



(51) International Patent Classification:

B01J 31/00 (2006.01) B01J 31/22 (2006.01)
B01J 31/20 (2006.01)

(21) International Application Number:

PCT/US2022/022488

(22) International Filing Date:

30 March 2022 (30.03.2022)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

63/171,150 06 April 2021 (06.04.2021) US

(71) Applicant: **NOVOMER, INC.** [US/US]; 275 Buell Rd,
Rochester, New York 14624 (US).

(72) Inventors: **TEDDER, Jonathan D.**; c/o Novomer, Inc.,
275 Buell Rd, Rochester, New York 14624 (US).
WILDERS, Alison M.; c/o Novomer, Inc., 275 Buell Rd,
Rochester, New York 14624 (US). **COATES, Geoffrey**

W.; 48 Lake Forest Drive, Lansing, New York 14882 (US).
FALKNER, Catherine A.; c/o Novomer, Inc., 275 Buell
Rd, Rochester, New York 14624 (US).

(74) Agent: **WOELKE, Ethan C.** et al.; YOUNG BASILE
HANLON & MACFARLANE, P.C., 3001 W. Big Beaver
Road, Suite 624, Troy, Michigan 48084 (US).

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

(54) Title: NOVEL CARBONYLATION CATALYSTS AND METHODS OF MAKING THE SAME

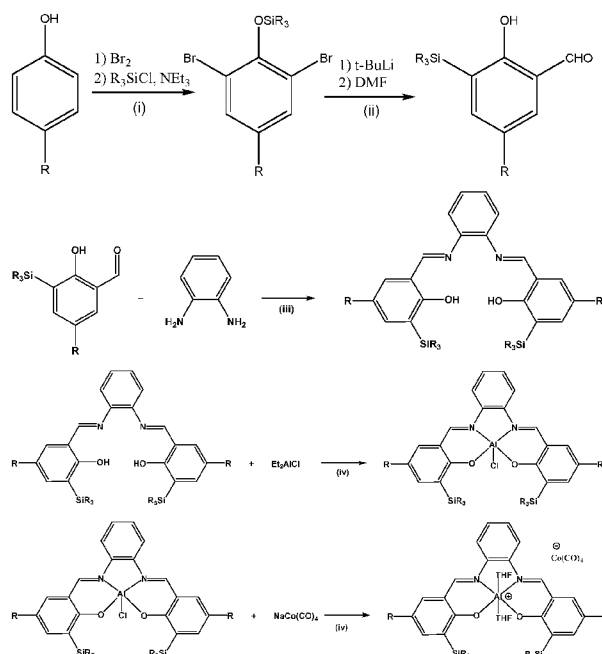


FIG. 1

(57) Abstract: Disclosed herein are compounds and methods useful as carbonylation catalysts that improve steric properties so that reaction with epoxide is improved, reaction with lactones is avoided, and polymer bonds to the metal centers are weakened, which facilitates faster ring closure, that improve stability of the carbonylation catalyst by not being susceptible to hydrolysis, which reduces side products and improves recovery yields of the carbonylation catalyst after using to make lactones, and that have improved steric and electron properties so that release time of a lactone product is minimized, which reduces side reactions.

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

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

NOVEL CARBONYLATION CATALYSTS AND METHODS OF MAKING THE SAME

Field

[0001] The present disclosure relates to novel catalyst used in the production of lactones from epoxides and methods of making the same.

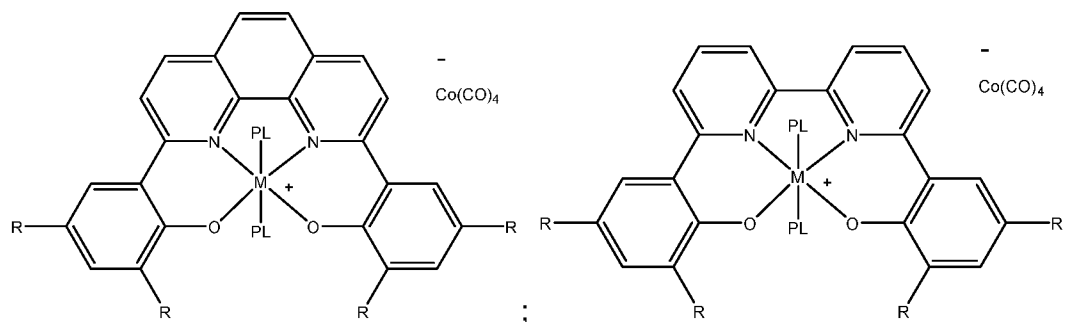
Background

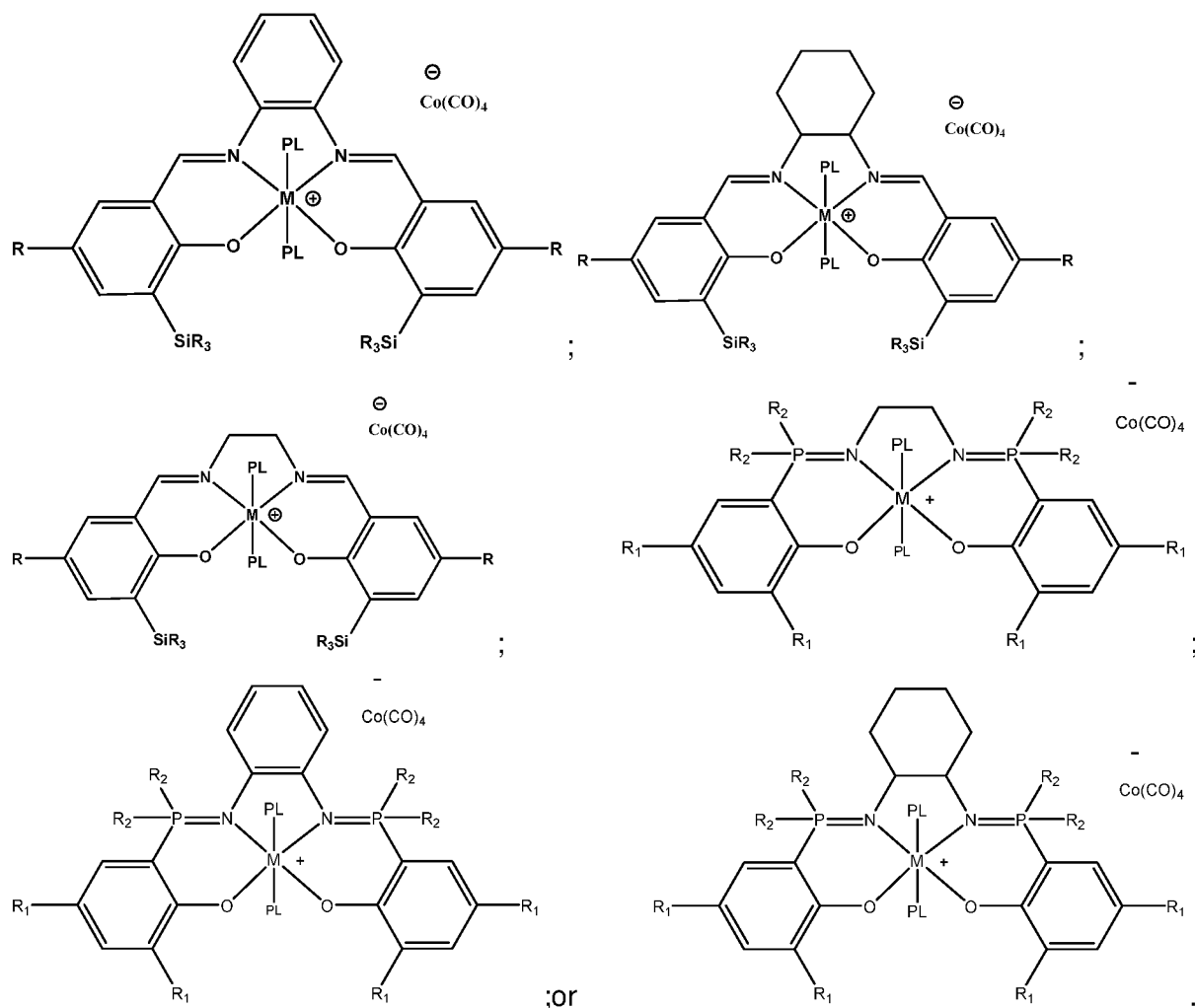
[0002] Carbonylation is a process that can be used to react carbon monoxide and an epoxide to make a lactone. In some cases, additional steps are taken to react the lactones to make polymers. These lactones or polymers thereof are often used as plastics and disinfectants. When making these lactones, a carbonylation catalyst is used to optimize the efficiency of the reaction to produce lactones at competitive prices. Carbonylation catalysts are expensive, and thus, new carbonylation catalysts and new techniques to synthesize the carbonylation catalysts from simple components are needed. Further, some current carbonylation catalysts can create unwanted side products that need to be later filtered out. Some carbonylation catalysts can be found in US Patent Nos. US 6,852,865, US 8,481,756, and US 8,633,123. Some of these carbonylation catalysts may provide slow reaction times, can become unstable, and can deactivate during the course of the catalytic carbonylation.

[0003] Accordingly, a catalyst is needed that can be used in a carbonylation reaction and that can be recycled, possesses a longer catalytic lifetime, has an increased rate of formation of lactone product, and/or avoid undesirable side products.

Summary

[0004] Disclosed are compounds that have catalytic activity with one or more of an epoxide, succinic anhydride, or a lactone according to one of the following formulas:

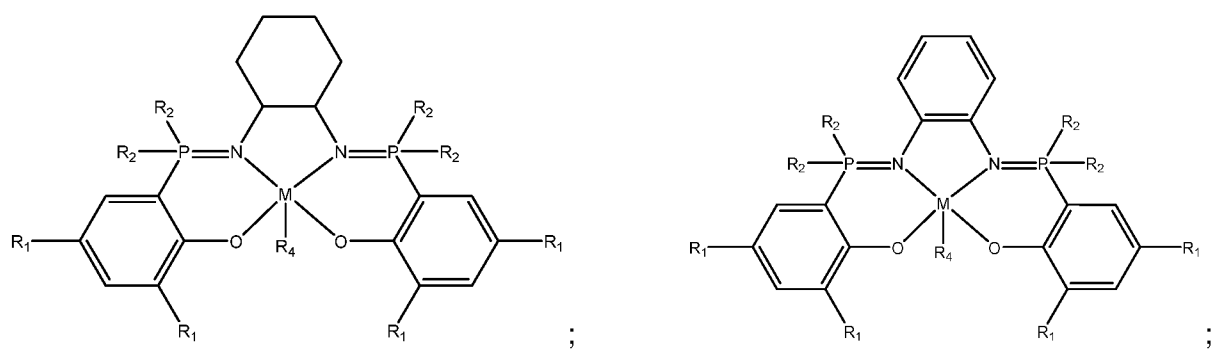
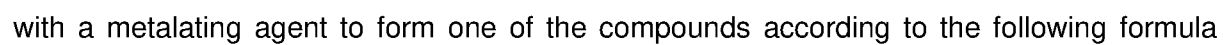




In these compounds, R is separately in each occurrence an hydrogen, alkyl, or aryl group; R_1 is separately in each occurrence hydrogen, alkyl, or aryl groups; R_2 is separately in each occurrence an alkyl, aryl, or alkoxide group; R_3 is separately in each occurrence an alkyl or aryl group; R_4 may be separately in each occurrence an alkyl group or a halogen; PL is the residue of a polar ligand; and M is separately in each occurrence a Lewis Acid metal.

[0005] Disclosed herein are methods for preparing the above compounds by contacting a compound according to one of the following formulas:

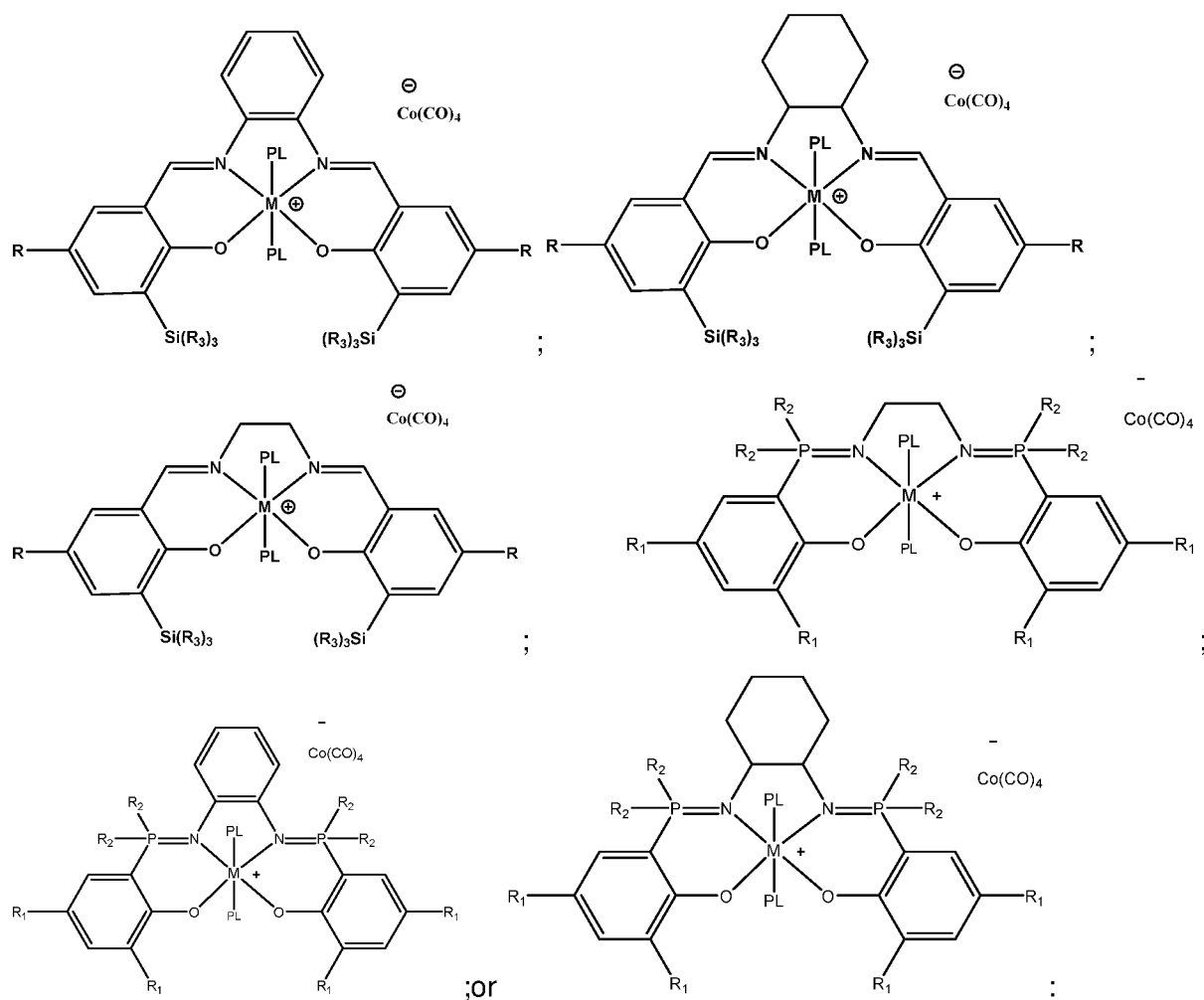






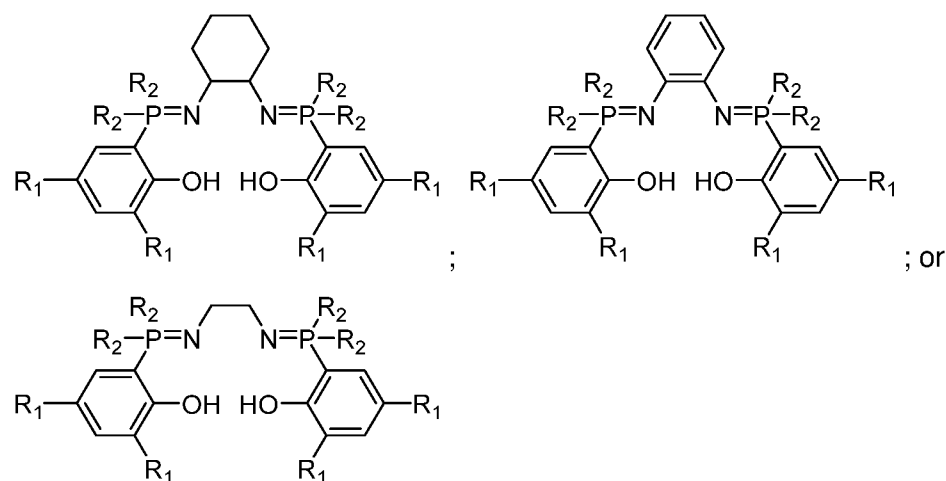
and contacting the formed compounds with a metal carbonyl under condition such that one of the following compounds are formed:





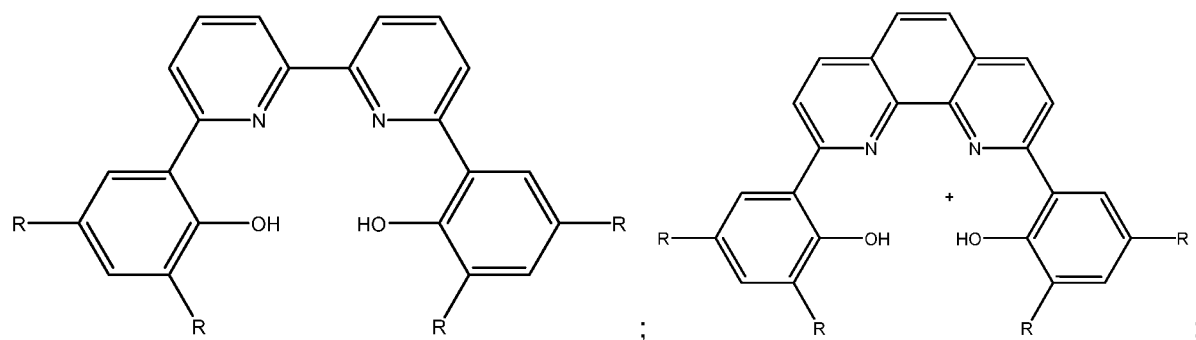
where R, R₁, R₂, R₃, R₄, PL, and M are described above. The methods may further include contacting the formed compounds, the metal carbonyl, or both with a polar ligand so that that one of the compounds are formed.

[0006] Disclosed herein are methods of preparing one of the compounds according to the one of the following formulas:



by contacting a phenol which may be substituted at the 2 and/or 4 position with a hydrogen, alkyl, or aryl group with a halogenating agent under conditions such that a halogen atom is added at the 6 carbon atom to form a halogenated phenol. The method further includes contacting the halogenated phenol with a halo-di(aryl or alkyl) phosphine in the presence of an alkyl lithium under conditions to replace the halogen on the phenol with di(alkyl or aryl) phosphate to form a dialkyl or diaryl phosphate substituted phenol. The method further includes contacting the dialkyl or diaryl phosphate substituted phenol with a diamine, an ortho phenylene amine or ortho cyclohexyl diamine in the presence of a source of bromine and a trialkyl amine to form a compound according to the formulas. The method may further include, first, contacting the dialkyl or diaryl phosphate substituted phenol with the source of bromine to form an activated dialkyl or diaryl phosphate substituted phenol, and second, contacting the activated dialkyl or diaryl phosphate substituted phenol with the ethylene diamine, ortho phenylene amine, or the cyclohexyl diamine in the presence of the trialkyl amine to form the compound according to the formulas.

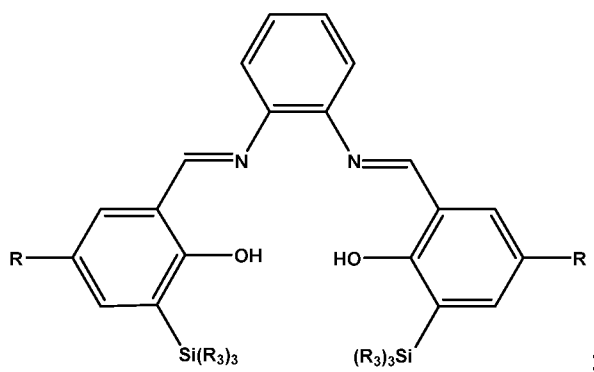
[0007] Disclosed herein are methods for preparing one of the compounds according to one of the following formulas:



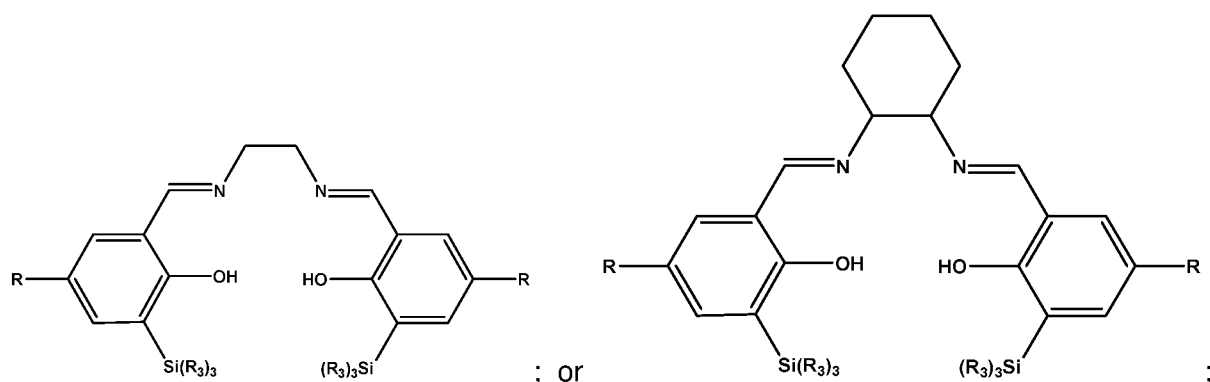
by:

by contacting a phenol which may be substituted at the 2 and/or 4 position with a hydrogen, alkyl, or aryl group with a halogenating agent under conditions such that a halogen atom is added at the 6 carbon atom to form a halogenated phenol. The method further includes contacting the formed halogenated phenol with a trialkyl borate in the presence of an alkyl lithium compound to replace the halogen atom with a boron dihydroxide group. The method further includes contacting phenol containing a boron dihydroxide group with bipyridine or phenanthroline having halogen groups on carbons adjacent to the nitrogen atoms in the presence of a palladium catalyst and an alkali metal carbonate under conditions to form one of the compounds of the formulas. The trialkyl amine may consume bromic acid to form an ammonium salt. The method may further include contacting the phenol containing a boron dihydroxide group with hydrochloric acid to quench the reaction.

