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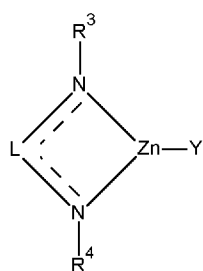
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(54) Title: HYDROGENATION CATALYST



(I)

(57) Abstract: Zinc complexes are described which find use in methods of selective hydrogenation of compounds which contain reducible double or triple bonds, such as the reduction of alkynes to alkenes. The zinc complexes have a general structure according to formula (I): (I) Methods of manufacturing such zinc complexes are also described.

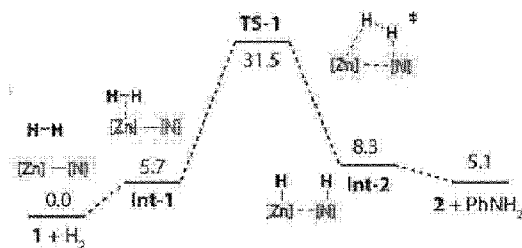


Fig. 1

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

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HYDROGENATION CATALYST

Field of the Invention

The present invention relates to zinc complexes and methods of manufacturing such complexes. The invention also relates to the use of such complexes in methods of selective hydrogenation of compounds containing reducible double or triple bonds and intermediates in such methods.

Background of the Invention

Alkynes are important starting materials in organic synthesis, particularly in the synthesis of bioactive compounds which contain carbon-carbon double bonds having a well-defined configuration. Non-limiting examples of such bioactive compounds include β -carotene, polyene antifungal drugs, crocaine, polyunsaturated fatty acids (PUFAs), pheromones and cruentaren. The stereoselective hydrogenation of alkynes to alkenes is an atom-economical method of synthesis of the carbon-carbon double bonds in these molecules.

The most widely used method for the selective hydrogenation of alkynes employs the Lindlar catalyst in heterogeneous catalysis. The Lindlar catalyst consists of Pd (5%) deposited on CaCO_3 , treated with lead acetate. The lead acetate poison is used to improve the *cis/trans* selectivity of the catalyst. Hydrogenation with the Lindlar catalyst is therefore highly stereoselective, producing almost exclusively the (*Z*)-isomer.

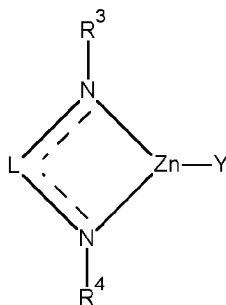
Despite the effectiveness of the Lindlar catalyst in such syntheses, there is a need for alternative stereoselective catalysts useful in the hydrogenation of alkynes to prepare carbon-carbon double bonds, due in part to the high relative cost of the Pd metal present in the catalyst and also to the toxicity of the Pb catalyst poison used in the Lindlar catalyst.

Such catalysts may find use in a wide range of applications in addition to the reduction of alkynes to alkenes. For example, such hydrogenation catalysts may also find use in the reduction of other functional groups containing reducible double or triple bonds, including but not limited to alkenes, nitriles, carbonyls (including aldehydes and ketones), esters and amides.

The present invention was developed with a view to providing alternative hydrogenation catalysts to address or ameliorate one or more of the problems mentioned above.

Summary of the Invention

A first aspect of the invention is a compound according to formula (I):



(I)

or a salt, solvate or hydrate thereof;

wherein:

Y is selected from $-QR^1R^2$, and OR^F ; wherein Q is selected from N, P and $P(=O)$;

L is selected from $-CR^8-CR^9-CR^{10}-$, $-CR^5-$, $-CR^6-CR^7-$, $-CR^{N3}-NR^G-CR^{N4}-$ and $-CR^{O1}-O-CR^{O2}-$;

either:

(A) R^1 is R^{1A} , R^2 is R^{2A} and R^4 is R^{4A} ; or

(B) R^4 is R^{4A} ; and R^1 and R^2 together with the Q moiety to which they are attached are joined to form a 3-6 membered heterocyclic group optionally substituted with one or more groups R^E ; or

(C) R^1 is R^{1A} ; and R^2 , R^4 and the atoms to which they are attached form a 5-8 membered heterocyclic group, optionally substituted with one or more groups R^D , and optionally being fused to one or more optionally substituted aryl groups;

R^3 is selected from

H;

linear or branched unsubstituted C_{1-12} aliphatic groups;

C_6 aryl, optionally substituted with one or more groups R^A , and

5-6 membered heteroaryl, optionally substituted with one or more groups R^B ;

R^5 , R^6 , R^7 , R^{N3} , R^{N4} , R^{O1} and R^{O2} are each independently selected from

H,

linear or branched unsubstituted C₁₋₁₂ aliphatic groups,
 C₅₋₆ unsubstituted aryl or heteroaryl groups, and
 -NR^{N1}R^{N2};

- 5 R⁸, R⁹ and R¹⁰ are each independently selected from
 H,
 linear or branched unsubstituted C₁₋₁₂ aliphatic groups,
 C₅₋₆ unsubstituted aryl or heteroaryl groups, and
 -NR^{N1}R^{N2};
- 10 or two or more of R⁸, R⁹ and R¹⁰, together with the atoms to which they are attached, are
 joined to form a monocyclic or bicyclic group, with any remaining groups of R⁸, R⁹ and R¹⁰
 being selected from H, linear or branched unsubstituted C₁₋₄ aliphatic groups, C₅₋₆
 unsubstituted aryl or heteroaryl groups, and -NR^{N1}R^{N2};
- 15 R^{1A}, R^{2A} and R^{4A} are each independently selected from
 H;
 linear or branched unsubstituted C₁₋₁₂ aliphatic groups;
 C₆ aryl, optionally substituted with one or more groups R^A;
 5-6 membered heteroaryl, optionally substituted with one or more groups R^B;
- 20 C₆₋₂₀ alkyl, optionally substituted with one or more groups R^C; and
 Si(C₁₋₆alkyl)₃;

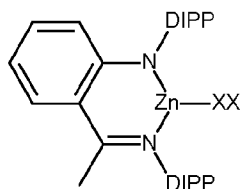
- R^{N1} and R^{N2} are each independently selected from linear or branched unsubstituted C₁₋₆
 aliphatic groups, or R^{N1} and R^{N2} together with the N atom to which they are attached are
 25 joined to form a 3-6 membered heterocyclic group optionally substituted with one or more
 groups R^E;

- R^A, R^B, R^C, R^D and R^E are each independently selected from
 linear or branched unsubstituted C₁₋₆ aliphatic groups;
 30 halo;
 O(C₁₋₆alkyl);
 -CF₃, -CF₂H, -CFH₂;
 -OCF₃, -OCF₂H and -OCFH₂;

- 35 R^F and R^G are independently selected from
 H;
 C₁₋₁₂ alkyl groups;

- C_6 aryl, optionally substituted with one or more groups R^A ;
 5-6 membered heteroaryl, optionally substituted with one or more groups R^B ;
 C_{6-20} aralkyl, optionally substituted with one or more groups R^C ;
 $-S(=O)_2CF_3$; and
 5 $-C(=O)R^H$, wherein R^H is linear or branched C_{1-6} alkyl optionally substituted with one or more groups independently selected from OH and halo;

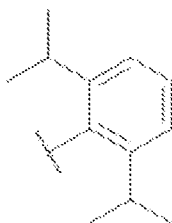
with the proviso that the compound is not a compound according to formula (X):



(X)

wherein the group XX is selected from $-N(SiMe_3)_2$ and $-NH(DIPP)$;

and wherein DIPP is the group:



It has been found that the zinc center facilitates the activation of dihydrogen through a 1,2-addition across the Zn-Y bond. The compounds therefore provide effective catalysts for the reduction of a wide range of compounds with functional groups containing reducible double or triple bonds. In particular, the compounds provide effective catalysts for the chemo- and stereo-selective semi-hydrogenation of alkynes to (Z)-alkenes. Herein, "semi-hydrogenation" refers to the hydrogenation of alkynes to alkenes, i.e. with little or no overhydrogenation to the alkane.

The compounds have been found to facilitate the production of alkenes from alkynes at relatively high yield, in a chemo- and stereo-selective manner. In particular, catalysts comprising the compounds provide for preferential synthesis of the alkene without over-reduction to the alkane, and also provide for stereoselective production of (Z)-alkenes.

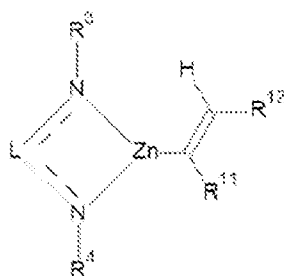
A second aspect of the invention is a catalyst comprising a compound according to the first aspect. In some embodiments, the catalyst is a hydrogenation catalyst. In some embodiments, the catalyst is an alkyne hydrogenation catalyst.

- 5 A third aspect of the invention is a method of reducing or hydrogenating a double or triple bond in the presence of a catalyst comprising a compound according to the first aspect.

A fourth aspect is a method of activating dihydrogen for hydrogenation, comprising reacting dihydrogen with a catalyst comprising a compound according to the first aspect.

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A fifth aspect is a compound according to formula (VII):



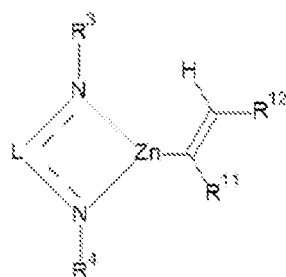
(VII)

wherein

- 15 L, R³ and R⁴ are as defined above under the first aspect;
and R¹¹ and R¹² are each independently selected from (hetero)hydrocarbyl groups.

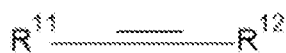
In some embodiments R¹¹ and R¹² are each independently selected from alkyl and aryl groups. In some embodiments, R¹¹ and R¹² are each independently selected from linear or
20 branched unsubstituted C₁₋₆ alkyl, and C₃₋₈ aromatic or heteroaromatic groups. However, the skilled person will understand that the hydrogenation may be carried out on any alkyne regardless of the identity of the groups R¹¹ and R¹², such that R¹¹ and R¹² may be selected from any suitable alkyne substituent.

- 25 A sixth aspect of the invention is a method of preparing an intermediate according to formula (VII):



(VII)

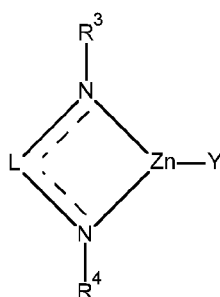
the method comprising reacting an alkyne according to formula (V):



(V)

5

with dihydrogen (H_2) in the presence of a catalyst comprising a compound according to formula (I):



(I)

10

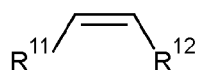
or a salt, solvate or hydrate thereof;

wherein L, Y, R^3 and R^4 , are as defined above under the first aspect;

and R^{11} and R^{12} are as defined under the fifth aspect.

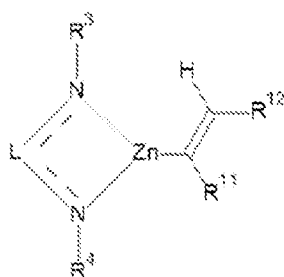
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A seventh aspect of the invention is therefore a method of preparing an alkene according to formula (VI):



(VI)

the method comprising protonating a compound according to formula (VII):

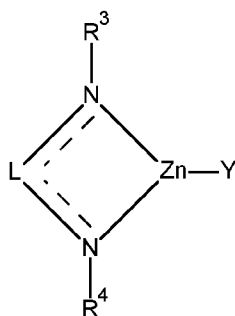


(VII)

wherein L, R³ and R⁴ are as defined above under the first aspect;
and R¹¹ and R¹² are as defined under the fifth aspect.

5

An eighth aspect of the invention is a method of making a compound according to formula (I):



(I)

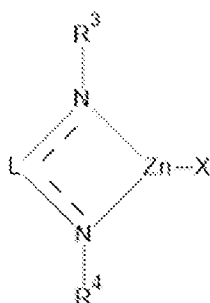
10 from starting materials comprising a compound according to formula (II):



(II)

wherein Y, L, R³ and R⁴ are as defined above under the first aspect.

15 A ninth aspect of the invention is an intermediate according to formula (IV):

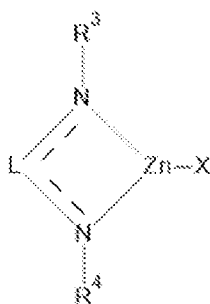


(IV)

wherein L, R³ and R⁴ are as defined above under the first aspect and X is a monovalent anion.

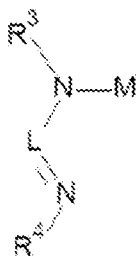
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A tenth aspect of the invention is a method of making an intermediate according to formula (IV):



(IV)

10 comprising reacting a compound according to formula (III) with ZnX₂



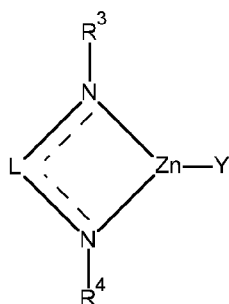
(III)

wherein L, R³ and R⁴ are as defined above under the first aspect, M is a metal atom selected from Li, Na and K, and X is as defined under the ninth aspect.

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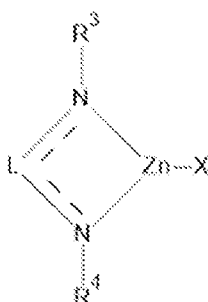
The skilled person will understand that the structure according to formula (III) is one possible representation of such compounds, but that in some cases the compound may adopt a configuration in which the M atom is bound to both N atoms to form a cyclic system.

- 5 An eleventh aspect of the invention is a method of making a compound according to formula (I):



(I)

from a compound according to formula (IV):

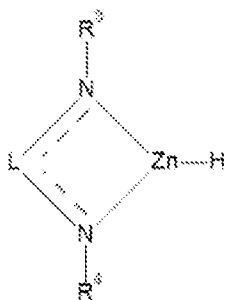


(IV)

wherein Y, L, R³ and R⁴ are as defined in the first aspect, and X is a monovalent anion.

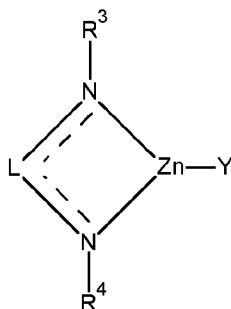
A twelfth aspect of the invention is a method of making a compound according to formula

- 15 (VIII):



(VIII)

comprising reacting a compound according to formula (I):



(I)

- 5 with dihydrogen (H₂), wherein L, Y, R³ and R⁴ are as defined under the first aspect.

The method according to the twelfth aspect may be used to prepare the hydride analogue (VIII) of the catalytic complex according to formula (I) *in situ*. The hydride analogue (VIII) may then go on to react with a compound containing a reducible double or triple bond which is present in the reaction mixture, e.g. an alkyne, in a first step towards semi-hydrogenation of the alkyne.

A thirteenth aspect of the invention is the use of a compound according to the first aspect or catalyst according to the second aspect in a hydrogenation process, for example an alkyne hydrogenation process. Another aspect is the use of a compound according to the first aspect as a catalyst a hydrogenation process, for example an alkyne hydrogenation process.

Definitions

Unless otherwise specified, the term “substituted” as used herein, pertains to a parent group which bears one or more substituents. The term “substituent” is used herein in the conventional sense and refers to a chemical moiety which is covalently attached to, or if appropriate, fused to, a parent group. A wide variety of substituents are well known, and methods for their formation and introduction into a variety of parent groups are also well known.

25

The term “C₄₋₂₀ aliphatic” as used herein, pertains to a monovalent moiety obtained by removing a hydrogen atom from a carbon atom of a hydrocarbon compound having from 4 to 20 carbon atoms, which may be saturated or unsaturated (e.g. partially unsaturated, fully unsaturated). The term “C₁₋₄ aliphatic” as used herein, pertains to a monovalent moiety obtained by removing a hydrogen atom from a carbon atom of a hydrocarbon compound

30

having from 1 to 4 carbon atoms, which may be saturated or unsaturated (e.g. partially unsaturated, fully unsaturated). Thus, the term “aliphatic” includes the sub-classes alkyl, alkenyl, alkynyl, cycloalkyl, etc.

- 5 The term “C₁₋₁₂ alkyl” as used herein, pertains to a monovalent moiety obtained by removing a hydrogen atom from a carbon atom of an aliphatic, acyclic hydrocarbon compound having from 1 to 12 carbon atoms, which is saturated. The term “C₁₋₄ alkyl” as used herein, pertains to a monovalent moiety obtained by removing a hydrogen atom from a carbon atom of an aliphatic, acyclic hydrocarbon compound having from 1 to 4 carbon atoms, which is
- 10 saturated.

Examples of saturated alkyl groups include, but are not limited to, methyl (C₁), ethyl (C₂), propyl (C₃), butyl (C₄), pentyl (C₅), hexyl (C₆), heptyl (C₇) and octyl (C₈).

- 15 Examples of saturated linear alkyl groups include, but are not limited to, methyl (C₁), ethyl (C₂), n-propyl (C₃), n-butyl (C₄), n-pentyl (amyl) (C₅), n-hexyl (C₆), n-heptyl (C₇) and n-octyl (C₈).

- Examples of saturated branched alkyl groups include iso-propyl (C₃), iso-butyl (C₄), sec-butyl
- 20 (C₄), tert-butyl (C₄), iso-pentyl (C₅), and neo-pentyl (C₅).

- Aryl: The term “C₆ aryl” or “6-membered aryl”, as used herein, pertains to a monovalent moiety obtained by removing a hydrogen atom from an aromatic ring atom of an aromatic compound, which moiety has 6 ring carbon atoms. The term “aryl” as used herein refers to
- 25 carboaryl moieties, i.e. does not include heteroaryl moieties.

Examples of aryl groups include, but are not limited to, phenyl, naphthyl, tolyl and xylyl.

- Heteroaryl: The term “6-membered heteroaryl”, as used herein, pertains to a monovalent
- 30 moiety obtained by removing a hydrogen atom from an aromatic ring atom of an aromatic compound, which moiety has 6 ring atoms, one or more of those ring atoms being a heteroatom.

- Heterocyclyl: The term “6-membered heterocyclyl” or “6-membered heterocyclic group”, as
- 35 used herein, pertains to a monovalent moiety obtained by removing a hydrogen atom from a ring atom of a heterocyclic compound, which moiety has 6 ring atoms, one or more of those ring atoms being a heteroatom.

(Hetero)hydrocarbyl: The term “(hetero)hydrocarbyl”, as used herein, includes hydrocarbyl and heterohydrocarbyl groups. The term “hydrocarbyl”, as used herein, pertains to a monovalent moiety obtained by removing a hydrogen atom from a hydrocarbon compound.

5 Thus, the term “hydrocarbyl” includes the sub-classes aliphatic, aromatic, alkyl, alkenyl, alkynyl, cycloalkyl, etc. The term “heterohydrocarbyl”, as used herein, pertains to a monovalent moiety obtained by removing a hydrogen atom from a hydrocarbon compound which also contains heteroatoms, e.g. a heteroaromatic compound, heterocyclic compound or a heteroaliphatic compound.

10

Aralkyl: The term “C₆₋₂₀ aralkyl”, as used herein, pertains to a monovalent moiety obtained by removing a hydrogen atom from a pendent alkyl group of an alkyl-substituted aromatic ring, wherein the total number of carbon atoms in the monovalent moiety is between 6 and 20. In other words, an aralkyl group is an aryl-substituted alkyl radical. Non-limiting examples of

15

Description of the drawings

Figure 1 shows a DFT-calculated Gibbs Free Energy profile for H₂ activation by a compound according to the invention, at standard conditions using the M06L functional and hybrid

20

Figure 2 shows initial and final ¹H NMR spectra for the protonolysis reaction of (DippBDI)ZnC(Ph)CHPh using aniline.

25 **Figure 3** shows initial and final ¹H NMR spectra for *cis*-stilbene hydrozincation reaction using (DippBDI)ZnH.

Figure 4 shows initial and final ¹H NMR spectra for *trans*-stilbene hydrozincation reaction using (DippBDI)ZnH.

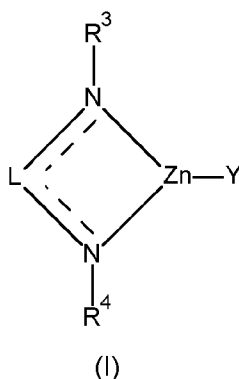
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Figure 5 shows the crystal structure of (DippBDI)ZnC(Ph)CHPh as determined by X-ray crystallography, with 50% probability ellipsoids.

Detailed Description

Preferred and/or optional features of the invention will now be set out. Any aspect of the invention may be combined with any other aspect of the invention unless the context demands otherwise. Any of the preferred and/or optional features of any aspect may be combined, either singly or in combination, with any aspect of the invention unless the context demands otherwise.

