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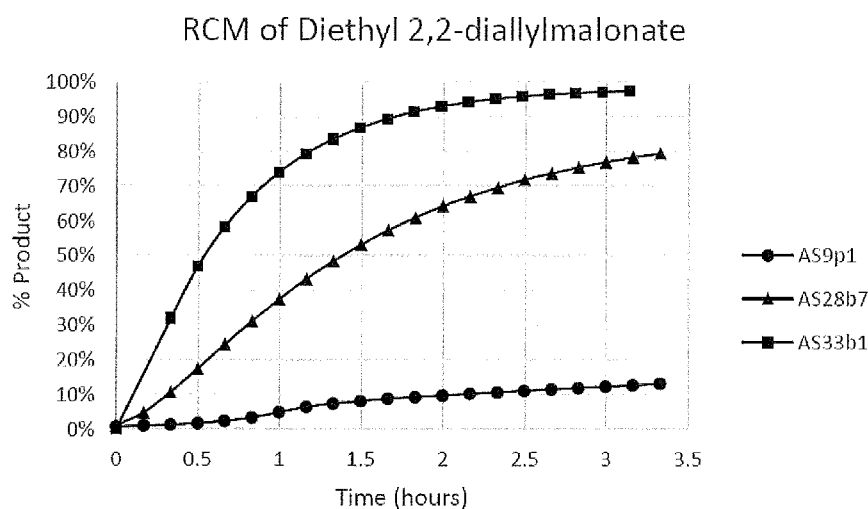
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(54) Title: METAL ORGANIC COMPOUNDS

Figure 1



(57) Abstract: This invention relates generally to olefin metathesis catalysts comprising cyclic alkyl amino carbenes, to the preparation of such compounds, compositions comprising such compounds, methods of using such compounds, and the use of such compounds in the metathesis of olefins. The invention has utility in the fields of catalysis, organic synthesis, polymer chemistry, and in industrial applications such as oil and gas, fine chemicals and pharmaceuticals.

METAL ORGANIC COMPOUNDS

TECHNICAL FIELD

[0001] This invention relates generally to olefin metathesis catalysts comprising cyclic alkyl amino carbenes, to the preparation of such compounds, compositions comprising such compounds, methods of using such compounds, and the use of such compounds in the metathesis of olefins. The invention has utility in the fields of catalysis, organic synthesis, polymer chemistry, and in industrial applications such as oil and gas, fine chemicals and pharmaceuticals.

BACKGROUND

[0002] Since its discovery in the 1950s, olefin metathesis has emerged as a valuable synthetic method for the formation of carbon-carbon double bonds. Recent advances in applications to organic syntheses and polymer syntheses mostly rely on developments of well-defined olefin metathesis catalysts.

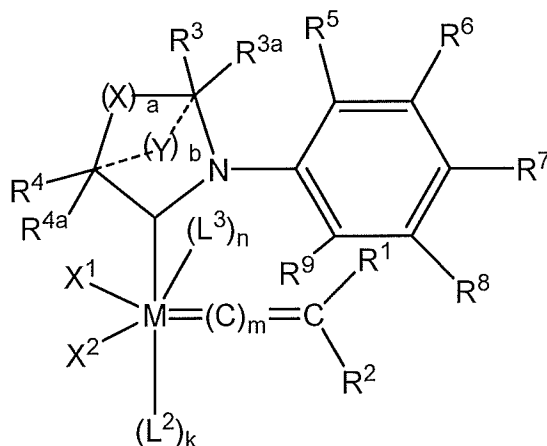
[0003] The technology of ruthenium metathesis catalysts has enabled the development of several research platforms including: ring opening metathesis polymerization (ROMP), ring opening cross metathesis (ROCM), cross metathesis (CM), ring closing metathesis (RCM).

[0004] The incorporation of N-Heterocyclic Carbene (NHC) ligands has played an essential role in the development of ruthenium metathesis catalysts. Metathesis catalysts, based on ruthenium, are known and have been studied.

[0005] However, there is an ongoing need for olefin metathesis catalysts, particularly ruthenium metathesis catalysts with improved characteristics which will further enable their use in a wider array of applications and olefin metathesis reactions, and for methods to prepare them.

SUMMARY OF THE INVENTION

[0006] To meet this need, the inventors have discovered various olefin metathesis catalysts, comprising cyclic alkyl amino carbenes, represented by the general structure of **Formula (I)**:

**Formula (I)**

wherein:

M is Ru or Os; typically, M is Ru;

L^2 and L^3 are independently neutral ligands;

m is 0, 1 or 2; generally, m is 0 or 1; typically, m is 0;

n is 0 or 1; generally, n is 0;

k is 0 or 1; generally, k is 1;

X^1 and X^2 are independently anionic ligands; generally, X^1 and X^2 are independently halogen, trifluoroacetate, per-fluorophenols, -NCO, -CN, -NCS, -N₃; or X^1 together with X^2 can form a nitrate; typically, X^1 and X^2 are independently halogen, or -NCO;

R^1 and R^2 are independently selected from hydrogen, optionally substituted hydrocarbyl, optionally substituted heteroatom-containing hydrocarbyl; or any two or more of X^1 , X^2 , L^2 , L^3 , R^1 , and R^2 are taken together to form one or more cyclic groups;

X is $-CR^{1a}R^{2a}$;

a is 1 or 2;

R^{1a} is H, optionally substituted C₁₋₂₄ alkyl, optionally substituted C₃₋₈ cycloalkyl, halogen, optionally substituted C₅₋₂₄ aryl, optionally substituted C₆₋₂₄ aralkyl, optionally substituted C₁₋₂₀ heteroalkyl, -C(O) R^{21} , -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, or together with R^{2a} forms an optionally substituted spiro monocyclic or spiro polycyclic C₃₋₁₀ cycloalkyl or spiro heterocyclic ring, with the carbon atom to which they are attached, or together with R^3 or together with R^4 forms an optionally substituted polycyclic ring;

R^{2a} is H, optionally substituted C₁₋₂₄ alkyl, optionally substituted C₃₋₈ cycloalkyl, halogen, optionally substituted C₅₋₂₄ aryl, optionally substituted C₆₋₂₄ aralkyl, optionally substituted C₁₋₂₀ heteroalkyl, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, or together with R^{1a} forms a spiro monocyclic or spiro polycyclic C₃₋₁₀ cycloalkyl or spiro heterocyclic ring, with the carbon atom to which they are attached, or together with R³ or together with R⁴ forms an optionally substituted polycyclic ring;

Y is -CR^{1b}R^{2b};

b is 0, 1 or 2;

R^{1b} is H, optionally substituted C₁₋₂₄ alkyl, optionally substituted C₃₋₈ cycloalkyl, halogen, optionally substituted C₅₋₂₄ aryl, optionally substituted C₆₋₂₄ aralkyl, optionally substituted C₁₋₂₀ heteroalkyl, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, or together with R^{2b} forms a five-, six-, or ten-membered cycloalkyl or heterocyclic ring, with the carbon atom to which they are attached;

R^{2b} is H, optionally substituted C₁₋₂₄ alkyl, optionally substituted C₃₋₈ cycloalkyl, halogen, optionally substituted C₅₋₂₄ aryl, optionally substituted C₆₋₂₄ aralkyl, optionally substituted C₁₋₂₀ heteroalkyl, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, or together with R^{1b} forms a five-, six-, or ten-membered cycloalkyl or heterocyclic ring, with the carbon atom to which they are attached;

R³ is H, optionally substituted C₁₋₂₄ alkyl, halogen, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, optionally substituted heterocycle, optionally substituted C₃₋₈ cycloalkyl, optionally substituted C₅₋₂₄ aryl, optionally substituted C₃₋₈ cycloalkenyl, or together with R^{1a} or together with R^{2a} can form an optionally substituted polycyclic ring, or together with R^{3a} can form an optionally substituted spiro monocyclic or spiro polycyclic C₃₋₁₀ cycloalkyl;

R^{3a} is H, optionally substituted C₁₋₂₄ alkyl, halogen, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, optionally substituted heterocycle, optionally substituted C₃₋₈ cycloalkyl, optionally substituted C₅₋₂₄ aryl, optionally substituted C₃₋₈ cycloalkenyl, or together with R^{1a} or together with R^{2a} can form an optionally substituted polycyclic ring, or together with R³ can form an optionally substituted spiro monocyclic or spiro polycyclic C₃₋₁₀ cycloalkyl;

R⁴ is H, optionally substituted C₁₋₂₄ alkyl, halogen, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, optionally substituted heterocycle, optionally substituted C₃₋₈ cycloalkyl, optionally substituted C₅₋₂₄ aryl, optionally substituted C₃₋₈ cycloalkenyl, or together with R^{1a} or together with R^{2a} can form an optionally substituted polycyclic ring, or together with R^{4a} can form an optionally substituted spiro monocyclic or spiro polycyclic C₃₋₁₀ cycloalkyl;

R^{4a} is H, optionally substituted C₁₋₂₄ alkyl, halogen, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, optionally substituted heterocycle, optionally substituted C₃₋₈ cycloalkyl, optionally substituted C₅₋₂₄ aryl, optionally substituted C₃₋₈ cycloalkenyl, or together with R^{1a} or together with R^{2a} can form an optionally substituted polycyclic ring, or together with R⁴ can form an optionally substituted spiro monocyclic or spiro polycyclic C₃₋₁₀ cycloalkyl;

R⁵ is H, optionally substituted C₁₋₂₄ alkyl, halogen, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, optionally substituted heterocycle, optionally substituted C₃₋₈ cycloalkyl, optionally substituted C₅₋₂₄ aryl, optionally substituted C₃₋₈ cycloalkenyl, or together with R⁶ can form an optionally substituted polycyclic ring;

R⁶ is H, optionally substituted C₁₋₂₄ alkyl, halogen, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, optionally substituted heterocycle, optionally substituted C₃₋₈ cycloalkyl, optionally substituted C₅₋₂₄ aryl, optionally substituted C₃₋₈ cycloalkenyl or together with R⁵ or together with R⁷ can form an optionally substituted polycyclic ring;

R⁷ is H, optionally substituted C₁₋₂₄ alkyl, halogen, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, optionally substituted heterocycle, optionally substituted C₃₋₈ cycloalkyl, optionally substituted C₅₋₂₄ aryl, optionally substituted C₃₋₈ cycloalkenyl, or together with R⁶ or together with R⁸ can form an optionally substituted polycyclic ring;

R⁸ is H, optionally substituted C₁₋₂₄ alkyl, halogen, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, optionally substituted heterocycle, optionally substituted C₃₋₈ cycloalkyl, optionally substituted C₅₋₂₄ aryl, optionally substituted C₃₋₈ cycloalkenyl, or together with R⁷ or together with R⁹ can form an optionally substituted polycyclic ring;

R⁹ is H, optionally substituted C₁₋₂₄ alkyl, halogen, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, optionally substituted heterocycle, optionally substituted C₃₋₈ cycloalkyl, optionally substituted C₅₋₂₄ aryl, optionally substituted C₃₋₈ cycloalkenyl, or together with R⁸ can form a polycyclic ring;

R²¹ is OH, OR²⁶, NR²³R²⁴, optionally substituted C₁₋₂₄ alkyl, optionally substituted C₃₋₈ cycloalkyl, optionally substituted heterocycle, optionally substituted C₅₋₂₄ aryl or optionally substituted C₃₋₈ cycloalkenyl;

R²² is H, optionally substituted C₁₋₂₄ alkyl, optionally substituted C₃₋₈ cycloalkyl, optionally substituted heterocycle, optionally substituted C₅₋₂₄ aryl or optionally substituted C₃₋₈ cycloalkenyl;

R²³ is H, optionally substituted C₁₋₂₄ alkyl, optionally substituted C₃₋₈ cycloalkyl, optionally substituted heterocycle, optionally substituted C₅₋₂₄ aryl or optionally substituted C₃₋₈ cycloalkenyl;

R²⁴ is H, optionally substituted C₁₋₂₄ alkyl, optionally substituted C₃₋₈ cycloalkyl, optionally substituted heterocycle, optionally substituted C₅₋₂₄ aryl or optionally substituted C₃₋₈ cycloalkenyl;

R²⁵ is H, optionally substituted C₁₋₂₄ alkyl, OR²², -NR²³R²⁴, optionally substituted heterocycle, optionally substituted C₃₋₈ cycloalkyl, optionally substituted C₅₋₂₄ aryl or optionally substituted C₃₋₈ cycloalkenyl;

R²⁶ is optionally substituted C₁₋₂₄ alkyl, optionally substituted C₃₋₈ cycloalkyl, optionally substituted heterocycle, optionally substituted C₅₋₂₄ aryl or optionally substituted C₃₋₈ cycloalkenyl;

R²⁷ is H, optionally substituted C₁₋₂₄ alkyl, optionally substituted C₃₋₈ cycloalkyl, optionally substituted heterocycle, optionally substituted C₅₋₂₄ aryl or optionally substituted C₃₋₈ cycloalkenyl;

x is 1 or 2; and with the provisos

- a. when a is 2, then the "X-X" bond can be saturated or unsaturated;
- b. when b is 2, the "Y-Y" bond can be saturated or unsaturated;
- c. when a is 2, and the "X-X" bond is unsaturated, then R^{2a} is nil;
- d. when b is 1, then R^{3a} and R^{4a} are both nil;
- e. when b is 2, then R^{3a} and R^{4a} are both nil;

f. when b is 2, and the "Y-Y" bond is unsaturated, then R^{2b} is nil.

[0007] In one embodiment, the invention provides a method of synthesizing the olefin metathesis catalysts of the invention.

[0008] In one embodiment, the invention provides a method of using the olefin metathesis catalysts of the invention in metathesis reactions. The olefin metathesis catalysts of the invention are of particular benefit for use in metathesis reactions, such as ring opening metathesis polymerization reactions, ring-opening cross metathesis reactions, cross metathesis reactions, ring-closing metathesis reactions, self-metathesis reactions, as well as combinations of such metathesis reactions.

[0009] The olefin metathesis catalysts of the invention are also key intermediates in the synthesis of a variety of ruthenium olefin metathesis catalysts.

[0010] These and other aspects of the present invention will be apparent to the skilled artisan in light of the following detailed description and examples. Furthermore, it is to be understood that none of the embodiments or examples of the invention described herein are to be interpreted as being limiting.

DETAILED DESCRIPTION

[0011] In this specification and in the claims that follow, reference will be made to a number of terms, which shall be defined to have the meanings as described herein.

[0012] The term "alkyl" as used herein, refers to a linear, branched, saturated hydrocarbon group typically containing 1 to 24 carbon atoms, preferably 1 to 12 carbon atoms, more preferably 1 to 6 carbon atoms: such as methyl (Me), ethyl (Et), n-propyl (Pr or n-Pr), isopropyl (i-Pr), n-butyl (Bu or n-Bu), isobutyl (i-Bu), t-butyl (t-Bu), octyl (Oct), decyl, and the like.

[0013] The term "cycloalkyl" refers to a cyclic alkyl group, can be monocyclic, bicyclic or polycyclic, typically having 3 to 10, preferably 5 to 7, carbon atoms, generally, cycloalkyl groups are cyclopentyl (Cp), cyclohexyl (Cy), adamantly.

[0014] The term "substituted alkyl" refers to alkyl substituted with one or more substituent groups, and the terms "heteroatom-containing alkyl" and "heteroalkyl" refer to alkyl in which at least one carbon atom is replaced with a heteroatom.

[0015] The term "alkylene" as used herein refers to a difunctional linear, branched alkyl group, where "alkyl" is as defined above.

[0016] The term "alkenyl" as used herein refers to a linear, branched hydrocarbon group of 2 to 24 carbon atoms containing at least one double bond, such as ethenyl, n-propenyl, iso-propenyl, n-butenyl, iso-butenyl, octenyl, decenyl, tetradecenyl, hexadecenyl, and the like. Preferred alkenyl groups herein contain 2 to 12 carbon atoms, more preferred alkenyl groups herein contain 2 to 6 carbon atoms.

[0017] The term "substituted alkenyl" refers to alkenyl substituted with one or more substituent groups, and the terms "heteroatom-containing alkenyl" and "heteroalkenyl" refer to alkenyl in which at least one carbon atom is replaced with a heteroatom.

[0018] The term "cycloalkenyl" refers to a cyclic alkenyl group, preferably having 3 to 8 carbon atoms.

[0019] The term "alkenylene" as used herein refers to a difunctional linear, branched, where "alkenyl" is as defined above.

[0020] The term "alkynyl" as used herein refers to a linear or branched hydrocarbon group of 2 to 24 carbon atoms containing at least one triple bond, such as ethynyl, n-propynyl, and the like. Preferred alkynyl groups herein contain 2 to 12 carbon atoms, more preferred alkynyl groups herein contain 2 to 6 carbon atoms.

[0021] The term "substituted alkynyl" refers to alkynyl substituted with one or more substituent groups, and the terms "heteroatom-containing alkynyl" and "heteroalkynyl" refer to alkynyl in which at least one carbon atom is replaced with a heteroatom.

[0022] The term "alkynylene" as used herein refers to a difunctional alkynyl group, where "alkynyl" is as defined above.

[0023] The term "alkoxy" as used herein refers to an alkyl group bound through a single, terminal ether linkage; that is, an "alkoxy" group may be represented as -O-alkyl where "alkyl" is as defined above. Analogously, "alkenyloxy" refer to an alkenyl group bound through a single, terminal ether linkage, and "alkynyloxy" refers to an alkynyl group bound through a single, terminal ether linkage.

[0024] The term "aryl" as used herein, and unless otherwise specified, refers to an aromatic substituent containing a single aromatic ring or multiple aromatic rings that are fused together, directly linked, or indirectly linked (such that the different aromatic rings are bound to a common group such as a methylene or ethylene moiety). Preferred aryl groups contain 5 to 24 carbon atoms, and particularly preferred aryl groups contain 6 to 10 carbon atoms. Exemplary aryl

groups contain one aromatic ring or two fused or linked aromatic rings, e.g., phenyl (Ph), naphthyl, biphenyl, diphenylether, diphenylamine, benzophenone, phenanthryl and the like.

[0025] "Substituted aryl" refers to an aryl moiety substituted with one or more substituent groups, and the terms "heteroatom containing aryl" and "heteroaryl" refer to aryl substituents in which at least one carbon atom is replaced with a heteroatom, as will be described in further detail herein.

[0026] The term "aryloxy" as used herein refers to an aryl group bound through a single, terminal ether linkage, wherein "aryl" is as defined above. An "aryloxy" group may be represented as -O-aryl where aryl is as defined above. Preferred aryloxy groups contain 5 to 24 carbon atoms, and particularly preferred aryloxy groups contain 6 to 10 carbon atoms. Examples of aryloxy groups include, without limitation, phenoxy, o-halo-phenoxy, m-halo-phenoxy, p-halo-phenoxy, o-methoxy-phenoxy, m-methoxy-phenoxy, p-methoxy-phenoxy, 2,4-dimethoxy-phenoxy, 3,4,5-trimethoxy-phenoxy, and the like.

[0027] The term "alkaryl" refers to an aryl group with an alkyl substituent, and the term "aralkyl" refers to an alkyl group with an aryl substituent, wherein "aryl" and "alkyl" are as defined above. Preferred alkaryl and aralkyl groups contain 6 to 24 carbon atoms, and particularly preferred alkaryl and aralkyl groups contain 6 to 16 carbon atoms. Alkaryl groups include, without limitation, p-methylphenyl, 2,4-dimethylphenyl, p-cyclohexylphenyl, 2,7-dimethylnaphthyl, 7-cyclooctylnaphthyl, 3-ethyl-cyclopenta-1,4-diene, and the like. Examples of aralkyl groups include, without limitation, benzyl, 2-phenyl-ethyl, 3-phenyl-propyl, 4-phenyl-butyl, 5-phenyl-pentyl, 4-phenylcyclohexyl, 4-benzylcyclohexyl, 4-phenylcyclohexylmethyl, 4-benzylcyclohexylmethyl, and the like.

[0028] The terms "alkaryloxy" and "aralkyloxy" refer to substituents of the formula -OR wherein R is alkaryl or aralkyl, respectively, as defined herein.

[0029] The term "acyl" refers to substituents having the formula -(CO)-alkyl, -(CO)-aryl, -(CO)-aralkyl, -(CO)-alkaryl, -(CO)-alkenyl, or -(CO)-alkynyl, and the term "acyloxy" refers to substituents having the formula -O(CO)-alkyl, -O(CO)-aryl, -O(CO)-aralkyl, -O(CO)-alkaryl, -O(CO)-alkenyl, or -(CO)-alkynyl wherein "alkyl," "aryl", "aralkyl", "alkaryl", "alkenyl", and "alkynyl" are as defined above. The acetoxy group (-O(CO)CH₃, often abbreviated as -OAc) is a common example of an acyloxy group.

[0030] The terms "cyclic" and "ring" refer to alicyclic or aromatic groups that may or may not be substituted and/or heteroatom containing, and that may be monocyclic, bicyclic, or polycyclic. The term "alicyclic" is used in the conventional sense to refer to an aliphatic cyclic moiety, as opposed to an aromatic cyclic moiety, and may be monocyclic, bicyclic or polycyclic.

[0031] The term "polycyclic ring" refers to alicyclic or aromatic groups that may or may not be substituted and/or heteroatom containing, and that have at least two closed rings tethered, fused, linked via a single bond or bridged. Polycyclic rings include without limitation naphthyl, biphenyl, phenanthryl and the like.

[0032] The term "spiro compound" refers to a chemical compound, that presents a twisted structure of two or more rings (a ring system), in which 2 or 3 rings are linked together by one common atom,

[0033] The terms "halo" and "halogen" and "halide" are used in the conventional sense to refer to a fluorine (F), chlorine (Cl), bromine (Br), or iodine (I) substituent.

[0034] "Hydrocarbyl" refers to univalent hydrocarbyl moieties containing 1 to 24 carbon atoms, preferably 1 to 12 carbon atoms, including linear, branched, cyclic, saturated and unsaturated species, such as alkyl groups, alkenyl groups, alkynyl groups, aryl groups, and the like. "Substituted hydrocarbyl" refers to hydrocarbyl substituted with one or more substituent groups.

[0035] "Hydrocarbylene" refers to divalent hydrocarbyl moieties containing 1 to 24 carbon atoms, preferably 1 to 12 carbon atoms, including linear, branched, cyclic, saturated and unsaturated species, formed by removal of two hydrogens from a hydrocarbon. "Substituted hydrocarbylene" refers to hydrocarbylene substituted with one or more substituent groups.

[0036] The term "heteroatom-containing" as in a "heteroatom-containing hydrocarbyl group" refers to a hydrocarbon molecule or a hydrocarbyl molecular fragment in which one or more carbon atoms is replaced with an atom other than carbon, e.g., nitrogen, oxygen, sulfur, phosphorus or silicon, typically nitrogen, oxygen or sulfur. The term "heteroatom-containing hydrocarbylene" and "heterohydrocarbylene" refer to hydrocarbylene in which at least one carbon atom is replaced with a heteroatom. Similarly, the term "heteroalkyl" refers to an alkyl substituent that is heteroatom-containing, the term "heterocyclic" refers to a cyclic substituent that is heteroatom-containing, the terms "heteroaryl" and "heteroaromatic" respectively refer to "aryl" and "aromatic" substituents that are heteroatom-containing, and the like. It should be noted

that a "heterocyclic" group or compound may or may not be aromatic, and further that "heterocycles" may be monocyclic, bicyclic, or polycyclic as described above with respect to the term "aryl." Examples of heteroalkyl groups include without limitation alkoxyaryl, alkylsulfanyl-substituted alkyl, N-alkylated amino alkyl, and the like. Examples of heteroaryl substituents include without limitation pyrrolyl, pyrrolidinyl, pyridinyl, quinolinyl, indolyl, pyrimidinyl, imidazolyl, 1,2,4-triazolyl, tetrazolyl, etc., and examples of heteroatom-containing alicyclic groups include without limitation pyrrolidino, morpholino, piperazino, piperidino, etc.

[0037] In addition, the aforementioned substituent groups may, if a particular group permits, be further substituted with one or more additional substituent groups or with one or more hydrocarbyl moieties such as those specifically enumerated above. Analogously, the above mentioned hydrocarbyl moieties may be further substituted with one or more substituent groups or additional hydrocarbyl moieties such as those specifically mentioned above. Analogously, the above-mentioned hydrocarbylene moieties may be further substituted with one or more substituent groups or additional hydrocarbyl moieties as noted above.

[0038] By "substituted" as in "substituted hydrocarbyl", "substituted alkyl", "substituted aryl", and the like, as alluded to in some of the aforementioned definitions, is meant that in the hydrocarbyl, alkyl, aryl, or other moiety, at least one hydrogen atom bound to a carbon (or other) atom is replaced with one or more non-hydrogen substituents. Examples of such substituents include, without limitation groups such as halo, hydroxyl, sulfhydryl, C₁-C₂₄ alkoxy, C₂-C₂₄ alkenyloxy, C₂-C₂₄ alkynyloxy, C₅-C₂₄ aryloxy, C₆-C₂₄ aralkyloxy, C₆-C₂₄ alkaryloxy, acyl (including C₂-C₂₄ alkylcarbonyl (-CO-alkyl) and C₆-C₂₄ arylcarbonyl (-CO-aryl)), acyloxy (-O-acyl, including C₂-C₂₄ alkylcarbonyloxy (-O-CO-alkyl) and C₆-C₂₄ arylcarbonyloxy (-O-CO-aryl)), C₂-C₂₄ alkoxycarbonyl (-(CO)-O-alkyl), C₆-C₂₄ aryloxycarbonyl (-(CO)-O-aryl), halocarbonyl (-CO)-X where X is halo), C₂-C₂₄ alkylcarbonato (-O-(CO)-O-alkyl), C₆-C₂₄ arylcarbonato (-O-(CO)-O-aryl), carboxylic acid (-COOH), carbamoyl (-(CO)-NH₂), mono-(C₁-C₂₄ alkyl)-substituted carbamoyl (-(CO)-NH(C₁-C₂₄ alkyl)), di-(C₁-C₂₄ alkyl)-substituted carbamoyl (-(CO)-N(C₁-C₂₄ alkyl)₂), mono-(C₁-C₂₄ haloalkyl)-substituted carbamoyl (-(CO)-NH(C₁-C₂₄ haloalkyl)), di-(C₁-C₂₄ haloalkyl)-substituted carbamoyl (-(CO)-N(C₁-C₂₄ haloalkyl)₂), mono-(C₅-C₂₄ aryl)-substituted carbamoyl (-(CO)-NH-aryl), di-(C₅-C₂₄ aryl)-substituted carbamoyl (-(CO)-N(C₅-C₂₄ aryl)₂), N(C₁-C₂₄ alkyl)(C₅-C₂₄ aryl)-substituted carbamoyl (-(CO)-N(C₁-C₂₄ alkyl)(C₅-C₂₄ aryl)), thiocarbamoyl (-(CS)-NH₂), mono-(C₁-C₂₄

alkyl)-substituted thiocarbamoyl $-(\text{CS})-\text{NH}(\text{C}_1\text{-C}_{24} \text{ alkyl})$, di- $(\text{C}_1\text{-C}_{24} \text{ alkyl})$ -substituted thiocarbamoyl $-(\text{CS})-\text{N}(\text{C}_1\text{-C}_{24} \text{ alkyl})_2$, mono- $(\text{C}_5\text{-C}_{24} \text{ aryl})$ -substituted thiocarbamoyl $-(\text{CS})-\text{NH-aryl}$, di- $(\text{C}_5\text{-C}_{24} \text{ aryl})$ -substituted thiocarbamoyl $-(\text{CS})-\text{N}(\text{C}_5\text{-C}_{24} \text{ aryl})_2$, $\text{N}(\text{C}_1\text{-C}_{24} \text{ alkyl})(\text{C}_5\text{-C}_{24} \text{ aryl})$ -substituted thiocarbamoyl $-(\text{CS})-\text{N}(\text{C}_1\text{-C}_{24} \text{ alkyl})(\text{C}_5\text{-C}_{24} \text{ aryl})$, carbamido $(-\text{NH}(\text{CO})-\text{NH}_2)$, cyano $(-\text{C}\equiv\text{N})$, cyanato $(-\text{O}-\text{C}\equiv\text{N})$, thiocyanato $(-\text{S}-\text{C}\equiv\text{N})$, isocyanate $(-\text{NCO})$, thioisocyanate $(-\text{NCS})$, formyl $(-\text{CO}-\text{H})$, thioformyl $(-\text{CS}-\text{H})$, amino $(-\text{NH}_2)$, mono- $(\text{C}_1\text{-C}_{24} \text{ alkyl})$ -substituted amino $(-\text{NH}(\text{C}_1\text{-C}_{24} \text{ alkyl}))$, di- $(\text{C}_1\text{-C}_{24} \text{ alkyl})$ -substituted amino $(-\text{N}(\text{C}_1\text{-C}_{24} \text{ alkyl})_2)$, mono- $(\text{C}_5\text{-C}_{24} \text{ aryl})$ -substituted amino $(-\text{NH}(\text{C}_5\text{-C}_{24} \text{ aryl}))$, di- $(\text{C}_5\text{-C}_{24} \text{ aryl})$ -substituted amino $(-\text{N}(\text{C}_5\text{-C}_{24} \text{ aryl})_2)$, $\text{C}_2\text{-C}_{24}$ alkylamido $(-\text{NH}(\text{CO})\text{-alkyl})$, $\text{C}_6\text{-C}_{24}$ arylamido $(-\text{NH}(\text{CO})\text{-aryl})$, imino $(-\text{CRNH}$ where, R includes without limitation H, $\text{C}_1\text{-C}_{24}$ alkyl, $\text{C}_5\text{-C}_{24}$ aryl, $\text{C}_6\text{-C}_{24}$ alkaryl, $\text{C}_6\text{-C}_{24}$ aralkyl, etc.), $\text{C}_2\text{-C}_{20}$ alkylimino $(-\text{CRN}(\text{alkyl}))$, where R includes without limitation H, $\text{C}_1\text{-C}_{24}$ alkyl, $\text{C}_5\text{-C}_{24}$ aryl, $\text{C}_6\text{-C}_{24}$ alkaryl, $\text{C}_6\text{-C}_{24}$ aralkyl, etc.), arylimino $(-\text{CRN}(\text{aryl}))$, where R includes without limitation H, $\text{C}_1\text{-C}_{20}$ alkyl, $\text{C}_5\text{-C}_{24}$ aryl, $\text{C}_6\text{-C}_{24}$ alkaryl, $\text{C}_6\text{-C}_{24}$ aralkyl, etc.), nitro $(-\text{NO}_2)$, nitroso $(-\text{NO})$, sulfo $(-\text{S}(\text{O})_2\text{OH})$, $\text{C}_1\text{-C}_{24}$ alkylsulfanyl $(-\text{S-alkyl})$; also termed "alkylthio"), $\text{C}_5\text{-C}_{24}$ arylsulfanyl $(-\text{S-aryl})$; also termed "arylthio"), $\text{C}_1\text{-C}_{24}$ alkylsulfanyl $(-\text{SO-alkyl})$, $\text{C}_5\text{-C}_{24}$ arylsulfanyl $(-\text{SO-aryl})$, $\text{C}_1\text{-C}_{24}$ alkylsulfonyl $(-\text{SO}_2\text{-alkyl})$, $\text{C}_1\text{-C}_{24}$ monoalkylaminosulfonyl $(-\text{SO}_2\text{-N(H) alkyl})$, $\text{C}_1\text{-C}_{24}$ dialkylaminosulfonyl $(-\text{SO}_2\text{-N(alkyl)}_2)$, $\text{C}_5\text{-C}_{24}$ arylsulfonyl $(-\text{SO}_2\text{-aryl})$, boryl $(-\text{BH}_2)$, borono $(-\text{B}(\text{OH})_2)$, boronato $(-\text{B}(\text{OR})_2)$ where R includes without limitation alkyl or other hydrocarbyl), phosphono $(-\text{P}(\text{O})(\text{OH})_2)$, phospho $(-\text{PO}_2)$, phosphino $(-\text{PH}_2)$, silyl $(-\text{SiR}_3)$ wherein R is H or hydrocarbyl), and silyloxy $(-\text{O-silyl})$; hydrocarbyl moieties $\text{C}_1\text{-C}_{24}$ alkyl (preferably $\text{C}_1\text{-C}_{12}$ alkyl, more preferably $\text{C}_1\text{-C}_6$ alkyl), $\text{C}_2\text{-C}_{24}$ alkenyl (preferably $\text{C}_2\text{-C}_{12}$ alkenyl, more preferably $\text{C}_2\text{-C}_6$ alkenyl), $\text{C}_2\text{-C}_{24}$ alkynyl (preferably $\text{C}_2\text{-C}_{12}$ alkynyl, more preferably $\text{C}_2\text{-C}_6$ alkynyl), $\text{C}_5\text{-C}_{24}$ aryl (preferably $\text{C}_6\text{-C}_{10}$ aryl), $\text{C}_6\text{-C}_{24}$ alkaryl (preferably $\text{C}_6\text{-C}_{16}$ alkaryl), or $\text{C}_6\text{-C}_{24}$ aralkyl (preferably $\text{C}_6\text{-C}_{16}$ aralkyl).