[0008] Disclosed herein are methods of preparing one of the compounds according to one



of the following formulas:



by contacting a phenol which may optionally be substituted at the 4 position with an hydrogen, alkyl, or aryl group with a halogenating agent and silyl halide under conditions such that a halogen atom is added at the 2 and 6 carbon atoms of the aromatic ring and the 1 hydroxyl group is converted to silyl ether group which may optionally be substituted at the 4 position with an hydrogen, alkyl, or aryl group. The method further includes contacting the formed 2, 6-halogenated 1-silylether substituted benzene with an alkyl lithium compound and dimethylformamide to form a phenol having a silyl and an acetaldehyde group at the 2 and 6 positions which may optionally be substituted at the 4 position with a hydrogen, alkyl, or aryl group. The method further includes contacting the phenol having a silyl and an acetaldehyde group at the 2 and 6 positions which may optionally be substituted at the 4 position with a hydrogen, alkyl, or aryl group with one of o-phenylene diamine, ethylene diamine, or cyclohexanediamine and optionally in the presence of a Lewis acid or Bronsted acid catalyst and an alkali metal or ammonium salt form one of the compounds corresponding to one of the formulas. The method may further include first contacting the phenol which may optionally be substituted with the halogenating agent to form a halogenated phenol, and second, contacting the halogenated phenol with the silyl halide under conditions such that 1 hydroxyl group is converted to silyl ether group which may optionally be substituted at the 4 position with an hydrogen, alkyl, or aryl group. The method may further include contacting the halogenated phenol and the silyl halide with a tertiary amine to consume any acid byproduct so that the phenol having a silyl and an acetaldehyde group at the 2 and 6 positions which may optionally

be substituted at the 4 position with a hydrogen, alkyl, or aryl group is formed. The method may further include first contacting the formed 2, 6-halogenated 1-silylether substituted benzene with the alkyl lithium compound to form the phenol having the silyl at the 2 or 6 position, and second, contacting the phenol having the silyl at the 2 or the 6 position with dimethylformamide to form the phenol having the silyl and the acetaldehyde group at the 2 and 6 positions which may optionally be substituted at the 4 position with a hydrogen, alkyl, or aryl group.

[0009] The present disclosure provides carbonylation catalysts containing phosphasalen, phosphasalph, phosphasalcy ligands, 6,6'-di(3,5-disubstituted-2-hydroxybenzene)-2,2'-bipyridine (" $^R\text{dhbpy}(\text{H})_2$ " where R is in each occurrence hydrogen, alkyl, or aryl) or 6,6'-di(3,5-disubstituted-2-hydroxybenzene)-2,2'-phenanthroline (" $^R\text{dhphen}(\text{H})_2$ " where R is in each occurrence hydrogen, alkyl, or aryl) ligands, and/or silyl substituted salen, salph or salcy ligands that possess catalytic activity with one or more of ethylene oxide, betapropiolactone, and/or succinic anhydride. The present disclosure provides carbonylation catalysts containing phosphasalen, phosphasalph, phosphasalcy ligands, $^R\text{dhbpy}(\text{H})_2$ or $^R\text{dhphen}(\text{H})_2$ ligands, and/or silyl substituted salen, salph or salcy ligands that have improved steric and electron qualities which improve reaction yields, reduce time of reaction, reduce side products, increase catalyst longevity, increase catalyst stability and are more easily recoverable after a carbonylation reaction.

Brief Description

[0010] FIG. 1 is a synthetic scheme to form a carbonylation catalyst with a Lewis acid containing a silyl substituted salen, salph or salcy ligands.

[0011] FIG. 2 is a synthetic scheme to form a carbonylation catalyst with a Lewis acid containing a phosphasalen, phosphasalph, phosphasalcy ligands.

[0012] FIG. 3 is a synthetic scheme to form a carbonylation catalyst with a Lewis acid containing a $^R\text{dhbpy}(\text{H})_2$ or $^R\text{dhphen}(\text{H})_2$ ligand.

[0013] FIG. 4 is a ^1H NMR spectrum of the isolated carbonylation catalyst with a Lewis acid containing a $^R\text{dhbpy}(\text{H})_2$ ligand.

[0014] FIG. 5 is a ReactIR spectrum showing the in-situ monitoring of beta-propiolactone (bPL) formation from the carbonylation catalyst with a Lewis acid containing a pyridine or phenanthroline ligand.

Detailed Description

[0015] While the disclosure has been described in connection with certain embodiments, it is to be understood that the disclosure is not to be limited to the disclosed embodiments but, on the contrary, is intended to cover various modifications and equivalent arrangements

included within the scope of the appended claims, which scope is to be accorded the broadest interpretation so as to encompass all such modifications and equivalent structures as is permitted under the law.

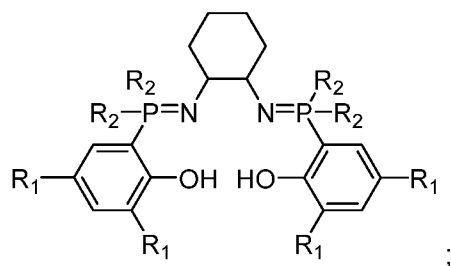
[0016] One or more as used herein means that at least one, or more than one, of the recited components may be used as disclosed. Residue with respect to an ingredient or reactant used to prepare the polymers or structures disclosed herein means that portion of the ingredient that remains in the polymers or structures after inclusion as a result of the methods disclosed herein. Substantially all as used herein means that greater than 90 percent of the referenced parameter, composition, structure or compound meet the defined criteria, greater than 95 percent, greater than 99 percent of the referenced parameter, composition or compound meet the defined criteria, or greater than 99.5 percent of the referenced parameter, composition or compound meet the defined criteria. Portion as used herein means less than the full amount or quantity of the component in the composition, stream, or both. Precipitate as used herein means a solid compound in a slurry or blend of liquid and solid compounds. Phase as used herein means a solid precipitate or a liquid or gaseous distinct and homogeneous state of a system with no visible boundary separating the phase into parts. Parts per weight means parts of a component relative to the total weight of the overall composition. A catalyst component as used herein means a metal centered compound, a metal carbonyl, a Lewis acid, a Lewis acid derivative, a metal carbonyl derivative, or any combination thereof. A catalyst as used herein includes at least cationic compound and an anionic compound. An organic compound as used herein includes any compound that is free of a metal atom. An inorganic compound as used herein includes compounds that include at least one metal atom. Composition as used herein includes all components in a stream, reactant stream, product stream, slurry, precipitate, liquid, solid, gas, or any combination thereof that are containable within a single vessel.

[0017] Disclosed herein are compounds and methods useful as carbonylation catalysts that improve steric properties so that reaction with epoxide is improved, reaction with lactones is avoided, and the polymer bonds to the metal centers are weakened, which facilitates faster ring closure and improves stability of the carbonylation catalyst by not being susceptible to hydrolysis. This provides an advantage of reduced side products, improved recovery yields of the carbonylation catalyst after using to make lactones, and improved steric and electron properties so that release time of a lactone product is minimized, which reduces side reactions.

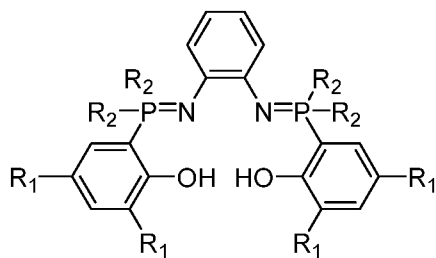
[0018] The carbonylation catalysts may include a Lewis acid containing phosphasalen, phosphasalph, or phosphasalcy ligands, ^Rdhbpy(H)₂ or ^Rdhphen(H)₂ ligands, silyl substituted salen, salph, or salcy ligands and may function to catalyze the carbonylation reactions where an epoxide and carbon monoxide react to form one or more lactones described herein. The carbonylation catalysts described herein may also be used to react an aziridine and carbon

monoxide to form a lactam.

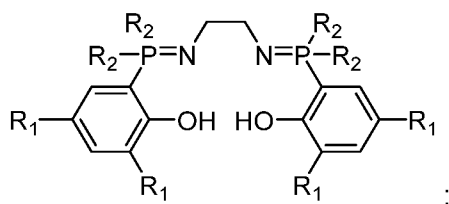
[0019] The phosphasalen, phosphasalph, or phosphasalcy ligands ligand may have the following structure according to Compounds 1, 2, and/or 3:



Compound 1:



Compound 2:

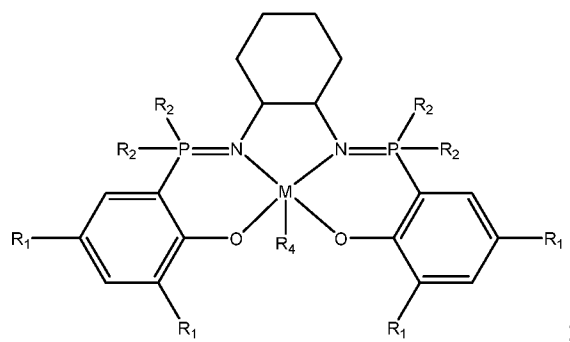


Compound 3:

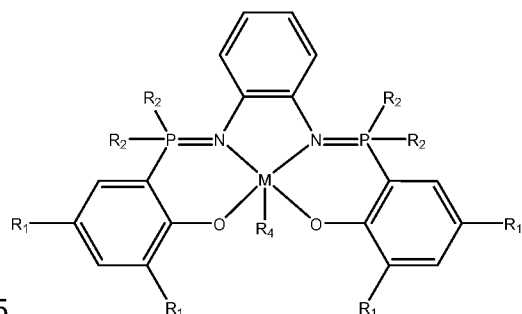
wherein R_1 may separately in each occurrence be hydrogen, alkyl or aryl, group; and

wherein R_2 may separately in each be occurrence an alkyl, aryl, or alkoxide group.

[0020] After a metalation step described below, as Lewis acid precursor containing the phosphasalen, phosphasalph, or phosphasalcy ligands is formed, which may have the following structure according to Compounds 4, 5, and/or 6:

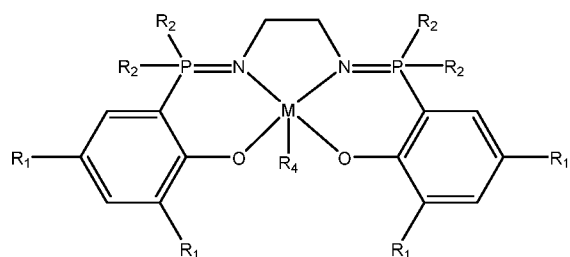


Compound 4



Compound 5

or



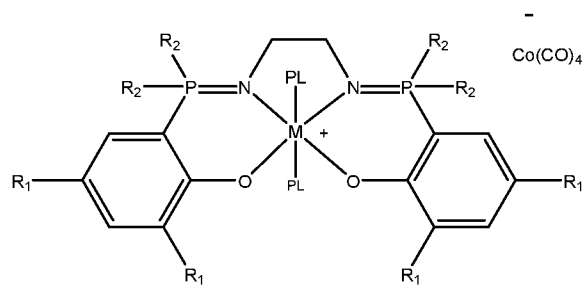
Compound 6

wherein R_1 and R_2 are described in Compounds 1, 2, and 3;

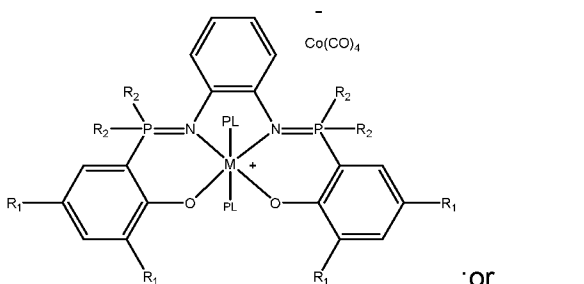
wherein R_4 may be separately in each occurrence an alkyl group or a halogen; and

wherein M may be separately in each occurrence a Lewis Acid metal.

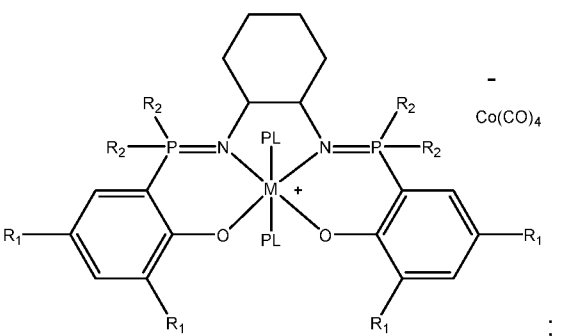
[0021] To form the carbonylation catalyst, the Lewis acid precursor containing the phosphasalen, phosphasalphen, or phosphasalcy ligands is reacted with a metal carbonyl additive, as described below. The final carbonylation catalyst having a Lewis acid precursor containing phosphasalen, phosphasalphen, or phosphasalcy may have the following structure according to compounds 7, 8, and/or 9:



Compound 7



Compound 8



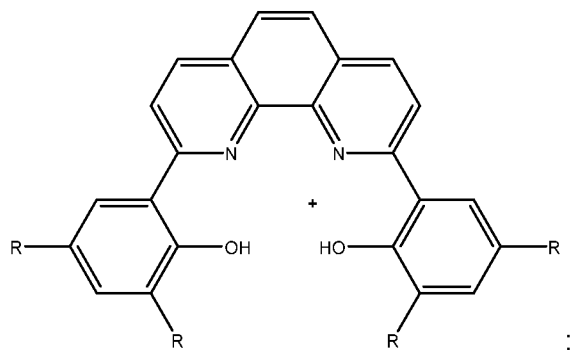
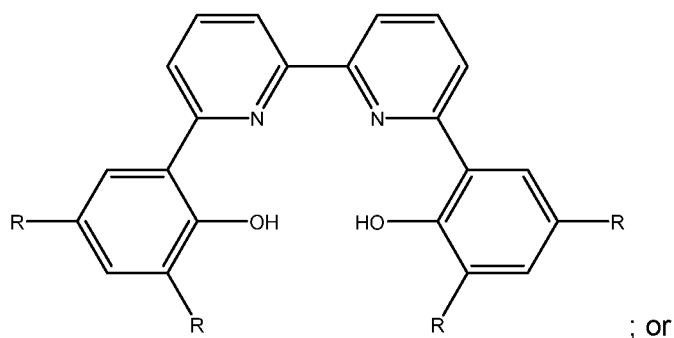
Compound 9

wherein R_1 , R_2 , and M are described in relation to compounds 1 to 6; and

wherein PL may be the residue of a polar ligand, such as diethyl ether, dioxane, or tetrahydrofuran.

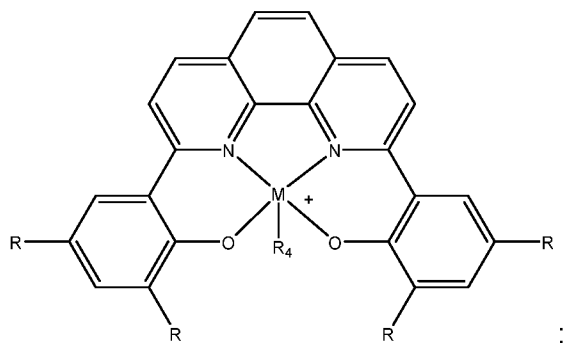
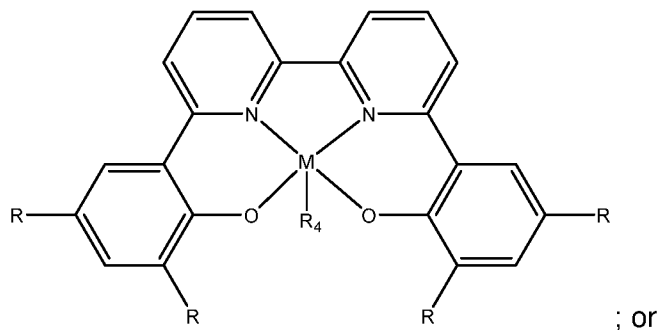
[0022] The R^d hbpy(H)₂ or R^d hphen(H)₂ ligands may have the following structure according

to compounds 10 and/or 11:



wherein R is separately in each occurrence an hydrogen, alkyl, or aryl group.

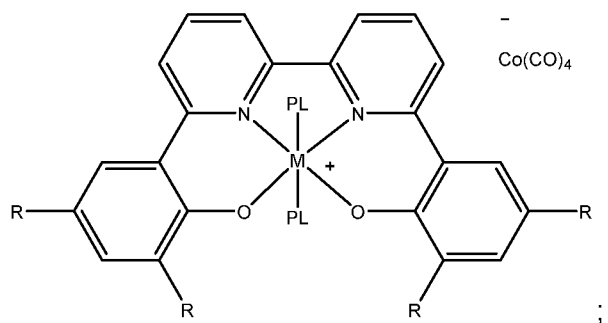
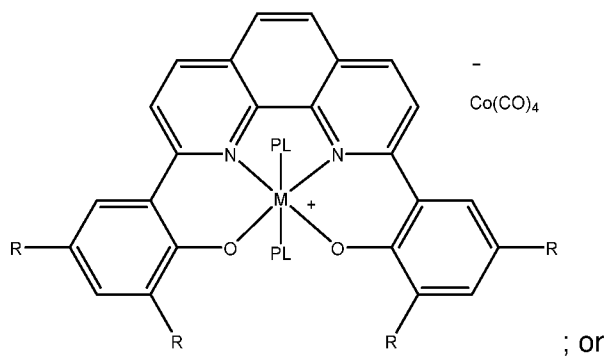
[0023] After a metalation step described below, as Lewis acid precursor containing the $R^d\text{hbpy}(\text{H})_2$ or $R^d\text{hphen}(\text{H})_2$ ligands is formed, which may have the following structure according to compounds 12 and/or 13:



wherein R, M, and R_4 are described in relation to compounds 1-11.

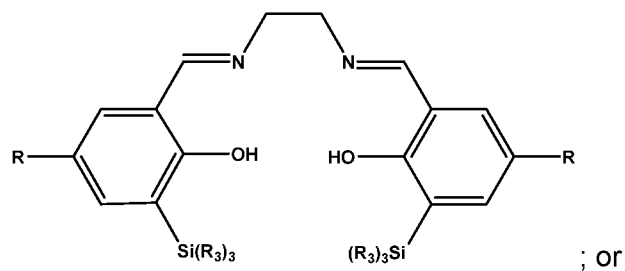
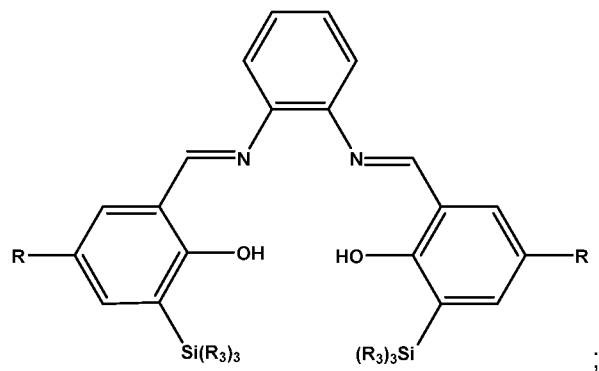
[0024] To form the carbonylation catalyst, the Lewis acid precursor containing the $R^d\text{hbpy}(\text{H})_2$ or $R^d\text{hphen}(\text{H})_2$ ligands is reacted with a metal carbonyl additive, as described below. The final carbonylation catalyst having a Lewis acid precursor containing the

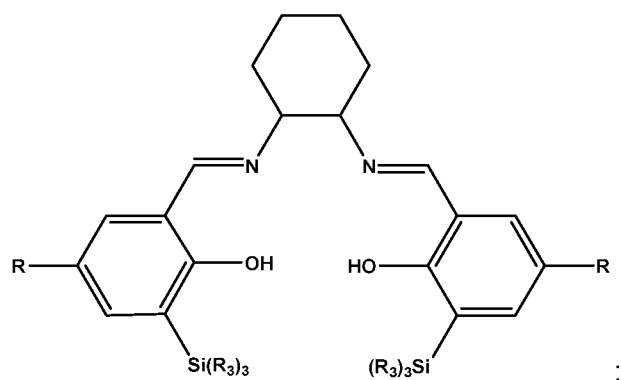
$^R\text{dhbpy}(\text{H})_2$ or $^R\text{dhphen}(\text{H})_2$ ligand may have the following structure according to compounds 14 and/or 15:



wherein R, M, and PL are described in relation to compounds 1-13.

[0025] The silyl substituted salen, salph, or salcy ligand may have the following structure according to compounds 16, 17, and/or 18:



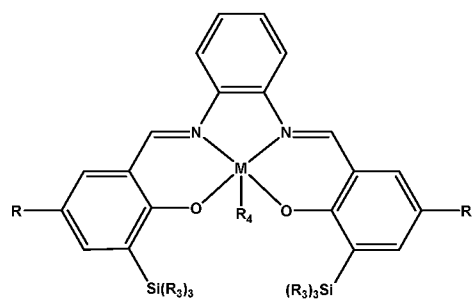


Compound 18

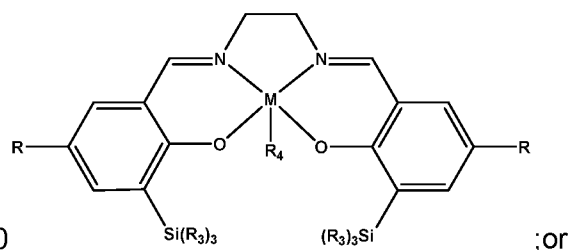
wherein R is described in compounds 1-15; and

wherein R_3 may be separately in each occurrence an alkyl or aryl group

[0026] After a metalation step described below, as Lewis acid precursor containing the silyl substituted salen, salph, or salcy ligand is formed, which may have the following structure according to compounds 19, 20, and/or 21:

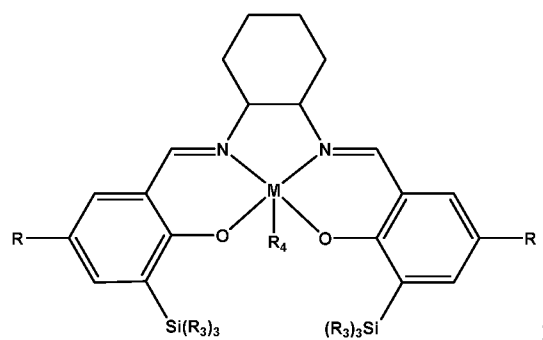


Compound 19



Compound 20

;or

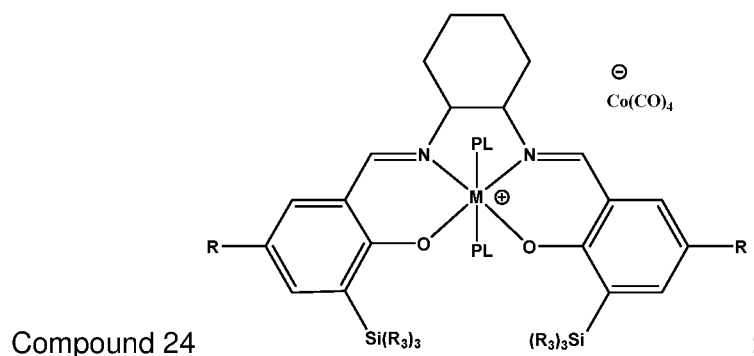
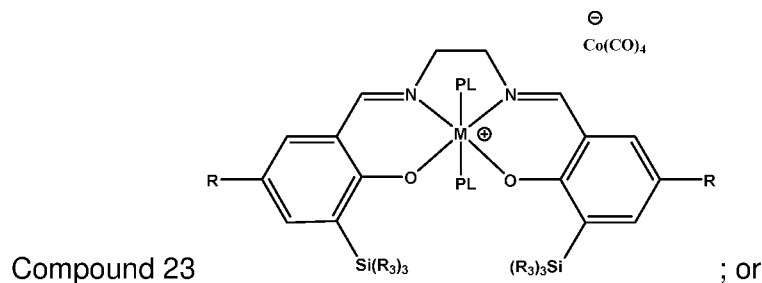
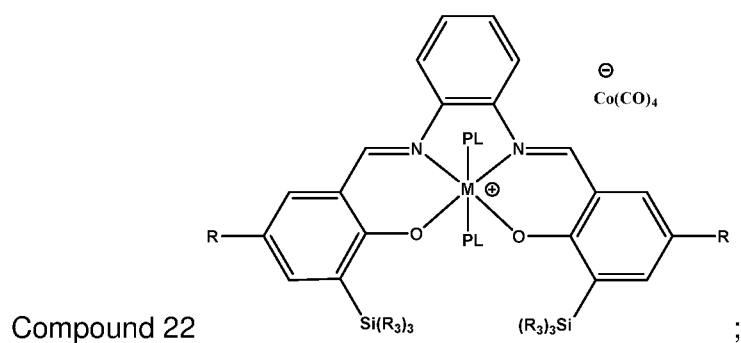


Compound 21

wherein R, R_3 , R_4 , and M are described in relation to compounds 1-18.

