



(51) International Patent Classification:

C07F 5/02 (2006.01) *H05B 33/14* (2006.01)
C07F 15/00 (2006.01) *H01L 51/00* (2006.01)
C09K 11/06 (2006.01)

(21) International Application Number:

PCT/US2013/048495

(22) International Filing Date:

28 June 2013 (28.06.2013)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

61/666,636 29 June 2012 (29.06.2012) US

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THROUGH THE ST. BOARD OF HIGHER EDUCA-
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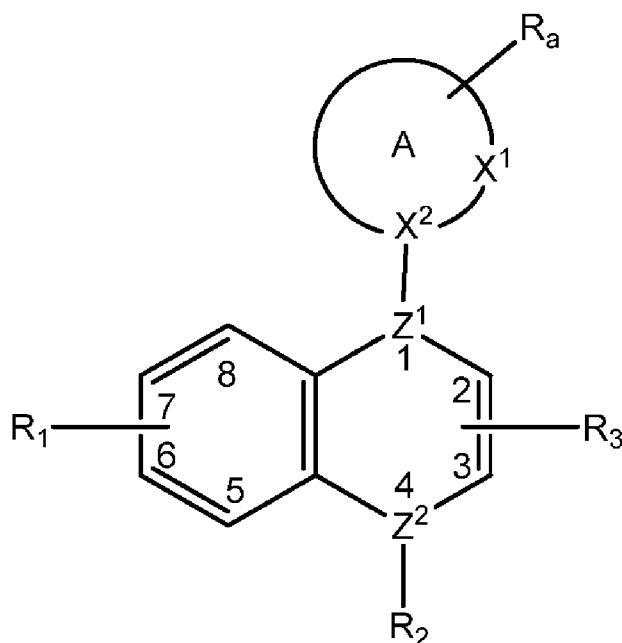
(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,
BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM,
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KN, KP, KR,
KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME,
MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ,
OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC,
SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN,
TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ,
UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ,
TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK,
EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV,
MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,

[Continued on next page]

(54) Title: 1,4-AZABORINE COMPOUNDS AND METHODS OF SYNTHESIS

(57) Abstract: A compound comprising a structure
of formula A





TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, **Published:**
KM, ML, MR, NE, SN, TD, TG).

— *with international search report (Art. 21(3))*

Declarations under Rule 4.17:

— *of inventorship (Rule 4.17(iv))*

1,4-AZABORINE COMPOUNDS AND METHODS OF SYNTHESIS

This application claims the benefit of U.S. Provisional Application No. 61/666,636, filed June 29, 2012, which is incorporated herein by reference in its entirety.

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BACKGROUND

Opto-electronic devices that make use of organic materials are becoming increasingly desirable for a number of reasons. Many of the materials used to make such devices are relatively inexpensive, so organic opto-electronic devices have the potential for cost advantages over inorganic devices. In addition, the inherent properties of organic materials, such as their flexibility, may make them well suited for particular applications such as fabrication on a flexible substrate. Examples of organic opto-electronic devices include organic light-emitting devices (OLEDs), organic phototransistors, organic photovoltaic cells, and organic photodetectors. For OLEDs, the organic materials may have performance advantages over conventional materials. For example, the wavelength at which an organic emissive layer emits light may generally be readily tuned with appropriate dopants.

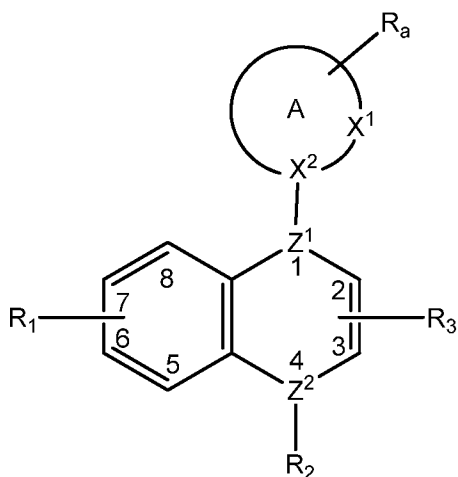
OLEDs make use of thin organic films that emit light when voltage is applied across the device. OLEDs are becoming an increasingly interesting technology for use in applications such as flat panel displays, illumination, and backlighting. Several OLED materials and configurations are described in U.S. Pat. Nos. 5,844,363, 6,303,238, and 5,707,745, which are incorporated herein by reference in their entirety.

One application for phosphorescent emissive molecules is a full color display. Industry standards for such a display call for pixels adapted to emit particular colors, referred to as "saturated" colors. In particular, these standards call for saturated red, green, and blue pixels. Color may be measured using CIE coordinates, which are well known to the art.

30

SUMMARY

Disclosed herein in one embodiment is a compound comprising a structure of formula A:



wherein ring A includes a 5-membered or 6-membered carbocycle or heterocycle;

each R_a is independently selected from hydrogen, deuterium, halide, optionally-substituted alkyl, optionally-substituted cycloalkyl, optionally-substituted heteroalkyl, optionally-substituted arylalkyl, optionally-substituted alkoxy, optionally-substituted aryloxy, optionally-substituted amino, silyl, optionally-substituted alkenyl, optionally-substituted cycloalkenyl, optionally-substituted heteroalkenyl, alkynyl, aryl, heteroaryl, acyl, carbonyl, carboxylic acid, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, optionally-substituted amido, optionally-substituted phosphoryl, optionally-substituted thiophosphoryl, optionally-substituted phosphinyl, optionally-substituted thiophosphinyl, thioester, nitro, azido, optionally-substituted hydrazinyl, optionally-substituted diazenyl, or thiocarbonyl;

X^1 represents C, N, S, O or Se;

X^2 represents C or N;

Z^1 is B and Z^2 is N, or Z^1 is N and Z^2 is B;

each R_1 is independently selected from hydrogen, deuterium, halide, optionally-substituted alkyl, optionally-substituted cycloalkyl, optionally-substituted heteroalkyl, optionally-substituted arylalkyl, optionally-substituted alkoxy, optionally-substituted aryloxy, optionally-substituted amino, silyl, optionally-substituted alkenyl, optionally-substituted cycloalkenyl, optionally-

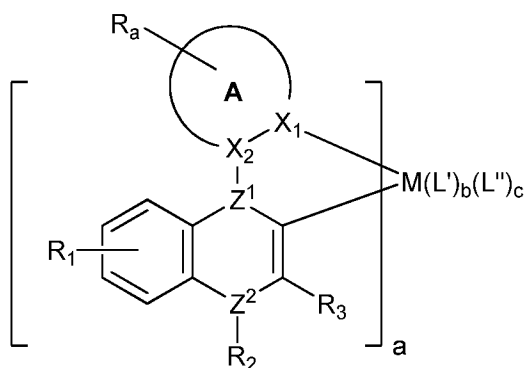
substituted heteroalkenyl, optionally-substituted alkynyl, optionally-substituted aryl, optionally-substituted heteroaryl, optionally-substituted acyl, carbonyl, carboxylic acid, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, optionally-substituted amido, optionally-substituted phosphoryl, optionally-substituted thiophosphoryl, optionally-substituted phosphinyl, optionally-substituted thiophosphinyl, thioester, nitro, azido, optionally-substituted hydrazinyl, optionally-substituted diazenyl, or thiocarbonyl;

R_2 is independently selected from hydrogen, deuterium, halide, optionally-substituted alkyl, optionally-substituted cycloalkyl, optionally-substituted heteroalkyl, optionally-substituted arylalkyl, optionally-substituted alkoxy, optionally-substituted aryloxy, optionally-substituted amino, silyl, optionally-substituted alkenyl, optionally-substituted cycloalkenyl, optionally-substituted heteroalkenyl, optionally-substituted alkynyl, optionally-substituted aryl, optionally-substituted heteroaryl, acyl, carbonyl, carboxylic acid, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, optionally-substituted amido, optionally-substituted phosphoryl, optionally-substituted thiophosphoryl, optionally-substituted phosphinyl, optionally-substituted thiophosphinyl, thioester, nitro, azido, optionally-substituted hydrazinyl, optionally-substituted diazenyl, or thiocarbonyl; and

each R_3 is independently selected from hydrogen, deuterium, halide, optionally-substituted alkyl, optionally-substituted cycloalkyl, optionally-substituted heteroalkyl, optionally-substituted arylalkyl, optionally-substituted alkoxy, optionally-substituted aryloxy, optionally-substituted amino, silyl, optionally-substituted alkenyl, optionally-substituted cycloalkenyl, optionally-substituted heteroalkenyl, optionally-substituted alkynyl, optionally-substituted aryl, optionally-substituted heteroaryl, acyl, carbonyl, carboxylic acid, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, optionally-substituted amido, optionally-substituted phosphoryl, optionally-substituted thiophosphoryl, optionally-substituted phosphinyl, optionally-substituted thiophosphinyl, thioester, nitro, azido, optionally-substituted hydrazinyl, optionally-substituted diazenyl, or thiocarbonyl.

Disclosed herein in a further embodiment is a compound comprising a structure of formula

B:



Formula B

wherein L' and L'' are mono, bi or tri ligands; M is a metal; a is 1, 2, or 3; b is 0, 1, or 2; c is 0, 1 or 2; a+b+c is n, wherein n is the oxidation state of the metal M;

ring A includes a 5-membered or 6-membered carbocycle or heterocycle;

each R_a is independently selected from hydrogen, deuterium, halide, optionally-substituted alkyl, optionally-substituted cycloalkyl, optionally-substituted heteroalkyl, optionally-substituted arylalkyl, optionally-substituted alkoxy, optionally-substituted aryloxy, optionally-substituted amino, silyl, optionally-substituted alkenyl, optionally-substituted cycloalkenyl, optionally-substituted heteroalkenyl, alkynyl, aryl, heteroaryl, acyl, carbonyl, carboxylic acid, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, optionally-substituted amido, optionally-substituted phosphoryl, optionally-substituted thiophosphoryl, optionally-substituted phosphinyl, optionally-substituted thiophosphinyl, thioester, nitro, azido, optionally-substituted hydrazinyl, optionally-substituted diazenyl, or thiocarbonyl;

X₁ represents C, N, S, O or Se;

X₂ represents C or N;

Z¹ is B and Z² is N, or Z¹ is N and Z² is B;

each R₁ is independently selected from hydrogen, deuterium, halide, optionally-substituted alkyl, optionally-substituted cycloalkyl, optionally-substituted heteroalkyl, optionally-substituted arylalkyl, optionally-substituted alkoxy, optionally-substituted aryloxy, optionally-substituted amino, silyl, optionally-substituted alkenyl, optionally-substituted cycloalkenyl, optionally-substituted heteroalkenyl, optionally-substituted alkynyl, optionally-substituted aryl, optionally-substituted heteroaryl, optionally-substituted acyl, carbonyl, carboxylic acid, ester, nitrile, isonitrile,

sulfanyl, sulfinyl, sulfonyl, optionally-substituted amido, optionally-substituted phosphoryl, optionally-substituted thiophosphoryl, optionally-substituted phosphinyl, optionally-substituted thiophosphinyl, thioester, nitro, azido, optionally-substituted hydrazinyl, optionally-substituted diazenyl, or thiocarbonyl;

5 R_2 is independently selected from hydrogen, deuterium, halide, optionally-substituted alkyl, optionally-substituted cycloalkyl, optionally-substituted heteroalkyl, optionally-substituted arylalkyl, optionally-substituted alkoxy, optionally-substituted aryloxy, optionally-substituted amino, silyl, optionally-substituted alkenyl, optionally-substituted cycloalkenyl, optionally-substituted heteroalkenyl, optionally-substituted alkynyl, optionally-substituted aryl, optionally-substituted heteroaryl, acyl, carbonyl, carboxylic acid, ester, nitrile, isonitrile, sulfanyl, sulfinyl, 10 sulfonyl, optionally-substituted amido, optionally-substituted phosphoryl, optionally-substituted thiophosphoryl, optionally-substituted phosphinyl, optionally-substituted thiophosphinyl, thioester, nitro, azido, optionally-substituted hydrazinyl, optionally-substituted diazenyl, or thiocarbonyl; and

 each R_3 is independently selected from hydrogen, deuterium, halide, optionally-substituted 15 alkyl, optionally-substituted cycloalkyl, optionally-substituted heteroalkyl, optionally-substituted arylalkyl, optionally-substituted alkoxy, optionally-substituted aryloxy, optionally-substituted amino, silyl, optionally-substituted alkenyl, optionally-substituted cycloalkenyl, optionally-substituted heteroalkenyl, optionally-substituted alkynyl, optionally-substituted aryl, optionally-substituted heteroaryl, acyl, carbonyl, carboxylic acid, ester, nitrile, isonitrile, sulfanyl, sulfinyl, 20 sulfonyl, optionally-substituted amido, optionally-substituted phosphoryl, optionally-substituted thiophosphoryl, optionally-substituted phosphinyl, optionally-substituted thiophosphinyl, thioester, nitro, azido, optionally-substituted hydrazinyl, optionally-substituted diazenyl, or thiocarbonyl.

 Further disclosed herein is an organic light emitting device comprising:

25 an anode;

 a cathode; and

 an organic layer disposed between the anode and the cathode, wherein the organic layer comprises a compound of formula A or formula B.

30 Also disclosed herein is a consumer product that includes the OLED devices disclosed herein.

An additional embodiment disclosed herein relates to a method for making a benzo-fused 1,4-azaborine, comprising:

performing an alkene isomerization of an aryl N-allylamine to produce an aryl enamine;

5 coupling the aryl enamine with a boron-containing electrophile to produce a ring-closing-metathesis aryl precursor having an enamine substituent and a boron-containing substituent, wherein the enamine substituent is at an *ortho* position relative to the boron-containing substituent; and

10 performing a ring-closing metathesis on the ring-closing-metathesis aryl precursor to produce a benzo-fused 1,4-azaborine.

Further disclosed herein is a method for making a benzo-fused 1,4-azaborine, comprising:

providing a N-protected ortho-substituted aryl amine;

15 subjecting the N-protected ortho-substituted aryl amine to an electrophilic borylation to provide an N-protected benzo-fused 1,4-azaborine intermediate;

removing the N-protecting group from the N-protected benzo-fused 1,4-azaborine intermediate; and

performing a Buchwald-Hartwig amination at the nitrogen heteroatom of the benzo-fused 1,4-azaborine to produce an N-pyridinyl substituted benzo-fused 1,4-azaborine.

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The foregoing will become more apparent from the following detailed description, which proceeds with reference to the accompanying figures.

BRIEF DESCRIPTION OF THE DRAWINGS

25

FIG. 1 shows an organic light-emitting device.

FIG. 2 shows an inverted organic light-emitting device that does not have a separate electron transport layer.

FIG. 3 shows a synthesis scheme of a novel B-pyridinyl 1,4-azaborine disclosed herein.

30 FIGS. 4-6 show synthesis schemes of novel N-pyridinyl 1,4-azaborines.

FIG. 7 shows the photoluminescence spectrum of compound Pt-PYAB-1.

DETAILED DESCRIPTION

Terminology

5 As used herein, the singular terms “a,” “an,” and “the” include plural referents unless context clearly indicates otherwise. Also, as used herein, the term “comprises” means “includes.”

Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present disclosure, suitable methods and materials are described below. In addition, the materials, methods, and examples are illustrative only and not intended to
10 be limiting.

To facilitate review of the various examples of this disclosure, the following explanations of specific terms are provided:

“Acyl” refers to a group having the structure --C(O)R , where R may be, for example, optionally substituted alkyl, optionally substituted aryl, or optionally substituted heteroaryl.

15 “Lower acyl” groups are those that contain one to six carbon atoms.

“Acyloxy” refers to a group having the structure --OC(O)R- , where R may be, for example, optionally substituted alkyl, optionally substituted aryl, or optionally substituted heteroaryl.

“Lower acyloxy” groups contain one to six carbon atoms.

“Alkenyl” refers to a cyclic, branched or straight chain group containing only carbon and hydrogen, and containing one or more double bonds that may or may not be conjugated. Alkenyl
20 groups may be unsubstituted or substituted. “Lower alkenyl” groups contain one to six carbon atoms.

The term “alkoxy” refers to a straight, branched or cyclic hydrocarbon configuration and combinations thereof, including from 1 to 20 carbon atoms, preferably from 1 to 8 carbon atoms
25 (referred to as a “lower alkoxy”), more preferably from 1 to 4 carbon atoms, that includes an oxygen atom at the point of attachment. An example of an “alkoxy group” is represented by the formula --OR , where R can be an alkyl group, optionally substituted with an alkenyl, alkynyl, aryl, aralkyl, cycloalkyl, halogenated alkyl, alkoxy or heterocycloalkyl group. Suitable alkoxy groups include methoxy, ethoxy, n-propoxy, i-propoxy, n-butoxy, i-butoxy, sec-butoxy, tert-butoxy
30 cyclopropoxy, cyclohexyloxy, and the like.

“Alkoxy carbonyl” refers to an alkoxy substituted carbonyl radical, $-C(O)OR$, wherein R represents an optionally substituted alkyl, aryl, aralkyl, cycloalkyl, cycloalkylalkyl or similar moiety.

The term “alkoxyaryl” refers to C_{1-6} alkoxyaryl such as benzyloxy.

5 The term “alkyl” refers to a branched or unbranched saturated hydrocarbon group of 1 to 24 carbon atoms, such as methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *t*-butyl, pentyl, hexyl, heptyl, octyl, decyl, tetradecyl, hexadecyl, eicosyl, tetracosyl and the like. A “lower alkyl” group is a saturated branched or unbranched hydrocarbon having from 1 to 6 carbon atoms. Preferred alkyl groups have 1 to 4 carbon atoms. Alkyl groups may be “substituted alkyls” wherein one or more

10 hydrogen atoms are substituted with a substituent such as halogen, cycloalkyl, alkoxy, amino, hydroxyl, aryl, alkenyl, or carboxyl. For example, a lower alkyl or (C_1-C_6) alkyl can be methyl, ethyl, propyl, isopropyl, butyl, iso-butyl, sec-butyl, pentyl, 3-pentyl, or hexyl; (C_3-C_6) cycloalkyl can be cyclopropyl, cyclobutyl, cyclopentyl, or cyclohexyl; (C_3-C_6) cycloalkyl (C_1-C_6) alkyl can be cyclopropylmethyl, cyclobutylmethyl, cyclopentylmethyl, cyclohexylmethyl, 2-cyclopropylethyl,

15 2-cyclobutylethyl, 2-cyclopentylethyl, or 2-cyclohexylethyl; (C_1-C_6) alkoxy can be methoxy, ethoxy, propoxy, isopropoxy, butoxy, iso-butoxy, sec-butoxy, pentoxy, 3-pentoxy, or hexyloxy; (C_2-C_6) alkenyl can be vinyl, allyl, 1-propenyl, 2-propenyl, 1-butenyl, 2-butenyl, 3-butenyl, 1-pentenyl, 2-pentenyl, 3-pentenyl, 4-pentenyl, 1-hexenyl, 2-hexenyl, 3-hexenyl, 4-hexenyl, or 5-hexenyl; (C_2-C_6) alkynyl can be ethynyl, 1-propynyl, 2-propynyl, 1-butylnyl, 2-butylnyl, 3-butylnyl,

20 1-pentylnyl, 2-pentylnyl, 3-pentylnyl, 4-pentylnyl, 1-hexynyl, 2-hexynyl, 3-hexynyl, 4-hexynyl, or 5-hexynyl; (C_1-C_6) alkanoyl can be acetyl, propanoyl or butanoyl; halo (C_1-C_6) alkyl can be iodomethyl, bromomethyl, chloromethyl, fluoromethyl, trifluoromethyl, 2-chloroethyl, 2-fluoroethyl, 2,2,2-trifluoroethyl, or pentafluoroethyl; hydroxy (C_1-C_6) alkyl can be hydroxymethyl, 1-hydroxyethyl, 2-hydroxyethyl, 1-hydroxypropyl, 2-hydroxypropyl, 3-hydroxypropyl, 1-

25 hydroxybutyl, 4-hydroxybutyl, 1-hydroxypentyl, 5-hydroxypentyl, 1-hydroxyhexyl, or 6-hydroxyhexyl; (C_1-C_6) alkoxy carbonyl can be methoxycarbonyl, ethoxycarbonyl, propoxycarbonyl, isopropoxycarbonyl, butoxycarbonyl, pentoxycarbonyl, or hexyloxycarbonyl; (C_1-C_6) alkylthio can be methylthio, ethylthio, propylthio, isopropylthio, butylthio, isobutylthio, pentylthio, or hexylthio; (C_2-C_6) alkanoyloxy can be acetoxyl, propanoyloxy, butanoyloxy, isobutanoyloxy, pentanoyloxy, or

30 hexanoyloxy.

“Alkynyl” refers to a cyclic, branched or straight chain group containing only carbon and hydrogen, and containing one or more triple bonds. Alkynyl groups may be unsubstituted or substituted. “Lower alkynyl” groups are those that contain one to six carbon atoms.

The term “amine” or “amino” refers to a group of the formula $-NRR'$, where R and R' can be, independently, hydrogen or an alkyl, alkenyl, alkynyl, aryl, aralkyl, cycloalkyl, halogenated alkyl, or heterocycloalkyl group. For example, an “alkylamino” or “alkylated amino” refers to $-NRR'$, wherein at least one of R or R' is an alkyl.

“Aminocarbonyl” alone or in combination, means an amino substituted carbonyl (carbamoyl) radical, wherein the amino radical may optionally be mono- or di-substituted, such as with alkyl, aryl, aralkyl, cycloalkyl, cycloalkylalkyl, alkanoyl, alkoxycarbonyl, aralkoxycarbonyl and the like. An aminocarbonyl group may be $-N(R)-C(O)-R$ (wherein R is a substituted group or H). A suitable aminocarbonyl group is acetamido.

The term “amide” or “amido” is represented by the formula $-C(O)NRR'$, where R and R' independently can be a hydrogen, alkyl, alkenyl, alkynyl, aryl, aralkyl, cycloalkyl, halogenated alkyl, or heterocycloalkyl group described above.

“Aryl” refers to a monovalent unsaturated aromatic carbocyclic group having a single ring (e.g., phenyl) or multiple condensed rings (e.g., naphthyl or anthryl), which can optionally be unsubstituted or substituted. A “heteroaryl group,” is defined as an aromatic group that has at least one heteroatom incorporated within the ring of the aromatic group. Examples of heteroatoms include, but are not limited to, nitrogen, oxygen, sulfur, and phosphorous. Heteroaryl includes, but is not limited to, pyridinyl, pyrazinyl, pyrimidinyl, pyrrolyl, pyrazolyl, imidazolyl, thiazolyl, oxazolyl, isooxazolyl, thiadiazolyl, oxadiazolyl, thiophenyl, furanyl, quinolinyl, isoquinolinyl, benzimidazolyl, benzooxazolyl, quinoxalinyl, and the like. The aryl or heteroaryl group can be substituted with one or more groups including, but not limited to, alkyl, alkynyl, alkenyl, aryl, halide, nitro, amino, ester, ketone, aldehyde, hydroxy, carboxylic acid, or alkoxy, or the aryl or heteroaryl group can be unsubstituted.

The term “aralkyl” or “arylalkyl” refers to an alkyl group wherein an aryl group is substituted for a hydrogen of the alkyl group. An example of an aralkyl group is a benzyl group.

“Aryloxy” or “heteroaryloxy” refers to a group of the formula $-OAr$, wherein Ar is an aryl group or a heteroaryl group, respectively.

“Carbocycle” refers to a carbon-based ring that includes at least three carbon atoms. A carbocycle may be, for example, a cycloalkyl, a cycloalkenyl, or an aryl group.

The term “carboxylate” or “carboxyl” refers to the group -COO^- or -COOH .

The term “cycloalkyl” refers to a non-aromatic carbon-based ring composed of at least three carbon atoms. Examples of cycloalkyl groups include, but are not limited to, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, and the like. The term “heterocycloalkyl group” is a cycloalkyl group as defined above where at least one of the carbon atoms of the ring is substituted with a heteroatom such as, but not limited to, nitrogen, oxygen, sulfur, or phosphorous.

The term “ester” refers to a carboxyl group having the hydrogen replaced with, for example, a C_{1-6} alkyl group (“carboxyl C_{1-6} alkyl” or “alkylester”), an aryl or aralkyl group (“arylester” or “aralkylester”) and so on. $\text{CO}_2\text{C}_{1-3}$ alkyl groups are preferred, such as for example, methylester (CO_2Me), ethylester (CO_2Et) and propylester (CO_2Pr) and includes reverse esters thereof (e.g. $-\text{OCOMe}$, $-\text{OCOEt}$ and $-\text{OCOPr}$).

The term “halogen” or “halide” refers to fluoro, bromo, chloro and iodo substituents.

The terms “halogenated alkyl” or “haloalkyl group” refer to an alkyl group as defined above with one or more hydrogen atoms present on these groups substituted with a halogen (F, Cl, Br, I).

“Heterocycle” refers to mono or bicyclic rings or ring systems that include at least one heteroatom. The rings or ring systems generally include 1 to 9 carbon atoms in addition to the heteroatom(s) and may be saturated, unsaturated or aromatic (including pseudoaromatic). The term “pseudoaromatic” refers to a ring system which is not strictly aromatic, but which is stabilized by means of delocalization of electrons and behaves in a similar manner to aromatic rings. Aromatic includes pseudoaromatic ring systems, such as pyrrolyl rings.

Examples of monocyclic heterocycle groups include, but are not limited to, those containing one nitrogen atom such as aziridine (3-membered ring), azetidine (4-membered ring), pyrrolidine (tetrahydropyrrole), pyrroline (e.g., 3-pyrroline, 2,5-dihydropyrrole), 2H-pyrrole or 3H-pyrrole (isopyrrole, isoazole) or pyrrolidinone (5-membered rings), piperidine, dihydropyridine, tetrahydropyridine (6-membered rings), and azepine (7-membered ring); those containing two nitrogen atoms such as imidazoline, pyrazolidine (diazolidine), imidazoline, pyrazoline (dihydropyrazole) (5-membered rings), piperazine (6-membered ring); those containing one oxygen atom such as oxirane (3-membered ring), oxetane (4-membered ring), oxolane (tetrahydrofuran), oxole (dihydrofuran) (5-membered rings), oxane (tetrahydropyran), dihydropyran, pyran (6-

membered rings), oxepin (7-membered ring); those containing two oxygen atoms such as dioxolane (5-membered ring), dioxane (6-membered ring), and dioxepane (7-membered ring); those containing three oxygen atoms such as trioxane (6-membered ring); those containing one sulfur atom such as thiirane (3-membered ring), thietane (4-membered ring), thiolane (tetrahydrothiophene) (5-membered ring), thiane (tetrahydrothiopyran) (6-membered ring), thiepane (7-membered ring); those containing one nitrogen and one oxygen atom such as tetrahydrooxazole, dihydrooxazole, tetrahydroisoxazole, dihydroisoxazole (5-membered rings), morpholine, tetrahydrooxazine, dihydrooxazine, oxazine (6-membered rings); those containing one nitrogen and one sulfur atom such as thiazoline, thiazolidine (5-membered rings), thiomorpholine (6-membered ring); those containing two nitrogen and one oxygen atom such as oxadiazine (6-membered ring); those containing one oxygen and one sulfur such as: oxathiole (5-membered ring) and oxathiane (thioxane) (6-membered ring); and those containing one nitrogen, one oxygen and one sulfur atom such as oxathiazine (6-membered ring).

Examples of 5-membered monocyclic heteroaryl groups include but are not limited to furanyl, thienyl, pyrrolyl, oxazolyl, oxadiazolyl (including 1,2,3 and 1,2,4 oxadiazolyls and furazanyl i.e. 1,2,5-oxadiazolyl), thiazolyl, isoxazolyl, isothiazolyl, pyrazolyl, imidazolyl, triazolyl (including 1,2,3, 1,2,4 and 1,3,4 triazolyls), oxatriazolyl, tetrazolyl, thiadiazolyl (including 1,2,3 and 1,3,4 thiadiazolyls) and the like.

Examples of 6-membered monocyclic heteroaryl groups include but are not limited to pyridinyl, pyrimidinyl, pyridazinyl, pyrazinyl, triazinyl, pyranal, oxazinyl, dioxinyl, thiazinyl, thiadiazinyl and the like. Examples of 6-membered aromatic heterocyclyls containing nitrogen include pyridyl (1 nitrogen), pyrazinyl, pyrimidinyl and pyridazinyl (2 nitrogens).

Aromatic heterocycle groups may also be bicyclic or polycyclic heteroaromatic ring systems such as fused ring systems (including purine, pteridinyl, naphthyridinyl, 1H thieno[2,3-c]pyrazolyl, thieno[2,3-b]furyl and the like) or linked ring systems (such as oligothiophene, polypyrrole and the like). Fused ring systems may also include aromatic 5-membered or 6-membered heterocycles fused to carbocyclic aromatic rings such as phenyl, naphthyl, indenyl, azulenyl, fluorenyl, anthracenyl and the like, such as 5-membered aromatic heterocycles containing nitrogen fused to phenyl rings, 5-membered aromatic heterocycles containing 1 or 2 nitrogens fused to phenyl ring.

A bicyclic heteroaryl group may be, for example, a group selected from: a) a benzene ring fused to a 5- or 6-membered ring containing 1, 2 or 3 ring heteroatoms; b) a pyridine ring fused to a 5- or 6-membered ring containing 1, 2 or 3 ring heteroatoms; c) a pyrimidine ring fused to a 5- or 6-membered ring containing 1 or 2 ring heteroatoms; d) a pyrrole ring fused to a 5- or 6-membered ring containing 1, 2 or 3 ring heteroatoms; e) a pyrazole ring fused to a 5- or 6-membered ring containing 1 or 2 ring heteroatoms; f) an imidazole ring fused to a 5- or 6-membered ring containing 1 or 2 ring heteroatoms; g) an oxazole ring fused to a 5- or 6-membered ring containing 1 or 2 ring heteroatoms; h) an isoxazole ring fused to a 5- or 6-membered ring containing 1 or 2 ring heteroatoms; i) a thiazole ring fused to a 5- or 6-membered ring containing 1 or 2 ring heteroatoms; j) an isothiazole ring fused to a 5- or 6-membered ring containing 1 or 2 ring heteroatoms; k) a thiophene ring fused to a 5- or 6-membered ring containing 1, 2 or 3 ring heteroatoms; l) a furan ring fused to a 5- or 6-membered ring containing 1, 2 or 3 ring heteroatoms; m) a cyclohexyl ring fused to a 5- or 6-membered ring containing 1, 2 or 3 ring heteroatoms; and n) a cyclopentyl ring fused to a 5- or 6-membered ring containing 1, 2 or 3 ring heteroatoms.

Particular examples of bicyclic heteroaryl groups containing a five membered ring fused to another five membered ring include but are not limited to imidazothiazole (e.g. imidazo[2,1-b]thiazole) and imidazoimidazole (e.g. imidazo[1,2-a]imidazole).

Particular examples of bicyclic heteroaryl groups containing a six membered ring fused to a five membered ring include but are not limited to benzofuran, benzothiophene, benzimidazole, benzoxazole, isobenzoxazole, benzisoxazole, benzothiazole, benzisothiazole, isobenzofuran, indole, isoindole, indolizine, indoline, isoindoline, purine (e.g., adenine, guanine), indazole, pyrazolopyrimidine (e.g. pyrazolo[1,5-a]pyrimidine), benzodioxole and pyrazolopyridine (e.g. pyrazolo[1,5-a]pyridine) groups. A further example of a six membered ring fused to a five membered ring is a pyrrolopyridine group such as a pyrrolo[2,3-b]pyridine group.

