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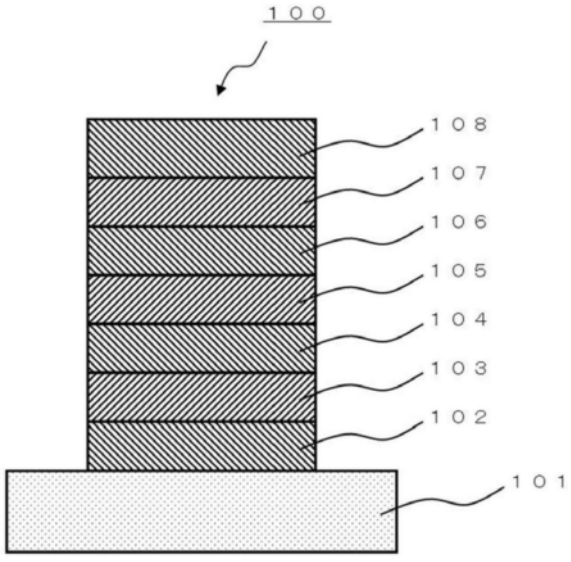
权利要求书7页 说明书352页 附图1页

(54)发明名称

化合物、有机元件用材料、油墨组合物、有机电致发光元件、显示装置及照明装置

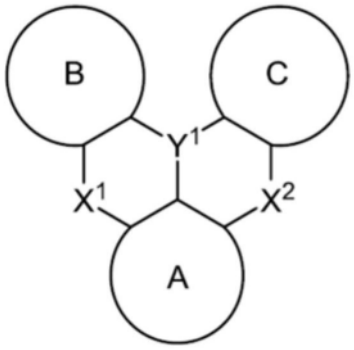
(57)摘要

本发明提供一种化合物、有机元件用材料、油墨组合物、有机电致发光元件、显示装置及照明装置。通过将环烷烃缩合于多环芳香族化合物，而增加有机EL元件用材料等有机元件用材料的选择项，所述多环芳香族化合物是利用硼原子与氧原子等将多个芳香族环连结而成。另外，通过将新颖的环烷烃缩合多环芳香族化合物用作有机EL元件用材料而提供例如发光效率或元件寿命优异的有机EL元件。



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1.一种多环芳香族化合物,其为单体或多聚体,所述单体由下述通式(1)表示,所述多聚体具有多个下述通式(1)所表示的结构;



(1)

所述式(1)中,

A环、B环及C环分别独立地为芳基环或杂芳基环,这些环中的至少一个氢可被取代,

Y^1为B、P、P=O、P=S、Al、Ga、As、Si-R或Ge-R,所述Si-R及Ge-R的R为芳基、烷基或环烷基,

X^1及X^2分别独立地为>O、>N-R、>$C(-R)_2$、>S或>Se,所述>N-R的R为可被取代的芳基、可被取代的杂芳基、可被取代的烷基或可被取代的环烷基,所述>$C(-R)_2$的R为氢、可被取代的芳基、可被取代的烷基或可被取代的环烷基,另外,所述>N-R的R及所述>$C(-R)_2$的R的至少一个可通过连结基或单键而与所述A环、B环及C环的至少一个键结,

式(1)所表示的化合物中的至少一个氢可由氘、氰基或卤素取代,而且,

式(1)所表示的化合物中的A环、B环、C环、芳基及杂芳基的至少一个由至少一个环烷烃缩合,所述环烷烃中的至少一个氢可被取代,所述环烷烃中的至少一个-CH_2-可由-O-取代。

2.根据权利要求1所述的多环芳香族化合物,其中,

所述式(1)中,

A环、B环及C环分别独立地为芳基环或杂芳基环,这些环中的至少一个氢可由经取代或未经取代的芳基、经取代或未经取代的杂芳基、经取代或未经取代的二芳基氨基、经取代或未经取代的二杂芳基氨基、经取代或未经取代的芳基杂芳基氨基、经取代或未经取代的二芳基硼基、经取代或未经取代的烷基、经取代或未经取代的环烷基、经取代或未经取代的烷氧基、经取代或未经取代的芳氧基、或者经取代的硅烷基取代,所述二芳基硼基的两个芳基可经由单键或连结基而键结,另外,这些环具有与包含Y^1、X^1及X^2的所述式(1)中央的缩合二环结构共有键结的5元环或6元环,

Y^1为B、P、P=O、P=S、Al、Ga、As、Si-R或Ge-R,所述Si-R及Ge-R的R为芳基、烷基或环烷基,

X^1及X^2分别独立地为>O、>N-R、>$C(-R)_2$、>S或>Se,所述>N-R的R为可由烷基或环烷基取代的芳基、可由烷基或环烷基取代的杂芳基、烷基或环烷基,所述>$C(-R)_2$的R为氢、可由烷基或环烷基取代的芳基、烷基或环烷基,另外,所述>N-R的R及所述>$C(-R)_2$的R的至少一个可通过-O-、-S-、-$C(-R)_2$-或单键而与所述A环、B环及C环的至少一个键结,所述-$C(-R)_2$-的R为氢、烷基或环烷基,

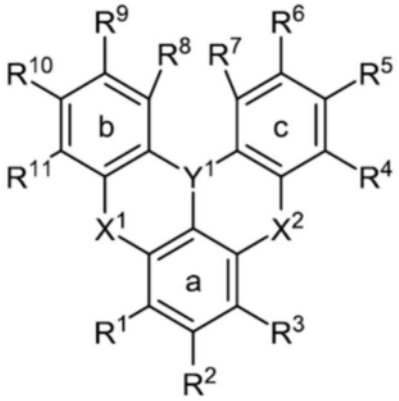
式(1)所表示的化合物中的至少一个氢可由氘、氰基或卤素取代,

在为多聚体的情况下,为具有2个或3个通式(1)所表示的结构的二聚体或三聚体,而

且,

式(1)所表示的化合物中的A环、B环、C环、芳基及杂芳基的至少一个由至少一个环烷烃缩合,所述环烷烃中的至少一个氢可被取代,所述环烷烃中的至少一个-CH_2-可由-O-取代。

3.根据权利要求1所述的多环芳香族化合物,其由下述通式(2)表示;



(2)

所述式(2)中,

a环、b环及c环中的任意的-C(-R)=可被取代为-N=,任意的-C(-R)=C(-R)-可被取代为-N(-R)-、-O-或-S-,所述-N(-R)-的R为芳基、烷基或环烷基,所述-C(-R)=的R为式(2)中的R^1~R^{11},所述-C(-R)=C(-R)-的R为式(2)中的R^1~R^{11},

R^1~R^{11}分别独立地为氢、芳基、杂芳基、二芳基氨基、二杂芳基氨基、芳基杂芳基氨基、二芳基硼基、烷基、环烷基、烷氧基、芳氧基、三芳基硅烷基、三烷基硅烷基、三环烷基硅烷基、二烷基环烷基硅烷基或烷基二环烷基硅烷基,这些中的至少一个氢可由芳基、杂芳基、烷基或环烷基取代,所述二芳基硼基的两个芳基可经由单键或连结基而键结,另外,R^1~R^{11}中的邻接的基彼此可键结并与a环、b环或c环一同形成芳基环或杂芳基环,所形成的环中的至少一个氢可由芳基、杂芳基、二芳基氨基、二杂芳基氨基、芳基杂芳基氨基、二芳基硼基、烷基、环烷基、烷氧基、芳氧基、三芳基硅烷基、三烷基硅烷基、三环烷基硅烷基、二烷基环烷基硅烷基或烷基二环烷基硅烷基取代,这些中的至少一个氢可由芳基、杂芳基、烷基或环烷基取代,所述二芳基硼基的两个芳基可经由单键或连结基而键结,

Y^1为B、P、P=O、P=S、Al、Ga、As、Si-R或Ge-R,所述Si-R及Ge-R的R为碳数6~12的芳基、碳数1~6的烷基或碳数3~14的环烷基,

X^1及X^2分别独立地为>O、>N-R、>C(-R)$_2$、>S或>Se,所述>N-R的R为碳数6~12的芳基、碳数2~15的杂芳基、碳数1~6的烷基或碳数3~14的环烷基,所述>C(-R)$_2$的R为氢、碳数6~12的芳基、碳数1~6的烷基或碳数3~14的环烷基,另外,所述>N-R的R及所述>C(-R)$_2$的R的至少一个可通过-O-、-S-、-C(-R)$_2$-或单键而与所述a环、b环及c环的至少一个键结,所述-C(-R)$_2$-的R为碳数1~6的烷基或碳数3~14的环烷基,

式(2)所表示的化合物中的至少一个氢可由氘、氰基或卤素取代,而且,

式(2)所表示的化合物中的所述a环、所述b环、所述c环、所述所形成的环、所述芳基及所述杂芳基的至少一个由碳数3~24的至少一个环烷烃缩合,所述环烷烃中的至少一个氢可由碳数6~30的芳基、碳数2~30的杂芳基、碳数1~24的烷基或碳数3~24的环烷基取代,所述环烷烃中的至少一个-CH_2-可由-O-取代。

4.根据权利要求3所述的多环芳香族化合物,其中,

所述式(2)中,

a环、b环及c环中的任意的-C(-R)＝可被取代为-N＝,任意的-C(-R)＝C(-R)-可被取代为-N(-R)-、-O-或-S-,所述-N(-R)-的R为碳数6～12的芳基、碳数1～6的烷基或碳数3～14的环烷基,所述-C(-R)＝的R为式(2)中的R^1～R^{11},所述-C(-R)＝C(-R)-的R为式(2)中的R^1～R^{11},

R^1～R^{11}分别独立地为氢、碳数6～30的芳基、碳数2～30的杂芳基、二芳基氨基、二芳基硼基、碳数1～24的烷基、碳数3～24的环烷基、三芳基硅烷基或三烷基硅烷基,所述二芳基氨基中芳基为碳数6～12的芳基,所述二芳基硼基中芳基为碳数6～12的芳基,且两个芳基可经由单键或连结基而键结,所述三芳基硅烷基中芳基为碳数6～12的芳基,所述三烷基硅烷基中烷基为碳数1～6的烷基,另外,R^1～R^{11}中的邻接的基彼此可键结并与a环、b环或c环一同形成碳数9～16的芳基环或碳数6～15的杂芳基环,所形成的环中的至少一个氢可由碳数6～10的芳基、碳数1～12的烷基、碳数3～16的环烷基、三芳基硅烷基或三烷基硅烷基取代,所述三芳基硅烷基中芳基为碳数6～12的芳基,所述三烷基硅烷基中烷基为碳数1～5的烷基,

Y^1为B、P、P＝O、P＝S或Si-R,所述Si-R的R为碳数6～10的芳基、碳数1～5的烷基或碳数5～10的环烷基,

X^1及X^2分别独立地为＞O、＞N-R、＞$C(-R)_2$或＞S,所述＞N-R的R为碳数6～10的芳基、碳数1～5的烷基或碳数5～10的环烷基,所述＞$C(-R)_2$的R为氢、碳数6～10的芳基、碳数1～5的烷基或碳数5～10的环烷基,

式(2)所表示的化合物中的至少一个氢可由氘、氰基或卤素取代,而且,

式(2)所表示的化合物中的所述a环、所述b环、所述c环、所述所形成的环、所述芳基及所述杂芳基的至少一个由碳数3～20的至少一个环烷烃缩合,所述环烷烃中的至少一个氢可由碳数6～16的芳基、碳数2～22的杂芳基、碳数1～12的烷基或碳数3～16的环烷基取代。

5.根据权利要求3所述的多环芳香族化合物,其中,

所述式(2)中,

a环、b环及c环中的任意的-C(-R)＝可被取代为-N＝,任意的-C(-R)＝C(-R)-可被取代为-N(-R)-、-O-或-S-,所述-N(-R)-的R为碳数6～10的芳基、碳数1～5的烷基或碳数5～10的环烷基,所述-C(-R)＝的R为式(2)中的R^1～R^{11},所述-C(-R)＝C(-R)-的R为式(2)中的R^1～R^{11},

R^1～R^{11}分别独立地为氢、碳数6～16的芳基、碳数2～20的杂芳基、二芳基氨基、碳数1～12的烷基或碳数3～16的环烷基,所述二芳基氨基中芳基为碳数6～10的芳基,

Y^1为B、P、P＝O或P＝S,

X^1及X^2分别独立地为＞O、＞N-R或＞$C(-R)_2$,所述＞N-R的R为碳数6～10的芳基、碳数1～5的烷基或碳数5～10的环烷基,所述＞$C(-R)_2$的R为氢、碳数6～10的芳基、碳数1～5的烷基或碳数5～10的环烷基,

式(2)所表示的化合物中的至少一个氢可由氘、氰基或卤素取代,而且,

式(2)所表示的化合物中的所述a环、所述b环、所述c环及作为所述＞N-R的R的碳数6～10的芳基的至少一个由碳数3～16的至少一个环烷烃缩合,所述环烷烃中的至少一个氢可由碳数1～6的烷基或碳数3～14的环烷基取代。

6.根据权利要求3所述的多环芳香族化合物,其中,

R^1～R^{11}分别独立地为氢、碳数6～16的芳基、二芳基氨基、碳数1～12的烷基或碳数3～16的环烷基,所述二芳基氨基中芳基为碳数6～10的芳基,

Y^1为B,

X^1及X^2均为>N-R,或者X^1为>N-R且X^2为>O,所述>N-R的R为碳数6～10的芳基、碳数1～5的烷基或碳数5～10的环烷基,

式(2)所表示的化合物中的至少一个氢可由氘或卤素取代,而且,

式(2)所表示的化合物中的所述a环、所述b环、所述c环及作为所述>N-R的R的碳数6～10的芳基的至少一个由碳数3～14的环烷烃缩合,所述环烷烃中的至少一个氢可由碳数1～5的烷基取代。

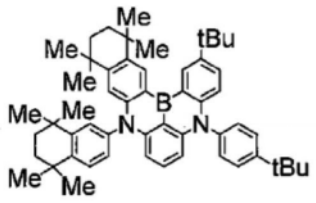
7.根据权利要求1至6中任一项所述的多环芳香族化合物,其被由环烷烃缩合的二芳基氨基、由环烷烃缩合的咔唑基或由环烷烃缩合的苯并咔唑基取代。

8.根据权利要求3至6中任一项所述的多环芳香族化合物,其中,R^2为由环烷烃缩合的二芳基氨基或由环烷烃缩合的咔唑基。

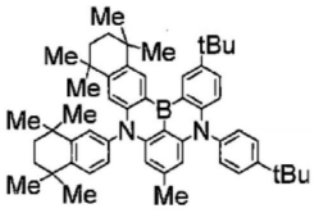
9.根据权利要求7或8所述的多环芳香族化合物,其中,所述环烷烃为碳数3～20的环烷烃。

10.根据权利要求1至8中任一项所述的多环芳香族化合物,其中,所述卤素为氟。

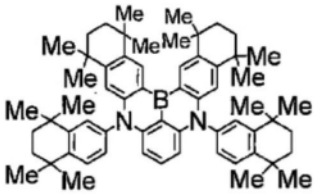
11.根据权利要求1所述的多环芳香族化合物,其由下述结构式的任一者表示;



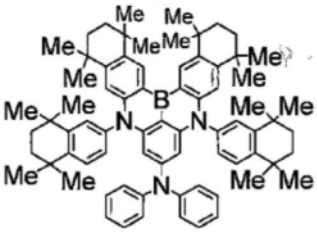
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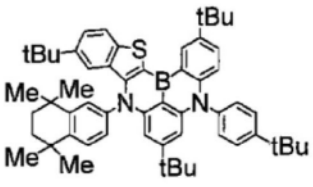
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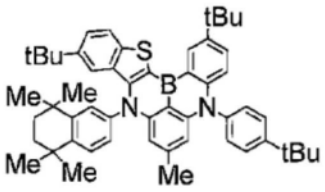
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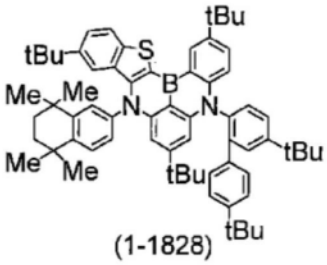


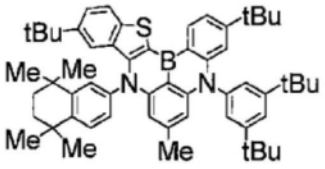
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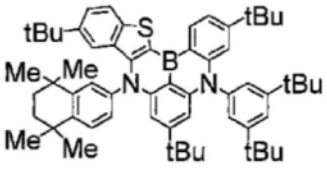


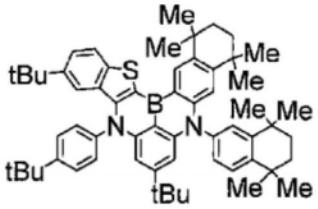
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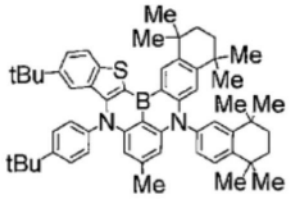

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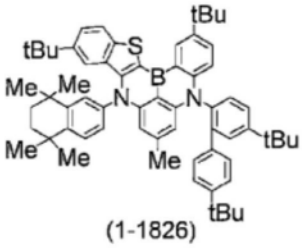

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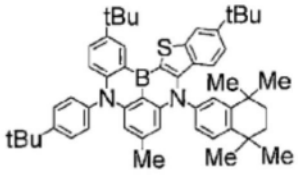

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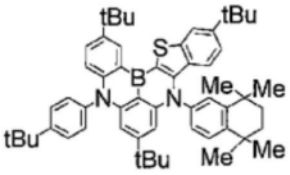

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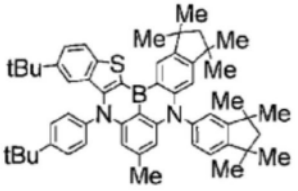

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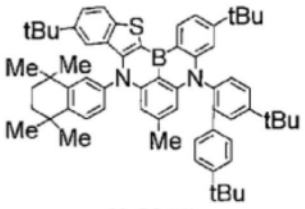

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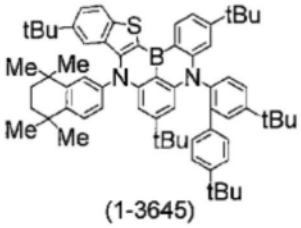

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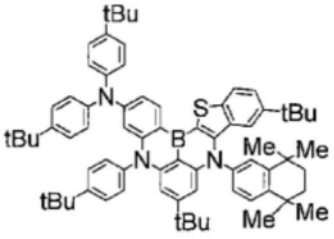

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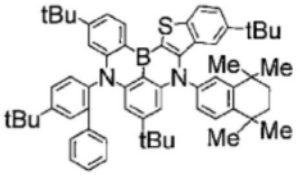

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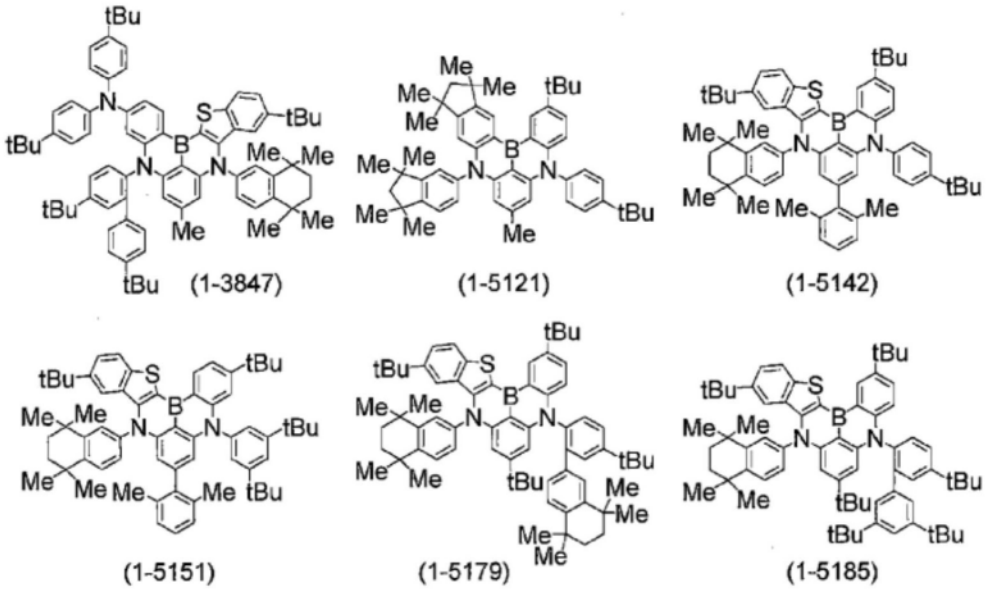

(1-2663)


(1-3644)


(1-3645)


(1-3812)


(1-3842)



各结构式中的Me表示甲基,tBu表示叔丁基。

12.一种反应性化合物,其是在如权利要求1至11中任一项所述的多环芳香族化合物中取代有反应性取代基而成。

13.一种高分子化合物,其是使如权利要求12所述的反应性化合物作为单体进行高分子化而成的高分子化合物,或是使所述高分子化合物进一步交联而成的高分子交联体。

14.一种悬挂型高分子化合物,其是在主链型高分子中使如权利要求12所述的反应性化合物取代而成的悬挂型高分子化合物,或是使所述悬挂型高分子化合物进一步交联而成的悬挂型高分子交联体。

15.一种有机元件用材料,含有如权利要求1至11中任一项所述的多环芳香族化合物。

16.一种有机元件用材料,含有如权利要求12所述的反应性化合物。

17.一种有机元件用材料,含有如权利要求13所述的高分子化合物。

18.一种有机元件用材料,含有如权利要求14所述的悬挂型高分子化合物。

19.根据权利要求15至18中任一项所述的有机元件用材料,其中,所述有机元件用材料为有机电致发光元件用材料、有机场效晶体管用材料或有机薄膜太阳电池用材料。

20.根据权利要求19所述的有机元件用材料,其中,所述有机电致发光元件用材料为发光层用材料。

21.一种油墨组合物,包含:如权利要求1至11中任一项所述的多环芳香族化合物;以及有机溶媒。

22.一种油墨组合物,包含:如权利要求12所述的反应性化合物;以及有机溶媒。

23.一种油墨组合物,包含:主链型高分子;如权利要求12所述的反应性化合物;以及有机溶媒。

24.一种油墨组合物,包含:如权利要求13所述的高分子化合物;以及有机溶媒。

25.一种油墨组合物,包含:如权利要求14所述的悬挂型高分子化合物;以及有机溶媒。

26.一种有机电致发光元件,具有:一对电极,包含阳极及阴极;以及有机层,配置于所述一对电极间,且含有如权利要求1至11中任一项所述的多环芳香族化合物、如权利要求12所述的反应性化合物、如权利要求13所述的高分子化合物、或者如权利要求14所述的悬挂

型高分子化合物。

27.根据权利要求26所述的有机电致发光元件,其中,所述有机层为发光层。

28.根据权利要求27所述的有机电致发光元件,其中,所述发光层包括:主体;以及作为掺杂剂的所述多环芳香族化合物、反应性化合物、高分子化合物或悬挂型高分子化合物。

29.根据权利要求28所述的有机电致发光元件,其中,所述主体为蒽系化合物、芴系化合物或二苯并䓛系化合物。

30.根据权利要求27至29中任一项所述的有机电致发光元件,其具有配置于所述阴极与所述发光层之间的电子传输层及电子注入层的至少一个层,且所述电子传输层及电子注入层的至少一个含有选自由硼烷衍生物、吡啶衍生物、荧蒽衍生物、BO系衍生物、蒽衍生物、苯并芴衍生物、氧化膦衍生物、嘧啶衍生物、咔唑衍生物、三嗪衍生物、苯并咪唑衍生物、菲咯啉衍生物及羟基喹啉系金属络合物所组成的群组中的至少一个。

31.根据权利要求30所述的有机电致发光元件,其中,所述电子传输层及电子注入层的至少一个层还含有选自由碱金属、碱土金属、稀土金属、碱金属的氧化物、碱金属的卤化物、碱土金属的氧化物、碱土金属的卤化物、稀土金属的氧化物、稀土金属的卤化物、碱金属的有机络合物、碱土金属的有机络合物及稀土金属的有机络合物所组成的群组中的至少一个。

32.根据权利要求26至31中任一项所述的有机电致发光元件,其中,空穴注入层、空穴传输层、发光层、电子传输层及电子注入层中的至少一个层包含:高分子化合物或高分子交联体、或者悬挂型高分子化合物或悬挂型高分子交联体,所述高分子化合物是使可形成各层的低分子化合物作为单体进行高分子化而成,所述高分子交联体是使所述高分子化合物进一步交联而成,所述悬挂型高分子化合物是使可形成各层的低分子化合物与主链型高分子反应而成,所述悬挂型高分子交联体是使所述悬挂型高分子化合物进一步交联而成。

33.一种显示装置,包括如权利要求26至32中任一项所述的有机电致发光元件。

34.一种照明装置,包括如权利要求26至32中任一项所述的有机电致发光元件。

化合物、有机元件用材料、油墨组合物、有机电致发光元件、显示装置及照明装置

[0001] 本申请为2020年04月14日递交的申请号为202080015059.1,发明名称为化合物、有机元件用材料、油墨组合物、有机电致发光元件、显示装置及照明装置的分案申请。

技术领域

[0002] 本发明涉及一种环烷烃缩合多环芳香族化合物及其多聚体(以下,也汇总称为“多环芳香族化合物”)、有机元件用材料、油墨组合物、与使用其的有机电致发光元件、有机场效晶体管及有机薄膜太阳电池、以及显示装置及照明装置。再者,本说明书中有时将“有机电致发光元件”表述为“有机EL(electroluminescence)元件”或仅表述为“元件”。

背景技术

[0003] 从前,使用了进行电致发光的发光元件的显示装置因可实现省电力化或薄型化而得到各种研究,进而,包含有机材料的有机电致发光元件因容易轻量化或大型化而得到积极研究。尤其,关于具有作为光的三原色之一的蓝色等的发光特性的有机材料的开发,以及关于具备空穴、电子等的电荷传输能力(具有成为半导体或超导体的可能性)的有机材料的开发,迄今为止,不论高分子化合物、低分子化合物均得到积极研究。

[0004] 有机EL元件具有如下结构,所述结构包括:包含阳极及阴极的一对电极,以及配置于所述一对电极间、且包含有机化合物的一层或多层。在包含有机化合物的层中,有发光层,或者传输或注入空穴、电子等电荷的电荷传输/注入层等,开发有对于这些层而言适当的各种有机材料。

[0005] 作为发光层用材料,例如开发有苯并芴系化合物等(国际公开第2004/061047号公报)。另外,作为空穴传输材料,例如开发有三苯基胺系化合物等(日本专利特开2001-172232号公报)。另外,作为电子传输材料,例如开发有蒽系化合物等(日本专利特开2005-170911号公报)。

[0006] 另外,近年来,作为用于有机EL元件或有机薄膜太阳电池的材料,也报告有对三苯基胺衍生物进行改良而成的材料(国际公开第2012/118164号公报)。所述材料为如下的材料,其中,参考已实用化的N,N’-二苯基-N,N’-双(3-甲基苯基)-1,1’-联苯-4,4’-二胺(TPD),使构成三苯基胺的芳香环彼此连结,由此提高其平面性。所述文献中,例如对NO连结系化合物(63页的化合物1)的电荷传输特性进行了评价,但关于NO连结系化合物以外的材料的制造方法并未进行记载,另外,若连结的元素不同则化合物整体的电子状态不同,因此,自NO连结系化合物以外的材料所获得的特性也仍未知。此种化合物的例子在别处也可看到(国际公开第2011/107186号公报)。例如,具有三重态激子的能量(T1)大的共轭结构的化合物可发出波长更短的磷光,因此作为蓝色的发光层用材料有益。另外,作为夹持发光层的电子传输材料或空穴传输材料,也需要具有T1大的新颖共轭结构的化合物。

[0007] 有机EL元件的主体(host)材料通常为利用单键或磷原子或硅原子将多个苯或咔唑等现有的芳香环连结而成的分子。其原因在于:通过将多个共轭系比较小的芳香环加以

连结,主体材料所需的大的最高占据分子轨道(Highest Occupied Molecular Orbital,HOMO)-最低未占分子轨道(Lowest Unoccupied Molecular Orbital,LUMO)间隙(薄膜的带隙Eg)得到担保。进而,在使用磷光材料或热活性型延迟荧光材料的有机EL元件的主体材料中,也需要高的三重态激发能量(E_T),但通过将施体性或受体性的芳香环或取代基连结于分子上,而使三重态激发状态(T1)的单占分子轨道(Singly Occupied Molecular Orbital,SOMO)1及SOMO2局部存在化,并减小两轨道间的交换相互作用,由此能够提升三重态激发能量(E_T)。但是,共轭系小的芳香环的氧化还原稳定性并不充分,将连结有现有的芳香环的分子用作主体材料的元件的寿命并不充分。另一方面,具有扩张π共轭系的多环芳香族化合物通常氧化还原稳定性优异,但HOMO-LUMO间隙(薄膜的带隙Eg)或三重态激发能量(E_T)低,因此被认为不适合主体材料。

[0008] 现有技术文献

[0009] 专利文献

[0010] 专利文献1:国际公开第2004/061047号公报

[0011] 专利文献2:日本专利特开2001-172232号公报

[0012] 专利文献3:日本专利特开2005-170911号公报

[0013] 专利文献4:国际公开第2012/118164号公报

[0014] 专利文献5:国际公开第2011/107186号公报

[0015] 专利文献6:国际公开第2015/102118号公报

发明内容

[0016] 发明所要解决的问题

[0017] 如上所述,作为用于有机EL元件的材料,开发有各种材料,为了增加有机EL元件用材料的选择项,期望开发包含与现有不同的化合物的材料。尤其,自专利文献1～专利文献4中所报告的NO连结系化合物以外的材料所获得的有机EL特性或其制造方法仍然未知。

[0018] 另外,专利文献6中报告有一种含有硼的多环芳香族化合物与使用其的有机EL元件,但为了进一步提升元件特性,谋求一种可提升发光效率或元件寿命的发光层用材料、特别是掺杂剂(dopant)材料。

[0019] 解决问题的技术手段

[0020] 本发明人等人为了解决所述课题而进行了努力研究,结果发现通过将含有缩合有环烷烃的多环芳香族化合物的层配置于一对电极间来构成例如有机EL元件,可获得优异的有机EL元件,从而完成了本发明。即,本发明提供如下的环烷烃缩合多环芳香族化合物或其多聚体、以及包含如下的环烷烃缩合多环芳香族化合物或其多聚体的有机EL元件用材料等有机元件用材料。

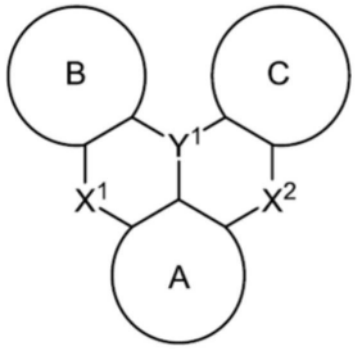
[0021] 再者,本说明书中有时以碳数来表示化学结构或取代基,但在化学结构中取代有取代基时、或者在取代基上进而取代有取代基时等的碳数是指化学结构或取代基各自的碳数,并非指化学结构与取代基的合计碳数、或取代基与取代基的合计碳数。例如,所谓“由碳数X的取代基A取代的碳数Y的取代基B”,是指“碳数X的取代基A”在“碳数Y的取代基B”上进行取代,碳数Y并非取代基A及取代基B的合计碳数。另外,例如所谓“由取代基A取代的碳数Y的取代基B”,是指“(不限定碳数的)取代基A”在“碳数Y的取代基B”上进行取代,碳数Y并非

取代基A及取代基B的合计碳数。

[0022] 项1.

[0023] 一种多环芳香族化合物或多环芳香族化合物的多聚体,其中,所述多环芳香族化合物由下述通式(1)表示,所述多环芳香族化合物的多聚体具有多个下述通式(1)所表示的结构。

[0024] [化7]

[0025] 

(1)

[0026] (所述式(1)中,

[0027] A环、B环及C环分别独立地为芳基环或杂芳基环,这些环中的至少一个氢可被取代,

[0028] Y^1为B、P、P=O、P=S、Al、Ga、As、Si-R或Ge-R,所述Si-R及Ge-R的R为芳基、烷基或环烷基,

[0029] X^1及X^2分别独立地为>O、>N-R、>C(-R)$_2$、>S或>Se,所述>N-R的R为可被取代的芳基、可被取代的杂芳基、可被取代的烷基或可被取代的环烷基,所述>C(-R)$_2$的R为氢、可被取代的芳基、可被取代的烷基或可被取代的环烷基,另外,所述>N-R的R及所述>C(-R)$_2$的R的至少一个可通过连结基或单键而与所述A环、B环及C环的至少一个键结,

[0030] 式(1)所表示的化合物或结构中的至少一个氢可由氘、氰基或卤素取代,而且,

[0031] 式(1)所表示的化合物或结构中的A环、B环、C环、芳基及杂芳基的至少一个由至少一个环烷烃缩合,所述环烷烃中的至少一个氢可被取代,所述环烷烃中的至少一个-CH_2-可由-O-取代)

[0032] 项2.

[0033] 根据项1所述的多环芳香族化合物或其多聚体,其中,

[0034] 所述式(1)中,

[0035] A环、B环及C环分别独立地为芳基环或杂芳基环,这些环中的至少一个氢可由经取代或未经取代的芳基、经取代或未经取代的杂芳基、经取代或未经取代的二芳基氨基、经取代或未经取代的二杂芳基氨基、经取代或未经取代的芳基杂芳基氨基、经取代或未经取代的二芳基硼基(两个芳基可经由单键或连结基而键结)、经取代或未经取代的烷基、经取代或未经取代的环烷基、经取代或未经取代的烷氧基、经取代或未经取代的芳氧基、或者经取代的硅烷基取代,另外,这些环具有与包含Y^1、X^1及X^2的所述式中央的缩合二环结构共有键结的5元环或6元环,

[0036] Y^1为B、P、P=O、P=S、Al、Ga、As、Si-R或Ge-R,所述Si-R及Ge-R的R为芳基、烷基或环烷基,

[0037] X^1及X^2分别独立地为>O、>N-R、>C(-R)$_2$、>S或>Se,所述>N-R的R为可由烷基或环烷基取代的芳基、可由烷基或环烷基取代的杂芳基、烷基或环烷基,所述>C(-R)$_2$的R为氢、可由烷基或环烷基取代的芳基、烷基或环烷基,另外,所述>N-R的R及所述>C(-R)$_2$的R的至少一个可通过-O-、-S-、-C(-R)$_2$-或单键而与所述A环、B环及C环的至少一个键结,所述-C(-R)$_2$-的R为氢、烷基或环烷基,

[0038] 式(1)所表示的化合物或结构中的至少一个氢可由氘、氰基或卤素取代,

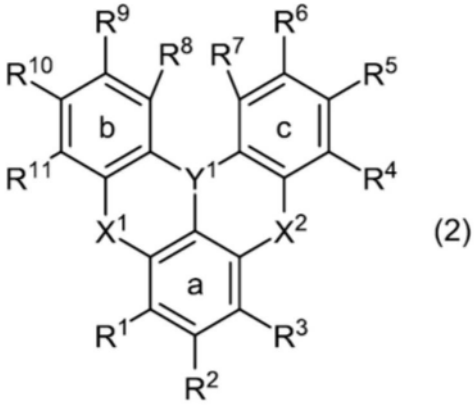
[0039] 在为多聚体的情况下,为具有2个或3个通式(1)所表示的结构的二聚体或三聚体,而且,

[0040] 式(1)所表示的化合物或结构中的A环、B环、C环、芳基及杂芳基的至少一个由至少一个环烷烃缩合,所述环烷烃中的至少一个氢可被取代,所述环烷烃中的至少一个-CH_2-可由-O-取代。

[0041] 项3.

[0042] 根据项1所述的多环芳香族化合物,其由下述通式(2)表示。

[0043] [化8]

[0044] 

(2)

[0045] (所述式(2)中,

[0046] a环、b环及c环中的任意的"-C(-R)=")(此处,R为式(2)中的R^1~R^{11})可被取代为"-N=",任意的"-C(-R)=C(-R)-")(此处,R为式(2)中的R^1~R^{11})可被取代为"-N(-R)-"、"-O-"或"-S-",所述"-N(-R)-"的R为芳基、烷基或环烷基,

[0047] R^1~R^{11}分别独立地为氢、芳基、杂芳基、二芳基氨基、二杂芳基氨基、芳基杂芳基氨基、二芳基硼基(两个芳基可经由单键或连结基而键结)、烷基、环烷基、烷氧基、芳氧基、三芳基硅烷基、三烷基硅烷基、三环烷基硅烷基、二烷基环烷基硅烷基或烷基二环烷基硅烷基,这些中的至少一个氢可由芳基、杂芳基、烷基或环烷基取代,另外,R^1~R^{11}中的邻接的基彼此可键结并与a环、b环或c环一同形成芳基环或杂芳基环,所形成的环中的至少一个氢可由芳基、杂芳基、二芳基氨基、二杂芳基氨基、芳基杂芳基氨基、二芳基硼基(两个芳基可经由单键或连结基而键结)、烷基、环烷基、烷氧基、芳氧基、三芳基硅烷基、三烷基硅烷基、三环烷基硅烷基、二烷基环烷基硅烷基或烷基二环烷基硅烷基取代,这些中的至少一个氢可由芳基、杂芳基、烷基或环烷基取代,

[0048] Y^1为B、P、P=O、P=S、Al、Ga、As、Si-R或Ge-R,所述Si-R及Ge-R的R为碳数6~12的芳基、碳数1~6的烷基或碳数3~14的环烷基,

[0049] X^1及X^2分别独立地为>O、>N-R、>C(-R)$_2$、>S或>Se,所述>N-R的R为碳数6~12

的芳基、碳数2～15的杂芳基、碳数1～6的烷基或碳数3～14的环烷基，所述＞C(-R)$_2$的R为氢、碳数6～12的芳基、碳数1～6的烷基或碳数3～14的环烷基，另外，所述＞N-R的R及所述＞C(-R)$_2$的R的至少一个可通过-O-、-S-、-C(-R)$_2$-或单键而与所述a环、b环及c环的至少一个键结，所述-C(-R)$_2$-的R为碳数1～6的烷基或碳数3～14的环烷基，

[0050] 式(2)所表示的化合物中的至少一个氢可由氘、氰基或卤素取代，而且，

[0051] 式(2)所表示的化合物中的所述a环、所述b环、所述c环、所述所形成的环、所述芳基及所述杂芳基的至少一个由碳数3～24的至少一个环烷烃缩合，所述环烷烃中的至少一个氢可由碳数6～30的芳基、碳数2～30的杂芳基、碳数1～24的烷基或碳数3～24的环烷基取代，所述环烷烃中的至少一个-CH_2-可由-O-取代)

[0052] 项4.

[0053] 根据项3所述的多环芳香族化合物，其中，

[0054] 所述式(2)中，

[0055] a环、b环及c环中的任意的“-C(-R)＝”(此处，R为式(2)中的R^1～R^{11})可被取代为“-N＝”，任意的“-C(-R)＝C(-R)-”(此处，R为式(2)中的R^1～R^{11})可被取代为“-N(-R)-”、“-O-”或“-S-”，所述“-N(-R)-”的R为碳数6～12的芳基、碳数1～6的烷基或碳数3～14的环烷基，

[0056] R^1～R^{11}分别独立地为氢、碳数6～30的芳基、碳数2～30的杂芳基、二芳基氨基(其中，芳基为碳数6～12的芳基)、二芳基硼基(其中，芳基为碳数6～12的芳基，且两个芳基可经由单键或连结基而键结)、碳数1～24的烷基、碳数3～24的环烷基、三芳基硅烷基(其中，芳基为碳数6～12的芳基)或三烷基硅烷基(其中，烷基为碳数1～6的烷基)，另外，R^1～R^{11}中的邻接的基彼此可键结并与a环、b环或c环一同形成碳数9～16的芳基环或碳数6～15的杂芳基环，所形成的环中的至少一个氢可由碳数6～10的芳基、碳数1～12的烷基、碳数3～16的环烷基、三芳基硅烷基(其中，芳基为碳数6～12的芳基)或三烷基硅烷基(其中，烷基为碳数1～5的烷基)取代，

[0057] Y^1为B、P、P＝O、P＝S或Si-R，所述Si-R的R为碳数6～10的芳基、碳数1～5的烷基或碳数5～10的环烷基，

[0058] X^1及X^2分别独立地为＞O、＞N-R、＞C(-R)$_2$或＞S，所述＞N-R的R为碳数6～10的芳基、碳数1～5的烷基或碳数5～10的环烷基，所述＞C(-R)$_2$的R为氢、碳数6～10的芳基、碳数1～5的烷基或碳数5～10的环烷基，

[0059] 式(2)所表示的化合物中的至少一个氢可由氘、氰基或卤素取代，而且，

[0060] 式(2)所表示的化合物中的所述a环、所述b环、所述c环、所述所形成的环、所述芳基及所述杂芳基的至少一个由碳数3～20的至少一个环烷烃缩合，所述环烷烃中的至少一个氢可由碳数6～16的芳基、碳数2～22的杂芳基、碳数1～12的烷基或碳数3～16的环烷基取代。

[0061] 项5.

[0062] 根据项3所述的多环芳香族化合物，其中，

[0063] 所述式(2)中，

[0064] a环、b环及c环中的任意的“-C(-R)＝”(此处，R为式(2)中的R^1～R^{11})可被取代为“-N＝”，任意的“-C(-R)＝C(-R)-”(此处，R为式(2)中的R^1～R^{11})可被取代为“-N(-R)-”、“-O-”或“-S-”，所述“-N(-R)-”的R为碳数6～10的芳基、碳数1～5的烷基或碳数5～10的环烷基，

[0065] R^1～R^{11}分别独立地为氢、碳数6～16的芳基、碳数2～20的杂芳基、二芳基氨基(其中,芳基为碳数6～10的芳基)、碳数1～12的烷基或碳数3～16的环烷基,

[0066] Y^1为B、P、P=O或P=S,

[0067] X^1及X^2分别独立地为>O、>N-R或>C(-R)$_2$,所述>N-R的R为碳数6～10的芳基、碳数1～5的烷基或碳数5～10的环烷基,所述>C(-R)$_2$的R为氢、碳数6～10的芳基、碳数1～5的烷基或碳数5～10的环烷基,

[0068] 式(2)所表示的化合物中的至少一个氢可由氘、氰基或卤素取代,而且,

[0069] 式(2)所表示的化合物中的所述a环、所述b环、所述c环及作为所述>N-R的R的碳数6～10的芳基的至少一个由碳数3～16的至少一个环烷烃缩合,所述环烷烃中的至少一个氢可由碳数1～6的烷基或碳数3～14的环烷基取代。

[0070] 项6.

[0071] 根据项3所述的多环芳香族化合物,其中,

[0072] R^1～R^{11}分别独立地为氢、碳数6～16的芳基、二芳基氨基(其中,芳基为碳数6～10的芳基)、碳数1～12的烷基或碳数3～16的环烷基,

[0073] Y^1为B,

[0074] X^1及X^2均为>N-R,或者X^1为>N-R且X^2为>O,所述>N-R的R为碳数6～10的芳基、碳数1～5的烷基或碳数5～10的环烷基,

[0075] 式(2)所表示的化合物中的至少一个氢可由氘或卤素取代,而且,

[0076] 式(2)所表示的化合物中的所述a环、所述b环、所述c环及作为所述>N-R的R的碳数6～10的芳基的至少一个由碳数3～14的环烷烃缩合,所述环烷烃中的至少一个氢可由碳数1～5的烷基取代。

[0077] 项7.

[0078] 根据项1至项6中任一项所述的多环芳香族化合物或其多聚体,其被由环烷烃缩合的二芳基氨基、由环烷烃缩合的咔唑基或由环烷烃缩合的苯并咔唑基取代。

[0079] 项8.

[0080] 根据项3至项6中任一项所述的多环芳香族化合物,其中,R^2为由环烷烃缩合的二芳基氨基或由环烷烃缩合的咔唑基。

[0081] 项9.

[0082] 根据项7或项8所述的多环芳香族化合物,其中,所述环烷烃为碳数3～20的环烷烃。

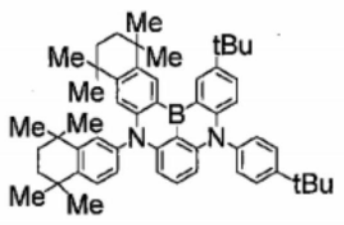
[0083] 项10.

[0084] 根据项1至项8中任一项所述的多环芳香族化合物或其多聚体,其中,所述卤素为氟。

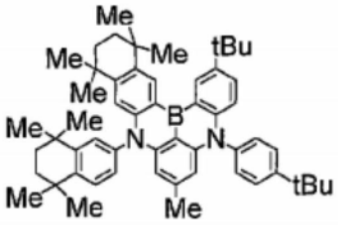
[0085] 项11.

[0086] 根据项1所述的多环芳香族化合物,其由下述结构式的任一者表示。

[0087] [化9]

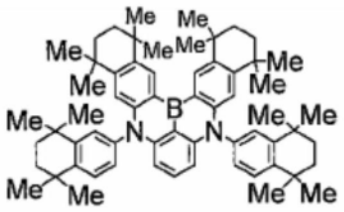


(1-411)

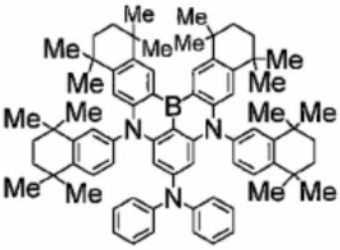


(1-590)

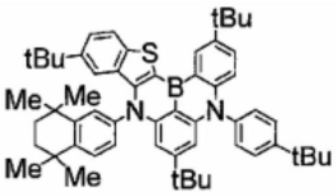
[0088]



(1-1301)

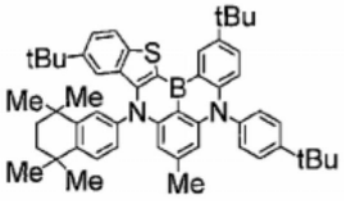


(1-1302)

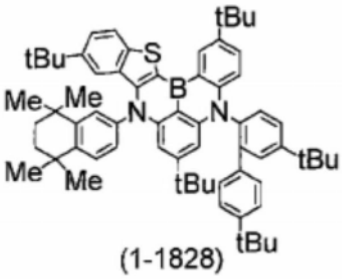


(1-1823)

[0089] [化10]

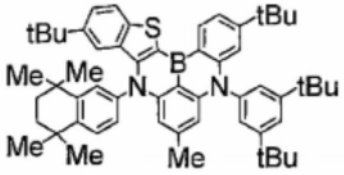


(1-1821)

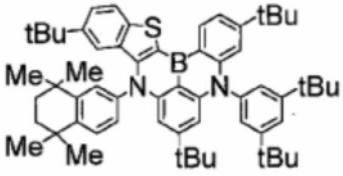


(1-1828)

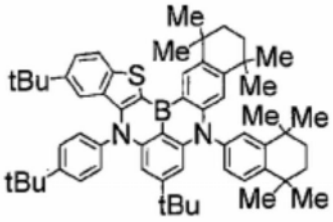
[0090]



(1-3621)

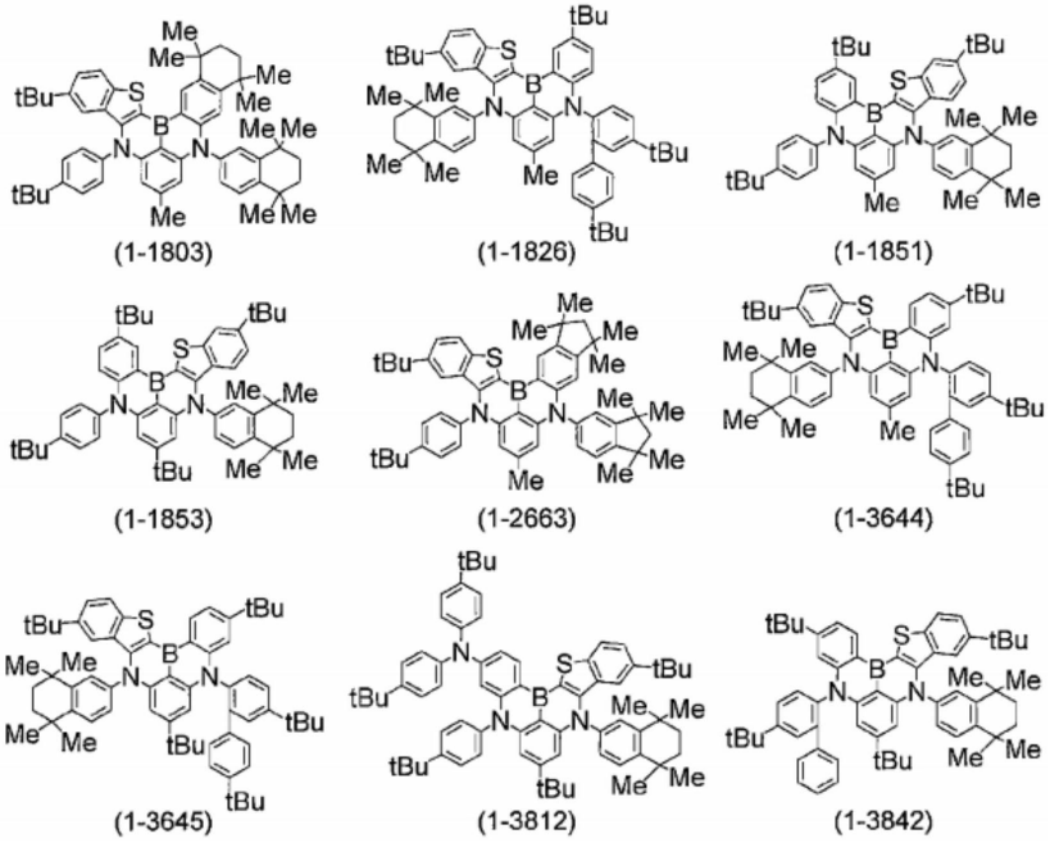


(1-3623)

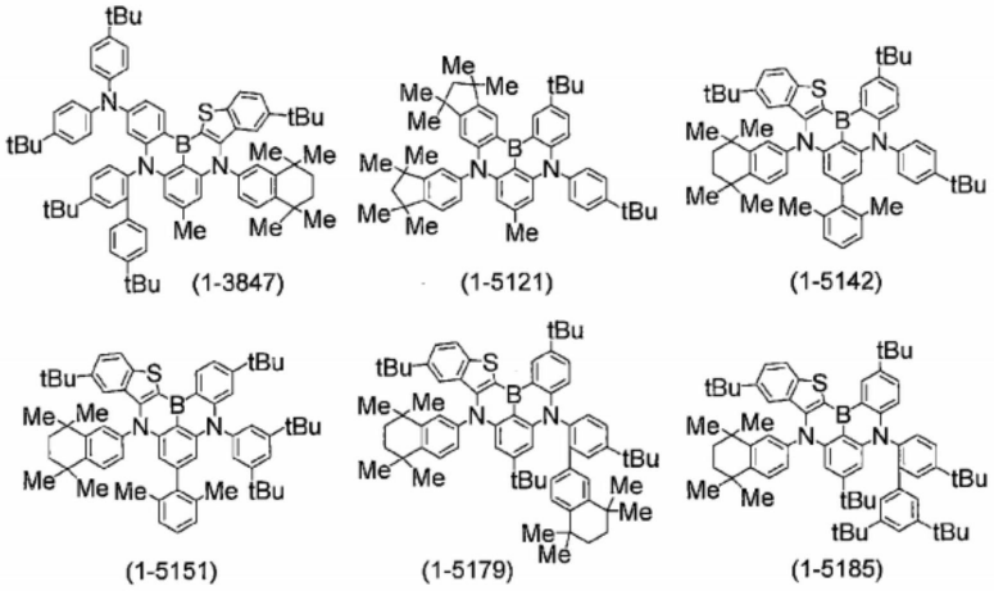


(1-3604)

[0091] [化11]

[0092] 

[0093] [化12]

[0094] 

[0095] (所述各结构式中的“Me”表示甲基,“tBu”表示叔丁基)

[0096] 项12.

[0097] 一种反应性化合物,其是在根据项1至项11中任一项所述的多环芳香族化合物或其多聚体中取代有反应性取代基而成。

[0098] 项13.

[0099] 一种高分子化合物或高分子交联体,其中,所述高分子化合物是使根据项12所述的反应性化合物作为单体进行高分子化而成,所述高分子交联体是使所述高分子化合物进

一步交联而成。

[0100] 项14.

[0101] 一种悬挂型高分子化合物或悬挂型高分子交联体,其中,所述悬挂型高分子化合物是在主链型高分子中使根据项12所述的反应性化合物取代而成,所述悬挂型高分子交联体是使所述悬挂型高分子化合物进一步交联而成。

[0102] 项15.

[0103] 一种有机元件用材料,含有根据项1至项11中任一项所述的多环芳香族化合物或其多聚体。

[0104] 项16.

[0105] 一种有机元件用材料,含有根据项12所述的反应性化合物。

[0106] 项17.

[0107] 一种有机元件用材料,含有根据项13所述的高分子化合物或高分子交联体。

[0108] 项18.

[0109] 一种有机元件用材料,含有根据项14所述的悬挂型高分子化合物或悬挂型高分子交联体。

[0110] 项19.

[0111] 根据项15至项18中任一项所述的有机元件用材料,其中,所述有机元件用材料为有机电致发光元件用材料、有机场效晶体管用材料或有机薄膜太阳电池用材料。

[0112] 项20.

[0113] 根据项19所述的有机元件用材料,其中,所述有机电致发光元件用材料为发光层用材料。

[0114] 项21.

[0115] 一种油墨组合物,包含:根据项1至项11中任一项所述的多环芳香族化合物或其多聚体;以及有机溶媒。

[0116] 项22.

[0117] 一种油墨组合物,包含:根据项12所述的反应性化合物;以及有机溶媒。

[0118] 项23.

[0119] 一种油墨组合物,包含:主链型高分子;根据项12所述的反应性化合物;以及有机溶媒。

[0120] 项24.

[0121] 一种油墨组合物,包含:根据项13所述的高分子化合物或高分子交联体;以及有机溶媒。

[0122] 项25.

[0123] 一种油墨组合物,包含:根据项14所述的悬挂型高分子化合物或悬挂型高分子交联体;以及有机溶媒。

[0124] 项26.

[0125] 一种有机电致发光元件,具有:一对电极,包含阳极及阴极;以及有机层,配置于所述一对电极间,且含有根据项1至项11中任一项所述的多环芳香族化合物或其多聚体、根据项12所述的反应性化合物、根据项13所述的高分子化合物或高分子交联体、或者根据项14

所述的悬挂型高分子化合物或悬挂型高分子交联体。

[0126] 项27.

[0127] 根据项26所述的有机电场发光元件,其中所述有机层为发光层。

[0128] 项28.

[0129] 根据项27所述的有机电致发光元件,其中,所述发光层包括:主体;以及作为掺杂剂的所述多环芳香族化合物、其多聚体、反应性化合物、高分子化合物、高分子交联体、悬挂型高分子化合物或悬挂型高分子交联体。

[0130] 项29.

[0131] 根据项28所述的有机电致发光元件,其中,所述主体为蒽系化合物、芴系化合物或二苯并䓛系化合物。

[0132] 项30.

[0133] 根据项26至项29中任一项所述的有机电致发光元件,其具有配置于所述阴极与所述发光层之间的电子传输层及电子注入层的至少一个层,且所述电子传输层及电子注入层的至少一个含有选自由硼烷衍生物、吡啶衍生物、荧蒽衍生物、BO系衍生物、蒽衍生物、苯并芴衍生物、氧化膦衍生物、嘧啶衍生物、咔唑衍生物、三嗪衍生物、苯并咪唑衍生物、菲咯啉衍生物及羟基喹啉(quinolinol)系金属络合物所组成的群组中的至少一个。

[0134] 项31.

[0135] 根据项30所述的有机电致发光元件,其中,所述电子传输层及电子注入层的至少一个层还含有选自由碱金属、碱土金属、稀土金属、碱金属的氧化物、碱金属的卤化物、碱土金属的氧化物、碱土金属的卤化物、稀土金属的氧化物、稀土金属的卤化物、碱金属的有机络合物、碱土金属的有机络合物及稀土金属的有机络合物所组成的群组中的至少一个。

[0136] 项32.

[0137] 根据项26至项31中任一项所述的有机电致发光元件,其中,空穴注入层、空穴传输层、发光层、电子传输层及电子注入层中的至少一个层包含:高分子化合物或高分子交联体、或者悬挂型高分子化合物或悬挂型高分子交联体,所述高分子化合物是使可形成各层的低分子化合物作为单体进行高分子化而成,所述高分子交联体是使所述高分子化合物进一步交联而成,所述悬挂型高分子化合物是使可形成各层的低分子化合物与主链型高分子反应而成,所述悬挂型高分子交联体是使所述悬挂型高分子化合物进一步交联而成。

[0138] 项33.

[0139] 一种显示装置或照明装置,包括根据项26至项32中任一项所述的有机电致发光元件。

[0140] 发明的效果

[0141] 根据本发明的优选的实施例,可提供一种可用作例如有机EL元件用材料等有机元件用材料的新颖的环烷烃缩合多环芳香族化合物,通过使用所述环烷烃缩合多环芳香族化合物,可提供一种优异的有机EL元件等有机元件。

[0142] 具体而言,本发明人等人发现利用硼、磷、氧、氮、硫等异质元素将芳香环连结而成的多环芳香族化合物(基本骨架部分)具有大的HOMO-LUMO间隙(薄膜的带隙Eg)与高的三重态激发能量(E_T)。认为其原因在于:含有异质元素的6元环的芳香族性低,因此伴随共轭系的扩张的HOMO-LUMO间隙的减少得到抑制,且因异质元素的电子扰动而使三重态激发状态

(T1)的SOMO1及SOMO2局部存在化。另外,本发明的含有异质元素的多环芳香族化合物(基本骨架部分)通过三重态激发状态(T1)下的SOMO1及SOMO2的局部存在化,而两轨道间的交换相互作用变小,因此三重态激发状态(T1)与单重态激发状态(S1)的能量差小,显示出热活性型延迟荧光,因此作为有机EL元件(包含利用了热活性型延迟荧光的元件)的荧光材料也有用。另外,具有高的三重态激发能量(E_T)的材料作为磷光有机EL元件或利用了热活性型延迟荧光的有机EL元件的电子传输层或空穴传输层也有用。进而,这些多环芳香族化合物(基本骨架部分)通过取代基的导入,而可任意地变动HOMO与LUMO的能量,因此可对应于周边材料而使电离电位(ionization potential)或电子亲和力最优选化。

[0143] 除此种基本骨架部分的特性以外,本发明的化合物通过缩合环烷烃,也可抑制浓度淬灭,还可期待元件寿命或发光效率的改善。元件寿命或发光效率为有机元件的重要的特性值,通过使用本申请的化合物,可期待对于提高元件的特性的效果。另外,可期待熔点或升华温度的降低。所述情况是指,在作为要求高纯度的有机EL元件等有机元件用的材料的精制法而几乎不可缺少的升华精制中,可在比较低的温度下进行精制,因此可避免材料的热分解等。另外,所述情况对于真空蒸镀工艺而言也相同,可在比较低的温度下实施工艺,因此可避免材料的热分解,结果可获得高性能的有机元件,所述真空蒸镀工艺是对于制作有机EL元件等有机元件而言有力的手段。另外,关于多环芳香族化合物的多聚体,由于分子量或平面性的高等而升华温度高的化合物多,因此由缩合环烷烃引起的升华温度的降低变得更有效。另外,通过环烷烃的缩合而在有机溶媒中的溶解性提高,因此也能够应用于利用了涂布工艺的元件制作。但是,本发明并不特别限定于这些原理。

附图说明

[0144] 图1是表示本实施方式的有机EL元件的概略剖面图。

[0145] [符号的说明]

[0146] 100:有机电致发光元件

[0147] 101:基板

[0148] 102:阳极

[0149] 103:空穴注入层

[0150] 104:空穴传输层

[0151] 105:发光层

[0152] 106:电子传输层

[0153] 107:电子注入层

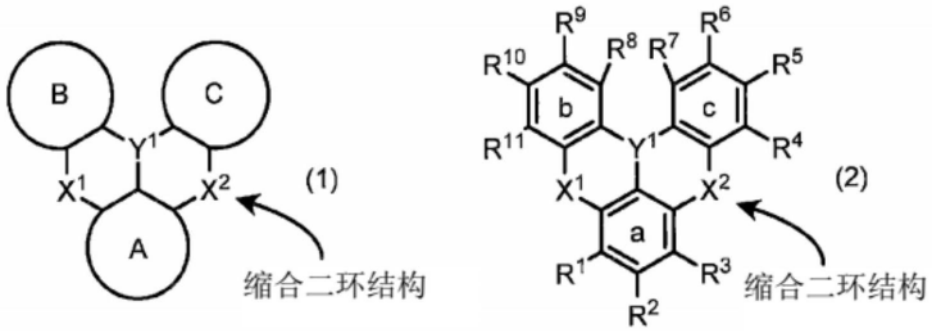
[0154] 108:阴极。

具体实施方式

[0155] 1.经环烷烃缩合的多环芳香族化合物及其多聚体

[0156] 本申请发明为下述通式(1)所表示的多环芳香族化合物、或具有多个下述通式(1)所表示的结构的多环芳香族化合物的多聚体,优选为下述通式(2)所表示的多环芳香族化合物、或具有多个下述通式(2)所表示的结构的多环芳香族化合物的多聚体,这些化合物或结构中的A环、B环、C环、芳基及杂芳基的至少一个由至少一个环烷烃缩合。

[0157] [化13]

[0158] 

[0159] 通式(1)中的A环、B环及C环分别独立地为芳基环或杂芳基环,这些环中的至少一个氢可由取代基取代。所述取代基优选为经取代或未经取代的芳基、经取代或未经取代的杂芳基、经取代或未经取代的二芳基氨基、经取代或未经取代的二杂芳基氨基、经取代或未经取代的芳基杂芳基氨基(具有芳基与杂芳基的氨基)、经取代或未经取代的二芳基硼基(两个芳基可经由单键或连结基而键结)、经取代或未经取代的烷基、经取代或未经取代的环烷基、经取代或未经取代的烷氧基、经取代或未经取代的芳氧基、或者经取代的硅烷基取代。作为这些基具有取代基时的取代基,可列举:芳基、杂芳基、烷基或环烷基。另外,所述芳基环或杂芳基环优选为具有与包含Y^1、X^1及X^2的通式(1)中央的缩合二环结构共有键结的5元环或6元环。

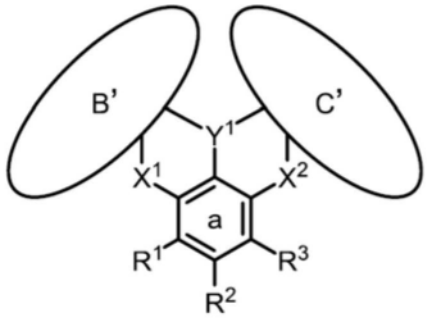
[0160] 此处,所谓“缩合二环结构”,是指通式(1)的中央所示的包含Y^1、X^1及X^2而构成的两个饱和烃环缩合而成的结构。另外,所谓“与缩合二环结构共有键结的6元环”,例如如所述通式(2)中所示那样,是指在所述缩合二环结构中缩合的a环(苯环(6元环))。另外,所谓“(A环)芳基环或杂芳基环具有所述6元环”,是指仅由所述6元环形成A环、或者以包含所述6元环的方式在所述6元环中进而缩合其他环等来形成A环。换言之,所谓此处所述的“具有6元环的(A环)芳基环或杂芳基环”,是指构成A环的全部或一部分的6元环在所述缩合二环结构中缩合。关于“B环(b环)”、“C环(c环)”及“5元环”,相同的说明也适用。

[0161] 通式(1)中的A环(或B环、C环)对应于通式(2)中的a环与其取代基R^1～R^3(或b环与其取代基R^8～R^{11}、c环与其取代基R^4～R^7)。即,通式(2)对应于选择“具有6元环的A环～C环”作为通式(1)的A环～C环的结构。以所述含义,由小写字母的a～c表示通式(2)的各环。

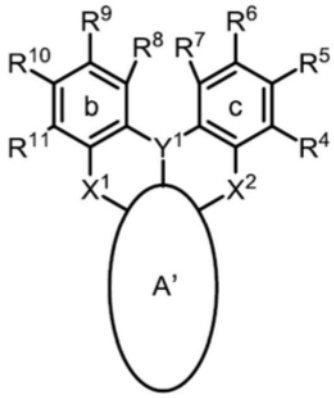
[0162] 通式(2)中,a环、b环及c环的取代基R^1～R^{11}中的邻接的基彼此可键结并与a环、b环或c环一同形成芳基环或杂芳基环,所形成的环中的至少一个氢可由芳基、杂芳基、二芳基氨基、二杂芳基氨基、芳基杂芳基氨基、二芳基硼基(两个芳基可经由单键或连结基而键结)、烷基、环烷基、烷氧基、芳氧基、三芳基硅烷基、三烷基硅烷基、三环烷基硅烷基、二烷基环烷基硅烷基或烷基二环烷基硅烷基取代,这些中的至少一个氢可由芳基、杂芳基、烷基或环烷基取代。因此,通式(2)所表示的多环芳香族化合物根据a环、b环及c环中的取代基的相互的键结形态,如下述式(2-1)及式(2-2)所示,构成化合物的环结构发生变化。各式中的A’环、B’环及C’环分别对应于通式(1)中的A环、B环及C环。

[0163] [化14]

[0164]



(2-1)



(2-2)

[0165] 若以通式(2)进行说明,则所述式(2-1)及式(2-2)中的A'环、B'环及C'环表示取代基R^1～R^{11}中的邻接的基彼此键结并分别与a环、b环及c环一同形成的芳基环或杂芳基环(也可称为其他环结构在a环、b环或c环中缩合而成的缩合环)。再者,虽然式中未表示,但也存在a环、b环及c环全部变化成A'环、B'环及C'环的化合物。另外,如根据所述式(2-1)及式(2-2)而可知那样,例如b环的R^8与c环的R^7、b环的R^{11}与a环的R^1、c环的R^4与a环的R^3等并不符合"邻接的基彼此",这些不会进行键结。即,所谓"邻接的基",是指在同一环上邻接的基。

[0166] 所述式(2-1)或式(2-2)所表示的化合物例如为具有苯环、吲哚环、吡咯环、苯并呋喃环或苯并噻吩环对于作为a环(或b环或c环)的苯环进行缩合而形成的A'环(或B'环或C'环)的化合物,所形成的缩合环A'(或缩合环B'或缩合环C')分别为萘环、咔唑环、吲哚环、二苯并呋喃环或二苯并噻吩环。

[0167] 通式(1)中的Y^1为B、P、P=O、P=S、Al、Ga、As、Si-R或Ge-R,所述Si-R及Ge-R的R为芳基、烷基或环烷基。在为P=O、P=S、Si-R或Ge-R的情况下,与A环、B环或C环进行键结的原子为P、Si或Ge。Y^1优选为B、P、P=O、P=S或Si-R,特别优选为B。所述说明也同样适用于通式(2)中的Y^1。

[0168] 通式(1)中的X^1及X^2分别独立地为>O、>N-R、>C(-R)$_2$、>S或>Se,所述>N-R的R为可被取代的芳基、可被取代的杂芳基、可被取代的烷基或可被取代的环烷基,所述>C(-R)$_2$的R为氢、可被取代的芳基、可被取代的烷基或可被取代的环烷基,所述>N-R的R及所述>C(-R)$_2$的R的至少一个可通过连结基或单键而与所述A环、B环及C环的至少一个键结,作为连结基,优选为-O-、-S-或-C(-R)$_2$-。再者,所述"-C(-R)$_2$-"的R为氢、烷基或环烷基。所述说明也同样适用于通式(2)中的X^1及X^2。

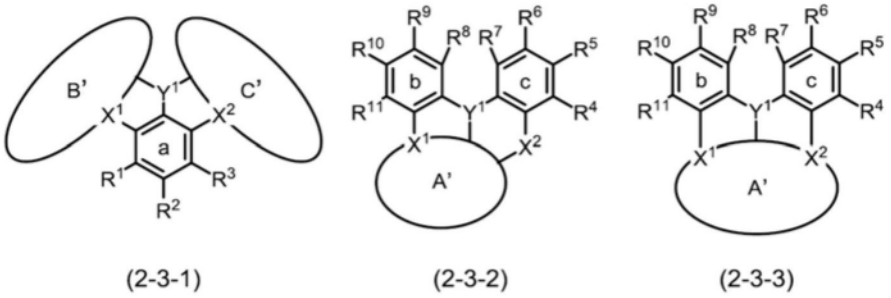
[0169] 此处,通式(1)中的"所述>N-R的R及所述>C(-R)$_2$的R的至少一个通过连结基或单键而与所述A环、B环及C环的至少一个键结"的规定对应于通式(2)中"所述>N-R的R及所述>C(-R)$_2$的R的至少一个通过-O-、-S-、-C(-R)$_2$-或单键而与所述a环、b环及c环的至少一个键结"的规定。

[0170] 所述规定可由如下的化合物来表现,所述化合物由下述式(2-3-1)表示、且具有X^1或X^2被导入至缩合环B'及缩合环C'中的环结构。即,例如为具有其他环以导入X^1(或X^2)的方式对于作为通式(2)中的b环(或c环)的苯环进行缩合而形成的B'环(或C'环)的化合物。所形成的缩合环B'(或缩合环C')例如为吩噁嗪环、吩噻嗪环或吖啶环。

[0171] 另外,所述规定也可由如下的化合物来表现,所述化合物由下述式(2-3-2)或式

(2-3-3)表示、且具有X^1及X^2的至少一个被导入至缩合环A'中的环结构。即,例如为具有其他环以导入X^1(或X^2或者X^1及X^2)的方式对于作为通式(2)中的a环的苯环进行缩合而形成的A'环的化合物。所形成的缩合环A'例如为吩噁嗪环、吩噻嗪环或吖啶环。

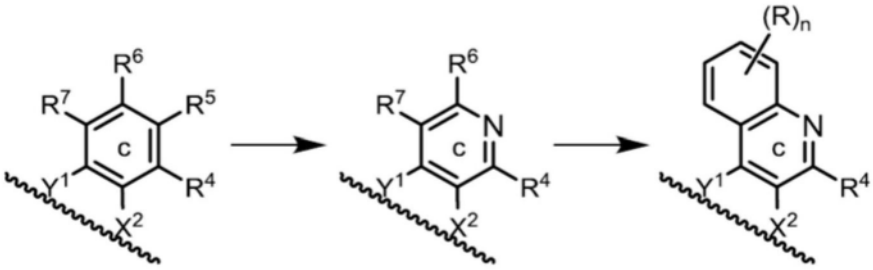
[0172] [化15]

[0173] 

(2-3-1) (2-3-2) (2-3-3)

[0174] 式(2)中,a环、b环及c环中的任意的"-C(-R)=”(此处,R为式(2)中的R^1~R^{11})可被取代为"-N=”。

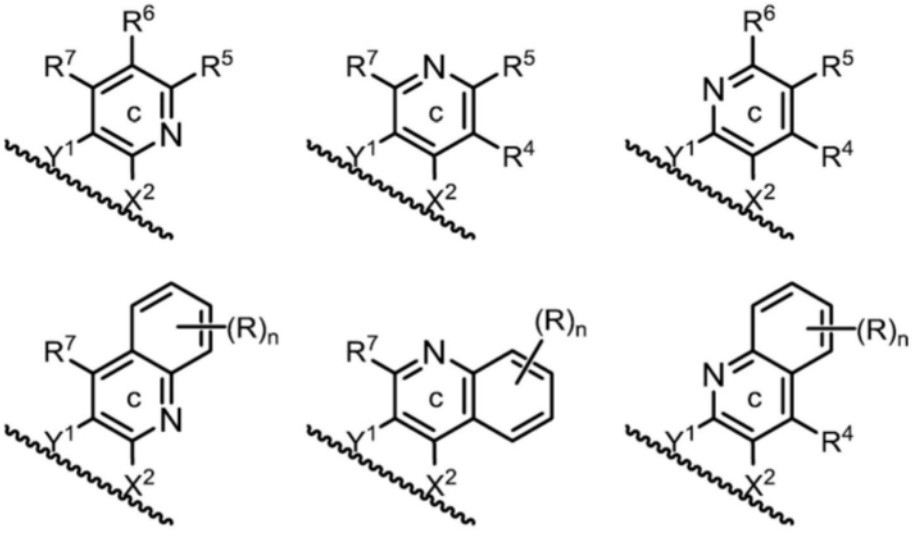
[0175] [化16]

[0176] 

[0177] 如上所示,例如c环中的"-C(-R^5)=”的部位可被取代为"-N=”,如此,在式(2)中表示为苯环的c环可变化为吡啶环、嘧啶环、哒嗪环、吡嗪环、其他含氮杂芳基环。另外,如上所述,在在c环上存在邻接的基的情况下(所述式中为R^6及R^7),这些键结并与c环一同形成杂芳基环(所述式中为喹啉环),所形成的环也可进而被取代(由n个R表示)。

[0178] 此外,也存在以下的变形例。

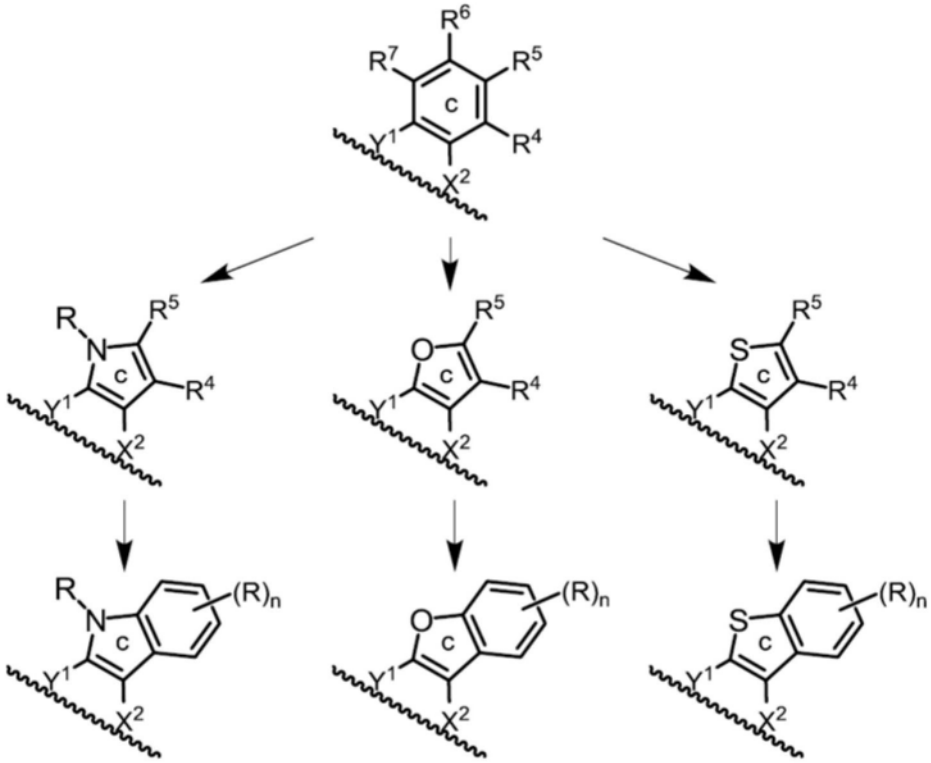
[0179] [化17]

[0180] 

[0181] 对于其他部位被取代为"-N=”的情况或者a环或b环发生了变化的情况而言也相同。

[0182] 式(2)中,a环、b环及c环中的任意的“-C(-R)=C(-R)-”(此处,R为式(2)中的R^1~R^{11})可被取代为“-N(-R)-”、“-O-”或“-S-”,所述“-N(-R)-”的R为芳基、烷基或环烷基。再者,关于此处所列举的取代基的详细内容,将在后汇总叙述。

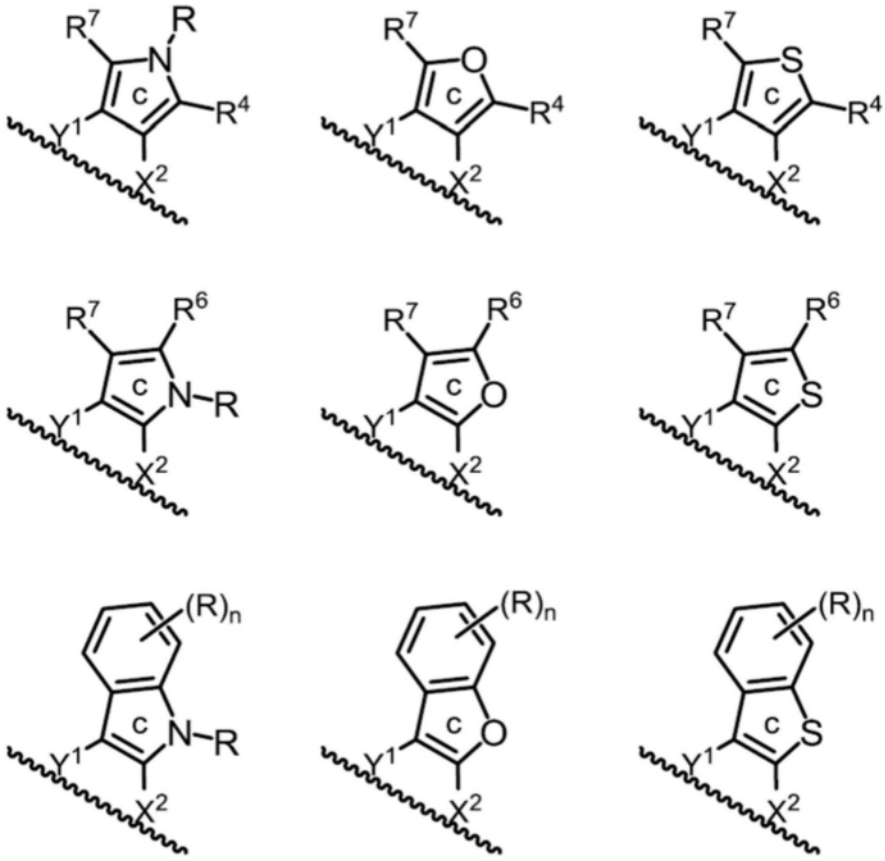
[0183] [化18]

[0184] 

[0185] 如上所示,例如c环中的“-C(-R^7)=C(-R^6)-”的部位可被取代为“-N(-R)-”、“-O-”或“-S-”,如此,在式(2)中表示为苯环的c环可变化为R取代的吡咯环、呋喃环、噻吩环、其他含氮/氧/硫杂芳基环。另外,如上所述,于在c环上存在邻接的基的情况下(所述式中为R^4及R^5),这些键结并与c环一同形成杂芳基环(所述式中为R取代的吲哚环、苯并呋喃环或苯并噻吩环),所形成的环也可进而被取代(由n个R表示)。

[0186] 此外,也存在以下的变形例。

[0187] [化19]

[0188] 

[0189] 对于其他部位被取代为“-N(-R)-”、“-O-”或“-S-”或者a环或b环发生了变化的情况而言也相同。

[0190] 再者,所述式(2-1)、式(2-2)、式(2-3-1)、式(2-3-2)及式(2-3-3)的说明中,将a环、b环及c环作为苯环来进行说明,对于a环～c环变化为含氮杂芳基环(6元环或5元环)或含氧/硫杂芳基环(5元环)的情况而言也相同。

[0191] 作为通式(1)的A环、B环及C环的“芳基环”例如可列举碳数6～30的芳基环,优选为碳数6～16的芳基环,更优选为碳数6～12的芳基环,特别优选为碳数6～10的芳基环。再者,所述“芳基环”对应于通式(2)中所规定的“R^1～R^{11}中的邻接的基彼此键结并与a环、b环或c环一同形成的芳基环”,另外,a环(或b环、c环)已包含碳数6的苯环,因此,5元环在其中进行缩合而成的缩合环的合计碳数9成为下限碳数。

[0192] 作为具体的“芳基环”,可列举:作为单环系的苯环,作为二环系的联苯环,作为缩合二环系的萘环,作为三环系的联三苯环(间联三苯基、邻联三苯基、对联三苯基),作为缩合三环系的苊环、芴环、非那烯环、菲环、蒽环,作为缩合四环系的三亚苯环、芘环、稠四苯(naphthacene)环,作为缩合五环系的苉环、稠五苯(pentacene)环等。

[0193] 作为通式(1)的A环、B环及C环的“杂芳基环”例如可列举碳数2～30的杂芳基环,优选为碳数2～25的杂芳基环,更优选为碳数2～20的杂芳基环,进而优选为碳数2～15的杂芳基环,特别优选为碳数2～10的杂芳基环。另外,作为“杂芳基环”,例如可列举除碳以外含有1个～5个选自氧、硫及氮中的杂原子作为环构成原子的杂环等。再者,所述“杂芳基环”对应于通式(2)中所规定的“R^1～R^{11}中的邻接的基彼此键结并与a环、b环或c环一同形成的杂芳基环”,另外,a环(或b环、c环)已包含碳数6的苯环,因此,5元环在其中进行缩合而成的缩合环的合计碳数6成为下限碳数。

[0194] 作为具体的“杂芳基环”,例如可列举:吡咯环、噁唑环、异噁唑环、噻唑环、异噻唑环、咪唑环、噁二唑环、噻二唑环、三唑环、四唑环、吡唑环、吡啶环、嘧啶环、哒嗪环、吡嗪环、三嗪环、吲哚环、异吲哚环、1H-吲唑环、苯并咪唑环、苯并噁唑环、苯并噻唑环、1H-苯并三唑环、喹啉环、异喹啉环、噌啉(cinnoline)环、喹唑啉环、喹噁啉环、菲咯啉环、酞嗪环、萘啶环、嘌呤环、蝶啶环、咔唑环、吖啶环、吩噁噻环、吩噁嗪环、吩噻嗪环、吩嗪环、环戊基硼酸(phenazasiline)环、吲嗪环、呋喃环、苯并呋喃环、异苯并呋喃环、二苯并呋喃环、萘并苯并呋喃环、噻吩环、苯并噻吩环、异苯并噻吩环、二苯并噻吩环、萘并苯并噻吩环、苯并磷杂环戊二烯(benzophosphole)环、二苯并磷杂环戊二烯环、苯并磷杂环戊二烯氧化物环、二苯并磷杂环戊二烯氧化物环、呋咱(furazan)环、噻蒽环、吲哚并咔唑环、苯并吲唑并咔唑环、苯并苯并吲哚并咔唑环、咪唑啉环、噁唑啉环等。

[0195] 所述“芳基环”或“杂芳基环”中的至少一个氢可由作为第一取代基的经取代或未经取代的“芳基”、经取代或未经取代的“杂芳基”、经取代或未经取代的“二芳基氨基”、经取代或未经取代的“二杂芳基氨基”、经取代或未经取代的“芳基杂芳基氨基”、经取代或未经取代的“二芳基硼基(两个芳基可经由单键或连结基而键结)”、经取代或未经取代的“烷基”、经取代或未经取代的“环烷基”、经取代或未经取代的“烷氧基”、经取代或未经取代的“芳氧基”或者经取代的“硅烷基”取代,作为所述第一取代基的“芳基”或“杂芳基”、“二芳基氨基”的芳基、“二杂芳基氨基”的杂芳基、“芳基杂芳基氨基”的芳基与杂芳基、“二芳基硼基”的芳基、及“芳氧基”的芳基可列举所述“芳基环”或“杂芳基环”的一价基。

[0196] 另外,作为第一取代基的“烷基”可为直链及分支链的任一种,例如可列举碳数1~24的直链烷基或碳数3~24的分支链烷基。优选为碳数1~18的烷基(碳数3~18的分支链烷基),更优选为碳数1~12的烷基(碳数3~12的分支链烷基),进而优选为碳数1~6的烷基(碳数3~6的分支链烷基),特别优选为碳数1~5的烷基(碳数3~5的分支链烷基)、碳数1~4的烷基(碳数3~4的分支链烷基)。

[0197] 作为具体的烷基,可列举:甲基、乙基、正丙基、异丙基、正丁基、异丁基、仲丁基、叔丁基、正戊基、异戊基、新戊基、叔戊基(t-amyl)、正己基、1-甲基戊基、3,3-二甲基丁基、2-乙基丁基、正庚基、1-甲基己基、正辛基、叔辛基(1,1,3,3-四甲基丁基)、1-甲基庚基、2-乙基己基、2-丙基戊基、正壬基、2,2-二甲基庚基、2,6-二甲基-4-庚基、3,5,5-三甲基己基、正癸基、正十一基、1-甲基癸基、正十二基、正十三基、1-己基庚基、正十四基、正十五基、正十六基、正十七基、正十八基、正二十基等。

[0198] 另外,例如也可列举:1-乙基-1-甲基丙基、1,1-二乙基丙基、1,1-二甲基丁基、1-乙基-1-甲基丁基、1,1,4-三甲基戊基、1,1,2-三甲基丙基、1,1-二甲基辛基、1,1-二甲基戊基、1,1-二甲基庚基、1,1,5-三甲基己基、1-乙基-1-甲基己基、1-乙基-1,3-二甲基丁基、1,1,2,2-四甲基丙基、1-丁基-1-甲基戊基、1,1-二乙基丁基、1-乙基-1-甲基戊基、1,1,3-三甲基丁基、1-丙基-1-甲基戊基、1,1,2-三甲基丙基、1-乙基-1,2,2-三甲基丙基、1-丙基-1-甲基丁基、1,1-二甲基己基等。

[0199] 另外,作为第一取代基的“环烷基”可列举:碳数3~24的环烷基、碳数3~20的环烷基、碳数3~16的环烷基、碳数3~14的环烷基、碳数3~12的环烷基、碳数5~10的环烷基、碳数5~8的环烷基、碳数5~6的环烷基、碳数5的环烷基等。

[0200] 作为具体的环烷基,可列举:环丙基、环丁基、环戊基、环己基、环庚基、环辛基、环

壬基、环癸基、以及这些的碳数1～4或碳数1～5的烷基(尤其是甲基)取代物、或降冰片烯基、双环[1.0.1]丁基、双环[1.1.1]戊基、双环[2.0.1]戊基、双环[1.2.1]己基、双环[3.0.1]己基、双环[2.1.2]庚基、双环[2.2.2]辛基、金刚烷基、双金刚烷基、十氢萘基(decahydronaphthalenyl)、十氢薁基(decahydroazulenyl)等。

[0201] 另外,作为第一取代基的“烷氧基”例如可列举:碳数1～24的直链的烷氧基或碳数3～24的分支链的烷氧基。优选为碳数1～18的烷氧基(碳数3～18的分支链的烷氧基),更优选为碳数1～12的烷氧基(碳数3～12的分支链的烷氧基),进而优选为碳数1～6的烷氧基(碳数3～6的分支链的烷氧基),特别优选为碳数1～5的烷氧基(碳数3～5的分支链的烷氧基)、碳数1～4的烷氧基(碳数3～4的分支链的烷氧基)。

[0202] 作为具体的烷氧基,可列举:甲氧基、乙氧基、丙氧基、异丙氧基、正丁氧基、异丁氧基、仲丁氧基、叔丁氧基、叔戊氧基(t-amyloxy)、正戊氧基、异戊氧基、新戊氧基、叔戊氧基(t-pentyloxy)、正己氧基、1-甲基戊氧基、3,3-二甲基丁氧基、2-乙基丁氧基、正庚氧基、1-甲基己氧基、正辛氧基、叔辛氧基、1-甲基庚氧基、2-乙基己氧基、2-丙基戊氧基、正壬氧基、2,2-二甲基庚氧基、2,6-二甲基-4-庚氧基、3,5,5-三甲基己氧基、正癸氧基、正十一烷氧基、1-甲基癸氧基、正十二烷氧基、正十三烷氧基、1-己基庚氧基、正十四烷氧基、正十五烷氧基、正十六烷氧基、正十七烷氧基、正十八烷氧基、正二十烷氧基等。

[0203] 另外,作为第一取代基的“经取代的硅烷基”例如可列举:作为由芳基、烷基及环烷基的至少一个取代的硅烷基的、三芳基硅烷基、三烷基硅烷基、三环烷基硅烷基、二烷基环烷基硅烷基或烷基二环烷基硅烷基。

[0204] 作为“三芳基硅烷基”,可列举硅烷基中的三个氢分别独立地由芳基取代的基,所述芳基可引用作为所述第一取代基中的“芳基”而说明的基。

[0205] 具体的“三芳基硅烷基”例如为三苯基硅烷基、二苯基单萘基硅烷基、单苯基二萘基硅烷基或三萘基硅烷基等。

[0206] 作为“三烷基硅烷基”,可列举硅烷基中的三个氢分别独立地由烷基取代的基,所述烷基可引用作为所述第一取代基中的“烷基”而说明的基。对于进行取代而言优选的烷基为碳数1～5或碳数1～4的烷基,具体而言,可列举:甲基、乙基、丙基、异丙基、丁基、仲丁基、叔丁基、环丁基等。

[0207] 作为具体的三烷基硅烷基,可列举:三甲基硅烷基、三乙基硅烷基、三丙基硅烷基、三异丙基硅烷基、三丁基硅烷基、三-仲丁基硅烷基、三-叔丁基硅烷基、乙基二甲基硅烷基、丙基二甲基硅烷基、异丙基二甲基硅烷基、丁基二甲基硅烷基、仲丁基二甲基硅烷基、叔丁基二甲基硅烷基、甲基二乙基硅烷基、丙基二乙基硅烷基、异丙基二乙基硅烷基、丁基二乙基硅烷基、仲丁基二乙基硅烷基、叔丁基二乙基硅烷基、甲基二丙基硅烷基、乙基二丙基硅烷基、丁基二丙基硅烷基、仲丁基二丙基硅烷基、叔丁基二丙基硅烷基、甲基二异丙基硅烷基、乙基二异丙基硅烷基、丁基二异丙基硅烷基、仲丁基二异丙基硅烷基、叔丁基二异丙基硅烷基等。

[0208] 作为“三环烷基硅烷基”,可列举硅烷基中的三个氢分别独立地由环烷基取代的基,所述环烷基可引用作为所述第一取代基中的“环烷基”而说明的基。对于进行取代而言优选的环烷基为碳数5～10的环烷基,具体而言,可列举:环戊基、环己基、环庚基、环辛基、环壬基、环癸基、双环[1.1.1]戊基、双环[2.0.1]戊基、双环[1.2.1]己基、双环[3.0.1]己

基、双环[2.1.2]庚基、双环[2.2.2]辛基、金刚烷基、十氢萘基、十氢薁基等。

[0209] 作为具体的三环烷基硅烷基，可列举三环戊基硅烷基、三环己基硅烷基等。

[0210] 作为两个烷基与一个环烷基取代而成的二烷基环烷基硅烷基、及一个烷基与两个环烷基取代而成的烷基二环烷基硅烷基的具体例，可列举：选自所述具体的烷基及环烷基中的基取代而成的硅烷基。

[0211] 另外，作为第一取代基的“二芳基硼基”中的“芳基”，可引用所述芳基的说明。另外，所述两个芳基可经由单键或连结基(例如>C(-R)$_2$、>O、>S或>N-R)而键结。此处，>C(-R)$_2$及>N-R的R为氢(仅在为>C(-R)$_2$时)、芳基、杂芳基、二芳基氨基、烷基、环烷基、烷氧基或芳氧基(以上为第一取代基)，在所述第一取代基上也可进而取代有芳基、杂芳基、烷基或环烷基(以上为第二取代基)，作为这些基的具体例，可引用作为所述第一取代基的芳基、杂芳基、二芳基氨基、烷基、环烷基、烷氧基或芳氧基的说明。

[0212] 作为第一取代基的经取代或未经取代的“芳基”、经取代或未经取代的“杂芳基”、经取代或未经取代的“二芳基氨基”、经取代或未经取代的“二杂芳基氨基”、经取代或未经取代的“芳基杂芳基氨基”、经取代或未经取代的“二芳基硼基(两个芳基可经由单键或连结基而键结)”、经取代或未经取代的“烷基”、经取代或未经取代的“环烷基”、经取代或未经取代的“烷氧基”、经取代或未经取代的“芳氧基”、或者经取代的“硅烷基”如说明为经取代或未经取代那样，这些中的至少一个氢可由第二取代基取代。作为所述第二取代基，例如可列举芳基、杂芳基、烷基或环烷基，这些的具体例可参照所述“芳基环”或“杂芳基环”的一价基及作为第一取代基的“烷基”或“环烷基”的说明。另外，在作为第二取代基的芳基或杂芳基中，这些中的至少一个氢由苯基等芳基(具体例为以上所述的基)、甲基等烷基(具体例为以上所述的基)或环己基等环烷基(具体例为以上所述的基)取代的结构也包含于作为第二取代基的芳基或杂芳基中。作为其一例，在第二取代基为咔唑基的情况下，9位上的至少一个氢由苯基等芳基、甲基等烷基或环己基等环烷基取代的咔唑基也包含于作为第二取代基的杂芳基中。

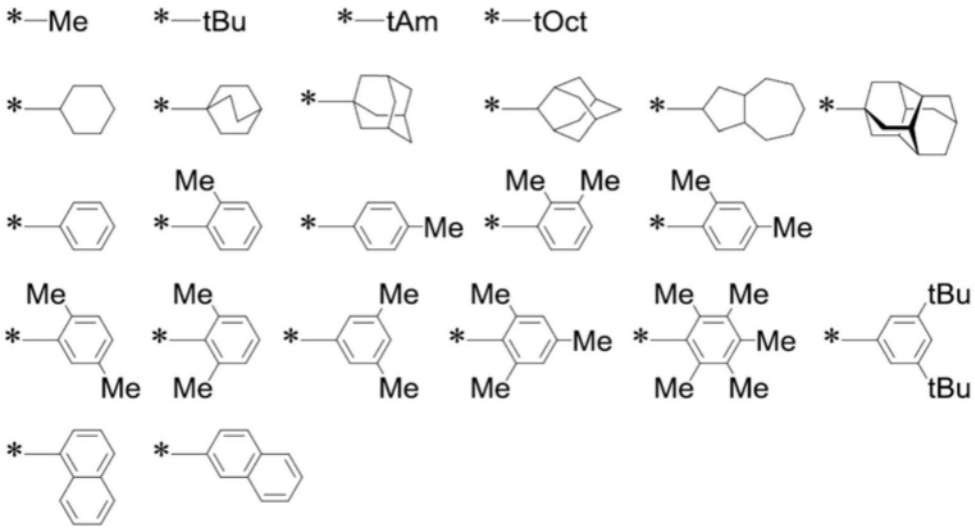
[0213] 作为通式(2)的R^1～R^{11}中的芳基、杂芳基、二芳基氨基的芳基、二杂芳基氨基的杂芳基、芳基杂芳基氨基的芳基与杂芳基、二芳基硼基的芳基、或芳氧基的芳基，可列举通式(1)中所说明的“芳基环”或“杂芳基环”的一价基。另外，作为R^1～R^{11}中的烷基、环烷基或烷氧基，可参照所述通式(1)的说明中的作为第一取代基的“烷基”、“环烷基”或“烷氧基”的说明。另外，作为R^1～R^{11}中的三芳基硅烷基、三烷基硅烷基、三环烷基硅烷基、二烷基环烷基硅烷基或烷基二环烷基硅烷基，可参照所述通式(1)的说明中的作为第一取代基的“经取代的硅烷基”的说明。进而，作为针对这些基的取代基的芳基、杂芳基、烷基或环烷基也相同。另外，对于作为R^1～R^{11}中的邻接的基彼此键结并与a环、b环或c环一同形成芳基环或杂芳基环时的针对这些环的取代基的杂芳基、二芳基氨基、二杂芳基氨基、芳基杂芳基氨基、二芳基硼基(两个芳基可经由单键或连结基而键结)、烷基、环烷基、烷氧基、芳氧基、三芳基硅烷基、三烷基硅烷基、三环烷基硅烷基、二烷基环烷基硅烷基或烷基二环烷基硅烷基、以及作为进一步的取代基的芳基、杂芳基、烷基或环烷基而言也相同。

[0214] 具体而言，可通过第一取代基的结构的位阻性、供电子性及拉电子性来调整发光波长，优选为以下结构式所表示的基，更优选为甲基、叔丁基、叔戊基、叔辛基、苯基、邻甲苯基、对甲苯基、2,4-二甲苯基、2,5-二甲苯基、2,6-二甲苯基、2,4,6-均三甲苯基、二苯基氨

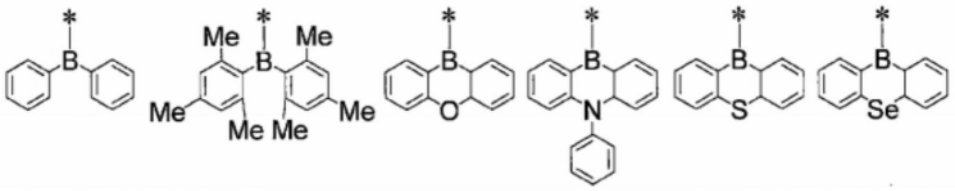
基、二-对甲苯基氨基、双(对(叔丁基)苯基)氨基、咔唑基、3,6-二甲基咔唑基、3,6-二-叔丁基咔唑基及苯氧基，进而优选为甲基、叔丁基、叔戊基、叔辛基、苯基、邻甲苯基、2,6-二甲苯基、2,4,6-均三甲苯基、二苯基氨基、二-对甲苯基氨基、双(对(叔丁基)苯基)氨基、咔唑基、3,6-二甲基咔唑基及3,6-二-叔丁基咔唑基。就合成容易性的观点而言，位阻大者对于选择性合成而言优选，具体而言，优选为叔丁基、叔戊基、叔辛基、邻甲苯基、对甲苯基、2,4-二甲苯基、2,5-二甲苯基、2,6-二甲苯基、2,4,6-均三甲苯基、二-对甲苯基氨基、双(对(叔丁基)苯基)氨基、3,6-二甲基咔唑基及3,6-二-叔丁基咔唑基。

[0215] 下述结构式中，“Me”表示甲基，“tBu”表示叔丁基，“tAm”表示叔戊基，“tOct”表示叔辛基，*表示键结位置。

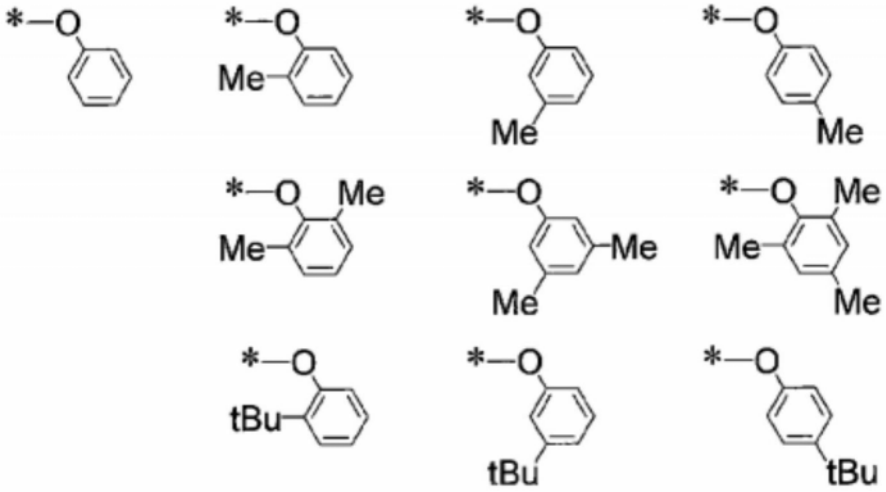
[0216] [化20]

[0217] 

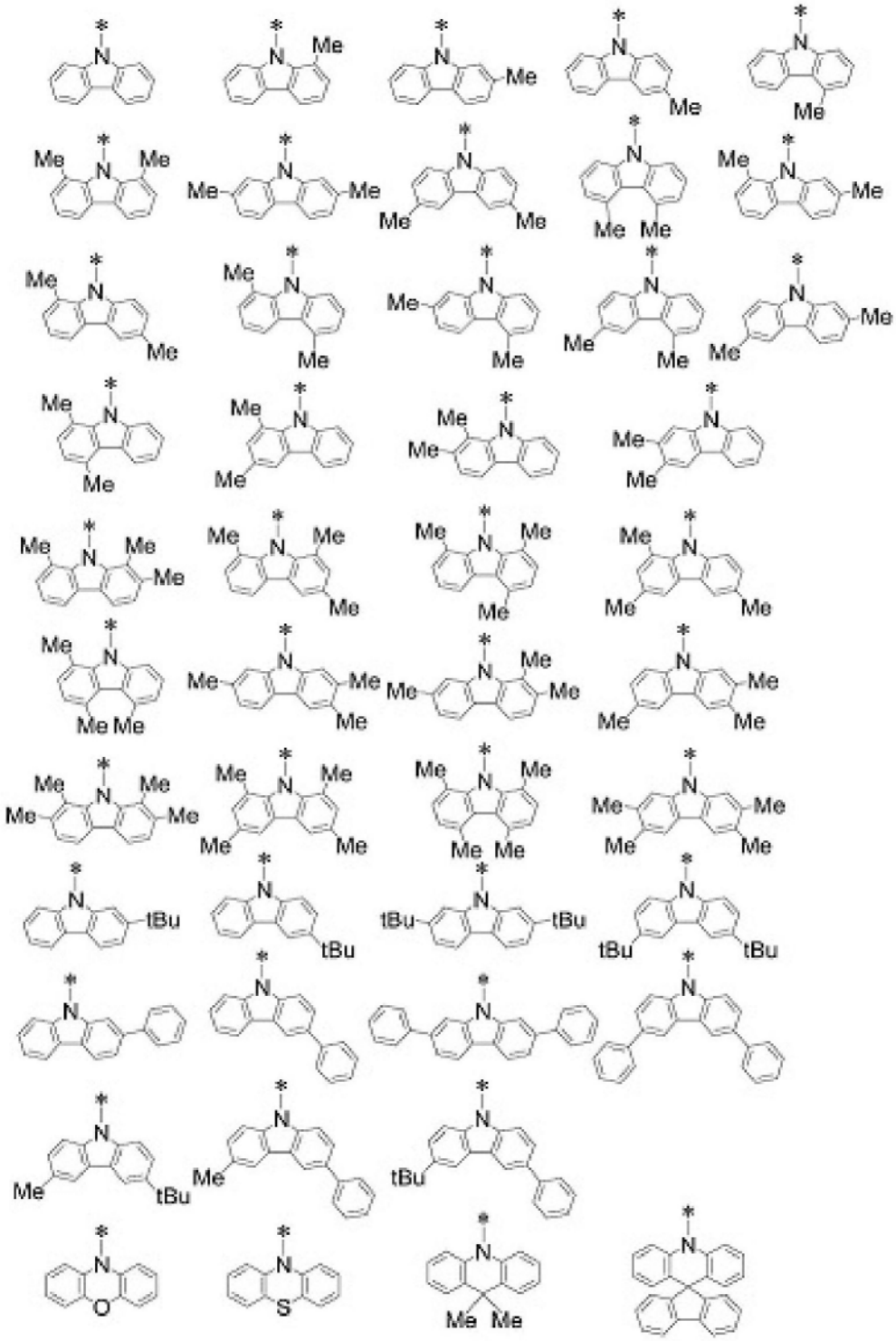
[0218] [化21]

[0219] 

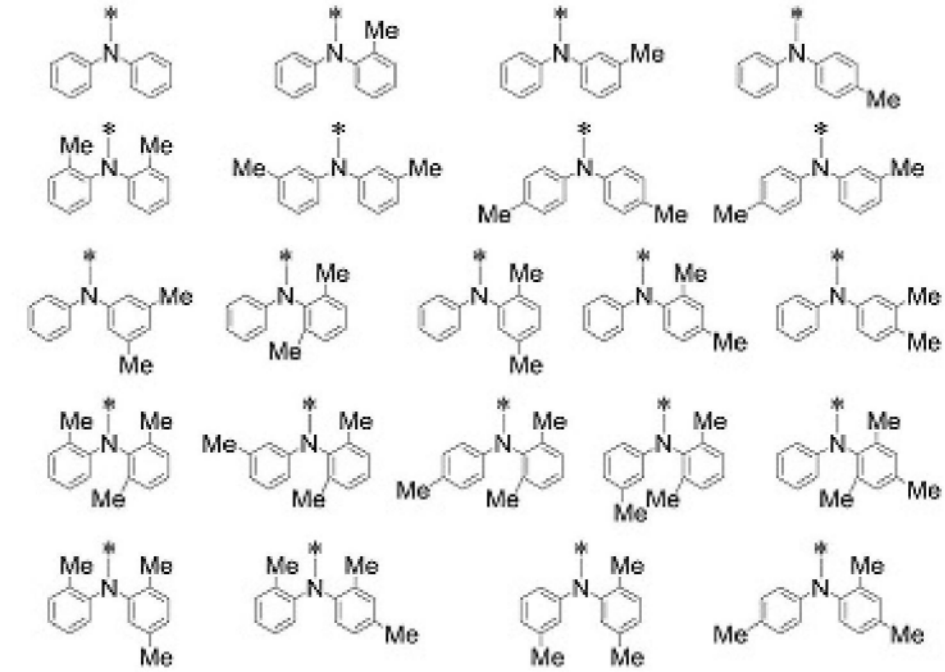
[0220] [化22]

[0221] 

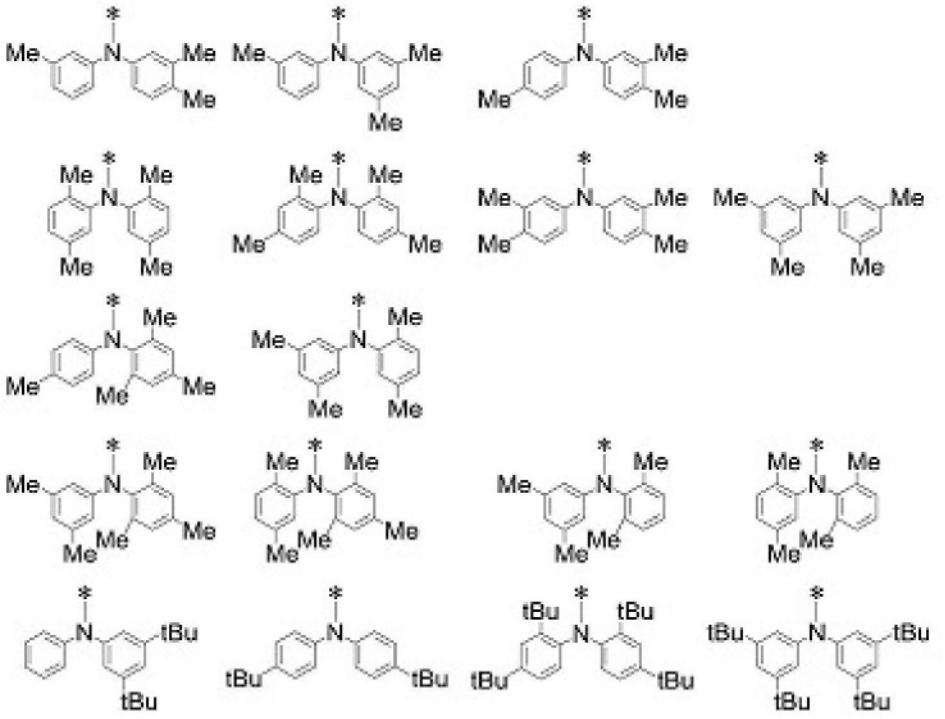
[0222] [化23]

[0223] 

[0224] [化24]



[0225]



[0226] 通式(2)中,可对任意的“-C(-R)=C(-R)-”(此处,R为式(2)中的R^1~R^{11})进行取代的“-N(-R)-”的R为芳基、烷基或环烷基,作为所述芳基、烷基或环烷基,可列举以上所述的基。特别优选为碳数6~10的芳基(例如苯基、萘基等)、碳数1~5或碳数1~4的烷基(例如甲基、乙基等)或者碳数5~10的环烷基(优选为环己基或金刚烷基)。

[0227] 通式(1)的Y^1中的Si-R及Ge-R的R为芳基、烷基或环烷基,作为所述芳基、烷基或环烷基,可列举以上所述的基。特别优选为碳数6~10的芳基(例如苯基、萘基等)、碳数1~5或碳数1~4的烷基(例如甲基、乙基等)或者碳数5~10的环烷基(优选为环己基或金刚烷基)。所述说明也同样适用于通式(2)中的Y^1。

[0228] 通式(1)的X^1及X^2中的>N-R的R为可由所述第二取代基取代的芳基、杂芳基、烷基

或环烷基,所述芳基、杂芳基、烷基或环烷基中的至少一个氢例如可由烷基或环烷基取代。作为所述芳基、杂芳基、烷基或环烷基,可列举以上所述的基。特别优选为碳数6～10的芳基(例如苯基、萘基等)、碳数2～15的杂芳基(例如咔唑基、二苯并呋喃基、二苯并噻吩基等)、碳数1～5或碳数1～4的烷基(例如甲基、乙基等)或者碳数5～10的环烷基(优选为环己基或金刚烷基),更优选为苯基、萘基、咔唑基、二苯并呋喃基或二苯并噻吩基,进而优选为二苯并呋喃基或二苯并噻吩基。另外,二苯并呋喃基或二苯并噻吩基特别优选为由第二取代基取代,具体而言,作为第二取代基,可列举叔丁基、苯基或d5-苯基等,这些取代基优选为在氧原子或硫原子的对位进行取代。所述说明也同样适用于通式(2)中的X^1及X^2。

[0229] 通式(1)的X^1及X^2中的>C(-R)$_2$的R为氢、可由所述第二取代基取代的芳基、烷基或环烷基,芳基中的至少一个氢例如可由烷基取代。作为所述芳基、烷基或环烷基,可列举以上所述的基。特别优选为碳数6～10的芳基(例如苯基、萘基等)、碳数1～5或碳数1～4的烷基(例如甲基、乙基等)或者碳数5～10的环烷基(优选为环己基或金刚烷基)。所述说明也同样适用于通式(2)中的X^1及X^2。

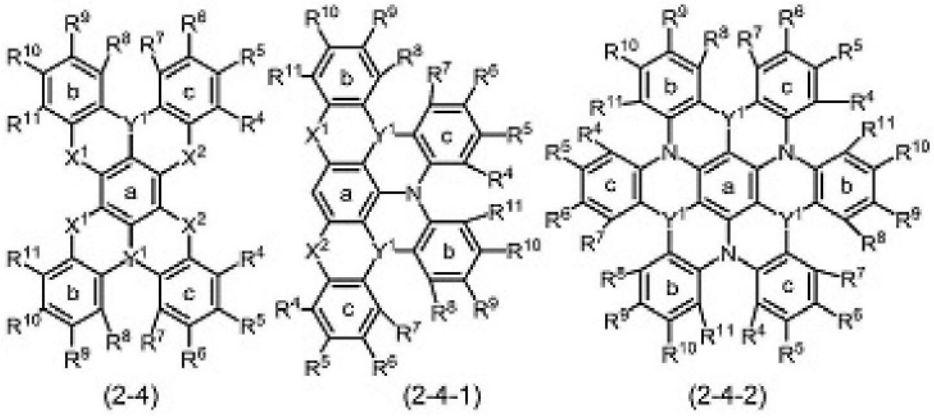
[0230] 作为通式(1)中的连结基的“-C(-R)$_2$-”的R为氢、烷基或环烷基,作为所述烷基或环烷基,可列举以上所述的基。特别优选为碳数1～5或碳数1～4的烷基(例如甲基、乙基等)或者碳数5～10的环烷基(优选为环己基或金刚烷基)。所述说明也同样适用于作为通式(2)中的连结基的“-C(-R)$_2$-”。

[0231] 另外,本申请发明为具有多个通式(1)所表示的单元结构的多环芳香族化合物的多聚体,优选为具有多个通式(2)所表示的单元结构的多环芳香族化合物的多聚体。多聚体优选为二聚体～六聚体,更优选为二聚体～三聚体,特别优选为二聚体。多聚体只要是在一个化合物中具有多个所述单元结构的形态即可,例如除利用单键、碳数1～3的亚烷基、亚苯基、亚萘基等连结基使多个所述单元结构键结而成的形态(连结型多聚体)以外,也可为以由多个单元结构共有所述单元结构中所含的任意的环(A环、B环或C环,a环、b环或c环)的方式进行键结的形态(环共有型多聚体),另外,也可为以所述单元结构中所含的任意的环(A环、B环或C环,a环、b环或c环)彼此进行缩合的方式进行键结的形态(环缩合型多聚体),优选为环共有型多聚体及环缩合型多聚体,更优选为环共有型多聚体。

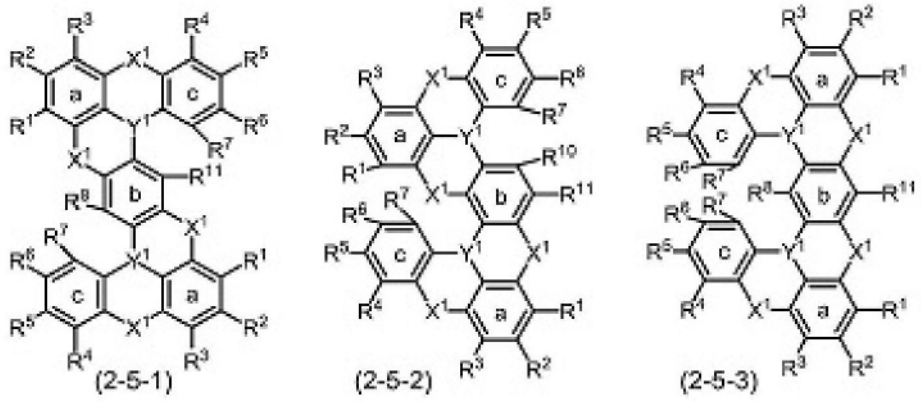
[0232] 作为此种多聚体,例如可列举下述式(2-4)、式(2-4-1)、式(2-4-2)、式(2-5-1)～式(2-5-4)或式(2-6)所表示的多聚体化合物。若以通式(2)进行说明,则下述式(2-4)所表示的多聚体化合物为以共有作为a环的苯环的方式,在一个化合物中具有多个通式(2)所表示的单元结构的多聚体化合物(环共有型多聚体)。另外,若以通式(2)进行说明,则下述式(2-4-1)所表示的多聚体化合物为以共有作为a环的苯环的方式,在一个化合物中具有两个通式(2)所表示的单元结构的多聚体化合物(环共有型多聚体)。另外,若以通式(2)进行说明,则下述式(2-4-2)所表示的多聚体化合物为以共有作为a环的苯环的方式,在一个化合物中具有三个通式(2)所表示的单元结构的多聚体化合物(环共有型多聚体)。另外,若以通式(2)进行说明,则下述式(2-5-1)～式(2-5-4)的任一者所表示的多聚体化合物为以共有作为b环(或c环)的苯环的方式,在一个化合物中具有多个通式(2)所表示的单元结构的多聚体化合物(环共有型多聚体)。另外,若以通式(2)进行说明,则下述式(2-6)所表示的多聚体化合物为以例如作为某一单元结构的b环(或a环、c环)的苯环与作为某一单元结构的b环(或a环、c环)的苯环进行缩合的方式,在一个化合物中具有多个通式(2)所表示的单元结构

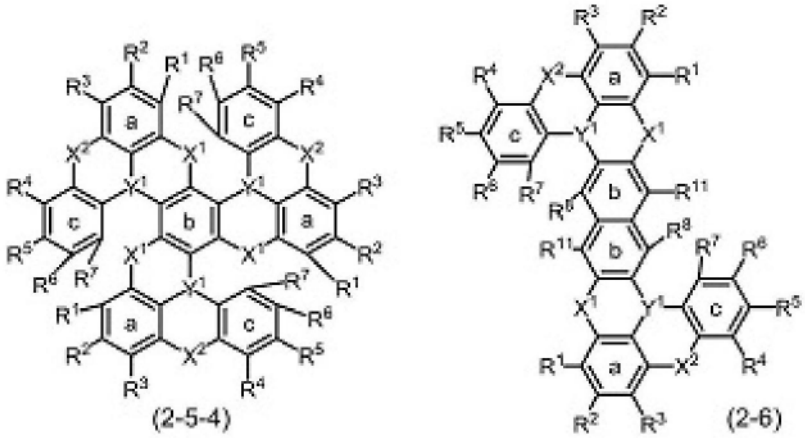
的多聚体化合物(环缩合型多聚体)。

[0233] [化25]



[0234]





[0235] 多聚体化合物可为将式(2-4)、式(2-4-1)或式(2-4-2)所表现的多聚化形态与式(2-5-1)～式(2-5-4)的任一者或式(2-6)所表现的多聚化形态组合而成的多聚体,也可为将式(2-5-1)～式(2-5-4)的任一者所表现的多聚化形态与式(2-6)所表现的多聚化形态组合而成的多聚体,也可为将式(2-4)、式(2-4-1)或式(2-4-2)所表现的多聚化形态与式(2-5-1)～式(2-5-4)的任一者所表现的多聚化形态,及式(2-6)所表现的多聚化形态组合而成的多聚体。

[0236] 另外,通式(1)或通式(2)所表示的多环芳香族化合物及其多聚体的化学结构中的氢的全部或一部分也可为氘、氰基或卤素。例如,式(1)中,A环、B环、C环(A环～C环为芳基环或杂芳基环)、针对A环～C环的取代基、Y^1为Si-R或Ge-R时的R(＝烷基、环烷基、芳基)、以及

X^1及X^2为＞N-R或＞C(-R)$_2$时的R(＝烷基、环烷基、芳基)中的氢可由氘、氰基或卤素取代,这些中,可列举芳基或杂芳基中的全部或一部分的氢由氘、氰基或卤素取代的形态。卤素为氟、氯、溴或碘,优选为氟、氯或溴,更优选为氟或氯。

[0237] 另外,本发明的多环芳香族化合物及其多聚体可用作有机元件用材料。作为有机元件,例如可列举:有机电致发光元件、有机场效晶体管或有机薄膜太阳电池等。尤其,在有机电致发光元件中,作为发光层的掺杂剂材料,优选为Y^1为B、X^1及X^2为＞N-R的化合物,Y^1为B、X^1为＞O、X^2为＞N-R的化合物,Y^1为B、X^1及X^2为＞O的化合物,作为发光层的主体材料,优选为Y^1为B、X^1为＞O、X^2为＞N-R的化合物,Y^1为B、X^1及X^2为＞O的化合物,作为电子传输材料,可优选地使用Y^1为B、X^1及X^2为＞O的化合物,Y^1为P＝O、X^1及X^2为＞O的化合物。

[0238] 另外,通式(1)或通式(2)所表示的多环芳香族化合物及其多聚体的化学结构中的芳香族环及杂芳香族环的至少一个由至少一个环烷烃缩合。

[0239] 例如,作为A环、B环、C环、a环、b环及c环的芳基环及杂芳基环、作为针对A环～C环的第一取代基及第二取代基的芳基(芳基、二芳基氨基、芳基杂芳基氨基、二芳基硼基或芳氧基中的芳基部分)及杂芳基(杂芳基、二杂芳基氨基或芳基杂芳基氨基中的杂芳基部分)、作为针对a环～c环的第一取代基及第二取代基的芳基(与所述相同)及杂芳基(与所述相同)、作为Y^1即Si-R及Ge-R的R的芳基(与所述相同)、以及作为X^1及X^2即＞N-R及＞C(-R)$_2$的R的芳基(与所述相同)及杂芳基(与所述相同)中的至少一个由至少一个环烷烃缩合。

[0240] 优选为作为A环、B环、C环、a环、b环及c环的芳基环及杂芳基环、作为针对A环～C环的第一取代基的芳基(芳基、二芳基氨基、二芳基硼基或芳氧基中的芳基部分)及杂芳基(杂芳基或二杂芳基氨基中的杂芳基部分)、作为针对a环～c环的第一取代基的芳基(与所述相同)及杂芳基(与所述相同)、以及作为X^1及X^2即＞N-R及＞C(-R)$_2$的R的芳基(与所述相同)及杂芳基(与所述相同)中的至少一个由至少一个环烷烃缩合。

[0241] 更优选为作为A环、B环、C环、a环、b环及c环的芳基环、作为针对A环～C环的第一取代基的芳基(芳基或二芳基氨基中的芳基部分)及杂芳基(杂芳基中的杂芳基部分)、作为针对a环～c环的第一取代基的芳基(与所述相同)及杂芳基(与所述相同)、以及作为X^1及X^2即＞N-R及＞C(-R)$_2$的R的芳基(与所述相同)中的至少一个由至少一个环烷烃缩合。

[0242] 进而优选为作为A环、B环、C环、a环、b环及c环的芳基环、作为针对A环～C环的第一取代基的芳基(芳基或二芳基氨基中的芳基部分)、作为针对a环～c环的第一取代基的芳基(与所述相同)、以及作为X^1及X^2即＞N-R及＞C(-R)$_2$的R的芳基(与所述相同)中的至少一个由至少一个环烷烃缩合。

[0243] 作为“环烷烃”,可列举:碳数3～24的环烷烃、碳数3～20的环烷烃、碳数3～16的环烷烃、碳数3～14的环烷烃、碳数5～10的环烷烃、碳数5～8的环烷烃、碳数5～6的环烷烃、碳数5的环烷烃等。

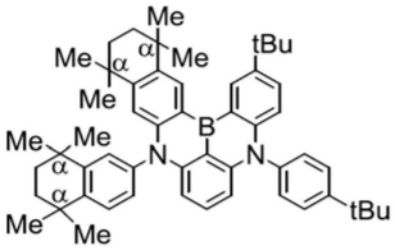
[0244] 作为具体的环烷烃,可列举:环丙烷、环丁烷、环戊烷、环己烷、环庚烷、环辛烷、环壬烷、环癸烷、降冰片烯、双环[1.0.1]丁烷、双环[1.1.1]戊烷、双环[2.0.1]戊烷、双环[1.2.1]己烷、双环[3.0.1]己烷、双环[2.1.2]庚烷、双环[2.2.2]辛烷、金刚烷、双金刚烷、十氢萘、十氢蒽、以及这些的碳数1～5或碳数1～4的烷基(尤其是甲基)取代物、卤素(尤其是氟)取代物及氘取代物等。

[0245] 这些中,例如优选为下述结构式所示的、环烷烃的α位的碳(于在芳香族环或杂芳

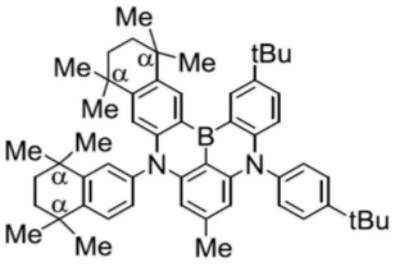
香族环中进行缩合的环烷烃中,与缩合部位的碳邻接的位置的碳)中的至少一个氢被取代的结构,更优选为α位的碳中的两个氢被取代的结构,进而优选为两个α位的碳中的合计四个氢被取代的结构。作为所述取代基,可列举碳数1～5或碳数1～4的烷基(尤其是甲基)取代物、卤素(尤其是氟)取代物及氘取代物等。

[0246] [化26]

[0247]



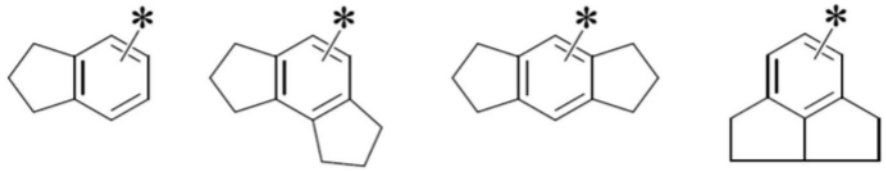
(1-411)



(1-590)

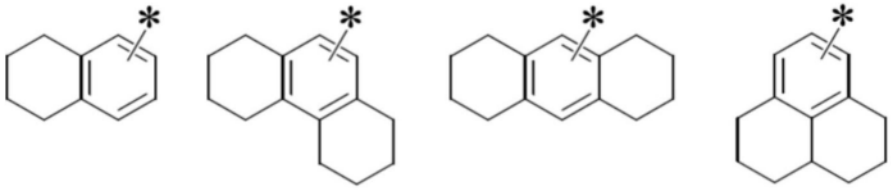
[0248] 在一个芳香族环或杂芳香族环中进行缩合的环烷烃的数量优选为1个～3个,更优选为1个或2个,进而优选为1个。例如,以下示出于一个苯环(苯基)中缩合有一个或多个环烷烃的例子。关于各结构式中的*,在为苯环的情况下是指化合物的骨架结构中所含的苯环,在为苯基的情况下是指在化合物的骨架结构中进行取代的键结键。如式(Cy-1-4)及式(Cy-2-4)那样缩合的环烷烃彼此也可缩合。不论是所缩合的环(基)为苯环(苯基)以外的其他芳香族环或杂芳香族环的情况,还是进行缩合的环烷烃为环戊烷或环己烷以外的其他环烷烃的情况,均相同。

[0249] [化27]



(Cy-1-1) (Cy-1-2) (Cy-1-3) (Cy-1-4)

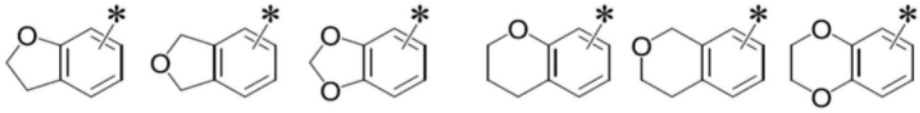
[0250]



(Cy-2-1) (Cy-2-2) (Cy-2-3) (Cy-2-4)

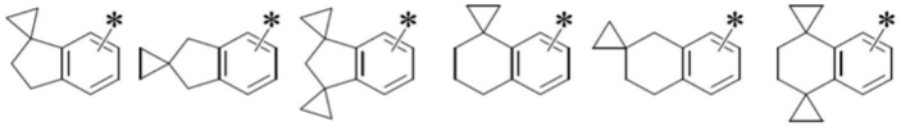
[0251] 环烷烃中的至少一个-CH_2-可由-O-取代。其中,在多个-CH_2-由-O-取代的情况下,邻接的-CH_2-不会由-O-取代。例如,以下示出缩合于一个苯环(苯基)的环烷烃中的一个或多个-CH_2-由-O-取代的例子。关于各结构式中的*,在为苯环的情况下是指化合物的骨架结构中所含的苯环,在为苯基的情况下是指在化合物的骨架结构中进行取代的键结键。不论是所缩合的环(基)为苯环(苯基)以外的其他芳香族环或杂芳香族环的情况,还是进行缩合的环烷烃为环戊烷或环己烷以外的其他环烷烃的情况,均相同。

[0252] [化28]

[0253] 

[0254] 环烷烃中的至少一个氢可被取代,作为所述取代基,例如可列举芳基、杂芳基、二芳基氨基、二杂芳基氨基、芳基杂芳基氨基、二芳基硼基(两个芳基可经由单键或连结基而键结)、烷基、环烷基、烷氧基、芳氧基、经取代的硅烷基、氘、氰基或卤素,这些详细情况可引用所述第一取代基的说明。这些取代基中,优选为烷基(例如碳数1~6的烷基)、环烷基(例如碳数3~14的环烷基)、卤素(例如氟)及氘等。另外,环烷基进行取代时,可为形成螺环结构的取代形态,例如,以下示出于缩合于一个苯环(苯基)中的环烷烃中形成螺环结构的例子。关于各结构式中的*,在为苯环的情况下是指化合物的骨架结构中所含的苯环,在为苯基的情况下是指在化合物的骨架结构中进行取代的键结键。

[0255] [化29]

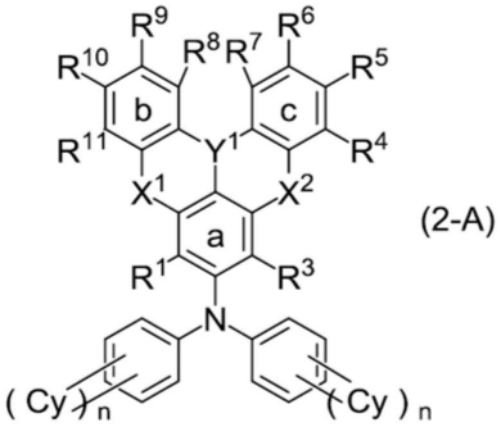
[0256] 

[0257] 作为环烷烃缩合的其他形态,可列举:通式(1)或通式(2)所表示的多环芳香族化合物及其多聚体例如被由环烷烃缩合的二芳氨基(缩合至其芳基部分)、由环烷烃缩合的咔唑基(缩合至其苯环部分)或由环烷烃缩合的苯并咔唑基(缩合至其苯环部分)取代的例子。关于“二芳基氨基”,可列举作为所述“第一取代基”而说明的基。

[0258] 另外,作为更具体的例子,可列举通式(2)所表示的多环芳香族化合物及其多聚体中的R^2为由环烷烃缩合的二芳氨基(缩合至其芳基部分)或由环烷烃缩合的咔唑基(缩合至其苯环部分)的例子。

[0259] 作为其一例,可列举下述通式(2-A)所表示的多环芳香族化合物、或具有多个下述通式(2-A)所表示的结构的多环芳香族化合物的多聚体。下述结构式中的Cy为环烷烃,n分别独立地为1~3(优选为1)的整数,“=(Cy)n”是指n个环烷烃在作为缩合对象的结构的任意位置进行缩合(下述结构式中为n个环烷烃在苯环(苯基)中进行缩合),结构式中的各符号的定义与通式(2)中的各符号的定义相同。

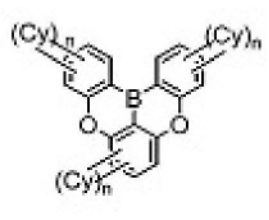
[0260] [化30]

[0261] 

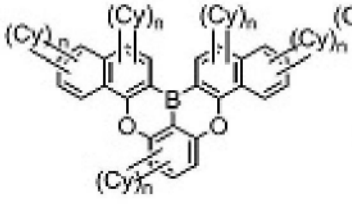
(2-A)

[0262] 具体而言,可列举以下的式“1-Cy-(1)”～式“1-Cy-(4401)”所表示的化合物。下述式中的“Cy”表示环烷烃,n分别独立地0～最大可缩合的数(其中,不会全部的n成为0),优选为0～2(其中,不会全部的n成为0),更优选为1,“＝(Cy)n”是指n个环烷烃在作为缩合对象的结构的任意位置进行缩合(例如下述式“1-Cy-(1)”中为n个环烷烃在各苯环的任意位置进行缩合)。再者,下述结构式中的“OPh”表示苯氧基,“Me”表示甲基,各化合物可由所述第一取代基及第二取代基取代。

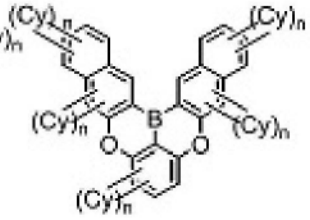
[0263] [化31]



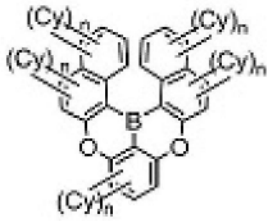
1-Cy-(1)



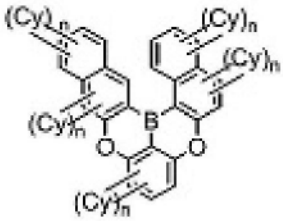
1-Cy-(2)



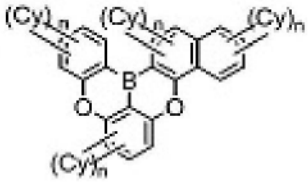
1-Cy-(3)



1-Cy-(4)

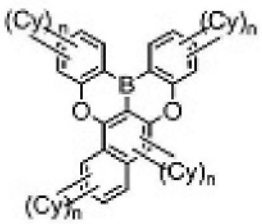


1-Cy-(5)

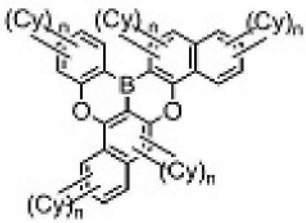


1-Cy-(6)

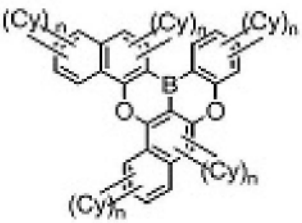
[0264]



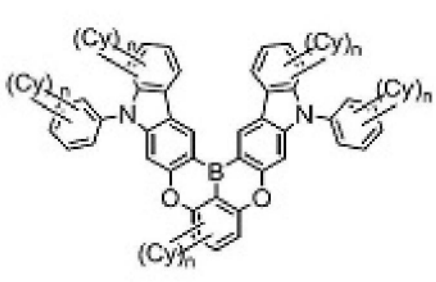
1-Cy-(7)



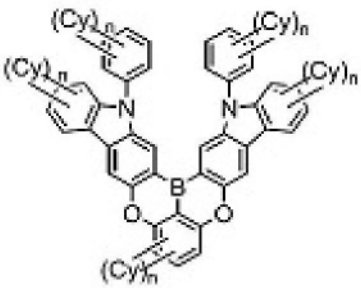
1-Cy-(8)



1-Cy-(9)

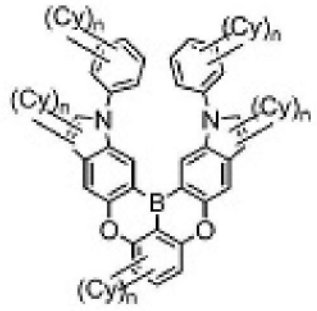


1-Cy-(10)

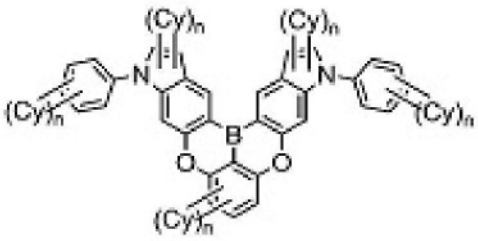


1-Cy-(11)

[0265] [化32]

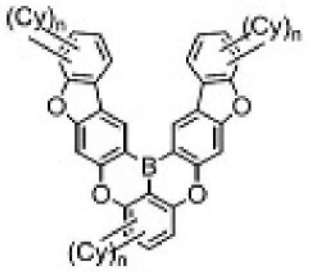


1-Cy-(12)

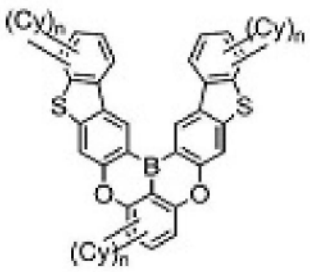


1-Cy-(13)

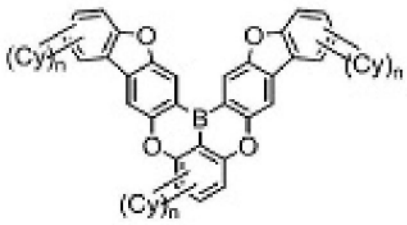
[0266]



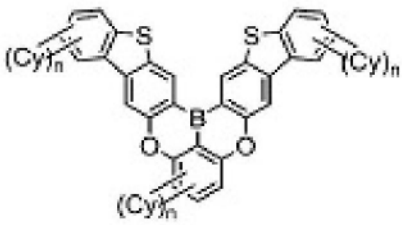
1-Cy-(14)



1-Cy-(15)

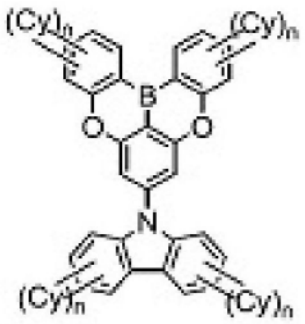


1-Cy-(16)

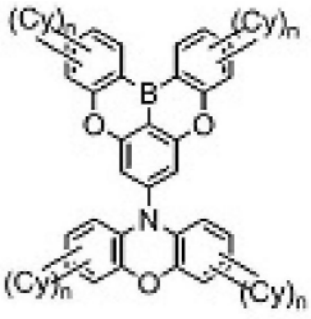


1-Cy-(17)

[0267] [化33]

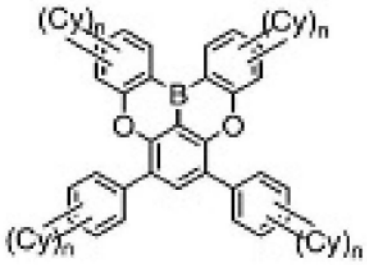


1-Cy-(49)

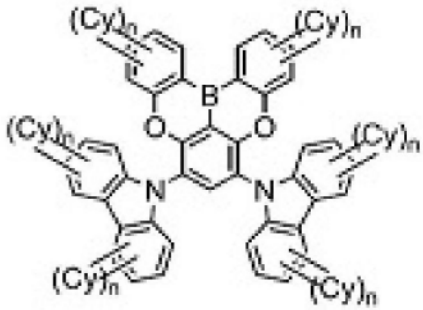


1-Cy-(81)

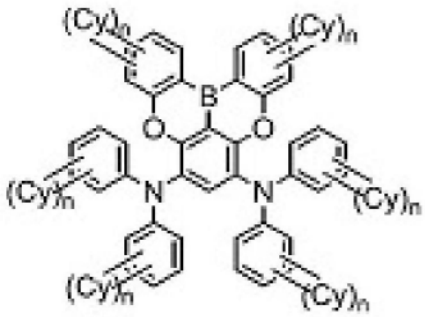
[0268]



1-Cy-(91)

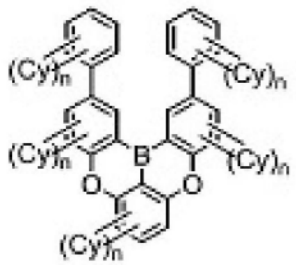


1-Cy-(100)

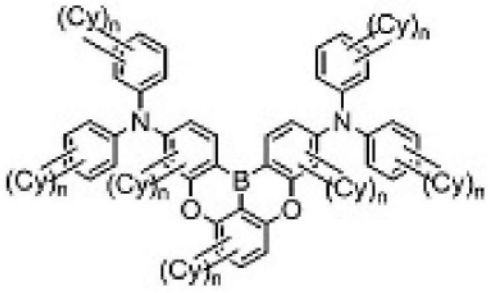


1-Cy-(141)

[0269] [化34]

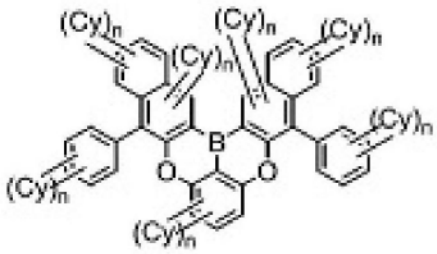


1-Cy-(151)

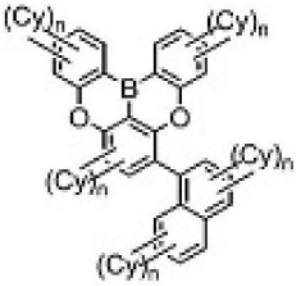


1-Cy-(176)

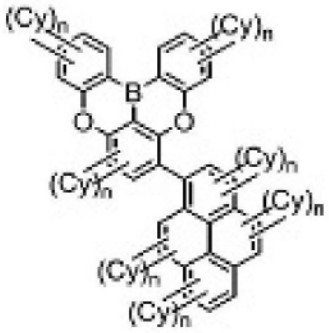
[0270]



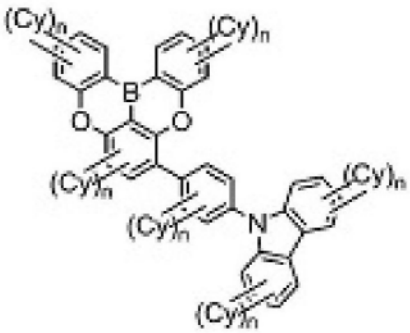
1-Cy-(1271)



1-Cy-(1084)

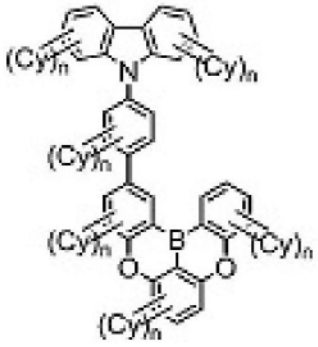


1-Cy-(1090)

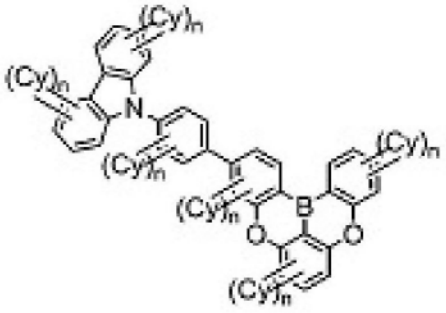


1-Cy-(1092)

[0271] [化35]

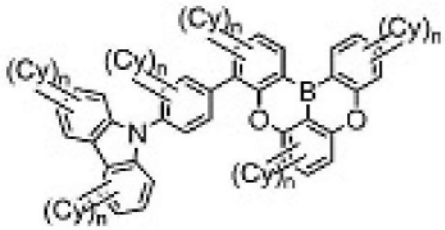


1-Cy-(1101)

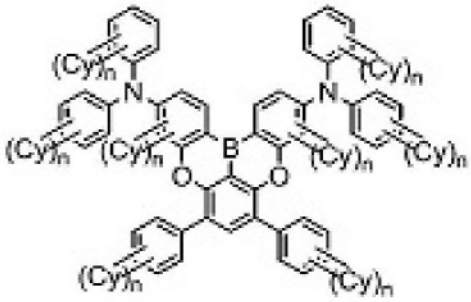


1-Cy-(1102)

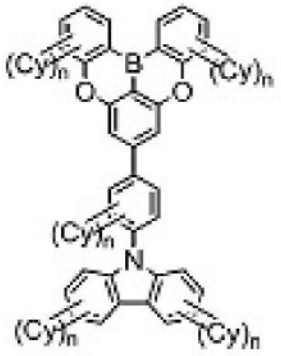
[0272]



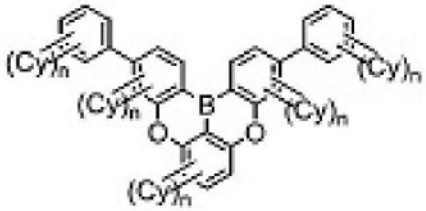
1-Cy-(1103)



1-Cy-(178)

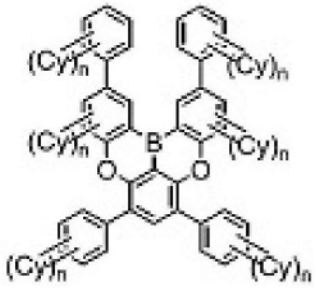


1-Cy-(50)

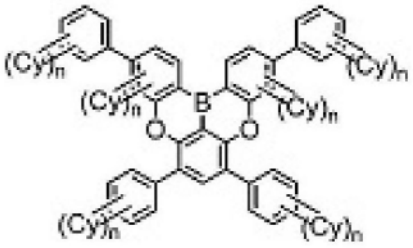


1-Cy-(152)

[0273] [化36]

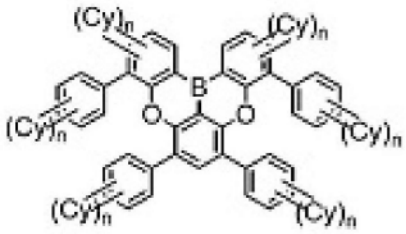


1-Cy-(1048)

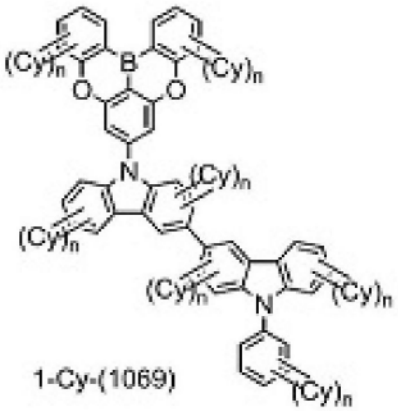


1-Cy-(1049)

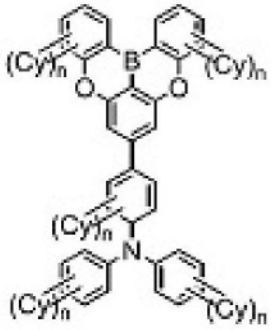
[0274]



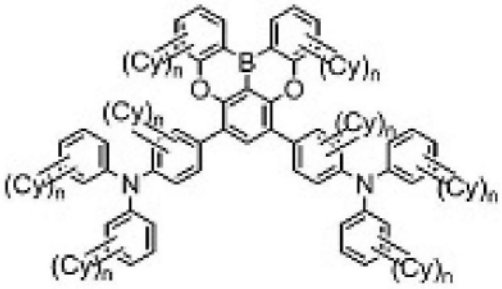
1-Cy-(1050)



1-Cy-(1069)

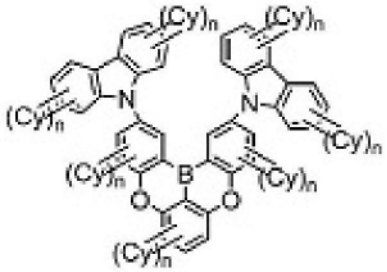


1-Cy-(79)

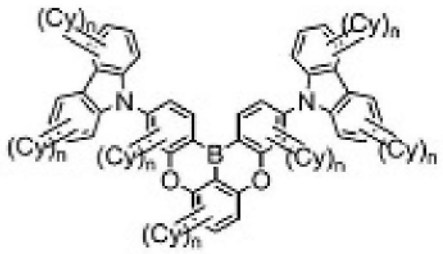


1-Cy-(142)

[0275] [化37]

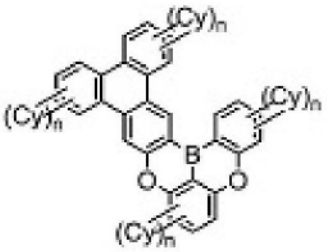


1-Cy-(158)

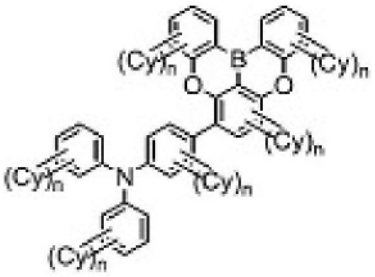


1-Cy-(159)

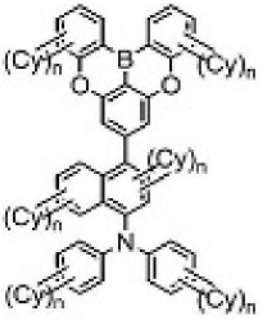
[0276]



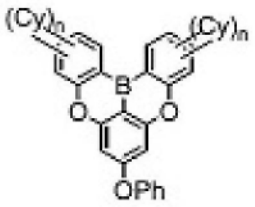
1-Cy-(1006)



1-Cy-(1104)

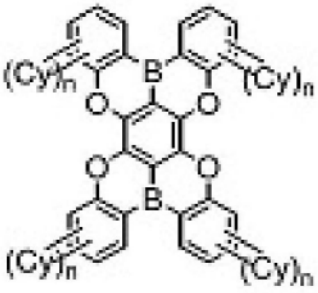


1-Cy-(2305)

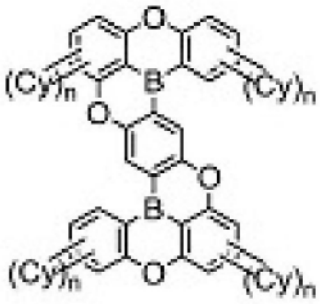


1-Cy-(4401)

[0277] [化38]

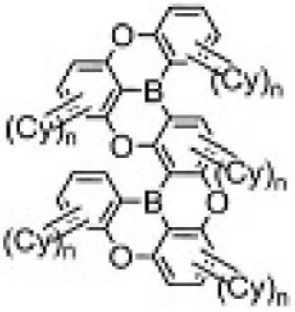


1-Cy-(21)

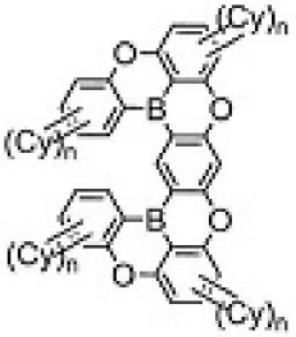


1-Cy-(22)

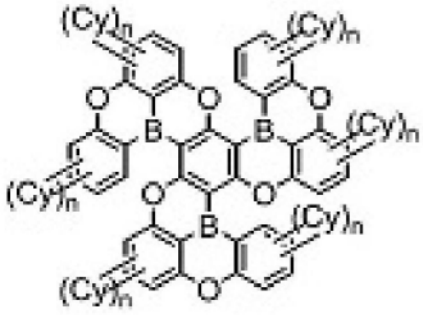
[0278]



1-Cy-(23)

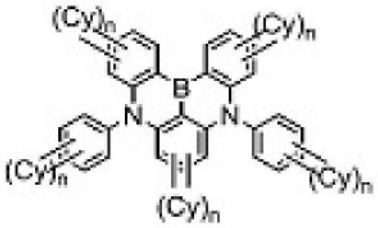


1-Cy-(24)

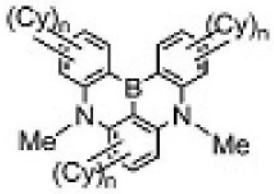


1-Cy-(25)

[0279] [化39]

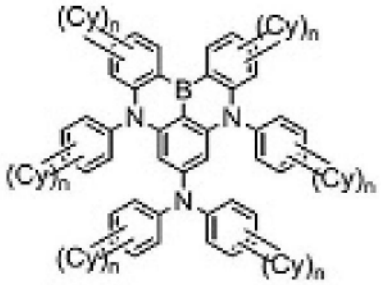


1-Cy-(401)

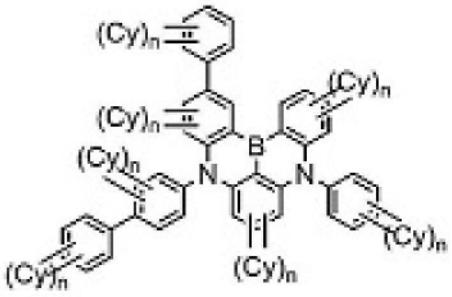


1-Cy-(411)

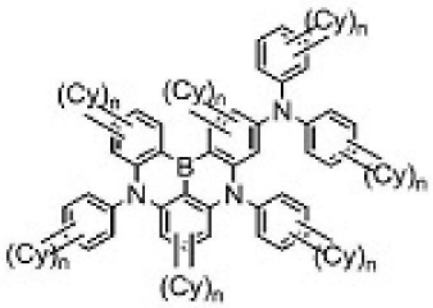
[0280]



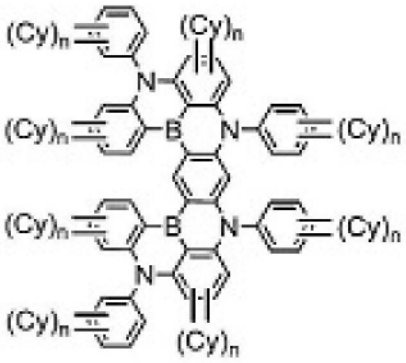
1-Cy-(447)



1-Cy-(1152)

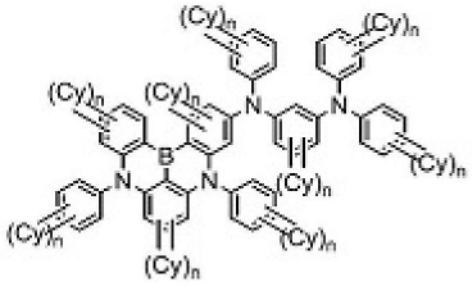


1-Cy-(2623)

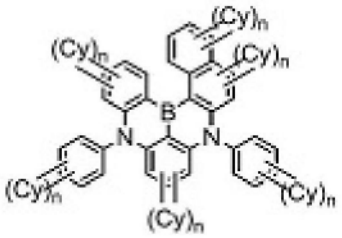


1-Cy-(422)

[0281] [化40]

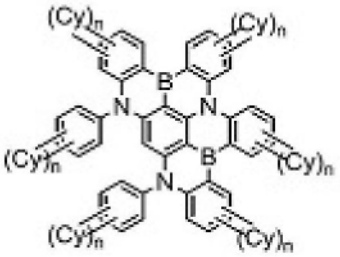


1-Cy-(1159)