[0027] To form the carbonylation catalyst, the Lewis acid precursor containing the silyl substituted salen, salph, or salcy ligand is reacted with a metal carbonyl additive, as described below. The final carbonylation catalyst having a Lewis acid precursor containing the silyl substituted salen, salph, or salcy ligand may have the following structure according to

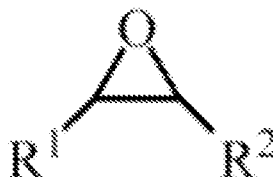
compounds 22, 23, and/or 24:



wherein R, R₃, M, and PL are described in relation to compounds 1-21.

[0028] The carbonylation reaction may include contacting one or more epoxides, lactones, or both with carbon monoxide in the presence of catalyst. This step may occur in a reactor that has one or more inlets, two or more inlets, three or more inlets, or a plurality of inlets. The one or more epoxides, the lactones, the carbon monoxide, and the catalyst may be added in a single inlet, multiple inlets, or each may be added in a separate inlet as separate or combined feed streams. The carbonylation reaction may produce one or more product streams or compositions.

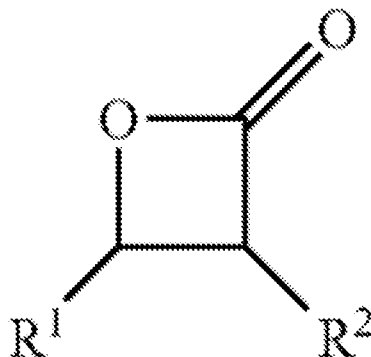
[0029] The epoxide used in the carbonylation reaction may be any cyclic alkoxide containing at least two carbon atoms and one oxygen atom. For example, the epoxide may have a structure shown by formula (I):



Formula (I):

where R^1 and R^2 in the context of formula (I) are each independently selected from the group consisting of: hydrogen; C_1 - C_{15} alkyl groups; halogenated alkyl chains; phenyl groups; optionally substituted aliphatic or aromatic alkyl groups; optionally substituted phenyl; optionally substituted heteroaliphatic alkyl groups; optionally substituted 3 to 6 membered carbocycle; and optionally substituted 3 to 6 membered heterocycle groups, where R^1 and R^2 can optionally be taken together with intervening atoms to form a 3 to 10 membered, substituted or unsubstituted ring optionally containing one or more hetero atoms; or any combination thereof.

[0030] The lactone formed from the carbonylation reaction may be any cyclic carboxylic ester having at least one carbon atom and two oxygen atoms. For example, the lactone may be an acetolactone, a propiolactone, a butyrolactone, a valerolactone, caprolactone, or a combination thereof. Anywhere in this application where a propiolactone or lactone is used or described, another lactone may be applicable or usable in the process, step, or method. Where a propiolactone is a used or produced in the carbonylation reaction, the propiolactone may have a structure corresponding to formula (II):



Formula (II):

where R^1 and R^2 in the context of formula (II) are each independently selected from the group consisting of: hydrogen; C_1 - C_{15} alkyl groups; halogenated alkyl chains; phenyl groups; optionally substituted aliphatic or aromatic alkyl groups; optionally substituted phenyl; optionally substituted heteroaliphatic alkyl groups; optionally substituted 3 to 6 membered carbocycle; and optionally substituted 3 to 6 membered heterocycle groups, where R^1 and R^2 can optionally be taken together with intervening atoms to form a 3 to 10 membered, substituted or unsubstituted ring optionally containing one or more hetero atoms; or any

combination thereof.

[0031] The product stream or composition may include one or more organic compounds including a propiolactone, a polypropiolactone, succinic anhydride, polyethylene glycol, poly-3-hydroxypropionate, 3-hydroxy propionic acid, 3-hydroxy propionaldehyde, a polyester, a polyethylene, a polyether, unreacted epoxides, any derivative thereof, any other monomer or polymer derived from the reaction of an epoxide and carbon monoxide, or any combination thereof. The product stream or composition may include one or more inorganic compounds that include catalyst components such as metal carbonyls, metal carbonyl derivatives, metal centered compounds, Lewis acids, Lewis acid derivatives, or any combination thereof. A metal carbonyl derivative is a compound that includes one or more metals and one or more carbonyl groups that can be processed to form an anionic metal carbonyl component for use in a carbonylation catalyst. A Lewis acid derivative is a compound that includes one or more metal centered Lewis acids bonded to one or more undesirable compounds at the metal center that can be processed into a cationic Lewis acid for use in a carbonylation catalyst. The product stream or composition may include a catalyst that has not been spent or used up in the process of forming propiolactones. The product stream or composition may include one or more unreacted epoxides or carbon monoxide.

[0032] To make the carbonylation catalysts described herein, a phenol may be halogenated to form the basis of the Lewis acid of the carbonylation catalyst in a halogenation step. The phenol may be contacted with a polar solvent a halogenating agent under conditions such that a halogen atom is added at the 4 and/or 6 carbon atom to form a halogenated phenol. The phenol and the halogenating agent may be added in a molar ratio of about 1:1 or more, about 2:3 or more, or about 1:2 or more. The phenol may be substituted at the 2 and/or 4 position with a hydrogen, alkyl, or aryl group. The halogenation step may be performed in a polar solvent that is aprotic or protic depending on halogenating agent and the substituted groups of the phenol. The halogenation step may be performed at room temperature and in ambient air. After mixing the phenol and the halogenating agent, the halogenation reaction may be stirred through a known means, such as with a magnetic stir bar. The halogenation reaction may be stirred for about 1 hour or more, about 1.5 hours or more or more, or about 2 hours or more. The halogenation reaction may be stirred for about 3.5 hours or less, about 3 hours or less, or about 2.5 hours or less. The reaction may be quenched, for example, by addition of sodium bicarbonate, which causes the aqueous and organic layers to separate. The halogenated phenol may be isolated using any technique described herein or any known technique. For example, the halogenated phenol may be isolated using simple organic/aqueous extraction to remove aqueous layers, and the organic layers can be dried by adding MgSO_4 or Na_2SO_4 , stirring with basic alumina, and then filtering over a combination of silica gel and diatomaceous earth.

[0033] After making and isolating the halogenated phenol, the halogenated phenol may be further modified with a silyl group in silylation step. The halogenated phenol may be contacted with a polar aprotic solvent and a silyl halide under such conditions such that the 1 hydroxyl group of the halogenated phenol is converted to a silyl ether group to form a 2, 6-halogenated 1-silylether substituted benzene. The halogenated phenol and the silyl halide may be added in a molar ratio of about 1:1. This silylation step may be performed in the presence of a catalyst that functions to facilitate conversion of the hydroxyl group to a silyl ether group. This silylation step may be performed in the presence of a scavenger that may consume any acid formed during the conversion of the hydroxyl to the silyl ether. The scavenger may include one or more of a tertiary amine. The scavenger may include one or more of triethylamine. The scavenger and the halogenated phenol may be added in a molar ratio of about 1:1, about 1.1:1, or about 1.2:1. Before addition of the silyl halide, the aprotic solvent and the halogenated phenol may be cooled to about -10 degrees Celsius or more, about -5 degrees Celsius or more, or about 0 degrees Celsius or more. The aprotic solvent and the halogenated phenol may be cooled to about 15 degrees Celsius or less, about 10 degrees Celsius or less, or about 5 degrees Celsius or less. After addition of the silyl halide, the silylation step then may be allowed to warm to room temperature and stirred. After addition of the ingredients, the silylation step may be stirred for about 3 hours or less, about 2.5 hours or less, or about 2.0 hours or less at room temperature. The silylation step may be stirred for about 0.5 hours or more, about 1.0 hours or more, or about 1.5 hours or more at room temperature. After stirring, the 2, 6-halogenated 1-silylether substituted benzene may be isolated using any known means or any means discussed herein. For example, the solvent may be removed by vacuum filtration, the remaining product stream may be dissolved in a nonpolar solvent, the product stream may be filtered over a filtration bed, such diatomaceous earth, and remove the nonpolar solvent by vacuum filtration.

[0034] After making and isolating the halogenated phenol, the halogenated phenol may be subjected to an elimination step to replace the halogen atom on the phenol with a di(aryl or alkyl) phosphate. The halogenated phenol may be contacted with an alkyl lithium compound and a halo-di(aryl or alkyl) phosphine in a polar aprotic solvent to form a dialkyl or diaryl phosphate substituted phenol. The halogenated phenol and the halo-di(aryl or alkyl) phosphine may be added in a molar ratio of about 1:1 or more. The alkyl lithium may be added in an amount sufficient to replace the halogen atom on the phenol. First, the halogenated phenol may be dissolved in the polar aprotic solvent and cooled to about 90 degrees Celsius or less, about 85 degrees Celsius or less, or about 80 degrees Celsius or less. The polar aprotic solvent and the halogenated phenol may be cooled to about 65 degrees Celsius or more, about 70 degrees Celsius or more, or about 75 degrees Celsius or more. After cooling, the halogenated phenol may be contacted with the alkyl lithium compound in the polar aprotic

solvent to form an intermediate composition. The intermediate composition may be allowed to warm to about room temperature (i.e., about 25 degrees Celsius) and may be stirred for about 0.5 hours or more, about 0.75 hours or more, or about 1.0 hour or more. The intermediate composition may be stirred for about 2.25 hours or less, about 1.75 hours or less, or about 1.25 hours or less.

[0035] After stirring and before addition of the halo-di(aryl or alkyl) phosphine, the intermediate composition including the halogenated phenol, the alkyl lithium compound, or residues thereof in the polar aprotic solvent may be cooled to about 90 degrees Celsius or less, about 85 degrees Celsius or less, or about 80 degrees Celsius or less. The intermediate composition may be cooled to about 65 degrees Celsius or more, about 70 degrees Celsius or more, or about 75 degrees Celsius or more. After cooling and without isolating any compound within the intermediate composition, the intermediate composition including the halogenated phenol, the alkyl lithium compound, or residues thereof in the polar aprotic solvent may be contacted with the halo-di(aryl or alkyl) phosphine to form the dialkyl or diaryl phosphate substituted phenol in a product composition. After contacting with the halo-di(aryl or alkyl) phosphine, the product composition may be allowed to warm to about room temperature (i.e., about 25 degrees Celsius) and may be stirred for about 0.5 hours or more, about 1.0 hours or more, or about 1.5 hours or more. The product composition may be stirred for about 3.0 hours or less, about 2.5 hours or less, or about 2.0 hours or less. The product composition may be washed with a buffer solution to and the organic phase may be removed by any means discussed herein or known by the skilled artisan, such as organic/aqueous extraction. The buffer solution may be potassium phosphate. Accordingly, the dialkyl or diaryl phosphate substituted phenol may be removed or isolated from the product stream by any other known isolation or extraction means. The elimination step may be performed under an inert gas, such as nitrogen, and/or in a dry box or a Schlenk line.

[0036] After making and isolating the halogenated phenol, the halogenated phenol may be subjected to an elimination step to replace the halogen atom on the phenol with a boron dihydroxide group. In this step, halogenated phenol may be contacted with an alkyl lithium compound and a trialkyl borate in a polar aprotic solvent to form a phenol containing a boron dihydroxide group at the 6 position. The halogenated phenol, the alkyl lithium, and the trialkyl borate may be added in a molar ratio of about 1:2:1 or more. First, the halogenated phenol may be dissolved in the polar aprotic solvent and cooled to about 90 degrees Celsius or less, about 85 degrees Celsius or less, or about 80 degrees Celsius or less. The polar aprotic solvent and the halogenated phenol may be cooled to about 65 degrees Celsius or more, about 70 degrees Celsius or more, or about 75 degrees Celsius or more. After cooling, the halogenated phenol may be contacted with the alkyl lithium compound in the aprotic polar solvent to form an intermediate composition. The intermediate composition may be warmed

to about room temperature (about 25 degrees Celsius) and may be stirred for about 0.5 hours or more, about 0.75 hours or more, or about 1.0 hour or more. The intermediate composition may be stirred for about 2.25 hours or less, about 1.75 hours or less, or about 1.25 hours or less. After stirring and before addition of the trialkyl borate, the intermediate composition may again be cooled to about 90 degrees Celsius or less, about 85 degrees Celsius or less, or about 80 degrees Celsius or less. The polar aprotic solvent and the halogenated phenol may be cooled to about 65 degrees Celsius or more, about 70 degrees Celsius or more, or about 75 degrees Celsius or more.

[0037] After cooling, the intermediate composition containing halogenated phenol, the alkyl lithium compound, or residues thereof in the aprotic polar solvent may be contacted with the trialkyl borate to form a phenol containing a borate ester at the 6 position in a product composition. After contacting with the trialkyl borate, the product composition may be allowed to warm to room temperature and stirred for about 30 hours or less, about 24 hours or less, or about 18 hours or less. The product composition may be stirred for about 6 hours or more, about 12 hours or more, or about 18 hours or more. Subsequently, an acid may be contacted with the product stream containing the phenol containing a borate ester at the 6 position in an aprotic solvent to catalyze hydrolysis and form the phenol containing a boron dihydroxide group at the 6 position. The acid may include acetic acid, hydrochloric acid, sulfuric acid, nitric acid, boric acid, perchloric acid, or any combination thereof. The acid may have a molarity of about 1.6 or more, about 1.8 or more, or about 2.0 or more. The acid may have a molarity of about 2.4 or less, about 2.2 or less, or about 2.0 or less. After hydrolyzing, the phenol containing a boron dihydroxide group at the 6 position may be isolated using any known technique or technique described herein, for example aqueous/organic extraction. The elimination step may be performed under an inert gas, such as nitrogen, and/or in a dry box or a Schlenk line.

[0038] After making the 2,6-halogenated 1-silylether substituted benzene, the 2,6-halogenated 1-silylether substituted benzene may be subjected to an elimination step to exchange one halogen with an aldehyde at the 2 position and rearrange the silyl group to exchange with the other halogen at the 6 position. In this step, the 2,6-halogenated 1-silylether substituted benzene may be contacted with an alkyl lithium compound and dimethylformamide in a polar aprotic solvent to form a phenol having a silyl and an acetaldehyde group at the 2 and 6 positions. The halogenated phenol, the alkyl lithium, and the dimethylformamide may be added in a molar ratio of about 1:4:4. First, 2,6-halogenated 1-silylether substituted benzene may be dissolved in the polar aprotic solvent and may be cooled to about 90 degrees Celsius or less, about 85 degrees Celsius or less, or about 80 degrees Celsius or less. The polar aprotic solvent and the 2,6-halogenated 1-silylether substituted benzene may be cooled to about 65 degrees Celsius or more, about 70 degrees Celsius or more, or about 75 degrees

Celsius or more. After cooling, the 2,6-halogenated 1-silylether substituted benzene is contacted with the alkyl lithium compound in the polar aprotic solvent to form an intermediate composition and may be allowed to warm to 0 degrees Celsius and stirred for about 0.5 hours or more, about 1.0 hours or more, or about 1.5 hours or more. In other examples, the intermediate composition may be allowed to warm to room temperature. The intermediate composition may be stirred for about 3.0 hours or less, about 2.5 hours or less, or about 2.0 hours or less.

[0039] After stirring and without an isolation step, the intermediate composition may be cooled to about 90 degrees Celsius or less, about 85 degrees Celsius or less, or about 80 degrees Celsius or less. The intermediate composition may be cooled to about 65 degrees Celsius or more, about 70 degrees Celsius or more, or about 75 degrees Celsius or more. After cooling, the intermediate composition containing the 2,6-halogenated 1-silylether substituted benzene, the alkyl lithium compound, and/or residues thereof in the polar aprotic solvent may be contacted with dimethylformamide to form phenol having a silyl and an acetaldehyde group at the 2 and 6 positions in a product composition. In addition to the dimethylformamide, a quenching agent diluted in a polar aprotic solvent may be added to form the phenol having a silyl and an acetaldehyde group at the 2 and 6 positions. Quenching agents may include NH_4Cl (aqueous). After cooling and after addition of the dimethylformamide, the product composition may be warmed to about 0 degrees Celsius and stirred for about 0.5 hours or more, about 0.75 hours or more, or about 1.0 hour or more. The product composition may be stirred for about 2.25 hours or less, about 1.75 hours or less, or about 1.25 hours or less. After formation of the phenol having a silyl and an acetaldehyde group at the 2 and 6 positions, the phenol having a silyl and an acetaldehyde group at the 2 and 6 positions may be purified or isolated using any known technique or any technique discussed herein, such as aqueous/organic extraction. The entire elimination step may be performed under an inert gas, such as nitrogen, and/or in a dry box or a Schlenk line.

[0040] After isolating the dialkyl or diaryl phosphate substituted phenol, the dialkyl or diaryl phosphate substituted phenol may be subjected to an addition step to form a phosphasalen, phosphasalph, or phosphasalcy ligand. For example, the phosphasalen, phosphasalph, or phosphasalcy ligand may have a structure according to compounds 1, 2, and/or 3 as described above.

[0041] In this step, the dialkyl or diaryl phosphate substituted phenol may be contacted with a bromine and a diamine in the presence of a polar aprotic solvent and a trialkyl amine to form the phosphasalen, phosphasalph, or phosphasalcy ligand. The dialkyl or diaryl phosphate substituted phenol, the bromine, and the diamine may be added in a molar ratio of about 2:2:1 or more. First and under a nitrogen stream (i.e., glove box or Schlenk line), the dialkyl or diaryl phosphate substituted phenol may be dissolved in the aprotic solvent and

cooled to about 90 degrees Celsius or less, about 85 degrees Celsius or less, or about 80 degrees Celsius or less. The polar aprotic solvent and the dialkyl or diaryl phosphate substituted phenol may be cooled to about 65 degrees Celsius or more, about 70 degrees Celsius or more, or about 75 degrees Celsius or more. After cooling, the dialkyl or diaryl phosphate substituted phenol may be contacted with the bromine in the polar aprotic solvent to form an intermediate composition, and the intermediate composition may be warmed to room temperature (i.e., about 25 degrees Celsius) and stirred for about 0.25 hours or more, about 0.50 hours or more, or about 0.75 hours or more. The intermediate composition may be stirred for about 2.0 hours or less, about 1.50 hours or less, or about 1.25 hours or less. After stirring, the intermediate composition may be cooled to about 90 degrees Celsius or less, about 85 degrees Celsius or less, or about 80 degrees Celsius or less. The intermediate composition may be cooled to about 65 degrees Celsius or more, about 70 degrees Celsius or more, or about 75 degrees Celsius or more.

[0042] After cooling, the intermediate composition containing the bromine, the dialkyl or diaryl phosphate substituted phenol, and/or residues thereof in the polar aprotic solvent may be contacted with the diamine in the presence of the trialkyl amine to form the phosphasalen, phosphasalp, or phosphasalcy ligand in a product composition. After contacting, the product composition may be warmed to room temperature (i.e., about 25 degrees Celsius) and stirred overnight. For example, the product composition may be stirred for about 12 hours or more, about 18 hours or more, or about 23 hours or more. The product composition may be stirred for about 36 hours or less, about 30 hours or less, or about 25 hours or less. After stirring, any byproducts, such as ammonium bromide, may be precipitated from the composition using any known filtration technique, such as gravity filtration. The phosphasalen, phosphasalp, or phosphasalcy ligand may be isolated from the product composition by any known technique or any technique described herein. For example, the phosphasalen, phosphasalp, or phosphasalcy ligand may be isolated from the product composition by removing solvent through rotary evaporation and subjecting the phosphasalen, phosphasalp, or phosphasalcy to an additional precipitation step and an additional purification step in column chromatography. The entire addition step may be performed under an inert gas, such as nitrogen, and/or in a dry box or a Schlenk line.

[0043] After isolating the phenol containing a boron dihydroxide group at the 6 position, the phenol containing a boron dihydroxide group at the 6 position may be subjected to a Suzuki reaction step to form a $R^d\text{hbpy}(\text{H})_2$ or $R^d\text{hphen}(\text{H})_2$ ligand. For example, the $R^d\text{hbpy}(\text{H})_2$ or $R^d\text{hphen}(\text{H})_2$ ligand may have a structure according to compounds 10 and/or 11.

