

CATALYSTS AND METHODS FOR POLYMER SYNTHESIS

Priority Claim

This application claims priority to United States Provisional Patent Application Serial No. 61/091,013, filed August 22, 2008; United States Provisional Patent Application Serial No. 61/096,313, filed September 11, 2008 and United States Provisional Patent Application Serial No. 61/098,739, filed September 19, 2008. The entire contents of each of these priority applications are incorporated herein by reference.

Background

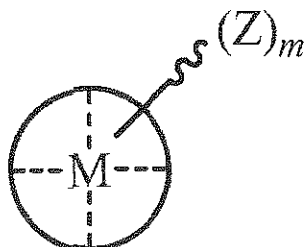
Catalysts capable of effecting the copolymerization of epoxides and carbon dioxide to form aliphatic polycarbonates (APCs) have been known in the art since the 1960s. The early catalysts were based on heterogeneous zinc compounds and suffered from low reactivity, a lack of selectivity for polymer formation vs. cyclic carbonate formation, and a tendency to produce polycarbonates contaminated with ether linkages.

Improved catalysts based on transition metals have been discovered over the past decade or so. These newer catalysts have increased reactivity and improved selectivity. Nevertheless, even using highly active catalysts such as those disclosed in US patent 7,304,172, the reaction times required to make high molecular weight polymer are typically quite long. In addition, the best-performing catalysts disclosed in the '172 patent require the addition of a separate co-catalyst to achieve optimum activity.

Attempts to address these shortcomings have been made. Catalysts described by Nozaki and co-workers (*Angew. Chem. Int. Ed.* **2006**, 45, 7274 -7277) tether an amine co-catalyst to a ligand of the catalyst. These next-generation catalytic systems suffer from lengthy and complicated syntheses and undesirable induction times prior to onset of polymerization. There remains a need for catalysts that have increased activity that will further reduce the polymerization time required to produce high molecular weight APCs.

Summary

In a first aspect of the present disclosure, there is provided a metal complex of the formula:



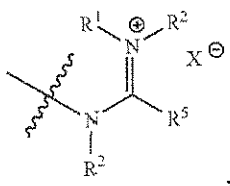
5 wherein:

M is cobalt;



comprises a salen ligand; and

10 $\text{---} \text{wavy line} \text{---} (Z)_m$ represents one or more activating moieties tethered to the salen ligand, where $\text{---} \text{wavy line} \text{---}$ represents a linker moiety; m is an integer between 1 and 4 inclusive and represents the number of Z groups present on a linker moiety; and each (Z) represents an activating moiety comprising an amidine or amidinium group of the formula:



wherein

15 X^- is an anion;

each of R^1 and R^2 is independently hydrogen or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon

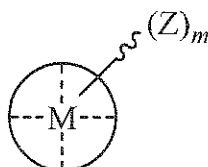
saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; and an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; wherein any two or more R^1 and R^2 groups can be taken together with intervening atoms to form one or more optionally substituted rings optionally containing one or more additional heteroatoms; and each occurrence of R^5 is independently hydrogen or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; and an 8- to 10-membered bicyclic heteroaryl ring having 1-5 R^5 can be taken with an R^1 or R^2 group to form one or more optionally substituted rings.

In a second aspect of the present disclosure, there is provided a method for the synthesis of aliphatic polycarbonate polymers comprising the step of contacting one or more epoxides with carbon dioxide in the presence of a metal complex as described herein.

The present disclosure provides, among other things, unimolecular catalyst systems having activity in the copolymerization of carbon dioxide and epoxides and methods of using the same. In some embodiments, the present disclosure

provides metal complexes having an activating species with co-catalytic activity tethered to a multidentate ligand that is coordinated to an active metal center of a metal complex. In certain embodiments, the present disclosure provides unimolecular metal complexes and methods for using the same in the copolymerization of carbon dioxide and epoxides.

5 In some embodiments, provided metal complexes have the structure:



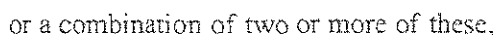
wherein:

M is a metal atom;

 comprises a multidentate ligand;

10 $\text{---}\text{~}\text{~}\text{~}\text{(Z)}_m$ represents one or more activating moieties attached to the multidentate ligand, where $\text{---}\text{~}\text{~}\text{~}$ is a linker moiety covalently coupled to the ligand, each Z is an activating functional group; and m is an integer from 1 to 4 representing the number of Z groups present on an individual linker moiety.

15 In some embodiments, tethered activating functional groups (Z) are neutral nitrogen-containing moieties. In certain embodiments, neutral nitrogen-containing moieties are selected from the group consisting of:



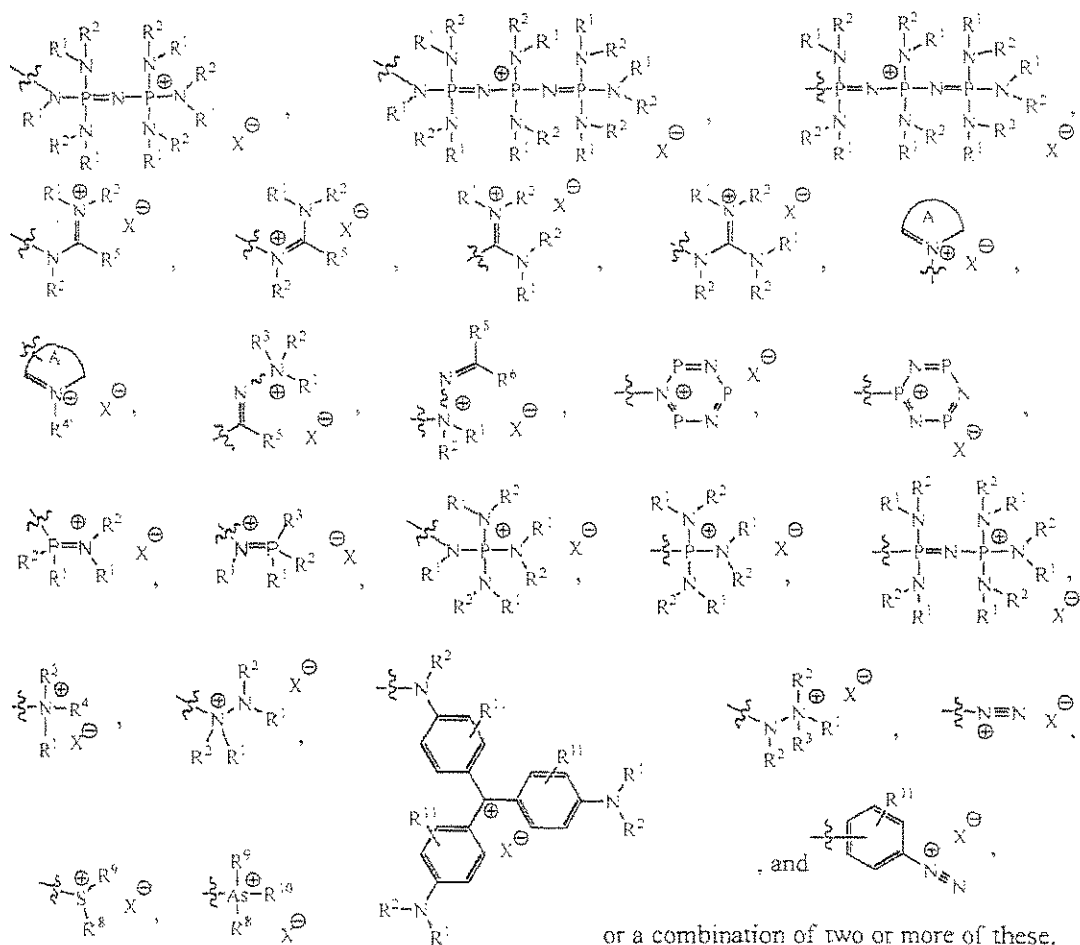
each occurrence of R¹, and R² is independently hydrogen or an optionally substituted radical selected from the group consisting of C₁₋₂₀ aliphatic; C₁₋₂₀ heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle; a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; wherein R¹ and R² groups can be taken together with intervening atoms to form one or more optionally substituted rings optionally containing one or more additional heteroatoms;

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selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms
5 independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; wherein an R⁵ group can be taken with an R¹ or R² group to form one or more optionally substituted rings; and

each occurrence of R⁷ is independently hydrogen, a hydroxyl protecting group, or an
10 optionally substituted radical selected from the group consisting of C₁₋₂₀ acyl; C₁₋₂₀ aliphatic; C₁₋₂₀ heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen,
15 oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring
20 having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur.

In some embodiments, tethered activating functional groups (Z) are cationic moieties. In certain embodiments, cationic moieties are selected from the group consisting of:



wherein:

- 5 each occurrence of R^1 , R^2 , and R^3 is independently hydrogen or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4
- 10 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to
- 15 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently

selected from nitrogen, oxygen, or sulfur; wherein any two or more R^1 , R^2 , and R^3 groups can be taken together with intervening atoms to form one or more optionally substituted rings optionally containing one or more additional heteroatoms;

5 R^4 is hydrogen or $-OR^7$;

R^4 is hydrogen, hydroxyl, or optionally substituted C_{1-20} aliphatic;

each occurrence of R^5 and R^6 is independently hydrogen or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4
10 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5
15 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; wherein R^5 and R^6 can be taken together with intervening atoms to form one or more optionally substituted rings optionally containing one or more heteroatoms, and an R^5 or R^6 group can be
20 taken with an R^1 or R^2 group to form one or more optionally substituted rings;

each occurrence of R^7 is independently hydrogen, a hydroxyl protecting group, or an optionally substituted radical selected from the group consisting of C_{1-20} acyl; C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or
25 partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen,
30 oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially

unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur;

each occurrence of R^8 , R^9 , and R^{10} is independently hydrogen or an optionally

5 substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4
10 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5
15 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; wherein any two or more R^8 , R^9 and R^{10} groups can be taken together with intervening atoms to form one or more optionally substituted rings;

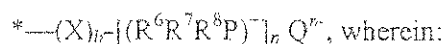
each occurrence of R^{11} is independently selected from the group consisting of:

20 halogen, $-NO_2$, $-CN$, $-SR^y$, $-S(O)R^y$, $-S(O)_2R^y$, $-NR^yC(O)R^y$, $-OC(O)R^y$, $-CO_2R^y$, $-NCO$, $-N_3$, $-OR^7$, $-OC(O)N(R^y)_2$, $-N(R^y)_2$, $-NR^yC(O)R^y$, $-NR^yC(O)OR^y$; or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially
25 unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a
30 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; where each occurrence

each R⁷ is independently hydrogen, a hydroxyl protecting group, or an optionally substituted radical selected from the group consisting of C₁₋₂₀ acyl; C₁₋₂₀ aliphatic; C₁₋₂₀ heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; and where two R⁷ groups can be taken together with intervening atoms to form an optionally substituted ring optionally containing one or more heteroatoms, and an R⁷ group can be taken with an R¹ or R² group to an optionally substituted ring;

In some embodiments, phosphorous containing functional groups include those disclosed in The Chemistry of Organophosphorus Compounds, Volume 4. Ter- and Quinquevalent Phosphorus Acids and their Derivatives, The Chemistry of Functional Group Series Edited by Frank R. Hartley (Cranfield University, Cranfield, U.K.). Wiley: New York, 1996. ISBN 0-471-95706-2, the entirety of which is hereby incorporated herein by reference.

In certain embodiments, a phosphorous-containing functional group has the structure



X is -O-, -N=, or -NR²-,

h is 1 or 0,

each of R⁶, R⁷ and R⁸ are independently present or absent and, if present, are independently selected from the group consisting of optionally substituted C₁-C₂₀ aliphatic, optionally substituted C₆-C₁₄ aryl, optionally substituted 3- to 14-

membered heterocyclic, optionally substituted 5- to 14-membered heteroaryl,
halogen, =O, -OR^z, =NR^z, and N(R^z)₂ where R^z is hydrogen, or an optionally
substituted C₁-C₂₀ aliphatic, optionally substituted 6- to 14-membered aryl,
optionally substituted 3- to 14-membered heterocyclic, or optionally substituted 5-
to 14-membered heteroaryl,

Q is any anion, and

n is an integer between 1 and 4.

In some embodiments, the present disclosure encompasses methods for the
copolymerization of epoxides and carbon dioxide, such methods comprising contacting
one or more epoxides with a catalyst described above in the presence of carbon dioxide.

In some embodiments, the present disclosure encompasses methods for the
formation of cyclic carbonates from epoxides and carbon dioxide, such methods
comprising contacting one or more epoxides with a catalyst described above in the
presence of carbon dioxide.

In some embodiments, the present disclosure encompasses methods for the
formation of polyethers, such methods comprising contacting one or more epoxides with
a catalyst described above.

Definitions

Definitions of specific functional groups and chemical terms are described in
more detail below. For purposes of this invention, the chemical elements are identified in
accordance with the Periodic Table of the Elements, CAS version, Handbook of
Chemistry and Physics, 75th Ed., inside cover, and specific functional groups are
generally defined as described therein. Additionally, general principles of organic
chemistry, as well as specific functional moieties and reactivity, are described in *Organic
Chemistry*, Thomas Sorrell, University Science Books, Sausalito, 1999; Smith and March
March's Advanced Organic Chemistry, 5th Edition, John Wiley & Sons, Inc., New York,

2001; Larock, *Comprehensive Organic Transformations*, VCH Publishers, Inc., New York, 1989; Carruthers, *Some Modern Methods of Organic Synthesis*, 3rd Edition, Cambridge University Press, Cambridge, 1987; the entire contents of each of which are incorporated herein by reference.

5 Certain compounds of the present invention can comprise one or more asymmetric centers, and thus can exist in various stereoisomeric forms, *e.g.*, enantiomers and/or diastereomers. Thus, inventive compounds and compositions thereof may be in the form of an individual enantiomer, diastereomer or geometric isomer, or may be in the form of a mixture of stereoisomers. In certain embodiments, the compounds of the
10 invention are enantiopure compounds. In certain embodiments, mixtures of enantiomers or diastereomers are provided.

 Furthermore, certain compounds, as described herein may have one or more double bonds that can exist as either a Z or E isomer, unless otherwise indicated. The invention additionally encompasses the compounds as individual isomers substantially
15 free of other isomers and alternatively, as mixtures of various isomers, *e.g.*, racemic mixtures of enantiomers. In addition to the above-mentioned compounds *per se*, this invention also encompasses compositions comprising one or more compounds.

 As used herein, the term "isomers" includes any and all geometric isomers and stereoisomers. For example, "isomers" include *cis*- and *trans*-isomers, *E*- and *Z*- isomers,
20 *R*- and *S*-enantiomers, diastereomers, (D)-isomers, (L)-isomers, racemic mixtures thereof, and other mixtures thereof, as falling within the scope of the invention. For instance, a compound may, in some embodiments, be provided substantially free of one or more corresponding stereoisomers, and may also be referred to as "stereochemically enriched."

 Where a particular enantiomer is preferred, it may, in some embodiments be
25 provided substantially free of the opposite enantiomer, and may also be referred to as "optically enriched." "Optically enriched," as used herein, means that the compound is made up of a significantly greater proportion of one enantiomer. In certain embodiments the compound is made up of at least about 90% by weight of an enantiomer. In some embodiments the compound is made up of at least about 95%, 97%, 98%, 99%, 99.5%,
30 99.7%, 99.8%, or 99.9% by weight of an enantiomer. In some embodiments the

enantiomeric excess of provided compounds is at least about 90%, 95%, 97%, 98%, 99%, 99.5%, 99.7%, 99.8%, or 99.9%. In some embodiments, enantiomers may be isolated from racemic mixtures by any method known to those skilled in the art, including chiral high pressure liquid chromatography (HPLC) and the formation and crystallization of chiral salts or prepared by asymmetric syntheses. See, for example, Jacques, et al., *Enantiomers, Racemates and Resolutions* (Wiley Interscience, New York, 1981); Wilen, S.H., et al., *Tetrahedron* 33:2725 (1977); Eliel, E.L. *Stereochemistry of Carbon Compounds* (McGraw-Hill, NY, 1962); Wilen, S.H. *Tables of Resolving Agents and Optical Resolutions* p. 268 (E.L. Eliel, Ed., Univ. of Notre Dame Press, Notre Dame, IN 1972).

The terms "halo" and "halogen" as used herein refer to an atom selected from fluorine (fluoro, -F), chlorine (chloro, -Cl), bromine (bromo, -Br), and iodine (iodo, -I).

The term "aliphatic" or "aliphatic group", as used herein, denotes a hydrocarbon moiety that may be straight-chain (i.e., unbranched), branched, or cyclic (including fused, bridging, and spiro-fused polycyclic) and may be completely saturated or may contain one or more units of unsaturation, but which is not aromatic. Unless otherwise specified, aliphatic groups contain 1-30 carbon atoms. In certain embodiments, aliphatic groups contain 1-12 carbon atoms. In certain embodiments, aliphatic groups contain 1-8 carbon atoms. In certain embodiments, aliphatic groups contain 1-6 carbon atoms. In some embodiments, aliphatic groups contain 1-5 carbon atoms, in some embodiments, aliphatic groups contain 1-4 carbon atoms, in yet other embodiments aliphatic groups contain 1-3 carbon atoms, and in yet other embodiments aliphatic groups contain 1-2 carbon atoms. Suitable aliphatic groups include, but are not limited to, linear or branched, alkyl, alkenyl, and alkynyl groups, and hybrids thereof such as (cycloalkyl)alkyl, (cycloalkenyl)alkyl or (cycloalkyl)alkenyl. In certain embodiments, the term aliphatic group encompasses aliphatic groups wherein one or more hydrogen atoms are replaced with a halogen atom. In certain embodiments, the term aliphatic group encompasses chlorinated or fluorinated aliphatic groups including perfluorinated compounds.

The term "epoxide", as used herein, refers to a substituted or unsubstituted oxirane. Such substituted oxiranes include monosubstituted oxiranes, disubstituted

oxiranes, trisubstituted oxiranes, and tetrasubstituted oxiranes. Such epoxides may be further optionally substituted as defined herein. In certain embodiments, epoxides comprise a single oxirane moiety. In certain embodiments, epoxides comprise two or more oxirane moieties.

5 The term "polymer", as used herein, refers to a molecule of high relative molecular mass, the structure of which comprises the multiple repetition of units derived, actually or conceptually, from molecules of low relative molecular mass. In certain embodiments, a polymer is comprised of only one monomer species (*e.g.*, polyethylene oxide). In certain embodiments, a polymer of the present invention is a copolymer,
10 terpolymer, heteropolymer, block copolymer, or tapered heteropolymer of one or more epoxides.

 The term "unsaturated", as used herein, means that a moiety has one or more double or triple bonds.

 The terms "cycloaliphatic", "carbocycle", or "carbocyclic", used alone or as part
15 of a larger moiety, refer to a saturated or partially unsaturated cyclic aliphatic monocyclic, bicyclic, or polycyclic ring systems, as described herein, having from 3 to 12 members, wherein the aliphatic ring system is optionally substituted as defined above and described herein. Cycloaliphatic groups include, without limitation, cyclopropyl, cyclobutyl, cyclopentyl, cyclopentenyl, cyclohexyl, cyclohexenyl, cycloheptyl,
20 cycloheptenyl, cyclooctyl, cyclooctenyl, and cyclooctadienyl. In some embodiments, the cycloalkyl has 3-6 carbons. The terms "cycloaliphatic", "carbocycle" or "carbocyclic" also include aliphatic rings that are fused to one or more aromatic or nonaromatic rings, such as decahydronaphthyl or tetrahydronaphthyl, where the radical or point of attachment is on the aliphatic ring. In some embodiments, a carbocyclic groups is
25 bicyclic. In some embodiments, a carbocyclic group is tricyclic. In some embodiments, a carbocyclic group is polycyclic.

 The term "alkyl," as used herein, refers to saturated, straight- or branched-chain hydrocarbon radicals derived by removal of a single hydrogen atom from an aliphatic moiety. Unless otherwise specified, alkyl groups contain 1-12 carbon atoms. In certain
30 embodiments, alkyl groups contain 1-8 carbon atoms. In certain embodiments, alkyl

groups contain 1-6 carbon atoms. In some embodiments, alkyl groups contain 1-5 carbon atoms, in some embodiments, alkyl groups contain 1-4 carbon atoms, in yet other embodiments alkyl groups contain 1-3 carbon atoms, and in yet other embodiments alkyl groups contain 1-2 carbon atoms. Examples of alkyl radicals include, but are not limited to, methyl, ethyl, n-propyl, isopropyl, n-butyl, iso-butyl, sec-butyl, sec-pentyl, iso-pentyl, tert-butyl, n-pentyl, neopentyl, n-hexyl, sec-hexyl, n-heptyl, n-octyl, n-decyl, n-undecyl, dodecyl, and the like.

The term "alkenyl," as used herein, denotes a monovalent group derived by the removal of a single hydrogen atom from a straight- or branched-chain aliphatic moiety having at least one carbon-carbon double bond. Unless otherwise specified, alkenyl groups contain 2-12 carbon atoms. In certain embodiments, alkenyl groups contain 2-8 carbon atoms. In certain embodiments, alkenyl groups contain 2-6 carbon atoms. In some embodiments, alkenyl groups contain 2-5 carbon atoms, in some embodiments, alkenyl groups contain 2-4 carbon atoms, in yet other embodiments alkenyl groups contain 2-3 carbon atoms, and in yet other embodiments alkenyl groups contain 2 carbon atoms. Alkenyl groups include, for example, ethenyl, propenyl, allyl, 1,3-butadienyl, butenyl, 1-methyl-2-buten-1-yl, allyl, 1,3-butadienyl, allenyl, and the like.

The term "alkynyl," as used herein, refers to a monovalent group derived by the removal of a single hydrogen atom from a straight- or branched-chain aliphatic moiety having at least one carbon-carbon triple bond. Unless otherwise specified, alkynyl groups contain 2-12 carbon atoms. In certain embodiments, alkynyl groups contain 2-8 carbon atoms. In certain embodiments, alkynyl groups contain 2-6 carbon atoms. In some embodiments, alkynyl groups contain 2-5 carbon atoms, in some embodiments, alkynyl groups contain 2-4 carbon atoms, in yet other embodiments alkynyl groups contain 2-3 carbon atoms, and in yet other embodiments alkynyl groups contain 2 carbon atoms. Representative alkynyl groups include, but are not limited to, ethynyl, 2-propynyl (propargyl), 1-propynyl, and the like.

The term "carbocycle" and "carbocyclic ring" as used herein, refer to monocyclic and polycyclic moieties wherein the rings contain only carbon atoms. Unless otherwise specified, carbocycles may be saturated, partially unsaturated or aromatic, and contain 3

to 20 carbon atoms. Representative carbocycles include cyclopropane, cyclobutane, cyclopentane, cyclohexane, bicyclo[2.2.1]heptane, norbornene, phenyl, cyclohexene, naphthalene, and spiro[4.5]decane, to name but a few.

The term "aryl" used alone or as part of a larger moiety as in "aralkyl",
5 "aralkoxy", or "aryloxyalkyl", refers to monocyclic and polycyclic ring systems having a total of six to 20 ring members, wherein at least one ring in the system is aromatic and wherein each ring in the system contains three to twelve ring members. The term "aryl" may be used interchangeably with the term "aryl ring". In certain embodiments of the present invention, "aryl" refers to an aromatic ring system which includes, but is not
10 limited to, phenyl, biphenyl, naphthyl, anthracyl and the like, which may bear one or more substituents. Also included within the scope of the term "aryl", as it is used herein, is a group in which an aromatic ring is fused to one or more additional rings, such as benzofuranyl, indanyl, phthalimidyl, naphthimidyl, phenanthridinyl, or tetrahydronaphthyl, and the like.

15 The term "heteroaliphatic," as used herein, refers to aliphatic groups wherein one or more carbon atoms are independently replaced by one or more atoms selected from the group consisting of oxygen, sulfur, nitrogen, phosphorus, or boron. In certain embodiments, one to six carbon atoms are independently replaced by one or more of oxygen, sulfur, nitrogen, or phosphorus. Heteroaliphatic groups may be substituted or
20 unsubstituted, branched or unbranched, cyclic or acyclic, and include saturated, unsaturated or partially unsaturated groups.

The terms "heteroaryl" and "heteroar-", used alone or as part of a larger moiety, e.g., "heteroaralkyl", or "heteroaralkoxy", refer to groups having 5 to 14 ring atoms, preferably 5, 6, or 9 ring atoms; having 6, 10, or 14 π electrons shared in a cyclic array;
25 and having, in addition to carbon atoms, from one to five heteroatoms. The term "heteroatom" refers to nitrogen, oxygen, or sulfur, and includes any oxidized form of nitrogen or sulfur, and any quaternized form of a basic nitrogen. Heteroaryl groups include, without limitation, thienyl, furanyl, pyrrolyl, imidazolyl, pyrazolyl, triazolyl, tetrazolyl, oxazolyl, isoxazolyl, oxadiazolyl, thiazolyl, isothiazolyl, thiadiazolyl, pyridyl,
30 pyridazinyl, pyrimidinyl, pyrazinyl, indolizinyl, purinyl, naphthyridinyl, benzofuranyl

and pteridinyl. The terms "heteroaryl" and "heteroar-", as used herein, also include groups in which a heteroaromatic ring is fused to one or more aryl, cycloaliphatic, or heterocyclyl rings, where the radical or point of attachment is on the heteroaromatic ring. Nonlimiting examples include indolyl, isoindolyl, benzothienyl, benzofuranyl, 5 dibenzofuranyl, indazolyl, benzimidazolyl, benzthiazolyl, quinolyl, isoquinolyl, cinnolinyl, phthalazinyl, quinazolinyl, quinoxalyl, 4*H*-quinoliziny, carbazolyl, acridinyl, phenazinyl, phenothiazinyl, phenoxazinyl, tetrahydroquinolinyl, tetrahydroisoquinolinyl, and pyrido[2,3-*b*]-1,4-oxazin-3(4*H*)-one. A heteroaryl group may be mono- or polycyclic. The term "heteroaryl" may be used interchangeably with 10 the terms "heteroaryl ring", "heteroaryl group", or "heteroaromatic", any of which terms include rings that are optionally substituted. The term "heteroaralkyl" refers to an alkyl group substituted by a heteroaryl, wherein the alkyl and heteroaryl portions independently are optionally substituted.

As used herein, the terms "heterocycle", "heterocyclyl", "heterocyclic radical", 15 and "heterocyclic ring" are used interchangeably and refer to a stable 5- to 7-membered monocyclic or 7-14-membered bicyclic heterocyclic moiety that is saturated, partially unsaturated, or aromatic and having, in addition to carbon atoms, one or more, preferably one to four, heteroatoms, as defined above. When used in reference to a ring atom of a heterocycle, the term "nitrogen" includes a substituted nitrogen. As an example, in a 20 saturated or partially unsaturated ring having 0-3 heteroatoms selected from oxygen, sulfur or nitrogen, the nitrogen may be N (as in 3,4-dihydro-2*H*-pyrrolyl), NH (as in pyrrolidinyl), or NR (as in *N*-substituted pyrrolidinyl).

A heterocyclic ring can be attached to its pendant group at any heteroatom or carbon atom that results in a stable structure and any of the ring atoms can be optionally 25 substituted. Examples of such saturated or partially unsaturated heterocyclic radicals include, without limitation, tetrahydrofuranyl, tetrahydrothienyl, pyrrolidinyl, pyrrolidonyl, piperidinyl, pyrrolinyl, tetrahydroquinolinyl, tetrahydroisoquinolinyl, decahydroquinolinyl, oxazolidinyl, piperazinyl, dioxanyl, dioxolanyl, diazepinyl, oxazepinyl, thiazepinyl, morpholinyl, and quinuclidinyl. The terms "heterocycle", 30 "heterocyclyl", "heterocyclyl ring", "heterocyclic group", "heterocyclic moiety", and "heterocyclic radical", are used interchangeably herein, and also include groups in which

a heterocyclyl ring is fused to one or more aryl, heteroaryl, or cycloaliphatic rings, such as indolyl, 3*H*-indolyl, chromanyl, phenanthridinyl, or tetrahydroquinolyl, where the radical or point of attachment is on the heterocyclyl ring. A heterocyclyl group may be mono- or bicyclic. The term "heterocyclylalkyl" refers to an alkyl group substituted by a heterocyclyl, wherein the alkyl and heterocyclyl portions independently are optionally substituted.

The term "acyl" as used herein refers to a group having a formula -C(O)R where R is hydrogen or an optionally substituted aliphatic, aryl, or heterocyclic group.

As used herein, the term "partially unsaturated" refers to a ring moiety that includes at least one double or triple bond. The term "partially unsaturated" is intended to encompass rings having multiple sites of unsaturation, but is not intended to include aryl or heteroaryl moieties, as herein defined.

One of ordinary skill in the art will appreciate that the synthetic methods, as described herein, utilize a variety of protecting groups. By the term "protecting group," as used herein, it is meant that a particular functional moiety, *e.g.*, O, S, or N, is masked or blocked, permitting, if desired, a reaction to be carried out selectively at another reactive site in a multifunctional compound. In preferred embodiments, a protecting group reacts selectively in good yield to give a protected substrate that is stable to the projected reactions; the protecting group is preferably selectively removable by readily available, preferably non-toxic reagents that do not attack the other functional groups; the protecting group forms a separable derivative (more preferably without the generation of new stereogenic centers); and the protecting group will preferably have a minimum of additional functionality to avoid further sites of reaction. As detailed herein, oxygen, sulfur, nitrogen, and carbon protecting groups may be utilized. By way of non-limiting example, hydroxyl protecting groups include methyl, methoxymethyl (MOM), methylthiomethyl (MTM), *t*-butylthiomethyl, (phenyldimethylsilyl)methoxymethyl (SMOM), benzyloxymethyl (BOM), *p*-methoxybenzyloxymethyl (PMBM), (4-methoxyphenoxy)methyl (*p*-AOM), guaiacolmethyl (GUM), *t*-butoxymethyl, 4-pentenylloxymethyl (POM), siloxymethyl, 2-methoxyethoxymethyl (MEM), 2,2,2-trichloroethoxymethyl, bis(2-chloroethoxy)methyl, 2-(trimethylsilyl)ethoxymethyl

(SEMOR), tetrahydropyranyl (THP), 3-bromotetrahydropyranyl, tetrahydrothiopyranyl, 1-methoxycyclohexyl, 4-methoxytetrahydropyranyl (MTHP), 4-methoxytetrahydrothiopyranyl, 4-methoxytetrahydrothiopyranyl S,S-dioxide, 1-[(2-chloro-4-methyl)phenyl]-4-methoxypiperidin-4-yl (CTMP), 1,4-dioxan-2-yl, 5 tetrahydrofuran-2-yl, tetrahydrothiofuran-2-yl, 2,3,3a,4,5,6,7,7a-octahydro-7,8,8-trimethyl-4,7-methanobenzofuran-2-yl, 1-ethoxyethyl, 1-(2-chloroethoxy)ethyl, 1-methyl-1-methoxyethyl, 1-methyl-1-benzyloxyethyl, 1-methyl-1-benzyloxy-2-fluorooctyl, 2,2,2-trichloroethyl, 2-trimethylsilyl ethyl, 2-(phenylselenenyl)ethyl, *t*-butyl, allyl, *p*-chlorophenyl, *p*-methoxyphenyl, 2,4- 10 dinitrophenyl, benzyl, *p*-methoxybenzyl, 3,4-dimethoxybenzyl, *o*-nitrobenzyl, *p*-nitrobenzyl, *p*-halobenzyl, 2,6-dichlorobenzyl, *p*-cyanobenzyl, *p*-phenylbenzyl, 2-picolyl, 4-picolyl, 3-methyl-2-picolyl *N*-oxido, diphenylmethyl, *p,p'*-dinitrobenzhydrazide, 5-dibenzosuberonyl, triphenylmethyl, α -naphthyl diphenylmethyl, *p*-methoxyphenyl diphenylmethyl, di(*p*-methoxyphenyl)phenylmethyl, 15 tri(*p*-methoxyphenyl)methyl, 4-(4'-bromophenacyloxyphenyl)diphenylmethyl, 4,4',4''-tris(4,5-dichlorophthalimidophenyl)methyl, 4,4',4''-tris(levulinoyloxyphenyl)methyl, 4,4',4''-tris(benzoyloxyphenyl)methyl, 3-(imidazol-1-yl)bis(4',4''-dimethoxyphenyl)methyl, 1,1-bis(4-methoxyphenyl)-1'-pyrenylmethyl, 9-anthryl, 9-(9-phenyl)xanthenyl. 20 9-(9-phenyl-10-oxo)anthryl, 1,3-benzodithiolan-2-yl, benzoisothiazolyl S,S-dioxide, trimethylsilyl (TMS), triethylsilyl (TES), triisopropylsilyl (TIPS), dimethylisopropylsilyl (IPDMS), diethylisopropylsilyl (DEIPS), dimethylhexylsilyl, *t*-butyldimethylsilyl (TBDMS), *t*-butyldiphenylsilyl (TBDPS), tribenzylsilyl, tri-*p*-xylylsilyl, triphenylsilyl, diphenylmethylsilyl (DPMS), *t*-butylmethoxyphenylsilyl (TBMPS), formate. 25 benzoylformate, acetate, chloroacetate, dichloroacetate, trichloroacetate, trifluoroacetate, methoxyacetate, triphenylmethoxyacetate, phenoxyacetate, *p*-chlorophenoxyacetate, 3-phenylpropionate, 4-oxopentanoate (levulinate), 4,4-(ethylenedithio)pentanoate (levulinoyldithioacetal), pivaloate, adamantate, crotonate, 4-methoxycrotonate, benzoate, *p*-phenylbenzoate, 2,4,6-trimethylbenzoate (mesitoate), alkyl methyl carbonate, 30 9-fluorenylmethyl carbonate (Fmoc), alkyl ethyl carbonate, alkyl 2,2,2-trichloroethyl carbonate (Troc), 2-(trimethylsilyl)ethyl carbonate (TMSEC), 2-(phenylsulfonyl) ethyl carbonate (Psec), 2-(triphenylphosphonio) ethyl carbonate (Peoc), alkyl isobutyl

carbonate, alkyl vinyl carbonate alkyl allyl carbonate, alkyl *p*-nitrophenyl carbonate, alkyl benzyl carbonate, alkyl *p*-methoxybenzyl carbonate, alkyl 3,4-dimethoxybenzyl carbonate, alkyl *o*-nitrobenzyl carbonate, alkyl *p*-nitrobenzyl carbonate, alkyl *S*-benzyl thiocarbonate, 4-ethoxy-1-naphthyl carbonate, methyl dithiocarbonate, 2-iodobenzoate, 5 4-azidobutyrate, 4-nitro-4-methylpentanoate, *o*-(dibromomethyl)benzoate, 2-formylbenzenesulfonate, 2-(methylthiomethoxy)ethyl, 4-(methylthiomethoxy)butyrate, 2-(methylthiomethoxymethyl)benzoate, 2,6-dichloro-4-methylphenoxyacetate, 2,6-dichloro-4-(1,1,3,3-tetramethylbutyl)phenoxyacetate, 2,4-bis(1,1-dimethylpropyl)phenoxyacetate, chlorodiphenylacetate, isobutyrate, 10 monosuccinoate, (*E*)-2-methyl-2-butenolate, *o*-(methoxycarbonyl)benzoate, α -naphthoate, nitrate, alkyl *N,N,N',N'*-tetramethylphosphorodiamidate, alkyl *N*-phenylcarbamate, borate, dimethylphosphinothioyl, alkyl 2,4-dinitrophenylsulfonate, sulfate, methanesulfonate (mesylate), benzyisulfonate, and tosylate (Ts). For protecting 1,2- or 1,3-diols, the protecting groups include methylene acetal, ethylidene acetal, 15 1-*t*-butylethylidene ketal, 1-phenylethylidene ketal, (4-methoxyphenyl)ethylidene acetal, 2,2,2-trichloroethylidene acetal, acetone, cyclopentylidene ketal, cyclohexylidene ketal, cycloheptylidene ketal, benzyidene acetal, *p*-methoxybenzyidene acetal, 2,4-dimethoxybenzyidene ketal, 3,4-dimethoxybenzyidene acetal, 2-nitrobenzyidene acetal, methoxymethylene acetal, ethoxymethylene acetal, dimethoxymethylene ortho ester, 20 1-methoxyethylidene ortho ester, 1-ethoxyethylidene ortho ester, 1,2-dimethoxyethylidene ortho ester, α -methoxybenzyidene ortho ester, 1-(*N,N*-dimethylamino)ethylidene derivative, α -(*N,N'*-dimethylamino)benzyidene derivative, 2-oxacyclopentylidene ortho ester, di-*t*-butylsilylene group (DTBS), 1,3-(1,1,3,3-tetraisopropylidisiloxanylidene) derivative (TIPDS), tetra-*t*-butoxydisiloxane-1,3- 25 diylidene derivative (TBDS), cyclic carbonates, cyclic boronates, ethyl boronate, and phenyl boronate. Amino-protecting groups include methyl carbamate, ethyl carbamate, 9-fluorenylmethyl carbamate (Fmoc), 9-(2-sulfo)fluorenylmethyl carbamate, 9-(2,7-dibromo)fluorenylmethyl carbamate, 2,7-di-*t*-butyl-[9-(10,10-dioxo-10,10,10,10-tetrahydrothioxanthyl)]methyl carbamate (DBD-Tmoc), 4-methoxyphenacyl carbamate (Phenoc), 2,2,2-trichloroethyl carbamate (Troc), 2-trimethylsilylethyl carbamate (Teoc), 2-phenylethyl carbamate (hZ), 30 1-(1-adamantyl)-1-methylethyl carbamate (Adpoc), 1,1-dimethyl-2-haloethyl carbamate,

1,1-dimethyl-2,2-dibromoethyl carbamate (DB-*t*-BOC), 1,1-dimethyl-2,2,2-trichloroethyl carbamate (TCBOC), 1-methyl-1-(4-biphenyl)ethyl carbamate (Bpoc), 1-(3,5-di-*t*-butylphenyl)-1-methylethyl carbamate (*t*-Bumeoc), 2-(2'- and 4'-pyridyl)ethyl carbamate (Pyoc), 2-(*N,N*-dicyclohexylcarboxamido)ethyl carbamate, *t*-butyl carbamate (BOC), 1-adamantyl carbamate (Adoc), vinyl carbamate (Voc), allyl carbamate (Alloc), 1-isopropylallyl carbamate (Ipaoc), cinnamyl carbamate (Coc), 4-nitrocinnamyl carbamate (Noc), 8-quinolyl carbamate, *N*-hydroxypiperidiny carbamate, alkylidithio carbamate, benzyl carbamate (Cbz), *p*-methoxybenzyl carbamate (Moz), *p*-nitrobenzyl carbamate, *p*-bromobenzyl carbamate, *p*-chlorobenzyl carbamate, 2,4-dichlorobenzyl carbamate, 4-methylsulfinylbenzyl carbamate (MsZ), 9-anthrylmethyl carbamate, diphenylmethyl carbamate, 2-methylthioethyl carbamate, 2-methylsulfonyl ethyl carbamate, 2-(*p*-toluenesulfonyl)ethyl carbamate, [2-(1,3-dithianyl)]methyl carbamate (Dmoc), 4-methylthiophenyl carbamate (Mtpc), 2,4-dimethylthiophenyl carbamate (Bmpc), 2-phosphonioethyl carbamate (Peoc), 2-triphenylphosphonioisopropyl carbamate (Ppoc), 1,1-dimethyl-2-cyanoethyl carbamate, *m*-chloro-*p*-acyloxybenzyl carbamate, *p*-(dihydroxyboryl)benzyl carbamate, 5-benzisoxazolylmethyl carbamate, 2-(trifluoromethyl)-6-chromonylmethyl carbamate (TcroC), *m*-nitrophenyl carbamate, 3,5-dimethoxybenzyl carbamate, *o*-nitrobenzyl carbamate, 3,4-dimethoxy-6-nitrobenzyl carbamate, phenyl(*o*-nitrophenyl)methyl carbamate, phenothiazinyl-(10)-carbonyl derivative, *N'*-*p*-toluenesulfonylaminocarbonyl derivative, *N'*-phenylaminothiocarbonyl derivative, *t*-amyl carbamate, *S*-benzyl thiocarbamate, *p*-cyanobenzyl carbamate, cyclobutyl carbamate, cyclohexyl carbamate, cyclopentyl carbamate, cyclopropylmethyl carbamate, *p*-decyloxybenzyl carbamate, 2,2-dimethoxycarbonylvinyl carbamate, *o*-(*N,N*-dimethylcarboxamido)benzyl carbamate, 1,1-dimethyl-3-(*N,N*-dimethylcarboxamido)propyl carbamate, 1,1-dimethylpropynyl carbamate, di(2-pyridyl)methyl carbamate, 2-furanylmethyl carbamate, 2-iodoethyl carbamate, isoborynl carbamate, isobutyl carbamate, isonicotiny carbamate, *p*-(*p'*-methoxyphenylazo)benzyl carbamate, 1-methylcyclobutyl carbamate, 1-methylcyclohexyl carbamate, 1-methyl-1-cyclopropylmethyl carbamate, 1-methyl-1-(3,5-dimethoxyphenyl)ethyl carbamate, 1-methyl-1-(*p*-phenylazophenyl)ethyl carbamate, 1-methyl-1-phenylethyl carbamate, 1-methyl-1-(4-pyridyl)ethyl carbamate, phenyl carbamate, *p*-(phenylazo)benzyl carbamate, 2,4,6-tri-*t*-butylphenyl carbamate, 4-

(trimethylammonium)benzyl carbamate, 2,4,6-trimethylbenzyl carbamate, formamide, acetamide, chloroacetamide, trichloroacetamide, trifluoroacetamide, phenylacetamide, 3-phenylpropanamide, picolinamide, 3-pyridylcarboxamide, *N*-benzoylphenylalanyl derivative, benzamide, *p*-phenylbenzamide, *o*-nitrophenylacetamide,

5 *o*-nitrophenoxyacetamide, acetoacetamide, (*N*'-dithiobenzoyloxycarbonylamino)acetamide, 3-(*p*-hydroxyphenyl)propanamide, 3-(*o*-nitrophenyl)propanamide, 2-methyl-2-(*o*-nitrophenoxy)propanamide, 2-methyl-2-(*o*-phenylazophenoxy)propanamide, 4-chlorobutanamide, 3-methyl-3-nitrobutanamide, *o*-nitrocinnamide, *N*-acetylmethionine derivative, *o*-nitrobenzamide,

10 *o*-(benzoyloxymethyl)benzamide, 4,5-diphenyl-3-oxazolin-2-one, *N*-phthalimide, *N*-dithiasuccinimide (Dts), *N*-2,3-diphenylmaleimide, *N*-2,5-dimethylpyrrole, *N*-1,1,4,4-tetramethyldisilylazacyclopentane adduct (STABASE), 5-substituted 1,3-dimethyl-1,3,5-triazacyclohexan-2-one, 5-substituted 1,3-dibenzyl-1,3,5-triazacyclohexan-2-one, 1-substituted 3,5-dinitro-4-pyridone, *N*-methylamine, *N*-allylamine,

15 *N*-[2-(trimethylsilyl)ethoxy]methylamine (SEM), *N*-3-acetoxypyrrolamine, *N*-(1-isopropyl-4-nitro-2-oxo-3-pyrroline-3-yl)amine, quaternary ammonium salts, *N*-benzylamine, *N*-di(4-methoxyphenyl)methylamine, *N*-5-dibenzosuberylamine, *N*-triphenylmethylamine (Tr), *N*-[(4-methoxyphenyl)diphenylmethyl]amine (MMTr), *N*-9-phenylfluorenylamine (PhF), *N*-2,7-dichloro-9-fluorenylmethylencamine,

20 *N*-ferrocenylmethylamino (Fcm), *N*-2-picolylamino *N*'-oxide, *N*-1,1-dimethylthiomethyleneamine, *N*-benzylideneamine, *N*-*p*-methoxybenzylideneamine, *N*-diphenylmethyleneamine, *N*-[(2-pyridyl)mesityl]methyleneamine, *N*-(*N*',*N*'-dimethylaminomethylene)amine, *N,N*'-isopropylidenediamine, *N*-*p*-nitrobenzylideneamine, *N*-salicylideneamine, *N*-5-chlorosalicylideneamine, *N*-(5-chloro-2-hydroxyphenyl)phenylmethyleneamine,

25 *N*-cyclohexylideneamine, *N*-(5,5-dimethyl-3-oxo-1-cyclohexenyl)amine, *N*-borane derivative, *N*-diphenylborinic acid derivative, *N*-[phenyl(pentacarbonylchromium- or tungsten)carbonyl]amine, *N*-copper chelate, *N*-zinc chelate, *N*-nitroamine, *N*-nitrosoamine, amine *N*-oxide, diphenylphosphinamide (Dpp),

30 dimethylthiophosphinamide (Mpt), diphenylthiophosphinamide (Ppt), dialkyl phosphoramidates, dibenzyl phosphoramidate, diphenyl phosphoramidate, benzenesulfenamide, *o*-nitrobenzenesulfenamide (Nps), 2,4-dinitrobenzenesulfenamide,

pentachlorobenzenesulfenamide, 2-nitro-4-methoxybenzenesulfenamide, triphenylmethylsulfenamide, 3-nitropyridinesulfenamide (Npys), *p*-toluenesulfonamide (Ts), benzenesulfonamide, 2,3,6-trimethyl-4-methoxybenzenesulfonamide (Mtr), 2,4,6-trimethoxybenzenesulfonamide (Mtb), 2,6-dimethyl-4-methoxybenzenesulfonamide (Pmc), 2,3,5,6-tetramethyl-4-methoxybenzenesulfonamide (Mte), 4-methoxybenzenesulfonamide (Mbs), 2,4,6-trimethylbenzenesulfonamide (Mts), 2,6-dimethoxy-4-methylbenzenesulfonamide (iMds), 2,2,5,7,8-pentamethylchroman-6-sulfonamide (Pmc), methanesulfonamide (Ms), β -trimethylsilylethanesulfonamide (SES), 9-anthracenesulfonamide, 4-(4',8'-dimethoxynaphthylmethyl)benzenesulfonamide (DNMBS), benzylsulfonamide, trifluoromethylsulfonamide, and phenacysulfonamide. Exemplary protecting groups are detailed herein, however, it will be appreciated that the present invention is not intended to be limited to these protecting groups; rather, a variety of additional equivalent protecting groups can be readily identified using the above criteria and utilized in the method of the present invention. Additionally, a variety of protecting groups are described in *Protecting Groups in Organic Synthesis*, T. W. Greene and P. G. M. Wuts, 3rd edition, John Wiley & Sons, 1999, the entirety of which is incorporated herein by reference.

When substituents are described herein, the term "radical" or "optionally substituted radical" is sometimes used. In this context, "radical" means a moiety or functional group having an available position for attachment to the structure on which the substituent is bound. In general the point of attachment would bear a hydrogen atom if the substituent were an independent neutral molecule rather than a substituent. The terms "radical" or "optionally-substituted radical" in this context are thus interchangeable with "group" or "optionally-substituted group".

As described herein, compounds of the invention may contain "optionally substituted" moieties. In general, the term "substituted", whether preceded by the term "optionally" or not, means that one or more hydrogens of the designated moiety are replaced with a suitable substituent. Unless otherwise indicated, an "optionally substituted group" or "optionally substituted radical" may have a suitable substituent at each substitutable position of the group, and when more than one position in any given structure may be substituted with more than one substituent selected from a specified

group, the substituent may be either the same or different at every position. Combinations of substituents envisioned by this invention are preferably those that result in the formation of stable or chemically feasible compounds. The term "stable", as used herein, refers to compounds that are not substantially altered when subjected to conditions to allow for their production, detection, and, in certain embodiments, their recovery, purification, and use for one or more of the purposes disclosed herein.

In some chemical structures herein, substituents are shown attached to a bond that crosses a bond in a ring of the depicted molecule. This convention indicates that one or more of the substituents may be attached to the ring at any available position (usually in place of a hydrogen atom of the parent structure). In cases where an atom of a ring so substituted has two substitutable positions, two groups may be present on the same ring atom. Unless otherwise indicated, when more than one substituent is present, each is defined independently of the others, and each may have a different structure. In cases where the substituent shown crossing a bond of the ring is -R, this has the same meaning as if the ring were said to be "optionally substituted" as described in the preceding paragraph.

Suitable monovalent substituents on a substitutable carbon atom of an "optionally substituted" group are independently halogen; $-(CH_2)_{0-4}R^\circ$; $-(CH_2)_{0-4}OR^\circ$; $-O-(CH_2)_{0-4}C(O)OR^\circ$; $-(CH_2)_{0-4}CH(OR^\circ)_2$; $-(CH_2)_{0-4}SR^\circ$; $-(CH_2)_{0-4}Ph$, which may be substituted with R° ; $-(CH_2)_{0-4}O(CH_2)_{0-1}Ph$ which may be substituted with R° ; $-CH=CHPh$, which may be substituted with R° ; $-NO_2$; $-CN$; $-N_3$; $-(CH_2)_{0-4}N(R^\circ)_2$; $-(CH_2)_{0-4}N(R^\circ)C(O)R^\circ$; $-N(R^\circ)C(S)R^\circ$; $-(CH_2)_{0-4}N(R^\circ)C(O)NR^\circ_2$; $-N(R^\circ)C(S)NR^\circ_2$; $-(CH_2)_{0-4}N(R^\circ)C(O)OR^\circ$; $-N(R^\circ)N(R^\circ)C(O)R^\circ$; $-N(R^\circ)N(R^\circ)C(O)NR^\circ_2$; $-N(R^\circ)N(R^\circ)C(O)OR^\circ$; $-(CH_2)_{0-4}C(O)R^\circ$; $-C(S)R^\circ$; $-(CH_2)_{0-4}C(O)OR^\circ$; $-(CH_2)_{0-4}C(O)N(R^\circ)_2$; $-(CH_2)_{0-4}C(O)SR^\circ$; $-(CH_2)_{0-4}C(O)OSiR^\circ_3$; $-(CH_2)_{0-4}OC(O)R^\circ$; $-OC(O)(CH_2)_{0-4}SR^\circ$; $-SC(S)SR^\circ$; $-(CH_2)_{0-4}SC(O)R^\circ$; $-(CH_2)_{0-4}C(O)NR^\circ_2$; $-C(S)NR^\circ_2$; $-C(S)SR^\circ$; $-SC(S)SR^\circ$; $-(CH_2)_{0-4}OC(O)NR^\circ_2$; $-C(O)N(OR^\circ)R^\circ$; $-C(O)C(O)R^\circ$; $-C(O)CH_2C(O)R^\circ$; $-C(NOR^\circ)R^\circ$; $-(CH_2)_{0-4}SSR^\circ$; $-(CH_2)_{0-4}S(O)_2R^\circ$; $-(CH_2)_{0-4}S(O)_2OR^\circ$; $-(CH_2)_{0-4}OS(O)_2R^\circ$; $-S(O)_2NR^\circ_2$; $-(CH_2)_{0-4}S(O)R^\circ$; $-N(R^\circ)S(O)_2NR^\circ_2$; $-N(R^\circ)S(O)_2R^\circ$; $-N(OR^\circ)R^\circ$; $-C(NH)NR^\circ_2$; $-P(O)_2R^\circ$; $-P(O)R^\circ_2$; $-OP(O)R^\circ_2$; $-OP(O)(OR^\circ)_2$; SiR°_3 ; $-(C_{1-4}$

straight or branched alkylene)O-N(R^o)₂; or -(C₁₋₄ straight or branched alkylene)C(O)O-N(R^o)₂, wherein each R^o may be substituted as defined below and is independently hydrogen, C₁₋₈ aliphatic, -CH₂Ph, -O(CH₂)₀₋₁Ph, or a 5-6-membered saturated, partially unsaturated, or aryl ring having 0-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur, or, notwithstanding the definition above, two independent occurrences of R^o, taken together with intervening atom(s), form a 3-12-membered saturated, partially unsaturated, or aryl mono- or polycyclic ring having 0-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur, which may be substituted as defined below.