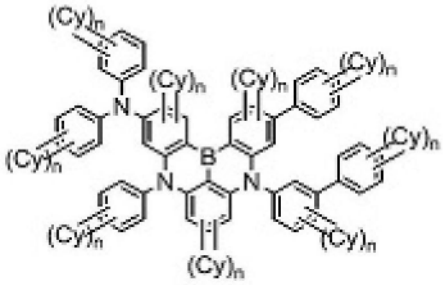


1-Cy-(2657)

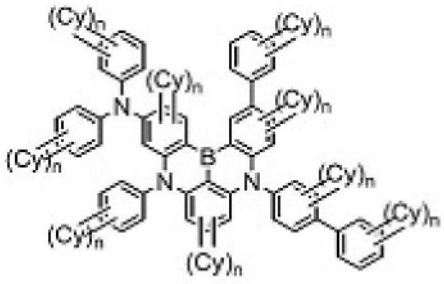
[0282]



1-Cy-(2665)

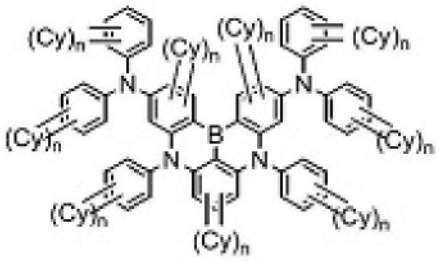


1-Cy-(2676)

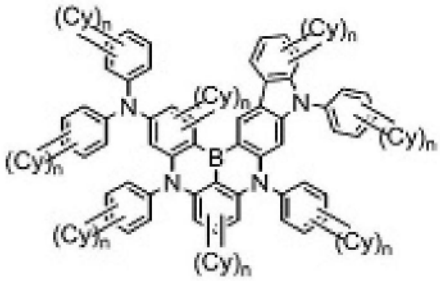


1-Cy-(2679)

[0283] [化41]

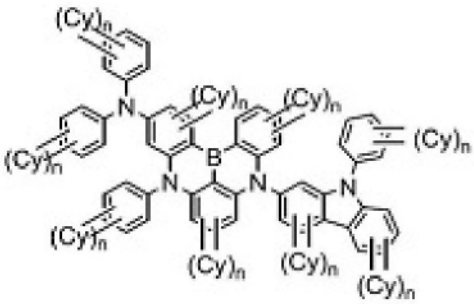


1-Cy-(2680)

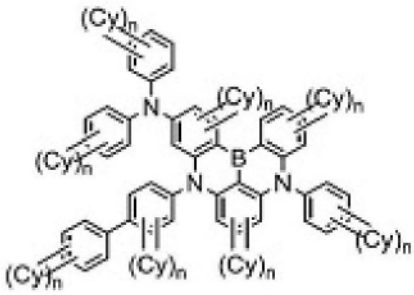


1-Cy-(2681)

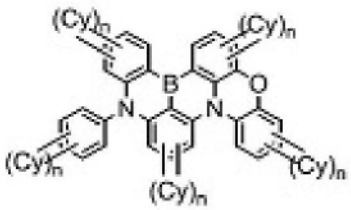
[0284]



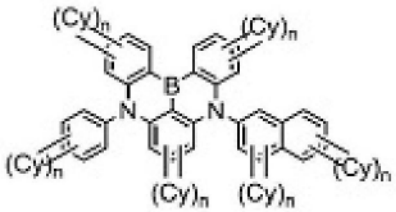
1-Cy-(2682)



1-Cy-(2683)

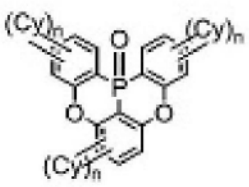


1-Cy-(2691)

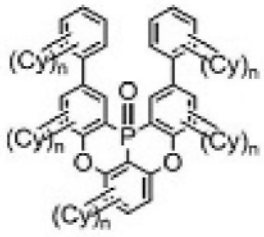


1-Cy-(2699)

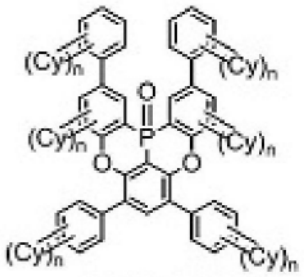
[0285] [化42]



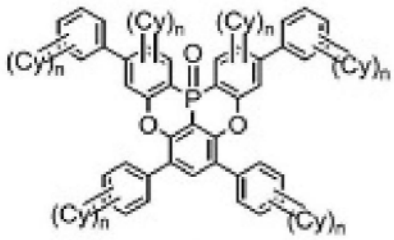
1-Cy-(601)



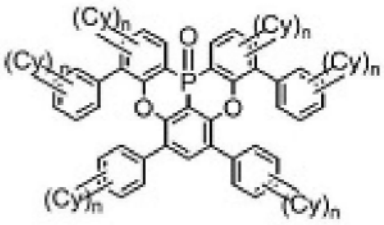
1-Cy-(1187)



1-Cy-(1190)

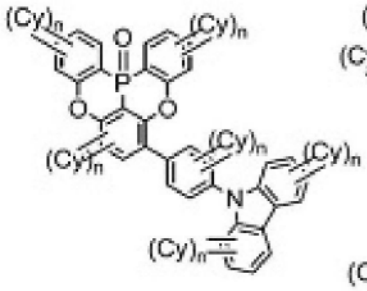


1-Cy-(1191)

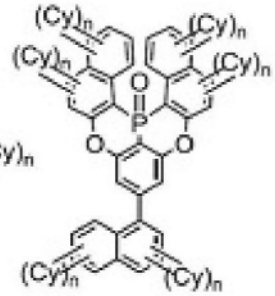


1-Cy-(1192)

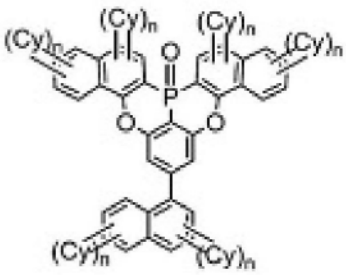
[0286]



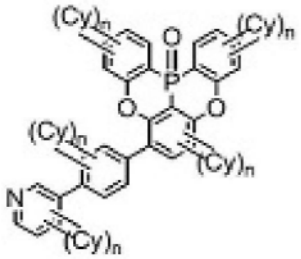
1-Cy-(3588)



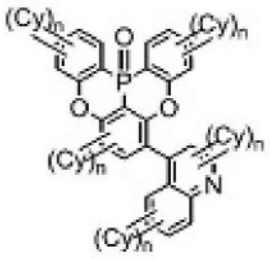
1-Cy-(3654)



1-Cy-(3690)

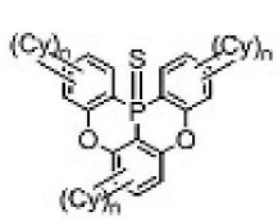


1-Cy-(3806)

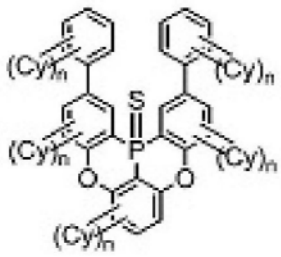


1-Cy-(3824)

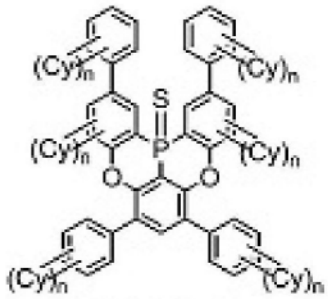
[0287] [化43]



1-Cy-(701)

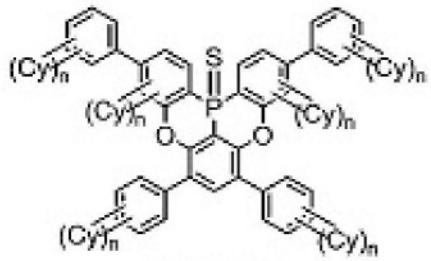


1-Cy-(1247)

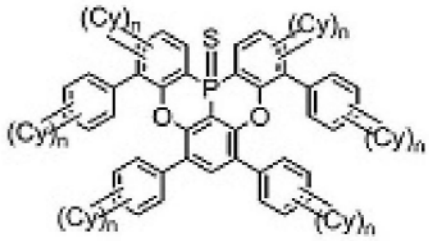


1-Cy-(1250)

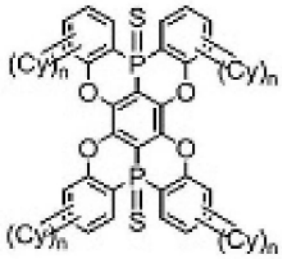
[0288]



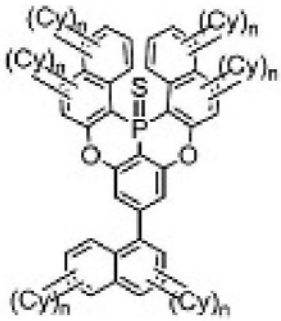
1-Cy-(1251)



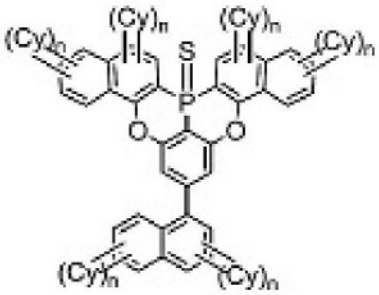
1-Cy-(1252)



1-Cy-(721)

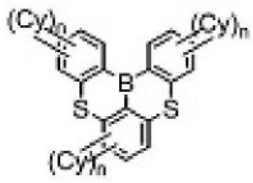


1-Cy-(4114)

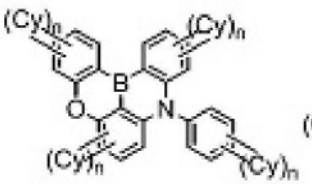


1-Cy-(4150)

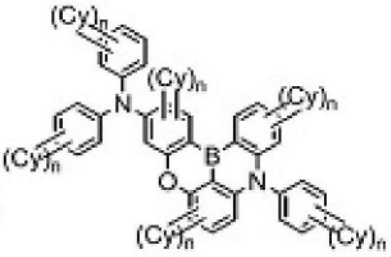
[0289] [化44]



1-Cy-(201)

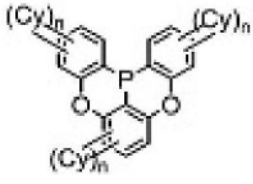


1-Cy-(1201)

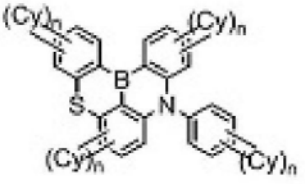


1-Cy-(1210)

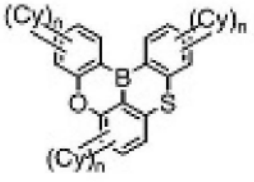
[0290]



1-Cy-(501)



1-Cy-(1301)

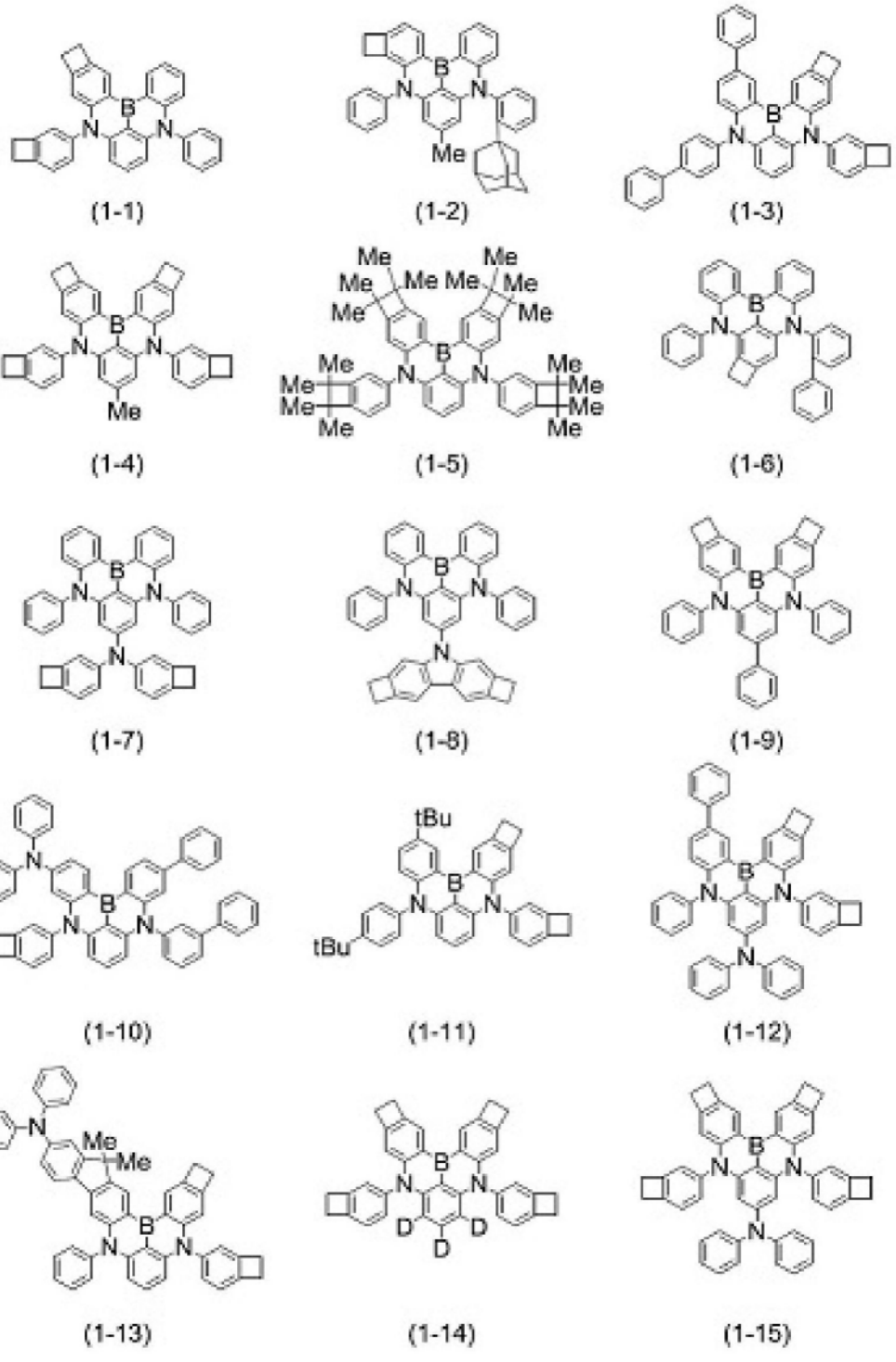


1-Cy-(1351)

[0291] 作为本发明的经环烷烃缩合的多环芳香族化合物的更具体的例子,可列举以下结构式所表示的化合物。再者,下述结构式中的“D”表示氘,“Me”表示甲基,“Et”表示乙基,“iPr”表示异丙基,“tBu”表示叔丁基,“tAm”表示叔戊基,“Ph”表示苯基,“F”表示氟,“CN”表示氰基,“TMS”表示三甲基硅烷基,“TPhS”表示三苯基硅烷基。再者,式(1-1001)～式(1-1265)中,省略结构式中的甲基(Me)的表述。

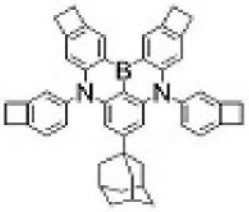
[0292] [化45]

[0293]

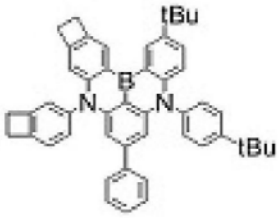


[0294] [化46]

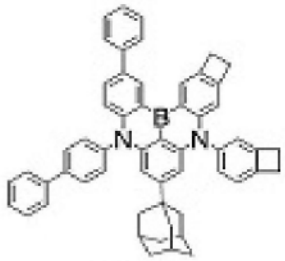
[0295]



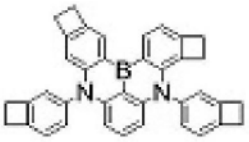
(1-21)



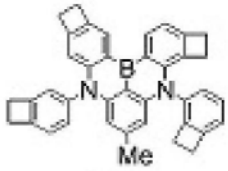
(1-22)



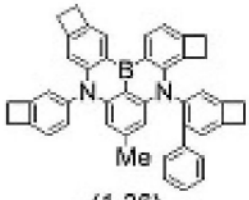
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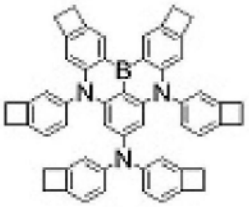
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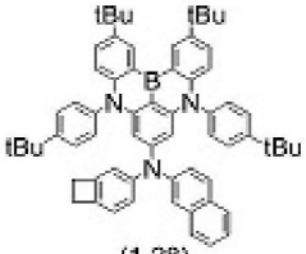
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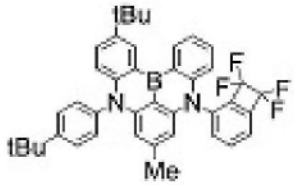
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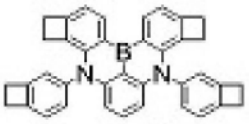
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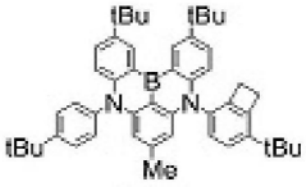
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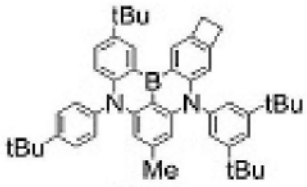
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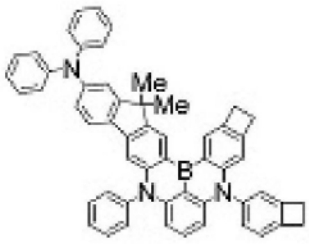
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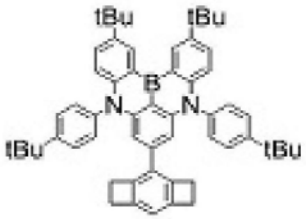
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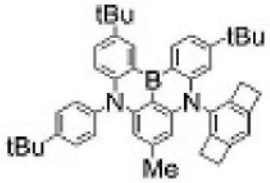
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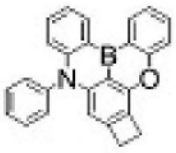
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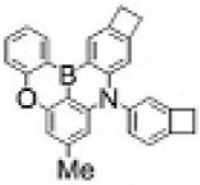
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[0296] [化47]

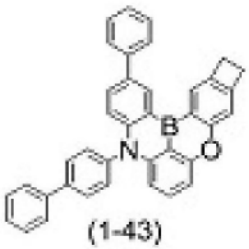
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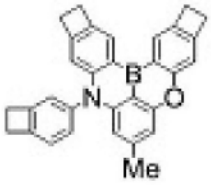
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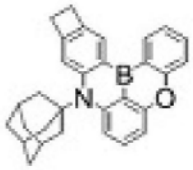
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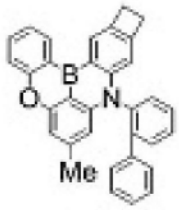
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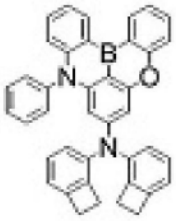
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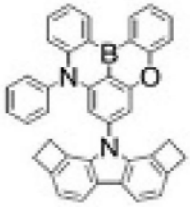
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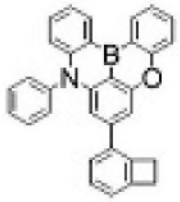
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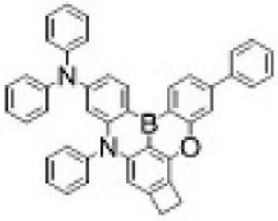
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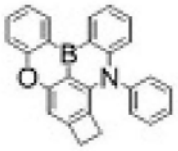
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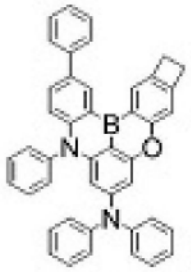
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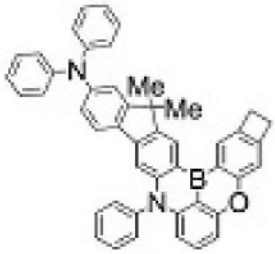
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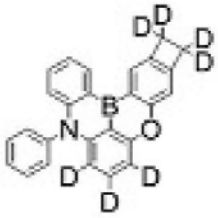
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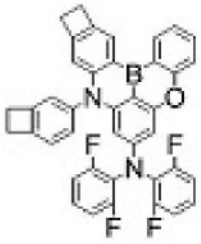
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(1-53)



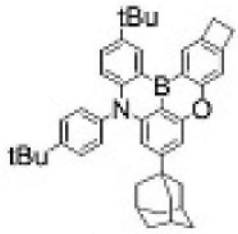
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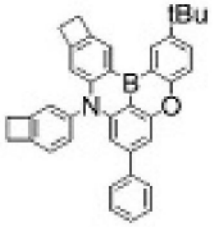
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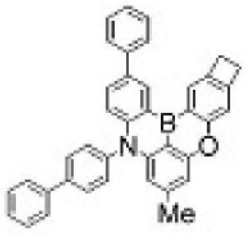
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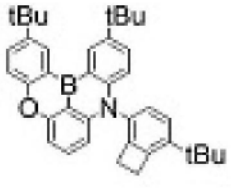
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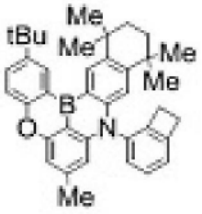
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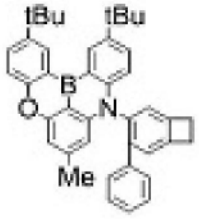
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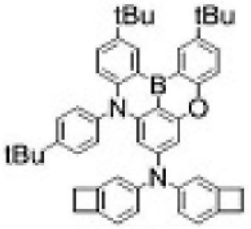
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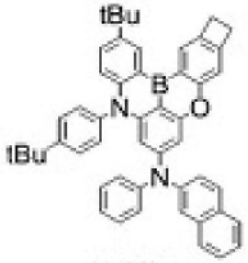
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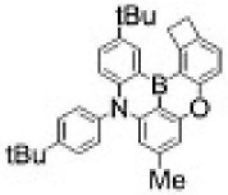
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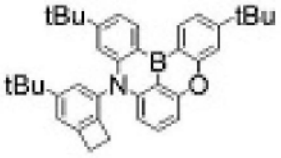
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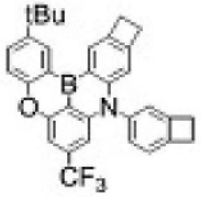
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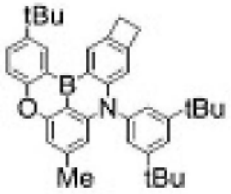
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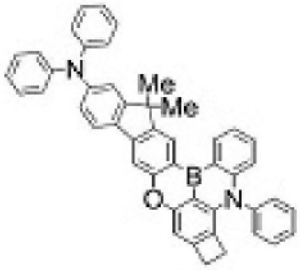
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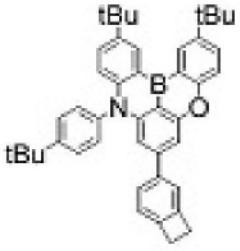
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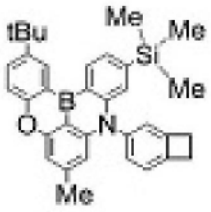
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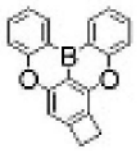
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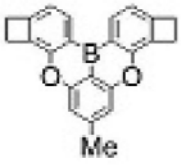
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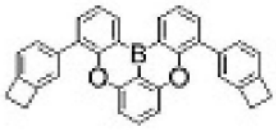
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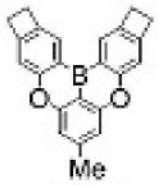
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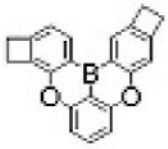
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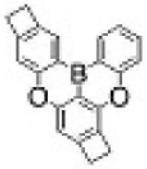
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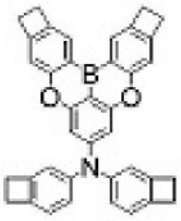
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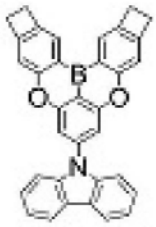
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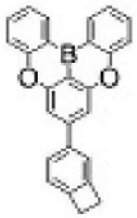
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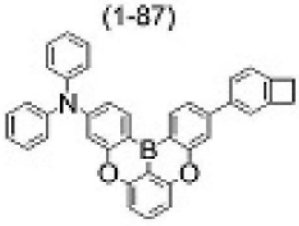
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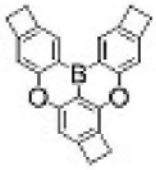
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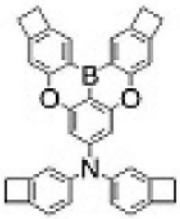
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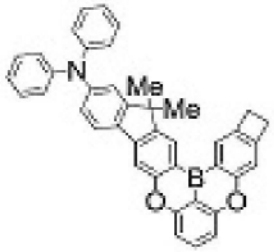
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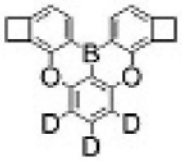
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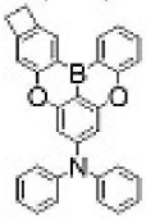
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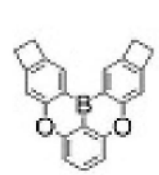
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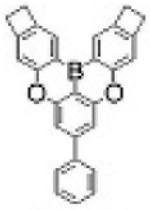


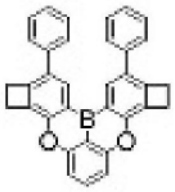
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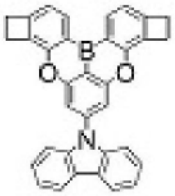
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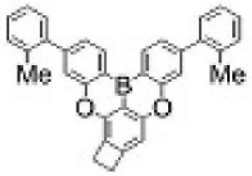
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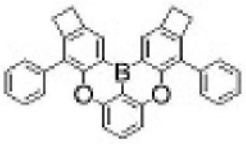

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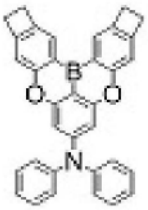

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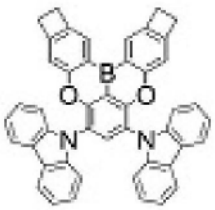

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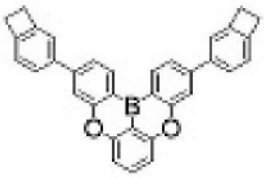

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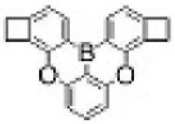

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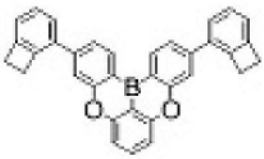

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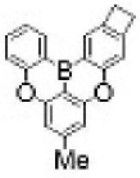

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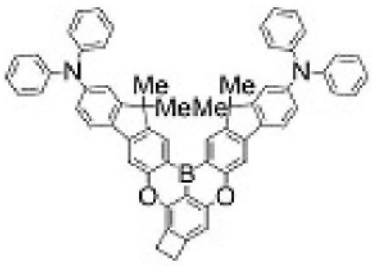

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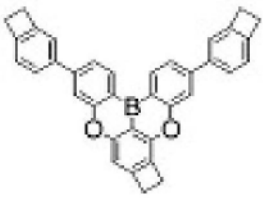

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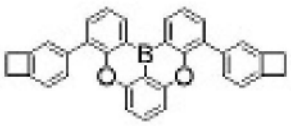

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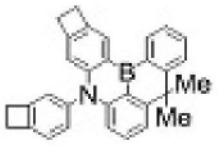

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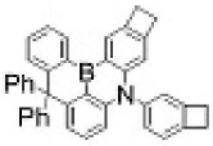

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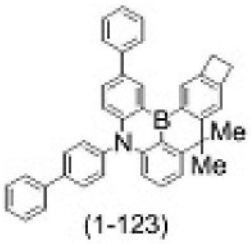
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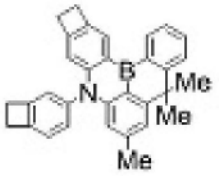
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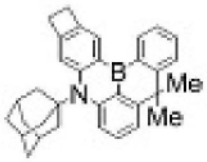
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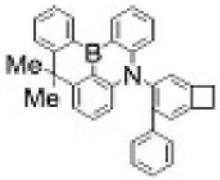
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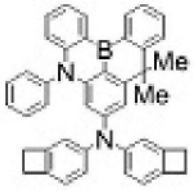
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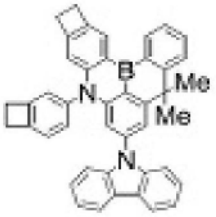
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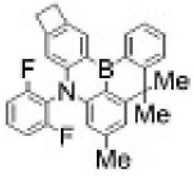
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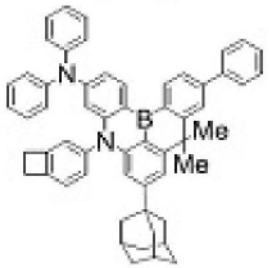
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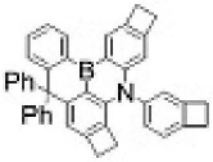
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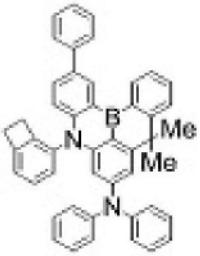
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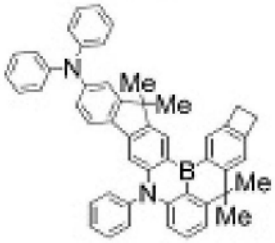
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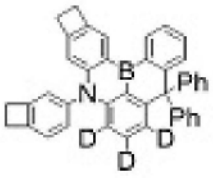
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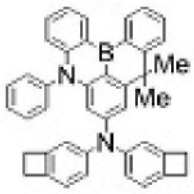
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(1-133)



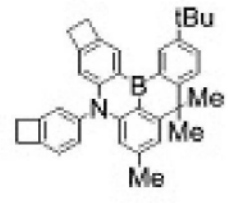
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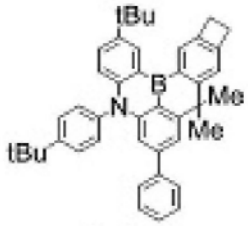


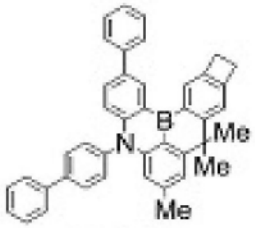
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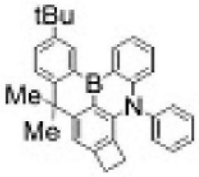
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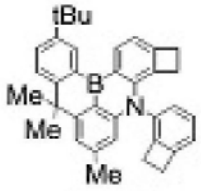
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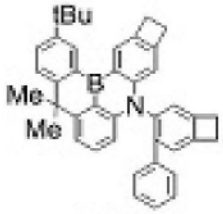

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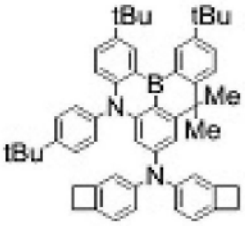

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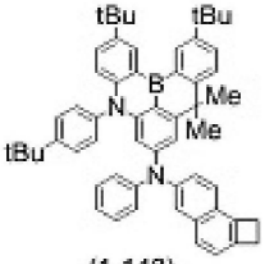

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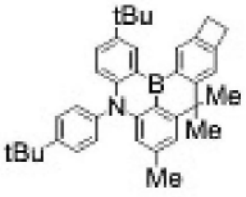

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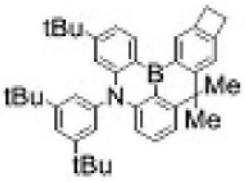

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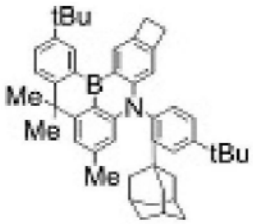

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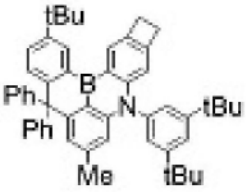

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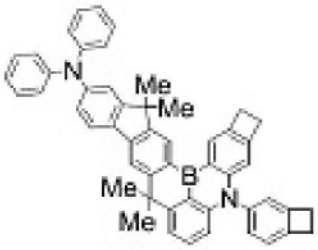

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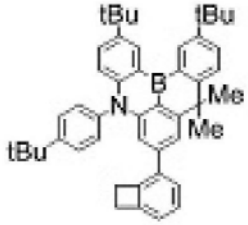

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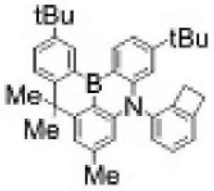

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(1-151)


(1-152)

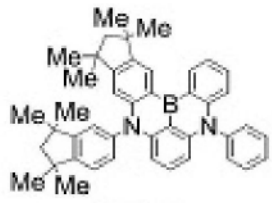

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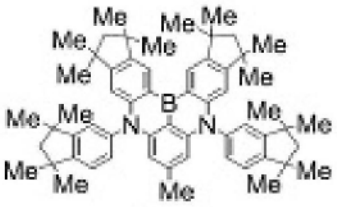

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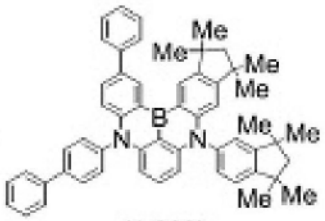

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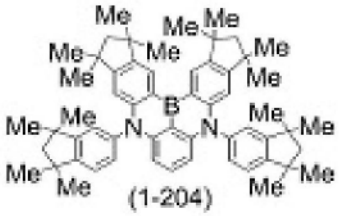
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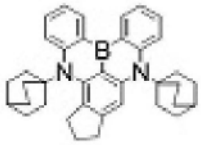
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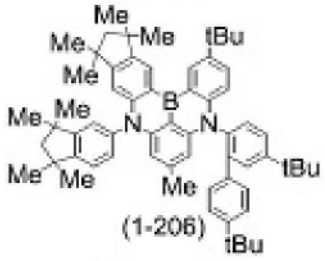

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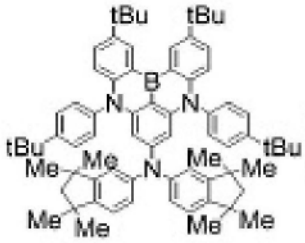

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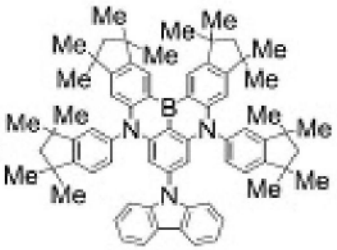

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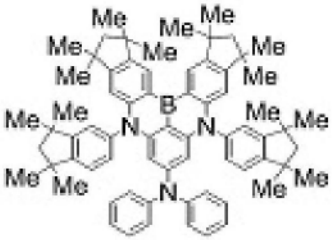

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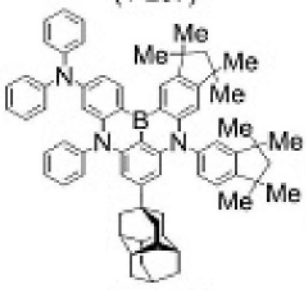

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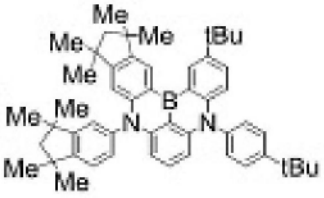

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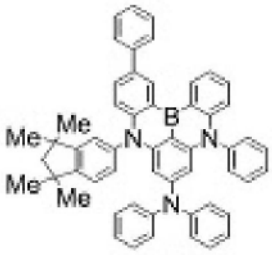

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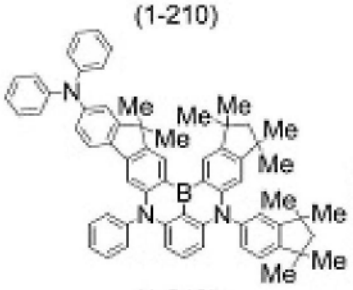

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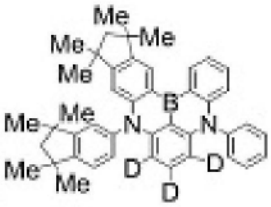

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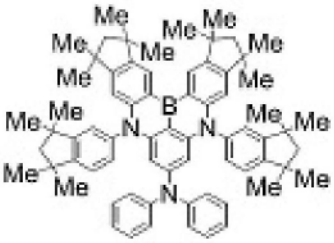

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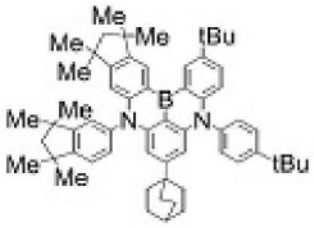

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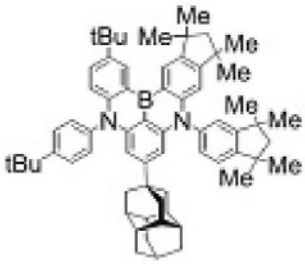

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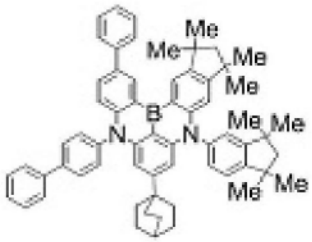
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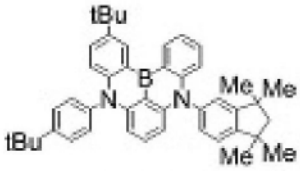
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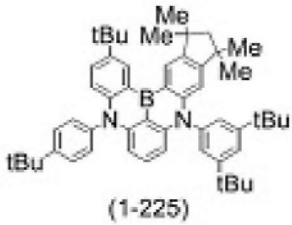
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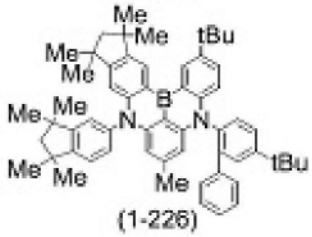
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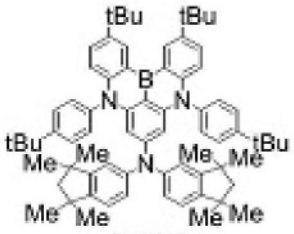
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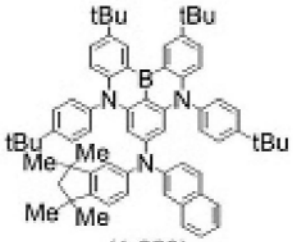
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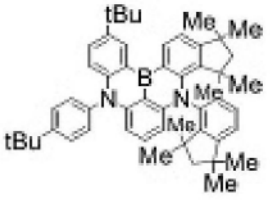
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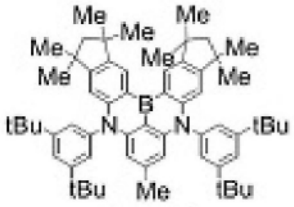
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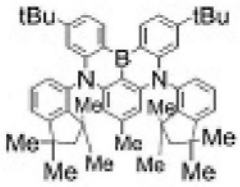
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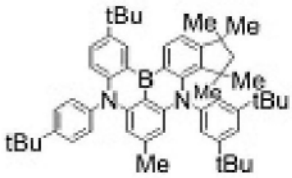
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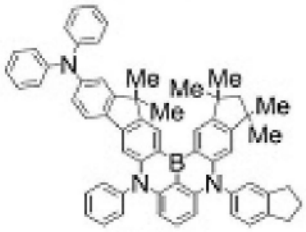
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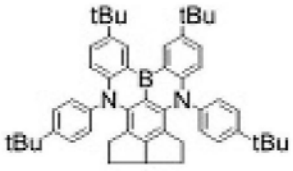
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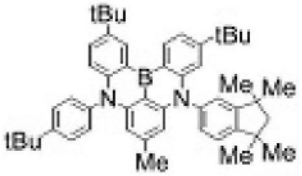
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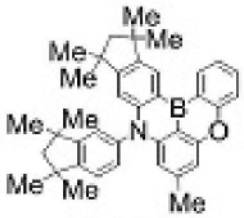
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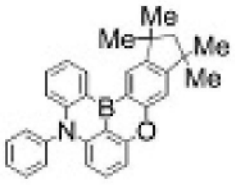


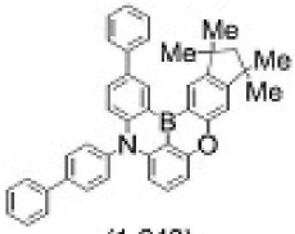
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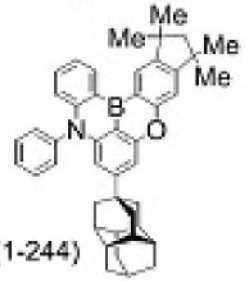
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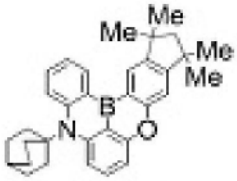
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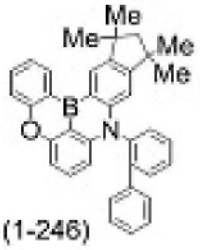

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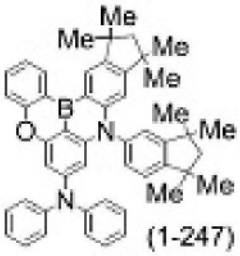

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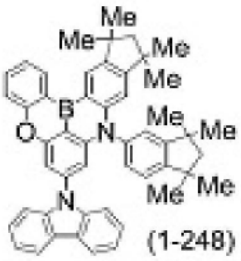

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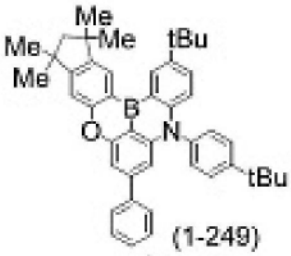

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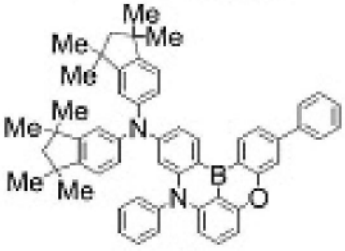

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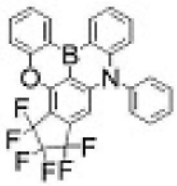

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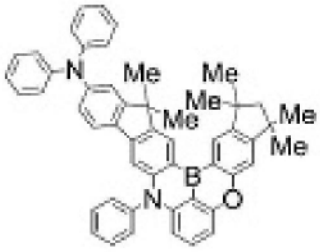

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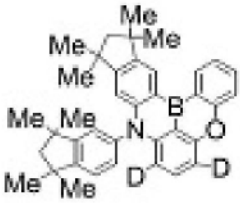

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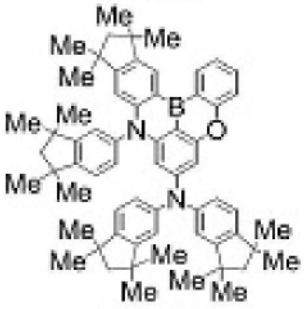

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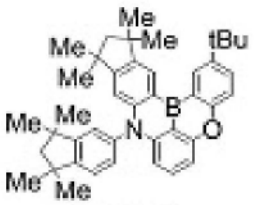

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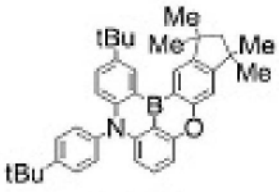

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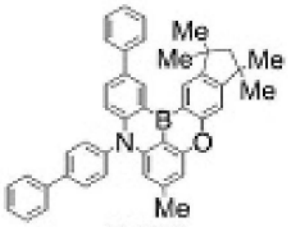

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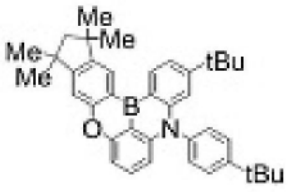
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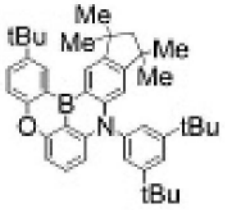
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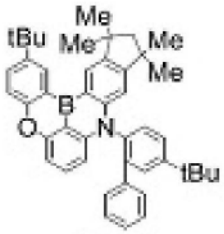

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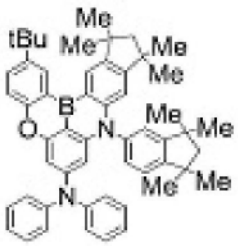

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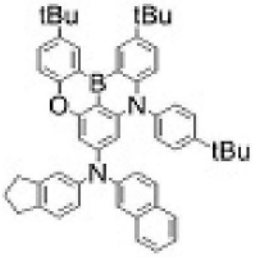

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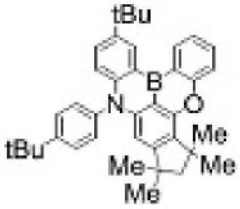

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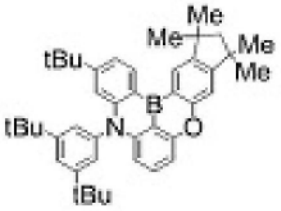

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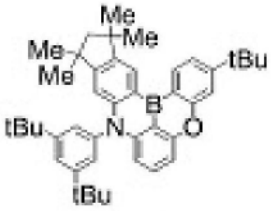

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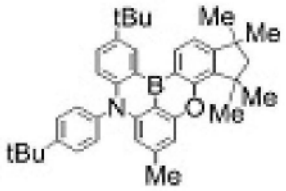

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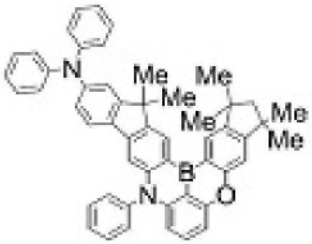

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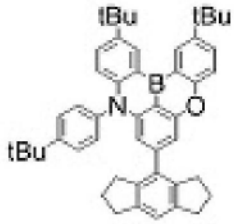

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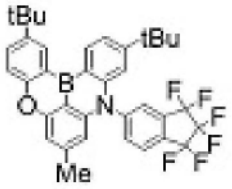

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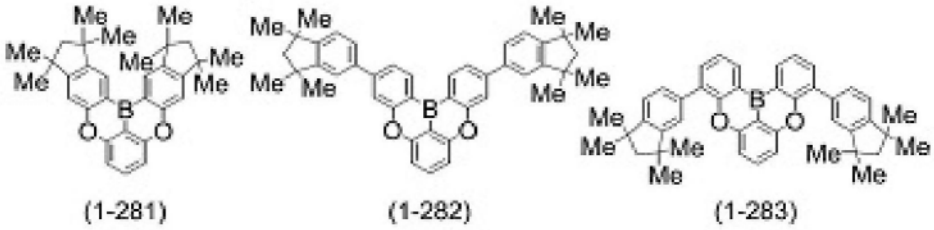

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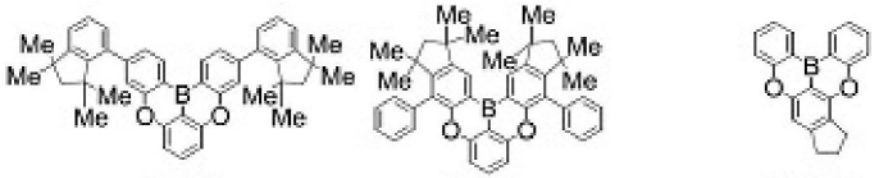

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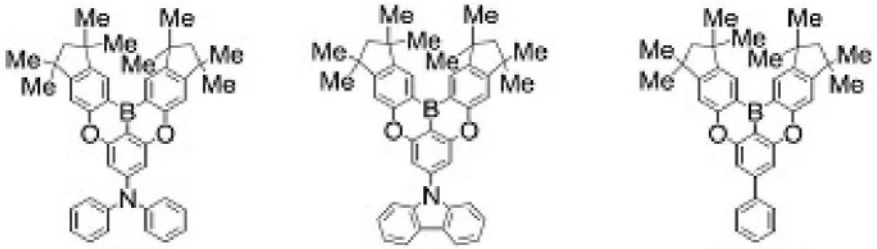
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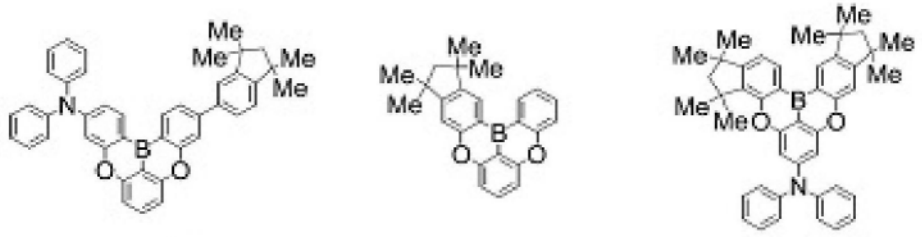
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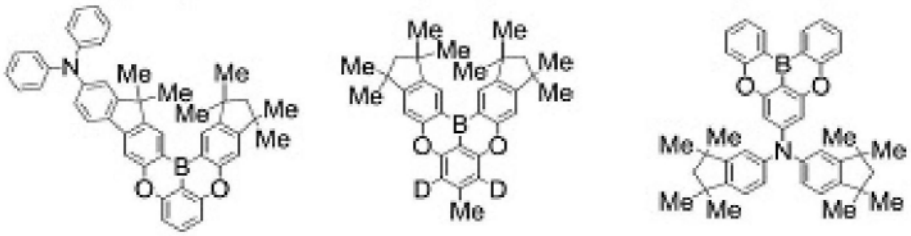
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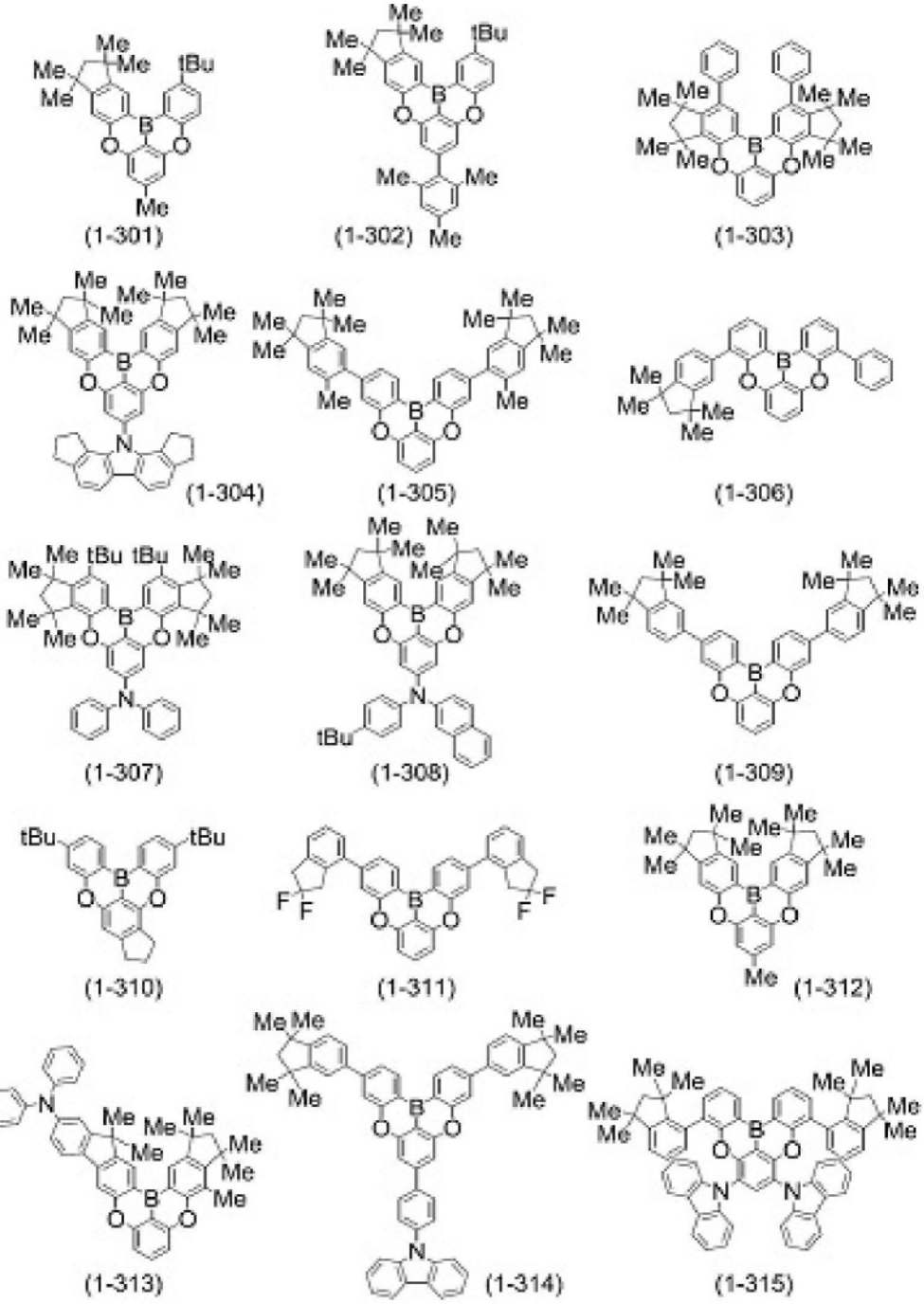
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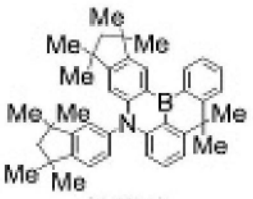
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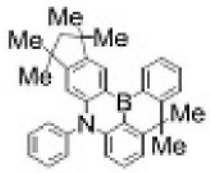
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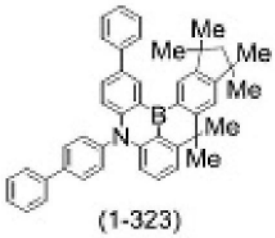


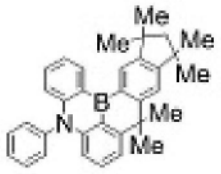
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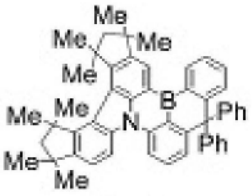
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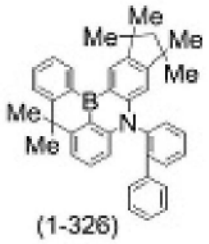

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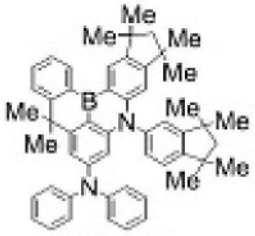

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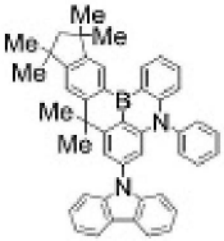

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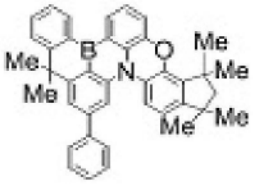

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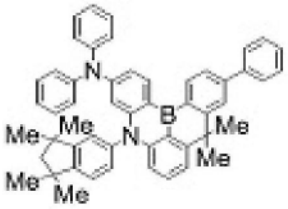

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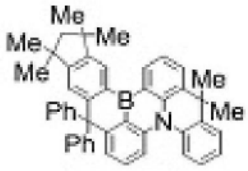

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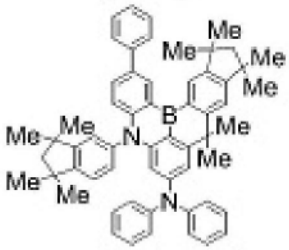

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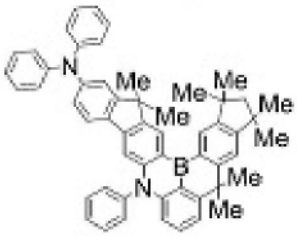

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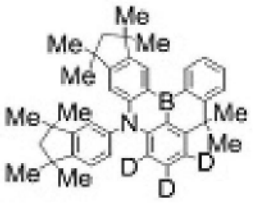

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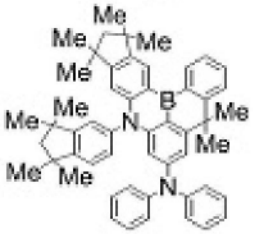

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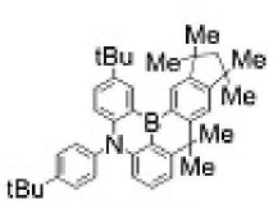

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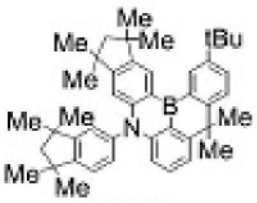

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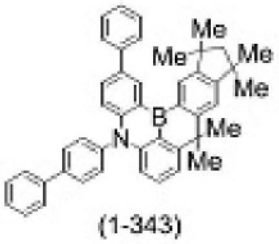

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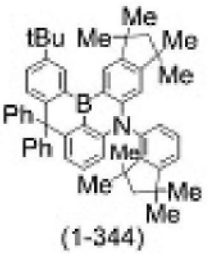
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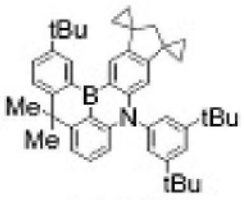
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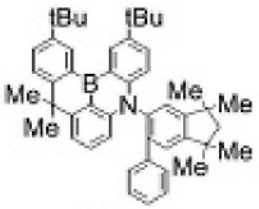

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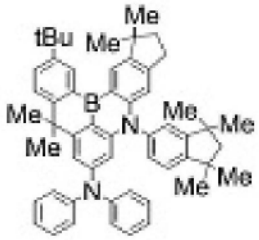

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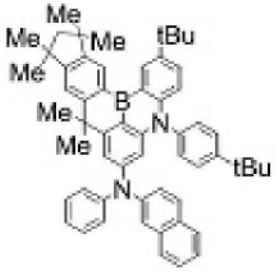

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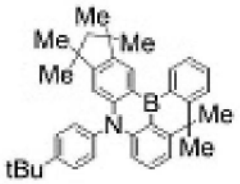

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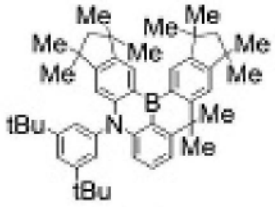

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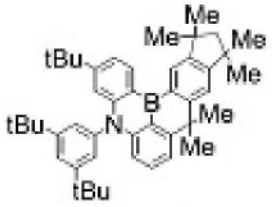

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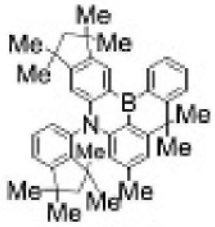

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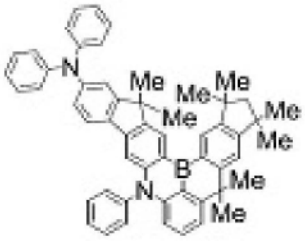

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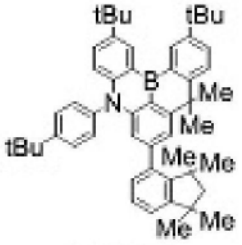

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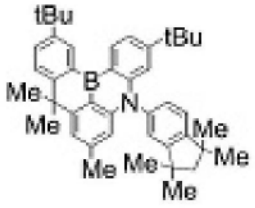

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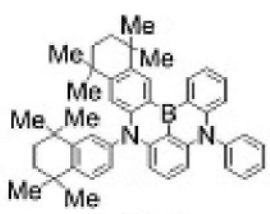

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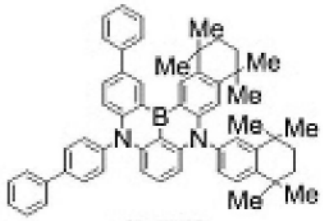

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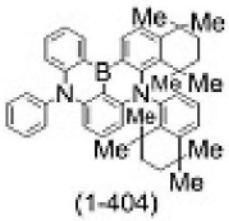
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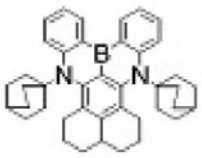
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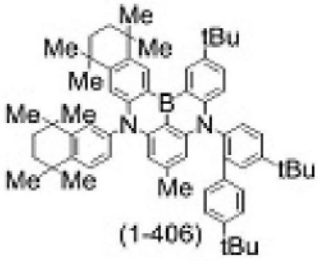

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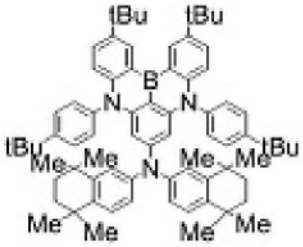

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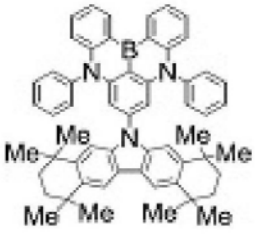

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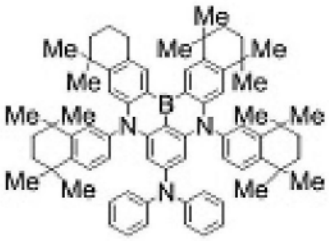

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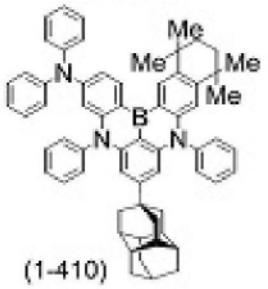

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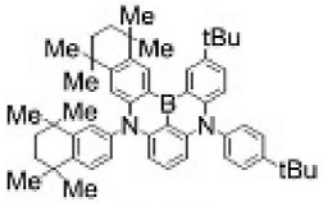

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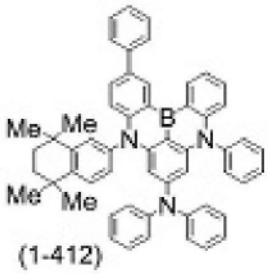

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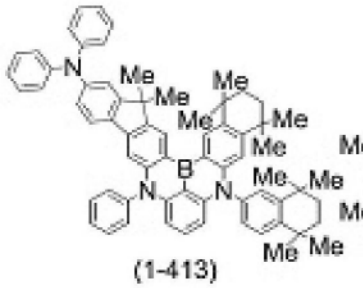

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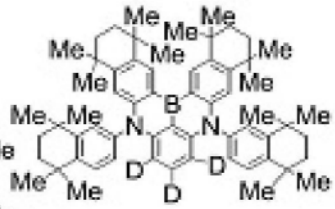

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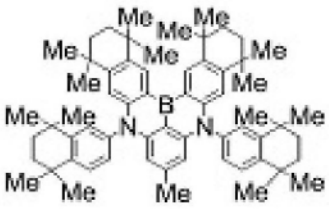

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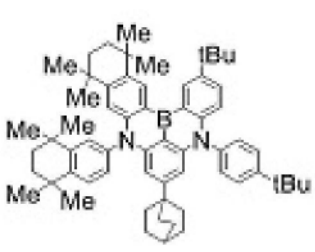

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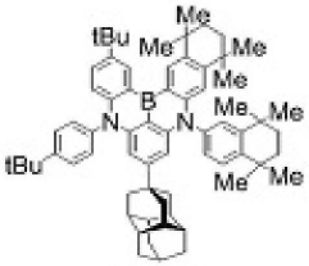

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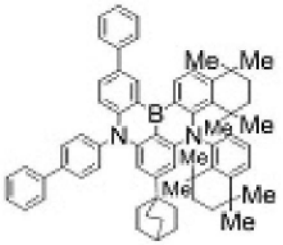
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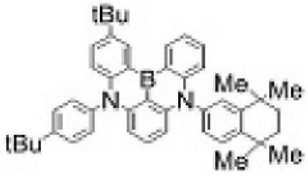
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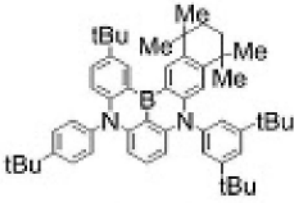
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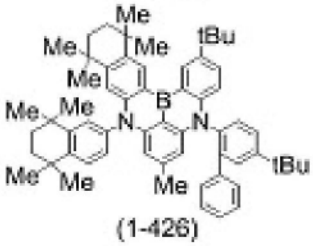
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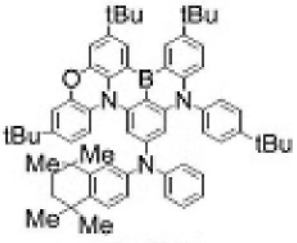
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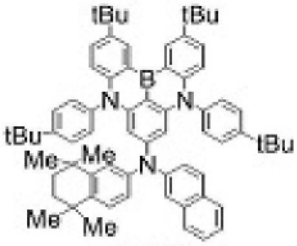
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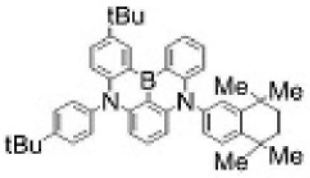
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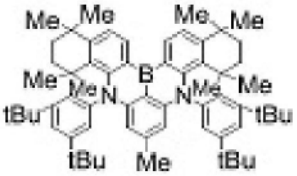
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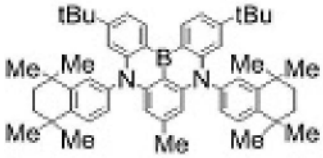
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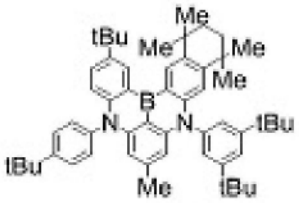
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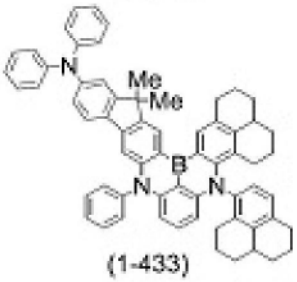
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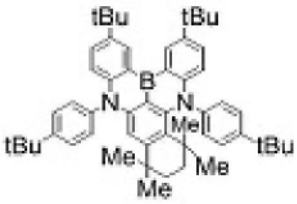
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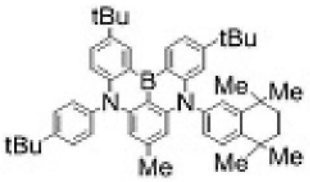
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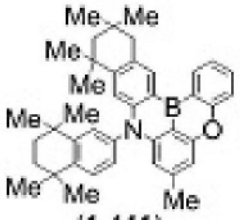
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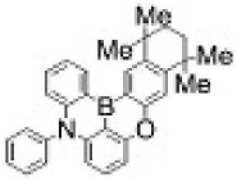


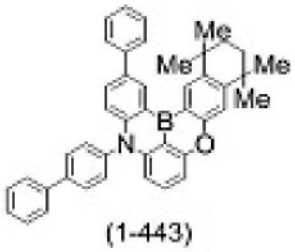
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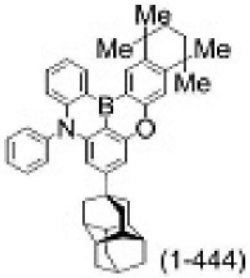
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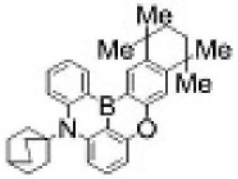
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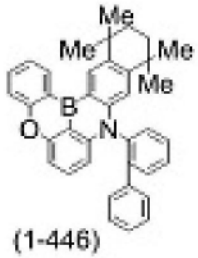

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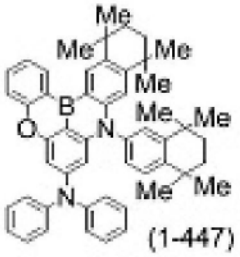

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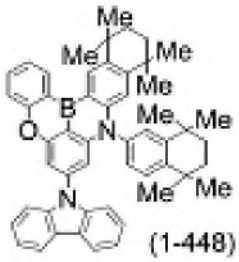

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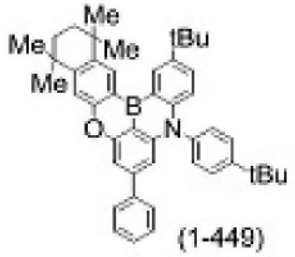

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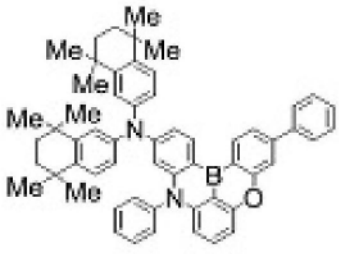

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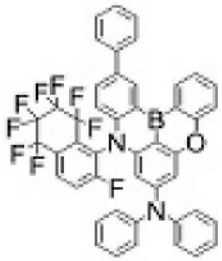

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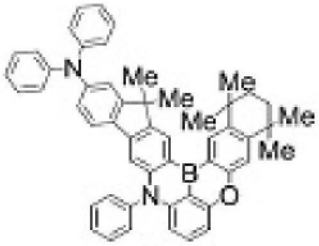

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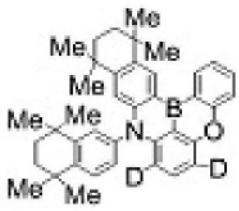

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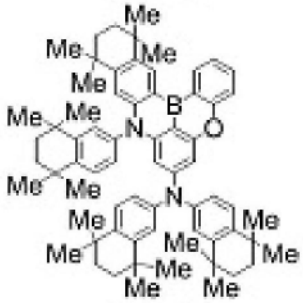

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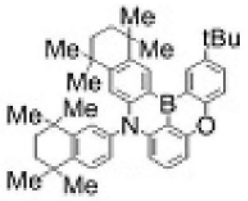

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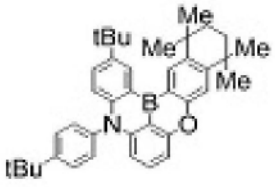

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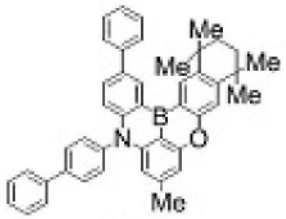

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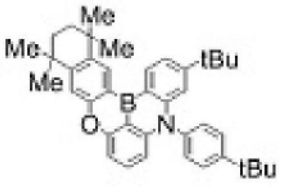
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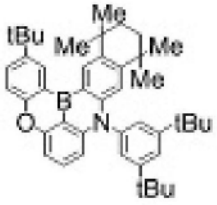
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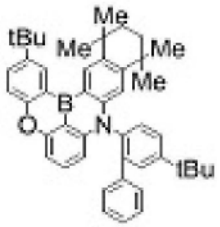

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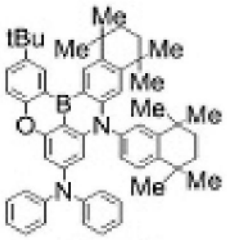

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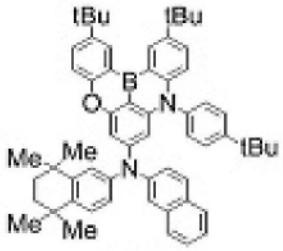

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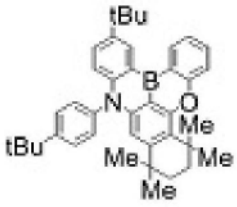

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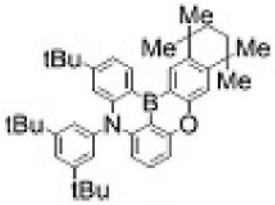

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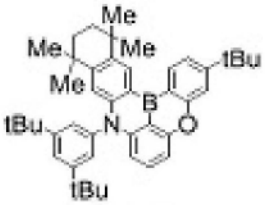

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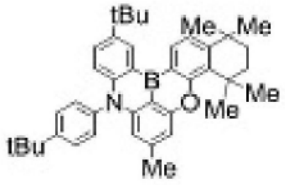

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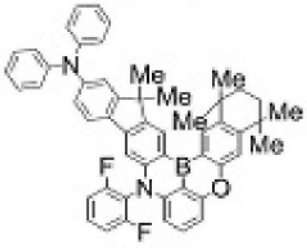

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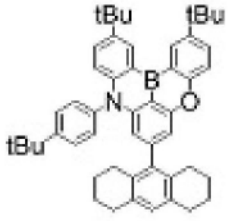

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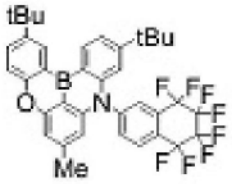

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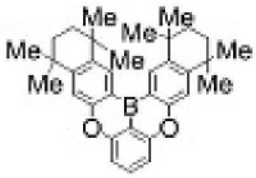

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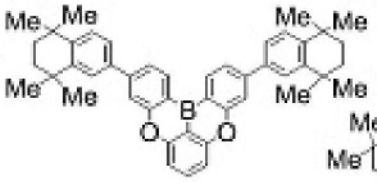

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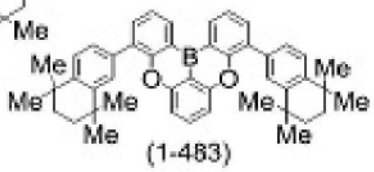

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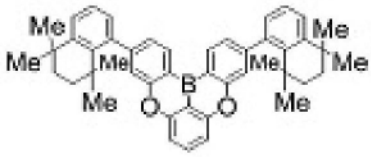
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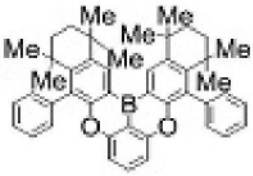
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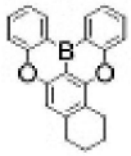

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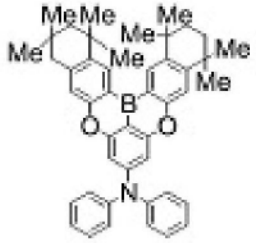

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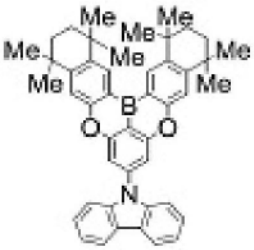

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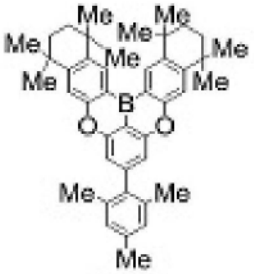

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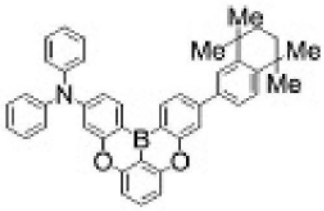

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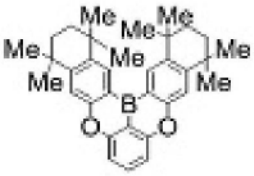

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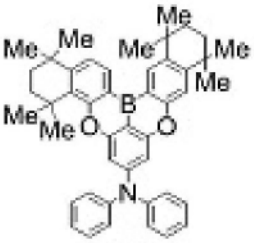

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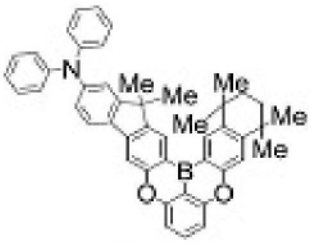

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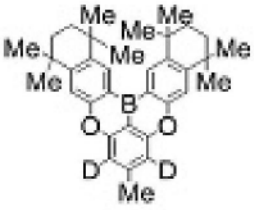

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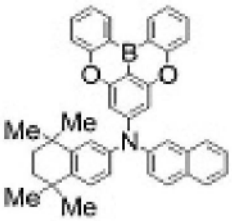

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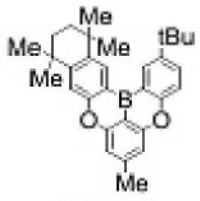

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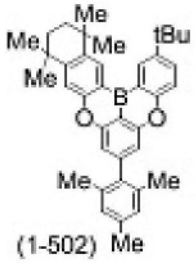

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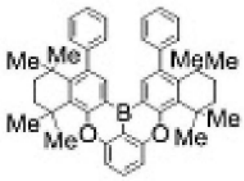

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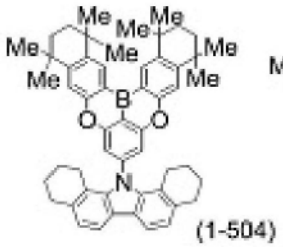
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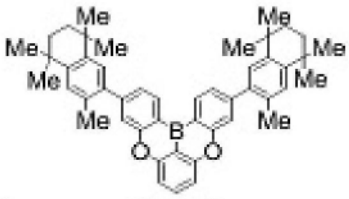
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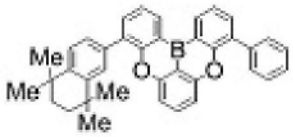

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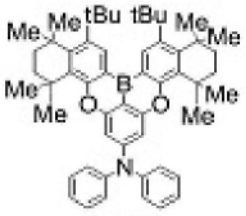

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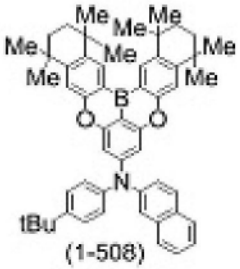

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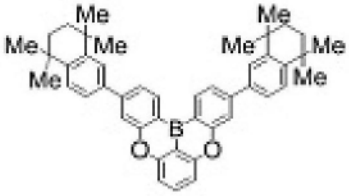

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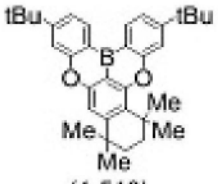

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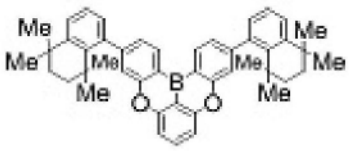

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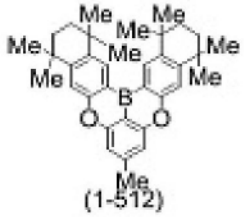

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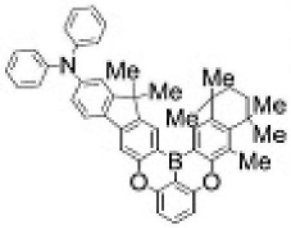

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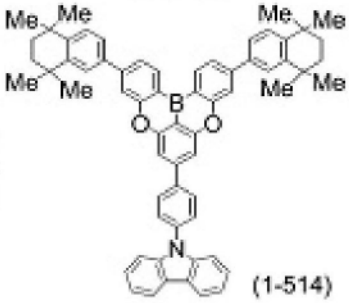

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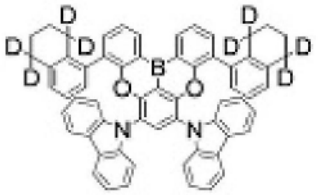

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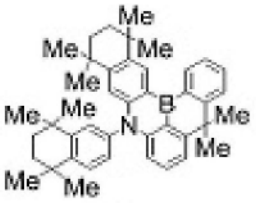

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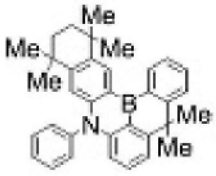

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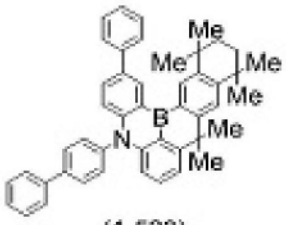

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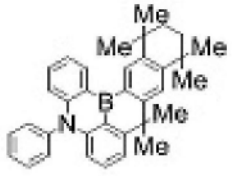
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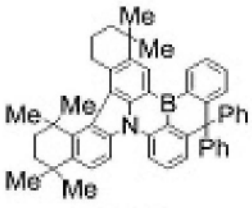
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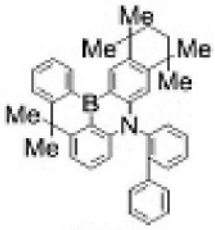

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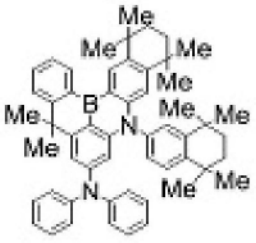

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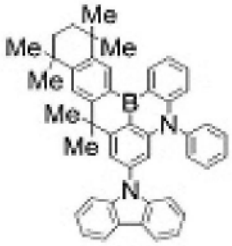

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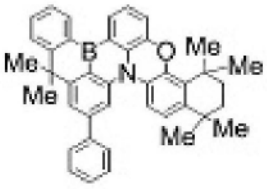

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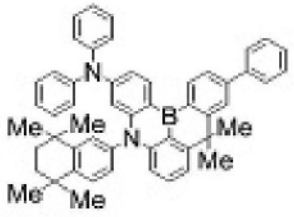

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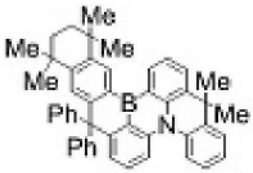

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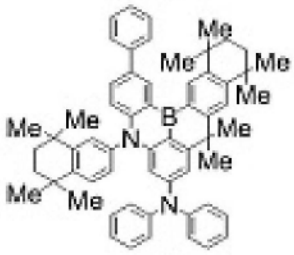

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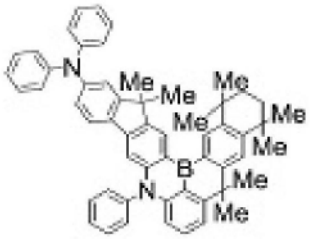

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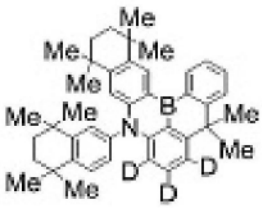

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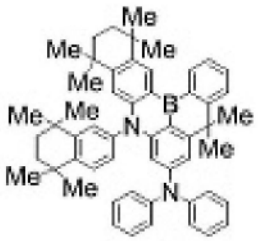

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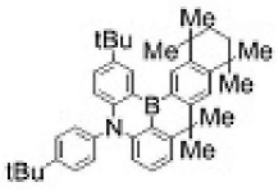

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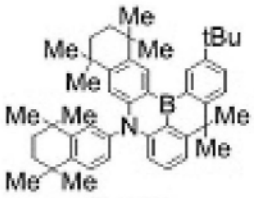

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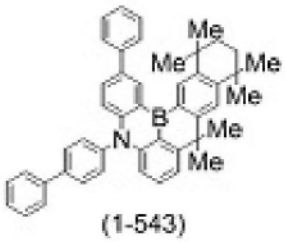

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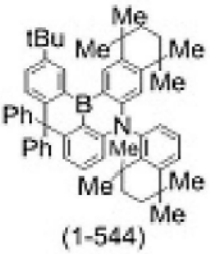
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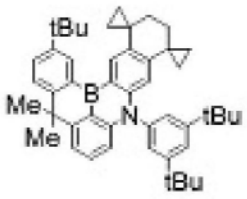
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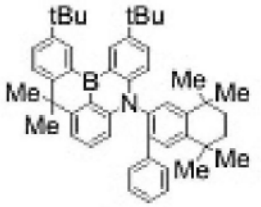

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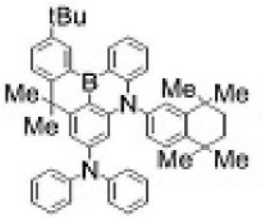

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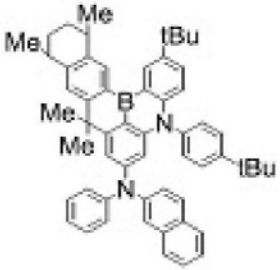

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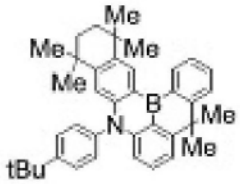

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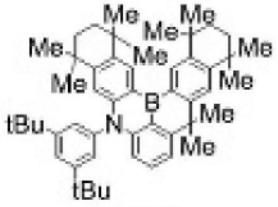

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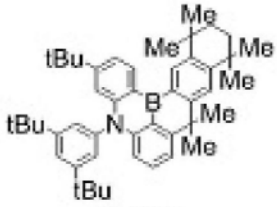

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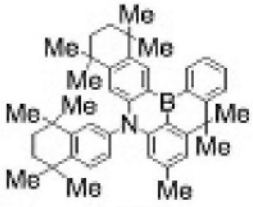

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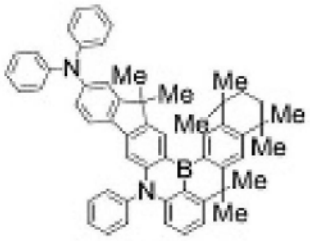

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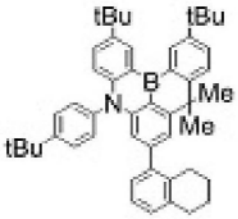

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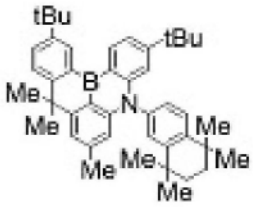

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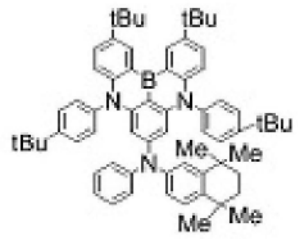

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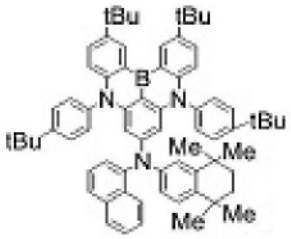

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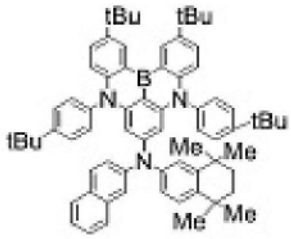
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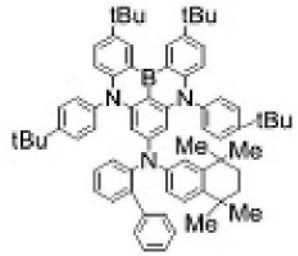
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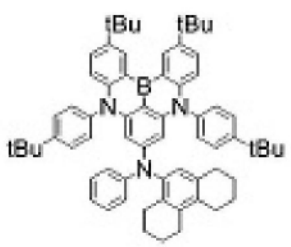
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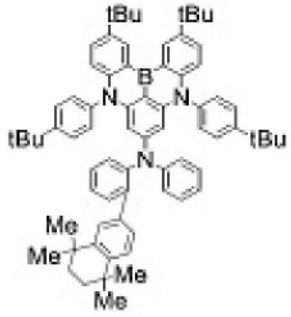
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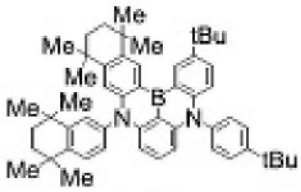


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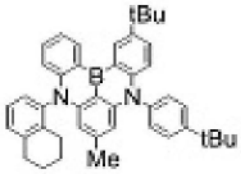


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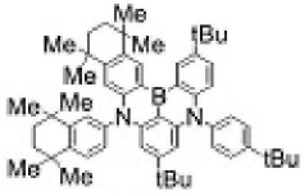
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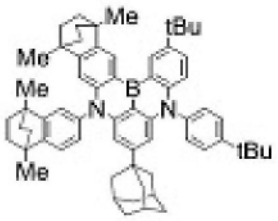
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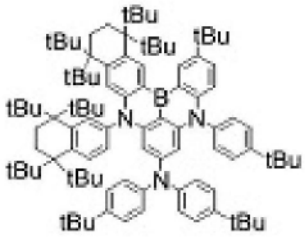
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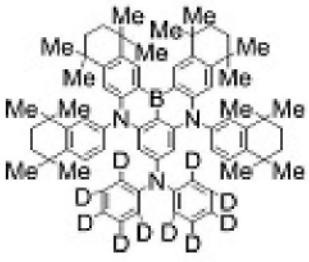
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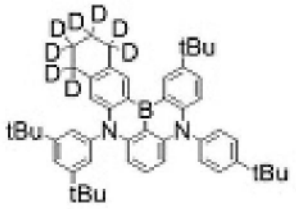


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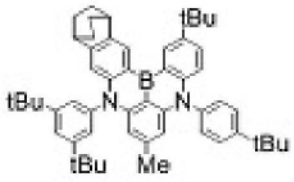


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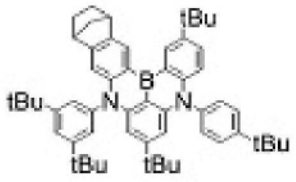
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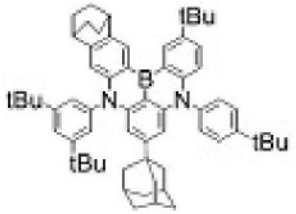
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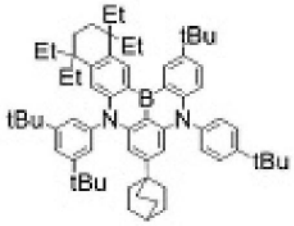
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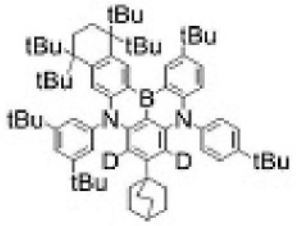
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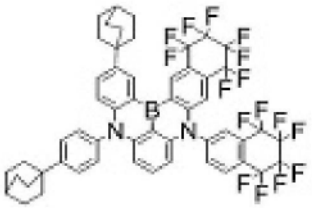


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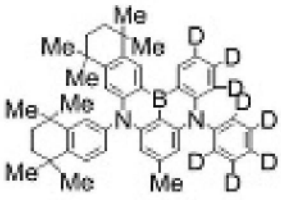


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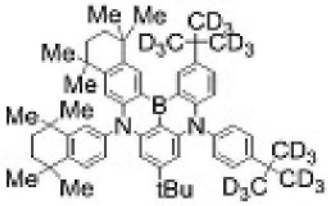
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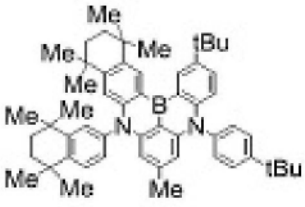
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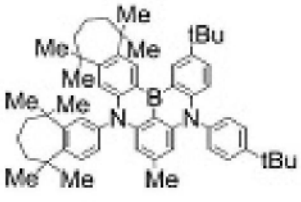
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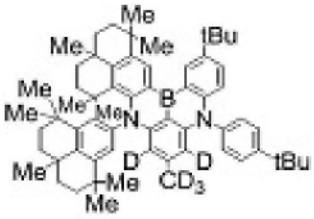
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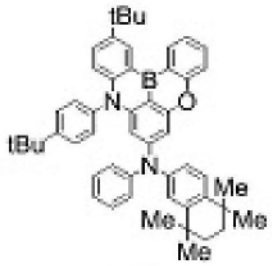


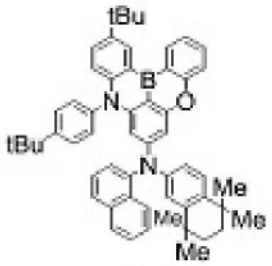
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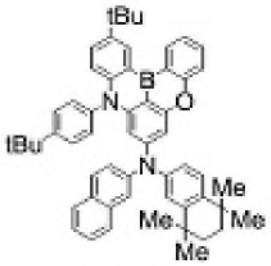


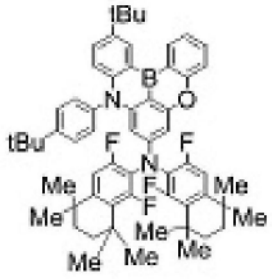
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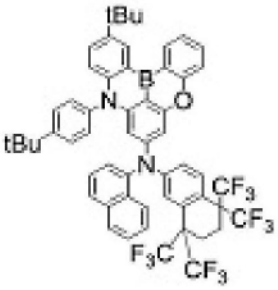
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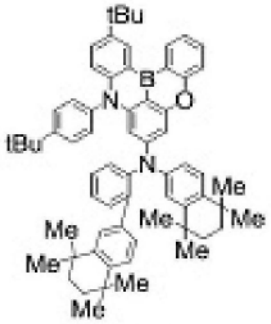

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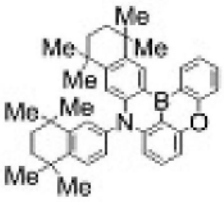

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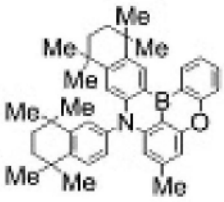

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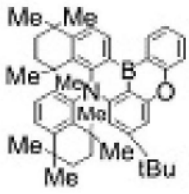

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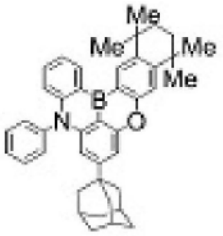

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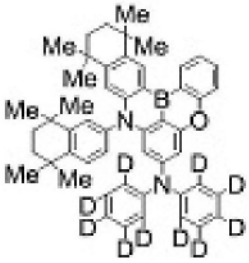
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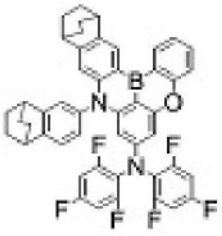

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(1-608)

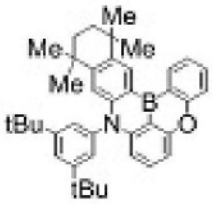

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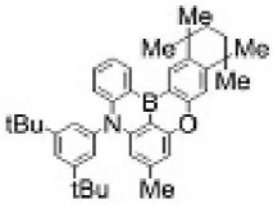

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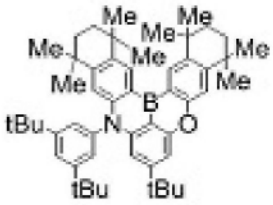
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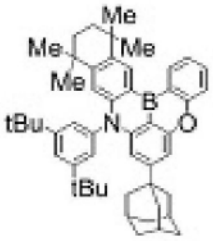
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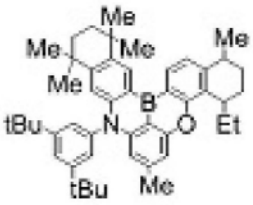
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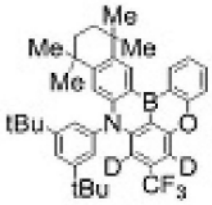
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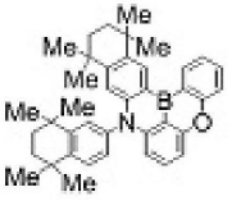


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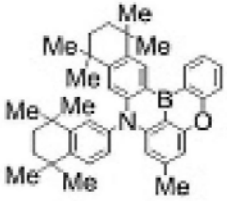


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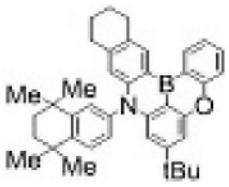
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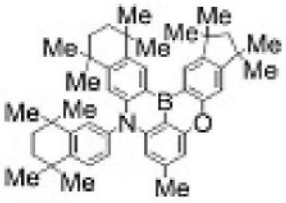
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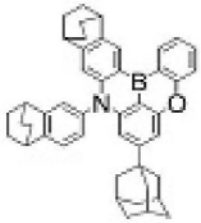
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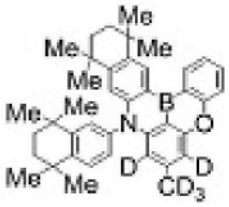
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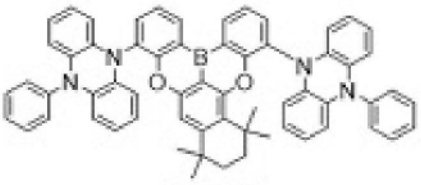


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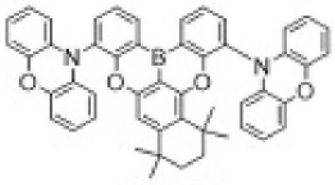


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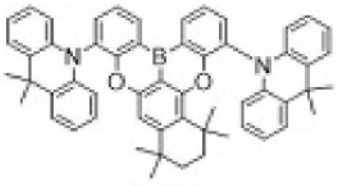
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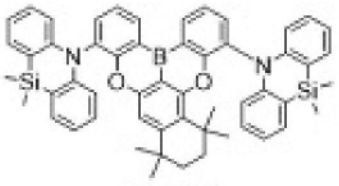
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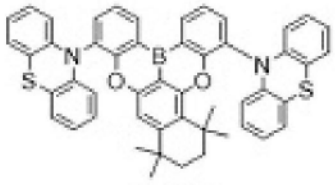
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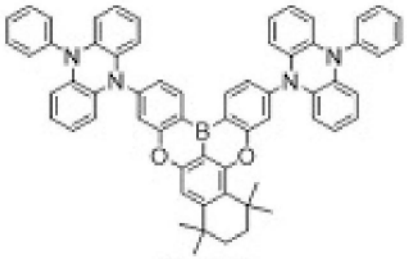


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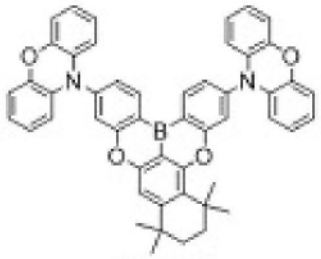


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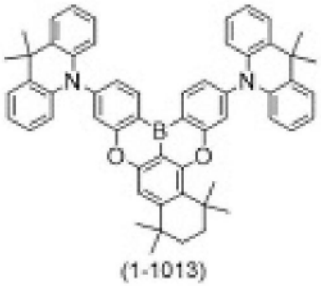
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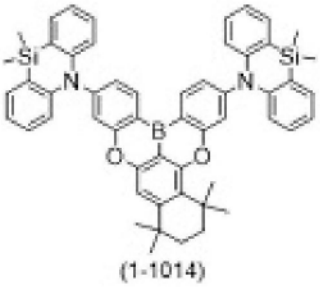
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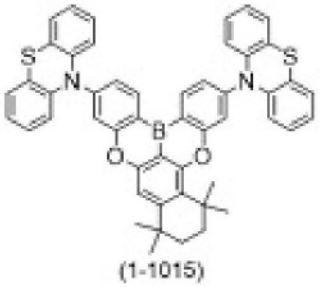
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(1-1013)



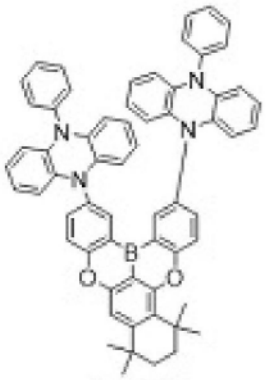
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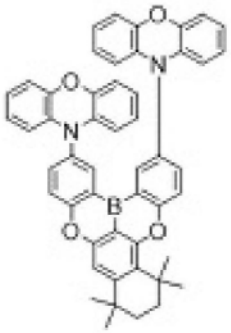
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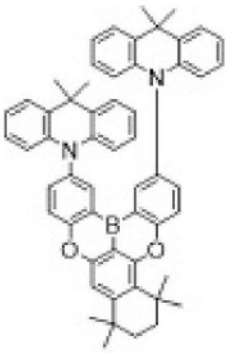
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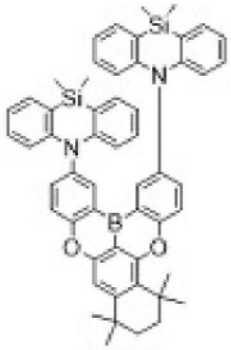
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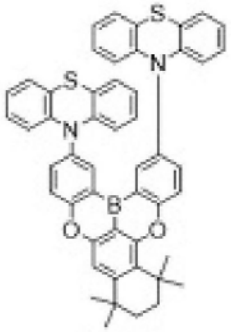
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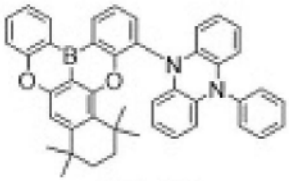
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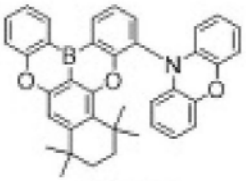
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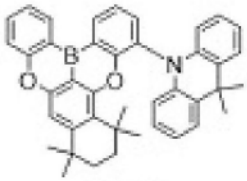
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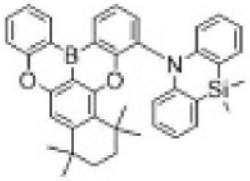
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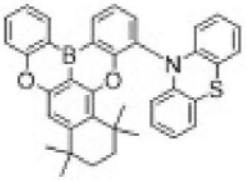
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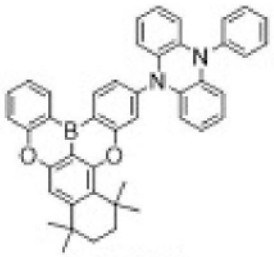


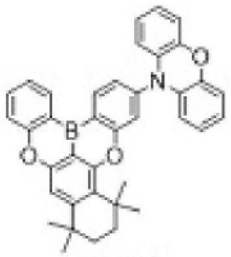
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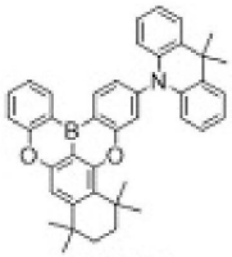


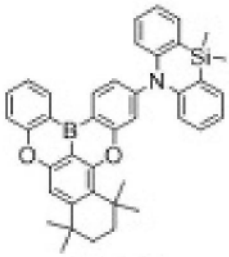
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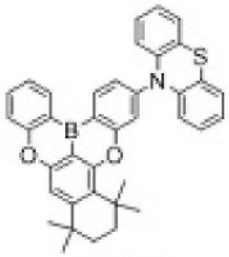
[0352] [化75]


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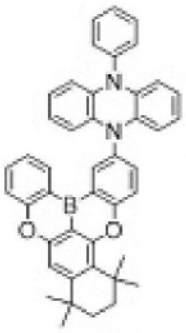

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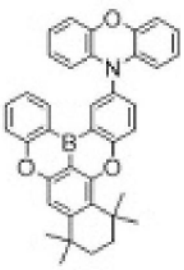

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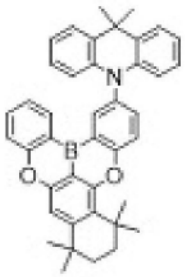

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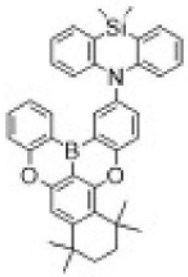

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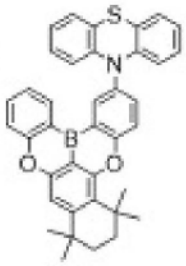
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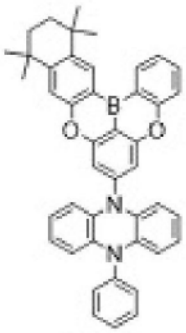

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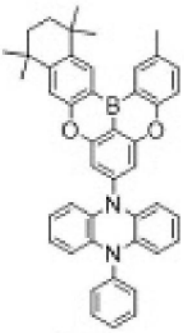

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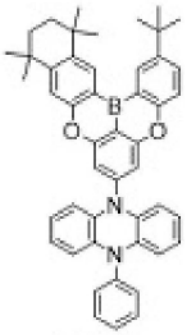

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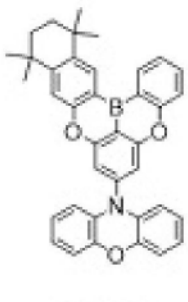

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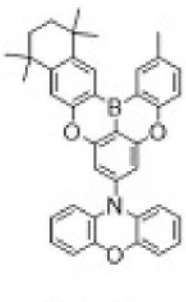

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(1-1062)

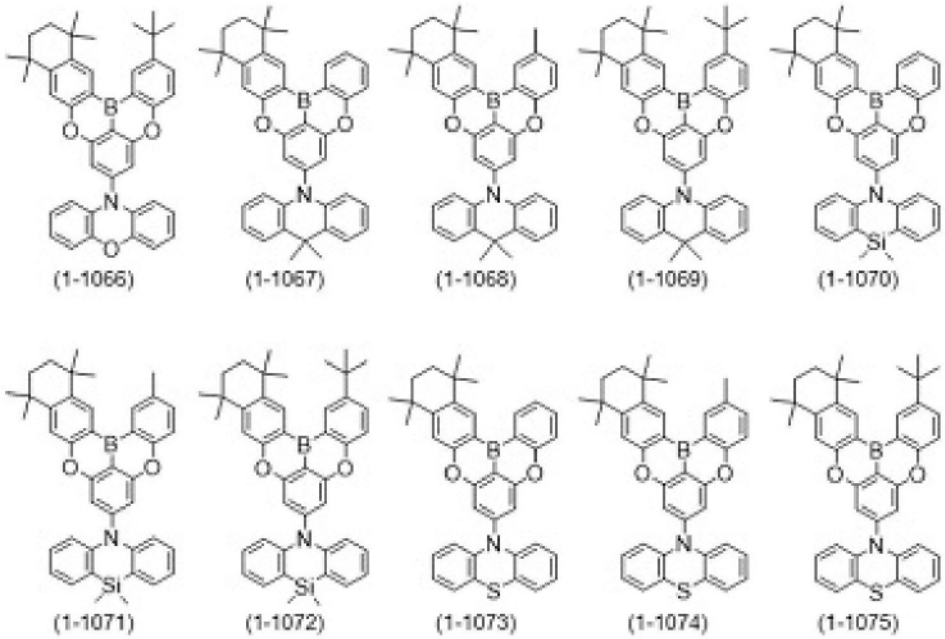

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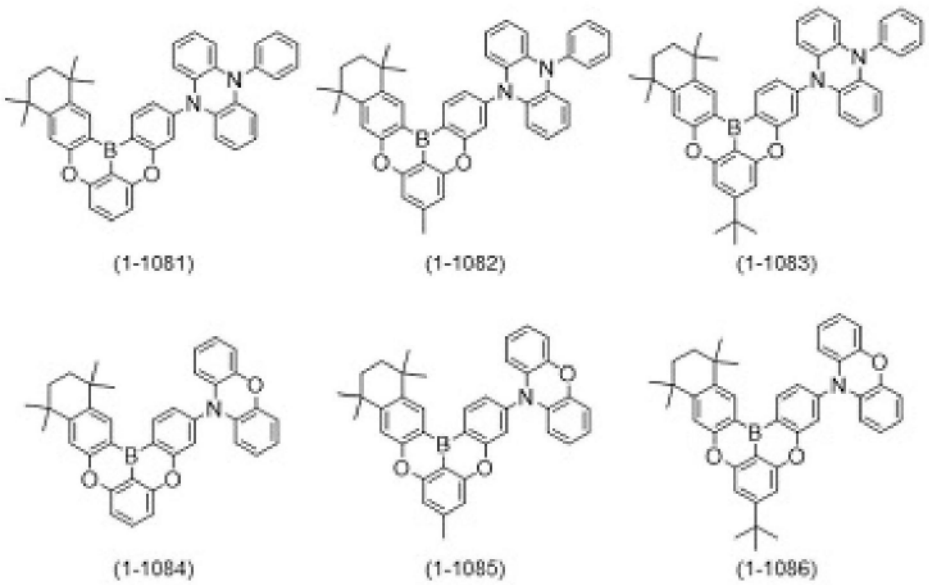

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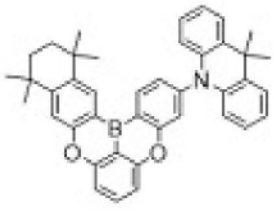
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[0355]

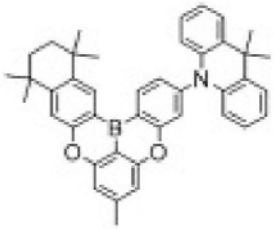




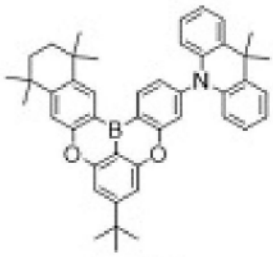
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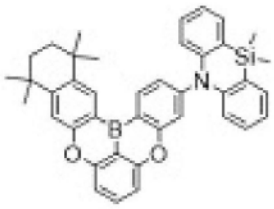
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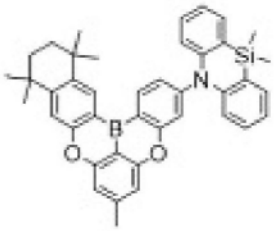
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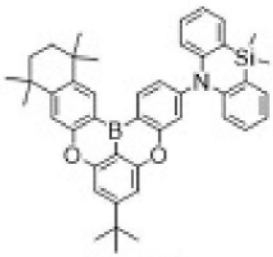
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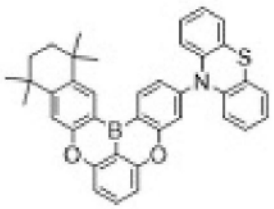


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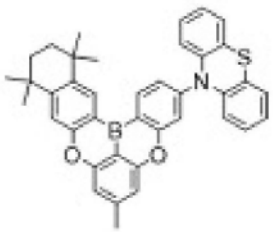


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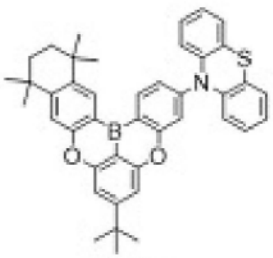
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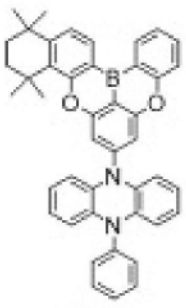
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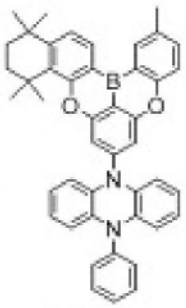
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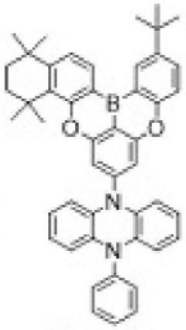
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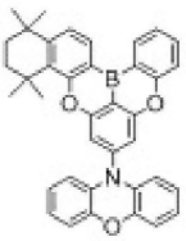
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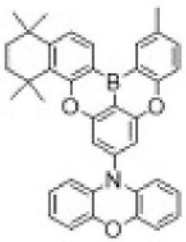
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(1-1103)

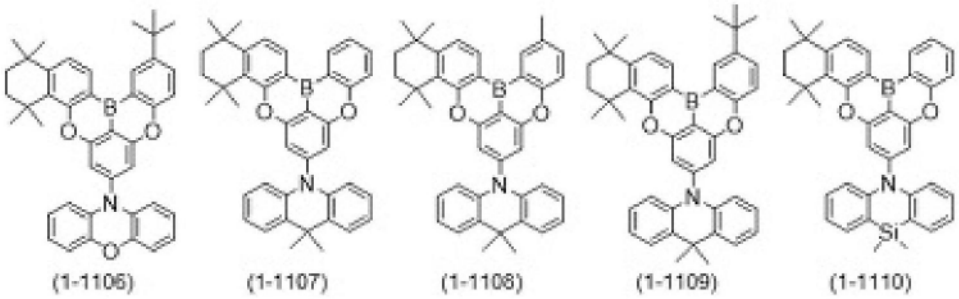


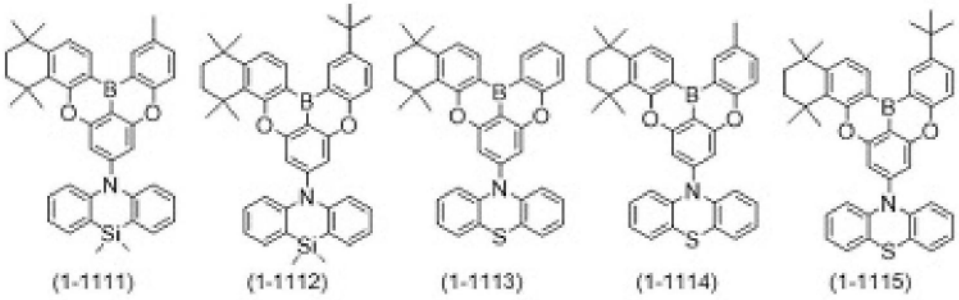
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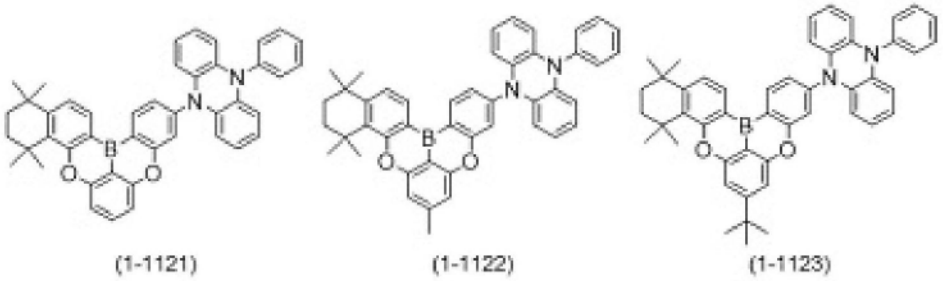
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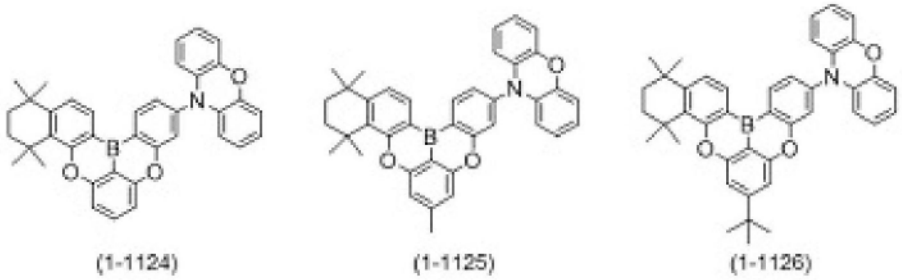
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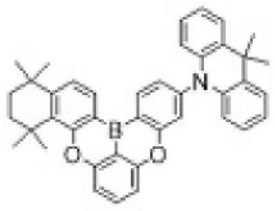


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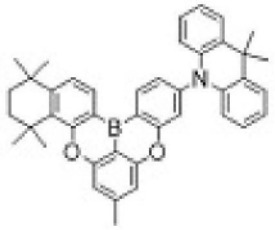




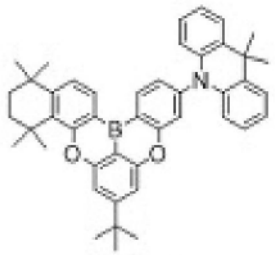
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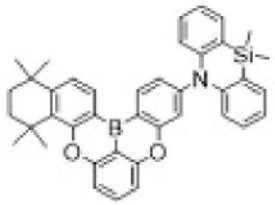
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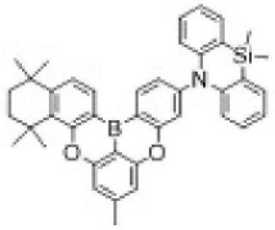
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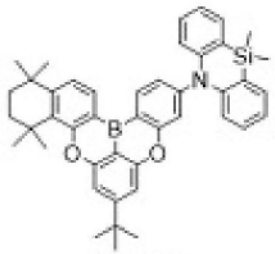
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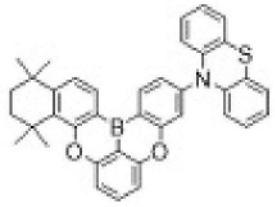


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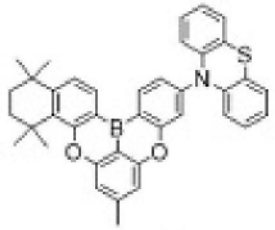


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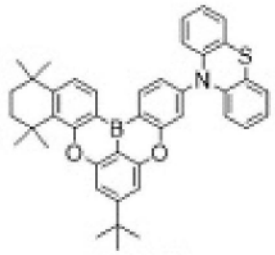
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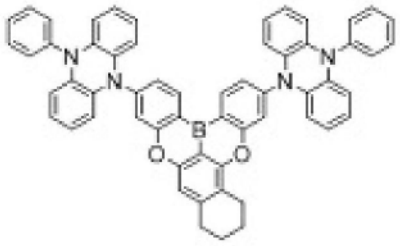
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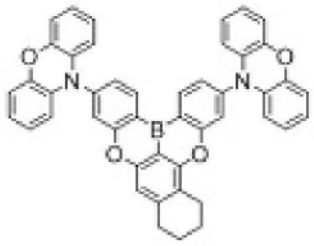
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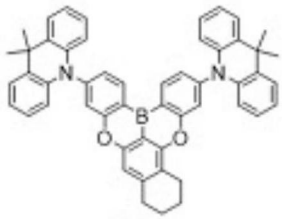


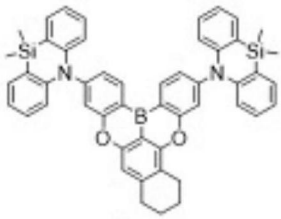
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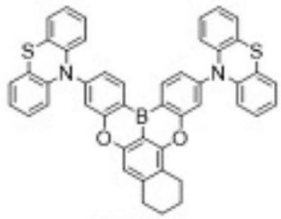


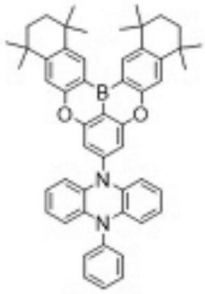
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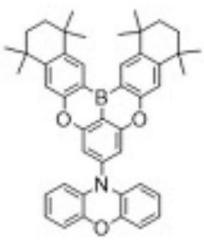
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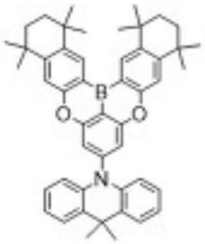

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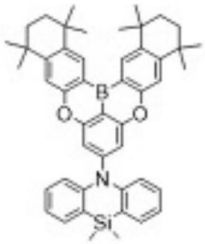

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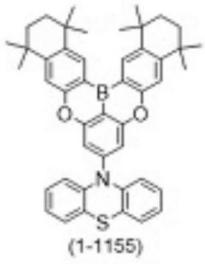

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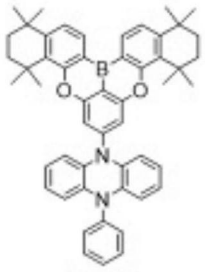

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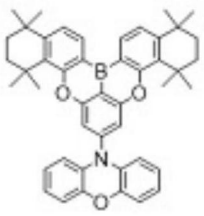

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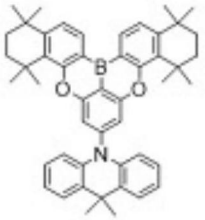

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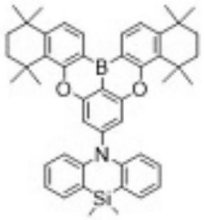
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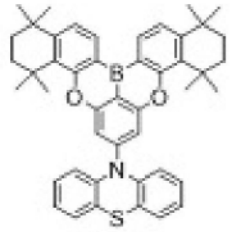

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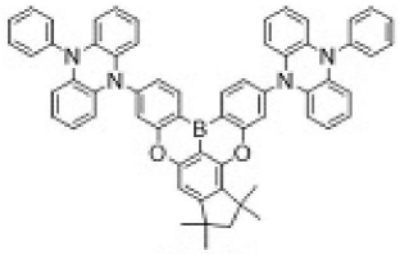

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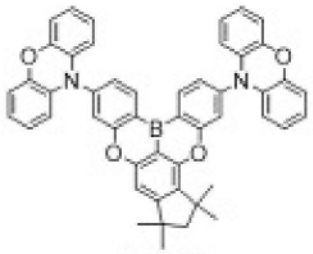

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(1-1164)

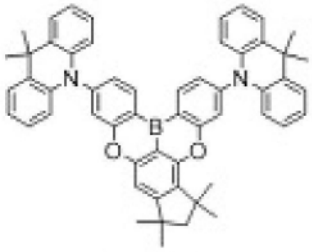
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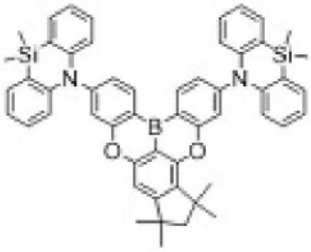

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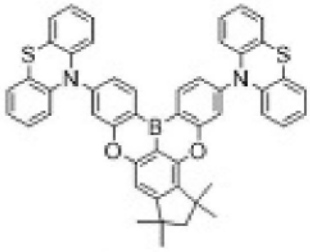

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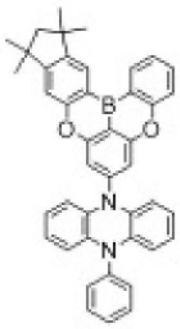

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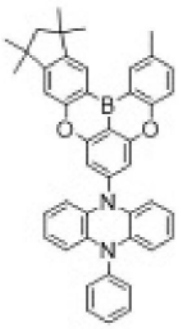
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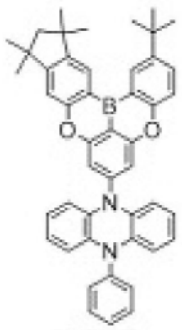

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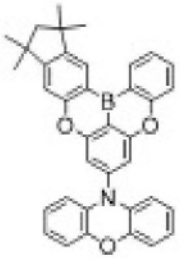

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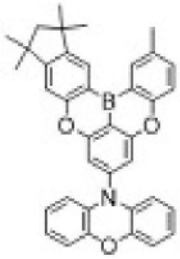

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(1-1181)

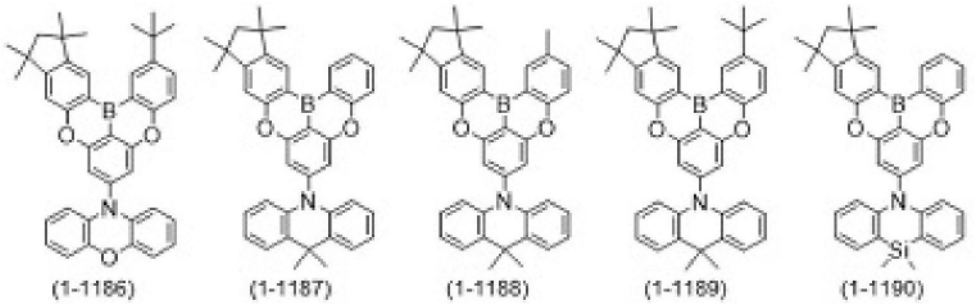

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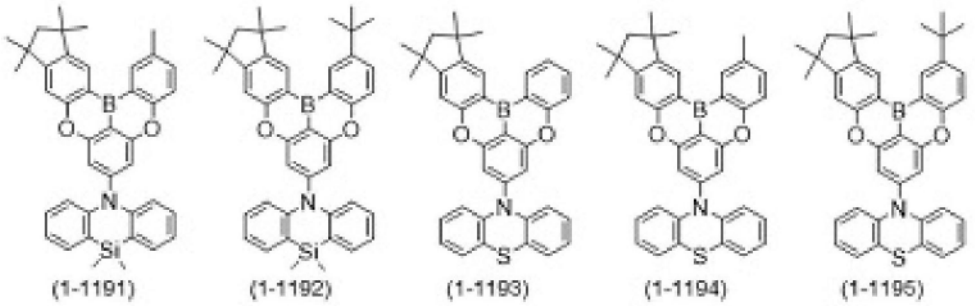

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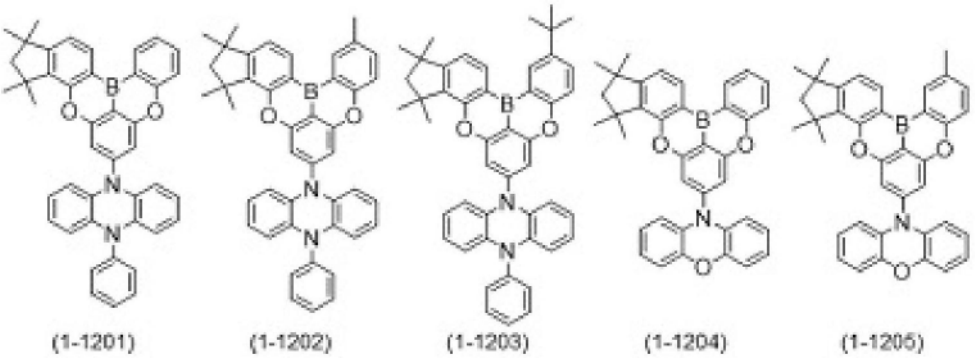

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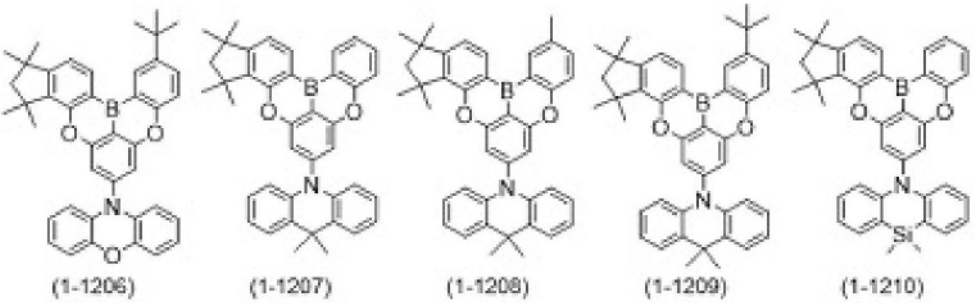
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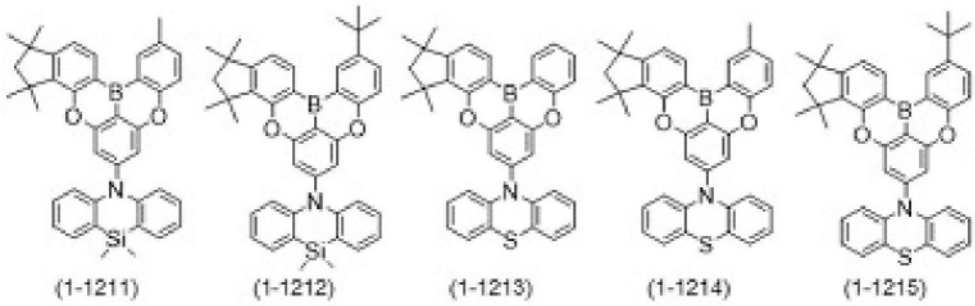


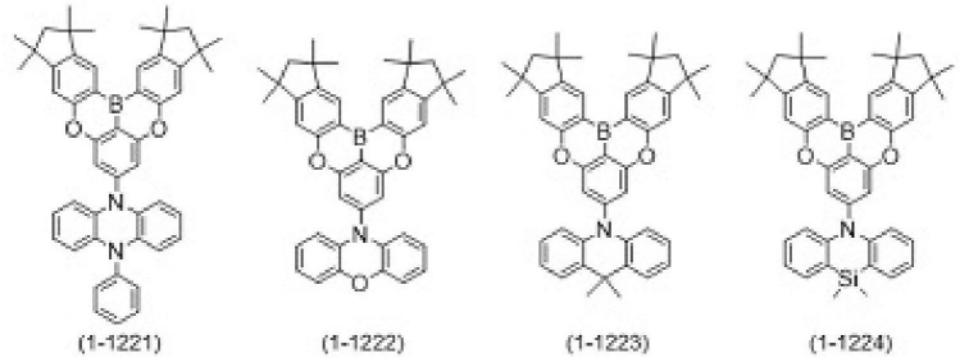
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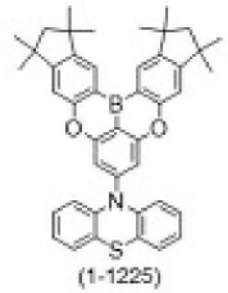


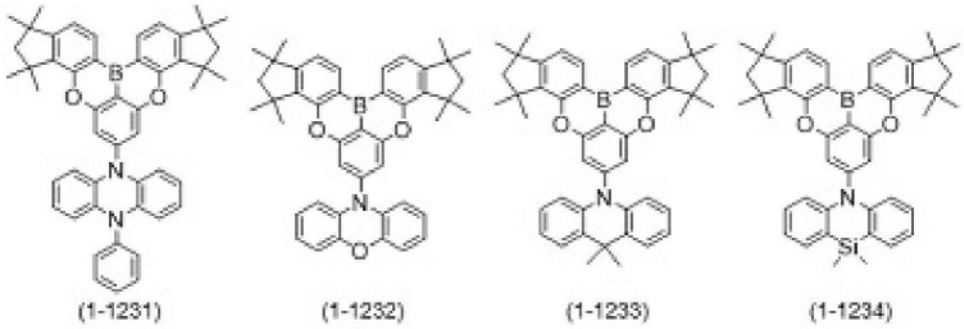
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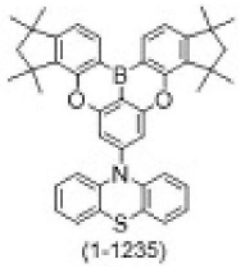


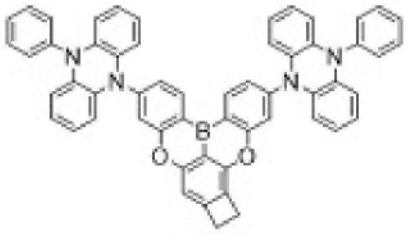
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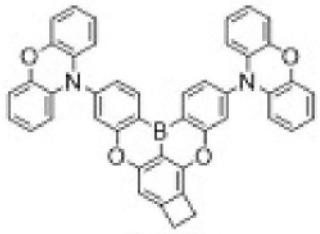




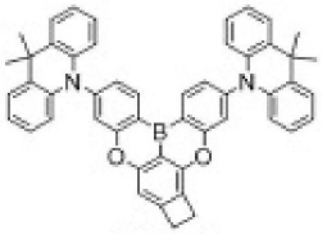
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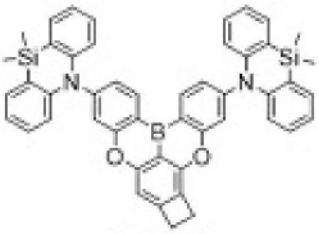

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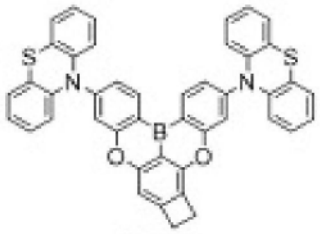

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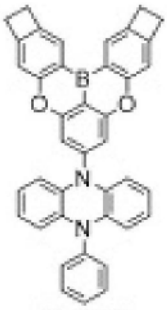

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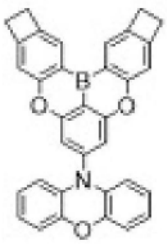
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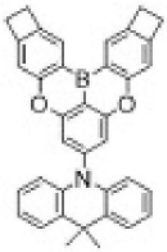

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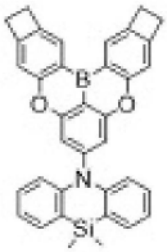

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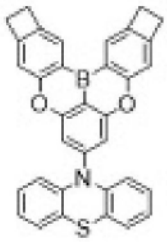

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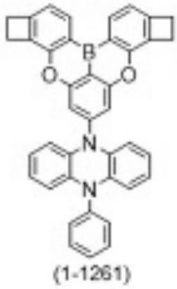

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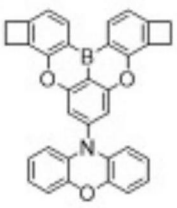

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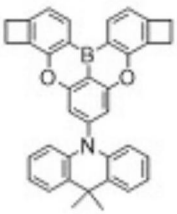

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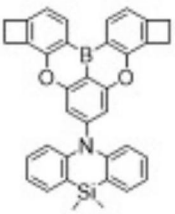
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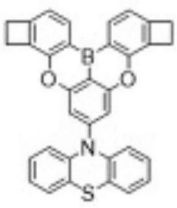
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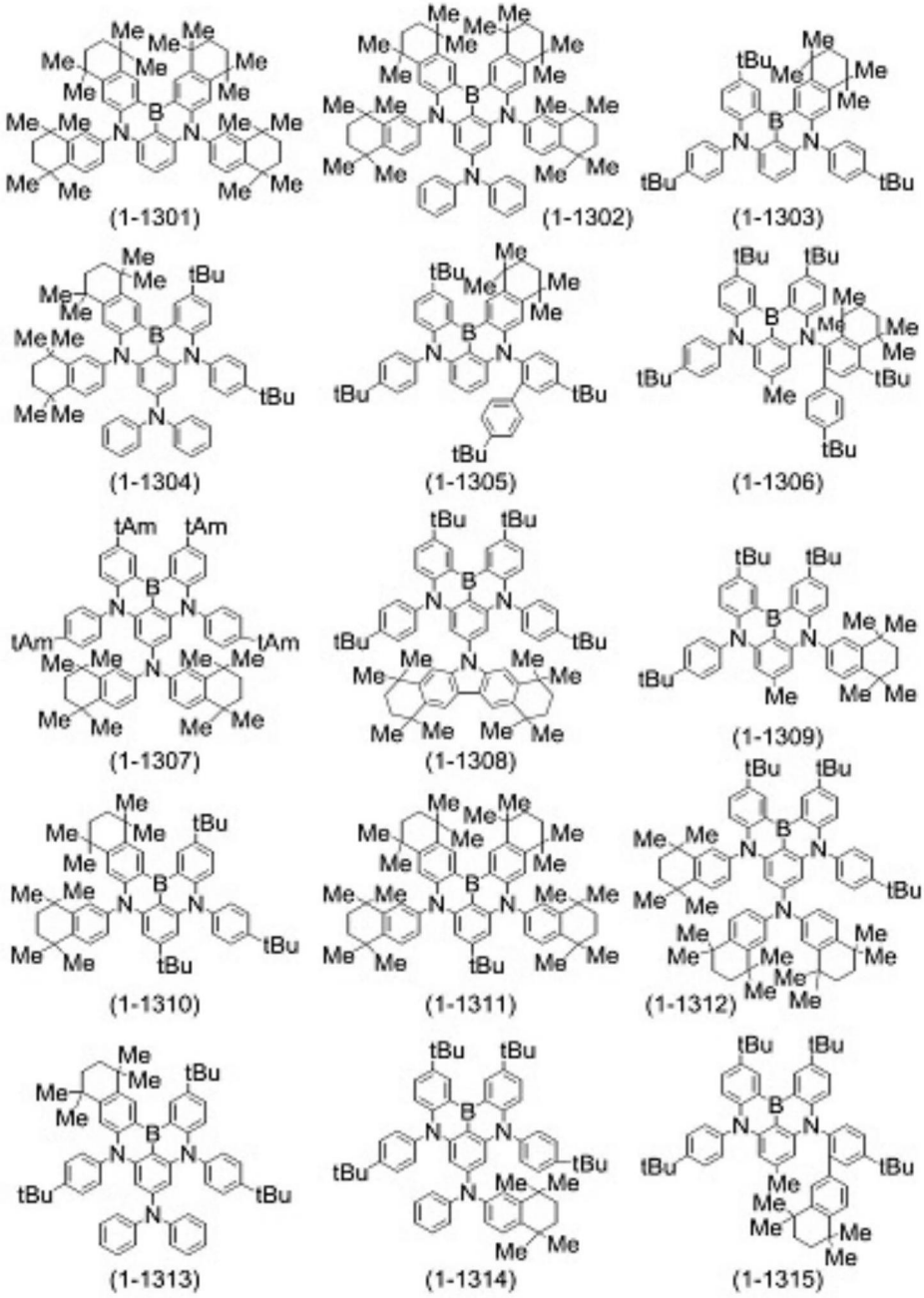

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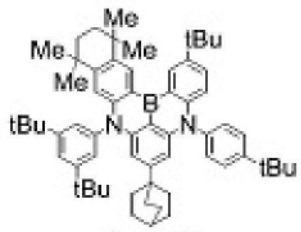
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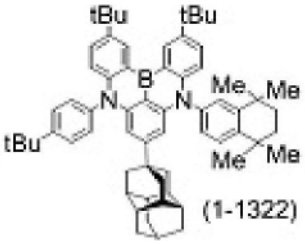
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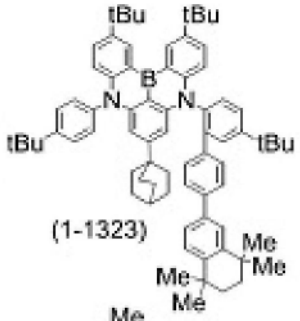


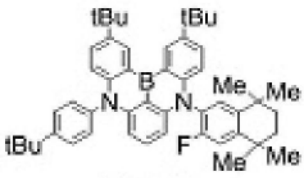
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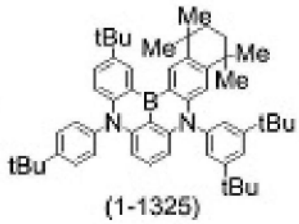
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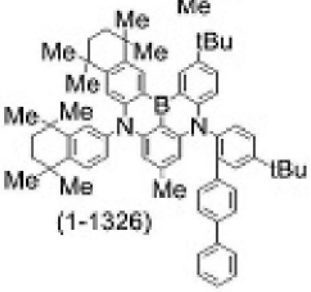

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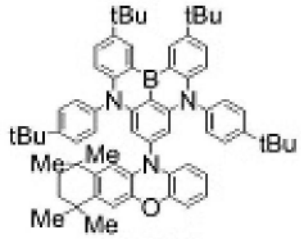

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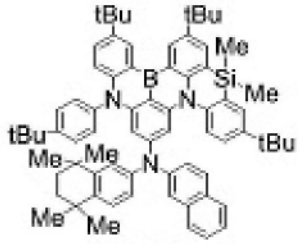

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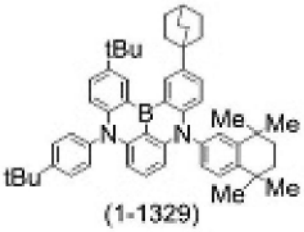

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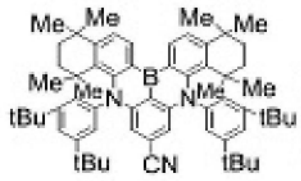

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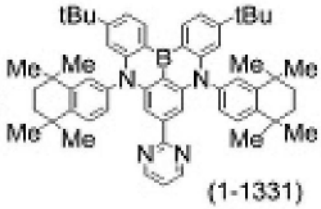

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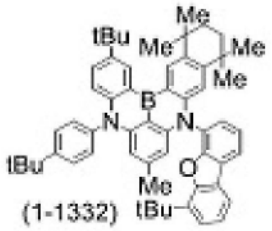

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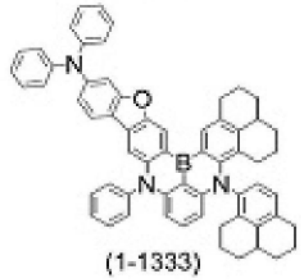

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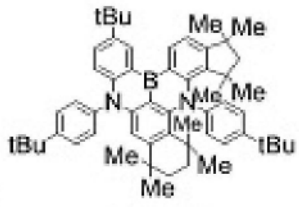

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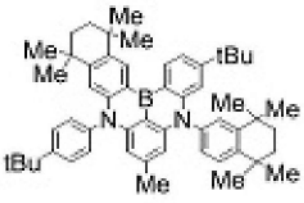

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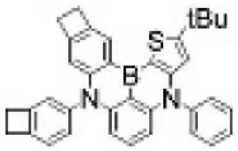

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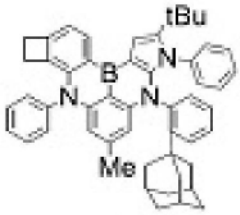

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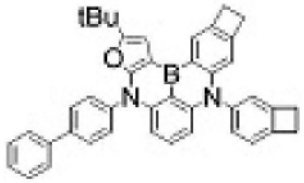
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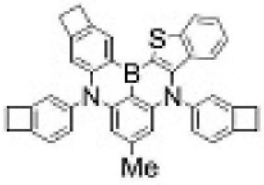
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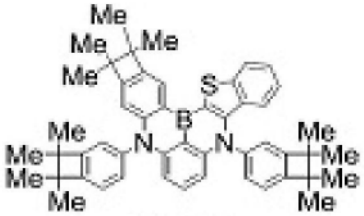
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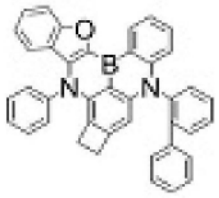
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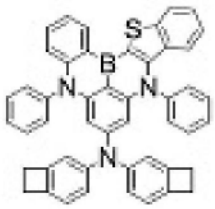
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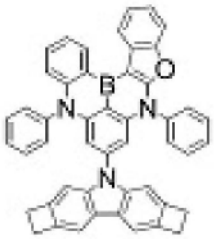
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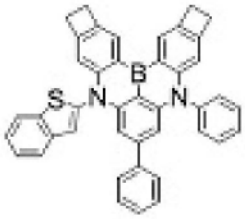
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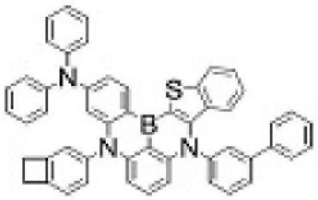
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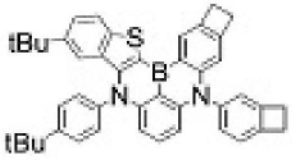
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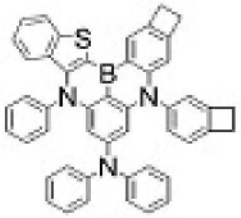
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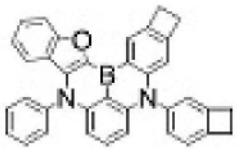
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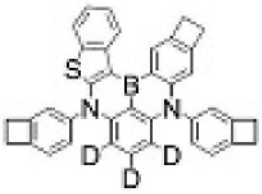
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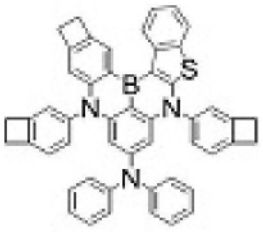
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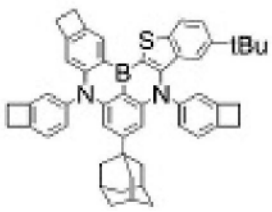
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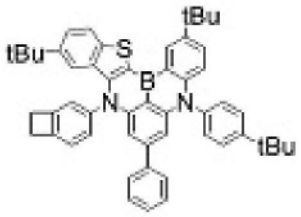
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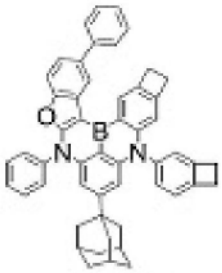
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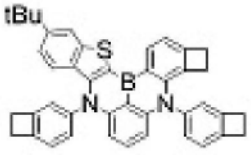
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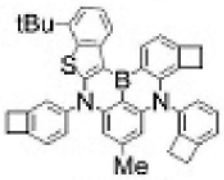
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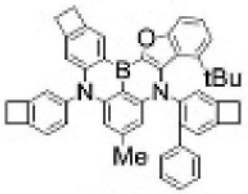
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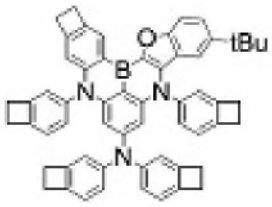
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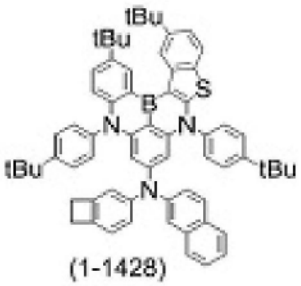
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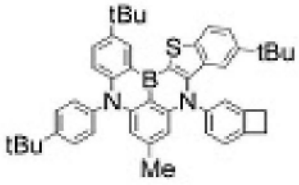
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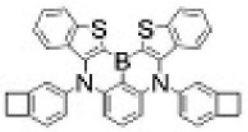
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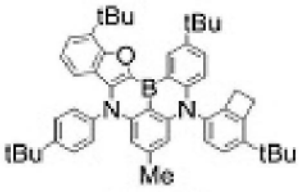
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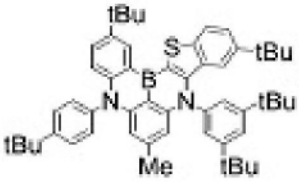
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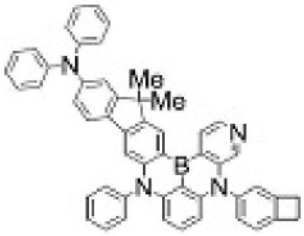
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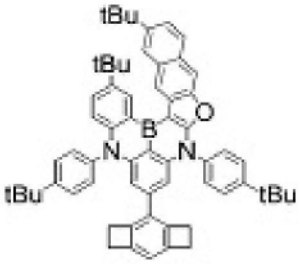
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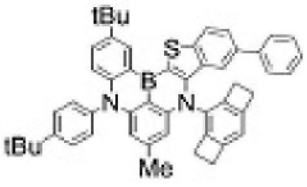
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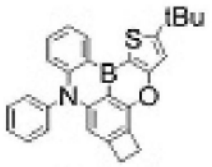
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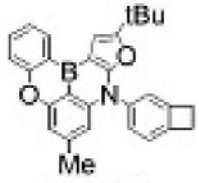


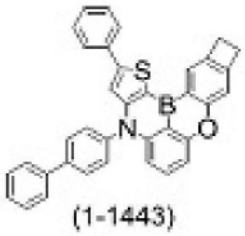
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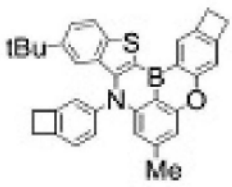
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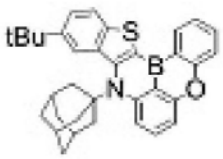
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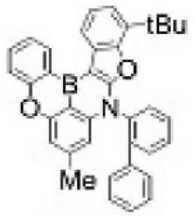

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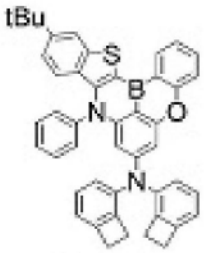

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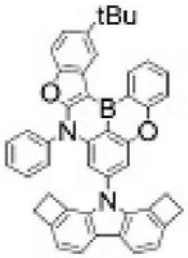

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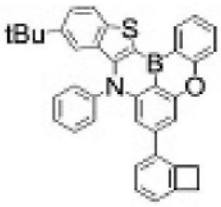

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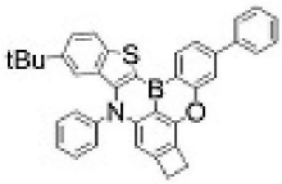

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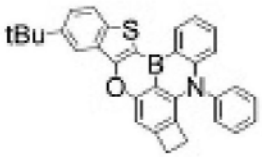

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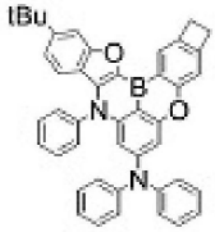

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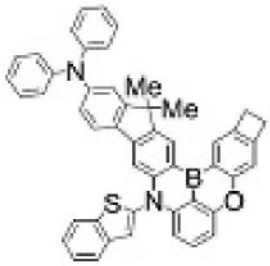

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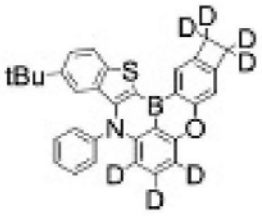

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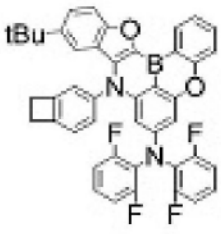

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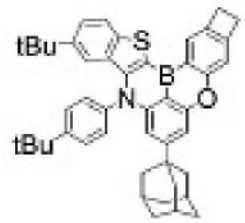

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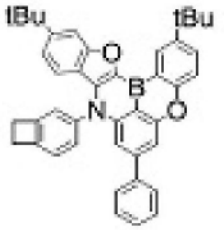

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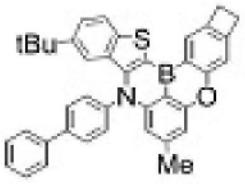

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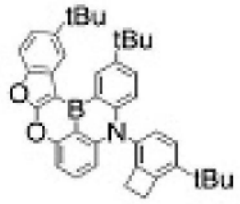
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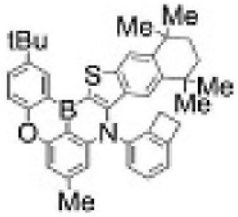
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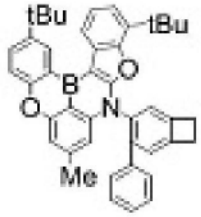

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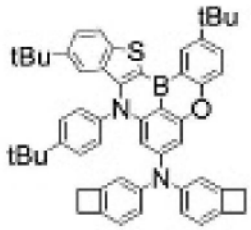

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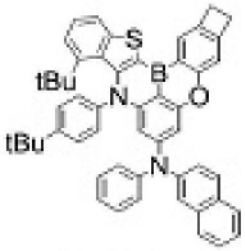

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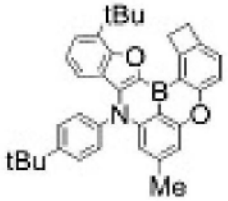

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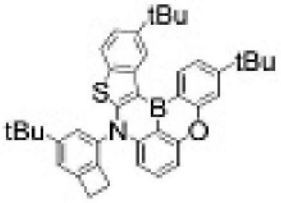

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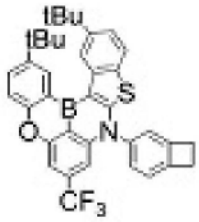

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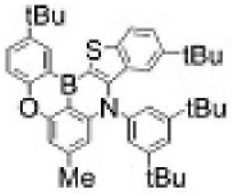

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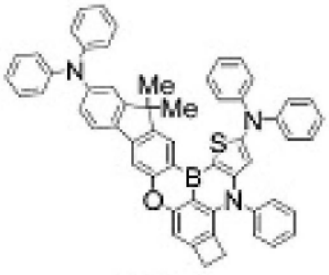

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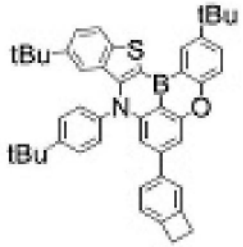

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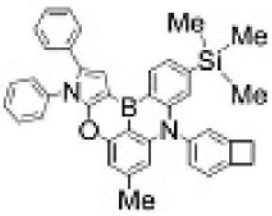

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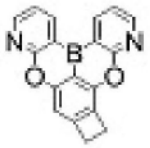

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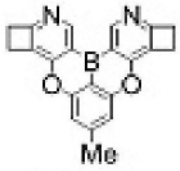