[0044] In this Suzuki reaction step, the phenol containing a boron dihydroxide group at the 6 position may be contacted with a dibromo bipyridine or a dibromo phenanthroline containing one or more halogens adjacent to the nitrogen atom in the presence of one or more polar

solvents, an alkali metal carbonate, and a palladium catalyst to form a ligand according to compound 10 and/or 11 in a product composition. The one or more polar solvents may be a combination of solvents to dissolve one or more compounds in the reaction. The one or more polar solvents may be protic, aprotic, or a combination of both protic and aprotic solvents. The phenol containing a boron dihydroxide group at the 6 position and the dibromo bipyridine or the dibromo phenanthroline containing one or more halogens adjacent to the nitrogen atom may be added in a molar ratio of about 2:1 or more. Additionally, bromic acid may be added to the combination of phenol containing a boron dihydroxide group at the 6 position and the dibromo bipyridine or dibromo phenanthroline in a molar ratio of about 2:2:1 or more. The palladium catalyst may be added in a solution of about 2 mole percent or more, about 3 mole percent or more, or about 4 mole percent or more. The palladium catalyst may be added in a solution of about 8 mole percent or less, about 7 mole percent or less, or about 6 mole percent or less. The alkali metal carbonate may be added in a solution of about 1.6 M or more, about 1.8 M or more, or about 2.0 M or more. The alkali metal carbonate may be added in a solution of 2.6 or less, about 2.4 or less, or about 2.2 or less. After contacting the ingredients, the Suzuki reaction step may be carried out at reflux for about 72 hours or less, about 96 hours or less, or about 120 hours or less. The Suzuki reaction step may be carried out at reflux for about 24 hours or more, about 48 hours or more, or about 70 hours or more. After reflux, the ligand according to compound 10 and/or 11 is removed from the product composition using any known extraction technique described herein or known by the skilled artisan. For example, the ligand according to compound 10 and/or 11 may be removed by adding a solvent that dissolves the ligand, such as a polar aprotic solvent, adding a brine (i.e., aqueous solution), extracting the brine, and evaporating the polar aprotic solvent to leave a dry ligand. The Suzuki reaction step may be conducted under an inert gas, such as nitrogen, and in a dry box and/or Schlenk line.

[0045] After isolating the phenol having a silyl and an acetaldehyde group at the 2 and 6 positions, the phenol having a silyl and an acetaldehyde group at the 2 and 6 positions may be subjected to a condensation step to form a silyl substituted salen, salph, or salcy ligand. For example, the silyl substituted salen, salph, or salcy ligand may have a structure according to compounds 16, 17, and/or 18. In this step, the phenol having a silyl and an acetaldehyde group at the 2 and 6 positions may be contacted with a diamine in the presence of a Lewis acid or Bronsted acid and a alkali metal or ammonium salt in the a polar solvent subjected to form the silyl substituted salen, salph, or salcy ligand in a product composition. In other examples, the reaction may be free of a Lewis acid or Bronsted acid so that the diamine and the phenol having a silyl and an acetaldehyde group at the 2 and 6 positions may be contacted in a polar solvent. These steps may be completed in ambient air and may be completed at room temperature (e.g., about 25 degrees Celsius) or may be completed at reflux of the polar

solvent. The phenol having a silyl and an acetaldehyde group at the 2 and 6 positions and the diamine, may be added in a molar ratio of about 1:2 or more. The Lewis acid or Bronsted acid may be added in an amount sufficient to catalyze the condensation reaction. The silyl substituted salen, salph, or salcy ligand may be isolated from the product composition by any known technique or any technique described herein. For example, the silyl substituted salen, salph, or salcy ligand may be collected as a precipitate by gravity filtration after the product composition has cooled.

[0046] After forming the phosphasalén, phosphasalph, or phosphasalcy ligand, the $R^d\text{hbpy}(\text{H})_2$ or $R^d\text{hphen}(\text{H})_2$ ligand, or the silyl substituted salen, salph, or salcy ligand, the ligands may be subjected to a metalation step to form a Lewis acid containing a halogen or an alkyl group. The Lewis acids containing the halogen or the alkyl group may have a structure according to compounds 4, 5, 6, 12, 13, 19, 20, and/or 21 described above. The halogen or the alkyl group of the Lewis acid may be bonded to the metal center of the Lewis acid. In the metalation step, a metal alkyl compound may be contacted with the phosphasalén, phosphasalph, or phosphasalcy ligand, the $R^d\text{hbpy}(\text{H})_2$ or $R^d\text{hphen}(\text{H})_2$ ligand, or the silyl substituted salen, salph, or salcy ligand in a nonpolar solvent at room temperature to form a Lewis acid containing a halogen or alkyl group. The metal alkyl compound and phosphasalén, phosphasalph, or phosphasalcy ligand, the $R^d\text{hbpy}(\text{H})_2$ or $R^d\text{hphen}(\text{H})_2$ ligand, or the silyl substituted salen, salph, or salcy ligand may be added in a molar ratio of about 1:1. The metalation step may be stirred for any amount of time sufficient to form the Lewis acid containing the halogen or the alkyl group. For example, the metalation step may be stirred for about 36 hours or less, about 30 hours or less, or about 24 hours or less. The metalation step may be stirred for about 12 hours or more, about 18 hours or more, or about 22 hours or more. The metalation step may be conducted under an inert gas, such as nitrogen, and in a dry box and/or Schlenk line. The metalation step may be conducted in open air or may be conducted in an inert atmosphere free of oxygen and water, such as a dry box or Schlenk line. The metalation step may be similar to the metalation steps described in US Patent No. 8,633,123, incorporated herein by reference in its entirety. After the metalation step is complete, the Lewis acid containing the halogen or the alkyl group may be isolated using any known technique, such as collecting the Lewis acid containing the halogen or the alkyl group by gravity filtration. The steps to form the Lewis acid containing the halogen or alkyl group may be performed under conditions that are moisture and oxygen free, for example, under an inert gas, like nitrogen, in a dry box or Schlenk line.

[0047] After forming and isolating one of the Lewis acids containing the halogen or the alkyl group above, the Lewis acids containing the halogen or the alkyl group may be subjected to a catalyst formation step to form the carbonylation catalyst. The carbonylation catalyst may have one of the structures described above in compounds 7, 8, 9, 14, 15, 22, 23, and/or 24.

The catalyst formation step may include contacting the Lewis acids containing the halogen or the alkyl group with a polar ligand, a metal carbonyl additive, or both to form the carbonylation catalyst. The Lewis acid containing the halogen or alkyl group may be added in a molar ratio of about 1:1. The metal carbonyl additive may contain at least a metal carbonyl that is anionic and a cationic group that is configured to cleave and bond with the alkyl group or the halogen of the metal centered compound. The cationic group may be one or more of an alkali metal, $(R_4)_3Si^-$, any counterion sufficient to ionically bond and/or balance the metal carbonyl, or any combination thereof, where R_4 is independently selected from a phenyl, halophenyl, hydrogen, alkyl, alkylhalo, alkoxy, or any combination thereof. In examples where the metal carbonyl additive cleaves or decouples the alkyl group, the alkyl group may couple with the cationic group, and the alkyl group and cationic group could be removed via any filtration or removal means described herein. In examples where the metal carbonyl additive cleaves the halogen from the metal centered compound and is contacted with the polar compound, the halogen bonds with the cationic group of the metal carbonyl additive and the Lewis acid containing the polar compound is formed. Any byproducts can be removed by any other removal or separation steps described herein. After the metal carbonyl additive cleaves or decouples the alkyl group, the Lewis acid may combine with the polar ligand to form a cationic species. The Lewis acid containing the polar ligand then contacts with the anionic metal carbonyl of the metal carbonyl additive and forms the regenerated carbonylation catalyst.

[0048] The steps to form the carbonylation catalyst may be performed under conditions that are moisture and oxygen free. For example, the catalyst formation steps may be performed within a dry glove box, on a Schlenk line, or in a reactor under an inert atmosphere (i.e., nitrogen). The catalyst formation steps may be performed under a nitrogen, argon, or any other inert gas. During the catalyst formation steps, the Lewis acid, the polar ligand, the metal carbonyl, or any combination thereof may be contacted and agitated by stirring for a period of time sufficient to form the carbonylation catalyst. The period of time for stirring the components may be about 5 minutes or more, about 30 minutes or more, about 60 minutes or more. The period of time for stirring the components may be about 24 hours or less, about 12 hours or less, or about 6 hours or less. The components in the catalyst formation steps may be completed under ambient temperature and/or pressure. Additional steps to make the regenerated catalyst can be found in US6,852,865B2 and US8,481,756B1, both of which are included herein by reference in their entirety.

[0049] The filtering, isolating, or removing steps taught herein function to remove from the composition any unwanted components that may interfere with the formation of a carbonylation catalyst or any precursor of the carbonylation catalyst. For example, one or more of solvents, polymers, unreacted acid compounds, inorganic compounds, organic compounds, or any combination thereof may be removed from the composition so that the carbonylation

catalyst may be regenerated from the Lewis acid containing a halogen or a alkyl compound and have catalytic activity with one or more of succinic anhydride, propiolactone, or an epoxide. The filtering, isolating, or removing steps may include one or more of vacuum filtration, gravity filtration, centrifugation, decantation, precipitation, phase layer extraction, or any combination thereof. The filtering, isolating, or removing steps may utilize any method sufficient to separate one or more of solvents, polymers, unreacted acid compounds, inorganic compounds, organic compounds, or any combination thereof and the Lewis acid containing the halogen or a alkyl group, the ligands, or any combination thereof. The filtering, isolating, or removing steps may remove a single type of compound at a time, such as a precipitate, or may remove a collection of compounds at a time, such as all components dissolved in a solvent. The filtering or removing steps may include forming multiple phases including one or more of one or more organic phases, an aqueous phase, a solid phase (i.e., a precipitate), one or more gaseous or vapor phases, or any combination thereof. The one or more separation or removal steps/methods described herein may be performed at any temperature, pressure, agitation rate, time, or any combination thereof sufficient to separate or remove any undesirable component from the composition including the ligands, the Lewis acid containing the halogen or alkyl group, or any combination thereof.

[0050] The carbonylation catalyst as described herein functions to catalyze a reaction of an epoxide and carbon monoxide to produce one or more propiolactones and other products. The carbonylation catalyst includes at least a metal carbonyl that is anionic and a Lewis acid that is cationic.

[0051] The metal carbonyl of the carbonylation catalyst functions to provide the anionic component of the carbonylation catalyst. The carbonylation catalyst may include one or more, two more, or a mixture of metal carbonyls. The metal carbonyl may be capable of ring-opening an epoxide and facilitating the insertion of CO into the resulting metal carbon bond. In some examples, the metal carbonyl may include an anionic metal carbonyl moiety. In other examples, the metal carbonyl compound may include a neutral metal carbonyl compound. The metal carbonyl may include a metal carbonyl hydride or a hydrido metal carbonyl compound. The metal carbonyl may be a pre-catalyst which reacts *in situ* with one or more reaction components to provide an active species different from the compound initially provided. The metal carbonyl includes an anionic metal carbonyl species. In some examples, the metal carbonyl may have the general formula $[Q_dM'_e(CO)_w]^{y+}$, where Q is an optional ligand, M' is a metal atom, d is an integer between 0 and 8 inclusive, e is an integer between 1 and 6 inclusive, w is a number such as to provide the stable anionic metal carbonyl complex, and y is the charge of the anionic metal carbonyl species. The metal carbonyl may include monoanionic carbonyl complexes of metals from groups 5, 7 or 9 of the periodic table or dianionic carbonyl complexes of metals from groups 4 or 8 of the periodic table. The metal

carbonyl may contain cobalt, manganese, ruthenium, or rhodium. Exemplary metal carbonyls may include $[\text{Co}(\text{CO})_4]^-$, $[\text{Ti}(\text{CO})_6]^{2-}$, $[\text{V}(\text{CO})_6]^-$, $[\text{Rh}(\text{CO})_4]^-$, $[\text{Fe}(\text{CO})_4]^{2-}$, $[\text{Ru}(\text{CO})_4]^{2-}$, $[\text{Os}(\text{CO})_4]^{2-}$, $[\text{Cr}_2(\text{CO})_{10}]^{2-}$, $[\text{Fe}_2(\text{CO})_8]^{2-}$, $[\text{Tc}(\text{CO})_5]^-$, $[\text{Re}(\text{CO})_5]^-$, and $[\text{Mn}(\text{CO})_5]^-$. The metal carbonyl may be a mixture of two or more anionic metal carbonyl complexes in the carbonylation catalysts used in the methods.

[0052] The halogenating agent may function to couple a halogen atom to a phenol. The halogenating agent may be any compound containing one or more halogens that can be coupled to a phenol. The halogenating agent may be one or more of N-bromosuccinimide, bromine (i.e., Br_2), dibromisocyanuric acid, or any combination thereof.

[0053] The alkyl lithium compound may function to replace a halogen group on a phenol with another compound. The alkyl lithium compound may be n-butyllithium, t-butyllithium, or any combination thereof. Where n-butyllithium is used, an additive to activate the n-butyllithium may be used, such as tetramethylethylenediamine, hexamethylphosphoramide, N,N'-Dimethylpropyleneurea, or any combination thereof.

[0054] The halo-di(aryl or alkyl) phosphine may function to form a disubstituted phosphine group on a phenol compound. The halo-di(aryl or alkyl) phosphine include one or more of chloro-di(aryl) phosphine, chloro-di(alkyl) phosphine, or both.

[0055] The silyl halide may function to form a silyl ether on a phenol group. The silyl halide may include one or more of fluorine, chlorine, bromine, and/or iodine. The silyl halide may contain a trisubstituted silicone group, for example, having a structure of $\text{Si}(\text{R}_3)_3$, where R_3 is described above in relation to compounds 1 to 24.

[0056] The trialkyl borate may function to form a compound suitable for a Suzuki coupling reaction. The trialkyl borate may be trimethyl borate, or any combination thereof.

[0057] The diamines used herein may function to form a ligand by connecting two substituted phenol groups. The diamine may be any substituted compound containing at least two amine groups that are separated by at least two carbon atoms. The diamine may be one or more of an ethylene diamine, an ortho phenylene amine, an ortho cyclohexyl diamine, or any combination thereof.

[0058] The trialkyl amine may be a compound sufficient to consume generated HBr in the form of an ammonium salt, such as tributylammonium bromide. The trialkyl amine may be one or more of tributyl amine, triethyl amine, trimethyl amine, or any combination thereof.

[0059] The Lewis acid or Bronsted acid catalyst may function to catalyze a condensation reaction. The Lewis acid or Bronsted acid catalyst may be one or more of formic acid, acetic acid, aluminum chloride, or any combination thereof.

[0060] The alkali metal carbonate may function to decompose a boron dihydroxide. The alkali metal carbonate may include one or more of Na_2CO_3 , or any combination thereof. In lieu of the alkali metal carbonate, a alkali metal, alkoxide, and/or alkali metal hydroxide could be

used to decompose the boron dihydroxide.

[0061] The metal alkyl compound may function to coordinate a metal in one or more ligands to form a Lewis acid containing a halogen or an alkyl group. The metal alkyl compound may be any compound containing a metal and/or one or more alkyl groups and/or halogen group. The metal of the metal alkyl compound may be one or more of aluminum, chromium, or any combination thereof. The metal alkyl compound may include one or more of CrCl_2 , $(\text{Et})_2\text{AlCl}$ or $(\text{Et})_3\text{Al}$, or any combination thereof.

[0062] A metal carbonyl additive functions to deliver a metal carbonyl to a Lewis acid that is suitable to combine and form the carbonylation catalyst. The metal carbonyl additive may function to decouple a halogen or a alkyl group from a Lewis acid to form the carbonylation catalyst that includes the Lewis acid and metal carbonyl combination. The metal carbonyl additive includes at least a metal carbonyl as described herein and a cationic compound. The cationic compound may include lithium, sodium, potassium, rubidium, cesium, beryllium, magnesium, calcium, strontium, barium, radium, or any combination thereof. The metal carbonyl additive may be a salt. The metal carbonyl additive may be a silicon salt in the form of R_3Si^- , where R is independently selected from a phenyl, halophenyl, hydrogen, alkyl, alkylhalo, alkoxy, or any combination thereof. The metal carbonyl additive may be $\text{NaCo}(\text{CO})_4$, $\text{Co}_2(\text{CO})_8$, $\text{HCo}(\text{CO})_4$, or any combination thereof. Where a Lewis acid containing a halogen is formed after the metalation step, $\text{NaCo}(\text{CO})_4$ may be used to form the carbonylation catalyst. Where a Lewis acid containing an alkyl group is formed, $\text{Co}_2(\text{CO})_8$ or $\text{HCo}(\text{CO})_4$ may be used to form the carbonylation catalyst.

[0063] In some Lewis acids, one or more polar ligands may coordinate to M, or a combination thereof and fill the coordination valence of the metal atom. The polar ligand may be a solvent. The polar ligand may be any compound with at least two free valence electrons. The polar ligand may be aprotic. The compound may be tetrahydrofuran, dioxane, diethyl ether, acetonitrile, carbon disulfide, pyridine, epoxide, ester, lactone, or a combination thereof.

[0064] The solvent may be a polar aprotic solvent, a polar protic solvent, or a nonpolar solvent that functions to dissolve one or more compounds described herein. One solvent may be soluble in one or more other solvents to increase solubility of one or more of the compounds described herein. A first solvent may be combined with a second solvent that is miscible in the first solvent to precipitate components that are insoluble in the second solvent. The solvents may be selected to form an organic phase or an aqueous phase layer that is distinct from another aqueous phase layer, another organic phase layer, a precipitate, or any some combination. The solvent may be one or more of water, methanol, ethanol, propanol, hexane, heptane, nonane, decane, tetrahydrofuran, methyltetrahydrofuran, diethyl ether, sulfolane, toluene, pyridine, diethyl ether, 1,4-dioxane, acetonitrile, ethyl acetate, dimethoxy ethane, acetone, chloroform, dichloromethane, or any combination thereof.

[0065] Several techniques have been theorized to illustrate the teaching of the present disclosure. Each teaching is simply an example of the disclosure and is not intended to limit the teachings to any single technique.

[0066] FIG. 1 is a synthetic scheme to form a carbonylation catalyst with a Lewis acid containing a silyl substituted salen, salph, or salcy ligand. After isolating two equivalents of Br_2 for one equivalent of appropriate 4-substituted phenol are added to a reaction vessel equipped with a stir bar in the amounts of 0.01 mol of appropriate pre-isolated 2,6-dibromophenol in 10 mL of THF solvent. The solution is cooled with an ice bath (0°C) and a slight excess of triethylamine (0.012 mol) is added and a subsequently a slight excess of appropriate trisubstituted chlorosilane. The mixture is stirred for 2 hours at room temperature and the solvent is then removed by reduced pressure methods. The residue is taken up into hexanes and filtered over diatomaceous earth and the solvent is once again removed to yield the desired product. In a reaction vessel equipped with a stir bar the appropriate 2,6-dibromophenol silylether (0.0015 mol) in diethyl ether (3.0 mL) is cooled to -78°C and treated with four equivalents of t-butyllithium (0.006 mol). The reaction is stirred for 1.5 h at 0°C . In the same reaction vessel, the reaction mixture is cooled to -78°C and 0.006 mol of DMF is added and stirred at 0°C for 1 h. The reaction is then quenched with 5.0 mL of saturated NH_4Cl solution and diluted with 75 mL diethyl ether. The organic and aqueous phases are separated, and the organic phase is dried to yield the desired product. The ligand synthesis is completed by reacting the silyl salicylaldehyde with orthophenylene diamine in a ratio of 2.2 to 1. Salicylaldehyde in an amount of 0.004 mol is dissolved in 30 mL of ethanol (EtOH) and added 0.00176 mol ortho-phenylene diamine and refluxed overnight. The temperature subsequently is reduced and the product is isolated by gravity filtration after precipitation of the ligand from the EtOH. using standard methods for condensation reaction between aldehyde of the salicylaldehyde precursor containing a silyl group and a diamine. After the ligand is formed, a reaction vessel under an inert atmosphere is charged with 0.1 mol of ligand in 100 mL toluene solvent (1.0 M). One equivalent of Et_2AlCl is added to the solution slowly and allowed to stir at room temperature overnight. Product is collected by filtration after precipitation from solution. To form the carbonylation catalyst, a reaction vessel under an inert atmosphere is charged with 0.1 mol of metalated ligand in 100 mL THF solvent (1.0 M). One equivalent of $\text{NaCo}(\text{CO})_4$ is added to the solution slowly and allowed to stir at room temperature overnight. Product is filtered to removed NaCl byproduct. The product is collected by precipitating the catalyst from THF solvent by addition of anti-solvent hexanes which is then collected by filtration.

[0067] FIG. 2 is a synthetic scheme to form a carbonylation catalyst with a Lewis acid containing phosphasalén, phosphasalph, or phosphasalcy ligand. A reaction vessel is charged with appropriate 2,4-disubstituted phenol (0.1 mol) in 300 mL of acetonitrile. The reaction is

cooled to 0 °C and 0.1 mol of *N*-bromosuccinimide is added and is stirred overnight at room temperature. The reaction mixture is washed with Na₂SO₃ and the phases are separated. The organic layer is then collected, and the solvent is removed by rotary evaporation. After isolating, to a reaction vessel under an inert atmosphere is added the appropriate 2-bromo-4,6-disubstituted phenol (0.014 mol) in 50 mL of diethyl ether and is reduced in temperature to -78 °C. To the cooled solution, 0.0295 mol of *n*-butyl lithium, a slight excess, is added slowly. The reaction mixture is brought back to room temperature for 1 hour. Subsequently, the reaction mixture is cooled to -78 °C and 0.014 mol of the appropriate chlorophosphine (R₂PCl) is added and stirred overnight at room temperature. The solution is washed with KH₂PO₄. The layers are separated and the organic is layer is dried and the solvent removed by rotary evaporation. To a reaction vessel under an inert atmosphere is added the appropriate 2,4-disubstituted-6-(R₂phosphaneyl)phenol (0.00512 mol) in 60 mL dichloromethane solvent. The temperature is reduced to -78 °C and liquid bromine (0.00512 mol) is added slowly and then stirred at room temperature for 2 hours. The reaction mixture is reduced in temperature again to -78 °C and 0.00256 mol of tributylamine and 0.00256 mol of ethylene diamine is added slowly and stirred at room temperature overnight. The reaction mixture is filtered, and the filtrate is dried by reduced pressure. The oil is the stirred in THF to afford a white solid that is further purified by column chromatography. After the ligand is formed, a reaction vessel under an inert atmosphere is charged with 0.1 mol of ligand in 100 mL toluene solvent (1.0 M). One equivalent of Et₂AlCl is added to the solution slowly and allowed to stir at room temperature overnight. Product is collected by filtration after precipitation from solution. To form the carbonylation catalyst, a reaction vessel under an inert atmosphere is charged with 0.1 mol of metalated ligand in 100 mL THF solvent (1.0 M). One equivalent of NaCo(CO)₄ is added to the solution slowly and allowed to stir at room temperature overnight. Product is filtered to removed NaCl byproduct. The product is collected by precipitating the catalyst from THF solvent by addition of anti-solvent hexanes which is then collected by filtration.