Suitable monovalent substituents on R^o (or the ring formed by taking two independent occurrences of R^o together with their intervening atoms), are independently halogen, -(CH₂)₀₋₂R*, -(haloR*), -(CH₂)₀₋₂OH, -(CH₂)₀₋₂OR*, -(CH₂)₀₋₂CH(OR*)₂; -O(haloR*), -CN, -N₃, -(CH₂)₀₋₂C(O)R*, -(CH₂)₀₋₂C(O)OH, -(CH₂)₀₋₂C(O)OR*, -(CH₂)₀₋₄C(O)N(R^o)₂; -(CH₂)₀₋₂SR*, -(CH₂)₀₋₂SH, -(CH₂)₀₋₂NH₂, -(CH₂)₀₋₂NHR*, -(CH₂)₀₋₂NR*₂, -NO₂, -SiR*₃, -OSiR*₃, -C(O)SR*, -(C₁₋₄ straight or branched alkylene)C(O)OR*, or -SSR* wherein each R* is unsubstituted or where preceded by "halo" is substituted only with one or more halogens, and is independently selected from C₁₋₄ aliphatic, -CH₂Ph, -O(CH₂)₀₋₁Ph, or a 5-6-membered saturated, partially unsaturated, or aryl ring having 0-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur. Suitable divalent substituents on a saturated carbon atom of R^o include =O and =S.

Suitable divalent substituents on a saturated carbon atom of an "optionally substituted" group include the following: =O, =S, =NNR*₂, =NNHC(O)R*, =NNHC(O)OR*, =NNHS(O)₂R*, =NR*, =NOR*, -O(C(R*₂))₂₋₃O-, or -S(C(R*₂))₂₋₃S-, wherein each independent occurrence of R* is selected from hydrogen, C₁₋₆ aliphatic which may be substituted as defined below, or an unsubstituted 5-6-membered saturated, partially unsaturated, or aryl ring having 0-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur. Suitable divalent substituents that are bound to vicinal substitutable carbons of an "optionally substituted" group include: -O(CR*₂)₂₋₃O-, wherein each independent occurrence of R* is selected from hydrogen, C₁₋₆ aliphatic

which may be substituted as defined below, or an unsubstituted 5-6-membered saturated, partially unsaturated, or aryl ring having 0-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur.

5 Suitable substituents on the aliphatic group of R^* include halogen, $-R^*$, $-(\text{halo}R^*)$, $-\text{OH}$, $-\text{OR}^*$, $-\text{O}(\text{halo}R^*)$, $-\text{CN}$, $-\text{C}(\text{O})\text{OH}$, $-\text{C}(\text{O})\text{OR}^*$, $-\text{NH}_2$, $-\text{NHR}^*$, $-\text{NR}^{*2}$, or $-\text{NO}_2$, wherein each R^* is unsubstituted or where preceded by "halo" is substituted only with one or more halogens, and is independently C_{1-4} aliphatic, $-\text{CH}_2\text{Ph}$, $-\text{O}(\text{CH}_2)_{0-1}\text{Ph}$, or a 5-6-membered saturated, partially unsaturated, or aryl ring having 0-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur.

10 Suitable substituents on a substitutable nitrogen of an "optionally substituted" group include $-\text{R}^\dagger$, $-\text{NR}^\dagger_2$, $-\text{C}(\text{O})\text{R}^\dagger$, $-\text{C}(\text{O})\text{OR}^\dagger$, $-\text{C}(\text{O})\text{C}(\text{O})\text{R}^\dagger$, $-\text{C}(\text{O})\text{CH}_2\text{C}(\text{O})\text{R}^\dagger$, $-\text{S}(\text{O})_2\text{R}^\dagger$, $-\text{S}(\text{O})_2\text{NR}^\dagger_2$, $-\text{C}(\text{S})\text{NR}^\dagger_2$, $-\text{C}(\text{NH})\text{NR}^\dagger_2$, or $-\text{N}(\text{R}^\dagger)\text{S}(\text{O})_2\text{R}^\dagger$; wherein each $\text{R}^\dagger$ is independently hydrogen, C_{1-6} aliphatic which may be substituted as defined below, unsubstituted $-\text{OPh}$, or an unsubstituted 5-6-membered saturated, partially unsaturated, or aryl ring having 0-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur, or, notwithstanding the definition above, two independent occurrences of $\text{R}^\dagger$, taken together with intervening atom(s) form an unsubstituted 3-12-membered saturated, partially unsaturated, or aryl mono- or bicyclic ring having 0-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur. A substitutable nitrogen may be substituted with three $\text{R}^\dagger$ substituents to provide a charged ammonium moiety $-\text{N}^+(\text{R}^\dagger)_3$, wherein the ammonium moiety is further complexed with a suitable counterion.

20 Suitable substituents on the aliphatic group of $\text{R}^\dagger$ are independently halogen, $-\text{R}^*$, $-(\text{halo}R^*)$, $-\text{OH}$, $-\text{OR}^*$, $-\text{O}(\text{halo}R^*)$, $-\text{CN}$, $-\text{C}(\text{O})\text{OH}$, $-\text{C}(\text{O})\text{OR}^*$, $-\text{NH}_2$, $-\text{NHR}^*$, $-\text{NR}^{*2}$, or $-\text{NO}_2$, wherein each R^* is unsubstituted or where preceded by "halo" is substituted only with one or more halogens, and is independently C_{1-4} aliphatic, $-\text{CH}_2\text{Ph}$, $-\text{O}(\text{CH}_2)_{0-1}\text{Ph}$, or a 5-6-membered saturated, partially unsaturated, or aryl ring having 0-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur.

30 As used herein, the term "catalyst" refers to a substance the presence of which increases the rate and/or extent of a chemical reaction, while not being consumed or undergoing a permanent chemical change itself.

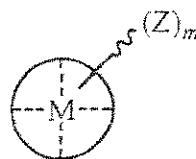
As used herein, the term “multidentate” refers to ligands having multiple sites capable of coordinating to a single metal center.

As used herein, the term “activating moiety” refers to a moiety comprising one or more activating functional groups. In certain embodiments, an activating moiety improves the catalytic activity of a metal complex. In some embodiments, such improved catalytic activity is characterized by higher conversion of starting materials compared to a metal complex lacking an activating moiety. In some embodiments, such improved catalytic activity is characterized by higher rate of conversion of starting materials compared to a metal complex lacking an activating moiety. In some embodiments, such improved catalytic activity is characterized by higher yield of product compared to a metal complex lacking an activating moiety.

Detailed Description of Certain Embodiments

The present invention provides, among other things, unimolecular metal complexes for the copolymerization of carbon dioxide and epoxides and methods of using the same. In certain embodiments, provided metal complexes contain a metal-ligand moiety tethered to one or more activating moieties. In some embodiments, an activating moiety comprises a linker and one or more activating functional groups. In some embodiments, provided metal complexes act as polymerization catalysts. In certain embodiments, at least one activating functional group present on the tethered moiety can act as a polymerization co-catalyst and thereby increase the rate of the copolymerization.

In certain embodiments, provided metal complexes include a metal atom coordinated to a multidentate ligand and at least one activating moiety tethered to the multidentate ligand. In certain embodiments, provided metal complexes have the structure:



wherein:

M is a metal atom;



comprises a multidentate ligand;

—(Z)_m represents one or more activating moieties attached to the multidentate
ligand, where — is a linker moiety covalently coupled to the ligand, each Z
is an activating functional group; and m is an integer from 1 to 4 representing the
number of Z groups present on an individual linker moiety.

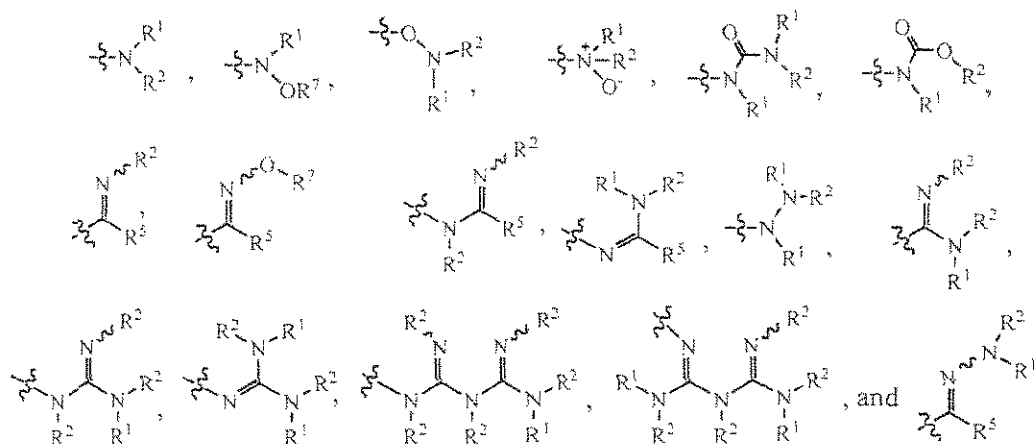
In certain embodiments, provided metal complexes include a metal atom
coordinated to a multidentate ligand and at least one activating moiety tethered to the
multidentate ligand. In some embodiments, there are 1 to 10 activating moieties
—(Z)_m tethered to the multidentate ligand. In certain embodiments, there are 1 to 8
such activating moieties tethered to the multidentate ligand. In certain embodiments,
there are 1 to 4 such activating moieties tethered to the multidentate ligand.

I. Activating Functional Groups

In some embodiments, an activating functional group is selected from the group
consisting of neutral nitrogen-containing functional groups, cationic moieties,
phosphorous-containing functional groups, and combinations of two or more of these.

I.a. Neutral Nitrogen-Containing Activating Groups

In some embodiments, one or more tethered activating functional groups on
provided metal complexes are neutral nitrogen-containing moieties. In some
embodiments, such moieties include one or more of the structures in Table Z-1:



or a combination of two or more of these,

TABLE Z-1

wherein:

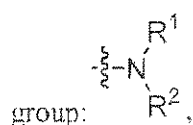
each occurrence of R^1 , and R^2 is independently hydrogen or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; wherein two or more R^1 and R^2 groups can be taken together with intervening atoms to form one or more optionally substituted rings optionally containing one or more additional heteroatoms;

each occurrence of R^5 is independently hydrogen or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5-

to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; wherein an R⁵ group can be taken with an R¹ or R² group to form one or more optionally substituted rings;

each occurrence of R⁷ is independently hydrogen, a hydroxyl protecting group, or an optionally substituted radical selected from the group consisting of C₁₋₂₀ acyl; C₁₋₂₀ aliphatic; C₁₋₂₀ heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur;

In some embodiments, an activating functional group is an *N*-linked amino



where R¹ and R² are as defined above.

In certain embodiments, R¹ and R² are both hydrogen. In some embodiments, only one of R¹ and R² is hydrogen. In certain embodiments, R¹ and R² are each independently an optionally substituted radical selected from the group consisting of C₁₋₂₀ aliphatic; C₁₋₂₀ heteroaliphatic, 5- to 14-membered heteroaryl, phenyl, 8- to 10-membered

aryl and 3- to 7-membered heterocyclic. In certain embodiments, R^1 and R^2 are each independently an optionally substituted radical selected from the group consisting of phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur.

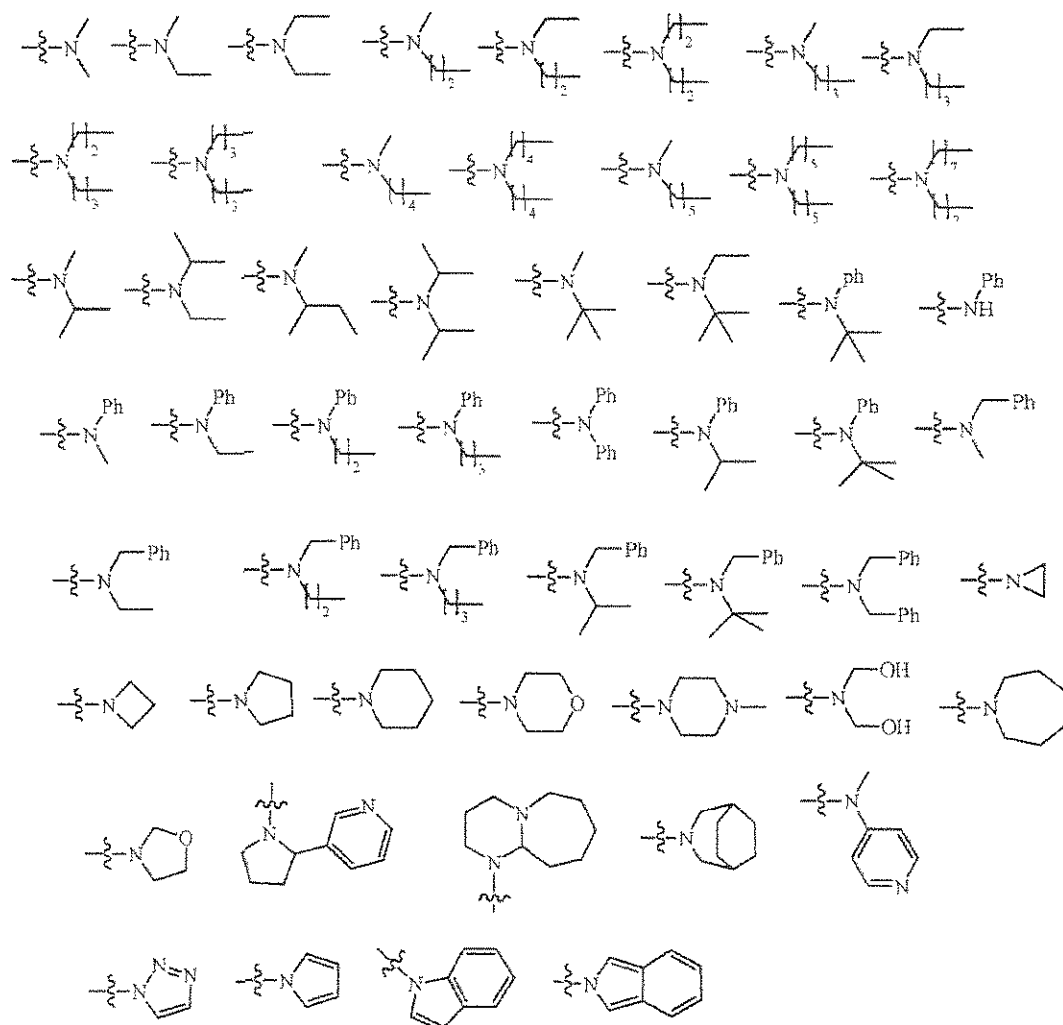
In certain embodiments, R^1 and R^2 are each independently an optionally substituted radical selected from the group consisting of C_{1-12} aliphatic and C_{1-12} heteroaliphatic. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted C_{1-20} aliphatic. In some embodiments, R^1 and R^2 are each independently optionally substituted C_{1-12} aliphatic. In some embodiments, R^1 and R^2 are each independently optionally substituted C_{1-6} aliphatic. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted C_{1-20} heteroaliphatic. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted C_{1-12} heteroaliphatic. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted phenyl. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted 8- to 10-membered aryl. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted phenyl group. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted 5- to 10-membered heteroaryl group. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted 3- to 7-membered heterocyclic.

In certain embodiments, R^1 and R^2 are each independently hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, optionally substituted phenyl, or optionally substituted benzyl. In certain embodiments, R^1 and R^2 are both methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, phenyl or benzyl. In some embodiments, R^1

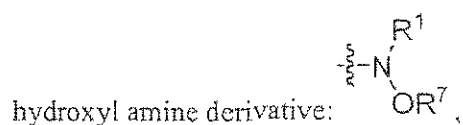
and R^2 are each butyl. In some embodiments, R^1 and R^2 are each isopropyl. In some embodiments, R^1 and R^2 are perfluoro. In some embodiments, R^1 and R^2 are $-\text{CF}_2\text{CF}_3$. In some embodiments, R^1 and R^2 are each phenyl. In some embodiments, R^1 and R^2 are each benzyl.

5 In some embodiments, R^1 and R^2 are taken together with intervening atoms to form one or more optionally substituted rings. In certain embodiments, R^1 and R^2 are taken together to form a ring fragment selected from the group consisting of: $-\text{C}(\text{R}^y)_2-$, $-\text{C}(\text{R}^y)_2\text{C}(\text{R}^y)_2-$, $-\text{C}(\text{R}^y)_2\text{C}(\text{R}^y)_2\text{C}(\text{R}^y)_2-$, $-\text{C}(\text{R}^y)_2\text{OC}(\text{R}^y)_2-$, and $-\text{C}(\text{R}^y)_2\text{NR}^y\text{C}(\text{R}^y)_2-$. In certain embodiments, R^1 and R^2 are taken together to form a ring fragment selected from
10 the group consisting of: $-\text{CH}_2-$, $-\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\text{OCH}_2-$, and $-\text{CH}_2\text{NR}^y\text{CH}_2-$. In some embodiments, R^1 and R^2 are taken together to form an unsaturated linker moiety optionally containing one or more additional heteroatoms. In some embodiments, the resulting nitrogen-containing ring is partially unsaturated. In certain embodiments, the resulting nitrogen-containing ring comprises a fused polycyclic
15 heterocycle.

 In specific embodiments, an *N*-linked amine activating functional group is selected from the group consisting of:



In some embodiments, one or more activating functional groups is an *N*-linked



wherein R^1 and R^7 are as defined above.

- 5 In certain embodiments, R^7 is hydrogen. In some embodiments, R^7 is an optionally substituted radical selected from the group consisting of C_{1-12} aliphatic, phenyl, 8- to 10-membered aryl, and 3- to 7-membered heterocyclic. In certain embodiments, R^7 is a C_{1-12} aliphatic. In certain embodiments, R^7 is a C_{1-6} aliphatic. In some embodiments, R^7 is an optionally substituted 8- to 10-membered aryl group. In

certain embodiments, R^7 is an optionally substituted phenyl. In some embodiments, R^7 is methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, phenyl or benzyl.

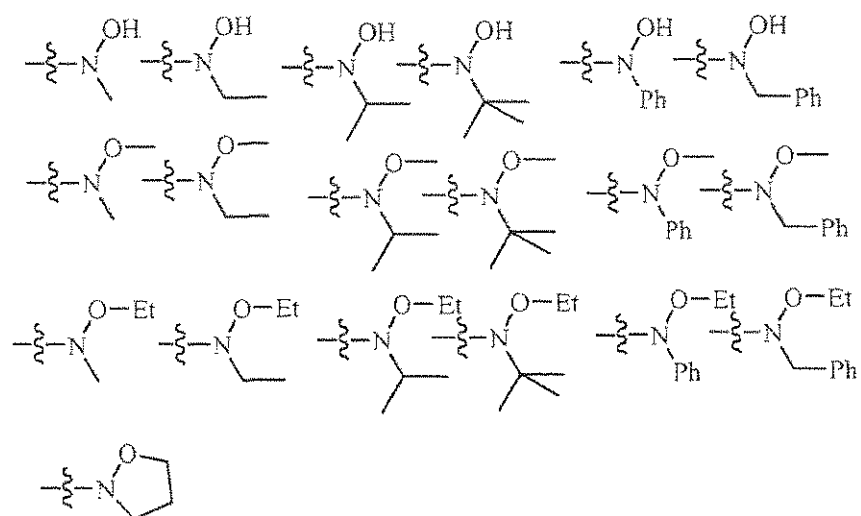
In certain embodiments, R^1 is hydrogen. In some embodiments, R^1 is an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic, 5- to 14-membered heteroaryl, phenyl, 8- to 10-membered aryl and 3- to 7-membered heterocyclic. In some embodiments, R^1 is an optionally substituted radical selected from the group consisting of phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur.

In some embodiments, R^1 is an optionally substituted radical selected from the group consisting of C_{1-12} aliphatic and C_{1-12} heteroaliphatic. In some embodiments, R^1 is an optionally substituted C_{1-20} aliphatic. In certain embodiments, R^1 is an optionally substituted C_{1-12} aliphatic. In some embodiments, R^1 is an optionally substituted C_{1-6} aliphatic. In some embodiments, R^1 is an optionally substituted C_{1-12} heteroaliphatic. In some embodiments, R^1 is an optionally substituted 8- to 10-membered aryl. In certain embodiments, R^1 is an optionally substituted phenyl. In some embodiments, R^1 is an optionally substituted 5- to 10-membered heteroaryl. In some embodiments, R^1 is an optionally substituted 3- to 7-membered heterocyclic.

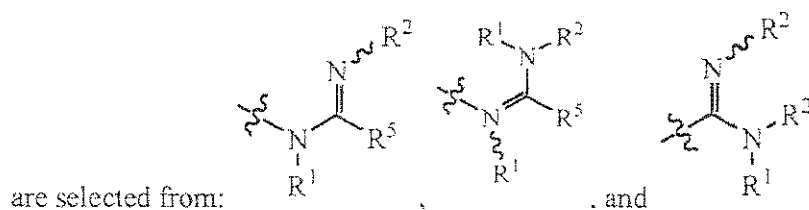
In certain embodiments, R^1 is methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, phenyl or benzyl. In some embodiments, R^1 is butyl. In some embodiments, R^1 is isopropyl. In some embodiments, R^1 is phenyl. In some embodiments, R^1 is benzyl. In some embodiments, R^1 is perfluoro. In some embodiments, R^1 is $-CF_2CF_3$.

In certain embodiments, R^1 and R^7 are taken together with intervening atoms to form one or more optionally substituted rings optionally containing one or more additional heteroatoms.

5 In certain embodiments, one or more *N*-linked hydroxyl amine activating functional groups are selected from the group consisting of:



In some embodiments, an activating functional group in a provided metal complex is an amidine. In certain embodiments, such amidine activating functional groups



10 where each occurrence of R^1 , R^2 and R^5 are as defined above.

In certain embodiments, each R^1 and R^2 is hydrogen. In some embodiments, only one of R^1 and R^2 is hydrogen. In certain embodiments, each R^1 and R^2 is independently an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic, 5- to 14-membered heteroaryl, phenyl, 8- to 10-membered aryl and 3- to 7-membered heterocyclic. In some embodiments, each R^1 and R^2 is independently an optionally substituted radical selected from the group consisting of phenyl; a 3- to 8-

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membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur.

In certain embodiments, R^1 and R^2 are each independently an optionally substituted radical selected from the group consisting of C_{1-12} aliphatic and C_{1-12} heteroaliphatic. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted C_{1-20} aliphatic. In some embodiments, R^1 and R^2 are each independently optionally substituted C_{1-12} aliphatic. In some embodiments, R^1 and R^2 are each independently optionally substituted C_{1-6} aliphatic. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted C_{1-20} heteroaliphatic. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted C_{1-12} heteroaliphatic. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted 8- to 10-membered aryl. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted phenyl group. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted 5- to 10-membered heteroaryl group. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted 3- to 7-membered heterocyclic.

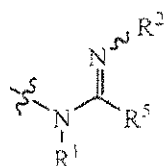
In certain embodiments, R^1 and R^2 are each independently hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, optionally substituted phenyl, or optionally substituted benzyl. In certain embodiments, R^1 and R^2 are both methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, phenyl or benzyl. In some embodiments, R^1 and R^2 are each butyl. In some embodiments, R^1 and R^2 are each isopropyl. In some embodiments, R^1 and R^2 are perfluoro. In some embodiments, R^1 and R^2 are $-CF_2CF_3$. In some embodiments, R^1 and R^2 are each phenyl. In some embodiments, R^1 and R^2 are each benzyl.

In some embodiments, R^1 and R^2 are taken together with intervening atoms to form one or more optionally substituted rings. In certain embodiments, R^1 and R^2 are taken together to form a ring fragment selected from the group consisting of: $-C(R^y)_2-$, $-C(R^y)_2C(R^y)_2-$, $-C(R^y)_2C(R^y)_2C(R^y)_2-$, $-C(R^y)_2OC(R^y)_2-$, and $-C(R^y)_2NR^yC(R^y)_2-$. In certain embodiments, R^1 and R^2 are taken together to form a ring fragment selected from the group consisting of: $-CH_2-$, $-CH_2CH_2-$, $-CH_2CH_2CH_2-$, $-CH_2OCH_2-$, and $-CH_2NR^yCH_2-$. In some embodiments, R^1 and R^2 are taken together to form an unsaturated linker moiety optionally containing one or more additional heteroatoms. In some embodiments, the resulting nitrogen-containing ring is partially unsaturated. In certain embodiments, the resulting nitrogen-containing ring comprises a fused polycyclic heterocycle.

In certain embodiments, R^5 is H. In certain embodiments, R^5 is optionally substituted C_{1-20} aliphatic. In some embodiments, R^5 is optionally substituted 6- to 14-membered aryl. In certain embodiments, R^5 is optionally substituted C_{1-12} aliphatic. In some embodiments, R^5 is optionally substituted C_{1-6} aliphatic. In certain embodiments, R^5 is optionally substituted phenyl.

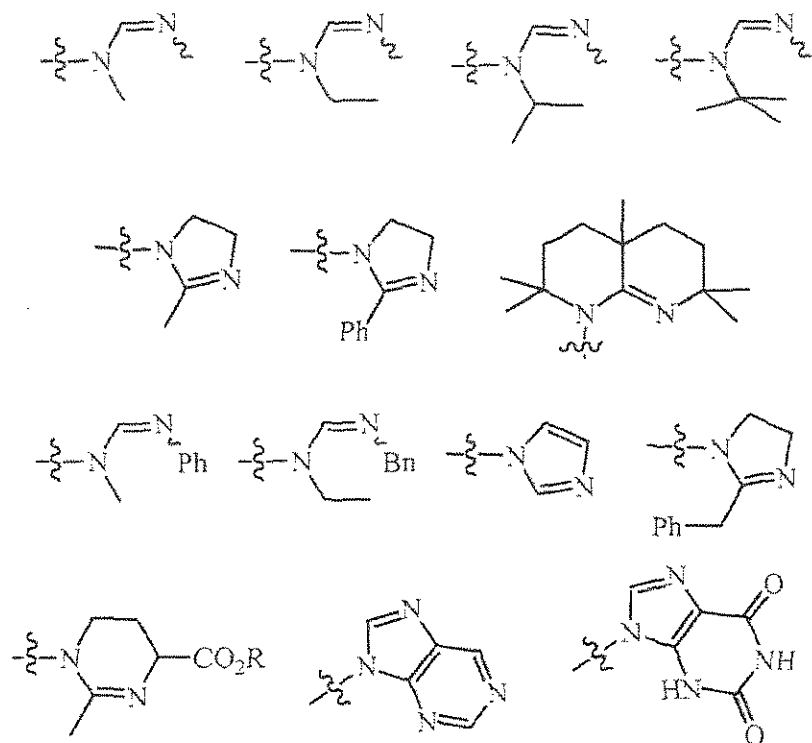
In some embodiments, one or more R^1 or R^2 groups are taken together with R^5 and intervening atoms to form an optionally substituted ring. In certain embodiments, R^1 and R^5 are taken together to form an optionally substituted 5- or 6-membered ring. In some embodiments, R^2 and R^5 are taken together to form an optionally substituted 5- or 6-membered ring optionally containing one or more additional heteroatoms. In some embodiments, R^1 , R^2 and R^5 are taken together to form an optionally substituted fused ring system. In some embodiments such rings formed by combinations of any of R^1 , R^2 and R^5 are partially unsaturated or aromatic.

In certain embodiments, an activating functional group is an *N*-linked amidine:

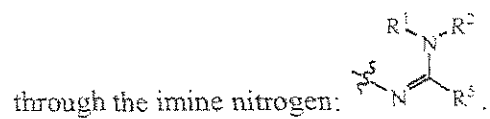


In certain embodiments, *N*-linked amidine groups are selected from the

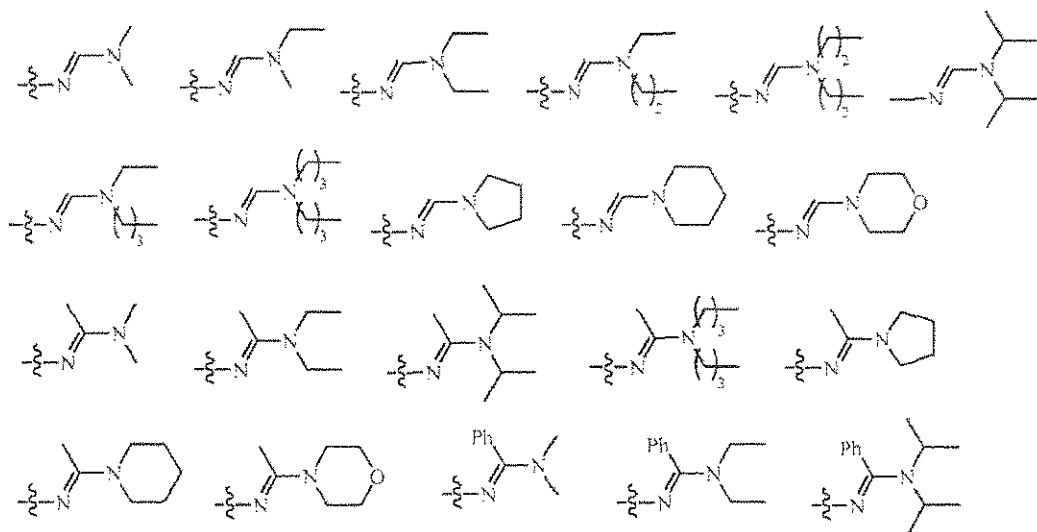
group consisting of:



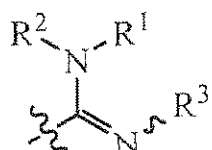
In certain embodiments, activating functional groups are amidine moieties linked



- 5 In certain embodiments, imine-linked amidine activating functional groups are selected from the group consisting of:



In certain embodiments, activating functional groups are amidine moieties linked

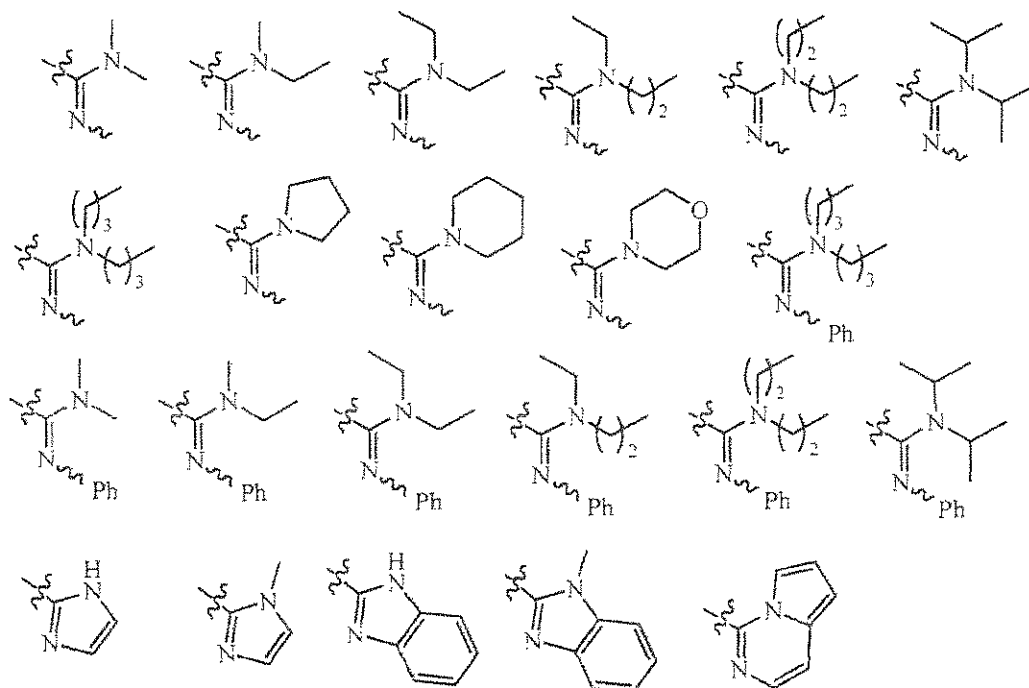


through a carbon atom:

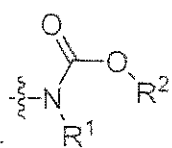
. In certain embodiments, carbon-linked

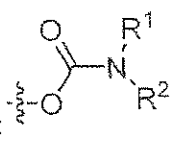
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amidine activating groups are selected from the group consisting of:



In some embodiments, one or more activating functional groups is a carbamate. In

certain embodiments, a carbamate is *N*-linked: , where R¹ and R² are as

defined above. In some embodiments, a carbamate is *O*-linked: , where R¹ and R² are as defined above.

In certain embodiments, R¹ and R² are both hydrogen. In some embodiments, only one of R¹ and R² is hydrogen. In certain embodiments, R¹ and R² are each independently an optionally substituted radical selected from the group consisting of C₁₋₂₀ aliphatic; C₁₋₂₀ heteroaliphatic, 5- to 14-membered heteroaryl, phenyl, 8- to 10-membered aryl and 3- to 7-membered heterocyclic. In some embodiments, R¹ and R² are each independently an optionally substituted radical selected from the group consisting of phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur.

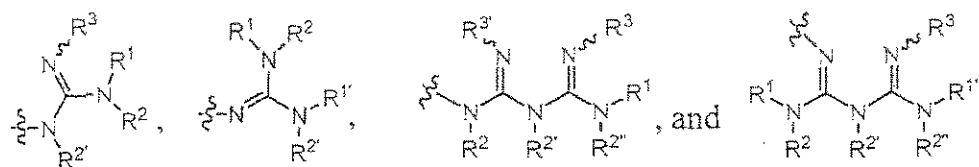
In certain embodiments, R¹ and R² are each independently an optionally substituted radical selected from the group consisting of C₁₋₁₂ aliphatic and C₁₋₁₂ heteroaliphatic. In some embodiments, each occurrence of R¹ and R² is independently an optionally substituted C₁₋₂₀ aliphatic. In some embodiments, R¹ and R² are each independently optionally substituted C₁₋₁₂ aliphatic. In some embodiments, R¹ and R² are each independently optionally substituted C₁₋₆ aliphatic. In some embodiments, each occurrence of R¹ and R² is independently an optionally substituted C₁₋₂₀ heteroaliphatic. In some embodiments, each occurrence of R¹ and R² is independently an optionally

substituted C₁₋₁₂ heteroaliphatic. In some embodiments, each occurrence of R¹ and R² is independently an optionally substituted 8- to 10-membered aryl. In some embodiments, each occurrence of R¹ and R² is independently an optionally substituted phenyl group. In some embodiments, each occurrence of R¹ and R² is independently an optionally substituted 5- to 10-membered heteroaryl group. In some embodiments, each occurrence of R¹ and R² is independently an optionally substituted 3- to 7-membered heterocyclic.

In certain embodiments, R¹ and R² are each independently hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, optionally substituted phenyl, or optionally substituted benzyl. In certain embodiments, R¹ and R² are both methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, phenyl or benzyl. In some embodiments, R¹ and R² are each butyl. In some embodiments, R¹ and R² are each isopropyl. In some embodiments, R¹ and R² are perfluoro. In some embodiments, R¹ and R² are -CF₂CF₃. In some embodiments, R¹ and R² are each phenyl. In some embodiments, R¹ and R² are each benzyl.

In some embodiments, R¹ and R² are taken together with intervening atoms to form one or more optionally substituted rings. In certain embodiments, R¹ and R² are taken together to form a ring fragment selected from the group consisting of: -C(R^y)₂-, -C(R^y)₂C(R^y)₂-, -C(R^y)₂C(R^y)₂C(R^y)₂-, -C(R^y)₂OC(R^y)₂-, and -C(R^y)₂NR^yC(R^y)₂-. In certain embodiments, R¹ and R² are taken together to form a ring fragment selected from the group consisting of: -CH₂-, -CH₂CH₂-, -CH₂CH₂CH₂-, -CH₂OCH₂-, and -CH₂NR^yCH₂-. In some embodiments, R¹ and R² are taken together to form an unsaturated linker moiety optionally containing one or more additional heteroatoms. In some embodiments, the resulting nitrogen-containing ring is partially unsaturated. In certain embodiments, the resulting nitrogen-containing ring comprises a fused polycyclic heterocycle. In some embodiments, R² is selected from the group consisting of: methyl, *t*-butyl, *t*-amyl, benzyl, adamantyl, allyl, 4-methoxycarbonylphenyl, 2-(methylsulfonyl)ethyl, 2-(4-biphenyl)-prop-2-yl, 2-(trimethylsilyl)ethyl, 2-bromoethyl, and 9-fluorenylmethyl.

In some embodiments, an activating functional group is a guanidine or bis-guanidine group:



where each occurrence of R^1 , $R^{1'}$, R^2 , $R^{2'}$, $R^{2''}$, R^3 , and $R^{3'}$ is independently hydrogen

5 or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 10 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms 15 independently selected from nitrogen, oxygen, or sulfur; wherein any two or more R^1 , $R^{1'}$, R^2 , $R^{2'}$, $R^{2''}$, R^3 , and $R^{3'}$ groups can be taken together with intervening atoms to form one or more optionally substituted rings optionally containing one or more additional heteroatoms;

In certain embodiments, each occurrence of R^1 , $R^{1'}$, R^2 , $R^{2'}$, $R^{2''}$, R^3 , and $R^{3'}$ is 20 hydrogen. In some embodiments, each occurrence of R^1 , $R^{1'}$, R^2 , $R^{2'}$, $R^{2''}$, R^3 , and $R^{3'}$ is hydrogen or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; 3- to 7-membered heterocyclic, phenyl, and 8- to 10-membered aryl. In some embodiments, each occurrence of R^1 , $R^{1'}$, R^2 , $R^{2'}$, $R^{2''}$, R^3 , and $R^{3'}$ is hydrogen or an optionally substituted radical selected from the group consisting of 25 phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated

heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur. In certain embodiments, each occurrence of R^1 , $R^{1'}$, R^2 , $R^{2'}$, $R^{2''}$, R^3 , and $R^{3'}$ is independently hydrogen or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic, phenyl, and 8- to 10-membered aryl. In certain embodiments, each occurrence of R^1 and R^2 is independently an optionally hydrogen or an optionally substituted C_{1-8} aliphatic, phenyl, or 8- to 10-membered aryl group. In some embodiments, each occurrence of R^1 , $R^{1'}$, R^2 , $R^{2'}$, $R^{2''}$, R^3 , and $R^{3'}$ is independently hydrogen or an optionally substituted C_{1-20} aliphatic. In some embodiments, each occurrence of R^1 and R^2 is independently hydrogen an optionally substituted aryl group or an optionally substituted C_{1-8} aliphatic group. In some embodiments, each occurrence of R^1 , $R^{1'}$, R^2 , $R^{2'}$, $R^{2''}$, R^3 , and $R^{3'}$ is independently hydrogen or an optionally substituted C_{1-6} aliphatic group. In some embodiments, each occurrence of R^1 , $R^{1'}$, R^2 , $R^{2'}$, $R^{2''}$, R^3 , and $R^{3'}$ is independently hydrogen or an optionally substituted C_{1-4} aliphatic group. In some embodiments, each occurrence of R^1 , $R^{1'}$, R^2 , $R^{2'}$, $R^{2''}$, R^3 , and $R^{3'}$ is independently an optionally substituted C_{1-20} aliphatic. In some embodiments, R^1 , $R^{1'}$, R^2 , $R^{2'}$, $R^{2''}$, R^3 , and $R^{3'}$ are each independently optionally substituted C_{1-12} aliphatic. In some embodiments, R^1 , $R^{1'}$, R^2 , $R^{2'}$, $R^{2''}$, R^3 , and $R^{3'}$ are each independently optionally substituted C_{1-6} aliphatic. In some embodiments, one or more occurrence of $R^{1'}$, R^2 , $R^{2'}$, $R^{2''}$, R^3 , and $R^{3'}$ is independently an optionally substituted C_{1-20} heteroaliphatic. In some embodiments, one or more occurrence of R^1 , $R^{1'}$, R^2 , $R^{2'}$, $R^{2''}$, R^3 , and $R^{3'}$ is independently hydrogen or an optionally substituted phenyl or 8- to 10-membered aryl. In some embodiments, one or more occurrence of R^1 , $R^{1'}$, R^2 , $R^{2'}$, $R^{2''}$, R^3 , and $R^{3'}$ is independently hydrogen, or an optionally substituted 5- to 10-membered heteroaryl.

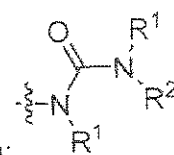
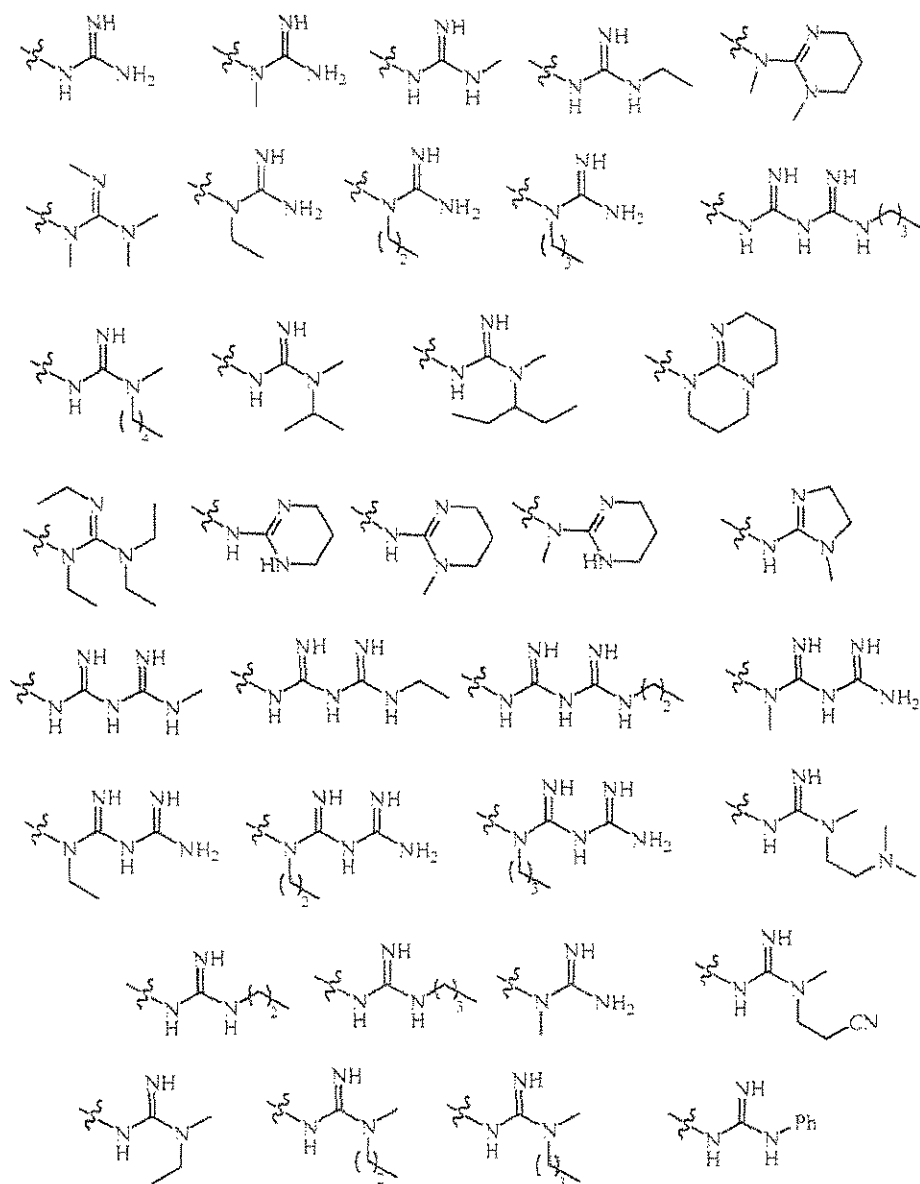
In some embodiments, R^1 is optionally substituted C_{1-6} aliphatic. In certain embodiments, $R^{1'}$ is optionally substituted C_{1-6} aliphatic. In certain embodiments, R^2 is optionally substituted C_{1-6} aliphatic. In certain embodiments, $R^{2'}$ is optionally substituted C_{1-6} aliphatic. In certain embodiments, $R^{2''}$ is optionally substituted C_{1-6} aliphatic. In certain embodiments, R^3 is optionally substituted C_{1-6} aliphatic. In certain embodiments,

$R^{3'}$ is optionally substituted C_{1-6} aliphatic. In some embodiments, each occurrence of R^1 , $R^{1'}$, R^2 , $R^{2'}$, $R^{2''}$, R^3 , and $R^{3'}$ is independently hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, phenyl or benzyl. In certain embodiments, R^1 , $R^{1'}$, R^2 , $R^{2'}$, $R^{2''}$, R^3 , and $R^{3'}$ are each methyl or ethyl. In some embodiments, one or more R^1 , $R^{1'}$, R^2 , $R^{2'}$, $R^{2''}$, R^3 , and $R^{3'}$ is perfluoro.

In some embodiments, any two or more R^1 , $R^{1'}$, R^2 , $R^{2'}$, $R^{2''}$, R^3 , and $R^{3'}$ groups are taken together with intervening atoms to form one or more optionally substituted rings.

In certain embodiments, R^1 and R^2 are taken together with intervening atoms to form an optionally substituted ring optionally containing one or more additional heteroatoms. In some embodiments, R^2 and $R^{2'}$ are taken together with intervening atoms to form an optionally substituted ring optionally containing one or more additional heteroatoms. In certain embodiments, R^1 and R^3 are taken together with intervening atoms to form an optionally substituted ring optionally containing one or more additional heteroatoms. In some embodiments, [R^2 and $R^{2'}$] and [R^1 and R^3] are taken together with intervening atoms to form an optionally substituted ring optionally containing one or more additional heteroatoms. In some embodiments, three or more R^1 , $R^{1'}$, R^2 , $R^{2'}$, $R^{2''}$, R^3 , and $R^{3'}$ groups are taken together with any intervening atoms to form optionally substituted rings. In certain embodiments, R^1 and R^2 groups are taken together to form an optionally substituted 5- or 6-membered ring. In some embodiments, three or more R^1 and/or R^2 groups are taken together to form an optionally substituted fused ring system.

In certain embodiments where an activating functional group is a guanidine or bis guanidine moiety, it is chosen from the group consisting of:



In some embodiments, an activating functional group is a urea:
 where R^1 , and R^2 are as defined above.

In certain embodiments, R^1 and R^2 are each hydrogen. In some embodiments,
 5 only one of R^1 and R^2 is hydrogen. In certain embodiments, R^1 and R^2 are each
 independently an optionally substituted radical selected from the group consisting of C_{1-20}

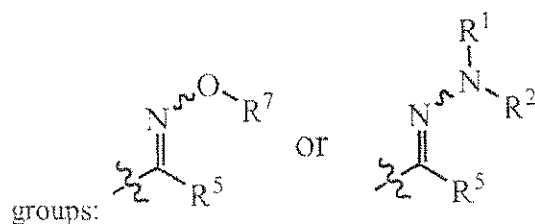
aliphatic; C₁₋₂₀ heteroaliphatic, phenyl: a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur.

In certain embodiments, R¹ and R² are each independently an optionally substituted radical selected from the group consisting of C₁₋₁₂ aliphatic and C₁₋₁₂ heteroaliphatic. In some embodiments, each occurrence of R¹ and R² is independently an optionally substituted C₁₋₂₀ aliphatic. In some embodiments, R¹ and R² are each independently optionally substituted C₁₋₁₂ aliphatic. In some embodiments, R¹ and R² are each independently optionally substituted C₁₋₆ aliphatic. In some embodiments, each occurrence of R¹ and R² is independently an optionally substituted C₁₋₂₀ heteroaliphatic. In some embodiments, each occurrence of R¹ and R² is independently an optionally substituted C₁₋₁₂ heteroaliphatic. In some embodiments, each occurrence of R¹ and R² is independently an optionally substituted 8- to 10-membered aryl. In some embodiments, each occurrence of R¹ and R² is independently an optionally substituted phenyl group. In some embodiments, each occurrence of R¹ and R² is independently an optionally substituted 5- to 10-membered heteroaryl group. In some embodiments, each occurrence of R¹ and R² is independently an optionally substituted 3- to 7-membered heterocyclic.

