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(54) Title: SILANE COMPOUNDS AND METHODS OF USING THEREOF

(57) Abstract: Provided herein are silane compounds. The silane compounds can be used as organocatalysts and as sensors. Accordingly, also provided are methods of using the silane compounds described herein as catalysts. Methods of using the silane compounds described herein as catalysts can involve contacting a first organic species and a second organic species with a catalytically effective amount of a silane compound or a catalyst composition comprising a silane compound under conditions effective to form the desired product. The product can preferably be enantioenriched.

SILANE COMPOUNDS AND METHODS OF USING THEREOF

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of priority to U.S. Provisional Application No. 61/978,402 filed April 11, 2014, which is hereby incorporated herein by reference in its entirety.

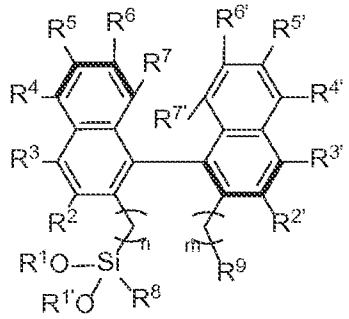
BACKGROUND

Many complex organic compounds, including many clinically approved pharmaceuticals, contain one or more chiral centers and may be provided in the form of one or more stereoisomers. In such cases, the multistep synthesis of complex organic compounds can employ stereoselective synthetic steps to provide, for example, enantioenriched compositions of a desired stereoisomer. For example, the synthesis of bioactive compounds such as Vinblastine, Lexapro, and Cialis can involve the stereoselective syntheses of arene rich triaryl- or diaryl- functionalities.

A variety of stereoselective synthetic methodologies are known in the art, including stereoselective methods for the preparation of triaryl- and diaryl- methanes. However, many existing methods for preparing compounds in a stereoselective manner are inefficient (e.g., low yielding) and/or require the use of enantioenriched substrates. Improved stereoselective synthetic methodologies for preparing a variety of complex organic compounds, including triaryl- and diaryl- methanes, are needed.

SUMMARY

Provided herein are compounds defined by Formula I:



I

wherein

n = 0 or 1;

m = 0 or 1;

R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl;

R^2, R^3, R^4, R^5, and R^6 (i.e., R^2-R^6) and $R^{2'}$, $R^{3'}$, $R^{4'}$, $R^{5'}$, and $R^{6'}$ (i.e., $R^{2'}$-$R^{6'}$) are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl, or wherein, as valence and stability permit, independently R^2 and R^3, R^3 and R^4, R^4 and R^5, R^5 and R^6, $R^{2'}$ and $R^{3'}$, $R^{3'}$ and $R^{4'}$, $R^{4'}$ and $R^{5'}$, $R^{5'}$ and $R^{6'}$, , or $R^{2'}$ and R^9, together with the atoms to which they are attached, form a 3-10 membered substituted or unsubstituted cyclic moiety optionally including between 1 and 3 heteroatoms; and

R^7 and $R^{7'}$ are each independently chosen from H, OH, and halogen; and

R^8 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

R^9 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl;

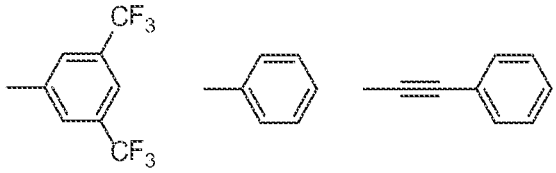
or wherein, as valence and stability permit, R^8 and R^9, together with the atoms to which they are attached, form a 7-9 membered silacycle;

with the proviso that when R^8 and R^9, together with the atoms to which they are attached, form a 7-membered silacycle, R^1, $R^{1'}$, R^3-R^7 and $R^{3'}$-$R^{7'}$ are not all H and R^2 and $R^{2'}$ are not both phenyl.

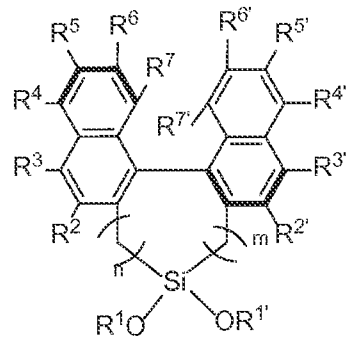
In some examples of Formula I, when R^8 and R^9, together with the atoms to which they are attached, form a 9-membered silacycle, R^1, $R^{1'}$, R^2-R^7 and $R^{2'}$-$R^{7'}$ are not all H.

In some examples of Formula I, when R^8 and R^9, together with the atoms to which they are attached, form a 9-membered silacycle, R^1 and $R^{1'}$ are not both $-CH_3$; and R^2-R^7 and $R^{2'}$-$R^{7'}$ are not all H.

In certain examples of Formula I, when R^8 and R^9, together with the atoms to which they are attached, form a 9-membered silacycle, R^1, $R^{1'}$, R^3-R^7 and $R^{3'}$-$R^{7'}$ are not all H and R^2 and $R^{2'}$ are not both chosen from the moieties shown below.



In some examples of Formula I, the compound can be defined by Formula II:



II

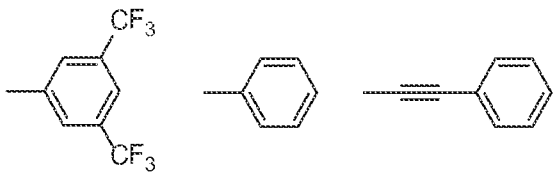
wherein n, m, R^1, $R^{1'}$, R^2, R^3, R^4, R^5, R^6, $R^{2'}$, $R^{3'}$, $R^{4'}$, $R^{5'}$, $R^{6'}$, R^7, and R7' are as defined above with respect to Formula I, with the proviso that when n=0 and m=0, R^1, $R^{1'}$, R^3-R^7 and $R^{3'}$-$R^{7'}$ are not all H and R^2 and $R^{2'}$ are not both phenyl.

In some examples of Formula II, the compound exhibits C_2-symmetry.

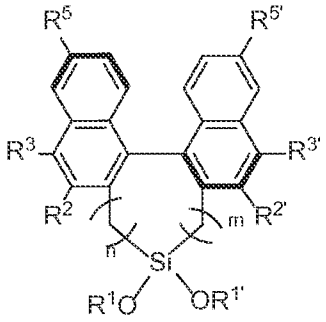
In some examples of Formula II, when n=1 and m=1, R^1, $R^{1'}$, R^2-R^7 and $R^{2'}$-$R^{7'}$ are not all H.

In some examples of Formula II, when n=1 and m=1; R^1 and $R^{1'}$ are not both $-CH_3$; and R^2-R^7 and $R^{2'}$-$R^{7'}$ are not all H.

In certain examples of Formula II, when n=1 and m=1, R^1, $R^{1'}$, R^3-R^7 and $R^{3'}$-$R^{7'}$ are not all H and R^2 and $R^{2'}$ are not both chosen from the moieties shown below.



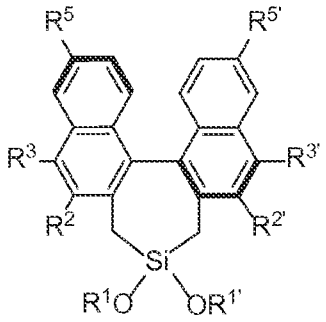
In some examples of Formula II, the compound can be defined by Formula III:



III

wherein n, m, R^1, $R^{1'}$, R^2, R^3, R^5, $R^{2'}$, $R^{3'}$, and $R^{5'}$ are as defined above with respect to Formula I, with the proviso that when n=0 and m=0, R^1, $R^{1'}$, R^3, R^5, $R^{3'}$ and $R^{5'}$ are not all H and R^2 and $R^{2'}$ are not both phenyl.

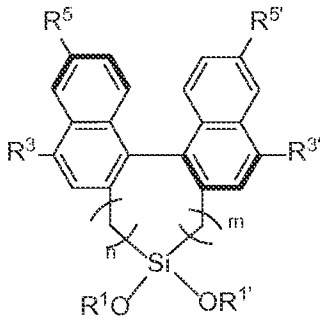
In some examples of Formula III, n and m are both 1 and the compound can be defined by Formula IIIa:



IIIa

wherein R^1, $R^{1'}$, R^2, R^3, R^5, $R^{2'}$, $R^{3'}$, and $R^{5'}$ are as defined above with respect to Formula I.

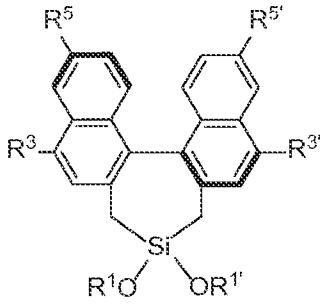
In some examples of Formula II, the compound can be defined by Formula IV:



IV

wherein n, m, R^1, $R^{1'}$, R^3, R^5, $R^{3'}$, and $R^{5'}$ are as defined above with respect to Formula I.

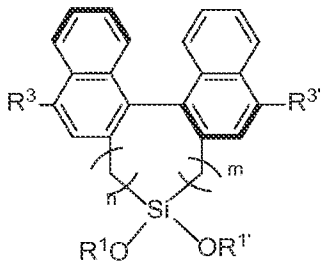
In some examples of Formula IV, n and m are both 1 and the compound can be defined by Formula IVa:



IVa

wherein R^1, $R^{1'}$, R^3, R^5, $R^{3'}$, and $R^{5'}$ are as defined above with respect to Formula I.

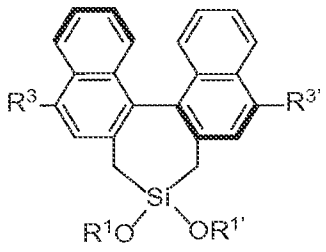
In some examples of Formula II, the compound can be defined by Formula V:



V

wherein n, m, R^1, $R^{1'}$, R^3, and $R^{3'}$ are as defined above with respect to Formula I.

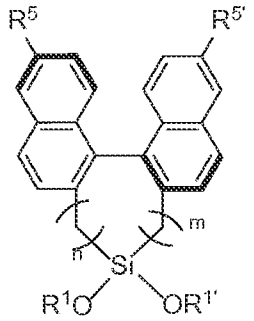
In some examples of Formula V, n and m are both 1 and the compound can be defined by Formula Va:



Va

wherein R^1, $R^{1'}$, R^3, and $R^{3'}$ are as defined above with respect to Formula I.

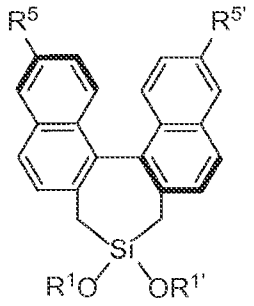
In some examples of Formula II, the compound can be defined by Formula VI:



VI

wherein n, m, R^1, $R^{1'}$, R^5, and $R^{5'}$ are as defined above with respect to Formula I.

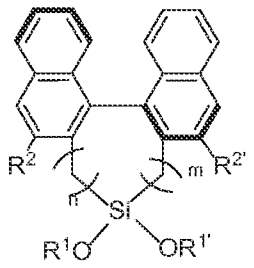
In some examples of Formula VI, n and m are both 1 and the compound can be defined by Formula VIa:



VIa

wherein R^1, $R^{1'}$, R^5, and $R^{5'}$ are as defined above with respect to Formula I.

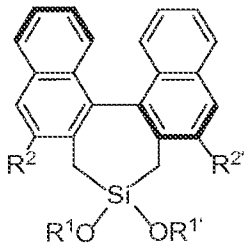
In some examples of Formula II, the compound can be defined by Formula VII:



VII

wherein n, m, R^1, $R^{1'}$, R^2, and $R^{2'}$ are as defined above with respect to Formula I, with the proviso that when n=0 and m=0, R^1 and $R^{1'}$ are not both H and R^2 and $R^{2'}$ are not both phenyl.

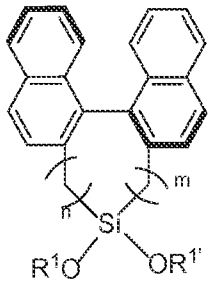
In some examples of Formula VII, n and m are both 1 and the compound can be defined by Formula VIIa:



VIIa

wherein R^1, $R^{1'}$, R^2, and $R^{2'}$ are as defined above with respect to Formula I.

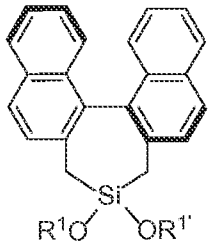
In some examples of Formula II, the compound can be defined by Formula VIII:



VIII

wherein n, m, R^1, and $R^{1'}$ are as defined above with respect to Formula I.

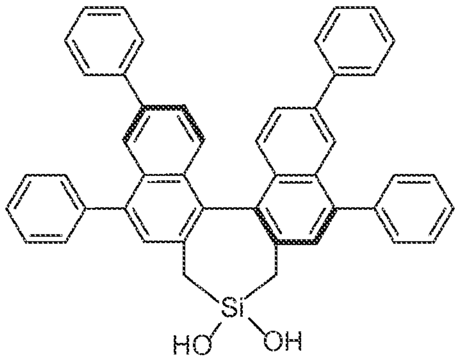
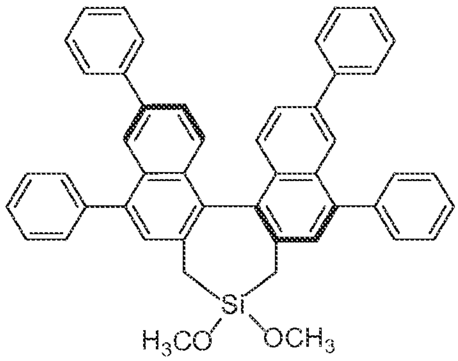
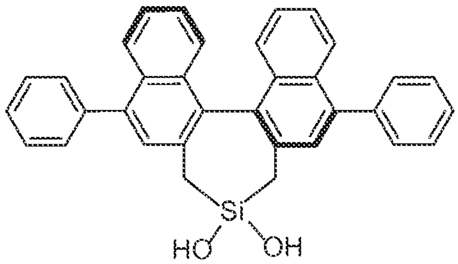
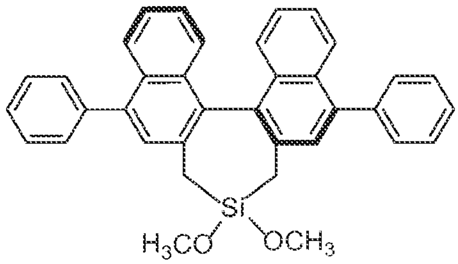
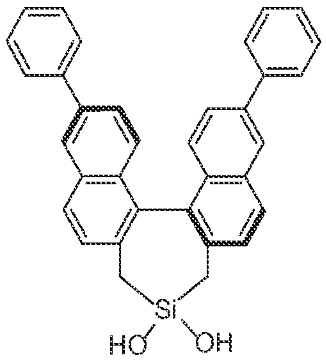
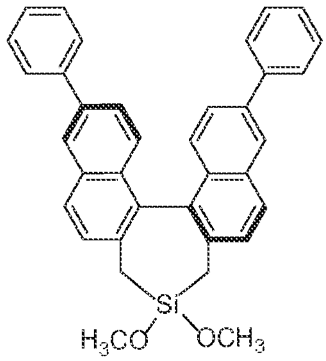
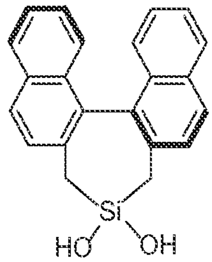
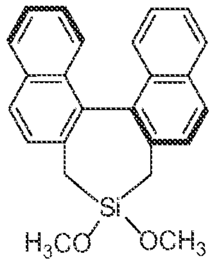
In some examples of Formula VIII, n and m are both 1 and the compound can be defined by Formula VIIIa:



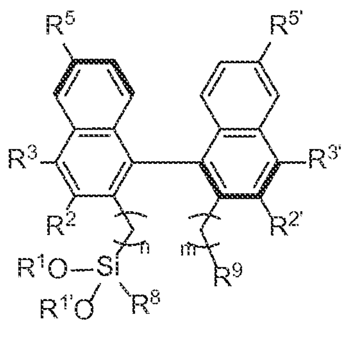
VIIIa

wherein R^1 and $R^{1'}$ are as defined above with respect to Formula I.

In some examples, the compound can be one of the following:

 ,
 ,
 ,
 ,
 ,
 ,
 , or
 .

In some examples of Formula I, the compound can be defined by Formula IX:

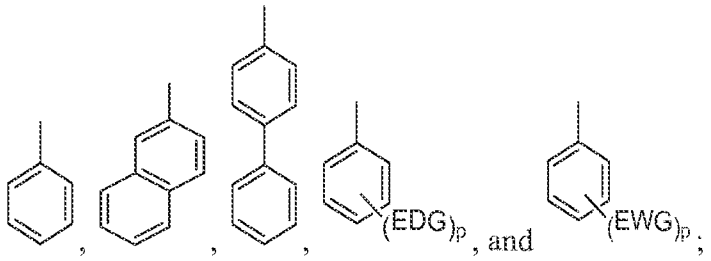


IX

wherein n, m, R^1, $R^{1'}$, R^2, R^3, R^5, $R^{2'}$, $R^{3'}$, $R^{5'}$, R^8, and R^9 are as defined above with respect to Formula I.

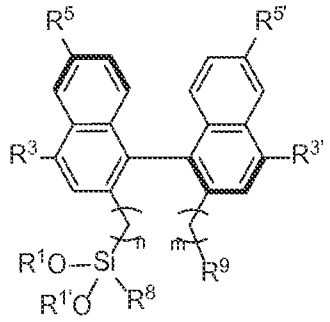
In some examples of Formula IX, m is 0. In some examples of Formula IX, R^9 is substituted or unsubstituted aryl. In certain examples of Formula IX, m is 0 and R^9 is substituted or unsubstituted aryl. For example, in certain examples of Formula IX, m is 0

and R^9 is substituted or unsubstituted phenyl. In certain examples of Formula IX, R^8 is chosen from the moieties shown below



wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5.

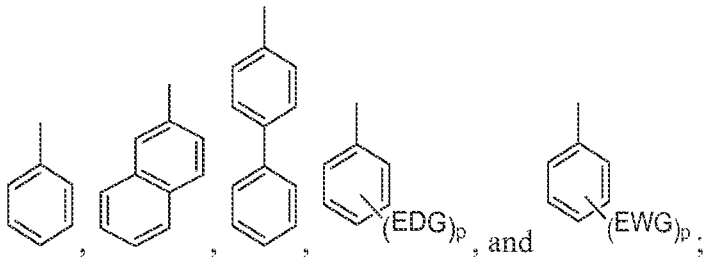
In some examples of Formula I, the compound can be defined by Formula X:



X

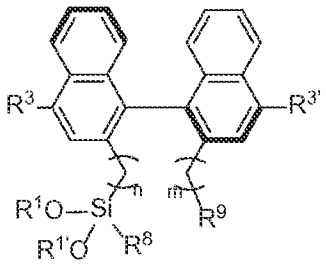
wherein n, m, R^1, $R^{1'}$, R^3, R^5, $R^{3'}$, $R^{5'}$, R^8, and R^9 are as defined above with respect to Formula I.

In some examples of Formula X, m is 0. In some examples of Formula X, R^9 is substituted or unsubstituted aryl. In certain examples of Formula X, m is 0 and R^9 is substituted or unsubstituted aryl. For example, in certain examples of Formula X, m is 0 and R^9 is substituted or unsubstituted phenyl. In certain examples of Formula X, R^8 is chosen from the moieties shown below



wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5.

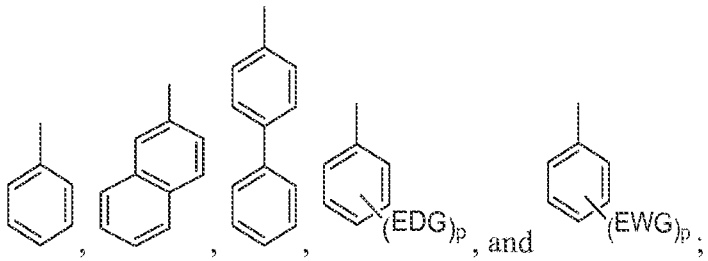
In some examples of Formula I, the compound can be defined by Formula XI:



XI

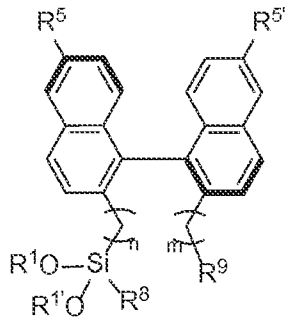
wherein n, m, R^1, $R^{1'}$, R^3, $R^{3'}$, R^8, and R^9 are as defined above with respect to Formula I.

In some examples of Formula XI, m is 0. In some examples of Formula XI, R^9 is substituted or unsubstituted aryl. In certain examples of Formula XI, m is 0 and R^9 is substituted or unsubstituted aryl. For example, in certain examples of Formula XI, m is 0 and R^9 is substituted or unsubstituted phenyl. In certain examples of Formula XI, R^8 is chosen from the moieties shown below



wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5.

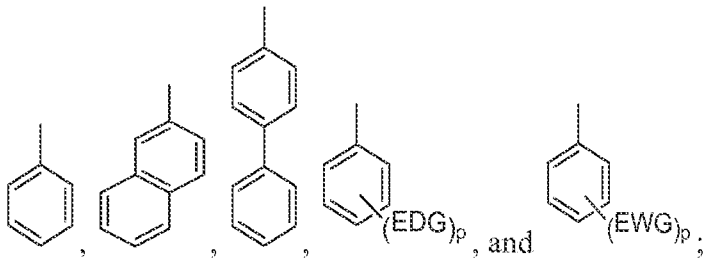
In some examples of Formula I, the compound can be defined by Formula XII:



XII

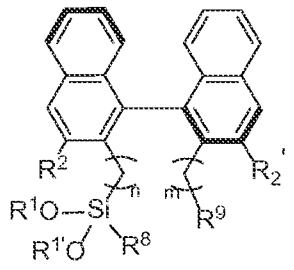
wherein n, m, R^1, $R^{1'}$, R^5, $R^{5'}$, R^8, and R^9 are as defined above with respect to Formula I.

In some examples of Formula XII, m is 0. In some examples of Formula XII, R^9 is substituted or unsubstituted aryl. In certain examples of Formula XII, m is 0 and R^9 is substituted or unsubstituted aryl. For example, in certain examples of Formula XII, m is 0 and R^9 is substituted or unsubstituted phenyl. In certain examples of Formula XII, R^8 is chosen from the moieties shown below



wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5.

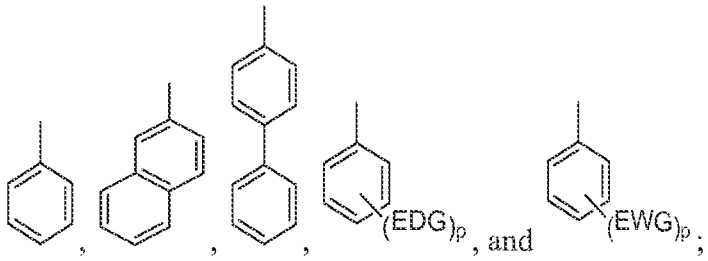
In some examples of Formula I, the compound can be defined by Formula XIII:



XIII

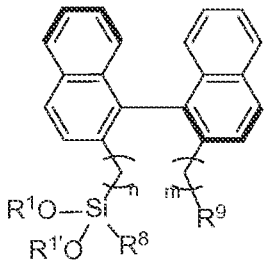
wherein n, m, R^1, $R^{1'}$, R^2, $R^{2'}$, R^8, and R^9 are as defined above with respect to Formula I.

In some examples of Formula XIII, m is 0. In some examples of Formula XIII, R^9 is substituted or unsubstituted aryl. In certain examples of Formula XIII, m is 0 and R^9 is substituted or unsubstituted aryl. For example, in certain examples of Formula XIII, m is 0 and R^9 is substituted or unsubstituted phenyl. In certain examples of Formula XIII, R^8 is chosen from the moieties shown below



wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5.

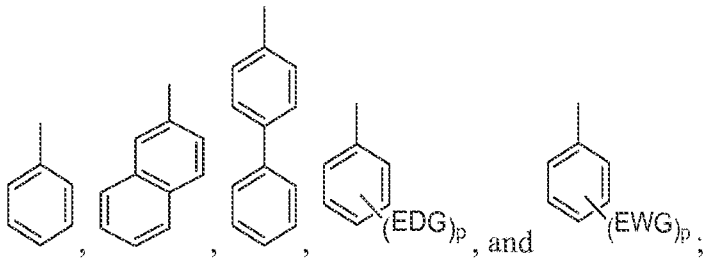
In some examples of Formula I, the compound can be defined by Formula XIV:



XIV

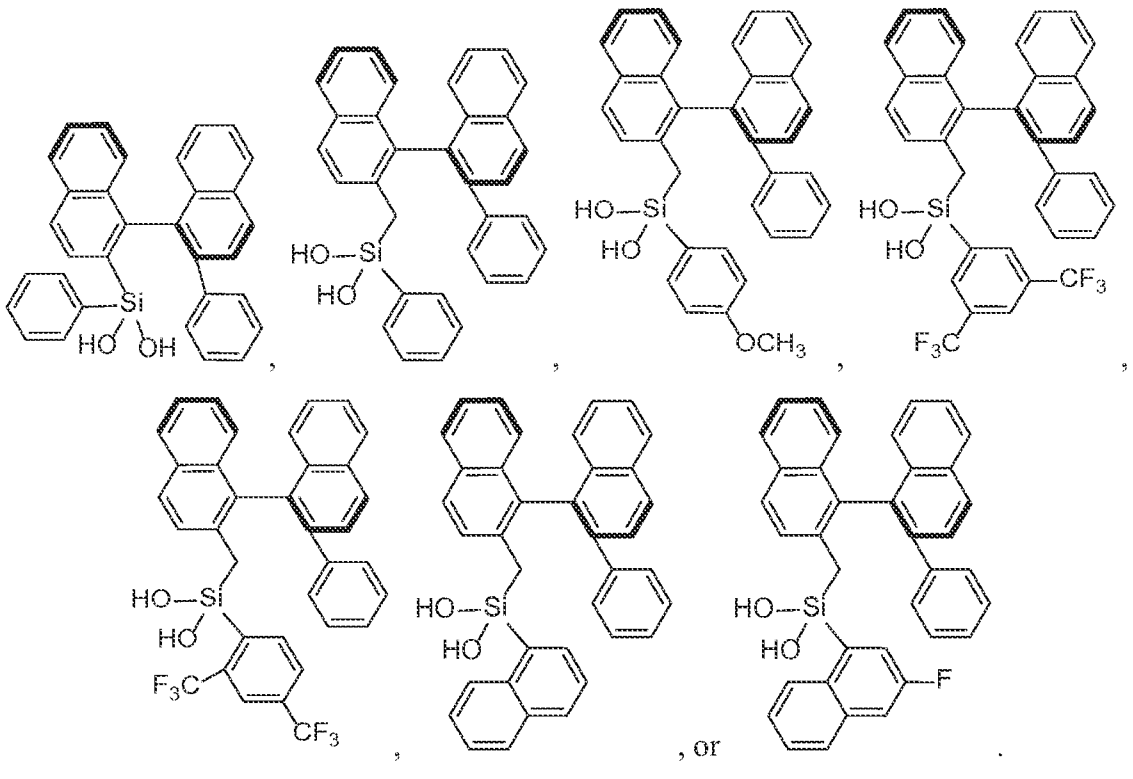
wherein n, m, R^1, $R^{1'}$, R^8, and R^9 are as defined above with respect to Formula I.

In some examples of Formula XIV, m is 0. In some examples of Formula XIV, R^9 is substituted or unsubstituted aryl. In certain examples of Formula XIV, m is 0 and R^9 is substituted or unsubstituted aryl. For example, in certain examples of Formula XIV, m is 0 and R^9 is substituted or unsubstituted phenyl. In certain examples of Formula XIV, R^8 is chosen from the moieties shown below

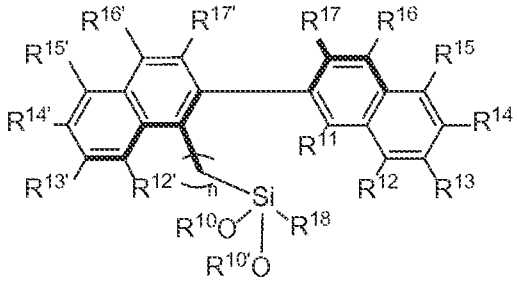


wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5.

In some examples, the compound can be one of the following:



Also disclosed herein are compounds defined by Formula XV:



XV

wherein

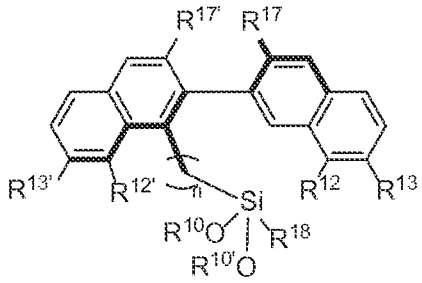
n = 0 or 1;

R^{10} and $R^{10'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl;

R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, R^{16}, R^{17}, $R^{12'}$, $R^{13'}$, $R^{14'}$, $R^{15'}$, $R^{16'}$, and $R^{17'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl, or wherein, as valence and stability permit, independently R^{11} and R^{12}, R^{12} and R^{13}, R^{13} and R^{14}, R^{14} and R^{15}, R^{15} and R^{16}, R^{16} and R^{17}, $R^{12'}$ and $R^{13'}$, $R^{13'}$ and $R^{14'}$, $R^{14'}$ and $R^{15'}$, $R^{15'}$ and $R^{16'}$, or $R^{16'}$ and $R^{17'}$, together with the atoms to which they are attached, form a 3-10 membered substituted or unsubstituted cyclic moiety optionally including between 1 and 3 heteroatoms; and

R^{18} is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

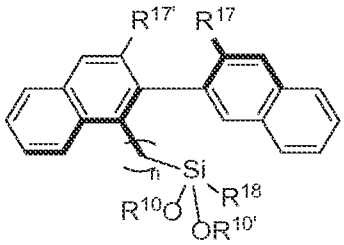
In some examples of Formula XV, the compound can be defined by Formula XVa:



XVa

wherein n, R^{10}, $R^{10'}$, R^{12}, R^{13}, R^{17}, $R^{12'}$, $R^{13'}$, $R^{17'}$, and R^{18} are as defined above with respect to Formula XV.

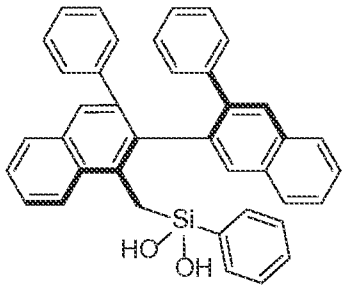
In some examples of Formula XVa, the compound can be defined by Formula XVb:



XVb

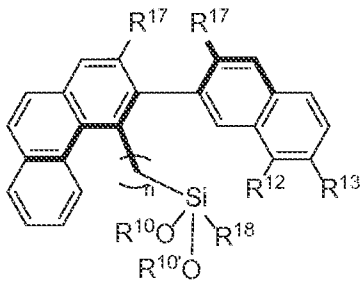
wherein n, R^{10}, $R^{10'}$, R^{17}, $R^{17'}$, and R^{18} are as defined above with respect to Formula XV.

In some examples of Formula XVb, the compound can be defined by the formula:



.

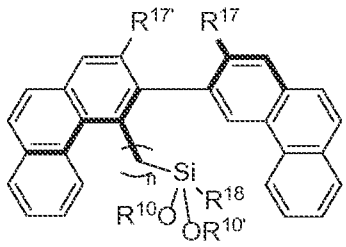
In some examples of Formula XVa, the compound can be defined by Formula XVc:



XVc

wherein n, R^{10}, $R^{10'}$, R^{12}, R^{13}, R^{17}, $R^{17'}$, and R^{18} are as defined above with respect to Formula XV.

In some examples of Formula XVc, the compound can be defined by Formula XVd:



XVd

wherein n, R^{10}, $R^{10'}$, R^{17}, $R^{17'}$, and R^{18} are as defined above with respect to Formula XV.

In certain examples, the compounds described above can be in a complex with a suitable solvent, such as diethyl ether. For example, in some cases, the compounds can be in a 2:1 complex with diethyl ether.

The silane compounds provided herein can be used as organocatalysts. For example, the silane compounds described herein can be used to catalyze a nucleophilic conjugate addition reaction in which a first organic species comprising a nitroalkene reacts with a second organic species comprising a nucleophile to provide a product. The silane compounds described herein can also be used to catalyze an acyl-Mannich type reaction in which a first organic species comprising an amine reacts with a second organic species comprising a carbonyl containing compound to provide a product.

Accordingly, also provided are methods of using the silane compounds described herein as catalysts. Methods of using the silane compounds described herein as catalysts can involve contacting a first organic species and a second organic species with a catalytically effective amount of a silane compound or a catalyst composition comprising a silane compound under conditions effective to form the desired product. The product can preferably be enantioenriched.

The silane compounds described herein can also be used as sensors for analytes. Examples of suitable analytes include, for example, anions and chiral compounds. Accordingly, also provided are methods for detecting, identifying, and/or quantifying an analyte in a sample. The methods comprise contacting the sample comprising an analyte with a silane compound described herein; and evaluating an optical property of the silane compound to detect, identify, or quantify the analyte.

DESCRIPTION OF FIGURES

Figure 1 displays the chiral HPLC of 9a formed using 8-TMS and 20 mol% R-3.

Figure 2 displays the chiral HPLC of 9a formed using 8-TBS and 20 mol% R-3.

Figure 3 displays the chiral HPLC of 9a formed using 8-TIPS and 20 mol% R-3.

Figure 4 displays the chiral HPLC of 9a formed using 8-TIPS and 100 mol% R-3.

Figure 5 displays the chiral HPLC of 2,2,2-trichloroethyl 5-bromo-1-(1-methoxy-2-methyl-1-oxopropan-2-yl)isoquinoline-2(1*H*)-carboxylate (9b) formed using 8-TIPS and 20 mol % R-3.

Figure 6 displays the chiral HPLC of 9b formed using 8-TBS, 20 mol% R-3.

Figure 7 displays the chiral HPLC of 2,2,2-trichloroethyl 5-chloro-1-(1-methoxy-2-methyl-1-oxopropan-2-yl)isoquinoline-2(1*H*)-carboxylate (9c) formed using 8-TIPS, 20 mol % R-3.

Figure 8 displays the chiral HPLC of 9c formed using 8-TBS and 20 mol% R-3.

Figure 9 displays the chiral HPLC of 2,2,2-trichloroethyl 1-(1-methoxy-2-methyl-1-oxopropan-2-yl)-5-nitroisoquinoline-2(1*H*)-carboxylate (9d) formed using 8-TIPS, 20 mol % R-3.

Figure 10 displays the chiral HPLC of 9d formed using 8-TBS, 20 mol% R-**3**.

Figure 11 displays the chiral HPLC of racemic mixture of **9a**.

Figure 12 displays the chiral HPLC of racemic mixture of **9b**.

Figure 13 displays the chiral HPLC of racemic mixture of **9c**.

Figure 14 displays the chiral HPLC of racemic mixture of **9d**.

Figure 15 displays the chiral HPLC of an enantiopure Bis(TMS) derivative of Silanediol R-3.

Figure 16 displays the chiral HPLC of racemic Bis(TMS) derivative of Silanediol R-3.

Figure 17 displays the chiral HPLC of S2 formed using S1, 20 mol% R-3.

Figure 18 displays the chiral HPLC of racemic S2.

Figure 19 displays the ORTEP representation of *bis*-trimethylsilyl protected (*R*)-**3**.

Figure 20 displays the ^{1}H NMR spectra of (*R*)-**3** with varying equivalents of tetrabutylammonium chloride (TBACl). The –OH chemical shifts are marked with a circle.

Figure 21 displays the ORTEP representation of an ion-pair between achiral silanediol **1** and the HCl salt of isoquinoline. In the solid state, the O1-Cl and N-Cl distances are 2.12 Å and 2.32 Å respectively, indicative of moderately strong hydrogen bonds (Steiner T, *Angew. Chem. Int. Ed.* **2002**, *41*, 48-76). The O2-Cl bond is longer, with a distance of 4.47 Å.

Figure 22 displays the crystal structure of H_2O complex of **(±)-21b**.

Figure 23 displays the crystal structure of bis-TMS derivative of **(*R*)-22**.

Figure 24 displays the crystal structure of a trimer derived from (*R*)-**22b**. The anisotropic displacement parameters are drawn at the 50% probability level.

Figure 25 displays the pK_as and anion binding constants for representative silanediols.

Figure 26 illustrates the ^{1}H NMR binding titration of silanediol (*R*)-**22b** with *n*-Bu_4NCl in $CDCl_3$.

Figure 27 illustrates the Job's plot analysis of (*R*)-**22b** and *n*-Bu_4NCl in $CDCl_3$.

Figure 28 displays the crystal structure of ion pair between di(naphthalen-1-yl)silanediol and the HCl salt of isoquinoline.

Figure 29 displays the proposed reaction pathway for silanediol-catalyzed *N*-acyl Mannich reaction of isoquinolines.

DETAILED DESCRIPTION

The materials, compounds, compositions, articles, devices, and methods described herein may be understood more readily by reference to the following detailed description of specific aspects of the disclosed subject matter and the Examples and Figures included therein.

Before the present materials, compounds, compositions, articles, devices, and methods are disclosed and described, it is to be understood that the aspects described below are not limited to specific synthetic methods or specific reagents, as such may, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular aspects only and is not intended to be limiting.

Also, throughout this specification, various publications are referenced. The disclosures of these publications in their entireties are hereby incorporated by reference into this application in order to more fully describe the state of the art to which the disclosed matter pertains. The references disclosed are also individually and specifically incorporated by reference herein for the material contained in them that is discussed in the sentence in which the reference is relied upon.

Definitions

In this specification and in the claims that follow, reference will be made to a number of terms, which shall be defined to have the following meanings:

Throughout the description and claims of this specification the word "comprise" and other forms of the word, such as "comprising" and "comprises," means including but not limited to, and is not intended to exclude, for example, other additives, components, integers, or steps.

As used in the description and the appended claims, the singular forms "a," "an," and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to "a composition" includes mixtures of two or more such compositions, reference to "an agent" includes mixtures of two or more such agents, reference to "the component" includes mixtures of two or more such components, and the like.

"Optional" or "optionally" means that the subsequently described event or circumstance can or cannot occur, and that the description includes instances where the event or circumstance occurs and instances where it does not.

Ranges can be expressed herein as from "about" one particular value, and/or to "about" another particular value. By "about" is meant within 5% of the value, e.g., within 4, 3, 2, or 1% of the value. When such a range is expressed, another aspect includes from the one particular value and/or to the other particular value. Similarly, when values are expressed as approximations, by use of the antecedent "about," it will be understood that the particular value forms another aspect. It will be further understood that the endpoints of each of the ranges are significant both in relation to the other endpoint, and independently of the other endpoint.

It is understood that throughout this specification the identifiers "first" and "second" are used solely to aid in distinguishing the various components and steps of the disclosed subject matter. The identifiers "first" and "second" are not intended to imply any particular order, amount, preference, or importance to the components or steps modified by these terms.

As used herein, the term "substituted" is contemplated to include all permissible substituents of organic compounds. In a broad aspect, the permissible substituents include acyclic and cyclic, branched and unbranched, carbocyclic and heterocyclic, and aromatic and nonaromatic substituents of organic compounds. Illustrative substituents include, for example, those described below. The permissible substituents can be one or more and the same or different for appropriate organic compounds. For purposes of this disclosure, heteroatoms present in a compound or moiety, such as nitrogen, can have hydrogen substituents and/or any permissible substituents of organic compounds described herein which satisfy the valency of the heteroatom. This disclosure is not intended to be limited in any manner by the permissible substituents of organic compounds. Also, the terms "substitution" or "substituted with" include the implicit proviso that such substitution is in accordance with permitted valence of the substituted atom and the substituent, and that the substitution results in a stable compound (e.g., a compound that does not spontaneously

undergo transformation such as by rearrangement, cyclization, elimination, etc.

"Z^1," "Z^2," "Z^3," and "Z^4" are used herein as generic symbols to represent various specific substituents. These symbols can be any substituent, not limited to those disclosed herein, and when they are defined to be certain substituents in one instance, they can, in another instance, be defined as some other substituents.

The term "aliphatic" as used herein refers to a non-aromatic hydrocarbon group and includes branched and unbranched, alkyl, alkenyl, or alkynyl groups.

The term "alkyl" as used herein is a branched or unbranched saturated hydrocarbon group of 1 to 24 carbon atoms, for example 1 to 3, 1 to 4, 1 to 5, 1 to 6, 1 to 7, 1 to 8, 1 to 9, 1 to 10, or 1 to 15 carbon atoms, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, t-butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, dodecyl, tetradecyl, hexadecyl, eicosyl, tetracosyl, and the like. The alkyl group can also be substituted or unsubstituted. The alkyl group can be substituted with one or more groups including, but not limited to, alkyl, halogenated alkyl, alkoxy, alkenyl, alkynyl, aryl, heteroaryl, aldehyde, amino, carboxylic acid, ester, ether, halide, hydroxy, ketone, nitro, silyl, sulfo-oxo, sulfonyl, sulfone, sulfoxide, or thiol, as described below.

Throughout the specification "alkyl" is generally used to refer to both unsubstituted alkyl groups and substituted alkyl groups; however, substituted alkyl groups are also specifically referred to herein by identifying the specific substituent(s) on the alkyl group. For example, the term "halogenated alkyl" specifically refers to an alkyl group that is substituted with one or more halides (halogens; e.g., fluorine, chlorine, bromine, or iodine). The term "alkoxyalkyl" specifically refers to an alkyl group that is substituted with one or more alkoxy groups, as described below. The term "alkylamino" specifically refers to an alkyl group that is substituted with one or more amino groups, as described below, and the like. When "alkyl" is used in one instance and a specific term such as "alkylalcohol" is used in another, it is not meant to imply that the term "alkyl" does not also refer to specific terms such as "alkylalcohol" and the like.

This practice is also used for other groups described herein. That is, while a term such as "cycloalkyl" refers to both unsubstituted and substituted cycloalkyl moieties, the substituted moieties can, in addition, be specifically identified herein; for example, a particular substituted cycloalkyl can be referred to as, *e.g.*, an "alkylcycloalkyl." Similarly, a substituted alkoxy can be specifically referred to as, *e.g.*, a "halogenated alkoxy," a particular substituted alkenyl can be, *e.g.*, an "alkenylalcohol," and the like. Again, the practice of using a general term, such as "cycloalkyl," and a specific term, such as

"alkylcycloalkyl," is not meant to imply that the general term does not also include the specific term.

The term "alkoxy" as used herein is an alkyl group bound through a single, terminal ether linkage; that is, an "alkoxy" group can be defined as —OZ^1 where Z^1 is alkyl as defined above.

The term "alkenyl" as used herein is a hydrocarbon group of from 2 to 24 carbon atoms, for example, 2 to 5, 2 to 10, 2 to 15, or 2 to 20 carbon atoms, with a structural formula containing at least one carbon-carbon double bond. Asymmetric structures such as $(Z^1Z^2)C=C(Z^3Z^4)$ are intended to include both the *E* and *Z* isomers. This can be presumed in structural formulae herein wherein an asymmetric alkene is present, or it can be explicitly indicated by the bond symbol C=C. The alkenyl group can be substituted with one or more groups including, but not limited to, alkyl, halogenated alkyl, alkoxy, alkenyl, alkynyl, aryl, heteroaryl, aldehyde, amino, carboxylic acid, ester, ether, halide, hydroxy, ketone, nitro, silyl, sulfo-oxo, sulfonyl, sulfone, sulfoxide, or thiol, as described below.

The term "alkynyl" as used herein is a hydrocarbon group of 2 to 24 carbon atoms, for example 2 to 5, 2 to 10, 2 to 15, or 2 to 20 carbon atoms, with a structural formula containing at least one carbon-carbon triple bond. The alkynyl group can be substituted with one or more groups including, but not limited to, alkyl, halogenated alkyl, alkoxy, alkenyl, alkynyl, aryl, heteroaryl, aldehyde, amino, carboxylic acid, ester, ether, halide, hydroxy, ketone, nitro, silyl, sulfo-oxo, sulfonyl, sulfone, sulfoxide, or thiol, as described below.

The term "aryl" as used herein is a group that contains any carbon-based aromatic group including, but not limited to, benzene, naphthalene, phenyl, biphenyl, phenoxybenzene, and the like. The term "heteroaryl" is defined as a group that contains 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 phosphorus. The term "non-heteroaryl," which is included in the term "aryl," defines a group that contains an aromatic group that does not contain a heteroatom. The aryl or heteroaryl group can be substituted or unsubstituted. The aryl or heteroaryl group can be substituted with one or more groups including, but not limited to, alkyl, halogenated alkyl, alkoxy, alkenyl, alkynyl, aryl, heteroaryl, aldehyde, amino, carboxylic acid, ester, ether, halide, hydroxy, ketone, nitro, silyl, sulfo-oxo, sulfonyl, sulfone, sulfoxide, or thiol as described herein. The term "biaryl" is a specific type of aryl group and is included in the definition of aryl. Biaryl refers to two aryl groups that are bound together *via* a fused ring

structure, as in naphthalene, or are attached *via* one or more carbon-carbon bonds, as in biphenyl.

The term "cycloalkyl" as used herein is 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, etc. The term "heterocycloalkyl" 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 phosphorus. The cycloalkyl group and heterocycloalkyl group can be substituted or unsubstituted. The cycloalkyl group and heterocycloalkyl group can be substituted with one or more groups including, but not limited to, alkyl, alkoxy, alkenyl, alkynyl, aryl, heteroaryl, aldehyde, amino, carboxylic acid, ester, ether, halide, hydroxy, ketone, nitro, silyl, sulfo-oxo, sulfonyl, sulfone, sulfoxide, or thiol as described herein.

The term "cycloalkenyl" as used herein is a non-aromatic carbon-based ring composed of at least three carbon atoms and containing at least one double bound, *i.e.*, C=C. Examples of cycloalkenyl groups include, but are not limited to, cyclopropenyl, cyclobutenyl, cyclopentenyl, cyclopentadienyl, cyclohexenyl, cyclohexadienyl, and the like. The term "heterocycloalkenyl" is a type of cycloalkenyl group as defined above, and is included within the meaning of the term "cycloalkenyl," 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 phosphorus. The cycloalkenyl group and heterocycloalkenyl group can be substituted or unsubstituted. The cycloalkenyl group and heterocycloalkenyl group can be substituted with one or more groups including, but not limited to, alkyl, alkoxy, alkenyl, alkynyl, aryl, heteroaryl, aldehyde, amino, carboxylic acid, ester, ether, halide, hydroxy, ketone, nitro, silyl, sulfo-oxo, sulfonyl, sulfone, sulfoxide, or thiol as described herein.

The term "cyclic group" is used herein to refer to either aryl groups, non-aryl groups (*i.e.*, cycloalkyl, heterocycloalkyl, cycloalkenyl, and heterocycloalkenyl groups), or both. Cyclic groups have one or more ring systems that can be substituted or unsubstituted. A cyclic group can contain one or more aryl groups, one or more non-aryl groups, or one or more aryl groups and one or more non-aryl groups.

The term "carbonyl as used herein is represented by the formula $-C(O)Z^1$ where Z^1 can be a hydrogen, hydroxyl, alkoxy, alkyl, halogenated alkyl, alkenyl, alkynyl, aryl, heteroaryl, cycloalkyl, cycloalkenyl, heterocycloalkyl, or heterocycloalkenyl group described above. Throughout this specification "C(O)" or "CO" is a short hand notation for C=O.

The term "aldehyde" as used herein is represented by the formula —C(O)H.

The terms "amine" or "amino" as used herein are represented by the formula —NZ^1Z^2, where Z^1 and Z^2 can each be substitution group as described herein, such as hydrogen, an alkyl, halogenated alkyl, alkenyl, alkynyl, aryl, heteroaryl, cycloalkyl, cycloalkenyl, heterocycloalkyl, or heterocycloalkenyl group described above. "Amido" is —$C(O)NZ^1Z^2$.

The term "carboxylic acid" as used herein is represented by the formula —C(O)OH. A "carboxylate" or "carboxyl" group as used herein is represented by the formula —$C(O)O^-$.

The term "ester" as used herein is represented by the formula —$OC(O)Z^1$ or —$C(O)OZ^1$, where Z^1 can be an alkyl, halogenated alkyl, alkenyl, alkynyl, aryl, heteroaryl, cycloalkyl, cycloalkenyl, heterocycloalkyl, or heterocycloalkenyl group described above.

The term "ether" as used herein is represented by the formula Z^1OZ^2, where Z^1 and Z^2 can be, independently, an alkyl, halogenated alkyl, alkenyl, alkynyl, aryl, heteroaryl, cycloalkyl, cycloalkenyl, heterocycloalkyl, or heterocycloalkenyl group described above.

The term "ketone" as used herein is represented by the formula $Z^1C(O)Z^2$, where Z^1 and Z^2 can be, independently, an alkyl, halogenated alkyl, alkenyl, alkynyl, aryl, heteroaryl, cycloalkyl, cycloalkenyl, heterocycloalkyl, or heterocycloalkenyl group described above.

The term "halide" or "halogen" as used herein refers to the fluorine, chlorine, bromine, and iodine.

The term "hydroxyl" as used herein is represented by the formula —OH.

The term "nitro" as used herein is represented by the formula —NO_2.

The term "silyl" as used herein is represented by the formula —$SiZ^1Z^2Z^3$, where Z^1, Z^2, and Z^3 can be, independently, hydrogen, alkyl, halogenated alkyl, alkoxy, alkenyl, alkynyl, aryl, heteroaryl, cycloalkyl, cycloalkenyl, heterocycloalkyl, or heterocycloalkenyl group described above.

The term "sulfonyl" is used herein to refer to the sulfo-oxo group represented by the formula —$S(O)_2Z^1$, where Z^1 can be hydrogen, an alkyl, halogenated alkyl, alkenyl, alkynyl, aryl, heteroaryl, cycloalkyl, cycloalkenyl, heterocycloalkyl, or heterocycloalkenyl group described above.

The term "sulfonylamino" or "sulfonamide" as used herein is represented by the formula —$S(O)_2NH$—.

The term "thiol" as used herein is represented by the formula —SH.

The term "thio" as used herein is represented by the formula —S—.

"R^1," "R^2," "R^3," "R^n," etc., where n is some integer, as used herein can, independently, possess one or more of the groups listed above. For example, if R^1 is a straight chain alkyl group, one of the hydrogen atoms of the alkyl group can optionally be substituted with a hydroxyl group, an alkoxy group, an amine group, an alkyl group, a halide, and the like. Depending upon the groups that are selected, a first group can be incorporated within second group or, alternatively, the first group can be pendant (i.e., attached) to the second group. For example, with the phrase "an alkyl group comprising an amino group," the amino group can be incorporated within the backbone of the alkyl group. Alternatively, the amino group can be attached to the backbone of the alkyl group. The nature of the group(s) that is (are) selected will determine if the first group is embedded or attached to the second group.

The term "electron donating group" (also abbreviated herein as EDG) is used herein to describe substituents (e.g., atoms or functional groups) that can donate some of their electron density into a conjugated π system to which they are attached (e.g., a benzene group) via resonance or inductive electron withdrawal, thus making the conjugated π system more nucleophilic. When attached to benzene, an electron donating group can, for example, make the benzene more likely to participate in electrophilic substitution reactions. Examples of electron donating groups include, but are not limited to, primary, secondary and tertiary amines; hydroxy groups; amides; alkoxy groups; alkyl groups; and aryl groups.

The term "electron withdrawing group" (also abbreviated herein as EWG) is used herein to describe substituents (e.g., atoms or functional groups) that can remove electron density from a conjugated π system to which they are attached (e.g., benzene) via resonance or inductive electron withdrawal, thus making the π system more electrophilic. When attached to a benzene, and electron withdrawing group can, for example, make electrophilic aromatic substitution reactions slower and more complex. Depending on their relative strengths, electron withdrawing groups can also determine the positions (relative to themselves) on the benzene ring where substitutions can take place. Examples of electron withdrawing groups include, but are not limited to, nitro, quaternary amines, trihalides (e.g., $-CF_3$), cyano, sulfonates, carboxylic acids, esters, aldehydes, and ketones.

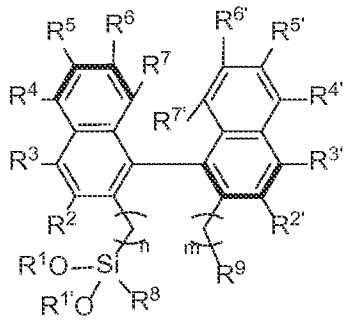
Unless stated to the contrary, a formula with chemical bonds shown only as solid lines and not as wedges or dashed lines contemplates each possible stereoisomer or mixture of stereoisomer (e.g., each enantiomer, each diastereomer, each meso compound, a racemic mixture, or scalemic mixture).

Reference will now be made in detail to specific aspects of the disclosed materials,

compounds, compositions, articles, and methods, examples of which are illustrated in the accompanying Examples and Figures.

Compounds

Provided herein are compounds defined by Formula I:



I

wherein

n = 0 or 1;

m = 0 or 1;

R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl;

R^2, R^3, R^4, R^5, and R^6 (i.e., R^2-R^6) and $R^{2'}$, $R^{3'}$, $R^{4'}$, $R^{5'}$, and $R^{6'}$ (i.e., $R^{2'}$-$R^{6'}$) are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl, or wherein, as valence and stability permit, independently R^2 and R^3, R^3 and R^4, R^4 and R^5, R^5 and R^6, $R^{2'}$ and $R^{3'}$, $R^{3'}$ and $R^{4'}$, $R^{4'}$ and $R^{5'}$, $R^{5'}$ and $R^{6'}$, or $R^{2'}$ and R^9, together with the atoms to which they are attached, form a 3-10 membered substituted or unsubstituted cyclic moiety optionally including between 1 and 3 heteroatoms; and

R^7 and $R^{7'}$ are each independently chosen from H, OH, and halogen; and

R^8 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or

unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

R^9 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl;

or wherein, as valence and stability permit, R^8 and R^9, together with the atoms to which they are attached, form a 7-9 membered silacycle;

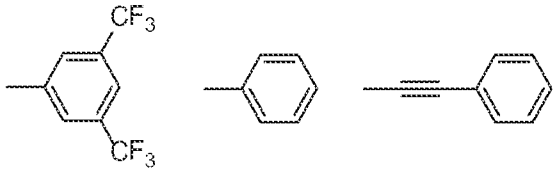
with the proviso that when R^8 and R^9, together with the atoms to which they are attached, form a 7-membered silacycle, R^1, $R^{1'}$, R^3-R^7 and $R^{3'}$-$R^{7'}$ are not all H and R^2 and $R^{2'}$ are not both phenyl.

In some examples of Formula I, when R^8 and R^9, together with the atoms to which they are attached, form a 9-membered silacycle, R^1, $R^{1'}$, R^2-R^7 and $R^{2'}$-$R^{7'}$ are not all H.

In some examples of Formula I, when R^8 and R^9, together with the atoms to which they are attached, form a 9-membered silacycle, R^1 and $R^{1'}$ are not both $-CH_3$; and R^2-R^7 and $R^{2'}$-$R^{7'}$ are not all H.

In some examples of Formula I, when R^8 and R^9, together with the atoms to which they are attached, form a 9-membered silacycle, R^1, $R^{1'}$, R^3-R^7 and $R^{3'}$-$R^{7'}$ are not all H and R^2 and $R^{2'}$ are not both chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

In some examples of Formula I, when R^8 and R^9, together with the atoms to which they are attached, form a 9-membered silacycle, R^1, $R^{1'}$, R^3-R^7 and $R^{3'}$-$R^{7'}$ are not all H and R^2 and $R^{2'}$ are not both substituted or unsubstituted aryl or substituted or unsubstituted alkylaryl. In certain examples of Formula I, when R^8 and R^9, together with the atoms to which they are attached, form a 9-membered silacycle, R^1, $R^{1'}$, R^3-R^7 and $R^{3'}$-$R^{7'}$ are not all H and R^2 and $R^{2'}$ are not both chosen from the moieties shown below.

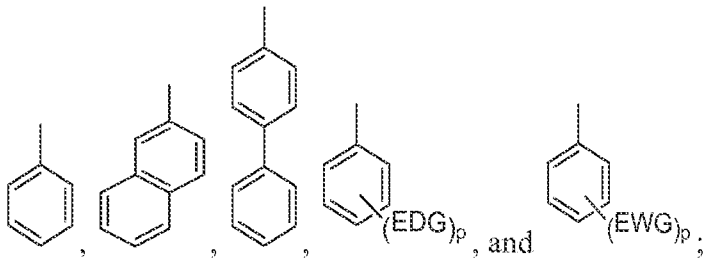


In some examples of Formula I, n is 0. In some examples of Formula I, m is 0. In some examples of Formula I, n and m are 0. In some examples of Formula I, n is 1. In some examples of Formula I, m is 1. In some examples of Formula I, at least one of n and m is 1. In some examples of Formula I, n and m are 1. In some examples of Formula I, n is 1 and m is 0.