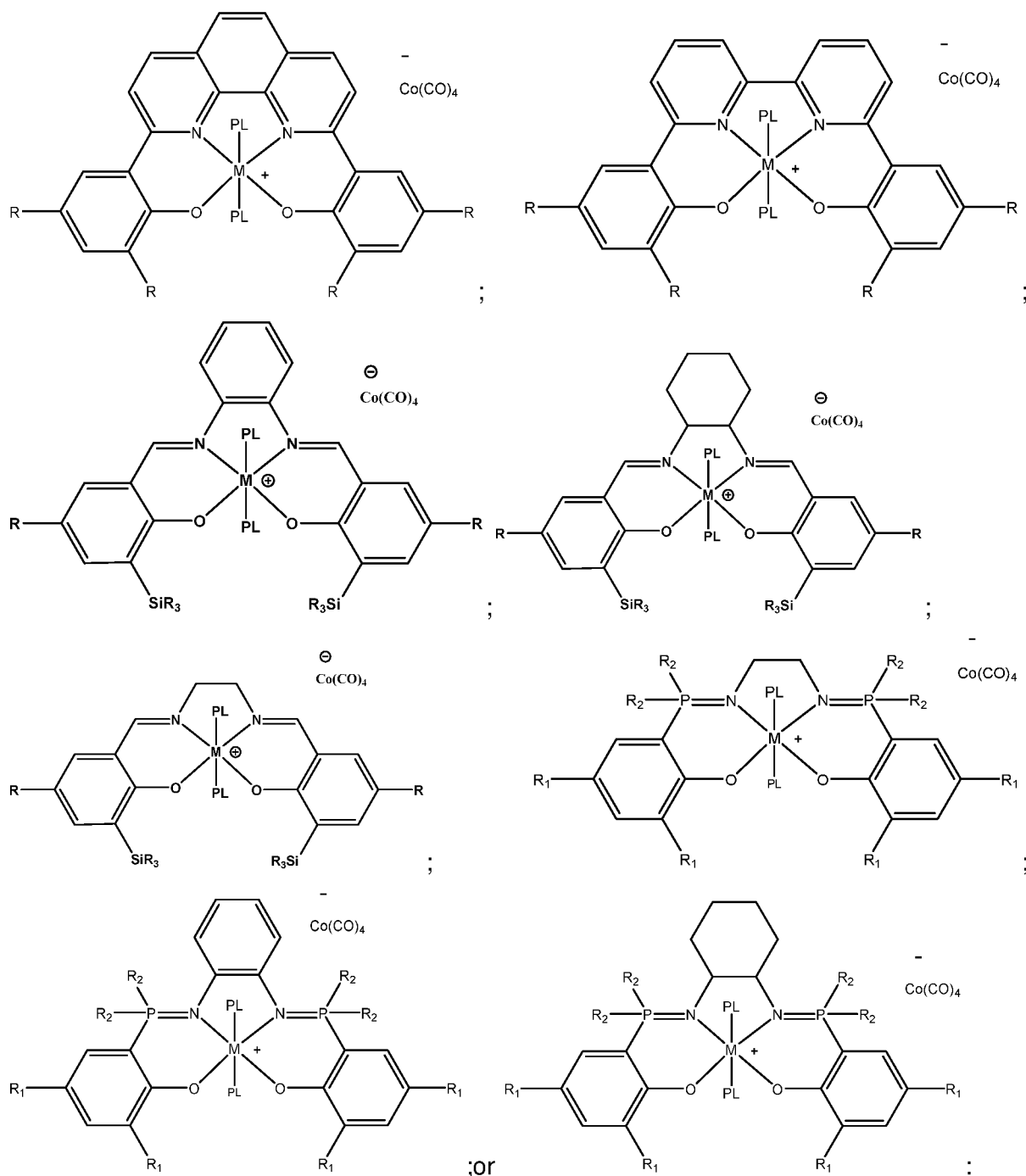
[0068] FIG. 3 is a synthetic scheme to form a carbonylation catalyst with a Lewis acid containing a ^Rdhbpy(H)₂ or ^Rdhphen(H)₂ ligand. A reaction vessel under an inert atmosphere is charged with 0.10 mol of 2,4-disubstituted phenol in 100 mL of solvent (1.0 M reaction). Added at -78 °C is one equivalent (0.10 mol) of Br₂ and stirred for 2 hours at room temperature. The reaction mixture is then quenched with 50 mL of sat. NaHCO₃ solution and the organic and aqueous layers are separated. The organic phase after drying with MgSO₄ or Na₂SO₄ is slurried with basic alumina and then is filtered over a combo of silica gel and diatomaceous earth. After isolating, a reaction vessel under an inert atmosphere is charged with the 2-bromo-4,6-disubstituted phenol (0.0175 mol) in 200 mL diethyl ether solvent (~0.1 M). Solution is reduced in temperature to -78 °C and a slight excess of *n*-butyllithium (0.042 mol) of *n*-BuLi is added to the reaction vessel slowly. After addition, the reaction is stirred at room temperature

for 2 hours. The reaction mixture is then reduced in temperature to $-78\text{ }^{\circ}\text{C}$ again 0.0282 mol of trimethylborate is added. The reaction is allowed to reach room temperature and is stirred for 18 hours. The reaction is then reduced in temperature to $0\text{ }^{\circ}\text{C}$ and is quenched with 2M HCl solution. The organic and aqueous phases are separated and the product is collected by reduced pressure evaporation of solvent. Subsequently, a reaction vessel under an inert atmosphere is charged with 0.00637 mol of dibromo pyridine linker ligand (either 6,6'-dibromobipyridine or 2,9-dibromo-1,10-phenanthroline) in 250 mL toluene with 0.0127 mol of the previously synthesized 3,5-disubstituted-2-hydroxy-phenylboronic acid, 30 mL of MeOH, 60 mL of 2M Na_2CO_3 , and 5 mol % $\text{Pd}(\text{PPh}_3)_4$. The mixture is refluxed for 72 h under an inert atmosphere. After cooling, the organic and aqueous phases are separated and the organic solvent is removed under reduced pressure to yield the desired ligand. After the ligand is formed, a reaction vessel under an inert atmosphere is charged with 0.1 mol of ligand in 100 mL toluene solvent (1.0 M). One equivalent of Et_2AlCl is added to the solution slowly and allowed to stir at room temperature overnight. Product is collected by filtration after precipitation from solution. To form the carbonylation catalyst, a reaction vessel under an inert atmosphere is charged with 0.1 mol of metalated ligand in 100 mL THF solvent (1.0 M). One equivalent of $\text{NaCo}(\text{CO})_4$ is added to the solution slowly and allowed to stir at room temperature overnight. Product is filtered to remove NaCl byproduct. The product is collected by precipitating the catalyst from THF solvent by addition of anti-solvent hexanes which is then collected by filtration.

ENUMERATED EMBODIMENTS

[0069] The following examples are provided to illustrate the invention but are not intended to limit the scope thereof. All parts and percentages are by weight unless otherwise indicated.

[0070] Embodiment 1. A compound according to one of the formulas:



wherein R is separately in each occurrence an hydrogen, alkyl, or aryl group;

R₁ is separately in each occurrence hydrogen, aryl, or alkyls group;

R₂ is separately in each occurrence an alkyl, aryl, or alkoxide group;

R₃ is separately in each occurrence an alkyl or aryl group

PL is the residue of a polar ligand; and

M is separately in each occurrence a Lewis Acid metal.

[0071] Embodiment 2. The compounds according to Embodiment 1 wherein:

R is separately in each occurrence an alkyl or aryl group;

R₁ is separately in each occurrence an alkyl group;

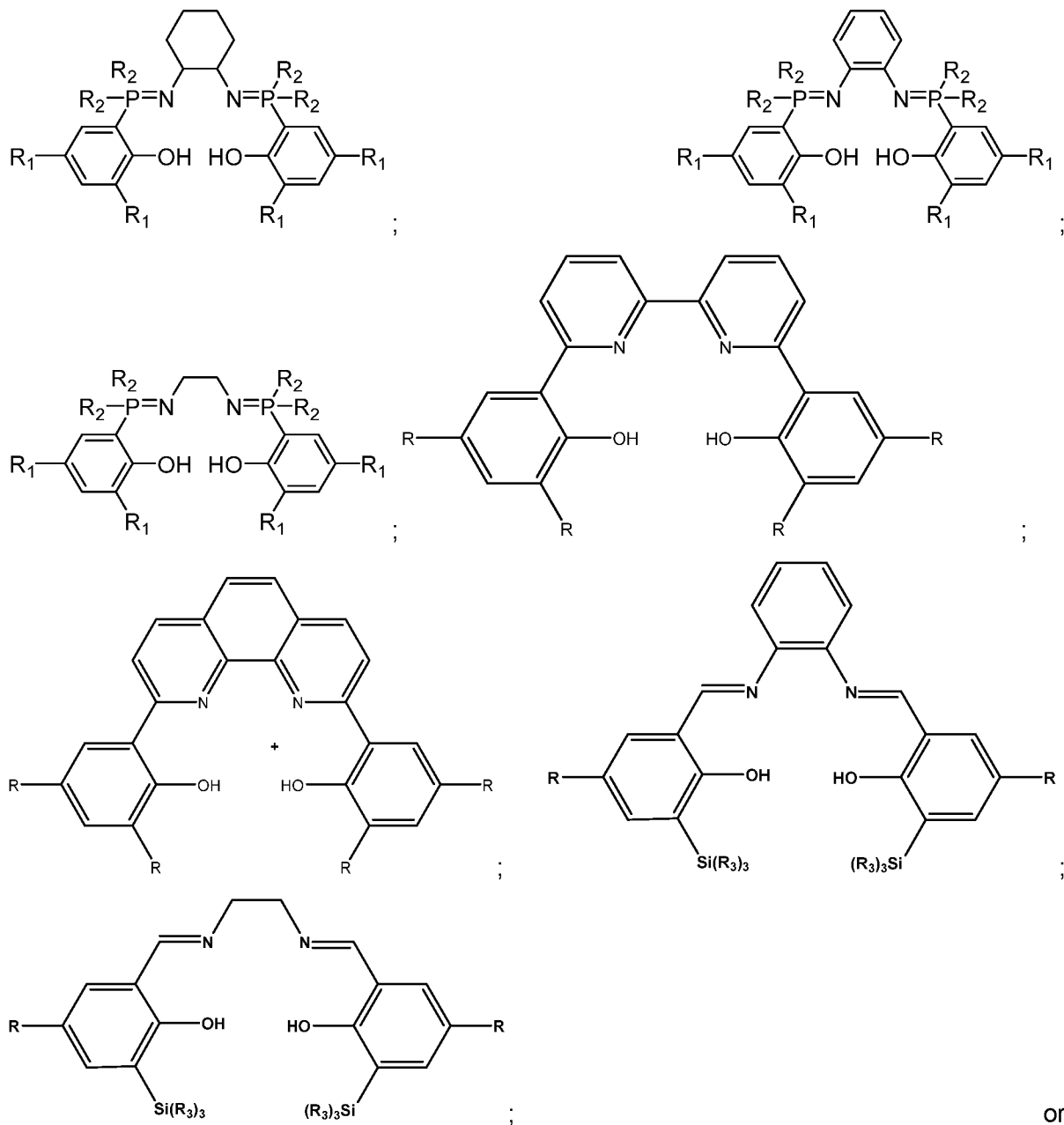
R₂ is separately in each occurrence an alkyl group;

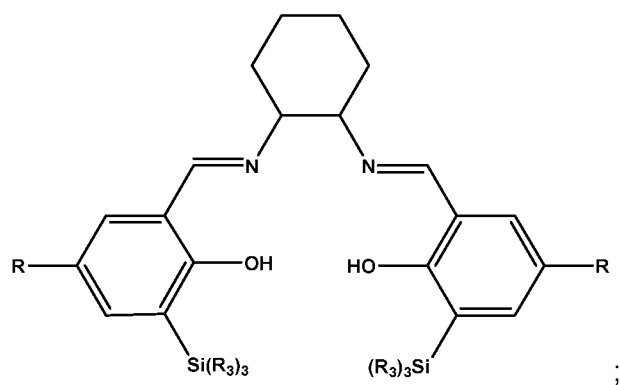
R₃ is separately in each occurrence an alkyl group

PL is the residue of tetrahydrofuran, diethyl ether, or a combination thereof; and

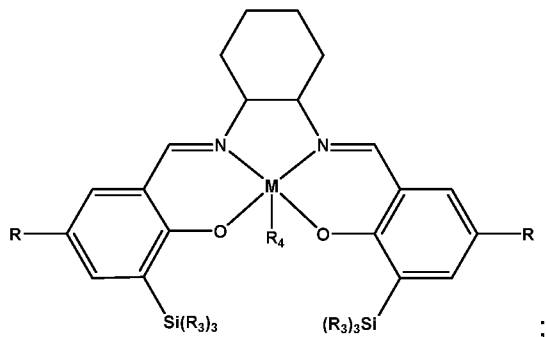
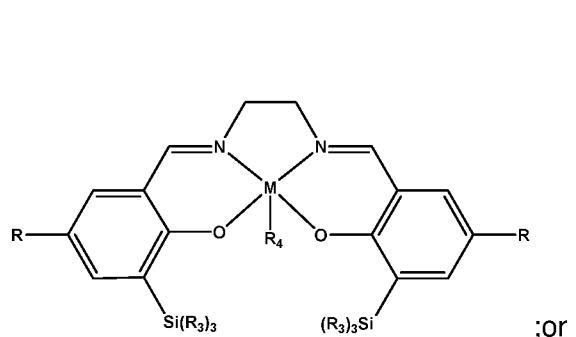
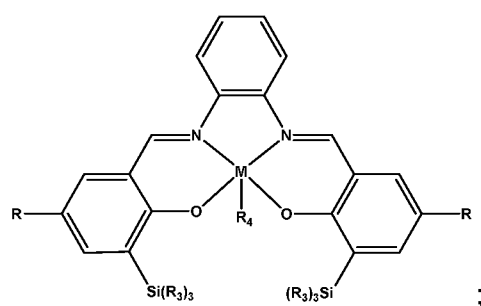
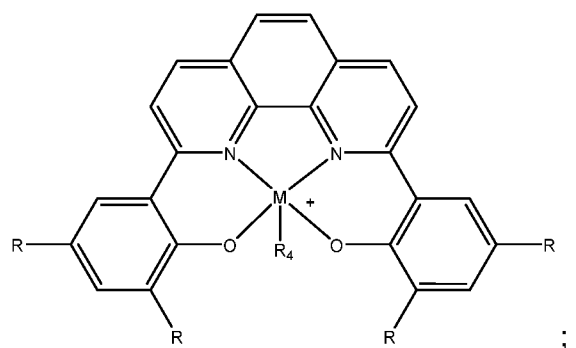
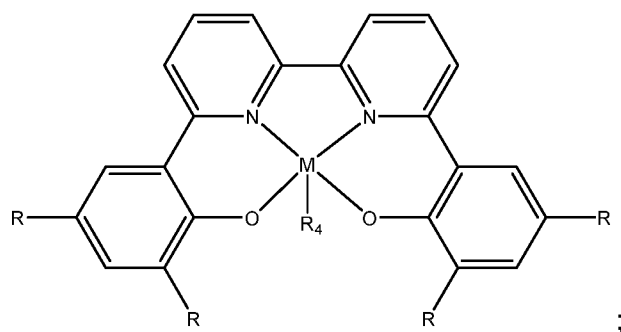
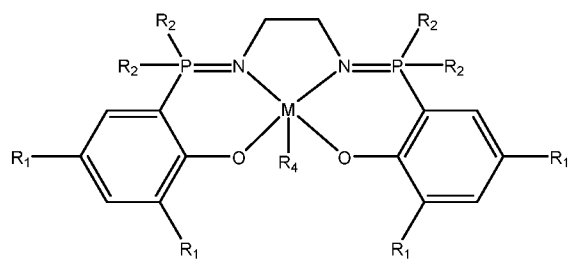
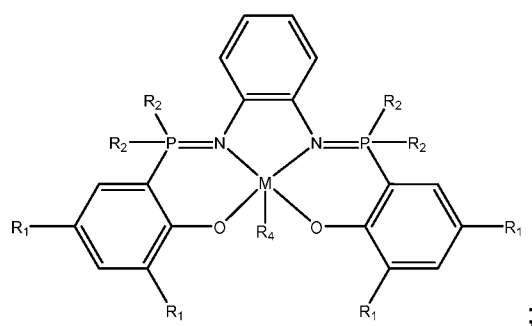
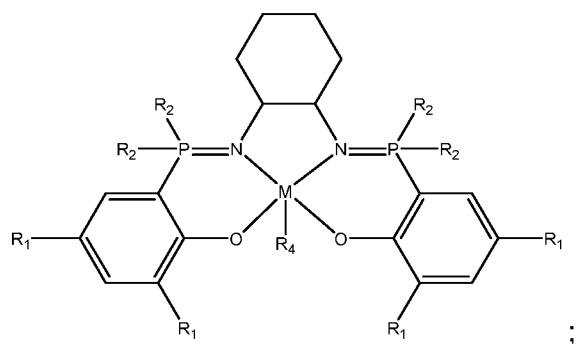
M is separately in each occurrence aluminum or chromium.

[0072] Embodiment 3. A method for preparing a compound according to Embodiment 1 or 2 comprising:
contacting of a compound according to one of the formulas:



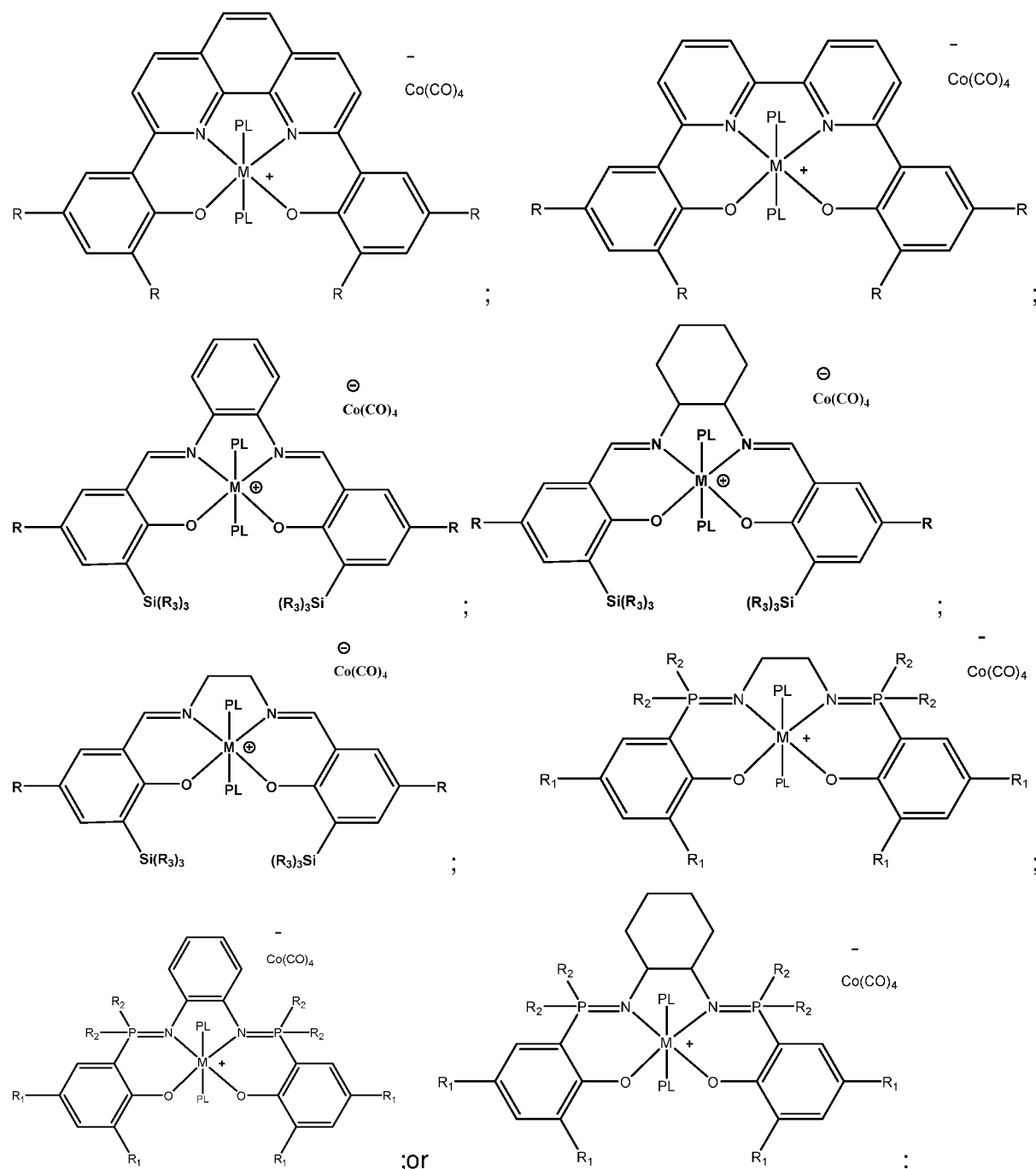


with a metalating agent to form one of the compounds according to the formula



;or

and contacting the formed compounds with a metal carbonyl under condition such that one of the following compounds are formed:



wherein R is separately in each occurrence an hydrogen, alkyl, or aryl group;

R_1 is separately in each occurrence hydrogen, aryl, or alkyl group;

R_2 is separately in each occurrence an alkyl, aryl, or alkoxide group;

R_3 is separately in each occurrence an alkyl or aryl group

R_4 is separately in each occurrence an alkyl group or a halogen

PL is the residue of a polar ligand; and

M is separately in each occurrence a Lewis Acid metal.

[0073] Embodiment 4. The method according to Embodiment 3 wherein:

R is separately in each occurrence an alkyl or aryl group;

R₁ is separately in each occurrence an alkyl group;

R₂ is separately in each occurrence an alkyl group;

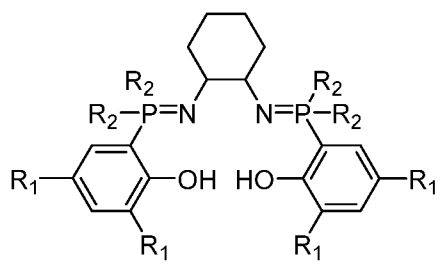
R₃ is separately in each occurrence an alkyl group;

R₄ is separately in each occurrence an alkyl group or a halogen

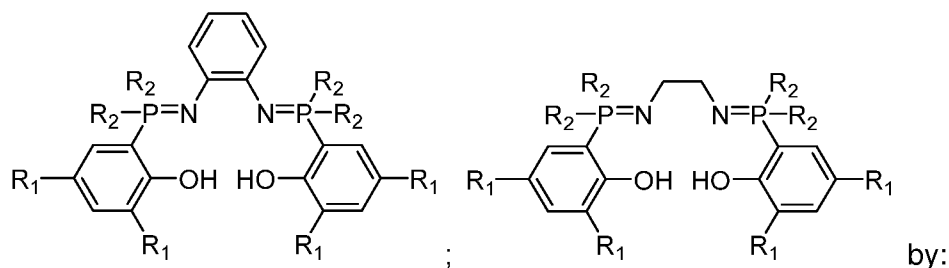
PL is the residue of tetrahydrofuran, diethyl ether, or a combination thereof; and

M is separately in each occurrence aluminum or chromium.