In certain embodiments, R¹ and R² are each independently hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, optionally substituted phenyl, or optionally substituted benzyl. In certain embodiments, R¹ and R² are both methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, phenyl or benzyl. In some embodiments, R¹ and R² are each butyl. In some embodiments, R¹ and R² are each isopropyl. In some embodiments, R¹ and R² are perfluoro. In some embodiments, R¹ and R² are -CF₂CF₃. In some embodiments, R¹ and R² are each phenyl. In some embodiments, R¹ and R² are each benzyl.

In some embodiments, R^1 and R^2 are taken together with intervening atoms to form one or more optionally substituted rings. In certain embodiments, R^1 and R^2 are taken together to form a ring fragment selected from the group consisting of: $-C(R^y)_2-$, $-C(R^y)_2C(R^y)_2-$, $-C(R^y)_2C(R^y)_2C(R^y)_2-$, $-C(R^y)_2OC(R^y)_2-$, and $-C(R^y)_2NR^yC(R^y)_2-$. In certain embodiments, R^1 and R^2 are taken together to form a ring fragment selected from the group consisting of: $-CH_2-$, $-CH_2CH_2-$, $-CH_2CH_2CH_2-$, $-CH_2OCH_2-$, and $-CH_2NR^yCH_2-$. In some embodiments, R^1 and R^2 are taken together to form an unsaturated linker moiety optionally containing one or more additional heteroatoms. In some embodiments, the resulting nitrogen-containing ring is partially unsaturated. In certain embodiments, the resulting nitrogen-containing ring comprises a fused polycyclic heterocycle.

In certain embodiments, activating functional groups are oxime or hydrazone



where R^1 , R^2 , R^5 , and R^7 are as defined above.

In certain embodiments, R^1 and R^2 are both hydrogen. In some embodiments, only one of R^1 and R^2 is hydrogen. In certain embodiments, R^1 and R^2 are each independently an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic, 5- to 14-membered heteroaryl, 8- to 10-membered aryl and 3- to 7-membered heterocyclic. In certain embodiments, R^1 and R^2 are each independently an optionally substituted radical selected from the group consisting of phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8-

to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur.

In certain embodiments, R^1 and R^2 are each independently an optionally substituted radical selected from the group consisting of C_{1-12} aliphatic and C_{1-12} heteroaliphatic. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted C_{1-20} aliphatic. In some embodiments, R^1 and R^2 are each independently optionally substituted C_{1-12} aliphatic. In some embodiments, R^1 and R^2 are each independently optionally substituted C_{1-6} aliphatic. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted C_{1-20} heteroaliphatic. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted C_{1-12} heteroaliphatic. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted 8- to 10-membered aryl. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted phenyl group. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted 5- to 10-membered heteroaryl group. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted 3- to 7-membered heterocyclic.

In certain embodiments, R^1 and R^2 are each independently hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, optionally substituted phenyl, or optionally substituted benzyl. In certain embodiments, R^1 and R^2 are both methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, phenyl or benzyl. In some embodiments, R^1 and R^2 are each butyl. In some embodiments, R^1 and R^2 are each isopropyl. In some embodiments, R^1 and R^2 are perfluoro. In some embodiments, R^1 and R^2 are $-CF_2CF_3$. In some embodiments, R^1 and R^2 are each phenyl. In some embodiments, R^1 and R^2 are each benzyl.

In some embodiments, R^1 and R^2 are taken together with intervening atoms to form one or more optionally substituted rings. In certain embodiments, R^1 and R^2 are taken together to form a ring fragment selected from the group consisting of: $-C(R^y)_2-$, $-C(R^y)_2C(R^y)_2-$, $-C(R^y)_2C(R^y)_2C(R^y)_2-$, $-C(R^y)_2OC(R^y)_2-$, and $-C(R^y)_2NR^yC(R^y)_2-$. In certain embodiments, R^1 and R^2 are taken together to form a ring fragment selected from the group consisting of: $-CH_2-$, $-CH_2CH_2-$, $-CH_2CH_2CH_2-$, $-CH_2OCH_2-$, and

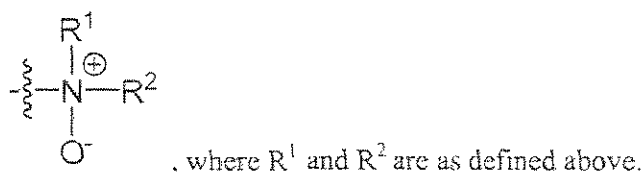
5 -CH₂NR¹CH₂-. In some embodiments, R¹ and R² are taken together to form an unsaturated linker moiety optionally containing one or more additional heteroatoms. In some embodiments, the resulting nitrogen-containing ring is partially unsaturated. In certain embodiments, the resulting nitrogen-containing ring comprises a fused polycyclic heterocycle.

10 In certain embodiments, R⁵ is H. In certain embodiments, R⁵ is optionally substituted C₁₋₂₀ aliphatic, and in some embodiments R⁵ is optionally substituted 6- to 14-membered aryl. In certain embodiments, R⁵ is optionally substituted C₁₋₁₂ aliphatic and in some embodiments, optionally substituted C₁₋₆ aliphatic. In certain embodiments, R⁵ is optionally substituted phenyl.

15 In some embodiments, one or more R¹ or R² groups are taken together with R⁵ and intervening atoms to form an optionally substituted ring. In certain embodiments, R¹ and R⁵ are taken together to form an optionally substituted 5- or 6-membered ring. In some embodiments, R² and R⁵ are taken together to form an optionally substituted 5- or 6-membered ring optionally containing one or more additional heteroatoms. In some embodiments, R¹, R² and R⁵ are taken together to form an optionally substituted fused ring system. In some embodiments such rings formed by combinations of any of R¹, R² and R⁵ are partially unsaturated or aromatic.

20 In certain embodiments, R⁷ is -H. In certain embodiments, R⁷ is optionally substituted C₁₋₂₀ aliphatic, while in some embodiments R⁵ is optionally substituted 6- to 14-membered aryl. In certain embodiments, R⁷ is optionally substituted C₁₋₁₂ aliphatic or in some embodiments, optionally substituted C₁₋₆ aliphatic. In certain embodiments, R⁷ is optionally substituted C₁₋₁₂ acyl or in some embodiments, optionally substituted C₁₋₆ acyl. In certain embodiments, R⁷ is optionally substituted phenyl. In some embodiments, R⁷ is a hydroxyl protecting group. In some embodiments, R⁷ is a silyl protecting group.

In some embodiments, an activating functional group is an N-oxide derivative:



In certain embodiments, R^1 and R^2 are both hydrogen. In some embodiments, only one of R^1 and R^2 is hydrogen. In certain embodiments, R^1 and R^2 are each independently an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic, 5- to 14-membered heteroaryl, phenyl, or 8- to 10-membered aryl and 3- to 7-membered heterocyclic.

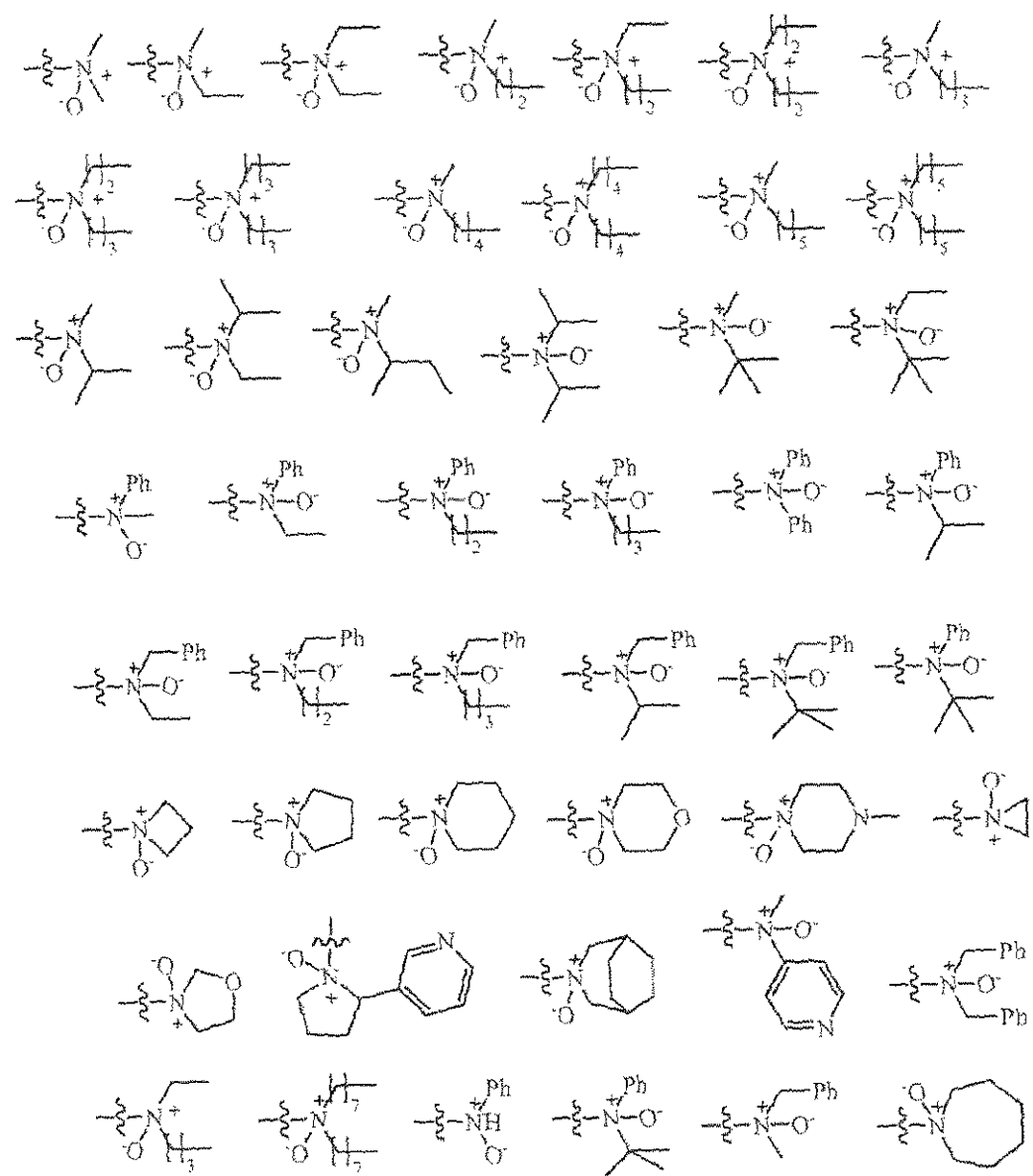
In certain embodiments, R^1 and R^2 are each independently an optionally substituted radical selected from the group consisting of C_{1-12} aliphatic and C_{1-12} heteroaliphatic. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted C_{1-20} aliphatic. In some embodiments, R^1 and R^2 are each independently optionally substituted C_{1-12} aliphatic. In some embodiments, R^1 and R^2 are each independently optionally substituted C_{1-6} aliphatic. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted C_{1-20} heteroaliphatic. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted C_{1-12} heteroaliphatic. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted 8- to 10-membered aryl. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted phenyl group. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted 5- to 10-membered heteroaryl group. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted 3- to 7-membered heterocyclic.

In certain embodiments, R^1 and R^2 are each independently hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, optionally substituted phenyl, or optionally substituted benzyl. In certain embodiments, R^1 and R^2 are both methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, phenyl or benzyl. In some embodiments, R^1 and R^2 are each butyl. In some embodiments, R^1 and R^2 are each isopropyl. In some embodiments, R^1 and R^2 are perfluoro. In some embodiments, R^1 and R^2 are $-CF_2CF_3$. In some embodiments, R^1 and R^2 are each phenyl. In some embodiments, R^1 and R^2 are each benzyl.

In some embodiments, R^1 and R^2 are taken together with intervening atoms to form one or more optionally substituted rings. In certain embodiments, R^1 and R^2 are taken together to form a ring fragment selected from the group consisting of: $-C(R^y)_2-$,

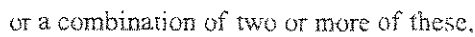
-C(R^y)₂C(R^y)₂-, -C(R^y)₂C(R^y)₂C(R^y)₂-, -C(R^y)₂OC(R^y)₂-, and -C(R^y)₂NR^yC(R^y)₂-. In certain embodiments, R¹ and R² are taken together to form a ring fragment selected from the group consisting of: -CH₂-, -CH₂CH₂-, -CH₂CH₂CH₂-, -CH₂OCH₂-, and -CH₂NR^yCH₂-. In some embodiments, R¹ and R² are taken together to form an unsaturated linker moiety optionally containing one or more additional heteroatoms. In some embodiments, the resulting nitrogen-containing ring is partially unsaturated. In certain embodiments, the resulting nitrogen-containing ring comprises a fused polycyclic heterocycle.

In specific embodiments, an *N*-oxide activating functional group is selected from the group consisting of:



I.b. Cationic Activating Groups

In some embodiments, one or more tethered activating functional groups on provided metal complexes are cationic moieties include cationic moieties. In some
5 embodiments, such moieties include one or more of the structures in Table Z-2:



wherein:

53

R^{4'} is hydrogen, hydroxyl, optionally substituted C₁₋₂₀ aliphatic;

each occurrence of R⁵ and R⁶ is independently hydrogen or an optionally substituted radical selected from the group consisting of C₁₋₂₀ aliphatic; C₁₋₂₀ heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; wherein R⁵ and R⁶ can be taken together with intervening atoms to form one or more optionally substituted rings optionally containing one or more heteroatoms, and an R⁵ or R⁶ group can be taken with an R¹ or R² group to form one or more optionally substituted rings;

each occurrence of R⁸, R⁹, and R¹⁰ is independently hydrogen or an optionally substituted radical selected from the group consisting of C₁₋₂₀ aliphatic; C₁₋₂₀ heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; wherein any two or more R⁸, R⁹ and R¹⁰ groups can be taken together with intervening atoms to form one or more optionally substituted rings;

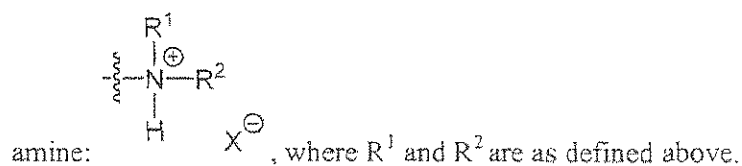
each occurrence of R^{11} is independently selected from the group consisting of:

halogen, $-\text{NO}_2$, $-\text{CN}$, $-\text{SR}^y$, $-\text{S}(\text{O})\text{R}^y$, $-\text{S}(\text{O})_2\text{R}^y$, $-\text{NR}^y\text{C}(\text{O})\text{R}^y$, $-\text{OC}(\text{O})\text{R}^y$, $-\text{CO}_2\text{R}^y$,
 $-\text{NCO}$, $-\text{N}_3$, $-\text{OR}^7$, $-\text{OC}(\text{O})\text{N}(\text{R}^y)_2$, $-\text{N}(\text{R}^y)_2$, $-\text{NR}^y\text{C}(\text{O})\text{R}^y$, $-\text{NR}^y\text{C}(\text{O})\text{OR}^y$; or an
optionally substituted radical selected from the group consisting of C_{1-20} aliphatic;
5 C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially
unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated
or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl
ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or
sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring
10 having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a
6- to 12-membered polycyclic saturated or partially unsaturated heterocycle
having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur;
or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms
independently selected from nitrogen, oxygen, or sulfur, where each occurrence
15 of R^y is independently hydrogen or an optionally substituted C_{1-6} aliphatic group,
and where two or more adjacent R^{11} groups can be taken together to form an
optionally substituted saturated, partially unsaturated, or aromatic 5- to 12-
membered ring containing 0 to 4 heteroatoms;

X^- is any anion, and

20 Ring A is an optionally substituted, 5- to 10-membered heteroaryl group.

In certain embodiments, a cationic activating functional group is a protonated



In certain embodiments, R^1 and R^2 are both hydrogen. In some embodiments,
only one of R^1 and R^2 is hydrogen. In certain embodiments, R^1 and R^2 are each
25 independently an optionally substituted radical selected from the group consisting of C_{1-20}
aliphatic; C_{1-20} heteroaliphatic, 5- to 14-membered heteroaryl, phenyl, or 8- to 10-
membered aryl and 3- to 7-membered heterocyclic. In certain embodiments, R^1 and R^2

are each independently an optionally substituted radical selected from the group consisting of phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur.

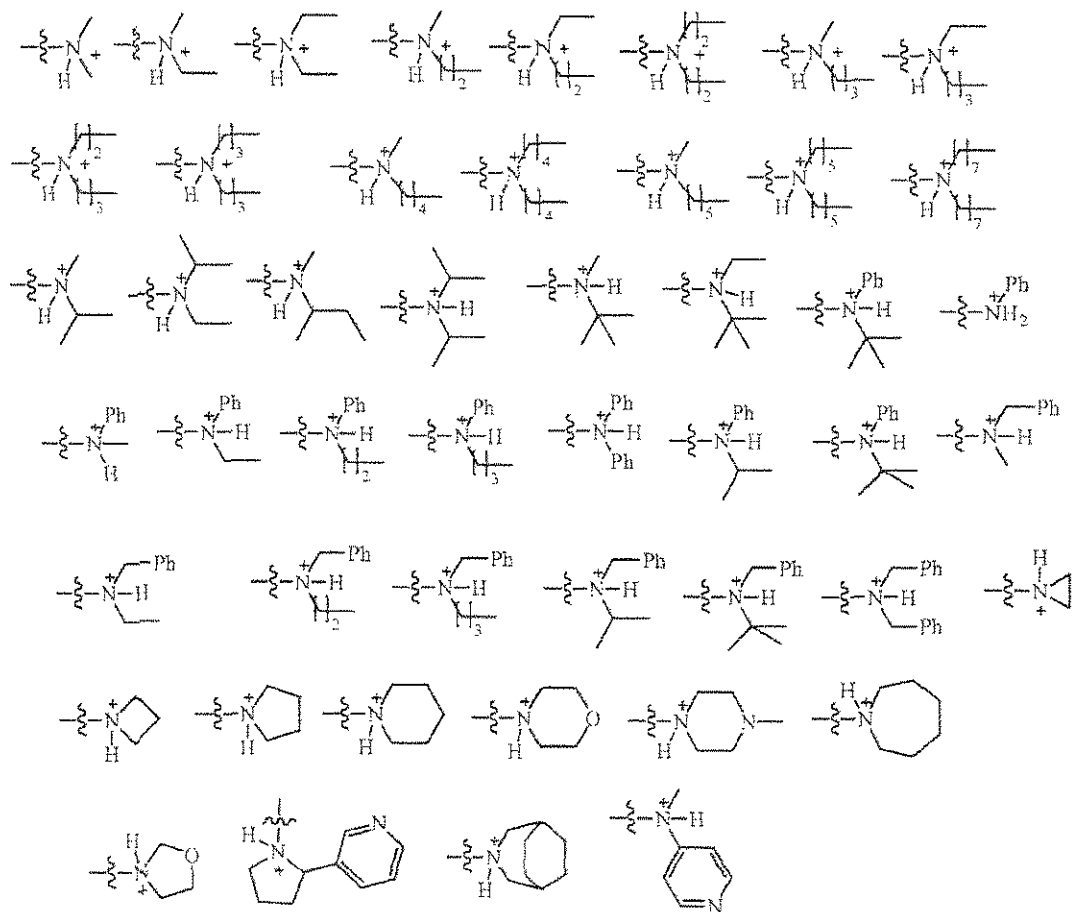
In certain embodiments, R^1 and R^2 are each independently an optionally substituted radical selected from the group consisting of C_{1-12} aliphatic and C_{1-12} heteroaliphatic. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted C_{1-20} aliphatic. In some embodiments, R^1 and R^2 are each independently optionally substituted C_{1-12} aliphatic. In some embodiments, R^1 and R^2 are each independently optionally substituted C_{1-6} aliphatic. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted C_{1-20} heteroaliphatic. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted C_{1-12} heteroaliphatic. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted 8- to 10-membered aryl. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted phenyl group. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted 5- to 10-membered heteroaryl group. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted 3- to 7-membered heterocyclic.

In certain embodiments, R^1 and R^2 are each independently hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, optionally substituted phenyl, or optionally substituted benzyl. In certain embodiments, R^1 and R^2 are both methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, phenyl or benzyl. In some embodiments, R^1 and R^2 are each butyl. In some embodiments, R^1 and R^2 are each isopropyl. In some embodiments, R^1 and R^2 are perfluoro. In some embodiments, R^1 and R^2 are $-CF_2CF_3$. In

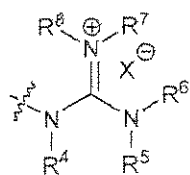
some embodiments, R^1 and R^2 are each phenyl. In some embodiments, R^1 and R^2 are each benzyl.

In some embodiments, R^1 and R^2 are taken together with intervening atoms to form one or more optionally substituted rings. In certain embodiments, R^1 and R^2 are taken together to form a ring fragment selected from the group consisting of: $-C(R^y)_2-$, $-C(R^y)_2C(R^y)_2-$, $-C(R^y)_2C(R^y)_2C(R^y)_2-$, $-C(R^y)_2OC(R^y)_2-$, and $-C(R^y)_2NR^yC(R^y)_2-$. In certain embodiments, R^1 and R^2 are taken together to form a ring fragment selected from the group consisting of: $-CH_2-$, $-CH_2CH_2-$, $-CH_2CH_2CH_2-$, $-CH_2OCH_2-$, and $-CH_2NR^yCH_2-$. In some embodiments, R^1 and R^2 are taken together to form an unsaturated linker moiety optionally containing one or more additional heteroatoms. In some embodiments, the resulting nitrogen-containing ring is partially unsaturated. In certain embodiments, the resulting nitrogen-containing ring comprises a fused polycyclic heterocycle.

In specific embodiments, a protonated amine activating functional group is selected from the group consisting of:



In certain embodiments, an activating functional group is a guanidinium



group: . In some embodiments, each of R^4 , R^5 , R^6 , R^7 , and R^8 is hydrogen.

In some embodiments, each occurrence of R^4 , R^5 , R^6 , R^7 , and R^8 is independently

5 hydrogen or C_{1-20} aliphatic. In some embodiments, each occurrence of R^4 , R^5 , R^6 , R^7 , and R^8 is independently hydrogen or C_{1-12} aliphatic. In some embodiments, each

occurrence of R^4 , R^5 , R^6 , R^7 , and R^8 is independently hydrogen or C_{1-20} heteroaliphatic.

In some embodiments, each occurrence of R^4 , R^5 , R^6 , R^7 , and R^8 is independently

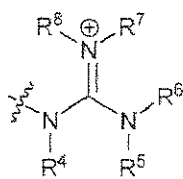
hydrogen or phenyl. In some embodiments, each occurrence of R^4 , R^5 , R^6 , R^7 , and R^8 is

10 independently hydrogen or 8- to 10-membered aryl. In some embodiments, each

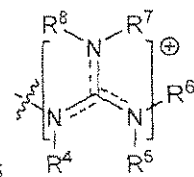
occurrence of R^4 , R^5 , R^6 , R^7 , and R^8 is independently hydrogen or 5- to 10-membered

heteroaryl. In some embodiments, each occurrence of R^4 , R^5 , R^6 , R^7 , and R^8 is independently hydrogen or 3- to 7-membered heterocyclic. In some embodiments, one or more of R^4 , R^5 , R^6 , and R^7 is optionally substituted C_{1-12} aliphatic. In certain embodiments, any of (R^4 and R^5), (R^5 and R^6), (R^6 and R^7), (R^7 and R^8), and (R^4 and R^7) can be taken together with intervening atoms to form one or more optionally substituted rings. In some embodiments, (R^4 and R^5) and (R^6 and R^7) are taken together to form rings.

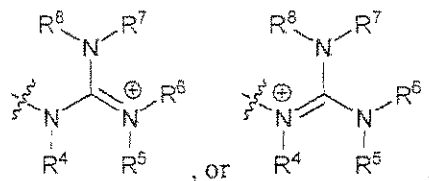
It will be appreciated that when a guanidinium cation is depicted as



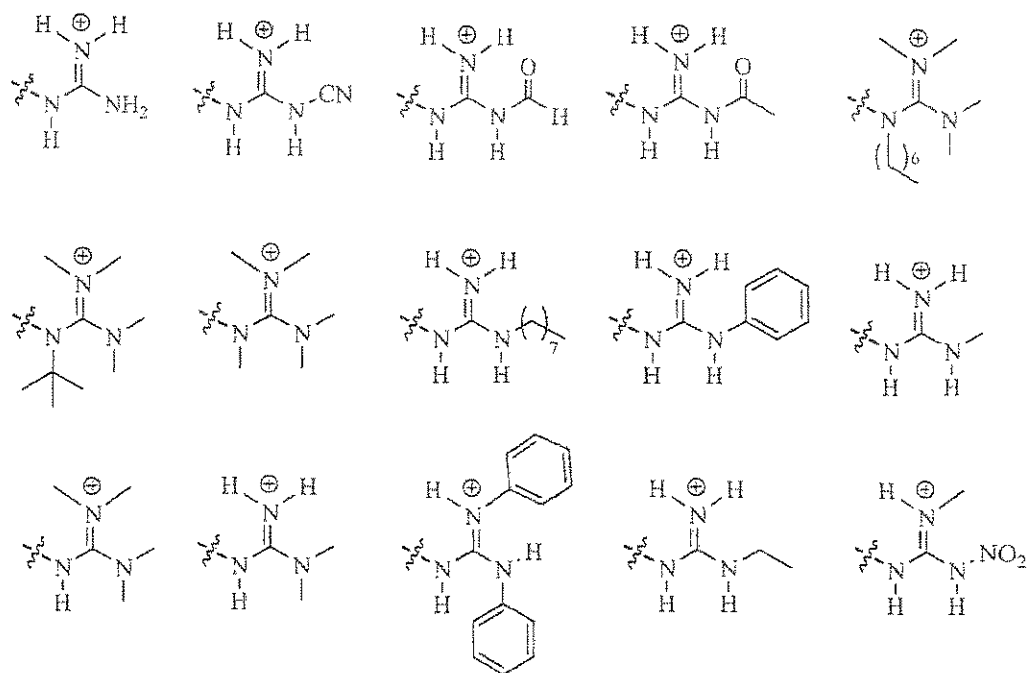
, all such resonance forms are contemplated and encompassed by the



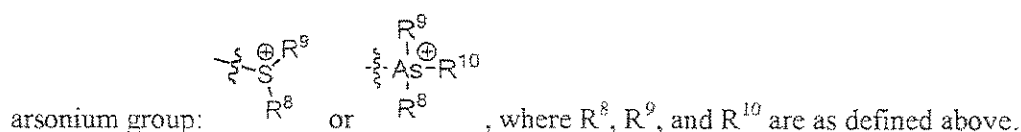
present disclosure. For example, such groups can also be depicted as



In specific embodiments, a guanidinium activating functional group is selected from the group consisting of:



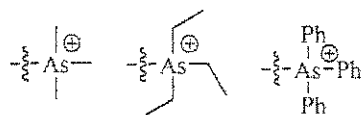
In some embodiments, an activating functional group is a sulfonium group or an



In certain embodiments, each occurrence of R^8 , R^9 , and R^{10} is independently
 5 optionally substituted C_{1-20} aliphatic. In some embodiments, each occurrence of R^8 , R^9 ,
 and R^{10} is independently hydrogen or optionally substituted C_{1-20} heteroaliphatic. In
 some embodiments, each occurrence of R^9 , R^{10} , and R^{11} is independently hydrogen or
 optionally substituted phenyl. In some embodiments, each occurrence of R^9 , R^{10} , and R^{11}
 10 is independently hydrogen or optionally substituted 8- to 10-membered aryl. In some
 embodiments, each occurrence of R^8 , R^9 , and R^{10} is independently hydrogen or optionally
 substituted 5- to 10-membered heteroaryl. In some embodiments, each occurrence of R^9 ,
 R^{10} , and R^{11} is independently hydrogen or optionally substituted 3- to 7-membered
 heterocyclic. In some embodiments, R^8 and R^9 are taken together with intervening atoms
 15 to form one or more rings selected from the group consisting of: optionally substituted
 $\text{C}_3\text{-C}_{14}$ carbocycle, optionally substituted 3- to 14-membered heterocycle, optionally
 substituted $\text{C}_6\text{-C}_{10}$ aryl, and optionally substituted 5- to 10-membered heteroaryl.

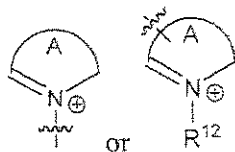
In certain embodiments, R^8 , R^9 and R^{10} are each methyl. In certain embodiments, R^8 , R^9 and R^{10} are each phenyl.

In specific embodiments, an arsonium activating functional group is selected from the group consisting of:



In some embodiments, an activating functional group is an optionally substituted nitrogen-containing heterocycle. In certain embodiments, the nitrogen-containing heterocycle is an aromatic heterocycle. In certain embodiments, the optionally substituted nitrogen-containing heterocycle is selected from the group consisting of: pyridine, imidazole, pyrrolidine, pyrazole, quinoline, thiazole, dithiazole, oxazole, triazole, pyrazolem, isoxazole, isothiazole, tetrazole, pyrazine, thiazine, and triazine.

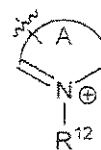
In some embodiments, a nitrogen-containing heterocycle includes a quaternarized nitrogen atom. In certain embodiments, a nitrogen-containing heterocycle includes an



iminium moiety such as or . In certain embodiments, the optionally substituted nitrogen-containing heterocycle is selected from the group consisting of pyridinium, imidazolium, pyrrolidinium, pyrazolium, quinolinium, thiazolium, dithiazolium, oxazolium, triazolium, isoxazolium, isothiazolium, tetrazolium, pyrazinium, thiazinium, and triazinium.

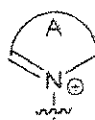
In certain embodiments, a nitrogen-containing heterocycle is linked to a metal complex via a ring nitrogen atom. In some embodiments, a ring nitrogen to which the attachment is made is thereby quaternized, and in some embodiments, linkage to a metal complex takes the place of an N-H bond and the nitrogen atom thereby remains neutral. In certain embodiments, an optionally substituted *N*-linked nitrogen-containing heterocycle is a pyridinium derivative. In certain embodiments, optionally substituted *N*-linked nitrogen-containing heterocycle is an imidazolium derivative. In certain

embodiments, optionally substituted N-linked nitrogen-containing heterocycle is a thiazolium derivative. In certain embodiments, optionally substituted N-linked nitrogen-containing heterocycle is a pyridinium derivative.



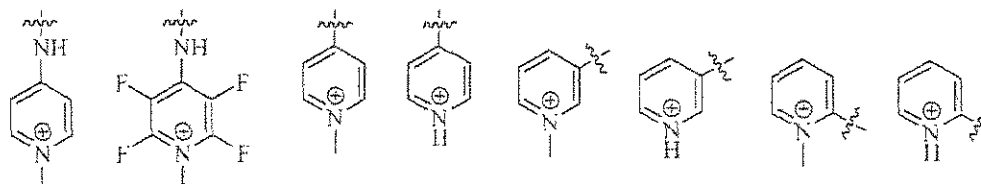
In some embodiments, an activating functional group is R^{12} . In certain
 5 embodiments, ring A is an optionally substituted, 5- to 10-membered heteroaryl group.
 In some embodiments, Ring A is an optionally substituted, 6-membered heteroaryl group.
 In some embodiments, Ring A is a ring of a fused heterocycle. In some embodiments,
 Ring A is an optionally substituted pyridyl group.

In some embodiments, R^{12} is hydrogen. In some embodiments, R^{12} is an
 10 optionally substituted C_{1-20} aliphatic group. In some embodiments, R^{12} is C_{1-20}
 heteroaliphatic. In some embodiments, R^{12} is optionally substituted phenyl, 8- to 10-
 membered aryl; 5- to 10-membered heteroaryl. In some embodiments, R^{12} is 3- to 7-
 membered heterocyclic. In some embodiments, R^{12} is an optionally substituted C_{1-12}
 aliphatic group. In some embodiments, R^{12} is neopentyl. In some embodiments, R^{12} is
 15 oxide or hydroxyl.

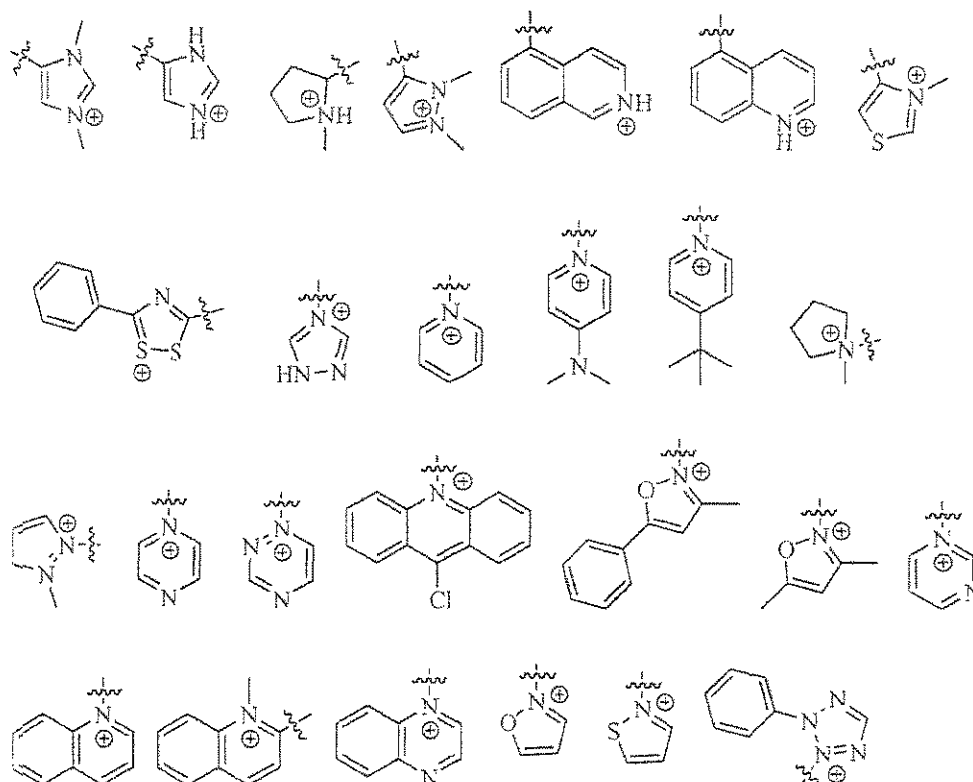


In some embodiments, when Z is Z , ring A is other than an imidazole, an
 oxazole, or a thiazole.

In specific embodiments, a nitrogen-containing heterocycle activating functional
 group is selected from the group consisting of:

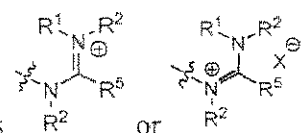


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In some embodiments, an activating functional group is where R^1 , R^2 and R^5 are as defined above.



10

In certain embodiments, R^1 and R^2 are each hydrogen. In some embodiments, only one of R^1 and R^2 is hydrogen. In certain embodiments, R^1 and R^2 are each independently an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic, 5- to 14-membered heteroaryl, phenyl, 8- to 10-membered aryl and 3- to 7-membered heterocyclic. In certain embodiments, R^1 and R^2 are each independently an optionally substituted radical selected from the group consisting of phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-
 15 membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen,

or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur.

5 In certain embodiments, R^1 and R^2 are each independently an optionally substituted radical selected from the group consisting of C_{1-12} aliphatic and C_{1-12} heteroaliphatic. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted C_{1-20} aliphatic. In some embodiments, R^1 and R^2 are each independently optionally substituted C_{1-12} aliphatic. In some embodiments, R^1 and R^2 are each independently optionally substituted C_{1-6} aliphatic. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted C_{1-20} heteroaliphatic. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted C_{1-12} heteroaliphatic. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted 8- to 10-membered aryl. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted phenyl group. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted 5- to 10-membered heteroaryl group. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted 3- to 7-membered heterocyclic.

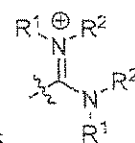
20 In certain embodiments, R^1 and R^2 are each independently hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, optionally substituted phenyl, or optionally substituted benzyl. In certain embodiments, R^1 and R^2 are both methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, phenyl or benzyl. In some embodiments, R^1 and R^2 are each butyl. In some embodiments, R^1 and R^2 are each isopropyl. In some embodiments, R^1 and R^2 are perfluoro. In some embodiments, R^1 and R^2 are $-CF_2CF_3$. In some embodiments, R^1 and R^2 are each phenyl. In some embodiments, R^1 and R^2 are each benzyl.

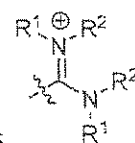
30 In some embodiments, R^1 and R^2 are taken together with intervening atoms to form one or more optionally substituted rings. In certain embodiments, R^1 and R^2 are taken together to form a ring fragment selected from the group consisting of: $-C(R^y)_2-$, $-C(R^y)_2C(R^y)_2-$, $-C(R^y)_2C(R^y)_2C(R^y)_2-$, $-C(R^y)_2OC(R^y)_2-$, and $-C(R^y)_2NR^yC(R^y)_2-$. In

certain embodiments, R^1 and R^2 are taken together to form a ring fragment selected from the group consisting of: $-\text{CH}_2-$, $-\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\text{OCH}_2-$, and $-\text{CH}_2\text{NR}^3\text{CH}_2-$. In some embodiments, R^1 and R^2 are taken together to form an unsaturated linker moiety optionally containing one or more additional heteroatoms. In some embodiments, the resulting nitrogen-containing ring is partially unsaturated. In certain embodiments, the resulting nitrogen-containing ring comprises a fused polycyclic heterocycle.

In certain embodiments, R^5 is H. In certain embodiments, R^5 is optionally substituted C_{1-20} aliphatic, and in some embodiments R^5 is optionally substituted 6- to 14-membered aryl. In certain embodiments, R^5 is optionally substituted C_{1-12} aliphatic and in some embodiments, optionally substituted C_{1-6} aliphatic. In certain embodiments, R^5 is methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, phenyl or benzyl. In some embodiments, R^5 is perfluoro. In some embodiments, R^5 is $-\text{CF}_2\text{CF}_3$. In certain embodiments, R^5 is optionally substituted phenyl.

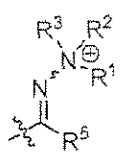
In some embodiments, one or more R^1 or R^2 groups are taken together with R^5 and intervening atoms to form an optionally substituted ring. In certain embodiments, R^1 and R^5 are taken together to form an optionally substituted 5- or 6-membered ring. In some embodiments, R^2 and R^5 are taken together to form an optionally substituted 5- or 6-membered ring optionally containing one or more additional heteroatoms. In some embodiments, R^1 , R^2 and R^5 are taken together to form an optionally substituted fused ring system. In some embodiments such rings formed by combinations of any of R^1 , R^2 and R^5 are partially unsaturated or aromatic.



In some embodiments, an activating functional group is , where R^1 and R^2 are as defined above.

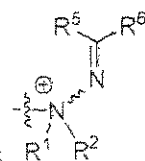
In certain embodiments, R^1 and R^2 are each independently an optionally substituted group selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; and 8-10-membered aryl. In some embodiments, R^1 and R^2 are each independently an optionally substituted 4-7-membered heterocyclic. In some

embodiments, R^1 and R^2 can be taken together with intervening atoms to form one or more rings selected from the group consisting of: optionally substituted C_3 - C_{14} carbocycle, optionally substituted C_3 - C_{14} heterocycle, optionally substituted C_6 - C_{10} aryl, and optionally substituted 5- to 10-membered heteroaryl. In some embodiments, R^1 and R^2 are each independently selected from the group consisting of methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, or benzyl. In some embodiments, each occurrence of R^1 and R^2 is independently perfluoro. In some embodiments, each occurrence of R^1 and R^2 is independently $-CF_2CF_3$.

In some embodiments, an activating functional group is  where R^1 , R^2 , R^3 , and R^5 are as defined above.

In certain embodiments, R^1 , R^2 , and R^3 are each independently an optionally substituted group selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; and 8-10-membered aryl. In certain embodiments, R^1 , R^2 , and R^3 are each independently an optionally substituted 4-7-membered heterocyclic. In some embodiments, R^1 and R^2 can be taken together with intervening atoms to form one or more rings selected from the group consisting of: optionally substituted C_3 - C_{14} carbocycle, optionally substituted C_3 - C_{14} heterocycle, optionally substituted C_6 - C_{10} aryl, and optionally substituted 5- to 10-membered heteroaryl. In certain embodiments, R^1 , R^2 , and R^3 are each independently an optionally substituted C_{1-6} aliphatic. In certain embodiments, R^1 , R^2 , and R^3 are each independently selected from the group consisting of methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, or benzyl. In certain embodiments, R^1 , R^2 , and R^3 are each independently perfluoro. In some embodiments, R^1 , R^2 , and R^3 are each independently $-CF_2CF_3$.

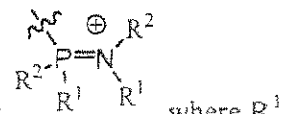
In certain embodiments, R^5 is hydrogen. In certain embodiments R^5 is an optionally substituted group selected from the group consisting of C_{1-12} aliphatic and C_{1-12} heteroaliphatic. In some embodiments, R^5 is an optionally substituted C_{1-12} aliphatic. In some embodiments, R^5 is optionally substituted C_{1-6} aliphatic.



In some embodiments, an activating functional group is R^1 R^2 . In certain embodiments, R^1 and R^2 are each independently an optionally substituted group selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; and 8-10-membered aryl. In some embodiments, R^1 and R^2 are each independently an optionally substituted 4-7-membered heterocyclic. In some embodiments, R^1 and R^2 can be taken together with intervening atoms to form one or more rings selected from the group consisting of: optionally substituted C_3 - C_{14} carbocycle, optionally substituted C_3 - C_{14} heterocycle, optionally substituted C_6 - C_{10} aryl, and optionally substituted 5- to 10-membered heteroaryl. In some embodiments, R^1 and R^2 are each independently selected from the group consisting of methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, or benzyl. In some embodiments, each occurrence of R^1 and R^2 is independently perfluoro. In some embodiments, each occurrence of R^1 and R^2 is independently $-\text{CF}_2\text{CF}_3$.

In certain embodiments, R^5 and R^6 are each independently an optionally substituted group selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl, and 8-10-membered aryl. In some embodiments, R^5 and R^6 are each independently an optionally substituted C_{1-20} aliphatic. In some embodiments, R^5 and R^6 are each independently an optionally substituted C_{1-20} heteroaliphatic having. In some embodiments, R^5 and R^6 are each independently an optionally substituted phenyl or 8-10-membered aryl. In some embodiments, R^5 and R^6 are each independently an optionally substituted 5- to 10-membered heteroaryl. In some embodiments, R^5 and R^6 can be taken together with intervening atoms to form one or more rings selected from the group consisting of: optionally substituted C_3 - C_{14} carbocycle, optionally substituted C_3 - C_{14} heterocycle, optionally substituted C_6 - C_{10} aryl, and optionally substituted 5- to 10-membered heteroaryl. In some embodiments, R^5 and R^6 are each independently an optionally substituted C_{1-6} aliphatic. In some embodiments, each occurrence of R^5 and R^6 is independently methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, or benzyl. In some embodiments, each occurrence of R^5 and R^6 is independently perfluoro. In some embodiments, each occurrence of R^5 and R^6 is independently $-\text{CF}_2\text{CF}_3$.

In some embodiments, an activating functional group is

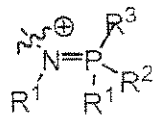


In certain embodiments, R^1 and R^2 are each hydrogen. In some embodiments, only one of R^1 and R^2 is hydrogen. In certain embodiments, R^1 and R^2 are each independently an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic, phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur.

In certain embodiments, R^1 and R^2 are each independently an optionally substituted radical selected from the group consisting of C_{1-12} aliphatic and C_{1-12} heteroaliphatic. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted C_{1-20} aliphatic. In some embodiments, R^1 and R^2 are each independently optionally substituted C_{1-12} aliphatic. In some embodiments, R^1 and R^2 are each independently optionally substituted C_{1-6} aliphatic. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted C_{1-20} heteroaliphatic. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted C_{1-12} heteroaliphatic. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted phenyl or 8- to 10-membered aryl. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted phenyl group. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted 5- to 10-membered heteroaryl group. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted 3- to 7-membered heterocyclic.

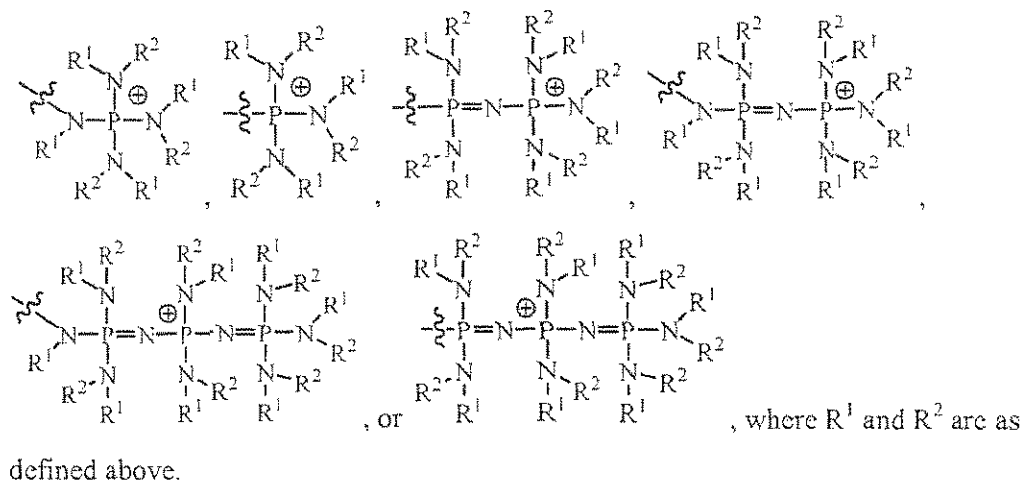
In certain embodiments, R^1 and R^2 are each independently hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, optionally substituted phenyl, or optionally substituted benzyl. In certain embodiments, R^1 and R^2 are both methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, phenyl or benzyl. In some embodiments, R^1 and R^2 are each butyl. In some embodiments, R^1 and R^2 are each isopropyl. In some
 5 embodiments, R^1 and R^2 are perfluoro. In some embodiments, R^1 and R^2 are $-\text{CF}_2\text{CF}_3$. In some embodiments, R^1 and R^2 are each phenyl. In some embodiments, R^1 and R^2 are each benzyl.

In some embodiments, R^1 and R^2 are taken together with intervening atoms to
 10 form one or more optionally substituted rings. In certain embodiments, R^1 and R^2 are taken together to form a ring fragment selected from the group consisting of: $-\text{C}(\text{R}^y)_2-$, $-\text{C}(\text{R}^y)_2\text{C}(\text{R}^y)_2-$, $-\text{C}(\text{R}^y)_2\text{C}(\text{R}^y)_2\text{C}(\text{R}^y)_2-$, $-\text{C}(\text{R}^y)_2\text{OC}(\text{R}^y)_2-$, and $-\text{C}(\text{R}^y)_2\text{NR}^y\text{C}(\text{R}^y)_2-$. In certain embodiments, R^1 and R^2 are taken together to form a ring fragment selected from the group consisting of: $-\text{CH}_2-$, $-\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\text{OCH}_2-$, and
 15 $-\text{CH}_2\text{NR}^y\text{CH}_2-$. In some embodiments, R^1 and R^2 are taken together to form an unsaturated linker moiety optionally containing one or more additional heteroatoms. In some embodiments, the resulting nitrogen-containing ring is partially unsaturated. In certain embodiments, the resulting nitrogen-containing ring comprises a fused polycyclic heterocycle.

In some embodiments, an activating functional group is . In certain
 20 embodiments, R^1 , R^2 , and R^3 are each independently an optionally substituted group selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; and 8-10-membered aryl. In certain embodiments, R^1 , R^2 , and R^3 are each independently an optionally substituted 4-7-membered heterocyclic. In some embodiments, R^1 and R^2 can
 25 be taken together with intervening atoms to form one or more rings selected from the group consisting of: optionally substituted C_3 - C_{14} carbocycle, optionally substituted C_3 - C_{14} heterocycle, optionally substituted C_6 - C_{10} aryl, and optionally substituted 5- to 10-membered heteroaryl. In certain embodiments, R^1 , R^2 , and R^3 are each independently an optionally substituted C_{1-6} aliphatic. In certain embodiments, R^1 , R^2 , and R^3 are each

independently selected from the group consisting of methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, or benzyl. In certain embodiments, R^1 , R^2 , and R^3 are each independently perfluoro. In some embodiments, R^1 , R^2 , and R^3 are each independently $-\text{CF}_2\text{CF}_3$.

5 In some embodiments, an activating functional group is



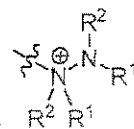
10 In certain embodiments, R^1 and R^2 are each hydrogen. In some embodiments, only one of R^1 and R^2 is hydrogen. In certain embodiments, R^1 and R^2 are each independently an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic, phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur.

20 In certain embodiments, R^1 and R^2 are each independently an optionally substituted radical selected from the group consisting of C_{1-12} aliphatic and C_{1-12} heteroaliphatic. In some embodiments, each occurrence of R^1 and R^2 is independently an optionally substituted C_{1-20} aliphatic. In some embodiments, R^1 and R^2 are each

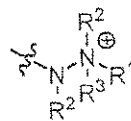
independently optionally substituted C₁₋₁₂ aliphatic. In some embodiments, R¹ and R² are each independently optionally substituted C₁₋₆ aliphatic. In some embodiments, each occurrence of R¹ and R² is independently an optionally substituted C₁₋₂₀ heteroaliphatic. In some embodiments, each occurrence of R¹ and R² is independently an optionally substituted C₁₋₁₂ heteroaliphatic. In some embodiments, each occurrence of R¹ and R² is independently an optionally substituted 8- to 10-membered aryl. In some embodiments, each occurrence of R¹ and R² is independently an optionally substituted phenyl group. In some embodiments, each occurrence of R¹ and R² is independently an optionally substituted 5- to 10-membered heteroaryl group. In some embodiments, each occurrence of R¹ and R² is independently an optionally substituted 3- to 7-membered heterocyclic.

