

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
21 September 2006 (21.09.2006)

PCT

(10) International Publication Number
WO 2006/099162 A2

(51) International Patent Classification:
C07F 1/08 (2006.01)

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(21) International Application Number:
PCT/US2006/008634

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

(22) International Filing Date: 13 March 2006 (13.03.2006)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/661,549 14 March 2005 (14.03.2005) US
60/661,550 14 March 2005 (14.03.2005) US
60/710,269 22 August 2005 (22.08.2005) US

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

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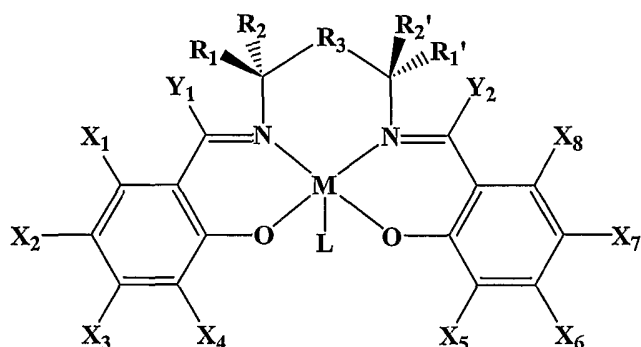
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Published:

— without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: POLYMERIC SALEN COMPOUNDS AND METHODS THEREOF



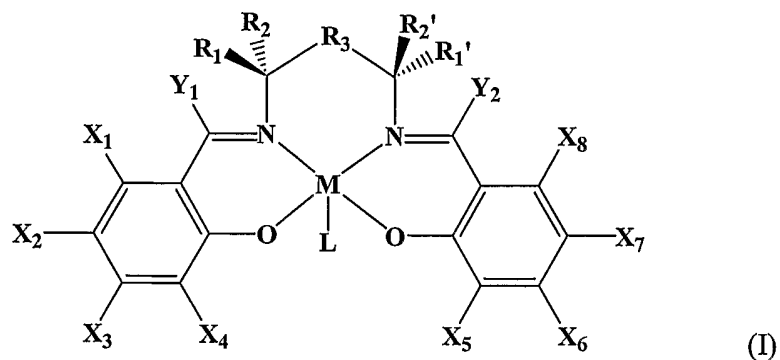
(I)

(57) Abstract: The present disclosure provides a polymerizable compound of the formula (I) where the R_1 , R_2 , R'_1 , R'_2 , X_1 to X_8 , Y_1 , Y_2 , M and L have any of values as defined in the specification. The disclosure also provides an oligomer, a homo-polymer, or a co-polymer of compound of the formula (I). The disclosure also provides methods for preparing the compound of the formula (I) and methods for preparing polymers of the compound of the formula (I), and to methods and intermediates

useful for preparing them. The disclosure also provides methods for the use of the polymers of formula (I) as chiral catalysts in enantioselective preparative processes.

Abstract

The present disclosure provides a polymerizable compound of the formula (I)



where the R_1 , R_2 , R'_1 , R'_2 , X_1 to X_8 , Y_1 , Y_2 , M and L have any of values as defined in the specification. The disclosure also provides an oligomer, a homo-polymer, or a co-polymer of compound of the formula (I). The disclosure also provides methods for preparing the compound of the formula (I) and methods for preparing polymers of the compound of the formula (I), and to methods and intermediates useful for preparing them. The disclosure also provides methods for the use of the polymers of formula (I) as chiral catalysts in enantioselective preparative processes.

POLYMERIC SALEN COMPOUNDS AND METHODS THEREOF

This application is being filed as a PCT International Patent Application on
5 13 March 2006, in the name of Georgia Tech Research Corporation, a U.S. national
corporation, applicant for the designation of all countries except the U.S., and
Xiaolai Zheng, citizen of China P.R., Michael Johannes Holbach and Marcus Weck,
both German citizens, and Christopher W. Jones, a U.S. citizen; applicants for the
designation of the U.S. only, and claims priority to U.S. Applications Serial Nos.
10 60/661,549, filed 14 March 2005, 60/661,550, filed 14 March 2005 and 60/710,269,
filed 22 August 2005.

Background

Methods for making and using chiral catalyst for use in stereoselective
15 chemical reaction processes are known, see for example, U.S. Patent Nos. 5,663,393
and 6,262,278, to Jacobsen, et al., and U.S. Patent No. 6,884,750, to Kim et al.
Supported chiral catalysts are also known, see for example, Reger, T.S., et al., *J. Am.*
Chem Soc., 2000, 122, 6929.

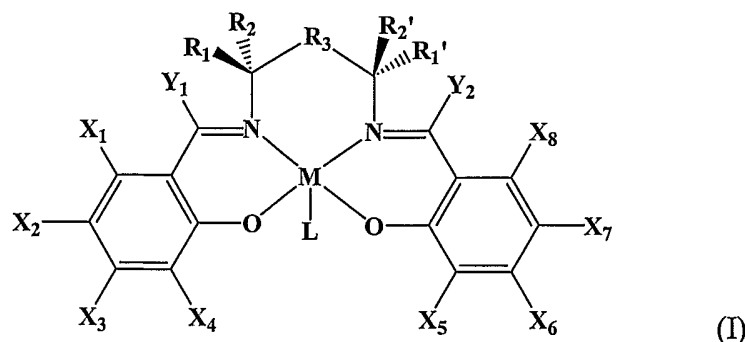
Challenges associated with supported chiral catalyst compositions and their
20 use can include, for example, difficult separation from product, non-reuse or poor
reuse (reusability) performance, low or reduced activity, and low or reduced
selectivity. These and other challenges can prohibit broad industrial application or
at least contribute to a higher total cost of manufacture and use of chiral catalyst
compositions and to higher total cost of manufacture of chemical products produced
25 therewith.

There is a need for improved supported chiral catalyst compositions and to
improved methods for making and using the compositions.

Summary

30 In general terms, the claimed invention relates to certain transition metal
salen complexes, polymers thereof, and use of the polymers as catalysts, for
example, in preparing organic compounds having high optical purity, such as in
asymmetric epoxidation or hydrolytic kinetic resolution processes.

One possible aspect of the disclosure is a polymerizable compound of the formula (I)



5 wherein

R_1 , R_2 , R'_1 , R'_2 , X_1 , X_2 , X_3 , X_4 , X_5 , X_6 , X_7 , X_8 , Y_1 and Y_2 are independently H, C₁-C₆ alkyl, C₃₋₁₂ cycloalkyl, C₁-C₆ alkoxy, halogen, -OH, -SH, -NO₂, -NH₂, amino, imine, amide, carbonyl, carboxy, silyl, ether, thio ether, seleno ether, ketone, aldehyde, ester, phosphoryl, phosphonate, phosphine, sulfonyl, or -(CH₂)_k-R₄ group, wherein R₄ is aryl, heteroaryl, cycloalkyl, heterocycle, or polycycle, and k is an integer of 0 to 8, or any two or more proximate R_1 , R_2 , R'_1 , R'_2 , X_1 , X_2 , X_3 , X_4 , X_5 , X_6 , X_7 , X_8 , Y_1 and Y_2 form a ring of a carbocycle or heterocycle comprising 4 to 10 atoms,

where at least one X_1 , X_2 , X_3 , X_4 , X_5 , X_6 , X_7 , X_8 , Y_1 and Y_2 is independently of the formula -L'-Z-P, where

L' is a divalent linker which is independently a single carbon-carbon bond, -(CH₂)_k-R₅-, -(CH=CH)_k-R₅-, or -(C≡C)_k-R₅-, wherein -R₅- is arylene, heteroarylene, cycloalkylene, heterocyclene, or polycyclene, and k is an integer of 0 to 8, -R₅- can optionally be further substituted,

Z is a divalent connector which is independently a single carbon-carbon bond, -C(=O)-, -C(=S)-, -C(=S)S-, -SC(=S)-, -SO₂-, -S(=O)₂O-, -O-S(=O)₂-, -C(=O)N(R_a)-, -C(=S)N(R_a)-, -SO₂N(R_a)-, -C(=O)O-, -O-C(=O)-, -C(=S)O-, C₁-C₈ alkylenyl, or alkyl substituted C₁-C₈ alkylenyl, where R_a is -H, alkyl, acyl, aryl, alkylaryl, arylalkyl, aryloxy, alkoxycarbonyl, or benzyloxycarbonyl, and

P is a polymerizable group which is independently C₂-C₆ alkenyl, C₂-C₆ alkynyl, arylene-C₂-C₆ alkenyl, cycloalkenyl, cycloalkynyl, heterocycloalkenyl, or polycycloalkenyl;

R_3 is independently which is a single carbon-carbon bond, $-\text{CH}_2-$, $-\text{CH}_2\text{CH}_2-$, $-\text{NH}-$, $-\text{O}-$, or $-\text{S}-$;

M is absent or a metal atom or ion of at least one of Co, Mn, Cr, Al, Zn, Ru, Fe, Mo, Ni, Ti, Zr, or mixtures thereof; and

- 5 L is absent, or a counter anion selected from F, Cl, Br, I, $-\text{O}(\text{C}=\text{O})\text{alkyl}$, $-\text{O}-\text{S}(=\text{O})_2-\text{R}'_4$, wherein R'_4 is aryl, $\text{arylC}_2-\text{C}_6$ alkyl, heteroaryl, C_1-C_6 alkyl, cycloalkyl, heterocycle, PF_6 , $\text{B}(\text{Ar})_4$, or $\text{B}(\text{halo})_4$, where halo is F, Cl, Br, or I; or a salt or hydrate thereof.

- 10 Another possible aspect of the disclosure is a polymerizable compound of the formula (I) wherein only one X_1 , X_2 , X_3 , X_4 , X_5 , X_6 , X_7 , X_8 , Y_1 and Y_2 is independently of the formula $-\text{L}'-\text{Z}-\text{P}$, that is, a single polymerizable group of the formula $-\text{L}'-\text{Z}-\text{P}$.

- 15 Another possible aspect of the disclosure is a polymer of the compound of the formula (I) wherein only one of the substituents X_1 , X_2 , X_3 , X_4 , X_5 , X_6 , X_7 , X_8 , Y_1 and Y_2 is of the formula $-\text{L}'-\text{Z}-\text{P}$, that is, each compound of formula (I) has a single polymerized group of the formula $-\text{L}'-\text{Z}-(\text{P})_n$.

Another possible aspect of the disclosure is a polymer of the compound of formula (I), such as an oligomer or homopolymer of formula (I), or an oligomer or a copolymer of formula (I) with other polymerizable monomers.

- 20 Another possible aspect of the disclosure is a preparative method for a homopolymer of the compound of formula (I).

Another possible aspect of the disclosure is a preparative method for a copolymer of the compound of formula (I).

- 25 Another possible aspect of the disclosure is a preparative method for an oligomeric-ring or macrocyclic-ring polymer of the compound of formula (I).

Another possible aspect of the disclosure is a preparative method for novel intermediates useful for preparing a compound of formula (I) and its polymers.

- 30 Another possible aspect of the disclosure is a catalytic preparative method, comprising reacting a suitable substrate molecule with a polymer of the compound of formula (I) to form a reaction product of the substrate molecule having high enantiomeric excess.

Another possible aspect of the disclosure is a supported compound of formula (I).

Another possible aspect of the disclosure is a supported polymer of the compound of formula (I), such as an oligomer, a homopolymer, or a copolymer of formula (I).

5

Detailed Description

Various embodiments of the present disclosure will be described in detail with reference to drawings, if any. Reference to various embodiments does not limit the scope of the invention, which is limited only by the scope of the claims attached hereto. Additionally, any examples set forth in this specification are not intended to be limiting and merely set forth some of the many possible embodiments for the claimed invention.

Definitions

Unless otherwise stated, the following terms used in the specification and claims have the meanings given below.

In various embodiments, halo includes fluoro, chloro, bromo, or iodo. Alkyl, alkoxy, etc., include both straight and branched groups; but reference to an individual radical such as "propyl" embraces only the straight chain radical, a branched chain isomer such as "isopropyl" being specifically referred to.

"Acyl" refers to a radical —C(O)R , where R is hydrogen, alkyl, cycloalkyl, cycloalkylalkyl, phenyl or phenylalkyl wherein alkyl, cycloalkyl, cycloalkylalkyl, and phenylalkyl are as defined herein. Representative examples include, but are not limited to formyl, acetyl, cyclohexylcarbonyl, cyclohexylmethylcarbonyl, benzoyl, benzylcarbonyl, and the like.

"Acylalkyl" refers to a radical —alkylene-C(O)R where R is hydrogen, alkyl, haloalkyl, cycloalkyl, cycloalkyl-alkyl, optionally substituted phenyl, benzyl, hydroxy, alkoxy, amino, monoalkylamino or dialkylamino. Representative examples include methylcarbonyl-methyl, 2-(ethoxycarbonyl)ethyl, 2-(methoxycarbonyl)ethyl, 2-carboxyethyl, and like radicals.

"Acylamino" or refers to an amide radical —NR'C(O)R , where R' is hydrogen or alkyl, and R is hydrogen, alkyl, cycloalkyl, cycloalkylalkyl, phenyl or phenylalkyl wherein alkyl, cycloalkyl, cycloalkylalkyl, and phenylalkyl are as defined herein. Representative examples include, but are not limited to formylamino,

acetylamino, cyclohexylcarbonylamino, cyclohexylmethylcarbonylamino, benzoylamino, benzylcarbonylamino, and like radicals.

"Alkoxy" refers to a radical —OR where R is an alkyl as defined herein, e.g., methoxy, ethoxy, propoxy, butoxy, and like radicals. Similarly, "alkenyloxy" refers to a radical —OR where R is instead an alkenyl as defined herein, e.g., ethenyloxy, propenyloxy, butenyloxy, and like radicals.

"Alkoxy carbonyl" refers to a radical —C(O)—R where R is alkoxy as defined herein.

"Alkenyl" means a linear monovalent hydrocarbon radical of two to six carbon atoms or a branched monovalent hydrocarbon radical of three to six carbon atoms, containing at least one double bond, e.g., ethenyl, propenyl, and like radicals.

"Alkyl" refers to a linear saturated monovalent hydrocarbon radical of one to ten carbon atoms or a branched saturated monovalent hydrocarbon radical of three to six carbon atoms, e.g., methyl, ethyl, propyl, 2-propyl, n-butyl, iso-butyl, tert-butyl, pentyl, and like radicals. "Alkyl" includes linear alkyls, branched alkyls, and cycloalkyls.

"Alkylamino" or "monoalkylamino" refers to a radical —NHR where R represents an alkyl, cycloalkyl or cycloalkyl-alkyl group as defined herein. Representative examples include, but are not limited to methylamino, ethylamino, isopropylamino, cyclohexylamino, and like radicals.

"Alkylene" refers to a linear saturated divalent hydrocarbon radical of one to six carbon atoms or a branched saturated divalent hydrocarbon radical of three to six carbon atoms, e.g., methylene, ethylene, 2,2-dimethylethylene, propylene, 2-methylpropylene, butylene, pentylene, and like radicals.

"Alkynyl" refers to a linear monovalent hydrocarbon radical of two to six carbon atoms or a branched monovalent hydrocarbon radical of three to six carbon atoms, containing at least one triple bond, e.g., ethynyl, propynyl, and like radicals.

"Alkylsulfonyl" refers to a radical $\text{—S(O)}_2\text{R}$ where R is an alkyl, cycloalkyl or cycloalkyl-alkyl group as defined herein, e.g., methylsulfonyl, ethylsulfonyl, propylsulfonyl, butylsulfonyl, cyclohexylsulfonyl, and like radicals.

"Alkylsulfinyl" refers to a radical —S(O)R where R is an alkyl, cycloalkyl or cycloalkylalkyl group as defined herein, e.g., methylsulfinyl, ethylsulfinyl, propylsulfinyl, butylsulfinyl, cyclohexylsulfinyl, and like radicals.

"Alkylthio" refers to a radical —SR where R is an alkyl as defined above, e.g., methylthio, ethylthio, propylthio, butylthio, and like radicals.

"Aryl" refers to a monocyclic, bicyclic, or polycyclic aromatic hydrocarbon radical which is optionally substituted with one or more substituents, preferably one, two or three, substituents preferably selected from the group consisting of alkyl, haloalkyl, hydroxyalkyl, heteroalkyl, acyl, acylamino, amino, alkylamino, dialkylamino, alkylthio, alkylsulfinyl, alkylsulfonyl, —SO₂NR'R" (where R' and R" are independently hydrogen or alkyl), alkoxy, haloalkoxy, alkoxycarbonyl, carbamoyl, hydroxy, halo, nitro, cyano, mercapto, methylenedioxy or ethylenedioxy. More specifically the term aryl includes, but is not limited to, phenyl, chlorophenyl, fluorophenyl, methoxyphenyl, 1-naphthyl, 2-naphthyl, and like radicals, and derivatives thereof. "Aryl" includes a phenyl radical or an ortho-fused bicyclic carbocyclic radical having about nine to twenty ring atoms in which at least one ring is aromatic. Aryl (Ar) can include substituted aryls, such as a phenyl radical having from 1 to 5 substituents, for example, alkyl, alkylene, alkoxy, halo, and like substituents.

"Arylene" refers to a divalent aryl group as defined above, e.g., 1,4-phenylene- (1,4--Ph-), 1,4-arylene-C₂-C₆ alkenyl such as -Ar-CH=CH₂, and like radical

"Arylalkyl" refers to an alkyl radical as defined herein in which one of the hydrogen atoms of the alkyl group is replaced with an aryl group. Typical arylalkyl groups include, but are not limited to, benzyl, 2-phenylethan-1-yl, naphthylmethyl, 2-naphthylethan-1-yl, naphthobenzyl, 2-naphthophenylethan-1-yl, and like radicals.

"Aryloxy" refers to a radical —O—R where R is an aryl group as defined herein.

"Cycloalkyl" refers to a saturated monovalent cyclic hydrocarbon radical of three to seven ring carbons e.g., cyclopropyl, cyclobutyl, cyclohexyl, 4-methylcyclohexyl, and like radicals.

"Cycloalkylene" refers to a divalent saturated monovalent cyclic hydrocarbon radical as defined above.

"Cycloalkenyl" refers to an unsaturated monovalent cyclic hydrocarbon radical of three to ten ring carbons and containing at least one double bond, e.g., cyclopropylene, cyclobutylene, cyclohexylene, 4-methylcyclohexylene, cyclo-octene, and like radicals.

"Cycloalkyl-alkyl" refers to a radical $-R^xR^y$ where R^x is an alkylene group and R^y is cycloalkyl group as defined herein, e.g., cyclohexylmethyl, and like radicals.

"Dialkylamino" refers to a radical $-NRR'$ where R and R' independently represent an alkyl, cycloalkyl, or cycloalkylalkyl group as defined herein. Representative examples include, but are not limited to dimethylamino, methylethylamino, di(1-methylethyl)amino, (cyclohexyl)(methyl)amino, (cyclohexylmethyl)(methyl)amino, and like radicals.

"Haloalkyl" refers to alkyl substituted with one or more same or different halo atoms, e.g., $-\text{CH}_2\text{Cl}$, $-\text{CF}_3$, $-\text{CH}_2\text{CF}_3$, $-\text{CH}_2\text{CCl}_3$, and like radicals.

"Het" includes a four- (4), five- (5), six- (6), seven- (7), or eight- (8) membered saturated or unsaturated heterocyclic ring having 1, 2, 3, or 4 heteroatoms of the group oxy, thio, sulfinyl, sulfonyl, silyl, or nitrogen, which ring is optionally fused to a benzene ring. Het also includes "heteroaryl," which encompasses a radical attached via a ring carbon of a monocyclic aromatic ring containing five or six ring atoms consisting of carbon and 1, 2, 3, or 4 heteroatoms each selected from the group consisting of non-peroxide oxy, thio, and N(X) wherein X is absent or is H, O, (C₁₋₄)alkyl, phenyl or benzyl, as well as a radical of an ortho-fused bicyclic heterocycle of about eight to ten ring atoms derived therefrom, particularly a benz-derivative or one derived by fusing a propylene, trimethylene, or tetramethylene diradical thereto. "Heteroaryl" refers to a monocyclic or bicyclic radical of 5 to 12 ring atoms having at least one aromatic ring containing one, two, or three ring heteroatoms such as N, O, or S, the remaining ring atoms being C, with the understanding that the attachment point of the heteroaryl radical will be on an aromatic ring. The heteroaryl ring can be optionally substituted independently with one or more substituents, preferably one or two substituents, such as alkyl, haloalkyl, hydroxyalkyl, heteroalkyl, acyl, acylamino, amino, alkylamino, dialkylamino, alkylthio, alkylsulfinyl, alkylsulfonyl, $-\text{SO}_2\text{NR}'\text{R}''$ (where R' and R'' are independently hydrogen or alkyl), alkoxy, haloalkoxy, alkoxycarbonyl, carbamoyl, hydroxy, halo, nitro, cyano, mercapto, methylenedioxy, ethylenedioxy, or optionally substituted phenyl. More specifically the term heteroaryl includes, but is not limited to, pyridyl, furanyl, thienyl, thiazolyl, isothiazolyl, triazolyl, imidazolyl, isoxazolyl, pyrrolyl, pyrazolyl, pyrimidinyl, benzofuranyl, tetrahydrobenzofuranyl, tetrahydropyranyl, isobenzofuranyl, benzothiazolyl,

benzothiazolyl, benzotriazolyl, indolyl, isoindolyl, benzoxazolyl, quinolyl, tetrahydroquinolinyl, isoquinolyl, benzimidazolyl, benzisoxazolyl, benzothienyl, and like radicals, or derivatives thereof.

"Heterocyclyl" or "heterocycle" refers to a saturated or unsaturated non-aromatic cyclic radical of 3 to 8 ring atoms in which one or two ring atoms can be a heteroatom, such as NR^x {wherein each R^x is independently hydrogen, alkyl, acyl, alkylsulfonyl, aminosulfonyl, (alkylamino)sulfonyl, (dialkylamino)sulfonyl, carbamoyl, (alkylamino)carbonyl, (dialkylamino)carbonyl, (carbamoyl)alkyl, (alkylamino)carbonylalkyl, or dialkylaminocarbonylalkyl}, O, or $\text{S}(\text{O})_n$ (where n is an integer from 0 to 2), the remaining ring atoms being C. The heterocyclyl ring may be optionally substituted independently with one, two, or three substituents selected from alkyl, haloalkyl, heteroalkyl, halo, nitro, cyanoalkyl, hydroxy, alkoxy, amino, monoalkylamino, dialkylamino, aralkyl, $-(\text{X})_n-\text{C}(\text{O})\text{R}$ (where X is O or NR' , n is 0 or 1, R is hydrogen, alkyl, haloalkyl, hydroxy, alkoxy, amino, monoalkylamino, dialkylamino or optionally substituted phenyl, and R' is hydrogen or alkyl), -alkylene- $\text{C}(\text{O})\text{R}$ (where R is hydrogen, alkyl, haloalkyl, hydroxy, alkoxy, amino, monoalkylamino, dialkylamino or optionally substituted phenyl) or $-\text{S}(\text{O})_n\text{R}^d$ (where n is an integer from 0 to 2, and R is hydrogen (provided that n is 0), alkyl, haloalkyl, cycloalkyl, cycloalkylalkyl, amino, monoalkylamino, dialkylamino, or hydroxyalkyl).

"Heterocyclene" refers to a divalent saturated or unsaturated non-aromatic heterocycle or heterocyclyl as defined herein.

"Heteroarylene" refers to a divalent heteroaryl group as defined above.

"Heteroarylalkyl" refers to an alkyl radical as defined herein in which one of the hydrogen atoms of the alkyl group is replaced with a heteroaryl group.

"Heteroalkyl" refers to an alkyl radical as defined herein wherein one, two or three hydrogen atoms have been replaced with a substituent independently selected from the group consisting of $-\text{OR}^a$, $-\text{NR}^b\text{R}^c$, and $-\text{S}(\text{O})_n\text{R}^d$ (where n is an integer from 0 to 2), with the understanding that the point of attachment of the heteroalkyl radical is through a carbon atom, wherein R^a is hydrogen, acyl, alkyl, cycloalkyl, or cycloalkylalkyl; R^b and R^c are independently of each other hydrogen, acyl, alkyl, cycloalkyl, or cycloalkylalkyl; when n is 0, R^d is hydrogen, alkyl, cycloalkyl, or cycloalkylalkyl, and when n is 1 or 2, R^d is alkyl, cycloalkyl, cycloalkylalkyl, amino, acylamino, monoalkylamino, or dialkylamino. Representative examples include, but

are not limited to, 2-hydroxyethyl, 3-hydroxypropyl, 2-hydroxy-1-hydroxymethylethyl, 2,3-dihydroxypropyl, 1-hydroxymethylethyl, 3-hydroxybutyl, 2,3-dihydroxybutyl, 2-hydroxy-1-methylpropyl, 2-aminoethyl, 3-aminopropyl, 2-methylsulfonylethyl, aminosulfonylmethyl, aminosulfonylethyl, 5 aminosulfonylpropyl, methylaminosulfonylmethyl, methylaminosulfonylethyl, methylaminosulfonylpropyl, and like radicals.

"Hydroxyalkyl" refers to an alkyl radical as defined herein, substituted with one or more, preferably one, two or three hydroxy groups, provided that the same carbon atom does not carry more than one hydroxy group. Representative examples 10 include, but are not limited to, 2-hydroxyethyl, 2-hydroxypropyl, 3-hydroxypropyl, 1-(hydroxymethyl)-2-methylpropyl, 2-hydroxybutyl, 3-hydroxybutyl, 4-hydroxybutyl, 2,3-dihydroxypropyl, 2-hydroxy-1-hydroxymethylethyl, 2,3-dihydroxybutyl, 3,4-dihydroxybutyl and 2-(hydroxymethyl)-3-hydroxypropyl, preferably 2-hydroxyethyl, 2,3-dihydroxypropyl and 1-(hydroxymethyl)-2- 15 hydroxyethyl. Accordingly, as used herein, the term "hydroxyalkyl" is used to define a subset of heteroalkyl groups.