[0074] Embodiment 5. The method according to Embodiment 3 or 4 comprising preparing



one of the compounds according to the one of the formulas

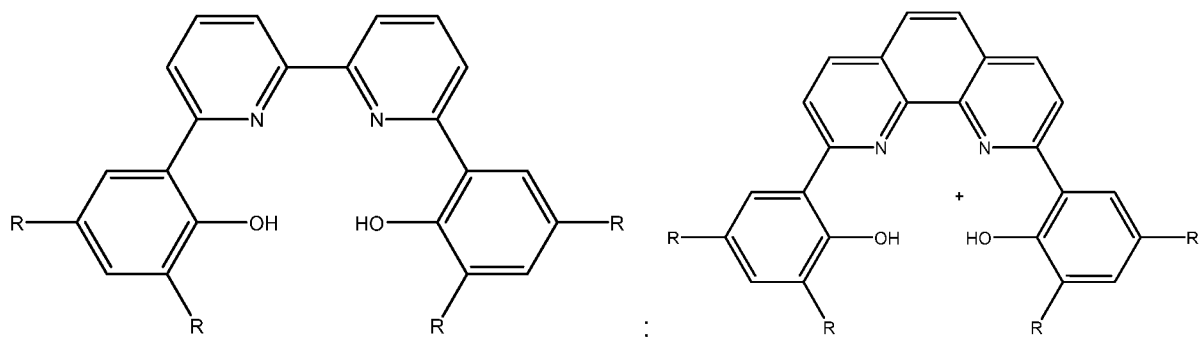


contacting a phenol which may be substituted at the 2 and/or 4 position with an hydrogen, alkyl, or aryl group with a halogenating agent under conditions such that a halogen atom is added at the 6 carbon atom to form a halogenated phenol;

contacting the halogenated phenol with a halo-di(aryl or alkyl) phosphine in the presents of an alkyl lithium under conditions to replace the halogen on the phenol with di(alkyl or aryl) phosphate to form a dialkyl or diaryl phosphate substituted phenol; and

contacting the dialkyl or diaryl phosphate substituted phenol with a diamine, an ortho phenylene amine or ortho cyclohexyl diamine in the presence of bromine and a trialkyl amine to form a compound according to the formulas.

[0075] Embodiment 6. The method according to Embodiment 3 or 4 comprising preparing one of the compounds according to one of the formulas:



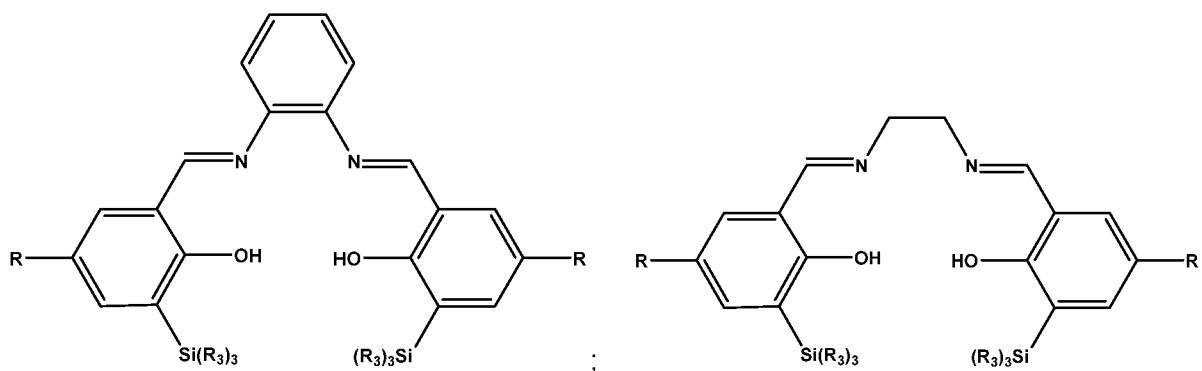
by:

contacting a phenol which may be substituted at the 2 and/or 4 position with an hydrogen, alkyl, or aryl group with a halogenating agent under conditions such that a halogen atom is added at the 6 carbon atom to form a halogenated phenol;

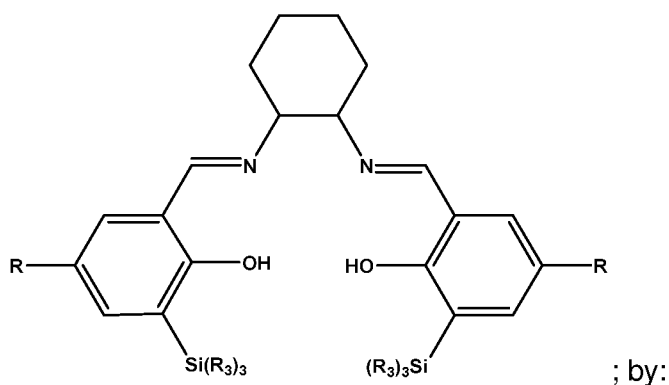
contacting the formed halogenated phenol with a trialkyl borate in the presence of an alkyl lithium compound to replace the halogen atom with a boron dihydroxide group; and

contacting phenol containing a boron dihydroxide group with bipyridine or phenanthroline having halogen groups on carbons adjacent to the nitrogen atoms in the presence of a palladium catalyst and an alkali metal carbonate under conditions to form one of the compounds of the formulas.

[0076] Embodiment 7. The method according to Embodiment 3 or 4 comprising preparing one of the compounds according to one of the formulas:



or



contacting a phenol which may optionally be substituted at the 4 position with an hydrogen, alkyl, or aryl group with a halogenating agent and silyl halide under conditions such that a halogen atom is added at the 2 and 6 carbon atoms of the aromatic ring and the 1 hydroxyl group is converted to silyl ether group which may optionally be substituted at the 4 position with an hydrogen, alkyl, or aryl group;

contacting the formed 2, 6-halogenated 1-silylether substituted benzene with an alkyl lithium compound and dimethylformamide to form a phenol having a silyl and an acetaldehyde group at the 2 and 6 positions which may optionally be substituted at the 4 position with an hydrogen, alkyl, or aryl group; and

contacting the phenol having a silyl and an acetaldehyde group at the 2 and 6 positions which may optionally be substituted at the 4 position with an hydrogen, alkyl, or aryl group with one of o-phenylene diamine, ethylene diamine, or cyclohexanediamine and optionally in the presence of a Lewis acid or Bronsted acid catalyst and an alkali metal or ammonium salt to form one of the compounds corresponding to one of the formulas.

[0077] Embodiment 8. The method of embodiment 5, wherein contacting the dialkyl or diaryl phosphate substituted phenol with the diamine, the ortho phenylene amine or the ortho cyclohexyl diamine in the presence of the bromine and the trialkyl amine to form a compound according to the formulas includes:

contacting the dialkyl or diaryl phosphate substituted phenol with the bromine to form an activated dialkyl or diaryl phosphate substituted phenol; and

contacting the activated dialkyl or diaryl phosphate substituted phenol with the ortho phenylene amine or the ortho cyclohexyl diamine in the presence of the trialkyl amine to form the compound according to the formulas.

[0078] Embodiment 9. The method of embodiments 5 or 8, wherein the halo-di(aryl or alkyl) phosphine is one or more of chloro-di(aryl) phosphine, chloro-di(alkyl) phosphine, chloro-di(alkoxide) phosphine, or any combination.

[0079] Embodiment 10. The method of any one of embodiments 5 or 8-9, wherein the trialkyl amine is configured to consume bromic acid to form an ammonium salt.

[0080] Embodiment 11. The method of any one of embodiments 5 or 8-10, wherein the trialkyl amine includes one or more of tributylamine.

[0081] Embodiment 12. The method of embodiment 6, wherein contacting the formed halogenated phenol with the trialkyl borate in the presence of an alkyl lithium compound to replace the halogen atom with a boron dihydroxide group:

contacting the phenol containing a boron dihydroxide group with hydrochloric acid to quench the reaction.

[0082] Embodiment 13. The method of embodiments 6 or 12, wherein the trialkyl borate includes one or more of trimethyl borate, triethyl borate, tripropyl borate, trisopropyl borate, or any combination thereof.

[0083] Embodiment 14. The method of any one of embodiments 6, 12, or 13, wherein the alkali metal carbonate includes sodium carbonate.

[0084] Embodiment 15. The method of embodiment 7, wherein contacting a phenol which may optionally be substituted at the 4 position with an hydrogen, alkyl, or aryl group with a halogenating agent and silyl halide under conditions such that a halogen atom is added at the 2 and 6 carbon atoms of the aromatic ring and the 1 hydroxyl group is converted to silyl ether group which may optionally be substituted at the 4 position with an hydrogen, alkyl, or aryl group includes:

contacting the phenol which may optionally be substituted with the halogenating agent to form a halogenated phenol; and

contacting the halogenated phenol with the silyl halide under conditions such that 1 hydroxyl group is converted to silyl ether group which may optionally be substituted at the 4 position with an hydrogen, alkyl, or aryl group.

[0085] Embodiment 16. The method of embodiments 7 or 15, wherein contacting the halogenated phenol with the silyl halide under conditions such that 1 hydroxyl group is converted to silyl ether group which may optionally be substituted at the 4 position with an hydrogen, alkyl, or aryl group includes:

contacting the halogenated phenol and the silyl halide with a tertiary amine to consume any acid byproduct so that the phenol having a silyl and an acetaldehyde group at the 2 and 6 positions which may optionally be substituted at the 4 position with an hydrogen, alkyl, or aryl group is formed.

[0086] Embodiment 17. The method of any one of embodiments 7 or 15-16, wherein contacting the formed 2, 6-halogenated 1-silylether substituted benzene with the alkyl lithium compound to form the phenol having the silyl and the acetaldehyde group at the 2 and 6 positions which may optionally be substituted at the 4 position with an hydrogen, alkyl, or aryl group includes:

contacting the formed 2, 6-halogenated 1-silylether substituted benzene with the alkyl lithium compound to form the phenol having the silyl at the 2 or 6 position; and

contacting the phenol having the silyl at the 2 or the 6 position with dimethylformamide to form the phenol having the silyl and the acetaldehyde group at the 2 and 6 positions which may optionally be substituted at the 4 position with an hydrogen, alkyl, or aryl group.

[0087] Embodiment 18. The method of any one of embodiments 7 or 15-17, wherein the

silyl halide is trisubstituted with one or more of aryl groups, alkyl groups, or both.

[0088] Embodiment 19. The method of any one of embodiments 7 or 15-19, wherein the silyl halide includes one or more of fluorine, chlorine, bromine, iodine, or any combination thereof.

[0089] Embodiment 20. The method of any one of the preceding embodiments, wherein contacting the formed compounds with the metal carbonyl under condition such that one of the compounds are formed includes:

contacting the formed compounds, the metal carbonyl, or both with a polar ligand so that that one of the compounds are formed.

[0090] Embodiment 21. The method of any one of the preceding embodiments, wherein the alkyl lithium compound includes one or more of *n*-butyllithium, *t*-butyllithium, or any combination thereof.

[0091] Embodiment 22. The method of any one of the preceding embodiments, wherein the halogenating agent includes one or more of bromine, *N*-bromosuccinimide, dibromoisocyanuric acid, or any combination thereof.

[0092] Embodiment 23. The method of any one of the preceding embodiments, wherein the metal carbonyl includes $\text{NaCo}(\text{CO})_4$, $\text{Co}_2(\text{CO})_8$, $\text{HCo}(\text{CO})_4$, or any combination thereof.

[0093] Embodiment 24. The method of any one of the preceding embodiments, wherein the polar ligand includes one or more of tetrahydrofuran, diethyl ether, or any combination thereof.

[0094] Embodiment 25. The method of any one of the preceding embodiments, wherein metalating agent is one or more of $(\text{Et})_2\text{AlCl}$, $(\text{Et})_3\text{Al}$, CrCl_2 , or any combination thereof

EXAMPLES

[0095] The following examples are provided to illustrate the invention but are not intended to limit the scope thereof. All parts and percentages are by weight unless otherwise indicated.

[0096] The NMR analysis is conducted on a Bruker Advance III-HD spectrometer operating at 400.3 MHz. The sample is dissolved in THF-*d*8 before testing.

[0097] The in-situ-FTIR analysis tracking the catalytic activity of the regenerated catalyst is conducted on a Mettler Toledo ReatIR 45m equipped with a silicone tipped sentinel that is directly affixed to the bottom of the reactor.

[0098] FIG. 4 is a ^1H NMR spectrum of the isolated carbonylation catalyst with a Lewis acid containing a bipyridine or phenanthroline ligand. This shows the desired catalyst from the $^{\text{tBu}}\text{dhbpy}(\text{H})_2$ ligand metalated with Et_2AlCl and reacted with $\text{NaCo}(\text{CO})_4$ that is successfully

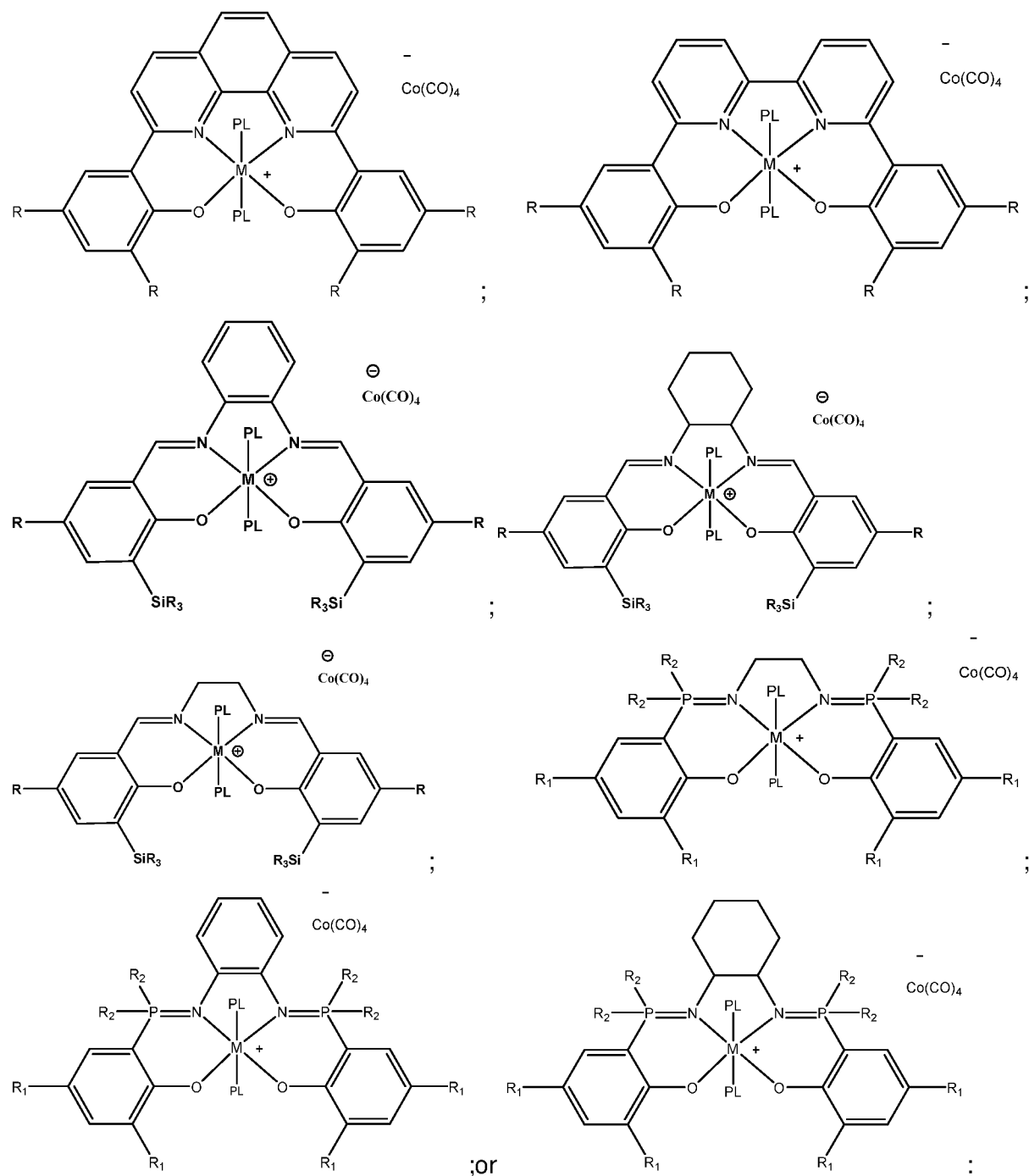
isolated. The inset image is a zoomed in view of the aromatic region of ^{tbu}dhbpy(H)₂ ligand metalated with Et₂AlCl.

[0099] FIG. 5 is a ReactIR spectrum showing the in-situ monitoring of beta-propiolactone (BPL) formation from the carbonylation catalyst with a Lewis acid containing a pyridine or phenanthroline ligand. The carbonylation catalyst is shown to have good catalytic activity with BPL (top line), some catalytic activity with ethylene oxide (middle line), and minimal activity with succinic anhydride (bottom line).

CLAIMS

What is Claimed

1. A compound according to one of the following formulas:



wherein R is separately in each occurrence an hydrogen, alkyl, or aryl group;
 R₁ is separately in each occurrence hydrogen, aryl, or alkyl group;
 R₂ is separately in each occurrence an alkyl, aryl, or alkoxide group;

R₃ is separately in each occurrence an alkyl or aryl group

PL is the residue of a polar ligand; and

M is separately in each occurrence a Lewis Acid metal.

2. The compounds according to Claim 1 wherein:

R is separately in each occurrence an alkyl or aryl group;

R₁ is separately in each occurrence an alkyl group;

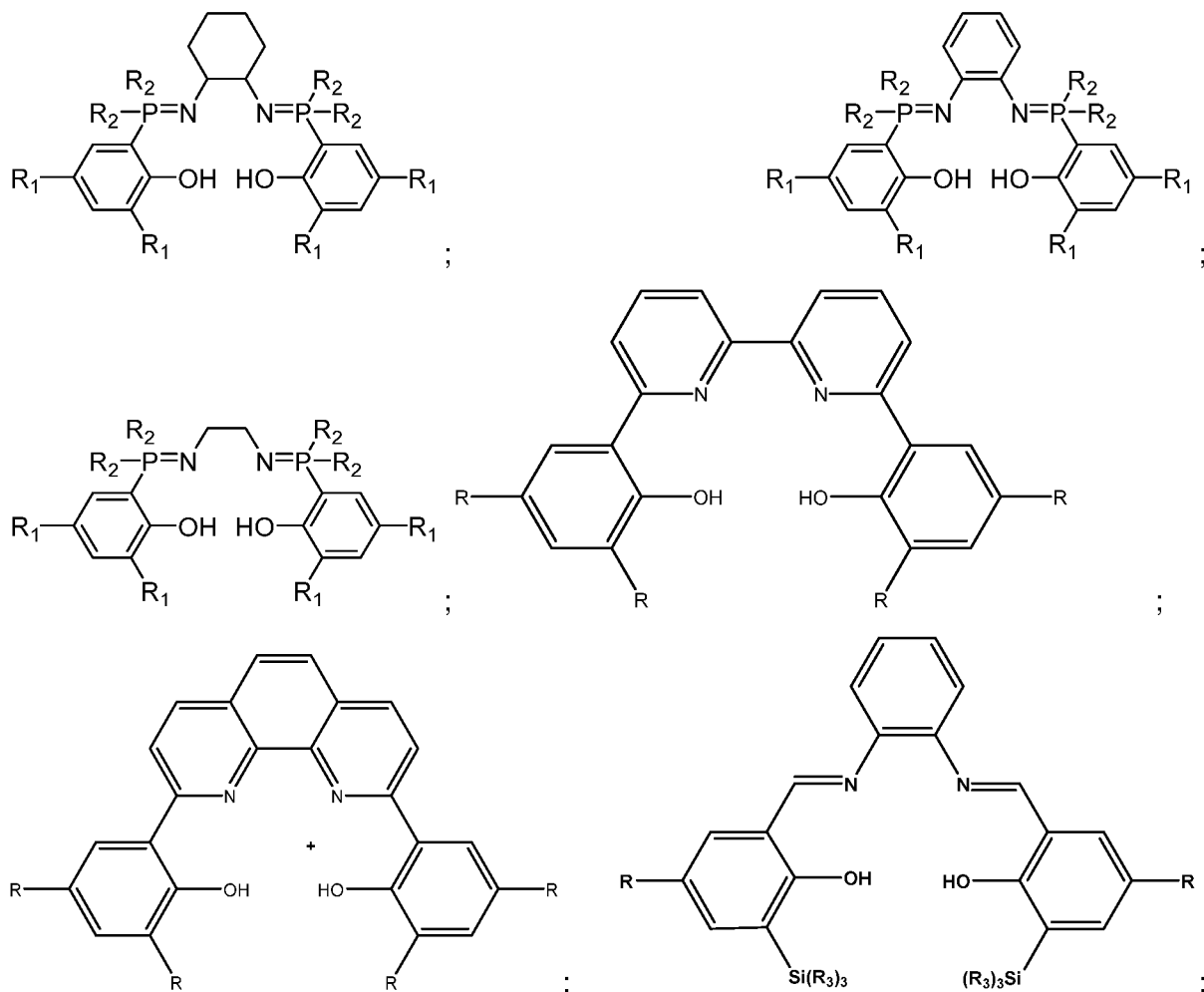
R₂ is separately in each occurrence an alkyl group;

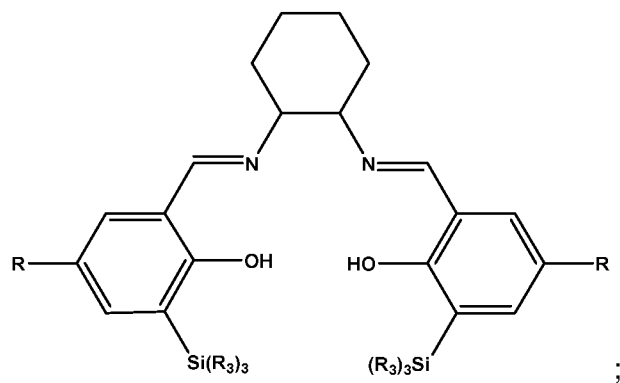
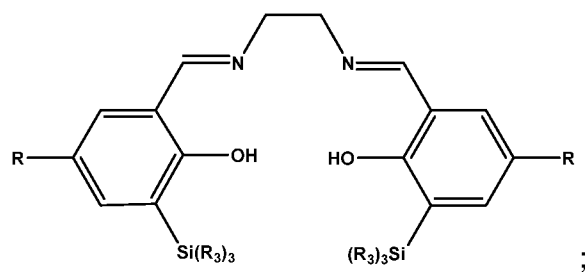
R₃ is separately in each occurrence an alkyl group

