Title: HIGHLY ACTIVE METATHESIS CATALYSIS SELECTIVE FOR ROMP AND RCM

Abstract: A kind of novel carbene ligand and corresponding novel ruthenium catalyst are provided. The ruthenium catalysts are highly active and selective for ROMP and RCM reactions. The significant electronic effects of different substituted carbene ligands on the catalytic activity and stability of corresponding carbene ruthenium complexes are disclosed. The methods for preparing new ruthenium complexes are disclosed. Moreover, efficient methods for making various functional polymers and quality modified nitrile butadiene rubbers via different metathesis and hydrogenation reactions in the presence of the new ruthenium catalysts are provided.
HIGHLY ACTIVE METATHESIS CATALYSTS SELECTIVE FOR ROMP
AND RCM REACTIONS

FIELD OF THE INVENTION

The present invention relates to novel carbene ligands and their incorporated ruthenium catalysts, which are highly active and selective for different kinds of metathesis reactions such as ROMP and RCM. The invention also relates to preparation of new ruthenium complexes and the use thereof in metathesis, especially effective for preparation of various functional polymers and rubbers.

BACKGROUND OF THE INVENTION

Since Richard R. Schrock and Robert H. Grubbs prepared two kinds of metathesis catalysts with transition metal carbene structure in the 1990’s, it has been drawing extensive attention in the development of more active and selective ruthenium catalysts for different kinds of olefin metathesis reactions, e.g., ring-opening metathesis polymerization (ROMP), ring-closing metathesis (RCM), and cross metathesis (CM).

So far, some useful ruthenium complexes have been reported as active metathesis catalysts (1a-1b and 2a-2f in Scheme 1) for RCM and ROMP reactions (Grubbs et al., *J. Am. Chem. Soc.* 1992, 114, 3974-3975, *Org. Lett.* 1999, 1, 953-956, WO2007081987A1; Hoveyda et al., *J. Am. Chem. Soc.* 1999, 121, 791-799, *J. Am. Chem. Soc.* 2000, 122, 8168-8179; Yamaguchi et al., *Chem. Commun.* 1998, 1399-1400; Zhan et al., US20070043180A1, WO 2007003135A1; Grela et al., WO2004035596A1; Slugovc et al., *Organometallics* 2004, 23(15), 3623-3626 for catalyst 2d; and *Organometallics* 2005, 24(10), 2255-2258 for catalyst 2e). However, a disadvantage of all reported ruthenium catalysts is obviously substrate-dependent for different kinds of ruthenium catalysts in metathesis reactions, and it is still very difficult to find some active metathesis catalysts selective for RCM and ROMP reactions, respectively. Moreover, only a few metathesis catalysts could be used effectively to make high-strength and high-stiffness polydicyclopentadiene (PDCPD) material by ROMP reaction.
Currently, ROMP reaction is broadly used for preparation of various high-strength and other functional polymers. To overcome the activity and selectivity problems for ROMP catalysts, it has become a goal to develop more active and selective metathesis catalysts as an alternative for ROMP and RCM reactions, especially in ROMP for effective preparation and modification of different functional polymer materials. It is significantly important to develop more active and selective ruthenium catalyst for ROMP reactions with different kinds of olefin substrates to prepare highly functional polymer materials and also to improve polymer properties.

**SUMMARY OF THE INVENTION**

The present invention relates to two classes of novel carbene ligands and their incorporated ruthenium complexes that can be used as highly active metathesis catalysts selective for RCM, CM, and ROMP reactions, respectively. The novel metathesis catalysts are ruthenium complexes with different kinds of new functionally substituted carbene ligands. The new ruthenium complexes of the invention can catalyze different kinds of metathesis reactions in a very effective manner and offer great advantage in activity and selectivity for different kinds of metathesis reactions, especially in ROMP effective for preparation of some functional polymer materials with unique chemical and physical properties. The novel ruthenium complexes of the
invention have broad uses in the polymeric and pharmaceutical industries.

In the first aspect, the present invention provides a kind of compounds to form carbene ligands having the following structure **la** or **lb**:

![Chemical Structure](image)

Wherein Z is CH2= or TsNHN=;

m = 0 or 1, n = 0 or 1;

When m = 0, Y is CH2, NH, oxygen, nitrogen, carbonyl, imino, C1-C20 alkoxy, C6-C20 arylxy, C2-C20 heterocyclic aryl, C1-C20 alkoxy carbonyl, C6-C20 aryl oxycarbonyl, C1-C20 alkyl imino, C1-C20 alkyl amino, C6-C20 aryl amino or C2-C20 heterocyclic amino group;

When m = 1, X is oxygen, nitrogen, sulfur, CH, CH2, carbonyl; Y is nitrogen, oxygen, CH, CH2, imino, NH, C1-C20 alkyl, C1-C20 alkoxy, C6-C20 aryl, C6-C20 arylxy, C3-C20 heteroaryl, C1-C20 alkyl carbonyl, C1-C20 alkoxy carbonyl, C6-C20 aryl carbonyl, C6-C20 aryl oxycarbonyl, C1-C20 alkyl imino, C1-C20 alkyl amino, C6-C20 aryl amino or C2-C20 heterocyclic amino group; “Y=X” is either single bond or double bond;

When n = 1, X1 and Y1 are each oxygen, nitrogen, sulfur, carbonyl, imino, CH, CH2, C1-C20 alkyl, C6-C20 aryl, C6-C20 arylxy, C2-C20 heterocyclic aryl, C1-C20 alkyl amino, C6-C20 aryl amino or C2-C20 heterocyclic amino group;

R1 is H, C1-C20 alkyl, C2-C20 alkenyl, C6-C20 aryl, C6-C20 arylxy, C1-C20 alkylthio, C6-C20 arylthio, C6-C20 arylxy, C3-C20 heteroaryl or C2-C20 heterocyclic group;

R2 is H, C1-C20 alkyl, C6-C20 aryl, C1-C20 alkyl carbonyl, C6-C20 aryl carbonyl, C1-C20 alkoxy carbonyl, C6-C20 aryl oxycarbonyl, C1-C20 aminocarbonyl, C3-C20 heteroaryl or C2-C20 heterocyclic group;

E, E1, E2, E3, E4, E5, E6 and E7 are each independently selected from the group consisting of H, halogen atom, nitro, amino, cyano, formyl, sulfinyl, sulfonyl, C1-C20
alkyl, C₁₋C₂₀ alkoxy, C₁₋C₂₀ alkylthio, C₂₋C₂₀ alkenyloxy, C₁₋C₂₀ silanyl, C₁₋C₂₀ alkylsilyloxy, C₆₋C₂₀ aryl, C₆₋C₂₀ aryloxy, C₁₋C₂₀ alkylcarbonyl, C₆₋C₂₀ arylcarbonyl, C₁₋C₂₀ alkoxy carbonyl, C₆₋C₂₀ aryloxycarbonyl, amino, C₁₋C₂₀ alkyaminocarbonyl, C₆₋C₂₀ arylaminocarbonyl, C₁₋C₂₀ alkylamido, C₆₋C₂₀ arylamido, C₁₋C₂₀ alkylaminosulfonyl, C₆₋C₂₀ arylaminosulfonyl, C₁₋C₂₀ sulfonylamido, C₃₋C₂₀ heteroaryl or C₂₋C₂₀ heterocyclic group; each optionally substituted with an alkyl, alkoxy, alkylthio, aryl, aryloxy, halogen atom or heterocyclic group;

In one preferred embodiment in the present invention, the formula Ia-Ib,

\[ Z = \text{CH}_2 \text{ or } \text{TsNHN}^-; \]

\[ m = 0 \text{ or } 1, n = 0 \text{ or } 1; \]

When \( m = 0 \), \( Y \) is \( \text{CH}_2 \), \( \text{NH} \), oxygen, nitrogen, carbonyl, imino, C₁₋C₁₅ alkoxy, C₆₋C₁₅ aryloxy, C₁₋C₁₅ alkoxy carbonyl, C₆₋C₁₅ aryloxycarbonyl, C₁₋C₁₅ alkylamino, C₆₋C₁₅ arylamino or C₂₋C₁₅ heterocyclic amino group;

When \( m = 1 \), \( X \) is oxygen, nitrogen, sulfur, CH, CH₂, carbonyl; \( Y \) is nitrogen, oxygen, CH, CH₂, imino, NH, C₁₋C₁₅ alkyl, C₁₋C₁₅ alkoxy, C₆₋C₁₅ aryloxy, C₃₋C₁₅ heteroaryl, C₁₋C₁₅ alkylcarbonyl, C₁₋C₁₅ alkoxy carbonyl, C₆₋C₁₅ arylcarbonyl, C₆₋C₁₅ aryloxycarbonyl, C₁₋C₁₅ alkylamino, C₆₋C₁₅ arylamino or C₂₋C₁₅ heterocyclic amino group; “\( Y = \text{X} \)” is either single bond or double bond.

When \( n = 1 \), \( X^1 \) and \( Y^1 \) are each oxygen, nitrogen, sulfur, carbonyl, imino, CH, CH₂, C₁₋C₁₅ alkyl, C₆₋C₁₅ aryl, C₂₋C₁₅ heterocyclic aryl, C₁₋C₁₅ alkylamino, C₆₋C₁₅ arylamino or C₂₋C₁₅ heterocyclic amino group;

\[ R^1 \text{ is } H, \text{C}_1\text{-C}_{15} \text{ alkyl, C}_2\text{-C}_{15} \text{ alkenyl, C}_6\text{-C}_{15} \text{ aryl, C}_6\text{-C}_{15} \text{ arylenyl, C}_1\text{-C}_{15} \text{ alkoxy, C}_1\text{-C}_{15} \text{ alkylthio, C}_6\text{-C}_{15} \text{ arythio, C}_6\text{-C}_{15} \text{ aryloxy, C}_3\text{-C}_{15} \text{ heteroaryl or C}_2\text{-C}_{15} \text{ heterocyclic group;} \]

\[ R^2 \text{ is } H, \text{C}_1\text{-C}_{15} \text{ alkyl, C}_6\text{-C}_{15} \text{ aryl, C}_1\text{-C}_{15} \text{ alkylcarbonyl, C}_6\text{-C}_{15} \text{ arylcarbonyl, C}_1\text{-C}_{15} \text{ alkoxy carbonyl, C}_6\text{-C}_{15} \text{ aryloxycarbonyl, C}_1\text{-C}_{15} \text{ aminocarbonyl, C}_3\text{-C}_{15} \text{ heteroaryl or C}_2\text{-C}_{15} \text{ heterocyclic group;} \]

\[ E, E^1, E^2, E^3, E^4, E^5, E^6 \text{ and } E^7 \text{ are each independently selected from the group consisting of } H, \text{halogen atom, nitro, amino, cyano, formyl, sulfinyl, sulfonyl, C}_1\text{-C}_{15} \]
alkyl, C_{1-15} alkoxyc, C_{1-15} alkythio, C_{2-15} alkenyloxy, C_{1-15} silanyl, C_{1-15} alkylsilyloxy, C_{6-15} aryl, C_{6-15} aryloxy, C_{1-15} alkyrcarbonyl, C_{6-15} arylcarbonyl, C_{1-15} alkoxycarbonyl, C_{6-15} aryloxy carbonyl, C_{1-15} alkylaminocarbonyl, C_{6-15} arylaminocarbonyl, C_{1-15} alkylamido, C_{6-15} arylamido, C_{1-15} alkylaminosulfonyl, C_{6-15} arylaminosulfonyl, C_{1-15} sulfonamido, C_{3-15} heteroaryl or C_{2-15} heterocyclic group; each optionally substituted with an alkyl, alkoxy, alkylthio, aryl, aryloxy, halogen atom or heterocyclic group.

In one more preferred embodiment in the present invention, in the formula Ia-Ib,

Z is CH_2= or TsNHN=;

m = 0 or 1, n = 0 or 1;

When m = 0, Y is oxygen, nitrogen, carbonyl, imino, C_{1-8} alkoxyc, C_{6-8} aryloxy, C_{1-8} alkoxycarbonyl, C_{6-8} aryloxy carbonyl, C_{1-8} alkylimino, C_{1-8} alkylamino, C_{6-12} arylamino or C_{2-12} heterocyclic amino group;

When m = 1, X is nitrogen, oxygen, sulfur, CH, CH_2, carbonyl; Y is oxygen, nitrogen, CH, CH_2, imino, NH, C_{1-15} alkyl, C_{1-8} alkoxy, C_{6-15} aryl, C_{6-12} aryloxy, C_{3-12} heteroaryl, C_{1-8} alkyrcarbonyl, C_{1-8} alkoxycarbonyl, C_{6-12} arylcarbonyl, C_{6-12} aryloxy carbonyl, C_{1-8} alkylamino, C_{6-12} arylamino or C_{2-12} heterocyclic amino group; “Y==X” is either single bond or double bond.

When n = 1, X^1 and Y^1 are each oxygen, nitrogen, sulfur, carbonyl, imino, CH, CH_2, C_{1-8} alkyl, C_{6-8} aryl, C_{6-8} aryloxy, C_{2-8} heterocyclic aryl, C_{1-8} alkylamino, C_{6-8} arylamino or C_{2-8} heterocyclic amino group;

R^1 is H, C_{1-8} alkyl, C_{2-8} alkenyl, C_{6-12} aryl or C_{6-12} arylenyl;

R^2 is methyl, ethyl, isopropyl, C_{1-8} alkyl or C_{6-12} aryl;

E, E^1, E^2, E^3, E^4, E^5, E^6 and E^7 are each independently selected from the group consisting of H, halogen atom, nitro, C_{1-8} alkyl, C_{1-8} alkoxy, C_{1-8} alkylthio, C_{2-8} alkenyloxy, C_{1-8} silanyl, C_{1-8} alkysilyloxy, C_{6-12} aryl, C_{6-12} aryloxy, C_{1-8} alkyrcarbonyl, C_{6-12} aryloxy carbonyl, C_{1-8} alkylaminocarbonyl, C_{6-12} arylaminocarbonyl, C_{1-8} alkylamido, C_{6-12} arylamido, C_{1-8} alkylaminosulfonyl, C_{6-12} arylaminosulfonyl,
C₃-C₈ sulfonylamido, C₃-C₁₂ heteroaryl or C₂-C₈ heterocyclic group; each optionally
substituted with an alkyl, alkoxy, alkylthio, aryl, aryloxy, halogen atom or
heterocyclic group.

In one most preferred embodiment in the present invention, the formula \textbf{Ia-Ib}

Z is CH₂⁻ or TsNHN⁻;

m = 0 or 1, n = 0 or 1;

When m = 0, Y is CH₂, NH, C₁-C₄ alkoxy, C₁-C₄ alkylamino or C₆-C₉ arylamino

group;

When m = 1, X is nitrogen, C₁-C₃ alkylamino, CH, CH₂, or carbonyl; Y is

oxygen, nitrogen, imino, NH, C₁-C₄ alkyl, C₁-C₄ alkoxy, C₁-C₄ alkylamino, or C₆-C₉

arylamino; "Y≡X" is either single bond or double bond;

When n = 1, X¹ is CH₂, substituted or unsubstituted phenyl, or carbonyl; Y¹ is

oxygen or carbonyl;

R¹ is H;

when n = 1, R² is methyl, ethyl, or isopropyl; and when n = 0, R² is H, halogen,

C₁-C₄ alkyl or C₁-C₄ alkoxy in structure \textbf{Ia}.

E is H, halogen, nitro, C₁-C₄ alkyl, C₁-C₄ alkoxy, C₁-C₄ alkoxycarbonyl, C₁-C₈

alkylaminosulfonyl, C₆-C₁₂ arylaminosulfonyl;

E¹ and E² are each H, halogen, C₁-C₄ alkyl or C₁-C₄ alkoxy;

E³ is H;

E⁴ is H or C₁-C₄ alkyl;

E⁵ and E⁶ is H, halogen, C₁-C₄ alkyl or C₁-C₆ alkoxy;

E⁷ is H or C₁-C₄ alkyl.

In the second aspect, the present invention provides a kind of transition metal

complex having the following structure \textbf{IIa} or \textbf{IIb}:
Wherein: \( m = 0 \) or 1, and \( n = 0 \) or 1;

When \( n = 0 \): \( p = 0 \) or 1; when \( n = 1 \), \( p = 0 \);

M is a transition metal;

\( L^1 \) and \( L^2 \) are the same or different and each selected from halogen anion (\( \text{Cl}^- \), \( \text{Br}^- \) or \( \text{I}^- \)), \( \text{RC(O)O}^- \) or \( \text{ArO}^- \) anion;

\( L \) is an electron-donating ligand;

When \( m = 1 \), \( X \) is oxygen, nitrogen, sulfur, CH, CH₂, carbonyl; \( Y \) is nitrogen, oxygen, CH, CH₂, imino, C₁-C₂₀ alkoxy, C₆-C₂₀ aryl, C₆-C₂₀ aryloxy, C₃-C₂₀ heteroaryl, C₁-C₂₀ alkylcarbonyl, C₁-C₂₀ alkoxy carbonyl, C₆-C₂₀ aryl carbonyl, C₆-C₂₀ aryloxy carbonyl, C₁-C₂₀ alkyl imino, C₁-C₂₀ alkyl amine, C₆-C₂₀ aryl amine or C₂-C₂₀ heterocyclic amino group; “\( \text{Y} \rightarrow \text{X} \)” is either single bond or double bond;

When \( m = 0 \), \( Y \) is oxygen, nitrogen, carbonyl, imino, C₁-C₂₀ alkoxy, C₆-C₂₀ aryloxy, C₂-C₂₀ heterocyclic aryl, C₁-C₂₀ alkoxy carbonyl, C₆-C₂₀ aryl carbonyl, C₁-C₂₀ alkyl imino, C₁-C₂₀ alkyl amine, C₆-C₂₀ aryl amine or C₂-C₂₀ heterocyclic amino group;

When \( n = 0 \) and \( p = 1 \), \( L^3 \) is an electron-donating ligand;

When \( n = 1 \) and \( p = 0 \), \( X^1 \) and \( Y^1 \) are each oxygen, nitrogen, sulfur, carbonyl, imino, CH, CH₂, C₁-C₂₀ alkyl, C₆-C₂₀ aryl, C₆-C₂₀ aryloxy, C₂-C₂₀ heterocyclic aryl, C₁-C₂₀ alkyl amine, C₆-C₂₀ aryl amine or C₂-C₂₀ heterocyclic amino group;

\( R^1 \) is H, C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, C₆-C₂₀ aryl, C₆-C₂₀ aryl enyl, C₁-C₂₀ alkoxy, C₁-C₂₀ alkylthio, C₆-C₂₀ arylthio, C₆-C₂₀ aryloxy, C₃-C₂₀ heteroaryl or C₂-C₂₀ heterocyclic group;

\( R^2 \) is H, C₁-C₂₀ alkyl, C₆-C₂₀ aryl, C₁-C₂₀ alkylcarbonyl, C₆-C₂₀ aryl carbonyl, C₁-C₂₀ alkoxy carbonyl, C₆-C₂₀ aryloxy carbonyl, C₁-C₂₀ amine carbonyl, C₃-C₂₀ heteroaryl or C₂-C₂₀ heterocyclic group;

\( E, E^1, E^2, E^3, E^4, E^5, E^6 \) and \( E^7 \) are each independently selected from the group consisting of H, halogen atom, nitro, amino, cyan, formyl, sulfinyl, sulfonyl, C₁-C₂₀ alkyl, C₁-C₂₀ alkoxy, C₁-C₂₀ alkylthio, C₂-C₂₀ alkenyloxy, C₁-C₂₀ silanyl, C₁-C₂₀ alkyl silyloxy, C₆-C₂₀ aryl, C₆-C₂₀ aryloxy, C₁-C₂₀ alkyl carbonyl, C₆-C₂₀ aryl carbonyl, C₁-C₂₀ alkoxy carbonyl, C₆-C₂₀ aryloxy carbonyl, amino, C₁-C₂₀ alkylaminocarbonyl,
C\textsubscript{6}-C\textsubscript{20} arylaminocarbonyl, C\textsubscript{1}-C\textsubscript{20} alkylamido, C\textsubscript{6}-C\textsubscript{20} arylamido, C\textsubscript{1}-C\textsubscript{20} alkylaminosulfonyl, C\textsubscript{6}-C\textsubscript{20} arylaminosulfonyl, C\textsubscript{1}-C\textsubscript{20} sulfonylamido, C\textsubscript{3}-C\textsubscript{20} heteroaryl or C\textsubscript{2}-C\textsubscript{20} heterocyclic group; each optionally substituted with an alkyl, alkoxy, alkylthio, aryl, aryloxy, halogen atom or heterocyclic group.

In preferred embodiment \textbf{IIa} or \textbf{IIb}, L is heterocyclic carbene ligand or phosphine P(R\textsuperscript{8})\textsubscript{2}(R\textsuperscript{9}) having the following structure \textbf{IIIa}, \textbf{IIIb}, \textbf{IIIc}, or \textbf{IIId}:

\[
\begin{align*}
\text{IIIa} & \quad \text{IIIb} & \quad \text{IIIc} & \quad \text{IIId} \\
R^4 & \quad N & \quad N & \quad R^5 \\
R^6 & \quad N & \quad N & \quad R^5 \\
R^7 & \quad N & \quad N & \quad R^5 \\
q & \quad \text{R}^8 & \quad \text{R}^8 & \quad \text{R}^8 \\
\end{align*}
\]

Wherein, q = 1, 2 or 3;

R\textsuperscript{4} and R\textsuperscript{5} are each C\textsubscript{1}-C\textsubscript{20} alkyl, C\textsubscript{6}-C\textsubscript{20} aryl, C\textsubscript{1}-C\textsubscript{20} alkylamido, C\textsubscript{6}-C\textsubscript{20} arylamido, C\textsubscript{3}-C\textsubscript{20} heteroaryl or C\textsubscript{2}-C\textsubscript{20} heterocyclic group;

R\textsuperscript{6} and R\textsuperscript{7} are each H, halogen atom, nitro, amino, cyano, formyl, sulfinyl, sulfonyl, C\textsubscript{1}-C\textsubscript{20} alkyl, C\textsubscript{1}-C\textsubscript{20} alkoxy, C\textsubscript{1}-C\textsubscript{20} alkylthio, C\textsubscript{2}-C\textsubscript{20} alkenyloxy, C\textsubscript{1}-C\textsubscript{20} silanyl, C\textsubscript{1}-C\textsubscript{20} alkylsilyloxy, C\textsubscript{2}-C\textsubscript{20} heterocyclic, C\textsubscript{6}-C\textsubscript{20} aryl, C\textsubscript{6}-C\textsubscript{20} arloxy, C\textsubscript{1}-C\textsubscript{20} alkylcarbonyl, C\textsubscript{6}-C\textsubscript{20} arylcarbonyl, C\textsubscript{1}-C\textsubscript{20} alkoxycarbonyl, C\textsubscript{6}-C\textsubscript{20} aryloxy carbonyl, amino, C\textsubscript{1}-C\textsubscript{20} alkylaminocarbonyl, C\textsubscript{6}-C\textsubscript{20} arylaminocarbonyl, C\textsubscript{1}-C\textsubscript{20} alkylamido, C\textsubscript{6}-C\textsubscript{20} ary lamido, C\textsubscript{1}-C\textsubscript{20} alkyaminosulfonyl, C\textsubscript{6}-C\textsubscript{20} arylaminosulfonyl, C\textsubscript{1}-C\textsubscript{20} sulfonylamido, C\textsubscript{3}-C\textsubscript{20} heteroaryl or C\textsubscript{2}-C\textsubscript{20} heterocyclic group;

R\textsuperscript{8} and R\textsuperscript{9} are each C\textsubscript{1}-C\textsubscript{20} alkyl, C\textsubscript{1}-C\textsubscript{20} alkoxy, C\textsubscript{6}-C\textsubscript{20} aryl, C\textsubscript{6}-C\textsubscript{20} aryloxy, C\textsubscript{3}-C\textsubscript{20} heteroaryl or C\textsubscript{2}-C\textsubscript{20} heterocyclic group.

In one preferred embodiment, wherein L is formula \textbf{IIIa} or \textbf{IIId}; and in \textbf{IIIa}, q = 1 or 2, R\textsuperscript{4} and R\textsuperscript{5} each is aryl, R\textsuperscript{6} and R\textsuperscript{7} each is H.

In one more preferred embodiment, wherein L is \textbf{IIIa} or \textbf{IIId}; and in \textbf{IIIa}, q = 1, R\textsuperscript{4} and R\textsuperscript{5} each is 2,4,6-trimethylphenyl, R\textsuperscript{6} and R\textsuperscript{7} each is H; or in \textbf{IIId}, R\textsuperscript{8} and R\textsuperscript{9} each is cyclohexyl (Cy).

In another preferred embodiment, in \textbf{IIa-IIb},

M is ruthenium (Ru), wolfram (W) or nickel (Ni);

m = 0 or 1, n = 0 or 1;
L¹ and L² each is chloride (Cl⁻);

L is \textbf{IIIa} or \textbf{IIIb}; wherein q, R¹, R², R³, R⁴, R⁶, R⁷, R⁸, R⁹, E, E¹, E², E³, E⁴, E⁵, E⁶ and E⁷ each is as defined above.

When n = 0, p = 0 or 1; when n = 1, p = 0;

When m = 0, Y is oxygen, nitrogen, carbonyl, imino, C₁-C₁₅ alkoxy, C₆-C₁₅ aryloxyl, C₁-C₁₅ alkoxy carbonyl, C₆-C₁₅ aryloxycarbonyl, C₁-C₁₅ alkylamino, C₆-C₁₅ arylamino or C₂-C₅₁ heterocyclic amino group;

When m = 1, X is oxygen, nitrogen, sulfur, CH, CH₂, carbonyl; Y is nitrogen, oxygen, CH, CH₂, imino, C₁-C₁₅ alkoxy, C₆-C₁₅ aryl, C₆-C₁₅ aryloxyl, C₃-C₁₅ heteroaryl, C₁-C₁₅ alkylcarbonyl, C₁-C₁₅ alkoxy carbonyl, C₆-C₁₅ arylcarbonyl, C₆-C₁₅ aryloxycarbonyl, C₁-C₁₅ alkylamino, C₆-C₁₅ arylamino or C₂-C₅₁ heterocyclic amino group; “Y≡X” is either single bond or double bond;

When n = 0 and p = 1, L³ is one or more substituted pyridine at the ortho-position, meta-position and/or para-position, and the nitrogen atom of the substituted pyridine donates a pair of electron to the transition metal cation, wherein the substituents at the ortho-position, meta-position and/or para-position of pyridine are each selected from halogen, nitro, cyano, C₁-C₁₅ alkyl, C₁-C₁₅ alkoxy, C₁-C₁₅ alkylthio, C₂-C₁₅ alkenyloxy, C₁-C₁₅ silanyl, C₁-C₁₅ alkylsilyloxy, C₆-C₁₅ aryl, C₆-C₁₅ aryloxyl, C₁-C₁₅ alkylcarbonyl, C₆-C₁₅ arylcarbonyl, C₁-C₁₅ alkoxy carbonyl, C₆-C₁₅ aryloxycarbonyl, C₁-C₁₅ alkylaminocarbonyl, C₆-C₁₅ aryaminocarbonyl, C₁-C₁₅ alkylamido, C₆-C₁₅ arylamido, C₁-C₁₅ alkyaminosulfonyl, C₆-C₁₅ aryaminosulfonyl, C₁-C₁₅ sulfonylamido, C₃-C₁₅ heteroaryl or C₂-C₅₁ heterocyclic group; each optionally substituted with an alkyl, alkoxy, aryl, aryloxyl, halogen atom or heterocyclic group.

When n = 1 and p = 0, X¹ and Y¹ are each oxygen, nitrogen, sulfur, carbonyl, imino, CH, CH₂, C₁-C₁₅ alkyl, C₆-C₁₅ aryl, C₆-C₁₅ aryloxyl, C₂-C₅₁ heterocyclic aryl, C₁-C₁₅ alkylamino, C₆-C₁₅ arylamino or C₂-C₅₁ heterocyclic amino group.

In one more preferred embodiment of the present invention, wherein the structure \textbf{IIa} or \textbf{Ib}: 

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When \( m = 0 \), \( Y \) is oxygen, nitrogen, carbonyl, imino, \( C_1-C_8 \) alkoxy, \( C_6-C_{12} \) aryloxy, \( C_1-C_8 \) alkoxy carbonyl, \( C_6-C_{12} \) aryloxy carbonyl, \( C_1-C_8 \) alkylimino, \( C_1-C_8 \) alkylamino, \( C_6-C_{12} \) arylamino or \( C_2-C_8 \) heterocyclic amino group;

When \( m = 1 \), \( X \) is oxygen, nitrogen, sulfur, CH, CH\(_2\), carbonyl; \( Y \) is nitrogen, oxygen, CH, CH\(_2\), imino, \( C_1-C_8 \) alkoxy, \( C_6-C_{12} \) aryl, \( C_6-C_{12} \) aryloxy, \( C_3-C_{12} \) heteroaryl, \( C_1-C_8 \) alkylcarbonyl, \( C_1-C_8 \) alkoxy carbonyl, \( C_6-C_{12} \) arylcarbonyl, \( C_6-C_{12} \) aryloxycarbonyl, \( C_1-C_8 \) alkylamino, \( C_6-C_{12} \) arylamino or \( C_2-C_8 \) heterocyclic amino group; “Y=-X” is either single bond or double bond;

When \( n = 0 \), \( p = 0 \) or 1; when \( n = 1 \), \( p = 0 \);

When \( n = 0 \) and \( p = 1 \), \( L^3 \) is one or more substituted pyridine at the ortho-position, meta-position and/or para-position, and the nitrogen atom of the substituted pyridine donates a pair of electron to the transition metal cation, wherein the substituents at the ortho-position, meta-position and/or para-position of pyridine are each selected from halogen, nitro, cyano, \( C_1-C_8 \) alkyl, \( C_1-C_8 \) alkoxy, \( C_1-C_8 \) alkylthio, \( C_2-C_8 \) alkenyloxy, \( C_1-C_8 \) silanyl, \( C_1-C_8 \) alkylsilyloxy, \( C_6-C_{12} \) aryl, \( C_6-C_{12} \) aryloxy, \( C_1-C_8 \) alkylcarbonyl, \( C_6-C_{12} \) arylcarbonyl, \( C_1-C_8 \) alkoxy carbonyl, \( C_6-C_{12} \) aryloxycarbonyl, \( C_1-C_8 \) alkylaminocarbonyl, \( C_6-C_{12} \) arylaminocarbonyl, \( C_1-C_8 \) alkylamido, \( C_6-C_{12} \) arylamido, \( C_1-C_8 \) alkylaminosulfonyl, \( C_6-C_{12} \) arylaminosulfonyl, \( C_1-C_8 \) sulfonlamido, \( C_3-C_{12} \) heteroaryl or \( C_2-C_8 \) heterocyclic group; each optionally substituted with an alkyl, alkoxy, alkylthio, aryl, aryloxy, halogen atom or heterocyclic group;

When \( n = 1 \) and \( p = 0 \), \( X^1 \) and \( Y^1 \) are each oxygen, nitrogen, sulfur, carbonyl, imino, CH, CH\(_2\), \( C_1-C_8 \) alkyl, \( C_6-C_{12} \) aryl, \( C_6-C_{12} \) aryloxy, \( C_2-C_{12} \) heterocyclic aryl, \( C_1-C_8 \) alkylimino, \( C_6-C_{12} \) arylamino or \( C_2-C_8 \) heterocyclic amino group;

\( R^1 \) is \( H, C_1-C_8 \) alkyl, \( C_2-C_8 \) alkenyl, \( C_6-C_{12} \) aryl or \( C_6-C_{12} \) aroylenyl;

\( R^2 \) is methyl, ethyl, isopropyl, \( C_1-C_8 \) alkyl or \( C_6-C_{12} \) aryl;

\( E, E^1, E^2, E^3, E^4, E^5, E^6 \) and \( E^7 \) are each independently selected from the group consisting of \( H \), halogen atom, nitro, \( C_1-C_8 \) alkyl, \( C_1-C_8 \) alkoxy, \( C_1-C_8 \) alkylthio, \( C_2-C_8 \) alkenyloxy, \( C_1-C_8 \) silanyl, \( C_1-C_8 \) alkylsilyloxy, \( C_6-C_{12} \) aryl, \( C_6-C_{12} \) aryloxy, \( C_1-C_8 \) alkylcarbonyl, \( C_6-C_{12} \) arylcarbonyl, \( C_1-C_8 \) alkoxy carbonyl, \( C_6-C_{12} \) aryloxycarbonyl,
C1-C8 alkylaminocarbonyl, C6-C12 arylaminocarbonyl, C1-C8 alkylamido, C6-C12 arylamido, C1-C8 alkylaminosulfonyl, C6-C12 arylaminosulfonyl, C1-C8 sulfonylamido, C3-C12 heteroaryl or C2-C8 heterocyclic group; each optionally substituted with an alkyl, alkoxy, alkylthio, aryl, arylxy, halogen atom or heterocyclic group.