A first aspect of the invention is a compound according to formula (I):



or a salt, solvate or hydrate thereof;
wherein:

Y is selected from $-QR^1R^2$ and OR^F ; wherein Q is selected from N, P and $P(=O)$;

L is selected from $-CR^8-CR^9-CR^{10}-$, $-CR^5-$, $-CR^6-CR^7-$, $-CR^{N3}-NR^G-CR^{N4}-$ and $-CR^{O1}-O-CR^{O2}-$;

either:

(A) R^1 is R^{1A} , R^2 is R^{2A} and R^4 is R^{4A} ; or

(B) R^4 is R^{4A} ; and R^1 and R^2 together with the Q moiety to which they are attached are joined to form a 3-6 membered heterocyclic group optionally substituted with one or more groups R^E ; or

(C) R^1 is R^{1A} ; and R^2 , R^4 and the atoms to which they are attached form a 5-8 membered heterocyclic group, optionally substituted with one or more groups R^D , and optionally being fused to one or more optionally substituted aryl groups;

R^3 is selected from

H;

linear or branched unsubstituted C_{1-12} aliphatic groups;

C₆ aryl, optionally substituted with one or more groups R^A, and
5-6 membered heteroaryl, optionally substituted with one or more groups R^B;

R⁵, R⁶, R⁷, R^{N3}, R^{N4}, R^{O1} and R^{O2} are each independently selected from

- 5 H,
linear or branched unsubstituted C₁₋₁₂ aliphatic groups,
C₅₋₆ unsubstituted aryl or heteroaryl groups, and
-NR^{N1}R^{N2};

- 10 R⁸, R⁹ and R¹⁰ are each independently selected from

H,
linear or branched unsubstituted C₁₋₁₂ aliphatic groups,
C₅₋₆ unsubstituted aryl or heteroaryl groups, and
-NR^{N1}R^{N2};

- 15 or two or more of R⁸, R⁹ and R¹⁰, together with the atoms to which they are attached, are
joined to form a monocyclic or bicyclic group, with any remaining groups of R⁸, R⁹ and R¹⁰
being selected from H, linear or branched unsubstituted C₁₋₄ aliphatic groups, C₅₋₆
unsubstituted aryl or heteroaryl groups, and -NR^{N1}R^{N2};

- 20 R^{1A}, R^{2A} and R^{4A} are each independently selected from

H;
linear or branched unsubstituted C₁₋₁₂ aliphatic groups;
C₆ aryl, optionally substituted with one or more groups R^A;
5-6 membered heteroaryl, optionally substituted with one or more groups R^B;

- 25 C₆₋₂₀ alkyl, optionally substituted with one or more groups R^C; and
Si(C₁₋₆alkyl)₃;

R^{N1} and R^{N2} are each independently selected from linear or branched unsubstituted C₁₋₆
aliphatic groups, or R^{N1} and R^{N2} together with the N atom to which they are attached are

- 30 joined to form a 3-6 membered heterocyclic group optionally substituted with one or more
groups R^E;

R^A, R^B, R^C, R^D and R^E are each independently selected from

linear or branched unsubstituted C₁₋₆ aliphatic groups;

- 35 halo;
O(C₁₋₆alkyl);
-CF₃, -CF₂H, -CFH₂;

-OCF₃, -OCF₂H and -OCFH₂;

R^F and R^G are independently selected from

H;

5 C₁₋₁₂ alkyl groups;

C₆ aryl, optionally substituted with one or more groups R^A;

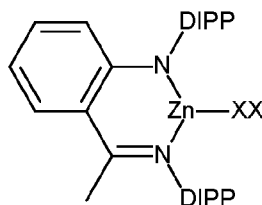
5-6 membered heteroaryl, optionally substituted with one or more groups R^B;

C₆₋₂₀ aralkyl, optionally substituted with one or more groups R^C;

-S(=O)₂CF₃; and

10 -C(=O)R^H, wherein R^H is linear or branched C₁₋₆ alkyl optionally substituted with one or more groups independently selected from OH and halo;

with the proviso that the compound is not a compound according to formula (X):

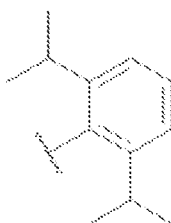


15

(X)

wherein the group XX is selected from -N(SiMe₃)₂ and -NH(DIPP);

and wherein DIPP is the group:



20

The group Y

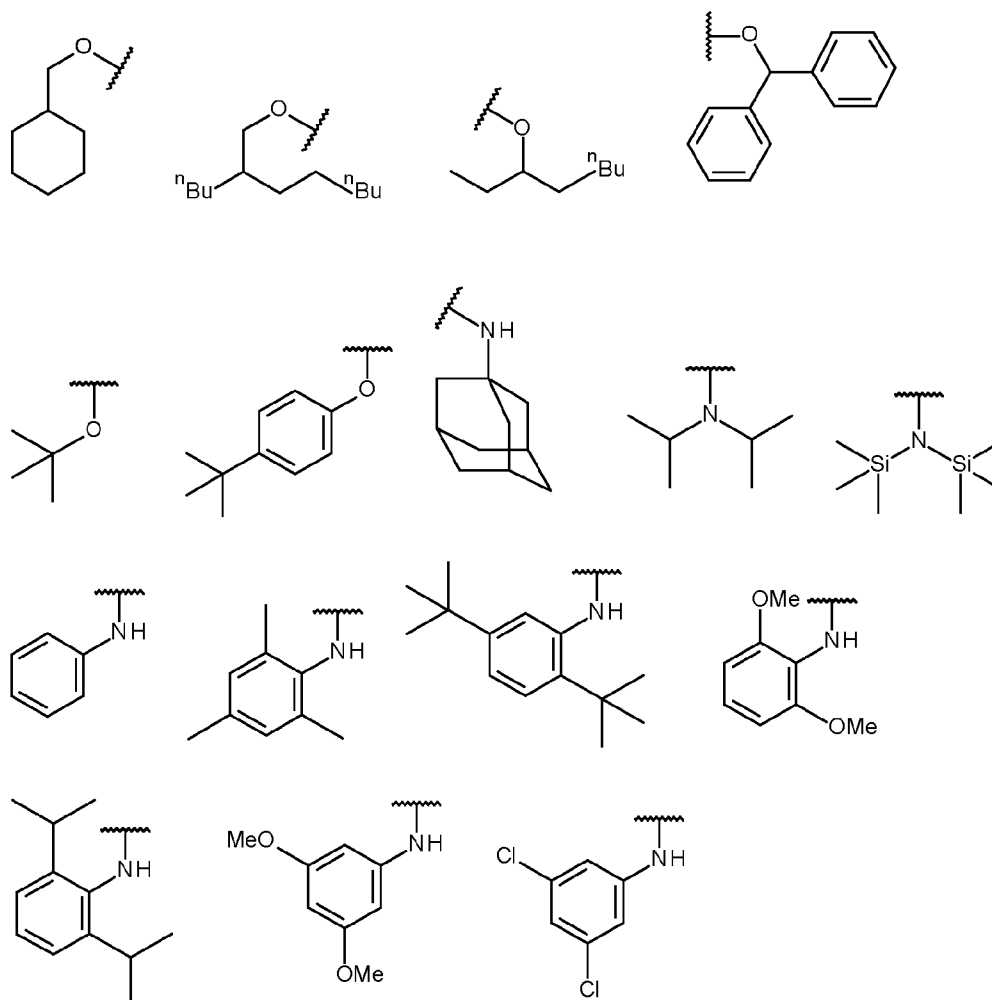
Y is selected from -QR¹R² and OR^F.

25 In some embodiments, Y is -QR¹R².

In some embodiments, R^F is selected from linear unsubstituted C_{1-4} alkyl groups. In some embodiments, R^F is methyl.

In some embodiments, Y is selected from one of the following groups:

5



10

The group Q

In preferred embodiments, Y is $-QR^1R^2$.

15 The group Q is selected from N, P and $P(=O)$.

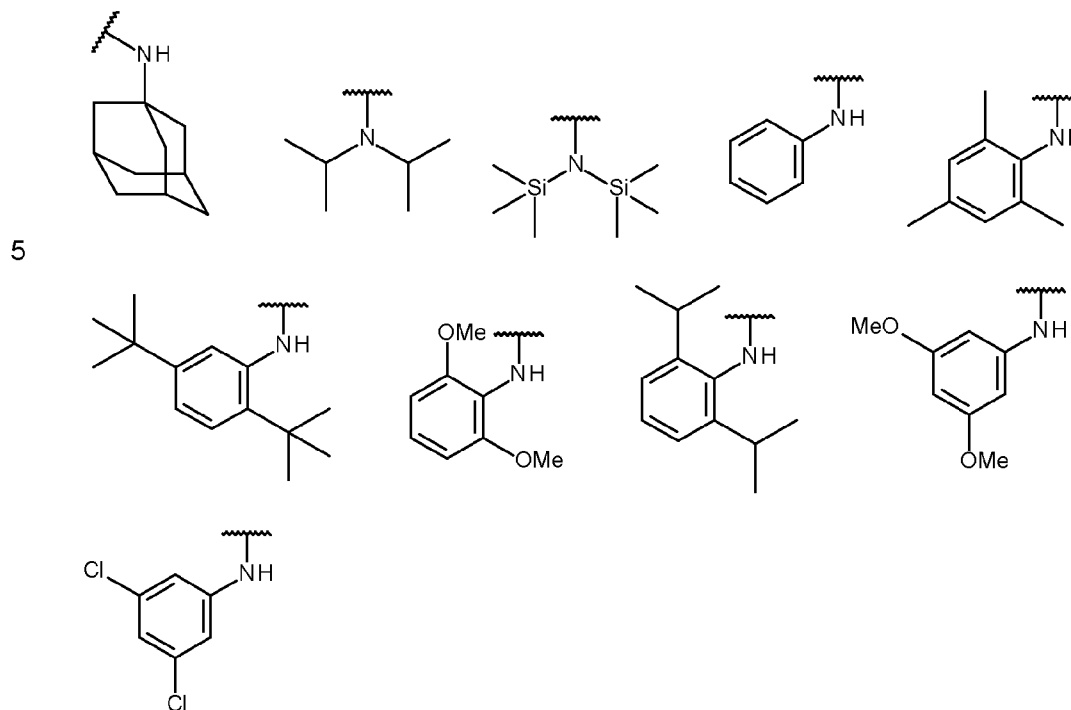
In some embodiments, Q is N. Thus in some embodiments, the group $-QR^1R^2$ is $-NR^1R^2$.

In some embodiments, Q is P. Thus in some embodiments, the group $-QR^1R^2$ is $-PR^1R^2$.

20

In some embodiments, Q is P(=O). Thus in some embodiments, the group $-QR^1R^2$ is $-P(=O)R^1R^2$.

In some embodiments, the group $-QR^1R^2$ is selected from one of the following groups:

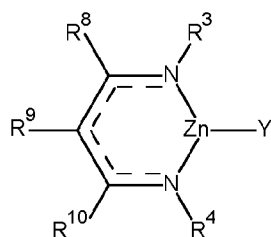


The group L

L is selected from $-CR^8-CR^9-CR^{10}-$, $-CR^5-$, $-CR^6-CR^7-$, $-CR^{N3}-NR^G-CR^{N4}-$ and $-CR^{O1}-O-CR^{O2}-$. In some embodiments, L is selected from $-CR^8-CR^9-CR^{10}-$, $-CR^5-$ and $-CR^6-CR^7-$.

10

In some embodiments, L is $-CR^8-CR^9-CR^{10}-$. Thus in some embodiments, the compound is a compound according to formula (IA):



(IA)

or a salt, solvate or hydrate thereof.

In some embodiments of formula (IA), Y is QR^1R^2 .

In some embodiments, L is $-\text{CR}^8-\text{CR}^9-\text{CR}^{10}-$, Y is QR^1R^2 and Q is N. In some embodiments, L is $-\text{CR}^8-\text{CR}^9-\text{CR}^{10}-$, Y is QR^1R^2 , Q is N, R^1 is R^{1A} and R^2 is R^{2A} .

5 In some embodiments, L is $-\text{CR}^5-$.

In some embodiments, L is $-\text{CR}^6-\text{CR}^7-$.

10 In some embodiments, L is $-\text{CR}^{\text{N}3}-\text{NR}^{\text{G}}-\text{CR}^{\text{N}4}-$. In some embodiments, L is $-\text{CR}^{\text{N}3}-\text{NR}^{\text{G}}-\text{CR}^{\text{N}4}-$ wherein R^{G} is methyl.

In some embodiments, L is $-\text{CR}^{\text{O}1}-\text{O}-\text{CR}^{\text{O}2}-$.

The groups R^1 , R^2 and R^4 ; and R^{1A} , R^{2A} and R^{4A}

15 In some embodiments, R^1 is R^{1A} , and R^{1A} is selected from

H;

linear or branched unsubstituted C_{1-12} aliphatic groups;

C_6 aryl, optionally substituted with one or more groups R^A ;

5-6 membered heteroaryl, optionally substituted with one or more groups R^B ;

20 C_{6-20} aralkyl, optionally substituted with one or more groups R^C ; and

$\text{Si}(\text{C}_{1-6}\text{alkyl})_3$.

In some embodiments, R^{1A} is H. Hence in some embodiments, the group Y is QHR^2 .

25 In some embodiments, R^{1A} is selected from linear or branched unsubstituted C_{1-12} aliphatic groups. In some embodiments, R^{1A} is selected from linear or branched unsubstituted C_{1-4} aliphatic groups. In some embodiments, R^{1A} is selected from methyl and ethyl.

In some embodiments, R^2 is R^{2A} , and R^{2A} is selected from

30 H;

linear or branched unsubstituted C_{1-12} aliphatic groups;

C_6 aryl, optionally substituted with one or more groups R^A ;

5-6 membered heteroaryl, optionally substituted with one or more groups R^B ;

C_{6-20} aralkyl, optionally substituted with one or more groups R^C ; and

35 $\text{Si}(\text{C}_{1-6}\text{alkyl})_3$.

In some embodiments, R^{2A} is selected from C_6 aryl, optionally substituted with one or more groups R^A ; and 5-6 membered heteroaryl, optionally substituted with one or more groups R^B .

In some embodiments, R^{2A} is phenyl optionally substituted with one or more groups R^A . In some embodiments, R^{2A} is phenyl optionally substituted with one or two groups R^A . In some embodiments, R^{2A} is phenyl substituted with one or more groups R^A . In some embodiments, R^{2A} is phenyl substituted with one or two groups R^A .

In some embodiments, R^{2A} is unsubstituted phenyl.

In some embodiments, R^{2A} is $Si(C_{1-6}alkyl)_3$. In some embodiments, R^{2A} is $Si(C_{1-4}alkyl)_3$. In some embodiments, R^{2A} is $Si(Me)_3$.

In some embodiments, R^{1A} is H and R^{2A} is selected from

H;
linear or branched unsubstituted C_{1-12} aliphatic groups;
 C_6 aryl, optionally substituted with one or more groups R^A ;
5-6 membered heteroaryl, optionally substituted with one or more groups R^B ;
 C_{6-20} aralkyl, optionally substituted with one or more groups R^C ; and
 $Si(C_{1-6}alkyl)_3$.

In some embodiments, R^{1A} is H and R^{2A} is selected from

linear or branched unsubstituted C_{1-12} aliphatic groups;
 C_6 aryl, optionally substituted with one or more groups R^A ;
5-6 membered heteroaryl, optionally substituted with one or more groups R^B ;
 C_{6-20} aralkyl, optionally substituted with one or more groups R^C ; and
 $Si(C_{1-6}alkyl)_3$.

In some embodiments, R^{1A} is H and R^{2A} is selected from C_6 aryl, optionally substituted with one or more groups R^A ; and 5-6 membered heteroaryl, optionally substituted with one or more groups R^B .

In some embodiments, R^{1A} is H and R^{2A} is phenyl optionally substituted with one or more groups R^A . In some embodiments, R^{1A} is H and R^{2A} is phenyl optionally substituted with one or two groups R^A . In some embodiments, R^{1A} is H and R^{2A} is phenyl substituted with one or more groups R^A . In some embodiments, R^{1A} is H and R^{2A} is phenyl substituted with one or two groups R^A .

In some embodiments, R^{1A} is H and R^{2A} is unsubstituted phenyl. Hence in some embodiments, the group Y is QH(Ph).

5 In some embodiments, when Y is QR^1R^2 , R^1 and R^2 together with the Q moiety to which they are attached are joined to form a 3-6 membered heterocyclic group optionally substituted with one or more groups R^E . In some embodiments, R^1 and R^2 together with the Q moiety to which they are attached are joined to form a 3-6 membered unsubstituted heterocyclic group. In some embodiments, R^1 and R^2 together with the Q moiety to which they are
 10 attached are joined to form a 5-6 membered heterocyclic group optionally substituted with one or more groups R^E . In some embodiments, R^1 and R^2 together with the Q moiety to which they are attached are joined to form a 5-6 membered unsubstituted heterocyclic group.

15 In some embodiments, R^1 and R^2 together with the Q moiety to which they are attached are joined to form a 3-6 membered heterocyclic group optionally substituted with one or more groups R^E . In some embodiments, R^1 and R^2 together with the Q moiety to which they are attached are joined to form a 3-6 membered heteroaromatic group optionally substituted with one or more groups R^E .

20

In some embodiments, Q is N, and R^1 and R^2 together with the N to which they are attached are joined to form a heterocyclic group selected from:

aziridinyl, diaziridinyl, azetidiny, diazetidinyl, pyrrolidinyl, pyrrolyl, oxazolidinyl, imidazolidinyl, pyrazolidinyl, imidazolyl, pyrazolyl, triazolyl, piperidinyl, diazinanyl, morpholinyl, thiomorpholinyl, thiazinyl and triazinanyl;
 25 optionally substituted with one or more groups R^E .

In some embodiments, Q is N, and R^1 and R^2 together with the N to which they are attached are joined to form an unsubstituted heterocyclic group selected from:

30 aziridinyl, diaziridinyl, azetidiny, diazetidinyl, pyrrolidinyl, pyrrolyl, oxazolidinyl, imidazolidinyl, pyrazolidinyl, imidazolyl, pyrazolyl, triazolyl, piperidinyl, diazinanyl, morpholinyl, thiomorpholinyl, thiazinyl and triazinanyl.

In some embodiments, R^4 is R^{4A} , and R^{4A} is selected from

35

H;

linear or branched unsubstituted C_{1-4} aliphatic groups;

C_{5-6} aryl, optionally substituted with one or more groups R^A ; and

C₅₋₆ heteroaryl, optionally substituted with one or more groups R^B.

In some embodiments, R⁴ is R^{4A}, and R^{4A} is selected from

linear or branched unsubstituted C₁₋₄ aliphatic groups;

5 C₅₋₆ aryl, optionally substituted with one or more groups R^A; and

C₅₋₆ heteroaryl, optionally substituted with one or more groups R^B.

In some embodiments, R^{4A} is independently selected from phenyl optionally substituted with one or more groups R^A. In some embodiments, R^{4A} is independently selected from phenyl

10 substituted with one or more groups R^A. In some embodiments, R^{4A} is independently selected from phenyl substituted with one or two groups R^A. In some embodiments, R^{4A} is independently selected from phenyl substituted with two groups R^A.

In some embodiments, R^{4A} is independently selected from phenyl substituted in both *ortho*-

15 positions with a group R^A. In some embodiments, R^{4A} is independently selected from phenyl substituted in both *ortho*-positions with a group R^A and unsubstituted in the *meta* and *para* positions.

In some embodiments, R^{4A} is independently selected from methyl, ethyl and mesityl.

20

In some embodiments, R¹ and R² are each independently selected from

H;

linear or branched unsubstituted C₁₋₁₂ aliphatic groups;

C₆ aryl, optionally substituted with one or more groups R^A;

25 5-6 membered heteroaryl, optionally substituted with one or more groups R^B;

C₆₋₂₀ aralkyl, optionally substituted with one or more groups R^C; and

Si(C₁₋₆alkyl)₃;

or R¹ and R² together with the Q moiety to which they are attached are joined to form a 3-6 membered heterocyclic group optionally substituted with one or more groups R^E;

30 and R⁴ is independently selected from

linear or branched unsubstituted C₁₋₄ aliphatic groups;

C₆ aryl, optionally substituted with one or more groups R^A; and

5-6 membered heteroaryl, optionally substituted with one or more groups R^B.

35 In some embodiments, R¹ and R² are each independently selected from

H;

linear or branched unsubstituted C₁₋₁₂ aliphatic groups;

C₆ aryl, optionally substituted with one or more groups R^A;
5-6 membered heteroaryl, optionally substituted with one or more groups R^B;
C₆₋₂₀ aralkyl, optionally substituted with one or more groups R^C; and
Si(C₁₋₆alkyl)₃;

5 and R⁴ is independently selected from

linear or branched unsubstituted C₁₋₄ aliphatic groups;
C₆ aryl, optionally substituted with one or more groups R^A; and
5-6 membered heteroaryl, optionally substituted with one or more groups R^B.