Particular examples of bicyclic heteroaryl groups containing two fused six membered rings include but are not limited to quinoline, isoquinoline, chroman, thiochroman, chromene, isochromene, isochroman, benzodioxan, quinolizine, benzoxazine, benzodiazine, pyridopyridine, quinoxaline, quinazoline, cinnoline, phthalazine, naphthyridine and pteridine groups.

Examples of heteroaryl groups containing an aromatic ring and a non-aromatic ring include tetrahydronaphthalene, tetrahydroisoquinoline, tetrahydroquinoline, dihydrobenzothiophene,

dihydrobenzofuran, 2,3-dihydro- benzo[1,4]dioxine, benzo[1,3]dioxole, 4,5,6,7-tetrahydrobenzofuran, indoiine, isoindoline and indane groups.

Examples of aromatic heterocycles fused to carbocyclic aromatic rings may therefore include but are not limited to benzothiophenyl, indolyl, isoindolyl, benzofuranyl, isobenzofuranyl, benzimidazolyl, indazolyl, benzoxazolyl, benzisoxazolyl, isobenzoxazolyl, benzothiazolyl, benzisothiazolyl, quinolinyl, isoquinolinyl, quinoxalyl, quinazolinyl, cinnolinyl, benzotriazinyl, phthalazinyl, carbolinyl and the like.

Examples of 5-membered non-aromatic heterocycle rings include 2H-pyrrolyl, 1-pyrrolinyl, 2-pyrrolinyl, 3-pyrrolinyl, pyrrolidinyl, 1-pyrrolidinyl, 2-pyrrolidinyl, 3-pyrrolidinyl, tetrahydrofuranyl, tetrahydrothiophenyl, pyrazolyl, 2-pyrazolyl, 3-pyrazolyl, pyrazolidinyl, 2-pyrazolidinyl, 3-pyrazolidinyl, imidazolidinyl, 3-dioxalanyl, thiazolidinyl, isoxazolidinyl, 2-imidazolinyl and the like.

Examples of 6-membered non-aromatic heterocycles include piperidinyl, piperidinonyl, pyranyl, dihydropyranyl, tetrahydropyranyl, 2H pyranyl, 4H pyranyl, thianyl, thianyl oxide, thianyl dioxide, piperazinyl, diozanyl, 1,4-dioxinyl, 1,4-dithianyl, 1,3,5-triozalanlyl, 1,3,5-trithianyl, 1,4-morpholinyl, thiomorpholinyl, 1,4-oxathianyl, triazinyl, 1,4-thiazinyl and the like.

Examples of 7-membered non-aromatic heterocycles include azepanyl, oxepanyl, thiepanyl and the like.

"N-heterocyclic" refers to mono or bicyclic rings or ring systems that include at least one nitrogen heteroatom. The rings or ring systems generally include 1 to 9 carbon atoms in addition to the heteroatom(s) and may be saturated, unsaturated or aromatic (including pseudoaromatic). The term "pseudoaromatic" refers to a ring system which is not strictly aromatic, but which is stabilized by means of delocalization of electrons and behaves in a similar manner to aromatic rings.

Aromatic includes pseudoaromatic ring systems, such as pyrrolyl rings.

Examples of 5-membered monocyclic N-heterocycles include pyrrolyl, H-pyrrolyl, pyrrolinyl, pyrrolidinyl, oxazolyl, oxadiazolyl, (including 1,2,3 and 1,2,4 oxadiazolyls) isoxazolyl, furazanyl, thiazolyl, isothiazolyl, pyrazolyl, pyrazolinyl, pyrazolidinyl, imidazolyl, imidazolinyl, triazolyl (including 1,2,3 and 1,3,4 triazolyls), tetrazolyl, thiadiazolyl (including 1,2,3 and 1,3,4 thiadiazolyls), and dithiazolyl

Examples of 6-membered monocyclic N-heterocycles include pyridyl, pyrimidinyl, pyridazinyl, pyrazinyl, piperidinyl, morpholinyl, thiomorpholinyl, piperazinyl, and triazinyl. The

heterocycles may be optionally substituted with a broad range of substituents, and preferably with C₁₋₆ alkyl, C₁₋₆ alkoxy, C₂₋₆ alkenyl, C₂₋₆ alkynyl, halo, hydroxy, mercapto, trifluoromethyl, amino, cyano or mono or di(C₁₋₆alkyl)amino. The N-heterocyclic group may be fused to a carbocyclic ring such as phenyl, naphthyl, indenyl, azulenyl, fluorenyl, and anthracenyl.

5 Examples of 8, 9 and 10-membered bicyclic heterocycles include 1H thieno[2,3-c]pyrazolyl, indolyl, isoindolyl, benzoxazolyl, benzothiazolyl, benzisoxazolyl, benzisothiazolyl, benzimidazolyl, indazolyl, isoquinolinyl, quinolinyl, quinoxalyl, purinyl, cinnolinyl, phthalazinyl, quinazolinyl, quinoxalyl, benzotriazinyl, and the like. These heterocycles may be optionally substituted, for example with C₁₋₆ alkyl, C₁₋₆ alkoxy, C₂₋₆ alkenyl, C₂₋₆ alkynyl, halo, hydroxy, mercapto, trifluoromethyl, amino, cyano or mono or di(C₁₋₆alkyl)amino. Unless
10 otherwise defined optionally substituted N-heterocyclics includes pyridinium salts and the N-oxide form of suitable ring nitrogens.

 The term "hydroxyl" is represented by the formula –OH.

 "Isonitrile" refers to –NC.

15 "Nitrile" refers to –CN.

 "Nitro" refers to an R-group having the structure –NO₂.

 As used herein, the term "organic" includes polymeric materials as well as small molecule organic materials that may be used to fabricate organic opto-electronic devices. "Small molecule" refers to any organic material that is not a polymer, and "small molecules" may actually be quite
20 large. Small molecules may include repeat units in some circumstances. For example, using a long chain alkyl group as a substituent does not remove a molecule from the "small molecule" class. Small molecules may also be incorporated into polymers, for example as a pendent group on a polymer backbone or as a part of the backbone. Small molecules may also serve as the core moiety of a dendrimer, which consists of a series of chemical shells built on the core moiety. The core
25 moiety of a dendrimer may be a fluorescent or phosphorescent small molecule emitter. A dendrimer may be a "small molecule," and it is believed that all dendrimers currently used in the field of OLEDs are small molecules.

 "Phosphinyl" refers to –PRR' wherein R and R' to substituted groups.

 "Silyl" refers to –SiH₃ or SiR₃, wherein R is a substituted group.

30 A "substituent" refers to a single atom (for example, a halogen atom) or a group of two or more atoms that are covalently bonded to each other, which are covalently bonded to an atom or

atoms in a molecule to satisfy the valency requirements of the atom or atoms of the molecule, typically in place of a hydrogen atom. Examples of substituents include alkyl groups, hydroxyl groups, alkoxy groups, acyloxy groups, mercapto groups, and aryl groups.

As used herein, "solution processible" means capable of being dissolved, dispersed, or transported in and/or deposited from a liquid medium, either in solution or suspension form.

"Substituted" or "substitution" refers to replacement of a hydrogen atom of a molecule or an R-group with one or more additional R-groups. Unless otherwise defined, the term "optionally substituted" or "optional substituent" as used herein refers to a group which may or may not be further substituted with 1, 2, 3, 4 or more groups, preferably 1, 2 or 3, more preferably 1 or 2 groups selected from the group consisting of C₁₋₆alkyl, C₂₋₆alkenyl, C₂₋₆alkynyl, C₃₋₈cycloalkyl, hydroxyl, oxo, C₁₋₆alkoxy, aryloxy, C₁₋₆alkoxyaryl, halo, C₁₋₆alkylhalo (such as CF₃ and CHF₂), C₁₋₆alkoxyhalo (such as OCF₃ and OCHF₂), carboxyl, esters, cyano, nitro, amino, substituted amino, disubstituted amino, acyl, ketones, amides, aminoacyl, substituted amides, disubstituted amides, thiol, alkylthio, thioxo, sulfates, sulfonates, sulfinyl, substituted sulfinyl, sulfonyl, substituted sulfonyl, sulfonylamides, substituted sulfonamides, disubstituted sulfonamides, aryl, arC₁₋₆alkyl, heterocyclyl and heteroaryl wherein each alkyl, alkenyl, alkynyl, cycloalkyl, aryl and heterocyclyl and groups containing them may be further optionally substituted. Optional substituents in the case of heterocycles containing N may also include but are not limited to C₁₋₆alkyl i.e. *N*-C₁₋₃alkyl, more preferably methyl particularly *N*-methyl.

The term "sulfinyl" refers to the group -S(=O)H.

The term "substituted sulfinyl" or "sulfoxide" refers to a sulfinyl group having the hydrogen replaced with, for example a C₁₋₆alkyl group ("C₁₋₆alkylsulfinyl" or "C₁₋₆alkylsulfoxide"), an aryl ("arylsulfinyl"), an aralkyl ("aralkyl sulfinyl") and so on. C₁₋₃alkylsulfinyl groups are preferred, such as for example, -SOMethyl, -SOethyl and -SOPropyl.

The term "sulfonyl" refers to the group -SO₂H.

The term "substituted sulfonyl" refers to a sulfonyl group having the hydrogen replaced with, for example a C₁₋₆alkyl group ("sulfonylC₁₋₆alkyl"), an aryl ("arylsulfonyl"), an aralkyl ("aralkylsulfonyl") and so on. SulfonylC₁₋₃alkyl groups are preferred, such as for example, -SO₂Me, -SO₂Et and -SO₂Pr.

The term "sulfonylamido" or "sulfonamide" refers to the group -SO₂NH₂.

The term "sulfate" refers to the group $-\text{OS}(\text{O})_2\text{OH}$ and includes groups having the hydrogen replaced with, for example a C_{1-6} alkyl group ("alkylsulfates"), an aryl ("arylsulfate"), an aralkyl ("aralkylsulfate") and so on. C_{1-3} sulfates are preferred, such as for example, $\text{OS}(\text{O})_2\text{OMe}$, $\text{OS}(\text{O})_2\text{OEt}$ and $\text{OS}(\text{O})_2\text{OPr}$.

5 The term "sulfonate" refers to the group $-\text{SO}_3\text{H}$ and includes groups having the hydrogen replaced with, for example a C_{1-6} alkyl group ("alkylsulfonate"), an aryl ("arylsulfonate"), an aralkyl ("aralkylsulfonate") and so on. C_{1-3} sulfonates are preferred, such as for example, SO_3Me , SO_3Et and SO_3Pr .

10 The term "thioether" refers to a $-\text{S}-\text{R}$ group, wherein R may be, for example, alkyl (including substituted alkyl), or aryl (including substituted aryl).

The term "thiol" refers to $-\text{SH}$. A "substituted thiol" refers to a $-\text{S}-\text{R}$ group wherein R is not an aliphatic or aromatic group. For instance, a substituted thiol may be a halogenated thiol such as, for example, $-\text{SF}_5$.

The term "thioxo" refers to the group $=\text{S}$.

15 As used herein, "top" means furthest away from the substrate, while "bottom" means closest to the substrate. Where a first layer is described as "disposed over" a second layer, the first layer is disposed further away from substrate. There may be other layers between the first and second layer, unless it is specified that the first layer is "in contact with" the second layer. For example, a cathode may be described as "disposed over" an anode, even though there are various organic layers in
20 between.

A ligand may be referred to as "photoactive" when it is believed that the ligand directly contributes to the photoactive properties of an emissive material. A ligand may be referred to as "ancillary" when it is believed that the ligand does not contribute to the photoactive properties of an emissive material, although an ancillary ligand may alter the properties of a photoactive ligand.

25 As used herein, and as would be generally understood by one skilled in the art, a first "Highest Occupied Molecular Orbital" (HOMO) or "Lowest Unoccupied Molecular Orbital" (LUMO) energy level is "greater than" or "higher than" a second HOMO or LUMO energy level if the first energy level is closer to the vacuum energy level. Since ionization potentials (IP) are measured as a negative energy relative to a vacuum level, a higher HOMO energy level
30 corresponds to an IP having a smaller absolute value (an IP that is less negative). Similarly, a higher LUMO energy level corresponds to an electron affinity (EA) having a smaller absolute value

(an EA that is less negative). On a conventional energy level diagram, with the vacuum level at the top, the LUMO energy level of a material is higher than the HOMO energy level of the same material. A "higher" HOMO or LUMO energy level appears closer to the top of such a diagram than a "lower" HOMO or LUMO energy level.

5 As used herein, and as would be generally understood by one skilled in the art, a first work function is "greater than" or "higher than" a second work function if the first work function has a higher absolute value. Because work functions are generally measured as negative numbers relative to vacuum level, this means that a "higher" work function is more negative. On a conventional energy level diagram, with the vacuum level at the top, a "higher" work function is illustrated as
10 further away from the vacuum level in the downward direction. Thus, the definitions of HOMO and LUMO energy levels follow a different convention than work functions.

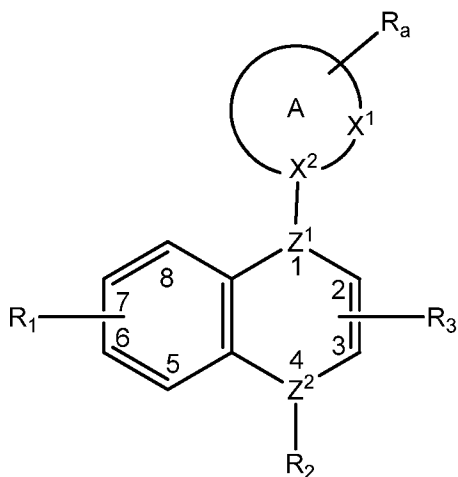
Overview

15 Using 1,4-azaborine to replace the regular aromatic in the ligands for metal complexes such as Ir(2-phenylpyridine)₃ offers a new avenue for novel aromatic, high triplet compounds for application in organic electronics. Novel azaborine compounds are provided that may be used as host, fluorescent emissive dopant, phosphorescent emissive dopant or charge transport materials in organic light-emitting devices. 1,4-azaborine compounds are particularly interesting heteroaromatic
20 molecules because of the boron and nitrogen heteroatoms in the core of the compound. These 1,4-azaborine compounds can display high singlet and triplet energies due to the reduced conjugation relative to their all-carbon congeners, and they may be luminescent. Metal complexes containing 1,4-azaborine ligands may be useful as the phosphorescent emitters in PHOLEDs. Compared to their all-carbon congeners, the 1,4-azaborine analogs may show higher photophysical and
25 electrochemical tunability because of the relatively higher polarized nature of the azaborine ring.

 In certain embodiments, metal complexes containing 1,4-azaborine ligands may be useful as blue luminescent materials or high triplet charge transport materials in OLEDs. For example, the metal complexes may exhibit strong blue, Gaussian type, phosphorescence (for example, $\lambda_{\text{max}} < 460 \text{ nm}$, PLQE > 80%). The metal complexes also can be used in phosphorescent devices, in
30 single color or multiple color devices. In certain embodiments, the materials disclosed herein can be vapor-evaporated or solution processed.

Compounds and Complexes

In one embodiment disclosed herein there is provided a 1,4-azaborine compound having a structure of formula A:



Ring A includes a 5-membered or 6-membered carbocycle or heterocycle. In certain embodiments, A is an optionally-substituted N-heterocycle, particularly a lower alkyl-substituted N-heterocycle.

Each R_a is independently selected from hydrogen, deuterium, halide, optionally-substituted alkyl, optionally-substituted cycloalkyl, optionally-substituted heteroalkyl, optionally-substituted arylalkyl, optionally-substituted alkoxy, optionally-substituted aryloxy, optionally-substituted amino, silyl, optionally-substituted alkenyl, optionally-substituted cycloalkenyl, optionally-substituted heteroalkenyl, alkynyl, aryl, heteroaryl, acyl, carbonyl, carboxylic acid, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, optionally-substituted amido, optionally-substituted phosphoryl, optionally-substituted thiophosphoryl, optionally-substituted phosphinyl, optionally-substituted thiophosphinyl, thioester, nitro, azido, optionally-substituted hydrazinyl, optionally-substituted diazenyl, or thiocarbonyl. The ring A substituents can join together to form one or more fused rings. For example, two of the substituents may join together to form a fused ring structure so that ring A is a naphthyl, indolyl, quinolinyl, isoquinolinyl, or other fused rings. In certain embodiments at least one R_a is a lower alkyl. In preferred embodiments, one R_a is a lower alkyl

and the remaining R_a are hydrogen atoms. In other preferred embodiments, R_a are all hydrogen atoms.

X^1 represents C, N, S, O or Se. X^2 represents C or N. In certain embodiments at least one of X^1 or X^2 is N. In preferred embodiments, X^2 is C, and X^1 is N.

5 Z^1 is B and Z^2 is N, or Z^1 is N and Z^2 is B.

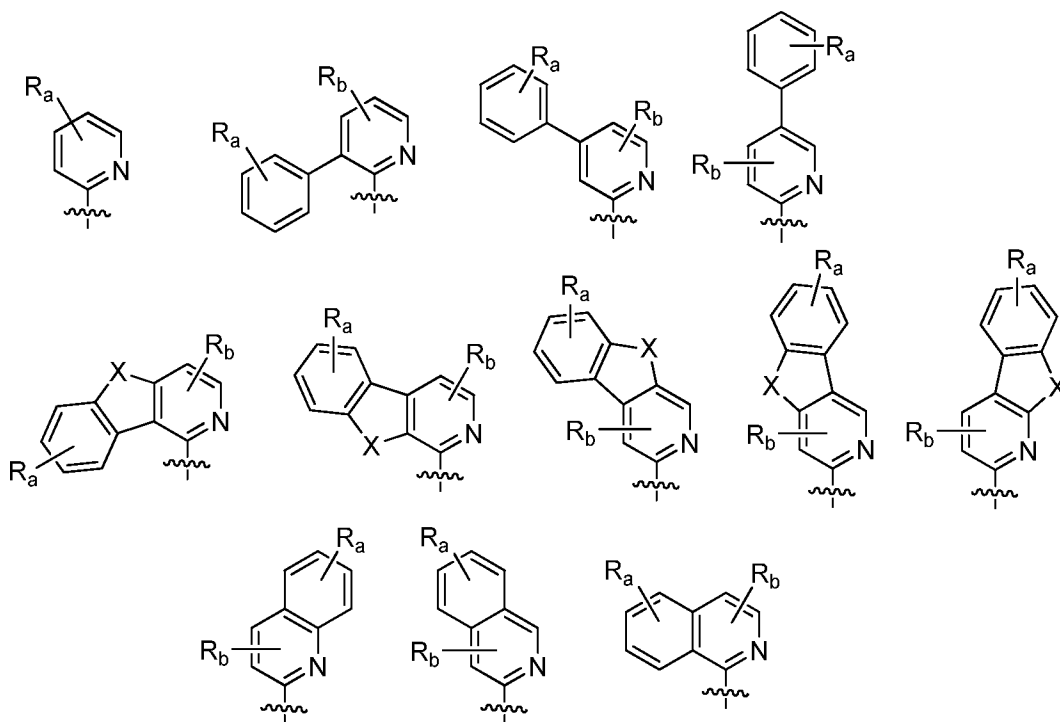
Each R_1 is independently selected from hydrogen, deuterium, halide, optionally-substituted alkyl, optionally-substituted cycloalkyl, optionally-substituted heteroalkyl, optionally-substituted arylalkyl, optionally-substituted alkoxy, optionally-substituted aryloxy, optionally-substituted amino, silyl, optionally-substituted alkenyl, optionally-substituted cycloalkenyl, optionally-substituted heteroalkenyl, optionally-substituted alkynyl, optionally-substituted aryl, optionally-substituted heteroaryl, optionally-substituted acyl, carbonyl, carboxylic acid, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, optionally-substituted amido, optionally-substituted phosphoryl, optionally-substituted thiophosphoryl, optionally-substituted phosphinyl, optionally-substituted thiophosphinyl, thioester, nitro, azido, optionally-substituted hydrazinyl, optionally-substituted diazenyl, or thiocarbonyl. The substituents can join together to form one or more fused rings. In preferred embodiments, R_1 are all hydrogen atoms.

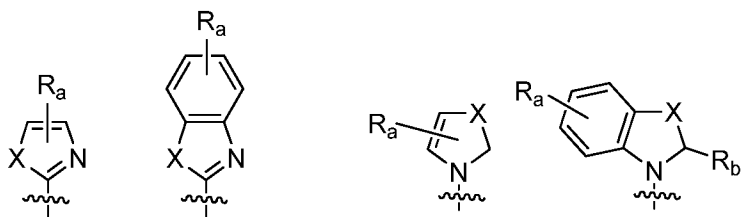
R_2 is independently selected from hydrogen, deuterium, halide, optionally-substituted alkyl, optionally-substituted cycloalkyl, optionally-substituted heteroalkyl, optionally-substituted arylalkyl, optionally-substituted alkoxy, optionally-substituted aryloxy, optionally-substituted amino, silyl, optionally-substituted alkenyl, optionally-substituted cycloalkenyl, optionally-substituted heteroalkenyl, optionally-substituted alkynyl, optionally-substituted aryl, optionally-substituted heteroaryl, acyl, carbonyl, carboxylic acid, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, optionally-substituted amido, optionally-substituted phosphoryl, optionally-substituted thiophosphoryl, optionally-substituted phosphinyl, optionally-substituted thiophosphinyl, thioester, nitro, azido, optionally-substituted hydrazinyl, optionally-substituted diazenyl, or thiocarbonyl. In certain embodiments, R_2 is hydrogen, lower alkyl (which may or may not be substituted), or aryl (which may or may not be substituted). In particularly preferred embodiments, R_2 is hydrogen, lower alkyl (which may or may not be substituted), or unsubstituted phenyl. In further embodiments, R_2 is substituted phenyl, particularly alkyl-substituted phenyl or phenyl-substituted phenyl. For example, R_2 may be 2,4,6-trialkyl-substituted phenyl (e.g., 2,4,6-trimethyl-phenyl (also referred to herein as mesityl (Mes) phenyl)), or R_2 may be 2,4,6-triphenyl-phenyl or 2,6-

diphenyl-phenyl. Although not bound by any theory, mesityl phenyl may impart significantly improved stability toward air and moisture.

Each R_3 is independently selected from hydrogen, deuterium, halide, optionally-substituted alkyl, optionally-substituted cycloalkyl, optionally-substituted heteroalkyl, optionally-substituted arylalkyl, optionally-substituted alkoxy, optionally-substituted aryloxy, optionally-substituted amino, silyl, optionally-substituted alkenyl, optionally-substituted cycloalkenyl, optionally-substituted heteroalkenyl, optionally-substituted alkynyl, optionally-substituted aryl, optionally-substituted heteroaryl, acyl, carbonyl, carboxylic acid, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, optionally-substituted amido, optionally-substituted phosphoryl, optionally-substituted thiophosphoryl, optionally-substituted phosphinyl, optionally-substituted thiophosphinyl, thioester, nitro, azido, optionally-substituted hydrazinyl, optionally-substituted diazenyl, or thiocarbonyl. In certain embodiments, R_3 are all hydrogen atoms.

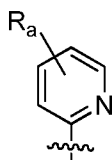
In certain embodiments, A is selected from:





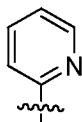
X in the above embodiments for A is selected from S, NZ, O, Se, BZ, CZZ', or C=O. Z and Z' are each independently selected from hydrogen, alkyl, or aryl. Each of R_a and R_b is independently selected from hydrogen, deuterium, halide, alkyl, cycloalkyl, heteroalkyl, arylalkyl, alkoxy, aryloxy, amino, silyl, alkenyl, cycloalkenyl, heteroalkenyl, alkynyl, aryl, heteroaryl, acyl, carbonyl, carboxyl, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, amido, phosphoryl, thiophosphoryl, phosphinyl, thiophosphinyl, thioester, nitro, azido, hydrazinyl, diazenyl, or thiocarbonyl. The substituents can join together to form one or more fused rings.

10 In one embodiment,



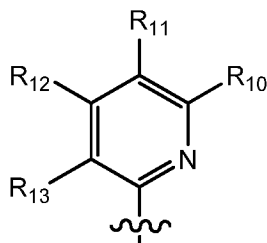
is preferred.

In a further embodiment,



is preferred.

In another preferred embodiment, A is



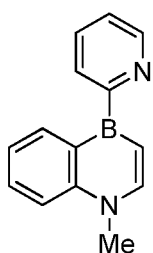
, wherein R_{10} is an alkyl, particularly a lower alkyl; and R_{11} - R_{13} are each H.

15 In a preferred embodiment, A is optionally-substituted pyridinyl; R_1 is hydrogen; R_2 is hydrogen, alkyl or aryl; and R_3 is hydrogen or alkyl. In a further preferred embodiment, A is optionally-substituted pyridinyl; Z^1 is N; Z^2 is B; R_1 is hydrogen; R_2 is hydrogen, lower alkyl or unsubstituted phenyl; and R_3 is hydrogen or alkyl. In an additional preferred embodiment, Z^1 is B; Z^2 is N; R_1 is hydrogen; R_2 is hydrogen, lower alkyl or aryl; and R_3 is hydrogen or lower alkyl. In

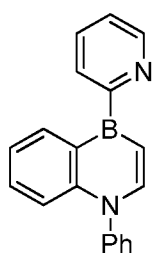
another preferred embodiment, A is optionally-substituted pyridinyl (particularly unsubstituted pyridinyl); Z^1 is N; Z^2 is B; R_1 is hydrogen; R_2 is substituted phenyl (particularly 2,4,6-trialkyl-phenyl, 2,4,6-triphenyl-phenyl, or 2,6-diphenyl-phenyl); and R_3 is hydrogen or alkyl.

Some specific examples are:

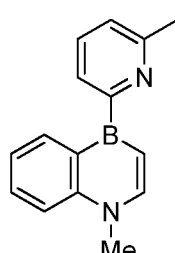
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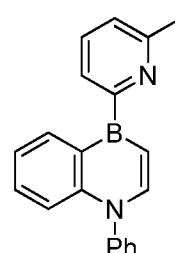
Compound 1L



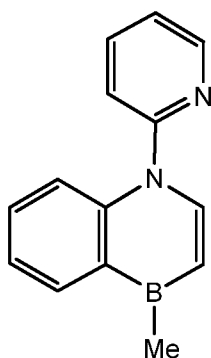
Compound 2L



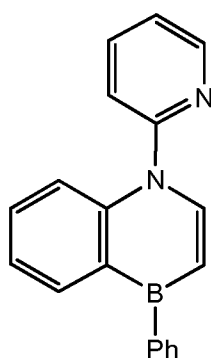
Compound 3L



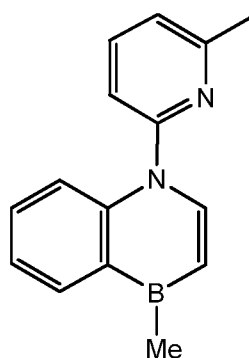
Compound 4L



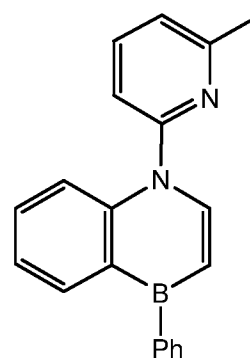
Compound 5L



Compound 6L

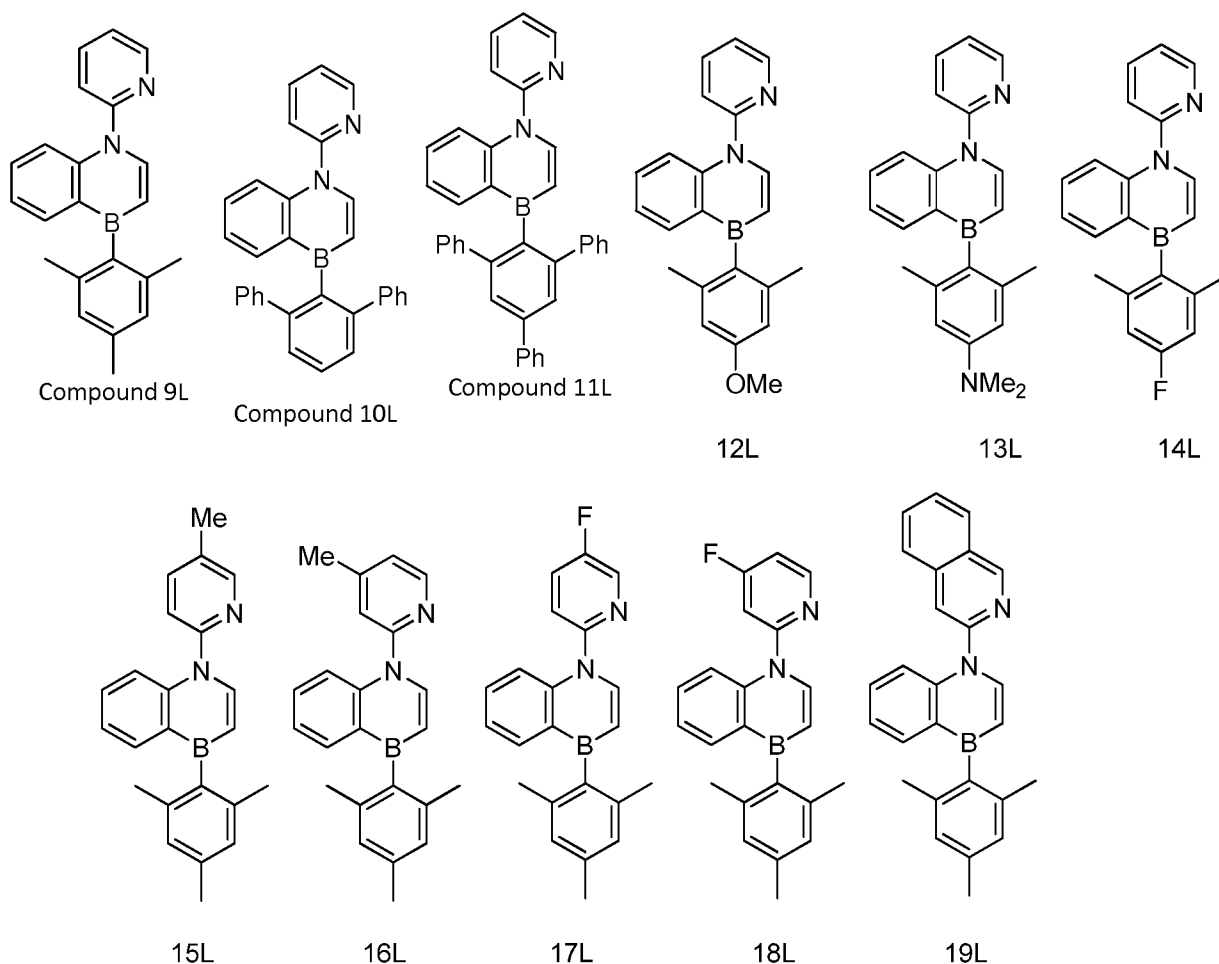


Compound 7L

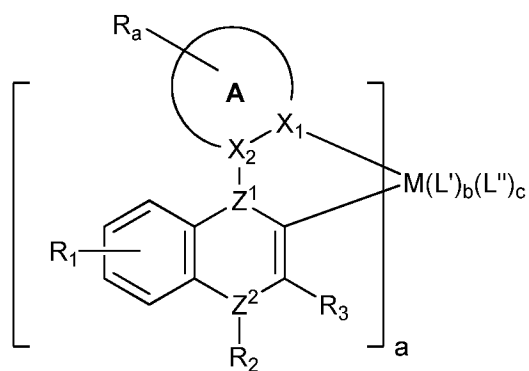


Compound 8L

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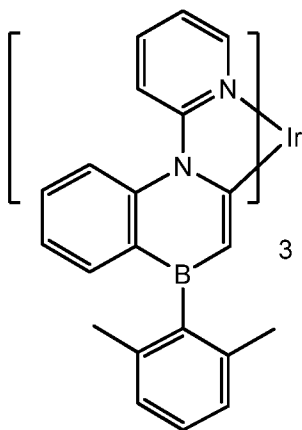


In certain embodiments, the compounds of formula A may be used as a moiety or ligand in forming metal complexes. Illustrative metal complexes of 1,4-azaborine ligands are:

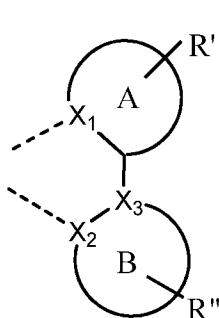


wherein L' and L'' are mono, bi or tri ligands; M is a metal; a is 1, 2, or 3; b is 0, 1, or 2; c is 0, 1 or 2; a+b+c is n, wherein n is the oxidation state of the metal M; and A, X₁, X₂, Z¹, Z², R_a, R₁, R₂ and R₃ are as described above in connection with Formula A. In certain embodiments, M is a second or third row transition metal. In particular embodiments, M is Ir. In further embodiments, M is Pt.