In one most preferred embodiment of the present invention, wherein the structure

IIa or IIb:

M is ruthenium;

L is IIIa or IIId; and in IIIa, \( q = 1 \), \( R^4 \) and \( R^5 \) each is 2,4,6-trimethylphenyl, \( R^6 \) and \( R^7 \) each is \( H \), or in IIId, \( R^8 \) and \( R^9 \) each is cyclohexyl (Cy).

\( L^1 \) and \( L^2 \) each is chloride anion;

\( m = 0 \) or 1, and \( n = 0 \) or 1;

When \( m = 0 \), \( Y \) is \( \text{CH}_2, \text{NH}, \text{C}_1-\text{C}_4 \text{ alkoxy}, \text{C}_1-\text{C}_4 \text{ alkylamino} \) or \( \text{C}_6-\text{C}_9 \text{ arylamino} \) group;

When \( m = 1 \), \( X \) is nitrogen, \( \text{C}_1-\text{C}_3 \text{ alkylamino}, \text{CH}, \text{CH}_2, \) or carbonyl; \( Y \) is oxygen, nitrogen, imino, \( \text{NH}, \text{C}_1-\text{C}_4 \text{ alkyl}, \text{C}_1-\text{C}_4 \text{ alkoxy}, \text{C}_1-\text{C}_4 \text{ alkylamino}, \) or \( \text{C}_6-\text{C}_9 \text{ arylamino} \); “\( \text{Y=Z} \)” is either single bond or double bond;

When \( n = 0 \), \( p = 0 \) or 1; when \( n = 1 \), \( p = 0 \).

When \( n = 0 \) and \( p = 1 \), \( L^3 \) is one substituted pyridine at the meta-position or para-position, and the nitrogen atom of the substituted pyridine donates a pair of electron to ruthenium cation, wherein the substituents at the meta-position or para-position of pyridine are each selected from halogen, nitro, \( \text{C}_1-\text{C}_3 \text{ alkyl}, \text{C}_1-\text{C}_3 \text{ alkoxy}, \text{C}_1-\text{C}_6 \text{ alkylamino}, \) unsubstituted or substituted \( \text{C}_6-\text{C}_{12} \text{ aryl} \);

When \( n = 1 \), \( X^1 \) is \( \text{CH}_2, \) substituted or unsubstituted phenyl, or carbonyl; \( Y^1 \) is oxygen or carbonyl;

\( R^1 \) is \( H \);

when \( n = 1 \), \( R^2 \) is methyl, ethyl, or isopropyl; when \( n = 0 \), \( R^2 \) is \( H \), halogen, \( \text{C}_1-\text{C}_4 \text{ alkyl} \) or \( \text{C}_1-\text{C}_4 \text{ alkoxy} \) in structure IIa.

E is \( H \), halogen, nitro, \( \text{C}_1-\text{C}_4 \text{ alkyl}, \text{C}_1-\text{C}_4 \text{ alkoxy}, \text{C}_1-\text{C}_4 \text{ alkoxy carbonyl}, \text{C}_1-\text{C}_8 \text{ alkylaminosulfonyl}, \text{C}_6-\text{C}_{12} \text{ arylaminosulfonyl};

\( E^1 \) and \( E^2 \) are each \( H \), halogen, \( \text{C}_1-\text{C}_4 \text{ alkyl} \) or \( \text{C}_1-\text{C}_4 \text{ alkoxy} \);
E³ is H;
E⁴ is H or C₁-C₄ alkyl;
E⁵ and E⁶ is H, halogen, C₁-C₄ alkyl or C₁-C₆ alkoxy;
E⁷ is H or C₁-C₄ alkyl.

The third aspect, the present invention provides the following synthetic methods of making different kinds of transition metal complexes IIa-IIb.

First of all, in the present invention, when Z is CH₂, the complex ligands Ia-Ib could be prepared by the following Suzuki reaction:

Wherein Y, Y¹, R¹, R², E, E¹, E² and E³ each is as defined above.

The ligands Ia-Ib can be prepared by the coupling of chemicals SM-1a or SM-1b with vinyl borane reagent in organic solvent such as DMF in the presence of Pd catalyst. SM-1a or SM-1b were ordered by custom synthesis from Zannan Pharma Ltd, in China.

Method 1 in the following Scheme 1:
The intermediate of transition metal complex (Va or Vb) having the following structure:

1. The Ru complex 2h is prepared by the reaction of reagent SM-2b and RuCl₂(PPh₃)₃ in anhydrous DCM in a three-neck flask filled with inert gas (Ar).

2. The Ru complex 2h obtained by step (1) is reacted with complex ligand Ia or Ib to prepare another Ru complex Va or Vb in a flask filled with inert gas (Ar); wherein, Va and Vb are compounds IIa or IIb when L is PPh₃; M, L₁, L₂, Y, Y¹, R¹, R², E, E¹, E² and E³ are each as defined above.

More preferred, L¹ and L² each is chloride anion (Cl⁻).

Wherein, in step (1), the preferred one of E and X¹ is hydrogen; the preferred usage of anhydrous organic solvent is 5-30 times weight of SM-2; the more preferred usage is 15 times; the preferred reaction temperature is 25-75°C, the more preferred temperature is 50-65°C.

In step (2), the preferred reaction temperature is -50°C to -85°C, the more preferred temperature is -60°C to -75°C; the preferred usage of ML¹L₂L₃ is 0.3-1.0 times molar ratio of SM-2, the more preferred usage is 0.6-0.7 times; the preferred compound of ML¹L₂L₃ is RuCl₂(PPh₃)₃.

In step (3) of method 1, the preferred reaction temperature is -50°C to -85°C, the more preferred temperature is -60°C to -75°C; the preferred usage of complex ligand Ia or Ib is 1-3 molar ratio of complex intermediate, the preferred usage is 1.5-2 eq.

When ML¹L₂L is RuCl₂(PPh₃)₃, the structure of product Va or Vb is as follows:
Method 2: the complex Va or Vb obtained by method 1 is reacted respectively with any electron-donating complex ligand L except PPh₃ to prepare following metal complexes IIa or IIb, wherein, p = 0, q = 1, definition of M, L, L¹, L², Y, Y¹, R¹, R², E, E¹, E² and E³ each is as defined above;

Wherein, the preferred one, in structure of transition metal complexes as the product IIa or IIb, where a preferred ligand L is IIIa or IIId. The preferred reaction temperature is 20°C to 75°C, the more preferred reaction temperature reacted with complex ligand IIIa is 60°C to 75°C, the more preferred reaction temperature reacted with complex ligand IIId is 20°C to 35°C; The preferred usage of IIIa or IIId is 1-3 times molar ratio of complex intermediate Va or Vb, the more preferred molar ratio is 1.5-2 eq;

Method 3: when L is PCy₃ or PPh₃, the IIa or IIb is reacted respectively with any electron-donating complex ligand L (IIIa) or L³ to prepare the metal complex IIa or IIb, wherein p = 0, M, L¹, L², Y, Y¹, R¹, R², E, E¹, E², E³ is each as defined above.

Method 4: when L is PCy₃ or IIIa, the IIa or IIb is reacted respectively with any electron-donating complex ligand L³ to prepare the metal complex IIa or IIb, wherein p = 1, M, L¹, L², Y, Y¹, R¹, R², E, E¹, E², E³ is each as defined above. In method 4, the preferred reaction temperature is 20°C to 35°C.

From method 1 to method 4, L¹ and L² each is chloride anion.
Based on currently developed technology, the metal complex IIa or IIb of the present invention could also be prepared by the following two alternative procedures described in Schemes 2 & 3:

**Scheme 2:**

\[
\begin{align*}
\text{Ia or Ib (Z = TsNHN)} & \xrightarrow{1) \text{NaOEt, EtOH}} \text{Va or Vb} \\
& \xrightarrow{2) \text{RuCl}_2(P\text{Ph}_3)\text{CuCl}} \text{PCy}_3 \text{(IIId)} \\
\text{IIa or IIb (L = PCy}_3) & \xrightarrow{} \text{IIa or IIb} \\
& \xrightarrow{} \text{Mes}^+\text{N}^\text{N-Mes} \text{(IIIa)} \\
\end{align*}
\]

L = Mes^+\text{N}^\text{N-Mes} \quad (\text{Mes = 2,4,6-trimethylphenyl})

In the above procedure, Z is TsNHN in structure Ia or Ib.

In Scheme 2, Ia or Ib reacts with NaOEt in anhydrous EtOH to form carbene in a flask filled with inert gas, followed by reacting with RuCl₂(PPh₃)₂ to form complex Va or Vb. The complex Va or Vb is reacted with IIIa or IIId effectively to obtain the complex IIa or IIb in inert gas, respectively.

**Scheme 3:**

\[
\begin{align*}
\text{Ia or Ib} & \xrightarrow{} \text{IIa or IIb} \\
& \xrightarrow{\text{CuCl, DCM}} \text{(L = PCy}_3 \text{ or Mes}^+\text{N}^\text{N-Mes})
\end{align*}
\]

Complexes IIa and IIb could also be prepared by other two alternative synthetic routes as shown in Scheme 3.
In Scheme 3, 1a or 1b reacts with ruthenium complex 1 or 2 directly to form the desired complex IIa or IIb in a flask filled with inert gas (Ar), respectively.

In the fourth aspect, the present invention provides a method of carrying out a metathesis reaction effectively with olefin substrate, comprising intramolecular ring-closing metathesis (RCM), intermolecular cross metathesis (CM), acyclic diene metathesis (ADMET), or ring-opening metathesis polymerization (ROMP) of cyclo-olefin substrate selectively in the presence of the novel ruthenium catalysts.

The preferred cyclo-olefin substrate for ROMP is optionally selected from dicyclopentadiene (DCPD), norbornene, cyclooctene, or a kind of tensional cycloolefin; each is optionally substituted or unsubstituted with one or more of F, Cl, Br, C1-C15 alkyl, C1-C15 alkoxy, C1-C15 alkylthio, C2-C15 alkenyloxy, C1-C15 silanyl, C1-C15 alkylsilyloxy, C6-C15 aryl, C6-C15 aryloxy, C1-C15 alkenylcarbonyl, C6-C15 arylcarbonyl, C1-C15 alkenoxycarbonyl, C6-C15 aryloxycarbonyl, C1-C15 alkylaminocarbonyl, C6-C15 arylaminocarbonyl, C1-C15 alkylamido, C6-C15 arylamido, C1-C15 alkylaminosulfonyl, C6-C15 arylaminosulfonyl, C1-C15 sulfonlamido, C3-C15 heteroaryl or C2-C15 heterocyclic group.

In one preferred embodiment of the present invention, wherein a kind of tensional cycloolefin substrates include the following structure VIa-VIc:

Wherein r = 1, 2, 3 or 4; s = 1, 2, 3 or 4;

A is O, S, C1-C15 alkyl, C1-C15 alkoxy, C1-C15 aryloxy, C1-C15 alkylthio, C1-C15 alkenyloxy, C1-C15 alkenylcarbonyl, C1-C15 alkylaminocarbonyl, C6-C15 arylamino, C1-C15 alkylamino, C6-C15 alkylaminocarbonyl, C1-C15 arylaminocarbonyl, C1-C15 alkylamido, C6-C15 arylamido, or C1-C15 heterocyclic amid group;

G is a group of compounds with specific properties and uses; each is optionally selected from commercial liquid crystal monomers or modified prodrugs;
R^{10} and R^{11} are each H, halogen, C_{1-15} alkyl, C_{1-15} alkoxy, C_{1-15} alkylthio, C_{1-15} alkylsilyloxy, C_{6-15} aryloxy, C_{6-15} aryl, C_{2-15} heterocyclic, C_{3-15} heterocyclic aryl, C_{1-15} alkylcarbonyl, C_{1-15} alkoxy carbonyl, C_{6-15} aryloxycarbonyl, C_{1-15} alkylaminocarbonyl, C_{6-15} arylaminocarbonyl, C_{1-15} alkylamido, C_{1-15} alkylsulfonyl, C_{1-15} alkylsulfonamido, liquid crystal monomer or modified pro-drug;

“Linker” is C_{1-15} alkyl, C_{1-15} alkoxy, C_{1-15} alkylthio, C_{1-15} alkylsilyloxy, C_{6-15} aryloxy, C_{6-15} aryl, C_{1-15} alkoxy carbonyl, C_{6-15} aryloxycarbonyl, C_{1-15} alkylaminocarbonyl, C_{6-15} arylaminocarbonyl, C_{1-15} alkylamido, C_{6-15} arylamido, C_{1-15} alkylsulfonamido, C_{6-15} arylsulfonamido, C_{3-15} heteroaryl or C_{2-15} heterocyclic group.

In one more preferred embodiment of the present invention, wherein in structure Vla-Vlc:

Wherein r = 1, 2, 3 or 4; s = 1, 2, 3 or 4;:

A is O, S, C_{1-8} alkyl, C_{1-8} alkoxy, C_{1-15} aryloxy, C_{1-15} alkylthio, C_{1-8} alkoxy carbonyl, C_{1-8} alkylamino, C_{6-12} arylamino, C_{1-8} alkylaminocarbonyl, C_{6-12} arylaminocarbonyl, C_{1-8} alkylamido, C_{6-12} arylamido, or C_{1-8} heterocyclic amido group;

G is a kind of compounds with specific properties and uses; each is optionally selected from commercial liquid crystal monomers or modified prodrugs;

R^{10} and R^{11} are each H, halogen, C_{1-8} alkyl, C_{1-8} alkoxy, C_{1-8} alkylthio, C_{1-8} alkylsilyloxy, C_{6-12} aryloxy, C_{6-12} aryl, C_{2-8} heterocyclic, C_{3-12} heterocyclic aryl, C_{1-8} alkylcarbonyl, C_{1-8} alkoxy carbonyl, C_{6-12} aryloxycarbonyl, C_{1-8} alkylaminocarbonyl, C_{6-12} arylaminocarbonyl, C_{1-8} alkylamido, C_{1-8} alkylsulfonyl, C_{1-8} alkylsulfonamido, liquid crystal monomer or modified pro-drug;

“Linker” is C_{1-8} alkyl, C_{1-8} alkoxy, C_{1-8} alkylthio, C_{1-8} alkylsilyloxy, C_{6-12} aryloxy, C_{6-12} aryl, C_{1-8} alkoxy carbonyl, C_{6-12} aryloxycarbonyl, C_{1-8} alkylaminocarbonyl, C_{6-12} arylaminocarbonyl, C_{1-8} alkylamido, C_{6-12} arylamido,
C₁-C₈ alkylsulfonamido, C₆-C₁₂ arylsulfonamido, C₃-C₁₂ heteroaryl or C₂-C₈ heterocyclic group.

In one most preferred embodiment of the present invention, wherein in structure VIa-VIc:

r = 1 or 2; s = 1 or 2;

A is O, CH₂, C₁-C₅ alkyl-amino, C₁-C₅ alkoxy, C₁-C₅ alkylaminocarbonyl or C₁-C₃ heterocyclic amido group;

“Linker” is C₁-C₆ alkyl, C₁-C₅ alkoxy, C₁-C₅ alkylthio, C₁-C₅ alkoxy carbonyl, C₁-C₅ alkylaminocarbonyl, C₆-C₁₂ arylaminocarbonyl, C₁-C₅ alkylamido or C₆-C₁₂ arylamido group;

G is a kind of optionally modified prodrug of commercial drug Lipitor having the following structure VIIa-VIIId:

Wherein R¹⁰ and R¹¹ are each H, C₁-C₅ alkoxy, C₆-C₁₂ aryloxy, C₁-C₅ alkoxycarbonyl, C₆-C₁₂ aryloxycarbonyl, C₁-C₅ alkylaminocarbonyl, C₆-C₁₂ arylaminocarbonyl, C₁-C₅ alkylamido, C₆-C₁₂ arylamido, liquid crystal monomer or modified pro-drug;

R¹² is cyclopropyl, C₁-C₆ alkyl, C₃-C₆ cycloalkyl, C₁-C₆ alkoxy, C₆-C₁₂ aryl, C₆-C₁₂ aryloxy, C₁-C₆ alkylamino, C₆-C₁₂ arylamino, C₁-C₆ alkylsulfonamido, C₆-C₁₂ arylsulfonamido, C₃-C₁₂ heterocyclic aryl or C₂-C₆ heterocyclic group.

In another preferred embodiment, the present invention provides a method of making a quality-modified polymer having the following structure VIIIa-VIIIb in the presence of one or two more mixed ruthenium catalysts;
The present invention provides a process of preparing functional polymers \textbf{VIIIa-VIIIb} in the presence of one or two more mixed catalysts.

In the third preferred embodiment, the present invention provides a method of making a modified nitrile butadiene rubber (NBR) or styrene-butadiene rubber (SBR) by depolymerization in the presence of one or more mixed catalysts of the present invention at 30-100°C.

In the fourth preferred embodiment, the present invention provides a method of making a depolymerized HNBR (hydrogenated nitrile butadiene rubber) or styrene-butadiene rubber by adding one or more mixed catalysts of the present invention first to carry out depolymerization of NBR, followed by adding hydrogen into the reaction under high pressure for hydrogenation at 60-150°C.

In the fifth preferred embodiment, the present invention provides a method of making a hydrogenated nitrile butadiene rubber (HNBR) or styrene-butadiene rubber by adding hydrogen under high pressure first, followed by adding one or more mixed catalysts of claim 5 at 60-150°C.

In the sixth preferred embodiment, the present invention provides a use of catalysts of the present invention in depolymerization of a rubber comprising at least one carbon-carbon double bond.

In the seventh preferred embodiment, the present invention provides a use of catalysts of the present invention in hydrogenation of a rubber comprising at least one carbon-carbon double bond.

The present invention also provides a useful method of making functional polymers, comprising reacting one or more monomers in the presence of the novel ruthenium catalysts.

In the fifth aspect, the present invention provides a composition of comprising a modified prodrug or functional group \textbf{G} having the following structure \textbf{IXa-IXc}:
Wherein: $r = 1, 2, 3$ or $4$; $s = 1, 2, 3$ or $4$;

A, G, “Linker”, $R^{11}$ and $R^{12}$ each is as defined above.

In the most preferred embodiment of the present invention, wherein a modified prodrug or functional group G having the following structures IXa-IXc:

$r = 1$ or $2$; $s = 1$ or $2$;

A, “Linker”, $R^{10}$ and $R^{11}$ each is as defined above;

G is a kind of optionally modified pro-drug of Lipitor having the following structure VIIa-VIIId:

Wherein $R^{12}$ is cyclopropyl, C$_1$-C$_6$ alky, C$_3$-C$_6$ cycloalkyl, C$_1$-C$_6$ alkoxy, C$_6$-C$_{12}$ aryl, C$_6$-C$_{12}$ aryloxy, C$_1$-C$_6$ alkylamino, C$_6$-C$_{12}$ arylamino, C$_1$-C$_6$ alkylsulfonamido, C$_6$-C$_{12}$ arylsulfonamido, C$_3$-C$_{12}$ heterocyclic aryl or C$_2$-C$_6$ heterocyclic group.

The present invention relates to two classes of novel carbene ligands and ruthenium complexes as catalysts in uses of carrying out metathesis reactions effectively, e.g., preparation of the high strength and/or stiffness polymer materials, functional polymers linked with small molecule pro-drugs and liquid crystal materials.

Currently, the present invention provides the following significant achievements:
1. Two classes of novel carbene ligands and ruthenium complexes have been designed and prepared, which has different structure and activity with five or six coordinate bonds, especially for the new Ru complexes with six coordinate bonds to form at least one “Ru-N” coordinate bond from the new developed ligands Ia or Ib. Moreover, the electronic and steric effect of different substituted ligands on the catalytic activity and stability of various new Ru complexes have been studied, and it is found that some of novel Ru catalysts in the present invention have much better catalytic selectivity and variable physical diversity than Grubbs and Hoveyda catalysts in the ROMP and RCM reactions.

2. The experimental results show that some of novel Ru catalysts in the present invention have high activity and selectivity for different olefin ROMP and RCM reactions, so the invention provides a useful synthetic method of carrying out olefin metathesis reactions effectively in preparation of polymer materials and pharmaceutical intermediates.

3. The present invention provides several developed methods for preparation of carbene ligands and Ru catalysts at lower cost, and it also provides some efficient methods for preparation of various functional polymer materials with different chemical and physical properties.

4. The present invention provides several developed processes of conducting ROMP reaction with one or two more mixed of novel active Ru catalysts for preparation of the high-strength polymer materials and some functional polymers linked with small molecule pro-drugs and/or liquid crystal materials.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1: Single-crystal X-ray Structure of Ru Catalyst 8m.

DETAILED DESCRIPTION OF THE INVENTION

The present invention comprises two novel classes of carbene ligands and ruthenium complexes as catalysts for metathesis reactions. To study the electronic and steric effects of multi-substituted benzylidene ligands on the stability and activity of
Ru complexes, based on the following reported procedure in Schemes 1-3, different kinds of the complex ligands (3a-3bf, 5a-5j, 7a-7r, 9a-9j) have been prepared and reacted with the Ru complex 1 to obtain different kinds of new Ru complex (4a-4bf, 6a-6j, 8a-8r, 10a-10j, 11a-11r). During preparation and activity evaluation of various Ru complexes with various substituted 2-aminobenzylidene ligands in the following Schemes 4-8, different kinds of the electron-withdrawing and/or electron-donating effect and steric effect on the stability and selective activity for ROMP and RCM reactions have been found as shown in Schemes 9-16 and Tables 1-6.

**Significant electronic effect of various substituted benzylidene ligands on the stability of Ru complexes:** Based on different described synthetic methods and procedures in Schemes 1-3, there are different kinds of new olefin or carbene ligands (Ia-Ib) and Ru complexes (IIa-IIb) prepared in the present invention. Moreover, significant substituent effect of different substituted benzylidene ligands on the stability and activity of Ru complexes has been observed and developed selectively for ROMP and RCM reactions, and some novel Ru catalysts have been prepared much more active and selective than prior reported Ru catalysts for different kinds of ROMP and RCM reactions.

According to previously described synthetic methods, various new Ru complexes 4a-4bf have been prepared by the reaction listed in Scheme 4, and the corresponding metathesis activity of each Ru complex has been studied for RCM and ROMP reactions with different olefin substrates, respectively.

**Scheme 4:**
Some selected structure of prepared ligands 3a-3bf and corresponding ruthenium complexes 4a-4bf (1a: Cy = cyclohexyl, 1b = 2,4,6-trimethylbenzene) are listed as follows:
According to previously described synthetic methods, various new Ru
complexes 6a-6j have been prepared by the reaction listed in Scheme 5, and the corresponding metathesis activity of each Ru complex has been studied for RCM and ROMP reactions with different olefin substrates, respectively.

Scheme 5:

Some selected structure of prepared ligands 5a-5j and corresponding ruthenium complexes 6a-6j (1a: Cy = cyclohexyl, 1b = 2,4,6,-trimethylbenzene) are listed as follows:

5a, 5b, 5c, 5d, 5e, 5f, 5g, 5h, 5j
According to previously described synthetic methods, various new Ru complexes 8a-8r have been prepared by the reaction listed in Scheme 6, and the corresponding metathesis activity of each Ru complex has been studied for RCM and ROMP reactions with different olefin substrates, respectively.

Scheme 6:

\[
\text{SM 7a-7r} \xrightarrow{\text{Pd catalyst (Suzuki Reaction)}} 7a-7r
\]

\[
\text{Cl}_2\text{Ru} \equiv \text{Ph} \xrightarrow{(1)} \text{Cl}_2\text{Ru} \equiv \text{Ph} \xrightarrow{(2)} \text{L = PCy}_3, \text{Mes}^+N\equiv N\text{Mes}
\]

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Some selected structure of prepared ligands 7a-7r and corresponding ruthenium
complexes 8a-8r (la: Cy = cyclohexyl, 1b = 2,4,6,- trimethylbenzene) are listed as follows:

7a

7b

7c

7d

7e

7f

7g

7h

7j

7k

7m

7n

7p

7q

7r

7s

7t

7u
The structure of Ru catalyst 8m is confirmed by single-crystal X-ray as shown in Figure 1.
According to previously described synthetic methods, various new Ru complexes 10a-10j have been prepared by the reaction listed in Scheme 7, and the corresponding metathesis activity of each Ru complex has been studied for RCM and ROMP reactions with different olefin substrates, respectively.

Scheme 7:

SM 9a-9j

\[
\text{Pd catalyst (Suzuki Reaction)}
\]

9a-9j

\[
\begin{align*}
\text{Cl}_2\text{Ru=Ph} & \quad \left( \text{or} \quad \text{Cl}_2\text{Ru=Ph} \right) \\
\text{Cl} & \quad \text{PCy}_3 (1) \\
\text{L} = \text{PCy}_3, \quad \text{Mes} & \quad \text{N} \quad \text{N-Mes}
\end{align*}
\]

10a-10j

(Mes = 2,4,6-trimethylbenzene)

Some selected structure of prepared ligands 9a-9j and corresponding ruthenium complexes 10a-10j (la: Cy = cyclohexyl, 1b = 2,4,6,- trimethylbenzene) are listed as follows:
According to previously described synthetic methods, various new Ru complexes 11a-11r have been prepared by the reaction listed in Scheme 8, and the
corresponding metathesis activity of each Ru complex has been studied for RCM and ROMP reactions with different olefin substrates, respectively.

Scheme 8:

Ru catalyst (IIa)  
(n = 0, p = 0)

Ligand: L³  
(n = 0)

Ru catalyst (IIb)  
(n = 0, p = 0)

Ligand: L³  
(n = 0)

11 (Ru catalyst IIa)  
(n = 0, p = 1)

11 (Ru catalyst IIb)  
(n = 0, p = 1)

Some selected structure of prepared ruthenium complexes 11a-11r (la: Cy = cyclohexyl, 1b = 2,4,6,- trimethylbenzene) is listed as follows:

11a  
11b  
11c  
11d  
11e  
11f
Two alternative production procedures for preparation of some highly active metathesis catalysts: In order to prepare different kinds of Ru catalyst at lower cost, based on some references (Zhan et al., US20070043180A1 and WO2007003135A1) and new process development as described in Schemes 9 and 10, there is the following alternative procedure developed in Scheme 9 for scale-up production of different Ru catalysts in the present invention.
Scheme 9: A convenient route for preparation of some Ru complexes

In Scheme 9, the starting material **4-SM** was reacted with sodium ethoxide to produce carbene intermediate **4-1** first, followed by reacting with RuCl$_2$(PPh$_3$)$_3$ directly to form Ru complex intermediate **4-2**. The triphenylphosphine ligand (PPh$_3$) of Ru intermediate **4-2** was replaced by another ligand PCy$_3$ (**4-3, IIId**) to form a new Ru complex **4i**. The phosphine ligand of Ru intermediate **4-2** or **4i** was further replaced by an NHC ligand (H$_2$IMes, **4-4, IIIa**) to form another Ru complex **4j**. The Ru complex **4j** could directly react with another ligand 4-chloro pyridine (**4-5**) to make the Ru complex **11h**.
Scheme 10: A convenient route for preparation of some Ru complexes

In Scheme 10, the Ru complex 2h is prepared by the reaction of reagents SM-2b and RuCl2(PPh3)3 in anhydrous DCM in a three-neck flask filled with inert gas (Ar), followed by reacting the Ru complex 2h with complex ligand 3x (Ia) to form another Ru complex 2j (Va) in a flask filled with inert gas (Ar). The triphenylphosphine ligand (PPh3) of Ru intermediate 2j was replaced by another phosphine ligand PCy3 (4-3, IIId) to form a new Ru complex 4x. The phosphine ligand of Ru intermediate 2j or 4x was further replaced by another NHC ligand (H2IMes, 4-4, IIIa) to form another Ru complex 4aa.

So far, to study the relative activity and catalytic selectivity of above prepared catalysts 4a-4bj, 6a-6j, 8a-8u, 10a-10j, and 11a-11r, two olefin substrates 15 and 17 in Equations 1 and 2 were chosen for RCM reactions, and different kinds of cyclic olefin substrates 19, 21, 23, 25, 27, 29 and 31 in Equations 3-9 were selected for ROMP reactions, and the kinetic results of different conducted RCM and ROMP reactions for each new catalyst are listed in Tables 1, 2, 3, 4 and 5, respectively. Other
eight prior known Ru catalysts 1a-1b and 2a-2f listed in Scheme 1 are also selected for evaluation of metathesis activity study with various substrates 15, 17, 19, 21, 23, 25, 27, 29 and 31 in comparison to all new Ru catalysts in the present invention.

The evaluation of catalytic activity for RCM in Equation 1 with different catalysts 4a-4bj, 6a-6j, 8a-8u, 10a-10j, and 11a-11r has been done under the same reaction condition, and the valuable experimental data for different Ru catalysts are selected and listed in Tables 1-1 to 1-4, respectively.

**Equation 1:**

```
<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conversion (% by HPLC)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>10 min</td>
</tr>
<tr>
<td>1</td>
<td>4a</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>4b</td>
<td>52</td>
</tr>
<tr>
<td>3</td>
<td>4e</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>4f</td>
<td>84</td>
</tr>
<tr>
<td>5</td>
<td>4g</td>
<td>94</td>
</tr>
<tr>
<td>6</td>
<td>4h</td>
<td>3</td>
</tr>
<tr>
<td>7</td>
<td>4u</td>
<td>96</td>
</tr>
<tr>
<td>8</td>
<td>4y</td>
<td>43</td>
</tr>
<tr>
<td>9</td>
<td>4aa</td>
<td>21</td>
</tr>
<tr>
<td>10</td>
<td>4ab</td>
<td>94</td>
</tr>
<tr>
<td>11</td>
<td>4ac</td>
<td>70</td>
</tr>
<tr>
<td>12</td>
<td>4af</td>
<td>93</td>
</tr>
<tr>
<td>13</td>
<td>4aj</td>
<td>95</td>
</tr>
<tr>
<td>14</td>
<td>4ap</td>
<td>71</td>
</tr>
<tr>
<td>15</td>
<td>4at</td>
<td>24</td>
</tr>
<tr>
<td>16</td>
<td>4ba</td>
<td>62</td>
</tr>
<tr>
<td>17</td>
<td>4bb</td>
<td>100</td>
</tr>
<tr>
<td>18</td>
<td>4bc</td>
<td>94</td>
</tr>
<tr>
<td>19</td>
<td>4bd</td>
<td>68</td>
</tr>
<tr>
<td>20</td>
<td>4be</td>
<td>100</td>
</tr>
</tbody>
</table>
```

Among Ru complexes 4a-4bj, only some of new complexes (such as 4f, 4g, 4u, 4ab, 4aj, 4bb and 4be) show high catalytic activity, the rest of them not listed in
Table 1-1 have lower or very poor activities for RCM reaction. Based on the
determined results in Table 1-1, the activity of Ru complexes **4a-4bj** for RCM is
significantly affected by the electronic and steric effect of different substituents
incorporated in various new ligands **3a-3bj**. However, some of complexes **4a-4bj**
non-active for RCM can be used effectively in the following ROMP (Equations 3-9)
with high activity and selectivity.

Table 1-2. Activity Results of Some Selected Complexes **6a-6j** for Substrate 15

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conversion (% by HPLC)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>10 min</td>
</tr>
<tr>
<td>1</td>
<td><strong>6e</strong></td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td><strong>6h</strong></td>
<td>95</td>
</tr>
<tr>
<td>3</td>
<td><strong>6j</strong></td>
<td>45</td>
</tr>
<tr>
<td>4</td>
<td><strong>2e</strong></td>
<td>0</td>
</tr>
</tbody>
</table>

Among complexes **6a-6j**, only a Ru complexes **6h** shows high catalytic activity
and much better than the known catalyst **2e**, the rest of them not listed in Table 1-2
have worse or very poor activities. Based on the determined results in Table 1-2, the
activity of Ru complexes **6a-6j** for RCM is significantly affected by the electronic and
steric effect of different substituents incorporated in various new ligands **5a-5j**.
However, some of complexes **6a-6j** non-active for RCM can be used effectively in the
following ROMP (Equations 3-9) with high activity and selectivity.