10 In some embodiments, R¹ is H and R² is selected from

H;
linear or branched unsubstituted C₁₋₁₂ aliphatic groups;
C₆ aryl, optionally substituted with one or more groups R^A;
5-6 membered heteroaryl, optionally substituted with one or more groups R^B;
15 C₆₋₂₀ aralkyl, optionally substituted with one or more groups R^C; and
Si(C₁₋₆alkyl)₃;

and R⁴ is independently selected from

linear or branched unsubstituted C₁₋₄ aliphatic groups;
C₆ aryl, optionally substituted with one or more groups R^A; and
20 5-6 membered heteroaryl, optionally substituted with one or more groups R^B.

In some embodiments, R¹ and R² together with the Q moiety to which they are attached are joined to form a 3-6 membered heterocyclic group optionally substituted with one or more groups R^E;

25 and R⁴ is independently selected from

linear or branched unsubstituted C₁₋₄ aliphatic groups;
C₆ aryl, optionally substituted with one or more groups R^A; and
5-6 membered heteroaryl, optionally substituted with one or more groups R^B.

30 In some embodiments, R¹ is selected from

H;
linear or branched unsubstituted C₁₋₁₂ aliphatic groups;
C₆ aryl, optionally substituted with one or more groups R^A;
5-6 membered heteroaryl, optionally substituted with one or more groups R^B;
35 C₆₋₂₀ aralkyl, optionally substituted with one or more groups R^C; and
Si(C₁₋₆alkyl)₃;

and R^2 , R^4 and the atoms to which they are attached form a 5-8 membered heterocyclic group, optionally substituted with one or more groups R^D , and optionally being fused to one or more optionally substituted aryl groups.

- 5 In some embodiments, R^1 is H;
and R^2 , R^4 and the atoms to which they are attached form a 5-8 membered heterocyclic group, optionally substituted with one or more groups R^D , and optionally being fused to one or more optionally substituted aryl groups.
- 10 When R^2 , R^4 and the atoms to which they are attached form a 5-8 membered heterocyclic group, said 5-8 membered heterocyclic group is optionally fused to one or more optionally substituted aryl groups. The one or more aryl groups may be unsubstituted. In some embodiments said 5-8 membered heterocyclic group is fused to two optionally substituted aryl groups. The term "fused" here means that the 5-8 membered heterocyclic group shares
- 15 two atoms with an adjacent ring structure, such that the 5-8 membered heterocyclic group and that adjacent ring form a bicyclic system (or a tricyclic system where two fused aryl groups are present).

The group R^3

- 20 R^3 is selected from
- H;
 - linear or branched unsubstituted C_{1-12} aliphatic groups;
 - C_6 aryl, optionally substituted with one or more groups R^A , and
 - 5-6 membered heteroaryl, optionally substituted with one or more groups R^B .

25

In some embodiments, R^3 is selected from

- H;
- linear or branched unsubstituted C_{1-4} aliphatic groups;
- C_6 aryl, optionally substituted with one or more groups R^A , and
- 30 5-6 membered heteroaryl, optionally substituted with one or more groups R^B .

In some embodiments, R^3 is selected from

- linear or branched unsubstituted C_{1-4} aliphatic groups;
- C_6 aryl, optionally substituted with one or more groups R^A , and
- 35 5-6 membered heteroaryl, optionally substituted with one or more groups R^B .

In some embodiments, R^3 is selected from

C₆ aryl, optionally substituted with one or more groups R^A, and
5-6 membered heteroaryl, optionally substituted with one or more groups R^B.

In some embodiments, R³ is phenyl, optionally substituted with one or more groups R^A.

5

In some embodiments, R³ is independently selected from phenyl optionally substituted with one or more groups R^A. In some embodiments, R³ is independently selected from phenyl substituted with one or more groups R^A. In some embodiments, R³ is independently selected from phenyl substituted with one or two groups R^A. In some embodiments, R³ is
10 independently selected from phenyl substituted with two groups R^A.

In some embodiments, R³ is independently selected from phenyl substituted in both *ortho*-positions with a group R^A. In some embodiments, R³ is independently selected from phenyl substituted in both *ortho*-positions with a group R^A and unsubstituted in the *meta* and *para*
15 positions.

In some embodiments, R³ is independently selected from methyl, ethyl and mesityl.

In some embodiments, R³ and R⁴ are the same, each being selected from any of the groups
20 set out above.

In some embodiments, R³ and R⁴ are each independently selected from phenyl optionally substituted with one or more groups R^A. In some embodiments, R³ and R⁴ are each independently selected from phenyl substituted in both *ortho*-positions with a group R^A. In
25 some embodiments, R³ and R⁴ are each independently selected from methyl, ethyl and mesityl.

The group R⁵

In some embodiments, L is -CR⁵-, wherein R⁵ is selected from

30

H,
linear or branched unsubstituted C₁₋₁₂ aliphatic groups,
C₅₋₆ unsubstituted aryl or heteroaryl groups, and
-NR^{N1}R^{N2}.

35 In some embodiments, R⁵ is selected from

H,
linear or branched unsubstituted C₁₋₄ aliphatic groups,

C₅₋₆ unsubstituted aryl or heteroaryl groups, and
-NR^{N1}R^{N2}.

In some embodiments, R⁵ is H.

5

In some embodiments, R⁵ is selected from linear or branched unsubstituted C₁₋₄ aliphatic groups. In some embodiments, R⁵ is methyl or ethyl. In some embodiments, R⁵ is methyl.

The groups R⁶ and R⁷

10 R⁶ and R⁷ are each independently selected from

H,
linear or branched unsubstituted C₁₋₁₂ aliphatic groups,
C₅₋₆ unsubstituted aryl or heteroaryl groups, and
-NR^{N1}R^{N2}.

15

In some embodiments, R⁶ and R⁷ are each independently selected from

H,
linear or branched unsubstituted C₁₋₄ aliphatic groups,
C₅₋₆ unsubstituted aryl or heteroaryl groups, and
20 -NR^{N1}R^{N2}.

20

When L is -CR⁶-CR⁷-, the ring system containing Zn and L is 5-membered. The skilled person will appreciate that complexes according to formula (I) containing such a 5-membered ring system may carry a charge or a radical. In embodiments where the compound according to formula (I) carries an overall charge, a counterion may be present to balance that charge. For example, where the compound carries an overall single negative charge and exists as an anion, a counter ion [M'']⁺ may be present to balance that charge. [M'']⁺ may be any suitable cation, for example a metal ion, such as an alkali metal ion.

25

30 *The groups R^{N3}, R^{N4}, R^{O1} and R^{O2}*

R^{N3}, R^{N4}, R^{O1} and R^{O2} are each independently selected from

H,
linear or branched unsubstituted C₁₋₁₂ aliphatic groups,
C₅₋₆ unsubstituted aryl or heteroaryl groups, and
35 -NR^{N1}R^{N2}.

35

In some embodiments, R^{N3}, R^{N4}, R^{O1} and R^{O2} are each independently selected from

H,
linear or branched unsubstituted C₁₋₄ aliphatic groups,
C₅₋₆ unsubstituted aryl or heteroaryl groups, and
-NR^{N1}R^{N2}.

5

In some embodiments, R^{N3}, R^{N4}, R^{O1} and R^{O2} are each independently selected from H, and linear or branched unsubstituted C₁₋₄ aliphatic groups.

The groups R⁸, R⁹ and R¹⁰

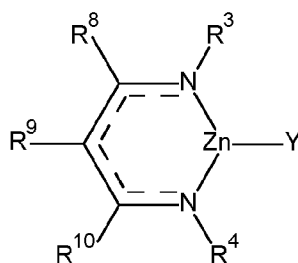
10 In some embodiments, L is -CR⁸-CR⁹-CR¹⁰-, and
R⁸, R⁹ and R¹⁰ are each independently selected from

H,
linear or branched unsubstituted C₁₋₁₂ aliphatic groups,
C₅₋₆ unsubstituted aryl or heteroaryl groups, and
15 -NR^{N1}R^{N2};

or two or more of R⁸, R⁹ and R¹⁰, together with the atoms to which they are attached, are joined to form a monocyclic or bicyclic group, with any remaining groups of R⁸, R⁹ and R¹⁰ being selected from H, linear or branched unsubstituted C₁₋₄ aliphatic groups, C₅₋₆ unsubstituted aryl or heteroaryl groups, and -NR^{N1}R^{N2}.

20

Thus in some embodiments, the compound is a compound according to formula (IA):



(IA)

or a salt, solvate or hydrate thereof;

25 wherein Y, R³, R⁴, R⁸, R⁹ and R¹⁰ are as defined above.

In some embodiments of formula (IA), R⁸, R⁹ and R¹⁰ are each independently selected from

H,
linear or branched unsubstituted C₁₋₄ aliphatic groups,
30 C₅₋₆ unsubstituted aryl or heteroaryl groups, and
-NR^{N1}R^{N2}.

In some embodiments of formula (IA), R^8 , R^9 and R^{10} are each independently selected from H, and linear or branched unsubstituted C_{1-4} aliphatic groups.

5

In some embodiments of formula (IA), R^8 , R^9 and R^{10} are each independently selected from H and methyl. In some embodiments of formula (IA), R^8 , R^9 and R^{10} are each independently selected from H and methyl; and Y is QR^1R^2 .

10 In some embodiments of formula (IA), R^9 is H. In some embodiments of formula (IA), one or both of R^8 and R^{10} is linear or branched unsubstituted C_{1-4} aliphatic groups. In some embodiments of formula (IA), one or both of R^8 and R^{10} is linear unsubstituted C_{1-4} aliphatic groups. In some embodiments of formula (IA), one or both of R^8 and R^{10} is methyl. In some
15 unsubstituted C_{1-4} aliphatic group. In some embodiments of formula (IA), R^9 is H and one or both of R^8 and R^{10} is methyl. In some embodiments of formula (IA), R^9 is H and both of R^8 and R^{10} are methyl.

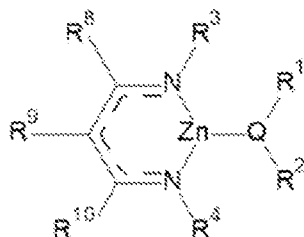
In some embodiments of formula (IA), two or more of R^8 , R^9 and R^{10} , together with the atoms
20 to which they are attached, are joined to form a monocyclic or bicyclic group, with any remaining groups of R^8 , R^9 and R^{10} being selected from H, linear or branched unsubstituted C_{1-4} aliphatic groups, C_{5-6} unsubstituted aryl or heteroaryl groups, and $-NR^{N1}R^{N2}$.

In some embodiments of formula (IA), R^8 and R^9 , together with the atoms to which they are
25 attached, are joined to form a monocyclic group, and R^{10} is selected from H, linear or branched unsubstituted C_{1-4} aliphatic groups, C_{5-6} unsubstituted aryl or heteroaryl groups, and $-NR^{N1}R^{N2}$. In some embodiments of formula (IA), R^8 and R^9 , together with the atoms to which they are attached, are joined to form a 6-membered monocyclic group, and R^{10} is
30 selected from H, linear or branched unsubstituted C_{1-4} aliphatic groups, C_{5-6} unsubstituted aryl or heteroaryl groups, and $-NR^{N1}R^{N2}$. In some embodiments of formula (IA), R^8 and R^9 , together with the atoms to which they are attached, are joined to form a 6-membered monocyclic group, and R^{10} is selected from H, and linear or branched unsubstituted C_{1-4} aliphatic groups.

35 In some embodiments of formula (IA), R^8 , R^9 and R^{10} , together with the atoms to which they are attached, are joined to form a bicyclic group. In some embodiments of formula (IA), R^8 ,

R⁹ and R¹⁰, together with the atoms to which they are attached, are joined to form a naphthyl group.

In some embodiments, the compound is a compound according to formula (IB):



5

(IB)

or a salt, solvate or hydrate thereof;

wherein:

10 Q is selected from N, P and P(=O);

R¹ and R² are each independently selected from

H;

linear or branched unsubstituted C₁₋₁₂ aliphatic groups;

15 C₆ aryl, optionally substituted with one or more groups R^A;

5-6 membered heteroaryl, optionally substituted with one or more groups R^B;

C₆₋₂₀ aralkyl, optionally substituted with one or more groups R^C; and

Si(C₁₋₆alkyl)₃;

20 R³ and R⁴ are each independently selected from

H;

linear or branched unsubstituted C₁₋₁₂ aliphatic groups;

C₆ aryl, optionally substituted with one or more groups R^A; and

5-6 membered heteroaryl, optionally substituted with one or more groups R^B;

25

R⁸, R⁹ and R¹⁰ are each independently selected from

H,

linear or branched unsubstituted C₁₋₁₂ aliphatic groups,

C₅₋₆ unsubstituted aryl or heteroaryl groups, and

30 -NR^{N1}R^{N2};

R^{N1} and R^{N2} are each independently selected from linear or branched unsubstituted C_{1-6} aliphatic groups, or R^{N1} and R^{N2} together with the N atom to which they are attached are joined to form a 3-6 membered heterocyclic group optionally substituted with one or more groups R^E ; and

5

R^A , R^B , R^C and R^E are each independently selected from linear or branched unsubstituted C_{1-6} aliphatic groups.

The groups R^{N1} and R^{N2}

10 In some embodiments, R^5 is $-NR^{N1}R^{N2}$. In some embodiments, one or more of R^6 and R^7 is $-NR^{N1}R^{N2}$. In some embodiments, one or more of R^8 , R^9 and R^{10} is $-NR^{N1}R^{N2}$.

R^{N1} and R^{N2} are each independently selected from linear or branched unsubstituted C_{1-6} aliphatic groups, or R^{N1} and R^{N2} together with the N atom to which they are attached are joined to form a 3-6 membered heterocyclic group optionally substituted with one or more groups R^E .

15

In some embodiments, R^{N1} and R^{N2} are each independently selected from linear or branched unsubstituted C_{1-6} aliphatic groups. In some embodiments, R^{N1} and R^{N2} are each independently selected from linear or branched unsubstituted C_{1-4} aliphatic groups. In some embodiments, R^{N1} and R^{N2} are each independently selected from linear unsubstituted C_{1-6} aliphatic groups. In some embodiments, R^{N1} and R^{N2} are each independently selected from linear unsubstituted C_{1-4} aliphatic groups. In some embodiments, R^{N1} and R^{N2} are each independently selected from methyl or ethyl.

20

25

In some embodiments, R^{N1} and R^{N2} together with the N atom to which they are attached are joined to form a 3-6 membered heterocyclic group optionally substituted with one or more groups R^E . In some embodiments, R^{N1} and R^{N2} together with the N atom to which they are attached are joined to form an unsubstituted 3-6 membered heterocyclic group.

30

In some embodiments, R^{N1} and R^{N2} together with the N atom to which they are attached are joined to form a heterocyclic group selected from:

aziridinyl, diaziridinyl, azetidiny, diazetidinyl, pyrrolidinyl, pyrrolyl, oxazolidinyl, imidazolidinyl, pyrazolidinyl, imidazolyl, pyrazolyl, triazolyl, piperidinyl, diazinanyl, morpholinyl, thiomorpholinyl, thiazinyl and triazinanyl; optionally substituted with one or more groups R^E .

35

In some embodiments, R^{N1} and R^{N2} together with the N atom to which they are attached are joined to form an unsubstituted heterocyclic group selected from:

aziridinyl, diaziridinyl, azetidiny, diazetidinyl, pyrrolidinyl, pyrrolyl, oxazolidinyl, imidazolidinyl, pyrazolidinyl, imidazolyl, pyrazolyl, triazolyl, piperidinyl, diazinanyl, morpholinyl, thiomorpholinyl, thiazinyl and triazinanyl.

The groups R^A , R^B , R^C , R^D and R^E

R^A , R^B , R^C , R^D and R^E are each independently selected from

linear or branched unsubstituted C_{1-6} aliphatic groups;

halo;

$O(C_{1-6}alkyl)$;

$-CF_3$, $-CF_2H$, $-CFH_2$;

$-OCF_3$, $-OCF_2H$ and $-OCFH_2$.

In some embodiments, R^A , R^B , R^C , R^D and R^E are each independently selected from

linear or branched unsubstituted C_{1-6} aliphatic groups;

halo; and

$O(C_{1-6}alkyl)$.

In some embodiments, R^A , R^B , R^C , R^D and R^E are each independently selected from

linear or branched unsubstituted C_{1-6} aliphatic groups;

halo; and

$O(Me)$.

In some embodiments, R^A , R^B , R^C , R^D and R^E are each independently selected from

linear or branched unsubstituted C_{1-6} aliphatic groups;

Cl; and

$O(Me)$.

In some embodiments, R^A , R^B , R^C , R^D and R^E are each independently selected from linear or branched unsubstituted C_{1-4} aliphatic groups. In some embodiments, R^A , R^B , R^C , R^D and R^E are each independently selected from linear unsubstituted C_{1-6} aliphatic groups. In some embodiments, R^A , R^B , R^C , R^D and R^E are each independently selected from linear unsubstituted C_{1-4} aliphatic groups. In some embodiments, R^A , R^B , R^C , R^D and R^E are each independently selected from methyl and ethyl.

The groups R^F and R^G

R^F and R^G are each independently selected from

H;

C_{1-12} alkyl groups;

5 C_6 aryl, optionally substituted with one or more groups R^A ;

5-6 membered heteroaryl, optionally substituted with one or more groups R^B ;

C_{6-20} aralkyl, optionally substituted with one or more groups R^C ;

$-S(=O)_2CF_3$; and

$-C(=O)R^H$, wherein R^H is linear or branched C_{1-6} alkyl optionally substituted with one

10 or more groups independently selected from OH and halo.

In some embodiments, R^F and R^G are each independently selected from

H;

C_{1-12} alkyl groups;

15 C_6 aryl, optionally substituted with one or more groups R^A ;

5-6 membered heteroaryl, optionally substituted with one or more groups R^B ; and

C_{6-20} aralkyl, optionally substituted with one or more groups R^C .

In some embodiments, R^F and R^G are each independently selected from

20 H;

branched C_{1-12} alkyl groups;

unsubstituted C_6 aryl; and

unsubstituted C_{6-20} aralkyl.

25 In some embodiments, Y is OR^F and R^F is selected from

H;

C_{1-12} alkyl groups;

C_6 aryl, optionally substituted with one or more groups R^A ;

5-6 membered heteroaryl, optionally substituted with one or more groups R^B ;

30 C_{6-20} aralkyl, optionally substituted with one or more groups R^C ;

$-S(=O)_2CF_3$; and

$-C(=O)R^H$, wherein R^H is linear or branched C_{1-6} alkyl optionally substituted with one or more groups independently selected from OH and halo.

35 In some embodiments, R^F is selected from

C_{1-12} alkyl groups;

C_6 aryl, optionally substituted with one or more groups R^A ;

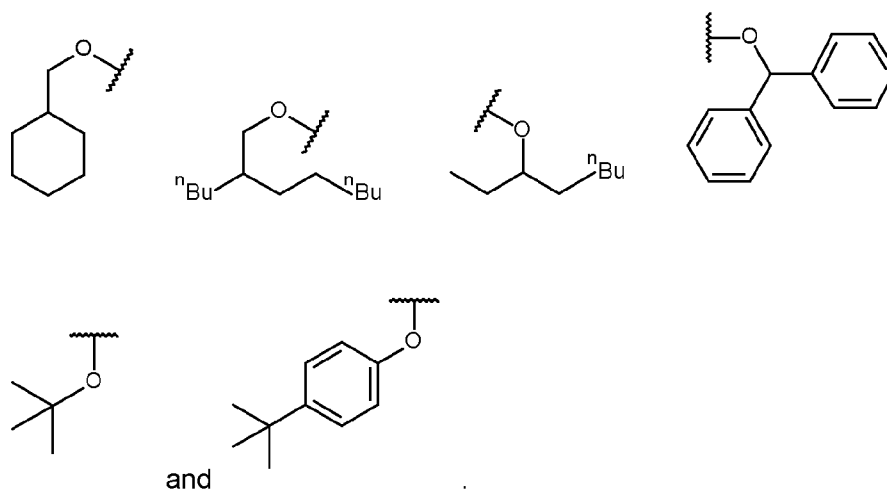
5-6 membered heteroaryl, optionally substituted with one or more groups R^B ; and
 C_{6-20} aralkyl, optionally substituted with one or more groups R^C .

In some embodiments, R^F is selected from

- 5 C_{1-12} unsubstituted alkyl groups;
 C_6 aryl, optionally substituted with one or more groups R^A ; and
 C_{6-20} aralkyl, optionally substituted with one or more groups R^C .

- 10 In some embodiments, R^F is C_6 aryl, optionally substituted with one or more groups R^A . In
some embodiments, R^F is unsubstituted C_6 aryl.