In some examples of Formula I, R^1 and $R^{1'}$ are the same. In some examples of Formula I, R^1 and $R^{1'}$ are both hydrogen or $-CH_3$. In some examples of Formula I, R^1 and $R^{1'}$ are both hydrogen. In some examples of Formula I, R^1 and $R^{1'}$ are both $-CH_3$.

In some examples of Formula I, R^2 and $R^{2'}$ are individually chosen from hydrogen, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula I, R^2 and $R^{2'}$ are individually chosen from hydrogen, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula I, R^2 and $R^{2'}$ are independently substituted or unsubstituted alkylaryl. In certain examples of Formula I, R^2 and $R^{2'}$ are independently substituted or unsubstituted aryl.

In some examples of Formula I, R^2 and $R^{2'}$ are independently chosen from the moieties shown below

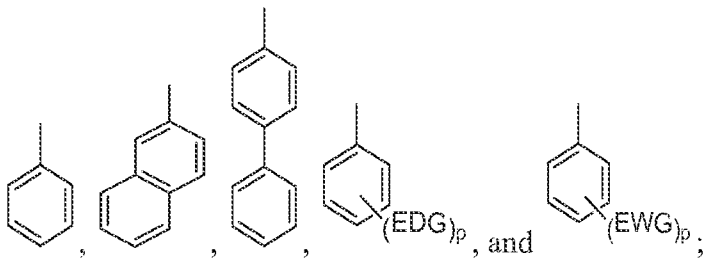


wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5. In certain examples of Formula II, R^2 and $R^{2'}$ are independently substituted or unsubstituted phenyl.

In some examples of Formula I, R^2 and $R^{2'}$ are the same. In some examples of Formula I, R^2 and $R^{2'}$ are both hydrogen.

In some examples of Formula I, R^3 and $R^{3'}$ are individually chosen from hydrogen, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula I, R^3 and $R^{3'}$ are individually chosen from hydrogen, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula I, R^3 and $R^{3'}$ are independently substituted or unsubstituted alkylaryl. In certain examples of Formula I, R^3 and $R^{3'}$ are independently substituted or unsubstituted aryl.

In some examples of Formula I, R^3 and $R^{3'}$ are independently chosen from the moieties shown below



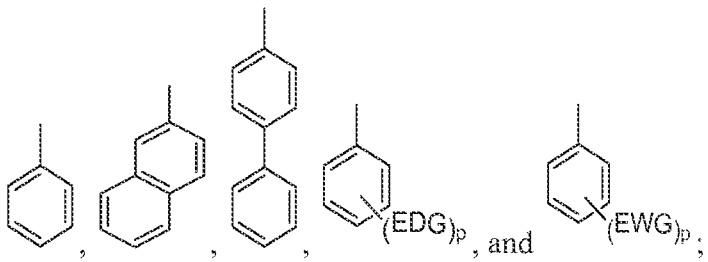
wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5. In certain examples of Formula I, R^3 and $R^{3'}$ are independently substituted or unsubstituted phenyl.

In some examples of Formula I, R^3 and $R^{3'}$ are the same. In some examples of Formula I, R^3 and $R^{3'}$ are both hydrogen.

In some examples of Formula I, R^4 and $R^{4'}$ are independently chosen from hydrogen, hydroxy, and halogen. In some examples of Formula I, R^4 and $R^{4'}$ are the same. In certain examples of Formula I, R^4 and $R^{4'}$ are both hydrogen.

In some examples of Formula I, R^5 and $R^{5'}$ are individually chosen from hydrogen, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula I, R^5 and $R^{5'}$ are individually chosen from hydrogen, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula I, R^5 and $R^{5'}$ are independently substituted or unsubstituted alkylaryl. In certain examples of Formula I, R^5 and $R^{5'}$ are independently substituted or unsubstituted aryl.

In some examples of Formula I, R^5 and $R^{5'}$ are independently chosen from the moieties shown below



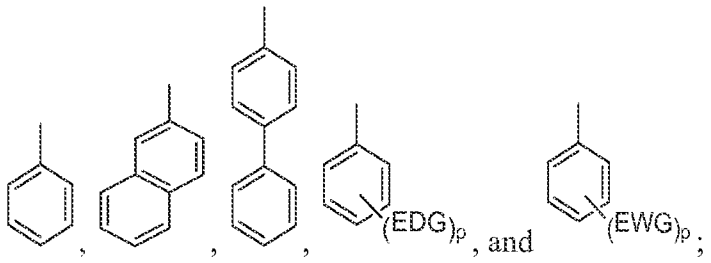
wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5. In certain examples of Formula I, R^5 and $R^{5'}$ are substituted or unsubstituted phenyl.

In some examples of Formula I, R^5 and $R^{5'}$ are the same. In some examples of Formula I, R^5 and $R^{5'}$ are both hydrogen.

In some examples of Formula I, R^3 and $R^{3'}$ are the same, and R^5 and $R^{5'}$ are the same. In some examples of Formula I, R^3, $R^{3'}$, R^5 and $R^{5'}$ are individually chosen from hydrogen, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula I, R^3, $R^{3'}$, R^5 and $R^{5'}$ are individually chosen from hydrogen, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or

unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula I, R^3, $R^{3'}$, R^5 and $R^{5'}$ are substituted or unsubstituted alkylaryl. In certain examples of Formula I, R^3, $R^{3'}$, R^5 and $R^{5'}$ are substituted or unsubstituted aryl.

In some examples of Formula I, R^3, $R^{3'}$, R^5 and $R^{5'}$ are chosen from the moieties shown below



wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5. In certain examples of Formula I, R^3, $R^{3'}$, R^5 and $R^{5'}$ are substituted or unsubstituted phenyl.

In some examples of Formula I, R^3 and $R^{3'}$ are both hydrogen, and R^5 and $R^{5'}$ are the same. In some examples of Formula I, R^3 and $R^{3'}$ are the same and R^5 and $R^{5'}$ are both hydrogen. In some examples of Formula I, R^3, $R^{3'}$, R^5 and $R^{5'}$ are all the same. In some examples of Formula I, R^3, $R^{3'}$, R^5, and $R^{5'}$ are all hydrogen.

In some examples of Formula I, R^6 and $R^{6'}$ are independently chosen from hydrogen, hydroxy, and halogen. In some examples of Formula I, R^6 and $R^{6'}$ are the same. In certain examples of Formula I, R^6 and $R^{6'}$ are both hydrogen.

In some examples of Formula I, R^7 and $R^{7'}$ are the same. In some examples of Formula I, R^7 and $R^{7'}$ are both hydrogen.

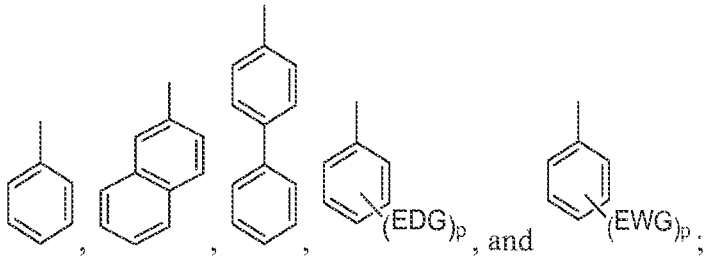
In some examples of Formula I, R^4, R^6, $R^{4'}$, and $R^{6'}$ are the same. In some examples of Formula I, R^4, R^6, $R^{4'}$, and $R^{6'}$ are all hydrogen. In some examples of Formula I, R^4, R^7, $R^{4'}$, and $R^{7'}$ are the same. In some examples of Formula I, R^4, R^7, $R^{4'}$, and $R^{7'}$ are all hydrogen. In some examples of Formula I, R^6, R^7, $R^{6'}$, and $R^{7'}$ are the same. In some examples of Formula I, R^6, R^7, $R^{6'}$, and $R^{7'}$ are all hydrogen.

In some examples of Formula I, R^4, R^6, R^7, $R^{4'}$, $R^{6'}$, and $R^{7'}$ are the same. In some examples of Formula I, R^4, R^6, R^7, $R^{4'}$, $R^{6'}$, and $R^{7'}$ are all hydrogen.

In some examples of Formula I, R^8 and R^9 are individually chosen from substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples

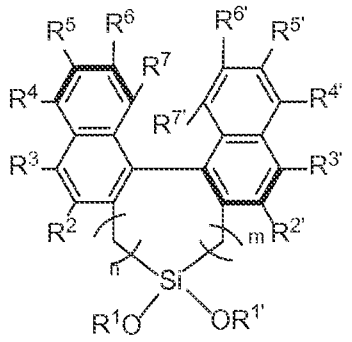
of Formula I, R^8 and R^9 are individually chosen from substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula I, R^8 and R^9 are substituted or unsubstituted alkylaryl. In certain examples of Formula I, R^8 and R^9 are substituted or unsubstituted aryl.

In some examples of Formula I, R^8 and R^9 are independently chosen from the moieties shown below



wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5. In certain examples of Formula I, R^8 and R^9 are independently substituted or unsubstituted phenyl.

In some examples of Formula I, R^8 and R^9, together with the atoms to which they are attached, form a 7-9 membered silacycle, and the compound can be defined by Formula II:



II

wherein

n = 0 or 1;

m = 0 or 1;

R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl;

R^2, R^3, R^4, R^5, and R^6 (i.e., R^2-R^6) and $R^{2'}$, $R^{3'}$, $R^{4'}$, $R^{5'}$, and $R^{6'}$ (i.e., $R^{2'}$-$R^{6'}$) are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl,

substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl, or wherein, as valence and stability permit, independently R^2 and R^3, R^3 and R^4, R^4 and R^5, R^5 and R^6, $R^{2'}$ and $R^{3'}$, $R^{3'}$ and $R^{4'}$, $R^{4'}$ and $R^{5'}$, or $R^{5'}$ and $R^{6'}$, together with the atoms to which they are attached, form a 3-10 membered substituted or unsubstituted cyclic moiety optionally including between 1 and 3 heteroatoms; and

R^7 and $R^{7'}$ are each independently chosen from H, OH, and halogen;

with the proviso that when n=0 and m=0, R^1, $R^{1'}$, R^3-R^7 and $R^{3'}$-$R^{7'}$ are not all H and R^2 and $R^{2'}$ are not both phenyl.

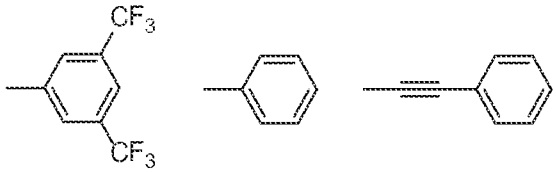
In some examples of Formula II, the compound exhibits C_2-symmetry.

In some examples of Formula II, when n=1 and m=1, R^1, $R^{1'}$, R^2-R^7 and $R^{2'}$-$R^{7'}$ are not all H.

In some examples of Formula II, when n=1 and m=1; R^1 and $R^{1'}$ are not both $-CH_3$; and R^2-R^7 and $R^{2'}$-$R^{7'}$ are not all H.

In some examples of Formula II, when n=1 and m=1, R^1, $R^{1'}$, R^3-R^7 and $R^{3'}$-$R^{7'}$ are not all H and R^2 and $R^{2'}$ are not both chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

In some examples of Formula II, when n=1 and m=1, R^1, $R^{1'}$, R^3-R^7 and $R^{3'}$-$R^{7'}$ are not all H and R^2 and $R^{2'}$ are not both substituted or unsubstituted aryl or substituted or unsubstituted alkylaryl. In certain examples of Formula II, when n=1 and m=1, R^1, $R^{1'}$, R^3-R^7 and $R^{3'}$-$R^{7'}$ are not all H and R^2 and $R^{2'}$ are not both chosen from the moieties shown below.

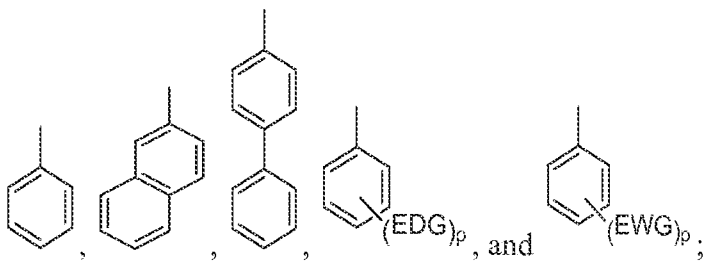


In some examples of Formula II, n is 0. In some examples of Formula II, m is 0. In some examples of Formula II, n and m are 0. In some examples of Formula II, n is 1. In some examples of Formula II, m is 1. In some examples of Formula II, at least one of n and m is 1. In some examples of Formula II, n and m are 1.

In some examples of Formula II, R^1 and $R^{1'}$ are the same. In some examples of Formula II, R^1 and $R^{1'}$ are both hydrogen or $-CH_3$. In some examples of Formula II, R^1 and $R^{1'}$ are both hydrogen. In some examples of Formula II, R^1 and $R^{1'}$ are both $-CH_3$.

In some examples of Formula II, R^2 and $R^{2'}$ are the same. In some examples of Formula II, R^2 and $R^{2'}$ are individually chosen from substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula II, R^2 and $R^{2'}$ are individually chosen from substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula II, R^2 and $R^{2'}$ are substituted or unsubstituted alkylaryl. In certain examples of Formula II, R^2 and $R^{2'}$ are substituted or unsubstituted aryl.

In some examples of Formula II, R^2 and $R^{2'}$ are chosen from the moieties shown below

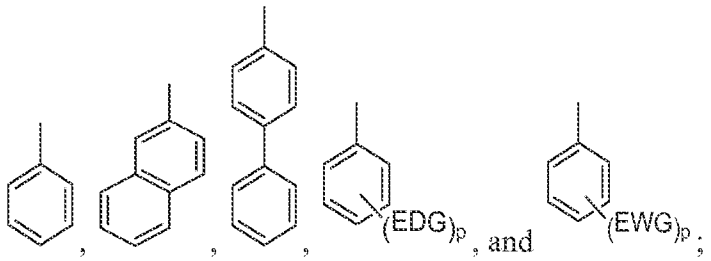


wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5. In certain examples of Formula II, R^2 and $R^{2'}$ are substituted or unsubstituted phenyl.

In some examples of Formula II, R^3 and $R^{3'}$ are the same. In some examples of Formula II, R^3 and $R^{3'}$ are individually chosen from substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl,

substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula II, R^3 and $R^{3'}$ are individually chosen from substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula II, R^3 and $R^{3'}$ are substituted or unsubstituted alkylaryl. In certain examples of Formula II, R^3 and $R^{3'}$ are substituted or unsubstituted aryl.

In some examples of Formula II, R^3 and $R^{3'}$ are chosen from the moieties shown below

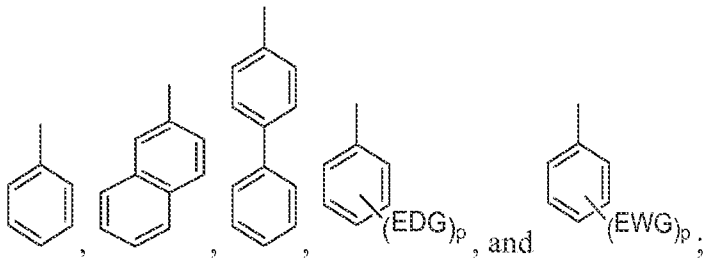


wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5. In certain examples of Formula II, R^3 and $R^{3'}$ are substituted or unsubstituted phenyl.

In some examples of Formula II, R^4 and $R^{4'}$ are the same. In some examples of Formula II, R^4 and $R^{4'}$ are both chosen from hydrogen, hydroxy, and halogen. In certain examples of Formula II, R^4 and $R^{4'}$ are both hydrogen.

In some examples of Formula II, R^5 and $R^{5'}$ are the same. In some examples of Formula II, R^5 and $R^{5'}$ are individually chosen from substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula II, R^5 and $R^{5'}$ are individually chosen from substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula II, R^5 and $R^{5'}$ are substituted or unsubstituted alkylaryl. In certain examples of Formula II, R^5 and $R^{5'}$ are substituted or unsubstituted aryl.

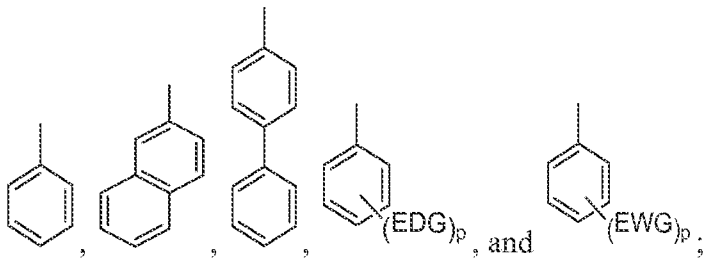
In some examples of Formula II, R^5 and $R^{5'}$ are chosen from the moieties shown below



wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5. In certain examples of Formula II, R^5 and $R^{5'}$ are substituted or unsubstituted phenyl.

In some examples of Formula II, R^3 and $R^{3'}$ are the same, and R^5 and $R^{5'}$ are the same. In some examples of Formula II, R^3, $R^{3'}$, R^5 and $R^{5'}$ are individually chosen from substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula II, R^3, $R^{3'}$, R^5 and $R^{5'}$ are individually chosen from substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula II, R^3, $R^{3'}$, R^5 and $R^{5'}$ are substituted or unsubstituted alkylaryl. In certain examples of Formula II, R^3, $R^{3'}$, R^5 and $R^{5'}$ are substituted or unsubstituted aryl.

In some examples of Formula II, R^3, $R^{3'}$, R^5 and $R^{5'}$ are chosen from the moieties shown below



wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5. In certain examples of Formula II, R^3, $R^{3'}$, R^5 and $R^{5'}$ are substituted or unsubstituted phenyl.

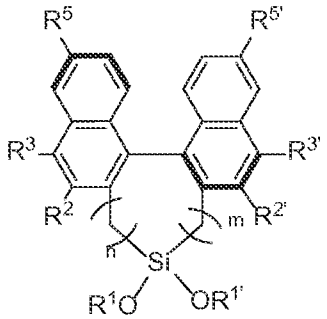
In some examples of Formula II, R^6 and $R^{6'}$ are the same. In some examples of Formula II, R^6 and $R^{6'}$ are both chosen from hydrogen, hydroxy, and halogen. In certain examples of Formula II, R^6 and $R^{6'}$ are both hydrogen.

In some examples of Formula II, R^7 and $R^{7'}$ are the same. In some examples of Formula II, R^7 and $R^{7'}$ are both hydrogen.

In some examples of Formula II, R^4, R^6, $R^{4'}$, and $R^{6'}$ are the same. In some examples of Formula II, R^4, R^6, $R^{4'}$, and $R^{6'}$ are all hydrogen. In some examples of Formula II, R^4, R^7, $R^{4'}$, and $R^{7'}$ are the same. In some examples of Formula II, R^4, R^7, $R^{4'}$, and $R^{7'}$ are all hydrogen. In some examples of Formula II, R^6, R^7, $R^{6'}$, and $R^{7'}$ are the same. In some examples of Formula II, R^6, R^7, $R^{6'}$, and $R^{7'}$ are all hydrogen.

In some examples of Formula II, R^4, R^6, R^7, $R^{4'}$, $R^{6'}$, and $R^{7'}$ are the same.

In some examples of Formula II, R^4, R^6, R^7, $R^{4'}$, $R^{6'}$ and $R^{7'}$ are all hydrogen, and the compound can be defined by Formula III:



III

wherein

n = 0 or 1;

m = 0 or 1;

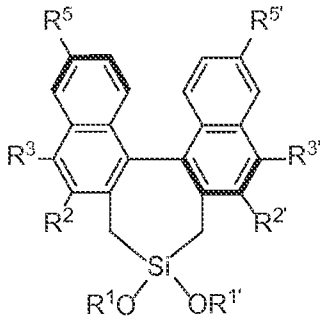
R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl; and

R^2, R^3, R^5, $R^{2'}$, $R^{3'}$, and $R^{5'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl, or wherein, as valence and stability permit, R^2 and R^3, and/or $R^{2'}$ and $R^{3'}$, together with the atoms to which they are attached, form a 3-10 membered substituted or unsubstituted cyclic moiety optionally including between 1 and 3 heteroatoms;

with the proviso that when n=0 and m=0, R^1, $R^{1'}$, R^3, R^5, $R^{3'}$ and $R^{5'}$ are not all H and R^2 and $R^{2'}$ are not both phenyl.

In some examples of Formula III, n is 0. In some examples of Formula III, m is 0. In some examples of Formula III, n and m are 0. In some examples of Formula III, n is 1. In some examples of Formula III, m is 1.

In some examples of Formula III, at least one of n and m is 1. In some examples of Formula III, n and m are both 1. In these examples, the compound of Formula III can be defined by Formula IIIa:



IIIa

wherein

R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl; and

R^2, R^3, R^5, $R^{2'}$, $R^{3'}$, and $R^{5'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl, or wherein, as valence and stability permit, R^2 and R^3, and/or $R^{2'}$ and $R^{3'}$, together with the atoms to which they are attached, form a 3-10 membered substituted or unsubstituted cyclic moiety optionally including between 1 and 3 heteroatoms.

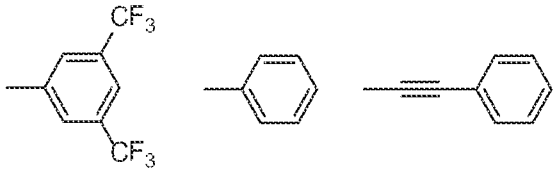
In some examples of Formula IIIa, R^1, $R^{1'}$, R^2, R^3, R^5, $R^{2'}$, $R^{3'}$, and $R^{5'}$ are not all H.

In some examples of Formula IIIa, when R^1 and $R^{1'}$ are both $-CH_3$, R^2, R^3, R^5, $R^{2'}$, $R^{3'}$, and $R^{5'}$ are not all H.

In some examples of Formula IIIa, when R^1, $R^{1'}$, R^3, R^5, $R^{3'}$, and $R^{5'}$ are all H, R^2 and $R^{2'}$ are not both chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl,

substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

In some examples of Formula IIIa, when R^1, $R^{1'}$, R^3, R^5, $R^{3'}$, and $R^{5'}$ are all H, R^2 and $R^{2'}$ are not both substituted or unsubstituted aryl or substituted or unsubstituted alkylaryl. In some examples of Formula IIIa, when R^1, $R^{1'}$, R^3, R^5, $R^{3'}$, and $R^{5'}$ are all H, R^2 and $R^{2'}$ are not both chosen from the moieties shown below.

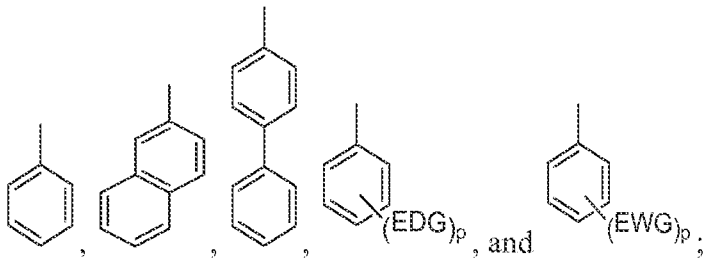


In some examples of Formula III and Formula IIIa, the compound exhibits C_2-symmetry.

In some examples of Formula III and Formula IIIa, R^1 and $R^{1'}$ are the same. In some examples of Formula III and Formula IIIa, R^1 and $R^{1'}$ are both hydrogen or $-CH_3$. In some examples of Formula III and Formula IIIa, R^1 and $R^{1'}$ are both hydrogen. In some examples of Formula III and Formula IIIa, R^1 and $R^{1'}$ are both $-CH_3$.

In some examples of Formula III and Formula IIIa, R^2 and $R^{2'}$ are the same. In some examples of Formula III and Formula IIIa, R^2 and $R^{2'}$ are individually chosen from substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula III and Formula IIIa, R^2 and $R^{2'}$ are individually chosen from substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula III and Formula IIIa, R^2 and $R^{2'}$ are substituted or unsubstituted alkylaryl. In certain examples of Formula III and Formula IIIa, R^2 and $R^{2'}$ are substituted or unsubstituted aryl.

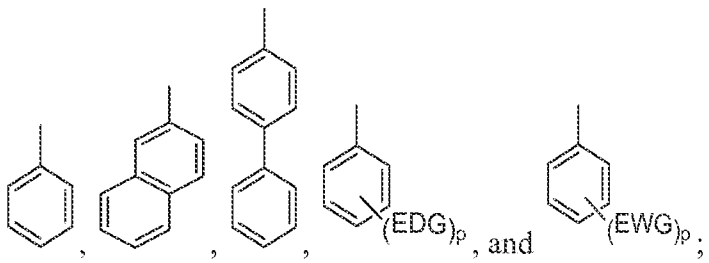
In some examples of Formula III and Formula IIIa, R^2 and $R^{2'}$ are chosen from the moieties shown below



wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5. In certain examples of Formula III and Formula IIIa, R^2 and $R^{2'}$ are substituted or unsubstituted phenyl.

In some examples of Formula III and Formula IIIa, R^3 and $R^{3'}$ are the same. In some examples of Formula III and Formula IIIa, R^3 and $R^{3'}$ are individually chosen from substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula III and Formula IIIa, R^3 and $R^{3'}$ are individually chosen from substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula III and Formula IIIa, R^3 and $R^{3'}$ are substituted or unsubstituted alkylaryl. In certain examples of Formula III and Formula IIIa, R^3 and $R^{3'}$ are substituted or unsubstituted aryl.

In some examples of Formula III and Formula IIIa, R^3 and $R^{3'}$ are chosen from the moieties shown below

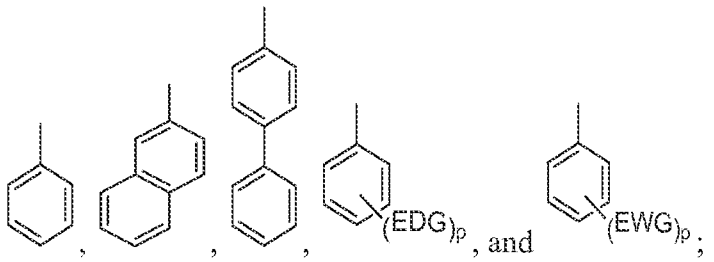


wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5. In certain examples of Formula III and Formula IIIa, R^3 and $R^{3'}$ are substituted or unsubstituted phenyl.

In some examples of Formula III and Formula IIIa, R^5 and $R^{5'}$ are the same. In some examples of Formula III and Formula IIIa, R^5 and $R^{5'}$ are individually chosen from substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted

alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula III and Formula IIIa, R^5 and $R^{5'}$ are individually chosen from substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula III and Formula IIIa, R^5 and $R^{5'}$ are substituted or unsubstituted alkylaryl. In certain examples of Formula III and Formula IIIa, R^5 and $R^{5'}$ are substituted or unsubstituted aryl.

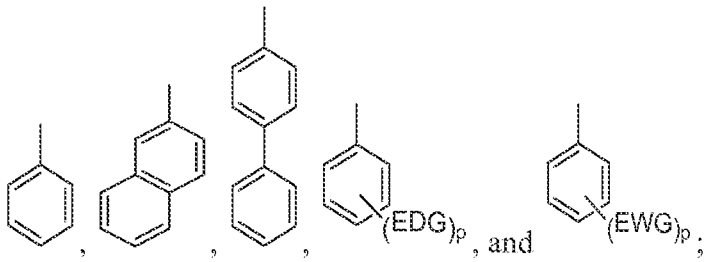
In some examples of Formula III and Formula IIIa, R^5 and $R^{5'}$ are chosen from the moieties shown below



wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5. In certain examples of Formula III and Formula IIIa, R^5 and $R^{5'}$ are substituted or unsubstituted phenyl.

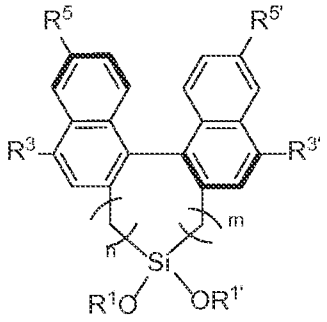
In some examples of Formula III and Formula IIIa, R^3 and $R^{3'}$ are the same, and R^5 and $R^{5'}$ are the same. In some examples of Formula III and Formula IIIa, R^3, $R^{3'}$, R^5 and $R^{5'}$ are individually chosen from substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula III and Formula IIIa, R^3, $R^{3'}$, R^5 and $R^{5'}$ are individually chosen from substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula III and Formula IIIa, R^3, $R^{3'}$, R^5 and $R^{5'}$ are substituted or unsubstituted alkylaryl. In certain examples of Formula III and Formula IIIa, R^3, $R^{3'}$, R^5 and $R^{5'}$ are substituted or unsubstituted aryl.

In some examples of Formula III and Formula IIIa, R^3, $R^{3'}$, R^5 and $R^{5'}$ are chosen from the moieties shown below



wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5. In certain examples of Formula III and Formula IIIa, R^3, $R^{3'}$, R^5 and $R^{5'}$ are substituted or unsubstituted phenyl.

In some examples of Formula II, R^2, R^4, R^6, R^7, $R^{2'}$, $R^{4'}$, $R^{6'}$ and $R^{7'}$ are all hydrogen, and the compound can be defined by Formula IV:



IV

wherein

n = 0 or 1;

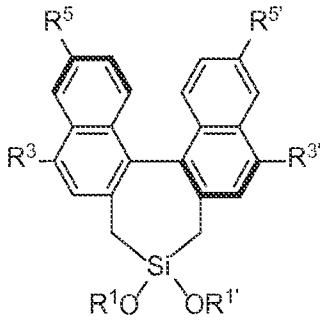
m = 0 or 1;

R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl; and

R^3, R^5, $R^{3'}$, and $R^{5'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

In some examples of Formula IV, n is 0. In some examples of Formula IV, m is 0. In some examples of Formula IV, n and m are 0. In some examples of Formula IV, n is 1. In some examples of Formula IV, m is 1.

In some examples of Formula IV, at least one of n and m is 1. In some examples of Formula IV, n and m are both 1. In these examples, the compound of Formula IV can be defined by Formula IVa:



IVa

wherein

R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl; and

R^3, R^5, $R^{3'}$, and $R^{5'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

In some examples of Formula IVa, R^1, $R^{1'}$, R^3, R^5, $R^{3'}$, and $R^{5'}$ are not all H.

In some examples of Formula IVa, when R^1 and $R^{1'}$ are both $-CH_3$, R^3, R^5, $R^{3'}$, and $R^{5'}$ are not all H.

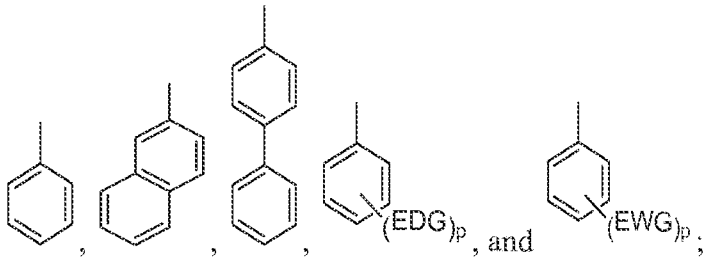
In some examples of Formula IV and Formula IVa, the compound exhibits C_2-symmetry.

In some examples of Formula IV and Formula IVa, R^1 and $R^{1'}$ are the same. In some examples of Formula IV and Formula IVa, R^1 and $R^{1'}$ are both hydrogen or $-CH_3$. In some examples of Formula IV and Formula IVa, R^1 and $R^{1'}$ are both hydrogen. In some examples of Formula IV and Formula IVa, R^1 and $R^{1'}$ are both $-CH_3$.

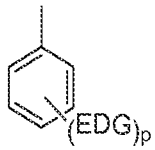
In some examples of Formula IV and Formula IVa, R^3 and $R^{3'}$ are the same. In some examples of Formula IV and Formula IVa, R^3 and $R^{3'}$ are individually chosen from substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl,

substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula IV and Formula IVa, R^3 and $R^{3'}$ are individually chosen from substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula IV and Formula IVa, R^3 and $R^{3'}$ are substituted or unsubstituted alkylaryl. In certain examples of Formula IV and Formula IVa, R^3 and $R^{3'}$ are substituted or unsubstituted aryl.

In some examples of Formula IV and Formula IVa, R^3 and $R^{3'}$ are chosen from the moieties shown below

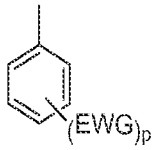


wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5. In some examples of Formula IV and Formula IVa, R^3 and $R^{3'}$ are



wherein EDG represents an electron donating group selected from hydroxy, substituted or unsubstituted amino, substituted or unsubstituted amido, substituted or unsubstituted alkyl, substituted or unsubstituted alkoxy, and substituted or unsubstituted aryl, and p is chosen from 1, 2, 3, 4 and 5.

In some examples of Formula IV and Formula IVa, R^3 and $R^{3'}$ are

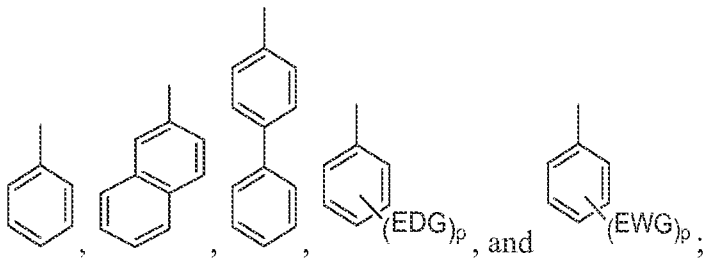


wherein EWG represents an electron withdrawing group selected from nitro, cyano, and trihalides (e.g., -C(halide)$_3$), and p is chosen from 1, 2, 3, 4 and 5.

In certain examples of Formula IV and Formula IVa, R^3 and $R^{3'}$ are substituted or unsubstituted phenyl.

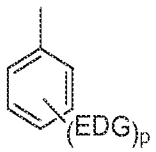
In some examples of Formula IV and Formula IVa, R^5 and $R^{5'}$ are the same. In some examples of Formula IV and Formula IVa, R^5 and $R^{5'}$ are individually chosen from substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula IV and Formula IVa, R^5 and $R^{5'}$ are individually chosen from substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula IV and Formula IVa, R^5 and $R^{5'}$ are substituted or unsubstituted alkylaryl. In certain examples of Formula IV and Formula IVa, R^5 and $R^{5'}$ are substituted or unsubstituted aryl.

In some examples of Formula IV and Formula IVa, R^5 and $R^{5'}$ are chosen from the moieties shown below



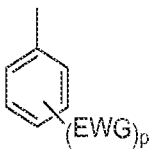
wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5.

In some examples of Formula IV and Formula IVa, R^5 and $R^{5'}$ are



wherein EDG represents an electron donating group selected from hydroxy, substituted or unsubstituted amino, substituted or unsubstituted amido, substituted or unsubstituted alkyl, substituted or unsubstituted alkoxy, and substituted or unsubstituted aryl, and p is chosen from 1, 2, 3, 4 and 5.

In some examples of Formula IV and Formula IVa, R^5 and $R^{5'}$ are

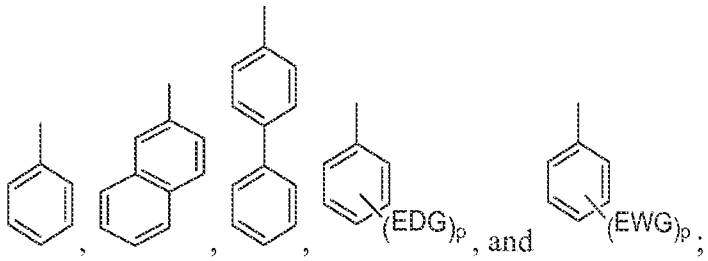


wherein EWG represents an electron withdrawing group selected from nitro, cyano, and trihalides (e.g., -C(halide)$_3$), and p is chosen from 1, 2, 3, 4 and 5.

In certain examples of Formula IV and Formula IVa, R^5 and $R^{5'}$ are substituted or unsubstituted phenyl.

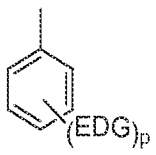
In some examples of Formula IV and Formula IVa, R^3 and $R^{3'}$ are the same, and R^5 and $R^{5'}$ are the same. In some examples of Formula IV and Formula IVa, R^3, $R^{3'}$, R^5 and $R^{5'}$ are individually chosen from substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula IV and Formula IVa, R^3, $R^{3'}$, R^5 and $R^{5'}$ are individually chosen from substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula IV and Formula IVa, R^3, $R^{3'}$, R^5 and $R^{5'}$ are substituted or unsubstituted alkylaryl. In certain examples of Formula IV and Formula IVa, R^3, $R^{3'}$, R^5 and $R^{5'}$ are substituted or unsubstituted aryl.

In some examples of Formula IV and Formula IVa, R^3, $R^{3'}$, R^5 and $R^{5'}$ are chosen from the moieties shown below



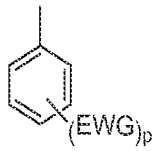
wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5.

In some examples of Formula IV and Formula IVa, R^3, $R^{3'}$, R^5 and $R^{5'}$ are



wherein EDG represents an electron donating group selected from hydroxy, substituted or unsubstituted amino, substituted or unsubstituted amido, substituted or unsubstituted alkyl, substituted or unsubstituted alkoxy, and substituted or unsubstituted aryl, and p is chosen from 1, 2, 3, 4 and 5.

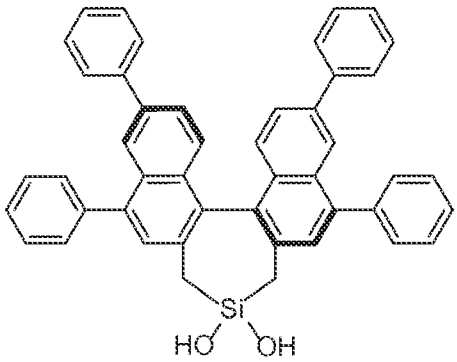
In some examples of Formula IV and Formula IVa, R^3, $R^{3'}$, R^5 and $R^{5'}$ are



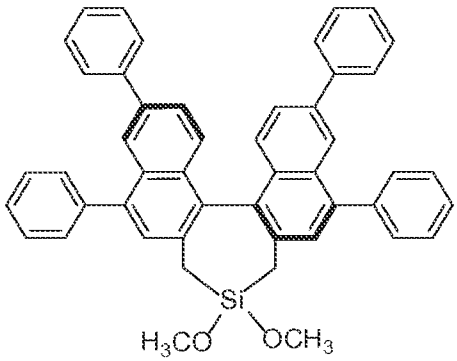
wherein EWG represents an electron withdrawing group selected from nitro, cyano, and trihalides (e.g., -C(halide)$_3$), and p is chosen from 1, 2, 3, 4 and 5.

In certain examples of Formula IV and Formula IVa, R^3, $R^{3'}$, R^5 and $R^{5'}$ are substituted or unsubstituted phenyl.

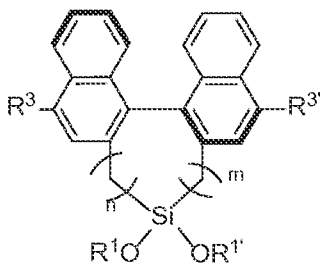
In some examples of Formula IVa, the compound can be defined by the formula:



In some examples of Formula IVa, the compound can be defined by the formula:



In some examples of Formula II, R^2, R^4, R^5, R^6, R^7, $R^{2'}$, $R^{4'}$, $R^{5'}$, $R^{6'}$ and $R^{7'}$ are all hydrogen, and the compound can be defined by Formula V:



V

wherein

n = 0 or 1;

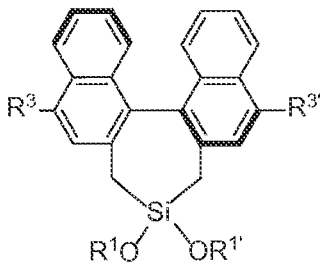
m = 0 or 1;

R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl; and

R^3 and $R^{3'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

In some examples of Formula V, n is 0. In some examples of Formula V, m is 0. In some examples of Formula V, n and m are 0. In some examples of Formula V, n is 1. In some examples of Formula V, m is 1.

In some examples of Formula V, at least one of n and m is 1. In some examples of Formula V, n and m are both 1. In these examples, the compound of Formula V can be defined by Formula Va:



Va

wherein

R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl; and

R^3 and $R^{3'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted

alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

In some examples of Formula Va, R^1, $R^{1'}$, R^3, and $R^{3'}$ are not all H.

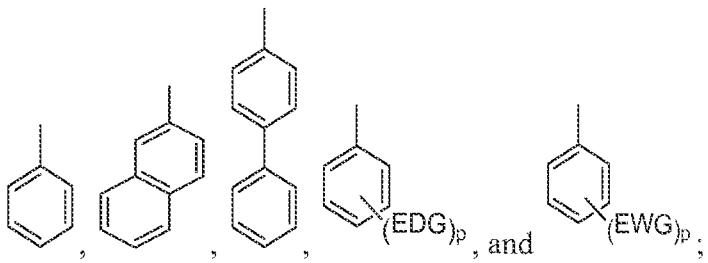
In some examples of Formula Va, when R^1 and $R^{1'}$ are both $-CH_3$, R^3 and $R^{3'}$ are not both H.

In some examples of Formula V and Formula Va, the compound exhibits C_2-symmetry.

In some examples of Formula V and Formula Va, R^1 and $R^{1'}$ are the same. In some examples of Formula V and Formula Va, R^1 and $R^{1'}$ are both hydrogen or $-CH_3$. In some examples of Formula V and Formula Va, R^1 and $R^{1'}$ are both hydrogen. In some examples of Formula V and Formula Va, R^1 and $R^{1'}$ are both $-CH_3$.

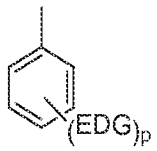
In some examples of Formula V and Formula Va, R^3 and $R^{3'}$ are the same. In some examples of Formula V and Formula Va, R^3 and $R^{3'}$ are individually chosen from substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula V and Formula Va, R^3 and $R^{3'}$ are individually chosen from substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula V and Formula Va, R^3 and $R^{3'}$ are substituted or unsubstituted alkylaryl. In certain examples of Formula V and Formula Va, R^3 and $R^{3'}$ are substituted or unsubstituted aryl.

In some examples of Formula V and Formula Va, R^3 and $R^{3'}$ are chosen from the moieties shown below



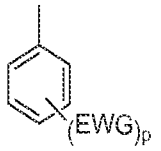
wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5.

In some examples of Formula V and Formula Va, R^3 and $R^{3'}$ are



wherein EDG represents an electron donating group selected from hydroxy, substituted or unsubstituted amino, substituted or unsubstituted amido, substituted or unsubstituted alkyl, substituted or unsubstituted alkoxy, and substituted or unsubstituted aryl, and p is chosen from 1, 2, 3, 4 and 5.

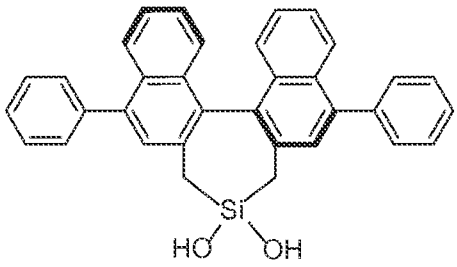
In some examples of Formula V and Formula Va, R^3 and $R^{3'}$ are



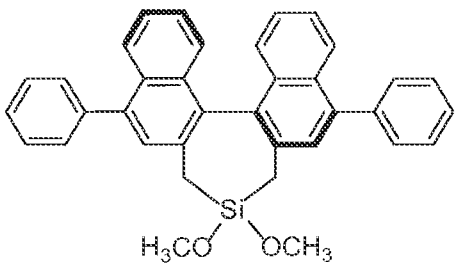
wherein EWG represents an electron withdrawing group selected from nitro, cyano, and trihalides (e.g., -C(halide)$_3$), and p is chosen from 1, 2, 3, 4 and 5.

In certain examples of Formula V and Formula Va, R^3 and $R^{3'}$ are substituted or unsubstituted phenyl.

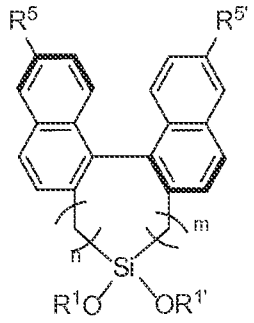
In some examples of Formula Va, the compound can be defined by the formula:



In some examples of Formula Va, the compound can be defined by the formula:



In some examples of Formula II, R^2, R^3, R^4, R^6, R^7, $R^{2'}$, $R^{3'}$, $R^{4'}$, $R^{6'}$ and $R^{7'}$ are all hydrogen, and the compound can be defined by Formula VI:



VI

wherein

n = 0 or 1;

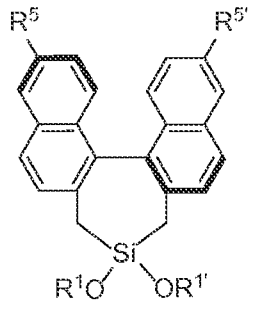
m = 0 or 1;

R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl; and

R^5 and $R^{5'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

In some examples of Formula VI, n is 0. In some examples of Formula VI, m is 0. In some examples of Formula VI, n and m are 0. In some examples of Formula VI, n is 1. In some examples of Formula VI, m is 1.

In some examples of Formula VI, at least one of n and m is 1. In some examples of Formula VI, n and m are both 1. In these examples, the compound of Formula VI can be defined by Formula VIa:



VIa

wherein

R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl; and

R^5 and $R^{5'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

In some examples of Formula VIa, R^1, $R^{1'}$, R^5, and $R^{5'}$ are not all H.

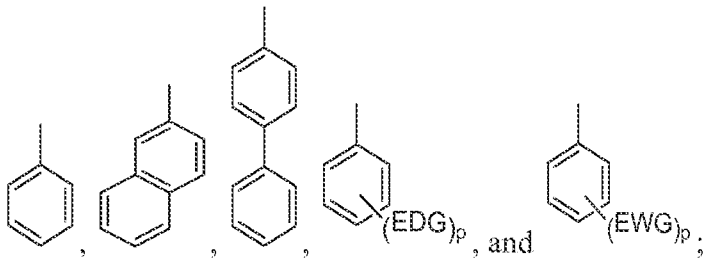
In some examples of Formula VIa, when R^1 and $R^{1'}$ are both $-CH_3$, R^3 and $R^{3'}$ $R^{5'}$ are not both H.

In some examples of Formula VI and Formula VIa, the compound exhibits C_2-symmetry.

In some examples of Formula VI and Formula VIa, R^1 and $R^{1'}$ are the same. In some examples of Formula VI and Formula VIa, R^1 and $R^{1'}$ are both hydrogen or $-CH_3$. In some examples of Formula VI and Formula VIa, R^1 and $R^{1'}$ are both hydrogen. In some examples of Formula VI and Formula VIa, R^1 and $R^{1'}$ are both $-CH_3$.

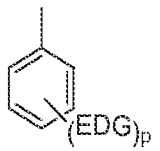
In some examples of Formula VI and Formula VIa, R^5 and $R^{5'}$ are the same. In some examples of Formula VI and Formula VIa, R^5 and $R^{5'}$ are individually chosen from substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula VI and Formula VIa, R^5 and $R^{5'}$ are individually chosen from substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula VI and Formula VIa, R^5 and $R^{5'}$ are substituted or unsubstituted alkylaryl. In certain examples of Formula VI and Formula VIa, R^5 and $R^{5'}$ are substituted or unsubstituted aryl.

In some examples of Formula VI and Formula VIa, R^5 and $R^{5'}$ are chosen from the moieties shown below



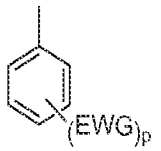
wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5.

In some examples of Formula VI and Formula VIa, R^5 and $R^{5'}$ are



wherein EDG represents an electron donating group selected from hydroxy, substituted or unsubstituted amino, substituted or unsubstituted amido, substituted or unsubstituted alkyl, substituted or unsubstituted alkoxy, and substituted or unsubstituted aryl, and p is chosen from 1, 2, 3, 4 and 5.

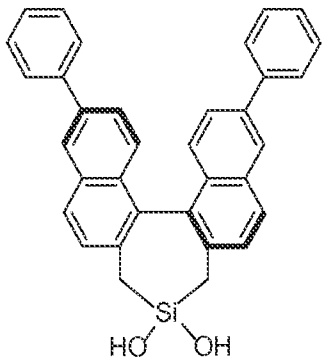
In some examples of Formula VI and Formula VIa, R^5 and $R^{5'}$ are



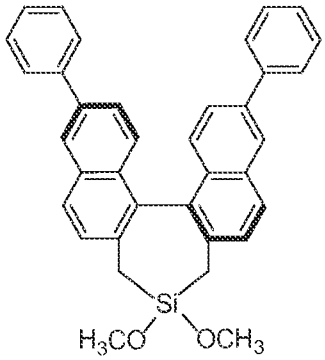
wherein EWG represents an electron withdrawing group selected from nitro, cyano, and trihalides (e.g., -C(halide)$_3$), and p is chosen from 1, 2, 3, 4 and 5.

In certain examples of Formula VI and Formula VIa, R^5 and $R^{5'}$ are substituted or unsubstituted phenyl.

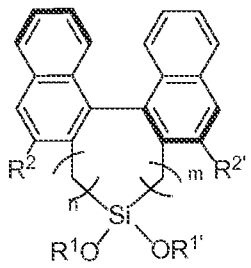
In some examples of Formula VIa, the compound can be defined be the formula:



In some examples of Formula VIa, the compound can be defined be the formula:



In some examples of Formula II, R^3, R^4, R^5, R^6, R^7, $R^{3'}$, $R^{4'}$, $R^{5'}$, $R^{6'}$ and $R^{7'}$ are all hydrogen, and the compound can be defined by Formula VII:



VII

wherein

n = 0 or 1;

m = 0 or 1;

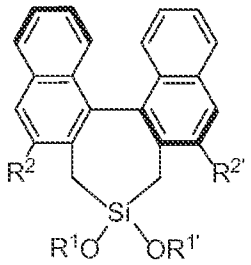
R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl; and

R^2 and $R^{2'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl;

with the proviso that when n=0 and m=0, R^1 and $R^{1'}$ are not both H and R^2 and $R^{2'}$ are not both phenyl.

In some examples of Formula VII, n is 0. In some examples of Formula VII, m is 0. In some examples of Formula VII, n and m are 0. In some examples of Formula VII, n is 1. In some examples of Formula VII, m is 1.

In some examples of Formula VII, at least one of n and m is 1. In some examples of Formula VII, n and m are both 1. In these examples, the compound of Formula VII can be defined by Formula VIIa:



VIIa

wherein

R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl; and

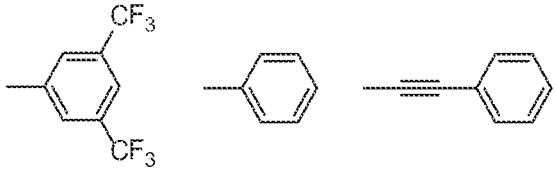
R^2 and $R^{2'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

In some examples of Formula VIIa, R^1, $R^{1'}$, R^2, and $R^{2'}$ are not all H.

In some examples of Formula VIIa, when R^1 and $R^{1'}$ are both $-CH_3$, R^2 and $R^{2'}$ are not both H.

In some examples of Formula VIIa, when R^1 and $R^{1'}$ are both H, R^2 and $R^{2'}$ are not both chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

In some examples of Formula VIIa, when R^1 and $R^{1'}$ are both H, R^2 and $R^{2'}$ are not both substituted or unsubstituted aryl or substituted or unsubstituted alkylaryl. In some examples of Formula VIIa, when R^1 and $R^{1'}$ are both H, R^2 and $R^{2'}$ are not both chosen from the moieties shown below.

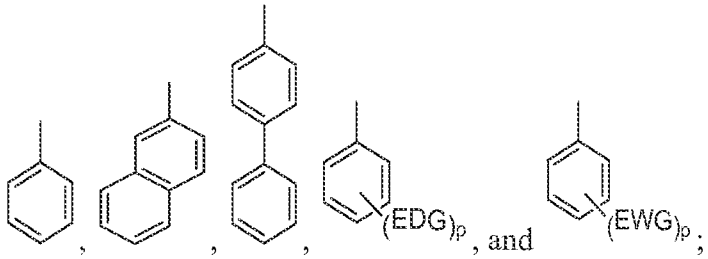


In some examples of Formula VII and Formula VIIa, the compound exhibits C_2-symmetry.

In some examples of Formula VII and Formula VIIa, R^1 and $R^{1'}$ are the same. In some examples of Formula VII and Formula VIIa, R^1 and $R^{1'}$ are both hydrogen or $-CH_3$. In some examples of Formula VII and Formula VIIa, R^1 and $R^{1'}$ are both hydrogen. In some examples of Formula VII and Formula VIIa, R^1 and $R^{1'}$ are both $-CH_3$.

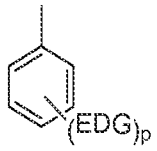
In some examples of Formula VII and Formula VIIa, R^2 and $R^{2'}$ are the same. In some examples of Formula VII and Formula VIIa, R^2 and $R^{2'}$ are individually chosen from substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula VII and Formula VIIa, R^2 and $R^{2'}$ are individually chosen from substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula VII and Formula VIIa, R^2 and $R^{2'}$ are substituted or unsubstituted alkylaryl. In certain examples of Formula VII and Formula VIIa, R^2 and $R^{2'}$ are substituted or unsubstituted aryl.

In some examples of Formula VII and Formula VIIa, R^2 and $R^{2'}$ are chosen from the moieties shown below



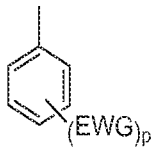
wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5.

In some examples of Formula VII and Formula VIIa, R^2 and $R^{2'}$ are



wherein EDG represents an electron donating group selected from hydroxy, substituted or unsubstituted amino, substituted or unsubstituted amido, substituted or unsubstituted alkyl, substituted or unsubstituted alkoxy, and substituted or unsubstituted aryl, and p is chosen from 1, 2, 3, 4 and 5.

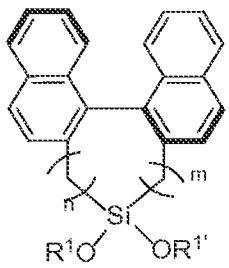
In some examples of Formula VII and Formula VIIa, R^2 and $R^{2'}$ are



wherein EWG represents an electron withdrawing group selected from nitro, cyano, and trihalides (e.g., -C(halide)$_3$), and p is chosen from 1, 2, 3, 4 and 5.

In certain examples of Formula VII and Formula VIIa, R^2 and $R^{2'}$ are substituted or unsubstituted phenyl.

In some examples of Formula II, R^2, R^3, R^4, R^5, R^6, R^7, $R^{2'}$, $R^{3'}$, $R^{4'}$, $R^{5'}$, $R^{6'}$ and $R^{7'}$ are all hydrogen, and the compound can be defined by Formula VIII:



VIII

wherein

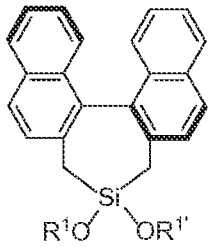
n = 0 or 1;

m = 0 or 1; and

R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl.

In some examples of Formula VIII, n is 0. In some examples of Formula VIII, m is 0. In some examples of Formula VIII, n and m are 0. In some examples of Formula VIII, n is 1. In some examples of Formula VIII, m is 1.

In some examples of Formula VIII, at least one of n and m is 1. In some examples of Formula VIII, n and m are both 1. In these examples, the compound of Formula VIII can be defined by Formula VIIIa:



VIIIa

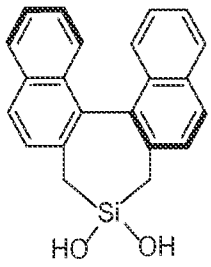
wherein

R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl.

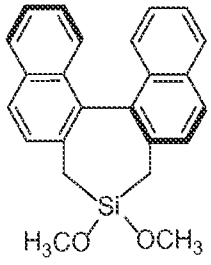
In some examples of Formula VIII and Formula VIIIa, the compound exhibits C_2-symmetry.

In some examples of Formula VIII and Formula VIIIa, R^1 and $R^{1'}$ are the same. In some examples of Formula VIII and Formula VIIIa, R^1 and $R^{1'}$ are both hydrogen or $-CH_3$. In some examples of Formula VIII and Formula VIIIa, R^1 and $R^{1'}$ are both $-CH_3$. In some examples of Formula VIII, R^1 and $R^{1'}$ are both hydrogen.

In some examples of Formula VIIIa, R^1 and $R^{1'}$ are both hydrogen, and the compound can be defined by the formula:

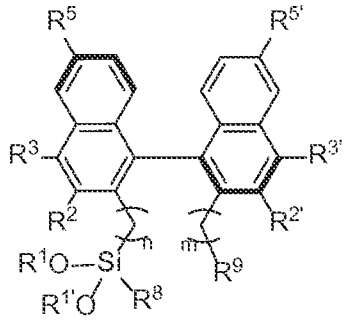


In some examples of Formula VIIIa, R^1 and $R^{1'}$ are both methoxy, and the compound can be defined by the formula:



In some examples of Formula VIIIa, R^1 and $R^{1'}$ are both hydrogen, and the compound is a complex with an ether. In some examples of Formula VIIIa, R^1 and $R^{1'}$ are both hydrogen, and the compound is a complex with a diethyl ether. In some examples of Formula VIIIa, R^1 and $R^{1'}$ are both hydrogen, and the compound is a 2:1 complex with a diethyl ether.