Table 1-3. Activity Results of Some Selected Complexes **8a-8u** for Substrate 15

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conversion (% by HPLC)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>10 min</td>
</tr>
<tr>
<td>1</td>
<td><strong>8b</strong></td>
<td>73</td>
</tr>
<tr>
<td>2</td>
<td><strong>8c</strong></td>
<td>21</td>
</tr>
<tr>
<td>3</td>
<td><strong>8g</strong></td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td><strong>8h</strong></td>
<td>96</td>
</tr>
<tr>
<td>5</td>
<td><strong>8t</strong></td>
<td>53</td>
</tr>
<tr>
<td>6</td>
<td><strong>8u</strong></td>
<td>79</td>
</tr>
<tr>
<td>7</td>
<td><strong>2c</strong></td>
<td>47</td>
</tr>
</tbody>
</table>

Among complexes **8a-8u**, only a few complexes (such as **8b, 8h** and **8r**) show
good activity and much better than the reported catalyst **2c**, the rest of them not listed
in Table 1-3 have worse or very poor activities. Based on the determined results in Table 1-3, the activity of Ru complexes 8a-8u for RCM is significantly affected by the electronic and steric effect of different substituents incorporated in various new ligands 7a-7u. However, some of non-active complexes 8a-8u for RCM can be used effectively in the following ROMP (Equations 3-9) with high activity and selectivity.

Table 1-4: Activity Results of Some Selected Complexes 10a-10j for Substrate 15

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conversion (% by HPLC)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>10 min</td>
</tr>
<tr>
<td>1</td>
<td>10c</td>
<td>90</td>
</tr>
<tr>
<td>2</td>
<td>10d</td>
<td>96</td>
</tr>
<tr>
<td>3</td>
<td>10e</td>
<td>91</td>
</tr>
<tr>
<td>4</td>
<td>10g</td>
<td>84</td>
</tr>
<tr>
<td>5</td>
<td>10j</td>
<td>86</td>
</tr>
<tr>
<td>6</td>
<td>2d</td>
<td>62</td>
</tr>
</tbody>
</table>

Among complexes 10a-10j, several complexes (such as 10c, 10d, 10e and 10g) show good or high catalytic activity and much better than the known catalyst 2d, the rest of them not listed in Table 1-4 have worse or very poor activities. Based on the determined results in Table 1-4, the activity of Ru complexes 10a-10j for RCM is significantly affected by the electronic and steric effect of different substituents incorporated in various new ligands 9a-9j. However, some of non-active complexes 10a-10j for RCM can be used effectively in the following ROMP (Equations 3-9) with high activity and selectivity.

Table 1-5: Activity Results of Some Selected Complexes 11a-11r for Substrate 15

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conversion (% by HPLC)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>10 min</td>
</tr>
<tr>
<td>1</td>
<td>11b</td>
<td>38</td>
</tr>
<tr>
<td>2</td>
<td>11e</td>
<td>44</td>
</tr>
<tr>
<td>3</td>
<td>11p</td>
<td>39</td>
</tr>
<tr>
<td>4</td>
<td>11q</td>
<td>32</td>
</tr>
</tbody>
</table>

Among complexes 11a-11r, only a few complexes (such as 11c, 11e and 11p) show lower catalytic activity, the rest of them not listed in Table 1-5 have worse or very poor activities. Based on the determined results in Table 1-5, the activity of Ru
complexes 11a-11r for RCM is significantly affected by the electronic effect of
different substituted pyridine ligands. However, some of complexes 11a-11r
non-active for RCM can be used effectively in the following ROMP (Equations 3-9)
with high activity and selectivity.

In order to find some new catalysts with better activity and selectivity, it is
designed to carry out a RCM reaction with a phenyl-substituted diene substrate 17 as
shown in Equation 2 instead of unsubstituted diene substrate 15 for further evaluation
of some active catalysts selected from the catalysts 4a-4bj, 6a-6j, 8a-8u, 10a-10j, and
11a-11r according to activity results in Tables 1-1 to 1-5. The experimental results of

**Equation 2:**

![Equation 2 Image]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conversion (% by HPLC)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>10 min</td>
</tr>
<tr>
<td>1</td>
<td>4f</td>
<td>67</td>
</tr>
<tr>
<td>2</td>
<td>4g</td>
<td>61</td>
</tr>
<tr>
<td>5</td>
<td>4ab</td>
<td>63</td>
</tr>
<tr>
<td>6</td>
<td>4ad</td>
<td>51</td>
</tr>
<tr>
<td>7</td>
<td>4af</td>
<td>72</td>
</tr>
<tr>
<td>8</td>
<td>4be</td>
<td>49</td>
</tr>
<tr>
<td>9</td>
<td>6h</td>
<td>70</td>
</tr>
<tr>
<td>10</td>
<td>8h</td>
<td>75</td>
</tr>
<tr>
<td>11</td>
<td>10a</td>
<td>42</td>
</tr>
<tr>
<td>12</td>
<td>10c</td>
<td>71</td>
</tr>
<tr>
<td>13</td>
<td>10d</td>
<td>82</td>
</tr>
<tr>
<td>14</td>
<td>10f</td>
<td>35</td>
</tr>
<tr>
<td>15</td>
<td>10g</td>
<td>46</td>
</tr>
</tbody>
</table>

To develop more effective ROMP catalysts and prepare better quality of new

43
functional polymers, and also better to measure the difference of various active Ru catalysts, the evaluation of catalytic activity for different ROMP reactions in Equations 3-9 with different catalysts 4a-4bj, 6a-6j, 8a-8u, 10a-10j, and 11a-11r has been done under the same reaction condition, and some valuable results for different Ru catalysts are selected or listed in Tables 3 to 6, respectively. Based on the broad test, it is useful to find some active and selective catalysts for ROMP and RCM reactions, respectively.

Equation 3:

After screening with most of new Ru catalysts, it is found that some catalysts such as 8g and 8m could selectively catalyze the ROMP reaction effectively.

Equation 4:

After screening with most of new Ru catalysts, it is found that some catalysts such as 4d and 8j could catalyze the ROMP reaction effectively.

Equation 5:

The ROMP results show that the catalysts 4b, 4f, 4v, 4y, 4aa, 8b and 8h of the present invention have better activity and selectivity for norbornene (23) polymerization. Catalytic polymerization was completed in 10-60 min, and the polymer product (24) has better tensile-strength when it is prepared as film.

Equation 6:
The ROMP results show that the catalysts 4b, 4f, 4v, 4y, 4aa, 4ag, 4ar, 4au, 8a, 8b, 8c, 8h, 8m and 8q of the present invention have better activity and selectivity for DCPD (25) polymerization. The ROMP polymerization was completed in 5-60 min for different Ru catalysts. The reaction temperature is preferred to be 40-60℃. By using one or two more mixed catalysts, it is surprised to obtain the high strength and high stiffness polymer PDCPD.

The property tests of various PDCPD (26) samples in the present invention show that several PDCPD products have more better tensile strength (55-62Mpa) and flexural strength (78-83Mpa) than those of commercial PDCPD products such as “Pentam, Metton, and Prometa” (tensile strength: 40-50Mpa, and flexural strength: 66-75Mpa) reported by other companies prepared with their own ROMP catalysts in Japan and USA, which advantage in the present invention will provide an alternative method of making high-quality of PDCPD material for broad uses in polymer industry.

Equation 7:

Some selected structure of prepared polymers 28a-28g is listed as follows, and ROMP results are listed in Table 3:
Table 3: Selected ROMP results

<table>
<thead>
<tr>
<th>SM</th>
<th>Amount (g)</th>
<th>Solvent</th>
<th>Catalyst (0.1%)</th>
<th>Yield (%)</th>
<th>Polymer</th>
<th>Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>27a</td>
<td>0.5</td>
<td>DCM</td>
<td>4d</td>
<td>90</td>
<td>28a</td>
<td>white solid</td>
</tr>
<tr>
<td>27b</td>
<td>0.5</td>
<td>DCM</td>
<td>4d</td>
<td>93</td>
<td>28b</td>
<td>white solid</td>
</tr>
<tr>
<td>27c</td>
<td>0.5</td>
<td>DCM</td>
<td>4d</td>
<td>97</td>
<td>28c</td>
<td>white solid</td>
</tr>
<tr>
<td>27d</td>
<td>0.5</td>
<td>DCM</td>
<td>4d</td>
<td>95</td>
<td>28d</td>
<td>white solid</td>
</tr>
<tr>
<td>27e</td>
<td>0.5</td>
<td>DCM</td>
<td>4d</td>
<td>93</td>
<td>28e</td>
<td>white solid</td>
</tr>
<tr>
<td>27f</td>
<td>0.5</td>
<td>DCM</td>
<td>4d</td>
<td>81</td>
<td>28f</td>
<td>white solid</td>
</tr>
<tr>
<td>27g</td>
<td>0.5</td>
<td>DCM</td>
<td>4d</td>
<td>87</td>
<td>28g</td>
<td>white solid</td>
</tr>
</tbody>
</table>

The results of Table 3 show that, small molecule liquid crystal or pro-drug monomer can react with new Ru catalysts selected from the present invention to form
polymerized macromolecule liquid crystal (28c and 28d) and polymer-linked prodrugs (28e, 28f and 28g) with special properties and applications. The results of activity test show that several new catalysts (such as 4d, 4f, 6g and 11a) of the present invention have better catalytic activity for olefin monomers (27a-27g), and the ROMP reactions were completed in 5-15 hrs. Yield is better than 80% with optimized polymerization conditions in the presence of new Ru catalyst 4d.

The results of polymerization test show that different Ru catalysts of the present invention have significantly different activity and selectivity for different cyclo-olefin monomers. In particular, some new Ru catalysts (e.g., 4d and 6g) have lower catalytic activities in RCM reaction, but have very good activity in ROMP reactions, which demonstrates that several new Ru catalysts in the present invention have the high selectivity and catalytic activity for ROMP and RCM, respectively.

Equation 8:

Some selected structure of prepared polymers 30a-30n is listed as follows, and some selected ROMP results are listed in Table 4:
Table 4: Selected ROMP results

<table>
<thead>
<tr>
<th>SM</th>
<th>Amount (g)</th>
<th>Solvent</th>
<th>Catalyst (0.1%)</th>
<th>Yield (%)</th>
<th>Polymer</th>
<th>Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>29a</td>
<td>0.5</td>
<td>DCM</td>
<td>4d</td>
<td>75</td>
<td>30a</td>
<td>white solid</td>
</tr>
<tr>
<td>29b</td>
<td>0.5</td>
<td>DCM</td>
<td>4d</td>
<td>90</td>
<td>30b</td>
<td>white solid</td>
</tr>
<tr>
<td>29c</td>
<td>0.5</td>
<td>DCM</td>
<td>4d</td>
<td>71</td>
<td>30c</td>
<td>white solid</td>
</tr>
<tr>
<td>29d</td>
<td>0.5</td>
<td>DCM</td>
<td>4d</td>
<td>60</td>
<td>30d</td>
<td>white solid</td>
</tr>
<tr>
<td>29e</td>
<td>0.5</td>
<td>DCM</td>
<td>6g</td>
<td>46</td>
<td>30e</td>
<td>white solid</td>
</tr>
<tr>
<td>29f</td>
<td>0.5</td>
<td>DCM</td>
<td>4d</td>
<td>85</td>
<td>30f</td>
<td>white solid</td>
</tr>
<tr>
<td>29g</td>
<td>0.5</td>
<td>DCM</td>
<td>4d</td>
<td>97</td>
<td>30g</td>
<td>white solid</td>
</tr>
<tr>
<td>29h</td>
<td>0.5</td>
<td>DCM</td>
<td>4d</td>
<td>98</td>
<td>30h</td>
<td>white solid</td>
</tr>
<tr>
<td>29j</td>
<td>0.5</td>
<td>DCM</td>
<td>4d</td>
<td>97</td>
<td>30j</td>
<td>white solid</td>
</tr>
<tr>
<td>92k</td>
<td>0.5</td>
<td>DCM</td>
<td>4d</td>
<td>96</td>
<td>30k</td>
<td>white solid</td>
</tr>
<tr>
<td>29m</td>
<td>0.5</td>
<td>DCM</td>
<td>4d</td>
<td>95</td>
<td>30m</td>
<td>white solid</td>
</tr>
<tr>
<td>29n</td>
<td>0.5</td>
<td>DCM</td>
<td>4d</td>
<td>93</td>
<td>30n</td>
<td>white solid</td>
</tr>
</tbody>
</table>
The results in Table 4 show that most of cyclo-olefin monomers with different functional groups (29a-29n) were polymerized in the presence of new Ru catalysts such as 4d or 6g selected from the present invention to form functional polymers with different chemical and physical properties.

Equation 9:

Some selected structure of prepared polymers 32a-32m is listed as follows, and some selected ROMP results are listed in Table 5:
Table 5: Selected ROMP results

<table>
<thead>
<tr>
<th>SM</th>
<th>Amount (g)</th>
<th>Solvent (mL)</th>
<th>Catalyst (0.1%)</th>
<th>Yield (%)</th>
<th>Polymer</th>
<th>Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>31a</td>
<td>0.5</td>
<td>DCM</td>
<td>4d</td>
<td>96</td>
<td>32a</td>
<td>white solid</td>
</tr>
<tr>
<td>31b</td>
<td>0.5</td>
<td>DCM</td>
<td>4d</td>
<td>92</td>
<td>32b</td>
<td>white solid</td>
</tr>
<tr>
<td>31c</td>
<td>0.5</td>
<td>DCM</td>
<td>4d</td>
<td>92</td>
<td>32c</td>
<td>white solid</td>
</tr>
<tr>
<td>31d</td>
<td>0.5</td>
<td>DCM</td>
<td>4d</td>
<td>89</td>
<td>32d</td>
<td>white solid</td>
</tr>
<tr>
<td>31e</td>
<td>0.5</td>
<td>DCM</td>
<td>4d</td>
<td>91</td>
<td>32e</td>
<td>white solid</td>
</tr>
<tr>
<td>31f</td>
<td>0.5</td>
<td>DCM</td>
<td>4d</td>
<td>87</td>
<td>32f</td>
<td>white solid</td>
</tr>
<tr>
<td>31g</td>
<td>0.5</td>
<td>DCM</td>
<td>4d</td>
<td>91</td>
<td>32g</td>
<td>white solid</td>
</tr>
<tr>
<td>31h</td>
<td>0.5</td>
<td>DCM</td>
<td>4d</td>
<td>85</td>
<td>32h</td>
<td>white solid</td>
</tr>
<tr>
<td>31i</td>
<td>0.5</td>
<td>DCM</td>
<td>4d</td>
<td>87</td>
<td>32i</td>
<td>white solid</td>
</tr>
<tr>
<td>31j</td>
<td>0.5</td>
<td>DCM</td>
<td>4d</td>
<td>97</td>
<td>32j</td>
<td>white solid</td>
</tr>
<tr>
<td>31k</td>
<td>0.5</td>
<td>DCM</td>
<td>4d</td>
<td>98</td>
<td>34k</td>
<td>white solid</td>
</tr>
<tr>
<td>31m</td>
<td>0.5</td>
<td>DCM</td>
<td>4d</td>
<td></td>
<td>32m</td>
<td>white solid</td>
</tr>
</tbody>
</table>

The results in Table 5 show that most of cyclo-olefin monomers with different functional groups (31a-31m) were polymerized in the presence of new Ru catalyst 4d selected from the present invention to form functional polymers with different chemical and physical properties. Moreover, several products 32a, 32b, 32c, and 34m could be used to form film with high strength (over 50 Mpa).

The catalysts of the present invention can be used for depolymerization of a rubber comprising at least one carbon-carbon double bond. The depolymerization is conducted by metathesis reaction of carbon-carbon double bond in the rubber in the presence of one or more of catalysts of the present invention. The depolymerized rubber has lower molecular weight and lower mooney viscosity, which can be better used at lower temperature as lower as -40°C.

The catalysts of the present invention can be used in hydrogenation of a rubber comprising at least one carbon-carbon double bond. The carbon-carbon double bond in the rubber is hydrogenated under high pressure of hydrogen in the presence of one or more of catalysts of the present invention. The hydrogenated rubber is obtained and could be used as more stable and higher strength rubber.

The rubber comprising at least one carbon-carbon double bond can be depolymerized, and followed by hydrogenation under high pressure of hydrogen to produce a lower molecular weight and lower mooney viscosity rubber in the presence
of one or more catalysts of the present invention, which can be used at lower temperature as lower as -55°C.

The rubber comprising at least one carbon-carbon double bond can be hydrogenated under high pressure of hydrogen and depolymerized simultaneously in the presence of one or more catalysts of the present invention, which can be used at lower temperature as lower as -55°C.

The representative examples of rubbers include but not limited to nitrile butadiene rubber, polybutadiene rubber, styrene-butadiene rubber (SBR), styrene-butadiene-styrene (SBS) or any rubber containing carbon-carbon double bond.

For example, the NBR is depolymerized by using catalyst 4ab at 30°C-100°C as shown in Equation 10; and the physical properties of depolymerized NBR are listed in Table 6.

Equation 10:

\[
\begin{align*}
&\text{Ru Catalyst(s)} \\
\text{Selected from Claim 5}
\end{align*}
\]

(In Equation, where \( q > q' \))

<table>
<thead>
<tr>
<th>Entry No.</th>
<th>Samples</th>
<th>Mw</th>
<th>Mn</th>
<th>Mooney viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NBR (N41), RM</td>
<td>4.11E+05</td>
<td>1.81E+05</td>
<td>77.5</td>
</tr>
<tr>
<td>2</td>
<td>0.04 wt% Catalyst (4ab)</td>
<td>2.78E+05</td>
<td>1.586E+5</td>
<td>60.3</td>
</tr>
<tr>
<td>3</td>
<td>0.07 wt% Catalyst (4ab)</td>
<td>2.16E+05</td>
<td>1.05E+05</td>
<td>54.1</td>
</tr>
<tr>
<td>4</td>
<td>0.10 wt% Catalyst (4ab)</td>
<td>1.11E+05</td>
<td>7.41E+04</td>
<td>37.9</td>
</tr>
</tbody>
</table>

Notes: Mw and Mn: Molecular weight. RM: Raw Material.

So far, it is determined that the molecular weight (Mw) and Mooney viscosity of various nitrile butadiene rubber (e.g., commercially available from Zeon company
(Japan) in trade name N41, DN3335, DN3350, and DN2850) are significantly reduced down about 30-70% as needed by metathesis depolymerization in chlorobenzene or chloroform in the presence of catalysts of the present invention (e.g., catalyst 4ab selected from 4a-4bj, 6a-6j, 8g-8u, 10e-10g).

Equation 11:

\[
\begin{align*}
\text{H}_2\text{C} & - \text{CH} \equiv \text{CH} - \text{CH}_2 \quad \text{CH}_2 \\
\text{CH}_3 & \\
1) \text{Ru Catalyst(s)} \\
2) \text{H}_2 \text{ (Hydrogenation)} \\
\text{H}_2\text{C} & - \text{CH} \equiv \text{CH} - \text{CH}_2 \\
\text{CH}_2 & - \text{CH}_2 \\
\text{CH}_3 & \\
\text{H}_2\text{C} & - \text{CH} \equiv \text{CH} - \text{CH}_2 \\
\text{CH}_2 & - \text{CH}_2 \\
\text{CH}_3 & \\
\text{H}_2\text{C} & - \text{CH} \equiv \text{CH} - \text{CH}_2 \\
\text{CH}_2 & - \text{CH}_2 \\
\text{CH}_3 & \\
\end{align*}
\]

In Equation 11, q > (t + u).

The process for Equation 11 was carried out by adding Ru metathesis catalyst (4aa) for depolymerization first at 60°C-150°C, followed by adding hydrogen under high pressure 2.0-15MPa for hydrogenation in chlorobenzene. It is determined that the molecular weight (Mw) and Mooney viscosity of various nitrile butadiene rubbers (e.g., commercially available from Zeon company (Japan) in trade name N41, DN3335, DN3350, and DN2850) are significantly reduced down about 30-70% as needed by depolymerization in chlorobenzene or chloroform in the presence of the catalysts of the present invention (e.g., 4a-4bj, 8g-8u, 10e-10g), and the hydrogenation degree is determined to be between 90-99.5% as needed. The depolymerization and hydrogenation results are listed in the following Table 7.

Table 7: Depolymerization and Hydrogenation Results by Ru Catalysts

<table>
<thead>
<tr>
<th>Entry No.</th>
<th>Samples</th>
<th>Mw</th>
<th>Mn</th>
<th>Iodine Value</th>
<th>[H] Degree</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NBR (N41), RM</td>
<td>4.11E+05</td>
<td>1.81E+05</td>
<td>290</td>
<td>---</td>
</tr>
<tr>
<td>2</td>
<td>0.04 wt% Catalyst (4aa)</td>
<td>2.70E+05</td>
<td>1.62E+05</td>
<td>23.5</td>
<td>&gt;90%</td>
</tr>
<tr>
<td>3</td>
<td>0.07 wt% Catalyst (4aa)</td>
<td>1.60E+05</td>
<td>1.12E+05</td>
<td>12.6</td>
<td>&gt;95%</td>
</tr>
<tr>
<td>4</td>
<td>0.10 wt% Catalyst (4aa)</td>
<td>2.10E+04</td>
<td>1.32E+04</td>
<td>3.5</td>
<td>&gt;99%</td>
</tr>
</tbody>
</table>

Notes: Mw and Mn: Molecular weight, [H]: Hydrogenation; RM: Raw Material, which is undepolymerized and unhydrogenated.
Equation 12:

\[
\begin{align*}
\left(\text{H}_2\text{C-CH=CH-CH}_2\right)_q\left(\text{CH}_2\text{-CH}\right)_s
\end{align*}
\]

1) H\textsubscript{2}\n
2) Ru Catalyst(s)

(Hydrogenation)

\[
\begin{align*}
\left(\text{H}_2\text{C-CH}_2\text{-CH}_2\text{-CH}_2\right)_t\left(\text{H}_2\text{C-CH=CH-CH}_2\right)_u\left(\text{CH}_2\text{-CH}\right)_s
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3
\end{align*}
\]

In Equation 12, q > (t+u’).

The process for Equation 12 was carried out by adding hydrogen under high pressure 2.0-15MPa first, followed by adding Ru metathesis catalyst (4aa) to conduct hydrogenation and depolymerization simultaneously in chlorobenzene at 60°C-150°C. It is determined that the hydrogenation degree is determined to be between 90-99.5% as needed (determined by IHNMR), and the molecular weight (Mw) and Mooney viscosity of various nitrile butadiene rubbers (e.g., commercially available from Zeon company (Japan) in trade name N41, DN3335, DN3350, and DN2850) are reduced down about 10-50% as needed by depolymerization in chlorobenzene or chloroform in the presence of catalysts (e.g., 4a-4bj, 8g-8u, 10e-10g). The depolymerization and hydrogenation results are listed in Table 8.

Table 8: Selected Hydrogenation and Depolymerization Results by Ru Catalysts

<table>
<thead>
<tr>
<th>Entry No.</th>
<th>Samples</th>
<th>Mw</th>
<th>Mn</th>
<th>Iodine Value</th>
<th>[H] Degree</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NBR (N41), RM</td>
<td>4.11E+05</td>
<td>1.81E+05</td>
<td>290</td>
<td>----</td>
</tr>
<tr>
<td>2</td>
<td>0.04 wt% Catalyst (4aa)</td>
<td>3.07E+05</td>
<td>1.87E+05</td>
<td>15.3</td>
<td>&gt;95%</td>
</tr>
<tr>
<td>3</td>
<td>0.07 wt% Catalyst (4aa)</td>
<td>2.10E+05</td>
<td>1.18E+05</td>
<td>11.8</td>
<td>&gt;96%</td>
</tr>
<tr>
<td>4</td>
<td>0.10 wt% Catalyst (4aa)</td>
<td>1.80E+05</td>
<td>1.07E+05</td>
<td>3.1</td>
<td>&gt;99%</td>
</tr>
</tbody>
</table>

RM: Raw Material, which is undepolymerized and unhydrogenated.

Based on the results from Equation 10 to Equation 12, it is determined that the molecular weight (Mw) and Mooney viscosity of various NBR brands (e.g., N41, DN3335, DN3350, and DN2850) are obviously reduced about 30-70% as needed by metathesis depolymerization and hydrogenation by adding hydrogen in chlorobenzene
or chloroform in the presence of the Ru catalysts (e.g., 4a-4bj, 8g-8u, 10e-10g) to obtain different kinds of HNBR products as needed with lower molecular weight (Mooney viscosity range: 20-100MU) and high hydrogenation degree (90-99.5%).

So far, it is found that most of the new developed Ru catalysts (4a-4bj, 6a-6j, 8a-8u, 10a-10j) can be used to reduce molecular weight of the nitrile butadiene rubber (NBR) and butyl rubber by catalytical depolymerization. Furthermore, the quality-modified hydrogenated nitrile butadiene rubber (HNBR) with different molecular weight has been prepared by adding different new Ru catalyst and hydrogen (H₂) under high pressure (2.0-15Mpa) in some organic solvents such as chlorobenzene or chloroform solution. Just as mentioned above, the depolymerized NBR can be used in lower temperature as lower as -40°C, and the depolymerized and hydrogenated NBR (HNBR) can be used in a temperature as lower as -55°C with an improved strength and a better UV-resistance.

Based on our broad study, it is found that some of novel Ru catalysts (such as 4a-4bj, 8g-8u, 10a-10j) have good activity for metathesis depolymerization to prepare different kinds of lower molecular NBR, followed by hydrogenation under high pressure of hydrogen (preferred between 4-9Mpa) to prepare high hydrogenation degree and various molecular weight of HNBR products.

Overall, based on the activity and selectivity studies in equations 1-10, it is found that some of novel Ru catalysts such as 4d, 4f, 4g, 4ab, 6h, 8g, 8h, 10c and 10e have much better activity and selectivity than other tested and reported metathesis catalysts for the ROMP and RCM reactions, respectively. Moreover, it is found that the electronic effect of multi-substituted benzylidene ligands on the activity and selectivity of Ru complexes is one of the most important factors for the development of new active and selective metathesis catalysts for ROMP and RCM reactions. Based on the intensive study, the present invention provides some useful methods of carrying out ROMP, RCM, CM, and ADMET reactions with one or two more mixed of novel active Ru catalysts for preparation of some functional polymers, lower molecular weight rubbers and/or pharmaceutical intermediates, respectively.
EXAMPLES

**General:** Infrared (IR) spectra were recorded on a Fourier Transform AVATAR™ 360 E.S.P™ spectrophotometer (Unit: cm⁻¹). Bands are characterized as broad (br), strong (s), medium (m), and weak (w). ¹H NMR spectra were recorded on a Varian-400 (400 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl₃: 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz), integration, and assignment. ¹⁹F and ³¹P NMR spectra were recorded on a Varian-400 (400 MHz) and Gemini-2000 (300MHz) spectrometers. The chemical shifts of the fluoro resonances were determined relative to trifluoroacetic acid as the external standard (CF₃CO₂H: 0.00 ppm), and the chemical shifts of the phosphorus resonances were determined relative to phosphoric acid as the external standard (H₃PO₄: 0.00 ppm). Mass spectra were obtained at Thermo Finnigan LCQ Advantage. Unless otherwise noted, all reactions were conducted in oven- (135°C) and flame-dried glassware with vacuum-line techniques under an inert atmosphere of dry Ar. THF and Et₂O were distilled from sodium metal dried flask, DCM, pentane, and hexanes were distilled from calcium hydride. Different substituted 2-alkoxy styrene ligands were prepared according to literature procedures as shown in Schemes 1-3. SM-Ia and SM-Ib chemicals were obtained from commercial sources or ordered by custom synthesis from Zannan Pharma Ltd., China. General procedures for preparation of different Ru complexes are described in examples 1 and 2, respectively. General procedures for evaluation of the RCM and ROMP reactions are described in examples 104-107, respectively.

**Example 1**

Synthesis of Ru complex 4a

SM-3a (5.0mmol) was added into a 50 mL of three-neck round-bottom flask filled with inert gas (Ar), and followed by adding DME (10 mL) and deionized water
(3 mL). K$_2$CO$_3$ (1.5 eq) was added and the solution was N$_2$ protected. The reaction was heated to 85°C, 2,4,6-Trivinyl-cyclotriboroxane pyridine complex (0.5 eq) and Pd(PPh$_3$)$_4$ (2%) were added until completed overnight. (monitored by TLC). The reaction mixture was filtered and extracted by DCM twice, then purified by flash column eluting with a gradient solvent (PE/EA 400/1 to 100/1) and dried under vacuum to obtain 0.9g of yellow oil products 3a (yield: 86%). The product was confirmed by $^1$HNMR.

Ligand 3a $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.56 (d, $J = 7.5$ Hz, 1H, aromatic H), 7.37-7.18 (m, 5H, aromatic H, CH=CH$_2$), 7.02 (dd, $J = 17.4$ Hz, 10.8 Hz, 1H, CH=CH$_2$), 6.76-6.64 (m, 3H, aromatic H), 5.72 (d, $J = 17.4$ Hz, 1H, CH=CH$_2$), 5.34 (d, $J = 10.8$ Hz, 1H, CH=CH$_2$), 4.33 (s, 2H, NCH$_2$), 3.83 (s, 1H, NH).

(H$_2$IMes)(PC$_3$)$_2$Ru=CHPh (formula 1b, 860mg, 1.0mmol) and CuCl (270 mg, 2.5mmol, 2.5 eq) were added into a 100 mL of two-neck round-bottom flask filled with inert gas (Ar), and followed by adding DCM (15 mL) and ligand 3a (250 mg, 1.2mmol, 1.2 eq) into the DCM solution at 20-25°C. The reaction was stirred until completed in 30-60 min. (monitored by TLC). The reaction mixture was filtered and concentrated, then purified by flash column eluting with a gradient solvent (Pentane/DCM 2/1 to DCM). The purified solid product was washed with methanol, and dried under vacuum to obtain 27mg of green solid product 4a, yield: 4%. The green product was confirmed by $^1$HNMR.

Ru complex (4a) $^1$HNMR (400 MHz, CDCl$_3$): $\delta$ 19.09 (s,1H, Ru=CH), 7.51-6.70 (m, 13H), 5.31 (m, 1H), 4.30 (d, $J = 12.9$ Hz, 1H), 4.04 (s, 4H, NCH$_2$CH$_2$N), 3.61 (d, $J = 12.9$ Hz, 1H), 2.45 (s, 12H), 2.33 (s, 6H).

Example 2

Synthesis of Ru complex 4b

The synthetic procedure for preparation of ligand 3b is the same as in Example 1 in 5.0 mmol scale. 1.15g of yellow oil product 3b was obtained (yield: 91%).

Ligand 3b $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.54 (d, $J = 6.6$ Hz, 1H), 7.27-7.23
(m, 3H), 7.02 (dd, J = 11.1 Hz, 17.0 Hz, 1H), 6.87-6.84 (m, 2H), 6.75-6.72 (m, 2H), 5.69 (dd, J = 1.5 Hz, 17.0 Hz, 1H), 5.35 (dd, J = 1.5 Hz, 11.1 Hz, 1H), 4.47 (s, 2H), 3.78 (s, 3H), 2.93 (s, 3H).

(PCy₃)₂Cl₂Ru-CHPh (formula 1a, 830mg, 1.0mmol) and CuCl (270 mg, 2.5mmol, 2.5 eq) were added into a 100 mL of two-neck round-bottom flask filled with inert gas (Ar), and followed by adding DCM (15 mL) and ligand 3b (250 mg, 1.2mmol, 1.2 eq) into the DCM solution at 20-25°C. The reaction was stirred until completed in 30-60 min. (monitored by TLC). The reaction mixture was filtered and concentrated, then purified by flash column eluting with a gradient solvent (Pentane/DCM 2/1 to DCM). The purified solid product was washed with methanol, and dried under vacuum to obtain 195mg of green solid product 4b, yield: 29%. The green product was confirmed by ¹H NMR.

Ru complex (4b) ¹H NMR (400 MHz, CDCl₃): δ 19.31 (d, J = 8.4 Hz, Ru=CH), 7.57-7.50 (m, 4H), 7.31-7.29 (m, 1H), 7.15 (d, J = 5.6 Hz, 1H), 6.84-6.81 (m, 2H), 5.78 (d, J = 12.0 Hz, 1H), 3.71 (s, 3H), 3.62 (d, J = 12.0 Hz, 1H), 2.51 (s, 3H), 2.22-1.13 (m, 33H, PCy₃).

Example 3

Synthesis of Ru complex 4c

The synthetic procedure for preparation of ligand 3c is the same as in Example 1 in 5.0 mmol scale. 0.66g of yellow oil product 3c was obtained (yield: 54%).

Ligand 3c ¹H-NMR (400 MHz, CDCl₃): δ 7.56 (d, J = 7.5 Hz, 1H, aromatic H), 7.34-7.26 (m, 3H, aromatic H, CH=CH₂), 7.13 (d, J = 9 Hz, 1H, CH=CH₂), 6.98 (dd, J = 17.4 Hz, 10.8 Hz, 1H, CH=CH₂), 6.56 (d, J = 9 Hz, 1H, CH=CH₂), 5.71 (dd, J = 17.4 Hz, 1.2 Hz, 1H, CH=CH₂), 5.35 (dd, J = 10.8 Hz, 1.2 Hz, 1H, CH=CH₂), 4.30 (s, 2H, NCH₂), 3.86 (s, 1H, NH).