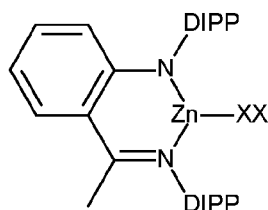
In some embodiments, the group OR^F is selected from one of the following groups:



15

Provisos

The compound according to formula (I) is not a compound according to formula (X):

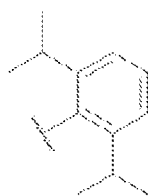


(X)

20

wherein the group XX is selected from $-N(SiMe_3)_2$ and $-NH(DIPP)$;

and wherein DIPP is the group:



In some embodiments, the compound according to formula (I) is not a compound according to formula (X), wherein the group XX is selected from $-NR^{1A}R^{2A}$, wherein R^{1A} and R^{2A} are as defined above. In some embodiments, the compound according to formula (I) is not a

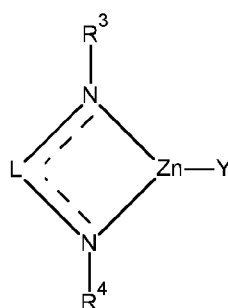
- 5 compound according to formula (X), wherein the group XX is selected from $-QR^1R^2$, wherein Q, R^1 and R^2 are as defined above. In some embodiments, the compound according to formula (I) is not a compound according to formula (X), wherein the group XX is Y, wherein Y is as defined above.

- 10 Certain specific compounds according to formula (X) are disclosed by Webb *et al.* in the article "Utilising an anilido-imino ligand to stabilise zinc-phosphanide complexes: reactivity and fluorescent properties", Dalton Trans, 2019, 48, 8094. However, this article does not teach or suggest any application of these complexes in the reduction or hydrogenation of compounds containing double or triple bonds, such as alkynes.

15

Further embodiments of formula (I)

In some embodiments, the invention provides a compound according to formula (I):



(I)

- 20 or a salt, solvate or hydrate thereof;
wherein:

Y is selected from $-QR^1R^2$, and OR^F ; wherein Q is selected from N, P and $P(=O)$;

- 25 L is selected from $-CR^8-CR^9-CR^{10}-$, $-CR^5-$, $-CR^6-CR^7-$, $-CR^{N3}-NR^G-CR^{N4}-$ and $-CR^{O1}-O-CR^{O2}-$;

either:

(A) R^1 is R^{1A} , R^2 is R^{2A} and R^4 is R^{4A} ; or

(B) R^4 is R^{4A} ; and R^1 and R^2 together with the Q moiety to which they are attached

5 are joined to form a 3-6 membered heterocyclic group optionally substituted with one or more groups R^E ; or

(C) R^1 is R^{1A} ; and R^2 , R^4 and the atoms to which they are attached form a 5-8 membered heterocyclic group, optionally substituted with one or more groups R^D , and optionally being fused to one or more optionally substituted aryl groups;

10

R^3 is selected from

H;

linear or branched unsubstituted C_{1-12} aliphatic groups;

C_6 aryl, optionally substituted with one or more groups R^A , and

15 5-6 membered heteroaryl, optionally substituted with one or more groups R^B ;

R^5 , R^6 , R^7 , R^{N3} , R^{N4} , R^{O1} and R^{O2} are each independently selected from

H,

linear or branched unsubstituted C_{1-12} aliphatic groups,

20 C_{5-6} unsubstituted aryl or heteroaryl groups, and

$-NR^{N1}R^{N2}$;

R^8 , R^9 and R^{10} are each independently selected from

H,

25 linear or branched unsubstituted C_{1-12} aliphatic groups,

C_{5-6} unsubstituted aryl or heteroaryl groups, and

$-NR^{N1}R^{N2}$;

R^{1A} , R^{2A} and R^{4A} are each independently selected from

30 H;

linear or branched unsubstituted C_{1-12} aliphatic groups;

C_6 aryl, optionally substituted with one or more groups R^A ;

5-6 membered heteroaryl, optionally substituted with one or more groups R^B ;

C_{6-20} alkyl, optionally substituted with one or more groups R^C ; and

35 $Si(C_{1-6}alkyl)_3$;

R^{N1} and R^{N2} are each independently selected from linear or branched unsubstituted C_{1-6} aliphatic groups, or R^{N1} and R^{N2} together with the N atom to which they are attached are joined to form a 3-6 membered heterocyclic group optionally substituted with one or more groups R^E ;

5

R^A , R^B , R^C , R^D and R^E are each independently selected from
linear or branched unsubstituted C_{1-6} aliphatic groups;

halo;

$O(C_{1-6}alkyl)$;

10

$-CF_3$, $-CF_2H$, $-CFH_2$;

$-OCF_3$, $-OCF_2H$ and $-OCFH_2$;

R^F and R^G are independently selected from

H;

15

C_{1-12} alkyl groups;

C_6 aryl, optionally substituted with one or more groups R^A ;

5-6 membered heteroaryl, optionally substituted with one or more groups R^B ;

C_{6-20} aralkyl, optionally substituted with one or more groups R^C ;

$-S(=O)_2CF_3$; and

20

$-C(=O)R^H$, wherein R^H is linear or branched C_{1-6} alkyl optionally substituted with one or more groups independently selected from OH and halo.

In some embodiments,

Y is $-NR^1R^2$;

25

L is $-CR^8-CR^9-CR^{10}-$;

R^1 is R^{1A} , R^2 is R^{2A} , R^4 is R^{4A} ;

R^3 and R^{4A} are each independently selected from

H;

linear or branched unsubstituted C_{1-12} aliphatic groups;

30

C_6 aryl, optionally substituted with one or more groups R^A , and

5-6 membered heteroaryl, optionally substituted with one or more groups R^B ;

R^8 , R^9 and R^{10} are each independently selected from

H,

linear or branched unsubstituted C_{1-12} aliphatic groups,

35

C_{5-6} unsubstituted aryl or heteroaryl groups, and

$-NR^{N1}R^{N2}$;

R^{1A} and R^{2A} are each independently selected from

- 5 H;
 linear or branched unsubstituted C₁₋₁₂ aliphatic groups;
 C₆ aryl, optionally substituted with one or more groups R^A;
 5-6 membered heteroaryl, optionally substituted with one or more groups R^B;
 5 C₆₋₂₀ aralkyl, optionally substituted with one or more groups R^C; and
 Si(C₁₋₆alkyl)₃;
 and R^A, R^B, R^C, R^{N1} and R^{N2} are as defined under the first aspect.

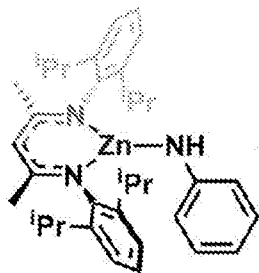
In some embodiments,

- 10 Y is -NR¹R²;
 L is -CR⁸-CR⁹-CR¹⁰-;
 R¹ is R^{1A}, R² is R^{2A}, R⁴ is R^{4A};
 R³ and R^{4A} are each independently selected from
 linear or branched unsubstituted C₁₋₁₂ aliphatic groups; and
 15 C₆ aryl, optionally substituted with one or more groups R^A;
 R⁸, R⁹ and R¹⁰ are each independently selected from
 H, and
 linear or branched unsubstituted C₁₋₁₂ aliphatic groups,
 R^{1A} and R^{2A} are each independently selected from
 20 H; and
 C₆ aryl, optionally substituted with one or more groups R^A;
 and R^A is as defined under the first aspect.

In some embodiments,

- 25 Y is -NR¹R²;
 L is -CR⁸-CR⁹-CR¹⁰-;
 R¹ is R^{1A}, R² is R^{2A}, R⁴ is R^{4A};
 R³ and R^{4A} are each independently selected from
 C₆ aryl, optionally substituted with one or more groups R^A;
 30 R⁸, R⁹ and R¹⁰ are each independently selected from
 H, and
 linear or branched unsubstituted C₁₋₆ aliphatic groups,
 R^{1A} and R^{2A} are each independently selected from
 H; and
 35 C₆ aryl, optionally substituted with one or more groups R^A;
 and R^A is as defined under the first aspect.

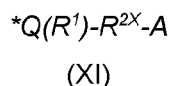
In some embodiments, the compound is:



A second aspect of the invention is a catalyst comprising a compound according to the first aspect. In some embodiments, the catalyst is a hydrogenation catalyst. In some
5 embodiments, the catalyst is an alkyne hydrogenation catalyst.

In some embodiments the catalyst comprises a compound according to the first aspect and a support. The support may be a solid support. The support may comprise a resin material. In some embodiments, the support comprises a functional group attached to the compound
10 of formula (I). In some embodiments, when Y is QR^1R^2 , the support comprises a functional group attached to the compound of formula (I) via the $Q-R^2$ group. In other words, the group Q^{R^2} in the compound according to formula (I) may act as a linker attaching the compound to a support.

15 In some embodiments, the supported form of the compound may have a structure according to formula (XI):



20

wherein the asterisk (*) represents the point of attachment to the Zn atom of the compound of formula (I);

Q and R^1 are as defined under the first aspect above;

R^{2X} is a divalent derivative of the R^2 group defined above; and

25 A is a support moiety.

In some embodiments the support moiety A is a solid support. In some embodiments the support moiety A is a resin.

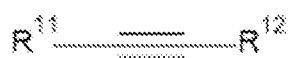
In some embodiments, R^{2X} is the group $-\text{Ph}-\text{O}-(\text{CH}_2)_n^*$, where the asterisk (*) represents the point of attachment to the support A; and wherein Ph is phenylene optionally substituted with one or more unsubstituted straight or branched C_{1-6} alkyl groups.

- 5 A third aspect of the invention is a method of reducing or hydrogenating a double or triple bond in the presence of a catalyst comprising a compound according to the first aspect. In some embodiments, the method is a method of reducing or hydrogenating a compound selected from alkyne, alkene, nitrile, carbonyl (including aldehydes and ketones), ester and amide in the presence of a catalyst comprising a compound according to the first aspect.
- 10 In some embodiments, the method is a method of semi-hydrogenation of an alkyne to provide an alkene. In some embodiments, the method is a method of manufacturing a compound selected from β -carotene, polyene antifungal drugs, crocaine, polyunsaturated fatty acids (PUFAs), pheromones and cruentaren.
- 15 In some embodiments, the method is a method of stereoselectively reducing or hydrogenating the double or triple bond to provide an excess of one stereoisomer. In some embodiments, the molar ratio of a first stereoisomer to a second stereoisomer is at least 55:45, for example at least 60:40, at least 70:30, at least 80:20, at least 90:10, at least 95:5 or at least 99:1. In some embodiments the first stereoisomer is a (*Z*)-alkene and the second stereoisomer is an (*E*)-alkene.
- 20

In some embodiments, the method is a method of chemoselectively reducing or hydrogenating the double or triple bond. In some embodiments, the molar ratio of a first product to a second product is at least 2:1, for example at least 5:1, at least 10:1, at least 20:1, at least 30:1, at least 50:1 or at least 99:1. In some embodiments the first product is an alkene and the second product is an alkane which results from further hydrogenation of the alkene.

25

In some embodiments, the method comprises reacting an alkyne according to formula (V):

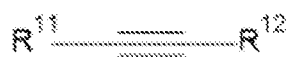


30

(V)

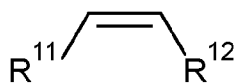
with dihydrogen (H_2), in the presence of a catalyst comprising a compound according to the first aspect.

- 35 In some embodiments, the method comprises reacting an alkyne according to formula (V):



(V)

with dihydrogen (H₂), in the presence of a catalyst comprising a compound according to the first aspect, to produce an alkene according to formula (VI):



5

(VI).

The catalyst facilitates the chemo- and stereo-selective production of the alkene according to formula (VI). In other words, semi-hydrogenation takes place with very little over-
 10 hydrogenation, producing preferentially the alkene (VI) with little or no overhydrogenation to the alkane (chemoselectivity), and the reaction preferentially produces the (Z)-alkene over the (E)-alkene (stereoselectivity).

In some embodiments the method of the third aspect comprises reducing or hydrogenating a
 15 double or triple bond in the presence of a catalyst comprising a supported catalyst with a structure according to formula (XI) described above. In such embodiments the method may be a flow process in which the supported catalyst forms part of a stationary phase, for example immobilised on a resin within a column. Reactants including hydrogen and a compound containing a double or triple bond (e.g. an alkyne) may then be contacted with the
 20 supported catalyst, for example through passing them through the column.

The skilled person is aware of suitable reaction conditions for carrying out catalytic hydrogenation reactions.

25 In some embodiments, the hydrogenation comprises first dissolving the catalyst comprising the compound according to formula (I) in a suitable solvent (Solvent A) to form a catalyst solution (Solution A), and combining Solution A with the compound to be hydrogenated, e.g. the alkyne according to formula (V). Solvent A may be an organic solvent, for example toluene.

30

The compound to be hydrogenated may also be dissolved in a solvent (Solvent B) to form a solution (Solution B) before combining with Solution A. Solvent A and Solvent B may be the same solvent. In some embodiments, both Solvent A and Solvent B are toluene.

After mixing Solution A with Solution B to form the reaction mixture, the reaction mixture may be pressurised with hydrogen and heated up to the reaction temperature.

- 5 Hydrogenation may be performed under a hydrogen pressure of from 100 kPa to 10 MPa, for example from 200 kPa to 8 MPa, 500 kPa to 5 MPa, 1 MPa to 5 MPa or 800 kPa to 2.5 MPa.

- 10 Hydrogenation may be performed at a temperature of from 50 °C to 200 °C, for example from 60 °C to 180 °C, from 80 °C to 160 °C or from 100 °C to 150 °C.

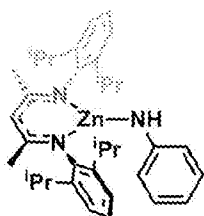
In some embodiments, the reaction mixture is stirred during the hydrogenation.

- 15 The reaction time may be from 1 h to 50 h, for example from 1 h to 50 h, from 2 h to 40 h, from 5 h to 30 h, from 5 h to 20 h, from 10 h to 20 h or from 12 h to 18 h.

- 20 In some embodiments, R^{11} and R^{12} are each independently selected from alkyl and aryl groups. In some embodiments, R^{11} and R^{12} are each independently selected from linear or branched unsubstituted C_{1-6} alkyl, and C_{3-8} aromatic or heteroaromatic groups. However, the skilled person will understand that the hydrogenation may be carried out on any alkyne regardless of the identity of the groups R^{11} and R^{12} .

- 25 A fourth aspect is a method of activating dihydrogen for hydrogenation, comprising reacting dihydrogen with a catalyst comprising a compound according to the first aspect. The inventors have found that compounds of formula (I) according to the invention provide for dihydrogen activation at zinc. The thus activated dihydrogen may then react with a reducible double or triple bond, such as an alkyne, in a hydrogenation reaction.

- 30 This has been confirmed by DFT studies into the dihydrogen activation process for Compound 1:

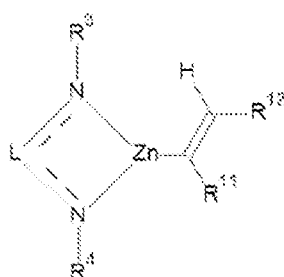


Compound 1

as explained in more detail in the appended examples.

5

A fifth aspect is a compound according to formula (VII):



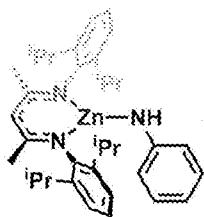
(VII)

wherein

10 L, R³, R⁴, R¹¹ and R¹² are as defined above.

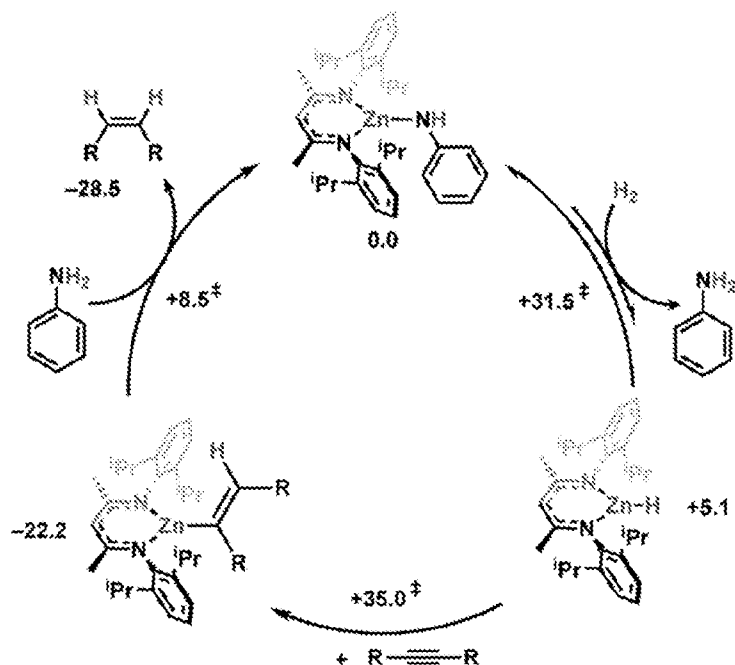
The inventors have determined that the zinc vinyl compound according to formula (VII) is formed as a key intermediate in the alkyne semi-hydrogenation reaction when an alkyne according to formula (V) is hydrogenated in the presence of a catalyst comprising a
 15 compound according to formula (I). This was confirmed by NMR characterisation of the intermediate of formula (VII).

Without wishing to be bound by theory, and using Compound 1 below as a specific example, the inventors believe that the catalytic hydrogenation of the alkyne proceeds according to the
 20 mechanism shown in Scheme A below:



Compound 1

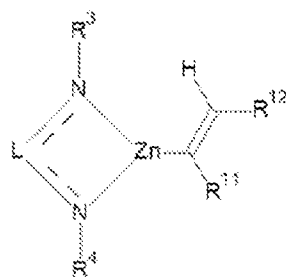
Scheme A



where the numbers indicate DFT calculated barriers and thermodynamics for R = Ph

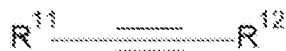
5 (kcal mol⁻¹).

Thus a sixth aspect of the invention is a method of preparing an intermediate according to formula (VII):



(VII)

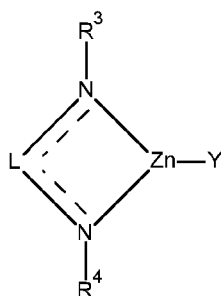
the method comprising reacting an alkyne according to formula (V):



(V)

with dihydrogen (H₂) in the presence of a catalyst comprising a compound according to

15 formula (I):



(I)

or a salt, solvate or hydrate thereof;

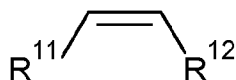
wherein L, Y, R³, R⁴, R¹¹ and R¹² are as defined above.

5

Protonation of the intermediate according to formula (VII) then provides the hydrogenated alkene product and the compound according to formula (I) may be regenerated.

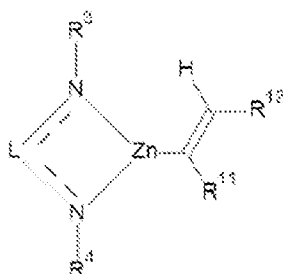
A seventh aspect of the invention is therefore a method of preparing an alkene according to formula (VI):

10



(VI)

the method comprising protonating a compound according to formula (VII):



(VII)

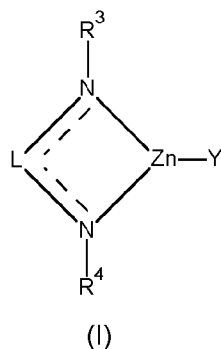
15

wherein L, R³, R⁴, R¹¹ and R¹² are as defined above.

The protonation may be performed by any suitable acid, but preferably the protonation is performed by the species HY (e.g. HQR¹R²) which is generated when the compound according to formula (I) is reacted with dihydrogen and therefore may be present in the reaction mixture. In this way, the compound according to formula (I) is regenerated by the reaction with HY (e.g. HQR¹R²) such that it may act as a catalyst for the process.

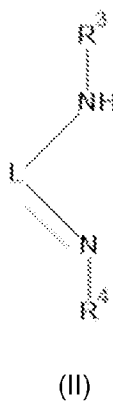
20

An eighth aspect of the invention is a method of making a compound according to formula (I):



5

from starting materials comprising a compound according to formula (II):



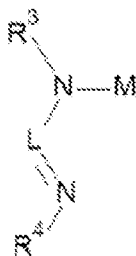
10 wherein Y, L, R³ and R⁴ are as defined in the first aspect above.

For the avoidance of doubt, all the options and preferences expressed above for all variables within the formula (I) apply equally to those same variables where they appear in other formulae herein (including, for example, formula (II)).

15

In some embodiments, the method of the eighth aspect comprises

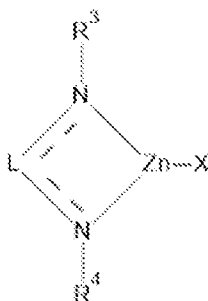
(a) reacting the compound according to formula (II) with a first metal-containing reagent to form a compound according to formula (III):



(III)

wherein M is a metal atom selected from Li, Na and K;

- (b) reacting the compound according to formula (III) with a zinc salt ZnX_2 to form a compound according to formula (IV):



(IV)

wherein X is a monovalent anion;

and

- (c) converting the compound according to formula (IV) into the compound according to formula (I).

In some embodiments, step (c) comprises reacting the compound according to formula (IV) with $M'Y$ to form the compound according to formula (I), wherein M' is a metal atom and Y is as defined under the first aspect. M' may be selected from Li, Na and K.