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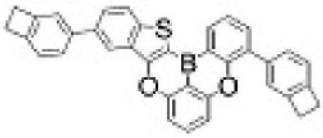
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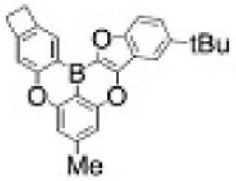
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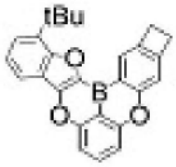
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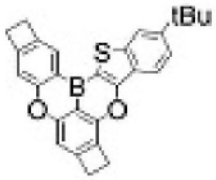
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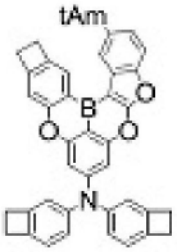
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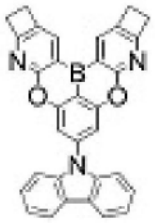
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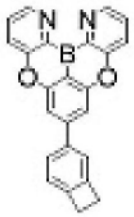
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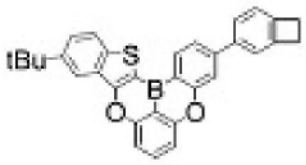
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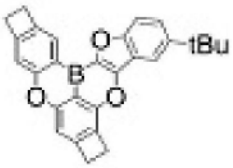
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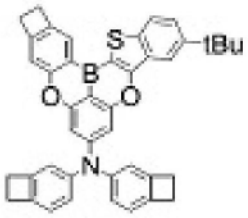
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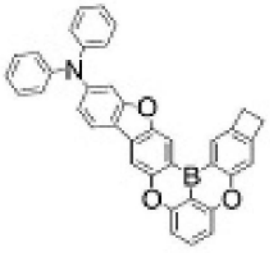
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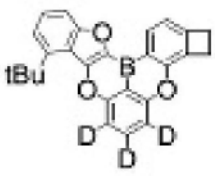
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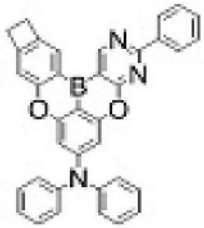
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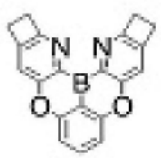
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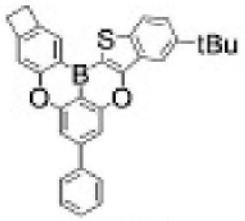
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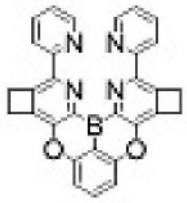
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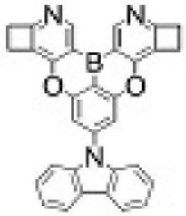
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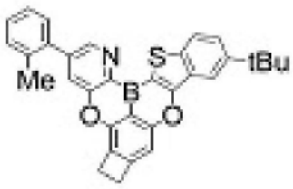
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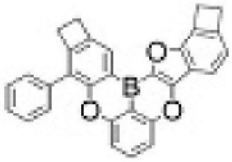
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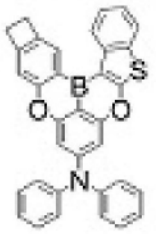
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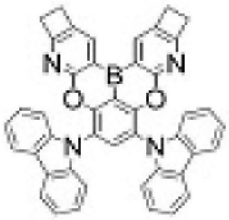
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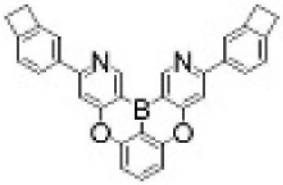
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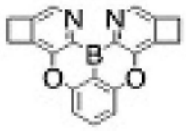
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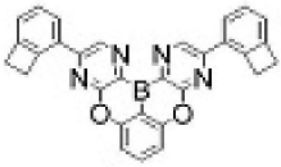
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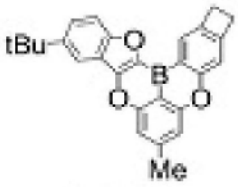
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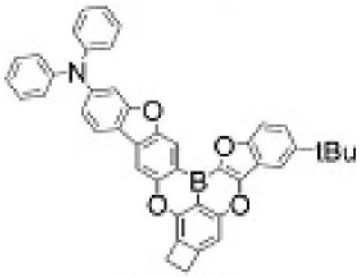
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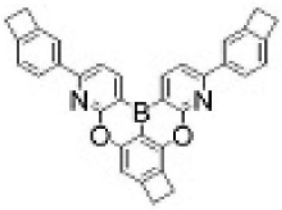
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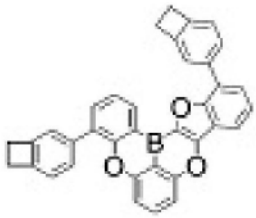
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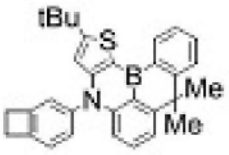
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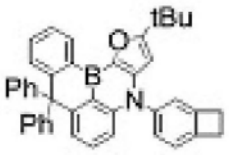


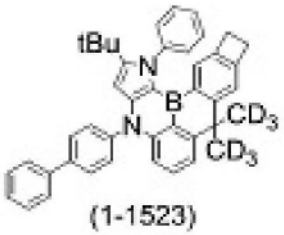
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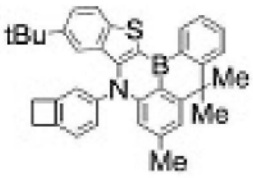
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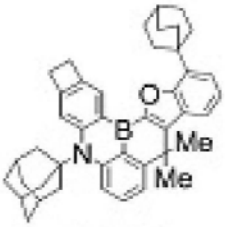
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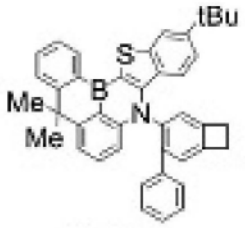

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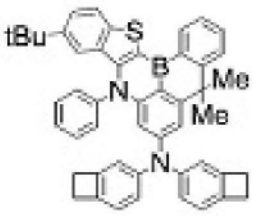

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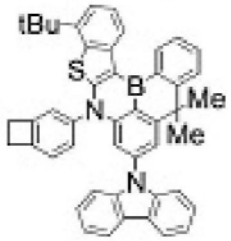

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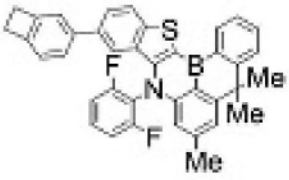

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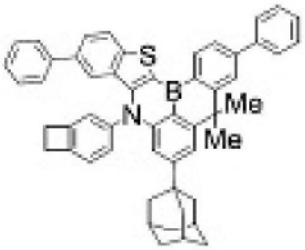

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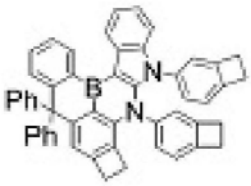

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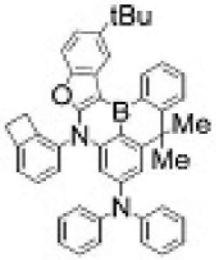

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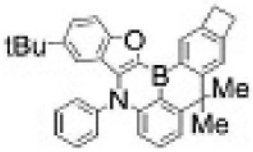

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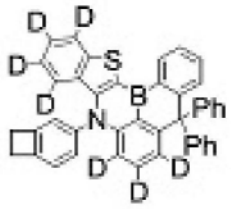

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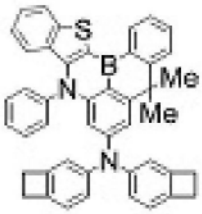

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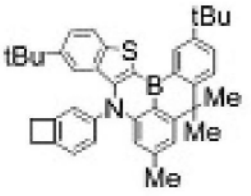

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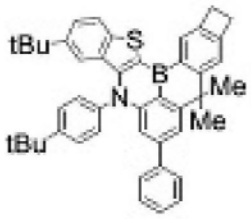

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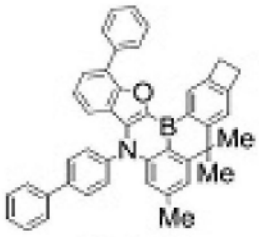

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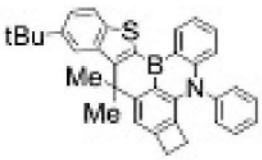
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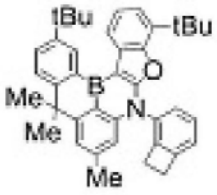
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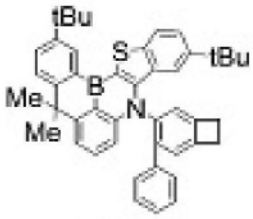

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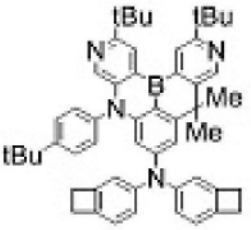

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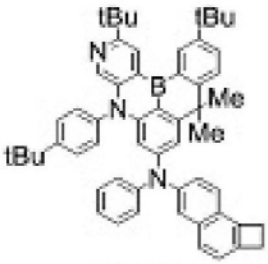

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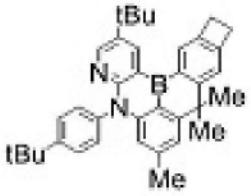

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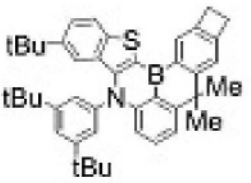

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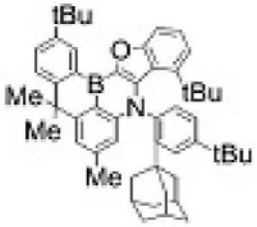

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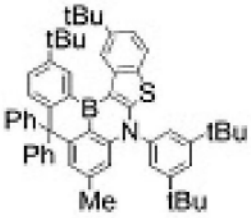

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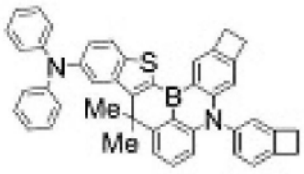

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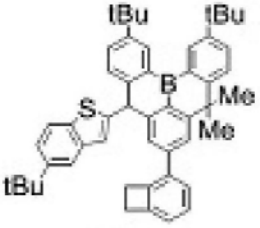

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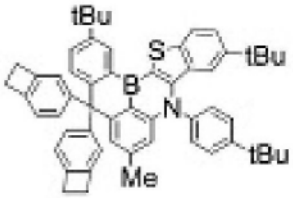

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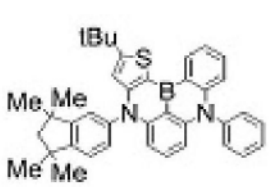

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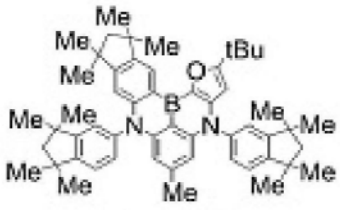

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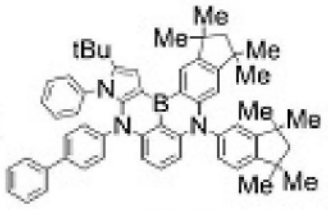

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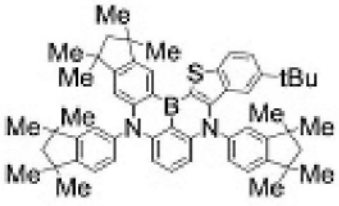
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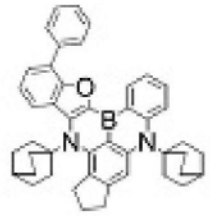
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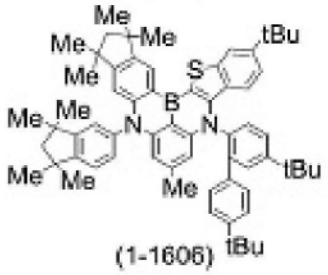

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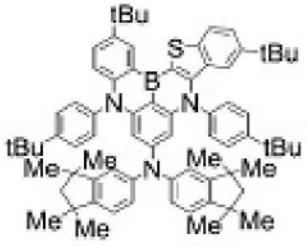

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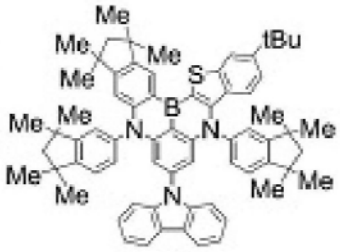

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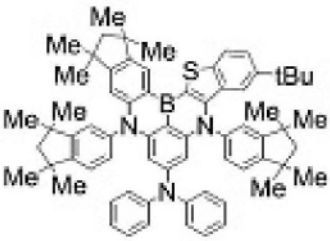

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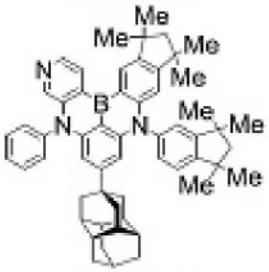

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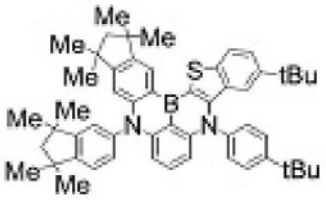

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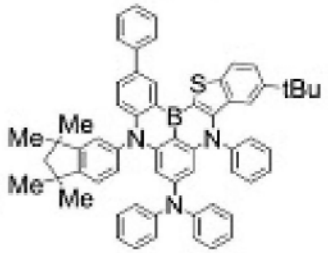

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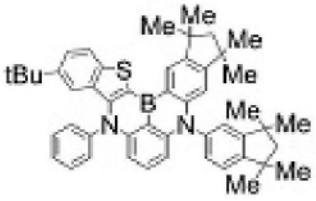

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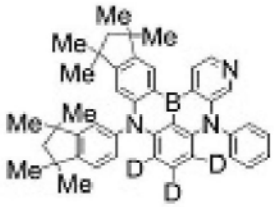

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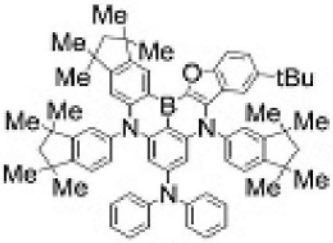

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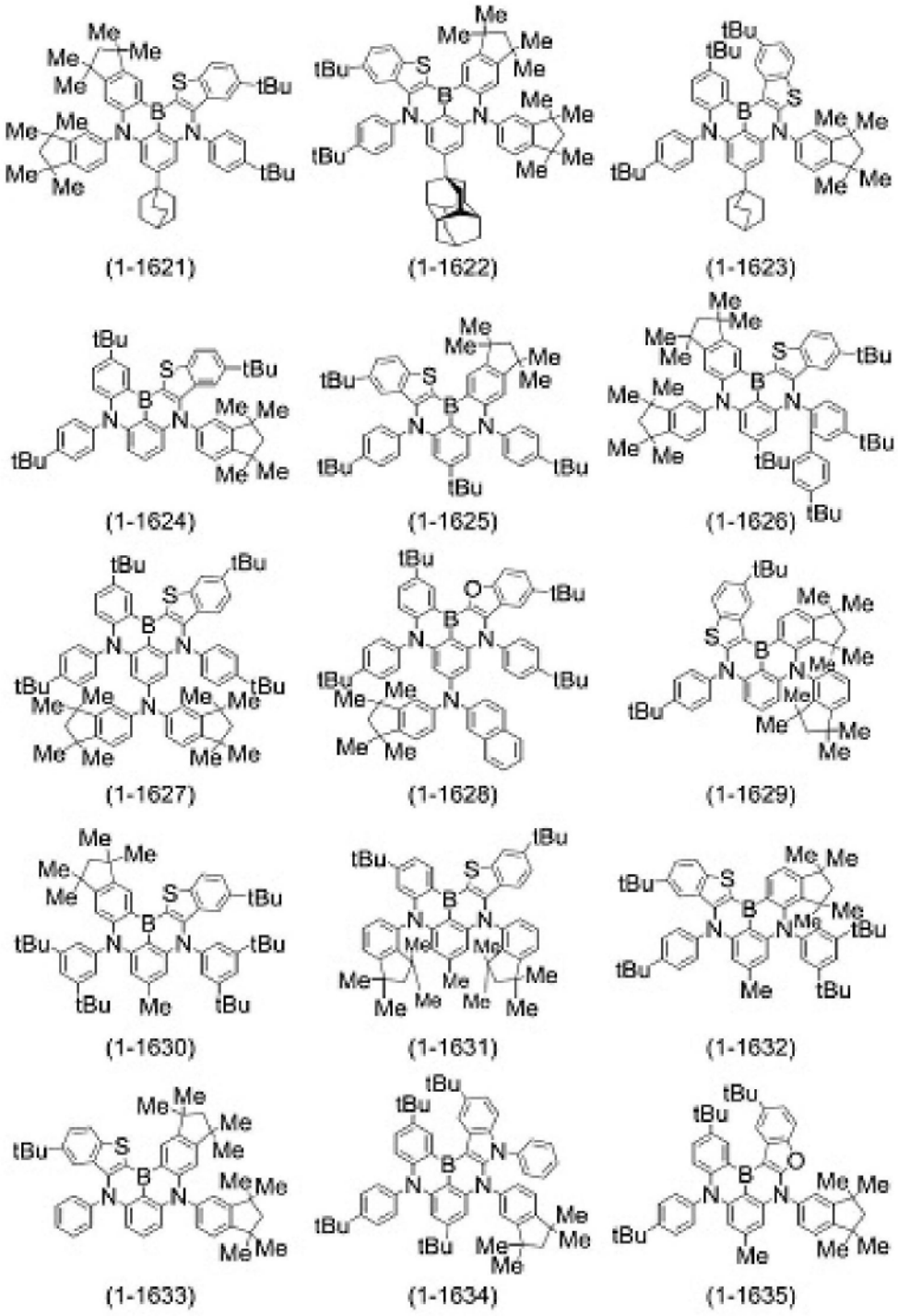

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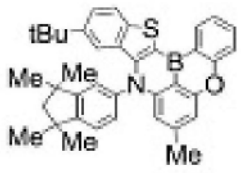
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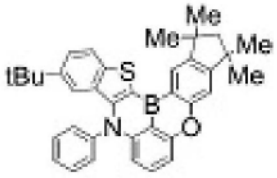
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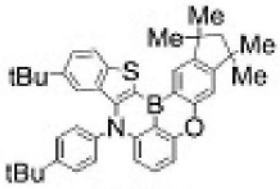


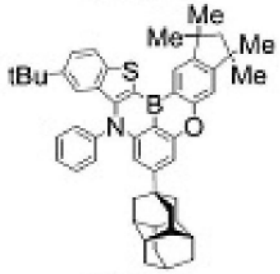
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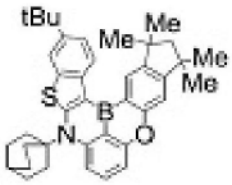
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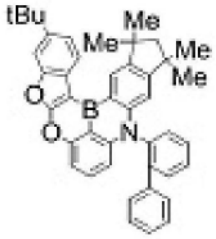

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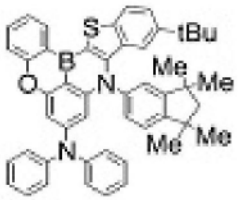

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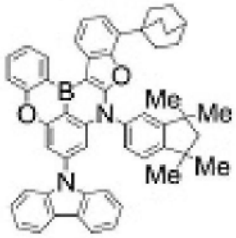

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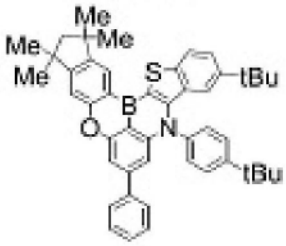

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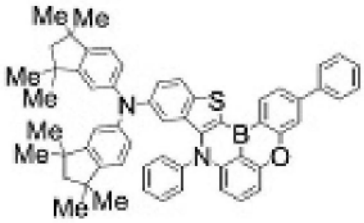

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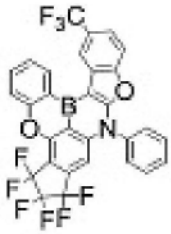

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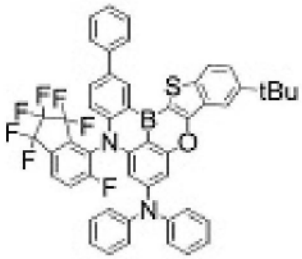

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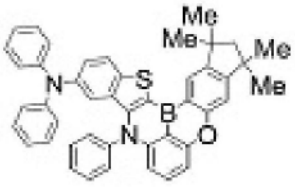

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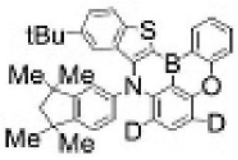

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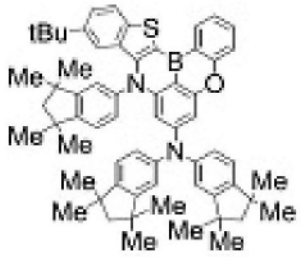

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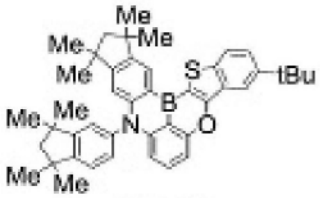

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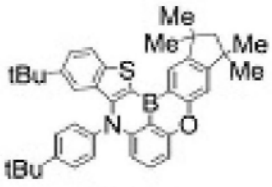

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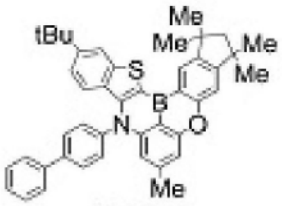

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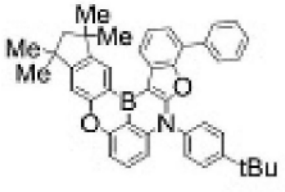
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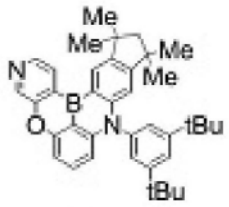
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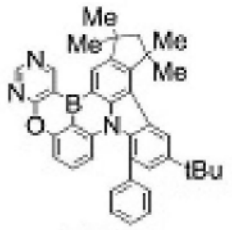

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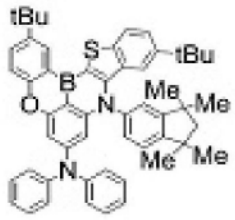

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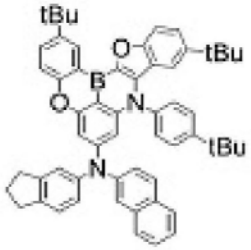

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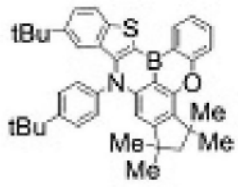

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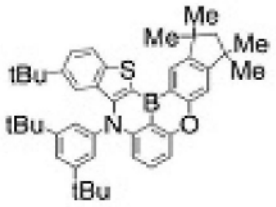

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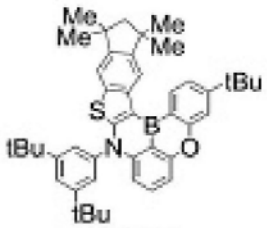

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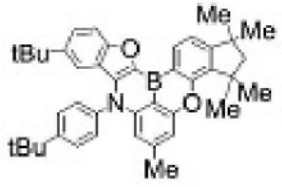

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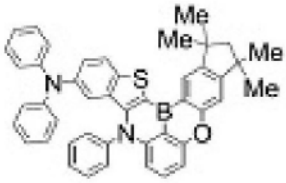

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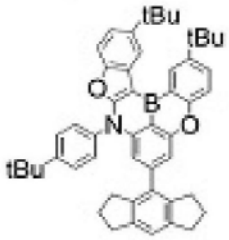

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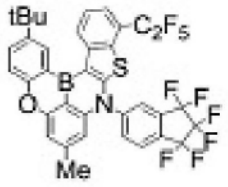

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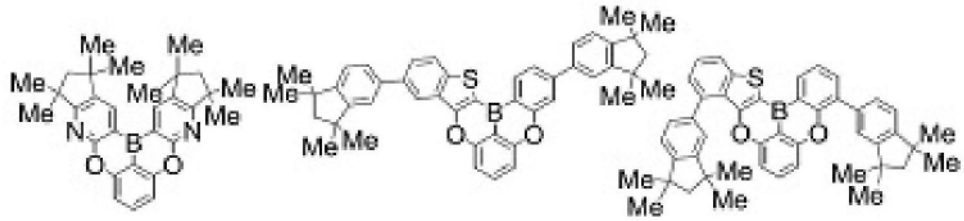

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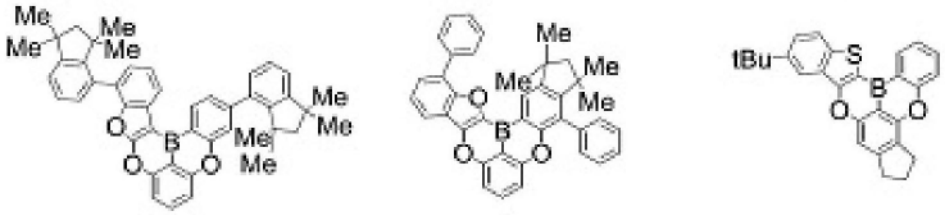

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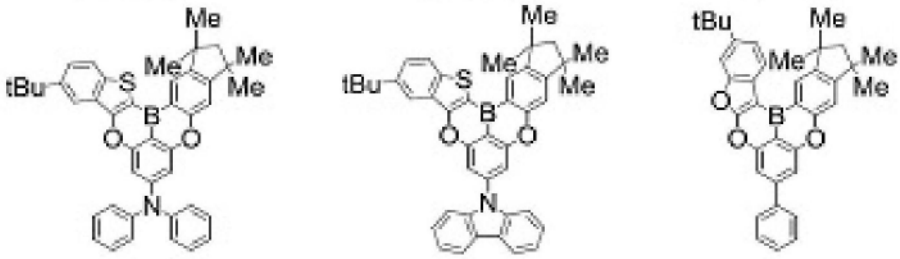
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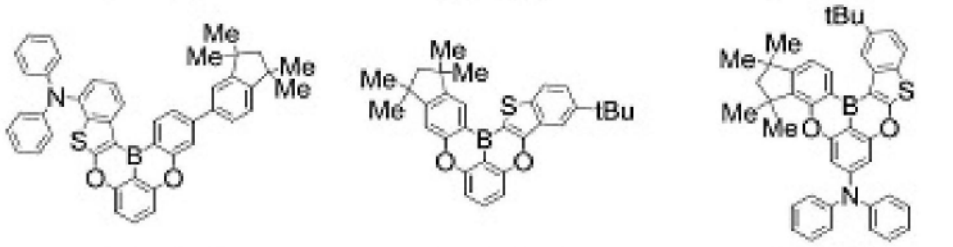
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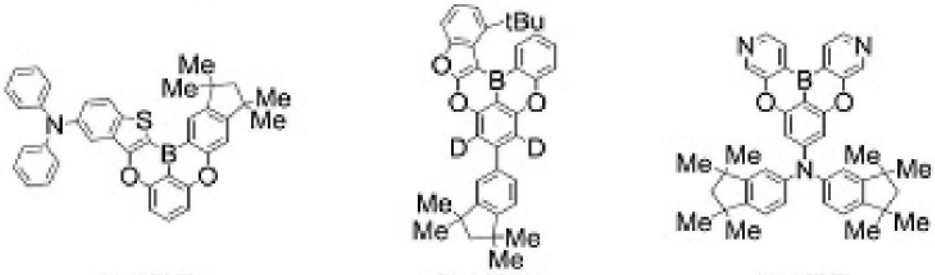
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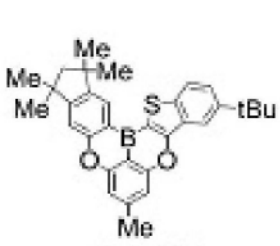
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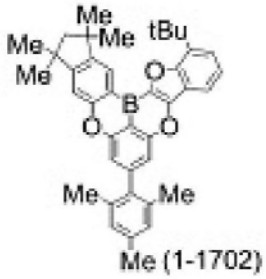


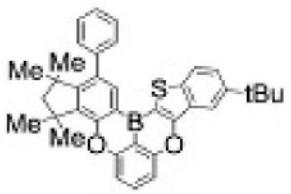
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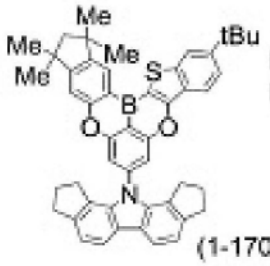
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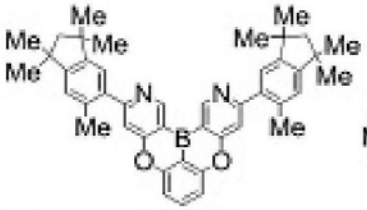
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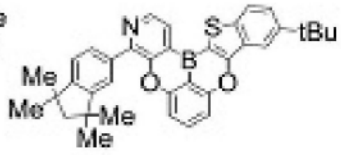

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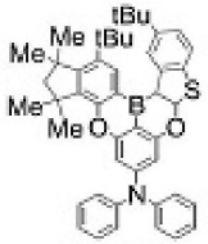

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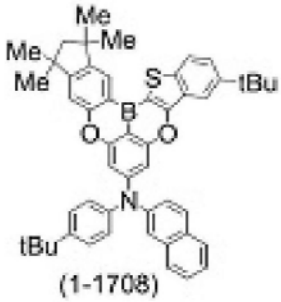

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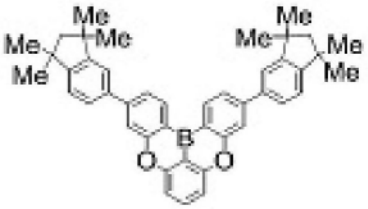

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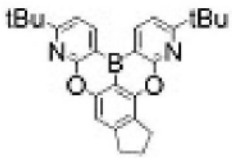

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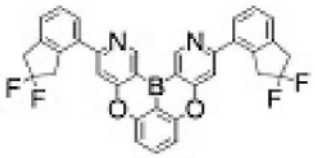

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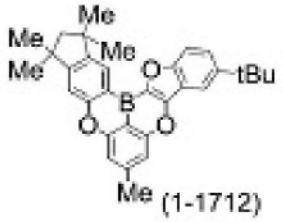

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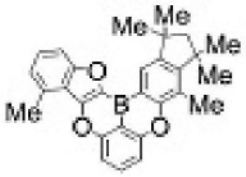

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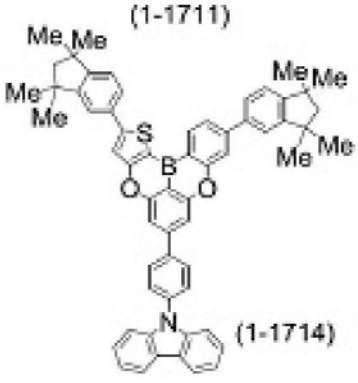

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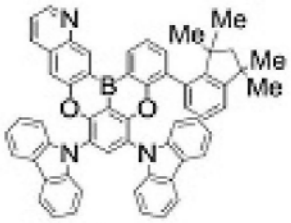

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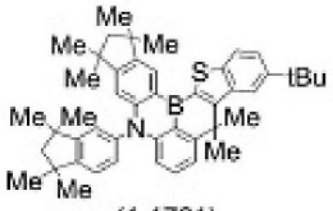

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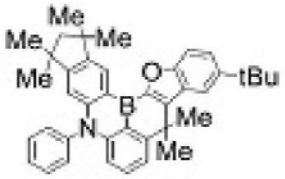

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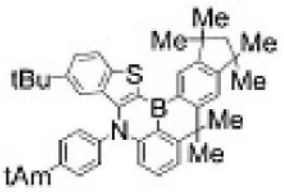

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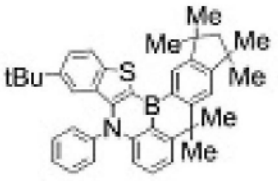
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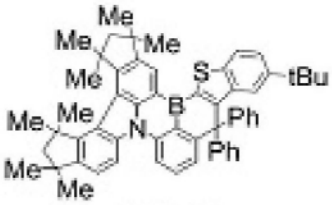
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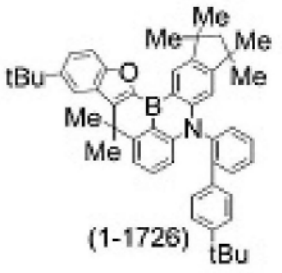

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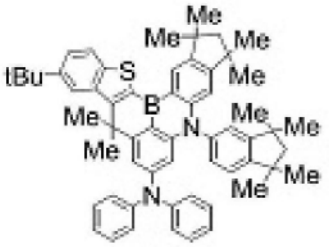

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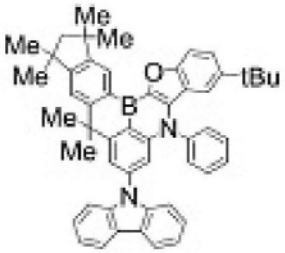

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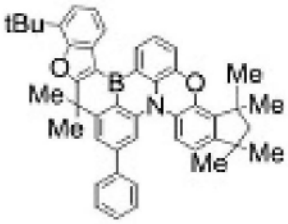

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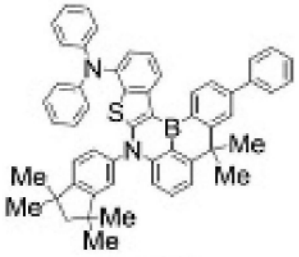

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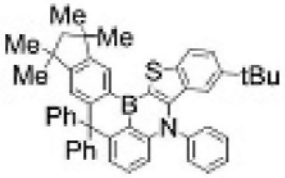

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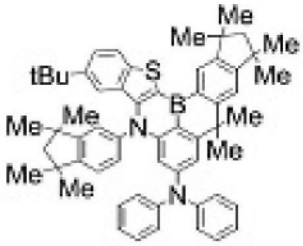

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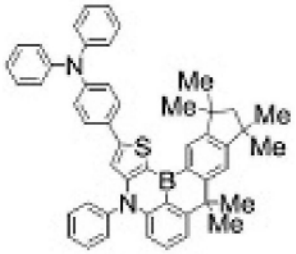

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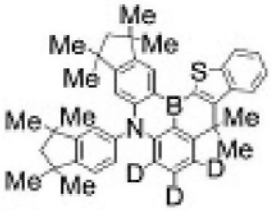

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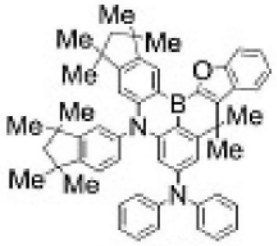

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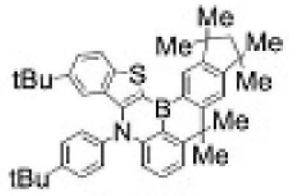

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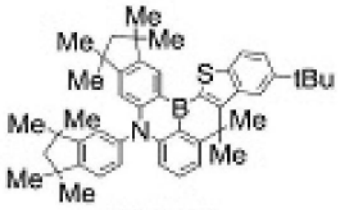

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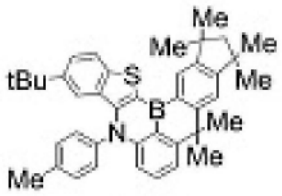

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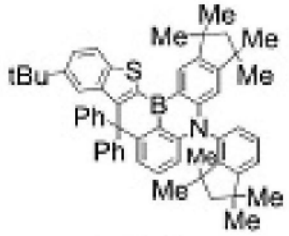
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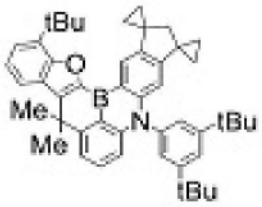
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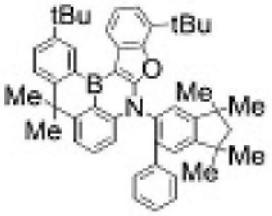

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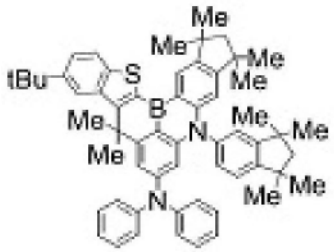

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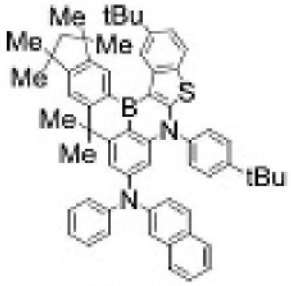

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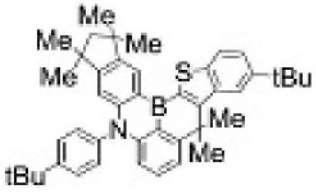

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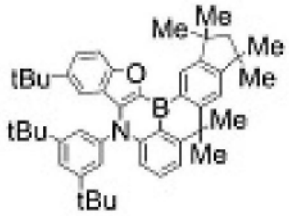

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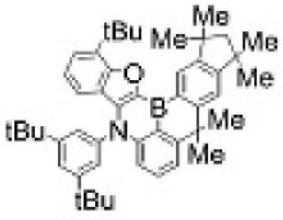

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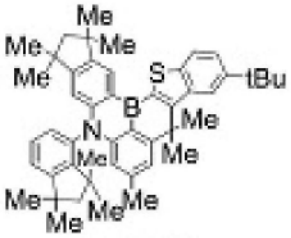

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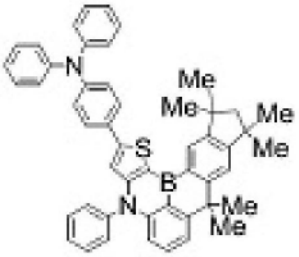

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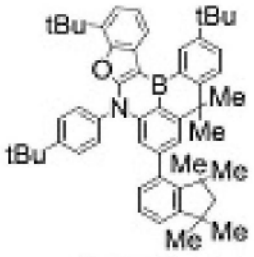

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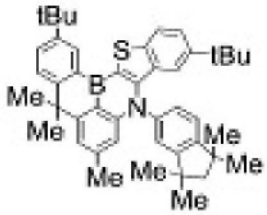

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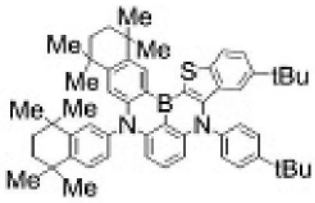

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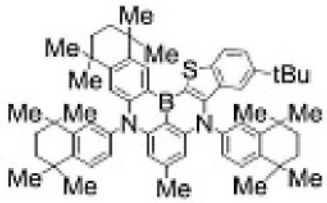

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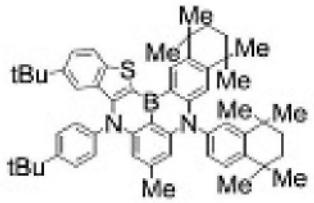

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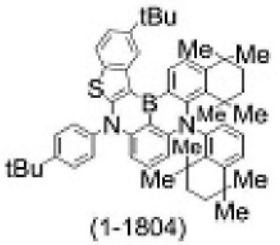
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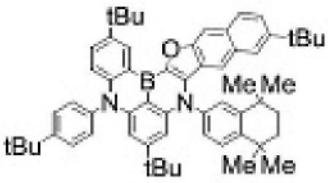
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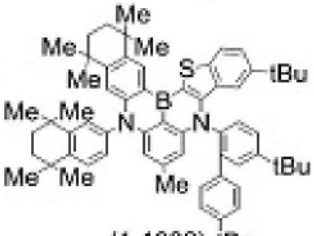

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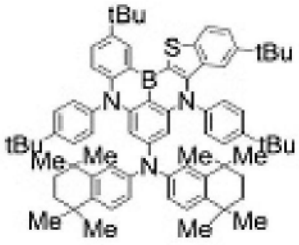

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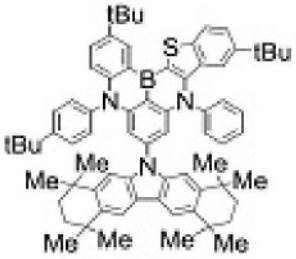

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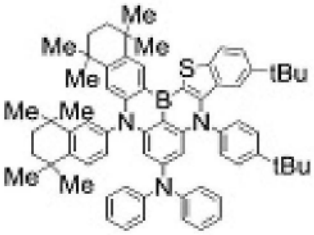

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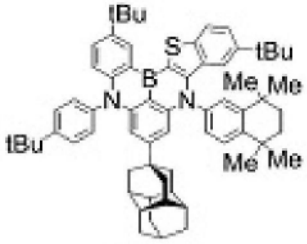

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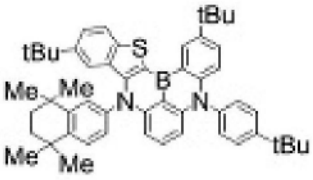

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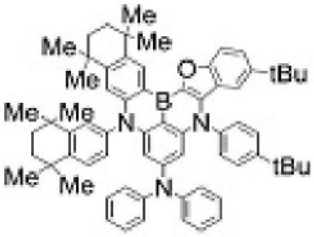

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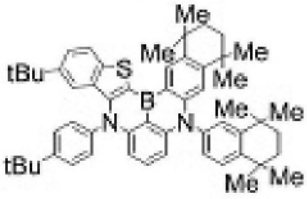

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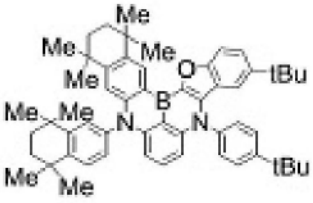

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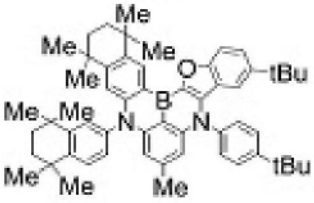

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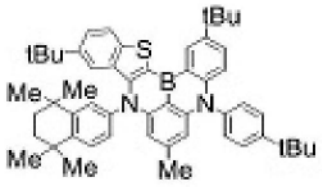

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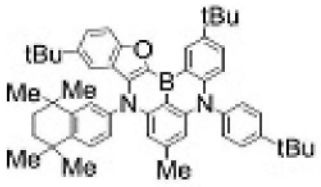

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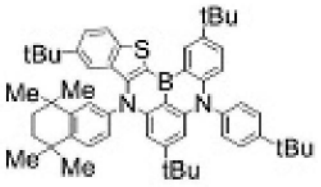
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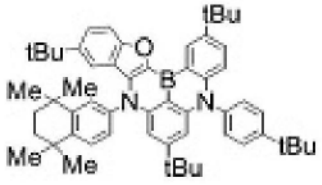
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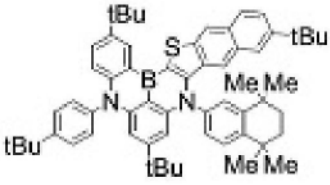
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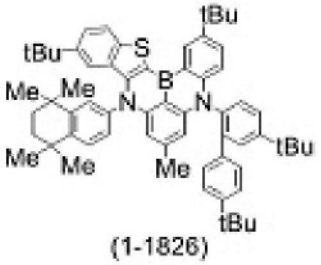
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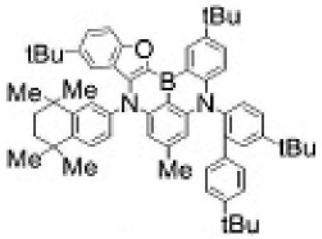
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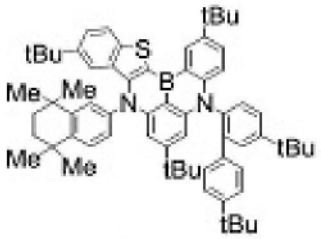
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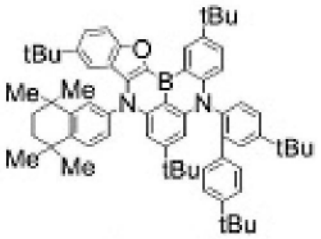
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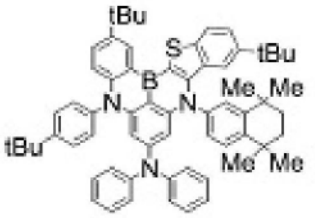
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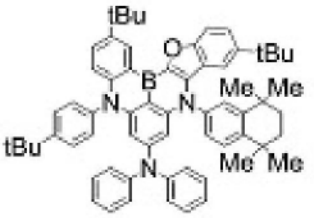
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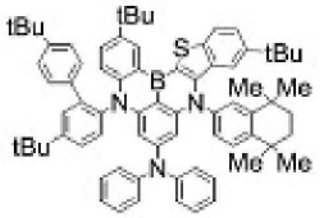
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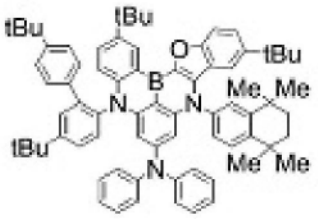
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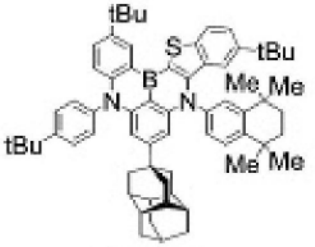
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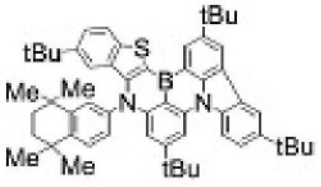
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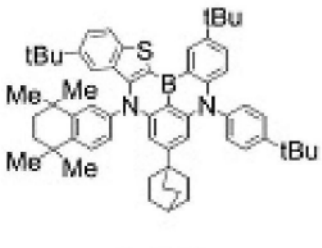


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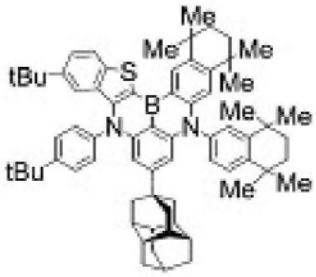


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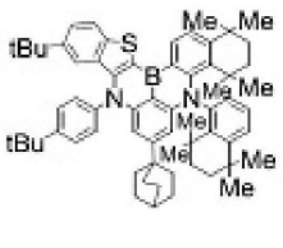
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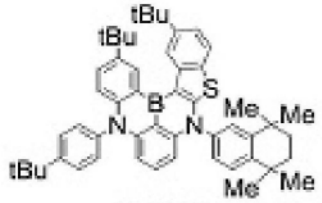
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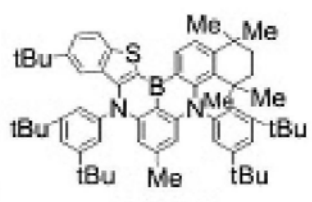
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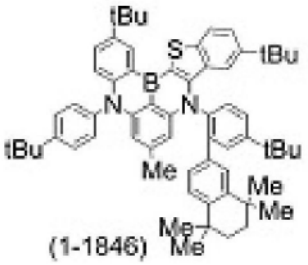
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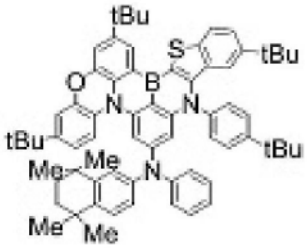


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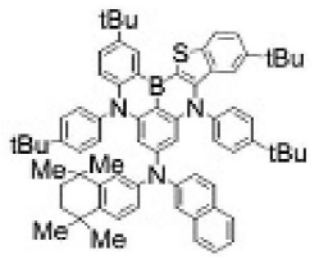


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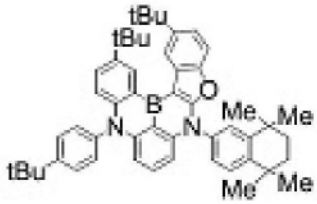
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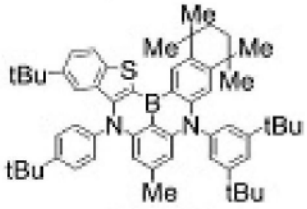
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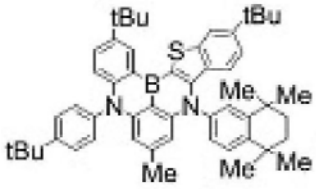
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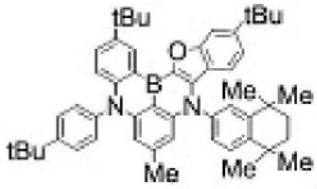
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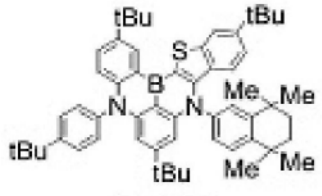
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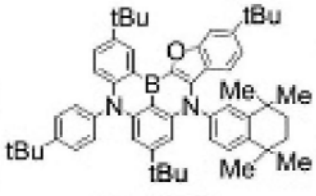
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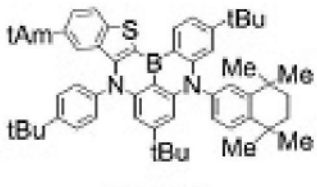
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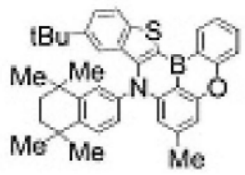
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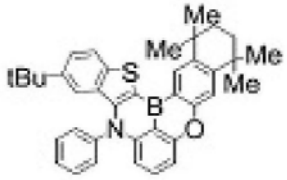


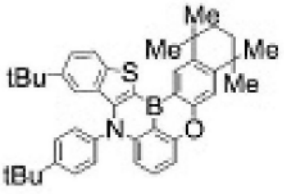
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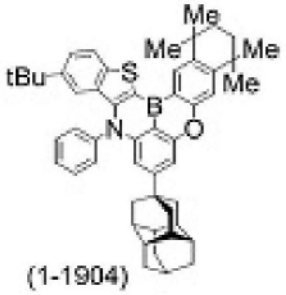
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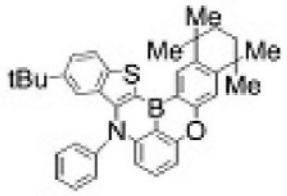
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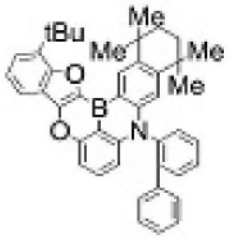

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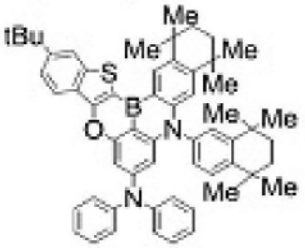

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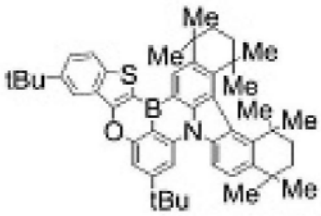

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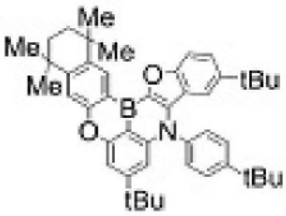

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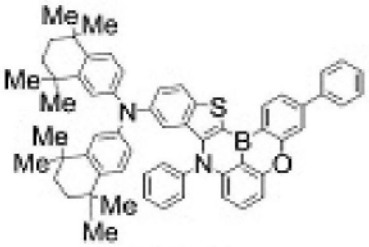

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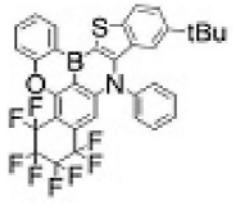

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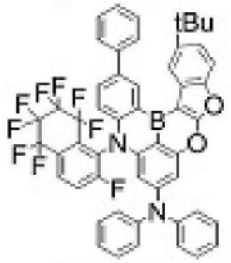

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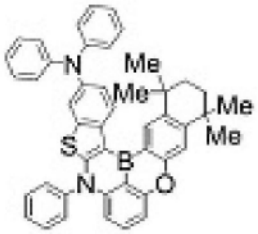

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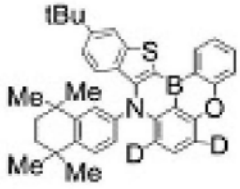

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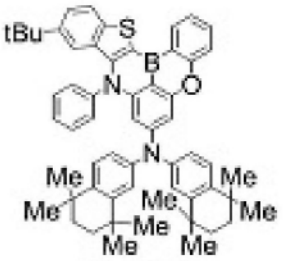

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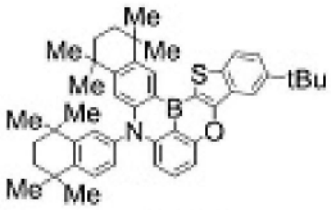

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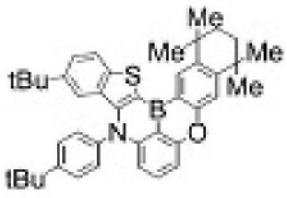

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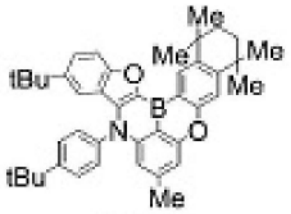

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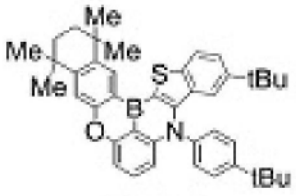

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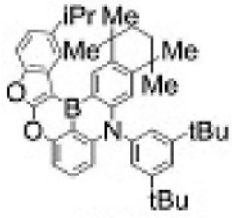
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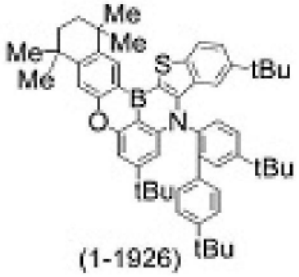

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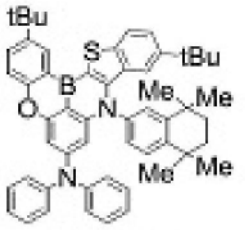

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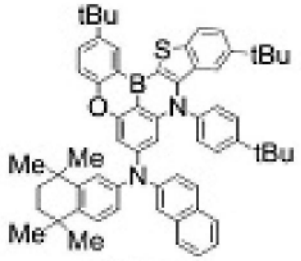

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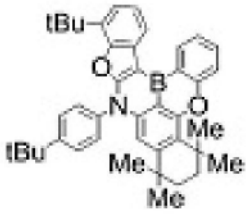

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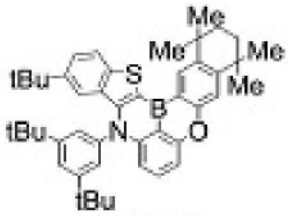

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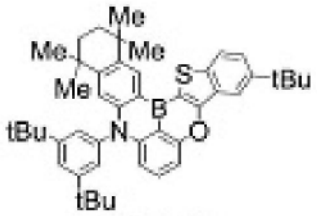
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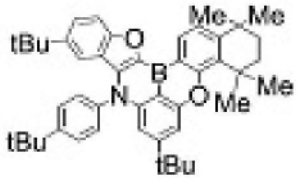

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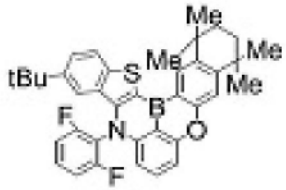

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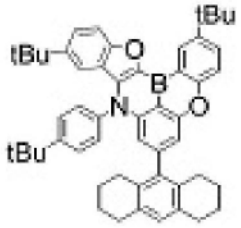

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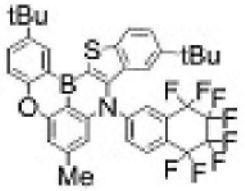

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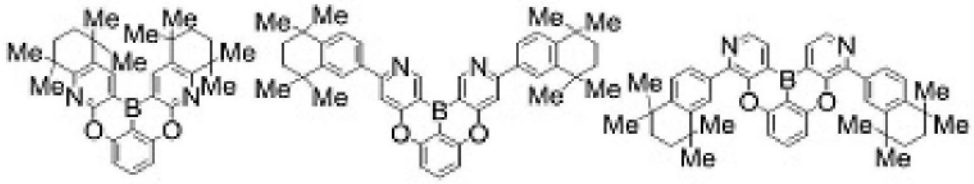

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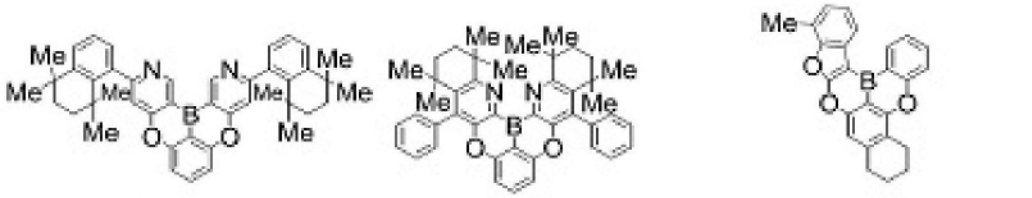

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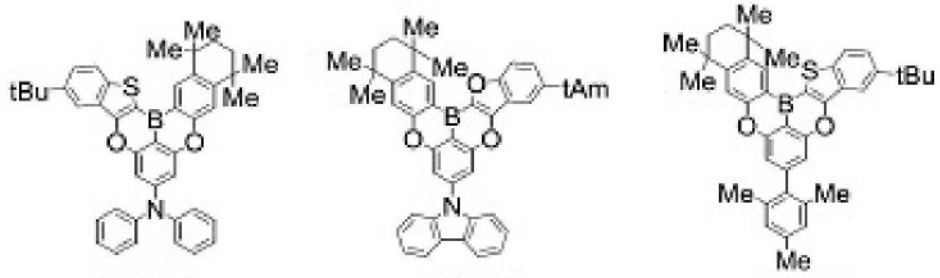
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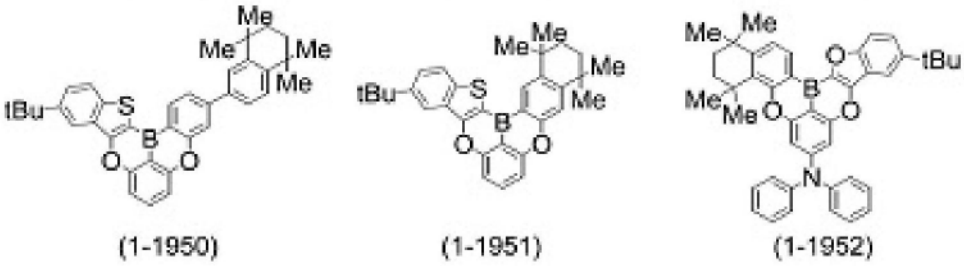
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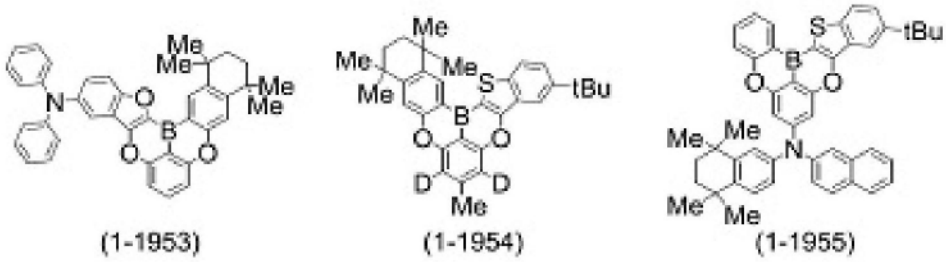
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(1-1947) (1-1948) (1-1949)



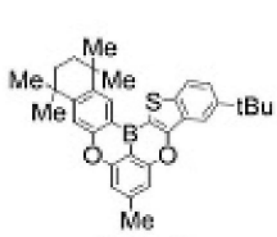
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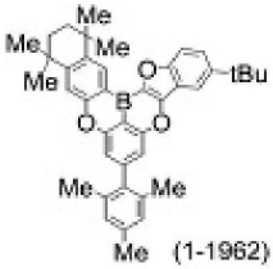


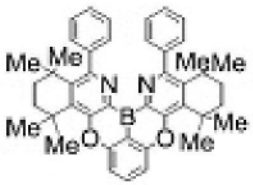
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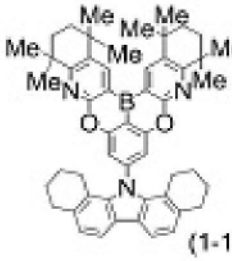
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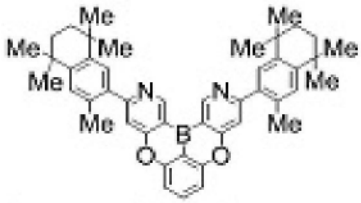
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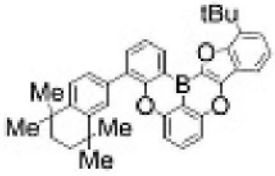

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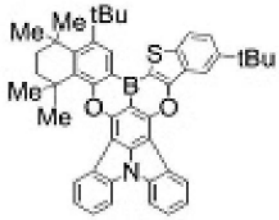

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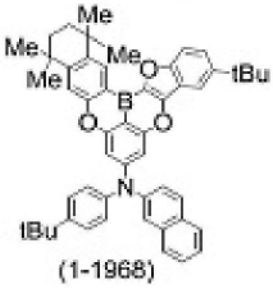

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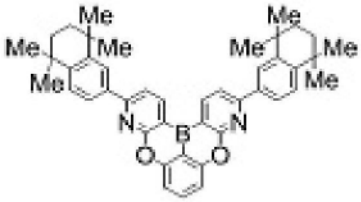

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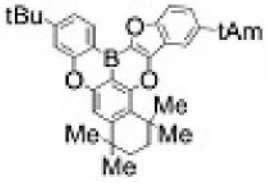

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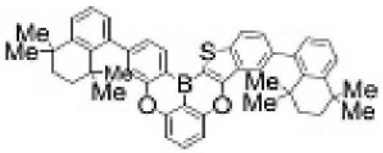

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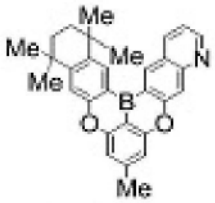

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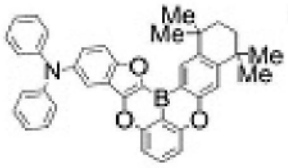

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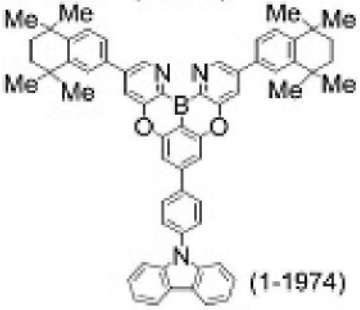

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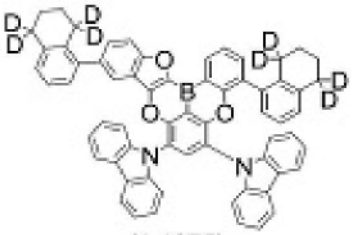

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(1-1971)


(1-1972)

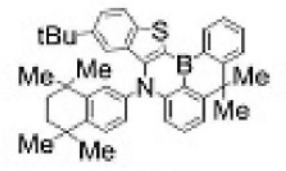

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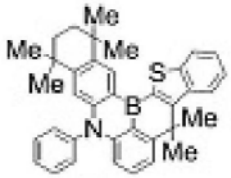

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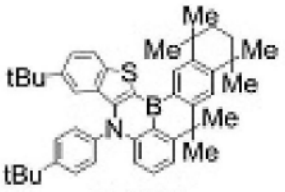

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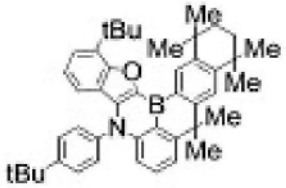
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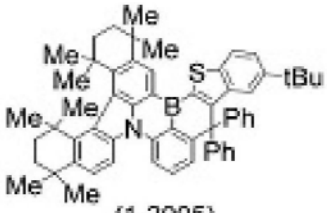
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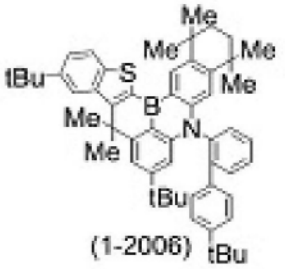

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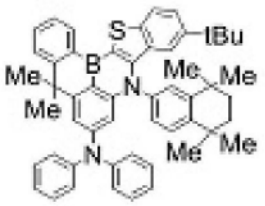

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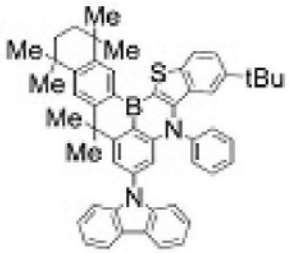

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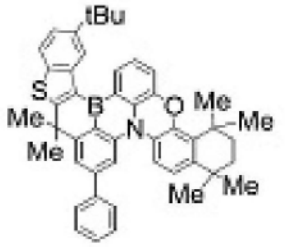

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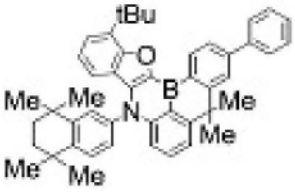

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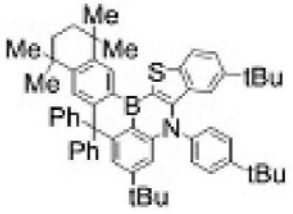

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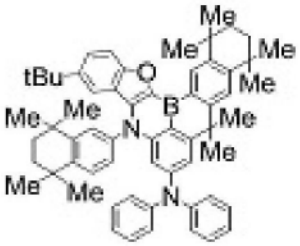

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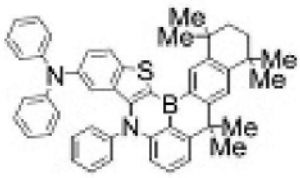

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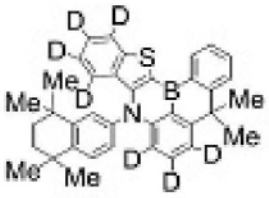

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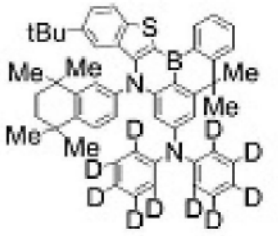

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(1-2011)


(1-2012)

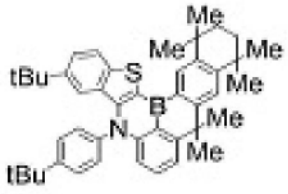

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(1-2014)

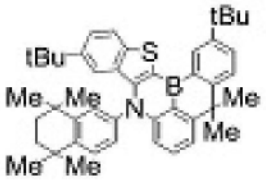

(1-2015)

[0426] [化112]

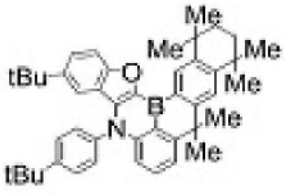
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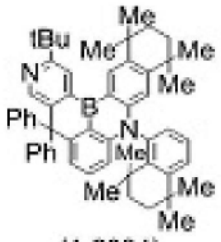
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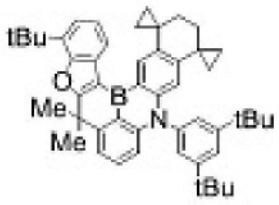
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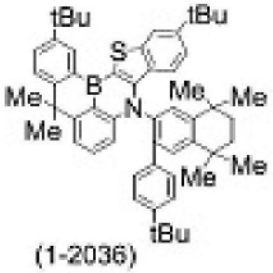
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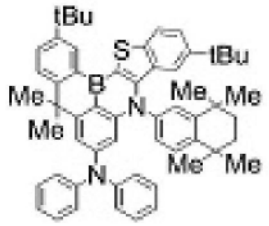
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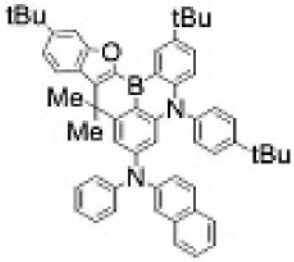
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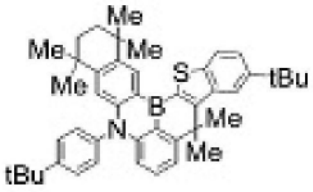
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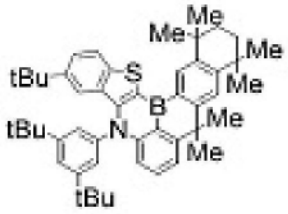
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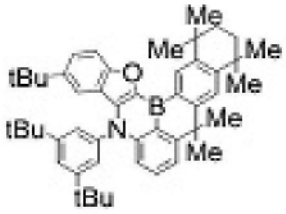
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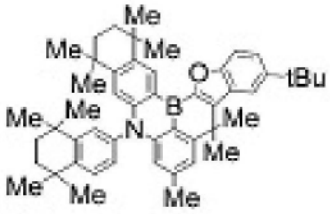
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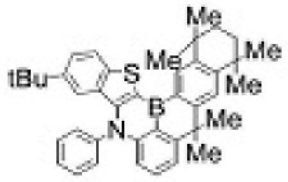
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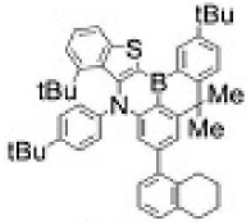
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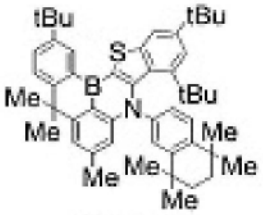
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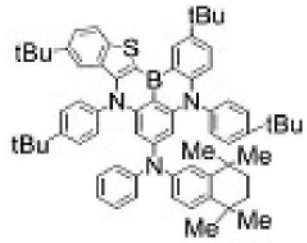


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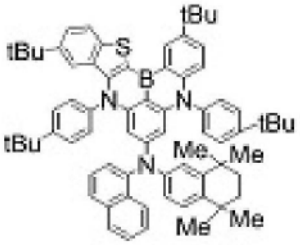


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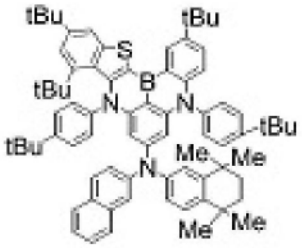
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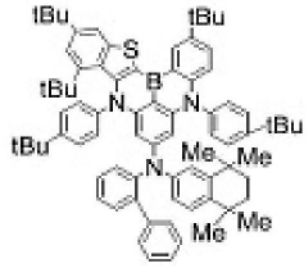
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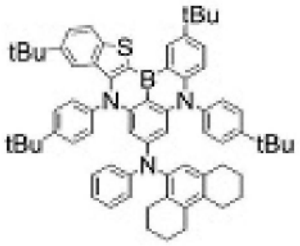
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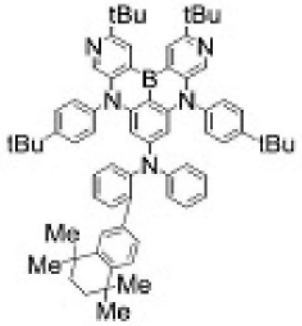
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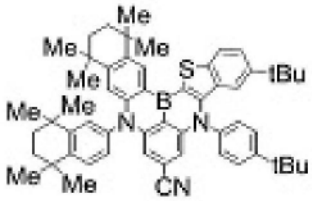


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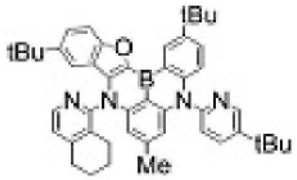


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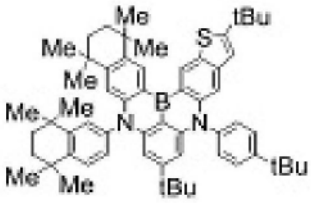
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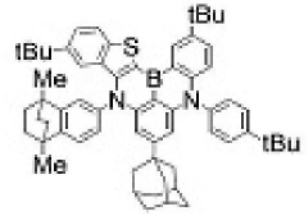
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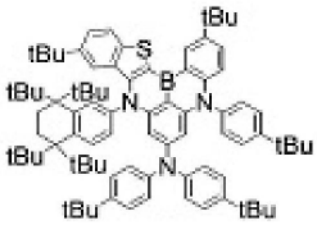
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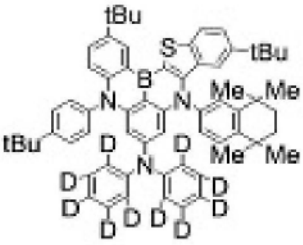
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(1-2110)

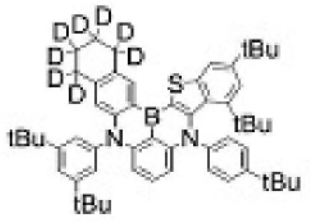


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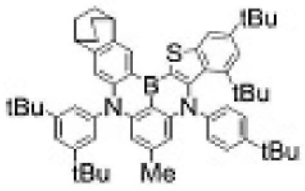


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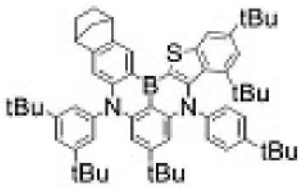
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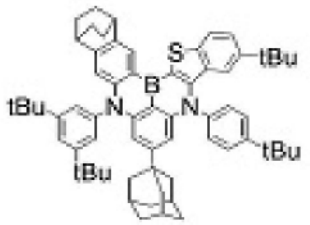
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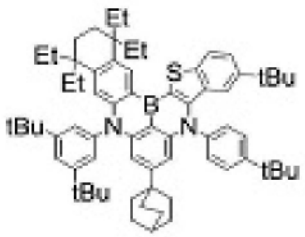
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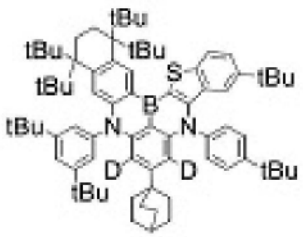
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(1-2154)

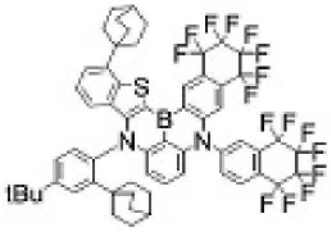


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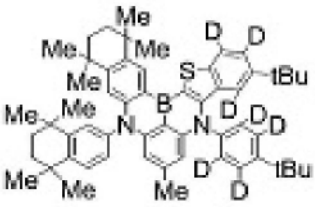


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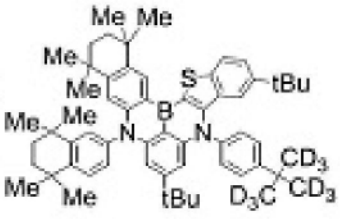
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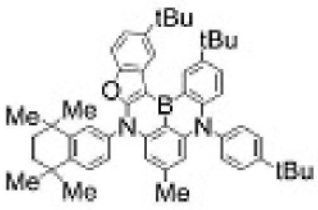
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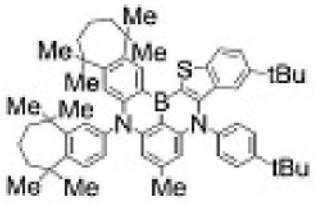
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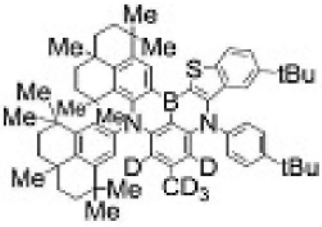
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(1-2160)

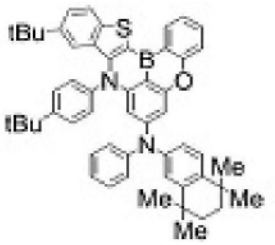


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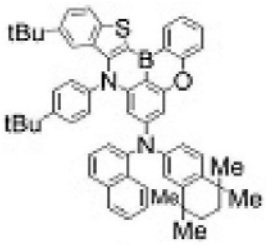


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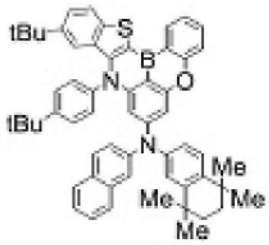
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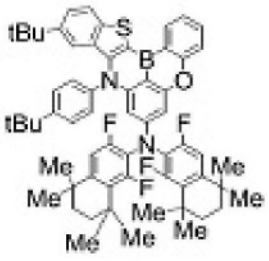
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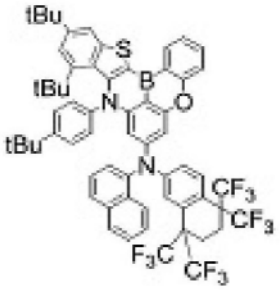
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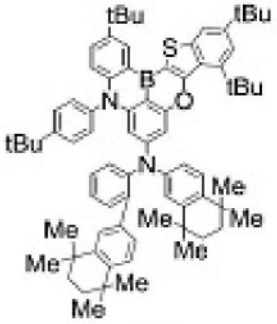
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(1-2204)

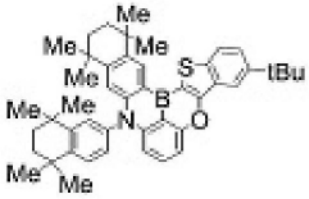


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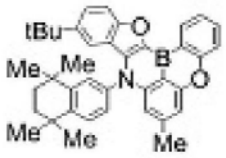


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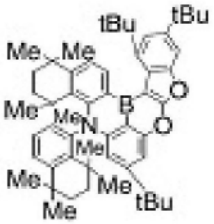
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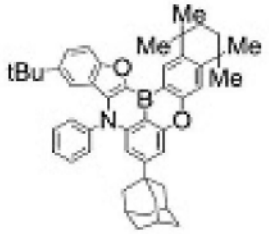
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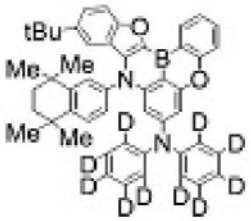
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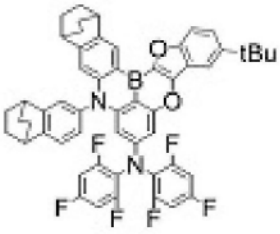
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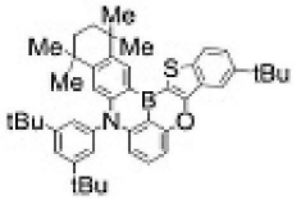


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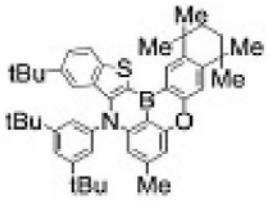


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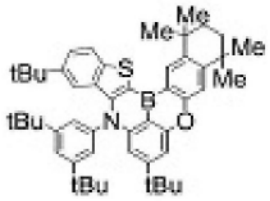
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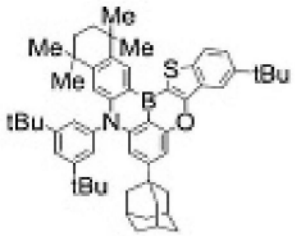
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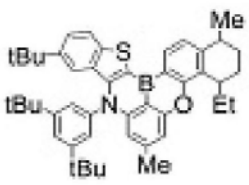
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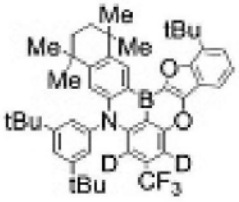
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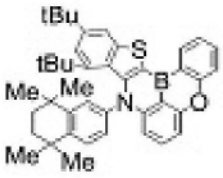


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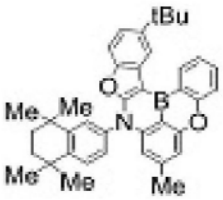


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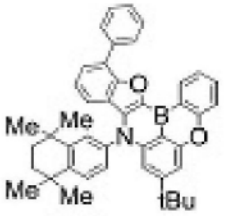
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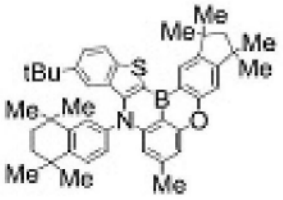
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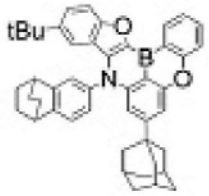
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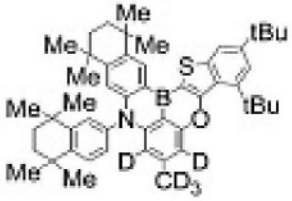
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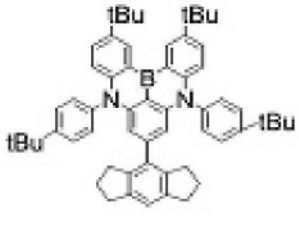


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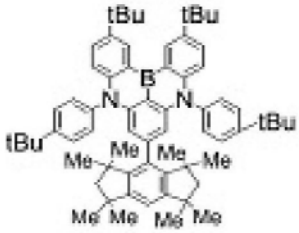


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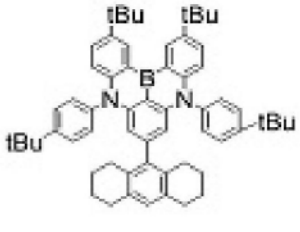
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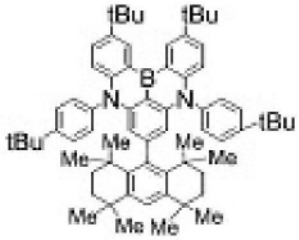
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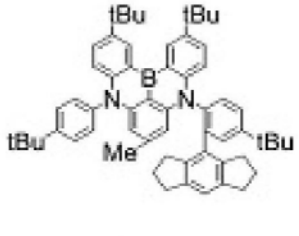
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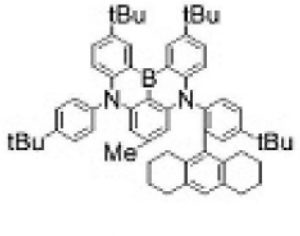
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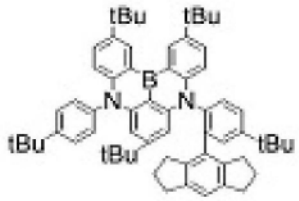


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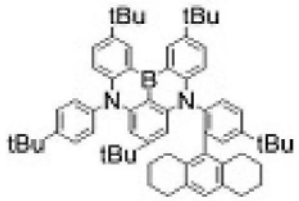


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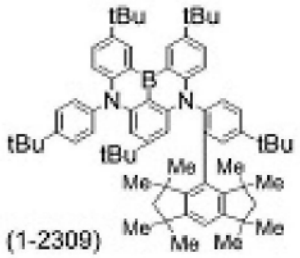
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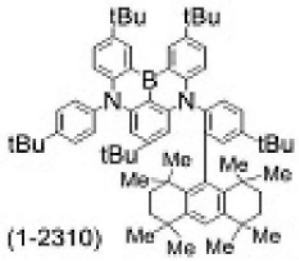
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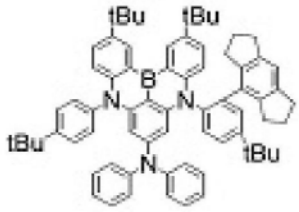
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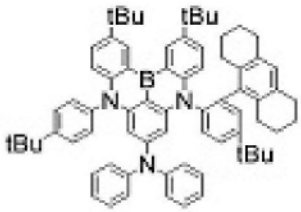
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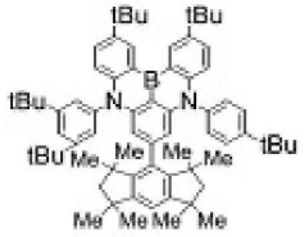


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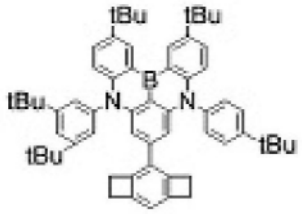


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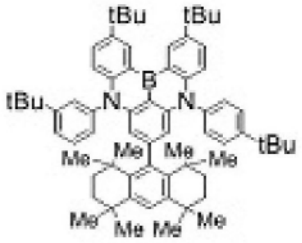
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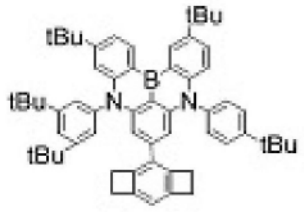
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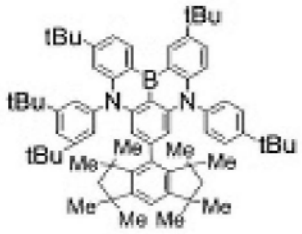
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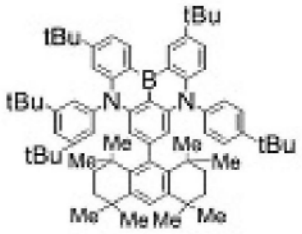
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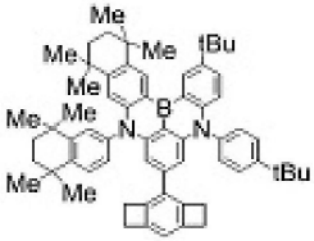


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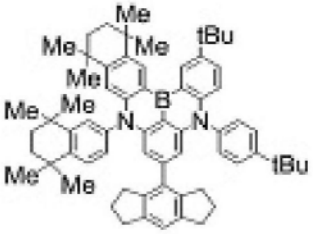


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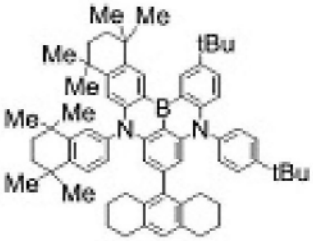
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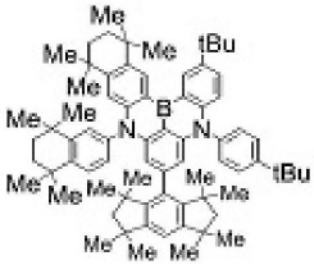
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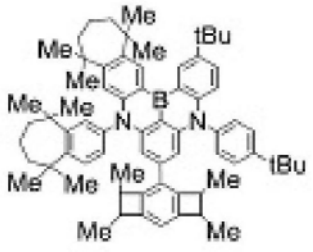
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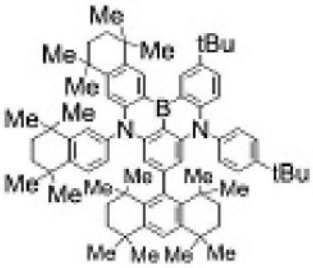
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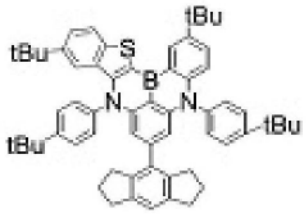


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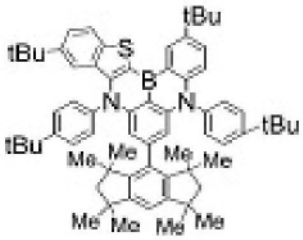


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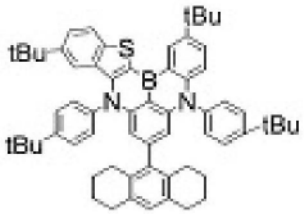
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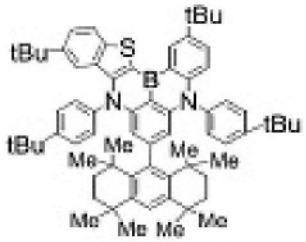
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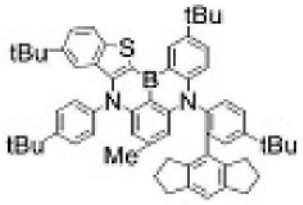
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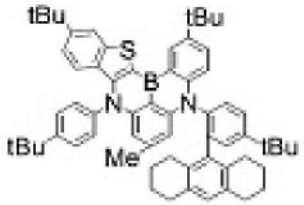
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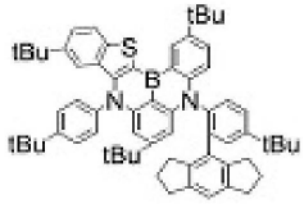


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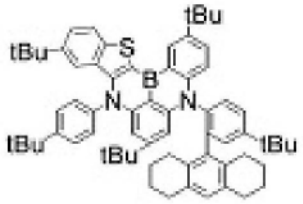


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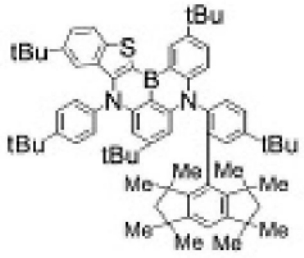
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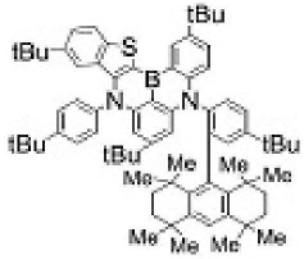
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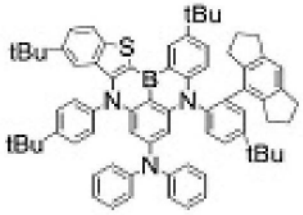
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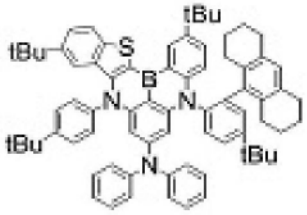
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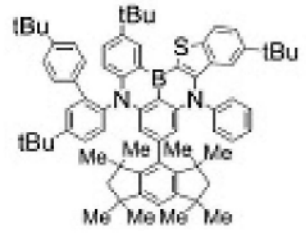


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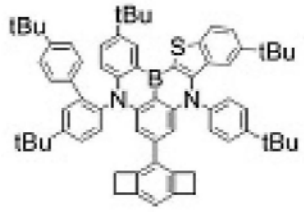


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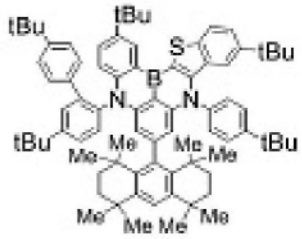
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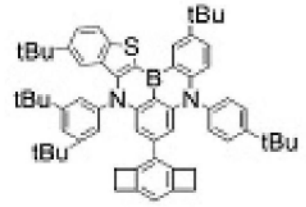
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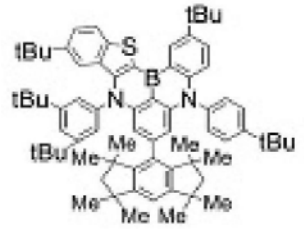
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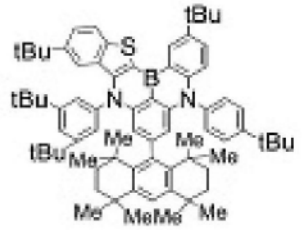
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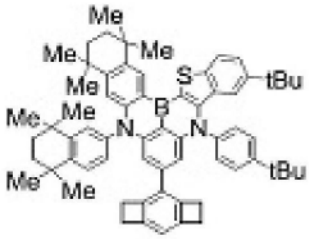


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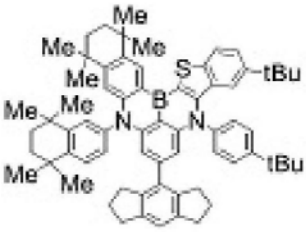


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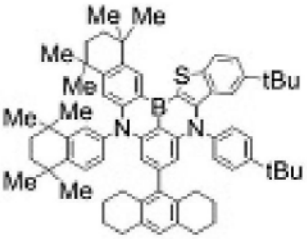
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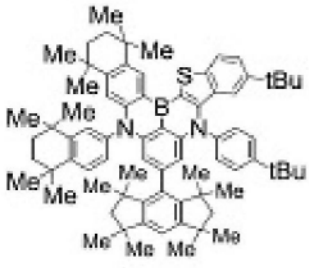
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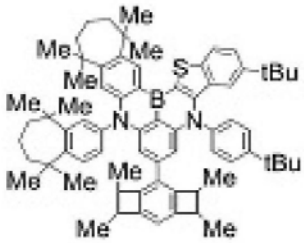
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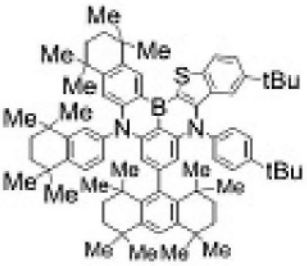
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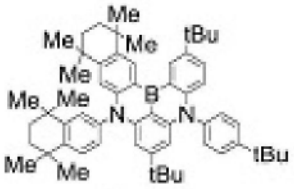
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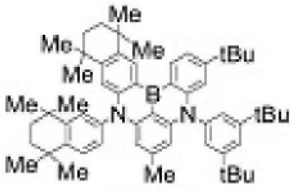


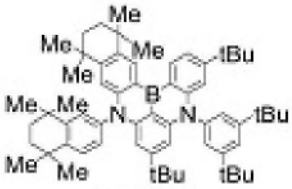
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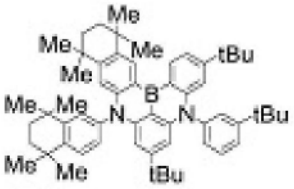
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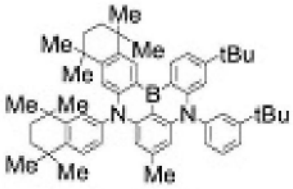
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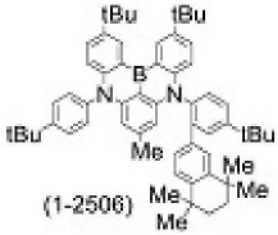

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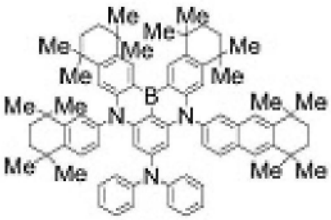

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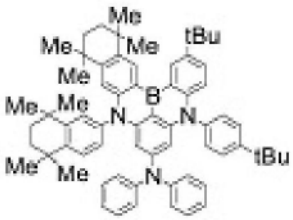

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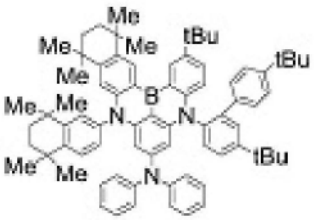

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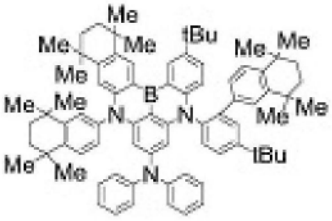

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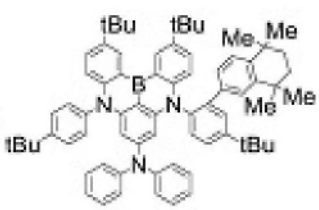

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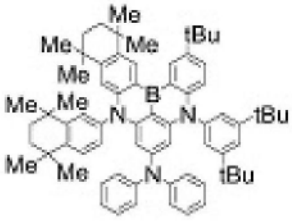

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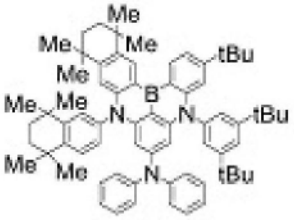

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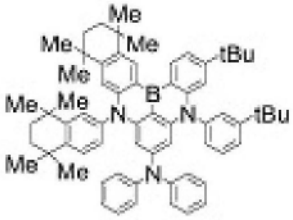

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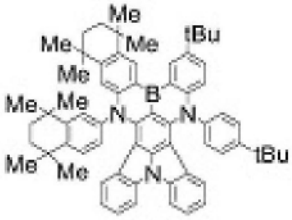

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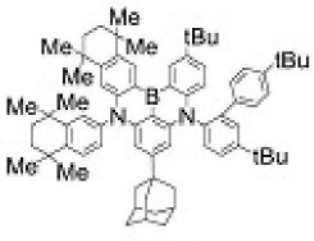

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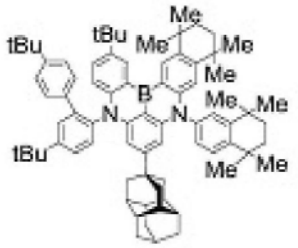

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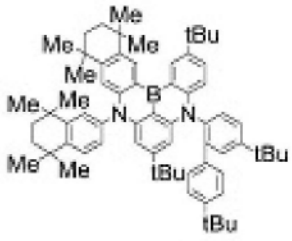
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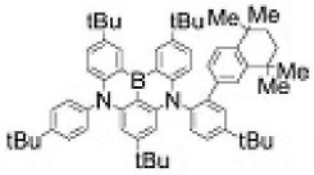
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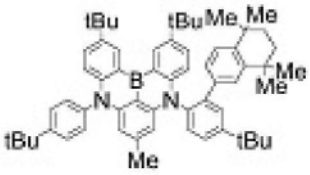
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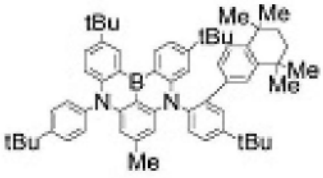
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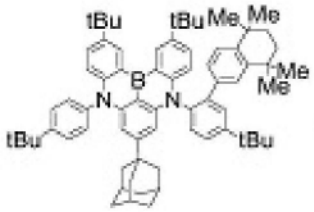
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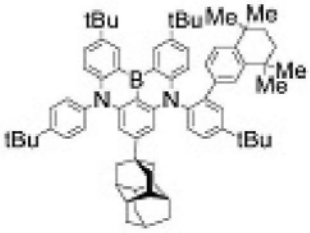
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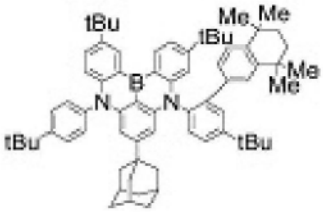
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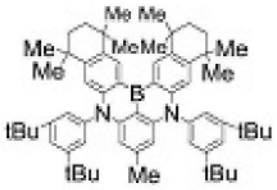
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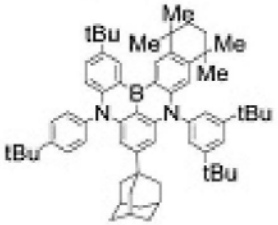
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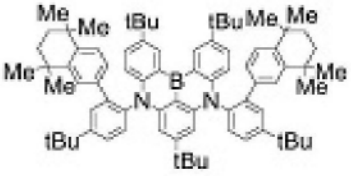
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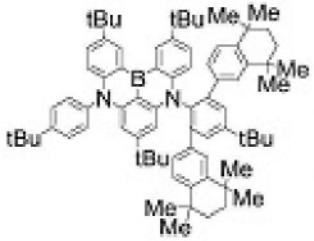
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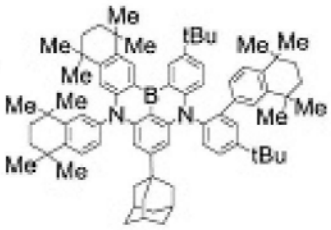
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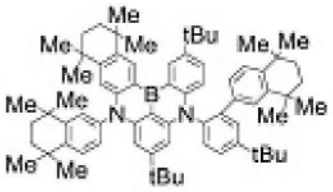
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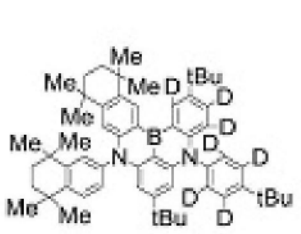
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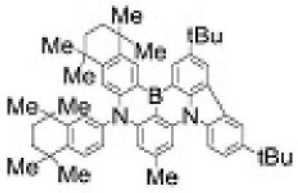


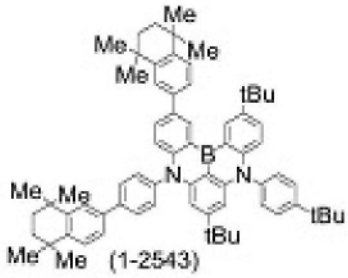
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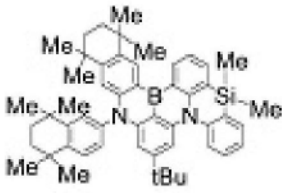
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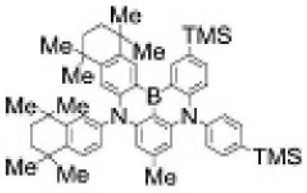
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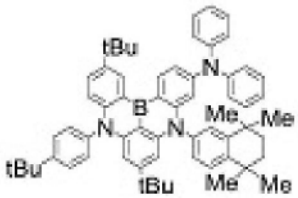

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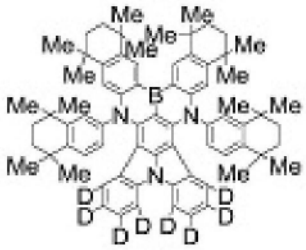

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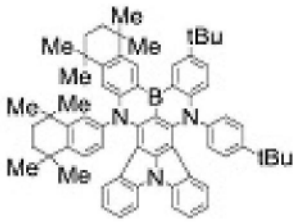

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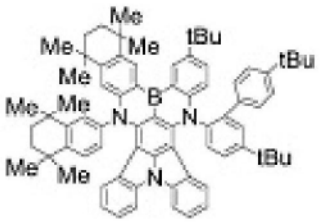

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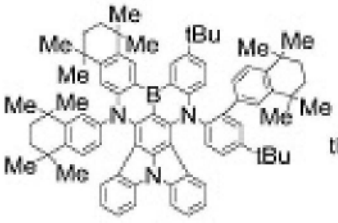

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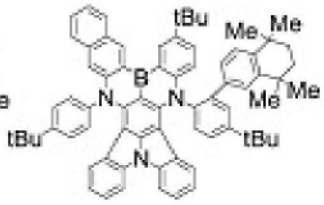

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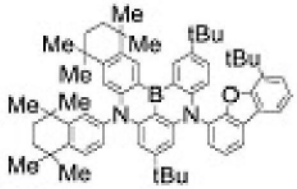

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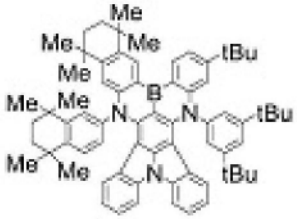

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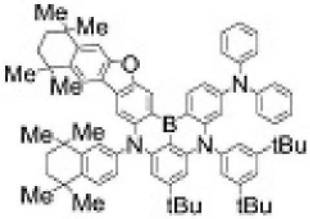

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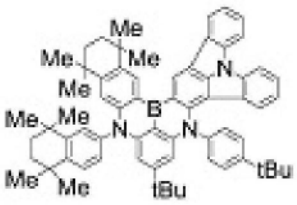

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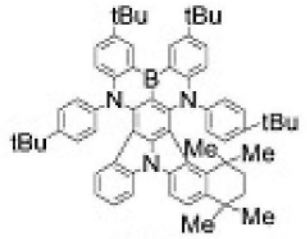

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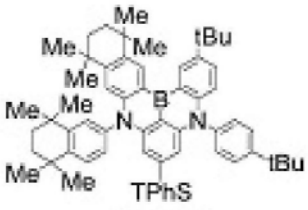

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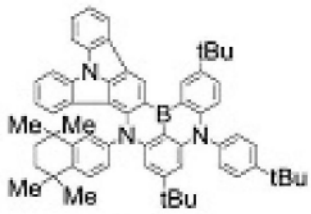

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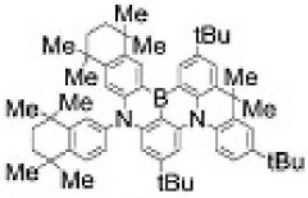
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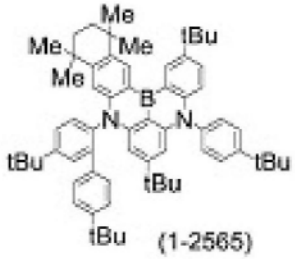
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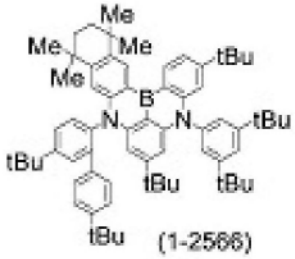

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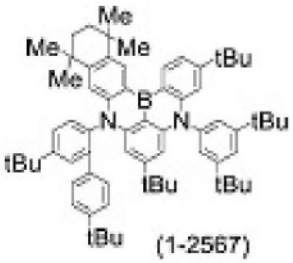

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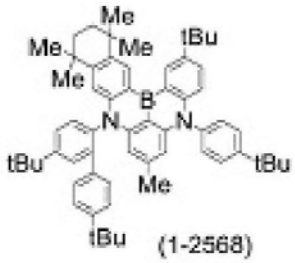

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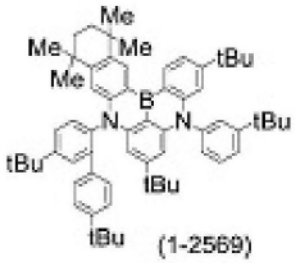

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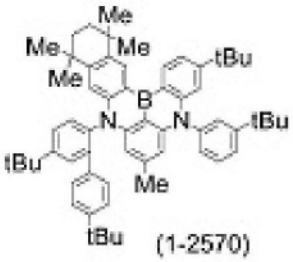

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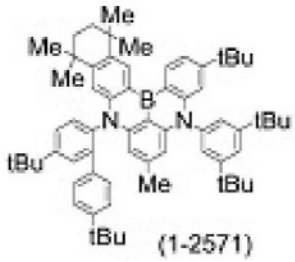

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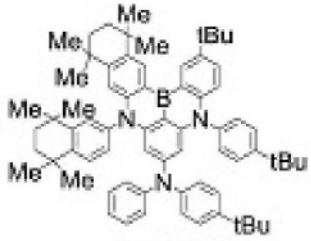

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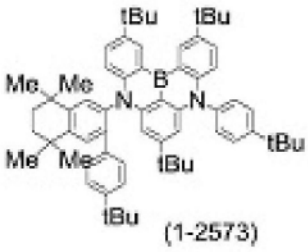

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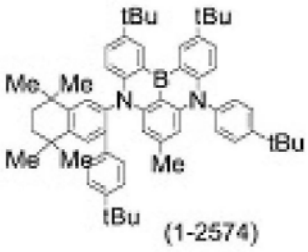

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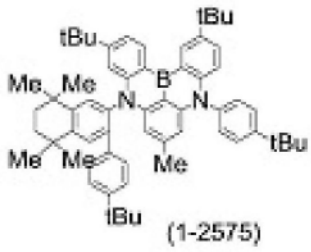

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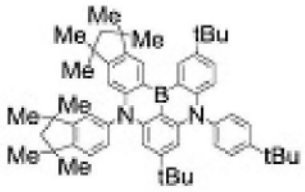

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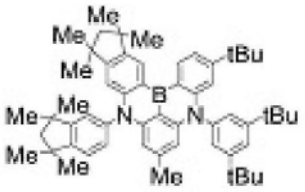

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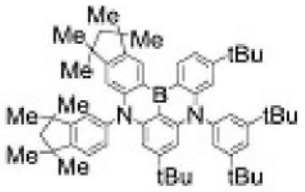

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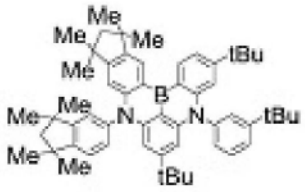

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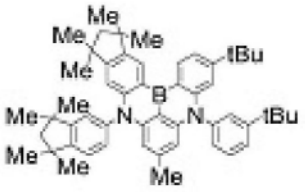
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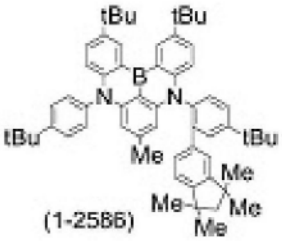

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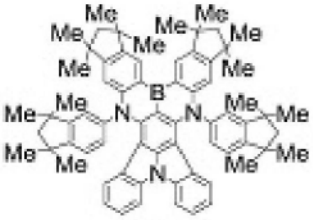

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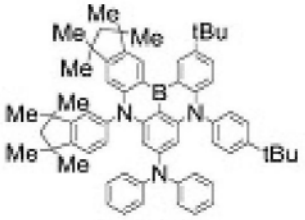

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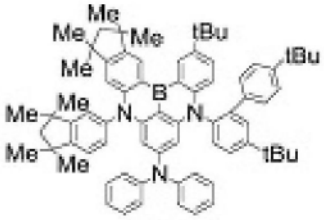

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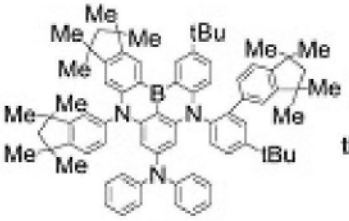

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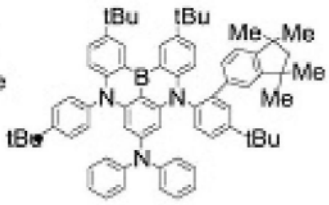
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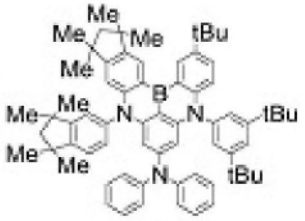

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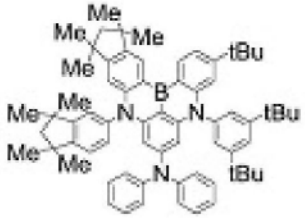

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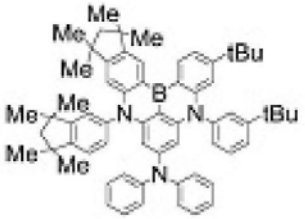

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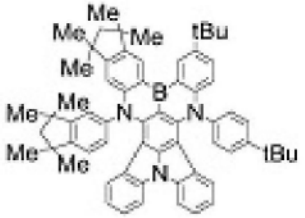

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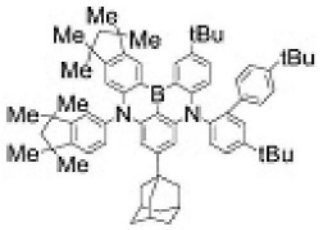

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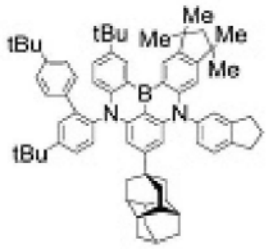

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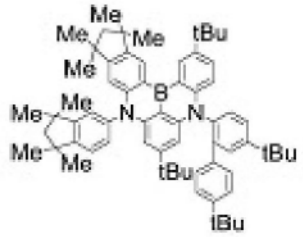
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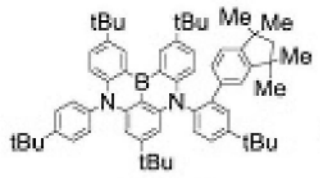
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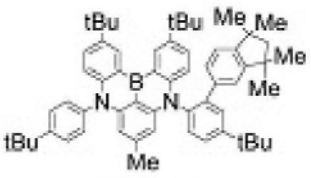
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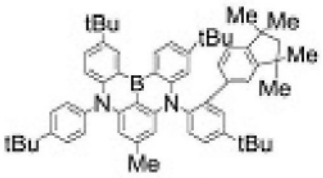
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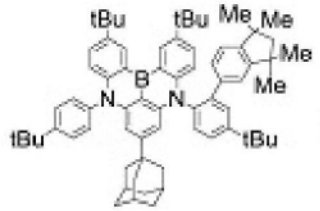
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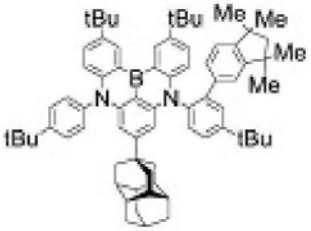
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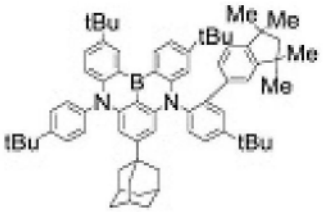
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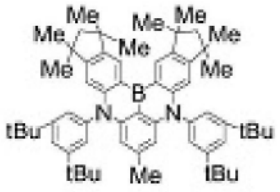
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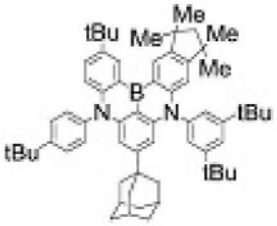
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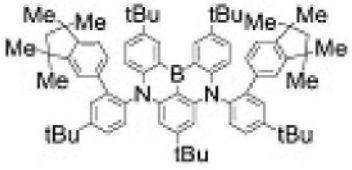
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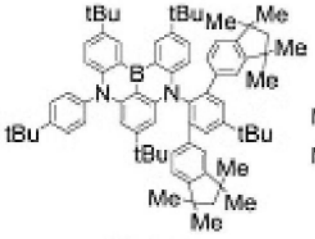
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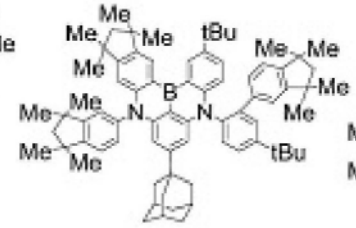
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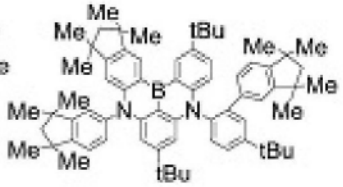
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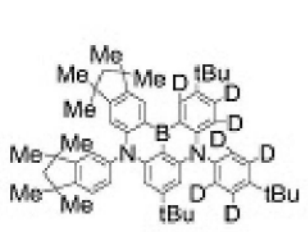
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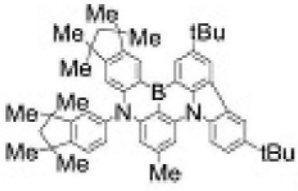


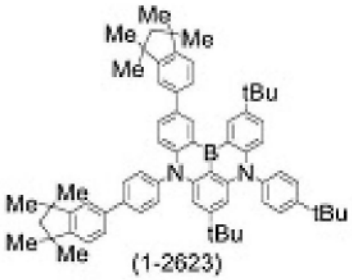
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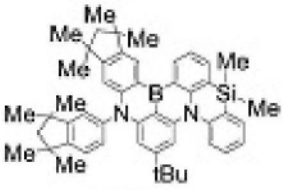
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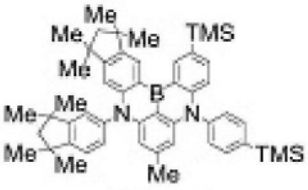
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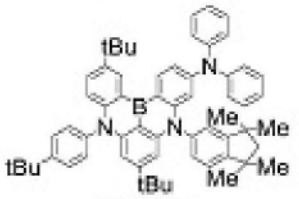

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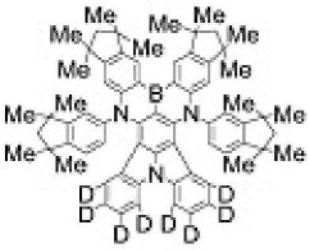

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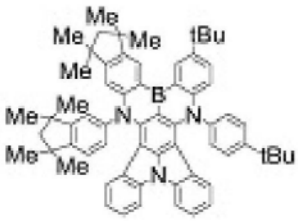

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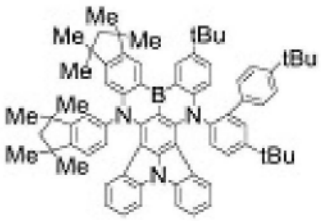

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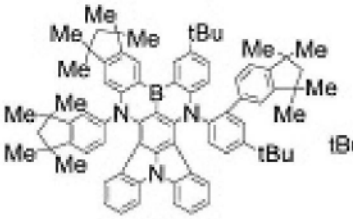

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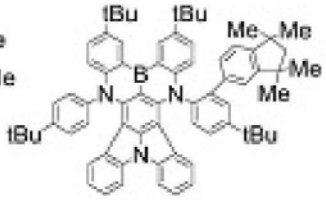

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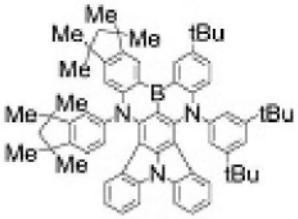

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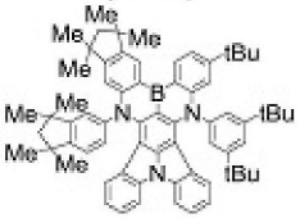

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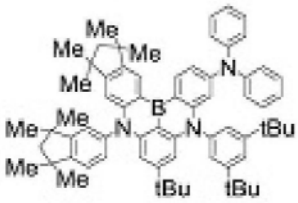

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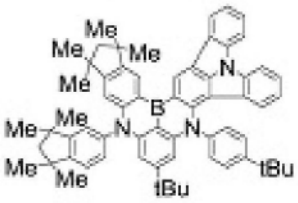

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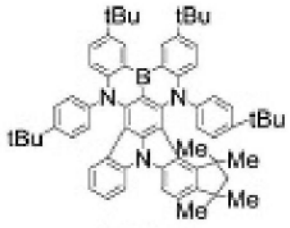

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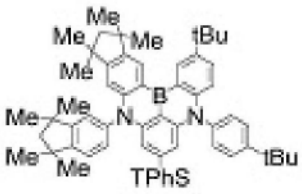

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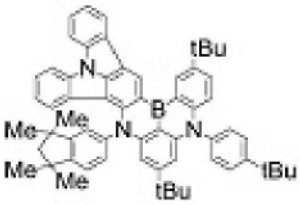

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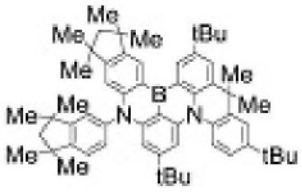
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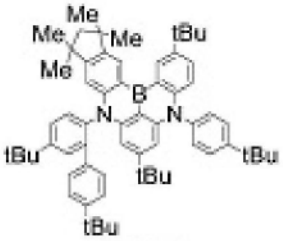
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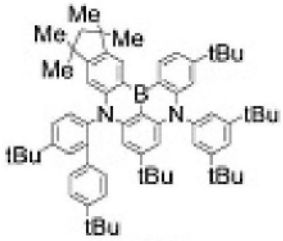

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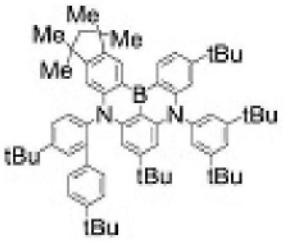

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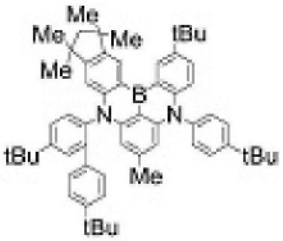

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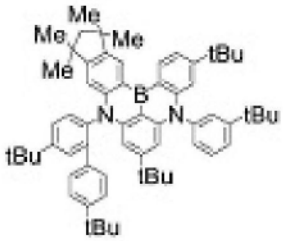

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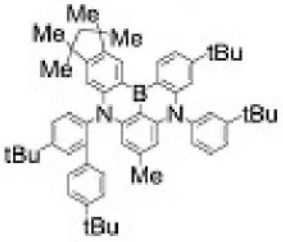

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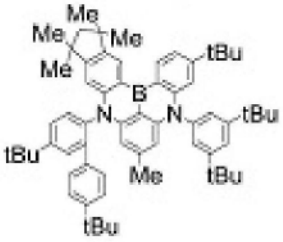

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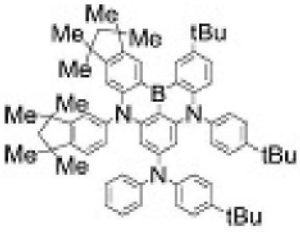

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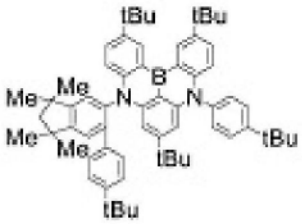

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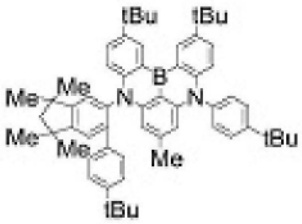

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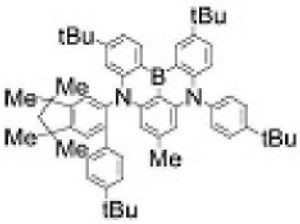

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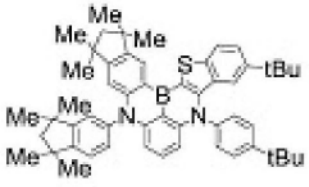

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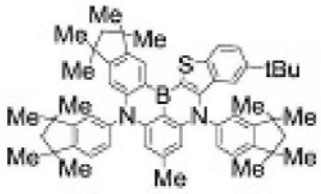

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[0460] [化129]

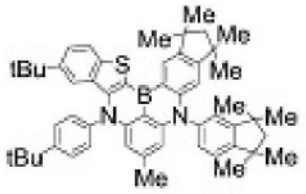
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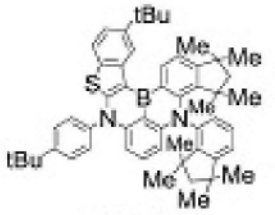
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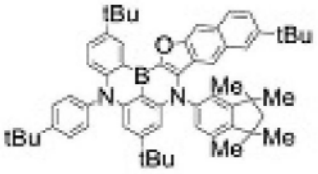
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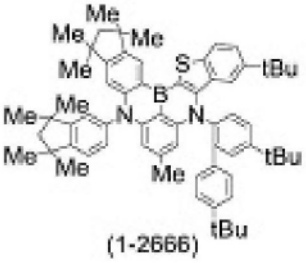
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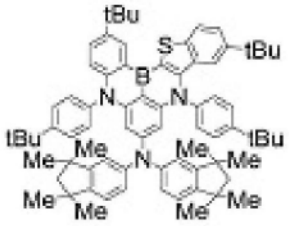
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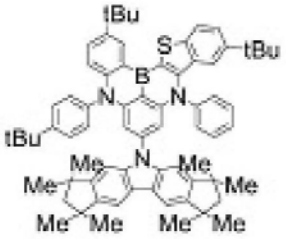
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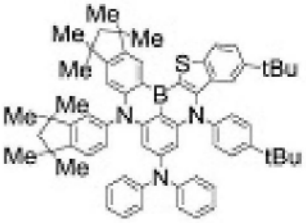
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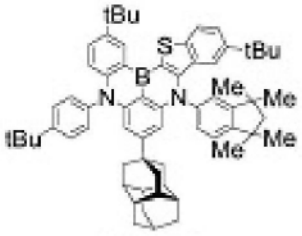
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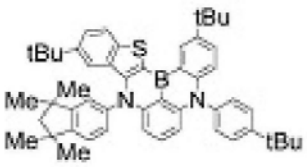
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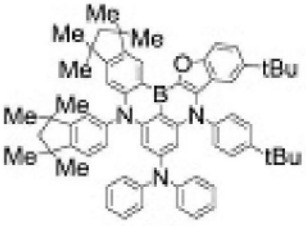
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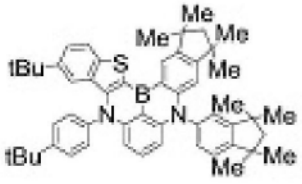
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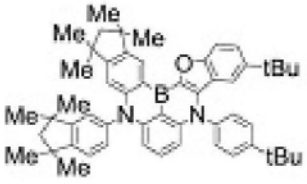
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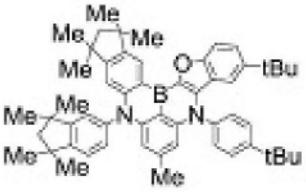
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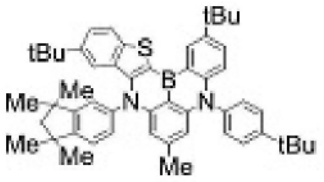
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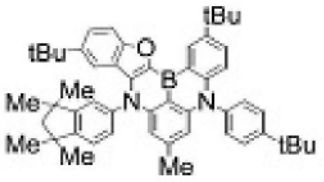
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[0462] [化130]

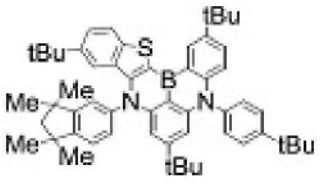
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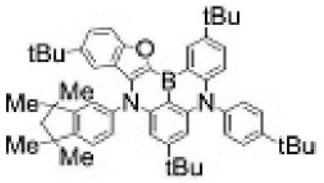
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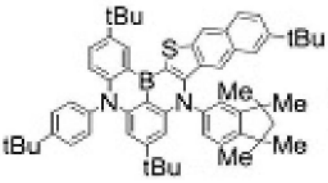
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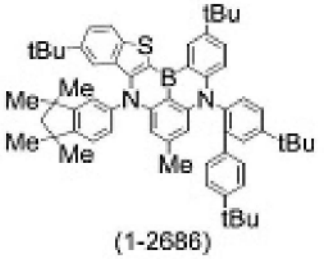
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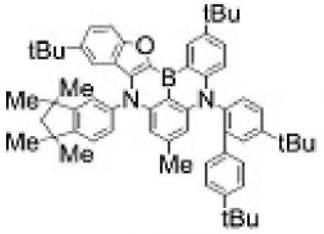
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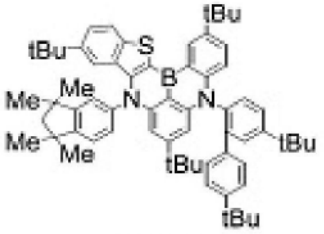
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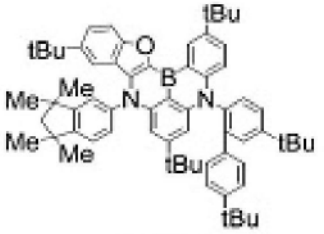
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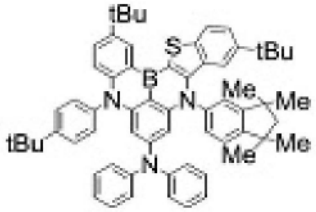
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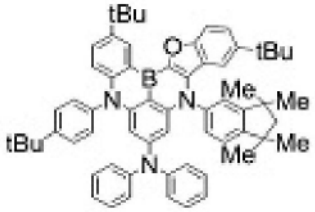
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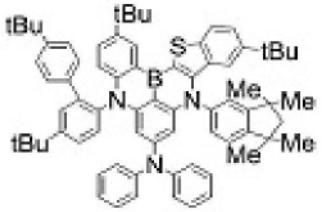
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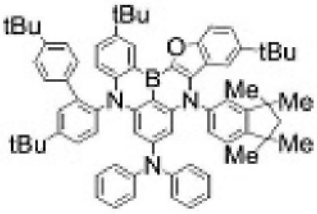
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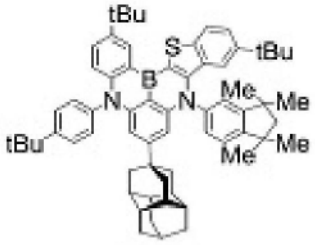
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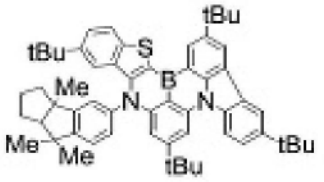
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(1-2693)



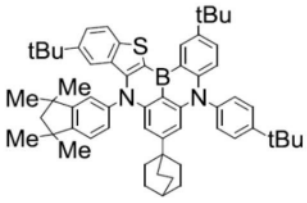
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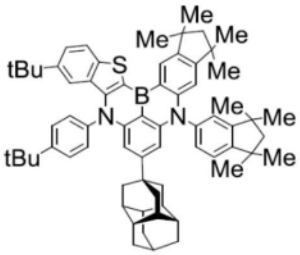
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[0464] [化131]

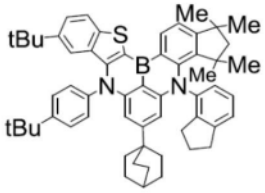
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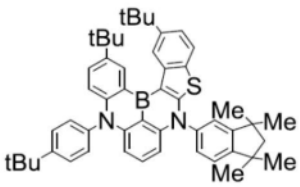
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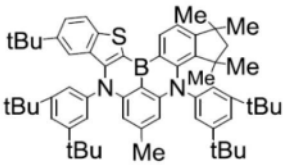
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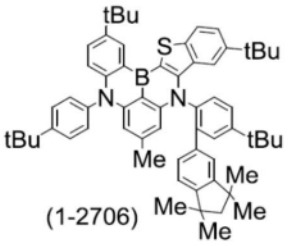
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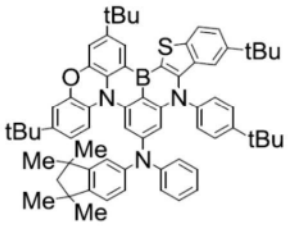
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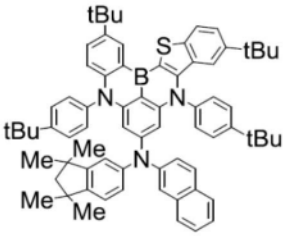
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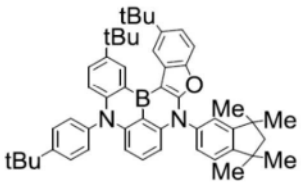
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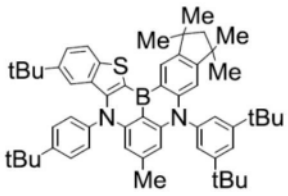
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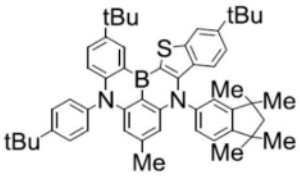
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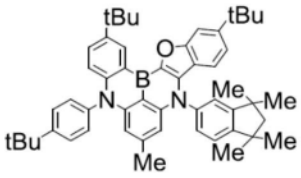
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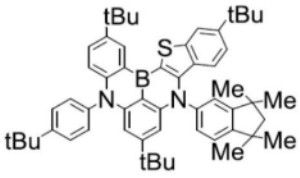
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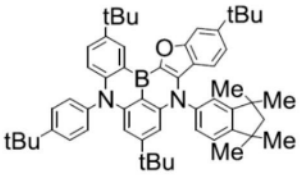
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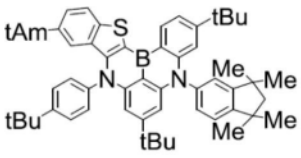
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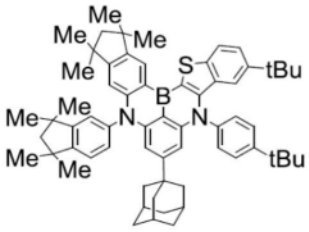
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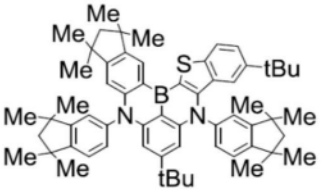
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[0466] [化132]

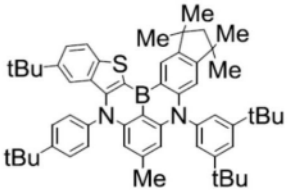
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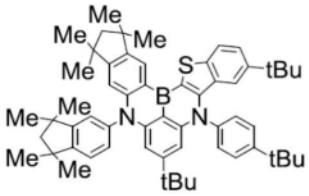
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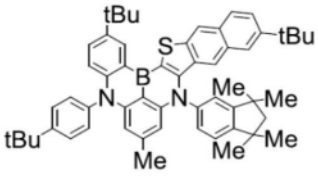
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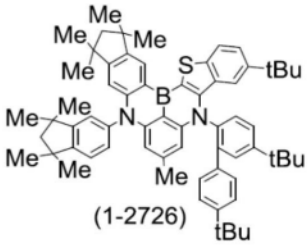
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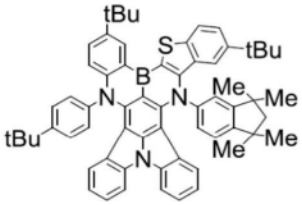
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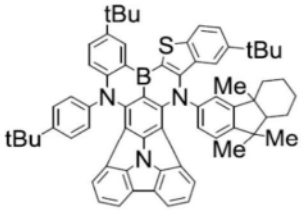
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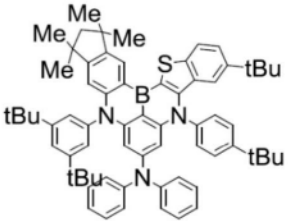
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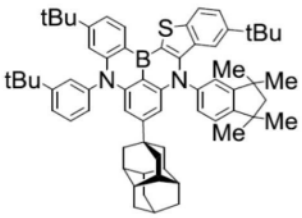
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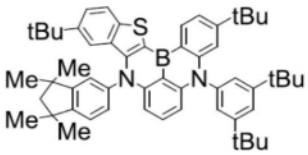
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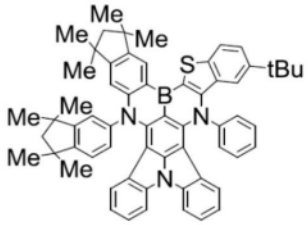
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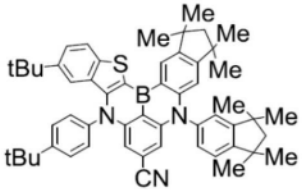
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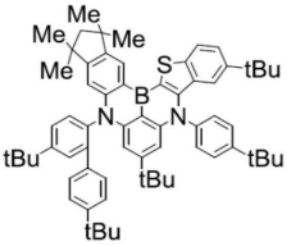
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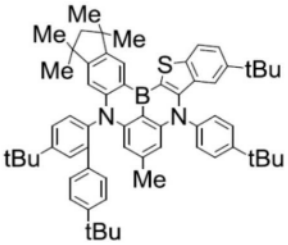
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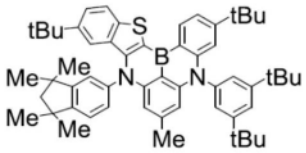
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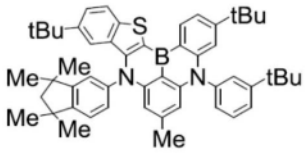
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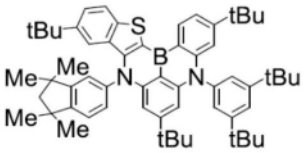
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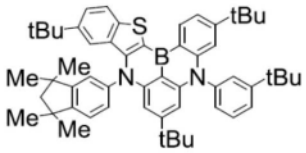
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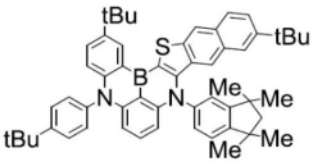
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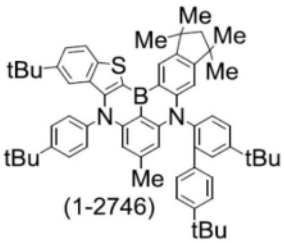
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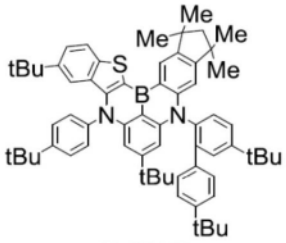
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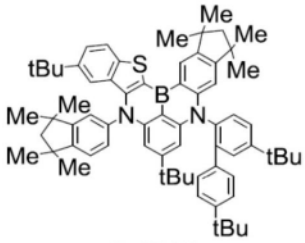
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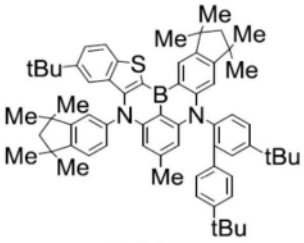
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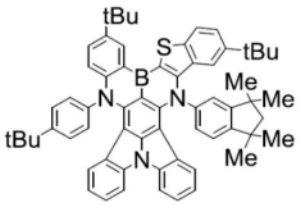
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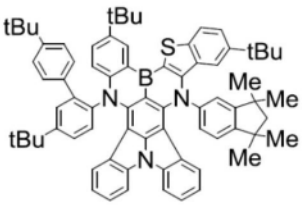
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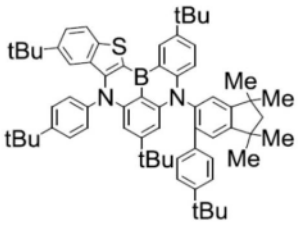
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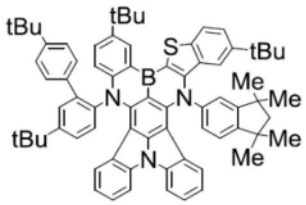
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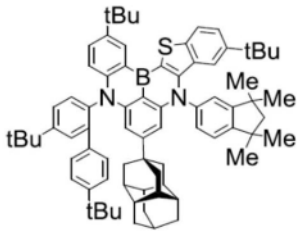
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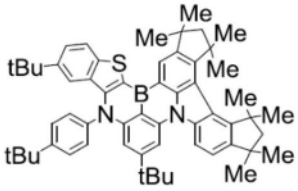
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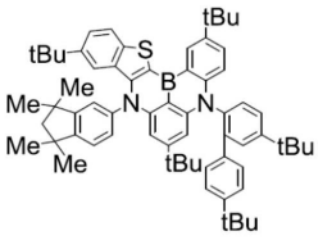


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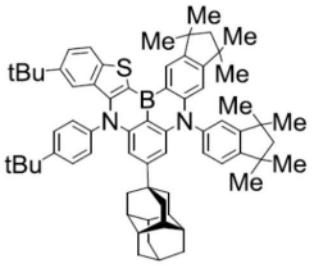


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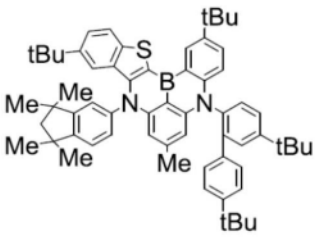
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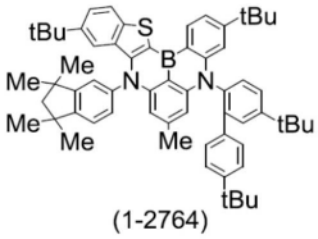
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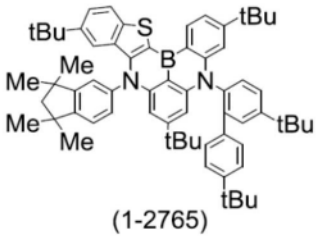
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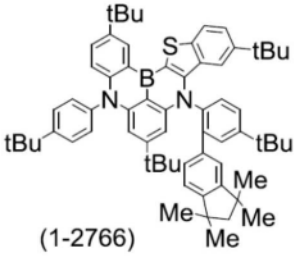
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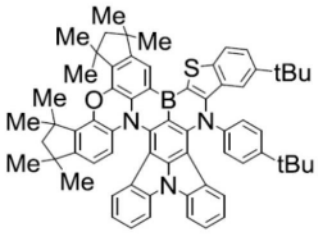


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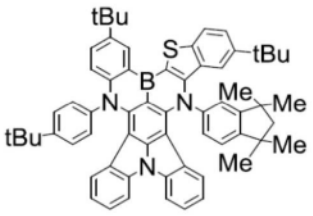


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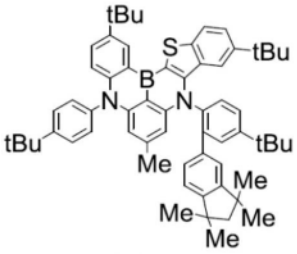
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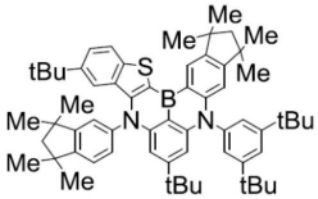
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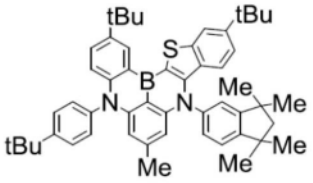
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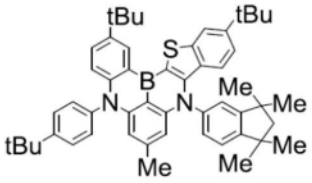
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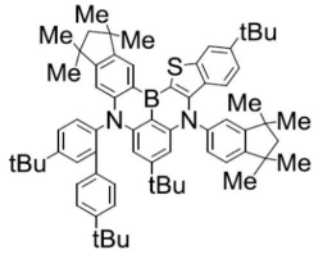
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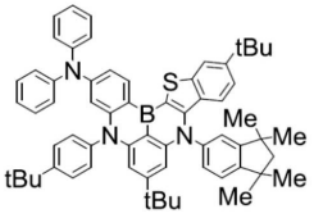
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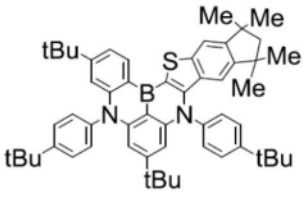
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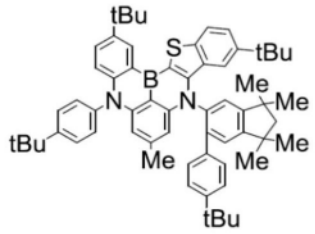


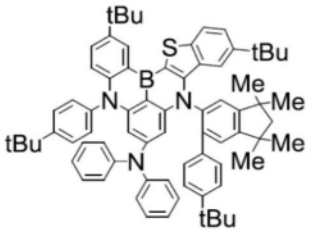
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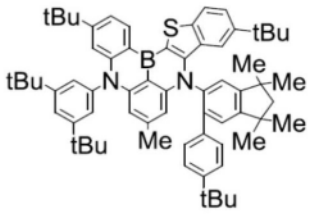


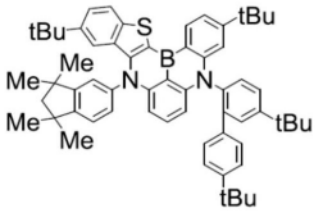
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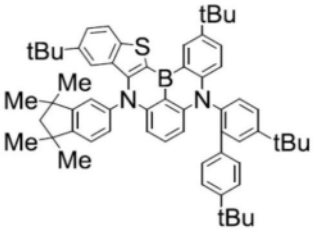
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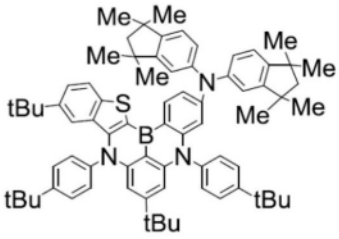

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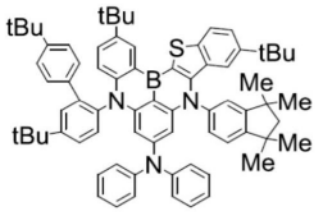

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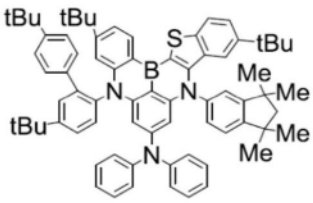

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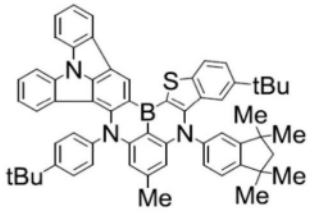

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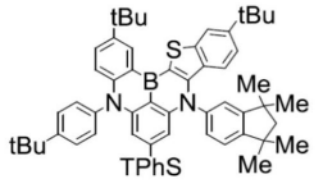

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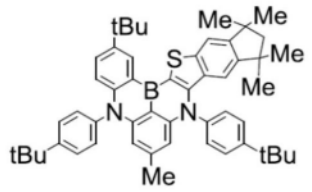
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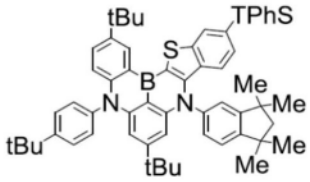

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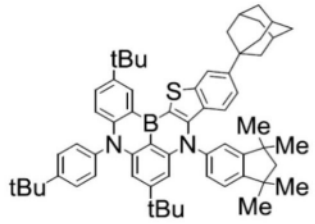

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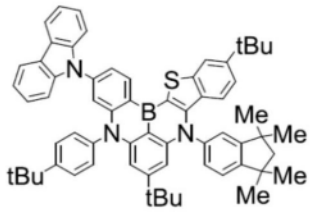

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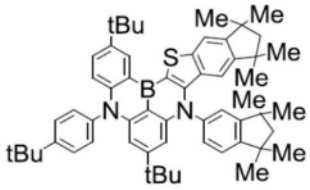

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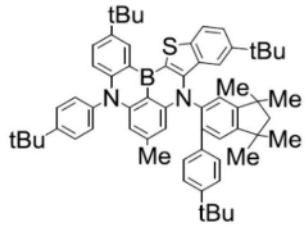

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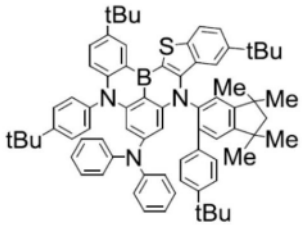

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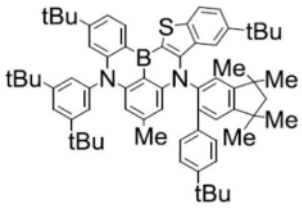

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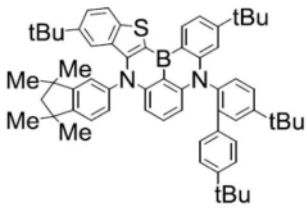

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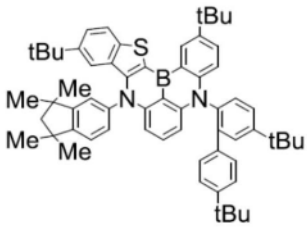
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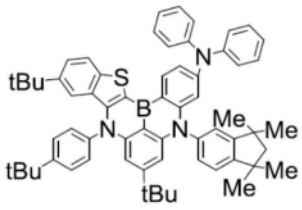

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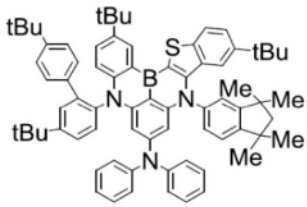

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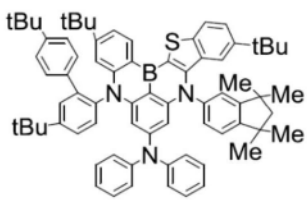

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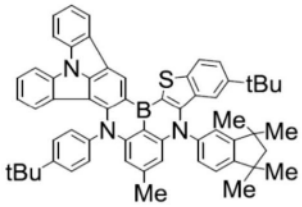

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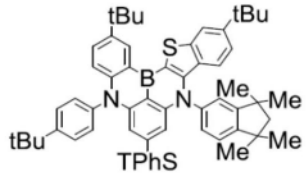

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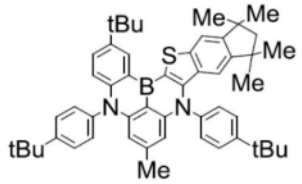
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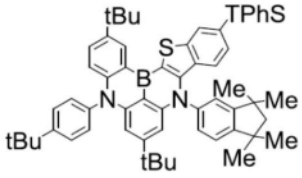

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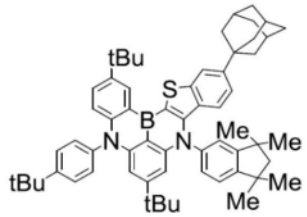

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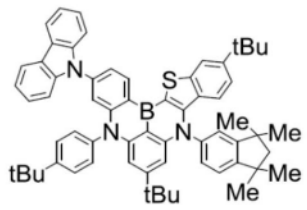

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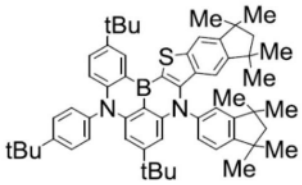

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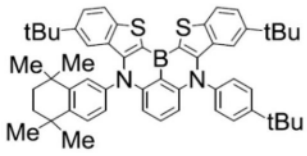

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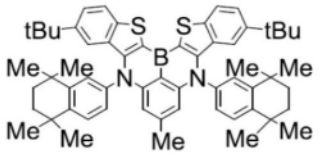

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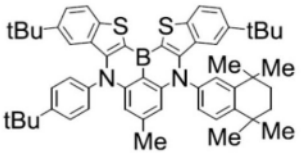
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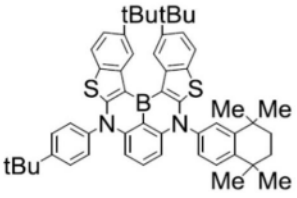
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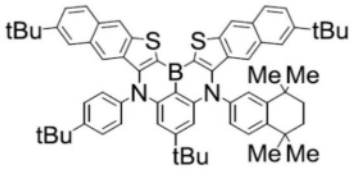
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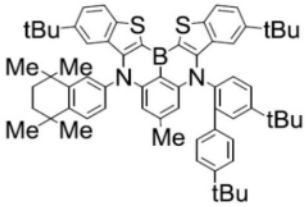
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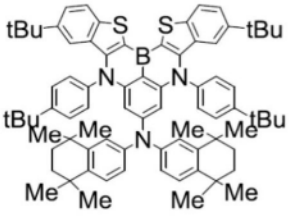


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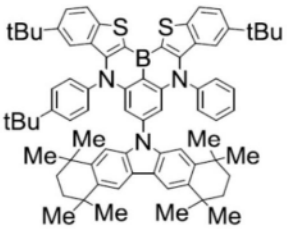


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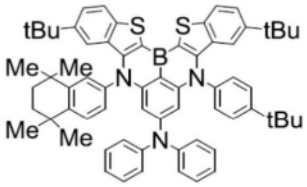
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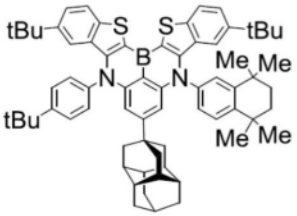
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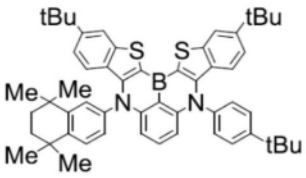
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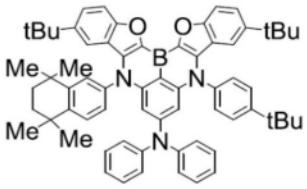
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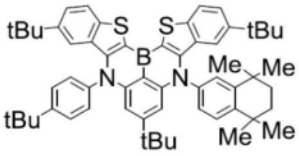
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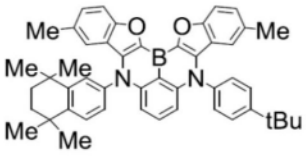
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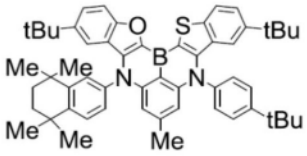
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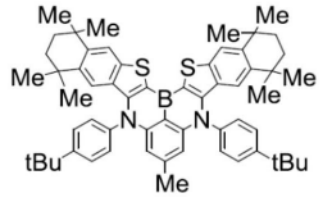
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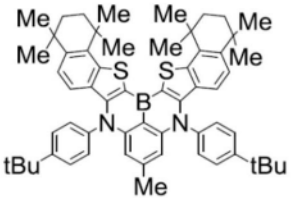
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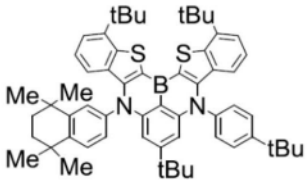
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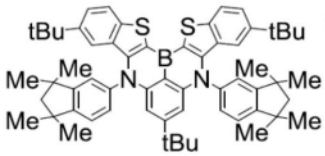
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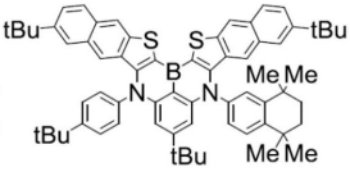
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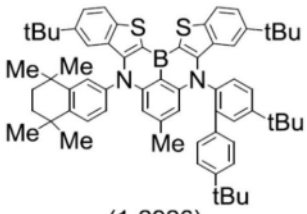
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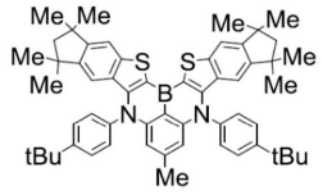
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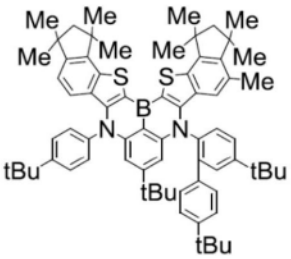
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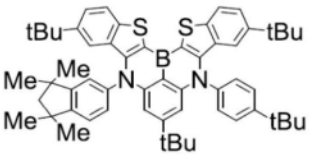
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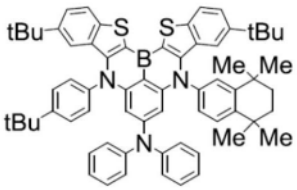
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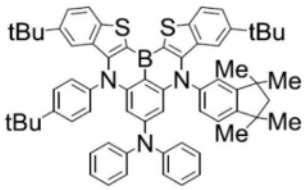
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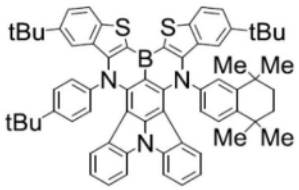
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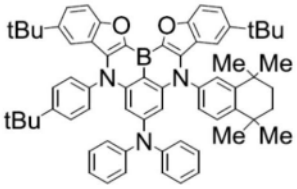
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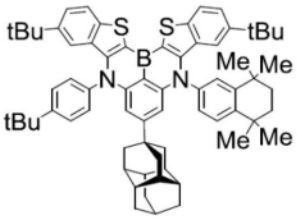
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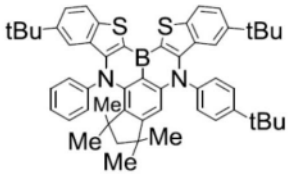
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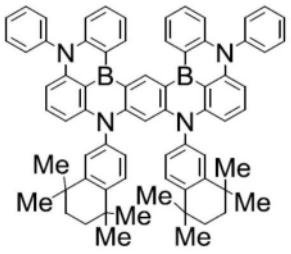