The procedure for preparation of Ru complex 4c is the same as in Example 1 in 1.0 mmol scale. 35 mg of green solid product 4c was obtained (yield: 5%).

Ru complex (4c) ¹H NMR (400 MHz): δ 19.09 (s,1H, Ru=CH), 7.50-6.69 (m, 12H), 5.27 (m, 1H), 4.33 (d, J = 12.9 Hz, 1H), 4.04 (s, 4H, NCH₂CH₂N), 3.59 (d, J =
12.9 Hz, 1H), 2.45 (s, 12H), 2.37 (s, 6H).

**Example 4**

**Synthesis of Ru complex 4d**

The synthetic procedure for preparation of ligand 3d is the same as in Example 1 in 5.0 mmol scale. 0.74g of yellow oil product 3d was obtained (yield: 62%).

Ligand 3d 1H-NMR (400 MHz, CDCl3): δ 7.32-7.23 (m, 2H), 7.04-6.91 (m, 2H), 6.82 (dd, J = 2.0 Hz, 6.6 Hz, 2H), 6.62 (dd, J = 2.4 Hz, 6.6 Hz, 2H), 5.73 (d, J = 17.1 Hz, 1H), 5.39 (d, J = 11.1 Hz, 1H), 4.25 (s, 2H), 3.77 (s, 3H).

The procedure for preparation of Ru complex 4d is the same as in Example 1 in 1.0 mmol scale. 231 mg of green solid product 4d was obtained (yield: 32%).

Ru complex (4d) 1H-NMR (400 MHz, CDCl3): δ 18.68 (s, Ru=CH), 7.23-6.65 (m, 10H), 6.36 (dd, J = 2.8, 9.6 Hz, 1H), 6.03 (d, J = 12.8 Hz, 1H), 4.14-3.90 (m, 4H, NCH₂CH₂N), 3.85 (s, 3H), 3.47 (d, J = 12.8 Hz, 1H), 2.89-1.62 (m, 18H).

**Example 5**

**Synthesis of Ru complex 4e**

The structure of ligand 3e is the same as 3d for preparation of Ru complex 4e, just another Ru complex reagent 1a was used instead of Ru reagent 1b.

The procedure for preparation of Ru complex 4e is the same as in Example 2 in 1.0 mmol scale. 243 mg of green solid product 4e was obtained (35% yield).

Ru complex (4e) 1H-NMR (400 MHz, CDCl3): δ 19.28 (d, J = 8.4 Hz, Ru=CH), 7.45 (d, J = 8.8 Hz, 2H), 7.31-7.16 (m, 3H), 6.83 (d, J = 8.8 Hz, 2H), 5.13 (t, J = 12.4 Hz, 1H), 7.96 (d, J = 12.4 Hz, 1H), 3.85 (d, J = 12.4 Hz, 1H), 3.80 (s, 3H), 2.28-1.24 (m, 33H, PCy₃).

**Example 6**

**Synthesis of Ru complex 4f**

The synthetic procedure for preparation of ligand 3f is the same as in Example 1 in 5.0 mmol scale. 0.79g of yellow oil product 3f was obtained (yield: 63%).
Ligand 3f $^1$H-NMR (400 MHz, CDCl$_3$): δ 7.21 (m, 2H), 6.94 (m, 2H), 6.85 (m, 2H), 6.73 (m, 2H), 5.68 (dd, $J = 1.2$ Hz, 16.8 Hz, 1H), 5.38 (dd, $J = 1.5$ Hz, 11.4 Hz, 1H), 4.40 (s, 2H), 3.77 (s, 3H), 2.89 (s, 3H).

The procedure for preparation of Ru complex 4f is the same as in Example 1 in 1.0 mmol scale. 103 mg of green solid product 4f was obtained (yield: 14%).

Ru complex (4f) $^1$H-NMR (400 MHz, CDCl$_3$): δ 18.99 (s, Ru=CH), 7.48-7.44 (m, 1H), 7.19-6.86 (m, 7H), 6.72-6.66 (m, 1H), 5.29 (t, $J = 13.2$ Hz, 1H), 4.19-3.58 (m, 8H), 2.52-2.37 (m, 18H).

**Example 7**

Synthesis of Ru complex 4g

The synthetic procedure for preparation of ligand 3g is the same as in Example 1 in 5.0 mmol scale. 0.70g of yellow oil product 3g was obtained (yield: 56%). The product 3g is confirmed by LC-MS (M+H$^+$): m/z calculated: 285.1, found: 285.1, and directly used for preparation of Ru complex 4g.

The procedure for preparation of Ru complex 4g is the same as in Example 1 in 1.0 mmol scale. 61 mg of green solid product 4g was obtained (yield: 8%).

Ru complex (4g) $^1$H-NMR (400 MHz, CDCl$_3$): δ 19.11 (s,1H, Ru=CH), 8.36 (dd, $J = 2.0$, 8.0 Hz, 1H), 7.29-6.65 (m, 10H ), 5.30 (t, $J = 13.6$ Hz, 1H), 4.23 (d, $J = 13.2$ Hz, 1H), 4.10 (s, 3H), 3.80 (s, 4H, NCH$_2$CH$_2$N), 3.69 (d, $J = 13.2$ Hz, 1H), 2.65-2.08 (m, 18H).

**Example 8**

Synthesis of Ru complex 4h

The synthetic procedure for preparation of ligand 3h is the same as in Example 1 in 5.0 mmol scale. 0.47g of yellow solid product 3h was obtained (yield: 32%).

Ligand 3h $^1$H-NMR (400 MHz, CDCl$_3$): δ 7.32 (dd, $J = 5.6$ Hz, 8.0 Hz, 1H), 7.25 (dd, $J = 2.8$ Hz, 10.4 Hz, 1H), 7.00-6.92 (m, 2H), 6.34 (s, 2H), 5.72 (d, $J = 17.2$ Hz, 1H), 5.38 (d, $J = 11.2$ Hz, 1H), 4.23 (s, 2H), 3.68 (s, 3H), 2.24 (s, 6H).
The procedure for preparation of Ru complex 4h is the same as in Example 1 in 1.0 mmol scale. 315 mg of green solid product 4h was obtained (yield: 42%).

Ru complex (4h) \(^1\)HNMR (400 MHz, CDCl\(_3\)): 19.02 (s, 1H, Ru=CH), 7.21-6.82 (m, 8H), 6.40 (dd, \(J = 9.6\) Hz, 1.6 Hz), 5.21 (m, 1H), 4.06-4.00 (m, 5H), 3.70 (s, 3H), 3.54 (d, \(J = 13.2\) Hz, 1H), 2.48-2.18 (m, 24H).

**Example 9**

Synthesis of Ru complex 4j

The synthetic procedure for preparation of ligand 3j is the same as in Example 1 in 5.0 mmol scale. 0.91g of yellow liquid product 3j was obtained (yield: 93%).

Ligand 3j \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta 7.34-7.26\) (m, 2H), 7.22-7.13 (m 2H), 6.98-6.95 (m, 2H), 6.81 (m, 1H), 6.70-6.68 (m, 1H), 5.73 (d, \(J = 17.2\) Hz, 1H), 5.36 (d, \(J = 11.2\) Hz, 1H), 4.32 (s, 2H), 2.81 (m, 1H), 1.24 (d, \(J = 6.8\) Hz, 6H).

The procedure for preparation of Ru complex 4j is the same as in Example 1 in 1.0 mmol scale. 353 mg of green solid product 4j was obtained (yield: 48%).

Ru complex (4j) \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta 18.88\) (s,1H, Ru=CH), 7.57-6.44 (m, 11H), 5.36 (t, \(J = 13.2\) Hz, 1H), 4.16-4.02 (m, 5H), 4.01 (d, \(J = 13.2\) Hz, 1H), 2.75-2.00 (m, 19H), 1.01-0.90 (m, 6H).

**Example 10**

Synthesis of Ru complex 4k

The synthetic procedure for preparation of ligand 3k is the same as in Example 1 in 5.0 mmol scale. 0.57g of yellow oil product 3k was obtained (yield: 83%).

Ligand 3k \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.26\) Hz) : 7.317 (dd, 1H, \(J = 6\) Hz,8.4 Hz), 7.256 (dd, \(J = 2.8\) Hz, 10.4 Hz, 1H), 7.094-7.017 (m, 3H), 6.961 (td, \(J = 2.8\) Hz, 8.8 Hz, 1H), 6.873 (t, 1H, \(J = 6.8\) Hz), 5.735 (d, \(J = 17.2\) Hz 1H.), 5.412 (d, \(J = 10.8\) Hz, 1H), 4.133(s, 2H), 2.276(s, 6H).

The procedure for preparation of Ru complex 4k is the same as in Example 1 in 1.0 mmol scale. 490 mg of green solid product 4k was obtained (yield: 68%).
Ru complex (4k) $^1$HNMR (400 MHz, CDCl$_3$): δ 18.90 (s, 1H, Ru=CH), 7.27-6.77 (m, 9H), 6.41 (d, J = 8.0 Hz, 1H), 5.43 (t, J = 13.2 Hz, 1H), 4.18-4.00 (m, 5H), 3.25 (d, J = 13.6 Hz, 1H), 2.76-1.27 (m, 24H).

Example 11

Synthesis of Ru complex 4m

The synthetic procedure for preparation of ligand 3m is the same as in Example 1 in 5.0 mmol scale. 0.76g of yellow oil product 3m was obtained (yield: 49%). The product 3m is confirmed by LC-MS (M+H$^+$): m/z calculated: 311.2, found: 311.2, and directly used for preparation of the Ru complex 4m.

The procedure for preparation of Ru complex 4m is the same as in Example 1 in 1.0 mmol scale. 404 mg of green solid product 4m was obtained (yield: 52%).

Ru complex (4m) $^1$HNMR (400 MHz, CDCl$_3$): δ 18.95 (s, 1H, Ru=CH), 7.43-6.36 (m, 10H), 4.00 (m, 6H), 2.67-2.06 (m, 20H), 0.90-0.83 (m, 12H).

Example 12

Synthesis of Ru complex 4n

The synthetic procedure for preparation of ligand 3n is the same as in Example 1 in 5.0 mmol scale. 0.63g of yellow oil product 3n was obtained (yield: 45%).

Ligand 3n $^1$H-NMR (400 MHz, CDCl$_3$): δ 7.33 (dd, J = 6.8 Hz, 6.8 Hz, 1H), 7.26 (d, J = 11.6 Hz, 1H), 7.08 (dd, J = 10.8 Hz, 17.6 Hz, 1H), 6.69 (t, J = 8.4 Hz, 1H), 6.86 (s, 2H), 5.74 (d, J = 17.6 Hz, 1H), 5.42 (d, J = 10.8 Hz, 1H), 4.08 (s, 2H), 2.25 (s, 9H).

The procedure for preparation of Ru complex 4n is the same as in Example 1 in 1.0 mmol scale. 470 mg of green solid product 4n was obtained (yield: 64%).

Ru complex (4n): $^1$H-NMR (400 MHz, CDCl$_3$): δ 18.88 (s, 1H, Ru=CH), 7.25-6.36 (m, 9H), 5.40 (t, J = 13.2 Hz, 1H), 4.14-4.00 (m, 6H), 2.77-1.90 (m, 27H).

Example 13

Synthesis of Ru complex 4p
The synthetic procedure for preparation of ligand 3p is the same as in Example 1 in 5.0 mmol scale. 0.85g of yellow oil product 3p was obtained (yield: 67%).

Ligand 3p $^1$H-NMR (400 MHz, CDCl$_3$): δ=7.26Hz):7.368 (dd, 1H, $J$=6.00 Hz, 8.40 Hz), 7.258-7.126 (m, 4H), 7.019-6.922 (m, 3H), 5.632 (dd, 1H, $J$ = 1.20 Hz, 17.60 Hz), 5.287 (dd, 1H, $J$ = 1.20 Hz, 11.20 Hz), 4.072 (s, 2H), 2.537 (s, 3H), 2.290 (s, 3H)

The procedure for preparation of Ru complex 4p is the same as in Example 1 in 1.0 mmol scale. 184 mg of green solid product 4p was obtained (yield: 26%).

Ru complex (4p) $^1$HNMR (400 MHz, CDCl$_3$): δ 18.91 (s,1H, Ru=CH), 7.63-6.42 (m, 10H), 5.27 (t, $J$ = 13.2 Hz, 1H), 4.13-4.01 (m, 5H), 3.44 (d, $J$ = 13.2 Hz, 1H), 2.46-2.00 (m, 21H).

Example 14

Synthesis of Ru complex 4q

The synthetic procedure for preparation of ligand 3q is the same as in Example 1 in 5.0 mmol scale. 0.69g of yellow oil product 3q was obtained (yield: 46%).

Ligand 3q $^1$H-NMR (400 MHz, CDCl$_3$): δ 7.21 (dd, $J$ = 2.8 Hz, 10.0 Hz, 1H), 7.15 (dd, $J$ = 5.6 Hz, 7.6 Hz, 1H), 6.97-6.88 (m, 2H), 6.39 (s, 2H), 5.68 (d, $J$ = 17.2 Hz, 1H), 5.36 (dd, $J$ = 0.8 Hz, 11.2 Hz, 1H), 4.40 (s, 2H), 3.67 (s, 3H), 2.87 (s, 3H), 2.24 (s, 6H).

The procedure for preparation of Ru complex 4q is the same as in Example 1 in 1.0 mmol scale. 291 mg of green solid product 4q was obtained (yield: 38%).

Ru complex (4q) $^1$HNMR (400 MHz, CDCl$_3$): δ 18.75 (s,1H, Ru=CH), 7.26-6.21 (m, 9H), 4.05-3.85 (m, 5H), 3.72 (s, 3H), 3.34 (d, $J$ = 13.2 Hz, 1H), 2.82-0.95 (m, 30H).

Example 15

Synthesis of Ru complex 4r

The synthetic procedure for preparation of ligand 3r is the same as in Example 1
in 5.0 mmol scale. 0.55g of yellow oil product 3r was obtained (yield: 44%).

Ligand 3r $^1$H-NMR (400 MHz, CDCl$_3$): δ 7.33-7.25 (m, 2H), 7.00-6.93 (m, 2H), 6.84 (bd, $J=8.4$ Hz, 2H), 6.55 (dd, $J=4.4$ Hz, 9.6 Hz, 1H), 5.74 (d, $J=17.2$ Hz, 1H), 5.40 (d, $J=11.2$ Hz, 1H), 4.29 (s, 2H), 3.46 (bs, 1H), 2.12 (s, 3H).

The procedure for preparation of Ru complex 4r is the same as in Example 1 in 1.0 mmol scale. 101 mg of green solid product 4r was obtained (yield: 14%).

Ru complex (4r)$^1$HNMR (400 MHz, CDCl$_3$): δ 18.89 (s,1H, Ru=CH), 7.69-6.43 (m, 10H), 5.23 (dd, $J=13.2$, 11.3 Hz, 1H), 4.16-3.94 (m, 5H), 3.46 (d, $J=11.3$ Hz, 1H), 2.62-1.00 (m, 21H).

**Example 16**

**Synthesis of Ru complex 4s**

The synthetic procedure for preparation of ligand 3s is the same as in Example 1 in 5.0 mmol scale. 0.83g of yellow oil product 3s was obtained (yield: 51%).

Ligand 3s $^1$H-NMR (400 MHz, CDCl$_3$): δ 7.30 (dd, $J=6.0$ Hz, 8.5 Hz, 1H), 7.23 (dd, $J=3.0$ Hz, 10.0 Hz, 1H), 6.70-6.90 (m, 2H), 6.79 (d, $J=8.5$ Hz, 2H), 6.58 (d, $J=8.5$ Hz, 2H), 5.70 (d, $J=18.0$ Hz, 1H), 5.37 (d, $J=11.0$ Hz, 1H), 4.23 (s, 2H), 3.88 (t, $J=6.5$ Hz, 2H), 1.73 (m, 2H), 1.44 (m, 2H), 1.35-1.31 (m, 4H), 0.90 (t, $J=6.0$ Hz, 3H).

The procedure for preparation of Ru complex 4s is the same as in Example 1 in 1.0 mmol scale. 679 mg of green solid product 4s was obtained (yield: 85%).

Ru complex (4s)$^1$HNMR (400 MHz, CDCl$_3$): δ 18.68 (s,1H, Ru=CH), 7.28-6.42 (m, 10H), 6.37 (d, $J=8.5$ Hz, 1H), 5.05 (m, 1H), 4.06-3.93 (m, 7H), 3.57 (d, $J=12.8$ Hz, 1H), 2.89-1.29 (m, 29H).

**Example 17**

**Synthesis of Ru complex 4t**

The synthetic procedure for preparation of ligand 3t is the same as in Example 1 in 5.0 mmol scale. 0.67g of yellow product 3t was obtained (yield: 38%). The product
3t is confirmed by LC-MS (M+H⁺): m/z calculated: 339.2, found: 339.2, and directly used for preparation of the Ru complex 4t.

The procedure for preparation of Ru complex 4t is the same as in Example 1 in 1.0 mmol scale. 185 mg of green solid product 4t was obtained (yield: 23%).

Ru complex (4t) 1H-NMR (300 MHz, CDCl3): δ 18.97 (s, 1H, Ru=CH), 8.54-8.45 (m, 2H), 6.66-6.96 (m, 8H), 4.16-4.10 (m, 1H), 4.03 (s, 4H, NCH₂CH₂N), 2.63-1.75 (m, 22H), 0.92 (d, J = 7.6Hz), 0.83 (d, J = 7.6Hz).

Example 18

Synthesis of Ru complex 4u

The synthetic procedure for preparation of ligand 3u is the same as in Example 1 in 5.0 mmol scale. 0.39g of yellow oil product 3u was obtained (yield: 28%).

Ligand 3u 1H-NMR (400 MHz, CDCl3): δ 7.53 (d, J = 2.0 Hz, 1H), 7.39 (d, J = 8.4 Hz, 1H), 7.28-7.26 (m, 1H), 7.21-7.12 (m, 3H), 7.03 (dd, J = 10.8 Hz, 17.6Hz, 1H), 5.73 (d, J = 17.6 Hz, 1H), 5.43 (d, J = 10.8 Hz, 1H), 4.07 (s, 2H), 3.26 (m, 2H), 1.25 (d, J = 6.4 Hz, 12 H).

The procedure for preparation of Ru complex 4u is the same as in Example 1 in 1.0 mmol scale. 254 mg of green solid product 4u was obtained (yield: 32%).

Ru complex (4u) 1H-NMR (300 MHz, CDCl3): δ 19.03 (s, 1H, Ru=CH), 7.48-6.63 (m, 10H), 5.53 (m, 1H), 4.81-4.78 (m, 1H), 4.00 (s, 4H, NCH₂CH₂N), 2.51-2.49 (m, 1H), 2.51-2.32 (m, 18H), 1.12 (d, J = 7.6Hz), 1.04 (d, J = 7.6Hz).

Example 19

Synthesis of Ru complex 4v

The synthetic procedure for preparation of ligand 3v is the same as in Example 1 in 5.0 mmol scale. 1.08g of yellow oil product 3v was obtained (yield: 81%).

Ligand 3v 1H-NMR (400 MHz, CDCl3): δ 7.56 (d, J = 7.2 Hz, 1H), 7.34 (dd, J = 1.6 Hz, 7.6 Hz, 1H), 7.30-7.26 (m, 2H), 7.03 (dd, J = 11.2 Hz, 17.2 Hz, 1H), 6.86-6.80 (m, 2H), 6.68-6.62 (m, 2H), 5.72 (dd, J = 1.2 Hz, 17.2 Hz, 1H), 5.33 (dd, J = 1.2 Hz, 11.2 Hz, 1H), 4.56 (m, 1H), 4.36 (s, 2H), 1.33 (d, J = 6 Hz, 6H).
The procedure for preparation of Ru complex 4v is the same as in Example 1 in 1.0 mmol scale. 73 mg of green solid product 4v was obtained (yield: 10%).

Ru complex (4v) $^1$HNMR (400 MHz, CDCl$_3$): $\delta$ 18.97 (s, Ru=CH), 7.50-6.58 (m, 11H), 5.26-3.52 (m, 8H), 3.48-2.07 (m, 18H), 1.23 (d, $J = 6.4$ Hz, 6H).

Example 20

Synthesis of Ru complex 4w

The structure of ligand 3w is the same as 3v for preparation of Ru complex 4w, just another Ru complex reagent 1a was used instead of Ru reagent 1b.

The procedure for preparation of Ru complex 4w is the same as in Example 2 in 1.0 mmol scale. 219 mg of green solid product 4w was obtained (yield: 31%).

Ru complex (4w) $^1$HNMR (400 MHz, CDCl$_3$): $\delta$ 19.56 (d, $J = 9.9$ Hz, Ru=CH), 8.20 (d, $J = 8.1$ Hz, 1H), 7.66-6.84 (m, 6H), 5.46 (d, $J = 12$ Hz, 1H), 5.22 (t, $J = 6$ Hz, 1H), 4.56 (m, 1H), 3.95 (d, $J = 12.0$ Hz, 1H), 2.34-0.87 (m, 39H, PCy$_3$).

Example 21

Synthesis of Ru complex 4x

The synthetic procedure for preparation of ligand 3x is the same as in Example 1 in 5.0 mmol scale. 0.96g of yellow oil product 3x was obtained (yield: 76%).

Ligand 3x $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.27 (dd, $J = 4.5$ Hz, 6.15 Hz, 1H), 7.21-7.17 (m, 1H), 6.95-6.88 (m, 2H), 6.82-6.75 (m, 2H), 6.64-6.60 (m, 1H), 6.55 (d, $J = 5.7$ Hz, 1H), 5.66 (d, $J = 12.9$ Hz, 1H), 5.32 (d, $J = 8.1$ Hz, 1H), 4.48 (m, 1H), 4.26 (s, 2H), 1.27 (d, $J = 4.5$ Hz, 6H).

The procedure for preparation of Ru complex 4x is the same as in Example 2 in 1.0 mmol scale. 420 mg of green solid product 4x was obtained (yield: 58%).

Ru complex (4x) $^1$HNMR (400 MHz, CDCl$_3$): $\delta$ 19.55 (d, $J = 9.9$ Hz, Ru=CH), 8.14 (d, $J = 8.1$ Hz, 1H), 7.36-6.83 (m, 6H), 5.46 (d, $J = 12.0$ Hz, 1H), 5.13 (t, $J = 6.0$ Hz, 1H), 4.56 (m, 1H), 3.90 (d, $J = 12.0$ Hz, 1H), 2.30-1.25 (m, 39H, PCy$_3$).

Example 22
Synthesis of Ru complex 4y

The synthetic procedure for preparation of ligand 3y is the same as in Example 1 in 5.0 mmol scale. 0.58g of yellow oil product 3y was obtained (yield: 47%).

Ligand 3y 1H-NMR (400 MHz, CDCl3): δ 7.33 (dd, J = 5.6 Hz, 8.4Hz, 1H), 7.25 (dd, J = 2.8 Hz, 10 Hz, 1H), 7.05-6.82 (m, 3H), 6.81 (dd, J = 1.6 Hz, 8 Hz, 1H), 6.74-6.69 (m, 1H), 6.62 (dd, J = 1.6 Hz, 8Hz, 1H), 5.57 (d, J = 17.6 Hz, 1H), 5.40 (d, J = 11.2 Hz, 1H), 4.31 (s, 2H), 3.84 (s, 3H).

The procedure for preparation of Ru complex 4y is the same as in Example 1 in 1.0 mmol scale. 267 mg of green solid product 4y was obtained (yield: 37%).

Ru complex (4y): 1H NMR (400 MHz, CDCl3): δ 18.83 (s, Ru=CH), 7.50-6.39 (m, 11H), 5.21 (t, J = 12.4 Hz, 1H), 4.69-3.46 (m, 9H), 2.62-2.08 (m, 18H).

Example 23

Synthesis of Ru complex 4z

The structure of ligand 3z is the same as 3y for preparation of Ru complex 4z, just another Ru complex intermediate 1a was used instead of Ru intermediate 1b.

The procedure for preparation of Ru complex 4z is the same as in Example 2 in 1.0 mmol scale. 362 mg of green solid product 4z was obtained (yield: 52%).

Ru complex (4z) 1H NMR (400 MHz, CDCl3): δ 19.35 (d, J = 9.9 Hz, Ru=CH), 8.11 (d, J = 8.1 Hz, 1H), 7.34-6.85 (m, 6H), 5.48 (d, J = 12.0 Hz, 1H), 5.27 (t, J = 6 Hz, 1H), 3.93 (d, J = 12.0 Hz, 1H), 3.88 (s, 3H), 2.33-1.24 (m, 33H, PCy3).

Example 24

Synthesis of Ru complex 4aa

The structure of ligand 3aa is the same as 3x for preparation of Ru complex 4aa, just another Ru complex intermediate 1b was used instead of Ru intermediate 1a.

The procedure for preparation of Ru complex 4aa is the same as in Example 1 in 1.0 mmol scale. 631 mg of green solid product 4aa was obtained (yield: 84%).

Ru complex (4aa) 1H NMR (400 MHz, CDCl3): δ 18.89 (s, Ru=CH), 7.60-6.45
(m, 11H), 5.13-3.52 (m, 8H), 2.95-2.10 (m, 18H), 0.95 (d, J = 6.4 Hz, 6H)

**Example 25**

Synthesis of Ru complex 4ab

The synthetic procedure for preparation of ligand 3ab is the same as in Example 1 in 5.0 mmol scale. 0.32g of yellow oil product 3ab was obtained (yield: 26%).

Ligand 3ab $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 8.36 (d, J = 2.8 Hz, 1H), 8.05 (dd, J = 2.8 Hz, 8.4 Hz, 1H), 7.54 (d, J = 8.4 Hz, 1H), 7.01 (dd, J = 10.5 Hz, 17.1 Hz, 1H), 6.85-6.69 (m, 3H), 6.44 (d, J = 7.5 Hz, 1H), 5.86 (dd, J = 0.9 Hz, 17.1 Hz, 1H), 5.53 (dd, J = 0.9Hz, 10.5 Hz, 1H), 4.46 (s, 2H), 3.87 (s, 3H)

The procedure for preparation of Ru complex 4ab is the same as in Example 1 in 1.0 mmol scale. 300 mg of green solid product 4ab was obtained (yield: 40%).

Ru complex (4ab) $^1$HNMR (400 MHz, CDCl$_3$): $\delta$ 16.52 (s, Ru=CH), 7.58 (m, 1H), 7.09 (s, 4H), 6.93-6.60 (m, 6H), 4.52 (m, 1H), 4.35 (s, 2H), 4.18 (s, 4H, NCH$_2$CH$_2$N), 3.89 (s, 6H), 2.49 (s, 12H), 2.40 (s, 6H).

**Example 26**

Synthesis of Ru complex 4ac

The synthetic procedure for preparation of ligand 3ac is the same as in Example 1 in 5.0 mmol scale. 1.09g of yellow oil product 3ac was obtained (yield: 91%).

Ligand 3ac $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.49 (s, 1H, NH), 7.27 (d, J = 7.5 Hz, 1H, aromatic H), 7.09-7.00 (m, 2H, aromatic H, CH=CH$_2$), 6.88-6.63 (m, 5H, aromatic H), 5.75 (d, J = 17.4 Hz, 1H, CH=CH$_2$), 5.38 (d, J = 10.8 Hz, 1H, CH=CH$_2$), 4.28 (s, 2H, NCH$_2$), 3.81 (s, 6H, OCH$_3$).

The procedure for preparation of Ru complex 4ac is the same as in Example 1 in 1.0 mmol scale. 367 mg of green solid product 4ac was obtained (yield: 50%).

Ru complex (4ac) $^1$HNMR (400 MHz, CDCl$_3$): $\delta$ 19.03 (s, Ru=CH), 8.38 (d, J = 2.0 Hz, 1H), 7.69 (d, J = 16.0 Hz, 1H), 7.44 (d, J = 7.6 Hz, 1H), 7.21-7.03 (m, 5H), 6.83-6.59 (m, 3H), 5.24 (t, J =12.0 Hz, 1H), 4.66 (d, J =12.0 Hz, 1H), 4.45 (m, 1H), 4.20-4.05 (m, 4H, NCH$_2$CH$_2$N), 3.62 (d, J =12.0 Hz, 1H), 2.69-2.03 (m, 18H), 1.18 (d,
\[ J = 5.6 \text{ Hz, 6H}. \]

**Example 27**

Synthesis of Ru complex 4ad

The synthetic procedure for preparation of ligand 3ad is the same as in Example 1 in 5.0 mmol scale. 1.01g of yellow oil product 3ad was obtained (yield: 79%).

Ligand 3ad \(^1^H\)-NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.48 (d, \( J = 2.1 \text{ Hz}, 1\text{H}, \text{aromatic H} \)), 7.27-7.24 (m, 1H, aromatic H), 7.04 (dd, \( J = 18\text{Hz}, 10.8 \text{ Hz}, 1\text{H}, \text{CH=CH}_2 \)), 6.85-6.79 (m, 3H, aromatic H), 6.67-6.61 (m, 2H, aromatic H), 5.74 (dd, \( J = 18 \text{ Hz}, 1.2 \text{ Hz}, 1\text{H}, \text{CH=CH}_2 \)), 5.28 (dd, \( J = 10.8 \text{ Hz}, 1.2 \text{ Hz}, 1\text{H}, \text{CH=CH}_2 \)), 4.59-4.53 (m, 2H, OCH, NH), 4.29 (s, 2H, NCH\(_2\)), 3.86 (s, 3H, OCH\(_3\)), 1.37 (d, \( J = 6.4 \text{ Hz}, 6\text{H}, \text{OCH(CH}_3\text{)_2} \)).

The procedure for preparation of Ru complex 4ad is the same as in Example 1 in 1.0 mmol scale. 374 mg of green solid product 4ad was obtained (yield: 49%).

Ru complex (4ad) \(^1^H\)NMR (400 MHz, CDCl\(_3\)): \( \delta \) 16.52 (s, Ru=CH), 7.59 (m, 1H), 7.09 (s, 4H), 6.92-6.84 (m, 4H), 6.75-6.66 (m, 2H), 4.59 (m, 1H), 4.35 (s, 2H), 4.18 (s, 4H, NCH\(_2\)CH\(_2\)N), 3.89 (s, 3H), 2.49 (s, 12H), 2.40 (s, 6H, 18H), 0.93 (m, 6H).

**Example 28**

Synthesis of Ru complex 4ae

The synthetic procedure for preparation of ligand 3ae is the same as in Example 1 in 5.0 mmol scale. 0.32g of yellow oil product 3ae was obtained (yield: 27%).

Ligand 3ae \(^1^H\)-NMR (400 MHz, CDCl\(_3\)): \( \delta \) 8.36 (d, \( J = 2.4 \text{ Hz}, 1\text{H} \)), 8.05 (dd, \( J = 2.4 \text{ Hz}, 8.4 \text{ Hz}, 1\text{H} \)), 7.54 (d, \( J = 8.4 \text{ Hz}, 1\text{H} \)), 7.01 (dd, \( J = 10.8 \text{ Hz}, 17.1 \text{ Hz}, 1\text{H} \)), 6.84-6.75 (m, 2H), 6.71-6.65 (m, 2H), 6.42 (dd, \( J = 1.8 \text{ Hz}, 7.8 \text{ Hz}, 1\text{H} \)), 5.85 (dd, \( J = 0.9 \text{ Hz}, 17.1 \text{ Hz}, 1\text{H} \)), 5.53 (dd, \( J = 0.9 \text{ Hz}, 10.8 \text{ Hz}, 1\text{H} \)), 4.58 (m, 1H), 4.47 (s, 1H), 1.36 (d, \( J = 6.0 \text{ Hz}, 6\text{H} \)).

The procedure for preparation of Ru complex 4ae is the same as in Example 1 in 1.0 mmol scale. 389 mg of green solid product 4ae was obtained (yield: 50%).
Ru complex (4ae) $^1$HNMR (400 MHz, CDCl$_3$): δ 19.03 (s, 1H, Ru=CH), 8.38 (d, $J$ = 2.0 Hz, 1H), 7.69 (d, $J$ = 16.0 Hz, 1H), 7.44 (d, $J$ = 7.6 Hz, 1H), 7.21-7.03 (m, 5H), 6.83-6.59 (m, 3H), 5.24 (t, $J$ = 12.0 Hz, 1H), 4.66 (d, $J$ = 12.0 Hz, 1H), 4.45 (m, 1H), 4.20-4.05 (m, 4H, NCH$_2$CH$_2$N), 3.62 (d, $J$ = 12.0 Hz, 1H), 2.69-2.03 (m, 18H), 1.18 (d, $J$ = 5.6 Hz, 6H).