[0039] By "functionalized" as in "functionalized hydrocarbyl", "functionalized alkyl", "functionalized olefin", "functionalized cyclic olefin", and the like, is meant that in the hydrocarbyl, alkyl, olefin, cyclic olefin, or other moiety, at least one H atom bound to a carbon (or other) atom is replaced with one or more functional group(s) such as those described hereinabove. The term "functional group" is meant to include any functional species that is suitable for the uses described herein. In some cases, the terms "substituent" and "functional group" are used interchangeably.

[0040] "Optional" or "optionally" means that the subsequently described circumstance may or may not occur, so that the description includes instances where the circumstance occurs and instances where it does not. For example, the phrase "optionally substituted" means that a non-hydrogen substituent may or may not be present on a given atom, and, thus, the description includes structures wherein a non-hydrogen substituent is present and structures wherein a non-hydrogen substituent is not present.

[0041] The term "nil", as used herein, means absent or nonexistent.

[0042] The term "sulfhydryl" as used herein, represents a group of formula -SH .

[0043] The term "hydroxyl" as used herein, represents a group of formula -OH .

[0044] The term "carbonyl" as used herein, represents a group of formula -C(O)- .

[0045] The term "ketone" as used herein, represents an organic compound having a carbonyl group linked to a carbon atom such as -C(O)R^x , wherein R^x can be alkyl, aryl, cycloalkyl, cycloalkenyl, heterocycle as defined above.

[0046] The term "ester" as used herein, represents an organic compound having a carbonyl group linked to a carbon atom such as -C(O)OR^x wherein R^x can be alkyl, aryl, cycloalkyl, cycloalkenyl, heterocycle as defined above.

[0047] The term "amine" as used herein, represents a group of formula $\text{-NR}^x\text{R}^y$, wherein R^x and R^y can be the same or independently H, alkyl, aryl, cycloalkyl, cycloalkenyl, heterocycle as defined above.

[0048] The term "carboxyl" as used herein, represents a group of formula -C(O)O- .

[0049] The term "sulfonyl" as used herein, represents a group of formula -SO_2 .

[0050] The term "sulfate" as used herein, represents a group of formula $\text{-O-S(O)}_2\text{-O-}$.

[0051] The term "sulfonate" as used herein, represents a group of the formula $\text{-S(O)}_2\text{-O-}$.

[0052] The term "amide" as used herein, represents a group of formula $\text{-C(O)NR}^x\text{R}^y$, wherein R^x and R^y can be the same or independently H, alkyl, aryl, cycloalkyl, cycloalkenyl, heterocycle as defined above.

[0053] The term "sulfonamide" as used herein, represents a group of formula $\text{-S(O)}_2\text{NR}^x\text{R}^y$ wherein R^x and R^y can be the same or independently H, alkyl, aryl, cycloalkyl, cycloalkenyl, heterocycle as defined above.

[0054] The term "sulfoxide" as used herein, represents a group of formula -S(O)- .

[0055] The term "phosphonic acid" as used herein, represents a group of formula -P(O)(OH)_2 .

[0056] The term "phosphoric acid" as used herein, represents a group of formula " OP(O)(OH)_2 ".

[0057] The term "sulphonic acid" as used herein, represents a group of formula " $\text{-S(O)}_2\text{OH}$ ".

[0058] The formula "H", as used herein, represents a hydrogen atom.

[0059] The formula "O", as used herein, represents an oxygen atom.

[0060] The formula "N", as used herein, represents a nitrogen atom.

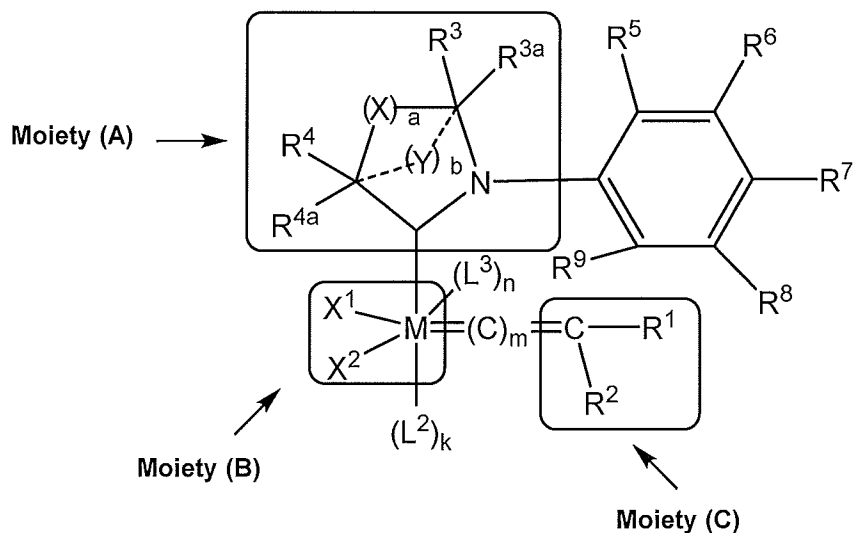
[0061] The formula "S", as used herein, represents a sulfur atom.

[0062] Functional groups may be protected in cases where the functional group interferes with the metal carbene olefin metathesis catalyst, and any of the protecting groups commonly used in the art may be employed. Acceptable protecting groups may be found, for example, in Greene et al., *Protective Groups in Organic Synthesis*, 5th Ed. (New York: Wiley, 2014). Examples of protecting groups include acetals, cyclic acetals, boronate esters (boronates), cyclic boronate esters (cyclic boronates), carbonates, or the like. Examples of protecting groups include cyclic acetals or cyclic boronate esters.

METAL CARBENE OLEFIN METATHESIS CATALYSTS OF THE INVENTION

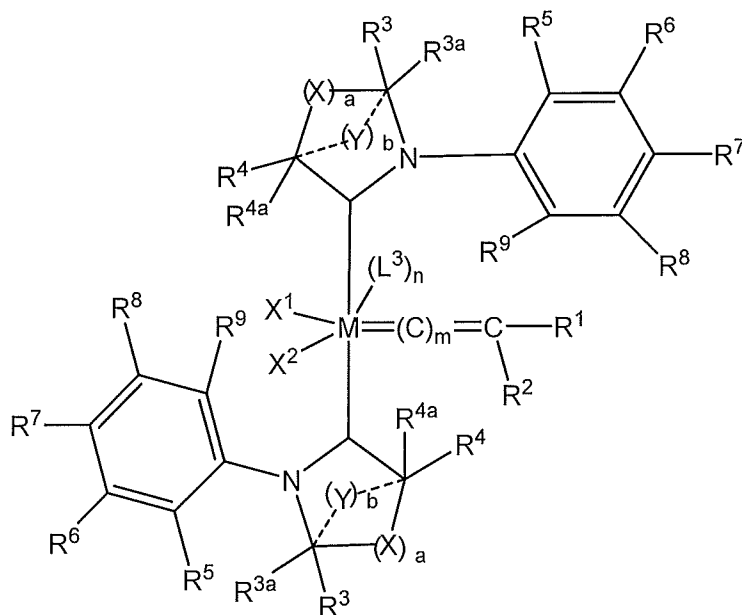
[0063] In one embodiment, the invention provides olefin metathesis catalysts, represented by the structure of **Formula (I)**, as described herein.

[0064] **Formula (I)** is formed by different moieties, as shown in **Scheme (1)**, below:



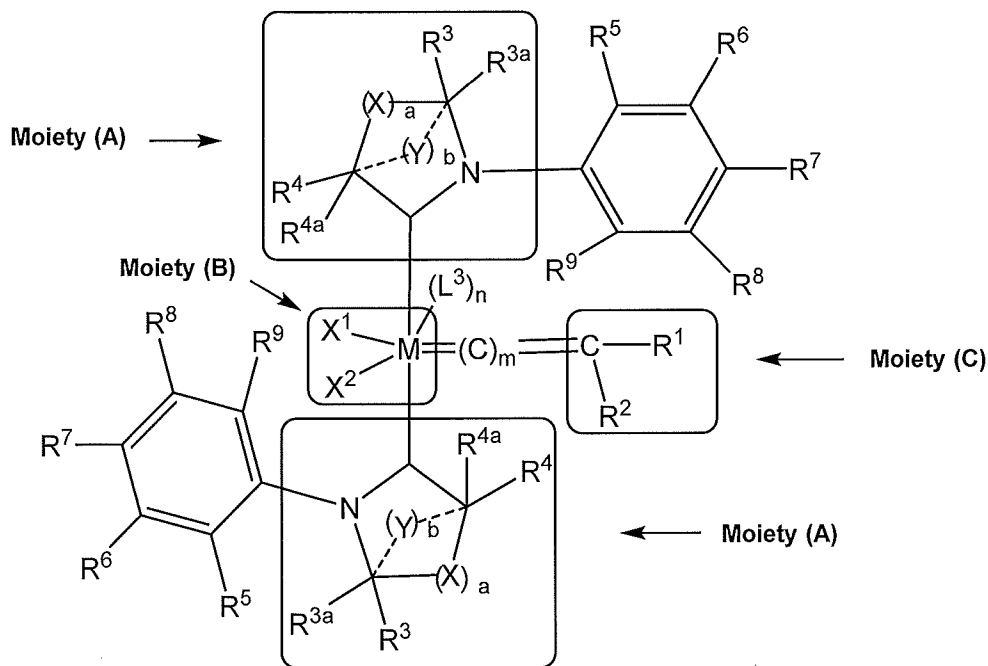
Scheme (1)

[0065] In one embodiment, the invention provides a metal carbene olefin metathesis catalyst, represented by the structure of **Formula (II)**, as represented below:



Formula (II)

[0066] Formula (II) is formed by different moieties, as shown in Scheme (2), below:

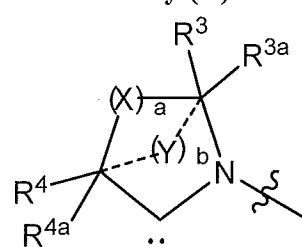
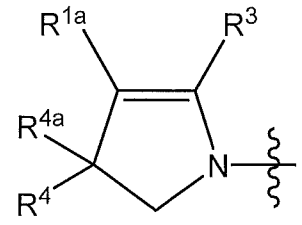
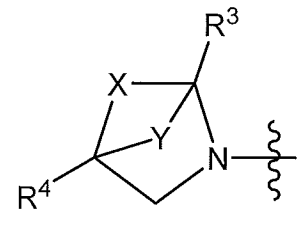
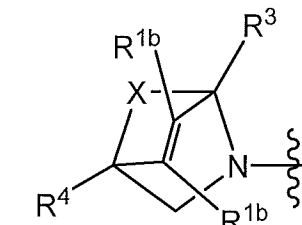
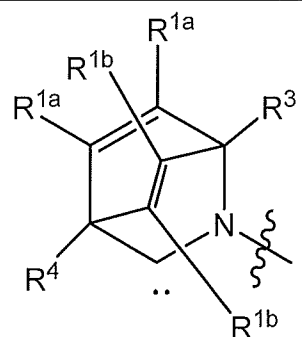
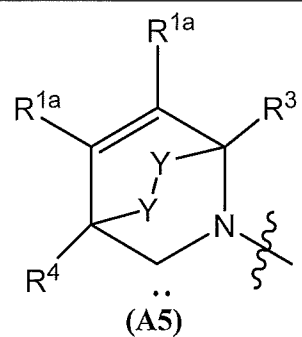
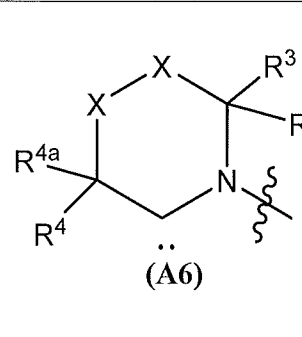
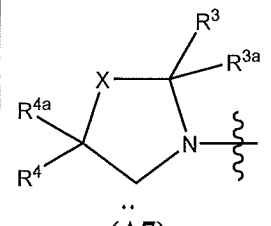
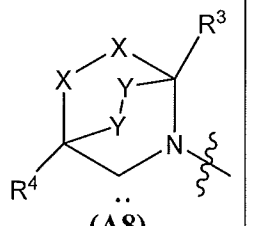
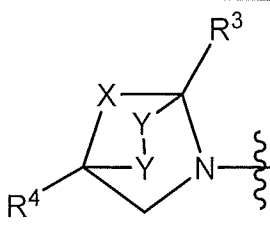
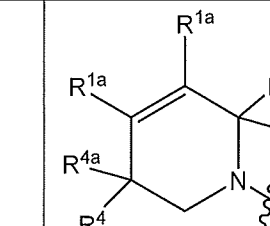


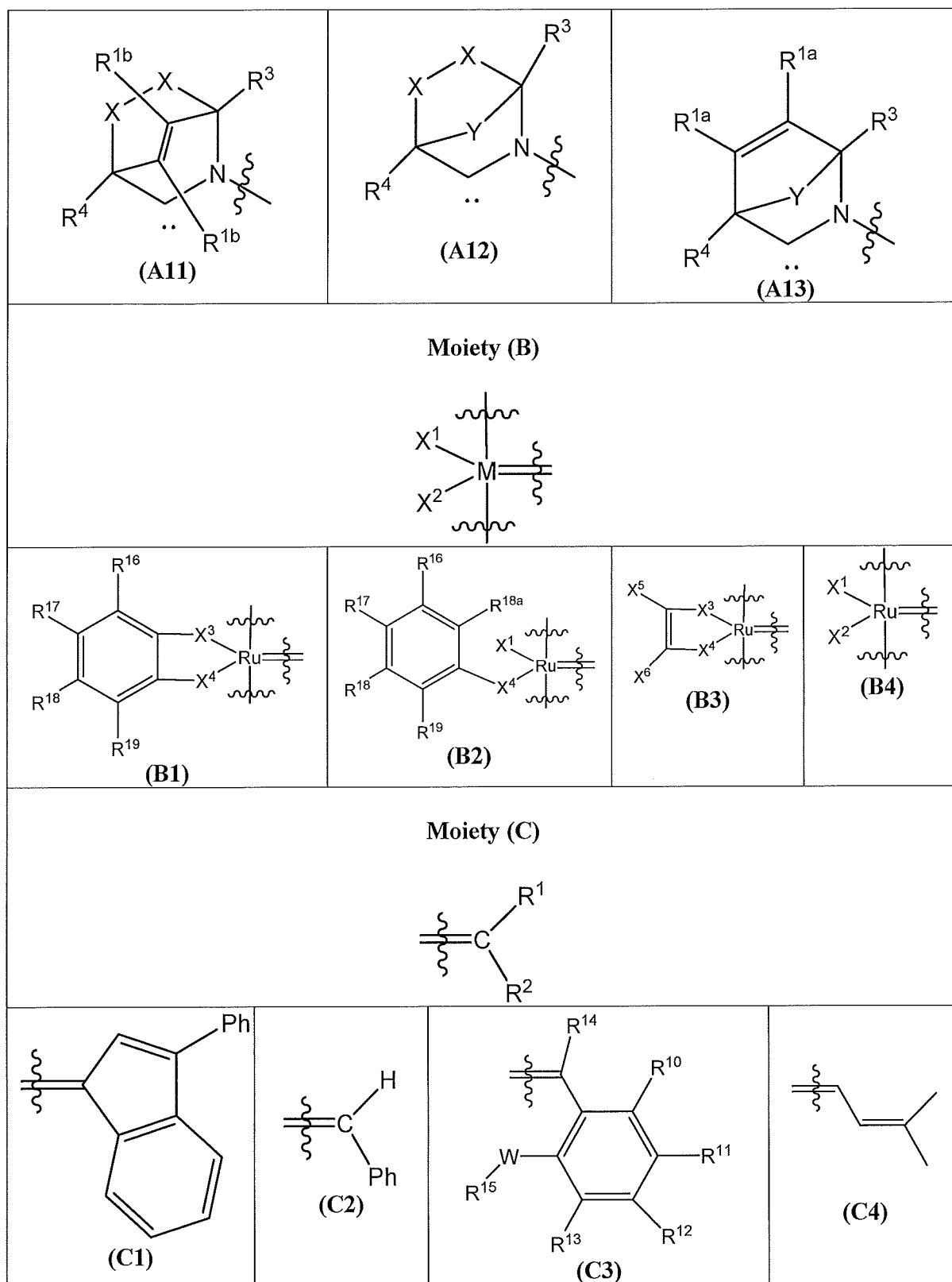
Scheme (2)

[0067] Table (1) illustrates possible moieties which form general Formula (I) and general Formula (II). Depending on the values of "a" and "b", substructures of the Moieties (A), are exemplified in Table (1). Depending on the values of X^1 and X^2 , substructures of Moieties (B) are

exemplified in **Table (1)**. Depending on the values of R^1 and R^2 , substructures of **Moiety (C)** are exemplified in **Table (1)**. Any combination of a **Moiety (A)**, **Moiety (B)** and **Moiety (C)** can form a ruthenium carbene olefin metathesis catalyst of the invention, according to **Formula (I)** and **Formula (II)**.

Table (1)

Moiety (A) 			
 (A1)	 (A2)	 (A3)	
 (A4)	 (A5)	 (A6)	
 (A7)	 (A8)	 (A9)	 (A10)

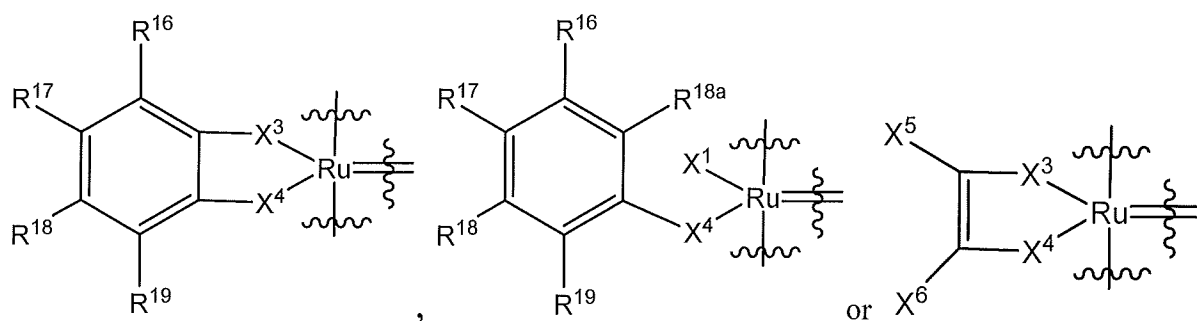


[0068] The values of the substituents described in **Table (1)** are as follows:

M is Ru;

X^1 is an anionic ligand; generally, X^1 is halogen, trifluoroacetate, per-fluorophenols, -NCO, -CN, -NCS, -N₃; or together with X^2 can form a nitrate; typically, X^1 is halogen, or -NCO; specifically, in the present case X^1 is Cl;

X^2 is an anionic ligand; generally, X^2 is halogen, trifluoroacetate, per-fluorophenols, -NCO, -CN, -NCS, -N₃; or together with X^1 can form a nitrate; typically, X^2 is halogen, or -NCO; specifically, in the present case X^2 is Cl; or X^1 and X^2 together with the ruthenium can form



R^1 is hydrogen, optionally substituted hydrocarbyl, or optionally substituted heteroatom-containing hydrocarbyl; generally, R^1 is H; or together with R^2 can form a substituted indenylidene;

R^2 is hydrogen, optionally substituted hydrocarbyl, optionally substituted heteroatom-containing hydrocarbyl; generally, R^2 is optionally substituted C₂₋₂₄ alkenyl or optionally substituted phenyl or together with R^1 can form a substituted indenylidene;

X is -CR^{1a}R^{2a}-;

a is 1 or 2; generally, a is 2;

R^{1a} is H, optionally substituted C₁₋₂₄ alkyl, optionally substituted C₃₋₈ cycloalkyl, halogen, optionally substituted C₅-C₂₄ aryl, optionally substituted C₆-C₂₄ aralkyl, optionally substituted C₁-C₂₀ heteroalkyl, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, or together with R^{2a} forms an optionally substituted spiro monocyclic or spiro polycyclic C₃₋₁₀ cycloalkyl or spiro heterocyclic ring, with the carbon atom to which they are attached, or together with R^3 or together with R^4 forms an optionally substituted polycyclic ring;

R^{2a} is H, optionally substituted C₁₋₂₄ alkyl, optionally substituted C₃₋₈ cycloalkyl, halogen, optionally substituted C₅-C₂₄ aryl, optionally substituted C₆-C₂₄ aralkyl, optionally substituted

C₁-C₂₀ heteroalkyl, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, or together with R^{1a} forms a spiro monocyclic or spiro polycyclic C₃₋₁₀ cycloalkyl or spiro heterocyclic ring, with the carbon atom to which they are attached, or together with R³ or together with R⁴ forms an optionally substituted polycyclic ring;

Y is -CR^{1b}R^{2b}-;

b is 0, 1 or 2; generally, b is 0 or 1; typically, b is 0;

R^{1b} is H, optionally substituted C₁₋₂₄ alkyl, optionally substituted C₃₋₈ cycloalkyl, halogen, optionally substituted C₅₋₂₄ aryl, optionally substituted C₆₋₂₄ aralkyl, optionally substituted C₁-C₂₀ heteroalkyl, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, or together with R^{2b} forms a five-, six-, or ten-membered cycloalkyl or heterocyclic ring, with the carbon atom to which they are attached;

R^{2b} is H, optionally substituted C₁₋₂₄ alkyl, optionally substituted C₃₋₈ cycloalkyl, halogen, optionally substituted C₅₋₂₄ aryl, optionally substituted C₆₋₂₄ aralkyl, optionally substituted C₁-C₂₀ heteroalkyl, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, or together with R^{1b} forms a five-, six-, or ten-membered cycloalkyl or heterocyclic ring, with the carbon atom to which they are attached;

R³ is H, optionally substituted C₁₋₂₄ alkyl, halogen, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, optionally substituted heterocycle, optionally substituted C₃₋₈ cycloalkyl, optionally substituted C₅₋₂₄ aryl, optionally substituted C₃₋₈ cycloalkenyl, or together with R^{3a} can form an optionally substituted spiro monocyclic or spiro polycyclic C₃₋₁₀ cycloalkyl or together with R^{1a} or together with R^{2a} can form an optionally substituted polycyclic ring;

R^{3a} is H, optionally substituted C₁₋₂₄ alkyl, halogen, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, optionally substituted heterocycle, optionally substituted C₃₋₈ cycloalkyl, optionally substituted C₅₋₂₄ aryl, optionally substituted C₃₋₈ cycloalkenyl, or together with R³ can form an optionally substituted spiro monocyclic or spiro polycyclic C₃₋₁₀ cycloalkyl or together with R^{1a} or together with R^{2a} can form an optionally substituted polycyclic ring;

R⁴ is H, optionally substituted C₁₋₂₄ alkyl, halogen, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, optionally substituted heterocycle, optionally substituted C₃₋₈ cycloalkyl, optionally substituted C₅₋₂₄ aryl, optionally substituted C₃₋₈

cycloalkenyl, or together with R^{4a} can form an optionally substituted spiro monocyclic or spiro polycyclic C₃₋₁₀ cycloalkyl or together with R^{1a} or together with R^{2a} can form an optionally substituted polycyclic ring;

R^{4a} is H, optionally substituted C₁₋₂₄ alkyl, halogen, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, optionally substituted heterocycle, optionally substituted C₃₋₈ cycloalkyl, optionally substituted C₅₋₂₄ aryl, optionally substituted C₃₋₈ cycloalkenyl, or together with R⁴ can form an optionally substituted spiro monocyclic or spiro polycyclic C₃₋₁₀ cycloalkyl or together with R^{1a} or together with R^{2a} can form an optionally substituted polycyclic ring;

W is O, NR²⁰ or S;

R¹⁰ is H, optionally substituted C₁₋₂₄ alkyl, halogen, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, optionally substituted heterocycle, optionally substituted C₃₋₈ cycloalkyl, optionally substituted C₅₋₂₄ aryl, optionally substituted C₃₋₈ cycloalkenyl or together with R¹¹ can form a polycyclic ring;

R¹¹ is H, optionally substituted C₁₋₂₄ alkyl, halogen, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, optionally substituted heterocycle, optionally substituted C₃₋₈ cycloalkyl, optionally substituted C₅₋₂₄ aryl, optionally substituted C₃₋₈ cycloalkenyl or together with R¹⁰ or together with R¹² can form a polycyclic ring;

R¹² is H, optionally substituted C₁₋₂₄ alkyl, halogen, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, -NHC(O)CF₃, optionally substituted heterocycle, optionally substituted C₃₋₈ cycloalkyl, optionally substituted C₅₋₂₄ aryl, optionally substituted C₃₋₈ cycloalkenyl or together with R¹¹ or together with R¹³ can form a polycyclic ring;

R¹³ is H, optionally substituted C₁₋₂₄ alkyl, halogen, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, optionally substituted heterocycle, optionally substituted C₃₋₈ cycloalkyl, optionally substituted C₅₋₂₄ aryl, optionally substituted C₃₋₈ cycloalkenyl or together with R¹² can form a polycyclic ring;

R¹⁴ is H, optionally substituted C₁₋₂₄ alkyl, halogen, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, optionally substituted heterocycle, optionally substituted C₃₋₈ cycloalkyl, optionally substituted C₅₋₂₄ aryl or optionally substituted C₃₋₈ cycloalkenyl;

R¹⁵ is H, optionally substituted C₁₋₂₄ alkyl, -C(R²⁸)(R²⁹)COOR³⁰, -C(R²⁸)(R²⁹)C(O)H, -C(R²⁸)(R²⁹)C(O)R³¹, -C(R²⁸)(R²⁹)CR³²(OR³³)(OR³⁴), -C(R²⁸)(R²⁹)C(O)NR³⁵R³⁶, -C(R²⁸)(R²⁹)C(O)NR³⁵OR³⁴, -C(O)R²¹, optionally substituted heterocycle, optionally substituted C₃₋₈ cycloalkyl, optionally substituted C₅₋₂₄ aryl, optionally substituted C₃₋₈ cycloalkenyl, or together with R²⁰ can form an optionally substituted heterocyclic ring or is nil when W is halogen;

R¹⁶ is H, optionally substituted C₁₋₂₄ alkyl, halogen, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, optionally substituted heterocycle, optionally substituted C₃₋₈ cycloalkyl, optionally substituted C₅₋₂₄ aryl or optionally substituted C₃₋₈ cycloalkenyl, or together with R¹⁷ can form an optionally substituted polycyclic ring;

R¹⁷ is H, optionally substituted C₁₋₂₄ alkyl, halogen, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, optionally substituted heterocycle, optionally substituted C₃₋₈ cycloalkyl, optionally substituted C₅₋₂₄ aryl or optionally substituted C₃₋₈ cycloalkenyl, or together with R¹⁶ or together with R¹⁸ can form an optionally substituted polycyclic ring;

R¹⁸ is H, optionally substituted C₁₋₂₄ alkyl, halogen, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, optionally substituted heterocycle, optionally substituted C₃₋₈ cycloalkyl, optionally substituted C₅₋₂₄ aryl or optionally substituted C₃₋₈ cycloalkenyl, or together with R¹⁷ or together with R¹⁹ can form an optionally substituted polycyclic ring;

R^{18a} is H, optionally substituted C₁₋₂₄ alkyl, halogen, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, optionally substituted heterocycle, optionally substituted C₃₋₈ cycloalkyl, optionally substituted C₅₋₂₄ aryl or optionally substituted C₃₋₈ cycloalkenyl, or together with R¹⁶ can form an optionally substituted polycyclic ring;

R¹⁹ is H, optionally substituted C₁₋₂₄ alkyl, halogen, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, optionally substituted heterocycle, optionally substituted C₃₋₈ cycloalkyl, optionally substituted C₅₋₂₄ aryl or optionally substituted C₃₋₈ cycloalkenyl, or together with R¹⁸ can form an optionally substituted polycyclic ring.