"Leaving group" has the meaning conventionally associated with it in synthetic organic chemistry, i.e., an atom or a group capable of being displaced by a nucleophile and includes halo (such as chloro, bromo, and iodo), alkanesulfonyloxy, 20 arenesulfonyloxy, alkylcarbonyloxy (e.g., acetoxy), arylcarbonyloxy, mesyloxy, tosyloxy, trifluoromethanesulfonyloxy, aryloxy (e.g., 2,4-dinitrophenoxy), methoxy, N,O-dimethylhydroxylamino, and the like.

"Phenylalkyl" refers to an alkyl radical as defined herein in which one of the hydrogen atoms of the alkyl radical has been replaced by an optionally substituted 25 phenyl.

"Polycycle" or "polycyclyl" refers to an alkyl radical having two or more joined rings or cycles.

"Polycyclene" refers to a divalent polycycle alkyl radical as defined herein.

"Polycycloalkenyl" refers to a monovalent polycyclic unsaturated 30 hydrocarbon radical of six to ten ring carbons and containing at least one double bond, e.g., norbornene, and like radicals.

"Homopolymer" and "copolymer" refer to polymer substances having substantially, respectively, homogeneous (i.e., the same) and heterogeneous (i.e., mixed) monomer contents in the polymer chain. A homopolymer of the disclosure

has at least two or more of the same monomers covalently-linked. A homopolymer of the disclosure can have, in embodiments, individual polymer chains having from 2 to about 200,000 total monomer units or more, from 2 to about 100,000 total monomers, from 2 to about 10,000 total monomers, from 2 to about 1,000 total monomers, from 2 to about 100 total monomers, from 2 to about 50 total monomers, and from 2 to more than about 25 total monomers, depending upon, for example, the monomer reactant and reaction conditions selected, the molecular weight, polydispersity, and like considerations. A copolymer of the disclosure has at least two or more different monomers covalently-linked. A copolymer of the disclosure can have, in embodiments, individual polymer chains with from 2 to about 200,000 total monomer units or more, from 2 to about 100,000 total monomers, from 2 to about 10,000 total monomers, from 2 to about 1,000 total monomers, from 2 to about 100 total monomers, from 2 to about 50 total monomers, and from 2 to more than about 25 total monomers, depending upon for example, the reactants and reaction conditions selected, the molecular weight, polydispersity, and like considerations. "Oligomer," "oligomeric," or like terms refer to a subset of either the above "homopolymer" or "copolymer" terms. An oligomer of the disclosure has at least two or more monomers, the monomers being the same or different, and are covalently-linked. An oligomer of the disclosure can have, in embodiments, individual polymer chains having, for example, from 2 to about 25 total monomers or less, such as from 2 to about 20 total monomers, from 2 to about 15 total monomers, from 2 to about 10 total monomers, and from 2 to about 5 total monomers, depending upon for example, the reactants and reaction conditions selected, the desired molecular weight, polydispersity, and like considerations.

"Supported" in the phrase "supported compound of formula (I)" refers to any compound of formula (I) of the disclosure being associated with a suitable carrier. A suitable carrier, in embodiments, can be an oligomeric, a polymeric, a non-polymeric material, or mixtures thereof. The support or carrier can be covalently attached to the compound of formula (I), physically associated with the compound of formula (I) such as coated with or imbibed with the compound or polymer of compound of formula (I), or both covalently attached and physically associated with the compound or polymer of compound of formula (I). A suitable carrier can be, for example, metal oxide or mixed metal oxide particles, such as silicas, aluminas, borates, and like particles, or mixtures thereof, particles having surface structure

such as pores or cavities, such as mesoporous silicas, zeolites, and like particles, magnetic nanoparticles, finely divided metals or metal salts, or mixtures or combinations of the above carriers. Similarly, "supported" in the phrase "supported polymer of the compound of formula (I)" refers to any oligomer, a homopolymer, or a copolymer of formula (I) of the disclosure being the carrier for an integral or covalently bonded catalytic site of the formula (I), or alternatively, being associated with a suitable carrier as defined above.

The indefinite article "a" or "an" and its corresponding definite article "the" as used herein means at least one, or one or more, unless specified otherwise.

"About" modifying, for example, the quantity of an ingredient in a composition, concentration, volume, process temperature, process time, yield, flow rate, pressure, and like values, and ranges thereof, employed in describing the embodiments of the disclosure, refers to variation in the numerical quantity that can occur, for example, through typical measuring and handling procedures used for making compounds, compositions, concentrates or use formulations; through inadvertent error in these procedures; through differences in the manufacture, source, or purity of starting materials or ingredients used to carry out the methods, and like proximate considerations. The term "about" also encompasses amounts that differ due to aging of a formulation with a particular initial concentration or mixture, and amounts that differ due to mixing or processing a formulation with a particular initial concentration or mixture. Whether modified by the term "about" the claims appended hereto include equivalents to these quantities.

"Consisting essentially of" in embodiments refers, for example, to a single compound, mixture of compounds, a polymer or polymers of a compound, or a composition, the method of using the compound or compounds to catalyze reactions, and the resulting enantioselective products of the catalysis of the disclosure, and can include the components or steps listed in the claim, plus other components or steps that do not materially affect the basic and novel properties of the compounds, polymers, compositions, and methods of use of the disclosure, such as the particular substrates, particular catalysts, the particular process conditions, or like structure or process variables selected. Items that may materially affect the basic properties of the components or steps of the disclosure may impart undesirable characteristics to the present disclosure include, for example, decreased enantioselection, decreased resolution, decreased yield, decreased recyclability of the catalyst, and like

characteristics. In embodiments, the compounds, the polymers, or the methods of the present disclosure preferably eliminate or avoid such undesirable characteristics.

"Optionally substituted" refers to any radical which is capable of substitution, such as an alkyl or phenyl group, is further substituted with one or more substituents, preferably one, two or three, substituents selected from, for example, alkyl, haloalkyl, hydroxyalkyl, heteroalkyl, acyl, acylamino, amino, alkylamino, dialkylamino, alkylthio, alkylsulfinyl, alkylsulfonyl, $\text{—SO}_2\text{NR}'\text{R}''$ (where R' and R'' are independently hydrogen or alkyl), alkoxy, haloalkoxy, alkoxycarbonyl, carbamoyl, hydroxy, halo, nitro, cyano, mercapto, methylenedioxy, or ethylenedioxy. More specifically the term includes, but is not limited to chlorophenyl, fluorophenyl, bromophenyl, methylphenyl, ethylphenyl, methoxyphenyl, cyanophenyl, 4-nitrophenyl, 4-trifluoromethylphenyl, 4-chlorophenyl, 3,4-difluorophenyl, 2,3-dichlorophenyl, 3-methyl-4-nitrophenyl, 3-chloro-4-methylphenyl, 3-chloro-4-fluorophenyl or 3,4-dichlorophenyl, and like substituted radicals.

"Optional" or "optionally" means that the subsequently described event or circumstance may but need not occur, and that the description includes instances where the event or circumstance occurs and instances in which it does not. For example, "aryl group optionally mono- or di-substituted with an alkyl group" means that the alkyl may but need not be present, and the description includes situations where the aryl group is mono- or disubstituted with an alkyl group and situations where the aryl group is not substituted with the alkyl group.

"Salt" of a compound refers to a salt that possesses the desired chemical activity of the parent compound or polymer. Such salts include: (1) acid addition salts, formed with inorganic acids such as hydrochloric acid, hydrobromic acid, sulfuric acid, nitric acid, phosphoric acid, and like acid salts, such as BF_3 , BCl_3 , BBr_3 or AlCl_3 ; or formed with organic acids such as acetic acid, propionic acid, hexanoic acid, cyclopentanepropionic acid, glycolic acid, pyruvic acid, lactic acid, malonic acid, succinic acid, malic acid, maleic acid, fumaric acid, tartaric acid, citric acid, benzoic acid, 3-(4-hydroxybenzoyl)benzoic acid, cinnamic acid, mandelic acid, methanesulfonic acid, ethanesulfonic acid, 1,2-ethane-disulfonic acid, 2-hydroxyethanesulfonic acid, benzenesulfonic acid, 4-chlorobenzenesulfonic acid, 2-naphthalenesulfonic acid, 4-toluenesulfonic acid, camphorsulfonic acid, 4-methylbicyclo[2.2.2]-oct-2-ene-1-carboxylic acid, glucoheptonic acid, 3-

phenylpropionic acid, trimethylacetic acid, tertiary butylacetic acid, lauryl sulfuric acid, gluconic acid, glutamic acid, hydroxynaphthoic acid, salicylic acid, stearic acid, muconic acid, and the like; or (2) salts formed when an acidic proton present in the parent compound either is replaced by a metal ion, e.g., an alkali metal ion, an alkaline earth ion, or an aluminum ion; or coordinates with an organic base such as ethanamine, diethanamine, triethanamine, nitromethamine, N-methylglucamine, and like salts. Salts may be obtained using standard procedures well known in the art, for example, by reacting a sufficiently basic compound such as an amine with a suitable acid affording an acceptable anion. Alkali metals, for example, sodium, potassium or lithium, or alkaline earth metal salts, for example, calcium, of carboxylic acids can also be made. In embodiments, certain of the abovementioned salts can be selected as a suitable L counterion or ligand in a compound or a polymer of the formula (I) of the disclosure.

The carbon atom content of various hydrocarbon-containing moieties is indicated by a prefix designating a lower and upper number of carbon atoms in the moiety, i.e., the prefix C_{i-j} indicates a moiety of the integer "i" to the integer "j" carbon atoms, inclusive. Thus, for example, (C₁-C₆)alkyl or C₁₋₆alkyl refers to alkyl of one to seven carbon atoms, inclusive, and (C₁-C₄)alkyl or C₁₋₄alkyl refers to alkyl of one to four carbon atoms, inclusive.

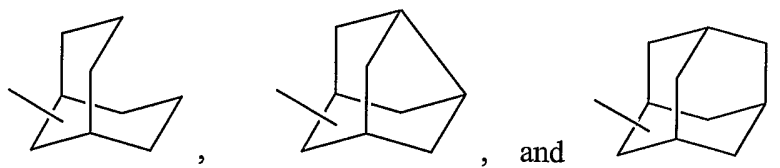
The compounds of the present disclosure are generally named according to the IUPAC nomenclature system. Abbreviations, which are well known to one of ordinary skill in the art, may be used (e.g., "Ph" for phenyl, "Me" for methyl, "Et" for ethyl, "h" for hour or hours, "g" or "gm" for gram(s), "mL" for milliliters, and "rt" for room temperature).

Compounds that have the same molecular formula but differ in the nature or sequence of bonding of their atoms or the arrangement of their atoms in space are termed "isomers." Isomers that differ in the arrangement of their atoms in space are termed "stereoisomers." Stereoisomers that are not mirror images of one another are termed "diastereomers" and those that are non-superimposable mirror images of each other are termed "enantiomers". When a compound has an asymmetric center, for example, if a carbon atom is bonded to four different groups, a pair of enantiomers is possible. An enantiomer can be characterized by the absolute configuration of its asymmetric center and is described by the R- and S-sequencing rules of Cahn and Prelog, or by the manner in which the molecule rotates the plane

of polarized light and designated as dextrorotatory or levorotatory (i.e., as (+) or (-)-isomers respectively). A chiral compound can exist as either individual enantiomer or as a mixture thereof. A mixture containing equal proportions of the enantiomers is called a "racemic mixture". The compounds of this disclosure may possess one or
5 more asymmetric centers; such compounds can therefore be produced as individual (R)- or (S)-stereoisomers or as mixtures thereof. Unless indicated otherwise, the description or naming of a particular compound in the specification and claims is intended to include both individual enantiomers and mixtures, racemic or otherwise, thereof. The methods for the determination of stereochemistry and the separation of
10 stereoisomers are well-known in the art (see discussion in Chapter 4 of "Advanced Organic Chemistry", 4th edition J. March, John Wiley and Sons, New York, 1992).

Specific and preferred values listed below for radicals, substituents, and ranges, are for illustration only; they do not exclude other defined values or other values within defined ranges for the radicals and substituents. The compounds of
15 the disclosure include compounds of formulas (I) and like compounds having any combination of the values, specific values, more specific values, and preferred values described herein. Specifically, aryl can be phenyl, naphthyl, anthracenyl, phenanthrenyl, fluorenyl, tetrahydronaphthyl, or indanyl.

Specifically, C₁-C₆ alkyl can be methyl, ethyl, propyl, isopropyl, butyl, iso-
20 butyl, sec-butyl, *tert*-butyl, pentyl, 3-pentyl, or hexyl; C₃₋₁₂ cycloalkyl can be cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, and bicyclic, or multi- or polycyclic substituents, such as of the formulas



25

and unsaturated or polycycloalkenyl analogs; C₁-C₆ alkoxy, can be methoxy, ethoxy, propoxy, isopropoxy, butoxy, iso-butoxy, sec-butoxy, pentoxy, 3-pentoxy, or hexyloxy; -C(=O)alkyl or (C₂₋₇)alkanoyl or ketone can be acetyl, propanoyl, butanoyl, pentanoyl, 4-methylpentanoyl, hexanoyl, or heptanoyl; aryl can be phenyl,
30 indenyl, or naphthyl; Het or heterocycle can be pyrrolidinyl, piperidinyl, morpholinyl, thiomorpholinyl, or heteroaryl; and heteroaryl can be furyl, imidazolyl,

triazolyl, triazinyl, oxazolyl, isoxazolyl, thiazolyl, isothiazolyl, pyrazolyl, pyrrolyl, pyrazinyl, tetrazolyl, pyridyl, (or its N-oxide), thienyl, pyrimidinyl (or its N-oxide), indolyl, isoquinolyl (or its N-oxide) or quinolyl (or its N-oxide).

Specifically, $-(CH_2)_k-$ can be a $-(C_{1-8}\text{alkylene})-$ when k is an integer from 1 to about 8, which can be methylenyl, ethylenyl, propylenyl, butylenyl, pentylenyl, 3-pentylenyl, hexylenyl, heptylenyl, or octylenyl.

A specific value for Het includes a five- (5), six- (6), or seven- (7) membered saturated or unsaturated ring containing 1, 2, 3, or 4 heteroatoms, for example, non-peroxide oxy, thio, sulfinyl, sulfonyl, and nitrogen; as well as a radical of an ortho-fused bicyclic heterocycle of about eight to twelve ring atoms derived therefrom, particularly a benz-derivative or one derived by fusing a propylene, trimethylene, tetramethylene or another monocyclic Het diradical thereto.

A specific value for the linker L' is $-(C\equiv C)_k-R_5$, wherein R_5 is arylene, and k is 1.

Another specific value for the linker L' is $-(C\equiv C)_k-R_5$, wherein R_5 is an optionally substituted arylene, and k is 0.

Another specific value for the linker L' is an optionally substituted -Ph-.

Another specific value for the linker L' is an optionally substituted -Ph-Ph-.

Another specific value for the linker L' is an optionally substituted naphthalyl.

Another specific value for the linker L' is $-C_1-C_6$ alkylene-O- C_1-C_6 alkylene-.

Another specific value for the linker L' is $-CH_2-O-(CH_2)_2-$.

Another specific value for L' is single carbon-carbon bond.

A specific value for the connector Z is $-C(=O)O-$ or $-O-C(=O)-$.

Another specific value for Z is $-C(=O)O-$.

Another specific value for Z is single carbon-carbon bond.

A specific value for the polymerizable group P is C_2-C_6 alkenyl.

Another specific value for P is C_2 alkenyl.

Another specific value for P is arylene- C_2-C_6 alkenyl.

Another specific value for P is $-\text{Ph}-CH_2=CH_2$.

Another specific value for P is cycloalkenyl.

Another specific value for P is cyclo-octene.

Another specific value for P is norbornene.

A specific value for R_3 is a single carbon-carbon bond.

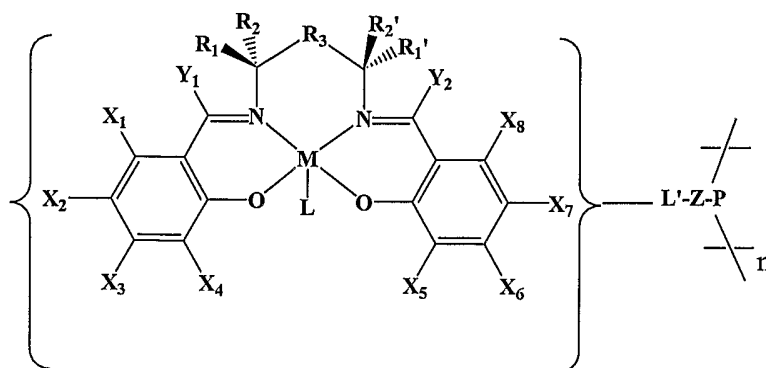
Another specific value for R_3 is $-\text{CH}_2-$.

- Another specific value for R_3 is —O— .
 A specific value for M is absent.
 Another specific value for M is Co.
 Another specific value for M is Mn.
 5 Another specific value for M is Ru.
 Another specific value for M is Cr.
 Another specific value for M is Al.
 A specific value for L is absent.
 Another specific value for L is halide.
 10 Another specific value for L is Cl.
 Another specific value for L is I.
 Another specific value for L is —OAc or acetate.
 Another specific value for L is —OTs or —tosylate .
 A specific compound of the formula (I) is the formula (I) wherein X_1 , X_2 , X_3 ,
 15 X_4 , X_5 , X_6 , X_7 , X_8 , Y_1 and Y_2 are independently H, $C_1\text{--}C_6$ alkyl, and $C_1\text{--}C_6$ alkoxy,
 and at least one X_1 , X_2 , X_3 , X_4 , X_5 , X_6 , X_7 , X_8 , Y_1 and Y_2 is —L'—Z—P .
 Another specific compound of the formula (I) is the formula (I) wherein X_1 ,
 X_3 , X_4 , X_5 , X_6 , X_7 and X_8 are independently H or t-butyl; Y_1 and Y_2 are H; R_1 and
 R'_2 are a carbocycle or heterocycle comprising 4 to 10 atoms, when R_2 and R'_1 are H,
 20 or R_1 and R'_2 are H, when R_2 and R'_1 are a carbocycle or heterocycle comprising 4 to
 10 atoms; R_3 is a single carbon-carbon bond; and X_2 is —L'—Z—P .
 Another specific compound of the formula (I) is formula (I) wherein X_1 , X_3 ,
 X_6 , and X_8 are H; X_4 , X_5 , and X_7 are t-butyl; Y_1 and Y_2 are H; R_1 and R'_2 are a -
 $(CH_2)_4\text{—}$, when R_2 and R'_1 are H, or R_1 and R'_2 are H, when R_2 and R'_1 are a $\text{—}(CH_2)_4\text{—}$;
 25 R_3 is a single carbon-carbon bond; X_2 is —L'—Z—P where
 L' is a single carbon-carbon bond or $\text{—}(C\equiv C)_k\text{—Ar—}$, where k is 1;
 Z is —C(=O)O— or —O—C(=O)— ;
 P is $C_2\text{--}C_6$ alkenyl, cycloalkenyl, or polycycloalkenyl;
 M is Co, Mn, or mixtures thereof; and
 30 L is absent or a halide anion selected from F, Cl, Br, and I; or a salt or hydrate
 thereof.
 Another specific compound of the formula (I) is formula (I) wherein X_2 is —L'—Z—P where L' is a single carbon-carbon bond or $\text{—}(C\equiv C)_k\text{—Ar—}$, where k is 1; Z is —C(=O)O— or —O—C(=O)— ; P is ethenyl, 5-cyclooctenyl, or 4-norbornenyl; M is Co or

Mn; and L is absent or a halide anion such as F, Cl, Br, and I; or a salt or hydrate thereof.

A specific homopolymer of the compound of the formula (I) is of the formula:

5



wherein

10 $R_1, R_2, R'_1, R'_2, X_1, X_2, X_3, X_4, X_5, X_6, X_7, X_8, Y_1$ and Y_2 are as defined herein, and at least one $X_1, X_2, X_3, X_4, X_5, X_6, X_7, X_8, Y_1$ and Y_2 is independently of the formula $-L'-Z-P$ as defined herein;

M is a metal atom or ion is at least one of Co, Mn, Cr, Al, Zn, Ru, Fe, Mo, Ni, or mixtures thereof;

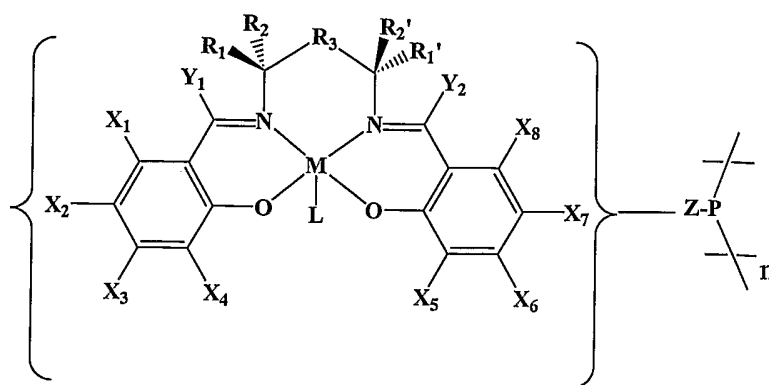
L is a halide anion selected from F, Cl, Br, and I; and

15 n is 2 to 2,500;

or a salt or hydrate thereof.

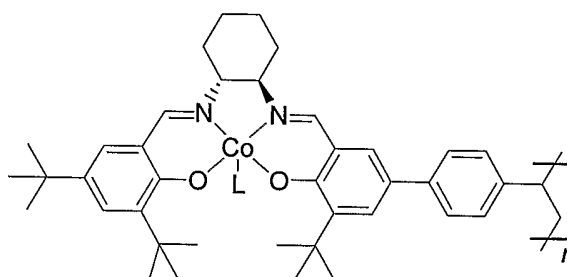
Another specific homopolymer of the compound of the formula (I) is of the above formula wherein $R_1, R_2, R'_1, R'_2, X_1, X_2, X_3, X_4, X_5, X_6, X_7, X_8, Y_1$ and Y_2 are as defined above, and only one of $X_1, X_2, X_3, X_4, X_5, X_6, X_7, X_8, Y_1$ and Y_2 is of the
20 formula $-L'-Z-P$ as defined herein.

Another specific homopolymer of the compound of the formula (I) is of the formula:



where R₁, R₂, R_{1'}, R_{2'}, X₁, X₂, X₃, X₄, X₅, X₆, X₇, X₈, Y₁ and Y₂ are as defined herein, and at least one X₁, X₂, X₃, X₄, X₅, X₆, X₇, X₈, Y₁ and Y₂ is independently of the formula -L'-Z-P as defined herein; and L' is a single carbon-carbon bond.

Another specific homopolymer of the compound of the formula (I) is of the formula:

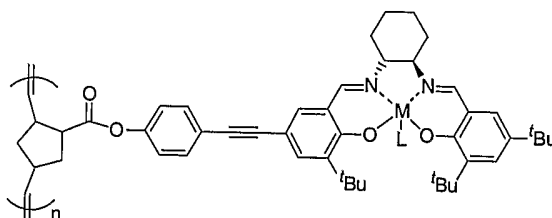


wherein

L is absent, or a tosylate, an acetate, or a halide anion selected from F, Cl, Br, and I; and

n is 2 to 2,500; or a salt or hydrate thereof.

Another specific homopolymer of the compound of the formula (I) is of the formula:



wherein

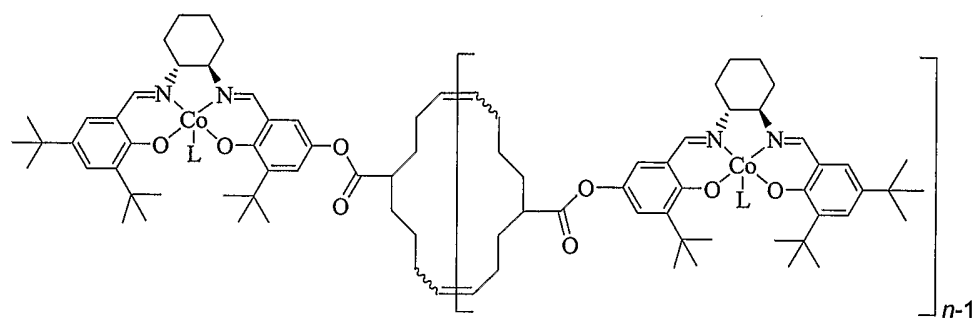
M is a metal atom or ion of at least one of Co, Mn, or mixtures thereof;

L is absent, or a tosylate, an acetate, or a halide anion selected from F, Cl, Br, and I; and

n is 2 to 2,500; or a salt or hydrate thereof.

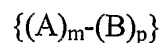
Another specific homopolymer or oligomer of the compound of the formula

5 (I) is the ring-expanded formula:



wherein L is a counterion as defined herein, for example, a tosylate, an acetate, or a
10 halide anion selected from F, Cl, Br, and I; and n is 2 to 100; or a salt or hydrate thereof.

A specific copolymer of the compound of the formula (I) is of the formula:



15

where

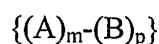
A is a mer representing the polymerized compound of formula (I);

B is a co-polymerized monomer;

m is an integer from 1 to about 1,000; and

20 p is an integer from 1 to about 10,000.

Another specific copolymer of the compound of the formula (I) is of the formula:



25

where

A is the polymerized compound of formula (I);

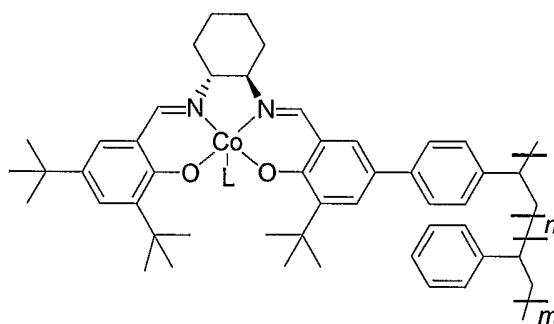
B is a co-polymerized monomer of at least one of an olefin, a perfluorinated olefin, a silane or siloxane substituted olefin, a diene, an alkenylaryl, an acrylate, or mixtures thereof;

m is an integer from 10 to about 100; and

5 p is an integer from 10 to about 1,000.