**Example 29**

Synthesis of Ru complex 4af

The synthetic procedure for preparation of ligand 3af is the same as in Example 1 in 5.0 mmol scale. 0.76g of yellow oil product 3af was obtained (yield: 65%).

Ligand 3af $^1$H-NMR (400 MHz, CDCl$_3$): δ 7.38-7.34 (m, 2H, aromatic H), 7.22-7.10 (m, 2H, aromatic H, CH=CH$_2$), 7.01-6.88 (m, 4H, aromatic H), 5.63 (d, $J$ = 17.1 Hz, 1H, CH=CH$_2$), 5.29 (d, $J$ = 10.8 Hz, 1H, CH=CH$_2$), 4.20 (s, 2H, NCH$_2$), 3.88 (s, 3H, OCH$_3$), 2.63 (s, 3H, NCH$_3$).

The procedure for preparation of Ru complex 4af is the same as in Example 1 in 1.0 mmol scale. 111 mg of green solid product 4af was obtained (yield: 15%).

Ru complex (4af) $^1$HNMR (400 MHz, CDCl$_3$): δ 18.54 (s, 1H, Ru=CH), 7.45 (d, $J$ = 8.0 Hz, 1H), 7.24-7.19 (m, 4H), 7.06-6.96 (m, 6H), 6.14 (d, $J$ = 13.2 Hz, 1H), 5.39 (d, $J$ = 13.2 Hz, 1H), 4.07-3.77 (m, 7H), 3.52 (s, 3H), 2.65-2.30 (m, 18H).

**Example 30**

Synthesis of Ru complex 4ag

The synthetic procedure for preparation of ligand 3ag is the same as in Example 1 in 5.0 mmol scale. 0.84g of yellow oil product 3ag was obtained (yield: 76%).

Ligand 3ag $^1$H-NMR (400 MHz, CDCl$_3$): δ = 7.26 Hz): 7.32 (dd, $J$ = 5.70 Hz, 8.40 Hz, 1H), 7.24 (dd, $J$ = 9.9 Hz, 2.4 Hz, 1H), 7.03-6.90 (m, 2H), 6.54-6.39 (m, 3H), 5.71 (dd, $J$ = 1.2 Hz, 17.4 Hz, 1H), 5.37 (dd, $J$ = 1.2 Hz, 10.8 Hz, 1H), 4.25 (s, 2H), 4.07 (bs, 1H), 3.81 (s, 3H), 3.76 (s, 3H).

The procedure for preparation of Ru complex 4ag is the same as in Example 1 in
1.0 mmol scale. 302 mg of green solid product \textbf{4ag} was obtained (40% yield).

Ru complex (\textbf{4ag}) $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 18.83 (s, 1H, Ru=CH), 7.36-6.14 (m, 10H), 5.12 (t, $J = 12.4$ Hz, 1H), 4.50-3.42 (m, 12H), 2.62-2.05 (m, 18H).

\textbf{Example 31}

Synthesis of Ru complex \textbf{4ah}

The synthetic procedure for preparation of ligand \textbf{3ah} is the same as in Example 1 in 5.0 mmol scale. 0.46g of yellow oil product \textbf{3ah} was obtained (yield: 38%).

Ligand \textbf{3ah} $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.34-7.23 (m, 2H), 7.03-6.91 (m, 2H), 6.69 (dd, $J = 1.2$ Hz, 8.10 Hz, 1H), 7.52-6.45 (m, 2H), 5.72 (d, $J = 17.4$ Hz, 1H), 5.38 (d, $J = 11.4$ Hz, 1H), 4.32 (bs, 1H), 4.28 (s, 2H), 2.27 (s, 3H).

The procedure for preparation of Ru complex \textbf{4ah} is the same as in Example 1 in 1.0 mmol scale. 376 mg of green solid product \textbf{4ah} was obtained (yield: 51%).

Ru complex (\textbf{4ah}) $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 18.90 (s, 1H, Ru=CH), 7.60-6.36 (m, 10H), 5.25 (t, $J = 12.0$ Hz, 1H), 4.78 (d, $J = 12.0$ Hz, 1H), 4.05 (s, 4H, NCH$_2$CH$_2$N), 3.53 (s, 3H), 3.43 (d, $J = 12.0$ Hz, 1H), 2.56-2.13 (m, 21H).

\textbf{Example 32}

Synthesis of Ru complex \textbf{4aj}

The synthetic procedure for preparation of ligand \textbf{3aj} is the same as in Example 1 in 5.0 mmol scale. 1.22g of yellow oil product \textbf{3aj} was obtained (yield: 90%).

Ligand \textbf{3aj} $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.35-7.21 (m, 2H), 7.03-6.77 (m, 4H), 6.71-6.58 (m, 2H), 5.71 (d, $J = 17.7$ Hz, 1H), 5.38 (d, $J = 11.1$ Hz, 1H), 4.31 (s, 2H), 4.06 (q, $J = 11.1$ Hz, 2H), 1.40 (t, $J = 11.1$ Hz, 3H).

The procedure for preparation of Ru complex \textbf{4aj} is the same as in Example 2 in 1.0 mmol scale. 390 mg of green solid product \textbf{4aj} was obtained (yield: 55%).

Ru complex (\textbf{4aj}) $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 19.45 (d, $J = 9.6$ Hz, Ru=CH), 8.18 (d, $J = 7.6$ Hz, 1H), 7.40-7.33 (m, 2H), 7.21-7.11 (m, 2H), 6.95-6.88 (m, 2H), 6.84 (d, $J = 7.8$ Hz, 2H), 4.82 (t, $J = 7.8$ Hz, 1H), 4.75 (d, $J = 7.8$ Hz, 2H), 4.31 (q, $J = 7.8$ Hz, 2H), 3.47 (q, $J = 7.8$ Hz, 2H), 2.56-2.13 (m, 21H).
5.52 (m, 1H), 5.23 (m, 1H), 4.16-3.94 (m, 3H), 2.36-0.81 (m, 36H, PCy₃).

**Example 33**

Synthesis of Ru complex 4ak

The synthetic procedure for preparation of ligand 3ak is the same as in Example 1 in 5.0 mmol scale. 0.65g of yellow oil product 3ak was obtained (yield: 52%).

Ligand 3ak ¹H-NMR (400 MHz, CDCl₃): δ 7.47 (dd, 3H, 6.0 Hz, 8.4 Hz, 1H), 7.21 (dd, 3H, 10.4 Hz, 2.4 Hz, 1H), 7.13 (dd, 3H, 11.2 Hz, 17.2 Hz, 1H), 6.97-6.92 (m, 3H), 6.79 (d, 3H, 8.4 Hz, 1H), 5.63 (d, 3H, 17.2 Hz, 1H), 5.28 (d, 3H, 11.2 Hz, 1H), 4.57 (m, 1H), 4.21 (s, 2H), 2.66 (s, 3H), 1.29-1.27 (m, 15H).

The procedure for preparation of Ru complex 4ak is the same as in Example 1 in 1.0 mmol scale. 299 mg of green solid product 4ak was obtained (yield: 37%).

Ru complex (4ak) ¹H-NMR (400 MHz, CDCl₃): δ 19.08 (s, 1H, Ru=CH), 7.97-6.33 (m, 10H), 5.08 (m, 2H), 4.34 (m, 1H), 4.02 (s, 4H, NCH₂CH₂N), 3.41 (m, 1H), 2.53-2.31 (m, 18H), 1.29 (s, 9H), 0.89-0.87 (m, 6H).

**Example 34**

Synthesis of Ru complex 4am

The synthetic procedure for preparation of ligand 3am is the same as in Example 1 in 5.0 mmol scale. 1.10g of yellow oil product 3am was obtained (yield: 86%).

Ligand 3am ¹H-NMR (400 MHz, CDCl₃): δ 7.32 (m, 1H), 7.26-7.21 (m, 1H), 7.00-6.93 (m, 2H), 6.52-6.42 (m, 3H), 5.71 (d, 3H, 17.4 Hz, 1H), 5.37 (d, 3H, 11.1 Hz, 1H), 4.50 (m, 1H), 4.38 (m, 1H), 4.26 (s, 2H), 1.31 (m, 12H).

The procedure for preparation of Ru complex 4am is the same as in Example 1 in 1.0 mmol scale. 437 mg of green solid product 4am was obtained (yield: 54%).

Ru complex (4am) ¹H-NMR (400 MHz, CDCl₃): δ 18.85 (s, 1H, Ru=CH), 7.26-6.07 (m, 10H), 5.04 (t, 3H, 13.2 Hz, 1H), 4.48 (m, 1H), 4.39-4.33 (m, 2H), 4.15-4.02 (m, 4H, NCH₂CH₂N), 3.65 (m, 1H), 2.66-2.05 (m, 18H), 1.55 (m, 6H), 1.38 (m, 6H).
Example 35

Synthesis of Ru complex 4an

The synthetic procedure for preparation of ligand 3an is the same as in Example 1 in 5.0 mmol scale. 0.66g of yellow oil product 3an was obtained (yield: 41%).

Ligand 3an $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.34-7.22 (m, 2H), 7.02-6.93 (m, 2H), 6.70 (d, $J = 7.8$ Hz, 1H), 6.48-6.43 (m, 1H), 5.71 (d, $J = 17.4$ Hz, 1H), 5.37 (d, $J = 10.8$ Hz, 1H), 4.46 (m, 1H), 4.40 (bs, 1H), 4.28 (s, 2H), 2.25 (s, 3H), 1.30 (d, $J = 6.0$ Hz, 6H).

The procedure for preparation of Ru complex 4an is the same as in Example 1 in 1.0 mmol scale. 359 mg of green solid product 4an was obtained (yield: 46%).

Ru complex (4an) $^1$HNMR (400 MHz, CDCl$_3$): $\delta$ 18.98 (s, 1H, Ru=CH), 7.66-6.39 (m, 10H), 5.17 (t, $J = 13.2$ Hz, 1H), 4.71 (d, $J = 13.2$ Hz, 1H), 4.36 (m, 1H), 4.06 (brs, 4H, NCH$_2$CH$_2$N), 3.42 (d, $J = 13.2$ Hz, 1H), 2.63-2.09 (m, 21H), 1.09 (m, 6H).

Example 36

Synthesis of Ru complex 4ap

The synthetic procedure for preparation of ligand 3ap is the same as in Example 1 in 5.0 mmol scale. 0.70g of yellow oil product 3ap was obtained (yield: 57%).

Ligand 3ap $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.33-7.25 (m, 2H), 7.04 (dd, $J = 10.8$ Hz, 17.2 Hz, 1H), 6.96-6.92 (m, 1H), 6.79 (d, $J = 2.4$ Hz, 1H), 6.54 (d, $J = 2.4$ Hz, 1H), 5.72 (d, $J = 17.2$ Hz, 1H), 5.37(d, $J = 10.8$ Hz, 1H), 4.55 (m, 1H), 4.23 (s, 2H), 3.99 (bs, 1H), 1.40 (s, 9H), 1.29 (s, 9H), 1.20 (d, $J = 6.0$ Hz, 6H).

The procedure for preparation of Ru complex 4ap is the same as in Example 1 in 1.0 mmol scale. 380 mg of green solid product 4ap was obtained (yield: 44%).

Ru complex (4ap) $^1$HNMR (400 MHz, CDCl$_3$): $\delta$ 18.99 (s, 1H, Ru=CH), 7.45-6.36 (m, 9H), 5.05 (m, 2H), 3.98-3.91 (m, 5H), 3.72 (d, $J = 13.2$ Hz, 1H), 2.48-2.34 (m, 19H), 1.45-0.95 (m, 21H).
Example 37

Synthesis of Ru complex 4aq

The synthetic procedure for preparation of ligand 3aq is the same as in Example 1 in 5.0 mmol scale. 0.63g of yellow oil product 3aq was obtained (yield: 52%).

Ligand 3aq $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.54 (d, $J = 2.0$ Hz, 1H), 7.32 (d, $J = 8.4$ Hz, 1H), 7.23 (dd, $J = 2.0$ Hz, 8.4 Hz, 1H), 6.98 (dd, $J = 11.2$ Hz, 17.2 Hz, 1H), 6.89 (td, $J = 1.6$ Hz, 7.6 Hz, 1H), 6.83 (td, $J = 1.6$ Hz, 8.0 Hz, 1H), 6.73 (td, $J = 1.6$ Hz, 8.0 Hz, 1H), 6.59 (dd, $J = 1.6$ Hz, 7.6 Hz, 1H), 5.74 (dd, $J = 0.80$ Hz, 17.2 Hz, 1H), 5.40 (dd, $J = 0.80$ Hz, 11.2 Hz, 1H), 4.33 (s, 2H), 3.86 (s, 3H).

The procedure for preparation of Ru complex 4aq is the same as in Example 1 in 1.0 mmol scale. 665 mg of green solid product 4aq was obtained (yield: 90%).

Ru complex (4aq) $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 18.75 (s, 1H, Ru=CH), 7.50-7.44 (m, 2H), 7.04-6.36 (m, 9H), 5.32-5.21 (m, 1H), 4.65 (d, $J = 13.2$ Hz, 1H), 4.16-4.04 (m, 4H, NCH$_2$CH$_2$N), 3.59 (s, 3H), 3.48 (d, $J = 13.2$ Hz, 1H), 2.62-2.32 (m, 18H).

Example 38

Synthesis of Ru complex 4ar

The synthetic procedure for preparation of ligand 3ar is the same as in Example 1 in 5.0 mmol scale. 0.56g of yellow oil product 3ar was obtained (yield: 44%).

Ligand 3ar $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.52 (d, $J = 2.0$ Hz, 1H), 7.31 (d, $J = 8.4$ Hz, 1H), 7.22 (dd, $J = 2.0$ Hz, 8.4 Hz, 1H), 6.96 (dd, $J = 11.2$ Hz, 17.2 Hz, 1H), 6.86-6.81 (m, 2H), 6.68 (td, $J = 1.2$ Hz, 7.6 Hz, 1H), 6.56 (dd, $J = 1.6$ Hz, 7.6 Hz, 1H), 5.73 (dd, $J = 0.8$ Hz, 17.2 Hz, 1H), 5.39 (dd, $J = 0.8$ Hz, 11.2 Hz, 1H), 4.56 (m, 1H), 4.33 (s, 3H), 1.35 (d, $J = 6.0$ Hz, 6H).

The procedure for preparation of Ru complex 4ar is the same as in Example 1 in 1.0 mmol scale. 499 mg of green solid product 4ar was obtained (yield: 65%).

Ru complex (4ar) $^1$HNMR (300 MHz, CDCl3): $\delta$ 18.82 (s, 1H, Ru=CH),
7.47-7.43 (m, 2H), 7.01-6.56 (m, 9H), 5.12-5.09 (m, 1H), 4.56-4.45 (m, 2H),
4.40-4.15 (m, 4H, NCH₂CH₂N), 3.48-3.45 (m, 1H), 2.64-2.04 (m, 18H), 1.10 (d, J =
6.4 Hz, 6H).

Example 39

Synthesis of Ru complex 4as

The synthetic procedure for preparation of ligand 3as is the same as in Example
1 in 5.0 mmol scale. 0.45g of yellow oil product 3as was obtained (yield: 34%).

Ligand 3as ¹H-NMR (400 MHz, CDCl₃): δ 8.20 (d, J = 1.5 Hz, 1H), 7.90 (dd, J =
1.5 Hz, 8.0 Hz, 1H), 7.45 (d, J = 8.0 Hz 1H.), 7.01 (dd, J = 11.5 Hz, 17.0 Hz, 1H),
6.83-6.80 (m, 2H), 6.67 (td, J = 2.0 Hz, 7.0 Hz, 1H), 6.52 (dd, J = 2.0 Hz, 7.5 Hz, 1H),
5.80 (d, J = 17.0 Hz, 1H), 5.42 (d, J = 11.5 Hz, 1H), 4.56 (m, 1H), 4.42 (s, 2H), 3.93
(s, 3H), 1.34 (d, J = 6.5 Hz, 6H).

The procedure for preparation of Ru complex 4as is the same as in Example 1 in
1.0 mmol scale. 467 mg of green solid product 4as was obtained (yield: 59%).

Ru complex (4as) ¹H-NMR (400 MHz, CDCl₃): δ 18.82 (s, 1H, Ru=CH), 8.15 (dd,
J = 6.4, 1.2 Hz, 2H), 7.51 (d, J = 1.2 Hz, 1H), 7.44 (d, J = 1.2 Hz, 1H), 7.05-6.99 (m,
5H), 8.15 (d, J = 6.4Hz, 2H), 6.59-6.56 (m, 1H), 5.22 (m, 1H), 4.63 (m, 1H),
4.41(m,1H), 3.96 (m, 4H, NCH₂CH₂N), 3.55-3.52 (m, 1H), 2.66-2.33 (m, 18H), 1.14
(d, J = 6.4 Hz, 6H).

Example 40

Synthesis of Ru complex 4at

The synthetic procedure for preparation of ligand 3at is the same as in Example
1 in 5.0 mmol scale. 0.53g of yellow oil product 3at was obtained (yield: 33%).

Ligand 3at ¹H-NMR (400 MHz, CDCl₃): δ 7.91 (s, 1H), 7.63 (d, J = 8.0 Hz, 1H),
7.56 (d, J = 8.0 Hz, 1H), 7.03 (dd, J = 11.2 Hz, 17.2 Hz, 1H), 6.88-6.82 (m, 2H), 6.74
(t, J = 8.0 Hz, 1H), 6.53 (d, J = 7.6 Hz, 1H), 5.81 (d, J = 17.2 Hz, 1H), 5.49 (d, J =
11.2 Hz, 1H), 4.44 (s, 2H), 3.88(s, 3H), 2.74 (s, 6H).
The procedure for preparation of Ru complex 4at is the same as in Example 1 in 1.0 mmol scale. 341 mg of green solid product 4at was obtained (yield: 42%).

Ru complex (4at) \(^1\)HNMR (400 MHz, CDCl\(_3\)): \(\delta\) 19.02 (s, 1H, Ru=CH), 7.87 (dd, \(J = 8.0, 1.2\) Hz, 1H), 7.44 (dd, \(J = 7.2, 1.2\) Hz, 1H), 7.25-7.03 (m, 9H), 5.37-5.30 (m, 1H), 4.76-4.74 (m, 1H), 4.16-4.01 (m, 4H, NCH\(_2\)CH\(_2\)N), 3.58-3.54 (m, 4H), 2.75 (s, 6H), 2.73-1.98 (m, 18H).

### Example 41

Synthesis of Ru complex 4au

The synthetic procedure for preparation of ligand 3au is the same as in Example 1 in 5.0 mmol scale. 0.58g of yellow oil product 3au was obtained (yield: 39%).

Ligand 3au \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.93 (s, 1H), 7.64 (d, \(J = 8.0\) Hz, 1H), 7.50 (d, \(J = 8.0\) Hz, 1H), 7.01 (dd, \(J = 10.8, 16.8\) Hz, 1H), 6.84-6.69 (m, 3H), 6.49 (d, \(J = 7.6\) Hz, 1H), 5.74 (d, \(J = 16.8\) Hz, 1H), 5.47 (d, \(J = 10.8\) Hz, 1H), 4.59-4.53 (m, 1H), 4.43 (s, 2H), 3.14 (t, \(J = 8\) Hz, 4H), 1.51 (m, 4H), 1.36 (d, \(J = 5.6\) Hz, 6H), 1.33-1.27 (m, 4H), 0.90 (t, \(J = 7.2\) Hz, 6H).

The procedure for preparation of Ru complex 4au is the same as in Example 1 in 1.0 mmol scale. 471 mg of green solid product 4au was obtained (yield: 51%).

Ru complex (4au) \(^1\)HNMR (300 MHz, CDCl\(_3\)): \(\delta\) 19.06 (s, 1H, Ru=CH), 7.87 (d, \(J = 7.6\) Hz, 1H), 7.42 (d, \(J = 7.6\) Hz, 1H), 7.29 (d, \(J = 12.0\) Hz, 1H), 7.11-6.56 (m, 8H), 5.22-5.19 (m, 1H), 4.63-4.64 (m, 1H), 4.45-4.42 (m, 1H), 4.14-4.01 (m, 4H, NCH\(_2\)CH\(_2\)N), 3.56-3.53 (m, 1H), 3.12-3.07 (m, 4H), 2.67-2.36 (m, 18H), 1.99-1.00 (m, 24H).

### Example 42

Synthesis of Ru complex 4av

The synthetic procedure for preparation of ligand 3av is the same as in Example 1 in 5.0 mmol scale. 0.65g of white solid product 3av was obtained (yield: 39%).

Ligand 3av \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) = 7.26 Hz) : 7.894 (s, 1H), 7.624
The procedure for preparation of Ru complex 4av is the same as in Example 1 in 1.0 mmol scale. 622 mg of green solid product 4av was obtained (yield: 74%).

Ru complex (4av)\(^1\)HNMR (300 MHz, CDCl\(_3\)): \(\delta\) 19.06 (s, 1H, Ru=CH), 7.87 (d, \(J = 7.6\) Hz, 1H), 7.42 (d, \(J = 7.6\) Hz, 1H), 7.11-6.56 (m, 9H), 5.27-5.20 (m, 1H), 4.64-4.61 (m, 1H), 4.46-4.44 (m, 1H), 4.14-4.01 (m, 4H, NCH\(_2\)CH\(_2\)N), 3.59-3.56 (m, 1H), 3.12-3.07 (m, 4H), 2.75 (s, 6H), 2.67-2.36 (m, 18H), 1.13 (d, \(J = 6.0\) Hz, 6H).

**Example 43**

Synthesis of Ru complex 4aw

The structure of ligand 3aw is the same as 3av for preparation of Ru complex 4aw, just another Ru complex reagent 1a was used instead of Ru reagent 1b.

The procedure for preparation of Ru complex 4aw is the same as in Example 2 in 1.0 mmol scale. 626 mg of green solid product 4aw was obtained (yield: 77%).

Ru complex (4aw)\(^1\)HNMR (400 MHz, CDCl\(_3\)): \(\delta\) 19.56 (d, \(J = 9.6\) Hz, Ru=CH), 8.21 (d, \(J = 8.0\) Hz, 1H), 8.09 (d, \(J = 2.0\) Hz, 1H), 8.10 (dd, \(J = 7.6, 2\) Hz, 1H), 7.34-6.87 (m, 4H), 5.47-5.44 (m, 1H), 5.33-5.27 (m, 1H), 4.62-4.56 (m, 1H), 3.99-3.96 (m, 1H), 2.80 (s, 6H), 2.30-1.24 (m, 39H, PCy\(_3\)).

**Example 44**

Synthesis of Ru complex 4ax

The synthetic procedure for preparation of ligand 3ax is the same as in Example 1 in 5.0 mmol scale. 0.77g of yellow product 3ax was obtained (yield: 55%). The product 3t is confirmed by LC-MS (M+H\(^+\)): m/z calculated: 431.2, found: 431.2, and directly used for preparation of the Ru complex 4ax.

The procedure for preparation of Ru complex 4ax is the same as in Example 1 in 1.0 mmol scale. 421 mg of green solid product 4ax was obtained (yield: 47%).
Ru complex (4ax) $^1$HNMR (400 MHz, CDCl$_3$): δ 18.99 (s, 1H, Ru=CH), 7.88 (dd, J = 8.0, 2.0 Hz, 1H), 7.44 (dd, J = 7.2, 1.2 Hz, 1H), 7.28-6.63 (m, 9H), 5.35-5.28 (m, 1H), 4.75-4.72 (m, 1H), 4.16-4.12 (m, 4H, NCH$_2$CH$_2$N), 3.61 (s, 3H), 3.56-3.52 (m, 4H), 3.10-3.06 (m, 4H), 2.63-2.05 (m, 18H), 1.37-0.98 (m, 14H).

Example 45

Synthesis of Ru complex 4ay

The synthetic procedure for preparation of ligand 3ay is the same as in Example 1 in 5.0 mmol scale. 0.56g of yellow oil product 3ay was obtained (yield: 31%).

Ligand 3ay $^1$H-NMR (400 MHz, CDCl$_3$): δ 8.02 (d, J = 1.6 Hz, 1H), 7.72 (dd, J = 1.6 Hz, 8.4 Hz, 1H), 7.51 (d, J = 8.4 Hz, 1H), 7.01 (dd, J = 10.8 Hz, 17.6 Hz, 1H), 6.84-6.80 (m, 2H), 6.70 (td, J = 1.2 Hz, 7.6 Hz, 1H), 6.48 (dd, J = 1.2 Hz, 8.0 Hz, 1H), 5.80 (d, J = 17.6 Hz, 1H), 5.48 (d, J = 10.8 Hz, 1H), 4.67 (bs, 1H), 4.58 (m, 1H), 4.44 (s, 2H), 3.22-3.15 (bm, 1H), 1.81-1.77 (bm, 2H), 1.68-1.63 (bm, 2H), 1.36 (d, J = 6 Hz, 6H), 1.32-1.12 (m, 6H).

The procedure for preparation of Ru complex 4ay is the same as in Example 1 in 1.0 mmol scale. 241 mg of green solid product 4ay was obtained (yield: 27%).

Ru complex (4ay) $^1$HNMR (400 MHz, CDCl$_3$): δ 19.03 (s, 1H, Ru=CH), 7.60 (d, J = 7.6 Hz, 1H), 7.43 (d, J = 3.6 Hz, 1H), 7.14 (s, 1H), 7.09-7.00 (m, 5H), 6.81-6.57(m, 3H), 5.22 (m, 1H), 4.64-4.61 (m, 1H), 4.64-4.42 (m, 2H), 4.15-4.02 (m, 4H, NCH$_2$CH$_2$N), 3.16 (m, 1H), 3.17 (m, 1H), 2.67-2.00 (m, 18H), 1.85-1.00 (m, 16H).

Example 46

Synthesis of Ru complex 4ba

The synthetic procedure for preparation of ligand 3ba is the same as in Example 1 in 5.0 mmol scale. 0.96g of yellow oil product 3ba was obtained (yield: 67%).

Ligand 3ba $^1$H NMR (CDCl$_3$, 400 MHz): δ 7.23 (m, 4H), 6.92 (m, 2H), 6.80 (m, 1H), 6.67 (m, 2H), 5.68 (d, 1H), 5.39 (d, 1H), 4.64 (s, 2H), 4.06 (s, 2H), 3.75 (s, 3H).
The procedure for preparation of Ru complex 4ba is the same as in Example 1 in 1.0 mmol scale. 176 mg of green solid product 4ba was obtained (yield: 22%).

Ru complex (4ba) $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 18.74 (s, 1H, Ru=CH), 7.25-7.24 (m, 1H), 7.19 (s, 1H), 7.14-7.04 (m, 7H), 6.93 (s, 1H), 6.71 (s, 1H), 6.41-6.40 (d, $J$=9.0 Hz, 1H), 6.10-6.07 (d, $J$=12.0 Hz, 1H), 4.52-4.49 (d, $J$=13.5Hz, 1H), 4.33-4.29 (d, $J$=18.5 Hz, 1H), 4.09 (s, 2H), 3.92 (s, 2H), 3.31 (s, 3H), 2.96-2.92 (d, $J$=19.0Hz, 1H), 2.83 (s, 3H), 2.71 (s, 3H), 2.47 (s, 3H), 2.39 (s, 3H), 2.06 (s, 3H), 2.02 (s, 3H).

Example 47

Synthesis of Ru complex 4bb

The synthetic procedure for preparation of ligand 3bb is the same as in Example 1 in 5.0 mmol scale. 1.13g of yellow oil product 3bb was obtained (yield: 71%).

Ligand 3bb $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.21 (m, 4H), 6.90 (m, 2H), 6.78 (m, 1H), 6.67 (d, 2H), 5.68 (d, 1H), 5.38 (d, 1H), 5.06 (m, 1H), 4.64 (s, 2H), 3.99 (s, 2H), 1.23 (d, 6H).

The procedure for preparation of Ru complex 4bb is the same as in Example 1 in 1.0 mmol scale. 237 mg of green solid product 4bb was obtained (yield: 30%).

Ru complex (4bb) $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 18.74 (s, 1H, Ru=CH), 7.27-7.25 (dd, $J$=8.0, 3.0 Hz, 1H), 7.19 (s, 1H), 7.14-7.05 (m, 7H), 6.93 (s, 1H), 6.71 (s, 1H), 6.42-6.40 (d, $J$=9.0 Hz, 1H), 6.07-6.05 (d, $J$=12.5 Hz, 1H), 4.65-4.61 (m, 1H), 4.51-4.49 (d, $J$=12.5 Hz, 1H), 4.24-4.20 (d, $J$=18.0 Hz, 1H), 4.10 (s, 2H), 3.92 (s, 2H), 2.90-2.86 (d, $J$=18 Hz, 1H), 2.83 (s, 3H), 2.71 (s, 3H), 2.47 (s, 3H), 2.39 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H), 0.90-0.82 (d, $J$=33.0, 6.5 Hz, 6H).

Example 48

Synthesis of Ru complex 4bc

The synthetic procedure for preparation of ligand 3bc is the same as in Example 1 in 5.0 mmol scale. 0.74g of yellow oil product 3bc was obtained (yield: 43%).
Ligand 3bc \( ^1H \) NMR (CDCl\(_3\), 400 MHz): \( \delta \) 7.23 (m, 2H), 6.92 (m, 2H), 6.81 (m, 2H), 6.67 (m, 2H), 5.67 (d, 1H), 5.37 (d, 1H), 5.05 (m, 1H), 4.57 (s, 2H), 3.98 (s, 2H), 3.77 (s, 3H), 1.22 (d, 6H).

The procedure for preparation of Ru complex 4bc is the same as in Example 1 in 1.0 mmol scale. 578 mg of green solid product 4bc was obtained (yield: 73%).

Ru complex (4bc) \(^1\)HNMR (400 MHz, CDCl\(_3\)): \( \delta \) 18.72 (s, 1H, Ru=CH), 7.24-7.22 (dd, \( J=8.5, 2.5 \) Hz, 1H), 7.16 (s, 1H), 7.07-7.04 (m, 4H), 6.91 (s, 1H), 6.75 (s, 1H), 6.66 (s, 1H), 6.64(s, 1H), 6.39-6.38 (d, \( J=8.0 \) Hz, 1H), 6.02-6.00 (d, \( J=12.0 \) Hz, 1H), 4.64-4.59 (m, 1H), 4.50-4.47 (d, \( J=13.0 \) Hz, 1H), 4.13-4.09 (d, \( J=18 \) Hz, 1H), 4.08 (s, 2H), 3.90 (s, 2H), 3.83(s, 3H), 2.81 (s, 3H), 2.81-2.79 (d, \( J=11.5 \) Hz, 1H), 2.69 (s, 3H), 2.45 (s, 3H), 2.39 (s, 3H), 2.08 (s, 3H), 2.01 (s, 3H), 0.89-0.81 (dd, \( J=34.0, 6.0 \) Hz, 6H).

Example 49

Synthesis of Ru complex 4bd

The synthetic procedure for preparation of ligand 3bd is the same as in Example 1 in 5.0 mmol scale. 0.96g of yellow oil product 3bd was obtained (yield: 52%).

Ligand 3bd \(^1H \) NMR (CDCl\(_3\), 400 MHz): \( \delta \) 7.21 (m, 2H), 7.16 (m, 2H ,), 6.86 (m, 2H), 6.58 (m, 2H), 5.68 (d, 1H), 5.39 (d, 1H), 5.06 (m, 1H), 4.60 (s, 2H), 3.97 (s, 2H), 1.23 (d, 6H).

The procedure for preparation of Ru complex 4bd is the same as in Example 1 in 1.0 mmol scale. 236 mg of green solid product 4bd was obtained (yield: 29%).

Ru complex (4bd) \(^1\)HNMR (400 MHz, CDCl\(_3\)): \( \delta \) 18.72 (s, 1H, Ru=CH), 7.28-7.26 (m, 1H), 7.19 (s, 1H), 7.10-7.05 (m, 6H), 6.94 (s, 1H), 6.82 (s, 1H), 6.41-6.39 (d, \( J=9.5 \) Hz, 1H), 6.07-6.04 (d, \( J=12.0 \) Hz, 1H), 4.68-4.64 (m, 1H), 4.45-4.43 (d, \( J=12.5 \) Hz, 1H), 4.24-4.20 (d, \( J=18.0 \) Hz, 1H), 4.09 (s, 2H), 3.93(s, 2H), 2.91-2.87 (d, \( J=18.5 \) Hz, 1H), 2.81 (s, 3H), 2.79 (s, 3H), 2.47 (s, 6H), 2.10 (s, 3H), 2.03 (s, 3H), 0.93-0.87 (dd, \( J=24.0, 7.0 \) Hz, 6H).
Example 50

Synthesis of Ru complex 4be

The synthetic procedure for preparation of ligand 3be is the same as in Example 1 in 5.0 mmol scale. 1.46g of yellow oil product 3be was obtained (yield: 84%).