In certain embodiments, R¹ and R² are each independently hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, optionally substituted phenyl, or optionally substituted benzyl. In certain embodiments, R¹ and R² are both methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, phenyl or benzyl. In some embodiments, R¹ and R² are each butyl. In some embodiments, R¹ and R² are each isopropyl. In some embodiments, R¹ and R² are perfluoro. In some embodiments, R¹ and R² are -CF₂CF₃. In some embodiments, R¹ and R² are each phenyl. In some embodiments, R¹ and R² are each benzyl.

In some embodiments, R¹ and R² are taken together with intervening atoms to form one or more optionally substituted rings. In certain embodiments, R¹ and R² are taken together to form a ring fragment selected from the group consisting of: -C(R^y)₂-, -C(R^y)₂C(R^y)₂-, -C(R^y)₂C(R^y)₂C(R^y)₂-, -C(R^y)₂OC(R^y)₂-, and -C(R^y)₂NR^yC(R^y)₂-. In certain embodiments, R¹ and R² are taken together to form a ring fragment selected from the group consisting of: -CH₂-, -CH₂CH₂-, -CH₂CH₂CH₂-, -CH₂OCH₂-, and -CH₂NR^yCH₂-. In some embodiments, R¹ and R² are taken together to form an unsaturated linker moiety optionally containing one or more additional heteroatoms. In some embodiments, the resulting nitrogen-containing ring is partially unsaturated. In certain embodiments, the resulting nitrogen-containing ring comprises a fused polycyclic heterocycle.

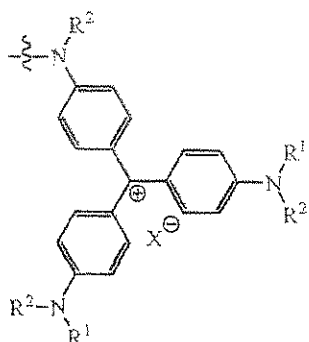


In some embodiments, an activating functional group is $\begin{array}{c} \text{R}^2 \\ | \\ \text{---S---N}^{\oplus}\text{---N---R}^1 \\ | \\ \text{R}^2 \end{array}$. In certain embodiments, R^1 and R^2 are each independently an optionally substituted group selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; and 8-10-membered aryl. In some embodiments, R^1 and R^2 are each independently an optionally substituted 4-7-membered heterocyclic. In some embodiments, R^1 and R^2 can be taken together with intervening atoms to form one or more rings selected from the group consisting of: optionally substituted $\text{C}_3\text{-C}_{14}$ carbocycle, optionally substituted $\text{C}_3\text{-C}_{14}$ heterocycle, optionally substituted $\text{C}_6\text{-C}_{10}$ aryl, and optionally substituted 5- to 10-membered heteroaryl. In some embodiments, R^1 and R^2 are each independently selected from the group consisting of methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, or benzyl. In some embodiments, each occurrence of R^1 and R^2 is independently perfluoro. In some embodiments, each occurrence of R^1 and R^2 is independently $-\text{CF}_2\text{CF}_3$.



In some embodiments, an activating functional group is $\begin{array}{c} \text{R}^2 \\ | \\ \text{---S---N}^{\oplus}\text{---N---R}^1 \\ | \quad | \\ \text{R}^2 \quad \text{R}^3 \end{array}$. In certain embodiments, R^1 , R^2 , and R^3 are each independently an optionally substituted group selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; and 8-10-membered aryl. In certain embodiments, R^1 , R^2 , and R^3 are each independently an optionally substituted 4-7-membered heterocyclic. In some embodiments, R^1 and R^2 can be taken together with intervening atoms to form one or more rings selected from the group consisting of: optionally substituted $\text{C}_3\text{-C}_{14}$ carbocycle, optionally substituted $\text{C}_3\text{-C}_{14}$ heterocycle, optionally substituted $\text{C}_6\text{-C}_{10}$ aryl, and optionally substituted 5- to 10-membered heteroaryl. In certain embodiments, R^1 , R^2 , and R^3 are each independently an optionally substituted C_{1-6} aliphatic. In certain embodiments, R^1 , R^2 , and R^3 are each independently selected from the group consisting of methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, or benzyl. In certain embodiments, R^1 , R^2 , and R^3 are each independently perfluoro. In some embodiments, R^1 , R^2 , and R^3 are each independently $-\text{CF}_2\text{CF}_3$.

In some embodiments, an activating functional group is



, where R^1 and R^2 are as defined above.

In certain embodiments, R^1 and R^2 are each independently an optionally substituted group selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; and 8-10-membered aryl. In some embodiments, R^1 and R^2 are each independently an optionally substituted 4-7-membered heterocyclic. In some embodiments, R^1 and R^2 can be taken together with intervening atoms to form one or more rings selected from the group consisting of: optionally substituted C_3-C_{14} carbocycle, optionally substituted C_3-C_{14} heterocycle, optionally substituted C_6-C_{10} aryl, and optionally substituted 5- to 10-membered heteroaryl. In some embodiments, R^1 and R^2 are each independently selected from the group consisting of methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, or benzyl. In some embodiments, each occurrence of R^1 and R^2 is independently perfluoro. In some embodiments, each occurrence of R^1 and R^2 is independently $-CF_2CF_3$.

In certain embodiments, X is any anion. In certain embodiments, X is a nucleophile. In some embodiments, X is a nucleophile capable of ring opening an epoxide. In certain embodiments, X is absent. In certain embodiments, X is a nucleophilic ligand. Exemplary nucleophilic ligands include, but are not limited to, $-OR^x$, $-SR^x$, $-O(C=O)R^x$, $-O(C=O)OR^x$, $-O(C=O)N(R^x)_2$, $-N(R^x)(C=O)R^x$, $-NC$, $-CN$, halo (e.g., $-Br$, $-I$, $-Cl$), $-N_3$, $-O(SO_2)R^x$ and $-OPR^x_3$, wherein each R^x is, independently, selected from hydrogen, optionally substituted aliphatic, optionally substituted heteroaliphatic, optionally substituted aryl and optionally substituted heteroaryl.

In certain embodiments, X is $-\text{O}(\text{C}=\text{O})\text{R}^x$, wherein R^x is selected from optionally substituted aliphatic, fluorinated aliphatic, optionally substituted heteroaliphatic, optionally substituted aryl, fluorinated aryl, and optionally substituted heteroaryl.

5 For example, in certain embodiments, X is $-\text{O}(\text{C}=\text{O})\text{R}^x$, wherein R^x is optionally substituted aliphatic. In certain embodiments, X is $-\text{O}(\text{C}=\text{O})\text{R}^x$, wherein R^x is optionally substituted alkyl and fluoroalkyl. In certain embodiments, X is $-\text{O}(\text{C}=\text{O})\text{CH}_3$ or $-\text{O}(\text{C}=\text{O})\text{CF}_3$.

10 Furthermore, in certain embodiments, X is $-\text{O}(\text{C}=\text{O})\text{R}^x$, wherein R^x is optionally substituted aryl, fluoroaryl, or heteroaryl. In certain embodiments, X is $-\text{O}(\text{C}=\text{O})\text{R}^x$, wherein R^x is optionally substituted aryl. In certain embodiments, X is $-\text{O}(\text{C}=\text{O})\text{R}^x$, wherein R^x is optionally substituted phenyl. In certain embodiments, X is $-\text{O}(\text{C}=\text{O})\text{C}_6\text{H}_5$ or $-\text{O}(\text{C}=\text{O})\text{C}_6\text{F}_5$.

15 In certain embodiments, X is $-\text{OR}^x$, wherein R^x is selected from optionally substituted aliphatic, optionally substituted heteroaliphatic, optionally substituted aryl, and optionally substituted heteroaryl.

For example, in certain embodiments, X is $-\text{OR}^x$, wherein R^x is optionally substituted aryl. In certain embodiments, X is $-\text{OR}^x$, wherein R^x is optionally substituted phenyl. In certain embodiments, X is $-\text{OC}_6\text{H}_5$ or $-\text{OC}_6\text{H}_4(2,4\text{-NO}_2)$.

20 In certain embodiments, X is halo. In certain embodiments, X is $-\text{Br}$. In certain embodiments, X is $-\text{Cl}$. In certain embodiments, X is $-\text{I}$.

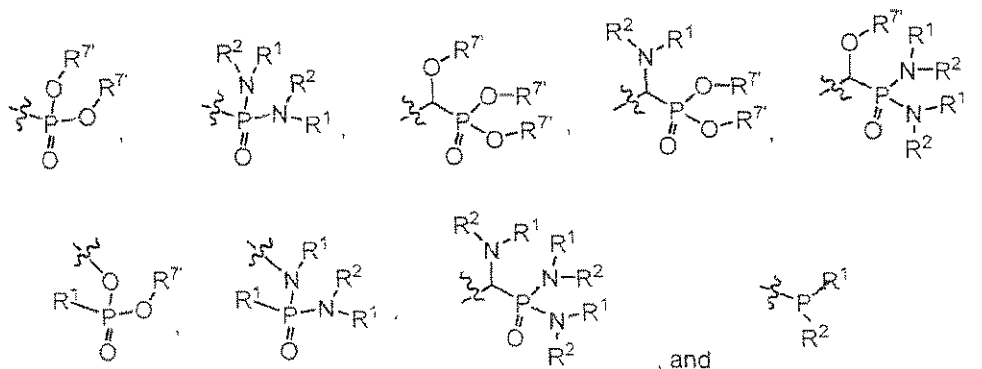
In certain embodiments, X is $-\text{O}(\text{SO}_2)\text{R}^x$. In certain embodiments X is $-\text{OTs}$. In certain embodiments X is $-\text{OSO}_2\text{Me}$. In certain embodiments X is $-\text{OSO}_2\text{CF}_3$. In some embodiments, X is a 2,4-dinitrophenolate anion.

25 *Lc. Phosphorous-Containing Activating Groups*

In some embodiments, activating functional groups Z are phosphorous containing groups.

In certain embodiments, a phosphorous-containing functional group is chosen from the group consisting of: phosphines ($-\text{PR}^{\text{Y}}_2$); Phosphine oxides $-\text{P}(\text{O})\text{R}^{\text{Y}}_2$; phosphinites $\text{P}(\text{OR}^{\text{Y}})\text{R}^{\text{Y}}_2$; phosphonites $\text{P}(\text{OR}^{\text{Y}})_2\text{R}^{\text{Y}}$; phosphites $\text{P}(\text{OR}^{\text{Y}})_3$; phosphinates $\text{OP}(\text{OR}^{\text{Y}})\text{R}^{\text{Y}}_2$; phosphonates: $\text{OP}(\text{OR}^{\text{Y}})_2\text{R}^{\text{Y}}$; phosphates $-\text{OP}(\text{OR}^{\text{Y}})_3$; phosphonium salts ($[-\text{PR}^{\text{Y}}_3]^+$) where a phosphorous-containing functional group may be linked to a metal complex through any available position (e.g. direct linkage via the phosphorous atom, or in some cases via an oxygen atom).

In certain embodiments, a phosphorous-containing functional group is chosen from the group consisting of:



or a combination of two or more of these

wherein R^1 and R^2 , are as defined above; and

each R^{Y} , is independently hydrogen, a hydroxyl protecting group, or an optionally substituted radical selected from the group consisting of C_{1-20} acyl; C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms

independently selected from nitrogen, oxygen, or sulfur; and where two R^7 groups can be taken together with intervening atoms to form an optionally substituted ring optionally containing one or more heteroatoms, and an R^7 group can be taken with an R^1 or R^2 group to an optionally substituted ring;

5 In some embodiments, phosphorous containing functional groups include those disclosed in The Chemistry of Organophosphorus Compounds, Volume 4, Ter- and Quinquevalent Phosphorus Acids and their Derivatives, The Chemistry of Functional Group Series Edited by Frank R. Hartley (Cranfield University, Cranfield, U.K.). Wiley: New York, 1996. ISBN 0-471-95706-2, the entirety of which is hereby incorporated
10 herein by reference.

$*-(X)_b-[(R^6R^7R^8P)^+]_nQ^{n-}$, wherein:

X is -O-, -N=, or -NR^z-,

b is 1 or 0,

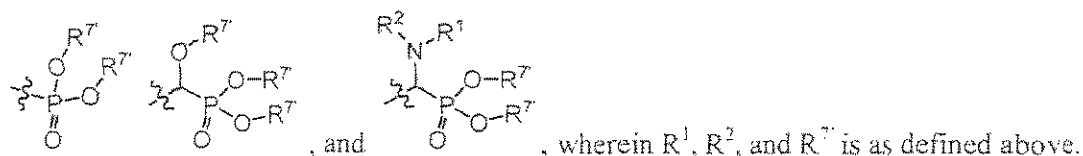
each of R^6 , R^7 and R^8 are independently present or absent and, if present, are

15 independently selected from the group consisting of optionally substituted C₁-C₂₀ aliphatic, optionally substituted phenyl, optionally substituted C₈-C₁₄ aryl, optionally substituted 3- to 14-membered heterocyclic, optionally substituted 5- to 14-membered heteroaryl, halogen, =O, -OR^z, =NR^z, and N(R^z)₂ where R^z is hydrogen, or an optionally substituted C₁-C₂₀ aliphatic, optionally substituted
20 phenyl, optionally substituted 8- to 14-membered aryl, optionally substituted 3- to 14-membered heterocyclic, or optionally substituted 5- to 14-membered heteroaryl,

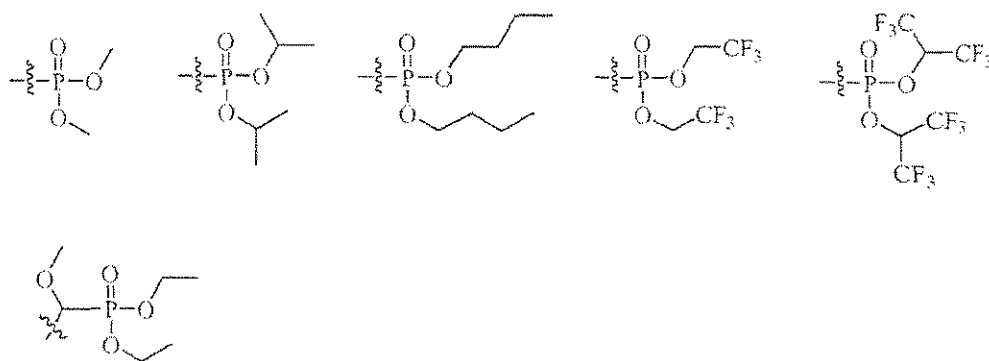
Q is any anion, and

n is an integer between 1 and 4.

In some embodiments, an activating functional group is a phosphonate group:

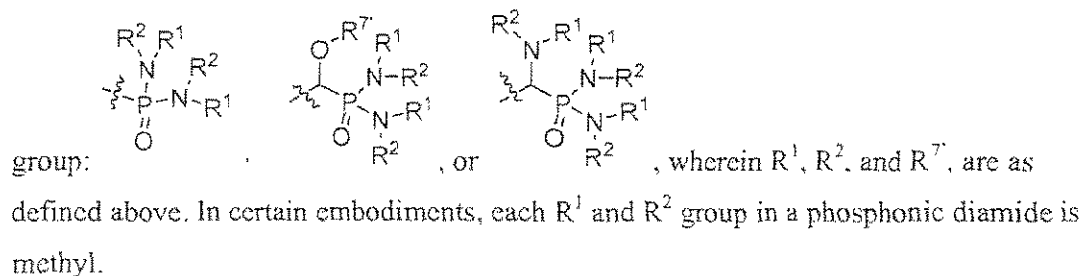


In specific embodiments, a phosphonate activating functional group is selected from the group consisting of:



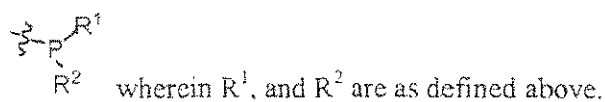
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In some embodiments, an activating functional group is a phosphonic diamide

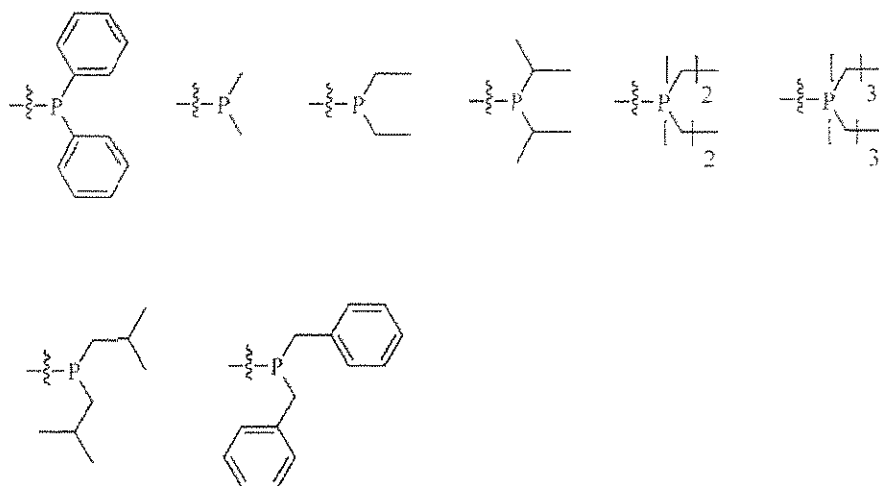


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In some embodiments, an activating functional group is a phosphine group:



In specific embodiments, a phosphine activating functional group is selected from the group consisting of:



II. Linker Moieties

As described above, each activating moiety $\text{---}\text{---}\text{---}(\text{Z})_m$ comprises a linker
 5 “ $\text{---}\text{---}\text{---}$ ” coupled to at least one activating functional group Z as described above, with m
 denoting the number of activating functional groups present on a single linker moiety.

As noted above there may be one or more activating moiety $\text{---}\text{---}\text{---}(\text{Z})_m$ tethered
 to a given metal complex, similarly, each activating moiety itself may contain more than
 one activating functional group Z. In certain embodiments, each activating moiety
 10 contains only one activating functional group (i.e. $m = 1$). In some embodiments, each
 activating moiety contains more than one activating functional groups (i.e. $m > 1$). In
 certain embodiments, an activating moiety contains two activating functional groups (i.e.
 $m = 2$). In certain embodiments, an activating moiety contains three activating functional
 groups (i.e. $m = 3$). In certain embodiments, an activating moiety contains four activating
 15 functional groups (i.e. $m = 4$). In certain embodiments where more than one activating
 functional group is present on an activating moiety, they are all the same functional
 group. In some embodiments where more than one activating functional group is present
 on an activating moiety, two or more of the activating functional groups are different.

In certain embodiments, each linker moiety $\text{---}\sim\text{---}$ contains 1-30 atoms including at least one carbon atom, and optionally one or more atoms selected from the group consisting of N, O, S, Si, B, and P.

5 In certain embodiments, the linker is an optionally substituted C_{2-30} aliphatic group wherein one or more methylene units are optionally and independently replaced by $\text{---NR}^y\text{---}$, $\text{---N(R}^y\text{)C(O)---}$, $\text{---C(O)N(R}^y\text{)---}$, ---O--- , ---C(O)--- , ---OC(O)--- , ---C(O)O--- , ---S--- , ---SO--- , $\text{---SO}_2\text{---}$, ---C(=S)--- , $\text{---C(=NR}^y\text{)---}$, or ---N=N--- , where each occurrence of R^y is independently ---H , or an optionally substituted radical selected from the group consisting of C_{1-6} aliphatic 3- to 7-membered heterocyclic, phenyl, and 8- to 10-membered aryl. In certain embodiments, a linker moiety is a $\text{C}_4\text{---C}_{12}$ aliphatic group substituted with one or more moieties selected from the group consisting of halogen, $\text{---NO}_2\text{---}$, ---CN--- , $\text{---SR}^y\text{---}$, $\text{---S(O)R}^y\text{---}$, $\text{---S(O)}_2\text{R}^y\text{---}$, $\text{---NR}^y\text{C(O)R}^y\text{---}$, $\text{---OC(O)R}^y\text{---}$, $\text{---CO}_2\text{R}^y\text{---}$, ---NCO--- , $\text{---N}_3\text{---}$, $\text{---OR}^y\text{---}$, $\text{---OC(O)N(R}^y\text{)}_2\text{---}$, $\text{---N(R}^y\text{)}_2\text{---}$, $\text{---NR}^y\text{C(O)R}^y\text{---}$, and $\text{---NR}^y\text{C(O)OR}^y\text{---}$, where R^y is ---H , or an optionally substituted radical selected from the group consisting of C_{1-6} aliphatic 3- to 7-membered heterocyclic, phenyl, and 8- to 10-membered aryl.

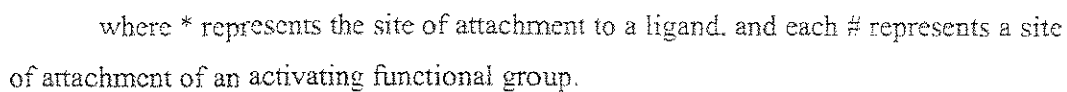
In certain embodiments, a linker moiety is an optionally substituted $\text{C}_3\text{---C}_{30}$ aliphatic group. In certain embodiments, a linker is an optionally substituted C_{4-24} aliphatic group. In certain embodiments, a linker moiety is an optionally substituted $\text{C}_4\text{---C}_{20}$ aliphatic group. In certain embodiments, a linker moiety is an optionally substituted $\text{C}_4\text{---C}_{12}$ aliphatic group. In certain embodiments, a linker is an optionally substituted C_{4-10} aliphatic group. In certain embodiments, a linker is an optionally substituted C_{4-8} aliphatic group. In certain embodiments, a linker moiety is an optionally substituted $\text{C}_4\text{---C}_6$ aliphatic group. In certain embodiments, a linker moiety is an optionally substituted $\text{C}_6\text{---C}_{12}$ aliphatic group. In certain embodiments, a linker moiety is an optionally substituted C_8 aliphatic group. In certain embodiments, a linker moiety is an optionally substituted C_7 aliphatic group. In certain embodiments, a linker moiety is an optionally substituted C_6 aliphatic group. In certain embodiments, a linker moiety is an optionally substituted C_5 aliphatic group. In certain embodiments, a linker moiety is an optionally substituted C_4 aliphatic group. In certain embodiments, a linker moiety is an optionally substituted C_3 aliphatic group. In certain embodiments, a aliphatic group in the linker moiety is an optionally substituted straight alkyl chain. In certain embodiments, the aliphatic group is

an optionally substituted branched alkyl chain. In some embodiments, a linker moiety is a C₄ to C₂₀ alkyl group having one or more methylene groups replaced by -C(R^aR^b)- where R^a and R^b are each, independently C₁-C₄ alkyl groups. In certain embodiments, a linker moiety consists of an aliphatic group having 4 to 30 carbons including one or more gem-dimethyl substituted carbon atoms.

In certain embodiments, a linker moiety includes one or more optionally substituted cyclic elements selected from the group consisting of saturated or partially unsaturated carbocyclic, aryl, heterocyclic, or heteroaryl. In certain embodiments, a linker moiety consists of the substituted cyclic element, in some embodiments the cyclic element is part of a linker with one or more non-ring heteroatoms or optionally substituted aliphatic groups comprising other parts of the linker moiety.

In some embodiments, a linker moiety is of sufficient length to allow one or more activating functional groups to be positioned near a metal atom of a metal complex. In certain embodiments, structural constraints are built into a linker moiety to control the disposition and orientation of one or more activating functional groups near a metal center of a metal complex. In certain embodiments such structural constraints are selected from the group consisting of cyclic moieties, bicyclic moieties, bridged cyclic moieties and tricyclic moieties. In some embodiments, such structural constraints are the result of acyclic steric interactions. In certain embodiments such structural constraints are selected from the group consisting of *cis* double bonds, *trans* double bonds, *cis* allenes, *trans* allenes, and triple bonds. In some embodiments, such structural constraints are selected from the group consisting of substituted carbons including geminally disubstituted groups such as spirocyclic rings, gem dimethyl groups, gem diethyl groups and gem diphenyl groups. In certain embodiments such structural constraints are selected from the group consisting of heteroatom-containing functional groups such as sulfoxides, amides, and oximes.

In certain embodiments, linker moieties are selected from the group consisting of:

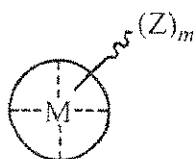


In some embodiments, s is 0. In some embodiments, s is 1. In some
embodiments, s is 2. In some embodiments, s is 3. In some embodiments, s is 4. In
some embodiments, s is 5. In some embodiments, s is 6.

5 In some embodiments, t is 1. In some embodiments, t is 2. In some
embodiments, t is 3. In some embodiments, t is 4.

III. Metal Complexes

As noted above, the present invention encompasses metal complexes that include
a metal atom coordinated to a multidentate ligand and at least one activating moiety
tethered to a multidentate ligand. In certain embodiments, provided metal complexes
10 have the structure:



where  represents a metal atom coordinated to a multidentate ligand.

III.a. Metal Atoms

15 In certain embodiments, M is a metal atom selected from periodic table groups 3-
13, inclusive. In certain embodiments, M is a transition metal selected from periodic
table groups 5-12, inclusive. In certain embodiments, M is a transition metal selected
from periodic table groups 4-11, inclusive. In certain embodiments, M is a transition
metal selected from periodic table groups 5-10, inclusive. In certain embodiments, M is a
20 transition metal selected from periodic table groups 7-9, inclusive. In some
embodiments, M is selected from the group consisting of Cr, Mn, V, Fe, Co, Mo, W, Ru,
Al, and Ni. In some embodiments, M is a metal atom selected from the group consisting
of: cobalt; chromium; aluminum; titanium; ruthenium, and manganese. In some

embodiments, M is cobalt. In some embodiments, M is chromium. In some embodiments, M is aluminum.

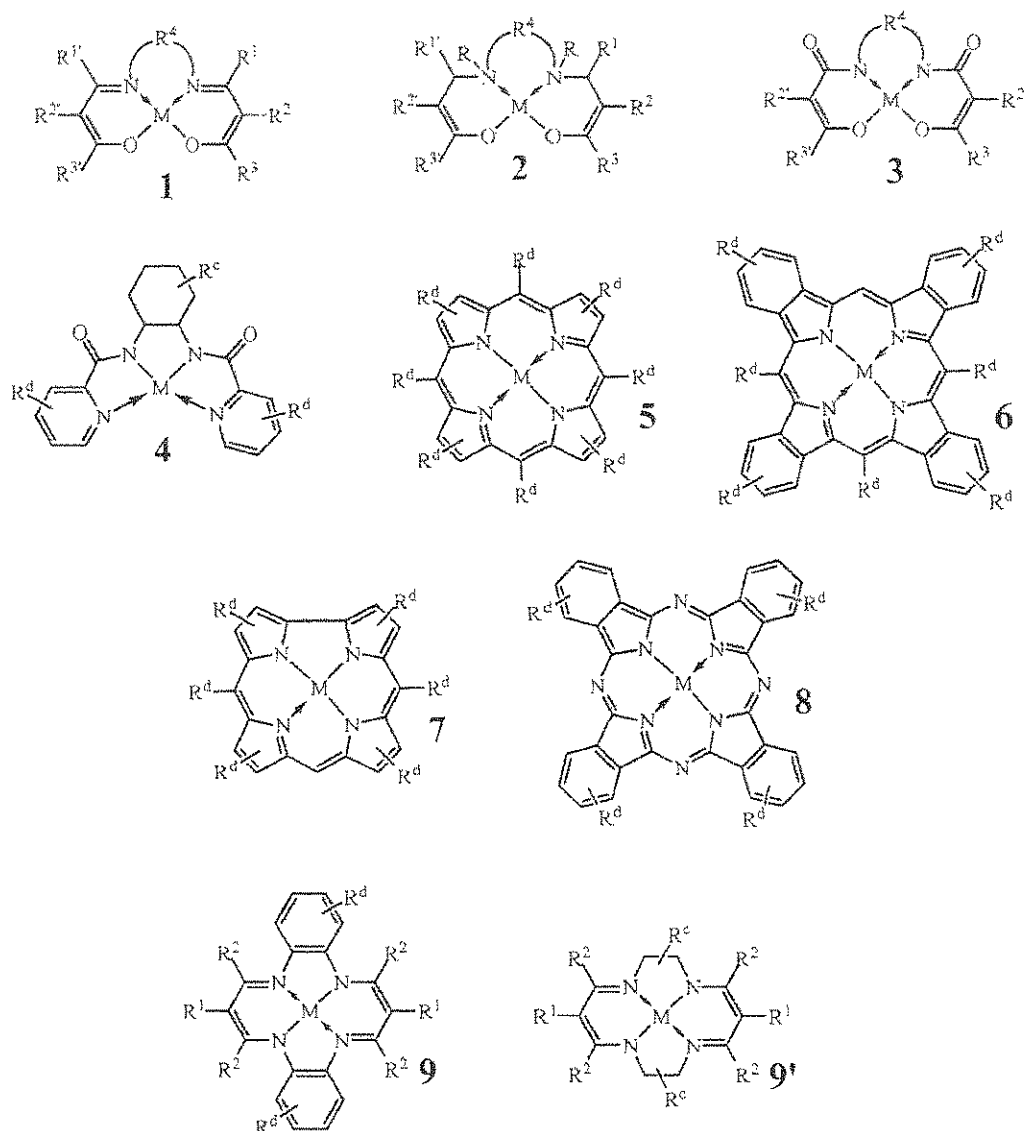
In certain embodiments, a metal complex is a zinc, cobalt, chromium, aluminum, titanium, ruthenium, or manganese complex. In certain embodiments, a metal complex is an aluminum complex. In some embodiments, a metal complex is a chromium complex. In some embodiments, a metal complex is a zinc complex. In certain some embodiments, a metal complex is a titanium complex. In some embodiments, a metal complex is a ruthenium complex. In certain embodiments, a metal complex is a manganese complex. In certain embodiments, a metal complex is cobalt complex. In certain embodiments where the metal complex is a cobalt complex, the cobalt metal has an oxidation state of 3+ (*i.e.*, Co(III)). In some embodiments, the cobalt metal has an oxidation state of 2+.

III.b. Ligands

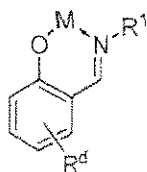
In some embodiments, a metal complex  comprises a metal atom coordinated to a single tetradentate ligand and in some embodiments, the metal complex comprises a chelate containing a plurality of individual ligands. In certain embodiments, a metal complex contains two bidentate ligands. In some embodiments, a metal complex contains a tridentate ligand.

In various embodiments, tetradentate ligands suitable for metal complexes of the present invention may include, but are not limited to: salen derivatives 1, derivatives of salan ligands 2, bis-2-hydroxybenzamido derivatives 3, derivatives of the Trost ligand 4, porphyrin derivatives 5, derivatives of tetrabenzoporphyrin ligands 6, derivatives of corrole ligands 7, phthalocyaninate derivatives 8, and

dibenzotetramethyltetraaza[14]annulene (tmtaa) derivatives 9 or 9'.

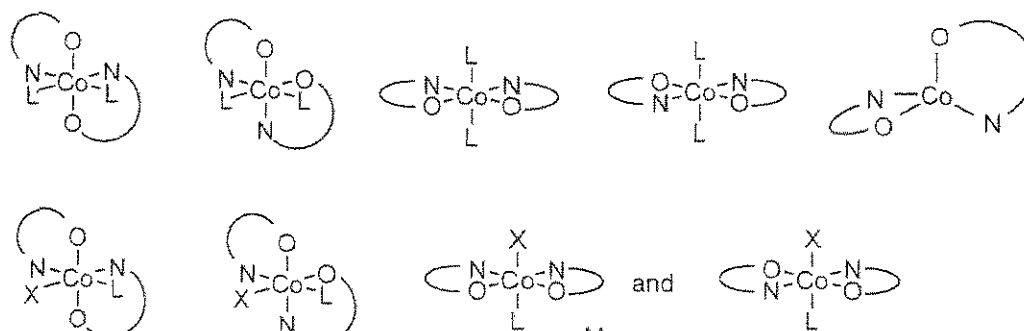


In some embodiments, a metal multidentate ligand coordinated with a metal complex may comprise a plurality of discrete ligands. In some embodiments, metal complexes include two bidentate ligands. In certain embodiments, such bidentate ligands may have the structure

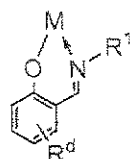


where R^d and R^1 are as defined above. Metal complexes having two such ligands may adopt one of several geometries, and the present disclosure encompasses such variations.

In certain embodiments, metal complexes including two bidentate ligands may have structures selected from the group consisting of:



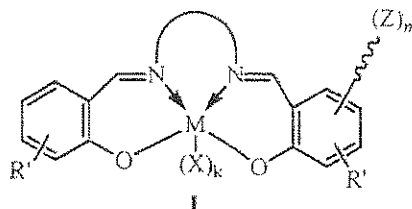
where each  represents a ligand:



In certain embodiments, a tetradentate ligand is a salen ligand. In certain embodiments, a metal complex is a metallosalenate. In certain embodiments, a metal complex is a cobalt salen complex. In certain embodiments, a metal complex is a chromium salen complex. In some embodiments, a metal complex is an aluminum salen complex.

In certain embodiments, at least one activating moiety is tethered to a carbon atom of a phenyl ring of the salicylaldehyde-derived portions of a salen ligand. In certain embodiments, at least one activating moiety is tethered to a carbon atom of a porphyrin ligand. In certain embodiments, at least one activating moiety is tethered to a pyrrole-carbon atom of a porphyrin ligand. In certain embodiments, at least one activating moiety is tethered to a carbon atom forming the bridge between the pyrrole rings of a porphyrin ligand.

In certain embodiments, at least one activating moiety is tethered to one or more carbon atoms of only one phenyl ring of the salicylaldehyde-derived portions of a salen ligand, as shown in formula I:



5 wherein:

M is a metal atom;

X is a nucleophile capable of ring opening an epoxide;

k is an integer from 0-2 inclusive;

10 R' represents one or more substituents optionally present on the phenyl rings and each R' is independently selected from the group consisting of: halogen, -NO₂, -CN, -SR^y, -S(O)R^y, -S(O)₂R^y, -NR^yC(O)R^y, -OC(O)R^y, -CO₂R^y, -NCO, -N₃, -OR⁷, -OC(O)N(R^y)₂, -N(R^y)₂, -NR^yC(O)R^y, -NR^yC(O)OR^y; or an optionally substituted radical selected from the group consisting of C₁₋₂₀ aliphatic; C₁₋₂₀ heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur, where two or more adjacent R' groups can be taken together to form an optionally

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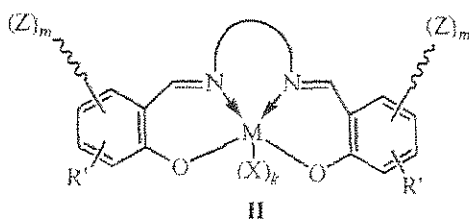
substituted saturated, partially unsaturated, or aromatic 5- to 12-membered ring containing 0 to 4 heteroatoms;

R^y is -H, or an optionally substituted radical selected from the group consisting of C_{1-6} aliphatic, 3- to 7-membered heterocyclic, phenyl, and 8- to 10- membered aryl;

 represents is an optionally substituted moiety linking the two nitrogen atoms of the diamine portion of the salen ligand, where  is selected from the group consisting of phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an optionally substituted C_{2-20} aliphatic group, wherein one or more methylene units are optionally and independently replaced by $-NR^y-$, $-N(R^y)C(O)-$, $-C(O)N(R^y)-$, $-OC(O)N(R^y)-$, $-N(R^y)C(O)O-$, $-OC(O)O-$, $-O-$, $-C(O)-$, $-OC(O)-$, $-C(O)O-$, $-S-$, $-SO-$, $-SO_2-$, $-C(=S)-$, $-C(=NR^y)-$, $-C(=NOR^y)-$ or $-N=N-$;

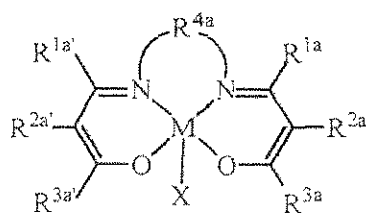
 $(Z)_m$ represents one or more activating moieties, where "" is a covalent linker containing one or more atoms selected from the group consisting of C, O, N, S, and Si; Z is a activating functional group and m is an integer from 1 to 4 indicating the number of individual activating functional groups present in each activating moiety.

In certain embodiments, both salicylaldehyde-derived portions of a salen ligand bear one or more activating moieties:



wherein M, X, k, R', , and $\text{---}\text{---}\text{---}(Z)_m$ are as defined above.

In some embodiments, provided metal complexes comprise a moiety that has the structure:



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wherein:

M is a metal atom,

R^{1a} , $R^{1a'}$, R^{2a} , $R^{2a'}$, R^{3a} , and $R^{3a'}$ are independently a $\text{---}\text{---}\text{---}(Z)_m$ group, hydrogen, halogen, -OR, -NR₂, -SR, -CN, -NO₂, -SO₂R, -SOR, -SO₂NR₂, -CNO, -NRSO₂R, -NCO, -N₃, -SiR₃; or an optionally substituted radical selected from the group consisting of C₁₋₂₀ aliphatic; C₁₋₂₀ heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle; a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur;

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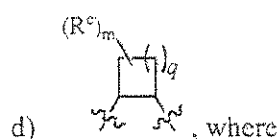
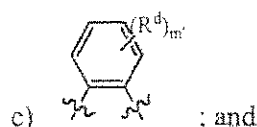
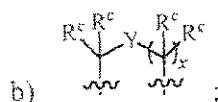
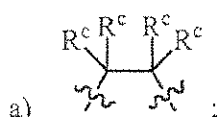
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each R is independently hydrogen, an optionally substituted radical selected the group consisting of acyl; carbamoyl; arylalkyl; phenyl, 8- to 10-membered aryl; C₁₋₁₂ aliphatic; C₁₋₁₂ heteroaliphatic; 5- to 10-membered heteroaryl; 4- to 7-membered heterocyclyl; an oxygen protecting group; and a nitrogen protecting group; or:

two R on the same nitrogen atom are taken with the nitrogen to form a 3- to 7-membered heterocyclic ring;

wherein any of [R^{2a'} and R^{3a'}], [R^{2a} and R^{3a}], [R^{1a} and R^{2a}], and [R^{1a'} and R^{2a'}] may optionally be taken together with the carbon atoms to which they are attached to form one or more rings which may in turn be substituted with one or more R^{20a} groups; and

R^{4a} is selected from the group consisting of:



R^c at each occurrence is independently a Z group, hydrogen, halogen, -OR, -NR₂, -SR, -CN, -NO₂, -SO₂R, -SOR, -SO₂NR₂, -CNO, -NRSO₂R, -NCO, -N₃, -SiR₃; or an optionally substituted radical selected from the group consisting of C₁₋₂₀ aliphatic; C₁₋₂₀ heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle; a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4

heteroatoms independently selected from nitrogen, oxygen, or sulfur;
a 3- to 8-membered saturated or partially unsaturated heterocyclic ring
having 1-3 heteroatoms independently selected from nitrogen, oxygen, or
sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated
heterocycle having 1-5 heteroatoms independently selected from
nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl
ring having 1-5 heteroatoms independently selected from nitrogen,
oxygen, or sulfur;

where:

two or more R^c groups may be taken together with the carbon atoms to
which they are attached and any intervening atoms to form one or
more rings;

when two R^c groups are attached to the same carbon atom, they may be
taken together along with the carbon atom to which they are
attached to form a moiety selected from the group consisting of: a 3-
to 8-membered spirocyclic ring, a carbonyl, an oxime, a hydrazone,
an imine;

X is a nucleophile capable of ring opening an epoxide;

Y is a divalent linker selected from the group consisting of: -NR-, -N(R)C(O)-,
-C(O)NR-, -O-, -C(O)-, -OC(O)-, -C(O)O-, -S-, -SO-, -SO₂-, -C(=S)-,
-C(=NR)-, or -N=N-; a polyether; a C₃ to C₈ substituted or unsubstituted
carbocycle; and a C₁ to C₈ substituted or unsubstituted heterocycle;

m' is 0 or an integer from 1 to 4, inclusive;

q is 0 or an integer from 1 to 4, inclusive; and

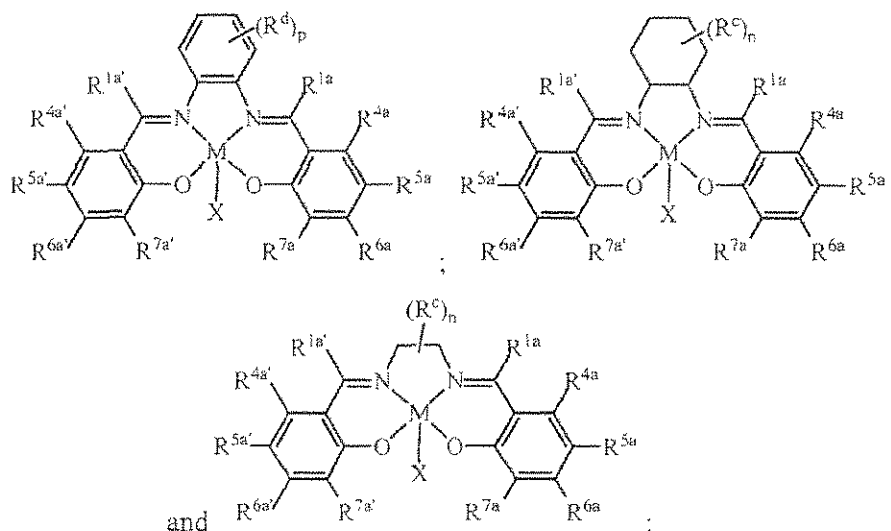
x is 0, 1, or 2.

In some embodiments, at least one of $[R^{2a}$ and $R^{3a}]$ and $[R^{2a'}$ and $R^{3a'}]$ are taken
together to form a ring. In some embodiments, both $[R^{2a}$ and $R^{3a}]$ and $[R^{2a'}$ and $R^{3a'}]$ are
taken together to form rings. In some embodiments, the rings formed by $[R^{2a}$ and $R^{3a}]$
and $[R^{2a'}$ and $R^{3a'}]$ are substituted phenyl rings.

In certain embodiments, one or more of R^{1a} , $R^{1a'}$, R^{2a} , $R^{2a'}$, R^{3a} , and $R^{3a'}$ are independently a $\text{---}\text{Z}$ group.



In certain embodiments of provided metal complexes, a  moiety has a structure selected from the group consisting of:



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wherein:

M is a metal atom;

R^{4a} , $R^{4a'}$, R^{5a} , $R^{5a'}$, R^{6a} , $R^{6a'}$, R^{7a} , and $R^{7a'}$ are each independently a $\text{---}\text{Z}$ group,

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hydrogen, halogen, -OR, -NR₂, -SR, -CN, -NO₂, -SO₂R, -SOR, -SO₂NR₂; -CNO, -NRSO₂R, -NCO, -N₃, -SiR₃; or an optionally substituted radical selected from the group consisting of C₁₋₂₀ aliphatic; C₁₋₂₀ heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having

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1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or
 an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms
 independently selected from nitrogen, oxygen, or sulfur;

wherein $[R^{1a}$ and $R^{4a}]$, $[R^{1a'}$ and $R^{4a'}]$ and any two adjacent R^{4a} , $R^{4a'}$, R^{5a} , $R^{5a'}$, R^{6a} ,
 $R^{6a'}$, R^{7a} , and $R^{7a'}$ groups can be taken together with intervening atoms to form
 one or more optionally substituted rings;

n is 0 or an integer from 1 to 8, inclusive; and

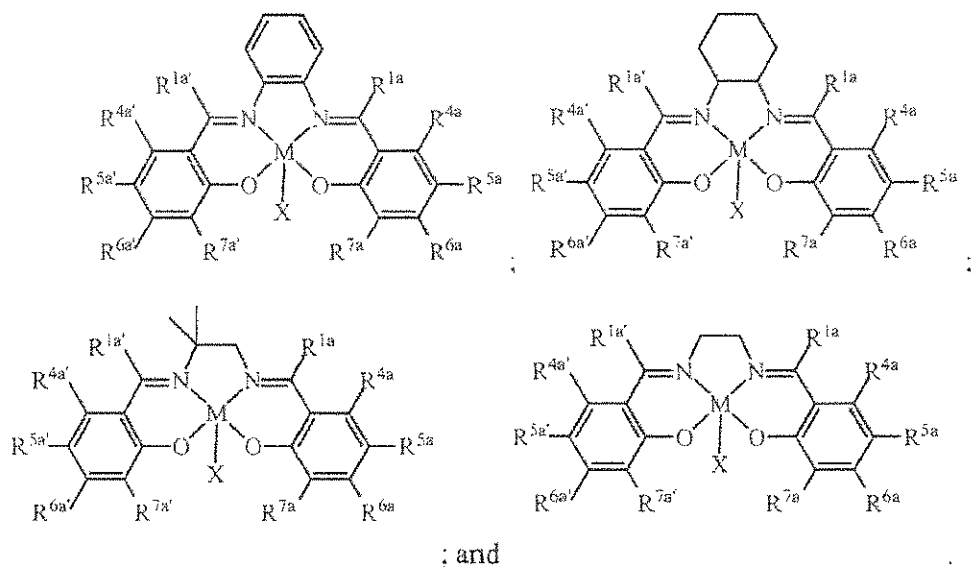
p is 0 or an integer from 1 to 4, inclusive.

In some embodiments, M is Co.

In some embodiments, R^{1a} , $R^{1a'}$, R^{4a} , $R^{4a'}$, R^{6a} , and $R^{6a'}$ are each -H. In some
 embodiments, R^{5a} , $R^{5a'}$, R^{7a} and $R^{7a'}$ are each optionally substituted C_1 - C_{12} aliphatic. In
 some embodiments, R^{4a} , $R^{4a'}$, R^{5a} , $R^{5a'}$, R^{6a} , $R^{6a'}$, R^{7a} , and $R^{7a'}$ are each independently
 selected from the group consisting of: -H, -SiR₃; methyl, ethyl, *n*-propyl, *i*-propyl,
n-butyl, *sec*-butyl, *t*-butyl, isoamyl, *t*-amyl, hexyl, and trityl. In some embodiments, R^{1a} ,
 $R^{1a'}$, R^{4a} , $R^{4a'}$, R^{6a} , and $R^{6a'}$ are each -H. In some embodiments, R^{7a} is selected from the
 group consisting of -H; methyl; ethyl; *n*-propyl; *i*-propyl; *n*-butyl; *sec*-butyl; *t*-butyl;
 isoamyl; *t*-amyl; hexyl; and trityl. In some embodiments, R^{5a} and R^{7a} are independently
 selected from the group consisting of -H; methyl; ethyl; *n*-propyl; *i*-propyl; *n*-butyl;
sec-butyl; *t*-butyl; isoamyl; *t*-amyl; hexyl; and trityl. In certain embodiments, one or
 more of R^{5a} , $R^{5a'}$, R^{7a} and $R^{7a'}$ is a $\text{---}\text{Z}$ group. In some embodiments, R^{5a} and $R^{5a'}$
 are a $\text{---}\text{Z}$ group.

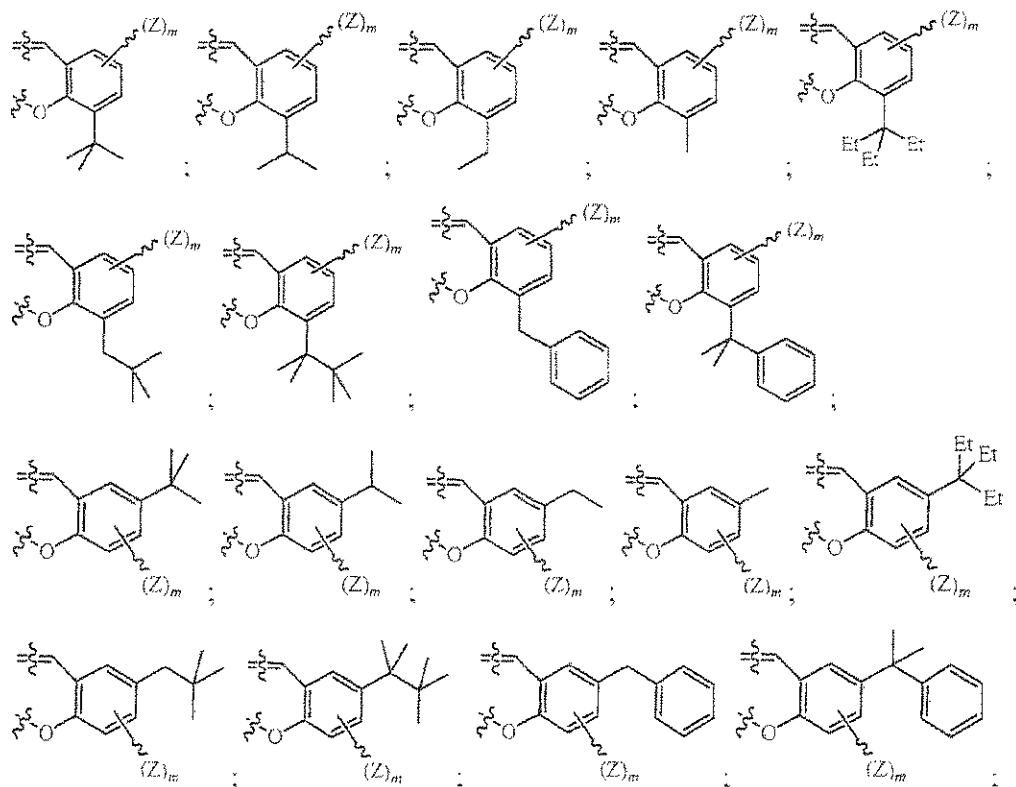


In certain embodiments of provided metal complexes, a moiety has a
 structure selected from the group consisting of:



In certain embodiments of complexes having formulae described above, at least one of the phenyl rings comprising a salicylaldehyde-derived portion of a catalyst is independently selected from the group consisting of:

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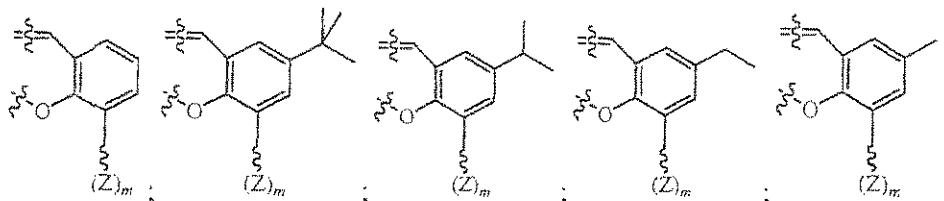


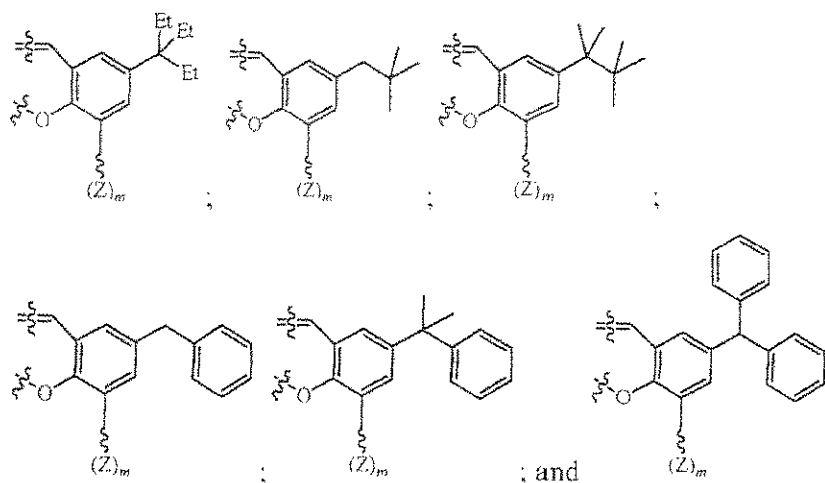
R^{4a} , $R^{4a'}$, R^{5a} , $R^{5a'}$, R^{6a} , and $R^{6a'}$ are each independently a $\sim Z$ group,
 hydrogen, halogen, -OR, -NR₂, -SR, -CN, -NO₂, -SO₂R, -SOR, -SO₂NR₂;
 -CNO, -NRSO₂R, -NCO, -N₃, -SiR₃; or an optionally substituted radical
 selected from the group consisting of C₁₋₂₀ aliphatic; C₁₋₂₀ heteroaliphatic;
 5 phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic
 carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic
 polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having
 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3-
 to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3
 10 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to
 12-membered polycyclic saturated or partially unsaturated heterocycle having
 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or
 an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms
 independently selected from nitrogen, oxygen, or sulfur;

15 wherein any two adjacent R^{4a} , $R^{4a'}$, R^{5a} , $R^{5a'}$, R^{6a} , and $R^{6a'}$ groups can be taken
 together with intervening atoms to form one or more optionally substituted
 rings.