R²⁰ is H, optionally substituted C₁₋₂₄ alkyl, optionally substituted C₃₋₈ cycloalkyl, optionally substituted heterocycle, optionally substituted C₅₋₂₄ aryl, optionally substituted C₃₋₈ cycloalkenyl, or together with R¹⁵ can form an optionally substituted heterocyclic ring;

R²¹ is OH, OR²⁶, NR²³R²⁴, optionally substituted C₁₋₂₄ alkyl, optionally substituted C₃₋₈ cycloalkyl, optionally substituted heterocycle, optionally substituted C₅₋₂₄ aryl or optionally substituted C₃₋₈ cycloalkenyl;

R²² is H, optionally substituted C₁₋₂₄ alkyl, optionally substituted C₃₋₈ cycloalkyl, optionally substituted heterocycle, optionally substituted C₅₋₂₄ aryl or optionally substituted C₃₋₈ cycloalkenyl;

R²³ is H, optionally substituted C₁₋₂₄ alkyl, optionally substituted C₃₋₈ cycloalkyl, optionally substituted heterocycle, optionally substituted C₅₋₂₄ aryl or optionally substituted C₃₋₈ cycloalkenyl;

R²⁴ is H, optionally substituted C₁₋₂₄ alkyl, optionally substituted C₃₋₈ cycloalkyl, optionally substituted heterocycle, optionally substituted C₅₋₂₄ aryl or optionally substituted C₃₋₈ cycloalkenyl;

x is 1 or 2;

R²⁵ is H, optionally substituted C₁₋₂₄ alkyl, OR²², - NR²³R²⁴, optionally substituted heterocycle, optionally substituted C₃₋₈ cycloalkyl, optionally substituted C₅₋₂₄ aryl or optionally substituted C₃₋₈ cycloalkenyl;

R²⁶ is optionally substituted C₁₋₂₄ alkyl, optionally substituted C₃₋₈ cycloalkyl, optionally substituted heterocycle, optionally substituted C₅₋₂₄ aryl or optionally substituted C₃₋₈ cycloalkenyl;

R²⁷ is H, optionally substituted C₁₋₂₄ alkyl, optionally substituted C₃₋₈ cycloalkyl, optionally substituted heterocycle, optionally substituted C₅₋₂₄ aryl or optionally substituted C₃₋₈ cycloalkenyl;

R²⁸ is H, optionally substituted C₁₋₂₄ alkyl, optionally substituted C₃₋₈ cycloalkyl, optionally substituted heterocycle, optionally substituted C₅₋₂₄ aryl or optionally substituted C₃₋₈ cycloalkenyl;

R²⁹ is H, optionally substituted C₁₋₂₄ alkyl, optionally substituted C₃₋₈ cycloalkyl, optionally substituted heterocycle, optionally substituted C₅₋₂₄ aryl, optionally substituted C₃₋₈ cycloalkenyl, or together with R¹⁹ can form an optionally substituted heterocyclic ring;

R³⁰ is H, optionally substituted C₁₋₂₄ alkyl, optionally substituted C₃₋₈ cycloalkyl, optionally substituted heterocycle, optionally substituted C₅₋₂₄ aryl or optionally substituted C₃₋₈ cycloalkenyl;

R^{31} is H, optionally substituted C_{1-24} alkyl, optionally substituted C_{3-8} cycloalkyl, optionally substituted heterocycle, optionally substituted C_{5-24} aryl or optionally substituted C_{3-8} cycloalkenyl;

R^{32} is H, optionally substituted C_{1-24} alkyl, optionally substituted C_{3-8} cycloalkyl, optionally substituted heterocycle, optionally substituted C_{5-24} aryl or optionally substituted C_{3-8} cycloalkenyl;

R^{33} is H, optionally substituted C_{1-24} alkyl, optionally substituted C_{3-8} cycloalkyl, optionally substituted heterocycle, optionally substituted C_{5-24} aryl or optionally substituted C_{3-8} cycloalkenyl;

R^{34} is H, optionally substituted C_{1-24} alkyl, optionally substituted C_{3-8} cycloalkyl, optionally substituted heterocycle, optionally substituted C_{5-24} aryl or optionally substituted C_{3-8} cycloalkenyl;

R^{35} is H, optionally substituted C_{1-24} alkyl, optionally substituted C_{3-8} cycloalkyl, optionally substituted heterocycle, optionally substituted C_{5-24} aryl or optionally substituted C_{3-8} cycloalkenyl;

R^{36} is H, optionally substituted C_{1-24} alkyl, -OR²², optionally substituted C_{3-8} cycloalkyl, optionally substituted heterocycle, optionally substituted C_{5-24} aryl or optionally substituted C_{3-8} cycloalkenyl;

X^3 is O or S; typically, X^3 is S;

X^4 is O or S; typically, X^4 is S;

X^5 is CN or NO₂; typically, X^5 is CN;

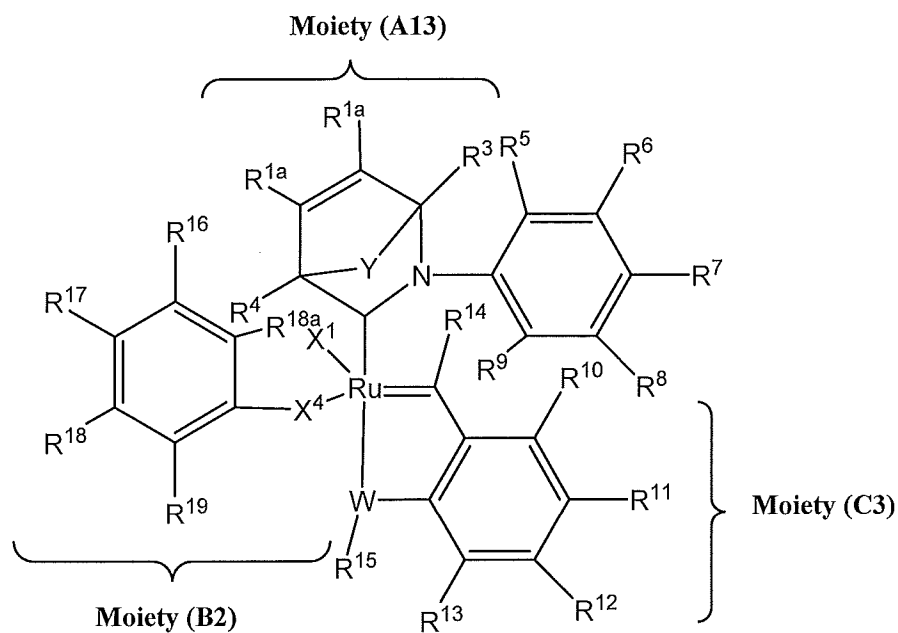
X^6 is CN or NO₂; typically, X^6 is CN; and

with the provisos:

- a. when a is 2, then the "X-X" bond can be saturated or unsaturated;
- b. when b is 2, the "Y-Y" bond can be saturated or unsaturated;
- c. when a is 2, and the "X-X" bond is unsaturated, then R^{2a} is nil;
- d. when b is 1, then R^{3a} and R^{4a} are both nil;
- e. when b is 2, then R^{3a} and R^{4a} are both nil;
- f. when b is 2, and the "Y-Y" bond is unsaturated, then R^{2b} is nil.

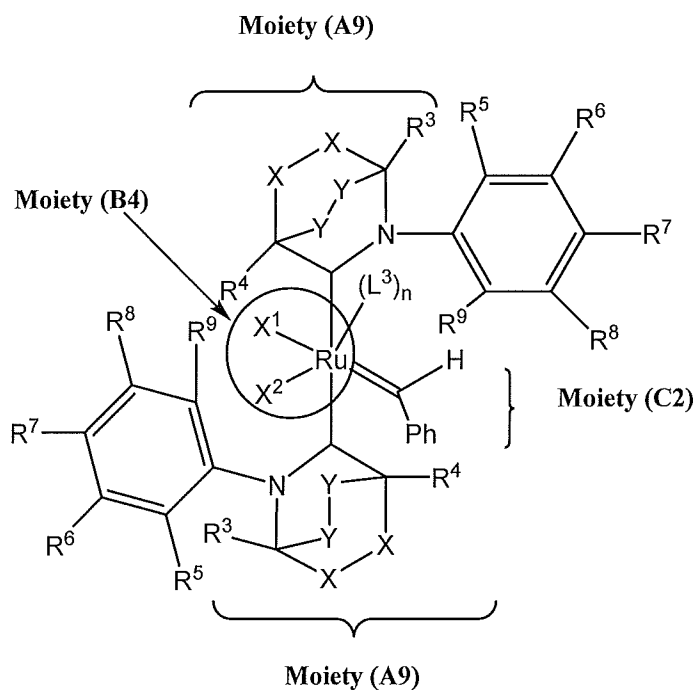
[0069] Therefore, the invention provides olefin metathesis catalysts, wherein the nomenclature of the olefin metathesis catalysts is determined by the combination of **Moiety (A)**, **(B)**, and **(C)** according to **Table (1)**.

[0070] For example, olefin metathesis catalyst represented by the structure shown below is of general **Formula (I)** and is composed of **Moiety (A13)**, **Moiety (B2)** and **Moiety (C3)**, therefore it is assigned **Formula (IA13B2C3)**:

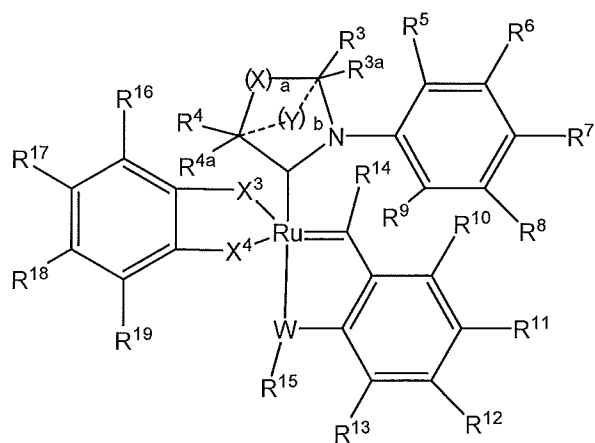


Formula (IA13B2C3)

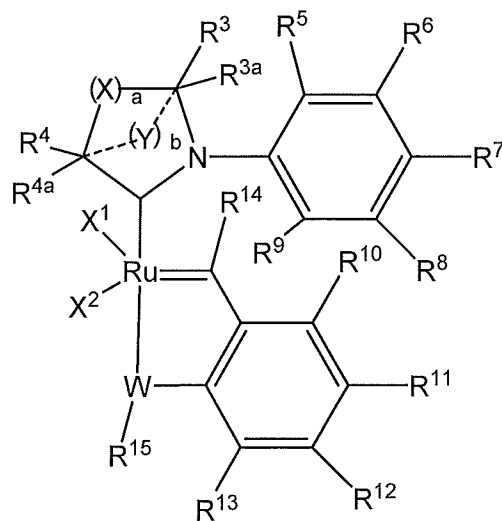
[0071] In another example, the olefin metathesis catalyst represented by the structure shown below, is of general **Formula (II)** and is composed of two **Moiety (A9)**, **Moiety (B4)** and **Moiety (C2)**, therefore it is assigned **Formula (IIA9B4C2A9)**:



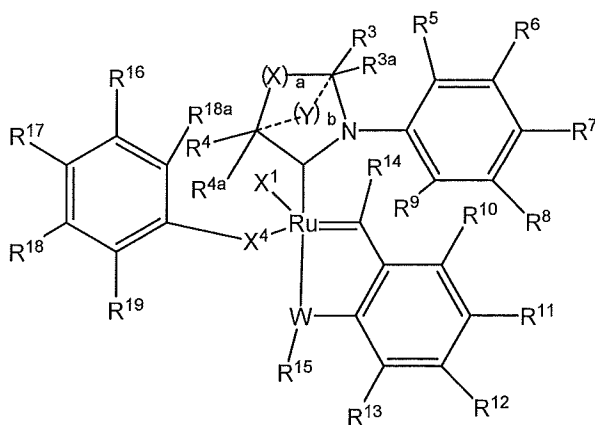
[0072] Other examples of olefin metathesis catalysts of the invention are represented by the structures shown below, wherein the nomenclature was assigned as described herein:



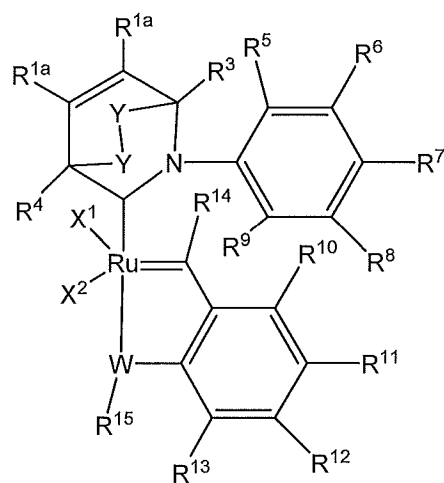
Formula (IAB1C3)



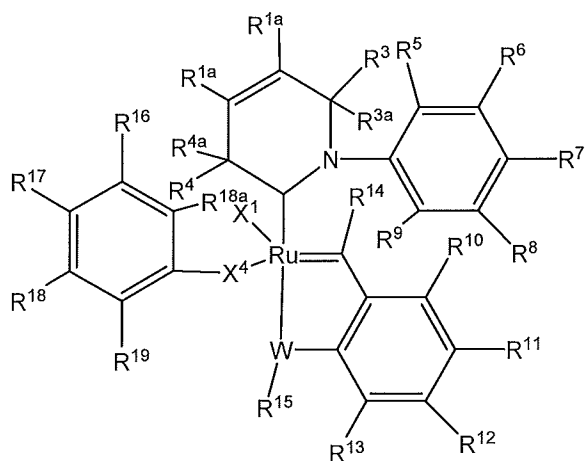
Formula (IAB4C3)



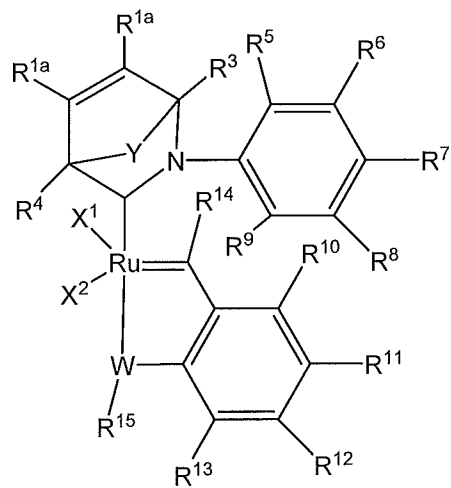
Formula (IAB2C3)



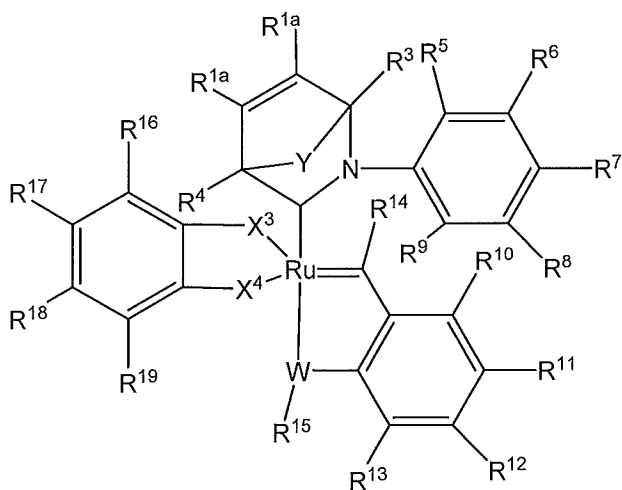
Formula (IA5B4C3)



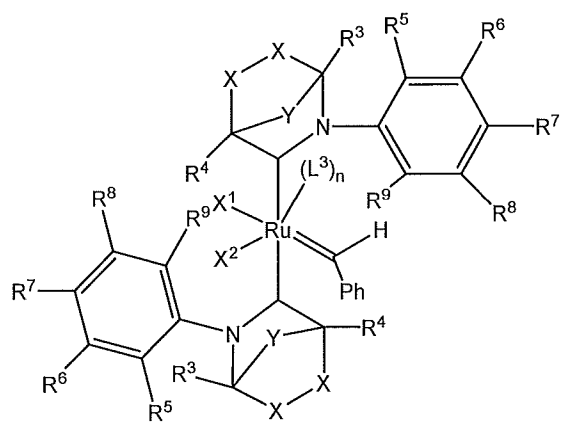
Formula (IA10B2C3)



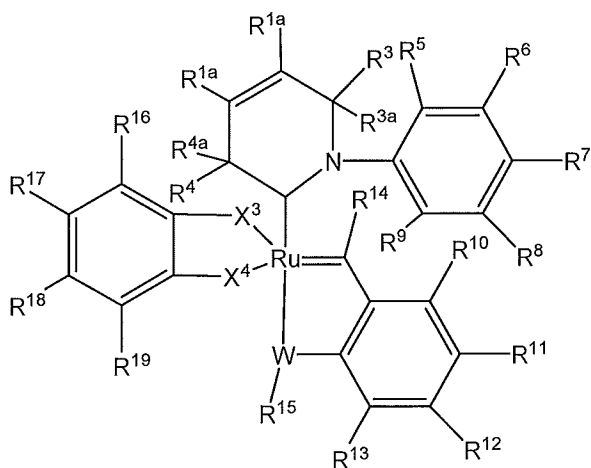
Formula (IA13B4C3)



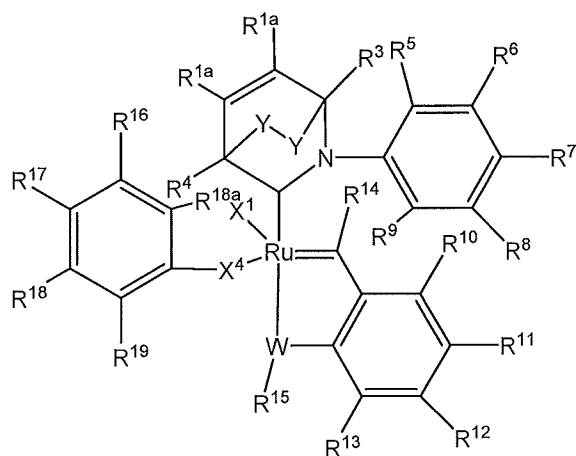
Formula (IA13B1C3)



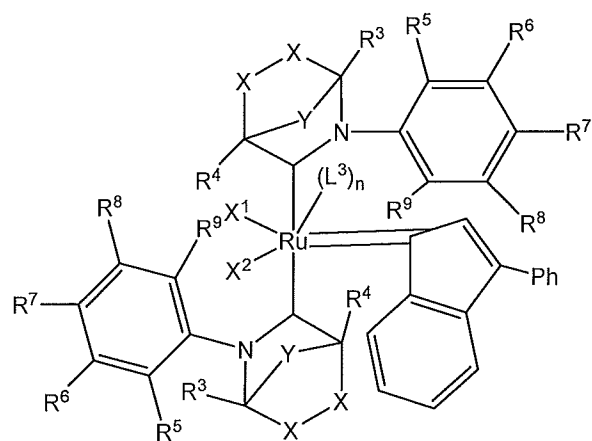
Formula (IIA12B4C2A12)



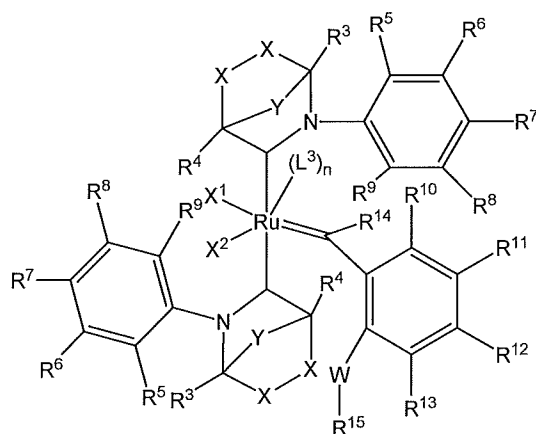
Formula (IA10B1C3)



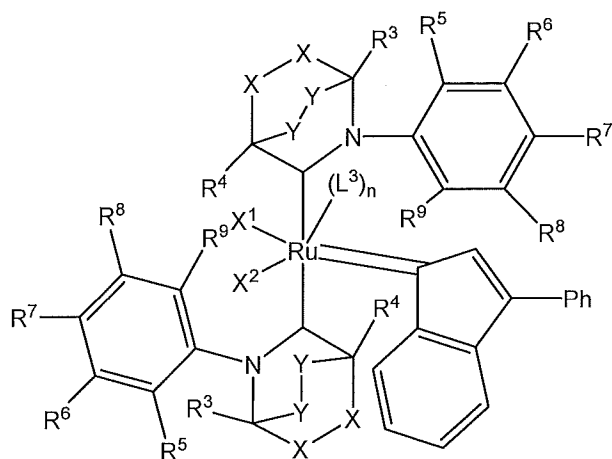
Formula (IA5B2C3)



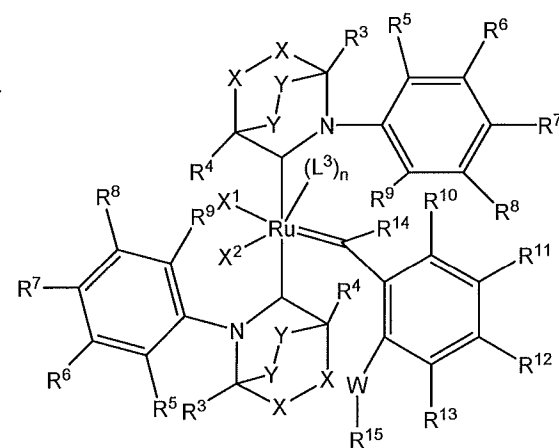
Formula (IIA12B4C1A12)



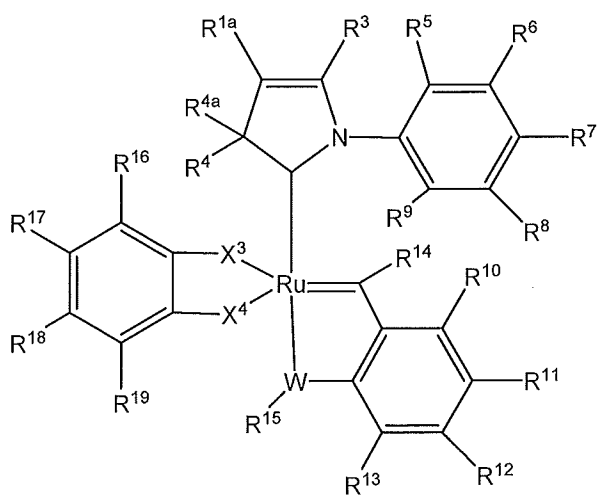
Formula (IIA12B4C3A12)



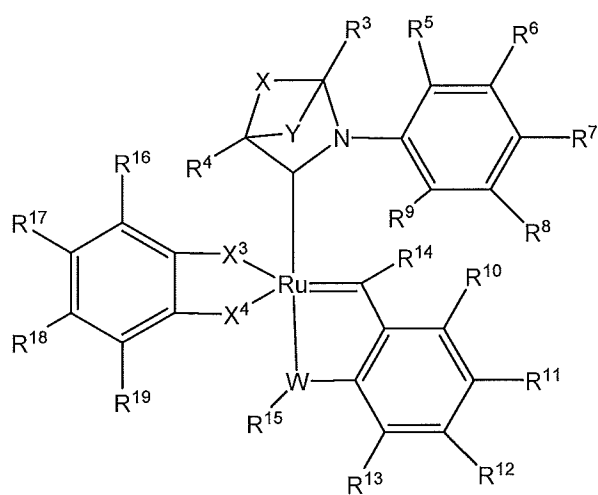
Formula (IIA9B4C1A9)



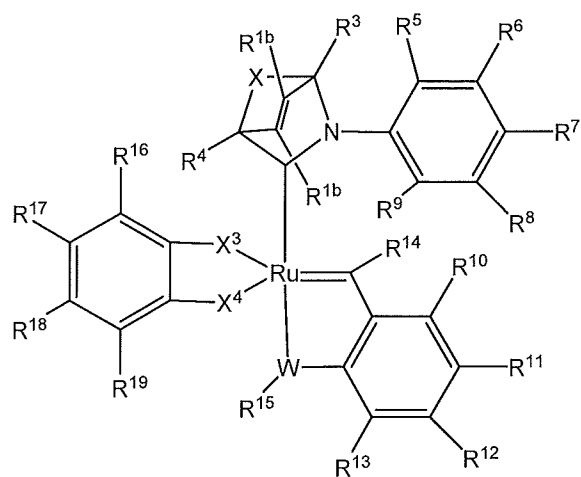
Formula (IIA9B4C3A9)



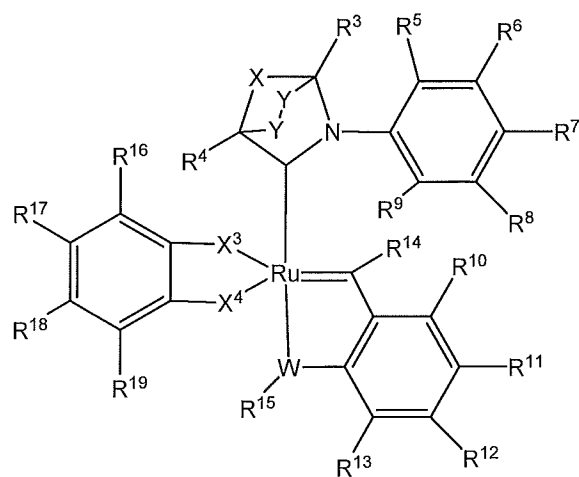
Formula (IA1B1C3)



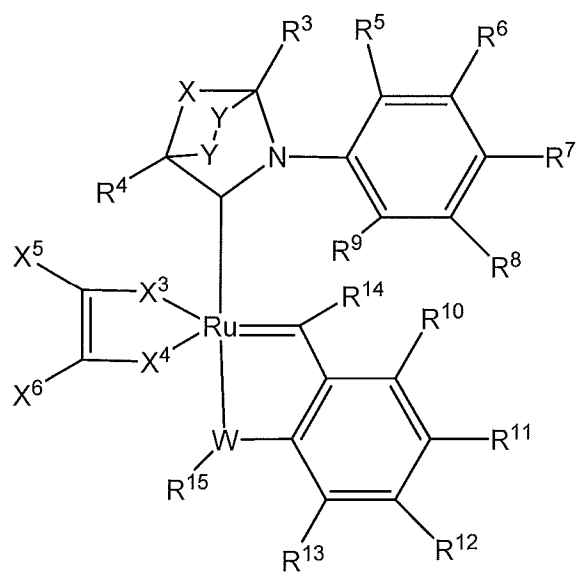
Formula (IA2B1C3)



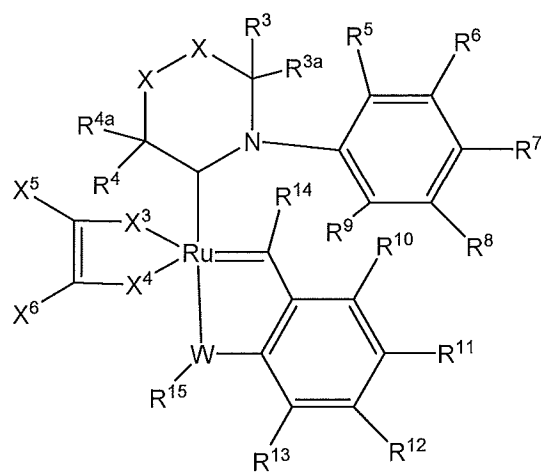
Formula (IA3B1C3)



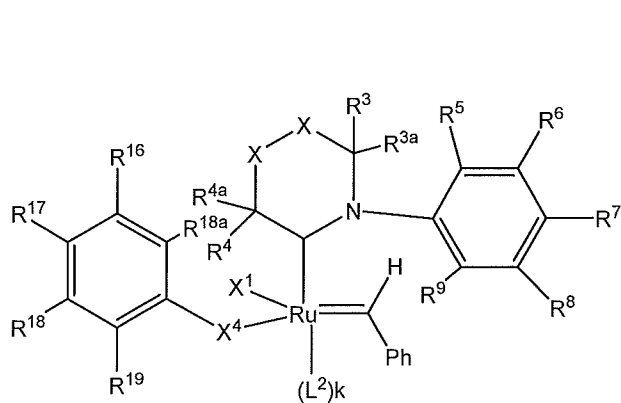
Formula (IA8B1C3)



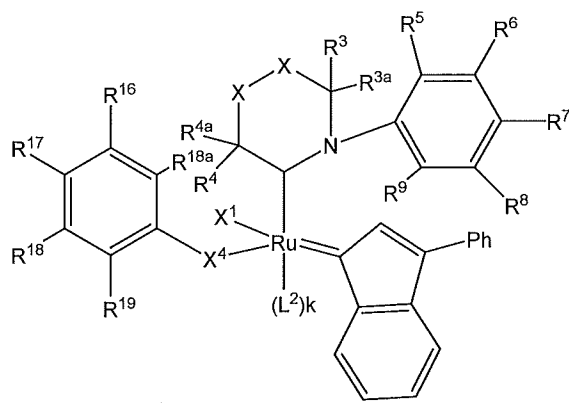
Formula (IA8B3C3)



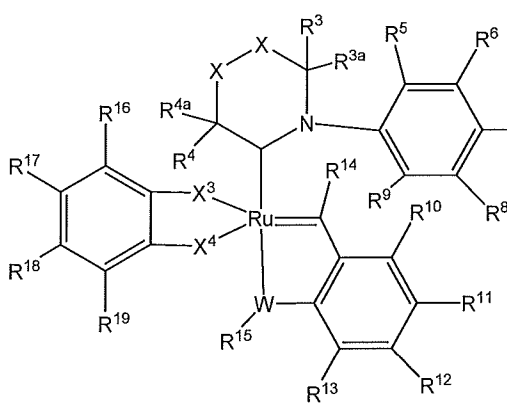
Formula (IA6B3C3)



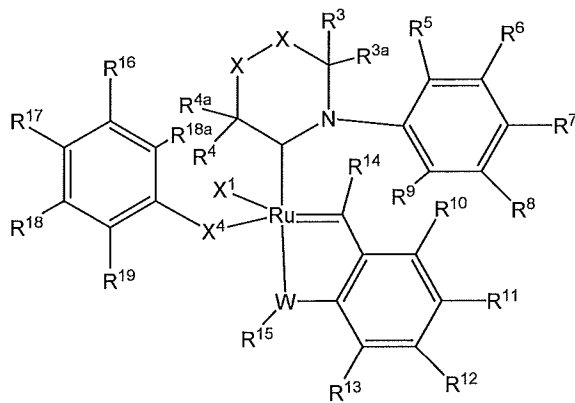
Formula (IA6B2C2)



Formula (IA6B2C1)

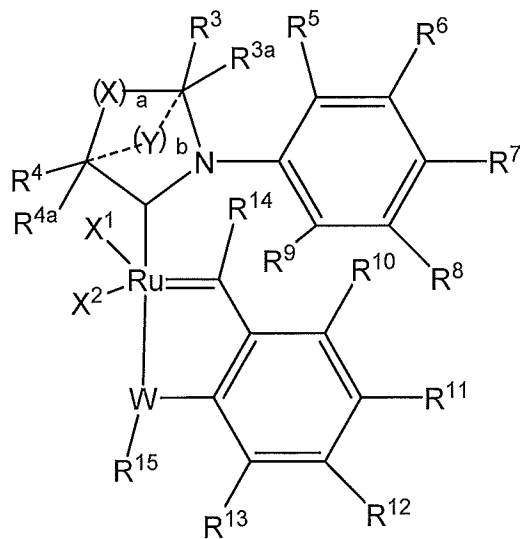


Formula (IA6B1C3)



Formula (IA6B2C3)

[0073] In one embodiment, the invention provides an olefin metathesis catalyst, represented by the structure of **Formula (IAB4C3)**,



Formula (IAB4C3)

wherein:

X¹ is halogen;

X² is halogen;

X is -CR^{1a}R^{2a}-;