Ligand 3be H NMR (CDCl₃, 400 MHz): δ 7.23 (m, 2H), 6.91 (m, 4H), 6.61 (m, 2H), 5.68 (d, 1H), 5.38 (d, 1H), 5.05 (m, 1H), 4.58 (s, 2H), 3.95 (s, 2H), 1.23 (d, 6H).

The procedure for preparation of Ru complex 4be is the same as in Example 1 in 1.0 mmol scale. 396 mg of green solid product 4be was obtained (yield: 49%).

Ru complex (4be) ¹H NMR (400 MHz, CDCl₃): δ 18.71 (s, 1H, Ru=CH), 7.29-7.25 (dd, J=8.5, 2.5 Hz, 1H), 7.19 (s, 1H), 7.13-7.06 (m, 4H), 6.94 (s, 1H), 6.82-6.77 (m, 3H), 6.42-6.39 (dd, J=9.5, 2.5 Hz, 1H), 6.08-6.05 (d, J=13.0 Hz, 1H), 4.66-4.64 (m, 1H), 4.47-4.45 (d, J=12.5 Hz, 1H), 4.21-4.18 (d, J=18 Hz, 1H), 4.10 (s, 2H), 3.93 (s, 2H), 3.89-3.86 (d, J=18 Hz, 1H), 2.83 (s, 3H), 2.70 (s, 3H), 2.48 (s, 3H), 2.42 (s, 3H), 2.11 (s, 3H), 2.02 (s, 3H), 0.92-0.85 (dd, J=26.5, 7.0 Hz, 3H).

Example 51

Synthesis of Ru complex 4bf

The synthetic procedure for preparation of ligand 3bf is the same as in Example 1 in 5.0 mmol scale. 0.68g of yellow oil product 3bf was obtained (yield: 51%).

Ligand 3bf ¹H NMR (CDCl₃, 400 MHz): δ 7.26 (m, 1H), 7.22 (m, 2H), 6.92 (m, 1H), 5.68 (d, 1H), 5.37 (d, 1H), 5.09 (m, 1H), 3.74 (s, 2H), 3.26 (s, 2H), 2.30 (m, 3H), 1.26 (d, 6H).

The procedure for preparation of Ru complex 4bf is the same as in Example 1 in 1.0 mmol scale. 76 mg of green solid product 4bf was obtained (yield: 10%).

Ru complex (4bf) ¹H NMR (400 MHz, CDCl₃): δ 18.54 (s, 1H, Ru=CH), 7.16-6.87 (m, 7H), 6.15-6.13 (dd, J=10.0, 2.0 Hz, 1H), 5.44-5.41 (d, J=13.5 Hz, 1H), 4.76-4.71 (m, 1H), 4.37-4.34 (d, J=15.5 Hz, 1H), 3.96 (s, 4H, NCH₂CH₂N), 3.07-3.05 (d, J=13 Hz, 1H), 2.75-2.40 (m, 18H), 1.66 (s, 3H), 1.21-1.17 (dd, J=13.0, 6.5 Hz, 6H).
Example 52

Synthesis of Ru complex 4bg

The synthetic procedure for preparation of ligand 3bg is the same as in Example 1 in 5.0 mmol scale. 0.83g of yellow oil product 3bg was obtained (yield: 59%).

Ligand 3bg \(^1^H\) NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.24 (m, 2H), 6.93 (m, 2H), 6.70 (m, 1H), 6.30 (m, 2H), 5.71 (d, 1H), 5.40 (d, 1H), 4.58 (s, 1H), 4.44 (m, 1H), 4.29 (s, 2H), 1.28 (d, 6H).

The procedure for preparation of Ru complex 4bg is the same as in Example 1 in 1.0 mmol scale. 302mg of green solid product 4bg was obtained (yield: 39%).

Ru complex (4bg) \(^1^H\) NMR (400 MHz, CDCl\(_3\)): \(\delta\) 18.91 (s, 1H, Ru=CH), 7.60-7.58 (dd, \(J = 9.5\), 2.5 Hz, 1H), 7.24-7.20 (m, 1H), 7.13-7.05 (m, 3H), 6.94-6.92 (dd, \(J = 8.0\), 6.0 Hz, 1H), 6.80 (brs, 1H), 6.74-6.70 (m, 1H), 6.64-6.61 (dd, \(J = 9.0\), 5.0 Hz, 1H), 6.45-6.43 (dd, \(J = 10.5\), 3.0 Hz, 1H), 5.20-5.15 (t, \(J = 13.5\), 1H, NCH\(_2\)), 4.69-4.67 (d, \(J = 12.5\) Hz, 1H, NCH\(_2\)), 4.38-4.33 (m, 1H, OCH(CH\(_3\))\(_2\)), 4.12-4.08(m, 4H, NCH\(_2\)CH\(_2\)N), 3.47-3.45 (d, \(J = 12.5\) Hz, 1H, NH), 2.65 (s, 6H), 2.56 (s, 6H), 2.26 (s, 3H), 2.09 (s, 3H), 1.14-1.12 (dd, \(J = 6.0\), 4.0 Hz, 6H, OCH(CH\(_3\))\(_2\)).

Example 53

Synthesis of Ru complex 4bh

The synthetic procedure for preparation of ligand 3bh is the same as in Example 1 in 5.0 mmol scale. 0.94g of yellow oil product 3bh was obtained (yield: 78%).

Ligand 3bh \(^1^H\) NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.99 (s, 1H), 7.95-7.93 (m, 1H), 7.55-7.53 (d, 1H), 7.36-7.32 (m, 2H), 7.30-7.23 (m, 2H), 7.03-6.98 (m, 1H), 6.66-6.61 (m, 2H), 5.72-5.68 (m, 1H), 5.36-5.34 (m, 1H), 4.46-4.45 (d, 2H), 3.85 (s, 3H).

The procedure for preparation of Ru complex 4bh is the same as in Example 1 in 1.0 mmol scale. 542mg of green solid product 4bh was obtained (yield: 74%).

Ru complex (4bh) \(^1^H\) NMR (400 MHz, CDCl\(_3\)): \(\delta\) 18.89 (s, 1H, Ru=CH), 7.91-7.89 (d, \(J = 8.0\) Hz, 1H), 7.76-7.74 (dd, \(J = 8.0\), 1.5 Hz, 1H), 7.51-7.48 (td, \(J = 8.5\), 7.0, 1.5 Hz,
1H), 7.25-7.21 (td, J = 13.5, 11.0, 2.0 Hz, 1H), 7.19-7.16 (t, J = 8.0 Hz, 1H), 7.12-7.09 (t, J = 7.5 Hz, 2H), 7.04-7.03 (d, J = 7.0 Hz, 1H), 7.00-6.88 (m, 3H), 6.78-6.76 (d, J = 7.0 Hz, 1H), 6.65 (brs, 1H, NH), 6.64-6.59 (t, J = 12.5 Hz, 1H, NCH2), 4.08 (brs, 2H, NCH2CH2N), 3.99 (brs, 2H, NCH2CH2N), 3.72-3.69 (dd, J = 13.5, 2.0 Hz, 1H, NCH2), 3.67 (s, 3H, COOCH3), 2.62-2.03 (m, 18H).

**Example 54**

Synthesis of Ru complex 4bj

The synthetic procedure for preparation of ligand 3bj is the same as in Example 1 in 5.0 mmol scale. 0.99g of yellow oil product 3bj was obtained (yield: 82%).

Ligand 3bj 1H NMR (CDCl3, 400 MHz): δ 7.58-7.57 (d, 1H), 7.38-7.36 (d, 1H), 7.32-7.25 (m, 2H), 7.08-7.00 (m, 3H), 6.74-6.70 (m, 1H), 6.65-6.63 (d, 1H), 5.73-5.69 (m, 1H), 5.33-5.30 (m, 1H), 4.90 (s, 1H), 4.35 (s, 2H), 2.63 (s, 6H).

The procedure for preparation of Ru complex 4bj is the same as in Example 1 in 1.0 mmol scale. 508mg of green solid product 4bj was obtained (yield: 69%).

Ru complex (4bj) 1HNMR (400 MHz, CDCl3): δ 18.90 (s, 1H, Ru=CH), 7.63-7.61 (d, J = 7.5 Hz, 1H), 7.49-7.46 (t, J = 7.0 Hz, 1H), 7.19-7.16 (t, J = 8.0 Hz, 1H), 7.11-6.95 (m, 6H), 6.87-6.84 (t, J = 8.0 Hz, 1H), 6.80-6.79 (d, J = 7.5 Hz, 1H), 6.72 (brs, 1H), 6.68-6.65 (d, J = 11.5 Hz, 1H, NCH2), 5.50-5.45 (t, J = 13.0 Hz, 1H, NCH2), 4.15-3.96 (m, 4H, NCH2CH2N), 3.51-3.48 (d, J = 13.5 Hz, 1H, NH), 2.66-2.30 (m, 21H, aromatic CH3, NCH3), 2.05 (brs, 3H, NCH3).

**Example 55**

Synthesis of Ru complex 6a

SM1-5a (5.0mmol) and SM2-5a (5.0mmol) was added into a 50 mL of three-neck round-bottom flask filled with inert gas (Ar), and followed by adding anhydrous DCM (10 mL) and Na2SO4 (5 eq) was added. The reaction was stirred until completed overnight (monitored by TLC). The reaction mixture was filtered, and the crude imine product 5a (1.25g, 97%) was obtained by removing all DCM solvent.
under vacuum. The crude imine product 5a was directly used for next step to prepare Ru complex 6a.

To a 50 mL two-necked round bottom flask, after filling with Ar atmosphere, were added ligand 5a (1.0mmol) and CuCl (3.0mmol, 3eq) and 30 mL dry DCM, followed by refilling with Ar three times and protected with Ar balloon in close system. Ru complex 1b (1.0mmol) was added under Ar protection, and the mixture was stirred for 0.5 hr at room temperature.

After the reaction was complete, the solution was filtered and the filtrate was concentrated and slurried with silica gel. The crude was obtained by silica gel column chromatography and washed with methanol or pentane-DCM to obtain 453mg of yellow-green solid product 6a, yield: 79%.

Ru complex (6a)\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 18.53 (s, 1H, Ru=CH), 8.59 (s, 1H), 7.28-6.49 (m, 11H), 4.160 (s, 4H, NCH\textsubscript{2}CH\textsubscript{2}N), 2.50 (s, 12H), 2.42 (s, 6H).

Example 56

Synthesis of Ru complex 6b

The synthetic procedure for preparation of ligand 5b is the same as in Example 52 in 5.0 mmol scale. 1.21g of crude imine product 5b was obtained (yield: 95%), and it was directly used for next step to prepare Ru complex 6b.

To a 50 mL two-necked round bottom flask, after filling with Ar atmosphere, were added ligand 5b (1.0mmol) and CuCl (3.0mmol, 3eq) and 30 mL dry DCM, followed by refilling with Ar three times and protected with Ar balloon in close system. Ru complex 1a (1.0mmol) was added under Ar protection, and the mixture was stirred for 0.5 hr at room temperature.

After the reaction was complete, the solution was filtered and the filtrate was concentrated and slurried with silica gel. The crude was obtained by silica gel column chromatography and washed with methanol or pentane-DCM to obtain 414mg yellow-green solid product 6b, yield: 77%.

Ru complex (6b)\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 19.20 (d, J = 10.8 Hz, Ru=CH), 8.82 (d, J = 9.2 Hz, 1H), 7.84 (m, 1H), 7.80 (d, J = 8.4 Hz, 1H), 7.45 (m, 4H),
2.46-1.29 (m, 33H, PCy,).

**Example 57**

Synthesis of Ru complex 6c

The synthetic procedure for preparation of ligand 5c is the same as in Example 52 in 5.0 mmol scale. 1.16g of crude imine product 5c was obtained (yield: 92%), and it was directly used for next step to prepare Ru complex 6c.

The synthetic procedure is the same as in Example 52 in 1.0 mmol scale. 664 mg of yellow-green solid product 6c was obtained (96% yield).

**Ru complex (6c)** \(^1\)HNM R (400 MHz, CDCl,): \(\delta\) 18.52 (s, 1H, Ru=CH), 8.60 (s, 1H), 7.28-7.13 (m, 7H), 7.02 (d, \(J = 8.8\) Hz, 1H), 6.80 (m, 1H), 6.09 (d, \(J = 8.8\) Hz, 1H), 4.16 (s, 4H, NCH,CH,2N), 3.84 (s, 3H), 2.51 (m, 18H).

**Example 58**

Synthesis of Ru complex 6d

The synthetic procedure for preparation of ligand 5d is the same as in Example 52 in 5.0 mmol scale. 1.18g of crude imine product 5d was obtained (yield: 94%), and it was directly used for next step to prepare Ru complex 6d.

The synthetic procedure is the same as in Example 52 in 1.0 mmol scale. 68 mg of yellow-green solid product 6d was obtained (31% yield).

**Ru complex (6d)** \(^1\)HNM R (400 MHz, CDCl,): \(\delta\) 18.73 (s, 1H, Ru=CH), 8.62 (s, 1H), 7.67-7.46 (m, 3H), 7.11 (s, 4H), 6.78-6.65 (m, 5H), 4.13 (s, 4H, NCH,CH,2N), 3.81 (s, 3H), 2.49 (m, 18H).

**Example 59**

Synthesis of Ru complex 6e

The synthetic procedure for preparation of ligand 5e is the same as in Example 52 in 5.0 mmol scale. 1.13g of crude imine product 5e was obtained (yield: 93%), and it was directly used for next step to prepare Ru complex 6e.

The synthetic procedure is the same as in Example 52 in 1.0 mmol scale. 41 mg
of yellow-green solid product 6e was obtained (24% yield).

Ru complex (6e)\(^1\)H-NMR (400 MHz, CDCl\(_3\)): δ 18.74 (s, 1H, Ru=CH), 8.60 (s, 1H), 7.69-7.49 (m, 3H), 7.12-7.04 (m, 8H), 6.80 (d, \(J = 8.7\) Hz, 1H), 4.13 (s, 4H, NCH\(_2\)CH\(_2\)N), 2.50 (m, 18H).

**Example 60**

Synthesis of Ru complex 6f

The synthetic procedure for preparation of ligand 5f is the same as in Example 52 in 5.0 mmol scale. 1.28 g of crude imine product 5f was obtained (yield: 94%), and it was directly used for next step to prepare Ru complex 6f.

The synthetic procedure is the same as in Example 52 in 1.0 mmol scale. 664 mg of yellow-green solid product 6f was obtained (17% yield).

Ru complex (6f)\(^1\)H-NMR (400 MHz, CDCl\(_3\)): δ 18.60 (s, 1H, Ru=CH), 8.58 (s, 1H), 7.48-7.29 (m, 2H), 7.02 (d, \(J = 8.8\) Hz, 2H), 6.74-6.69 (m, 3H), 4.17 (s, 4H, NCH\(_2\)CH\(_2\)N), 3.85 (s, 3H), 2.52 (m, 18H).

**Example 61**

Synthesis of Ru complex 6g

The synthetic procedure for preparation of ligand 5g is the same as in Example 52 in 5.0 mmol scale. 1.23 g of crude imine product 5g was obtained (yield: 96%), and it was directly used for next step to prepare Ru complex 6g.

The synthetic procedure is the same as in Example 52 in 1.0 mmol scale. 35 mg of green solid product 6g was obtained (22% yield).

Ru complex (6g)\(^1\)H-NMR (400 MHz, CDCl\(_3\)): δ 18.66 (s, 1H, Ru=CH), 8.56 (s, 1H), 7.50-7.34 (m, 2H), 7.26 (s, 4H), 7.00-6.40 (m, 5H), 4.14 (s, 4H, NCH\(_2\)CH\(_2\)N), 3.81 (s, 3H), 2.49 (m, 18H).

**Example 62**

Synthesis of Ru complex 6h

The synthetic procedure for preparation of ligand 5h is the same as in Example
52 in 5.0 mmol scale. 1.29g of crude imine product 5h was obtained (yield: 96%), and it was directly used for next step to prepare Ru complex 6h.

The synthetic procedure is the same as in Example 52 in 1.0 mmol scale. 106 mg of yellow-green solid product 6h was obtained (37% yield).

Ru complex (6h) \(^1\)HNMR (400 MHz, CDCl\(_3\)): \(\delta\) 16.52 (s, 1H, Ru=CH), 8.43 (s, 1H, N=CH), 8.10 (s, 1H), 7.46-7.22 (m, 2H), 7.73-6.96 (m, 8H), 4.19 (s, 4H, NCH\(_2\)CH\(_2\)N), 3.95 (s, 3H), 3.87 (s, 3H), 2.49 (s, 12H), 2.48 (s, 6H).

**Example 63**

Synthesis of Ru complex 6j

The synthetic procedure for preparation of ligand 5j is the same as in Example 52 in 5.0 mmol scale. 1.31g of crude imine product 5j was obtained (yield: 97%), and it was directly used for next step to prepare Ru complex 6j.

The synthetic procedure is the same as in Example 52 in 1.0 mmol scale. 190 mg of red solid product 6j was obtained, and the product 6j is unstable and difficult to detect the structure by \(^1\)HNMR. But the crude Ru complex 6j could be directly used for metathesis reaction.

**Example 64**

Synthesis of Ru complex 8a

The synthetic procedure for preparation of ligand 7a is the same as in Example 1 in 5.0 mmol scale. 0.26g of oily product 7a was obtained (yield: 28%).

Ligand 7a \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.21 (dd, \(J = 18.0, 11.20\) Hz, 1H), 7.00 (td, \(J = 9.2, 2.8, 1.6\) Hz, 1H), 6.73-6.67 (m, 1H), 5.67 (dd, \(J = 18.0, 1.2\) Hz, 1H), 5.34 (d, \(J = 11.2\) Hz, 1H), 2.77 (d, \(J = 2.4\) Hz, 6H).

The procedure for preparation of Ru complex 8a is the same as in Example 1 in 1.0 mmol scale. 208 mg of green solid product 8a was obtained, yield: 32%.

Ru complex (8a) \(^1\)HNMR (400 MHz, CDCl\(_3\)): \(\delta\)16.80 (s, 1H, Ru=CH), 7.07 (s, 4H, aromatic H), 6.94 (m, 1H), 6.30 (d, \(J = 6.4\) Hz, 1H), 4.11 (s, 4H, NCH\(_2\)CH\(_2\)N),
2.69 (s, 6H), 2.49 (s, (s, 12H), 2.42 (s, 6H).

**Example 65**

Synthesis of Ru complex 8b

The synthetic procedure for preparation of ligand 7b is the same as in Example 1 in 5.0 mmol scale. 0.89g of solid product 7b was obtained (yield: 92%).

Ligand 7b \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.25 (d, \(J = 2.7\) Hz, 1H), 8.05 (dd, \(J = 8.7\) Hz, 2.4 Hz, 1H), 6.90 (d, \(J = 9.0\) Hz, 1H), 6.82 (dd, \(J = 17.4, 11.1\) Hz, 1H), 5.77 (dd, \(J = 17.7, 0.9\) Hz, 1H), 5.37 (dd, \(J = 10.8, 0.6\) Hz, 1H), 2.92 (s, 6H).

The procedure for preparation of Ru complex 8b is the same as in Example 1 in 1.0 mmol scale. 59 mg of green solid product 8b was obtained (yield: 9%).

Ru complex (8b) \(^1\)HNMR (400 MHz, CDCl\(_3\)): \(\delta\) 16.97 (s, 1H, Ru=CH), 8.40 (dd, \(J = 8.8, 2.4\) Hz, 1H), 7.65 (d, \(J = 2.4\) Hz, 1H), 7.29 (d, \(J = 8.8\) Hz, 1H), 7.07 (s, 4H), 4.20 (s, 4H, NCH\(_2\)CH\(_2\)N), 2.57 (s, 6H), 2.47 (s, 12H), 2.39 (s, 6H).

**Example 66**

Synthesis of Ru complex 8c

The synthetic procedure for preparation of ligand 7c is the same as in Example 1 in 5.0 mmol scale. 0.96g of yellow oil product 7c was obtained (yield: 96%).

Ligand 7c \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.19 (d, \(J = 2.8\) Hz, 1H), 7.98 (dd, \(J = 9.0, 2.8\) Hz, 1H), 6.86 (d, \(J = 9.0\) Hz, 1H), 6.73 (dd, \(J = 17.6, 11.2\) Hz, 1H), 5.69 (d, \(J = 17.6\) Hz, 1H), 5.29 (d, \(J = 11.2\) Hz, 1H), 3.12 (q, 2H, \(J = 6.8\) Hz), 2.78 (s, 3H), 1.09 (t, \(J = 6.8\) Hz, 3H).

The procedure for preparation of Ru complex 8c is the same as in Example 1 in 1.0 mmol scale. 161 mg of green solid product 8c was obtained (24% yield).

Ru complex (8c) \(^1\)HNMR (400 MHz, CDCl\(_3\)): \(\delta\) 16.69 (s, 1H, Ru=CH), 8.36 (dd, \(J = 8.8, 2.4\) Hz, 1H), 7.62 (d, \(J = 2.4\) Hz, 1H), 7.18 (d, \(J = 8.8\) Hz, 1H), 7.17-7.00 (m, 4H, 4.16-3.80 (m, 6H), 2.84-2.08 (m, 21H), 0.57 (t, \(J = 6.8\) Hz, 3H).
Example 67

Synthesis of Ru complex 8d

The synthetic procedure for preparation of ligand 7d is the same as in Example 1 in 5.0 mmol scale. 1.02g of yellow oil product 7d was obtained (yield: 92%).

Ligand 7d $^1$H NMR (400 MHz, CDCl$_3$): 8.27 (d, $J = 2.7$ Hz, 1H), 8.05 (dd, $J = 9.0$, 3.0 Hz, 1H), 6.92 (d, $J = 9.0$ Hz, 1H), 6.75 (dd, $J = 18.0$, 10.8 Hz, 1H), 5.77 (dd, $J = 17.7$, 0.9 Hz, 1H), 5.34 (dd, $J = 1.2$ Hz, 10.8 Hz, 1H), 3.71 (m, 1H), 2.74 (s, 3H), 1.13 (d, $J = 6.6$ Hz, 6H).

The procedure for preparation of Ru complex 8d is the same as in Example 1 in 1.0 mmol scale. 103mg green solid product 8d was obtained, yield: 15%.

The product is unstable, so it is difficult to detect the structure by $^1$HNMR. But the crude Ru complex 8d could be directly used for metathesis reaction.

Example 68

Synthesis of Ru complex 8e

The synthetic procedure for preparation of ligand 7e is the same as in Example 1 in 5.0 mmol scale. 0.63g of yellow oil product 7e was obtained (yield: 37%).

Ligand 7e $^1$H-NMR (400 MHz, CDCl$_3$): δ 8.11-8.06 (m, 2H, aromatic H), 6.65-6.55 (m, 2H, aromatic H, CH=CH$_2$), 5.61 (d, $J = 17.1$ Hz, CH=CH$_2$), 5.47 (d, $J = 10.8$ Hz, CH=CH$_2$), 4.43 (s, 1H, NH), 3.78-3.74 (m, 1H, NCH), 1.28 (d, $J = 7.8$ Hz, NCH(CH$_3$)$_2$).

The procedure for preparation of Ru complex 8e is the same as in Example 1 in 1.0 mmol scale. 74mg green solid product 8e was obtained, yield: 15%.

The product is unstable, so it is difficult to detect the structure by $^1$HNMR. But the crude Ru complex 8e could be directly used for metathesis reaction.

Example 69

Synthesis of Ru complex 8f

The synthetic procedure for preparation of ligand 7f is the same as in Example 1
in 5.0 mmol scale. 0.68g of yellow oil product 7f was obtained (yield: 66%).

Ligand 7f $^1$HNMR (400 MHz, CDCl$_3$): δ 8.11 (d, $J = 2.0$ Hz, 1H), 7.89 (dd, $J = 8.8$, 2.0 Hz, 1H), 6.96 (d, $J = 8.8$ Hz, 1H), 6.91 (dd, $J = 12.0$, 18.4 Hz, 1H), 5.76 (dd, $J = 18.40$, 1.20 Hz, 1H), 5.31 (dd, $J = 12.0$, 1.2 Hz, 1H), 3.90 (s, 3H), 2.83 (s, 6H).

The procedure for preparation of Ru complex 8f is the same as in Example 1 in 1.0 mmol scale. 396 mg of green solid product 8f was obtained (yield: 59%).

Ru complex (8f) $^1$HNMR (400 MHz, CDCl$_3$): δ 16.80 (s, 1H, Ru=CH), 8.18 (dd, $J = 8.8$, 2.4 Hz, 1H), 7.46 (d, $J = 2.4$ Hz, 1H), 7.23 (d, $J = 8.8$ Hz, 1H), 7.07 (s, 4H), 4.11 (s, 4H, NCH$_2$CH$_2$N), 3.91 (s, 3H), 2.58 (s, 6H), 2.47 (s, 12H), 2.43 (s, 6H).

**Example 70**

Synthesis of Ru complex 8g

The synthetic procedure for preparation of ligand 7g is the same as in Example 1 in 5.0 mmol scale. 1.03g of yellow oil product 7g was obtained (yield: 96%).

Ligand 7g $^1$H NMR (CDCl$_3$, 400Hz): δ 7.45-7.44 (m, 1H), 7.25-7.21 (m, 1H), 7.12-7.10 (m, 1H), 7.05-6.99 (m, 2H), 5.69-5.65 (m, 1H), 5.27-5.25 (m, 1H), 3.80 (s, 2H), 3.70 (s, 3H), 2.90 (s, 3H).

The procedure for preparation of Ru complex 8g is the same as in Example 1 in 1.0 mmol scale. 530 mg of green solid product 8g was obtained (yield: 79%).

Ru complex (8g) $^1$HNMR (400 MHz, CDCl$_3$): δ 16.70 (s, 1H, Ru=CH), 7.37 (m, 1H), 7.04-6.91 (m, 6H), 6.72 (d, $J = 7.6$ Hz, 1H), 5.05 (d, $J = 11.6$ Hz, 1H), 3.88-3.85 (m, 4H, NCH$_2$CH$_2$N), 3.52 (s, 3H), 3.44 (d, $J = 11.6$ Hz, 1H), 2.85-1.50 (m, 21H).

**Example 71**

Synthesis of Ru complex 8h

The synthetic procedure for preparation of ligand 7h is the same as in Example 1 in 5.0 mmol scale. 0.64g of product 7h was obtained (yield: 51%). The product 7h is confirmed by LC-MS (M+H$^+$): m/z calculated: 251.2, found: 251.2, and directly used for preparation of the Ru complex 8h.
The procedure for preparation of Ru complex **8h** is the same as in Example 1 in 1.0 mmol scale. 530 mg of green solid product **8h** was obtained (yield: 74%).

Ru complex (**8h**)<sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>): δ 16.56 (s, 1H, Ru=CH), 8.33 (dd, J = 8.4, 2.4 Hz, 1H), 7.56 (d, J = 2.4 Hz), 7.20-6.94 (m, 5H), 5.22 (d, J = 11.2 Hz, 1H), 4.21-3.96 (m, 4H, NCH<sub>2</sub>CH<sub>2</sub>N), 3.56 (s, 3H), 3.54 (d, J = 11.2 Hz, 1H), 2.94-0.92 (m, 21H).

**Example 72**

**Synthesis of Ru complex 8j**

The synthetic procedure for preparation of ligand **7j** is the same as in Example 1 in 5.0 mmol scale. 0.58g of yellow oil product **7j** was obtained (yield: 46%).

Ligand **7j**<sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>): δ 8.24 (d, J = 2.8 Hz, 1H), 8.08 (dd, J = 8.8, 8.2 Hz, 1H), 7.03 (d, J = 8.8 Hz, 1H), 6.79 (dd, J = 17.6, 10.8 Hz, 1H), 5.79 (dd, J = 17.6, 1.2 Hz, 1H), 5.4 (dd, J = 10.8, 1.2 Hz, 1H), 5.05 (m, 1H), 3.94 (s, 2H), 3.024 (s, 3H), 1.24 (d, J = 6.4 Hz, 6H).

The procedure for preparation of Ru complex **8j** is the same as in Example 1 in 1.0 mmol scale. 320 mg of green solid product **8j** was obtained (yield: 43%).

Ru complex (**8j**)<sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>): δ 16.64 (s, 1H, Ru=CH), 8.34 (dd, J = 8.4, 2.4 Hz, 1H), 7.54 (d, J = 2.4 Hz, 1H), 7.25-6.93 (m, 5H), 5.17 (d, J = 11.2 Hz, 1H), 4.84-4.83 (m, 1H), 4.14-3.93 (m, 4H, NCH<sub>2</sub>CH<sub>2</sub>N), 3.45 (d, J = 11.2 Hz, 1H), 2.89-1.19 (m, 27 H).

**Example 73**

**Synthesis of Ru complex 8k**

The synthetic procedure for preparation of ligand **7k** is the same as in Example 1 in 5.0 mmol scale. 0.53g of product **7k** was obtained (yield: 44%). The product **7k** is confirmed by LC-MS (M+H<sup>+</sup>): m/z calculated: 251.2, found: 251.2, and directly used for preparation of the Ru complex **8k**.

The procedure for preparation of Ru complex **8k** is the same as in Example 1 in
1.0 mmol scale. 530 mg of green solid product 8k was obtained (yield: 74%).

Ru complex (8k) $^1$HNMR (400MHz, CDCl$_3$): $\delta$ 16.70 (s, 1H, Ru=CH), 7.18-7.13 (m, 3H), 7.05 (s, 1H), 6.96-6.94 (m, 2H), 6.48-6.45 (dd, J=8.0, 2.0 Hz, 1H), 5.19-5.16 (d, J=15.5 Hz, 1H), 4.17 (s, 2H), 3.94 (s, 2H), 3.62 (s, 3H), 3.50-3.47 (d, J=15.5 Hz, 1H), 2.94 (s, 3H), 2.80 (s, 3H), 2.49 (s, 3H), 2.32 (s, 6H), 2.00 (s, 6H).

Example 74

Synthesis of Ru complex 8m

The synthetic procedure for preparation of ligand 7m is the same as in Example 1 in 5.0 mmol scale. 0.76g of yellow oil product 7m was obtained (yield: 68%).

Ligand 7m $^1$H-NMR (CDCl$_3$, 400Hz): $\delta$ 7.15-7.13 (m, 1H), 7.11-7.08 (m, 1H), 7.05-6.99 (m, 1H), 6.93-6.89 (m, 1H), 5.68-5.65 (m, 1H), 5.32-5.30 (d, 1H), 3.74 (s, 2H), 3.69 (s, 3H), 2.86 (s, 3H).

The procedure for preparation of Ru complex 8m is the same as in Example 1 in 1.0 mmol scale. 430 mg of green solid product 8m was obtained (yield: 41%).

Ru complex (8m) $^1$HNMR (400MHz, CDCl$_3$): $\delta$ 16.67 (s, 1H, Ru=CH), 7.10-7.16 (m, 3H), 7.02 (s, 1H), 6.91-6.94 (m, 2H), 6.43-6.45 (dd, J=8.75, 2.5 Hz, 1H), 5.13-5.16 (d, J=15.5 Hz, 1H), 4.15 (s, 2H), 3.91(s, 2H), 3.59 (s, 3H), 3.44-3.47 (d, J=15.0 Hz, 1H), 2.92 (s, 3H), 2.77(s, 3H), 2.47 (s, 3H), 2.29 (s, 6H), 1.97 (s, 6H).

Example 75

Synthesis of Ru complex 8n

The synthetic procedure for preparation of ligand 7n is the same as in Example 1 in 5.0 mmol scale. 0.79g of yellow oil product 7n was obtained (yield: 71%).

Ligand 7n $^1$H-NMR (400 MHz, CDC13): $\delta$ 7.02 (dd, J = 9.6, 3.2 Hz, 1H), 6.87 (td, J = 8.8, 3.2 Hz, 1H), 6.79 (dd, J = 17.2, 11.2 Hz, 1H), 6.43 (dd, J = 8.8, 4.8 Hz, 1H), 5.65 (dd, J = 17.2, 1.6 Hz, 1H), 5.39 (dd, J = 11.2, 1.6 Hz, 1H), 5.11 (m, 1H), 3.85 (s, 2H), 1.27 (d, J = 6.4 Hz, 6H).

The procedure for preparation of Ru complex 8n is the same as in Example 1 in
1.0 mmol scale. 599 mg of green solid product 8n was obtained (yield: 87%).

Ru complex (8n) \(^1\)HNMR (400 MHz, CDCl\(_3\)): \(\delta\) 16.82 (s, 1H, Ru=CH), 7.12-7.02 (m, 5H), 6.64 (m, 1H), 6.51-6.48 (m, 1H), 4.15 (s, 4H, NCH\(_2\)CH\(_2\)N), 3.95-3.92 (m, 1H), 3.74 (s, 3H), 2.50-2.37 (m, 18H), 0.96 (d, \(J = 6.4\) Hz, 1H).