In some embodiments, step (c) comprises reacting the compound according to formula (IV) with $MgYX'$ to form the compound according to formula (I), wherein X' is a monovalent anion and Y is as defined under the first aspect.

- In some embodiments, X' is a halogen anion. In some embodiments, X' is Cl.

In some embodiments, step (c) comprises reacting the compound according to formula (IV) with a Grignard reagent and HY to form the compound according to formula (I), wherein Y is as defined under the first aspect. The skilled person is aware of suitable Grignard reagents,

but non-limiting examples are reagents of the formula $R^{13}MgX''$, wherein R^{13} is selected from aliphatic and aryl groups (for example, C_{1-20} alkyl, aryl or vinyl) and X'' is a monovalent anion, for example Cl.

- 5 In some embodiments, M is Li. In some embodiments, the first metal-containing reagent is a lithiating reagent. In some embodiments, the first metal-containing reagent is an organolithium reagent. In some embodiments, the first metal-containing reagent is n-BuLi.

- 10 In some embodiments, M is Na. In some embodiments, the first metal-containing reagent is selected from NaH and $NaOR^{Na}$, wherein R^{Na} is an alkyl group.

In some embodiments, M is K. In some embodiments, the first metal-containing reagent is selected from KH and KOR^K , wherein R^K is an alkyl group.

- 15 In some embodiments, M' is Li. In some embodiments, M' is Na. In some embodiments, M' is K.

- In some embodiments, $M'Y$ is made by reacting a second metal-containing reagent with HY. In some embodiments, M' is Li and the second metal-containing reagent is a lithiating reagent. In some embodiments, M' is Li and the second metal-containing reagent is an organolithium reagent. In some embodiments, M' is Li and the second metal-containing reagent is n-BuLi.
- 20

- In some embodiments, M' is Na and the second metal-containing reagent is selected from NaH and $NaOR^{Na}$, wherein R^{Na} is an alkyl group.
- 25

In some embodiments, M' is K and the second metal-containing reagent is selected from KH and KOR^K , wherein R^K is an alkyl group.

- 30 In some embodiments, both of the first organolithium reagent and the second metal-containing reagent comprises $nBuLi$.

- In some embodiments, the method of the eighth aspect comprises, in step (a), dissolving the compound according to formula (II) in a solvent (Solvent C) to form a solution (Solution C), then adding the first metal-containing reagent to Solvent C. The first metal-containing reagent may be added drop-wise to Solution C. In some embodiments, Solvent C is an
- 35

organic solvent, e.g. tetrahydrofuran (THF). In some embodiments the addition of the first metal-containing reagent to Solvent C is performed at low temperature, e.g. below -70 °C.

The reaction mixture may then be allowed to warm, for example to around room

- 5 temperature. In some embodiments the reaction mixture is stirred after warming. The stirring may be performed for at least 1 h, for example at least 5 h, at least 8 h or at least 10 h.

- 10 Step (b) of the method according to the eighth aspect may include dissolving ZnX_2 in a solvent (Solvent D) to form a solution (Solution D). In some embodiments, Solvent D is the same solvent as Solvent C. In some embodiments, Solvent D is an organic solvent, e.g. tetrahydrofuran (THF). The solution from step (a) containing the compound according to formula (III) may then be added to Solution D. In some embodiments, it is added dropwise to Solution D. In some embodiments the addition to Solvent D is performed at low
- 15 temperature, e.g. below -70 °C. The reaction mixture may then be allowed to warm, for example to around room temperature. In some embodiments the reaction mixture is stirred after warming. The stirring may be performed for at least 1 h, for example at least 5 h, at least 8 h or at least 10 h.

- 20 Step (c) of the method according to the eighth aspect may comprise first forming the compound $M'Y$ by reacting a second metal-containing reagent with YH. In some embodiments, this comprises adding the second metal-containing reagent to a solution of YH. The addition may be dropwise addition of the second metal-containing reagent. In some embodiments the addition is performed at low temperature, e.g. below -70 °C. The
- 25 solution of YH may be a solution in organic solvent, e.g. THF. The reaction mixture may then be allowed to warm, for example to around room temperature. In some embodiments the reaction mixture is stirred after warming. The stirring may be performed for at least 1 h, for example at least 5 h, at least 8 h or at least 10 h.

- 30 The compound $M'Y$ may then be added to the compound according to formula (IV) to complete step (c) of the method. This addition may be performed at a temperature of from 5 °C to 40 °C, for example from 10 °C to 30 °C, from 15 °C to 30 °C, 20 °C to 30 °C, or at about room temperature. In some embodiments the reaction mixture is stirred after the addition. The stirring may be performed for at least 1 h, for example at least 5 h, at least 8 h
- 35 or at least 10 h.

Optional purification steps may then be performed, including for example one or more recrystallisation and/or washing steps.

The product may then be dried, for example by drying under vacuum.

5

A ninth aspect of the invention is an intermediate according to formula (IV):



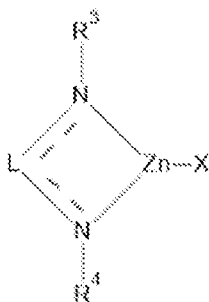
(IV)

wherein L, R³ and R⁴ are as defined in the first aspect and X is a monovalent anion.

10

In some embodiments, X is Cl.

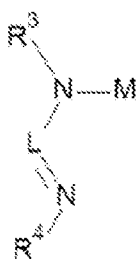
A tenth aspect of the invention is a method of making an intermediate according to formula (IV):



15

(IV)

comprising reacting a compound according to formula (III) with ZnX₂



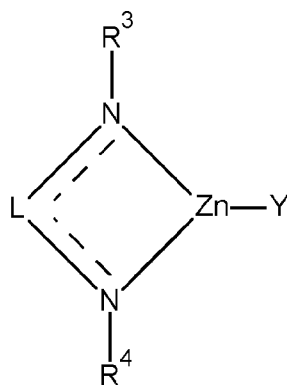
(III)

wherein L, R³ and R⁴ are as defined in the first aspect, M is a metal atom selected from Li, Na and K, and X is as defined under the ninth aspect.

5

In some embodiments, M is Li.

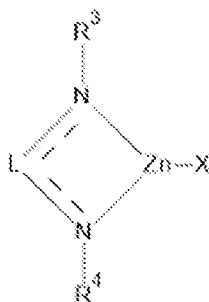
An eleventh aspect of the invention is a method of making a compound according to formula (I):



10

(I)

from a compound according to formula (IV):



(IV)

15 wherein Y, L, R³ and R⁴ are as defined in the first aspect, and X is a monovalent anion.

In some embodiments, the method of the eleventh aspect comprises reacting the compound according to formula (IV) with $M'Y$ to form the compound according to formula (I), wherein M' is a metal atom and Y is as defined under the first aspect. M' may be selected from Li, Na and K.

5

In some embodiments, the method of the eleventh aspect comprises reacting the compound according to formula (IV) with $MgYX'$ to form the compound according to formula (I), wherein X' is a monovalent anion and Y is as defined under the first aspect.

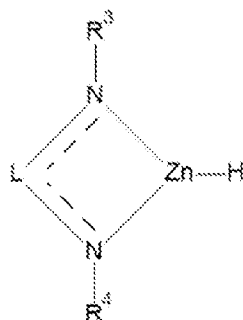
10 In some embodiments, X and X' are each independently selected from halogens and monovalent organic anions. In some embodiments, X and X' are each independently selected from halogens, $-OAc$, $-OTf$ and $-OC(=O)CF_3$. In some embodiments, X and X' are each independently selected from halogens. In some embodiments, X is Cl. In some embodiments, X' is Cl.

15

In some embodiments, M' is Li.

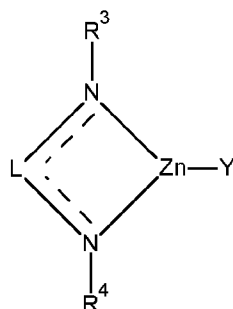
In some embodiments, the method of the eleventh aspect comprises reacting the compound according to formula (IV) with a Grignard reagent and HY to form the compound according to
 20 formula (I), wherein Y is as defined under the first aspect. The skilled person is aware of suitable Grignard reagents, but non-limiting examples are reagents of the formula $R^{13}MgX''$, wherein R^{13} is selected from aliphatic and aryl groups (for example, C_{1-20} alkyl, aryl or vinyl) and X'' is a monovalent anion, for example Cl.

25 A twelfth aspect of the invention is a method of making a compound according to formula (VIII):



(VIII)

comprising reacting a compound according to formula (I):



(I)

with dihydrogen (H_2), wherein L, Y, R^3 and R^4 are as defined under the first aspect.

5

A thirteenth aspect of the invention is the use of a compound according to the first aspect or catalyst according to the second aspect in a hydrogenation process, for example an alkyne hydrogenation process. Another aspect is the use of a compound according to the first aspect as a catalyst in a hydrogenation process, for example an alkyne hydrogenation process.

10

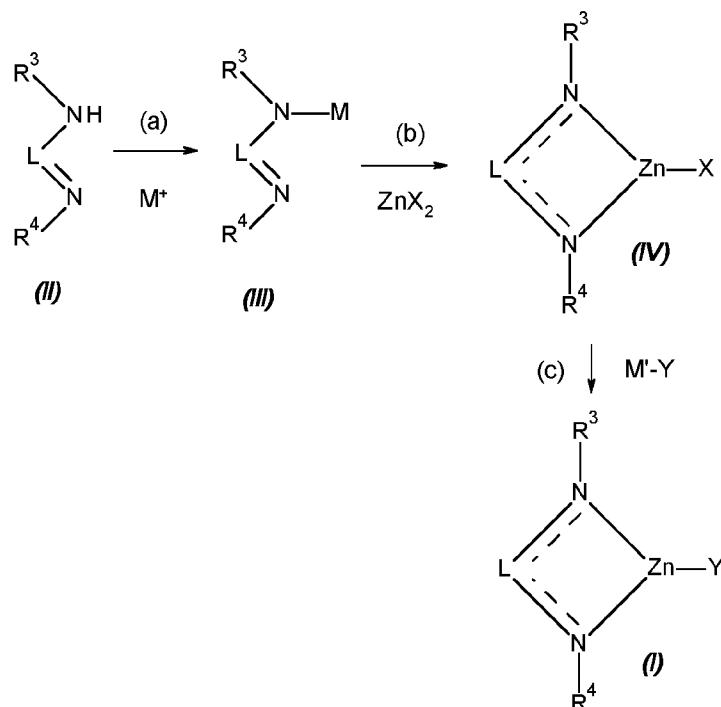
General synthetic methods

A number of synthetic routes are available for the preparation of compounds according to the invention. The skilled person will be able to select a suitable synthetic route based on the particular target compound.

15

In some embodiments, synthesis may involve a stepwise reaction starting from a proligand compound (II), as shown in Scheme 1 below.

Scheme 1



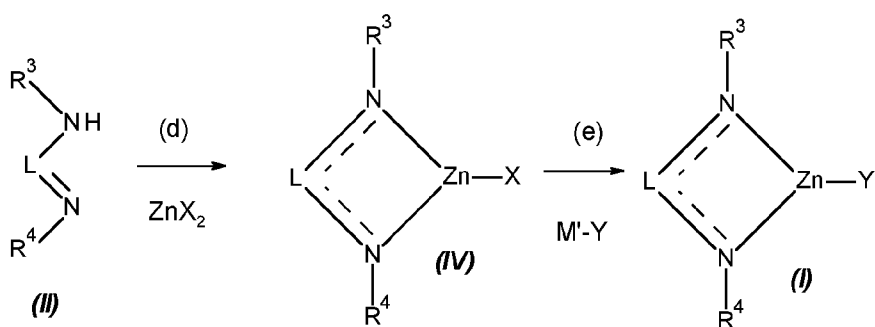
In the reaction according to Scheme 1, pro-ligand compound of formula (II) is first reacted with a metal salt comprising a metal ion M⁺, to form the derivative according to formula (III).

- 5 The metal ion M⁺ may be any suitable ion including Li, Na or K. The metal salt which provides the ion M⁺ may be, for example, a lithiating agent, such as an organolithium reagent, e.g. nBuLi. Alternatively, the salt may be NaH, NaOR, KH or KOR (wherein R is alkyl).
- 10 The derivative according to formula (III) is then reacted with zinc salt ZnX₂, where X is any suitable monovalent anion. For example, X may be Cl, triflate or a carbanion such as an alkyl anion. Reacting the derivative according to formula (III) with ZnX₂ provides the complex according to formula (IV).
- 15 Finally, the complex according to formula (IV) is reacted with M'-Y (for example, M'-QR¹R²) to form the compound according to formula (I). In the compound M'-Y, M' is a metal atom such as Li, Na or K. M'-Y may be formed by the reaction of HY with a suitable reagent for introducing the metal atom, such as a lithiating reagent e.g. nBuLi.
- 20 As an alternative in step (c), a Grignard reagent MgYX' may be reacted with the compound according to formula (IV), where X' is a halogen, for example Cl.

An alternative method of synthesis for the compounds according to formula (I) involves the direct reaction of the proligand compound with a suitable zinc salt, as shown in Scheme 2 below.

5

Scheme 2



In the reaction according to Scheme 2, pro-ligand compound of formula (II) is first reacted with zinc salt ZnX₂, where X is any suitable monovalent anion. For example, X may be Cl, triflate or a carbanion such as an alkyl anion. Reacting the proligand according to formula (II) with ZnX₂ provides the complex according to formula (IV).

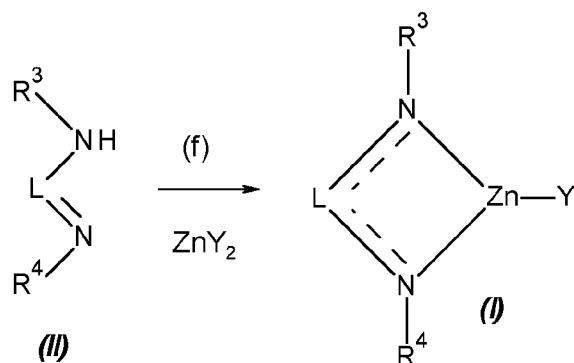
Finally, the complex according to formula (IV) is reacted with M'-Y to form the compound according to formula (I). In the compound M'-Y, M' is a metal atom such as Li, Na or K. M'-QR¹R² may be formed by the reaction of HY with a suitable reagent for introducing the metal atom, such as a lithiating reagent e.g. nBuLi.

As an alternative in step (e), a Grignard reagent MgYX' may be reacted with the compound according to formula (IV), where X' is a halogen, for example Cl. In an alternative synthesis, step (e) may involve the reaction of the compound according to formula (IV) with a Grignard reagent R¹³MgX'', wherein R¹³ is selected from aliphatic and aryl groups (for example, C₁-alkyl, aryl or vinyl) and X'' is a monovalent anion, for example Cl. Reaction with HY then gives the compound according to formula (I). The order of addition of R¹³MgX'' and HY may not be critical.

25

An alternative method of synthesis for the compounds according to formula (I) involves the reaction of a zinc compound Zn(Y)₂ with the proligand compound as shown in Scheme 3 below.

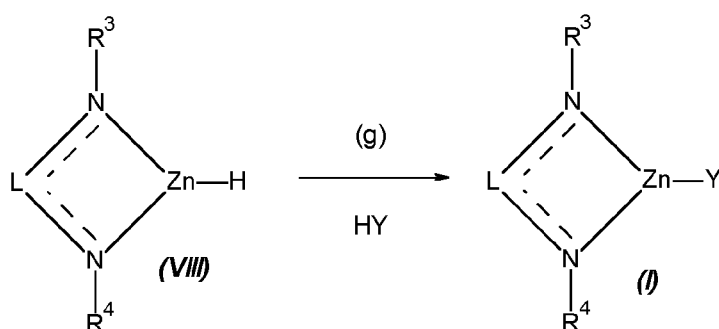
Scheme 3



An alternative method of synthesis for the compounds according to formula (I) involves the reaction of a zinc hydride complex of formula (VIII) with HY as shown in Scheme 4 below.

5

Scheme 4

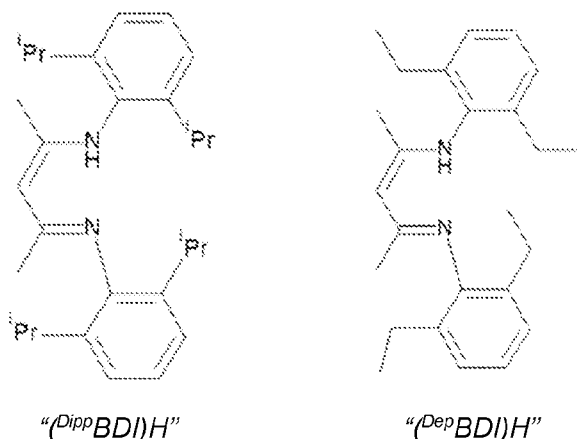


Specific compound synthesis

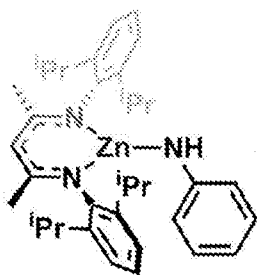
In the following examples, all manipulations were carried out under standard Schlenk-line and glovebox techniques under an inert atmosphere of argon or dinitrogen. An MBraun Labmaster glovebox was employed operating at <0.1 ppm O_2 and <0.1 ppm H_2O . NMR scale reactions were performed in J. Young tap NMR tubes equipped with internal standard capillaries of ferrocene or *bis*(trimethylsilyl)methane in C_6D_6 and were prepared in a glovebox. Solvents were dried over activated alumina from an SPS (solvent purification system) based upon the Grubbs design and degassed before use. Glassware was dried for 12 hours at 120°C prior to use. Benzene- d_6 and toluene- d_8 were freeze-pump-thaw degassed and stored over $3\text{ \AA}$ molecular sieves prior to use. NMR spectra were obtained on BRUKER 400 or 500 MHz machines, all peaks are referenced against residual solvent peak ($\text{C}_6\text{D}_5\text{H}$ δ 7.16 ppm, $\text{C}_6\text{D}_5\text{CD}_2\text{H}$ δ 2.09 ppm) with values quoted in ppm. Data were processed in MestReNova. Crystallographic data was collected using Agilent Xcalibur

PX Ultra A or Agilent Xcalibur 3E diffractometers, and the structures were refined using the SHELXTL and SHELX-2013 program systems.

- 5 The β -diketiminato proligands (^{Dipp}BDI)H and (^{Dep}BDI)H, complex and diarylethyne substrates were prepared according to literature procedures.

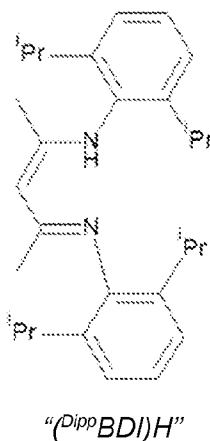


- 10 Solvents were freeze-pump-thaw degassed and stored over 3 Å molecular sieves prior to use. Chemicals were purchased from Sigma Aldrich, Alfa Aesar, Honeywell or Fluorochem and used without further purification unless stated. Where liquids at 25 °C, reagents were dried over 3 Å sieves and freeze-pump-thaw degassed prior to use. All gases were supplied by BOC and used without further purification or drying.
- 15 Quantitative gas chromatography (GC) analyses were performed with an Agilent Technologies 7820A GC with FID detector using either an Agilent DB-WAX or HP-PLOT Q column. The carrier gas used was helium. Durene was used as internal standard.
- 20 High pressure (>10 bar) reactions were performed in either a Parr Instrument Company Series 5500 HPCL 300 mL reactor or Series 4790 GP 25 mL reactor with a 4848 reactor controller. Heating was supplied by a hot plate stirrer and metal bead bath or aluminium heating block and monitored using an internal thermocouple. Stirring was provided using PTFE coated magnetic stirrers (3.0 x 0.8 x 0.8 cm for 300 mL vessel and 1.2 x 0.4 x 0.4 cm for 25 mL vessel) and both reactors were fitted with PTFE liners. Due to issues with contamination and background catalysis all PTFE liners and stirrers were subject to a
- 25 rigorous cleaning procedure after each reaction. This procedure was: an acetone rinse, then an aqua regia soak (10 – 20 minutes) followed by a thorough wash with distilled water and a final rinse with acetone. This cleaning procedure was coupled with appropriate control reactions to minimise background catalysis.

Example 1Compound 1"(DippBDI)ZnNHPh"

5

To a clean, dry Schlenk under argon, (DippBDI)H (5 g, 11.9 mmol) was added and dissolved in THF (20 mL).

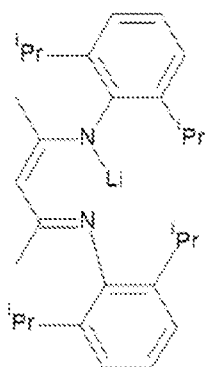


10

ⁿBuLi (1.6 M in hexanes, 7.5 mL, 11.9 mmol) was added dropwise at -78 °C, the reaction was then allowed to warm to 25 °C and stirred for 16 h.