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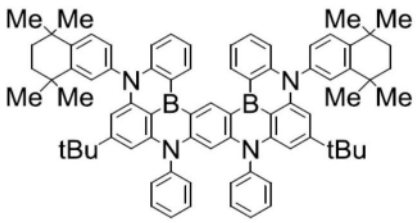


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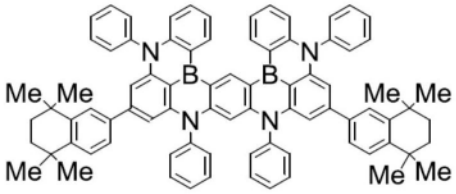
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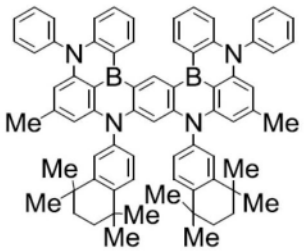
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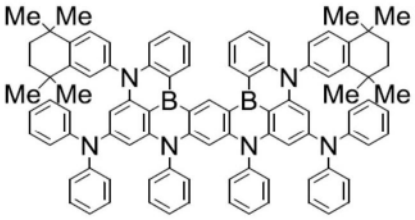


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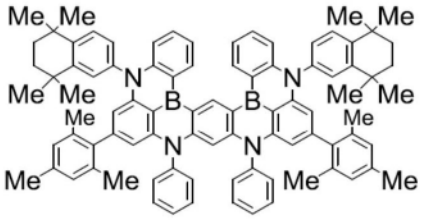


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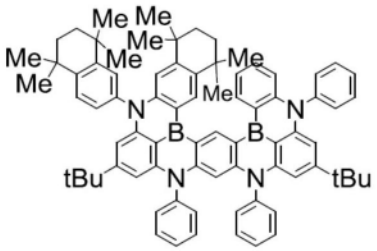
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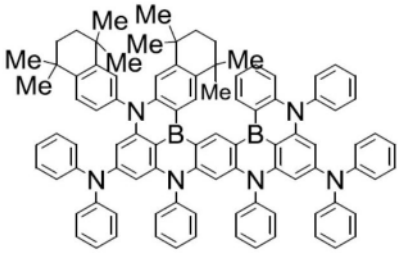
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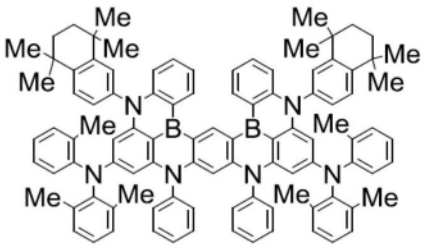
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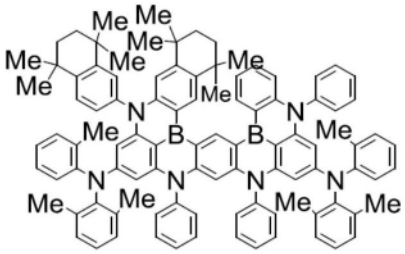
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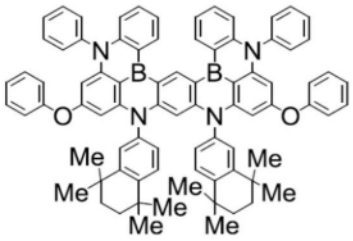
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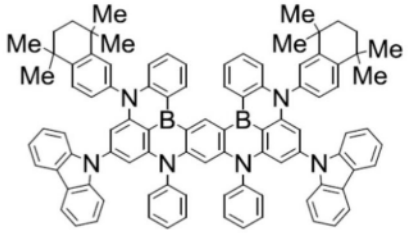
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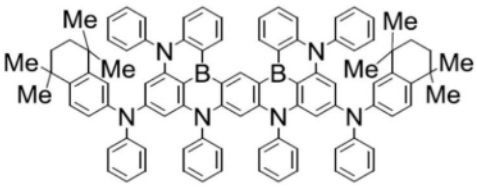
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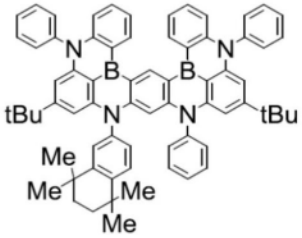
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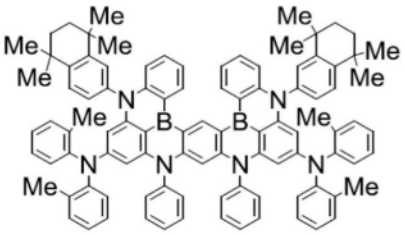
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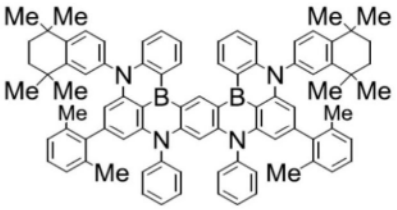
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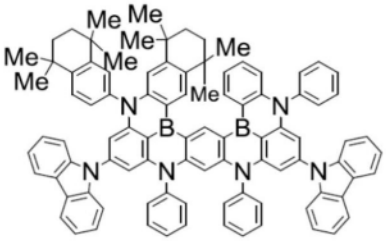
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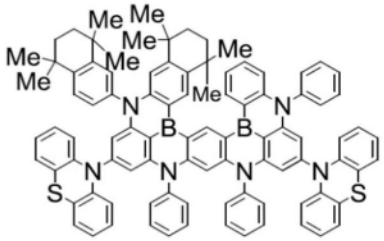
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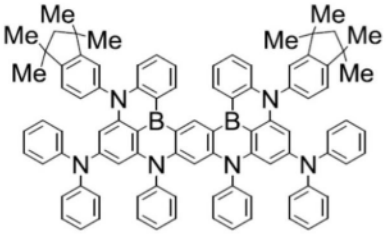
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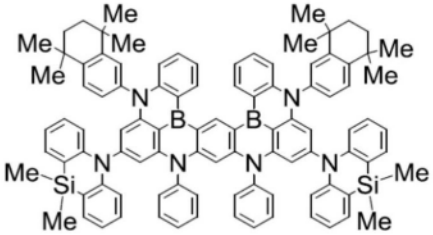
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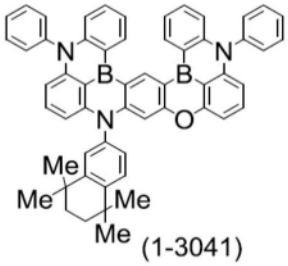


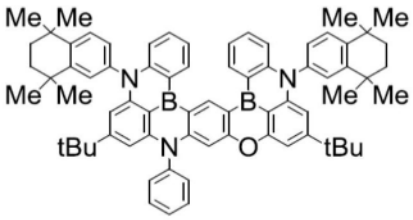
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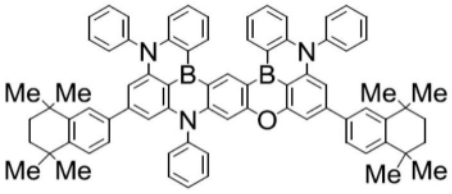


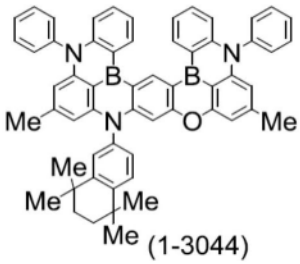
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[0484] [化141]

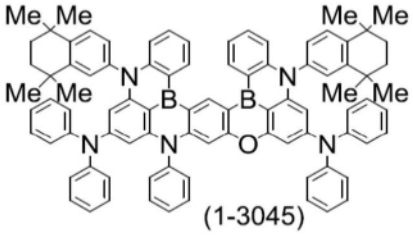

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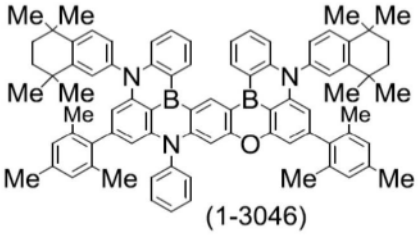

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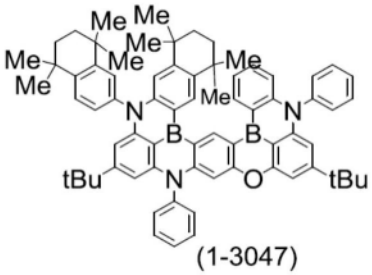

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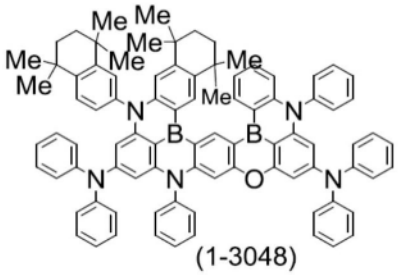

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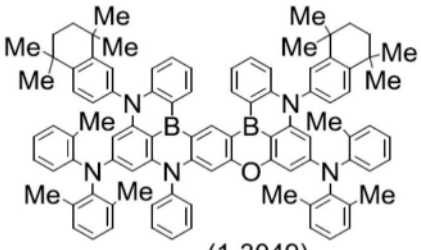
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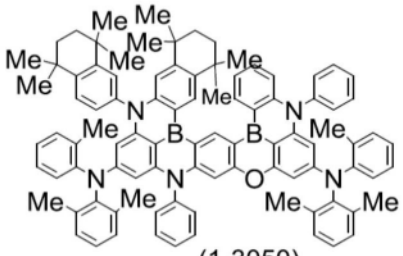

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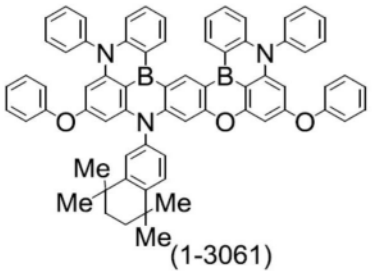

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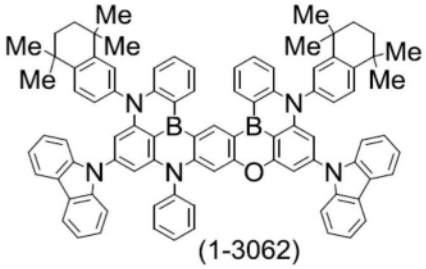

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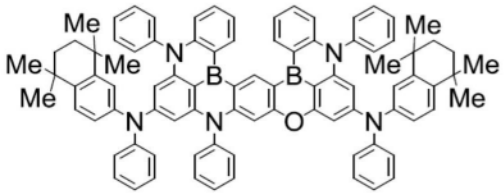

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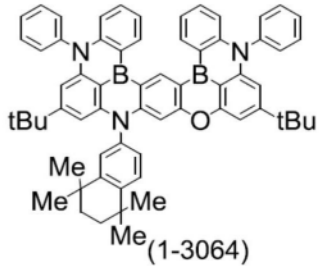

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[0486] [化142]

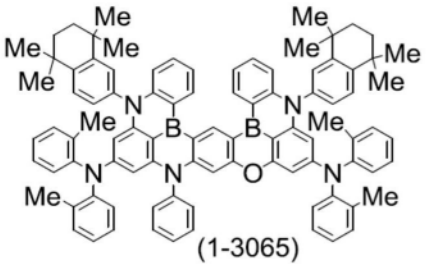

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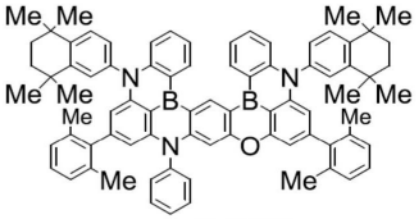

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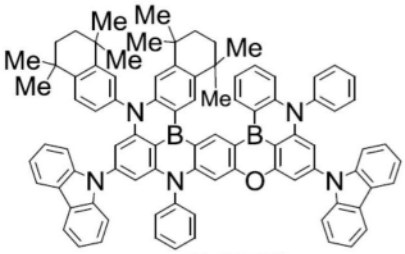

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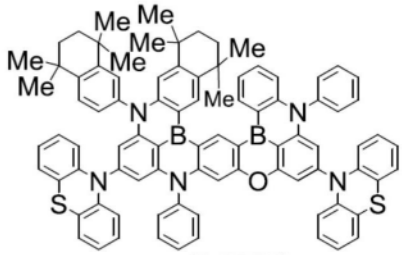

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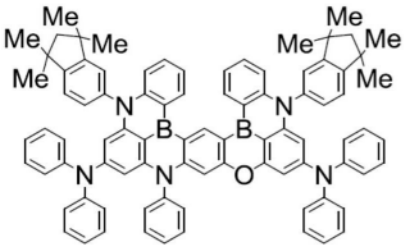
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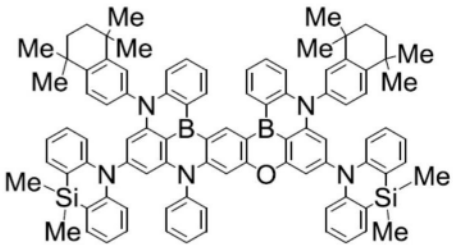

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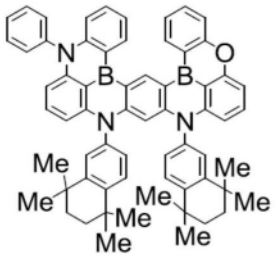

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(1-3068)

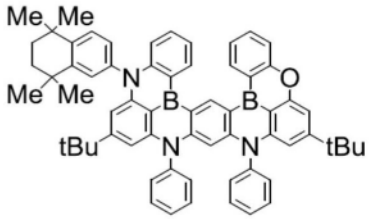

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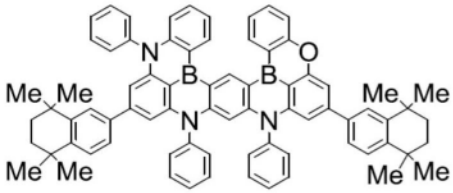
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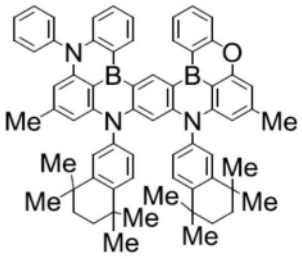
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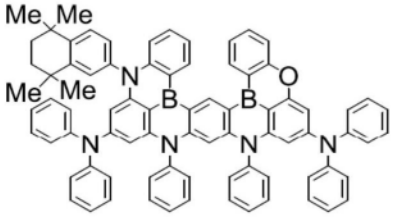


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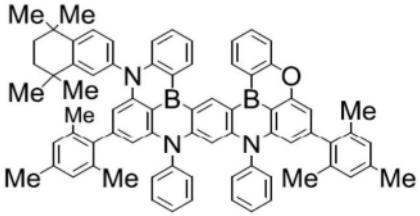


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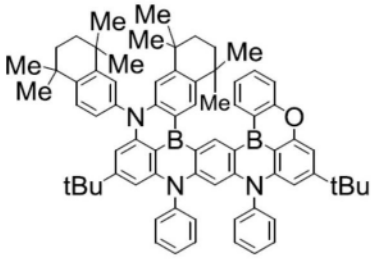
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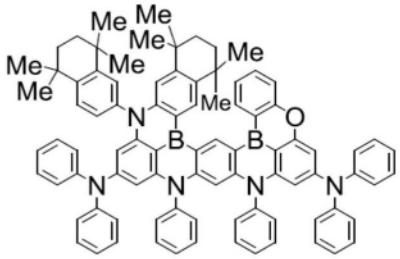
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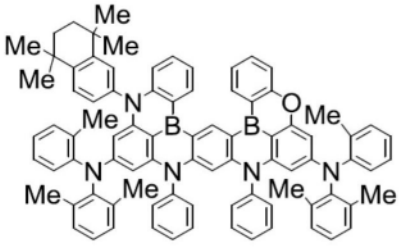
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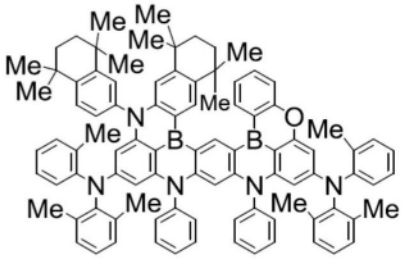
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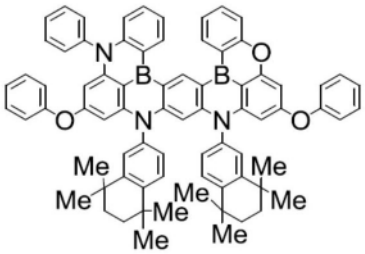


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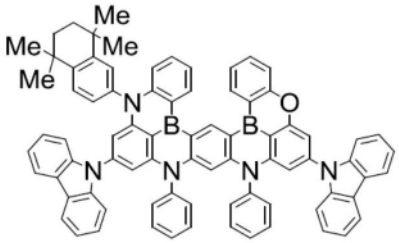


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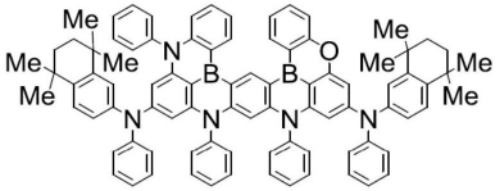
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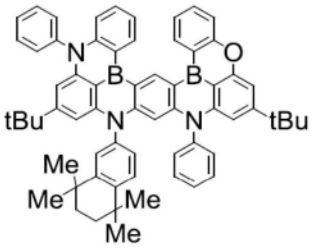
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(1-3102)

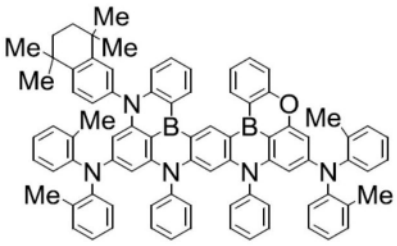


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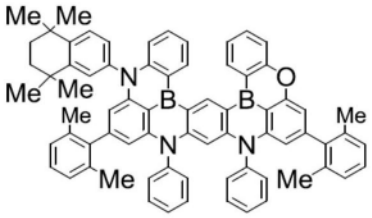


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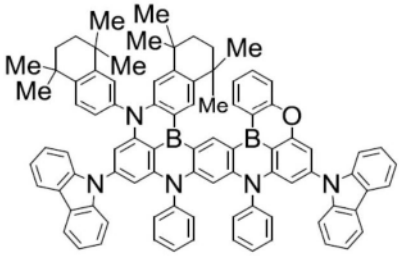
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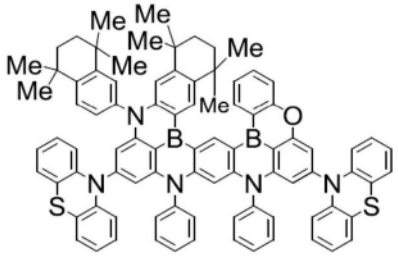
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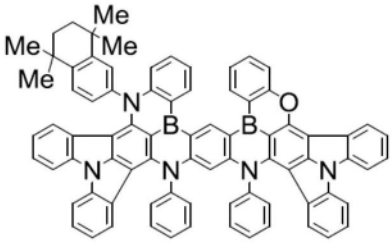
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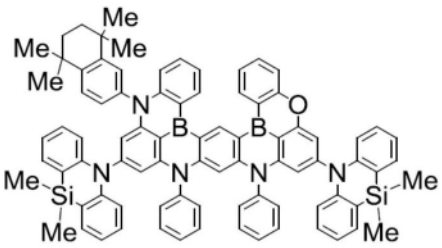
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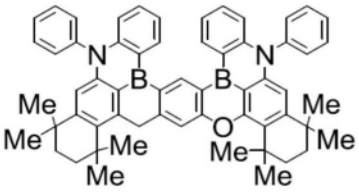


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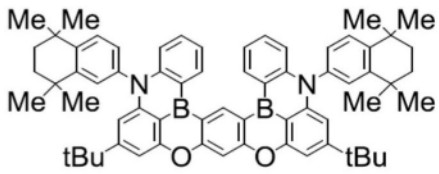


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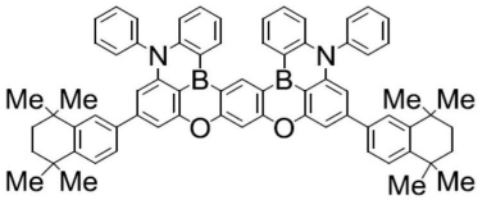
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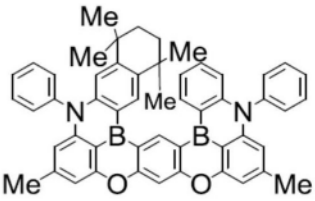
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(1-3122)

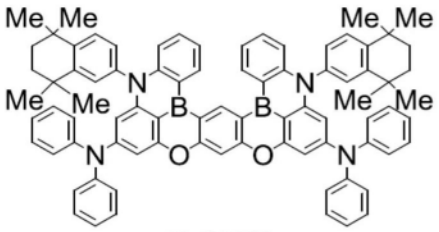


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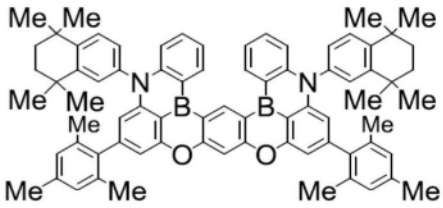


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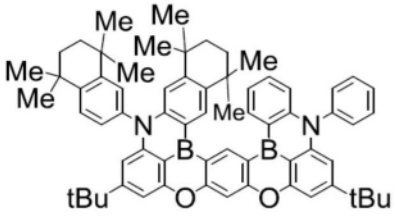
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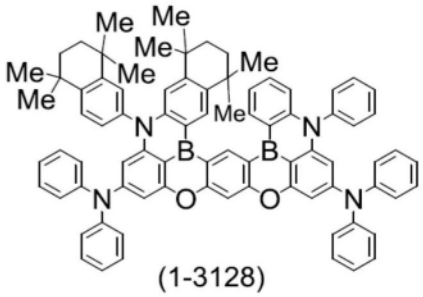
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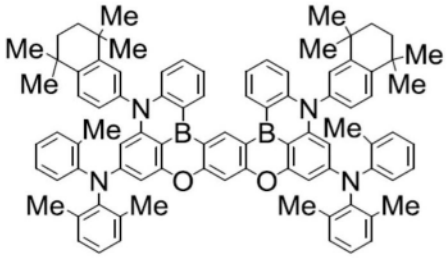
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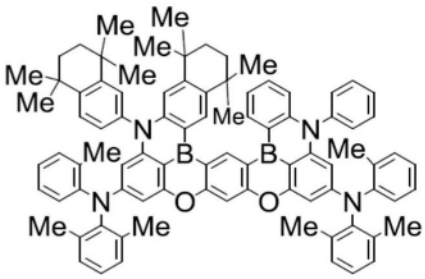
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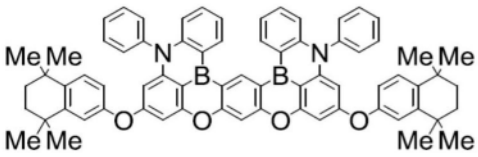
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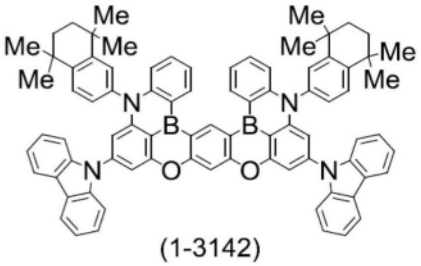
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[0494] [化146]

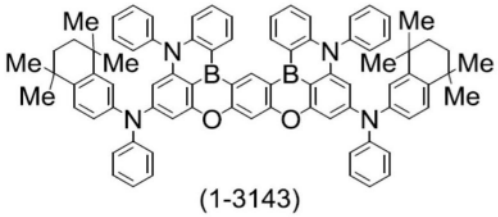
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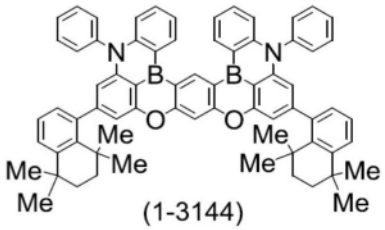
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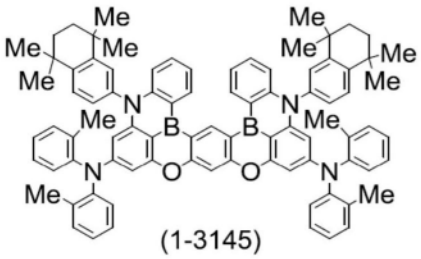
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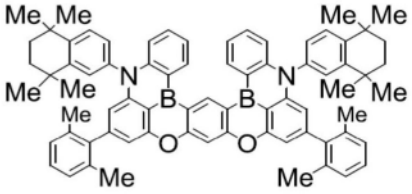
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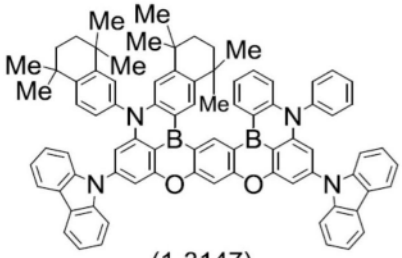
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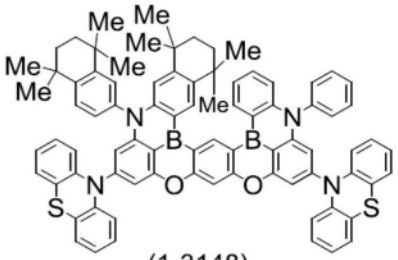
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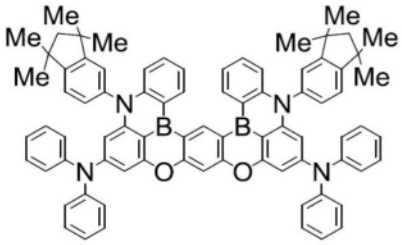
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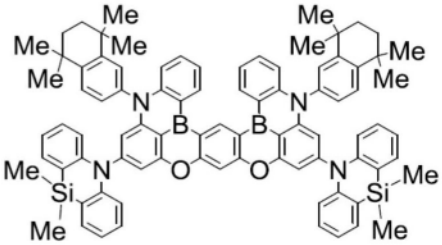
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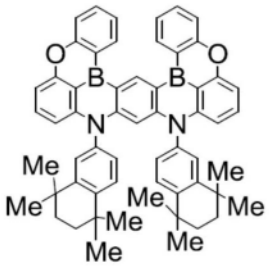


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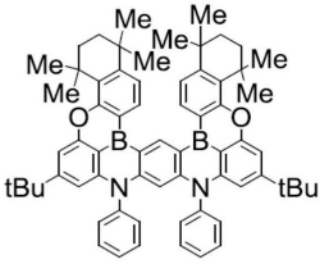


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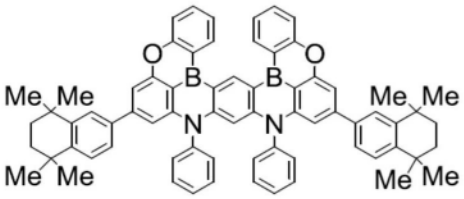
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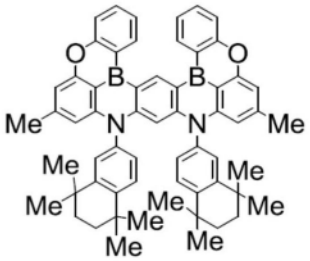
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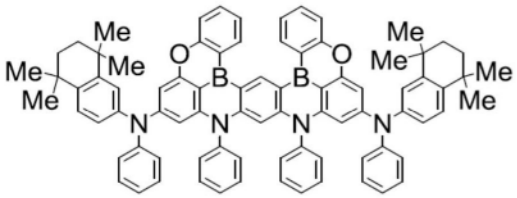


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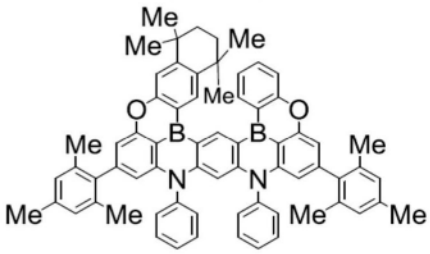


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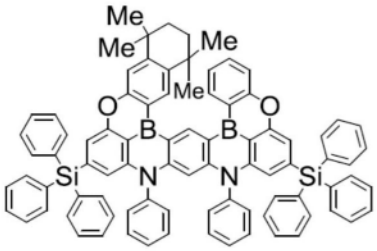
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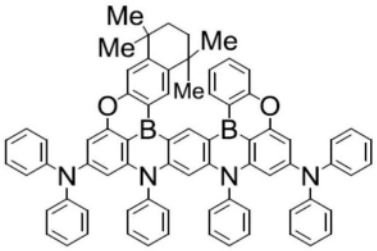
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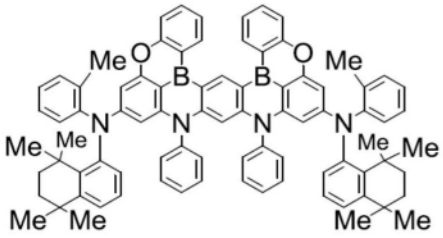
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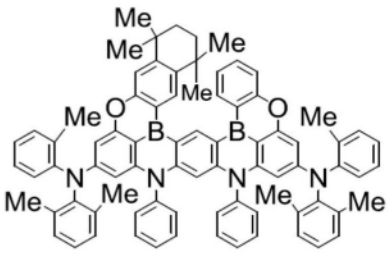
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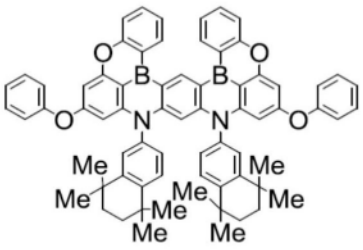


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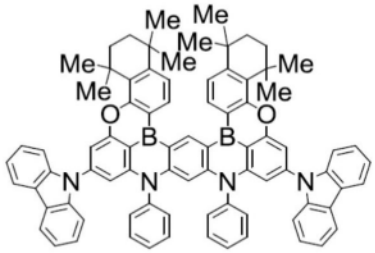


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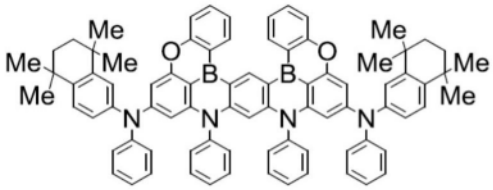
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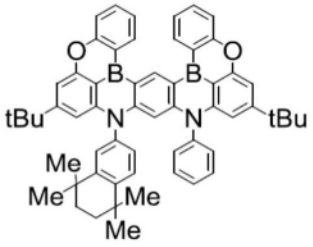
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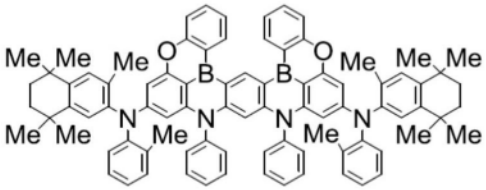


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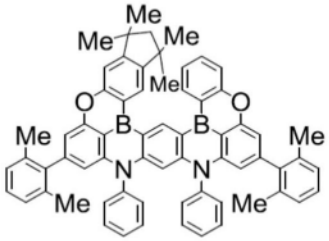


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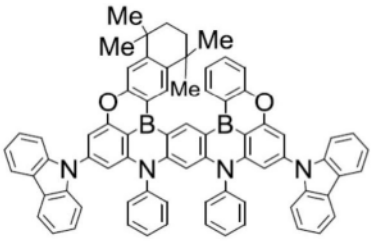
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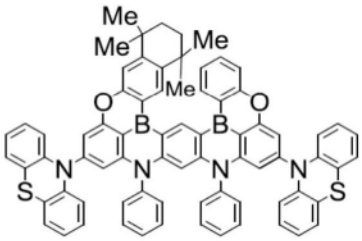
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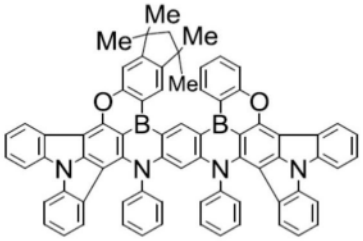
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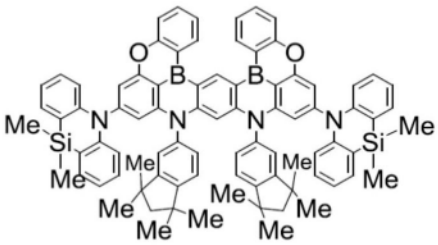
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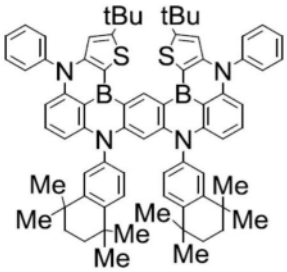


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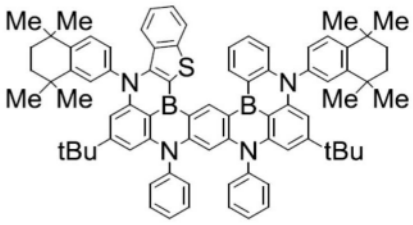


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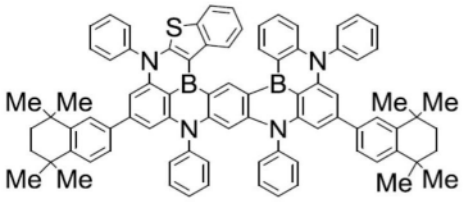
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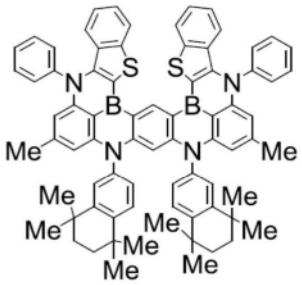
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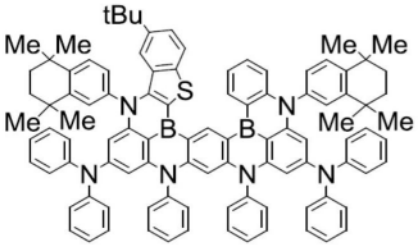


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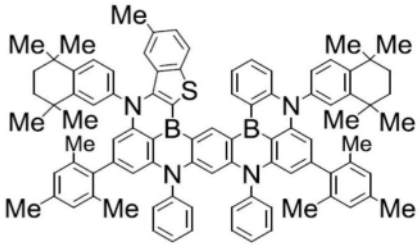


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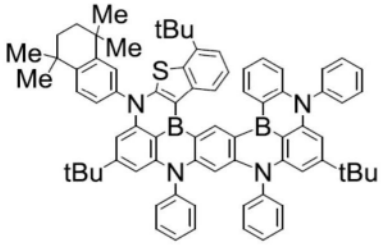
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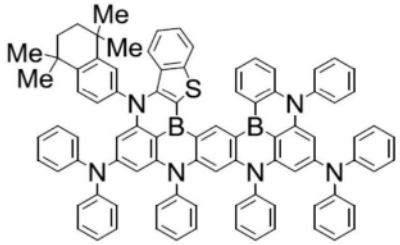
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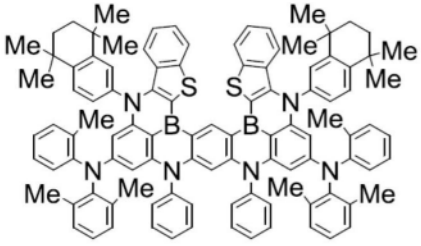
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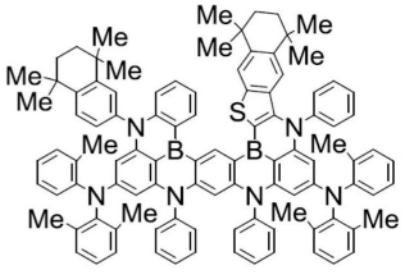
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(1-3308)



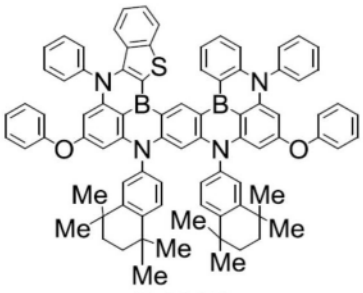
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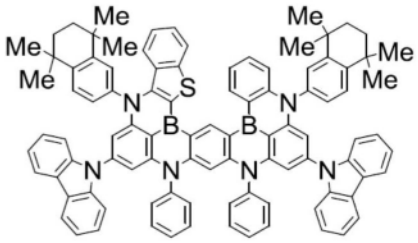
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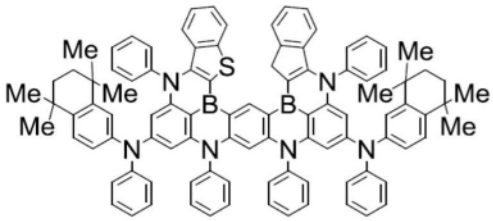
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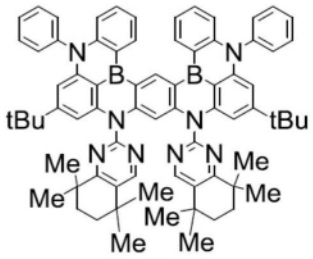
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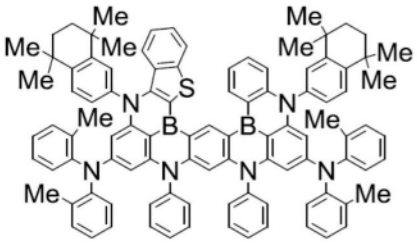
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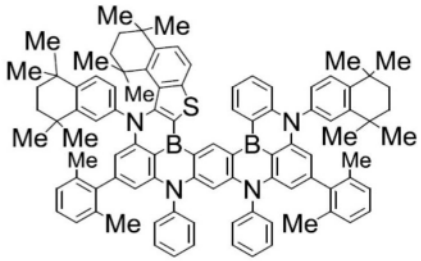
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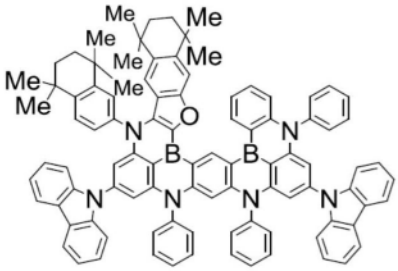
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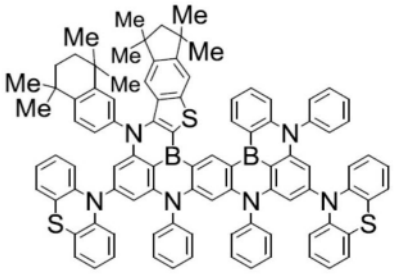
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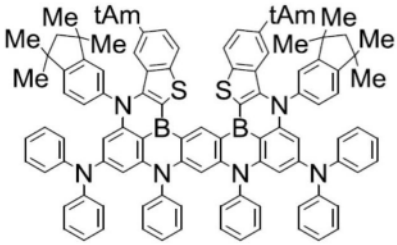
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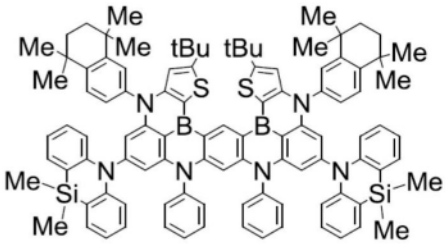
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(1-3328)

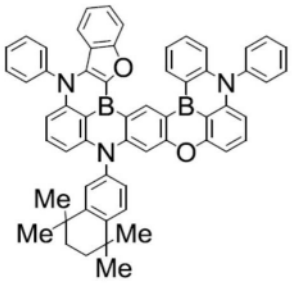


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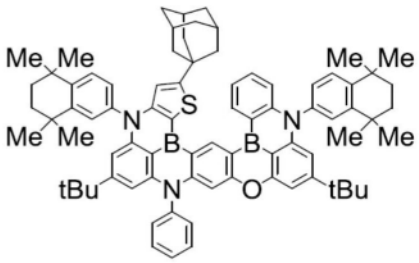


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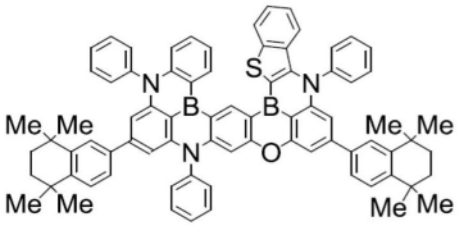
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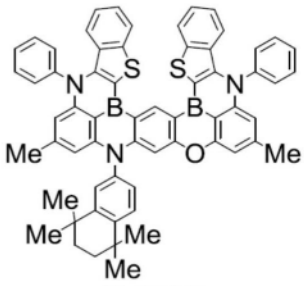
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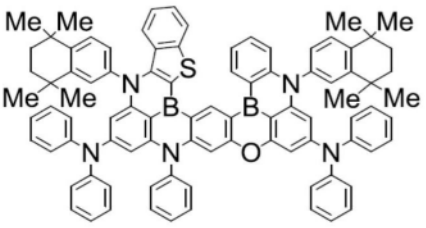


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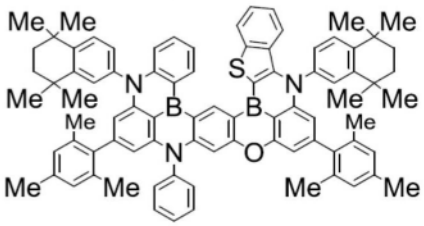


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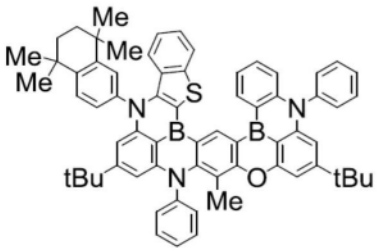
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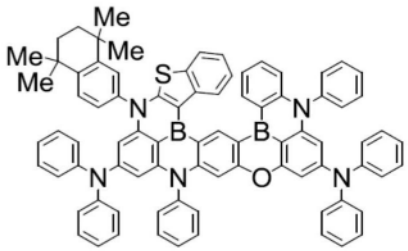
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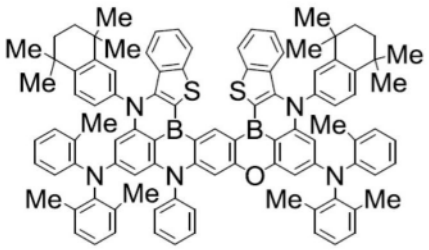
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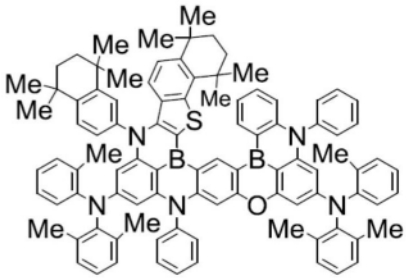
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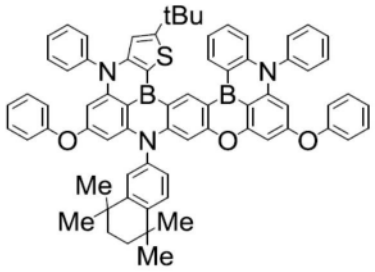


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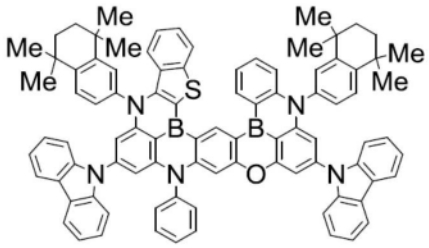


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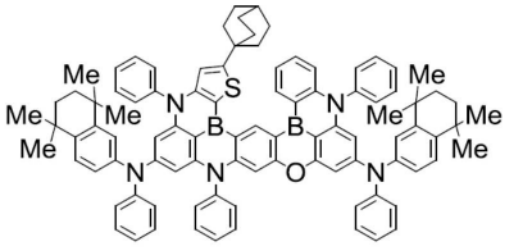
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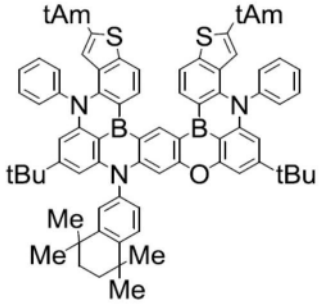
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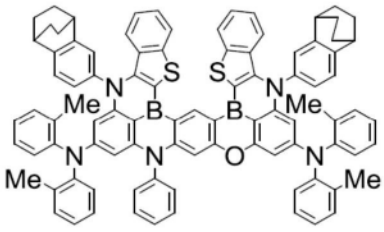


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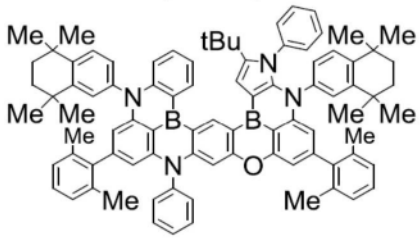


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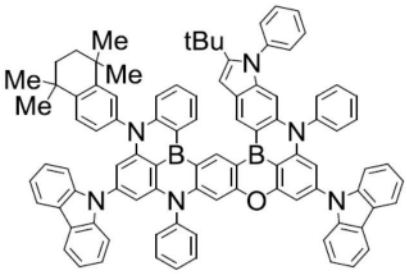
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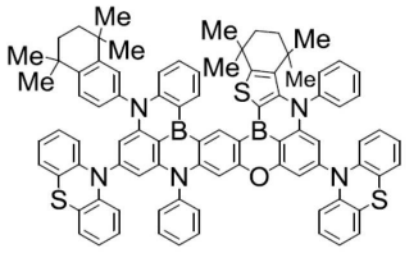
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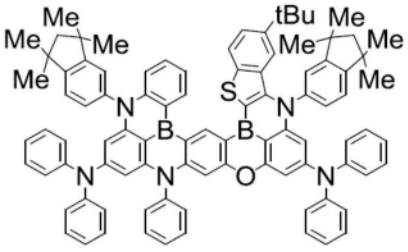
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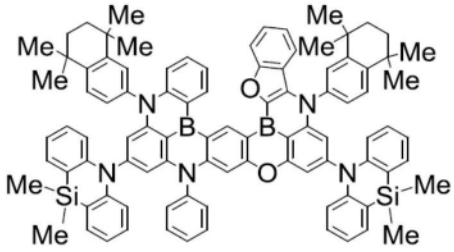
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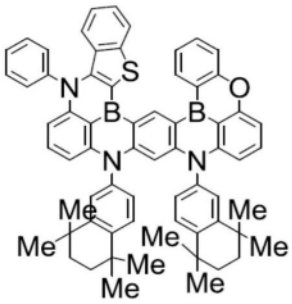


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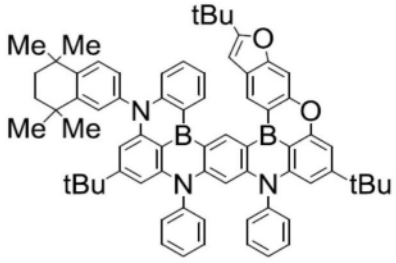


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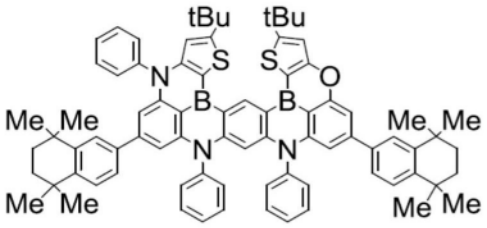
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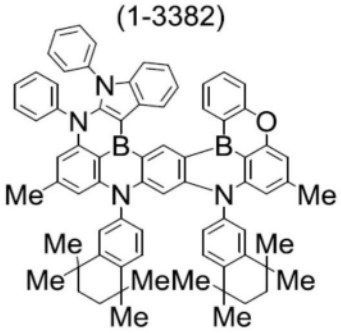
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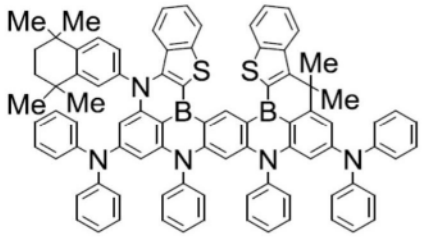


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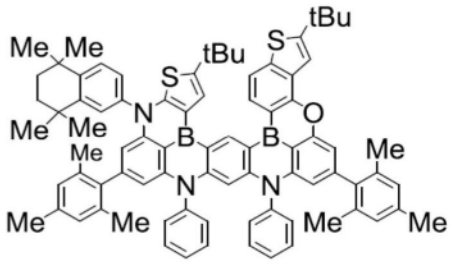


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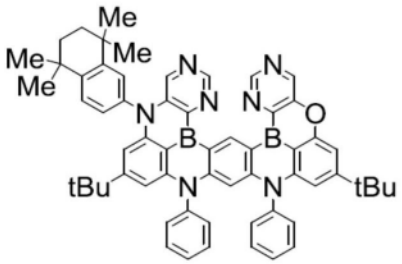
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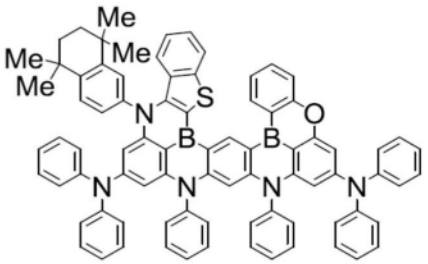
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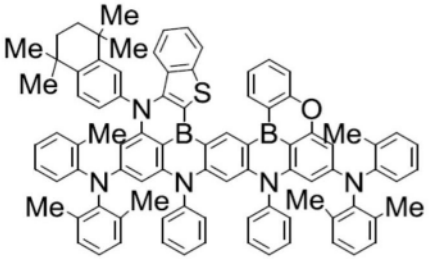
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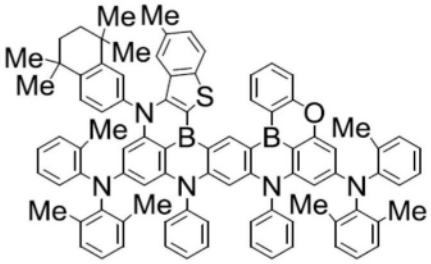
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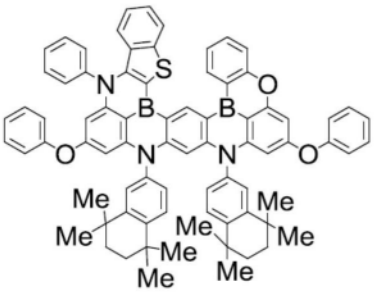


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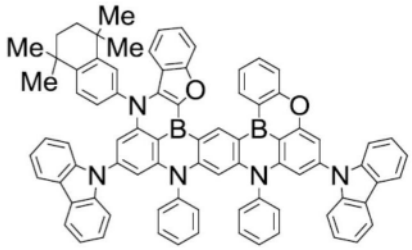


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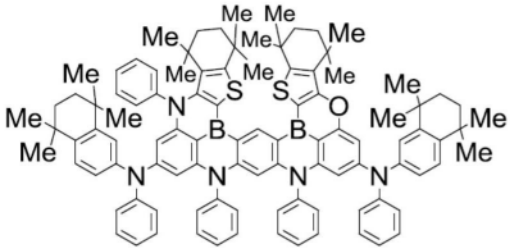
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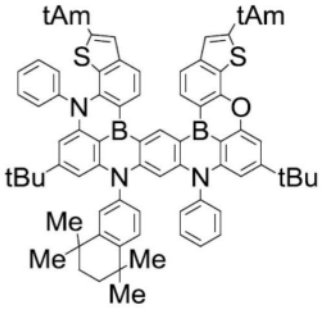
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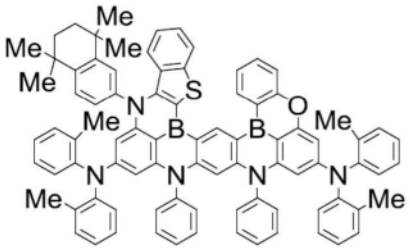


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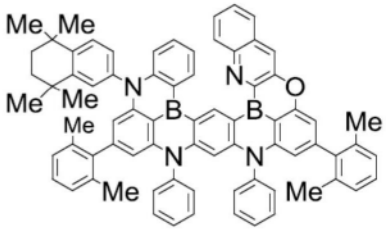


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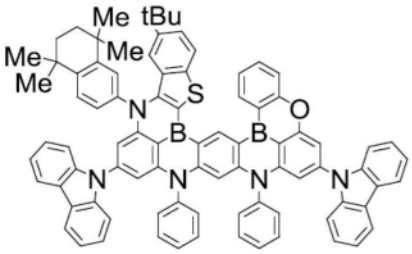
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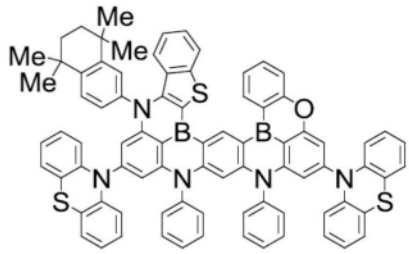
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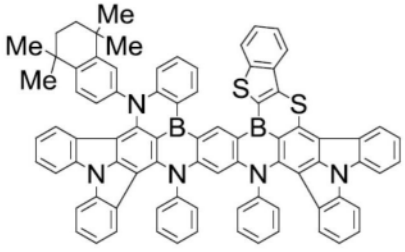
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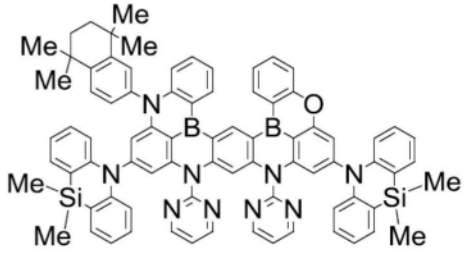
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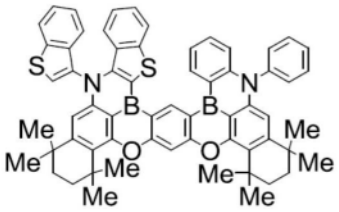


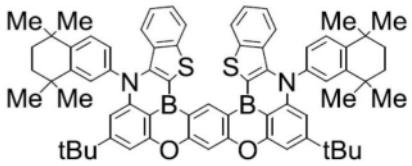
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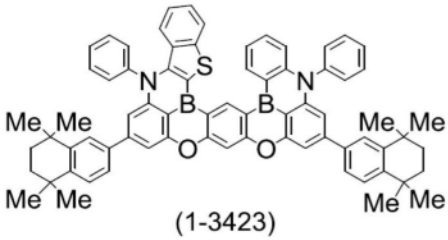


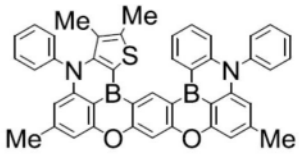
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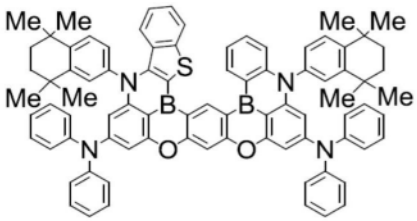

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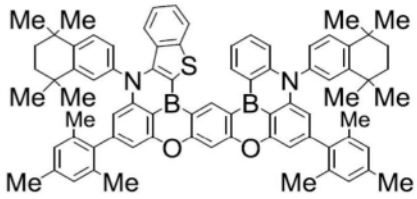

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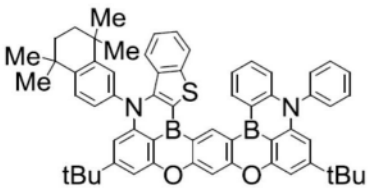

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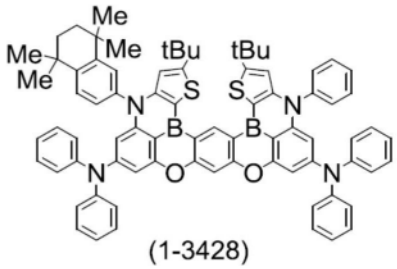

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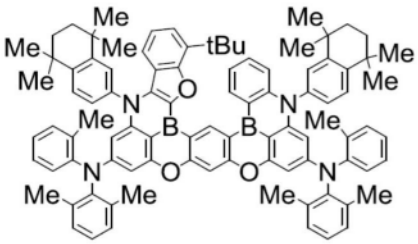
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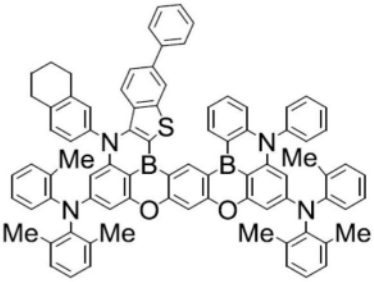

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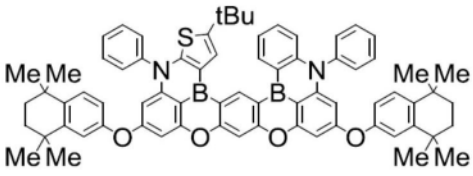

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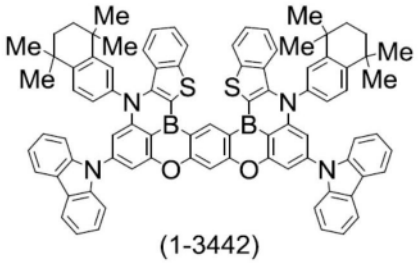

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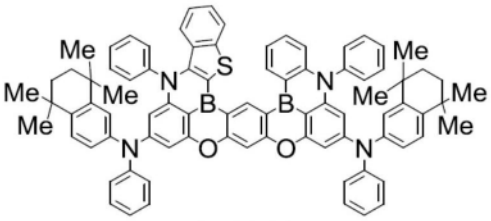
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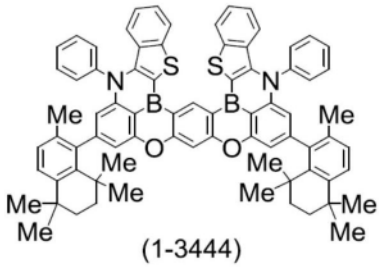
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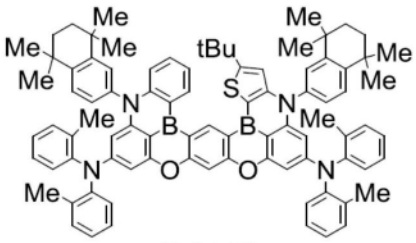


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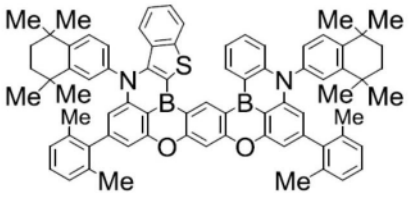


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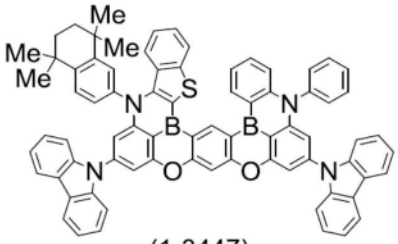
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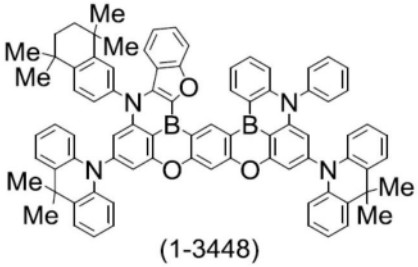
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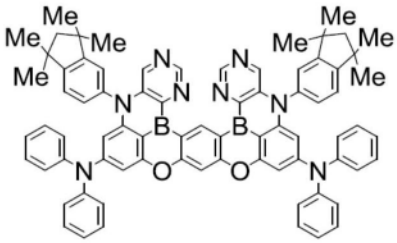
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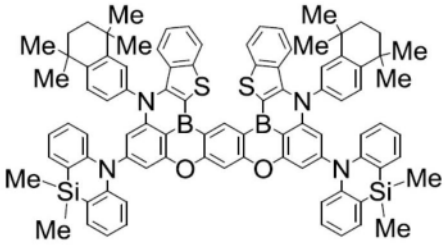
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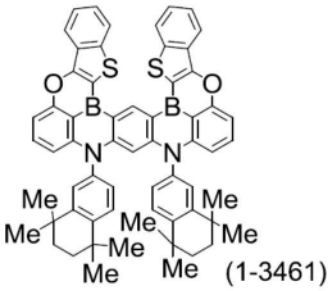


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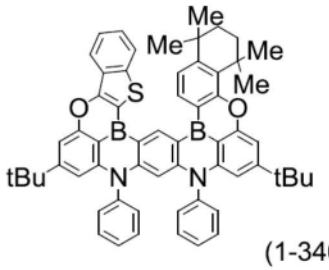


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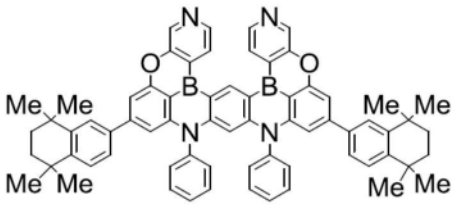
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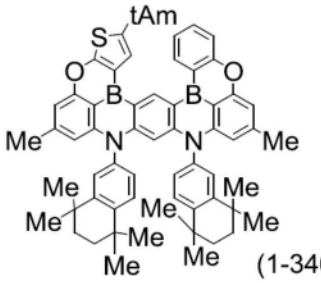
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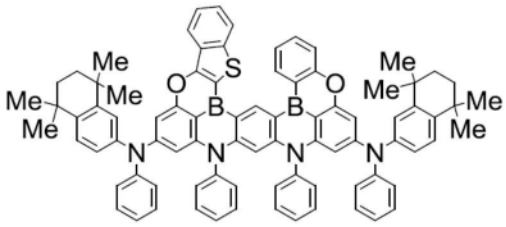


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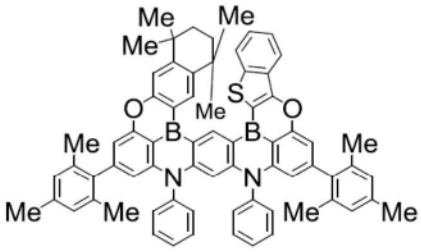


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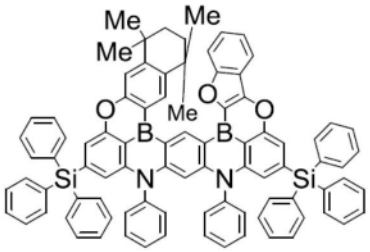
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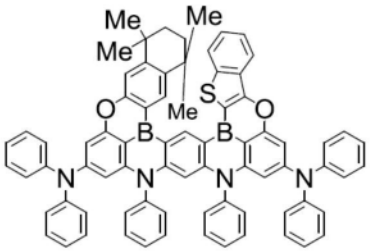
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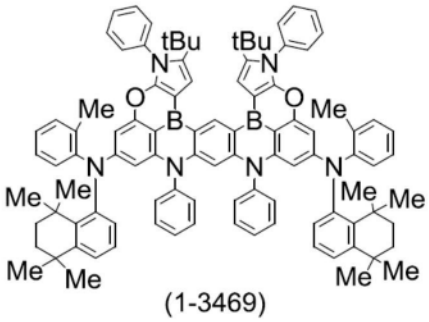
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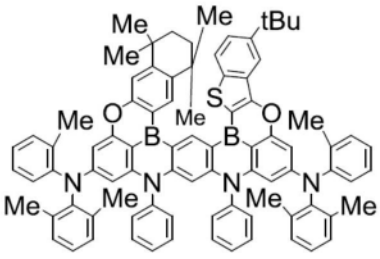
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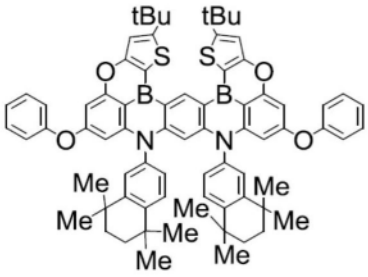


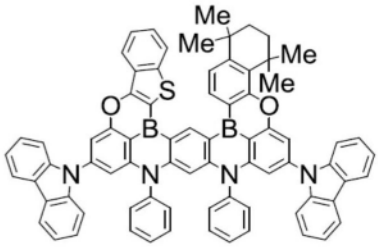
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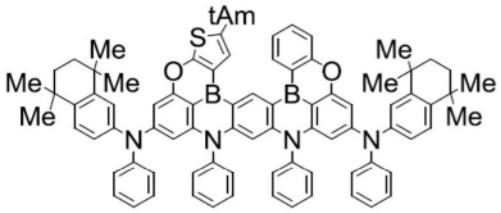


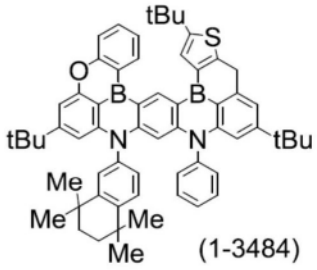
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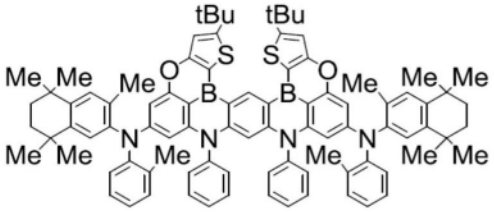

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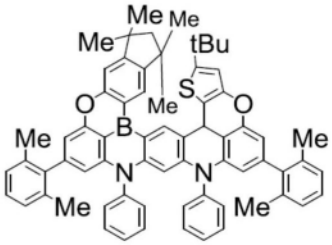

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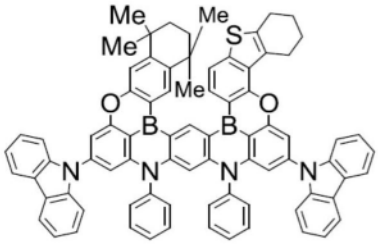

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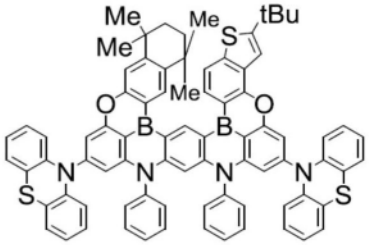

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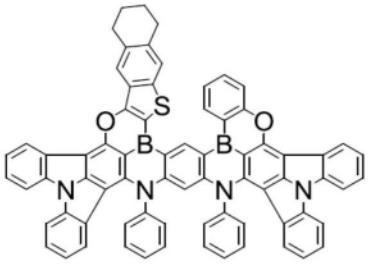
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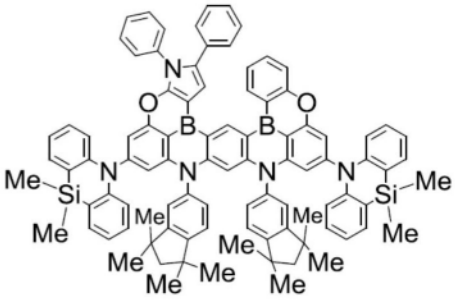

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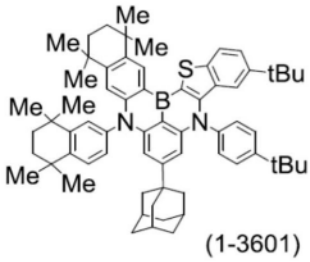

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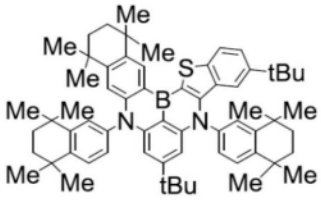

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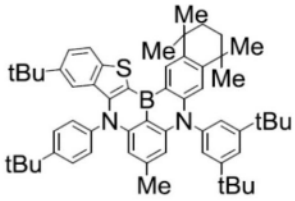

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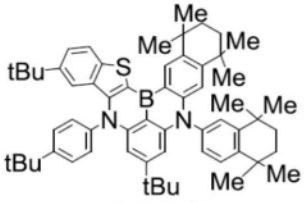

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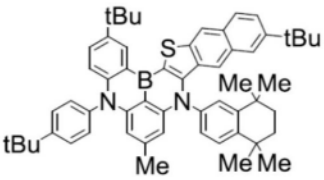
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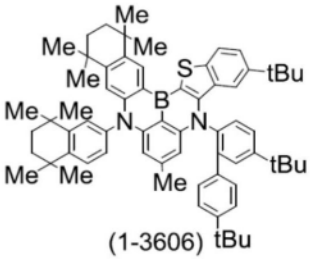

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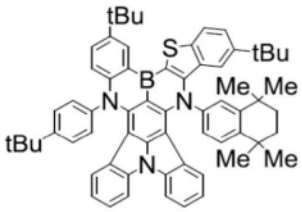

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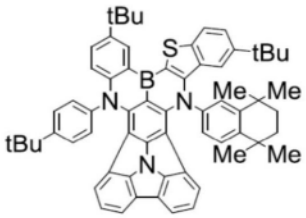

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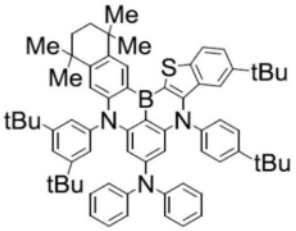

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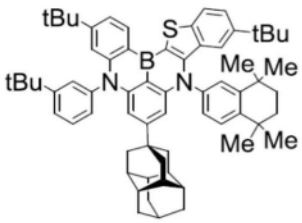

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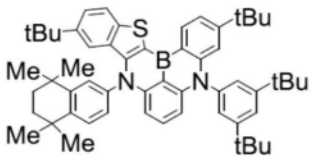

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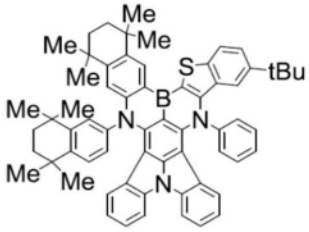

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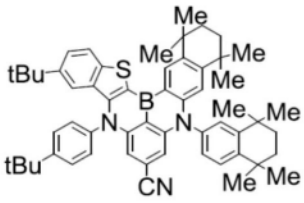

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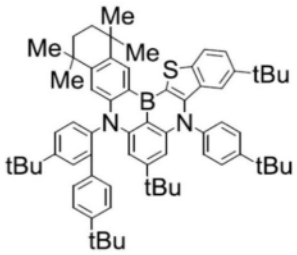
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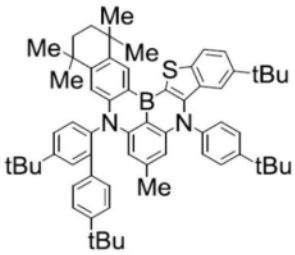

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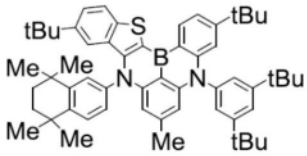

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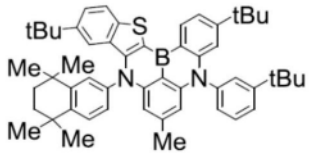

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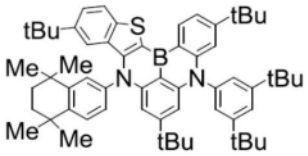

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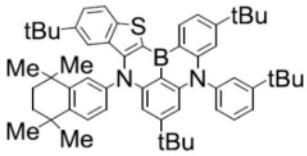
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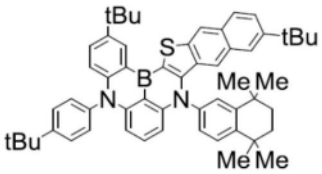
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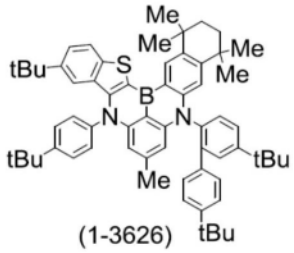

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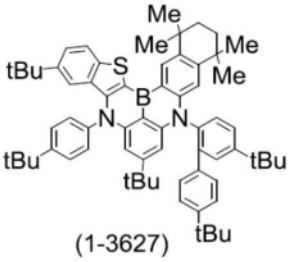

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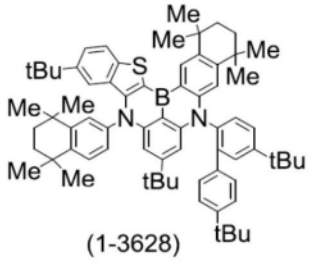

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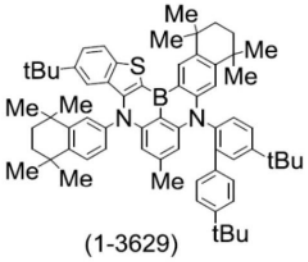

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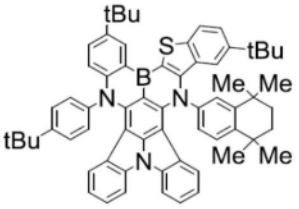

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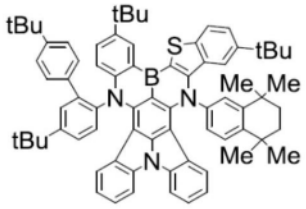

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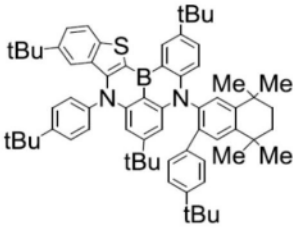

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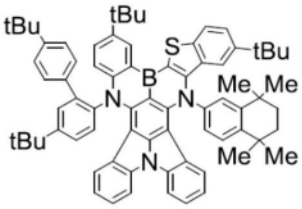

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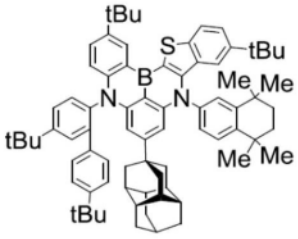

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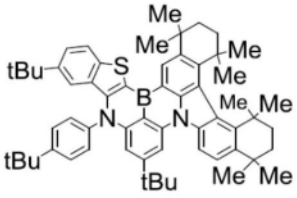

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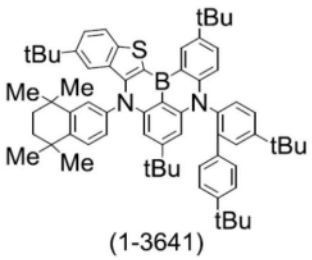

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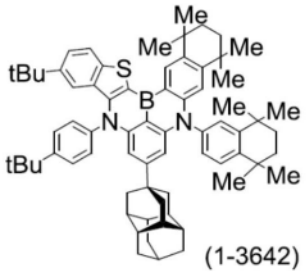

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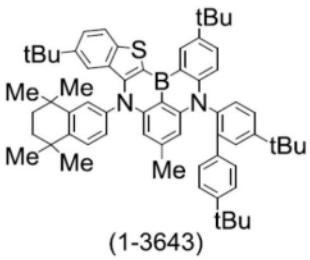

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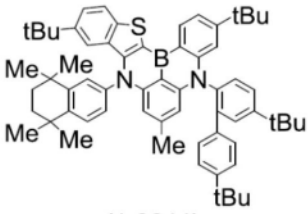
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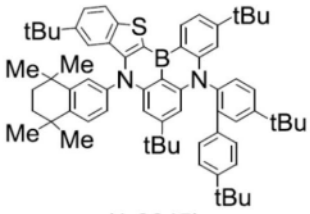
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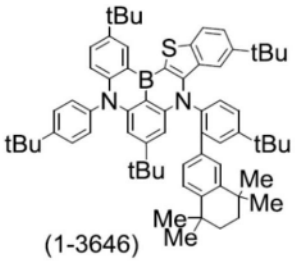

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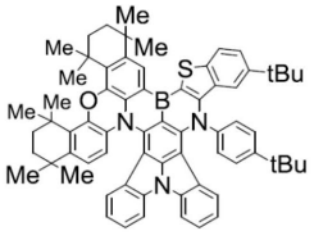

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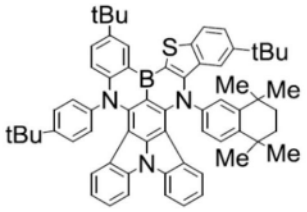

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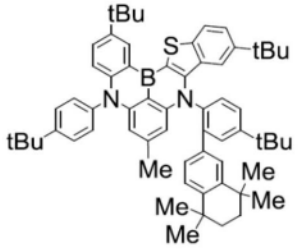

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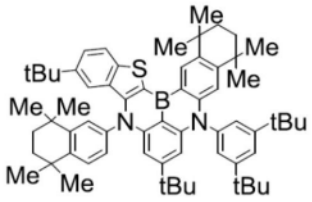

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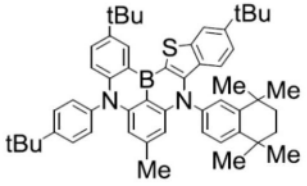

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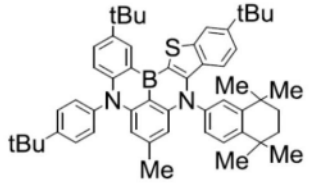

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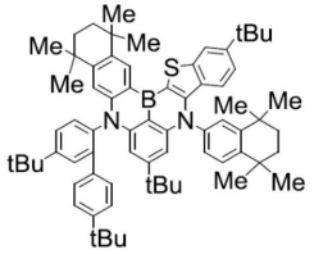

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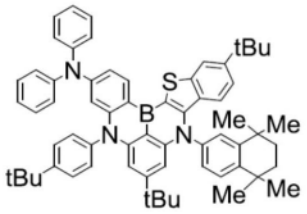

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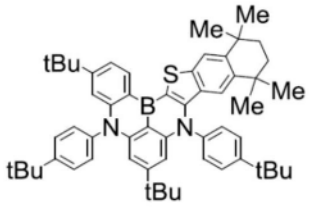

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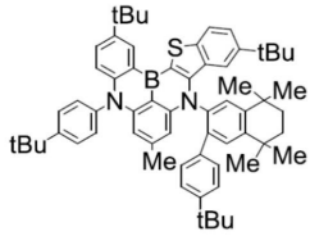

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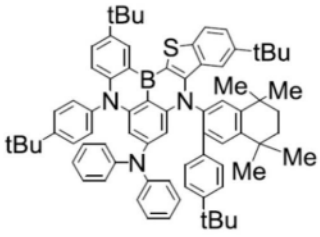

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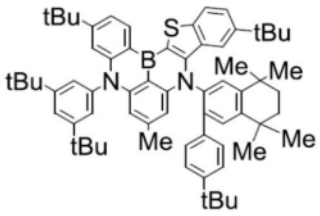
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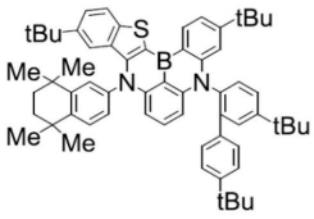
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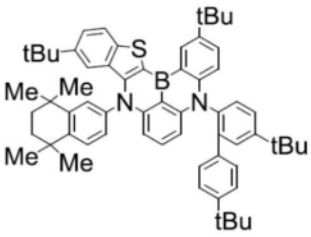
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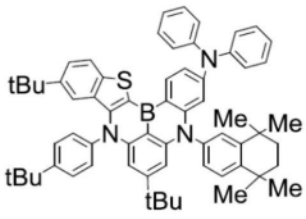
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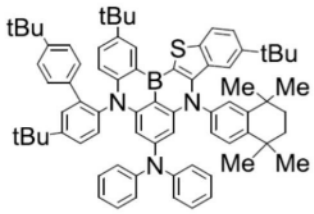


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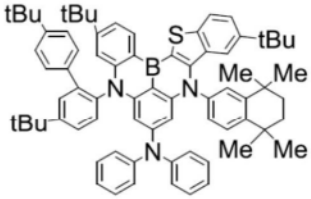


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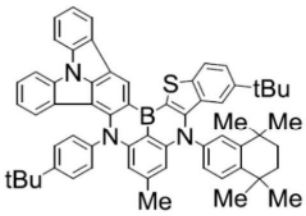
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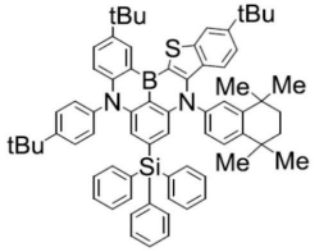
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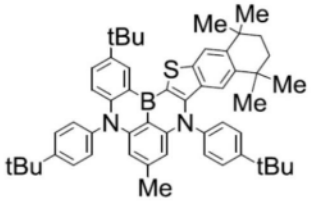
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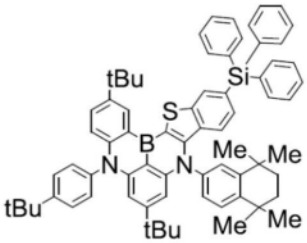
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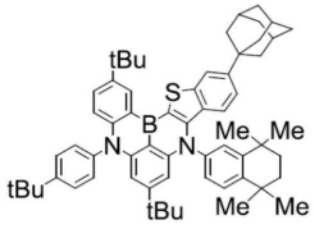
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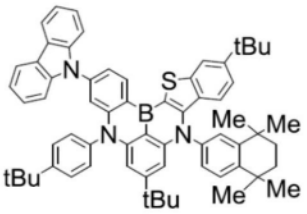
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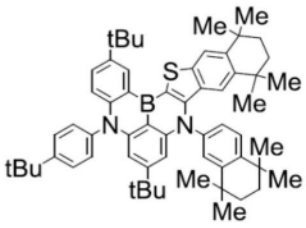
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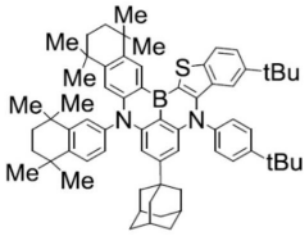
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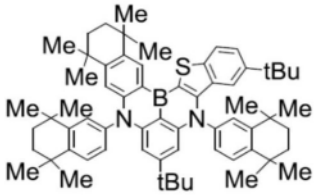
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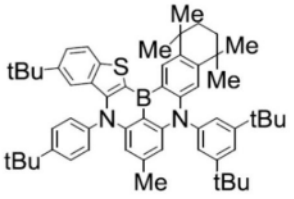
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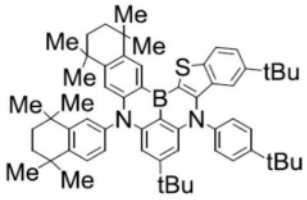
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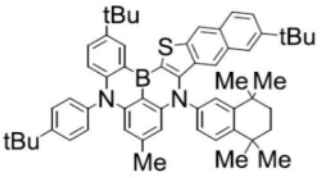
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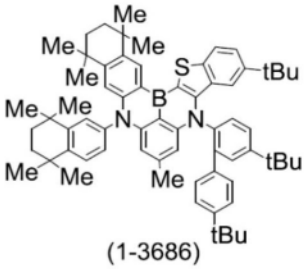
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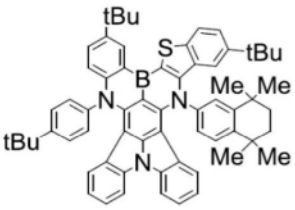
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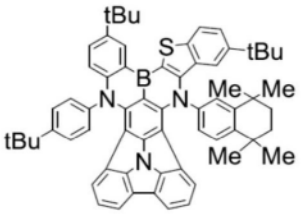
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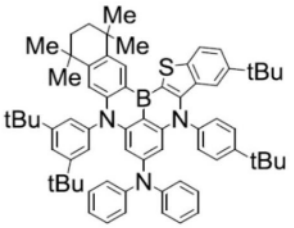
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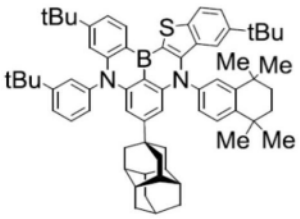
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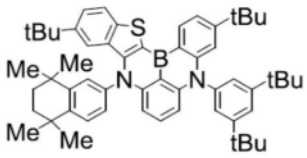
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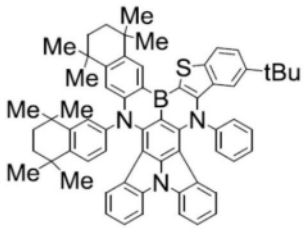
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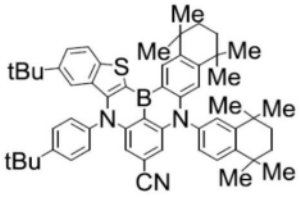
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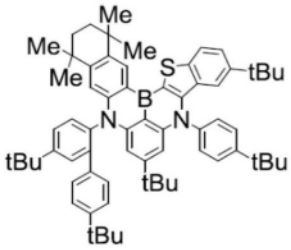
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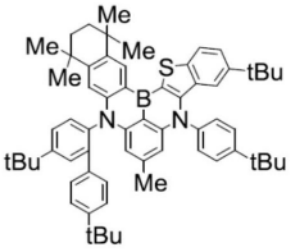
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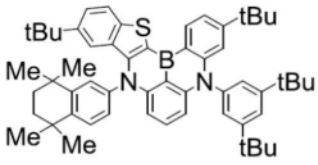
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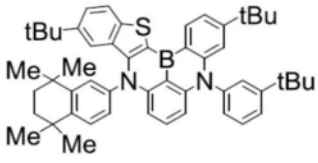
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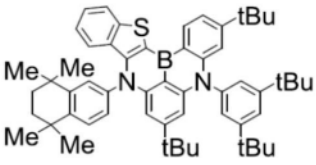
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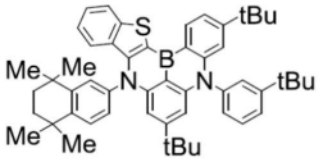
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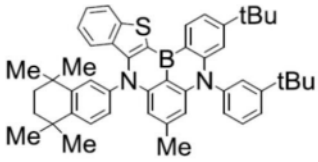
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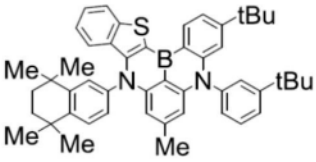
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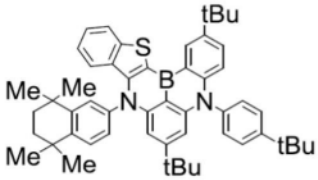
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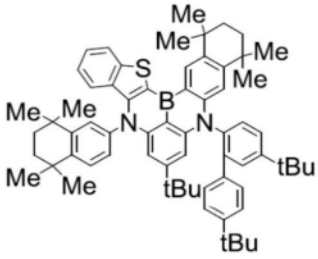
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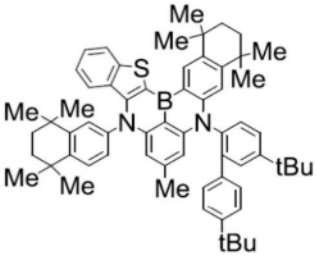
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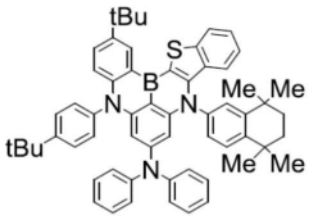
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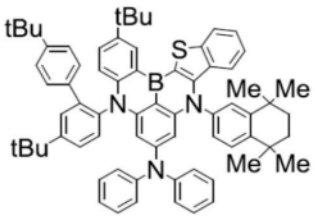
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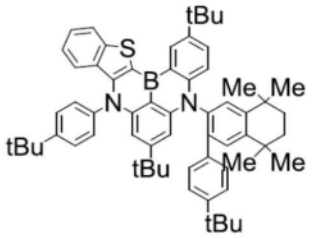
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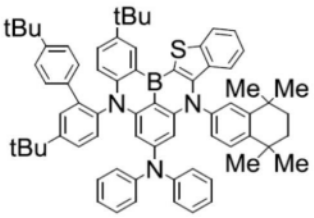
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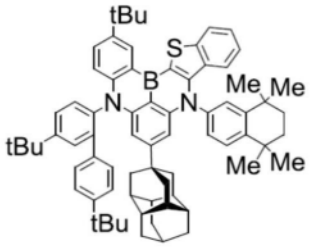
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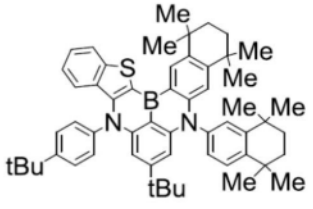
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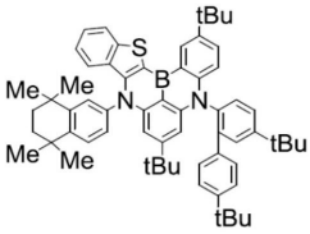


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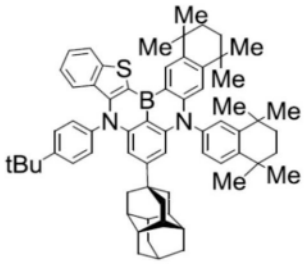


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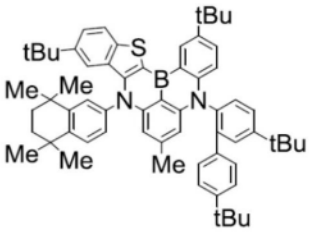
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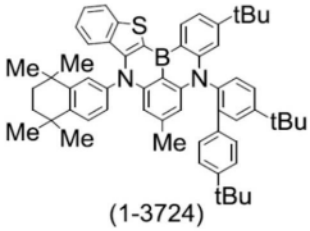
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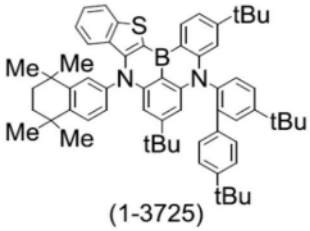
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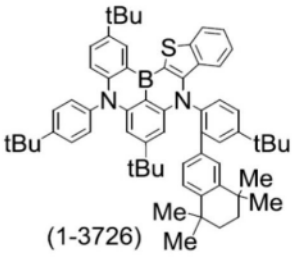
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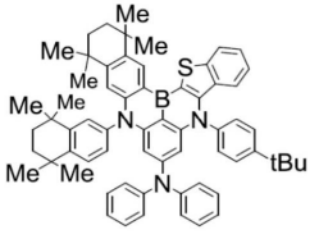


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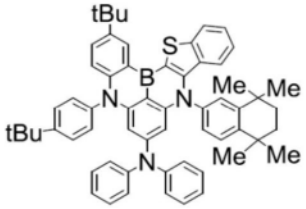


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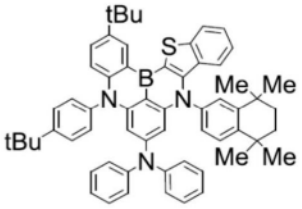
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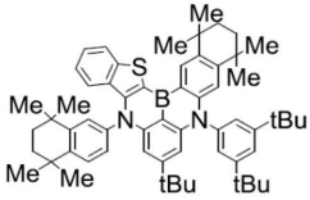
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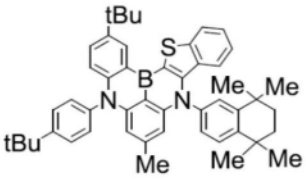
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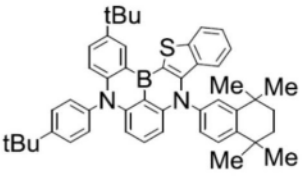
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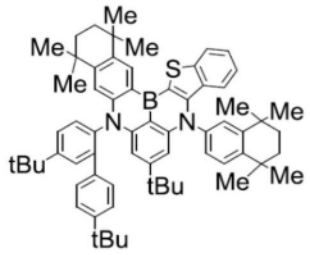
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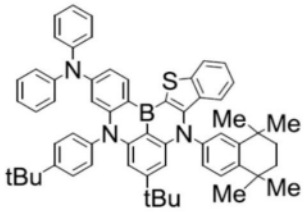
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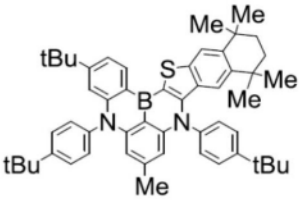
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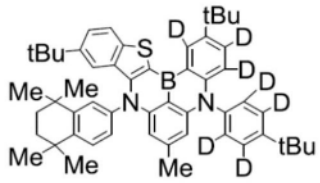
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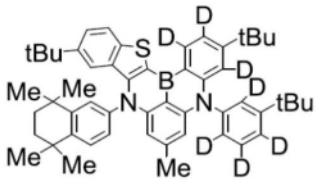
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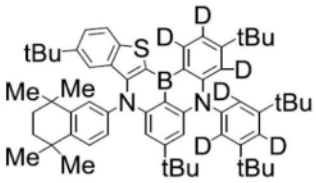
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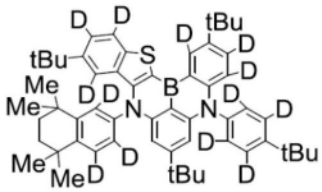
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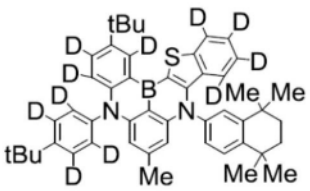
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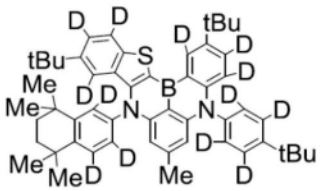
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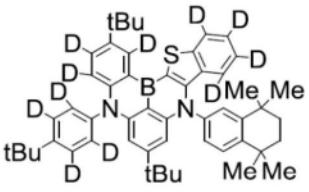
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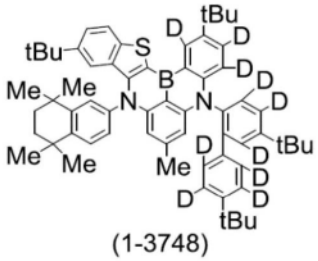
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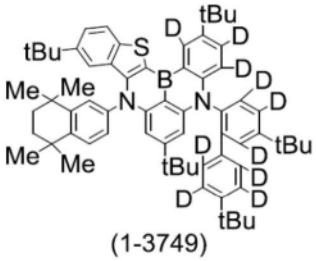
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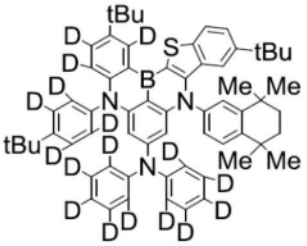
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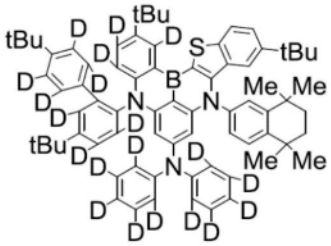
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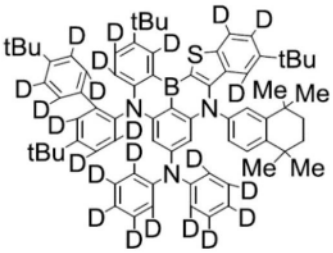
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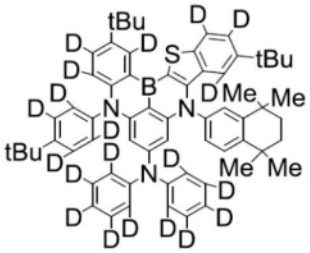
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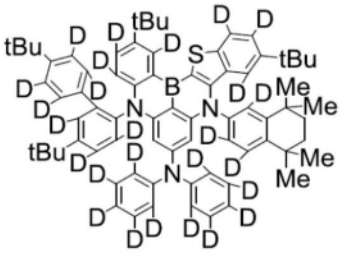
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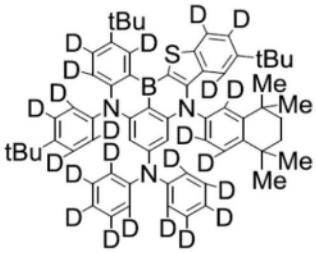
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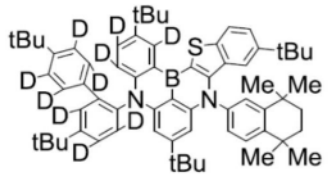


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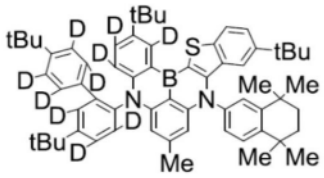


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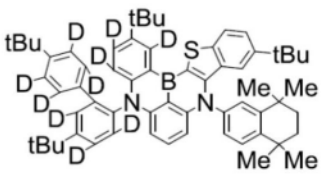
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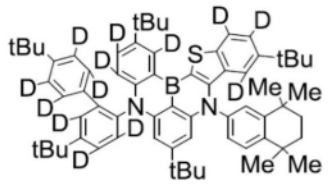
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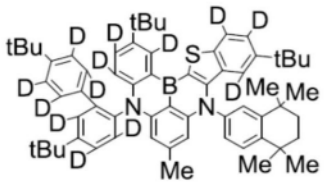
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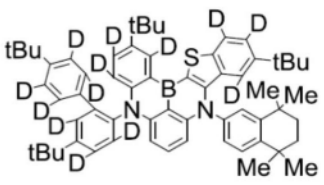
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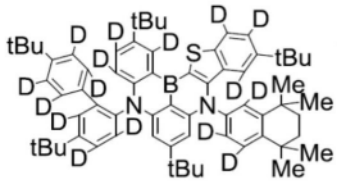


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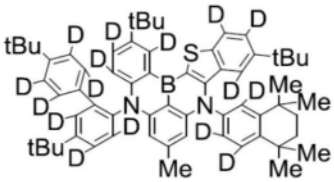


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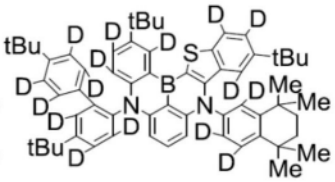
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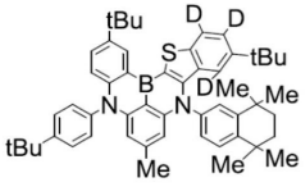
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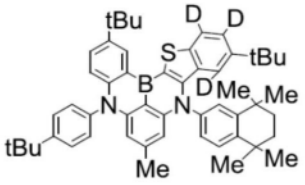
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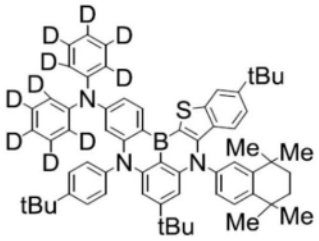
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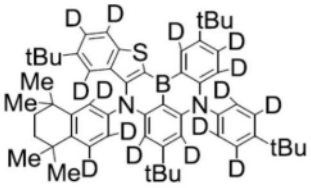
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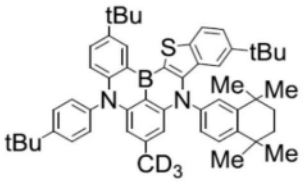
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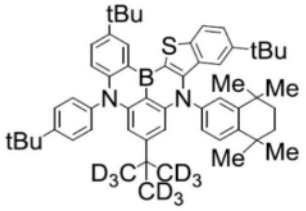
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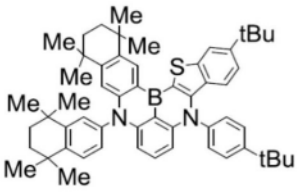


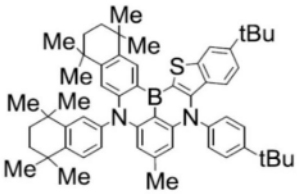
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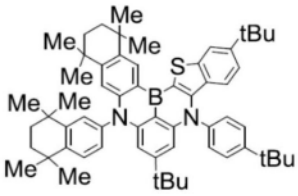


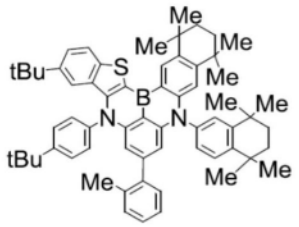
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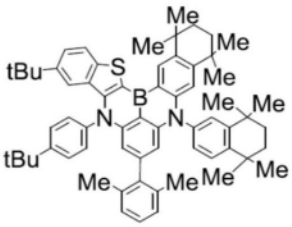
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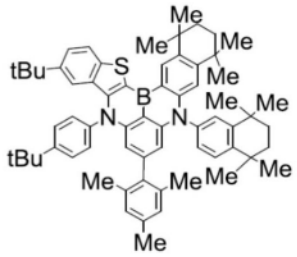

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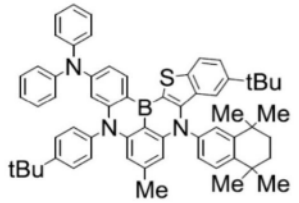

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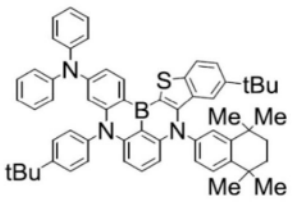

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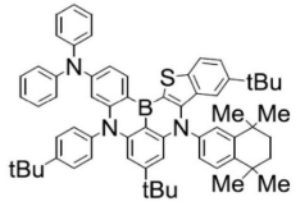

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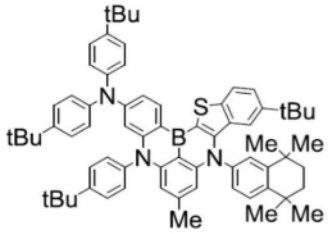

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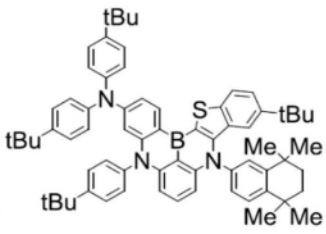
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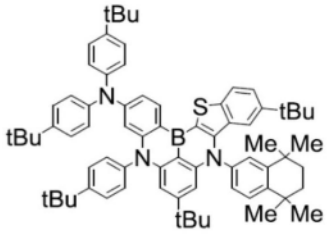

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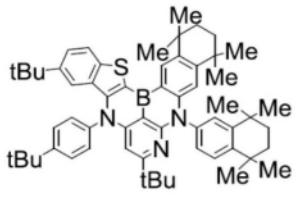

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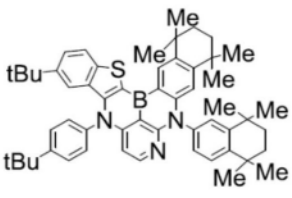

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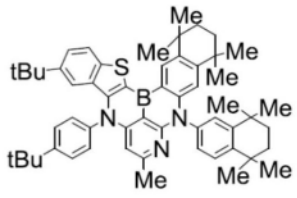

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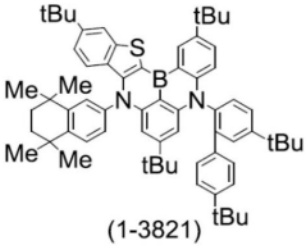

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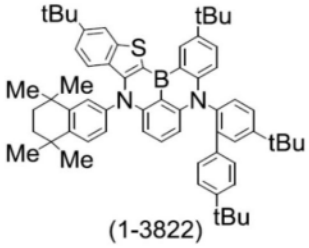

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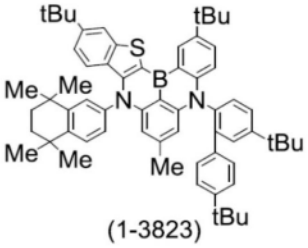

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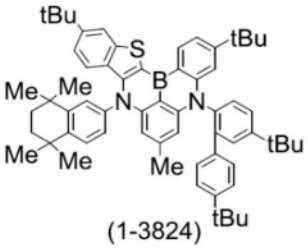
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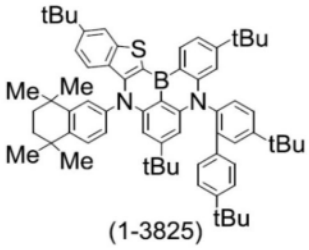
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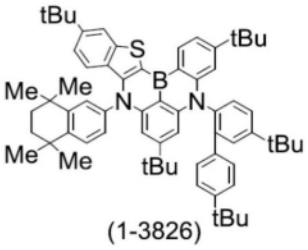

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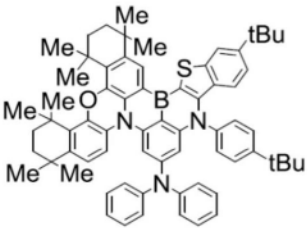

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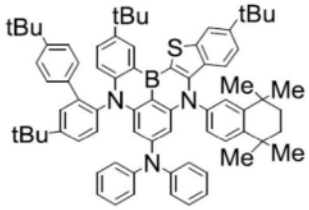

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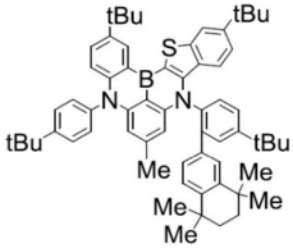

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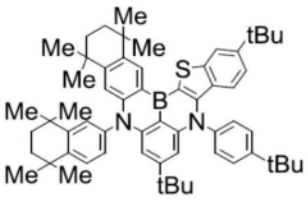

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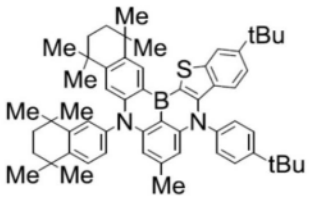

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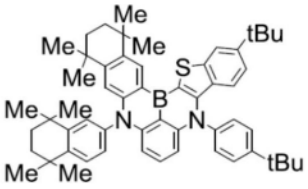

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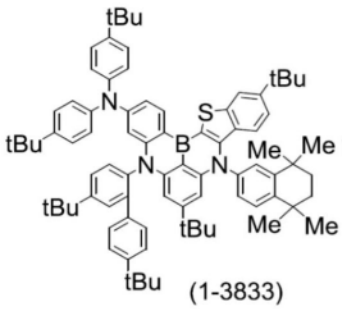

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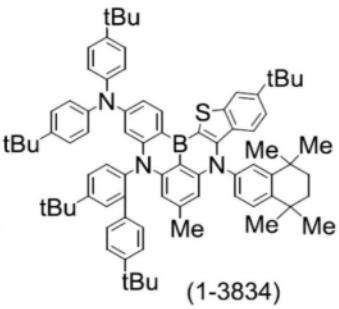

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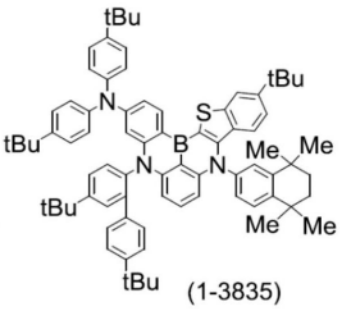

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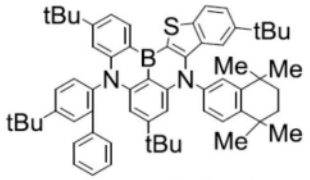

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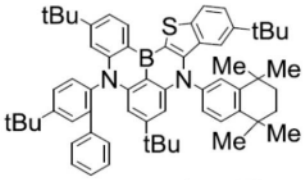

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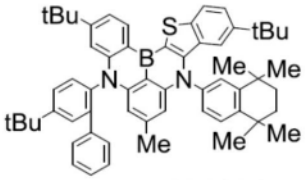

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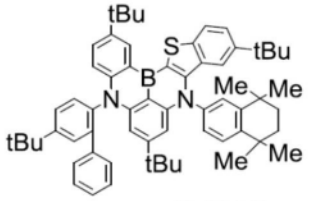
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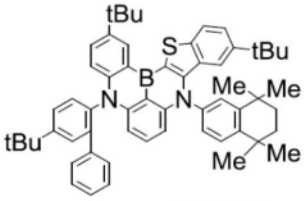
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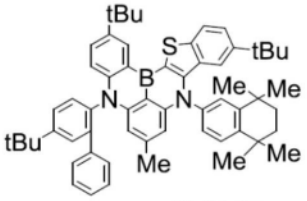

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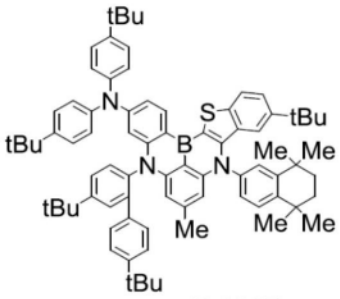

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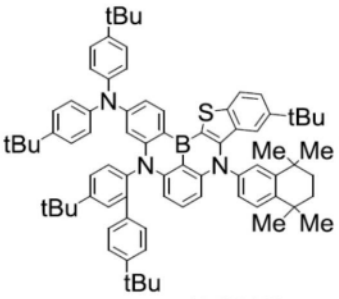

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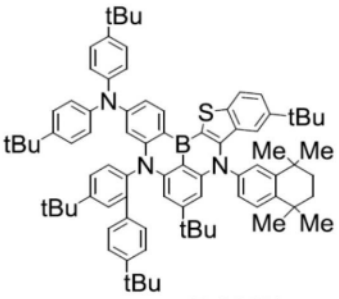

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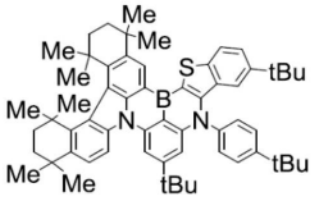

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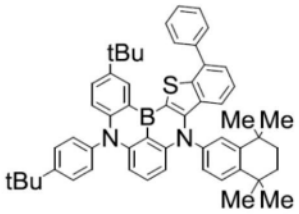

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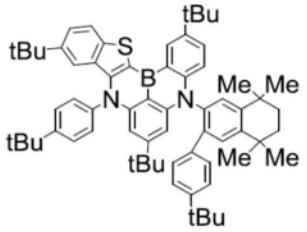

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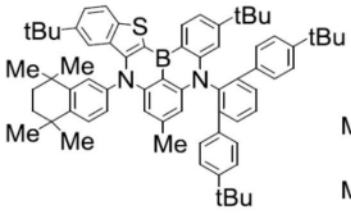

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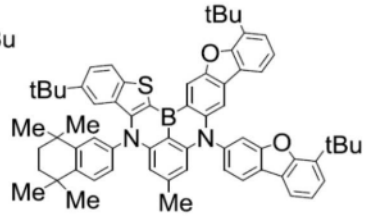

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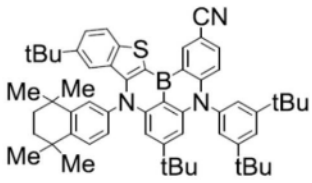

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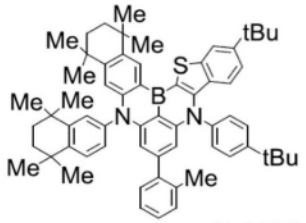

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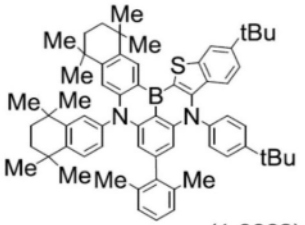

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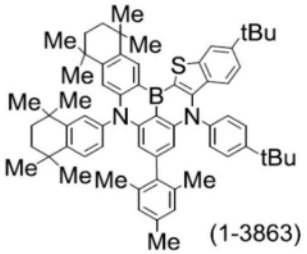

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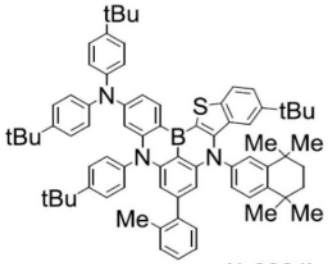
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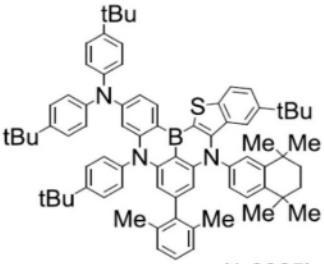
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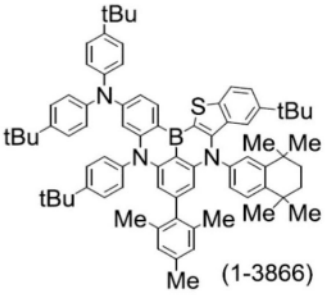

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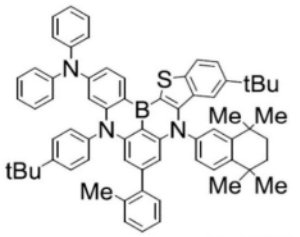

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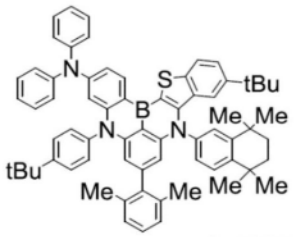

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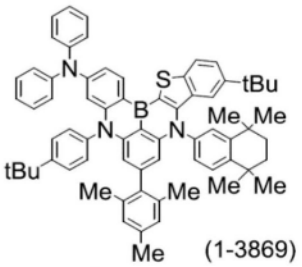

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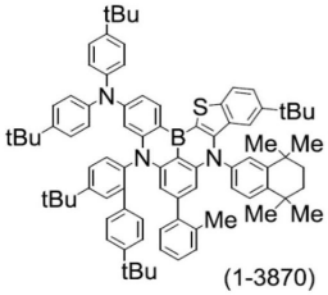

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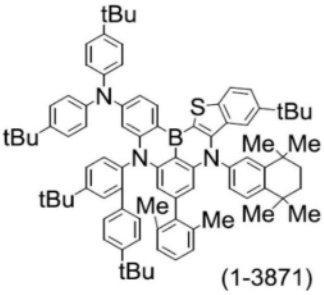

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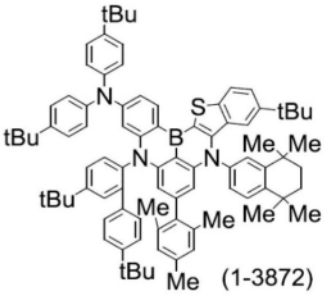

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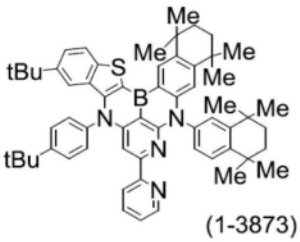

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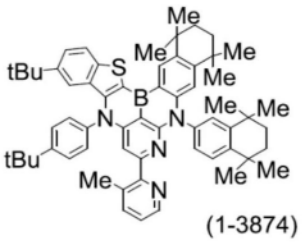

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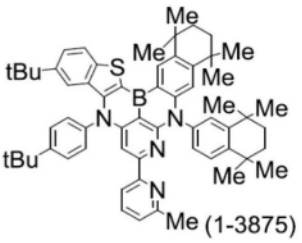

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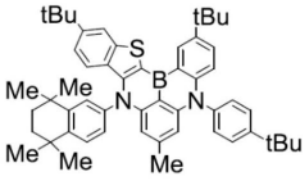

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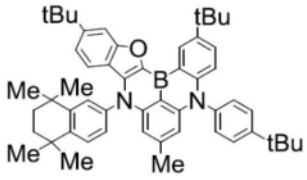

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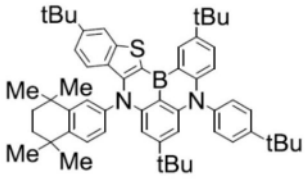
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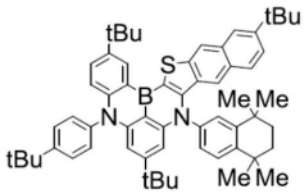
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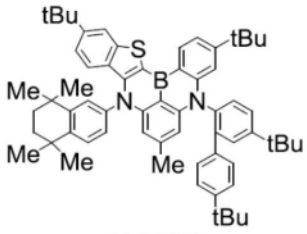
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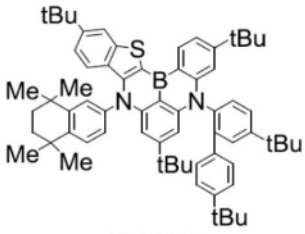
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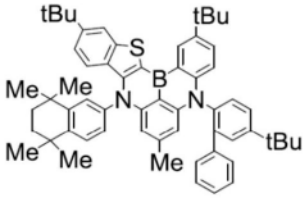
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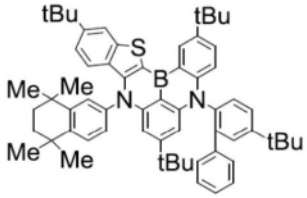
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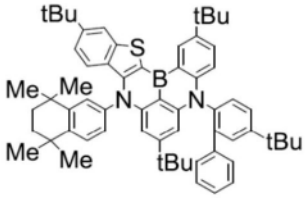
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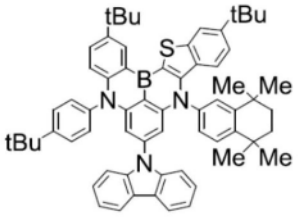
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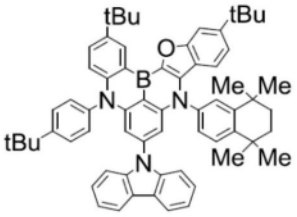
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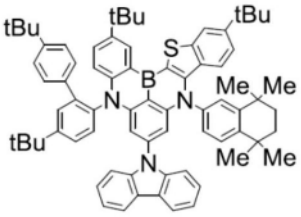
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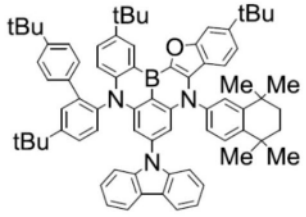
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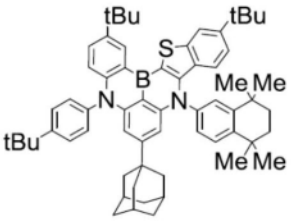
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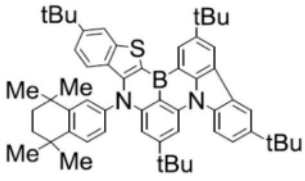
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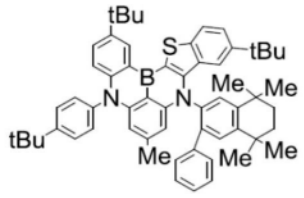


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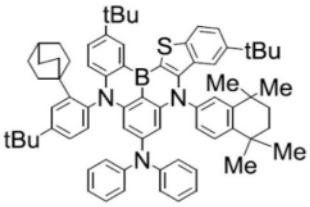


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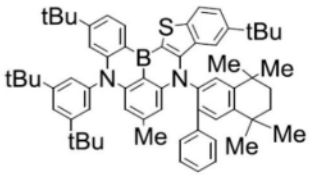
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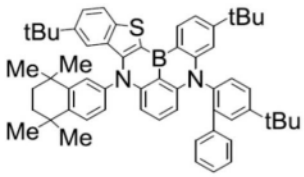
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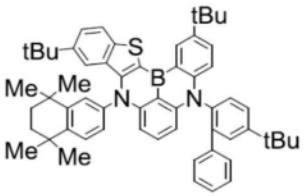
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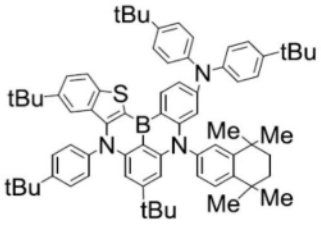
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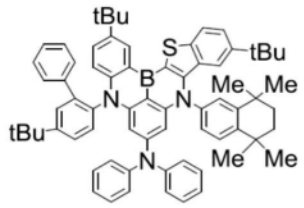


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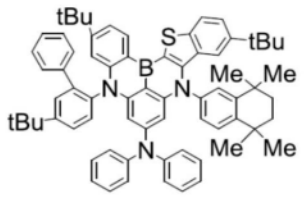


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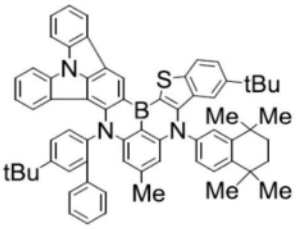
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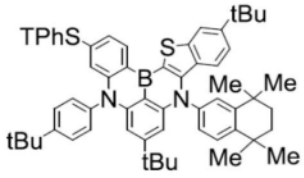
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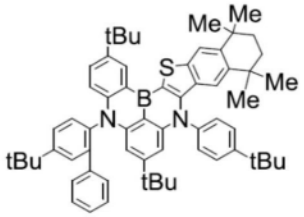
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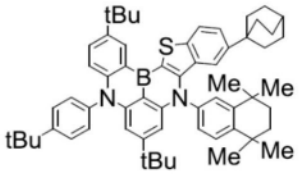
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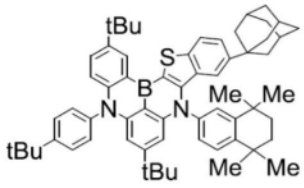
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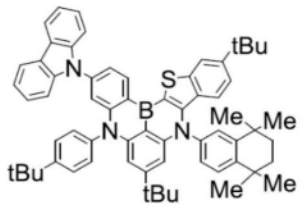
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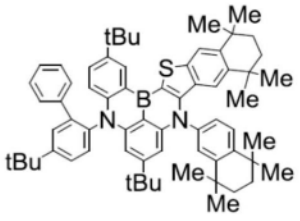
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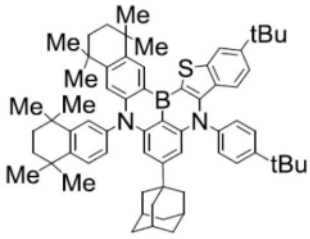
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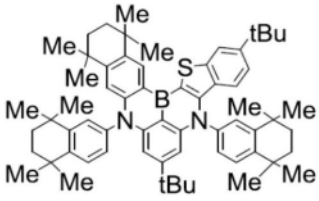
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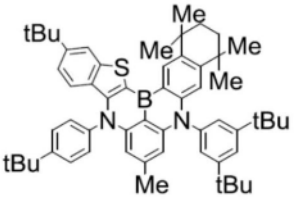
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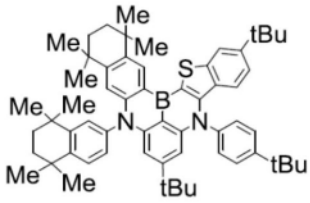
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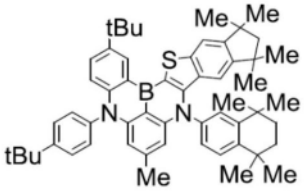
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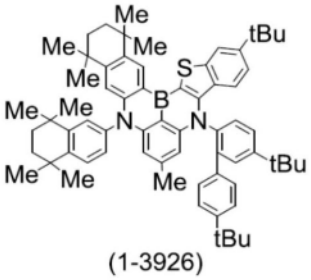
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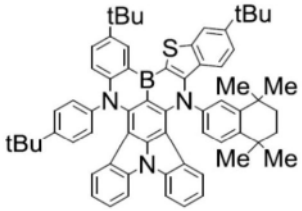
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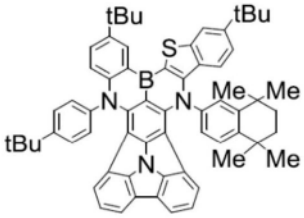
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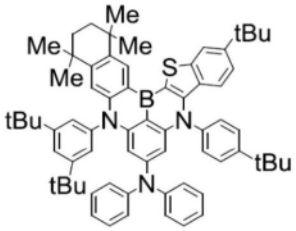
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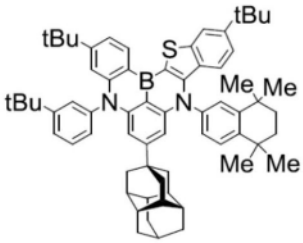
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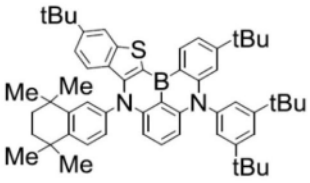
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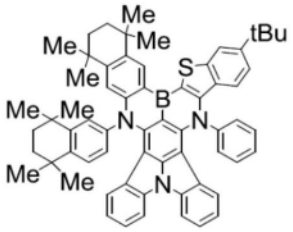
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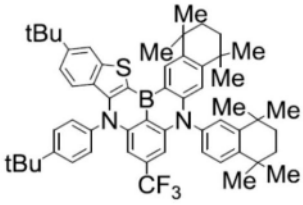
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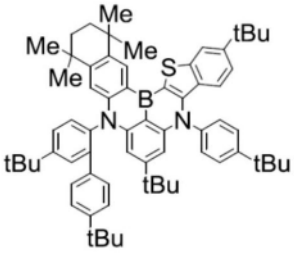
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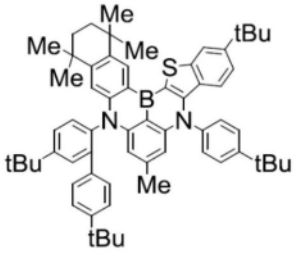
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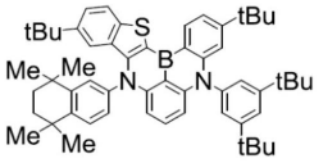


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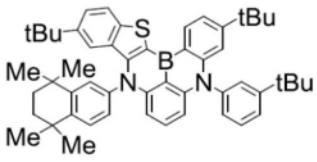


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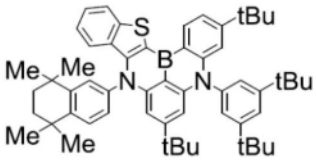
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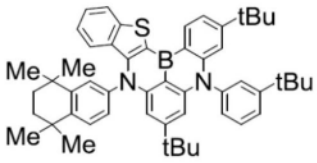
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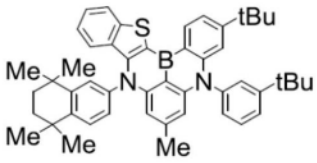
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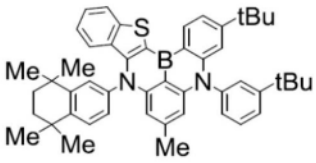
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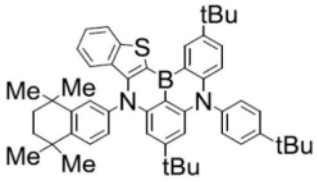


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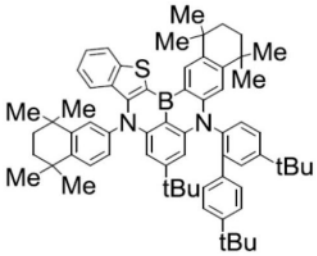


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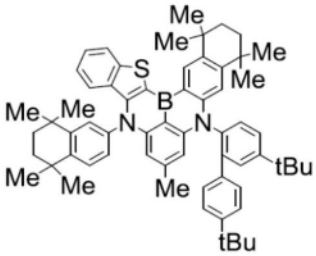
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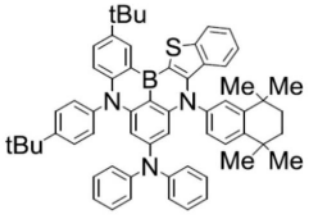
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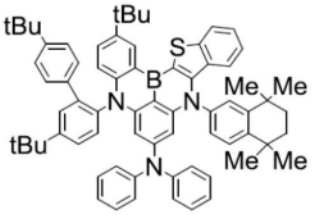
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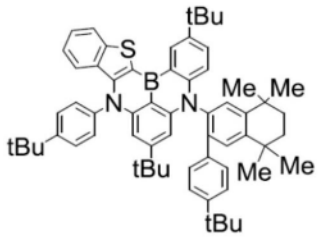
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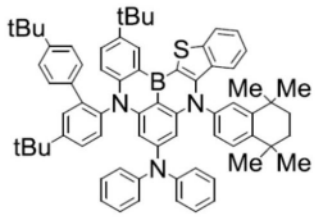
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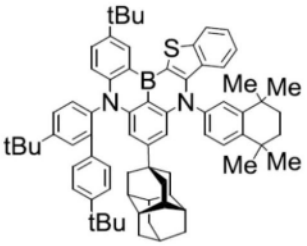
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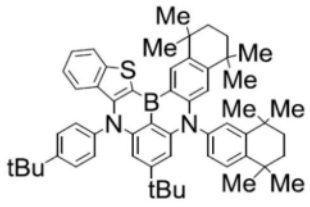
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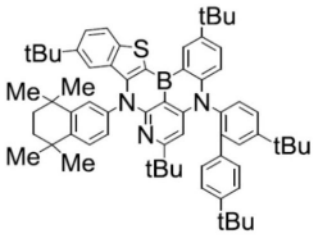


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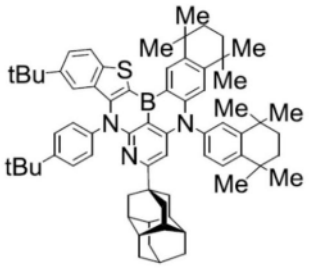


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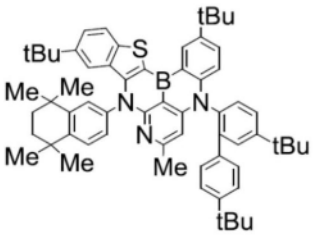
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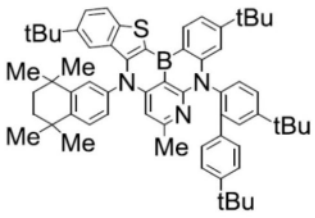
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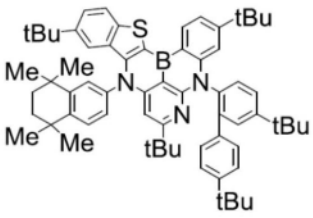
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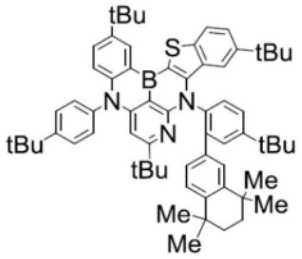
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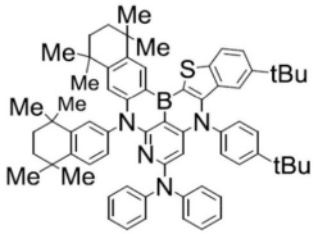


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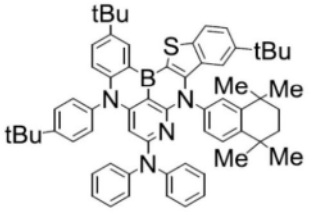


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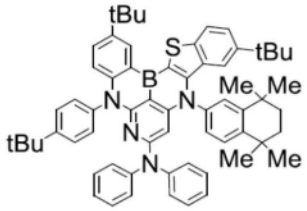
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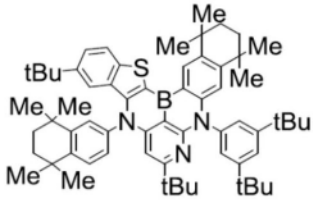
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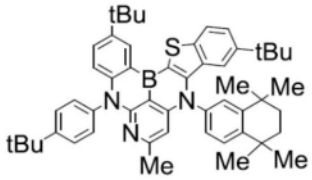
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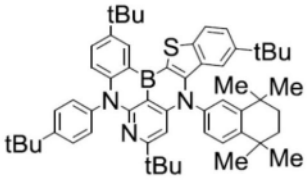
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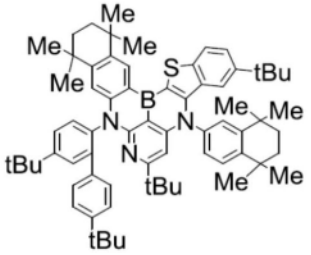
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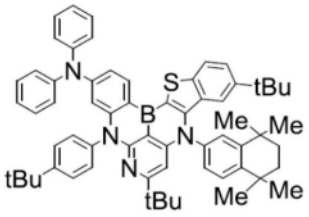
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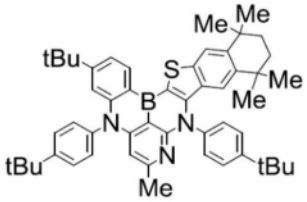
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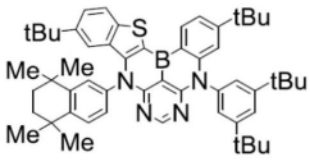
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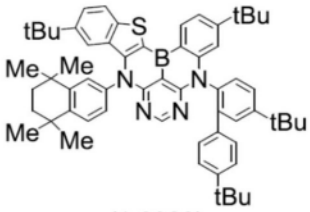
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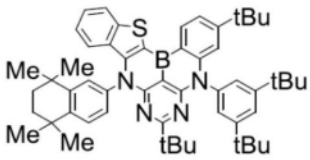
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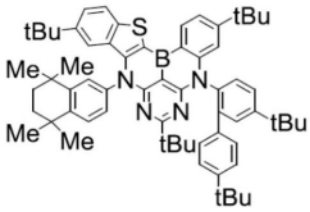
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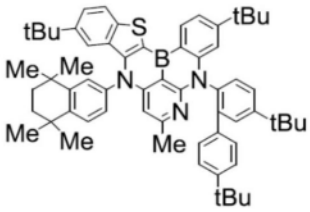
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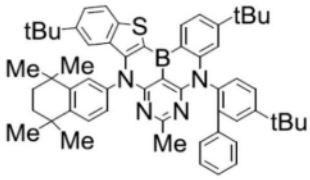
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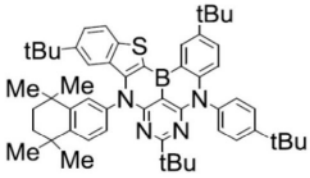
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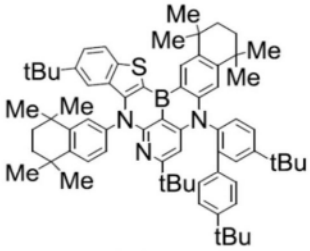
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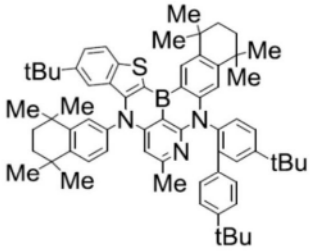
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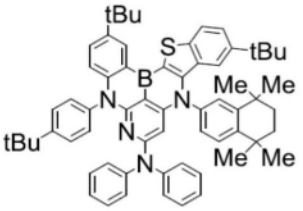
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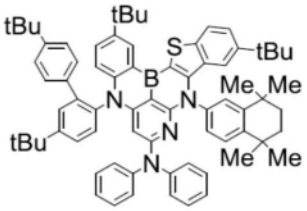
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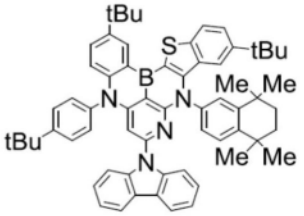
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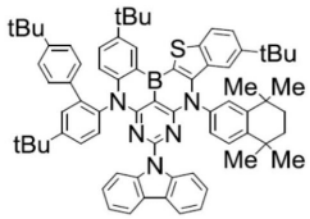
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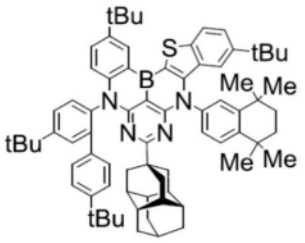
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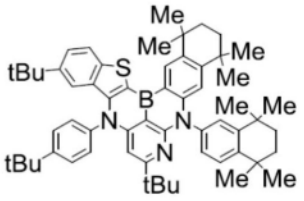
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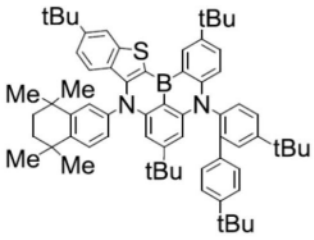


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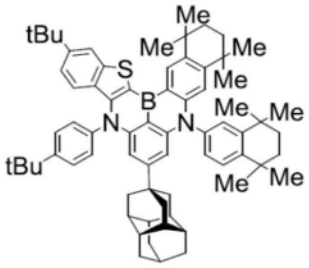


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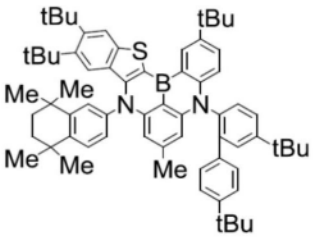
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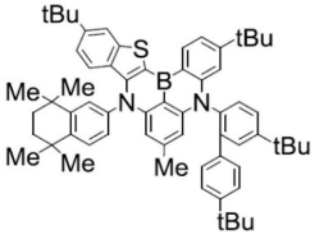
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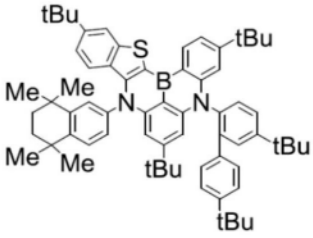
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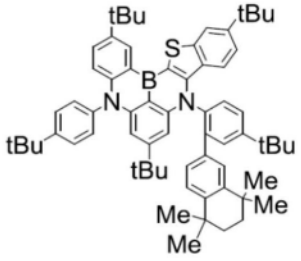
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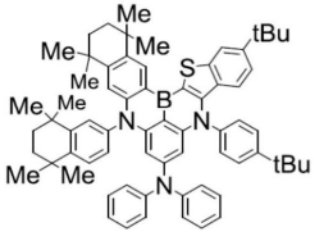


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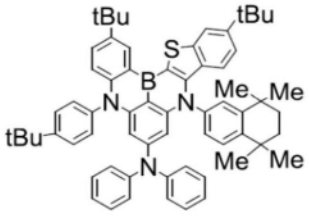


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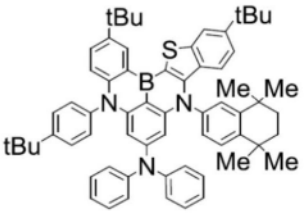
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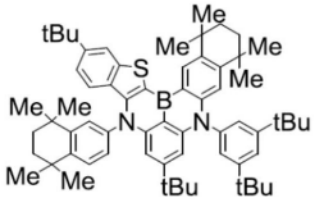
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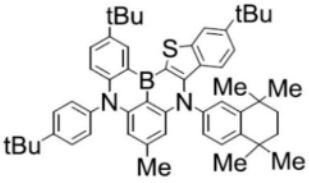
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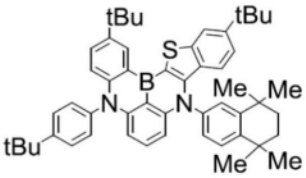
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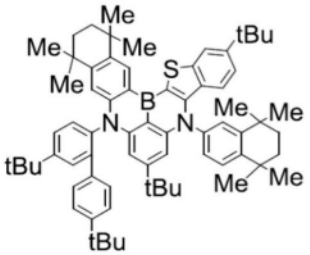
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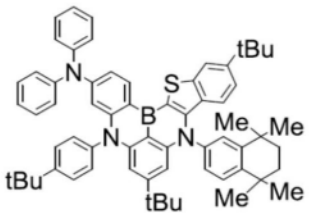
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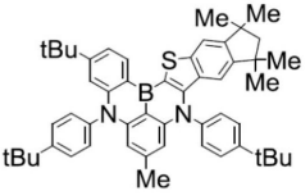
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(1-4013)



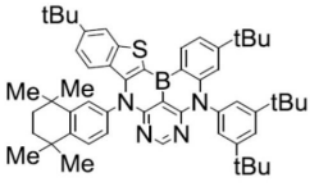
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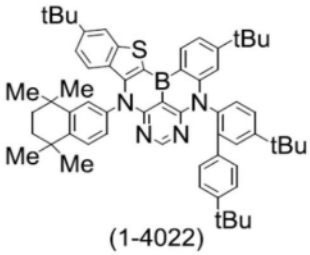


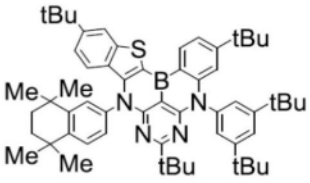
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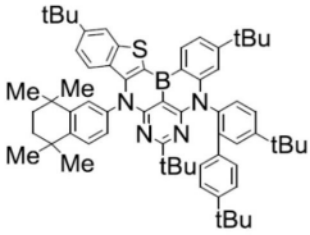
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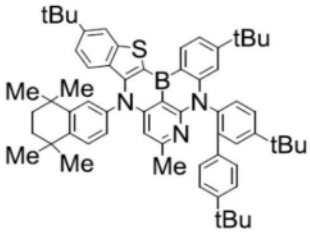
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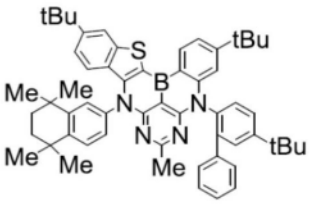

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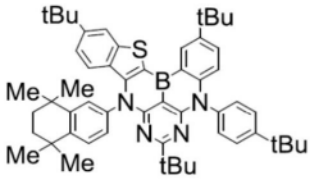

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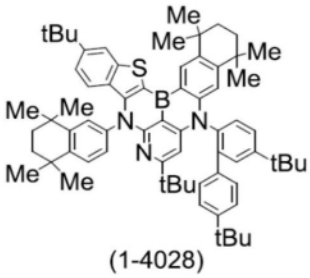

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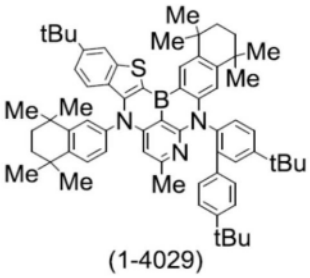

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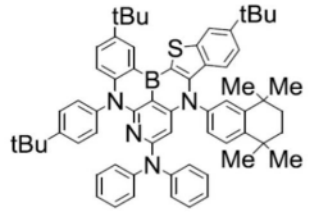

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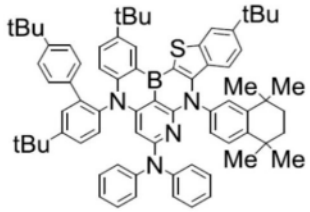

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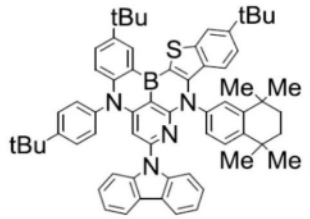

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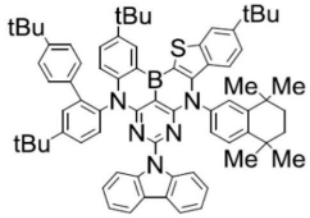

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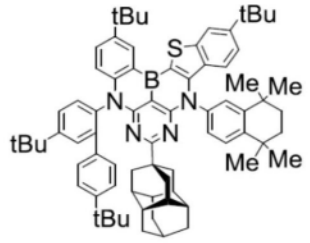

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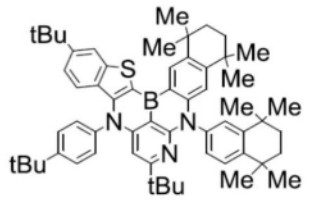

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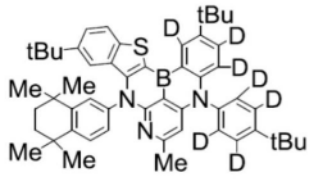

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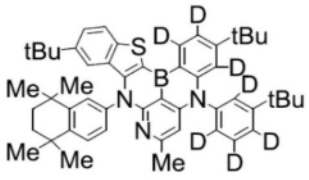

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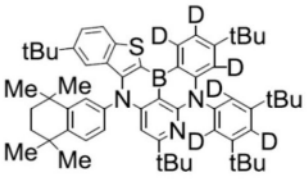
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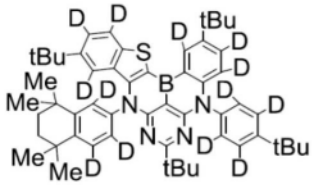
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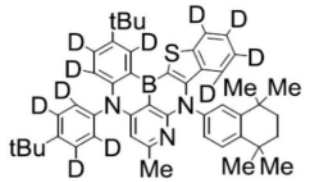
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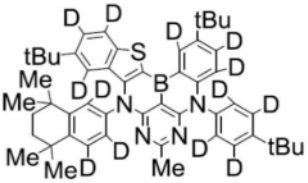
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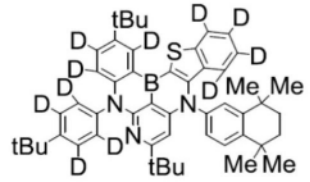
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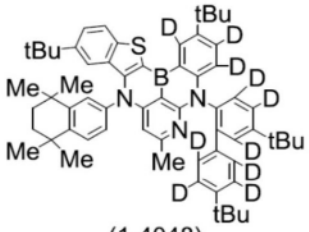
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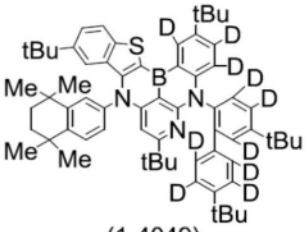
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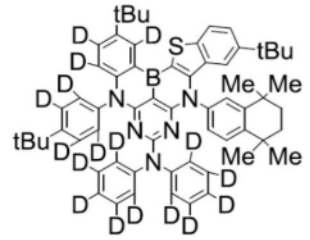
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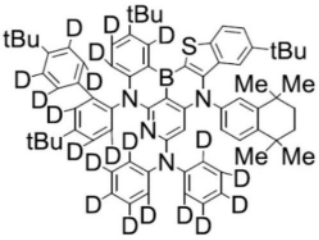
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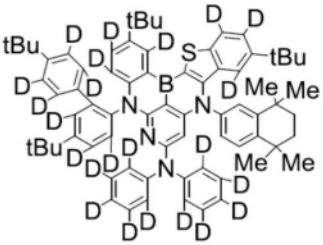
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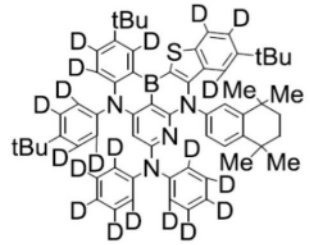
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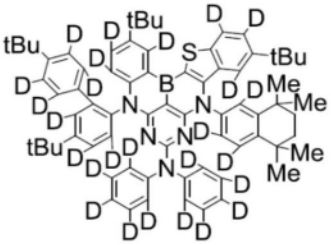
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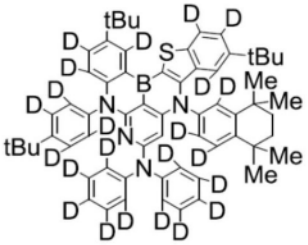
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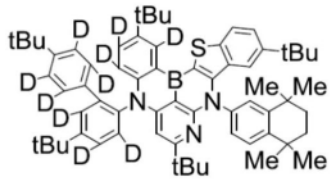


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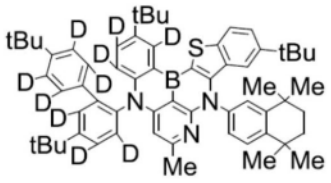


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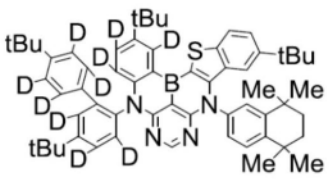
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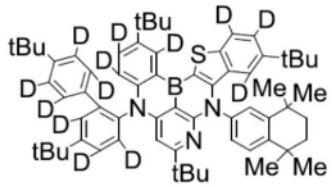
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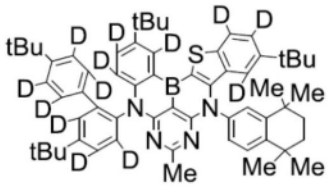
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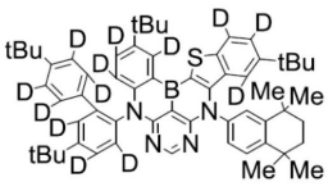
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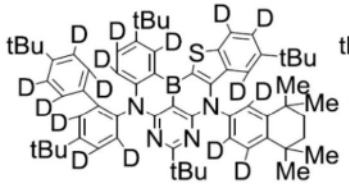


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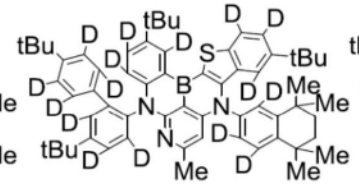


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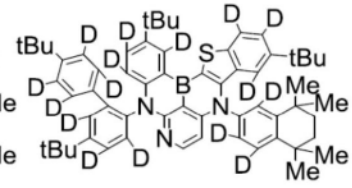
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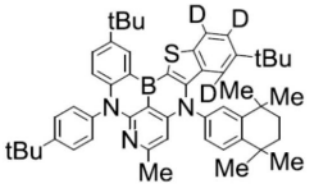
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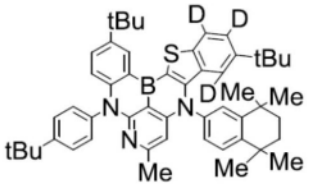
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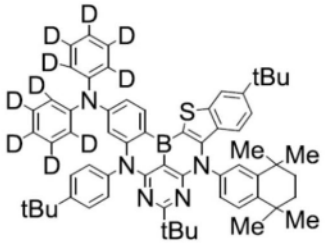
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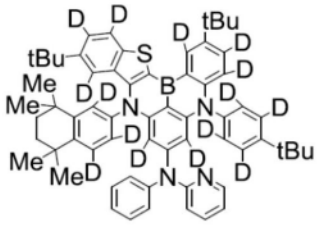
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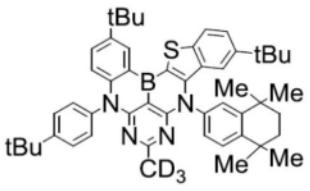
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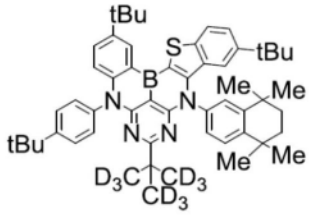
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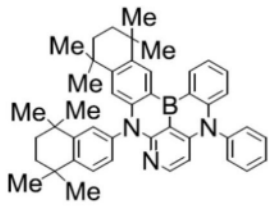
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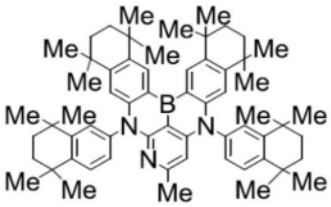


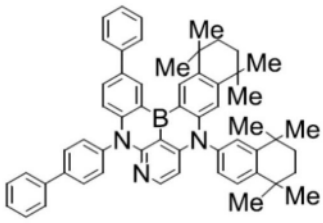
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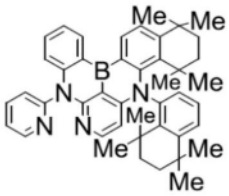
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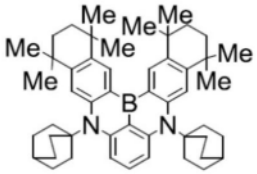
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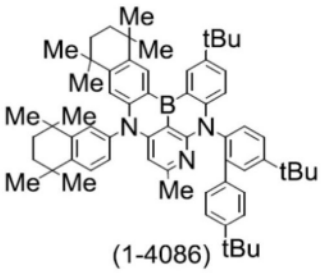

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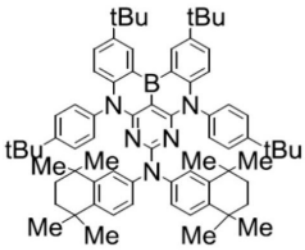

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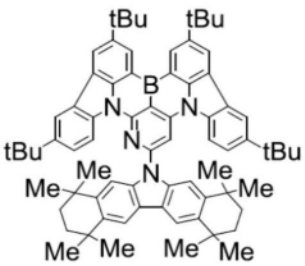

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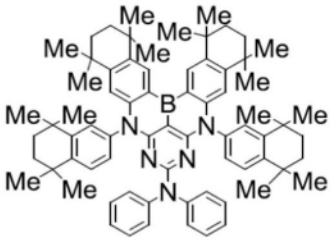

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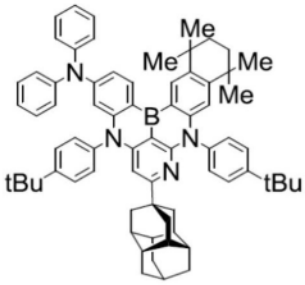

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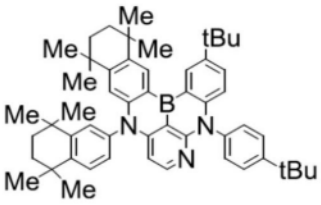

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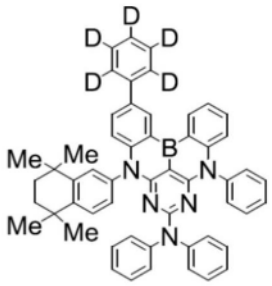