**Example 76**

Synthesis of Ru complex 8p

The synthetic procedure for preparation of ligand 7p is the same as in Example 1 in 5.0 mmol scale. 0.365g of product 7p was obtained (yield: 27%).

Ligand 7p \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.42 (m, 1H), 7.17-7.15 (m, 1H), 7.09-7.06 (m, 1H), 7.04-6.98 (m, 1H), 5.69-5.65 (m, 1H), 5.30-5.27 (m, 1H), 5.0-4.95 (m, 1H), 3.75 (s, 2H), 3.23-3.19 (m, 2H), 1.19-1.18 (d, 6H), 1.07-1.04 (m, 3H).

The procedure for preparation of Ru complex 8p is the same as in Example 1 in 1.0 mmol scale. 167 mg of green solid product 8p was obtained (yield: 23%).

Ru complex (8p) \(^1\)HNMR (400 MHz, CDCl\(_3\)): \(\delta\) 16.52 (s, 1H, Ru=CH), 7.34-32 (dd, \(J = 8.5, 2.0\) Hz, 1H), 7.17 (s, 1H), 7.08 (s, 1H), 7.03 (s, 1H), 6.93 (s, 1H), 6.79-6.77 (d, \(J = 8.0\) Hz, 1H), 6.66 (s, 1H), 5.08-5.05 (d, \(J = 14.5\) Hz, 1H), 4.81-4.76 (m, 1H), 4.16 (s, 2H, NCH\(_2\)CH\(_2\)N), 3.90 (s, 2H, NCH\(_2\)CH\(_2\)N), 3.62-3.59 (d, \(J = 16.0\) Hz, 1H, NCH\(_2\)), 2.91 (s, 3H), 2.81 (s, 3H), 2.48 (s, 3H), 2.32 (s, 3H), 2.30 (s, 3H), 2.16-2.09 (m, 2H, NCH\(_2\)CH\(_3\)), 1.95 (s, 3H), 1.24-1.19 (dd, \(J = 17.5, 6.0\) Hz, 6H, OCH(CH\(_3\))\(_2\)), 0.53-0.50 (t, \(J = 5.5\) Hz, 3H, NCH\(_2\)CH\(_3\)).

**Example 77**

Synthesis of Ru complex 8q

The synthetic procedure for preparation of ligand 7q is the same as in Example 1 in 5.0 mmol scale. 487mg of yellow oil product 7q was obtained (yield: 38%).

Ligand 7q \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.29-7.26 (m, 1H), 7.17-7.14 (m, 1H), 6.85-6.14 (m, 2H), 6.56-6.55 (d, 1H), 5.65-5.62 (m, 1H), 5.37-5.30 (m, 1H), 4.19-4.15 (m, 1H), 3.74 (s, 3H), 1.57-1.50 (d, 3H).

The procedure for preparation of Ru complex 8q is the same as in Example 1 in
1.0 mmol scale. 147mg of brown solid product 8q was obtained (yield: 21%).

Ru complex (8q)\textsuperscript{1}HNMR (400 MHz, CDCl\textsubscript{3}): 8 16.91 (s, 1H, Ru=CH), 7.43-7.40 (m, 1H), 7.08-7.03 (m, 5H), 6.85-6.84 (d, J = 6.5 Hz, 1H), 6.72-6.70 (d, J = 7.5 Hz, 1H), 4.12 (s, 4H, NCH\textsubscript{2}CH\textsubscript{2}N), 4.07 (s, 1H, NH), 4.02-3.98 (m, 1H, NCH), 3.76 (s, 3H, COOCH\textsubscript{3}), 2.52 (s, 9H), 2.39 (brs, 9H), 1.02-1.01 (d, J = 6.0 Hz, 3H)

Example 78

Synthesis of Ru complex 8r

The synthetic procedure for preparation of ligand 7r is the same as in Example 1 in 5.0 mmol scale. 1.06g of yellow oil product 7r was obtained (yield: 83%). The product 7r is confirmed by LC-MS (M+H\textsuperscript{+}): m/z calculated: 285.1, found: 285.1, and directly used for preparation of Ru complex 8r.

The synthetic procedure for preparation of Ru complex 8r is the same as in Example 1 in 1.0 mmol scale. 386 mg of brown solid product 8r was obtained by precipitation in hexane and MeOH, and the crude product 8r is unstable and difficult to detect the structure by \textsuperscript{1}HNMR. But the crude Ru complex 6j could be directly used for metathesis reaction.

Example 79

Synthesis of Ru complex 8s

The synthetic procedure for preparation of ligand 7s is the same as in Example 1 in 5.0 mmol scale. 1.18g of yellow oil product 7s was obtained (yield: 67%).

Ligand 7s \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}): 8 7.44 (d, J = 2.7Hz, 1H, aromatic H), 7.64 (d, J = 3.0 Hz, 1H, aromatic H), 7.16-7.12 (m, 2H, aromatic H), 7.08-6.92 (m, 2H, aromatic H, CH=CH\textsubscript{2}), 6.76 (d, J = 8.7 Hz, 1H, aromatic H), 5.66 (dd, J = 17.7, 1.5Hz, 1H, CH=CH\textsubscript{2}), 5.25 (dd, J = 10.8, 0.9 Hz, 1H, CH=CH\textsubscript{2}), 4.46 (t, J = 6.0 Hz, 1H, OCH), 4.06 (s, 2H, NCH\textsubscript{2}), 2.63 (d, J = 8.4 Hz, 3H, NCH\textsubscript{3}), 1.31-1.26 (m, 6H, OCH(CH\textsubscript{3})\textsubscript{2}).

The procedure for preparation of Ru complex 8s is the same as in Example 1 in
1.0 mmol scale. 379 mg of green solid product 8s was obtained (yield: 48%).

Ru complex (8s) \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}): δ17.58 (d, \( J = 6.0 \) Hz, 1H, Ru=CH), 7.59-7.55 (m, 2H), 7.48 (d, \( J = 8.4 \) Hz, 1H), 7.22 (dd, \( J = 2.4, 8.8 \) Hz, 1H), 7.14 (d, \( J = 8.4 \) Hz, 1H), 6.78 (d, \( J = 8.8 \) Hz, 1H), 4.80 (d, \( J = 12.8 \) Hz, 1H), 4.50-4.47 (m, 1H), 4.05 (d, \( J = 12.8 \) Hz, 1H), 2.704 (s, 3H), 2.38-0.78 (m, 39H, PCy\textsubscript{3}).

Example 80

Synthesis of Ru complex 8t

The synthetic procedure for preparation of ligand 7t is the same as in Example 1 in 5.0 mmol scale. 0.83g of product 7t was obtained (yield: 51%). The product 7q is confirmed by LC-MS (M+H\textsuperscript{+}): m/z calculated: 316.1, found: 316.1, and directly used for preparation of the Ru complex 8t.

The procedure for preparation of Ru complex 8t is the same as in Example 1 in 1.0 mmol scale. 602 mg of green solid product 8t was obtained (yield: 77%).

Ru complex (8t) \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}): δ16.87 (s, 1H, Ru=CH), 7.41 (dd, \( J = 2, 8.4 \) Hz, 1H), 7.19-7.13 (m, 5H), 7.031 (d, \( J = 8.4 \) Hz, 1H), 6.93 (d, \( J = 7.2 \) Hz, 1H), 6.77-6.76 (m, 2H), 6.65 (t, \( J = 7.2 \) Hz, 1H), 4.66 (d, \( J = 12.4 \) Hz, 1H), 4.48-4.43 (m, 1H), 4.02-3.98 (m, 5H), 2.54-2.30 (m, 18H), 2.25 (s, 3H), 1.29 (d, \( J = 6 \) Hz, 6H).

Example 81

Synthesis of Ru complex 8u

The synthetic procedure for preparation of ligand 7u is the same as in Example 1 in 5.0 mmol scale. 1.21g of yellow oil product 7u was obtained (yield: 71%).

Ligand 7u \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}): δ 7.44 (d, \( J = 2.7 \)Hz, 1H, aromatic H), 7.64 (d, \( J = 3.0 \) Hz, 1H, aromatic H), 7.16-7.12 (m, 2H, aromatic H), 7.08-6.92 (m, 2H, aromatic H, CH=CH\textsubscript{2}), 6.76 (d, \( J = 8.7 \) Hz, 1H, aromatic H), 5.66 (dd, \( J = 17.7, 1.5 \)Hz, 1H, CH=CH\textsubscript{2}), 5.25 (dd, \( J = 10.8, 0.9 \) Hz, 1H, CH=CH\textsubscript{2}), 4.46 (t, \( J = 6.0 \) Hz, 1H, OCH), 4.06 (s, 2H, NCH\textsubscript{2}), 2.63 (d, \( J = 8.4 \) Hz, 3H, NCH\textsubscript{3}), 1.31-1.26 (m, 6H, OCH(CH\textsubscript{3})\textsubscript{2}).

The procedure for preparation of Ru complex 8u is the same as in Example 1 in
1.0 mmol scale. 302 mg of green solid product 8u was obtained (yield: 37%).

Ru complex (8u) \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}): \( \delta \) 16.84 (s, 1H, Ru=CH), 7.18 (d, \( J = 8.4 \) Hz, 1H), 7.81 (m, 5H), 6.75 (m, 1H), 6.62 (d, \( J = 8.8 \) Hz, 1H), 6.32 (d, \( J = 8.4 \) Hz, 1H), 4.29-4.24 (m, 1H), 4.11 (s, 4H, NCH\textsubscript{2}CH\textsubscript{2}N), 3.85 (d, \( J = 14.0 \) Hz, 1H), 3.09 (d, \( J = 14.0 \) Hz, 1H), 2.74 (s, 3H), 2.43-2.28 (m, 18H), 1.10 (d, \( J = 6.0 \) Hz, 6H).

**Example 82**

Synthesis of Ru complex 10a

The synthetic procedure for preparation of ligand 9a is the same as in Example 1 in 5.0 mmol scale. 0.97g of yellow oil product 9a was obtained (yield: 93%).

Ligand 9a \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}): \( \delta \) 7.80 (dd, \( J = 8.4, 5.7 \) Hz, 1H), 7.38 (dd, \( J = 17.7, 11.1 \) Hz, 1H), 7.14 (dd, \( J = 10.5, 2.7 \) Hz, 1H), 6.90 (td, \( J = 8.4, 2.1 \) Hz, 1H), 5.55 (d, \( J = 17.7 \) Hz, 1H), 5.30 (d, \( J = 11.1 \) Hz, 1H), 5.17-5.09 (m, 1H), 1.27 (d, \( J = 6.3 \) Hz, 6H).

The procedure for preparation of Ru complex 10a is the same as in Example 1 in 1.0 mmol scale. 128 mg of green solid product 10a was obtained (yield: 19%). The product is unstable, so it is difficult to detect the structure by \textsuperscript{1}H-NMR. But the crude Ru complex 10a could be directly used for metathesis reaction.

**Example 83**

Synthesis of Ru complex 10b

The synthetic procedure for preparation of ligand 9b is the same as in Example 1 in 5.0 mmol scale. 0.89g of yellow oil product 9b was obtained (yield: 87%).

Ligand 9b \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}): \( \delta \) 7.80 (dd, \( J = 8.4, 5.7 \) Hz, 1H), 7.38 (dd, \( J = 17.7, 11.1 \) Hz, 1H), 7.14 (dd, \( J = 10.5, 2.7 \) Hz, 1H), 6.90 (td, \( J = 8.4, 2.1 \) Hz, 1H), 5.55 (d, \( J = 17.7 \) Hz, 1H), 5.30 (d, \( J = 11.1 \) Hz, 1H), 5.17-5.09 (m, 1H), 1.27 (d, \( J = 6.3 \) Hz, 6H).

The procedure for preparation of Ru complex 10b is the same as in Example 1 in 1.0 mmol scale. 97 mg of green solid product 10b was obtained (yield: 15%). The
product is unstable, so it is difficult to detect the structure by $^1$HNMR. But the crude Ru complex 10b could be directly used for metathesis reaction.

**Example 84**

5 Synthesis of Ru complex 10c

The synthetic procedure for preparation of ligand 9c is the same as in Example 1 in 5.0 mmol scale. 0.82g of product 9c was obtained (yield: 76%). The product 9c is confirmed by LC-MS (M+H$^+$): m/z calculated: 208.1, found: 208.0, and directly used for preparation of the Ru complex 10c.

The procedure for preparation of Ru complex 10c is the same as in Example 1 in 1.0 mmol scale. 29 mg of green solid product 10c was obtained (yield: 5%).

Ru complex (10c) $^1$HNMR (400 MHz, CDCl$_3$): $\delta$ 18.68 (s, 1H, Ru=CH), 8.44 (dd, $J = 8.4$, 2.4 Hz, 1H), 8.20 (d, $J = 8.4$ Hz, 1H), 7.60 (d, $J = 2.4$ Hz, 1H), 7.13 (s, 4H), 4.14 (s, 4H, NCH$_2$CH$_2$N), 3.97 (s, 3H), 2.48 (s, 12H), 2.459 (s, 6H).

**Example 85**

Synthesis of Ru complex 10d

The synthetic procedure for preparation of ligand 9d is the same as in Example 1 in 5.0 mmol scale. 0.78g of product 9d was obtained (yield: 72%). The product 9d is confirmed by LC-MS (M+H$^+$): m/z calculated: 236.1, found: 236.1, and directly used for preparation of the Ru complex 10d.

The procedure for preparation of Ru complex 10d is the same as in Example 1 in 1.0 mmol scale. 238 mg of green solid product 10d was obtained (yield: 34%).

Ru complex (10d) $^1$HNMR (400 MHz, CDCl$_3$): $\delta$ 18.71 (s, 1H, Ru=CH), 8.42 (dd, $J = 9.0$, 2.4 Hz, 1H), 8.18 (d, $J = 9.0$ Hz, 1H), 7.60 (d, $J = 2.4$ Hz, 1H), 7.13 (s, 4H), 5.25 (m, 1H), 4.13 (s, 4H, NCH$_2$CH$_2$N), 2.46 (m, 18H), 1.24 (d, $J = 6.0$ Hz, 6H).

**Example 86**

Synthesis of Ru complex 10e

The synthetic procedure for preparation of ligand 9e is the same as in Example 1
in 5.0 mmol scale. 0.92g of product 9e was obtained (yield: 82%). The product 9e is confirmed by LC-MS (M+H\(^+\)): m/z calculated: 225.1, found: 225.1, and directly used for preparation of the Ru complex 10e.

The procedure for preparation of Ru complex 10e is the same as in Example 1 in 1.0 mmol scale. 235 mg of green solid product 10e was obtained (yield: 34%).

Ru complex (10e) \(^1\)H-NMR (400 MHz, CDCl\(_3\)): δ 18.56 (s, 1H, Ru=CH), 7.98 (d, \(J = 8.8\) Hz, 1H), 8.18 (dd, \(J = 8.8, 2.4\) Hz, 1H), 7.11 (s, 4H), 7.06 (d, \(J = 2.4\) Hz, 1H), 5.23 (m, 1H), 4.11 (s, 4H, NCH\(_2\)CH\(_2\)N), 2.45 (m, 18H), 1.28 (d, \(J = 6.0\) Hz, 6H).

Example 87

Synthesis of Ru complex 10f

The synthetic procedure for preparation of ligand 9f is the same as in Example 1 in 5.0 mmol scale. 1.13g of yellow oil product 9f was obtained (yield: 81%).

Ligand 9f \(^1\)H-NMR (400 MHz, CDCl\(_3\)): δ 7.52 (d, \(J = 3.0\) Hz, 1H), 7.26 (dd, \(J = 8.7\) Hz, 3.0 Hz, 1H), 6.89 (d, \(J = 8.7\) Hz, 1H), 5.75 (m, 1H), 5.21 (m, 1H), 5.07-4.97 (m, 2H), 3.17-3.16 (m, 2H), 2.82 (s, 3H), 2.35-2.28 (m, 2H), 1.35 (d, \(J = 6.0\) Hz, 6H).

The procedure for preparation of Ru complex 10f is the same as in Example 1 in 1.0 mmol scale. 274 mg of green solid product 10f was obtained (yield: 37%).

Ru complex (10f) \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(^1\)H-NMR (400 MHz, CDCl\(_3\)): δ 18.74 (s, 1H, Ru=CH), 8.21 (dd, \(J = 8.0, 2.4\) Hz, 1H), 8.08 (d, \(J = 8.0\) Hz, 1H), 7.54 (d, \(J = 2.4\) Hz, 1H), 7.12 (s, 4H), 5.32 (m, 1H), 5.25 (m, 1H), 4.13 (s, 4H, NCH\(_2\)CH\(_2\)N), 2.47 (m, 18H), 1.43 (d, \(J = 6.0\) Hz), 1.24 (d, \(J = 6.0\) Hz, 6H).

Example 88

Synthesis of Ru complex 10g

The synthetic procedure for preparation of ligand 9g is the same as in Example 1 in 5.0 mmol scale. 1.43g of yellow oil product 9g was obtained (yield: 79%).

Ligand 9g \(^1\)H-NMR (400 MHz, CDCl\(_3\)): δ 7.88 (d, \(J = 9.6\) Hz, 1H, aromatic H), 7.86-7.21 (m, 5H, aromatic H, CH=CH\(_2\)), 6.83 (d, \(J = 9.3\) Hz, 1H, aromatic H), 5.68
(d, $J = 16.8$ Hz, 1H, CH=CH$_2$), 5.40 (d, $J = 11.1$ Hz, 1H, CH=CH$_2$), 5.32 (s, 2H, OCH$_2$), 4.55 (m, 1H, OCH(CH$_3$)$_2$), 1.31 (d, $J = 8.1$ Hz, 6H, OCH(CH$_3$)$_2$).

The procedure for preparation of Ru complex 10g is the same as in Example 1 in 1.0 mmol scale. 440 mg of green solid product 10g was obtained (yield: 53%).

Ru complex (10g) $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 18.60 (s, 1H, Ru=CH), 8.01 (d, $J = 8.4$ Hz, 1H), 7.59 (dd, $J = 1.6$, 8.4 Hz, 1H), 7.31-7.23 (m, 1H), 7.24 (dd, $J = 2.8$, 8.8 Hz, 1H), 6.81 (d, $J = 8.8$ Hz, 1H), 6.71 (d, $J = 2.0$ Hz, 1H), 5.33 (s, 2H), 4.52 (m, 1H), 4.16 (s, 4H, NCH$_2$CH$_2$N), 2.51 (s, 12H), 2.48 (s, 6H), 1.28 (d, 6H, $J = 6.0$ Hz).

**Example 89**

Synthesis of Ru complex 10h

The synthetic procedure for preparation of ligand 9h is the same as in Example 1 in 5.0 mmol scale. 1.38g of yellow oil product 9h was obtained (yield: 83%).

Ligand 9h $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.87 (d, $J = 8.4$ Hz, 1H, aromatic H), 7.55-7.24 (m, 6H, aromatic H, CH=CH$_2$), 6.95-6.90 (m, 1H, aromatic H), 5.66 (d, $J = 21.6$ Hz, 1H, CH=CH$_2$), 5.42-5.32 (m, 3H, CH=CH$_2$, OCH$_2$), 4.60 (m, 1H, OCH(CH$_3$)$_2$), 1.25 (d, $J = 8.1$ Hz, 6H, OCH(CH$_3$)$_2$).

The procedure for preparation of Ru complex 10h is the same as in Example 1 in 1.0 mmol scale. 183 mg of green solid product 10h was obtained (yield: 23%).

Ru complex (10h) $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 18.60 (s, 1H, Ru=CH), 8.00 (d, $J = 8.8$ Hz, 1H), 7.55 (d, $J = 8.4$ Hz, 1H), 7.32-7.29 (m, 1H), 7.14 (s, 4H), 7.01-6.70 (m, 4H), 5.38 (s, 2H), 4.56 (m, 1H), 4.16 (s, 4H, NCH$_2$CH$_2$N), 2.71 (s, 12H), 2.52 (s, 6H), 1.32 (d, $J = 6.0$ Hz, 6H).

**Example 90**

Synthesis of Ru complex 10j

The synthetic procedure for preparation of ligand 9j is the same as in Example 1 in 5.0 mmol scale. 1.19g of yellow oil product 9j was obtained (yield: 63%).

Ligand 9j $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ 8.42 (d, $J = 2.1$ Hz, 1H, aromatic H),
8.14 (d, J = 2.1 Hz, 1H, aromatic H), 8.11 (d, J = 2.4 Hz, 1H, aromatic H), 7.48-7.24 (m, 3H, aromatic H, CH=CH₂), 6.84 (d, J = 9.0 Hz, 1H, aromatic H), 5.84 (d, J = 17.7 Hz, 1H, CH=CH₂), 5.53 (d, J = 10.8 Hz, 1H, CH=CH₂), 5.37 (s, 2H, OCH₂), 4.57 (m, 1H, OCH(CH₃)₂), 1.32 (d, J = 8.1 Hz, 6H, OCH(CH₃)₂).

The procedure for preparation of Ru complex 10j is the same as in Example 1 in 1.0 mmol scale. 345 mg of yellow solid product 10j was obtained (yield: 41%).

It is confirmed by Ru complex (10j)¹HNMR (400 MHz, CDCl₃): δ 18.75 (s, 1H, Ru=CH), 8.45 (dd, J =8.8, 1.6 Hz, 1H), 8.21 (d, J =8.8 Hz, 1H), 7.64 (d, J =1.6 Hz, 1H), 7.39-7.25 (m, 2H), 7.17 (s, 4H), 6.83 (d, J =8.8 Hz, 1H), 5.37 (s, 2H), 4.53 (m, 1H), 4.15 (s, 4H, NCH₂CH₂N), 2.51 (m, 18H), 1.40 (d, J = 6.0 Hz, 6H).

Example 91

Synthesis of Ru complex 11a

The Ru complex (Grela catalyst 2f, 1.0mmol) and 4-chlorin pyridine ligand (10mmol) were reacted directly to form another Ru complex 11a in 20 mL of anhydrous DCM in a 100 mL of three-neck flask filled with inert gas (Ar), and the reaction mixture was stirred for 0.5 hr at room temperature. After complete, 20mL of pentane (-10°C) was added into reaction solution, then filtered and washed with MeOH to obtain 747 mg of yellow-green solid product 11a, yield: 95%.

Ru complex (11a)¹HNMR (400 MHz, CDCl₃): δ 17.00 (s, 1H), 8.47-6.83 (m, 11H), 4.91 (m, 1H), 4.17 (s, 4H), 2.48-2.41 (m, 18H), 1.26 (d, J = 4.4 Hz, 6H).

Example 92

Synthesis of Ru complex 11b

The synthetic procedure is the same as in Example 85. 394 mg of yellow-green solid product 11b was obtained (yield: 48%).

Ru complex (11b)¹HNMR (400 MHz, CDCl₃): δ 16.49 (s, 1H), 8.90-8.50 (m, 2H), 7.86 (d, J = 7.2 Hz, 1H), 7.47 (dd, J = 2.0, 7.2Hz, 1H), 7.33 (m, 1H), 7.27 (m, 1H), 7.08 (s, 3H), 6.90 (d, J = 1.6 Hz, 1H), 6.74-6.72 (m, 1H), 4.87-4.84 (m, 1H),
4.19 (s, 4H), 2.48-2.42 (m, 18H), 1.27 (d, $J = 4.0$ Hz, 6H).

**Example 93**

Synthesis of Ru complex 11c

The synthetic procedure is the same as in Example 85. 733 mg of yellow-green solid product 11c was obtained (yield: 95%).

Ru complex (11c)$^1$HNMR (400 MHz, CDCl$_3$): $\delta$ 16.56 (s, 1H), 7.47 (dd, $J = 2.0$, 7.2 Hz, 1H), 7.31-7.27 (m, 5H), 7.20-7.19 (m, 3H), 7.08-6.94 (m, 1H), 6.72 (d, $J = 6.4$ Hz, 1H), 4.85-4.81 (m, 1H), 4.18 (s, 3H), 3.85 (s, 4H), 2.48-2.61 (m, 18H), 1.26 (d, $J = 6.0$ Hz, 6H).

**Example 94**

Synthesis of Ru complex 11d

The synthetic procedure is the same as in Example 85. 403 mg of yellow-green solid product 11d was obtained (yield: 52%).

Ru complex (11d)$^1$HNMR (400 MHz, CDCl$_3$): $\delta$ 16.49 (s, 1H), 8.67 (m, 2H), 7.47 (d, $J = 5.6$ Hz, 1H), 7.37 (m, 3H), 7.08 (s, 3H), 6.73 (d, $J = 6.8$ Hz, 1H), 4.85-4.83 (m, 1H), 4.19 (s, 4H), 2.48-2.41 (m, 18H), 1.26 (d, $J = 4.4$ Hz, 6H).

**Example 95**

Synthesis of Ru complex 11e

The synthetic procedure is the same as in Example 85. 458 mg of yellow-green solid product 11e was obtained (yield: 59%).

It is confirmed by Ru complex (11e)$^1$HNMR (400 MHz, CDCl$_3$): $\delta$ 16.52 (s, 1H), 8.60-8.51 (m, 2H), 7.67 (d, $J = 8.0$ Hz, 2H), 7.46 (d, $J = 2.4$ Hz, 1H), 7.06 (s, 4H), 6.88 (d, $J = 2.4$ Hz, 1H), 6.71 (d, $J = 8.0$ Hz, 2H), 4.84-4.81 (m, 1H), 4.16 (s, 4H), 2.45-2.39 (m, 18H), 1.24 (d, $J = 4.0$ Hz, 6H).

**Example 96**

Synthesis of Ru complex 11f
The synthetic procedure is the same as in Example 85. 733 mg of yellow-green solid product 11f was obtained (yield: 97%).

Ru complex (11f) \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 16.57 (s, 1H), 7.63-6.69 (m, 11H), 4.83-4.81 (m, 1H), 4.16 (s, 4H), 2.45-2.39 (m, 21H), 1.24 (d, \(J = 4.0\) Hz, 6H).

**Example 97**

Synthesis of Ru complex 11g

The synthetic procedure is the same as in Example 85. 330 mg of yellow-green solid product 11g was obtained (yield: 37%).

Ru complex (11g) \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 18.67 (s, 1H), 8.40 (m, 1H), 7.47-6.91 (m, 13H), 6.58 (m, 1H), 4.12 (m, 6H), 2.63-2.27 (m, 19H), 1.00 (d, \(J = 4.0\) Hz, 6H).

**Example 98**

Synthesis of Ru complex 11h

The synthetic procedure is the same as in Example 85. 619 mg of yellow-green solid product 11h was obtained (yield: 73%).

Ru complex (11h) \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 18.67 (s, 1H), 8.43 (s, 1H), 7.45-7.35 (m, 3H), 7.19-6.93 (m, 10H), 6.60 (d, \(J = 7.6\) Hz, 1H), 4.15 (m, 6H), 2.52-2.28 (m, 19H), 1.08-0.89 (m, 6H).

**Example 99**

Synthesis of Ru complex 11j

The synthetic procedure is the same as in Example 85. 416 mg of yellow-green solid product 11j was obtained (yield: 49%).

Ru complex (11j) \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 18.67 (s, 1H), 8.40 (m, 1H), 7.69-6.90 (m, 13H), 6.60 (m, 1H), 4.12 (m, 6H), 2.62-2.17 (m, 19H), 1.00 (d, \(J = 4.0\) Hz, 6H).

**Example 100**
Synthesis of Ru complex 11k

The synthetic procedure is the same as in Example 85. 561 mg of yellow-green solid product 11k was obtained (yield: 63%).

Ru complex (11k) $^1$HNMR (400 MHz, CDCl$_3$): $\delta$ 18.69 (s, 1H), 8.42 (s, 2H), 7.62-6.93 (m, 16H), 6.60 (dd, $J = 2.0$, 7.6 Hz, 2H), 4.14 (s, 6H), 2.52-2.27 (m, 18H), 0.98 (d, $J = 4.4$ Hz, 6H).

Example 101

Synthesis of Ru complex 11m

The synthetic procedure is the same as in Example 85. 685 mg of yellow-green solid product 11m was obtained (yield: 78%).

Ru complex (11m) $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 16.85 (s, 1H), 8.42-7.07 (m, 15H), 4.95 (m, 1H), 4.19 (s, 4H), 2.45-2.29 (m, 18H), 1.29 (d, $J = 4.4$ Hz, 6H).

Example 102

Synthesis of Ru complex 11n

The synthetic procedure is the same as in Example 85. 704 mg of yellow-green solid product 11n was obtained (yield: 85%).

Ru complex (11n) $^1$HNMR (400 MHz, CDCl$_3$): $\delta$ 16.85 (s, 1H), 8.47-6.85 (m, 16H), 4.94 (m, 1H), 4.19 (s, 4H), 2.40-2.29 (m, 18H), 1.29 (d, $J = 4.4$ Hz, 6H).

Example 103

Synthesis of Ru complex 11p

The synthetic procedure is the same as in Example 85. 797 mg of yellow-green solid product 11p was obtained (yield: 96%).

Ru complex (11p) $^1$HNMR (400 MHz, CDCl$_3$): $\delta$ 17.00 (s, 1H), 8.47-6.82 (m, 11H), 4.90 (m, 1H), 4.17 (s, 4H), 2.48-2.41 (m, 18H), 1.26 (d, $J = 4.4$ Hz, 6H).

Example 104

Synthesis of Ru complex 11q
The synthetic procedure is the same as in Example 85. 365 mg of yellow-green solid product 11q was obtained (yield: 47%).

Ru complex (11q) \(^1\)HNMR (400 MHz, CDCl\(_3\)): \(\delta\) 17.33 (s, 1H), 8.71 (s, 1H), 8.56 (d, \(J = 3.2\) Hz, 1H), 7.84 (d, \(J = 6.0\) Hz, 1H), 7.41-7.34 (m, 1H), 7.23-7.21 (m, 1H), 7.01 (dd, \(J = 3.2, 9.6\) Hz), 5.23-5.21 (m, 1H), 2.37-0.90 (m, 33H).

**Example 105**

Synthesis of Ru complex 11r

The synthetic procedure is the same as in Example 85. 604 mg of yellow-green solid product 11r was obtained (yield: 69%).

Ru complex (11r) \(^1\)HNMR (400 MHz, CDCl\(_3\)): \(\delta\) 18.65 (s, 1H), 8.56 (s, 1H), 7.50-6.39 (m, 20H), 4.14 (s, 4H), 3.80 (s, 3H), 2.42-2.29 (m, 18H).

**Example 106**

Synthesis of Ru complex 4i

Starting material 4-SM (44g, 100mmol) and anhydrous ethanol (250mL) were added into a 500 mL three-necked flask filled with inert gas (Ar), followed by adding NaOEt (400mmol, 4.0eq) was quickly added with agitation. The reaction mixture was heated to 60°C. After the reaction was completed in 0.5-1.0 hr, 120 mL of water was added into flask, and the aqueous layer was extracted with pentane (200 mL×3), and the combined organic layers were washed with brine (150 mL×2) solution, then dried over NaSO\(_4\) and concentrated to obtain about 50 mL of crude carbine intermediate 4-1 directly for next step at 0-5°C.

RuCl\(_2\)(PPh\(_3\))\(_3\) (29g, 30mmol) was dissolved in 250 mL of anhydrous DCM in a 500 mL three-neck flask filled with inert gas (Ar), and the DCM solution was cooled to -70°C, then the previously prepared crude carbine intermediate 4-1 (50 mL) was added into the DCM solution at -70°C. After 10 min, the solution was heated to room temperature, and CuCl (100mmol) was added. After completed in 30 min, the reaction solution was filtered and purified by silica gel column chromatography (eluting solution: n-hexane:DCM = 2:1 to pure DCM). The product was concentrated and
washed by anhydrous n-hexane. After dried by vacuum, the Ru complex intermediate 4-2 (19.3g) was obtained.

The intermediate 4-2 (10.0mmol) and tricyclohexylphosphine (PCy₃, 20mmol, 2.0eq.) were dissolved in DCM (30mL) in a 250 mL three-neck flask filled with inert gas (Ar), then stirred at 20°C for about 30 min. After completed, the crude product was purified by flash column to obtain dark-green solid. The solid product was washed with anhydrous methanol and n-hexane to obtain green solid product 4i (crude yield: 60-70%). The product 4i is not stable and difficult to analyze the structure by ¹HNMR. But the crude Ru complex 4i can be used directly to prepare 4j in next step.

**Example 107**

Synthesis of Ru complex 4j

The Ru complex 4i (5.0mmol) and a ligand H₂IMes(H)(CCl₃) (4-4, 10.0mmol, 2.0eq.) were dissolved in anhydrous toluene (30mL) in a 100 mL two-necked flask filled with Ar gas. The reaction mixture was heated to 80°C for 1.5hr. After the reaction was completed, the solution was cooled and filtered, then purified by flash column to obtain dark-green product. The crude product was washed by methanol and pentane-DCM to offer 2.3g of stable green solid product 4j (yield: 59%).