Another specific copolymer of the compound of the formula (I) is of the formula $\{(A)_m-(B)_p\}$ where A is a mer representing the polymerized compound of formula (I) and B is a co-polymerized monomer of, for example, ethylene, propylene, butadiene, styrene, norbornene, an alkylcarboxy substituted norbornene, an acrylate, or mixtures thereof;

Another specific copolymer of the compound of the formula (I) is of the formula:



15

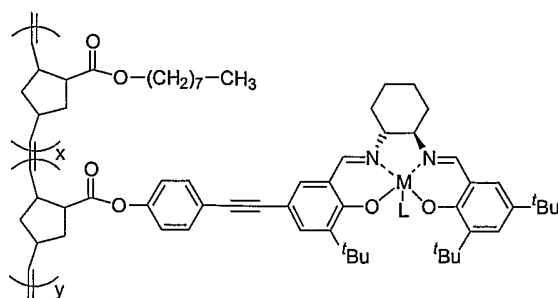
wherein

L is a counterion as defined herein, for example, a tosylate, an acetate, or a halide anion selected from F, Cl, Br, and I;

m is 2 to 100; and

20 n is 2 to 50; or a salt or hydrate thereof.

Another specific copolymer of the compound of the formula (I) is of the formula:



wherein

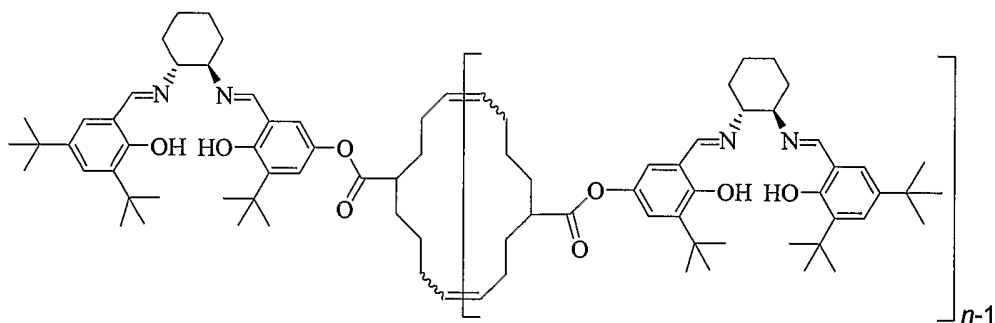
M is Mn, Co, or mixtures thereof;

5 L is absent, or a counterion as defined herein, for example, a tosylate, an acetate, or a halide anion selected from F, Cl, Br, and I;

x is 2 to 100; and

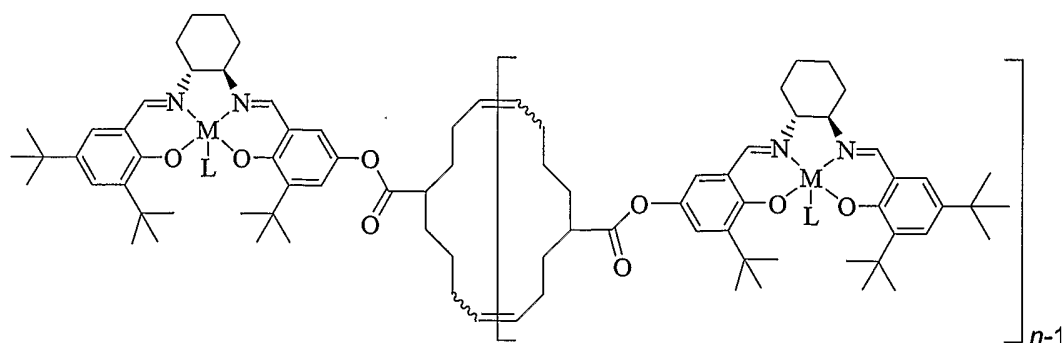
y is 2 to 50; or a salt or hydrate thereof.

A specific homopolymer or oligomer of formula (I) is the unsymmetrical
10 oligomeric macrocycle of the formula:



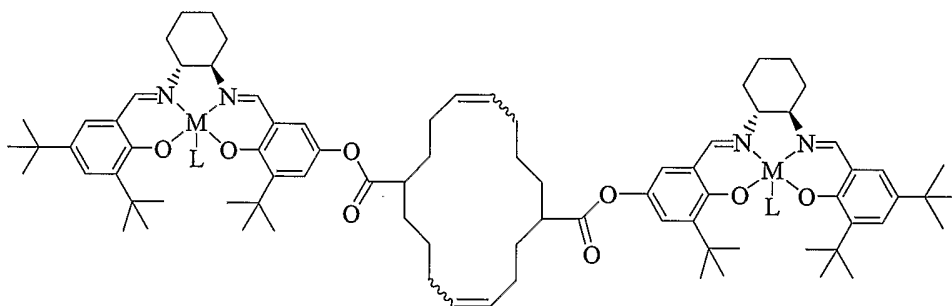
15 where M and L are absent, and n is from 2 to about 2,500.

Another specific cyclic homopolymer or oligomer of formula (I) is the metalated unsymmetrical oligomeric macrocycle catalyst of the formula:



where M is Co, L is absent or a counter ion, and n is from 2 to about 100.

Another specific oligomer of formula (I) is the metalated unsymmetrical
 5 dimeric macrocycle of the formula:



where M is Co, and L is absent or a counter ion.

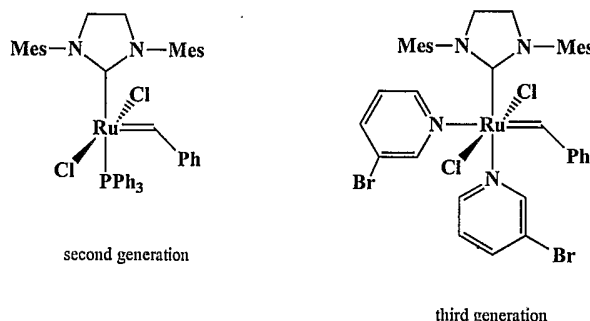
10 Another specific oligomer of formula (I) is the unmetalated unsymmetrical
 dimer macrocycle of the above formula, i.e., M and L absent.

The abovementioned specific and preferred compounds and polymers can
 include, for example, individual isomers, racemic and non-racemic mixtures of
 isomers, and salts and solvates thereof.

15 In embodiments, the present disclosure provides a method for preparing a
 homo-polymer of the compound of formula (I), comprising: heating the compound
 of formula (I) with a free radical initiator, for example, a carbon centered free
 radical source such as AIBN, or like carbon centered free radical source, or an
 oxygen centered free radical source such as an benzoyloxy radical (Ph-CO-O·), or
 20 like oxygen centered free radical source.

In embodiments, the present disclosure provides a method for preparing an
 oligomeric-ring or macrocyclic-ring homo-polymer of the compound of formula (I)

comprising: reacting the compound of formula (I) with a second or a third generation (3^o) Grubbs catalyst, for example, of the formulas:



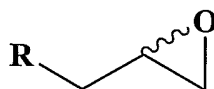
5

where Mes is a mesylate radical, $-\text{O}(\text{S}=\text{O})_2\text{CH}_3$, or like substituents.

In embodiments, the present disclosure provides a method for preparing a co-polymer of the compound of formula (I) comprising: heating the compound of formula (I) with a free radical initiator and at least one monomer selected from olefin, diene, alkenylaryl, acrylate, or mixtures thereof.

10

In embodiments, the present disclosure provides a method of preparing a chiral epoxide or chiral 1,2-diol by stereoselective hydrolysis (HKR) of a racemic epoxide of the formula



15

wherein R is hydrogen, C₁-C₁₀ alkyl, C₂-C₆ alkenyl, C₂-C₆ alkynyl, C₃-C₈ cycloalkyl, C₁-C₁₀ alkoxy, aryl, carbonyl, carboxy, ketone, aldehyde, ester, phosphoryl, phosphonate, phosphine, sulfonyl, or $-(\text{CH}_2)_k\text{R}_5$ wherein, R₅ is C₂-C₆ alkenyl, C₂-C₆ alkynyl, C₂-C₆ alkoxy, unsaturated alkoxy, aryl, cycloalkyl, cycloalkenyl, heterocycle, polycycle, halogen, hydroxy, amino, thiol, nitro, amine, imine, amide, carbonyl, carboxy, silyl, ether, thioether, seleno ether, ketone, aldehyde, ester, phosphoryl, phosphonate, phosphine, sulfonyl and k is an integer of 0 to 8, the method comprising:

20

contacting the racemic epoxide with water in the presence of a catalytic amount of a chiral homo-polymer, a chiral copolymer, or a chiral oligomer of the compound of formula (I) as defined herein,

wherein

$X_1, X_3, X_6,$ and X_8 are H;

$X_4, X_5,$ and X_7 are t-butyl;

Y_1 and Y_2 are H;

5 R_1 and R'_2 are a $-(CH_2)_4-$, when R_2 and R'_1 are H, or R_1 and R'_2 are H, when R_2 and R'_1 are a $-(CH_2)_4-$;

R_3 is a single carbon-carbon bond;

X_2 is $-L'-Z-P$ where

L' is $-(C\equiv C)_k-Ar-$ where k is 1;

10 Z is $-C(=O)O-$ or $-O-C(=O)-$;

P is a polymerized C_2-C_6 alkenyl, or polycycloalkenyl;

M is Co; and

L is absent or a counterion as defined herein, for example, a tosylate, an acetate, or a halide anion;

15 or a salt or hydrate thereof;

In embodiments, the present disclosure also provides a method of preparing an asymmetric epoxide of an olefin comprising:

contacting the olefin with a catalytic amount of a chiral homo-polymer or chiral copolymer of the compound of formula (I) as defined herein, and optionally in
20 the presence of an oxygen source, such as N-methyl-morpholino-N-oxide,

wherein

$X_1, X_3, X_6,$ and X_8 are H;

$X_4, X_5,$ and X_7 are t-butyl;

Y_1 and Y_2 are H;

25 R_1 and R'_2 are a $-(CH_2)_4-$, when R_2 and R'_1 are H, or R_1 and R'_2 are H, when R_2 and R'_1 are a $-(CH_2)_4-$;

R_3 is a single carbon-carbon bond;

X_2 is $-L'-Z-P$ where

L' is $-(C\equiv C)_k-Ar-$;

30 Z is $-C(=O)O-$ or $-O-C(=O)-$;

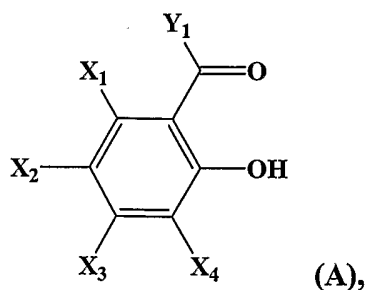
P is C_2-C_6 alkenyl, or polycycloalkenyl;

M is Mn; and

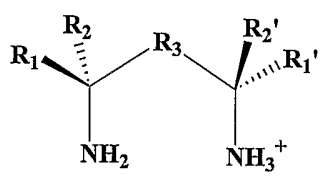
L is absent or as define herein;

or a salt or hydrate thereof.

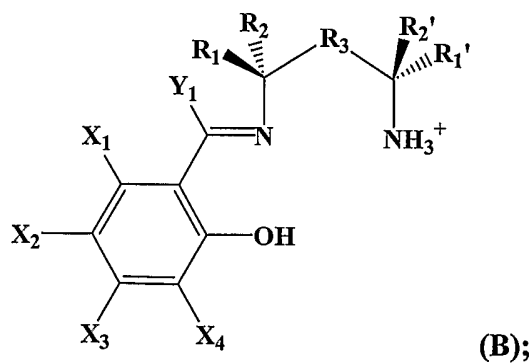
In embodiments, the present disclosure provides a single-pot method for preparing the compound of formula (I), the method comprising:
 reacting a salicylaldehyde compound of the formula (A):



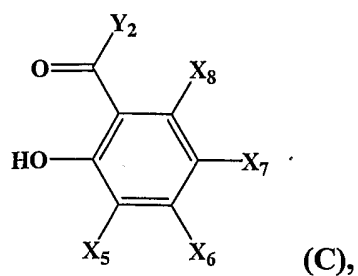
with an (R,R)-diamino mono-ammonium salt of the formula:



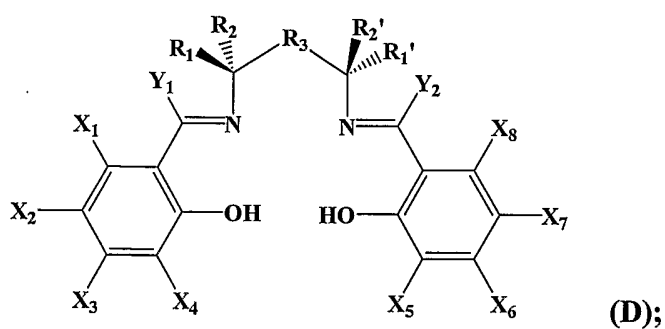
to form a mono-ammonium imine of the formula (B):



deprotecting the mono-ammonium imine of formula (B) with a base and thereafter reacting the deprotected imine with an aldehyde of formula (C):

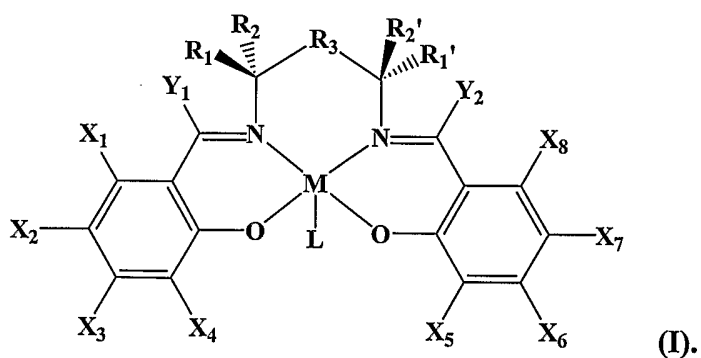


to form an unsymmetrical substituted salen of formula (D):

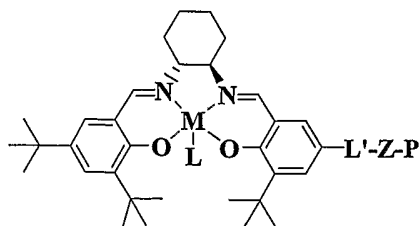


and

optionally reacting the salen of formula (D) with a metal salt to form the metalated-salen complex of the formula (I):



In embodiments, the present disclosure provides a single-pot method for preparing a compound of formula (I) in high yield, wherein the compound of formula (I) can be, for example:



where -L'-Z-P, M, and L can be any of the values as defined herein.

In embodiments, the above methods for preparing the compound of formula
 5 (I) can include isolation of intermediate compounds, if desired, although generally unnecessary.

General Synthetic Schemes

The compounds of the present invention can be prepared in a number of
 10 ways known to one skilled in the art. Preferred methods include, but are not limited to, the general synthetic procedures described below. These schemes are merely illustrative of some methods by which the compounds of this disclosure can be synthesized, and various modifications to these schemes can be made and will be suggested to one skilled in the art having referred to this disclosure. The starting
 15 materials and the intermediates of the reaction may be isolated and purified if desired using conventional techniques, including but not limited to filtration, distillation, crystallization, chromatography, and like methods. Such materials may be characterized using conventional means, including physical constants and spectral data.

20 The starting materials and reagents used in preparing these compounds are either available from commercial suppliers, such as Sigma-Aldrich Chemical Co., (St. Louis, Mo., USA), Maybridge (Dist: Ryan Scientific, P.O. Box 6496, Columbia, S.C. 92960), Bionet Research Ltd., (Cornwall PL32 9QZ, UK), Menai Organics Ltd., (Gwynedd, N. Wales, UK), or are prepared by methods known to those skilled
 25 in the art following procedures set forth in references such as Fieser and Fieser's Reagents for Organic Synthesis, Volumes 1-17 (John Wiley and Sons, 1991); Rodd's Chemistry of Carbon Compounds, Volumes 1-5 and Supplementals (Elsevier Science Publishers, 1989), Organic Reactions, Volumes 1-40 (John Wiley and Sons, 1991), March's Advanced Organic Chemistry, (John Wiley and Sons, 1992), House's
 30 Modern Synthetic Reactions (W. A. Benjamin, New York, 1972); and Larock's

Comprehensive Organic Transformations (VCH Publishers Inc., 1989). It may be desirable to optionally use a protecting group during all or portions of the above described or alternative synthetic procedures. Such protecting groups and methods for their introduction and removal are well known in the art. See Greene's

5 "Protecting Groups In Organic Synthesis," (John Wiley & Sons, 1991).

Styrene is one of the monomers used in the example co-polymerizations. Many other monomers are also equally suitable, and include for example, a substituted styrene such as vinyltoluene and bromostyrene, an acrylic acid, an acrylonitrile, an acrylamide, an alkylacrylate such as methyl methacrylate, a diene

10 such as a butadiene, an isoprene, a vinyl ester, a vinyl ether, a vinyl pyridine, a vinylidene chloride, a vinyl chloride, a fluorinated or perfluorinated alkylene such as tetrafluoroethylene, a silane substituted monomer, a siloxane substituted monomer, an epoxy monomer, and derivatives of these compounds. Other suitable monomers can include, for example, cyclic, bicyclic, or polycyclic monomers, for example,

15 norbornene, cyclooctene, cyclooctadiene, cyclcooctatetraene, cyclobutene, cyclopentene, cyclopentadiene, barrelenes such as bicyclo[2.2.2]octenes, and functionalized versions thereof. Functionalized versions include, for example, optionally substituted olefins or dienes, such as substituted with an acid, ester, aldehyde, ketone, amide, C₁-C₆ alkyl, C₃₋₁₂ cycloalkyl, aryl, het, C₁-C₆ alkoxy,

20 halogen, -OH, -SH, -NO₂, -NH₂, amino, imine, carboxy, silyl, ether, thio ether, seleno ether, phosphoryl, phosphonate, phosphine, sulfonyl, and like functional groups, or combinations thereof. Additionally, suitable co-monomers can include mixtures of two or more different monomer, such as styrene/butadiene, styrene/vinyltoluene, vinyltoluene/tert-butylstyrene, and like combinations.

25 Copolymers can include two or more monomers in combination with a polymerizable catalyst monomer to form for example, terpolymers, and like mixed copolymers, and including all permutations of monomer combinations and geometries, such as random, alternating, block, di-block, multi-block, graded, tapered, linear, branched, comb, dendritic, and like forms. If desired, known cross-

30 linking agents, such as divinylbenzene, and cross-linking methodologies can be used, either during polymerization or in post-polymerization processing, to further tailor the physical parameters and catalytic properties of the catalyst complexes. Similarly, known branching agents and branching methodologies can be used, either during polymerization or in post-polymerization processing, to further tailor the

physical parameters and catalytic properties of the catalyst complexes. In addition to ring-opening metathesis polymerization (ROMP) and the polymerizations processes illustrated herein, other polymerization methodologies can be used in conjunction with a compound of formula (I), if desired, to obtain the polymer or oligomer products of the disclosure, for example, other olefin metathesis methods such as ADMET (acyclic diene metathesis), controlled radical polymerization techniques such as ATRP (atom transfer radical polymerization), RAFT (reversible addition fragmentation transfer polymerization), NMP (nitroxide mediate polymerizations), or SFR (stable free radical polymerizations, see for example USP 5,322,912 and its progeny).

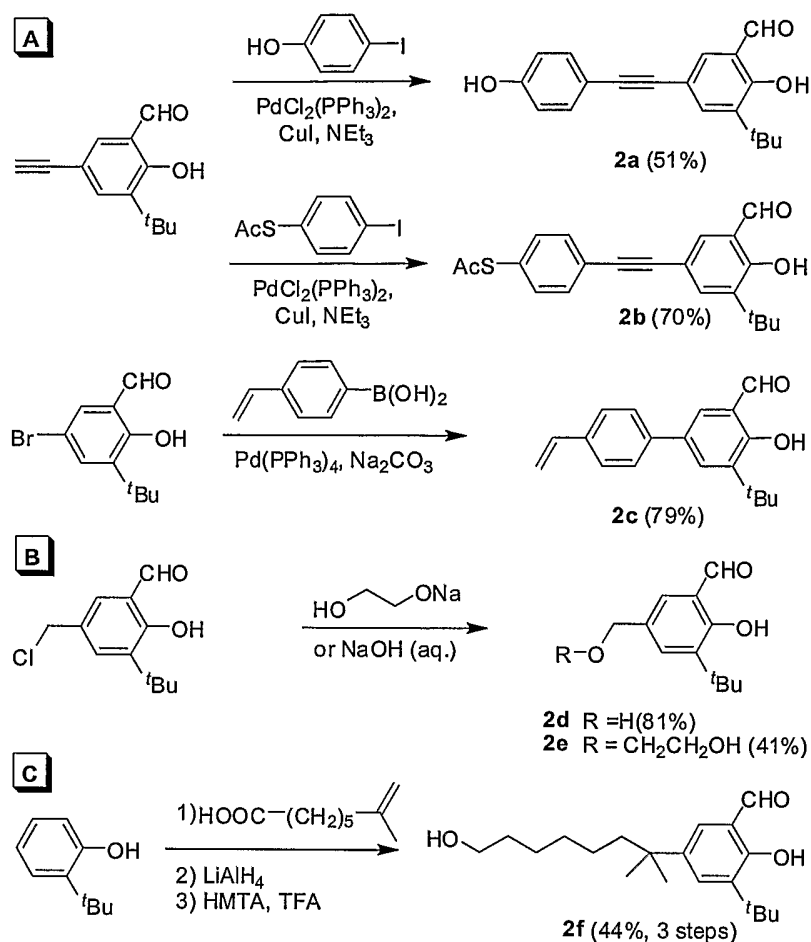
Preparation of compounds of formula (I) and their conversion to homopolymers, copolymers, and oligomers, are illustrated in Schemes 1-9.

Synthesis of Compounds of formula (I) - Monomer Ligands

Compounds of formula (I) are generally prepared as shown schematically below and as described in greater detail in the Experimental and Examples section.

Several salicylaldehydes functionalized with an immobilizing or coupling group, such as, -OH, -SAc, or -CH=CH₂, and a linker (L') of either a rigid spacer (phenylacetylene or phenylene) or a flexible spacer (alkyl or ethylene glycol) were prepared as precursors in the synthesis of unsymmetrical salen ligands, as outlined in Scheme 1.

For the preparation rigid of linker-based compounds, a Pd-catalyzed Sonogashira or Suzuki coupling reactions to yield **2a-c** (Path A) was employed. Both coupling reactions showed tolerance to the presence of hydroxy, acetylsulfanyl, vinyl, or formyl functional groups. Salicylaldehydes **2d** and **2e** were produced by nucleophilic substitutions of 3-*tert*-butyl-5-chloromethylsalicylaldehyde with RNa (R = -H, -CH₂CH₂OH) (Path B). Friedel-Crafts alkylation of 2-*tert*-butylphenol with 7-methyl-7-octenoic acid, followed by the reduction of the carboxylic acid with LiAlH₄ and the acid-catalyzed formylation reaction produced **2f** with a long alkyl chain (Path C).



Scheme 1. Synthesis of the salicylaldehydes 2.

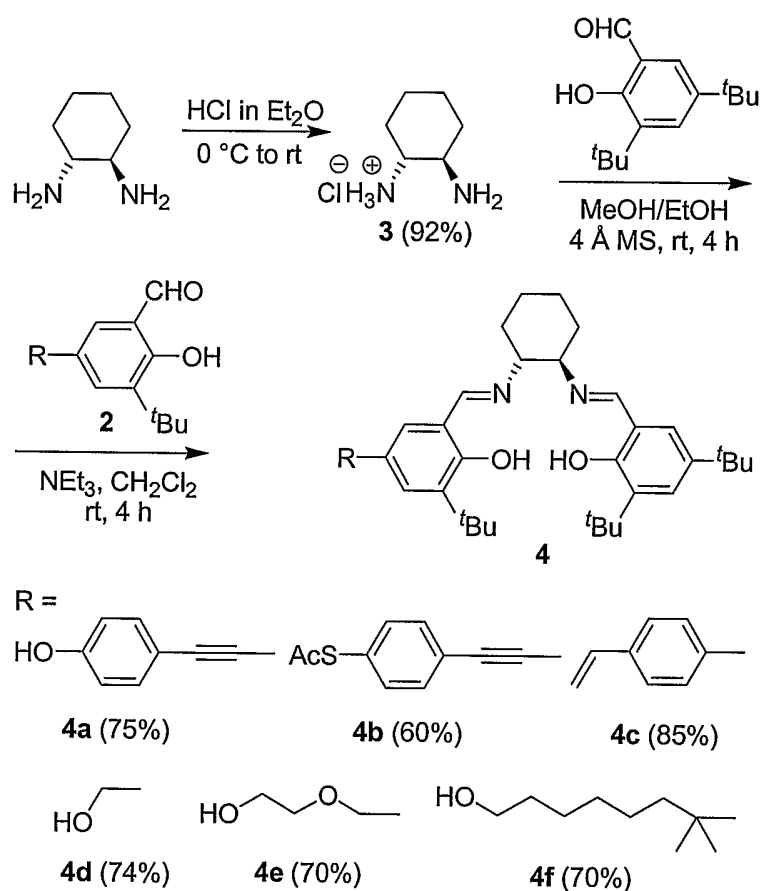
5 As shown in Scheme 2, for the preparation of enantiopure unsymmetrical salen ligands, a one-pot approach was used to avoid the isolation step of the mono-imine intermediate that is prone to the undesired disproportionation reaction. Hydrogen chloride was selected to form a protective acid salt of one amine group of the diamine. The mono-ammonium salt 3 was prepared in near quantitative yield from a 1:1 molar ratio of (*R,R*)-diaminocyclohexane and 2.0 M hydrogen chloride in ether. The first condensation between 3 and 3,5-di-*tert*-butylsalicylaldehyde was carried out in a 1:1 (v/v) mixture of anhydrous methanol and ethanol at ambient temperature. Use of activated 4 Å molecular sieves to remove the water formed during the reaction was found significant in reducing the reaction time to four hours and depressing the exchange of the salicylidene moieties. After the first condensation was complete, a solution of the functionalized salicylaldehyde 2 in dichloromethane was added to the reaction system, followed by the slow addition of

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an excess of anhydrous triethylamine as a deprotective base. The TLC analysis and ^1H NMR spectra showed that the second condensation was completed within four hours and only traces of symmetrical salens were detected.