In some examples of Formula I, the compound can be defined by Formula IX:



IX

wherein

n = 0 or 1;

m = 0 or 1;

R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl;

R^2, R^3, R^5, $R^{2'}$, $R^{3'}$, and $R^{5'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl, or wherein, as valence and stability permit, independently R^2 and R^3, $R^{2'}$ and $R^{3'}$, or $R^{2'}$ and R^9, together with the atoms to which they are attached, form a 3-10 membered substituted or unsubstituted cyclic moiety optionally including between 1 and 3 heteroatoms; and

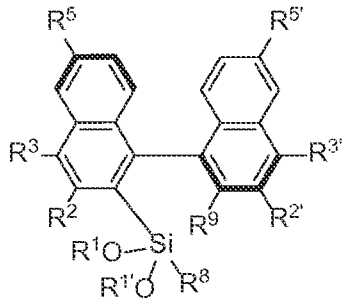
R^8 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted

heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

R^9 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

In some examples of Formula IX, n is 0. In some examples of Formula IX, m is 0. In some examples of Formula IX, n is 1. In some examples of Formula IX, m is 1. In some examples of Formula IX, at least one of n and m is 1. In some examples of Formula IX, n and m are both 1.

In some examples of Formula IX, n and m are both 0. In these examples, the compound of Formula IX can be defined by Formula IXa:



IXa

wherein

R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl; and

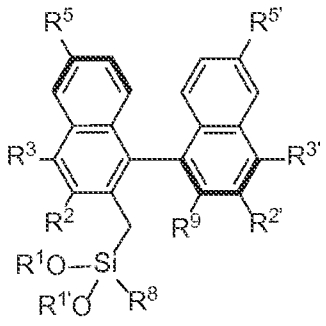
R^2, R^3, R^5, $R^{2'}$, $R^{3'}$, and $R^{5'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted

aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl, or wherein, as valence and stability permit, independently R^2 and R^3, $R^{2'}$ and $R^{3'}$, or $R^{2'}$ and R^9, together with the atoms to which they are attached, form a 3-10 membered substituted or unsubstituted cyclic moiety optionally including between 1 and 3 heteroatoms;

R^8 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

R^9 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

In some examples of Formula IX, n is 1 and m is 0. In these examples, the compound of Formula IX can be defined by Formula IXb:



IXb

wherein

R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl;

R^2, R^3, R^5, $R^{2'}$, $R^{3'}$, and $R^{5'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted

thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl, or wherein, as valence and stability permit, independently R^2 and R^3, $R^{2'}$ and $R^{3'}$, or $R^{2'}$ and R^9, together with the atoms to which they are attached, form a 3-10 membered substituted or unsubstituted cyclic moiety optionally including between 1 and 3 heteroatoms; and

R^8 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

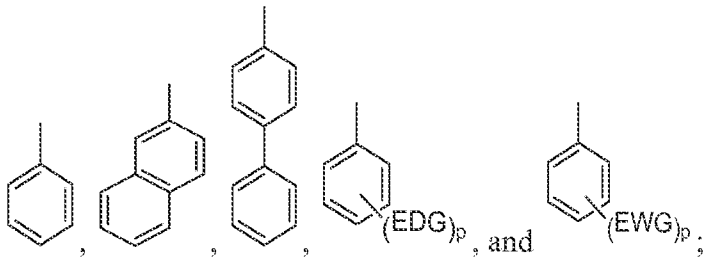
R^9 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl;.

In some examples of Formula IX, Formula IXa, and Formula IXb, R^1 and $R^{1'}$ are the same. In some examples of Formula IX, Formula IXa, and Formula IXb, R^1 and $R^{1'}$ are both hydrogen or $-CH_3$. In some examples of Formula IX, Formula IXa, and Formula IXb, R^1 and $R^{1'}$ are both hydrogen. In some examples of Formula IX, Formula IXa, and Formula IXb, R^1 and $R^{1'}$ are both $-CH_3$.

In some examples of Formula IX, Formula IXa, and Formula IXb, R^2 and $R^{2'}$ are individually chosen from hydrogen, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or

unsubstituted heteroaryl. In some examples of Formula IX, Formula IXa, and Formula IXb, R^2 and $R^{2'}$ are individually chosen from hydrogen, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula IX, Formula IXa, and Formula IXb, R^2 and $R^{2'}$ are substituted or unsubstituted alkylaryl. In certain examples of Formula IX, Formula IXa, and Formula IXb, R^2 and $R^{2'}$ are substituted or unsubstituted aryl.

In some examples of Formula IX, Formula IXa, and Formula IXb, R^2 and $R^{2'}$ are chosen from the moieties shown below

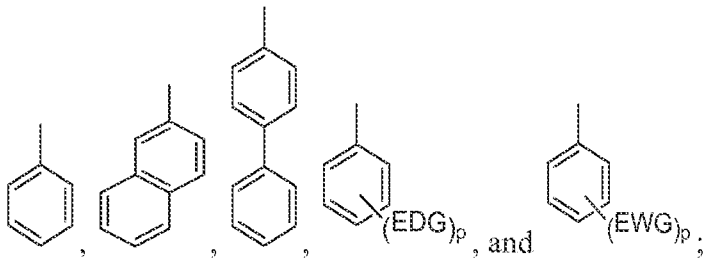


wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5. In certain examples of Formula IX, Formula IXa, and Formula IXb, R^2 and $R^{2'}$ are substituted or unsubstituted phenyl.

In some examples of Formula IX, Formula IXa, and Formula IXb, R^2 and $R^{2'}$ are the same. In certain examples of Formula IX, Formula IXa, and Formula IXb, R^2 and $R^{2'}$ are hydrogen.

In some examples of Formula IX, Formula IXa, and Formula IXb, R^3 and $R^{3'}$ are individually chosen from hydrogen, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula IX, Formula IXa, and Formula IXb, R^3 and $R^{3'}$ are individually chosen from hydrogen, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula IX, Formula IXa, and Formula IXb, R^3 and $R^{3'}$ are substituted or unsubstituted alkylaryl. In certain examples of Formula IX, Formula IXa, and Formula IXb, R^3 and $R^{3'}$ are substituted or unsubstituted aryl.

In some examples of Formula IX, Formula IXa, and Formula IXb, R^3 and $R^{3'}$ are chosen from the moieties shown below

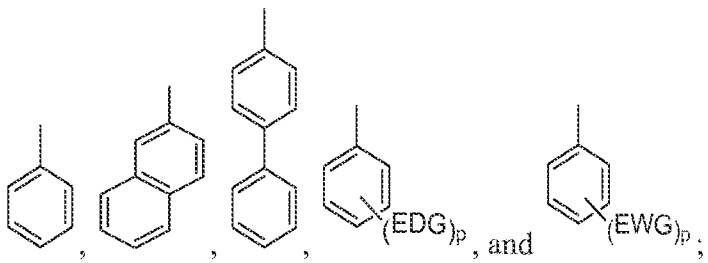


wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5. In certain examples of Formula IX, Formula IXa, and Formula IXb, R^3 and $R^{3'}$ are substituted or unsubstituted phenyl.

In some examples of Formula IX, Formula IXa, and Formula IXb, R^3 and $R^{3'}$ are the same. In some examples of Formula IX, Formula IXa, and Formula IXb, R^3 and $R^{3'}$ are hydrogen.

In some examples of Formula IX, Formula IXa, and Formula IXb, R^5 and $R^{5'}$ are individually chosen from hydrogen, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula IX, Formula IXa, and Formula IXb, R^5 and $R^{5'}$ are individually chosen from hydrogen, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula IX, Formula IXa, and Formula IXb, R^5 and $R^{5'}$ are substituted or unsubstituted alkylaryl. In certain examples of Formula IX, Formula IXa, and Formula IXb, R^5 and $R^{5'}$ are substituted or unsubstituted aryl.

In some examples of Formula IX, Formula IXa, and Formula IXb, R^5 and $R^{5'}$ are chosen from the moieties shown below

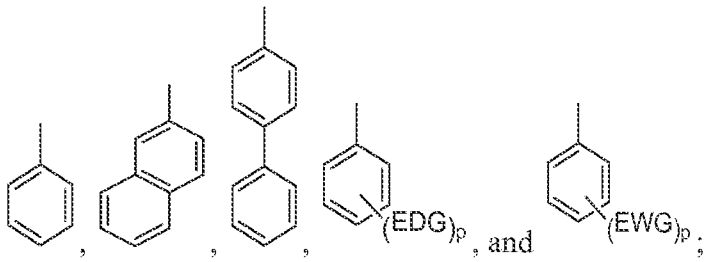


wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5. In certain examples of Formula IX, Formula IXa, and Formula IXb, R^5 and $R^{5'}$ are substituted or unsubstituted phenyl.

In some examples of Formula IX, Formula IXa, and Formula IXb, R^5 and $R^{5'}$ are the same. In some examples of Formula IX, Formula IXa, and Formula IXb, R^5 and $R^{5'}$ are hydrogen.

In some examples of Formula IX, Formula IXa, and Formula IXb, R^3, $R^{3'}$, R^5 and $R^{5'}$ are individually chosen from hydrogen, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula IX, Formula IXa, and Formula IXb, R^3, $R^{3'}$, R^5 and $R^{5'}$ are individually chosen from hydrogen, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula IX, Formula IXa, and Formula IXb, R^3, $R^{3'}$, R^5 and $R^{5'}$ are substituted or unsubstituted alkylaryl. In certain examples of Formula IX, Formula IXa, and Formula IXb, R^3, $R^{3'}$, R^5 and $R^{5'}$ are substituted or unsubstituted aryl.

In some examples of Formula IX, Formula IXa, and Formula IXb, R^3, $R^{3'}$, R^5 and $R^{5'}$ are chosen from the moieties shown below



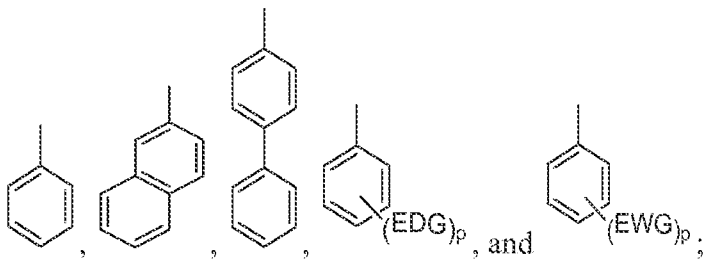
wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5. In certain examples of Formula IX, Formula IXa, and Formula IXb, R^3, $R^{3'}$, R^5 and $R^{5'}$ are substituted or unsubstituted phenyl.

In some examples of Formula IX, Formula IXa, and Formula IXb, R^3 and $R^{3'}$ are the same, and R^5 and $R^{5'}$ are the same. In some examples of Formula IX, Formula IXa, and Formula IXb, R^3 and $R^{3'}$ are hydrogen, and R^5 and $R^{5'}$ are the same. In some examples of Formula IX, Formula IXa, and Formula IXb, R^3 and $R^{3'}$ are the same, and R^5 and $R^{5'}$ are hydrogen.

In some examples of Formula IX, Formula IXa, and Formula IXb, R^3, $R^{3'}$, R^5, and $R^{5'}$ are the same. In some examples of Formula IX, Formula IXa, and Formula IXb, R^3, $R^{3'}$, R^5, and $R^{5'}$ are the hydrogen.

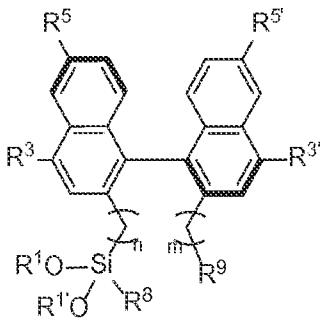
In some examples of Formula IX, Formula IXa, and Formula IXb, R^8 and R^9 are individually chosen from substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula IX, Formula IXa, and Formula IXb, R^8 and R^9 are individually chosen from substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula IX, Formula IXa, and Formula IXb, R^8 and R^9 are substituted or unsubstituted alkylaryl. In certain examples of Formula IX, Formula IXa, and Formula IXb, R^8 and R^9 are substituted or unsubstituted aryl.

In some examples of Formula IX, Formula IXa, and Formula IXb, R^8 and R^9 are independently chosen from the moieties shown below



wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5. In certain examples of Formula IX, Formula IXa, and Formula IXb, R^8 and R^9 are substituted or unsubstituted phenyl.

In some examples of Formula I, the compound can be defined by Formula X:



X

wherein

n = 0 or 1;

m = 0 or 1;

R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl;

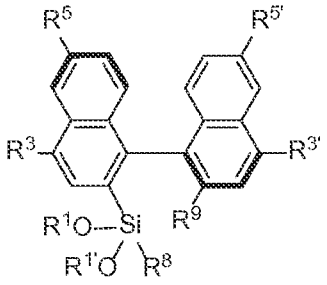
R^3, R^5, $R^{3'}$, and $R^{5'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

R^8 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

R^9 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

In some examples of Formula X, n is 0. In some examples of Formula X, m is 0. In some examples of Formula X, n is 1. In some examples of Formula X, m is 1. In some examples of Formula X, at least one of n and m is 1. In some examples of Formula X, n and m are both 1.

In some examples of Formula X, n and m are both 0. In these examples, the compound of Formula X can be defined by Formula Xa:



Xa

wherein

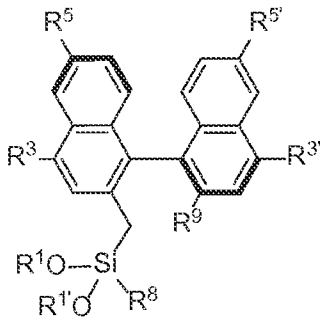
R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl;

R^3, R^5, $R^{3'}$, and $R^{5'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

R^8 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

R^9 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

In some examples of Formula X, n is 1 and m is 0. In these examples, the compound of Formula X can be defined by Formula Xb:



Xb

wherein

R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl;

R^3, R^5, $R^{3'}$, and $R^{5'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

R^8 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

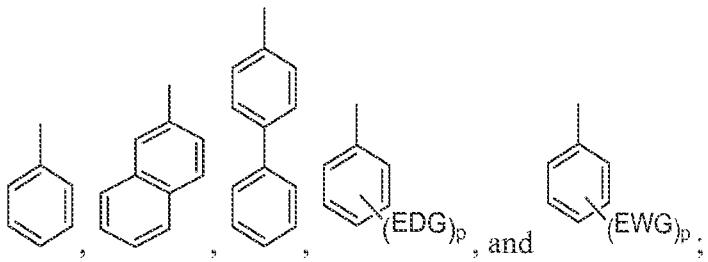
R^9 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted

heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

In some examples of Formula X, Formula Xa, and Formula Xb, R^1 and $R^{1'}$ are the same. In some examples of Formula X, Formula Xa, and Formula Xb, R^1 and $R^{1'}$ are both hydrogen or $-CH_3$. In some examples of Formula X, Formula Xa, and Formula Xb, R^1 and $R^{1'}$ are both hydrogen. In some examples of Formula X, Formula Xa, and Formula Xb, R^1 and $R^{1'}$ are both $-CH_3$.

In some examples of Formula X, Formula Xa, and Formula Xb, R^3 and $R^{3'}$ are individually chosen from hydrogen, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula X, Formula Xa, and Formula Xb, R^3 and $R^{3'}$ are individually chosen from hydrogen, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula X, Formula Xa, and Formula Xb, R^3 and $R^{3'}$ are substituted or unsubstituted alkylaryl. In certain examples of Formula X, Formula Xa, and Formula Xb, R^3 and $R^{3'}$ are substituted or unsubstituted aryl.

In some examples of Formula X, Formula Xa, and Formula Xb, R^3 and $R^{3'}$ are chosen from the moieties shown below



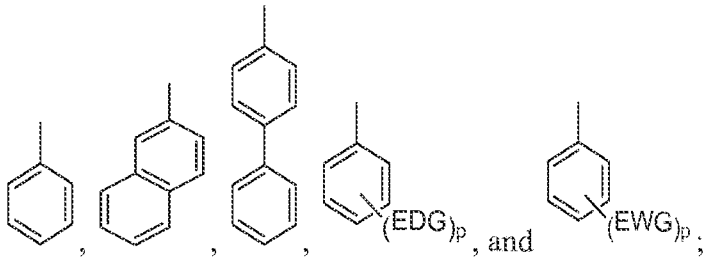
wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5. In certain examples of Formula X, Formula Xa, and Formula Xb, R^3 and $R^{3'}$ are substituted or unsubstituted phenyl.

In some examples of Formula X, Formula Xa, and Formula Xb, R^3 and $R^{3'}$ are the same. In some examples of Formula X, Formula Xa, and Formula Xb, R^3 and $R^{3'}$ are hydrogen.

In some examples of Formula X, Formula Xa, and Formula Xb, R^5 and $R^{5'}$ are individually chosen from hydrogen, substituted or unsubstituted cycloalkyl, substituted or

unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula X, Formula Xa, and Formula Xb, R^5 and $R^{5'}$ are individually chosen from hydrogen, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula X, Formula Xa, and Formula Xb, R^5 and $R^{5'}$ are substituted or unsubstituted alkylaryl. In certain examples of Formula X, Formula Xa, and Formula Xb, R^5 and $R^{5'}$ are substituted or unsubstituted aryl.

In some examples of Formula X, Formula Xa, and Formula Xb, R^5 and $R^{5'}$ are chosen from the moieties shown below

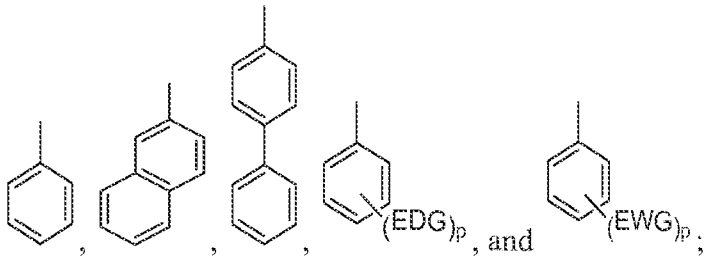


wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5. In certain examples of Formula X, Formula Xa, and Formula Xb, R^5 and $R^{5'}$ are substituted or unsubstituted phenyl.

In some examples of Formula X, Formula Xa, and Formula Xb, R^5 and $R^{5'}$ are the same. In some examples of Formula X, Formula Xa, and Formula Xb, R^5 and $R^{5'}$ are hydrogen.

In some examples of Formula X, Formula Xa, and Formula Xb, R^3, $R^{3'}$, R^5 and $R^{5'}$ are individually chosen from hydrogen, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula X, Formula Xa, and Formula Xb, R^3, $R^{3'}$, R^5 and $R^{5'}$ are individually chosen from hydrogen, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula X, Formula Xa, and Formula Xb, R^3, $R^{3'}$, R^5 and $R^{5'}$ are substituted or unsubstituted alkylaryl. In certain examples of Formula X, Formula Xa, and Formula Xb, R^3, $R^{3'}$, R^5 and $R^{5'}$ are substituted or unsubstituted aryl.

In some examples of Formula X, Formula Xa, and Formula Xb, R^3, $R^{3'}$, R^5 and $R^{5'}$ are chosen from the moieties shown below



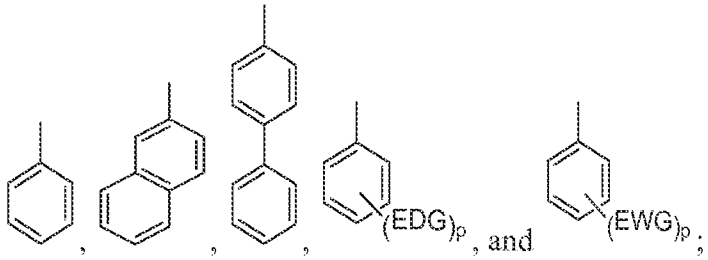
wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5. In certain examples of Formula X, Formula Xa, and Formula Xb, R^3, $R^{3'}$, R^5 and $R^{5'}$ are substituted or unsubstituted phenyl.

In some examples of Formula X, Formula Xa, and Formula Xb, R^3 and $R^{3'}$ are the same, and R^5 and $R^{5'}$ are the same. In some examples of Formula X, Formula Xa, and Formula Xb, R^3 and $R^{3'}$ are hydrogen, and R^5 and $R^{5'}$ are the same. In some examples of Formula X, Formula Xa, and Formula Xb, R^3 and $R^{3'}$ are the same, and R^5 and $R^{5'}$ are hydrogen.

In some examples of Formula X, Formula Xa, and Formula Xb, R^3, $R^{3'}$, R^5, and $R^{5'}$ are the same. In some examples of Formula X, Formula Xa, and Formula Xb, R^3, $R^{3'}$, R^5, and $R^{5'}$ are the hydrogen.

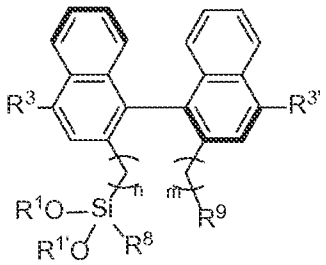
In some examples of Formula X, Formula Xa, and Formula Xb, R^8 and R^9 are individually chosen from substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula X, Formula Xa, and Formula Xb, R^8 and R^9 are individually chosen from substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula X, Formula Xa, and Formula Xb, R^8 and R^9 are substituted or unsubstituted alkylaryl. In certain examples of Formula X, Formula Xa, and Formula Xb, R^8 and R^9 are substituted or unsubstituted aryl.

In some examples of Formula X, Formula Xa, and Formula Xb, R^8 and R^9 are independently chosen from the moieties shown below



wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5. In certain examples of Formula X, Formula Xa, and Formula Xb, R^8 and R^9 are substituted or unsubstituted phenyl.

In some examples of Formula I, the compound can be defined by Formula XI:



XI

wherein

n = 0 or 1;

m = 0 or 1;

R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl;

R^3 and $R^{3'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

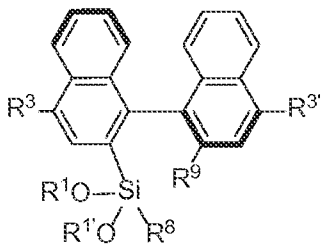
R^8 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted

heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

R^9 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

In some examples of Formula XI, n is 0. In some examples of Formula XI, m is 0. In some examples of Formula XI, n is 1. In some examples of Formula XI, m is 1. In some examples of Formula XI, at least one of n and m is 1. In some examples of Formula XI, n and m are both 1.

In some examples of Formula XI, n and m are both 0. In these examples, the compound of Formula XI can be defined by Formula XIa:



XIa

wherein

R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl;

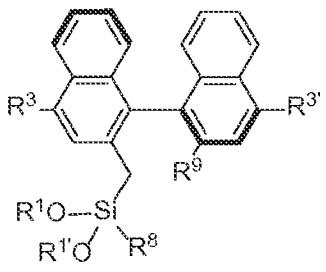
R^3 and $R^{3'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted

aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

R^8 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

R^9 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

In some examples of Formula XI, n is 1 and m is 0. In these examples, the compound of Formula XI can be defined by Formula XIb:



XIb

wherein

R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl;

R^3 and $R^{3'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl,

substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

R^8 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

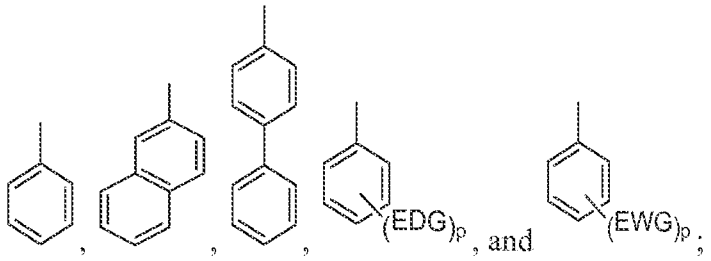
R^9 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

In some examples of Formula XI, Formula XIa, and Formula XIb, R^1 and $R^{1'}$ are the same. In some examples of Formula XI, Formula XIa, and Formula XIb, R^1 and $R^{1'}$ are both hydrogen or $-CH_3$. In some examples of Formula XI, Formula XIa, and Formula XIb, R^1 and $R^{1'}$ are both hydrogen. In some examples of Formula XI, Formula XIa, and Formula XIb, R^1 and $R^{1'}$ are both $-CH_3$.

In some examples of Formula XI, Formula XIa, and Formula XIb, R^3 and $R^{3'}$ are individually chosen from hydrogen, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula XI, Formula XIa, and Formula XIb, R^3 and $R^{3'}$ are individually chosen from hydrogen, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula XI, Formula XIa, and Formula

XIb, R^3 and $R^{3'}$ are substituted or unsubstituted alkylaryl. In certain examples of Formula XI, Formula XIa, and Formula XIb, R^3 and $R^{3'}$ are substituted or unsubstituted aryl.

In some examples of Formula XI, Formula XIa, and Formula XIb, R^3 and $R^{3'}$ are chosen from the moieties shown below

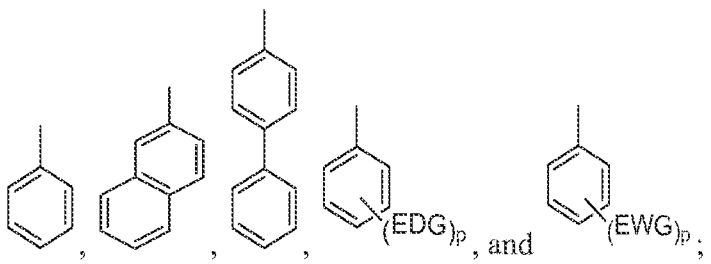


wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5. In certain examples of Formula XI, Formula XIa, and Formula XIb, R^3 and $R^{3'}$ are substituted or unsubstituted phenyl.

In some examples of Formula XI, Formula XIa, and Formula XIb, R^3 and $R^{3'}$ are the same. In some examples of Formula XI, Formula XIa, and Formula XIb, R^3 and $R^{3'}$ are hydrogen.

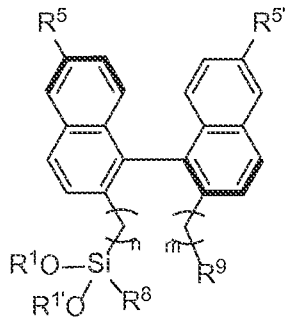
In some examples of Formula XI, Formula XIa, and Formula XIb, R^8 and R^9 are individually chosen from substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula XI, Formula XIa, and Formula XIb, R^8 and R^9 are individually chosen from substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula XI, Formula XIa, and Formula XIb, R^8 and R^9 are substituted or unsubstituted alkylaryl. In certain examples of Formula XI, Formula XIa, and Formula XIb, R^8 and R^9 are substituted or unsubstituted aryl.

In some examples of Formula XI, Formula XIa, and Formula XIb, R^8 and R^9 are independently chosen from the moieties shown below



wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5. In certain examples of Formula XI, Formula XIa, and Formula XIb, R^8 and R^9 are substituted or unsubstituted phenyl.

In some examples of Formula I, the compound can be defined by Formula XII:



XII

wherein

n = 0 or 1;

m = 0 or 1;

R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl;

R^5 and $R^{5'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

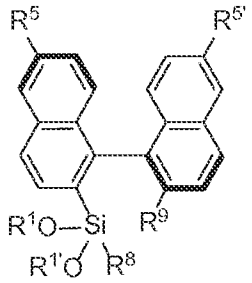
R^8 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

R^9 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl,

substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

In some examples of Formula XII, n is 0. In some examples of Formula XII, m is 0. In some examples of Formula XII, n is 1. In some examples of Formula XII, m is 1. In some examples of Formula XII, at least one of n and m is 1. In some examples of Formula XII, n and m are both 1.

In some examples of Formula XII, n and m are both 0. In these examples, the compound of Formula XII can be defined by Formula XIIa:



XIIa

wherein

R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl;

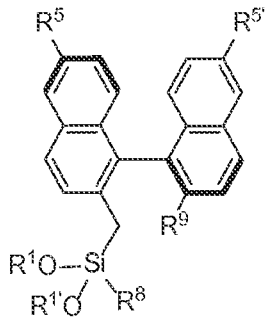
R^5 and $R^{5'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

R^8 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted

cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

R^9 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

In some examples of Formula XII, n is 1 and m is 0. In these examples, the compound of Formula XII can be defined by Formula XIIb:



XIIb

wherein

R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl;

R^5 and $R^{5'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

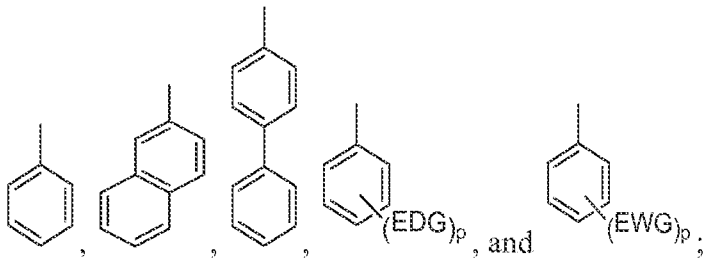
R^8 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

R^9 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

In some examples of Formula XII, Formula XIIa, and Formula XIIb, R^1 and $R^{1'}$ are the same. In some examples of Formula XII, Formula XIIa, and Formula XIIb, R^1 and $R^{1'}$ are both hydrogen or $-CH_3$. In some examples of Formula XII, Formula XIIa, and Formula XIIb, R^1 and $R^{1'}$ are both hydrogen. In some examples of Formula XII, Formula XIIa, and Formula XIIb, R^1 and $R^{1'}$ are both $-CH_3$.

In some examples of Formula XII, Formula XIIa, and Formula XIIb, R^5 and $R^{5'}$ are individually chosen from hydrogen, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula XII, Formula XIIa, and Formula XIIb, R^5 and $R^{5'}$ are individually chosen from hydrogen, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula XII, Formula XIIa, and Formula XIIb, R^5 and $R^{5'}$ are substituted or unsubstituted alkylaryl. In certain examples of Formula XII, Formula XIIa, and Formula XIIb, R^5 and $R^{5'}$ are substituted or unsubstituted aryl.

In some examples of Formula XII, Formula XIIa, and Formula XIIb, R^5 and $R^{5'}$ are chosen from the moieties shown below

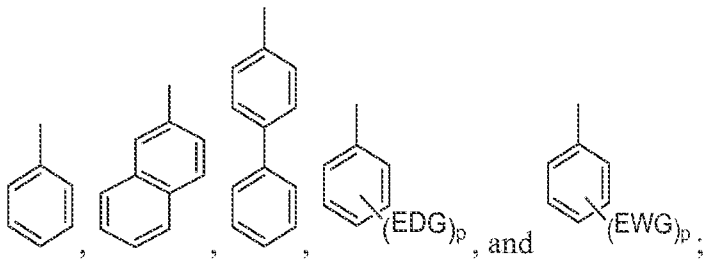


wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5. In certain examples of Formula XII, Formula XIIa, and Formula XIIb, R^5 and $R^{5'}$ are substituted or unsubstituted phenyl.

In some examples of Formula XII, Formula XIIa, and Formula XIIb, R^5 and $R^{5'}$ are the same. In some examples of Formula XII, Formula XIIa, and Formula XIIb, R^5 and $R^{5'}$ are hydrogen.

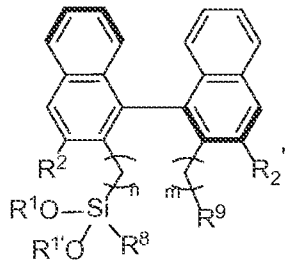
In some examples of Formula XII, Formula XIIa, and Formula XIIb, R^8 and R^9 are individually chosen from substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula XII, Formula XIIa, and Formula XIIb, R^8 and R^9 are individually chosen from substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula XII, Formula XIIa, and Formula XIIb, R^8 and R^9 are substituted or unsubstituted alkylaryl. In certain examples of Formula XII, Formula XIIa, and Formula XIIb, R^8 and R^9 are substituted or unsubstituted aryl.

In some examples of Formula XII, Formula XIIa, and Formula XIIb, R^8 and R^9 are independently chosen from the moieties shown below



wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5. In certain examples of Formula XII, Formula XIIa, and Formula XIIb, R^8 and R^9 are substituted or unsubstituted phenyl.

In some examples of Formula I, the compound can be defined by Formula XIII:



XIII

wherein

n = 0 or 1;

m = 0 or 1;

R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl;

R^2 and $R^{2'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

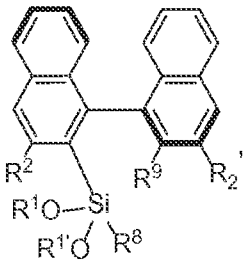
R^8 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

R^9 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or

unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

In some examples of Formula XIII, n is 0. In some examples of Formula XIII, m is 0. In some examples of Formula XIII, n is 1. In some examples of Formula XIII, m is 1. In some examples of Formula XIII, at least one of n and m is 1. In some examples of Formula XIII, n and m are both 1.

In some examples of Formula XIII, n and m are 0. In these examples, the compound of Formula XIII can be defined by Formula XIIIa:



XIIIa

wherein

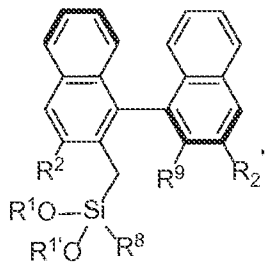
R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl;

R^2 and $R^{2'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

R^8 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

R^9 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

In some examples of Formula XIII, n is 1 and m is 0. In these examples, the compound of Formula XIII can be defined by Formula XIIIb:



XIIIb

wherein

R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl;

R^2 and $R^{2'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

R^8 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or

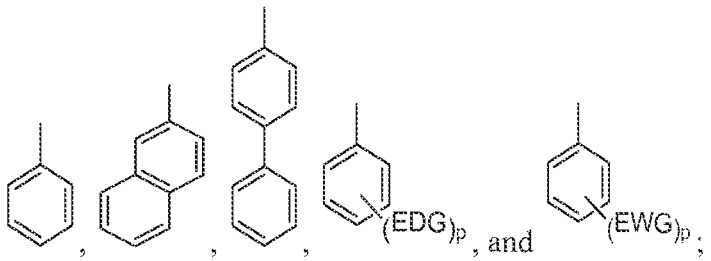
unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

R^9 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

In some examples of Formula XII, Formula XIIa, and Formula XIIb, R^1 and $R^{1'}$ are the same. In some examples of Formula XII, Formula XIIa, and Formula XIIb, R^1 and $R^{1'}$ are both hydrogen or $-CH_3$. In some examples of Formula XII, Formula XIIa, and Formula XIIb, R^1 and $R^{1'}$ are both hydrogen. In some examples of Formula XII, Formula XIIa, and Formula XIIb, R^1 and $R^{1'}$ are both $-CH_3$.

In some examples of Formula XII, Formula XIIa, and Formula XIIb, R^2 and $R^{2'}$ are individually chosen from hydrogen, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula XII, Formula XIIa, and Formula XIIb, R^2 and $R^{2'}$ are individually chosen from hydrogen, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula XII, Formula XIIa, and Formula XIIb, R^2 and $R^{2'}$ are substituted or unsubstituted alkylaryl. In certain examples of Formula XII, Formula XIIa, and Formula XIIb, R^2 and $R^{2'}$ are substituted or unsubstituted aryl.

In some examples of Formula XII, Formula XIIa, and Formula XIIb, R^2 and $R^{2'}$ are chosen from the moieties shown below

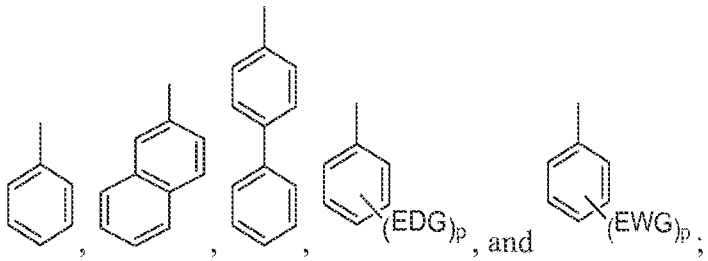


wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5. In certain examples of Formula XII, Formula XIIa, and Formula XIIb, R^2 and $R^{2'}$ are substituted or unsubstituted phenyl.

In some examples of Formula XII, Formula XIIa, and Formula XIIb, R^2 and $R^{2'}$ are the same. In certain examples of Formula XII, Formula XIIa, and Formula XIIb, R^2 and $R^{2'}$ are hydrogen.

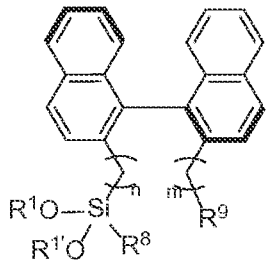
In some examples of Formula XII, Formula XIIa, and Formula XIIb, R^8 and R^9 are individually chosen from substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula XII, Formula XIIa, and Formula XIIb, R^8 and R^9 are individually chosen from substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula XII, Formula XIIa, and Formula XIIb, R^8 and R^9 are substituted or unsubstituted alkylaryl. In certain examples of Formula XII, Formula XIIa, and Formula XIIb, R^8 and R^9 are substituted or unsubstituted aryl.

In some examples of Formula XII, Formula XIIa, and Formula XIIb, R^8 and R^9 are independently chosen from the moieties shown below



wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5. In certain examples of Formula XII, Formula XIIa, and Formula XIIb, R^8 and R^9 are substituted or unsubstituted phenyl.

In some examples of Formula I, the compound can be defined by Formula XIV:



XIV

wherein

n = 0 or 1;

m = 0 or 1; and

R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl; and

R^8 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

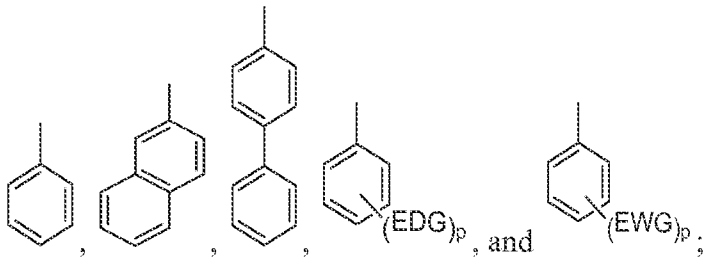
R^9 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

In some examples of Formula XIV, R^1 and $R^{1'}$ are the same. In some examples of Formula XIV, R^1 and $R^{1'}$ are both hydrogen or $-CH_3$. In some examples of Formula XIV, R^1 and $R^{1'}$ are both hydrogen. In some examples of Formula XIV, R^1 and $R^{1'}$ are both $-CH_3$.

In some examples of Formula XIV, R^8 and R^9 are individually chosen from substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted

aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula XIV, R^8 and R^9 are individually chosen from substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula XIV, R^8 and R^9 are substituted or unsubstituted alkylaryl. In certain examples of Formula XIV, R^8 and R^9 are substituted or unsubstituted aryl.

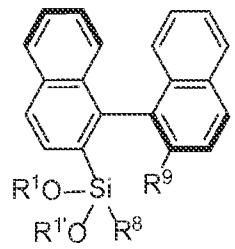
In some examples of Formula XIV, R^8 and R^9 are independently chosen from the moieties shown below



wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5. In certain examples of Formula XIV, R^8 and R^9 are substituted or unsubstituted phenyl.

In some examples of Formula XIV, n is 0. In some examples of Formula XIV, m is 0. In some examples of Formula XIV, n is 1. In some examples of Formula XIV, m is 1. In some examples of Formula XIV, at least one of n and m is 1. In some examples of Formula XIV, n and m are both 1.

In some examples of Formula XIV, n and m are both 0. In these examples, the compound of Formula XIV can be defined by Formula XIVa:



XIVa

wherein

R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl; and

R^8 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted

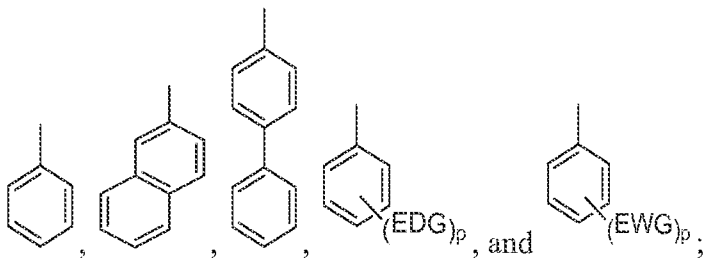
cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

R^9 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

In some examples of Formula XIVa, R^1 and $R^{1'}$ are the same. In some examples of Formula XIVa, R^1 and $R^{1'}$ are both hydrogen or $-CH_3$. In some examples of Formula XIVa, R^1 and $R^{1'}$ are both hydrogen. In some examples of Formula XIVa, R^1 and $R^{1'}$ are both $-CH_3$.

In some examples of Formula XIVa, R^8 and R^9 are individually chosen from substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula XIVa, R^8 and R^9 are individually chosen from substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula XIVa, R^8 and R^9 are substituted or unsubstituted alkylaryl. In certain examples of Formula XIVa, R^8 and R^9 are substituted or unsubstituted aryl.

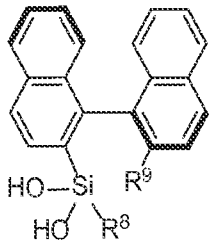
In some examples of Formula XIVa, R^8 and R^9 are independently chosen from the moieties shown below



wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5.

In certain examples of Formula XIVa, R^8 is substituted or unsubstituted phenyl. In certain examples of Formula XIVa, R^9 is substituted or unsubstituted phenyl.

In some examples of Formula XIVa, R^1 and $R^{1'}$ are both hydrogen. In these examples, the compound of Formula XIVa can be defined by Formula XIVb:



XIVb

wherein

R^8 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

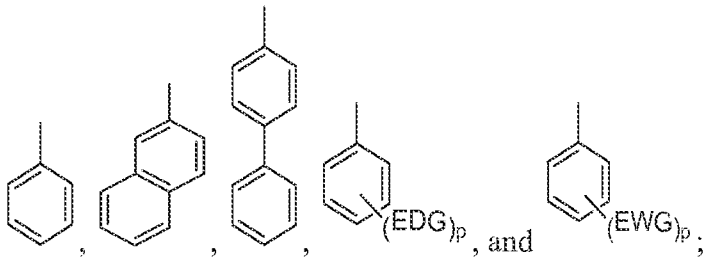
R^9 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

In some examples of Formula XIVb, R^8 and R^9 are individually chosen from substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

In some examples of Formula XIVb, R^8 and R^9 are individually chosen from substituted or

unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula XIVb, R^8 and R^9 are substituted or unsubstituted alkylaryl. In certain examples of Formula XIVb, R^8 and R^9 are substituted or unsubstituted aryl.

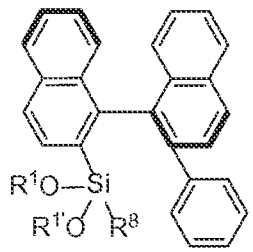
In some examples of Formula XIVb, R^8 and R^9 are independently chosen from the moieties shown below



wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5.

In certain examples of Formula XIVb, R^8 is substituted or unsubstituted phenyl. In certain examples of Formula XIVb, R^9 is substituted or unsubstituted phenyl.

In some examples of Formula XIVa, R^9 is phenyl. In these examples, the compound of Formula XIVa can be defined by Formula XIVc:



XIVc

wherein

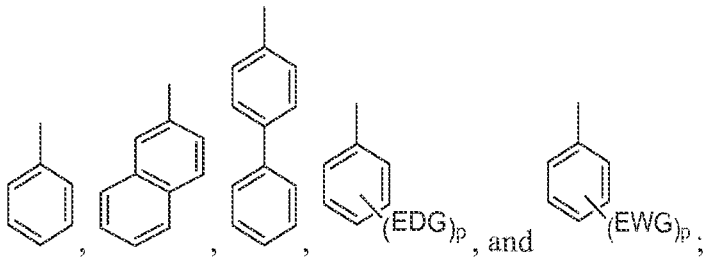
R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl; and

R^8 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

In some examples of Formula XIVc, R^1 and $R^{1'}$ are the same. In some examples of Formula XIVc, R^1 and $R^{1'}$ are both hydrogen or $-CH_3$. In some examples of Formula XIVc, R^1 and $R^{1'}$ are both hydrogen. In some examples of Formula XIVc, R^1 and $R^{1'}$ are both $-CH_3$.

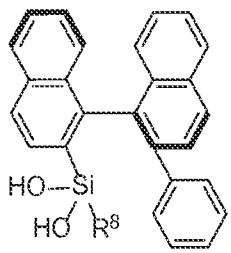
In some examples of Formula XIVc, R^8 is chosen from substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula XIVc, R^8 is chosen from substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula XIVc, R^8 is substituted or unsubstituted alkylaryl. In certain examples of Formula XIVc, R^8 is substituted or unsubstituted aryl.

In some examples of Formula XIVc, R^8 is independently chosen from the moieties shown below



wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5. In certain examples of Formula XIVc, R^8 is substituted or unsubstituted phenyl.

In some examples of Formula XIVa, R^1 and $R^{1'}$ are both hydrogen and R^9 is phenyl. In these examples, the compound of Formula XIVa can be defined by Formula XIVd:



XIVd

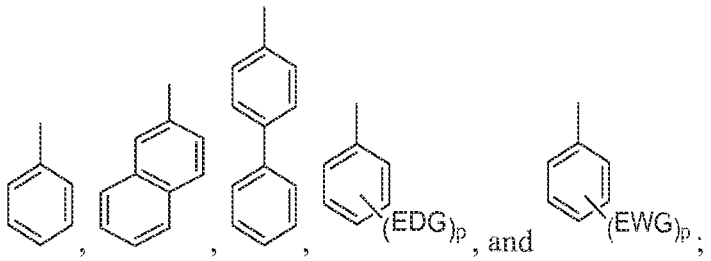
wherein

R^8 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or

unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

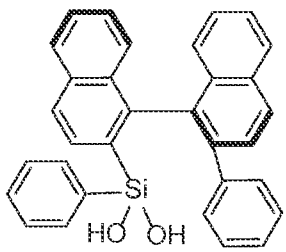
In some examples of Formula XIVd, R^8 is chosen from substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula XIVd, R^8 is chosen from substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula XIVd, R^8 is substituted or unsubstituted alkylaryl. In certain examples of Formula XIVd, R^8 is substituted or unsubstituted aryl.

In some examples of Formula XIVd, R^8 is chosen from the moieties shown below

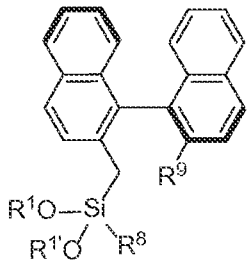


wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5. In certain examples of Formula XIVd, R^8 is substituted or unsubstituted phenyl.

In certain examples of Formula XIVd, R^8 is phenyl, and the compound can be defined by the formula below.



In some examples of Formula XIV, n is 1 and m is 0. In these examples, the compound of Formula XIV can be defined by Formula XIVe:



XIVe

wherein

R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl; and

R^8 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

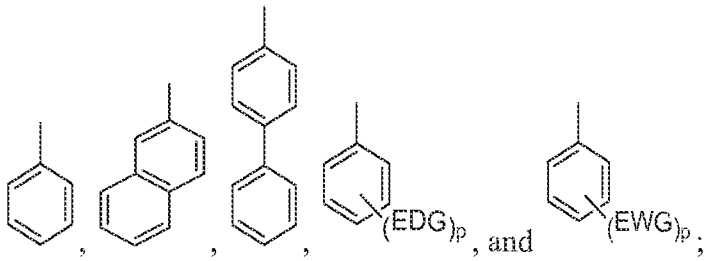
R^9 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

In some examples of Formula XIVe, R^1 and $R^{1'}$ are the same. In some examples of Formula XIVe, R^1 and $R^{1'}$ are both hydrogen or $-CH_3$. In some examples of Formula XIVe, R^1 and $R^{1'}$ are both hydrogen. In some examples of Formula XIVe, R^1 and $R^{1'}$ are both $-CH_3$.

In some examples of Formula XIVe, R^8 and R^9 are independently chosen from substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula XIVe, R^8 and R^9 are independently chosen from substituted

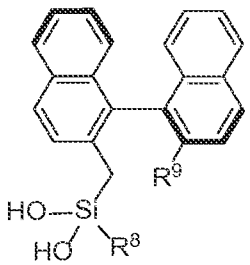
or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula XIVe, R^8 and R^9 are independently substituted or unsubstituted alkylaryl. In certain examples of Formula XIVe, R^8 and R^9 are independently substituted or unsubstituted aryl.

In some examples of Formula XIVe, R^8 and R^9 are independently is chosen from the moieties shown below



wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5. In certain examples of Formula XIVe, R^8 is substituted or unsubstituted phenyl. In certain examples of Formula XIVe, R^9 is substituted or unsubstituted phenyl.

In some examples of Formula XIVe, R^1 and $R^{1'}$ are both hydrogen. In these examples, the compound of Formula XIVe can be defined by Formula XIVf:



XIVf

wherein

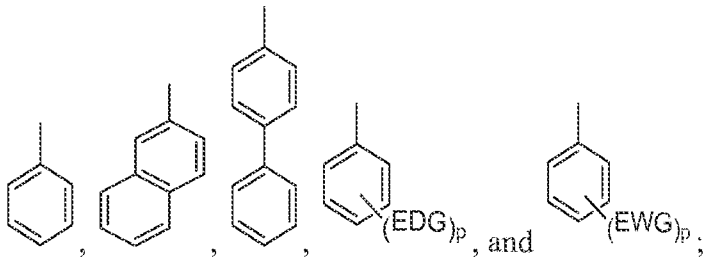
R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl; and

R^8 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

R^9 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

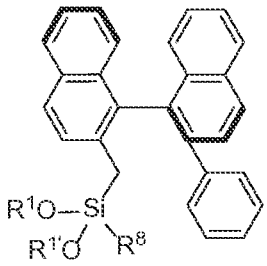
In some examples of Formula XIVf, R^8 and R^9 are independently chosen from substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula XIVf, R^8 and R^9 are independently chosen from substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula XIVf, R^8 and R^9 are independently substituted or unsubstituted alkylaryl. In certain examples of Formula XIVf, R^8 and R^9 are independently substituted or unsubstituted aryl.

In some examples of Formula XIVf, R^8 and R^9 are independently chosen from the moieties shown below



wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5. In certain examples of Formula XIVf, R^8 is substituted or unsubstituted phenyl. In certain examples of Formula XIVf, R^9 is substituted or unsubstituted phenyl.

In certain examples of Formula XIVe, R^9 is phenyl. In these examples, the compound of Formula XIVe can be defined by Formula XIVg:



XIVg

wherein

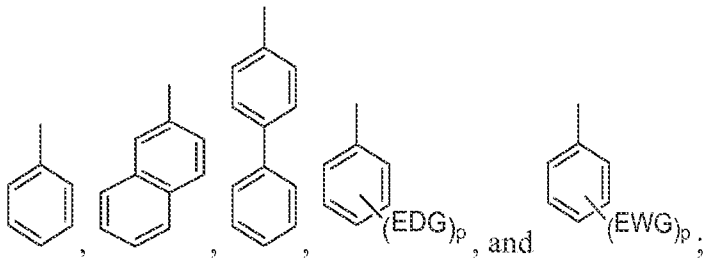
R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl; and

R^8 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

In some examples of Formula XIVg, R^1 and $R^{1'}$ are the same. In some examples of Formula XIVg, R^1 and $R^{1'}$ are both hydrogen or $-CH_3$. In some examples of Formula XIVg, R^1 and $R^{1'}$ are both hydrogen. In some examples of Formula XIVg, R^1 and $R^{1'}$ are both $-CH_3$.

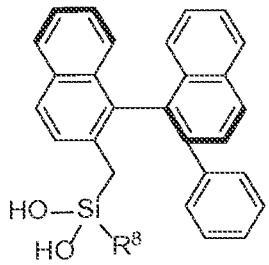
In some examples of Formula XIVg, R^8 is chosen from substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula XIVg, R^8 is chosen from substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula XIVg, R^8 is substituted or unsubstituted alkylaryl. In certain examples of Formula XIVg, R^8 is substituted or unsubstituted aryl.

In some examples of Formula XIVg, R^8 is chosen from the moieties shown below



wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5. In certain examples of Formula XIVg, R^8 is substituted or unsubstituted phenyl.

In certain examples of Formula XIVe, R^1 and $R^{1'}$ are both hydrogen and R^9 is phenyl. In these examples, the compound of Formula XIVe can be defined by Formula XIVh:



XIVh

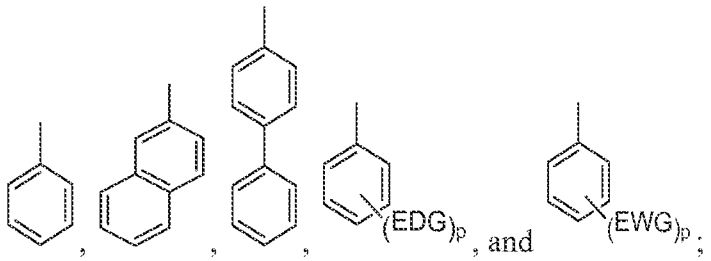
wherein

R^8 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

In some examples of Formula XIVh, R^8 is chosen from substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula XIVh, R^8 is chosen from substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

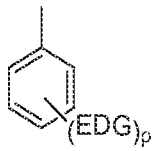
In certain examples of Formula XIVh, R^8 is substituted or unsubstituted alkylaryl. In certain examples of Formula XIVh, R^8 is substituted or unsubstituted aryl.

In some examples of Formula XIVh, R^8 is chosen from the moieties shown below



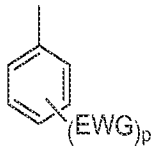
wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5.

In some examples of Formula XIVh, R^8 is



wherein EDG represents an electron donating group selected from hydroxy, substituted or unsubstituted amino, substituted or unsubstituted amido, substituted or unsubstituted alkyl, substituted or unsubstituted alkoxy, and substituted or unsubstituted aryl, and p is chosen from 1, 2, 3, 4 and 5.

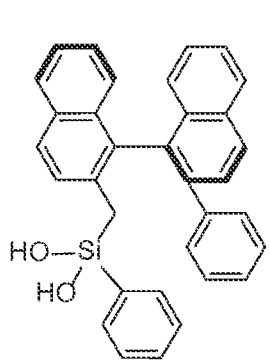
In some examples of Formula XIVh, R^8 is

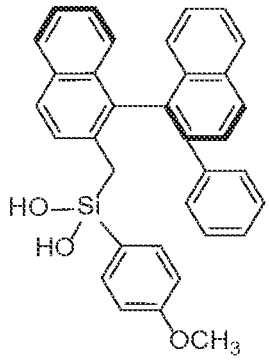


wherein EWG represents an electron withdrawing group selected from nitro, cyano, and trihalides (e.g., -C(halogen)$_3$), and p is chosen from 1, 2, 3, 4 and 5.

In certain examples of Formula XIVh, R^8 is substituted or unsubstituted phenyl.

In some examples of Formula XIVh, the compound can be selected from one of the formulas below:



,


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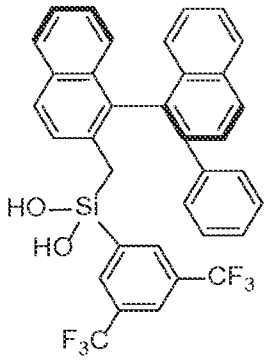

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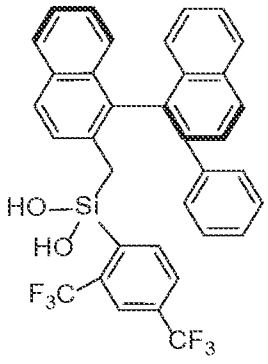
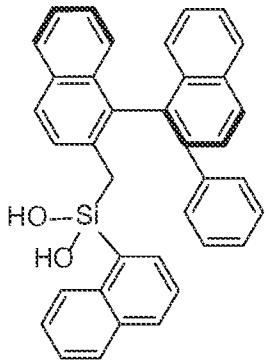
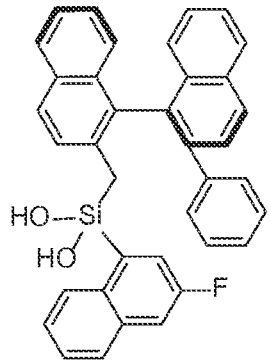
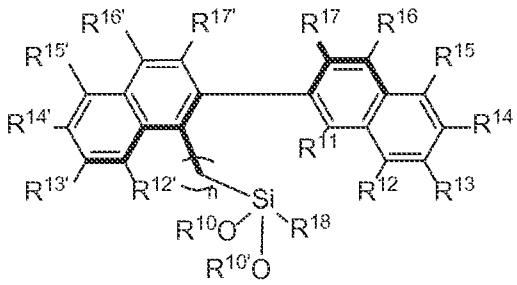


,




, or .