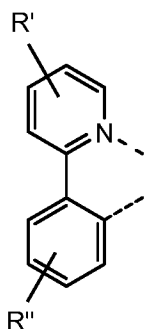
5 In certain embodiments, Formula B does not include:



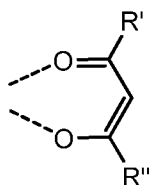
In one embodiment, L' and L'' are independently selected from:



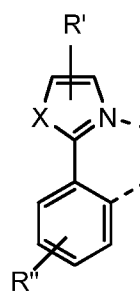
FORMULA I



FORMULA IV

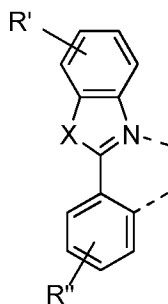


FORMULA V

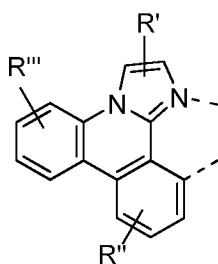


FORMULA VI

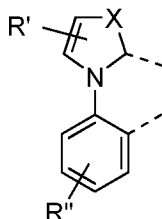
10



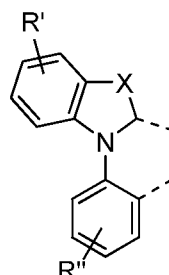
FORMULA VII



FORMULA VIII



FORMULA IX

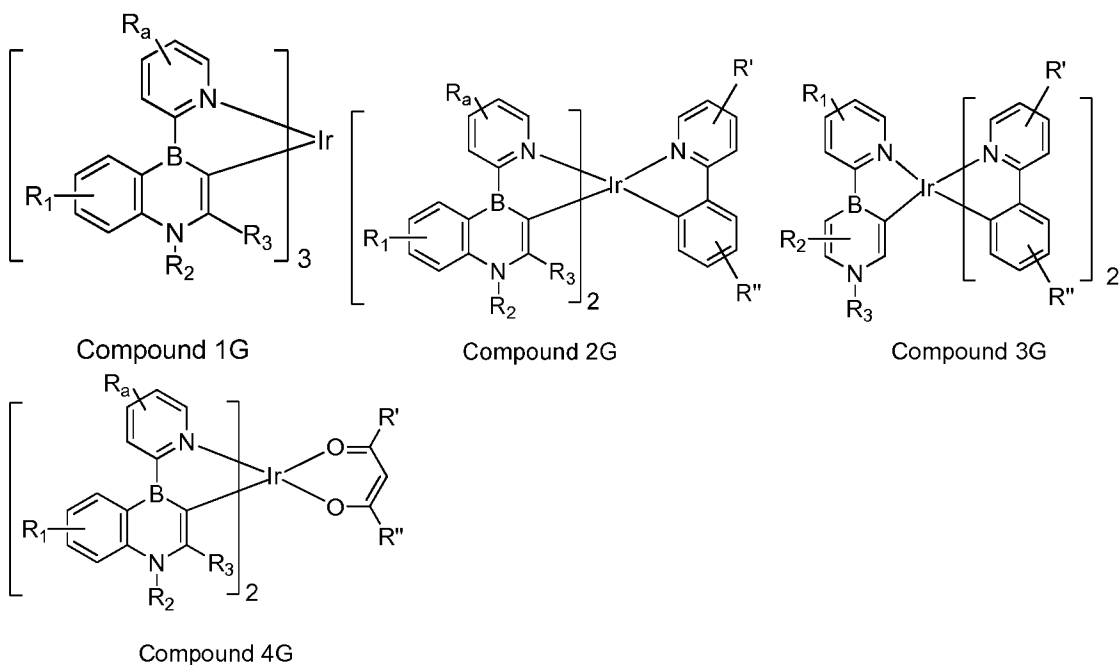


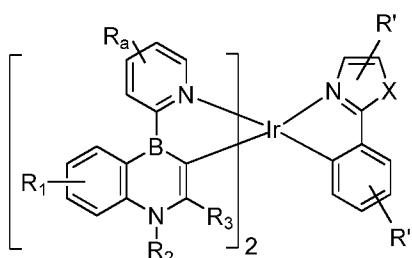
FORMULA X

wherein each R', R'', and R''' is independently selected from hydrogen, alkyl, alkoxy, amino, alkenyl, alkynyl, arylalkyl, aryl, or heteroaryl. X is selected from S, NZ, O, Se, BZ, CZZ', or C=O. Z and Z' are independently selected from hydrogen, alkyl, or aryl. R', R'', and R''' can join to

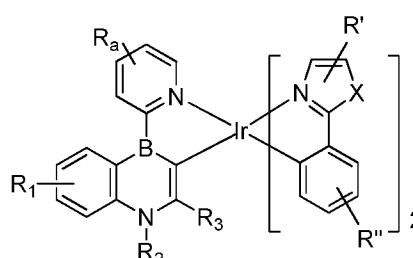
5 form one or more fused rings.

Illustrative metal complexes include:

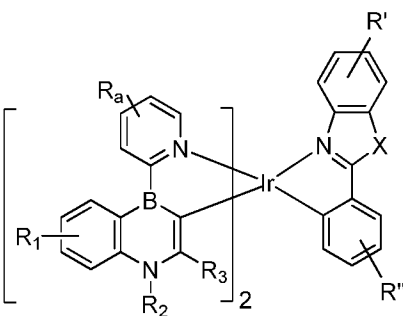




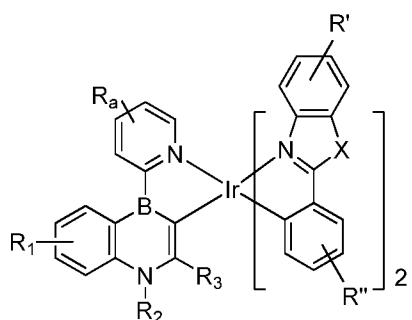
Compound 5G



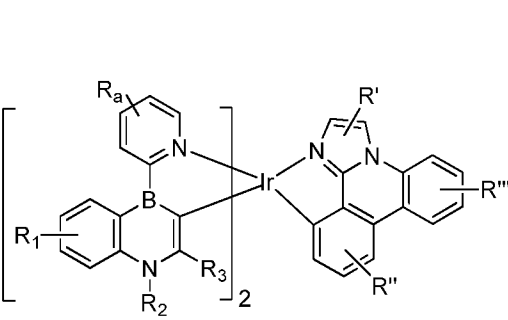
Compound 6G



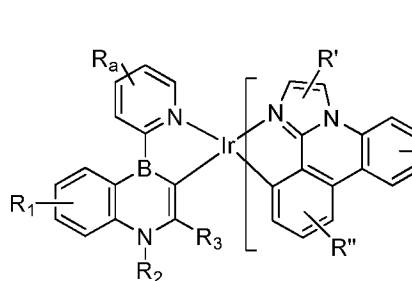
Compound 7G



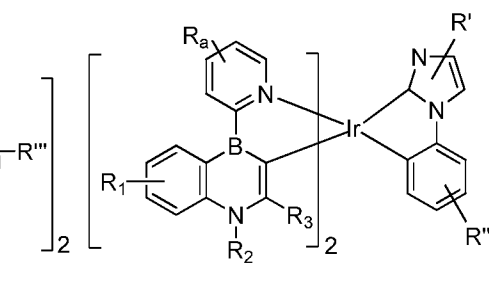
Compound 8G



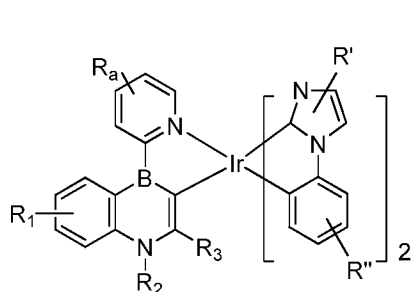
Compound 9G



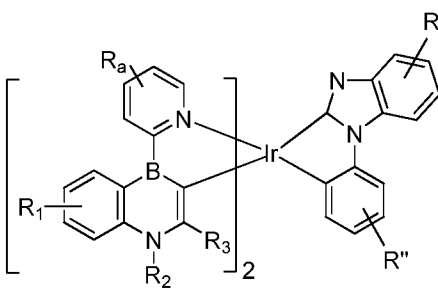
Compound 10G



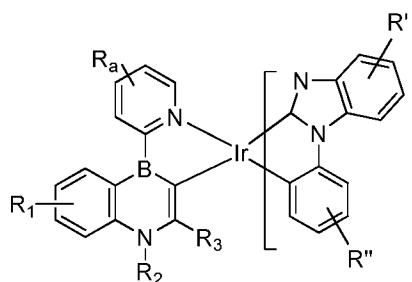
Compound 11G



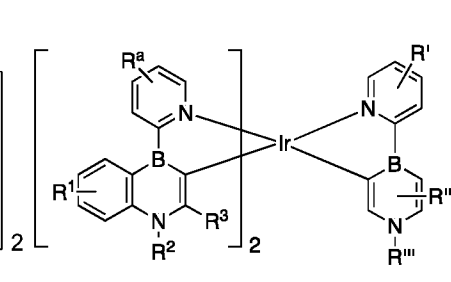
Compound 12G



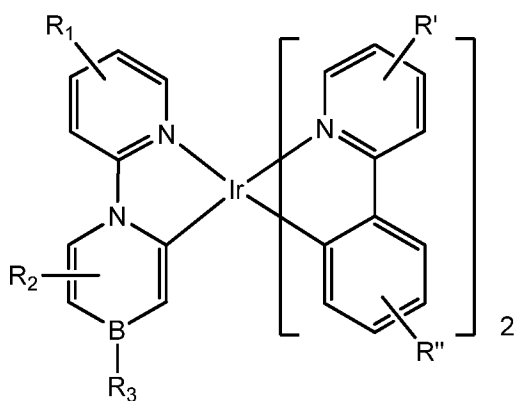
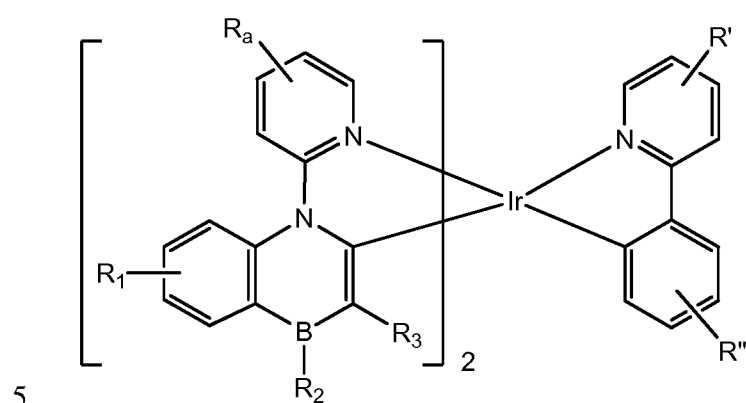
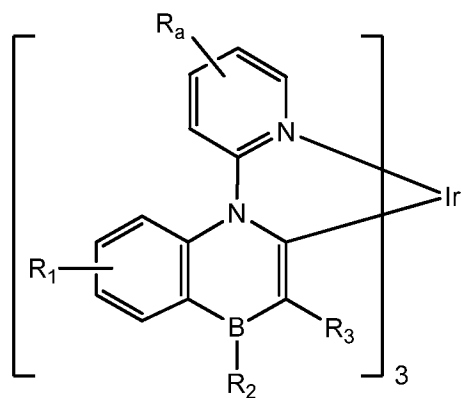
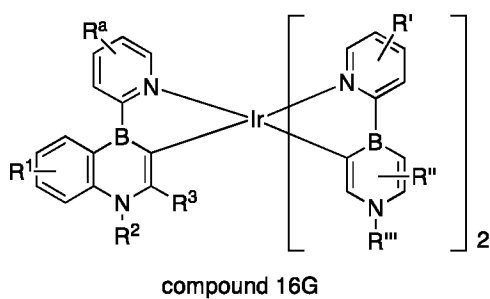
Compound 13G

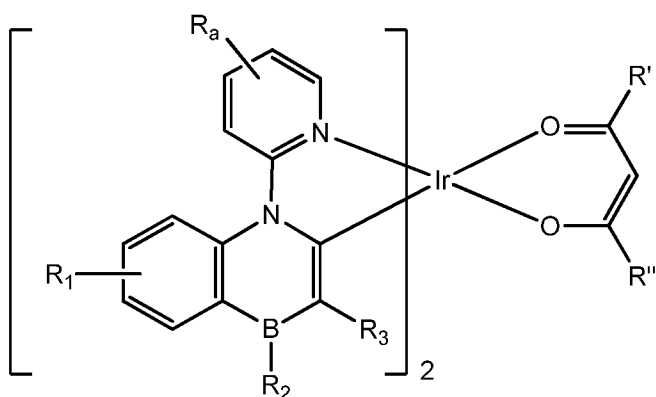


Compound 14G

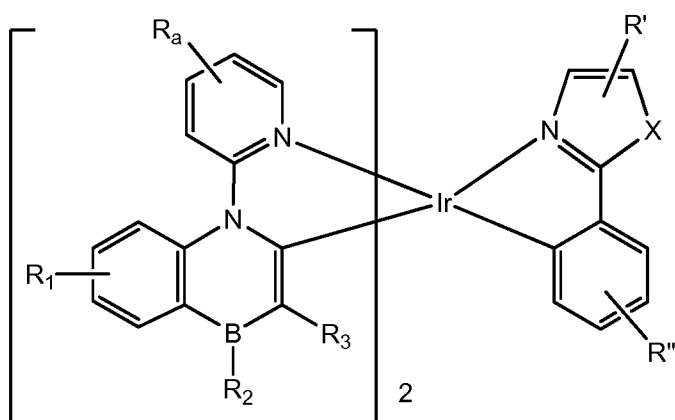


Compound 15G



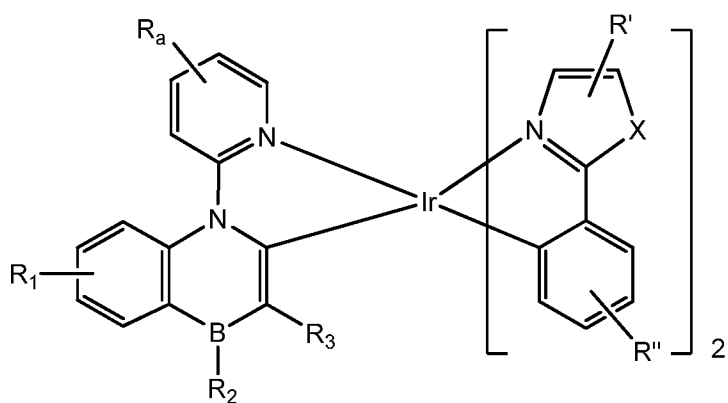


Compound 20G

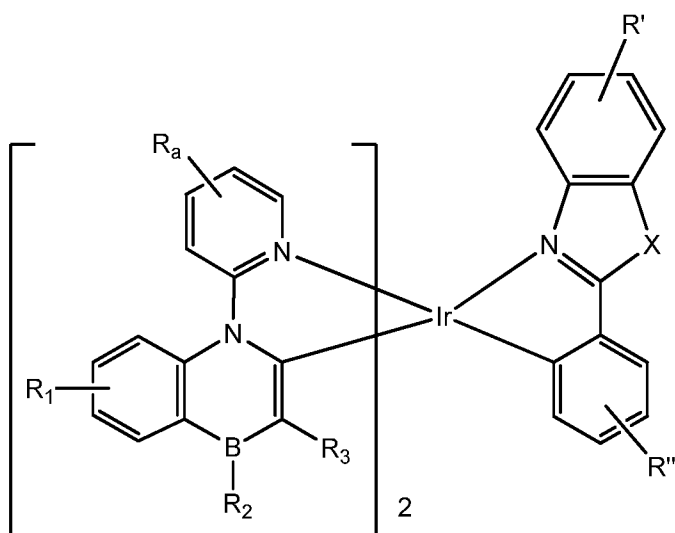


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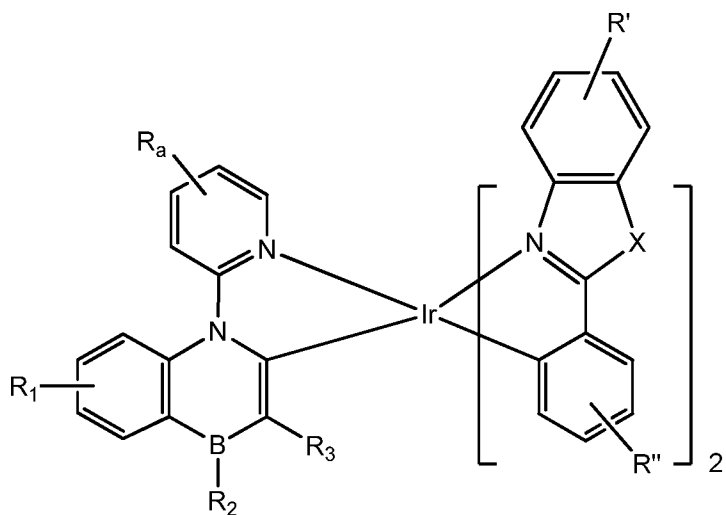
Compound 21G



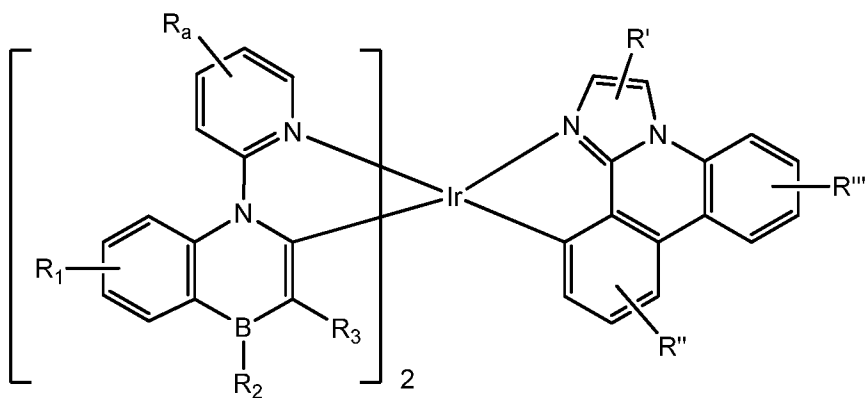
Compound 22G



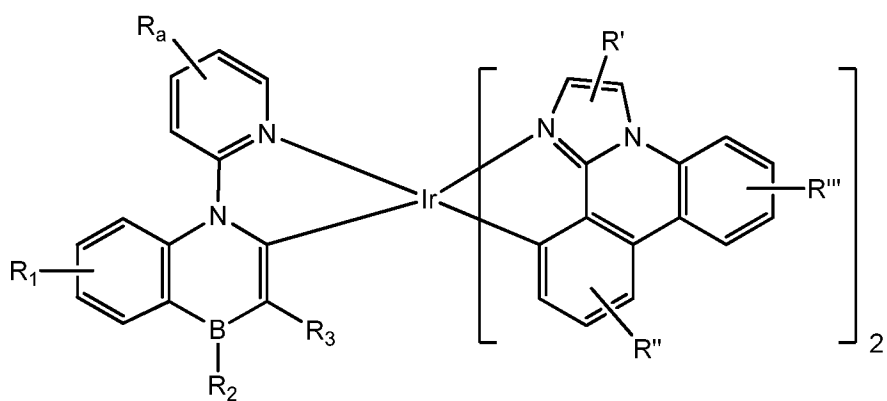
Compound 23G



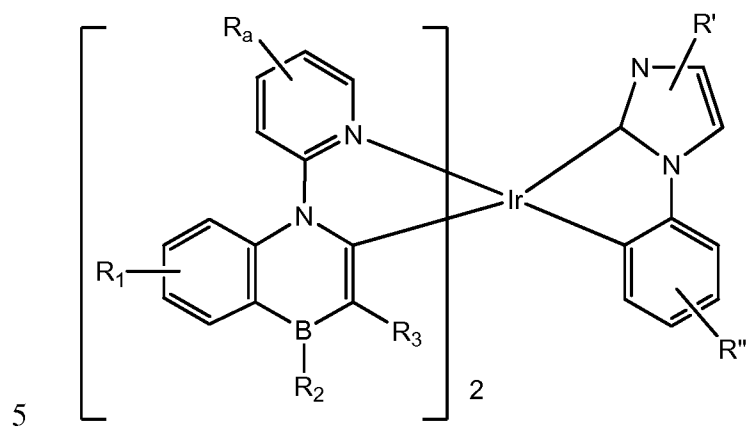
5 Compound 24G



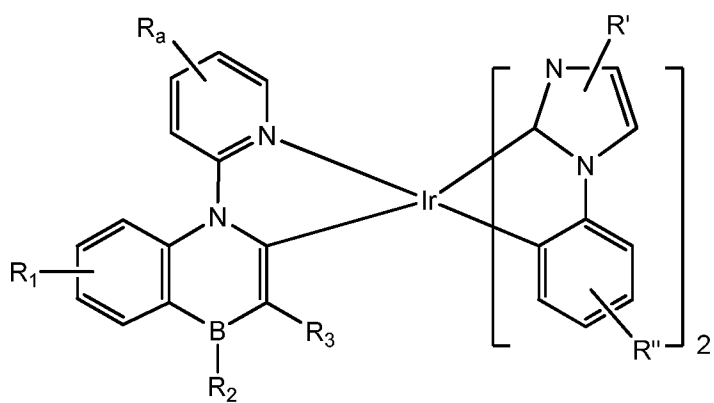
Compound 25G



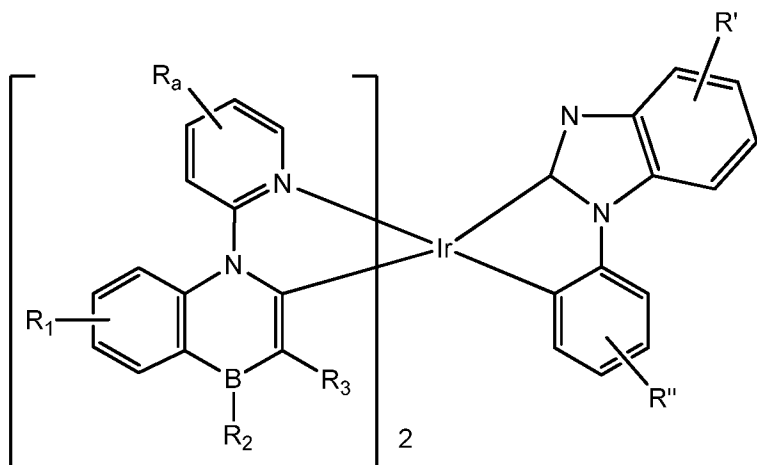
Compound 26G



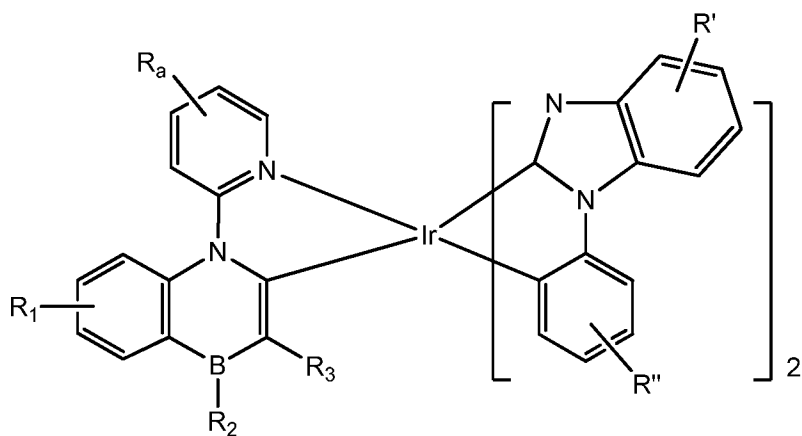
Compound 27G



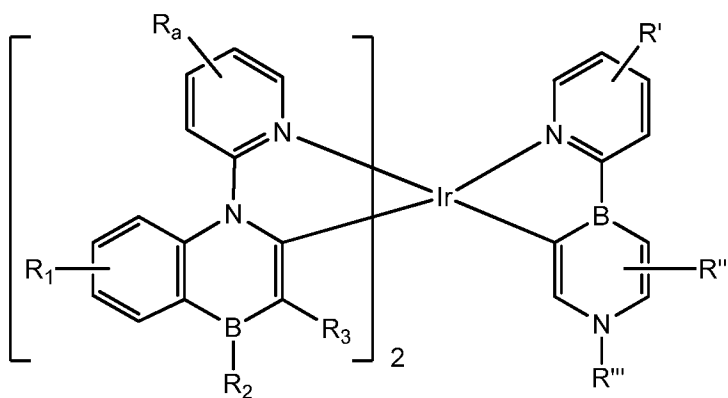
Compound 28G



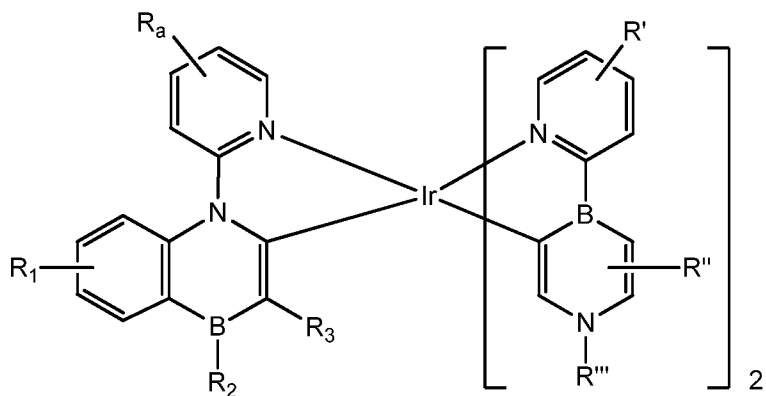
Compound 29G



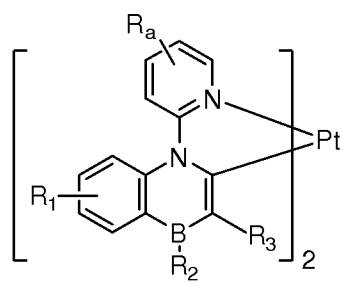
5 Compound 30G



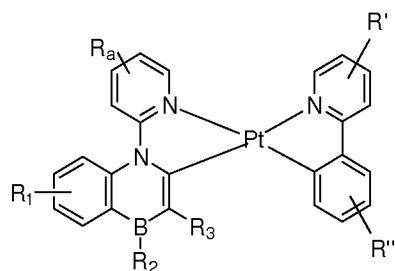
Compound 31G



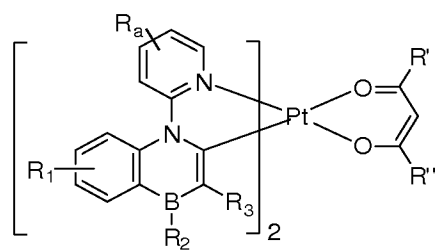
Compound 32G



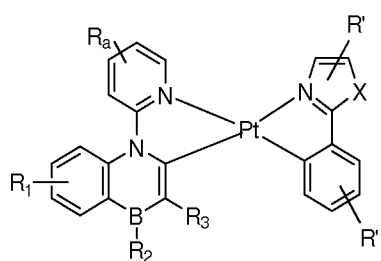
Compound 33G



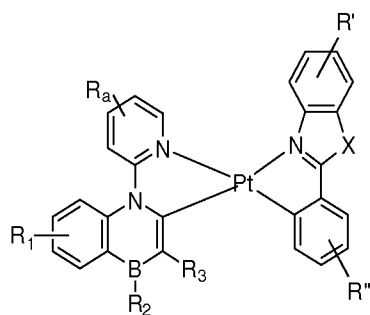
Compound 34G



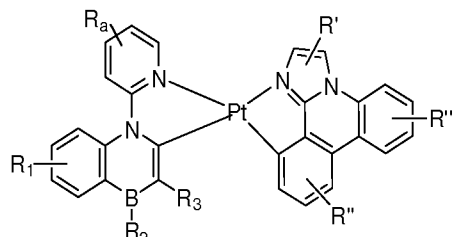
Compound 35G



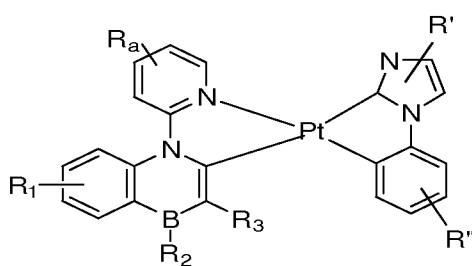
Compound 36G



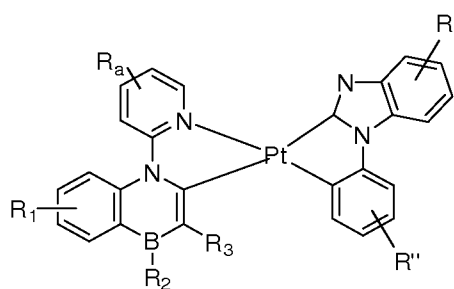
Compound 37G



Compound 38G

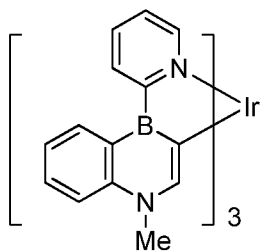


Compound 39G

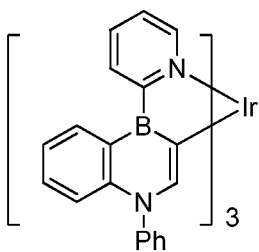


Compound 40G

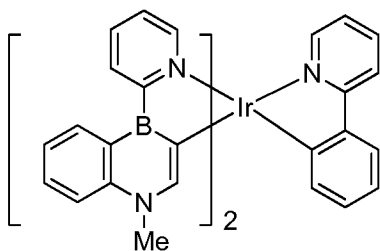
5 Specific examples include:



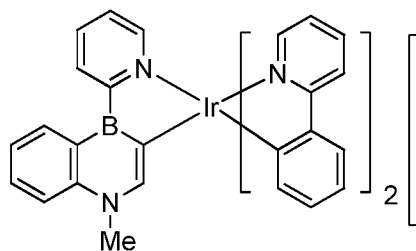
Compound 1



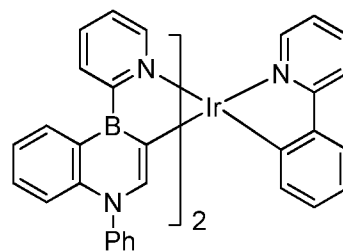
Compound 2



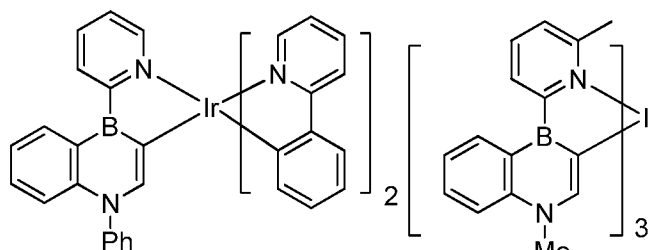
Compound 3



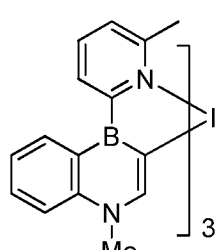
Compound 4



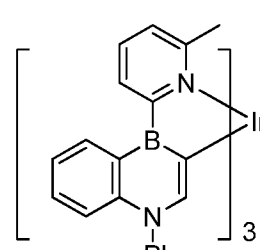
Compound 5



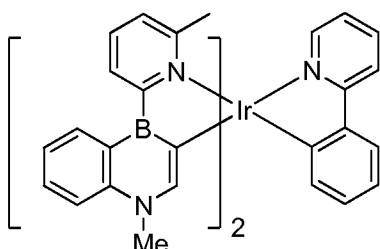
Compound 6



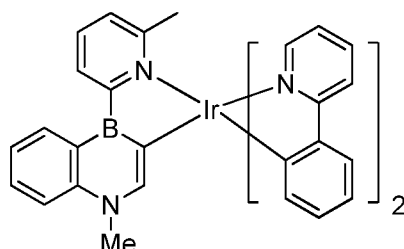
Compound 7



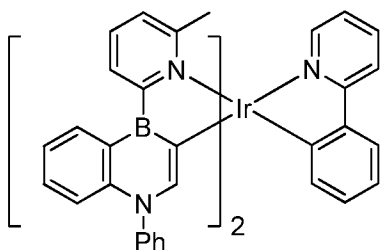
Compound 8



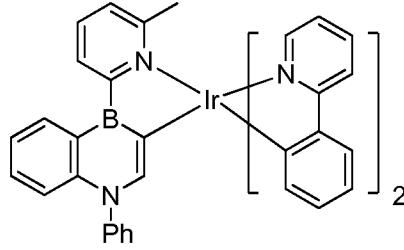
Compound 9



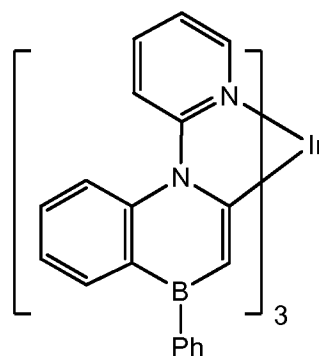
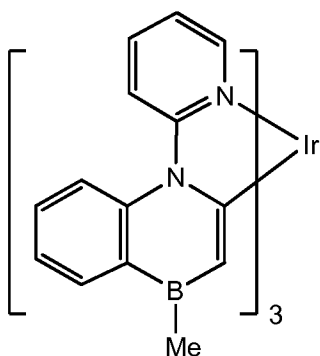
Compound 10



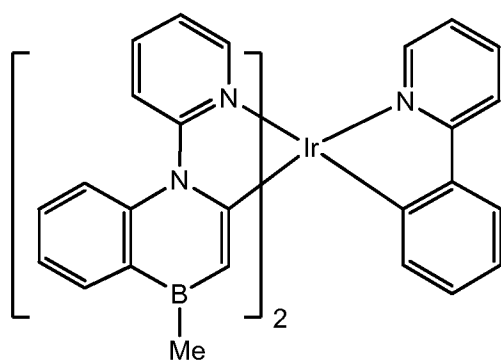
Compound 11



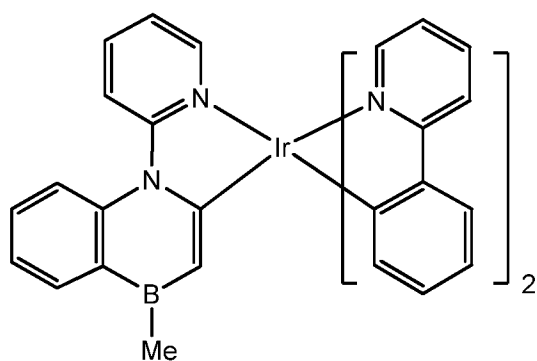
Compound 12



Compound 13



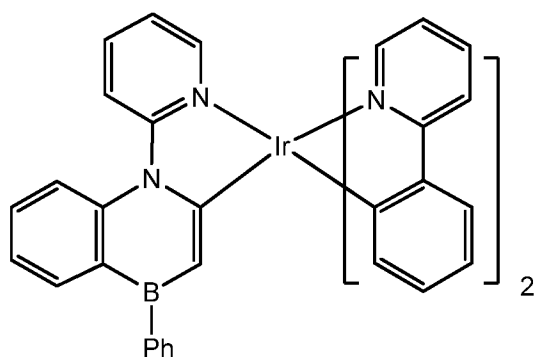
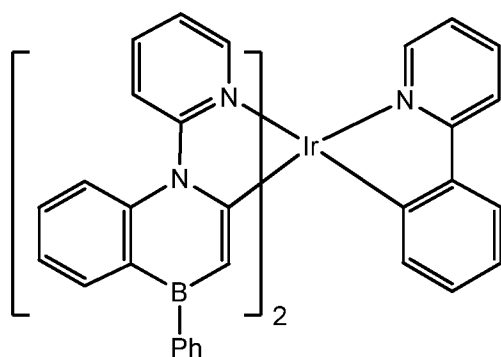
Compound 14



Compound 15

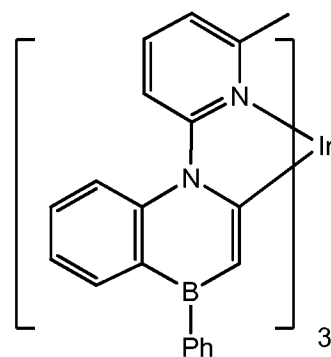
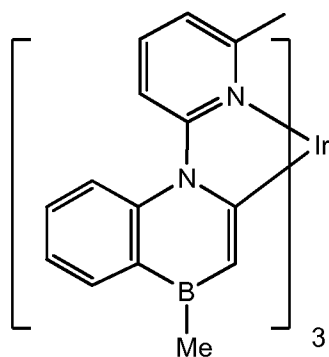
Compound 16

5



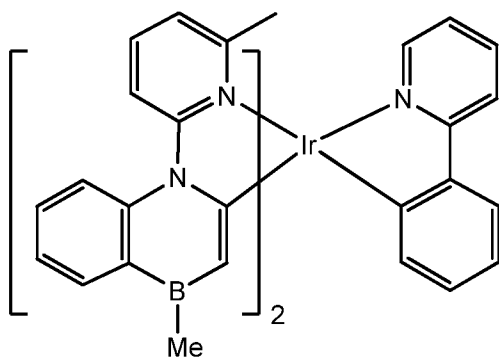
Compound 17

Compound 18

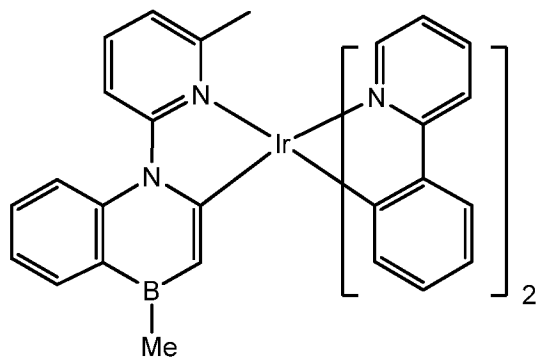


10 Compound 19

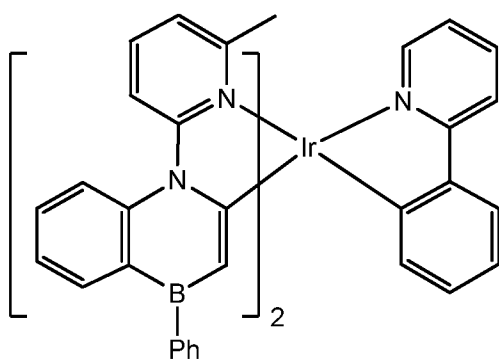
Compound 20



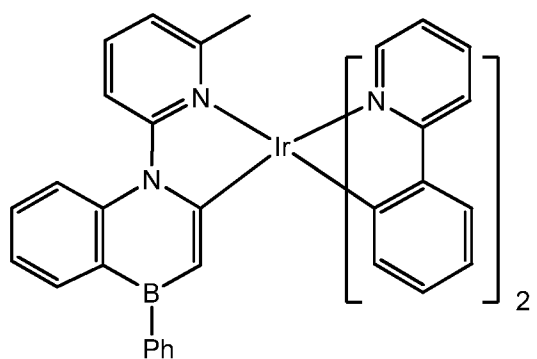
Compound 21



Compound 22

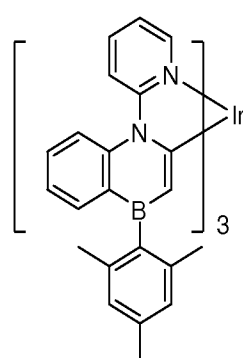


Compound 23

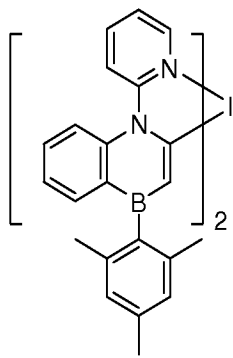


Compound 24

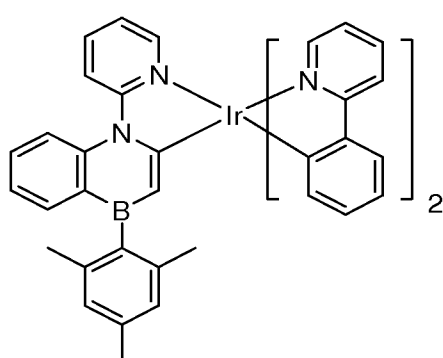
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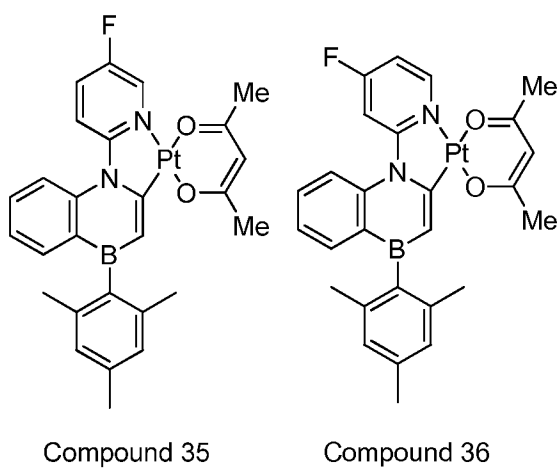
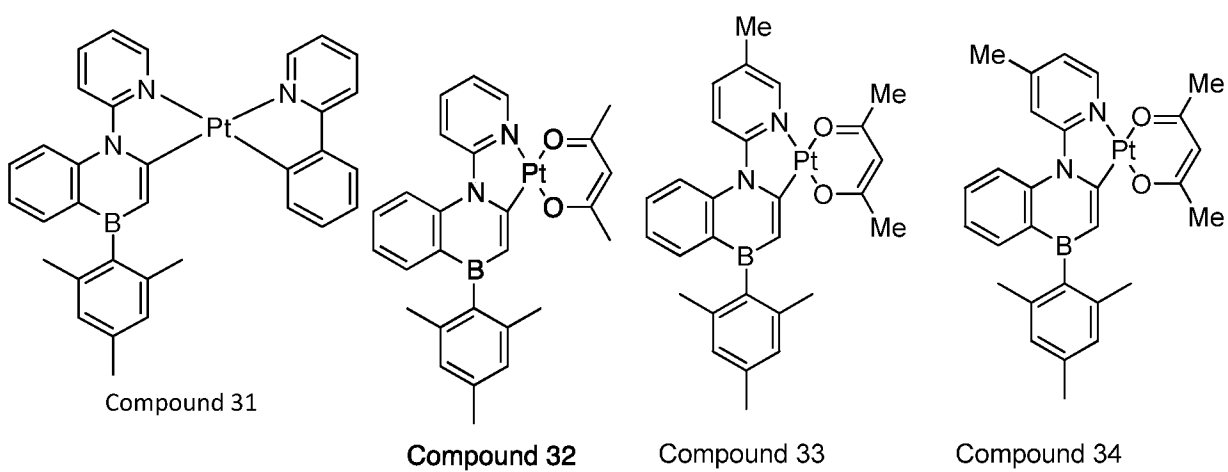
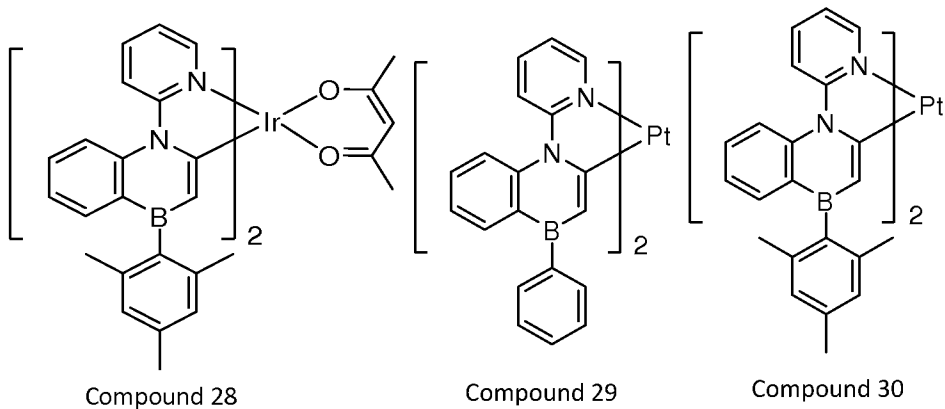
Compound 25

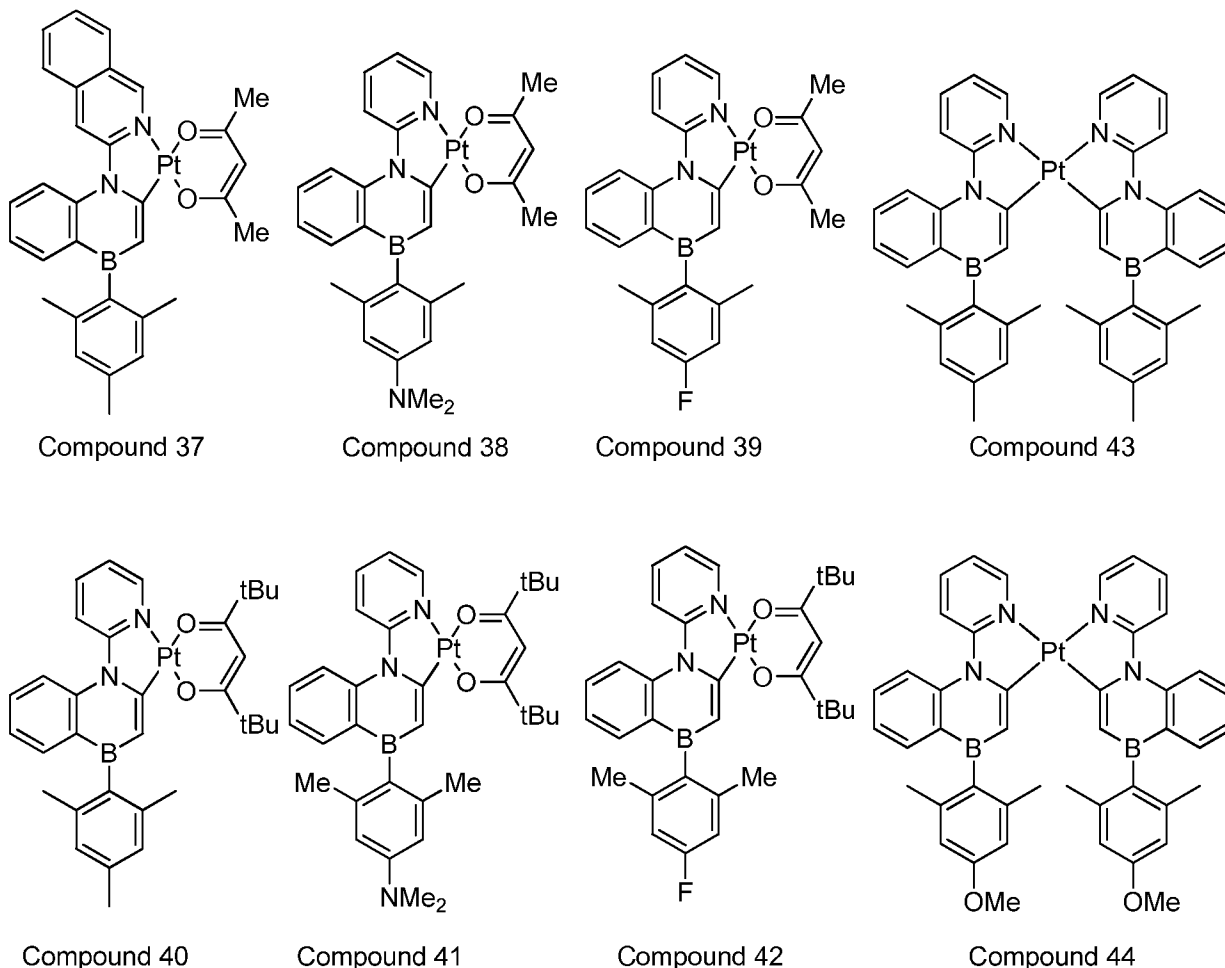


Compound 26



Compound 27





5

The 1,4-azaborines disclosed herein may be synthesized by the procedure shown in FIG. 3. In general, an ortho-substituted aryl amine (e.g., aniline) may be the starting compound. In certain embodiments, the aryl group is a benzene ring. An N-allylation of the ortho-substituted aryl amine (2-bromoaniline in FIG.3) is performed to produce an N-allyl compound **1A**. Compound **1A** undergoes N-methylation to generate an N-methylallyl compound **2A**. A ruthenium-mediated alkene isomerization is conducted on **2A** to furnish the enamine **3A**. Coupling of enamine **3A** with a boron-containing electrophile (e.g., vinylboronchloride **4A**) produces the crucial ring-closing-metathesis precursor **5A**. Ring closing metathesis of diene **5A** using, for example, using a Grubbs second-generation catalyst, generates the benzo-fused 1,4-azaborine **6A**. Methanolysis of 1,4-azaborine **6A** at the boron heteroatom produces B-OMe substituted 1,4-azaborine **7A**. Compound **7A** is then coupled with 2-optionally substituted Li pyridine derivatives (e.g. a 2-methyl pyridine)

to furnish the corresponding target benzofused-pyridine 1,4-azaborines **8A** and **9A**. For non-sterically encumbered compound **8A**, dimer formation was readily observed. However, when a methyl group was introduced at the 6-position on the pyridine (e.g., in compound **9A**), this dimerization was minimized in solution.

5 The synthesis shown in FIG. 3 can be adapted to generate 1,4-azaborines wherein the A ring (e.g., a pyridinyl) is attached to the N-heteroatom. Instead of N-methylation in the second step one could use an N-protecting group which then would be removed at a later stage. This would generate an NH-1,4-azaborine which could be functionalized using Buchwald-Hartwig amination protocols as shown in FIG 4.

10 An alternative synthesis for N-pyridinyl benzo-fused 1,4-azaborines that utilizes an electrophilic borylation approach is shown in FIG. 5 and 6. In this synthesis, the amino group of an ortho-substituted aryl amine (e.g., 2-bromoaniline) may be provided with protecting group(s) such as an alkenyl group (e.g., propenyl, isobutenyl). In certain embodiments, the aryl is a benzene ring. The N-protected intermediate then is subjected to an electrophilic borylation to provide an N-protected benzofused 1,4-azaborine. The N-protecting group could then be removed, and the resulting NH-benzofused 1,4-azaborine could be functionalized using Buchwald-Hartwig amination protocols as shown in FIG 4.

15 A further embodiment for synthesizing N-pyridinyl benzo-fused 1,4-azaborines includes the use of Petasis reagent to produce an enamine bearing an NH group; performing a metal-catalyzed stannylation of an aryl bromide to generate an aryltin compound; one pot transmetallation (Sn to B) / electrophilic borylation cyclization procedure followed by quenching with a nucleophile to produce a benzo-fused 1,4-azaborine bearing the free NH group; and cross-coupling with 2-bromo pyridine to furnish the N-pyridinyl 1,4-azaborine. A specific illustration of this embodiment is described below for synthesizing compound 9L (also referred to as "compound PYAB-1") as well
25 as its Pt-complex 32 (also referred to as "compound Pt-PYAB-1").

OLEDs

30 Generally, an OLED comprises at least one organic layer disposed between and electrically connected to an anode and a cathode. When a current is applied, the anode injects holes and the cathode injects electrons into the organic layer(s). The injected holes and electrons each migrate

toward the oppositely charged electrode. When an electron and hole localize on the same molecule, an "exciton," which is a localized electron-hole pair having an excited energy state, is formed. Light is emitted when the exciton relaxes via a photoemissive mechanism. In some cases, the exciton may be localized on an excimer or an exciplex. Non-radiative mechanisms, such as thermal relaxation, may also occur, but are generally considered undesirable.

The initial OLEDs used emissive molecules that emitted light from their singlet states ("fluorescence") as disclosed, for example, in U.S. Pat. No. 4,769,292, which is incorporated by reference in its entirety. Fluorescent emission generally occurs in a time frame of less than 10 nanoseconds.

More recently, OLEDs having emissive materials that emit light from triplet states ("phosphorescence") have been demonstrated. Baldo et al., "Highly Efficient Phosphorescent Emission from Organic Electroluminescent Devices," *Nature*, vol. 395, pp. 151-154, 1998; ("Baldo-I") and Baldo et al., "Very high-efficiency green organic light-emitting devices based on electrophosphorescence," *Appl. Phys. Lett.*, vol. 75, No. 3, pp. 4-6, 1999 ("Baldo-II"), which are incorporated by reference in their entireties. Phosphorescence is described in more detail in U.S. Pat. No. 7,279,704 at cols. 5-6, which are incorporated by reference.

FIG. 1 shows an organic light-emitting device 100. The figures are not necessarily drawn to scale. Device 100 may include a substrate 110, an anode 115, a hole injection layer 120, a hole transport layer 125, an electron blocking layer 130, an emissive layer 135, a hole blocking layer 140, an electron transport layer 145, an electron injection layer 150, a protective layer 155, and a cathode 160. Cathode 160 is a compound cathode having a first conductive layer 162 and a second conductive layer 164. Device 100 may be fabricated by depositing the layers described, in order. The properties and functions of these various layers, as well as example materials, are described in more detail in U.S. Pat. No. 7,279,704 at cols. 6-10, which are incorporated by reference.

More examples for each of these layers are available. For example, a flexible and transparent substrate-anode combination is disclosed in U.S. Pat. No. 5,844,363, which is incorporated by reference in its entirety. An example of a p-doped hole transport layer is m-MTDATA doped with F₄-TCNQ at a molar ratio of 50:1, as disclosed in U.S. Patent Application Publication No. 2003/0230980, which is incorporated by reference in its entirety. Examples of emissive and host materials are disclosed in U.S. Pat. No. 6,303,238 to Thompson et al., which is incorporated by reference in its entirety. An example of an n-doped electron transport layer is

BPhen doped with Li at a molar ratio of 1:1, as disclosed in U.S. Patent Application Publication No. 2003/0230980, which is incorporated by reference in its entirety. U.S. Pat. Nos. 5,703,436 and 5,707,745, which are incorporated by reference in their entireties, disclose examples of cathodes including compound cathodes having a thin layer of metal such as Mg:Ag with an overlying transparent, electrically-conductive, sputter-deposited ITO layer. The theory and use of blocking layers is described in more detail in U.S. Pat. No. 6,097,147 and U.S. Patent Application Publication No. 2003/0230980, which are incorporated by reference in their entireties. Examples of injection layers are provided in U.S. Patent Application Publication No. 2004/0174116, which is incorporated by reference in its entirety. A description of protective layers may be found in U.S. Patent Application Publication No. 2004/0174116, which is incorporated by reference in its entirety.

FIG. 2 shows an inverted OLED 200. The device includes a substrate 210, a cathode 215, an emissive layer 220, a hole transport layer 225, and an anode 230. Device 200 may be fabricated by depositing the layers described, in order. Because the most common OLED configuration has a cathode disposed over the anode, and device 200 has cathode 215 disposed under anode 230, device 200 may be referred to as an "inverted" OLED. Materials similar to those described with respect to device 100 may be used in the corresponding layers of device 200. FIG. 2 provides one example of how some layers may be omitted from the structure of device 100.

The simple layered structure illustrated in FIGS. 1 and 2 is provided by way of non-limiting example, and it is understood that embodiments of the invention may be used in connection with a wide variety of other structures. The specific materials and structures described are exemplary in nature, and other materials and structures may be used. Functional OLEDs may be achieved by combining the various layers described in different ways, or layers may be omitted entirely, based on design, performance, and cost factors. Other layers not specifically described may also be included. Materials other than those specifically described may be used. Although many of the examples provided herein describe various layers as comprising a single material, it is understood that combinations of materials, such as a mixture of host and dopant, or more generally a mixture, may be used. Also, the layers may have various sublayers. The names given to the various layers herein are not intended to be strictly limiting. For example, in device 200, hole transport layer 225 transports holes and injects holes into emissive layer 220, and may be described as a hole transport layer or a hole injection layer. In one embodiment, an OLED may be described as having an

"organic layer" disposed between a cathode and an anode. This organic layer may comprise a single layer, or may further comprise multiple layers of different organic materials as described, for example, with respect to FIGS. 1 and 2.

Structures and materials not specifically described may also be used, such as OLEDs comprised of polymeric materials (PLEDs) such as disclosed in U.S. Pat. No. 5,247,190 to Friend et al., which is incorporated by reference in its entirety. By way of further example, OLEDs having a single organic layer may be used. OLEDs may be stacked, for example as described in U.S. Pat. No. 5,707,745 to Forrest et al, which is incorporated by reference in its entirety. The OLED structure may deviate from the simple layered structure illustrated in FIGS. 1 and 2. For example, the substrate may include an angled reflective surface to improve out-coupling, such as a mesa structure as described in U.S. Pat. No. 6,091,195 to Forrest et al., and/or a pit structure as described in U.S. Pat. No. 5,834,893 to Bulovic et al., which are incorporated by reference in their entireties.

Unless otherwise specified, any of the layers of the various embodiments may be deposited by any suitable method. For the organic layers, preferred methods include thermal evaporation, ink-jet, such as described in U.S. Pat. Nos. 6,013,982 and 6,087,196, which are incorporated by reference in their entireties, organic vapor phase deposition (OVPD), such as described in U.S. Pat. No. 6,337,102 to Forrest et al., which is incorporated by reference in its entirety, and deposition by organic vapor jet printing (OVJP), such as described in U.S. patent application Ser. No. 10/233,470, which is incorporated by reference in its entirety. Other suitable deposition methods include spin coating and other solution based processes. Solution based processes are preferably carried out in nitrogen or an inert atmosphere. For the other layers, preferred methods include thermal evaporation. Preferred patterning methods include deposition through a mask, cold welding such as described in U.S. Pat. Nos. 6,294,398 and 6,468,819, which are incorporated by reference in their entireties, and patterning associated with some of the deposition methods such as ink jet and OVJD. Other methods may also be used. The materials to be deposited may be modified to make them compatible with a particular deposition method. For example, substituents such as alkyl and aryl groups, branched or unbranched, and preferably containing at least 3 carbons, may be used in small molecules to enhance their ability to undergo solution processing. Substituents having 20 carbons or more may be used, and 3-20 carbons is a preferred range. Materials with asymmetric structures may have better solution processibility than those having symmetric structures, because asymmetric

materials may have a lower tendency to recrystallize. Dendrimer substituents may be used to enhance the ability of small molecules to undergo solution processing.

Devices fabricated in accordance with embodiments of the invention may be incorporated into a wide variety of consumer products, including flat panel displays, computer monitors, 5 televisions, billboards, lights for interior or exterior illumination and/or signaling, heads up displays, fully transparent displays, flexible displays, laser printers, telephones, cell phones, personal digital assistants (PDAs), laptop computers, digital cameras, camcorders, viewfinders, micro-displays, vehicles, a large area wall, theater or stadium screen, or a sign. Various control mechanisms may be used to control devices fabricated in accordance with various embodiments of 10 the present invention, including passive matrix and active matrix. Many of the devices are intended for use in a temperature range comfortable to humans, such as 18 °C. to 30 °C., and more preferably at room temperature (20-25 °C.).

The materials and structures described herein may have applications in devices other than OLEDs. For example, other optoelectronic devices such as organic solar cells and organic 15 photodetectors may employ the materials and structures. More generally, organic devices, such as organic transistors, may employ the materials and structures.

In one embodiment, the organic layer is a blocking layer and the material having Formula A or B is a blocking material.

In another embodiment, the organic layer is an emissive layer and the material comprising 20 Formula A or B is a host. The organic layer may further comprise an emissive dopant. In yet another aspect, the organic layer is an emissive layer and the material comprising Formula A or B is an emitter.

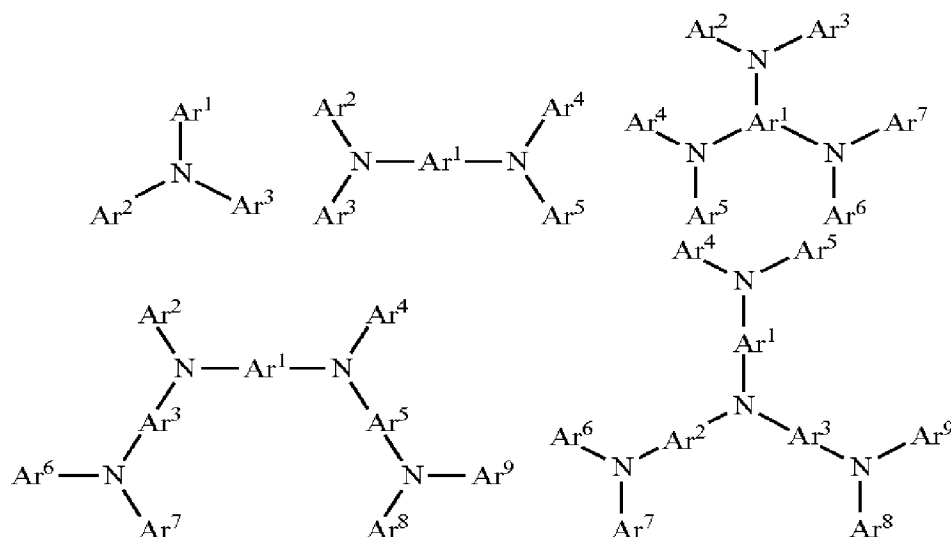
In one embodiment, the first device is a consumer product. In another aspect, the first device is an organic light-emitting device.