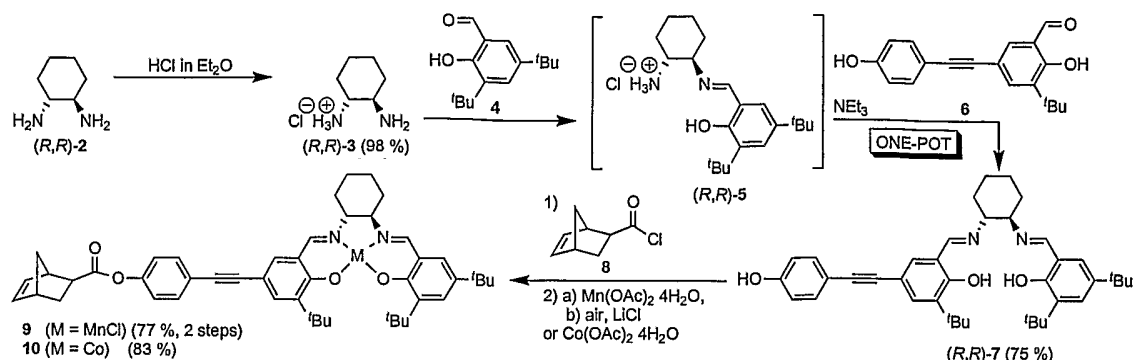
The target unsymmetrical salen ligands **4** were isolated in 60–85% yields as
5 light yellow solids by means of column chromatography on silica gel pretreated with
methanol or methanol/triethylamine. The reaction was very time and reproducibility
efficient and was easily scaled up and carried out on a multigram scale.



Scheme 2. Synthesis of unsymmetrical salen ligands.

The preparation of mono-functionalized Mn- and Co-salen complexes **9** and **10** attached to a norbornene monomer *via* a stable phenylacetylene linker are shown in Scheme 3. The *mono*-functionalized salens were obtained by the de-symmetrization of 1,2-diaminocyclohexane **2** with HCl to yield the mono-ammonium salt **3**. After reaction of **3** with **4**, the resulting mono-ammonium imine **5** was deprotected with NEt₃ in the above described one-pot procedure and reacted

with the functionalized aldehyde **6**. After an esterification of the resulting unsymmetrically substituted salen **7** with **8** and subsequent metalation, the functionalized Mn- and Co-salen norbornenes **9** and **10** were obtained in good yield.



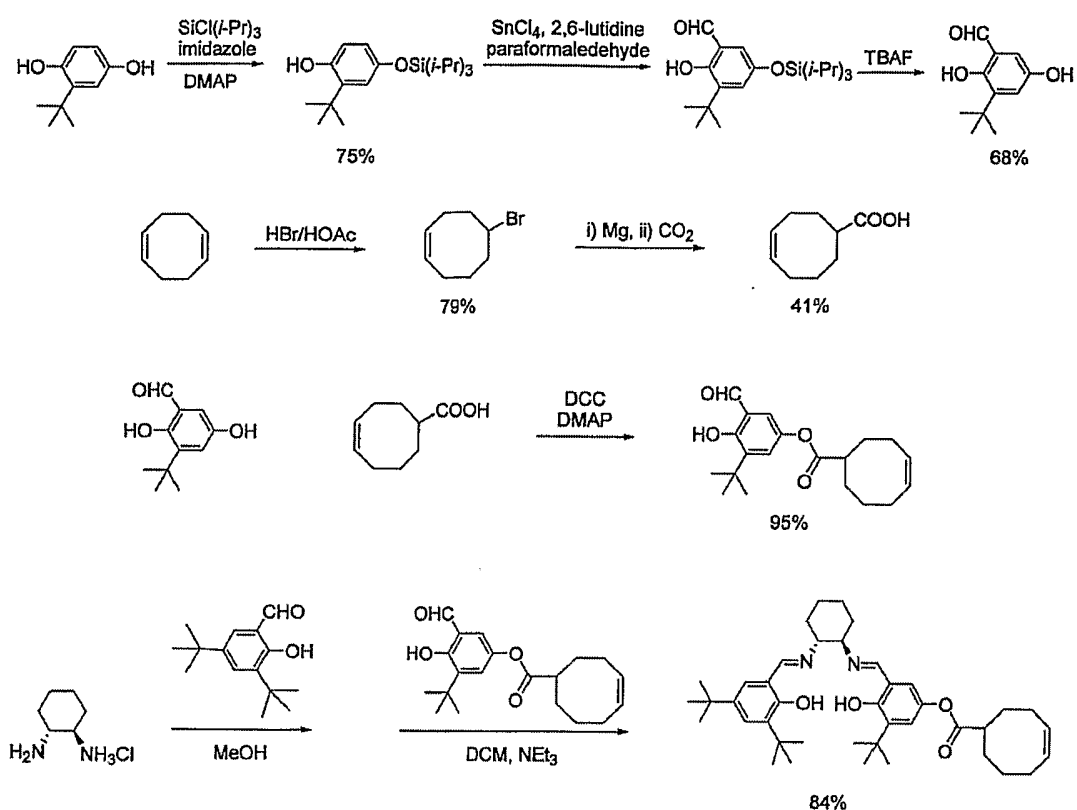
Scheme 3. Synthesis of the norbornene-functionalized salen ligand and their manganese- and cobalt complexes **9** and **10**.

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Cyclooctene-functionalized salen ligands were prepared, for example, as shown Scheme 4. Esterification of 3-*t*-butyl-2,5-dihydroxybenzaldehyde and cyclooct-4-enecarboxylic acid in the presence of 1,3-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) yield the salicylaldehyde cyclooct-4-enecarboxylate product. A one-pot stepwise condensation of (R,R)-diaminocyclohexane mono-ammonium salt with 3,5-di-*t*-butylsalicylaldehyde and the salicylaldehyde cyclooct-4-enecarboxylate in a 1:1:1 molar ratio afforded cyclooct-4-en-1-yl substituted unsymmetrical salen ligand in 84% yield.

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Scheme 4. Synthesis of cyclooctene-functionalized salen ligands.

5 Polymerization of Compounds of Formula (I)

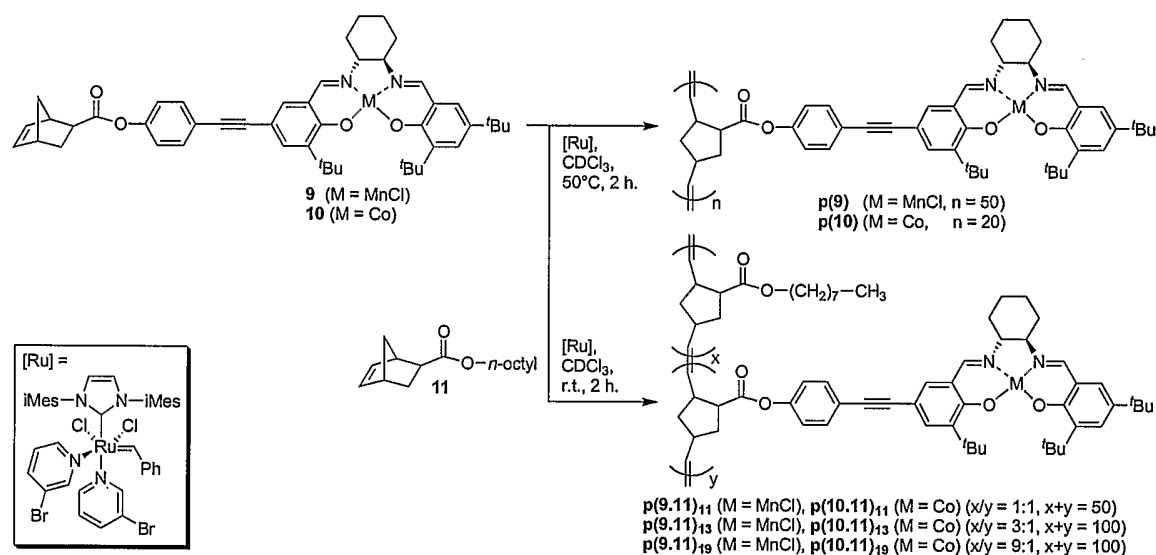
Synthesis and Polymerization of the Mono-Norbornene Functionalized Salens

The monomeric metalized complexes **9** and **10** were homo- and co-polymerized using a controlled polymerization method, such as ring-opening metathesis polymerization (ROMP), and thereby avoided a post-polymerization metal complexation step. The polymeric manganese and cobalt complexes were used as supported catalysts, for example, for asymmetric epoxidations of different olefins and for the hydrolytic kinetic resolution of epoxides. The polymeric catalysts showed excellent catalytic activity and selectivity. Unexpectedly, the activity and selectivity of the catalyst was found to depend upon the density of the catalytic moieties along the polymer backbones. In general, the copolymer complexes were slightly more active and selective as catalysts compared to the homopolymer complex analogues. This was true for both the manganese and the cobalt-based

catalysts. When the cobalt-salen moieties were present in the copolymer chain at less than about 15 % (i.e., cobalt-salen derived monomer:co-monomer molar ratio) in the polymer backbone a drop in catalytic activity was observed.

ROMP of the analytically pure and fully characterized monomers using the [Ru] 3^o-generation Grubbs catalyst, yielded **p(9)** and **p(10)** as shown in Scheme 5. Furthermore, copolymers of **9** and **10** were prepared with the unfunctionalized norbornene **11** to (i) site-isolate individual catalyst sites and (ii) probe the effect of catalyst loadings on the catalytic activity.

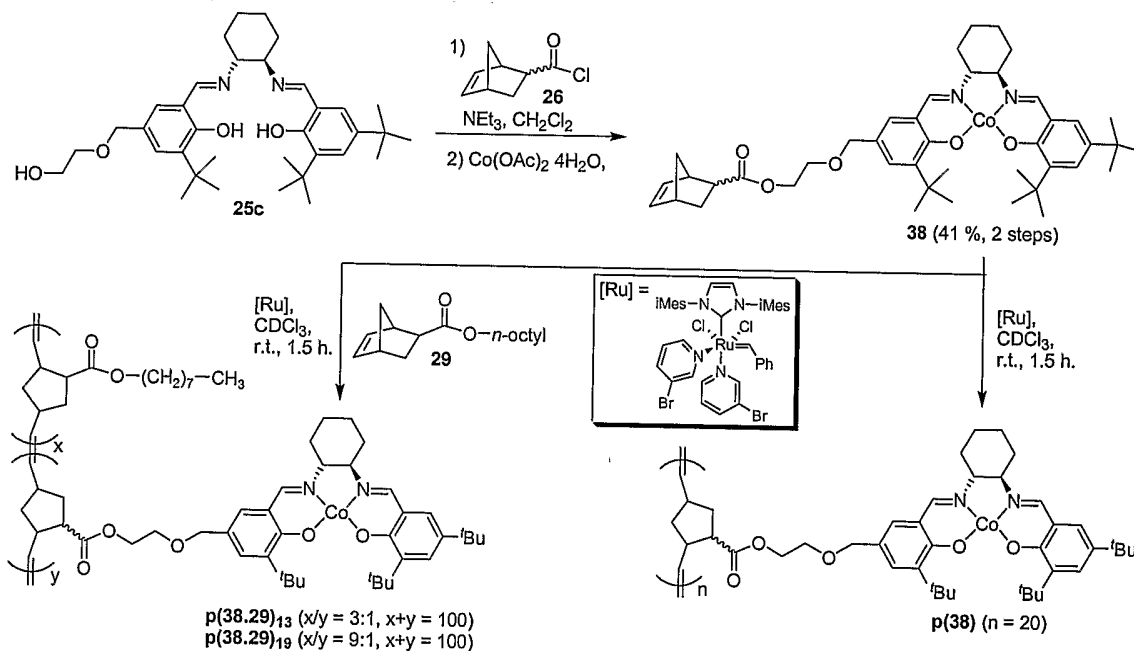
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Scheme 5. Ring-opening metathesis polymerization (ROMP) of the norbornene-functionalized metal-salen-complexes **9** and **10**.

As shown in Scheme 6 the monomeric cobalt salen complex **38** was obtained *via* an acylation of salen ligand **25c** with norbornene chloride **26**, followed by a
20 complexation of Co(OAc)₂. ROMP of the analytically pure and fully characterized metalated monomer using the 3^o-generation Grubbs catalyst, yielded homopolymer **p(38)**. Copolymers of **38** were prepared with the unfunctionalized norbornene **29** to (i) site-isolate individual catalyst sites and (ii) probe the effect of catalyst loadings on the catalytic activity. The polymerization rates were followed using ¹H-NMR
25 spectroscopy by focusing on the signals of the olefin protons. In all cases, monomer

conversions (monomer to catalyst ratios up to 100:1) were quantitative after one to two hours. Moreover, $^1\text{H-NMR}$ spectroscopy of the homopolymerizations of ten equivalents of **29** and **38** using the 3 $^\circ$ -generation Grubbs catalyst revealed that the polymerization kinetics were similar with complete monomer-conversion achieved after about 2-5 minutes. The results suggest that the copolymerization of **38** and **29** yield statistical copolymers **p(38,29)**, i.e., the monomers containing the catalytic moiety of formula (I) are randomly dispersed in the alkyl-norbornene copolymer matrix. These polymeric Co(II)-complexes could be oxidized to the corresponding Co(III) compounds **p(38a)** and **p(38a-co-29)** by O_2 in the presence of acetic acid to afford the corresponding acetate ($\text{L} = -\text{OAc}$).



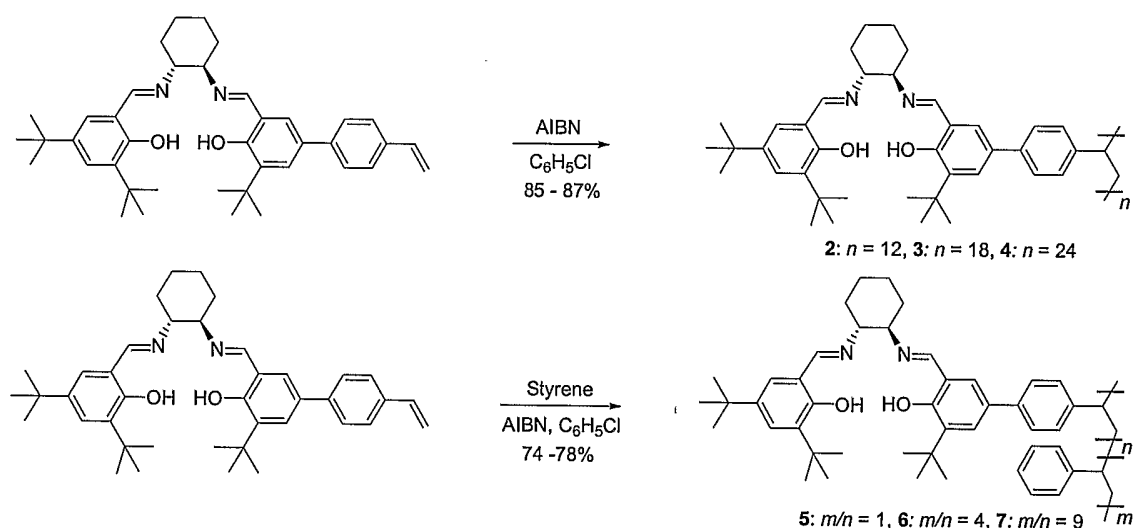
Scheme 6. Preparation of the polymeric Co(II)-salen complexes **p(38)** and **p(38-co-29)**.

Homopolymer and Poly(styrene)-Supported Co(Salen) Complexes

The reuse (reusability or recyclability) of a metal-based catalyst is a fundamental characteristic for the broad commercial acceptance of homogeneous or heterogeneous catalysts. One reaction that has potentially large industrial implication is the hydrolytic kinetic resolution (HKR) of diols from racemic epoxide

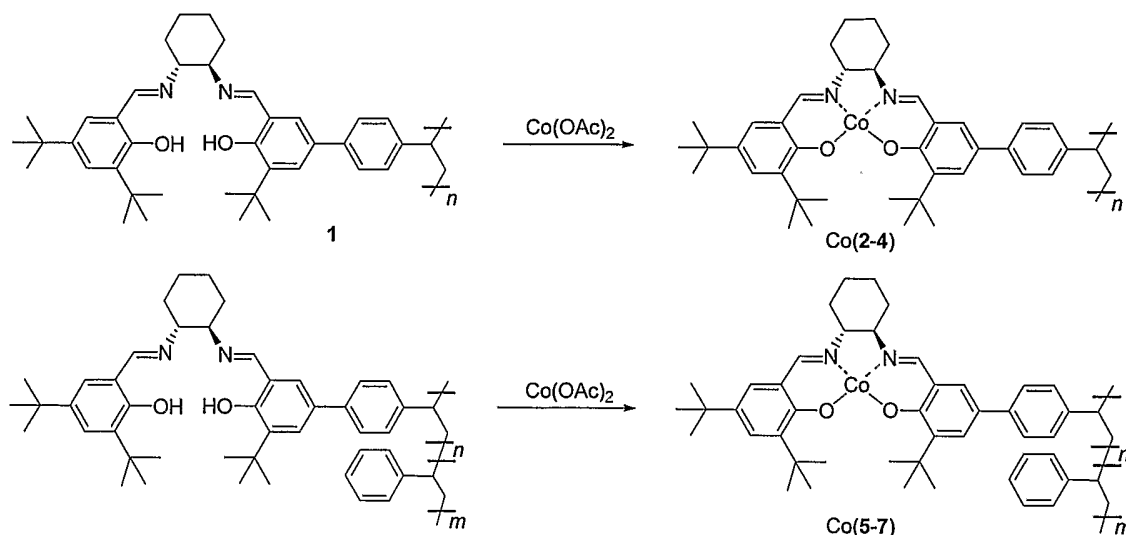
mixtures using cobalt-salen complexes. While a wide variety of supported Co-salen complexes have been reported, they often decompose (at least partially) under the catalyzed reaction conditions. Thus, the robust poly(norbornene) and poly(styrene) supported salen ligands of the present disclosure were prepared. The polymer supported ligands could be metalated, for example, with cobalt to yield the fully supported Co-salen complexes that were as active as their non-supported analogs. This complex can be recycled and reused without decomposition.

Homopolymer chiral Co(salen) and copoly(styrene)-immobilized chiral Co(salen) complexes were prepared by the free radical polymerization of a styryl-substituted unsymmetrical salen monomer, alone or with a styrene co-monomer, as shown in Scheme 7.



Scheme 7. Synthesis of homopolymeric salen ligands and co-polymeric polystyrene-supported salen ligands.

Subsequent metalation with $\text{Co}(\text{OAc})_2$ provided the metalated products as shown in Scheme 8, which products exhibited desirable catalytic properties in, for example, the hydrolytic kinetic resolution of racemic epichlorohydrin.



Scheme 8. Metalation of homopolymeric salen ligands and polystyrene-supported salen ligands.

For example, a one-pot condensation reaction of (1*R*,2*R*)-1,2-diaminocyclohexane monohydrochloride salt, 3,5-di-*t*-butyl-2-hydroxybenzaldehyde, and 3-(4-vinylphenyl)-5-*t*-butyl-2-hydroxybenzaldehyde in a 1:1:1 ratio afforded the desired unsymmetrical mono-styryl substituted salen ligand (1) of Scheme 7 in 85% isolated yield. Free radical polymerization of 1 in the presence of various amounts of the initiator AIBN gave the corresponding homopolymers 2-4 with different chain lengths. Copolymerization of the styryl-salen and styrene in the absence or presence of divinylstyrene produced soluble linear copolymers (5-7) or insoluble cross-linked resins of Scheme 8, respectively. Metalation of the polymers and the copolymers of the styryl-salen with cobalt(II) acetate generated the corresponding polymer-supported cobalt-salen precatalysts (Co(2-7)) in quantitative yields with cobalt loadings of 0.38-1.53 mmol/g.

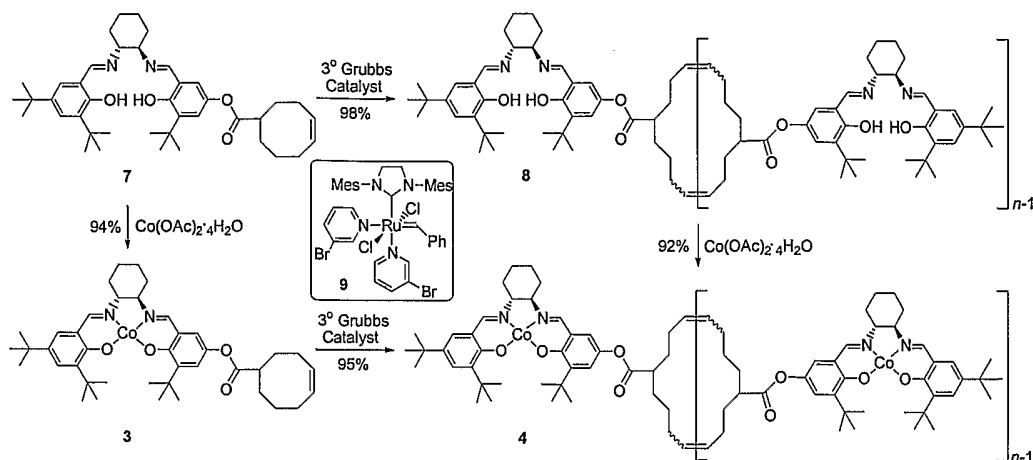
Synthesis of oligomeric Co(salen) complexes via ring-expanded olefin metathesis of cyclooctene substituted salen monomers.

As shown in Scheme 9, catalyst 4 was prepared on multi-gram scale from starting materials described above in Scheme 4. Treatment of the cyclooct-4-en-1-

yl substituted unsymmetrical salen ligand **7** with $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, produced the corresponding Co(II) complex **3** as a brick red solid. In the presence of 2-4 mol% of the third generation (3^o) Grubbs catalyst **9**, both **7** and **3** underwent the ring-expanding olefin metathesis in dichloromethane to give unsymmetrical oligomeric macrocycles **8** and **4**, respectively. These ring-expanding reactions were found to be rather fast and clean. *In situ* ^1H NMR revealed that the metathesis of **7** was complete in 20 min, as evidenced by the up-field shift of the alkenyl proton signals from 5.72 ppm for oligomer **7** to 5.42 ppm for oligomer **8** and line-broadening of almost all peaks. The oligomeric nature of **8** was verified by an analysis with the gel permeation chromatography (GPC) although the absolute value of the number-average molecular weight (M_n) would have a substantial error due to the lack of appropriate standards. However, the MALDI mass spectrometry provided unambiguous details of the structures of these oligomers at a molecular level. The spectrum of **4** (not shown) indicated the exclusive formation of oligomeric macrocycles as a mixture of predominantly dimeric to tetrameric species with observable traces of higher homologues up to a decamer (3: $m/z = 700$, 4: $m/z = 1,400$ (dimer), 2,099 (trimer), 2,799 (tetramer), and so forth). Furthermore, **4** can alternatively be prepared from the metalation of the oligomeric ligand **8** with $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, and demonstrated an identical mass spectrum to that obtained from the metathesis route.

HKR of allyl glycidyl ether with polymeric co-salen catalysts was also evaluated. The resolution reactions were carried out at ambient temperature with 0.6 equiv of water and 0.01 mol% loading of catalysts calculated on the basis of cobalt. The resolution was completed in 12 h in the presence of **4**(OAc) as the catalyst as shown in Scheme 10. The remaining allyl glycidyl ether was determined by the chiral GC method to have an enantiomeric excess (*ee*) of over 99% in a conversion of 51%. Despite a brief induction period in the initial HKR, catalyst **4**(OTs) of Scheme 9 readily completed the resolution in 6 h with over 99% *ee* for the epoxide. In comparison, the monometallic unsupported complex **3**(OAc) gave less than 1% *ee* for the epoxide in 12 h, suggesting that complex **3** had little if any affect on the HKR of allyl glycidyl ether in such a low catalyst loading.

A number of other HKR examples were accomplished on various terminal epoxide substrates and the conditions and results are tabulated in Table 1.



Scheme 9. Synthesis of oligomeric salens and oligomeric Co(salen) complexes via ring-expanded olefin metathesis of cyclooctene substituted salen monomers.

Supported Metal-Salen Catalyzed Preparative Processes

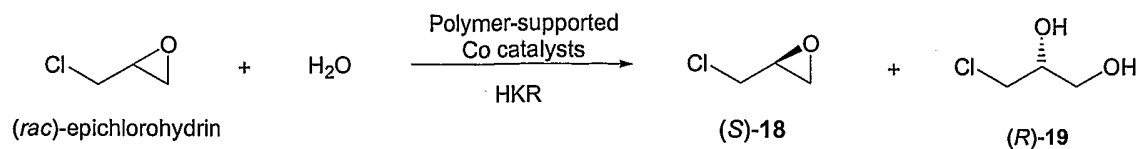
The cobalt-salen polymer supported catalysts were discovered to be useful as generally highly active for hydrolytic kinetic resolution (HKR) of terminal epoxides. The manganese-salen polymer supported catalysts were discovered to be useful as generally highly active for the asymmetric epoxidation (AE) of olefins. In embodiments, design criteria for salen polymer supported catalysts of the disclosure include: (i) the supported catalyst should possess an optimized salen ligand sphere, (ii) the salen ligand preferably can be attached to the support *via* a single linker (L') to minimize steric restrictions; (iii) for Mn-salen species, the catalyst loading should be sufficiently low to maximize site isolation of the catalytic centers to minimize the formation of catalytic inactive *oxo*-bridged dimers, whereas for Co-salen species, the active catalyst is preferably selected at a high enough density to permit the proposed simultaneous activation of epoxide and nucleophile *via* two different cobalt centers; and (iv) the morphology of the supports should ensure free access of reactants to all active sites. Accordingly, in embodiments, mono-functionalized salen cores were attached *via* a single site to a soluble poly(norbornene) backbone. For the attachment, chemically inert C-C bond linkages *via* a phenylene-acetylene linker were used and were found to minimize catalyst degradation during the epoxidation reactions. Variations of the catalyst active site density could be readily achieved by

homo- or co-polymerizing metalated salen monomers having a polymerizable group by, for example, ROMP.