Also disclosed herein are compounds defined by Formula XV:



XV

wherein

n = 0 or 1;

R^{10} and $R^{10'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl;

R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, R^{16}, R^{17}, $R^{12'}$, $R^{13'}$, $R^{14'}$, $R^{15'}$, $R^{16'}$, and $R^{17'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or

unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl, or wherein, as valence and stability permit, independently R^{11} and R^{12}, R^{12} and R^{13}, R^{13} and R^{14}, R^{14} and R^{15}, R^{15} and R^{16}, R^{16} and R^{17}, $R^{12'}$ and $R^{13'}$, $R^{13'}$ and $R^{14'}$, $R^{14'}$ and $R^{15'}$, $R^{15'}$ and $R^{16'}$, or $R^{16'}$ and $R^{17'}$, together with the atoms to which they are attached, form a 3-10 membered substituted or unsubstituted cyclic moiety optionally including between 1 and 3 heteroatoms; and

R^{18} is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

In some examples of Formula XV, n is 0. In some examples of Formula XV, n is 1.

In some examples of Formula XV, R^{10} and $R^{10'}$ are the same. In some examples of Formula XV, R^{10} and $R^{10'}$ are both hydrogen or $-CH_3$. In some examples of Formula XV, R^{10} and $R^{10'}$ are both hydrogen. In some examples of Formula XV, R^{10} and $R^{10'}$ are both $-CH_3$.

In some examples of Formula XV, R^{11} is selected from hydrogen, hydroxy, and halogen. In some examples of Formula XV, R^{11} is hydrogen.

In some examples of Formula XV, R^{12} and $R^{12'}$ are independently chosen from hydrogen, hydroxy, and halogen. In some examples of Formula XV, R^{12} is hydrogen. In some examples of Formula XV, $R^{12'}$ is hydrogen. In some examples of Formula XV, R^{12} and $R^{12'}$ are the same. In some examples of Formula XV, R^{12} and $R^{12'}$ are both hydrogen.

In some examples of Formula XV, R^{13} and $R^{13'}$ are independently chosen from hydrogen, hydroxy, and halogen. In some examples of Formula XV, R^{13} is hydrogen. In some examples of Formula XV, $R^{13'}$ is hydrogen. In some examples of Formula XV, R^{13} and $R^{13'}$ are the same. In some examples of Formula XV, R^{13} and $R^{13'}$ are both hydrogen.

In some examples of Formula XV, R^{12}, $R^{12'}$, R^{13} and $R^{13'}$ are independently chosen from hydrogen, hydroxy, and halogen. In some examples of Formula XV, R^{12}, $R^{12'}$, R^{13} and $R^{13'}$ are the same. In some examples of Formula XV, R^{12}, $R^{12'}$, R^{13} and $R^{13'}$ are all hydrogen.

In some examples of Formula XV, R^{12} and R^{13} together with the atoms to which they are attached, form a 3-10 membered substituted or unsubstituted cyclic moiety

optionally including between 1 and 3 heteroatoms. In some examples of Formula XV, R^{12} and R^{13} together with the atoms to which they are attached, form a 5-7 membered substituted or unsubstituted cyclic moiety optionally including between 1 and 3 heteroatoms. In some examples of Formula XV, R^{12} and R^{13} together with the atoms to which they are attached, form a 5-7 membered substituted or unsubstituted cyclic moiety. In some examples of Formula XV, R^{12} and R^{13} together with the atoms to which they are attached, form a 6 membered substituted or unsubstituted cyclic moiety. In some examples of Formula XV, R^{12} and R^{13} together with the atoms to which they are attached, form a substituted or unsubstituted phenyl moiety.

In some examples of Formula XV, $R^{12'}$ and $R^{13'}$ together with the atoms to which they are attached, form a 3-10 membered substituted or unsubstituted cyclic moiety optionally including between 1 and 3 heteroatoms. In some examples of Formula XV, $R^{12'}$ and $R^{13'}$ together with the atoms to which they are attached, form a 5-7 membered substituted or unsubstituted cyclic moiety optionally including between 1 and 3 heteroatoms. In some examples of Formula XV, $R^{12'}$ and $R^{13'}$ together with the atoms to which they are attached, form a 5-7 membered substituted or unsubstituted cyclic moiety. In some examples of Formula XV, $R^{12'}$ and $R^{13'}$ together with the atoms to which they are attached, form a 6 membered substituted or unsubstituted cyclic moiety. In some examples of Formula XV, $R^{12'}$ and $R^{13'}$ together with the atoms to which they are attached, form a substituted or unsubstituted phenyl moiety.

In some examples of Formula XV, R^{14} and $R^{14'}$ are independently chosen from hydrogen, hydroxy, and halogen. In some examples of Formula XV, R^{14} is hydrogen. In some examples of Formula XV, $R^{14'}$ is hydrogen. In some examples of Formula XV, R^{14} and $R^{14'}$ are the same. In some examples of Formula XV, R^{14} and $R^{14'}$ are both hydrogen.

In some examples of Formula XV, R^{15} and $R^{15'}$ are independently chosen from hydrogen, hydroxy, and halogen. In some examples of Formula XV, R^{15} is hydrogen. In some examples of Formula XV, $R^{15'}$ is hydrogen. In some examples of Formula XV, R^{15} and $R^{15'}$ are the same. In some examples of Formula XV, R^{15} and $R^{15'}$ are both hydrogen.

In some examples of Formula XV, R^{16} and $R^{16'}$ are independently chosen from hydrogen, hydroxy, and halogen. In some examples of Formula XV, R^{16} is hydrogen. In some examples of Formula XV, $R^{16'}$ is hydrogen. In some examples of Formula XV, R^{16} and $R^{16'}$ are the same. In some examples of Formula XV, R^{16} and $R^{16'}$ are both hydrogen.

In some examples of Formula XV, R^{14}, $R^{14'}$, R^{15}, and $R^{15'}$ are independently chosen from hydrogen, hydroxy, and halogen. In some examples of Formula XV, R^{14}, $R^{14'}$, R^{15},

and $R^{15'}$ are the same. In some examples of Formula XV, R^{14}, $R^{14'}$, R^{15}, and $R^{15'}$ are all hydrogen.

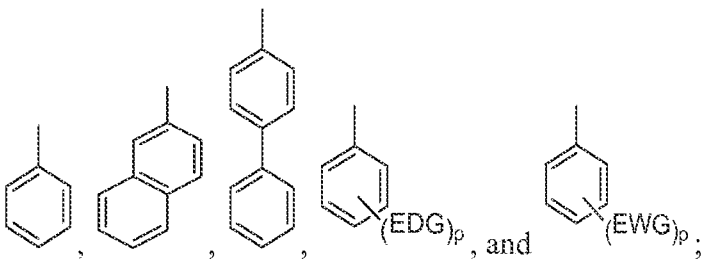
In some examples of Formula XV, R^{14}, $R^{14'}$, R^{16}, and $R^{16'}$ are independently chosen from hydrogen, hydroxy, and halogen. In some examples of Formula XV, R^{14}, $R^{14'}$, R^{16}, and $R^{16'}$ are the same. In some examples of Formula XV, R^{14}, $R^{14'}$, R^{16}, and $R^{16'}$ are all hydrogen.

In some examples of Formula XV, R^{15}, $R^{15'}$, R^{16}, and $R^{16'}$ are independently chosen from hydrogen, hydroxy, and halogen. In some examples of Formula XV, R^{15}, $R^{15'}$, R^{16}, and $R^{16'}$ are the same. In some examples of Formula XV, R^{15}, $R^{15'}$, R^{16}, and $R^{16'}$ are all hydrogen.

In some examples of Formula XV, R^{14}, $R^{14'}$, R^{15}, $R^{15'}$, R^{16}, and $R^{16'}$ are independently chosen from hydrogen, hydroxy, and halogen. In some examples of Formula XV, R^{14}, $R^{14'}$, R^{15}, $R^{15'}$, R^{16}, and $R^{16'}$ are the same. In some examples of Formula XV, R^{14}, $R^{14'}$, R^{15}, $R^{15'}$, R^{16}, and $R^{16'}$ are all hydrogen.

In some examples of Formula XV, R^{17} and $R^{17'}$ are individually chosen from hydrogen, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula XV, R^{17} and $R^{17'}$ are individually chosen from hydrogen, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula XV, R^{17} and $R^{17'}$ are independently substituted or unsubstituted alkylaryl. In certain examples of Formula XV, R^{17} and $R^{17'}$ are independently substituted or unsubstituted aryl.

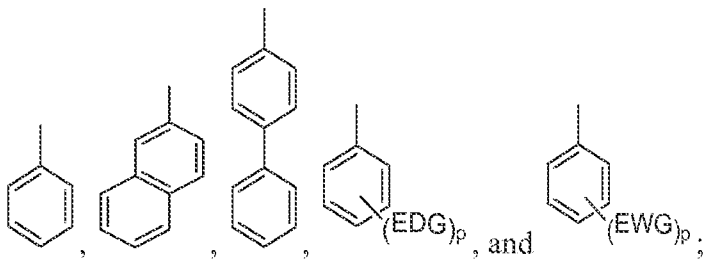
In some examples of Formula XV, R^{17} and $R^{17'}$ are independently chosen from the moieties shown below



wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5. In certain examples of Formula XV, R^{17} and $R^{17'}$ are independently substituted or unsubstituted phenyl.

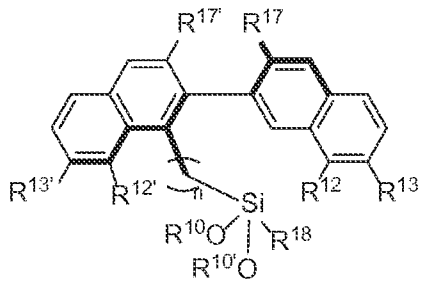
In some examples of Formula XV, R^{18} is chosen from substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula XV, R^{18} is chosen from substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula XV, R^{18} is substituted or unsubstituted alkylaryl. In certain examples of Formula XV, R^{18} is substituted or unsubstituted aryl.

In some examples of Formula XV, R^{18} is chosen from the moieties shown below



wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5. In certain examples of Formula XV, R^{18} is substituted or unsubstituted phenyl.

In some examples of Formula XV, the compound can be defined by Formula XVa:



XVa

wherein

n = 0 or 1;

R^{10} and $R^{10'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl;

R^{12}, R^{13}, R^{17}, $R^{12'}$, $R^{13'}$, and $R^{17'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl, or wherein, as valence and stability permit, independently R^{12} and R^{13}, or $R^{12'}$ and $R^{13'}$, together with the atoms to which they are attached, form a 3-10 membered substituted or unsubstituted cyclic moiety optionally including between 1 and 3 heteroatoms; and

R^{18} is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

In some examples of Formula XVa, n is 0. In some examples of Formula XVa, n is 1.

In some examples of Formula XVa, R^{10} and $R^{10'}$ are the same. In some examples of Formula XVa, R^{10} and $R^{10'}$ are both hydrogen or $-CH_3$. In some examples of Formula XVa, R^{10} and $R^{10'}$ are both hydrogen. In some examples of Formula XVa, R^{10} and $R^{10'}$ are both $-CH_3$.

In some examples of Formula XVa, R^{12} and $R^{12'}$ are independently chosen from hydrogen, hydroxy, and halogen. In some examples of Formula XVa, R^{12} is hydrogen. In some examples of Formula XVa, $R^{12'}$ is hydrogen. In some examples of Formula XVa, R^{12} and $R^{12'}$ are the same. In some examples of Formula XVa, R^{12} and $R^{12'}$ are both hydrogen.

In some examples of Formula XVa, R^{13} and $R^{13'}$ are independently chosen from hydrogen, hydroxy, and halogen. In some examples of Formula XVa, R^{13} is hydrogen. In some examples of Formula XVa, $R^{13'}$ is hydrogen. In some examples of Formula XVa, R^{13} and $R^{13'}$ are the same. In some examples of Formula XVa, R^{13} and $R^{13'}$ are both hydrogen.

In some examples of Formula XVa, R^{12}, $R^{12'}$, R^{13} and $R^{13'}$ are independently chosen from hydrogen, hydroxy, and halogen. In some examples of Formula XVa, R^{12}, $R^{12'}$, R^{13} and $R^{13'}$ are the same. In some examples of Formula XVa, R^{12}, $R^{12'}$, R^{13} and $R^{13'}$ are all hydrogen.

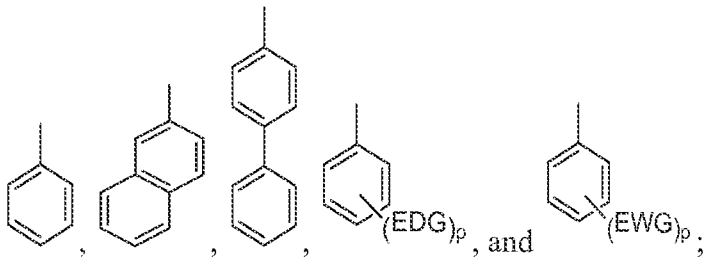
In some examples of Formula XVa, R^{12} and R^{13} together with the atoms to which they are attached, form a 3-10 membered substituted or unsubstituted cyclic moiety optionally including between 1 and 3 heteroatoms. In some examples of Formula XVa, R^{12} and R^{13} together with the atoms to which they are attached, form a 5-7 membered substituted or unsubstituted cyclic moiety optionally including between 1 and 3 heteroatoms. In some examples of Formula XVa, R^{12} and R^{13} together with the atoms to which they are attached, form a 5-7 membered substituted or unsubstituted cyclic moiety. In some examples of Formula XVa, R^{12} and R^{13} together with the atoms to which they are attached, form a 6 membered substituted or unsubstituted cyclic moiety. In some examples of Formula XVa, R^{12} and R^{13} together with the atoms to which they are attached, form a substituted or unsubstituted phenyl moiety.

In some examples of Formula XVa, $R^{12'}$ and $R^{13'}$ together with the atoms to which they are attached, form a 3-10 membered substituted or unsubstituted cyclic moiety optionally including between 1 and 3 heteroatoms. In some examples of Formula XVa, $R^{12'}$ and $R^{13'}$ together with the atoms to which they are attached, form a 5-7 membered substituted or unsubstituted cyclic moiety optionally including between 1 and 3 heteroatoms. In some examples of Formula XVa, $R^{12'}$ and $R^{13'}$ together with the atoms to which they are attached, form a 5-7 membered substituted or unsubstituted cyclic moiety. In some examples of Formula XVa, $R^{12'}$ and $R^{13'}$ together with the atoms to which they are attached, form a 6 membered substituted or unsubstituted cyclic moiety. In some examples of Formula XVa, $R^{12'}$ and $R^{13'}$ together with the atoms to which they are attached, form a substituted or unsubstituted phenyl moiety.

In some examples of Formula XVa, R^{17} and $R^{17'}$ are individually chosen from hydrogen, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula XVa, R^{17} and $R^{17'}$ are individually chosen from hydrogen, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain

examples of Formula XVa, R^{17} and $R^{17'}$ are independently substituted or unsubstituted alkylaryl. In certain examples of Formula XVa, R^{17} and $R^{17'}$ are independently substituted or unsubstituted aryl.

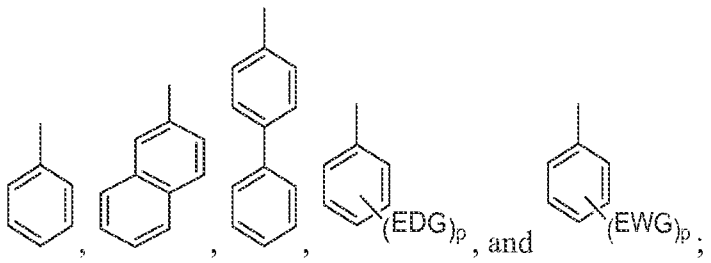
In some examples of Formula XVa, R^{17} and $R^{17'}$ are independently chosen from the moieties shown below



wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5. In certain examples of Formula XVa, R^{17} and $R^{17'}$ are independently substituted or unsubstituted phenyl.

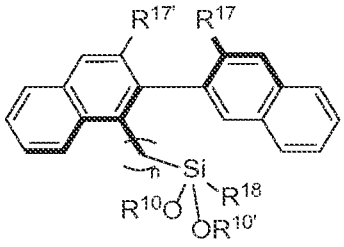
In some examples of Formula XVa, R^{18} is chosen from substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula XVa, R^{18} is chosen from substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula XVa, R^{18} is substituted or unsubstituted alkylaryl. In certain examples of Formula XVa, R^{18} is substituted or unsubstituted aryl.

In some examples of Formula XVa, R^{18} is chosen from the moieties shown below



wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5. In certain examples of Formula XVa, R^{18} is substituted or unsubstituted phenyl.

In some examples of Formula XVa, the compound can be defined by Formula XVb:



XVb

wherein

n = 0 or 1;

R^{10} and $R^{10'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl;

R^{17} and $R^{17'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

R^{18} is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

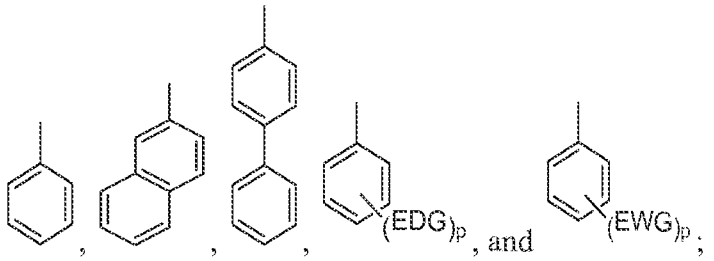
In some examples of Formula XVb, n is 0. In some examples of Formula XVb, n is 1.

In some examples of Formula XVb, R^{10} and $R^{10'}$ are the same. In some examples of Formula XVb, R^{10} and $R^{10'}$ are both hydrogen or $-CH_3$. In some examples of Formula XVb, R^{10} and $R^{10'}$ are both hydrogen. In some examples of Formula XVb, R^{10} and $R^{10'}$ are both $-CH_3$.

In some examples of Formula XVb, R^{17} and $R^{17'}$ are individually chosen from hydrogen, substituted or unsubstituted cycloalkyl, substituted or unsubstituted

alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula XVb, R^{17} and $R^{17'}$ are individually chosen from hydrogen, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula XVb, R^{17} and $R^{17'}$ are independently substituted or unsubstituted alkylaryl. In certain examples of Formula XVb, R^{17} and $R^{17'}$ are independently substituted or unsubstituted aryl.

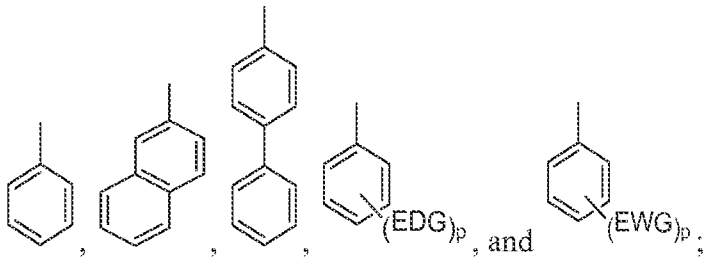
In some examples of Formula XVb, R^{17} and $R^{17'}$ are independently chosen from the moieties shown below



wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5. In certain examples of Formula XVb, R^{17} and $R^{17'}$ are independently substituted or unsubstituted phenyl.

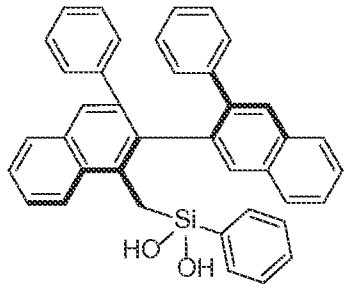
In some examples of Formula XVb, R^{18} is chosen from substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula XVb, R^{18} is chosen from substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula XVb, R^{18} is substituted or unsubstituted alkylaryl. In certain examples of Formula XVb, R^{18} is substituted or unsubstituted aryl.

In some examples of Formula XVb, R^{18} is chosen from the moieties shown below



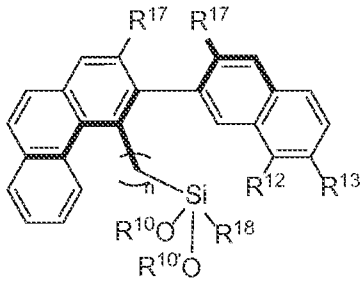
wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5. In certain examples of Formula XVb, R^{18} is substituted or unsubstituted phenyl.

In some examples of Formula XVb, the compound can be defined by the formula:



.

In some examples of Formula XVa, the compound can be defined by Formula XVc:



XVc

wherein

n = 0 or 1;

R^{10} and $R^{10'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl;

R^{12}, R^{13}, R^{17}, and $R^{17'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl, or wherein, as valence and stability permit, R^{12} and R^{13}, together with the atoms to which they are attached, form a 3-10 membered substituted or unsubstituted cyclic moiety optionally including between 1 and 3 heteroatoms; and

R^{18} is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

In some examples of Formula XVc, n is 0. In some examples of Formula XVc, n is 1.

In some examples of Formula XVc, R^{10} and $R^{10'}$ are the same. In some examples of Formula XVc, R^{10} and $R^{10'}$ are both hydrogen or $-CH_3$. In some examples of Formula XVc, R^{10} and $R^{10'}$ are both hydrogen. In some examples of Formula XVc, R^{10} and $R^{10'}$ are both $-CH_3$.

In some examples of Formula XVc, R^{12} is chosen from hydrogen, hydroxy, and halogen. In some examples of Formula XVc, R^{12} is hydrogen.

In some examples of Formula XVc, R^{13} is chosen from hydrogen, hydroxy, and halogen. In some examples of Formula XVc, R^{13} is hydrogen.

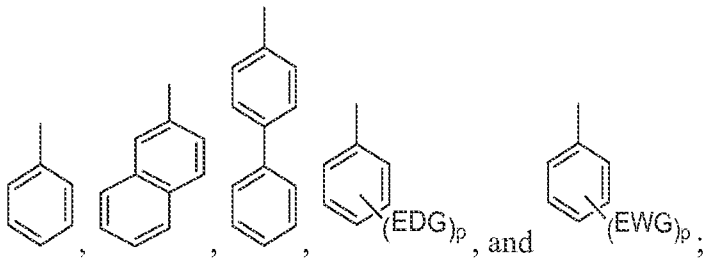
In some examples of Formula XVc, R^{12} and R^{13} are independently chosen from hydrogen, hydroxy, and halogen. In some examples of Formula XVc, R^{12} and R^{13} are the same. In some examples of Formula XVc, R^{12} and R^{13} are both hydrogen.

In some examples of Formula XVc, R^{12} and R^{13} together with the atoms to which they are attached, form a 3-10 membered substituted or unsubstituted cyclic moiety optionally including between 1 and 3 heteroatoms. In some examples of Formula XVc, R^{12} and R^{13} together with the atoms to which they are attached, form a 5-7 membered substituted or unsubstituted cyclic moiety optionally including between 1 and 3 heteroatoms. In some examples of Formula XVc, R^{12} and R^{13} together with the atoms to which they are attached, form a 5-7 membered substituted or unsubstituted cyclic moiety. In some examples of Formula XVc, R^{12} and R^{13} together with the atoms to which they are attached, form a 6 membered substituted or unsubstituted cyclic moiety. In some examples of Formula XVc, R^{12} and R^{13} together with the atoms to which they are attached, form a substituted or unsubstituted phenyl moiety.

In some examples of Formula XVc, R^{17} and $R^{17'}$ are individually chosen from hydrogen, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted

alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula XVc, R^{17} and $R^{17'}$ are individually chosen from hydrogen, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula XVc, R^{17} and $R^{17'}$ are independently substituted or unsubstituted alkylaryl. In certain examples of Formula XVc, R^{17} and $R^{17'}$ are independently substituted or unsubstituted aryl.

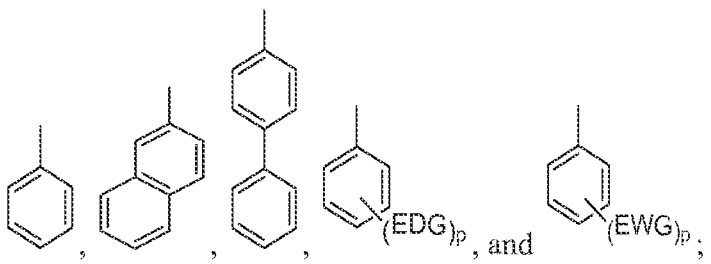
In some examples of Formula XVc, R^{17} and $R^{17'}$ are independently chosen from the moieties shown below



wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5. In certain examples of Formula XVc, R^{17} and $R^{17'}$ are independently substituted or unsubstituted phenyl.

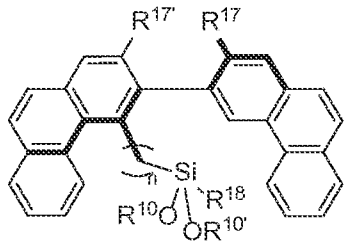
In some examples of Formula XVc, R^{18} is chosen from substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula XVc, R^{18} is chosen from substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula XVc, R^{18} is substituted or unsubstituted alkylaryl. In certain examples of Formula XVc, R^{18} is substituted or unsubstituted aryl.

In some examples of Formula XVc, R^{18} is chosen from the moieties shown below



wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5. In certain examples of Formula XVc, R^{18} is substituted or unsubstituted phenyl.

In some examples of Formula XVc, the compound can be defined by Formula XVd:



XVd

wherein

n = 0 or 1;

R^{10} and $R^{10'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl;

R^{17} and $R^{17'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

R^{18} is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

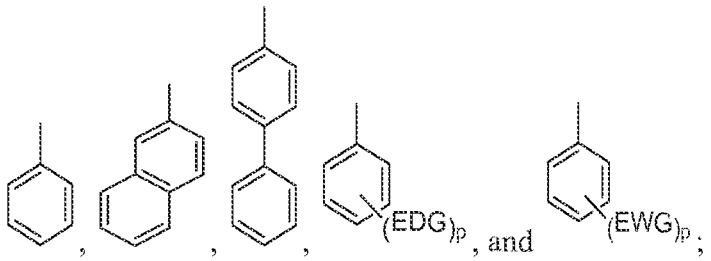
In some examples of Formula XVd, n is 0. In some examples of Formula XVd, n is 1.

In some examples of Formula XVd, R^{10} and $R^{10'}$ are the same. In some examples of Formula XVd, R^{10} and $R^{10'}$ are both hydrogen or $-CH_3$. In some examples of Formula

XVd, R^{10} and $R^{10'}$ are both hydrogen. In some examples of Formula XVd, R^{10} and $R^{10'}$ are both $-CH_3$.

In some examples of Formula XVd, R^{17} and $R^{17'}$ are individually chosen from hydrogen, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula XVd, R^{17} and $R^{17'}$ are individually chosen from hydrogen, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula XVd, R^{17} and $R^{17'}$ are independently substituted or unsubstituted alkylaryl. In certain examples of Formula XVd, R^{17} and $R^{17'}$ are independently substituted or unsubstituted aryl.

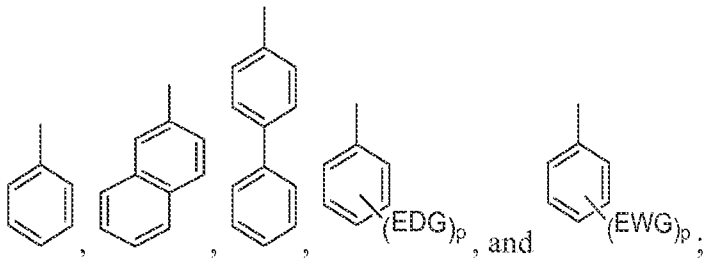
In some examples of Formula XVd, R^{17} and $R^{17'}$ are independently chosen from the moieties shown below



wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5. In certain examples of Formula XVd, R^{17} and $R^{17'}$ are independently substituted or unsubstituted phenyl.

In some examples of Formula XVd, R^{18} is chosen from substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In some examples of Formula XVd, R^{18} is chosen from substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl. In certain examples of Formula XVd, R^{18} is substituted or unsubstituted alkylaryl. In certain examples of Formula XVd, R^{18} is substituted or unsubstituted aryl.

In some examples of Formula XVd, R^{18} is chosen from the moieties shown below



wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5. In certain examples of Formula XVd, R^{18} is substituted or unsubstituted phenyl.

Methods of Making

The silane compounds described herein can be prepared using synthetic methodologies that involve chemical reactions known to one skilled in the art of organic synthesis or variations thereon as appreciated by those skilled in the art. The silane compounds can be prepared from readily available starting materials. Optimum reaction conditions can vary with the particular reactants or solvents used, but such conditions can be determined by one skilled in the art.

Variations on the compounds discussed herein include the addition, subtraction, or movement of the various constituents as described for each compound. Similarly, when one or more chiral centers are present in a molecule, the chirality of the molecule can be changed. Additionally, compound synthesis can involve the protection and deprotection of various chemical groups. The use of protection and deprotection, and the selection of appropriate protecting groups can be determined by one skilled in the art. The chemistry of protecting groups can be found, for example, in Wuts and Greene, *Protective Groups in Organic Synthesis*, 4th Ed., Wiley & Sons, 2006, which is incorporated herein by reference in its entirety.

The starting materials and reagents used in preparing the disclosed compounds and compositions are either available from commercial suppliers such as Aldrich Chemical Co., (Milwaukee, WI), Acros Organics (Morris Plains, NJ), Fisher Scientific (Pittsburgh, PA), Sigma (St. Louis, MO), Pfizer (New York, NY), GlaxoSmithKline (Raleigh, NC), Merck (Whitehouse Station, NJ), Johnson & Johnson (New Brunswick, NJ), Aventis (Bridgewater, NJ), AstraZeneca (Wilmington, DE), Novartis (Basel, Switzerland), Wyeth (Madison, NJ), Bristol-Myers-Squibb (New York, NY), Roche (Basel, Switzerland), Lilly (Indianapolis, IN), Abbott (Abbott Park, IL), Schering Plough (Kenilworth, NJ), or Boehringer Ingelheim (Ingelheim, Germany), or are prepared by methods known to those skilled in the art using

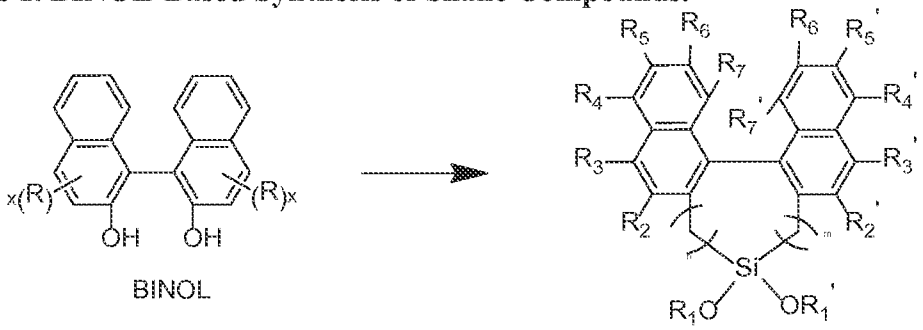
procedures set forth in references such as Fieser and Fieser's Reagents for Organic Synthesis, Volumes 1-17 (John Wiley and Sons, 1991); Rodd's Chemistry of Carbon Compounds, Volumes 1-5 and Supplementals (Elsevier Science Publishers, 1989); Organic Reactions, Volumes 1-40 (John Wiley and Sons, 1991); March's Advanced Organic Chemistry, (John Wiley and Sons, 4th Edition); and Larock's Comprehensive Organic Transformations (VCH Publishers Inc., 1989).

Reactions to produce the compounds described herein can be carried out in solvents, which can be selected by one of skill in the art of organic synthesis. Solvents can be substantially nonreactive with the starting materials (reactants), the intermediates, or products under the conditions at which the reactions are carried out (e.g., temperature and pressure). Reactions can be carried out in one solvent or a mixture of more than one solvent.

Product or intermediate formation can be monitored according to any suitable method known in the art. For example, product formation can be monitored by spectroscopic means, such as nuclear magnetic resonance spectroscopy (e.g., ^{1}H NMR and/or ^{13}C NMR), infrared spectroscopy (e.g., FT-IR spectroscopy), spectrophotometry (e.g., UV-visible spectrometry), mass spectrometry, and/or by chromatography such as high performance liquid chromatography (HPLC) or thin layer chromatography.

By way of example, silane compounds can be prepared from 1,1'-Bi-2-naphthol (BINOL) or derivatives thereof, as generally illustrated in Scheme 1.

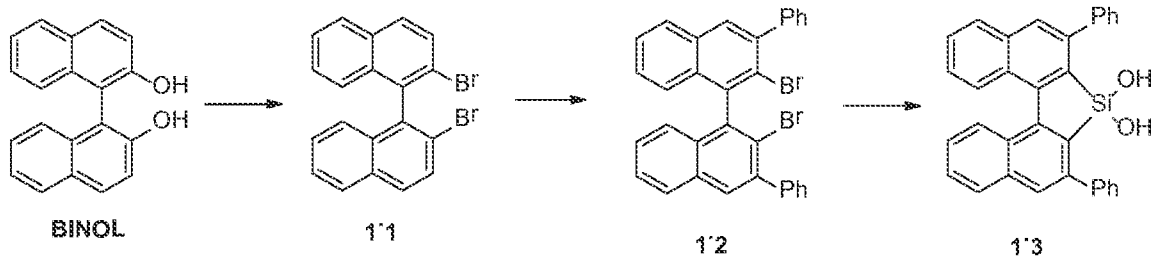
Scheme 1. BINOL-Based Synthesis of Silane Compounds.



Example silane compounds wherein n=m=0 can be prepared using the methodology described in Scheme 2. Starting from BINOL, halogenation using methods known in the art (*see*, for example, Takaya H et al., *Org. Syn.* **1989**, *67*, 20–32) can afford compound 1.1 (dibromobinaphthalene). Compound 1.1 can then be converted to compound 1.2 by treatment with lithium tetramethylpiperidide (LiTMP) and trimethylsilyl chloride (TMSCl), followed by reaction with ICl to form an aryl iodide intermediate, followed by palladium-

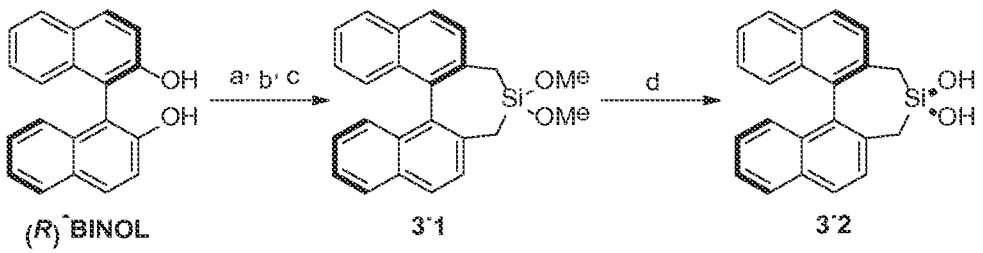
catalyzed cross-coupling of the aryl iodide intermediate with phenyl boronic acid. Finally, silacyclization of 1.2 can be accomplished, for example, by lithium halogen exchange (e.g., effected with *n*-BuLi) followed by treatment with silicon tetrachloride to generate a dichlorosilane intermediate *in situ*. The dichlorosilane intermediate can then be hydrolyzed (e.g., by subjection to ether and water) to afford compound 1.3.

Scheme 2. Synthetic Route to Example Silane Compounds Including 5-Membered Silacycles.



Compounds containing 7-membered silacyclic silanediols can also be prepared from BINOL using methods known in the art. An example strategy for preparing silane compounds wherein n=m=1 is illustrated in Scheme 3. BINOL (e.g., (*R*)-BINOL) can be triflated (e.g., by treatment with Tf_2O). Subsequently, a nickel-catalyzed Kumada cross-coupling with MeMgBr can afford provide (*R*)-2,2'-dimethyl-1,1'-binaphthlene. Deprotonation of both benzylic methyl groups with *n*-BuLi/TMEDA, followed by quenching with $Si(OMe)_4$, can afford silane compound 3.1. Subsequent hydrolysis with dilute HCl can afford silane compound 3.2.

Scheme 3. Synthetic Route to Example Silane Compounds Including 7-Membered Silacycles.

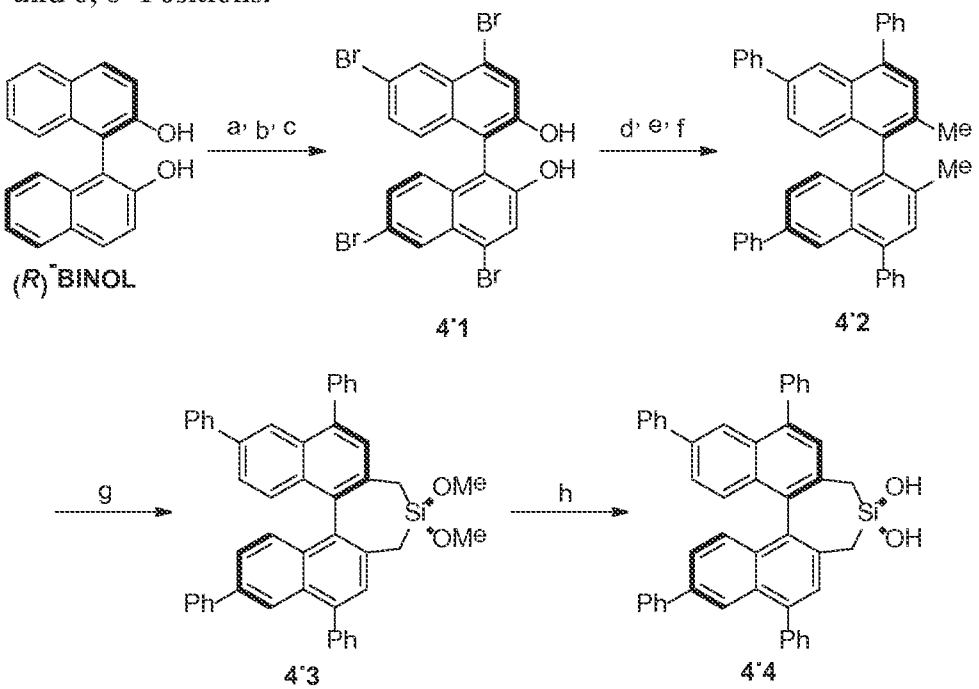


(a) Tf_2O, NEt_3, CH_2Cl_2, −78°C; (b) $NiCl_2$(dppp), MeMgBr, Et_2O; (c) *n*-BuLi, TMEDA, Et_2O, then $Si(OMe)_4$, 0 °C; (d) 1 M HCl (aq.), Me_2CO, 0°C.

Silane compounds containing a variety of substituents at various positions on the binaphthyl back bone can be prepared using modified versions of the methodologies

outlined above. For example, silane compounds including substituents at both the 4, 4' and 6, 6' positions can be prepared using the methods outlined in Scheme 4. Drawing from established protocols (*see*, for example, Hu QS et al., *J. Org. Chem.* **1999**, *64*, 7528–7536), (*R*)-BINOL can be bis-*O*-hexylated, followed by four-fold bromination and dealkylation with BBr_3 to afford compound 4.1. Suzuki-Miyaura cross-coupling with $PhB(OH)_2$, subsequent triflation of the free alcohols, and Nickel-catalyzed Kumada cross-coupling with MeMgBr can provides compound 4.2. Silacyclization can then be performed as described above to prepare the silane compounds. Briefly, deprotonation of both benzylic methyl groups with *n*-BuLi/TMEDA, followed by quenching with $Si(OMe)_4$, can afford silane compound 4.1. Subsequent hydrolysis with dilute HCl can afford silane compound 4.2.

Scheme 4. Synthetic Route to Example Silane Compounds Including Substituents at the 4, 4' and 6, 6' Positions.

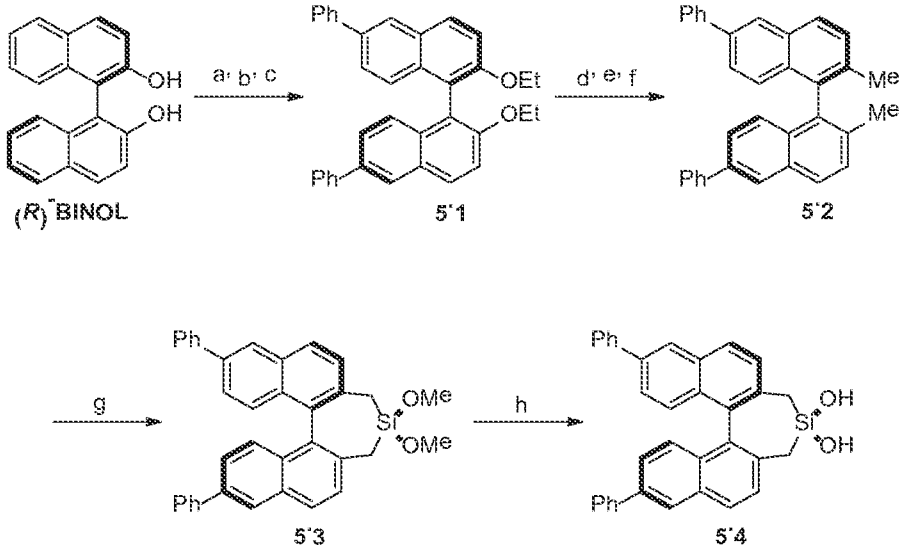


(a) *n*-$C_6H_{13}Br$, K_2CO_3, MeCN, Δ; (b) Br_2, AcOH; (c) BBr_3, CH_2Cl_2, −78 °C to r.t.; (d) $PhB(OH)_2$, $Pd(PPh_3)_4$, K_2CO_3, THF/H_2O, Δ; (e) Tf_2O, NEt_3, CH_2Cl_2, −78 °C to r.t.; (f) $NiCl_2$(dppp), MeMgBr, Et_2O, Δ; (g) *n*-BuLi, TMEDA, Et_2O, then $Si(OMe)_4$, 0 °C to r.t.; (h) 1 M HCl (aq.), Me_2CO, 0 °C.

By way of example, 6,6'-diphenyl substituted silane compounds can be prepared using a procedure similar to the procedure outlined for preparation of the 4, 4', 6, 6' tetrasubstituted compounds. An example methodology is outlined in Scheme 5. The methodology can involve a regio-controlled dibromination of a bis-ethylated (*R*)-BINOL

intermediate at the 6 and 6' positions, followed by a Suzuki-Miyaura cross-coupling proceeding dealkylation to affix substituents at the 6 and 6' positions.

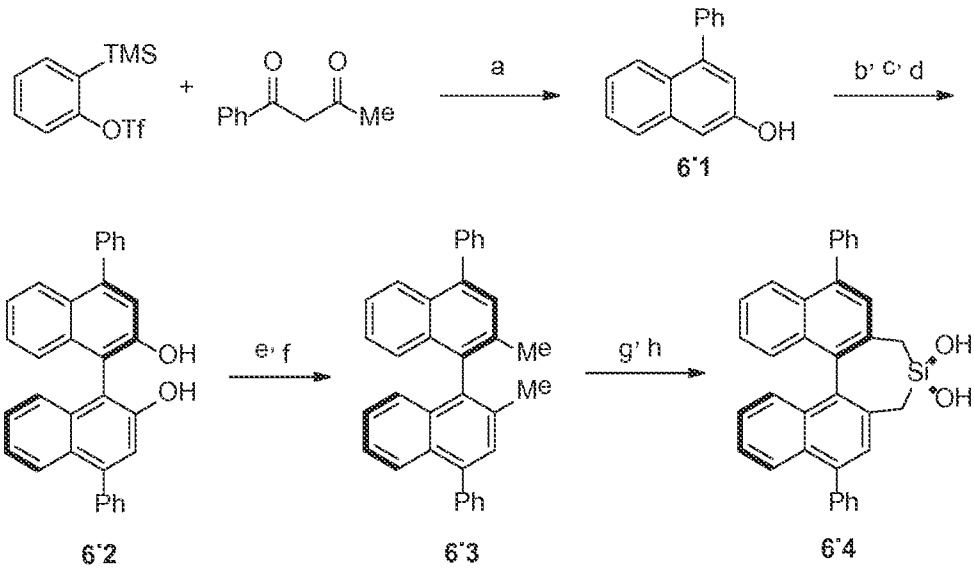
Scheme 5. Synthetic Route to Example Silane Compounds Including Substituents at the 6 and 6' Positions.



(a) C_2H_5Br, K_2CO_3, MeCN, Δ; (b) Br_2, CH_2Cl_2, 0 °C to r.t.; (c) $PhB(OH)_2$, $Pd(PPh_3)_4$, K_2CO_3, THF/H_2O, Δ; (d) BBr_3, CH_2Cl_2, −78 °C to r.t.; (e) Tf_2O, NEt_3, CH_2Cl_2, −78 °C to r.t.; (f) $NiCl_2$(dppp), MeMgBr, Et_2O, Δ; (g) *n*-BuLi, TMEDA, Et_2O, then $Si(OMe)_4$, 0 °C to r.t.; (h) 1 M HCl (aq.), Me_2CO, 0 °C.

By way of example, 4,4'-diphenyl substituted silane compounds can be prepared using the synthetic methodology outlined in Scheme 6. Using known methods (*see*, for example, Okuma K et al., *Chem. Commun.* **2012**, *48*, 11145–11147), 2-(trimethylsilyl)phenyltriflate can be reacted with benzoylacetone in the presence of CsF to afford 4-phenyl-2-naphthol (compound 6.1). Oxidative coupling with CuTMEDA, followed by resolution with *S*-(+)-camphorsulfonyl chloride, can provide, after removal of the chiral auxiliary, enantiopure 6.2. As described above, triflation and Nickel-catalyzed Kumada cross-coupling with MeMgBr can afford 6.3; silacycle formation and hydrolysis can afford silane compound 6.4.

Scheme 6. Synthetic Route to Example Silane Compounds Including Substituents at the 4 and 4' Positions.



(a) CsF, MeCN; (b) CuTMEDA, CH_2Cl_2, r.t.; (c) *S*-(+)-camphorsulfonyl chloride, CH_2Cl_2, r.t.; (d) MeOH, KOH, 60°C, 20 h; (e) Tf_2O, NEt_3, CH_2Cl_2, −78°C to r.t.; (f) $NiCl_2$(dppp), MeMgBr, Et_2O; (g) *n*-BuLi, TMEDA, Et_2O, 0°C to r.t.; (h) 1 M HCl (aq.), Me_2CO, 0°C.

Methods of Use

The silane compounds described herein can be used as enantioselective organocatalysts. Accordingly, also provided are catalyst compositions comprising a silane compound described herein.

For example, the silane compounds described herein can be used to catalyze a nucleophilic conjugate addition reaction, in which a first organic species comprising a nitroalkene reacts with a second organic species comprising a nucleophile to provide a product. The silane compounds described herein can also be used to catalyze an acyl-Mannich type reaction in which a first organic species comprising an amine reacts with a second organic species comprising a carbonyl containing compound to provide a product. The silane compounds described herein can also be used to catalyze an epoxide ring opening reaction, in which a first organic species comprising an epoxide reacts with a second organic species comprising a nucelophile to provide a product. In some examples, the silane compounds described herein can be used to catalyze the sequestration of carbon dioxide, in which a first organic species comprising carbon dioxide reacts with a second organic species comprising a reservoir to provide a product. In some embodiments, the silane compounds described herein can be used to catalyze an enantioselective reaction. In these cases, the first organic species reacts with the second organic species to form a chiral product. The product can preferably be enantioentriched.

Methods of using the silane compounds described herein as catalysts can involve contacting the first organic species and the second organic species with a catalytically effective amount of a silane compound or a catalyst composition comprising a silane compound under conditions effective to form the product.

The silane compounds described herein can also be used as sensors for analytes. Examples of suitable analytes include, for example, anions and chiral compounds. Accordingly, also provided are methods for detecting, identifying, and/or quantifying an analyte in a sample. The methods comprise contacting the sample comprising an analyte with a silane compound described herein; and evaluating an optical property of the silane compound to detect, identify, or quantify the analyte.

By way of example, the silane compounds can exhibit a spectroscopically observable change (e.g., a colorimetric and/or fluorometric response) in the presence of the analyte of interest. In some embodiments, the silane compound can be a luminophore. The spectroscopically observable change can be a change in the absorbance of the silane compound (*i.e.*, color), a change in the fluorescence of the silane compound, a change in the phosphorescence of the silane compound, or a combination thereof.

In these cases, methods for detecting, identifying, and/or quantifying an analyte in a sample can comprise (a) contacting the sample comprising an analyte with a silane compound described herein; and (b) evaluating the optical properties of the silane compound to elucidate the presence of an analyte, to identity an analyte, to determine the concentration of an analyte, or combinations thereof. In certain embodiments, the methods can comprise evaluating the optical properties of the silane compound to determine the concentration of an analyte.

In some cases, one or more spectroscopically observable changes in a silane compound are qualitatively observed to detect the presence of an analyte in a sample. For example, the absorbance of the silane compound (*i.e.*, color) or the fluorescence of the silane compound (under irradiation by, for example a UV blacklight) can be observed by the naked eye to qualitatively assess the presence of an analyte in a sample. In other embodiments, one or more spectroscopically observable changes in a silane compound are measured as part of an assay to quantify the amount of analyte in a sample.

In certain embodiments, the silane compounds can be used in a fluorescence-based assay for the detection and/or quantification of an analyte. Fluorescence assays involve the observation and/or measurement of changes in the fluorescence of a silane compound upon contact with an analyte. The change may take one or more of several forms, including a

change in emission spectra, a change in the intensity of the fluorescence (*i.e.*, fluorescence quantum yield), and a change in the fluorescence lifetime. These changes may be either in the positive or negative direction and may be of a range of magnitudes, which preferably will be detectable as described below.

The emission spectra of a fluorophore sensor can be measured using a spectrofluorometer. The spectrofluorometer uses a high intensity light source with a particular wavelength (or interval of wavelengths) to excite the fluorophore. The spectrofluorometer then measures the intensity of light emitted by the fluorophore at a range of different wavelengths, called an emission spectra. Changes in the maximum emission wavelength or the shape of the emission spectra that are caused by an analyte of interest in a sample may be used to determine the presence or concentration of the analyte of interest in the sample.

In embodiments where an analyte is detected or quantified by measuring the change in the maximum emission wavelength of the silane compound, the silane compound can be designed to exhibit a large change in maximum emission wavelength upon exposure to the analyte of interest. In some embodiments, the maximum emission wavelength of the silane compound shifts by more than 50 nm, more preferably by more than 75 nm, most preferably by more than 100 nm upon exposure to the analyte of interest.

Changes in the maximum emission wavelength can also be observed with the naked eye, for example with the use of a handheld blacklight, to qualitatively determine the presence of the analyte of interest in a sample.

The fluorescence quantum yield of a silane compound can be measured using methods known in the art. *See*, for example, Lakowicz, J. R. "Principles of Fluorescence Spectroscopy", 2nd Ed., Plenum Press, New York, 1999. Generally, the fluorescence quantum yield of the silane compound is obtained by comparison of the integrated area of the corrected emission spectrum of the sensor with that of a reference solution.

A change in the fluorescence quantum yield of the silane compound upon exposure to an analyte of interest may be used as the basis for detecting the presence of the analyte of interest in a sample, and may optionally be used to determine the concentration of the analyte of interest in a sample.

In some embodiments, the silane compound will preferably be selected so as to exhibit a large change in fluorescence quantum yield upon exposure to the analyte of interest. In some embodiments, exposure of the silane compound to the analyte of interest results in at least a 10% reduction in the fluorescence quantum yield of the silane compound

(e.g., at least a 25% reduction in the fluorescence quantum yield of the silane compound, at least a 50% reduction in the fluorescence quantum yield of the silane compound, at least a 75% reduction in the fluorescence quantum yield of the silane compound, or at least a 90% reduction in the fluorescence quantum yield of the silane compound).

In other embodiments, exposure of the silane compound to the analyte of interest can result in at least a 25% increase in the fluorescence quantum yield of the silane compound (e.g., at least a 50% increase in the fluorescence quantum yield of the silane compound, at least a 75% increase in the fluorescence quantum yield of the silane compound, at least a 100% increase in the fluorescence quantum yield of the silane compound, at least a 500% increase in the fluorescence quantum yield of the silane compound, or at least a 1000% increase in the fluorescence quantum yield of the silane compound).

The fluorescence lifetime of a silane compound can also be measured using methods known in the art. Changes in the fluorescence lifetime of a silane compound upon exposure to an analyte can also be used to determine the presence or concentration of an analyte in the sample.

EXAMPLES

The following examples are set forth below to illustrate the methods and results according to the disclosed subject matter. These examples are not intended to be inclusive of all aspects of the subject matter disclosed herein, but rather to illustrate representative methods and results. These examples are not intended to exclude equivalents and variations of the present invention which are apparent to one skilled in the art.

Efforts have been made to ensure accuracy with respect to numbers (*e.g.*, amounts, temperature, etc.) but some errors and deviations should be accounted for. Unless indicated otherwise, parts are parts by weight based on the total weight of the composition in which the component is present, temperature is in °C or is at ambient temperature, and pressure is at or near atmospheric. There are numerous variations and combinations of reaction conditions (e.g., component concentrations, temperatures, pressures and other reaction ranges and conditions) that can be used to optimize the product purity and yield obtained from the described process.

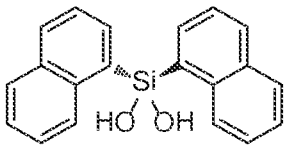
Example 1. Chiral Silanediols in Anion-Binding Catalysis

Background

Hydrogen bond donor (HBD) catalysis is evolving as a powerful direction in organic catalysis. Two avenues through which HBD organocatalysts are proposed to operate include the more traditional hydrogen-bonding activation of appropriate functional groups found on electrophiles, and the more recently introduced ion-pairing catalysis. Herein, halide-binding is discussed as a promising new direction for enantioselective silanediol catalysis.

Materials and Methods

General Methods: Diethyl ether, tetrahydrofuran, methylene chloride, and toluene were purified by passage through a bed of activated alumina (Pangborn AB et al., *Organometallics* **1996**, *15*, 1518–1520). $CHCl_3$ was purchased from Aldrich and used as received. Methanol was freshly distilled from CaH_2. Purification of reaction products was carried out by flash chromatography using Sigma-Aldrich 60 Å silica gel (40- 63 μm). Analytical thin layer chromatography was performed on EMD Chemicals 0.25 μm silica gel 60-F254 plates. Visualization was accomplished with UV light and ceric ammonium molybdate stain followed by heating. Melting points (mp) were obtained on a Fisher Scientific Mel-Temp apparatus and are uncorrected. Infrared spectra (IR) were obtained on a Perkin Elmer Spectrum 100R spectrophotometer. Infrared spectra for liquid products were obtained as a thin film on a NaCl disk, and spectra for solid products were collected by preparing a KBr pellet containing the title compound. Proton nuclear magnetic resonances (^{1}H NMR) were recorded in deuterated solvents on a Bruker Avance DPX 400 (400 MHz) spectrometer. Chemical shifts are reported in parts per million (ppm, δ) using the solvent as internal standard ($CHCl_3$, δ 7.26 and DMSO, δ 2.50). ^{1}H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), or quartet (q). Splitting patterns that could not be interpreted or easily visualized are designated as multiplet (m) or broad (br). Coupling constants are reported in Hertz (Hz). Proton-decoupled carbon (^{13}C NMR) spectra were recorded on a Bruker Avance DPX 400 (100 MHz) spectrometer and are reported in ppm using the solvent as an internal standard ($CHCl_3$, δ 77.0; DMSO, δ 39.5). Electrospray mass spectra (ESI-MS) were obtained using a Bruker MicrOTOF Mass Spectrometer. Unless otherwise noted, all other commercially available reagents and solvents were used without further purification. HPLC analyses were obtained on a Perkin Elmer Series 200 HPLC with multiple wavelength detector.



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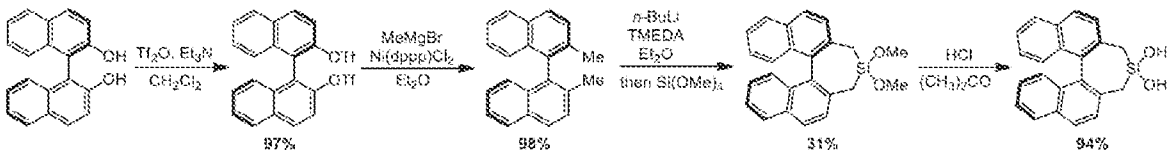
Preparation of 1: A 250 mL round bottom flask was equipped with a stir bar, flame dried, and placed under N_2 atmosphere. A 100 mL pear shape flask was flame dried and placed under N_2 atmosphere. The round bottom flask was charged with freshly distilled 1-bromonaphthalene (3.4 mL, 24.4 mmol) and 100 mL of dry Et_2O. The solution was stirred and cooled to -78°C. The pear shape flask was charged with 20 mL of dry Et_2O and $SiCl_4$ (1.4 mL, 12.2 mmol). A solution of *n*-BuLi in hexanes (1.5 *M*, 17.9 mL, 26.8 mmol) was added to the 1-bromonaphthalene/Et_2O solution dropwise with stirring at -78°C to afford an off white suspension. The cold bath was removed and the mixture was allowed to warm to 23°C over an hour. The mixture was recooled to -78°C and the $SiCl_4/Et_2O$ solution was added dropwise with stirring to afford a clear, light yellow solution. The yellow solution was stirred overnight allowing it to come to 23°C. The mixture was concentrated to afford a yellow oil with a white ppt. About 50 mL of Et_2O and 9 mL of H_2O were added to the oil and this mixture was stirred at 23°C for 2 h. Saturated $NaHCO_3$ (aq) was added to neutralize the mixture to pH 7. This solution was extracted with Et_2O/brine, concentrated, and dried over Na_2SO_4 to afford a light yellow oil which was crystallized from Et_2O/hexanes to afford a white powder which was washed twice with hexanes (2.89 g, 67%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.0 Hz, 2H); 8.00 (dd, *J*= 8.0 Hz, 1.2 Hz, 2H); 7.94 (d, *J* = 8.4 Hz, 2H); 7.86 (dd, *J* = 8.4 Hz, 1.2 Hz, 2H); 7.48–7.40 (m, 6H). All spectral data matched that previously reported (Schafer AG et al., *Org. Lett.* **2011**, *13*, 5228–5231).