R^{1a} is H, optionally substituted C₁₋₆ alkyl, optionally substituted cyclopentyl or optionally substituted cyclohexyl, halogen, optionally substituted phenyl, optionally substituted benzyl, optionally substituted C_{1-C6} heteroalkyl, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, or -SR²⁷;

R^{2a} is H, optionally substituted C₁₋₆ alkyl, optionally substituted cyclopentyl, optionally substituted cyclohexyl, halogen, optionally substituted phenyl, optionally substituted benzyl, optionally substituted C_{1-C6} heteroalkyl, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, or -SR²⁷;

a is 1 or 2;

Y is -CR^{1b}R^{2b}-;

R^{1b} is H, optionally substituted C₁₋₆ alkyl, optionally substituted cyclopentyl, optionally substituted cyclohexyl, halogen, optionally substituted phenyl, optionally substituted benzyl, optionally substituted C_{1-C6} heteroalkyl, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, or -SR²⁷;

R^{2b} is H, optionally substituted C₁₋₆ alkyl, optionally substituted cyclopentyl, optionally substituted cyclohexyl, halogen, optionally substituted phenyl, optionally substituted benzyl, optionally substituted C_{1-C6} heteroalkyl, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, or -SR²⁷;

b is 0, 1 or 2;

R³ is H, optionally substituted C₁₋₆ alkyl, optionally substituted cyclopentyl, optionally substituted cyclohexyl, halogen, optionally substituted phenyl, optionally substituted benzyl, optionally substituted C_{1-C6} heteroalkyl, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, or -SR²⁷;

R^{3a} is H, optionally substituted C₁₋₆ alkyl, optionally substituted cyclopentyl, optionally substituted cyclohexyl, halogen, optionally substituted phenyl, optionally substituted benzyl, optionally substituted C_{1-C6} heteroalkyl, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, or -SR²⁷;

R⁴ is H, optionally substituted C₁₋₆ alkyl, optionally substituted cyclopentyl, optionally substituted cyclohexyl, halogen, optionally substituted phenyl, optionally substituted benzyl, optionally substituted C₁₋₆ heteroalkyl, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, or together with R^{4a} forms an optionally substituted spiro cyclohexyl or adamantyl;

R^{4a} is H, optionally substituted C₁₋₆ alkyl, optionally substituted cyclopentyl, optionally substituted cyclohexyl, halogen, optionally substituted phenyl, optionally substituted benzyl, optionally substituted C₁₋₆ heteroalkyl, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, or together with R⁴ forms an optionally substituted spiro cyclohexyl or adamantyl;

R⁵ is H, optionally substituted C₁₋₆ alkyl, halogen, optionally substituted phenyl, or together with R⁶ can form an optionally substituted polycyclic ring;

R⁶ is H, optionally substituted C₁₋₆ alkyl, halogen, optionally substituted phenyl, or together with R⁵ or together with R⁷ can form an optionally substituted polycyclic ring;

R⁷ is H, optionally substituted C₁₋₆ alkyl, halogen, optionally substituted phenyl, or together with R⁶ or together with R⁸ can form an optionally substituted polycyclic ring;

R⁸ is H, optionally substituted C₁₋₆ alkyl, halogen, optionally substituted phenyl, or together with R⁷ or together with R⁹ can form an optionally substituted polycyclic ring;

R⁹ is H, optionally substituted C₁₋₆ alkyl, halogen, optionally substituted phenyl, or together with R⁸ can form a polycyclic ring;

W is O, S, or NR²⁰;

R¹⁰ is H, optionally substituted C₁₋₆ alkyl, halogen, optionally substituted phenyl, or together with R¹¹ can form a polycyclic ring;

R¹¹ is H, optionally substituted C₁₋₆ alkyl, halogen, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, optionally substituted cyclohexyl, optionally substituted cyclopentyl, optionally substituted phenyl, optionally substituted benzyl or together with R¹⁰ or together with R¹² can form a polycyclic ring;

R¹² is H, optionally substituted C₁₋₆ alkyl, halogen, optionally substituted phenyl, or together with R¹¹ or together with R¹³ can form a polycyclic ring;

R¹³ is H, optionally substituted C₁₋₆ alkyl, optionally substituted phenyl, or together with R¹² can form a polycyclic ring;

R^{14} is H, or optionally substituted C_{1-6} alkyl;

R^{15} is optionally substituted C_{1-6} alkyl, $-C(R^{28})(R^{29})COOR^{30}$, $-C(R^{28})(R^{29})C(O)H$, $-C(R^{28})(R^{29})C(O)R^{31}$, $-C(R^{28})(R^{29})CR^{32}(OR^{33})(OR^{34})$, $-C(R^{28})(R^{29})C(O)NR^{35}R^{36}$, $-C(R^{28})(R^{29})C(O)NR^{35}OR^{34}$, $C(R^{28})(R^{29})C(O)NR^{35}OR^{34}$, $-C(O)R^{21}$, optionally substituted heterocycle, optionally substituted C_{3-8} cycloalkyl, optionally substituted phenyl, optionally substituted cyclopentyl, optionally substituted cyclohexyl, or together with R^{20} can form an optionally substituted heterocyclic ring;

R^{20} is H, optionally substituted C_{1-6} alkyl, optionally substituted C_{3-8} cycloalkyl, optionally substituted phenyl, or together with R^{15} can form an optionally substituted heterocyclic ring;

R^{21} is OH, OR^{26} , $NR^{23}R^{24}$, or optionally substituted C_{1-6} alkyl;

R^{22} is H, or optionally substituted C_{1-6} alkyl;

R^{23} is H, or optionally substituted C_{1-6} alkyl;

R^{24} is H, or optionally substituted C_{1-6} alkyl;

R^{25} is H, or optionally substituted C_{1-6} alkyl, OR^{22} , $-NR^{23}R^{24}$;

R^{26} is optionally substituted C_{1-6} alkyl;

R^{27} is H, or optionally substituted C_{1-6} alkyl;

R^{28} is H, or optionally substituted C_{1-6} alkyl;

R^{29} is H, or optionally substituted C_{1-6} alkyl;

R^{30} is H, or optionally substituted C_{16} alkyl;

R^{31} is H, or optionally substituted C_{1-6} alkyl;

R^{32} is H, or optionally substituted C_{1-6} alkyl;

R^{33} is H, or optionally substituted C_{1-6} alkyl;

R^{34} is H, or optionally substituted C_{1-6} alkyl;

R^{35} is H, or optionally substituted C_{1-6} alkyl;

R^{36} is H, or optionally substituted C_{1-6} alkyl; and

x is 1 or 2.

[0074] In one embodiment, the invention provides an olefin metathesis catalyst, represented by the structure of **Formula (IAB4C3)**:

X is $-CR^{1a}R^{2a}$;

R^{1a} is H, phenyl, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, s-Bu, -NR²³R²⁴, F, Cl, Br, or I;

R^{2a} is H, phenyl, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, s-Bu, -NR²³R²⁴, F, Cl, Br, or I;

a is 2;

Y is -CR^{1b}R^{2b}-;

R^{1b} is H, phenyl, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, s-Bu, -NR²³R²⁴, F, Cl, Br, or I;

R^{2b} is H, phenyl, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, s-Bu, -NR²³R²⁴, F, Cl, Br, or I;

b is 0, 1 or 2;

W is O;

R³ is H, phenyl, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, or s-Bu;

R^{3a} is H, phenyl, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, or s-Bu;

R⁴ is H, phenyl, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, or s-Bu;

R^{4a} is H, phenyl, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, or s-Bu;

R⁵ is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, s-Bu, F, optionally substituted phenyl, or together with R⁵ or together with R⁷ can form an optionally substituted polycyclic ring;

R⁷ is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, s-Bu, optionally substituted phenyl, or together with R⁶ or together with R⁸ can form an optionally substituted polycyclic ring;

R⁸ is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, s-Bu, optionally substituted phenyl, or together with R⁷ or together with R⁹ can form an optionally substituted polycyclic ring;

R⁹ is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, s-Bu, F, optionally substituted phenyl, or together with R⁸ can form a polycyclic ring;

R¹⁰ is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, s-Bu, optionally substituted phenyl, or together with R¹¹ can form a polycyclic ring;

R¹¹ is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, s-Bu, NO₂, -NHC(O)CF₃, -S(O)₂NMe₂, optionally substituted phenyl, or together with R¹⁰ or together with R¹² can form a polycyclic ring;

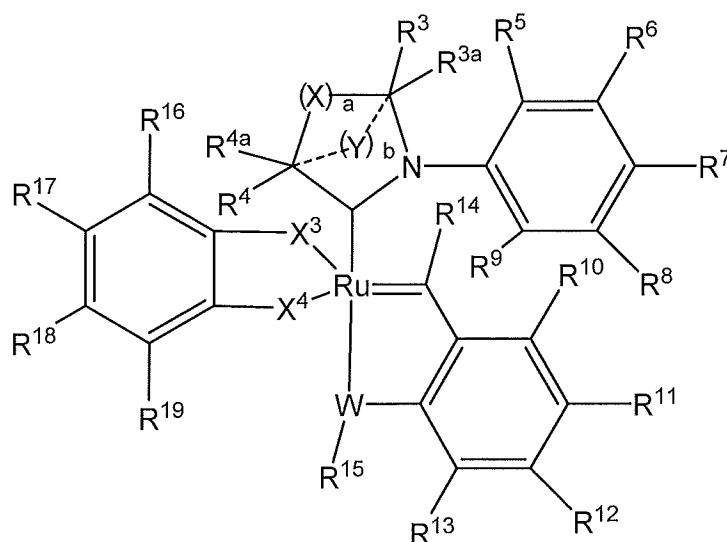
R¹² is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, s-Bu, halogen optionally substituted phenyl, or together with R¹¹ or together with R¹³ can form a polycyclic ring;

R¹³ is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, s-Bu, optionally substituted phenyl, or together with R¹² can form a polycyclic ring;

R¹⁴ is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, or s-Bu;

R^{15} is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, s-Bu, -C(O) R^{25} , -OR²⁶, CN, -NR²⁷R²⁸, NO₂, -CF₃, -S(O)_xR²⁹, -P(O)(OH)₂, C(R²⁸)(R²⁹)C(O)NR³⁵OR³⁴, -OP(O)(OH)₂, -SR³¹, pyridine, piperidine, imidazole, indolizine, indazole, cyclohexyl, phenyl, naphthalene, cyclohexene, F, Cl, Br, or I;
 R^{21} is OH, OR²⁶, NR²³R²⁴, or optionally substituted C₁₋₆ alkyl;
 R^{22} is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, or s-Bu;
 R^{23} is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, or s-Bu;
 R^{24} is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, or s-Bu;
 R^{25} is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, s-Bu, OR²², or -NR²³R²⁴;
 R^{26} is Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, or s-Bu;
 R^{27} is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, or s-Bu;
 R^{28} is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, or s-Bu;
 R^{29} is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, or s-Bu;
 R^{30} is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, or s-Bu;
 R^{31} is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, or s-Bu;
 R^{32} is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, or s-Bu;
 R^{33} is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, or s-Bu;
 R^{34} is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, or s-Bu;
 R^{35} is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, or s-Bu;
 R^{36} is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, or s-Bu;
x is 1 or 2;
X¹ is Cl; and
X² is Cl.

[0075] In one embodiment, the invention provides an olefin metathesis catalyst, represented by the structure of **Formula (IAB1C3)**,

**Formula (IAB1C3)**

wherein:

X^3 is O or S;

X^4 is O or S;

X is $-CR^{1a}R^{2a}-$;

R^{1a} is H, optionally substituted C_{1-6} alkyl, optionally substituted cyclopentyl or optionally substituted cyclohexyl, halogen, optionally substituted phenyl, optionally substituted benzyl, optionally substituted C_1-C_6 heteroalkyl, $-C(O)R^{21}$, $-OR^{22}$, CN, $-NR^{23}R^{24}$, NO_2 , $-CF_3$, $-S(O)_xR^{25}$, $-P(O)(OH)_2$, $-OP(O)(OH)_2$, or $-SR^{27}$;

R^{2a} is H, optionally substituted C_{1-6} alkyl, optionally substituted cyclopentyl, optionally substituted cyclohexyl, halogen, optionally substituted phenyl, optionally substituted benzyl, optionally substituted C_1-C_6 heteroalkyl, $-C(O)R^{21}$, $-OR^{22}$, CN, $-NR^{23}R^{24}$, NO_2 , $-CF_3$, $-S(O)_xR^{25}$, $-P(O)(OH)_2$, $-OP(O)(OH)_2$, or $-SR^{27}$;

a is 1 or 2;

Y is $-CR^{1b}R^{2b}-$;

R^{1b} is H, optionally substituted C_{1-6} alkyl, optionally substituted cyclopentyl, optionally substituted cyclohexyl, halogen, optionally substituted phenyl, optionally substituted benzyl, optionally substituted C_1-C_6 heteroalkyl, $-C(O)R^{21}$, $-OR^{22}$, CN, $-NR^{23}R^{24}$, NO_2 , $-CF_3$, $-S(O)_xR^{25}$, $-P(O)(OH)_2$, $-OP(O)(OH)_2$, or $-SR^{27}$;

R^{2b} is H, optionally substituted C_{1-6} alkyl, optionally substituted cyclopentyl, optionally substituted cyclohexyl, halogen, optionally substituted phenyl, optionally substituted benzyl, optionally substituted C_1 - C_6 heteroalkyl, -C(O) R^{21} , -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, or -SR²⁷;

b is 0, 1 or 2;

W is O, halogen, NR²⁰ or S;

R^3 is H, optionally substituted C_{1-6} alkyl, optionally substituted cyclopentyl, optionally substituted cyclohexyl, halogen, optionally substituted phenyl, optionally substituted benzyl, optionally substituted C_1 - C_6 heteroalkyl, -C(O) R^{21} , -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, or -SR²⁷;

R^{3a} is H, optionally substituted C_{1-6} alkyl, optionally substituted cyclopentyl, optionally substituted cyclohexyl, halogen, optionally substituted phenyl, optionally substituted benzyl, optionally substituted C_1 - C_6 heteroalkyl, -C(O) R^{21} , -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, or -SR²⁷;

R^4 is H, optionally substituted C_{1-6} alkyl, optionally substituted cyclopentyl, optionally substituted cyclohexyl, halogen, optionally substituted phenyl, optionally substituted benzyl, optionally substituted C_1 - C_6 heteroalkyl, -C(O) R^{21} , -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, or together with R^{4a} forms an optionally substituted spiro cyclohexyl or adamantyl;

R^{4a} is H, optionally substituted C_{1-6} alkyl, optionally substituted cyclopentyl, optionally substituted cyclohexyl, halogen, optionally substituted phenyl, optionally substituted benzyl, optionally substituted C_1 - C_6 heteroalkyl, -C(O) R^{21} , -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, or together with R^4 forms an optionally substituted spiro cyclohexyl or adamantyl;

R^5 is H, optionally substituted C_{1-6} alkyl, halogen, optionally substituted phenyl, or together with R^6 can form an optionally substituted polycyclic ring;

R^6 is H, optionally substituted C_{1-6} alkyl, halogen, optionally substituted phenyl, or together with R^5 or together with R^7 can form an optionally substituted polycyclic ring;

R^7 is H, optionally substituted C_{1-6} alkyl, halogen, optionally substituted phenyl, or together with R^6 or together with R^8 can form an optionally substituted polycyclic ring;

R⁸ is H, optionally substituted C₁₋₆ alkyl, halogen, optionally substituted phenyl, or together with R⁷ or together with R⁹ can form an optionally substituted polycyclic ring;

R⁹ is H, optionally substituted C₁₋₆ alkyl, halogen, optionally substituted phenyl, or together with R⁸ can form a polycyclic ring;

R¹⁰ is H, optionally substituted C₁₋₆ alkyl, halogen, optionally substituted phenyl, or together with R¹¹ can form a polycyclic ring;

R¹¹ is H, optionally substituted C₁₋₆ alkyl, halogen, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -NHC(O)CF₃, -SR²⁷, optionally substituted phenyl, or together with R¹⁰ or together with R¹² can form a polycyclic ring;

R¹² is H, optionally substituted C₁₋₆ alkyl, halogen, optionally substituted phenyl, or together with R¹¹ or together with R¹³ can form a polycyclic ring;

R¹³ is H, optionally substituted C₁₋₆ alkyl, halogen, optionally substituted phenyl, or together with R¹² can form a polycyclic ring;

R¹⁴ is H, or optionally substituted C₁₋₆ alkyl;

R¹⁵ is optionally substituted C₁₋₆ alkyl, -C(R²⁸)(R²⁹)COOR³⁰, -C(R²⁸)(R²⁹)C(O)H, -C(R²⁸)(R²⁹)C(O)R³¹, -C(R²⁸)(R²⁹)CR³²(OR³³)(OR³⁴), -C(R²⁸)(R²⁹)C(O)NR³⁵R³⁶, -C(R²⁸)(R²⁹)C(O)NR³⁵OR³⁴, -C(O)R²¹, optionally substituted heterocycle, optionally substituted C₃₋₈ cycloalkyl, optionally substituted phenyl, optionally substituted cyclopentyl, optionally substituted cyclohexyl, or together with R²⁰ can form an optionally substituted heterocyclic ring;

R¹⁶ is H, optionally substituted C₁₋₆ alkyl, halogen, -C(O)R²⁵, -OR²⁶, CN, -NR²⁷R²⁸, NO₂, -CF₃, -S(O)_xR²⁹, -P(O)(OH)₂, -OP(O)(OH)₂, -SR³¹, optionally substituted heterocycle, optionally substituted C₃₋₈ cycloalkyl, optionally substituted phenyl or together with R¹⁷ can form an optionally substituted polycyclic ring;

R¹⁷ is H, optionally substituted C₁₋₆ alkyl, halogen, -C(O)R²⁵, -OR²⁶, CN, -NR²⁷R²⁸, NO₂, -CF₃, -S(O)_xR²⁹, -P(O)(OH)₂, -OP(O)(OH)₂, -SR³¹, optionally substituted phenyl or optionally substituted C₃₋₈ cycloalkenyl, or together with R¹⁶ or together with R¹⁸ can form an optionally substituted polycyclic ring;

R¹⁸ is H, optionally substituted C₁₋₆ alkyl, halogen, -C(O)R²⁵, -OR²⁶, CN, -NR²⁷R²⁸, NO₂, -CF₃, -S(O)_xR²⁹, -P(O)(OH)₂, -OP(O)(OH)₂, -SR³¹, optionally substituted phenyl or together with R¹⁷ or together with R¹⁹ can form an optionally substituted polycyclic ring;

R¹⁹ is H, optionally substituted C₁₋₆ alkyl, halogen, -C(O)R²⁵, -OR²⁶, CN, -NR²⁷R²⁸, NO₂, -CF₃, -S(O)_xR²⁹, -P(O)(OH)₂, -OP(O)(OH)₂, -SR³¹, optionally substituted heterocycle, optionally substituted C₃₋₈ cycloalkyl, optionally substituted phenyl or optionally substituted C₃₋₈ cycloalkenyl, or together with R¹⁸ can form an optionally substituted polycyclic ring;

R²⁰ is H, optionally substituted C₁₋₆ alkyl, optionally substituted C₃₋₈ cycloalkyl, optionally substituted phenyl, or together with R¹⁵ can form an optionally substituted heterocyclic ring;

R²¹ is OH, OR²⁶, NR²³R²⁴, or optionally substituted C₁₋₆ alkyl;

R²² is H, or optionally substituted C₁₋₆ alkyl;

R²³ is H, or optionally substituted C₁₋₆ alkyl;

R²⁴ is H, or optionally substituted C₁₋₆ alkyl;

R²⁵ is H, optionally substituted C₁₋₆ alkyl, OR²², or -NR²³R²⁴;

R²⁶ is optionally substituted C₁₋₆ alkyl;

R²⁷ is H, or optionally substituted C₁₋₆ alkyl;

R²⁸ is H, or optionally substituted C₁₋₆ alkyl;

R²⁹ is H, or optionally substituted C₁₋₆ alkyl;

R³⁰ is H, or optionally substituted C₁₆ alkyl;

R³¹ is H, or optionally substituted C₁₋₆ alkyl;

R³² is H, or optionally substituted C₁₋₆ alkyl;

R³³ is H, or optionally substituted C₁₋₆ alkyl;

R³⁴ is H, or optionally substituted C₁₋₆ alkyl;

R³⁵ is H, or optionally substituted C₁₋₆ alkyl;

R³⁶ is H, or optionally substituted C₁₋₆ alkyl;

x is 1 or 2;

X¹ is halogen; and

X² is halogen.

[0076] In one embodiment, the invention provides an olefin metathesis catalyst, represented by the structure of **Formula (IAB1C3)**, wherein:

X³ is S;

X⁴ is S;

X is $-\text{CR}^{1a}\text{R}^{2a}-$;

R^{1a} is H, phenyl, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, s-Bu, $-\text{NR}^{23}\text{R}^{24}$, F, Cl, Br, or I;

R^{2a} is H, phenyl, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, s-Bu, $-\text{NR}^{23}\text{R}^{24}$, F, Cl, Br, or I;

a is 2;

Y is $-\text{CR}^{1b}\text{R}^{2b}-$;

R^{1b} is H, phenyl, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, s-Bu, $-\text{NR}^{23}\text{R}^{24}$, F, Cl, Br, or I;

R^{2b} is H, phenyl, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, s-Bu, $-\text{NR}^{23}\text{R}^{24}$, F, Cl, Br, or I;

b is 0, 1 or 2;

W is O;

R^3 is H, phenyl, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, or s-Bu;

R^{3a} is H, phenyl, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, or s-Bu;

R^4 is H, phenyl, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, or s-Bu;

R^{4a} is H, phenyl, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, or s-Bu;

R^5 is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, s-Bu, F, optionally substituted phenyl, or together with R^6 can form an optionally substituted polycyclic ring;

R^6 is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, s-Bu, optionally substituted phenyl, or together with R^5 or together with R^7 can form an optionally substituted polycyclic ring;

R^7 is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, s-Bu, optionally substituted phenyl, or together with R^6 or together with R^8 can form an optionally substituted polycyclic ring;

R^8 is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, s-Bu, optionally substituted phenyl, or together with R^7 or together with R^9 can form an optionally substituted polycyclic ring;

R^9 is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, s-Bu, F, optionally substituted phenyl, or together with R^8 can form a polycyclic ring;

R^{10} is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, s-Bu, optionally substituted phenyl, or together with R^{11} can form a polycyclic ring;

R^{11} is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, s-Bu, halogen, $-\text{C}(\text{O})\text{R}^{21}$, $-\text{OR}^{22}$, CN, $-\text{NR}^{23}\text{R}^{24}$, NO_2 , $-\text{CF}_3$, $-\text{S}(\text{O})_x\text{R}^{25}$, $-\text{P}(\text{O})(\text{OH})_2$, $-\text{OP}(\text{O})(\text{OH})_2$, $-\text{NHC}(\text{O})\text{CF}_3$, $-\text{SR}^{27}$, optionally substituted cyclopentyl, optionally substituted cyclohexyl, optionally substituted benzyl, optionally substituted phenyl, or together with R^{10} or together with R^{12} can form a polycyclic ring;

R^{12} is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, s-Bu, halogen, optionally substituted phenyl, or together with R^{11} or together with R^{13} can form a polycyclic ring;

R¹³ is H, optionally substituted C₁₋₆ alkyl, optionally substituted phenyl, or together with R¹² can form a polycyclic ring;

R¹⁴ is H, or optionally substituted C₁₋₆ alkyl;

R¹⁵ is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, s-Bu, -C(O)R²⁵, -OR²⁶, CN, -NR²⁷R²⁸, NO₂, -CF₃, -S(O)_xR²⁹, -P(O)(OH)₂, -OP(O)(OH)₂, -SR³¹, pyridine, piperidine, imidazole, indolizine, indazole, cyclohexyl, phenyl, naphthalene, cyclohexene, F, Cl, Br, or I;

R¹⁶ is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, s-Bu, F, Cl, Br, I, -C(O)R²⁵, -OR²⁶, CN, -NR²⁷R²⁸, NO₂, -CF₃, -S(O)_xR²⁹, -P(O)(OH)₂, -OP(O)(OH)₂, -SR³¹, pyridine, piperidine, imidazole, indolizine, indazole, cyclohexyl, naphthalene, cyclohexene, optionally substituted phenyl or together with R¹⁷ can form an optionally substituted polycyclic ring;

R¹⁷ is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, s-Bu, F, Cl, Br, I, -C(O)R²⁵, -OR²⁶, CN, -NR²⁷R²⁸, NO₂, -CF₃, -S(O)_xR²⁹, -P(O)(OH)₂, -OP(O)(OH)₂, -SR³¹, pyridine, piperidine, imidazole, indolizine, indazole, cyclohexyl, naphthalene, cyclohexene, optionally substituted phenyl, or together with R¹⁶ or together with R¹⁸ can form an optionally substituted polycyclic ring;

R¹⁸ is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, s-Bu, F, Cl, Br, I, -C(O)R²⁵, -OR²⁶, CN, -NR²⁷R²⁸, NO₂, -CF₃, -S(O)_xR²⁹, -P(O)(OH)₂, -OP(O)(OH)₂, -SR³¹, pyridine, piperidine, imidazole, indolizine, indazole, cyclohexyl, naphthalene, cyclohexene, optionally substituted phenyl or together with R¹⁷ or together with R¹⁹ can form an optionally substituted polycyclic ring;

R¹⁹ is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, s-Bu, F, Cl, Br, I, -C(O)R²⁵, -OR²⁶, CN, -NR²⁷R²⁸, NO₂, -CF₃, -S(O)_xR²⁹, -P(O)(OH)₂, -OP(O)(OH)₂, -SR³¹, pyridine, piperidine, imidazole, indolizine, indazole, cyclohexyl, naphthalene, cyclohexene, optionally substituted phenyl or together with R¹⁸ can form an optionally substituted polycyclic ring;

R²¹ is OH, OR²⁶, NR²³R²⁴, or optionally substituted C₁₋₆ alkyl;

R²² is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, or s-Bu;

R²³ is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, or s-Bu;

R²⁴ is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, or s-Bu;

R²⁵ is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, s-Bu, OR²², or -NR²³R²⁴;

R²⁶ is Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, or s-Bu;

R²⁷ is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, or s-Bu;

R²⁸ is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, or s-Bu;

R²⁹ is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, or s-Bu;

R^{30} is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, or s-Bu;

R^{31} is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, or s-Bu;

R^{32} is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, or s-Bu;

R^{33} is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, or s-Bu;

R^{34} is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, or s-Bu;

R^{35} is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, or s-Bu;

R^{36} is H, Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, or s-Bu;

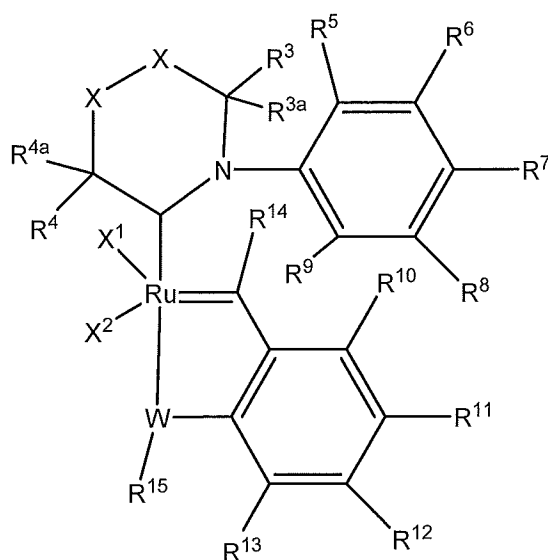
x is 1 or 2;

X^1 is Cl; and

X^2 is Cl.

[0077] Examples of olefin metathesis catalysts represented by the structure of **Formula**

(IA6B4C3), wherein: $X^1 = Cl$, $X^2 = Cl$, $W = O$, $b = 0$, $a = 2$, $X = -CR^{1a}R^{2a}$, $R^{1a} = H$, $R^{2a} = H$, $R^6 = H$, $R^8 = H$, $R^{10} = H$, $R^{11} = H$, $R^{12} = H$, $R^{13} = H$, $R^{14} = H$, and $R^{15} = i\text{-Pr}$, are found in **Table (2)**.

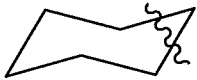
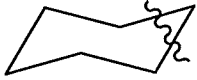
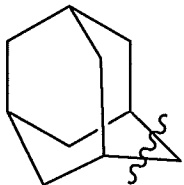
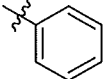
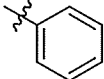
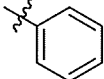
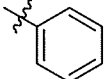
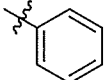


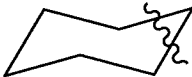
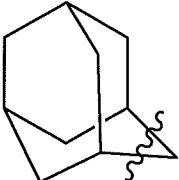
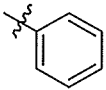
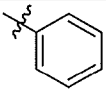
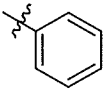
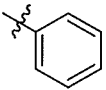
Formula (IA6B4C3)

Table (2)

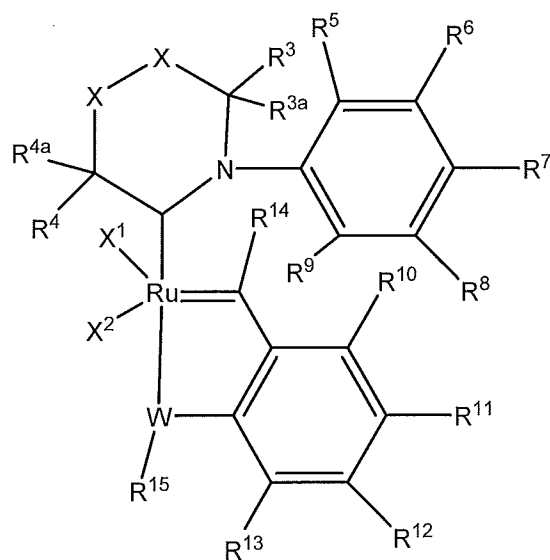
Examples of olefin metathesis catalysts represented by **Formula (IA6B4C3)**

Catalyst	R^3	R^{3a}	R^4	R^{4a}	R^5	R^7	R^9
1	Me	Me	Me	Me	Et	H	Me

2	Me	Me	Me	Me	Et	H	Et
3	Me	Me	Me	Me	i-Pr	H	Me
4	Me	Me	Me	Me	t-Bu	H	Me
5	Me	Me	Me	Me	i-Pr	H	i-Pr
6	Me	Me	Et	Et	i-Pr	H	H
7	Me	Me	Et	Et	Me	Me	Me
8	Me	Me	Et	Et	i-Pr	H	Me
9	Me	Me			Me	Me	Me
10	Me	Me			i-Pr	H	i-Pr
11	Me	Me	n-Pr	Me	i-Pr	H	i-Pr
12	Me	Me			Et	H	Et
13	Me	Me		Me	Me	Me	Me
14	Me	Me	Me		Et	H	Me
15	Me	Me	Me		Et	H	Et
16	Me	Me	Me		i-Pr	H	Me
17	Me	Me	Me		i-Pr	H	i-Pr
18	Me	Me	Me	Me	Me	Me	Me
19	Me	Me	Me	Me	i-Pr	H	H
20	Me	Me	Et	Et	Et	H	Me

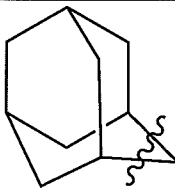
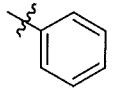
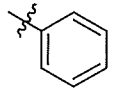
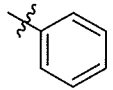
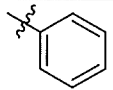
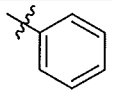
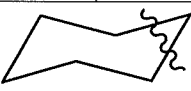
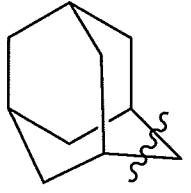
21	Me	Me	Me	Et	i-Pr	H	Me
22	Me	Me	Me	Et	t-Bu	H	Me
23	Me	Me	Et	n-Pr	i-Pr	H	i-Pr
24	Me	Me	n-Pr	n-Pr	i-Pr	H	Me
25	Me	Me	Et	n-Pr	i-Pr	H	H
26	Me	Me	Et	Et	Me	Me	Me
27	Me	Me			Me	Me	Me
28	Me	Me			Me	Me	Me
29	Me	Me		Et	Me	Me	Me
30	Me	Me		Et	Et	H	Me
31	Me	Me		Et	Et	H	Et
32	Me	Me		Et	i-Pr	H	Me

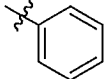
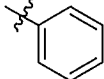
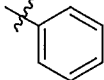
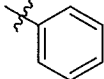
[0078] Examples of olefin metathesis catalysts represented by the structure of **Formula (IA6B4C3)**, wherein, $X^1 = \text{Cl}$, $X^2 = \text{Cl}$, $W = \text{O}$, $b = 0$, $a = 2$, $X = -\text{CR}^{1a}\text{R}^{2a}-$, $\text{R}^{1a} = \text{H}$, $\text{R}^{2a} = \text{H}$, $\text{R}^6 = \text{H}$, $\text{R}^8 = \text{H}$, $\text{R}^{10} = \text{H}$, $\text{R}^{11} = \text{NHC(O)CF}_3$, $\text{R}^{12} = \text{H}$, $\text{R}^{13} = \text{H}$, $\text{R}^{14} = \text{H}$, and $\text{R}^{15} = \text{i-Pr}$, are found in **Table (3)**.