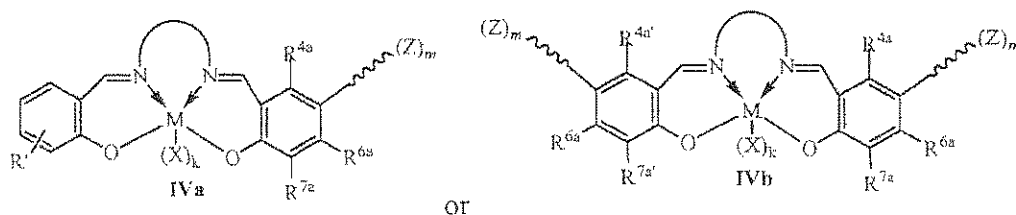
In certain embodiments of compounds having formulac **IIIa** or **IIIb**, R^{4a} , $R^{4a'}$,
 R^{6a} , and $R^{6a'}$ are each hydrogen, and R^{5a} , $R^{5a'}$ are, independently, optionally substituted
 20 C₁-C₂₀ aliphatic.

In certain embodiments of complexes **IIIa** and **IIIb**, at least one of the phenyl
 rings comprising a salicylaldehyde-derived portion of a catalyst is independently selected
 from the group consisting of:





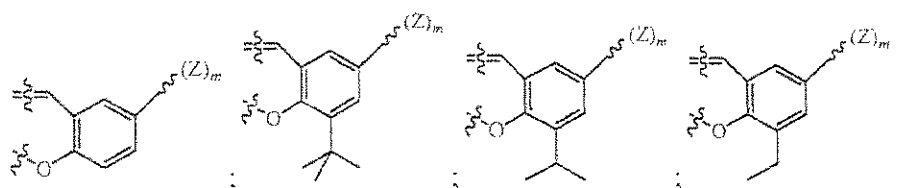
In certain embodiments, there is an activating moiety tethered to the position para to the phenolic oxygen of one or both of a salicylaldehyde-derived phenyl rings of the salen ligand as in structures **IVa** and **IVb**:

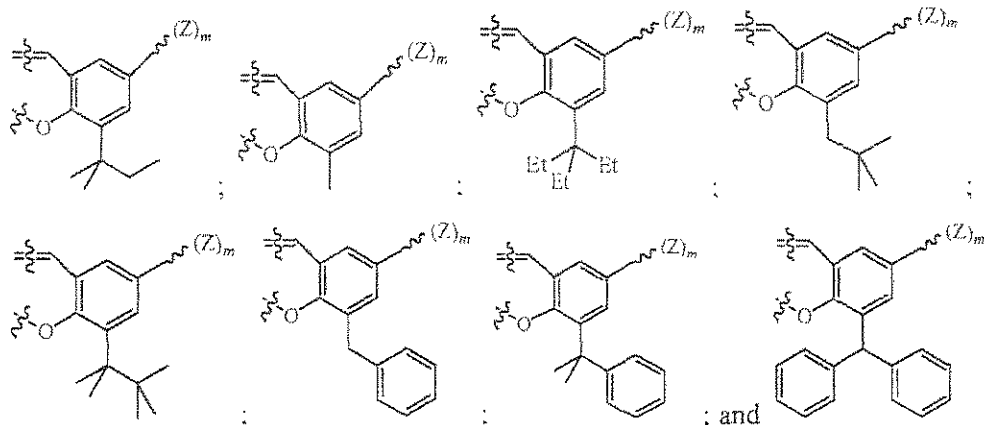


where M, X, k, R', R^{4a}, R^{4a'}, R^{6a}, R^{6a'}, R^{7a}, R^{7a'}, , and  (Z)_m are as defined above.

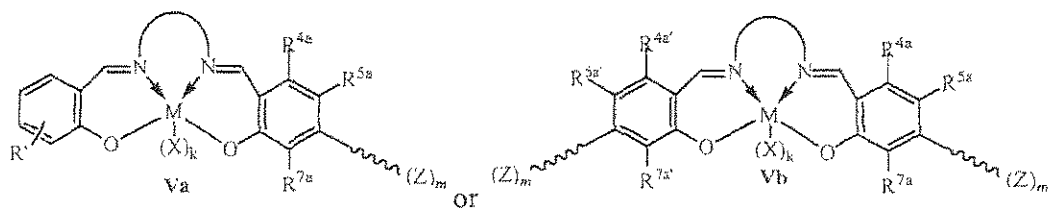
In certain embodiments of compounds having formulae **IVa** or **IVb**, R^{4a}, R^{4a'}, R^{6a}, and R^{6a'} are hydrogen, and each R^{7a}, R^{7a'} is, independently, optionally substituted C₁-C₂₀ aliphatic.

In certain embodiments of catalysts **IVa** and **IVb**, at least one of the phenyl rings comprising a salicylaldehyde-derived portion of a catalyst is independently selected from the group consisting of:





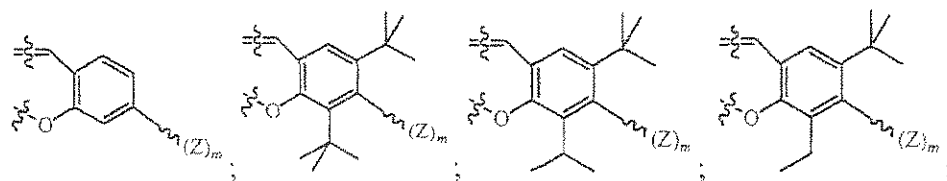
In some embodiments, there is an activating moiety tethered to the position para to the imine substituent of one or both of the salicylaldehyde-derived phenyl rings of a salen ligand as in formulae **Va** or **Vb**:

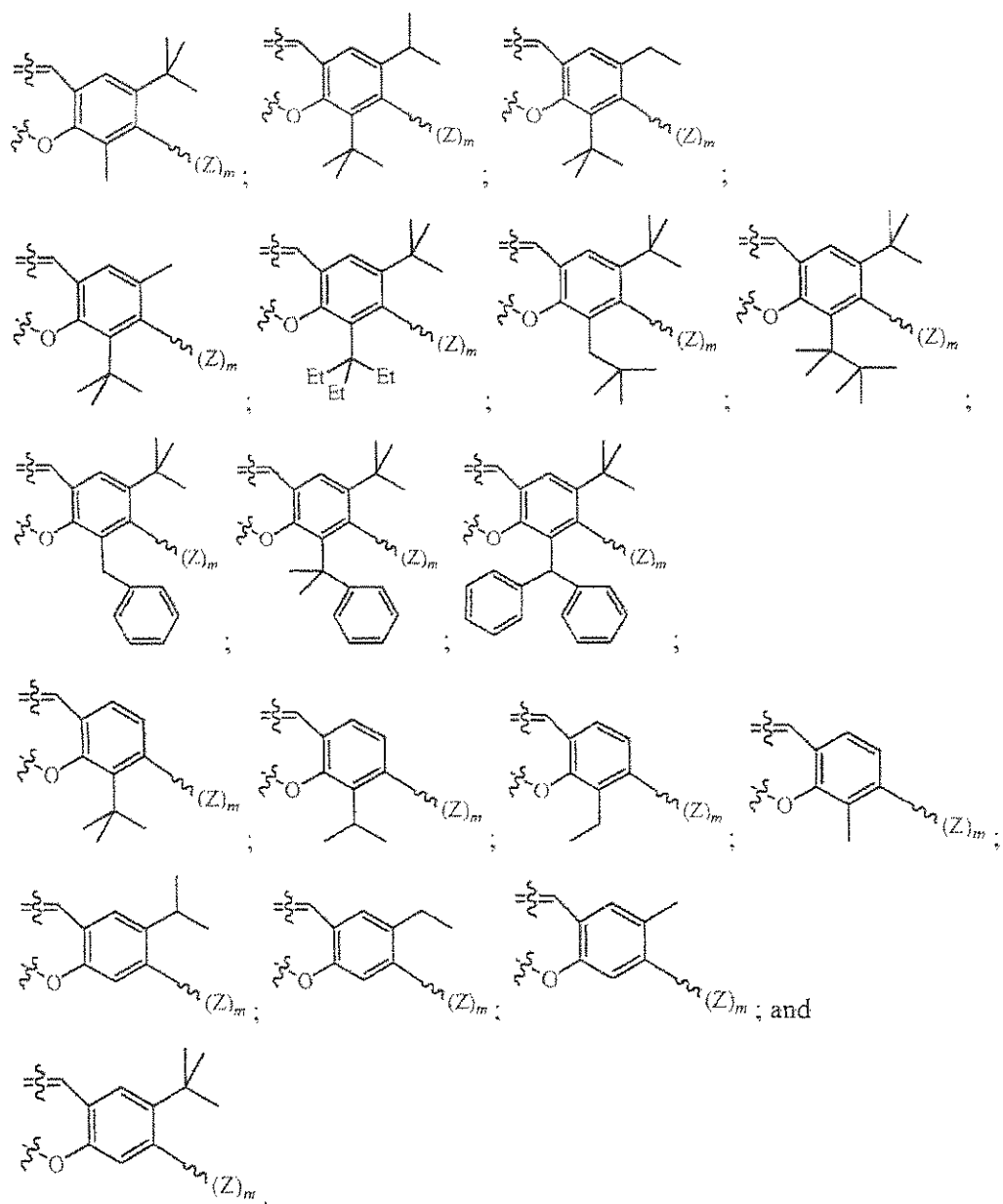


where M , X , k , R^1 , R^{4a} , $R^{4a'}$, R^{5a} , $R^{5a'}$, R^{7a} , $R^{7a'}$, , and $\text{---}(Z)_m$ are as defined above.

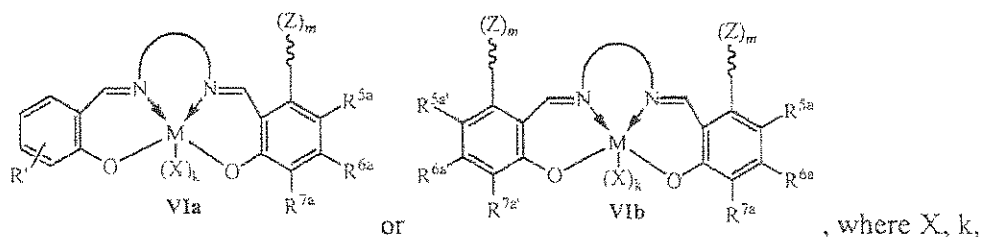
In certain embodiments of compounds having formulae **Va** or **Vb**, each R^4 and R^{4a} is hydrogen, and each R^{5a} , $R^{5a'}$, R^{7a} , $R^{7a'}$ is, independently, hydrogen or optionally substituted C_1 - C_{20} aliphatic.

In certain embodiments of catalysts **Va** and **Vb**, at least one of the phenyl rings comprising a salicylaldehyde-derived portion of a catalyst is independently selected from the group consisting of:





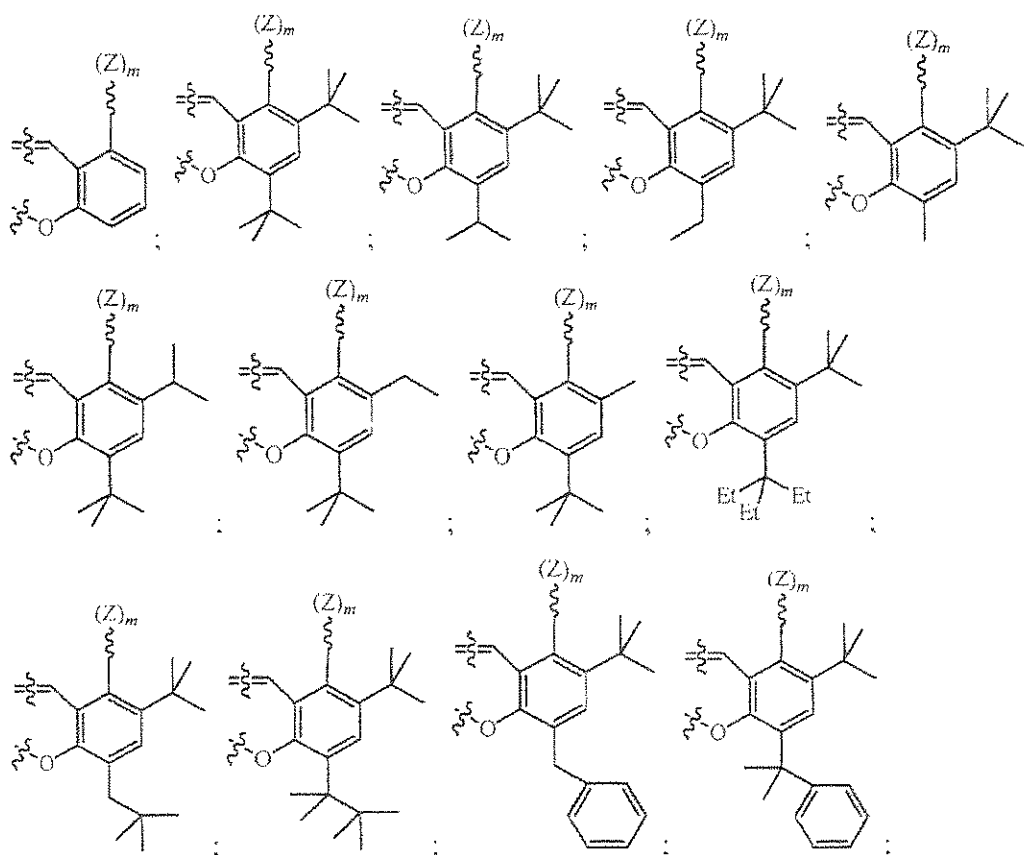
In some embodiments, there is an activating moiety tethered to the position ortho to the imine substituent of one or both of the salicylaldehyde-derived phenyl rings of a salen ligand as in formulae **VIa** and **VIb**:

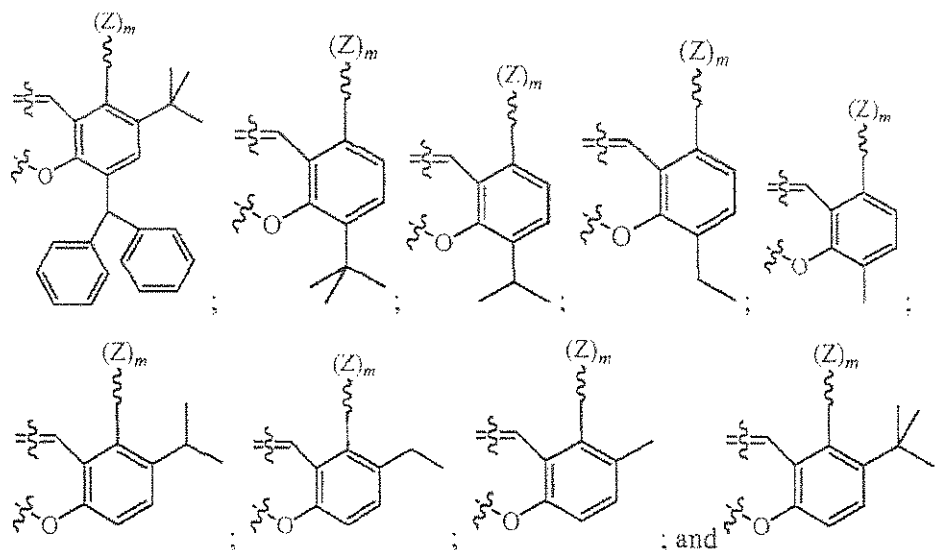


M, R', R^{5a}, R^{5a'}, R^{6a}, R^{6a'}, R^{7a}, R^{7a'}, , and (Z)_m are as defined above.

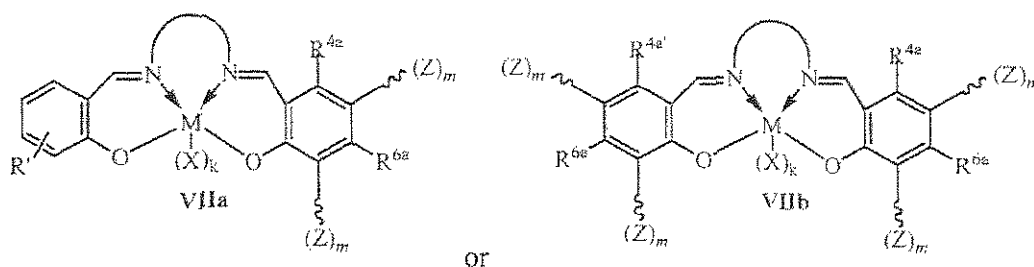
In certain embodiments of compounds having formulae **VIa** or **VIb**, each R^{6a} and R^{6a'} is hydrogen, and each R^{5a}, R^{5a'}, R^{7a}, and R^{7a'} is, independently, hydrogen or optionally substituted C₁-C₂₀ aliphatic.

In certain embodiments of catalysts **VIa** and **VIb**, at least one of the phenyl rings comprising a salicylaldehyde-derived portion of a catalyst is independently selected from the group consisting of:





In some embodiments, there are activating moieties tethered to the positions ortho and para to the phenolic oxygen of one or both of the salicylaldehyde-derived phenyl rings of a salen ligand as in formulae **VIIa** and **VIIb**:

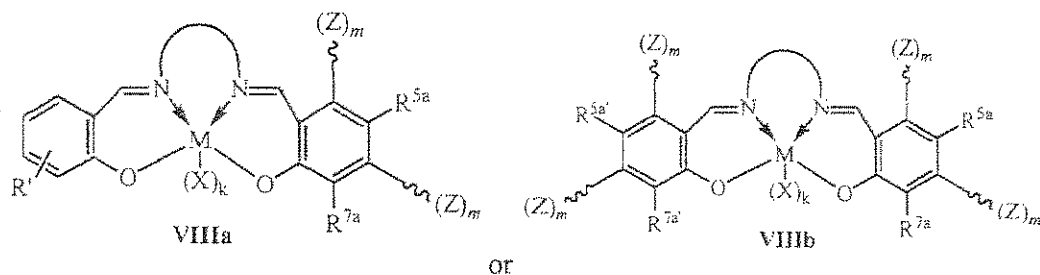


where M, X, k, R', R^{4a}, R^{4a'}, R^{6a}, R^{6a'}, , and  (Z)_m are as defined above.

In certain embodiments of compounds having formulae **VIa** or **VIb**, each R^{6a}, R^{6a'}, R^{4a}, and R^{4a'} is, independently, hydrogen or optionally substituted C₁-C₂₀ aliphatic.

In certain embodiments of compounds having formulae **VIIa** or **VIIb**, each R^{6a}, R^{6a'}, R^{4a}, and R^{4a'} is hydrogen.

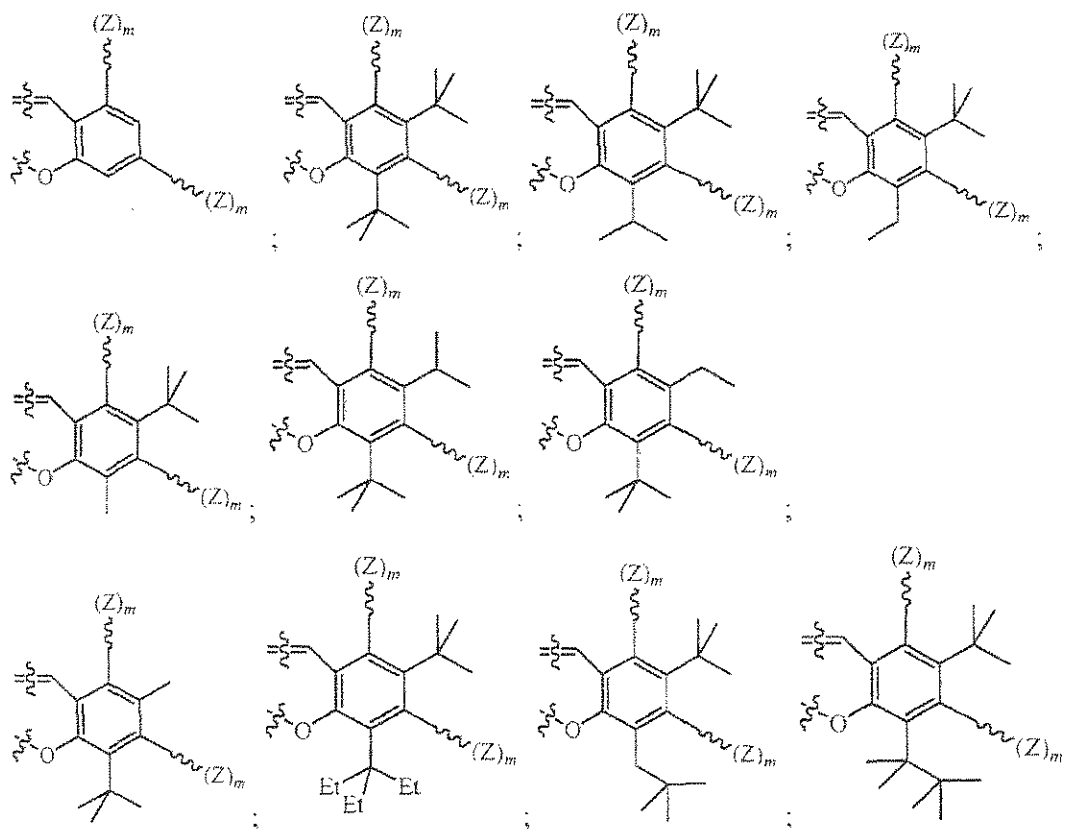
In some embodiments, there are activating moieties tethered to the positions ortho and para to the imine substituent of one or both of the salicylaldehyde-derived phenyl rings of a salen ligand as in formulae **VIIIa** and **VIIIb**:

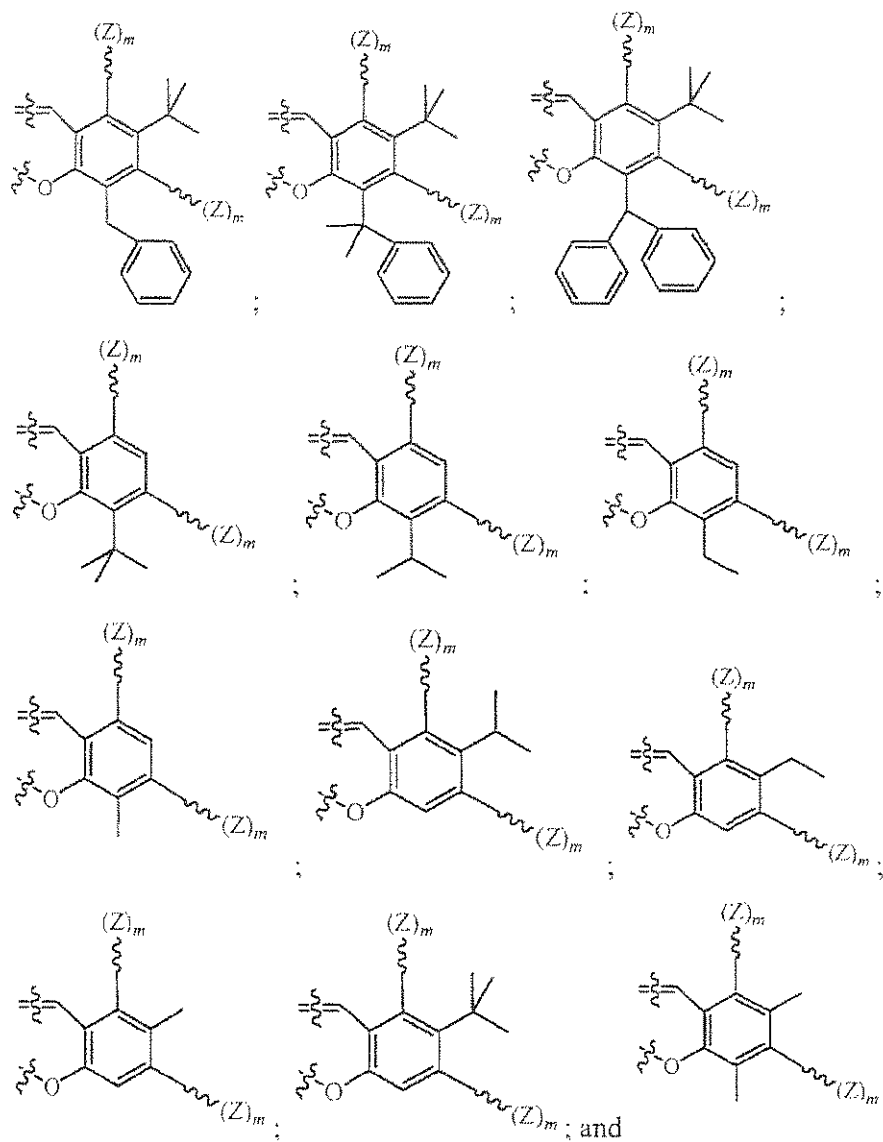


where X, k, M, R', R^{5a}, R^{5a'}, R^{7a}, R^{7a'}, , and (Z)_m are as defined above.

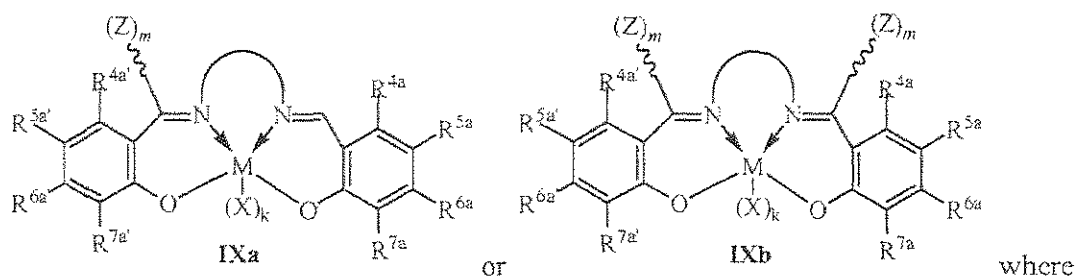
In certain embodiments of compounds having formulae **VIIIa** or **VIIIb**, each R^{5a}, R^{5a'}, R^{7a}, and R^{7a'} is, independently, optionally, hydrogen or substituted C₁-C₂₀ aliphatic.

- 5 In certain embodiments of the present invention, catalysts of structures **VIIIa** or **VIIIb** above, at least one of the phenyl rings comprising the salicylaldehyde-derived portion of a catalyst is independently selected from the group consisting of:





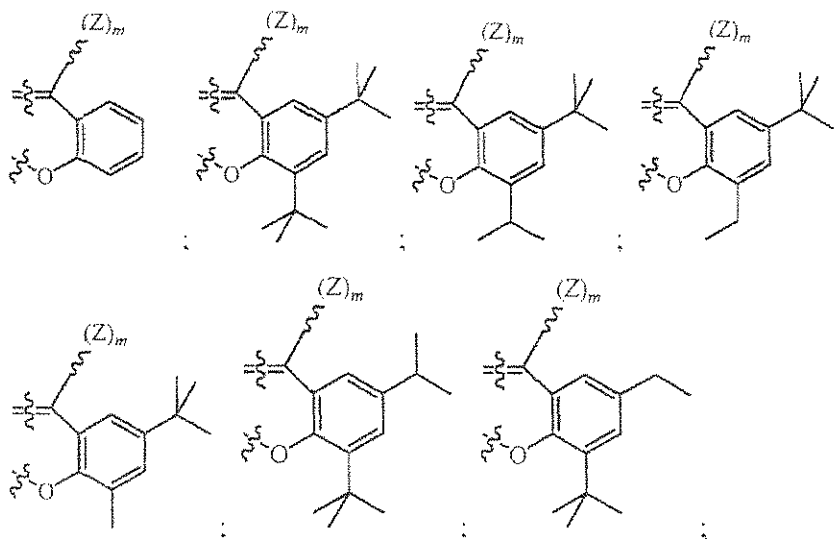
5 In some embodiments, there is an activating moiety tethered to the imine carbon of a salen ligand as in formulae **IXa** and **IXb**:

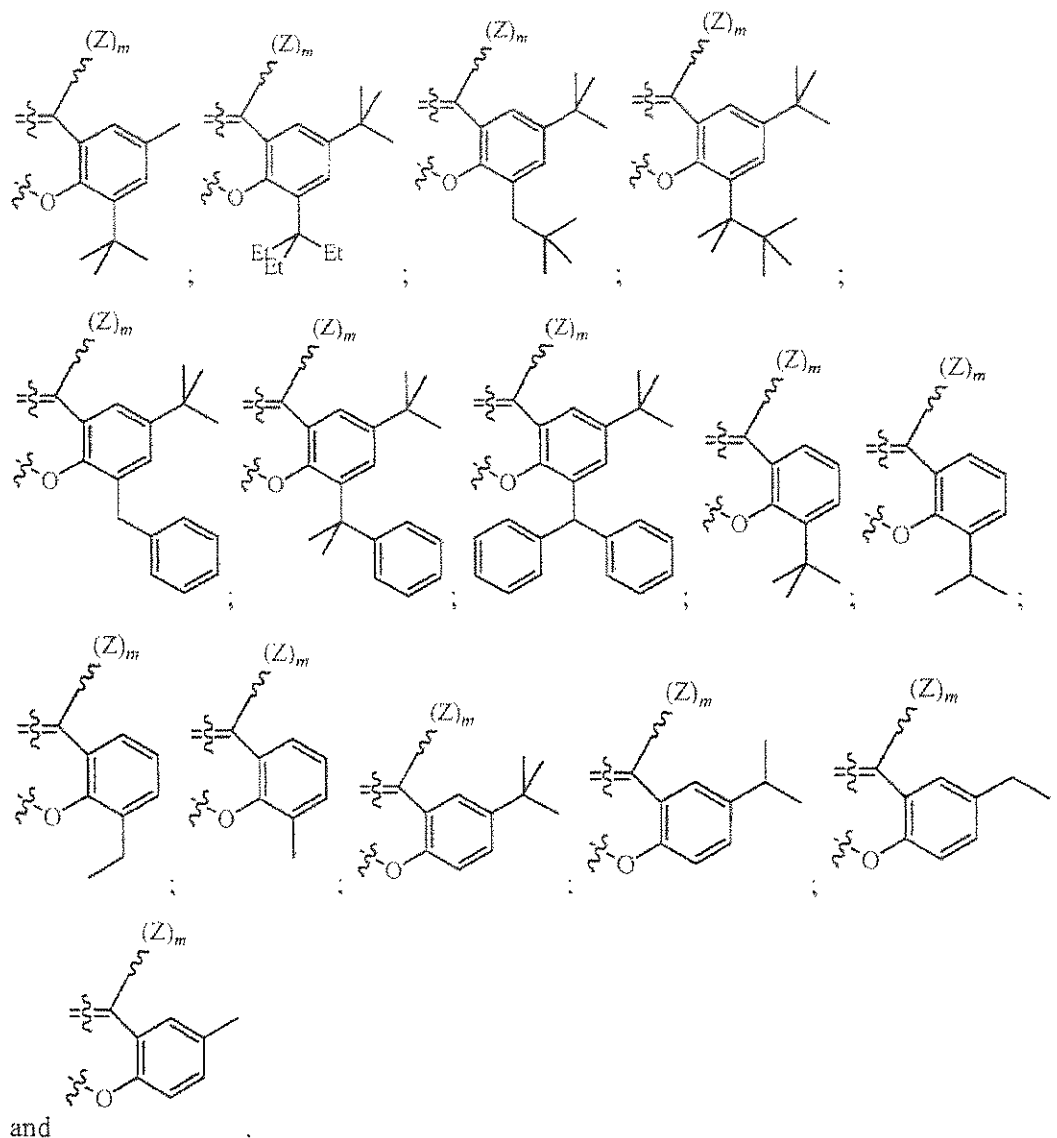


M, X, k, R^{4a} , $R^{4a'}$, R^{5a} , $R^{5a'}$, R^{6a} , $R^{6a'}$, R^{7a} , $R^{7a'}$, $\bigcirc$, and $\text{---}\text{---}\text{---}(Z)_m$ are as defined above with the proviso that the atom of the activating moiety attached to the salen ligand is a carbon atom.

- 5 In certain embodiments of compounds having formulae **IXa** or **IXb**, each R^{4a} , $R^{4a'}$, R^{6a} , and $R^{6a'}$ is hydrogen, and each R^{5a} , $R^{5a'}$, R^{7a} , and $R^{7a'}$ is, independently, hydrogen or optionally substituted C_1 - C_{20} aliphatic.

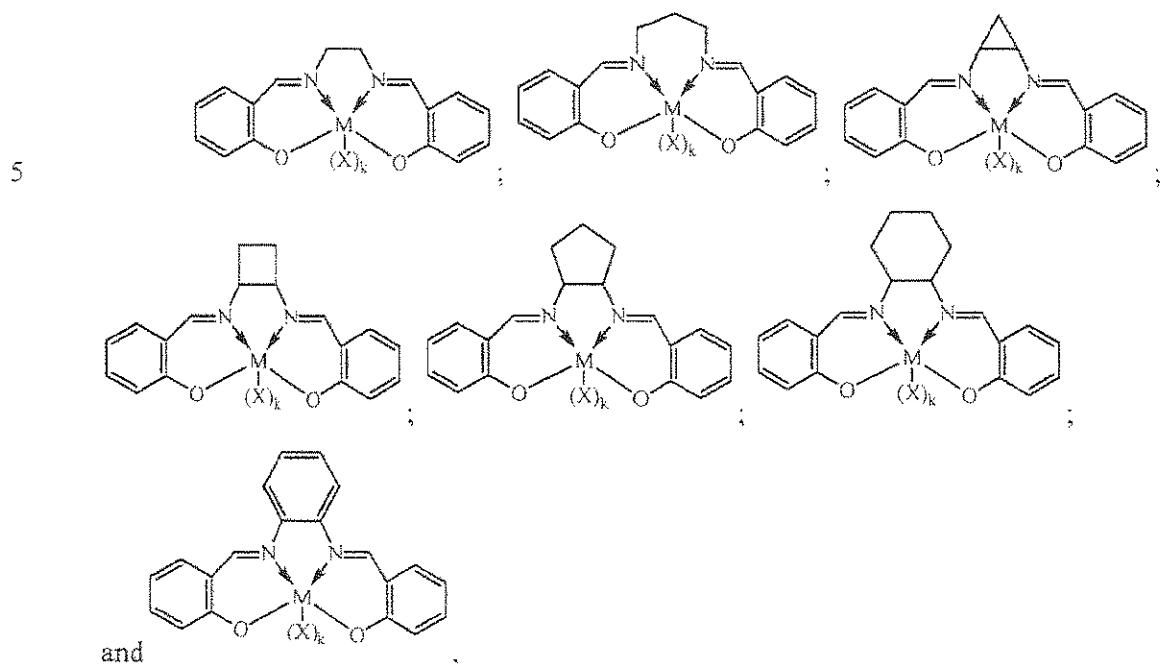
- 10 In certain embodiments of the present invention, metal complexes of structures **IXa** or **IXb** above, at least one of the phenyl rings comprising a salicylaldehyde-derived portion of a catalyst is independently selected from the group consisting of:





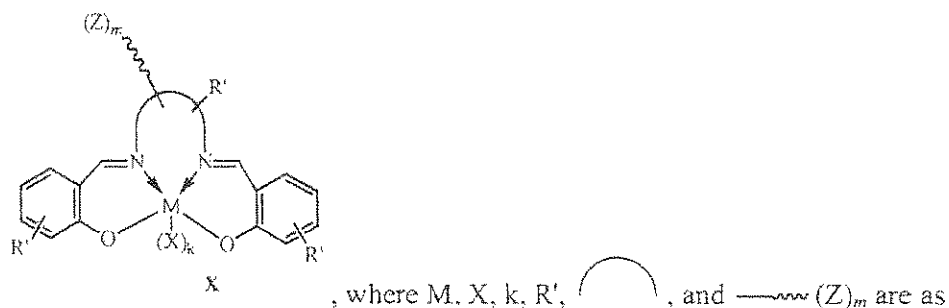
5 As shown above, the two phenyl rings derived from salicylaldehyde in the core
salen structures need not be the same. Though not explicitly shown in formulae **Ia**
through **IXb** above, it is to be understood that a catalyst may have an activating moiety
attached to different positions on each of the two rings, and such compounds are
specifically encompassed within the scope of the present invention. Furthermore,
10 activating moieties can be present on multiple parts of the ligand, for instance activating
moieties can be present on the diamine bridge and on one or both phenyl rings in the
same catalyst.

In certain embodiments, the salen ligand cores of catalysts **Ia** through **IXb** above are selected from the group shown below wherein any available position may be independently substituted with one or more R-groups or one or more activating moieties as described above.

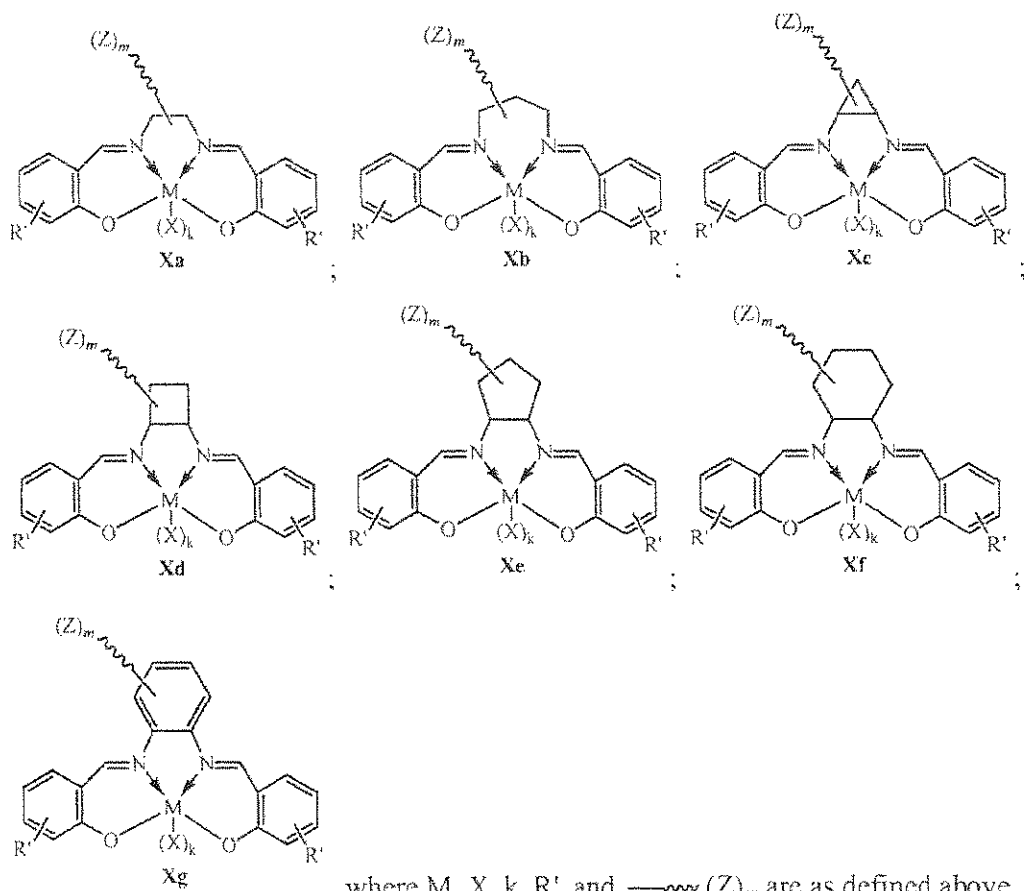


where M, X, and k, are as defined above.

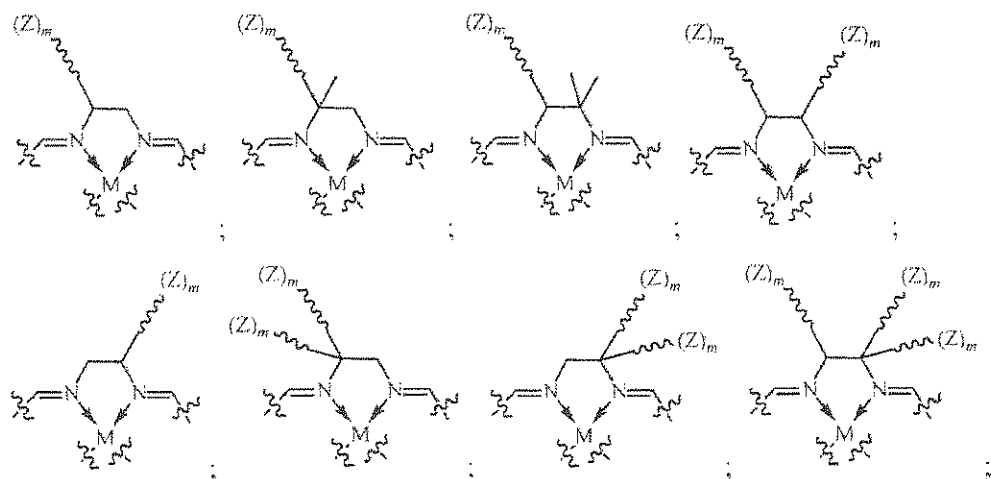
10 In some embodiments, at least one activating moiety is tethered to the diamine-derived portion of the salen ligand, as shown in formula X:

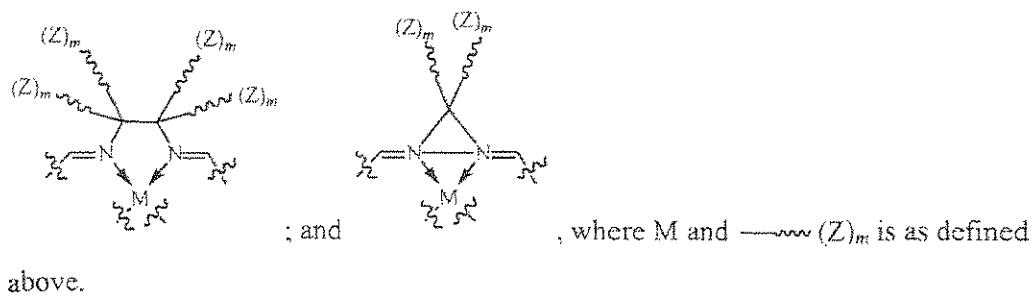


In certain embodiments, salen ligands of formula X are selected from an optionally substituted moiety consisting of:



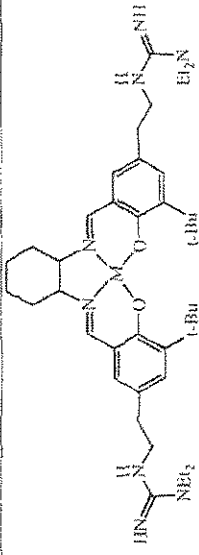
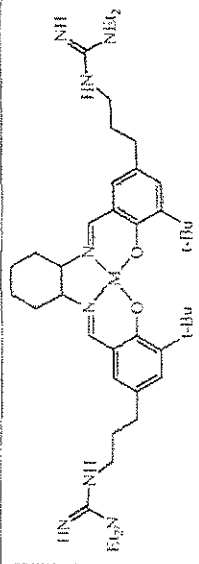
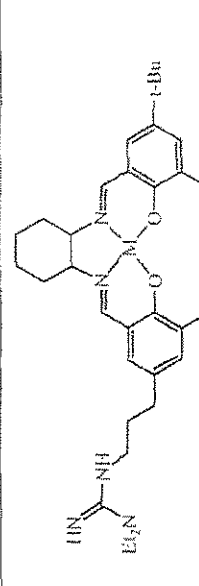
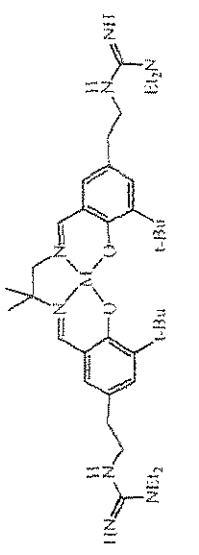
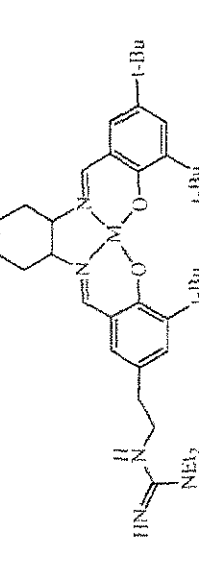
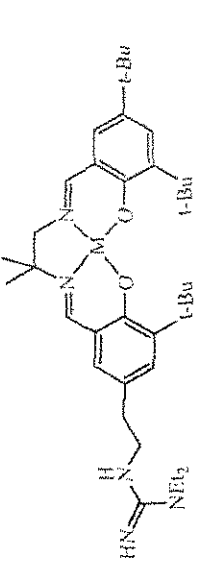
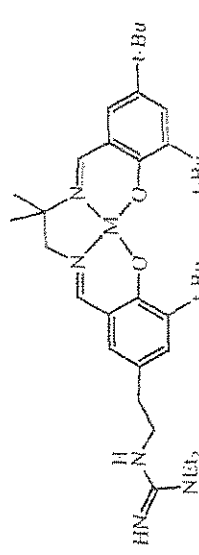
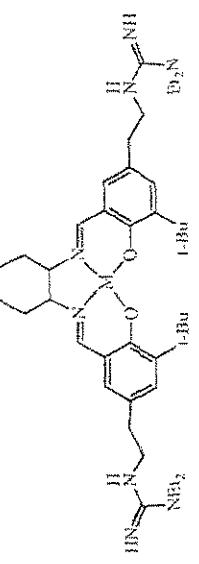
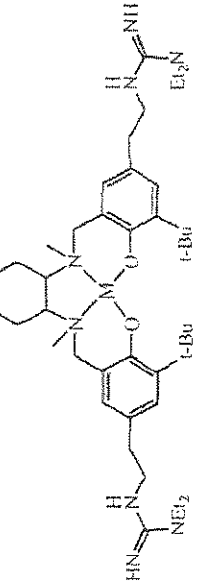
In certain embodiments, the diamine bridge of catalysts of formula **Xa** an optionally substituted moiety selected from the group consisting of:

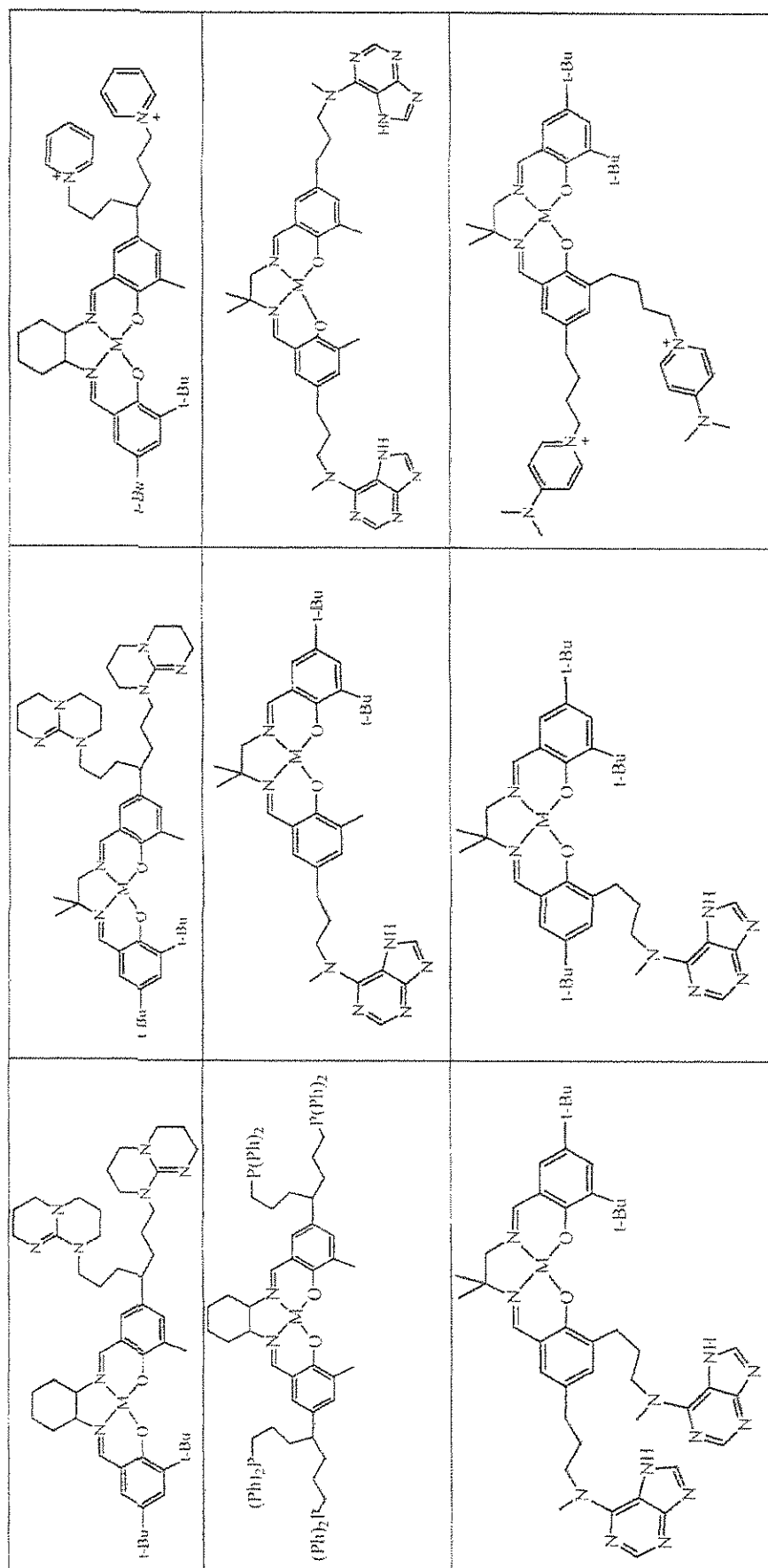


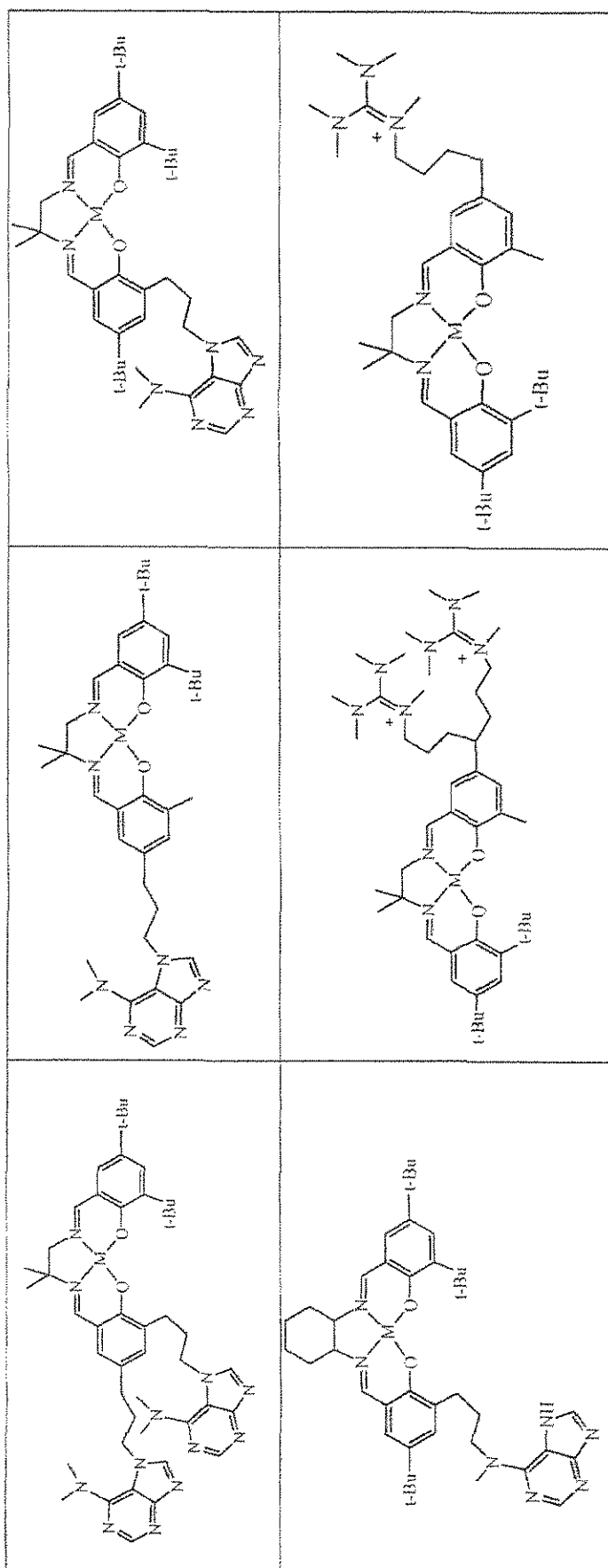


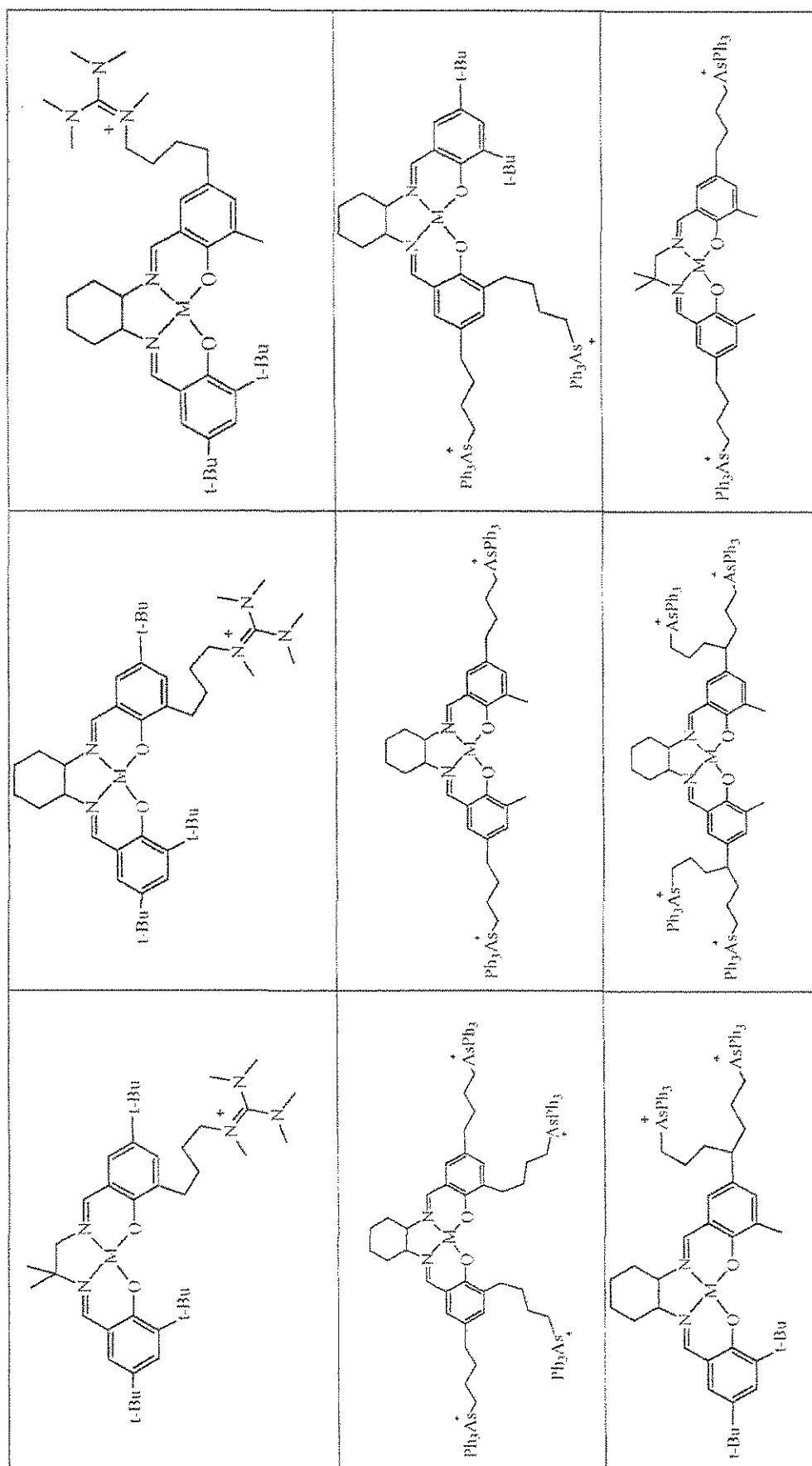
In certain embodiments, metallosalenate complexes of the present invention include, but are not limited to those in Table 1 below:

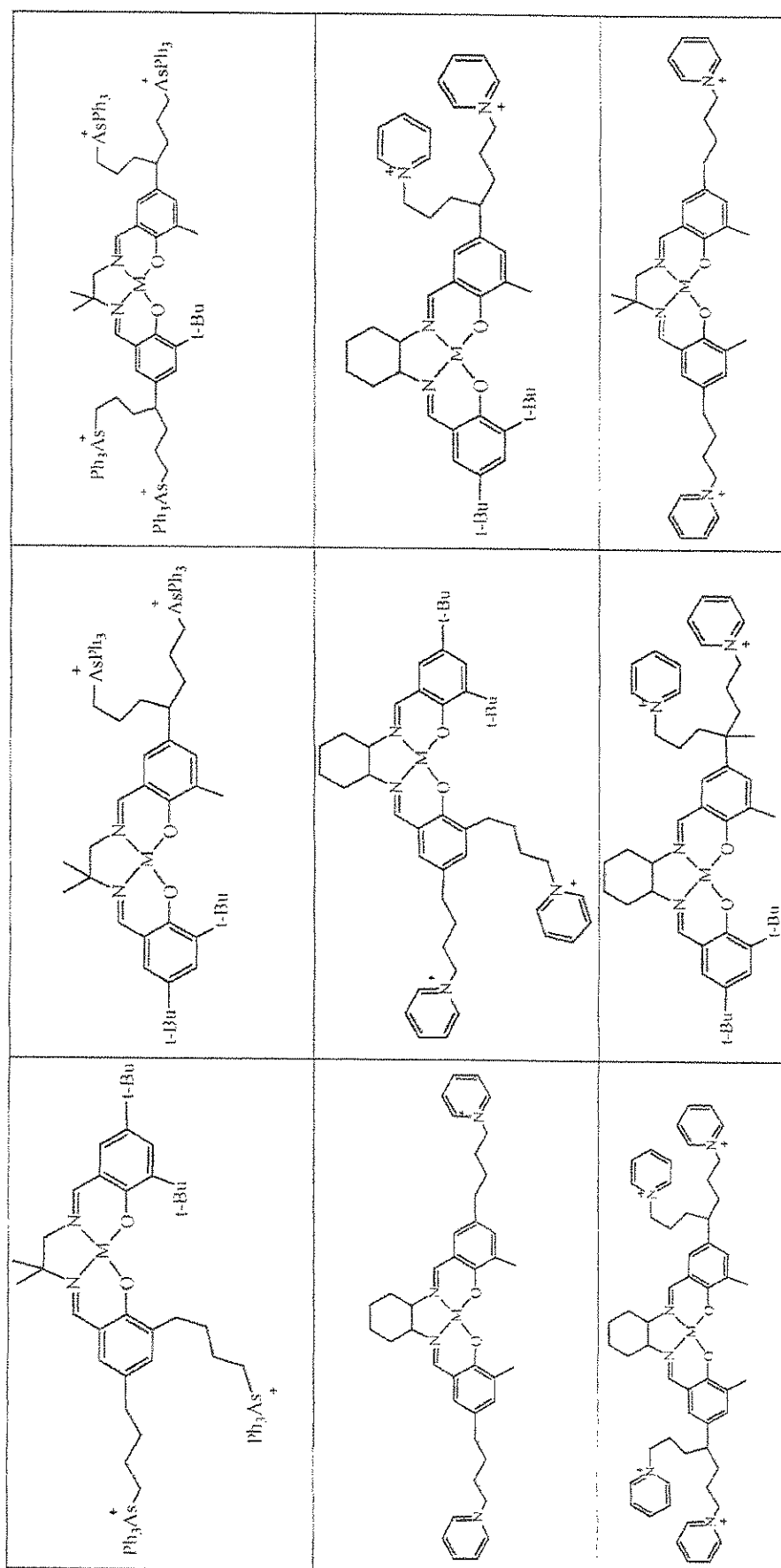
Table I

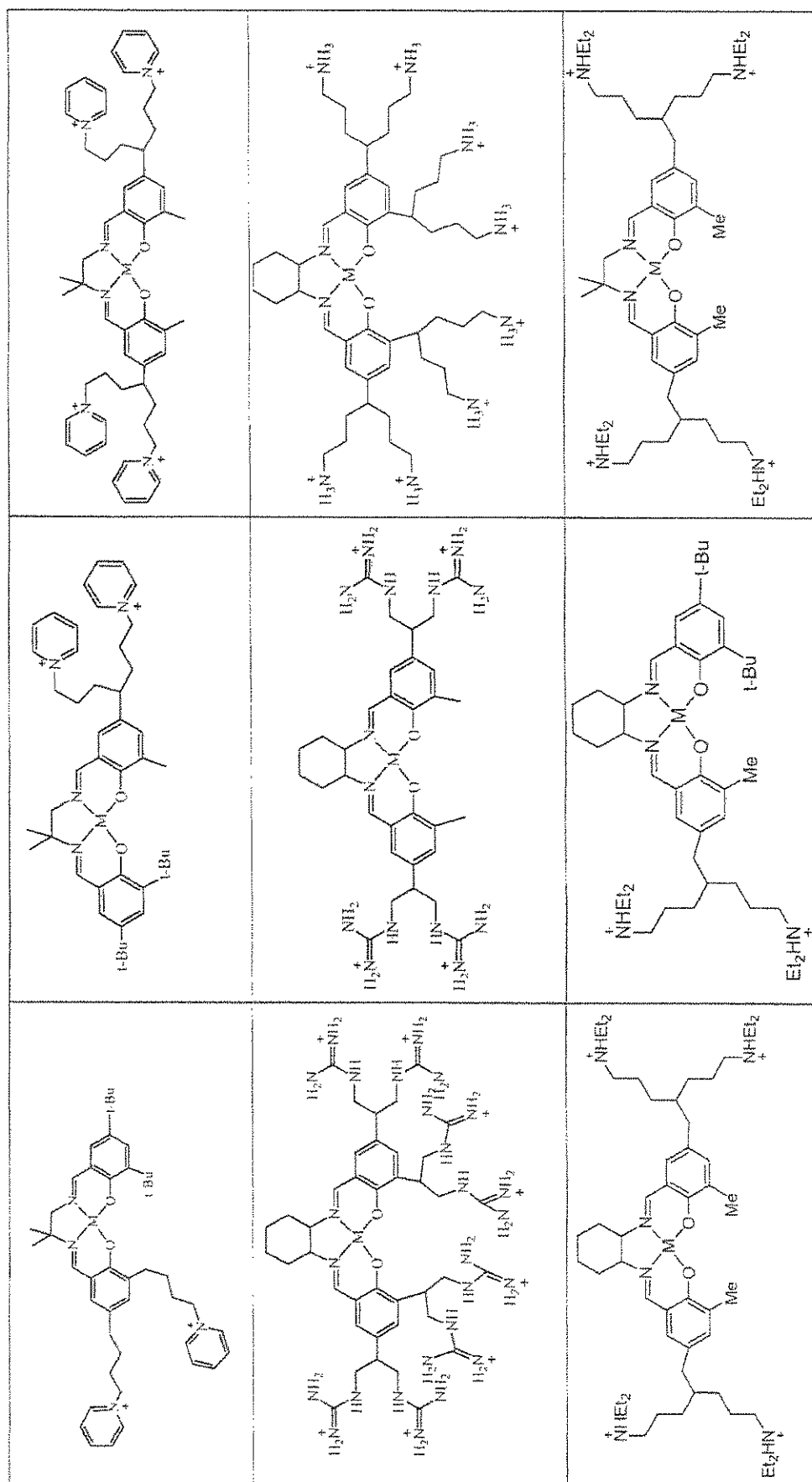
		
		
		

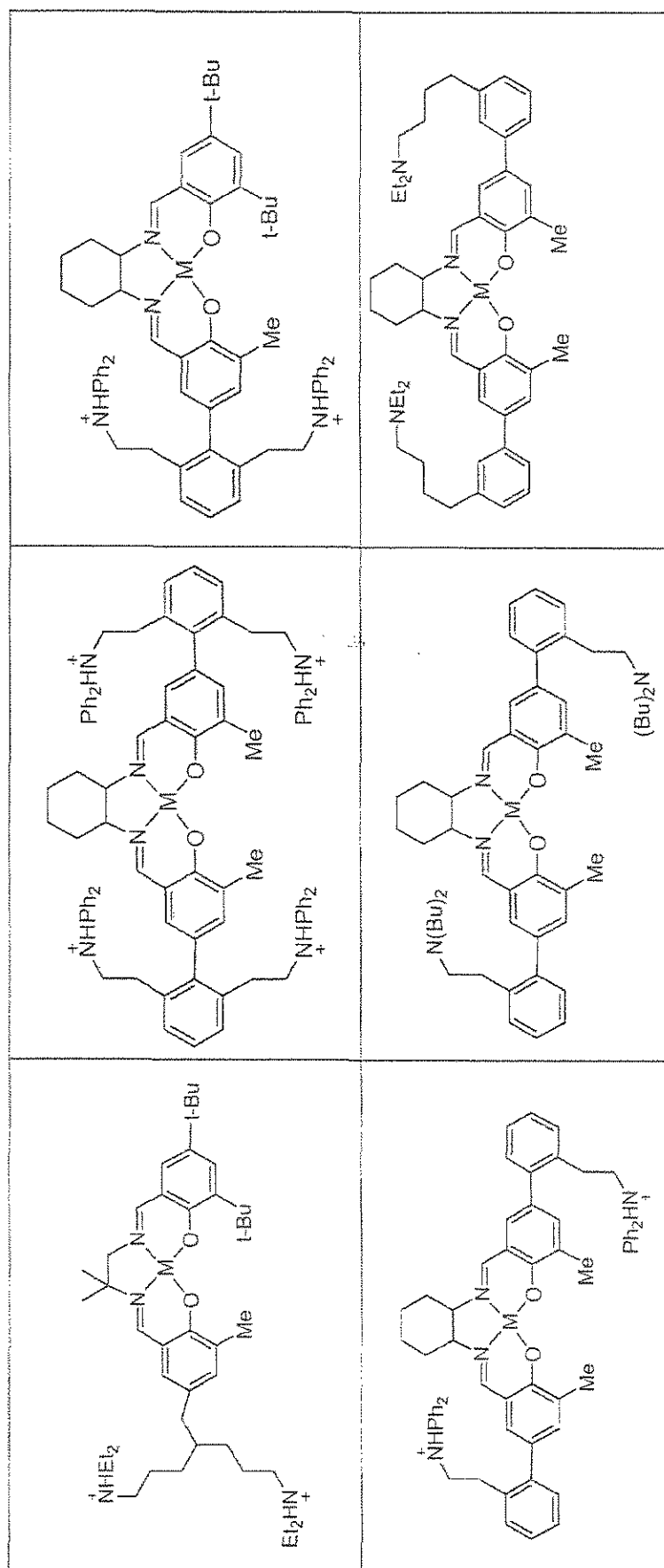


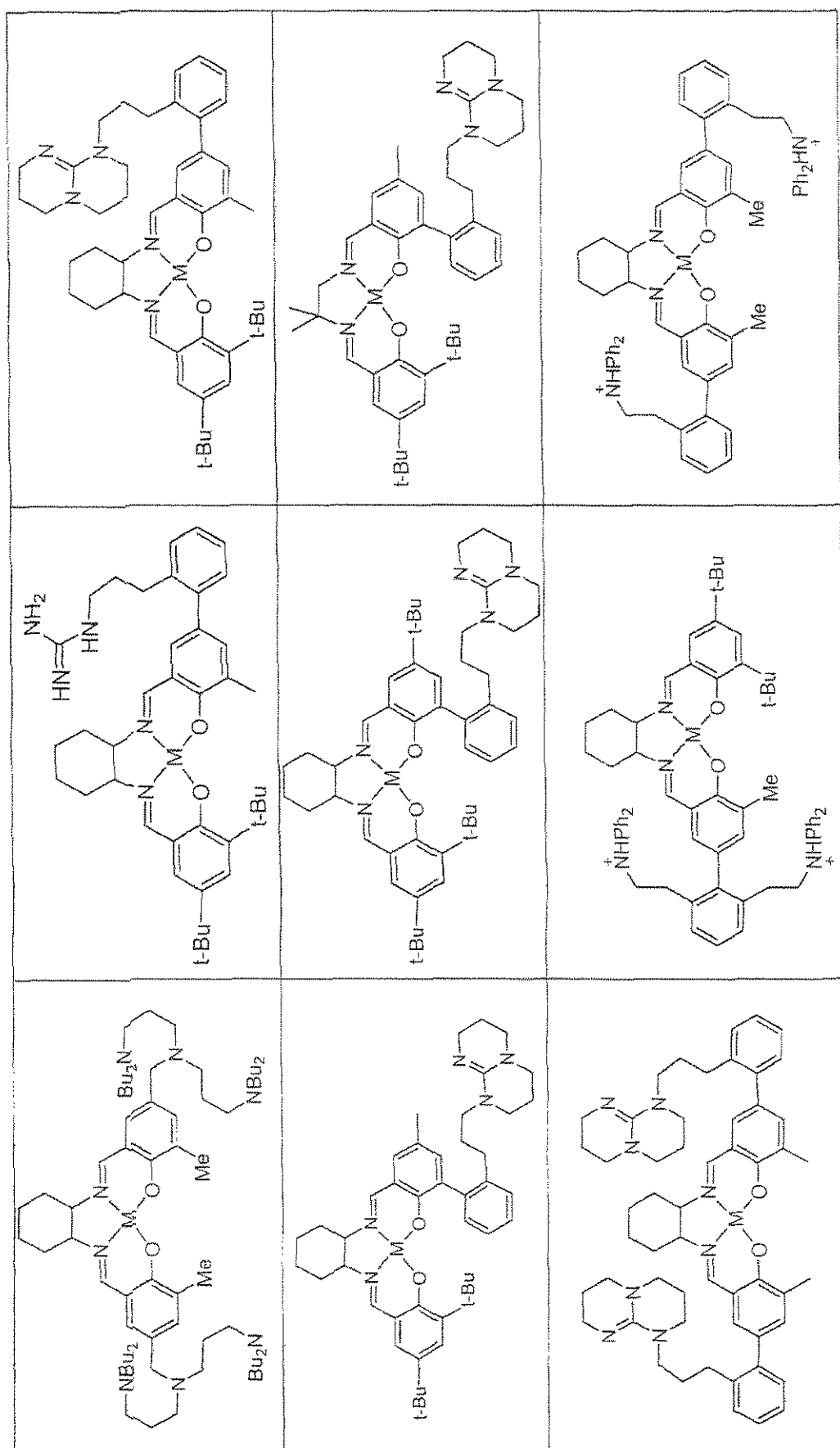


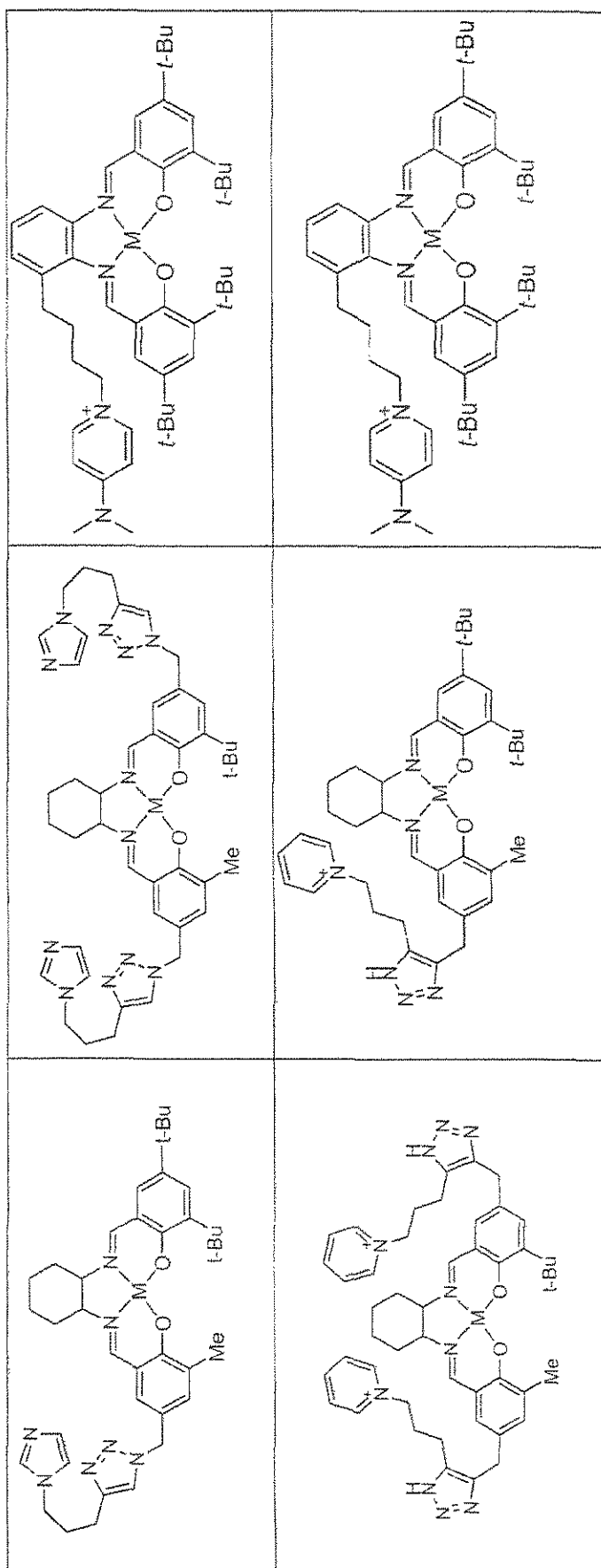


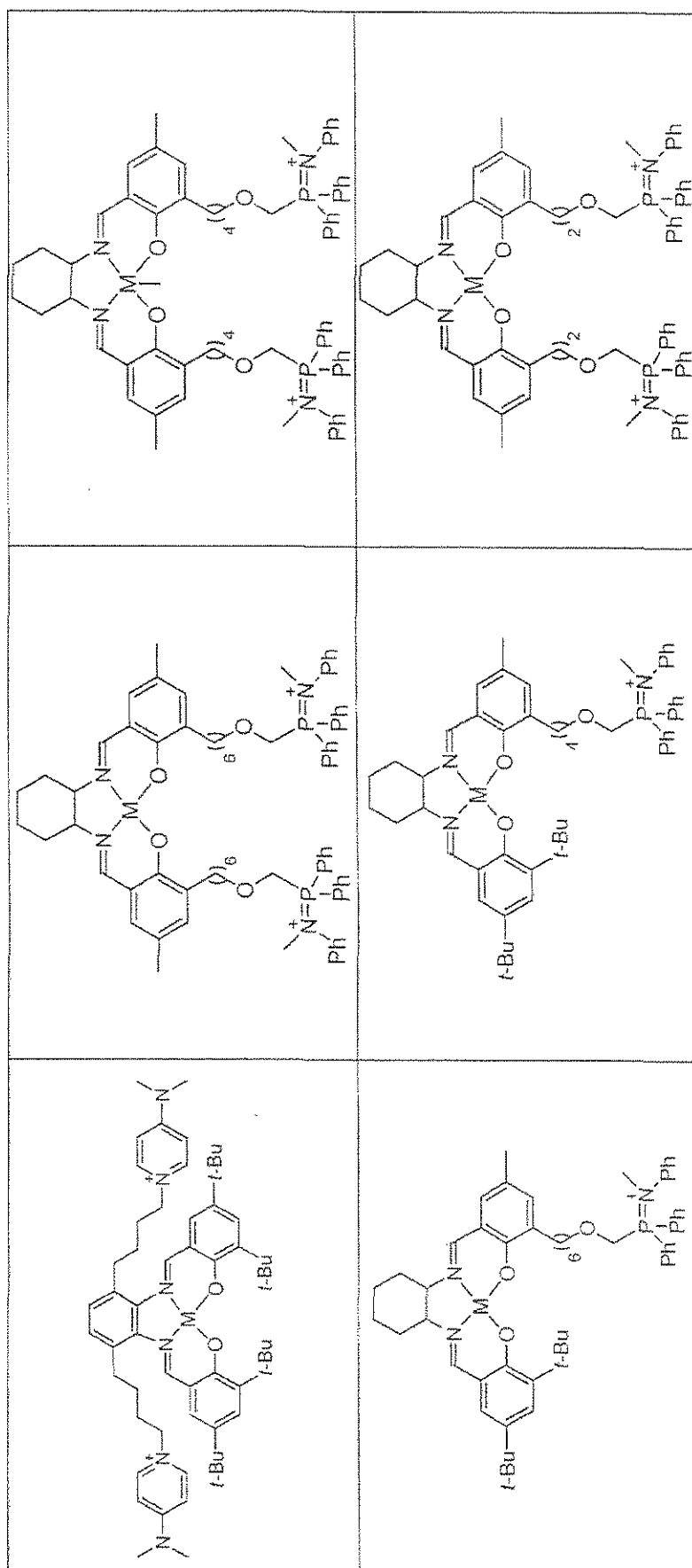


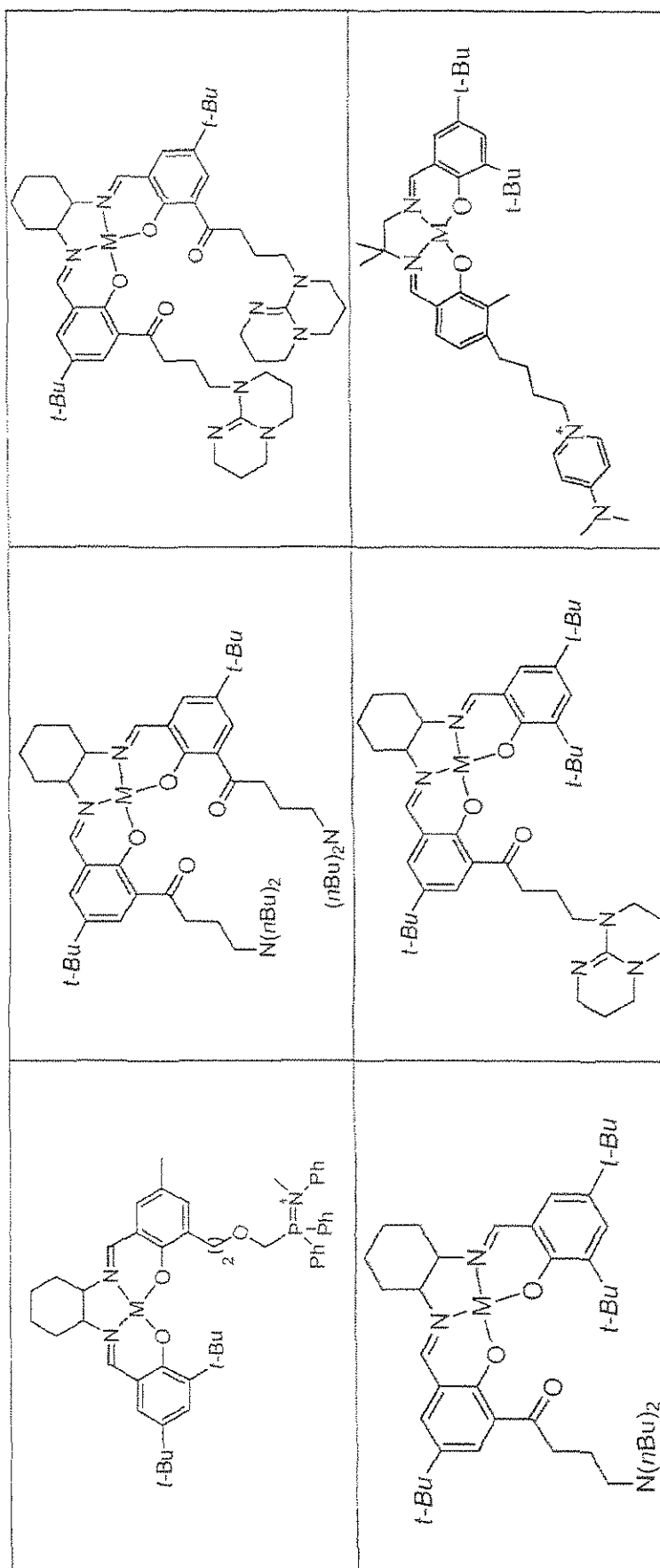


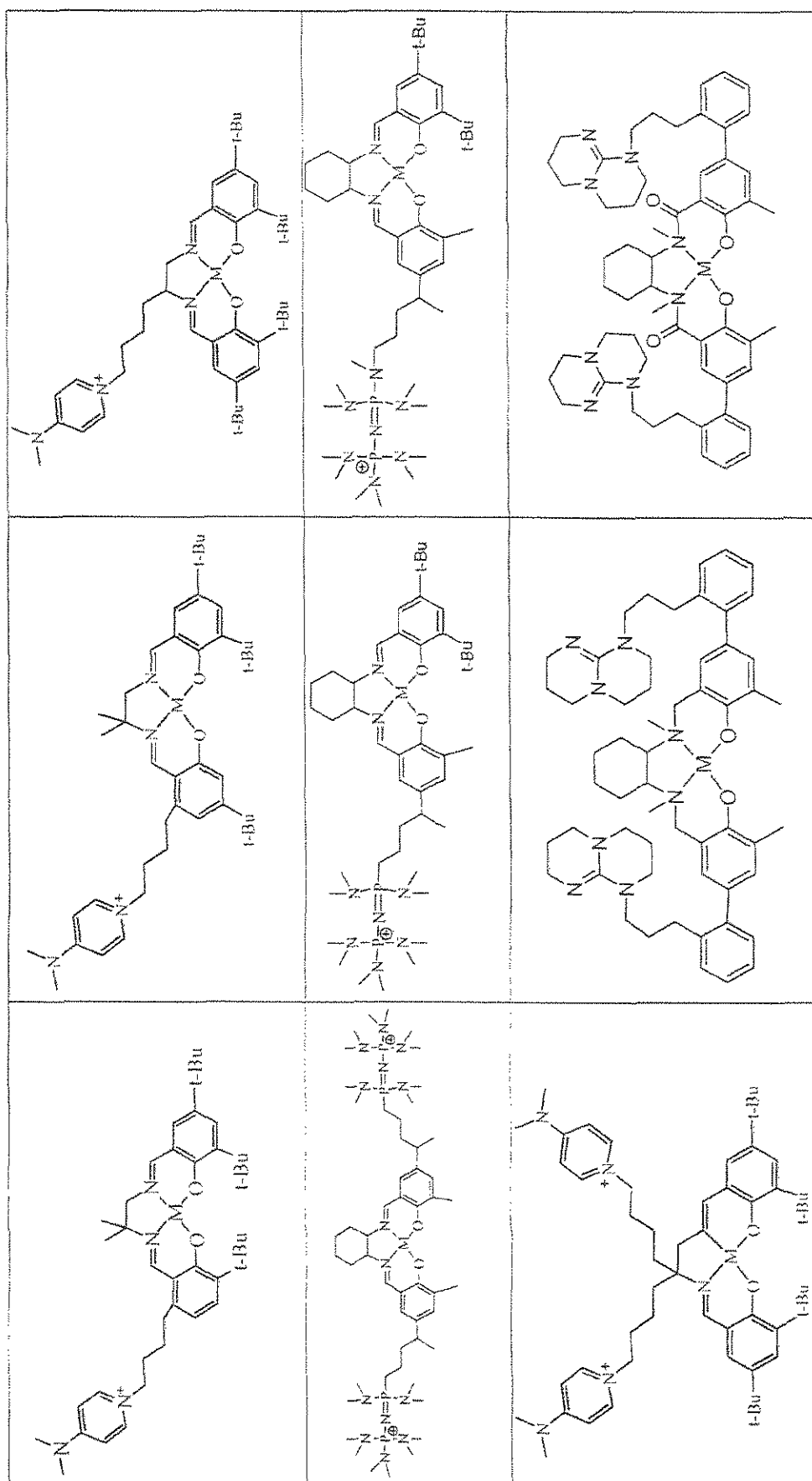










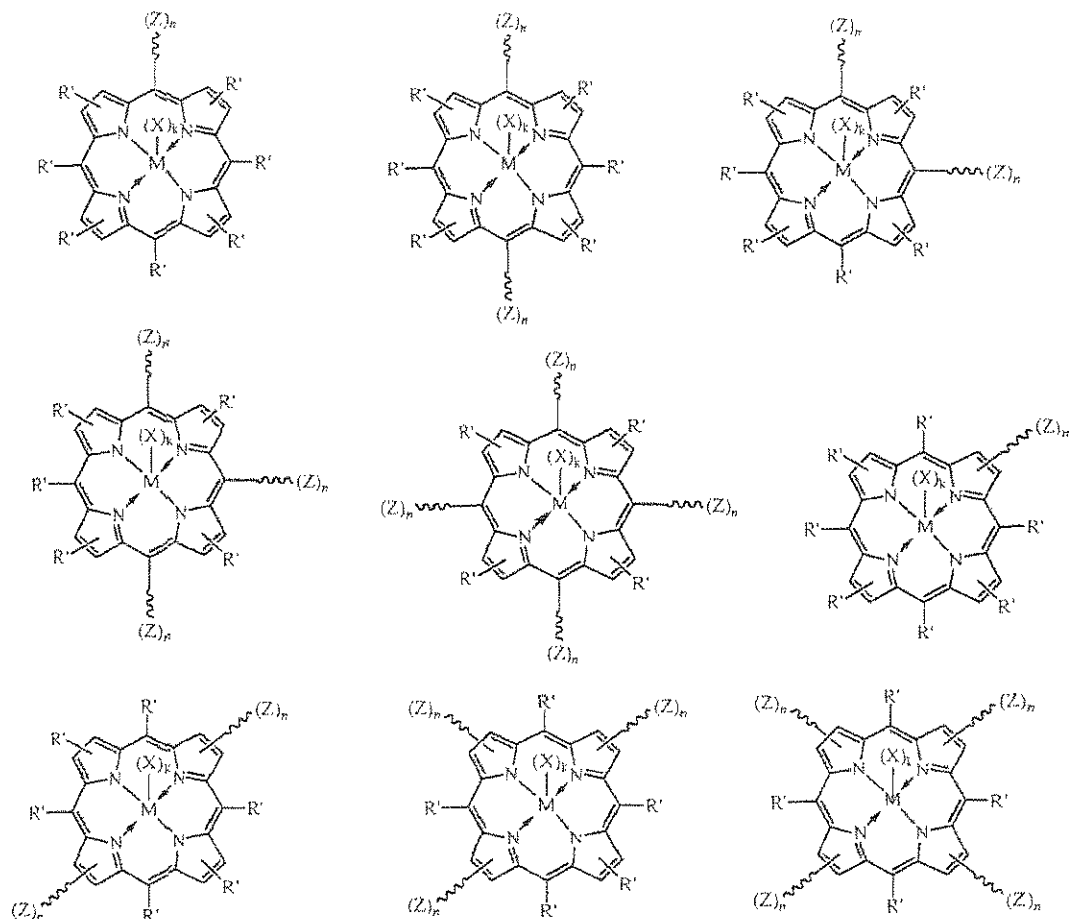


In certain embodiments, for complexes of Table 1, M is Co-X, where X is as defined above. In certain embodiments, for complexes of Table 1, M is Co-OC(O)CF₃. In certain embodiments, for complexes of Table 1, M is Co-OAc. In certain embodiments, for complexes of Table 1, M is Co-OC(O)C₆F₅. In certain embodiments, for complexes of Table 1, M is Co-N₃. In certain embodiments, for complexes of Table 1, M is Co-Cl. In certain embodiments, for complexes of Table 1, M is Co-nitrophenoxy. In certain embodiments, for complexes of Table 1, M is Co-dinitrophenoxy.

In some embodiments, for complexes of Table 1, M is Cr-X, where X is as defined above.

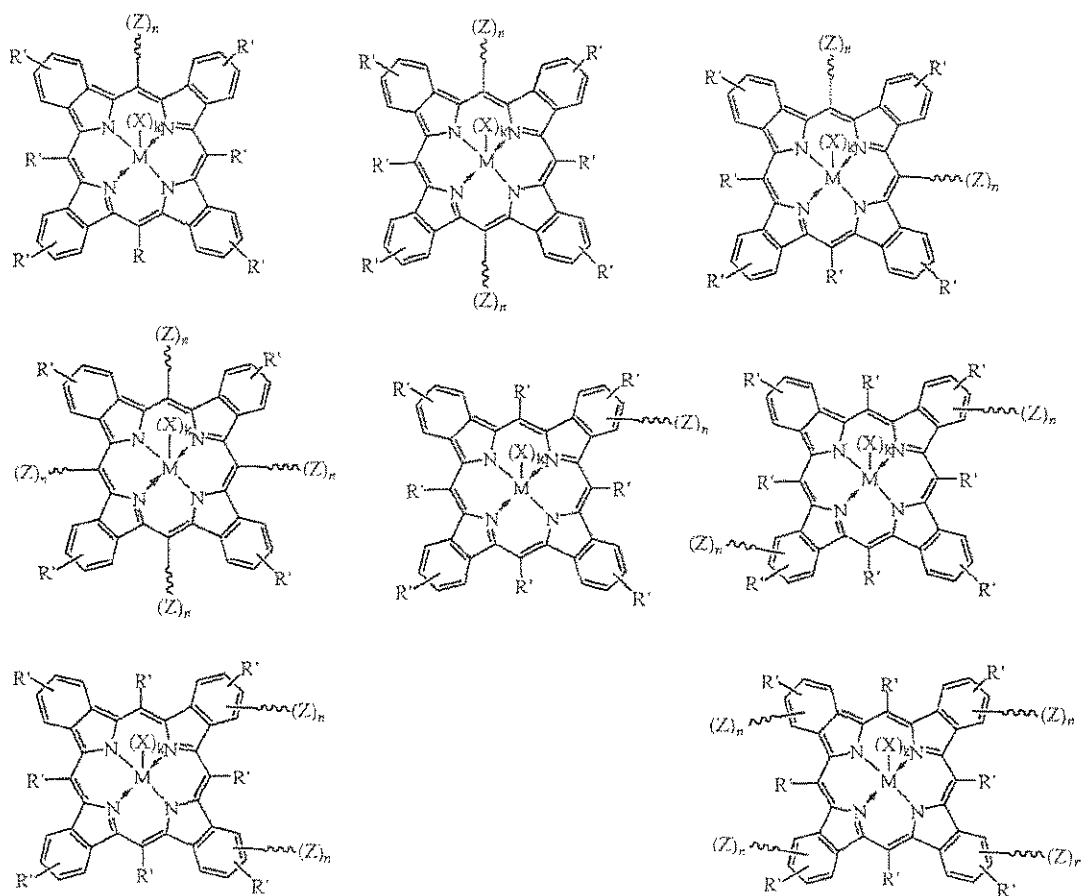
10 In certain embodiments, a tetradentate ligand is a porphyrin ligand. In some embodiments, a metal complex is a cobalt porphyrin complex. In certain embodiments, a metal complex is a chromium porphyrin complex. In some embodiments, a metal complex is an aluminum porphyrin complex.

Examples of porphyrin containing metal complexes of the present invention include, but are not limited to:



wherein each of M, X, k, R', and $\text{---}(Z)_n$ is as defined above.

5 In certain embodiments, a multidentate ligand is an optionally substituted tetrabenzoporphyrin. Suitable examples include, but are not limited to:

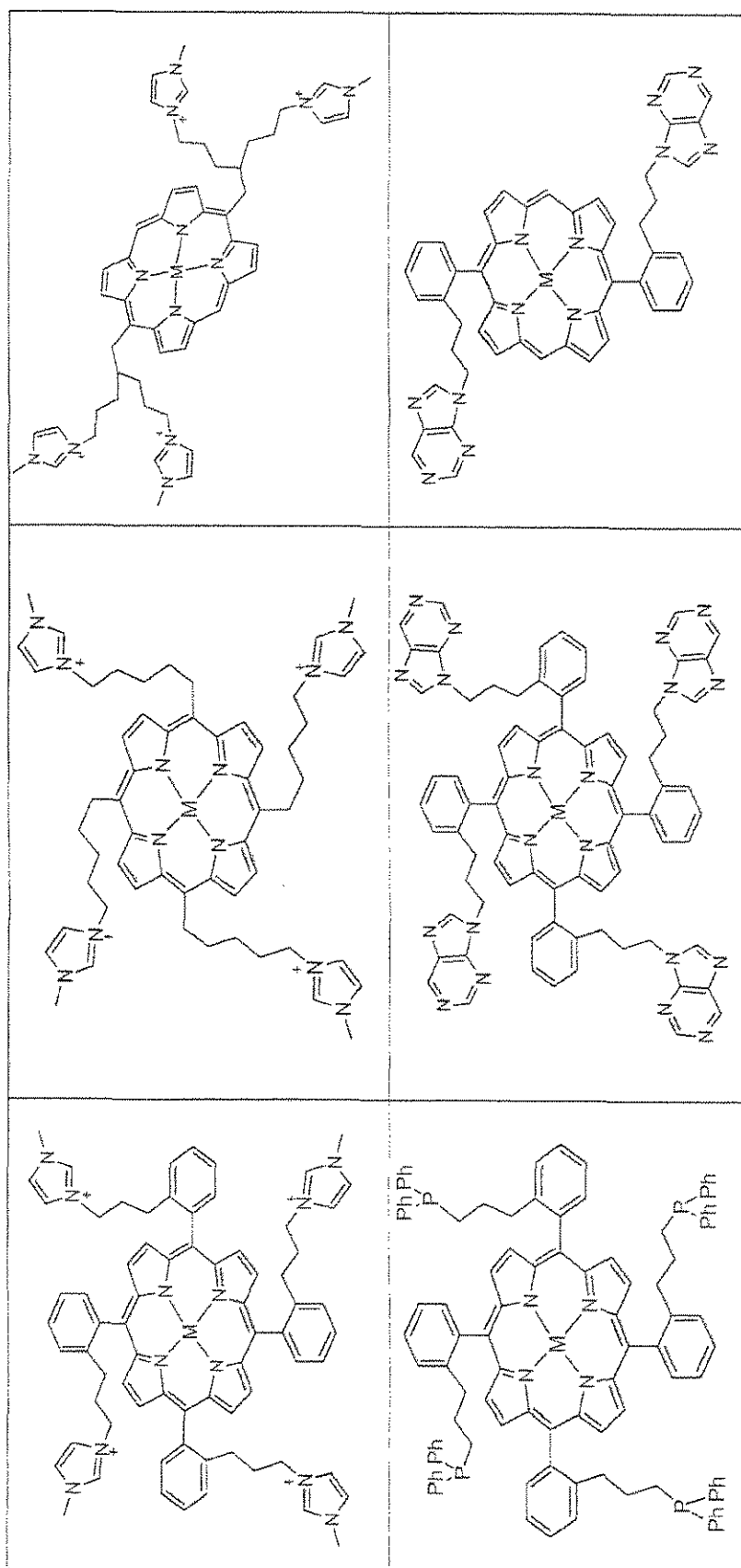


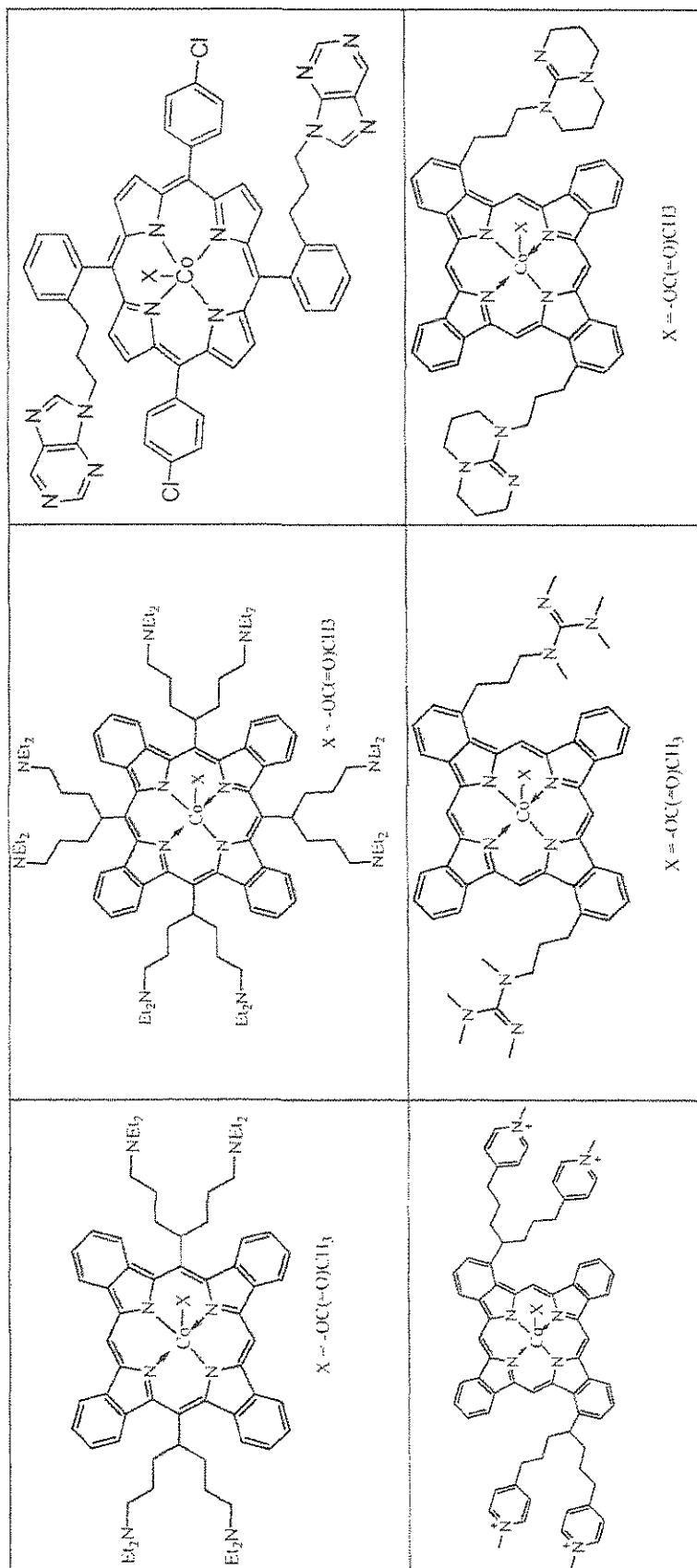
wherein M , R' , and $\text{---}(Z)_n$ are as previously defined.