25 The materials described herein as useful for a particular layer in an organic light-emitting device may be used in combination with a wide variety of other materials present in the device. For example, emissive dopants disclosed herein may be used in conjunction with a wide variety of hosts, transport layers, blocking layers, injection layers, electrodes and other layers that may be present. The materials described or referred to below are non-limiting examples of materials that 30 may be useful in combination with the compounds disclosed herein, and one of skill in the art can readily consult the literature to identify other materials that may be useful in combination.

HIL/HTL:

A hole injecting/transporting material to be used in various embodiments of the present invention is not particularly limited, and any compound may be used as long as the compound is typically used as a hole injecting/transporting material. Examples of the material include, but not limit to: a phthalocyanine or porphyrin derivative; an aromatic amine derivative; an indolocarbazole derivative; a polymer containing fluorohydrocarbon; a polymer with conductivity dopants; a conducting polymer, such as PEDOT/PSS; a self-assembly monomer derived from compounds such as phosphonic acid and silane derivatives; a metal oxide derivative, such as MoO.sub.x; a p-type semiconducting organic compound, such as 1,4,5,8,9,12-Hexaazatriphenylenehexacarbonitrile; a metal complex, and a cross-linkable compounds.

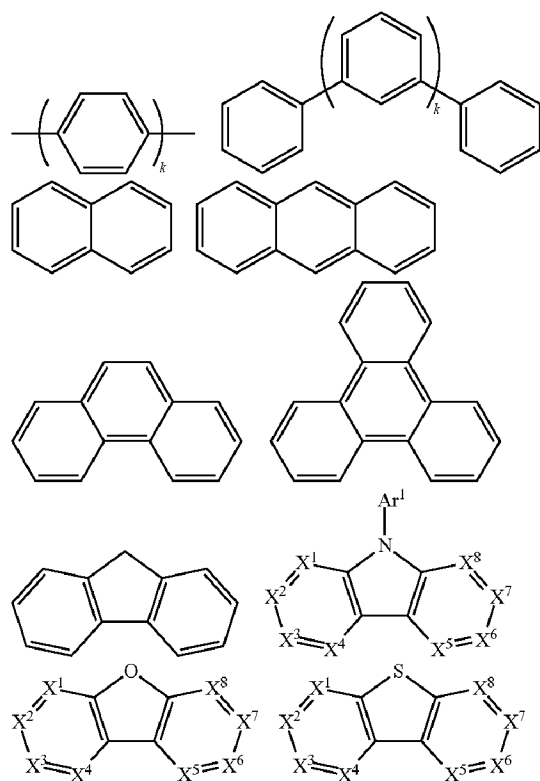
Examples of aromatic amine derivatives used in HIL or HTL include, but not limit to the following general structures:



Each of Ar¹ to Ar⁹ is selected from aromatic hydrocarbon cyclic compounds such as benzene, biphenyl, triphenyl, triphenylene, naphthalene, anthracene, phenalene, phenanthrene, fluorene, pyrene, chrysene, perylene, azulene; group consisting aromatic heterocyclic compounds such as dibenzothiophene, dibenzofuran, dibenzoselenophene, furan, thiophene, benzofuran, benzothiophene, benzoselenophene, carbazole, indolocarbazole, pyridylindole, pyrrolodipyridine,

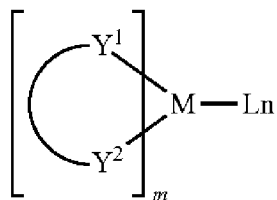
pyrazole, imidazole, triazole, oxazole, thiazole, oxadiazole, oxatriazole, dioxazole, thiadiazole, pyridine, pyridazine, pyrimidine, pyrazine, triazine, oxazine, oxathiazine, oxadiazine, indole, benzimidazole, indazole, indoxazine, benzoxazole, benzisoxazole, benzothiazole, quinoline, isoquinoline, cinnoline, quinazoline, quinoxaline, naphthyridine, phthalazine, pteridine, xanthene, acridine, phenazine, phenothiazine, phenoxazine, benzofuropyridine, furodipyrindine, benzothienopyridine, thienodipyrindine, benzoselenophenopyridine, or selenophenodipyrindine; or 2 to 10 cyclic structural units which are groups of the same type or different types selected from the aromatic hydrocarbon cyclic group and the aromatic heterocyclic group and are bonded to each other directly or via at least one of oxygen atom, nitrogen atom, sulfur atom, silicon atom, phosphorus atom, boron atom, chain structural unit and the aliphatic cyclic group, wherein each Ar is further substituted by a substituent selected from the group consisting of hydrogen, alkyl, alkoxy, amino, alkenyl, alkynyl, arylalkyl, heteroalkyl, aryl and heteroaryl.

In one aspect, Ar¹ to Ar⁹ is independently selected from:



wherein k is an integer from 1 to 20; X¹ to X⁸ is CH or N; Ar¹ has the same group defined above.

Examples of metal complexes used in HIL or HTL include, but are not limited to the following general formula:



M is a metal, having an atomic weight greater than 40; (Y¹-Y²) is a bidentate ligand, Y¹ and Y² are independently selected from C, N, O, P, and S; L is an ancillary ligand; m is an integer value from 1 to the maximum number of ligands that may be attached to the metal; and m+n is the maximum number of ligands that may be attached to the metal.

In one embodiment, (Y¹-Y²) is a 2-phenylpyridine derivative.

In another embodiment, (Y¹-Y²) is a carbene ligand.

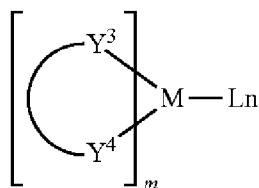
In another embodiment, M is selected from Ir, Pt, Os, and Zn.

In a further embodiment, the metal complex has a smallest oxidation potential in solution vs. Fc⁺/Fc couple less than about 0.6 V.

Host:

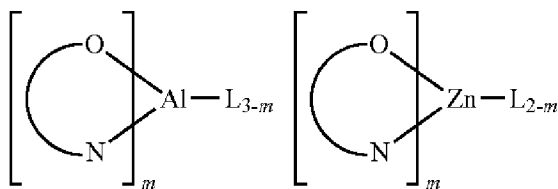
The light-emitting layer of the organic EL device of various embodiments of the present invention preferably contains at least a metal complex as light-emitting material, and may contain a host material using the metal complex as a dopant material. Examples of the host material are not particularly limited, and any metal complexes or organic compounds may be used as long as the triplet energy of the host is larger than that of the dopant.

Examples of metal complexes used as host are preferred to have the following general formula



M is a metal; (Y^3 - Y^4) is a bidentate ligand, Y^3 and Y^4 are independently selected from C, N, O, P, and S; L is an ancillary ligand; m is an integer value from 1 to the maximum number of ligands that may be attached to the metal; and m+n is the maximum number of ligands that may be attached to the metal.

5 In one aspect, the metal complexes are:



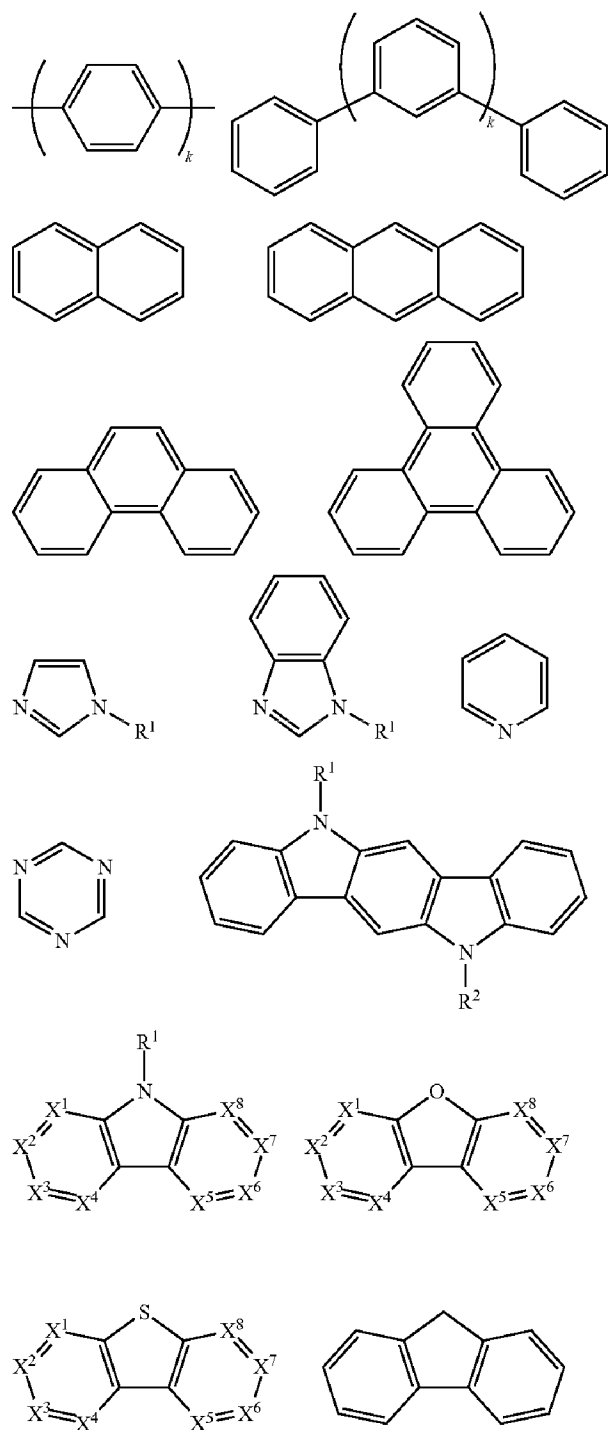
wherein (O--N) is a bidentate ligand, having metal coordinated to atoms O and N.

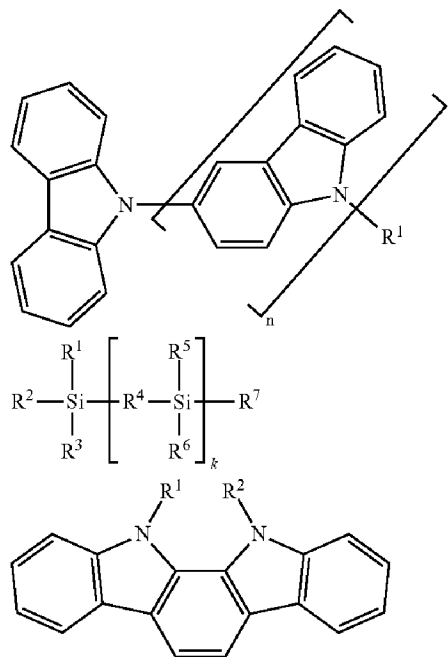
In another embodiment, M is selected from Ir and N.

In a further embodiment, (Y^3 - Y^4) is a carbene ligand.

10 Examples of organic compounds used as host are selected from aromatic hydrocarbon cyclic compounds such as benzene, biphenyl, triphenyl, triphenylene, naphthalene, anthracene, phenalene, phenanthrene, fluorene, pyrene, chrysene, perylene, azulene; group consisting aromatic heterocyclic compounds such as dibenzothiophene, dibenzofuran, dibenzoselenophene, furan, thiophene, benzofuran, benzothiophene, benzoselenophene, carbazole, indolocarbazole,
 15 pyridylindole, pyrrolodipyridine, pyrazole, imidazole, triazole, oxazole, triazole, oxadiazole, oxatriazole, dioxazole, thiadiazole, pyridine, pyridazine, pyrimidine, pyrazine, triazine, oxazine, oxathiazine, oxadiazine, indole, benzimidazole, indazole, indoxazine, benzoxazole, benzisoxazole, benzothiazole, quinoline, isoquinoline, cinnoline, quinazoline, quinoxaline, naphthyridine, phthalazine, pteridine, xanthene, acridine, phenazine, phenothiazine, phenoxazine,
 20 benzofuopyridine, furodipyridine, benzothienopyridine, thienodipyridine, benzoselenophenopyridine, and selenophenodipyridine; or 2 to 10 cyclic structural units which are groups of the same type or different types selected from the aromatic hydrocarbon cyclic group and the aromatic heterocyclic group and are bonded to each other directly or via at least one of oxygen atom, nitrogen atom, sulfur atom, silicon atom, phosphorus atom, boron atom, chain structural unit
 25 and the aliphatic cyclic group. Wherein each group is further substituted by a substituent selected from the group consisting of hydrogen, alkyl, alkoxy, amino, alkenyl, alkynyl, arylalkyl, heteroalkyl, aryl and heteroaryl.

In one embodiment, the host compound contains at least one of the following groups in the molecule:





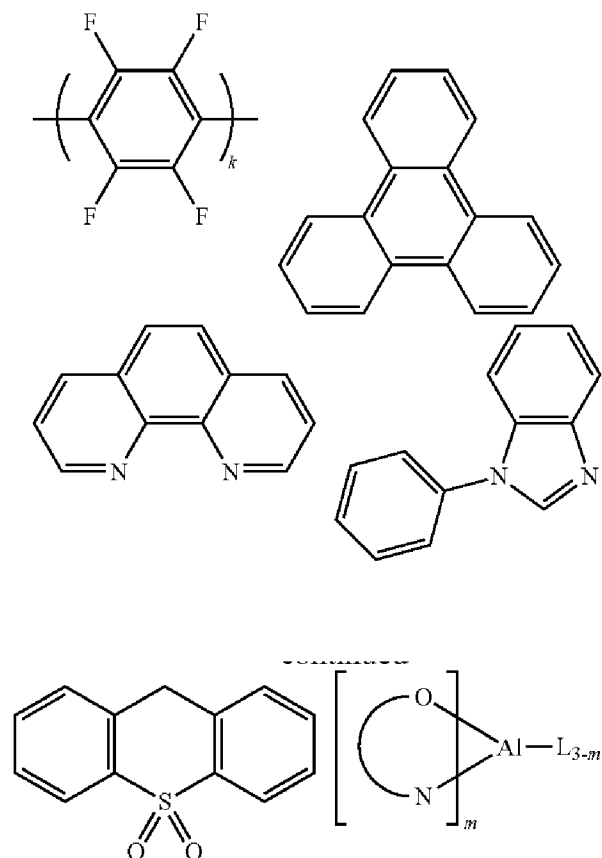
wherein R¹ to R⁷ is independently selected from hydrogen, alkyl, alkoxy, amino, alkenyl, alkynyl, arylalkyl, heteroalkyl, aryl and heteroaryl, when it is aryl or heteroaryl, it has the similar definition as Ar's mentioned above; k is an integer from 0 to 20 ; and X¹ to X⁸ is selected from CH or N.

HBL:

A hole blocking layer (HBL) may be used to reduce the number of holes and/or excitons that leave the emissive layer. The presence of such a blocking layer in a device may result in substantially higher efficiencies as compared to a similar device lacking a blocking layer. Also, a blocking layer may be used to confine emission to a desired region of an OLED.

In one embodiment, compounds used in a HBL contain the same molecule used as a host as described above.

In another embodiment, compounds used in a HBL contain at least one of the following groups in the molecule:



wherein k is an integer from 0 to 20; L is an ancillary ligand; and m is an integer from 1 to 3.

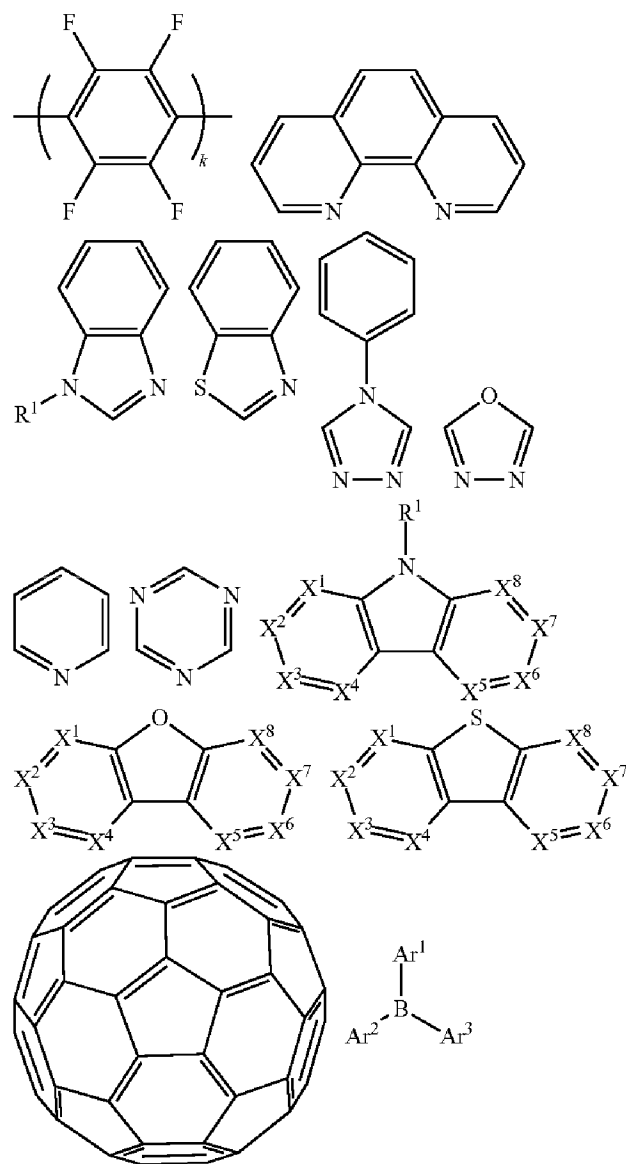
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ETL:

Electron transport layer (ETL) may include a material capable of transporting electrons. Electron transport layer may be intrinsic (undoped), or doped. Doping may be used to enhance conductivity. Examples of the ETL material are not particularly limited, and any metal complexes or organic compounds may be used as long as they are typically used to transport electrons.

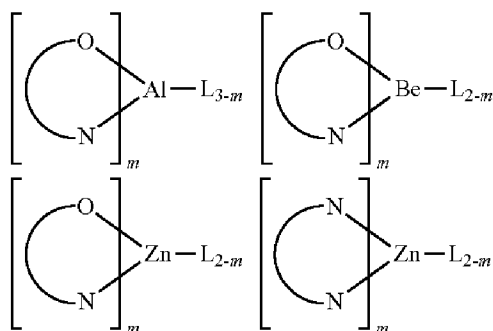
10

In one embodiment, compounds used in an ETL contain at least one of the following groups in the molecule



wherein R^1 is selected from hydrogen, alkyl, alkoxy, amino, alkenyl, alkynyl, arylalkyl, heteroalkyl, aryl and heteroaryl, when it is aryl or heteroaryl, it has the similar definition as Ar's mentioned above; Ar^1 to Ar^3 has the similar definition as Ar's mentioned above; k is an integer from 0 to 20; and X^1 to X^8 is selected from CH or N.

In another embodiment, the metal complexes used in ETL contain, but are not limited to the following general formula



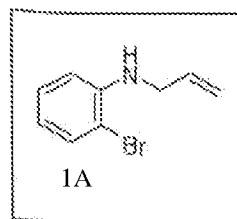
wherein (O--N) or (N--N) is a bidentate ligand, having metal coordinated to atoms O, N or N,N; L is an ancillary ligand; m is an integer value from 1 to the maximum number of ligands that may be attached to the metal.

More details on OLEDs, and the definitions described above, can be found in U.S. Pat. No. 7,279,704, which is incorporated herein by reference in its entirety.

Experimental

Synthesis of compound 1A

Compound 1A. To a 500-mL flask charged with 2-bromoaniline (17.2 g, 100 mmol) and THF (200 mL) was added 2.5 M *n*-BuLi hexane solution (40 mL, 100 mmol)

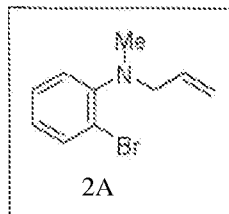


dropwise at -78° C. The resulting mixture was then stirred at the same temperature for 0.5 h. Allylbromide (12.1 g, 100 mmol) was then introduced in one portion at -78 °C and the reaction mixture was allowed to stir at room temperature for 16 h. Water (100 mL) was then added to quench the reaction. After removal of most of the THF, the residue was then extracted with Et₂O three times. The combined organic phase was dried over Na₂SO₄ and concentrated. The residue was purified by distillation under attenuated pressure to furnish **1A** as yellow oil (20.5 g, 96%).

¹HNMR (600 MHz, CDCl₃) δ 7.43 (m, 1H), 7.18 (m, 1H), 6.63 (d, *J* = 7.8 Hz, 1H), 6.56 (m, 1 H), 5.98 (m, 1H), 5.30 (d, *J* = 17.4, 1.2 Hz, 1H), 5.21 (m, 1 H), 4.48 (br, 1H), 3.84 (m, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 144.7, 134.6, 132.3, 128.4, 117.8, 116.4, 111.5, 109.7, 46.2.

Synthesis of compound 2A

Compound 2A. To a 500-mL flask charged with **1A** (20.5 g, 96.7 mmol) and THF (200 mL) was added 2.5 M *n*-BuLi hexane solution (38.7 mL, 96.7 mmol) dropwise at -78 °C.

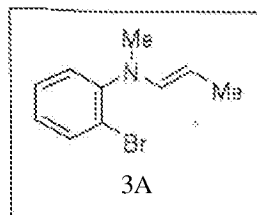


The resulting mixture was then stirred at the same temperature for 0.5 h. Iodomethane (13.7 g, 96.7 mmol) was then introduced in one portion at -78° C and the reaction mixture was allowed to stir at room temperature for 16 h. Water (100 mL) was then added to quench the reaction. After removal of most of the THF, the residue was then extracted with Et₂O three times. The combined organic phase was dried over Na₂SO₄ and concentrated. The residue was purified by distillation under attenuated pressure to furnish **2A** as light yellow oil (20.8 g, 95%).

¹H NMR (600 MHz, CDCl₃) δ 7.56 (d, *J* = 7.8 Hz, 1H), 7.26 (m, 1H), 7.08 (d, *J* = 7.8 Hz, 1H), 6.89 (m, 1 H), 5.95 (m, 1H), 5.26 (d, *J* = 16.8, 1H), 5.19(d, *J* = 10.8 Hz, 1H), 3.62, (d, *J* = 6.6 Hz, 2H), 2.74 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 150.9, 135.0, 133.8, 127.8, 123.9, 121.7, 119.7, 117.7, 59.4, 40.1.

Synthesis of compound 3A

Compound 3A. To a 500-mL pressure flask charged with **2A** (8.30 g, 36.7 mmol) and benzene (50 mL) was added Ru(CO)ClH(PPh₃)₃ (0.70 g, 0.74 mmol). The resulting mixture was then sealed and allowed to stir at 85 °C for 2 h. After cooled to room temperature and removal of

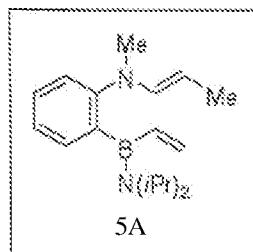


benzene, the residue was purified by distillation under attenuated pressure to furnish **3A** as light yellow oil (7.60 g, 91%).

¹H NMR (600 MHz, CD₂Cl₂) δ 7.57 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.27 (m, 1H), 7.10 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.98 (m, 1H), 6.19 (dd, *J* = 13.8, 7.2 Hz, 1H), 4.53 (m, 1H), 2.96 (s, 3H), 1.70 (dd, *J* = 6.6, 1.2 Hz, 3H); ¹³C NMR (150 MHz, CD₂Cl₂) δ 148.8, 137.4, 137.3, 134.3, 128.8, 126.9, 126.1, 120.3, 97.2, 38.7.

Synthesis of compound 5A

5 **Compound 5A.** To a 500-mL flask charged with **3** (10.6 g, 47.0 mmol) and THF (200 mL) was added 2.5 M n-BuLi hexane solution (18.7 mL, 47.0 mmol) dropwise at –78 °C. The resulting mixture was then stirred at the same temperature for 0.5 h. Electrophile **4A** (8.2 g, 47 mmol)

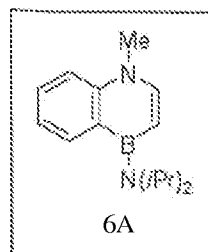


10 was then introduced in one portion at -78 °C. The reaction mixture was allowed to stir -78 °C for 0.5 h and then room temperature for 16 h. After removal of THF, the residue was filtrated through a pad of silica gel with Et₂O as the eluent. After removal of the Et₂O, the residue was purified by distillation under attenuated pressure to furnish **5** as yellow oil (10.4 g, 78%).

¹H NMR (600 MHz, CD₂Cl₂) δ 7.19 (m, 1H), 7.09 (m, 1H), 6.90 (m, 2H), 6.80 (m, 1H), 6.38 (m, 1H), 5.78 (d, *J* = 14.4Hz, 1H), 5.18(d, *J*= 19.2 Hz, 1H), 4.30(m, 1H), 3.70 (m, 1H), 3.43 (m, 1H), 2.95 (s, 3H), 1.65 (m, 3H), 1.41 (m, 6H), 1.04 (m, 3H), 1.00 (m, 3H); ¹³C NMR (150 MHz, CD₂Cl₂) δ 152.1, 141.5 (br), 137.2, 136.5 (br), 133.5, 133.4, 133.2, 128.1, 121.2, 120.4, 94.5, 52.6, 45.2, 37.5, 26.1, 25.2, 22.5, 20.8; ¹¹B NMR (96 MHz, CD₂Cl₂) δ 38.9.

Synthesis of compound 6A

20 **Compound 6A.** To a 500-mL flask charged with **5A** (10.4 g, 36.6 mmol) and DCM (300 mL) was added Grubbs 2nd generation catalyst (3.1 g, 3.7 mmol). The resulting mixture was then stirred at room temperature for 36 h. After removal of DCM, the residue was purified by distillation under



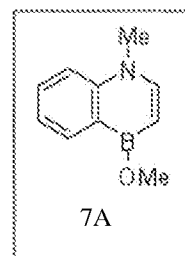
25 attenuated pressure to furnish crude **6A**. The crude **6A** was further purified by filtrated through a pad of silica gel with DCM/Et₂O/Et₃N (1/1/0.2) as the eluent to furnish **6A** as yellow solid (4.6 g, 52%).

¹H NMR (600 MHz, CD₂Cl₂) δ 7.93 (dd, *J* = 7.8. 0.6 Hz 1H), 7.43 (m, 1H), 7.19 (m, 2H), 7.07 (m, 1H), 5.59 (d, *J*= 10.2 Hz. 1H), 3.99 (br. 2H), 3.52(s, 3H), 1.34 (d, *J* = 6.6 Hz. 12H); ¹³C NMR (150

MHz. CD_2Cl_2) δ 146.6, 143.9, 133.9, 129.0, 119.7, 114.2, 106.4 (br), 47.9, 40.7, 23.9; ^{11}B NMR (96 MHz, CD_2Cl_2) δ 33.3; HRMS (CI) calcd for $\text{C}_{15}\text{H}_{24}\text{BN}_2$ ($[\text{M} + \text{H}]^+$) 243.2033, found 243.2022.

Synthesis of compound 7A

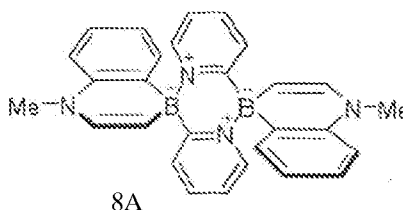
5 **Compound 7A.** To a 50-mL flask charged with **6A** (484 mg, 2.0 mmol) and THF (10 mL) was added MeOH (81 μL , 2.0 mmol). The resulting mixture was allowed to stir at room temperature for 24 h. Removal of THF furnished **7A** as pale yellow oil (340 mg, 99%). **7A** is pure enough without any further purification.



10 ^1H NMR (600 MHz, CD_2Cl_2) δ 8.08 (d, $J = 7.2$ Hz, 1H), 7.71 (d, $J = 9.6$ Hz, 1H), 7.58 (m, 1H), 7.35 (d, $J = 8.4$ Hz, 1H), 7.20 (m, 1H), 5.59 (d, $J = 9.6$ Hz, 1H), 3.87 (s, 3H), 3.70 (s, 3H); ^{13}C NMR (150 MHz, CD_2Cl_2) δ 151.3, 145.9, 131.8, 130.8, 125.8 (br), 121.2, 114.9, 99.8 (br), 54.1, 41.6; ^{11}B NMR (96 MHz, CD_2Cl_2) δ 37.1; HRMS (CI) calcd for $\text{C}_{15}\text{H}_{24}\text{BN}_2$ ($[\text{M} + \text{H}]^+$) 174.1090, found 174.1085.

Synthesis of compound 8A

Compound 8A. To a 20-mL drum charged



20 with 2-bromopyridine (316 mg, 2.0 mmol) and THF (5 mL) was added 2.5 M *n*-BuLi hexane solution (0.8 mL, 2.0 mmol) at -78°C . The resulting mixture was then stirred at the same temperature for 0.5 h. Compound **7A** (344 mg, 2.0 mmol) in THF (2 mL) was then introduced to the reaction system. After stirring at -78°C for 15 min, the mixture was allowed to stir at room temperature for additional 2 h. After removal of THF, DCM (5 mL) was added. The resulting suspension was continued to stir at room temperature for 10 min. After filtrated through the

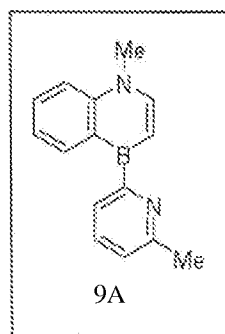
25 Acrodisc, the combined DCM solution was then concentrated and washed by pentane to furnish **8A** as pale yellow powder (220 mg, 50%). ^1H NMR shows there are two isomers (*trans* (major initial) and *cis* (minor initial)). ^1H NMR (600 MHz, CD_2Cl_2) δ 8.31 (d, $J = 6.0$ Hz, 1H), 7.49 (m, 2H),

7.07 (m, 1H), 7.01 (m, 1H), 6.87 (d, $J = 8.4$ Hz, 1H), 6.82 (d, $J = 9.6$ Hz, 1H), 6.74 (m, 1H). 6.58 (m, 1H), 4.90 (d, $J = 10.2$ Hz, 1H). 3.38 (s, 3H). ^{13}C NMR (150 MHz, CD_2Cl_2) δ 179.5 (br), 145.6, 145.2, 145.0, 144.2, 138.9, 137.3, 136.1, 136.0, 135.9, 135.3, 133.4, 133.3, 127.4, 127.1, 120.9, 120.8, 120.1, 119.8, 111.5, 111.4, 109.7 (br), 39.9: ^{11}B NMR (96MHz, CD_2Cl_2) δ -6.1.