**Formula (IA6B4C3)****Table (3)**

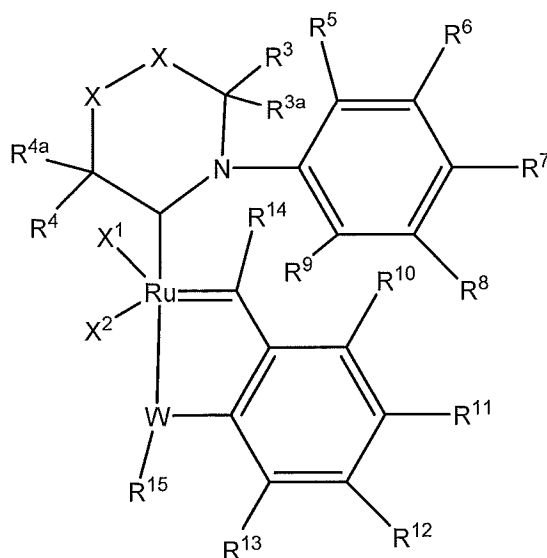
Examples of olefin metathesis catalysts represented by **Formula (IA6B4C3)**

Catalyst	R ₃	R ^{3a}	R ⁴	R ^{4a}	R ⁵	R ⁷	R ⁹
33	Me	Me	Me	Me	Et	H	Me
34	Me	Me	Me	Me	Et	H	Et
35	Me	Me	Me	Me	i-Pr	H	Me
36	Me	Me	Me	Me	t-Bu	H	Me
37	Me	Me	Me	Me	i-Pr	H	i-Pr
38	Me	Me	Et	Et	i-Pr	H	H
39	Me	Me	Et	Et	Me	Me	Me
40	Me	Me	Et	Et	i-Pr	H	Me
41	Me	Me			Me	Me	Me
42	Me	Me			i-Pr	H	i-Pr
43	Me	Me	n-Pr	Me	i-Pr	H	i-Pr
44	Me	Me			Et	H	Et

							
45	Me	Me		Me	Me	Me	Me
46	Me	Me	Me		Et	H	Me
47	Me	Me	Me		Et	H	Et
48	Me	Me	Me		i-Pr	H	Me
49	Me	Me	Me		i-Pr	H	i-Pr
50	Me	Me	Me	Me	Me	Me	Me
51	Me	Me	Me	Me	i-Pr	H	H
52	Me	Me	Et	Et	Et	H	Me
53	Me	Me	Me	Et	i-Pr	H	Me
54	Me	Me	Me	Et	t-Bu	H	Me
55	Me	Me	Et	n-Pr	i-Pr	H	i-Pr
56	Me	Me	n-Pr	n-Pr	i-Pr	H	Me
57	Me	Me	Et	n-Pr	i-Pr	H	H
58	Me	Me	Et	Et	Me	Me	Me
59	Me	Me			Me	H	Me
60	Me	Me			Me	Me	Me

61	Me	Me		Et	Me	Me	Me
62	Me	Me		Et	Et	H	Me
63	Me	Me		Et	Et	H	Et
64	Me	Me		Et	i-Pr	H	Me

[0079] Examples of olefin metathesis catalysts represented by the structure of **Formula (IA6B4C3)**, wherein, $X^1 = \text{Cl}$, $X^2 = \text{Cl}$, $W = \text{O}$, $b = 0$, $a = 2$, $X = -\text{CR}^{1a}\text{R}^{2a}$, $\text{R}^{1a} = \text{H}$, $\text{R}^{2a} = \text{H}$, $\text{R}^6 = \text{H}$, $\text{R}^8 = \text{H}$, $\text{R}^{10} = \text{H}$, $\text{R}^{11} = \text{S}(\text{O})_2\text{NMe}_2$, $\text{R}^{12} = \text{H}$, $\text{R}^{13} = \text{H}$, $\text{R}^{14} = \text{H}$, and $\text{R}^{15} = \text{i-Pr}$, are found in **Table (4)**.

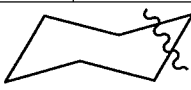
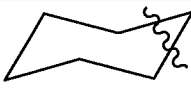
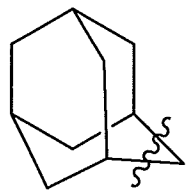
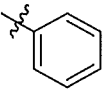
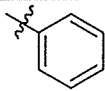
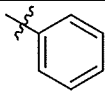
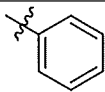
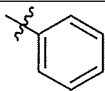


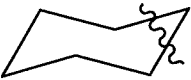
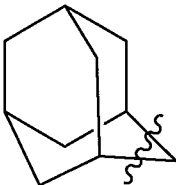
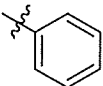
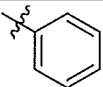
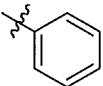
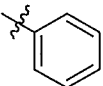
Formula (IA6B4C3)

Table (4)

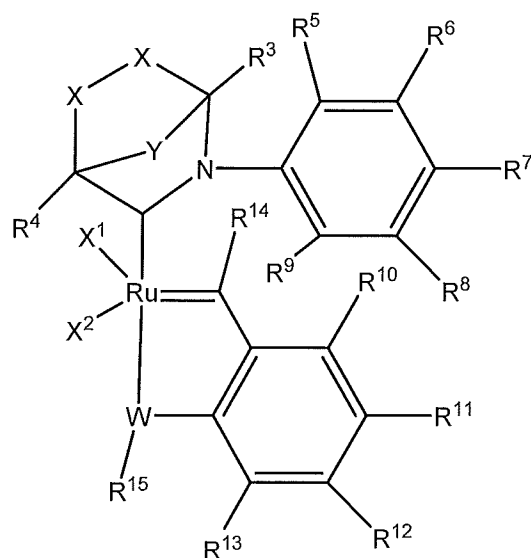
Examples of olefin metathesis catalysts represented by Formula **(IA6B4C3)**

Catalyst	R_3	R^{3a}	R^4	R^{4a}	R^5	R^7	R^9
----------	--------------	-----------------	--------------	-----------------	--------------	--------------	--------------

65	Me	Me	Me	Me	Et	H	Me
66	Me	Me	Me	Me	Et	H	Et
67	Me	Me	Me	Me	i-Pr	H	Me
68	Me	Me	Me	Me	t-Bu	H	Me
69	Me	Me	Me	Me	i-Pr	H	i-Pr
70	Me	Me	Et	Et	i-Pr	H	H
71	Me	Me	Et	Et	Me	Me	Me
72	Me	Me	Et	Et	i-Pr	H	Me
73	Me	Me			Me	Me	Me
74	Me	Me			i-Pr	H	i-Pr
75	Me	Me	n-Pr	Me	i-Pr	H	i-Pr
76	Me	Me			Et	H	Et
77	Me	Me		Me	Me	Me	Me
78	Me	Me	Me		Et	H	Me
79	Me	Me	Me		Et	H	Et
80	Me	Me	Me		i-Pr	H	Me
81	Me	Me	Me		i-Pr	H	i-Pr
82	Me	Me	Me	Me	Me	Me	Me
83	Me	Me	Me	Me	i-Pr	H	H

84	Me	Me	Et	Et	Et	H	Me
85	Me	Me	Me	Et	i-Pr	H	Me
86	Me	Me	Me	Et	t-Bu	H	Me
87	Me	Me	Et	n-Pr	i-Pr	H	i-Pr
88	Me	Me	n-Pr	n-Pr	i-Pr	H	Me
89	Me	Me	Et	n-Pr	i-Pr	H	H
90	Me	Me	Et	Et	Me	Me	Me
91	Me	Me			Me	Me	Me
92	Me	Me			Me	Me	Me
93	Me	Me		Et	Me	Me	Me
94	Me	Me		Et	Et	H	Me
95	Me	Me		Et	Et	H	Et
96	Me	Me		Et	i-Pr	H	Me

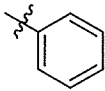
[0080] Examples of olefin metathesis catalysts represented by the structure of **Formula (IA12B4C3)**, wherein: $X^1 = Cl$, $X^2 = Cl$, $W = O$, $R^{15} = i\text{-Pr}$, $b = 1$, $Y = -CR^{1b}R^{2b}-$, $a = 2$, $X = -CR^{1a}R^{2a}-$, $R^{1a} = H$, $R^{2a} = H$, $R^{1b} = H$, $R^{2b} = H$, $R^6 = H$, $R^8 = H$, $R^{10} = H$, $R^{11} = H$, $R^{12} = H$, $R^{13} = H$, $R^{14} = H$.

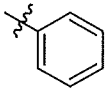
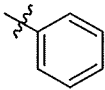
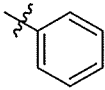
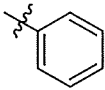


Formula (IA12B4C3)

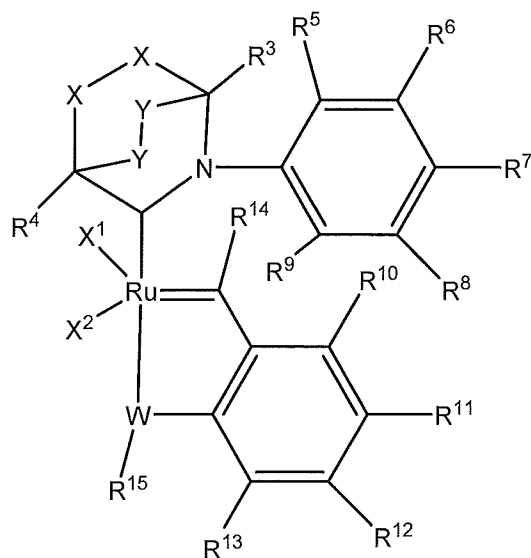
Table (5)

Examples of olefin metathesis catalysts represented by **Formula (IA12B4C3)**

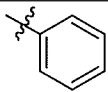
Catalyst	R ³	R ⁴	R ⁵	R ⁷	R ⁹
97	Me	Me	Et	H	Me
98	Me	Me	Et	H	Et
99	Me	Me	i-Pr	H	Me
100	Me	Me	t-Bu	H	Me
101	Me	Me	i-Pr	H	H
102	Me	Et	i-Pr	H	H
103	Me	Et	Me	Me	Me
104	Me	Et	i-Pr	H	Me
105	Me	n-Pr	i-Pr	H	i-Pr
106	Me		Me	H	Me
107	Me	Et	Et	H	Me
108	Me	Et	Et	H	Et

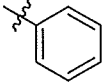
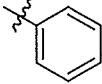
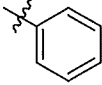
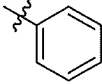
109	Me	Me	Me	H	H
110	Me	Me	i-Pr	H	i-Pr
111	Me	Me	Me	Me	Me
112	Me	Me	i-Pr	H	H
113	Me	n-Pr	Et	H	Me
114	Me	n-Pr	i-Pr	H	Me
115	Me	n-Pr	t-Bu	H	Me
116	Me	n-Pr	i-Pr	H	i-Pr
117	Me	n-Pr	i-Pr	H	Me
118	Me	n-Pr	i-Pr	H	H
119	Me	n-Pr	Me	Me	Me
120	Me		Me	Me	Me
121	Me		Et	H	Me
122	Me		Et	H	Et
123	Me		i-Pr	H	Me

[0081] Examples of olefin metathesis catalysts represented by the structure of **Formula (IA9B4C3)** wherein: $X^1 = \text{Cl}$, $X^2 = \text{Cl}$, $W = \text{O}$, $R^{15} = i\text{-Pr}$, $b = 2$, $Y = -\text{CR}^{1b}\text{R}^{2b}-$, $a = 2$, $X = -\text{CR}^{1a}\text{R}^{2a}-$, $R^{1a} = \text{H}$, $R^{2a} = \text{H}$, $R^{1b} = \text{H}$, $R^{2b} = \text{H}$, $R^6 = \text{H}$, $R^8 = \text{H}$, $R^{10} = \text{H}$, $R^{11} = \text{H}$, $R^{12} = \text{H}$, $R^{13} = \text{H}$, and $R^{14} = \text{H}$, are found in **Table (6)**.

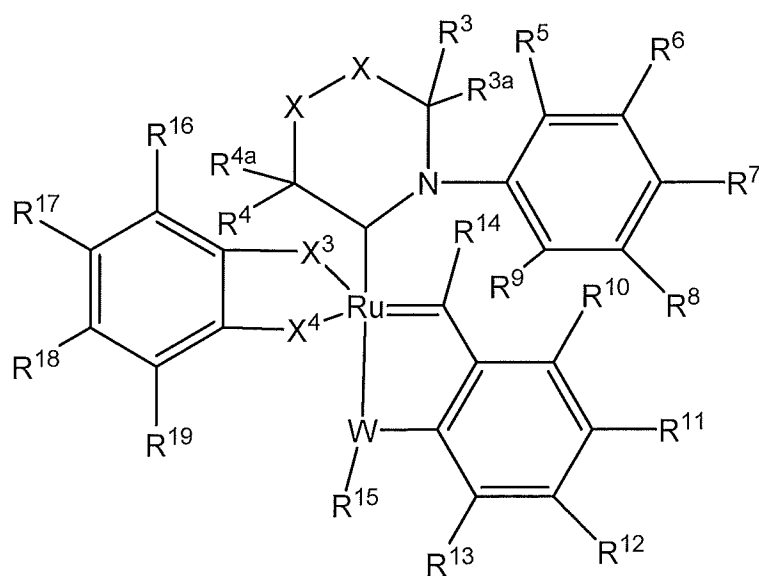
**Formula (IA9B4C3)****Table (6)**

Examples of olefin metathesis catalysts represented by **Formula (IA9B4C3)**

Catalyst	R ³	R ⁴	R ⁵	R ⁷	R ⁹
124	Me	Me	Et	H	Me
125	Me	Me	Et	H	Et
126	Me	Me	i-Pr	H	Me
127	Me	Me	t-Bu	H	Me
128	Me	Me	i-Pr	H	i-Pr
129	Me	Et	i-Pr	H	H
130	Me	Et	Me	Me	Me
131	Me	Et	i-Pr	H	Me
132	Me	n-Pr	i-Pr	H	i-Pr
133	Me		Me	H	Me
134	Me	Et	Et	H	Me
135	Me	Et	Et	H	Et
136	Me	Et	i-Pr	H	Me

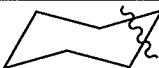
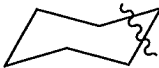
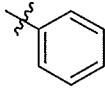
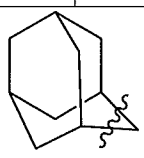
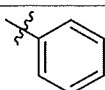
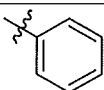
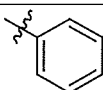
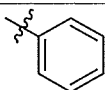
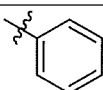
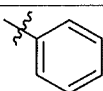
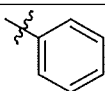
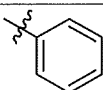
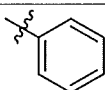
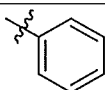
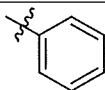
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138	Me	Me	Me	Me	Me
139	Me	Me	i-Pr	H	H
140	Me	n-Pr	Et	H	Me
141	Me	n-Pr	i-Pr	H	Me
142	Me	n-Pr	t-Bu	H	Me
143	Me	Et	i-Pr	H	i-Pr
144	Me	n-Pr	i-Pr	H	Me
145	Me	Et	i-Pr	H	H
146	Me	Et	Me	Me	Me
147	Me		Me	Me	Me
148	Me		Et	H	Me
149	Me		Et	H	Et
150	Me		i-Pr	H	Me

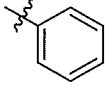
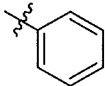
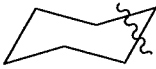
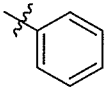
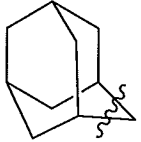
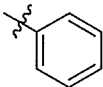
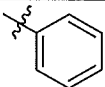
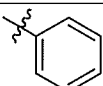
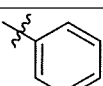
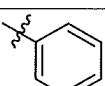
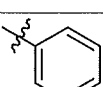
[0082] Examples of olefin metathesis catalysts represented by the structure of **Formula (IA6B1C3)**, wherein: $W = O$, $R^{15} = i\text{-Pr}$, $b = 0$, $a = 2$, $X = -CR^{1a}R^{2a}$, $R^{1a} = H$, $R^{2a} = H$, $R^6 = H$, $R^8 = H$, $X^3 = S$, $X^4 = S$, $R^{10} = H$, $R^{11} = H$, $R^{12} = H$, $R^{13} = H$, $R^{14} = H$, $R^{17} = H$, and $R^{18} = H$, are found in **Table (7)**.

**Formula (IA6B1C3)****Table (7)**

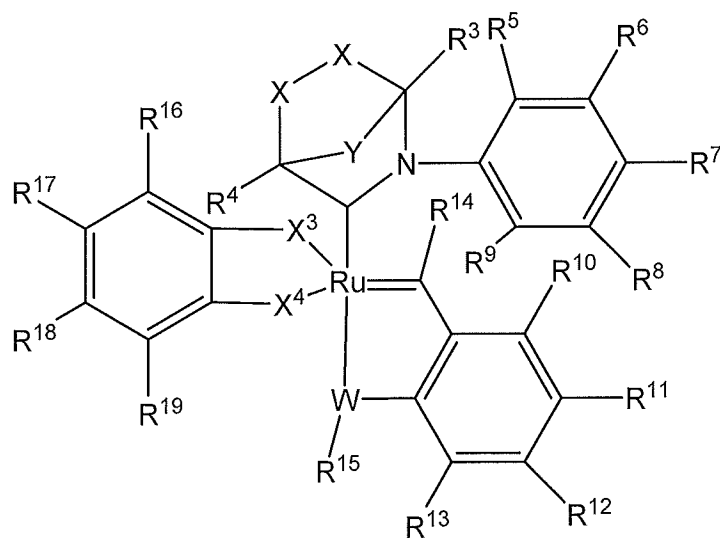
Examples of olefin metathesis catalysts represented by **Formula (IA6B1C3)**

Catalyst	R³	R^{3a}	R⁴	R^{4a}	R⁵	R⁷	R⁹	R¹⁶	R¹⁹
151	Me	Me	Me	Me	Et	H	Me	Cl	Cl
152	Me	Me	Me	Me	Et	H	Et	H	
153	Me	Me	Me	Me	i-Pr	H	Me	Cl	Cl
154	Me	Me	Me	Me	t-Bu	H	Me	H	
155	Me	Me	Me	Me	i-Pr	H	i-Pr	Cl	Cl
156	Me	Me	Et	Et	i-Pr	H	H	H	
157	Me	Me	Et	Et	Me	Me	Me	Cl	Cl
158	Me	Me	Et	Et	i-Pr	H	Me	H	

159	Me	Me			Me	Me	Me	Cl	Cl
160	Me	Me			i-Pr	H	i-Pr	H	
161	Me	Me	n-Pr	Me	i-Pr	H	i-Pr	Cl	Cl
162	Me	Me			Et	H	Et	H	
163	Me	Me		Me	Me	Me	Me	Cl	Cl
164	Me	Me	Me		Et	H	Me	H	
165	Me	Me	Me		Et	H	Et	Cl	Cl
166	Me	Me	Me		i-Pr	H	Me	H	
167	Me	Me	Me		i-Pr	H	i-Pr	Cl	Cl
168	Me	Me	Me	Me	Me	Me	Me	H	
169	Me	Me	Me	Me	i-Pr	H	H	Cl	Cl
170	Me	Me	Me	Me	Et	H	Me	H	
171	Me	Me	Me	Me	i-Pr	H	Et	Cl	Cl
172	Me	Me	Me	Me	t-Bu	H	Me	Cl	Cl
173	Me	Me	Me	n-Pr	i-Pr	H	i-Pr	H	
174	Me	Me	Et	Et	i-Pr	H	Me	Cl	Cl

175	Me	Me	Et	Et	i-Pr	H	H	H	
176	Me	Me	Et	Et	Me	Me	Me	Cl	
177	Me	Me			Me	Me	Me	H	
178	Me	Me			Et	H	Et	Cl	Cl
179	Me	Me		Me	Me	Me	Me	H	
180	Me	Me		Me	Et	H	Me	Cl	Cl
181	Me	Me		Me	Et	H	Et	H	
182	Me	Me		Me	i-Pr	H	Me	Cl	Cl

[0083] Examples of olefin metathesis catalysts represented by the structure of **Formula (IA12B1C3)**, wherein: $W = O$, $R^{15} = i\text{-Pr}$, $b = 1$, $a = 2$, $X = -CR^{1a}R^{2a}-$, $R^{1a} = H$, $R^{2a} = H$, $Y = -CR^{1b}R^{2b}-$, $R^{1b} = H$, $R^{2b} = H$, $R^6 = H$, $R^8 = H$, $R^{10} = H$, $R^{11} = H$, $R^{12} = H$, $R^{13} = H$, $R^{14} = H$, $X^3 = S$, $X^4 = S$, $R^{17} = H$, and $R^{18} = H$, are found in **Table (8)**.

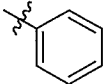
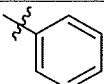
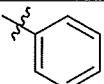
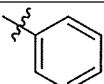
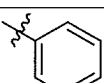
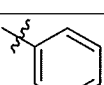
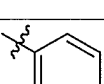
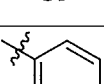
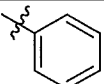
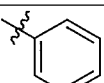


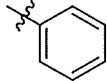
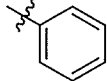
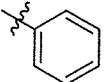
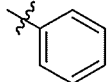
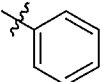
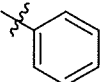
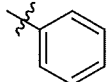
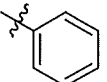
Formula (IA12B1C3)

Table (8)

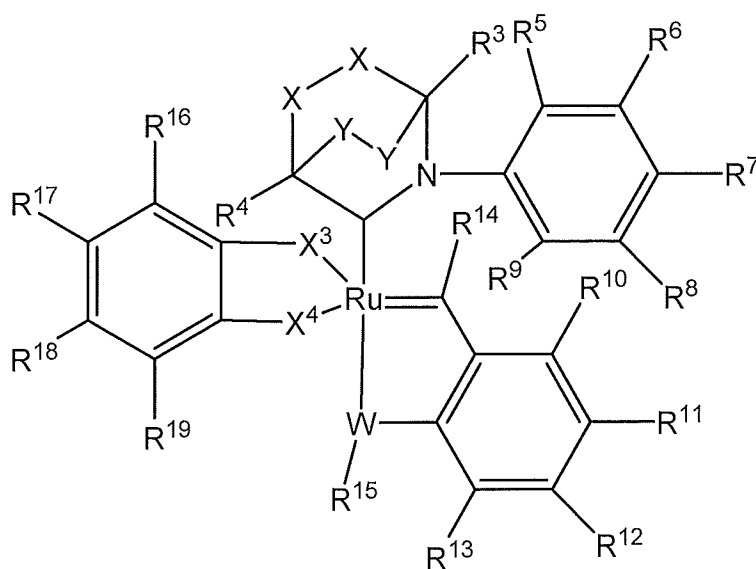
Examples of olefin metathesis catalysts represented by **Formula (IA12B1C3)**

Catalyst	R ³	R ⁴	R ⁵	R ⁷	R ⁹	R ¹⁶	R ¹⁹
183	Me	Me	Et	H	Me	Cl	Cl
184	Me	Me	Et	H	Et	H	
185	Me	Me	i-Pr	H	Me	Cl	Cl
186	Me	Me	t-Bu	H	Me	H	
187	Me	Me	i-Pr	H	i-Pr	Cl	Cl
188	Me	Et	i-Pr	H	H	H	
189	Me	Et	Me	Me	Me	Cl	Cl
190	Me	Et	i-Pr	H	Me	H	

191	Me	Me	Me	Me	Me	Cl	Cl
191	Me	Me	i-Pr	H	i-Pr	H	
192	Me	n-Pr	i-Pr	H	i-Pr	Cl	Cl
193	Me	Me	Et	H	Et	Cl	
194	Me		Me	Me	Me	Cl	Cl
195	Me	Et	Et	H	Me	H	
196	Me	Et	Et	H	Et	Cl	Cl
197	Me	Et	i-Pr	H	Me	H	
198	Me	Et	i-Pr	H	i-Pr	Cl	Cl
199	Me	Me	Me	Me	Me	H	
200	Me	Me	i-Pr	H	H	Cl	Cl
201	Me	Me	Et	H	Me	H	
202	Me	Me	i-Pr	H	Me	Cl	Cl
203	Me	Me	t-Bu	H	Me	H	
204	Me	Me	i-Pr	H	i-Pr	H	
205	Me	Et	i-Pr	H	Me	Cl	Cl
206	Me	Et	i-Pr	H	H	H	

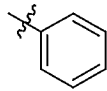
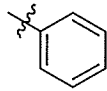
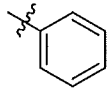
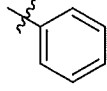
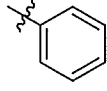
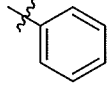
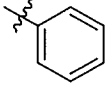
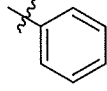
207	Me	Et	Me	Me	Me	Cl	
208	Me	Me	Me	H	Me	H	
209	Me	Me	Et	H	Et	Cl	Cl
300	Me		Me	Me	Me	H	
301	Me		Et	H	Me	Cl	Cl
302	Me		Et	H	Et	H	
303	Me		i-Pr	H	Me	Cl	Cl

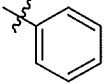
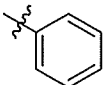
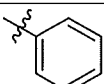
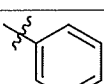
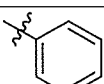
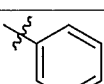
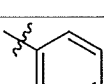
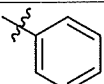
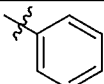
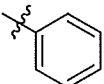
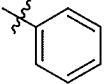
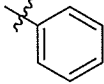
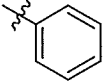
[0084] Examples of olefin metathesis catalysts represented by the structure of **Formula (IA9B1C3)**, wherein: $W = O$, $R^{15} = i\text{-Pr}$, $b = 2$, $Y = -CR^{1b}R^{2b}-$, $a = 2$, $X = -CR^{1a}R^{2a}-$, $R^{1a} = H$, $R^{2a} = H$, $R^{1b} = H$, $R^{2b} = H$, $R^6 = H$, $R^8 = H$, $R^{10} = H$, $R^{11} = H$, $R^{12} = H$, $R^{13} = H$, $R^{14} = H$, are found in **Table (9)**.



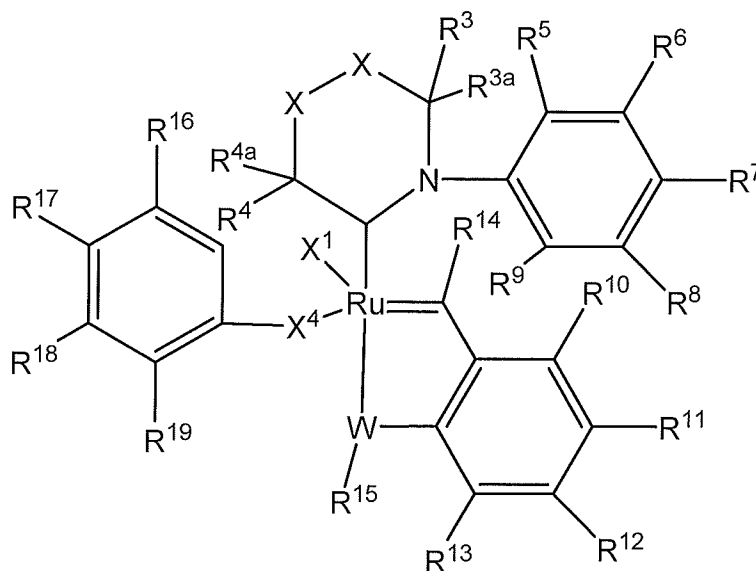
Formula (IA9B1C3)

Table (9)Examples of olefin metathesis catalysts represented by **Formula (IA9B1C3)**

Catalyst	R ³	R ⁴	R ⁵	R ⁷	R ⁹	R ¹⁶	R ¹⁹
304	Me	Me	Et	H	Me	Cl	Cl
305	Me	Me	Et	H	Et	H	
306	Me	Me	i-Pr	H	Me	Cl	Cl
307	Me	Me	t-Bu	H	Me	H	
308	Me	Me	i-Pr	H	i-Pr	Cl	Cl
309	Me	Et	i-Pr	H	H	H	
310	Me	Et	Me	Me	Me	Cl	Cl
311	Me	Et	i-Pr	H	Me	H	
312	Me	Me	Me	Me	Me	Cl	Cl
313	Me	Me	i-Pr	H	i-Pr	H	
314	Me	n-Pr	i-Pr	H	i-Pr	Cl	Cl
315	Me	Me	Et	H	Et	H	
316	Me		Me	Me	Me	Cl	Cl
317	Me	Et	Et	H	Me	H	

318	Me	Et	Et	H	Et	Cl	Cl
319	Me	Et	i-Pr	H	Me	H	
320	Me	Et	i-Pr	H	i-Pr	Cl	Cl
321	Me	Me	Me	Me	Me	H	
322	Me	Me	i-Pr	H	H	Cl	Cl
323	Me	Me	Et	H	Me	H	
324	Me	Me	i-Pr	H	Me	Cl	Cl
325	Me	n-Pr	t-Bu	H	Me	H	
326	Me	n-Pr	i-Pr	H	i-Pr	H	
327	Me	Et	i-Pr	H	Me	Cl	Cl
328	Me	n-Pr	i-Pr	H	H	H	
329	Me	n-Pr	Me	Me	Me	Cl	Cl
330	Me	Me	Me	Me	Me	H	
331	Me	Me	Et	H	Et	Cl	Cl
332	Me		Me	Me	Me	H	
333	Me		Et	H	Me	Cl	Cl
334	Me		Et	H	Et	H	
335	Me		i-Pr	H	Me	Cl	Cl

[0085] Examples of olefin metathesis catalysts represented by the structure of **Formula (IA6B2C3)**, wherein: W = O, R¹⁵ = *i*-Pr, b = 0, a = 2, X = -CR^{1a}R^{2a}-, R^{1a} = H, R^{2a} = H, R⁶ = H, R⁸ = H, R¹⁰ = H, R¹¹ = H, R¹² = H, R¹³ = H, R¹⁴ = H, X¹ = Cl, X⁴ = S, R¹⁷ = H, and R¹⁸ = H are found in **Table (10)**.