In certain embodiments of porphyrin and phthalocyanine-based complexes described herein, M is aluminum. In certain embodiments of porphyrin and phthalocyanine-based complexes described herein, M is cobalt. In certain embodiments of porphyrin and phthalocyanine-based complexes described herein, M is manganese.

In certain embodiments, porphyrin complexes of the present invention include, but are not limited to those in Table 2 below:

Table 2

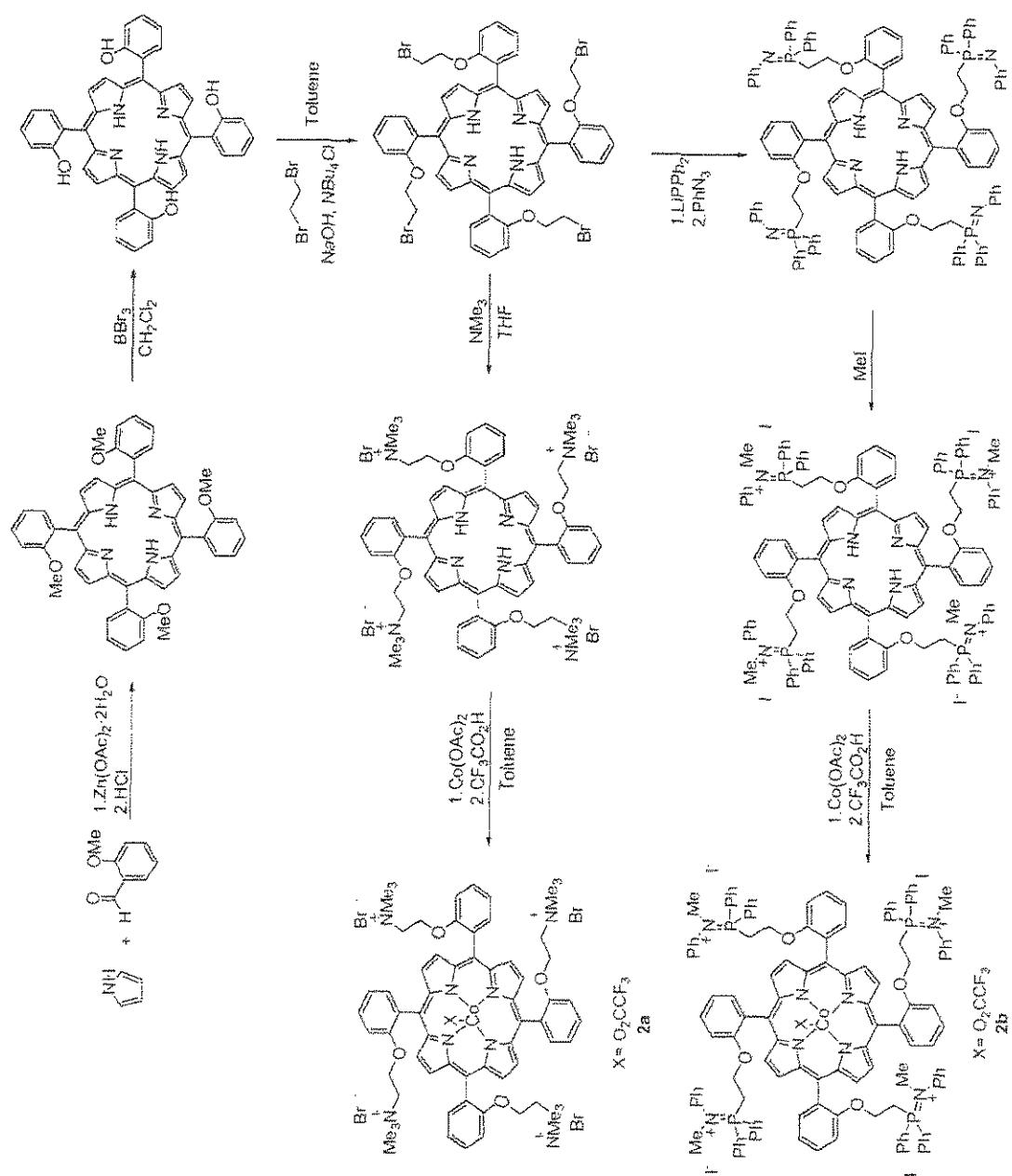


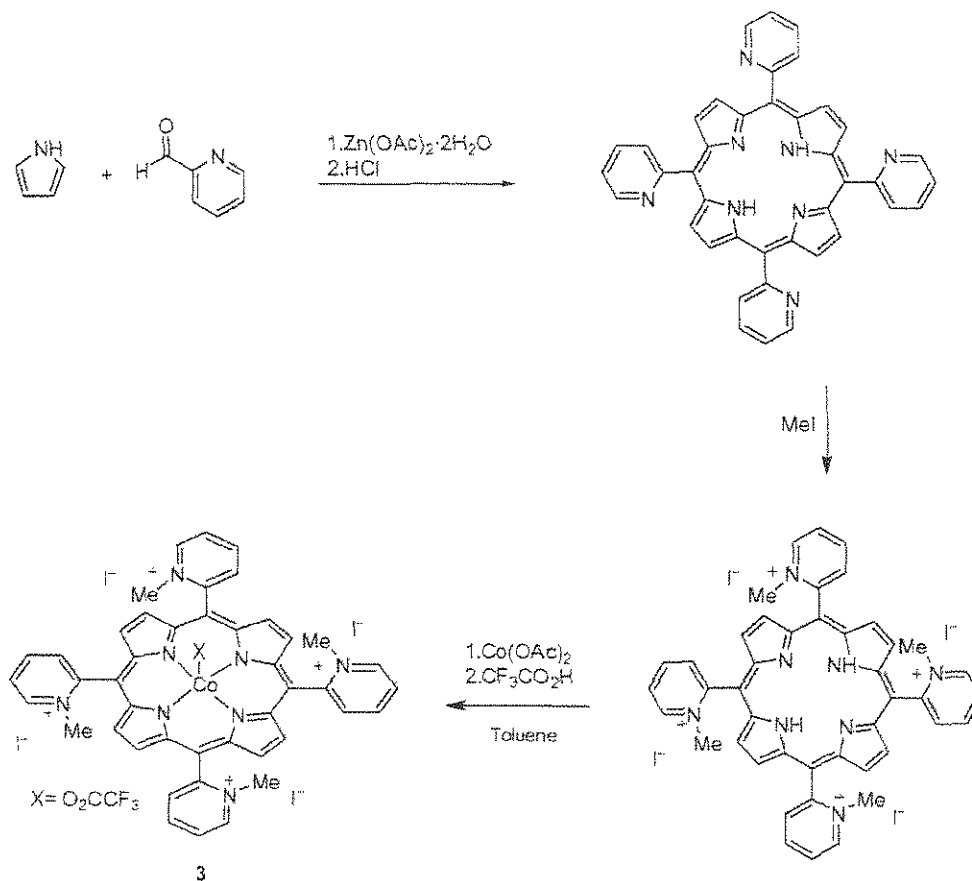


In certain embodiments, for complexes of Table 2, M is Co-X, where X is as defined above. In certain embodiments, for complexes of Table 2, M is Co-OC(O)CF₃. In certain embodiments, for complexes of Table 2, M is Co-OAc. In certain embodiments, for complexes of Table 1, M is Co-OC(O)C₆F₅. In certain embodiments, for complexes of Table 2, M is Co-N₃. In certain embodiments, for complexes of Table 2, M is Co-Cl. In certain embodiments, for complexes of Table 2, M is Co-nitrophenoxy. In certain embodiments, for complexes of Table 2, M is Co-dinitrophenoxy.

In certain embodiments, for complexes of Table 2, M is Al-X, where X is as defined above. In certain embodiments, for complexes of Table 2, M is Cr-X, where X is as defined above.

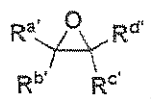
In certain embodiments, porphyrin complexes of the present invention are synthesized as shown in the following schemes:





In some embodiments, the present disclosure provides methods of polymerization comprising contacting an epoxide with carbon dioxide in the presence of a provided metal complex to form a polycarbonate. In some embodiments, the present invention provides a method of polymerization, the method comprising:

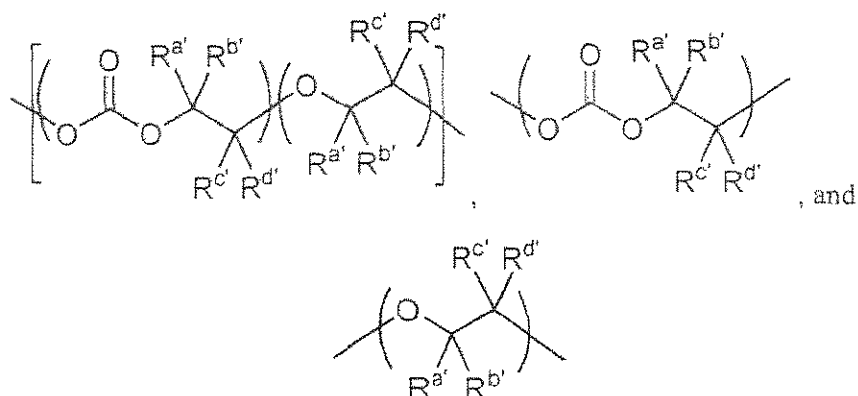
a) providing an epoxide of formula:



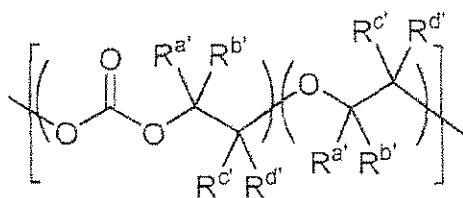
wherein:

$\text{R}^{\text{a}'}$ is hydrogen or an optionally substituted radical selected from the group consisting of C_{1-30} aliphatic; C_{1-30} heteroaliphatic; phenyl; a 3- to 8-membered

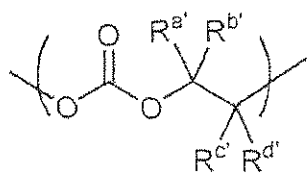
- 5 saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; and
- 10 each of $R^{b'}$, $R^{c'}$, and $R^{d'}$ is independently hydrogen or an optionally substituted radical selected from the group consisting of C_{1-12} aliphatic; C_{1-12} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur;
- 15 wherein any of ($R^{a'}$ and $R^{c'}$), ($R^{c'}$ and $R^{d'}$), and ($R^{a'}$ and $R^{b'}$) can be taken together with intervening atoms to form one or more optionally substituted rings;
- 20 b) contacting the epoxide and carbon dioxide in the presence of a metal complex as described herein to provide a polymer having a formula selected from the group consisting of:
- 25



In some embodiments, a provided polymer has a formula:

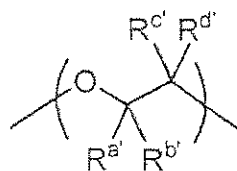


. In some embodiments, a provided polymer has a



5 formula:

. In some embodiments, carbon dioxide is optional



and a provided polymer has a formula:

In certain embodiments, $\text{R}^{\text{b}'}$, $\text{R}^{\text{c}'}$, and $\text{R}^{\text{d}'}$ are each hydrogen. In some
embodiments, $\text{R}^{\text{a}'}$ is optionally substituted C_{1-12} aliphatic. In some embodiments, $\text{R}^{\text{a}'}$ is
optionally substituted C_{1-12} heteroaliphatic. In some embodiments, the epoxide is
10 ethylene oxide, propylene oxide, or cyclohexene oxide.

In certain embodiments, one of $\text{R}^{\text{a}'}$, $\text{R}^{\text{b}'}$, $\text{R}^{\text{c}'}$, and $\text{R}^{\text{d}'}$ is hydrogen. In certain
embodiments, two of $\text{R}^{\text{a}'}$, $\text{R}^{\text{b}'}$, $\text{R}^{\text{c}'}$, and $\text{R}^{\text{d}'}$ are hydrogen. In certain embodiments, three of
 $\text{R}^{\text{a}'}$, $\text{R}^{\text{b}'}$, $\text{R}^{\text{c}'}$, and $\text{R}^{\text{d}'}$ are hydrogen.

In certain embodiments, R^{a'} is hydrogen. In certain embodiments, R^{b'} is hydrogen. In certain embodiments, R^{c'} is hydrogen. In certain embodiments, R^{d'} is hydrogen.

5 In certain embodiments, R^{a'}, R^{b'}, R^{c'}, and R^{d'} are each independently an optionally substituted C₁₋₃₀ aliphatic group. In certain embodiments, R^{a'}, R^{b'}, R^{c'}, and R^{d'} are each independently an optionally substituted C₁₋₂₀ aliphatic group. In certain embodiments, R^{a'}, R^{b'}, R^{c'}, and R^{d'} are each independently an optionally substituted C₁₋₁₂ aliphatic group. In certain embodiments, R^{a'}, R^{b'}, R^{c'}, and R^{d'} are each independently an optionally substituted C₁₋₈ aliphatic group. In certain embodiments, R^{a'}, R^{b'}, R^{c'}, and R^{d'} are each independently an optionally substituted C₃₋₈ aliphatic group. In certain embodiments, R^{a'}, R^{b'}, R^{c'}, and R^{d'} are each independently an optionally substituted C₃₋₁₂ aliphatic group.

15 In certain embodiments, R^{a'} is an optionally substituted C₁₋₃₀ aliphatic group. In certain embodiments, R^{b'} is an optionally substituted C₁₋₃₀ aliphatic group. In certain embodiments, R^{c'} is an optionally substituted C₁₋₃₀ aliphatic group. In certain embodiments, R^{d'} is an optionally substituted C₁₋₃₀ aliphatic group.

20 In some embodiments, an R^{a'} and an R^{b'} attached to the same carbon are taken together to form one or more optionally substituted 3-12-membered carbocyclic rings. In some embodiments, an R^{a'} and an R^{b'} attached to the same carbon are taken together to form a polycyclic carbocycle comprising two or more optionally substituted 3-8-membered carbocyclic rings. In some embodiments, an R^{a'} and an R^{b'} attached to the same carbon are taken together to form a polycyclic carbocycle comprising two or more optionally substituted 5-7-membered carbocyclic rings.

25 In some embodiments, an R^{a'} and an R^{b'} attached to the same carbon are taken together to form a bicyclic carbocycle comprising two optionally substituted 3-12-membered carbocyclic rings. In some embodiments, an R^{a'} and an R^{b'} attached to the same carbon are taken together to form a bicyclic carbocycle comprising two optionally substituted 3-8-membered carbocyclic rings. In some embodiments, an R^{a'} and an R^{b'} attached to the same carbon are taken together to form a bicyclic carbocycle comprising two optionally substituted 5-7-membered carbocyclic rings.

In certain embodiments, an $R^{a'}$ and an $R^{b'}$ attached to the same carbon are taken together to form an optionally substituted 3-12-membered carbocyclic ring. In certain embodiments, an $R^{a'}$ and an $R^{b'}$ attached to the same carbon are taken together to form an optionally substituted 3-8-membered carbocyclic ring. In certain embodiments,
5 an $R^{a'}$ and an $R^{b'}$ attached to the same carbon are taken together to form an optionally substituted 5-7-membered carbocyclic ring.

In some embodiments, an $R^{b'}$ and an $R^{c'}$ attached to adjacent carbons are taken together to form one or more optionally substituted 3-12-membered carbocyclic rings. In some embodiments, an $R^{b'}$ and an $R^{c'}$ attached to adjacent carbons are taken
10 together to form a polycyclic carbocycle comprising two or more optionally substituted 3-8-membered carbocyclic rings. In some embodiments, an $R^{b'}$ and an $R^{c'}$ attached to adjacent carbons are taken together to form a polycyclic carbocycle comprising two or more optionally substituted 5-7-membered carbocyclic rings.

In some embodiments, an $R^{b'}$ and an $R^{c'}$ attached to adjacent carbons are taken together to form a bicyclic carbocycle comprising two optionally substituted 3-12-membered carbocyclic rings. In some embodiments, an $R^{b'}$ and an $R^{c'}$ attached to adjacent carbons are taken together to form a bicyclic carbocycle comprising two optionally substituted 3-8-membered carbocyclic rings. In some embodiments, an $R^{b'}$ and an $R^{c'}$ attached to adjacent carbons are taken together to form a bicyclic carbocycle
15 comprising two optionally substituted 5-7-membered carbocyclic rings.
20

In certain embodiments, an $R^{b'}$ and an $R^{c'}$ attached to adjacent carbons are taken together to form an optionally substituted 3-12-membered carbocyclic ring. In certain embodiments, an $R^{b'}$ and an $R^{c'}$ attached to adjacent carbons are taken together to form an optionally substituted 3-8-membered carbocyclic ring. In certain embodiments, an $R^{b'}$ and an $R^{c'}$ attached to adjacent carbons are taken together to form an optionally substituted 5-7-membered carbocyclic ring.
25

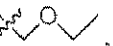
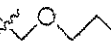
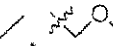
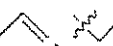
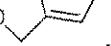
In certain embodiments, the polymer comprises a copolymer of two different repeating units where $R^{a'}$, $R^{b'}$, and $R^{c'}$ of the two different repeating units are not all the same. In some embodiments, a polymer comprises a copolymer of three or more
30 different repeating units wherein $R^{a'}$, $R^{b'}$, and $R^{c'}$ of each of the different repeating units

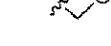
are not all the same as R^a , R^b , and R^c of any of the other different repeating units. In some embodiments, a polymer is a random copolymer. In some embodiments, a polymer is a tapered copolymer.

In some embodiments, a polymer contains a metal complex as described herein.
 5 In some embodiments, a polymer comprises residue of a metal complex as described herein. In some embodiments, a polymer comprises a salt of an organic cation and X, wherein X is a nucleophile or counterion. In some embodiments, X is 2,4-dinitrophenolate anion.

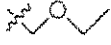
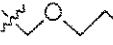
In some embodiments, R^a is optionally substituted C_{1-12} aliphatic. In
 10 some embodiments, R^a is optionally substituted C_{1-12} heteroaliphatic. In some embodiments, R^a is optionally substituted phenyl. In some embodiments, R^a is optionally substituted 8- to 10-membered aryl. In some embodiments, R^a is optionally substituted 5- to 10-membered heteroaryl. In some embodiments, R^a is optionally substituted 3- to 7-membered heterocyclic.

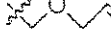
15 In certain embodiments, R^a is selected from methyl, ethyl, propyl, butyl, vinyl,

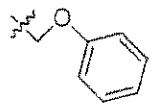
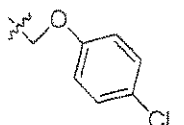
allyl, phenyl, trifluoromethyl, , , , , ,

, , , or any two or more of the above. In certain

embodiments, R^a is methyl. In certain embodiments, R^a is ethyl. In certain
 20 embodiments, R^a is propyl. In certain embodiments, R^a is butyl. In certain
 embodiments, R^a is vinyl. In certain embodiments, R^a is allyl. In certain embodiments,
 R^a is phenyl. In certain embodiments, R^a is trifluoromethyl. In certain embodiments,

R^a is . In certain embodiments, R^a is . In certain embodiments,

R^a is . In certain embodiments, R^a is . In certain embodiments,

$R^{a'}$ is . In certain embodiments, $R^{a'}$ is . In certain


 embodiments, $R^{a'}$ is

In some embodiments, $R^{b'}$ is hydrogen. In some embodiments, $R^{b'}$ is optionally substituted C_{1-12} aliphatic. In some embodiments, $R^{b'}$ is optionally substituted C_{1-12} heteroaliphatic. In some embodiments, $R^{b'}$ is optionally substituted phenyl. In some
 5 embodiments, $R^{b'}$ is optionally substituted 8- to 10-membered aryl. In some
 embodiments, $R^{b'}$ is optionally substituted 5- to 10-membered heteroaryl. In some
 embodiments, $R^{b'}$ is optionally substituted 3- to 7-membered heterocyclic.

In some embodiments, $R^{c'}$ is hydrogen. In some embodiments, $R^{c'}$ is optionally
 10 substituted C_{1-12} aliphatic. In some embodiments, $R^{c'}$ is optionally substituted C_{1-12}
 heteroaliphatic. In some embodiments, $R^{c'}$ is optionally substituted phenyl. In some
 embodiments, $R^{c'}$ is optionally substituted 8- to 10-membered aryl. In some
 embodiments, $R^{c'}$ is optionally substituted 5- to 10-membered heteroaryl. In some
 embodiments, $R^{c'}$ is optionally substituted 3- to 7-membered heterocyclic.

15 In some embodiments, $R^{a'}$ and $R^{c'}$ are taken together with intervening atoms to
 form one or more rings selected from the group consisting of: optionally substituted C_3 -
 C_{14} carbocycle, optionally substituted 3- to 14-membered heterocycle, optionally
 substituted phenyl, optionally substituted C_8 - C_{10} aryl, and optionally substituted 5- to 10-
 membered heteroaryl.

20 In some embodiments, $R^{b'}$ and $R^{c'}$ are taken together with intervening atoms to
 form one or more rings selected from the group consisting of: optionally substituted C_3 -
 C_{14} carbocycle, optionally substituted 3- to 14-membered heterocycle, optionally
 substituted phenyl, optionally substituted C_8 - C_{10} aryl, and optionally substituted 5- to 10-
 membered heteroaryl.

5 In some embodiments, R^a and R^b are taken together with intervening atoms to form one or more rings selected from the group consisting of: optionally substituted C₃-C₁₄ carbocycle, optionally substituted 3- to 14-membered heterocycle, optionally substituted phenyl, optionally substituted C₈-C₁₀ aryl, and optionally substituted 5- to 10-membered heteroaryl.

In some embodiments, the invention includes methods for synthesizing polyethers from epoxides. Suitable methods of performing these reactions are disclosed in US Patent No. 7,399,822, the entire contents of which are hereby incorporated herein by reference.

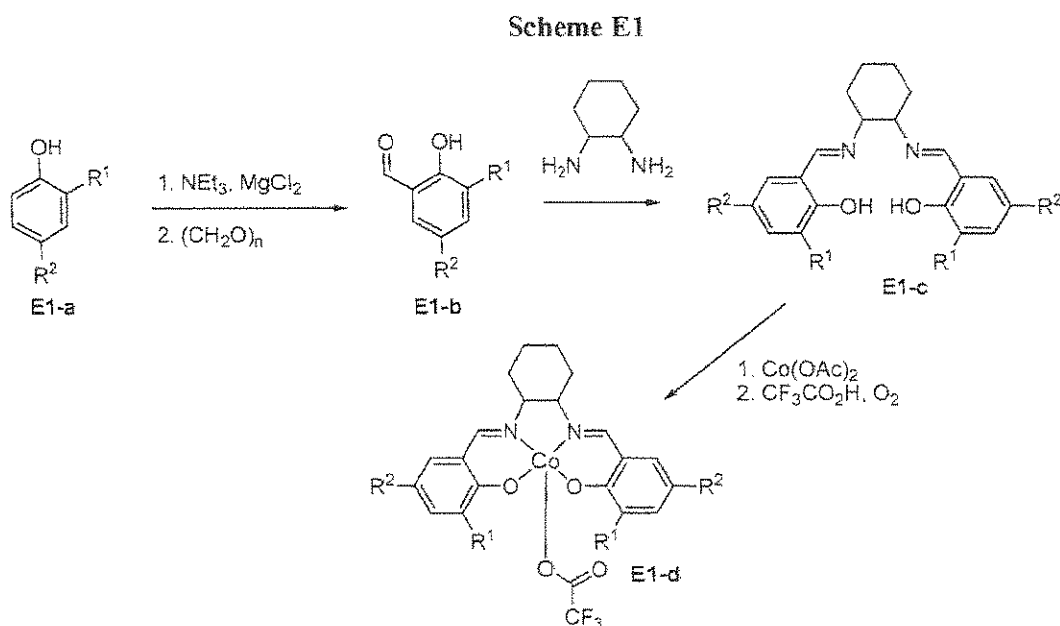
10 In some embodiments, the invention includes methods for synthesizing cyclic carbonates from carbon dioxide and epoxides using catalysts described above, suitable methods of performing this reaction are disclosed in US Patent No. 6,870,004 which is incorporated herein by reference.

15

EXAMPLES

Example 1

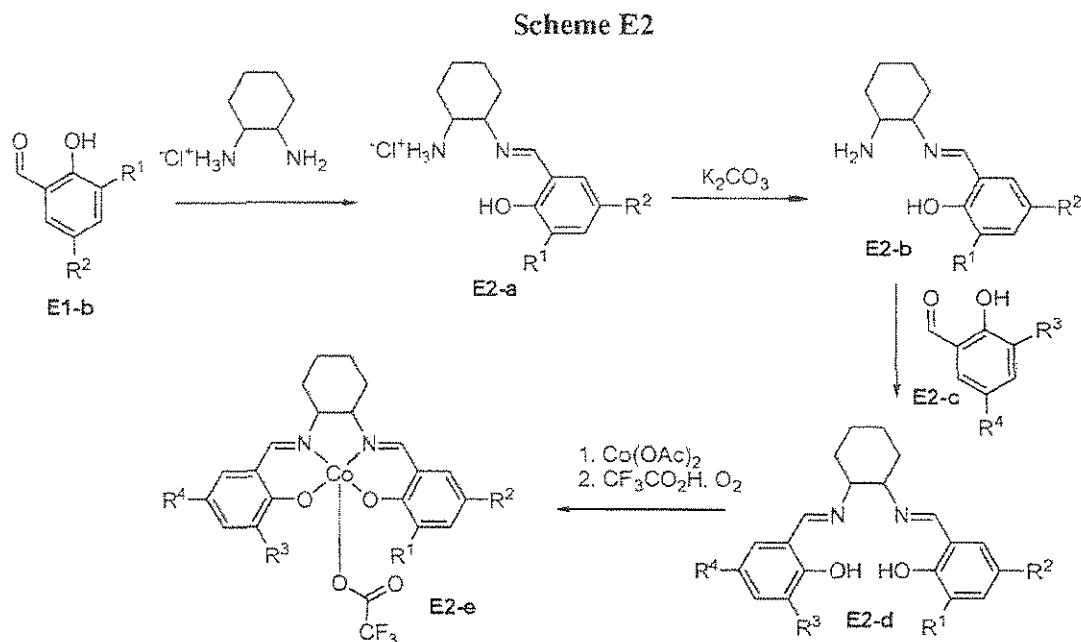
A general route to a symmetric cobalt (III) salen ligand of the present invention is shown in Schemes E1 and E2, below:



As shown in Scheme E1, disubstituted phenol **E1-a** is formylated to provide salicylaldehyde derivative **E1-b**. Two equivalents of this aldehyde are then reacted with a diamine (in this case 1,2-diaminocyclohexane) to afford Schiff base **E1-c**. This compound is then reacted with cobalt (II) acetate to give the Co(II)-salen complex (not shown) which is oxidized by air in the presence of trifluoroacetic acid to afford the active cobalt (III) catalyst. Similar chemistries can be applied to synthesis of the catalysts described hereinabove. One skilled in the art of organic synthesis can adapt this chemistry as needed to provide the specific catalysts described herein.

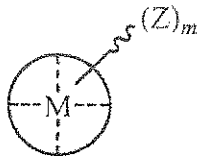
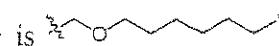
Example 2

A typical route to an asymmetric cobalt (III) salen ligand is shown in Scheme E2:



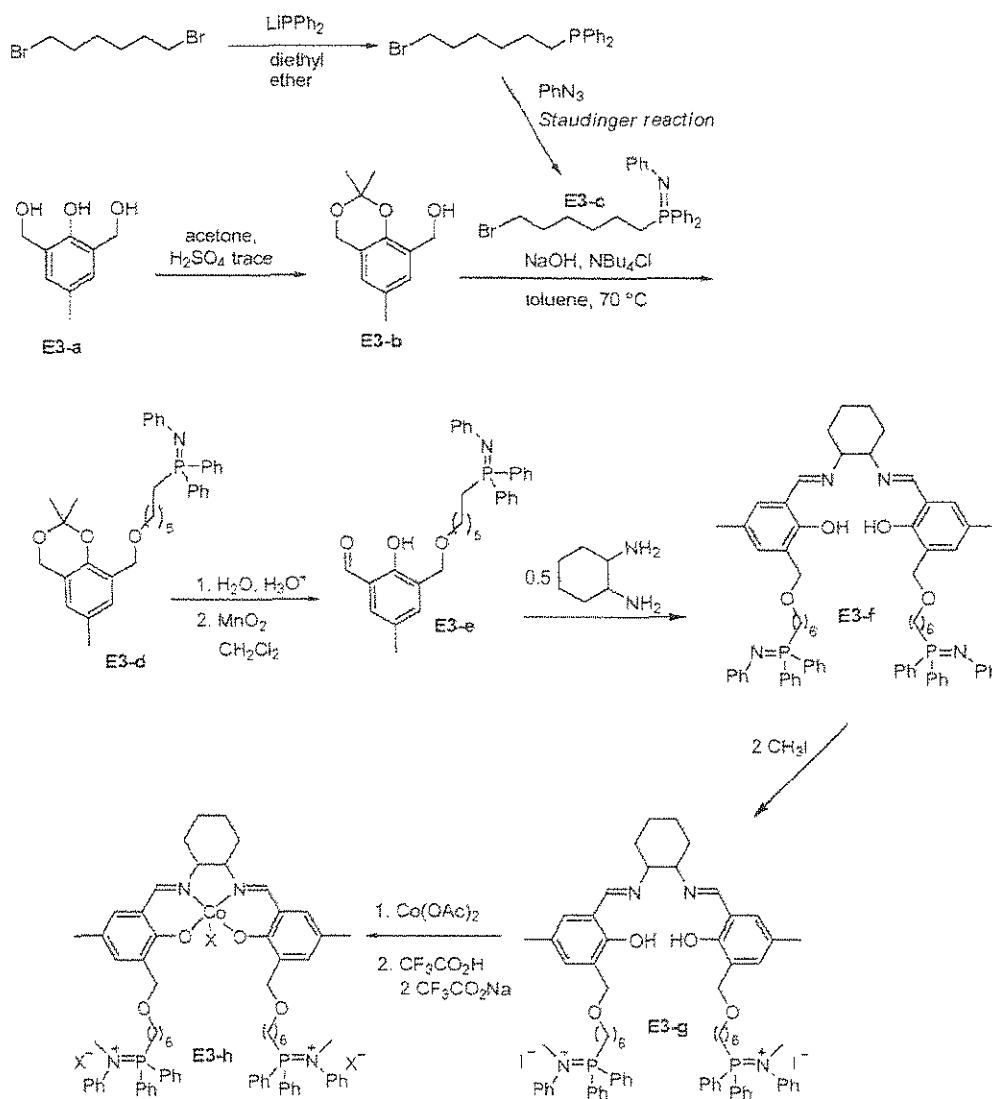
As shown in Scheme E2, disubstituted salicylaldehyde derivative **E1-b** is treated with one equivalent of a monohydrochloride salt of 1,2 cyclohexanediamine, the resulting Schiff base **E2-a** is then neutralized and a second different salicylaldehyde derivative is added. This compound is then reacted with cobalt (II) acetate to give the Co(II)-salen complex which is oxidized by air in the presence of trifluoroacetic acid to afford the active cobalt (III) catalyst. Similar chemistries can be applied to synthesis of the catalysts described hereinabove. One skilled in the art of organic synthesis can adapt this chemistry as needed to provide the specific catalysts described herein.

Example 3

Example 3 describes the synthesis of a catalyst , where M is Co(III),  is salcy,  is $\text{-(CH}_2\text{)}_6\text{-O-}$, Z is a P-linked phosphorimine

moiety $\text{P}^+(\text{Ph})_2$, and m is 1, wherein there are one or two ---(Z)_m groups present (Scheme E4 and E3, respectively).

Scheme E3

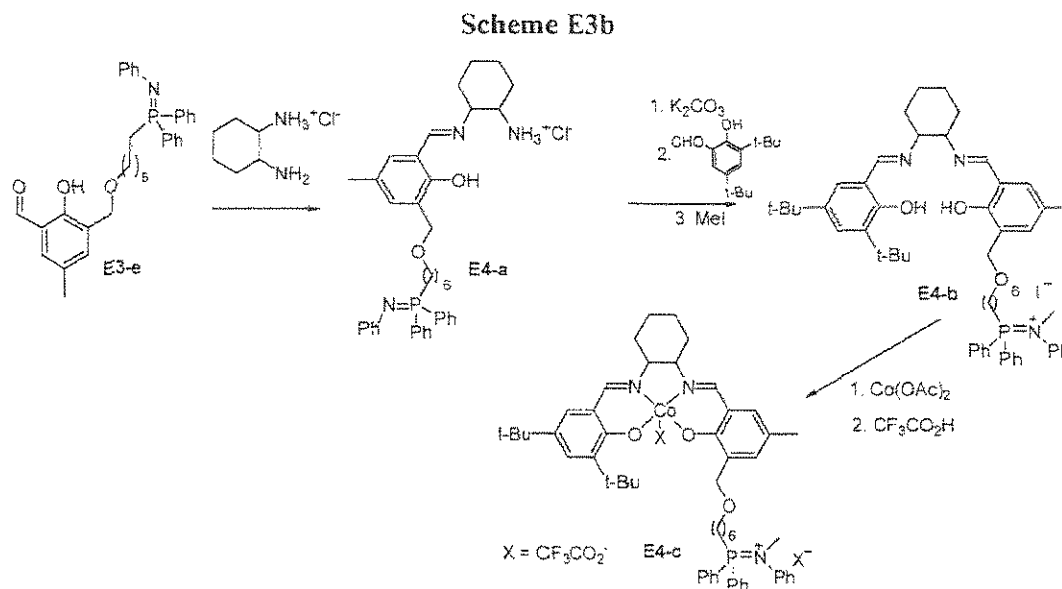


5

As shown in Scheme E3, triol **E3-a** is protected as a ketal to afford monohydric alcohol **E3-b**, this compound is then alkylated with bromide **E3-c** to afford benzyl ether **E3-d**. Deprotection and oxidation of the other benzylic alcohol affords salicylaldehyde

E3-e which is condensed with cyclohexanediamine as described above to give ligand E3-f. The phosphorimine nitrogen is then quaternized and the metal complex formed as before to provide catalyst E3-h. In an alternative route not shown here the metal is first inserted and then quaternization is performed.

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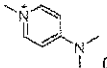


As shown in Scheme E3b, salicylaldehyde E3-e (described above) is condensed with cyclohexanediamine monohydrochloride to afford the mono-Schiff base hydrochloride E4a. This salt is then neutralized, condensed with di-*t*-butyl salicaldehyde, and methylated to give E4-b. The resulting ligand is metallated and oxidized as described above for Scheme E3 to give catalyst E4-c.

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Example 4

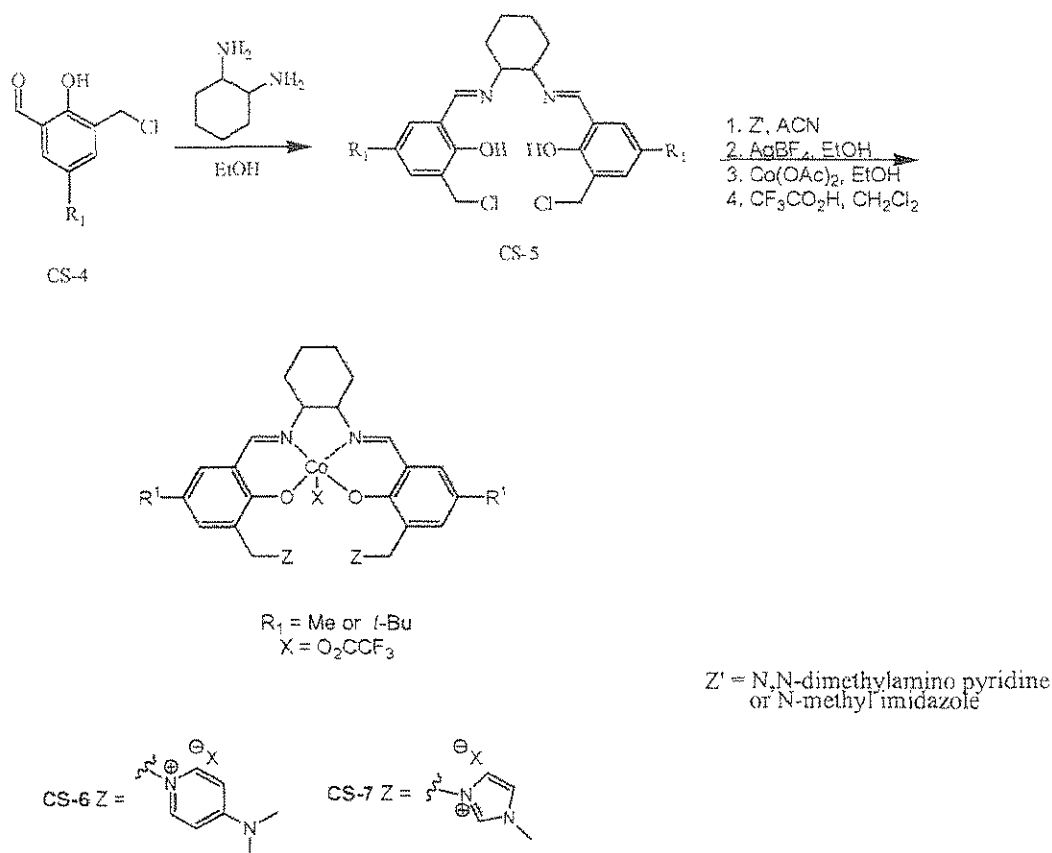
Example 4 describes the synthesis of catalysts where M is Co(III),  is salcy,

 is , Z is a 1-[4-dimethylamino-pyridinium]  or 1-[N-

15

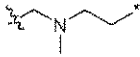
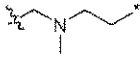
methylimidazolium],  and *m* is 1, wherein there are one or two  (Z)_{*m*} groups present (Scheme E5 and E6, respectively).

Scheme E4

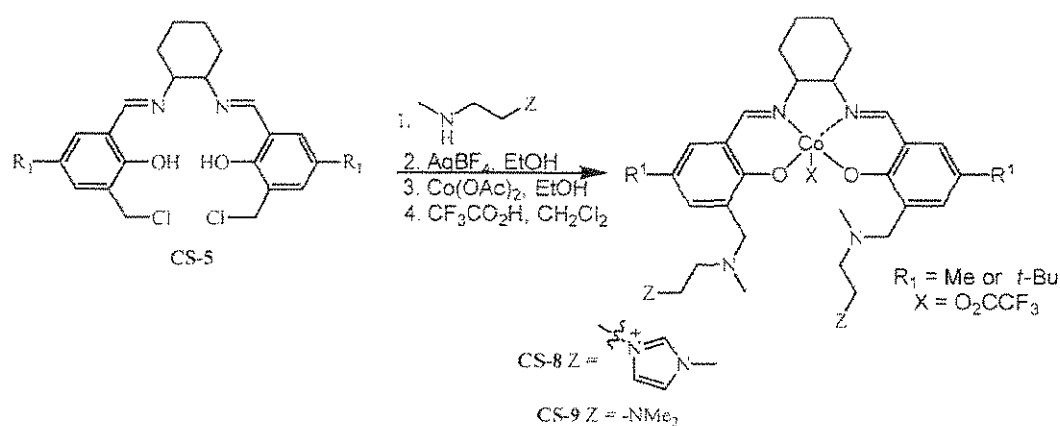


Scheme E4 shows the synthesis of compounds CS-6 and CS-7. For each compound *trans*-1,2-Diaminocyclohexane (2.0 mol) is slowly added to an anhydrous ethanol solution of benzyl chloride CS-4 (1.0 mol). The reaction is stirred and heated to reflux for 3 h, then cooled to rt and diluted with water. This mixture is cooled overnight in the freezer and solids are collected by filtration to afford dichloride CS-5. The dichloride CS-5 (1.0 mol) is reacted with N,N-Dimethylamino pyridine (2.0 mol) or N-methyl imidazole in acetonitrile. The reactions are heated at 80 °C for 18 h and then the solvent is removed in vacuo to provide the respective ammonium salts. These salts are metallated and oxidized as described previously to provide catalysts CS-6 and CS-7.

Example 5

Example 5 describes the synthesis of catalysts where M is Co(III),  is salcy,  is , Z is a 1-[N-methylimidazolium] (CS-8), or dimethylamino (CS-9) and m is 1, wherein there are two  (Z)_m groups present (Scheme E5 and E6, respectively).

Scheme E5



Scheme E5 shows the synthesis of compounds CS-8 and CS-9 using conditions similar to those described above. **Synthesis of CS-8:** The known compound 1-(2-methylaminoethyl)-3-methylimidazole (2.0 mol) is combined with CS-5 (1.0 mol) in acetonitrile. The reaction is heated to 80 °C for 18 h and then the solvent is removed in vacuo, metallation with Co(OAc)₂ and oxidation in TFA are then performed as described above to afford catalyst CS-8. **Synthesis of CS-9:** N,N,N'-Trimethyl-1,2-ethanediamine (4.0 mol) is combined with CS-5 (1.0 mol) in acetonitrile. The reaction is heated to 80 °C for 18 h, cooled, and the solvent is removed in vacuo. The crude product is diluted with ether, filtered to remove amine salts, and concentrated in vacuo. The residue is dissolved in degassed methanol and combined with Co(OAc)₂ (1.0 mol). After stirring for 3 h the residue is filtered and washed with methanol. Trifluoroacetic acid (1.0 mol) is added slowly to a stirring solution of the solid residue in dichloromethane. After stirring open to air for 3 h, the solids are filtered and dried in vacuo to produce CS-9.

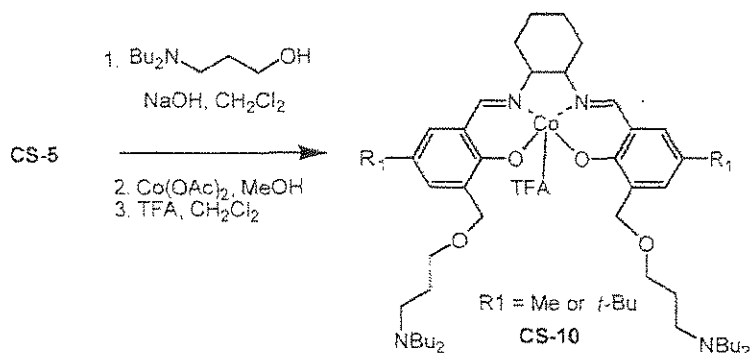
Example 6

Example 6 and Scheme E6 describe the synthesis of catalysts where M is Co(III),

 is salcy,  is , Z is dibutylamino and *m* is 1, wherein there are two  (Z)_{*m*} groups present.

5

Scheme E6



Synthesis of CS-10: Ligand CS-5 (1.0 mol), 3-(dibutylamino)-1-propanol (2.0 mol), a 50% NaOH solution (10 mol), tetrabutylammonium bisulphate (4 mol %), and dichloromethane are combined and heated at 65 °C overnight. The reaction mixture is concentrated in vacuo to remove the bulk of the solvent and the aqueous layer is extracted with ethyl acetate. The organic layer is separated, dried with magnesium sulfate, filtered, and concentrated in vacuo. After purification using silica gel the product is dissolved in degassed methanol and combined with Co(OAc)₂ (1.0 mol). After stirring for 3 h, the residue is filtered and washed with methanol. Trifluoroacetic acid (1.0 mol) is added slowly to a dichloromethane solution of the solid residue. After stirring open to air for 3 h, the solids are filtered and dried in vacuo to produce CS-10.

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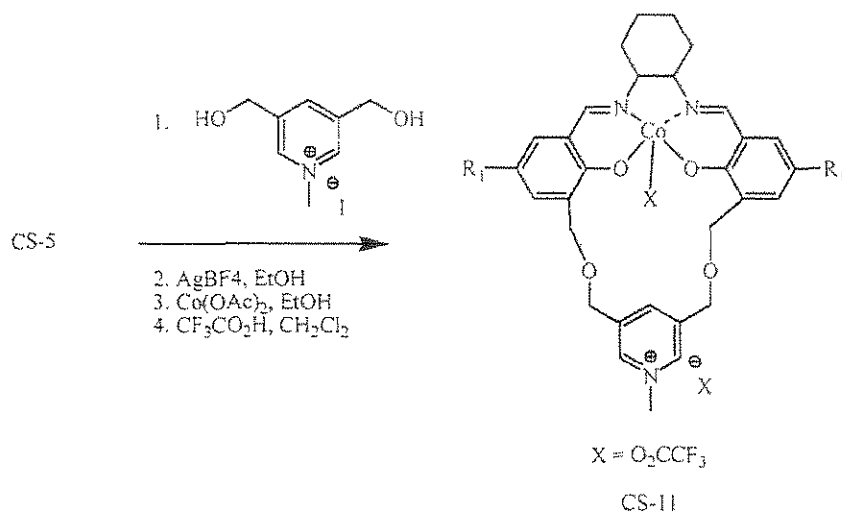
Example 7

Example 7 and Scheme E7 describe the synthesis of catalysts where M is Co(III),

 is salcy,  includes two  groups taken together to form a ring including the Z group, Z is 3-[N-methylpyridinium] and *m* is 1, wherein there is one  (Z)_{*m*} group present.

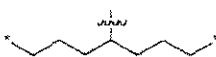
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Scheme E7

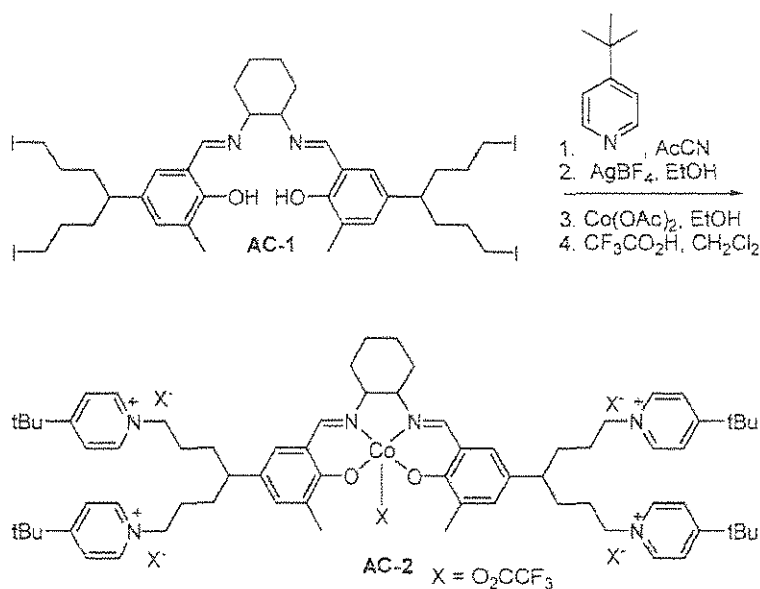


Synthesis of CS-11. Ligand CS-5 (1.0 mol), 3,5-bis(hydroxymethyl)-N-methylpyridinium iodide (2.0 mol), a 50% NaOH solution (10 mol), tetrabutylammonium bisulphate (4 mol %), and dichloromethane are combined and heated at 65 °C overnight. The reaction mixture is concentrated in vacuo to remove the bulk of the solvent and the aqueous layer is extracted with ethyl acetate. The organic layer is separated, dried with magnesium sulfate, filtered, and concentrated in vacuo. The procedure detailed above for the metallation and oxidation is followed to produce CS-11.

Example 8

Example 8 and Scheme E8 describe the synthesis of catalysts where M is Co(III),  is salcy,  is $\text{---}^*\text{---}^*$, Z is 1-[4-t-butylpyridinium], and m is 2, wherein there are two $\text{---}^*(\text{Z})_m$ groups present.

Scheme E8



Synthesis of AC-2. Intermediate **AC-1** (0.37 g, 0.35 mmol), 4-*t*-butylpyridine (0.21 mL, 1.41 mmol), and AcCN (4 mL) were combined in a sealed vial and heated to 80 °C with stirring for 18 h. The solvent was removed in vacuo, leaving a yellow residue (0.61 g, 110% yield, AcCN present). ^1H NMR (400 MHz, CDCl_3 , δ): 9.53 (t, 8H), 8.21 (s, 2H), 7.94 (t, 8H), 7.08 (s, 2H), 6.83 (s, 2H), 4.81 (m, 8H), 3.29 (m, 2H), 2.78 (m, 2H), 2.15 (s, 6H), 1.5–2.0 (m, 24 H), 1.36 (s, 36H); IR (ATR, film cast from AcCN): $\nu_{\text{C}=\text{N}} = 1637 \text{ cm}^{-1}$. A solution of the residue (0.30 g, 0.19 mmol) in dry EtOH (5 mL) was added to AgBF_4 (0.19 g, 0.85 mmol) in a schlenk tube and stirred overnight shielded from the light. The solution was filtered through Celite and the solvent was removed in vacuo, giving a solid residue. This residue was flashed over a small plug of silica gel with 5:1 CH_2Cl_2 :EtOH as eluant. The solvent was removed to give a solid residue (0.18 g, 67% yield). ^1H NMR (400 MHz, CDCl_3 , δ): 8.75 (t, 8H), 7.98 (d, 2H), 7.92 (t, 8H), 7.1–7.3 (m, 4H), 4.52 (m, 8H), 3.6 (m, 2H), 2.7 (m, 2H), 2.19 (s, 6H), 1.5–2.0 (m, 24 H), 1.38 (s, 36H); IR (ATR, film cast from CH_2Cl_2): $\nu_{\text{C}=\text{N}} = 1641 \text{ cm}^{-1}$, $\nu_{\text{BF}_4} = 1050 \text{ cm}^{-1}$. A solution of the residue (0.18 g, 0.12 mmol) in dry EtOH (4 mL) was added to $\text{Co}(\text{OAc})_2$ (0.022 g, 0.12 mmol) in a schlenk tube under N_2 . The solution was stirred for 3 h at room temperature, and the solvent was removed in vacuo. The residue was triturated with ether, dried in vacuo, and redissolved in CH_2Cl_2 . A solution of $\text{CF}_3\text{CO}_2\text{H}$ (9 μL , 0.12 mmol) in

CH₂Cl₂ (80 μ L) was added and the solution stirred for 3 h open to air. Solid NaO₂CCF₃ (0.067 g, 0.49 mmol) was added, and the solution was stirred under N₂ for 2 days. The solution was filtered through Celite and the solvent was removed in vacuo to leave a brown residue (0.071 g, 37% yield). ¹H NMR (400 MHz, DMSO-d₆, δ): 8.86 (t, 8H), 8.08 (t, 8H), 8.07 (s, 2H), 7.30 (m, 4H), 4.44 (m, 8H), 3.54 (m, 2H), 2.9 (m, 2H), 2.47 (s, 6H), 1.5-2.0 (m, 24 H), 1.29(s, 36H); IR (ATR): $\nu_{\text{C=O}}$ = 1682 cm⁻¹, $\nu_{\text{C=N}}$ = 1641 cm⁻¹.