Scheme 7. Preparation of Binaphthyl-Derived Silanediol



Preparation of Binaphthyl-Derived Silanediol (Scheme 7)

(R)-Trifluoro-methanesulfonic acid 2'-trifluoromethanesulfonyloxy [1,1'] binapthalenyl-2-yl ester: A 500 mL round bottom flask was equipped with a stir bar, flame dried, placed under N_2 atmosphere, charged with R-(+)-BINOL (10.00 g, 35.0 mmol) and CH_2Cl_2 (145 mL), and was cooled to –78°C. Et_3N (12.2 mL, 87.5 mmol, 2.5 equiv) freshly

distilled from CaH_2 was then added dropwise. This mixture was stirred at –78°C for 5 min, and Tf_2O (14.6 mL, 86.8 mmol, 2.5 equiv) was added dropwise at –78°C. This solution was stirred overnight while warming to 23°C. The resulting black solution was then cooled to 0°C, and 10 mL 1 M HCl(aq) was added. The organic layer was separated, and the aqueous layer was extracted 3 times with CH_2Cl_2. The organic layers were combined, washed with saturated $NaHCO_3$ (aq), dried with Na_2SO_4, and concentrated to afford a thick black oil. The oil was passed through a short silica gel plug using 90/10 hexanes/EtOAc as the eluent. The resulting off white solid was recrystallized from 15 mL of hexanes to afford a flaky, white product (18.68 g, 33.9 mmol, 97%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 9.2 Hz, 2H); 8.01 (d, J = 8 Hz, 2H); 7.62 (d, J = 9.2 Hz, 2H); 7.59 (ddd, J = 8.4 Hz, 7.2 Hz, 1.2 Hz, 2H); 7.41 (ddd, J = 8.4 Hz, 7.2 Hz, 1.2 Hz, 2H); 7.25 (d, J = 8.4 Hz, 2H). All spectral data matched that previously reported (Bulman Page PC et al., *Org. Lett.* **2004**, *6*, 1543–1546).

(R)-2,2'-Dimethyl-1,1'-binaphthyl (11): A 250 mL 2-necked round bottom flask was equipped with a stir bar, flame dried, placed under N_2 atmosphere, and charged with (R)-Trifluoromethanesulfonic acid 2'-trifluoromethanesulfonyloxy [1,1']binapthalenyl-2-yl ester (12.83 g, 23.3 mmol). Dry Et_2O (160 mL) was added, followed by Ni(dppp)Cl_2 (631 mg, 1.16 mmol, 0.05 equiv.). The mixture was cooled to 0°C and MeMgBr (36 mL, 3.0 M, 108 mmol, 4.6 equiv) was added dropwise with stirring. The mixture became clear and yellow during the addition, and after complete addition of the MeMgBr, was refluxed overnight. The solution became black, and after complete conversion by TLC, was carefully poured into ice-cooled 1 M HCl(aq). The reaction was filtered through a pad of celite, the layers separated, and the aqueous layer extracted 3 times with Et_2O. The organic layers were combined, dried with Na_2SO_4, and concentrated to afford an off-white oil. The oil was passed through a short silica gel plug using hexanes as the eluent to afford a white powder upon concentration (6.49 g, 22.9 mmol, 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.4 Hz, 2H); 7.88 (d, J = 8 Hz, 2H); 7.51 (d, J = 8.4 Hz, 2H); 7.39 (ddd, J = 8.4 Hz, 7.2 Hz, 1.2 Hz, 2H); 7.21 (ddd, J = 8.4 Hz, 6.9 Hz, 1.3 Hz, 2H); 7.05 (d, J = 8.0 Hz, 2H); 2.04 (s, 6H). All spectral data matched that previously reported (Bulman Page PC et al., *Org. Lett.* **2004**, *6*, 1543–1546).

4,4-dimethoxy-4,5-dihydro-3H-dinaphtho[2,1-c:1',2'-e]silepine (4): Adapting a procedure by Oestreich (Mewald M et al., *Chem. Eur. J.* **2011**, *17*, 9406–9414), a 100 mL round bottom flask was equipped with a large stir bar, flame dried, and placed under N_2 atmosphere. The flask was charged with a solution of *n*-BuLi in hexanes (8.9 mL, 1.2 M,

10.7 mmol, 3.0 equiv) and cooled to 0°C. 11 (990 mg, 3.51 mmol) was added in dry Et_2O (8 mL) dropwise. This solution was stirred at 0°C for 5 min, then N,N,N',N'-tetramethylethylenediamine (TMEDA, 1.6 mL, 10.7 mmol, 3.0 equiv) previously distilled from CaH_2 was added dropwise at 0°C. The resulting yellow solution was allowed to come to 23°C, and was stirred for 24 h after complete addition of TMEDA. The now very dark red *n*-BuLi/TMEDA/binaphthalene mixture was cooled to 0°C, and distilled $Si(OMe)_4$ (2.0 mL, 13.6 mmol, 3.9 equiv) in Et_2O (8 mL) was added dropwise. The mixture was allowed to come to 23°C and stirred overnight to afford an opaque yellow mixture. This mixture was filtered through celite using Et_2O (80 mL) and CH_2Cl_2 (20 mL) to afford a clear, neon green solution. The solution was concentrated, diluted in 5 mL CH_2Cl_2, and quickly run through a short silica gel plug packed with hexanes using 1500 mL of 80/20 hexanes/EtOAc as the eluent. The eluent was concentrated to afford a yellow oil which was placed under an Ar atmosphere. The crude mixture stood undisturbed under Ar for 24 h, during which time clear, colorless crystals formed. After 24 h, the crystals were carefully triturated with 3 x 3 mL portions of hexanes to afford 396 mg of the desired silacycle (1.07 mmol, 31%). After trituration, a small amount of silacycle with an ethoxy group and a methoxy group was left, presumably from the cleavage of Et_2O during the course of the lithiation (Jung ME, Hogan KT, *Tetrahedron Lett.* **1988**, *29*, 6199–6202). This was carried through to the hydrolysis step. R*f* = 0.51 (4:1 hexanes/EtOAc); mp 197–202°C; IR (KBr) 3055, 2936, 2834, 1307, 1185, 1149, 1092 cm-1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.4 Hz, 2H); 7.87 (d, *J* = 8.4 Hz, 2H); 7.47 (d, *J* = 8.4 Hz, 2H); 7.36 (ddd, *J* = 8.0 Hz, 6.8 Hz, 1.2 Hz, 2H); 7.17 (ddd, *J* = 8.0 Hz, 6.8 Hz, 1.2 Hz, 2H); 7.07 (d, *J* = 7.4 Hz, 2 H); 3.50 (s, 6H); 2.22 (d, *J* = 14 Hz, 2 H), 2.08 (d, *J* = 14.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.4, 132.8, 132.7, 131.8, 128.3, 128.1, 128.0, 126.4, 125.9, 124.5, 50.9, 19.9; HRMS (ESI): Mass calculated for $C_{24}H_{22}O_2SiNa$ $[M^+Na]^+$, 393.1281. Found $[M^+Na]^+$, 393.1264. $[\alpha]^{23}_D$ = -195.2 (c 0.985, $CHCl_3$).

3H-dinaphtho[2,1-c:1',2'-e]silepine-4,4(5H)-diol (3): Adapting a procedure by Tacke (Tacke R et al., *Organometallics* **2004**,*23*, 4915–4923), a 250 mL round bottom flask was equipped with a stir bar, placed under N_2 atmosphere, and charged with 4 (378.0 mg, 1.02 mmol). ACS grade acetone (40 mL) was added and the solution was cooled to 0°C. Freshly prepared 1 M HCl (aq) (10 mL) was added to the solution dropwise at 0°C. The solution was stirred at 0°C until TLC showed complete consumption of starting material, generally within 1–2 h. Et_2O (50 mL) was added at 0°C, followed by saturated $NaHCO_3$ slowly until pH 7 was achieved. The mixture was shaken vigorously, the layers were

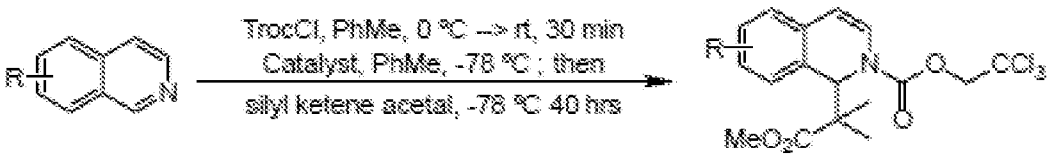
separated, and the aqueous layer extracted 3 times with Et_2O, checking to ensure pH 7 is maintained throughout the extraction. The organic layers were combined, dried with Na_2SO_4, and concentrated to afford a white powder (364 mg, 94%) as a 2:1 complex with Et_2O. This compound was used directly as the Et_2O complex, taking into account the residual solvent when calculating catalyst loadings. R_f = 0.28 (1:1 hexanes/EtOAc), will significantly tail; IR (KBr) 3401, 3051, 2969, 1232, 1143, 912, 822, 837 cm-1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.4 Hz, 4H); 7.47 (d, *J* = 8.4 Hz, 2H); 7.37 (ddd, *J* = 8.4 Hz, 6.8 Hz, 1.2 Hz, 2H); 7.18 (ddd, *J* = 10 Hz, 6.8 Hz, 1.2 Hz, 2H); 7.09 (d, *J* = 7.6 Hz, 2 H); 2.18 (d, *J* = 14 Hz, 2 H), 2.12 (d, *J* = 14.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.5, 132.9, 132.8, 132.0, 128.6, 128.2, 128.0, 126.6, 126.2, 124.8, 23.4; HRMS (ESI): Mass calculated for $C_{22}H_{18}O_2SiNa$ $[M^+Na]^+$, 365.0968. Found $[M^+Na]^+$, 365.0974. $[\alpha]^{24}_D$ = -280.3 (c 0.90, $CHCl_3$).

General Procedure for Titration of Silane Diol 3 and 4 with Tetrabutylammonium Chloride: A solution of *R*-**3** (5.0 x 10-3 *M*) in $CDCl_3$ was prepared in a 2 mL volumetric flask. Portions of TBACl were quantitatively transferred to the flask and ^{1}H NMR spectra of the solutions were recorded after the addition of each equivalent, ensuring that the concentration of *R*-**3** did not change.

Confirmation that the O–H peak was shifting was achieved by washing a solution of *R*-**3** in $CDCl_3$ with D_2O, drying the sample with Na_2SO_4, and recording the NMR spectrum, which lacks the peak at 2.4 ppm. No changes in methylene or aromatic proton resonances were observed during the TBACl titration of **4**.

General Procedure for Silanediol Catalyzed Acyl-Mannich Reactions

Scheme 8. General Procedure for Silanediol Catalyzed Acyl-Mannich Reactions



General Procedure for Table 1

(9a): An oven dried 2-dram vial with screw top cap and septa was equipped with a stir bar and flushed with argon. The vial was sealed and covered further with parafilm. Isoquinoline (11.8 μL, 0.1 mmol, 1.0 equiv) was added via syringe, solvent (2 mL) was added and the solution was cooled to 0 °C. 2,2,2-Trichloroethyl chloroformate (15.0 μL,

0.11 mmol, 1.1 equiv) was added, the ice bath was removed and the solution was warmed to room temperature while stirring for 30 minutes. The cloudy suspension was cooled to –78°C and catalyst (0.02 mmol, 0.2 equiv) was added as a solution in solvent followed by **8-TBS** (33 mg, 0.15 mmols, 1.5 equiv). The reaction vessel was transferred to a –78°C acetone bath equipped with immersion cooling coil and stirred for 40 hours. The reaction was quenched at –78 °C by the addition of NaOMe (0.2 ml, 0.5 M in MeOH, 1.0 equiv) and then warmed to room temperature before filtration through a short silica gel plug with EtOAc as the eluent. Removal of the solvent *in vacuo* and subsequent purification via flash column chromatography on silica gel (0:100 EtOAc:Hexanes to 4:96 EtOAc:Hexanes) yielded the title compound as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): the compound exists as a 3:1 mixture of carbamate rotamers. Signals corresponding to the major rotamer: δ 7.28−7.19 (m, 2H), 7.10−6.95 (m, 2H), 6.96 (d, J = 7.6 Hz, 1H), 5.95 (d, J = 7.6 Hz, 1 H), 5.74 (s, 1H), 4.97 (d, J = 12.0 Hz, 1H), 4.70 (d, J = 12.0 Hz, 1H), 3.64 (s, 3H), 1.20 (s, 3H), 1.12 (s, 3H). Representative signals of the minor rotamer: δ 6.05 (d, J = 7.6 Hz, 1H), 5.79 (s, 1H), 4.86 (s, 2H), 3.61 (s, 3H), 1.29 (s, 3H), 1.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) Signals correspond to major rotamer: δ 175.9, 152.3, 131.3, 128.4, 128.0, 127.2, 125.6, 124.9, 112.0, 95.2, 75.7, 60.9, 52.2, 50.3, 22.6, 21.5. IR (neat) 2991, 2924, 2357, 2343, 1724, 1717, 1627, 1448, 1374, 1322, 1225, 1128, 1046, 941 cm^{-1}; HRMS (ESI): Mass Calculated for $C_{17}H_{18}Cl_3NO_4$ $[M^+Na]^+$, 428.0199. Found $[M^+Na]^+$, 428.0189.

General Procedure for Table 2

(9a) Table 2, entry 1: An oven dried 2-dram vial with screw top cap and septa was equipped with a stir bar and flushed with argon. The vial was sealed and covered further with parafilm. Isoquinoline (11.8 μL, 0.1 mmol, 1.0 equiv) was added via syringe, PhMe (2 mL) was added and the solution was cooled to 0°C. 2,2,2-Trichloroethyl chloroformate (15.0 μL, 0.11 mmol, 1.1 equiv) was added, the ice bath was removed and the solution was warmed to room temperature while stirring for 30 minutes. The cloudy suspension was cooled to –78°C. *R*-(3) (6.8 mg, 0.02 mmol, 0.2 equiv) was added as a solution in PhMe followed by methyl trimethylsilyl dimethylketene acetal 8-TMS (30.5 μL, 0.15 mmols, 1.5 equiv). The reaction vessel was transferred to a –78°C acetone bath equipped with immersion cooling coil and stirred for 40 hours. The reaction was quenched at –78°C by the addition of NaOMe (0.2 ml, 0.5 M in MeOH, 1.0 equiv) and then warmed to room temperature before filtration through a short silica gel plug with EtOAc as the eluent. Removal of the solvent *in vacuo* and subsequent purification via flash column

chromatography on silica gel (0:100 EtOAc:Hexanes to 4:96 EtOAc:Hexanes) yielded the title compound as a colorless oil (32.4 mg, 0.080 mmols, 80% yield). All spectral data matched spectra for 9a as reported above. (R_f = 0.45 in 10:90 EtOAc:Hexanes), enantiomeric excess was found to be 8% by chiral HPLC (Chiralpak OD-H, 1% isopropanol/99% hexane 0.7 mL/min, *tr* (minor): 12.8 min, *tr* (major): 15.7 min.; Figure 1) $[\alpha]^{24}_D$ = –24.5 (c 1.11, $CHCl_3$).

(9a) Table 2, entry 2: The general procedure was repeated with 8-TBS as the nucleophile. All spectral data matched spectra for 9a as reported above. Purification via flash column chromatography on silica gel (0:100 EtOAc:Hexanes to 4:96 EtOAc:Hexanes) yielded the title compound as a colorless oil (28.9 mg, 0.071 mmols, 71% yield) (R_f = 0.45 in 10:90 EtOAc:Hexanes), enantiomeric excess was found to be 18% by chiral HPLC (Chiralpak OD-H, 1% isopropanol/99% hexane 0.7 mL/min, *tr* (minor): 13.3 min, *tr* (major): 16.2 min.; Figure 2) $[\alpha]^{24}_D$ = –57.4 (c 0.63, $CHCl_3$).

(9a) Table 2, entry 3: The general procedure was repeated with 8-TIPS as the nucleophile. All spectral data matched spectra for 9a as reported above. Purification via flash column chromatography on silica gel (0:100 EtOAc:Hexanes to 4:96 EtOAc:Hexanes), subsequent concentration under reduced pressure and filtration through a plug of activity II neutral alumina with CH_2Cl_2 to remove TIPSOH, yielded the title compound as a colorless oil (22.4 mg, 0.055 mmols, 55% yield) (R_f = 0.45 in 10:90 EtOAc:Hexanes), enantiomeric excess was found to be 28% by chiral HPLC (Chiralpak OD-H, 1% isopropanol/99% hexane 0.7 mL/min, *tr* (minor): 12.8 min, *tr* (major): 15.6 min.; Figure 3) $[\alpha]^{24}_D$ = –128.2 (c 0.60, $CHCl_3$).

(9a) Table 2, entry 4: The general procedure was repeated with 8-TIPS as the nucleophile as well as 100 mol% *R*-(3) (34.2 mg, 0.10 mmol). All spectral data matched spectra for 9a as reported above. Purification via flash column chromatography on silica gel (0:100 EtOAc:Hexanes to 4:96 EtOAc:Hexanes), subsequent concentration under reduced pressure and filtration through a plug of activity II neutral alumina with CH_2Cl_2 to remove TIPSOH, yielded the title compound as a colorless oil (30.2 mg, 0.074 mmols, 74% yield) (R_f = 0.45 in 10:90 EtOAc:Hexanes), enantiomeric excess was found to be 28% by chiral HPLC (Chiralpak OD-H, 1% isopropanol/99% hexane 0.7 mL/min, *tr* (minor): 14.1 min, *tr* (major): 17.7 min., Figure 4) $[\alpha]^{24}_D$ = –128.2 (c 1.00, $CHCl_3$).

(9b) Table 2, entry 5: The general procedure was repeated with 8-TIPS as the nucleophile. Purification via flash column chromatography on silica gel (0:100 ethyl acetate:hexanes to 4:96 ethyl acetate hexanes), subsequent concentration under reduced

pressure and filtration through a plug of activity II neutral alumina with CH_2Cl_2 to remove TIPSOH, yielded the title compound as a colorless oil (27.7 mg, 0.057 mmols, 57% yield) (R_f = 0.45 in 10:90 EtOAc:Hexanes), enantiomeric excess was determined to be 26% by chiral HPLC (Chiralpak OD-H, 1% isopropanol/99% hexane 0.7 mL/min, *tr*(minor): 12.5 min, *tr*(major): 18.3 min.; Figure 5) $[\alpha]^{24}_D$ = -54.3° (c 0.96, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): the compound exists as a 3:1 mixture of carbamate rotamers. Signals corresponding to the major rotamer: δ 7.49 (dd, *J* = 7.6 Hz, 1.6 Hz, 1H), 7.10−7.00 (m, 3H), 6.33 (d, *J* = 8.0 Hz, 1H), 5.70 (s, 1H), 4.98 (d, *J* = 12.0 Hz, 1H), 4.71 (d, *J* = 12.0 Hz, 1H), 3.62 (s, 3H), 1.19 (s, 3H), 1.12 (s, 3H). Representative signals of the minor rotamer: δ 6.43 (d, *J* = 12.0 Hz, 1H), 5.74 (s, 1H), 4.86 (s, 2H), 3.60 (s, 3H), 1.28 (s, 3H), 1.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) Signals correspond to major rotamer: δ 175.5, 152.0 132.4, 130.7, 130.0, 127.9, 127.1, 120.4, 110.4, 75.6, 60.9, 52.2, 50.1, 22.7, 21.5. IR (neat) 3110, 2976, 2946, 2357, 2335, 1724, 1627, 1553, 1441 1381, 1322, 1269, 1120, 770, 718 cm^{-1}; HRMS (ESI): Mass Calculated for $C_{17}H_{17}BrCl_3NO_4$ $[M^+Na]^+$, 505.9304. Found $[M^+Na]^+$, 505.9299.

(9b) Table 2, entry 6: The general procedure was repeated with 8-TBS as the nucleophile. All spectral data matched spectra for 9b as reported above. Purification via flash column chromatography on silica gel (0:100 EtOAc:Hexanes to 4:96 EtOAc:Hexanes) yielded the title compound as a colorless oil (32.1 mg, 0.066 mmols, 66% yield) (R_f = 0.45 in 10:90 EtOAc:Hexanes), enantiomeric excess was found to be 18% by chiral HPLC (Chiralpak OD-H, 1% isopropanol/99% hexane 0.7 mL/min, *tr* (minor): 14.5 min, *tr* (major): 22.2 min.; Figure 6) $[\alpha]^{24}_D$ = -44.5 (c 1.85, $CHCl_3$).

(9c) Table 2 entry 7: The general procedure was repeated with 8-TIPS as the nucleophile. Purification via flash column chromatography on silica gel (0:100 ethyl acetate:hexanes to 5:95 ethyl acetate hexanes) yielded the title compound as a colorless oil (26.9 mg, 0.061 mmols, 61% yield) (R_f = 0.45 in 10:90 EtOAc:Hexanes), enantiomeric excess was determined to be 32% by chiral HPLC (Chiralpak OD-H, 1% isopropanol/99% hexane 0.7 mL/min, *tr*(minor): 11.4 min, *tr*(major): 17.0 min.; Figure 7) $[\alpha]^{24}_D$ = –71.3° (c 0.99, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): the compound exists as a 3:1 mixture of carbamate rotamers. Signals corresponding to the major rotamer: δ 7.31 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.13 (t, *J* = 8.0 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.98 (app d, *J* = 8.0 Hz, 1H), 6.35 (d, *J* = 7.6 Hz, 1H), 5.72 (s, 1H), 4.98 (d, *J* = 12.0 Hz,) 4.71 (d, *J* = 12.0 Hz, 1H), 3.63 (s, 3H), 1.20 (s, 3H), 1.12 (s, 3H). Representative signals of the minor rotamer: δ 6.45 (d, *J* = 12.0 Hz, 1H), 5.76 (s, 1H), 4.87 (s, 2H), 3.61 (s, 3H), 1.29 (s, 3H), 1.26 (s, 3H). ^{13}C NMR (100

MHz, $CDCl_3$) Signals correspond to major rotamer: δ 175.5, 152.0, 129.9, 129.1, 127.6, 126.9, 126.4, 125.7, 107.9, 94.9, 75.6, 60.7, 52.1, 50.1, 29.7, 22.6, 21.4. IR (neat) 2984, 2946, 1724, 1627, 1553, 1448, 1381, 1120, 770 cm^{-1}; HRMS (ESI): Mass Calculated for $C_{17}H_{17}Cl_4NO_4$ $[M^+Na]^+$, 461.9809. Found $[M^+Na]^+$, 461.9804.

(9c) Table 2 entry 8: The general procedure was repeated with 8-TBS as the nucleophile. All spectral data matched spectra for 9c as reported above. Purification via flash column chromatography on silica gel (0:100 EtOAc:Hexanes to 4:96 EtOAc:Hexanes) yielded the title compound as a colorless oil (35.2 mg, 0.080 mmols, 80% yield) (R_f = 0.45 in 10:90 EtOAc:Hexanes), enantiomeric excess was found to be 20% by chiral HPLC (Chiralpak OD-H, 1% isopropanol/99% hexane 0.7 mL/min, *tr* (minor): 13.3 min, *tr* (major): 20.5 min.; Figure 8) $[\alpha]^{24}_D$ = –58.1 (c 1.57, $CHCl_3$).

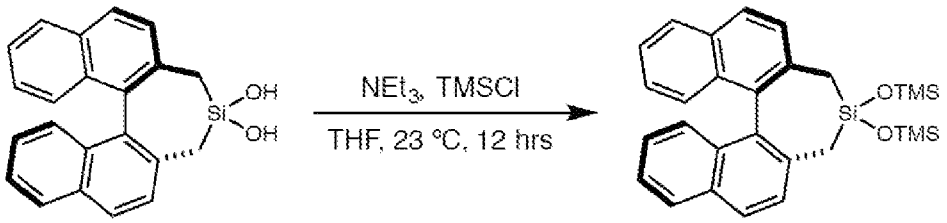
(9d) Table 2 entry 9: The general procedure was repeated with 8-TIPS as the nucleophile. Purification via flash column chromatography on silica gel (0:100 diethyl ether:hexanes to 15:85 diethyl ether:hexanes) yielded the title compound as a bright yellow oil (29.5 mg, 0.065 mmols, 65% yield) (R_f = 0.16 in 20:80 Et_2O:Hexanes), enantiomeric excess was determined to be 17% by chiral HPLC (Chiralpak OD-H, 4% isopropanol/96% hexane 0.7 mL/min, *tr*(major): 15.7 min, *tr*(minor): 22.1 min.; Figure 9) $[\alpha]^{24}_D$ = +26.1 (c 0.91, $CHCl_3$) ^1H NMR (400 MHz, $CDCl_3$): the compound exists as a 4:1 mixture of carbamate rotamers. Signals corresponding to the major rotamer: δ 7.94 (dd, *J* = 7.2, 2.4 Hz, 1H), 7.40−7.30 (m, 2H), 7.18 (d, *J* = 8.0 Hz, 1H), 6.70 (d, *J* = 8.4 Hz, 1H), 5.77 (s, 1H), 5.00 (d, *J* = 11.6 Hz, 1H), 4.73 (d, *J* = 11.6 Hz, 1H), 3.63 (s, 3H), 1.21 (s, 3H), 1.16 (s, 3H). Representative signals of the minor rotamer: δ 6.79 (d, *J* = 8.4 Hz, 1H), 4.88 (s, 2H), 1.29 (s, 3H), 1.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) Signals correspond to major rotamer: δ 175.1, 151.7, 144.8, 132.8, 130.4, 129.5, 126.7, 125.9, 124.8, 105.8, 94.7, 75.7, 60.84, 52.3, 49.9, 22.8, 21.5 IR (neat) 2954, 2924, 2857, 1724, 1627, 1515, 1456, 1381, 1329, 1262, 1120, 897 cm^{-1}; HRMS (ESI): Mass Calculated for $C_{17}H_{17}Cl_4NO_4$ $[M^+Na]^+$, 473.0050. Found $[M^+Na]^+$, 473.0044.

(9d) Table 2 entry 10: The general procedure was repeated with 8-TBS as the nucleophile. All spectral data matched spectra for 9d as reported above. Purification via flash column chromatography on silica gel (0:100 diethyl ether:hexanes to 15:85 diethyl ether:hexanes) yielded the title compound as a colorless oil (32.7 mg, 0.072 mmols, 72% yield) (R_f = 0.45 in 10:90 EtOAc:Hexanes), enantiomeric excess was found to be 50% by chiral HPLC (Chiralpak OD-H, 1% isopropanol/99% hexane 0.7 mL/min, *tr* (major): 16.2 min, *tr* (minor): 23.0 min.; Figure 10) $[\alpha]^{24}_D$ = +70.1 (c 1.60, $CHCl_3$).

Preparation of Racemic Samples for HPLC Analysis: In an oven dried 2-dram vial with stir bar, a solution of the appropriate isoquinoline (0.1 mmol) in 2 mL dichloromethane was prepared and cooled to 0 °C. 2,2,2-Trichloroethyl chloroformate (15.0 µL, 0.11 mmol, 1.1 equiv) was added, the ice bath was removed and the solution was warmed to room temperature while stirring for 30 minutes. The reaction was then cooled to – 78°C and the appropriate silyl ketene acetal (0.15 mmol, 1.5 equiv) was added. The reaction was allowed to warm to room temperature and stir overnight (14–18 hrs). The products were isolated under the same column conditions as their enantioenriched counterparts (see Figure 11, Figure 12, Figure 13, and Figure 14 for racemic samples of 9a, 9b, 9c, and 9d, respectively).

Synthesis of Bis(TMS) Derivative of Silanediol R-3 (3H-dinaphtho[2,1-c:1',2'-e]silepine-4,4(5H)-diol) for HPLC Analysis (Scheme 9)

Scheme 9. Synthesis of Bis(TMS) Derivative of 3H-dinaphtho[2,1-c:1',2'-e]silepine-4,4(5H)-diol for HPLC Analysis

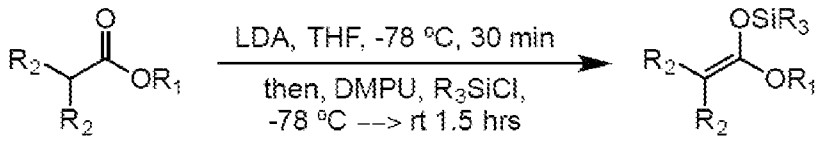


A 25 mL round bottom flask equipped with a Teflon coated magnetic stir bar was flame dried under vacuum and purged with nitrogen gas. The flask was then fitted with a rubber septa and placed under argon atmosphere. The flask was then charged with (*R*)-**3** (27.4 mg, 0.08 mmols, 1.0 equiv) followed by THF (0.27 mL). NEt_3 (40 µL, 0.32 mmols, 4.0 equiv) was added to the reaction mixture via syringe, followed by TMSCl (22 µL, 0.17 mmols, 2.2 equiv). The reaction stirred at room temperature for 12 hours, then diluted with 15 mL of diethyl ether and washed with water (10 mL), saturated sodium bicarbonate (2 x 10 mL), and brine (2 x 10 mL). The organic layer was dried with anhydrous sodium sulfate, and the solvent was removed *in vacuo* resulting in a clear yellow oil. Purification via flash column chromatography on silica gel (100% hexanes as eluent) yielded the title compound as a white solid (18.3 mg, 0.038 mmols, 48% yield) (R_f = 0.30 in 99:1 Hexanes:EtOAc), enantiomeric excess was determined to be >99% by chiral HPLC (Chiralpak OD-H, 100% hexane 0.5 mL/min, *tr*(minor): 11.2 min, *tr*(major): 15.7 min.; Figure 15; see also Figure 16 for racemic sample) $[\alpha]^{24}_D$ = –155.9° (c 1.01, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 7.87

(d, J = 8.4 Hz, 2H), 7.84 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 7.35 (ddd, J = 8.0, 6.8, 1.2 Hz, 2H), 7.16 (ddd, J = 8.8, 6.8, 1.2 Hz, 2H), 7.09 (d, J = 8.8 Hz, 2H), 2.00 (d, J = 13.6 Hz, 2H), 1.96 (d, J = 13.6 Hz, 2H), 0.02 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.7, 132.8, 132.7, 131.8, 128.4, 128.1, 128.0, 126.7, 125.8, 124.3, 24.5, 2.0. IR (KBR) 3049, 2946, 2898, 1500, 1395, 1250, 1147, 1067 (br), 917, 837, 750, 735 cm^{-1}. Mass Calculated for $C_{28}H_{34}O_2Si_3$ $[M^+Na]^+$, 509.1764. Found $[M^+Na]^+$, 509.1766.

Synthesis of Silyl Ketene Acetals (Scheme 10)

Scheme 10. Synthesis of Silyl Ketene Acetals



Triisopropyl((1-methoxy-2-methylprop-1-en-1-yl)oxy)silane (8-TIPS): Using the method reported by the Jacobsen group (Wenzel AG, Jacobsen EN, *J. Am. Chem. Soc.* **2002**, 124, 12964–12965), a 200 mL round bottom flask equipped with a stir bar was flame dried under vacuum and purged with nitrogen gas. The flask was placed under positive pressure of argon gas and fitted with a rubber septa. The reaction vessel was charged with 50 mL of anhydrous THF and diisopropyl amine (4.2 mL, 30 mmol, 1.2 equiv.), and cooled to 0 °C. A solution of 1.3 M *n*-BuLi (21.2 mL, 27.5 mmol, 1.1 equiv) in hexanes was added dropwise to the reaction mixture and stirred for 20 minutes at 0 °C. The reaction was cooled to –78 °C and methyl isobutyrate (2.87 mL, 25 mmol, 1.0 equiv) was added over a 10-minute period. The reaction was stirred for 30 mins at –78 °C, followed by the addition 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU) (4.53 mL, 37.5 mmol, 1.5 equiv) and triisopropylsilyl chloride (6.42 mL, 30 mmol, 1.2 equiv). The reaction stirred at –78 °C for 30 min then warmed to room temperature for 1 h. Solvent was removed under reduced pressure and the resulting mixture was taken up in 200 mL of pentane, washed sequentially with water (1 x 100 mL), saturated $CuSO_4$ (1 x 100 mL), saturated $NaHCO_3$ (1 x 100 mL), and brine (1 x 100 mL). The organic layer was dried over anhydrous Na_2SO_4, and concentrated *in vacuo*, resulting in an oil which was purified via fractional distillation to yield the title compound (5.62 g, 21.7 mmol, 87% yield) as a clear colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.56 (s, 3H), 1.57 (s, 6H), 1.09–1.18 (m, 21H). All spectral data

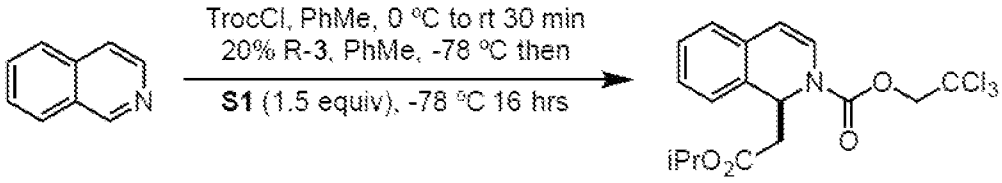
matched that previously reported (Liu SY et al., *J. Am. Chem. Soc.* **2005**, 127, 15352–15353).

tert-Butyl((1-methoxy-2-methylprop-1-en-1-yl)oxy)dimethylsilane (8-TBS): Using the method reported by the Jacobsen group (Wenzel AG, Jacobsen EN, *J. Am. Chem. Soc.* **2002**, 124, 12964–12965), the title compound (4.04 g, 18.7 mmol, 75% yield) was obtained as a clear colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.51 (s, 3H), 1.57 (s, 3H), 1.53 (s, 3H), 0.96 (s, 9H), 0.14 (s, 6H). All spectral data matched that previously reported (Schäeckel R et al., *Angew. Chem. Int. Ed.* **2010**, 49, 1619–1622).

tert-butyl((1-isopropoxyvinyl)oxy)dimethylsilane (S1): Following the same procedure as above, the title compound was prepared on a 30 mmol scale to yield the title compound (5.24 g, 24.2 mmol, 81% yield) as a clear colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.19 (sep, J = 6.4 Hz, 1H), 3.27 (d, J = 2.4 Hz, 1H), 3.08 (d, J = 2.4 Hz, 1H), 1.25 (d, J = 6.4 Hz, 6H), 0.93 (s, 9H), 0.17 (s, 6H). All spectral data matched that previously reported (Wenzel AG, Jacobsen EN, *J. Am. Chem. Soc.* **2002**, 124, 12964–12965).

Tentative Assignment of Absolute Stereochemistry (Scheme 11)

Scheme 11. Tentative assignment of absolute stereochemistry



2,2,2-trichloroethyl (*S*)-1-(2-isopropoxy-2-oxoethyl)isoquinoline-2(1*H*)-carboxylate (S2): Using the same general procedure for silanediol catalyzed acyl-Mannich reactions above, the title compound was purified via flash column chromatography on silica gel (0:100 EtOAc:Hexanes to 4:96 EtOAc:Hexanes) yielded the title compound as a colorless oil (30.5 mg, 0.075 mmols, 75% yield) (R_f = 0.45 in 10:90 EtOAc:Hexanes), enantiomeric excess was found to be 14% by chiral HPLC (Chiralpak OD-H, 1% isopropanol/99% hexane 0.7 mL/min, *tr* (minor): 13.8 min, *tr* (major): 18.2 min.; Figure 17, see also Figure 18 for racemic sample) $[\alpha]^{24}_D$ = +27.8° (c 0.78, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): The compound exists at a 1.7:1 mixture of carbamate rotamers. Signals corresponding to the major rotamer: δ 7.27–7.19 (m, 3H), 7.10 (d, J = 7.6 Hz, 1H), 6.90 (d, J = 7.6 Hz, 1H), 5.98 (d, J = 7.6 Hz, 1 H), 5.89–5.81 (m, 1H), 4.97–4.76 (m, 3H), 2.67–2.58 (m, 2H), 1.20 (d, J =

6.0 Hz, 3H), 1.16 (d, J = 6.4 Hz, 3 H). Representative signals of the minor rotamer: δ 6.90 (d, J = 7.6 Hz, 1H), 6.04 (d, J = 7.6 Hz, 1H), 2.77 (dd, J = 14.4, 9.2 Hz, 1H) 1.11 (d, J = 6.4 Hz, 3H). All spectral data matched that previously reported with exception of optical rotation: Literature $[\alpha]^{24}{}_{D}$ for 86% 2,2,2-trichloroethyl (*R*)-1-(2-isopropoxy-2-oxoethyl)isoquinoline-2(1*H*)- carboxylate: –240° (86% ee, c 1.1, CH_2Cl_2).

Results and Discussion

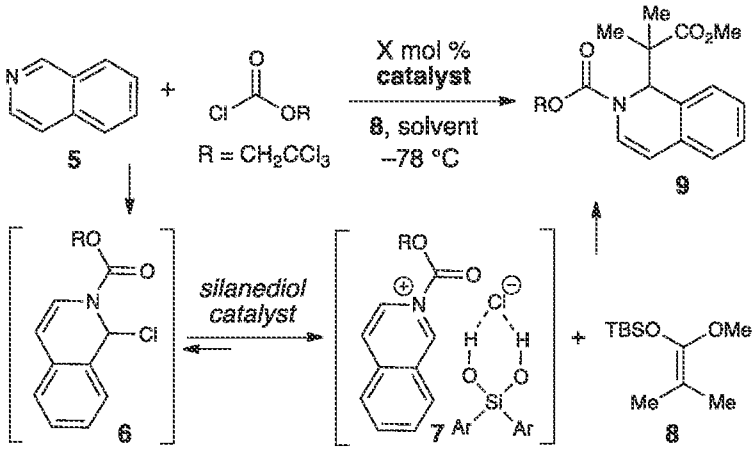
The feasibility of silanediol ion-pair catalysis was studied in the addition of silyl ketene acetal **8** to in situ generated *N*-acylisoquinoline **6** through proposed ion pair **7** (Table 1). This reaction was selected as a testing ground as it is a process that has documented benefits under the influence of HBD catalysis. Of particular interest were the observations of Taylor and Jacobsen demonstrating thiourea-activation of *N*-acylisoquinolines (Taylor MS et al., *Angew. Chem. Int. Ed.* **2005**, *44*, 6700–6704) and subsequent studies on related systems pointing to thiourea anion binding in the catalytic pathway (Raheem IT et al., *JACS*, **2007**, *129*, 13404–13405; Raheem IT et al., *Org. Lett.* **2008**, *10*, 1577–1580; Peterson EA, Jacobsen EN, *Angew. Chem. Int. Ed.* **2009**, *48*, 6328–6331). Early on, it was found that the solvent played a role in the reaction of **8** with **6** (entries 1–5, Table 1). Ethereal solvents, such as diethyl ether and methyl *tert*-butyl ether (MTBE), afforded low yields of product **9** after 40 h with 20 mol % of silanediol **1** (entries 1 and 2). Dichloromethane gave rise to a good yield of **9** (entry 3); however, the background rate was also high at 88%. Toluene was selected as the solvent to explore in this system as moderate yields of **9** were observed with 20 mol % of silanediol **1** while the background rate remained low at just 12% (entries 4 and 5).

With the solvent identified with achiral silanediol **1**, attention was turned toward the effect of chiral silanediols on catalytic activity for studies on enantioselective catalysis. Catalyst **2**, a previously developed chiral C_2-symmetric variant of catalyst **1**, promoted the reaction in 50% yield (entry 6) (Schafer AG et al., *Org. Lett.* **2011**, *13*, 5228–5231). Concerned that the steric bulk of silanediol **2** was preventing sufficient catalysis, the less sterically encumbered chiral silanediol catalyst **3** was explored. It was found that 20 mol % of silanediol **3** afforded a 75% yield of **9** at –78 °C in toluene (entry 7). The silanediol functionality was determined to affect catalyst activity: dimethoxysilacycle **4** was unable to catalyze the reaction, affording just 14% of **9** (entry 8).

Following the successful catalysis of the addition of silyl ketene acetal **8** to in situ generated *N*-acylisoquinolinium **7** with racemic silanediol **3**, the use of enantiopure silanediols to control the absolute stereochemistry of the acyl Mannich reaction was

investigated. Prior to this study, asymmetric catalysis achieved solely through the HBD activity of a chiral silanediol had not been reported. A factor likely inhibiting advances in asymmetric silanediol catalysis is the difficulty of synthesizing enantioenriched chiral silanediols.

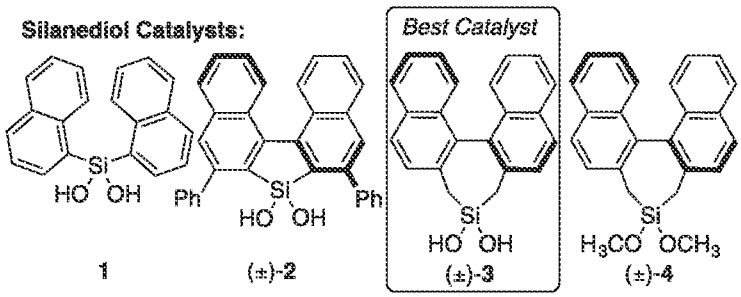
Table 1. **Silanediol ion-pair catalysis**[a]



Entry	Catalyst	Solvent	Yield (%)[b]
1	20 mol % **1**	Et_2O	3
2	20 mol % **1**	MTBE	3
3	20 mol % **1**	CH_2Cl_2	74
4	20 mol % **1**	Toluene	74
5	0 mol % **1**	Toluene	12
6	20 mol % **2**	Toluene	50
7	20 mol % **3**	Toluene	75
8	20 mol % **4**	Toluene	14

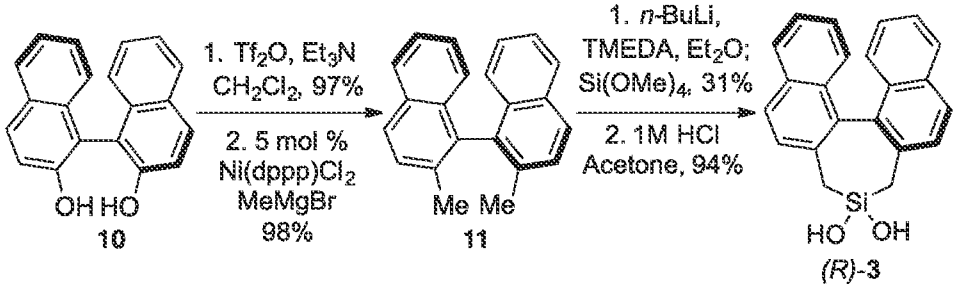
[a] Reactions performed at a concentration of 0.025 M in the solvent listed.

[b] Isolated yields



Enantiopure silanediol **3** could be prepared from commercial BINOL (**10**, Scheme 12). The triflation of **10** (Bulman Page PC, *Org. Lett.* **2004**, *6*, 1543–1546) followed by a Kumada cross-coupling reaction (Kasak P, Putala M, *Tetrahedron Lett.* **2004**, *45*, 5279–5282) gives rise to (*R*)-2,2'-dimethyl-1,1'-binaphthalene **11** in high yield. Dilithiation of **11** followed by treatment of with tetramethoxysilane affords an intermediate dimethoxysilacycle that readily converts to silanediol (*R*)-**3** upon treatment with hydrochloric acid in acetone.

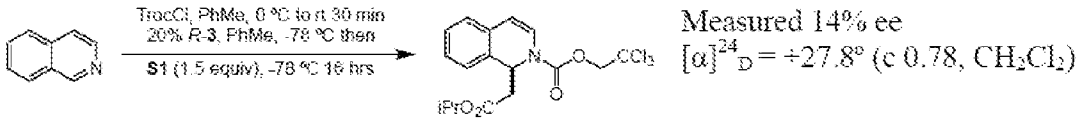
Scheme 12. Synthesis of enantiopure chiral C_2-symmetric silanediol.



An X-ray quality crystal of *bis*-trimethylsilyl protected (*R*)-**3** was obtained from hexanes and the ORTEP representation is depicted in Figure 19. An X-ray quality crystal of the unprotected silanediol (*R*)-**3** has yet to be isolated. *Bis*-trimethylsilyl protected (*R*)-**3** was found to be 99% enantioenriched by HPLC analysis.

The enantiopure silanediol (*R*)-**3** was able to catalyze the addition of silyl ketene acetals to *N*-acylisoquinolines with promising levels of stereocontrol (Table 2). The silyl group on **8** had a significant effect on the stereochemical outcome: the larger the silyl group the better the enantiomeric excess (entries 1–3). The best enantioselectivity obtained for **9a** in this study occurred with the addition of triisopropylsilyl protected **8** to isoquinoline in the presence of 2,2,2-trichloroethyl chloroformate and 1 equiv of (*R*)-**3** (38% ee, entry 4). The absolute stereochemistry of **9a** was tentatively assigned (Scheme 13) by analogy to literature precedent (Taylor MS et al., *Angew. Chem. Int. Ed.* **2005**, 44, 6700–6704) (Scheme 14). High yields and encouraging levels of enantiocontrol were also observed with several isoquinolines tested (entries 5–10). For example, 5-bromoisoquinolinium ions were easily incorporated into the process, giving rise to the corresponding products **9b** in 57% and 66% yields, with the TIPS and TBS silyl ketene acetals (**8**) respectively, and up to 26% ee when 20 mol % of (*R*)-**3** was used (entries 5 and 6). 5-Chloroisoquinoline gave rise to **9c** in high yield and up to 31% ee with 20 mol % of (*R*)-**3** (entries 7 and 8). Good yields of **9d** were isolated (87%) with 50% enantiomeric excess from the incorporation of 5-nitroisoquinoline into the reaction system (entries 9 and 10).

Scheme 13. Tentative stereochemistry based on this work



Scheme 14. Tentative stereochemistry based on Jacobsen's work (Taylor MS et al., *Angew. Chem. Int. Ed.* 2005, 44, 6700–6704)

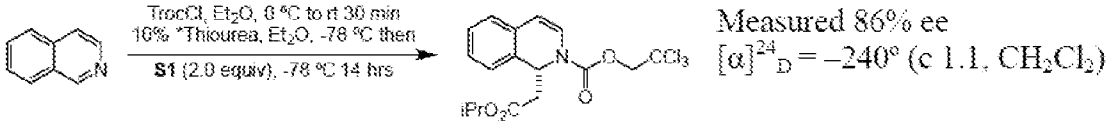
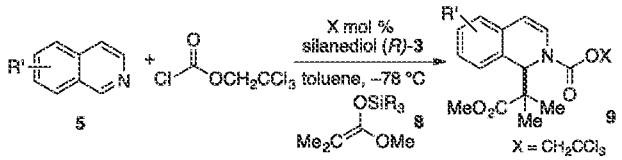


Table 2. Enantioselective acyl Mannich with silanediol (*R*)-3.[a]



entry	**8** (SiR_3)	**5** (R')	mol % (*R*)-3	**9**	Yield (%)[b]	Er
1	TMS	H	20 mol %	**9a**	80	54:46
2	TBS	H	20 mol %	**9a**	71	59:41
3	TIPS	H	20 mol%	**9a**	55	64:36
4	TIPS	H	100 mol %	**9a**	74	69:31
5	TIPS	5-Br	20 mol %	**9b**	57	63:37
6	TBS	5-Br	20 mol %	**9b**	66	59:41
7	TIPS	5-Cl	20 mol %	**9c**	61	66:34
8	TBS	5-Cl	20 mol %	**9c**	80	60:40
9	TIPS	5-NO_2	20 mol %	**9d**	65	58:42
10	TBS	5-NO_2	20 mol %	**9d**	72	75:25

[a] Reactions performed at a concentration of 0.025 M in toluene.

[b] Isolated yields

Evidence supporting a reaction pathway involving silanediol recognition of chloride ions was collected by ^{1}H NMR spectroscopy and X-ray crystallographic analysis. First, ^{1}H NMR spectroscopic analysis found an effect on the OH signals of (*R*)-**3** upon the addition of varying amounts of tetrabutylammonium chloride (TBACl). In the ^{1}H NMR spectrum of pure (*R*)-**3**, the OH chemical shift was observed at 2.3 ppm (spectrum (a), Figure 20). As equivalents of TBACl were added to the silanediol, clear downfield shifting of the OH peak (spectra (b)-(f)) was observed. For example, the addition of 5 equiv of TBACl caused the OH chemical shift to be observed at 4.7 ppm, a change of more than 2 ppm (compare spectra (a) vs. (f)). There were also small changes in the chemical shifts observed for the methylene and aromatic hydrogens. Further support of silanediol ion-pair catalysis was

found in the capture of achiral silanediol **1** in a solid-state ion-pair with the hydrochloride salt of isoquinoline (Figure 21).

Conclusions

In summary, silanediols can promote the reaction of silyl ketene acetals with *N*-acylisoquinolines in good yield, conceivably through anion-binding catalysis. In addition, C2-symmetric silanediols also were shown to exhibit promising levels of enantiocontrol in the title reaction.

Example 2:

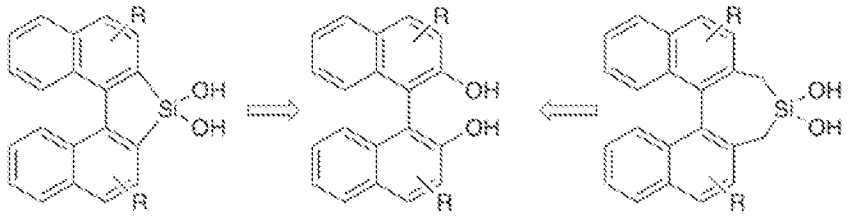
Introduction

The versatility of the silanediol functionality (Si–$(OH)_2$) continues to grow in organic synthesis. Attractive characteristics of the silanediol functionalities include their hydrogen bonding abilities and their preference to exist as diols, not silanones. The conversion of silanediols into polysiloxanes, polymers with useful properties, is possibly their most well-known function. Albeit less popular, stable silanediols are also accessible and possess their own useful applications. For example, chemists have taken advantage of silanediols to advance new therapeutic agents.

Enantioselective hydrogen bond donor (HBD) organocatalysis is emerging as a powerful tool in complex target construction. Given their hydrogen bonding abilities, silanediols may benefit from improved activities and selectivities versus other HBD catalysts, ultimately enabling unique bond-forming reactions.

Silanediols derived from BINOL-backbones were investigated as catalysts (Scheme 15). There are many advantages of BINOL: it is a readily available, inexpensive source of chirality that is highly customizable in terms of both steric hindrance and electronic nature so as to enable the achievement of optimal reactivity.

Scheme 15. BINOL-Based Silanediol Catalyst Designs



21 23 (BINOL) 22

Experimental

2,2'-bis(hexyloxy)-1,1'-binaphthalene: To a flame-dried 1000 mL round bottom flask was added (*R*)-BINOL (30.0 g, 105 mmol, 1 equiv), *n*-bromohexane (73.3 mL, 524 mmol, 5 equiv), MeCN (500 mL), and K_2CO_3 (72.3 g, 524 mmol, 5 equiv). The flask was equipped with a water-cooled condenser and the reaction was heated to reflux overnight. The reaction was cooled to 23°C, diluted with H_2O, and extracted with hexanes (3x). The combined organic layers were dried with Na_2SO_4, concentrated *in vacuo*, and distilled to remove excess *n*-bromohexane (120°C, ~300 mTorr) to provide the title compound as colorless viscous oil (46.7 g, 103 mmol, 98%; contains ~5% residual *n*-bromohexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 9.0 Hz, 2H), 7.89 (d, J = 8.1 Hz, 2H), 7.45 (d, J = 9.0 Hz, 2H), 7.34 (ddd, J = 1.9 Hz, 6.1 Hz, 8.0 Hz, 2H), 7.20–7.23 (4H), 3.97 (4H), 1.40–1.44 (4H), 0.95–1.10 (12H), 0.79 (t, J = 7.1, 6H). All other spectra data matched that previously reported (Gong Z *et al. J. Org. Chem.* **2001**, *66*, 2358-2367).

4,4',6,6'-tetrabromo-2,2'-bis(hexyloxy)-1,1'-binaphthalene: To a flamed-dried 500 mL round bottom flask was added 2,2'-bis(hexyloxy)-1,1'-binaphthalene (16.9 g, 37.1 mmol, equiv) followed by AcOH (300 mL). Bromine (20.1 mL, 390.5 mmol, 10.5 equiv) was added slowly to the solution at 23°C and the reaction was stirred for 4.5 h at 23°C. The reaction was cooled to 0°C, quenched with saturated $NaHSO_3$, and extracted with CH_2Cl_2 (3x). The combined organic layers were washed with $NaHCO_3$, then brine, dried with Na_2SO_4, and concentrated *in vacuo*. The compound was purified via flash column chromatography (dry load) on silica gel (100% hexanes) to provide the title compound as a light yellow oil (18.2 g, 23.6 mmol, 64%). R_f = 0.65 (10:90 ethyl acetate:hexanes), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, J = 1.9 Hz, 2H), 7.71 (s, 2H), 7.31 (dd, J = 2.0, 9.1 Hz, 2H), 6.97 (d, J = 9.0 Hz, 2H), 3.92 (4H), 1.37–1.44 (4H), 0.88–1.12 (12H), 0.76 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 133.2, 130.7, 129.5, 128.9, 127.4, 122.5, 120.5, 119.3, 69.9, 31.3, 29.2, 25.4, 22.6, 14.0. All other spectra data matched that previously reported (Gong Z *et al. J. Org. Chem.* **2001**, *66*, 2358-2367).

4,4',6,6' tetrabromo-[1,1'-binaphthalene]-2,2'-diol (***R*)-26**: Adapting a procedure by Lin (Mi L *et al. JACS* **2009**, *131*, 4610-4613), to a flame-dried 250 mL round bottom flask was added 4,4',6,6'-tetrabromo-2,2'-bis(hexyloxy)-1,1'-binaphthalene (20.9 g, 27.1 mmol, 1 equiv) followed by CH_2Cl_2 (60 mL). The solution was cooled to –78°C and BBr_3 (2.26 mL, 23.8 mmol, 6 equiv) was added dropwise. The reaction was warmed to 23°C and stirred overnight. The reaction was cooled to 0°C, quenched with water (~20 mL), and extracted with CH_2Cl_2 (3x). The organic layers were combined, washed with brine, dried with

Na_2SO_4, and concentrated *in vacuo*. The resulting compound was purified via silica plug (CH_2Cl_2) to afford (*R*)-**26** as a white solid (16.1 g, 26.7 mmol, 99%). R_f = 0.56 (30:70 ethyl acetate:hexanes), ^1H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 1.9 Hz, 2H), 7.75 (s, 2H), 7.43 (dd, *J* = 1.9 Hz, 8.9, 2H), 6.96 (d, *J* = 8.9 Hz, 2H), 4.95 (s, 2H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 132.5, 132.1, 130.3, 129.6, 126.3, 125.1, 123.2, 120.1, 110.4; m.p. 293–294°C; IR (NaCl) 3500, 3080, 2916, 1580, 1493, 1373, 1176, 937, 733 cm^{-1}; HRMS (ESI): Mass calculated for $C_{20}H_{10}Br_4O_2Na$ $[M+Na]^+$, 620.7307. Found $[M+Na]^+$, 620.7300; $[\alpha]^{23}_D$ = –49.8° (c 1.00, $CHCl_3$).

4,4',6,6'-tetraphenyl-[1,1'-binaphthalene]-2,2'-diol: To a 150 mL flame-dried round bottom flask was added (*R*)-**26** (6.66 g, 11.1 mmol, 1 equiv), phenylboronic acid (5.94 g, 48.7 mmol, 4.4 equiv), K_2CO_3 (9.17 g, 66.4 mmol, 6 equiv), THF (35 mL), $Pd(PPh_3)_4$ (1.92 g, 1.66 mmol, 0.15 equiv) and H_2O (33 mL). The flask was equipped with a water-cooled condenser and the reaction was heated to reflux overnight. The reaction was cooled to 23°C and extracted with CH_2Cl_2 (3x). The combined organic layers were washed with brine, dried with Na_2SO_4, and concentrated *in vacuo*. The resulting residue was first subjected to flash column chromatography on silica gel (100% CH_2Cl_2) to remove the black colored impurity followed by additional purification via flash column chromatography on silica gel (30:70 CH_2Cl_2:hexanes to 100% CH_2Cl_2) to provide the title compound as an off-white solid (4.03 g, 6.82 mmol, 62%). R_f = 0.46 (30:70 ethyl acetate:hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 8.18 (br d, *J* = 8.2 Hz, 2H), 7.49–7.69 (16H), 7.39–7.47 (8H), 7.30–7.34 (2H), 5.20 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 144.4, 141.2, 140.0, 137.1, 133.3, 130.1, 129.0, 128.7, 128.4, 128.0, 127.4, 127.33, 127.27, 125.4, 125.0, 119.3, 110.5; $[\alpha]^{23}_D$ = –49.8° (c 0.26, CHCl3) All other spectra data matched that previously reported (Gong Z *et al. J. Org. Chem.* **2001**, *66*, 2358-2367).