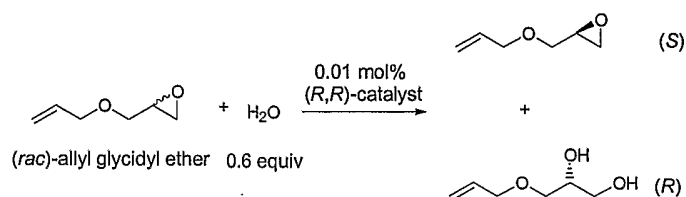
Hydrolytic Kinetic Resolution (HKR)

5 The oligo(cyclooctene)-supported Co(II)(salen) complex **4** of Scheme 9 was examined for catalytic efficiency in the HKR of terminal epoxides. Two methods were developed to generate the Co(III)(salen) species, the active catalytic species for the HKR, with different counterions. Method A involved the aerobic oxidation in the presence of an excessive amount of acetic acid. After the mixture was stirred in
10 dichloromethane in the open air for 30 min, all volatiles were removed *in vacuo* to afford **4**(OAc) as a brown solid. Method B used 1.05 equiv of *p*-toluenesulfonic acid in THF as the acid reagent. The oxidation and workup under the similar conditions gave green **4**(OTs) as the crude catalyst. Both of these catalysts were
15 highly soluble in common epoxides and enabled the resolution reactions to be performed neat.

 In embodiments, the polymeric cobalt-salen catalysts of the disclosure were used in HKR of racemic substrates, such as *rac*-epichlorohydrin or allyl glycidyl ether as shown in Scheme 10. HKR of *rac*-epichlorohydrin was accomplished with, for example, 0.5% of the polymeric cobalt-salen catalyst of Scheme 8 and afforded
20 the (S)-epichlorohydrin in 44% yield (88% theoretical yield) and >99% ee. The catalyst could be reused with almost identical reactivity and enantio-selectivity after isolation and reactivation.



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Scheme 10. Hydrolytic kinetic resolution of substrates epichlorohydrin and allyl glycidyl ether.

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Table 1. Hydrolytic kinetic resolution of various terminal epoxides.^a

Entry	R	Method ^b	Loading (mol%)	Time (h)	<i>ee</i> ^c (%)	Yield ^d (%)
1a	<i>n</i> -Bu	A	0.01	2.0	>99	43
2a	Cl	A	0.01	2.5	>99	44
2b	Cl	B	0.01	2.5	>99	43
3a	AllylOCH ₂	A	0.01	12	>99	48
3b	AllylOCH ₂	B	0.01	6.0	>99	46
4a	PhOCH ₂	A	0.01	20	>99	46
5a ^[e]	Ph	A	0.1	24	>99	45
5b	Ph	B	0.1	18	>99	48

^a Reactions were performed on 0.05–0.1 mol scales under solvent-free (neat) conditions.

^b Method A: 4(OAc) as the catalyst; Method B: 4(OTs) as the catalyst.

^c Determined by chiral GC or HPLC methods.

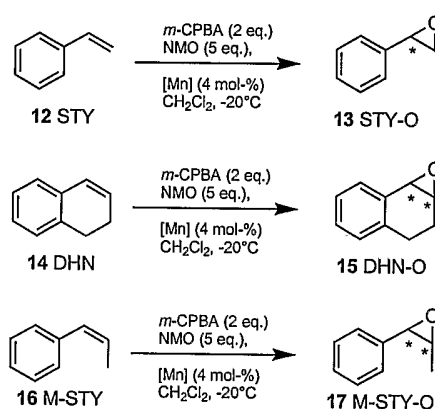
^d Isolated yield.

^e 1 mol% (based on the epoxide) of HOAc was added.

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Asymmetric Epoxidation

As shown in Scheme 11, the polymeric Mn-salen complexes were evaluated as asymmetric epoxidation catalysts. The olefins styrene **12**, 1,2-dihydronaphthalene **14**, and *cis*- β -methyl styrene **16**, were selected as substrates, representing a terminal, a cyclic and a *cis*-disubstituted, non-cyclic olefin, respectively. Following published procedures, the polymeric catalysts of the present disclosure, N-methyl-morpholino-N-oxide (NMO), the olefin, and chlorobenzene or dodecane as an internal standard, were dissolved in methylene chloride, cooled the solutions to $-20\text{ }^{\circ}\text{C}$, and the peracid *meta*-chloroperoxybenzoic acid (*m*-CPBA) was added in three equal portions over a period of two minutes.



Scheme 11. Epoxidations of unfunctionalized olefins.

Kinetic studies of the reactions *via* GC-analysis showed the high activities of the polymer-supported Mn-salen catalyst systems of Scheme 5 with quantitative conversion using four mol% Mn after 150-300 seconds. The epoxidations of styrene **12** and *cis*- β -methyl styrene **16** were as fast as control experiments that used an original non-supported Jacobsen complex. Only in the case of 1,2-dihydronaphthalene **14**, the epoxidation rate with **p(9)** is somewhat slower than the rate of the original Jacobsen-catalyst. The copolymer complexes **p(9.11)** had catalytic activities that were higher than the homopolymer complex analog **p(9)**. All reactions are quantitative after five minutes or less, suggesting excellent substrate access to metal-complex catalytic sites. Table 2 lists additional results for catalytic epoxidation of olefins **12**, **14**, and **16**.

Table 2. Epoxidation of unfunctionalized olefins.¹

Entry	Olefin ²	Epoxide	Catalyst	Temp. (°C)	Conv. ₃ (%)	ee (%)
1	12	13	Jacobsen	-20	100	34
2	12	13	p(9)	-20	100	32
3	12	13	p(9.11) ₁₁	-20	100	33
4	12	13	p(9.11) ₁₃	-20	100	32
5	12	13	p(9.11) ₁₉	-20	100	33
6	14	15	Jacobsen	-20	100	88
7	14	15	p(9)	-20	100	76
8	14	15	p(9.11) ₁₁	-20	100	81
9	14	15	Cycle 2	-20	100	47
10	14	15	Cycle 3	-20	85	6
11	14	15	p(9.11) ₁₃	-20	100	81
12	14	15	p(9.11) ₁₉	-20	100	82
13	16	17	Jacobsen	-20	100	93
14	16	17	p(9.11) ₁₁	-20	100	92

All epoxidations were carried out at -20 °C:

1) with m-CPBA (2 eq.), NMO (5 eq.) and 4 mol-% Mn-catalyst in CH₂Cl₂.

5 2) Styrene (STY) or 1,2-dihydronaphthalene (DHN).

3) after five minutes.

The supported catalysts also had outstanding selectivities. For the epoxidation of styrene 12 and *cis*- β -methyl styrene 16 the enantiomeric excesses (ee's) are comparable to the unsupported Jacobsen catalyst (32-33% ee vs. 34% ee for 13 and 92% ee vs. 93% ee for 17). For the epoxidation of 1,2-dihydronaphthalene 14, the ee's with the polymeric catalysts are slightly lower than with the Jacobsen catalyst (76-82% ee vs. 88% ee) but among the highest ee's reported for any immobilized salen complexes (10-84% ee). Although not limited by theory, a possible reason for the somewhat lower selectivities of the presently disclosed supported systems is their slower reaction rate, which increases the amount of racemic epoxide produced by a slow background reaction without the

need of a catalyst. As observed for the epoxidation rates, the enantioselectivities of the copolymers **p(9.11)** are very similar (81-82% *ee*) and higher than the homopolymer **p(9)** (76% *ee*), suggesting a good site-isolation of the manganese centers even for the 1:1-copolymer.

5 The polymeric Mn-complexes could be separated easily from the reaction mixtures by precipitation into Et₂O/MeOH and subsequent centrifugation. In all cases, the polymer catalyst was recovered quantitatively. In one study of the reusability, **p(9.11)**₁₁ was selected and represented the copolymer system with the best catalytic performance and the highest manganese loading. Unfortunately, after
10 separating the polymer by precipitation, the residue was no longer completely soluble in methylene chloride. When the resulting suspension was used as a catalyst for the epoxidation of **14**, the epoxidation rate was slower than the one with the non-recycled polymer. This drop of activity after recycling is even more pronounced in the third cycle, where only 85% conversion of **14** after 300 seconds was achieved.
15 Even more dramatic was the decline of enantioselectivity from 81% *ee* over 47% *ee* (second cycle) to only 6% *ee* after the third cycle, demonstrating that **p(9.11)**₁₁ was not reusable. Whether the observed reduced solubilities and the subsequent drops in activity and selectivity are a result of the dimerization of Mn(III)- and Mn(V)=O centers (i.e., leading to cross-links between different polymer chains), or a
20 degradation/chemical modification of the catalyst, i.e., the backbone olefins of the poly(norbornene)s could be crosslinked or epoxidized, remains uncertain.

 The results with the Mn-poly(norbornene)s as chiral epoxidation catalysts clearly reveal that by following the above described criteria, immobilized catalysts with outstanding activities and selectivities that are comparable with the catalytic
25 activities and selectivities of the original non-polymeric Jacobsen catalyst, can be prepared and utilized. Furthermore, the polymeric Mn-salen complexes can be easily removed by precipitation and subsequent centrifugation allowing for the removal of the vast majority of the metal species after complete reactions.

 Similarly, the polymeric Co-catalysts of the disclosure can be easily and
30 readily removed or separated from a reaction mixture and desired reaction products. The separated polymeric cobalt-salen catalysts can be reused or recycled, for example, at least once in a second reaction with high retention of activity and selectivity. Although not limited by theory, the effect of the linker group (L') and polymer backbone flexibility on the activity and selectivity of immobilized metal-

salen catalysts is believed to be significant in bi-metallic processes with polymeric Co-catalysts, and less significant or insignificant in mono-metallic processes with polymeric Mn-catalysts.

5 Experimental Section

All reactions with air- and moisture sensitive compounds were carried out under an argon atmosphere using standard Schlenk techniques. Diethylether (Et₂O), tetrahydrofuran (THF), methanol (MeOH) and ethanol (EtOH) were distilled over sodium/benzophenone, and dichloromethane (CH₂Cl₂) and triethylamine (NEt₃) were distilled over calcium hydride and stored in dry Schlenk-flasks under argon. All other reagents and solvents were purchased from commercial sources and used as received unless otherwise noted.

Gas-chromatographic analyses were performed on a gas chromatograph equipped with a flame-ionization detector and a HP-5 column (30m x 0.25mm x 0.25μm). The temperature program for GC analysis was as follows: 2 min. 50 °C followed by heating to 140 °C at 30K/min and heating to 300 °C at 40 K/min under constant pressure with inlet and detector temperatures kept constant at 330 °C. The enantiomeric excess of the epoxides of styrene **12**, 1,2-dihydronaphthalene **14** and *cis*-β-methylstyrene **16** were determined using a GC-MS with a Dex 120 column (30m x 0.25mm x 0.25μm). The temperature programs were as follows: for Sty-O **13**: 80 °C for 50 min, 20 K/min to 200 °C (*t_R*(first enantiomer) = 46.3 min, *t_R*(second enantiomer) = 49.5 min); for DHN-O **15**: 125 °C for 40 min, 20 K/min to 205 °C (*t_R*(first enantiomer) = 34.9 min, *t_R*(second enantiomer) = 36.8 min); for MSty-O **17**: 90 °C for 40 min, 20 K/min to 190 °C (*t_R*(first enantiomer) = 33.3 min, *t_R*(second enantiomer) = 36.4 min).

Kinetics and selectivities of the hydrolytic kinetic resolution of epichlorohydrin **18** was analyzed on a GC-FID with a γ-TA column (30m x 0.25mm x 0.25μm). The temperature was kept at 60 °C for 15 min followed by heating at 10 K/min to 160 °C (*t_R*(*S*-**18**) = 10.2 min, *t_R*(*R*-**18**) = 11.7 min, *t_R*(diol *R*-**19**) = 25.1 min).

NMR spectra were recorded on a 300 MHz or a 500 MHz instrument. Chemical shifts (ppm) of ¹H- and ¹³C-spectra are referenced to residual solvent signals as internal standards. The fine structure of the proton signals were specified

with "s" (singlet), "d" (doublet), "t" (triplet), "q" (quartet), "m" (multiplet), "dd" (double-doublet) and "br s" (broad singlet).

Gel-permeation Chromatography analyses (GPC) were carried out using a binary pump coupled to a refractive index detector. The GPC was calibrated using poly(styrene) standards using a column set with CH₂Cl₂ as the eluent.

Column-chromatography was carried out on technical grade silica gel (60 Å, 40-63 µm) at a pressure of ca. 50 kPa.

Polymer Characterization Although the metal complexes **9** and **10** are paramagnetic, it was possible to investigate the polymerization rates using ¹H-NMR spectroscopy by solely focusing on the signals of the olefin protons. In all cases, monomer conversions (monomer to catalyst ratios up to 100:1) were quantitative after one to two hours. Moreover, following the homopolymerizations of ten equivalents of **9**, **10** or **11** by ¹H-NMR, it was found that the polymerization kinetics of all three monomers using the 3^o-generation Grubbs catalyst were similar with complete monomer-conversion after about 2-5 minutes. These results suggest that the copolymerization of **9** and **11** and **10** and **11** yield statistical copolymers **p(9.11)** and **p(10.11)**, *i.e.*, the monomers containing the catalytic moiety are randomly dispersed within the alkyl-norbornene matrix.

It is well known that polyelectrolyte and metal-salt containing polymers cannot be characterized by gel-permeation chromatography (GPC), most likely due to interactions of the polymers with the packing material and the formation of aggregates during the process. The same limitation holds true for the present metal-containing polymers and no GPC results of any polymer containing more than ten repeating units could be obtained in either THF, chloroform, or methylene chloride. Therefore, no polydispersities (PDIs) or molecular weights for the high molecular weight polymers are included. However, the values for the molecular weights and the polydispersities of **p(9)** (M_w=5,900, M_n=4,400, PDI=1.34) and **p(10)** (M_w=55,400, M_n=18,300, PDI=3.03) confirmed a successful and quantitative ROMP of the monomeric complexes.

Three different analysis methods were used to determine the metal contents of all monomers and polymers. First, all compounds were ICP. Second, the C, H, N, and O-contents were analyzed by elemental analysis. Since the monomers contain only the elements C, H, N, and O but for the metal and its ligands (such as

chlorine, etc.) one can calculate the metal content by subtracting the C, H, N, O - (and in case of the Mn-complexes Cl) contents from 100 percent. The remaining contents are the metal complex. The results of these two methods are shown in Table 3.

5

Table 3. Elemental analysis and ICP-data of the polymers.

Entry	Polymer	% -found / (% -calcd.)						
		C ¹	H ¹	N ¹	O ¹	Cl / S ₂	Me ³	Me ⁴
1	p(9)	68.67 (70.71)	7.02 (6.92)	3.27 (3.44)	9.09 (7.85)	n.d. ⁵ -	11.95 ⁶ (11.09)	5.00 (6.74)
2	p(9.11) ₁₁	71.10 (72.13)	7.65 (7.78)	2.64 (2.63)	9.72 (9.01)	2.26 (3.33)	5.68 (5.15)	4.68 (5.15)
3	p(9.11) ₁₃	n.d. ⁵	n.d. ⁵	n.d. ⁵	n.d. ⁵	n.d. ⁵	n.d. ⁵	3.86 (3.51)
4	p(9.11) ₁₉	75.05 (75.15)	9.63 (9.53)	0.84 (0.91)	11.69 (11.47)	0.96 (1.16)	1.83 (1.79)	1.39 (1.79)
5	10	73.33 (73.54)	7.21 (7.20)	3.49 (3.57)	8.33 (8.16)	- -	7.64 (7.52)	8.00 (7.52)
6	p(10)	71.06 (73.54)	7.06 (7.20)	3.57 (3.57)	8.95 (8.16)	-	9.36 (7.52)	6.96 (7.52)
7	p(10.11) ₁₁	72.88 (74.32)	7.89 (7.99)	2.76 (2.71)	9.89 (9.28)	-	6.58 (5.70)	5.96 (5.70)
8	p(10.11) ₁₃	74.25 (75.11)	8.73 (8.80)	1.95 (1.82)	11.15 (10.42)	-	3.92 (3.84)	3.95 (3.84)
9	p(10.11) ₁₉	75.50 (75.92)	9.50 (9.62)	0.90 (0.92)	11.96 (11.59)	-	2.14 (1.94)	2.02 (1.94)
10	p(10c)	65.42 (69.16)	6.79 (6.65)	2.60 (2.93)	15.02 (11.73)	3.97 (3.36)	6.20 (6.17)	5.60 (6.17)

11	p(10c)_rec	57.65	6.27	2.58	20.47	5.10	7.93	4.27
		(69.16)	(6.65)	(2.93)	(11.73)	(3.36)	(6.17)	(6.17)

1) Determined by elemental analysis.

2) Determined by elemental analysis, S only for p(10c.11) and p(10c.11)_rec (entry 10,11).

3) Determined by 100 – (sum of percentages of other elements).

4) Determined by ICP.

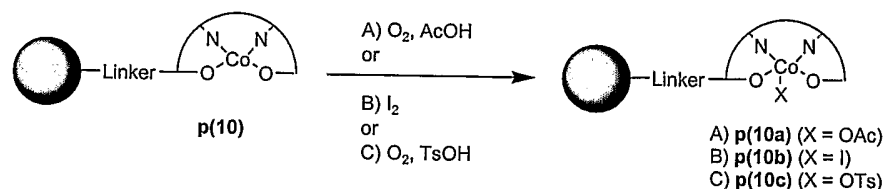
5) Not determined due to lack of sample material.

6) Content of MnCl, determined by 100 – (sum of percentages of other elements).

Finally, where possible, the chlorine content of all polymers was determined. The manganese compounds generally contain one Cl ligand on all metals. Therefore, by analyzing the chlorine content, one can calculate the metal content. Using this methodology, the manganese contents of p(9.11)₁₁ was calculated to be 3.50 % (calcd. 5.15 %) and that of p(9.11)₁₉ to be 1.48 % (calcd. 1.79 %). While one should expect these three methods to agree in the metal contents, it was found that all three methods slightly diverge from the theoretical expected metal values (some methods suggest a higher metal content while others suggest a lower one), which is attribute to the error of the three analytical methods due to the small sample sizes and the low metal percentage of all polymers. With these limitations in mind, the values for the metal loadings of the polymers are within the error range (in most cases $\pm 0.5\%$ for all three methods) in good agreement with the theoretical values. These results suggest that the metalated salen complexes do not decompose during the ROMP. It is important to note that always fully characterized and purified, i.e., by column chromatography, metalated monomers were employed during the ROMP, and that the co-monomer ratios are approximately the same as the theoretical targeted ratios.

Hydrolytic Kinetic Resolution Reaction Analysis The catalytic performance of the polymeric cobalt complexes p(10) and p(10.11) were studied in the HKR of racemic epichlorohydrin (ECH) 18 (Scheme 10). Since only the Co(III) complexes are catalytically active in this reaction, we oxidized the obtained Co(II) polymers p(10) and p(10.11) were oxidized by stirring methylene chloride solutions of the polymers with acetic acid under an atmosphere of air (X = OAc). After removal of the solvent and the excess AcOH *in vacuo*, the desired Co(III)-salen polymers p(10a) and p(10a.11) with acetates as counterions were obtained. For the HKR reactions, the Co(III)-polymers were dissolved in a mixture of methylene chloride, 18, and chlorobenzene as an internal standard, followed by the addition of 0.7

equivalents of water to start the resolution. The addition of some methylene chloride as a solvent was necessary because the copolymers were not fully soluble in **18**. Similar procedures were used to obtain **p(10b)**(X=I) and **p(10c)**(X= OTs).

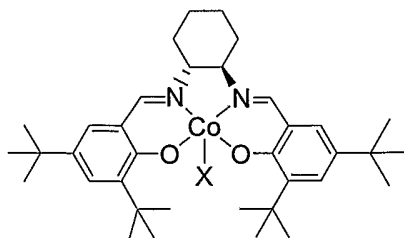


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The reaction kinetics of the HKR were studied *via* chiral GC-analysis. Using either the homopolymer **p(10a)** (X = OAc) or the two copolymers **p(10a.11)₁₁** and **p(10a.11)₁₃**, epoxide (*R*)-**18** was fully converted after five hours to its corresponding diol, leaving pure (*S*)-**18** in the reaction mixture in above 99% enantiomeric excesses. After this time period, 55% of the racemic **18** is converted, i.e., all of the unwanted R enantiomer is converted to the diol while only 5% of the desired epoxide has been converted, indicating selectivities similar to the original Jacobsen CoOAc catalyst (53% conversion, >99% *ee* under solvent-free conditions). The epoxidation rates with **p(10a.11)₁₁** and **p(10a.11)₁₃** are slightly higher than the ones using **p(10a)**. This finding, at first impression contradicts the assumption of a bimetallic mechanism for the HKR, and may be the result of a higher backbone flexibility of the copolymers in comparison to the sterically more congested homopolymers. However, further dilution of the salen-moieties along the polymer backbone (polymers **p(10a.11)₁₉**) resulted in a dramatic drop of the activity (only 43% conversion and 80% *ee* after five hours), while the selectivities remained the same (e.g., **p(10a.11)₁₁**: 44.5% conv., 78.4% *ee* and **p(10a.11)₁₃**: 45.5% conv., 81.0% *ee* after one hour). This result suggests that the extreme dilution of the catalytic moieties along the polymer backbone results in the deactivation of the catalysts due to the unlikelihood of two catalytic moieties being in close proximity to each other, a prerequisite for the bimetallic catalytic pathway.

Using **p(10a)**, the HKR of **18** can also be carried out under solvent-free conditions. In this case, the reaction rates are faster than the rate with **p(10a)** using CH₂Cl₂ as the solvent as well as the rate of the original Jacobsen complex, resulting in (*S*)-**18** with >99 % *ee* after less than two hours. However, an increase in conversion (62%) suggests that the polymeric catalyst is less selective under these

reaction conditions. When comparing the kinetics of the non-polymeric Jacobsen CoOAc-salen catalyst ($X = \text{OAc}$) of the formula:



5

with the monomeric catalysts **10a**, it was found that **10a** is slightly less selective than the Jacobsen catalyst indicating that the lower selectivity of the polymers are primarily a result of the different catalyst structure (phenylene-acetylene linker instead of a *tert*-butyl group in the 5-position of one of the aromatic rings) and not based on the polymeric support. This result suggests that even small changes in the structure of the salen core can have a significant effect on the catalytic properties of the resulting complexes.

Another important variable that has been studied with Co-salen catalysts is the choice of the counterion on the metal center. It has been reported that very nucleophilic counterions like Cl can attack the epoxide very fast resulting in small amounts of byproduct, while catalyst activity can be increased dramatically with more electronegative counterions, such as -OTs, and like counterions. Finally, non-coordinating counterions like PF_6^- or BF_4^- can suppress the undesired reduction of Co(III) to Co(II). To investigate if this counterion effect holds true in the present polymeric system and to investigate whether changes to counterion of the polymeric catalyst can be used to control their activities and selectivities, polymers **p(10b)** and **p(10c)** were prepared with iodide and tosylate counterions, respectively. Polymer **p(10b)** was obtained by oxidizing **10** with iodine and subsequent ROMP of **10-I**. In contrast, **p(10c)** ($X = \text{OTs}$) was obtained by oxidizing the polymer **p(10)** with O_2/p -toluenesulfonic acid. Interestingly, when either **p(10b)** or **p(10c)** were employed as catalysts in the HKR of **18** under solvent-free conditions, both catalysts showed higher activities than **p(10a)**. In particular **p(10b)** was highly active, with (*S*)-**18** being obtained in >99% *ee* after less than one hour. However, the selectivities of **p(10b)** and **p(10c)** are somewhat lower than that of **p(10a)** (conversions for obtaining (*S*)-**18** with >99% *ee*: 66.7% using **p(10b)**, 69.7% using **p(10c)** and 62.0%

using **p(10a)**). These results demonstrate that a counterion effect exists for the polymer-supported Co-salen catalysts of the present disclosure.

As a result of the outstanding activities of **p(10c)**, this polymeric catalyst was used to optimize other reaction conditions. In an attempt to improve selectivities, CH_2Cl_2 was added to the reaction as a solvent. Unfortunately, the reaction was significantly slower with only about 49.0% **18** converted after 11.5 hours (87.9% *ee* of (*S*)-**18**). Nevertheless, higher enantiomeric excess of (*S*)-**18** at 50% conversion observed under these reaction conditions indicate an increase in selectivity of **p(10c)** when a solvent is added. The effect of decreasing catalyst loading on the activities and the selectivities was also investigated. When the catalyst loading of the polymeric CoOTs-catalyst was decreased to 0.2 mol-% Co for the HKR of **18**, a decrease in activity (the reaction took eleven hours for a complete conversion of (*R*)-**18**) and a decrease in selectivity were observed (after 11 hours, 67.2% of the racemic epoxide was converted). Moreover, a comparison of the enantiomeric excess of the remaining (*S*)-**18** at similar conversions suggested an increased selectivity with a decrease of the CoOTs-amount (0.2 mol-% **p(10c)**: 47.4% conv., 78.2% *ee*, 0.5 mol%: 51.4% conv., 64.4% *ee*). These results demonstrate that for the CoOTs-poly(norbornene) catalyst the use of less catalyst loading can be advantageous in embodiments.