PL is the residue of tetrahydrofuran, diethyl ether, or a combination thereof; and

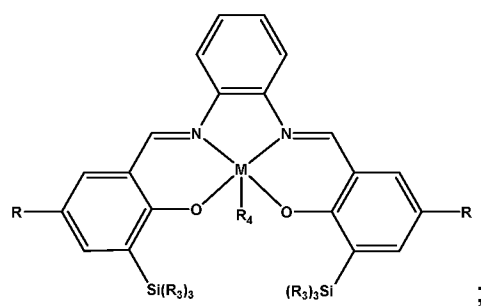
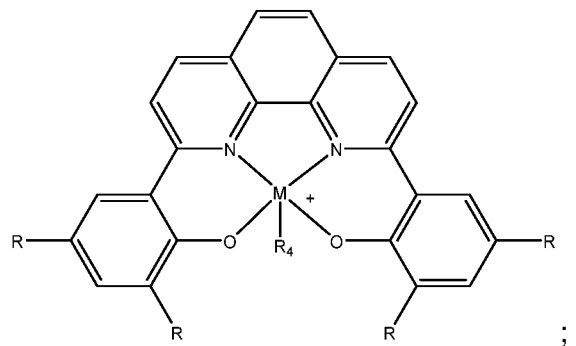
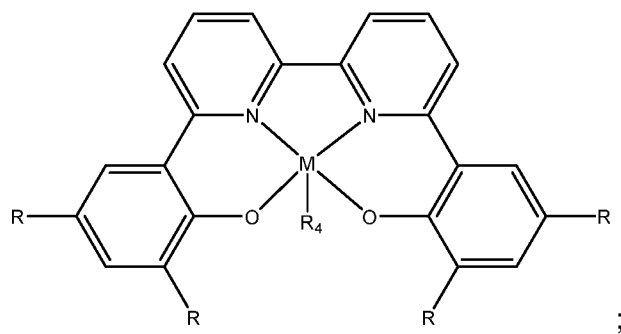
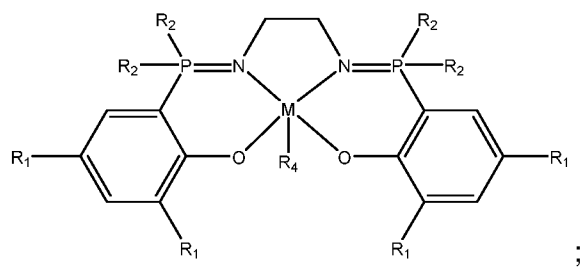
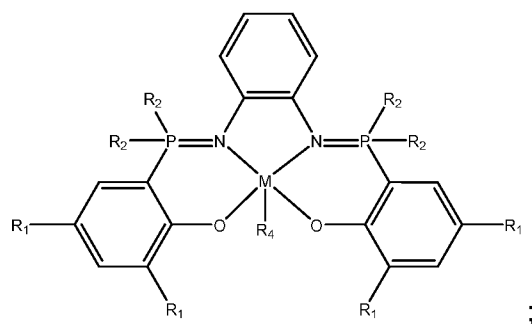
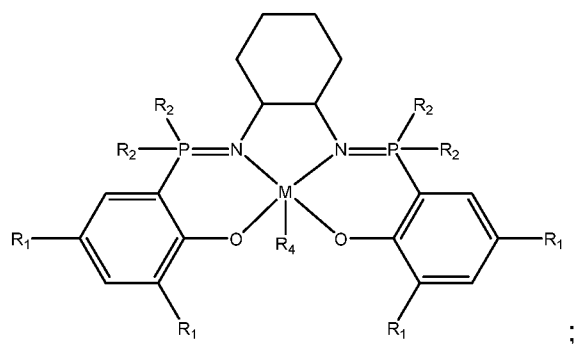
M is separately in each occurrence aluminum or chromium.

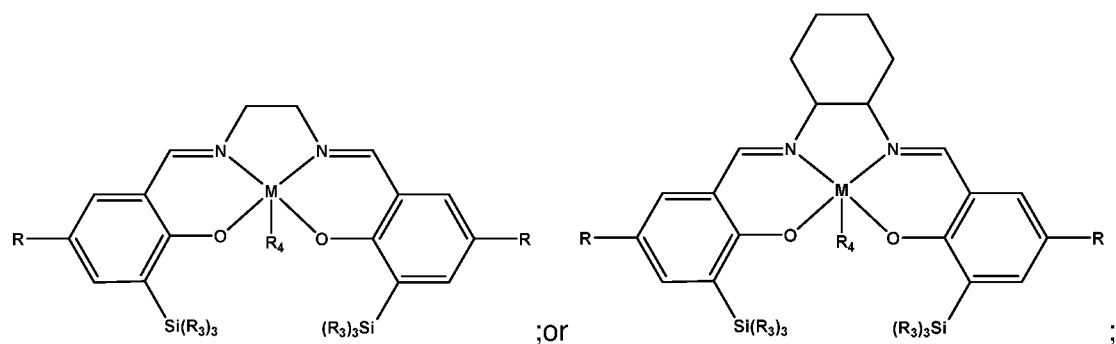
3. A method for preparing a compound according to Claim 1 or 2 comprising:
contacting of a compound according to one of the formulas:



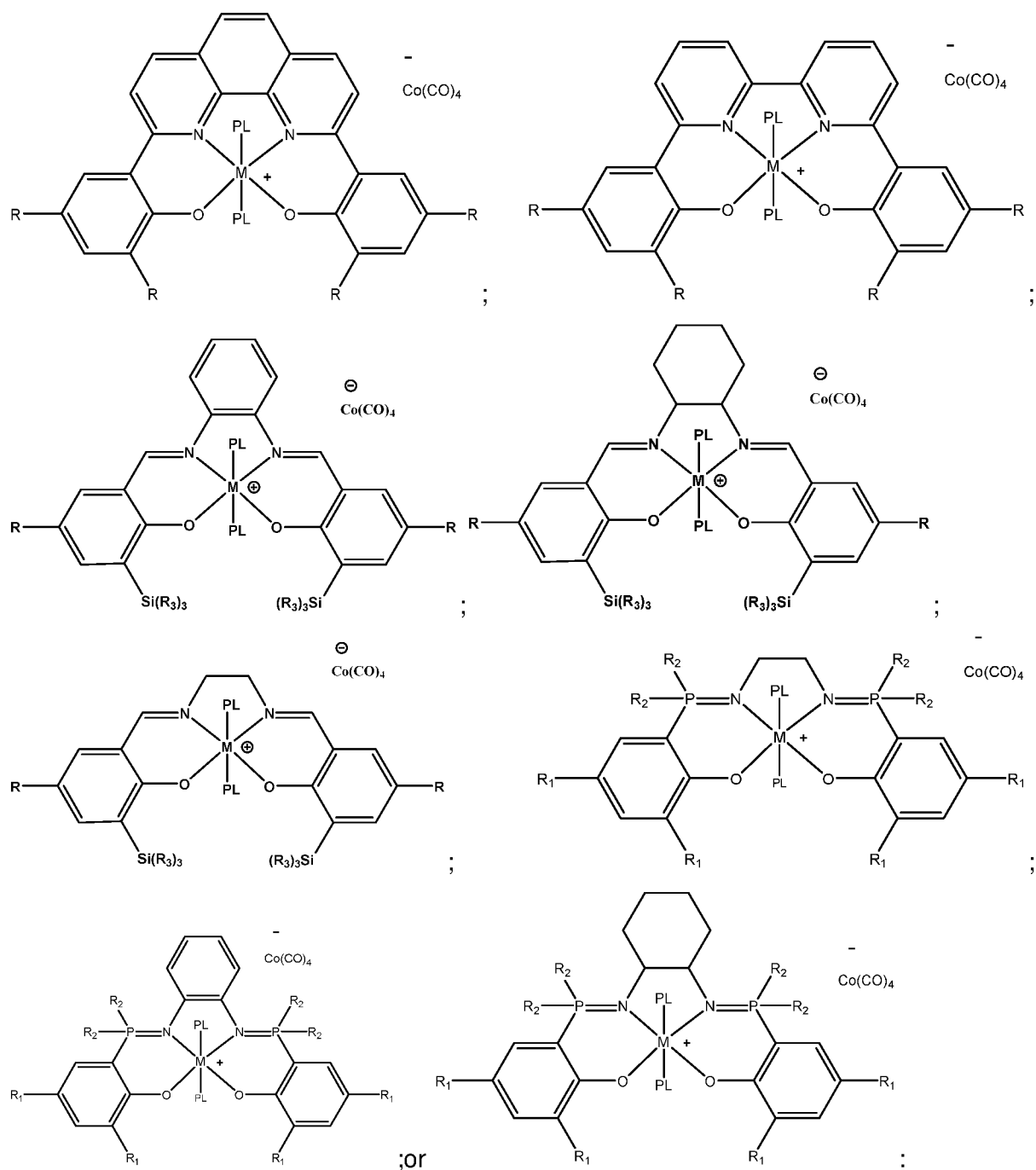


with a metalating agent to form one of the compounds according to the formula





and contacting the formed compounds with a metal carbonyl under condition such that one of the following compounds are formed:



wherein R is separately in each occurrence an hydrogen, alkyl, or aryl group;

R₁ is separately in each occurrence hydrogen, aryl, or alkyl group;

R₂ is separately in each occurrence an alkyl, aryl, or alkoxide group;

R₃ is separately in each occurrence an alkyl or aryl group

R₄ is separately in each occurrence an alkyl group or a halogen

PL is the residue of a polar ligand; and

M is separately in each occurrence a Lewis Acid metal.

4. The method according to Claim 3 wherein:

R is separately in each occurrence an alkyl or aryl group;

R₁ is separately in each occurrence an alkyl group;

R₂ is separately in each occurrence an alkyl group;

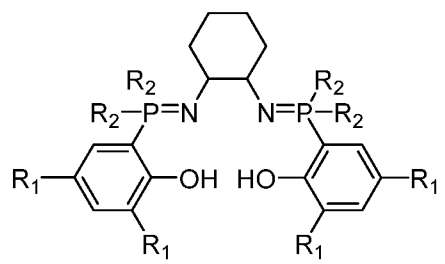
R₃ is separately in each occurrence an alkyl group;

R₄ is separately in each occurrence an alkyl group or a halogen

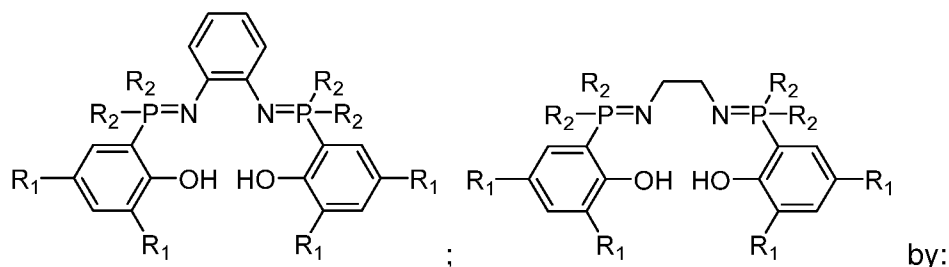
PL is the residue of tetrahydrofuran, diethyl ether, or a combination thereof; and

M is separately in each occurrence aluminum or chromium.

5. The method according to Claim 3 or 4 comprising preparing one of the compounds



according to the one of the formulas

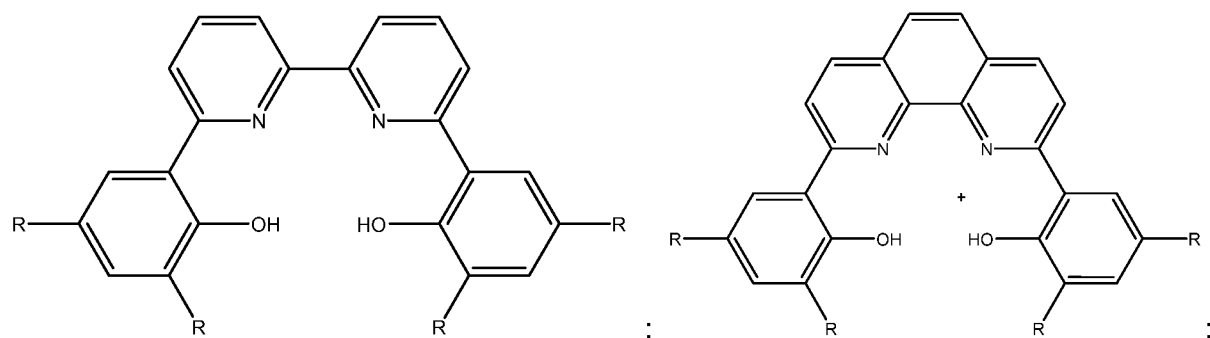


contacting a phenol which may be substituted at the 2 and/or 4 position with an hydrogen, alkyl, or aryl group with a halogenating agent under conditions such that a halogen atom is added at the 6 carbon atom to form a halogenated phenol;

contacting the halogenated phenol with a halo-di(aryl or alkyl) phosphine in the presents of an alkyl lithium under conditions to replace the halogen on the phenol with di(alkyl or aryl) phosphate to form a dialkyl or diaryl phosphate substituted phenol; and

contacting the dialkyl or diaryl phosphate substituted phenol with a diamine, an ortho phenylene amine or ortho cyclohexyl diamine in the presence of bromine and a trialkyl amine to form a compound according to the formulas.

6. The method according to Claim 3 or 4 comprising preparing one of the compounds according to one of the formulas:



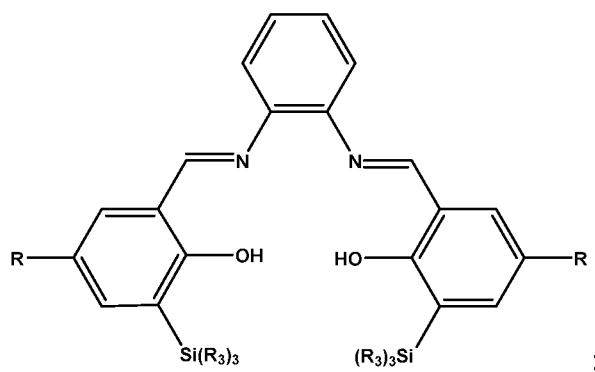
by:

contacting a phenol which may be substituted at the 2 and/or 4 position with an hydrogen, alkyl, or aryl group with a halogenating agent under conditions such that a halogen atom is added at the 6 carbon atom to form a halogenated phenol;

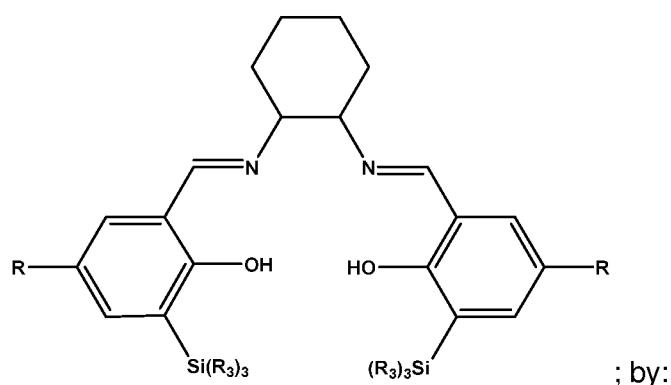
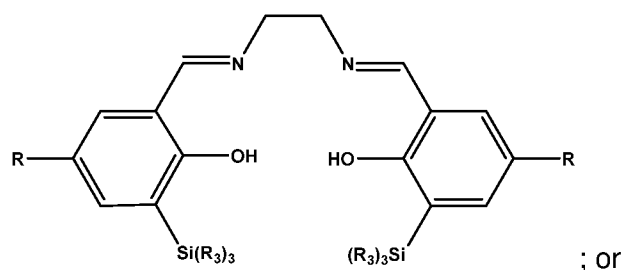
contacting the formed halogenated phenol with a trialkyl borate in the presence of an alkyl lithium compound to replace the halogen atom with a boron dihydroxide group; and

contacting phenol containing a boron dihydroxide group with bipyridine or phenanthroline having halogen groups on carbons adjacent to the nitrogen atoms in the presence of a palladium catalyst and an alkali metal carbonate under conditions to form one of the compounds of the formulas.

7. The method according to Claim 3 or 4 comprising preparing one of the compounds



according to one of the formulas:



contacting a phenol which may optionally be substituted at the 4 position with an hydrogen, alkyl, or aryl group with a halogenating agent and silyl halide under conditions such that a halogen atom is added at the 2 and 6 carbon atoms of the aromatic ring and the 1 hydroxyl group is converted to silyl ether group which may optionally be substituted at the 4 position with an hydrogen, alkyl, or aryl group;

contacting the formed 2, 6-halogenated 1-silylether substituted benzene with an alkyl lithium compound and dimethylformamide to form a phenol having a silyl and an acetaldehyde group at the 2 and 6 positions which may optionally be substituted at the 4 position with hydrogen, alkyl, or aryl group; and

contacting the phenol having a silyl and an acetaldehyde group at the 2 and 6 positions which may optionally be substituted at the 4 position with an hydrogen, alkyl, or aryl group with one of o-phenylene diamine, ethylene diamine, or cyclohexanediamine and optionally in

the presence of a Lewis acid or Bronsted acid catalyst and an alkali metal or ammonium salt form one of the compounds corresponding to one of the formulas.

8. The method of claim 5, wherein contacting the dialkyl or diaryl phosphate substituted phenol with the diamine, the ortho phenylene amine or the ortho cyclohexyl diamine in the presence of the bromine and the trialkyl amine to form a compound according to the formulas includes:

contacting the dialkyl or diaryl phosphate substituted phenol with the bromine to form an activated dialkyl or diaryl phosphate substituted phenol; and

contacting the activated dialkyl or diaryl phosphate substituted phenol with the ortho phenylene amine or the ortho cyclohexyl diamine in the presence of the trialkyl amine to form the compound according to the formulas.

9. The method of claims 5 or 8, wherein the halo-di(aryl or alkyl) phosphine is one or more of chloro-di(aryl) phosphine, chloro-di(alkyl) phosphine, chloro-di(alkoxide) phosphine, or any combination.

10. The method of any one of claims 5 or 8-9, wherein the trialkyl amine is configured to consume bromic acid to form an ammonium salt.

11. The method of any one of claims 5 or 8-10, wherein the trialkyl amine includes one or more of tributylamine.

12. The method of claim 6, wherein contacting the formed halogenated phenol with the trialkyl borate in the presence of an alkyl lithium compound to replace the halogen atom with a boron dihydroxide group:

contacting the phenol containing a boron dihydroxide group with hydrochloric acid to quench the reaction.

13. The method of claims 6 or 12, wherein the trialkyl borate includes one or more of trimethyl borate, triethyl borate, tripropyl borate, trisopropyl borate, or any combination thereof.

14. The method of any one of claims 6, 12, or 13, wherein the alkali metal carbonate includes sodium carbonate.

15. The method of claim 7, wherein contacting a phenol which may optionally be substituted at the 4 position with an hydrogen, alkyl, or aryl group with a halogenating agent and silyl halide under conditions such that a halogen atom is added at the 2 and 6 carbon

atoms of the aromatic ring and the 1 hydroxyl group is converted to silyl ether group which may optionally be substituted at the 4 position with an hydrogen, alkyl, or aryl group includes:

contacting the phenol which may optionally be substituted with the halogenating agent to form a halogenated phenol; and

contacting the halogenated phenol with the silyl halide under conditions such that 1 hydroxyl group is converted to silyl ether group which may optionally be substituted at the 4 position with an hydrogen, alkyl, or aryl group.

16. The method of claims 7 or 15, wherein contacting the halogenated phenol with the silyl halide under conditions such that 1 hydroxyl group is converted to silyl ether group which may optionally be substituted at the 4 position with an hydrogen, alkyl, or aryl group includes:

contacting the halogenated phenol and the silyl halide with a tertiary amine to consume any acid byproduct so that the phenol having a silyl and an acetaldehyde group at the 2 and 6 positions which may optionally be substituted at the 4 position with an hydrogen, alkyl, or aryl group is formed.

17. The method of any one of claims 7 or 15-16, wherein contacting the formed 2, 6-halogenated 1-silylether substituted benzene with the alkyl lithium compound to form the phenol having the silyl and the acetaldehyde group at the 2 and 6 positions which may optionally be substituted at the 4 position with an hydrogen, alkyl, or aryl group includes:

contacting the formed 2, 6-halogenated 1-silylether substituted benzene with the alkyl lithium compound to form the phenol having the silyl at the 2 or 6 position; and

contacting the phenol having the silyl at the 2 or the 6 position with dimethylformamide to form the phenol having the silyl and the acetaldehyde group at the 2 and 6 positions which may optionally be substituted at the 4 position with an hydrogen, alkyl, or aryl group.

18. The method of any one of claims 7 or 15-17, wherein the silyl halide is trisubstituted with one or more of aryl groups, alkyl groups, or both.

19. The method of any one of claims 7 or 15-19, wherein the silyl halide includes one or more of fluorine, chlorine, bromine, iodine, or any combination thereof.

20. The method of any one of the preceding claims, wherein contacting the formed compounds with the metal carbonyl under condition such that one of the compounds are formed includes:

contacting the formed compounds, the metal carbonyl, or both with a polar ligand so that that one of the compounds are formed.

21. The method of any one of the preceding claims, wherein the alkyl lithium compound includes one or more of *n*-butyllithium, *t*-butyllithium, or any combination thereof.
22. The method of any one of the preceding claims, wherein the halogenating agent includes one or more of bromine, *N*-bromosuccinimide, dibromoisocyanuric acid, or any combination thereof.
23. The method of any one of the preceding claims, wherein the metal carbonyl includes $\text{NaCo}(\text{CO})_4$, $\text{Co}_2(\text{CO})_8$, $\text{HCo}(\text{CO})_4$, or any combination thereof.
24. The method of any one of the preceding claims, wherein the polar ligand includes one or more of tetrahydrofuran, diethyl ether, or any combination thereof.
25. The method of any one of the preceding claims, wherein metalating agent is one or more of $(\text{Et})_2\text{AlCl}$, $(\text{Et})_3\text{Al}$, CrCl_2 , or any combination thereof.