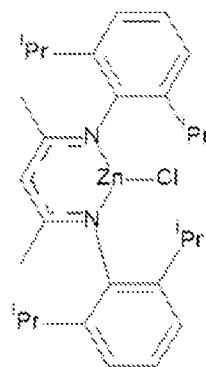
In a separate Schlenk, anhydrous ZnCl₂ (1.6 g, 11.9 mmol) was dissolved in THF (10 mL).

15 The solution of (DippBDI)Li was transferred dropwise via cannula onto the solution of ZnCl₂ at -78 °C. This mixture was allowed to warm to 25 °C and stirred for 16 h.



“(DippBDI)Li”

- 5 In a separate Schlenk, ⁿBuLi (1.6 M in n-hexane, 7.5 mL, 11.9 mmol) was added dropwise at -78 °C to a stirred solution of aniline (1.1 mL, 11.9 mmol) in THF (15 mL), this solution was allowed to warm to 25 °C and stirred for 16 h. The solution of LiNHPPh was transferred dropwise via cannula onto the solution of (DippBDI)ZnCl at 25 °C and stirred for 16 h.



“(DippBDI)ZnCl”

10

Recrystallisation from toluene, washing with n-hexane (2 x 5 mL) and drying under vacuum yielded pure product **Compound 1** as an off-white crystalline solid (3.2 g, 5.6 mmol, 42% yield).

- 15 ¹H NMR (400 MHz, C₆D₆) δ 7.21 – 7.18 (m, 2H, *p*-Dipp), 7.14 – 7.12 (m, 4H, *m*-Dipp), 6.80 (dd, ³J_{HH} = 8.5, 7.2 Hz, 2H, Zn-N(*m*-Ph)), 6.47 (tt, ³J_{HH} = 7.2 Hz, ⁴J_{HH} = 1.1 Hz, 1H, Zn-N(*p*-Ph)), 5.59 (d, ³J_{HH} = 7.6 Hz, 2H, Zn-N(*o*-Ph)), 4.95 (s, 1H, backbone CH), 3.15 (hept, ³J_{HH} =

6.9 Hz, 4H, ⁱPr-CH), 2.98 (s, 1H, Zn-N(H)), 1.67 (s, 6H, backbone CH₃), 1.24 (d, ³J_{HH} = 6.9 Hz, 12H, ⁱPr-CH₃), 1.14 (d, ³J_{HH} = 6.9 Hz, 12H, ⁱPr-CH₃).

¹³C{¹H} NMR (100 MHz, C₆D₆) δ 168.9 (backbone CCH₃), 154.6 (Zn-N(*ipso*-Ph)), 143.2

- 5 (*ipso*-Dipp), 141.6 (*o*-Dipp), 128.8 (Zn-N(*m*-Ph)), 126.4 (*p*-Dipp), 124.0 (*m*-Dipp), 115.8 (Zn-N(*o*-Ph)), 113.6 (Zn-N(*p*-Ph)), 94.8 (backbone CH), 28.2 (ⁱPr-CH), 23.9 (ⁱPr-CH₃), 23.1 (backbone CH₃), 23.0 (ⁱPr-CH₃).

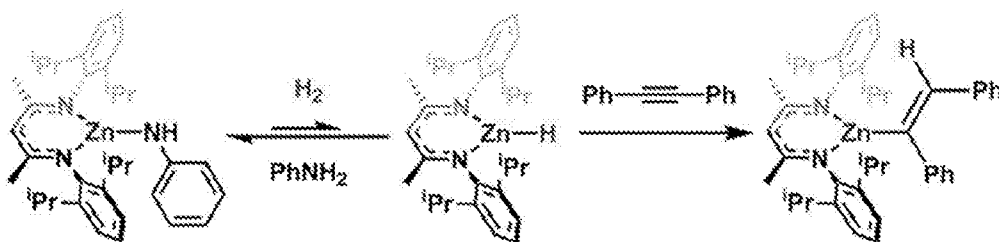
Anal. Calc. (found) for C₃₅H₄₇N₃Zn: C 73.09 (72.91) H 8.24 (8.39) N 7.31 (6.91) %.

10

Stoichiometric reactions

To investigate the activation of H₂ by Compound 1, stoichiometric reactions with alkyne were performed, followed by protonolysis of the resultant vinyl complex using aniline.

- 15 Example 2 – H₂ activation using Compound 1, and subsequent hydrozincation of diphenylacetylene



- In a N₂ glovebox, **Compound 1** (10 mg, 0.017 mmol) and diphenylacetylene (3.1 mg, 0.017 mmol) were added to a weighing vial via C₆D₆ stock solutions. *Bis*(trimethylsilyl)methane (1 μL, 0.005 mmol) was added directly as an internal standard. The reaction volume was made up to 0.6 mL with C₆D₆, before being transferred to a clean, dry J. Young tap NMR tube. The tube contents were freeze-pump-thaw degassed inside the glovebox and the tube was sealed under vacuum. The tube was removed from the glovebox and ~1 atm H₂ added. An initial ¹H NMR spectrum was recorded, and then the tube was heated to 100 °C for 18 h. A final ¹H NMR spectrum was recorded.
- 20
- 25

The resultant the vinyl complex (^{Dipp}BDI)ZnC(Ph)CHPh was submitted for crystal structure analysis by X-ray crystallography.

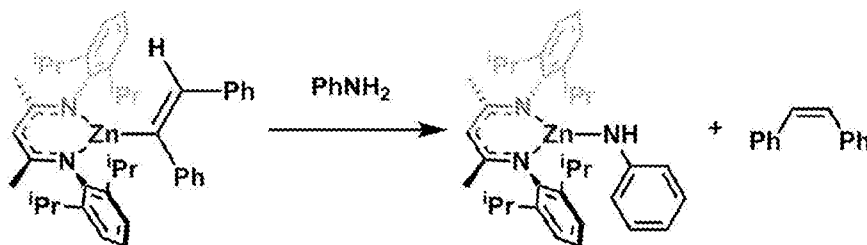
- 30 *Crystal data*: C₄₃H₅₂N₂Zn, *M* = 662.23, monoclinic, *P*2₁/*n* (no. 14), *a* = 11.3784(2), *b* = 15.3573(3), *c* = 21.4017(4) Å, β = 92.5051(17)°, *V* = 3736.18(13) Å³, *Z* = 4, *D*_c = 1.177 g cm⁻³, μ(Mo-Kα) = 0.688 mm⁻¹, *T* = 173 K, colourless blocks, Agilent Xcalibur 3 E diffractometer;

7500 independent measured reflections ($R_{\text{int}} = 0.0187$), F^2 refinement, $R_1(\text{obs}) = 0.0368$, $wR_2(\text{all}) = 0.0921$, 5912 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$], completeness to $\theta_{\text{full}}(25.2^\circ) = 98.9\%$, 436 parameters. CCDC 2004167.

The C24-based isopropyl group in the structure was found to be disordered. Two

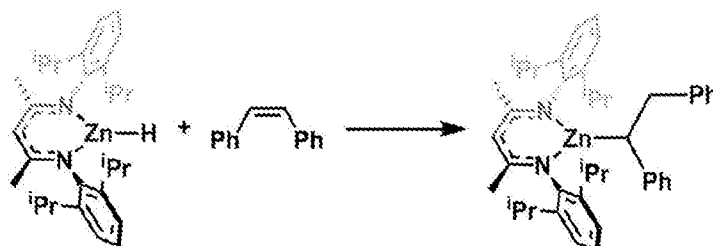
- 5 orientations were identified of ca. 56 and 44% occupancy, their geometries were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically (those of the minor occupancy orientation were refined isotropically).
- 10 The crystal structure of $(^{\text{Dipp}}\text{BDI})\text{ZnC}(\text{Ph})\text{CHPh}$ is shown in Figure 5, with 50% probability ellipsoids.

Example 3 – Protonolysis of $(^{\text{Dipp}}\text{BDI})\text{ZnC}(\text{Ph})\text{CHPh}$ using aniline



- 15 In a N_2 glovebox, the vinyl complex $(^{\text{Dipp}}\text{BDI})\text{ZnC}(\text{Ph})\text{CHPh}$ (10 mg, 0.015 mmol) and aniline (1.4 μL , 0.015 mmol) were added directly to a clean, dry J. Young NMR tube. *Bis*(trimethylsilyl)methane (1 μL , 0.005 mmol) was added directly as an internal standard. The reaction volume was made up to 0.6 mL with C_6D_6 , and the tube was sealed and removed from the glovebox. An initial ^1H NMR spectrum was recorded, and then the
- 20 reaction mixture was heated to 100°C for 4 days. A final ^1H NMR spectrum was recorded. These initial and final NMR spectra are shown in Figure 2.

Example 4 – *Cis*-alkene hydrozincation using $(^{\text{Dipp}}\text{BDI})\text{ZnH}$

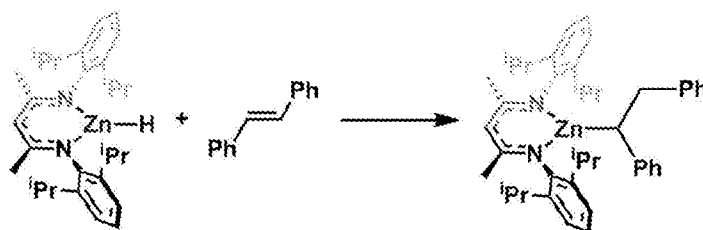


- 25 In a N_2 glovebox, hydride complex $(^{\text{Dipp}}\text{BDI})\text{ZnH}$ (7 mg, 0.014 mmol) and *cis*-stilbene (2.6 μL , 0.014 mmol) were added via C_6D_6 stock solutions to a clean, dry J. Young NMR tube. *Bis*(trimethylsilyl)methane (1 μL , 0.005 mmol) was added directly to the tube as an internal

standard. The reaction volume was made up to 0.6 mL with C₆D₆, and the tube was sealed and removed from the glovebox. An initial ¹H NMR spectrum was recorded, and then the reaction mixture was heated to 100 °C for 19 h. A final ¹H NMR spectrum was recorded. These initial and final NMR spectra are shown in Figure 3. The NMR yield was 8%.

5

Example 5 – Trans-alkene hydrozincation using (^{Dipp}BDI)ZnH



In a N₂ glovebox, hydride complex (^{Dipp}BDI)ZnH (7 mg, 0.014 mmol) and *trans*-stilbene (2.6 mg, 0.014 mmol) were added via C₆D₆ stock solutions to a clean, dry J. Young NMR tube. *Bis*(trimethylsilyl)methane (1 μL, 0.005 mmol) was added directly to the tube as an internal standard. The reaction volume was made up to 0.6 mL with C₆D₆, and the tube was sealed and removed from the glovebox. An initial ¹H NMR spectrum was recorded, and then the reaction mixture was heated to 100 °C for 15 h. A final ¹H NMR spectrum was recorded. These initial and final NMR spectra are shown in Figure 4. The NMR yield was 14%.

15

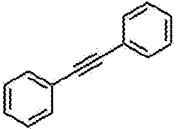
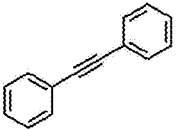
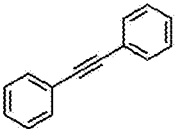
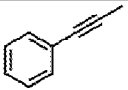
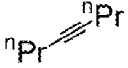
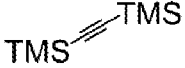
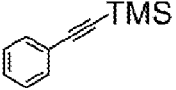
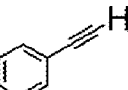
Catalytic alkyne hydrogenation

Examples 6-13 – High pressure (>10 bar) catalytic reactions at 30 mL scale

In a N₂ glovebox, **Compound 1**, (^{Dipp}BDI)ZnNHPh (293 mg, 0.5 mmol) was weighed into a scintillation vial, dissolved in toluene (15 mL) and transferred to a clean, dry Schlenk. Alkyne (10 equiv., 5.1 mmol) was weighed into a separate scintillation vial, dissolved in toluene (15 mL) and added to the Schlenk. The alkyne compounds used are set out in Table 1 below. ~0.5 mL was taken for NMR analysis. The Schlenk was sealed and removed from the glovebox. The Schlenk was attached to a N₂ line and the side-arm purged for 5 minutes before being opened to the gas line. The Schlenk was fitted with a subaseal and the reaction mixture transferred into the purged 300 mL pressure vessel (N₂ 10 x 5 bar, followed by H₂ 3 x 3 bar) using a 20 mL syringe and needle. The vessel was pressurised to 16 bar with H₂ and sealed. The reaction was heated to 145 °C to give a final pressure of 23 bar (measured using digital manometer). Stirring was set to 900 rpm and the reaction was run for 18 h. The reaction mixture was then analysed by NMR and gas chromatography.

25

Table 1

Example	Alkyne substrate	T / °C	P / bar	Yield / %	Z:E	Alkene:alkane
6		100	21	6	>99:1	30:1
7		125	22	23	>99:1	33:1
8		145	23	83	>99:1	48:1
9		145	23	21	>99:1	>99:1
10		145	23	44	>99:1	>99:1
11		145	23	1	>99:1	2:1
12		145	23	5	1:2	>99:1
13		145	23	9	N/A	>99:1

TMS = -SiMe₃ⁿPr = -CH₂CH₂CH₃

5

Examples 14-15 – High pressure (>10 bar) catalytic reactions at 7 mL scale

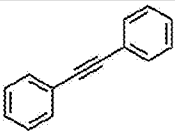
In a N₂ glovebox, **Compound 1**, (DippBDI)ZnNHPh (75 mg, 0.1 mmol) and alkyne (10 equiv., 1.3 mmol) were weighed into separate scintillation vials, dissolved in toluene (7.5 mL) and added to a 25 mL pressure vessel. ~0.5 mL was taken for NMR analysis. The alkyne compounds used are set out in Table 2 below. The pressure vessel was sealed and removed from the glovebox. Inlet and outlet lines were fitted to the vessel, and the inlet valve was purged for 5 minutes with N₂ before the vessel was opened to the gas line. The vessel was then purged with N₂ (10 x 5 bar) followed by H₂ (3 x 3 bar), before being pressurised to 16 bar with H₂ and sealed. The reaction was heated to 145 °C to give a final pressure of 23 bar (measured using a digital manometer). Stirring was set to 900 rpm and

10

15

the reaction was run for 18 h. The reaction mixture was then analysed by NMR and gas chromatography.

Table 2

<i>Example</i>	<i>Alkyne substrate</i>	<i>Alkyne conversion / %</i>	<i>Z:E</i>	<i>Alkene:alkane</i>
14		100	2.8:1	1.5:1
15	Et-C≡C-Et	88	96:4	98:1

5

The reduced selectivity with diphenylacetylene in Example 14 relative to diethylacetylene in Example 15 was attributed to unoptimized reaction conditions in the particular reactor used. It is suspected that in this particular Example the reaction was left to run for too long resulting in complete conversion to Z-alkene followed by some over-hydrogenation or isomerisation. This could be addressed by tailoring the reaction time.

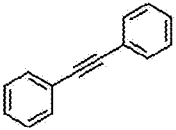
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Comparative Example 1 - High pressure (>10 bar) reaction at 30 mL scale without catalyst

The procedure as in Example 2 was carried out but in the absence of the catalyst

Compound 1. The results were as follows:

15

<i>Example</i>	<i>Alkyne substrate</i>	<i>T / °C</i>	<i>P / bar</i>	<i>Yield / %</i>	<i>Z:E</i>	<i>Alkene:alkane</i>
CE1		145	23	1	>99:1	2:1

DFT studies into dihydrogen activation at zinc

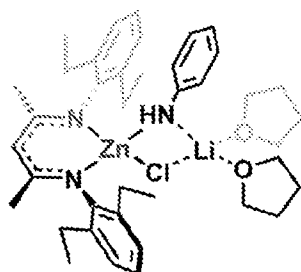
In order to explore the energetic feasibility of the dihydrogen activation process, DFT calculations were performed using the M06L functional and a hybrid basis set. In the solid state, **Compound 1** possesses an arrangement in which the core of the β-diketiminato ligand, the Zn–N motif, and the phenyl ring of the anilide all lie within the same plane. This conformation is reproduced by DFT calculations and results in an electronic structure in

20

which the frontier molecular orbitals of **Compound 1** are set up to react with dihydrogen.

Hence, the natural localized molecular orbitals (NLMOs) of **Compound 1** allow the visualization the 2p-orbital on N and the 4s-orbital on Zn, which have been found to contribute to the HOMO and LUMO+1, respectively. The dual Lewis acidic / Lewis basic

- 5 behavior of the Zn–N bond of **Compound 1** was further supported by attempts to prepare an analogue of this compound. Variation of the steric demands of the ligand on zinc (Ar = 2,6-diisopropylphenyl vs 2,6-diethylphenyl) led to the isolation of the zincate complex **Compound 2**, in which an equiv. of Li–Cl is coordinated to the Zn–N bond:

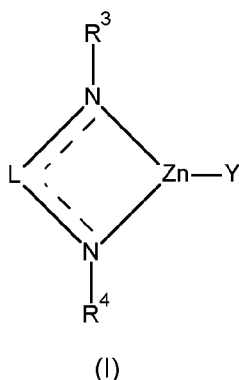


Compound 2

As shown in Figure 1, dihydrogen activation by **Compound 1** was found to occur through a stepwise process involving the formation of a weakly bound encounter complex **Int-1** which leads to **TS-1**. **Int-1** is an unstable encounter complex of zinc with dihydrogen. While there is component of bonding that involves donation of electron density from the H–H bond to the vacant 4s-orbital of Zn in **Int-1** it is not significant enough to assign this as a dihydrogen complex of zinc. Dihydrogen splitting occurs by translation of the H₂ molecule across the zinc center, towards the anilide nitrogen atom, elongating both the H–H and Zn–N distances as it nears the transition state geometry. In **TS-1** population of the s*-orbital of H₂ occurs through donation of electron density from the N-based LP, breaking the H–H bond and forming **Int-2** a weakly bound adduct of **2** and H₂NPh.

Further aspects and embodiments of the present disclosure are set out in the following numbered clauses:

1. A compound according to formula (I):



or a salt, solvate or hydrate thereof;

wherein:

5

Y is selected from $-QR^1R^2$, and OR^F ; wherein Q is selected from N, P and $P(=O)$;

L is selected from $-CR^8-CR^9-CR^{10}-$, $-CR^5-$, $-CR^6-CR^7-$, $-CR^{N3}-NR^G-CR^{N4}-$ and $-CR^{O1}-O-CR^{O2}-$;

10

either:

(A) R^1 is R^{1A} , R^2 is R^{2A} and R^4 is R^{4A} ; or

(B) R^4 is R^{4A} ; and R^1 and R^2 together with the Q moiety to which they are attached are joined to form a 3-6 membered heterocyclic group optionally substituted with one or more groups R^E ; or

15

(C) R^1 is R^{1A} ; and R^2 , R^4 and the atoms to which they are attached form a 5-8 membered heterocyclic group, optionally substituted with one or more groups R^D , and optionally being fused to one or more optionally substituted aryl groups;

20

R^3 is selected from

H;

linear or branched unsubstituted C_{1-12} aliphatic groups;

C_6 aryl, optionally substituted with one or more groups R^A , and

5-6 membered heteroaryl, optionally substituted with one or more groups R^B ;

25

R^5 , R^6 , R^7 , R^{N3} , R^{N4} , R^{O1} and R^{O2} are each independently selected from

H,

linear or branched unsubstituted C_{1-12} aliphatic groups,

C_{5-6} unsubstituted aryl or heteroaryl groups, and

30

$-NR^{N1}R^{N2}$;

R^8 , R^9 and R^{10} are each independently selected from

H,

linear or branched unsubstituted C_{1-12} aliphatic groups,

5 C_{5-6} unsubstituted aryl or heteroaryl groups, and

$-NR^{N1}R^{N2}$;

or two or more of R^8 , R^9 and R^{10} , together with the atoms to which they are attached, are joined to form a monocyclic or bicyclic group, with any remaining groups of R^8 , R^9 and R^{10} being selected from H, linear or branched unsubstituted C_{1-4} aliphatic groups, C_{5-6}

10 unsubstituted aryl or heteroaryl groups, and $-NR^{N1}R^{N2}$;

R^{1A} , R^{2A} and R^{4A} are each independently selected from

H;

linear or branched unsubstituted C_{1-12} aliphatic groups;

15 C_6 aryl, optionally substituted with one or more groups R^A ;

5-6 membered heteroaryl, optionally substituted with one or more groups R^B ;

C_{6-20} aralkyl, optionally substituted with one or more groups R^C ; and

$Si(C_{1-6}alkyl)_3$;

20 R^{N1} and R^{N2} are each independently selected from linear or branched unsubstituted C_{1-6} aliphatic groups, or R^{N1} and R^{N2} together with the N atom to which they are attached are joined to form a 3-6 membered heterocyclic group optionally substituted with one or more groups R^E ;

25 R^A , R^B , R^C , R^D and R^E are each independently selected from

linear or branched unsubstituted C_{1-6} aliphatic groups;

halo;

$O(C_{1-6}alkyl)$;

$-CF_3$, $-CF_2H$, $-CFH_2$;

30 $-OCF_3$, $-OCF_2H$ and $-OCFH_2$;

R^F and R^G are independently selected from

H;

C_{1-12} alkyl groups;

35 C_6 aryl, optionally substituted with one or more groups R^A ;

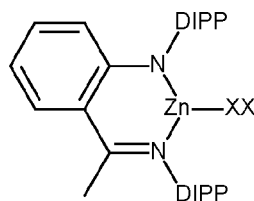
5-6 membered heteroaryl, optionally substituted with one or more groups R^B ;

C_{6-20} aralkyl, optionally substituted with one or more groups R^C ;

-S(=O)₂CF₃; and

-C(=O)R^H, wherein R^H is linear or branched C₁₋₆ alkyl optionally substituted with one or more groups independently selected from OH and halo;

5 with the proviso that the compound is not a compound according to formula (X):

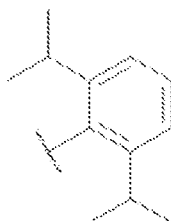


(X)

wherein the group XX is selected from -N(SiMe₃)₂ and -NH(DIPP);

10

and wherein DIPP is the group:



2. A compound according to clause 1, wherein Y is QR^1R^2 .

15

3. A compound according to clause 2, wherein Q is N.

4. A compound according to clause 2 or 3, wherein R¹ is H.

20

5. A compound according to any one of clauses 2 to 4, wherein R² is unsubstituted phenyl.

6. A compound according to any one of clauses 1 to 5, wherein R³ and R⁴ are the same.

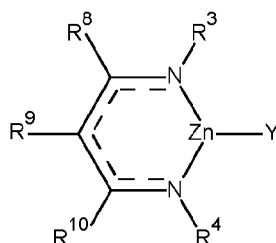
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7. A compound according to any one of clauses 1 to 6, wherein R³ and R⁴ are each independently selected from phenyl optionally substituted with one or more groups R^A.