5

Synthesis of compound 9A

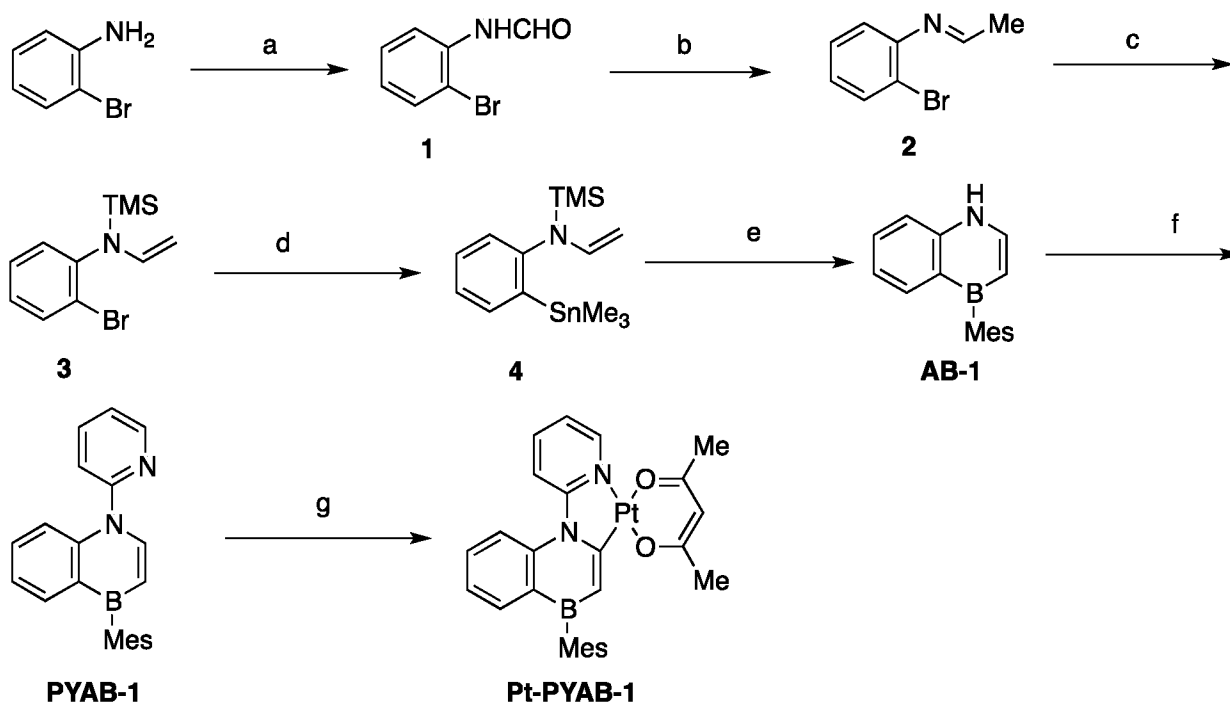
Compound 9A. The preparation of **9A** is similar to the **8A** but instead uses TMSCl as a promoter for re-aromatization from (80%).



10 ^1H NMR (600 MHz, CD_2Cl_2) δ 8.76 (dd, $J = 7.8, 1.2$ Hz 1H). 8.01 (d, $J = 9.0$ Hz, 1H), 7.70 (m, 1H), 7.60 (m, 3H), 7.33 (m, 1H), 7.10 (d, $J = 1.8$ Hz, 1H), 6.49 (d, $J = 8.0$ Hz, 1H), 3.95 (s, 3H), 2.64 (s, 3H); ^{13}C NMR (150 MHz, CD_2Cl_2) δ 168.8 (br), 158.2, 149.3, 144.7, 136.9, 134.8, 131.4, 127.0, 121.9, 121.6, 115.5, 114.7 (br), 42.8, 25.5: ^{11}B NMR (96 MHz, CD_2Cl_2) δ 43.5.

15

Synthesis of compounds PYAB-1 and Pt-PYAB-1



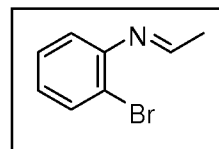
Reaction conditions: a) HCO_2H , Toluene, 110 °C, 4 h, 95%; b) Cp_2TiMe_2 , Toluene, 85 °C, 12 h, 29%; c) KHMDS, TMSCl, THF/Toluene (5/1), -78 °C, 12h, 55%; d) $\text{Pd}(\text{PPh}_3)_4$ (20 mol%), $\text{Me}_3\text{SnSnMe}_3$, Toluene, 110 °C, 24 h, 73%; e) 1. BCl_3 , toluene, -78°C, 16 h; 2. MesLi, THF, -78 °C, 4 h, 50% over 2 steps; f) 2-bromopyridine, 5 mol% Pd_2dba_3 , 20 mol% *t*ButylXphos, NaOtBu, Toluene, 110 °C, 24 h, 65%; g) 1. $\text{Pt}_2(\text{SMe}_2)_2\text{Me}_2$, THF, rt, 12 h; 2. TfOH, rt, 0.5 h; 3. Na(AcAc), THF-MeOH, rt, 1 h, 54% over 3 steps.

Synthesis of compound 1. Compound 1 was synthesized according to the literature procedures.¹
All the characterization data are consistent with literature.²

¹ Mitamura, T.; Iwata, K.; Ogawa, A. *J. Org. Chem.* **2011**, 76, 3880-3887.

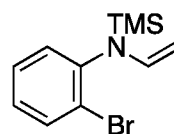
² Lygin, A.; de Meijere, A. *Org. Lett.* **2009**, 11, 389-392.

Synthesis of Compound 2. To a 500-mL flask charged with fresh prepared Cp_2TiMe_2 (14.5 g, 70 mmol) and benzene (200 mL) was added 14.0 g formamide **1** (14.0 g, 70 mmol). The resulting mixture was then refluxed for 14 hours. After cooled down to room temperature, the benzene was removed by vacuum. The residue was then washed by ether 3 times. The combined ethereal solution was then filtrated through the glass frit. After removal of the ether, the residue was then purified distillation under attenuated pressure (72-75 °C, 0.3 torr) to afford **2** as yellow oil. (4.0 g, yield, 29%).



¹H NMR (500 MHz, CD_2Cl_2) δ 7.80 (m, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.28 (m, 1H), 7.02 (m, 1H), 6.84 (m, 1H), 2.20 (d, J = 6.0 Hz, 3H); ¹³C NMR (125 MHz, CD_2Cl_2) δ 165.0, 151.8, 133.2, 128.9, 126.7, 120.8, 117.1, 23.5; IR (thin film) ν 3403, 3059, 2986, 2870, 1657, 1585, 1468, 1429, 1374, 1024, 810, 752, 663 cm^{-1} .

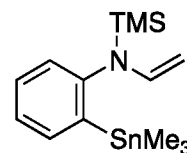
Synthesis of Compound 3. To a 1-L flask charged with KHMDS (82 mL, 0.5 M in toluene, 41 mmol) and THF (380 mL) was added **2** (8.1 g, 41 mmol) in THF (20 mL) at -78 °C. The resulting mixture was allowed to stir at -78 °C for 1.5 h. TMSCl was then introduced



at the same temperature. The reaction system was then stirred overnight. After removal of solvent, the residue was redissolved in THF and vinylMgBr (12 mL, 1 M in THF, 12 mmol) was then added. The reaction mixture was allowed to stir at rt for 0.5 h. After removal of the solvent, the residue was washed by pentane 3 times. After removal of pentane, the residue was purified by
 5 distillation under attenuated pressure (65-70 °C, 0.3 torr) to afford **3** as the colorless oil (5.9 g, 55%).

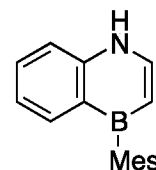
¹H NMR (500 MHz, C₆D₆): δ 7.45 (d, *J* = 8.0 Hz, 1H), 6.95 (d, *J* = 7.0 Hz, 1H), 6.88 (m, 1H), 6.63 (m, 1H), 6.48 (m, 1H), 4.03 (d, *J* = 10.5 Hz, 1H), 3.63 (d, *J* = 15.0 Hz, 1H), 0.08 (s, 9H); ¹H NMR (125 MHz, C₆D₆) δ 143.4, 139.7, 134.3, 132.4, 128.9, 128.7, 126.3, 87.2, 0.06; IR (thin film) 3102,
 10 3062, 2951, 2896, 1630, 1604, 1463, 1320, 1246, 1146, 1057, 906, 836 cm⁻¹.

Synthesis of Compound 4. To a 250-mL flask charged with **3** (3.1 g, 11 mmol), Pd(PPh₃)₄ (2.54 g, 2.20 mmol), and Me₃SnSnMe₃ (3.6 mL, 16.5 mmol) was added toluene (60 mL). The resulting mixture was
 15 then allowed to stir at 110 °C for 24 h. After cooling down to room temperature, the mixture was filtrated through the glass frit. After removal of the solvent, the residue was then purified by distillation under attenuated pressure (75-80 °C, 0.3 torr) to afford **4** as the colorless oil (2.83 g, 73%)



¹H NMR (500 MHz, CD₂Cl₂): δ 7.52 (dd, *J* = 6.5, 1.5 Hz, 1H), 7.33 (m, 1H), 7.20 (m, 1H), 7.05 (d, *J* = 8.5 Hz, 1H), 6.55 (dd, *J* = 15.0, 8.5 Hz, 1H), 3.77 (d, *J* = 8.5 Hz, 1H), 3.29 (d, *J* = 15.0 Hz, 1H), 0.20 (s, 9H), 0.15 (s, 9H); ¹³C NMR (125 MHz, CD₂Cl₂): δ 150.1, 144.8, 142.7, 137.9, 130.1, 129.3, 126.1, 87.1, 0.1, -7.5; IR (thin film) 3058, 2956, 2897, 1600, 1459, 1259, 1139, 1064, 916, 830, 762 cm⁻¹.

Synthesis of Compound AB-1. To a 250-mL flask charged with **4** (2.3 g, 6.4 mmol) and toluene (100 mL) was added BCl₃ (19.2 mL, 1 M in hexane, 19.2 mmol). The resulting mixture was allowed to stir at room temperature for 16 h. After removal of the solvent, the residue
 25 was then dissolved in THF (10 mL) and added to the MesLi solution



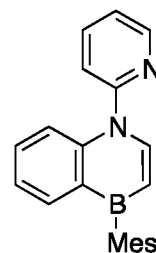
(32 mmol in 100 mL THF) at -78 °C. The reaction was allowed to stir at -78 °C for 2 h then at room temperature for 2 h. Sat. aq. NH₄Cl (20 mL) was then added to quench the reaction. The
 30

biphasic mixture was extracted with Et₂O (30 mL) 3 times. The combined ethereal solution was then dried over Na₂SO₄. After removal of the solvent, the residue was then purified with column chromatography on silica gel with hexanes/EtOAc as the eluent to furnish the desired AB-1 as a yellow solid (800 mg, 50%)

5 ¹H NMR (500 MHz, CDCl₃): δ 8.52 (br, 1H), 7.92 (m, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.58 (t, *J* = 7.0 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.15 (t, *J* = 7.0 Hz, 1H), 6.91 (s, 2H), 6.38 (d, *J* = 8.0 Hz, 1H), 2.36 (s, 3H), 2.06 (s, 6H); ¹³C NMR (125 MHz, CDCl₃): δ 141.9, 140.8, 138.9, 136.0, 135.5, 130.9, 126.8, 121.5, 117.0, 114.4 (br), 23.2, 21.2; ¹¹B NMR (96.2 MHz, CDCl₃) δ 49.6; IR (thin film) 3349, 3027, 2977, 2914, 2854, 2358, 2338, 1562, 1454, 1396, 754, 673 cm⁻¹.

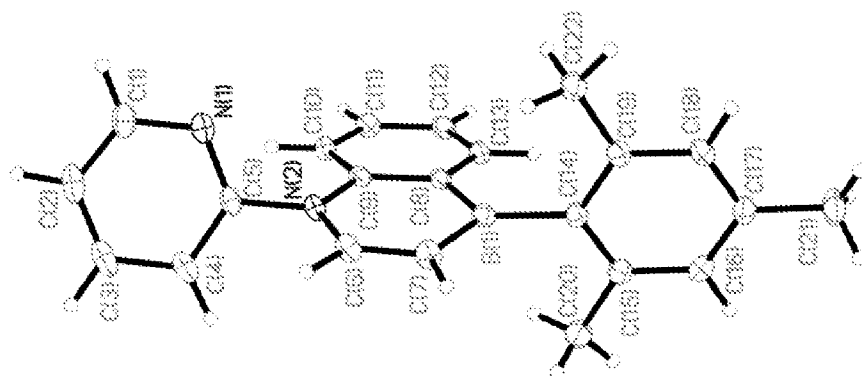
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Synthesis of Compound PYAB-1 (9L). To a 100-mL flask charged with AB-1 (800 mg, 3.2 mmol), 2-bromopyridine (0.46 mL, 4.8 mmol), Pd₂dba₃ (146 mg, 0.16 mmol), *t*ButylXphos (271 mg, 0.64 mmol), and NaO*t*Bu (614 mg, 6.4 mmol) was added toluene (20 mL). The resulting mixture was then allowed to

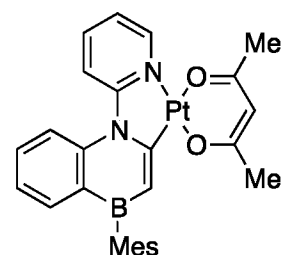


15 stir at 110 °C for 24 h. After cooling down to room temperature and removal of the solvent, the residue was purified by column chromatography on silica gel with hexanes/EtOAc (10/1) as the eluent to afford the PYAB-1 (9L) as the yellow solid (678 mg, 65%).

20 ¹H NMR (500 MHz, CDCl₃): δ 8.78 (d, *J* = 5.0 Hz, 1H), 8.07 (d, *J* = 9.5 Hz, 1H), 8.02 (m, 1H), 7.82 (d, *J* = 6.5 Hz, 1H), 7.56 (d, *J* = 7.5 Hz, 1H), 7.49 (m, 2H), 7.20 (m, 2H), 6.95 (s, 2H), 6.51 (d, *J* = 9.0 Hz, 1H), 2.40 (s, 3H), 2.13 (s, 6H); ¹³C NMR (125 MHz, CDCl₃): δ 156.1, 150.2, 145.5, 143.1, 139.0, 138.9, 136.1, 136.0, 130.7, 128.8 (br), 126.8, 123.7, 122.5, 121.8, 116.3, 114.9 (br), 23.2, 21.2; ¹¹B NMR (96.2 MHz, CDCl₃) δ 51.6; IR (thin film) 2912, 2859, 2364, 2332, 1580, 1559, 1533, 1454, 1430, 1352, 1234, 1160, 804, 773 cm⁻¹.

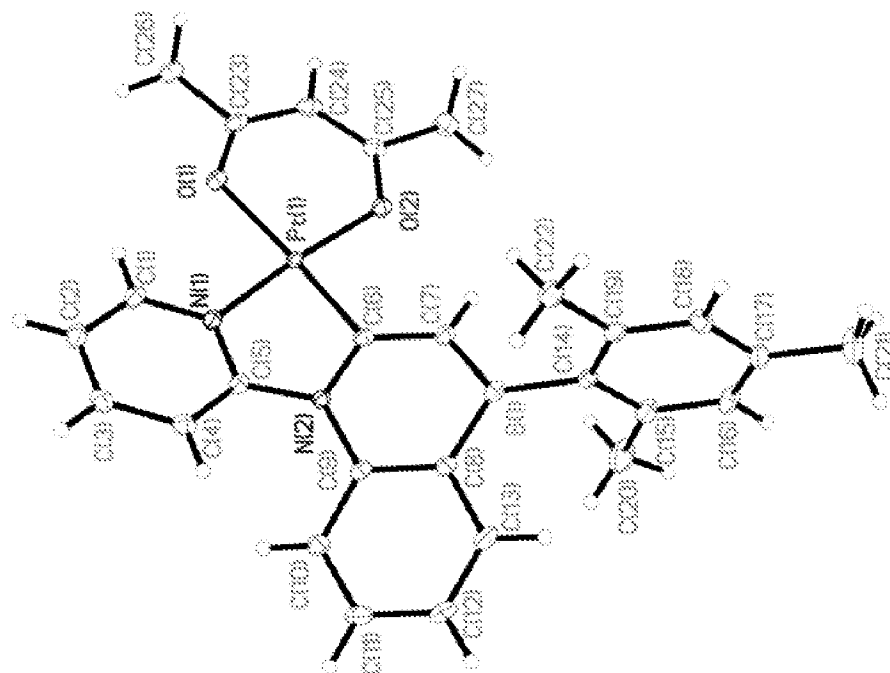


Synthesis of Compound Pt-PYAB-1 (32). To a 20-mL drum in glovebox charged with PYAB-1 (108 mg, 0.334) and $\text{Pt}(\text{SMe}_2)_2\text{Me}_2$ (96 mg, 0.167 mmol) was added THF (3 mL). The resulting mixture was allowed to stir at room temperature for 12 h. After addition of TfOH (29 μL , 0.334 mmol), the reaction mixture was stirred at room temperature for 0.5 h. Na(AcAc) (85 mg, 0.67 mmol) in



MeOH (1 mL) was added and the reaction was continued to stir at same temperature for 1 h. After removal the solvent, the residue was purified with column chromatography on silica gel with $\text{CH}_2\text{Cl}_2/\text{hexanes}$ (1/1) as the eluent to afford the Pt-PYAB-1 (32) as yellow powder (111 mg, 54%)

^1H NMR (500 MHz, CDCl_3): δ 8.97 (d, $J = 6.0$ Hz, 1H), 7.96 (d, $J = 8.5$ Hz, 1H), 7.90 (m, 1H), 7.86 (m, 1H), 7.67 (dd, $J = 7.5, 1.5$ Hz, 1H), 7.47 (m, 1H), 7.23 (m, 1H), 7.03 (t, $J = 6.0$ Hz, 1H), 6.94 (s, 2H), 6.75 (s, 1H), 5.51 (s, 1H), 2.39 (s, 3H), 2.18 (s, 6H), 2.07 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 186.3, 185.4, 160.4, 154.4, 146.0, 142.6, 141.7, 139.1, 138.2, 136.0, 133.3, 129.3, 126.8, 126.7, 123.1, 120.8, 117.4, 117.3, 113.8, 102.5, 27.8, 27.1, 23.1, 21.2; ^{11}B NMR (96.2 MHz, CDCl_3) δ 51.7; IR (thin film) 2912, 2849, 2364, 2332, 1611, 1585, 1562, 1507, 1483, 1433, 1320, 1153, 1061, 1027, 759, 741 cm^{-1} .



Photoluminescence of compound Pt-PYAB-1

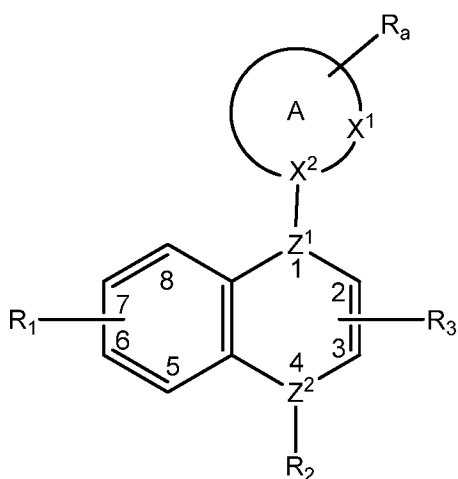
- 5 The photoluminescence spectrum of Compound Pt-PYAB-1 is shown in Figure 7. Blue emission was observed in both solution (2-MeTHF) and 5 weight % doped film with PMMA as the matrix. In PMMA film, the excited state lifetime was 50 μ s (50%) and 6.6 μ s (50%), with a photoluminescence quantum yield of 10%. Electrochemistry showed E_{ox} at 0.55 V and E_{red} at -2.31 V vs Fc/Fc⁺. The long excited state lifetime confirmed the phosphorescence nature of emission. Unlike most
- 10 cyclometallated Ir complexes with vibronic emissions, Compound Pt-PYAB-1 shows a featureless emission, at room temperature. It suggests a strong bond between the metal and the nitrogen. This feature may help the construction of stable blue phosphorescent OLEDs.

In view of the many possible embodiments to which the principles of the disclosed

15 invention may be applied, it should be recognized that the illustrated embodiments are only preferred examples of the invention and should not be taken as limiting the scope of the invention.

What is claimed is:

1. A compound comprising a structure of formula A:



wherein ring A includes a 5-membered or 6-membered carbocycle or heterocycle;

each R_a is independently selected from hydrogen, deuterium, halide, optionally-substituted alkyl, optionally-substituted cycloalkyl, optionally-substituted heteroalkyl, optionally-substituted arylalkyl, optionally-substituted alkoxy, optionally-substituted aryloxy, optionally-substituted amino, silyl, optionally-substituted alkenyl, optionally-substituted cycloalkenyl, optionally-substituted heteroalkenyl, alkynyl, aryl, heteroaryl, acyl, carbonyl, carboxylic acid, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, optionally-substituted amido, optionally-substituted phosphoryl, optionally-substituted thiophosphoryl, optionally-substituted phosphinyl, optionally-substituted thiophosphinyl, thioester, nitro, azido, optionally-substituted hydrazinyl, optionally-substituted diazenyl, or thiocarbonyl;

X^1 represents C, N, S, O or Se;

X^2 represents C or N;

Z^1 is B and Z^2 is N, or Z^1 is N and Z^2 is B;

each R_1 is independently selected from hydrogen, deuterium, halide, optionally-substituted alkyl, optionally-substituted cycloalkyl, optionally-substituted heteroalkyl, optionally-substituted arylalkyl, optionally-substituted alkoxy, optionally-substituted aryloxy, optionally-substituted amino, silyl, optionally-substituted alkenyl, optionally-substituted cycloalkenyl, optionally-

substituted heteroalkenyl, optionally-substituted alkynyl, optionally-substituted aryl, optionally-substituted heteroaryl, optionally-substituted acyl, carbonyl, carboxylic acid, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, optionally-substituted amido, optionally-substituted phosphoryl, optionally-substituted thiophosphoryl, optionally-substituted phosphinyl, optionally-substituted thiophosphinyl, thioester, nitro, azido, optionally-substituted hydrazinyl, optionally-substituted diazenyl, or thiocarbonyl;

R_2 is independently selected from hydrogen, deuterium, halide, optionally-substituted alkyl, optionally-substituted cycloalkyl, optionally-substituted heteroalkyl, optionally-substituted arylalkyl, optionally-substituted alkoxy, optionally-substituted aryloxy, optionally-substituted amino, silyl, optionally-substituted alkenyl, optionally-substituted cycloalkenyl, optionally-substituted heteroalkenyl, optionally-substituted alkynyl, optionally-substituted aryl, optionally-substituted heteroaryl, acyl, carbonyl, carboxylic acid, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, optionally-substituted amido, optionally-substituted phosphoryl, optionally-substituted thiophosphoryl, optionally-substituted phosphinyl, optionally-substituted thiophosphinyl, thioester, nitro, azido, optionally-substituted hydrazinyl, optionally-substituted diazenyl, or thiocarbonyl; and

each R_3 is independently selected from hydrogen, deuterium, halide, optionally-substituted alkyl, optionally-substituted cycloalkyl, optionally-substituted heteroalkyl, optionally-substituted arylalkyl, optionally-substituted alkoxy, optionally-substituted aryloxy, optionally-substituted amino, silyl, optionally-substituted alkenyl, optionally-substituted cycloalkenyl, optionally-substituted heteroalkenyl, optionally-substituted alkynyl, optionally-substituted aryl, optionally-substituted heteroaryl, acyl, carbonyl, carboxylic acid, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, optionally-substituted amido, optionally-substituted phosphoryl, optionally-substituted thiophosphoryl, optionally-substituted phosphinyl, optionally-substituted thiophosphinyl, thioester, nitro, azido, optionally-substituted hydrazinyl, optionally-substituted diazenyl, or thiocarbonyl.

2. The compound of claim 1, wherein ring A is an optionally-substituted N-heterocycle.

3. The compound of claim 1 or 2, wherein ring A includes at least two fused rings.

4. The compound of any one of claims 1 to 3, wherein at least one of X^1 or X^2 is N.

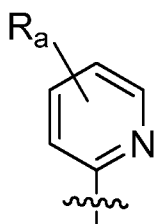
5. The compound of any one of claims 1 to 3, wherein X^2 is C, and X^1 is N.

6. The compound of any one of claims 1 to 5, wherein Z^1 is B and Z^2 is N.

5

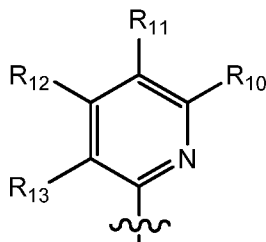
7. The compound of any one of claims 1 to 5, wherein Z^1 is N and Z^2 is B.

8. The compound of any one of claims 1, 2 or 4 to 7, wherein A is:



10

9. The compound of any one of claims 1, 2 or 4 to 8, wherein A is:



wherein R_{10} is an alkyl; and R_{11} - R_{13} are each H.

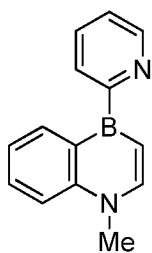
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10. The compound of claim 1, wherein A is optionally-substituted pyridinyl; Z^1 is N; Z^2 is B; R_1 is hydrogen; R_2 is hydrogen, lower alkyl or unsubstituted phenyl; and R_3 is hydrogen or alkyl.

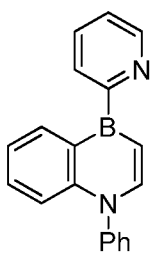
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11. The compound of claim 1, wherein A is optionally-substituted pyridinyl; Z^1 is B; Z^2 is N; R_1 is hydrogen; R_2 is hydrogen, lower alkyl or aryl; and R_3 is hydrogen or lower alkyl.

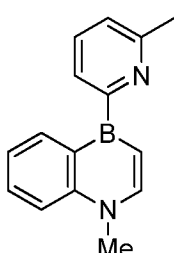
12. The compound of claim 1, wherein the compound is selected from:



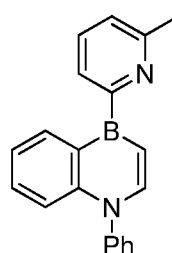
Compound 1L ,



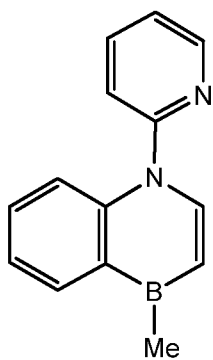
Compound 2L ,



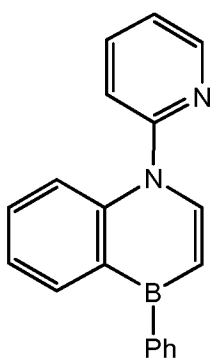
Compound 3L ,



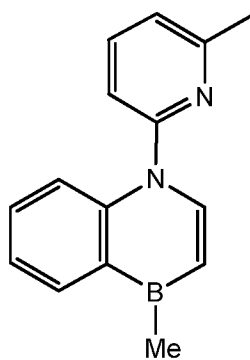
Compound 4L ,



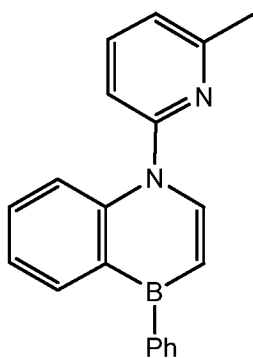
Compound 5L



Compound 6L ,



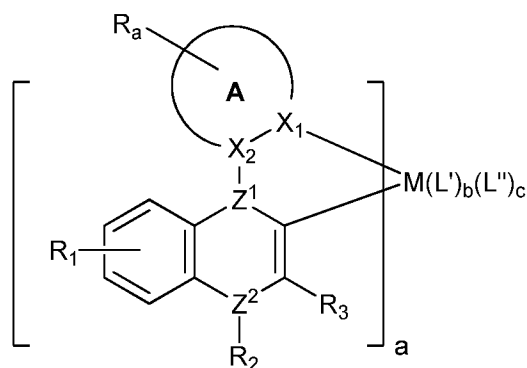
Compound 7L , or



5 Compound 8L

13. A compound comprising a metal M coordinated to a ligand, wherein the ligand comprises any one of the compounds of claims 1 to 12.

10 14. A compound comprising a structure of formula B:



Formula B

wherein L' and L'' are mono, bi or tri ligands; M is a metal; a is 1, 2, or 3; b is 0, 1, or 2; c is 0, 1 or 2; a+b+c is n, wherein n is the oxidation state of the metal M;

ring A includes a 5-membered or 6-membered carbocycle or heterocycle;

5 each R_a is independently selected from hydrogen, deuterium, halide, optionally-substituted alkyl, optionally-substituted cycloalkyl, optionally-substituted heteroalkyl, optionally-substituted arylalkyl, optionally-substituted alkoxy, optionally-substituted aryloxy, optionally-substituted amino, silyl, optionally-substituted alkenyl, optionally-substituted cycloalkenyl, optionally-substituted heteroalkenyl, alkynyl, aryl, heteroaryl, acyl, carbonyl, carboxylic acid, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, optionally-substituted amido, optionally-substituted
10 phosphoryl, optionally-substituted thiophosphoryl, optionally-substituted phosphinyl, optionally-substituted thiophosphinyl, thioester, nitro, azido, optionally-substituted hydrazinyl, optionally-substituted diazenyl, or thiocarbonyl;

X₁ represents C, N, S, O or Se;

15 X₂ represents C or N;

Z¹ is B and Z² is N, or Z¹ is N and Z² is B;

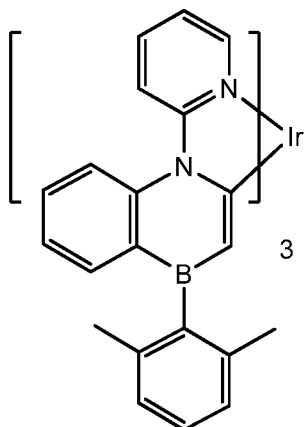
each R₁ is independently selected from hydrogen, deuterium, halide, optionally-substituted alkyl, optionally-substituted cycloalkyl, optionally-substituted heteroalkyl, optionally-substituted arylalkyl, optionally-substituted alkoxy, optionally-substituted aryloxy, optionally-substituted
20 amino, silyl, optionally-substituted alkenyl, optionally-substituted cycloalkenyl, optionally-substituted heteroalkenyl, optionally-substituted alkynyl, optionally-substituted aryl, optionally-substituted heteroaryl, optionally-substituted acyl, carbonyl, carboxylic acid, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, optionally-substituted amido, optionally-substituted phosphoryl, optionally-substituted thiophosphoryl, optionally-substituted phosphinyl, optionally-substituted

thiophosphinyl, thioester, nitro, azido, optionally-substituted hydrazinyl, optionally-substituted diazenyl, or thiocarbonyl;

R_2 is independently selected from hydrogen, deuterium, halide, optionally-substituted alkyl, optionally-substituted cycloalkyl, optionally-substituted heteroalkyl, optionally-substituted
5 arylalkyl, optionally-substituted alkoxy, optionally-substituted aryloxy, optionally-substituted amino, silyl, optionally-substituted alkenyl, optionally-substituted cycloalkenyl, optionally-substituted heteroalkenyl, optionally-substituted alkynyl, optionally-substituted aryl, optionally-substituted heteroaryl, acyl, carbonyl, carboxylic acid, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, optionally-substituted amido, optionally-substituted phosphoryl, optionally-substituted
10 thiophosphoryl, optionally-substituted phosphinyl, optionally-substituted thiophosphinyl, thioester, nitro, azido, optionally-substituted hydrazinyl, optionally-substituted diazenyl, or thiocarbonyl; and
each R_3 is independently selected from hydrogen, deuterium, halide, optionally-substituted alkyl, optionally-substituted cycloalkyl, optionally-substituted heteroalkyl, optionally-substituted
15 arylalkyl, optionally-substituted alkoxy, optionally-substituted aryloxy, optionally-substituted amino, silyl, optionally-substituted alkenyl, optionally-substituted cycloalkenyl, optionally-substituted heteroalkenyl, optionally-substituted alkynyl, optionally-substituted aryl, optionally-substituted heteroaryl, acyl, carbonyl, carboxylic acid, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, optionally-substituted amido, optionally-substituted phosphoryl, optionally-substituted
20 thiophosphoryl, optionally-substituted phosphinyl, optionally-substituted thiophosphinyl, thioester, nitro, azido, optionally-substituted hydrazinyl, optionally-substituted diazenyl, or thiocarbonyl.