4,4',6,6'-tetraphenyl-[1,1'-binaphthalene]-2,2'-diyl bis(trifluoromethanesulfonate) (Hashimoto T *et al. Tetrahedron:Aymmetry* **2003**, *14*, 1599-1602): To a 150 mL flame-dried round bottom flask was added 4,4',6,6'-tetraphenyl-[1,1'-binaphthalene]-2,2'-diol (5.13 g, 8.68 mmol, 1 equiv) followed by CH_2Cl_2 (50 mL). The solution was cooled to –78°C and Et_3N (3.60 mL, 26.04 mmol, 3 equiv) was added followed by the addition of Tf_2O (4.37 mL, 26.04 mmol, 3 equiv) dropwise. The reaction was warmed to 23°C and stirred overnight. The reaction was cooled to 0°C, quenched with 2 M HCl (~10 mL), and extracted with CH_2Cl_2 (3x). The combined organic layers were washed with $NaHCO_3$, brine, dried with Na_2SO_4, and concentrated *in vacuo*. The resulting compound was run through a silica gel plug (CH_2Cl_2 as eluent) and then purified via flash column

chromatography on silica gel (100% hexanes to 5:95 Et_2O:hexanes) to provide the title compound as a white solid (6.21 g, 7.26 mmol, 84%). R_f = 0.35 (10:90 ethyl acetate:hexanes); m.p. 205–207°C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.25 (br d *J* = 1.6 Hz, 2H), 7.54–7.74 (20H), 7.41–7.45 (4H), 7.34–7.38 (2H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 145.0, 140.4, 140.2, 138.9, 133.1, 131.4, 130.2, 129.1, 128.9, 128.6, 128.1, 128.0, 127.7, 127.6, 124.6, 122.7, 120.7, 118.4 (q, JCF = 320 Hz); m.p. 205–207°C; IR (NaCl) 3058, 3028, 1560, 1486, 1419, 1210, 1136, 942 cm^{-1}; HRMS (ESI): Mass calculated for $C_{46}H_{28}F_6O_6S_2Na$ $[M+Na]^+$, 877.1124. Found $[M+Na]^+$, 877.1112; $[\alpha]^{23}_D$ = –67.3° (c 1.00, $CHCl_3$).

2,2'-dimethyl-4,4',6,6'-tetraphenyl-1,1'-binaphthalene **(*R*)-27** (Hashimoto T *et al. Tetrahedron:Aymmetry* **2003**, *14*, 1599-1602): To a 150 mL flame-dried round bottom flask was added 4,4',6,6'-tetraphenyl-[1,1'-binaphthalene]-2,2'-diyl bis(trifluoromethanesulfonate) (6.21 g, 7.26 mmol, 1 equiv), Et_2O (65 mL), and Ni(dppp)Cl_2 (197 mg, 0.363 mmol, 0.05 equiv). The mixture was cooled to 0°C and 2.44 M MeMgBr (13.7 mL, 33.4 mmol, 4.6 equiv) was added drop wise. The flask was equipped with a water-cooled condenser and the reaction was heated to reflux overnight. The reaction was cooled to 23°C and slowly poured in a chilled flask of 2 M HCl (~25 mL). The mixture was filtered through celite and extracted with Et_2O (3x). The combined organic layers were washed with $NaHCO_3$, brine, dried with Na_2SO_4, and concentrated *in vacuo*. The resulting compound was purified with flash column chromatography on silica gel (5:95 Et_2O:hexanes to 10:90 Et_2O:hexanes) to afford (*R*)-**27** as a white solid (3.88 g, 6.61 mmol, 91%), R_f = 0.43 (10:90 ethyl acetate:hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (br d, *J* = 1.7 Hz, 2H), 7.68–7.71 (4H), 7.46–7.59 (14H), 7.28–7.42 (8H), 2.18 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5, 141.0, 140.2, 137.8, 134.8, 134.3, 132.6, 130.8, 130.6, 130.4, 128.9, 128.6, 127.51, 127.47, 127.3, 126.9, 125.8, 124.3, 20.4; m.p. 198–201°C; IR (NaCl) 3056, 3029, 2917, 1598, 1471, 1449, 1382 cm^{-1}; HRMS (ESI): Mass calculated for $C_{46}H_{34}Na$ $[M+Na]^+$, 609.2553. Found $[M+Na]^+$, 609.2538; $[\alpha]^{23}_D$ = –89.0° (c 0.200, $CHCl_3$).

1,7,9,14-tetraphenyl-3,5-dihydro-4H-dinaphtho[2,1-c:1',2'-e]silepine-4,4-diol **(*R*)-22b:** Adapting a procedure by Mattson (Schafer AG *et al. Angew. Chem. Int. Ed.* **2013**, *52*, 11321-11324), to a 250 mL flame-dried round bottom flask was added (*R*)-**27** (4.51 g, 7.69 mmol, 1 equiv) followed by Et_2O (70 mL). The solution was cooled to 0°C and 1.6 M n-BuLi (14.4 mL, 23.07 mmol, 3 equiv) was added dropwise followed by the addition of TMEDA (3.44 mL, 23.07 mmol, 3 equiv) dropwise. The reaction was warmed to 23°C and stirred overnight. The reaction was then cooled to 0°C and $Si(OMe)_4$ (4.55 mL, 30.8 mmol,

4 equiv) was added drop-wise followed by Et_2O (35 mL). The reaction was warmed to 23°C and stirred for 24 h. The mixture was pushed through a pad of silica gel using Et_2O as the eluent. After concentration *in vacuo*, the compound was partially purified via flash column chromatography on silica gel (100% hexanes to 80:20 hexanes:Et_2O) to afford slightly impure (*R*)-**25b** (2.88 g), which was carried on to the next hydrolysis step. To a flame dried 1000 mL flame-dried round bottom flask was added crude (*R*)-**25b** (2.88 g) and acetone (300 mL). The solution was cooled to 0°C followed by the dropwise addition of 1 M HCl (75 mL). The mixture was stirred at 0°C for 6 h. The reaction was diluted with Et_2O (~150 mL), neutralized to pH 7 using $NaHCO_3$, and extracted with Et_2O (3x). The organic layers were combined, dried with Na_2SO_4 and concentrated *in vacuo*. Evaporation under high vacuum was necessary to remove a volatile white liquid before purification. The resulting compound was purified via flash column chromatography on silica gel (40:60 Et_2O:hexanes to 80:20 Et_2O:hexanes) to afford a white solid (*R*)-**22b** (1.46 g, 2.17 mmol, 28% over 2 steps) as a 3:1 Et_2O complex. R_f = 0.42 (50:50 ethyl acetate:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (br d, *J* = 1.7 2H), 7.68–7.70 (4H), 7.46–7.58 (14H), 7.38–7.42 (6H), 7.29–7.33 (2H), 2.43 (s, 2H), 2.31 (d, *J* = 13.7 Hz, 2H), 2.25 (d, 13.7, *J* = 13.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 140.9, 140.6, 137.3, 134.3, 132.4, 132.2, 130.4, 130.3, 129.5, 128.8, 128.4, 127.6, 127.4, 127.3, 127.1, 125.6, 124.1, 23.5; m.p. 344–346 °C; IR (KBr) 3416, 3051, 3021, 2954, 2917, 1628, 1590, 1561, 1486, 1158, 1143, 830, 756, 696 cm^{-1}; HRMS (ESI): Mass calculated for $C_{46}H_{34}O_2SiNa$ $[M+Na]^+$, 669.2220. Found $[M+Na]^+$, 669.2207; $[\alpha]^{23}_D$ = –201° (c 1.00, $CHCl_3$).

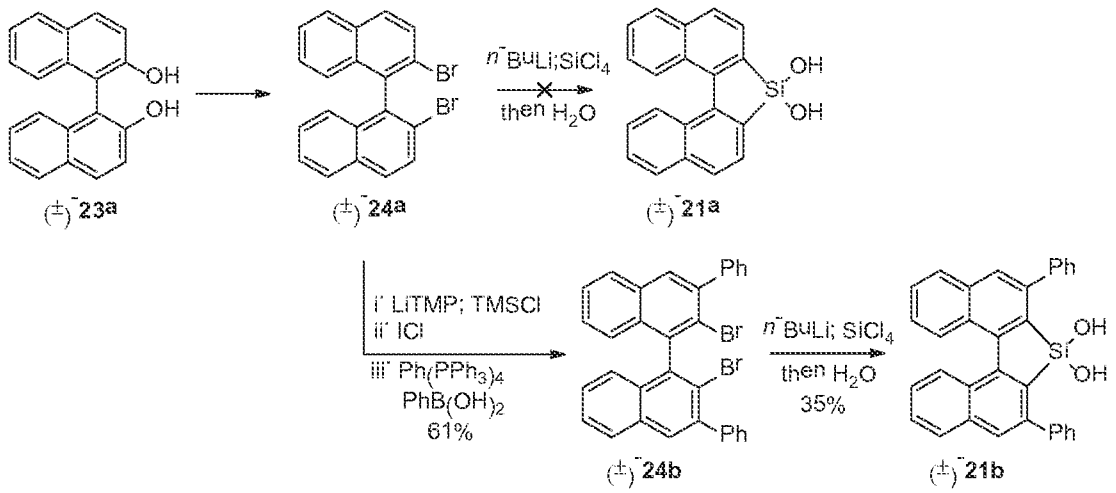
General procedure for N-acyl Mannich Reaction: An 8 mL vial was equipped with a magnetic stir bar and screw cap was sealed with a virgin septum, flame dried under vacuum, purged with N_2, and then placed under a positive pressure of argon. A 0.10 M stock solution of the appropriate freshly purified isoquinoline was prepared in toluene which had been passed through a bed of active alumina and freshly distilled from CaH_2. Isoquinoline solution (1.0 mL, 0.10 mmol, 1.0 equiv) was transferred to the reaction vial and placed in an ice bath. A 0.11 M stock solution of the appropriate chloroformate was prepared in toluene. Chloroformate solution (1.0 mL, 0.11 mmol, 1.1 equiv) was added drop-wise to the cold isoquinoline solution, the ice bath was removed and the reaction mixture warmed to r.t over 30 min. The reaction mixture was diluted with toluene (1.50 mL). A 0.020 M solution of catalyst (*R*)-**22b** was prepared in toluene. The reaction mixture was cooled in a dry ice acetone bath, and the catalyst (*R*)-**22b** solution (1.0 mL, 0.020 mmols, 0.20 equiv) was added to the reaction mixture and stirred for 5 mins. A 0.30 M solution of the appropriate

silyl ketene acetal was prepared in toluene, and was added (0.50 mL, 0.15 mmols, 1.5 equiv) drop-wise to the reaction mixture, which was immediately transferred to a –55°C acetone bath equipped with immersion cooling coil or a –35°C freezer. The reaction stirred for either 6 or 14 h, after which it was quenched by the addition of NaOMe (0.20 mL of 0.5 M in MeOH). The reaction mixture was filtered through a silica gel plug using ethyl acetate as the eluent, and solvent was removed *in vacuo*. The product was isolated via flash column chromatography on silica gel using the conditions detailed in the supporting information. Further purification through an activity II alumina plug with minimal dichloromethane (~2 mL) as the eluent yielded the pure product. Enantiomeric ratios were determined by HPLC analysis under the conditions detailed in the supporting information.

BINOL-Based Silanediol Synthesis

Studies herein began with the synthesis of 5-membered silacycles **21** (Scheme 16). Following literature protocols (Takaya H et al., *Org. Syn.* **1989**, *67*, 20–32), **23a** (R = H) was readily converted to **24a**. Silacyclization of **24a** attempted under numerous conditions met with no success. It was reasoned that the difficult preparation of **21a** might lie in its low stability, plausibly due to the location of the silicon in the highly strained 5-membered ring. It was hypothesized that silanediol **21b**, with phenyl substituents in the 3,3'-positions stabilizing the silacycle, would be more synthetically accessible. Indeed, silanediol **21b** was prepared in four steps from BINOL. The silacyclization protocol was found to be lithiation with *n*-BuLi followed by reaction with silicon tetrachloride then aqueous workup. The structure of **21b** was confirmed by small molecule X-ray crystallographic analysis (Figure 22).

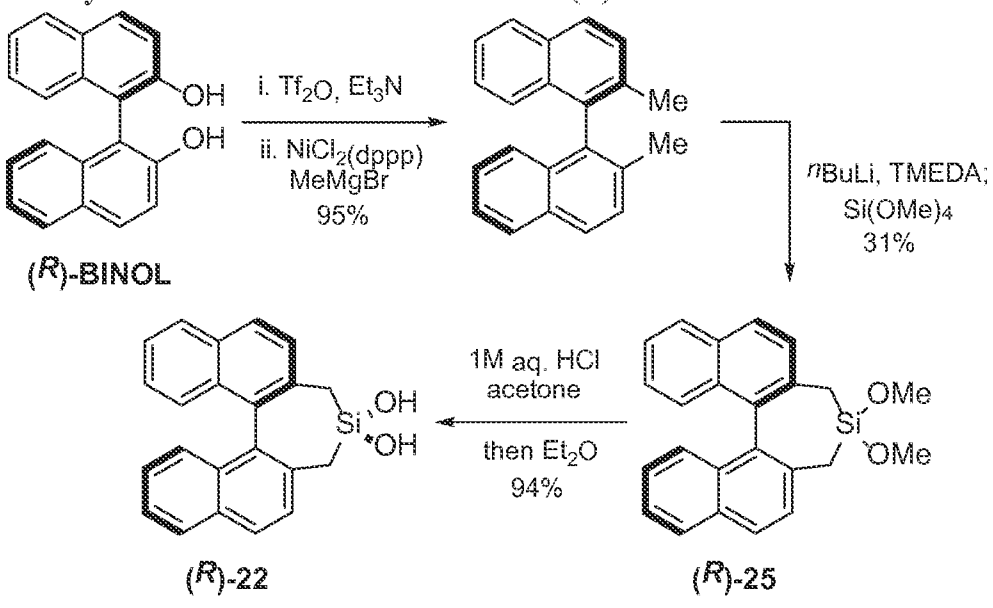
Scheme 16. Synthetic Route to Silanediols (±)-21a and (±)-21b.



It was discovered that problems inherent to **21** could make its straightforward synthesis in enantiopure form difficult. Specifically, intermediate **24a** is prone to racemization. While the resolution of racemic **21** is one possible solution, accessing silanediol catalysts directly in enantiopure form was further investigated.

Given the possible limitations of 5-membered silacycles **21**, efforts were redirected to 7-membered silacyclic silanediols **22** derived from (*R*)-2,2'-binaphthlene (e.g., (*R*)-BINOL). The advantage of this scaffold is that the chirality of the BINOL starting material is retained over the course of the synthetic sequence enabling direct access to enantiopure silanediols, meaning issues with enantioerosion due to unstable intermediates are avoided. Starting from (*R*)-BINOL, a straightforward four-step protocol was established, detailed in Scheme 17. (*R*)-BINOL is treated with Tf_2O, followed by nickel-catalyzed Kumada cross-coupling with MeMgBr to provide (*R*)-2,2'-dimethyl-1,1'-binaphthlene. Deprotonation of both benzylic methyl groups with *n*-BuLi/TMEDA, followed by quenching with $Si(OMe)_4$, affords dimethoxysilacycle **(*R*)-25**. Simple hydrolysis with dilute HCl gives silanediol **(*R*)-22**. After neutralization with sodium bicarbonate, dissolution and concentration from anhydrous Et_2O, the silane diol **22** was obtained as a 2:1 complex with diethyl ether. Silanediol (*R*)-**22**-Et_2O is an air and moisture stable white solid at room temperature that can be stored on the benchtop for several weeks. Attempts at removing the ethereal solvent of complexation led to rapid decomposition of the silanediol. Using this procedure, enantiopure **(*R*)-22** can be produced on a multi gram scale. (The structure of bis-TMS protected **(*R*)-22** was confirmed by X-ray crystallographic analysis (Figure 23).

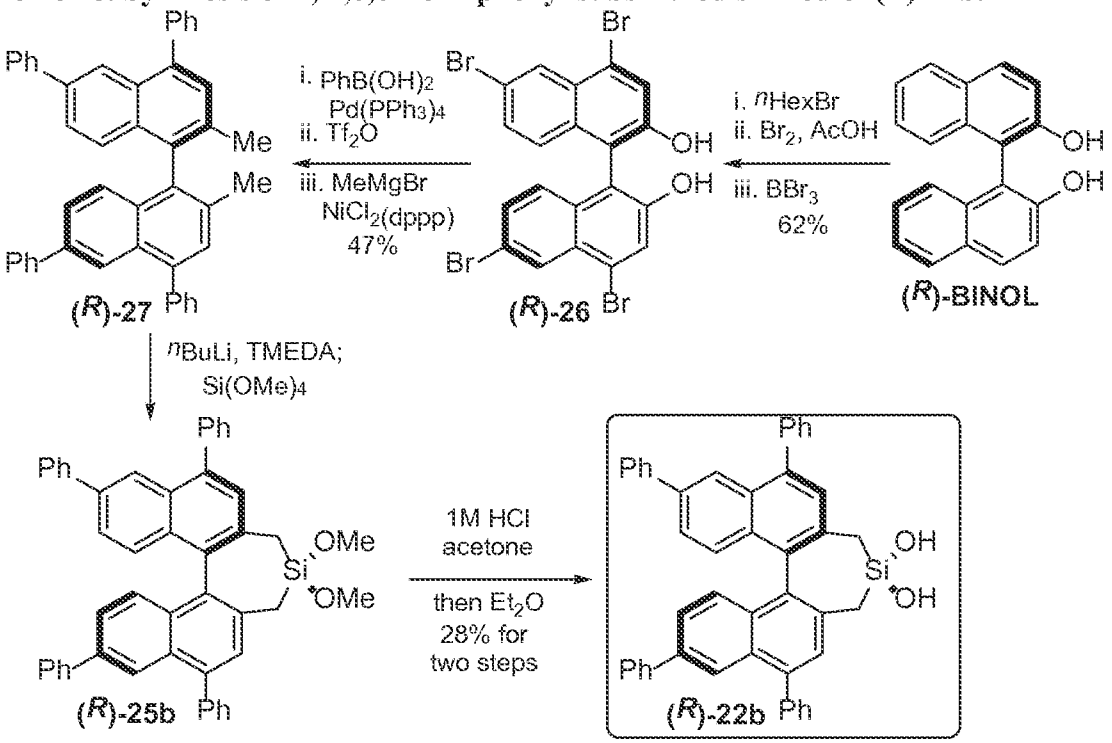
Scheme 17. Synthesis of unsubstituted silanediol (*R*)-22.



After successful synthesis of the unsubstituted silacyclic silanediol **(*R*)-22**, the possibility of adding substitution at various positions on the binaphthyl back bone was then investigated. The rationale being that a highly customizable catalyst scaffold will enable rapid identification of the ideal silanediol catalyst for a given reaction. The synthesis of catalysts substituted with phenyl groups at either or both the 4, 4' and 6, 6' positions was then studied.

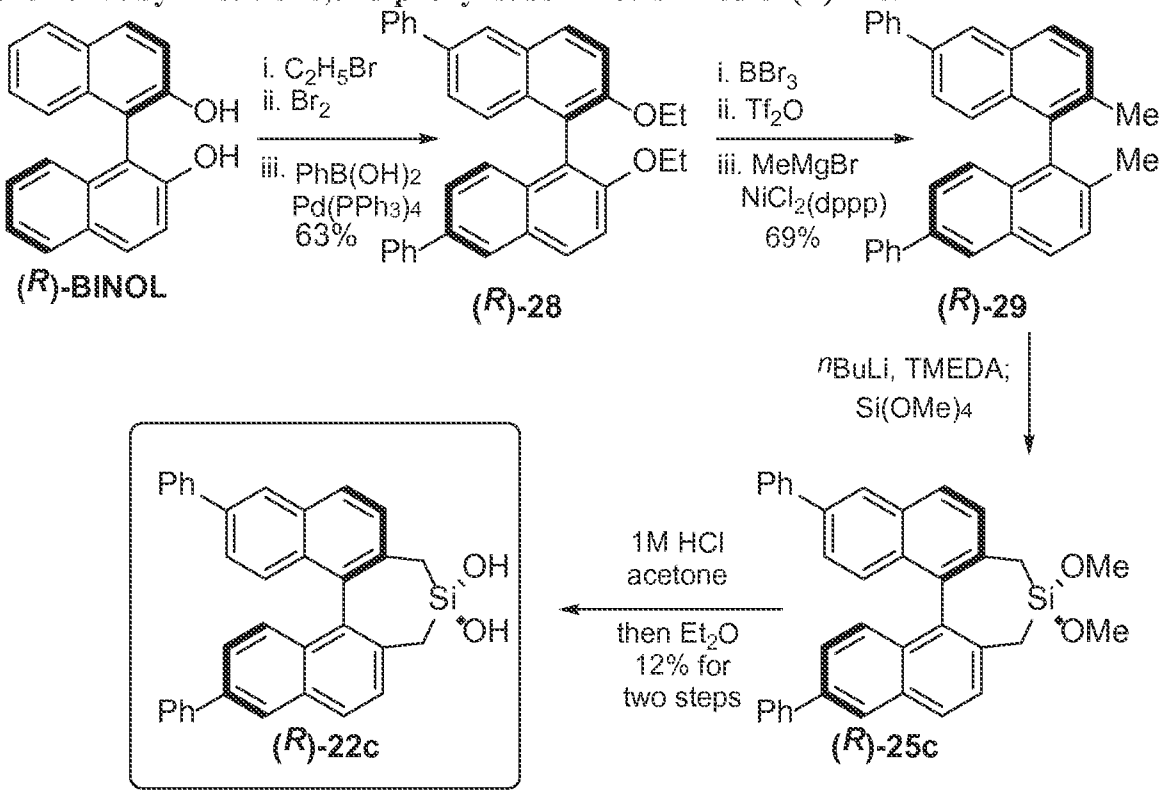
Scheme 18 outlines the general route to the 4,4',6,6'-tetrasubstituted catalysts. Drawing from the established protocols (Hu QS et al., *J. Org. Chem.* **1999**, *64*, 7528–7536), (*R*)-BINOL is bis-*O*-hexylated, followed by four-fold bromination and dealkylation with BBr_3 to provide **(*R*)-26**. A Suzuki-Miyaura cross-coupling with $PhB(OH)_2$ provided the phenyl substituents. Subsequent triflation of the free alcohols in the 2,2' positions enabled a nickel-catalyzed Kumada cross-coupling with MeMgBr provides access to the **(*R*)-27**, the precursor to silacyclization. Deprotonation of the 2,2' methyl groups, affected with *n*-BuLi and TMEDA, was followed with the addition of excess $Si(OMe)_4$ to give the dimethoxysilacycle (*R*)-**25b**. Simple hydrolysis of (*R*)-**25b** with aqueous HCl followed by treatment with diethyl ether and neutralization then afforded silanediol **(*R*)-22b** as a 3:1 complex with Et_2O. Attempts to confirm the structure of (*R*)-**22b** in the solid state led to the formation of a siloxane trimer (Figure 24).

Scheme 18. Synthesis of 4,4',6,6'-tetraphenyl substituted silanediol (*R*)-22b.



Synthesis of the 6,6'-diphenyl substituted silanediol **(*R*)-22c** proceeded in a similar fashion as the tetraphenyl substituted variant (Scheme 19). The notable differences being the regio controlled two-fold bromination of the bis-*O*-ethylated (*R*)-BINOL intermediate at the 6 and 6' positions. A subsequent Suzuki-Miyaura cross-coupling gave rise to intermediate (*R*)-**28**. The deprotection and triflation of the 2,2' hydroxyl groups allowed for their conversion to the requisite methyl group via a nickel-catalyzed cross coupling. The silacyclization of (*R*)-**29** occurred under standard reaction conditions to afford dimethoxysilacycle (*R*)-**25c**. Hydrolysis of (*R*)-**25c** was achieved under standard conditions and (*R*)-**22c** was isolated as a 2:1 complex with Et_2O.

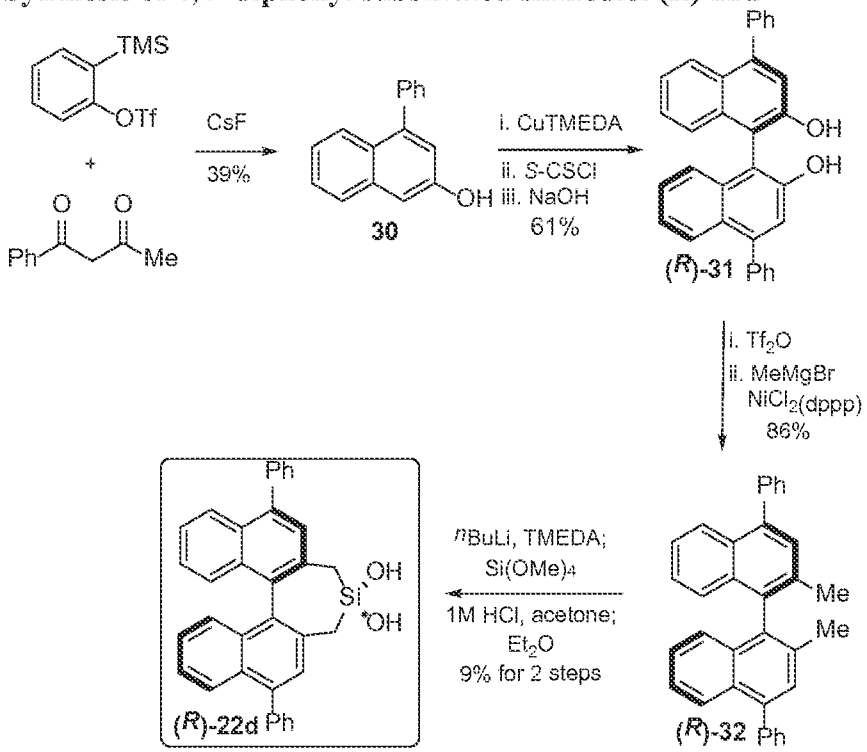
Scheme 19. Synthesis of 6,6'-diphenyl substituted silanediol (*R*)-22c.



Synthesis of the 4,4'-diphenyl substituted silanediol **(*R*)-22d** was planned to proceed in a similar fashion as above, drawing upon literature precedence (Lee SJ et al., *JACS*, **2002**, *124*, 12948–12949). However, difficulties were encountered in obtaining several of the intermediates in sufficient purity. Therefore, a different synthetic route to access this compound was developed. Using a known protocol (Okuma K et al., *Chem. Commun.* **2012**, *48*, 11145–11147), reaction of 2-(trimethylsilyl)phenyltriflate with benzoylacetone in the presence of CsF affords 4-phenyl-2-naphthol (**30**) in 39% yield (Scheme 20). Oxidative coupling with CuTMEDA was followed by resolution with *S*-(+)-camphorsulfonyl chloride

to give, after removal of the chiral auxiliary, enantiopure BINOL **(*R*)-31**. As before, triflation, and Nickel-catalyzed Kumada cross-coupling with MeMgBr provided **(*R*)-32**. After lithiation, silacycle formation and hydrolysis readily afforded the 4,4'-diphenyl substituted silanediol **(*R*)-22d** as a 1:1 complex with ether.

Scheme 20. Synthesis of 4,4'-diphenyl substituted silanediol (*R*)-22d



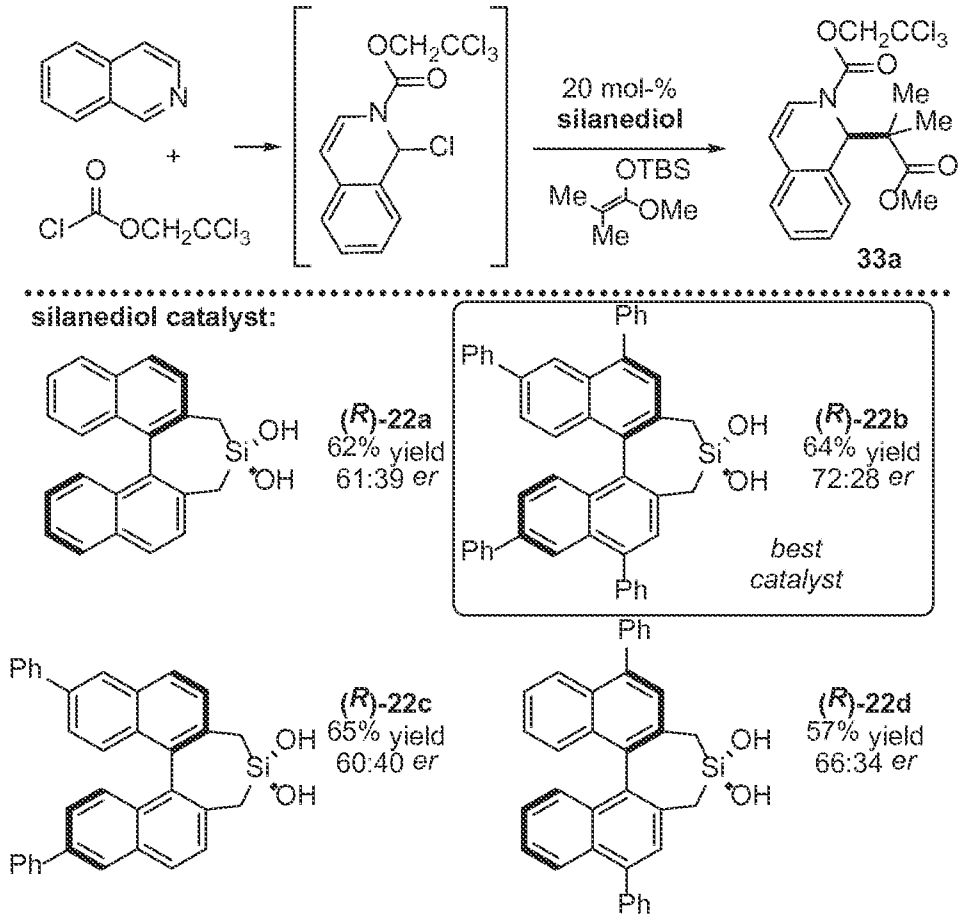
Catalysis with BINOL-Derived Silanediols

With a small family of BINOL-based silanediols in hand, the effect of catalyst structure on activity and stereoselectivity in the addition of silyl ketene acetals to *N*-acyl isoquinolinium ions was studied. This *N*-acyl Mannich reaction was selected as the platform for the structure activity relationship studies as it has been found that silanediols can effect this transformation, possibly via anion-binding catalysis (Schafer AG *et al. Angew. Chem. Int. Ed.* **2013**, *52*, 11321-11324). In general, enantioselective anion-binding catalysis is a relatively new mode of action for HBD catalysts, and previously only ureas and related thioureas had been shown to act as catalysts in this fashion (Brak K *et al. Angew. Chem. Int. Ed.* **2013**, 52, 534-561).

This *N*-acyl Mannich reaction system presented a platform for studying the effect of substitution patterns on the catalytic ability of the silacyclic catalyst (Table 3). The initial finding with unsubstituted silanediol **(*R*)-22a** gave rise to **33a** in 62% yield in an enantiomeric ratio of 61:39. Silanediol (*R*)-**22c** with phenyl rings solely in the 6,6' positions

afforded little improvement over this result, leading to **33a** in 65% yield and 20% enantiomeric excess. On the other hand, adding phenyl rings in the 4,4' positions provided a significant increase in enantiomeric enrichment. Specifically, catalyst (*R*)-**22d** gave rise to 57% of **33a** with a 10% improvement in enantiomeric excess over catalyst (*R*)-**22a**. Adding substitution at the 4,4' and 6,6' positions, e.g. silane diol (*R*)-**22b**, afforded **33a** in good yield with the best enantiomeric ratio (72:28 e.r.). It was impressive that the addition of four phenyl rings to the 4, 4', 6, 6' positions of the silane diol scaffold was able to more than double enantiomeric excess compared to substitution only at the 6,6' position as in catalyst (*R*)-**22c**.

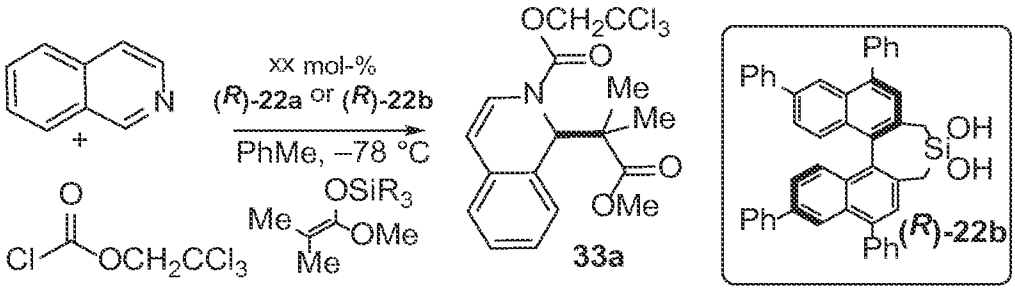
Table 3. Influence of Silanediol Backbone on Enantioselectivity.



Next, it was attempted to alter the reaction conditions to increase both the yield and enantioselectivity. Beginning with unsubstituted silanediol **(*R*)-22a**, the influence of the OR group of the silyl ketene acetal was evaluated (Table 4). Replacing the TBS group with TIPS leads to an increase in e.r. While the ethyl group is tolerated, a slight decrease in selectivity is observed; an increase in steric bulk to an *i*Pr group prevents conversion under

the standard conditions. Diluting the reaction five-fold, and extending the reaction time with 50 mol% of silanediol **(*R*)-22b**, the e.r. is improved to 89:11. Increasing the catalyst loading to 100 mol % of **(*R*)-22b** does not increase the enantioselectivity.

Table 4. Optimization of N-Acyl Mannich Reaction.



entry	cat (mol %)	R_1	conc. (M)	*t* (h)	yield (%)	e.r.
1	(*R*)-22a (20)	Me	0.025	40	71	64:36
2	(*R*)-22a (20)	Et	0.025	40	72	61:39
3	(*R*)-22a (20)	*i*Pr	0.025	40	0	--
5	(*R*)-22b (20)	Me	0.025	40	33	74:26
6	(*R*)-22b (20)	Me	0.0125	40	0	--
7	(*R*)-22b (50)	Me	0.025	40	68	75:25
8	(*R*)-22b (50)	Me	0.0125	72	79	77:23
9	(*R*)-22b (50)	Me	0.005	120	55	89:11
10	(*R*)-22b (100)	Me	0.005	120	43	89:11

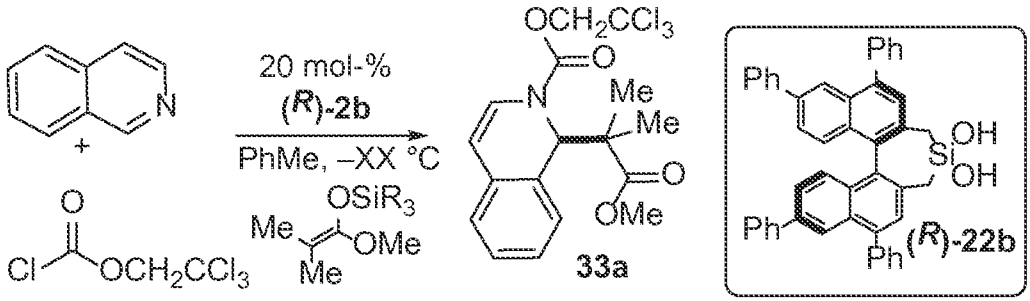
yield determined by ^{1}H NMR analysis; e.r. determined by chiral HPLC analysis.

With tetraphenyl-substituted silane diol (*R*)-**22b** selected as the best catalyst from the small series, next the reaction's sensitivity to other factors, including the effect of the silyl group, concentration, and temperature, was investigated (Table 5). In previous work with the unsubstituted catalyst (*R*)-**22a**, it was observed that more bulky silyl ketene acetals led to improved enantiomeric excesses (Schafer AG *et al. Angew. Chem. Int. Ed.* **2013**, *52*, 11321-11324). Herein, the trimethylsilyl ketene acetal prepared from methyl isobutyrate performed quite poorly, while the triisopropyl silyl keten acetal afforded **33a** in high yield and good enantiomeric excess (entries 1 and 3 in Table 5). A reaction concentration of 0.02 M in toluene proved to be optimal: **33a** was isolated in 69% yield and 83:17 er (entry 5 in Table 5). Diluting the reaction from 0.02 M to 0.005 M gave rise to **33a** in a lower yield and slightly reduced enantiomeric excess (entry 4 in Table 5).

A reaction temperature of -55°C was identified as optimal for both yield and enantioselectivity (entries 5-8 of Table 5). At -45°C, **33a** was isolated in 55% yield with an

enantiomeric ratio of 78:22 under the influence of 20 mol% **22b** (entry 6 in Table 5). At a catalyst loading of 50 mol%, **33a** was isolated in nearly 80% ee at -78°C in 0.005 M toluene, although the yield was just 39% after 120 hours (entry 8 in Table 5).

Table 5. Optimization of *N*-acyl Mannich reaction.

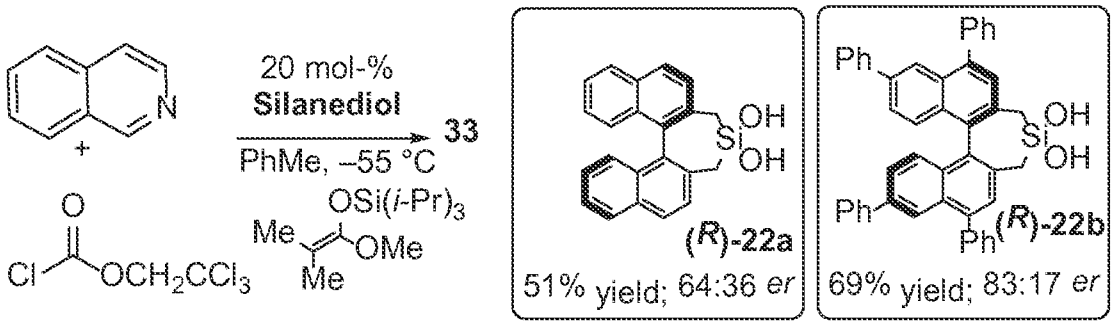


entry	SiR_3	conc. (M)	temp. (°C)	yield(%)	*er*	
1	$SiMe_3$	0.025	–55	68	55:45	*silyl group*
2	$SiMe_2(t\text{-Bu})$	0.025	–55	65	68:32	
3	$Si(i\text{-Pr})_3$	0.025	–55	70	71:29	
4	$Si(i\text{-Pr})_3$	0.005	–55	40	81:19	*concentration*
5	**$Si(i\text{-Pr})_3$**	**0.02**	**–55**	**69**	**83:17**	
6	$Si(i\text{-Pr})_3$	0.02	–45	55	78:22	*temperature*
7	$Si(i\text{-Pr})_3$	0.02	–78	56	70:30	
8[b]	$Si(i\text{-Pr})_3$	0.005	–78	39	89:11	

[b]50 mol % of **(*R*)-22b** added.

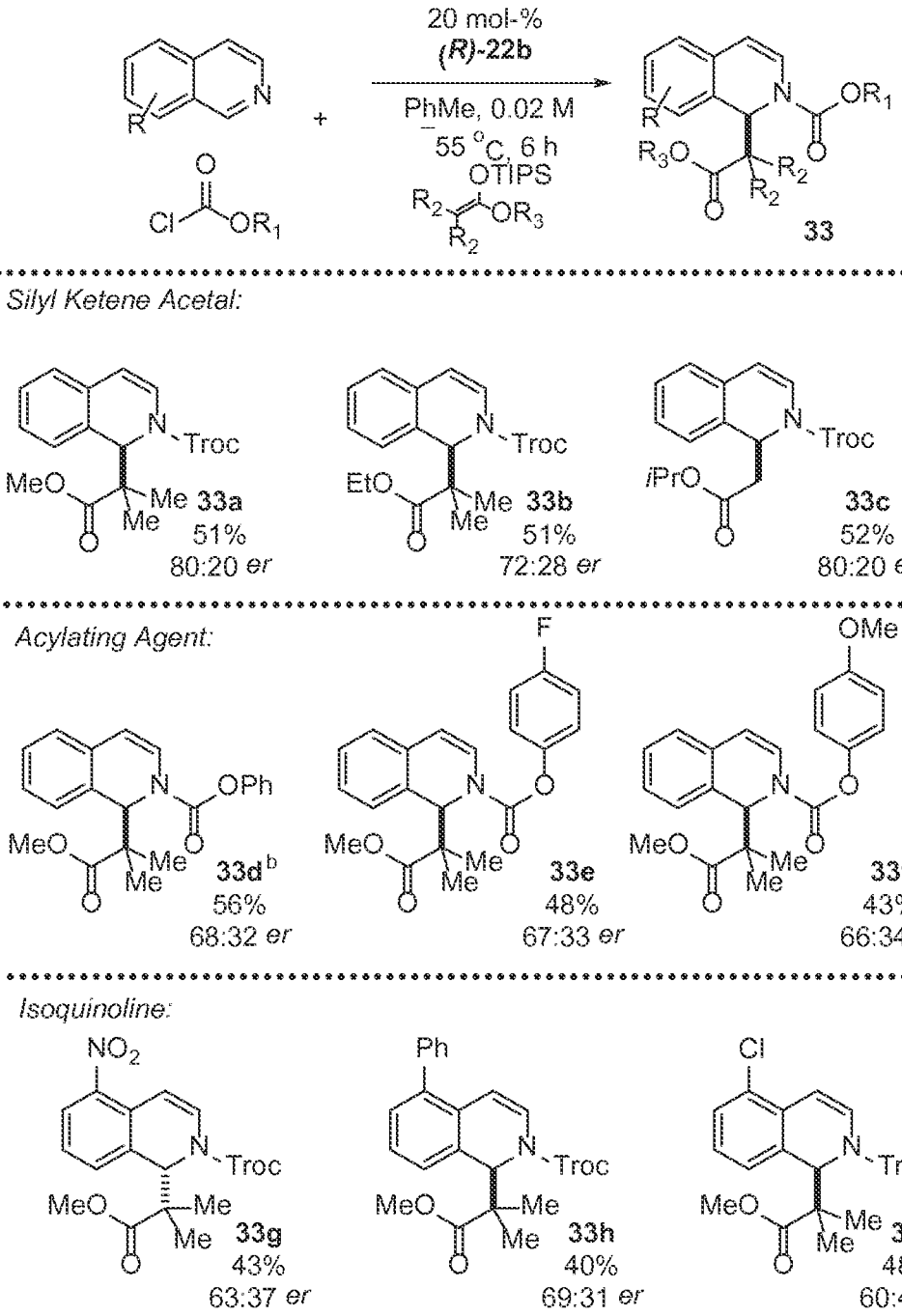
With a set of optimal conditions identified, the effect of substituents in the 4,4',6,6' positions of the BINOL scaffold was re-evaluated (Scheme 21). The more substituted catalyst (*R*)-**22b** was advantageous over the unsubstituted catalyst (*R*)-**22a** in terms of both yield and enantioselectivity.

Scheme 21. Comparison of silane diol catalysts (*R*)-22a to (*R*)-22b under optimized reaction conditions.



A short study of the reaction with respect to silyl ketene acetal, acetylating agent and isoquiniline was also conducted (Table 6). A variety of silyl ketene acetals operated well in the reaction. For instance, the acetal from ethyl isobutyrate gave rise to **33b** in 51% yield and 72:28 er, while the acetal from isopropyl acetate gave rise to **33c** in high yield with excellent levels of enantiocontrol (52% yield, 80:20 er). Although the highest enantiomeric enrichment was observed with the TROC acylating agent, phenyl chloroformate also provided an acceptable yield and enantiomeric enrichment of **33d** (62% yield, 38% ee). The addition of an electron-withdrawing fluoro substituent on the phenyl ring improved conversion by gave rise to **33e** in slightly lower enantiomeric excess. The reaction was least tolerant of substitution patterns on the isoquinoline; only substitution at the 5-position provided reasonable results. 5-Nitoisoquinoline, 5-phenylisoquinoline and 5-chloroisoquinoline afforded **33g-33i** in modest yield and enantiomeric excess.

Table 6. Substrate scope of *N*-acyl Mannich reaction.



[a] Yields after column chromatography on silica gel. [b] –35°C, 14 h.

Silanediol Properties

In order to gain more insight into the salient structural and mechanistic aspects of these catalysts, absolute values for the pK_as and the binding constants with a variety of anions, both of which have been shown to be important properties in HBD organocatalysis reactivity and selectivity (Li X et al., *Chem.–Eur. J.* **2010**, *16*, 450–455), were studied. The Brodwell method has previously been used to determine the pK_as of several urea-based

hydrogen bond donors (Jakab G *et al. Org. Lett.* **2012**, *14*, 1724-1727), the same approach was used to find the pK_as of achiral di(naphthalen-1-yl)silanediol **34**, **(*R*)-22a**, and **(*R*)-22b** (Figure 25). The pK_a values of these three representative silanediols were all ~19 in DMSO. This is in the same range as Jacobsen's chiral thiourea, a catalyst able to induce similar enantioselective *N*-acyl Mannich reactions (Taylor MS *et al. Angew. Chem. Int. Ed.* **2005**, *41*, 6700-6704; Jakab G *et al. Org. Lett.* **2012**, *14*, 1724-1727). Since both reactivity and selectivity are associated with a low pK_a of the HBD catalyst, the fact that the pK_a of all three silanediols tested was ~19 might indicate a lack of tunability within the catalyst structure. However, despite similarities in pK_a, the differences in enantioselectivity of *N*-acyl Mannich observed between the (*R*)-**22a** and (*R*)-**22b** catalysts suggests that factors outside of acidity can influence the ability of silane diols to impart sterocontrol over *N*-acyl Mannich reactions.

The binding affinities for the same silanediols above (e.g., (*R*)-**22a** and (*R*)-**22b**) with chloride in $CDCl_3$ were also determined. Kondo has previously reported the binding constant between chloride and achiral di(naphthalen-1-yl)silanediol **34** to be $1.44 \pm 0.11 \times 10^2$ mol^{-1} dm^3 (Figure 25) (Kondo S et al., *Org. Lett.* **2006**, *8*, 4621–4624). The binding constant for **(*R*)-22a** and **(*R*)-22b** were determined using the same approach as reported by Kondo *et al.* (Kondo S et al., *Org. Lett.* **2006**, *8*, 4621–4624): a ^1H NMR titration of the silanediols with tetrabutylammonium chloride was conducted and the change in chemical shift of the O-H protons was measured. From this data, the binding constant of (*R*)-**22a** and (*R*)-**22b** were determined to be $2.19 \pm 0.03 \times 10^2$ M^{-1} and $3.10 \pm 0.10 \times 10^2$ M^{-1}, respectively (Figure 25).

Figure 26 illustrates the ^1H NMR titration of **(*R*)-22b** with tetrabutylammonium chloride. The binding stoichiometry was determined to be 1:1 silanediol:chloride as can be seen from the maximum at ~ 0.5 in the Job's plot (Figure 27).

Solid state data regarding the silanediols bound with both anions alone (Kondo S *et al. Org. Lett.* **2006**, *8*, 4621-4624) and with isoquinolinium ion pairs also support their anion-binding mode of action and offers insight into potential non-covalent interactions supporting the transition state of the major reaction pathway. The crystal structure of the bis TMS ether **(*R*)-22a** is shown in Figure 23. Additionally, a single crystal of an ion pair composed of di(naphthalen-1-yl)silanediol **34** and the HCl salt of isoquinoline was obtained (Figure 28) (Schafer AG *et al. Angew. Chem. Int. Ed.* **2013**, *52*, 11321-11324).

All of the evidence taken together strongly suggests an anion-binding mode of catalysis (Figure 29). The proposed reaction pathway begins with *in situ* formation of the

acyl isoquinoline (**A**). The silane diol catalyst is then able to encourage formation of the isoquinolinium ion-pair **B** through hydrogen bonding to the chloride. Formation of the carbon-carbon bond occurs upon reaction of **B** with the silyl ketene acetal to yield ion pair **C**. The desilylation of the oxocarbenium ion with chloride then generates the product and frees the silanediol to initiate another reaction.

Conclusions

To conclude, a class of anion-binding organocatalysts that efficiently catalyze enantioselective *N*-acyl Mannich reactions was developed. These modifiable silanediols are readily prepared in enantiopure form and are bench stable indefinitely. The studies herein further suggest a network of noncovalent interactions such as π- π , π-cation, hydrogen bonding and electrostatic forces can contribute to the stabilization of the transition state leading to the major enantiomer.

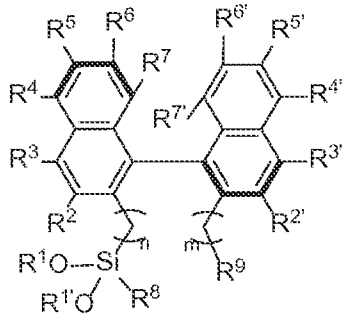
Throughout this application, various publications are referenced. The disclosures of these publications in their entireties are hereby incorporated by reference into this application in order to more fully describe the state of the art to which this invention pertains.

It will be apparent to those skilled in the art that various modifications and variations can be made in the present invention without departing from the scope or spirit of the invention. Other embodiments of the invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with a true scope and spirit of the invention being indicated by the following claims.

CLAIMS

What is claimed is:

1. A compound defined by Formula I:



I

wherein

n = 0 or 1;

m = 0 or 1;

R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl;

R^2, R^3, R^4, R^5, R^6, $R^{2'}$, $R^{3'}$, $R^{4'}$, $R^{5'}$, and $R^{6'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl, or wherein, as valence and stability permit, independently R^2 and R^3, R^3 and R^4, R^4 and R^5, R^5 and R^6, $R^{2'}$ and $R^{3'}$, $R^{3'}$ and $R^{4'}$, $R^{4'}$ and $R^{5'}$, $R^{5'}$ and $R^{6'}$, or $R^{2'}$ and R^9, together with the atoms to which they are attached, form a 3-10 membered substituted or unsubstituted cyclic moiety optionally including between 1 and 3 heteroatoms;

R^7 and $R^{7'}$ are each independently chosen from H, OH, and halogen;

R^8 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy,

substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

R^9 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl;

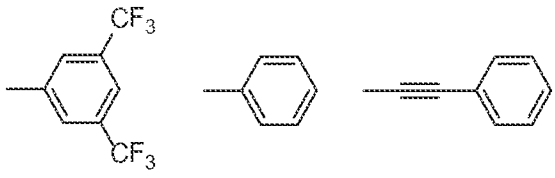
or wherein, as valence and stability permit, R^8 and R^9, together with the atoms to which they are attached, form a 7-9 membered silacycle;

with the proviso that when R^8 and R^9, together with the atoms to which they are attached, form a 7-membered silacycle, R^1, $R^{1'}$, R^3-R^7 and $R^{3'}$-$R^{7'}$ are not all H and R^2 and $R^{2'}$ are not both phenyl.

2. The compound of claim 1, wherein when R^8 and R^9, together with the atoms to which they are attached, form a 9-membered silacycle, R^1, $R^{1'}$, R^2-R^7 and $R^{2'}$-$R^{7'}$ are not all H.

3. The compound of claim 1 or 2, wherein when R^8 and R^9, together with the atoms to which they are attached, form a 9-membered silacycle, R^1 and $R^{1'}$ are not both -CH_3; and R^2-R^7 and $R^{2'}$-$R^{7'}$ are not all H.

4. The compound of any of claims 1-3, wherein when R^8 and R^9, together with the atoms to which they are attached, form a 9-membered silacycle, R^1, $R^{1'}$, R^3-R^7 and $R^{3'}$-$R^{7'}$ are not all H and R^2 and $R^{2'}$ are not both chosen from the moieties shown below.

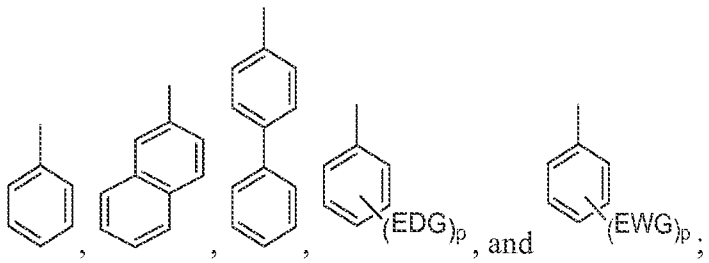


5. The compound of any of claims 1-4, wherein R^1 and $R^{1'}$ are chosen from hydrogen and $-CH_3$.

6. The compound of any of claims 1-5, wherein R^1 and $R^{1'}$ are both hydrogen.

7. The compound of any of claims 1-6, wherein R^2 and $R^{2'}$ are individually chosen from hydrogen, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

8. The compound of any of claims 1-7, wherein R^2 and $R^{2'}$ are independently chosen from the moieties shown below

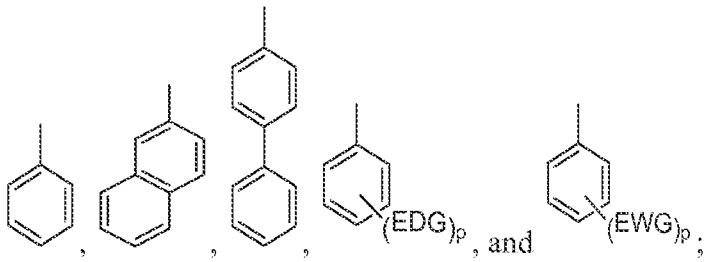


wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and

p is chosen from 1, 2, 3, 4 and 5.

9. The compound of any of claims 1-8, wherein R^3 and $R^{3'}$ are individually chosen from hydrogen, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

10. The compound of any of claims 1-9, wherein R^3 and $R^{3'}$ are independently chosen from the moieties shown below



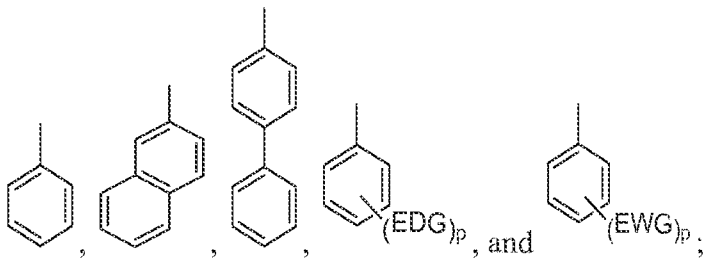
wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and

p is chosen from 1, 2, 3, 4 and 5.

11. The compound of any of claims 1-10, wherein R^4 and $R^{4'}$ are independently chosen from hydrogen, hydroxy, and halogen.

12. The compound of any of claims 1-11, wherein R^5 and $R^{5'}$ are individually chosen from hydrogen, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

13. The compound of any of claims 1-12, wherein R^5 and $R^{5'}$ are independently chosen from the moieties shown below



wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and

p is chosen from 1, 2, 3, 4 and 5.

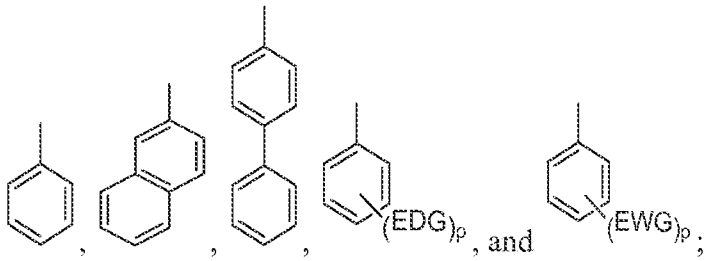
14. The compound of any of claims 1-13, wherein R^6 and $R^{6'}$ are independently chosen from hydrogen, hydroxy, and halogen.

15. The compound of any of claims 1-14, wherein R^7 and $R^{7'}$ are both hydrogen.

16. The compound of any of claims 1-15, wherein R^8 and R^9 are individually chosen from substituted or unsubstituted cycloalkyl, substituted or unsubstituted

alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

17. The compound of any of claims 1-16, wherein R^8 and R^9 are independently chosen from the moieties shown below



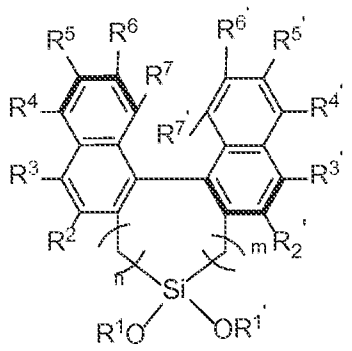
wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and

p is chosen from 1, 2, 3, 4 and 5.