8. A compound according to clause 7, wherein R^3 and R^4 are each independently selected from phenyl substituted in both *ortho*-positions with a group R^A .

5 9. A compound according to any one of clauses 1 to 8, wherein R^A is selected from unsubstituted branched C_{3-6} alkyl.

10. A compound according to any one of clauses 1 to 9, wherein L is $-CR^8-CR^9-CR^{10}-$, such that the compound is a compound according to formula (IA):



(IA)

or a salt, solvate or hydrate thereof.

11. A compound according to clause 10, wherein R^8 , R^9 and R^{10} are each independently selected from

H,
linear or branched unsubstituted C_{1-4} aliphatic groups,
 C_{5-6} unsubstituted aryl or heteroaryl groups, and
 $-NR^{N1}R^{N2}$.

12. A compound according to clause 10, wherein R^8 , R^9 and R^{10} are each independently selected from H and methyl.

13. A compound according to any one of clauses 10 to 12, wherein R^9 is H.

14. A compound according to any one of clauses 10 to 13, wherein one or both of R^8 and R^{10} is methyl.

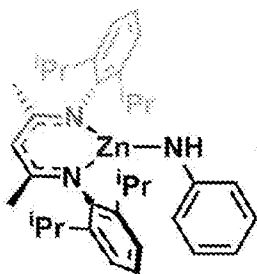
15. A compound according to any one of clauses 1 to 14, wherein R^{4A} is selected from linear or branched unsubstituted C_{1-4} aliphatic groups;
 C_6 aryl, optionally substituted with one or more groups R^A ; and

C₅₋₆ heteroaryl, optionally substituted with one or more groups R^B.

16. A compound according to any one of clauses 1 to 15, wherein R³ is selected from linear or branched unsubstituted C₁₋₄ aliphatic groups;

5 C₆ aryl, optionally substituted with one or more groups R^A; and
C₅₋₆ heteroaryl, optionally substituted with one or more groups R^B.

17. A compound according to any one of clauses 1 to 16, wherein the compound is:

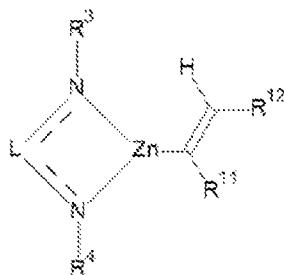


10 18. A hydrogenation catalyst comprising a compound according to any one of clauses 1 to 17.

19. A method of hydrogenation of reducing or hydrogenating a double or triple bond by reaction with dihydrogen in the presence of a catalyst comprising a compound according to
15 any one of clauses 1 to 17.

20. A method of activating dihydrogen for hydrogenation, comprising reacting dihydrogen with a catalyst comprising a compound according to any one of clauses 1 to 17.

20 21. A compound according to formula (VII):



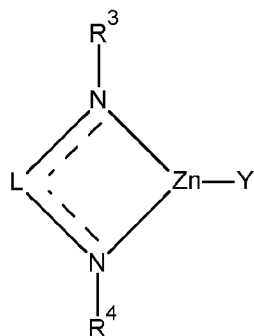
(VII)

wherein

L, R³ and R⁴ are as defined in any one of clauses 1 to 17; and

R^{11} and R^{12} are each independently selected from optionally substituted (hetero)hydrocarbyl groups.

22. A method of making a compound according to formula (I):



(I)

from starting materials comprising a compound according to formula (II):

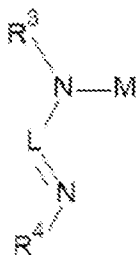


(II)

wherein Y, L, R^3 and R^4 are as defined in any one of clauses 1 to 17.

23. A method according to clause 22, comprising:

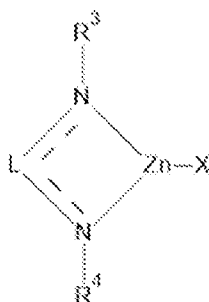
(a) reacting the compound according to formula (II) with a first metal-containing reagent to form a compound according to formula (III):



(III)

wherein M is a metal atom selected from Li, Na and K;

(b) reacting the compound according to formula (III) with a zinc salt ZnX_2 to form a compound according to formula (IV):



(IV)

5 wherein X is a monovalent anion;
and

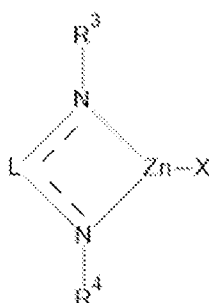
(c) converting the compound according to formula (IV) into the compound according to formula (I);

10 wherein one or both of the first metal-containing reagent and the second metal-containing reagent optionally comprises $n\text{BuLi}$.

24. A method according to clause 23, wherein step (c) comprises reacting the compound according to formula (IV) with $\text{M}'\text{Y}$, wherein $\text{M}'\text{Y}$ is optionally made by reacting a second metal-containing reagent with YH .

15

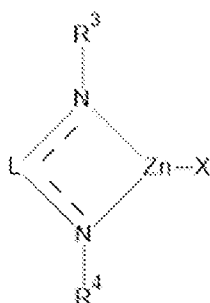
25. An intermediate according to formula (IV):



(IV)

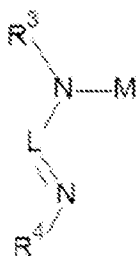
20 wherein L, R³ and R⁴ are as defined in any one of clauses 1 to 17 and X is a monovalent anion.

26. A method of making an intermediate according to formula (IV):



(IV)

comprising reacting a compound according to formula (III) with ZnX_2

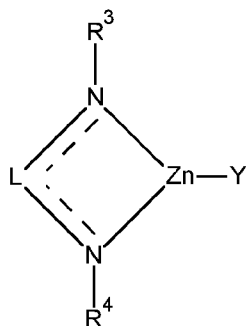


(III)

5

wherein L, R^3 and R^4 are as defined in any one of clauses 1 to 17, M is a metal atom selected from Li, Na and K and X is a monovalent anion.

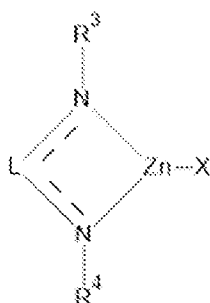
27. A method of making a compound according to formula (I):



(I)

10

from a compound according to formula (IV):

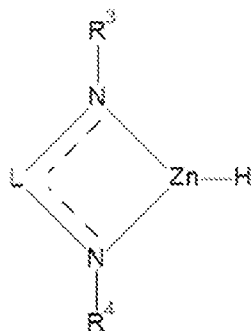


(IV)

wherein Y, L, R³ and R⁴ are as defined in any one of clauses 1 to 17, and X is a monovalent anion.

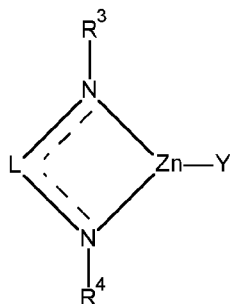
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28. A method of making a compound according to formula (VIII):



(VIII)

10 comprising reacting a compound according to formula (I):

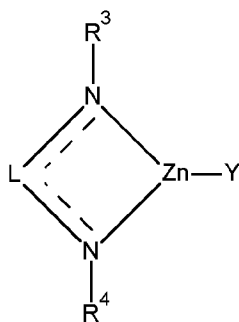


(I)

with dihydrogen (H₂), wherein L, Y, R³ and R⁴ are as defined in any one of clauses 1 to 17.

Claims

1. A compound according to formula (I):



5

(I)

or a salt, solvate or hydrate thereof;

wherein:

10 Y is -NHR²;

L is selected from -CR⁸-CR⁹-CR¹⁰-, -CR⁵-, -CR⁶-CR⁷-, -CR^{N3}-NR^G-CR^{N4}- and -CR^{O1}-O-CR^{O2}-;

15 either:

(A) R² is R^{2A} and R⁴ is R^{4A}; or

(B) R² and R⁴ and the atoms to which they are attached form a 5-8 membered heterocyclic group, optionally substituted with one or more groups R^D, and optionally being
20 fused to one or more optionally substituted aryl groups;

R³ is selected from

H;

linear or branched unsubstituted C₁₋₁₂ aliphatic groups;

25 C₆ aryl, optionally substituted with one or more groups R^A, and

5-6 membered heteroaryl, optionally substituted with one or more groups R^B;

R⁵, R⁶, R⁷, R^{N3}, R^{N4}, R^{O1} and R^{O2} are each independently selected from

H,

30 linear or branched unsubstituted C₁₋₁₂ aliphatic groups,

C₅₋₆ unsubstituted aryl or heteroaryl groups, and
-NR^{N1}R^{N2};

R⁸, R⁹ and R¹⁰ are each independently selected from

- 5 H,
 linear or branched unsubstituted C₁₋₁₂ aliphatic groups,
 C₅₋₆ unsubstituted aryl or heteroaryl groups, and
 -NR^{N1}R^{N2};

- or two or more of R⁸, R⁹ and R¹⁰, together with the atoms to which they are attached, are
10 joined to form a monocyclic or bicyclic group, with any remaining groups of R⁸, R⁹ and R¹⁰
 being selected from H, linear or branched unsubstituted C₁₋₄ aliphatic groups, C₅₋₆
 unsubstituted aryl or heteroaryl groups, and -NR^{N1}R^{N2};

R^{2A} and R^{4A} are each independently selected from

- 15 H;
 linear or branched unsubstituted C₁₋₁₂ aliphatic groups;
 C₆ aryl, optionally substituted with one or more groups R^A;
 5-6 membered heteroaryl, optionally substituted with one or more groups R^B;
 C₆₋₂₀ aralkyl, optionally substituted with one or more groups R^C; and
20 Si(C₁₋₆alkyl)₃;

- R^{N1} and R^{N2} are each independently selected from linear or branched unsubstituted C₁₋₆
 aliphatic groups, or R^{N1} and R^{N2} together with the N atom to which they are attached are
25 joined to form a 3-6 membered heterocyclic group optionally substituted with one or more
 groups R^E;

R^A, R^B, R^C, R^D and R^E are each independently selected from

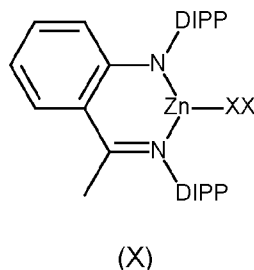
- linear or branched unsubstituted C₁₋₆ aliphatic groups;
 halo;
30 O(C₁₋₆alkyl);
 -CF₃, -CF₂H, -CFH₂;
 -OCF₃, -OCF₂H and -OCFH₂;

R^F and R^G are independently selected from

- 35 H;
 C₁₋₁₂ alkyl groups;
 C₆ aryl, optionally substituted with one or more groups R^A;

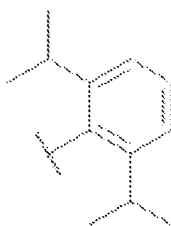
- 5-6 membered heteroaryl, optionally substituted with one or more groups R^B ;
 C_{6-20} aralkyl, optionally substituted with one or more groups R^C ;
 $-S(=O)_2CF_3$; and
 $-C(=O)R^H$, wherein R^H is linear or branched C_{1-6} alkyl optionally substituted with one
 5 or more groups independently selected from OH and halo;

with the proviso that the compound is not a compound according to formula (X):



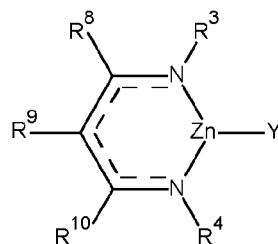
wherein the group XX is $-NH(DIPP)$;

and wherein DIPP is the group:



2. A compound according to claim 1, wherein R^2 is unsubstituted phenyl.
3. A compound according to claim 1 or claim 2, wherein R^3 and R^4 are the same.
4. A compound according to any one of claims 1 to 3, wherein R^3 and R^4 are each
 20 independently selected from phenyl optionally substituted with one or more groups R^A .
5. A compound according to claim 4, wherein R^3 and R^4 are each independently
 selected from phenyl substituted in both *ortho*-positions with a group R^A .
6. A compound according to any one of claims 1 to 5, wherein R^A is selected from
 25 unsubstituted branched C_{3-6} alkyl.

7. A compound according to any one of claims 1 to 6, wherein L is $-\text{CR}^8-\text{CR}^9-\text{CR}^{10}-$, such that the compound is a compound according to formula (IA):



5

(IA)

or a salt, solvate or hydrate thereof.

8. A compound according to claim 7, wherein R^8 , R^9 and R^{10} are each independently selected from

10

H,
linear or branched unsubstituted C_{1-4} aliphatic groups,
 C_{5-6} unsubstituted aryl or heteroaryl groups, and
 $-\text{NR}^{\text{N}1}\text{R}^{\text{N}2}$.

15

9. A compound according to claim 7, wherein R^8 , R^9 and R^{10} are each independently selected from H and methyl.

10. A compound according to any one of claims 7 to 9, wherein R^9 is H.

20

11. A compound according to any one of claims 7 to 10, wherein one or both of R^8 and R^{10} is methyl.

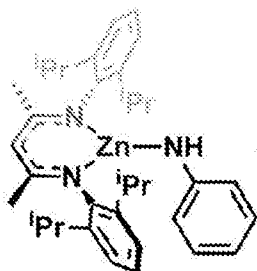
12. A compound according to any one of claims 1 to 11, wherein $\text{R}^{4\text{A}}$ is selected from linear or branched unsubstituted C_{1-4} aliphatic groups;
 C_6 aryl, optionally substituted with one or more groups R^{A} ; and
 C_{5-6} heteroaryl, optionally substituted with one or more groups R^{B} .

25

13. A compound according to any one of claims 1 to 12, wherein R^3 is selected from linear or branched unsubstituted C_{1-4} aliphatic groups;
 C_6 aryl, optionally substituted with one or more groups R^{A} ; and
 C_{5-6} heteroaryl, optionally substituted with one or more groups R^{B} .

30

14. A compound according to any one of claims 1 to 13, wherein the compound is:

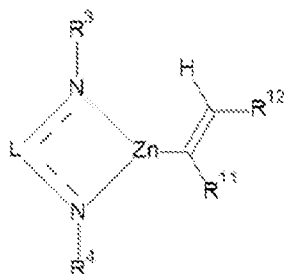


15. A hydrogenation catalyst comprising a compound according to any one of claims 1 to 14.

16. A method of hydrogenation of reducing or hydrogenating a double or triple bond by reaction with dihydrogen in the presence of a catalyst comprising a compound according to any one of claims 1 to 14.

17. A method of activating dihydrogen for hydrogenation, comprising reacting dihydrogen with a catalyst comprising a compound according to any one of claims 1 to 14.

18. A compound according to formula (VII):



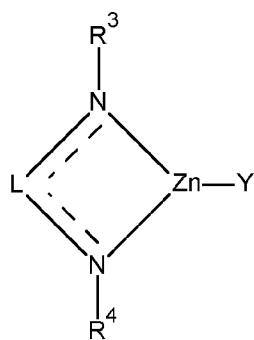
(VII)

wherein

L, R³ and R⁴ are as defined in any one of claims 1 to 14; and

R¹¹ and R¹² are each independently selected from optionally substituted (hetero)hydrocarbyl groups.

19. A method of making a compound according to formula (I):



(I)

from starting materials comprising a compound according to formula (II):



(II)

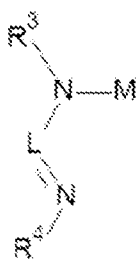
5

wherein Y, L, R³ and R⁴ are as defined in any one of claims 1 to 14.

20. A method according to claim 19, comprising:

- (a) reacting the compound according to formula (II) with a first metal-
containing reagent to form a compound according to formula (III):

10

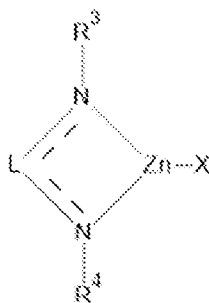


(III)

wherein M is a metal atom selected from Li, Na and K;

- (b) reacting the compound according to formula (III) with a zinc salt ZnX₂ to form a
compound according to formula (IV):

15



(IV)

wherein X is a monovalent anion;

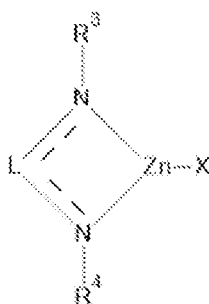
and

- 5 (c) converting the compound according to formula (IV) into the compound according to formula (I);

wherein one or both of the first metal-containing reagent and the second metal-containing reagent optionally comprises ⁿBuLi.

- 10 21. A method according to claim 20, wherein step (c) comprises reacting the compound according to formula (IV) with M'Y, wherein M'Y is optionally made by reacting a second metal-containing reagent with YH.

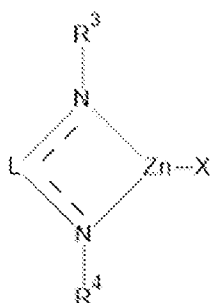
22. An intermediate according to formula (IV):



(IV)

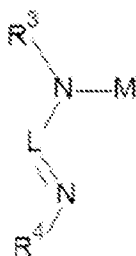
wherein L, R³ and R⁴ are as defined in any one of claims 1 to 14 and X is a monovalent anion.

- 20 23. A method of making an intermediate according to formula (IV):



(IV)

comprising reacting a compound according to formula (III) with ZnX_2

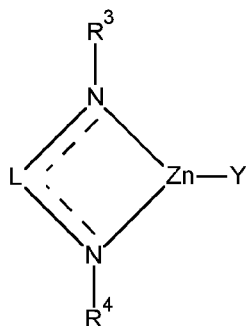


(III)

5

wherein L, R^3 and R^4 are as defined in any one of claims 1 to 14, M is a metal atom selected from Li, Na and K and X is a monovalent anion.

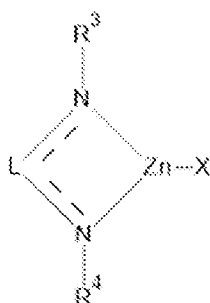
24. A method of making a compound according to formula (I):



(I)

10

from a compound according to formula (IV):

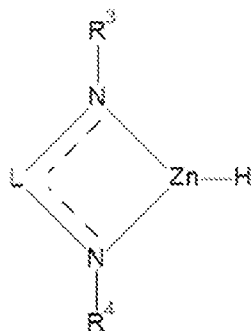


(IV)

wherein Y, L, R³ and R⁴ are as defined in any one of claims 1 to 14, and X is a monovalent anion.

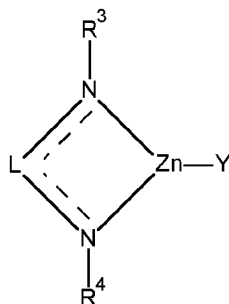
5

25. A method of making a compound according to formula (VIII):



(VIII)

10 comprising reacting a compound according to formula (I):



(I)

with dihydrogen (H₂), wherein L, Y, R³ and R⁴ are as defined in any one of claims 1 to 14.