15. The compound of claim 14, wherein M is Ir.

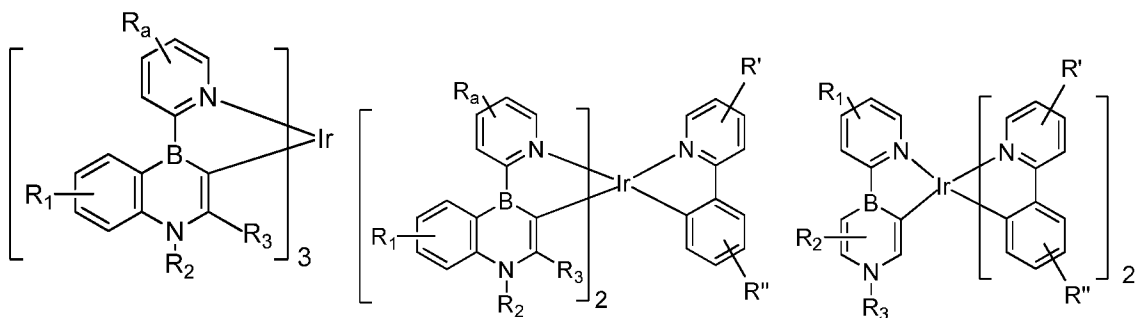
16. The compound of claim 14, wherein the compound is not:



17. The compound of claim 14, wherein A is optionally-substituted pyridinyl; Z^1 is N;
 Z^2 is B; R_1 is hydrogen; R_2 is hydrogen, lower alkyl or unsubstituted phenyl; and R_3 is hydrogen or
 5 alkyl.

18. The compound of claim 14, wherein A is optionally-substituted pyridinyl; Z^1 is B;
 Z^2 is N; R_1 is hydrogen; R_2 is hydrogen, lower alkyl or aryl; and R_3 is hydrogen or lower alkyl.

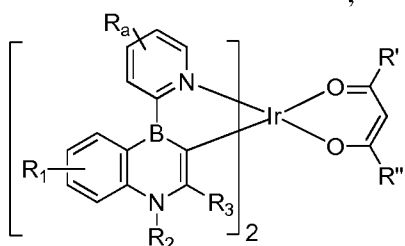
10 19. The compound of claim 14, wherein the compound is selected from:



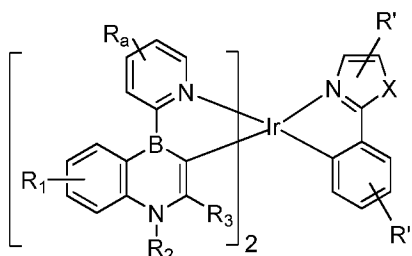
Compound 1G

Compound 2G

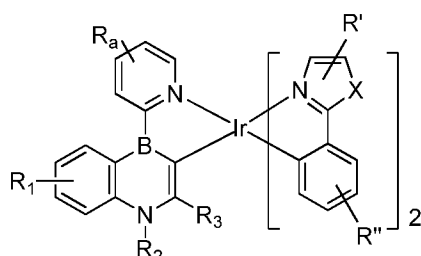
Compound 3G



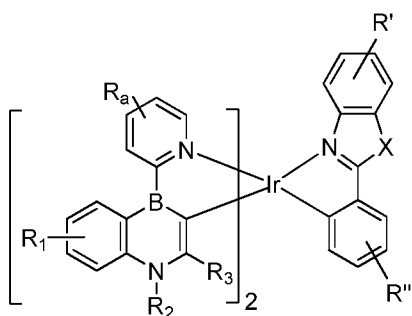
Compound 4G



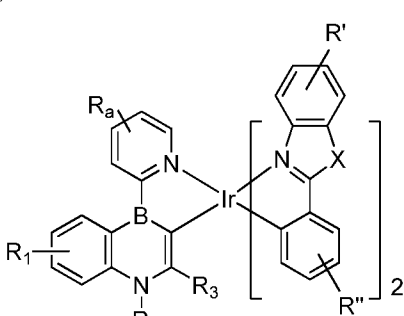
Compound 5G



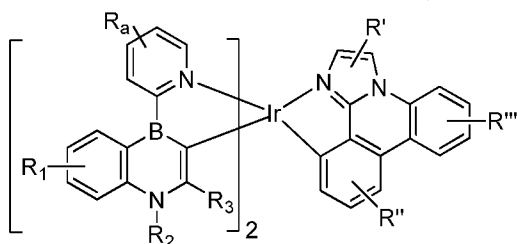
Compound 6G



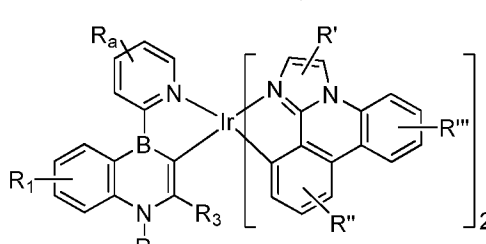
Compound 7G



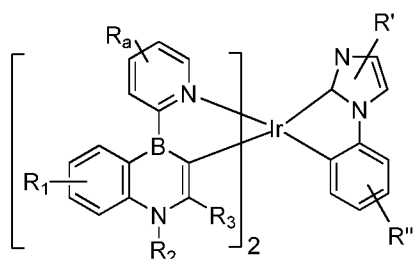
Compound 8G



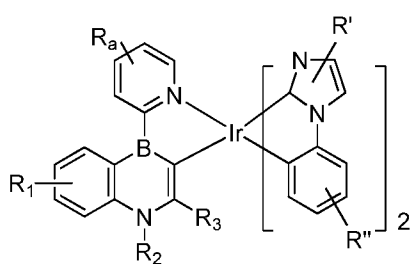
Compound 9G



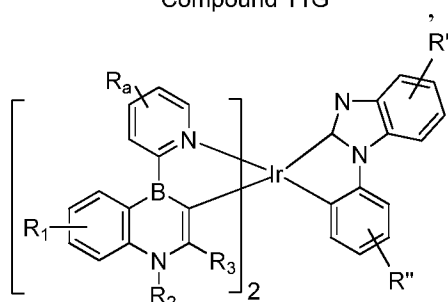
Compound 10G



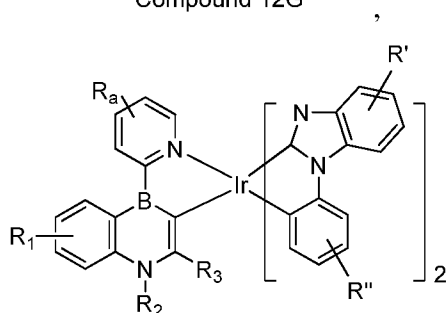
Compound 11G



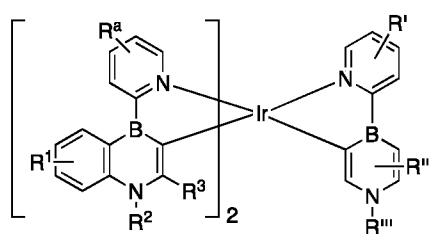
Compound 12G



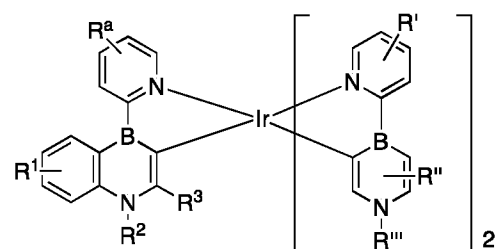
Compound 13G



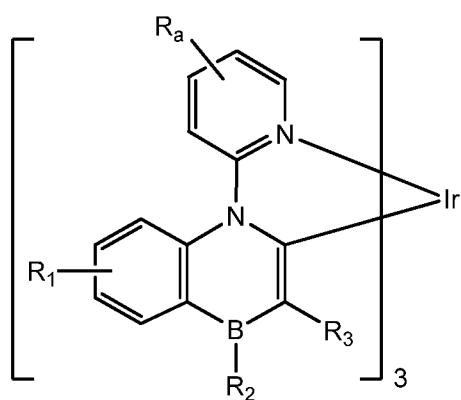
Compound 14G



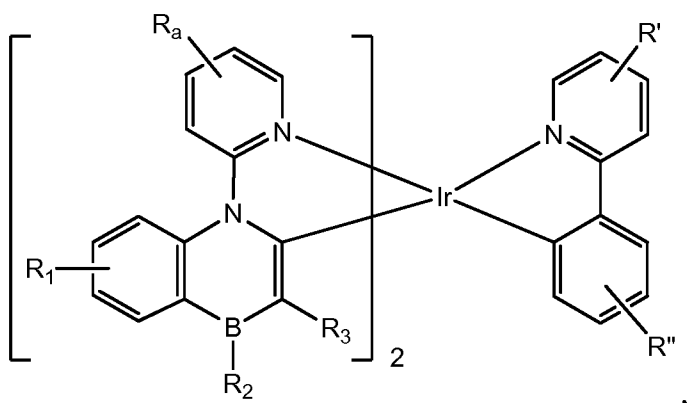
Compound 15G



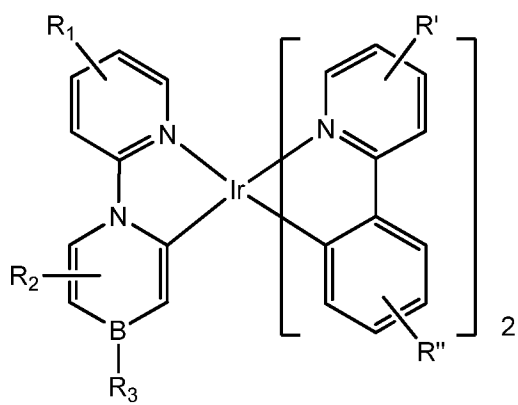
compound 16G



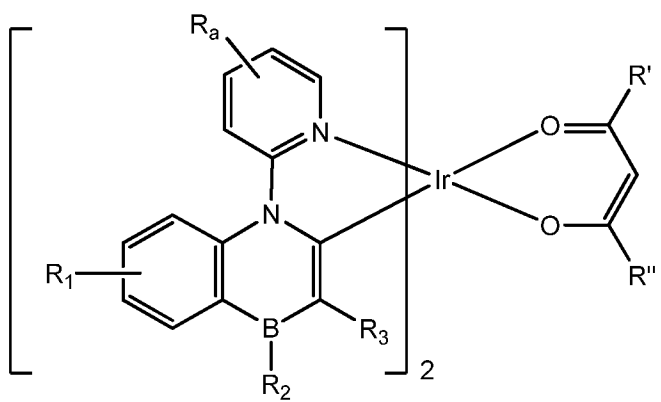
Compound 17G



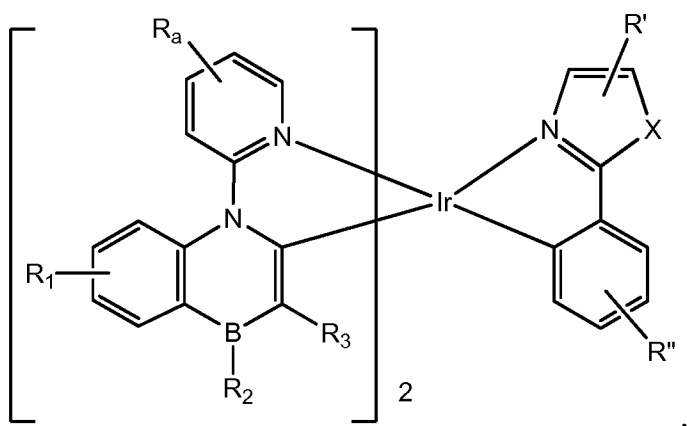
Compound 18G



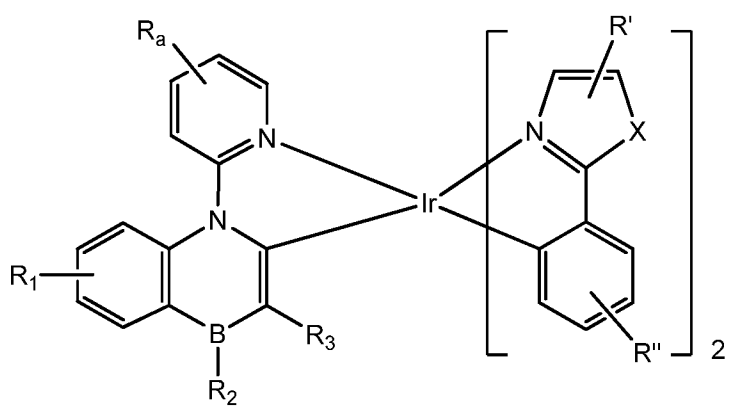
Compound 19G



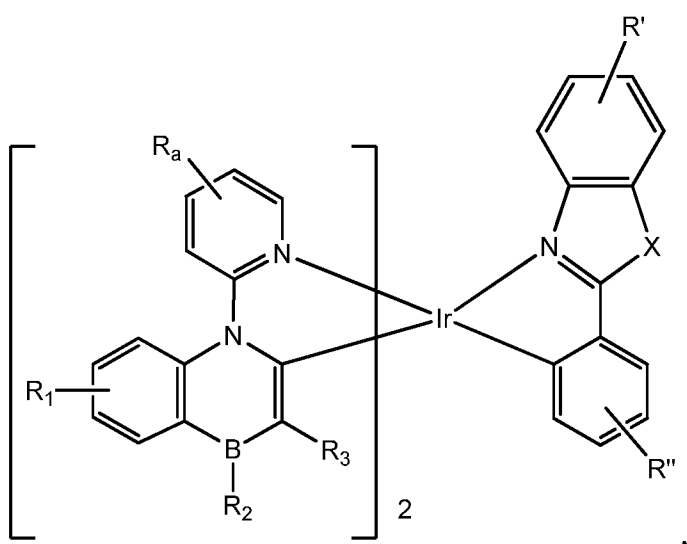
Compound 20G



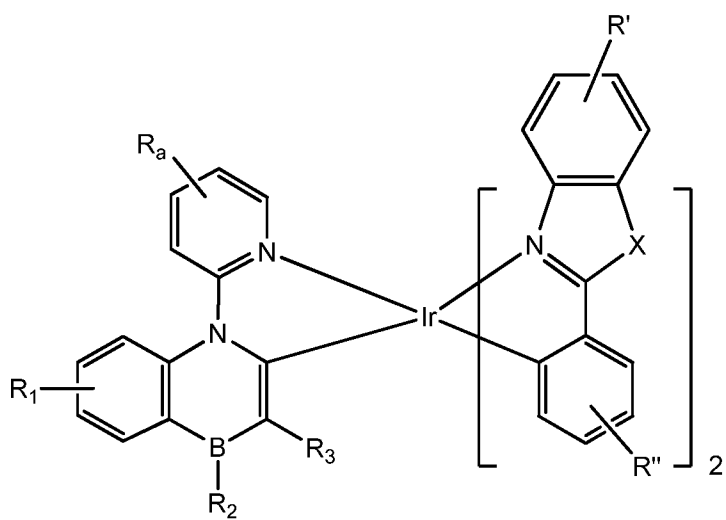
Compound 21G



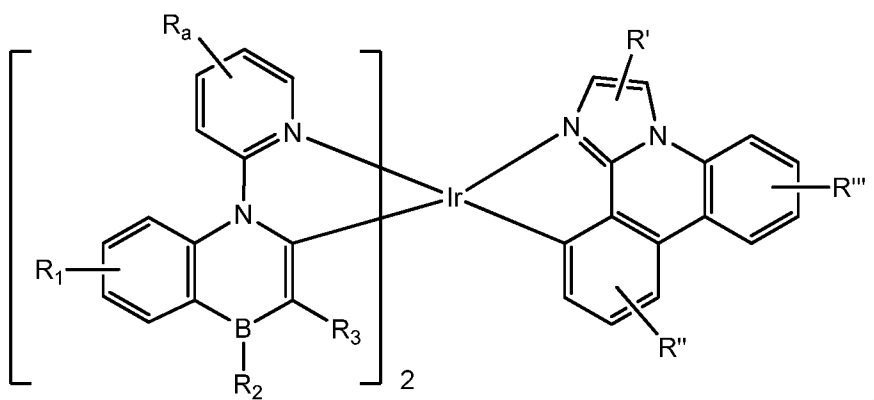
Compound 22G



Compound 23G

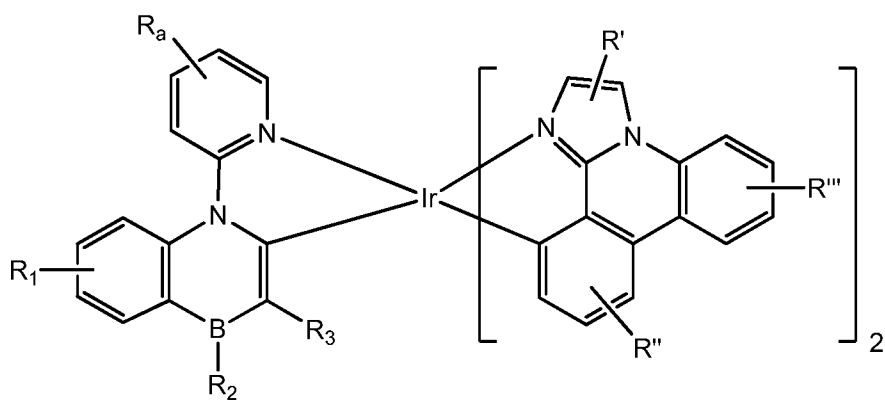


Compound 24G

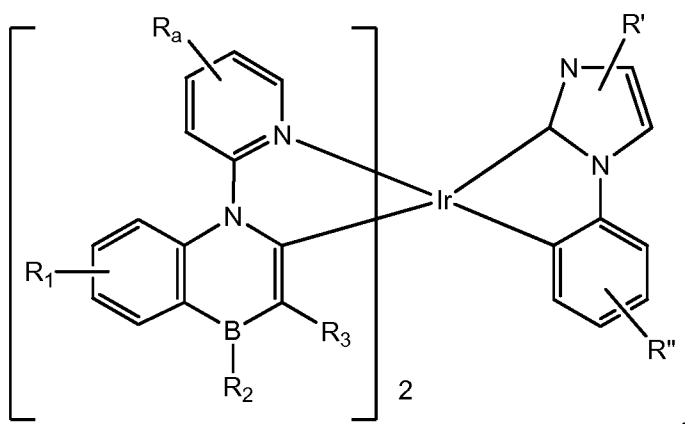


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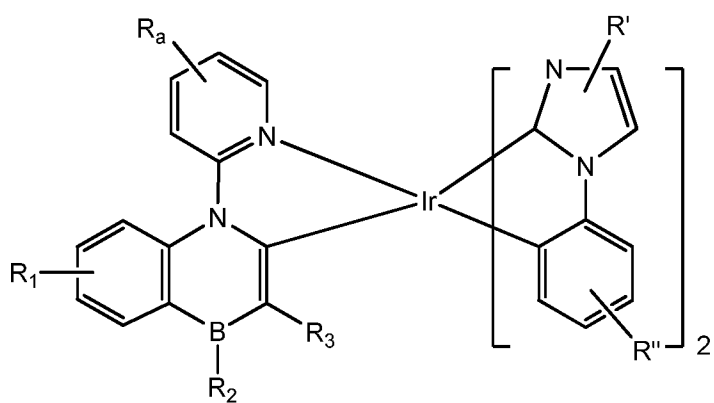
Compound 25G



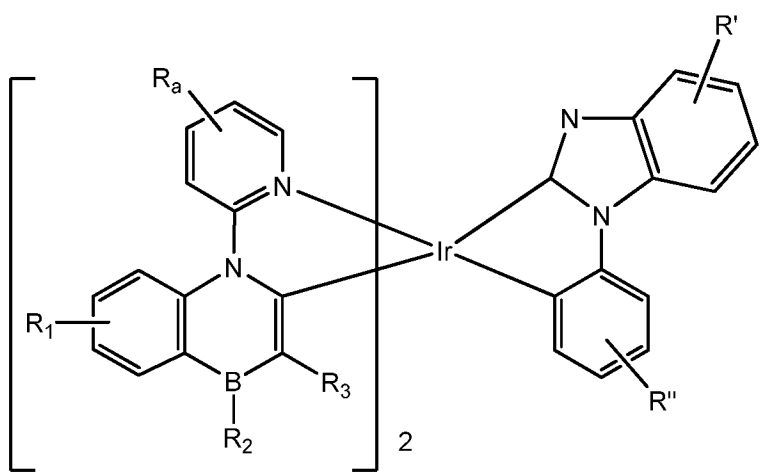
Compound 26G



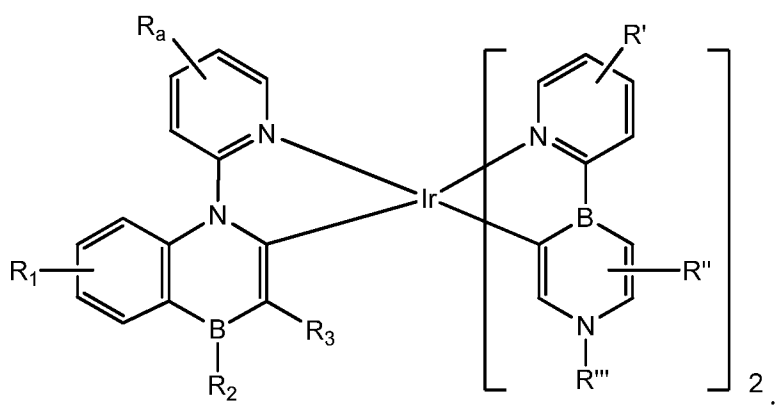
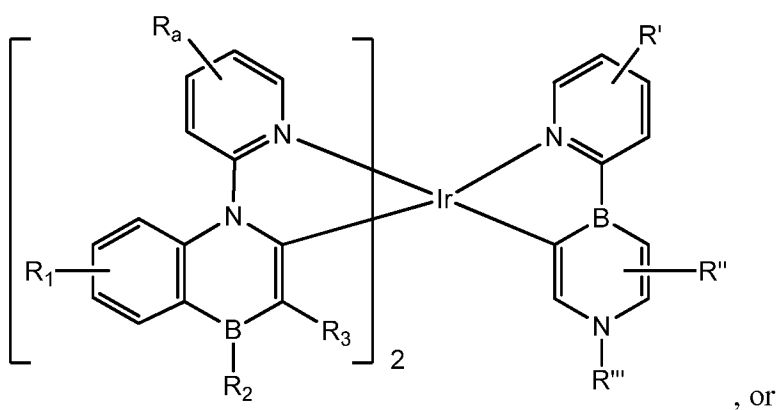
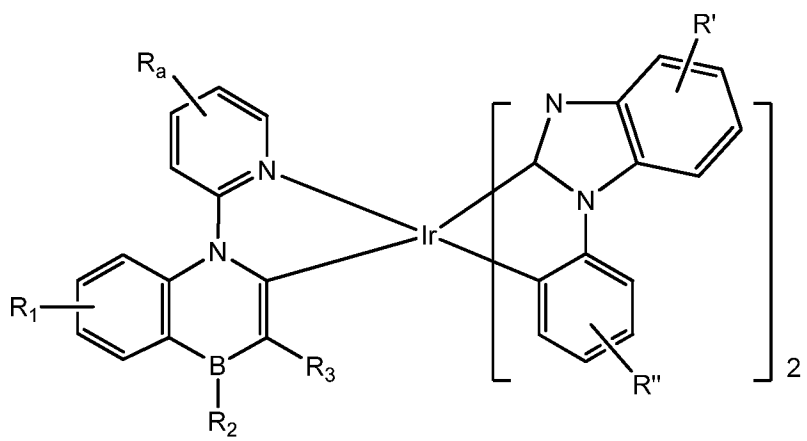
Compound 27G



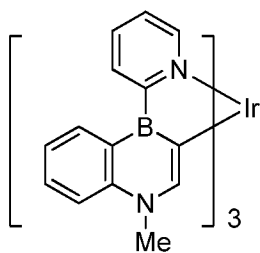
Compound 28G



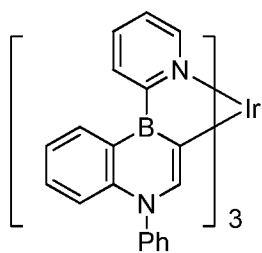
Compound 29G



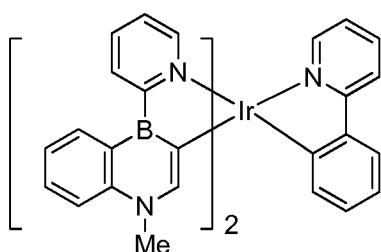
20. The compound of claim 14, wherein the compound is selected from:



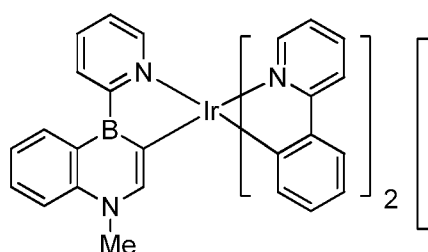
Compound 1



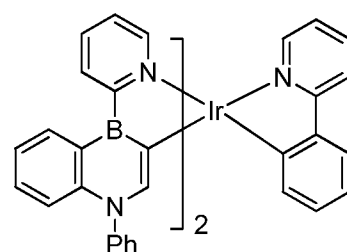
Compound 2



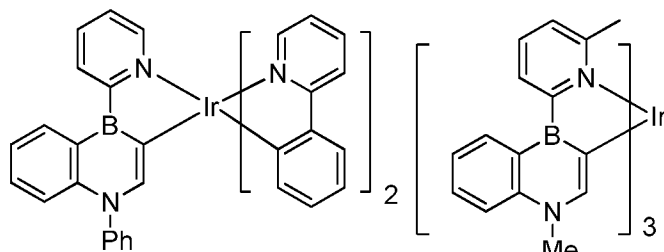
Compound 3



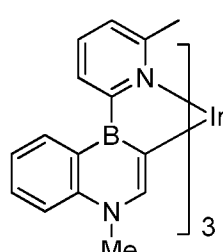
Compound 4



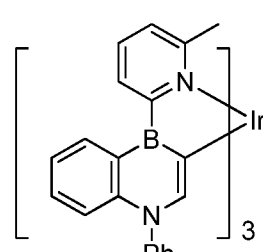
Compound 5



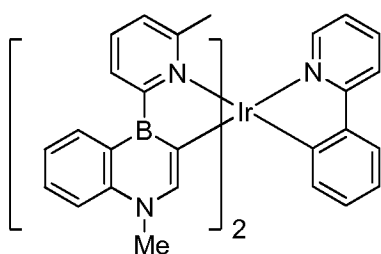
Compound 6



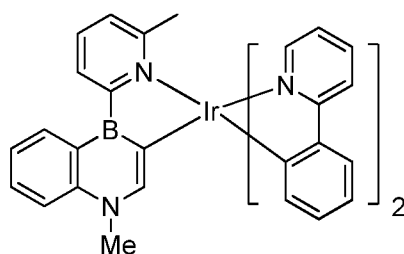
Compound 7



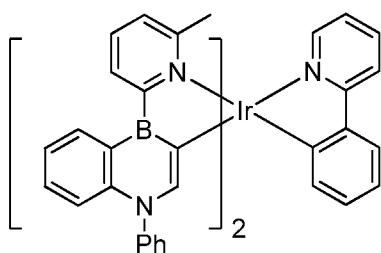
Compound 8



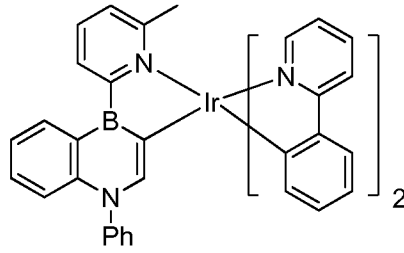
Compound 9



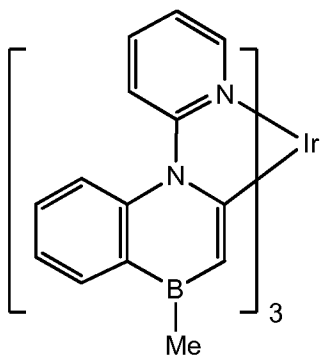
Compound 10



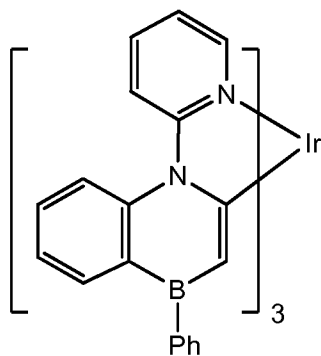
Compound 11



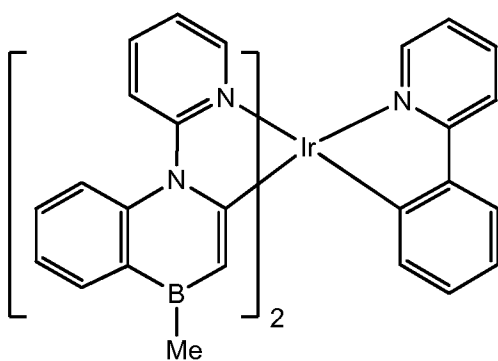
Compound 12



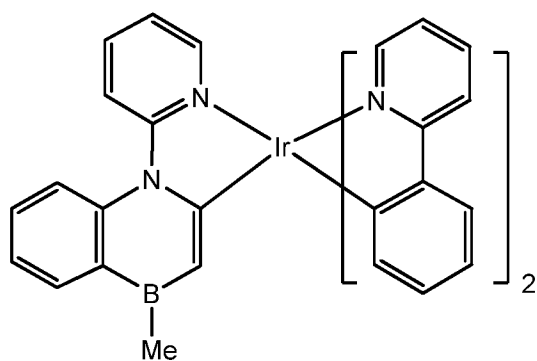
Compound 13



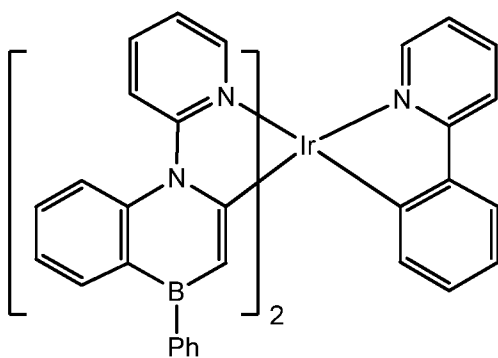
Compound 14



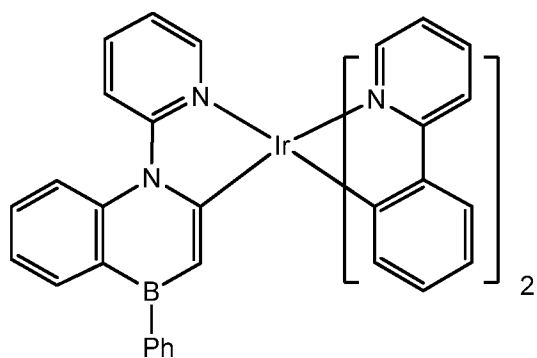
5 Compound 15



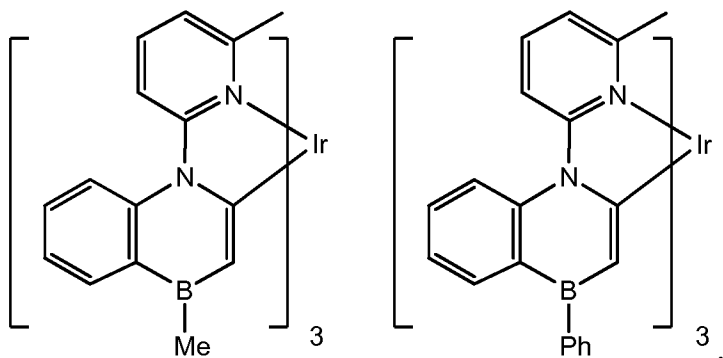
Compound 16



Compound 17

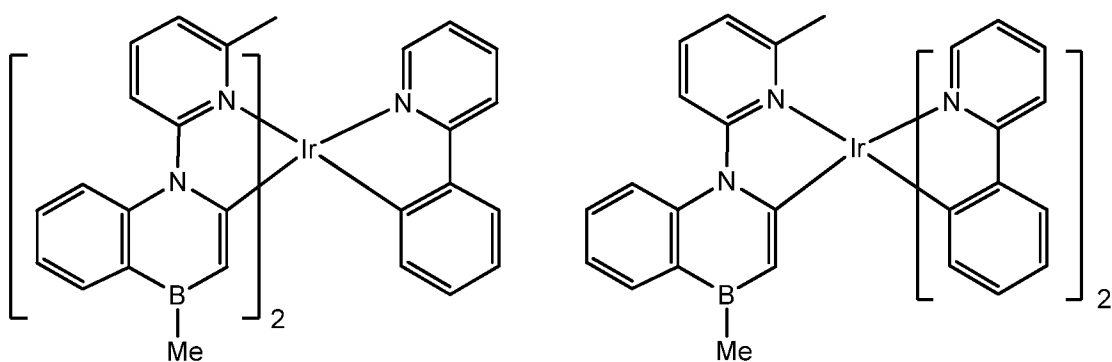


Compound 18



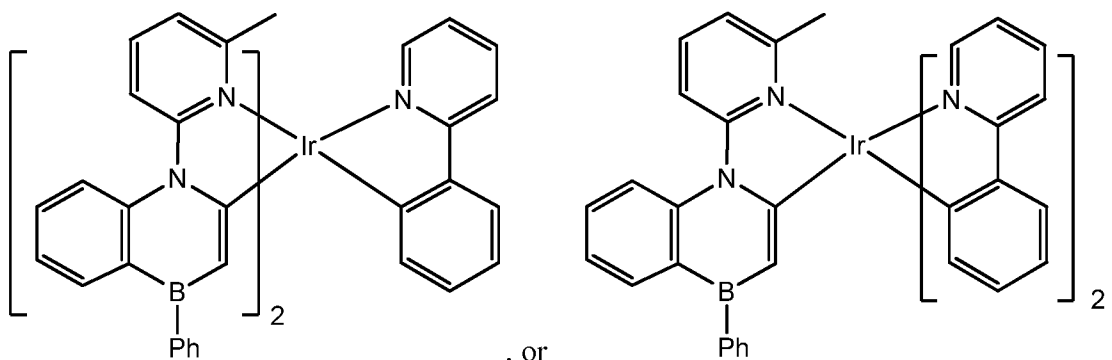
Compound 19

Compound 20



5 Compound 21

Compound 22



Compound 23

Compound 24

21. An organic light emitting device comprising:

an anode;

a cathode; and

an organic layer disposed between the anode and the cathode, wherein the organic layer comprises a compound of any one of claims 1 to 20.