Additional ligands AC-6 through AC-11 were synthesized using the conditions described for compound AC-2 and are summarized in Scheme E8b and Table E8:

Scheme E8b

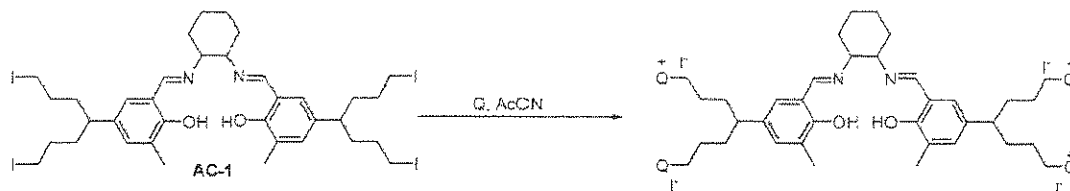


TABLE E8

Compound	Q (Scheme E8b)	¹ H NMR spectra ^a (δ, ppm)	IR ^b (cm ⁻¹)
AC-6 ^c		9.0 (d, 8H), 8.6 (t, 4H), 8.5 (s, 2H), 8.1 (t, 8H), 6.9 (s, 2H), 6.8 (s, 2H), 4.5 (t, 8H), 3.4 (m, 2H), 2.1 (s, 6H), 1.4-2.9 (m, 24H).	ν _{C=N} = 1629
AC-7		8.61 (d, 8H), 8.29 (s, 2H), 6.99 (s, 2H), 6.92 (d, 8H), 6.85 (s, 2H), 4.30 (t, 8H), 3.34 (m, 2H), 3.23 (s, 24H), 2.65 (m, 2H), 2.18 (s, 6H), 1.4-2.9 (m, 16H).	ν _{C=N} = 1649
AC-8			ν _{C=N} = 1627
AC-9			ν _{C=N} = 1610
AC-10			ν _{C=N} = 1627
AC-11			ν _{C=N} = 1628

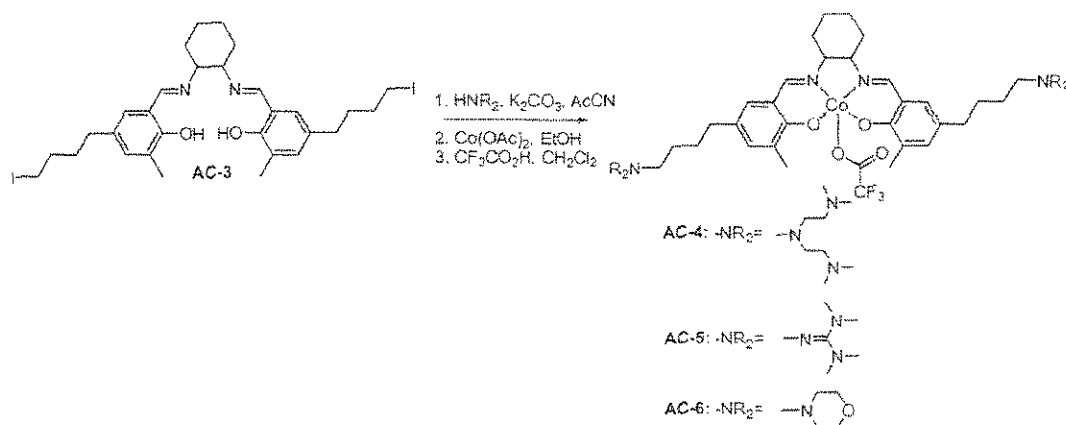
^a400 MHz, CDCl₃. ^bAll compounds exhibited the loss of a peak at 1213 cm⁻¹ attributed to the CH₂ group in AC-1. ^cNMR spectrum is in DMSO-d₆.

Example 9

Example 9 and Scheme E9 describe the synthesis of catalysts where M is Co(III),
 5  is salcy,  is , Z is *N,N*-bis-(3-dimethylaminopropyl)amino (AC-4),
 tetramethyl guanidino (AC-5), N-linked morpholino (AC-6), or N-linked piperidino (AC-
 14), and *m* is 2, wherein there are two (Z)_{*m*} groups present.

Scheme

E9



10 **Synthesis of AC-4.** Intermediate AC-3 (0.45 g, 0.63 mmol), 3,3'-iminobis(*N,N'*-
 dimethylpropylamine) (0.28 mL, 1.26 mmol), K₂CO₃ (0.35 g, 2.52 mmol) and AcCN (5
 mL) were combined in a sealed vial and heated to 80 °C with stirring for 18 h. The
 solution was filtered and the solvent was removed in vacuo, triturated with ether, and
 dried in vacuo to leave a yellow residue (0.48 g, 91% yield). ¹H NMR (400 MHz, CDCl₃,
 15 δ): 8.21 (m, 2H), 6.8-7.2 (m, 4H), 3.75 (m, 2H), 3.0-3.4 (m, 20H), 2.0-2.8 (m, 28H), 2.18
 (s, 6H), 1.4-2.0 (m, 24 H); IR (ATR): ν_{C=N} = 1600 cm⁻¹. A solution of the residue (0.21 g,
 0.25 mmol) in dry EtOH (10 mL) was added to Co(OAc)₂ (0.045 g, 0.25 mmol) in a
 schlenk tube under N₂. CH₂Cl₂ (3 mL) was added to completely dissolve the solution.
 The solution was stirred for 18 h at room temperature, and the solvent was removed in
 20 vacuo. The residue was triturated with ether, dried in vacuo, and redissolved in CH₂Cl₂
 (10 mL). CF₃CO₂H (20 μL, 0.25 mmol) was added and the solution stirred for 3.5 h open
 to air. The solvent was removed in vacuo, triturated with ether, and dried in vacuo to

leave a brown residue (0.28 g, 108% yield, residual CH_2Cl_2). ^1H NMR (400 MHz, $\text{DMSO}-d_6$, δ): 7.92 (m, 2H), 7.1-7.4 (m, 4H), 3.58 (m, 2H), 3.0-3.4 (m, 20H), 2.0-2.8 (m, 28H), 2.3 (s, 6H), 1.4-2.0 (m, 24 H); IR (ATR): $\nu_{\text{C=O}} = 1688\text{ cm}^{-1}$, $\nu_{\text{C=N}} = 1616\text{ cm}^{-1}$.

Synthesis of AC-5. Intermediate AC-3 (0.20 g, 0.29 mmol), 1,1,3,3-tetramethylguanidine (0.21 mL, 1.71 mmol), K_2CO_3 (0.39 g, 2.85 mmol) and AcCN (2 mL) were combined in a sealed vial and reacted as in AC-4, except that the residue was also washed with hexanes. ^1H NMR (400 MHz, CDCl_3 , δ): 8.23 (d, 2H), 6.95 (s, 2H), 6.80 (s, 2H), 3.35 (m, 2H), 3.1 (m, 4H), 2.7-2.8 (m, 24H), 2.48 (m, 4H), 2.20 (s, 6H), 1.4-2.0 (m, 16 H); IR (ATR): $\nu_{\text{C=N}} = 1594\text{ cm}^{-1}$. The residue was reacted as in AC-4. IR (ATR): $\nu_{\text{C=O}} = 1690\text{ cm}^{-1}$, $\nu_{\text{C=N}} = 1610\text{ cm}^{-1}$.

Synthesis of AC-6. Intermediate AC-3 (0.32 g, 0.44 mmol), morpholine (0.16 mL, 1.77 mmol), K_2CO_3 (0.61 g, 4.4 mmol) and AcCN (4 mL) were combined in a sealed vial and reacted as in AC-4, except that the residue was also washed with a NaOAc buffer (pH=4) solution to remove residual morpholine. ^1H NMR (400 MHz, CDCl_3 , δ): 8.22 (s, 2H), 6.92 (s, 2H), 6.79 (s, 2H), 3.69 (m, 8H), 3.28 (m, 2H), 2.2-2.5 (m, 16H), 2.19 (s, 6H), 1.4-2.0 (m, 16 H). The residue was reacted as in AC-4. ^1H NMR (400 MHz, $\text{DMSO}-d_6$, δ): 7.91 (s, 2H), 7.23 (s, 2H), 7.14 (s, 2H), 3.6 (m, 2H), 3.52 (m, 8H), 2.99 (m, 2H), 2.57 (s, 6H), 2.47 (m, 4H), 2.2-2.5 (m, 12H), 1.4-2.0 (m, 16 H); IR (ATR): $\nu_{\text{C=O}} = 1671\text{ cm}^{-1}$, $\nu_{\text{C=N}} = 1630\text{ cm}^{-1}$.

Additional ligands AC-13 and AC-14 were synthesized using the conditions described for compounds AC-4 through AC-6 and are summarized in Scheme E9b and Table E9:

Scheme E9b

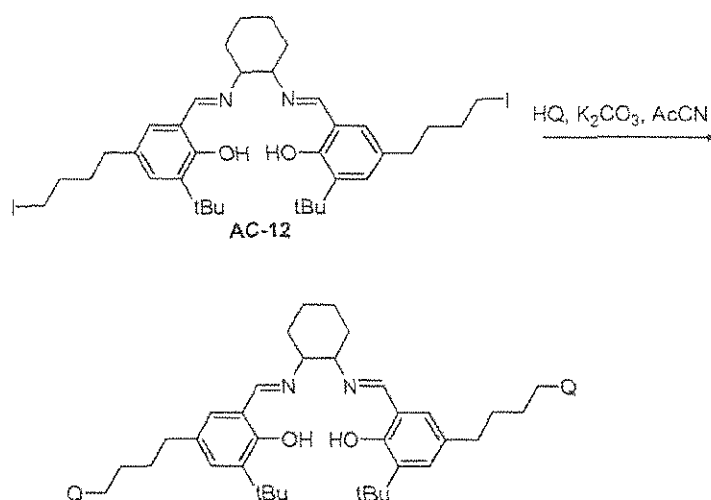


TABLE E9

Compound	Q (Scheme E9b)	¹ H NMR spectra ^a (δ, ppm)	IR ^b (cm ⁻¹)
AC-13		8.25 (s, 2H), 7.02 (d, 2H), 6.77 (d, 2H), 3.7 (m, 8H), 3.3 (m, 2H), 2.2-2.6 (m, 12H), 1.3-2.0 (m, 20H), 1.37 (s, 18H)	$\nu_{C=N} = 1628$
AC-14			$\nu_{C=N} = 1629$

^a400 MHz, CDCl₃. ^bAll compounds exhibited the loss of a peak at 1213 cm⁻¹ attributed to the CH₂I group in AC-1.

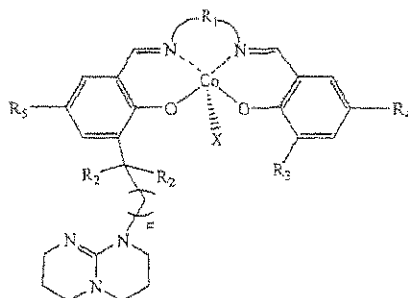
Example 10

Confirmation of inventive concepts, processes, methods, and compositions described herein has been provided, among other ways, through publication by others after the priority date of the present case. For example, Examples 10-27 describe working Examples presented in Chinese Patent Application No. 200810229276.1, published as CN 101412809A. Additional experimental and characterization data are described by Lu and co-workers, *J. Am. Chem. Soc.*, **2009**, *131*, 11509-11518, and

supporting information available at www.pubs.acs.org, the entirety each of which is hereby incorporated by reference.

In certain embodiments, provided catalysts and/or methods for the preparation of polycarbonate are characterized by one or more of the following: retaining high catalytic activity at low catalyst concentration; reaction conditions that are relatively mild; high catalytic activity with high selectivity for polymer product; alternate structure in the polycarbonate product higher than 97% with relatively narrow distribution of molecular weight; retaining high catalytic activity for copolymerization of carbon dioxide and epoxides at higher reaction temperatures (e.g., above 50 °C, above 75 °C, or above 100 °C); and catalysts that can be used to catalyze the polymerization of carbon dioxide with two or more alkylene oxides for the synthesis of polycarbonate polymer.

The following materials were added sequentially into a stainless steel high pressure reactor of effective volume of 200 mL at ambient temperature: 0.1 mmole of cobalt complex **I-a** (R_1 is cyclohexyl diamine, X is NO_3^{-1} anion; $R_2=\text{H}$; R_3 , R_4 and R_5 are tertiary butyl; group containing organic base group is at position 3 of the benzene ring in the ligand, n is 2) and one mole of propylene oxide. The reactor was then filled with carbon dioxide and the pressure is maintained constant at 2.0 MPa. The temperature was controlled at 25 °C. The content was stirred with a magnetic stirring bar for 6 hours and the remaining carbon dioxide was slowly released. The remaining alkylene oxide was collected in -20 °C cold trap and a certain amount of mixture of methanol/chloroform was added to dissolve the high polymer. Then a large amount of diethyl ether was added to precipitate the polycarbonate. The precipitate was filtered and washed several times with diethyl ether and dried in vacuum to constant weight to afford 27 grams of polycarbonate as a white solid. The average molecular weight of the polymer was determined by gel permeation chromatography to be 101,000 g/mol with a molecular weight distribution of 1.24. A Varian INOVA-400MHz Nuclear Magnetic Resonance spectrometer was used to determine its ^1H -NMR and the result showed that the alternate structure is over 99%.



I-a

Example 11

5 The same equipment and reaction conditions were employed as in Example 10 with the same catalyst and the same conditions except that the molar ratio of catalyst to propylene oxide was changed from 1:10000 to 1:50000 (0.02 mmole of catalyst and 1 mole of propylene oxide were used). The reaction was carried out at 25 °C for 24 hours to afford 21 grams of poly(propylene carbonate) with a molecular weight of 223,000 g/mol and a molecular weight distribution of 1.29. The polymer formed contained more than
10 99% carbonate linkages.

Example 12

 The same equipment and reaction conditions were employed as in Example 10 with the same catalyst and the same conditions except that the molar ratio of catalyst to propylene oxide was changed from 1:10000 to 1:200000 (0.008 mmole of catalyst and 1.6 mole of propylene oxide were used). The reaction was carried out at 50 °C for 10 hours to afford 19 grams of poly(propylene carbonate) with a molecular weight of 318,000 g/mol and a molecular weight distribution of 1.37. The polymer formed contained more than
15 99% carbonate linkages.

20

Example 13

 The same equipment and reaction conditions were employed as in Example 10 with the same catalyst and the same conditions except that the molar ratio of catalyst to

propylene oxide was changed from 1:10000 to 1:2000 (0.5 mmole of catalyst and 1 mole of propylene oxide were used). The reaction was carried out at 25 °C for 3 hours to afford 48 grams of poly(propylene carbonate) with a molecular weight of 52,800 g/mol and a molecular weight distribution of 1.30. The polymer formed contained more than 99% carbonate linkages.

Example 14

The same equipment and reaction conditions were employed as in Example 10 with the same catalyst and the same conditions except that the reaction temperature was changed from 25 °C to 100 °C and the reaction was carried out for 0.5 hours to afford 34 grams of poly(propylene carbonate) with a molecular weight of 112,400 g/mol and a molecular weight distribution of 1.38. The polymer formed contained more than 99% carbonate linkages.

Example 15

The same equipment and reaction conditions were employed as in Example 10 with the same catalyst and the same conditions except that the reaction temperature was changed from 25 °C to 10 °C and the reaction was carried out for 10 hours to afford 18 grams of poly(propylene carbonate) with a molecular weight of 914,000 g/mol and a molecular weight distribution of 1.38. The polymer formed contained more than 99% carbonate linkages.

Example 16

The same equipment and reaction conditions were employed as in Example 10 with the same catalyst and the same conditions except that the propylene oxide was replaced with 1,2-butylene oxide. The reaction was carried out at 25 °C for 6 hours to afford 31 grams of poly(butylene carbonate) with a molecular weight of 127,000 g/mol and a molecular weight distribution of 1.21. The polymer formed contained more than 99% carbonate linkages.

Example 17

The same equipment and reaction conditions were employed as in Example 10 with the same catalyst and the same conditions except that the propylene oxide was replaced with 1,2-octylene oxide. The reaction was carried out at 25 °C for 10 hours to afford 34 grams of poly(octylene carbonate) with a molecular weight of 109,000 g/mol and a molecular weight distribution of 1.38. The polymer formed contained more than 99% carbonate linkages.

Example 18

The same equipment and reaction conditions were employed as in Example 10 with the same catalyst and the same conditions except that the propylene oxide was replaced with a mixture of propylene oxide and cyclohexylene oxide (the molar ratio of the catalyst to propylene oxide and cyclohexylene oxide was 1:5000:5000). The reaction was carried out at 50 °C for 6 hours to afford 59 grams of poly(propylene-co-cyclohexylene carbonate) with a molecular weight of 187,000 g/mol and a molecular weight distribution of 1.29. The polymer formed contained more than 99% carbonate linkages.

Example 19

The same equipment and reaction conditions were employed as in Example 10 with the same catalyst and the same conditions except that the axial anion in the cobalt complex **I-a** was changed from nitrate radical to acetate moiety. The reaction was carried out at 25 °C for 6 hours to afford 34 grams of poly(propylene carbonate) with a molecular weight of 95,000 g/mol and a molecular weight distribution of 1.28. The polymer formed contained more than 99% carbonate linkages.

Example 20

The same equipment and reaction conditions were employed as in Example 10 with the same catalyst and the same conditions except that the diamine skeleton in the cobalt complex **I-a** was changed from cyclohexane diamine to ethylene diamine. The reaction was carried out at 25 °C for 6 hours to afford 29 grams of poly(propylene

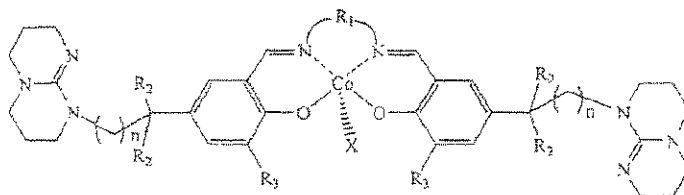
carbonate) with a molecular weight of 112,000 g/mol and a molecular weight distribution of 1.20. The polymer formed contained more than 99% carbonate linkages.

Example 21

The same equipment and reaction conditions were employed as in Example 10 with the same catalyst and the same conditions except that the diamine skeleton in the cobalt complex **I-a** was changed from cyclohexane diamine to o-phenylene diamine. The reaction was carried out at 25 °C for 6 hours to afford 25 grams of poly (propylene carbonate) with a molecular weight of 92,000 g/mol and a molecular weight distribution of 1.15. The polymer formed contained more than 99% carbonate linkages.

Example 22

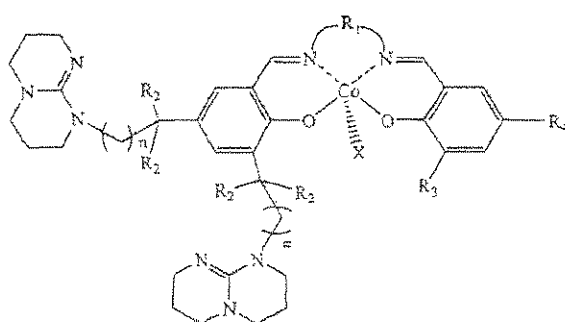
The following materials were added sequentially into a stainless steel high pressure reactor of volume of 200 mL at ambient temperature: 0.1 mmole of cobalt complex **I-b** (R_1 is 1,2-propylene diamine, X is dinitrophenyl anion; $R_2=H$; R_1 is tertiary butyl; there are organic base groups at position 5 of the two benzene rings in the ligand, n is 0) and 1 mole of propylene oxide. The reactor was then filled with carbon dioxide and the pressure was maintained constant at 2.0 MPa. The reaction was carried out at 25 °C for 6 hours to afford 23 grams of polycarbonate as a white solid. The average molecular weight of the polymer was determined by gel permeation chromatography to be 81,000 g/mol with a molecular weight distribution of 1.34. The polymer formed contained more than 99% carbonate linkages.



I-b

Example 23

5 The following materials were added sequentially into a stainless steel high pressure reactor of volume of 200 mL at ambient temperature: 0.1 mmole of cobalt complex I-c (R_1 is ethylene diamine, X is dinitrophenyl anion; $R_2=H$; R_3 is tertiary butyl; there are organic base groups at position 3 and position 5 of one of the benzene rings in the ligand, n is 0) and 1 mole of propylene oxide. The reactor was then filled with carbon
 10 dioxide and the pressure was maintained constant at 2.0 MPa. The reaction was carried out at 25 °C for 6 hours to afford 23 grams of polycarbonate as a white solid. The average molecular weight of the polymer was determined by gel permeation chromatography to be 81,000 g/mol with a molecular weight distribution of 1.34. The polymer formed contained more than 99% carbonate linkages.



I-c

Example 24

The following materials are added sequentially into a stainless steel high pressure reactor of volume of 200 mL at ambient temperature: 0.1 mmole of cobalt complex **I-b** (R_1 is ethylene diamine, X is dinitrophenyl anion; $R_2=H$; R_3 and R_4 are tertiary butyl; there are organic base groups at position 5 of the two benzene rings in the ligand, n is 0) and 1 mole of propylene oxide. The reactor was then filled with carbon dioxide and the pressure was maintained constant at 2.0 MPa. The reaction was carried out at 25 °C for 6 hours to afford 26 grams of polycarbonate as a white solid. The average molecular weight of the polymer was determined by gel permeation chromatography to be 83,000 g/mol with a molecular weight distribution of 1.19. The polymer formed contained more than 99% carbonate linkages. The polymer formed contained more than 99% carbonate linkages.

Example 25

The following materials are added sequentially onto a stainless steel high pressure reactor of volume of 200 mL at ambient temperature: 0.1 mmole of cobalt complex **I-a** (R_1 is 2,3-butylene diamine, X is nitrate anion; $R_2=H$; R_3 and R_4 are methoxyl group; R_1 is tertiary butyl; there is an organic base group at position 3 of one of the benzene rings in the ligand, n is 2) and 1 mole of propylene oxide. The reactor was then filled with carbon dioxide and the pressure is maintained constant at 2.0 MPa. The reaction was carried out at 25 °C for 6 hours to afford 22 grams of polycarbonate as a white solid. The average molecular weight of the polymer was determined by gel permeation chromatography to be 73,000 g/mol with a molecular weight distribution of 1.14. The polymer formed contained more than 99% carbonate linkages.

Example 26

The same equipment and reaction conditions were employed as in Example 10 with the same catalyst and the same conditions except that the pressure was changed from 2.0 MPa to 0.1 MPa. The reaction was carried out at 25 °C for 10 hours to afford 25 grams of poly(propylene carbonate) with a molecular weight of 100,400 g/mol and a molecular

weight distribution of 1.17. The polymer formed contained more than 99% carbonate linkages.

Example 27

5 The same equipment and reaction conditions were employed as in Example 10 with the same catalyst and the same conditions except that the pressure was changed from 2.0 MPa to 6.0 MPa. The reaction was carried out at 25 °C for 6 hours to afford 29 grams of poly(propylene carbonate) with a molecular weight of 125,000 g/mol and a molecular weight distribution of 1.25. The polymer formed contained more than 99% carbonate
10 linkages.

Table E10. Summary of Examples 10-27.

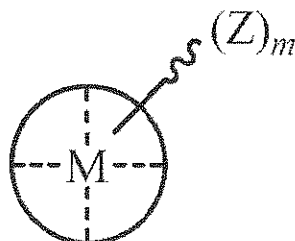
Catalyst							Reaction Conditions					Results									
Ex	Cat	R1	R2	R3	R4	R5	X	P	Epoxide	Cat.	Yield	T	t	PPC	TON	TOF	MW	PDI	g PC/g Cat	kg PC/mol Cat	
									(mmol)	(mg)	(mmol)	(deg C)	(h)	yield [g]	conv. [%]	(h ⁻¹)	(kDa)				
10								2	290	70.5	2	25	6	27	26.4	2644	441	101	1.2	383	270
11								2	290	14.1	2	25	24	21	20.6	10284	429	233	1.3	1489	1050
12								2	290	5.64	2	50	10	19	11.6	23262	2326	318	1.4	3369	2375
13								2	290	353	2	25	3	48	47.0	940	313	53	1.3	136	96
14								2	290	70.5	2	100	0.5	34	33	3330	6660	112	1.4	482	340
15								2	290	70.5	2	10	10	18	17.6	1763	176	914	1.4	255	180
16								0.1	15	70.5	0.1	25	10	25	24.5	2449	244.9	100	1.2	355	250
17								6	870	70.5	6	25	6	29	28.4	2840	473.4	125	1.3	411	290
18								2	290	70.5	2	25	6	31	26.7	2669	444.9	127	1.2	440	310
19								2	290	70.5	2	25	10	34	19.7	1974	197.4	109	1.4	482	340
20								2	290	70.5	2	50	6	59					837	590	390
21								2	290	70.2	2	25	6	34	33.3	3330	555	95	1.3	484	340
22								2	290	63.1	2	25	6	29	28.4	2840	473	112	1.2	446	290
23								2	290	69.9	2	25	6	25	24.5	2449	408	92	1.2	358	250
24								2	290	62.7	2	25	6	22	21.5	2155	359.1	73	1.1	351	220
25								2	290	89	2	25	6	23	22.5	2253	375	81	1.3	258	230
26								2	290	87.7	2	25	6	26	25.5	2547	424.4	83	1.2	296	260
27								2	290	88.2	2	25	6	23	22.5	2253	375.4	81	1.3	261	230

While we have described a number of embodiments of this invention, it is apparent that our basic examples may be altered to provide other embodiments that utilize the compounds and methods of this invention. Therefore, it will be appreciated that the scope of this invention is to be defined by the appended claims rather than by the
5 specific embodiments that have been presented by way of example.

CLAIMS

What is claimed is:

1. A metal complex of the formula:



wherein:

M is cobalt;



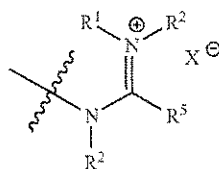
comprises a salen ligand; and

— (Z)_m represents one or more activating moieties tethered to the salen ligand, where — represents a linker moiety;

m is an integer between 1 and 4 inclusive and represents the number of Z groups present on a linker moiety;

and

each (Z) represents an activating moiety comprising an amidine or amidinium group of the formula:



wherein

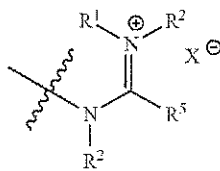
X⁻ is an anion;

each of R¹ and R² is independently hydrogen or an optionally substituted radical selected from the group consisting of C₁₋₂₀ aliphatic; C₁₋₂₀ heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; and an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; wherein any two or more R¹ and R² groups can be taken together with intervening atoms to form

one or more optionally substituted rings optionally containing one or more additional heteroatoms; and

each occurrence of R^5 is independently hydrogen or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; and an 8- to 10-membered bicyclic heteroaryl ring having 1-5 R^5 can be taken with an R^1 or R^2 group to form one or more optionally substituted rings.

2. The metal complex of claim 1, wherein the activating moiety comprises an amidinium group of the formula:

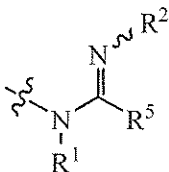


wherein X^- , R^1 , R^2 , and R^5 are as defined in claim 1.

3. The metal complex of claim 1, wherein each occurrence of R^1 and R^2 is independently an optionally substituted C_{1-20} aliphatic group.
4. The metal complex of claim 1, wherein each occurrence of R^1 and R^2 is independently an optionally substituted phenyl group.
5. The metal complex of claim 1, wherein R^1 and R^2 are taken together with intervening atoms to form one or more optionally substituted rings.
6. The metal complex of claim 5, wherein R^1 and R^2 are taken together to form a ring fragment selected from the group consisting of: $-C(R^y)_2-$, $-C(R^y)_2C(R^y)_2-$, $-C(R^y)_2C(R^y)_2C(R^y)_2-$, $-C(R^y)_2OC(R^y)_2-$, and $-C(R^y)_2NR^yC(R^y)_2-$, wherein each occurrence of R^y is independently $-H$, or an optionally substituted radical selected from the group consisting of C_{1-6} aliphatic, 3- to 7-membered heterocyclic, phenyl, and 8- to 10-membered aryl.

7. The metal complex of claim 6, wherein R¹ and R² are taken together to form a ring fragment selected from the group consisting of: -CH₂-, -CH₂CH₂-, -CH₂CH₂CH₂-, -CH₂OCH₂-, and -CH₂NR^yCH₂-.
8. The metal complex of claim 7, wherein the resulting nitrogen-containing ring formed by the combination of R¹ and R² is partially unsaturated.
9. The metal complex of claim 7, wherein the resulting nitrogen-containing ring formed by the combination of R¹ and R² comprises a fused polycyclic heterocycle.
10. The metal complex of claim 1, wherein R⁵ is H.
11. The metal complex of claim 1, wherein R⁵ is optionally substituted C₁₋₂₀ aliphatic.
12. The metal complex of claim 1, wherein R⁵ is optionally substituted C₁₋₆ aliphatic.
13. The metal complex of claim 1, wherein one or more R¹ or R² groups are taken together with R⁵ and intervening atoms to form an optionally substituted ring.
14. The metal complex of claim 13, wherein R¹ and R⁵ are taken together to form an optionally substituted 5- or 6-membered ring.
15. The metal complex of claim 13, wherein R² and R⁵ are taken together to form an optionally substituted 5- or 6-membered ring optionally containing one or more additional heteroatoms.
16. The metal complex of claim 1, wherein R¹, R² and R⁵ are taken together to form an optionally substituted fused ring system.
17. The metal complex of claim 16, wherein a ring in the fused ring system formed by combinations of any of R¹, R² and R⁵ is partially unsaturated or aromatic.
18. The metal complex of claim 1, wherein the activating moiety comprises an amidine.

19. The metal complex of claim 18, wherein the amidine has a formula:



where each of R^1 and R^2 is independently hydrogen or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; and an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; wherein any two or more R^1 and R^2 groups can be taken together with intervening atoms to form one or more optionally substituted rings optionally containing one or more additional heteroatoms; and

each occurrence of R^5 is independently hydrogen or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; and an 8- to 10-membered bicyclic heteroaryl ring having 1-5 R^5 can be taken with an R^1 or R^2 group to form one or more optionally substituted rings.

20. The metal complex of claim 19, wherein each R^1 and R^2 is independently an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic, 5- to 14-membered heteroaryl, phenyl, 8- to 10-membered aryl and 3- to 7-membered heterocyclic.

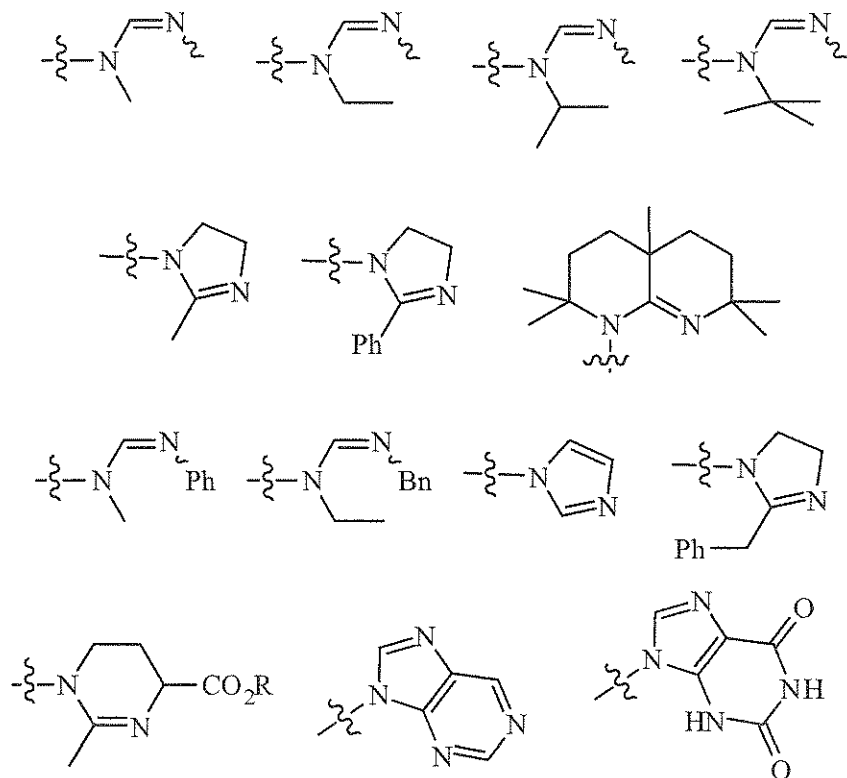
21. The metal complex of claim 19, wherein R^1 and R^2 are each independently an optionally substituted radical selected from the group consisting of C_{1-12} aliphatic and C_{1-12} heteroaliphatic.

22. The metal complex of claim 19, wherein each occurrence of R^1 and R^2 is independently an optionally substituted C_{1-12} aliphatic.

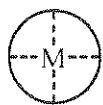
23. The metal complex of claim 19, wherein R^1 and R^2 are each independently optionally substituted C_{1-6} aliphatic.
24. The metal complex of claim 19, wherein R^1 and R^2 are both methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, phenyl or benzyl.
25. The metal complex of claim 19, wherein R^1 and R^2 are taken together with intervening atoms to form one or more optionally substituted rings.
26. The metal complex of claim 25, wherein R^1 and R^2 are taken together to form a ring fragment selected from the group consisting of: $-C(R^y)_2-$, $-C(R^y)_2C(R^y)_2-$, $-C(R^y)_2C(R^y)_2C(R^y)_2-$, $-C(R^y)_2OC(R^y)_2-$, and $-C(R^y)_2NR^yC(R^y)_2-$, wherein each occurrence of R^y is independently -H, or an optionally substituted radical selected from the group consisting of C_{1-6} aliphatic, 3- to 7-membered heterocyclic, phenyl, and 8- to 10- membered aryl.
27. The metal complex of claim 26, wherein R^1 and R^2 are taken together to form a ring fragment selected from the group consisting of: $-CH_2-$, $-CH_2CH_2-$, $-CH_2CH_2CH_2-$, $-CH_2OCH_2-$, and $-CH_2NR^yCH_2-$.
28. The metal complex of claim 19, wherein R^5 is H.
29. The metal complex of claim 19, wherein R^5 is optionally substituted C_{1-12} aliphatic.
30. The metal complex of claim 19, wherein R^5 is optionally substituted phenyl.
31. The metal complex of claim 19, wherein one or more R^1 or R^2 groups are taken together with R^5 and intervening atoms to form an optionally substituted ring.
32. The metal complex of claim 31, wherein R^1 and R^5 are taken together to form an optionally substituted 5- or 6-membered ring.
33. The metal complex of claim 32, wherein R^1 , R^2 and R^5 are taken together to form an optionally substituted fused ring system.

34. The metal complex of claim 33, wherein a ring formed by combinations of any of R^1 , R^2 and R^5 is partially unsaturated or aromatic.

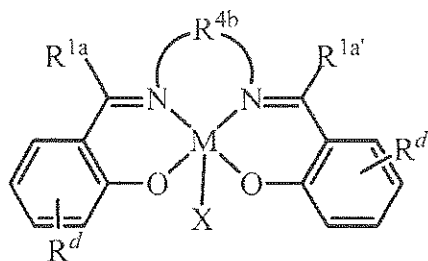
35. The metal complex of claim 19, wherein the amidine is selected from the group consisting of:



36. The metal complex of claim 1, wherein



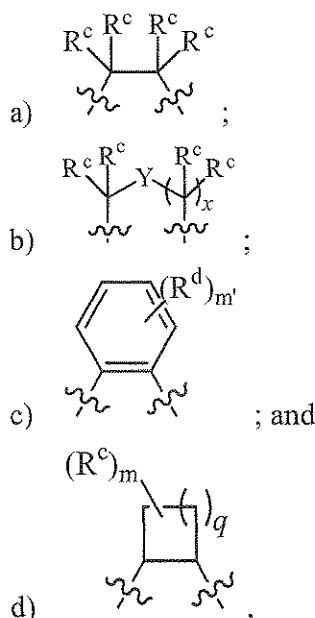
comprises:



R^{1a} and $R^{1a'}$ are independently a $\text{---}\sim(Z)_m$ group, hydrogen, or an optionally substituted radical selected from the group consisting of: C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle; a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen and sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 atoms independently selected from nitrogen, oxygen and sulfur; and a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms selected from nitrogen, oxygen and sulfur;

R^d at each occurrence is independently a $\text{---}\sim(Z)_m$ group, hydrogen, halogen, -OR, -NR₂, -SR, -CN, -NO₂, -SO₂R, -SOR, -SO₂NR₂; -CNO, -NRSO₂R, -NCO, -N₃, -SiR₃; or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle; a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; and an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; where two or more R^d groups may be taken together with intervening atoms to form one or more optionally substituted rings optionally containing one or more heteroatoms,

R^{4b} is selected from the group consisting of:



where

R^c at each occurrence is independently a $\text{---}\sim(Z)_m$ group, hydrogen, halogen, -OR, -NR₂, -SR, -CN, -NO₂, -SO₂R, -SOR, -SO₂NR₂, -CNO, -NRSO₂R, -NCO, -N₃, -SiR₃; or an optionally substituted radical selected from the group consisting of C₁₋₂₀ aliphatic; C₁₋₂₀ heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; and an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; where two or more R^c groups may be taken together with the carbon atoms to which they are attached and any intervening atoms to form one or more optionally substituted rings; when two R^c groups are attached to the same carbon atom, they may optionally be taken together along with the carbon atom to which they are attached to form an optionally substituted moiety selected from the group consisting of: a 3- to 8-membered spirocyclic ring, a carbonyl, an oxime, a hydrazone, and an imine;

Y is a divalent linker selected from the group consisting of: -NR-, -N(R)C(O)-, -C(O)NR-, -O-, -C(O)-, -OC(O)-, -C(O)O-, -S-, -SO-, -SO₂-, -SiR₂-, -C(=S)-, -C(=NR)-, or -N=N-; a polyether; a C₃ to C₈ substituted or unsubstituted carbocycle; and a C₁ to C₈ substituted or unsubstituted heterocycle;

R at each occurrence is independently hydrogen, an optionally substituted radical selected the group consisting of acyl; C₁₋₆ aliphatic; C₁₋₆ heteroaliphatic; carbamoyl; arylalkyl; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; and an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; an oxygen protecting group; and a nitrogen protecting group, where two R groups on the same nitrogen atom can optionally be taken together to form an optionally substituted 3- to 7-membered ring,

X' is a nucleophile capable of ring opening an epoxide;

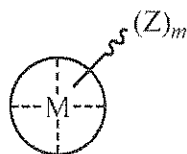
m' is 0 or an integer from 1 to 4, inclusive;

m'' is 0 or an integer from 1 to 6, inclusive;

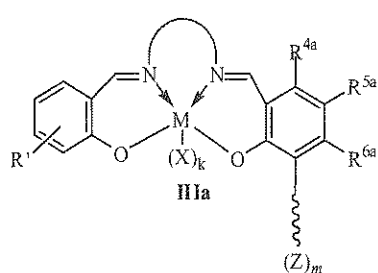
q is 0 or an integer from 1 to 4, inclusive; and

x is 0, 1, or 2.

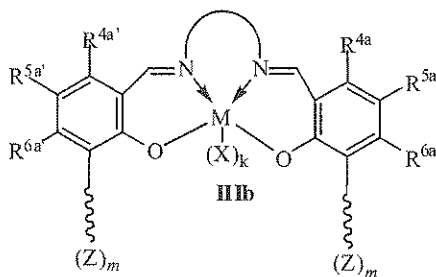
37. The metal complex of claim 1, wherein



, is selected from the group consisting of:



and



where



represents an optionally substituted moiety linking the two nitrogen atoms, and is selected from the group consisting of: phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; and an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an optionally substituted C₂₋₂₀ aliphatic group, wherein one or more methylene units are optionally and independently replaced by -NR^y-, -N(R^y)C(O)-, -C(O)N(R^y)-, -OC(O)N(R^y)-, -N(R^y)C(O)O-, -OC(O)O-, -O-, -C(O)-, -OC(O)-, -C(O)O-, -S-, -SO-, -SO₂-, -C(=S)-, -C(=NR^y)-, -C(=NOR^y)-, or -N=N;

R^{4a}, R^{4a'}, R^{5a}, R^{5a'}, R^{6a}, and R^{6a'} are each independently a $\text{---}\text{---}\text{---}(\text{Z})_m$ group, hydrogen, halogen, -OR, -NR₂, -SR, -CN, -NO₂, -SO₂R, -SOR, -SO₂NR₂; -CNO, -NRSO₂R, -NCO, -N₃, -SiR₃; or an optionally substituted radical selected from the group consisting of C₁₋₂₀ aliphatic; C₁₋₂₀ heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon

saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; and an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; wherein any two adjacent R^{4a} , $R^{4a'}$, R^{5a} , $R^{5a'}$, R^{6a} , and $R^{6a'}$ groups can be taken together with intervening atoms to form one or more optionally substituted rings,

R' represents one or more substituents optionally present on the phenyl ring and each R' is independently selected from the group consisting of: halogen, $-\text{NO}_2$, $-\text{CN}$, $-\text{SR}^y$, $-\text{S}(\text{O})\text{R}^y$, $-\text{S}(\text{O})_2\text{R}^y$, $-\text{NR}^y\text{C}(\text{O})\text{R}^y$, $-\text{OC}(\text{O})\text{R}^y$, $-\text{CO}_2\text{R}^y$, $-\text{NCO}$, $-\text{N}_3$, $-\text{OR}^7$, $-\text{OC}(\text{O})\text{N}(\text{R}^y)_2$, $-\text{N}(\text{R}^y)_2$, $-\text{NR}^y\text{C}(\text{O})\text{R}^3$, $-\text{NR}^y\text{C}(\text{O})\text{OR}^y$; and an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; and an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur, where two or more adjacent R' groups can be taken together to form an optionally substituted saturated, partially unsaturated, or aromatic 5- to 12-membered ring containing 0 to 4 heteroatoms;

R at each occurrence is independently hydrogen, an optionally substituted radical selected the group consisting of acyl; C_{1-6} aliphatic; C_{1-6} heteroaliphatic; carbamoyl; arylalkyl; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; and an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; an oxygen protecting group; and a nitrogen protecting group, where two R groups on the same nitrogen atom can optionally be taken together to form an optionally substituted 3- to 7-membered ring;

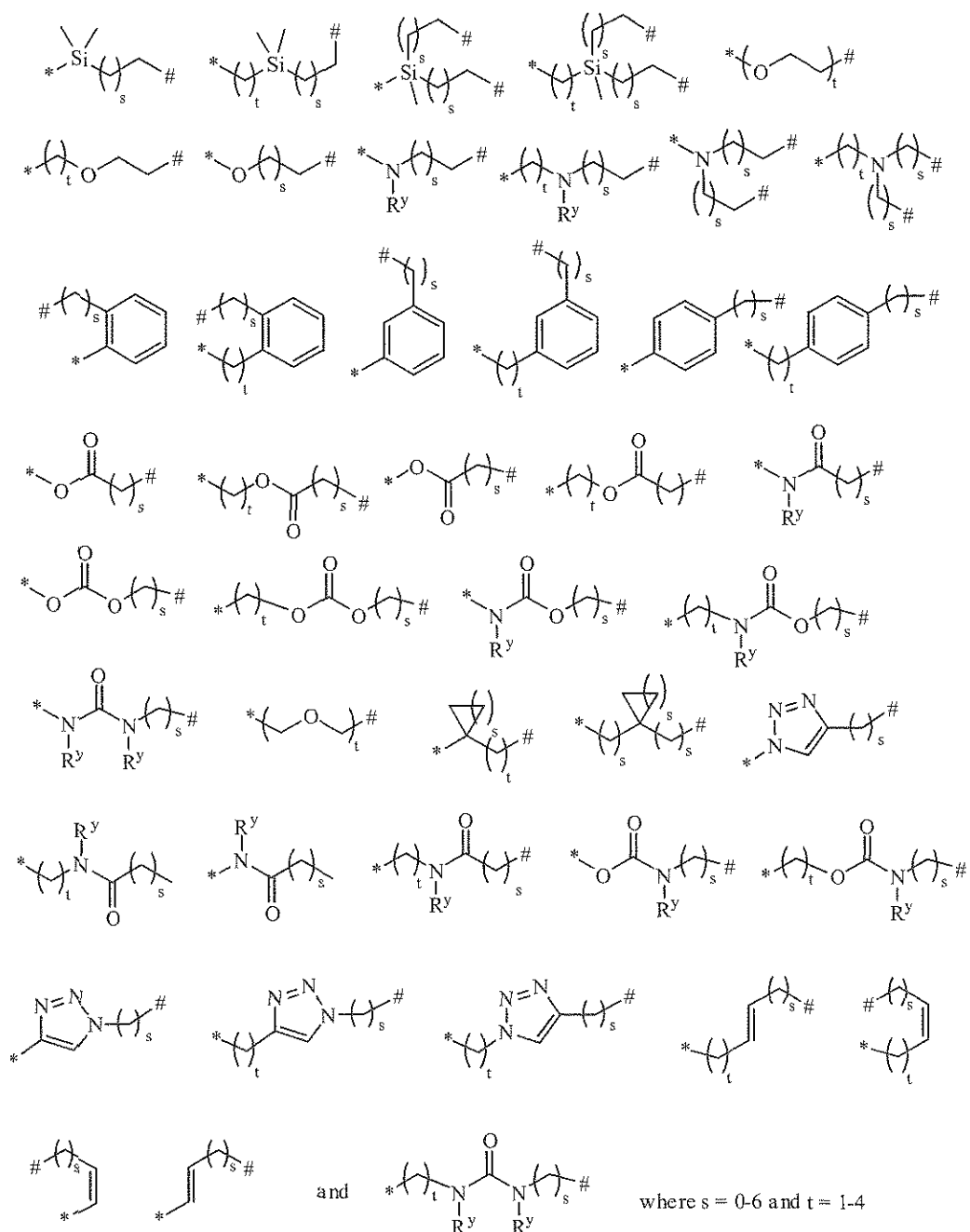
X' is a nucleophile capable of ring opening an epoxide; and k is 1.

40. The metal complex of claim 38, wherein  comprises a C₃₋₃₀ aliphatic group.

41. The metal complex of claim 38, wherein  comprises a C₄₋₈ aliphatic group.

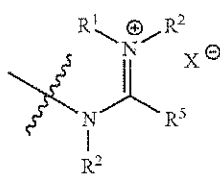
42. The metal complex of claim 38, wherein  comprises a C₃ aliphatic group.

43. The metal complex of claim 38, wherein $\text{---}\sim\sim\sim$ is selected from the group consisting of:



where * represents the site of attachment to the ligand, and each # represents a site of attachment to the amidine or amidinium activating moiety.

44. The metal complex of claim 36, wherein X' is selected from the group consisting of: chlorine, bromine, an optionally substituted C₁₋₁₂ carboxylate, azide, an optionally substituted phenoxide, and sulfonate.
45. The metal complex of claim 36, wherein X' is selected from the group consisting of: chloride, acetate, trifluoroacetate, azide, pentafluorobenzoate, and a nitrophenolate.
46. A method for the synthesis of aliphatic polycarbonate polymers comprising the step of contacting one or more epoxides with carbon dioxide in the presence of a metal complex of claim 1.
47. The method of claim 46, wherein the activating moiety comprises an amidinium group of the formula:



wherein

X⁻ is an anion;

each of R¹ and R² is independently hydrogen or an optionally substituted radical selected from the group consisting of C₁₋₂₀ aliphatic; C₁₋₂₀ heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; and an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; wherein any two or more R¹ and R² groups can be taken together with intervening atoms to form one or more optionally substituted rings optionally containing one or more additional heteroatoms; and

each occurrence of R⁵ is independently hydrogen or an optionally substituted radical selected from the group consisting of C₁₋₂₀ aliphatic; C₁₋₂₀ heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; and an 8- to 10-membered bicyclic heteroaryl ring having

1-5 R⁵ can be taken with an R¹ or R² group to form one or more optionally substituted rings.

48. The method of claim 46, wherein the activating moiety comprises an amidine group.
49. The method of claim 46, wherein the epoxide is ethylene oxide, propylene oxide, or cyclohexene oxide.
50. The method of claim 46, wherein the epoxide is ethylene oxide.
51. The method of claim 46, wherein the epoxide is propylene oxide.
52. The method of claim 46, wherein a pressure of carbon dioxide is between about 50 and 800 psi.
53. The method of claim 46, wherein a molar ratio of complex to epoxide is between about 1:1000 and about 1:100,000.

CATALYSTS AND METHODS FOR POLYMER SYNTHESIS

Abstract

- 5 The present invention provides unimolecular metal complexes having increased activity in the copolymerization of carbon dioxide and epoxides. Also provided are methods of using such metal complexes in the synthesis of polymers. According to one aspect, the present invention provides metal complexes comprising an activating species with co-catalytic activity tethered to a multidentate ligand that is
- 10 coordinated to the active metal center of the complex.

(no suitable figure)