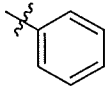
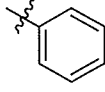
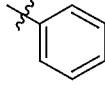
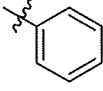
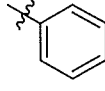
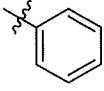
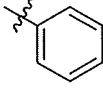
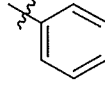
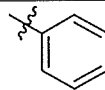
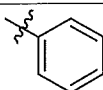
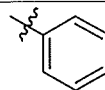
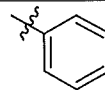


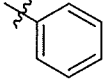
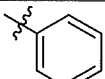
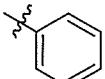
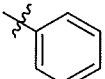
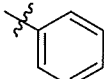
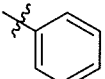
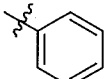
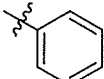
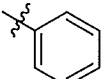
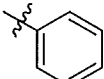
Formula (IA6B2C3)

Table (10)

Examples of olefin metathesis catalysts represented by **Formula (IA6B2C3)**

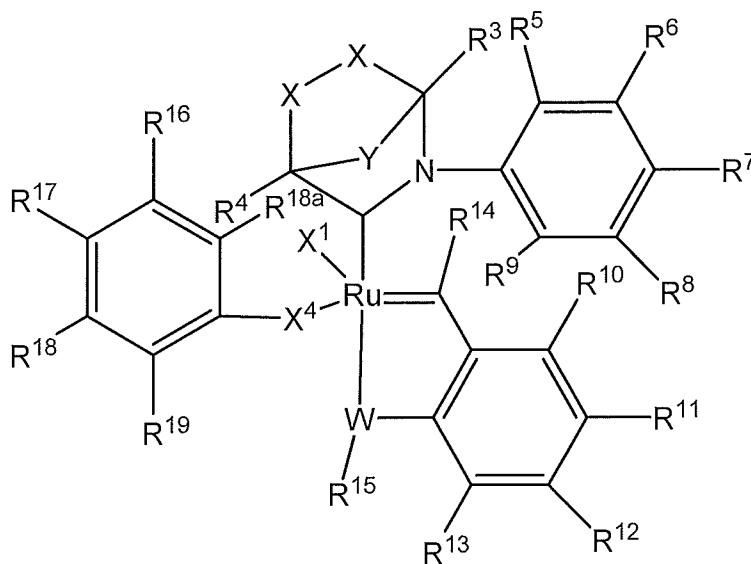
Catalyst	R ³	R ^{3a}	R ⁴	R ^{4a}	R ⁵	R ⁷	R ⁹	R ¹⁶	R ¹⁹
336	Me	Me	Me	Me	Et	H	Me	Cl	Cl
337	Me	Me	Me	Me	Et	H	Et	H	
338	Me	Me	Me	Me	i-Pr	H	Me	Cl	Cl
339	Me	Me	Me	Me	t-Bu	H	Me	H	
340	Me	Me	Me	Me	i-Pr	H	i-Pr	Cl	Cl

341	Me	Me	Et	Et	i-Pr	H	H	H	
342	Me	Me	Et	Et	Me	Me	Me	Cl	Cl
343	Me	Me	Et	Et	i-Pr	H	Me	H	
344	Me	Me	Me	Me	Me	Me	Me	Cl	Cl
345	Me	Me	Me	Me	i-Pr	H	i-Pr	H	
346	Me	Me	n-Pr	Me	i-Pr	H	i-Pr	Cl	Cl
347	Me	Me	Me		Et	H	Et	H	
348	Me	Me		Me	Me	Me	Me	Cl	Cl
349	Me	Me	Me		Et	H	Me	H	
350	Me	Me	Me	Me	Et	H	Et	Cl	Cl
351	Me	Me	Me	Me	i-Pr	H	Me	H	
352	Me	Me	Me		i-Pr	H	i-Pr	Cl	Cl
353	Me	Me	Me	Me	Me	Me	Me	H	
354	Me	Me	Me	Me	i-Pr	H	H	Cl	Cl
355	Me	Me	Me	n-Pr	Et	H	Me	H	
356	Me	Me	Me	Et	i-Pr	H	Me	Cl	Cl

357	Me	Me	Me	Et	t-Bu	H	Me	H	
358	Me	Me	Me	Et	i-Pr	H	i-Pr	H	
359	Me	Me	n-Pr	Me	i-Pr	H	Me	Cl	Cl
360	Me	Me	Et	Me	i-Pr	H	H	H	
361	Me	Me	Et	Me	Me	Me	Me	Cl	Cl
362	Me	Me	Me	Me	Me	Me	Me	H	
363	Me	Me	Me	n-Pr	Et	H	Et	Cl	Cl
364	Me	Me		Me	Me	Me	Me	H	
365	Me	Me		Me	Et	H	Me	Cl	Cl
366	Me	Me		Me	Et	H	Et	H	
367	Me	Me		Me	i-Pr	H	Me	Cl	Cl

[0086] Examples of olefin metathesis catalysts represented by the structure of **Formula**

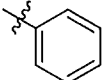
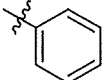
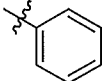
(IA12B2C3) wherein: $X^1 = \text{Cl}$, $W = \text{O}$, $R^{15} = i\text{-Pr}$, $b = 1$, $a = 2$, $X = -\text{CR}^{1a}\text{R}^{2a}$, $R^{1a} = \text{H}$, $R^{2a} = \text{H}$, $Y = -\text{CR}^{1b}\text{R}^{2b}$, $R^{1b} = \text{H}$, $R^{2b} = \text{H}$, $R^6 = \text{H}$, $R^8 = \text{H}$, $R^{10} = \text{H}$, $R^{11} = \text{H}$, $R^{12} = \text{H}$, $R^{13} = \text{H}$, $R^{14} = \text{H}$, $X^4 = \text{S}$, $R^{17} = \text{H}$, $R^{18} = \text{H}$, and $R^{18a} = \text{H}$ are found in **Table (11)**.

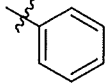
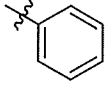
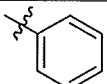
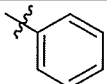
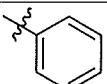
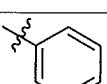
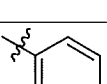
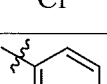
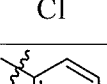
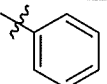


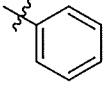
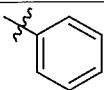
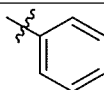
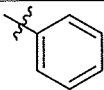
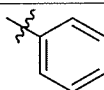
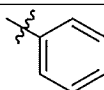
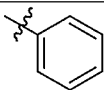
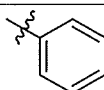
Formula (IA12B2C3)

Table (11)

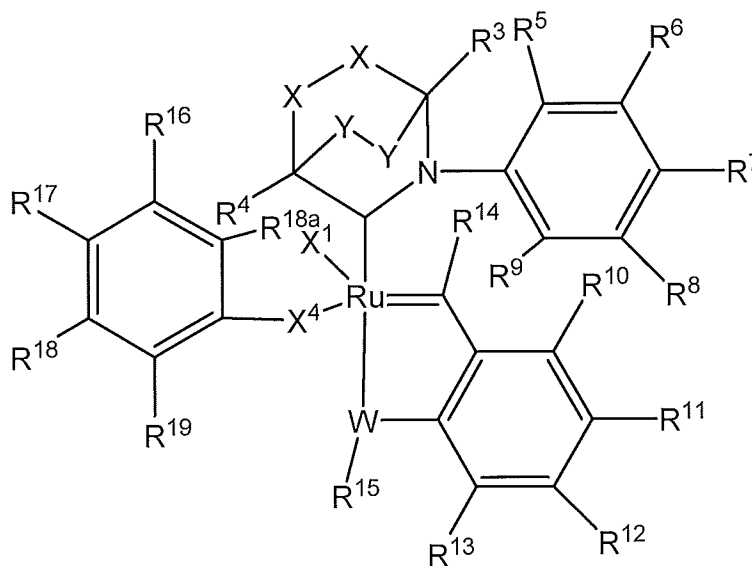
Examples of olefin metathesis catalysts represented by **Formula (IA12B2C3)**

Catalyst	R ³	R ⁴	R ⁵	R ⁷	R ⁹	R ¹⁶	R ¹⁹
368	Me	Me	Et	H	Me	Cl	Cl
369	Me	Me	Et	H	Et	H	
370	Me	Me	i-Pr	H	Me	Cl	Cl
371	Me	Me	t-Bu	H	Me	H	
372	Me	Me	i-Pr	H	i-Pr	Cl	Cl
373	Me	Et	i-Pr	H	H	H	
374	Me	Et	Me	Me	Me	Cl	Cl

375	Me	Et	i-Pr	H	Me	H	
376	Me	Me	Me	Me	Me	Cl	Cl
377	Me	Me	i-Pr	H	i-Pr	H	
378	Me	n-Pr	i-Pr	H	i-Pr	Cl	Cl
379	Me	n-Pr	Et	H	Et	H	
380	Me		Me	Me	Me	Cl	Cl
381	Me	Et	Et	H	Me	H	
382	Me	Et	Et	H	Et	Cl	Cl
383	Me	n-Pr	i-Pr	H	Me	H	
384	Me	Et	i-Pr	H	i-Pr	Cl	Cl
385	Me	Me	Me	Me	Me	H	
386	Me	Me	i-Pr	H	H	Cl	Cl
387	Me	Me	Et	H	Me	H	
388	Me	n-Pr	i-Pr	H	Me	Cl	Cl
389	Me	n-Pr	t-Bu	H	Me	H	
390	Me	n-Pr	i-Pr	H	i-Pr	H	
391	Me	Et	i-Pr	H	Me	Cl	Cl

392	Me	Et	i-Pr	H	H	H	
393	Me	Et	Me	Me	Me	Cl	Cl
394	Me	n-Pr	Me	Me	Me	H	
395	Me	Me	Et	H	Et	Cl	Cl
396	Me		Me	Me	Me	H	
397	Me		Et	H	Me	Cl	Cl
398	Me		Et	H	Et	H	
399	Me		i-Pr	H	Me	Cl	Cl

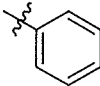
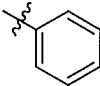
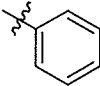
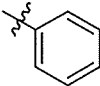
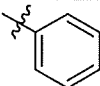
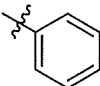
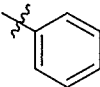
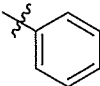
[0087] Examples of olefin metathesis catalysts represented by the structure of **Formula (IA12B2C3)** wherein: $X^1 = \text{Cl}$, $W = \text{O}$, $R^{15} = i\text{-Pr}$, $b = 2$, $Y = -\text{CR}^{1b}\text{R}^{2b}-$, $a = 2$, $X = -\text{CR}^{1a}\text{R}^{2a}-$, $R^{1a} = \text{H}$, $R^{2a} = \text{H}$, $R^{1b} = \text{H}$, $R^{2b} = \text{H}$, $R^6 = \text{H}$, $R^8 = \text{H}$, $R^{10} = \text{H}$, $R^{11} = \text{H}$, $R^{12} = \text{H}$, $R^{13} = \text{H}$, $R^{14} = \text{H}$, $X^4 = \text{S}$, $R^{17} = \text{H}$, $R^{18} = \text{H}$, and $R^{18a} = \text{H}$, are found in **Table (12)**.

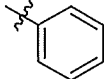
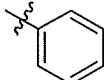
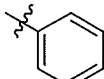
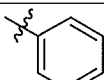
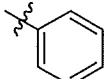
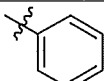
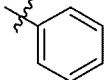
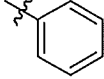
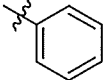
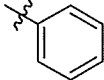
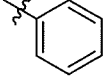
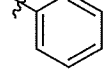
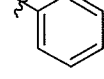
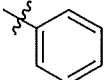


Formula (IA12B2C3)

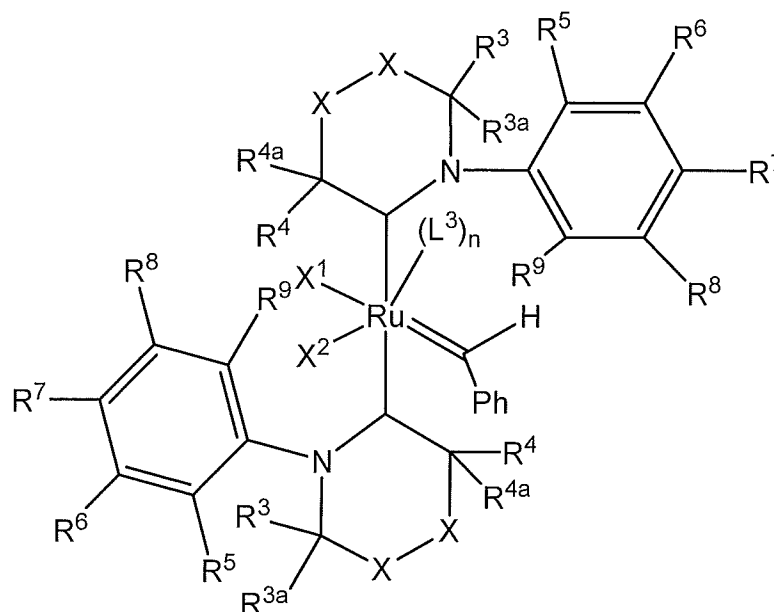
Table (12)

Examples of olefin metathesis catalysts represented by Formula (IA12B2C3)

Catalyst	R ³	R ⁴	R ⁵	R ⁷	R ⁹	R ¹⁶	R ¹⁹
400	Me	Me	Et	H	Me	Cl	Cl
401	Me	Me	Et	H	Et	H	
402	Me	Me	i-Pr	H	Me	Cl	Cl
403	Me	Me	t-Bu	H	Me	H	
404	Me	Me	i-Pr	H	i-Pr	Cl	Cl
405	Me	Et	i-Pr	H	H	H	
406	Me	Et	Me	Me	Me	Cl	Cl
407	Me	Et	i-Pr	H	Me	H	
408	Me	Me	Me	Me	Me	Cl	Cl
409	Me	Me	i-Pr	H	i-Pr	H	
410	Me	n-Pr	i-Pr	H	i-Pr	Cl	Cl
411	Me	n-Pr	Et	H	Et	H	
412	Me		Me	Me	Me	Cl	Cl
413	Me	n-Pr	Et	H	Me	H	
414	Me	Me	Et	H	Et	Cl	Cl

415	Me	Me	i-Pr	H	Me	H	
416	Me	Me	i-Pr	H	i-Pr	Cl	Cl
417	Me	Me	Me	Me	Me	H	
418	Me	n-Pr	i-Pr	H	H	Cl	Cl
419	Me	Me	Et	H	Me	H	
420	Me	Me	i-Pr	H	Me	Cl	Cl
421	Me	Me	t-Bu	H	Me	H	
422	Me	Me	i-Pr	H	i-Pr	H	
423	Me	Et	i-Pr	H	Me	Cl	Cl
424	Me	n-Pr	i-Pr	H	H	H	
425	Me	Et	Me	Me	Me	Cl	
426	Me	Me	Me	Me	Me	Cl	
427	Me	n-Pr	Et	H	Et	Cl	Cl
428	Me		Me	Me	Me	H	
429	Me		Et	H	Me	Cl	Cl
430	Me		Et	H	Et	H	
431	Me		i-Pr	H	Me	Cl	Cl

[0088] Examples of olefin metathesis catalysts represented by the structure of **Formula (IIA6B4C2A6)**, wherein: $X^1 = \text{Cl}$, $X^2 = \text{Cl}$, $b = 0$, $a = 2$, $X = -\text{CR}^{1a}\text{R}^{2a}$, $\text{R}^{1a} = \text{H}$, $\text{R}^{2a} = \text{H}$, $\text{R}^6 = \text{H}$, and $\text{R}^8 = \text{H}$ are found in **Table (13)**.

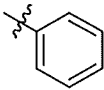
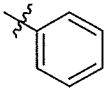
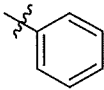
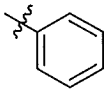
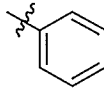
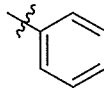


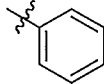
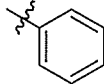
Formula (IIA6B4C2A6)

Table (13)

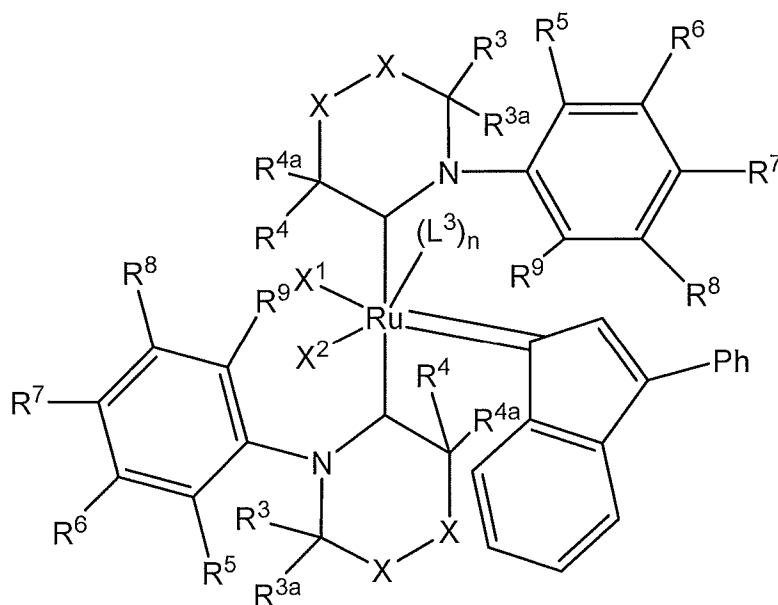
Examples of olefin metathesis catalysts represented by **Formula (IIA6B4C2A6)**

Catalyst	R ³	R ^{3a}	R ⁴	R ^{4a}	R ⁵	R ⁷	R ⁹
432	Me	Me	Me	Me	Et	H	Me
433	Me	Me	Me	Me	Et	H	Et
434	Me	Me	Me	Me	i-Pr	H	Me
435	Me	Me	Me	Me	t-Bu	H	Me
436	Me	Me	Me	Me	i-Pr	H	i-Pr
437	Me	Me	Et	Et	i-Pr	H	H
438	Me	Me	Et	Et	Me	Me	Me
439	Me	Me	Et	Et	i-Pr	H	Me

440	Me	Me	Me	Me	Me	Me	Me
441	Me	Me	Et	Et	i-Pr	H	i-Pr
442	Me	Me	n-Pr	n-Pr	i-Pr	H	i-Pr
443	Me	Me	Et	Et	Et	H	Et
444	Me	Me	Me		Me	Me	Me
445	Me	Me	Et	Et	Et	H	Me
446	Me	Me	Me		Et	H	Et
447	Me	Me	Me		i-Pr	H	Me
448	Me	Me	Me		i-Pr	H	i-Pr
449	Me	Me	Me	Et	Me	Me	Me
450	Me	Me	Me	Me	i-Pr	H	H
451	Me	Me	n-Pr	n-Pr	Et	H	Me
452	Me	Me	Me	n-Pr	i-Pr	H	Me
453	Me	Me	Me	n-Pr	t-Bu	H	Me
454	Me	Me	Me	Et	i-Pr	H	i-Pr
455	Me	Me	Me	Et	i-Pr	H	Me
456	Me	Me	Me	Et	i-Pr	H	H
457	Me	Me	Et	Et	Me	Me	Me
458	Me	Me	Me	n-Pr	Me	Me	Me
459	Me	Me	n-Pr	n-Pr	Et	H	Et
460	Me	Me	Et		Me	Me	Me
461	Me	Me	Me		Et	H	Me

462	Me	Me	Me		Et	H	Et
463	Me	Me	Me		i-Pr	H	Me

[0089] Examples of olefin metathesis catalysts represented by the structure of **Formula (IIA6B4C1A6)**, wherein: $X^1 = \text{Cl}$, $X^2 = \text{Cl}$, $b = 0$, $a = 2$, $X = -\text{CR}^{1a}\text{R}^{2a}$, $\text{R}^{1a} = \text{H}$, $\text{R}^{2a} = \text{H}$, $\text{R}^6 = \text{H}$, and $\text{R}^8 = \text{H}$ are found in **Table (14)**.

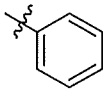
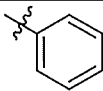


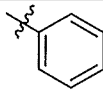
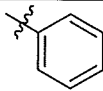
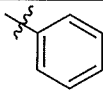
Formula (IIA6B4C1A6)

Table (14)

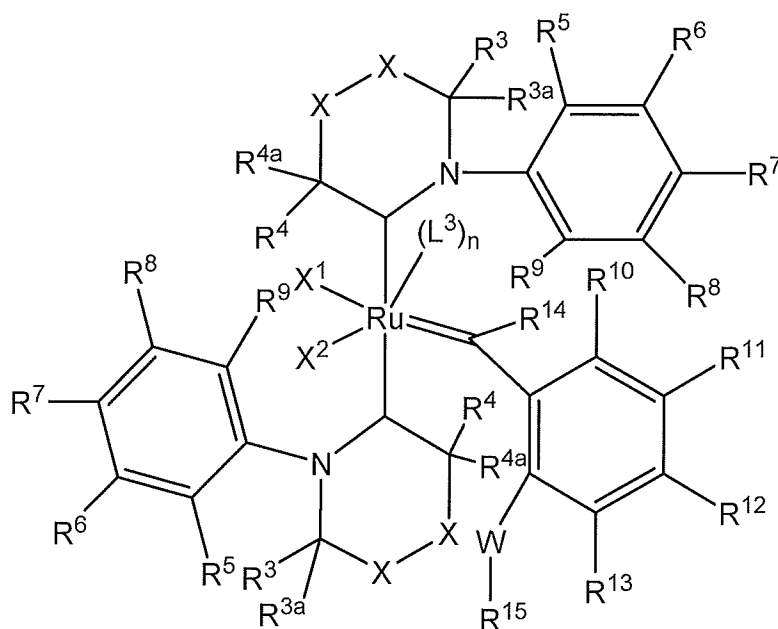
Examples of olefin metathesis catalysts represented by **Formula (IIA6B4C1A6)**

Catalyst	R^3	R^{3a}	R^4	R^{4a}	R^5	R^7	R^9
464	Me	Me	Me	Me	Et	H	Me
465	Me	Me	Me	Me	Et	H	Et
466	Me	Me	Me	Me	i-Pr	H	Me
467	Me	Me	Me	Me	t-Bu	H	Me

468	Me	Me	Me	Me	i-Pr	H	i-Pr
469	Me	Me	Et	Et	i-Pr	H	H
470	Me	Me	Et	Et	Me	Me	Me
471	Me	Me	Et	Et	i-Pr	H	Me
472	Me	Me	Me	Me	Me	Me	Me
473	Me	Me	Et	Et	i-Pr	H	i-Pr
474	Me	Me	n-Pr	n-Pr	i-Pr	H	i-Pr
475	Me	Me	Et	Et	Et	H	Et
476	Me	Me		Me	Me	Me	Me
477	Me	Me	Me	Me	Et	H	Me
478	Me	Me	Me	Me	Et	H	Et
479	Me	Me	Me	Me	i-Pr	H	Me
480	Me	Me	Me	Me	i-Pr	H	i-Pr
481	Me	Me	Me	Et	Me	Me	Me
482	Me	Me	Me	Me	i-Pr	H	H
483	Me	Me	n-Pr	n-Pr	Et	H	Me
484	Me	Me	Me	n-Pr	i-Pr	H	Me
485	Me	Me	Me	n-Pr	t-Bu	H	Me
486	Me	Me	Me	Et	i-Pr	H	i-Pr
487	Me	Me	Me	Et	i-Pr	H	Me
488	Me	Me	Me	Et	i-Pr	H	H
489	Me	Me	Et	Et	Me	Me	Me
490	Me	Me	Me	n-Pr	Me	Me	Me
491	Me	Me	n-Pr	n-Pr	Et	H	Et
492	Me	Me		Et	Me	Me	Me

494	Me	Me		Me	Et	H	Me
495	Me	Me		Me	Et	H	Et
496	Me	Me		Me	i-Pr	H	Me

[0090] Examples of olefin metathesis catalysts represented by the structure of **Formula (IIA6B4C3A6)**, wherein: $X^1 = \text{Cl}$, $X^2 = \text{Cl}$, $b = 0$, $a = 2$, $X = -\text{CR}^{1a}\text{R}^{2a}$, $\text{R}^{1a} = \text{H}$, $\text{R}^{2a} = \text{H}$, $\text{R}^6 = \text{H}$, $\text{R}^8 = \text{H}$, $\text{R}^{10} = \text{H}$, $\text{R}^{11} = \text{H}$, $\text{R}^{12} = \text{H}$, $\text{R}^{13} = \text{H}$, $\text{R}^{14} = \text{H}$, $\text{W} = \text{O}$, and $\text{R}^{15} = \text{i-Pr}$, are found in **Table (15)**.