1/5

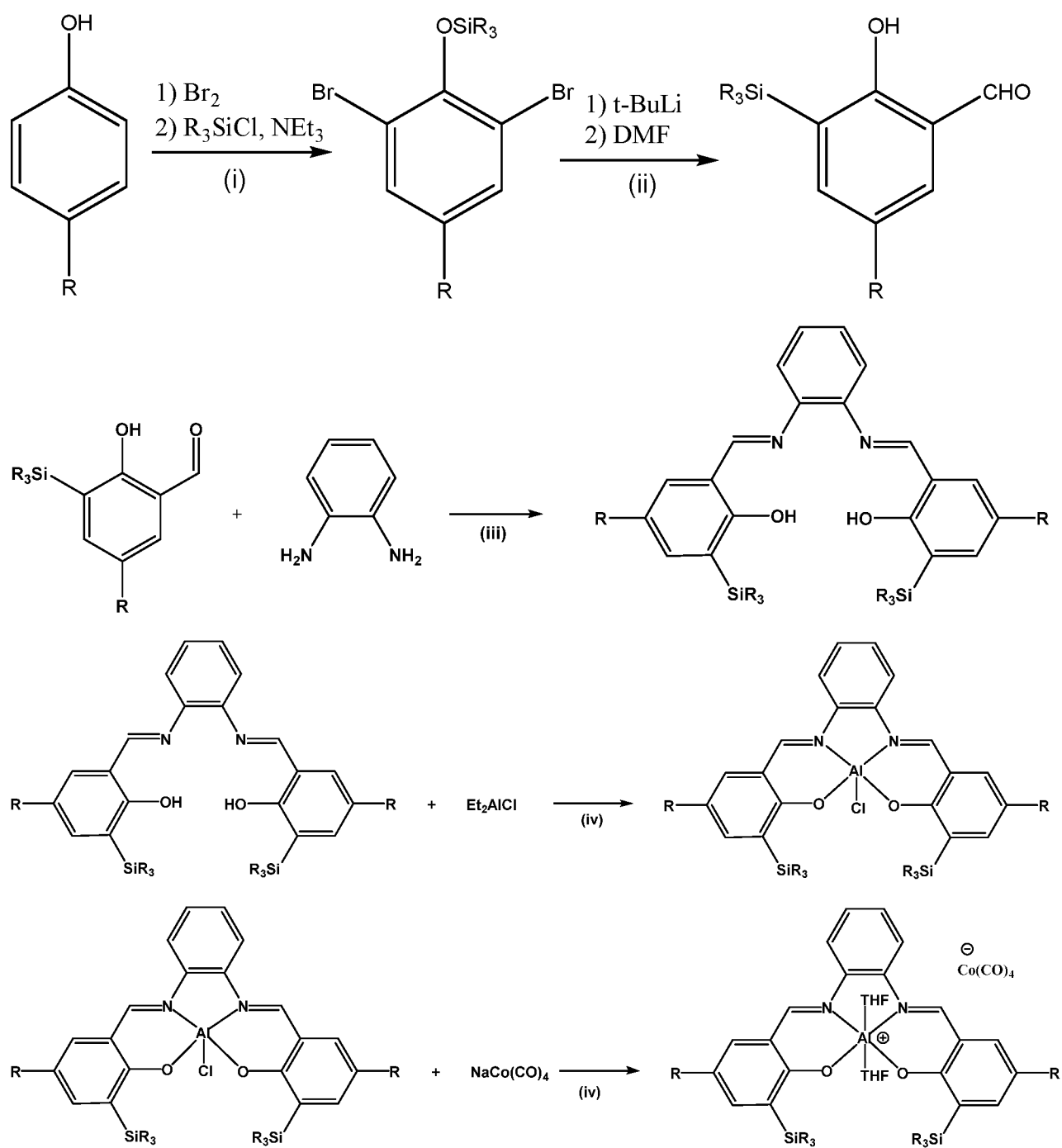


FIG. 1

2/5

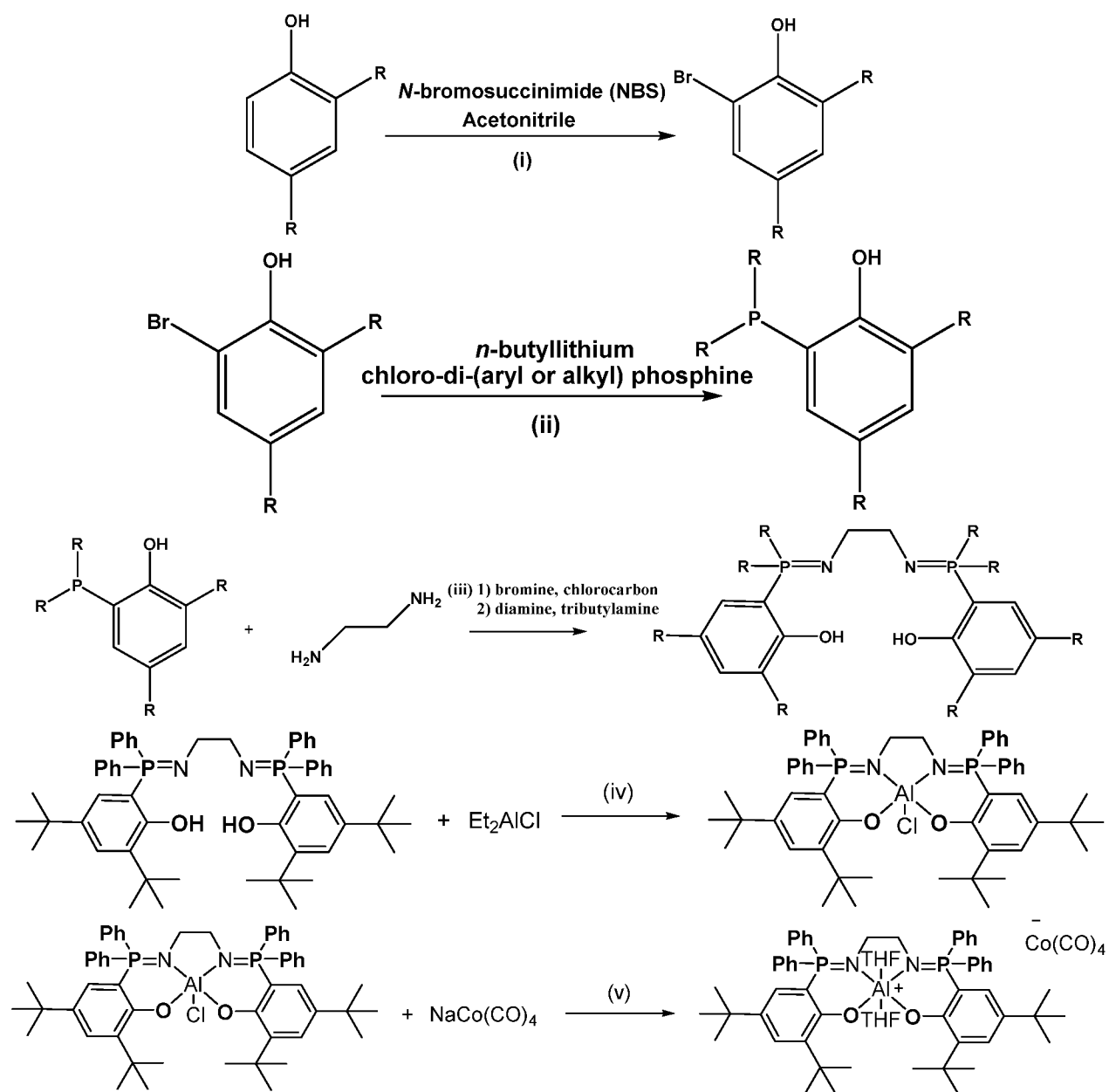


FIG. 2

3/5

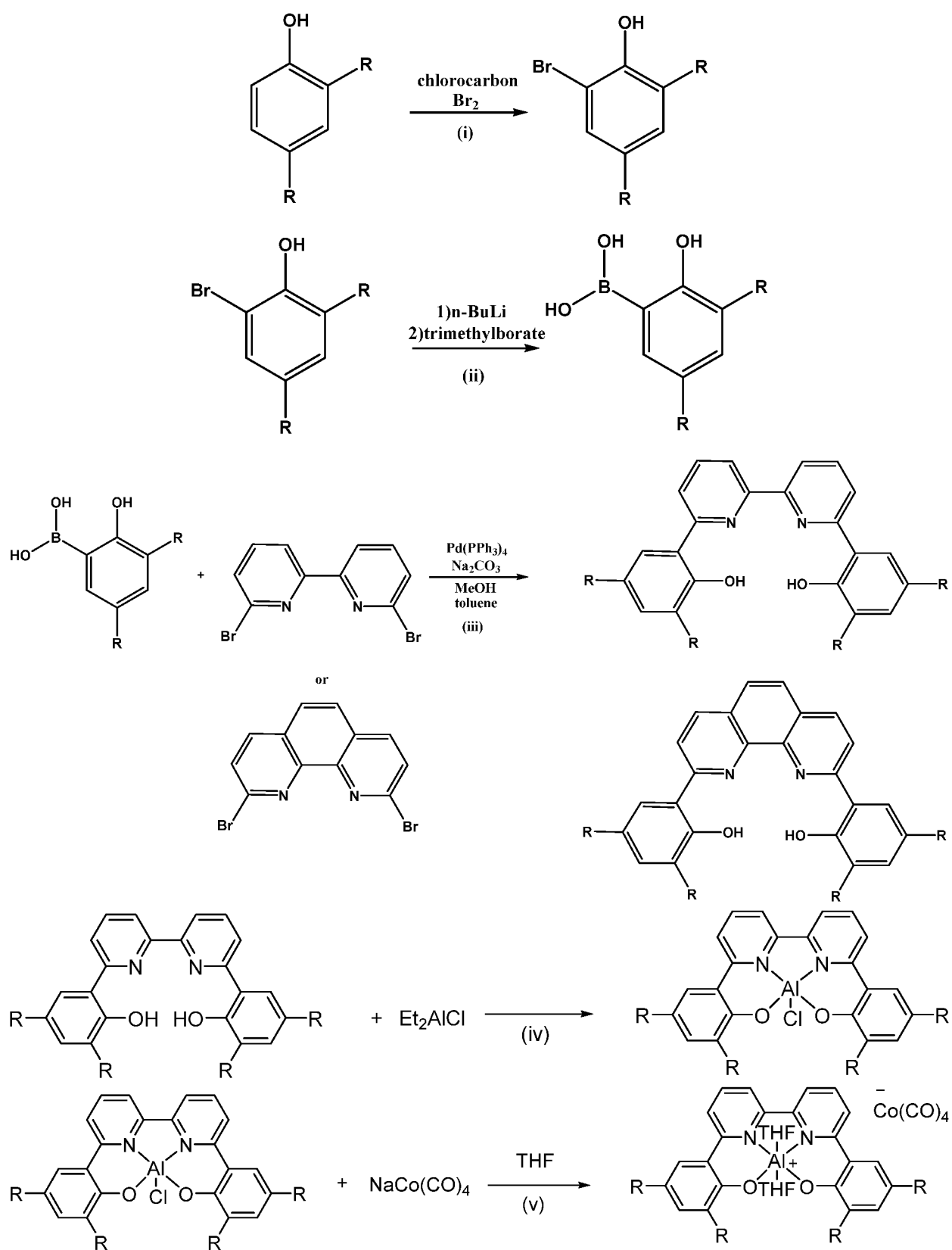


FIG. 3

4/5

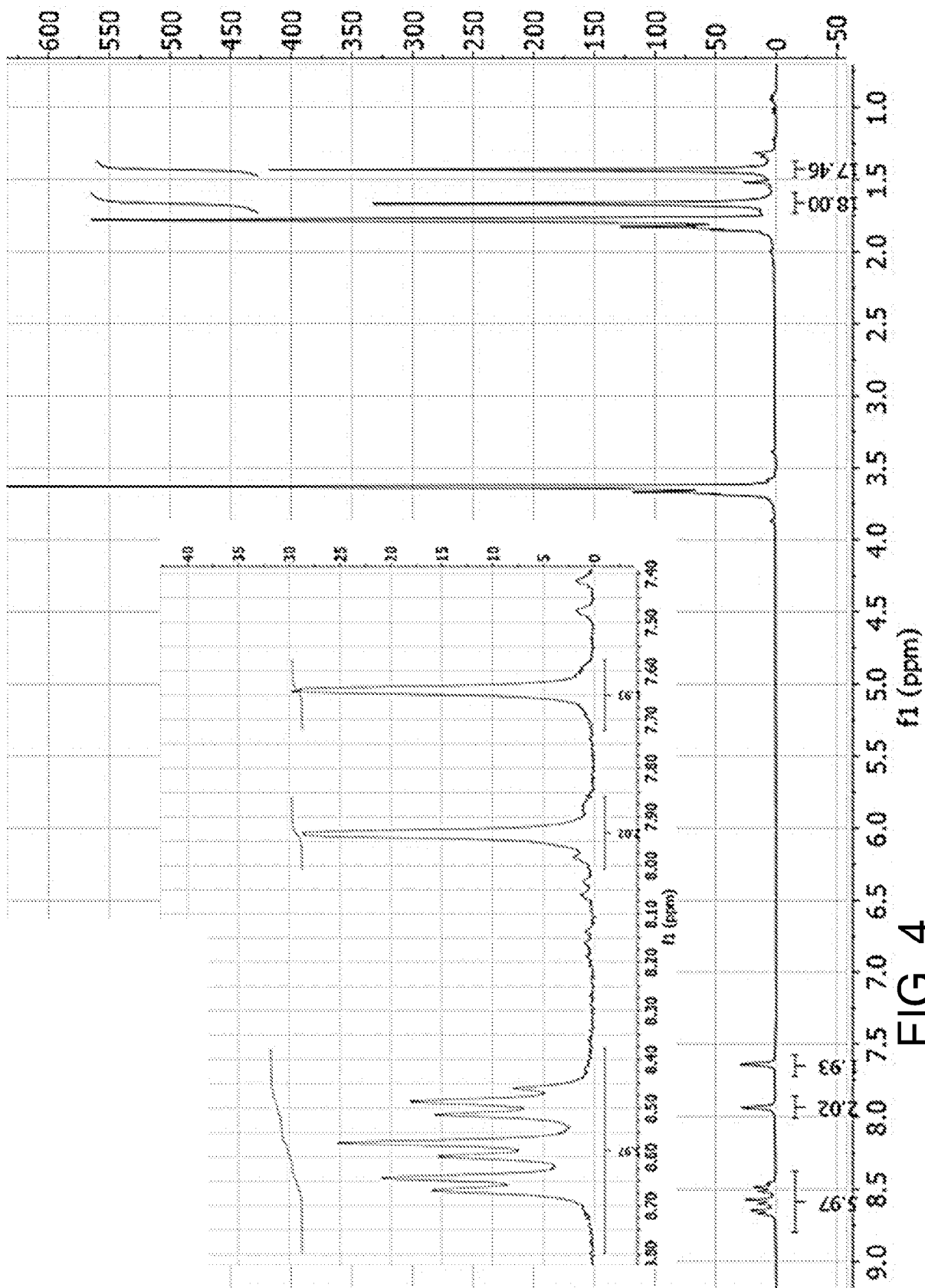


FIG. 4

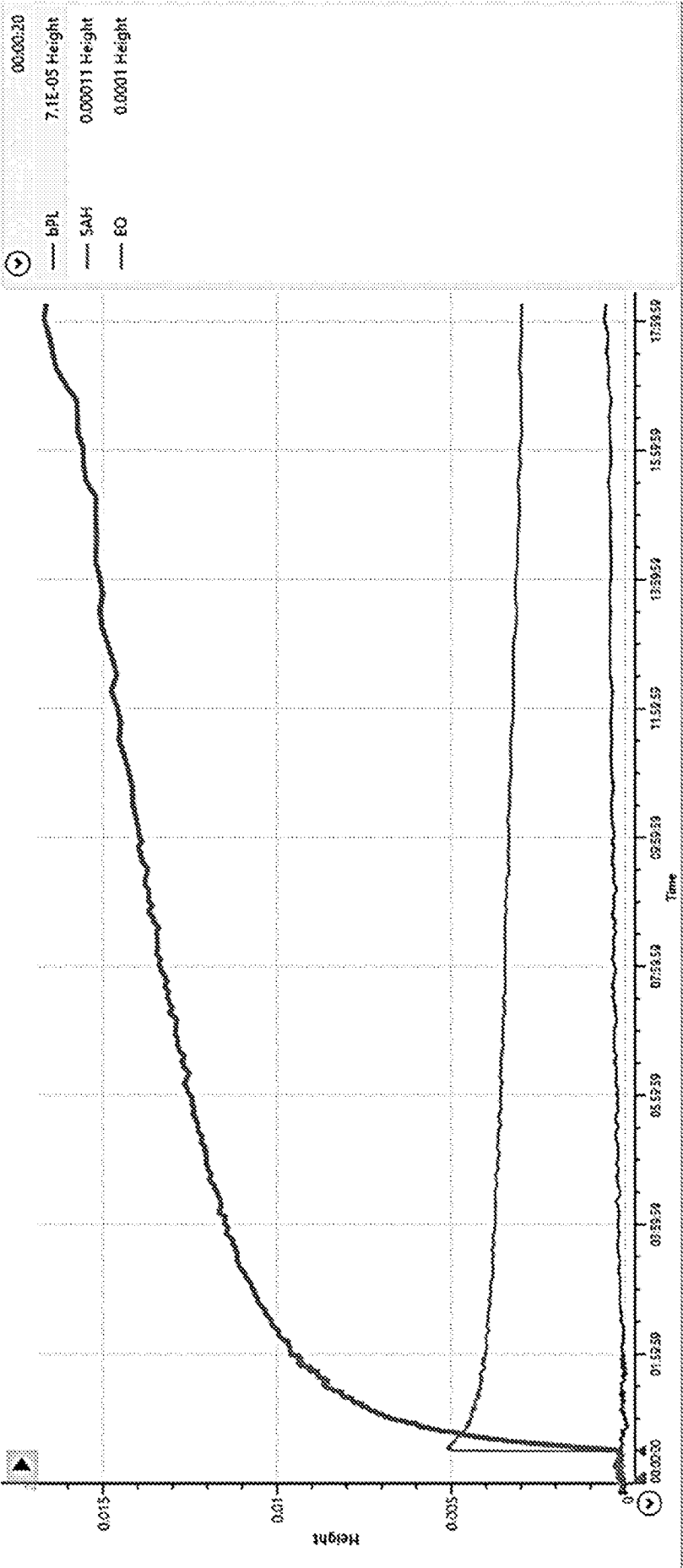


FIG. 5

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2022/022488

A. CLASSIFICATION OF SUBJECT MATTER INV. B01J31/00 B01J31/20 B01J31/22 ADD. 		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) B01J		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data, CHEM ABS Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 03/050154 A2 (CORNELL RES FOUNDATION INC [US]) 19 June 2003 (2003-06-19) cited in the application Family member of US6852865, referred to by the applicant Formulae V, VII, X; claims 3,17,45,70,76,79; tables 1-3 -----	1-25
X	WO 2010/022388 A2 (NOVOMER INC [US]; ALLEN SCOTT D [US] ET AL.) 25 February 2010 (2010-02-25) cited in the application Family member of US8633123, referred to by the applicant Tables and specific formulas; claims 81,83,87 ----- -/--	1-25
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 13 July 2022		Date of mailing of the international search report 22/07/2022
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Goss, Ilaria

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2022/022488

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 8 481 756 B1 (COATES GEOFFREY W [US] ET AL) 9 July 2013 (2013-07-09) cited in the application columns 12,13, lines 5-20 -----	1-25
X	CN 112 142 775 A (WANHUA CHEMICAL GROUP CO LTD) 29 December 2020 (2020-12-29) Claims Formula I according to claim 1 -----	1, 3
X	FENG MAOQI ET AL: "Synthesis and Reactivity of Nonbridged Metal-Metal Bonded Rhodium and Iridium Phenanthroline-Based N 2 O 2 Dimers", ORGANOMETALLICS, vol. 21, no. 13, 22 May 2002 (2002-05-22), pages 2743-2750, XP055941371, ISSN: 0276-7333, DOI: 10.1021/om010903g the whole document figure 1 -----	1, 3
X	MIYATA A ET AL: "Catalytic aerobic oxidation of diols under photo-irradiation: highly efficient synthesis of lactols", TETRAHEDRON LETTERS, ELSEVIER, AMSTERDAM , NL, vol. 43, no. 19, 6 May 2002 (2002-05-06), pages 3481-3484, XP004349420, ISSN: 0040-4039, DOI: 10.1016/S0040-4039(02)00605-6 Two compounds protected by TPS (tris(1-methylethyl)silyl) and having CAS Rn 470464-92-7 and 470464-91-6; compounds 5, 6 -----	1-25
X	NORMAND ADRIEN T. ET AL: "Phosphasalen group IV metal complexes: synthesis, characterization and ring opening polymerization of lactide", DALTON TRANSACTIONS, vol. 49, no. 21, 1 January 2020 (2020-01-01), pages 6989-7004, XP055941925, Cambridge ISSN: 1477-9226, DOI: 10.1039/D0DT00972E Scheme 2, scheme 3; table 1 the whole document -----	1-25

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2022/022488

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 03050154	A2	19-06-2003	AT 437854 T 15-08-2009
		AU 2002356929 A1 23-06-2003	
		DK 1461315 T3 16-11-2009	
		EP 1461315 A2 29-09-2004	
		ES 2330930 T3 17-12-2009	
		JP 5187929 B2 24-04-2013	
		JP 2005511753 A 28-04-2005	
		JP 2011074076 A 14-04-2011	
		US 2003162961 A1 28-08-2003	
		WO 03050154 A2 19-06-2003	
WO 2010022388	A2	25-02-2010	BR PI0917785 A2 01-03-2016
		CN 102164987 A 24-08-2011	
		CN 104888857 A 09-09-2015	
		CN 109734893 A 10-05-2019	
		CN 109734894 A 10-05-2019	
		EP 2321364 A2 18-05-2011	
		EP 2966108 A2 13-01-2016	
		ES 2552721 T3 01-12-2015	
		ES 2879498 T3 22-11-2021	
		HK 1219287 A1 31-03-2017	
		JP 5832288 B2 16-12-2015	
		JP 6031145 B2 24-11-2016	
		JP 2012500867 A 12-01-2012	
		JP 2015129306 A 16-07-2015	
		JP 2017031427 A 09-02-2017	
		JP 2019203133 A 28-11-2019	
		KR 20110079622 A 07-07-2011	
		KR 20180011873 A 02-02-2018	
		KR 20190026054 A 12-03-2019	
		PL 2321364 T3 29-01-2016	
		PL 2966108 T3 23-08-2021	
		SG 193220 A1 30-09-2013	
		SG 10201701421P A 27-04-2017	
		US 2011152497 A1 23-06-2011	
		US 2013144031 A1 06-06-2013	
		US 2013144032 A1 06-06-2013	
		US 2013144033 A1 06-06-2013	
		US 2015252145 A1 10-09-2015	
		US 2017183369 A1 29-06-2017	
		US 2018179242 A1 28-06-2018	
		WO 2010022388 A2 25-02-2010	
US 8481756	B1	09-07-2013	US 8481756 B1 09-07-2013
			US 8921581 B1 30-12-2014
			US 9376413 B1 28-06-2016
CN 112142775	A	29-12-2020	NONE