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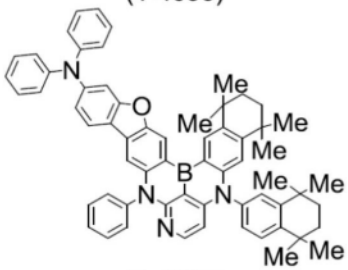

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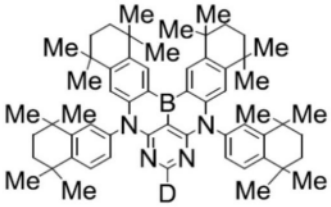

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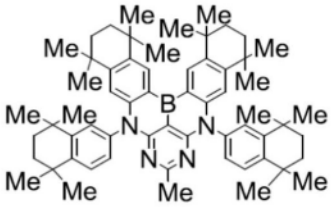

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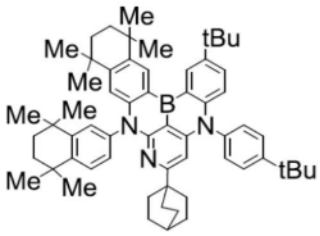

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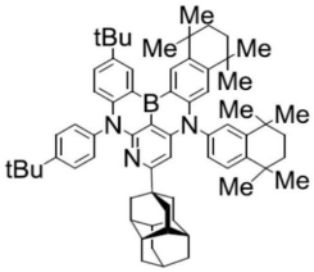

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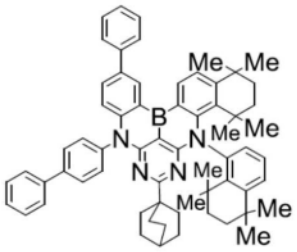
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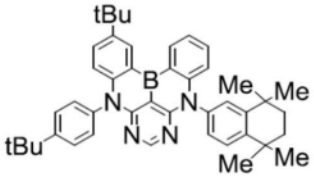
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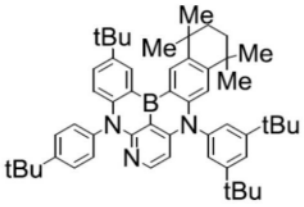
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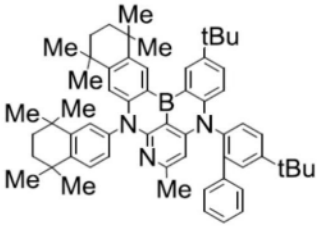
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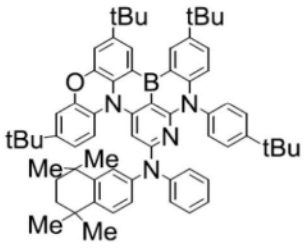


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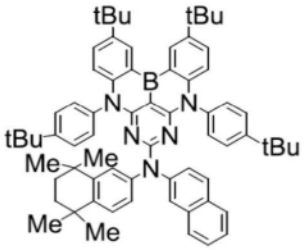


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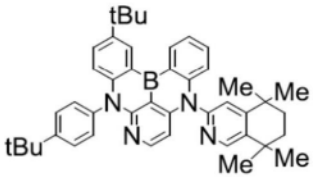
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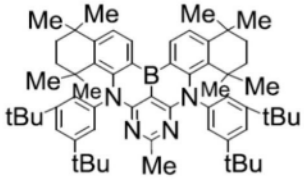
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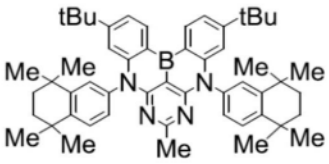
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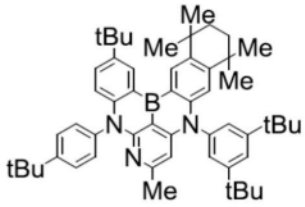
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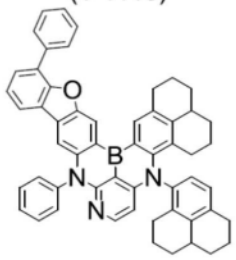
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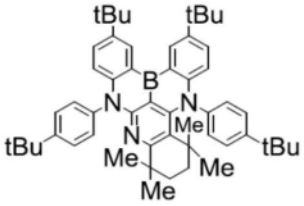
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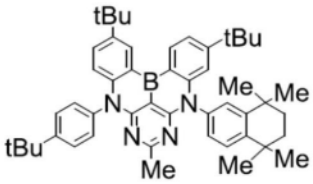
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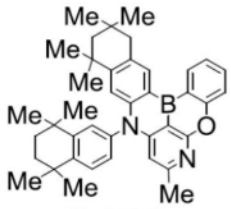
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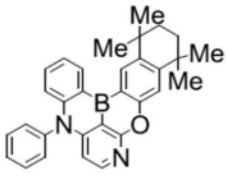


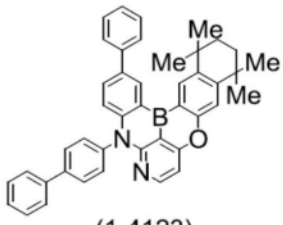
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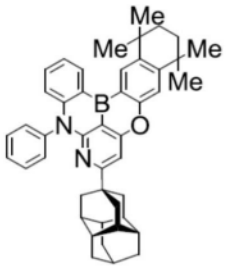
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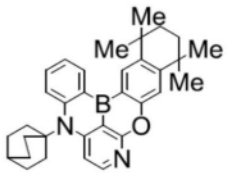
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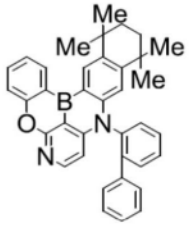

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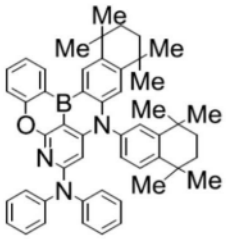

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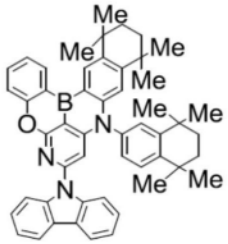

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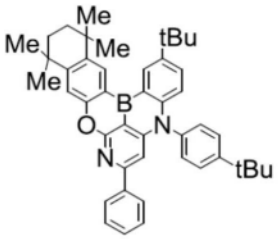

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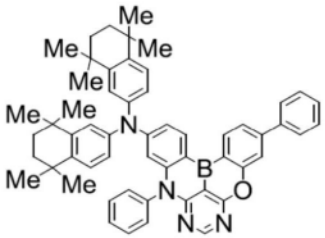

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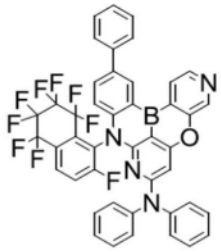

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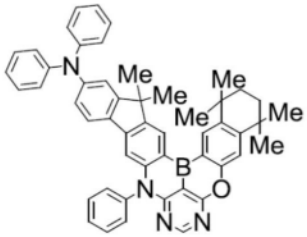

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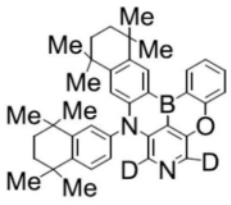

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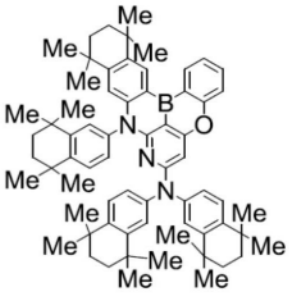

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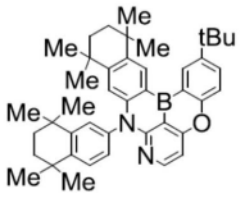

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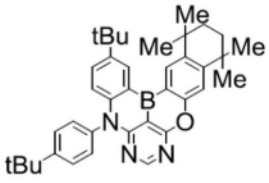

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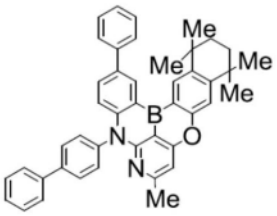

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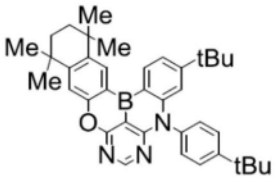

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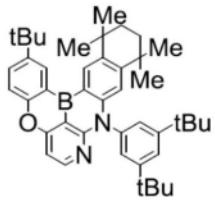
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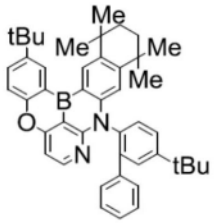

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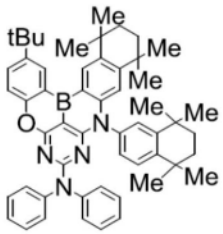

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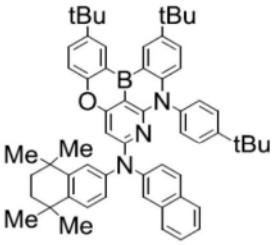

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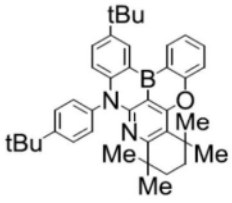

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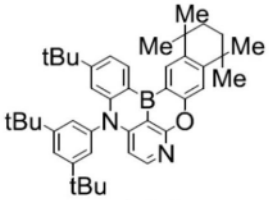

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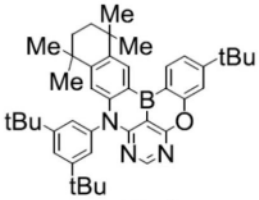
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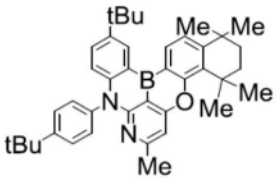

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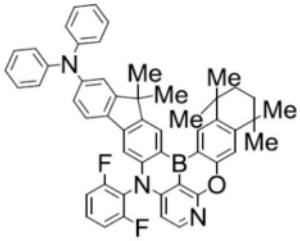

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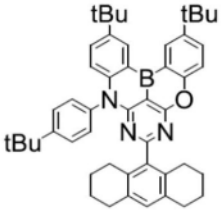

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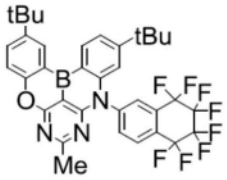

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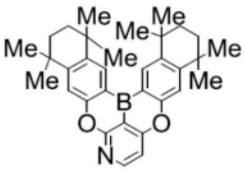

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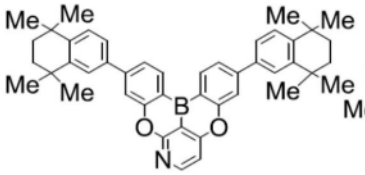

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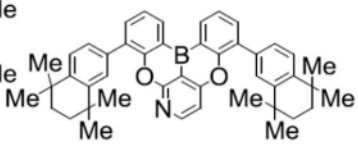

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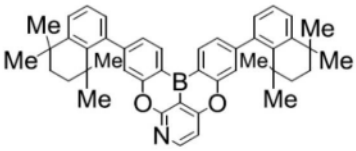
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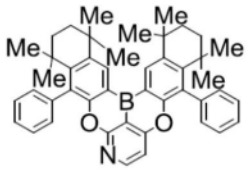
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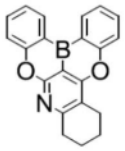

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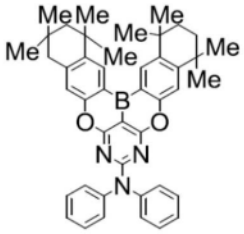

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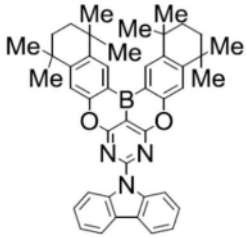

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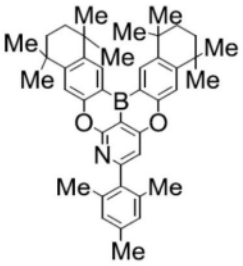

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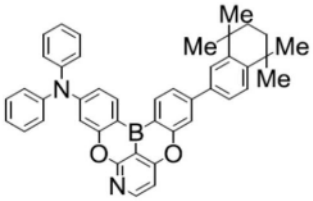

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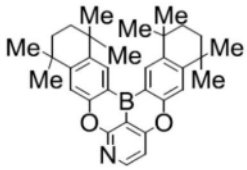

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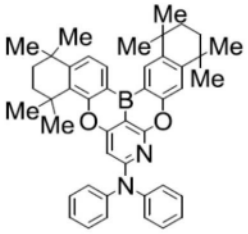

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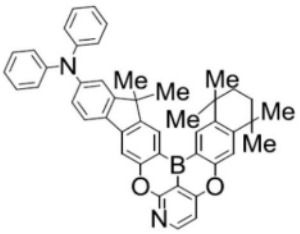

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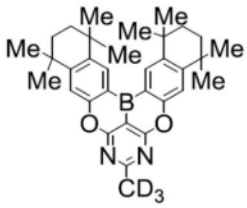

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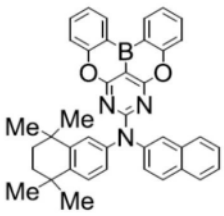

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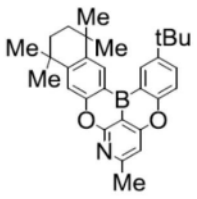

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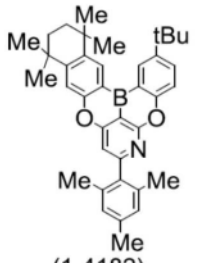

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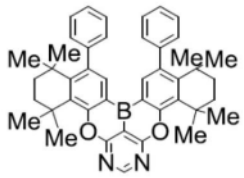
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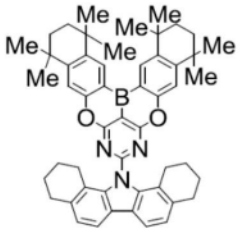
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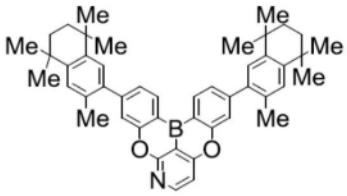
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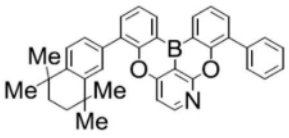
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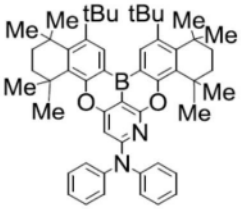
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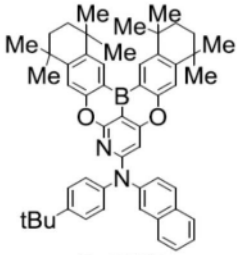
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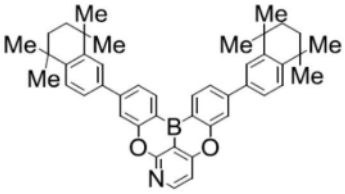
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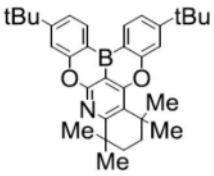
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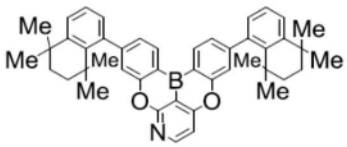
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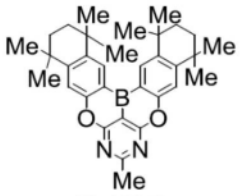
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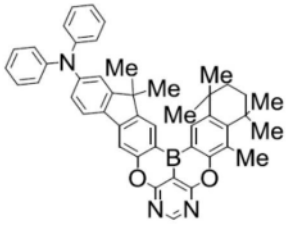
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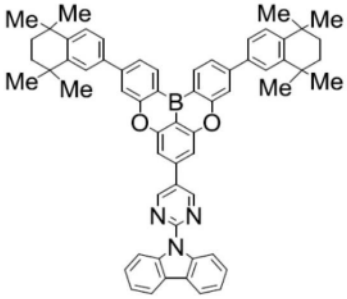
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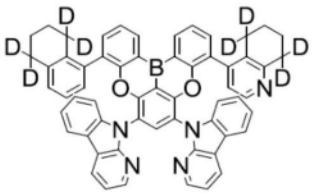
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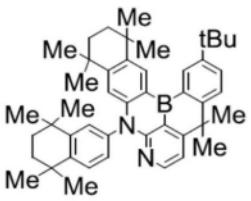


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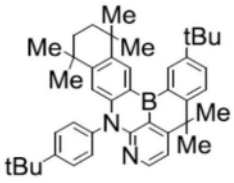


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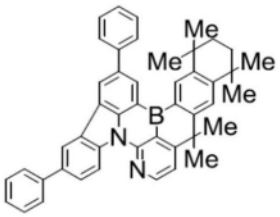
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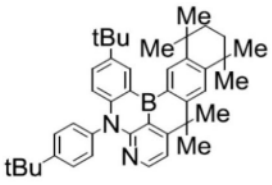
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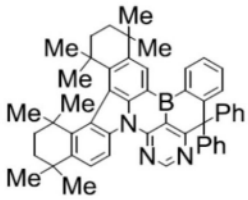
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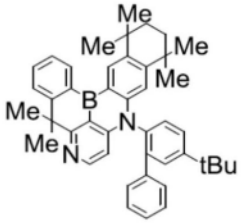
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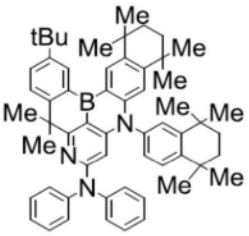


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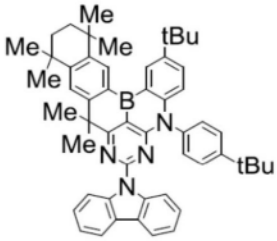


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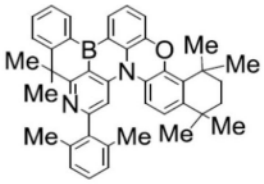
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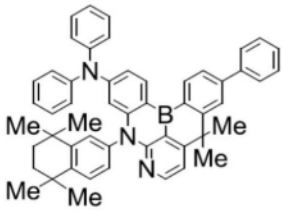
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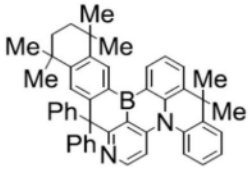
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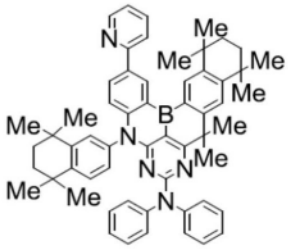
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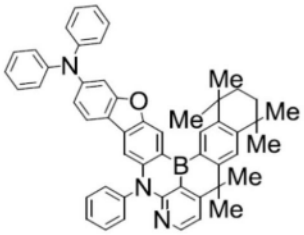
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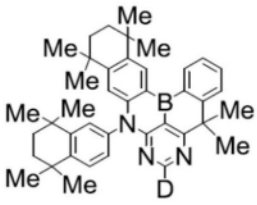
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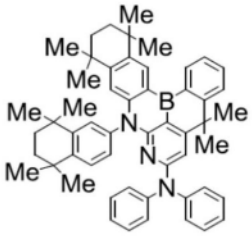
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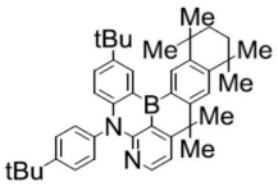
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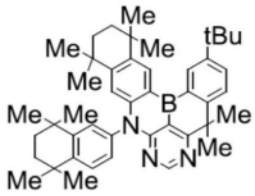


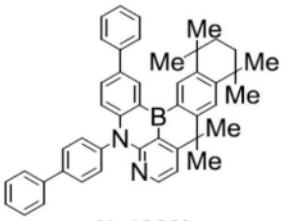
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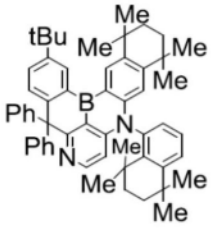
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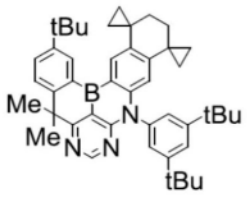
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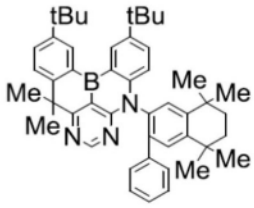

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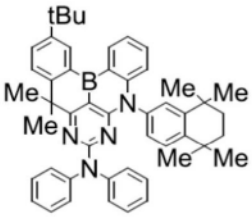

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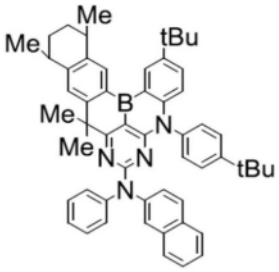

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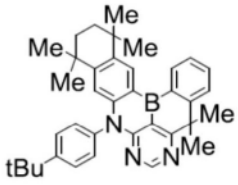

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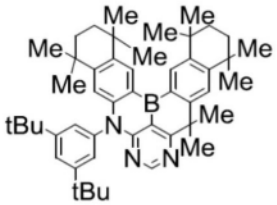

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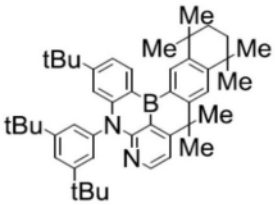

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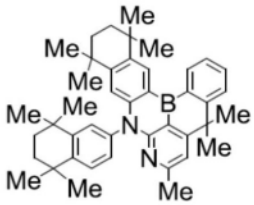

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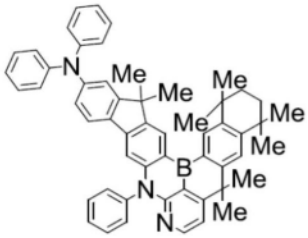

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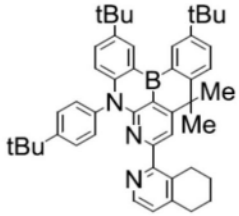

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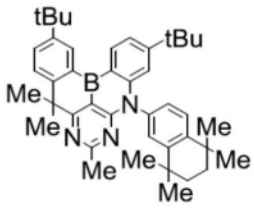

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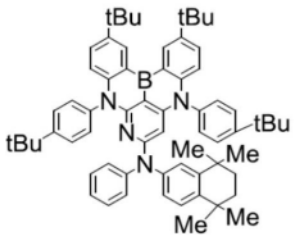

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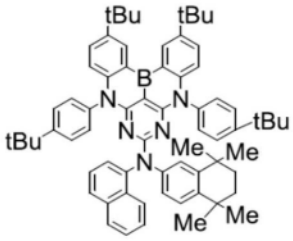

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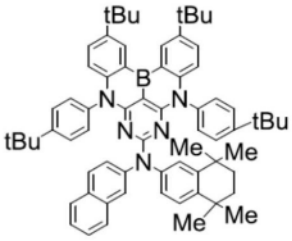
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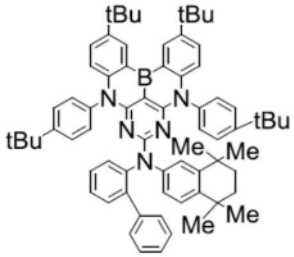
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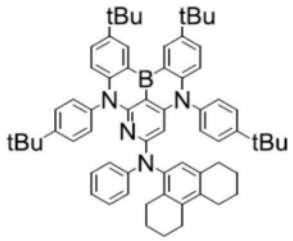
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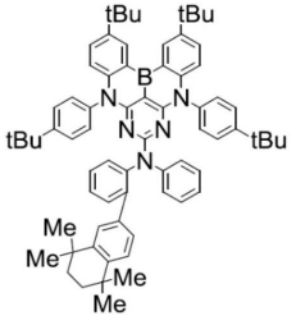
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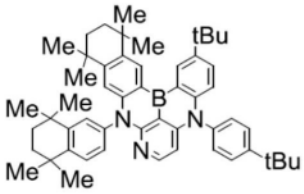


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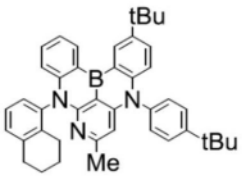


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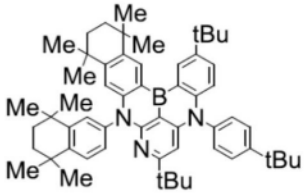
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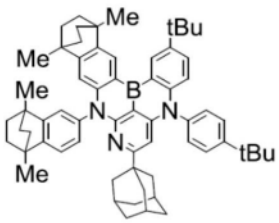
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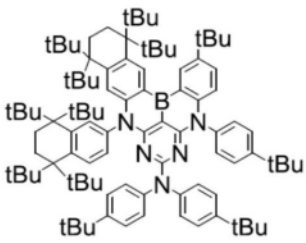
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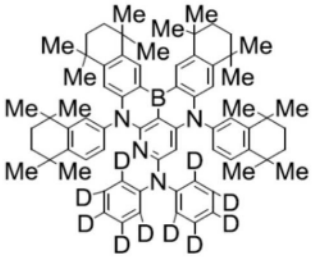
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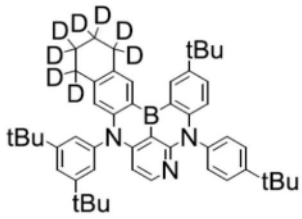


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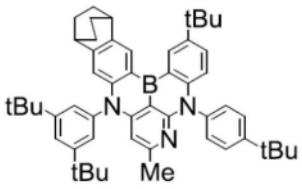


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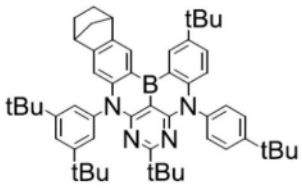
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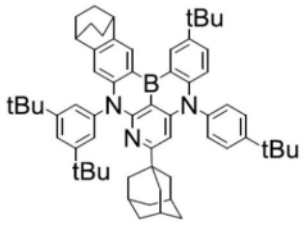
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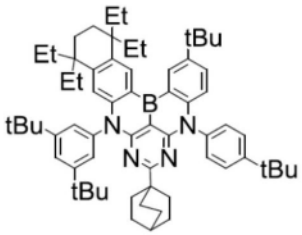
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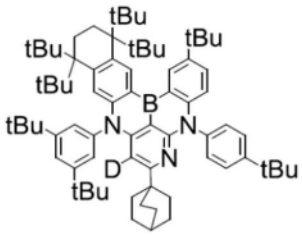
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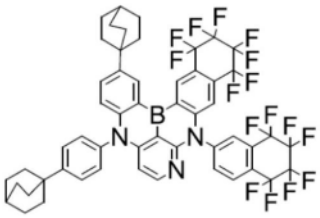


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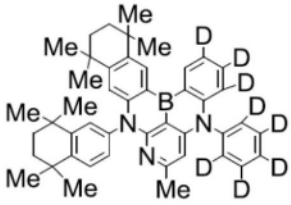


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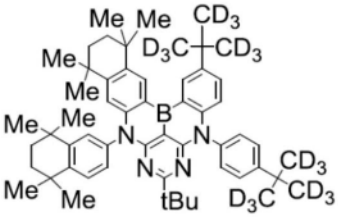
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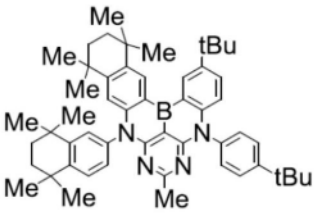
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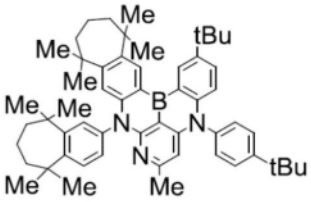
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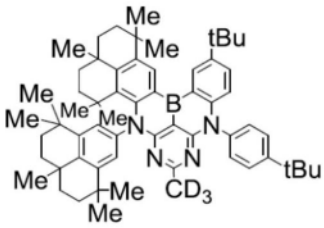
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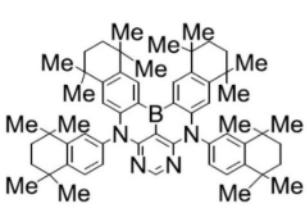


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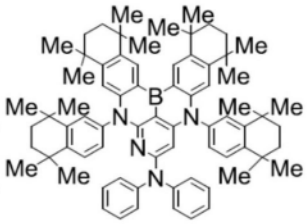


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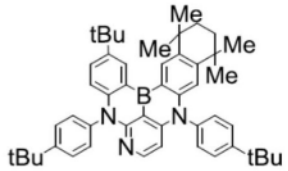
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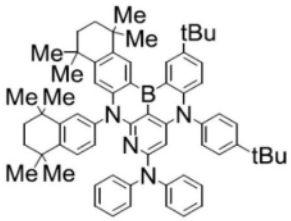
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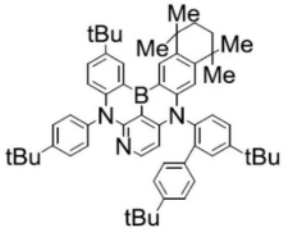
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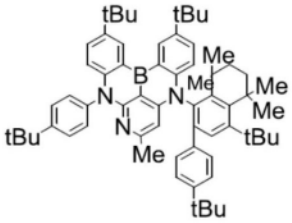
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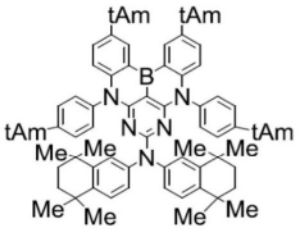


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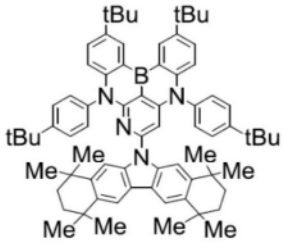


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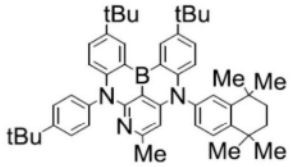
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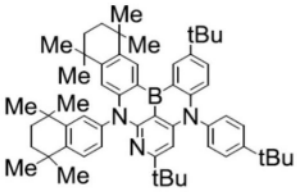
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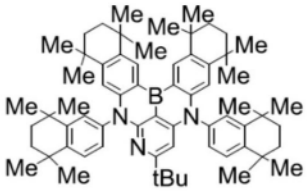
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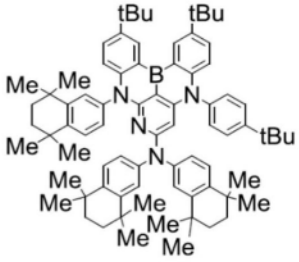
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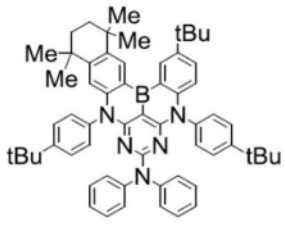
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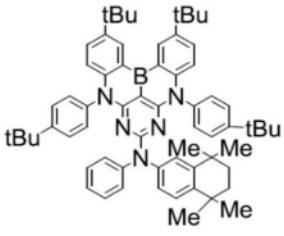
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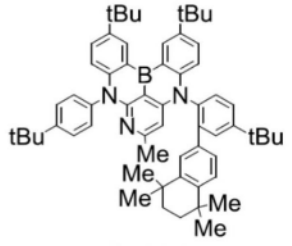
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(1-4293)



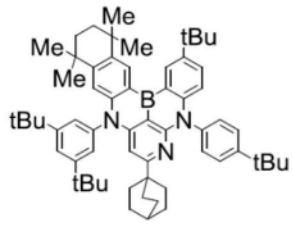
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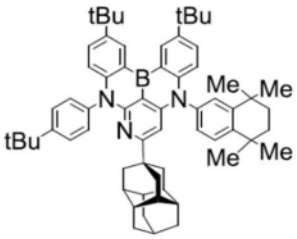


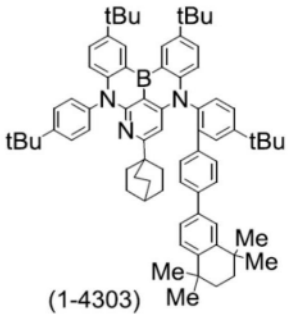
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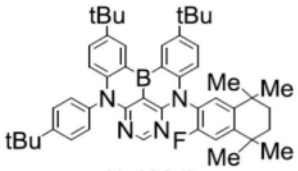
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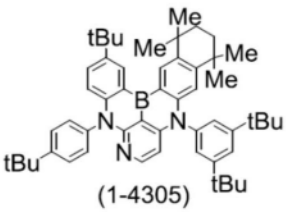
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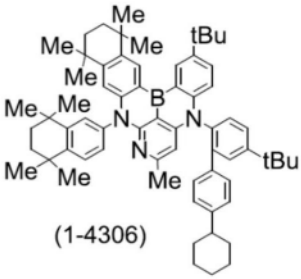

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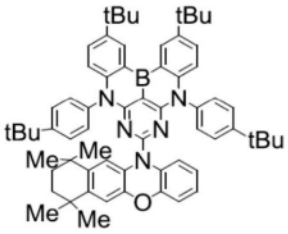

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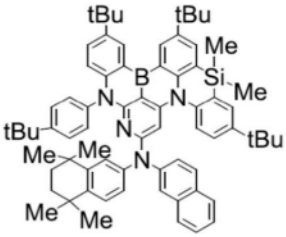

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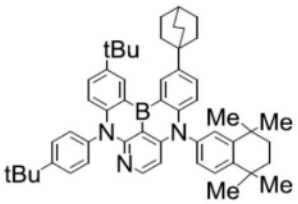

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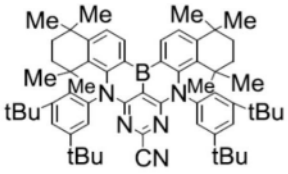

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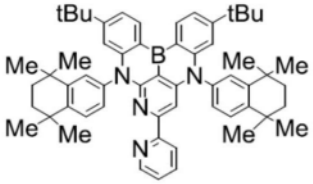

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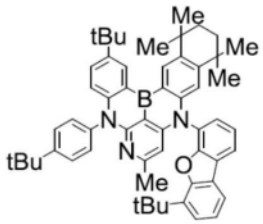

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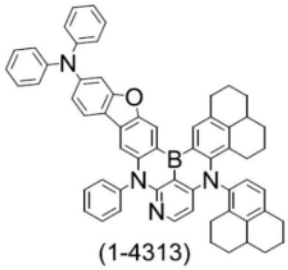

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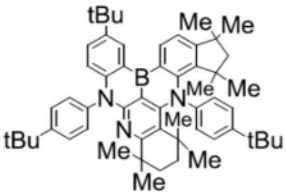

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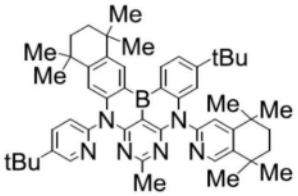

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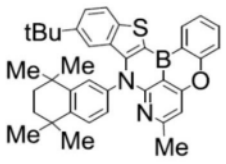

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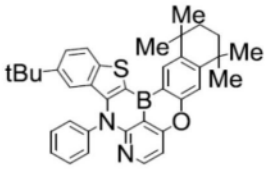

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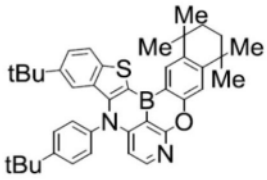
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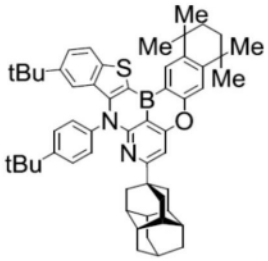
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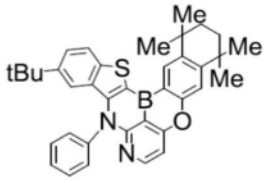
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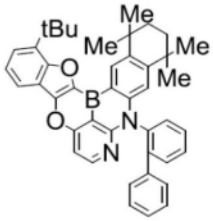
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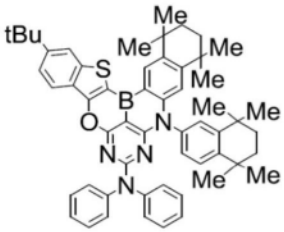
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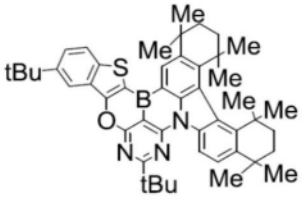
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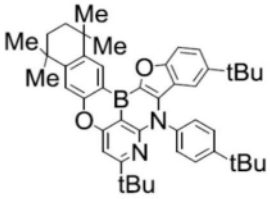
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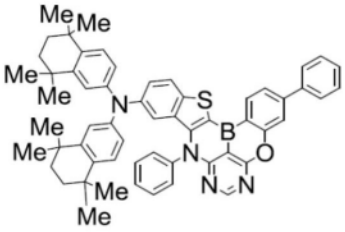
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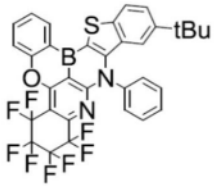
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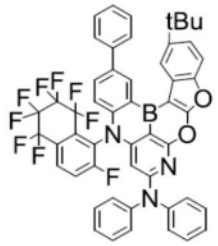
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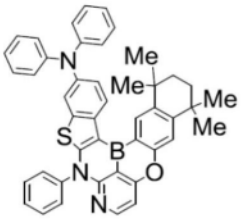
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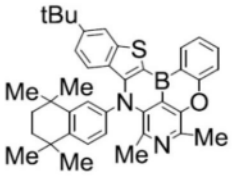
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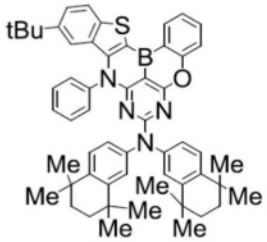
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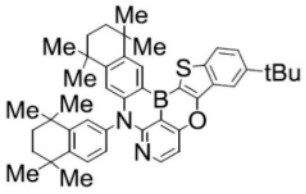


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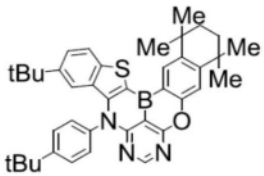


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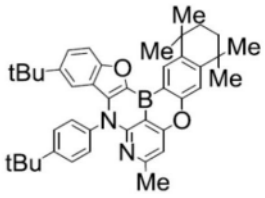
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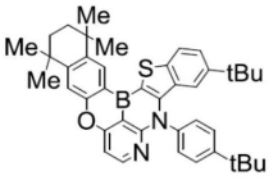
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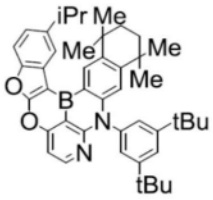
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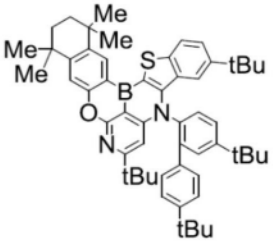
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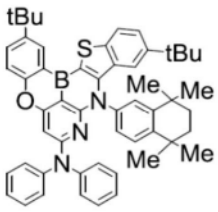


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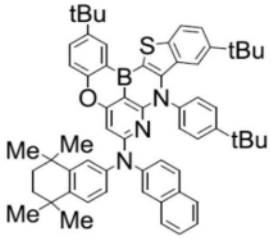


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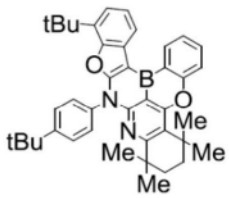
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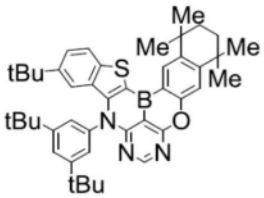
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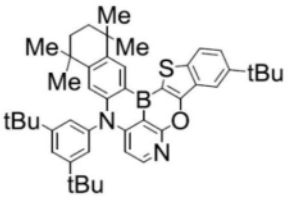
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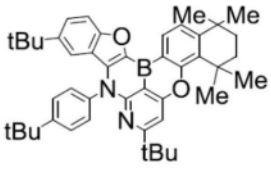
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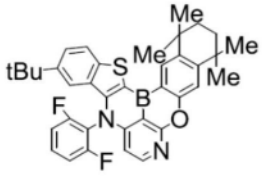
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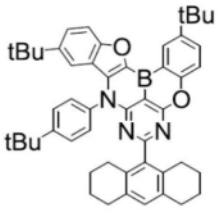
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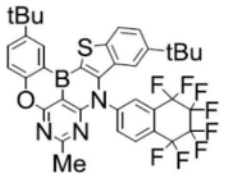
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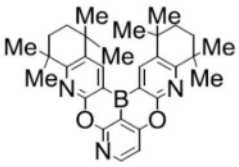


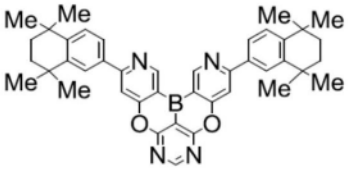
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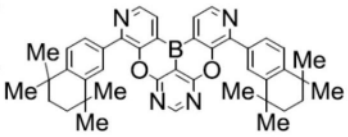


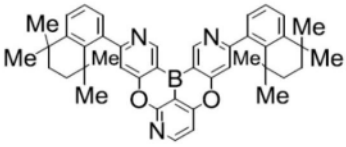
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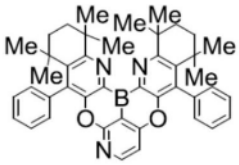
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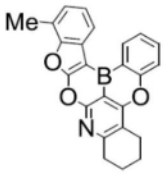

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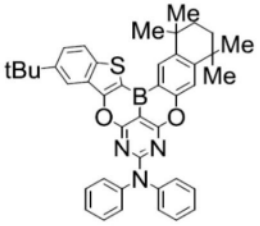

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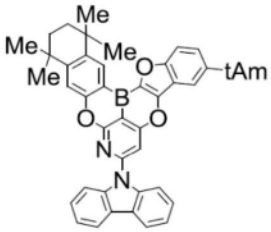

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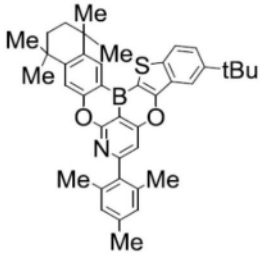

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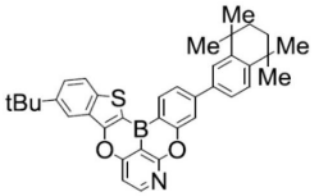

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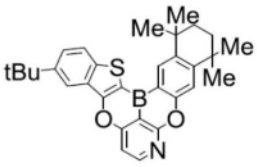
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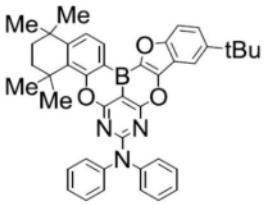

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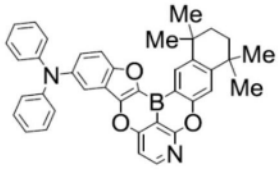

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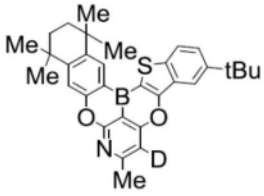

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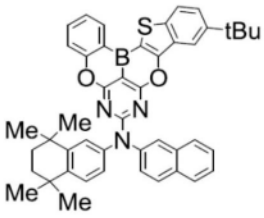

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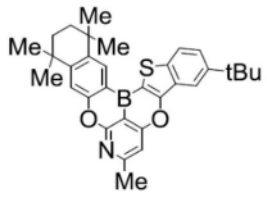

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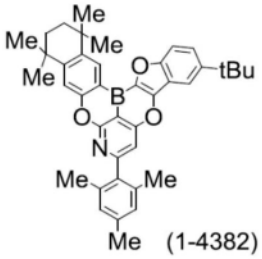

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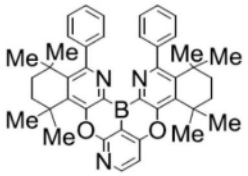
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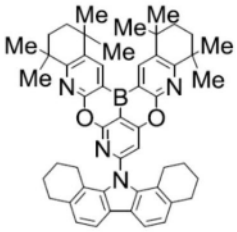
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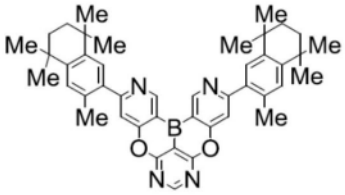
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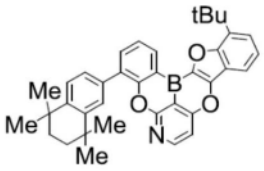
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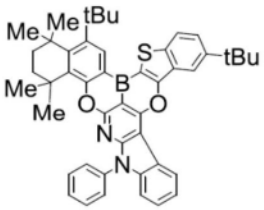
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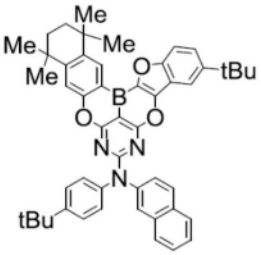
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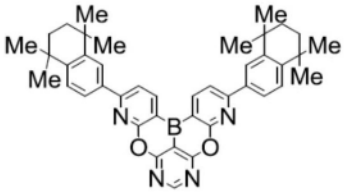
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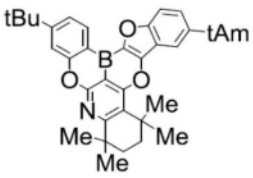
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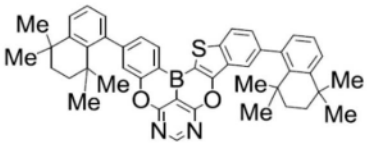
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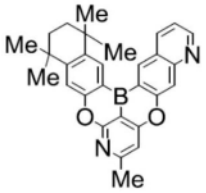
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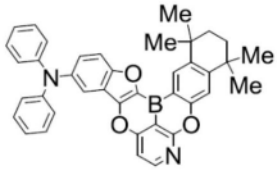
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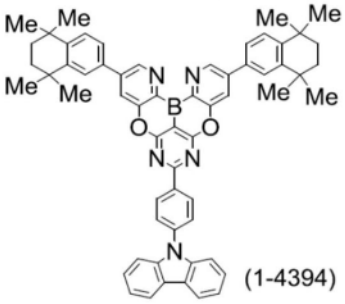
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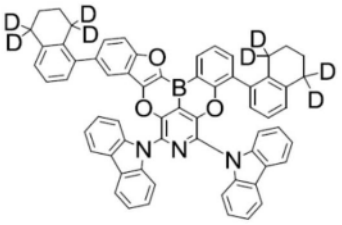
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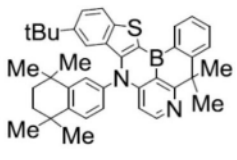


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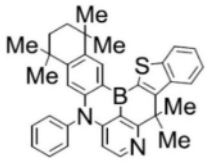


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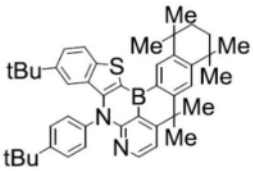
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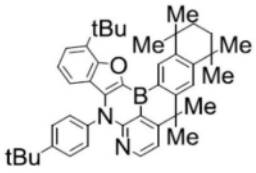
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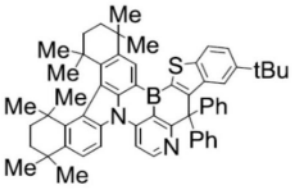
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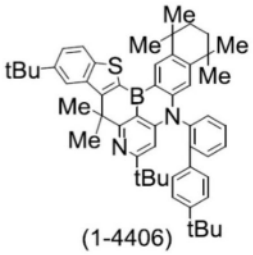
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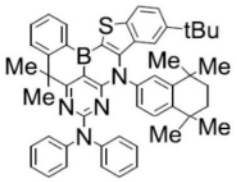


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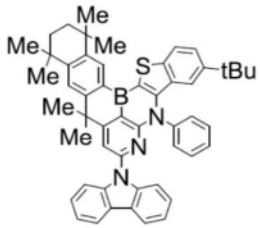


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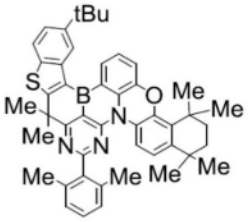
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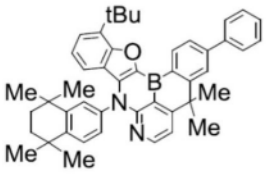
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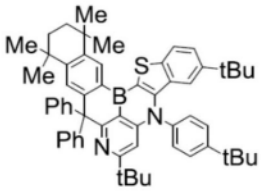
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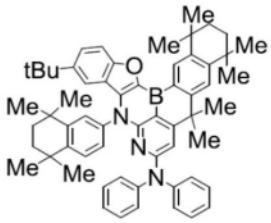
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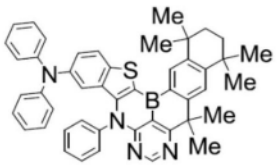
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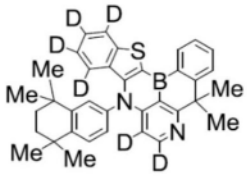
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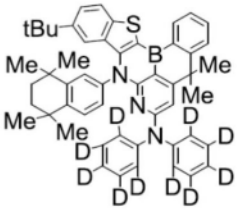
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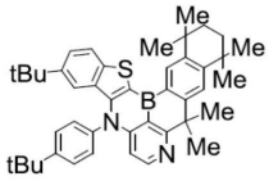
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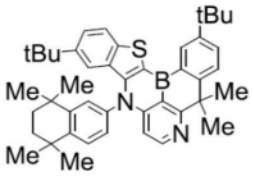


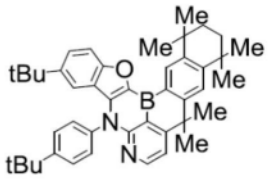
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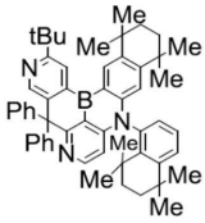
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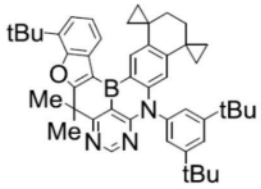
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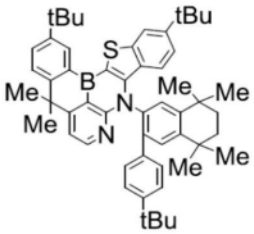

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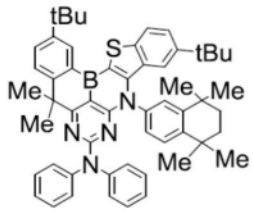

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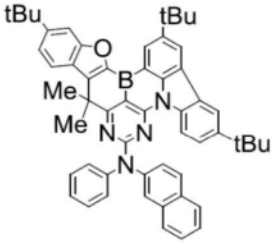

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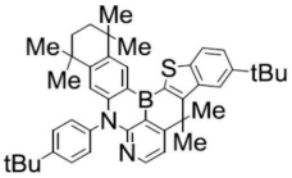

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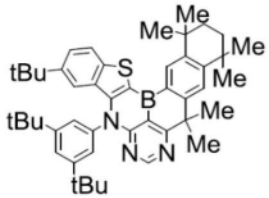

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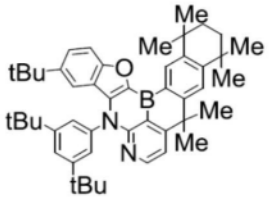

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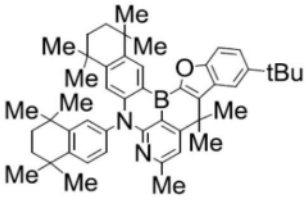

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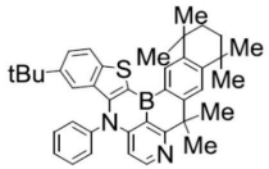

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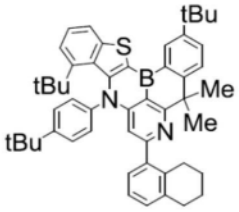

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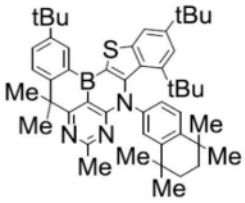

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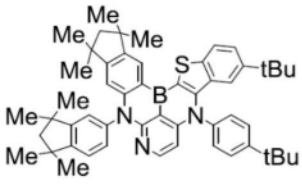

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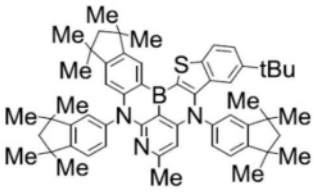

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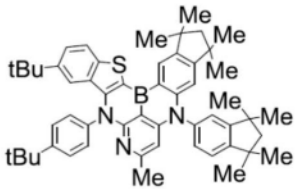
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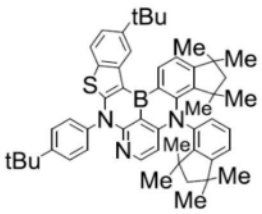
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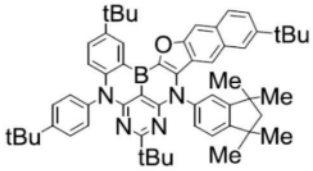
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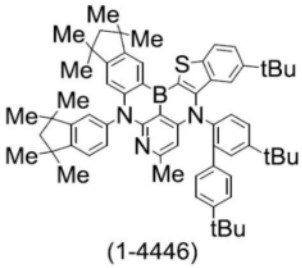
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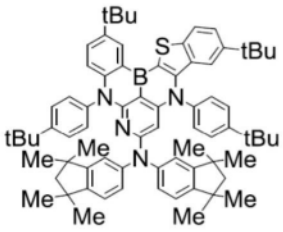


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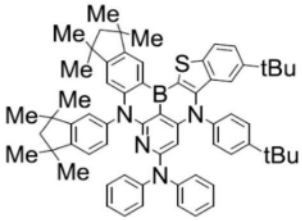
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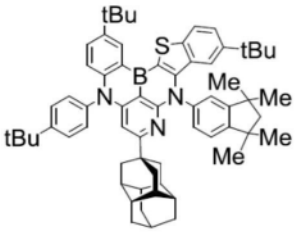
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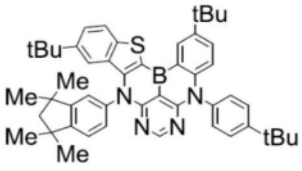
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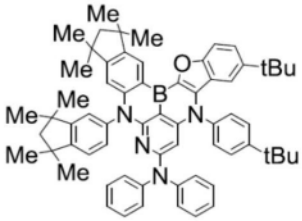
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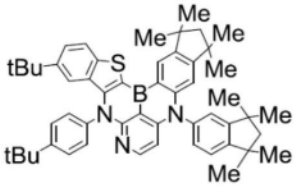
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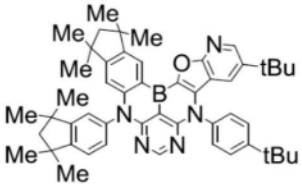
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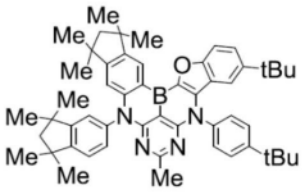
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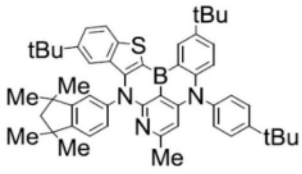


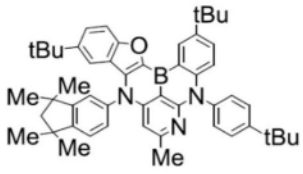
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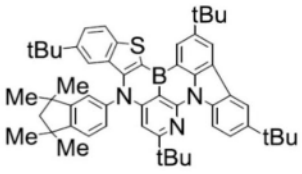


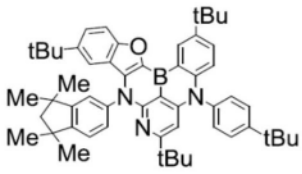
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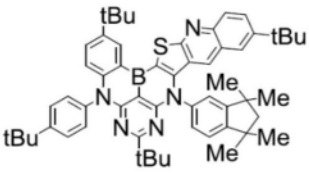
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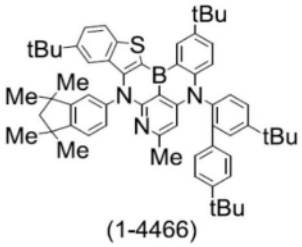

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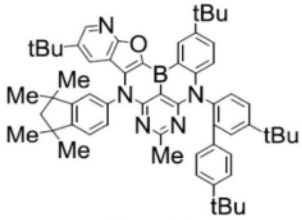

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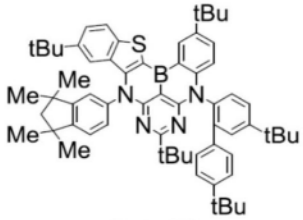

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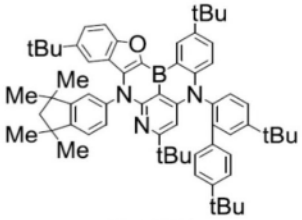

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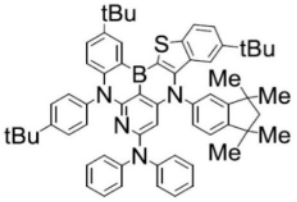

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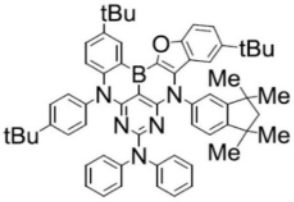
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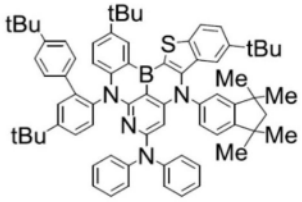

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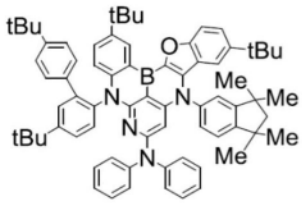

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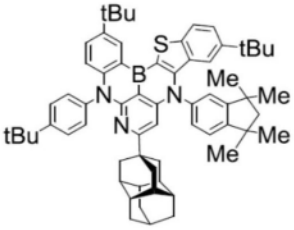

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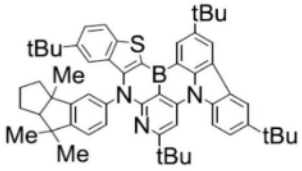

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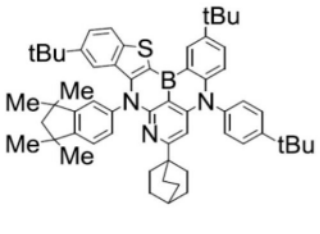

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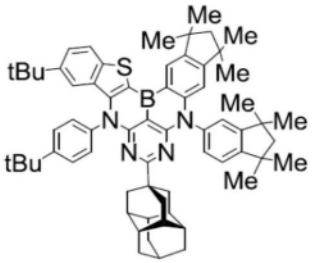

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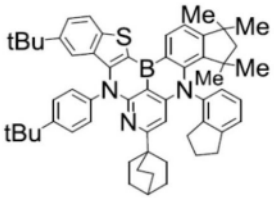
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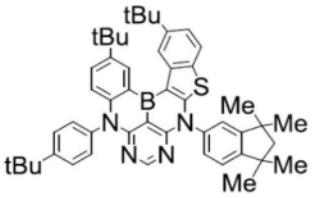
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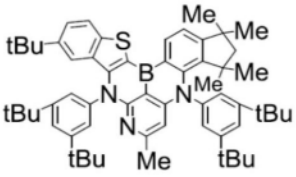
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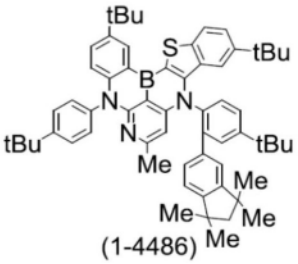
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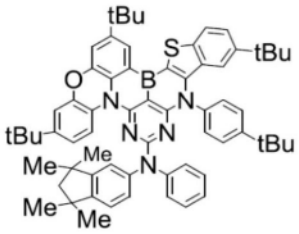


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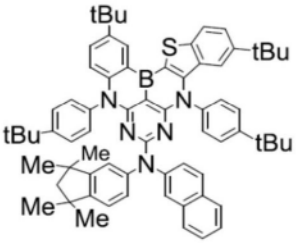


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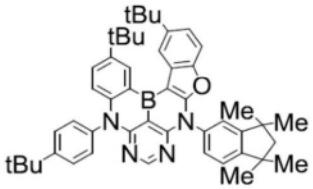
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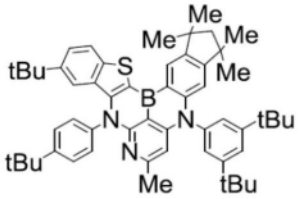
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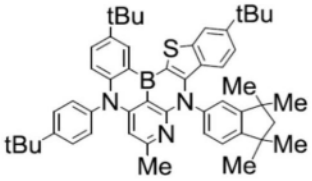
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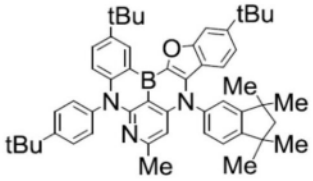
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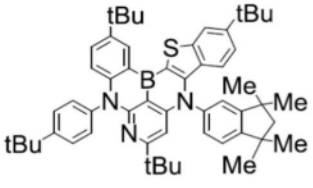
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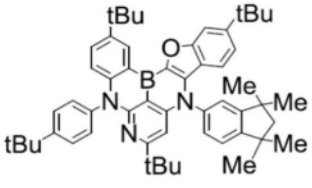
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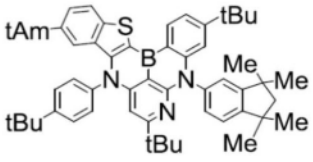
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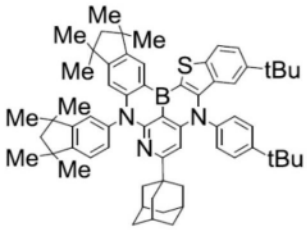


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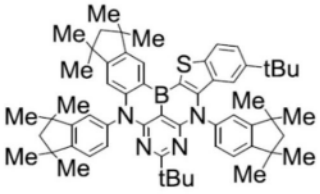


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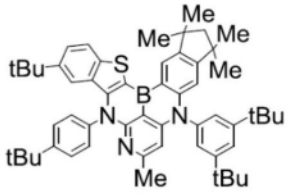
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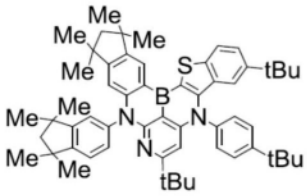
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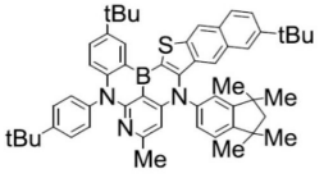
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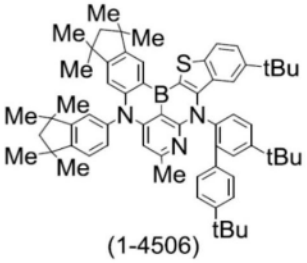
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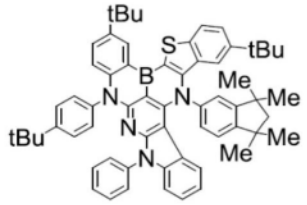


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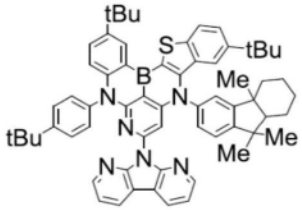


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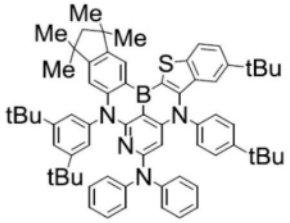
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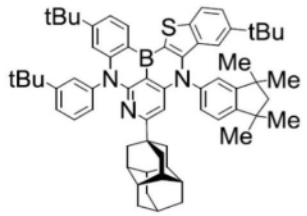
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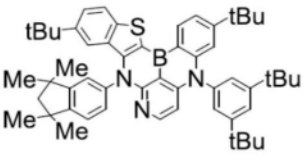
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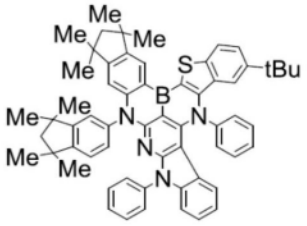
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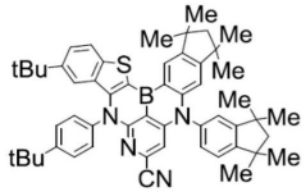
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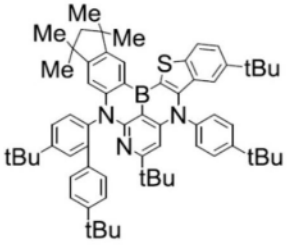
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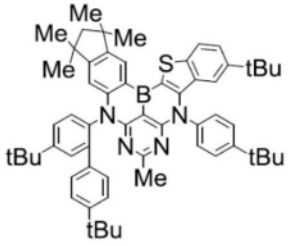
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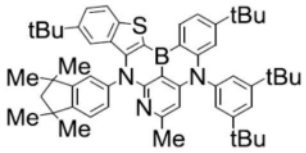
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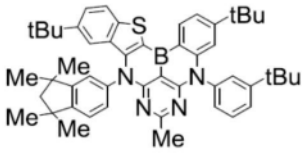


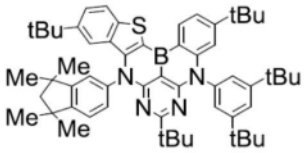
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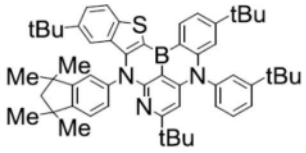
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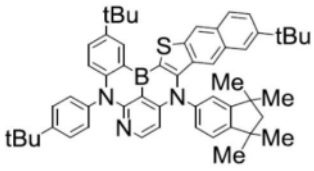
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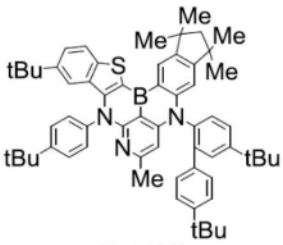

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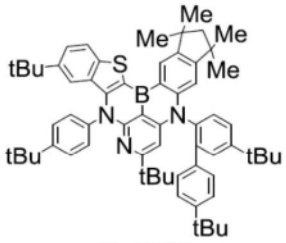

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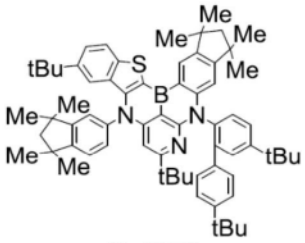

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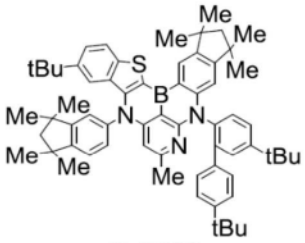

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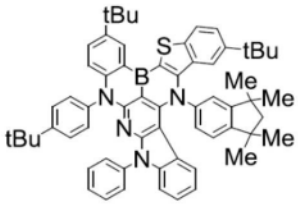

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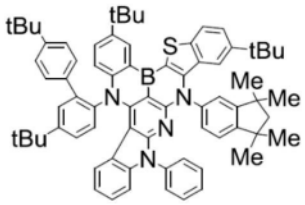

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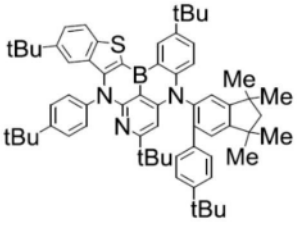

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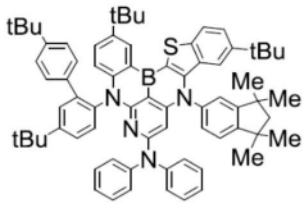

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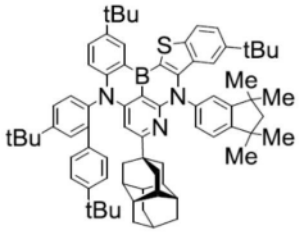

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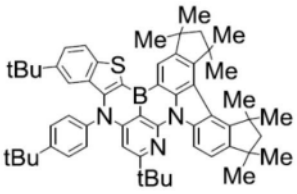

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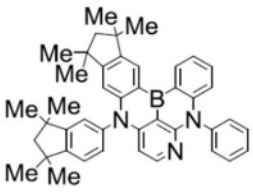

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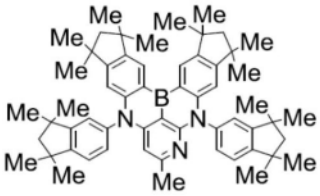

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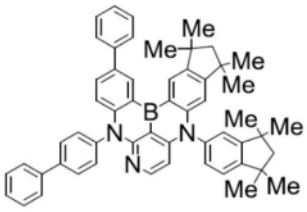
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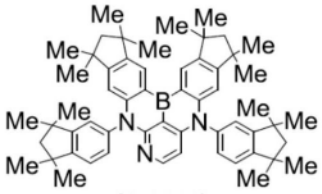
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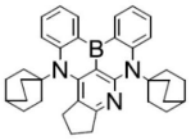
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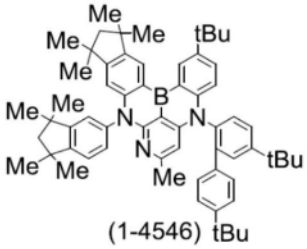
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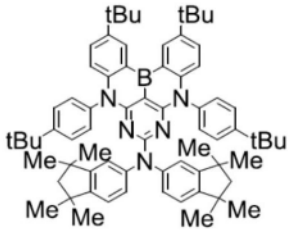
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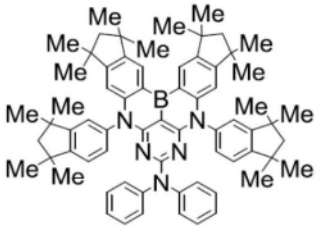
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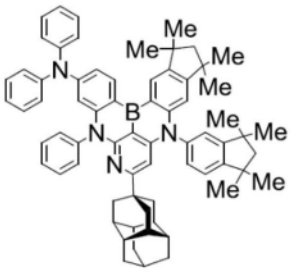
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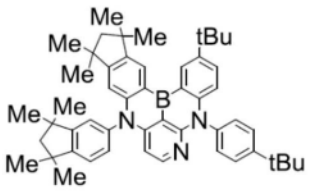
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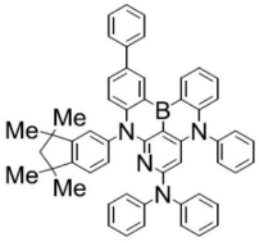
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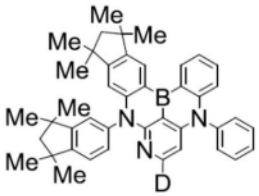
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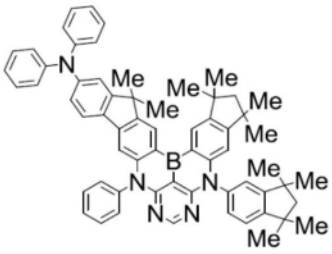
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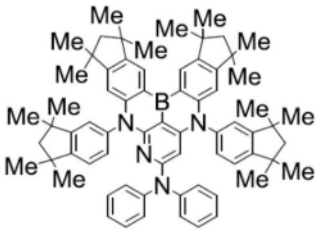
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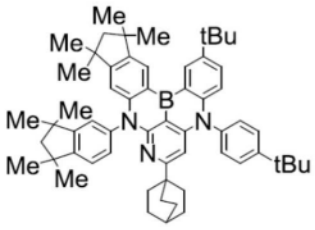


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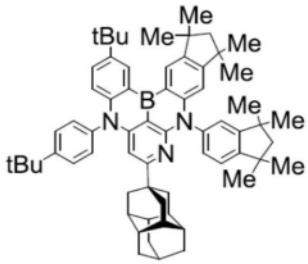


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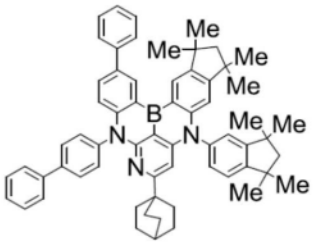
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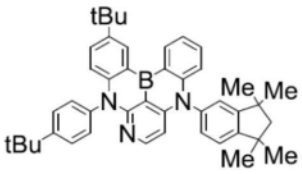
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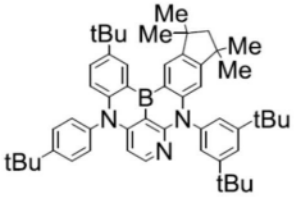
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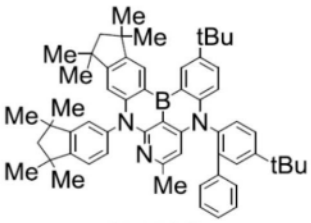
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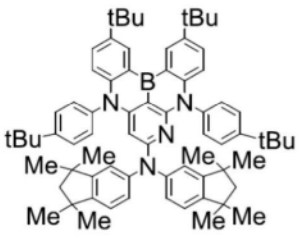


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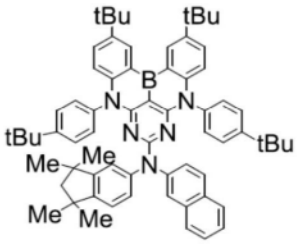


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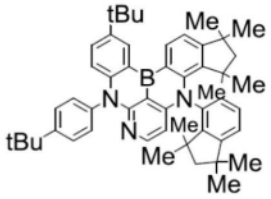
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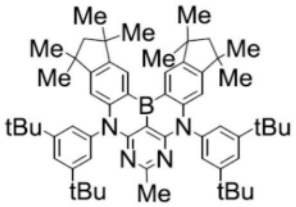
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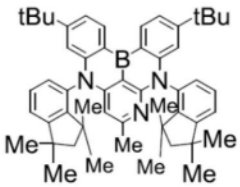
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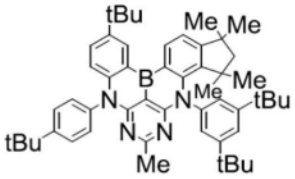
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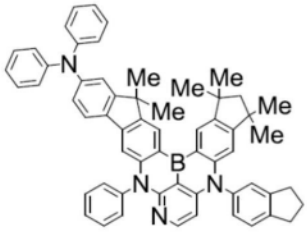
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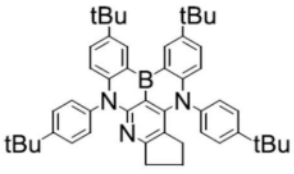
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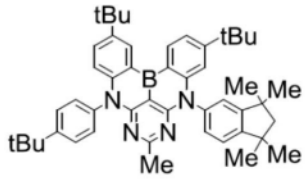
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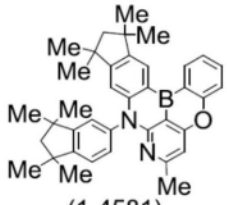
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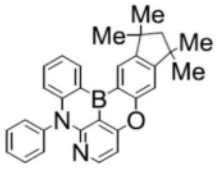


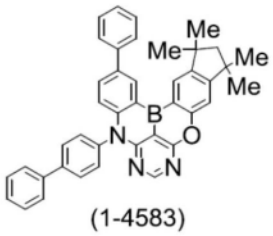
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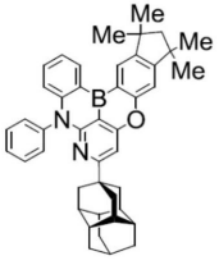
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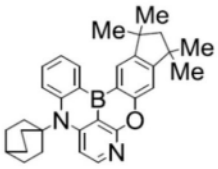
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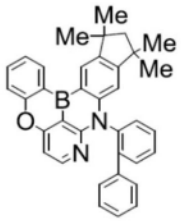

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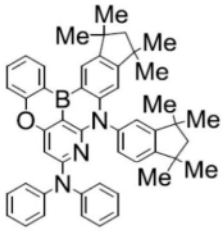

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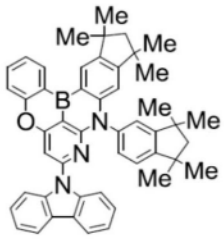

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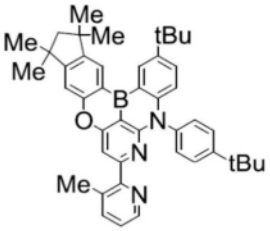

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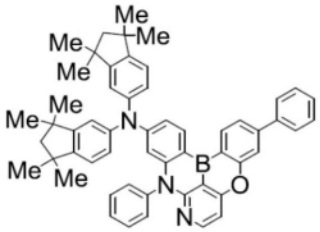

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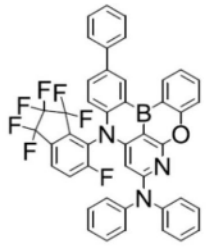

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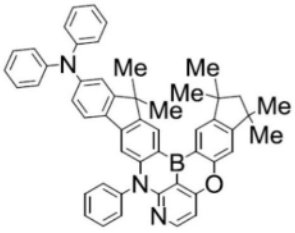

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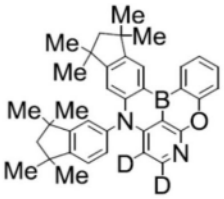

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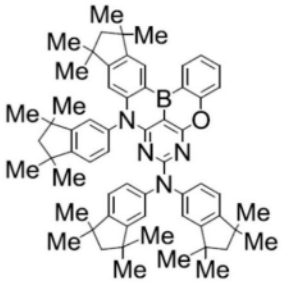

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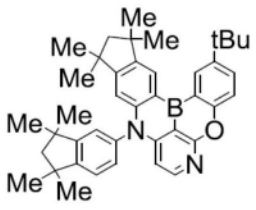

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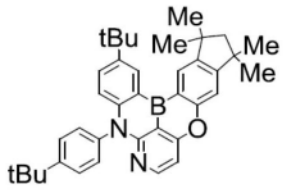

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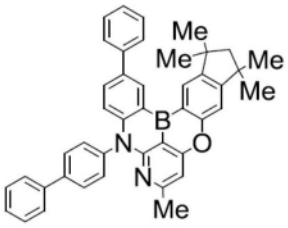
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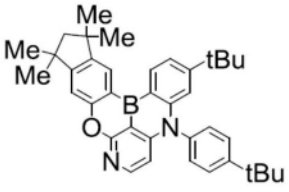
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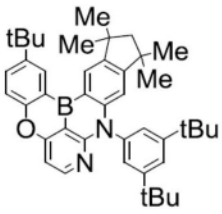
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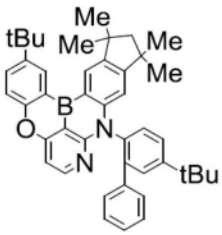
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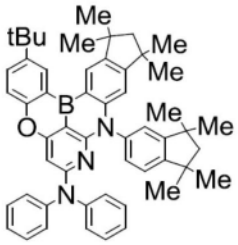


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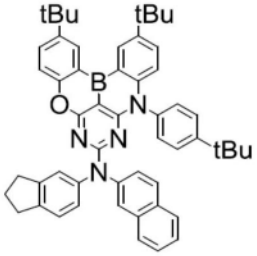


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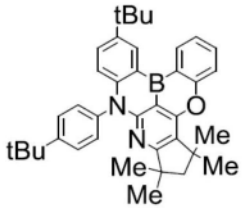
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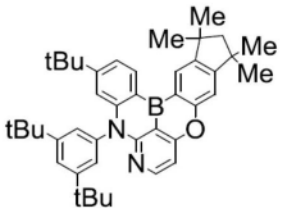
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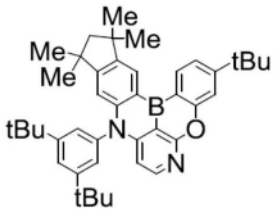
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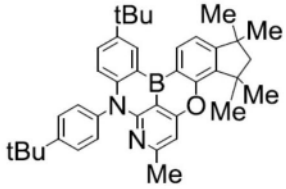
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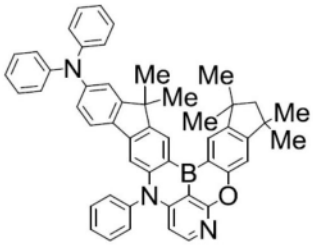
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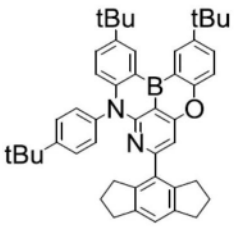
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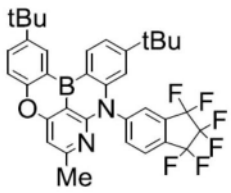
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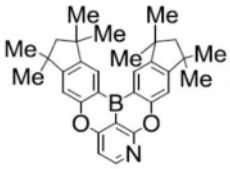
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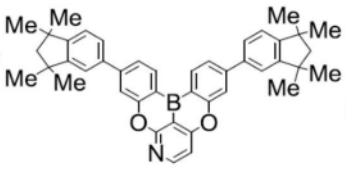
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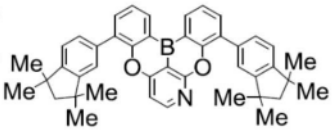
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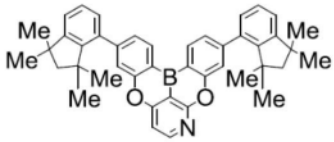
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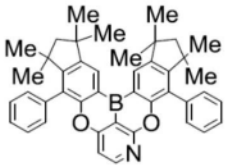
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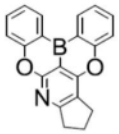
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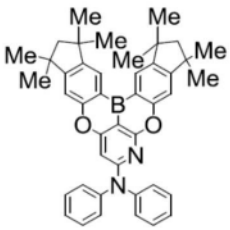
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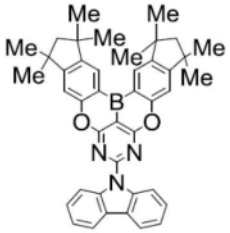
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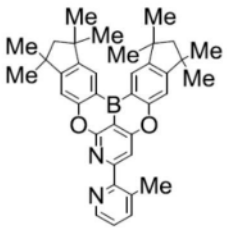
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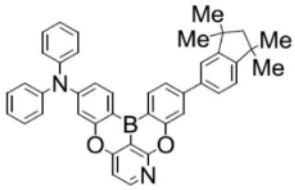
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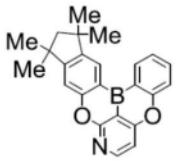
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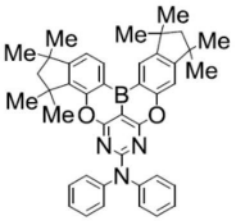
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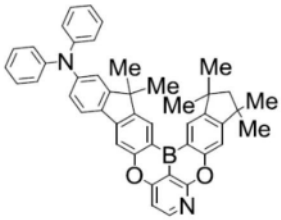
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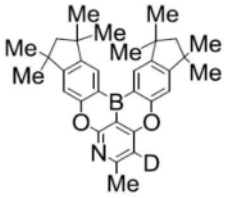
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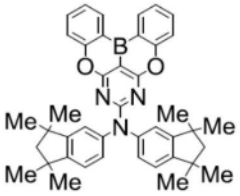
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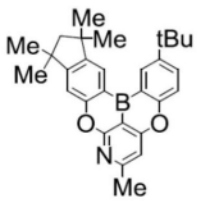
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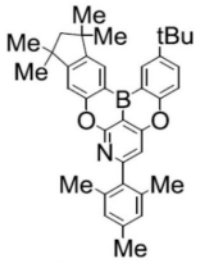
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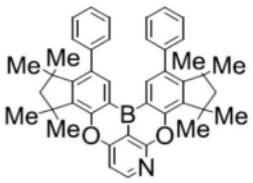
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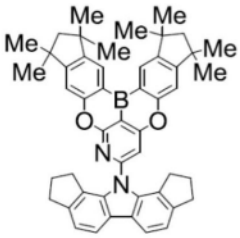
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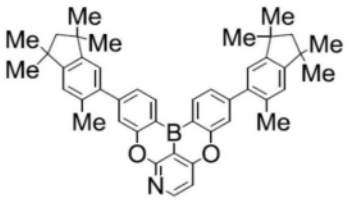
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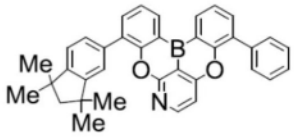
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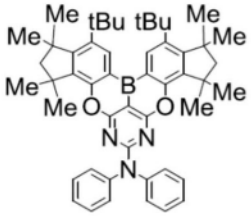
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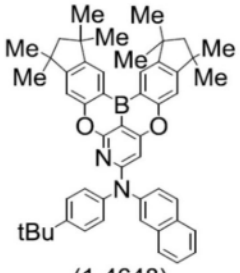
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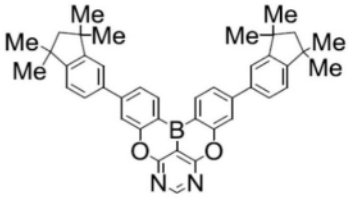
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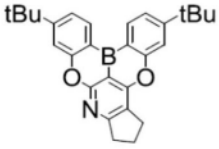
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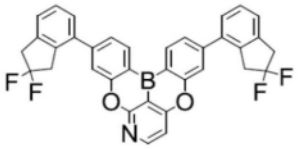
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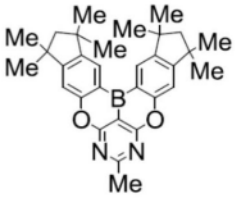
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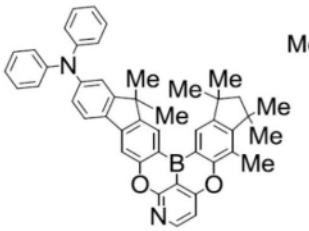
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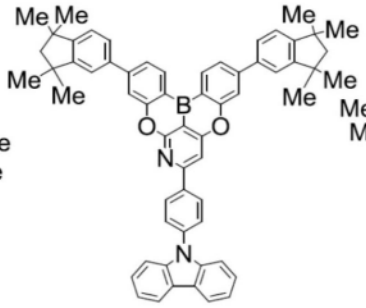
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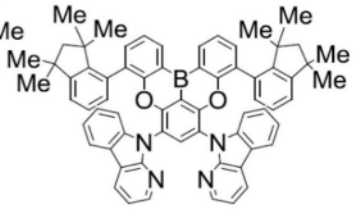
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(1-4653)



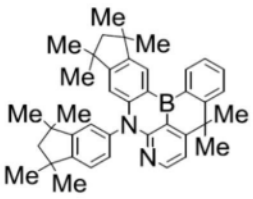
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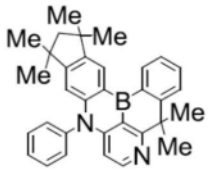


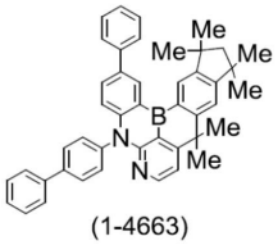
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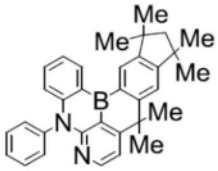
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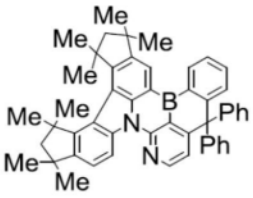
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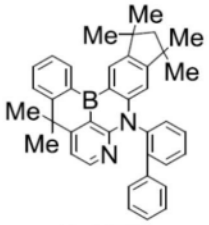

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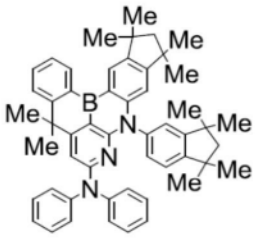

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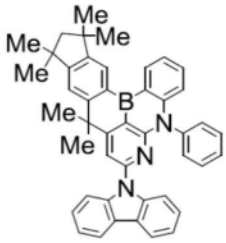

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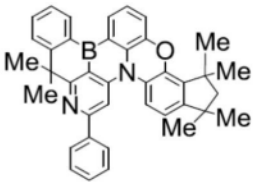

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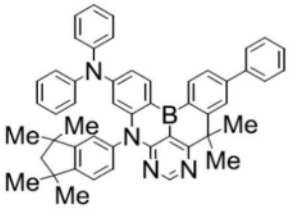

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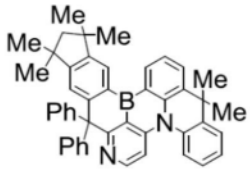

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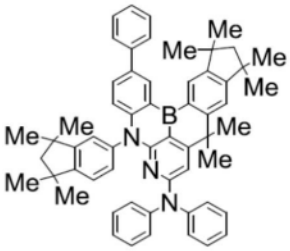

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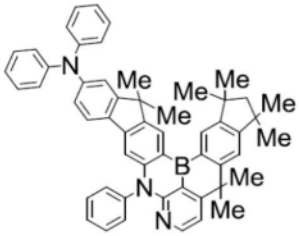

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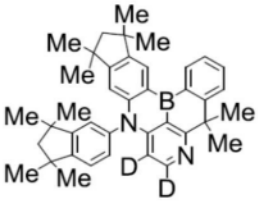

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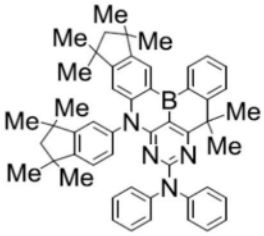

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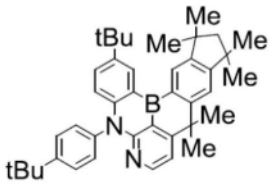

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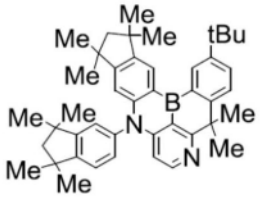

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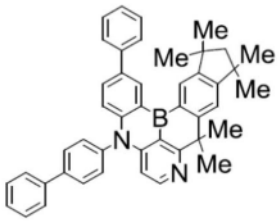
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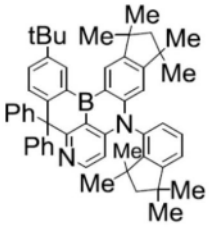
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(1-4682)



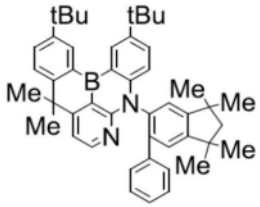
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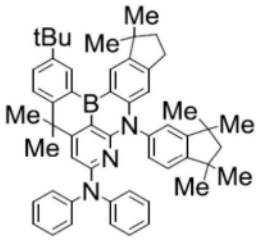


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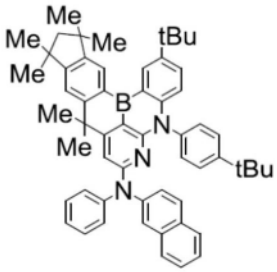


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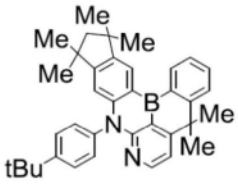
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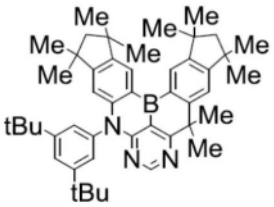
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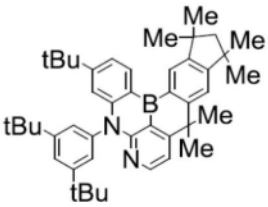
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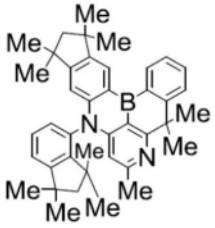
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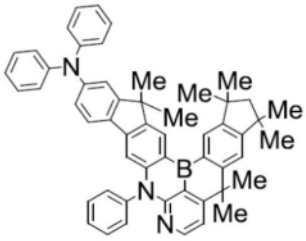
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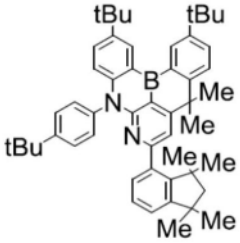
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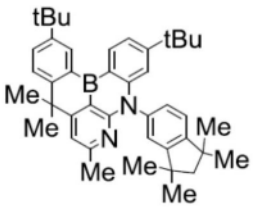
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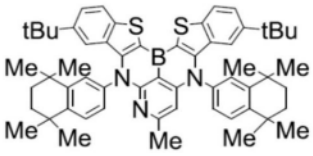


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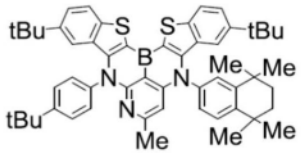
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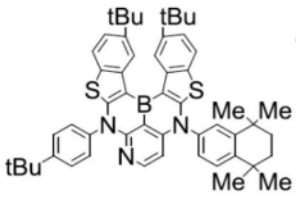
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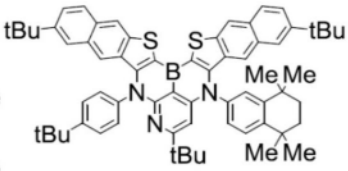
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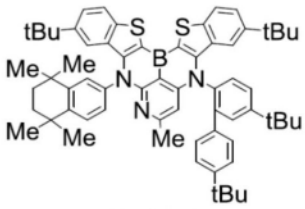
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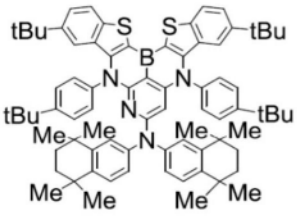


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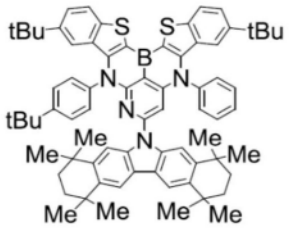


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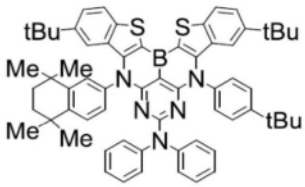
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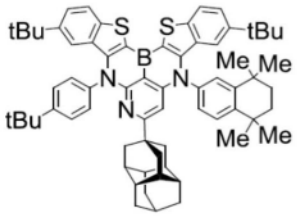
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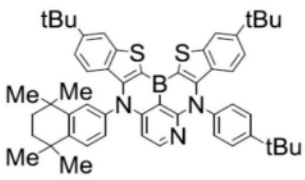
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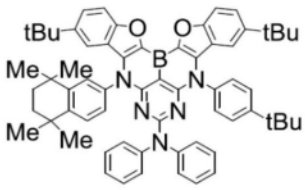
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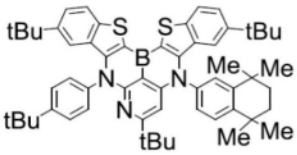
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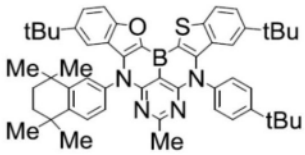
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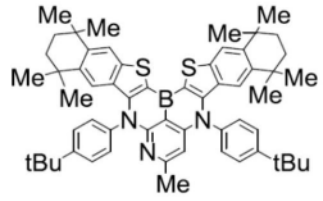
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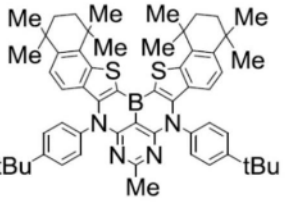
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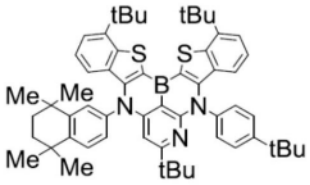
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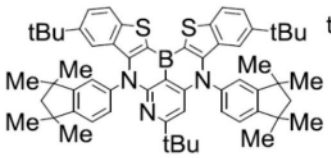
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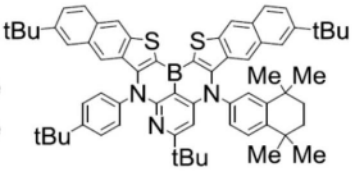
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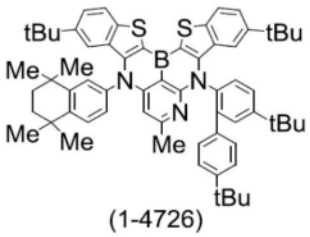
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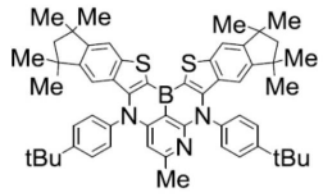
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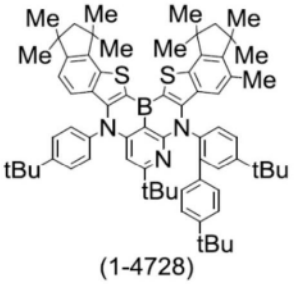
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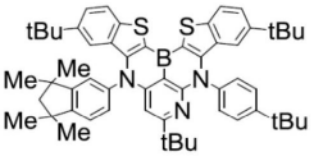
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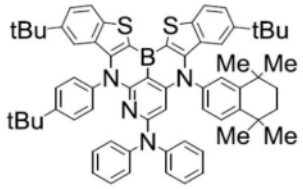
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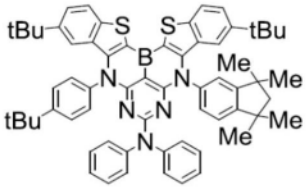
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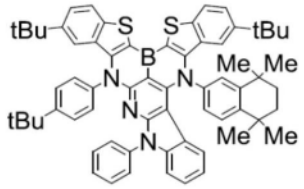
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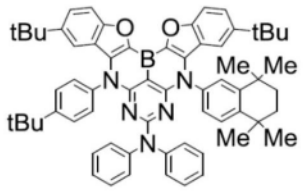
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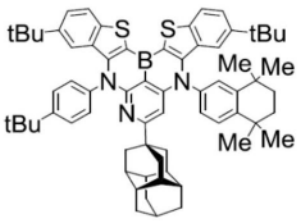
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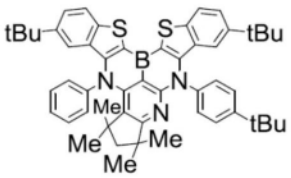
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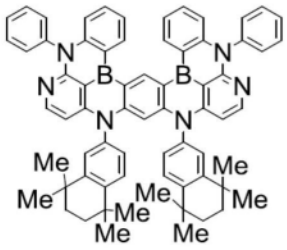


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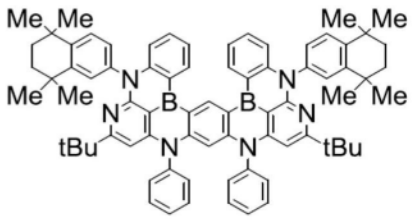


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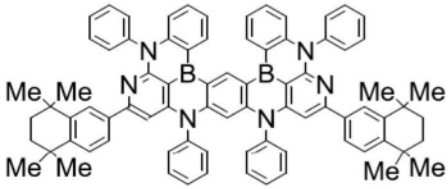
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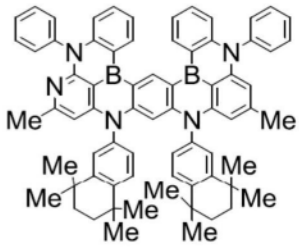
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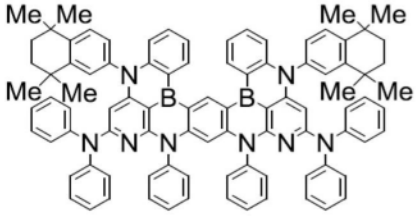


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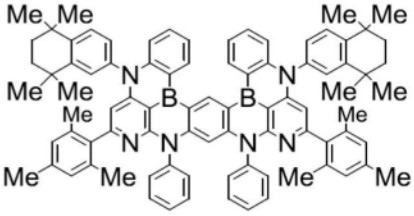


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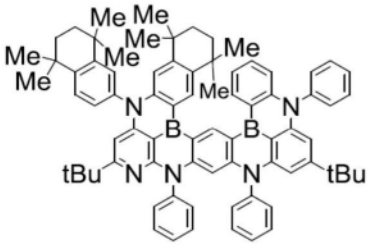
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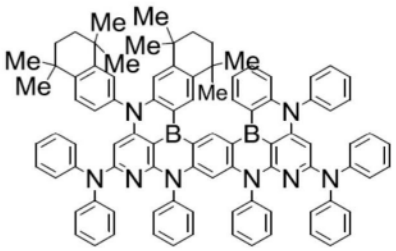
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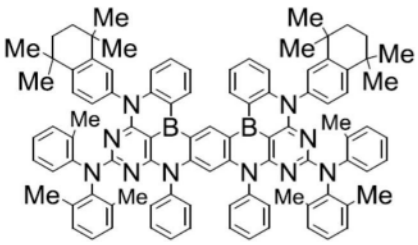
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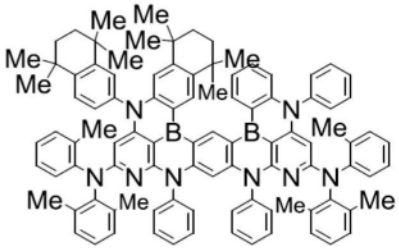
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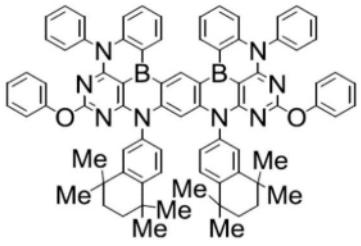
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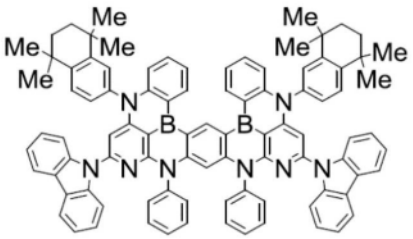
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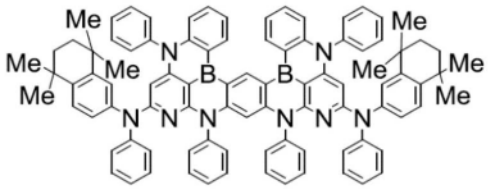
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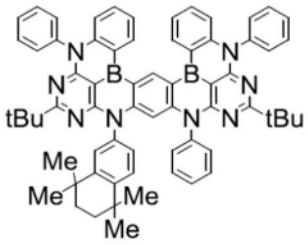
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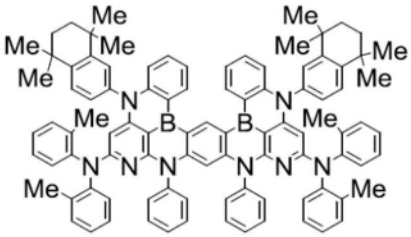
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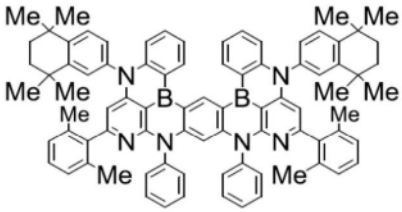
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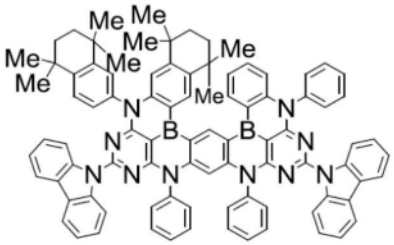
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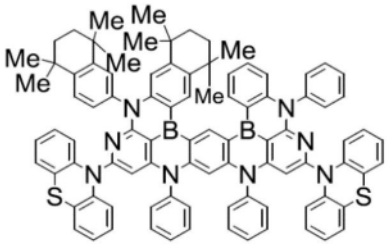
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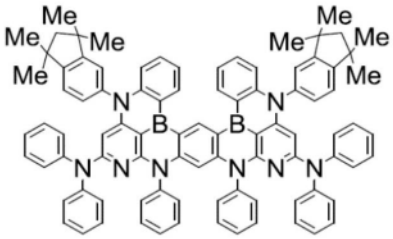
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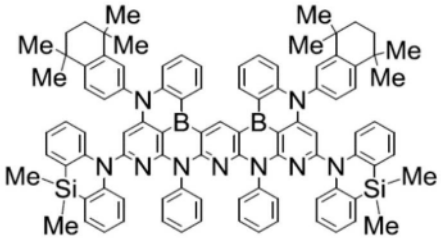
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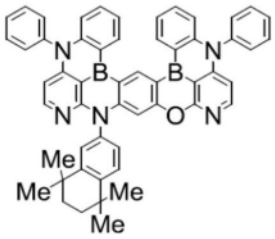


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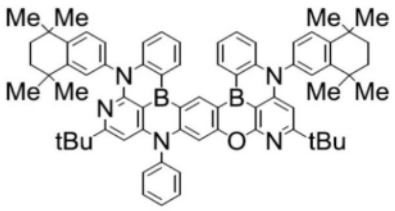


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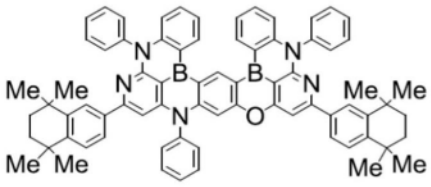
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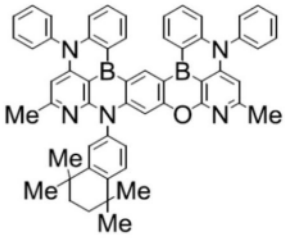
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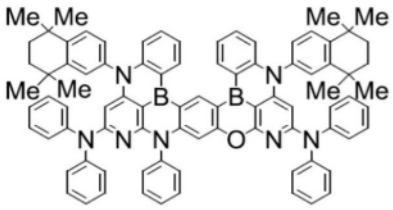


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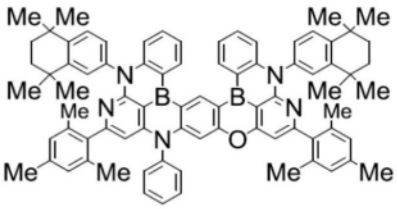


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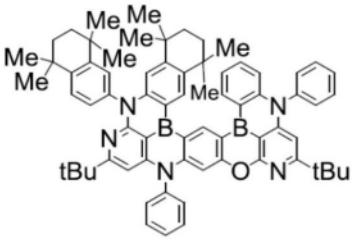
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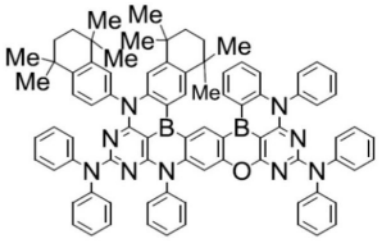
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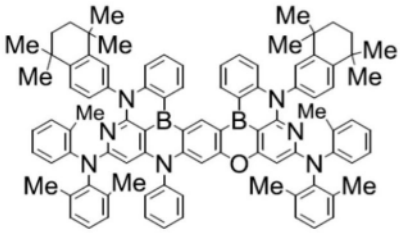
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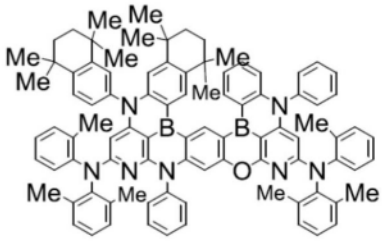
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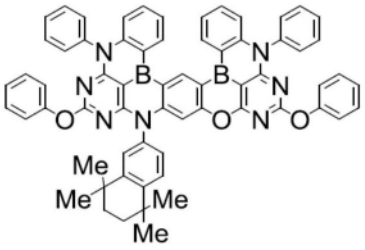


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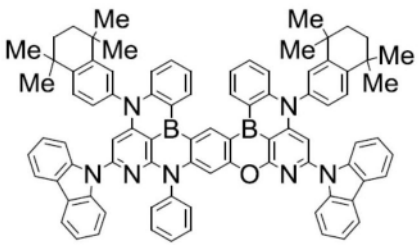


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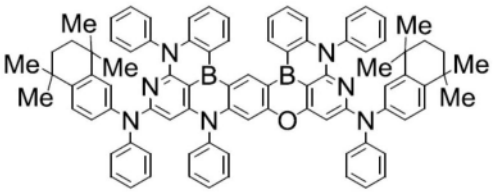
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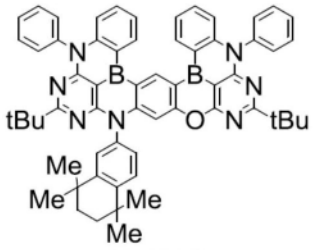
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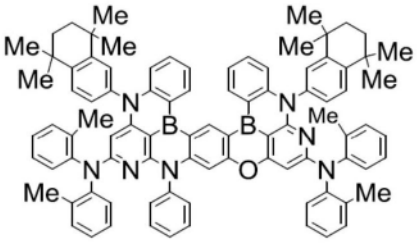


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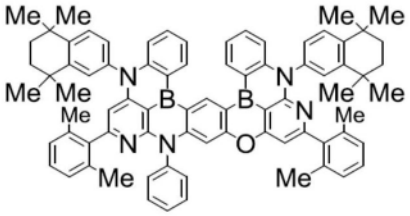


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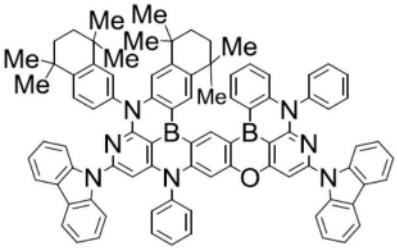
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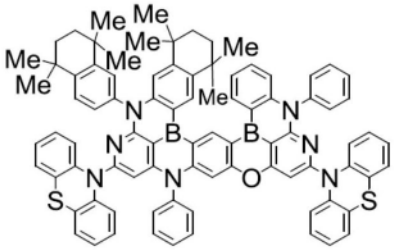
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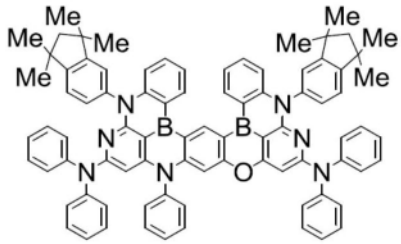
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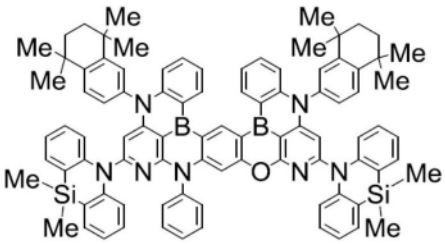
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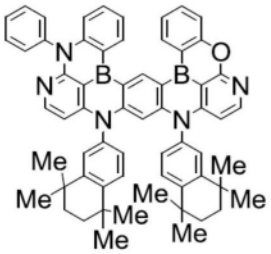


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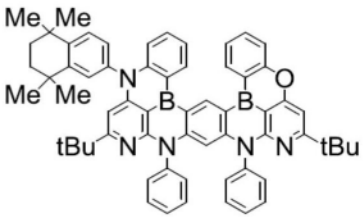


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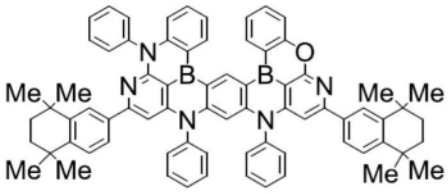
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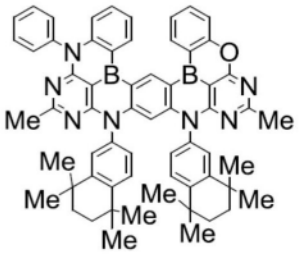
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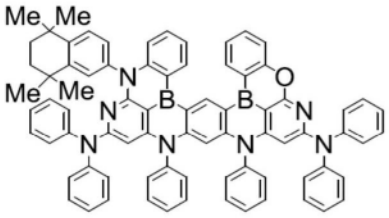


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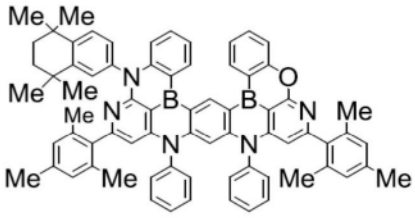


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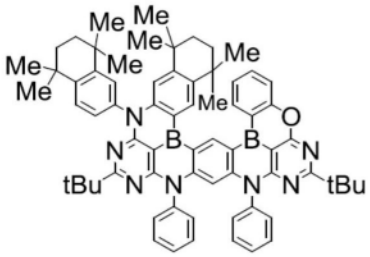
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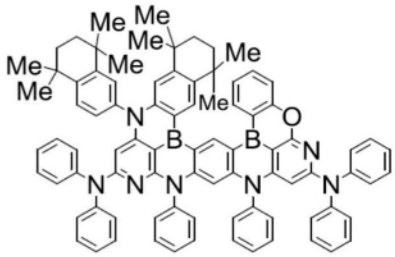
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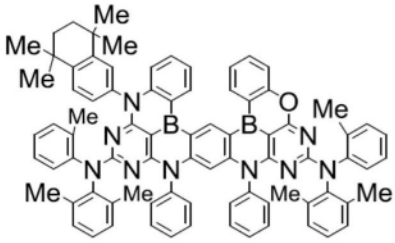
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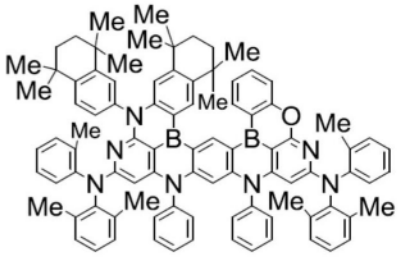
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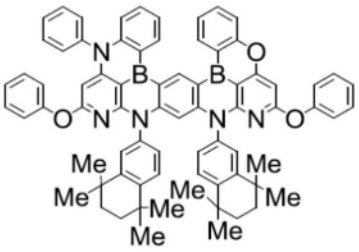


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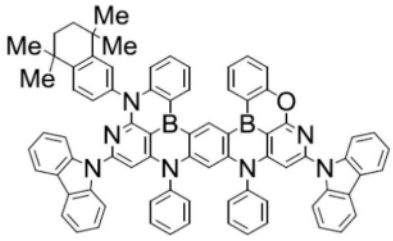


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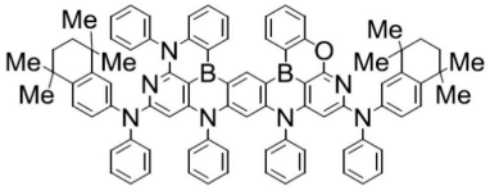
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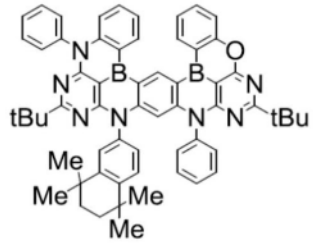
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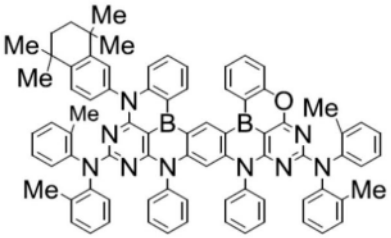


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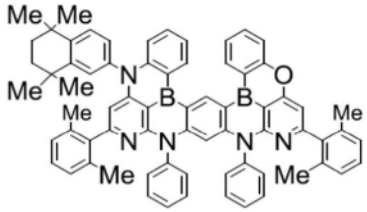


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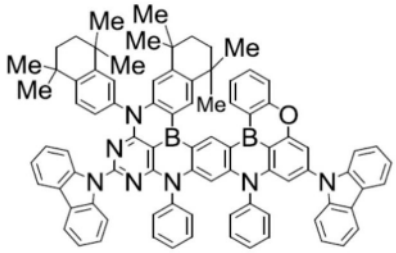
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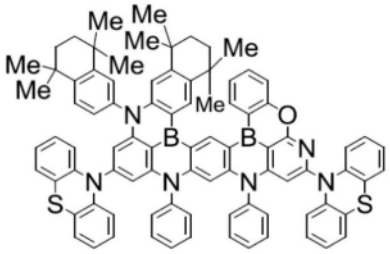
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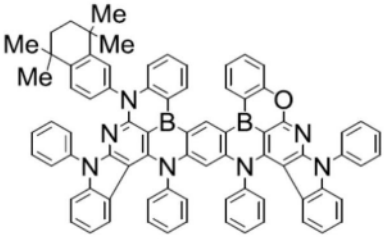
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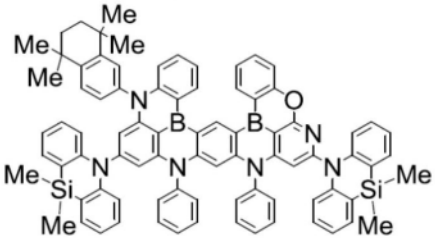
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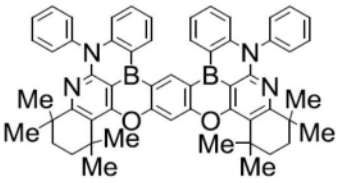


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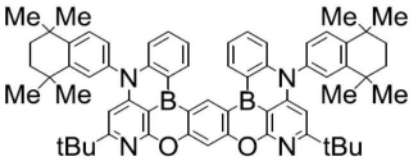


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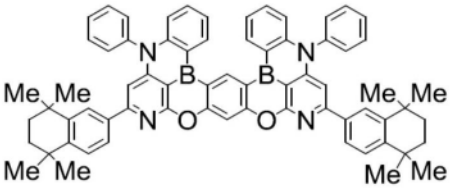
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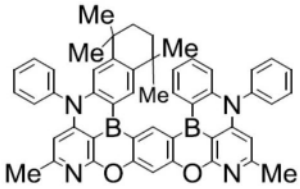
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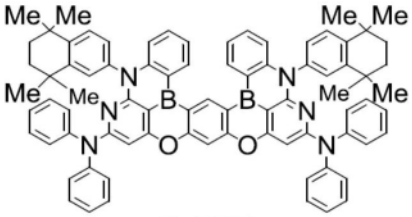


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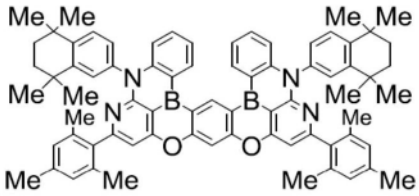


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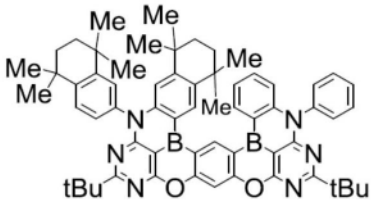
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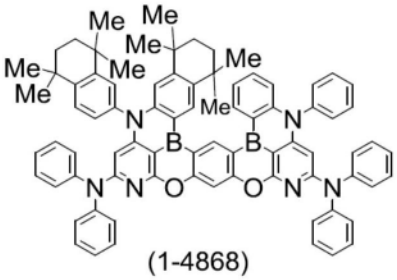
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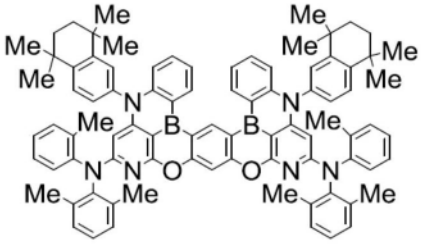
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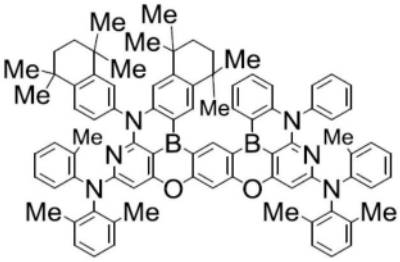
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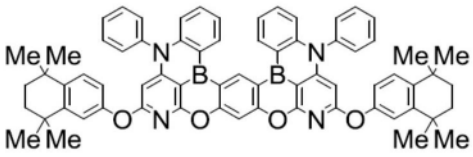
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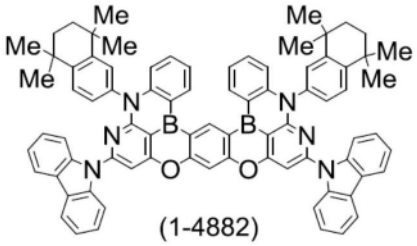
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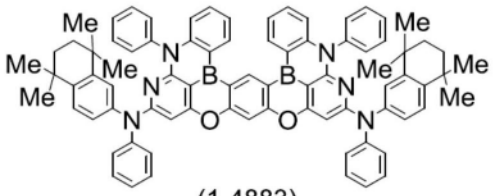
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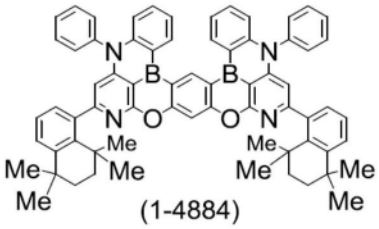
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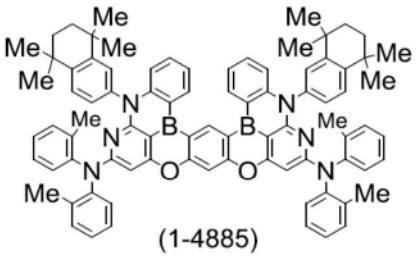
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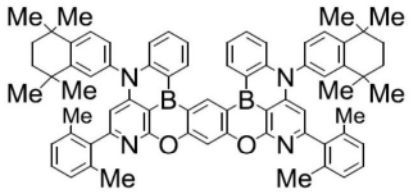
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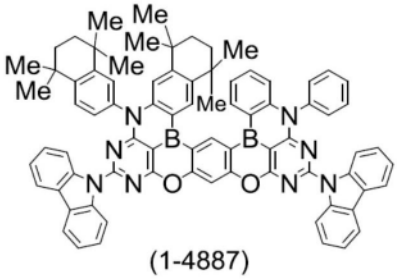
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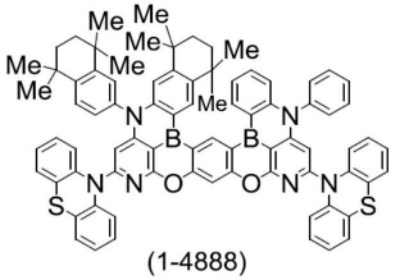
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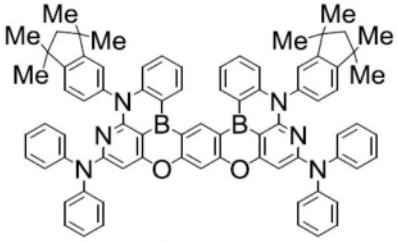
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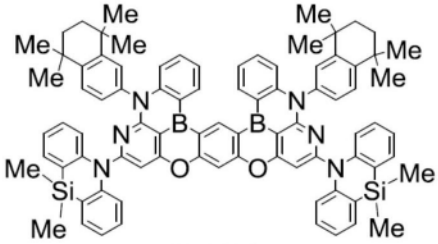
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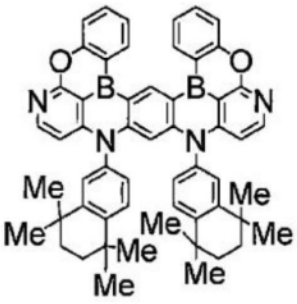


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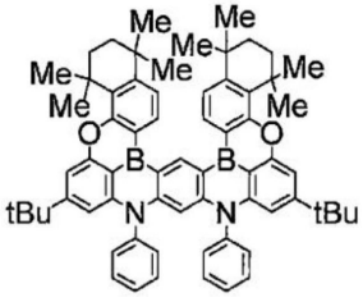


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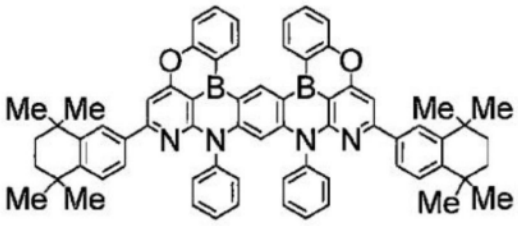
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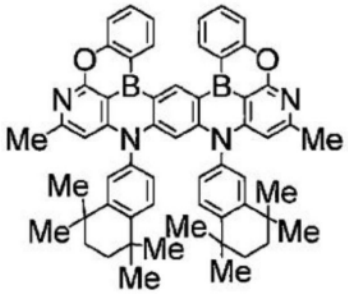
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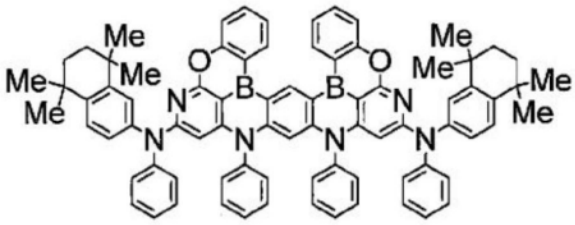


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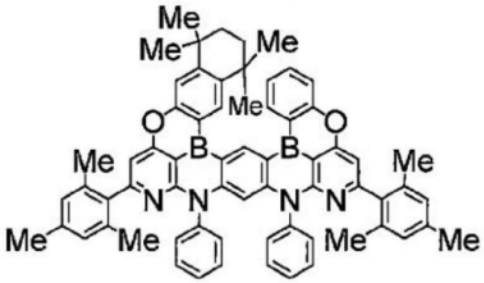


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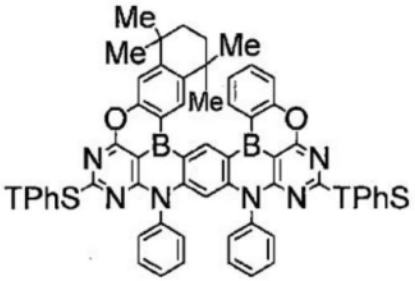
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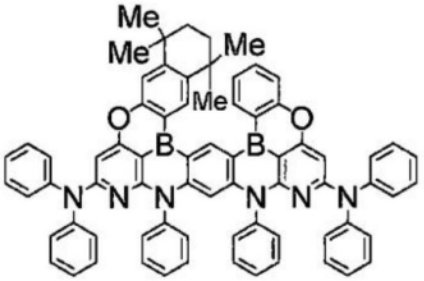
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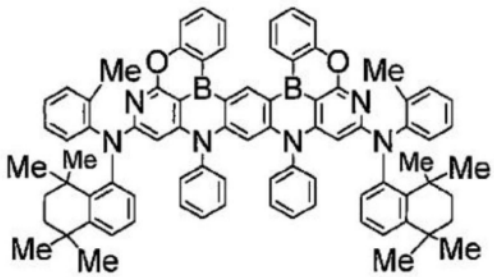
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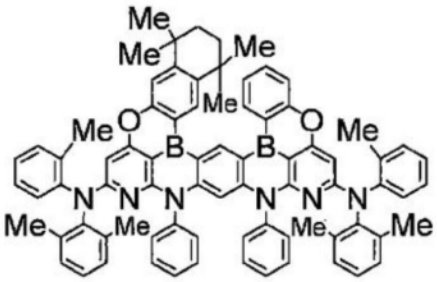
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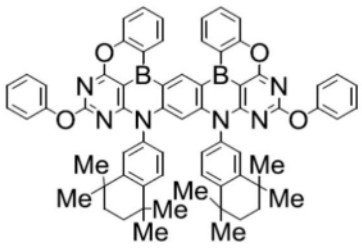


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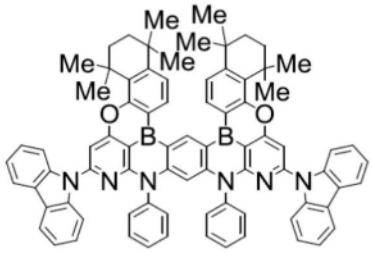


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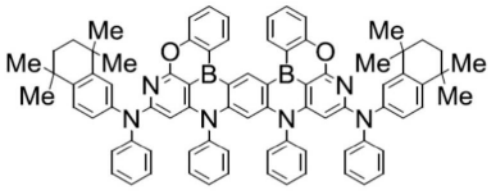
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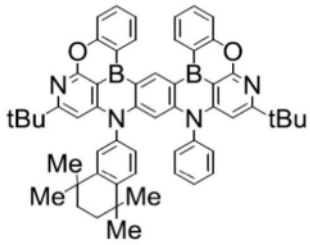
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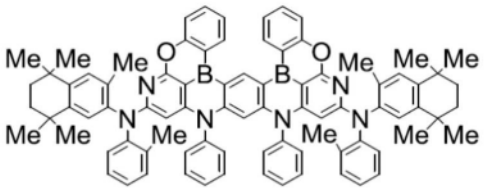


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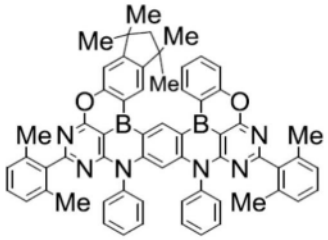


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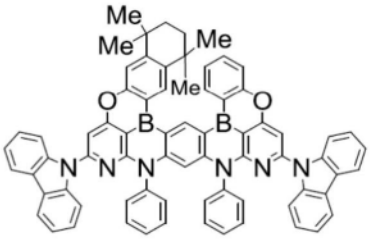
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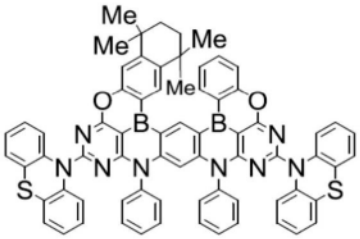
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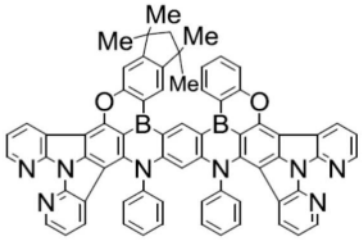
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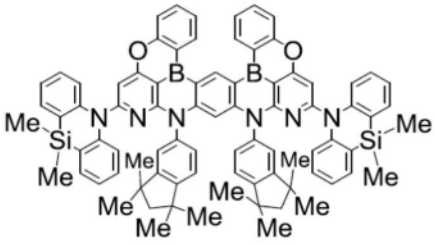
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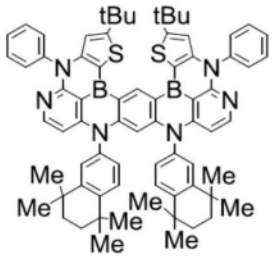


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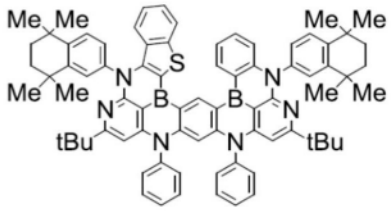


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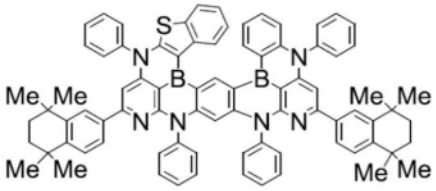
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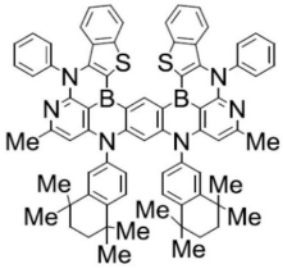
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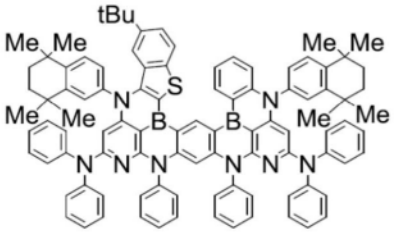


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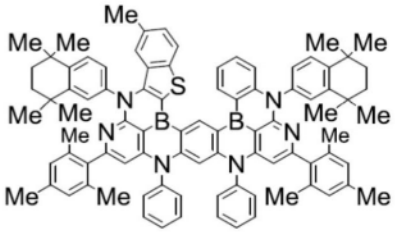


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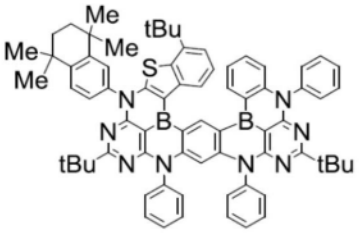
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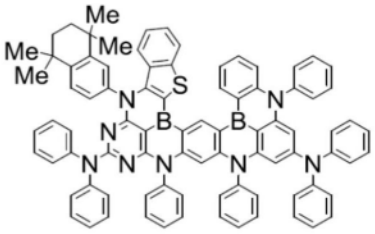
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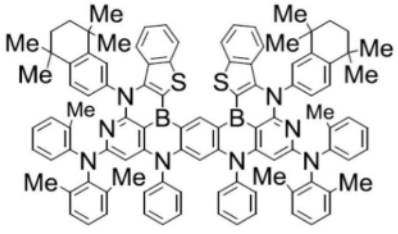
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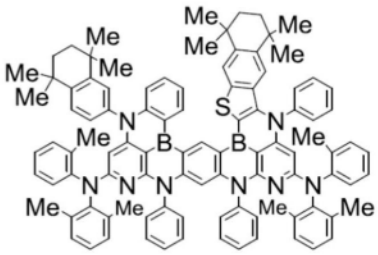
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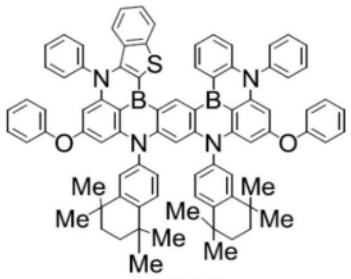


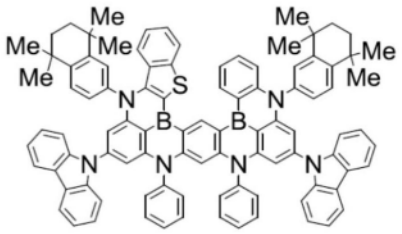
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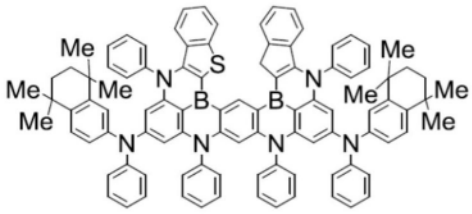


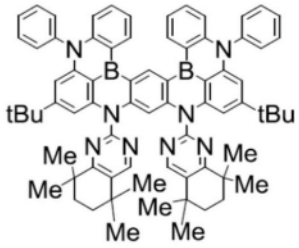
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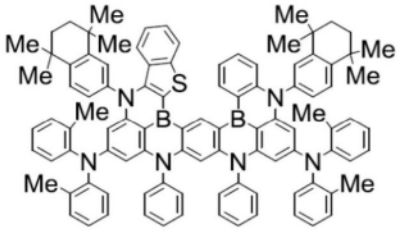

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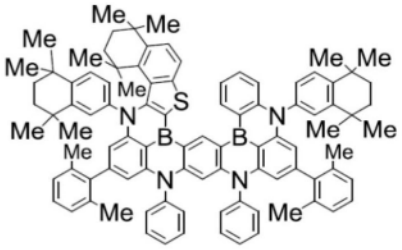

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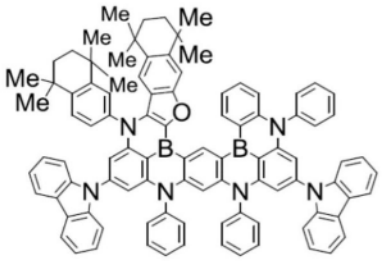

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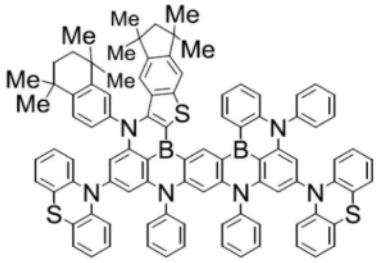

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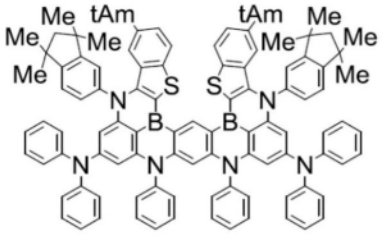
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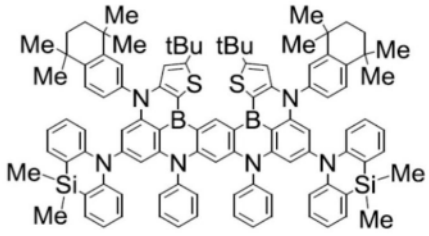

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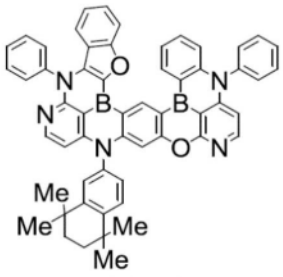

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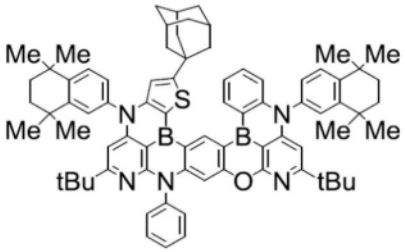

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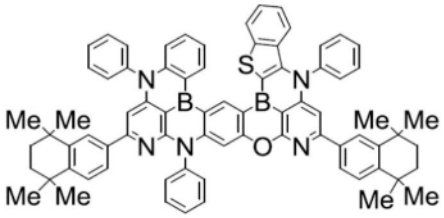
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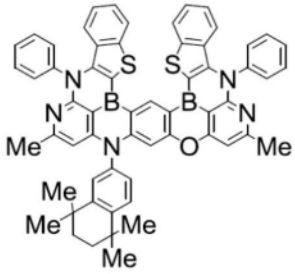
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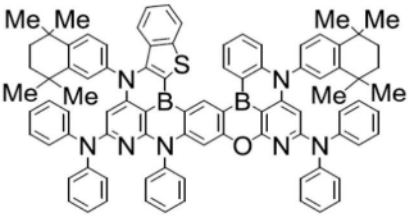


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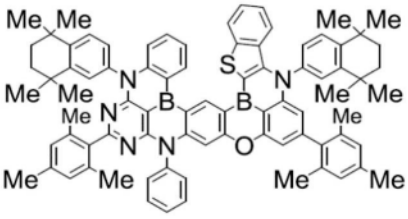


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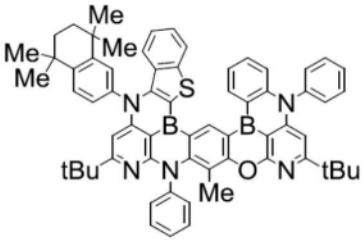
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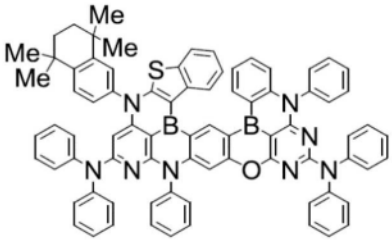
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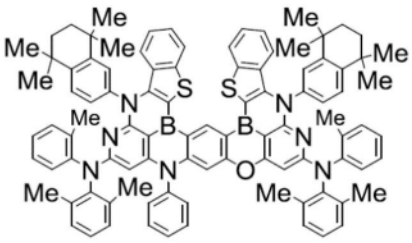
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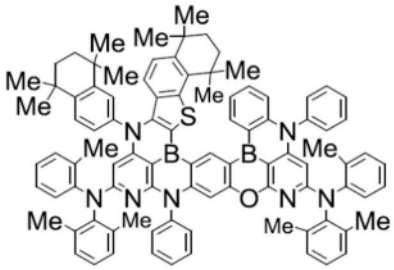
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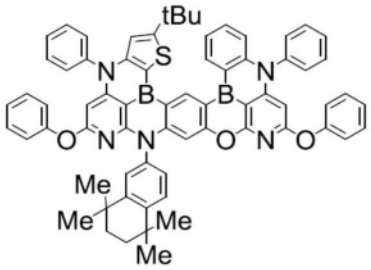


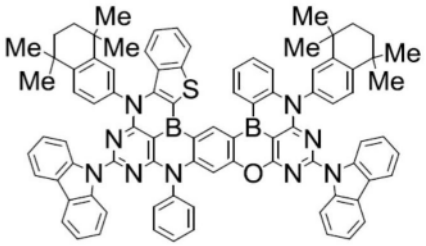
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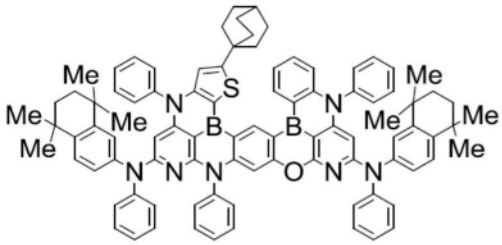


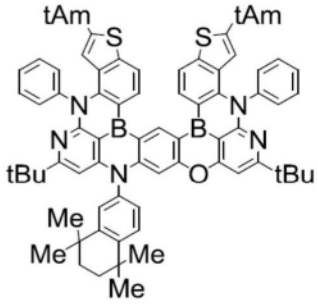
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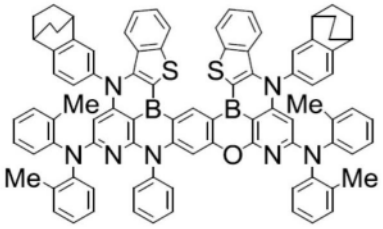

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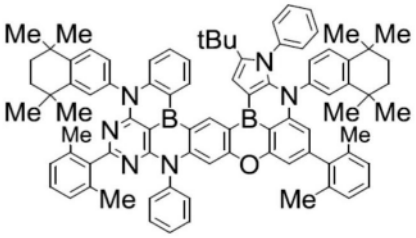

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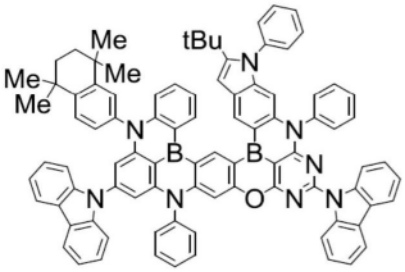

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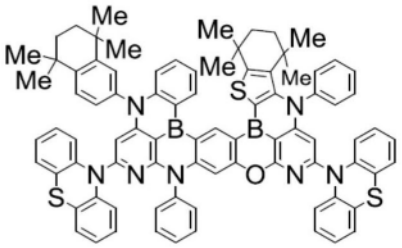

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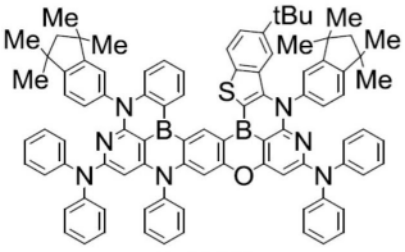
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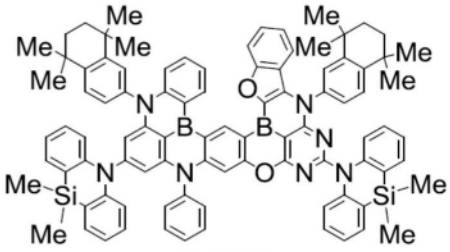

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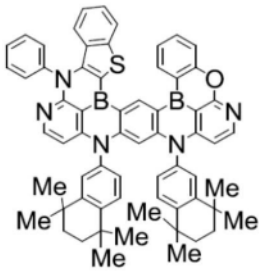

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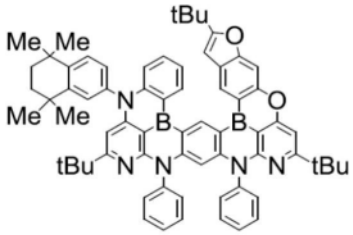

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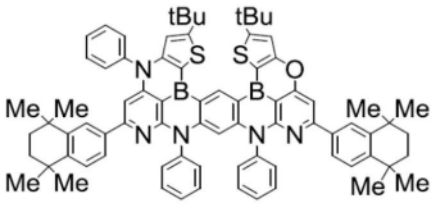
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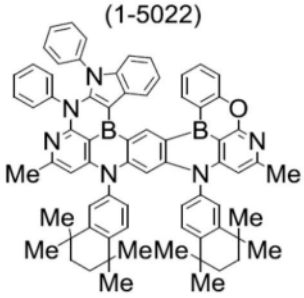
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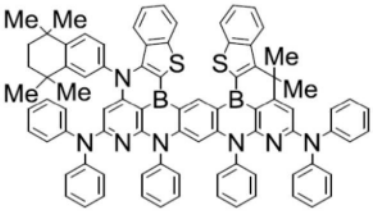


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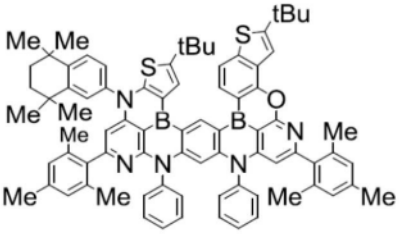


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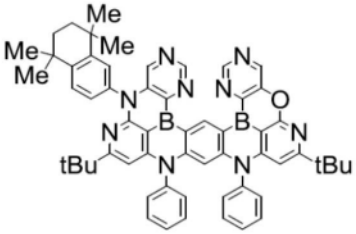
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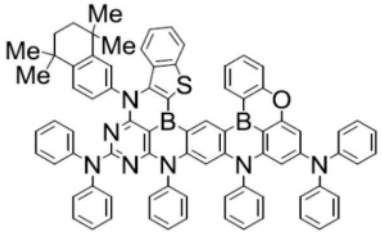
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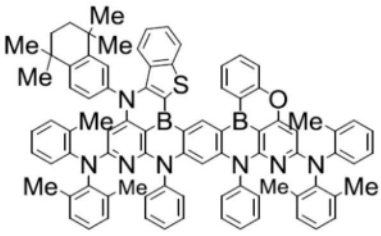
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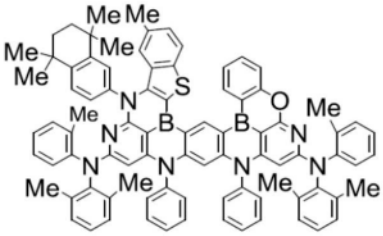
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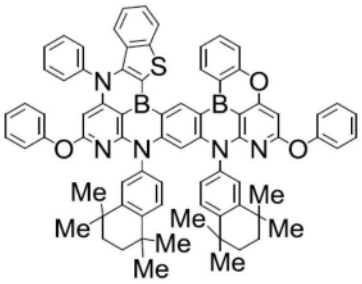


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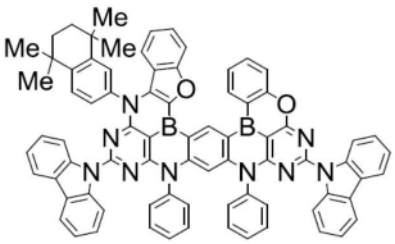


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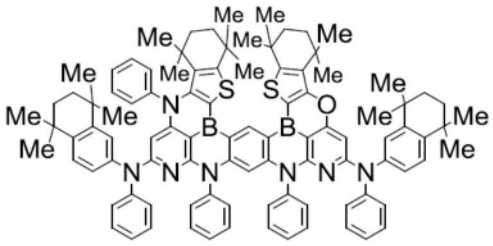
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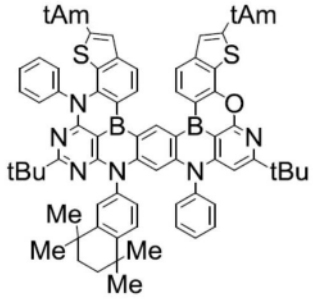
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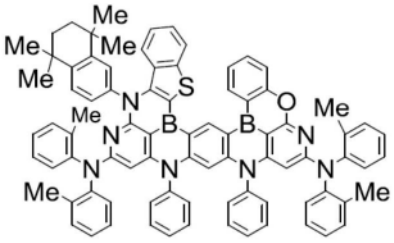


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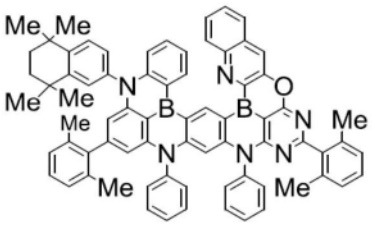


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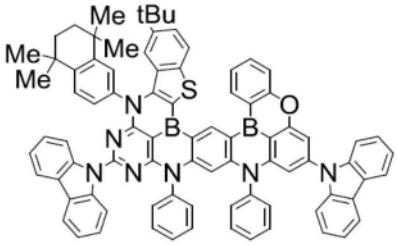
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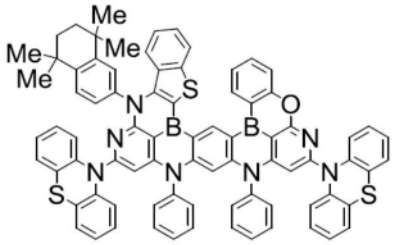
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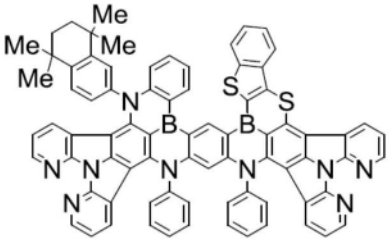
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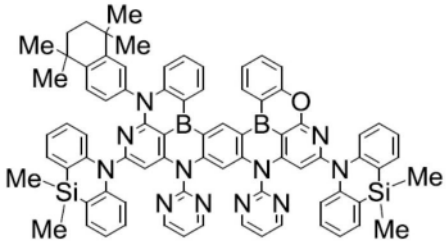
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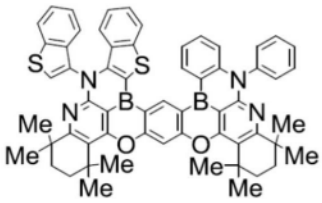


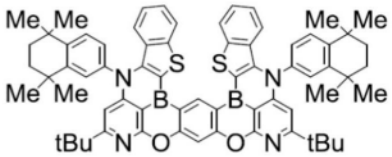
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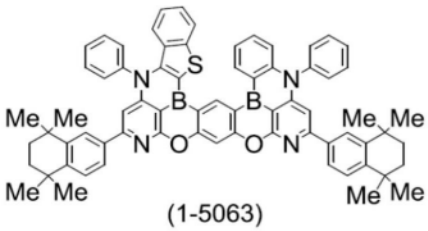


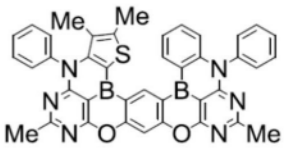
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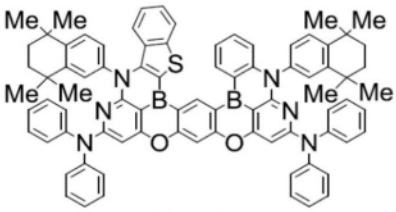

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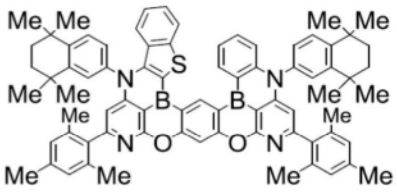

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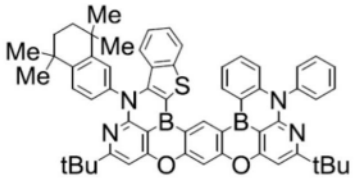

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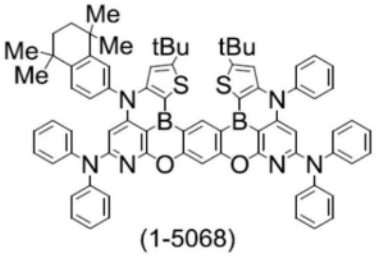

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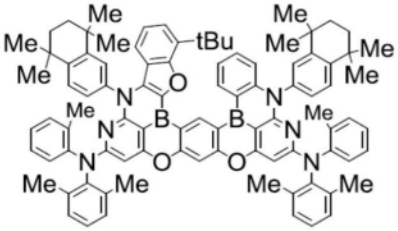
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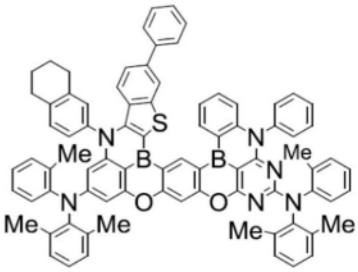

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(1-5066)


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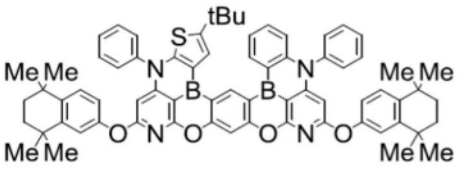

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(1-5070)