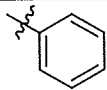
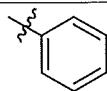
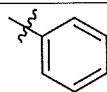
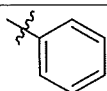
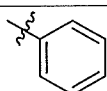


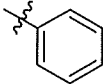
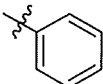
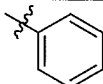
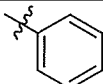
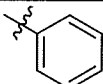
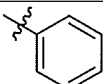
Formula (IIA6B4C3A6)

Table (15)

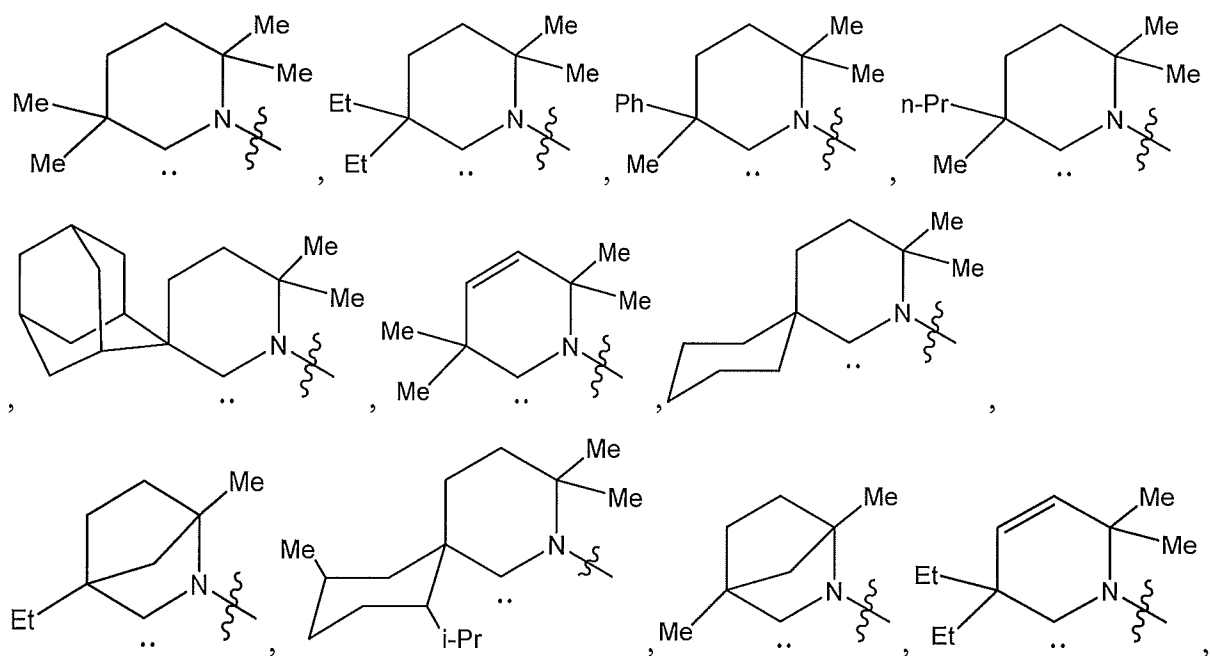
Examples of olefin metathesis catalysts represented by **Formula (IIA6B4C3A6)**

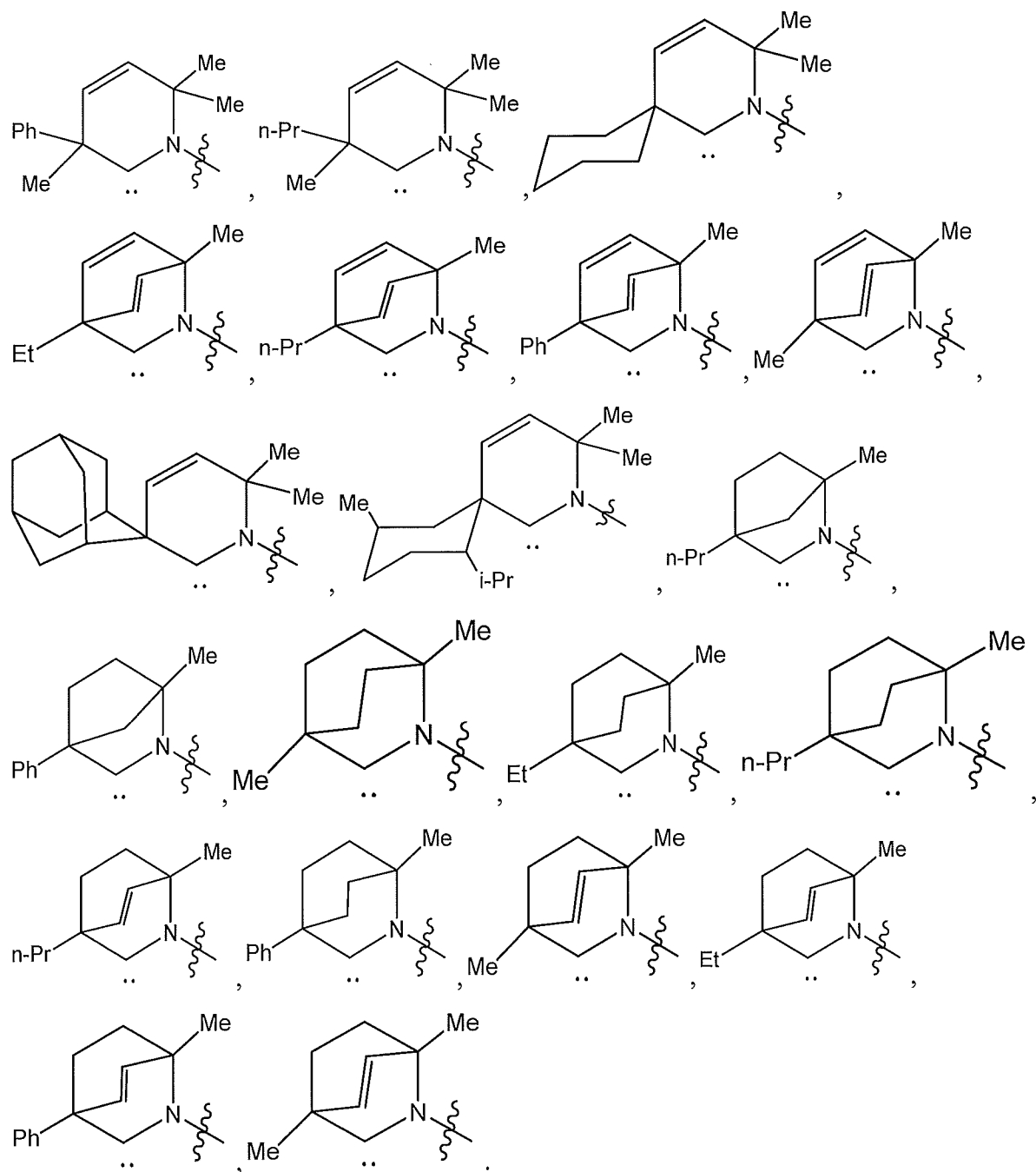
Catalyst	R^3	R^{3a}	R^4	R^{4a}	R^5	R^7	R^9
497	Me	Me	Me	Me	Et	H	Me
498	Me	Me	Me	Me	Et	H	Et

499	Me	Me	Me	Me	i-Pr	H	Me
500	Me	Me	Me	Me	t-Bu	H	Me
501	Me	Me	Me	Me	i-Pr	H	i-Pr
502	Me	Me	Et	Et	i-Pr	H	H
503	Me	Me	Et	Et	Me	Me	Me
504	Me	Me	Et	Et	i-Pr	H	Me
505	Et	Me	Me	Me	Me	Me	Me
506	Me	Me	Et	Et	i-Pr	H	i-Pr
507	Me	Me	n-Pr	n-Pr	i-Pr	H	i-Pr
508	Me	Et	Me	Me	Et	H	Et
509	Me	Me	Me		Me	Me	Me
510	Me	Me	Et	Et	Et	H	Me
511	Me	Me	Et	Et	Et	H	Et
512	Me	Me	n-Pr	n-Pr	i-Pr	H	Me
513	Me	Me	n-Pr	n-Pr	i-Pr	H	i-Pr
514	Me	Me	Me	Me	Me	H	Me
515	Me	Me	Me	Me	i-Pr	H	H
516	Me	Me	Me	Me	Et	H	H
517	Me	Me	Me	Me	i-Pr	H	Me
518	Me	Me	Me		t-Bu	H	Me
519	Me	Me	Me		i-Pr	H	i-Pr
520	Me		Et	Et	i-Pr	H	Me
521	Me		Et	Et	i-Pr	H	H

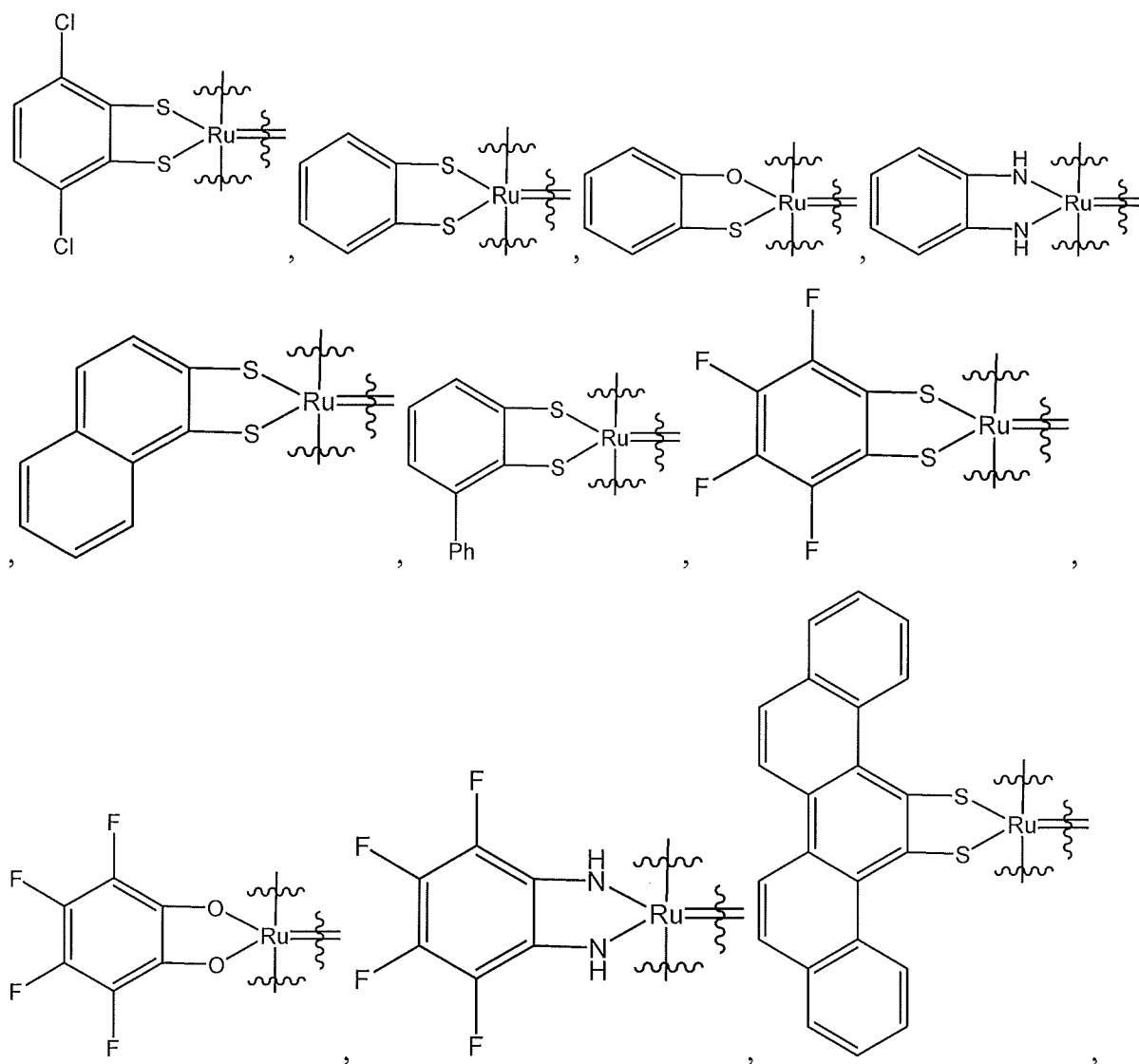
522	Me		Et	Et	Me	Me	Me
523	Me	Me	Me	Me	Me	Me	Me
524	Me		Me	Me	Et	H	Et
525	Me	Et	Me		Me	Me	Me
526	Me	Me	Me		Et	H	Me
527	Me	Me	Me		Et	H	Et
528	Me	Me	Me		i-Pr	H	Me

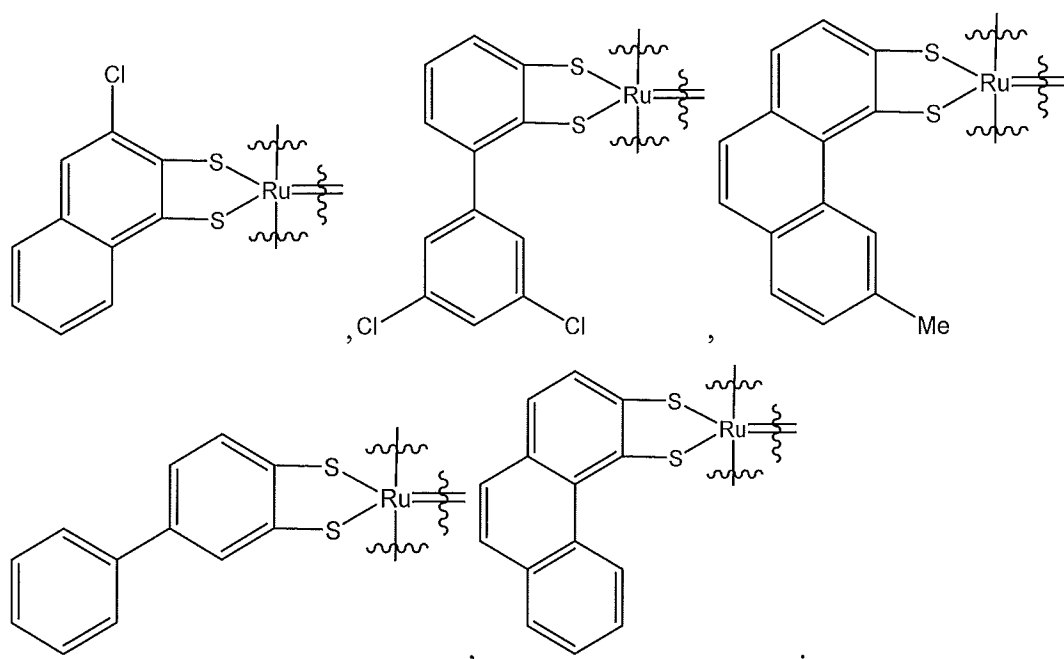
[0091] In one embodiment, the invention provides an olefin metathesis catalyst wherein the **Moiety (A)** is represented by:



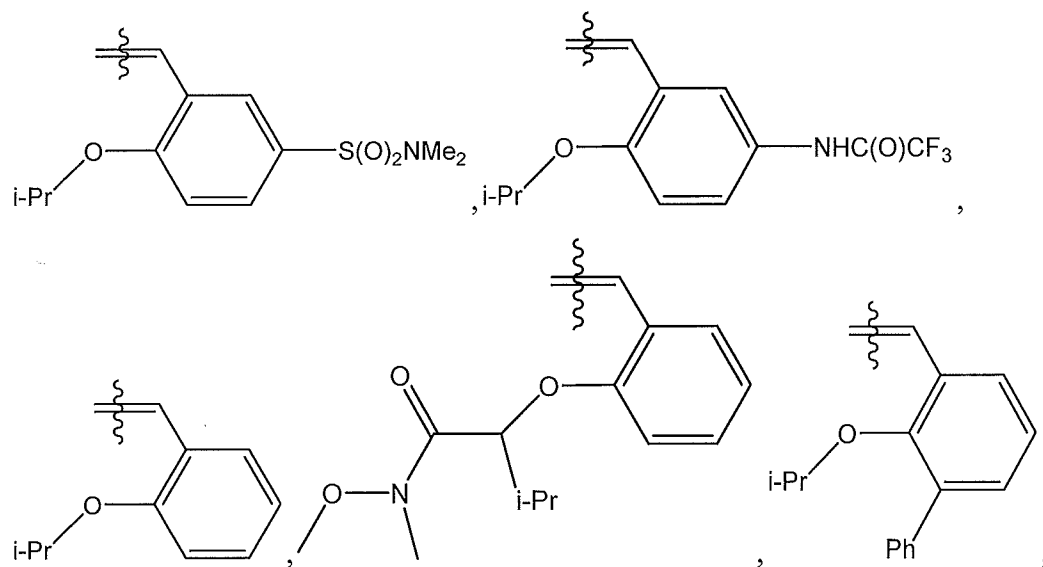


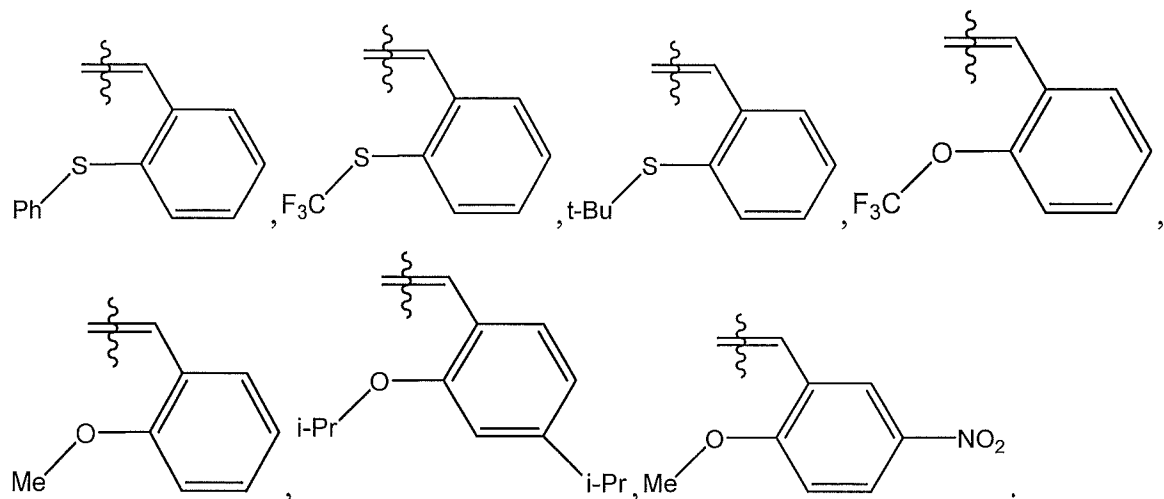
[0092] In one embodiment, the invention provides an olefin metathesis catalyst wherein the **Moiety (B)** is represented by:





[0093] In one embodiment, the invention provides an olefin metathesis catalyst wherein the **Moiety (C)** is represented by:

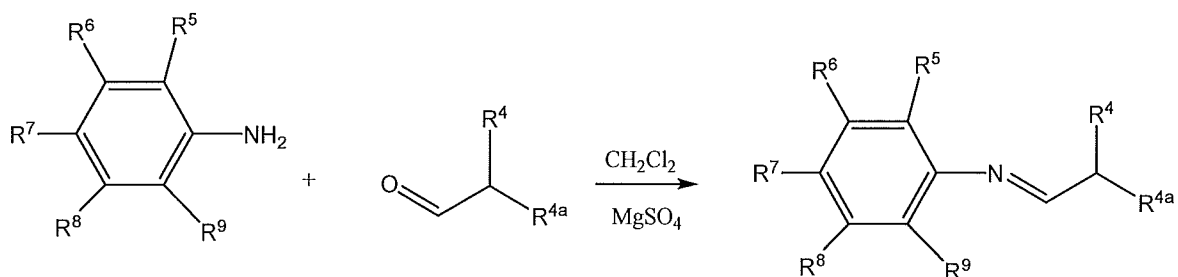




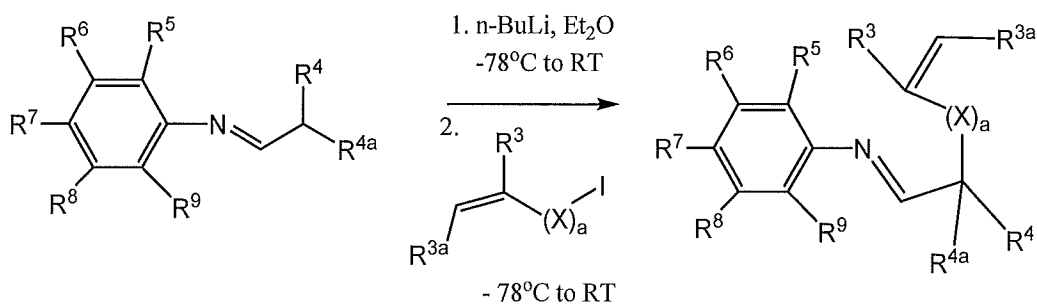
[0094] The present invention concerns also processes for preparing the olefin metathesis catalysts described herein. The olefin metathesis catalysts according to the invention can be prepared analogously to conventional methods as understood by the person skilled in the art of synthetic organic chemistry.

[0095] The following synthetic schemes illustrate how the olefin metathesis catalysts of the invention can be generally synthesized.

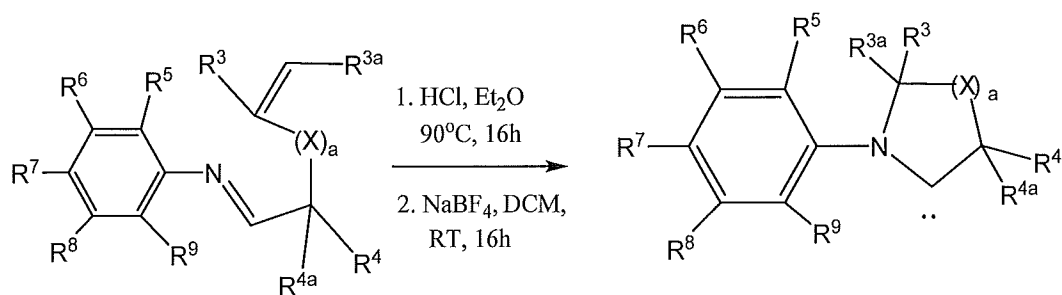
Scheme 3



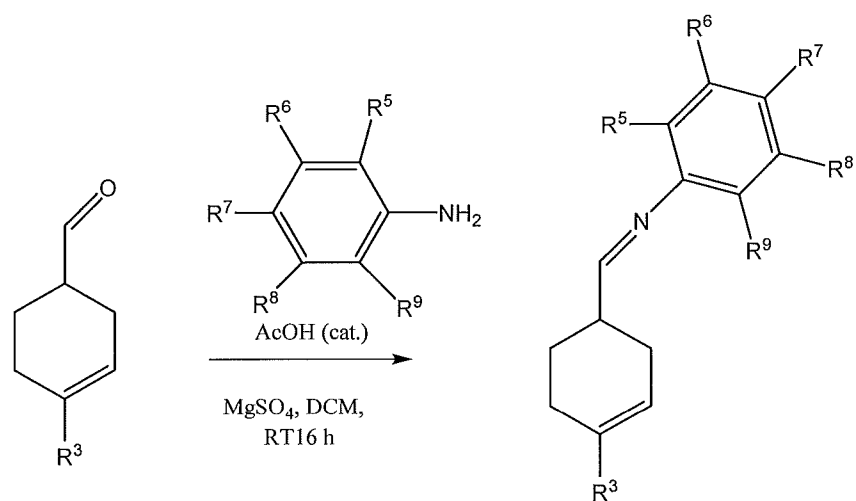
Scheme 4



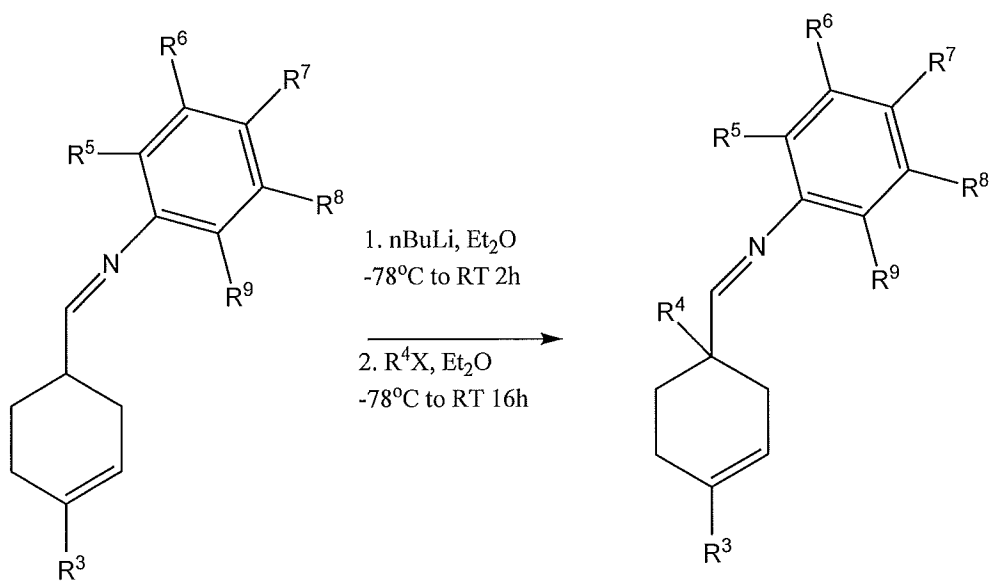
Scheme 5



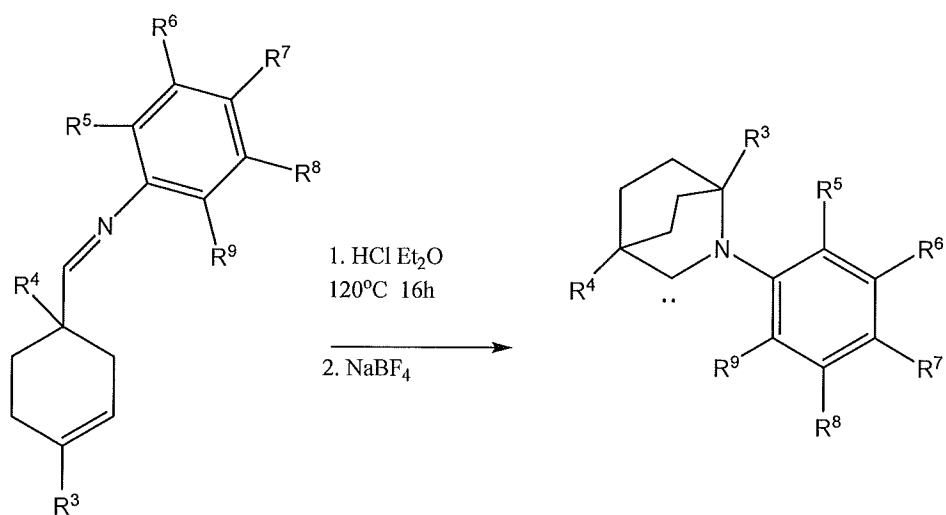
Scheme 6



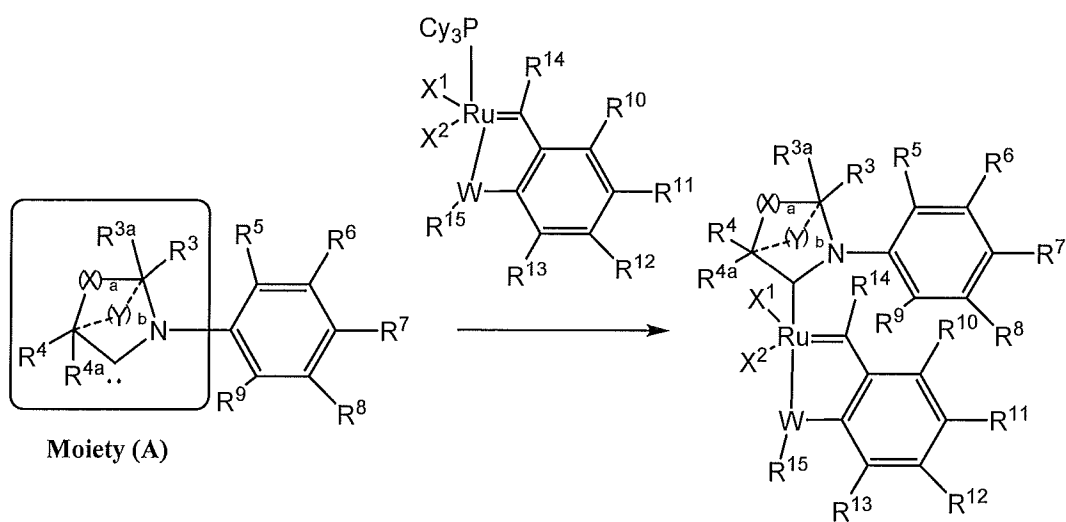
Scheme 7



Scheme 8

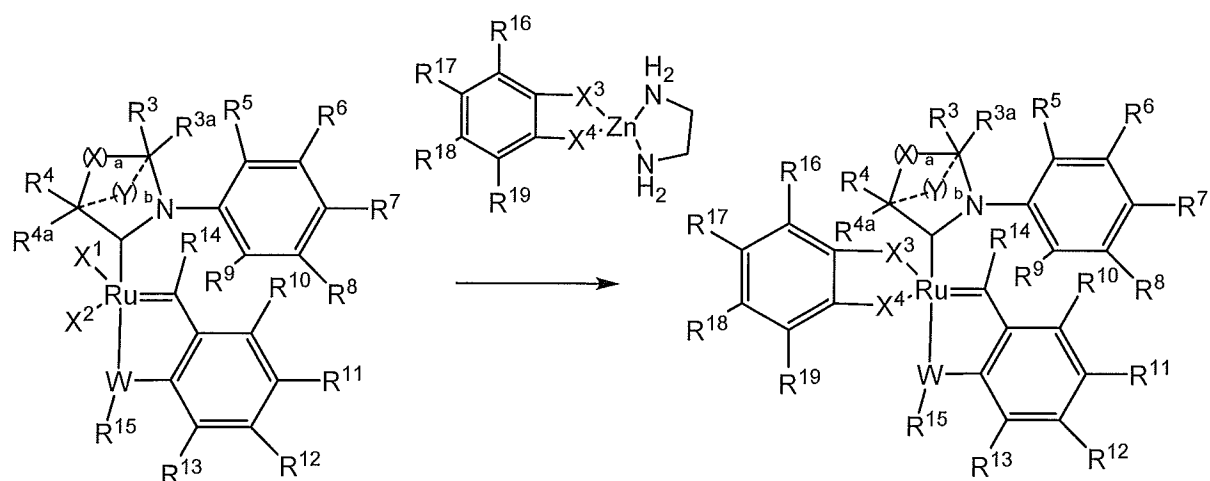


Scheme 9

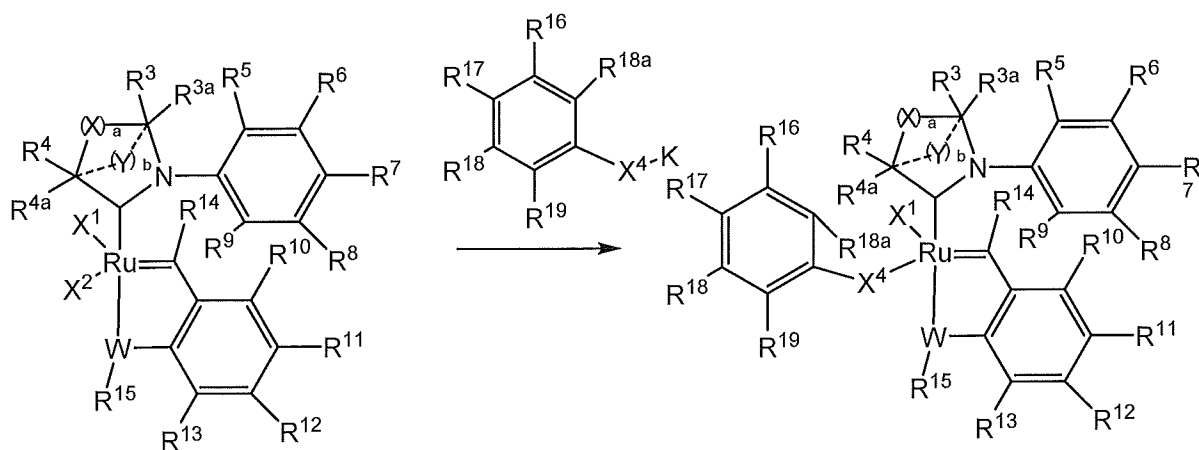


Moiety (A)

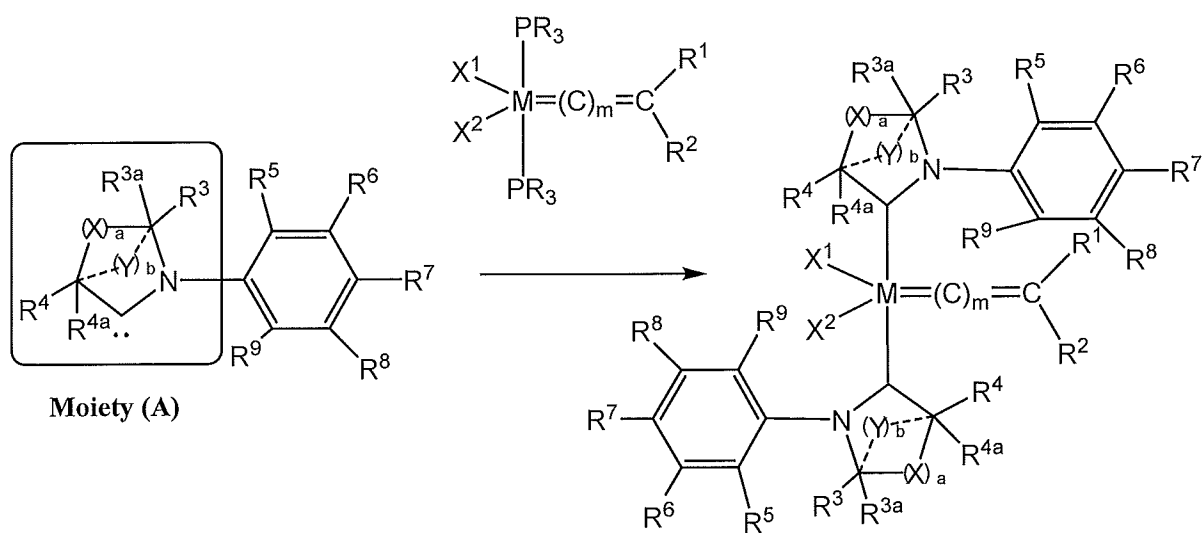
Scheme 10



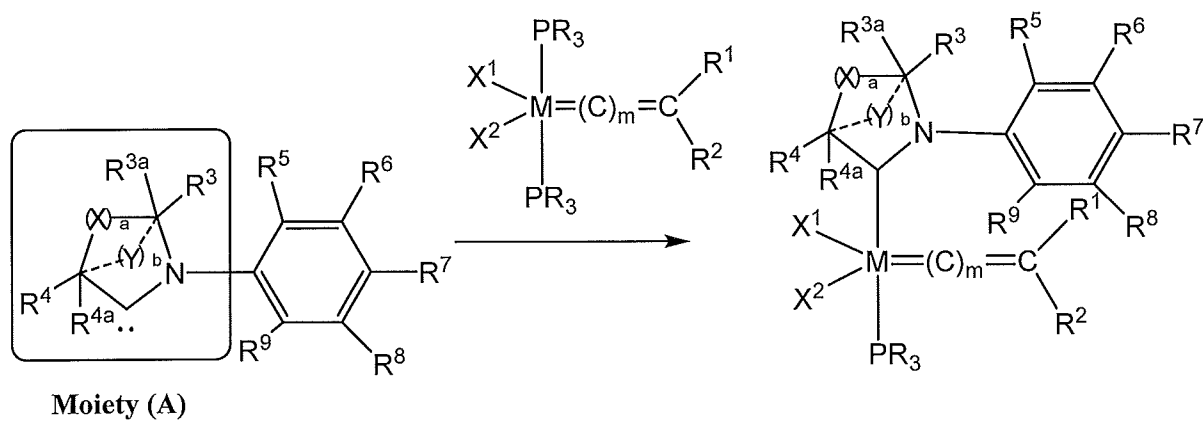
Scheme 11



Scheme 12



Scheme 13



[0096] Generally, the reactions take place under degassed N₂ at room temperature or at high temperature. Once the reaction is completed, the mixture is cooled to room temperature, the solvent is removed under high vacuum, and the residue is purified on a silica gel column and then recrystallized to afford the new olefin metathesis catalysts.