All polymeric Co-complexes could be easily separated from the reaction mixtures by precipitation into Et_2O and subsequent centrifugation. By simply washing the obtained Et_2O -solution with water (*R*)-3-chloro-1,2-propanediol **19** was removed nearly quantitatively resulting in pure (*S*)-**18**. This protocol is considered to be an important advantage to the normally used methodology of distilling off **18** from the crude reaction mixture since remaining Co(III)-salen complexes are reported to catalyze the decomposition and the racemization of the epoxide during the purification process. Since the polymeric Co-OAc complex **p(10a)** gave the best selectivities, this catalyst was selected to study the reusability of polymeric Co-salen catalysts. After re-oxidation with O_2 in the presence of acetic acid, recycled **p(10c)** showed the same resolution rate and selectivities as the original polymeric catalyst **p(10c)** (i.e., 61.8% conv. > 99% *ee* of (*S*)-**18** after 150 min). However, the need of ultra-sonication in order to dissolve **p(10a)** fully in a solution of **18** and chlorobenzene before the catalysis indicated reduced solubility. The solubility of the polymeric catalyst declined further for the third catalytic cycle. It was not

possible to dissolve the twice-recycled **p(10a)** fully in the reaction mixture, even after the addition of CH₂Cl₂ as solvent and ultra-sonicating the mixture. As a result of the lower solubility, the reaction rate dropped for the third cycle with only 78.8% *ee* after three hours (49.6% conversion). However, after 11 hours 61.0% of the racemic epoxide was converted and (*S*)-**18** was obtained with 97.8% *ee*, indicating that the polymeric catalyst was still active and very selective, and that after an appropriate reaction time enantiomerically pure (*S*)-**18** could be isolated in good yields. Similar results for the reusability (i.e., the solubility problems and subsequent low resolution rates) were obtained with the polymeric Co-OTs-salen **p(10c)**. Analysis of **p(10c)** by ICP before starting the recycling experiments and after the third catalysis cycle showed that the metal content of the polymer decreased from 5.60% to 4.27%. This decrease in metal content cannot be explained with the error range of the elemental analysis. Since a leaching of metallic cobalt has not been reported in the literature, it is suggested that this slight decrease in metal content may be due to a cleavage of the ester bonds resulting in a loss of a complete salen moiety from the polymer. Accordingly, more chemically robust or inert Z connector groups are suggested, such as a -CH₂- or -Ar- in place of -C(=O)O-. Nevertheless, in a recent report on the stability of the norbornene ester linkages under a variety of reaction conditions, one cannot completely rule out (although unlikely) some metal leaching of the cobalt from the polymer. Additionally, the percentages of carbon, oxygen, and sulfur increased, indicating that either *para*-toluenesulfonic acid is not completely separated during the precipitation or that the acid may be reacting with the double bond along the polymer backbone.

A second recycling method in the literature involves removal of the substrates by fractionated distillation followed by the addition of more starting material to the metal containing residue. While this method suggests repeated usability of the Co-catalysts, it has several disadvantages including the potential for the undetected decomposition of the catalyst (i.e., leaching of cobalt) and that epoxides such as (*S*)-**18** may racemize during this process. However, because of the solubility-issues encountered during the separation of the catalyst by precipitation, this recycling method was also investigated whereby CH₂Cl₂ was also used as a solvent. Starting with 11 mg **p(10a)** in the first cycle, 56 mg of an red-brown solid were obtained after distilling off CH₂Cl₂, (*S*)-**18** and **19**. Subsequently, the residue was dried *in vacuo* and the Co(II)-complex reoxidized with O₂/AcOH. The

increased mass indicates an incomplete removal of the substrates, in particular 3-chloro-propane-1,2-diol (boiling point 213 °C). The recycled polymeric catalyst showed a somewhat lower activity in the second cycle. It took eleven hours instead of five to obtain (*S*)-18 with >99% *ee* (57% conv.). After recycling and reoxidation, 99 mg of a brown residue were isolated after the second catalysis cycle. In the third cycle this residue showed a catalytic performance that was comparable to the one described for the second cycle. Interestingly, no solubility problems were observed using this methodology in contrast to the results with the precipitation method. Thus, the method of recycling selected may be an important factor in determining the properties and performance of a recycled catalyst.

The polymeric cobalt-salen results demonstrate a highly active and selective supported cobalt salen catalyst. Furthermore, copolymer complexes were slightly more active than their homopolymer analogs. Finally, a counterion effect was observed in the present supported catalyst systems that enable a tailoring of their activities and selectivities. The present supported catalysts can be easily removed from the reaction mixture and allow for the easy removal of metal species from the product. However, using the precipitation method, the supported catalysts were recycled once as a result of their decreased solubility after the reoxidation step.

Preparation of Starting Materials

(*R,R*)-*N*-(3,5-Di-*tert*-butylsalicylidene)-*N'*-[3-*tert*-butyl-5-(4'-hydroxyphenylethynyl) salicylidene]-1,2-cyclohexanediamine (4a)(Scheme 2).
(*R,R*)-1,2-Diaminocyclohexane mono(hydrogen chloride) (108 mg, 0.72 mmol), 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (168 mg, 0.72 mmol), and 4 Å molecular sieves (100 mg) were charged into a 25 mL flask equipped with a magnetic stir bar and a septum. Anhydrous ethanol (3 mL) and anhydrous methanol (3 mL) were added and the bright yellow solution was stirred at room temperature for four hours. A solution of 5-(4'-hydroxyphenylethynyl)-3-*tert*-butyl-2-hydroxy-benzaldehyde (211 mg, 0.72 mmol) in anhydrous CH₂Cl₂ (6 mL) and anhydrous NEt₃ (0.20 mL, 1.44 mmol) were added. The red solution was stirred at room temperature for additional four hours. The reaction mixture was filtered through a short pad of dry silica gel and the silica gel was flushed with CH₂Cl₂. The solvent was removed under reduced pressure. The residue was purified by column chromatography on

silica gel (ethyl acetate/hexanes = 1:5) to afford **4a** (323 mg, 75 %) as a yellow-orange powder. R_F (SiO₂, ethyl acetate / hexanes = 1:5) = 0.13. $[\alpha]_D^{20} - 136^\circ$ (c 0.5, DCM). ¹H NMR (500 MHz, CDCl₃): δ = 1.26 (s, 9 H), 1.44 (s, 9 H), 1.46 (s, 9 H), 1.40 - 1.53 (m, 2 H), 1.82 - 1.93 (m, 2 H), 1.66 - 1.81 (m, 2 H), 1.93 - 2.05 (m, 2 H), 3.25 - 3.77 (m, 4H), 6.81 (d, J = 8.7 Hz), 7.00 (d, J = 2.5 Hz), 7.19 (d, J = 2.0 Hz, 1 H), 7.35 (d, J = 2.5 Hz, 1 H), 7.40 (d, J = 8.7 Hz, 2 H), 7.41 (d, J = 2.0 Hz, 1 H), 8.22 (s, 1 H), 8.28 (s, 1 H). ¹³C NMR (125 MHz, CDCl₃): δ = 24.4, 29.4, 29.6, 31.5, 33.1, 33.2, 35.0, 34.2, 35.1, 72.0, 2.2, 87.2, 88.3, 112.5, 115.7, 115.6, 117.7, 118.4, 126.1, 127.3, 132.7, 133.1, 133.2, 136.7, 137.9, 140.1, 155.7, 158.4, 161.5, 165.2, 166.2. MS (ESI): m/z (I_{rel}) = 607 (56, $[M + 1]^+$), 291 (84, C₂₅H₃₁N₂O₂⁺). HRMS (ESI) calcd for C₄₀H₅₁N₂O₃ ($[M + 1]^+$): 607.3899; found: 607.3888. Anal. Calcd for C₄₀H₅₀N₂O₃ (606.38): C 79.17, H 8.30, N 4.62, O 7.91; found: C 78.61, H 8.26, N 4.63, O 8.03.

(R,R)-N-(3,5-Di-*tert*-butylsalicylidene)-N'-[5-(4'-acetylsulfanylphenylethynyl)-3-*tert*-butylsalicylidene]-1,2-cyclohexanediamine (4b)(Scheme 2). (R,R)-1,2-Diaminocyclohexane mono(hydrogen chloride) (128 mg, 0.85 mmol), 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (199 mg, 0.85 mmol), and 4 Å molecular sieves (100 mg) were charged into a 25 mL flask equipped with a magnetic stir bar and a septum. Anhydrous ethanol (3 mL) and anhydrous methanol (3 mL) were added and the bright yellow solution was stirred at room temperature for four hours. A solution of 3-*tert*-butyl-5-(4'-acetylsulfanylphenylethynyl)-2-hydroxybenzaldehyde (300 mg, 0.85 mmol) in anhydrous CH₂Cl₂ (6 mL) and anhydrous NEt₃ (0.27 mL, 1.9 mmol) were added. The red solution was stirred at room temperature for additional four hours. The reaction mixture was filtered through a short pad of dry silica gel and the silica gel was flushed with CH₂Cl₂. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (ethyl acetate/hexanes = 1:10) to afford **4b** (339 mg, 60 %) as a yellow powder. R_F (SiO₂, ethyl acetate/hexanes = 1:5) = 0.47. $[\alpha]_D^{20} - 144^\circ$ (c 0.5, DCM). ¹H NMR (300 MHz, CDCl₃): δ = 1.24 (s, 9 H), 1.42 (s, 9 H), 1.43 (s, 9 H), 1.43 - 1.60 (m, 2 H), 1.84 - 1.94 (m, 2 H), 1.66 - 1.83 (m, 2 H), 1.94 - 2.08 (m, 2 H), 2.43 (s, 3 H), 3.24 - 3.44 (m, 2 H), 6.96 (d, J = 2.4 Hz, 1 H), 7.21 (d, J = 2.0 Hz, 1 H), 7.32 (d, J = 2.4 Hz, 1 H), 7.37 (d, J = 8.4 Hz, 2 H), 7.40 (d, J = 2.4 Hz, 1 H), 7.51 (d,

$J = 8.4$ Hz, 1 H), 8.26 (s, 4 H), 8.28 (s, 4H), 13.60 (br s, 1 H), 14.33 (br s, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): $\delta = 24.4, 29.3, 29.6, 30.4, 31.6, 33.1, 33.3, 34.2, 35.0, 35.1, 72.4, 72.5, 86.7, 91.6, 111.9, 117.8, 118.6, 125.2, 126.0, 127.1, 127.5, 132.1, 134.3, 132.7, 133.5, 136.6, 137.9, 140.2, 158.0, 161.5, 165.0, 166.2, 193.8$.

- 5 MS (ESI): m/z (I_{rel}) = 665 (59, $[\text{M} + 1]^+$), 449 (69, $\text{C}_{27}\text{H}_{33}\text{N}_2\text{O}_2\text{S}^+$), 331 (100, $\text{C}_{21}\text{H}_{35}\text{N}_2\text{O}$). Anal. Calcd for $\text{C}_{42}\text{H}_{52}\text{N}_2\text{O}_3\text{S}$ (664.37): C 75.86, H 7.88, N 4.21, O 7.22; found: C 75.79, H 7.93, N 4.06, O 7.19.

- (*R,R*)-*N*-(3,5-Di-*tert*-butylsalicylidene)-*N'*-[3-*tert*-butyl-5-(4'-**
 10 **vinylbenzene)salicylidene]-1,2-cyclohexanediamine (4c)(Scheme 2).** A 250 mL flask was charged with (1*R*,2*R*)-1,2-diaminocyclohexane monohydrochloride salt (1.51 g, 10 mmol), activated 4 Å molecular sieves (4.0 g), anhydrous methanol (40 mL), and anhydrous ethanol (40 mL). 3,5-Di-*tert*-butyl-2-hydroxybenzaldehyde (2.34 g, 10 mmol) was added in one portion and the reaction mixture was stirred at
 15 room temperature for four hours. After complete consumption of the aldehyde as monitored by the TLC, a solution of 3-*tert*-butyl-2-hydroxy-5-(4'-vinylphenyl)benzaldehyde (2.74 g, 10 mmol) in dichloromethane (80 mL) was added to the reaction system, followed by the slow addition of triethylamine (2.8 mL, 20 mmol). The reaction mixture was stirred at room temperature for additional
 20 four hours followed by the removal of the solvents. The residue was dissolved in dichloromethane (100 mL), washed with aqueous hydrochloric acid (1 M, 50 mL) and water (2×50 mL), and dried with magnesium sulfate. Flash chromatography of the crude product with (ether/hexanes = 1:50) afforded **4c** (5.05 g, 85%) as a yellow solid. Mp: 177–178 °C; $[\alpha]_{\text{D}}^{20} - 156^\circ$ (c 0.5, DCM). ^1H NMR (400 MHz, CDCl_3): $\delta = 1.22$ (s, 9 H), 1.42 (s, 9 H), 1.44 – 1.51 (m, 2 H), 1.46 (s, 9 H), 1.70 – 1.84 (m, 2 H), 1.88 – 1.91 (m, 2 H), 1.97 – 2.02 (m, 2 H), 3.30 – 3.38 (m, 2 H), 5.25 (d, $J =$
 25 11.0 Hz, 1 H), 5.77 (d, $J = 17.6$ Hz, 1 H), 6.74 (dd, $J = 11.0, 17.6$ Hz, 1 H), 6.97 (d, $J = 2.5$ Hz, 1 H), 7.21 (d, $J = 2.5$ Hz, 1 H), 7.31 (d, $J = 2.5$ Hz, 1 H), 7.40 – 7.45 (m, 4 H), 7.49 (d, $J = 2.5$ Hz, 1 H), 8.30 (s, 1 H), 8.35 (s, 1 H), 13.69 (s, br, 1 H), 14.01
 30 (s, br, 1 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): $\delta = 24.5, 24.6, 29.5, 29.6, 31.6, 33.3, 33.4, 34.2, 35.1, 35.2, 72.6, 113.6, 118.0, 119.0, 126.2, 126.7, 126.9, 127.1, 128.2, 128.3, 130.5, 136.0, 136.6, 136.7, 137.8, 140.2, 140.7, 158.2, 160.2, 165.8, 166.2$. IR: $\nu = 3082, 2999, 2952, 2933, 2860, 1628, 1467, 1440, 1390, 1271, 1252, 1171,$

840 cm⁻¹. UV-vis (THF): λ = 262, 300, 340 nm. MS (FAB): m/z (I_{rel}) = 592 (100, M^+). Anal. Calcd for C₄₀H₅₂N₂O₂ (592.85): C 81.04, H 8.84, N 4.73.; found: C 81.06, H 8.95, N 4.72.

- 5 **(*R,R*)-*N*-(3,5-Di-*tert*-butylsalicylidene)-*N'*-[3-*tert*-butyl-5-(hydroxymethyl)salicylidene]-1,2-cyclohexanediamine (4d)(Scheme 2).** A 100 mL flask was charged with (1*R*,2*R*)-1,2-diaminocyclohexane monohydrochloride salt (151 mg, 1.0 mmol), activated 4 Å molecular sieves (200 mg), and anhydrous methanol (10 mL). 3,5-Di-*tert*-butyl-2-hydroxybenzaldehyde (234 mg, 1.0 mmol)
- 10 was added in one portion and the reaction mixture was stirred at room temperature for four hours. A solution of 3-*tert*-butyl-2-hydroxy-5-(hydroxymethyl)benzaldehyde (208 mg, 1.0 mmol) in dichloromethane (10 mL) was added to the reaction mixture, followed by the slow addition of triethylamine (0.27 mL, 2.0 mmol). The reaction mixture was stirred at room temperature for additional
- 15 four hours followed by the removal of the solvents. The residue was dissolved in dichloromethane (20 mL), washed with water (2 × 20 mL), and dried with magnesium sulfate. Flash chromatography of the crude product on silica gel (ether/hexanes = 1:4 to 1:1) afforded **4d** (0.39 g, 75%) as a light yellow solid. $[\alpha]_D^{20}$ -318° (c 0.5, DCM). ¹H NMR (400 MHz, CDCl₃): δ = 1.23 (s, 9 H), 1.41 (s, 9 H), 1.42 (s, 9 H), 1.43 – 1.51 (m, 2 H), 1.70 – 1.80 (m, 2 H), 1.88 – 1.92 (m, 2 H), 1.96 – 2.02 (m, 2 H), 3.29 – 3.38 (m, 2 H), 4.52 (s, 2 H), 6.96 (d, J = 2.2 Hz, 1 H), 7.01 (d, J = 2.0 Hz, 1 H), 7.25 (d, J = 2.0 Hz, 1 H), 7.31 (d, J = 2.4 Hz, 1 H), 8.28 (s, 1 H), 8.29 (s, 1 H), 13.68 (s br, 1 H), 13.97 (s br, 1 H). ¹³C{¹H}NMR (100 MHz, CDCl₃): δ = 24.5, 24.6, 29.5, 29.6, 31.6, 33.3, 33.4, 34.2, 35.0, 35.2, 65.6, 72.60,
- 20 72.61, 118.0, 118.5, 126.2, 127.0, 129.0 (2 overlapping lines), 130.1, 136.6, 137.7, 140.1, 158.1, 160.3, 165.5, 166.1. MS (EI): m/z (I_{rel}) = 520 (100, M^+). Anal. Calcd for C₃₃H₄₈N₂O₃: C 76.11, H 9.29, N 5.38, found: C 76.19, H 9.51, N 5.07.

- 30 **(*R,R*)-*N*-(3,5-Di-*tert*-butylsalicylidene)-*N'*-[3-*tert*-butyl-5-(2'-hydroxyethoxymethyl) salicylidene]-1,2-cyclohexanediamine (4e)(Scheme 2).** (*R,R*)-1,2-Diaminocyclohexane mono(hydrogen chloride) (276 mg, 1.83 mmol), 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (460 mg, 1.83 mmol), and 4 Å molecular sieves (200 mg) were charged into a 50 mL flask equipped with a magnetic stir bar

and a septum. Anhydrous ethanol (5 mL) and anhydrous methanol (5 mL) were added and the bright yellow solution was stirred at room temperature for four hours. A solution of 3-*tert*-butyl-2-hydroxy-5-(2'-hydroxyethoxymethyl)benzaldehyde (460 mg, 1.83 mmol) in anhydrous CH₂Cl₂ (10 mL) and anhydrous NEt₃ (0.51 mL, 3.66 mmol) were added. The red solution was stirred at room temperature for additional four hours. The reaction mixture was filtered through a short pad of dry silica gel and the silica gel was flushed with CH₂Cl₂. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (ethyl acetate/hexanes = 1:3) to afford **4e** (725 mg, 70 %) as a yellow powder. R_F (SiO₂, ethyl acetate / hexanes = 1:3) = 0.23. $[\alpha]_D^{20} - 262^\circ$ (c 0.5, DCM) ¹H NMR (500 MHz, CDCl₃): δ = 1.24 (s, 9 H), 1.41 (s, 9 H), 1.42 (s, 9 H), 1.43 - 1.55 (m, 2 H), 1.83 - 1.92 (m, 2 H), 1.61 - 1.81 (m, 2 H), 1.93 - 2.08 (m, 2 H), 2.01 (br s), 3.28 - 3.38 (m, 2 H), 3.54 (m, 2 H), 3.72 (br s, 2 H), 4.40 (s, 2 H), 6.98 (d, J = 2.3 Hz, 1 H), 7.01 (d, J = 1.6 Hz, 1 H), 7.22 (d, J = 1.6 Hz, 1 H), 7.31 (d, J = 2.3 Hz, 1 H), 8.29 (s, 1 H), 8.30 (s, 1 H), 13.70, (br s, 1 H), 14.00 (br s, 1 H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 24.3, 29.4, 29.5, 31.5, 33.3, 34.2, 34.9, 35.1, 63.0, 71.2, 72.5, 72.6, 73.4, 117.9, 118.4, 126.1, 126.8, 126.9, 129.6, 129.8, 136.5, 137.4, 140.0, 158.1, 160.3, 165.3, 166.0. MS (ESI): m/z (I_{rel}) = 565 (13, [M + 1]⁺), 349 (48, C₂₀H₃₃N₂O₃⁺), 331 (100, C₂₁H₃₅N₂O⁺). HRMS (ESI) calcd for C₃₅H₅₃N₂O₄ ([M + 1]⁺): 565.4005; found: 565.4001. Anal. Calcd for C₃₅H₅₂N₂O₄ (564.39): C 74.43, H 9.28, N 4.96; found: C 74.38, H 9.30, N 4.85.

(*R,R*)-*N*-(3,5-Di-*tert*-butylsalicylidene)-*N'*-[3-*tert*-butyl-5-(7'-hydroxy-1',1'-dimethylheptyl)salicylidene]-1,2-cyclohexanediamine (4f**)(Scheme 2).** (*R,R*)-1,2-Diaminocyclohexane mono(hydrogen chloride) (59 mg, 0.39 mmol), 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (92 mg, 0.39 mmol), and 4 Å molecular sieves (200 mg) were charged into a 25 mL flask equipped with a magnetic stir bar and a septum. Anhydrous methanol (5 mL) was added and the bright yellow solution was stirred at room temperature for four hours. A solution of 3-*tert*-butyl-2-hydroxy-5-(7'-hydroxy-1',1'-dimethylheptyl)benzaldehyde (125 mg, 0.39 mmol) in anhydrous CH₂Cl₂ (10 mL) and anhydrous NEt₃ (0.15 mL, 0.90 mmol) were added. The red solution was stirred at room temperature for additional four hours. The reaction mixture was filtered through a short pad of dry silica gel and the silica gel was

flushed with ethyl acetate. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (ethyl acetate/hexanes = 1:3) to afford **4f** (208 mg, 84 %) as a bright yellow powder. $[\alpha]_D^{20} - 200^\circ$ (c 0.5, DCM). ^1H NMR (300 MHz, CDCl_3): δ = 1.00 - 1.15 (m, 2 H), 1.16 - 1.31 (m, 2 H), 1.25 (s, 6 H), 1.23 (s, 9 H), 1.28 (s, 9 H), 1.42 (s, 9 H), 1.43 - 1.59 (m, 6 H), 1.70 - 1.80 (m, 2 H), 1.88 - 1.92 (m, 2 H), 1.93 - 2.08 (m, 4 H), 2.01 (s, 1H), 3.29 - 3.38 (m, 2 H), 3.54 (t, 2 H), 6.98 (d, J = 2.2 Hz, 1 H), 7.01 (d, J = 1.8 Hz, 1 H), 7.25 (d, J = 2.0 Hz, 1 H), 7.31 (d, J = 2.4 Hz, 1 H), 8.29 (s, 1 H), 8.31 (s, 1 H), 13.71 (s br, 2 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ = 24.6, 24.8, 25.7, 29.1, 29.2, 29.3, 29.6, 29.7, 30.3, 31.6, 31.7, 33.0, 33.4, 33.5, 33.6, 34.3, 35.2, 37.2, 44.6, 63.2, 72.6, 76.8, 77.3, 77.7, 118.1, 126.2, 126.9, 127.0, 136.5, 136.6, 138.7, 140.1, 158.1, 158.2, 165.9, 166.0, 166.1, 220.2. MS (ESI): m/z (I_{rel}) = 635.6 (13, $[\text{M}^+1]^+$). HRMS (ESI) calcd for $\text{C}_{41}\text{H}_{64}\text{N}_2\text{O}_3$ ($[\text{M} + 1]^+$): 633.4996; found: 633.4995. Anal. Calcd for $\text{C}_{41}\text{H}_{64}\text{N}_2\text{O}_3$ (633.49): C 77.80, H 10.19, N 4.43; found: C 77.88, H 10.20, N 4.39.

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The following examples serve to more fully describe the manner of using the above-described disclosure, as well as to set forth the best modes contemplated for carrying out various aspects of the disclosure. It is understood that these examples in no way serve to limit the true scope of this disclosure, but rather are presented for illustrative purposes.

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Example 1

(*R,R*)-*N*-(3,5-Di-*tert*-butylsalicylidene)-*N'*-(3-(4'-vinylbenzene)-5-*tert*-butylsalicylidene)-1,2-cyclohexanediamine (1)(4c of Scheme 2). To a 500 mL flask was charged with (1*R*,2*R*)-1,2-diaminocyclohexane monohydrochloride salt (1.51 g, 10 mmol), activated 4A molecular sieve (4.0 g), anhydrous methanol (40 mL) and ethanol (40 mL). 3,5-Di-*t*-butyl-2-hydroxybenzaldehyde (2.34 g, 10 mmol) was added in one portion and the reaction mixture was stirred at rt for 4 h. TLC showed that all the aldehyde was consumed. A solution of 3-(4'-vinylphenyl)-5-*t*-butyl-2-hydroxybenzaldehyde (2.74 g, 10 mmol) in dichloromethane (80 mL) was added to reaction system, followed by the addition of triethylamine (2.8 mL, 20 mmol) in a dropwise fashion. After the reaction mixture was stirred at rt for additional 4 h, all the solvents were removed by rotovap. The residue was dissolved

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in dichloromethane (100 mL), washed with aqueous hydrochloric acid (1 M, 50 mL) and water (2 x 50 mL), and dried with magnesium sulfate. The desired compound 1 (5.05 g, 85.2%) was isolated by flash chromatography of the crude product with 1/50 ether/hexanes.

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Example 2

Polymerization of (*R,R*)-*N*-(3,5-Di-*tert*-butylsalicylidene)-*N'*-(3-(4'-vinylbenzene)-5-*tert*-butylsalicylidene)-1,2-cyclohexanediamine (Scheme 7).

The monomer 1 (237 mg, 0.40 mmol) of Example 1 and AIBN (2.5 mol %, 1.7 mg, 0.010 mmol) were charged into a Schlenk tube. The system was purged with argon for three times. Under the protection of positive pressure of argon, degassed chlorobenzene (2 mL) was added to the system. The reaction mixture was stirred at 80 °C for 48 h. After it was cooled to rt, the solution was poured in to methanol (20 mL) and a yellow solid precipitated. The solid was collected by filtration and washed with 1/20 dichloromethane/methanol (3 x 10 mL). It was dissolved in dichloromethane (2 mL) and reprecipitated with methanol (20 mL). The solid was collected on a frit, washed with methanol (10 mL), and dried under high vacuum to afford the desired polymer 4 as a yellow powder (201 mg, 85%). Using a similar procedure, homopolymers (2,3) and copolymers (5-7) with styrene were synthesized with different chain lengths and ratios of monomers.

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Example 3

Metalation of Polymers with Cobalt(II) Acetate (Scheme 8). The reaction was carried out in a glove box and solvents were degassed prior to use. The polymer 4 (95 mg, 0.16 mmol) was dissolved in dichloromethane (2 mL) in a vial charged with a stir bar. A solution of cobalt acetate tetrahydrate (49.8 mg, 0.20 mmol) in methanol (2 mL) was added slowly to the vial, resulting in precipitation of a red-brown powder. After the suspension was stirred at rt for 3 h, additional methanol (6 mL) was added to precipitate more solid. The solid was collected by filtration, washed with 1/10 dichloromethane/methanol (2 x 10 mL) and methanol (10 mL), and dried under high vacuum to give the desired product Co(II)(4) (99 mg, 95%). Using a similar procedure, Co(II)(2), Co(II)(3), Co(II)(5), Co(II)(6), and Co(II)(7) were synthesized.