18. The compound of any of claims 8-17, wherein the electron donating group is selected from hydroxy, substituted or unsubstituted amino, substituted or unsubstituted amido, substituted or unsubstituted alkyl, substituted or unsubstituted alkoxy, and substituted or unsubstituted aryl.

19. The compound of any of claims 8-18, wherein the electron withdrawing group is selected from nitro, cyano, and trihalides.

20. The compound of any of claims 1-19, wherein the compound is defined by Formula II



II

wherein

n = 0 or 1;

m = 0 or 1;

R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl;

R^2, R^3, R^4, R^5, R^6, $R^{2'}$, $R^{3'}$, $R^{4'}$, $R^{5'}$, and $R^{6'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl, or wherein, as valence and stability permit, independently R^2 and R^3, R^3 and R^4, R^4 and R^5, R^5 and R^6, $R^{2'}$ and $R^{3'}$, $R^{3'}$ and $R^{4'}$, $R^{4'}$ and $R^{5'}$, or $R^{5'}$ and $R^{6'}$, together with the atoms to which they are attached, form a 3-10 membered substituted or unsubstituted cyclic moiety optionally including between 1 and 3 heteroatoms; and

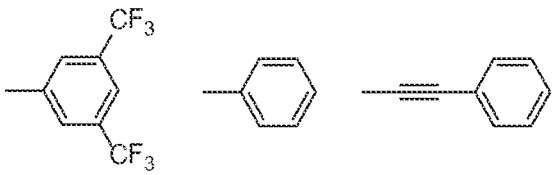
R^7 and $R^{7'}$ are each independently chosen from H, OH, and halogen;

with the proviso that when n=0 and m=0, R^1, $R^{1'}$, R^3-R^7 and $R^{3'}$-$R^{7'}$ are not all H and R^2 and $R^{2'}$ are not both phenyl.

21. The compound of claim 20, wherein when n is 1 and m is 1, R^1, $R^{1'}$, R^2-R^7 and $R^{2'}$-$R^{7'}$ are not all H.

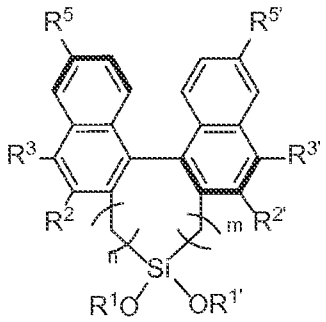
22. The compound of claim 20 or 21, wherein when n is 1 and m is 1, R^1 and $R^{1'}$ are both $-CH_3$; and R^2-R^7 and $R^{2'}$-$R^{7'}$ are not all H.

23. The compound of any of claims 20-22, wherein when n is 1 and m is 1, R^1, $R^{1'}$, R^3-R^7 and $R^{3'}$-$R^{7'}$ are not all H and R^2 and $R^{2'}$ are not both chosen from the moieties below:



24. The compound of any of claims 20-23, wherein n is 1 and m is 1.

25. The compound of any of claims 20-24, wherein the compound is defined by Formula III:



III

wherein

n = 0 or 1;

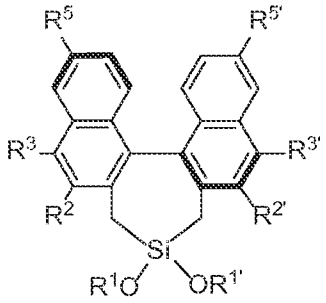
m = 0 or 1;

R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl; and

R^2, R^3, R^5, $R^{2'}$, $R^{3'}$, and $R^{5'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl, or wherein, as valence and stability permit, R^2 and R^3, and/or $R^{2'}$ and $R^{3'}$, together with the atoms to which they are attached, form a 3-10 membered substituted or unsubstituted cyclic moiety optionally including between 1 and 3 heteroatoms;

with the proviso that when n=0 and m=0, R^1, $R^{1'}$, R^3, R^5, $R^{3'}$, and $R^{5'}$ are not all H, and R^2 and $R^{2'}$ are not both phenyl.

26. The compound of claim 25, wherein the compound is defined by Formula IIIa:



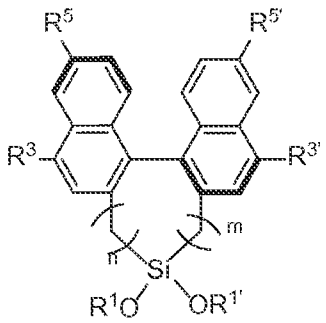
IIIa

wherein

R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl; and

R^2, R^3, R^5, $R^{2'}$, $R^{3'}$, and $R^{5'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl, or wherein, as valence and stability permit, independently R^2 and R^3, and/or $R^{2'}$ and $R^{3'}$ together with the atoms to which they are attached, form a 3-10 membered substituted or unsubstituted cyclic moiety optionally including between 1 and 3 heteroatoms.

27. The compound of any of claims 20-25, wherein the compound is defined by Formula IV:



IV

wherein

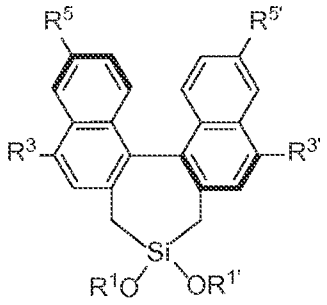
n = 0 or 1;

m = 0 or 1;

R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl; and

R^3, R^5, $R^{3'}$, and $R^{5'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

28. The compound of claim 27, wherein the compound is defined by Formula IVa:



IVa

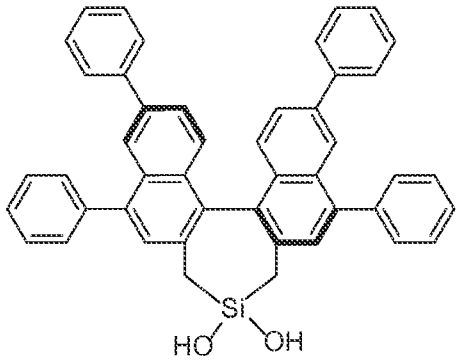
wherein

R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl; and

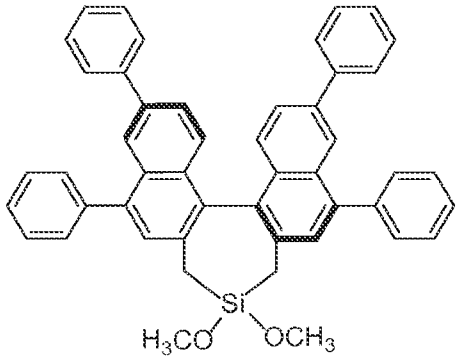
R^3, R^5, $R^{3'}$, and $R^{5'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or

unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

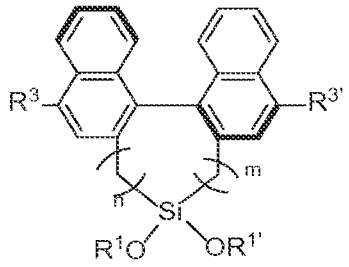
29. The compound of claim 27 or 28, wherein the compound is defined by the formula:



30. The compound of claim 27 or 28, wherein the compound is defined by the formula:



31. The compound of any of claims 20-26, wherein the compound is defined by Formula V:



V

wherein

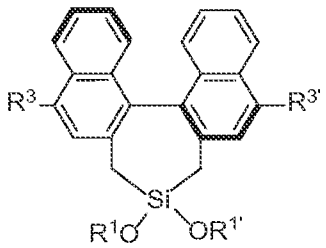
n = 0 or 1;

m = 0 or 1;

R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl; and

R^3 and $R^{3'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

32. The compound of claim 31, wherein the compound is defined by Formula Va:



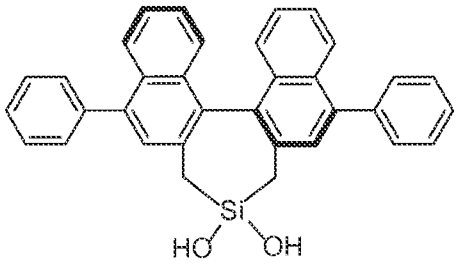
Va

wherein

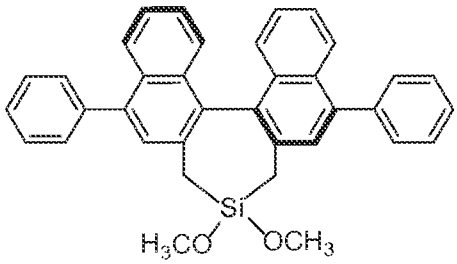
R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl; and

R^3 and $R^{3'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

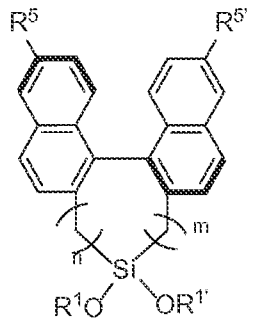
33. The compound of claim 31 or 32, wherein the compound is defined the formula:



34. The compound of claim 31 or 32, wherein the compound is defined by the formula:



35. The compound of any of claims 20-26, wherein the compound is defined by Formula VI:



VI

wherein

n = 0 or 1;

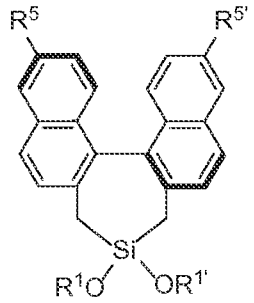
m = 0 or 1;

R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl; and

R^5 and $R^{5'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted

or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl..

36. The compound of claim 35, wherein the compound is defined by Formula VIa:



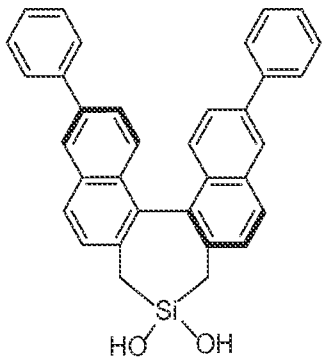
VIa

wherein

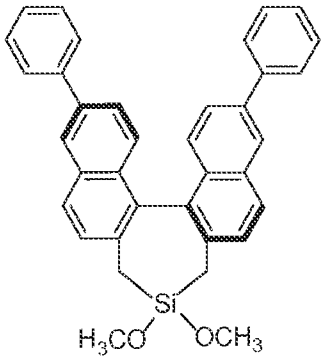
R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl; and

R^5 and $R^{5'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

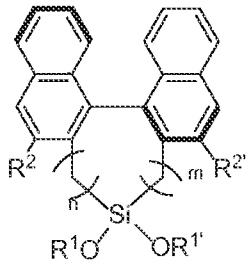
37. The compound of claim 35 or 36, wherein compound is defined be the formula:



38. The compound of claim 35 or 36, wherein the compound is defined be the formula:



39. The compound of any of claims 20-26, wherein the compound is defined by Formula VII:



VII

wherein

n = 0 or 1;

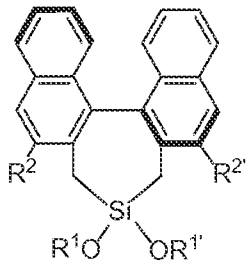
m = 0 or 1;

R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl; and

R^2 and $R^{2'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl;

with the proviso that when n=0 and m=0, R^1 and $R^{1'}$ are both H and R^2 and $R^{2'}$ are not both phenyl.

40. The compound of claim 39, wherein the compound is defined by Formula VIIa:



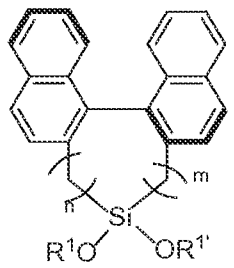
VIIa

wherein

R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl; and

R^2 and $R^{2'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

41. The compound of any of claims 20-26, wherein the compound is defined by Formula VIII:



VIII

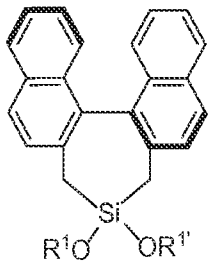
wherein

n = 0 or 1;

m = 0 or 1; and

R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl.

42. The compound of claim 41, wherein the compound is defined by Formula VIIIa:

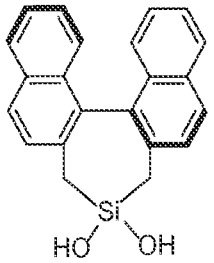


VIIIa

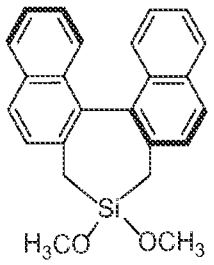
wherein

R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl.

43. The compound of claim 41 or 42, wherein the compound is defined by the formula:



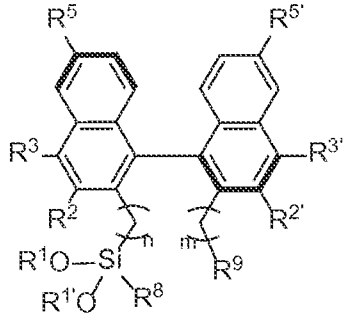
44. The compound of claim 41 or 42, wherein the compound is defined by the formula:



45. The compound of any of claims 20-44, wherein the compound is a complex with diethyl ether.

46. The compound of claim 45, wherein the compound is a 2:1 complex with diethyl ether.

47. The compound of any of claims 1-19, wherein the compound is defined by Formula IX:



IX

wherein

n = 0 or 1;

m = 0 or 1;

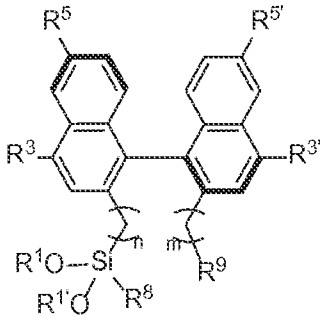
R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl;

R^2, R^3, R^5, $R^{2'}$, $R^{3'}$, and $R^{5'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl, or wherein, as valence and stability permit, independently R^2 and R^3, $R^{2'}$ and $R^{3'}$, or $R^{2'}$ and R^9, together with the atoms to which they are attached, form a 3-10 membered substituted or unsubstituted cyclic moiety optionally including between 1 and 3 heteroatoms; and

R^8 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

R^9 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

48. The compound of any of claims 1-19, wherein the compound is defined by Formula X:



X

wherein

n = 0 or 1;

m = 0 or 1;

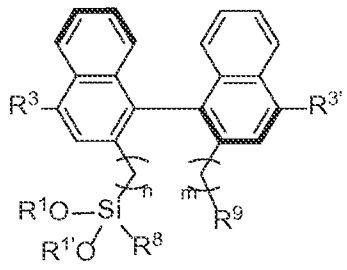
R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl;

R^3, R^5, $R^{3'}$, and $R^{5'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

R^8 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

R^9 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

49. The compound of any of claims 1-19, wherein the compound is defined by Formula XI:



XI

wherein

n = 0 or 1;

m = 0 or 1;

R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl;

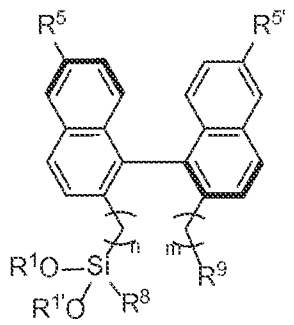
R^3 and $R^{3'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl,

substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

R^8 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

R^9 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

50. The compound of any claims 1-19, wherein the compound is defined by Formula XII:



XII

wherein

n = 0 or 1;

m = 0 or 1;

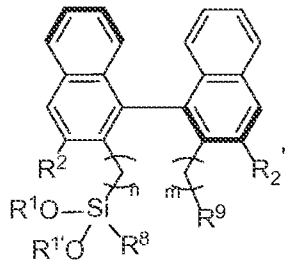
R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl;

R^5 and $R^{5'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

R^8 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

R^9 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

51. The compound of any of claims 1-19, wherein the compound is defined by Formula XIII:



XIII

wherein

n = 0 or 1;

m = 0 or 1;

R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl;

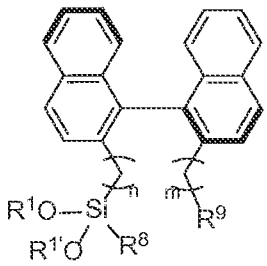
R^2 and $R^{2'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

R^8 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

R^9 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or

unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

52. The compound of any of claims 1-19, wherein the compound is defined by Formula XIV:



XIV

wherein

n = 0 or 1;

m = 0 or 1; and

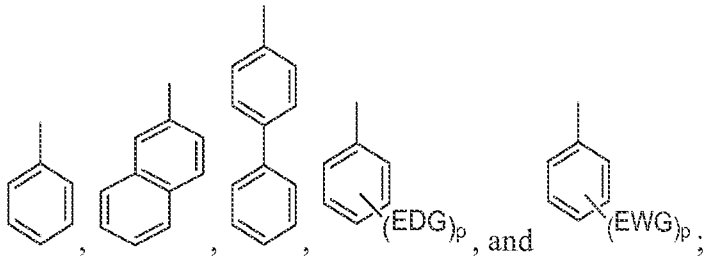
R^1 and $R^{1'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl; and

R^8 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

R^9 is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

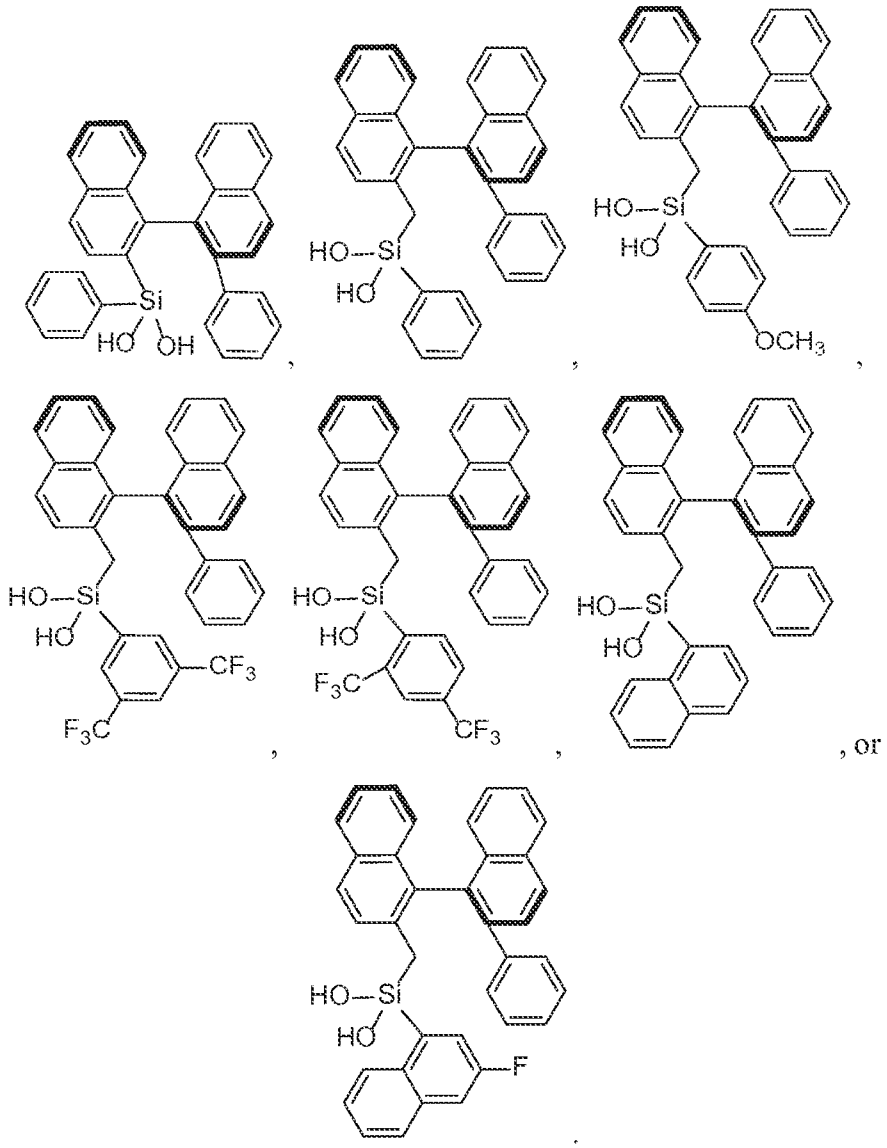
53. The compound of any of claims 48-52, wherein m is 0 and R^9 is substituted or unsubstituted aryl.

54. The compound of any of claims 48-53, wherein R^8 is chosen from the moieties shown below

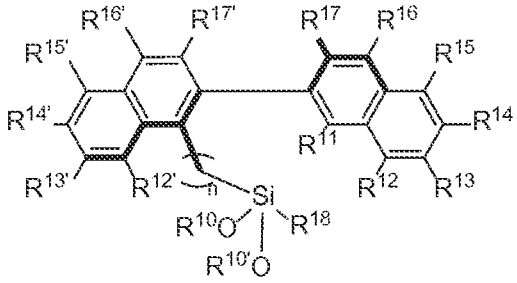


wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5

55. The compound of any of claims 48-54, wherein the compound is



56. A compound defined by Formula XV:



XV

wherein

n = 0 or 1;

R^{10} and $R^{10'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl;

R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, R^{16}, R^{17}, $R^{12'}$, $R^{13'}$, $R^{14'}$, $R^{15'}$, $R^{16'}$, and $R^{17'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl, or wherein, as valence and stability permit, independently R^{11} and R^{12}, R^{12} and R^{13}, R^{13} and R^{14}, R^{14} and R^{15}, R^{15} and R^{16}, R^{16} and R^{17}, $R^{12'}$ and $R^{13'}$, $R^{13'}$ and $R^{14'}$, $R^{14'}$ and $R^{15'}$, $R^{15'}$ and $R^{16'}$, or $R^{16'}$ and $R^{17'}$, together with the atoms to which they are attached, form a 3-10 membered substituted or unsubstituted cyclic moiety optionally including between 1 and 3 heteroatoms; and

R^{18} is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl,

substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

57. The compound of claim 56, wherein R^{10} and $R^{10'}$ are chosen from hydrogen and $-CH_3$.

58. The compound of any of claims 56 or 57, wherein R^{11} is selected from hydrogen, hydroxy, and halogen.

59. The compound of any of claims 56-58, wherein R^{12} and $R^{12'}$ are independently chosen from hydrogen, hydroxy, and halogen.

60. The compound of any of claims 56-59, wherein R^{13} and $R^{13'}$ are independently chosen from hydrogen, hydroxy, and halogen.

61. The compound of any of claims 56-58, wherein R^{12} and R^{13} together with the atoms to which they are attached, form a 5-7 membered substituted or unsubstituted cyclic moiety optionally including between 1 and 3 heteroatoms.

62. The compound of claim 61, wherein R^{12} and R^{13} together with the atoms to which they are attached, form a substituted or unsubstituted phenyl moiety.

63. The compound of any of claims 56-58 or 59-60, wherein $R^{12'}$ and $R^{13'}$ together with the atoms to which they are attached, form a 5-7 membered substituted or unsubstituted cyclic moiety optionally including between 1 and 3 heteroatoms.

64. The compound of claim 63, wherein $R^{12'}$ and $R^{13'}$ together with the atoms to which they are attached, form a substituted or unsubstituted phenyl moiety.

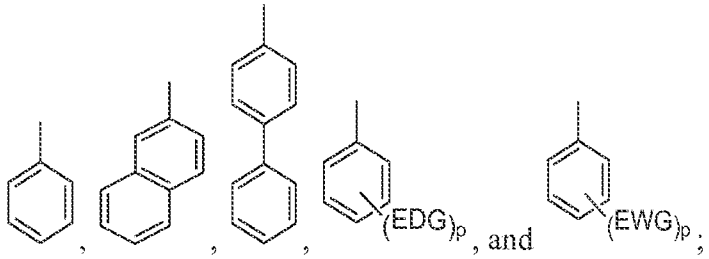
65. The compound of any of claims 56-64, wherein R^{14} and $R^{14'}$ are independently chosen from hydrogen, hydroxy, and halogen.

66. The compound of any of claims 56-65, wherein R^{15} and $R^{15'}$ are independently chosen from hydrogen, hydroxy, and halogen.

67. The compound of any of claims 56-66, wherein R^{16} and $R^{16'}$ are independently chosen from hydrogen, hydroxy, and halogen.

68. The compound of any of claims 56-67, wherein R^{17} and $R^{17'}$ are individually chosen from hydrogen, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

69. The compound of any of claims 56-68, wherein R^{17} and $R^{17'}$ are independently chosen from the moieties shown below

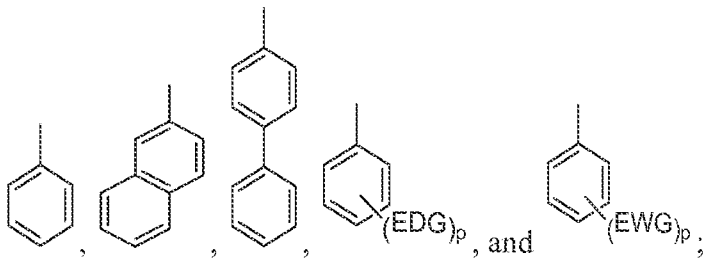


wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and

p is chosen from 1, 2, 3, 4 and 5.

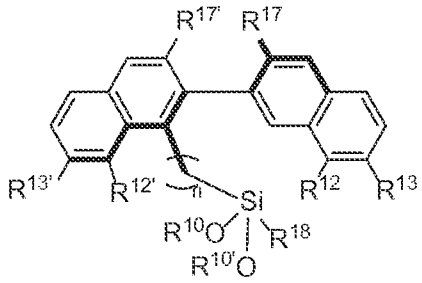
70. The compound of any of claims 56-69, wherein R^{18} is chosen from substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

71. The compound of any of claims 56-70, wherein R^{18} is chosen from the moieties shown below



wherein EDG represents an electron donating group and EWG represents an electron withdrawing group, and p is chosen from 1, 2, 3, 4 and 5.

72. The compound of any of claims 56-71, wherein the compound is defined by Formula XVa:



XVa

wherein

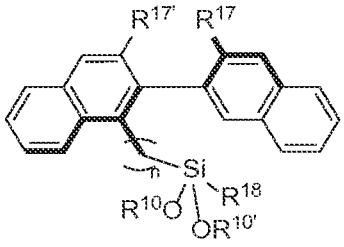
n = 0 or 1;

R^{10} and $R^{10'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl;

R^{12}, R^{13}, R^{17}, $R^{12'}$, $R^{13'}$, and $R^{17'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl, or wherein, as valence and stability permit, independently R^{12} and R^{13}, or $R^{12'}$ and $R^{13'}$, together with the atoms to which they are attached, form a 3-10 membered substituted or unsubstituted cyclic moiety optionally including between 1 and 3 heteroatoms; and

R^{18} is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

73. The compound of claim 72, wherein the compound is defined by Formula XVb:



XVb

wherein

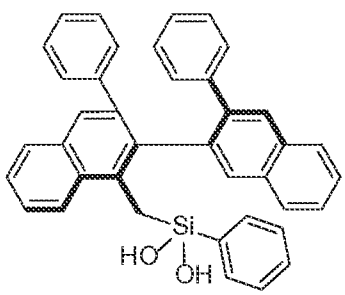
n = 0 or 1;

R^{10} and $R^{10'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl;

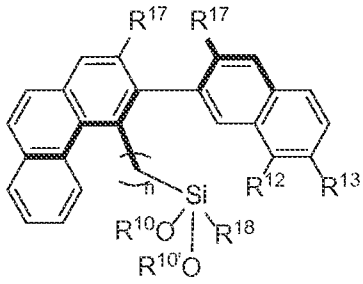
R^{17} and $R^{17'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

R^{18} is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

74. The compound of claim 73, wherein the compound is defined by the formula:



75. The compound of claim 72, wherein the compound is defined by Formula XVc:



XVc

wherein

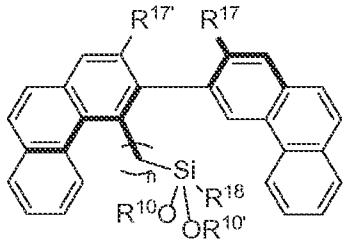
n = 0 or 1;

R^{10} and $R^{10'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl;

R^{12}, R^{13}, R^{17}, and $R^{17'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl, or wherein, as valence and stability permit, R^{12} and R^{13}, together with the atoms to which they are attached, form a 3-10 membered substituted or unsubstituted cyclic moiety optionally including between 1 and 3 heteroatoms; and

R^{18} is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

76. The compound of claim 75, wherein the compound is defined by Formula XVd:



XVd

wherein

n = 0 or 1;

R^{10} and $R^{10'}$ are each independently chosen from H and substituted or unsubstituted C_1-C_4 alkyl;

R^{17} and $R^{17'}$ are each independently chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted amino, silyl, thiol, substituted or unsubstituted thioalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl; and

R^{18} is chosen from hydrogen, halogen, hydroxy, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted haloalkyl, substituted or unsubstituted alkoxy, substituted or unsubstituted cycloalkyl, substituted or unsubstituted alkylcycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted alkylheterocycloalkyl, substituted or unsubstituted alkylaryl, substituted or unsubstituted aryl, substituted or unsubstituted alkylheteroaryl, or substituted or unsubstituted heteroaryl.

77. A catalytic composition comprising a compound defined by any of claims 1-76.

78. A method of performing a reaction selected from

(a) a nucleophilic conjugate addition reaction, in which a first organic species comprising a nitroalkene reacts with a second organic species comprising a nucleophile to provide a product; or

(b) an acyl Mannich type reaction in which a first organic species comprising an amine reacts with a second organic species comprising a carbonyl containing compound to provide a product;

(c) an epoxide ring opening reaction, in which a first organic species comprising an epoxide reacts with a second organic species comprising a nucelophile to provide a product;

(d) a sequestration of carbon dioxide reaction, in which a first organic species comprising carbon dioxide reacts with a second organic species comprising a reservoir to provide a product;

the method comprising contacting the first organic species and the second organic species with a catalytically effective amount of a compound defined by any of claims 1-76 or the catalyst composition defined by claim 77 under conditions effective to form the product.

79. A method of detecting an analyte comprising contacting the analyte with a compound defined by any of claims 1-76, and evaluating an optical property of the compound to detect, identify, or quantify the analyte.

80. The method of claim 79, wherein the optical property of the compound comprises luminescence.

81. The method of claim 79 or 80, wherein the luminescence comprises fluorescence.

82. The method of any of claims 79-81, wherein the optical property includes a change in the fluorescence of the compound upon contacting the analyte.

83. The method of any of claims 79-82, wherein the analyte comprises a chiral compound.

84. The method of any of claims 79-83, wherein the analyte comprises an anion.

9a WITH 8-TMS, 20 mol% *R*-3

DEFAULT REPORT

PEAK#	TIME[min]	AREA[μV·s]	HEIGHT [μV]	AREA[%]	NORM. AREA[%]	BL	AREA/HEIGHT [s]
1	12.782	28679960.44	1.19e+06	45.76	45.76	*BB	24.0364
2	15.667	33994943.81	1.01e+06	54.24	54.24	*BB	33.5116

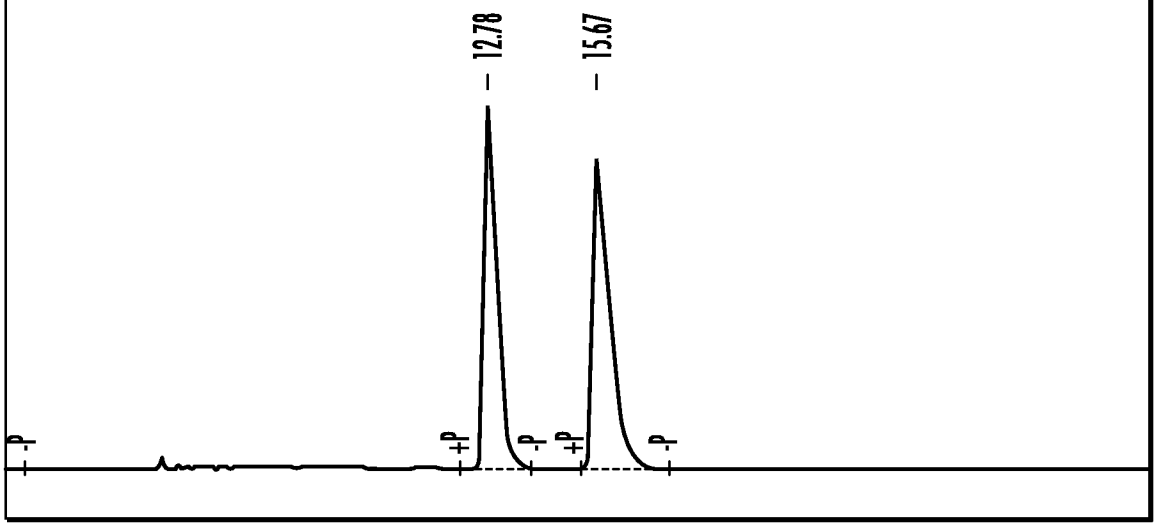


FIG. 1

9a WITH 8-TBS, 20 mol% *R*-3

DEFAULT REPORT

PEAK#	TIME[min]	AREA[μV·s]	HEIGHT [μV]	AREA[%]	NORM. AREA[%]	BL	AREA/HEIGHT [s]
1	13.288	29567891.85	1.18e+06	41.14	41.14	*BB	25.1374
2	16.240	42310266.64	1.15e+06	58.86	58.86	*BB	36.9046

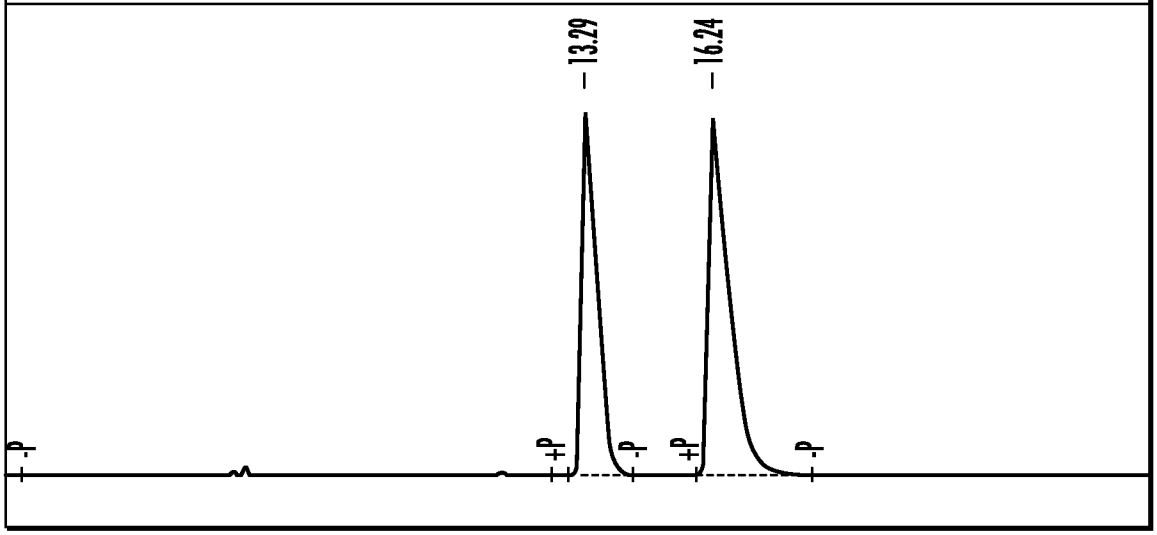


FIG. 2

9a WITH 8-TIPS, 20 mol% *R*-3

DEFAULT REPORT

PEAK#	TIME[min]	AREA[μV·s]	HEIGHT [μV]	AREA[%]	NORM. AREA[%]	BL	AREA/HEIGHT [s]
1	12.812	4635149.86	210635.39	36.48	36.48	BB	22.0056
2	15.575	8069534.84	243971.82	63.52	63.52	BB	33.0757

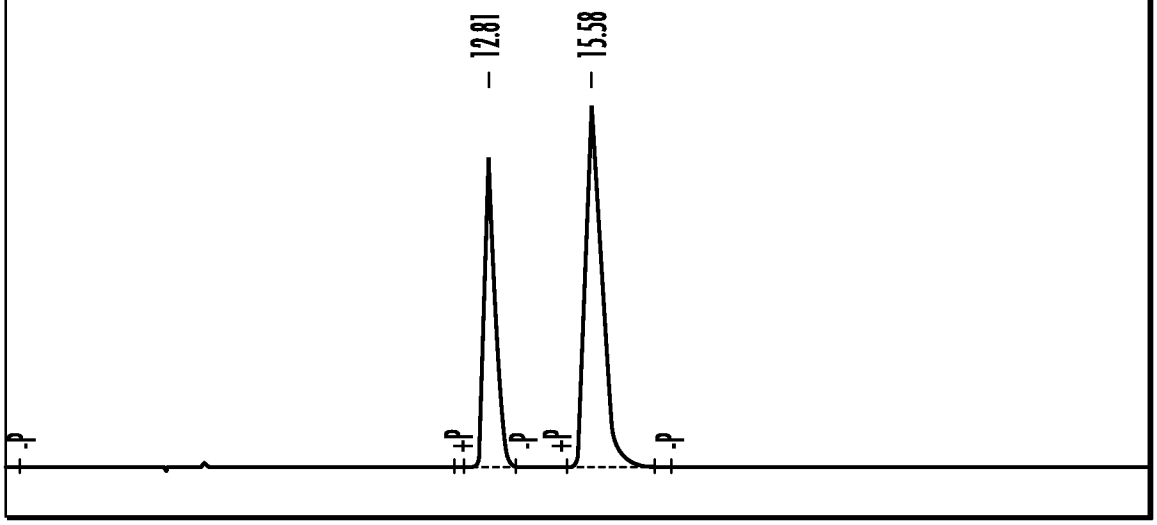


FIG. 3

9a WITH 8-TIPS, 100 mol% *R*-3

DEFAULT REPORT

PEAK#	TIME[min]	AREA[μV·s]	HEIGHT [μV]	AREA[%]	NORM. AREA[%]	BL	AREA/HEIGHT [s]
1	14.134	2421693.24	109385.42	31.26	31.26	BB	22.1391
2	17.695	5324340.30	179739.69	68.74	68.74	BB	29.6225

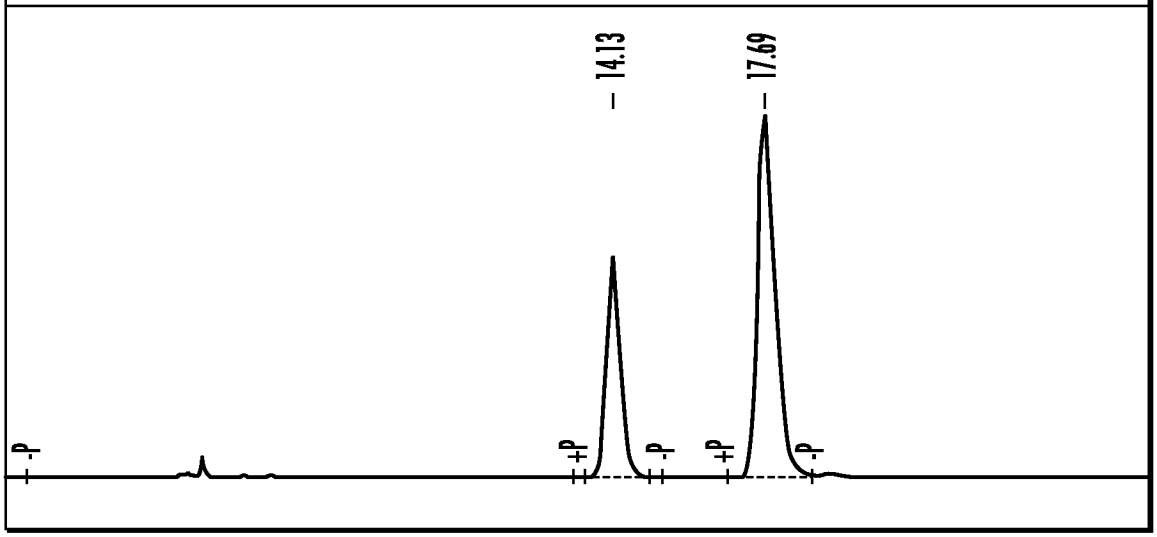


FIG. 4

9b WITH 8-TIPS, 20 mol% *R*-3

DEFAULT REPORT

PEAK#	TIME[min]	AREA[μV·s]	HEIGHT [μV]	AREA[%]	NORM. AREA[%]	BL	AREA/HEIGHT [s]
1	12.457	23459602.16	1.01e+06	37.27	37.27	*BB	23.1815
2	18.256	39483225.46	910085.55	62.73	62.73	BB	43.3841

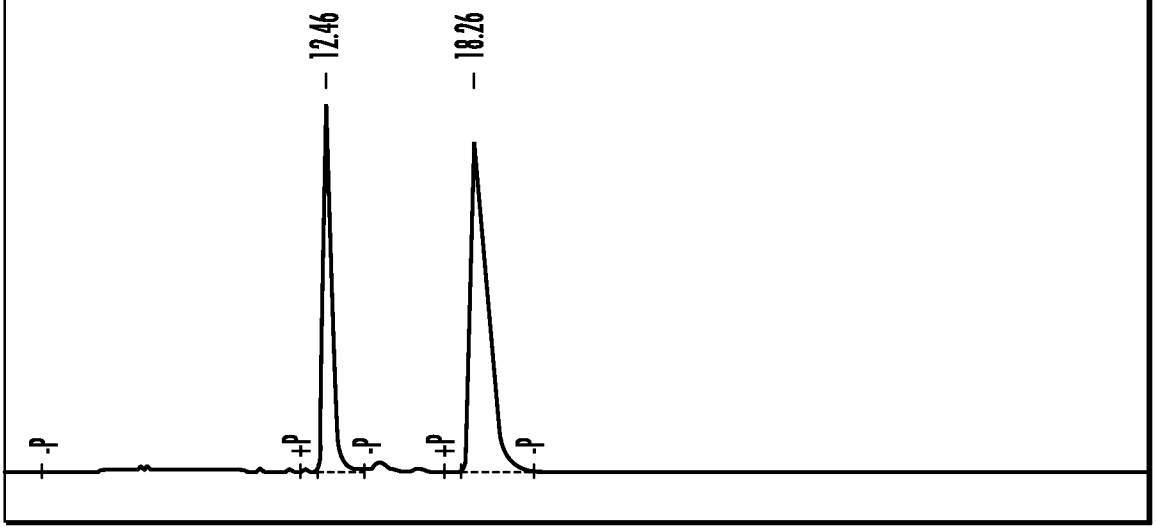


FIG. 5

9b WITH 8-TBS, 20 mol% *R*-3

DEFAULT REPORT

PEAK#	TIME[min]	AREA[μV·s]	HEIGHT [μV]	AREA[%]	NORM. AREA[%]	BL	AREA/HEIGHT [s]
1	14.486	1541333.63	62017.62	41.43	41.43	BB	24.8532
2	22.225	2178579.89	55269.36	58.57	58.57	BB	39.4175

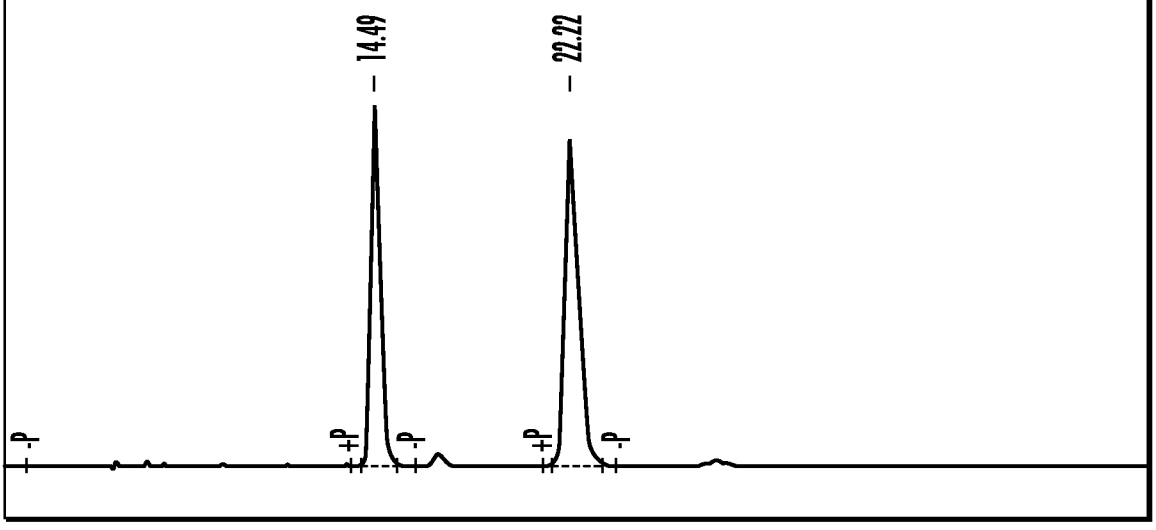


FIG. 6

9c WITH 8-TIPS, 20 mol% *R*-3

DEFAULT REPORT

PEAK#	TIME[min]	AREA[μV·s]	HEIGHT [μV]	AREA[%]	NORM. AREA[%]	BL	AREA/HEIGHT [s]
1	11.360	2698375.00	133355.93	33.96	33.96	BB	20.2344
2	17.037	5247996.32	169385.43	66.04	66.04	BB	30.9826

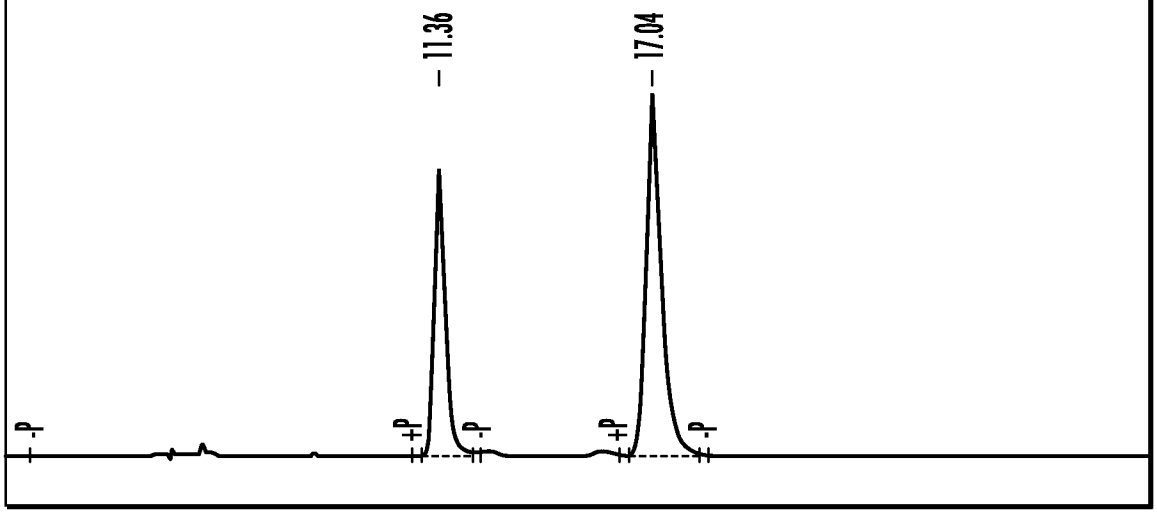


FIG. 7

9c WITH 8-TBS, 20 mol% *R*-3

DEFAULT REPORT

PEAK#	TIME[min]	AREA[μV·s]	HEIGHT [μV]	AREA[%]	NORM. AREA[%]	BL	AREA/HEIGHT [s]
1	13.296	4713093.97	208206.82	39.45	39.45	BB	22.6366
2	20.475	7232556.24	187814.49	60.55	60.55	BB	38.5090

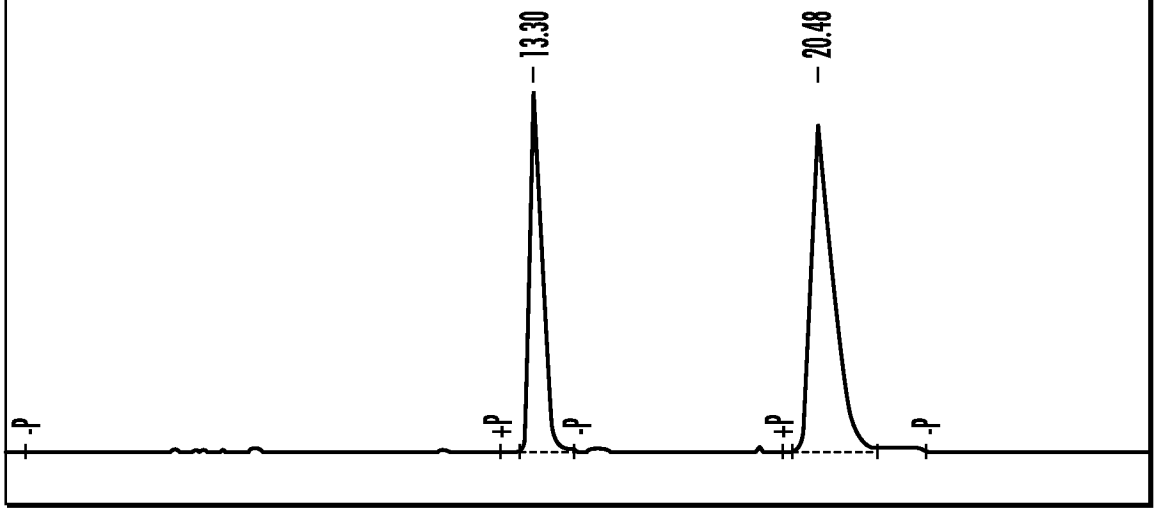


FIG. 8

9d WITH 8-TIPS, 20 mol% *R*-3

DEFAULT REPORT

PEAK#	TIME[min]	AREA[μV·s]	HEIGHT [μV]	AREA[%]	NORM. AREA[%]	BL	AREA/HEIGHT [s]
1	15.660	11867230.28	309409.58	58.29	58.29	BB	38.3544
2	22.068	8492864.29	170617.58	41.71	41.71	BB	49.7772

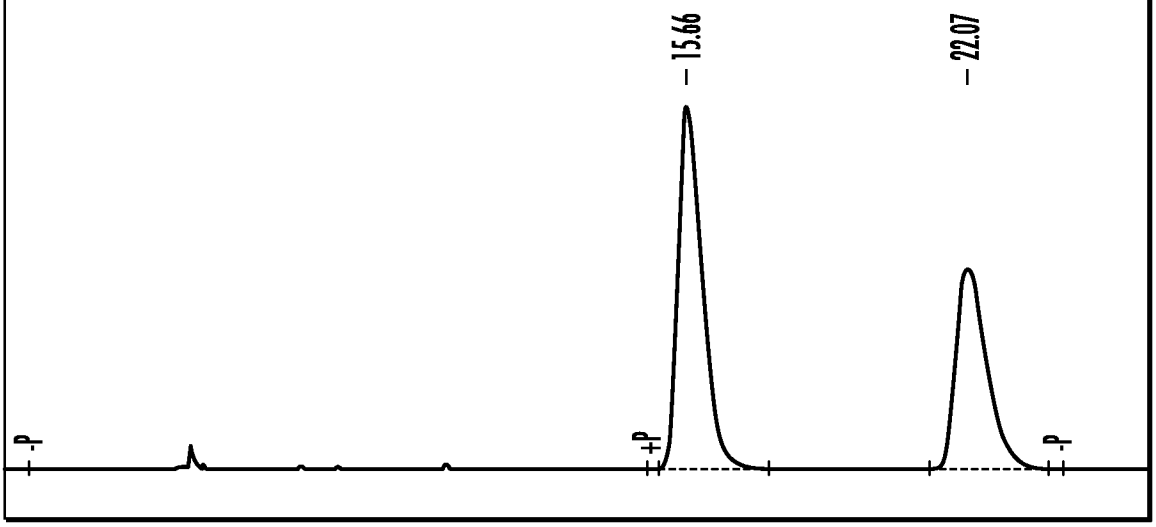


FIG. 9

9d WITH 8-TIPS, 20 mol% *R*-3

DEFAULT REPORT

PEAK#	TIME[min]	AREA[μV·s]	HEIGHT [μV]	AREA[%]	NORM. AREA[%]	BL	AREA/HEIGHT [s]
1	16.220	39139450.27	1.24e+06	74.94	74.94	BB	31.6089
2	23.048	13091334.15	296417.46	25.06	25.06	BB	44.1652

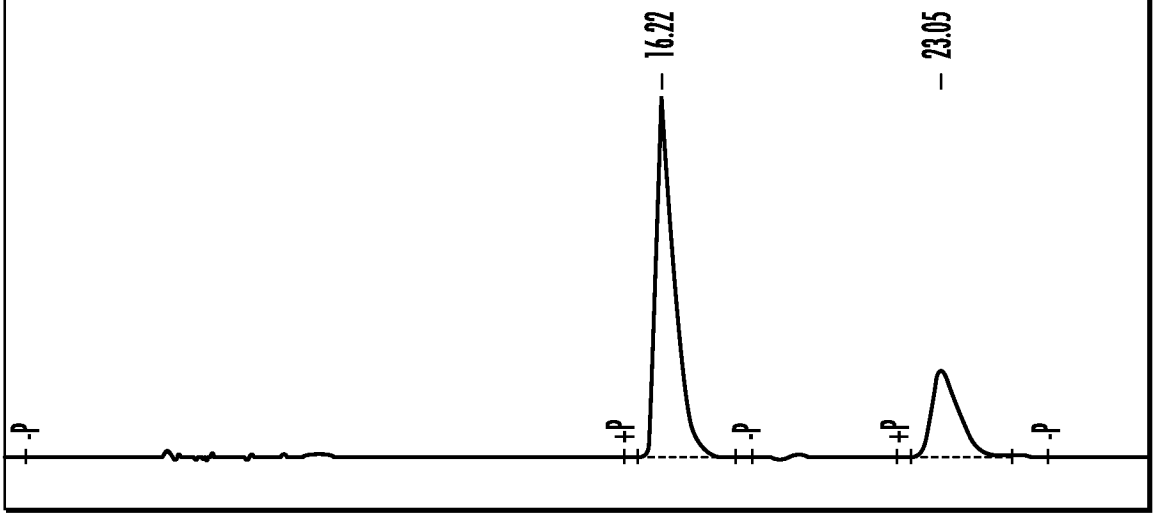


FIG. 10

rac-9a

DEFAULT REPORT

PEAK#	TIME[min]	AREA[μV·s]	HEIGHT [μV]	AREA[%]	NORM. AREA[%]	BL	AREA/HEIGHT [s]
1	13.096	7114271.78	292813.79	49.93	49.93	BB	24.2962
2	16.288	7134041.06	234817.62	50.07	50.07	BB	30.3812

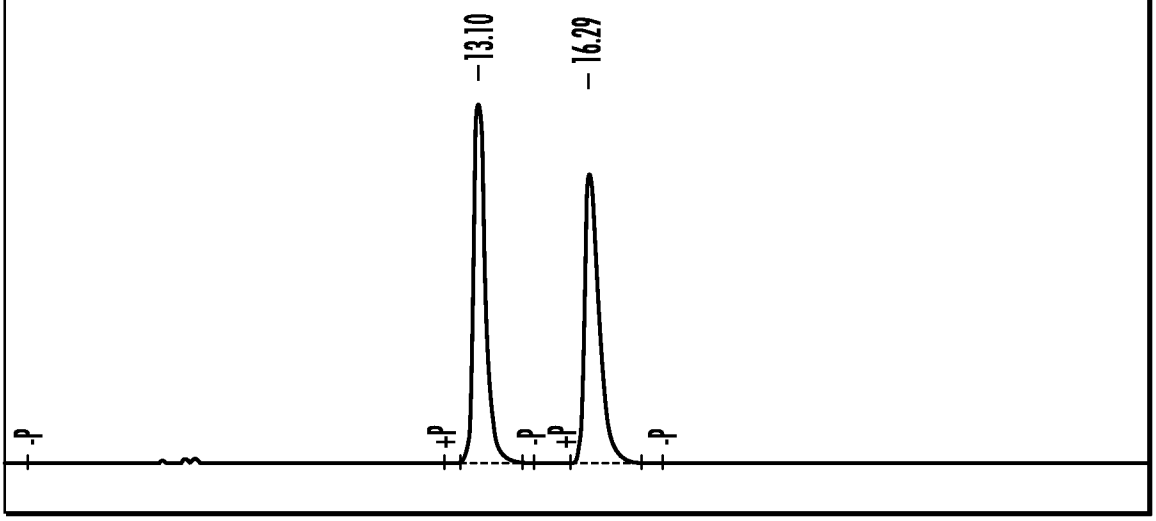


FIG. 11

rac-9b

DEFAULT REPORT

PEAK#	TIME[min]	AREA[μV·s]	HEIGHT [μV]	AREA[%]	NORM. AREA[%]	BL	AREA/HEIGHT [s]
1	13.610	1791978.49	78418.37	50.66	50.66	BB	22.8515
2	20.576	1745024.17	48778.30	49.34	49.34	BB	35.7746