22. The device of claim 21, wherein the organic layer is an emissive layer and the compound of any one of claims 1 to 20 is an emitting dopant, and the organic layer further comprises a host.

5

23. The device of claim 21, wherein the organic layer is an emissive layer and the compound of any one of claims 1 to 20 is a host.

24. The device of claim 21, wherein the organic layer is an emissive layer and the compound of any one of claims 1 to 20 is a fluorescent emitter.

10

25. The device of claim 21, wherein the organic layer is an emissive layer and the compound of any one of claims 1 to 20 is a phosphorescent emitter.

15

26. The device of claim 21 wherein the compound of any one of claims 1 to 20 is a charge transport material.

27. A consumer product comprising the device of any one of claims 21 to 26.

20

28. A method for making a benzo-fused 1,4-azaborine, comprising:
performing an alkene isomerization of an aryl N-allylamine to produce an aryl enamine;
coupling the aryl enamine with a boron-containing electrophile to produce a ring-closing-metathesis aryl precursor having an enamine substituent and a boron-containing substituent,
wherein the enamine substituent is at an *ortho* position relative to the boron-containing substituent;
and

25

performing a ring-closing metathesis on the ring-closing-metathesis aryl precursor to produce a benzo-fused 1,4-azaborine.

30

29. The method of claim 28, further comprising:

performing a methanolysis of the benzo-fused 1,4-azaborine at the boron heteroatom resulting in a B-OMe substituted 1,4-azaborine; and

coupling the B-OMe substituted 1,4-azaborine with a 2-optionally substituted pyridine derivative to produce a B-pyridinyl substituted benzo-fused 1,4-azaborine.

5

30. The method of claim 28, further comprising:

performing a Buchwald-Hartwig amination at the nitrogen heteroatom of the benzo-fused 1,4-azaborine to produce an N-pyridinyl substituted benzo-fused 1,4-azaborine.

10

31. The method of claim 28, wherein the aryl N-allylamine is an aryl N-alkylallylamine, the method further comprising:

performing an N-allylation of an ortho-substituted aryl amine to produce an aryl N-allylamine; and

performing an N-alkylation of the aryl N-allylamine to produce the aryl N-alkylallylamine.

15

32. A method for making a benzo-fused 1,4-azaborine, comprising:

providing a N-protected ortho-substituted aryl amine;

subjecting the N-protected ortho-substituted aryl amine to an electrophilic borylation to provide an N-protected benzo-fused 1,4-azaborine intermediate;

20

removing the N-protecting group from the N-protected benzo-fused 1,4-azaborine intermediate; and

performing a Buchwald-Hartwig amination at the nitrogen heteroatom of the benzo-fused 1,4-azaborine to produce an N-pyridinyl substituted benzo-fused 1,4-azaborine.

25

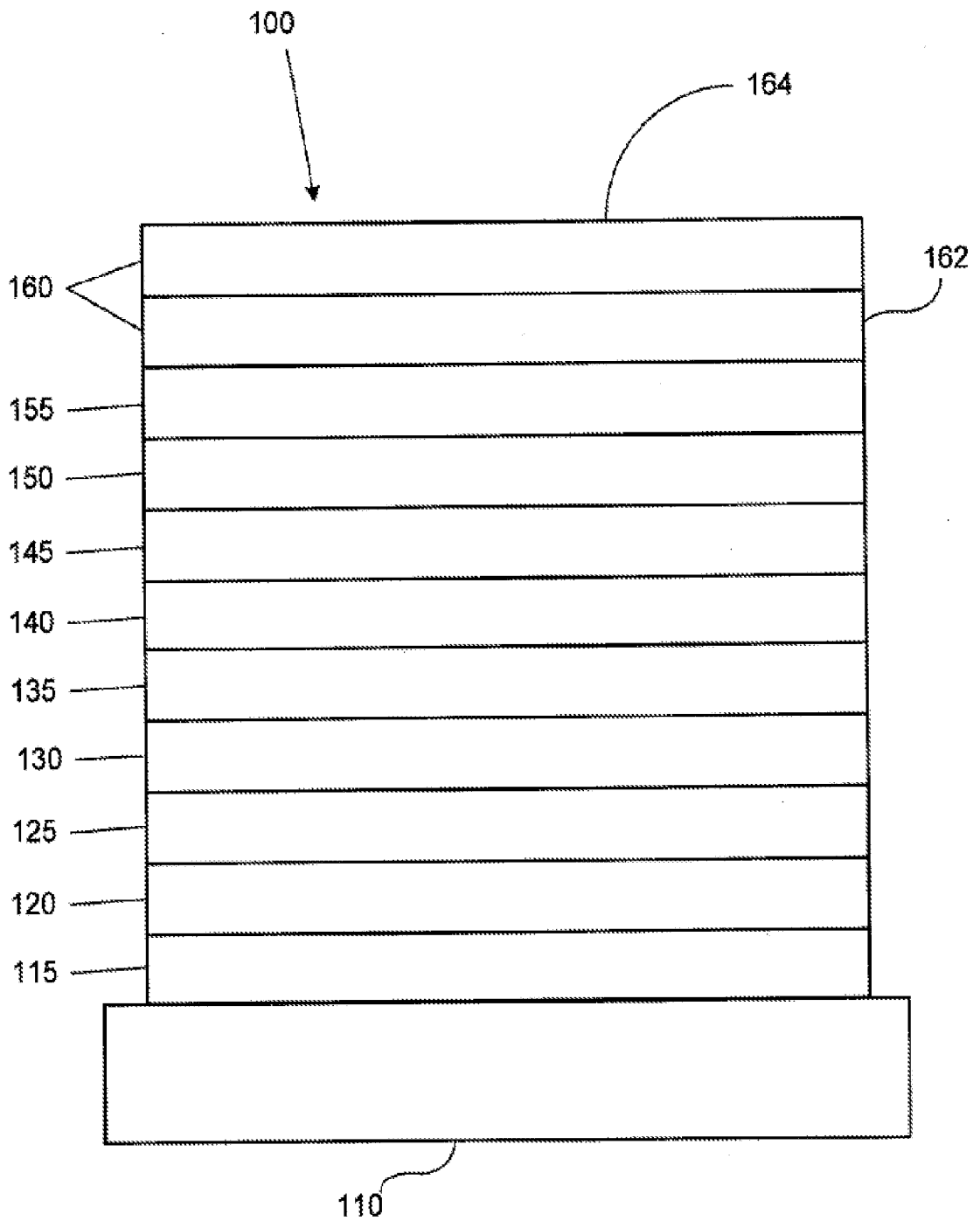


FIG. 1

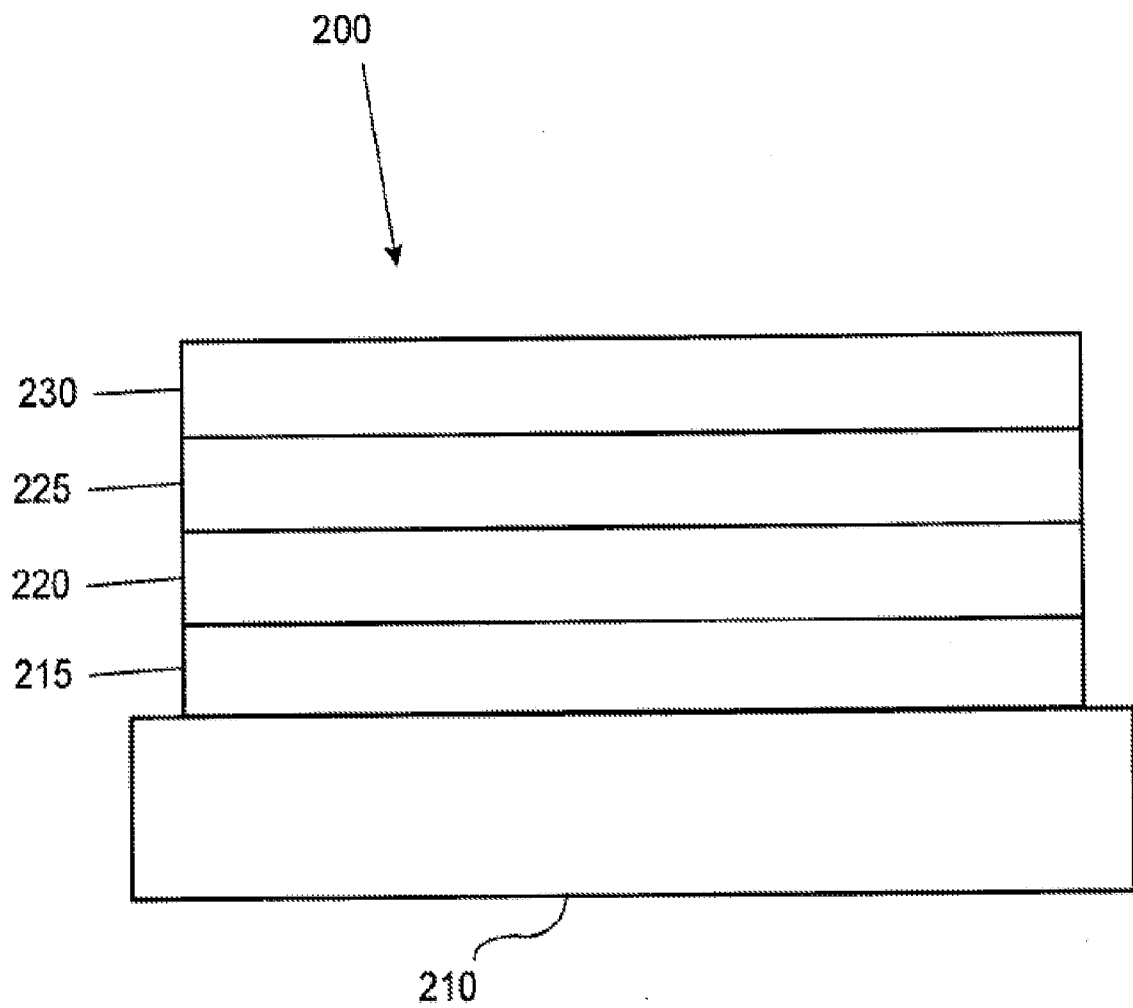


FIG. 2

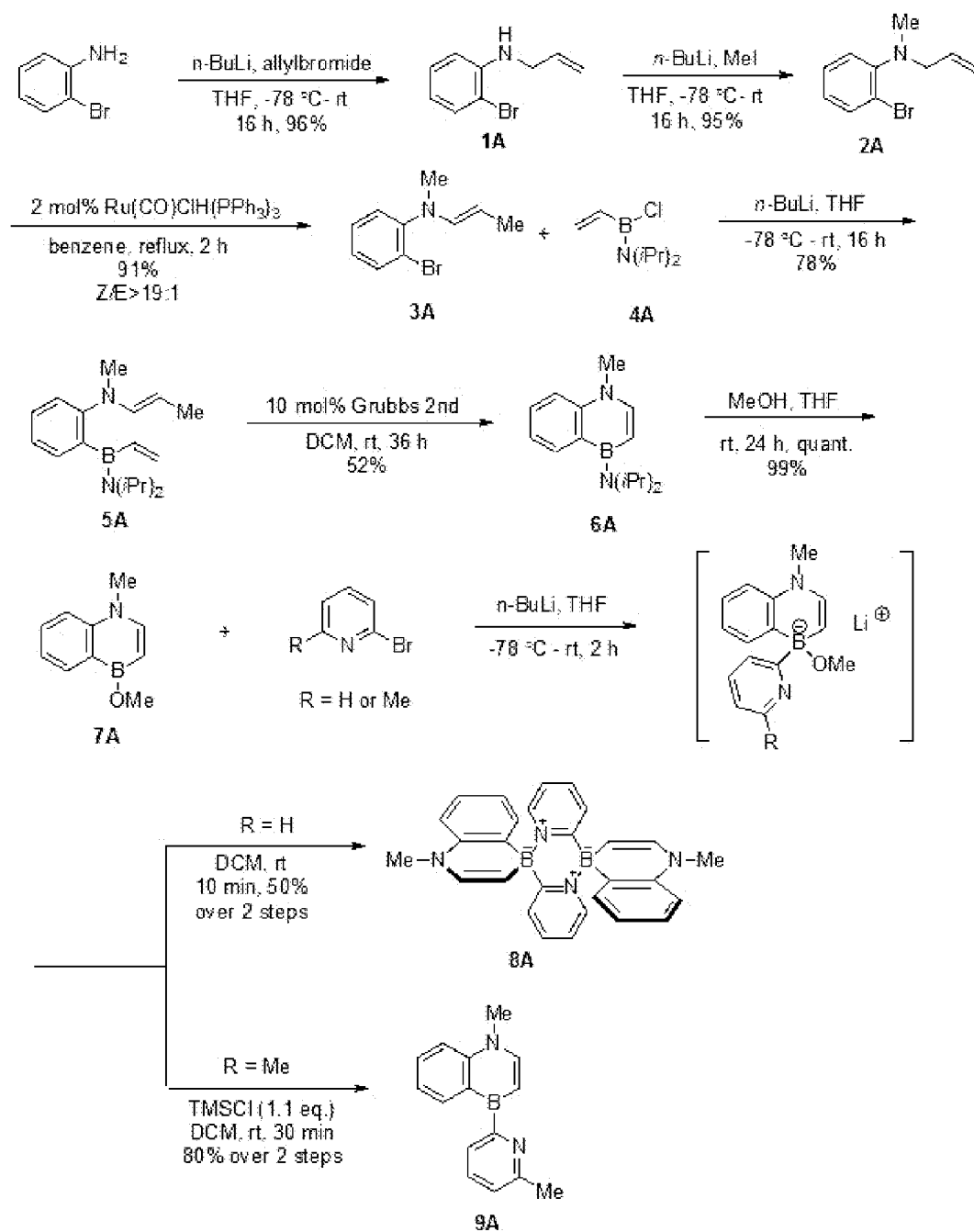


FIG. 3

N-Pyridyl 1,4-Azaborine

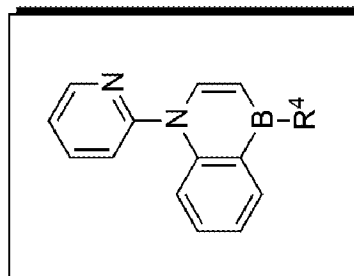
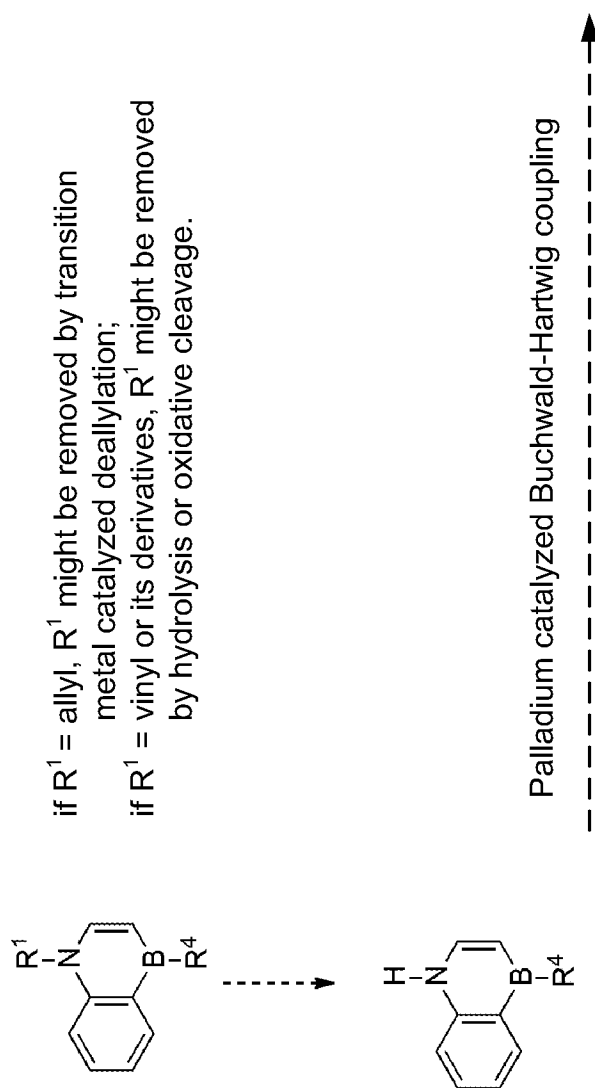


FIG. 4

Electrophilic Borylation Approach

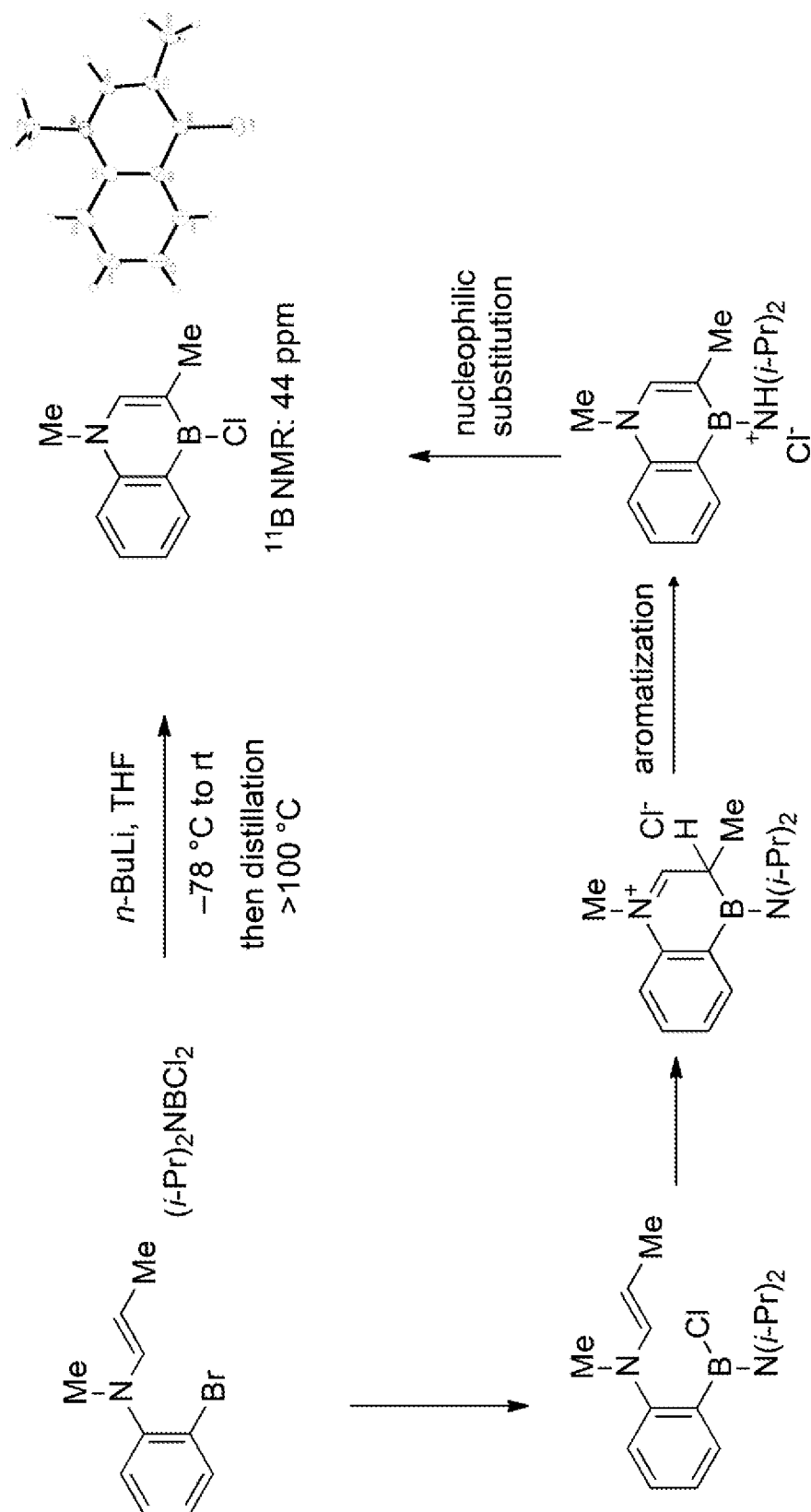


FIG. 5

N-Pyridyl 1,4-Azaborine

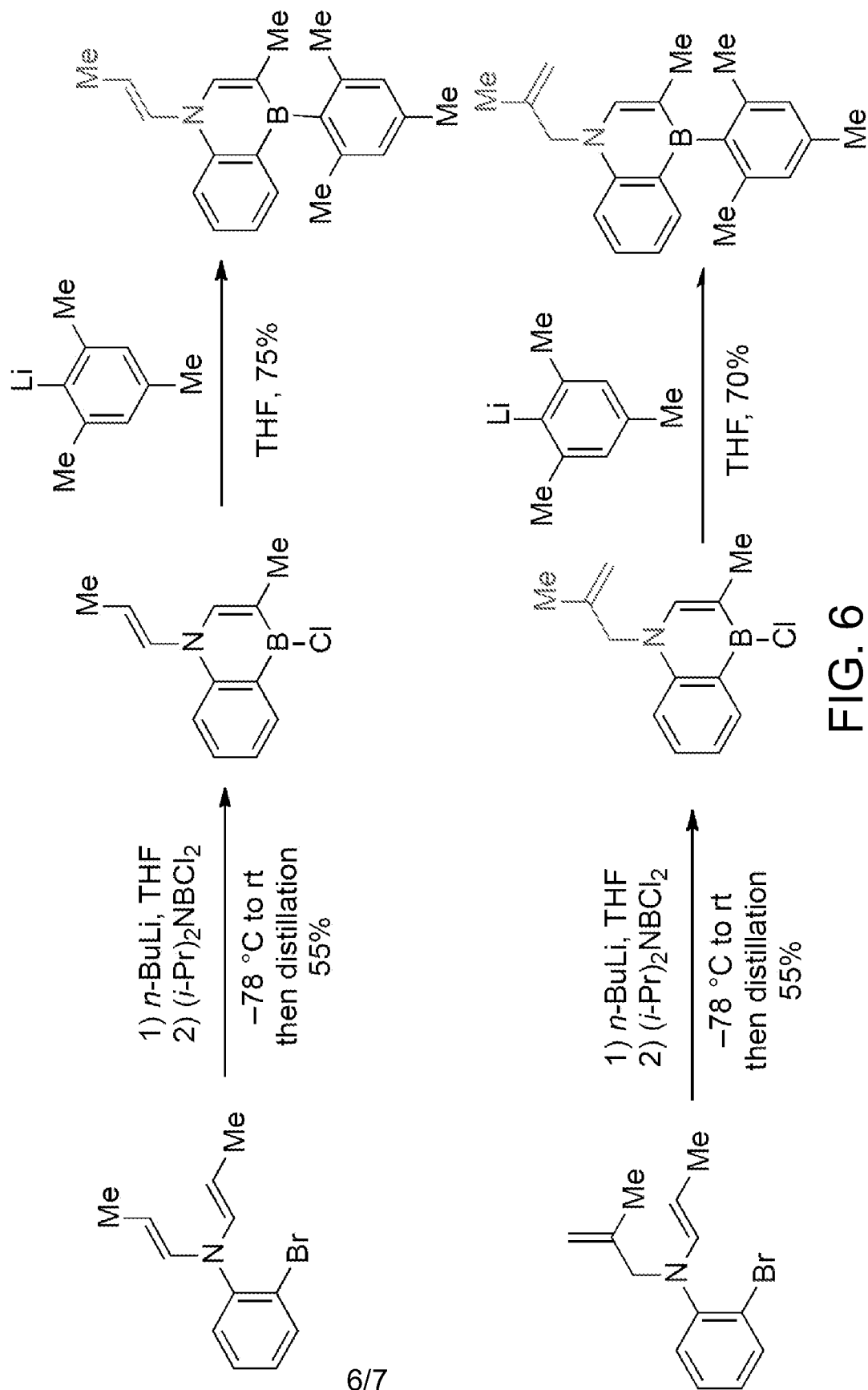


FIG. 6

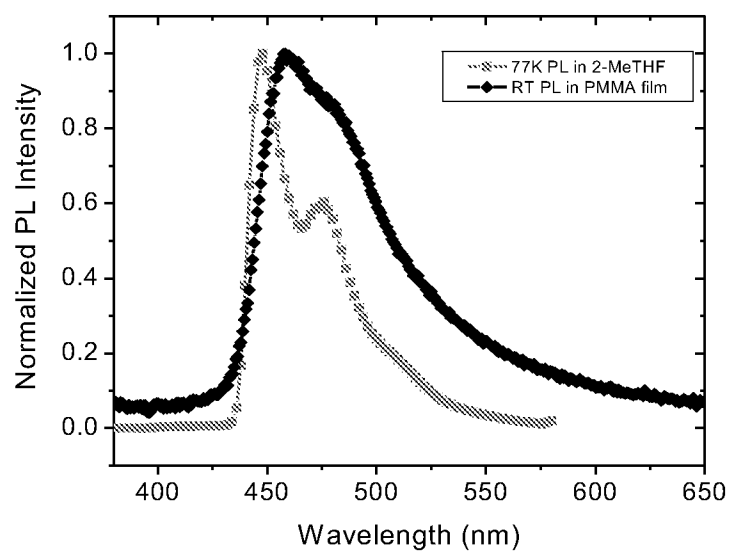


FIG. 7

INTERNATIONAL SEARCH REPORT

 International application No.
PCT/US2013/048495

A. CLASSIFICATION OF SUBJECT MATTER

C07F 5/02 (2006.01) C07F 15/00 (2006.01) C09K 11/06 (2006.01) H05B 33/14 (2006.01) H01L 51/00 (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPODOC, WPI, MEDLINE, HCA, BIOSIS, STN REGISTRY: (azaborine)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	



Further documents are listed in the continuation of Box C



See patent family annex

* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed		"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family	
Date of the actual completion of the international search 10 September 2013		Date of mailing of the international search report 10 September 2013	
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaustalia.gov.au Facsimile No.: +61 2 6283 7999		Authorised officer Neal Dalton AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. 0399359615	

INTERNATIONAL SEARCH REPORT C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		International application No. PCT/US2013/048495
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2010/135519 A1 (UNIVERSAL DISPLAY CORPORATION) 25 November 2010 see 0003, 0034-0036, Table 2 page 17	1-27
A	WO 2011/143563 A2 (UNIVERSAL DISPLAY CORPORATION) 17 November 2011	1-32
A	Campbell, P. G. et al. "Recent advances in azaborine chemistry" Angew Chem Int Ed Engl. 2012. Vol. 51, No. 25, pages 6074-6092.	1-32

INTERNATIONAL SEARCH REPORT		International application No.	
Information on patent family members		PCT/US2013/048495	
This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.			
Patent Document/s Cited in Search Report		Patent Family Member/s	
Publication Number	Publication Date	Publication Number	Publication Date
WO 2010/135519 A1	25 Nov 2010	EP 2448947 A1	09 May 2012
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End of Annex			
Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.			