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Example 4

Preparation of Norbornene Linked Ligands: 5-(4-Hydroxyphenyl ethynyl)-3-*tert*-butyl-2-hydroxybenzaldehyde, 6 (Scheme 3; 4a of Scheme 2). An *in-vacuo* flame-dried 100 mL Schlenk-flask under argon, equipped with a magnetic stir bar and a septum was charged with 1.714 g 4-iodophenol (7.79 mmol, 1.0 eq.), 278 mg [PdCl₂(PPh₃)₂] (0.397 mmol, 5 mol-%) and 51 mg triphenylphosphine (0.195 mmol, 2.5 mol-%). The flask was evacuated and subsequently flushed with Ar. After the evacuating-flushing procedure had been repeated twice, 10 mL of anhydrous THF, a solution of 1.576 g 5-ethynyl-3-*tert*-butyl-2-hydroxybenzaldehyde 23 (7.79 mmol, 1.0 eq.) in 15 mL anhydrous THF and 2.2 mL of NEt₃ (1.58 g, 15.54 mmol, 2.0 eq.) were added *via* a syringe, respectively, and the slurry was stirred at room temperature for 20 minutes. 28 mg CuI (0.117 mmol, 1.5 mol%) were added and the dark red solution was stirred at room temperature for 27 hours. The mixture was diluted with 100 mL H₂O and 50 mL Et₂O and the phases were separated. The aqueous layer was extracted with Et₂O (2 x 50 mL), the combined organic layers were washed with brine (40 mL) and dried over MgSO₄. After removal of the solvent under reduced pressure, 4.16 g of the crude product were obtained as a red oil. Purification by column chromatography (SiO₂, 4x58 cm², ethyl acetate/hexanes = 1:7) yielded 1.224 g product (51%) as yellow powder. ¹H-NMR (500 MHz, CDCl₃/CD₂Cl₂): δ = 1.41 (s), 5.19 (br. s.), 6.80 (d), 7.40 (d), 7.57 (d), 7.63 (dd), 9.84 (br. s.), 11.88 (dd). ¹³C-NMR (125 MHz, CDCl₃/CD₂Cl₂): δ = 29.0, 35.0, 86.9, 88.1, 114.6, 115.4, 115.6, 120.5, 133.2, 134.9, 137.0, 138.8, 155.9, 161.0, 196.9. HRMS (ESI): calcd for C₁₉H₁₈O₃: 294.1256, obsd 295.1341 [M+1]⁺. Anal. Calcd. for C₁₉H₁₈O₃: C, 77.53, H, 6.16, O, 16.31. Found: C, 77.20, H, 6.37, O, 16.27.

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Salen Linker Compound 7 (Scheme 3). Under an argon atmosphere in a flame-dried 25 mL three-necked flask, equipped with a magnetic stir bar, a septum and a gas-inlet, 301 mg (*R,R*)-1,2-diaminocyclohexane-*mono*-aminochloride 3 (2 mmol, 1.0 eq.) and some 4Å molecular sieve were slurried up in 7 mL anhydrous ethanol and 7 mL anhydrous methanol. To this slurry, 487 mg 5-(4-hydroxyphenyl ethynyl)-3-*tert*-butyl-2-hydroxy-benzaldehyde 6 (2 mmol, 1.0 eq.) was added. The bright yellow solution was stirred at room temperature. After four hours, a solution of 589 mg 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde 4 (2 mmol, 1.0 eq.) in 15 mL

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anhydrous CH_2Cl_2 and 0.56 mL anhydrous NEt_3 (4 mmol, 2.0 eq.) were added. The red solution was stirred at room temperature for an additional four hours. The mixture was filtered, the solvent removed under reduced pressure and the residue purified by column chromatography (dry SiO_2 , $2.5 \times 40 \text{ cm}^2$, ethyl acetate / hexanes = 1:5). 910 mg of the product (64%) could be isolated as a yellow-orange powder. ^1H -NMR (500 MHz, $\text{CDCl}_3/\text{CD}_2\text{Cl}_2$): δ = 1.26 (s), 1.44 (s), 1.46 (s), 1.40-1.53 (m), 1.82-1.93 (m), 1.66-1.81 (m), 1.93-2.05 (m), 3.25-3.77 (m), 6.81 (d), 7.00 (d), 7.19 (d), 7.35 (d), 7.40 (d), 7.41 (d), 8.22 (s), 8.28 (s). ^{13}C -NMR (125 MHz, $\text{CDCl}_3/\text{CD}_2\text{Cl}_2$): δ = 24.4, 29.4, 29.6, 31.5, 33.1, 33.2, 35.0, 34.2, 35.1, 72.0, 72.2, 87.2, 88.3, 112.5, 115.7, 115.7, 117.7, 118.4, 126.1, 127.3, 132.7, 133.2, 133.2, 136.7, 137.9, 140.1, 155.7, 158.4, 161.5, 165.2, 166.2. MS (ESI) m/z (%): 607.3888 (± 0.025) (56, $[\text{M}+1]^+$), 391.2 ($\text{C}_{25}\text{H}_{31}\text{N}_2\text{O}_2$, 100), 331.3 ($\text{C}_{21}\text{H}_{35}\text{N}_2\text{O}$, 72). Anal. Calcd. for $\text{C}_{40}\text{H}_{50}\text{N}_2\text{O}_3$: C, 79.17, H, 8.30, N, 4.62, O, 7.91. Found: C, 78.61, H, 8.26, N, 4.63, O, 8.06.

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Salen-Norbornene Compound (Scheme 3). Under an argon atmosphere, 720 mg salen linker compound 7 (1.186 mmol, 1.0 eq.) was dissolved in 20 mL anhydrous CH_2Cl_2 in a dry 50 mL Schlenk-flask, equipped with a magnetic stir bar and a septum. The red solution was cooled to 0 °C. A solution of 204 mg norbornene carbonyl chloride 8 (1.31 mmol, 1.1 eq.) in 8 mL anhydrous CH_2Cl_2 and 0.18 mL anhydrous NEt_3 (1.31 mmol, 1.1 eq.) were added dropwise *via* a syringe, respectively. The yellow solution was stirred at 0 °C for 30 minutes and was then allowed to warm up to room temperature over a period of 30 minutes. The reaction mixture was filtered through a pad of dry silica and the silica was flushed with CH_2Cl_2 . After removal of the solvent under reduced pressure, 913 mg product (96%) were obtained as a yellow solid. Usually, the crude product was used in the following steps. For characterization purposes, a part of the norbornene was purified by column chromatography (dry SiO_2 , Et_2O /hexanes = 1:10). ^1H -NMR (500 MHz, $\text{CDCl}_3/\text{CD}_2\text{Cl}_2$): δ = 1.24 (s), 1.42 (s), 1.43 (s), 1.35-1.39 (m), 1.45-1.50 (m), 1.83-1.94 (m), 1.50-1.64 (m), 1.68-1.82 (m), 1.94-2.01 (m), 2.01-2.10 (m), 2.97-3.02 (m), 3.19-3.25 (m), 3.22-3.37 (m), 3.37-3.41 (m), 6.09 (dd), 6.28 (dd), 6.18 (dd), 6.21 (dd), 6.96 (d), 7.01 (d), 7.08 (d), 7.19 (d), 7.32 (d), 7.39 (d), 7.47 (d), 7.80 (d), 8.25 (s), 8.28 (s), 13.62 (br. s.), 14.28 (br. s.). ^{13}C -NMR (125 MHz,

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CDCl₃/CD₂Cl₂): δ = 24.4, 29.3, 29.6, 29.5, 30.7, 31.6, 33.1, 33.3, 34.2, 35.0, 35.1, 41.9, 42.8, 43.5, 43.8, 46.1, 46.5, 46.9, 49.9, 72.4, 72.5, 86.7, 89.7, 112.2, 117.8, 118.6, 121.2, 121.7, 126.0, 127.1, 132.3, 132.6, 132.7, 133.4, 135.8, 136.6, 137.9, 138.4, 140.2, 150.5, 158.0, 161.3, 165.1, 166.2, 173.2. MS (ESI) m/z (%): 727.5 (100, [M+1]⁺), 525.4 (19). Anal. Calcd. for C₄₀H₅₈N₂O₄: C, 79.30, H, 8.04, N, 3.85, O, 8.80. Found: C, 79.07, H, 8.06, N, 3.79, O, 8.86.

Mn-Salen-Norbornene Compound 9 (Scheme 3). Under an argon atmosphere, an *in-vacuo* flame-dried 100 mL three-necked flask, equipped with a magnetic stir bar, a septum, an addition funnel and a reflux-condenser with gas-inlet, was charged with 923 mg Mn(OAc)₂·4H₂O (3.77 mmol, 3.0 eq.) and 15 mL anhydrous ethanol. The white slurry was heated to reflux (90 °C oil bath temperature) and a solution of 913 mg salen-norbornene (1.26 mmol, 1.0 eq.) in 15 mL anhydrous toluene was filled into the addition funnel. The ligand-solution was added dropwise to the manganese solution and the addition funnel was washed with anhydrous ethanol (2 x 5 mL). The reaction mixture was heated under reflux for two hours. Then, a needle connected to an air cylinder was placed in the solution through the septum, air was slowly bubbled through the refluxing mixture and the conversion of the ligand was monitored by TLC-analysis of the red solution. After one hour, TLC-analysis indicated complete conversion of the free ligand. Then, 160 mg lithium chloride (3.77 mmol, 3.0 eq.) was added and the mixture was allowed to cool down to room temperature over a period of one hour. The mixture was transferred into a separatory funnel and the toluene layer was washed with H₂O (3 x 50 mL) and brine (50 mL) and dried over MgSO₄. After removal of the solvent under reduced pressure, 1.93 g crude product were obtained as a dark red oil. Purification by column chromatography (dry SiO₂, 4x30 cm², CH₂Cl₂ -> CH₂Cl₂/ethyl acetate = 5:1) yielded 813 mg product (79%) as a dark red solid. MS (ESI) m/z (%): 779.35 (100, [M-Cl]⁺). Anal. Calcd. for C₄₀H₅₆ClMnN₂O₃: C, 70.71, H, 6.92, N, 3.44. Found: C, 70.34, H, 7.11, N, 3.37.

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Example 5

Poly(Mn-salen-norbornene), p(9) (where "p" refers to a polymer of compound "9") (Synthesis of a 50-mer)(Scheme 5). In an *in-vacuo* flame-dried 50 mL three-

necked flask equipped with a magnetic stir bar, a septum and a reflux-condenser with gas-inlet, 122 mg Mn-salen-norbornene **9** (150 μmol , 50 eq.) was dissolved in 3 mL anhydrous CDCl_3 and the solution was heated to 40 $^\circ\text{C}$. 2.7 mg Grubbs-catalyst (3 $^\circ$ -generation) (3 μmol , 1 eq.) was added as a solid and the mixture was stirred for 2.5 hours at 40 $^\circ\text{C}$. The polymerization was quenched by adding three drops of ethyl vinyl ether and the polymer was precipitated by adding 30 mL of Et_2O . The polymer was separated by centrifugation and washed with Et_2O three times (the polymer was suspended in Et_2O and subsequently separated by centrifugation). After drying the residue *in vacuo*, 96 mg (79%) of an ether-insoluble polymer-fraction were obtained as a dark, red-brown powder. Anal. Calcd. for $\text{C}_{40}\text{H}_{56}\text{ClMnN}_2\text{O}_3$: C, 70.71, H, 6.92, N, 3.44, O, 7.85. Found: C, 68.67, H, 7.02, N, 3.27, O, 9.09. ICP: calcd: Mn, 6.74. Found: Mn, 5.00.

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Example 6

Poly(Mn-salen-norbornene-co- n-octyl-norbornenecarbonyl ester), p(9.11)(where "p" refers to copolymer of "9.11") (x/y = 1:1, x+y = 50)(Scheme 5). In an *in vacuo* flame-dried 25 mL three-necked flask under Ar, equipped with a magnetic stir bar, a septum and a reflux-condenser with gas-inlet, 79 mg Mn-salen-norbornene **9** (94 μmol , 25 eq.) and 24 mg *n*-octyl-norbornenecarbonyl ester **11** (94 μmol , 25 eq.) were dissolved in 4 mL anhydrous CDCl_3 . Then, 3.3 mg Grubbs-catalyst (3 $^\circ$ -generation) (3.75 μmol , 1 eq.) were added as a solid and the mixture was stirred at room temperature. After 20 minutes, TLC-analysis as well as analysis of an aliquot by ^1H -NMR spectroscopy indicated complete conversion of both monomers. The polymerization was quenched by adding two drops of ethyl vinyl ether and the polymer was precipitated by adding 20 mL of Et_2O . After separation of the solid by centrifugation and drying *in vacuo*, 82 mg (82%) of an ether-insoluble polymer-fraction was obtained as a dark, red-brown powder. Anal. Calcd.: C, 72.13, H, 7.78, N, 2.63, O, 9.01, Cl, 3.33. Found: C, 71.10, H, 7.65, N, 2.64, O, 9.72, Cl, 2.26. ICP: calcd: Mn, 5.15. Found: Mn, 4.68.

Example 7

Co-Salen-Norbornene, 10 (Scheme 5). In an *in vacuo* flame-dried 10 mL Schlenk-flask under Ar, equipped with a magnetic stir bar and a septum, 146 mg salen-norbornene (0.20 mmol, 1.0 eq.) were dissolved in 1.5 mL anhydrous CH_2Cl_2 . A solution of 60 mg $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.24 mmol, 1.1 eq.) in 2 mL of anhydrous MeOH was added dropwise *via* a syringe. The resulting red suspension was stirred for 30 min. at room temperature, cooled in a ice-bath and stirred for another 30 min. at 0 °C. The orange-red precipitate was separated by vacuum-filtration, washed with cold MeOH and dried *in vacuo* to yield 121 mg (77%) **10** as an orange-red powder. MS (ESI) *m/z* (%): 783.3517 (± 0.01) (100, $[\text{M}]^+$) – calcd.: 783.3572. Anal. Calcd. for $\text{C}_{48}\text{H}_{56}\text{CoN}_2\text{O}_4$: C, 73.54, H, 7.20, N, 3.57, O, 7.52. Found: C, 73.33, H, 7.21, N, 3.49, O, 7.64. ICP: calcd: Co, 7.52. Found: Co, 8.00.

Example 8

Poly(Co(II)-salen-norbornene) p(10)' (Synthesis of a 20-mer) (Scheme 5). In an *in vacuo* flame-dried 25 mL three-necked flask under Ar, equipped with a magnetic stir bar, a septum and a gas-inlet, 111 mg Co(II)-salen-norbornene **10** (151 μmol , 20 eq.) were dissolved in 10 mL anhydrous CDCl_3 . Then, 6.7 mg Grubbs-catalyst (3rd-generation) (7.5 μmol , 1 eq.) were added as a solid and the mixture was stirred at room temperature. After two hours, analysis of an aliquot by ^1H -NMR-spectroscopy showed complete conversion of the monomer (absence of monomeric olefin peaks). The polymerization was quenched by adding three drops of ethyl vinyl ether and mixture was poured into 50 mL of cold Et_2O . The precipitated polymer was separated by centrifugation and washed with Et_2O (the polymer was suspended in Et_2O and subsequently separated by centrifugation). After drying the residue *in vacuo*, 105 mg (94%) of an ether-insoluble polymer-fraction were obtained as a dark, red powder. Anal. Calcd. for $\text{C}_{48}\text{H}_{56}\text{CoN}_2\text{O}_4$: C, 73.54, H, 7.20, N, 3.57, O, 7.52. Found: C, 71.06, H, 7.06, N, 3.57, O, 8.16. ICP: calcd: Co, 7.52. Found: Co, 6.96.

Example 9

Poly(Co-salen-norbornene-co- n-octyl-norbornenecarbonyl ester) p(10.11) (x/y = 1:1, x+y = 50) (Scheme 5). In an *in vacuo* flame-dried 10 mL Schlenk-flask under Ar, equipped with a magnetic stir bar and a septum, 78 mg Co-salen-norbornene 10 (100 μ mol, 25 eq.) and 25 mg *n*-octyl-norbornenecarbonyl ester 11 (100 μ mol, 25 eq.) were dissolved in 5 mL anhydrous CDCl_3 . Then, 3.5 mg Grubbs-catalyst (3^o-generation) (4 μ mol, 1 eq.) was added as a solid and the mixture was stirred at room temperature. After 40 minutes, TLC-analysis as well as analysis of an aliquot by ^1H -NMR spectroscopy indicated complete conversion of both monomers. The polymerization was quenched by adding two drops of ethyl vinyl ether. The solvent was removed under reduced pressure, the residue was redissolved in some CH_2Cl_2 , and the polymer was precipitated by adding 40 mL of cold Et_2O . After separation of the solid by centrifugation and drying *in vacuo*, 94 mg (91 m-%) of an ether-insoluble polymer-fraction were obtained as a dark, brown powder. Anal. Calcd.: C, 75.11, H, 8.80, N, 7.82, O, 10.42. Found: C, 74.25, H, 8.73, N, 1.95, O, 11.15. ICP: calcd: Co, 3.84. Found: Co, 3.95.

Example 10

Synthesis of the Co-salen-norbornene monomer 10·I (M= Co, L= I)(Scheme 5). In an *in vacuo* flame-dried 10 mL Schlenk-flask under Ar, equipped with a magnetic stir bar and a septum, 73 mg salen-norbornene (0.10 mmol, 1.0 eq.) was dissolved 1 mL in anhydrous CH_2Cl_2 . A solution of 27 mg $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.11 mmol, 1.1 eq.) in 1 mL anhydrous MeOH was added dropwise *via* a syringe. The resulting red suspension was stirred for 60 min. at room temperature. TLC-analysis of the reaction mixture showed complete conversion of the ligand to the Co complex. Next, 27 mg iodine I_2 (0.2 mmol I, 2.0 eq.) was added as a solid and the dark solution was stirred for another 60 min. at room temperature. The reaction mixture was filtered through a pad of dry silica and the silica was flushed with CH_2Cl_2 . After removal of the solvent under reduced pressure, the obtained dark powder was purified by column-chromatography over dry silica (CH_2Cl_2 / ethyl acetate = 5:1) to yield 78 mg (86%) 10·I as a dark powder. R_F (SiO_2 , Et_2O / hexanes = 1:10) = 0. ESI-MS m/z (%): 7. 783.3 (100, $[\text{M-I}]^+$) – calcd.: 910.8.

Polymerization of 10-I to Poly(Co-I-salen-norbornene) p(10b).

In an *in vacuo* flame-dried 10 mL three-necked flask under Ar, equipped with a magnetic stir bar, a septum and a gas-inlet, 56 mg Co-I-salen-norbornene **10-I** (62 micromol, 20 eq.) were dissolved in 2.5 mL anhydrous CDCl₃. 2.7 mg Grubbs-catalyst (3^o-generation) (3.1 micromol, 1 eq.) were added as a solid and the mixture was stirred at room temperature. After two hours, analysis of an aliquot by ¹H-NMR-spectroscopy showed complete conversion of the monomer (absent monomeric olefin signals). The polymerization was quenched by adding 3 drops of ethyl vinyl ether and the polymer was precipitated by adding 20 mL of cold Et₂O. The precipitated polymer was then separated by centrifugation and washed with Et₂O (i.e., the polymer was suspended in Et₂O and subsequently separated by centrifugation). After drying the residue *in vacuo*, 35 mg (62 m-%) of an ether-insoluble polymer-fraction were obtained. GPC: M_n = 43,000, M_w = 66,100, M_w/M_n = 1.54.

Example 11

Hydrolytic kinetic resolution of racemic epichlorohydrin *rac*-18 with poly(Co(III)(OTs)-salen-norbornene) p(10c)(Scheme 10). In a vial with a magnetic stir bar, 48.7 mg poly(Co(III)(OTs)-salen-norbornene) **p(10c)** (50 μmol, 0.5 mol-%) were dissolved in 100 μL chlorobenzene (as an internal standard) and 784 μL epichlorohydrin (10 mmol, 1.0 eq.). After taking an aliquot (2 μL), 126 μL of water (7 mmol, 0.7 eq.) were added. Aliquots (2 μL) were taken after 5, 10, 15, 20, 30, 60, 120 and 180 minutes. All aliquots were filtered through a pipette with cotton and some silica and the silica was flushed with 1.5-2 mL Et₂O. The resulting solutions were analyzed *via* chiral GC-FID (γ-TA). After three hours, the dark mixture was diluted with 2 mL CH₂Cl₂ and added drop-wise to cold Et₂O (ca. 40 mL). The resulting precipitate was separated by centrifugation and washed with cold Et₂O, i.e., the polymer was suspended in Et₂O and subsequently separated by centrifugation, then dried *in vacuo*.

Hydrolytic Kinetic Resolution of (rac)-Epichlorohydrin (Scheme 10). The above procedure was repeated with the exception that a Co(II) salen-norbornene was

selected as the starting catalyst instead of a Co(III). The precatalyst Co(II)(**2-7**) (Scheme 8) (25.5 mg, 0.025 mmol) was dissolved in dichloromethane (1 mL) in 10 mL flask. Glacial acetic acid (0.10 mL) was added and the reaction mixture was stirred in the open air for 30 min. The solvent and excess acetic acid were
5 completely removed under high vacuum. To the residue was added epichlorohydrin (391 microliter, 5.0 mmol) and chlorobenzene (50 microliter, internal reference). The flask was immersed in a water bath at rt. Deionized water (0.70 eq., 63 microl, 3.5 mmol) was injected into the system to start the reaction and the reaction process was monitored by means of GC (G-TA column). With a reaction time of 1 h, the
10 conversion and the ee of epichlorohydrin were 55% and >99%, respectively.

Hydrolytic Kinetic Resolution with polymeric Co-OAc-salen complexes p(38) and p(38.29) The above procedure was repeated with the exception that polymeric Co-OAc-salen complexes **p(38)** and **p(38.29)** were selected and other conditions or
15 procedural variations as indicated. The catalytic performances of the polymeric cobalt complexes **p(38)** and **p(38.29)** prepared as shown in Scheme 6 were studied in the HKR of racemic epichlorohydrin, where dichloromethane was added as a cosolvent due to the insolubility of the copolymers in ECH. The reaction kinetics of the HKR were studied *via* chiral GC-analysis. Using the homopolymer **p(38a)**,
20 epoxide (*R*)-**36** (*R*)-epichlorohydrin was fully converted after less than two hours to its corresponding diol, leaving pure (*S*)-**36** in the reaction mixture in above 99% *ee*. After this time period, 55 % of the racemic **36** is converted, showing that **p(38a)** with the flexible ethylene glycol linker is more active than its analogue **p(28a)** with a rigid phenylene acetylene linker (>99 % *ee* , 55 % conv. after five hours, while the
25 selectivity is comparable. In contrast to the results with the copolymers of **28**, the activity of **p(38a-co-29)** decreases with increasing dilution (i.e., decreased content of copolymerized monomer compound of formula (I)) of the catalytic centers along the polymer chain. With **p(38a-co-29)₁₃** it took three hours to obtain (*S*)-**36** with >99 % *ee* (54 % conv.), while with **p(38a-co-29)₁₉** a complete conversion of *rac*-**36**
30 could not even be achieved after 40 hours (49 % conv., 92 % *ee*). These results reflect the expectations for a cooperative bimetallic mechanism for the HKR and can thus be interpreted as confirmation of this mechanism.

Under solvent-free condition of the HKR, **p(38a)** was not only more active but also more selective than its analog with a rigid linker **p(28a)**. Using the

polymeric catalyst **p(38a)**, (*S*)- **36** with >99 % *ee* was obtained after only 30 minutes and with 54 % conversion of the *rac*-**36** (**p(28a)**: two hours, 62 % conv.). Moreover, activity and selectivity of **p(38a)** were also higher than of the corresponding monomer **38a** (complete resolution after two hours and 56 % conv. of *rac*-**36**), indicating a positive polymer effect by an easier (intramolecular) interaction of two cobalt moieties in **p(38a)**.

Comparisons of the reaction rates for the degradation of the (*R*)-epoxide **36** reveals that the rate of the monomer **38a** was comparable to those of **28a** and **p(28a)** and slightly faster than for a Jacobsen catalyst, indicating that (i) slight diversity of structures **28a** and **38a** to that of the Jacobsen Co-salen are responsible for the different rates, and (ii) that the polymerization of **28a** did not result in a more active catalyst. In contrast to the similar activities of **28a** and **p(28a)**, the resolution rate with **p(38a)** is significantly higher than for monomer **38a** (according to the slopes by a factor of around two). Because the salen cores of **38a** and **p(38a)** have exactly the same structure, this increase can only be a result of a better intramolecular interaction of two cobalt centers in the polymer.

The activity differences between monomeric and polymeric **38a** as well as between **p(38a)** and **p(28a)**, that only differ in the linker flexibility, confirm the assumed bimetallic mechanism for the HKR. Moreover, the comparison of the catalytic performances of **p(28a)** and **p(38a)** shows that for polymer-supported catalysts for reactions, such as the HKR, where the interaction of two catalytic centers is significant for high performance, the use of flexible linkers and homopolymer-supports is preferred if not compulsory.

Because of the high activity of **p(38a)** the concentration of cobalt can be reduced from 0.5 mol-% to up to 0.01 mol-%, whereby only the resolution rate but not the selectivity was affected. When the cobalt amount was decreased from 0.5 mol-% to 0.1 mol-% the reaction time for obtaining (*S*)-**36** with >99 % *ee* increased from 30 minutes to five hours (54 % conv. of *rac*-**36** in both cases). A further reduction of the Co-concentration to 0.01 mol-% resulted in an even slower HKR. Nevertheless, after 46 hours, 53 % of the racemic epichlorohydrin is converted and (*S*)-**36** with 99 % *ee* is obtained, showing that even with a low concentration of **p(38a)** complete resolution is feasible.