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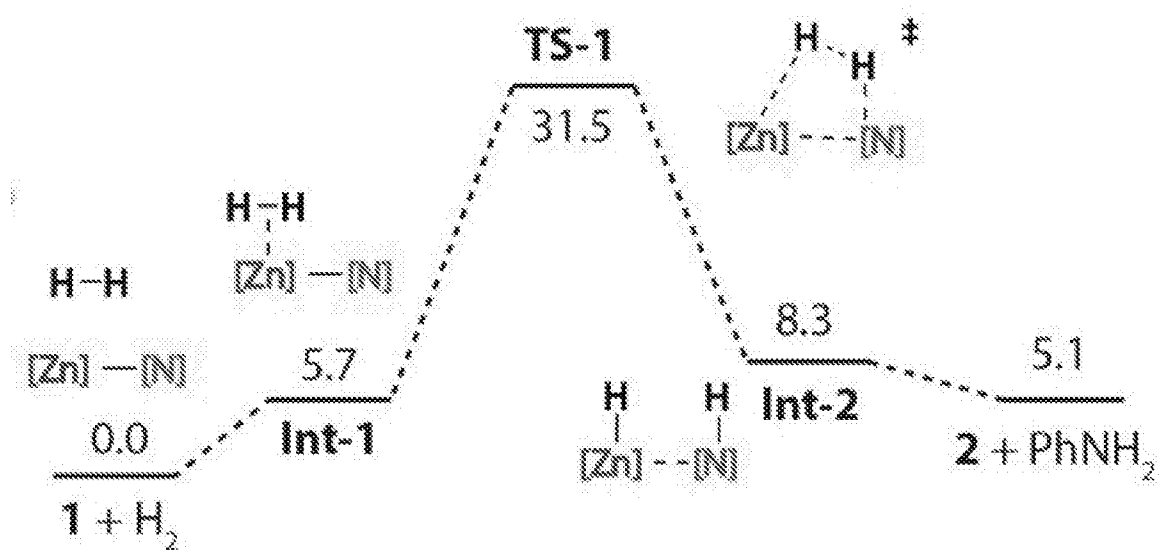


Fig. 1

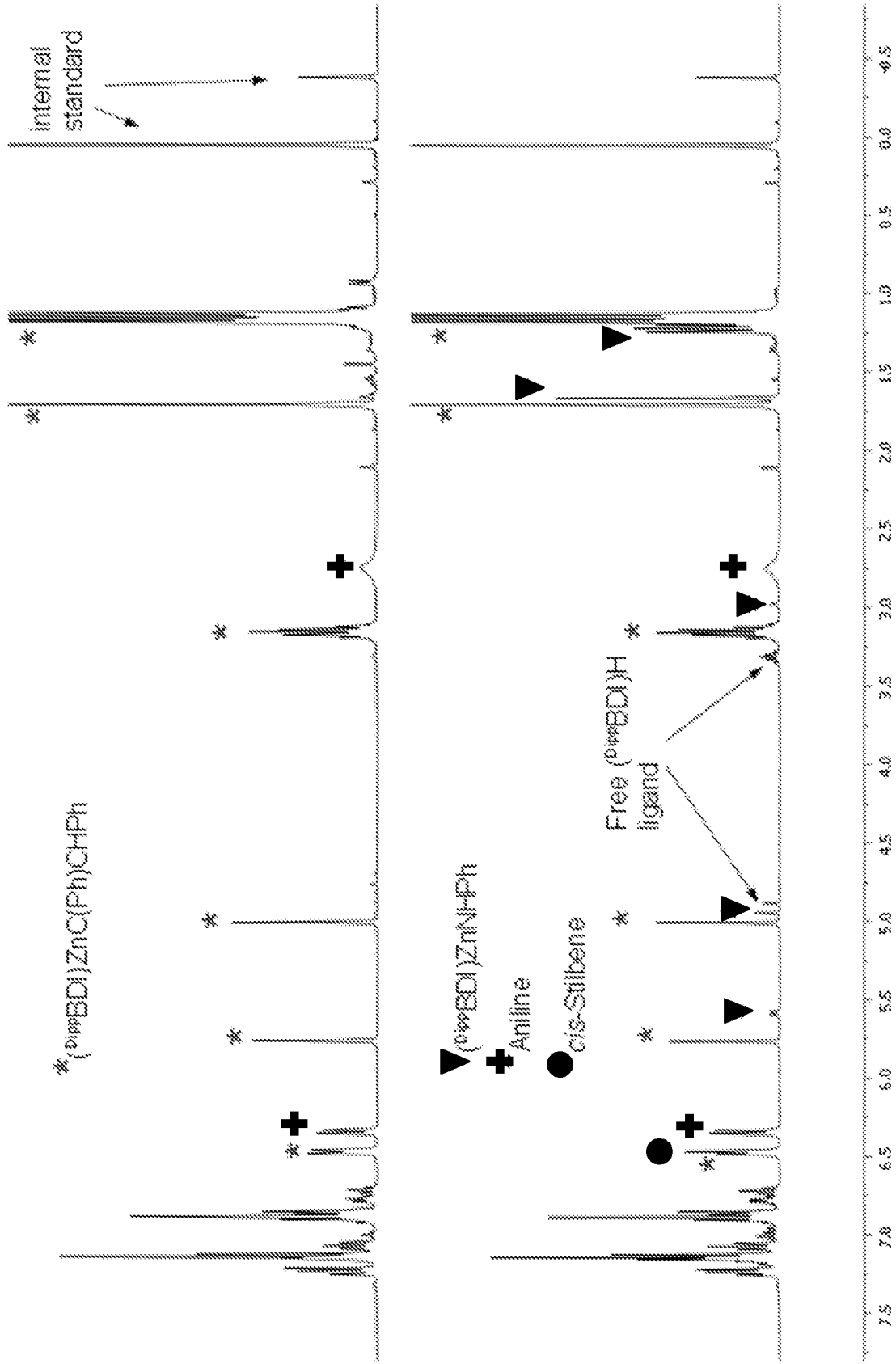


Fig. 2

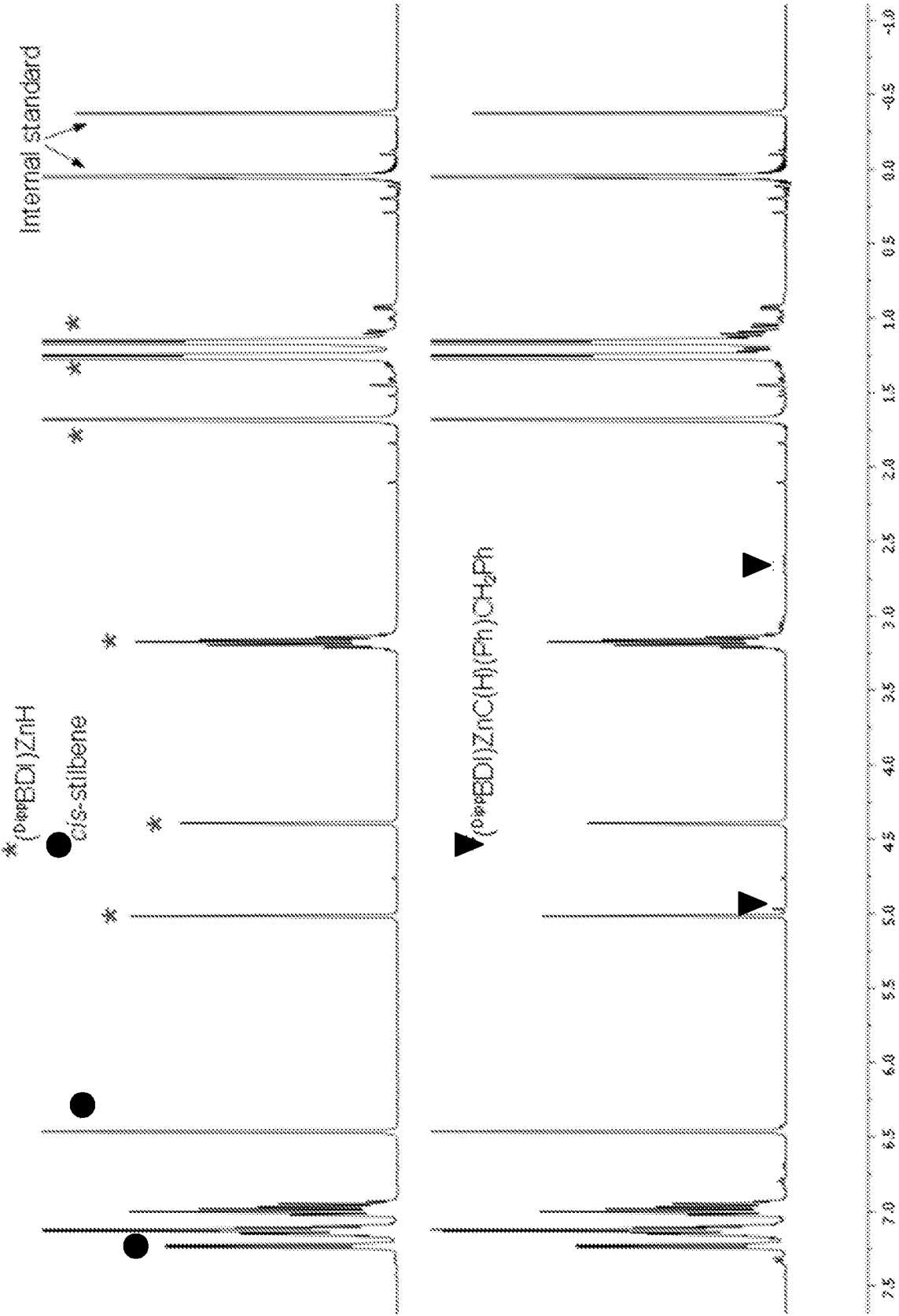


Fig. 3

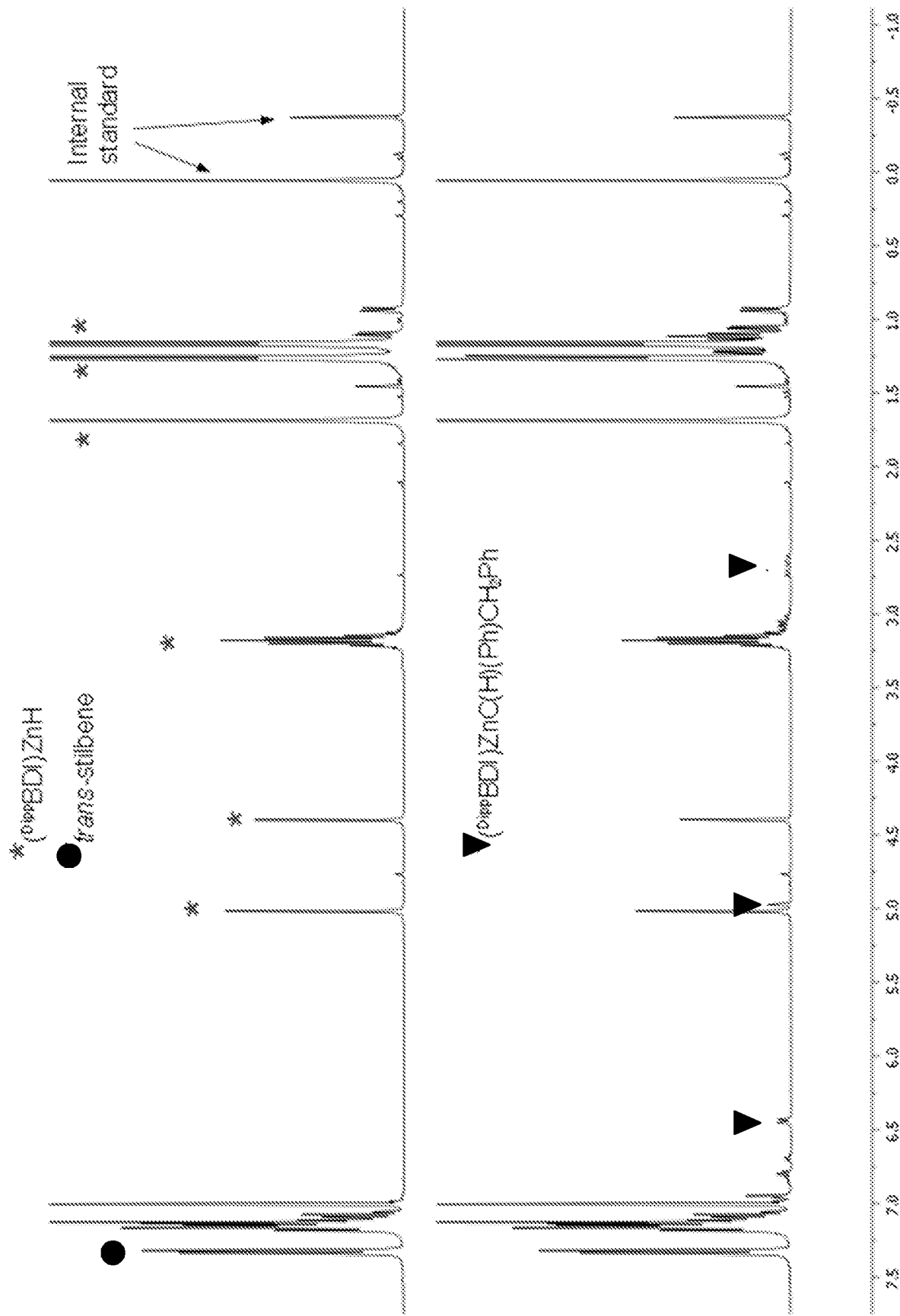


Fig. 4

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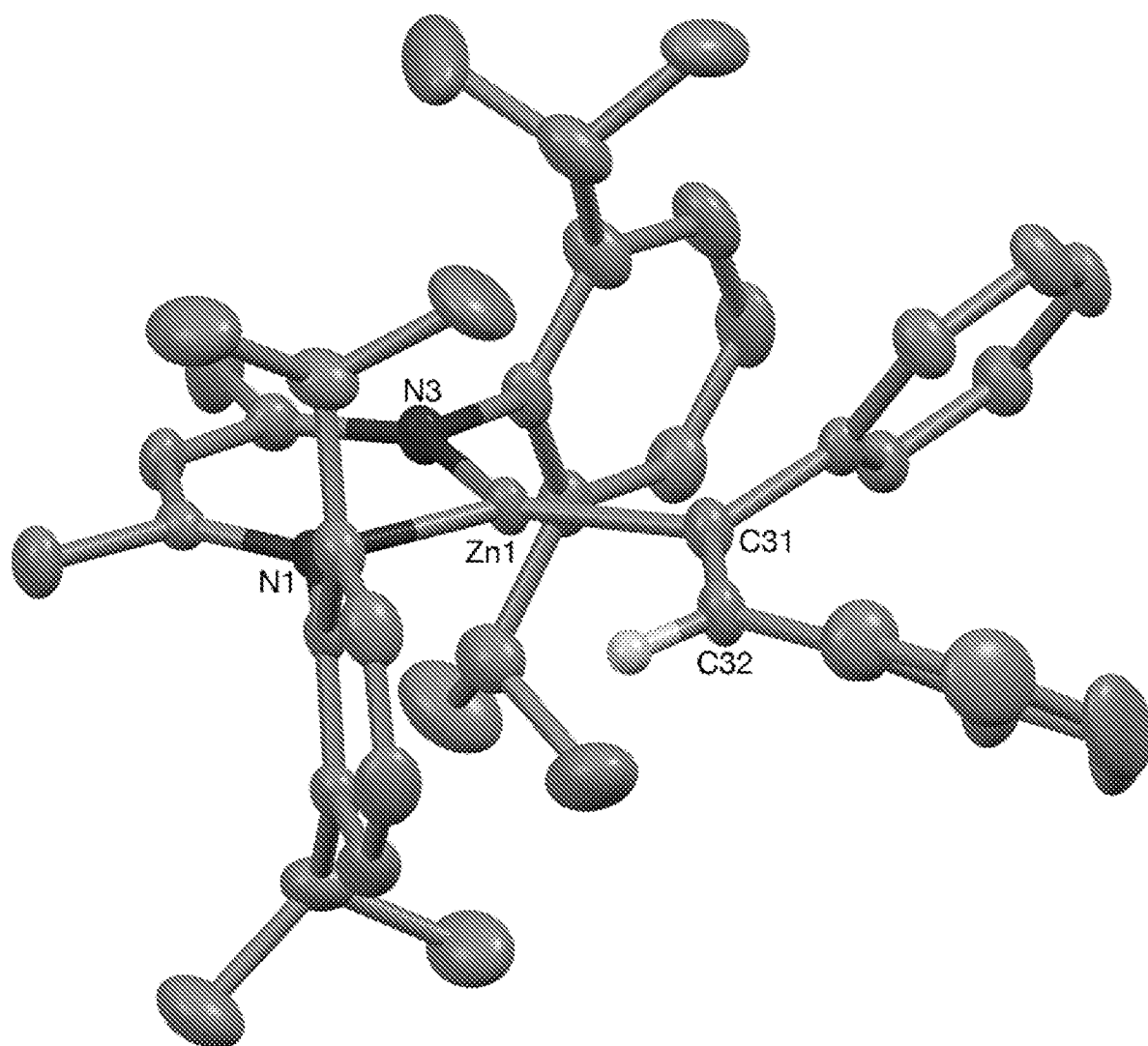


Fig. 5

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2021/051856

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07F3/00 C07C5/09 B01J23/06
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 C07C

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, 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	SCHMIDT SARAH ET AL: "Synthesis and Structural Characterization of New Zinc Amidinate Complexes", ORGANOMETALLICS, vol. 29, no. 22, 28 October 2010 (2010-10-28), pages 6097-6103, XP55852512, ISSN: 0276-7333, DOI: 10.1021/om1008549 compounds 2,3,6,7 ----- -/--	22,23



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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"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

19 October 2021

Date of mailing of the international search report

29/10/2021

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Fax: (+31-70) 340-3016

Authorized officer

Diederer, Jeroen

INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2021/051856

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	SCHULZ STEPHAN ET AL: "X-Ray crystal structure of a heterobimetallic Al-Zn-oxide complex", CHEMICAL COMMUNICATIONS, vol. 47, no. 9, 1 January 2011 (2011-01-01), pages 2676-2678, XP55852517, UK ISSN: 1359-7345, DOI: 10.1039/c0cc05599a Retrieved from the Internet: URL:https://pubs.rsc.org/en/content/articlepdf/2011/cc/c0cc05599a> Scheme 2	22,23
X	----- LORTIE JOHN L. ET AL: "Zinc-Catalyzed Hydrosilylation and Hydroboration of N-Heterocycles", ACS CATALYSIS, vol. 7, no. 12, 1 December 2017 (2017-12-01), pages 8454-8459, XP55852528, US ISSN: 2155-5435, DOI: 10.1021/acscatal.7b02811 Retrieved from the Internet: URL:https://pubs.acs.org/doi/pdf/10.1021/acscatal.7b02811> NaCNZnCl	22,23
X	& LORTIE JOHN L ET AL: "Supporting Information Zinc-Catalyzed Hydrosilylation and Hydroboration of N-Heterocycles Contents", ACS CATALYSIS, vol. 7, no. 12, 1 January 2017 (2017-01-01), pages 1-79, XP55852666,	22,23
X	----- PRUST JÖRG ET AL: "Synthesis and Structural Characterization of Monomeric Three-Coordinated [beta]-Diketoiminate Organozinc Derivatives", ORGANOMETALLICS, vol. 20, no. 17, 1 August 2001 (2001-08-01), pages 3825-3828, XP55852568, ISSN: 0276-7333, DOI: 10.1021/om010301x compounds 1-4 ----- -/--	22,23

INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2021/051856

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DOVE ANDREW P. ET AL: "Magnesium and zinc complexes of a potentially tridentate [beta]-diketiminat ligand", DALTON TRANSACTIONS, no. 4, 1 January 2004 (2004-01-01), pages 570-578, XP55852574, Cambridge ISSN: 1477-9226, DOI: 10.1039/B314760F compounds 8,10 -----	22,23
X	JONES CAMERON ET AL: "Synthesis and characterisation of zinc gallyl complexes: First structural elucidations of Zn-Ga bonds", DALTON TRANSACTIONS, no. 28, 1 January 2007 (2007-01-01), pages 2997-2999, XP55852580, Cambridge ISSN: 1477-9226, DOI: 10.1039/B706402K compound 2 -----	22,23
X	SCHULZ STEPHAN ET AL: "Synthesis and Characterization of [beta] -Diketiminat Zinc Complexes", ZEITSCHRIFT FUR ANORGANISCHE UND ALLGEMEINE CHEMIE, vol. 635, no. 2, 1 February 2009 (2009-02-01), pages 216-220, XP55852582, ISSN: 0044-2313, DOI: 10.1002/zaac.200800374 compounds 1-3 -----	22,23
A	BARTH JOHANN AMBROSIUS ET AL: "The Reagent (Z)-Selektive Reduktion von konjugierten Dreifachbindungen rnit Zn (Cu/Ag)l) (Z-)-Selective Reduction of Conjugated Alkynes with Zn (CdAg)", JOURNAL FUR PRAKTISCHE CHEMIE CHEMIKER-ZEITUNG DAS REAGENZ *, vol. 336, 1 January 1994 (1994-01-01), pages 714-715, XP55852711, the whole document -----	1-25