[0097] At this stage, those skilled in the art will appreciate that many additional compounds that fall under the scope of the invention can be prepared by performing various common chemical reactions.

[0098] For example, the olefin metathesis catalysts are typically added to a resin composition as a solid, a solution, or as a suspension. When the olefin metathesis catalysts are added to a resin composition as a suspension, the olefin metathesis catalysts are suspended in a dispersing carrier such as mineral oil, paraffin oil, soybean oil, tri-*iso*-propyl-benzene, or any hydrophobic liquid which has an appropriately high viscosity so as to permit effective dispersion of the catalyst(s), and which is inert and which has a sufficiently high boiling point so that it does not act as a low-boiling impurity in the olefin metathesis reaction.

OLEFINS

[0099] Resin compositions that may be formed, comprise one or more cyclic olefins, besides the olefin metathesis catalysts of the invention. The cyclic olefin may generally be any strained or unstrained cyclic olefin, provided the cyclic olefin is able to participate in a ROMP reaction either individually or as part of a ROMP cyclic olefin composition. Such cyclic olefins may be optionally substituted, optionally heteroatom-containing, mono-unsaturated, di-unsaturated, or poly-unsaturated C₅ to C₂₄ hydrocarbons that may be mono-, di-, or poly-cyclic.

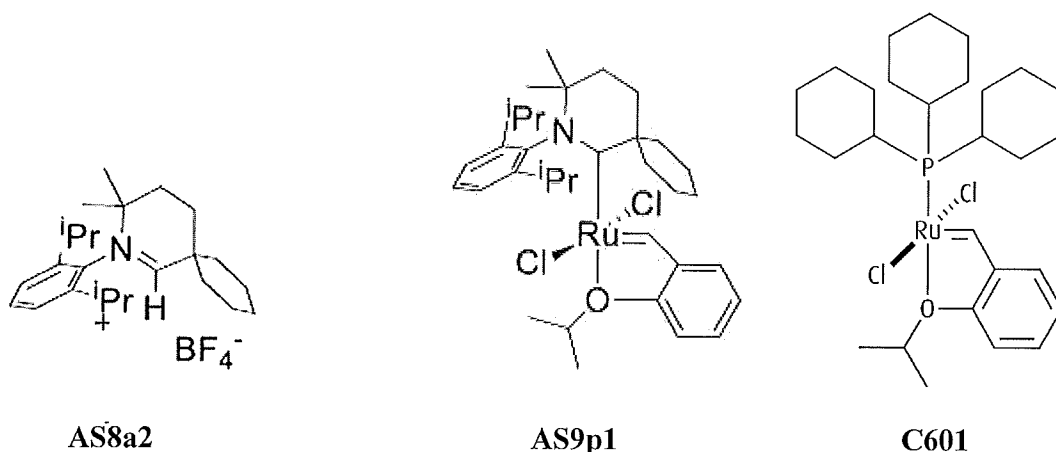
[0100] Examples of bicyclic and polycyclic olefins thus include, without limitation, dicyclopentadiene (DCPD); trimer and other higher order oligomers of cyclopentadiene including without limitation tricyclopentadiene (cyclopentadiene trimer), cyclopentadiene tetramer, and cyclopentadiene pentamer; ethylenenorbornene; dicyclohexadiene; norbornene; C₂-C₁₂ hydrocarbyl substituted norbornenes; 5-butyl-2-norbornene; 5-hexyl-2-norbornene; 5-octyl-2-norbornene; 5-decyl-2-norbornene; 5-dodecyl-2-norbornene; 5-vinyl-2-norbornene; 5-ethylidene-2-norbornene; 5-*isopropenyl*-2-norbornene; 5-propenyl-2-norbornene; 5-butenyl-2-norbornene; 5-tolyl-norbornene; 5-methyl-2-norbornene; 5-ethyl-2-norbornene; 5-*isobutyl*-2-norbornene; 5,6-dimethyl-2-norbornene; 5-phenylnorbornene; 5-benzylnorbornene; 5-

acetylnorbornene; 5-methoxycarbonylnorbornene; 5-ethoxycarbonyl-1-norbornene; 5-methyl-5-methoxy-carbonylnorbornene; bicyclo[2.2.1]hept-2-ene-2-carboxylic acid, 2-ethylhexyl ester; 5-cyanonorbornene; 5,5,6-trimethyl-2-norbornene; cyclo-hexenylnorbornene; endo, exo-5,6-dimethoxynorbornene; endo, endo-5,6-dimethoxynorbornene; endo, exo-5,6-dimethoxy carbonylnorbornene; endo,endo-5,6-dimethoxycarbonylnorbornene; 2,3-dimethoxynorbornene; norbornadiene; tricycloundecene; tetracyclododecene; 8-methyl tetracyclododecene; 8-ethyltetracyclododecene; 8-methoxy carbonyltetracyclo dodecene; 8-methyl-8-tetra cyclododecene; 8-cyanotetracyclo dodecene; pentacyclopentadecene; pentacyclo hexadecene; bicyclo[2.2.1]hept-2-ene-5-phenoxyethyl; 2-ethylhexyl ester-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid; 2-hydroxyethyl ester-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid; bicyclo[2.2.1]hept-5-ene-2-methanol; bicyclo[2.2.1]hept-5-ene-2-heptanoic acid-methyl ester; bicyclo[2.2.1]hept-5-ene-2-hexanoic acid-methyl ester; 1,4:5,8-dimethanonaphthalene, 2-hexyl-1,2,3,4,4a,5,8,8a-octahydro; bicyclo[2.2.1]hept-5-ene-2-octanoic acid-methyl ester; 1,4:5,8-dimethano naphthalene; 2-butyl-1,2,3,4,4a,5,8,8a-octahydro; ethylidenetetracyclododecene; 2-vinyl-1,2,3,4,4a,5,8,8a-octahydro-1,4:5,8-dimethano naphthalene; and the like, and their structural isomers, stereoisomers, and mixtures thereof.

EXAMPLES

6-membered CAAC Ruthenium complexes for Ethenolysis

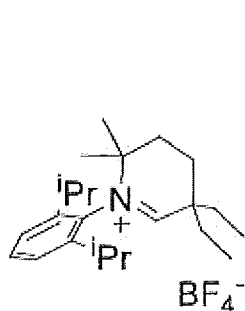
Example 1



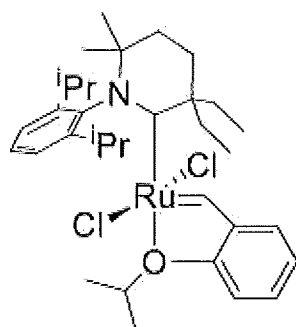
AS9p1. To a 4 mL vial in a glovebox loaded with salt **AS8a2** (107.0 mg, 0.25 mmol, 3.0 equiv) was added a solution of Lithium bis(trimethylsilyl)amide (38.9 mg, 0.23 mmol, 2.8 equiv) in benzene (2.2 mL). The solution was stirred vigorously for 1 h at room temperature then filtered into a solution of **C601** (50 mg, 0.083 mmol, 1.0 equiv) in benzene (0.5 mL). The solution was heated for 48 h at 45 °C then brought to room temperature and concentrated under reduced pressure. The residue was taken up in benzene (0.3 mL), the product precipitated with pentane (2 mL), and filtered to afford **AS9p1** (37 mg, 67%) as green solid. The product can be further purified by recrystallization from CH_2Cl_2 /Ethanol.

^1H NMR (benzene- d_6 , 500 MHz): δ = 16.24 (s, 1H), 7.32 (dd, J = 8.3, 7.0 Hz, 1H), 7.23 (d, J = 7.7 Hz, 2H), 7.20 – 7.17 (m, 1H), 7.12 (dd, J = 7.5, 1.7 Hz, 1H), 6.70 (t, J = 7.4 Hz, 1H), 6.42 (d, J = 8.3 Hz, 1H), 4.60 (hept, J = 6.1 Hz, 1H), 4.26 – 4.19 (m, 2H), 3.29 (p, J = 6.6 Hz, 2H), 2.66 (d, J = 12.1 Hz, 2H), 2.08 – 2.02 (m, 2H), 1.93 (d, J = 13.4 Hz, 2H), 1.66 (d, J = 6.1 Hz, 6H), 1.74 – 1.52 (m, 4H), 1.17 – 1.10 (m, 12H), 1.01 (s, 3H), 1.00 (s, 3H).

Example 2



AS22a2

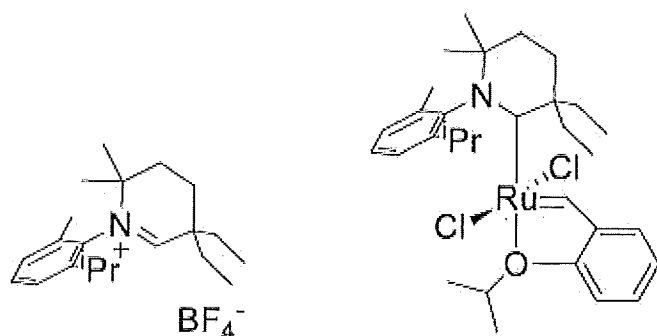


AS28b7

AS28b7 To a 4 mL vial in a glovebox loaded with salt **AS22a2** (41.4 mg, 0.10 mmol, 3.0 equiv) was added a solution of Lithium bis(trimethylsilyl)amide (15.6 mg, 0.09 mmol, 2.8 equiv) in benzene (0.6 mL). The solution was stirred vigorously for 1 h at room temperature then filtered into a solution of C601 (20 mg, 0.03 mmol, 1.0 equiv) in benzene (0.2 mL). The solution was heated for 72 h at 45 °C then brought to room temperature and concentrated under reduced pressure. The residue was taken up in benzene (0.1 mL), the product precipitated with pentane (2 mL), and then crystallized from CH₂Cl₂/Ethanol to afford **AS28b7** (5.3 mg, 25%) as a green-brown solid.

¹H NMR (Benzene-*d*₆, 400 MHz): δ = 16.20 (s, 1H), 7.31 (dd, J = 8.5, 6.8 Hz, 1H), 7.25 – 7.21 (m, 2H), 7.20 – 7.17 (m, 1H), 7.12 – 7.06 (m, 1H), 6.69 (td, J = 7.4, 0.7 Hz, 1H), 6.41 (d, J = 8.3 Hz, 1H), 4.59 (hept, J = 6.2 Hz, 1H), 3.84 (dq, J = 14.5, 7.3 Hz, 2H), 3.32 (hept, J = 6.5 Hz, 2H), 3.08 (dq, J = 14.6, 7.4 Hz, 2H), 1.96 – 1.91 (m, 2H), 1.66 – 1.63 (m, 2H), 1.64 (d, J = 6.1 Hz, 6H), 1.24 (t, J = 7.4 Hz, 6H), 1.13 (d, J = 6.7 Hz, 6H), 1.10 (s, 6H), 1.00 (d, J = 6.4 Hz, 6H).

Example 3

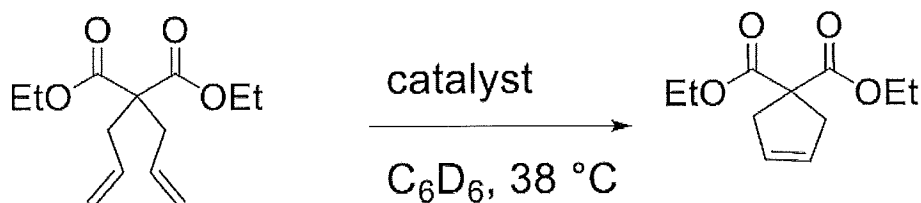


AS19a5

AS33b1

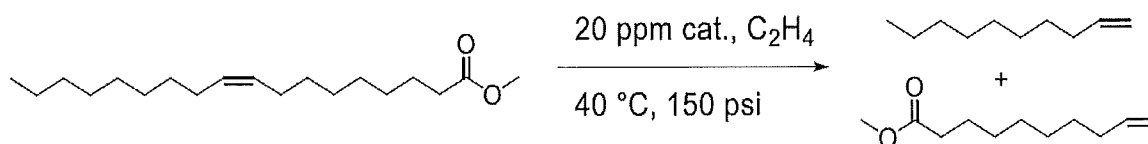
AS33b1 To a 4 mL vial in a glovebox loaded with salt **AS19a5** (100.0 mg, 0.26 mmol, 2.2 equiv) was added a solution of Lithium bis(trimethylsilyl)amide (39 mg, 0.24 mmol, 2.0 equiv) in benzene (3.0 mL). The solution was stirred vigorously for 1 h at room temperature then filtered into a solution of C601 (70 mg, 0.117 mmol, 1.0 equiv) in benzene (0.5 mL). The solution was heated for 26 h at 45 °C then brought to room temperature and concentrated under reduced pressure. The residue was purified on a silica plug (benzene/diethyl ether) and crystallized from pentane to afford **AS33b1** (50 mg, 68%) as green solid.

^1H NMR (Benzene- d_6 , 400 MHz): δ = 16.16 (s, 1H), 7.24 – 7.20 (m, 5H), 7.14 – 7.10 (m, 2H), 6.71 (t, J = 7.4 Hz, 1H), 6.43 (d, J = 8.4 Hz, 1H), 4.61 (p, J = 6.3 Hz, 1H), 3.91 (dt, J = 14.4, 7.2 Hz, 1H), 3.75 (dd, J = 14.3, 7.3 Hz, 1H), 3.62 (dd, J = 13.9, 6.9 Hz, 1H), 3.19 (p, J = 6.6 Hz, 1H), 2.59 (dd, J = 14.2, 7.2 Hz, 1H), 2.28 (s, 3H), 1.84 – 1.53 (m, 4H), 1.65 (d, J = 6.1 Hz, 6H), 1.28 (t, J = 7.3 Hz, 3H), 1.17 (d, J = 6.6 Hz, 3H), 1.12 (t, J = 7.5 Hz, 3H), 1.03 (s, 3H), 1.02 (d, J = 6.7 Hz, 3H), 0.93 (s, 3H).

Example 4**Ring Closing Metathesis of diallyl malonate**

The data charted in Fig. 1 shows the results of Ring-Closing Metathesis of diethyl 2,2-diallylmalonate. The compounds AS9p1, AS28b7 and AS33b1 obtained in Examples 1, 2 and 3 were employed as catalysts.

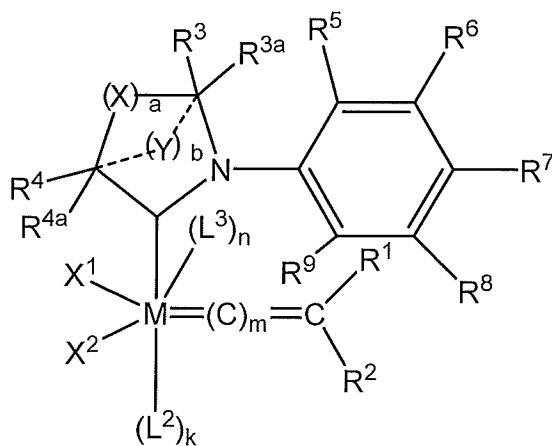
Conditions were kept constant and the same for all catalysts: A 0.1M solution of the malonate in C₆D₆ with 0.02 equivalents catalyst and internal standard (anthracene) were loaded into a screw top NMR tube. The tube was loaded into a Varian NMR spectrometer and heated to temperature. Timepoints were taken using the Varian array function. It can be seen from Figure 1 that all three catalysts are active in Ring-Closing Metathesis.

Example 5**Ethenolysis of Methyl Oleate**

Neutral alumina, Brockmann I, is activated by heating to 180 °C for 3 days under high vacuum. Methyl oleate is run through a plug of the neutral alumina and stored over fresh activated neutral alumina for 3 days. The reactions are run in a Fischer-porter flask with a dip-tube for taking aliquots under the conditions given in the equation above. Aliquots are diluted with hexane and cooled to -78 °C immediately and stored cold until analysis by gas chromatography. The compounds AS9p1, AS28b7 and AS33b1 obtained in Examples 1, 2 and 3 are employed as catalysts, showing ethenolysis activity as in the reaction equation given above.

What is claimed is:

1. An olefin metathesis catalyst comprising cyclic alkyl amino carbenes, represented by the structure of **Formula (I)**:



Formula (I)

wherein:

M is Ru or Os;

L^2 and L^3 are independently neutral ligands;

m is 0, 1 or 2;

n is 0 or 1;

k is 0 or 1;

X^1 and X^2 are independently anionic ligands; generally, X^1 and X^2 are independently halogen, trifluoroacetate, per-fluorophenols, -NCO, -CN, -NCS, -N₃; or X^1 together with X^2 can form a nitrate; typically, X^1 and X^2 are independently halogen, or -NCO;

R^1 and R^2 are independently selected from hydrogen, optionally substituted hydrocarbyl, optionally substituted heteroatom-containing hydrocarbyl; or any two or more of X^1 , X^2 , L^2 , L^3 , R^1 , and R^2 are taken together to form one or more cyclic groups;

X is $-CR^{1a}R^{2a}-$;

a is 1 or 2;

R^{1a} is H, optionally substituted C₁₋₂₄ alkyl, optionally substituted C₃₋₈ cycloalkyl, halogen, optionally substituted C₅₋₂₄ aryl, optionally substituted C₆₋₂₄ aralkyl, optionally substituted C₁₋₂₀ heteroalkyl, -C(O) R^{21} , -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, or together with R^{2a} forms an optionally substituted spiro

monocyclic or spiro polycyclic C₃₋₁₀ cycloalkyl or spiro heterocyclic ring, with the carbon atom to which they are attached, or together with R³ or together with R⁴ forms an optionally substituted polycyclic ring;

R^{2a} is H, optionally substituted C₁₋₂₄ alkyl, optionally substituted C₃₋₈ cycloalkyl, halogen, optionally substituted C₅₋₂₄ aryl, optionally substituted C₆₋₂₄ aralkyl, optionally substituted C₁₋₂₀ heteroalkyl, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, or together with R^{1a} forms a spiro monocyclic or spiro polycyclic C₃₋₁₀ cycloalkyl or spiro heterocyclic ring, with the carbon atom to which they are attached, or together with R³ or together with R⁴ forms an optionally substituted polycyclic ring;

Y is -CR^{1b}R^{2b}-;

b is 0, 1 or 2;

R^{1b} is H, optionally substituted C₁₋₂₄ alkyl, optionally substituted C₃₋₈ cycloalkyl, halogen, optionally substituted C₅₋₂₄ aryl, optionally substituted C₆₋₂₄ aralkyl, optionally substituted C₁₋₂₀ heteroalkyl, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, or together with R^{2b} forms a five-, six-, or ten-membered cycloalkyl or heterocyclic ring, with the carbon atom to which they are attached;

R^{2b} is H, optionally substituted C₁₋₂₄ alkyl, optionally substituted C₃₋₈ cycloalkyl, halogen, optionally substituted C₅₋₂₄ aryl, optionally substituted C₆₋₂₄ aralkyl, optionally substituted C₁₋₂₀ heteroalkyl, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, or together with R^{1b} forms a five-, six-, or ten-membered cycloalkyl or heterocyclic ring, with the carbon atom to which they are attached;

R³ is H, optionally substituted C₁₋₂₄ alkyl, halogen, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, optionally substituted heterocycle, optionally substituted C₃₋₈ cycloalkyl, optionally substituted C₅₋₂₄ aryl, optionally substituted C₃₋₈ cycloalkenyl, or together with R^{1a} or together with R^{2a} can form an optionally substituted polycyclic ring, or together with R^{3a} can form an optionally substituted spiro monocyclic or spiro polycyclic C₃₋₁₀ cycloalkyl;

R^{3a} is H, optionally substituted C₁₋₂₄ alkyl, halogen, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, optionally substituted heterocycle, optionally substituted C₃₋₈ cycloalkyl, optionally substituted C₅₋₂₄ aryl, optionally substituted

C₃₋₈ cycloalkenyl, or together with R^{1a} or together with R^{2a} can form an optionally substituted polycyclic ring, or together with R³ can form an optionally substituted spiro monocyclic or spiro polycyclic C₃₋₁₀ cycloalkyl;

R⁴ is H, optionally substituted C₁₋₂₄ alkyl, halogen, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, optionally substituted heterocycle, optionally substituted C₃₋₈ cycloalkyl, optionally substituted C₅₋₂₄ aryl, optionally substituted C₃₋₈ cycloalkenyl, or together with R^{1a} or together with R^{2a} can form an optionally substituted polycyclic ring, or together with R^{4a} can form an optionally substituted spiro monocyclic or spiro polycyclic C₃₋₁₀ cycloalkyl;

R^{4a} is H, optionally substituted C₁₋₂₄ alkyl, halogen, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, optionally substituted heterocycle, optionally substituted C₃₋₈ cycloalkyl, optionally substituted C₅₋₂₄ aryl, optionally substituted C₃₋₈ cycloalkenyl, or together with R^{1a} or together with R^{2a} can form an optionally substituted polycyclic ring, or together with R⁴ can form an optionally substituted spiro monocyclic or spiro polycyclic C₃₋₁₀ cycloalkyl;

R⁵ is H, optionally substituted C₁₋₂₄ alkyl, halogen, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, optionally substituted heterocycle, optionally substituted C₃₋₈ cycloalkyl, optionally substituted C₅₋₂₄ aryl, optionally substituted C₃₋₈ cycloalkenyl, or together with R⁶ can form an optionally substituted polycyclic ring;

R⁶ is H, optionally substituted C₁₋₂₄ alkyl, halogen, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, optionally substituted heterocycle, optionally substituted C₃₋₈ cycloalkyl, optionally substituted C₅₋₂₄ aryl, optionally substituted C₃₋₈ cycloalkenyl or together with R⁵ or together with R⁷ can form an optionally substituted polycyclic ring;

R⁷ is H, optionally substituted C₁₋₂₄ alkyl, halogen, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, optionally substituted heterocycle, optionally substituted C₃₋₈ cycloalkyl, optionally substituted C₅₋₂₄ aryl, optionally substituted C₃₋₈ cycloalkenyl, or together with R⁶ or together with R⁸ can form an optionally substituted polycyclic ring;

R⁸ is H, optionally substituted C₁₋₂₄ alkyl, halogen, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, optionally substituted heterocycle,

optionally substituted C₃₋₈ cycloalkyl, optionally substituted C₅₋₂₄ aryl, optionally substituted C₃₋₈ cycloalkenyl, or together with R⁷ or together with R⁹ can form an optionally substituted polycyclic ring;

R⁹ is H, optionally substituted C₁₋₂₄ alkyl, halogen, -C(O)R²¹, -OR²², CN, -NR²³R²⁴, NO₂, -CF₃, -S(O)_xR²⁵, -P(O)(OH)₂, -OP(O)(OH)₂, -SR²⁷, optionally substituted heterocycle, optionally substituted C₃₋₈ cycloalkyl, optionally substituted C₅₋₂₄ aryl, optionally substituted C₃₋₈ cycloalkenyl, or together with R⁸ can form a polycyclic ring;

R²¹ is OH, OR²⁶, NR²³R²⁴, optionally substituted C₁₋₂₄ alkyl, optionally substituted C₃₋₈ cycloalkyl, optionally substituted heterocycle, optionally substituted C₅₋₂₄ aryl or optionally substituted C₃₋₈ cycloalkenyl;

R²² is H, optionally substituted C₁₋₂₄ alkyl, optionally substituted C₃₋₈ cycloalkyl, optionally substituted heterocycle, optionally substituted C₅₋₂₄ aryl or optionally substituted C₃₋₈ cycloalkenyl;

R²³ is H, optionally substituted C₁₋₂₄ alkyl, optionally substituted C₃₋₈ cycloalkyl, optionally substituted heterocycle, optionally substituted C₅₋₂₄ aryl or optionally substituted C₃₋₈ cycloalkenyl;

R²⁴ is H, optionally substituted C₁₋₂₄ alkyl, optionally substituted C₃₋₈ cycloalkyl, optionally substituted heterocycle, optionally substituted C₅₋₂₄ aryl or optionally substituted C₃₋₈ cycloalkenyl;

R²⁵ is H, optionally substituted C₁₋₂₄ alkyl, OR²², -NR²³R²⁴, optionally substituted heterocycle, optionally substituted C₃₋₈ cycloalkyl, optionally substituted C₅₋₂₄ aryl or optionally substituted C₃₋₈ cycloalkenyl;

R²⁶ is optionally substituted C₁₋₂₄ alkyl, optionally substituted C₃₋₈ cycloalkyl, optionally substituted heterocycle, optionally substituted C₅₋₂₄ aryl or optionally substituted C₃₋₈ cycloalkenyl;

R²⁷ is H, optionally substituted C₁₋₂₄ alkyl, optionally substituted C₃₋₈ cycloalkyl, optionally substituted heterocycle, optionally substituted C₅₋₂₄ aryl or optionally substituted C₃₋₈ cycloalkenyl;

x is 1 or 2; with the provisos

- a. when a is 2, then the "X-X" bond can be saturated or unsaturated;
- b. when a is 2, and the "X-X" bond is unsaturated, then R^{2a} is nil;

- c. when b is 1, then R^{3a} and R^{4a} are both nil;
 - d. when b is 2, then R^{3a} and R^{4a} are both nil;
 - e. when b is 2, the "Y-Y" bond can be saturated or unsaturated;
 - f. when b is 2, and the "Y-Y" bond is unsaturated, then R^{2b} is nil.
2. An olefin metathesis catalyst of claim 1, wherein M is Ru.
 3. An olefin metathesis catalyst of claim 1 or 2, wherein L² and L³ are a phosphine, an NHC ligand, another cyclic alkyl amino carbene ligand or, is linked together with at least one of R¹ or R² or a cyclic group formed by R¹ and R².
 4. An olefin metathesis catalyst of any of claims 1 to 3, wherein a is 1 or 2, b is 0, n is 0, k is 1, m is 0 or 1 or combinations thereof.
 5. An olefin metathesis catalyst of any of claims 1 to 4, wherein X¹ and X² are the same or different and are independently selected from Cl, Br, I, trifluoroacetate.
 6. An olefin metathesis catalyst of any of claims 1 to 5, wherein R¹ and R² are independently selected from hydrogen, methyl, ethyl, ethenyl, 1,1-dimethylethenyl, or R¹ and R² are taken together to form one or more cyclic groups selected from indenyl, phenylindenyl or phenyl, and wherein optionally any two or more of R¹ and R², X¹, X², L², L³ are forming a ring.
 7. An olefin metathesis catalyst of any of claims 1 to 6, wherein R¹ and R² are taken together to form one or more cyclic groups and said cyclic group is substituted with a group W- R¹⁵, wherein said group -W-R¹⁵ is L², W is oxygen and R¹⁵ is alkyl.
 8. An olefin metathesis catalyst of any of claims 1 to 7, wherein R⁵ and R⁹ are alkyl, in particular with one to five carbon atoms, preferably methyl, ethyl or isopropyl.
 9. An olefin metathesis catalyst of any of claims 1 to 8, wherein R³ and R^{3a} are selected from methyl, ethyl, isopropyl or R³ and R^{3a} together are forming a cyclopentyl or cyclohexyl ring.
 10. An olefin metathesis catalyst of any of claims 1 to 9, wherein R⁴ and R^{4a} are selected from methyl, ethyl, isopropyl or R⁴ and R^{4a} together are forming a cyclopentyl or cyclohexyl ring.
 11. An olefin metathesis catalyst of any of claims 1 to 10, wherein X is CH₂, and a is 1 or 2.

12. An olefin metathesis catalyst of any of claims 1 to 11, wherein R^1 and R^2 are taken together are forming a phenyl ring that is substituted up to three times with a group selected from C_{1-24} alkyl, halogen, $-C(O)R^{21}$, $-OR^{22}$, CN , $-NR^{23}R^{24}$, NO_2 , $-CF_3$, $-S(O)_xR^{25}$, $-P(O)(OH)_2$, $-OP(O)(OH)_2$, $-SR^{27}$, and R^{21} is OH , OR^{26} , $NR^{23}R^{24}$, optionally substituted C_{1-24} alkyl, optionally substituted C_{3-8} cycloalkyl, R^{22} , R^{23} , R^{24} and R^{27} are, independently from each other, H , optionally substituted C_{1-24} alkyl, optionally substituted C_{3-8} cycloalkyl, R^{25} is H , optionally substituted C_{1-24} alkyl, OR^{22} , $-NR^{23}R^{24}$, optionally substituted heterocycle, optionally substituted C_{3-8} cycloalkyl, R^{26} is optionally substituted C_{1-24} alkyl, optionally substituted C_{3-8} cycloalkyl.
13. An olefin metathesis catalyst of any of claims 1 to 12, wherein R^{15} is selected from H , Me , Et , $i-Pr$, $n-Pr$, $n-Bu$, $t-Bu$, $s-Bu$.
14. An olefin metathesis catalyst of any of claims 1 to 13, wherein R^{21} is OH , OR^{26} , $NR^{23}R^{24}$, or optionally substituted C_{1-6} alkyl; R^{22} , R^{23} , R^{24} , R^{26} are H , Me , Et , $i-Pr$, $n-Pr$, $n-Bu$, $t-Bu$, or $s-Bu$; R^{25} is H , Me , Et , $i-Pr$, $n-Pr$, $n-Bu$, $t-Bu$, $s-Bu$, OR^{22} , or $-NR^{23}R^{24}$.
15. An olefin metathesis catalyst of any of claims 1 to 13, wherein R^6 , R^7 and R^8 are, independently from each other, are H , optionally substituted C_{1-6} alkyl, halogen, optionally substituted phenyl.

Figure 1