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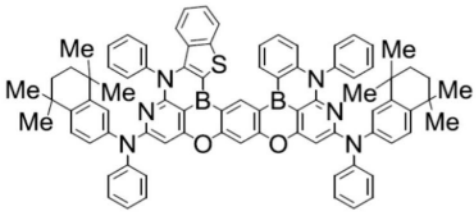
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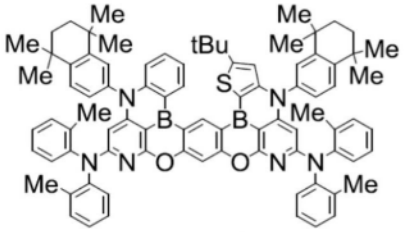
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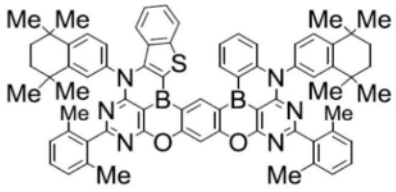
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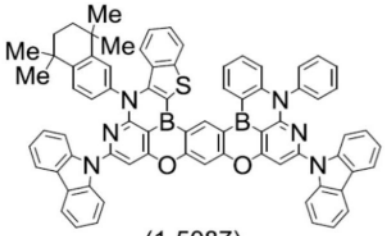
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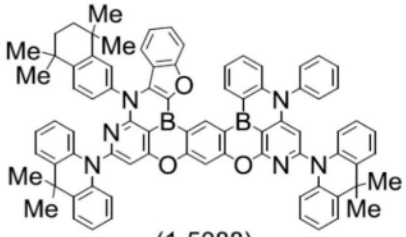
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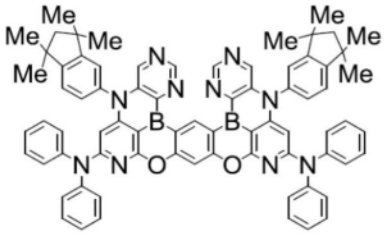
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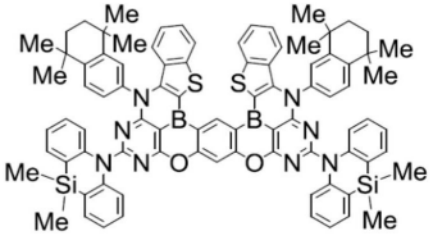
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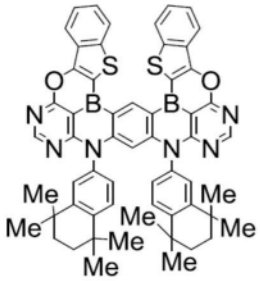


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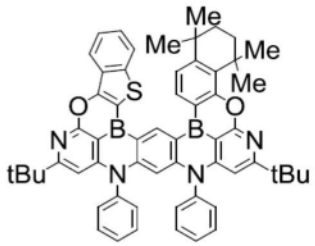


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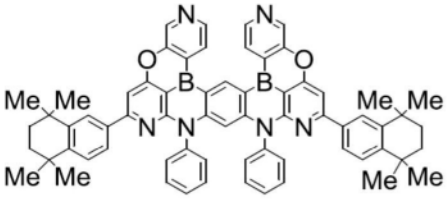
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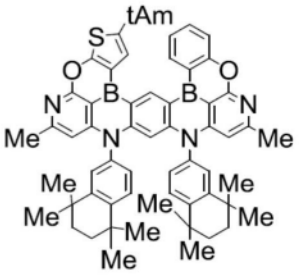
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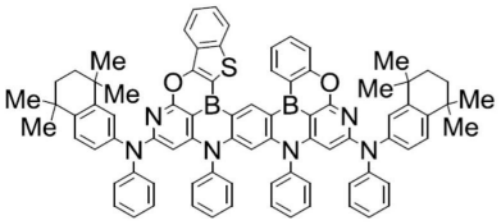


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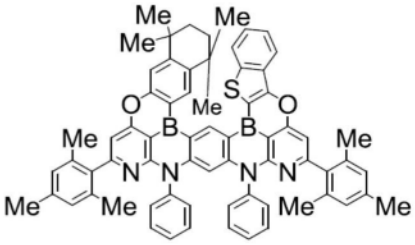


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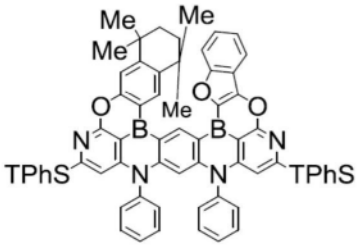
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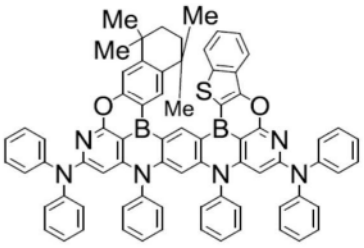
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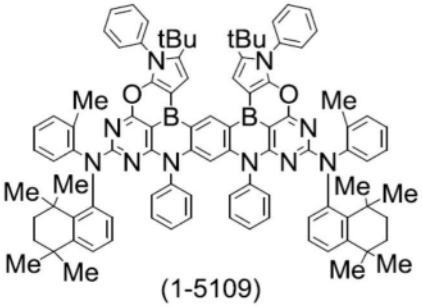
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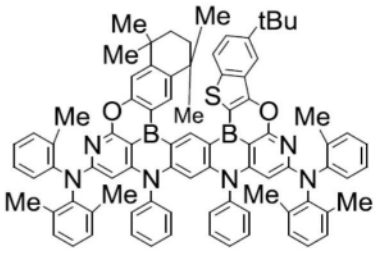
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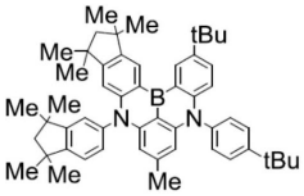
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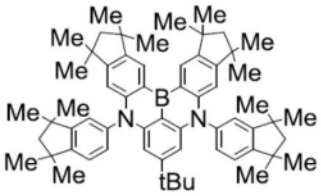


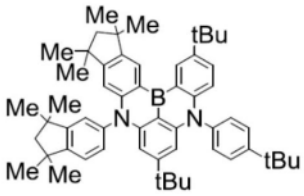
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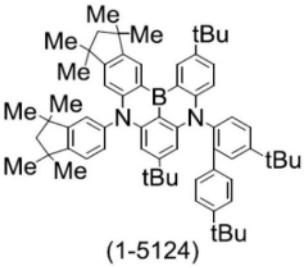
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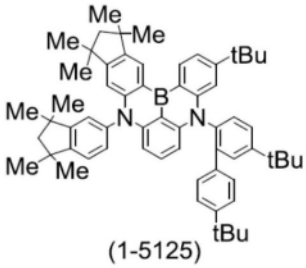
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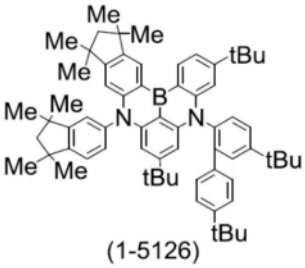

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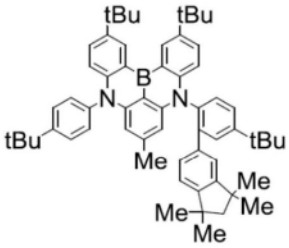

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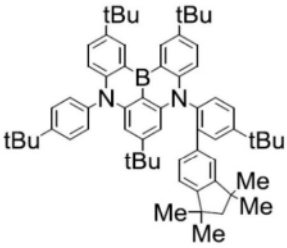

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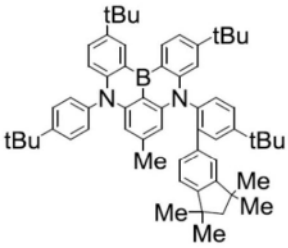

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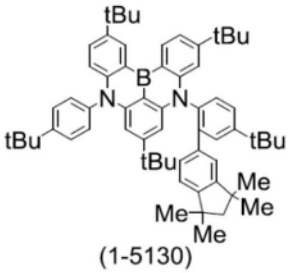

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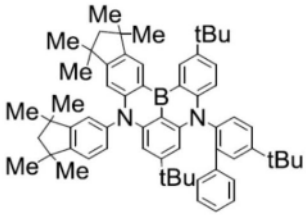

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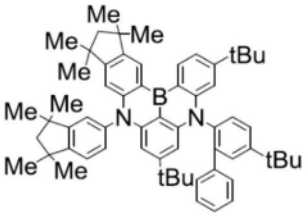

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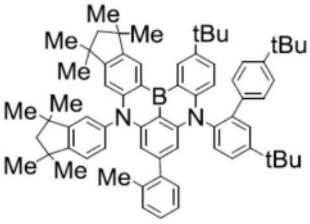

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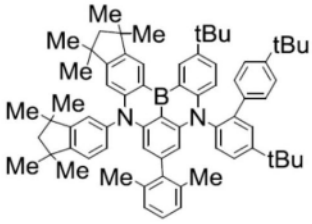

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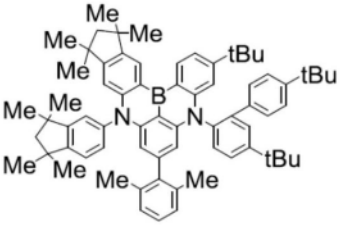

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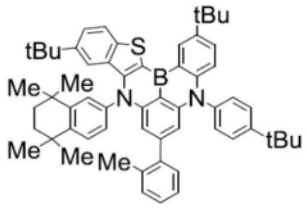

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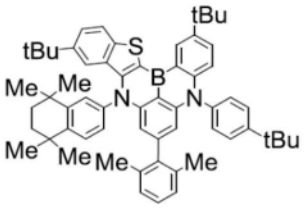

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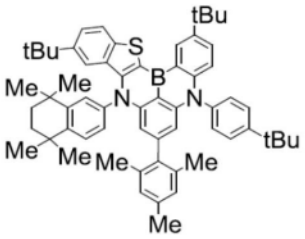
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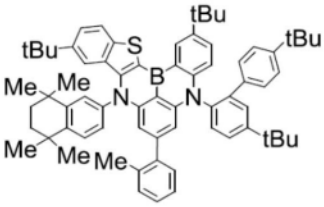
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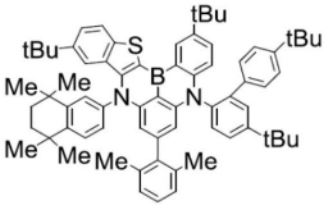
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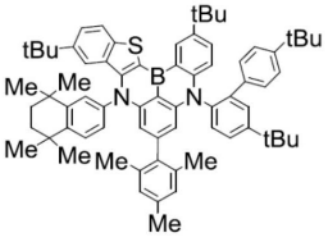
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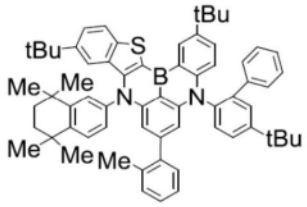


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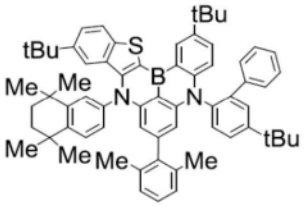


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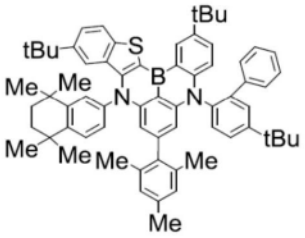
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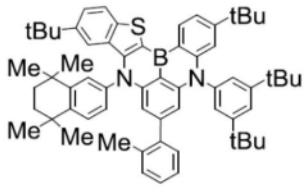
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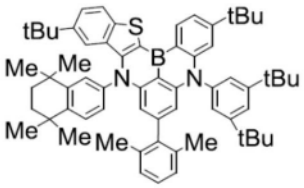
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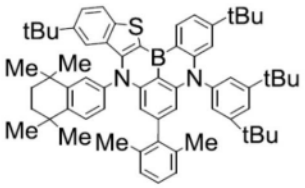
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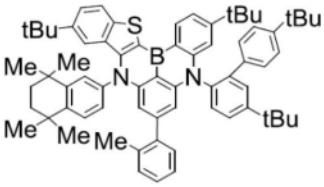
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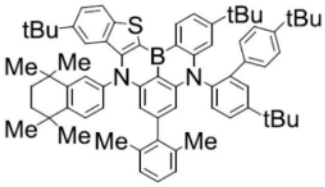
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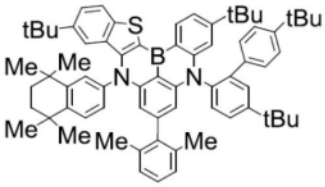
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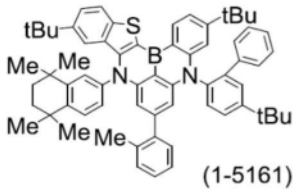


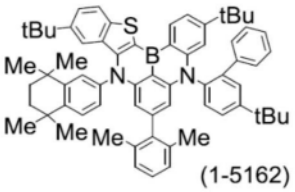
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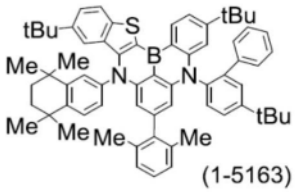


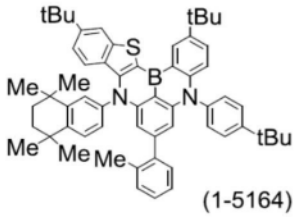
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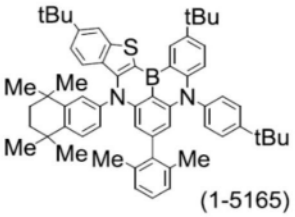
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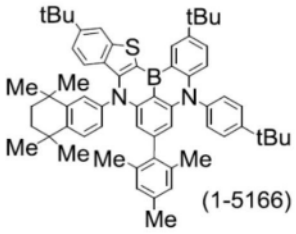

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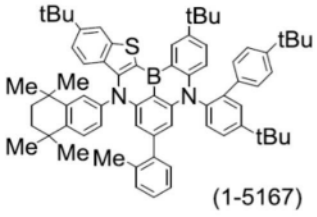

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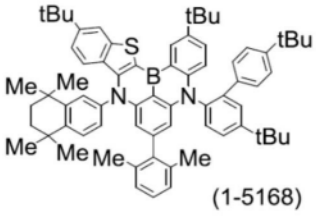

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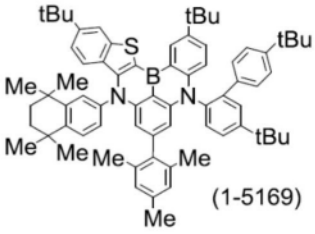

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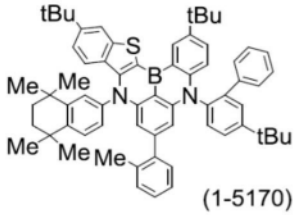

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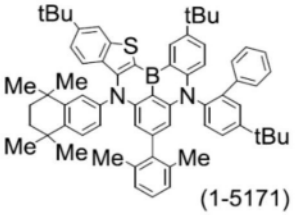

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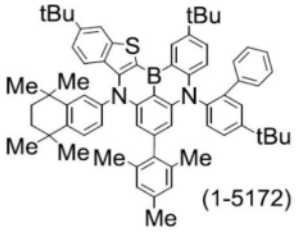

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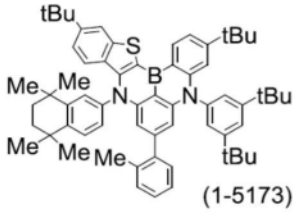

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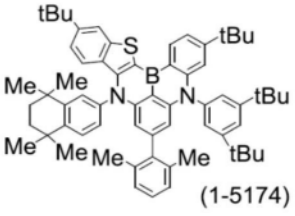
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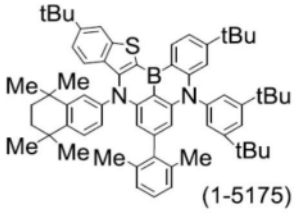

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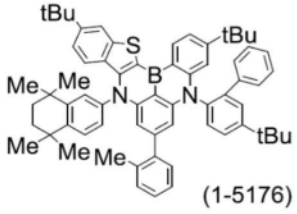

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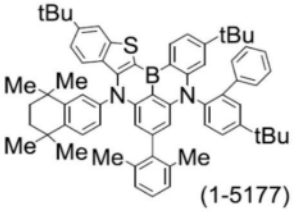

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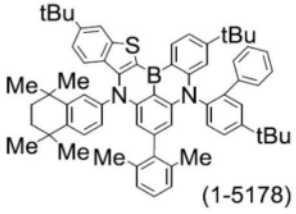

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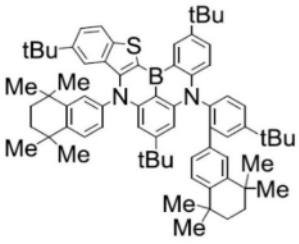

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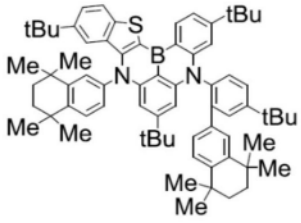

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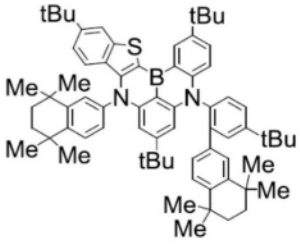

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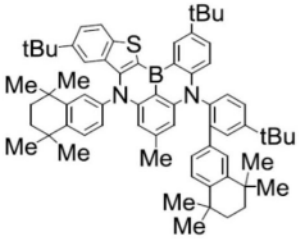
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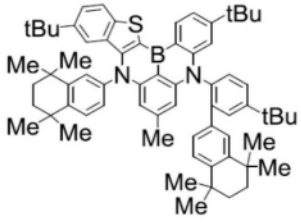
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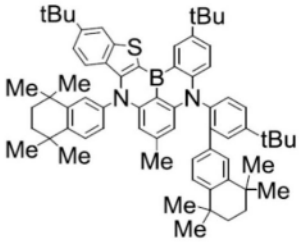

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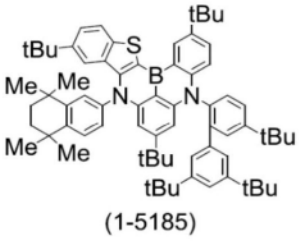

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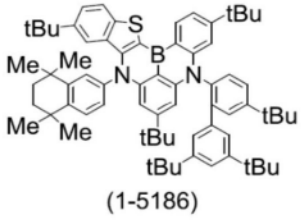

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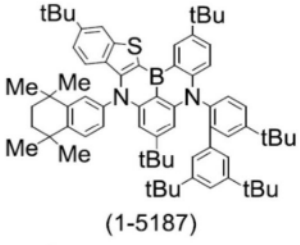

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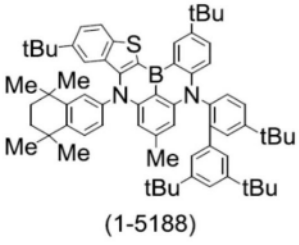

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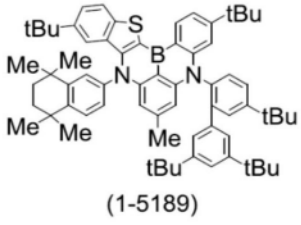

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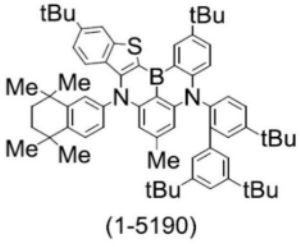

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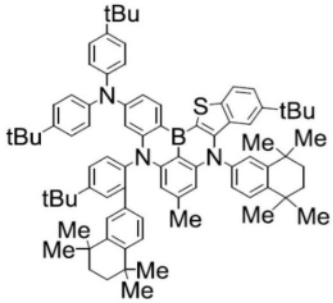

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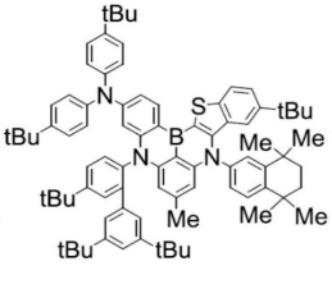

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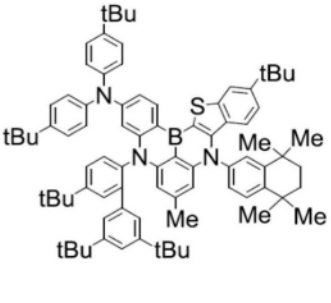

(1-5188)


(1-5189)


(1-5190)


(1-5191)


(1-5192)


(1-5193)

[0678] 再者,

[0679] (A)优选为所述式(1)中的A环、B环、C环及>N-R的R中的至少一个为杂芳基环或杂芳基,优选为所述式(2)中的a环、b环、c环、R^1～R^{11}中的邻接的基彼此键结并与a环、b环或c环一同形成的环、及>N-R的R中的至少一个为杂芳基环或杂芳基。

[0680] 另外,

[0681] (B)优选为所述式(2)中的a环、b环及c环中的至少一个“-C(-R)=”(此处,R为式(2)中的R^1～R^{11})由“-N=”取代,或至少一个“-C(-R)=C(-R)-”(此处,R为式(2)中的R^1～R^{11})由“-N(-R)-”、“-O-”或“-S-”取代。

[0682] 进而,

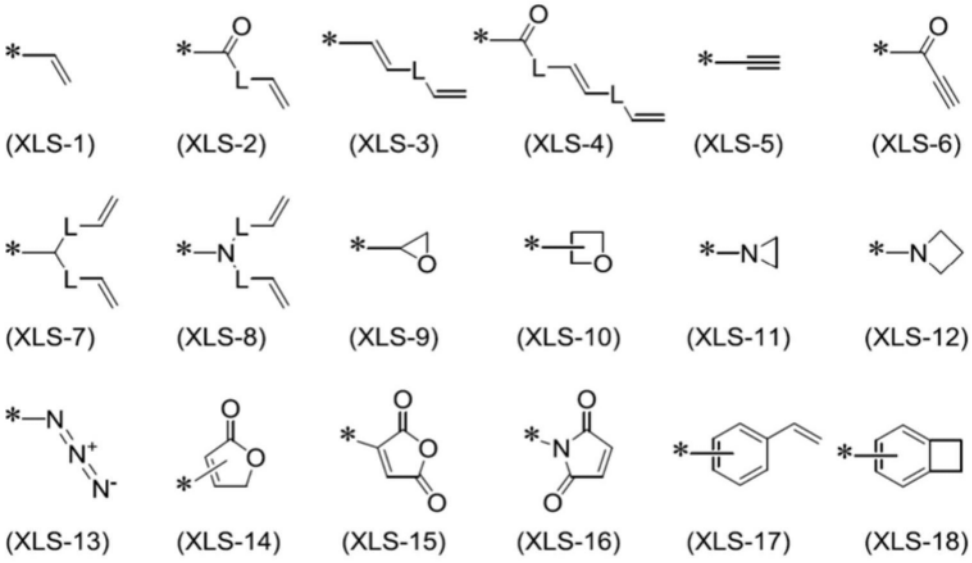
[0683] (C)优选为所述式(2)中的a环、b环及c环中的至少一个“-C(-R)=C(-R)-”(此处,R为式(2)中的R^1～R^{11})由“-S-”取代。

[0684] 以上的(A)～(C)更优选为Y^1为B且X^1及X^2为>N-R的情况。

[0685] 本发明的通式(1)所表示的多环芳香族化合物及其多聚体也可作为如下的高分子化合物(用于获得所述高分子化合物的所述单体具有聚合性取代基)或高分子交联体(用于获得所述高分子交联体的所述高分子化合物具有交联性取代基)、或者如下的悬挂型高分子化合物(用于获得所述悬挂型高分子化合物的所述反应性化合物具有反应性取代基)或悬挂型高分子交联体(用于获得所述悬挂型高分子交联体的所述悬挂型高分子化合物具有交联性取代基)而用于有机元件用材料、例如有机电致发光元件用材料、有机场效晶体管用材料或有机薄膜太阳电池用材料,其中,所述高分子化合物是使在所述通式(1)所表示的多环芳香族化合物及其多聚体中取代有反应性取代基的反应性化合物作为单体进行高分子化而成,所述高分子交联体是使所述高分子化合物进一步交联而成,所述悬挂型高分子化合物是使主链型高分子与所述反应性化合物反应而成,所述悬挂型高分子交联体是使所述悬挂型高分子化合物进一步交联而成。

[0686] 作为所述反应性取代基(包含所述聚合性取代基、所述交联性取代基、及用于获得悬挂型高分子的反应性取代基,以下,也简称为“反应性取代基”),若为可使所述多环芳香族化合物或其多聚体进行高分子量化的取代基、可使以此种方式获得的高分子化合物进一步交联化的取代基、以及可在主链型高分子中进行悬挂反应的取代基,则无特别限定,优选为以下结构的取代基。各结构式中的*表示键结位置。

[0687] [化238]

[0688] 

[0689] L分别独立地为单键、-O-、-S-、>C=O、-O-C(=O)-、碳数1～12的亚烷基、碳数1～12的氧化烯基及碳数1～12的聚氧化烯基。在所述取代基中,优选为式(XLS-1)、式(XLS-2)、式(XLS-3)、式(XLS-9)、式(XLS-10)或式(XLS-17)所表示的基,更优选为式(XLS-1)、式(XLS-3)或式(XLS-17)所表示的基。

[0690] 关于此种高分子化合物、高分子交联体、悬挂型高分子化合物及悬挂型高分子交联体(以下,也简称为“高分子化合物及高分子交联体”)的用途的详细情况,在后文叙述。

[0691] 2.经环烷烃缩合的多环芳香族化合物及其多聚体的制造方法

[0692] 关于通式(1)或通式(2)所表示的多环芳香族化合物及其多聚体,基本而言首先利用键结基(包含X^1或X^2的基)使A环(a环)与B环(b环)及C环(c环)键结,由此制造中间物(第一反应),其后,利用键结基(包含Y^1的基)使A环(a环)、B环(b环)及C环(c环)键结,由此可制造最终产物(第二反应)。第一反应中,例如若为醚化反应,则可利用亲核取代反应、乌尔曼反应(Ullmann Reaction)等通常的反应,若为氨基化反应,则可利用布赫瓦尔德-哈特维希反应(Buchwald-Hartwig Reaction)等通常的反应。另外,第二反应中,可利用串联式杂夫里德耳-夸夫特反应(Tandem Hetero-Friedel-Crafts Reaction)(连续的芳香族亲电子取代反应,以下相同)。另外,在这些反应步骤中的某处,使用经环烷烃缩合的原料、或者追加缩合环烷烃的步骤,由此,可制造所期望的位置经环烷烃缩合的本发明的化合物。

[0693] 如下述流程(1)或流程(2)所示,第二反应为将键结A环(a环)、B环(b环)及C环(c环)的Y^1导入的反应,作为例子,以下表示Y^1为硼原子、X^1及X^2为氧原子的情况。首先,利用正丁基锂、仲丁基锂或叔丁基锂等对X^1与X^2之间的氢原子进行邻位金属化。继而,加入三氯化硼或三溴化硼等,进行锂-硼的金属交换后,加入N,N-二异丙基乙胺等布忍斯特碱(Bronsted base),由此进行串联式硼杂夫里德耳-夸夫特反应(Tandem Bora-Friedel-Crafts Reaction),从而可获得目标物。在第二反应中,为了促进反应,也可加入三氯化铝等路易斯酸(Lewis acid)。再者,下述流程(1)及流程(2)中、进而其后的流程(3)~流程(28)中的各结构式的符号的定义与所述定义相同。

[0694] [化239]

流程(1)

[0695] 

(中间物) 通式(1)系化合物

[0696] [化240]

流程(2)

[0697] 

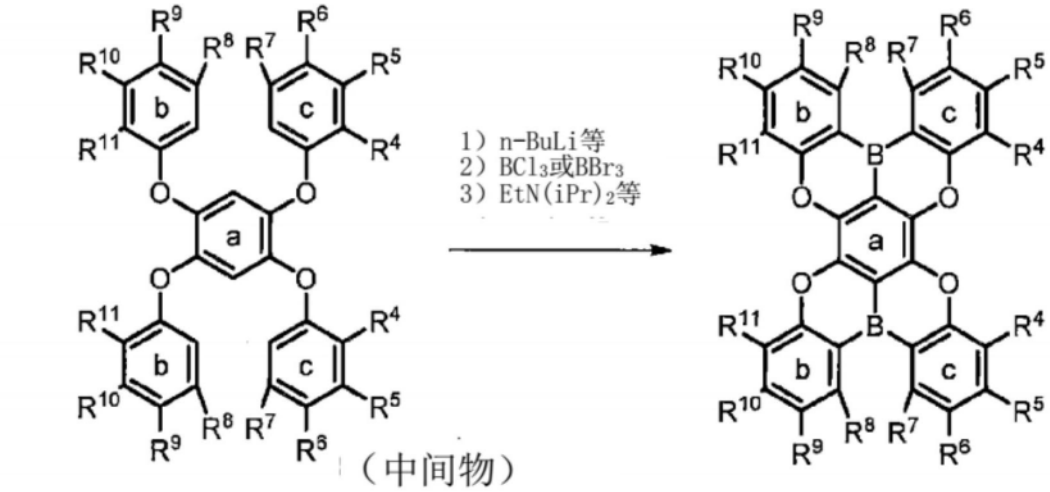
(中间物) 通式(2)系化合物

[0698] 再者,所述流程(1)或流程(2)主要表示通式(1)或通式(2)所表示的多环芳香族化合物的制造方法,但关于其多聚体,可通过使用具有多个A环(a环)、B环(b环)及C环(c环)的

中间物来制造。详细而言,通过下述流程(3)～流程(5)进行说明。所述情况下,通过将所使用的丁基锂等试剂的量设为2倍量、3倍量,可获得目标物。

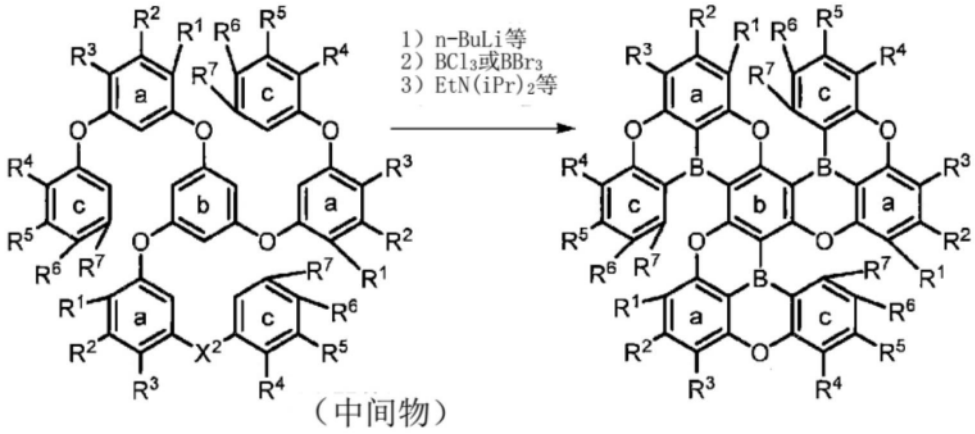
[0699] [化241]

流程(3)

[0700] 

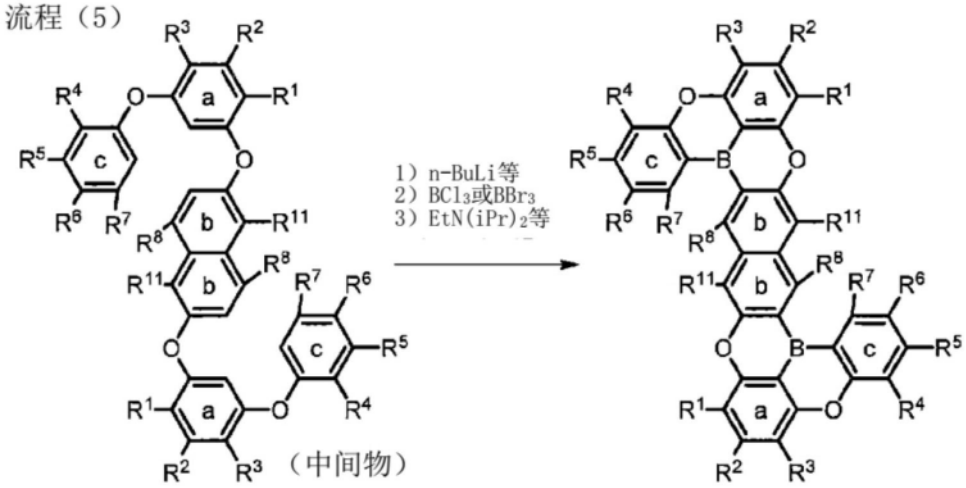
[0701] [化242]

流程(4)

[0702] 

[0703] [化243]

流程(5)

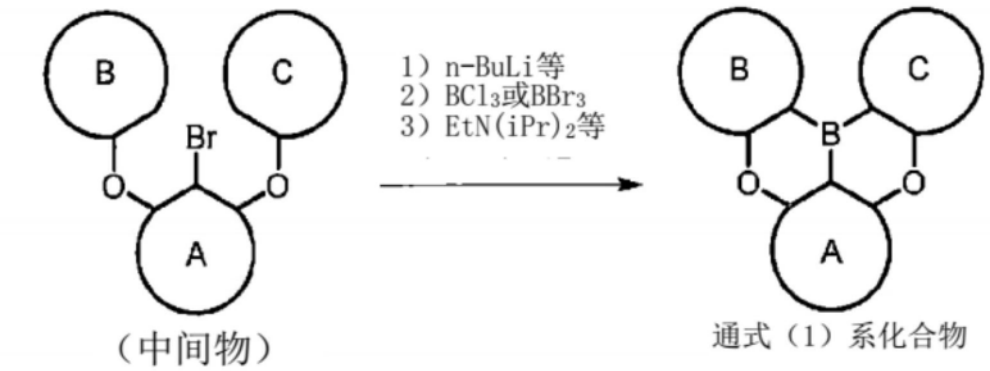
[0704] 

[0705] 在所述流程中,通过邻位金属化而朝所期望的位置上导入锂,但可如下述流程(6)

及流程(7)那样在欲导入锂的位置上导入溴原子等,并也通过卤素-金属交换而朝所期望的位置上导入锂。

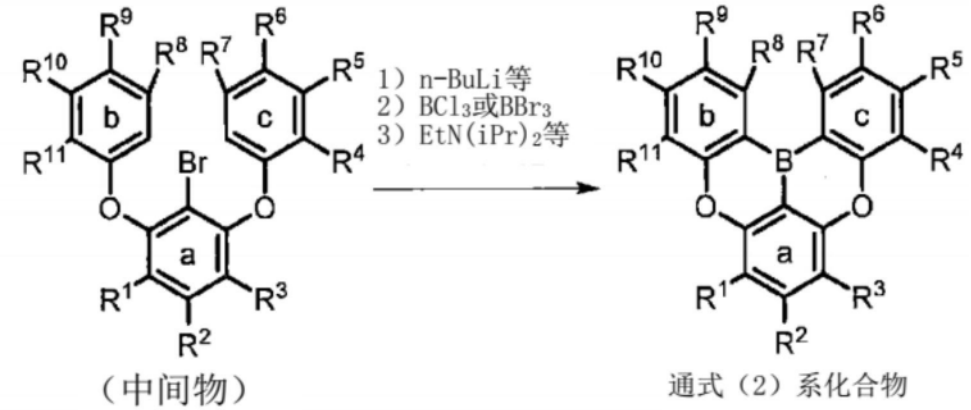
[0706] [化244]

流程（6）

[0707] 

[0708] [化245]

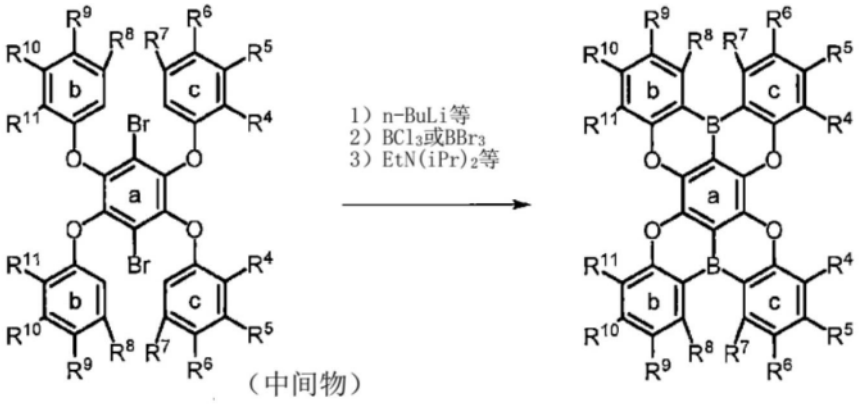
流程（7）

[0709] 

[0710] 另外,关于流程(3)中说明的多聚体的制造方法,也可如所述流程(6)及流程(7)那样在欲导入锂的位置上导入溴原子或氯原子等卤素,并也通过卤素-金属交换而朝所期望的位置上导入锂(下述流程(8)、流程(9)及流程(10))。

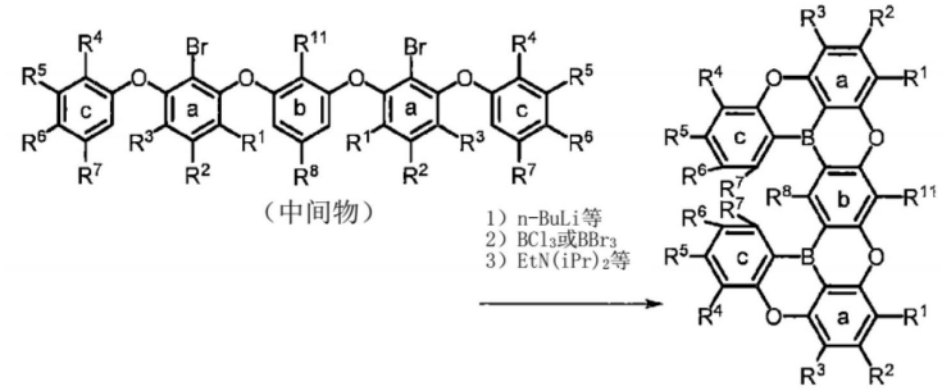
[0711] [化246]

流程（8）

[0712] 

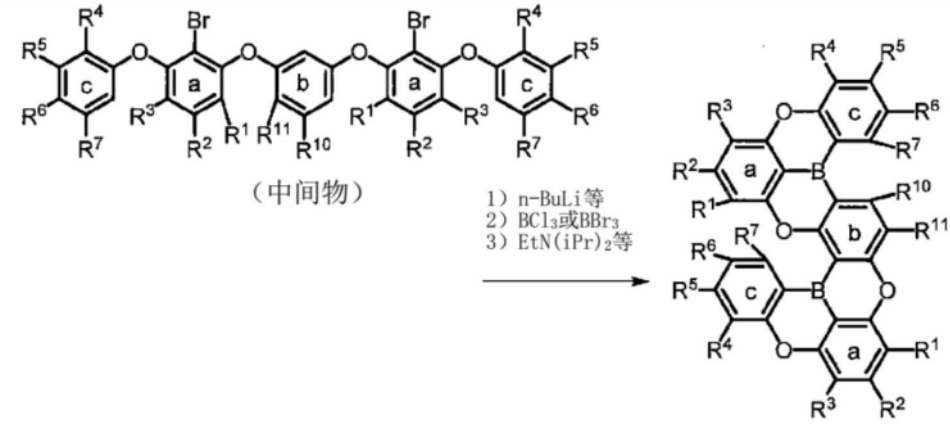
[0713] [化247]

流程（9）

[0714] 

[0715] [化248]

流程（10）

[0716] 

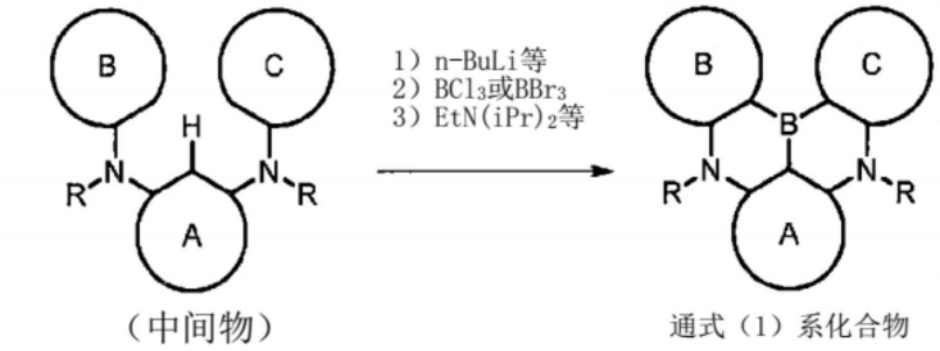
[0717] 根据所述方法,即便在因取代基的影响而无法进行邻位金属化的情况下也可合成目标物,从而有用。

[0718] 通过适当选择所述合成法,且也适当选择所使用的原料,可合成所期望的位置经环烷烃缩合、在所期望的位置上具有取代基、且Y^1为硼原子、X^1及X^2为氧原子的多环芳香族化合物及其多聚体。

[0719] 继而,将Y^1为硼原子、X^1及X^2为氮原子的情况作为例子而示于下述流程(11)及流程(12)中。与X^1及X^2为氧原子的情况同样地,首先,利用正丁基锂等对X^1与X^2之间的氢原子进行邻位金属化。继而,加入三溴化硼等,进行锂-硼的金属交换后,加入N,N-二异丙基乙胺等布忍斯特碱,由此进行串联式硼杂夫里德耳-夸夫特反应,从而可获得目标物。此处,为了促进反应,也可加入三氯化铝等路易斯酸。另外,在这些反应步骤中的某处,使用经环烷烃缩合的原料、或者追加缩合环烷烃的步骤,由此,可制造所期望的位置经环烷烃缩合的本发明的化合物。

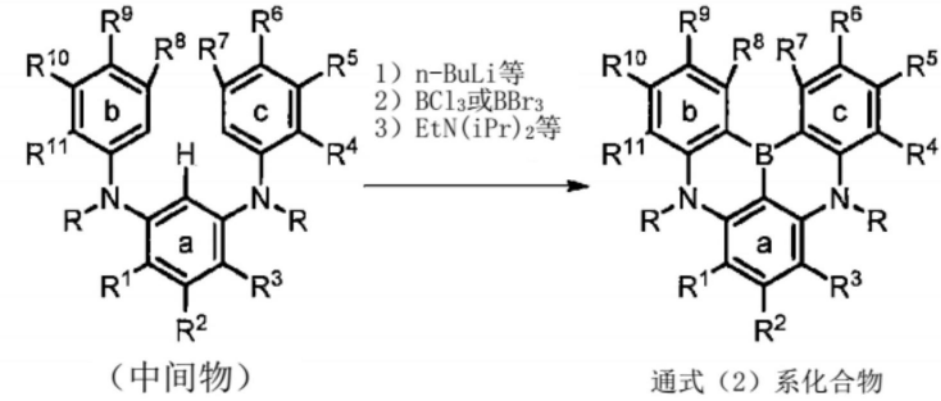
[0720] [化249]

流程（11）

[0721] 

[0722] [化250]

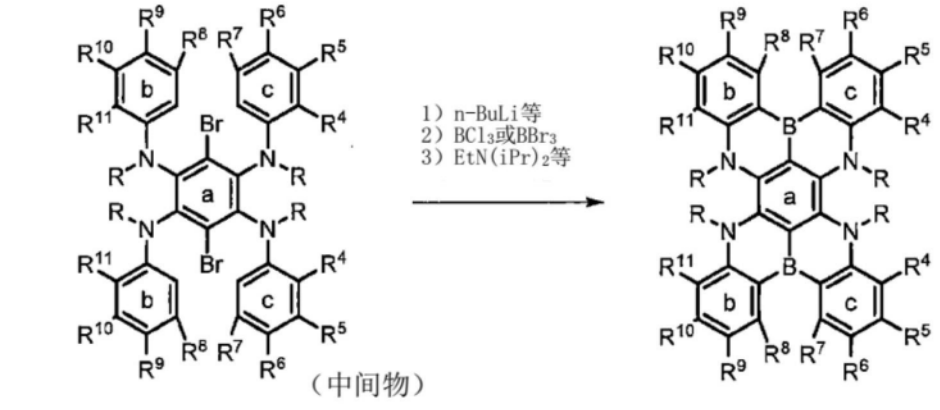
流程（12）

[0723] 

[0724] 另外，关于Y^1为硼原子、X^1及X^2为氮原子时的多聚体，也可如所述流程(6)及流程(7)那样在欲导入锂的位置上导入溴原子或氯原子等卤素，并也通过卤素-金属交换而朝所期望的位置上导入锂(下述流程(13)、流程(14)及流程(15))。

[0725] [化251]

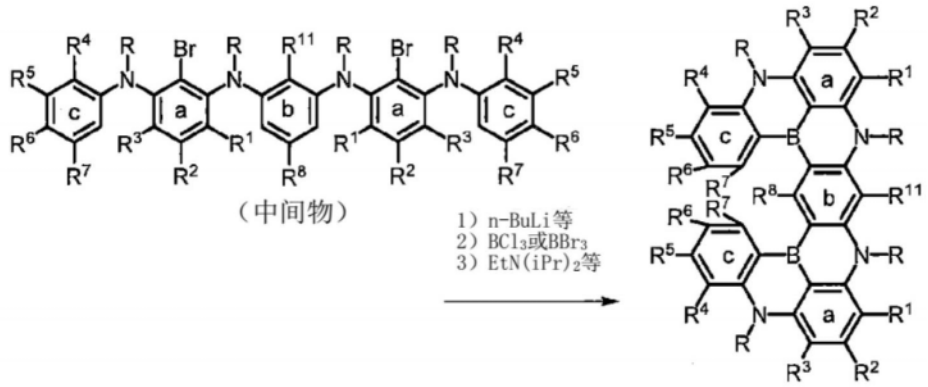
流程（13）

[0726] 

[0727] [化252]

流程（14）

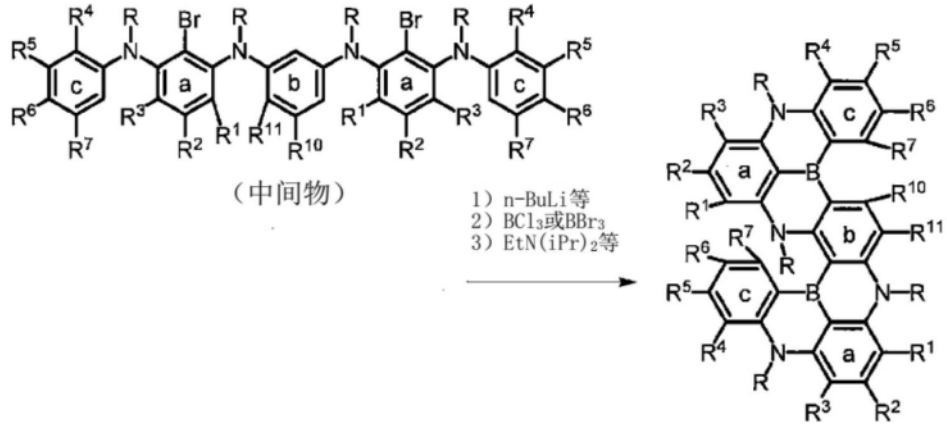
[0728]



[0729] [化253]

流程（15）

[0730]

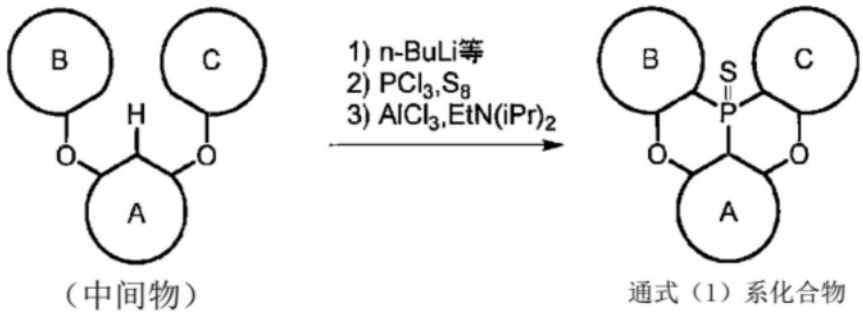


[0731] 继而，将Y^1为硫化磷、氧化磷或磷原子，X^1及X^2为氧原子的情况作为例子而示于下述流程(16)～流程(19)中。与迄今为止同样地，首先利用正丁基锂等对X^1与X^2之间的氢原子进行邻位金属化。继而，依次添加三氯化磷、硫，最后加入三氯化铝等路易斯酸及N,N-二异丙基乙胺等布忍斯特碱，由此进行串联式磷杂夫里德耳-夸夫特反应(Tandem Phospha-Friedel-Crafts Reaction)，从而可获得Y^1为硫化磷的化合物。另外，通过利用间氯过苯甲酸(m-chloroperbenzoic acid,m-CPBA)对所获得的硫化磷化合物进行处理而可获得Y^1为氧化磷的化合物，通过利用三乙基膦进行处理而可获得Y^1为磷原子的化合物。另外，在这些反应步骤中的某处，使用经环烷烃缩合的原料、或者追加缩合环烷烃的步骤，由此，可制造所期望的位置经环烷烃缩合的本发明的化合物。

[0732] [化254]

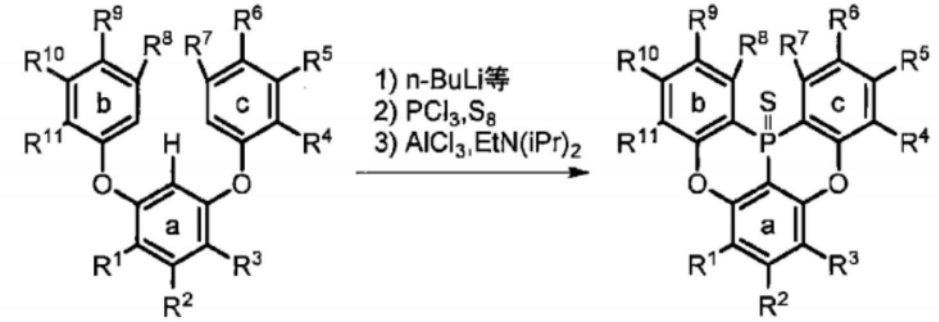
流程（16）

[0733]



[0734] [化255]

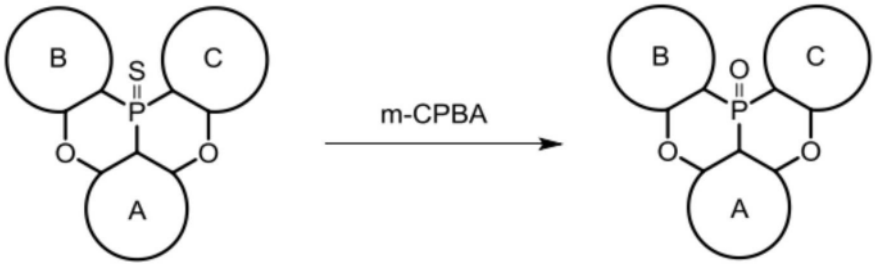
流程（17）

[0735] 

（中间物） 通式（2）系化合物

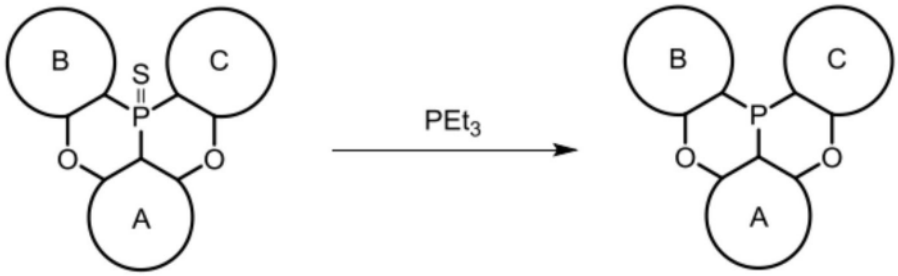
[0736] [化256]

流程（18）

[0737] 

[0738] [化257]

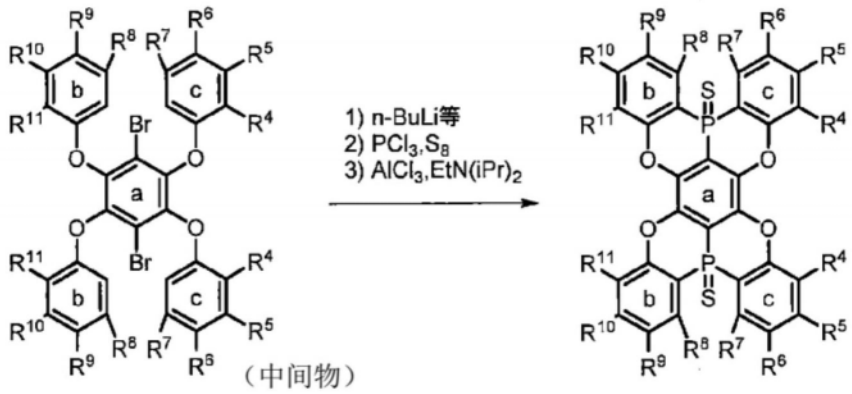
流程（19）

[0739] 

[0740] 另外,关于Y^1为硫化磷、X^1及X^2为氧原子时的多聚体,也可如所述流程(6)及流程(7)那样在欲导入锂的位置上导入溴原子或氯原子等卤素,并也通过卤素-金属交换而朝所期望的位置上导入锂(下述流程(20)、流程(21)及流程(22))。另外,以所述方式形成的Y^1为硫化磷、X^1及X^2为氧原子时的多聚体也如所述流程(18)及流程(19)那样,通过利用间氯过苯甲酸(m-CPBA)进行处理而可获得Y^1为氧化磷的化合物,通过利用三乙基膦进行处理而可获得Y^1为磷原子的化合物。

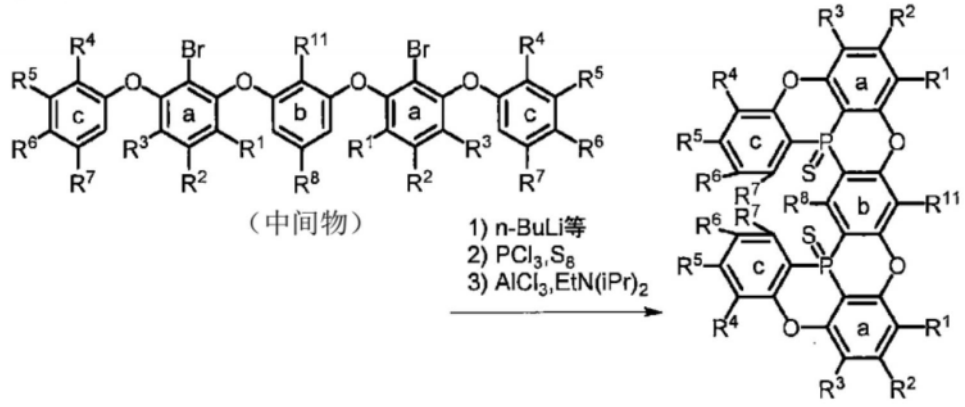
[0741] [化258]

[0742] 流程（20）



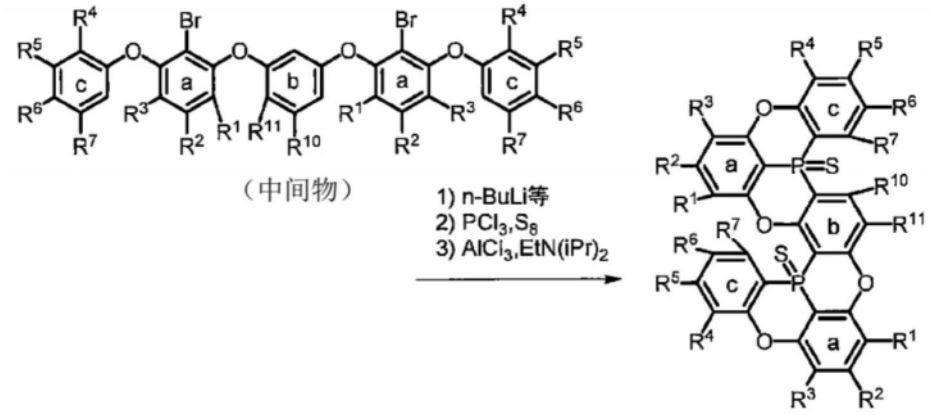
[0743] [化259]

[0744] 流程（21）



[0745] [化260]

[0746] 流程（22）



[0747] 此处，记载了Y^1为B、P、P＝O或P＝S，X^1及X^2为O或NR的例子，但通过适当变更原料，也可合成Y^1为Al、Ga、As、Si-R或Ge-R，或者X^1及X^2为S的化合物。

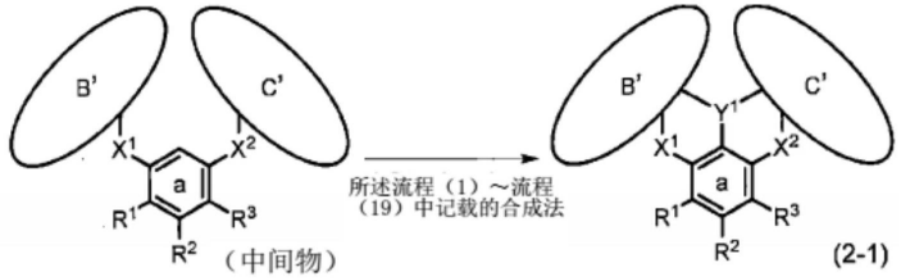
[0748] 以上的反应中所使用的溶媒的具体例为叔丁基苯或二甲苯等。

[0749] 另外，通式(2)中，a环、b环及c环的取代基R^1～R^{11}中的邻接的基彼此可键结并与a环、b环或c环一同形成芳基环或杂芳基环，所形成的环中的至少一个氢可由芳基或杂芳基取代。因此，通式(2)所表示的多环芳香族化合物根据a环、b环及c环中的取代基的相互的键结形态，如下述流程(23)及流程(24)的式(2-1)及式(2-2)所示，构成化合物的环结构发生变化。这些化合物可通过将所述流程(1)～流程(19)中示出的合成法应用于下述流程(23)

及流程(24)中所示的中间物来合成。另外,在这些反应步骤中的某处,使用经环烷烃缩合的原料、或者追加缩合环烷烃的步骤,由此,可制造所期望的位置经环烷烃缩合的本发明的化合物。

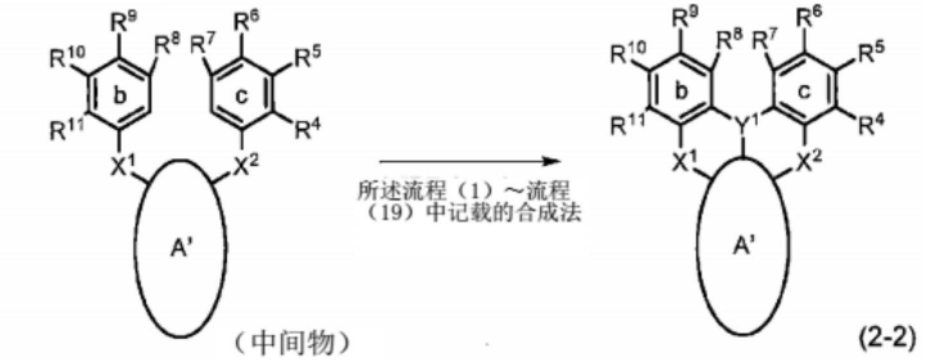
[0750] [化261]

[0751] 流程(23)



[0752] [化262]

[0753] 流程(24)

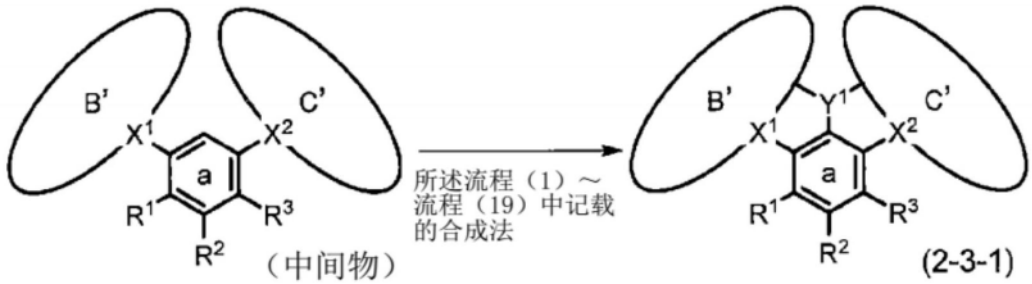


[0754] 所述式(2-1)及式(2-2)中的A'环、B'环及C'环表示取代基R^1～R^{11}中的邻接的基彼此键结并分别与a环、b环及c环一同形成的芳基环或杂芳基环(也可称为其他环结构在a环、b环或c环中缩合而成的缩合环)。再者,虽然式中未表示,但也存在a环、b环及c环全部变化成A'环、B'环及C'环的化合物。

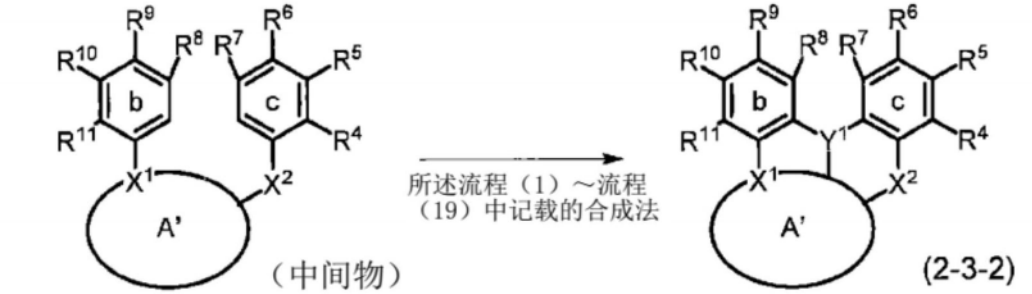
[0755] 另外,通式(2)中的"所述＞N-R的R及所述＞-C(-R)$_2$-的R的至少一个通过-O-、-S-、-C(-R)$_2$-或单键而与所述a环、b环及c环的至少一个键结"的规定可由如下的化合物来表现,所述化合物是由下述流程(25)的式(2-3-1)表示、且具有X^1或X^2被导入至缩合环B'及缩合环C'的环结构,或者由式(2-3-2)或式(2-3-3)表示、且具有X^1或X^2被导入至缩合环A'的环结构。这些化合物可通过将所述流程(1)～流程(19)中示出的合成法应用于下述流程(25)中示出的中间物来合成。另外,在这些反应步骤中的某处,使用经环烷烃缩合的原料、或者追加缩合环烷烃的步骤,由此,可制造所期望的位置经环烷烃缩合的本发明的化合物。

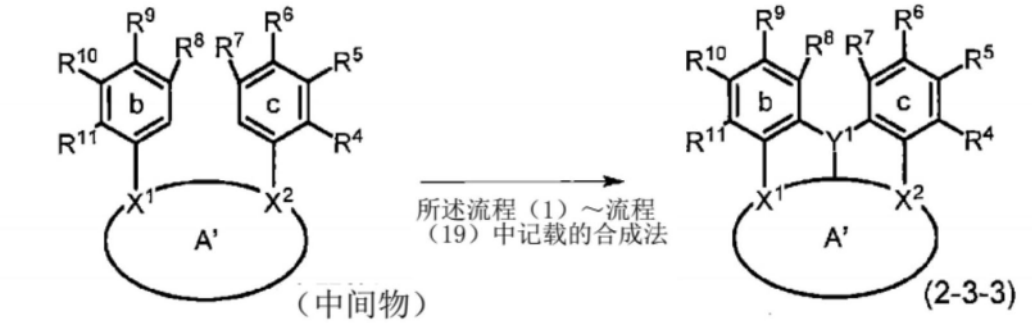
[0756] [化263]

流程（25）



[0757]



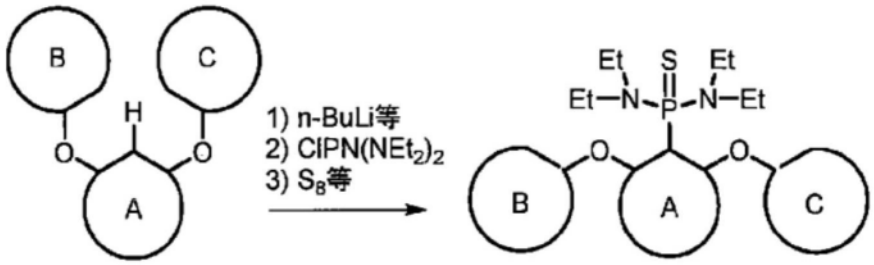


[0758] 另外,在所述流程(1)～流程(17)及流程(20)～流程(25)的合成法中,表示在加入三氯化硼或三溴化硼等之前,利用丁基锂等对X^1与X^2之间的氢原子(或卤素原子)进行邻位金属化,由此进行串联式杂夫里德耳-夸夫特反应的例子,但也可不进行利用丁基锂等的邻位金属化,而通过添加三氯化硼或三溴化硼等来进行反应。

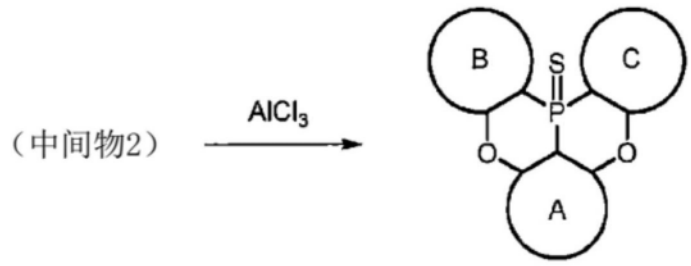
[0759] 另外,在Y^1为磷系的情况下,如下述流程(26)或流程(27)所示,利用正丁基锂、仲丁基锂或叔丁基锂等对X^1与X^2(下述式中为O)之间的氢原子进行邻位金属化,继而加入双(二乙氨基)氯膦,进行锂-磷的金属交换后,加入三氯化铝等路易斯酸,由此进行串联式磷杂夫里德耳-夸夫特反应,从而可获得目标物。所述反应方法在国际公开第2010/104047号公报(例如27页)中也有记载。另外,在这些反应步骤中的某处,使用经环烷烃缩合的原料、或者追加缩合环烷烃的步骤,由此,可制造所期望的位置经环烷烃缩合的本发明的化合物。

[0760] [化264]

流程（26）



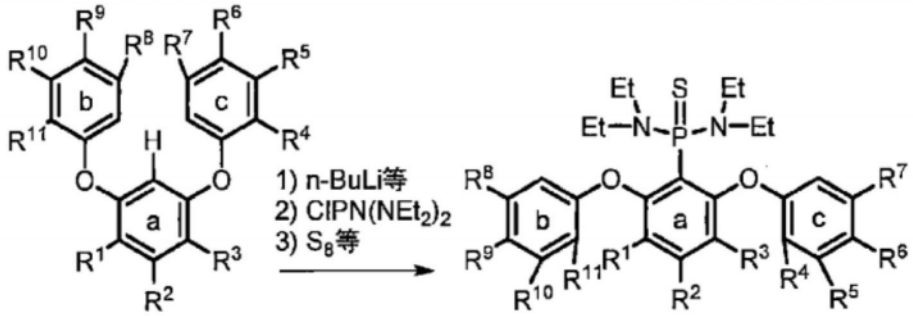
[0761] （中间物1） （中间物2）



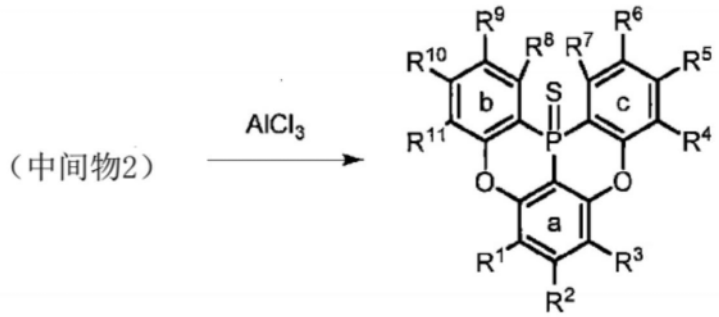
通式（1）系化合物

[0762] [化265]

流程（27）



[0763] （中间物1） （中间物2）



通式（2）系化合物

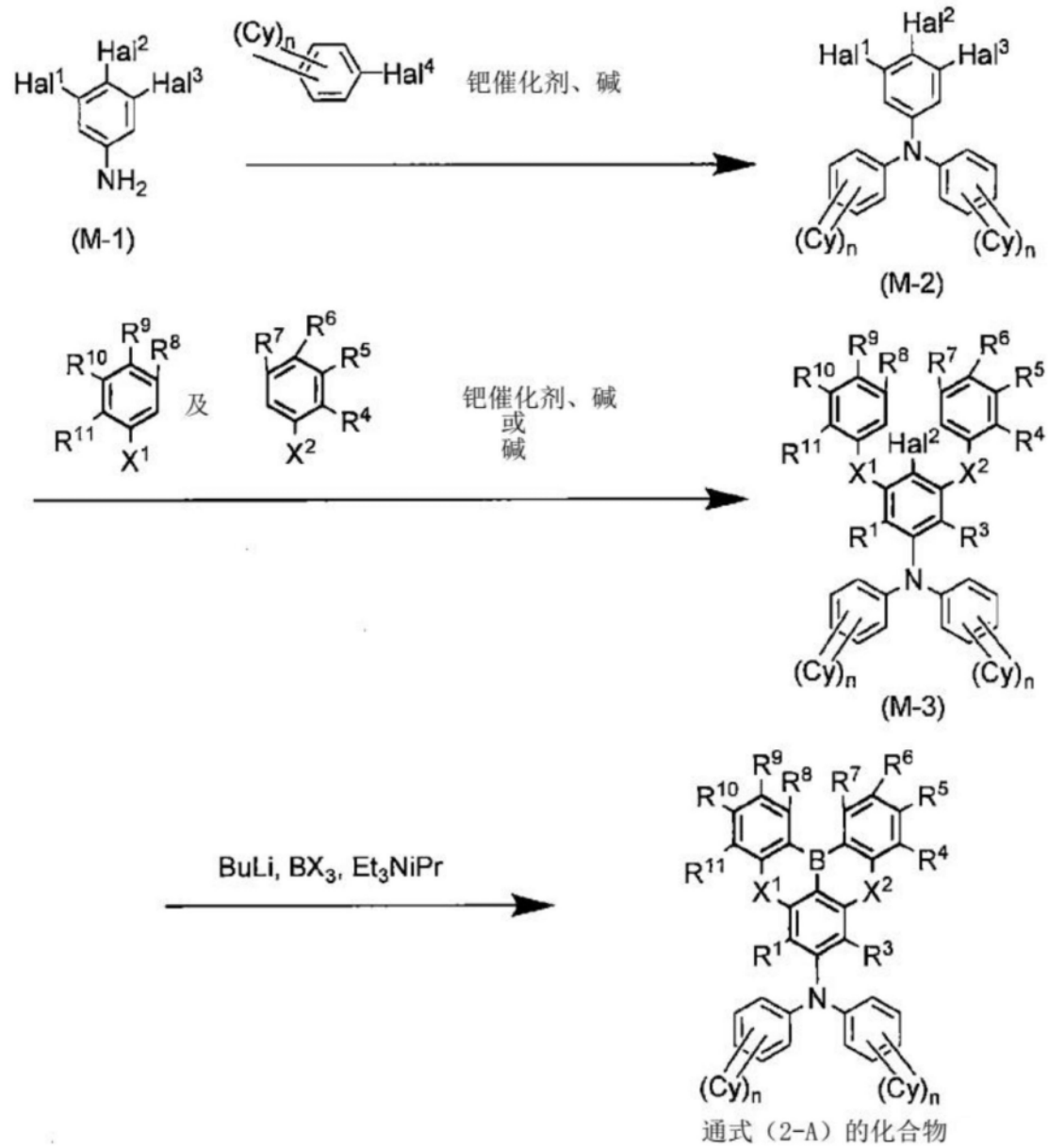
[0764] 再者，在所述流程(26)或流程(27)中，相对于中间物1的摩尔量，使用2倍、3倍的摩尔量的丁基锂等邻位金属化试剂，由此也可合成多聚体化合物。另外，在欲导入锂等金属的位置上事先导入溴原子或氯原子等卤素，并进行卤素-金属交换，由此可朝所期望的位置上导入金属。

[0765] 此外，关于通式(2-A)所表示的多环芳香族化合物，如下述流程(28)那样，合成经

环烷烃缩合的中间物,并使其环化,由此可合成所期望的位置由环烷烃缩合的多环芳香族化合物。流程(28)中,X表示卤素或氢,其他符号的定义与通式(20)中的符号的定义相同。

[0766] [化266]

流程(28)



[0767]

[0768] 流程(28)中的环化前的中间物也可利用流程(1)等所示的方法来合成。即,可通过将布赫瓦尔德-哈特维希反应或铃木偶合反应、或者利用亲核取代反应或乌尔曼反应等的醚化反应等适当组合来合成具有所期望的取代基的中间物。在这些反应中,成为经环烷烃缩合的前体的原料也可利用市售品。

[0769] 具有经环烷烃缩合的二苯基氨基的通式(2-A)的化合物例如也可利用如下方法来合成。即,对环烷烃缩合溴苯与三卤化苯胺通过如布赫瓦尔德-哈特维希反应那样的氨基化反应导入经环烷烃缩合的二苯基氨基后,在X^1、X^2为N-R的情况下,利用如布赫瓦尔德-哈特维希反应那样的氨基化反应而衍生为中间物(M-3),在X^1、X^2为O的情况下,通过使用苯酚的醚化而衍生为中间物(M-3),其后,例如通过使丁基锂那样的金属化试剂发挥作用并进行反

式金属化、之后使三溴化硼那样的卤化硼发挥作用、之后使二乙基异丙基胺那样的布忍斯特碱发挥作用的串联式硼杂夫里德耳-夸夫特反应,而可合成通式(2-A)的化合物。这些反应也可应用于其他经环烷烃缩合的化合物。

[0770] 再者,作为所述流程(1)~流程(28)中所使用的邻位金属化试剂,可列举:甲基锂、正丁基锂、仲丁基锂、叔丁基锂等烷基锂,二异丙基酰胺锂、四甲基哌啶化锂、六甲基二硅胺化锂、六甲基二硅胺化钾等有机碱性化合物、有机溶媒分散Na等分散碱金属。

[0771] 再者,作为所述流程(1)~流程(28)中所使用的金属-Y^1的金属交换试剂,可列举:Y^1的三氟化物、Y^1的三氯化物、Y^1的三溴化物、Y^1的三碘化物等Y^1的卤化物,$ClPN(NEt_2)_2$等Y^1的氨基化卤化物,Y^1的烷氧基化物,Y^1的芳氧基化物等。

[0772] 再者,作为所述流程(1)~流程(28)中所使用的布忍斯特碱,可列举:N,N-二异丙基乙胺、三乙胺、2,2,6,6-四甲基哌啶、1,2,2,6,6-五甲基哌啶、N,N-二甲基苯胺、N,N-二甲基甲苯胺、2,6-二甲吡啶、四苯基硼酸钠、四苯基硼酸钾、三苯基硼烷、四苯基硅烷、Ar_4BNa、Ar_4BK、Ar_3B、Ar_4Si(再者,Ar为苯基等芳基)等。

[0773] 作为所述流程(1)~流程(28)中所使用的路易斯酸,可列举:$AlCl_3$、$AlBr_3$、AlF_3、$BF_3 \cdot OEt_2$、BCl_3、BBr_3、$GaCl_3$、$GaBr_3$、$InCl_3$、$InBr_3$、$In(OTf)_3$、$SnCl_4$、$SnBr_4$、AgOTf、$ScCl_3$、$Sc(OTf)_3$、$ZnCl_2$、$ZnBr_2$、$Zn(OTf)_2$、$MgCl_2$、$MgBr_2$、$Mg(OTf)_2$、LiOTf、NaOTf、KOTf、Me_3SiOTf、$Cu(OTf)_2$、$CuCl_2$、YCl_3、$Y(OTf)_3$、$TiCl_4$、$TiBr_4$、$ZrCl_4$、$ZrBr_4$、$FeCl_3$、$FeBr_3$、$CoCl_3$、$CoBr_3$等。

[0774] 在所述流程(1)~流程(28)中,为了促进串联式杂夫里德耳-夸夫特反应,也可使用布忍斯特碱或路易斯酸。其中,在使用Y^1的三氟化物、Y^1的三氯化物、Y^1的三溴化物、Y^1的三碘化物等Y^1的卤化物的情况下,随着芳香族亲电子取代反应的进行,而生成氟化氢、氯化氢、溴化氢、碘化氢等酸,因此使用捕捉酸的布忍斯特碱是有效的。另一方面,在使用Y^1的氨基化卤化物、Y^1的烷氧基化物的情况下,随着芳香族亲电子取代反应的进行,而生成胺、醇,因此在多数情况下,无需使用布忍斯特碱,但因氨基或烷氧基的脱离能力低,因此使用促进其脱离的路易斯酸是有效的。

[0775] 另外,本发明的多环芳香族化合物或其多聚体中也包含至少一部分的氢原子由氘或氰基取代的化合物或者由氟或氯等卤素取代的化合物,此种化合物等可通过使用所期望的位置被氘化、氰化、氟化或氯化的原料而与所述同样地合成。

[0776] 3.有机元件

[0777] 本发明的经环烷烃缩合的多环芳香族化合物可用作有机元件用材料。作为有机元件,例如可列举:有机电致发光元件、有机场效晶体管或有机薄膜太阳电池等。

[0778] 3-1.有机电致发光元件

[0779] 以下,基于附图对本实施方式的有机EL元件进行详细说明。图1是表示本实施方式的有机EL元件的概略剖面图。

[0780] <有机电致发光元件的结构>

[0781] 图1所示的有机EL元件100包括:基板101、设置于基板101上的阳极102、设置于阳极102上的空穴注入层103、设置于空穴注入层103上的空穴传输层104、设置于空穴传输层104上的发光层105、设置于发光层105上的电子传输层106、设置于电子传输层106上的电子注入层107、以及设置于电子注入层107上的阴极108。

[0782] 再者,有机EL元件100也可使制作顺序相反而形成例如以下的结构,所述结构包

括:基板101、设置于基板101上的阴极108、设置于阴极108上的电子注入层107、设置于电子注入层107上的电子传输层106、设置于电子传输层106上的发光层105、设置于发光层105上的空穴传输层104、设置于空穴传输层104上的空穴注入层103、以及设置于空穴注入层103上的阳极102。

[0783] 并非需要所述各层的全部,将最小构成单元设为包括阳极102、发光层105及阴极108的结构,空穴注入层103、空穴传输层104、电子传输层106、电子注入层107是任意设置的层。另外,所述各层可分别包含单一层,也可包含多层。

[0784] 作为构成有机EL元件的层的形态,除所述“基板/阳极/空穴注入层/空穴传输层/发光层/电子传输层/电子注入层/阴极”的结构形态以外,也可为“基板/阳极/空穴传输层/发光层/电子传输层/电子注入层/阴极”、“基板/阳极/空穴注入层/发光层/电子传输层/电子注入层/阴极”、“基板/阳极/空穴注入层/空穴传输层/发光层/电子注入层/阴极”、“基板/阳极/空穴注入层/空穴传输层/发光层/电子传输层/阴极”、“基板/阳极/发光层/电子传输层/电子注入层/阴极”、“基板/阳极/空穴传输层/发光层/电子注入层/阴极”、“基板/阳极/空穴传输层/发光层/电子传输层/阴极”、“基板/阳极/空穴注入层/发光层/电子注入层/阴极”、“基板/阳极/空穴注入层/发光层/电子传输层/阴极”、“基板/阳极/发光层/电子传输层/阴极”、“基板/阳极/发光层/电子注入层/阴极”的结构形态。

[0785] <有机电致发光元件中的基板>

[0786] 基板101为有机EL元件100的支撑体,通常使用石英、玻璃、金属、塑料等。基板101根据目的而形成为板状、膜状或片状,例如可使用玻璃板、金属板、金属箔、塑料膜、塑料片等。其中,优选为玻璃板及聚酯、聚甲基丙烯酸酯、聚碳酸酯、聚砜等的透明的合成树脂制的板。若为玻璃基板,则可使用钠钙玻璃或无碱玻璃等,另外,厚度也只要有足以保持机械强度的厚度即可,因此例如只要有0.2mm以上即可。厚度的上限值例如为2mm以下,优选为1mm以下。关于玻璃的材质,因来自玻璃的溶出离子越少越好,因此优选为无碱玻璃,由于施加了SiO_2等的隔离涂层的钠钙玻璃也有市售,因此可使用所述钠钙玻璃。另外,为了提高阻气性,也可在基板101的至少一面上设置细密的氧化硅膜等阻气膜,尤其在将阻气性低的合成树脂制的板、膜或片用作基板101的情况下,优选为设置阻气膜。

[0787] <有机电致发光元件中的阳极>

[0788] 阳极102发挥朝发光层105中注入空穴的作用。再者,在在阳极102与发光层105之间设置有空穴注入层103及空穴传输层104的至少一个层的情况下,经由这些层朝发光层105中注入空穴。

[0789] 作为形成阳极102的材料,可列举无机化合物及有机化合物。作为无机化合物,例如可列举:金属(铝、金、银、镍、钯、铬等)、金属氧化物(铟的氧化物、锡的氧化物、铟-锡氧化物(Indium Tin Oxide,ITO)、铟-锌氧化物(Indium Zinc Oxide,IZO)等)、卤化金属(碘化铜等)、硫化铜、碳黑、ITO玻璃或奈塞(NESA)玻璃等。作为有机化合物,例如可列举:聚(3-甲基噻吩)等聚噻吩、聚吡咯、聚苯胺等导电性聚合物等。此外,可自用作有机EL元件的阳极的物质中适当选择来使用。

[0790] 透明电极的电阻只要可供给对于发光元件的发光而言充分的电流即可,因此并无限定,但就发光元件的消耗电力的观点而言,理想的是低电阻。例如,若为300Ω/Y以下的ITO基板,则作为元件电极发挥功能,但现在也能够供给10Ω/Y左右的基板,因此特别理想

的是使用例如100Ω/Y～5Ω/Y,优选为50Ω/Y～5Ω/Y的低电阻品。ITO的厚度可配合电阻值而任意地选择,但通常在50nm～300nm之间使用的情况多。

[0791] ＜有机电致发光元件中的空穴注入层、空穴传输层＞

[0792] 空穴注入层103发挥将自阳极102迁移而来的空穴高效地注入至发光层105内或空穴传输层104内的作用。空穴传输层104发挥将自阳极102所注入的空穴或自阳极102经由空穴注入层103所注入的空穴高效地传输至发光层105的作用。空穴注入层103及空穴传输层104分别将空穴注入·传输材料的一种或两种以上加以层叠、混合而形成,或者由空穴注入·传输材料与高分子粘结剂的混合物形成。另外,也可向空穴注入·传输材料中添加如氯化铁(III)那样的无机盐来形成层。

[0793] 作为空穴注入·传输性物质,需要在施加有电场的电极间高效地注入·传输来自正极的空穴,理想的是空穴注入效率高且高效地传输所注入的空穴。因此,优选为电离电位小、且空穴迁移率大、进而稳定性优异、在制造时及使用时不易产生成为陷阱(trap)的杂质的物质。

[0794] 作为形成空穴注入层103及空穴传输层104的材料,可自在光导电材料中作为空穴的电荷传输材料一直以来所惯用的化合物,用于p型半导体、有机EL元件的空穴注入层及空穴传输层的已知的化合物中选择任意的化合物来使用。这些材料的具体例为咔唑衍生物(N-苯基咔唑、聚乙烯咔唑等)、双(N-芳基咔唑)或双(N-烷基咔唑)等双咔唑衍生物、三芳基胺衍生物(主链或侧链上具有芳香族三级氨基的聚合物、1,1-双(4-二-对甲苯基氨基苯基)环已烷、N,N'-二苯基-N,N'-二(3-甲基苯基)-4,4'-二氨基联苯、N,N'-二苯基-N,N'-二萘基-4,4'-二氨基联苯、N,N'-二苯基-N,N'-二(3-甲基苯基)-4,4'-二苯基-1,1'-二胺、N,N'-二萘基-N,N'-二苯基-4,4'-二苯基-1,1'-二胺、N^4,N^4'-二苯基-N^4,N^4'-双(9-苯基-9H-咔唑-3-基)-[1,1'-联苯基]-4,4'-二胺、N^4,N^4,N^4',N^4'-四[1,1'-联苯]-4-基)-[1,1'-联苯基]-4,4'-二胺、4,4',4"-三(3-甲基苯基(苯基)氨基)三苯基胺等三苯基胺衍生物、星爆状胺衍生物等)、二苯乙烯衍生物、酞青衍生物(无金属、铜酞青等)、吡唑啉衍生物、腙系化合物、苯并呋喃衍生物或噻吩衍生物、噁二唑衍生物、喹噁啉衍生物(例如1,4,5,8,9,12-六氮杂三亚苯-2,3,6,7,10,11-六碳腈等)、卟啉衍生物等杂环化合物、聚硅烷等。聚合物系中,优选为侧链上具有所述单体的聚碳酸酯或苯乙烯衍生物、聚乙烯咔唑及聚硅烷等,但只要是形成发光元件的制作所需的薄膜,可自阳极注入空穴,进而可传输空穴的化合物,则并无特别限定。

[0795] 另外,有机半导体的导电性因其掺杂而受到强烈影响这一点也为人所知。此种有机半导体基质物质包含供电子性良好的化合物、或电子接受性良好的化合物。为了掺杂供电子物质,已知有四氰基醌二甲烷(Tetracyanoquinodimethane,TCNQ)或2,3,5,6-四氟四氰基-1,4-苯醌二甲烷(2,3,5,6-tetrafluorotetracyano-1,4-benzoquinodimethane,F4TCNQ)等强电子接受体(例如,参照文献《M.法伊弗,A.拜尔,T.弗里茨,K.利奥(M.Pfeiffer,A.Beyer,T.Fritz,K.Leo),应用物理学快报(Appl.Phys.Lett.),73(22),3202-3204(1998)》及文献《J.布洛赫维茨,M.法伊弗,T.弗里茨,K.利奥(J.Blochwitz,M.Pheiffer,T.Fritz,K.Leo),应用物理学快报(Appl.Phys.Lett.),73(6),729-731(1998)》)。这些通过供电子型基础物质(空穴传输物质)的电子迁移过程而生成所谓的空穴。基础物质的传导性根据空穴的数量及迁移率而产生相当大的变化。作为具有空穴传输

特性的基质物质,已知有例如联苯胺衍生物(TPD等)或星爆状胺衍生物(4,4',4"-三(N,N-二苯基氨基)三苯胺(4,4',4"-tris(N,N-diphenylamino)triphenylamine,TDATA)等)、或者特定的金属酞青(尤其是锌酞青(ZnPc)等)(日本专利特开2005-167175号公报)。

[0796] 所述空穴注入层用材料及空穴传输层用材料也可作为如下的高分子化合物或其高分子交联体、或者如下的悬挂型高分子化合物或其悬挂型高分子交联体而用于空穴层用材料,其中,所述高分子化合物是使在所述空穴注入层用材料及空穴传输层用材料中取代有反应性取代基的反应性化合物作为单体进行高分子化而成,所述悬挂型高分子化合物是使主链型高分子与所述反应性化合物反应而成。作为所述情况下的反应性取代基,可引用式(1)所表示的多环芳香族化合物中的说明。

[0797] 关于此种高分子化合物及高分子交联体的用途的详细情况,在后文叙述。

[0798] <有机电致发光元件中的发光层>

[0799] 发光层105是通过在施加有电场的电极间,使自阳极102所注入的空穴与自阴极108所注入的电子再结合而发光的层。形成发光层105的材料只要为通过空穴与电子的再结合而得到激发来发光的化合物(发光性化合物)即可,优选为可形成稳定的薄膜形状、且在固体状态下显示强的发光(荧光)效率的化合物。在本发明中,作为发光层用的材料,可使用主体材料、与例如作为掺杂剂材料的所述通式(1)所表示的多环芳香族化合物。

[0800] 发光层可为单一层,也可包含多层,任一者均可,且分别由发光层用材料(主体材料、掺杂剂材料)形成。主体材料与掺杂剂材料分别可为一种,也可为多种的组合,任一者均可。掺杂剂材料可包含于主体材料整体内,也可包含于部分主体材料内,任一者均可。作为掺杂方法,可通过与主体材料的共蒸镀法来形成,也可事先与主体材料混合后同时蒸镀。

[0801] 主体材料的使用量根据主体材料的种类而不同,只要配合所述主体材料的特性来决定即可。主体材料的使用量的基准优选为发光层用材料整体的50重量%~99.999重量%,更优选为80重量%~99.95重量%,进而优选为90重量%~99.9重量%。

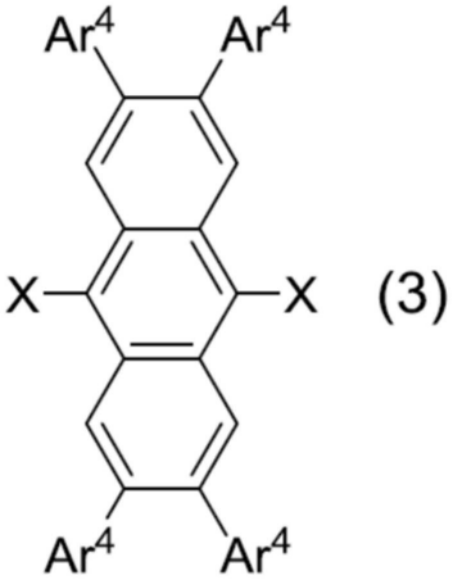
[0802] 掺杂剂材料的使用量根据掺杂剂材料的种类而不同,只要配合所述掺杂剂材料的特性来决定即可。掺杂剂的使用量的基准优选为整个发光层用材料的0.001重量%~50重量%,更优选为0.05重量%~20重量%,进而优选为0.1重量%~10重量%。若为所述范围,则例如就可防止浓度淬灭现象的方面而言优选。

[0803] 主体材料可列举自以前作为发光体已知的蒽、芘、二苯并䓛或芴等缩合环衍生物、双苯乙烯基蒽衍生物或二苯乙烯基苯衍生物等双苯乙烯基衍生物、四苯基丁二烯衍生物、环戊二烯衍生物等。特别优选为蒽系化合物、芴系化合物或二苯并䓛系化合物。

[0804] <蒽系化合物>

[0805] 作为主体的蒽系化合物例如为下述通式(3)所表示的化合物。

[0806] [化267]

[0807] 

[0808] 式(3)中,

[0809] X及Ar^4分别独立地为氢、可被取代的芳基、可被取代的杂芳基、可被取代的二芳基氨基、可被取代的二杂芳基氨基、可被取代的芳基杂芳基氨基、可被取代的烷基、可被取代的环烷基、可被取代的烯基、可被取代的烷氧基、可被取代的芳氧基、可被取代的芳硫基或可被取代的硅烷基,全部的X及Ar^4不会同时成为氢,

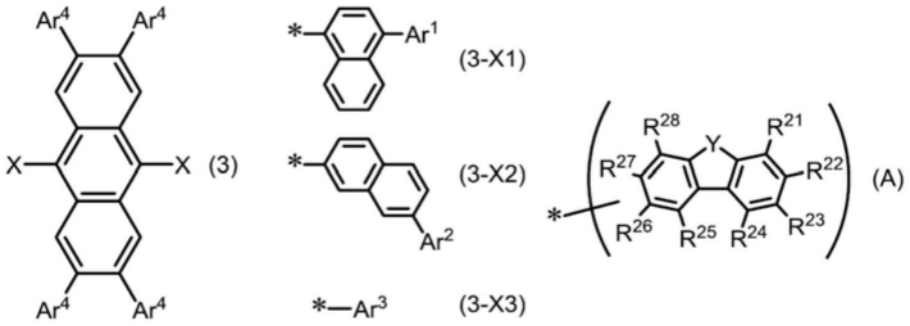
[0810] 式(3)所表示的化合物中的至少一个氢可由卤素、氰基、氘或可被取代的杂芳基取代。

[0811] 另外,也可将式(3)所表示的结构作为单元结构来形成多聚体(优选为二聚体)。所述情况下,例如可列举式(3)所表示的单元结构彼此经由X而键结的形态,作为所述X,可列举:单键、亚芳基(亚苯基、亚联苯基及亚萘基等)及亚杂芳基(吡啶环、二苯并呋喃环、二苯并噻吩环、咔唑环、苯并咔唑环及苯基取代咔唑环等具有二价成键价的基)等。

[0812] 所述芳基、杂芳基、二芳基氨基、二杂芳基氨基、芳基杂芳基氨基、烷基、环烷基、烯基、烷氧基、芳氧基、芳硫基或硅烷基的详细情况在以下的优选形态一栏中进行说明。另外,作为针对这些基的取代基,可列举:芳基、杂芳基、二芳基氨基、二杂芳基氨基、芳基杂芳基氨基、烷基、环烷基、烯基、烷氧基、芳氧基、芳硫基或硅烷基等,这些基的详细情况也在以下的优选形态一栏中进行说明。

[0813] 以下对所述蒽系化合物的优选形态进行说明。下述结构中的符号的定义与以上所述的定义相同。

[0814] [化268]

[0815] 

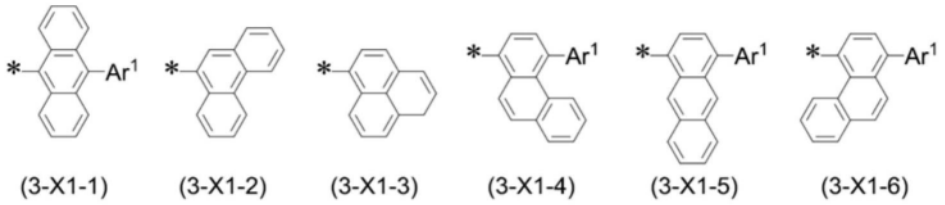
[0816] 通式(3)中,X分别独立地为所述式(3-X1)、式(3-X2)或式(3-X3)所表示的基,式(3-X1)、式(3-X2)或式(3-X3)所表示的基于*处与式(3)的蒽环键结。优选为两个X不会同时成为式(3-X3)所表示的基。更优选为两个X也不会同时成为式(3-X2)所表示的基。

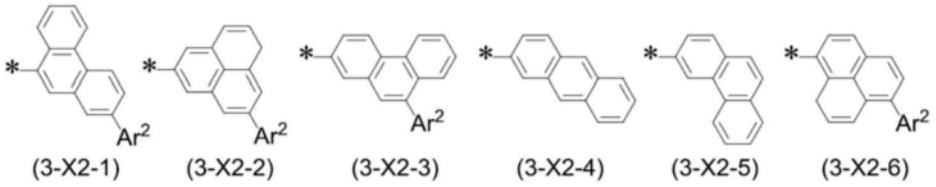
[0817] 另外,也可将式(3)所表示的结构作为单元结构来形成多聚体(优选为二聚体)。所述情况下,例如可列举式(3)所表示的单元结构彼此经由X而键结的形态,作为所述X,可列举:单键、亚芳基(亚苯基、亚联苯基及亚萘基等)及亚杂芳基(吡啶环、二苯并呋喃环、二苯并噻吩环、咔唑环、苯并咔唑环及苯基取代咔唑环等具有二价成键价的基)等。

[0818] 式(3-X1)及式(3-X2)中的亚萘基部位可由一个苯环缩合。以所述方式缩合而成的结构如下所示。

[0819] [化269]

[0820]





[0821] Ar^1及Ar^2分别独立地为氢、苯基、联苯基、联三苯基、联四苯基、萘基、菲基、芴基、苯并芴基、䓛基、三亚苯基、芘基、或所述式(A)所表示的基(也包含咔唑基、苯并咔唑基及苯基取代咔唑基)。再者,在Ar^1或Ar^2为式(A)所表示的基的情况下,式(A)所表示的基于其*处与式(3-X1)或式(3-X2)中的萘环键结。

[0822] Ar^3为苯基、联苯基、联三苯基、联四苯基、萘基、菲基、芴基、苯并芴基、䓛基、三亚苯基、芘基、或所述式(A)所表示的基(也包含咔唑基、苯并咔唑基及苯基取代咔唑基)。再者,在Ar^3为式(A)所表示的基的情况下,式(A)所表示的基在其*处与式(3-X3)中的直线所表示的单键键结。即,式(3)的蒽环与式(A)所表示的基直接键结。

[0823] 另外,Ar^3也可具有取代基,Ar^3中的至少一个氢进而可由碳数1~4的烷基、碳数5~10的环烷基、苯基、联苯基、联三苯基、萘基、菲基、芴基、䓛基、三亚苯基、芘基、或所述式(A)所表示的基(也包含咔唑基及苯基取代咔唑基)取代。再者,在Ar^3所具有的取代基为式(A)所表示的基的情况下,式(A)所表示的基在其*处与式(3-X3)中的Ar^3键结。

[0824] Ar^4分别独立地为氢、苯基、联苯基、联三苯基、萘基、或由碳数1~4的烷基(甲基、乙基、叔丁基等)和/或碳数5~10的环烷基取代的硅烷基。

[0825] 在硅烷基中进行取代的碳数1~4的烷基可列举甲基、乙基、丙基、异丙基、丁基、仲丁基、叔丁基、环丁基等,硅烷基中的三个氢分别独立地由这些烷基取代。

[0826] 作为具体的"由碳数1~4的烷基取代的硅烷基",可列举:三甲基硅烷基、三乙基硅烷基、三丙基硅烷基、三异丙基硅烷基、三丁基硅烷基、三-仲丁基硅烷基、三-叔丁基硅烷基、乙基二甲基硅烷基、丙基二甲基硅烷基、异丙基二甲基硅烷基、丁基二甲基硅烷基、仲丁

基二甲基硅烷基、叔丁基二甲基硅烷基、甲基二乙基硅烷基、丙基二乙基硅烷基、异丙基二乙基硅烷基、丁基二乙基硅烷基、仲丁基二乙基硅烷基、叔丁基二乙基硅烷基、甲基二丙基硅烷基、乙基二丙基硅烷基、丁基二丙基硅烷基、仲丁基二丙基硅烷基、叔丁基二丙基硅烷基、甲基二异丙基硅烷基、乙基二异丙基硅烷基、丁基二异丙基硅烷基、仲丁基二异丙基硅烷基、叔丁基二异丙基硅烷基等。

[0827] 在硅烷基中进行取代的碳数5～10的环烷基可列举:环戊基、环己基、环庚基、环辛基、环壬基、环癸基、降冰片烯基、双环[1.1.1]戊基、双环[2.0.1]戊基、双环[1.2.1]己基、双环[3.0.1]己基、双环[2.1.2]庚基、双环[2.2.2]辛基、金刚烷基、十氢萘基、十氢蒽基等,硅烷基中的三个氢分别独立地由这些环烷基取代。

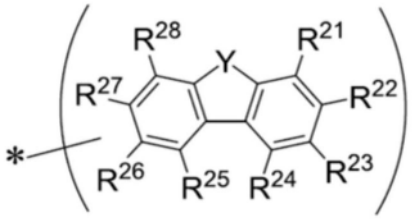
[0828] 作为具体的“由碳数5～10的环烷基取代的硅烷基”,可列举:三环戊基硅烷基、三环己基硅烷基等。

[0829] 作为经取代的硅烷基,也有两个烷基与一个环烷基取代而成的二烷基环烷基硅烷基、及一个烷基与两个环烷基取代而成的烷基二环烷基硅烷基,作为进行取代的烷基及环烷基的具体例,可列举所述基。

[0830] 另外,通式(3)所表示的蒽系化合物的化学结构中的氢也可由所述式(A)所表示的基取代。在由式(A)所表示的基取代的情况下,式(A)所表示的基在其*处与式(3)所表示的化合物中的至少一个氢进行取代。

[0831] 式(A)所表示的基为式(3)所表示的蒽系化合物可具有的取代基的一个。

[0832] [化270]

[0833] 

(A)

[0834] 所述式(A)中,Y为-O-、-S-或>N-R^{29},R^{21}～R^{28}分别独立地为氢、可被取代的烷基、可被取代的环烷基、可被取代的芳基、可被取代的杂芳基、可被取代的烷氧基、可被取代的芳氧基、可被取代的芳硫基、三烷基硅烷基、三环烷基硅烷基、二烷基环烷基硅烷基、烷基二环烷基硅烷基、可被取代的氨基、卤素、羟基或氰基,R^{21}～R^{28}中的邻接的基可彼此键结而形成烃环、芳基环或杂芳基环,R^{29}为氢或可被取代的芳基。

[0835] 作为R^{21}～R^{28}中的“可被取代的烷基”的“烷基”,可为直链及分支链的任一种,例如可列举碳数1～24的直链烷基或碳数3～24的分支链烷基。优选为碳数1～18的烷基(碳数3～18的分支链烷基),更优选为碳数1～12的烷基(碳数3～12的分支链烷基),进而优选为碳数1～6的烷基(碳数3～6的分支链烷基),特别优选为碳数1～4的烷基(碳数3～4的分支链烷基)。

[0836] 作为具体的“烷基”,可列举:甲基、乙基、正丙基、异丙基、正丁基、异丁基、仲丁基、叔丁基、正戊基、异戊基、新戊基、叔戊基(t-amyl)、正己基、1-甲基戊基、3,3-二甲基丁基、2-乙基丁基、正庚基、1-甲基己基、正辛基、叔辛基(1,1,3,3-四甲基丁基)、1-甲基庚基、2-乙基己基、2-丙基戊基、正壬基、2,2-二甲基庚基、2,6-二甲基-4-庚基、3,5,5-三甲基己基、正癸基、正十一基、1-甲基癸基、正十二基、正十三基、1-己基庚基、正十四基、正十五基、正

十六基、正十七基、正十八基、正二十基等。

[0837] 作为R^{21}～R^{28}中的“可被取代的环烷基”的“环烷基”,可列举:碳数3～24的环烷基、碳数3～20的环烷基、碳数3～16的环烷基、碳数3～14的环烷基、碳数5～10的环烷基、碳数5～8的环烷基、碳数5～6的环烷基、碳数5的环烷基等。

[0838] 作为具体的“环烷基”,可列举:环丙基、环丁基、环戊基、环己基、环庚基、环辛基、环壬基、环癸基、以及这些基的碳数1～4的烷基(尤其是甲基)取代物、或降冰片烯基、双环[1.0.1]丁基、双环[1.1.1]戊基、双环[2.0.1]戊基、双环[1.2.1]己基、双环[3.0.1]己基、双环[2.1.2]庚基、双环[2.2.2]辛基、金刚烷基、二金刚烷基、十氢萘基、十氢薁基等。

[0839] 作为R^{21}～R^{28}中的“可被取代的芳基”的“芳基”,例如可列举碳数6～30的芳基,优选为碳数6～16的芳基,更优选为碳数6～12的芳基,特别优选为碳数6～10的芳基。

[0840] 作为具体的“芳基”,可列举:作为单环系的苯基;作为二环系的联苯基;作为缩合二环系的萘基;作为三环系的联三苯基(间联三苯基、邻联三苯基、对联三苯基);作为缩合三环系的苊基、芴基、非那烯基、菲基;作为缩合四环系的三亚苯基、苉基、并四苯基;作为缩合五环系的苝基、稠五苯基等。

[0841] 作为R^{21}～R^{28}中的“可被取代的杂芳基”的“杂芳基”,例如可列举碳数2～30的杂芳基,优选为碳数2～25的杂芳基,更优选为碳数2～20的杂芳基,进而优选为碳数2～15的杂芳基,特别优选为碳数2～10的杂芳基。另外,作为杂芳基,例如可列举除碳以外含有1个～5个选自氧、硫及氮中的杂原子作为环构成原子的杂环等。

[0842] 作为具体的“杂芳基”,例如可列举:吡咯基、噁唑基、异噁唑基、噻唑基、异噻唑基、咪唑基、噁二唑基、噻二唑基、三唑基、四唑基、吡唑基、吡啶基、嘧啶基、哒嗪基、吡嗪基、三嗪基、吲哚基、异吲哚基、1H-吲唑基、苯并咪唑基、苯并噁唑基、苯并噻唑基、1H-苯并三唑基、喹啉基、异喹啉基、噌啉基、喹唑啉基、喹喔啉基、酞嗪基、萘啶基、嘌呤基、喋啶基、咔唑基、吖啶基、吩噁噻基、吩噁嗪基、吩噻嗪基、吩嗪基、环戊基硼酸基(phenazasiliny1)、吲嗪基、呋喃基、苯并呋喃基、异苯并呋喃基、二苯并呋喃基、萘并苯并呋喃基、噻吩基、苯并噻吩基、异苯并噻吩基、二苯并噻吩基、萘并苯并噻吩基、苯并磷酰基、二苯并磷酰基、苯并磷杂环戊二烯氧化物环的一价基、二苯并磷杂环戊二烯氧化物环的一价基、呋咱基、噻蒽基、吲哚并咔唑基、苯并吲唑并咔唑基及苯并苯并吲哚并咔唑基等。

[0843] 作为R^{21}～R^{28}中的“可被取代的烷氧基”的“烷氧基”,例如可列举碳数1～24的直链的烷氧基或碳数3～24的分支链的烷氧基。优选为碳数1～18的烷氧基(碳数3～18的分支链的烷氧基),更优选为碳数1～12的烷氧基(碳数3～12的分支链的烷氧基),进而优选为碳数1～6的烷氧基(碳数3～6的分支链的烷氧基),特别优选为碳数1～4的烷氧基(碳数3～4的分支链的烷氧基)。

[0844] 作为具体的“烷氧基”,可列举:甲氧基、乙氧基、丙氧基、异丙氧基、丁氧基、异丁氧基、仲丁氧基、叔丁氧基、戊氧基、己氧基、庚氧基、辛氧基等。

[0845] 作为R^{21}～R^{28}中的“可被取代的芳氧基”的“芳氧基”,为-OH基的氢由芳基取代的基,所述芳基可引用作为所述R^{21}～R^{28}中的“芳基”而说明的基。

[0846] 作为R^{21}～R^{28}中的“可被取代的芳硫基”的“芳硫基”,为-SH基的氢由芳基取代的基,所述芳基可引用作为所述R^{21}～R^{28}中的“芳基”而说明的基。

[0847] 作为R^{21}～R^{28}中的“三烷基硅烷基”,可列举硅烷基中的三个氢分别独立地由烷基

取代的基,所述烷基可引用作为所述R^{21}～R^{28}中的“烷基”而说明的基。对于进行取代而言优选的烷基为碳数1～4的烷基,具体而言,可列举:甲基、乙基、丙基、异丙基、丁基、仲丁基、叔丁基、环丁基等。

[0848] 作为具体的“三烷基硅烷基”,可列举:三甲基硅烷基、三乙基硅烷基、三丙基硅烷基、三异丙基硅烷基、三丁基硅烷基、三-仲丁基硅烷基、三-叔丁基硅烷基、乙基二甲基硅烷基、丙基二甲基硅烷基、异丙基二甲基硅烷基、丁基二甲基硅烷基、仲丁基二甲基硅烷基、叔丁基二甲基硅烷基、甲基二乙基硅烷基、丙基二乙基硅烷基、异丙基二乙基硅烷基、丁基二乙基硅烷基、仲丁基二乙基硅烷基、叔丁基二乙基硅烷基、甲基二丙基硅烷基、乙基二丙基硅烷基、丁基二丙基硅烷基、仲丁基二丙基硅烷基、叔丁基二丙基硅烷基、甲基二异丙基硅烷基、乙基二异丙基硅烷基、丁基二异丙基硅烷基、仲丁基二异丙基硅烷基、叔丁基二异丙基硅烷基等。

[0849] 作为R^{21}～R^{28}中的“三环烷基硅烷基”,可列举硅烷基中的三个氢分别独立地由环烷基取代的基,所述环烷基可引用作为所述R^{21}～R^{28}中的“环烷基”而说明的基。对于进行取代而言优选的环烷基为碳数5～10的环烷基,具体而言,可列举:环戊基、环己基、环庚基、环辛基、环壬基、环癸基、双环[1.1.1]戊基、双环[2.0.1]戊基、双环[1.2.1]己基、双环[3.0.1]己基、双环[2.1.2]庚基、双环[2.2.2]辛基、金刚烷基、十氢萘基、十氢蒽基等。

[0850] 作为具体的“三环烷基硅烷基”,可列举:三环戊基硅烷基、三环己基硅烷基等。

[0851] 作为两个烷基与一个环烷基取代而成的二烷基环烷基硅烷基、及一个烷基与两个环烷基取代而成的烷基二环烷基硅烷基的具体例,可列举:选自所述具体的烷基及环烷基中的基取代而成的硅烷基。

[0852] 作为R^{21}～R^{28}中的“可被取代的氨基”的“被取代的氨基”,例如可列举两个氢由芳基或杂芳基取代的氨基。两个氢由芳基取代的氨基为二芳基取代氨基,两个氢由杂芳基取代的氨基为二杂芳基取代氨基,两个氢由芳基与杂芳基取代的氨基为芳基杂芳基取代氨基。所述芳基或杂芳基可引用作为所述R^{21}～R^{28}中的“芳基”或“杂芳基”而说明的基。

[0853] 作为具体的“被取代的氨基”,可列举:二苯基氨基、二萘基氨基、苯基萘基氨基、二吡啶基氨基、苯基吡啶基氨基、萘基吡啶基氨基等。

[0854] 作为R^{21}～R^{28}中的“卤素”,可列举:氟、氯、溴、碘。

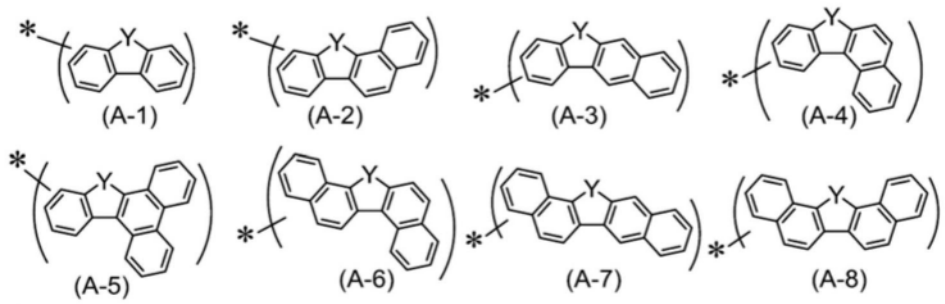
[0855] 作为R^{21}～R^{28}而说明的基中,若干基也可如所述那样被取代,作为所述情况下的取代基,可列举:烷基、环烷基、芳基或杂芳基。所述烷基、环烷基、芳基或杂芳基可引用作为所述R^{21}～R^{28}中的“烷基”、“环烷基”、“芳基”或“杂芳基”而说明的基。

[0856] 作为Y的“>N-R^{29}”中的R^{29}为氢或可被取代的芳基,作为所述芳基,可引用作为所述R^{21}～R^{28}中的“芳基”而说明的基,另外,作为所述取代基,可引用作为针对R^{21}～R^{28}的取代基而说明的基。

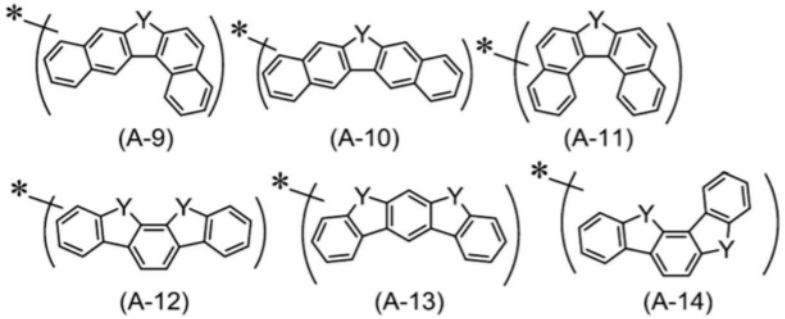
[0857] R^{21}～R^{28}中的邻接的基可彼此键结而形成烃环、芳基环或杂芳基环。未形成环的情况为下述式(A-1)所表示的基,作为形成环的情况,例如可列举下述式(A-2)～式(A-14)的任一者所表示的基。式中的Y及*与所述为相同定义。再者,式(A-1)～式(A-14)的任一者所表示的基中的至少一个氢可由烷基、环烷基、芳基、杂芳基、烷氧基、芳氧基、芳硫基、三烷基硅烷基、三环烷基硅烷基、二烷基环烷基硅烷基、烷基二环烷基硅烷基、二芳基取代氨基、二杂芳基取代氨基、芳基杂芳基取代氨基、卤素、羟基或氰基取代。各结构式中的*表示键结位

置。

[0858] [化271]



[0859]



[0860] 作为邻接的基彼此键结而成的环,若为烃环,则例如可列举环己烷环,作为芳基环或杂芳基环,可列举所述R^{21}～R^{28}中的“芳基”或“杂芳基”中所说明的环结构,这些环以与所述式(A-1)中的一个或两个苯环进行缩合的方式形成。

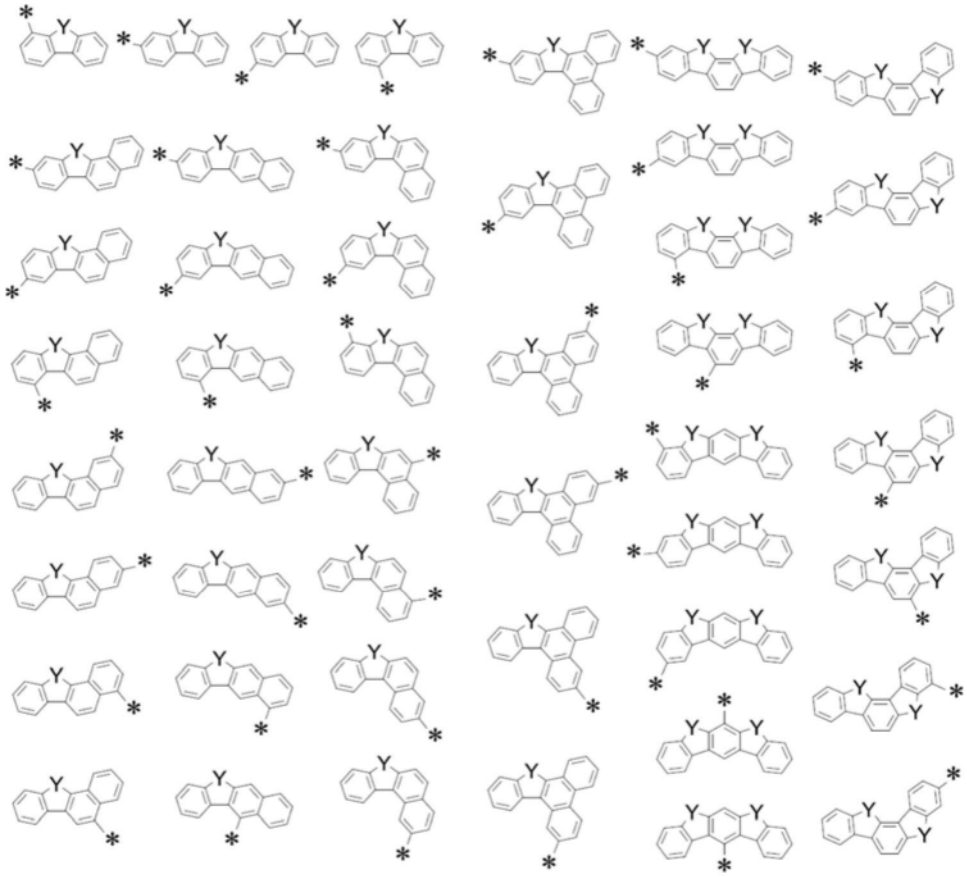
[0861] 作为式(A)所表示的基,例如可列举所述式(A-1)～式(A-14)的任一者所表示的基,优选为所述式(A-1)～式(A-5)及式(A-12)～式(A-14)的任一者所表示的基,更优选为所述式(A-1)～式(A-4)的任一者所表示的基,进而优选为所述式(A-1)、式(A-3)及式(A-4)的任一者所表示的基,特别优选为所述式(A-1)所表示的基。

[0862] 式(A)所表示的基在式(A)中的*处与式(3-X1)或式(3-X2)中的萘环、式(3-X3)中的单键、式(3-X3)中的Ar^3键结,另外,与式(3)所表示的化合物中的至少一个氢进行取代的情况如上所述,但这些键结形态中,优选为与式(3-X1)或式(3-X2)中的萘环、式(3-X3)中的单键及式(3-X3)中的Ar^3的至少一个键结的形态。

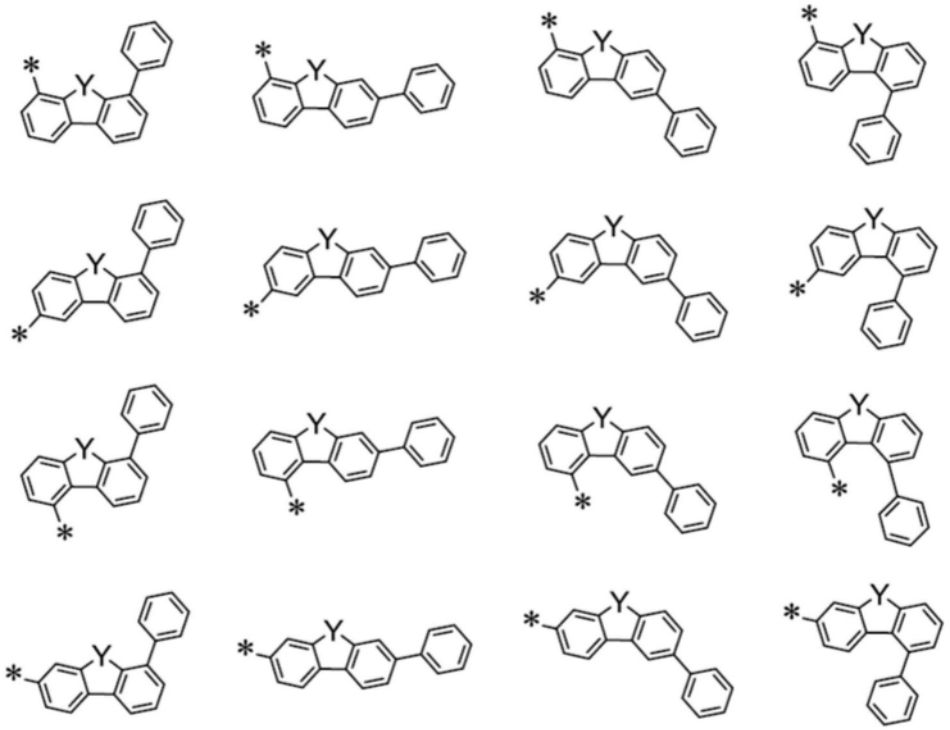
[0863] 另外,关于式(A)所表示的基的结构中,式(3-X1)或式(3-X2)中的萘环、式(3-X3)中的单键、式(3-X3)中的Ar^3进行键结的位置,及式(A)所表示的基的结构中,与式(3)所表示的化合物中的至少一个氢进行取代的位置,可为式(A)的结构中的任意位置,例如可在式(A)的结构中的两个苯环的任一个、或式(A)的结构中的R^{21}～R^{28}中的邻接的基彼此键结而形成的任一环、或式(A)的结构中的作为Y的“>N-R^{29}”的R^{29}中的任一位置进行键结。

[0864] 作为式(A)所表示的基,例如可列举以下的基。式中的Y及*与所述为相同定义。

[0865] [化272]

[0866] 

[0867] [化273]

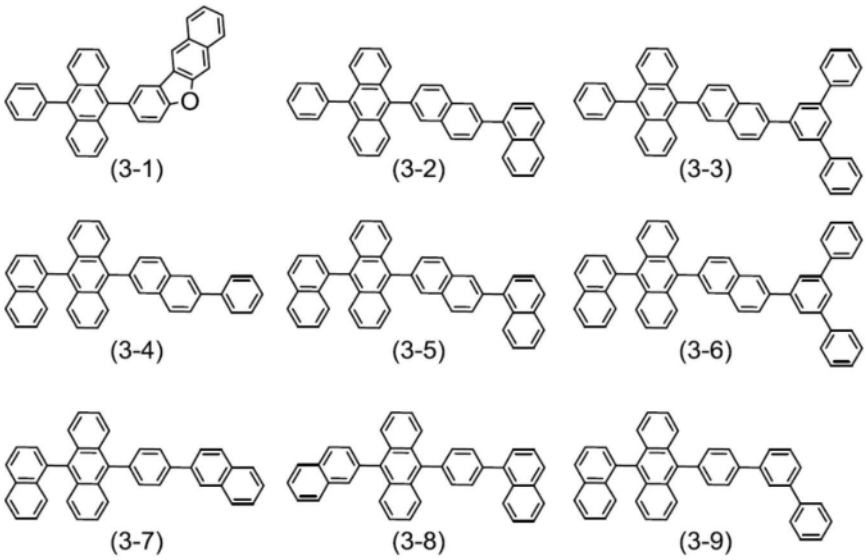


[0868]

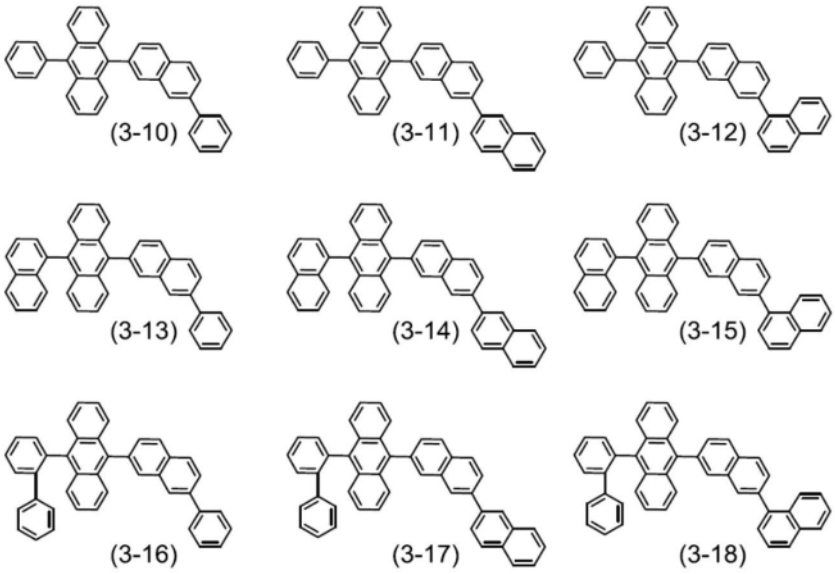
[0869] 另外,通式(3)所表示的蒽系化合物的化学结构中的氢的全部或一部分可为氘。

[0870] 作为蒽系化合物的具体例,例如可列举下述式(3-1)～式(3-142)的任一者所表示的化合物。再者,下述结构式中的“Me”表示甲基,“D”表示氘,“tBu”表示叔丁基。

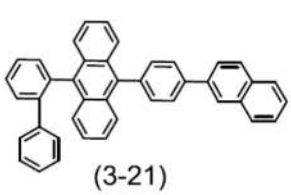
[0871] [化274]

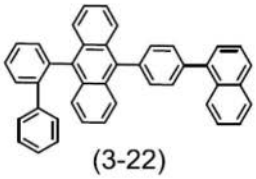


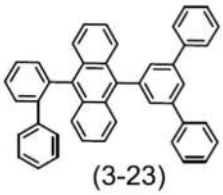
[0872]

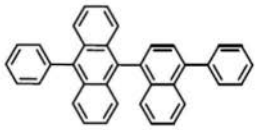


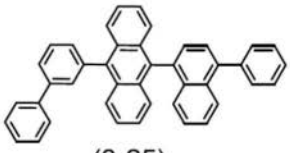
[0873] [化275]

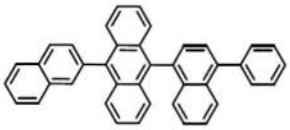

(3-21)

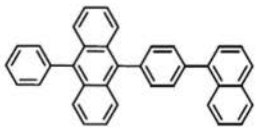

(3-22)

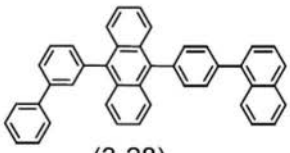

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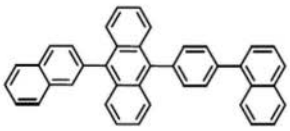

(3-24)


(3-25)

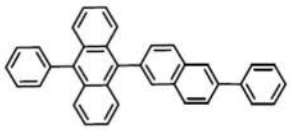

(3-26)

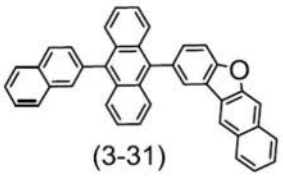

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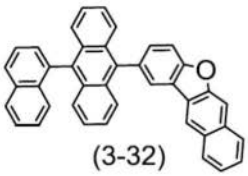

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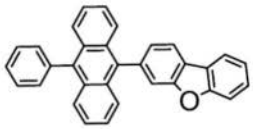

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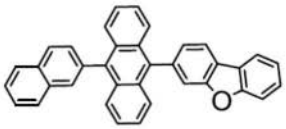
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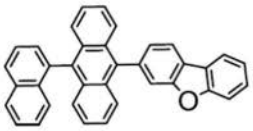

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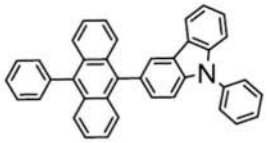

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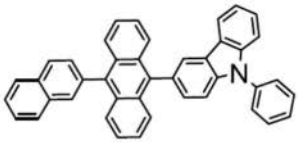

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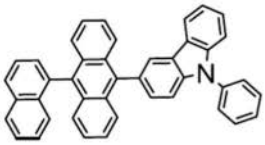

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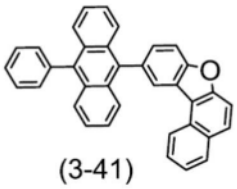

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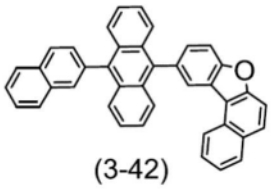

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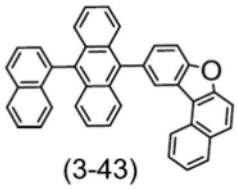

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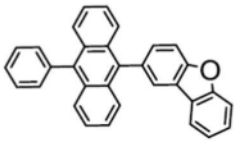

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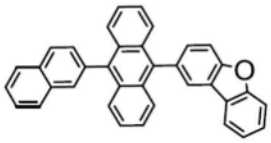
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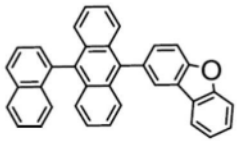

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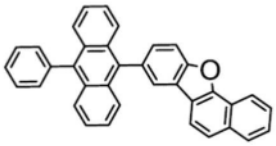

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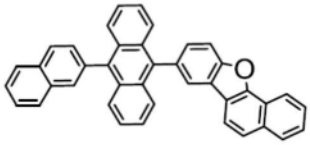

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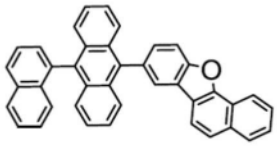

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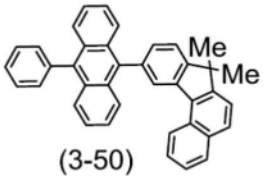

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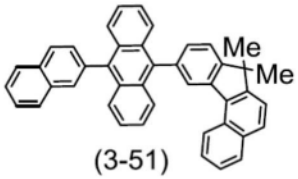

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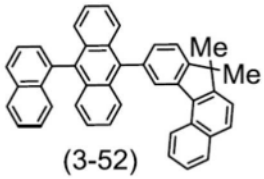

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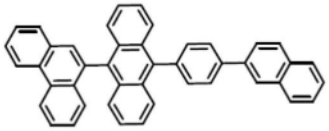

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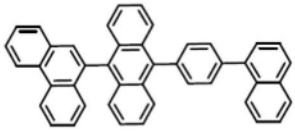
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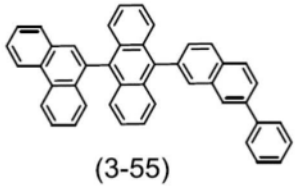

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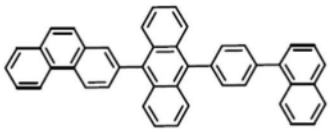

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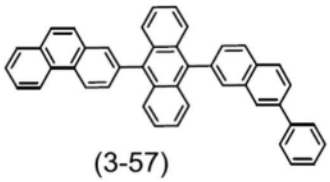

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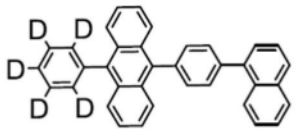

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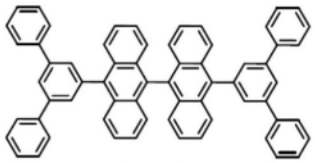

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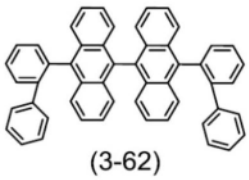

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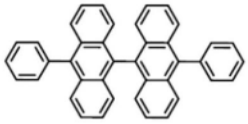
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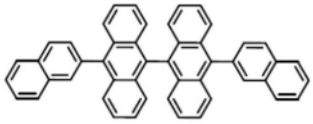
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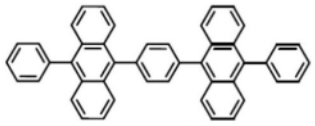


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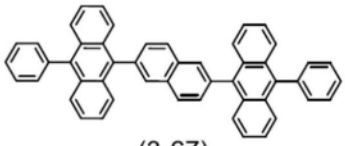


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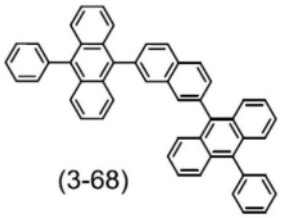
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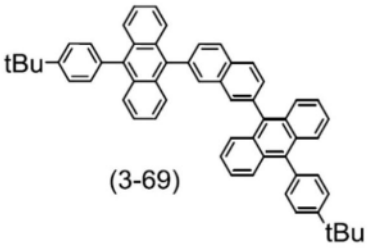
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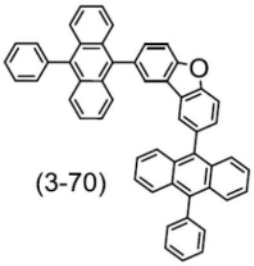
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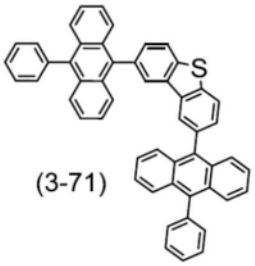
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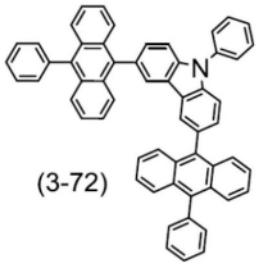
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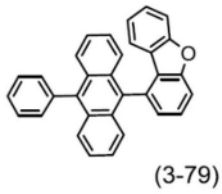


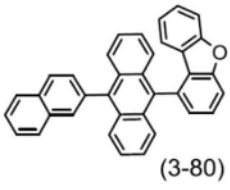
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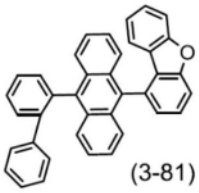


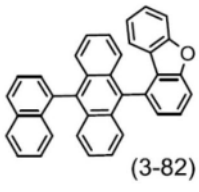
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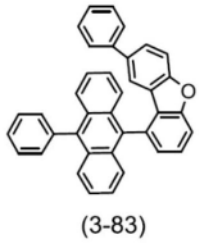
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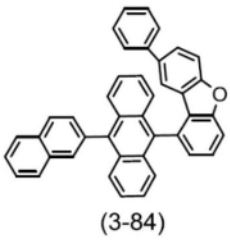

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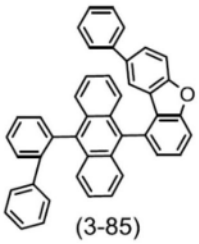

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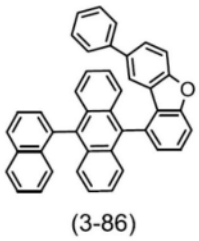

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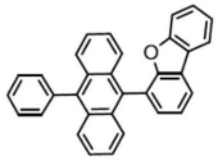

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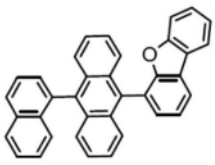

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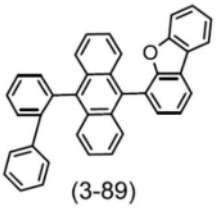

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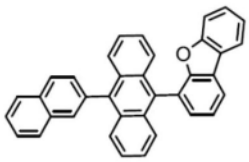

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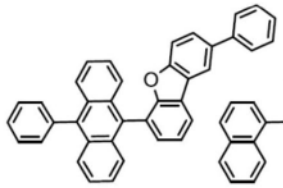

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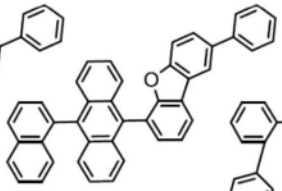

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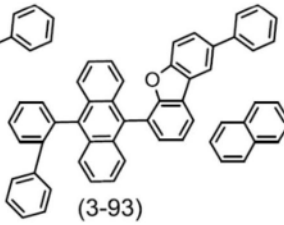

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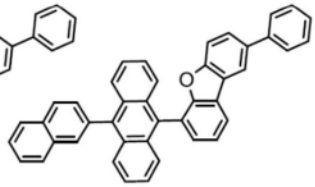

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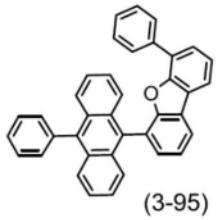
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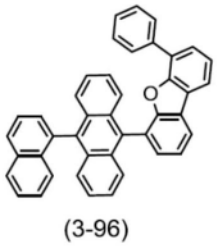

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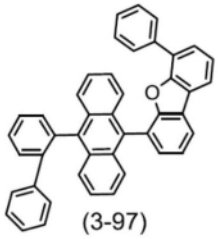

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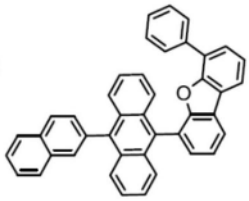

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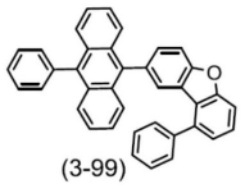

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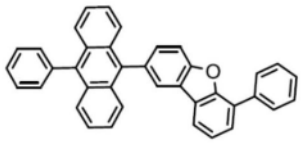

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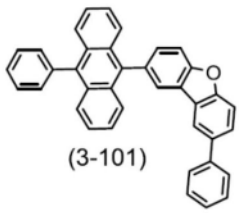

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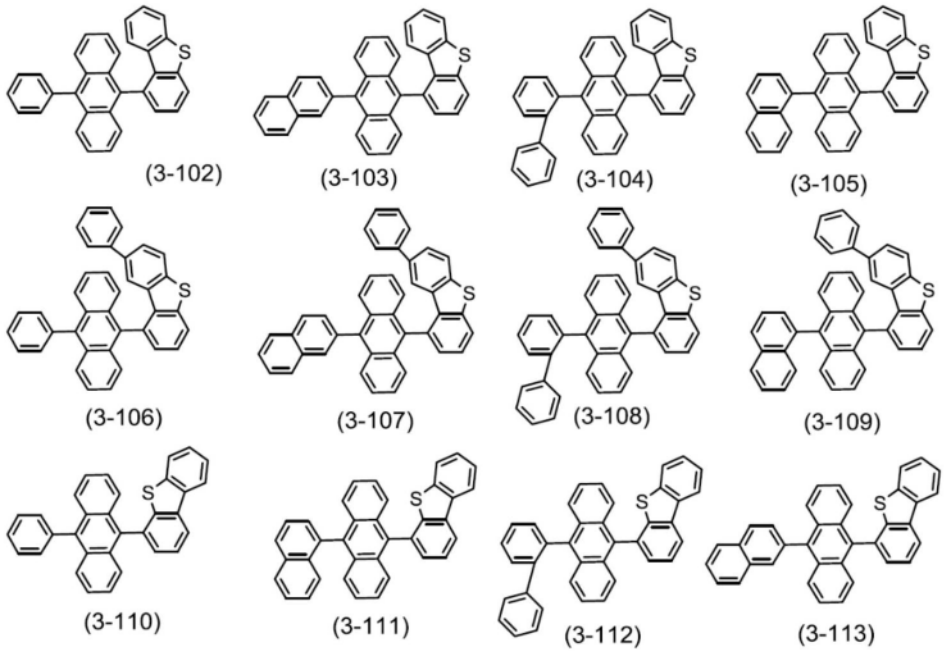

(3-98)


(3-99)

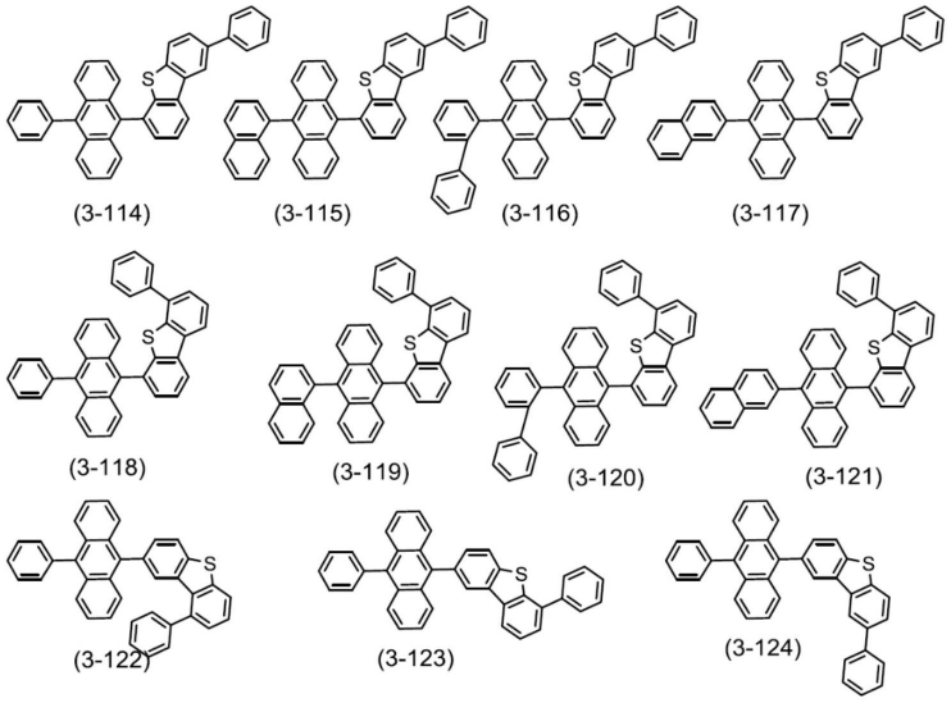

(3-100)


(3-101)

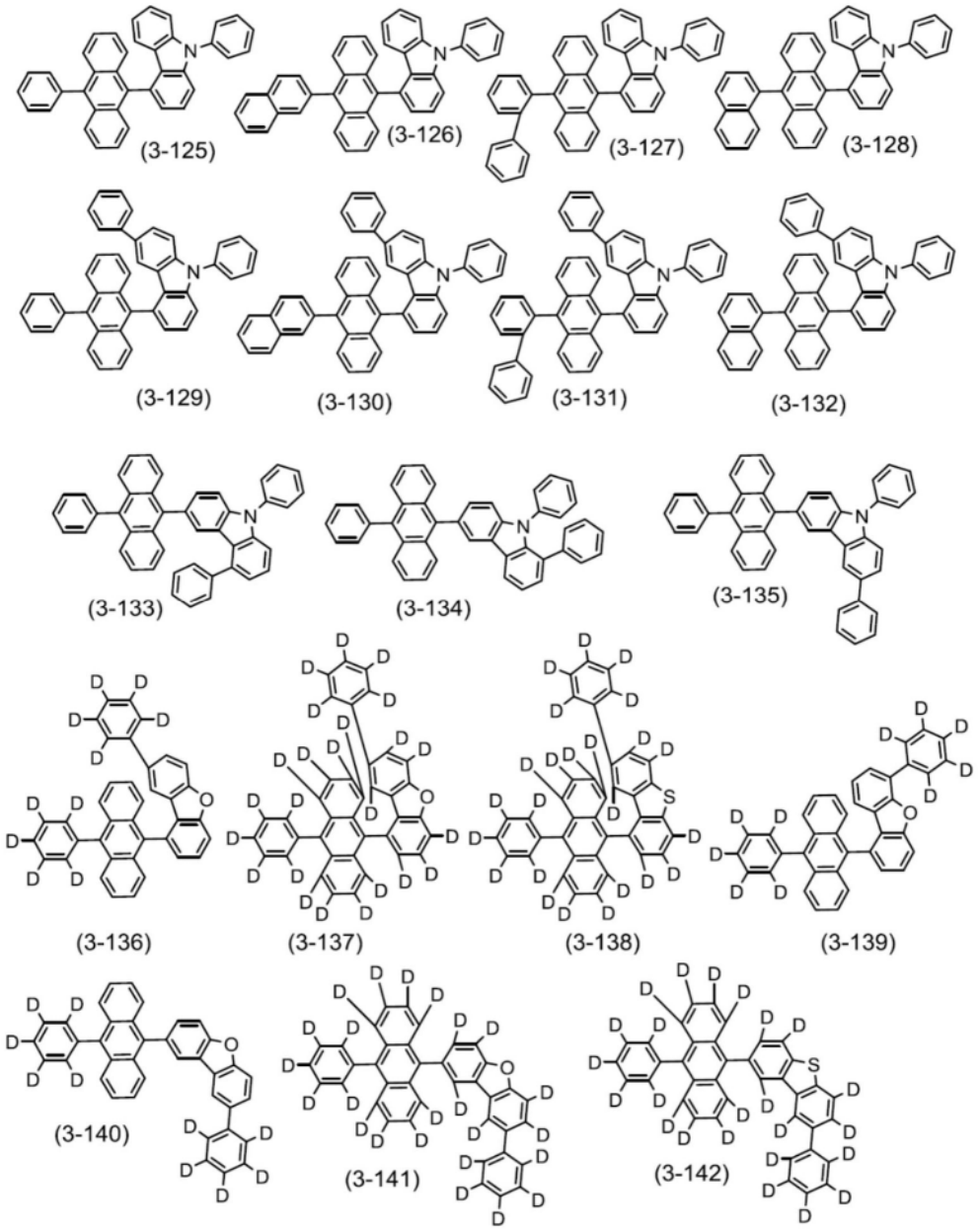
[0881] [化279]



[0882]



[0883] [化280]

[0884] 

[0885] 式(3)所表示的蒽系化合物可将在蒽骨架的所期望的位置上具有反应性基的化合物、以及在X、Ar^4及式(A)的结构等部分结构上具有反应性基的化合物作为引发原料,并应用铃木偶合、根岸偶合、其他已知的偶合反应来制造。作为这些反应性化合物的反应性基,可列举卤素或硼酸等。作为具体的制造方法,例如可参考:国际公开第2014/141725号公报的段落[0089]~[0175]的合成法。

[0886] <芴系化合物>

[0887] 通式(4)所表示的化合物基本上作为主体发挥功能。

[0888] [化281]

[0889] 

(4)

[0890] 所述式(4)中,

[0891] R^1至R^{10}分别独立地为氢、芳基、杂芳基(所述杂芳基可经由连结基而与所述式(4)中的芴骨架键结)、二芳基氨基、二杂芳基氨基、芳基杂芳基氨基、烷基、环烷基、烯基、烷氧基或芳氧基,这些中的至少一个氢可由芳基、杂芳基、烷基或环烷基取代,

[0892] 另外,R^1与R^2、R^2与R^3、R^3与R^4、R^5与R^6、R^6与R^7、R^7与R^8或R^9与R^{10}可分别独立地键结而形成缩合环或螺环,所形成的环中的至少一个氢可由芳基、杂芳基(所述杂芳基可经由连结基而与所述所形成的环键结)、二芳基氨基、二杂芳基氨基、芳基杂芳基氨基、烷基、环烷基、烯基、烷氧基或芳氧基取代,这些中的至少一个氢可由芳基、杂芳基、烷基或环烷基取代,而且,

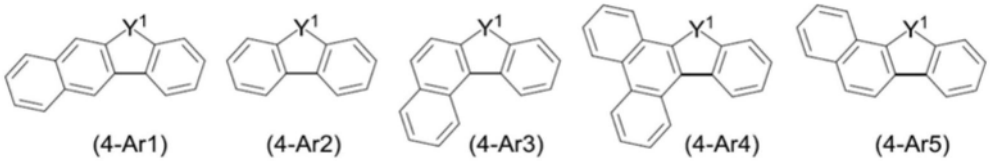
[0893] 式(4)所表示的化合物中的至少一个氢可由卤素、氰基或氘取代。

[0894] 所述式(4)的定义的各基的详细情况可引用以上所述的式(1)的多环芳香族化合物的说明。

[0895] 作为R^1至R^{10}中的烯基,例如可列举碳数2~30的烯基,优选为碳数2~20的烯基,更优选为碳数2~10的烯基,进而优选为碳数2~6的烯基,特别优选为碳数2~4的烯基。优选的烯基为乙烯基、1-丙烯基、2-丙烯基、1-丁烯基、2-丁烯基、3-丁烯基、1-戊烯基、2-戊烯基、3-戊烯基、4-戊烯基、1-己烯基、2-己烯基、3-己烯基、4-己烯基或5-己烯基。

[0896] 再者,作为杂芳基的具体例,也可列举自下述式(4-Ar1)、式(4-Ar2)、式(4-Ar3)、式(4-Ar4)或式(4-Ar5)的化合物中去除任意一个氢原子而表示的一价基。

[0897] [化282]

[0898] 

(4-Ar1) (4-Ar2) (4-Ar3) (4-Ar4) (4-Ar5)

[0899] 式(4-Ar1)至式(4-Ar5)中,Y^1分别独立地为O、S或N-R,R为苯基、联苯基、萘基、蒽基或氢,

[0900] 所述式(4-Ar1)至式(4-Ar5)的结构中的至少一个氢可由苯基、联苯基、萘基、蒽基、菲基、甲基、乙基、丙基或丁基取代。

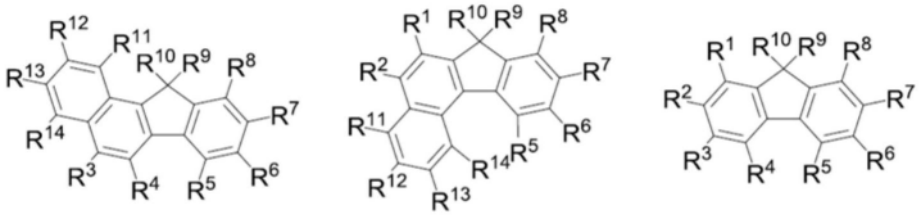
[0901] 这些杂芳基可经由连结基而与所述式(4)中的芴骨架键结。即,式(4)中的芴骨架与所述杂芳基不仅可直接键结,而且也可在这些之间经由连结基而键结。作为所述连结基,可列举:亚苯基、亚联苯基、亚萘基、亚蒽基、亚甲基、亚乙基、$-OCH_2CH_2-$、$-CH_2CH_2O-$或$-OCH_2CH_2O-$等。

[0902] 另外,式(4)中的R^1与R^2、R^2与R^3、R^3与R^4、R^5与R^6、R^6与R^7或R^7与R^8可分别独立地键结而形成缩合环,R^9与R^{10}可键结而形成螺环。由R^1至R^8所形成的缩合环为与式(4)中的苯环缩合的环且为脂肪族环或芳香族环。优选为芳香族环,作为包含式(4)中的苯环的结构,可列

举萘环或菲环等。由R^9与R^{10}所形成的螺环为与式(4)中的5元环螺键结的环且为脂肪族环或芳香族环。优选为芳香族环,可列举芴环等。

[0903] 通式(4)所表示的化合物优选为下述式(4-1)、式(4-2)或式(4-3)所表示的化合物,且分别为在通式(4)中R^1与R^2键结而形成的苯环缩合而成的化合物、在通式(4)中R^3与R^4键结而形成的苯环缩合而成的化合物、在通式(4)中R^1至R^8的任一者均未键结的化合物。

[0904] [化283]

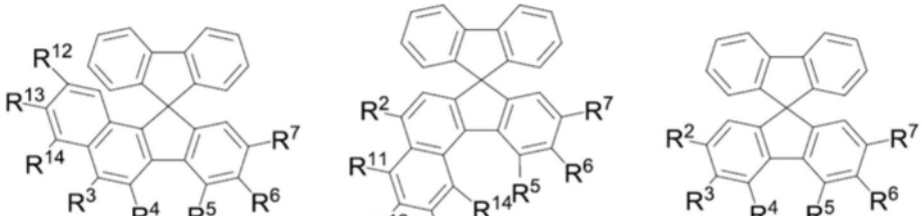
[0905] 

(4-1) (4-2) (4-3)

[0906] 式(4-1)、式(4-2)及式(4-3)中的R^1至R^{10}的定义与在式(4)中所对应的R^1至R^{10}相同,且式(4-1)及式(4-2)中的R^{11}至R^{14}的定义也与式(4)中的R^1至R^{10}相同。

[0907] 通式(4)所表示的化合物进而优选为下述式(4-1A)、式(4-2A)或式(4-3A)所表示的化合物,且分别为在式(4-1)、式(4-2)或式(4-3)中R^9与R^{10}键结而形成螺-芴环的化合物。

[0908] [化284]

[0909] 

(4-1A) (4-2A) (4-3A)

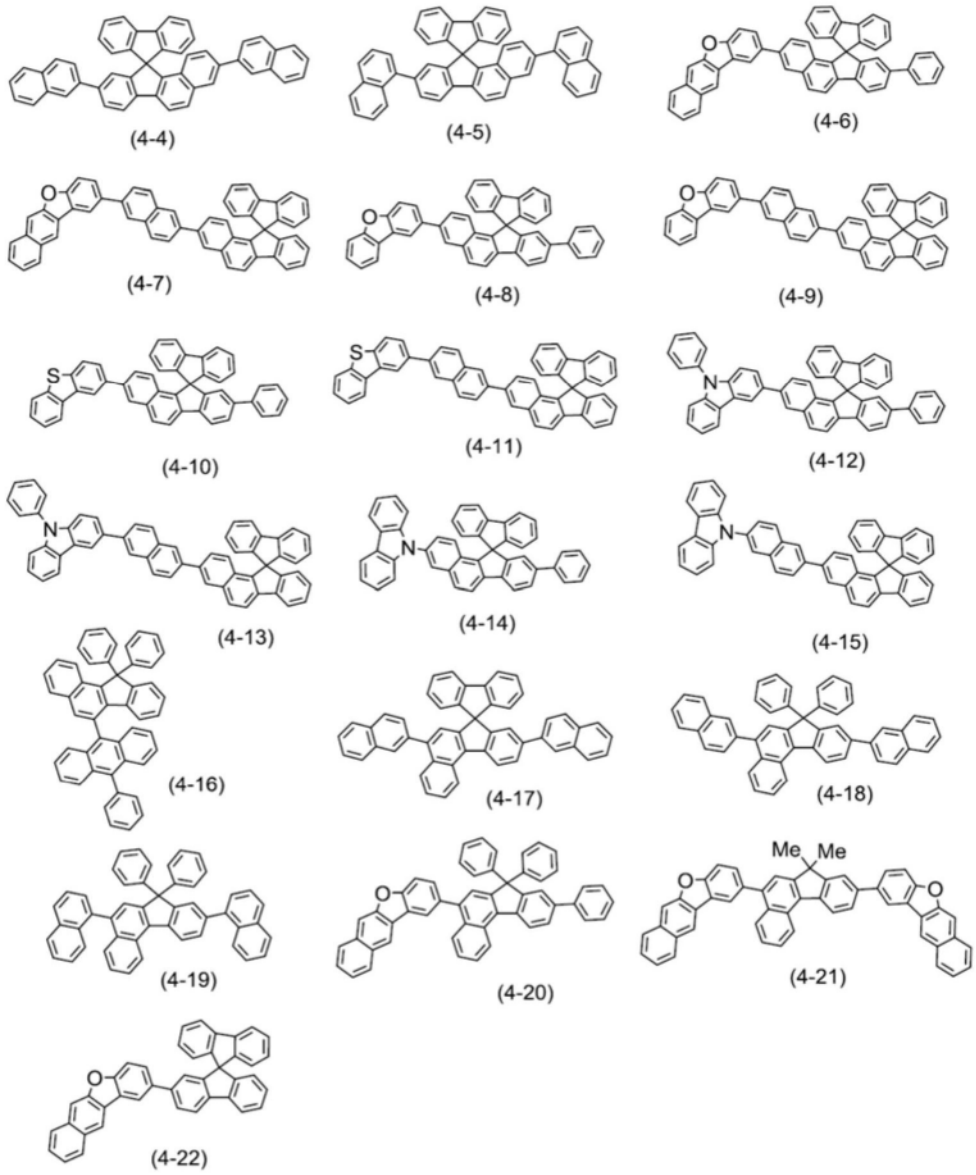
[0910] 式(4-1A)、式(4-2A)及式(4-3A)中的R^2至R^7的定义与在式(4-1)、式(4-2)及式(4-3)中所对应的R^2至R^7相同,且式(4-1A)及式(4-2A)中的R^{11}至R^{14}的定义也与式(4-1)及式(4-2)中的R^{11}至R^{14}相同。