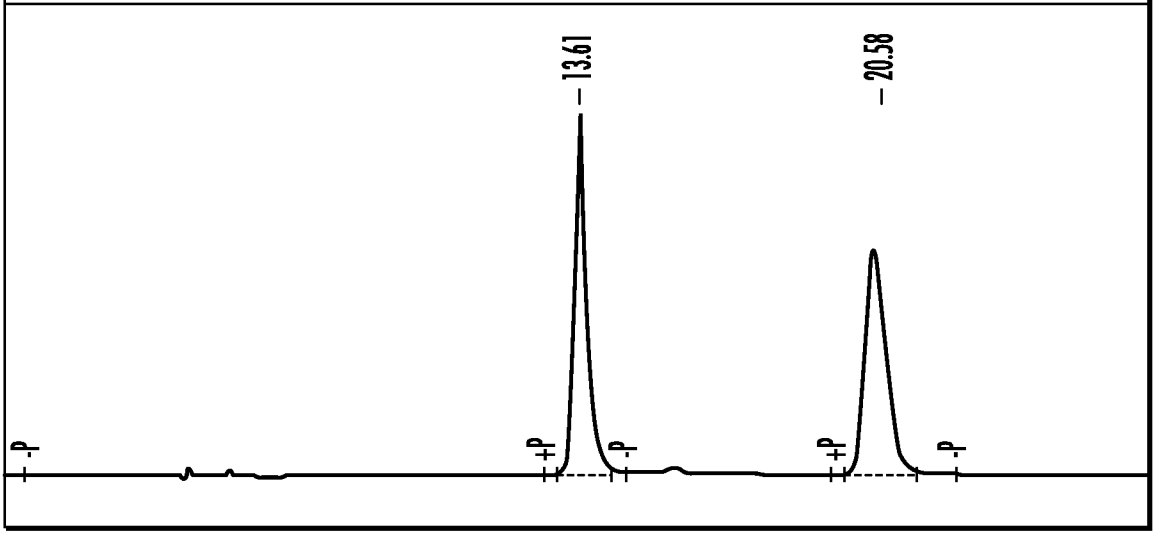


FIG. 12

rac-9c

DEFAULT REPORT

PEAK#	TIME[min]	AREA[μV·s]	HEIGHT [μV]	AREA[%]	NORM. AREA[%]	BL	AREA/HEIGHT [s]
1	12.806	4458550.77	204047.29	50.01	50.01	BB	21.8506
2	19.475	4456804.12	123606.51	49.99	49.99	BB	36.0564

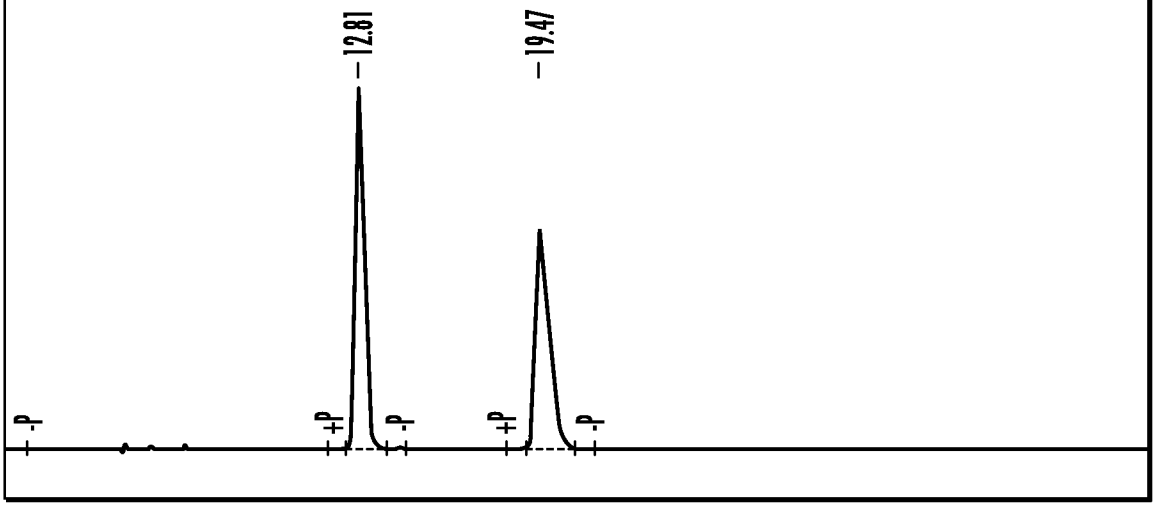


FIG. 13

rac-9d

DEFAULT REPORT

PEAK#	TIME[min]	AREA[μV·s]	HEIGHT [μV]	AREA[%]	NORM. AREA[%]	BL	AREA/HEIGHT [s]
1	16.113	18281303.65	642695.52	49.96	49.96	BB	28.4447
2	22.591	18308784.48	430444.29	50.04	50.04	BB	29.5346

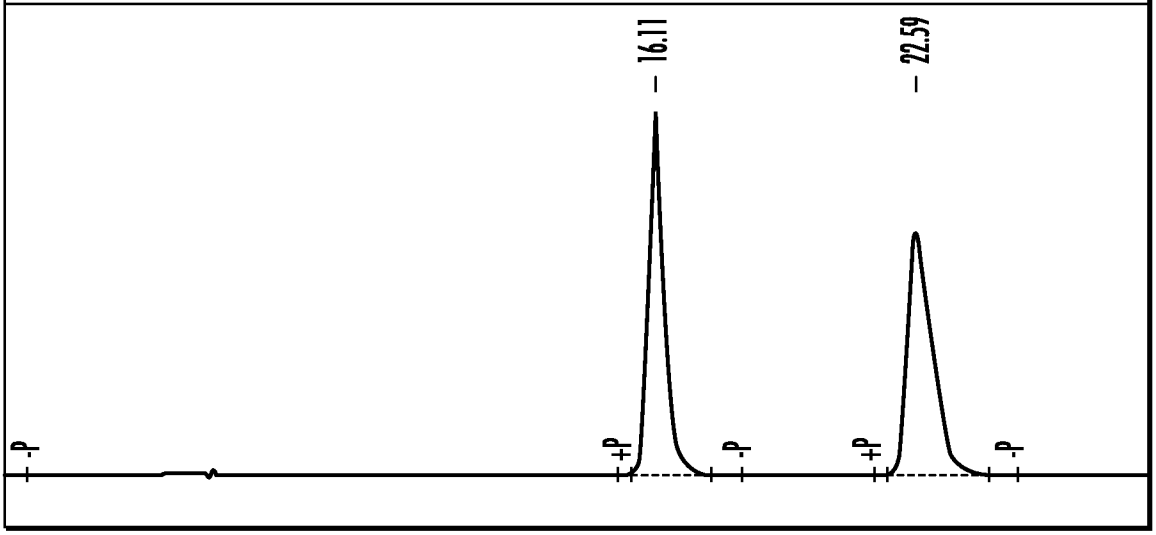


FIG. 14

ENANTIOPURE Bis(TMS) DERIVATIVE OF SILANEDIOL *R*-3

DEFAULT REPORT

PEAK#	TIME[min]	AREA[μV·s]	HEIGHT [μV]	AREA[%]	NORM. AREA[%]	BL	AREA/HEIGHT [s]
1	11.550	22.74	40.35	0.00	0.00	BB	0.5635
2	15.522	21941088.34	845486.56	100.00	100.00	BB	25.9508

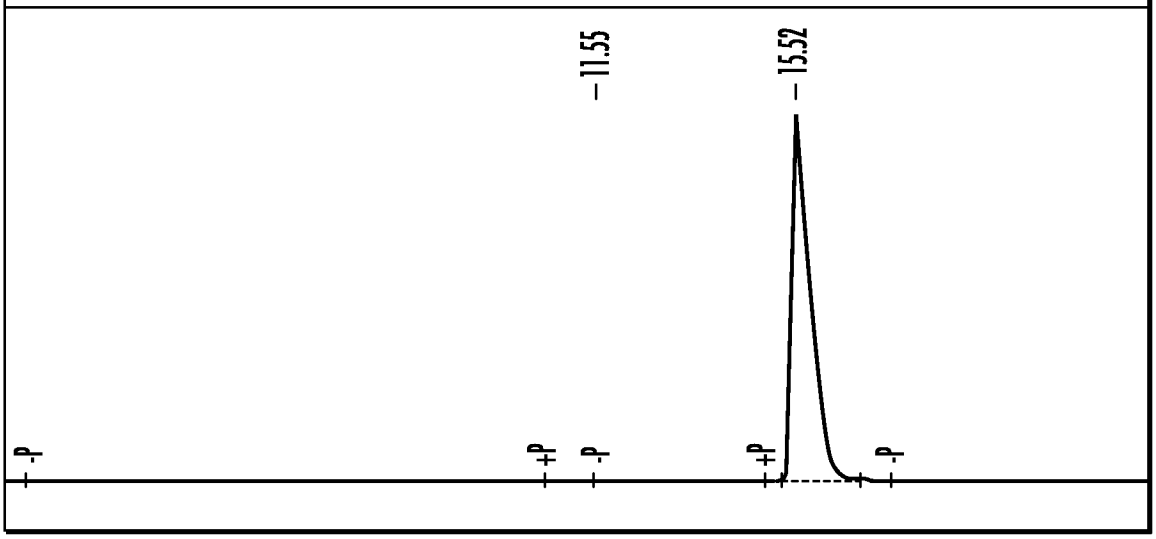


FIG. 15

rac-Bis(TMS) DERIVATIVE OF SILANEDIOL *R*-3

DEFAULT REPORT

PEAK#	TIME[min]	AREA[μV·s]	HEIGHT [μV]	AREA[%]	NORM. AREA[%]	BL	AREA/HEIGHT [s]
1	11.153	5987991.21	366702.80	49.72	49.72	BB	16.3293
2	15.671	6055330.74	253443.57	50.28	50.28	BB	23.8922

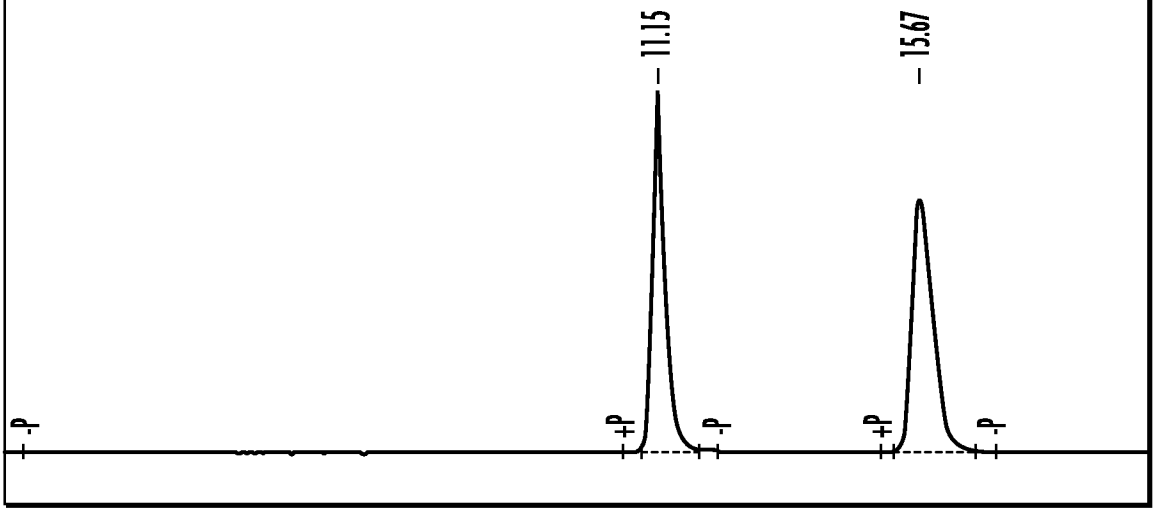


FIG. 16

S2 WITH S1, 20 mol% *R*-3

DEFAULT REPORT

PEAK#	TIME[min]	AREA[μV·s]	HEIGHT [μV]	AREA[%]	NORM. AREA[%]	BL	AREA/HEIGHT [s]
1	13.820	13364166.23	508444.23	57.14	57.14	BB	26.2844
2	18.160	10022876.66	269253.51	42.86	42.86	BB	37.2247

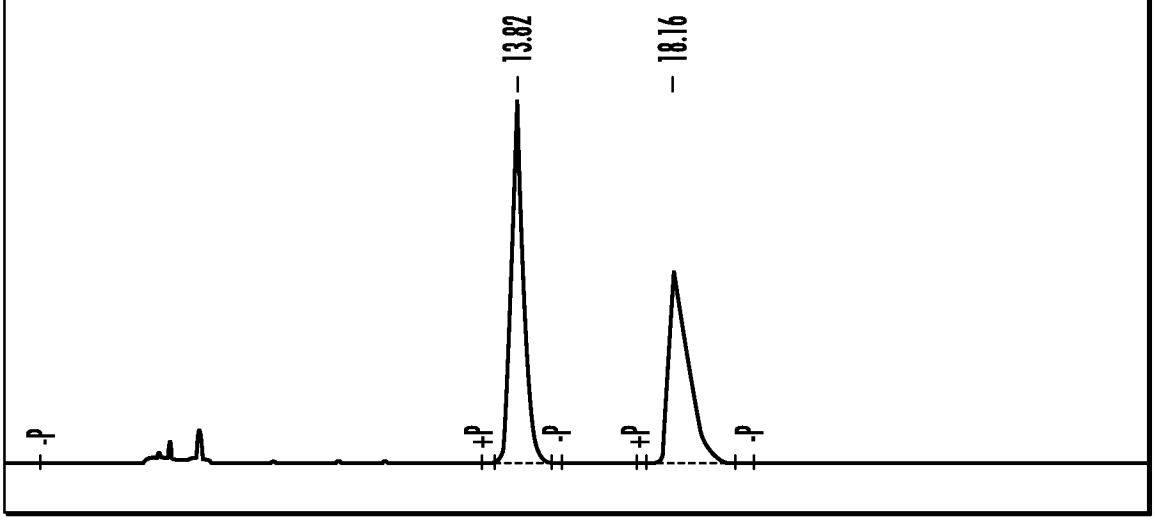


FIG. 17

rac-S2

DEFAULT REPORT

PEAK#	TIME[min]	AREA[μV·s]	HEIGHT [μV]	AREA[%]	NORM. AREA[%]	BL	AREA/HEIGHT [s]
1	14.128	5945417.46	264658.38	50.18	50.18	BB	22.4645
2	18.780	5903297.09	173531.00	49.82	49.82	BB	34.0187

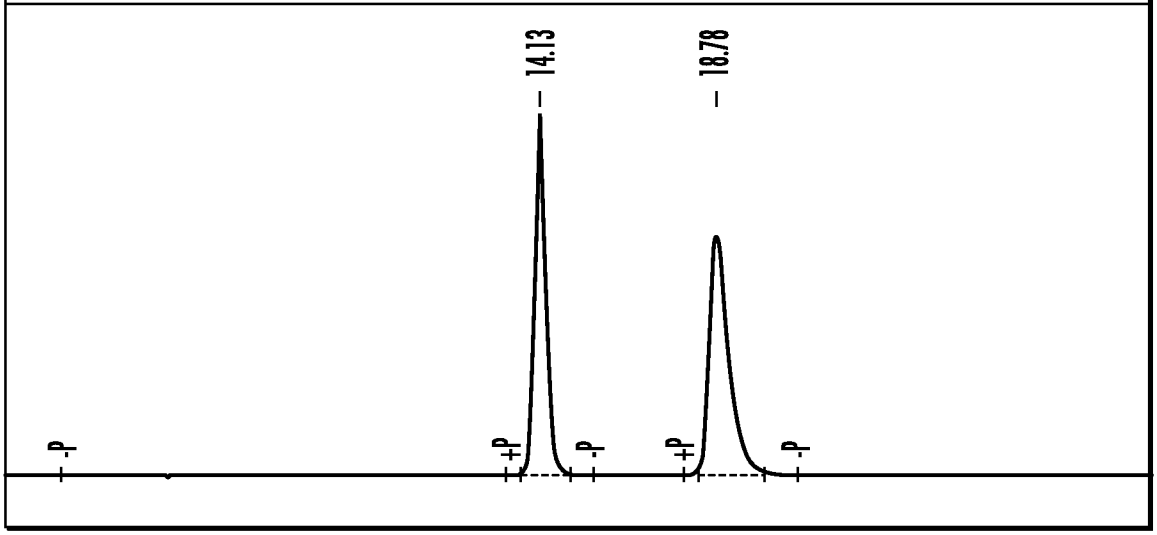


FIG. 18

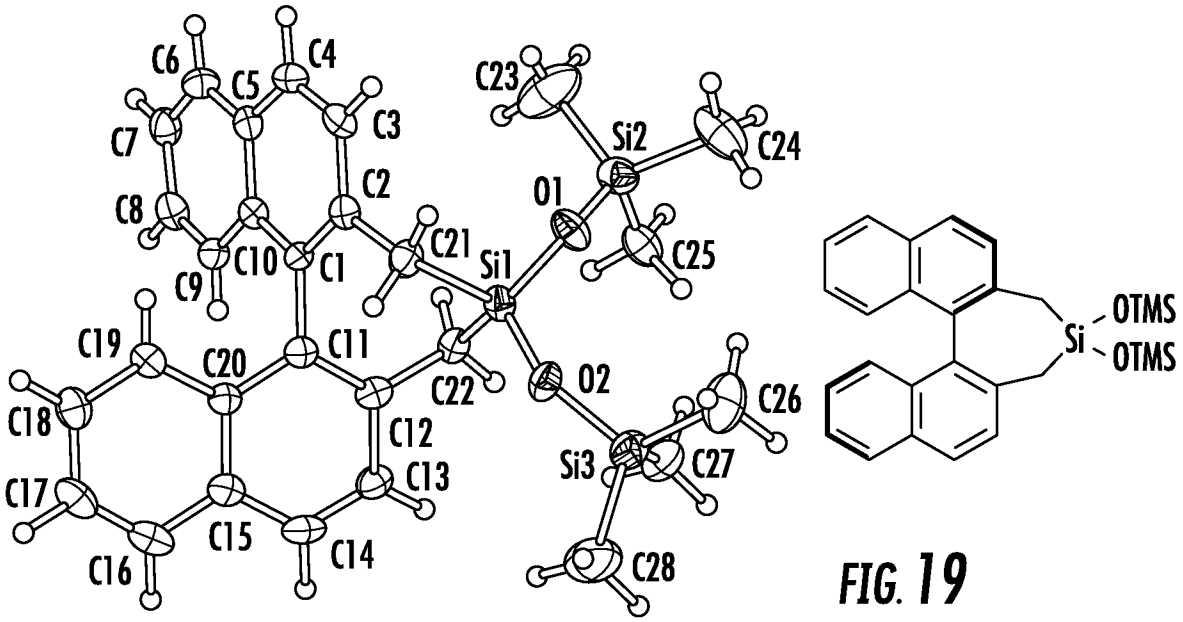

C6
C5
C4
C3
C7
C2
C8
C10
C1
C9
C21
Si1
C23
Si2
C24
O1
C25
C19
C20
C11
C22
O2
C26
C18
C12
Si3
C27
C17
C13
C15
C14
C16
C28
OTMS
Si
OTMS

FIG. 19

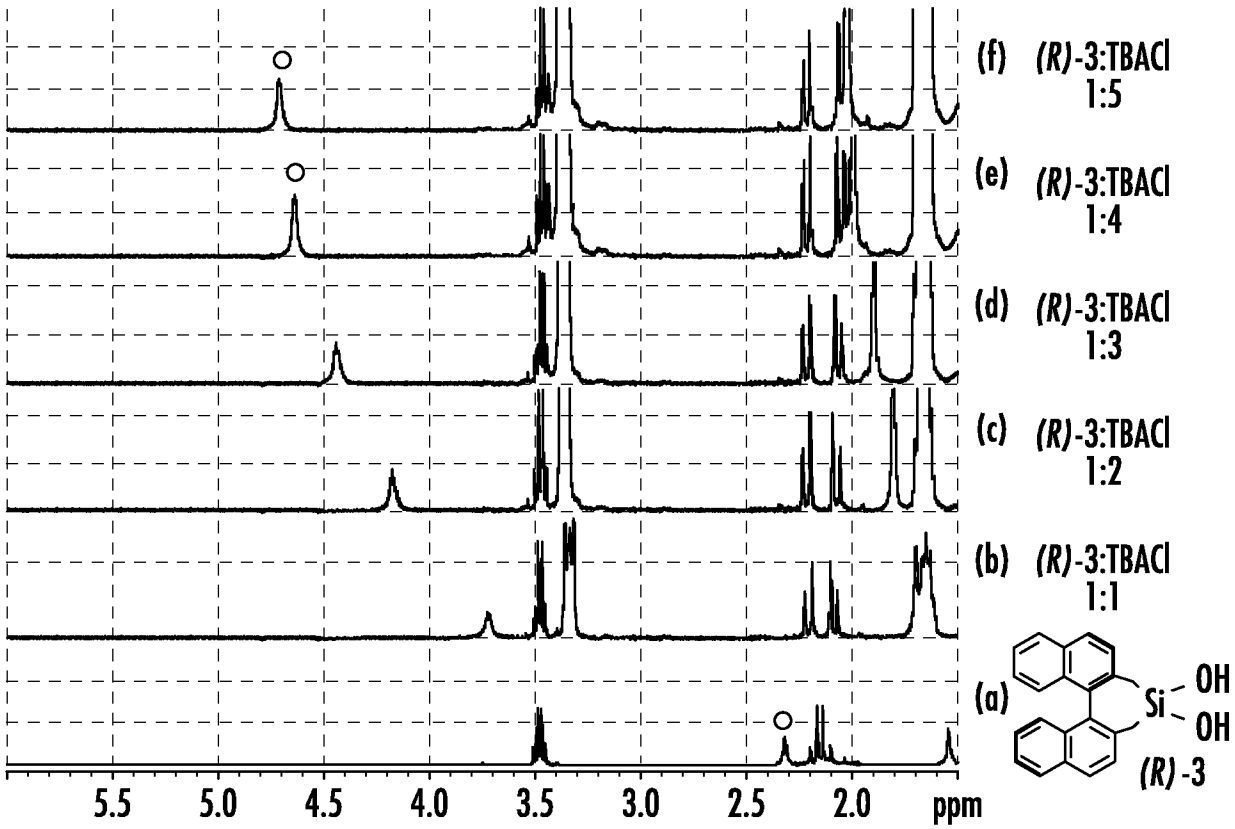

(f) (R)-3:TBACl 1:5
(e) (R)-3:TBACl 1:4
(d) (R)-3:TBACl 1:3
(c) (R)-3:TBACl 1:2
(b) (R)-3:TBACl 1:1
(a)
OH
Si
OH
(R)-3
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm

FIG. 20

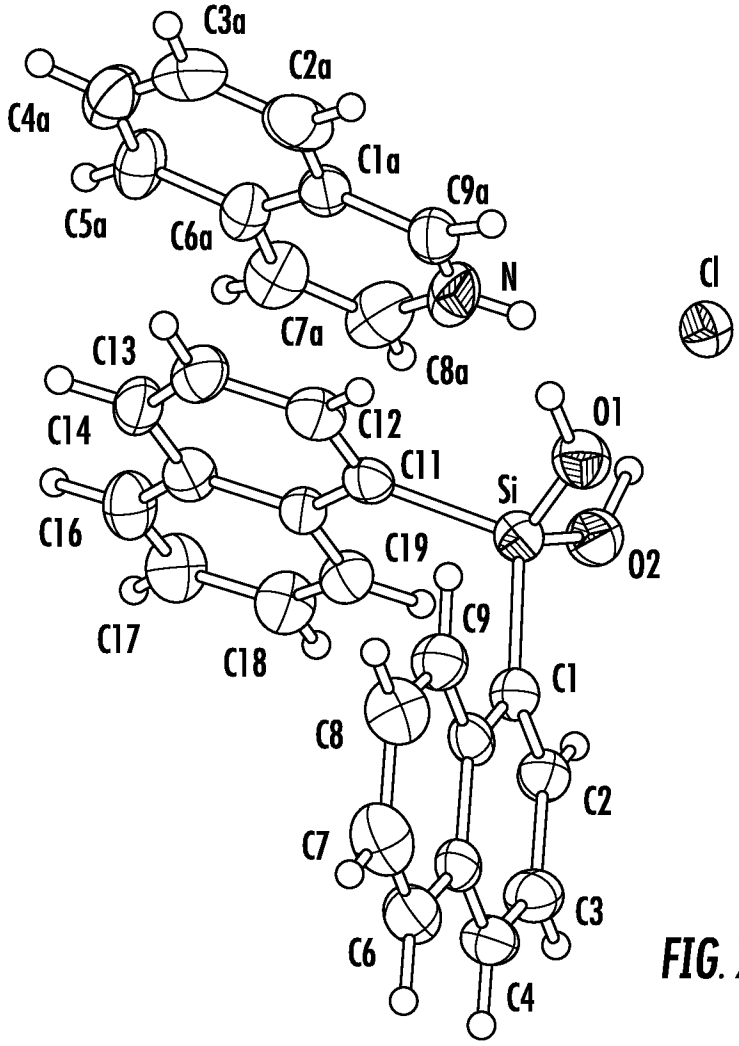

C3a
C2a
C4a
C1a
C9a
C5a
C6a
N
Cl
C7a
C8a
C13
C12
O1
C14
C11
Si
C16
C19
O2
C9
C17
C18
C1
C8
C2
C7
C3
C6
C4

FIG. 21

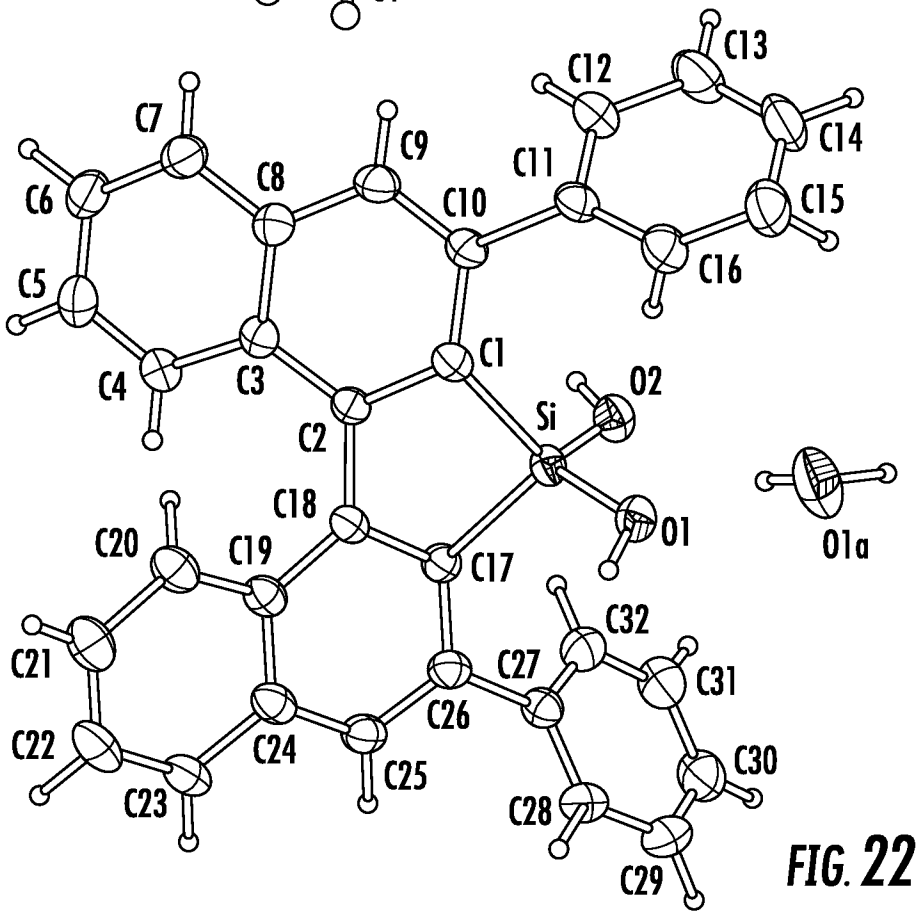

C13
C12
C7
C14
C9
C11
C8
C6
C10
C15
C5
C16
C1
C4
C3
O2
Si
C2
C18
O1
O1a
C20
C19
C17
C32
C21
C27
C31
C26
C22
C24
C30
C25
C23
C28
C29

FIG. 22

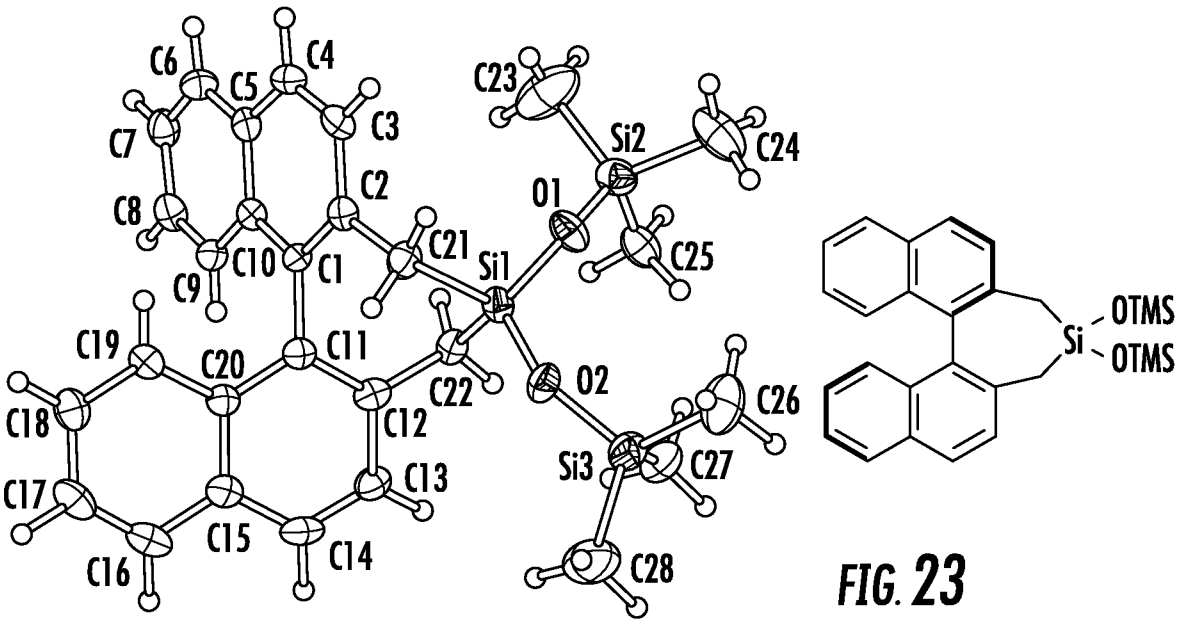

C6
C5
C4
C3
C7
C2
C8
C10
C1
C9
C21
Si1
C23
Si2
C24
O1
C25
C19
C20
C11
C22
O2
C26
C18
C12
Si3
C27
C17
C13
C15
C14
C16
C28
Si
OTMS
OTMS

FIG. 23

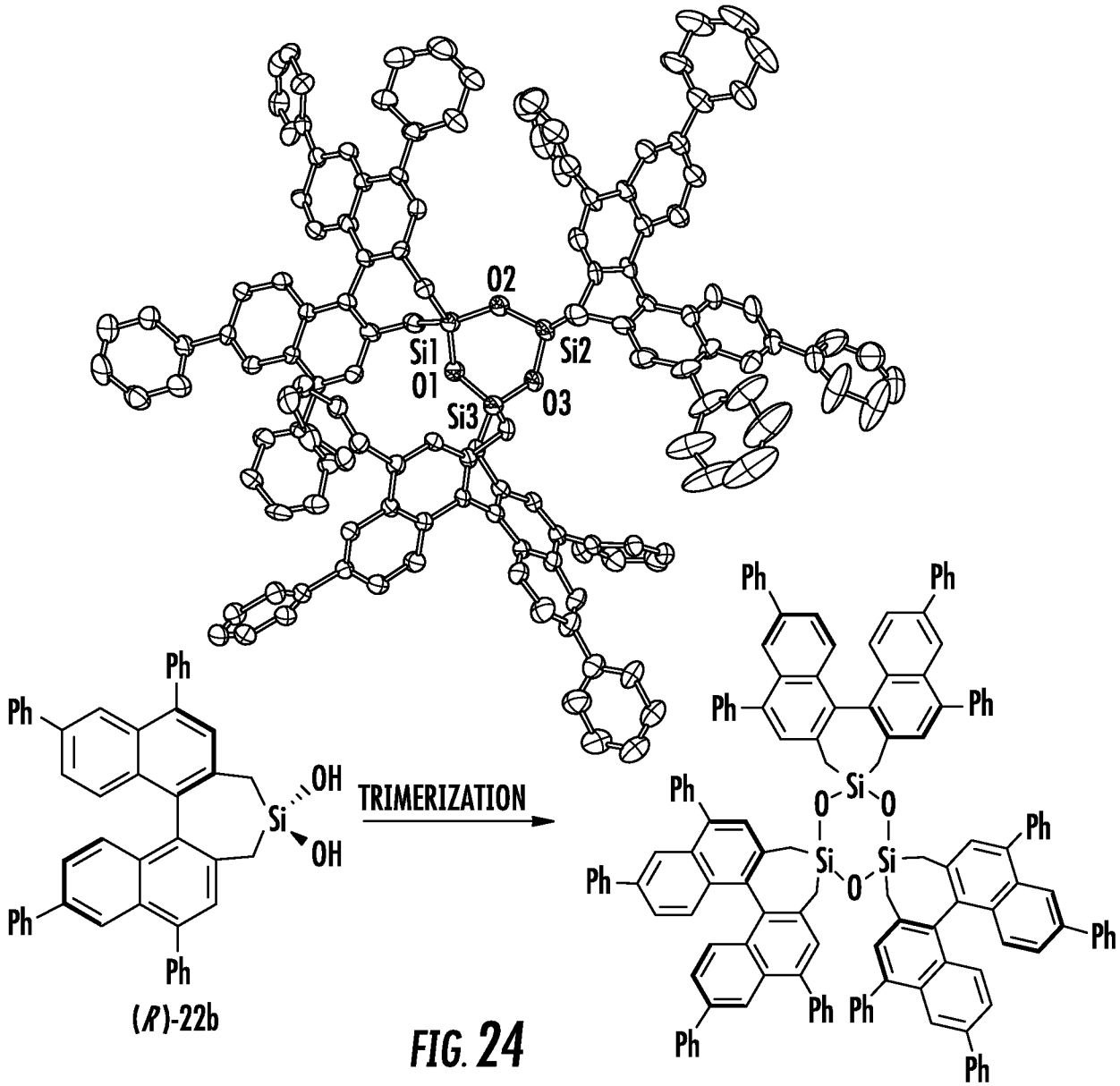
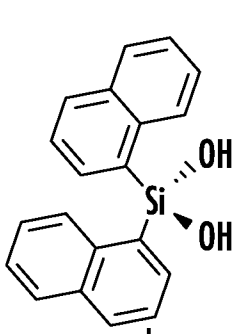
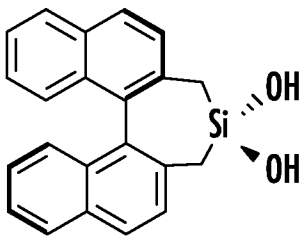

O2
Si1
Si2
O1
O3
Si3
Ph
OH
Si
OH
TRIMERIZATION
(R)-22b
O
Si

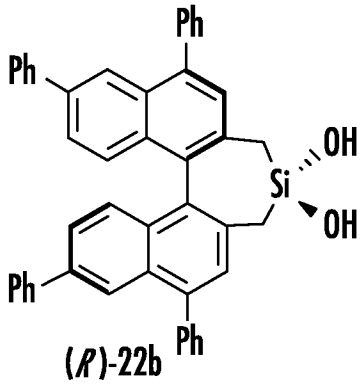
FIG. 24



34[b]



(*R*)-22a



(*R*)-22b

p*K*a (DMSO)	19.1 ± 0.3	19.3 ± 0.1	18.7 ± 0.3
BINDING CONSTANT $(M^{-1})^a$	1.44 ± 0.11 X 10^2	2.19 ± 0.03 X 10^2	3.10 ± 0.10 X 10^2

[a] WITH Cl^-, [b] FOR BINDING CONSTANT DATA SEE KONDO et al. Org. Lett 2006, 8, 4621-4624.

FIG. 25

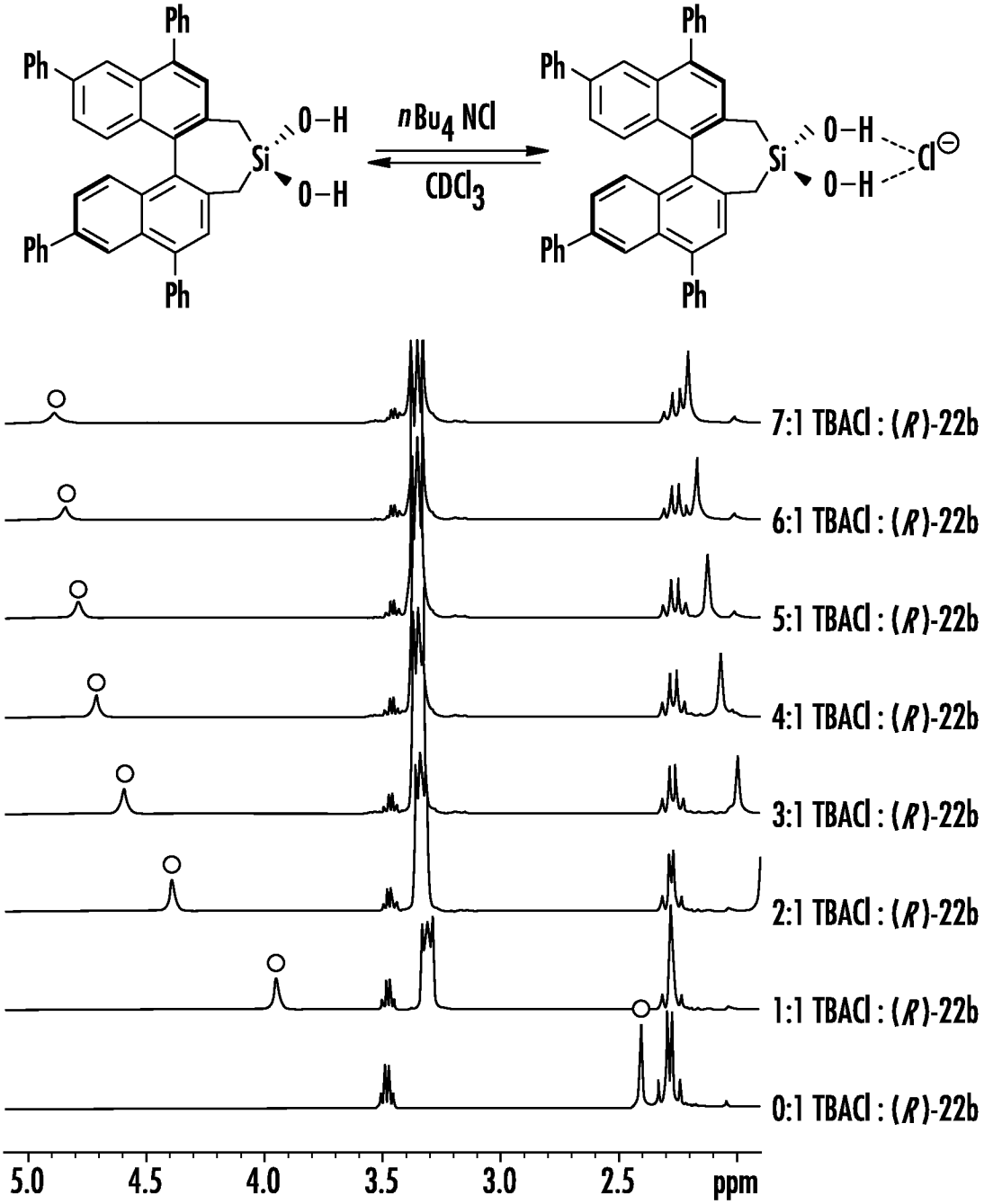

Ph
Ph
Ph
Ph
Ph
O–H
Si
O–H
nBu4 NCl
CDCl3
Ph
Ph
Ph
Ph
Ph
O–H
Si
O–H
Cl⊖
7:1 TBACl : (R)-22b
6:1 TBACl : (R)-22b
5:1 TBACl : (R)-22b
4:1 TBACl : (R)-22b
3:1 TBACl : (R)-22b
2:1 TBACl : (R)-22b
1:1 TBACl : (R)-22b
0:1 TBACl : (R)-22b
5.0
4.5
4.0
3.5
3.0
2.5
ppm

FIG. 26

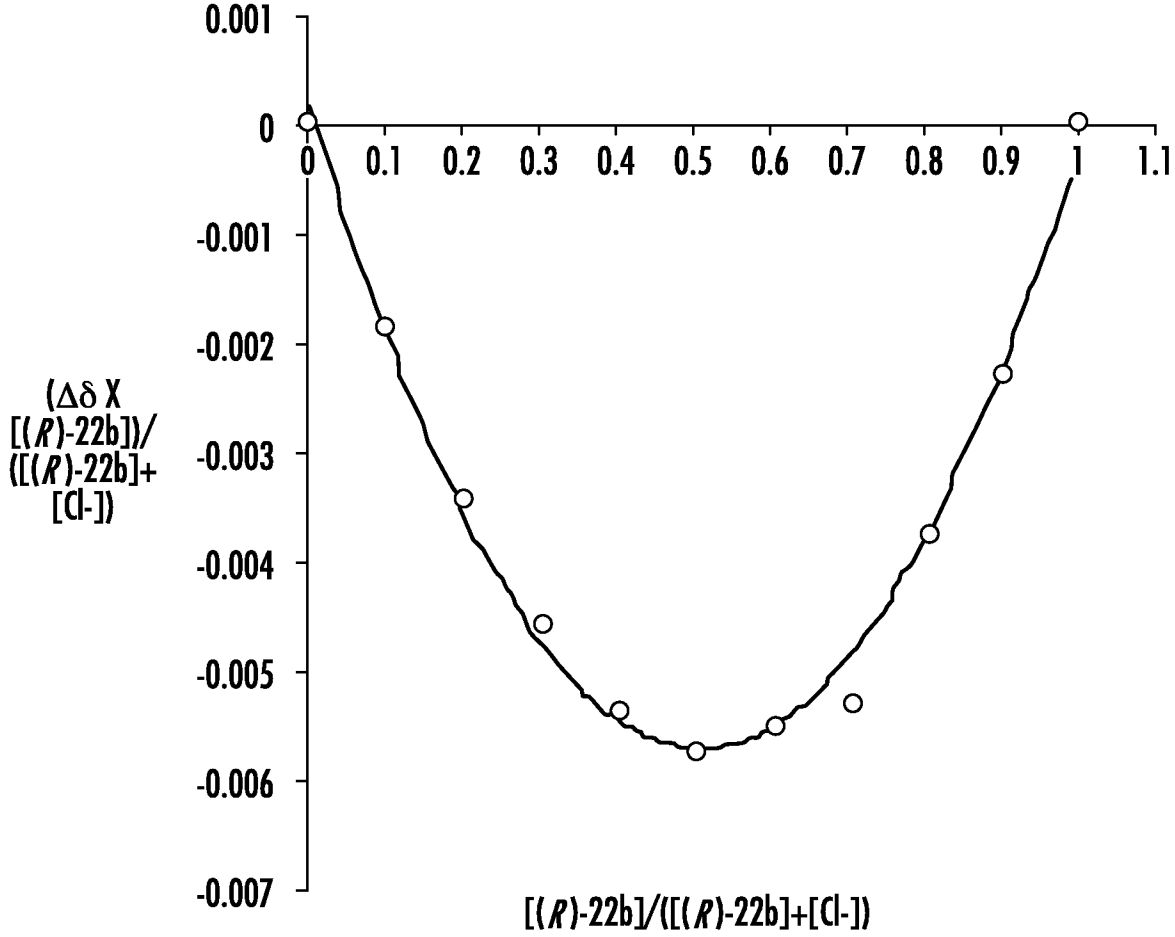

0.001
0
-0.001
-0.002
-0.003
-0.004
-0.005
-0.006
-0.007
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
1.1
(Δδ X [(R)-22b])/([(R)-22b]+[Cl-])
[(R)-22b]/([(R)-22b]+[Cl-])

FIG. 27

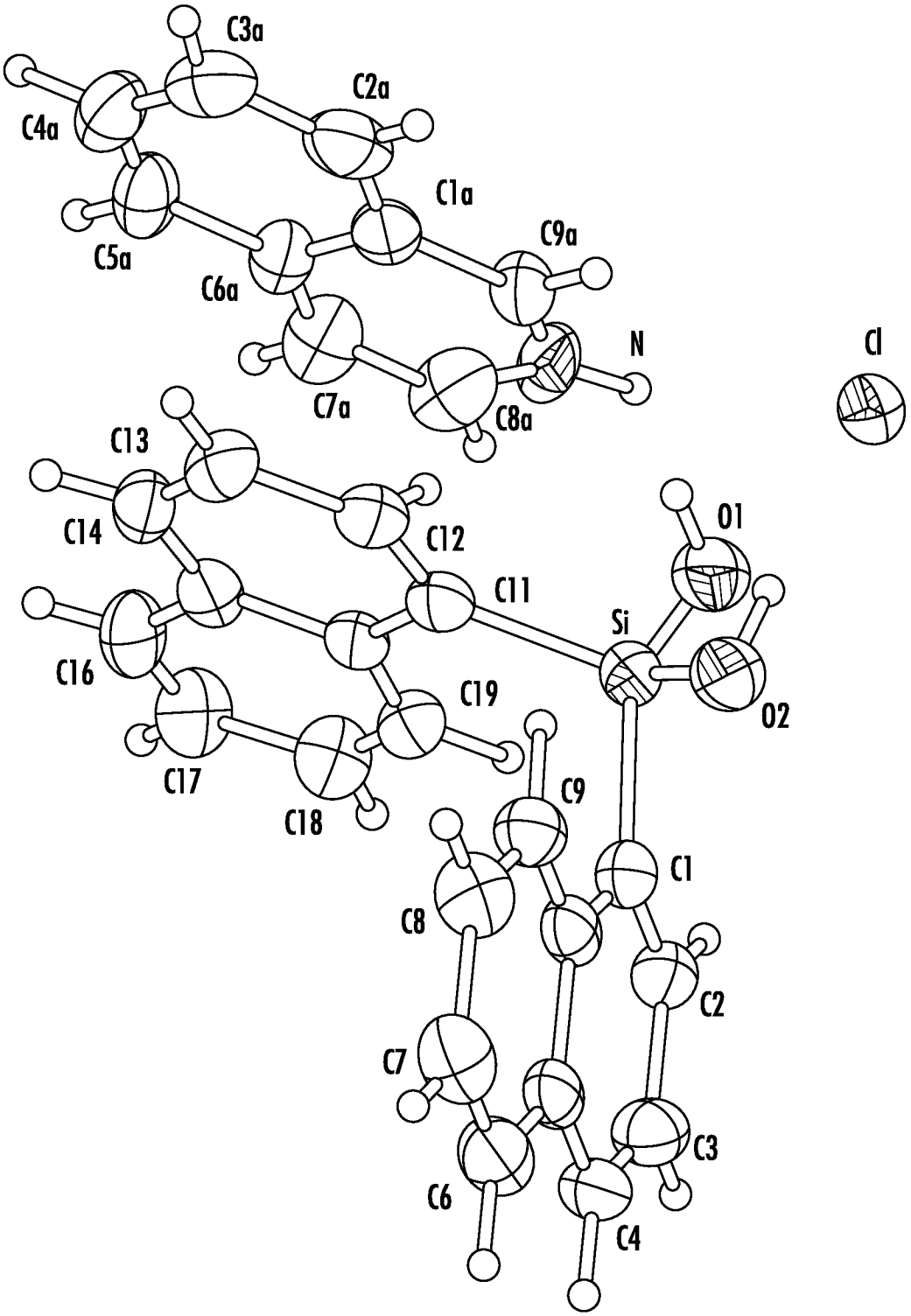

C3a
C2a
C4a
C1a
C9a
C5a
C6a
N
Cl
C7a
C8a
C13
O1
C14
C12
C11
Si
C16
C19
O2
C17
C9
C18
C1
C8
C2
C7
C3
C6
C4

FIG. 28

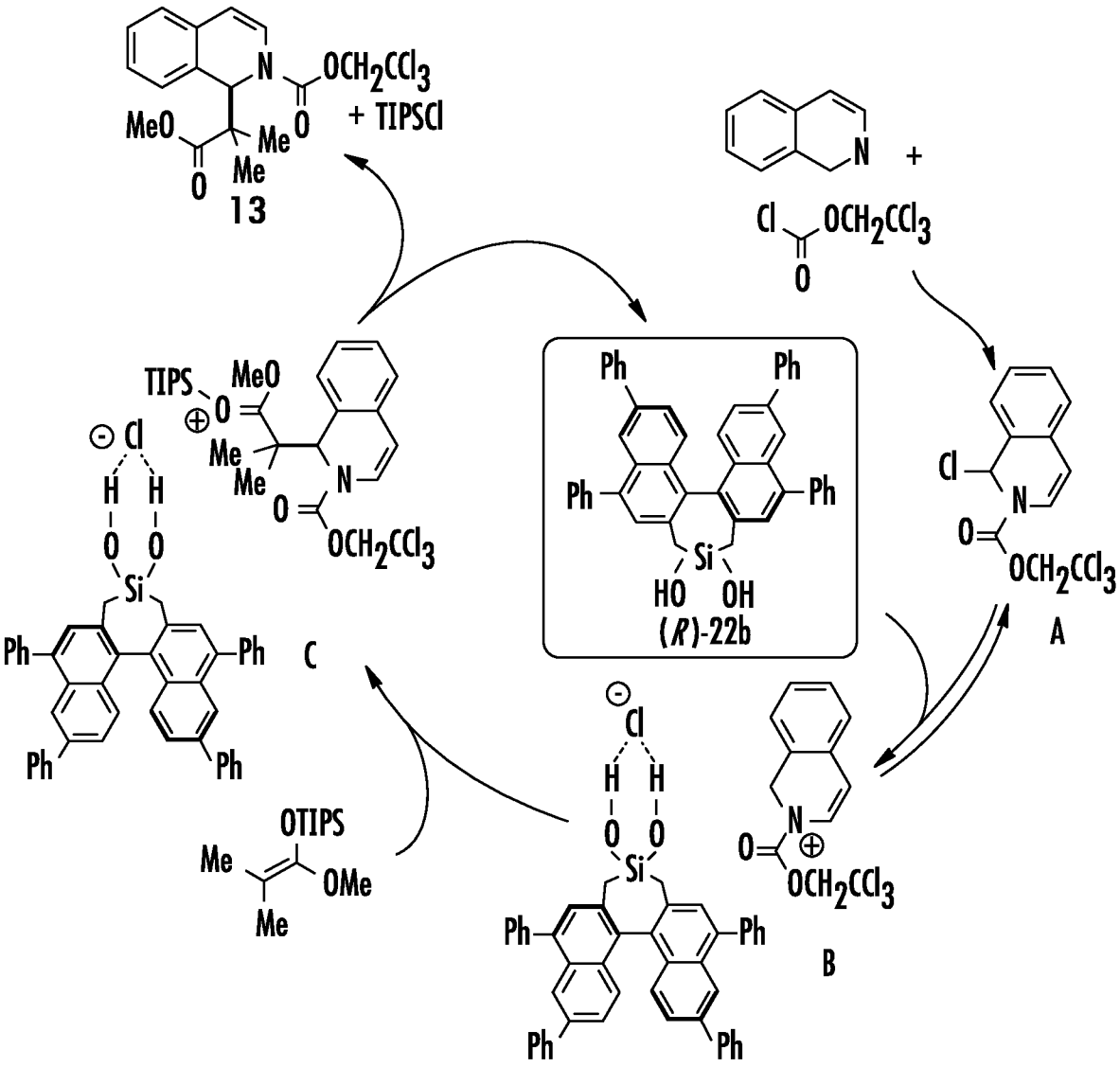


FIG. 29

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2015/025587

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C07F 7/08 (2015.01)
CPC - C07F 7/08 (2015.05)
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)
IPC(8) - C07C 15/20, 15/38, 15/56, 15/62; C07F 7/08 (2015.01)
CPC - C07C 15/20, 15/38, 15/56, 15/62; C07F 7/08 (2015.05) (keyword delimited)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC - 502/158 (keyword delimited)

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

Orbit, STN, Google Patents, PubChem, SureChEMBL, Google, Google Scholar
Search terms used: bipnaphthyl+, dinaphthyl+, dihydroxysilane, dihydroxysilicon, silanediol, BINOL

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	SCHAFER et al. Chiral Silanediols in Anion-binding Catalysis. Angew. Chem. Int. Ed. 52(43): 11321-11324, 2013. [retrieved on 20 May 2015]. Retrieved from the Internet. <URL: http://onlinelibrary.wiley.com/doi/10.1002/anie.201305496/abstract>. see abstract	1
A	MATTSON. Sustainable Catalysts for Feedstock Chemical Functionalization. 58th Annual Report on Research 2013, Under Sponsorship of the ACS Petroleum Research Fund 52183-DNI1: 1-5, 2013. [retrieved on 07 August 2015]. Retrieved from the Internet. <URL: https://acswebcontent.acs.org/prfar/2013/Paper12228.html>. entire document	1
A	US 5,360,938 A (BABIN et al) 01 November 1994 (01.11.1994) entire document	1
A, P	SCHAFER. Silanediols As Hydrogen Bond Donor Catalysts. Doctor of Philosophy, Ohio State University, Chemistry 1-286, 2014. [retrieved on 07 August 2015]. Retrieved from the Internet. <URL: https://etd.ohiolink.edu/ap/10?0::NO:10:P10_ETD_SUBID:93419>. see abstract	1

☐ Further documents are listed in the continuation of Box C. ☐

* 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	Date of mailing of the international search report
07 August 2015	08 SEP 2015
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer: Blaine R. Copenheaver PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2015/025587

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 4-55, 59-84
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Claim 1 has been analyzed subject to the restriction that the claim reads on the compound defined by instant Formula 1 as described in the Lack of Unity of Invention (See Extra Sheet). The claims are restricted to a compound defined by instant Formula I: wherein n is 0; m is 0; R1 and R1' are each independently H; R2, R3, R4, R5, R6, R2', R3', R4', R5' and R6' are each independently hydrogen; R7 and R7' are each independently H; R8 is hydrogen; R9 is hydrogen.

<See Extra Sheet>

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2015/025587

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees need to be paid.

Group I+: Claims 1-3 are drawn to a compound defined by Formula I.

Group II: Claims 56-58 are drawn to a compound defined by Formula XV.

The first invention of Group I+ is restricted to a compound defined by Formula I: wherein n is 0; m is 0; R1 and R1' are each independently H; R2, R3, R4, R5, R6, R2', R3', R4', R5' and R6' are each independently hydrogen; R7 and R7' are each independently H; R8 is hydrogen; R9 is hydrogen. It is believed that claim 1 reads on this first named invention and thus these claims will be searched without fee to the extent that they read on the above embodiment.

Applicant is invited to elect additional formula(e) for each additional compound to be searched in a specific combination by paying an additional fee for each set of election. An exemplary election would be a compound defined by Formula I: wherein n is 1; m is 0; R1 and R1' are each independently H; R2, R3, R4, R5, R6, R2', R3', R4', R5' and R6' are each independently hydrogen; R7 and R7' are each independently H; R8 is hydrogen; R9 is hydrogen. Additional formula(e) will be searched upon the payment of additional fees. Applicants must specify the claims that read on any additional elected inventions. Applicants must further indicate, if applicable, the claims which read on the first named invention if different than what was indicated above for this group. Failure to clearly identify how any paid additional invention fees are to be applied to the "+" group(s) will result in only the first claimed invention to be searched/examined.

The inventions listed in Groups I+ and II do not relate to a single general inventive concept under PCT Rule 13.1, because under PCT Rule 13.2 they lack the same or corresponding special technical features for the following reasons:

The special technical features of Group I+, a compound defined by Formula I, are not present in Group II; and the special technical features of Group II, a compound defined by Formula XV, are not present in Groups I+.

The Groups I+ and II formulae do not share a significant structural element, requiring the selection of alternative formulae as well as the compound variables n, m, R1, R1', R2, R3, R4, R5, R6, R2', R3', R4', R5', R6', R7, R7', R8, R9, R10, R10', R11, R12, R13, R14, R15, R16, R17, R12', R13', R14', R15', R16', R17', and R18.

The Groups I+ and II share the technical features of a compound defined by the core structure of Formula I; and a compound comprising a silane-containing naphthyl ring. However, these shared technical features do not represent a contribution over the prior art.

Specifically, "Chiral Silanediols in Anion-Binding Catalysis" to Schafer et al. teach a compound defined by the core structure of Formula I: wherein n is 1; m is 1; R1 and R2 are each independently H; R3, R4, R5, R6, R2', R3', R4', R5' and R6' are each independently hydrogen; R7 and R7' are each independently H; R8 and R9 together with the atoms which they are attached, form a 7 membered silacycle (See Pg. 2, Abstract Fig. silanediol catalyst (1);...see shown structure...); and a compound comprising a silane-containing naphthyl ring (See Pg. 2, Abstract Fig. silanediol catalyst (1);...see shown structure...).

The inventions listed in Groups I+ and II therefore lack unity under Rule 13 because they do not share a same or corresponding special technical feature.