The removal and recycling properties of **p(38a)** are comparable those of **p(28a)**. The polymeric Co-complexes could be separated easily from the reaction

mixtures by precipitation into Et₂O and subsequent centrifugation. After reoxidation with O₂/HOAc, the resolution rate of the recycled **p(38a)** is somewhat less than that of the original polymer and comparable to Jacobsen's cobalt-salen catalyst. The HKR was complete after three hours with 57 % conversion of *rac*-**36**, showing that selectivity of the catalyst also decreased slightly upon reuse. In the third cycle the polymeric catalyst was not fully soluble in the reaction mixture any more, even after adding CH₂Cl₂ as a co-solvent, and the reaction rate dropped significantly. However, after 14 hours (*S*)-**36** with 98 % *ee* was obtained (55 % conv. of *rac*-**36**), indicating that the polymeric catalyst was still active and very selective and that after an appropriate reaction time enantiomerically pure (*S*)-**36** could be isolated in good yields. Because of the solubility problems after precipitation and reoxidation of **p(38a)** and experience reusing **p(28a)** after pumping-off the substrates, the latter methodology was used to recycle **p(38a)**, using CH₂Cl₂ as a solvent. Although the solubility issues after recycling could be circumvented this way, activities and selectivities of the reused catalysts **p(38a)** decreased in each cycle. While the resolution in the first cycle was complete after two hours (55 % conv.), it took about 16 hours and almost 66 % conversion of *rac*-**36** in the second cycle. In the third cycle, only 30 % *rac*-**36** were converted after 23 hours (37 % *ee* of (*S*)-**36**), showing that **p(38a)** is not recyclable this way in contrast to **p(28a)**.

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Example 12

Asymmetric Epoxidation of 1,2-dihydronaphthalene 14 with poly(Mn-salen-norbornene) p(9) of Scheme 5 (Scheme 11). Under an argon atmosphere in a dry 10 mL Schlenk-flask, 13 mg poly(Mn-salen-norbornene) **p(9)** (16 μmol, 4 mol-%) and 234 mg *N*-methylmorpholine-*N*-oxide (NMO) (2 mmol, 5.0 eq.) were dissolved in 2 mL of anhydrous CH₂Cl₂. Then, 52 μL 1,2-dihydronaphthalene **14** (52 mg, 0.4 mmol, 1.0 eq.) and ca. 0.04 mL chlorobenzene as an internal standard were added *via* a microsyringe, respectively, and the solution was cooled to -20 °C. 138 mg *meta*-chloroperoxybenzoic acid (*m*CPBA) (0.8 mmol, 2.0 eq.) were added in three equal portions at *t* = 0, 60, 120 sec.. Aliquots (ca. 0.2 mL) were taken after 0, 30, 90, 150, 210 and 300 seconds. All aliquots were filtered through a pipette with cotton and some Al₂O₃ and the Al₂O₃ was flushed with ca. 1.5 mL CH₂Cl₂. The

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resulting solutions were analyzed *via* chiral GC-FID (HP-5). The aliquots at $t=210$ sec. and $t=300$ sec. were also analyzed by chiral GC-MS (β -CD).

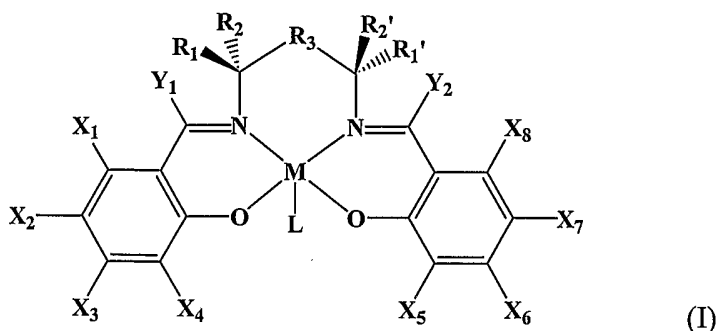
Example 13

- 5 **Recycling and reoxidation of the cobalt-polymers.** Polymeric Co-complexes were separated from the reaction mixtures by precipitation into Et₂O and subsequent centrifugation. The residue obtained after centrifugation was dissolved in CH₂Cl₂, 9.5 mg *para*-toluenesulfonic acid monohydrate (50 μ mol, 1.0 eq. according to Co) was added and the mixture was stirred under an atmosphere of air for one hour. The
- 10 CH₂Cl₂-solution was added dropwise to cold Et₂O (ca. 40 mL), the precipitate separated by centrifugation and “washed” with cold Et₂O. The obtained residue was dried *in vacuo* to yield 45 mg (93%) of re-oxidized **p(10c)_rec** as a dark green powder. The polymeric catalysts could be recovered quantitatively. For example for CoOAc-salen complex **p(10a)**, we started with 23 mg for the first catalytic cycle,
- 15 and obtained 24 mg after recycling and reoxidation in the second cycle and also 24 mg for the third cycle. This data clearly proves that the polymer was recycled quantitatively.

- 20 The disclosure has been described with reference to various specific embodiments and techniques. However, it should be understood that many variations and modifications are possible while remaining within the spirit and scope of the disclosure.

THE CLAIMED INVENTION IS:

1. A polymerizable chiral compound of formula (I)



wherein

R_1 , R_2 , R'_1 , R'_2 , X_1 , X_2 , X_3 , X_4 , X_5 , X_6 , X_7 , X_8 , Y_1 and Y_2 are independently H, C_1 - C_6 alkyl, C_3 - C_{12} cycloalkyl, C_1 - C_6 alkoxy, halogen, -OH, -SH, -NO₂, -NH₂, amino, imine, amide, carbonyl, carboxy, silyl, ether, thio ether, seleno ether, ketone, aldehyde, ester, phosphoryl, phosphonate, phosphine, sulfonyl, or $-(CH_2)_k-R_4$ group, wherein R_4 is aryl, heteroaryl, cycloalkyl, heterocycle, or polycycle, and k is an integer of 0 to 8, or any two or more proximate R_1 , R_2 , R'_1 , R'_2 , X_1 , X_2 , X_3 , X_4 , X_5 , X_6 , X_7 , X_8 , Y_1 and Y_2 form a ring of a carbocycle or heterocycle comprising 4 to 10 atoms,

where at least one X_1 , X_2 , X_3 , X_4 , X_5 , X_6 , X_7 , X_8 , Y_1 and Y_2 is independently of the formula -L'-Z-P, where

L' is a divalent linker independently a single carbon-carbon bond, $-(CH_2)_k-R_5$ -, $-(CH=CH)_k-R_5$ -, or $-(C\equiv C)_k-R_5$ -, wherein R_5 - is arylene, heteroarylene, cycloalkylene, heterocyclene, or polycyclene, and k is an integer of 0 to 8, $-R_5$ - can optionally be further substituted,

Z is a divalent connector independently a single carbon-carbon bond, $-C(=O)-$ -, $-C(=S)-$ -, $-C(=S)S-$ -, $-SC(=S)-$ -, $-SO_2-$ -, $-S(=O)_2O-$ -, $-O-S(=O)_2-$ -, $-C(=O)N(R_a)-$ -, $-C(=S)N(R_a)-$ -, $-SO_2N(R_a)-$ -, $-C(=O)O-$ -, $-O-C(=O)-$ -, $-C(=S)O-$ -, C_1 - C_8 alkylenyl, or alkyl substituted C_1 - C_8 alkylenyl, where R_a is -H, alkyl, acyl, aryl, alkylaryl, arylalkyl, aryloxy, alkoxycarbonyl, or benzyloxycarbonyl, and

P is a polymerizable group independently C₂-C₆ alkenyl, C₂-C₆ alkynyl, arylene-C₂-C₆ alkenyl, cycloalkenyl, cycloalkynyl, heterocycloalkenyl, or polycycloalkenyl;

R₃ is independently a single carbon-carbon bond, —CH₂—, —CH₂CH₂—, —NH—, —O—, or —S—;

5 M is absent or a metal atom or ion is at least one of Co, Mn, Cr, Al, Zn, Ru, Fe, Mo, Ni, Ti, Zr, or mixtures thereof; and

L is absent, or a counterion selected from F, Cl, Br, I, -O(C=O)alkyl, -O-S(=O)₂-R'₄, wherein R'₄ is aryl, arylC₂-C₆ alkyl, heteroaryl, C₁-C₆ alkyl, cycloalkyl, heterocycle, PF₆, B(Ar)₄, or B(halo)₃, where halo is F, Cl, Br, or I;

10 or a salt or hydrate thereof.

2. The compound of claim 1, wherein X₁, X₂, X₃, X₄, X₅, X₆, X₇, X₈, Y₁ and Y₂ are independently H, C₁-C₆ alkyl, and C₁-C₆ alkoxy, and at least one X₁, X₂, X₃, X₄, X₅, X₆, X₇, X₈, Y₁ and Y₂ is -L'-Z-P.

15

3. The compound of claim 1, wherein

X₁, X₃, X₄, X₅, X₆, X₇ and X₈ are independently H or t-butyl;

Y₁ and Y₂ are H;

R₁ and R'₂ are a carbocycle or heterocycle comprising 4 to 10 atoms, when R₂ and R'₁ are H, or R₁ and R'₂ are H, when R₂ and R'₁ are a carbocycle or heterocycle comprising 4 to 10 atoms;

R₃ is a single carbon-carbon bond; and

X₂ is -L'-Z-P.

25 4. The compound of claim 1, wherein

X₁, X₃, X₆, and X₈ are H;

X₄, X₅, and X₇ are t-butyl;

Y₁ and Y₂ are H;

R₁ and R'₂ are a -(CH₂)₄-, when R₂ and R'₁ are H, or R₁ and R'₂ are H, when R₂ and R'₁ are a -(CH₂)₄-;

30

R₃ is a single carbon-carbon bond;

X_2 is $-L'-Z-P$ where

L' is a single carbon-carbon bond or $-(C\equiv C)_k-Ar-$, where k is 1;

Z is $-C(=O)O-$ or $-O-C(=O)-$;

P is C_2-C_6 alkenyl, cycloalkenyl, or polycycloalkenyl;

5 M is Co, Mn, or mixtures thereof; and

L is absent, or a counterion selected from F, Cl, Br, I, $-O(C=O)alkyl$, $-O-S(=O)_2-$
 R'_4 , wherein R'_4 is aryl, aryl C_2-C_6 alkyl, heteroaryl, C_1-C_6 alkyl, cycloalkyl, heterocycle,
 PF_6 , $B(Ar)_4$, or $B(halo)_3$, where halo is F, Cl, Br, or I;
 or a salt or hydrate thereof.

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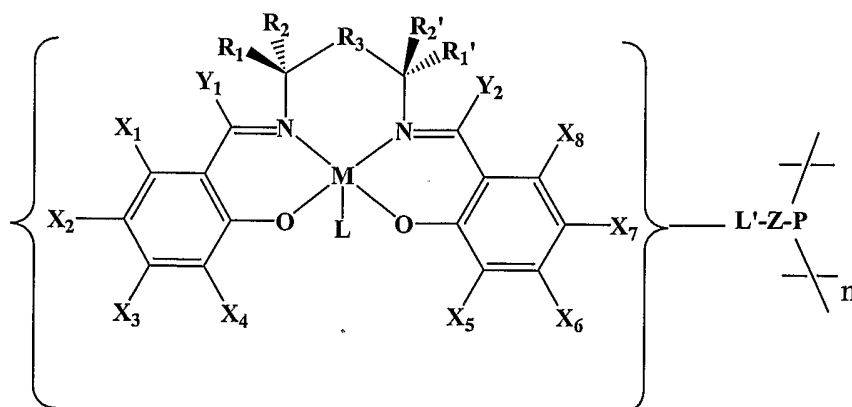
5. The compound of claim 1, wherein

P is ethylenyl, cyclooctenyl, or norbornenyl;

M is Co or Mn; and

15 L is absent or a halide anion selected from F, Cl, Br, and I; or a salt or hydrate thereof.

6. A homopolymer of the compound of claim 1 of the formula:



20

wherein

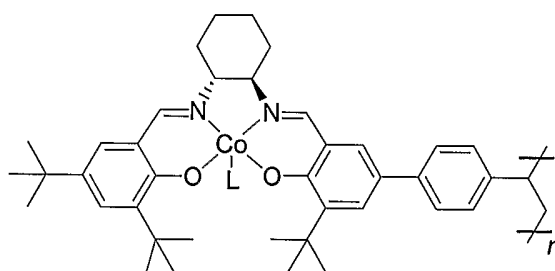
M is a metal atom or ion is at least one of Co, Mn, Cr, Al, Zn, Ru, Fe, Mo, Ni, Ti, Zr, or mixtures thereof;

L is absent, or a counterion selected from F, Cl, Br, I, $-\text{O}(\text{C}=\text{O})\text{alkyl}$, $-\text{O}-\text{S}(=\text{O})_2-$
 R'_4 , wherein R'_4 is aryl, aryl $\text{C}_2\text{-C}_6$ alkyl, heteroaryl, $\text{C}_1\text{-C}_6$ alkyl, cycloalkyl, heterocycle,
 PF_6 , $\text{B}(\text{Ar})_4$, or $\text{B}(\text{halo})_3$, where halo is F, Cl, Br, or I; and

n is 2 to 250;

5 or a salt or hydrate thereof.

7. The homopolymer of claim 6 of the formula:



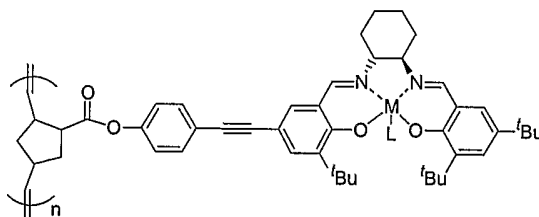
10

wherein

L is absent, or a counterion selected from F, Cl, Br, I, $-\text{O}(\text{C}=\text{O})\text{alkyl}$, $-\text{O}-\text{S}(=\text{O})_2-$
 R'_4 , wherein R'_4 is aryl, aryl $\text{C}_2\text{-C}_6$ alkyl, $\text{C}_1\text{-C}_6$ alkyl; and n is 2 to 250;
 or a salt or hydrate thereof.

15

8. The homopolymer of claim 6 of the formula:



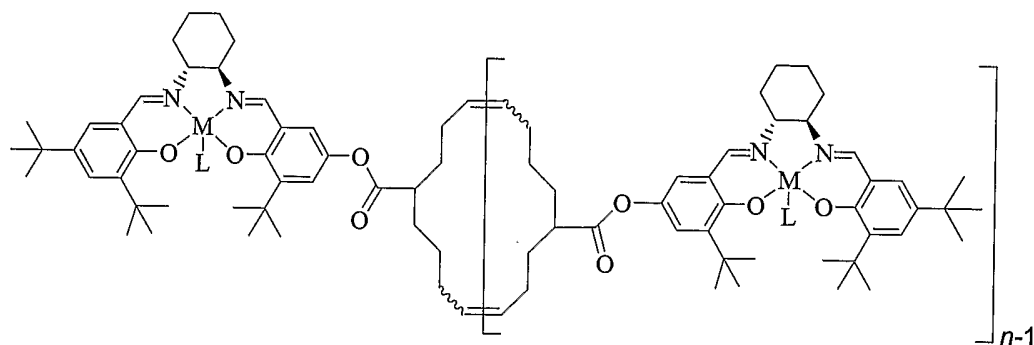
20

wherein

M is a metal atom or ion of at least one of Co, Mn, or mixtures thereof;

L is absent, or a counterion selected from F, Cl, Br, I, $-\text{O}(\text{C}=\text{O})\text{alkyl}$, $-\text{O}-\text{S}(=\text{O})_2-$
 R'_4 , wherein R'_4 is aryl, aryl $\text{C}_2\text{-C}_6$ alkyl, $\text{C}_1\text{-C}_6$ alkyl; and
 n is 2 to 250; or a salt or hydrate thereof.

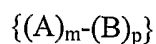
5 9. The homopolymer of claim 6 of the formula:



wherein

M is absent or a metal atom or ion of at least one of Co, Mn, Cr, Al, Zn, Ru, Fe,
 10 Mo, Ni, Ti, Zr, or mixtures thereof;
 L is absent or a counter ion; and
 n is 2 to 20;
 or a salt or hydrate thereof.

15 10. A copolymer of the formula:



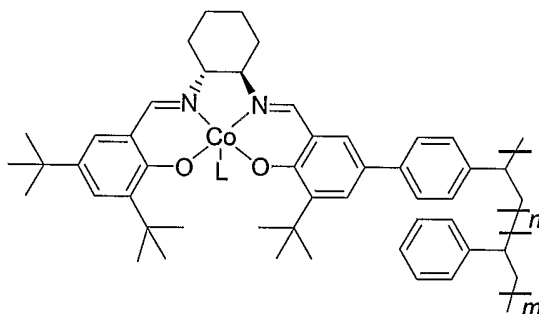
where

20 A is the polymerized compound of claim 1 of formula (I);
 B is a co-polymerized monomer;
 m is an integer from 1 to about 1,000; and
 p is an integer from 1 to about 10,000.

25

11. The copolymer of claim 10 where
 A is the polymerized compound of claim 1 of formula (I);
 B is a co-polymerized monomer of at least one olefin, perfluorinated olefin, silane
 or siloxane substituted olefin, diene, alkenylaryl, acrylate, or mixtures thereof;
 5 m is an integer from 10 to about 100; and
 p is an integer from 10 to about 1,000.

12. The copolymer of claim 10 of the formula:



wherein

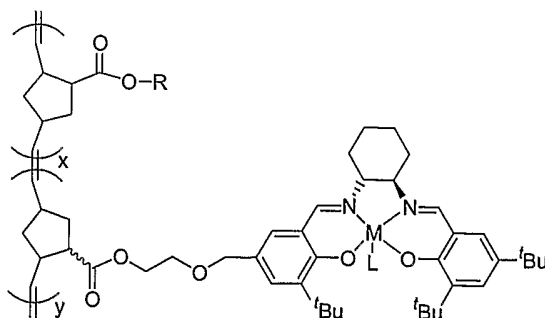
L is absent, or a counterion selected from F, Cl, Br, I, $-O(C=O)alkyl$, $-O-S(=O)_2-$
 R'_4 , wherein R'_4 is aryl, aryl C_2-C_6 alkyl, C_1-C_6 alkyl;

m is 2 to 100; and

n is 2 to 50;

or a salt or hydrate thereof.

13. The copolymer of claim 10 of the formula:



wherein

M is Mn, Co, or mixtures thereof;

L is absent or a halide anion selected from F, Cl, Br, and I;

5 R is C₁₋₈alkyl;

x is 2 to 1,000; and

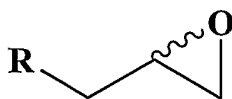
y is 2 to 250; or a salt or hydrate thereof.

14. A method for preparing a homo-polymer of the compound of formula (I) of claim
10 1, comprising: heating the compound of formula (I) with a free radical initiator.

15. A method for preparing an oligomeric-ring or macrocyclic-ring homo-polymer of
the compound of formula (I) of claim 1, comprising: reacting the compound of formula
(I) with a 3° Grubbs catalyst.

16. A method for preparing a co-polymer of the compound of formula (I) of claim 1,
comprising: heating the compound of formula (I) with a free radical initiator and at least
one monomer selected from olefin, diene, alkenylaryl, acylate, or mixtures thereof.

20 17. A method of preparing a chiral epoxide or chiral 1,2-diol by stereoselective
hydrolysis of a racemic epoxide of the formula



25 wherein R is hydrogen, C₁-C₁₀ alkyl, C₂-C₆ alkenyl, C₂-C₆ alkynyl, C₃-C₈ cycloalkyl, C₁-
C₁₀ alkoxy, C₁-C₁₀ alkenyloxy, aryl, carbonyl, carboxy, ketone, aldehyde, ester,
phosphoryl, phosphonate, phosphine, sulfonyl, or -(CH₂)_k-R₅ wherein, R₅ is C₂-C₆
alkenyl, C₂-C₆ alkynyl, C₂-C₆ alkoxy, unsaturated alkoxy, aryl, cycloalkyl, cycloalkenyl,
heterocycle, polycycle, halogen, hydroxy, amino, thiol, nitro, amine, imine, amide,

carbonyl, carboxy, silyl, ether, thioether, seleno ether, ketone, aldehyde, ester, phosphoryl, phosphonate, phosphine, sulfonyl and k is an integer of 0 to 8, comprising:

contacting the racemic epoxide with water in the presence of a catalytic amount of a chiral homo-polymer or chiral copolymer of the compound of formula (I) of claim 1,

5 wherein

$X_1, X_3, X_6,$ and X_8 are H;

$X_4, X_5,$ and X_7 are t-butyl;

Y_1 and Y_2 are H;

10 R_1 and R'_2 are a $-(CH_2)_4-$, when R_2 and R'_1 are H, or R_1 and R'_2 are H, when R_2 and R'_1 are a $-(CH_2)_4-$;

R_3 is a single carbon-carbon bond;

X_2 is $-L'-Z-P$ where

L' is $-(C\equiv C)_k-Ar-$ and k is 1;

Z is $-C(=O)O-$ or $-O-C(=O)-$;

15 P is a polymerized C_2-C_6 alkenyl, or polycycloalkenyl radical;

M is Co; and

L is absent, or a counterion;

or a salt or hydrate thereof.

20 18. A method of preparing an asymmetric epoxide from an unsaturated substrate comprising:

contacting the unsaturated substrate with a catalytic amount of a chiral homo-polymer or chiral copolymer of the compound of formula (I) of claim 1, wherein

$X_1, X_3, X_6,$ and X_8 are H;

25 $X_4, X_5,$ and X_7 are t-butyl;

Y_1 and Y_2 are H;

R_1 and R'_2 are a $-(CH_2)_4-$, when R_2 and R'_1 are H, or R_1 and R'_2 are H, when R_2 and R'_1 are a $-(CH_2)_4-$;

R_3 is a single carbon-carbon bond;

30 X_2 is $-L'-Z-P$ where

L' is $-(C\equiv C)_k-Ar-$, where k is 1;

Z is $-\text{C}(=\text{O})\text{O}-$ or $-\text{O}-\text{C}(=\text{O})-$;

P is $\text{C}_2\text{-C}_6$ alkenyl, cycloalkenyl, or polycycloalkenyl;

M is Mn; and

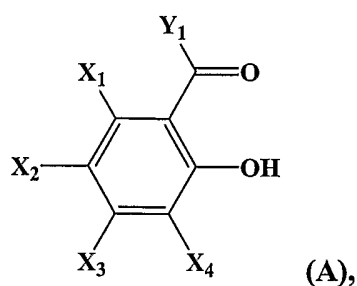
L is absent, or a counterion;

5 or a salt or hydrate thereof.

19. A single-pot method for preparing the compound of formula (I) of claim 1, comprising:

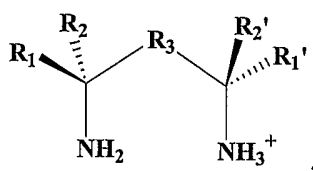
reacting a salicylaldehyde compound of the formula (A):

10

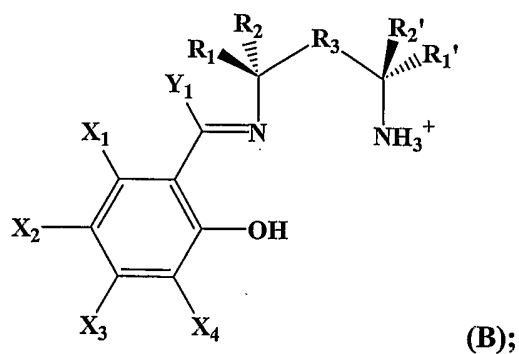


with an (R,R)-diamino mono-ammonium salt of the formula:

15

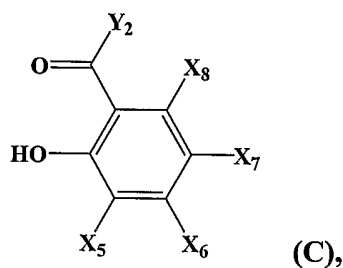


to form a mono-ammonium imine of the formula (B):

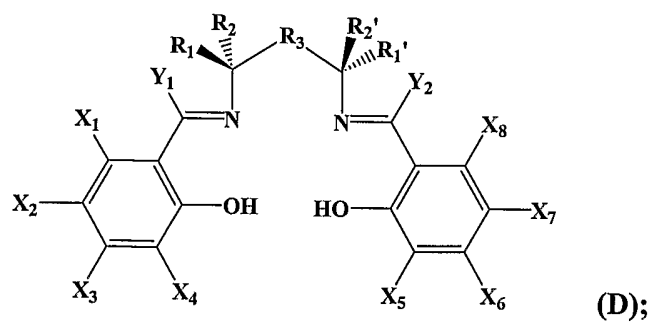


deprotecting the mono-ammonium imine of formula (B) with a base and thereafter reacting the deprotected imine with an aldehyde of formula (C):

5



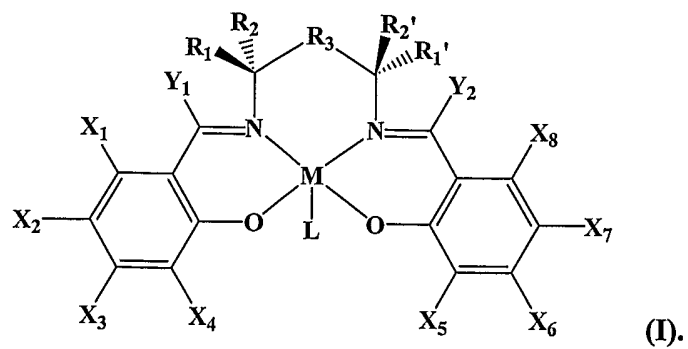
to form an unsymmetrical substituted salen of formula (D):



10

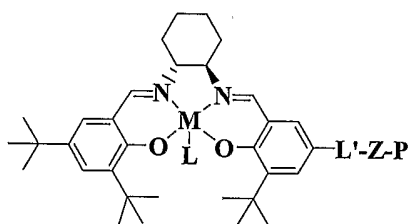
and

optionally reacting the salen of formula (D) with a metal salt to form a metalated-salen complex of the formula (I):



5

20. The method of claim 19 wherein formula (I) is



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