[0911] 另外,式(4)所表示的化合物中的氢的全部或一部分可由卤素、氰基或氘取代。

[0912] 作为芴系化合物的具体例,例如可列举下述式(4-4)～式(4-22)的任一者所表示的化合物。再者,下述结构式中的“Me”表示甲基。

[0913] [化285]

[0914]

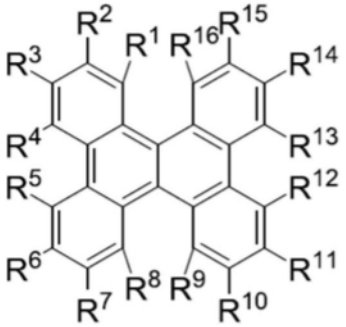


[0915] ＜二苯并蒀系化合物＞

[0916] 作为主体的二苯并蒀系化合物例如为下述通式(5)所表示的化合物。

[0917] [化286]

[0918]



(5)

[0919] 所述式(5)中，

[0920] R^1至R^{16}分别独立地为氢、芳基、杂芳基(所述杂芳基可经由连结基而与所述式(5)中的二苯并蒀骨架键结)、二芳基氨基、二杂芳基氨基、芳基杂芳基氨基、烷基、环烷基、烯

基、烷氧基或芳氧基,这些中的至少一个氢可由芳基、杂芳基、烷基或环烷基取代,

[0921] 另外,R^1至R^{16}中的邻接的基彼此可键结而形成缩合环,所形成的环中的至少一个氢可由芳基、杂芳基(所述杂芳基可经由连结基而与所述所形成的环键结)、二芳基氨基、二杂芳基氨基、芳基杂芳基氨基、烷基、环烷基、烯基、烷氧基或芳氧基取代,这些中的至少一个氢可由芳基、杂芳基、烷基或环烷基取代,而且,

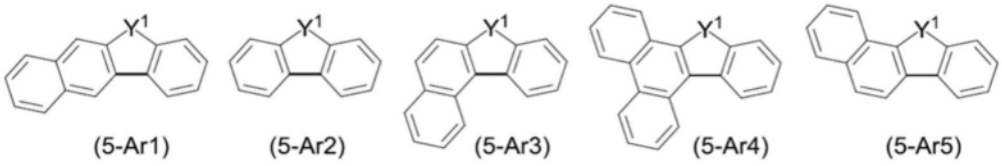
[0922] 式(5)所表示的化合物中的至少一个氢可由卤素、氰基或氘取代。

[0923] 所述式(5)的定义的各基的详细情况可引用以上所述的式(1)的多环芳香族化合物的说明。

[0924] 作为所述式(5)的定义的烯基,例如可列举碳数2~30的烯基,优选为碳数2~20的烯基,更优选为碳数2~10的烯基,进而优选为碳数2~6的烯基,特别优选为碳数2~4的烯基。优选的烯基为乙烯基、1-丙烯基、2-丙烯基、1-丁烯基、2-丁烯基、3-丁烯基、1-戊烯基、2-戊烯基、3-戊烯基、4-戊烯基、1-己烯基、2-己烯基、3-己烯基、4-己烯基或5-己烯基。

[0925] 再者,作为杂芳基的具体例,也可列举自下述式(5-Ar1)、式(5-Ar2)、式(5-Ar3)、式(5-Ar4)或式(5-Ar5)的化合物中去除任意一个氢原子而表示的一价基。

[0926] [化287]

[0927] 

[0928] 式(5-Ar1)至式(5-Ar5)中,Y^1分别独立地为O、S或N-R,R为苯基、联苯基、萘基、蒽基或氢,

[0929] 所述式(5-Ar1)至式(5-Ar5)的结构中的至少一个氢可由苯基、联苯基、萘基、蒽基、菲基、甲基、乙基、丙基或丁基取代。

[0930] 这些杂芳基可经由连结基而与所述式(5)中的二苯并䓛骨架键结。即,式(5)中的二苯并䓛骨架与所述杂芳基不仅可直接键结,而且也可在这些之间经由连结基而键结。作为所述连结基,可列举:亚苯基、亚联苯基、亚萘基、亚蒽基、亚甲基、亚乙基、$-OCH_2CH_2-$、$-CH_2CH_2O-$或$-OCH_2CH_2O-$等。

[0931] 通式(5)所表示的化合物优选为R^1、R^4、R^5、R^8、R^9、R^{12}、R^{13}及R^{16}为氢。所述情况下,式(5)中的R^2、R^3、R^6、R^7、R^{10}、R^{11}、R^{14}及R^{15}优选为分别独立地为氢、苯基、联苯基、萘基、蒽基、菲基、具有所述式(5-Ar1)、式(5-Ar2)、式(5-Ar3)、式(5-Ar4)或式(5-Ar5)的结构的一价基(具有所述结构的一价基可经由亚苯基、亚联苯基、亚萘基、亚蒽基、亚甲基、亚乙基、$-OCH_2CH_2-$、$-CH_2CH_2O-$或$-OCH_2CH_2O-$而与所述式(5)中的二苯并䓛骨架键结)、甲基、乙基、丙基或丁基。

[0932] 通式(5)所表示的化合物更优选为R^1、R^2、R^4、R^5、R^7、R^8、R^9、R^{10}、R^{12}、R^{13}、R^{15}及R^{16}为氢。所述情况下,式(5)中的R^3、R^6、R^{11}及R^{14}的至少一个(优选为一个或两个,更优选为一个)为具有经由单键、亚苯基、亚联苯基、亚萘基、亚蒽基、亚甲基、亚乙基、$-OCH_2CH_2-$、$-CH_2CH_2O-$或$-OCH_2CH_2O-$的所述式(5-Ar1)、式(5-Ar2)、式(5-Ar3)、式(5-Ar4)或式(5-Ar5)的结构的一价基,

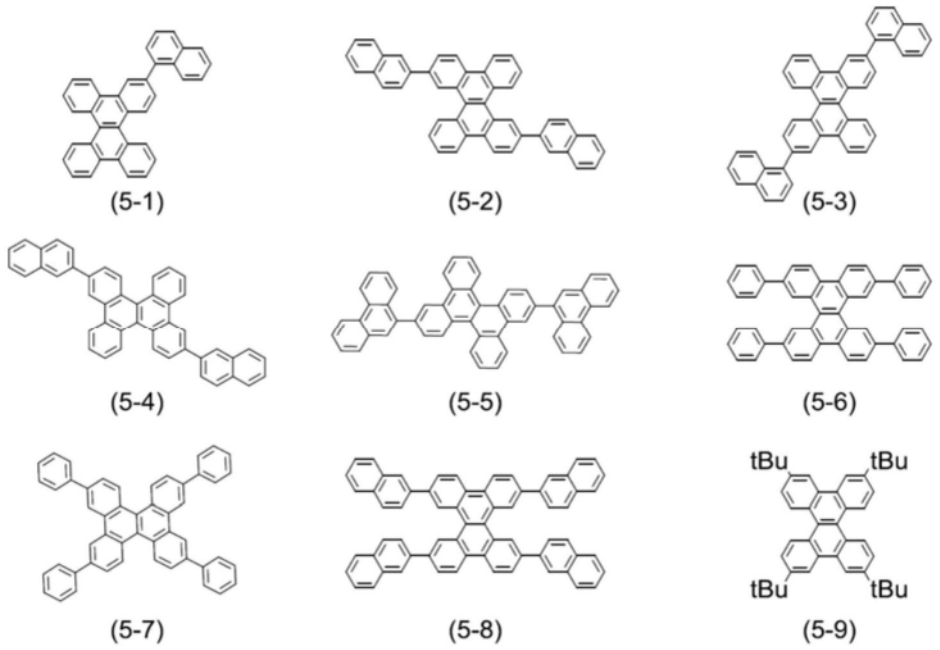
[0933] 所述至少一个以外(即,具有所述结构的一价基所取代的位置以外)为氢、苯基、联

苯基、萘基、蒽基、甲基、乙基、丙基或丁基，这些中的至少一个氢可由苯基、联苯基、萘基、蒽基、甲基、乙基、丙基或丁基取代。

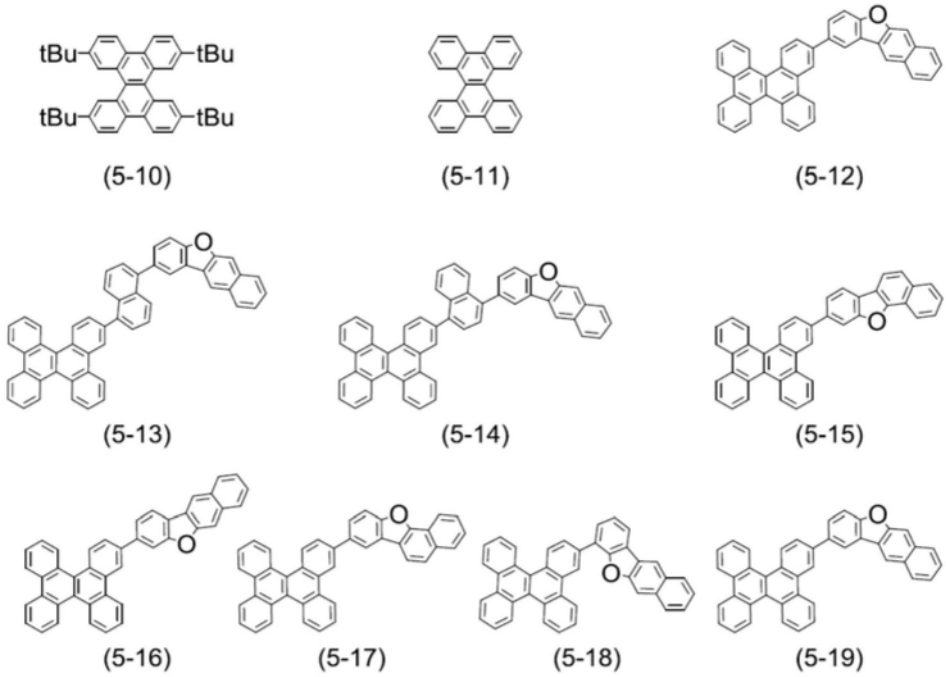
[0934] 另外，在选择具有所述式(5-Ar1)至式(5-Ar5)所表示的结构的一价基作为式(5)中的R^2、R^3、R^6、R^7、R^{10}、R^{11}、R^{14}及R^{15}的情况下，所述结构中的至少一个氢可与式(5)中的R^1至R^{16}的任一者键结而形成单键。

[0935] 作为二苯并[a,h]蒽系化合物的具体例，例如可列举下述式(5-1)～式(5-39)的任一者所表示的化合物。再者，下述结构式中的“tBu”表示叔丁基。

[0936] [化288]

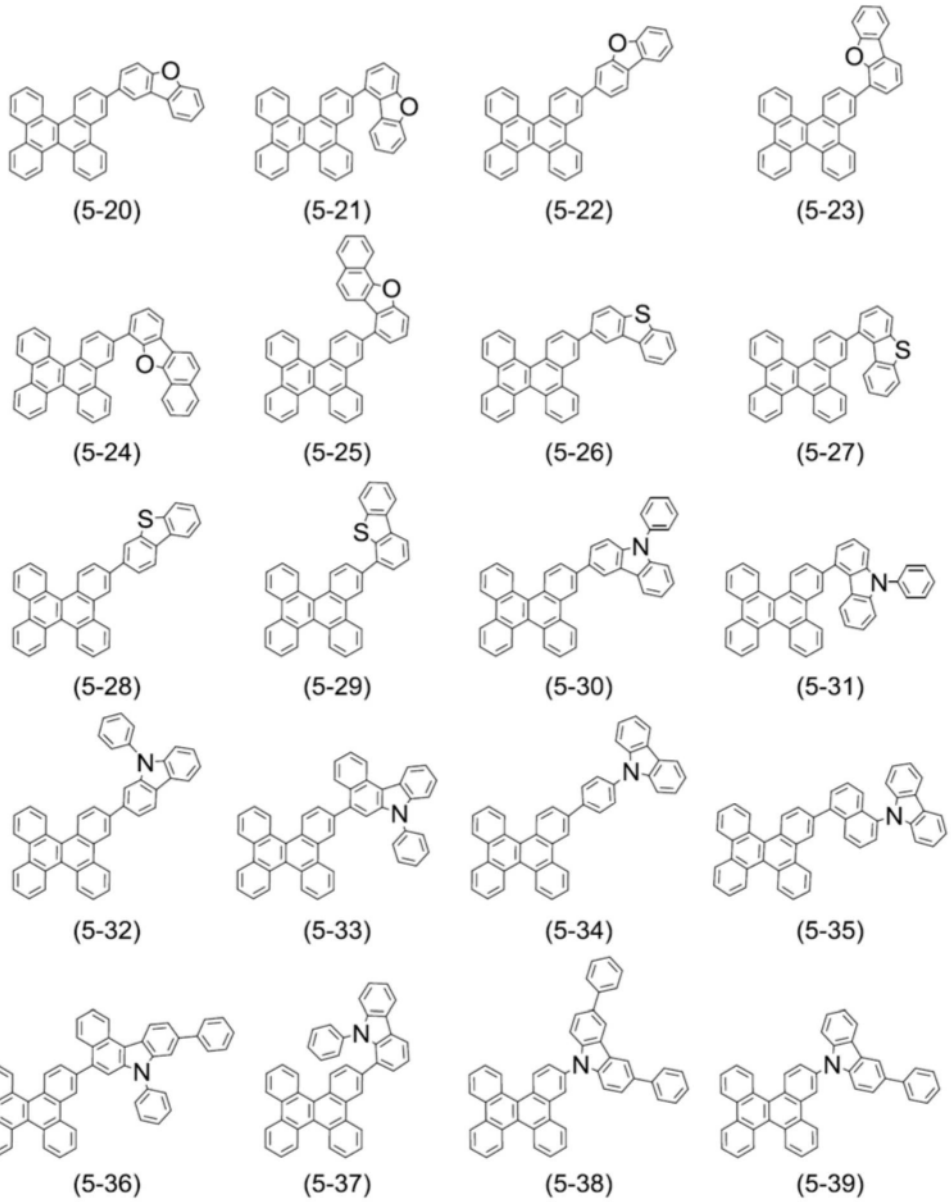


[0937]



[0938] [化289]

[0939]

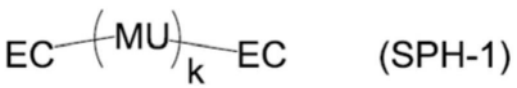


[0940] 所述发光层用材料(主体材料及掺杂剂材料)也可作为如下的高分子化合物或其高分子交联体、或者如下的悬挂型高分子化合物或其悬挂型高分子交联体而用于发光层用材料,其中,所述高分子化合物是使在所述发光层用材料(主体材料及掺杂剂材料)中取代有反应性取代基的反应性化合物作为单体进行高分子化而成,所述悬挂型高分子化合物是使主链型高分子与所述反应性化合物反应而成。作为所述情况下的反应性取代基,可引用式(1)所表示的多环芳香族化合物中的说明。

[0941] 关于此种高分子化合物及高分子交联体的用途的详细情况,在后文叙述。

[0942] <高分子主体材料的一例>

[0943] [化290]

[0944] 

(SPH-1)

[0945] 式(SPH-1)中,

[0946] MU分别独立地为自芳香族化合物中去除任意两个氢原子而表示的二价基,EC分别

独立地为自芳香族化合物中去除任意一个氢原子而表示的一价基,MU中的两个氢与EC或MU进行取代,k为2～50000的整数。

[0947] 更具体而言,

[0948] MU分别独立地为亚芳基、亚杂芳基、二亚芳基芳基氨基、二亚芳基芳基硼基、氧杂硼烷-二基、氮杂硼烷-二基,

[0949] EC分别独立地为氢、芳基、杂芳基、二芳基氨基、二杂芳基氨基、芳基杂芳基氨基或芳氧基,

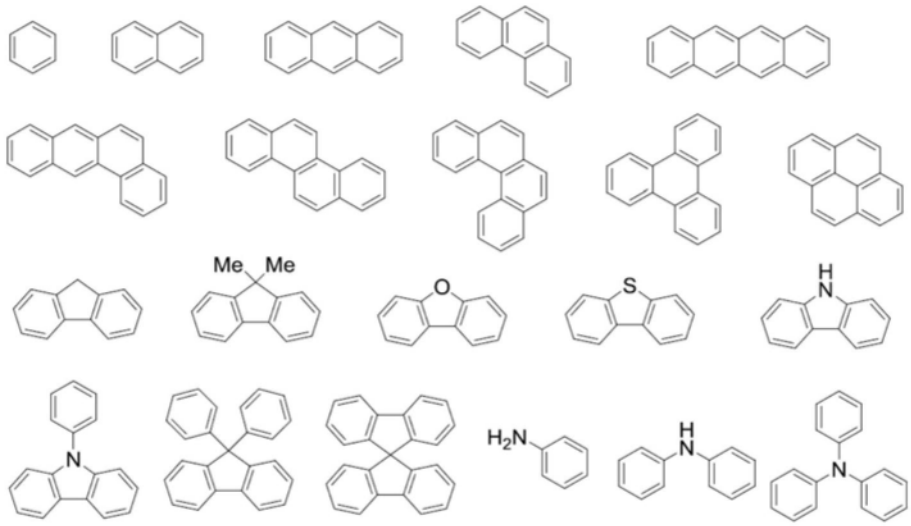
[0950] MU及EC中的至少一个氢可进而由芳基、杂芳基、二芳基氨基、烷基及环烷基取代,k为2～50000的整数。

[0951] k优选为20～50000的整数,更优选为100～50000的整数。

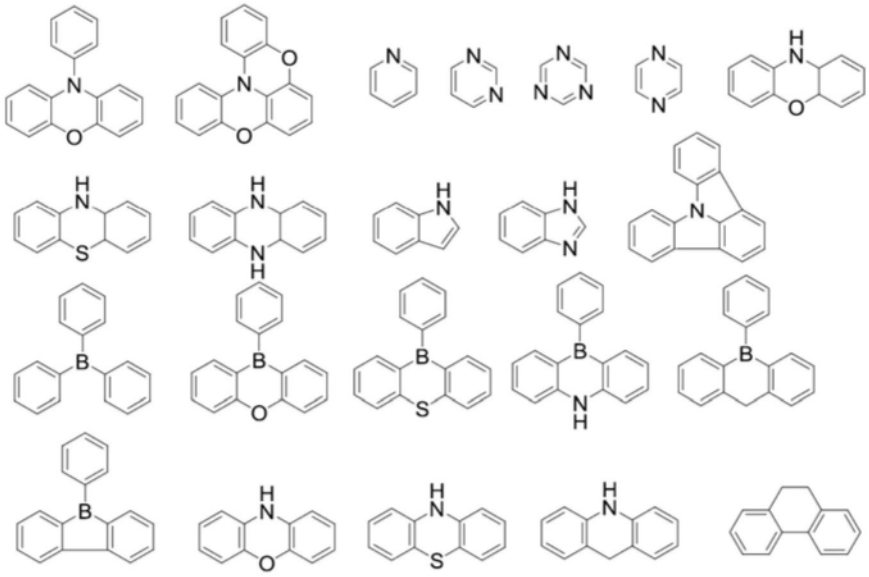
[0952] 式(SPH-1)中的MU及EC中的至少一个氢可由碳数1～24的烷基、碳数3～24的环烷基、卤素或氘取代,进而,所述烷基中的任意的-CH_2-可由-O-或-$Si(CH_3)_2$-取代,所述烷基中的除直接键结于式(SPH-1)中的EC的-CH_2-以外的任意的-CH_2-可由碳数6～24的亚芳基取代,所述烷基中的任意的氢可由氟取代。

[0953] 作为MU,例如可列举自以下的任一化合物中去除任意两个氢原子而表示的二价基。

[0954] [化291]



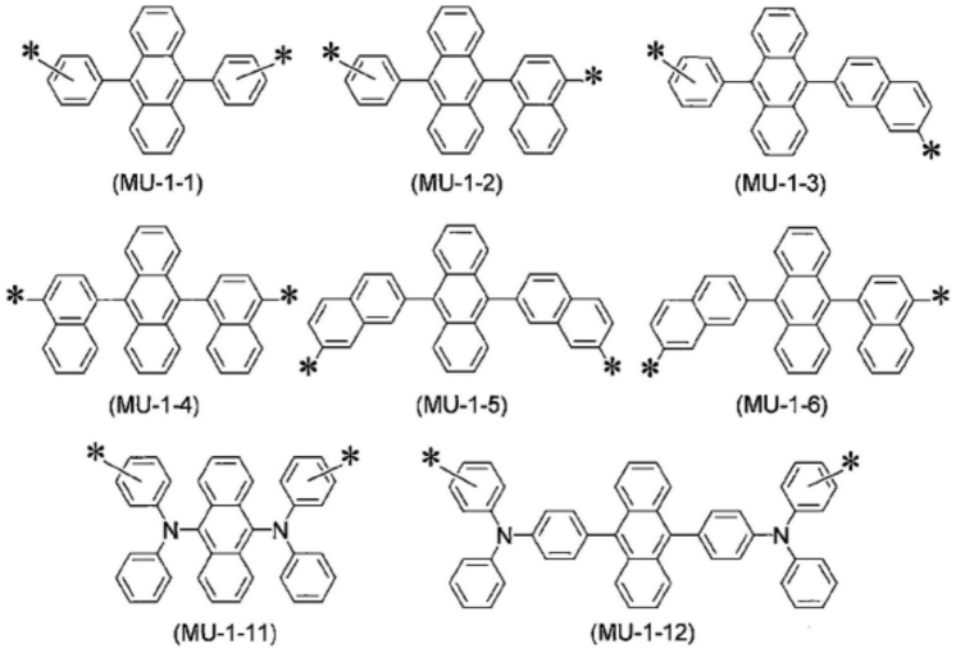
[0955]



[0956] 更具体而言,可列举以下的任一结构所表示的二价基。这些中,MU在*处与其他MU或EC键结。

[0957] [化292]

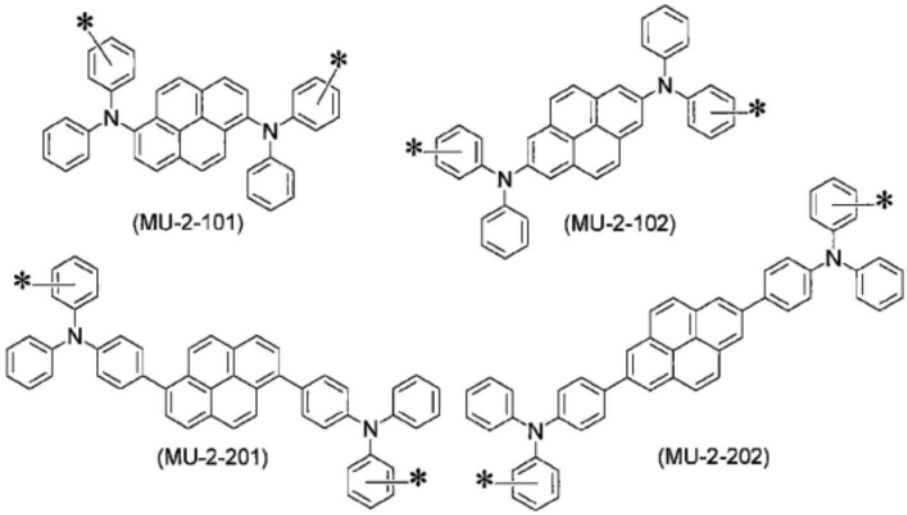
[0958]



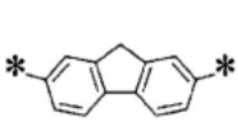
[0959] [化293]



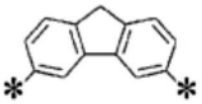
[0960]



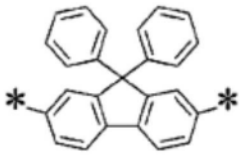
[0961] [化294]



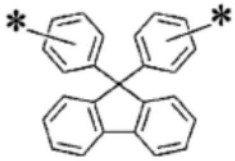
(MU-3-1)



(MU-3-2)



(MU-3-11)



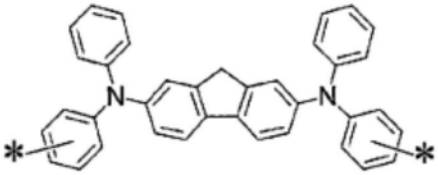
(MU-3-12)



(MU-3-21)

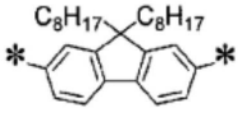


(MU-3-22)

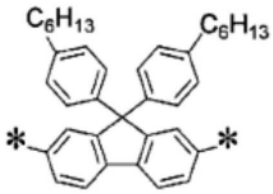


(MU-3-101)

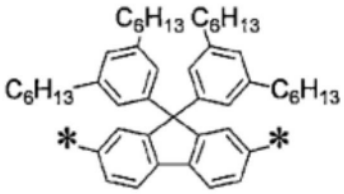
[0962]



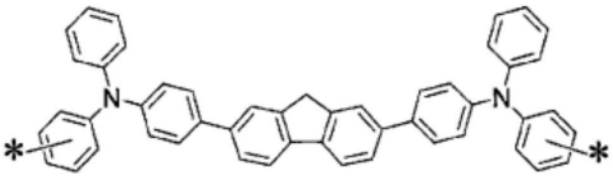
(MU-3-102)



(MU-3-111)

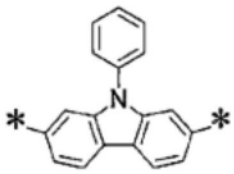


(MU-3-112)

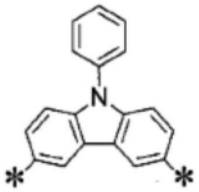


(MU-3-201)

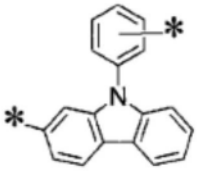
[0963] [化295]



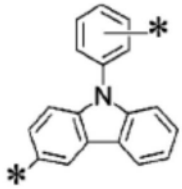
(MU-4-1)



(MU-4-2)

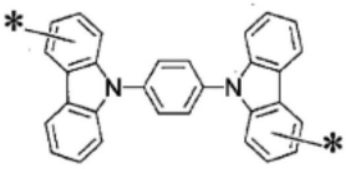


(MU-4-11)

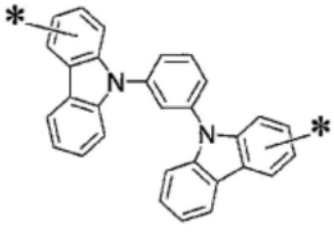


(MU-4-12)

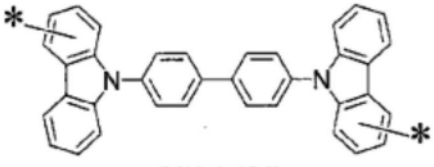
[0964]



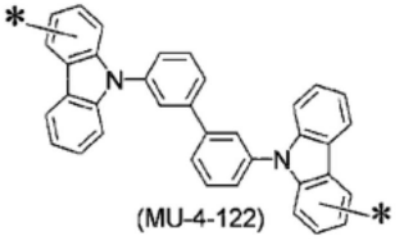
(MU-4-101)



(MU-4-102)



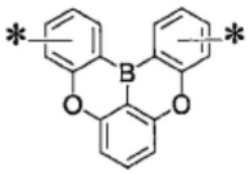
(MU-4-121)



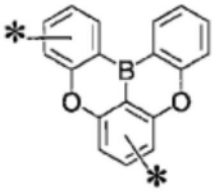
(MU-4-122)

[0965] [化296]

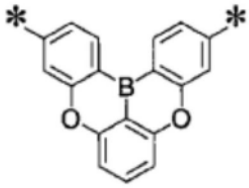
[0966]



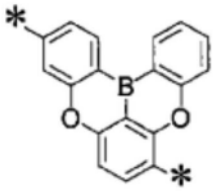
(MU-5-1)



(MU-5-2)



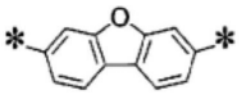
(MU-5-11)



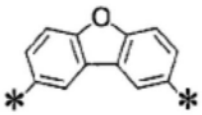
(MU-5-12)

[0967] [化297]

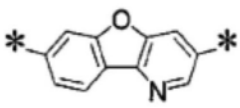
[0968]



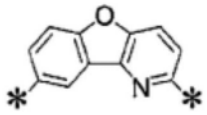
(MU-6-1)



(MU-6-2)

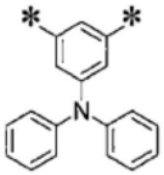


(MU-6-3)

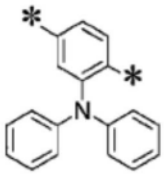


(MU-6-4)

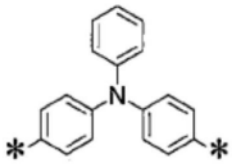
[0969] [化298]



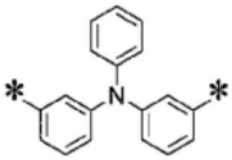
(MU-7-1)



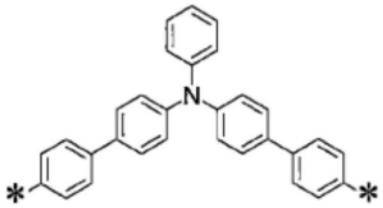
(MU-7-2)



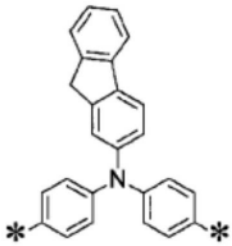
(MU-7-3)



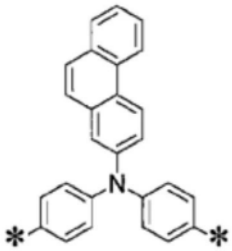
(MU-7-4)



(MU-7-31)

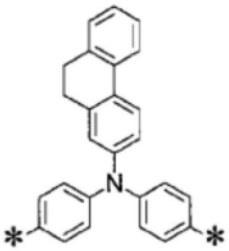


(MU-7-32)

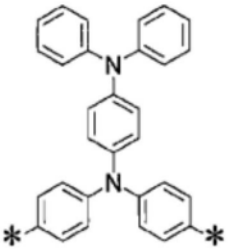


(MU-7-33)

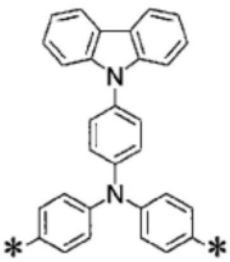
[0970]



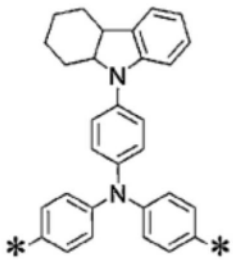
(MU-7-34)



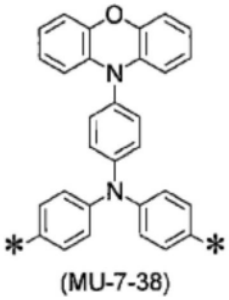
(MU-7-35)



(MU-7-36)

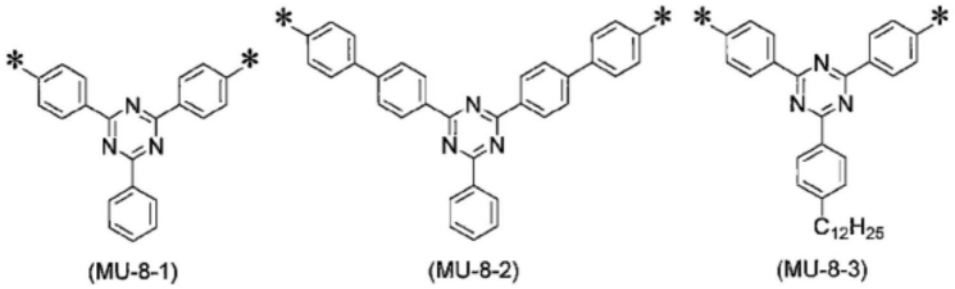


(MU-7-37)

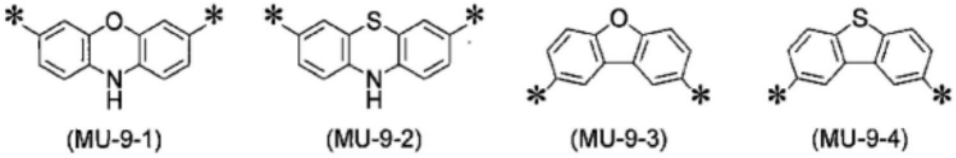


(MU-7-38)

[0971] [化299]

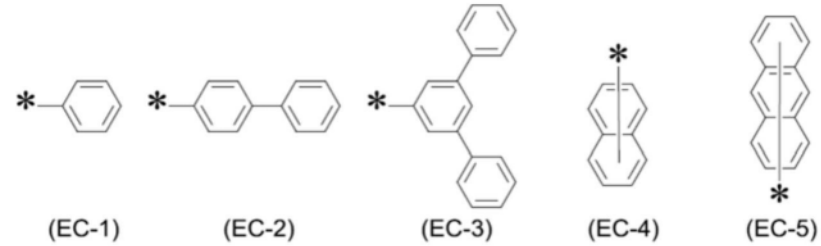
[0972] 

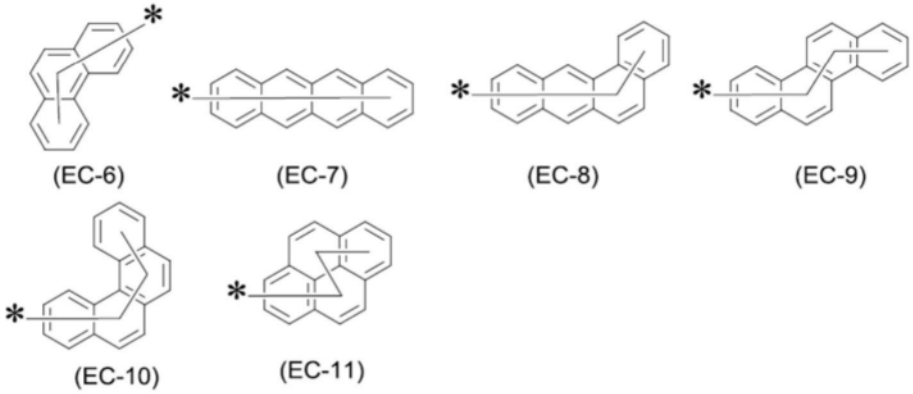
[0973] [化300]

[0974] 

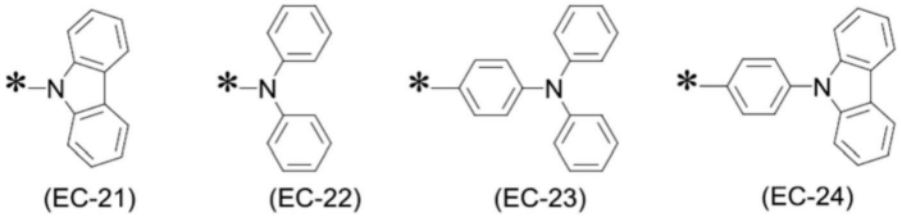
[0975] 另外,作为EC,例如可列举以下的任一结构所表示的一价基。这些中,EC在*处与MU键结。

[0976] [化301]

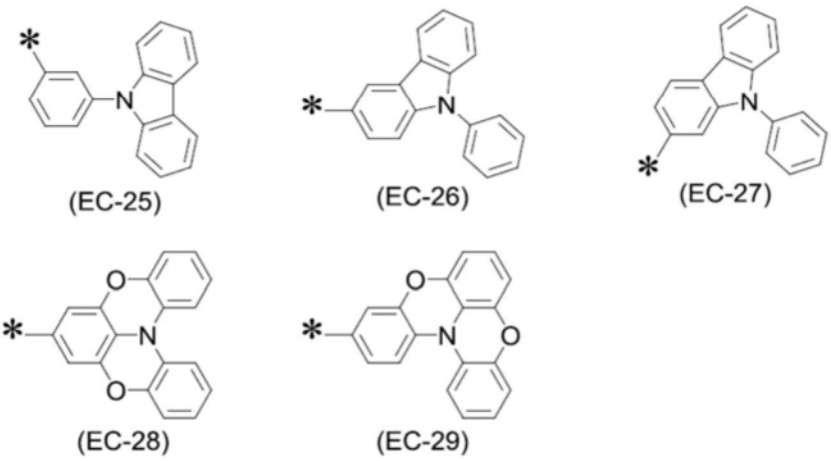


[0977] 

[0978] [化302]



[0979]



[0980] 就溶解性及涂布成膜性的观点而言,式(SPH-1)所表示的化合物优选为分子中的MU总数(k)的10%～100%的MU具有碳数1～24的烷基,更优选为分子中的MU总数(k)的30%～100%的MU具有碳数1～18的烷基(碳数3～18的分支链烷基),进而优选为分子中的MU总数(k)的50%～100%的MU具有碳数1～12的烷基(碳数3～12的分支链烷基)。另一方面,就面内取向性及电荷传输的观点而言,优选为分子中的MU总数(k)的10%～100%的MU具有碳数7～24的烷基,更优选为分子中的MU总数(k)的30%～100%的MU具有碳数7～24的烷基(碳数7～24的分支链烷基)。

[0981] 关于此种高分子化合物及高分子交联体的用途的详细情况,在后文叙述。

[0982] ＜有机电致发光元件中的电子注入层、电子传输层＞

[0983] 电子注入层107发挥将自阴极108迁移而来的电子高效地注入至发光层105内或电子传输层106内的作用。电子传输层106发挥将自阴极108所注入的电子或自阴极108经由电子注入层107所注入的电子高效地传输至发光层105的作用。电子传输层106及电子注入层107分别将电子传输・注入材料的一种或两种以上加以层叠、混合而形成,或者由电子传输・注入材料与高分子粘结剂的混合物形成。

[0984] 所谓电子注入・传输层,为担负自阴极注入电子、进而传输电子的层,理想的是电子注入效率高且高效地传输所注入的电子。因此,优选为电子亲和力大、且电子迁移率大、进而稳定性优异、在制造时及使用时不易产生成为陷阱的杂质的物质。但是,在考虑了空穴与电子的传输平衡的情况下,在主要发挥可高效地阻止来自阳极的空穴未再结合而流向阴极侧的作用的情况下,即便电子传输能力并不那么高,也与电子传输能力高的材料同等地具有提高发光效率的效果。因此,本实施方式中的电子注入・传输层也可包含能够高效地阻止空穴迁移的层的功能。

[0985] 作为形成电子传输层106或电子注入层107的材料(电子传输材料),可自在光导电材料中作为电子传递化合物一直以来所惯用的化合物、用于有机EL元件的电子注入层及电子传输层的已知的化合物中任意地选择来使用。

[0986] 作为电子传输层或电子注入层中所使用的材料,优选为含有选自如下化合物中的至少一种:含有包含选自碳、氢、氧、硫、硅及磷中的一种以上的原子的芳香族环或杂芳香族环的化合物、吡咯衍生物及其缩合环衍生物以及具有电子接受性氮的金属络合物。具体而言,可列举:萘、蒽等缩合环系芳香族环衍生物,以4,4'-双(二苯基乙烯基)联苯为代表的苯乙烯基系芳香族环衍生物,紫环酮衍生物,香豆素衍生物,萘二甲酰亚胺衍生物,蒽醌或联苯醌等醌衍生物,氧化磷衍生物,咔唑衍生物及吲哚衍生物等。作为具有电子接受性氮的金属络合物,例如可列举:羟基苯基噁唑络合物等羟基唑络合物、甲亚胺络合物、环庚三烯酚酮金属络合物、黄酮醇金属络合物及苯并喹啉金属络合物等。这些材料可单独使用,也可与不同的材料混合使用。

[0987] 另外,作为其他电子传递化合物的具体例,可列举:吡啶衍生物、萘衍生物、蒽衍生物、菲咯啉衍生物、紫环酮衍生物、香豆素衍生物、萘二甲酰亚胺衍生物、蒽醌衍生物、联苯醌衍生物、二苯基醌衍生物、芘衍生物、噁二唑衍生物(1,3-双[(4-叔丁基苯基)1,3,4-噁二唑基]亚苯基等)、噻吩衍生物、三唑衍生物(N-萘基-2,5-二苯基-1,3,4-三唑等)、噻二唑衍生物、8-羟基喹啉(oxine)衍生物的金属络合物、羟基喹啉系金属络合物、喹噁啉衍生物、喹噁啉衍生物的聚合物、吲哚(benzazole)类化合物、镓络合物、吡唑衍生物、全氟化亚苯基衍生物、三嗪衍生物、吡嗪衍生物、苯并喹啉衍生物(2,2'-双(苯并[h]喹啉-2-基)-9,9'-螺二芴等)、咪唑并吡啶衍生物、硼烷衍生物、苯并咪唑衍生物(三(N-苯基苯并咪唑-2-基)苯等)、苯并噁唑衍生物、苯并噻唑衍生物、喹啉衍生物、三联吡啶等寡聚吡啶衍生物、联吡啶衍生物、三联吡啶衍生物(1,3-双(4'-(2,2':6',2"-三联吡啶基))苯等)、萘啶衍生物(双(1-萘基)-4-(1,8-萘啶-2-基)苯基氧化膦等)、醛连氮衍生物、咔唑衍生物、吲哚衍生物、氧化磷衍生物、双苯乙烯基衍生物等。

[0988] 另外,也可使用具有电子接受性氮的金属络合物,例如可列举:羟基喹啉系金属络合物或羟基苯基噁唑络合物等羟基唑络合物、甲亚胺络合物、环庚三烯酚酮金属络合物、黄酮醇金属络合物及苯并喹啉金属络合物等。

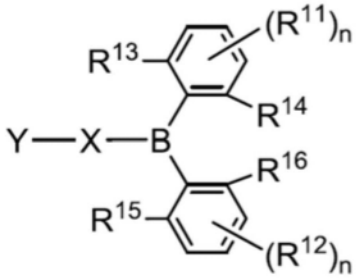
[0989] 所述材料可单独使用,也可与不同的材料混合使用。

[0990] 所述材料中,优选为硼烷衍生物、吡啶衍生物、荧蒽衍生物、BO系衍生物、蒽衍生物、苯并芴衍生物、氧化膦衍生物、嘧啶衍生物、咔唑衍生物、三嗪衍生物、苯并咪唑衍生物、菲咯啉衍生物、及羟基喹啉系金属络合物。

[0991] <硼烷衍生物>

[0992] 硼烷衍生物例如为下述通式(ETM-1)所表示的化合物,详细而言在日本专利特开2007-27587号公报中有公开。

[0993] [化303]

[0994] 

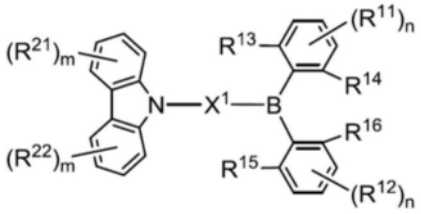
(ETM-1)

[0995] 所述式(ETM-1)中,R^{11}及R^{12}分别独立地为氢、烷基、环烷基、可被取代的芳基、经取

代的硅烷基、可被取代的含氮杂环或氰基的至少一者，R^{13}～R^{16}分别独立地为可被取代的烷基、可被取代的环烷基或可被取代的芳基，X为可被取代的亚芳基，Y为可被取代的碳数16以下的芳基、经取代的硼基或可被取代的咔唑基，而且，n分别独立地为0～3的整数。另外，作为“可被取代”或“经取代”的情况下的取代基，可列举：芳基、杂芳基、烷基或环烷基等。

[0996] 所述通式(ETM-1)所表示的化合物中，优选为下述通式(ETM-1-1)所表示的化合物或下述通式(ETM-1-2)所表示的化合物。

[0997] [化304]

[0998]  (ETM-1-1)

[0999] 式(ETM-1-1)中，R^{11}及R^{12}分别独立地为氢、烷基、环烷基、可被取代的芳基、经取代的硅烷基、可被取代的含氮杂环或氰基的至少一者，R^{13}～R^{16}分别独立地为可被取代的烷基、可被取代的环烷基、或可被取代的芳基，R^{21}及R^{22}分别独立地为氢、烷基、环烷基、可被取代的芳基、经取代的硅烷基、可被取代的含氮杂环、或氰基的至少一者，X^1为可被取代的碳数20以下的亚芳基，n分别独立地为0～3的整数，而且，m分别独立地为0～4的整数。另外，作为“可被取代”或“经取代”的情况下的取代基，可列举：芳基、杂芳基、烷基或环烷基等。

[1000] [化305]

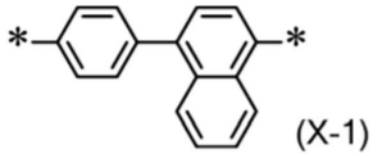
[1001]  (ETM-1-2)

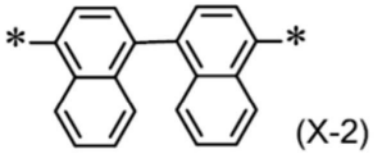
[1002] 式(ETM-1-2)中，R^{11}及R^{12}分别独立地为氢、烷基、环烷基、可被取代的芳基、经取代的硅烷基、可被取代的含氮杂环或氰基的至少一者，R^{13}～R^{16}分别独立地为可被取代的烷基、可被取代的环烷基或可被取代的芳基，X^1为可被取代的碳数20以下的亚芳基，而且，n分别独立地为0～3的整数。另外，作为“可被取代”或“经取代”的情况下的取代基，可列举：芳基、杂芳基、烷基或环烷基等。

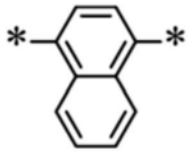
[1003] 作为X^1的具体例，可列举下述式(X-1)～式(X-9)的任一者所表示的二价基。各结构式中的*表示键结位置。

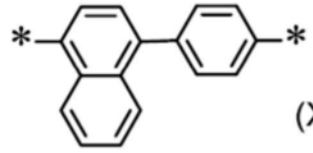
[1004] [化306]

[1005]

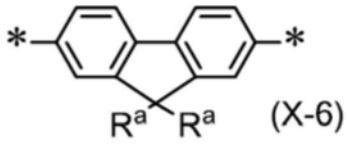

(X-1)

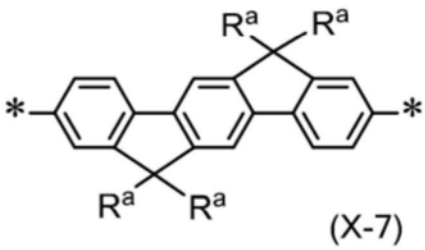

(X-2)

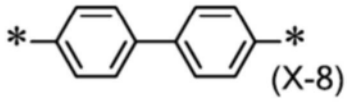

(X-3)

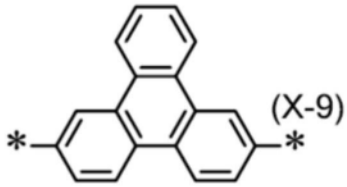

(X-4)


(X-5)


(X-6)


(X-7)


(X-8)

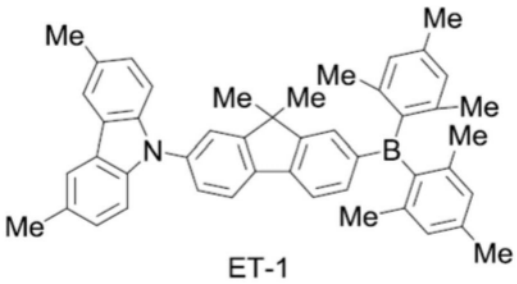

(X-9)

[1006] (各式中,R^a分别独立地为烷基、环烷基或可被取代的苯基)

[1007] 作为所述硼烷衍生物的具体例,例如可列举以下的化合物。

[1008] [化307]

[1009]


ET-1

[1010] 所述硼烷衍生物可使用已知的原料与已知的合成方法来制造。

[1011] <吡啶衍生物>

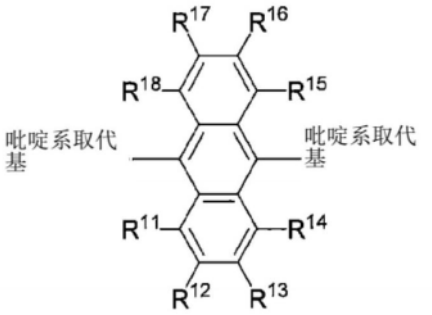
[1012] 吡啶衍生物例如为下述式(ETM-2)所表示的化合物,优选为式(ETM-2-1)或式(ETM-2-2)所表示的化合物。

[1013] [化308]

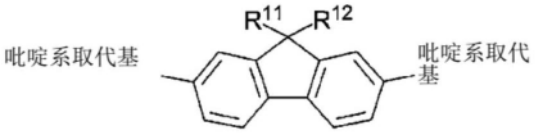


(ETM-2)

[1014]



(ETM-2-1)



(ETM-2-2)

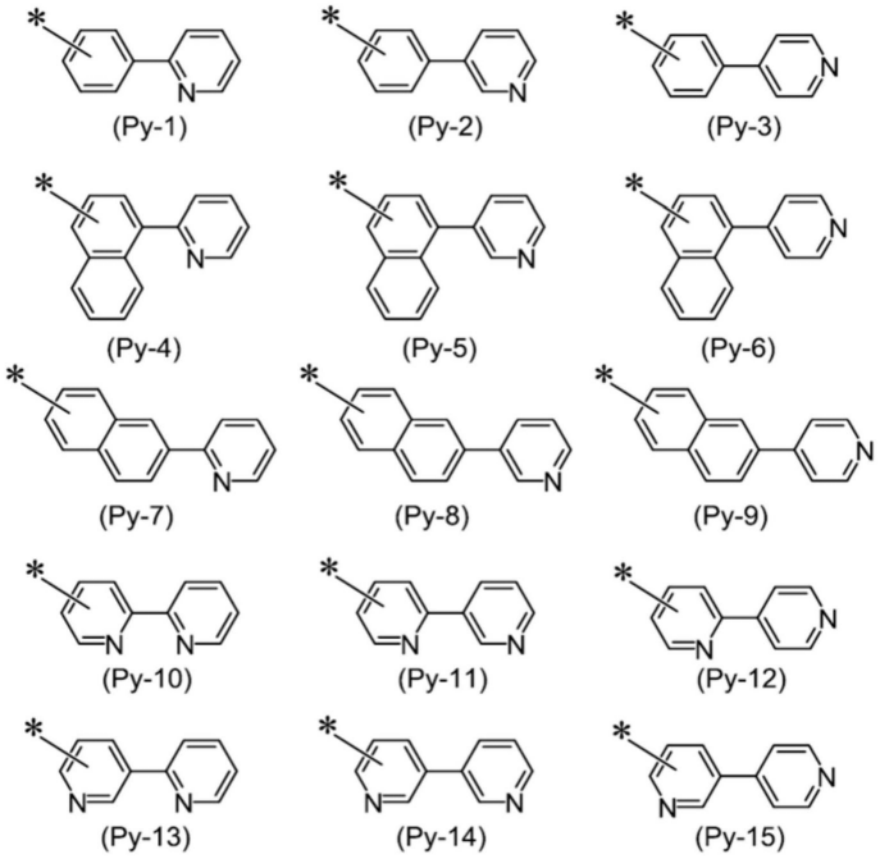
[1015] φ为n价的芳基环(优选为n价的苯环、萘环、蒽环、芴环、苯并芴环、非那烯环、菲环或三亚苯环),n为1～4的整数。

[1016] 所述式(ETM-2-1)中,R^{11}～R^{18}分别独立地为氢、烷基(优选为碳数1～24的烷基)、环烷基(优选为碳数3～12的环烷基)或芳基(优选为碳数6～30的芳基)。

[1017] 在所述式(ETM-2-2)中,R^{11}及R^{12}分别独立地为氢、烷基(优选为碳数1～24的烷基)、环烷基(优选为碳数3～12的环烷基)或芳基(优选为碳数6～30的芳基),R^{11}及R^{12}可键结而形成环。

[1018] 在各式中,“吡啶系取代基”为下述式(Py-1)～式(Py-15)的任一者,吡啶系取代基可分别独立地由碳数1～4的烷基或碳数5～10的环烷基取代。另外,吡啶系取代基可经由亚苯基或亚萘基而与各式中的φ、蒽环或芴环键结。各结构式中的*表示键结位置。

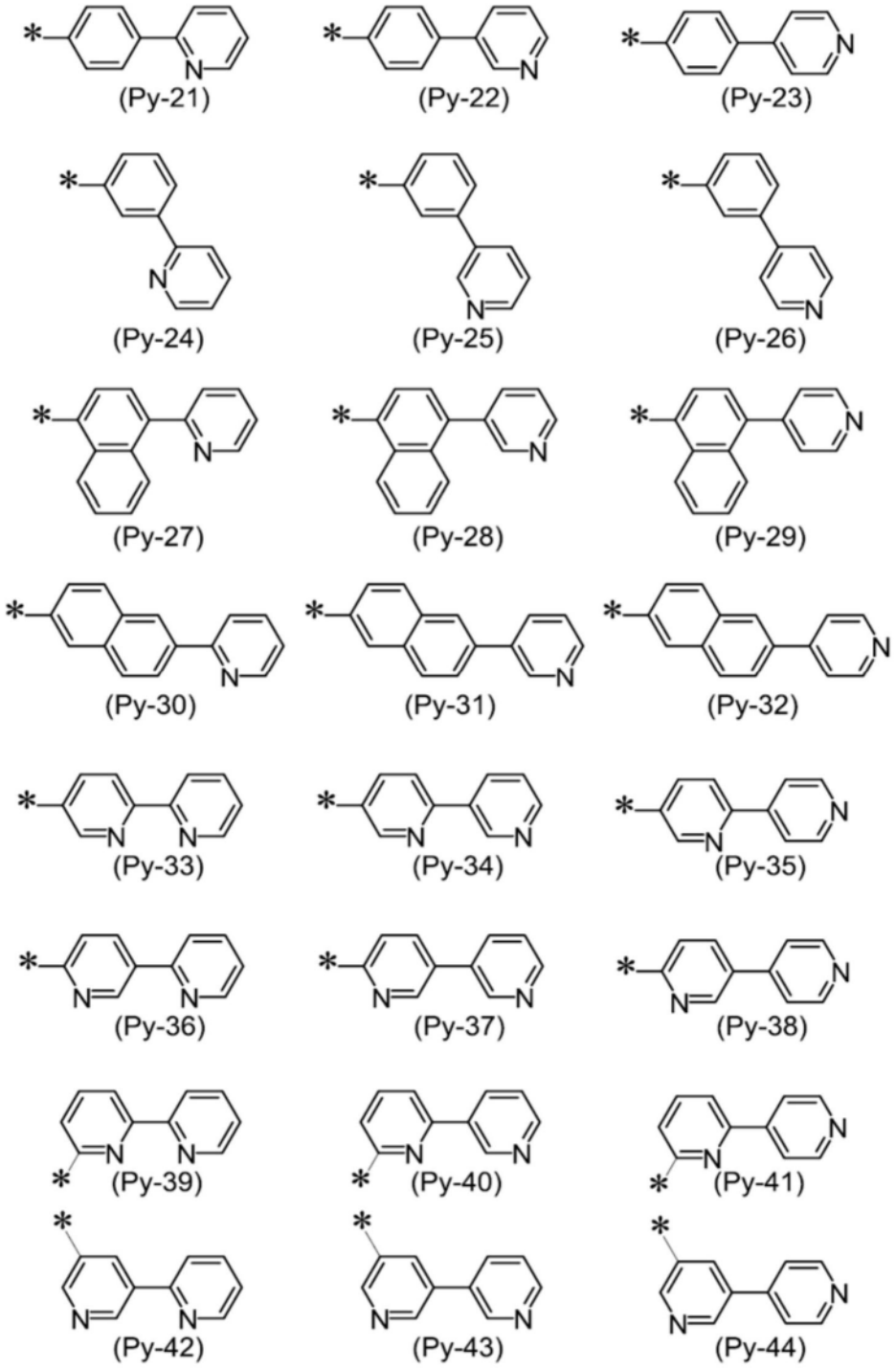
[1019] [化309]

[1020] 

[1021] 吡啶系取代基为所述式(Py-1)～式(Py-15)的任一者,这些中优选为下述式(Py-21)～式(Py-44)的任一者。各结构式中的*表示键结位置。

[1022] [化310]

[1023]



[1024] 各吡啶衍生物中的至少一个氢可由氘取代,另外,所述式(ETM-2-1)及式(ETM-2-2)中的两个“吡啶系取代基”中的一者可由芳基取代。

[1025] 作为R^{11}～R^{18}中的“烷基”,可为直链及分支链的任一种,例如可列举碳数1～24的直链烷基或碳数3～24的分支链烷基。优选的“烷基”为碳数1～18的烷基(碳数3～18的分支链烷基)。更优选的“烷基”为碳数1～12的烷基(碳数3～12的分支链烷基)。进而优选的“烷基”为碳数1～6的烷基(碳数3～6的分支链烷基)。特别优选的“烷基”为碳数1～4的烷基(碳数3～4的分支链烷基)。

[1026] 作为具体的“烷基”,可列举:甲基、乙基、正丙基、异丙基、正丁基、异丁基、仲丁基、叔丁基、正戊基、异戊基、新戊基、叔戊基(t-amyl)、正己基、1-甲基戊基、3,3-二甲基丁基、

2-乙基丁基、正庚基、1-甲基己基、正辛基、叔辛基(1,1,3,3-四甲基丁基)、1-甲基庚基、2-乙基己基、2-丙基戊基、正壬基、2,2-二甲基庚基、2,6-二甲基-4-庚基、3,5,5-三甲基己基、正癸基、正十一基、1-甲基癸基、正十二基、正十三基、1-己基庚基、正十四基、正十五基、正十六基、正十七基、正十八基、正二十基等。

[1027] 另外,例如也可列举:1-乙基-1-甲基丙基、1,1-二乙基丙基、1,1-二甲基丁基、1-乙基-1-甲基丁基、1,1,4-三甲基戊基、1,1,2-三甲基丙基、1,1-二甲基辛基、1,1-二甲基戊基、1,1-二甲基庚基、1,1,5-三甲基己基、1-乙基-1-甲基己基、1-乙基-1,3-二甲基丁基、1,1,2,2-四甲基丙基、1-丁基-1-甲基戊基、1,1-二乙基丁基、1-乙基-1-甲基戊基、1,1,3-三甲基丁基、1-丙基-1-甲基戊基、1,1,2-三甲基丙基、1-乙基-1,2,2-三甲基丙基、1-丙基-1-甲基丁基、1,1-二甲基己基等。

[1028] 作为在吡啶系取代基中进行取代的碳数1～4的烷基,可引用所述烷基的说明。

[1029] 作为R^{11}～R^{18}中的“环烷基”,例如可列举碳数3～12的环烷基。优选的“环烷基”为碳数3～10的环烷基。更优选的“环烷基”为碳数3～8的环烷基。进而优选的“环烷基”为碳数3～6的环烷基。

[1030] 作为具体的“环烷基”,可列举:环丙基、环丁基、环戊基、环己基、甲基环戊基、环庚基、甲基环己基、环辛基或二甲基环己基等。

[1031] 作为R^{11}～R^{18}中的“芳基”,优选的芳基为碳数6～30的芳基,更优选的芳基为碳数6～18的芳基,进而优选为碳数6～14的芳基,特别优选为碳数6～12的芳基。

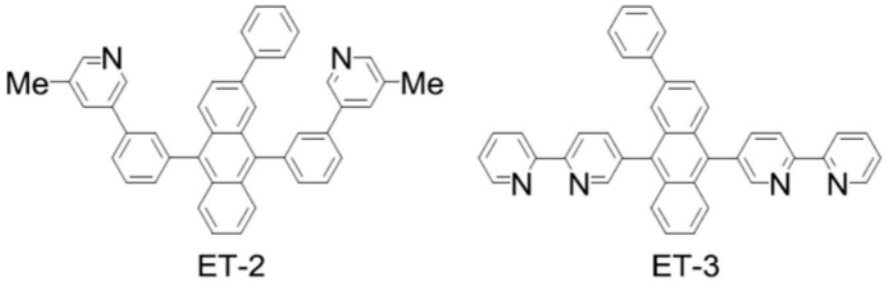
[1032] 作为具体的“碳数6～30的芳基”,可列举:作为单环系芳基的苯基、作为缩合二环系芳基的(1-、2-)萘基、作为缩合三环系芳基的苊-(1-、3-、4-、5-)基、芴-(1-、2-、3-、4-、9-)基、非那烯-(1-、2-)基、(1-、2-、3-、4-、9-)菲基、作为缩合四环系芳基的三亚苯-(1-、2-)基、芘-(1-、2-、4-)基、稠四苯-(1-、2-、5-)基、作为缩合五环系芳基的苝-(1-、2-、3-)基、稠五苯-(1-、2-、5-、6-)基等。

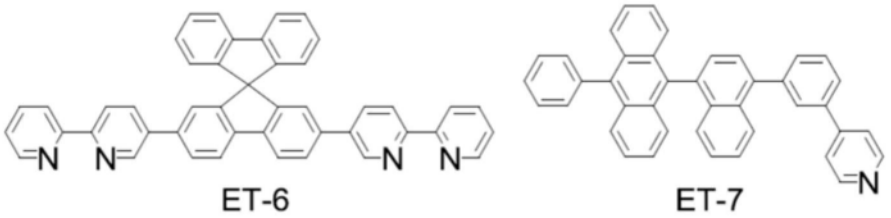
[1033] 优选的“碳数6～30的芳基”可列举苯基、萘基、菲基、䓛基或三亚苯基等,进而优选为可列举苯基、1-萘基、2-萘基或菲基,特别优选为可列举苯基、1-萘基或2-萘基。

[1034] 所述式(ETM-2-2)中的R^{11}及R^{12}可键结而形成环,其结果为,可在芴骨架的5元环上螺键结环丁烷、环戊烷、环戊烯、环戊二烯、环己烷、芴或茚等。

[1035] 作为所述吡啶衍生物的具体例,例如可列举以下的化合物。

[1036] [化311]

[1037] 

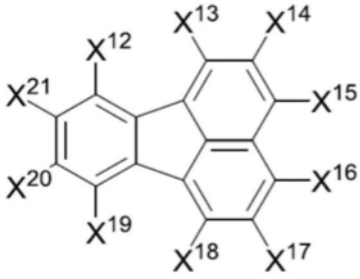


[1038] 所述吡啶衍生物可使用已知的原料与已知的合成方法来制造。

[1039] ＜荧蒽衍生物＞

[1040] 荧蒽衍生物例如为下述通式(ETM-3)所表示的化合物,详细而言在国际公开第2010/134352号公报中有公开。

[1041] [化312]

[1042] 

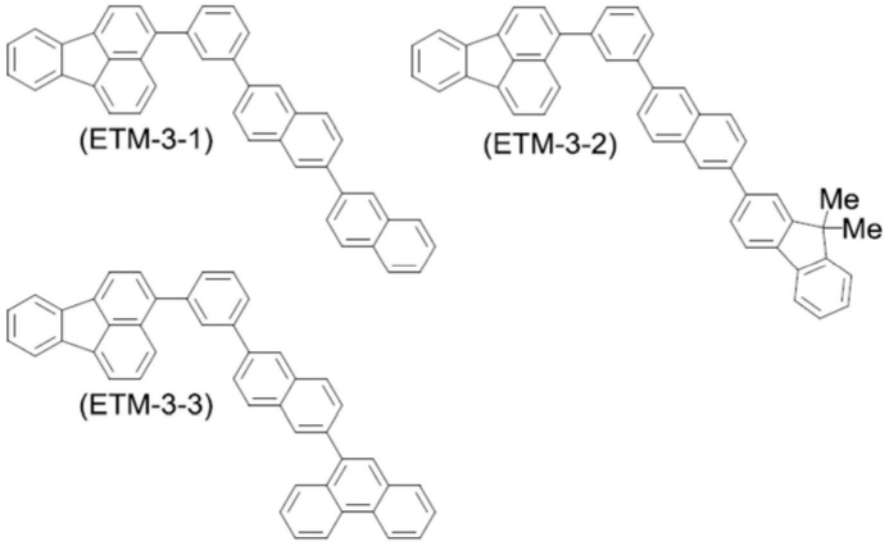
(ETM-3)

[1043] 所述式(ETM-3)中,X^{12}～X^{21}表示氢、卤素、直链、分支或环状的烷基、直链、分支或环状的烷氧基、经取代或未经取代的芳基、或者经取代或未经取代的杂芳基。此处,作为经取代的情况下的取代基,可列举:芳基、杂芳基、烷基或环烷基等。

[1044] 作为所述荧蒽衍生物的具体例,例如可列举以下的化合物。

[1045] [化313]

[1046]

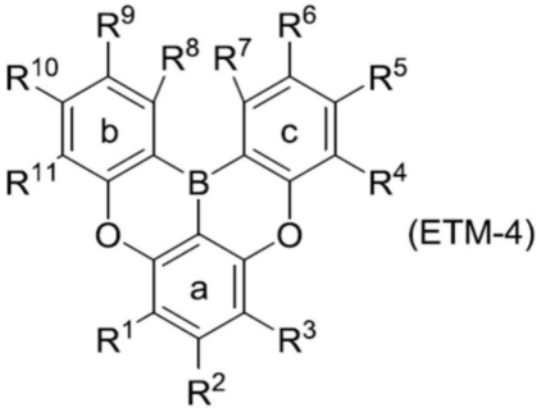


[1047] ＜BO系衍生物＞

[1048] BO系衍生物例如为下述式(ETM-4)所表示的多环芳香族化合物、或具有多个下述式(ETM-4)所表示的结构的多环芳香族化合物的多聚体。

[1049] [化314]

[1050]



(ETM-4)

[1051] R^1～R^{11}分别独立地为氢、芳基、杂芳基、二芳基氨基、二杂芳基氨基、芳基杂芳基氨基、烷基、环烷基、烷氧基或芳氧基,这些中的至少一个氢可由芳基、杂芳基、烷基或环烷基取代。

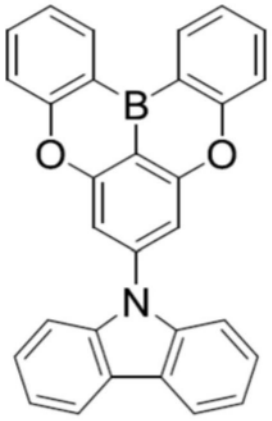
[1052] 另外,R^1～R^{11}中的邻接的基彼此可键结并与a环、b环或c环一同形成芳基环或杂芳基环,所形成的环中的至少一个氢可由芳基、杂芳基、二芳基氨基、二杂芳基氨基、芳基杂芳基氨基、烷基、环烷基、烷氧基或芳氧基取代,这些中的至少一个氢可由芳基、杂芳基、烷基或环烷基取代。

[1053] 另外,式(ETM-4)所表示的化合物或结构中的至少一个氢可由卤素或氘取代。

[1054] 关于式(ETM-4)中的取代基或环形成的形态的说明,可引用所述通式(1)或通式(2)所表示的多环芳香族化合物的说明。

[1055] 作为所述BO系衍生物的具体例,例如可列举以下的化合物。

[1056] [化315]

[1057] 

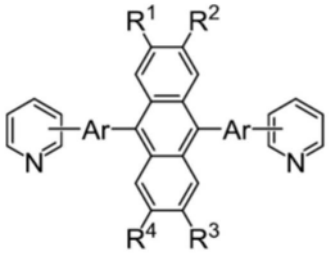
ET-5

[1058] 所述BO系衍生物可使用已知的原料与已知的合成方法来制造。

[1059] ＜蒽衍生物＞

[1060] 蒽衍生物之一例如为下述式(ETM-5-1)所表示的化合物。

[1061] [化316]

[1062] 

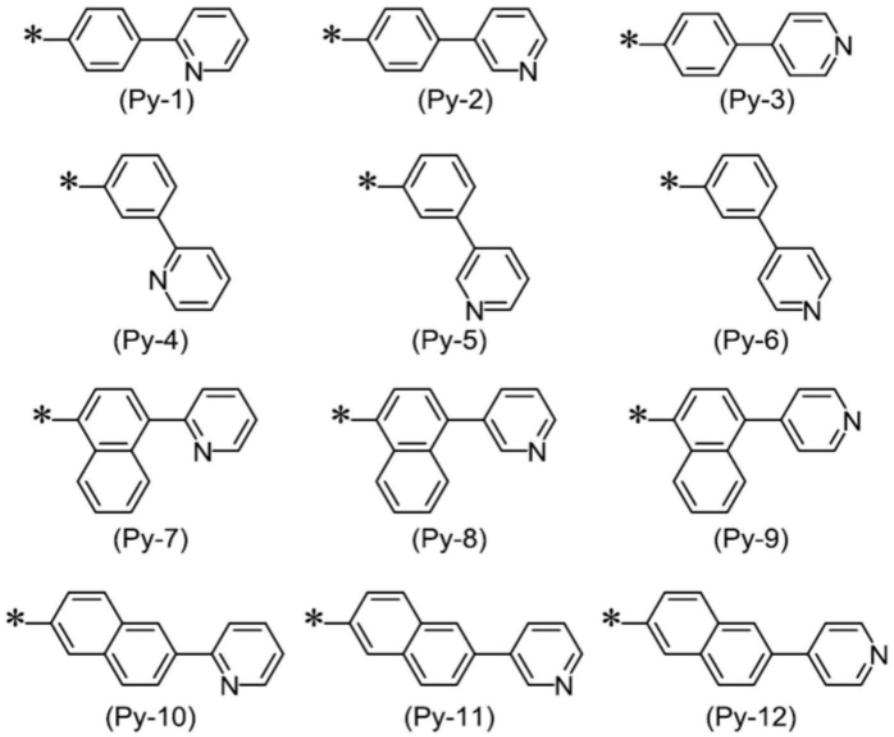
(ETM-5-1)

[1063] Ar分别独立地为二价的苯或萘,R^1～R^4分别独立地为氢、碳数1～6的烷基、碳数3～6的环烷基或碳数6～20的芳基。

[1064] Ar可分别独立地自二价的苯或萘中适当选择,两个Ar可不同也可相同,就蒽衍生物的合成容易性的观点而言,优选为相同。Ar与吡啶键结而形成“包含Ar及吡啶的部位”,所述部位例如作为下述式(Py-1)～式(Py-12)的任一者所表示的基而与蒽键结。各结构式中的*表示键结位置。

[1065] [化317]

[1066]



[1067] 这些基中,优选为所述式(Py-1)～式(Py-9)的任一者所表示的基,更优选为所述式(Py-1)～式(Py-6)的任一者所表示的基。键结于蒽的两个“包含Ar及吡啶的部位”的结构可相同也可不同,就蒽衍生物的合成容易性的观点而言,优选为相同结构。其中,就元件特性的观点而言,无论两个“包含Ar及吡啶的部位”的结构相同还是不同均优选。

[1068] 关于R^1～R^4中的碳数1～6的烷基,可为直链及分支链的任一种。即,为碳数1～6的直链烷基或碳数3～6的分支链烷基。更优选为碳数1～4的烷基(碳数3～4的分支链烷基)。作为具体例,可列举甲基、乙基、正丙基、异丙基、正丁基、异丁基、仲丁基、叔丁基、正戊基、异戊基、新戊基、叔戊基(t-amyl)、正己基、1-甲基戊基、3,3-二甲基丁基或2-乙基丁基等,优选为甲基、乙基、正丙基、异丙基、正丁基、异丁基、仲丁基或叔丁基,更优选为甲基、乙基或叔丁基。

[1069] 作为R^1～R^4中的碳数3～6的环烷基的具体例,可列举:环丙基、环丁基、环戊基、环己基、甲基环戊基、环庚基、甲基环己基、环辛基或二甲基环己基等。

[1070] 关于R^1～R^4中的碳数6～20的芳基,优选为碳数6～16的芳基,更优选为碳数6～12的芳基,特别优选为碳数6～10的芳基。

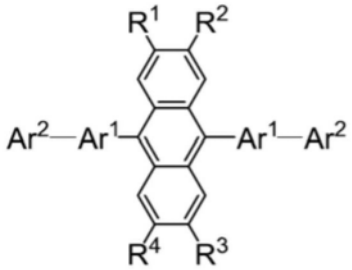
[1071] 作为“碳数6～20的芳基”的具体例,可列举:作为单环系芳基的苯基、(邻、间、对)甲苯基、(2,3-、2,4-、2,5-、2,6-、3,4-、3,5-)二甲苯基、均三甲苯基(2,4,6-三甲基苯基)、(邻、间、对)枯烯基、作为二环系芳基的(2-、3-、4-)联苯基、作为缩合二环系芳基的(1-、2-)萘基、作为三环系芳基的联三苯基(间联三苯-2'-基、间联三苯-4'-基、间联三苯-5'-基、邻联三苯-3'-基、邻联三苯-4'-基、对联三苯-2'-基、间联三苯-2-基、间联三苯-3-基、间联三苯-4-基、邻联三苯-2-基、邻联三苯-3-基、邻联三苯-4-基、对联三苯-2-基、对联三苯-3-基、对联三苯-4-基)、作为缩合三环系芳基的蒽-(1-、2-、9-)基、苊-(1-、3-、4-、5-)基、芴-(1-、2-、3-、4-、9-)基、非那烯-(1-、2-)基、(1-、2-、3-、4-、9-)菲基、作为缩合四环系芳基的三亚苯-(1-、2-)基、芘-(1-、2-、4-)基、稠四苯-(1-、2-、5-)基、作为缩合五环系芳基的苝-

(1-、2-、3-)基等。

[1072] 优选的“碳数6～20的芳基”为苯基、联苯基、联三苯基或萘基,更优选为苯基、联苯基、1-萘基、2-萘基或间联三苯-5’-基,进而优选为苯基、联苯基、1-萘基或2-萘基,最优选为苯基。

[1073] 蒽衍生物之一例如为下述式(ETM-5-2)所表示的化合物。

[1074] [化318]

[1075] 

(ETM-5-2)

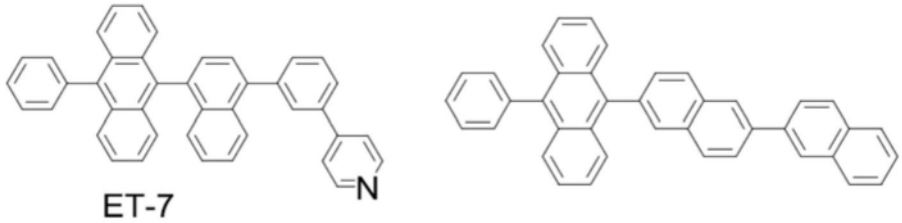
[1076] Ar^1分别独立地为单键、二价的苯、萘、蒽、芴、或非那烯。

[1077] Ar^2分别独立地为碳数6～20的芳基,可引用与所述式(ETM-5-1)中的“碳数6～20的芳基”相同的说明。优选为碳数6～16的芳基,更优选为碳数6～12的芳基,特别优选为碳数6～10的芳基。作为具体例,可列举:苯基、联苯基、萘基、联三苯基、蒽基、苊基、芴基、非那烯基、菲基、三亚苯基、芘基、并四苯基(tetracenyl)、苝基等。

[1078] R^1～R^4分别独立地为氢、碳数1～6的烷基、碳数3至6的环烷基或碳数6～20的芳基,可引用所述式(ETM-5-1)中的说明。

[1079] 作为这些蒽衍生物的具体例,例如可列举以下的化合物。

[1080] [化319]

[1081] 

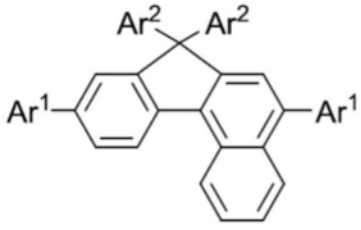
ET-7

[1082] 这些蒽衍生物可使用已知的原料与已知的合成方法来制造。

[1083] ＜苯并芴衍生物＞

[1084] 苯并芴衍生物例如为下述式(ETM-6)所表示的化合物。

[1085] [化320]

[1086] 

(ETM-6)

[1087] Ar^1分别独立地为碳数6～20的芳基,可引用与所述式(ETM-5-1)中的“碳数6～20的芳基”相同的说明。优选为碳数6～16的芳基,更优选为碳数6～12的芳基,特别优选为碳数6～10的芳基。作为具体例,可列举:苯基、联苯基、萘基、联三苯基、蒽基、苊基、芴基、非那烯基、菲基、三亚苯基、芘基、并四苯基(tetracenyl)、苝基等。

[1088] Ar^2分别独立地为氢、烷基(优选为碳数1～24的烷基)、环烷基(优选为碳数3～12的环烷基)或芳基(优选为碳数6～30的芳基),两个Ar^2可键结而形成环。

[1089] 作为Ar^2中的“烷基”,可为直链及分支链的任一种,例如可列举碳数1～24的直链烷基或碳数3～24的分支链烷基。优选的“烷基”为碳数1～18的烷基(碳数3～18的分支链烷基)。更优选的“烷基”为碳数1～12的烷基(碳数3～12的分支链烷基)。进而优选的“烷基”为碳数1～6的烷基(碳数3～6的分支链烷基)。特别优选的“烷基”为碳数1～4的烷基(碳数3～4的分支链烷基)。作为具体的“烷基”,可列举:甲基、乙基、正丙基、异丙基、正丁基、异丁基、仲丁基、叔丁基、正戊基、异戊基、新戊基、叔戊基(t-amyl)、正己基、1-甲基戊基、3,3-二甲基丁基、2-乙基丁基、正庚基、1-甲基己基等。

[1090] 作为Ar^2中的“环烷基”,例如可列举碳数3～12的环烷基。优选的“环烷基”为碳数3～10的环烷基。更优选的“环烷基”为碳数3～8的环烷基。进而优选的“环烷基”为碳数3～6的环烷基。作为具体的“环烷基”,可列举:环丙基、环丁基、环戊基、环己基、甲基环戊基、环庚基、甲基环己基、环辛基或二甲基环己基等。

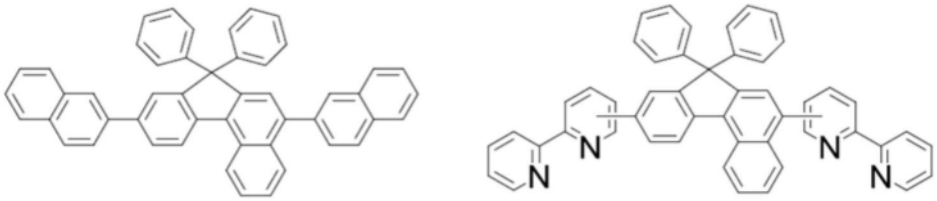
[1091] 作为Ar^2中的“芳基”,优选的芳基为碳数6～30的芳基,更优选的芳基为碳数6～18的芳基,进而优选为碳数6～14的芳基,特别优选为碳数6～12的芳基。

[1092] 作为具体的“碳数6～30的芳基”,可列举:苯基、萘基、苊基、芴基、非那烯基、菲基、三亚苯基、芘基、并四苯基、苉基、稠五苯基等。

[1093] 两个Ar^2可键结而形成环,其结果为,可在芴骨架的5元环上螺键结环丁烷、环戊烷、环戊烯、环戊二烯、环己烷、芴或茚等。

[1094] 作为所述苯并芴衍生物的具体例,例如可列举以下的化合物。

[1095] [化321]

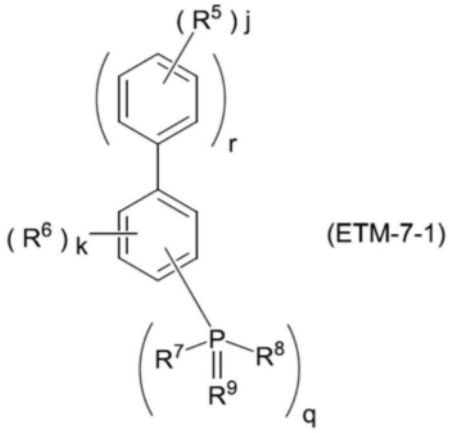
[1096] 

[1097] 所述苯并芴衍生物可使用已知的原料与已知的合成方法来制造。

[1098] ＜氧化膦衍生物＞

[1099] 氧化膦衍生物例如为下述式(ETM-7-1)所表示的化合物。详细情况在国际公开第2013/079217号公报中也有记载。

[1100] [化322]

[1101] 

(ETM-7-1)

[1102] R^5为经取代或未经取代的碳数1～20的烷基、碳数3～16的环烷基、碳数6～20的芳基或碳数5～20的杂芳基，

[1103] R^6为CN、经取代或未经取代的、碳数1～20的烷基、碳数3～16的环烷基、碳数1～20的杂烷基、碳数6～20的芳基、碳数5～20的杂芳基、碳数1～20的烷氧基或碳数6～20的芳氧基，

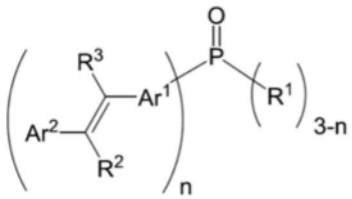
[1104] R^7及R^8分别独立地为经取代或未经取代的碳数6～20的芳基或碳数5～20的杂芳基，R^9为氧或硫，

[1105] j为0或1，k为0或1，r为0～4的整数，q为1～3的整数。

[1106] 此处，作为经取代的情况下的取代基，可列举：芳基、杂芳基、烷基或环烷基等。

[1107] 氧化膦衍生物例如可为下述式(ETM-7-2)所表示的化合物。

[1108] [化323]

[1109] 

(ETM-7-2)

[1110] R^1～R^3可相同也可不同，选自于与氢、烷基、环烷基、芳烷基、烯基、环烯基、炔基、烷氧基、烷硫基、环烷硫基、芳基醚基、芳硫基醚基、芳基、杂环基、卤素、氰基、醛基、羰基、羧基、氨基、硝基、硅烷基及邻接取代基之间所形成的缩合环中。

[1111] Ar^1可相同也可不同，为亚芳基或亚杂芳基。Ar^2可相同也可不同，为芳基或杂芳基。其中，Ar^1及Ar^2中的至少一者具有取代基，或在与邻接取代基之间形成缩合环。n为0～3的整数，n为0时，并不存在不饱和结构部分，n为3时，并不存在R^1。

[1112] 这些取代基中，所谓烷基，例如表示甲基、乙基、丙基、丁基等饱和脂肪族烃基，其可未经取代也可经取代。经取代的情况下的取代基并无特别限制，例如可列举烷基、芳基、杂环基等，所述方面在以下的记载中也共通。另外，烷基的碳数并无特别限定，就获取的容易性或成本的方面而言，通常为1～20的范围。

[1113] 另外，所谓环烷基，例如表示环丙基、环己基、降冰片基、金刚烷基等饱和脂环式烃基，其可未经取代也可经取代。烷基部分的碳数并无特别限定，通常为3～20的范围。

[1114] 另外，所谓芳烷基，例如表示苄基、苯基乙基等经由脂肪族烃的芳香族烃基，脂肪族烃与芳香族烃均可未经取代也可经取代。脂肪族部分的碳数并无特别限定，通常为1～20

的范围。

[1115] 另外,所谓烯基,例如表示乙烯基、烯丙基、丁二烯基等包含双键的不饱和脂肪族烃基,其可未经取代也可经取代。烯基的碳数并无特别限定,通常为2～20的范围。

[1116] 另外,所谓环烯基,例如表示环戊烯基、环戊二烯基、环己烯基等包含双键的不饱和脂环式烃基,其可未经取代也可经取代。

[1117] 另外,所谓炔基,例如表示乙炔基等包含三键的不饱和脂肪族烃基,其可未经取代也可经取代。炔基的碳数并无特别限定,通常为2～20的范围。

[1118] 另外,所谓烷氧基,例如表示甲氧基等经由醚键的脂肪族烃基,脂肪族烃基可未经取代也可经取代。烷氧基的碳数并无特别限定,通常为1～20的范围。

[1119] 另外,所谓烷硫基,为烷氧基的醚键的氧原子被取代为硫原子的基。

[1120] 另外,所谓环烷硫基,为环烷氧基的醚键的氧原子被取代为硫原子的基。

[1121] 另外,所谓芳基醚基,例如表示苯氧基等经由醚键的芳香族烃基,芳香族烃基可未经取代也可经取代。芳基醚基的碳数并无特别限定,通常为6～40的范围。

[1122] 另外,所谓芳硫基醚基,为芳基醚基的醚键的氧原子被取代为硫原子的基。

[1123] 另外,所谓芳基,例如表示苯基、萘基、联苯基、菲基、联三苯基、芘基等芳香族烃基。芳基可未经取代也可经取代。芳基的碳数并无特别限定,通常为6～40的范围。

[1124] 另外,所谓杂环基,例如表示呋喃基、噻吩基、噁唑基、吡啶基、喹啉基、咔唑基等具有碳以外的原子的环状结构基,其可未经取代也可经取代。杂环基的碳数并无特别限定,通常为2～30的范围。

[1125] 所谓卤素,表示氟、氯、溴、碘。

[1126] 醛基、羰基、氨基中也可包含由脂肪族烃、脂环式烃、芳香族烃、杂环等取代而成的基。

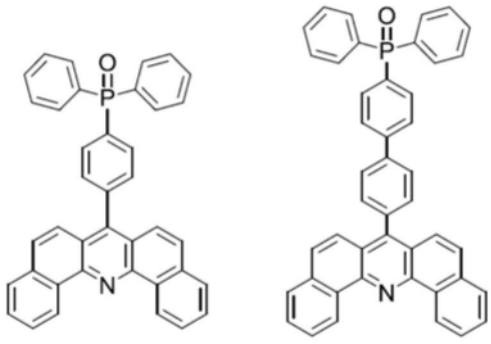
[1127] 另外,脂肪族烃、脂环式烃、芳香族烃、杂环可未经取代也可经取代。

[1128] 所谓硅烷基,例如表示三甲基硅烷基等硅化合物基,其可未经取代也可经取代。硅烷基的碳数并无特别限定,通常为3～20的范围。另外,硅数通常为1～6。

[1129] 所谓在与邻接取代基之间所形成的缩合环,例如为在Ar^1与R^2、Ar^1与R^3、Ar^2与R^2、Ar^2与R^3、R^2与R^3、Ar^1与Ar^2等之间形成的共轭或非共轭的缩合环。此处,在n为1的情况下,两个R^1彼此可形成共轭或非共轭的缩合环。这些缩合环可在环内结构中包含氮原子、氧原子、硫原子,进而也可与其他环缩合。

[1130] 作为所述氧化膦衍生物的具体例,例如可列举以下的化合物。

[1131] [化324]

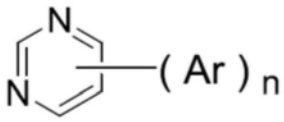
[1132] 

[1133] 所述氧化膦衍生物可使用已知的原料与已知的合成方法来制造。

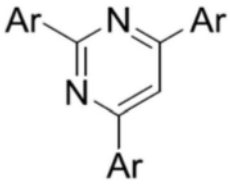
[1134] ＜嘧啶衍生物＞

[1135] 嘧啶衍生物例如为下述式(ETM-8)所表示的化合物,优选为下述式(ETM-8-1)所表示的化合物。详细情况在国际公开第2011/021689号公报中也有记载。

[1136] [化325]

[1137] 

(ETM-8)



(ETM-8-1)

[1138] Ar分别独立地为可被取代的芳基、或可被取代的杂芳基。n为1～4的整数,优选为1～3的整数,更优选为2或3。

[1139] 作为“可被取代的芳基”的“芳基”,例如可列举碳数6～30的芳基,优选为碳数6～24的芳基,更优选为碳数6～20的芳基,进而优选为碳数6～12的芳基。

[1140] 作为具体的“芳基”,可列举:作为单环系芳基的苯基、作为二环系芳基的(2-、3-、4-)联苯基、作为缩合二环系芳基的(1-、2-)萘基、作为三环系芳基的联三苯基(间联三苯-2'-基、间联三苯-4'-基、间联三苯-5'-基、邻联三苯-3'-基、邻联三苯-4'-基、对联三苯-2'-基、间联三苯-2-基、间联三苯-3-基、间联三苯-4-基、邻联三苯-2-基、邻联三苯-3-基、邻联三苯-4-基、对联三苯-2-基、对联三苯-3-基、对联三苯-4-基)、作为缩合三环系芳基的苊-(1-、3-、4-、5-)基、芴-(1-、2-、3-、4-、9-)基、非那烯-(1-、2-)基、(1-、2-、3-、4-、9-)菲基、作为四环系芳基的联四苯基(5'-苯基-间联三苯-2-基、5'-苯基-间联三苯-3-基、5'-苯基-间联三苯-4-基、间联四苯基)、作为缩合四环系芳基的三亚苯-(1-、2-)基、苝-(1-、2-、4-)基、稠四苯-(1-、2-、5-)基、作为缩合五环系芳基的苉-(1-、2-、3-)基、稠五苯-(1-、2-、5-、6-)基等。

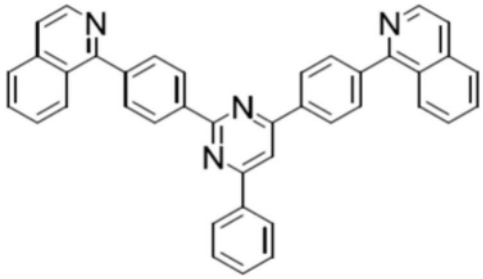
[1141] 作为“可被取代的杂芳基”的“杂芳基”,例如可列举碳数2～30的杂芳基,优选为碳数2～25的杂芳基,更优选为碳数2～20的杂芳基,进而优选为碳数2～15的杂芳基,特别优选为碳数2～10的杂芳基。另外,作为杂芳基,例如可列举除碳以外含有1个～5个选自氧、硫及氮中的杂原子作为环构成原子的杂环等。

[1142] 作为具体的杂芳基,例如可列举:吡咯基、噁唑基、异噁唑基、噻唑基、异噻唑基、咪唑基、噁二唑基、噻二唑基、三唑基、四唑基、吡唑基、吡啶基、嘧啶基、哒嗪基、吡嗪基、三嗪基、吲哚基、异吲哚基、1H-吲唑基、苯并咪唑基、苯并噁唑基、苯并噻唑基、1H-苯并三唑基、喹啉基、异喹啉基、噌啉基、喹唑啉基、喹喔啉基、酞嗪基、萘啶基、嘌呤基、喋啶基、咔唑基、吖啶基、吩噁噻基、吩噁嗪基、吩噻嗪基、吩嗪基、环戊基硼酸基(phenazasilinyl)、吲嗪基、呋喃基、苯并呋喃基、异苯并呋喃基、二苯并呋喃基、萘并苯并呋喃基、噻吩基、苯并噻吩基、异苯并噻吩基、二苯并噻吩基、萘并苯并噻吩基、噻蒽基、苯并磷杂环戊二烯氧化物环的一价基、二苯并磷杂环戊二烯氧化物环的一价基、呋咱基、噻蒽基、吲哚并咔唑基、苯并吲唑并咔唑基及苯并苯并吲哚并咔唑基等。

[1143] 另外,所述芳基及杂芳基可被取代,可分别例如由所述芳基或杂芳基取代。

[1144] 作为所述嘧啶衍生物的具体例,例如可列举以下的化合物。

[1145] [化326]

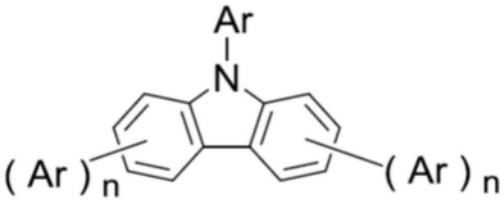
[1146] 

[1147] 所述嘧啶衍生物可使用已知的原料与已知的合成方法来制造。

[1148] <咔唑衍生物>

[1149] 咔唑衍生物例如为下述式(ETM-9)所表示的化合物或通过单键等将其键结多个而成的多聚体。详细情况在美国公开公报2014/0197386号公报中有记载。

[1150] [化327]

[1151] 

(ETM-9)

[1152] Ar分别独立地为可被取代的芳基、或可被取代的杂芳基。n分别独立地为0～4的整数,优选为0～3的整数,更优选为0或1。

[1153] 作为“可被取代的芳基”的“芳基”,例如可列举碳数6～30的芳基,优选为碳数6～24的芳基,更优选为碳数6～20的芳基,进而优选为碳数6～12的芳基。

[1154] 作为具体的“芳基”,可列举:作为单环系芳基的苯基、作为二环系芳基的(2-、3-、4-)联苯基、作为缩合二环系芳基的(1-、2-)萘基、作为三环系芳基的联三苯基(间联三苯-2'-基、间联三苯-4'-基、间联三苯-5'-基、邻联三苯-3'-基、邻联三苯-4'-基、对联三苯-2'-基、间联三苯-2-基、间联三苯-3-基、间联三苯-4-基、邻联三苯-2-基、邻联三苯-3-基、邻联三苯-4-基、对联三苯-2-基、对联三苯-3-基、对联三苯-4-基)、作为缩合三环系芳基的苊-(1-、3-、4-、5-)基、芴-(1-、2-、3-、4-、9-)基、非那烯-(1-、2-)基、(1-、2-、3-、4-、9-)菲基、作为四环系芳基的联四苯基(5'-苯基-间联三苯-2-基、5'-苯基-间联三苯-3-基、5'-苯基-间联三苯-4-基、间联四苯基)、作为缩合四环系芳基的三亚苯-(1-、2-)基、芘-(1-、2-、4-)基、稠四苯-(1-、2-、5-)基、作为缩合五环系芳基的苝-(1-、2-、3-)基、稠五苯-(1-、2-、5-、6-)基等。

[1155] 作为“可被取代的杂芳基”的“杂芳基”,例如可列举碳数2～30的杂芳基,优选为碳数2～25的杂芳基,更优选为碳数2～20的杂芳基,进而优选为碳数2～15的杂芳基,特别优选为碳数2～10的杂芳基。另外,作为杂芳基,例如可列举除碳以外含有1个～5个选自氧、硫及氮中的杂原子作为环构成原子的杂环等。

[1156] 作为具体的杂芳基,例如可列举:吡咯基、噁唑基、异噁唑基、噻唑基、异噻唑基、咪唑基、噁二唑基、噻二唑基、三唑基、四唑基、吡唑基、吡啶基、嘧啶基、哒嗪基、吡嗪基、三嗪

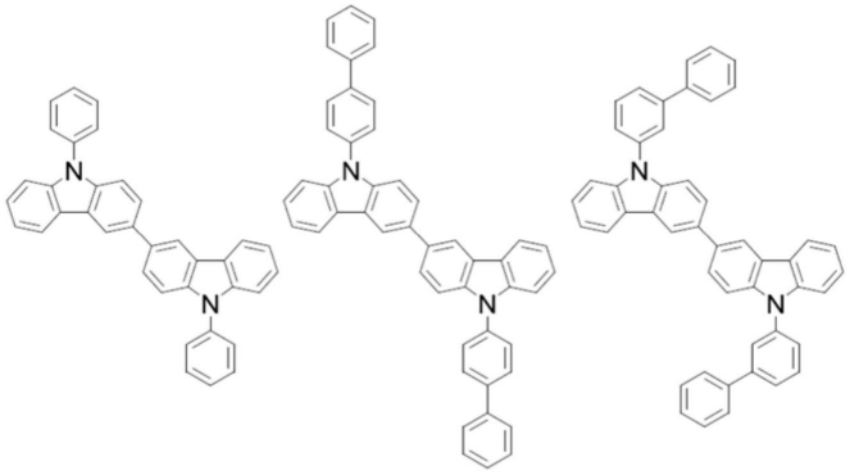
基、吲哚基、异吲哚基、1H-吲唑基、苯并咪唑基、苯并噁唑基、苯并噻唑基、1H-苯并三唑基、喹啉基、异喹啉基、噌啉基、喹唑啉基、喹喔啉基、酞嗪基、萘啶基、嘌呤基、喋啶基、咔唑基、吖啶基、吩噁噻基、吩噁嗪基、吩噻嗪基、吩嗪基、环戊基硼酸基(phenazasilinyl)、吲嗪基、呋喃基、苯并呋喃基、异苯并呋喃基、二苯并呋喃基、萘并苯并呋喃基、噻吩基、苯并噻吩基、异苯并噻吩基、二苯并噻吩基、萘并苯并噻吩基、苯并磷酰基、二苯并磷酰基、苯并磷杂环戊二烯氧化物环的一价基、二苯并磷杂环戊二烯氧化物环的一价基、呋咱基、噻蒽基、吲哚并咔唑基、苯并吲唑并咔唑基及苯并苯并吲哚并咔唑基等。

[1157] 另外,所述芳基及杂芳基可被取代,可分别例如由所述芳基或杂芳基取代。

[1158] 咔唑衍生物可为通过单键等将所述式(ETM-9)所表示的化合物键结多个而成的多聚体。所述情况下,除单键以外,也可通过芳基环(优选为多价的苯环、萘环、蒽环、芴环、苯并芴环、非那烯环、菲环或三亚苯环)键结。

[1159] 作为所述咔唑衍生物的具体例,例如可列举以下的化合物。

[1160] [化328]

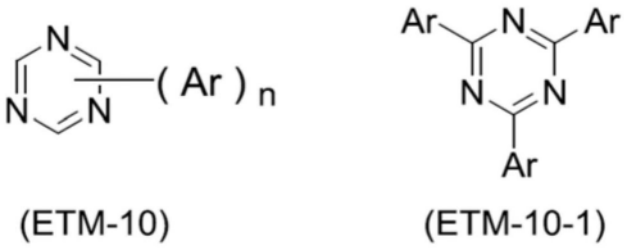
[1161] 

[1162] 所述咔唑衍生物可使用已知的原料与已知的合成方法来制造。

[1163] <三嗪衍生物>

[1164] 三嗪衍生物例如为下述式(ETM-10)所表示的化合物,优选为下述式(ETM-10-1)所表示的化合物。详细情况在美国公开公报2011/0156013号公报中有记载。

[1165] [化329]

[1166] 

(ETM-10) (ETM-10-1)

[1167] Ar分别独立地为可被取代的芳基、或可被取代的杂芳基。n为1~3的整数,优选为2或3。

[1168] 作为“可被取代的芳基”的“芳基”,例如可列举碳数6~30的芳基,优选为碳数6~24的芳基,更优选为碳数6~20的芳基,进而优选为碳数6~12的芳基。

[1169] 作为具体的“芳基”,可列举:作为单环系芳基的苯基、作为二环系芳基的(2-、3-、

4-)联苯基、作为缩合二环系芳基的(1-、2-)萘基、作为三环系芳基的联三苯基(间联三苯-2'-基、间联三苯-4'-基、间联三苯-5'-基、邻联三苯-3'-基、邻联三苯-4'-基、对联三苯-2'-基、间联三苯-2-基、间联三苯-3-基、间联三苯-4-基、邻联三苯-2-基、邻联三苯-3-基、邻联三苯-4-基、对联三苯-2-基、对联三苯-3-基、对联三苯-4-基)、作为缩合三环系芳基的苊-(1-、3-、4-、5-)基、芴-(1-、2-、3-、4-、9-)基、非那烯-(1-、2-)基、(1-、2-、3-、4-、9-)菲基、作为四环系芳基的联四苯基(5'-苯基-间联三苯-2-基、5'-苯基-间联三苯-3-基、5'-苯基-间联三苯-4-基、间联四苯基)、作为缩合四环系芳基的三亚苯-(1-、2-)基、苊-(1-、2-、4-)基、稠四苯-(1-、2-、5-)基、作为缩合五环系芳基的苉-(1-、2-、3-)基、稠五苯-(1-、2-、5-、6-)基等。

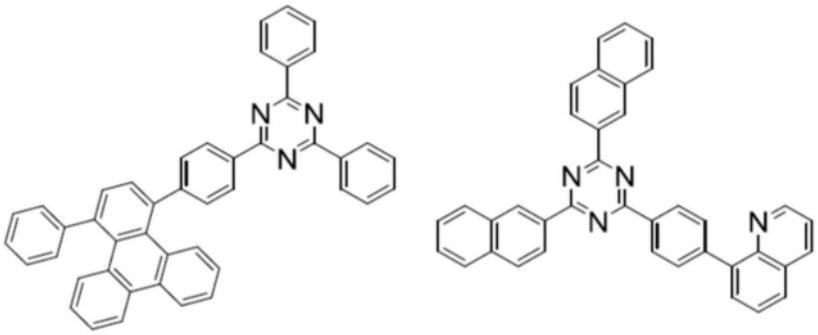
[1170] 作为"可被取代的杂芳基"的"杂芳基",例如可列举碳数2～30的杂芳基,优选为碳数2～25的杂芳基,更优选为碳数2～20的杂芳基,进而优选为碳数2～15的杂芳基,特别优选为碳数2～10的杂芳基。另外,作为杂芳基,例如可列举除碳以外含有1个～5个选自氧、硫及氮中的杂原子作为环构成原子的杂环等。

[1171] 作为具体的杂芳基,例如可列举:吡咯基、噁唑基、异噁唑基、噻唑基、异噻唑基、咪唑基、噁二唑基、噻二唑基、三唑基、四唑基、吡唑基、吡啶基、嘧啶基、哒嗪基、吡嗪基、三嗪基、吲哚基、异吲哚基、1H-吲唑基、苯并咪唑基、苯并噁唑基、苯并噻唑基、1H-苯并三唑基、喹啉基、异喹啉基、噌啉基、喹唑啉基、喹喔啉基、酞嗪基、萘啶基、嘌呤基、喋啶基、咔唑基、吖啶基、吩噁噻基、吩噁嗪基、吩噻嗪基、吩嗪基、环戊基硼酸基(phenazasilinyl)、吲嗪基、呋喃基、苯并呋喃基、异苯并呋喃基、二苯并呋喃基、萘并苯并呋喃基、噻吩基、苯并噻吩基、异苯并噻吩基、二苯并噻吩基、萘并苯并噻吩基、苯并磷酰基、二苯并磷酰基、苯并磷杂环戊二烯氧化物环的一价基、二苯并磷杂环戊二烯氧化物环的一价基、呋喃基、噻蒽基、吲哚并咔唑基、苯并吲唑并咔唑基及苯并苯并吲哚并咔唑基等。

[1172] 另外,所述芳基及杂芳基可被取代,可分别例如由所述芳基或杂芳基取代。

[1173] 作为所述三嗪衍生物的具体例,例如可列举以下的化合物。

[1174] [化330]

[1175] 

[1176] 所述三嗪衍生物可使用已知的原料与已知的合成方法来制造。

[1177] <苯并咪唑衍生物>

[1178] 苯并咪唑衍生物例如为下述式(ETM-11)所表示的化合物。

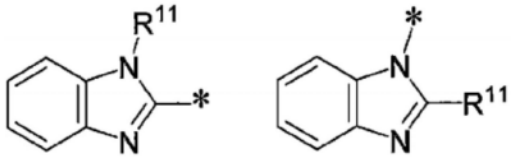
[1179] [化331]

[1180] φ-(苯并咪唑系取代基)n (ETM-11)

[1181] φ为n价的芳基环(优选为n价的苯环、萘环、蒽环、芴环、苯并芴环、非那烯环、菲环或三亚苯环),n为1～4的整数,"苯并咪唑系取代基"为将所述式(ETM-2)、式(ETM-2-1)及式

(ETM-2-2)的“吡啶系取代基”中的吡啶基取代为苯并咪唑基的取代基,苯并咪唑衍生物中的至少一个氢可由氘取代。下述结构式中的*表示键结位置。

[1182] [化332]

[1183] 

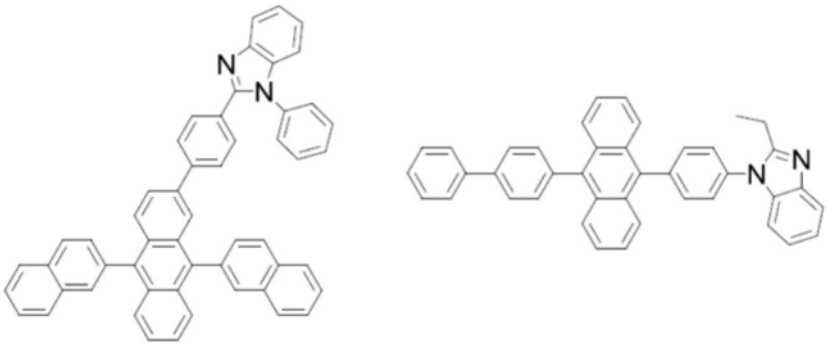
苯并咪唑基

[1184] 所述苯并咪唑基中的R^{11}为氢、碳数1～24的烷基、碳数3～12的环烷基或碳数6～30的芳基,可引用所述式(ETM-2-1)及式(ETM-2-2)中的R^{11}的说明。

[1185] φ进而优选为蒽环或芴环,所述情况下的结构可引用所述式(ETM-2-1)或式(ETM-2-2)中的说明,各式中的R^{11}～R^{18}可引用所述式(ETM-2-1)或式(ETM-2-2)中的说明。另外,所述式(ETM-2-1)或式(ETM-2-2)中以键结有两个吡啶系取代基的形态进行了说明,但将这些取代为苯并咪唑系取代基时,可由苯并咪唑系取代基取代两个吡啶系取代基(即n＝2),也可由苯并咪唑系取代基取代任一个吡啶系取代基而由R^{11}～R^{18}取代另一个吡啶系取代基(即n＝1)。进而,例如可由苯并咪唑系取代基取代所述式(ETM-2-1)中的R^{11}～R^{18}的至少一个而由R^{11}～R^{18}取代“吡啶系取代基”。

[1186] 作为所述苯并咪唑衍生物的具体例,例如可列举:1-苯基-2-(4-(10-苯基蒽-9-基)苯基)-1H-苯并[d]咪唑、2-(4-(10-(萘-2-基)蒽-9-基)苯基)-1-苯基-1H-苯并[d]咪唑、2-(3-(10-(萘-2-基)蒽-9-基)苯基)-1-苯基-1H-苯并[d]咪唑、5-(10-(萘-2-基)蒽-9-基)-1,2-二苯基-1H-苯并[d]咪唑、1-(4-(10-(萘-2-基)蒽-9-基)苯基)-2-苯基-1H-苯并[d]咪唑、2-(4-(9,10-二(萘-2-基)蒽-2-基)苯基)-1-苯基-1H-苯并[d]咪唑、1-(4-(9,10-二(萘-2-基)蒽-2-基)苯基)-2-苯基-1H-苯并[d]咪唑、5-(9,10-二(萘-2-基)蒽-2-基)-1,2-二苯基-1H-苯并[d]咪唑等。

[1187] [化333]

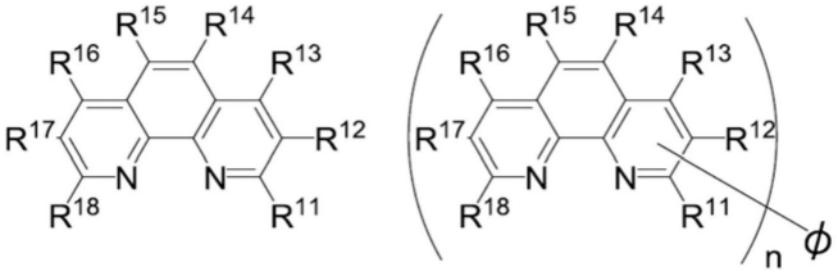
[1188] 

[1189] 所述苯并咪唑衍生物可使用已知的原料与已知的合成方法来制造。

[1190] ＜菲咯啉衍生物＞

[1191] 菲咯啉衍生物例如为下述式(ETM-12)或式(ETM-12-1)所表示的化合物。详细情况在国际公开2006/021982号公报中有记载。

[1192] [化334]

[1193] 

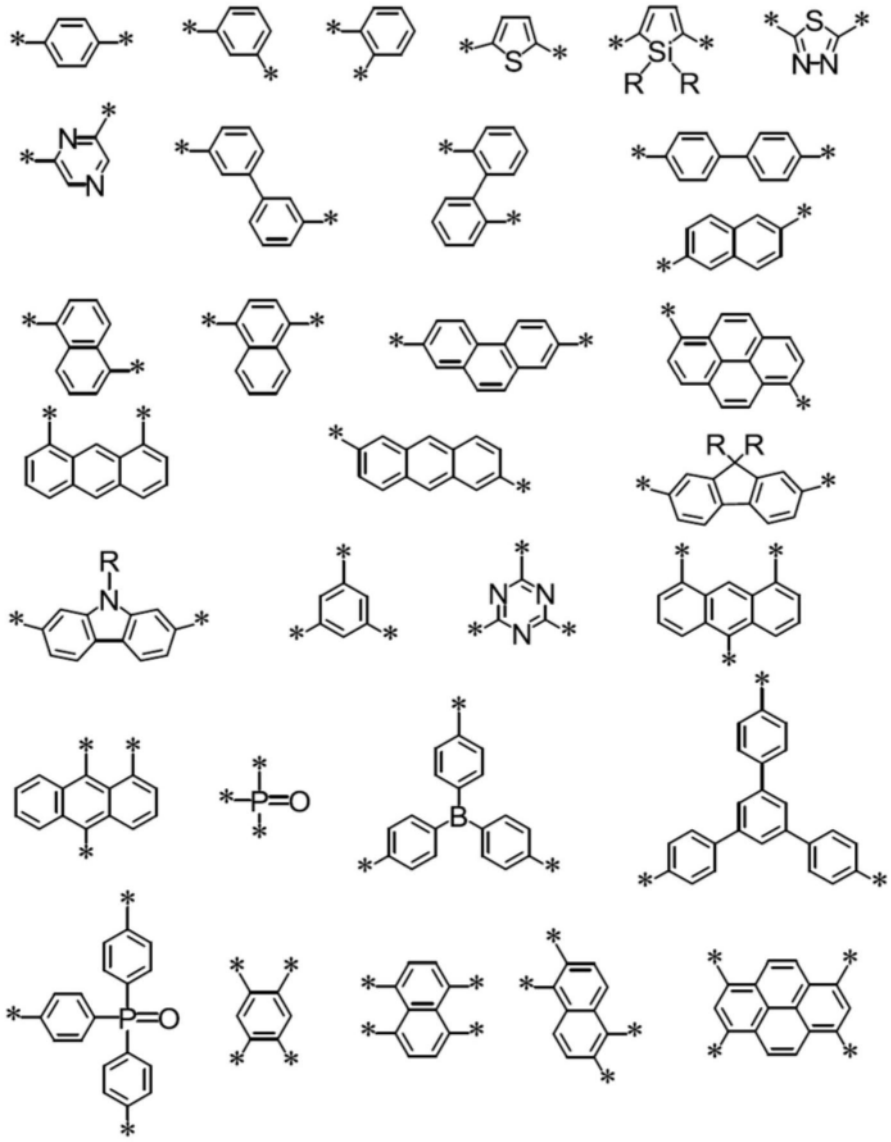
[1194] φ为n价的芳基环(优选为n价的苯环、萘环、蒽环、芴环、苯并芴环、非那烯环、菲环或三亚苯环),n为1～4的整数。

[1195] 各式的R^{11}～R^{18}分别独立地为氢、烷基(优选为碳数1～24的烷基)、环烷基(优选为碳素3～12的环烷基)或芳基(优选为碳数6～30的芳基)。另外,在所述式(ETM-12-1)中,R^{11}～R^{18}的任一者与作为芳基环的φ键结。

[1196] 各菲咯啉衍生物中的至少一个氢可由氘取代。

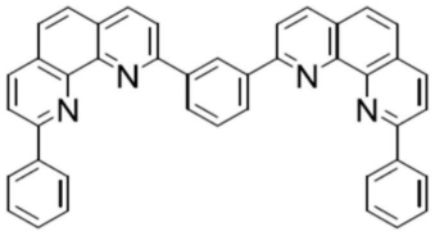
[1197] 作为R^{11}～R^{18}中的烷基、环烷基及芳基,可引用所述式(ETM-2)中的R^{11}～R^{18}的说明。另外,关于φ,除所述例子以外,例如可列举以下结构式。再者,下述结构式中的R分别独立地为氢、甲基、乙基、异丙基、环己基、苯基、1-萘基、2-萘基、联苯基或联三苯基。另外,各结构式中的*表示键结位置。

[1198] [化335]

[1199] 

[1200] 作为所述菲咯啉衍生物的具体例,例如可列举:4,7-二苯基-1,10-菲咯啉、2,9-二甲基-4,7-二苯基-1,10-菲咯啉、9,10-二(1,10-菲咯啉-2-基)蒽、2,6-二(1,10-菲咯啉-5-基)吡啶、1,3,5-三(1,10-菲咯啉-5-基)苯、9,9'-二氟-双(1,10-菲咯啉-5-基)、2,9-二甲基-4,7-联苯-1,10-菲咯啉(bathocuproine)、1,3-双(2-苯基-1,10-菲咯啉-9-基)苯或下述结构式所表示的化合物等。

[1201] [化336]

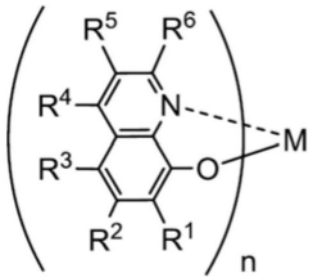
[1202] 

[1203] 所述菲咯啉衍生物可使用已知的原料与已知的合成方法来制造。

[1204] <羟基喹啉系金属络合物>

[1205] 羟基喹啉系金属络合物例如为下述通式(ETM-13)所表示的化合物。

[1206] [化337]

[1207]  (ETM-13)

[1208] 式中,R^1～R^6分别独立地为氢、氟、烷基、环烷基、芳烷基、烯基、氰基、烷氧基或芳基,M为Li、Al、Ga、Be或Zn,n为1～3的整数。

[1209] 作为羟基喹啉系金属络合物的具体例,可列举:8-羟基喹啉锂、三(8-羟基喹啉)铝、三(4-甲基-8-羟基喹啉)铝、三(5-甲基-8-羟基喹啉)铝、三(3,4-二甲基-8-羟基喹啉)铝、三(4,5-二甲基-8-羟基喹啉)铝、三(4,6-二甲基-8-羟基喹啉)铝、双(2-甲基-8-羟基喹啉)(苯酚)铝、双(2-甲基-8-羟基喹啉)(2-甲基苯酚)铝、双(2-甲基-8-羟基喹啉)(3-甲基苯酚)铝、双(2-甲基-8-羟基喹啉)(4-甲基苯酚)铝、双(2-甲基-8-羟基喹啉)(2-苯基苯酚)铝、双(2-甲基-8-羟基喹啉)(3-苯基苯酚)铝、双(2-甲基-8-羟基喹啉)(4-苯基苯酚)铝、双(2-甲基-8-羟基喹啉)(2,3-二甲基苯酚)铝、双(2-甲基-8-羟基喹啉)(2,6-二甲基苯酚)铝、双(2-甲基-8-羟基喹啉)(3,4-二甲基苯酚)铝、双(2-甲基-8-羟基喹啉)(3,5-二甲基苯酚)铝、双(2-甲基-8-羟基喹啉)(3,5-二-叔丁基苯酚)铝、双(2-甲基-8-羟基喹啉)(2,6-二苯基苯酚)铝、双(2-甲基-8-羟基喹啉)(2,4,6-三苯基苯酚)铝、双(2-甲基-8-羟基喹啉)(2,4,6-三甲基苯酚)铝、双(2-甲基-8-羟基喹啉)(2,4,5,6-四甲基苯酚)铝、双(2-甲基-8-羟基喹啉)(1-萘酚)铝、双(2-甲基-8-羟基喹啉)(2-萘酚)铝、双(2,4-二甲基-8-羟基喹啉)(2-苯基苯酚)铝、双(2,4-二甲基-8-羟基喹啉)(3-苯基苯酚)铝、双(2,4-二甲基-8-羟基喹啉)(4-苯基苯酚)铝、双(2,4-二甲基-8-羟基喹啉)(3,5-二甲基苯酚)铝、双(2,4-二甲基-8-羟基喹啉)(3,5-二-叔丁基苯酚)铝、双(2-甲基-8-羟基喹啉)铝-μ-氧代-双(2-甲基-8-羟基喹啉)铝、双(2,4-二甲基-8-羟基喹啉)铝-μ-氧代-双(2,4-二甲基-8-羟基喹啉)铝、双(2-甲基-4-乙基-8-羟基喹啉)铝-μ-氧代-双(2-甲基-4-乙基-8-羟基喹啉)铝、双(2-甲基-4-甲氧基-8-羟基喹啉)铝-μ-氧代-双(2-甲基-4-甲氧基-8-羟基喹啉)铝、双(2-甲基-5-氰基-8-羟基喹啉)铝-μ-氧代-双(2-甲基-5-氰基-8-羟基喹啉)铝、双(2-甲基-5-三氟甲基-8-羟基喹啉)铝-μ-氧代-双(2-甲基-5-三氟甲基-8-羟基喹啉)铝、双(10-羟基苯并[h]喹啉)铍等。

[1210] 所述羟基喹啉系金属络合物可使用已知的原料与已知的合成方法来制造。

[1211] <噻唑衍生物及苯并噻唑衍生物>

[1212] 噻唑衍生物例如为下述式(ETM-14-1)所表示的化合物。

[1213] [化338]

[1214] φ-(噻唑系取代基)n (ETM-14-1)

[1215] 苯并噻唑衍生物例如为下述式(ETM-14-2)所表示的化合物。

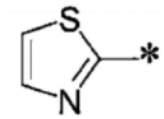
[1216] [化339]

[1217] φ-(苯并噻唑系取代基)n (ETM-14-2)

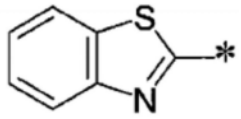
[1218] 各式的φ为n价的芳基环(优选为n价的苯环、萘环、蒽环、芴环、苯并芴环、非那烯

环、菲环或三亚苯环),n为1～4的整数,“噻唑系取代基”或“苯并噻唑系取代基”为将所述式(ETM-2)、式(ETM-2-1)及式(ETM-2-2)的“吡啶系取代基”中的吡啶基取代为下述噻唑基或苯并噻唑基的取代基,噻唑衍生物及苯并噻唑衍生物中的至少一个氢可由氘取代。下述结构式中的*表示键结位置。

[1219] [化340]

[1220] 

噻唑基



苯并噻唑基

[1221] φ进而优选为蒽环或芴环,所述情况下的结构可引用所述式(ETM-2-1)或式(ETM-2-2)中的说明,各式中的R^{11}～R^{18}可引用所述式(ETM-2-1)或式(ETM-2-2)中的说明。另外,所述式(ETM-2-1)或式(ETM-2-2)中以键结有两个吡啶系取代基的形态进行了说明,但将这些取代为噻唑系取代基(或苯并噻唑系取代基)时,可由噻唑系取代基(或苯并噻唑系取代基)取代两个吡啶系取代基(即n＝2),也可由噻唑系取代基(或苯并噻唑系取代基)取代任一个吡啶系取代基而由R^{11}～R^{18}取代另一个吡啶系取代基(即n＝1)。进而,例如可由噻唑系取代基(或苯并噻唑系取代基)取代所述式(ETM-2-1)中的R^{11}～R^{18}的至少一个而由R^{11}～R^{18}取代“吡啶系取代基”。

[1222] 这些噻唑衍生物或苯并噻唑衍生物可使用已知的原料与已知的合成方法来制造。

[1223] 在电子传输层或电子注入层中,进而可包含能够将形成电子传输层或电子注入层的材料还原的物质。所述还原性物质只要是具有一定的还原性的物质,则可使用各种物质,例如可适当地使用选自由碱金属、碱土金属、稀土金属、碱金属的氧化物、碱金属的卤化物、碱土金属的氧化物、碱土金属的卤化物、稀土金属的氧化物、稀土金属的卤化物、碱金属的有机络合物、碱土金属的有机络合物及稀土金属的有机络合物所组成的群组中的至少一者。

[1224] 作为优选的还原性物质,可列举:Na(功函数为2.36eV)、K(功函数为2.28eV)、Rb(功函数为2.16eV)或Cs(功函数为1.95eV)等碱金属、或Ca(功函数为2.9eV)、Sr(功函数为2.0eV～2.5eV)、或者Ba(功函数为2.52eV)等碱土金属,特别优选为功函数为2.9eV以下的物质。这些还原性物质中,更优选的还原性物质是K、Rb或Cs的碱金属,进而优选为Rb或Cs,最优选为Cs。这些碱金属的还原能力特别高,通过向形成电子传输层或电子注入层的材料中添加比较少量的这些碱金属,可谋求有机EL元件中的发光亮度的提高或长寿命化。另外,作为功函数为2.9eV以下的还原性物质,两种以上的所述碱金属的组合也优选,特别优选为包含Cs的组合,例如Cs与Na、Cs与K、Cs与Rb、或Cs与Na及K的组合。通过包含Cs,可有效率地发挥还原能力,通过添加至形成电子传输层或电子注入层的材料中,可谋求有机EL元件中的发光亮度的提高或长寿命化。

[1225] 所述电子注入层用材料及电子传输层用材料也可作为如下的高分子化合物或其高分子交联体、或者如下的悬挂型高分子化合物或其悬挂型高分子交联体而用于电子层用材料,其中,所述高分子化合物是使在所述电子注入层用材料及电子传输层用材料中取代有反应性取代基的反应性化合物作为单体进行高分子化而成,所述悬挂型高分子化合物是使主链型高分子与所述反应性化合物反应而成。作为所述情况下的反应性取代基,可引用

式(1)所表示的多环芳香族化合物中的说明。

[1226] 关于此种高分子化合物及高分子交联体的用途的详细情况,在后文叙述。

[1227] ＜有机电致发光元件中的阴极＞

[1228] 阴极108发挥经由电子注入层107及电子传输层106而将电子注入至发光层105的作用。

[1229] 作为形成阴极108的材料,若为可将电子高效地注入至有机层的物质,则并无特别限定,可使用与形成阳极102的材料相同的材料。其中,优选为锡、铟、钙、铝、银、铜、镍、铬、金、铂、铁、锌、锂、钠、钾、铯及镁等金属或这些的合金(镁-银合金、镁-铟合金、氟化锂/铝等的铝-锂合金等)等。为了提高电子注入效率来提高元件特性,有效的是锂、钠、钾、铯、钙、镁或包含这些低功函数金属的合金。但是,这些低功函数金属通常在大气中不稳定的情况多。为了改善这一点,已知有例如向有机层中掺杂微量的锂、铯或镁,并使用稳定性高的电极的方法。作为其他掺杂剂,也可使用氟化锂、氟化铯、氧化锂及氧化铯之类的无机盐。其中,并不限定于这些。

[1230] 进而,可列举如下的优选例:为了保护电极而将铂、金、银、铜、铁、锡、铝及铟等金属,或使用这些金属的合金,及二氧化硅、二氧化钛及氮化硅等无机物,聚乙烯醇,氯乙烯,烃系高分子化合物等进行层叠。这些电极的制作方法只要为电阻加热、电子束蒸镀、溅射、离子镀及涂布等可取得导通的方法,则也无特别限制。

[1231] ＜可用于各层的粘结剂＞

[1232] 用于以上的空穴注入层、空穴传输层、发光层、电子传输层及电子注入层的材料可单独地形成各层,也可分散于作为高分子粘结剂的聚氯乙烯、聚碳酸酯、聚苯乙烯、聚(N-乙烯咔唑)、聚甲基丙烯酸甲酯、聚甲基丙烯酸丁酯、聚酯、聚砜、聚苯醚(polyphenylene oxide)、聚丁二烯、烃树脂、酮树脂、苯氧基树脂、聚酰胺、乙基纤维素、乙酸乙烯酯树脂、丙烯腈-丁二烯-苯乙烯(Acrylonitrile Butadiene Styrene,ABS)树脂、聚氨基甲酸酯树脂等溶剂可溶性树脂,或者酚树脂、二甲苯树脂、石油树脂、脲树脂、三聚氰胺树脂、不饱和聚酯树脂、醇酸树脂、环氧树脂、硅酮树脂等硬化性树脂等中来使用。

[1233] ＜有机电致发光元件的制作方法＞

[1234] 构成有机EL元件的各层可通过利用蒸镀法、电阻加热蒸镀、电子束蒸镀、溅射、分子层叠法、印刷法、旋涂法或浇铸法、涂布法等方法将应构成各层的材料制成薄膜来形成。以所述方式形成的各层的膜厚并无特别限定,可对应于材料的性质而适当设定,但通常为2nm～5000nm的范围。膜厚通常可利用水晶振荡式膜厚测定装置等来测定。在使用蒸镀法进行薄膜化的情况下,其蒸镀条件根据材料的种类、膜的目标结晶结构及缔合结构等而不同。蒸镀条件通常优选为在舟皿加热温度+50℃～+400℃、真空度10^{-6}Pa～10^{-3}Pa、蒸镀速度0.01nm/sec～50nm/sec、基板温度-150℃～+300℃、膜厚2nm～5μm的范围内适当设定。

[1235] 在对以所述方式获得的有机EL元件施加直流电压的情况下,只要将阳极作为+的极性,将阴极作为-的极性来施加即可,若施加2V～40V左右的电压,则可自透明或半透明的电极侧(阳极或阴极、及两者)观测到发光。另外,所述有机EL元件在施加有脉冲电流或交流电流的情况下也发光。再者,施加的交流的波形可为任意。

[1236] 继而,作为制作有机EL元件的方法的一例,对包括阳极/空穴注入层/空穴传输层/包含主体材料与掺杂剂材料的发光层/电子传输层/电子注入层/阴极的有机EL元件的制作

方法进行说明。

[1237] ＜蒸镀法＞

[1238] 在适当的基板上,利用蒸镀法等形成阳极材料的薄膜来制作阳极后,在所述阳极上形成空穴注入层及空穴传输层的薄膜。在其上对主体材料与掺杂剂材料进行共蒸镀而形成薄膜来作为发光层,在所述发光层上形成电子传输层、电子注入层,进而利用蒸镀法等形成包含阴极用物质的薄膜来作为阴极,由此获得目标有机EL元件。再者,在所述有机EL元件的制作中,也能够使制作顺序相反,而以阴极、电子注入层、电子传输层、发光层、空穴传输层、空穴注入层、阳极的顺序制作。

[1239] ＜湿式成膜法＞

[1240] 准备可形成有机EL元件的各有机层的低分子化合物作为液状的有机层形成用组合物,并使用其来实施湿式成膜法。在不存在将所述低分子化合物溶解的适当的有机溶媒的情况下,也可由如下的高分子化合物等来准备有机层形成用组合物,所述高分子化合物是与作为在所述低分子化合物中取代有反应性取代基的反应性化合物而具有溶解性功能的其他单体或主链型高分子一同进行高分子化而成。

[1241] 湿式成膜法通常通过经过如下步骤而形成涂膜,所述步骤为在基板上涂布有机层形成用组合物的涂布步骤以及自经涂布的有机层形成用组合物中去除溶媒的干燥步骤。在所述高分子化合物具有交联性取代基的情况(也将其称为交联性高分子化合物)下,通过所述干燥步骤进一步进行交联而形成高分子交联体。根据涂布步骤的不同,将使用旋涂机的方法称为旋涂法,将使用狭缝涂布机的方法称为狭缝涂布法,将使用版的方法称为凹版、平版、反向平版、柔版印刷法,将使用喷墨打印机的方法称为喷墨法,将吹附为雾状的方法称为喷雾法。干燥步骤中有风干、加热、减压干燥等方法。干燥步骤可仅进行一次,也可使用不同的方法或条件而进行多次。另外,例如可如在减压下的煅烧那样并用不同的方法。

[1242] 所谓湿式成膜法,为使用溶液的成膜法,例如为一部分印刷法(喷墨法)、旋涂法或浇铸法、涂布法等。湿式成膜法与真空蒸镀法不同,无需使用昂贵的真空蒸镀装置,可在大气压下进行成膜。并且,湿式成膜法可大面积化或连续生产,从而带来制造成本的降低。

[1243] 另一方面,当与真空蒸镀法比较时,存在湿式成膜法难以层叠化的情况。在使用湿式成膜法制作层叠膜的情况下,需要防止由上层的组合物引起的底层的溶解,且运用控制了溶解性的组合物、底层的交联及正交溶媒(Orthogonal solvent,彼此不溶解的溶媒)等。但是,即便使用这些技术,也存在难以将湿式成膜法用于所有的膜的涂布的情况。

[1244] 因此,通常采用如下方法:使用湿式成膜法仅制成若干层,利用真空蒸镀法制成剩余层,从而制作有机EL元件。

[1245] 例如,以下表示一部分应用湿式成膜法而制作有机EL元件的程序。

[1246] (程序1)阳极的利用真空蒸镀法进行的成膜

[1247] (程序2)包含空穴注入层用材料的空穴注入层形成用组合物的利用湿式成膜法进行的成膜

[1248] (程序3)包含空穴传输层用材料的空穴传输层形成用组合物的利用湿式成膜法进行的成膜

[1249] (程序4)包含主体材料与掺杂剂材料的发光层形成用组合物的利用湿式成膜法进行的成膜

[1250] (程序5)电子传输层的利用真空蒸镀法进行的成膜

[1251] (程序6)电子注入层的利用真空蒸镀法进行的成膜

[1252] (程序7)阴极的利用真空蒸镀法进行的成膜

[1253] 通过经过所述程序,可获得包括阳极/空穴注入层/空穴传输层/包含主体材料与掺杂剂材料的发光层/电子传输层/电子注入层/阴极的有机EL元件。

[1254] 当然,通过存在防止底层的发光层溶解的手段,并且使用与所述程序相反地自阴极侧进行成膜的手段等,作为包含电子传输层用材料或电子注入层用材料的层形成用组合物来准备,可通过湿式成膜法对这些进行成膜。

[1255] <其他成膜法>

[1256] 有机层形成用组合物的成膜化中可使用激光加热描绘法(激光感热成像(Laser Induced Thermal Imaging,LITI))。所谓LITI,为利用激光对附着于基材的化合物进行加热蒸镀的方法,且可将有机层形成用组合物用于涂布在基材上的材料中。

[1257] <任意的步骤>

[1258] 在成膜的各步骤的前后,也可适宜加入适当的处理步骤、清洗步骤及干燥步骤。作为处理步骤,例如可列举:曝光处理、等离子体表面处理、超声波处理、臭氧处理、使用适当的溶媒的清洗处理及加热处理等。进而也可列举制作堤部的一系列的步骤。

[1259] 堤部的制作中可使用光刻技术。作为可利用光刻的堤部材料,可使用正型抗蚀剂材料及负型抗蚀剂材料。另外,也可使用喷墨法、凹版平版印刷、反向平版印刷、网版印刷等可制成图案的印刷法。此时,也可使用永久抗蚀剂材料。

[1260] 作为用于堤部的材料,可列举多糖类及其衍生物、具有羟基的乙烯性单体的均聚物及共聚物、生物高分子化合物、聚丙烯酰基化合物、聚酯、聚苯乙烯、聚酰亚胺、聚酰胺酰亚胺、聚醚酰亚胺、聚硫醚、聚砜、聚亚苯(polyphenylene)、聚苯醚(polyphenyl ether)、聚氨基甲酸酯、(甲基)丙烯酸环氧酯、(甲基)丙烯酸三聚氰胺酯、聚烯烃、环状聚烯烃、丙烯腈-丁二烯-苯乙烯共聚聚合物(ABS)、硅酮树脂、聚氯乙烯、氯化聚乙烯、氯化聚丙烯、聚乙酸酯、聚降冰片烯、合成橡胶、聚偏二氟乙烯、聚四氟乙烯、聚六氟丙烯等氟化聚合物、氟烯烃-碳氢烯烃的共聚聚合物、氟碳聚合物,但并不仅限定于此。

[1261] <湿式成膜法中所使用的有机层形成用组合物>

[1262] 有机层形成用组合物是使可形成有机EL元件的各有机层的低分子化合物、或将所述低分子化合物加以高分子化而成的高分子化合物溶解于有机溶媒中而获得。例如,发光层形成用组合物含有至少一种作为掺杂剂材料的多环芳香族化合物(或其高分子化合物)作为第一成分、至少一种主体材料作为第二成分、至少一种有机溶媒作为第三成分。第一成分作为由所述组合物所获得的发光层的掺杂剂成分而发挥功能,第二成分作为发光层的主体成分而发挥功能。第三成分作为使组合物中的第一成分与第二成分溶解的溶媒而发挥功能,并在涂布时通过第三成分自身的经控制的蒸发速度而获得平滑且均匀的表面形状。

[1263] <有机溶媒>

[1264] 有机层形成用组合物包含至少一种有机溶媒。在成膜时控制有机溶媒的蒸发速度,由此可控制及改善成膜性及涂膜的缺陷的有无、表面粗糙度、平滑性。另外,在使用喷墨法成膜时,可控制喷墨头的针孔处的弯液面(meniscus)稳定性,并可控制·改善喷出性。并且,通过控制膜的干燥速度及衍生物分子的取向,可改善具有由所述有机层形成用组合物

所获得的有机层的有机EL元件的电特性、发光特性、效率及寿命。

[1265] (1)有机溶媒的物性

[1266] 至少一种有机溶媒的沸点为130℃～300℃,更优选为140℃～270℃,进而优选为150℃～250℃。就喷墨的喷出性的观点而言,优选为沸点高于130℃的情况。另外,就涂膜的缺陷、表面粗糙度、残留溶媒及平滑性的观点而言,优选为沸点低于300℃的情况。就良好的喷墨喷出性、成膜性、平滑性及低残留溶媒的观点而言,有机溶媒更优选为包含两种以上的有机溶媒的结构。另一方面,视情况,考虑到搬运性等,也可为通过自有机层形成用组合物中去除溶媒而制成为固体状态的组合物。

[1267] 进而,有机溶媒包含对于溶质的至少一种而言的良溶媒(good solvent,GS)与不良溶媒(poor solvent,PS),特别优选为良溶媒(GS)的沸点(BP_{GS})低于不良溶媒(PS)的沸点(BP_{PS})的结构。

[1268] 通过加入高沸点的不良溶媒,而在成膜时低沸点的良溶媒先挥发,组合物中的含有物的浓度与不良溶媒的浓度增加并促进快速成膜。由此,可获得缺陷少、表面粗糙度小、平滑性高的涂膜。

[1269] 溶解度的差(S_{GS}-S_{PS})优选为1%以上,更优选为3%以上,进而优选为5%以上。沸点的差(BP_{PS}-BP_{GS})优选为10℃以上,更优选为30℃以上,进而优选为50℃以上。

[1270] 有机溶媒在成膜后通过真空、减压、加热等干燥步骤而自涂膜中去除。在进行加热的情况下,就改善涂布成膜性的观点而言,优选为以溶质的至少一种的玻璃转移温度(Tg)+30℃以下进行。另外,就削减残留溶媒的观点而言,优选为以溶质的至少一种的玻璃转移温度(Tg)-30℃以上进行加热。即便加热温度低于有机溶媒的沸点,由于膜薄,因此有机溶媒也充分地被去除。另外,可在不同的温度下进行多次干燥,也可并用多种干燥方法。

[1271] (2)有机溶媒的具体例

[1272] 作为用于有机层形成用组合物中的有机溶媒,可列举烷基苯系溶媒、苯基醚系溶媒、烷基醚系溶媒、环状酮系溶媒、脂肪族酮系溶媒、单环性酮系溶媒、具有二酯骨架的溶媒及含氟系溶媒等,作为具体例,可列举戊醇、己醇、庚醇、辛醇、壬醇、癸醇、十一醇、十二醇、十四醇、己烷-2-醇、庚烷-2-醇、辛烷-2-醇、癸烷-2-醇、十二烷-2-醇、环己醇、α-松油醇(α-terpineol)、β-松油醇、γ-松油醇、δ-松油醇、松油醇(混合物)、乙二醇单甲醚乙酸酯、丙二醇单甲醚乙酸酯、二乙二醇二甲醚、二丙二醇二甲醚、二乙二醇乙基甲基醚、二乙二醇异丙基甲基醚、二丙二醇单甲醚、二乙二醇二乙醚、二乙二醇单甲醚、二乙二醇丁基甲基醚、三丙二醇二甲醚、三乙二醇二甲醚、二乙二醇单丁醚、乙二醇单苯醚、三乙二醇单甲醚、二乙二醇二丁醚、三乙二醇丁基甲基醚、聚乙二醇二甲醚、四乙二醇二甲醚、对二甲苯、间二甲苯、邻二甲苯、2,6-二甲吡啶、2-氟-间二甲苯、3-氟-邻二甲苯、2-氯苯并三氟化物、枯烯、甲苯、2-氯-6-氟甲苯、2-氟苯甲醚、苯甲醚、2,3-二甲基吡嗪、溴苯、4-氟苯甲醚、3-氟苯甲醚、3-三氟甲基苯甲醚、均三甲苯、1,2,4-三甲基苯、叔丁基苯、2-甲基苯甲醚、苯乙醚、苯并二噁茂(benzodioxole)、4-甲基苯甲醚、仲丁基苯、3-甲基苯甲醚、4-氟-3-甲基苯甲醚、异丙基甲苯(cymene)、1,2,3-三甲基苯、1,2-二氯苯、2-氟苯甲腈、4-氟邻二甲氧苯(4-fluoroveratrole)、2,6-二甲基苯甲醚、正丁基苯、3-氟苯甲腈、十氢萘(decahydronaphthalene)、新戊基苯、2,5-二甲基苯甲醚、2,4-二甲基苯甲醚、苯甲腈、3,5-二甲基苯甲醚、二苯醚、1-氟-3,5-二甲氧基苯、苯甲酸甲酯、异戊基苯、3,4-二甲基苯甲醚、

邻甲苯甲腈(o-tolunitrile)、正戊基苯、邻二甲氧苯(veratrole)、1,2,3,4-四氢萘、苯甲酸乙酯、正己基苯、苯甲酸丙酯、环己基苯、1-甲基萘、苯甲酸丁酯、2-甲基联苯、3-苯氧基甲苯、2,2'-二甲基联苯(2,2'-bitolyl)、十二基苯、二戊基苯、四甲基苯、三甲氧基苯、三甲氧基甲苯、2,3-二氢苯并呋喃、1-甲基-4-(丙氧基甲基)苯、1-甲基-4-(丁氧基甲基)苯、1-甲基-4-(戊氧基甲基)苯、1-甲基-4-(己氧基甲基)苯、1-甲基-4-(庚氧基甲基)苯、苄基丁基醚、苄基戊基醚、苄基己基醚、苄基庚基醚、苄基辛基醚等,但并不仅限定于此。另外,溶媒可单独使用,也可进行混合。

[1273] ＜任意成分＞

[1274] 有机层形成用组合物也可在不损及其性质的范围内含有任意成分。作为任意成分,可列举粘合剂及表面活性剂等。

[1275] (1)粘合剂

[1276] 有机层形成用组合物也可含有粘合剂。关于粘合剂,在成膜时,在形成膜的同时将所获得的膜与基板接合。另外,在所述有机层形成用组合物中发挥使其他成分溶解及分散以及粘结的作用。

[1277] 作为用于有机层形成用组合物中的粘合剂,例如可列举丙烯酸树脂、聚对苯二甲酸乙二酯、乙烯-乙酸乙烯酯共聚物、乙烯-乙烯基醇共聚物、丙烯腈-乙烯-苯乙烯共聚物(Acrylonitrile-ethylene-styrene,AES)树脂、离聚物(ionomer)、氯化聚醚、邻苯二甲酸二烯丙酯树脂、不饱和聚酯树脂、聚乙烯、聚丙烯、聚氯乙烯、聚偏二氯乙烯(polyvinylidene chloride)、聚苯乙烯、聚乙酸乙烯酯、特氟龙(Teflon)、丙烯腈-丁二烯-苯乙烯共聚物(ABS)树脂、丙烯腈-苯乙烯共聚物(Acrylonitrile-Styrene,AS)树脂、酚树脂、环氧树脂、三聚氰胺树脂、脲树脂、醇酸树脂、聚氨基甲酸酯、以及所述树脂及聚合物的共聚物,但并不仅限定于此。

[1278] 用于有机层形成用组合物中的粘合剂可仅为一种,也可混合使用多种。

[1279] (2)表面活性剂

[1280] 例如为了控制有机层形成用组合物的膜面均匀性、膜表面的亲溶媒性及拨液性,有机层形成用组合物也可含有表面活性剂。表面活性剂根据亲水性基的结构被分类为离子性及非离子性,进而根据疏水性基的结构被分类为烷基系及硅系以及氟系。另外,根据分子的结构,被分类为分子量比较小的具有单纯结构的单分子系及分子量大的具有侧链或分支的高分子系。另外,根据组成被分类为单一系、混合有两种以上的表面活性剂及基材的混合系。作为可用于所述有机层形成用组合物的表面活性剂,可使用所有种类的表面活性剂。

[1281] 作为表面活性剂,例如可列举:珀利弗洛(Polyflow)No.45、珀利弗洛(Polyflow)KL-245、珀利弗洛(Polyflow)No.75、珀利弗洛(Polyflow)No.90、珀利弗洛(Polyflow)No.95(商品名,共荣社化学工业(股)制造),迪斯帕毕克(Disperbyk)161、迪斯帕毕克(Disperbyk)162、迪斯帕毕克(Disperbyk)163、迪斯帕毕克(Disperbyk)164、迪斯帕毕克(Disperbyk)166、迪斯帕毕克(Disperbyk)170、迪斯帕毕克(Disperbyk)180、迪斯帕毕克(Disperbyk)181、迪斯帕毕克(Disperbyk)182、毕克(BYK)300、毕克(BYK)306、毕克(BYK)310、毕克(BYK)320、毕克(BYK)330、毕克(BYK)342、毕克(BYK)344、毕克(BYK)346(商品名,日本毕克化学(BYK-Chemie Japan)(股)制造),KP-341、KP-358、KP-368、KF-96-50CS、KF-50-100CS(商品名,信越化学工业(股)制造),沙福隆(Surflon)SC-101、沙福隆(Surflon)

KH-40(商品名,清美化学(Seimi Chemical)(股)制造),福杰特(Ftergent)222F、福杰特(Ftergent)251、FTX-218(商品名,尼奥斯(NEOS)(股)制造),艾福拓(EFTOP)EF-351、艾福拓(EFTOP)EF-352、艾福拓(EFTOP)EF-601、艾福拓(EFTOP)EF-801、艾福拓(EFTOP)EF-802(商品名,三菱材料(Mitsubishi Material)(股)制造),美佳法(Megafac)F-470、美佳法(Megafac)F-471、美佳法(Megafac)F-475、美佳法(Megafac)R-08、美佳法(Megafac)F-477、美佳法(Megafac)F-479、美佳法(Megafac)F-553、美佳法(Megafac)F-554(商品名,迪爱生(DIC)(股)制造),氟烷基苯磺酸盐、氟烷基羧酸盐、氟烷基聚氧乙烯醚、氟烷基碘化铵、氟烷基甜菜碱、氟烷基磺酸盐、二甘油四(氟烷基聚氧乙烯醚)、氟烷基三甲基铵盐、氟烷基氨基磺酸盐、聚氧乙烯壬基苯基醚、聚氧乙烯辛基苯基醚、聚氧乙烯烷基醚、聚氧乙烯月桂酸酯、聚氧乙烯油酸酯、聚氧乙烯硬脂酸酯、聚氧乙烯月桂基胺、脱水山梨糖醇月桂酸酯、脱水山梨糖醇棕榈酸酯、脱水山梨糖醇硬脂酸酯、脱水山梨糖醇油酸酯、脱水山梨糖醇脂肪酸酯、聚氧乙烯脱水山梨糖醇月桂酸酯、聚氧乙烯脱水山梨糖醇棕榈酸酯、聚氧乙烯脱水山梨糖醇硬脂酸酯、聚氧乙烯脱水山梨糖醇油酸酯、聚氧乙烯萘基醚、烷基苯磺酸盐及烷基二苯基醚二磺酸盐。

[1282] 另外,表面活性剂可使用一种,也可并用两种以上。

[1283] ＜有机层形成用组合物的组成及物性＞

[1284] 考虑到有机层形成用组合物中各成分的良好的溶解性、保存稳定性及成膜性以及由所述有机层形成用组合物所获得的涂膜的优质膜质且使用喷墨法时的良好喷出性、具有使用所述组合物而制作的有机层的有机EL元件的良好的电特性、发光特性、效率、寿命的观点来决定有机层形成用组合物中的各成分的含量。例如,在为发光层形成用组合物的情况下,优选为:第一成分相对于发光层形成用组合物的总重量而为0.0001重量％～2.0重量％,第二成分相对于发光层形成用组合物的总重量而为0.0999重量％～8.0重量％,第三成分相对于发光层形成用组合物的总重量而为90.0重量％～99.9重量％。

[1285] 更优选为:第一成分相对于发光层形成用组合物的总重量而为0.005重量％～1.0重量％,第二成分相对于发光层形成用组合物的总重量而为0.095重量％～4.0重量％,第三成分相对于发光层形成用组合物的总重量而为95.0重量％～99.9重量％。进而更优选为:第一成分相对于发光层形成用组合物的总重量而为0.05重量％～0.5重量％,第二成分相对于发光层形成用组合物的总重量而为0.25重量％～2.5重量％,第三成分相对于发光层形成用组合物的总重量而为97.0重量％～99.7重量％。

[1286] 有机层形成用组合物可通过利用已知的方法对所述成分适当选择进行搅拌、混合、加热、冷却、溶解、分散等而制造。另外,也可在制备后适当选择进行过滤、脱气(也称为脱气(degas))、离子交换处理及惰性气体置换・封入处理等。

[1287] 关于有机层形成用组合物的粘度,高粘度者可获得良好的成膜性与使用喷墨法时的良好的喷出性。另一方面,低粘度者容易制作薄膜。因此,所述有机层形成用组合物的粘度优选为在25℃下的粘度为0.3mPa・s～3mPa・s,更优选为1mPa・s～3mPa・s。本发明中,粘度是使用圆锥平板型旋转粘度计(cone-plate type)而测定的值。

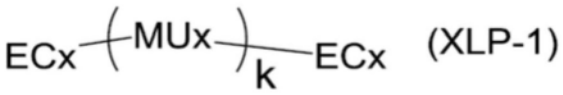
[1288] 关于有机层形成用组合物的表面张力,低者可获得良好的成膜性及无缺陷的涂膜。另一方面,高者可获得良好的喷墨喷出性。因此,所述有机层形成用组合物的粘度优选为在25℃下的表面张力为20mN/m～40mN/m,更优选为20mN/m～30mN/m。本发明中,表面张力

是使用悬滴法而测定的值。

[1289] ＜交联性高分子化合物:通式(XLP-1)所表示的化合物＞

[1290] 继而,对所述高分子化合物具有交联性取代基的情况进行说明。此种交联性高分子化合物例如为下述通式(XLP-1)所表示的化合物。

[1291] [化341]

[1292] 

(XLP-1)

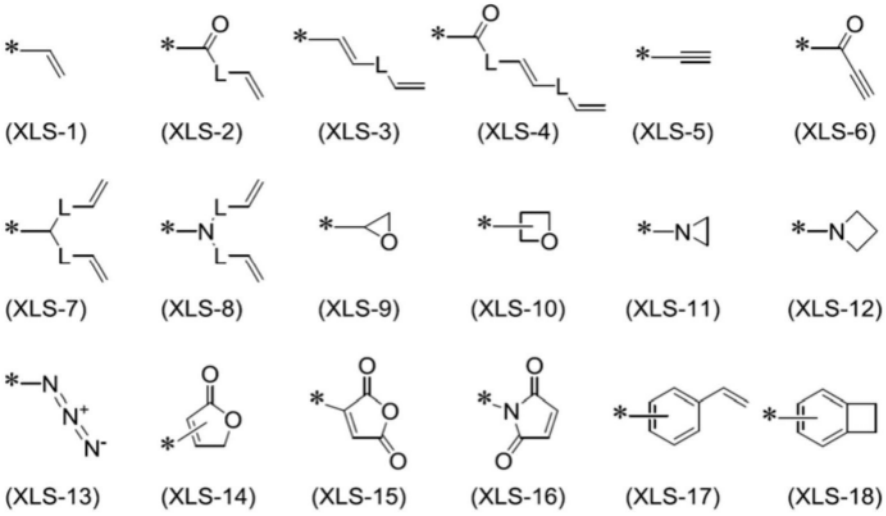
[1293] 式(XLP-1)中,

[1294] MUx、ECx及k与所述式(SPH-1)中的MU、EC及k为相同定义,其中,式(XLP-1)所表示的化合物具有至少一个交联性取代基(XLS),优选为具有交联性取代基的一价或二价的芳香族化合物的含量在分子中为0.1重量%～80重量%。

[1295] 具有交联性取代基的一价或二价的芳香族化合物的含量优选为0.5重量%～50重量%,更优选为1重量%～20重量%。

[1296] 作为交联性取代基(XLS),若为可使所述高分子化合物进一步交联化的基,则无特别限定,优选为以下结构的取代基。各结构式中的*表示键结位置。

[1297] [化342]

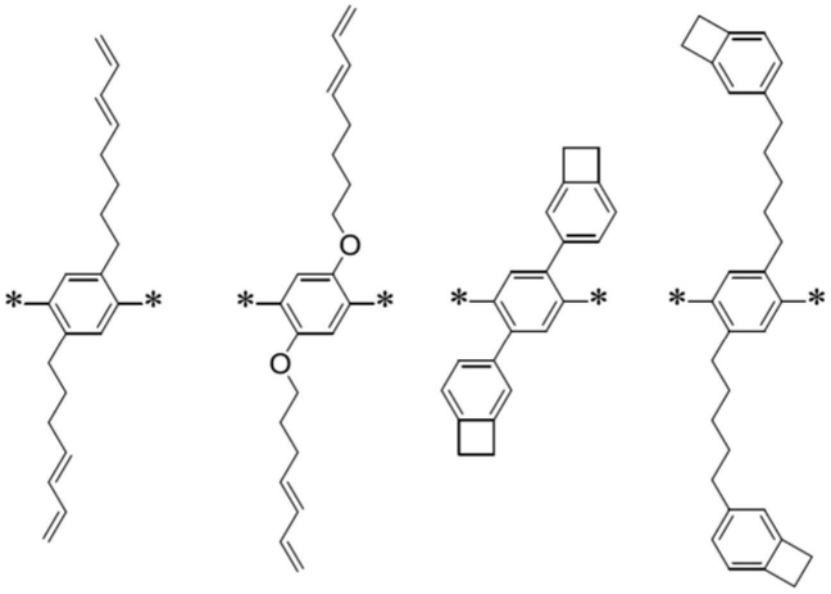
[1298] 

[1299] L分别独立地为单键、-O-、-S-、＞C＝O、-O-C(＝O)-、碳数1～12的亚烷基、碳数1～12的氧化烯基及碳数1～12的聚氧化烯基。在所述取代基中,优选为式(XLS-1)、式(XLS-2)、式(XLS-3)、式(XLS-9)、式(XLS-10)或式(XLS-17)所表示的基,更优选为式(XLS-1)、式(XLS-3)或式(XLS-17)所表示的基。

[1300] 作为具有交联性取代基的二价的芳香族化合物,例如可列举具有下述部分结构的化合物。下述结构式中的*表示键结位置。

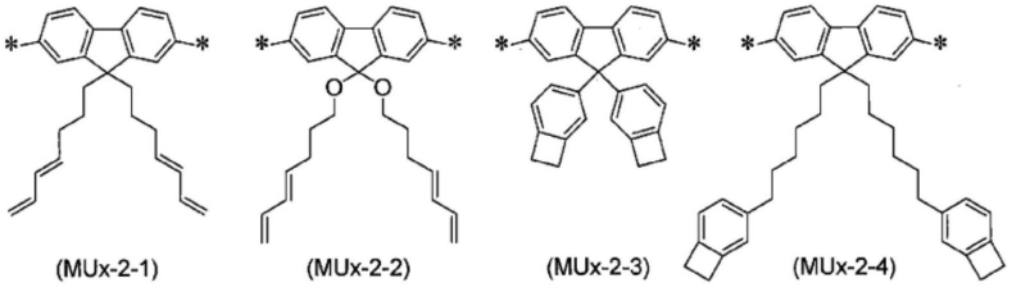
[1301] [化343]

[1302]



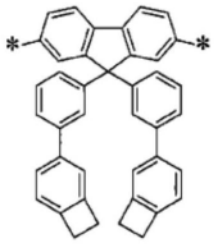
(MUx-1-1) (MUx-1-2) (MUx-1-3) (MUx-1-4)

[1303] [化344]



(MUx-2-1) (MUx-2-2) (MUx-2-3) (MUx-2-4)

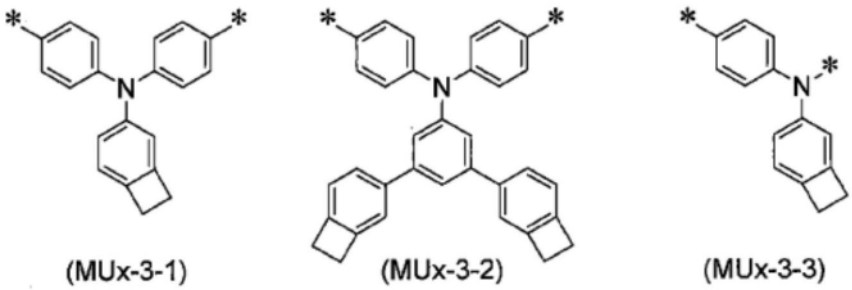
[1304]



(MUx-2-5)

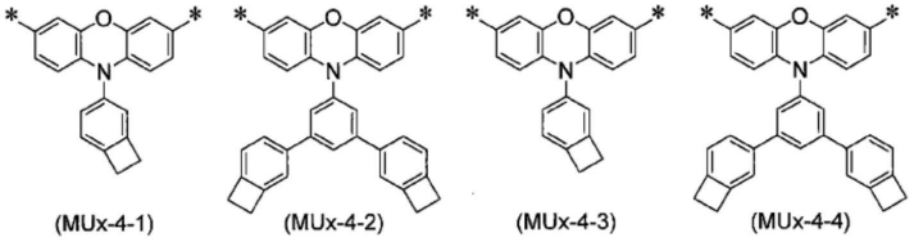
[1305] [化345]

[1306]



(MUx-3-1) (MUx-3-2) (MUx-3-3)

[1307] [化346]

[1308] 

[1309] ＜高分子化合物及交联性高分子化合物的制造方法＞

[1310] 关于高分子化合物及交联性高分子化合物的制造方法,以所述式(SPH-1)所表示的化合物及式(XLP-1)所表示的化合物为例进行说明。这些化合物可将已知的制造方法适当组合而合成。

[1311] 作为反应中所使用的溶媒,可列举芳香族溶媒、饱和/不饱和烃溶媒、醇溶媒、醚系溶媒等,例如可列举:二甲氧基乙烷、2-(2-甲氧基乙氧基)乙烷、2-(2-乙氧基乙氧基)乙烷等。

[1312] 另外,反应也可以两相系统进行。在以两相系统进行反应的情况下,视需要也可加入四级铵盐等相间转移催化剂。

[1313] 当制造式(SPH-1)的化合物及式(XLP-1)的化合物时,可以一阶段来制造,也可经由多阶段来制造。另外,可通过将原料全部放入至反应容器后开始反应的总括聚合法来进行,也可通过将原料滴加至反应容器的滴加聚合法来进行,还可通过产物随着反应的进行而沉淀的沉淀聚合法来进行,可适当组合这些来合成。例如,当以一阶段来合成式(SPH-1)所表示的化合物时,通过在将单体单元(MU)及封端单元(EC)加入至反应容器的状态下进行反应而获得目标物。另外,当以多阶段来合成通式(SPH-1)所表示的化合物时,通过在使单体单元(MU)聚合至目标分子量后加入封端单元(EC)并加以反应而获得目标物。若以多阶段加入不同种类的单体单元(MU)来进行反应,则可制作对于单体单元的结构而言具有浓度梯度的聚合物。另外,制备前体聚合物后,可通过后续反应而获得作为目标物的聚合物。

[1314] 另外,若选择单体单元(MU)的聚合性基,则可控制聚合物的一次结构。例如,如合成流程的1～3所示,能够合成具有无规的一次结构的聚合物(合成流程的1)、具有规则的一次结构的聚合物(合成流程的2及3)等,且可根据目标物进行适当组合来使用。进而,若使用具有三个以上的聚合性基的单体单元,则可合成超支化聚合物(hyperbranched polymer)或树枝状聚合物(dendrimer)。

[1315] [化347]

a、b=MU或MUx
聚合性基=x、y（分别为x与y键结）

1）使用两种单体（x-a-y）及单体（x-b-y）合成的聚合物



合成使a与b无规地连结的聚合物。

2）使用两种单体（x-a-x）及单体（y-b-y）合成的聚合物

[1316]



合成使a与b交替连结的聚合物。

3）使用两种单体（x-a-y）及单体（y-b-y）合成的聚合物



合成使b不相邻的聚合物。

[1317] 作为本发明中可使用的单体单元,可依据日本专利特开2010-189630号公报、国际公报第2012/086671号、国际公开第2013/191088号、国际公开第2002/045184号、国际公开第2011/049241号、国际公开第2013/146806号、国际公开第2005/049546号、国际公开第2015/145871号、日本专利特开2010-215886号、日本专利特开2008-106241号公报、日本专利特开2010-215886号公报、国际公开第2016/031639号、日本专利特开2011-174062号公报、国际公开第2016/031639号、国际公开第2016/031639号、国际公开第2002/045184号中记载的方法来合成。

[1318] 另外,关于具体的聚合物合成程序,可依据日本专利特开2012-036388号公报、国际公开第2015/008851号、日本专利特开2012-36381号公报、日本专利特开2012-144722号公报、国际公开第2015/194448号、国际公开第2013/146806号、国际公开第2015/145871号、国际公开第2016/031639号、国际公开第2016/125560号、国际公开第2016/031639号、国际公开第2016/031639号、国际公开第2016/125560号、国际公开第2015/145871号、国际公开第2011/049241号、日本专利特开2012-144722号公报中记载的方法来合成。

[1319] ＜有机电致发光元件的应用例＞

[1320] 另外,本发明也可应用于具备有机EL元件的显示装置或具备有机EL元件的照明装置等。

[1321] 具备有机EL元件的显示装置或照明装置可通过将本实施方式的有机EL元件与已知的驱动装置连接等已知的方法来制造,且可适当使用直流驱动、脉冲驱动、交流驱动等已知的驱动方法来进行驱动。

[1322] 作为显示装置,例如可列举:彩色平板显示器等面板显示器、挠性彩色有机电致发光(EL)显示器等挠性显示器等(例如,参照日本专利特开平10-335066号公报、日本专利特开2003-321546号公报、日本专利特开2004-281086号公报等)。另外,作为显示器的显示方式,例如可列举矩阵及分段方式等。再者,矩阵显示与分段显示可在相同的面板中共存。

[1323] 矩阵是将用于显示的像素二维地配置成格子状或马赛克状等,其通过像素的集合

来显示文字或图像。像素的形状或尺寸是根据用途来决定。例如在个人计算机、监视器、电视机的图像及文字显示中,通常使用一边为300μm以下的四边形的像素,另外,在为显示面板之类的大型显示器的情况下,使用一边为mm级的像素。在为单色显示的情况下,只要排列相同颜色的像素即可,在为彩色显示的情况下,使红、绿、蓝的像素并列来进行显示。在此情况下,典型的有三角型与条纹型。而且,作为所述矩阵的驱动方法,可为线序(line-sequential)驱动方法或有源矩阵的任一者。线序驱动有结构简单这一优点,但在考虑了动作特性的情况下,有时有源矩阵更优异,因此驱动方法也需要根据用途而区分使用。

[1324] 在分段方式(类型)中,以显示事先所决定的信息的方式形成图案,并使所决定的区域发光。例如可列举:数字时钟或温度计中的时刻或温度显示、声频机器或电磁炉等的动作状态显示及汽车的面板显示等。

[1325] 作为照明装置,例如可列举:室内照明等的照明装置、液晶显示装置的背光源等(例如,参照日本专利特开2003-257621号公报、日本专利特开2003-277741号公报、日本专利特开2004-119211号公报等)。背光源主要为了提高不进行自发光的显示装置的视认性而使用,其用于液晶显示装置、时钟、声频装置、汽车面板、显示板及标识等。尤其,作为液晶显示装置中薄型化正成为课题的个人计算机用途的背光源,若考虑到现有方式因包含荧光灯或导光板而难以薄型化,则使用了本实施方式的发光元件的背光源具有薄型、轻量的特征。

[1326] 3-2.其他有机元件

[1327] 除所述有机电致发光元件以外,本发明的多环芳香族化合物可用于有机场效晶体管或有机薄膜太阳电池等的制作。

[1328] 有机场效晶体管是利用通过电压输入所产生的电场来控制电流的晶体管,除源电极与漏电极以外,设置有栅电极。为若对栅电极施加电压,则产生电场,可任意地阻断在源电极与漏电极间流动的电子(或空穴)的流动来控制电流的晶体管。与单一晶体管(双极晶体管)相比,场效晶体管容易小型化,而常用作构成集成电路等的元件。

[1329] 有机场效晶体管的结构通常只要使源电极及漏电极接触使用本发明的多环芳香族化合物所形成的有机半导体活性层来设置,进而隔着接触有机半导体活性层的绝缘层(介电体层)来设置栅电极即可。作为其元件结构,例如可列举以下的结构。

[1330] (1)基板/栅电极/绝缘体层/源电极·漏电极/有机半导体活性层

[1331] (2)基板/栅电极/绝缘体层/有机半导体活性层/源电极·漏电极

[1332] (3)基板/有机半导体活性层/源电极·漏电极/绝缘体层/栅电极

[1333] (4)基板/源电极·漏电极/有机半导体活性层/绝缘体层/栅电极

[1334] 如此结构的有机场效晶体管可用作有源矩阵驱动方式的液晶显示器、或有机电致发光显示器的像素驱动开关元件等。

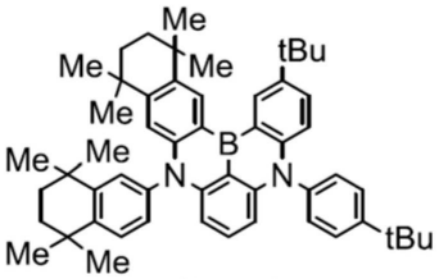
[1335] 有机薄膜太阳电池具有在玻璃等透明基板上层叠有ITO等的阳极、空穴传输层、光电转换层、电子传输层、阴极的结构。光电转换层在阳极侧具有p型半导体层,在阴极侧具有n型半导体层。本发明的多环芳香族化合物根据其物性,可用作空穴传输层、p型半导体层、n型半导体层、电子传输层的材料。在有机薄膜太阳电池中,本发明的多环芳香族化合物可作为空穴传输材料或电子传输材料而发挥功能。有机薄膜太阳电池除所述以外,也可适当具备空穴阻挡层、电子阻挡层、电子注入层、空穴注入层、平滑化层等。在有机薄膜太阳电池中,可适当选择用于有机薄膜太阳电池的已知的材料来组合使用。

[1336] 实施例

[1337] 以下,通过实施例对本发明进一步进行具体说明,但本发明并不限定于这些实施例。首先,关于多环芳香族化合物的合成例,在以下进行说明。

[1338] 合成例(1):化合物(1-411)的合成

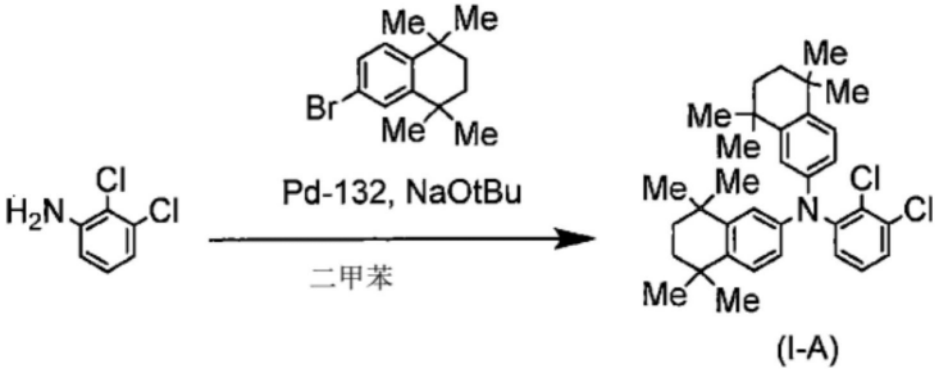
[1339] [化348]

[1340] 

(1-411)

[1341] 在氮气环境下,将2,3-二氯苯胺(6.0g)、6-溴-1,1,4,4-四甲基-2,3-二氢萘(25g)、二氯双(二-叔丁基(4-二甲基氨基苯基)膦基)钯(Pd-132、0.44g)、叔丁醇钠(NaOtBu、14.8g)及二甲苯(120ml)放入至烧瓶中,在120℃下加热2小时。反应后,向反应液中加入水与乙酸乙酯并进行搅拌后,将有机层分离并进行水洗。其后,将有机层浓缩而获得粗产物。利用硅胶短管柱(洗脱液:甲苯)对粗产物进行精制后,将溶媒浓缩,向所获得的粗产物中加入甲醇并进行冰浴冷却,对所析出的结晶进行过滤并利用甲醇来清洗结晶,由此获得化合物(I-A)(17.0g)。

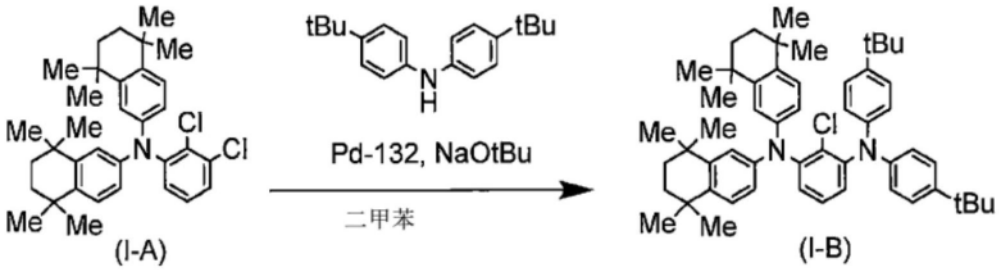
[1342] [化349]

[1343] 

(I-A)

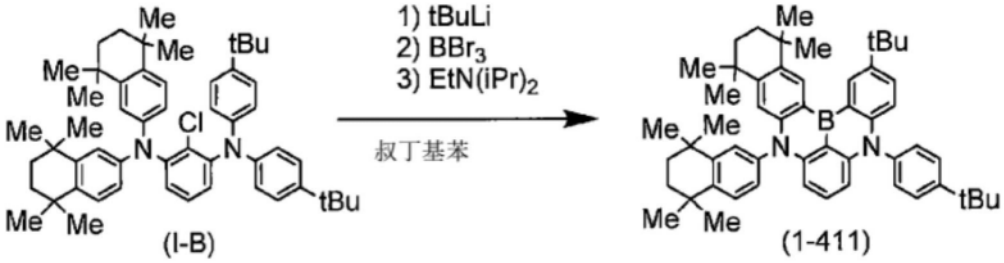
[1344] 在氮气环境下,将化合物(I-A)(8.0g)、双(4-叔丁基苯基)胺(25g)、Pd-132(0.10g)、NaOtBu(2.1g)及二甲苯(40ml)放入至烧瓶中,在120℃下加热1小时。反应后,向反应液中加入水与乙酸乙酯并进行搅拌后,将有机层分离并进行水洗。其后,将有机层浓缩而获得粗产物。利用硅胶短管柱(洗脱液:甲苯)对粗产物进行精制后,将溶媒浓缩,向所获得的粗产物中加入甲醇并进行冰浴冷却,对所析出的结晶进行过滤并利用甲醇来清洗结晶,由此获得化合物(I-B)(9.7g)。

[1345] [化350]

[1346] 

[1347] 在氮气环境下,且在0℃下向放入有化合物(I-B)(8.6g)及叔丁基苯(80ml)的烧瓶中加入1.53M的叔丁基锂戊烷溶液(15.2ml)。滴加结束后,升温至60℃并搅拌0.5小时后,将沸点低于叔丁基苯的成分减压馏去。冷却至-50℃并加入三溴化硼(5.8g),升温至室温并搅拌0.5小时。其后,再次冷却至0℃并加入N,N-二异丙基乙胺(2.6g),在室温下搅拌至发热结束后,升温至100℃并加热搅拌1小时。将反应液冷却至室温,依次加入利用冰浴进行了冷却的乙酸钠水溶液、乙酸乙酯并搅拌1小时。对黄色悬浮液进行过滤并利用甲醇来清洗其沉淀。将黄色结晶加热溶解于甲苯中后,利用硅胶短管柱(洗脱液:甲苯)进行精制。将所获得的粗产物加入甲苯中而进行浓缩后,加入索尔米克斯(Solmix)(A-11),对所析出的结晶进行过滤,进而利用甲醇来清洗结晶,由此获得化合物(1-411)(3.0g)。

[1348] [化351]

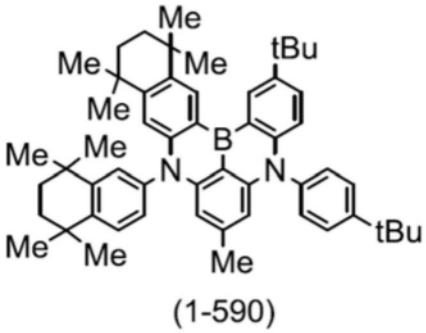
[1349] 

[1350] 通过核磁共振(nuclear magnetic resonance,NMR)测定来确认所获得的化合物的结构。

[1351] ^{1}H-NMR($CDCl_3$):δ=1.09(s,6H),1.27(s,6H),1.42(s,6H),1.46(s,9H),1.48(s,9H),1.49(s,6H),1.71-1.80(m,8H),6.11(d,1H),6.23(d,1H),6.59(s,1H),6.73(d,1H),7.09(dd,1H),7.25-7.30(m,5H),7.51(dd,1H),7.59(d,1H),7.67(d,2H),8.92(s,1H),8.99(d,1H).

[1352] 合成例(2):化合物(1-590)的合成

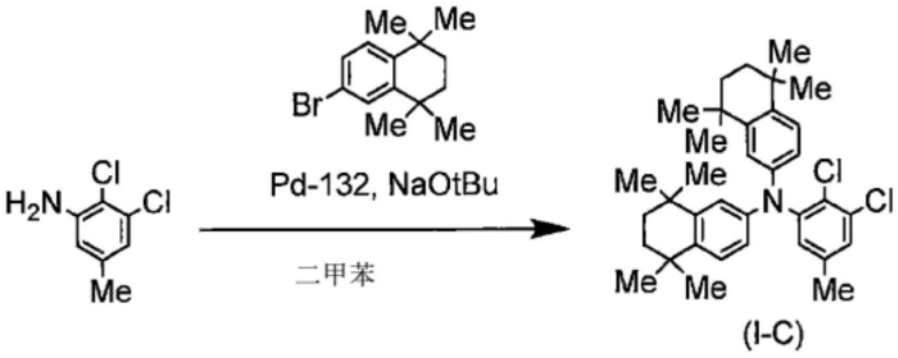
[1353] [化352]

[1354] 

[1355] 在氮气环境下,将2,3-二氯-5-甲基苯胺(6.6g)、6-溴-1,1,4,4-四甲基-2,3-二氢萘(25g)、Pd-132(0.54g)、NaOtBu(9.0g)及二甲苯(90ml)放入至烧瓶中,在120℃下加热2小

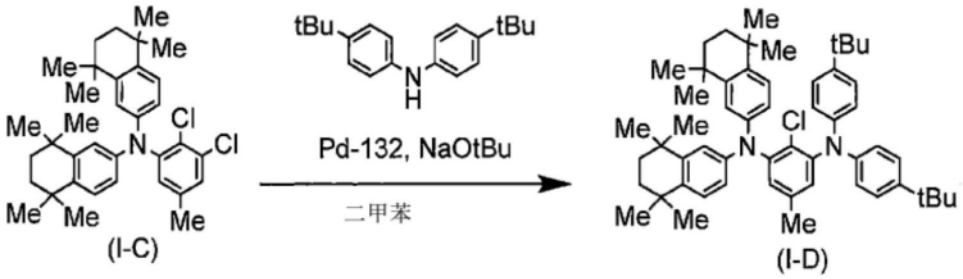
时。反应后,向反应液中加入水与乙酸乙酯并进行搅拌后,将有机层分离并进行水洗。其后,将有机层浓缩而获得粗产物。利用硅胶短管柱(洗脱液:甲苯)对粗产物进行精制后,将溶媒浓缩,向所获得的粗产物中加入甲醇并进行冰浴冷却,对所析出的结晶进行过滤并利用甲醇来清洗结晶,由此获得化合物(I-C)(13.0g)。

[1356] [化353]

[1357] 

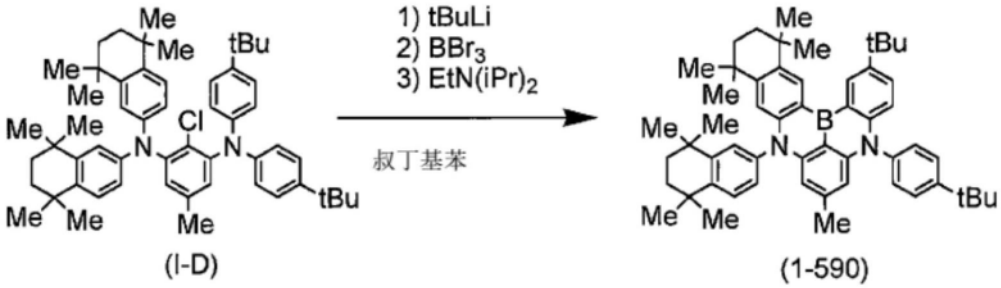
[1358] 在氮气环境下,将化合物(I-C)(8.0g)、双(4-叔丁基苯基)胺(4g)、Pd-132(0.10g)、NaOtBu(2.1g)及二甲苯(40ml)放入至烧瓶中,在120℃下加热1小时。反应后,向反应液中加入水与乙酸乙酯并进行搅拌后,将有机层分离并进行水洗。其后,将有机层浓缩而获得粗产物。利用硅胶短管柱(洗脱液:甲苯)对粗产物进行精制后,将溶媒浓缩,向所获得的粗产物中依次加入乙酸乙酯、甲醇,对所析出的结晶进行过滤并利用甲醇来清洗所述结晶,由此获得化合物(I-D)(11.0g)。

[1359] [化354]

[1360] 

[1361] 在氮气环境下,且在0℃下向放入有化合物(I-D)(11.0g)及叔丁基苯(110ml)的烧瓶中加入1.53M的叔丁基锂戊烷溶液(18.9ml)。滴加结束后,升温至60℃并搅拌0.5小时后,将沸点低于叔丁基苯的成分减压馏去。冷却至-50℃并加入三溴化硼(7.3g),升温至室温并搅拌0.5小时。其后,再次冷却至0℃并加入N,N-二异丙基乙胺(2.6g),在室温下搅拌至发热结束后,升温至100℃并加热搅拌1小时。将反应液冷却至室温,依次加入利用冰浴进行了冷却的乙酸钠水溶液、乙酸乙酯并搅拌1小时。将有机层分液后,进行水洗(2次)并将溶媒减压馏去。向所获得的残渣中加入甲醇并进行冰浴冷却,对其沉淀进行过滤并利用甲醇进行清洗。将黄色结晶加热溶解于甲苯中后,利用硅胶短管柱(洗脱液:甲苯)进行精制。将所获得的粗产物加入甲苯而进行浓缩后,依次加入乙酸乙酯、索尔米克斯(Solmix)(A-11),然后将乙酸乙酯馏去,对所析出的结晶进行过滤,进而利用甲醇来清洗结晶,由此获得化合物(1-590)(4.0g)。

[1362] [化355]

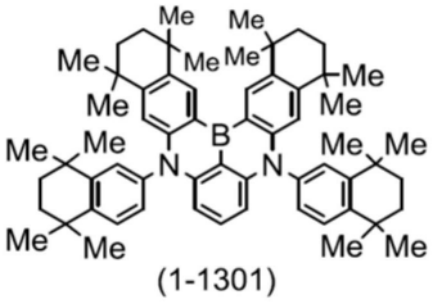
[1363] 

[1364] 通过NMR测定来确认所获得的化合物的结构。

[1365] ^{1}H-NMR($CDCl_3$):δ=1.08(s,6H),1.27(s,6H),1.42(s,6H),1.46(s,9H),1.47(s,9H),1.48(s,6H),1.69-1.81(m,8H),2.18(s,3H),5.97(s,1H),6.06(s,1H),6.52(s,1H),6.67(d,1H),7.08(dd,1H),7.25-7.29(m,3H),7.48(dd,1H),7.59(d,1H),7.67(d,2H),8.89(s,1H),8.97(d,1H).

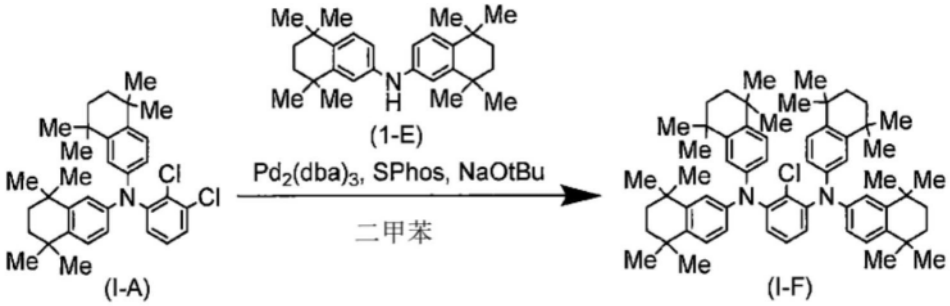
[1366] 合成例(3):化合物(1-1301)的合成

[1367] [化356]

[1368] 

[1369] 在氮气环境下,将化合物(I-A)(8.0g)、化合物(I-E)(5.6g)、三(二亚苄基丙酮)二钯(0)[$Pd_2(dba)_3$、0.16g]、二环己基(2',6'-二甲氧基-[1,1'-联苯]-2-基)膦(SPhos、0.24g)、NaOtBu(2.1g)及二甲苯(40ml)放入至烧瓶中,在120℃下加热1小时。反应后,向反应液中加入水与甲苯并进行搅拌后,将有机层分离并进行水洗。其后,将有机层浓缩而获得粗产物。利用硅胶短管柱(洗脱液:甲苯)对粗产物进行精制后,将溶媒浓缩,向所获得的粗产物中加入庚烷并进行冰浴冷却,对所析出的结晶进行过滤并利用庚烷进行清洗,由此获得化合物(I-F)(10.5g)。

[1370] [化357]

[1371] 

[1372] 在氮气环境下,且在0℃下向放入有化合物(I-F)(10.5g)及叔丁基苯(200ml)的烧瓶中加入1.53M的叔丁基锂戊烷溶液(14.4ml)。滴加结束后,升温至60℃并搅拌0.5小时后,将沸点低于叔丁基苯的成分减压馏去。冷却至-50℃并加入三溴化硼(5.9g),升温至室温并搅拌0.5小时。其后,再次冷却至0℃并加入N,N-二异丙基乙胺(3.1g),在室温下搅拌至发热

结束后,升温至100℃并加热搅拌1小时。将反应液冷却至室温,依次加入利用冰浴进行了冷却的乙酸钠水溶液、乙酸乙酯并搅拌1小时。将有机层分离并进行2次水洗。其后,将有机层浓缩,利用硅胶(NH二氧化硅)短管柱(洗脱液:甲苯/庚烷=1/9(容量比))对所获得的粗产物进行精制。将所获得的粗产物浓缩后,加入庚烷并对所析出的结晶进行过滤,进而利用庚烷进行清洗,由此获得化合物(1-1301)(1.9g)。

[1373] [化358]

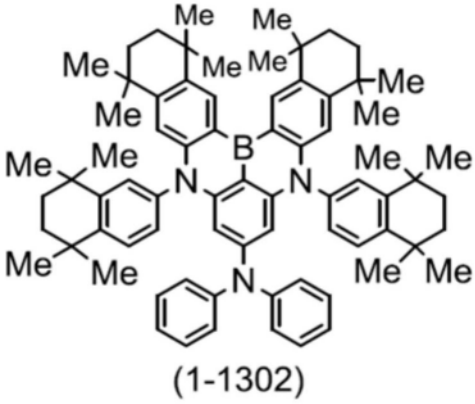
[1374] 

[1375] 通过NMR测定来确认所获得的化合物的结构。

[1376] ^{1}H-NMR($CDCl_3$):δ=1.09(s,12H),1.27(s,12H),1.42(s,12H),1.49(s,12H),1.70-1.80(m,16H),6.20(d,2H),6.56(s,2H),7.09(dd,2H),7.25-7.30(m,3H),7.58(d,2H),8.91(s,2H).

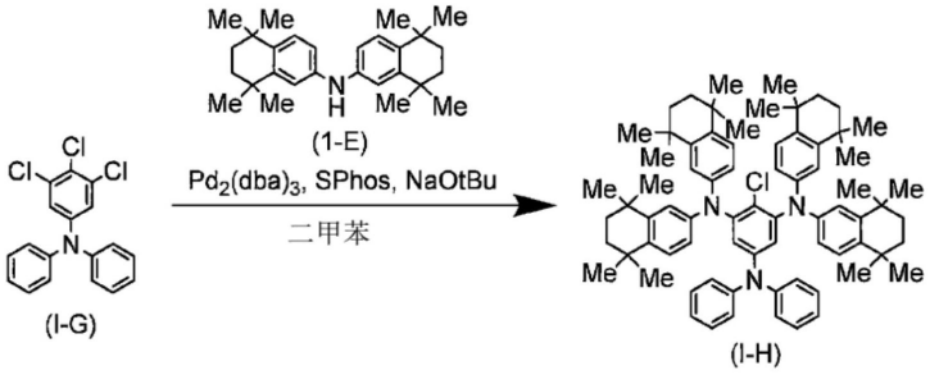
[1377] 合成例(4):化合物(1-1302)的合成

[1378] [化359]

[1379] 

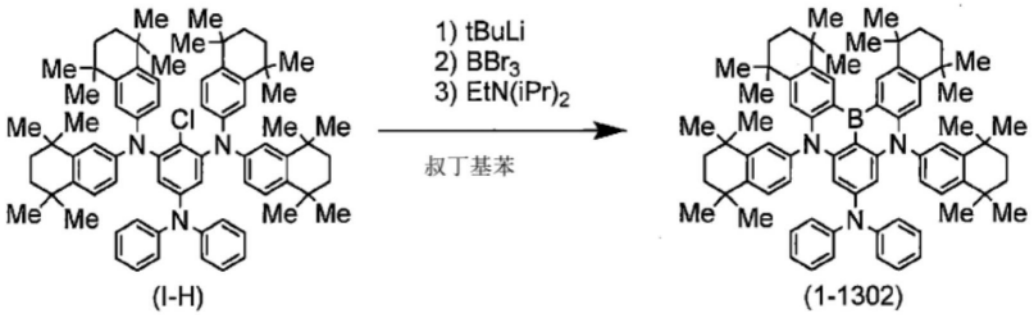
[1380] 在氮气环境下,将化合物(I-G)(8.0g)、化合物(I-E)(19.7g)、$Pd_2(dba)_3$(0.52g)、SPhos(0.94g)、NaOtBu(5.5g)及二甲苯(80ml)放入至烧瓶中,在120℃下加热搅拌3小时后,在130℃下搅拌1小时。反应后,向反应液中加入水与甲苯并进行搅拌后,将有机层分离并进行水洗。其后,将有机层浓缩而获得粗产物。利用硅胶管柱(洗脱液:甲苯/庚烷=10/90(容量比)→15/85(容量比))对粗产物进行精制后,将溶媒浓缩而获得化合物(I-H)(15.3g)。

[1381] [化360]

[1382] 

[1383] 在氮气环境下,且在0℃下向放入有化合物(I-H)(15.3g)及叔丁基苯(100ml)的烧瓶中加入1.53M的叔丁基锂戊烷溶液(13.2ml)。滴加结束后,升温至60℃并搅拌0.5小时后,将沸点低于叔丁基苯的成分减压馏去。冷却至-50℃并加入三溴化硼(5.3g),升温至室温并搅拌0.5小时。其后,再次冷却至0℃并加入N,N-二异丙基乙胺(2.7g),在室温下搅拌至发热结束后,升温至100℃并加热搅拌1小时。将反应液冷却至室温,依次加入利用冰浴进行了冷却的乙酸钠水溶液、乙酸乙酯并搅拌1小时。将有机层分液后,进行水洗(2次),并对通过加入庚烷而析出的沉淀进行过滤。利用甲醇及水对其沉淀物进行清洗,将所获得的黄色结晶加热溶解于甲苯中后,利用硅胶短管柱(洗脱液:甲苯)进行精制。将溶媒馏去,向所获得的粗产物中加入庚烷,对所获得的结晶进行过滤后,进而利用庚烷进行清洗,由此获得化合物(1-1302)(7.23g)。

[1384] [化361]

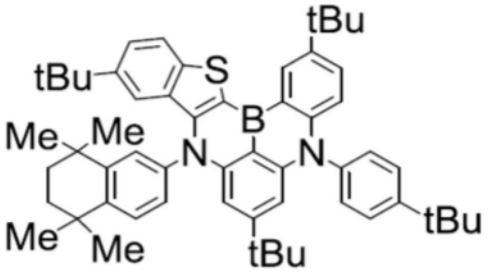
[1385] 

[1386] 通过NMR测定来确认所获得的化合物的结构。

[1387] ^{1}H-NMR($CDCl_3$):δ=1.07(s,12H),1.11(s,6H),1.19(s,6H),1.24(s,6H),1.35(s,6H),1.48(s,12H),1.68-1.75(m,16H),5.63(s,2H),6.55(s,2H),6.89(t,2H),6.91-6.92(m,2H),6.93-6.95(m,4H),7.04(t,4H),7.13(dd,2H),7.37(d,2H),8.85(s,2H).

[1388] 合成例(5):化合物(1-1823)的合成

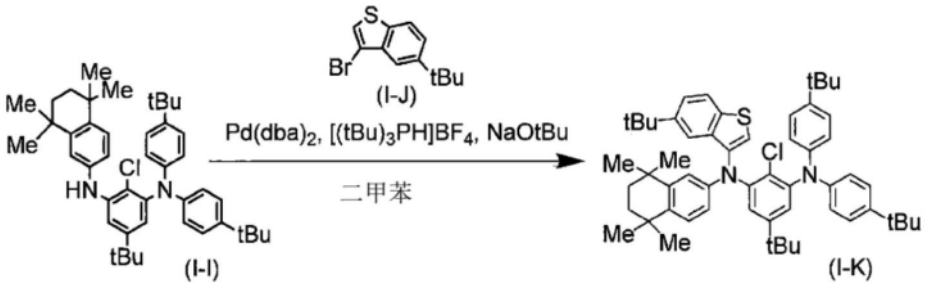
[1389] [化362]

[1390] 

(1-1823)

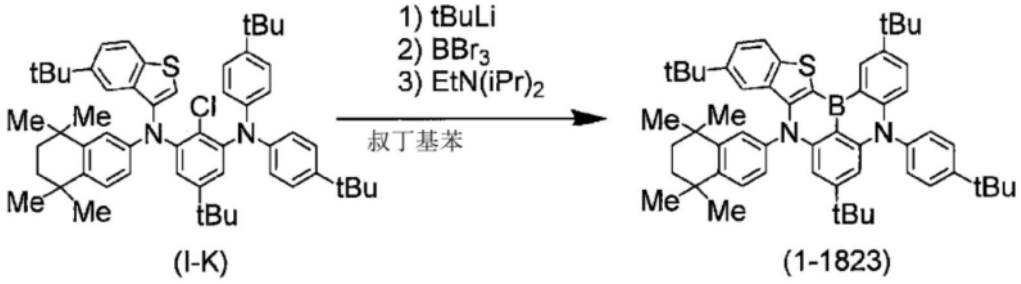
[1391] 在氮气环境下,将化合物(I-I)(35.0g)、3-溴-5-叔丁基-苯并[b]噻吩(化合物I-J:17.4g)、$Pd(dba)_2$(1.86g)、NaOtBu(10.4g)、三-叔丁基鏻四氟硼酸盐($[(tBu)_3PH]BF_4$):1.87g及二甲苯(300ml)放入至烧瓶中,在120℃下加热1小时。反应后,向反应液中加入水与甲苯并进行搅拌后,将有机层分离并进行水洗。其后,将有机层浓缩而获得粗产物。利用硅胶管柱(洗脱液:甲苯/庚烷=1/4(容量比))对粗产物进行精制后,将溶媒浓缩。利用真空泵对玻璃状的固体进行干燥,由此获得化合物(I-K)(35g)。

[1392] [化363]

[1393] 

[1394] 在氮气环境下,且在0℃下向放入有化合物(I-K)(16.7g)及叔丁基苯(400ml)的烧瓶中加入1.60M的叔丁基锂戊烷溶液(25.0ml)。滴加结束后,升温至60℃并搅拌0.5小时后,将沸点低于叔丁基苯的成分减压馏去。冷却至-50℃并加入三溴化硼(10.0g),升温至室温并搅拌0.5小时。其后,再次冷却至0℃并加入N,N-二异丙基乙胺(5.2g),在室温下搅拌至发热结束后,升温至90℃并加热搅拌1小时。将反应液冷却至室温,依次加入利用冰浴进行了冷却的乙酸钠水溶液、甲苯并搅拌1小时。将甲苯溶液浓缩后,添加庚烷并利用硅胶管柱(洗脱液:甲苯/庚烷=1/4(容量比))进行精制。利用甲苯对所获得的粗产物反复进行再结晶,由此获得化合物(1-1823)(2.8g)。

[1395] [化364]

[1396] 

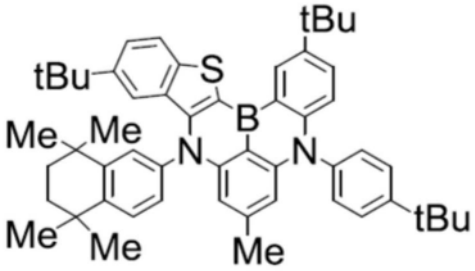
[1397] 通过NMR测定来确认所获得的化合物的结构。

[1398] ^1H-NMR($CDCl_3$):δ=0.99(s,9H),1.11(s,9H),1.30(s,6H),1.43(s,3H),1.46(m,

12H),1.51(s,9H),1.78-1.86(m,4H),6.15(s,1H),6.65(s,1H),6.74(s,1H),7.23-7.29(d,4H),7.41(d,1H),7.46(d,1H),7.53(s,1H),7.66-7.68(m,3H),7.90(d,1H),8.78(s,1H).

[1399] 合成例(6):化合物(1-1821)的合成

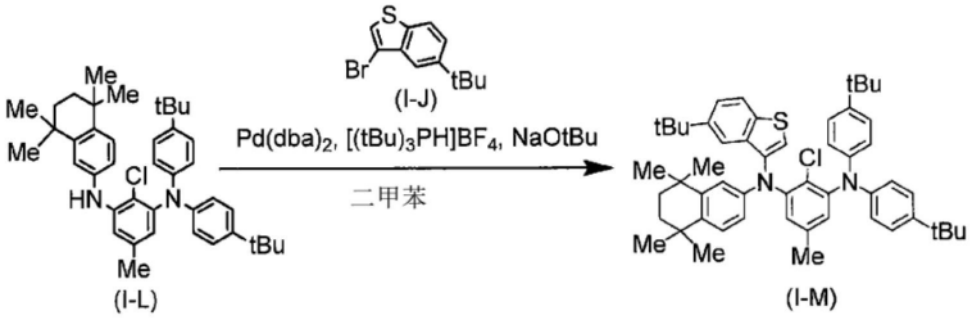
[1400] [化365]

[1401] 

(1-1821)

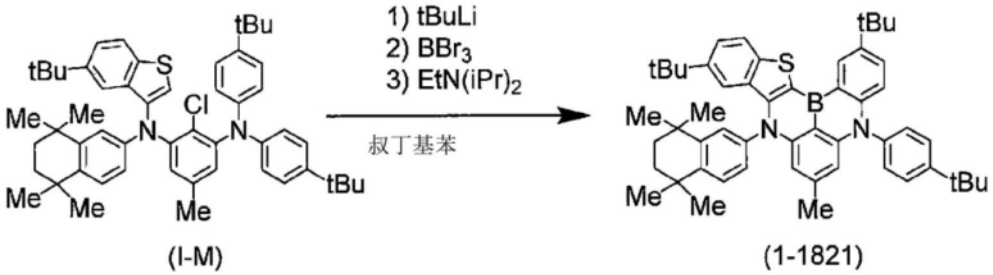
[1402] 在氮气环境下,将化合物(I-L)(71.0g)、化合物(I-J)(37.8g)、$Pd(dba)_2$(2.14g)、NaOtBu(16.9g)、$[(tBu)_3PH]BF_4$(1.36g)及二甲苯(710ml)放入至烧瓶中,在130℃下进行1小时加热回流。将反应液冷却至室温后,加入水与甲苯,将有机层分离并进行水洗。在减压下将所述溶液浓缩,利用硅胶管柱(洗脱液:甲苯)对残渣进行精制,进而利用庚烷进行清洗,由此获得化合物(I-M)(71.3g)。

[1403] [化366]

[1404] 

[1405] 在氮气环境下,且在0℃下向放入有化合物(I-M)(32.0g)及叔丁基苯(400ml)的烧瓶中加入1.60M的叔丁基锂戊烷溶液(50.0ml)。滴加结束后,升温至60℃并搅拌0.5小时后,将沸点低于叔丁基苯的成分减压馏去。冷却至-50℃并加入三溴化硼(20.0g),升温至室温并搅拌0.5小时。其后,再次冷却至0℃并加入N,N-二异丙基乙胺(10.4g),在室温下搅拌至发热结束后,升温至70℃并加热搅拌1小时。将反应液冷却至室温,依次加入利用冰浴进行了冷却的乙酸钠水溶液、乙酸乙酯并搅拌1小时,将有机层分离并进行水洗。在减压下将所述溶液浓缩,利用乙酸乙酯对残渣进行清洗后,利用硅胶管柱(洗脱液:甲苯/庚烷=1/1(容量比))进行精制。利用庚烷对所获得的粗产物进行清洗,由此获得化合物(1-1821)(7.1g)。

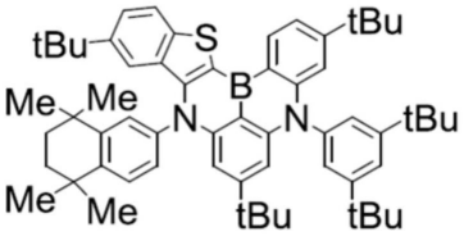
[1406] [化367]

[1407] 

(I-M) (1-1821)

[1408] 合成例(7):化合物(1-3623)的合成

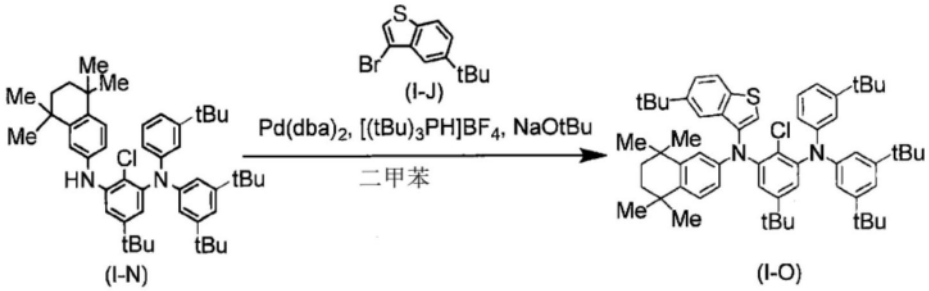
[1409] [化368]

[1410] 

(1-3623)

[1411] 在氮气环境下,将化合物(I-N)(60.0g)、化合物(I-J)(28.6g)、$Pd(dba)_2$(2.93g)、NaOtBu(12.3g)、$[(tBu)_3PH]BF_4$(2.96g)及二甲苯(660ml)放入至烧瓶中,在120℃下加热2小时。将反应液冷却至室温后,加入水与甲苯,将有机层分离并进行水洗。在减压下将所述溶液浓缩,利用硅胶管柱(洗脱液:甲苯/庚烷=1/3(容量比))对残渣进行精制,进而利用甲醇进行清洗,由此获得化合物(I-O)(68.0g)。

[1412] [化369]

[1413] 

(I-J) (I-N) (I-O)

[1414] 在氮气环境下,且在0℃下向放入有化合物(I-O)(35.8g)及叔丁基苯(800ml)的烧瓶中加入1.61M的叔丁基锂戊烷溶液(50.0ml)。滴加结束后,升温至60℃并搅拌0.5小时后,将沸点低于叔丁基苯的成分减压馏去。冷却至-50℃并加入三溴化硼(20.0g),升温至室温并搅拌0.5小时。其后,升温至50℃并加热搅拌0.5小时。将反应液冷却至室温,依次加入利用冰浴进行了冷却的乙酸钠水溶液、乙酸乙酯并搅拌1小时,将有机层分离并进行水洗。在减压下将所述溶液浓缩,利用乙酸乙酯对残渣进行清洗后,利用硅胶管柱(洗脱液:甲苯)进行精制。进而,通过自甲苯的再结晶而进行精制,由此获得化合物(1-3623)(9.3g)。

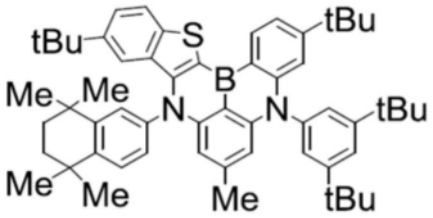
[1415] [化370]

[1416] 

(I-O) (1-3623)

[1417] 合成例(8):化合物(1-3621)的合成

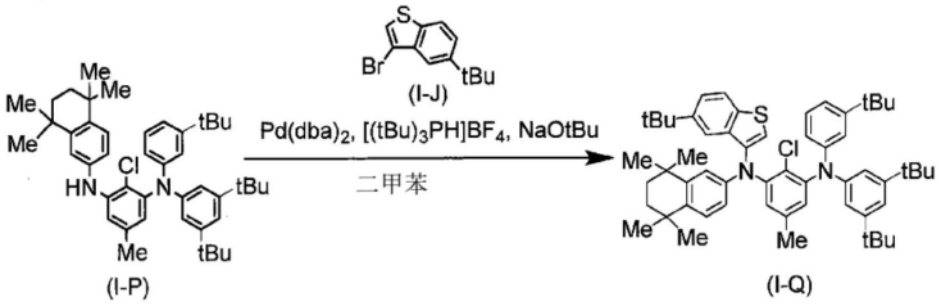
[1418] [化371]

[1419] 

(1-3621)

[1420] 在氮气环境下,将化合物(I-P)(65.0g)、化合物(I-J)(31.7g)、$Pd(dba)_2$(1.79g)、NaOtBu(14.1g)、$[(tBu)_3PH]BF_4$(1.14g)及二甲苯(520ml)放入至烧瓶中,在130℃下加热2小时。将反应液冷却至室温后,加入水与甲苯,将有机层分离并进行水洗。在减压下将所述溶液浓缩,利用硅胶管柱(洗脱液:甲苯/庚烷=1/4(容量比))对残渣进行精制。利用真空泵对玻璃状的固体进行干燥,由此获得化合物(I-Q)(52g)。

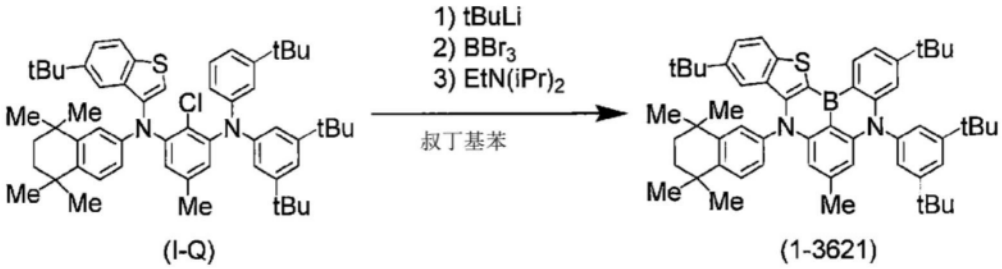
[1421] [化372]

[1422] 

(I-P) (I-Q)

[1423] 在氮气环境下,且在0℃下向放入有化合物(I-Q)(35.0g)及叔丁基苯(280ml)的烧瓶中加入1.60M的叔丁基锂戊烷溶液(50.0ml),升温至60℃并搅拌0.5小时。继而,冷却至-50℃并加入三溴化硼(20.6g),升温至室温并搅拌0.5小时。其后,再次冷却至0℃并加入N,N-二异丙基乙胺(10.6g),在室温下搅拌至发热结束后,升温至90℃并加热搅拌1小时。将反应液冷却至室温,依次加入利用冰浴进行了冷却的乙酸钠水溶液、乙酸乙酯并搅拌1小时,将有机层分离并进行水洗。在减压下将所述溶液浓缩,利用乙酸乙酯对残渣进行清洗后,利用硅胶管柱(洗脱液:甲苯/庚烷=1/1(容量比))进行精制。进而,通过自甲苯的再结晶而进行精制,由此获得化合物(1-3621)(7.2g)。

[1424] [化373]

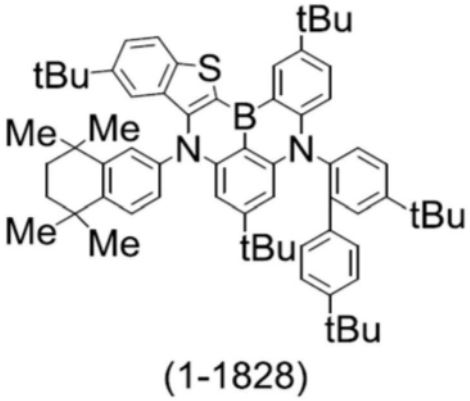
[1425] 

[1426] 通过NMR测定来确认所获得的化合物的结构。

[1427] ^{1}H-NMR($CDCl_3$):δ=1.11(s,9H),1.19(s,9H),1.26(s,3H),1.28(s,3H),1.37(s,18H),1.44-1.47(m,6H),1.77-1.86(m,4H),2.21(s,3H),6.08(s,1H),6.10(s,1H),6.53(d,1H),6.61(d,1H),7.20(d,2H),7.26(dd,1H),7.31(dd,1H),7.40(dd,1H),7.48(d,1H),7.61(t,1H),7.66(d,1H),7.88(d,1H),8.69(d,1H).

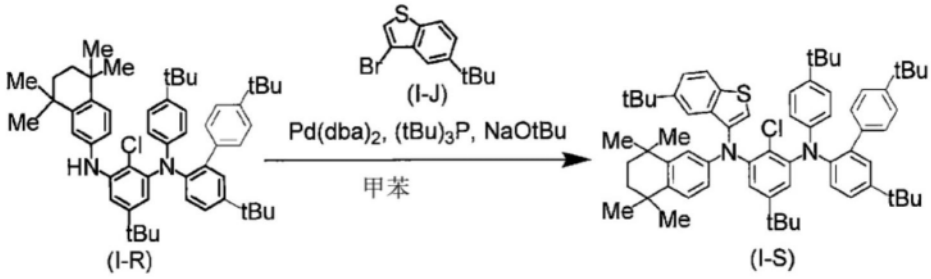
[1428] 合成例(9):化合物(1-1828)的合成

[1429] [化374]

[1430] 

[1431] 在氮气环境下,将化合物(I-R)(63.8g)、化合物(I-J)(24.2g)、$Pd(dba)_2$(0.939g)、NaOtBu(11.8g)、三-叔丁基膦($(tBu)_3P$:3.27ml)及甲苯(630ml)放入至烧瓶中,在110℃下加热4小时。将反应液冷却至室温后,加入水与甲苯,将有机层分离并进行水洗。在减压下将所述溶液浓缩,利用硅胶管柱(洗脱液:甲苯/庚烷=1/6(容量比))对残渣进行精制。利用真空泵对玻璃状的固体进行干燥,由此获得化合物(I-S)(44g)。

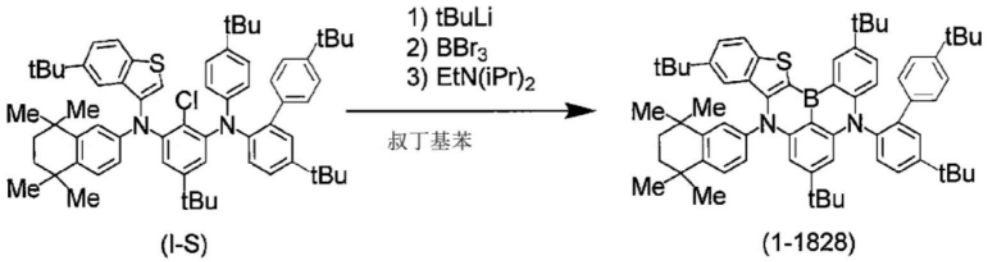
[1432] [化375]

[1433] 

[1434] 在氮气环境下,且在0℃下向放入有化合物(I-S)(44.3g)及叔丁基苯(400ml)的烧瓶中加入1.61M的叔丁基锂戊烷溶液(56.7ml)。滴加结束后,升温至60℃并搅拌0.5小时后,将沸点低于叔丁基苯的成分减压馏去。冷却至-50℃并加入三溴化硼(22.9g),升温至室温并搅拌0.5小时。其后,再次冷却至0℃并加入N,N-二异丙基乙胺(16.0g),在室温下搅拌至发热结束后,升温至120℃并加热搅拌1小时。将反应液冷却至室温,加入利用冰浴进行了冷

却的乙酸钠水溶液及甲苯并进行搅拌后,将有机层分离并进行水洗。其后,将有机层浓缩,利用硅胶管柱(洗脱液:甲苯/庚烷=1/4(容量比))对所获得的粗产物进行精制,进而,通过自甲苯及庚烷的混合溶媒(甲苯/庚烷=1/1(容量比))的再结晶而进行精制,由此获得化合物(1-1828)(5.0g)。

[1435] [化376]

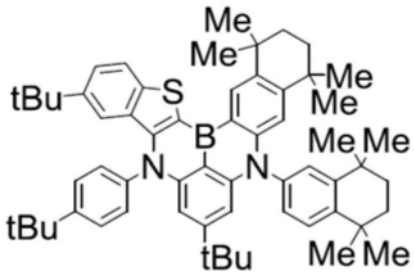
[1436] 

[1437] 通过NMR测定来确认所获得的化合物的结构。

[1438] ^{1}H-NMR($CDCl_3$):δ=0.96-0.99(m,9H),1.10(s,9H),1.12(s,9H),1.25-1.32(m,6H),1.39-1.51(m,24H),1.76-1.86(m,4H),6.05-6.28(m,2H),6.66-6.80(m,2H),7.01-7.08(m,2H),7.12-7.24(m,4H),7.37-7.47(m,2H),7.48-7.69(m,3H),7.70(s,1H),7.88(d,1H),8.70(s,1H).

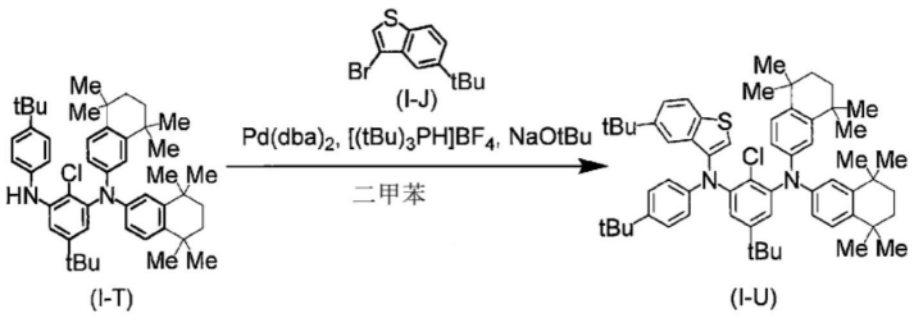
[1439] 合成例(10):化合物(1-3604)的合成

[1440] [化377]

[1441] 

[1442] 在氮气环境下,将化合物(I-T)(49.7g)、化合物(I-J)(22.8g)、$Pd(dba)_2$(2.44g)、NaOtBu(13.6g)、$[(tBu)_3PH]BF_4$(2.46g)及二甲苯(600ml)放入至烧瓶中,在120℃下加热3小时。将反应液冷却至室温后,加入水与甲苯,将有机层分离并进行水洗。在减压下将所述溶液浓缩,利用硅胶管柱(洗脱液:庚烷)对残渣进行精制,进而,通过自庚烷的再结晶而进行精制,由此获得化合物(I-U)(45g)。

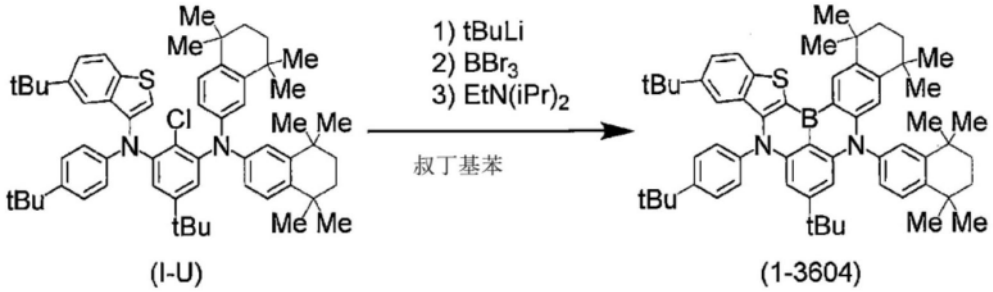
[1443] [化378]

[1444] 

[1445] 在氮气环境下,且在0℃下向放入有化合物(I-U)(40.4g)及叔丁基苯(270ml)的烧

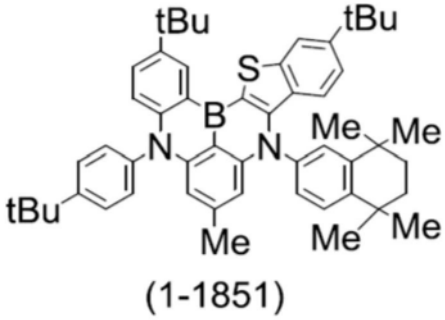
瓶中加入1.60M的叔丁基锂戊烷溶液(50.0ml)。滴加结束后,升温至60℃并搅拌0.5小时后,将沸点低于叔丁基苯的成分减压馏去。冷却至-50℃并加入三溴化硼(20.0g),升温至50℃并搅拌0.5小时。其后,再次冷却至0℃并加入N,N-二异丙基乙胺(10.4g),在室温下搅拌至发热结束后,升温至80℃并加热搅拌0.5小时。将反应液冷却至室温,依次加入利用冰浴进行了冷却的乙酸钠水溶液、乙酸乙酯并搅拌1小时,将有机层分离并进行水洗。在减压下将所述溶液浓缩,利用乙酸乙酯对残渣进行清洗后,利用硅胶管柱(洗脱液:甲苯)进行精制。进而,通过自甲苯的再结晶而进行精制,由此获得化合物(1-3604)(3.8g)。

[1446] [化379]

[1447] 

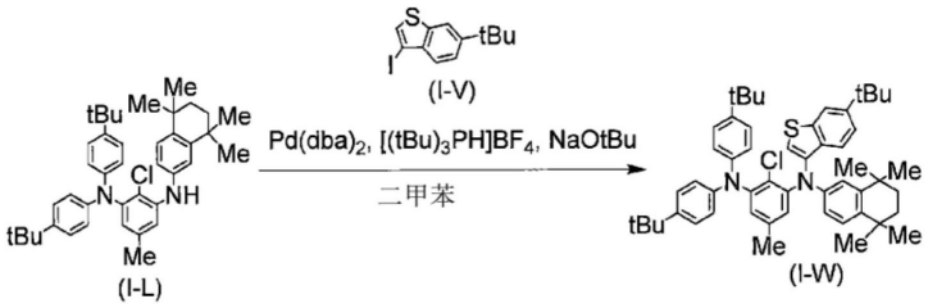
[1448] 合成例(11):化合物(1-1851)的合成

[1449] [化380]

[1450] 

[1451] 在氮气环境下,将化合物(I-L)(29.0g)、化合物(I-V)(18.9g)、$Pd(dba)_2$(0.55g)、NaOtBu(6.9g)、$[(tBu)_3PH]BF_4$(0.55g)及二甲苯(100ml)放入至烧瓶中,在120℃下进行1小时加热回流。将反应液冷却至室温后,加入水与乙酸乙酯,将有机层分离并进行水洗。在减压下将所述溶液浓缩,利用硅胶管柱(洗脱液:甲苯/庚烷=1/1(容量比))对残渣进行精制,在浓缩后加入乙酸乙酯,对所获得的结晶进行过滤后,利用甲醇进行清洗,由此获得化合物(I-W)(25.0g)。

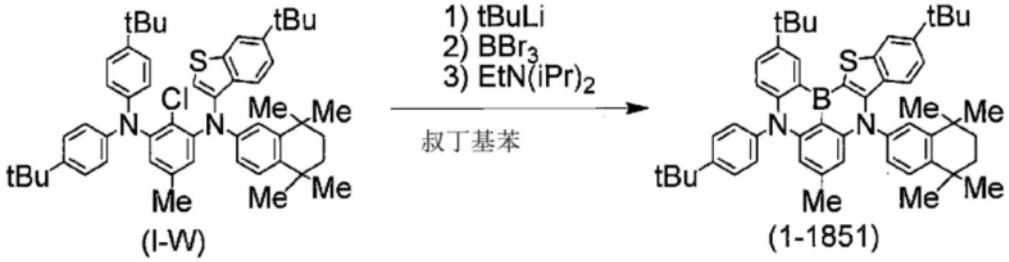
[1452] [化381]

[1453] 

[1454] 在氮气环境下,且在0℃下向放入有化合物(I-W)(25.0g)及叔丁基苯(160ml)的烧瓶中加入1.60M的叔丁基锂戊烷溶液(39.3ml)。滴加结束后,升温至60℃并搅拌0.5小时后,

将沸点低于叔丁基苯的成分减压馏去。冷却至-50℃并加入三溴化硼(15.7g),升温至室温并搅拌0.5小时。其后,再次冷却至0℃并加入N,N-二异丙基乙胺(8.1g),在室温下搅拌至发热结束后,升温至80℃并加热搅拌1小时。将反应液冷却至室温,依次加入利用冰浴进行了冷却的乙酸钠水溶液、乙酸乙酯并搅拌1小时,将有机层分离并进行水洗。在减压下将所述溶液浓缩,利用乙酸乙酯对残渣进行清洗后,利用硅胶管柱(洗脱液:甲苯/庚烷=2/8(容量比))进行精制。利用庚烷对所获得的粗产物进行清洗,由此获得化合物(1-1851)(7.5g)。

[1455] [化382]

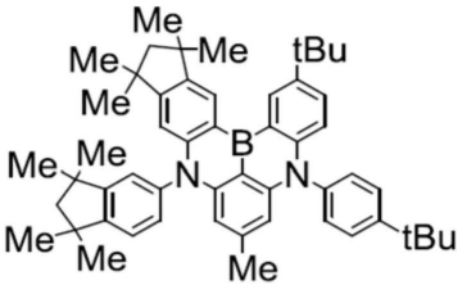
[1456] 

[1457] 通过NMR测定来确认所获得的化合物的结构。

[1458] ^{1}H-NMR($CDCl_3$):δ=1.23(s,3H),1.29(s,3H),1.36(s,9H),1.46(s,9H),1.49(s,6H),1.51(s,9H),1.82-1.89(m,4H),2.22(s,3H),5.80(d,1H),5.99(s,1H),6.24(s,1H),6.56(d,1H),6.92(d,1H),7.20(dd,1H),7.22-7.28(m,2H),7.44-7.47(m,2H),7.63(d,1H),7.68(d,2H),7.96(s,1H),8.78(d,1H).

[1459] 合成例(12):化合物(1-5121)的合成

[1460] [化383]

[1461] 

(1-5121)

[1462] 在氮气环境下,将化合物(I-X)(10.0g)、双(4-叔丁基苯基)胺(5.15g)、Pd-132(0.13g)、NaOtBu(2.6g)及二甲苯(40ml)放入至烧瓶中,在120℃下加热1小时。反应后,向反应液中加入水与乙酸乙酯并进行搅拌后,将有机层分离并进行水洗。其后,将有机层浓缩而获得粗产物。向粗产物中加入索尔米克斯(Solmix),对所析出的固体进行过滤分离,并利用甲醇对固体进行清洗。其后,利用硅胶短管柱(洗脱液:甲苯/庚烷=1/1(容积比))进行精制后,将溶媒浓缩,向所获得的粗产物中加入乙酸乙酯,对所析出的结晶进行过滤并利用甲醇来清洗结晶,由此获得化合物(I-Y)(8.5g)。

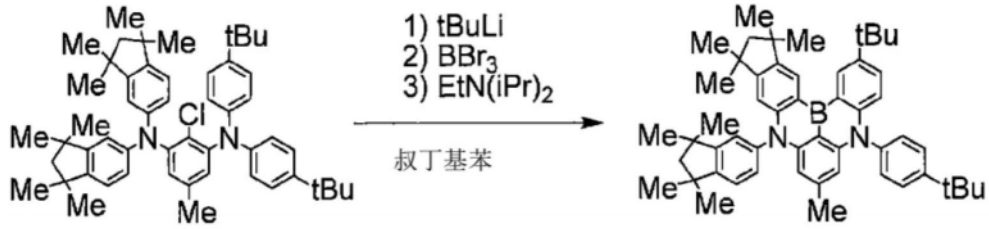
[1463] [化384]

[1464] 

(I-X) (I-Y)

[1465] 在氮气环境下,且在0℃下向放入有化合物(I-Y)(8.5g)及叔丁基苯(85ml)的烧瓶中加入1.60M的叔丁基锂戊烷溶液(13.9ml)。滴加结束后,升温至60℃并搅拌0.5小时后,将沸点低于叔丁基苯的成分减压馏去。冷却至-50℃并加入三溴化硼(5.6g),升温至室温并搅拌0.5小时。其后,再次冷却至0℃并加入N,N-二异丙基乙胺(2.9g),在室温下搅拌至发热结束后,升温至80℃并加热搅拌1小时。将反应液冷却至室温,依次加入利用冰浴进行了冷却的乙酸钠水溶液、乙酸乙酯并搅拌1小时。将有机层水洗2次后,将有机层浓缩而获得粗产物。在浓缩后添加索尔米克斯(Solmix),对所析出的固体进行过滤。其后,利用硅胶管柱(洗脱液:甲苯/庚烷=1/1(容量比))对粗体进行精制。反复进行向所获得的粗产物中加入索尔米克斯(Solmix),并对所获得的结晶进行过滤的步骤,由此获得化合物(1-5121)(3.0g)。

[1466] [化385]

[1467] 

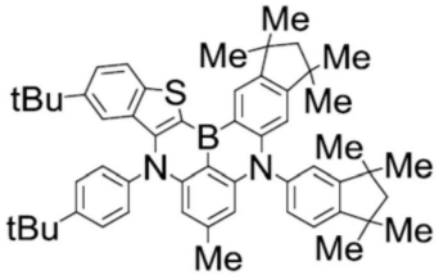
(I-Y) (1-5121)

[1468] 通过NMR测定来确认所获得的化合物的结构。

[1469] ^{1}H-NMR($CDCl_3$):δ=1.19(s,6H),1.32(s,6H),1.46(s,30H),1.97(s,2H),2.06(s,2H),2.18(s,3H),5.95(s,1H),6.05(s,1H),6.36(s,1H),6.66(d,1H),7.10(d,1H),7.18(dd,1H),7.27(d,2H),7.39(d,1H),7.48(d,1H),7.67(d,2H),8.67(s,1H),8.96(d,1H).

[1470] 合成例(13):化合物(1-2663)的合成

[1471] [化386]

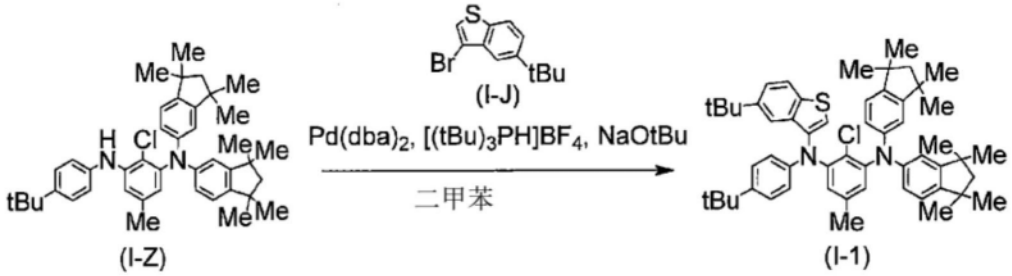
[1472] 

(1-2663)

[1473] 在氮气环境下,将化合物(I-Z)(20.0g)、化合物(I-J)(10.2g)、$Pd(dba)_2$(0.54g)、NaOtBu(4.6g)、$[(tBu)_3PH]BF_4$(0.55g)及二甲苯(60ml)放入至烧瓶中,在120℃下进行1小时加热回流。将反应液冷却至室温后,加入水与乙酸乙酯,将有机层分离并进行水洗。在减压

下将所述溶液浓缩,利用硅胶管柱(洗脱液:甲苯/庚烷=1/1(容量比))对残渣进行精制,在浓缩后加入索尔米克斯(Solmix),对所获得的结晶进行过滤后,利用甲醇进行清洗,由此获得化合物(I-1)(24.0g)。

[1474] [化387]

[1475] 

[1476] 在氮气环境下,且在0℃下向放入有化合物(I-1)(24.0g)及叔丁基苯(200ml)的烧瓶中加入1.60M的叔丁基锂戊烷溶液(36.5ml)。滴加结束后,升温至60℃并搅拌0.5小时后,将沸点低于叔丁基苯的成分减压馏去。冷却至-50℃并加入三溴化硼(14.6g),升温至室温并搅拌0.5小时。其后,再次冷却至0℃并加入N,N-二异丙基乙胺(7.6g),在室温下搅拌至发热结束后,升温至80℃并加热搅拌1小时。将反应液冷却至室温,依次加入利用冰浴进行了冷却的乙酸钠水溶液、乙酸乙酯并搅拌1小时,将有机层分离并进行水洗。在减压下将所述溶液浓缩,向残渣中加入庚烷,利用庚烷对所析出的固体进行清洗后,利用硅胶管柱(洗脱液:甲苯/庚烷=1/1(容量比))进行精制。向所获得的粗产物中加入庚烷,利用庚烷对所析出的固体进行清洗,反复进行所述操作而获得化合物(1-2663)(5.7g)。

[1477] [化388]

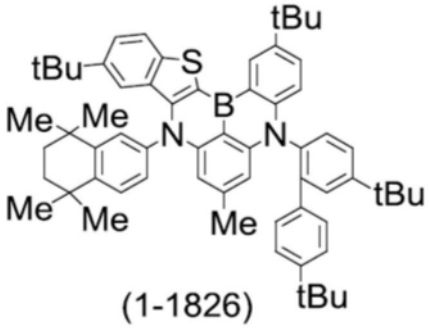
[1478] 

[1479] 通过NMR测定来确认所获得的化合物的结构。

[1480] ^{1}H-NMR($CDCl_3$):δ=1.09(s,9H),1.18(d,6H),1.32(d,6H),1.46(d,6H),1.50(s,9H),1.52(s,6H),1.96(s,2H),2.06(s,2H),2.21(s,3H),6.07(s,2H),6.25(s,1H),6.51(s,1H),7.08(d,1H),7.17(dd,1H),7.38-7.41(m,2H),7.47(d,2H),7.65(d,2H),7.88(d,1H),8.51(s,1H).

[1481] 合成例(14):化合物(1-1826)的合成

[1482] [化389]

[1483] 

[1484] 在氮气环境下,且在0℃下向放入有化合物(I-2)(55.5g)及叔丁基苯(450ml)的烧瓶中加入1.60M的叔丁基锂戊烷溶液(75.0ml)。滴加结束后,升温至60℃并搅拌0.5小时后,将沸点低于叔丁基苯的成分减压馏去。冷却至-50℃并加入三溴化硼(30.0g),升温至室温并搅拌0.5小时后,升温至80℃并加热搅拌1小时。将反应液冷却至室温,加入利用冰浴进行了冷却的乙酸钠水溶液及甲苯并进行搅拌后,将有机层分离并进行水洗。其后,将有机层浓缩,利用硅胶管柱(洗脱液:甲苯/庚烷=1/1(容量比))对残渣进行精制。依次利用丙酮及庚烷对所获得的粗产物进行清洗,由此获得化合物(1-1826)(6.60g)。

[1485] [化390]

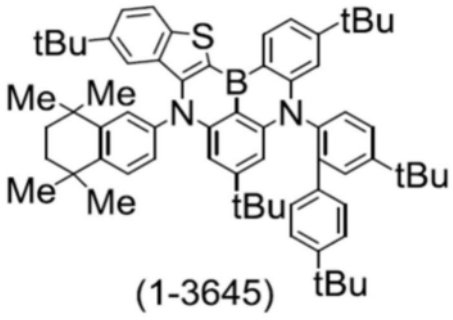
[1486] 

[1487] 通过NMR测定来确认所获得的化合物的结构。

[1488] ^{1}H-NMR($CDCl_3$):δ=1.09-1.16(m,18H),1.25-1.34(m,6H),1.42-1.50(m,24H),1.76-1.86(m,4H),2.19(s,3H),6.03-6.12(m,2H),6.57-6.66(m,2H),7.01-7.08(m,2H),7.12-7.25(m,4H),7.37-7.44(m,2H),7.48-7.54(m,1H),7.58(dd,1H),7.60-7.67(m,1H),7.67-7.71(m,1H),7.88(d,1H),8.68-8.72(m,1H).

[1489] 合成例(15):化合物(1-3645)的合成

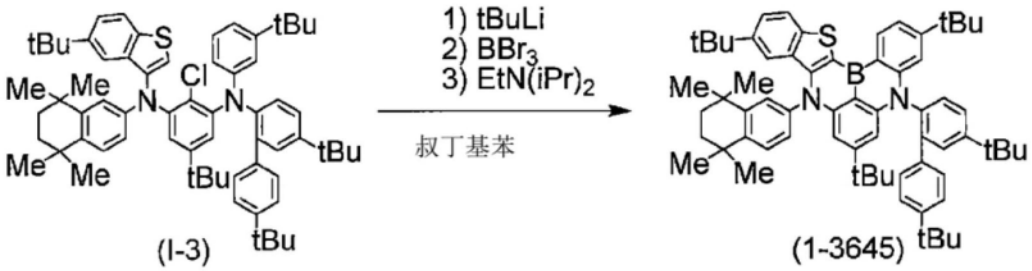
[1490] [化391]

[1491] 

[1492] 在氮气环境下,且在0℃下向放入有化合物(I-3)(58.5g)及叔丁基苯(300ml)的烧瓶中加入1.60M的叔丁基锂戊烷溶液(75.0ml)。滴加结束后,升温至60℃并搅拌0.5小时后,将沸点低于叔丁基苯的成分减压馏去。冷却至-50℃并加入三溴化硼(30.0g),升温至室温

并搅拌0.5小时。其后,再次冷却至0℃并加入N,N-二异丙基乙胺(15.6g),在室温下搅拌至发热结束后,升温至80℃并加热搅拌1小时。将反应液冷却至室温,加入利用冰浴进行了冷却的乙酸钠水溶液及甲苯并进行搅拌后,将有机层分离并进行水洗。其后,将有机层浓缩,利用硅胶管柱(洗脱液:甲苯/庚烷=1/1(容量比))对残渣进行精制。利用庚烷对所获得的粗产物进行清洗,由此获得化合物(1-3645)(10.2g)。

[1493] [化392]

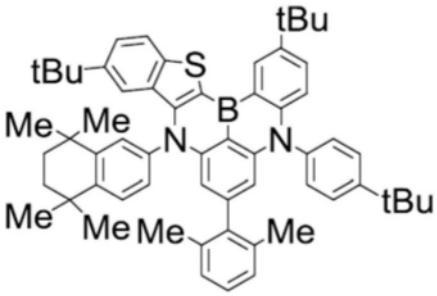
[1494] 

[1495] 通过NMR测定来确认所获得的化合物的结构。

[1496] ^{1}H-NMR($CDCl_3$):δ=0.98-1.02(m,9H),1.09-1.14(m,18H),1.20(s,9H),1.26-1.34(m,6H),1.39-1.50(m,15H),1.75-1.88(m,4H),6.13-6.35(m,2H),6.66-6.73(m,2H),7.00-7.07(m,2H),7.12-7.26(m,5H),7.39(dd,1H),7.48-7.79(m,3H),7.71(s,1H),7.86(d,1H),8.58(d,1H).

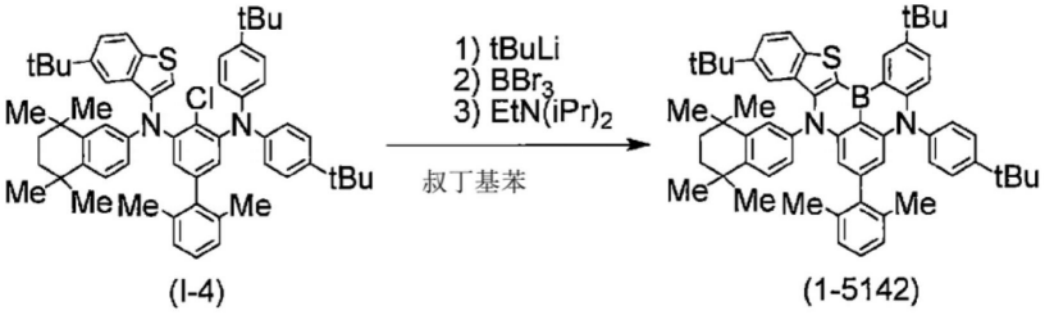
[1497] 合成例(16):化合物(1-5142)的合成

[1498] [化393]

[1499] 

[1500] 在氮气环境下,且在0℃下向放入有化合物(I-4)(51.0g)及叔丁基苯(610ml)的烧瓶中加入1.61M的叔丁基锂戊烷溶液(75.0ml)。滴加结束后,升温至60℃并搅拌0.5小时后,将沸点低于叔丁基苯的成分减压馏去。冷却至-50℃并加入三溴化硼(30.0g),升温至室温并搅拌0.5小时。其后,再次冷却至0℃并加入N,N-二异丙基乙胺(14.9g),在室温下搅拌至发热结束后,升温至80℃并加热搅拌1小时。将反应液冷却至室温,加入利用冰浴进行了冷却的乙酸钠水溶液及甲苯并进行搅拌后,将有机层分离并进行水洗。其后,将有机层浓缩,利用硅胶管柱(洗脱液:甲苯/庚烷=7/1(容量比))对残渣进行精制。利用庚烷对所获得的粗产物进行清洗,进而,通过自甲苯的再结晶而进行精制,由此获得化合物(1-5142)(6.51g)。

[1501] [化394]

[1502] 

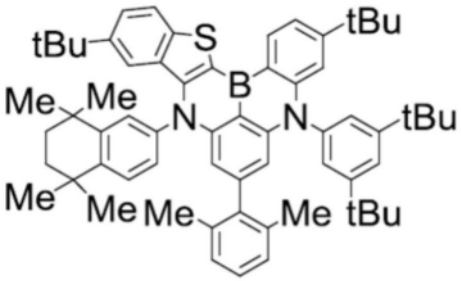
(I-4) (1-5142)

[1503] 通过NMR测定来确认所获得的化合物的结构。

[1504] ^{1}H-NMR($CDCl_3$):δ＝1.11(s,9H),1.18-1.24(m,6H),1.37-1.45(m,15H),1.51(s,9H),1.71-1.80(m,4H),1.94(s,6H),6.07(s,1H),6.11(s,1H),6.48-6.55(m,2H),6.97-7.09(m,3H),7.23(d,2H),7.30(dd,1H),7.39-7.43(m,2H),7.46(dd,1H),7.57-7.64(m,3H),7.91(d,1H),8.82(d,1H).

[1505] 合成例(17):化合物(1-5151)的合成

[1506] [化395]

[1507] 

(1-5151)

[1508] 在氮气环境下,且在0℃下向放入有化合物(I-5)(56.5g)及叔丁基苯(670ml)的烧瓶中加入1.61M的叔丁基锂戊烷溶液(75.0ml)。滴加结束后,升温至60℃并搅拌0.5小时后,将沸点低于叔丁基苯的成分减压馏去。冷却至-50℃并加入三溴化硼(30.0g),升温至室温并搅拌0.5小时。其后,再次冷却至0℃并加入N,N-二异丙基乙胺(15.5g),在室温下搅拌至发热结束后,升温至80℃并加热搅拌1小时。将反应液冷却至室温,加入利用冰浴进行了冷却的乙酸钠水溶液及甲苯并进行搅拌后,将有机层分离并进行水洗。其后,将有机层浓缩,利用硅胶管柱(洗脱液:甲苯/庚烷＝7/1(容量比))对残渣进行精制。依次利用丙酮及庚烷对所获得的粗产物进行清洗,由此获得化合物(1-5151)(6.34g)。

[1509] [化396]

[1510] 

(I-5) (1-5151)

[1511] 通过NMR测定来确认所获得的化合物的结构。

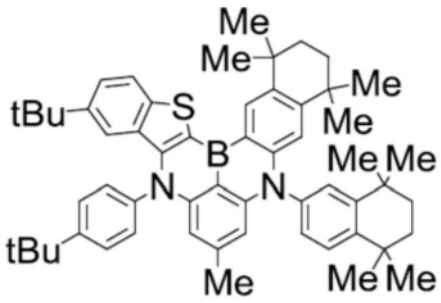
[1512] ^{1}H-NMR($CDCl_3$):δ＝1.11(s,9H),1.17-1.24(m,15H),1.32(s,18H),1.37-1.45(m,

6H),1.71-1.80(m,4H),1.97(s,6H),6.11(s,1H),6.14(s,1H),6.52(dd,2H),6.97-7.09(m,3H),7.18(d,2H),7.28-7.34(m,2H),7.38-7.43(m,2H),7.52(t,1H),7.60(d,1H),7.89(d,1H),8.72(d,1H).

[1513] 合成例(18):化合物(1-1803)的合成

[1514] [化397]

[1515]

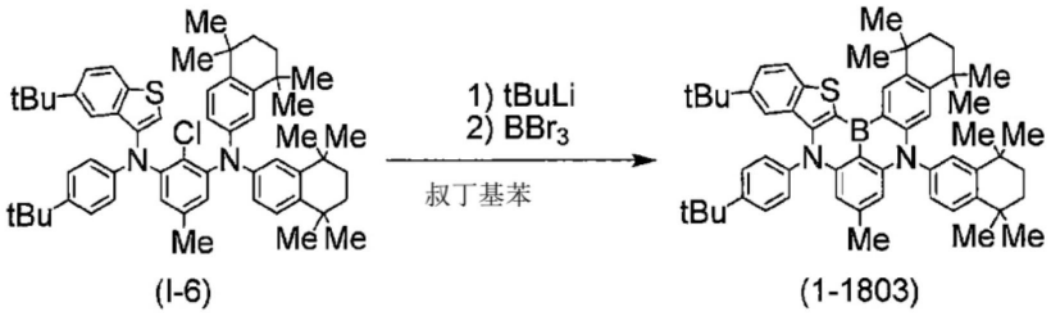


(1-1803)

[1516] 在氮气环境下,且在0℃下向放入有化合物(I-6)(86.6g)及叔丁基苯(520ml)的烧瓶中加入1.61M的叔丁基锂戊烷溶液(125ml)。滴加结束后,升温至60℃并搅拌0.5小时后,将沸点低于叔丁基苯的成分减压馏去。冷却至-50℃并加入三溴化硼(51.1g),升温至室温并搅拌2.5小时。加入利用冰浴进行了冷却的乙酸钠水溶液及甲苯并进行搅拌后,将有机层分离并进行水洗。其后,将有机层浓缩,利用硅胶管柱(洗脱液:甲苯/庚烷=1/1(容量比))对残渣进行精制。依次利用乙腈及庚烷对所获得的粗产物进行清洗,进而,通过自甲苯的再结晶而进行精制,由此获得化合物(1-1803)(10.2g)。

[1517] [化398]

[1518]



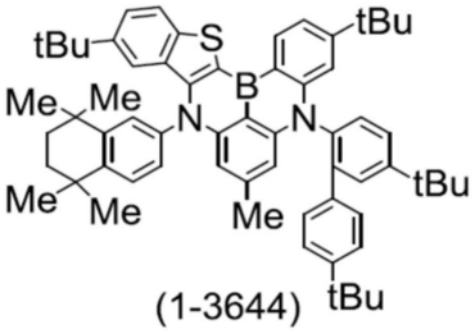
(I-6) (1-1803)

[1519] 通过NMR测定来确认所获得的化合物的结构。

[1520] ^{1}H-NMR($CDCl_3$):δ=1.04-1.10(m,15H),1.25(s,6H),1.38-1.45(m,6H),1.49(s,9H),1.53(s,6H),1.66-1.83(m,8H),2.20(s,3H),6.06(d,2H),6.41(s,1H),6.50(d,1H),7.07(dd,1H),7.26(d,1H),7.38(dd,1H),7.46(d,2H),7.59(d,1H),7.74(d,2H),7.88(d,1H),8.70(d,1H).

[1521] 合成例(19):化合物(1-3644)的合成

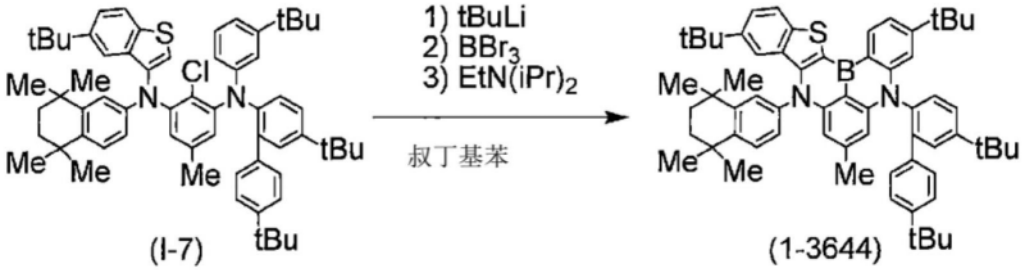
[1522] [化399]

[1523] 

(1-3644)

[1524] 在氮气环境下,且在0℃下向放入有化合物(I-7)(110g)及叔丁基苯(1000ml)的烧瓶中加入1.61M的叔丁基锂戊烷溶液(150ml)。滴加结束后,升温至60℃并搅拌0.5小时后,将沸点低于叔丁基苯的成分减压馏去。冷却至-50℃并加入三溴化硼(60.0g),升温至室温并搅拌0.5小时。其后,再次冷却至0℃并加入N,N-二异丙基乙胺(30.6g),在室温下搅拌至发热结束后,升温至80℃并加热搅拌1小时。将反应液冷却至室温,加入利用冰浴进行了冷却的乙酸钠水溶液及甲苯并进行搅拌后,将有机层分离并进行水洗。其后,将有机层浓缩,利用硅胶管柱(洗脱液:甲苯/庚烷=1/5(容量比))对残渣进行精制。依次利用乙腈、丙酮及庚烷对所获得的粗产物进行清洗,由此获得化合物(1-3644)(11.1g)。

[1525] [化400]

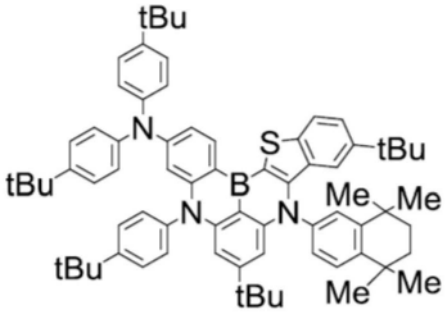
[1526] 

[1527] 通过NMR测定来确认所获得的化合物的结构。

[1528] ^{1}H-NMR($CDCl_3$):δ=1.10(s,9H),1.11-1.13(m,9H),1.16-1.18(m,9H),1.25-1.36(m,6H),1.43-1.47(m,6H),1.48(s,9H),1.77-1.87(m,4H),2.22(s,3H),6.07-6.11(m,1H),6.20(s,1H),6.54-6.62(m,2H),6.99-7.08(m,2H),7.15-7.30(m,5H),7.37(dd,1H),7.46-7.56(m,1H),7.58-7.68(m,2H),7.69-7.73(m,1H),7.85(d,1H),8.59-8.55(m,1H).

[1529] 合成例(20):化合物(1-3812)的合成

[1530] [化401]

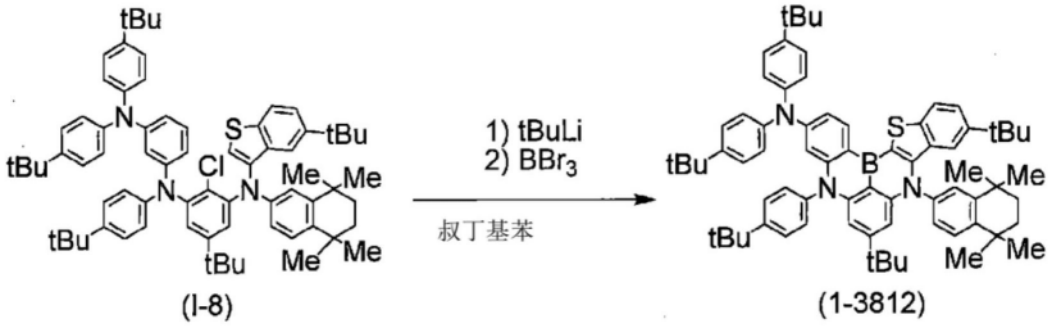
[1531] 

(1-3812)

[1532] 在氮气环境下,且在0℃下向放入有化合物(I-8)(21.2g)及叔丁基苯(170ml)的烧

瓶中加入1.61M的叔丁基锂戊烷溶液(25.0ml)。滴加结束后,升温至60℃并搅拌0.5小时后,将沸点低于叔丁基苯的成分减压馏去。冷却至-50℃并加入三溴化硼(10.0g),升温至室温并搅拌0.5小时。其后,升温至80℃并加热搅拌1小时。将反应液冷却至室温,加入利用冰浴进行了冷却的乙酸钠水溶液及甲苯并进行搅拌后,将有机层分离并进行水洗。其后,将有机层浓缩,利用硅胶管柱(洗脱液:甲苯)对所获得的粗产物进行精制,进而利用丙酮进行清洗,由此获得化合物(1-3812)(5.0g)。

[1533] [化402]

[1534] 

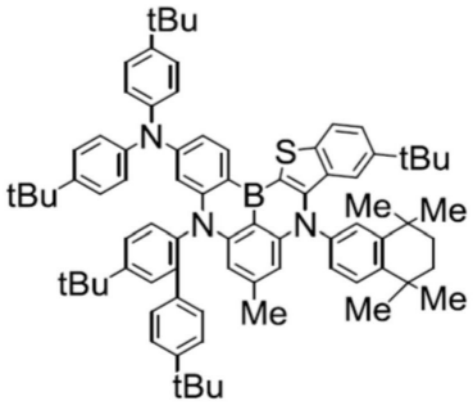
(I-8) (1-3812)

[1535] 通过NMR测定来确认所获得的化合物的结构。

[1536] ^{1}H-NMR($CDCl_3$):δ=0.97(s,9H),1.10(s,9H),1.27-1.34(m,33H),1.40-1.47(m,6H),1.75-1.90(m,4H),6.00-6.28(m,2H),6.36(s,1H),6.65-6.80(m,1H),6.80-6.96(m,1H),7.00(d,4H),7.14(d,2H),7.18-7.26(m,5H),7.38(d,1H),7.43-7.58(m,3H),7.65(d,1H),7.85(d,1H),8.53(s,1H).

[1537] 合成例(21):化合物(1-3847)的合成

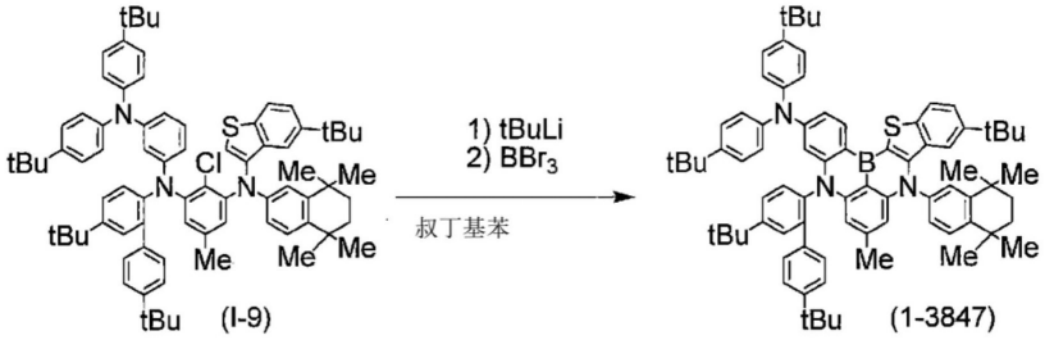
[1538] [化403]

[1539] 

(1-3847)

[1540] 在氮气环境下,且在0℃下向放入有化合物(I-9)(23.0g)及叔丁基苯(140ml)的烧瓶中加入1.61M的叔丁基锂戊烷溶液(25.0ml)。滴加结束后,升温至60℃并搅拌0.5小时后,将沸点低于叔丁基苯的成分减压馏去。冷却至-50℃并加入三溴化硼(10.0g),升温至室温并搅拌0.5小时。其后,升温至80℃并加热搅拌1小时。将反应液冷却至室温,加入利用冰浴进行了冷却的乙酸钠水溶液及甲苯并进行搅拌后,将有机层分离并进行水洗。其后,将有机层浓缩,利用硅胶管柱(洗脱液:甲苯/庚烷=1/3(容量比))对所获得的粗产物进行精制,进而利用丙酮进行清洗,由此获得化合物(1-3847)(2.5g)。

[1541] [化404]

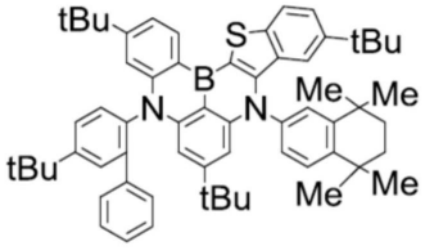
[1542] 

[1543] 通过NMR测定来确认所获得的化合物的结构。

[1544] ^{1}H-NMR($CDCl_3$):δ=1.10(s,9H),1.17-1.20(m,9H),1.25-1.38(m,33H),1.42-1.48(m,6H),1.76-1.88(m,4H),2.19(s,3H),6.02-6.16(m,3H),6.57-6.62(m,2H),6.86-6.96(m,7H),7.01-7.14(m,3H),7.20(d,4H),7.36(dd,1H),7.39-7.50(m,3H),7.60-7.67(m,1H),7.83(d,1H),8.47(d,1H).

[1545] 合成例(22):化合物(1-3842)的合成

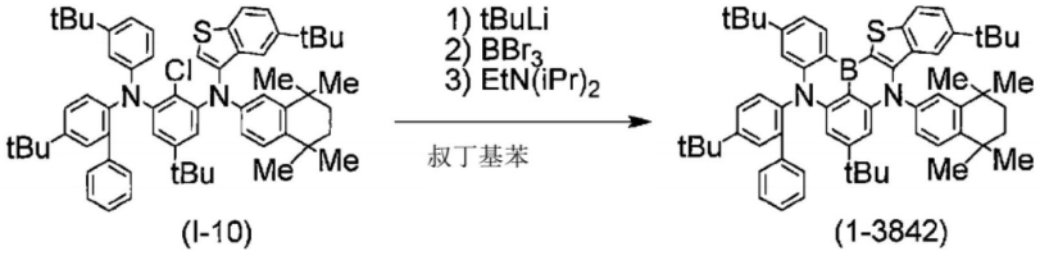
[1546] [化405]

[1547] 

(1-3842)

[1548] 在氮气环境下,且在0℃下向放入有化合物(I-10)(36.6g)及叔丁基苯(290ml)的烧瓶中加入1.61M的叔丁基锂戊烷溶液(50.0ml)。滴加结束后,升温至60℃并搅拌0.5小时后,将沸点低于叔丁基苯的成分减压馏去。冷却至-50℃并加入三溴化硼(20.0g),升温至室温并搅拌0.5小时。其后,再次冷却至0℃并加入N,N-二异丙基乙胺(30.6g),在室温下搅拌至发热结束后,升温至60℃并加热搅拌1小时。将反应液冷却至室温,加入利用冰浴进行了冷却的乙酸钠水溶液及甲苯并进行搅拌后,将有机层分离并进行水洗。其后,将有机层浓缩,利用庚烷对残渣进行清洗。利用硅胶管柱(洗脱液:甲苯)对所获得的粗产物进行精制,进而利用庚烷进行清洗,由此获得化合物(1-3842)(9.80g)。

[1549] [化406]

[1550] 

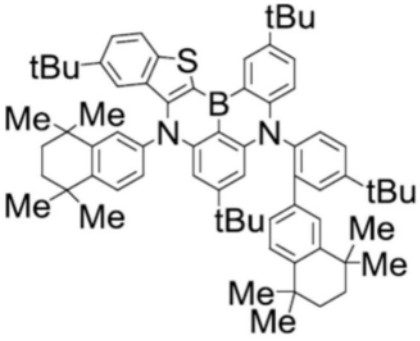
[1551] 通过NMR测定来确认所获得的化合物的结构。

[1552] ^{1}H-NMR($CDCl_3$):δ=0.99-1.02(m,9H),1.10(s,9H),1.21(s,9H),1.25-1.34(m,6H),1.38-1.47(m,6H),1.49(s,9H),1.75-1.88(m,4H),6.02-6.45(m,2H),6.62-6.78(m,

2H),6.96-7.50(m,3H),7.14-7.29(m,5H),7.38(dd,1H),7.47-7.73(m,4H),7.85(d,1H),8.58(d,1H).

[1553] 合成例(23):化合物(1-5179)的合成

[1554] [化407]

[1555] 

(1-5179)

[1556] 在氮气环境下,且在0℃下向放入有化合物(I-11)(63.0g)及叔丁基苯(440ml)的烧瓶中加入1.61M的叔丁基锂戊烷溶液(75.0ml)。滴加结束后,升温至60℃并搅拌0.5小时后,将沸点低于叔丁基苯的成分减压馏去。冷却至-50℃并加入三溴化硼(30.0g),升温至室温并搅拌1.5小时。加入利用冰浴进行了冷却的乙酸钠水溶液及甲苯并进行搅拌后,将有机层分离并进行水洗。其后,将有机层浓缩,利用硅胶管柱(洗脱液:甲苯/庚烷=1/2(容量比))对所获得的粗产物进行精制,进而通过自庚烷的再结晶而进行精制,由此获得化合物(1-5179)(16.0g)。

[1557] [化408]

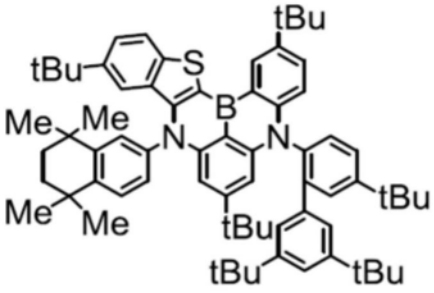
[1558] 

[1559] 通过NMR测定来确认所获得的化合物的结构。

[1560] ^{1}H-NMR($CDCl_3$):δ=0.53-0.60(m,6H),0.99(s,9H),1.04-1.09(m,6H),1.10(s,9H),1.29(s,6H),1.40-1.58(m,28H),1.86-1.76(m,4H),6.05-6.38(m,2H),6.72(d,2H),6.96-7.04(m,2H),7.06(d,1H),7.14-7.31(m,2H),7.36-7.55(m,3H),7.56-7.74(m,3H),7.88(d,1H),8.66(s,1H).

[1561] 合成例(24):化合物(1-5185)的合成

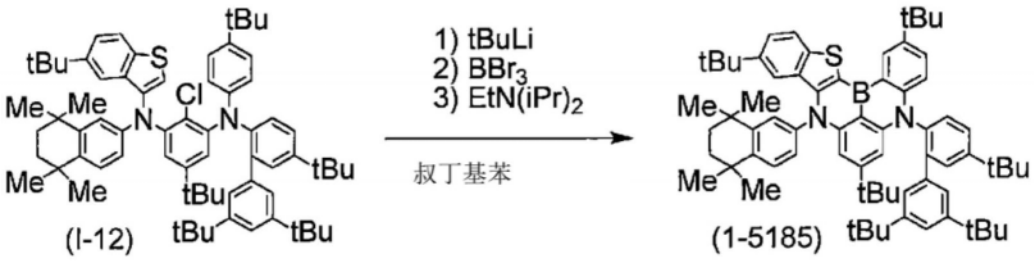
[1562] [化409]

[1563] 

(1-5185)

[1564] 在氮气环境下,且在0℃下向放入有化合物(I-12)(78.0g)及叔丁基苯(780ml)的烧瓶中加入1.61M的叔丁基锂戊烷溶液(100ml)。滴加结束后,升温至60℃并搅拌0.5小时后,将沸点低于叔丁基苯的成分减压馏去。冷却至-50℃并加入三溴化硼(40.0g),升温至室温并搅拌0.5小时。其后,再次冷却至0℃并加入N,N-二异丙基乙胺(19.7g),在室温下搅拌至发热结束后,升温至80℃并加热搅拌1小时。将反应液冷却至室温,加入利用冰浴进行了冷却的乙酸钠水溶液及甲苯并进行搅拌后,将有机层分离并进行水洗。其后,将有机层浓缩,依次利用乙酸乙酯及庚烷对残渣进行清洗。利用硅胶管柱(洗脱液:甲苯)对所获得的粗产物进行精制,进而通过自甲苯的再结晶而进行清洗,由此获得化合物(1-5185)(13.8g)。

[1565] [化410]

[1566] 

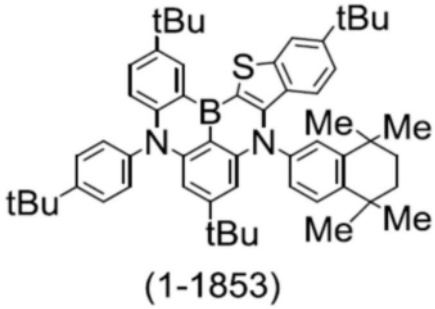
(I-12) (1-5185)

[1567] 通过NMR测定来确认所获得的化合物的结构。

[1568] ^{1}H-NMR($CDCl_3$):δ=0.86-0.90(m,18H),1.02(s,9H),1.10(s,9H),1.27-1.30(m,6H),1.40-1.50(m,24H),1.76-1.86(m,4H),6.02-6.38(m,2H),6.55-6.80(m,2H),6.84-90(m,2H),6.93-6.96(m,2H),7.08-7.24(m,1H),7.30-7.54(m,4H),7.58-7.73(m,2H),7.86(d,1H),8.61(s,1H).

[1569] 合成例(25):化合物(1-1853)的合成

[1570] [化411]

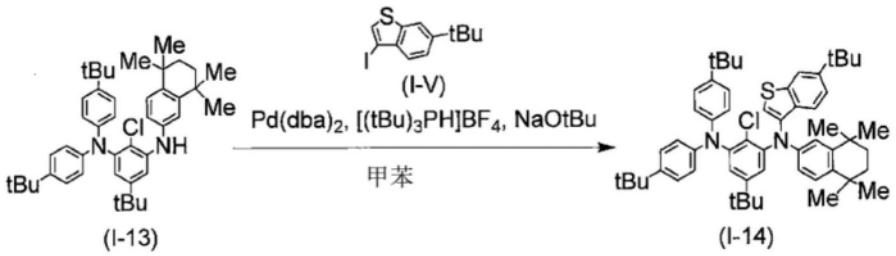
[1571] 

(1-1853)

[1572] 在氮气环境下,将化合物(I-13)(20.0g)、化合物(I-V)(12.0g)、$Pd(dba)_2$(0.53g)、NaOtBu(4.4g)、$[(tBu)_3PH]BF_4$(0.54g)及二甲苯(60ml)放入至烧瓶中,在120℃下

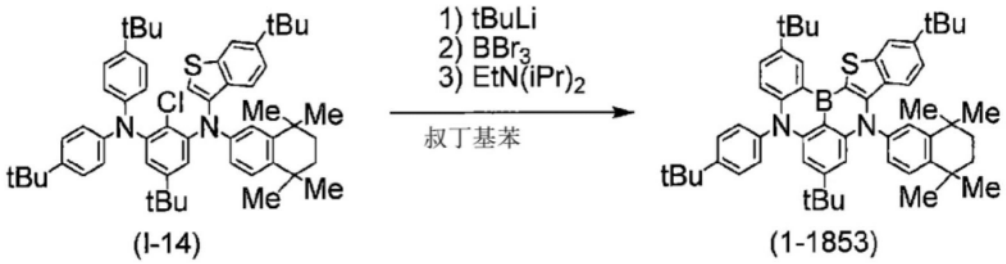
进行0.5小时加热回流。将反应液冷却至室温后,加入水与乙酸乙酯,将有机层分离并进行水洗。在减压下将所述溶液浓缩,利用硅胶管柱(洗脱液:甲苯/庚烷=1/1(容量比))对残渣进行精制,在浓缩后加入庚烷,对所获得的结晶进行过滤后,利用庚烷进行清洗,由此获得化合物(I-14)(30.0g)。

[1573] [化412]

[1574] 

[1575] 在氮气环境下,且在0℃下向放入有化合物(I-14)(30.0g)及叔丁基苯(180ml)的烧瓶中加入1.60M的叔丁基锂戊烷溶液(44.8ml)。滴加结束后,升温至60℃并搅拌0.5小时后,将沸点低于叔丁基苯的成分减压馏去。冷却至-50℃并加入三溴化硼(17.9g),升温至室温并搅拌0.5小时。其后,再次冷却至0℃并加入N,N-二异丙基乙胺(9.3g),在室温下搅拌至发热结束后,升温至80℃并加热搅拌1小时。将反应液冷却至室温,依次加入利用冰浴进行了冷却的乙酸钠水溶液、乙酸乙酯并搅拌1小时,将有机层分离并进行水洗。在减压下将所述溶液浓缩,利用庚烷对残渣进行清洗后,利用硅胶管柱(洗脱液:甲苯/庚烷=1/1(容量比))进行精制。利用庚烷对所获得的粗产物进行清洗,由此获得化合物(1-1853)(4.7g)。

[1576] [化413]

[1577] 

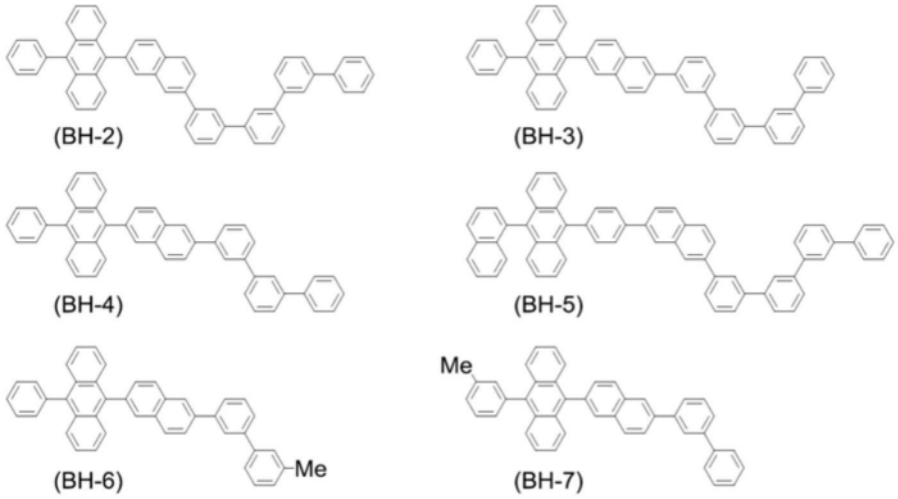
[1578] 通过NMR测定来确认所获得的化合物的结构。

[1579] ^{1}H-NMR($CDCl_3$):δ=1.01(s,9H),1.27(s,3H),1.29(s,3H),1.36(s,9H),1.45(s,3H),1.46(s,9H),1.49(s,3H),1.51(s,9H),1.81-1.89(m,4H),6.05(d,1H),6.14(br,1H),6.36(br,1H),6.64(br,1H),6.96(dd,1H),7.19(dd,1H),7.28(d,2H),7.46(dd,1H),7.49(d,1H),7.63(d,1H),7.68(d,2H),7.97(d,1H),8.76(s,1H).

[1580] 通过适当变更原料的化合物,可利用依据所述合成例的方法来合成本发明的其他多环芳香族化合物。

[1581] 化合物(BH-2)是依据日本专利特开2016-88927号公报的合成例1中所记载的方法来合成。另外,使用相同的方法来合成下述式(BH-3)至式(BH-7)所表示的化合物。

[1582] [化414]

[1583] 

[1584] 继而,为了更详细地说明本发明而示出使用了本发明的化合物的有机EL元件的实施例,但本发明并不限定于这些实施例。

[1585] <蒸镀型有机EL元件的评价>

[1586] 制作实施例1-1～实施例1-13的有机EL元件,测定作为1000cd/m^2发光时的特性的电压(V)、发光波长(nm)、外部量子效率(%),继而测定以下时间:以10mA/cm^2的电流密度进行恒定电流驱动时保持初期亮度的90%以上的亮度的时间。

[1587] 发光元件的量子效率有内部量子效率与外部量子效率,内部量子效率表示作为电子(或空穴)注入至发光元件的发光层的外部能量纯粹地转换为光子的比例。另一方面,外部量子效率是基于所述光子释放至发光元件的外部的量而算出,发光层中所产生的光子的一部分由发光元件的内部吸收或者持续反射而不释放至发光元件的外部,因此外部量子效率低于内部量子效率。

[1588] 外部量子效率的测定方法如下所述。使用爱德万测试(Advantest)公司制造的电压/电流产生器R6144,施加元件的亮度达到1000cd/m^2的电压而使元件发光。使用拓普康(TOPCON)公司制造的分光放射亮度计SR-3AR,自相对于发光面垂直的方向测定可见光区域的分光放射亮度。假定发光面为完全扩散面,将所测定的各波长成分的分光放射亮度的值除以波长能量并乘以π所获得的数值为各波长下的光子数。继而,在所观测的全波长区域累计光子数,并设为自元件释放的总光子数。将施加电流值除以元电荷(elementary charge)所获得的数值设为注入至元件的载流子(carrier)数,并且将自元件释放的总光子数除以注入至元件的载流子数所获得的数值为外部量子效率。

[1589] <实施例1-1～实施例1-13>

[1590] 将实施例1-1～实施例1-13的有机EL元件的各层的材料结构示于下述表1A中。

[1591] [表1A]

[1592]

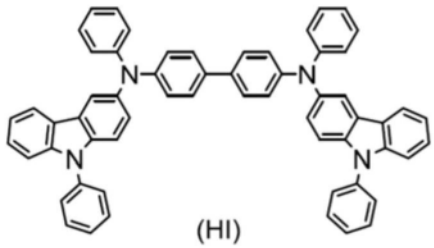
	空穴注入层 1 40 nm	空穴注入层 2 5 nm	空穴传输层 1 45 nm	空穴传输层 2 10 nm	发光层 25 nm		电子传输层 1 5 nm	电子传输层 2 25 nm	阴极 1 nm/100 nm
					主体	掺杂剂			
实施例 1-1	HI	HAT-CN	HT-1	HT-2	BH-1	化合物（1-411）	ET-1	ET-2+Liq	LiF/Al
实施例 1-2	HI	HAT-CN	HT-1	HT-2	BH-1	化合物（1-590）	ET-1	ET-2+Liq	LiF/Al
实施例 1-3	HI	HAT-CN	HT-1	HT-2	BH-1	化合物（1-1301）	ET-1	ET-2+Liq	LiF/Al
实施例 1-4	HI	HAT-CN	HT-1	HT-2	BH-1	化合物（1-1823）	ET-1	ET-2+Liq	LiF/Al
实施例 1-5	HI	HAT-CN	HT-1	HT-2	化合物（3-44）	化合物（1-1821）	ET-1	ET-2+Liq	LiF/Al
实施例 1-6	HI	HAT-CN	HT-1	HT-2	化合物（3-44）	化合物（1-1826）	ET-1	ET-2+Liq	LiF/Al
实施例 1-7	HI	HAT-CN	HT-1	HT-2	化合物（3-44）	化合物（1-3645）	ET-1	ET-2+Liq	LiF/Al
实施例 1-8	HI	HAT-CN	HT-1	HT-2	化合物（3-44）	化合物（1-1851）	ET-1	ET-2+Liq	LiF/Al
实施例 1-9	HI	HAT-CN	HT-1	HT-2	BH-1	化合物（1-1853）	ET-1	ET-2+Liq	LiF/Al
实施例 1-10	HI	HAT-CN	HT-1	HT-2	BH-1	化合物（1-3644）	ET-1	ET-2+Liq	LiF/Al
实施例 1-11	HI	HAT-CN	HT-1	HT-2	BH-1	化合物（1-3812）	ET-1	ET-2+Liq	LiF/Al
实施例 1-12	HI	HAT-CN	HT-1	HT-2	化合物（3-44）	化合物（1-3604）	ET-1	ET-2+Liq	LiF/Al
实施例 1-13	HI	HAT-CN	HT-1	HT-2	BH-1	化合物（1-3842）	ET-1	ET-2+Liq	LiF/Al

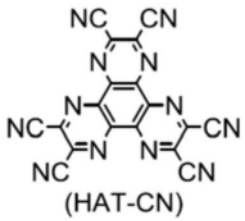
[1593] 表1A中，“HI”为N^4,N^4'-二苯基-N^4,N^4'-双(9-苯基-9H-咔唑-3-基)-[1,1'-联苯基]-4,4'-二胺，“HAT-CN”为1,4,5,8,9,12-六氮杂三亚苯六碳腈，“HT-1”为N-([1,1'-联

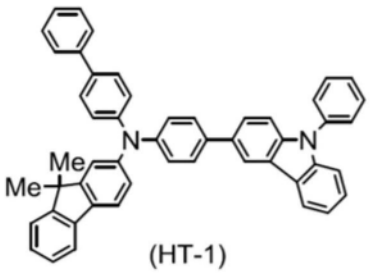
苯]-4-基-9,9-二甲基-N-4-(9-苯基-9H-咔唑-3-基)苯基)-9H-芴-2-胺[1,1'-联苯基]-4-胺,“HT-2”为N,N-双(4-(二苯并[b,d]呋喃-4-基)苯基)-[1,1':4',1"-联三苯基]-4-胺,“BH-1”为2-(10-苯基蒽-9-基)萘并[2,3-b]苯并呋喃,“ET-1”为4,6,8,10-四苯基[1,4]苯并氧杂硼杂环己烯并[2,3,4-kl]苯氧硼杂环己烯,“ET-2”为3,3'-((2-苯基蒽-9,10-二基)双(4,1-亚苯基))双(4-甲基吡啶)。以下与“Liq”一同示出化学结构。

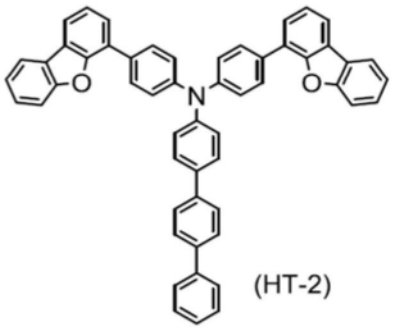
[1594] [化415]

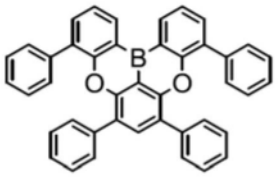
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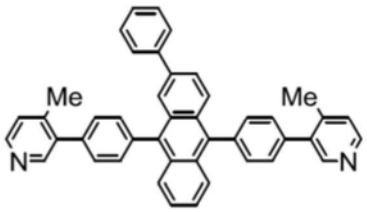


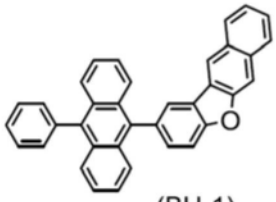


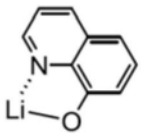












[1596] <实施例1-1>

[1597] 以将通过溅射来成膜为180nm厚度的ITO研磨至150nm的26mm×28mm×0.7mm的玻璃基板(光科学(Opto Science)(股)制造)作为透明支撑基板。将所述透明支撑基板固定于市售的蒸镀装置(昭和真空(股)制造)的基板固定器上,并安装分别放入有HI、HAT-CN、HT-1、HT-2、BH-1、化合物(1-411)、ET-1及ET-2的钼制蒸镀用舟皿、分别放入有Liq、LiF及铝的氮化铝制蒸镀用舟皿。

[1598] 在透明支撑基板的ITO膜上依次形成下述各层。将真空槽减压至5×10^{-4}Pa为止,首先,对HI进行加热且以使膜厚成为40nm的方式进行蒸镀,继而,对HAT-CN进行加热且以使膜厚成为5nm的方式进行蒸镀,继而,对HT-1进行加热且以使膜厚成为45nm的方式进行蒸镀,继而,对HT-2进行加热且以使膜厚成为10nm的方式进行蒸镀,从而形成包含四层的空穴层。

继而,对BH-1与化合物(1-411)同时进行加热且以使膜厚成为25nm的方式进行蒸镀来形成发光层。以使BH-1与化合物(1-411)的重量比大致成为98对2的方式调节蒸镀速度。进而,对ET-1进行加热且以使膜厚成为5nm的方式进行蒸镀,继而,对ET-2与Liq同时进行加热且以使膜厚成为25nm的方式进行蒸镀,从而形成包含两层的电子层。以使ET-2与Liq的重量比大致成为50对50的方式调节蒸镀速度。各层的蒸镀速度为0.01nm/sec～1nm/sec。其后,对LiF进行加热且以使膜厚成为1nm的方式以0.01nm/sec～0.1nm/sec的蒸镀速度进行蒸镀,继而,对铝进行加热且以使膜厚成为100nm的方式进行蒸镀来形成阴极,从而获得有机EL元件。

[1599] 将ITO电极作为阳极、LiF/铝电极作为阴极来施加直流电压,测定1000cd/m^2发光时的特性(发光波长、驱动电压及外部量子效率),另外,测定保持初期亮度的90％以上的亮度的时间。

[1600] ＜实施例1-2～实施例1-4＞

[1601] 与实施例1-1同样地制作有机EL元件,并评价EL特性。

[1602] ＜实施例1-5～实施例1-13＞

[1603] 与实施例1-1同样地制作有机EL元件,并评价EL特性。

[1604] 将实施例1-1～实施例1-13中所确认到的EL特性示于下述表1B中。

[1605] [表1B]

[1606]

	波长 (nm)	驱动电压 (V)	外部量子效率 (%)
实施例 1-1	466 (蓝色发光)	3.77	8.57
实施例 1-2	463 (蓝色发光)	3.72	7.93
实施例 1-3	465 (蓝色发光)	3.71	8.09
实施例 1-4	463 (蓝色发光)	3.57	8.05
实施例 1-5	459 (蓝色发光)	3.93	7.33
实施例 1-6	459 (蓝色发光)	3.94	7.61
实施例 1-7	457 (蓝色发光)	3.88	7.36
实施例 1-8	456 (蓝色发光)	3.99	7.44
实施例 1-9	460 (蓝色发光)	3.89	7.23
实施例 1-10	456 (蓝色发光)	3.71	8.07
实施例 1-11	458 (蓝色发光)	3.60	8.59
实施例 1-12	464 (蓝色发光)	3.55	8.26
实施例 1-13	456 (蓝色发光)	3.92	7.60

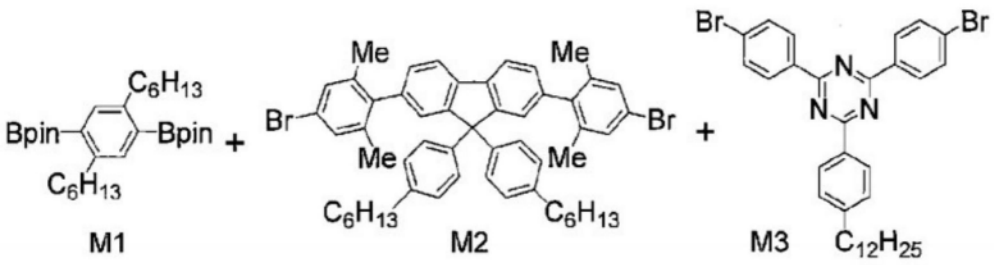
[1607] ＜涂布型有机EL元件的评价＞

[1608] 继而,对涂布形成有机层而获得的有机EL元件进行说明。

[1609] ＜高分子主体化合物:SPH-101的合成＞

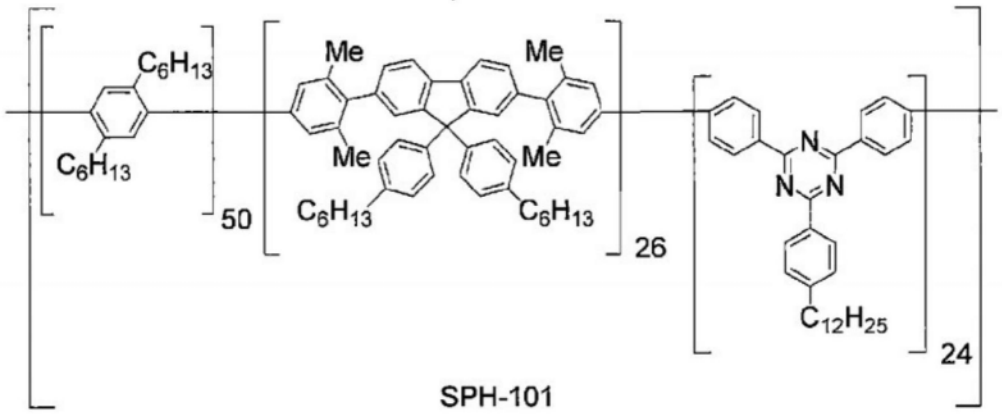
[1610] 依据国际公开第2015/008851号中记载的方法来合成SPH-101。获得在M1的相邻处键结有M2或M3的共聚物,根据投入比推测各单元为50:26:24(摩尔比)。

[1611] [化416]



聚合作用

[1612]

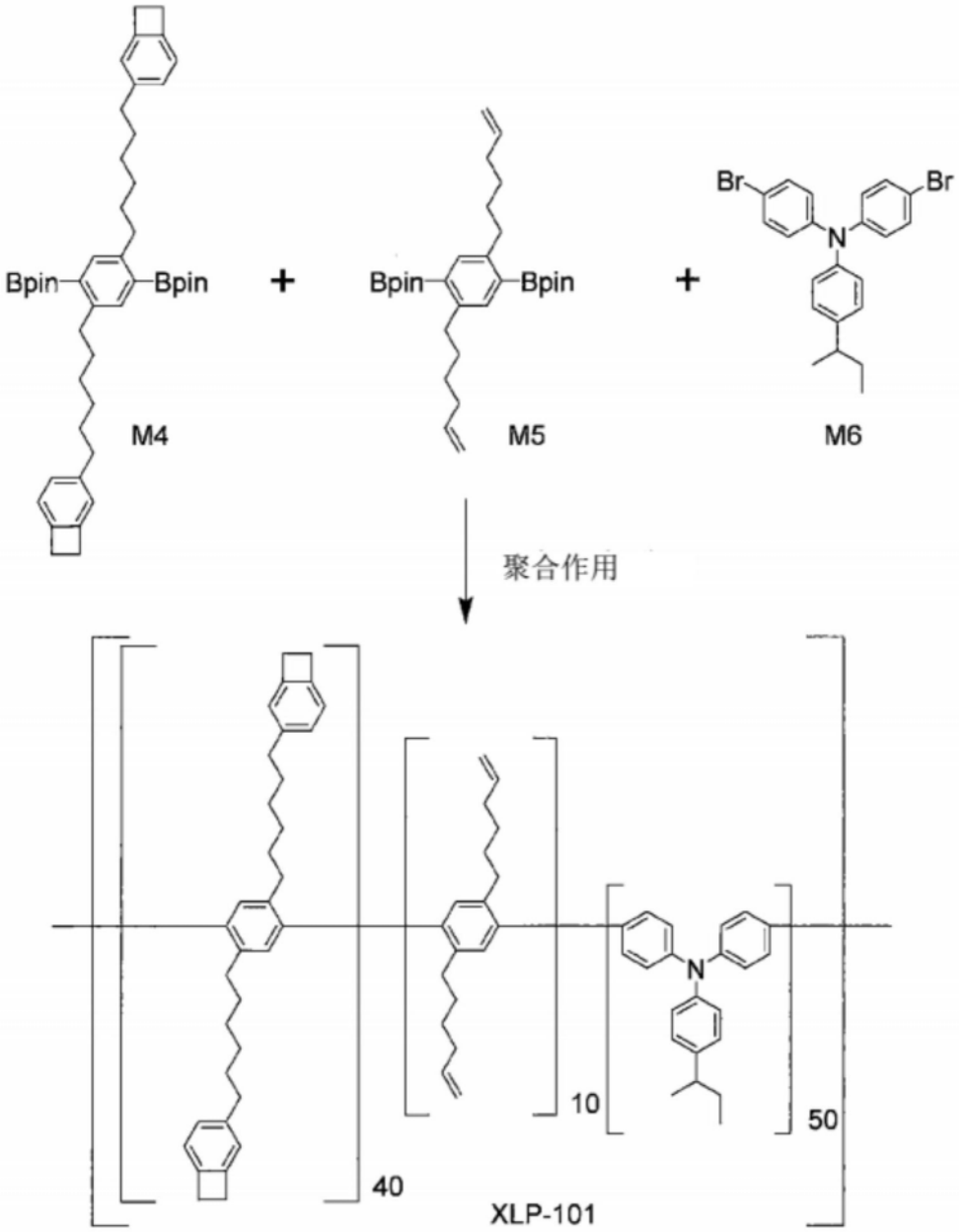


[1613] ＜高分子空穴传输化合物:XLP-101的合成＞

[1614] 依据日本专利特开2018-61028号公报中记载的方法来合成XLP-101。获得在M4的相邻处键结有M5或M6的共聚物,根据投入比推测各单元为40:10:50(摩尔比)。

[1615] [化417]

[1616]



[1617] ＜实施例2～实施例10＞

[1618] 对形成各层的材料的涂布用溶液进行制备,并制作涂布型有机EL元件。

[1619] ＜实施例2～实施例4的有机EL元件的制作＞

[1620] 将有机EL元件中的各层的材料结构示于表2中。

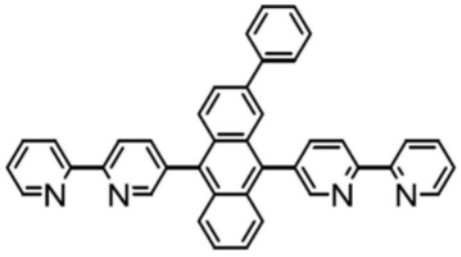
[1621] [表2]

[1622]

	空穴注入层（40 nm）	空穴传输层（30 nm）	发光层（20 nm）		电子传输层（30 nm）	阴极（1 nm/100 nm）
			主体	掺杂剂		
实施例 2	PEDOT：PSS	OTPD	SPH-101	（A）	ET1	LiF/Al
实施例 3	PEDOT：PSS	XLP-101	SPH-101	（A）	ET1	LiF/Al
实施例 4	PEDOT：PSS	PCz	SPH-101	（A）	ET1	LiF/Al

[1623] 以下示出表2中的“ET1”的结构。

[1624] [化418]

[1625] 

ET1

[1626] ＜发光层形成用组合物(1)的制备＞

[1627] 通过将下述成分搅拌至成为均匀的溶液为止,从而制备发光层形成用组合物(1)。将所制备的发光层形成用组合物旋涂于玻璃基板,且在减压下进行加热干燥,由此获得不存在膜缺陷、平滑性优异的涂布膜。

[1628]

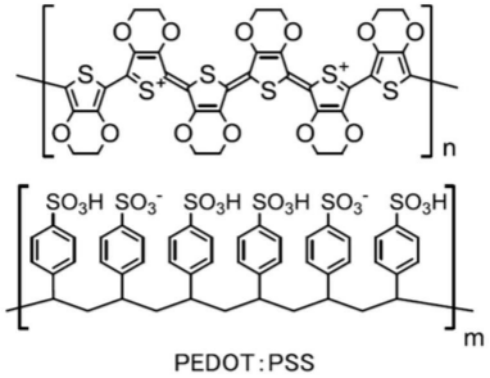
化合物（A）	0.04 重量%
SPH-101	1.96 重量%
二甲苯	69.00 重量%
十氢萘	29.00 重量%

[1629] 再者,化合物(A)为使通式(1)所表示的多环芳香族化合物、其多聚体、所述多环芳香族化合物或其多聚体作为单体(即,所述单体具有反应性取代基)加以高分子化而成的高分子化合物、或者使所述高分子化合物进一步交联而成的高分子交联体。用以获得高分子交联体的高分子化合物具有交联性取代基。

[1630] ＜PEDOT:PSS溶液＞

[1631] 使用市售的PEDOT:PSS溶液(克莱沃斯(Clevios)(TM)P VP AI4083、PEDOT:PSS的水分散液、贺利氏控股(Heraeus Holdings)公司制造)。

[1632] [化419]

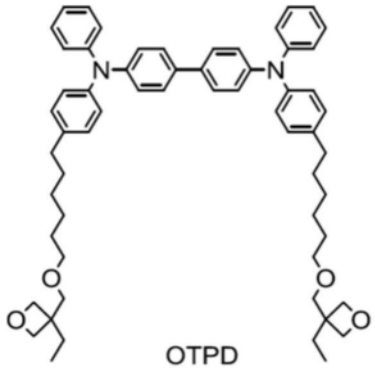
[1633] 

PEDOT:PSS

[1634] ＜OTPD溶液的制备＞

[1635] 使OTPD(LT-N159、发光技术公司(Luminescence Technology Corp)制造)及IK-2(光阳离子聚合引发剂、桑亚普罗(Sanapro)公司制造)溶解于甲苯中,从而制备OTPD浓度为0.7重量%、IK-2浓度为0.007重量%的OTPD溶液。

[1636] [化420]

[1637] 

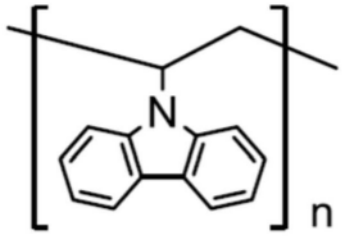
[1638] ＜XLP-101溶液的制备＞

[1639] 使XLP-101以0.6重量％的浓度溶解于二甲苯中,从而制备0.7重量％的XLP-101溶液。

[1640] ＜PCz溶液的制备＞

[1641] 使PCz(聚乙烯咔唑)溶解于二氯苯中,从而制备0.7重量％的PCz溶液。

[1642] [化421]

[1643] 

PCz

[1644] ＜实施例2＞

[1645] 在蒸镀有厚度为150nm的ITO的玻璃基板上旋涂PEDOT:PSS溶液,在200℃的热板上煅烧1小时,由此制成膜厚40nm的PEDOT:PSS膜(空穴注入层)。继而,旋涂OTPD溶液,在80℃的热板上干燥10分钟后,利用曝光机以曝光强度100mJ/cm^2进行曝光,在100℃的热板上煅烧1小时,由此制成不溶于溶液的膜厚30nm的OTPD膜(空穴传输层)。继而,旋涂发光层形成用组合物(1),在120℃的热板上煅烧1小时,由此制成膜厚20nm的发光层。

[1646] 将所制作的多层膜固定于市售的蒸镀装置(昭和真空(股)制造)的基板固定器上,安装放入有ET1的钼制蒸镀用舟皿、放入有LiF的钼制蒸镀用舟皿、放入有铝的钨制蒸镀用舟皿。将真空槽减压至5×10^{-4}Pa为止,然后,对ET1进行加热且以使膜厚成为30nm的方式进行蒸镀,从而形成电子传输层。将形成电子传输层时的蒸镀速度设为1nm/sec。其后,对LiF进行加热且以使膜厚成为1nm的方式以0.01nm/sec～0.1nm/sec的蒸镀速度进行蒸镀。继而,对铝进行加热且以使膜厚成为100nm的方式进行蒸镀而形成阴极。以所述方式获得有机EL元件。

[1647] ＜实施例3＞

[1648] 利用与实施例2相同的方法来获得有机EL元件。再者,关于空穴传输层,旋涂XLP-101溶液,在200℃的热板上煅烧1小时,由此制成膜厚30nm的膜。

[1649] ＜实施例4＞

[1650] 利用与实施例2相同的方法来获得有机EL元件。再者,关于空穴传输层,旋涂PCz溶

液,在120℃的热板上煅烧1小时,由此制成膜厚30nm的膜。

[1651] ＜实施例5～实施例7的有机EL元件的制作＞

[1652] 将有机EL元件中的各层的材料结构示于表3中。

[1653] [表3]

[1654]

	空穴注入层（50 nm）	空穴传输层（20 nm）	发光层（20 nm）		电子传输层（30 nm）	阴极（1 nm/100 nm）
			主体	掺杂剂		
实施例 5	ND-3202	XLP-101	mCBP	（A）	TSPO1	LiF/Al
实施例 6	ND-3202	XLP-101	SPH-101	（A）	TSPO1	LiF/Al
实施例 7	ND-3202	XLP-101	DOBNA	（A）	TSPO1	LiF/Al

[1655] ＜发光层形成用组合物(2)～发光层形成用组合物(4)的制备＞

[1656] 通过将下述成分搅拌至成为均匀的溶液为止,从而制备发光层形成用组合物(2)。

[1657] 化合物(A) 0.02重量%

[1658] mCBP 1.98重量%

[1659] 甲苯 98.00重量%

[1660] 通过将下述成分搅拌至成为均匀的溶液为止,从而制备发光层形成用组合物(3)。

[1661] 化合物(A) 0.02重量%

[1662] SPH-101 1.98重量%

[1663] 二甲苯 98.00重量%

[1664] 通过将下述成分搅拌至成为均匀的溶液为止,从而制备发光层形成用组合物(4)。

[1665] 化合物(A) 0.02重量%

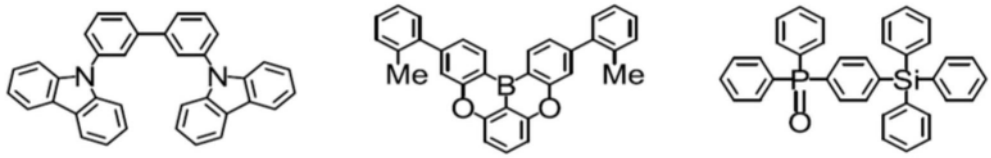
[1666] DOBNA 1.98重量%

[1667] 甲苯 98.00重量%

[1668] 表3中,“mCBP”为3,3'-双(N-咔唑基)-1,1'-联苯,“DOBNA”为3,11-二邻甲苯基-5,9-二氧杂-13b-硼杂萘并[3,2,1-de]蒽,“TSPO1”为二苯基[4-(三苯基硅烷基)苯基]氧化膦。以下示出化学结构。

[1669] [化422]

[1670]



mCBP DOBNA TSPO1

[1671] ＜实施例5＞

[1672] 在成膜有厚度为45nm的ITO的玻璃基板上旋涂ND-3202(日产化学工业制造)溶液后,在大气环境下以50℃加热3分钟,进而以230℃加热15分钟,由此制成膜厚50nm的ND-3202膜(空穴注入层)。继而,旋涂XLP-101溶液,在氮气环境下,在热板上以200℃加热30分钟,由此制成膜厚20nm的XLP-101膜(空穴传输层)。继而,旋涂发光层形成用组合物(2),在氮气环境下,以130℃加热10分钟,由此制成20nm的发光层。

[1673] 将所制作的多层膜固定于市售的蒸镀装置(昭和真空(股)制造)的基板固定器上,安装放入有TSPO1的钼制蒸镀用舟皿、放入有LiF的钼制蒸镀用舟皿、放入有铝的钨制蒸镀

用舟皿。将真空槽减压至5×10^{-4}Pa为止,然后,对TSPO1进行加热且以使膜厚成为30nm的方式进行蒸镀,从而形成电子传输层。将形成电子传输层时的蒸镀速度设为1nm/sec。其后,对LiF进行加热且以使膜厚成为1nm的方式以0.01nm/sec～0.1nm/sec的蒸镀速度进行蒸镀。继而,对铝进行加热且以使膜厚成为100nm的方式进行蒸镀而形成阴极。以所述方式获得有机EL元件。

[1674] ＜实施例6及实施例7＞

[1675] 使用发光层形成用组合物(3)或发光层形成用组合物(4)并利用与实施例5相同的方法来获得有机EL元件。

[1676] ＜实施例8～实施例10的有机EL元件的制作＞

[1677] 将有机EL元件中的各层的材料结构示于表4中。

[1678] [表4]

[1679]

	空穴注入层 50 nm	空穴传输层 20 nm	发光层 20 nm			电子传输层 30 nm	阴极 1 nm/100 nm
			主体	辅助掺杂剂	掺杂剂		
实施例 8	ND-3202	XLP-101	mCBP	2PXZ-TAZ	（A）	TSPO1	LiF/Al
实施例 9	ND-3202	XLP-101	SPH-101	2PXZ-TAZ	（A）	TSPO1	LiF/Al
实施例 10	ND-3202	XLP-101	DOBNA	2PXZ-TAZ	（A）	TSPO1	LiF/Al

[1680] ＜发光层形成用组合物(5)～发光层形成用组合物(7)的制备＞

[1681] 通过将下述成分搅拌至成为均匀的溶液为止,从而制备发光层形成用组合物(5)。

[1682]

化合物（A）	0.02 重量%
2PXZ-TAZ	0.18 重量%
mCBP	1.80 重量%
甲苯	98.00 重量%

[1683] 通过将下述成分搅拌至成为均匀的溶液为止,从而制备发光层形成用组合物(6)。

[1684]

化合物（A）	0.02 重量%
2PXZ-TAZ	0.18 重量%
SPH-101	1.80 重量%
二甲苯	98.00 重量%

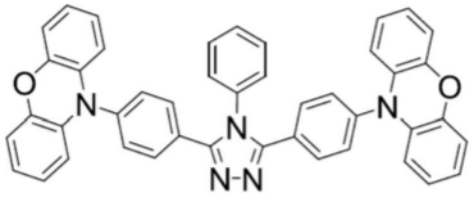
[1685] 通过将下述成分搅拌至成为均匀的溶液为止,从而制备发光层形成用组合物(7)。

[1686]

化合物（A）	0.02 重量%
2PXZ-TAZ	0.18 重量%
DOBNA	1.80 重量%
甲苯	98.00 重量%

[1687] 表4中,“2PXZ-TAZ”为10,10'-((4-苯基-4H-1,2,4-三唑-3,5-二基)双(4,1-苯基的))双(10H-吩噁嗪)。以下示出化学结构。

[1688] [化423]

[1689] 

(2PXZ-TAZ)

[1690] ＜实施例8＞

[1691] 在成膜有厚度为45nm的ITO的玻璃基板上旋涂ND-3202(日产化学工业制造)溶液后,在大气环境下以50℃加热3分钟,进而以230℃加热15分钟,由此制成膜厚50nm的ND-3202膜(空穴注入层)。继而,旋涂XLP-101溶液,在氮气环境下,在热板上以200℃加热30分钟,由此制成膜厚20nm的XLP-101膜(空穴传输层)。继而,旋涂发光层形成用组合物(5),在氮气环境下,以130℃加热10分钟,由此制成20nm的发光层。

[1692] 将所制作的多层膜固定于市售的蒸镀装置(昭和真空(股)制造)的基板固定器上,安装放入有TSPO1的钼制蒸镀用舟皿、放入有LiF的钼制蒸镀用舟皿、放入有铝的钨制蒸镀用舟皿。将真空槽减压至5×10^{-4}Pa为止,然后,对TSPO1进行加热且以使膜厚成为30nm的方式进行蒸镀,从而形成电子传输层。将形成电子传输层时的蒸镀速度设为1nm/sec。其后,对LiF进行加热且以使膜厚成为1nm的方式以0.01nm/sec～0.1nm/sec的蒸镀速度进行蒸镀。继而,对铝进行加热且以使膜厚成为100nm的方式进行蒸镀而形成阴极。以所述方式获得有机EL元件。

[1693] ＜实施例9及实施例10＞

[1694] 使用发光层形成用组合物(6)或发光层形成用组合物(7)并利用与实施例8相同的方法来获得有机EL元件。

[1695] ＜实施例11～实施例29＞

[1696] ＜发光层形成用组合物的制备＞

[1697] 对实施例11～实施例29的发光层形成用组合物进行制备。分别将表5A及表5B中记载的化合物混合并加以搅拌,由此制备发光层形成用组合物。

[1698] [表5A]

[1699]

	浓度				第一成分	第二成分	第三成分
	固体成分浓度	第一成分	第二成分	第三成分			
实施例11	1	0.01	0.99	99.0	化合物（1-411）	化合物（3-44）	环己基苯/3-苯氧基甲苯 7/3
实施例12	1	0.01	0.99	99.0	化合物（1-590）	化合物（3-44）	环己基苯/3-苯氧基甲苯 7/3
实施例13	2	0.02	1.98	98.0	化合物（1-590）	化合物（3-44）	环己基苯/3-苯氧基甲苯 7/3
实施例14	1	0.01	0.99	99.0	化合物（1-590）	化合物（3-44）	甲苯/十氢萘 9/1
实施例15	1	0.01	0.99	99.0	化合物（1-590）	化合物（3-44）	3-苯氧基甲苯/环己基苯 9/1
实施例16	1	0.01	0.99	99.0	化合物（1-590）	化合物（3-44）	苯甲醚/十氢萘 7/3
实施例17	1	0.01	0.99	99.0	化合物（1-590）	化合物（3-44）	二甲苯/1-甲基萘 7/3
实施例18	1	0.01	0.99	99.0	化合物（1-590）	化合物（3-44）	3-苯氧基甲苯/环己基苯 7/3
实施例19	1	0.01	0.99	99.0	化合物（1-590）	化合物（3-44）	正辛基苯/二苯基醚 7/3
实施例20	1	0.01	0.99	99.0	化合物（1-590）	化合物（3-44）	环己基苯/二苯基醚 7/3
实施例21	1	0.01	0.99	99.0	化合物（1-590）	化合物（3-44）	环己基苯/3-苯氧基甲苯/4-氟苯甲醚 6/3/1
实施例22	1	0.01	0.99	99.0	化合物（1-590）	化合物（3-44）	苯甲酸乙酯/3-苯氧基甲苯 5/5

[1700] [表5B]

[1701]

	浓度				第一成分	第二成分	第三成分
	固体成分浓度	第一成分	第二成分	第三成分			
实施例23	1	0.01	0.99	99.0	化合物（1-411）	化合物（BH-2）	环己基苯/3-苯氧基甲苯 7/3
实施例24	1	0.01	0.99	99.0	化合物（1-590）	化合物（BH-2）	环己基苯/3-苯氧基甲苯 7/3
实施例25	1	0.01	0.99	99	化合物（1-590）	化合物（BH-3）	环己基苯/3-苯氧基甲苯 7/3
实施例26	1	0.01	0.99	99	化合物（1-590）	化合物（BH-4）	环己基苯/3-苯氧基甲苯 7/3
实施例27	1	0.01	0.99	99	化合物（1-590）	化合物（BH-5）	环己基苯/3-苯氧基甲苯 7/3
实施例28	1	0.01	0.99	99	化合物（1-590）	化合物（BH-6）	环己基苯/3-苯氧基甲苯 7/3
实施例29	1	0.01	0.99	99	化合物（1-590）	化合物（BH-7）	环己基苯/3-苯氧基甲苯 7/3

[1702] ＜评价＞

[1703] 针对所获得的实施例11～实施例29的发光层形成用组合物,对溶解性及涂布性进行评价。

[1704] (溶解性的评价)

[1705] 将化合物全部溶解而获得均匀的溶液的例子设为“溶解”,将残留有不溶物的例子设为“不溶”。

[1706] (涂布性的评价)

[1707] 针对在所制备的油墨组合物的溶解性的评价中为“溶解”者,对旋涂成膜后或喷墨印刷后所获得的膜的制膜性进行评价。将在制膜后,膜中有针孔、化合物的析出或不均者示为“不良”,将无针孔、化合物的析出或不均者示为“良好”。

[1708] ＜利用旋涂的涂布方法＞

[1709] 通过对厚度0.5mm、尺寸28mm×26mm的洁净的玻璃基板照射照射能量1000mJ/cm^2(低压水银灯(254纳米))来进行UV-03处理。继而,将0.3mL～0.6mL的油墨组合物滴加至玻璃上,并进行旋涂(倾斜(slope)、5秒→500rpm～5000rpm、10秒→倾斜、5秒)。进而,在120℃的热板上干燥10分钟。

[1710] ＜利用喷墨的涂布方法＞

[1711] 针对涂布性,使用喷墨向100ppi的像素内喷出,对在100℃下干燥而成的涂膜的成膜性进行评价。

[1712] ＜粘度的测定方法＞

[1713] 粘度是使用圆锥平板型旋转粘度计(cone-plate type)来测定。

[1714] ＜表面张力的测定方法＞

[1715] 表面张力是使用悬滴法来测定。

[1716] [表6A]

[1717]

	溶解	涂布性		喷墨喷出稳定性		粘度	表面张力
		旋涂	喷墨	初期	24 小时后	mPa·s	mN/m
实施例 11	溶解	良好	良好	良好	良好	-	-
实施例 12	溶解	良好	良好	良好	良好	-	-
实施例 13	溶解	良好	良好	良好	良好	-	-
实施例 14	溶解	良好	良好	良好	良好	-	-
实施例 15	溶解	良好	良好	良好	良好	-	-
实施例 16	溶解	良好	良好	良好	良好	-	-
实施例 17	溶解	良好	良好	良好	良好	-	-
实施例 18	溶解	良好	良好	良好	良好	3.9	35.4
实施例 19	溶解	良好	良好	良好	良好		
实施例 20	溶解	良好	良好	良好	良好	-	-
实施例 21	溶解	良好	良好	良好	良好	-	-
实施例 22	溶解	良好	良好	良好	良好	-	-

[1718] [表6B]

[1719]

	溶解	涂布性		喷墨喷出稳定性		粘度	表面张力
		旋涂	喷墨	初期	24 小时后	mPa·s	mN/m
实施例 23	溶解	良好	良好	良好	良好	-	-
实施例 24	溶解	良好	良好	良好	良好	-	-
实施例 25	溶解	良好	良好	良好	良好	-	-
实施例 26	溶解	良好	良好	良好	良好	-	-
实施例 27	溶解	良好	良好	良好	良好	-	-
实施例 28	溶解	良好	良好	良好	良好	-	-
实施例 29	溶解	良好	良好	良好	良好	-	-

[1720] 本申请实施例均显示出良好的溶解性、涂布性。

[1721] ＜实施例30、实施例31＞

[1722] ＜涂布型有机EL元件的评价＞

[1723] 继而，对涂布形成有机层而获得的有机EL元件进行说明。将所制作的有机EL元件中的各层的材料结构示于表7中。

[1724] [表7]

[1725]

	空穴注入层（40 nm）	空穴传输层（30 nm）	发光层（20 nm）			电子传输层（30 nm）	阴极 1 nm/100 nm	发光波长 [nm]	效率 [%]
			第二成分	第一成分	组合物				
实施例 30	PEDOT：PSS	XLP-101	化合物（3-44）	化合物（1-411）	实施例 11	ET1	LiF/Al	464	6.3
实施例 31	PEDOT：PSS	XLP-101	化合物（BH-2）	化合物（1-590）	实施例 24	ET1	LiF/Al	464	6.3

[1726] ＜实施例30＞

[1727] 在蒸镀有厚度为150nm的ITO的玻璃基板上旋涂PEDOT:PSS溶液，在200℃的热板上煅烧1小时，由此制成膜厚40nm的PEDOT:PSS膜（空穴注入层）。继而，旋涂XLP-101溶液，在200℃的热板上煅烧1小时，由此制成膜厚30nm的膜（空穴传输层）。继而，旋涂实施例11中所制备的发光层形成用组合物，在120℃的热板上煅烧1小时，由此制成膜厚20nm的发光层。

[1728] 将所制作的多层膜固定于市售的蒸镀装置（昭和真空（股）制造）的基板固定器上，安装放入有ET1的钼制蒸镀用舟皿、放入有LiF的钼制蒸镀用舟皿、放入有铝的钨制蒸镀用舟皿。将真空槽减压至5×10^{-4}Pa为止，然后，对ET1进行加热且以使膜厚成为30nm的方式进行蒸镀，从而形成电子传输层。将形成电子传输层时的蒸镀速度设为1nm/sec。其后，对LiF进行加热且以使膜厚成为1nm的方式以0.01nm/sec～0.1nm/sec的蒸镀速度进行蒸镀。继而，对铝进行加热且以使膜厚成为100nm的方式进行蒸镀而形成阴极。以所述方式获得有机EL元件。

[1729] ＜实施例31＞

[1730] 除使用实施例24中所制备的发光层形成用组合物来代替实施例11中所制备的发光层形成用组合物以外，利用与实施例30相同的程序来制作有机EL元件。

[1731] 如上所述，认为：通常使用湿式成膜法所形成的有机EL元件可获得与使用真空蒸镀法所形成的相同的元件构成的有机EL元件同等的特性。这些元件只要进行涂布步骤、干燥步骤的最优选化，则可获得与具有相同的发光层的材料构成的蒸镀型有机EL元件同等的特性。

[1732] 以上，对本发明的化合物的一部分进行作为有机EL元件用材料的评价，且显示出

为优异的材料,但未进行评价的其他化合物也为具有相同的基本骨架且整体而言也具有类似结构的化合物,对于本领域技术人员而言,可同样地理解为是优异的有机EL元件用材料。

[1733] 产业上的可利用性

[1734] 本发明中,通过提供新颖的环烷烃缩合多环芳香族化合物,而可增加例如有机EL元件用材料等有机元件用材料的选择项。另外,通过将新颖的环烷烃缩合多环芳香族化合物用作有机EL元件用材料,而可提供例如发光效率或元件寿命优异的有机EL元件、具备其的显示装置及具备其的照明装置等。

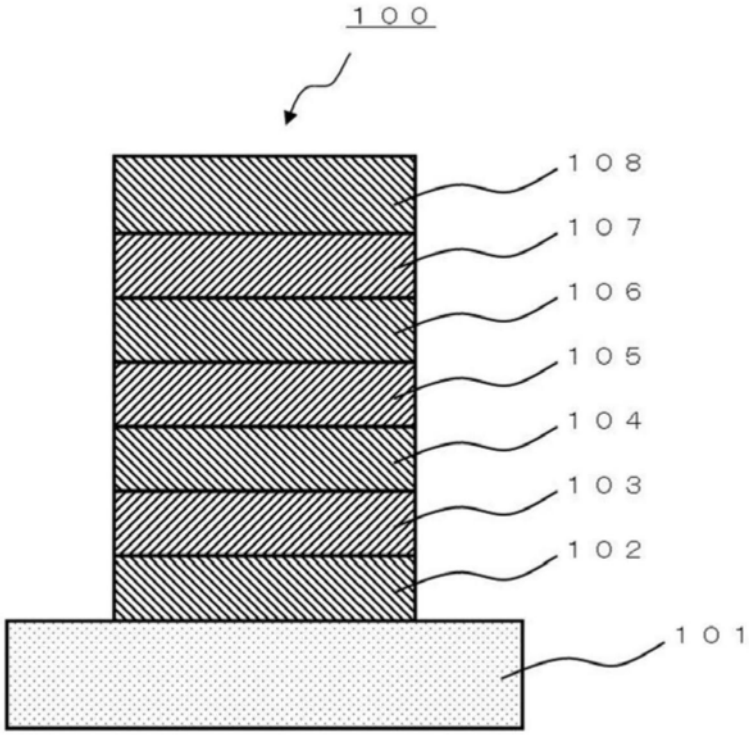


图1