Ru complex 4j is confirmed by ¹HNMR (400 MHz, CDCl₃): δ 18.88 (s, 1H, Ru=CH), 7.57-6.44 (m, 11H, aromatic H), 5.36 (t, J = 13.2 Hz, 1H, NH), 4.16-4.02 (m, 5H, NCH₂, NCH₂CH₂N), 4.01 (d, J = 13.2 Hz, 1H, NCH₂), 2.75-2.00 (m, 19H, CH(CH₃)₂, aromatic CH₃), 1.01-0.90 (m, 6H, CH(CH₃)₂).

**Example 108**

Synthesis of Ru complex 11h

The Ru complex 4j (0.2mmol) and 4-chlorin pyridine 4-chlorin pyridine ligand (4-5, 2.0mmol) were reacted directly to form another Ru complex 11h in 10 mL of anhydrous DCM in a 100 mL three-neck flask filled with inert gas (Ar). Preparation method and result of the Ru complex 11h was the same as described in Example 92. 619 mg of yellow-green solid product 11h was obtained (yield: 73%).
Ru complex 11h is confirmed by $^1$HNMR (400 MHz, CDCl$_3$): δ 18.67 (s, 1H), 8.43 (s, 1H), 7.45-7.35 (m, 3H), 7.19-6.93 (m, 10H), 6.60 (d, $J$ = 7.6 Hz, 1H), 4.15 (m, 6H), 2.52-2.28 (m, 19H), 1.08-0.89 (m, 6H).

**Example 109**

**Synthesis of Ru complex 2j**

SM-2b (10.4g, 50 mmol) and RuCl$_2$(PPh$_3$)$_3$ (48g, 50 mmol) were dissolved in 250 mL of anhydrous THF in a 500mL three-neck round-bottom flask filled with inert gas (Ar) and reacted to form the Ru complex 2h. The reaction mixture was stirred at room temperature until completed (monitored by TLC), and the reaction product 2h was worked out by precipitation in hexane and dried over 42g (yield: 95%).

2h (8.9g, 10 mmol) and a new ligand 3x (3.1g, 11 mmol) with CuCl (12 mmol) were dissolved in 100 mL of anhydrous DCM in a 500mL three-neck round-bottom flask filled with inert gas (Ar) and reacted to form another Ru complex 2j. The reaction mixture was stirred until complete (monitored by TLC), and the reaction product 2j was worked out and dried over (6.2g, yield: 89%). The product 2j is not very stable and directly used for next step to prepare new developed Ru complexes IIa and IIb.

**Example 110**

**Synthesis of Ru complex 4x**

2j (0.71g, 1.0 mmol) and a phosphine ligand PCy$_3$ (4-3, 1.5 mmol) were dissolved in 10 mL of anhydrous DCM in a 50mL three-neck flask filled with inert gas (Ar) and reacted to form the Ru complex 4x. The reaction mixture was stirred until completed (monitored by TLC), the reaction product was precipitated in MeOH and filtered and purified by flask column. 0.56g of green solid product 4x was obtained, yield: 78%.

The Ru complex 4x prepared in this Example 110 is confirmed by $^1$HNMR as the same as in Example 21.
Example 111

Synthesis of Ru complex 4aa

Ru complex 4x (0.72g, 1.0 mmol) and heterocyclic ligand H3IMes(H)(CCl3) (4-4, 48g, 50 mmol) were dissolved in 10 mL of anhydrous Toluene in a 50mL three-neck flask filled with inert gas (Ar) and reacted to form the Ru complex 4x. The reaction mixture was stirred until complete (monitored by TLC), the reaction solution was filtered and purified by flask column. 0.55g of green solid product 4x was obtained (yield: 73%).

The Ru complex 4aa prepared in this Example 111 is confirmed by 1HNMR as the same as in Example 24.

Example 112

RCM reaction

RCM test by selecting the Ru Complexes of Examples 1-108 as Catalyst

**General Procedure** for RCM Catalyzed by Ru Complex in DCM: Olefin substrate (15 or 17, 50mg/each, respectively) was dissolved in 1.0 mL of freshly distilled DCM in a 15mL two-neck round-bottom flask under Ar at 20-25 °C, then Ru catalyst (2 mol% of Ru complex selected from Examples 1-103, respectively) was added into the DCM solution. The kinetic data for conversion of RCM reactions in Equations 1-2 were determined by HPLC at 10 min., 30 min. 1.5 hr, 3.0 hr and until completed overnight. The RCM product (16 and 18, respectively) was determined and the conversion results of RCM reactions were listed in Tables 1-1, 1-2, 1-3, 1-4, 1-5, and 2 above, respectively.

The RCM product 16 is confirmed by 1HNMR (400 MHz, CDCl3): δ 7.72 (d, J = 8.2 Hz, 1H), 7.32 (d, J = 8.0 Hz, 1H), 5.66 (d, J = 4.4 Hz, 1H), 4.11 (d, J = 4.4 Hz, 1H), 2.42 (s, 3H). m/z calculated: 222.1; found: 222.2.

The RCM product 18 is confirmed by 1HNMR (400 MHz, CDCl3): δ 7.78 (d, 2H, J = 8.21Hz), 7.31 (m, 7H), 6.01 (m, 1H), 4.47 (m, 2H), 4.30 (m, 2H), 2.41 (s, 3H). (M+H’): m/z calculated: 300.1, found: 300.2.
Example 113
Catalyst Screening for Cross Metathesis Reaction

CM test by selecting Ru Complexes of Examples 1-108 as Catalyst(s)

**General Procedure** for CM Catalyzed by Ru Complex in DCM: Olefin substrate 19, 200mg/each, respectively) was dissolved in 3.0 mL of freshly distilled DCM in a 15mL two-neck round-bottom flask under Ar at 20-25 °C, then Ru catalyst (0.1 mol% of Ru complex selected from Examples 1-103, respectively) was added into the DCM solution. The CM reaction results are described in section of Equation 3 above.

Example 114
Catalyst Screening for ROMP reaction without solvent

ROMP test by selecting Ru Complexes of Examples 1-108 as Catalyst(s)

**General Procedure** for ROMP Catalyzed by Ru Complex without solvent for some liquid olefin substrates: Olefin substrate (21, 23 or 25, 5mL/each, respectively) was added into a 25mL flat-bottom bottle under Ar at 40-50°C, then Ru catalyst (0.1 mol% of Ru complex selected from Examples 1-103, respectively) was added with agitation. The kinetic data and ROMP results for products 22, 24 and 26 are described in each section of Equation 4-6 above, respectively.

Example 115
Catalyst Screening for ROMP reaction with solvent

ROMP test by selecting Ru Complexes of Examples 1-108 as Catalyst(s)

**General Procedure** for ROMP Catalyzed by Ru Complex in solution: 0.5g of cyclo-olefin substrate (21, 23, 25, 27, 29, or 31, respectively) was dissolved in 10 mL of freshly distilled DCM in a 25mL two-neck round-bottom flask under Ar at 20-25 °C, then Ru catalyst (0.1 mol% of Ru complex selected from Examples 1-103, respectively) was added into the DCM solution. The ROMP results for products 22, 24, 26, 28, 30 and 32 are described in each section of Equation 4-9 above, respectively.
Example 116
Catalyst Screening for Depolymerization of nitrile butadiene rubber by Metathesis

Metathesis Depolymerization test by selecting Ru Complexes from Examples 1-108 as Catalyst(s)

General Procedure for depolymerization Catalyzed by Ru Complex: 60g of nitrile butadiene rubber (NBR) was dissolved in 500 mL of anhydrous chlorobenzene in a 1.0L well-sealed steel reactor under Ar at 30 °C, then the Ru catalyst (4ab, 0.04 wt%, one of Ru complexes selected from Examples 1-108) was added into chlorobenzene solution. The depolymerization by Ru catalyst was conducted overnight to produce lower molecular weight rubber as shown in Equation 10. The depolymerized butyl rubber product was precipitated in MeOH, and dried over 97% of yield. The final rubber product has a Mw of 2.78E+05, a Mn of 1.586E+5, and a Mooney viscosity of 60.3.

Example 117
Catalyst Screening for Metathesis and Hydrogenation reactions of nitrile butadiene rubber

Metathesis and Hydrogenation test by selecting Ru Complexes from Examples 1-108 as Catalyst(s)

General Procedure for Metathesis and Hydrogenation Catalyzed by Ru Complex in solution: 60g of nitrile butadiene rubber (NBR, Raw Material) substrate was dissolved in 500 mL of anhydrous chlorobenzene in a 1.0L steel well-sealed reactor under Ar, then Ru catalyst (4aa, 0.07 wt% of Ru complex selected from Examples 1-108, respectively) was added into chlorobenzene solution, followed by adding hydrogen under high pressure 5MPa, and finally heated upto 130°C overnight. The hydrogenated nitrile butadiene rubber product (HNBR) by Ru catalyst was prepared with lower molecular weight and higher hydrogination degree as shown in Equation 11. The depolymerized and hydrogenated butyl rubber product was precipitated in MeOH, and dried over 98% of yield. The final product has a Mw of 1.60E+05, a Mn of 1.12E+05, an Iodine value of 12.6, and a hydrogenation degree of greater than 95%.

Example 118

108
Catalyst Screening for Hydrogenation and Metathesis reactions of nitrile butadiene rubber

Metathesis and Hydrogenation test by selecting selecting Ru Complexes from Examples 1-108 as Catalyst(s)

**General Procedure** for Metathesis and Hydrogenation Catalyzed by Ru Complex in solution: 60g of nitrile butadiene rubber (NBR) substrate was dissolved in 500 mL of anhydrous chlorobenzene in a 1.0L steel well-sealed reactor under Ar, then hydrogen was added under high pressure 5MPa, followed by adding Ru catalyst (4aa, 0.1 wt% of Ru complex selected from Examples 1-108) into chlorobenzene solution, then heated upto 130°C overnight. The hydrogenated nitrile butadiene rubber product (HNBR) by Ru catalyst was prepared with higher hydrogenation degree and lower molecular weight as shown in Equation 12. The hydrogenated butyl rubber product was precipitated in MeOH, and dried over 98% of yield. The final product has a Mw of 1.80E+05, a Mn of 1.07E+05, an Iodine value of 3.1, and a hydrogenation degree of greater than 99%.
What is claimed is:

1. A ligand of metal complex having the following structure \( \text{Ia or Ib} \)

\[
\begin{align*}
\text{Ia} & \quad \text{Ib}
\end{align*}
\]

Wherein:

\[ Z = \text{CH}_2= \text{ or } \text{TsNHN=} \]

\[ m = 0 \text{ or } 1, \quad n = 0 \text{ or } 1; \]

When \( m = 0 \), \( Y \) is \( \text{CH}_2, \text{NH, oxygen, nitrogen, carbonyl, imino, C}_1-\text{C}_{20} \text{ alkoxy, } \)
\( \text{C}_6-\text{C}_{20} \text{ aryloxy, } \text{C}_2-\text{C}_{20} \text{ heterocyclic aryl, } \text{C}_1-\text{C}_{20} \text{ alkoxy carbonyl, } \text{C}_6-\text{C}_{20} \text{ aryloxy carbonyl, } \text{C}_1-\text{C}_{20} \text{ alkylimino, } \text{C}_1-\text{C}_{20} \text{ alkylamino, } \text{C}_6-\text{C}_{20} \text{ arylamino or } \text{C}_2-\text{C}_{20} \text{ heterocyclic amino group;} \]

When \( m = 1 \), \( X \) is \( \text{oxygen, nitrogen, sulfur, CH, CH}_2, \text{ carbonyl; } Y \) is \( \text{nitrogen, oxygen, CH, CH}_2, \text{ imino, NH, C}_1-\text{C}_{20} \text{ alkyl, } \text{C}_1-\text{C}_{20} \text{ alkoxy, } \text{C}_6-\text{C}_{20} \text{ aryl, } \text{C}_6-\text{C}_{20} \text{ aryloxy, } \text{C}_3-\text{C}_{20} \text{ heteroaryl, } \text{C}_1-\text{C}_{20} \text{ alkylcarbonyl, } \text{C}_1-\text{C}_{20} \text{ alkoxy carbonyl, } \text{C}_6-\text{C}_{20} \text{ arylcarbonyl, } \text{C}_6-\text{C}_{20} \text{ aryloxy carbonyl, } \text{C}_1-\text{C}_{20} \text{ alkylimino, } \text{C}_1-\text{C}_{20} \text{ alkylamino, } \text{C}_6-\text{C}_{20} \text{ arylamino or } \text{C}_2-\text{C}_{20} \text{ heterocyclic amino group; } \quad \text{“Y=X” is either single bond or double bond;} \]

When \( n = 1 \), \( X^1 \) and \( Y^1 \) are each \( \text{oxygen, nitrogen, sulfur, carbonyl, imino, CH, CH}_2, \text{ C}_1-\text{C}_{20} \text{ alkyl, } \text{C}_6-\text{C}_{20} \text{ aryl, } \text{C}_6-\text{C}_{20} \text{ aryloxy, } \text{C}_2-\text{C}_{20} \text{ heterocyclic aryl, } \text{C}_1-\text{C}_{20} \text{ alkylamino, } \text{C}_6-\text{C}_{20} \text{ arylamino or } \text{C}_2-\text{C}_{20} \text{ heterocyclic amino group;} \]

\[ R^1 \text{ is } \text{H, C}_1-\text{C}_{20} \text{ alkyl, } \text{C}_2-\text{C}_{20} \text{ alkenyl, } \text{C}_6-\text{C}_{20} \text{ aryl, } \text{C}_6-\text{C}_{20} \text{ arylidenyl, } \text{C}_1-\text{C}_{20} \text{ alkoxy, } \text{C}_1-\text{C}_{20} \text{ alkylthio, } \text{C}_6-\text{C}_{20} \text{ arylthio, } \text{C}_6-\text{C}_{20} \text{ aryloxy, } \text{C}_3-\text{C}_{20} \text{ heteroaryl or } \text{C}_2-\text{C}_{20} \text{ heterocyclic group;} \]

\[ R^2 \text{ is } \text{H, C}_1-\text{C}_{20} \text{ alkyl, } \text{C}_6-\text{C}_{20} \text{ aryl, } \text{C}_1-\text{C}_{20} \text{ alkylcarbonyl, } \text{C}_6-\text{C}_{20} \text{ arylcarbonyl, } \text{C}_1-\text{C}_{20} \text{ alkoxy carbonyl, } \text{C}_6-\text{C}_{20} \text{ aryloxy carbonyl, } \text{C}_1-\text{C}_{20} \text{ aminocarbonyl, } \text{C}_3-\text{C}_{20} \text{ heteroaryl or } \text{C}_2-\text{C}_{20} \text{ heterocyclic group;} \]

\[ E, \text{ E}^1, \text{ E}^2, \text{ E}^3, \text{ E}^4, \text{ E}^5, \text{ E}^6 \text{ and E}^7 \text{ are each independently selected from the group consisting of } \text{H, halogen atom, nitro, amino, cyano, formyl, sulfinyl, sulfonyl, C}_1-\text{C}_{20} \text{}}
alkyl, C₁-C₂₀ alkoxy, C₁-C₂₀ alkylthio, C₂-C₂₀ alkenyloxy, C₁-C₂₀ silanyl, C₁-C₂₀ alkylsilyloxy, C₆-C₂₀ aryl, C₆-C₂₀ aryloxy, C₁-C₂₀ alkylcarbonyl, C₆-C₂₀ arylcarbonyl, C₁-C₂₀ alkoxy carbonyl, C₆-C₂₀ aryloxycarbonyl, amino, C₁-C₂₀ alkanaminocarbonyl, C₆-C₂₀ arylaminocarbonyl, C₁-C₂₀ alkylamido, C₆-C₂₀ arylamido, C₁-C₂₀ alkylaminosulfonyl, C₆-C₂₀ arylaminosulfonyl, C₁-C₂₀ sulfonlamido, C₃-C₂₀ heteroaryl or C₂-C₂₀ heterocyclic group; each optionally substituted with an alkyl, alkoxy, alkylthio, aryl, aryloxy, halogen atom or heterocyclic group.

2. The ligand of metal complex according to claim 1, wherein the structure Ⅰa-Ⅰb, Ⅰc-Ⅰd,

\[ Z = CH₂ = or TsNH = \]

m = 0 or 1, n = 0 or 1;

When m = 0, Y is CH₂, NH, oxygen, nitrogen, carbonyl, imino, C₁-C₁₅ alkoxy, C₆-C₁₅ aryloxy, C₁-C₁₅ alkoxy carbonyl, C₆-C₁₅ aryloxycarbonyl, C₁-C₁₅ alkylimino, C₁-C₁₅ alkylamino, C₆-C₁₅ arylamino or C₂-C₁₅ heterocyclic amino group;

When m = 1, X is oxygen, nitrogen, sulfur, CH, CH₂, carbonyl; Y is nitrogen, oxygen, CH, CH₂, imino, NH, C₁-C₁₅ alkyl, C₁-C₁₅ alkoxy, C₆-C₁₅ aryloxy, C₃-C₁₅ heteroaryl, C₁-C₁₅ alkylcarbonyl, C₁-C₁₅ alkoxy carbonyl, C₆-C₁₅ arylcarbonyl, C₆-C₁₅ aryloxycarbonyl, C₁-C₁₅ alkylimino, C₁-C₁₅ alkylamino, C₆-C₁₅ arylamino or C₂-C₁₅ heterocyclic amino group; “Y==X” is either single bond or double bond.

When n = 1, X¹ and Y¹ are each oxygen, nitrogen, sulfur, carbonyl, imino, CH, CH₂, C₁-C₁₅ alkyl, C₆-C₁₅ aryloxy, C₂-C₁₅ heterocyclic aryl, C₁-C₁₅ alkoxy carbonyl, C₆-C₁₅ arylamino or C₂-C₁₅ heterocyclic amino group;

\[ R¹ = H, C₁-C₁₅ alkyl, C₂-C₁₅ alkenyl, C₆-C₁₅ aryl, C₆-C₁₅ arylenyl, C₁-C₁₅ alkoxy, C₁-C₁₅ alkylthio, C₆-C₁₅ arythio, C₆-C₁₅ aryloxy, C₃-C₁₅ heteroaryl or C₂-C₁₅ heterocyclic group; \]

\[ R² = H, C₁-C₁₅ alkyl, C₆-C₁₅ aryl, C₁-C₁₅ alkylcarbonyl, C₆-C₁₅ arylcarbonyl, C₁-C₁₅ alkoxy carbonyl, C₆-C₁₅ aryloxycarbonyl, C₁-C₁₅ aminocarbonyl, C₃-C₁₅ heteroaryl or C₂-C₁₅ heterocyclic group; \]

E, E¹, E², E³, E⁴, E⁵, E⁶ and E⁷ are each independently selected from the group consisting of H, halogen atom, nitro, amino, cyano, formyl, sulfinyl, sulfonyl, C₁-C₁₅
alkyl, C_{1}-C_{15} alkoxy, C_{1}-C_{15} alkylthio, C_{2}-C_{15} alkenyloxy, C_{1}-C_{15} silanyl, C_{1}-C_{15} alkysilyloxy, C_{6}-C_{15} aryl, C_{6}-C_{15} aryloxy, C_{1}-C_{15} alkylcarbonyl, C_{6}-C_{15} arylcarbonyl, C_{1}-C_{15} alkoxy carbonyl, C_{6}-C_{15} aryloxy carbonyl, C_{1}-C_{15} alkylaminocarbonyl, C_{6}-C_{15} arylaminocarbonyl, C_{1}-C_{15} alkylamido, C_{6}-C_{15} arylamido, C_{1}-C_{15} alkylaminosulfonyl, C_{6}-C_{15} arylaminosulfonyl, C_{1}-C_{15} sulfonlamido, C_{3}-C_{15} heteroaryl or C_{2}-C_{15} heterocyclic group; each optionally substituted with an alkyl, alkoxy, alkylthio, aryl, aryloxy, halogen atom or heterocyclic group.

3. The ligand of metal complex according to claim 2, wherein the structure Ia-Ib, Z is CH_{2}= or TsNHN=;

m = 0 or 1, n = 0 or 1;

When m = 0, Y is oxygen, nitrogen, carbonyl, imino, C_{1}-C_{8} alkoxy, C_{6}-C_{8} arloxy, C_{1}-C_{8} alkoxy carbonyl, C_{6}-C_{8} aryloxy carbonyl, C_{1}-C_{8} alkylimino, C_{1}-C_{8} alkylamino, C_{6}-C_{12} arylamino or C_{2}-C_{12} heterocyclic amino group;

When m = 1, X is nitrogen, oxygen, sulfur, CH, CH_{2}, carbonyl; Y is oxygen, nitrogen, CH, CH_{2}, imino, NH, C_{1}-C_{15} alkyl, C_{1}-C_{8} alkoxy, C_{6}-C_{15} aryl, C_{6}-C_{12} aryloxy, C_{3}-C_{12} heteroaryl, C_{1}-C_{8} alkylcarbonyl, C_{1}-C_{8} alkoxy carbonyl, C_{6}-C_{12} arylcarbonyl, C_{6}-C_{12} aryloxy carbonyl, C_{1}-C_{8} alkylamino, C_{1}-C_{8} alkylamino, C_{6}-C_{12} arylamino or C_{2}-C_{8} heterocyclic amino group; “Y={X}” is either single bond or double bond.

When n = 1, X^1 and Y^1 are each oxygen, nitrogen, sulfur, carbonyl, imino, CH, CH_{2}, C_{1}-C_{8} alkyl, C_{6}-C_{8} aryl, C_{6}-C_{8} aryloxy, C_{2}-C_{8} heterocyclic aryl, C_{1}-C_{8} alkylamino, C_{6}-C_{8} arylamino or C_{2}-C_{8} heterocyclic amino group;

R^1 is H, C_{1}-C_{8} alkyl, C_{2}-C_{8} alkenyl, C_{6}-C_{12} aryl or C_{6}-C_{12} arlenylenyl;

R^2 is methyl, ethyl, isopropyl, C_{1}-C_{8} alkyl or C_{6}-C_{12} aryl;

E, E^1, E^2, E^3, E^4, E^5, E^6 and E^7 are each independently selected from the group consisting of H, halogen atom, nitro, C_{1}-C_{8} alkyl, C_{1}-C_{8} alkoxy, C_{1}-C_{8} alkylthio, C_{2}-C_{8} alkenyloxy, C_{1}-C_{8} silanyl, C_{1}-C_{8} alkysilyloxy, C_{6}-C_{12} aryl, C_{6}-C_{12} aryloxy, C_{1}-C_{8} alkylcarbonyl, C_{6}-C_{12} arylcarbonyl, C_{1}-C_{8} alkoxy carbonyl, C_{6}-C_{12} aryloxy carbonyl, C_{1}-C_{8} alkylaminocarbonyl, C_{6}-C_{12} arylaminocarbonyl, C_{1}-C_{8} alkylamido, C_{6}-C_{12} arylamido, C_{1}-C_{8} alkylaminosulfonyl, C_{6}-C_{12} arylaminosulfonyl,
C₁-C₈ sulfonylamido, C₃-C₁₂ heteroaryl or C₂-C₈ heterocyclic group; each optionally substituted with an alkyl, alkoxy, alkylthio, aryl, aryloxy, halogen atom or heterocyclic group.

4. The ligand of metal complex according to claim 3, wherein the structure Ia-Ib,

Z is CH₂= or TsNHN=;

m = 0 or 1, n = 0 or 1;

When m = 0, Y is CH₂, NH, C₁-C₄ alkoxy, C₁-C₄ alkylamino or C₆-C₉ arylamino group;

When m = 1, X is nitrogen, C₁-C₃ alkylamino, CH, CH₂, or carbonyl; Y is oxygen, nitrogen, imino, NH, C₁-C₄ alkyl, C₁-C₄ alkoxy, C₁-C₄ alkylamino, or C₆-C₉ arylamino; “Y=–X” is either single bond or double bond;

When n = 1, X₁ is CH₂, substituted or unsubstituted phenyl, or carbonyl; Y₁ is oxygen or carbonyl;

R₁ is H;

when n = 1, R₂ is methyl, ethyl, or isopropyl; when n = 0, R₂ is H, halogen, C₁-C₄ alkyl or C₁-C₄ alkoxy in structure Ia.

E is H, halogen, nitro, C₁-C₄ alkyl, C₁-C₄ alkoxy, C₁-C₄ alkoxy-carbonyl, C₁-C₈ alkylaminosulfonyl, C₆-C₁₂ arylaminosulfonyl;

E₁ and E₂ are each H, halogen, C₁-C₄ alkyl or C₁-C₄ alkoxy;

E₃ is H;

E₄ is H or C₁-C₄ alkyl;

E₅ and E₆ is H, halogen, C₁-C₄ alkyl or C₁-C₆ alkoxy;

E₇ is H or C₁-C₄ alkyl.

5. A transition metal complex having the following structure IIa or IIb,

wherein:
m = 0 or 1, n = 0 or 1;
When n = 0:  p = 0 or 1; when n = 1, p = 0;
M is a transition metal;
L¹ and L² are the same or different and each selected from halogen anion (Cl⁻, Br⁻ or I⁻), RC(O)O⁻ or ArO⁻ anion;
L is an electron-donating ligand;
When m = 1, X is oxygen, nitrogen, sulfur, CH, CH₂, carbonyl; Y is nitrogen, oxygen, CH, CH₂, imino, C₁-C₂₀ alkoxy, C₆-C₂₀ aryl, C₆-C₂₀ aryloxy, C₃-C₂₀ heteroaryl, C₁-C₂₀ alkylcarbonyl, C₁-C₂₀ alkoxy carbonyl, C₆-C₂₀ aryl carbonyl, C₆-C₂₀ aryloxycarbonyl, C₁-C₂₀ alkyl imino, C₁-C₂₀ alkylamino, C₆-C₂₀ arylamino or C₂-C₂₀ heterocyclic amino group; “X=Y” is either single bond or double bond;
When m = 0, Y is oxygen, nitrogen, carbonyl, imino, C₁-C₂₀ alkoxy, C₆-C₂₀ aryloxy, C₂-C₂₀ heterocyclic aryl, C₁-C₂₀ alkoxy carbonyl, C₆-C₂₀ aryloxycarbonyl, C₁-C₂₀ alkyl imino, C₁-C₂₀ alkylamino, C₆-C₂₀ arylamino or C₂-C₂₀ heterocyclic amino group;
When n = 0 and p = 1, L³ is an electron-donating ligand;
When n = 1 and p = 0, X¹ and Y¹ are each oxygen, nitrogen, sulfur, carbonyl, imino, CH, CH₂, C₁-C₂₀ alkyl, C₆-C₂₀ aryl, C₆-C₂₀ aryloxy, C₂-C₂₀ heterocyclic aryl, C₁-C₂₀ alkylamino, C₆-C₂₀ arylamino or C₂-C₂₀ heterocyclic amino group;
R¹ is H, C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, C₆-C₂₀ aryl, C₆-C₂₀ arylenyl, C₁-C₂₀ alkoxy, C₁-C₂₀ alkylthio, C₆-C₂₀ arylthio, C₆-C₂₀ aryloxy, C₃-C₂₀ heteroaryl or C₂-C₂₀ heterocyclic group;
R² is H, C₁-C₂₀ alkyl, C₆-C₂₀ aryl, C₁-C₂₀ alkylcarbonyl, C₆-C₂₀ aryl carbonyl, C₁-C₂₀ alkoxycarbonyl, C₆-C₂₀ aryloxycarbonyl, C₁-C₂₀ aminocarbonyl, C₃-C₂₀ heteroaryl or C₂-C₂₀ heterocyclic group;
E, E¹, E², E³, E⁴, E⁵, E⁶ and E⁷ are each independently selected from the group consisting of H, halogen atom, nitro, amino, cyano, formyl, sulfinyl, sulfonyl, C₁-C₂₀ alkyl, C₁-C₂₀ alkoxy, C₁-C₂₀ alkylthio, C₂-C₂₀ alkenyloxy, C₁-C₂₀ silanyl, C₁-C₂₀ alkylsilyl oxy, C₆-C₂₀ aryl, C₆-C₂₀ aryloxy, C₁-C₂₀ alkylcarbonyl, C₆-C₂₀ aryl carbonyl, C₁-C₂₀ alkoxy carbonyl, C₆-C₂₀ aryloxycarbonyl, C₁-C₂₀ aminocarbonyl, C₀-C₂₀ alkylaminocarbonyl,
C_{6}-C_{20} arylaminocarbonyl, C_{1}-C_{20} alkylamido, C_{6}-C_{20} arylamido, C_{1}-C_{20} alkylaminosulfanyl, C_{6}-C_{20} arylaminosulfanyl, C_{1}-C_{20} sulfonlamido, C_{3}-C_{20} heteroaryl or C_{2}-C_{20} heterocyclic group; each optionally substituted with an alkyl, alkoxy, alkylthio, aryl, aryloxy, halogen atom or heterocyclic group.

6. The transition metal complex according to claim 5, wherein L is heterocyclic carbene ligand or phosphine P(R^{3}_{2}(R^{3}) having the following structure IIIa, IIIb, IIIc, or IIIId:

![Diagram](image)

Wherein, q = 1, 2 or 3;

R^{4} and R^{5} are each C_{1}-C_{20} alkyl, C_{6}-C_{20} aryl, C_{1}-C_{20} alkylamido, C_{6}-C_{20} arylamido, C_{3}-C_{20} heteroaryl or C_{2}-C_{20} heterocyclic group;

R^{6} and R^{7} are each H, halogen atom, nitro, amino, cyano, formyl, sulfinyl, sulfanyl, C_{1}-C_{20} alkyl, C_{1}-C_{20} alkoxy, C_{1}-C_{20} alkylthio, C_{2}-C_{20} alkenyloxy, C_{1}-C_{20} silanyl, C_{1}-C_{20} alkylsilyloxy, C_{2}-C_{20} heterocyclic, C_{6}-C_{20} aryl, C_{6}-C_{20} aryloxy, C_{1}-C_{20} alklycarbonyl, C_{6}-C_{20} arylcarbonyl, C_{1}-C_{20} alkoxy carbonyl, C_{6}-C_{20} aryloxycarbonyl, amino, C_{1}-C_{20} alkenaminocarbonyl, C_{6}-C_{20} alkylaminocarbonyl, C_{1}-C_{20} alkylamido, C_{6}-C_{20} arylamido, C_{1}-C_{20} alkenaminosulfanyl, C_{6}-C_{20} alkylaminosulfanyl, C_{1}-C_{20} sulfonlamido, C_{3}-C_{20} heteroaryl or C_{2}-C_{20} heterocyclic group;

R^{8} and R^{9} are each C_{1}-C_{20} alkyl, C_{1}-C_{20} alkoxy, C_{6}-C_{20} aryl, C_{6}-C_{20} aryloxy, C_{3}-C_{20} heteroaryl or C_{2}-C_{20} heterocyclic group.

7. The transition metal complex according to claim 6, wherein L is formula IIIa or IIIId, and in IIIa, q = 1 or 2, R^{4} and R^{5} each is aryl, R^{6} and R^{7} each is H.

8. The transition metal complex according to claim 6, wherein L is IIIa or IIIId; and in IIIa, q = 1, R^{4} and R^{5} each is 2,4,6-trimethylphenyl, R^{6} and R^{7} each is H; or in IIIId, R^{8} and R^{9} each is cyclohexyl (Cy).

9. The transition metal complex according to claim 5, wherein the structure IIa or IIb.
M is ruthenium (Ru), wolfram (W) or nickel (Ni);

m = 0 or 1, n = 0 or 1;

L₁ and L₂ each is chloride (Cl⁻);

L is IIIa or IIId, wherein q, R⁴, R⁵, R⁶, R⁷, R⁸ and R⁹ each is as defined in claim 6; R¹, R², E, E¹, E², E³, E⁴, E⁵, E⁶ and E⁷ each is as defined in claim 2.

When m = 0, Y is oxygen, nitrogen, carbonyl, imino, C₁-C₁₅ alkoxy, C₆-C₁₅ aryloxy, C₁-C₁₅ alkoxy carbonyl, C₆-C₁₅ aryloxycarbonyl, C₁-C₁₅ alkylmino, C₁-C₁₅ alkylamino, C₆-C₁₅ arylamino or C₂-C₁₅ heterocyclic amino group;

When m = 1, X is oxygen, nitrogen, sulfur, CH, CH₂, carbonyl; Y is nitrogen, oxygen, CH, CH₂, imino, C₁-C₁₅ alkoxy, C₆-C₁₅ aryl, C₆-C₁₅ aryloxy, C₃-C₁₅ heteroaryl, C₁-C₁₅ alkylcarbonyl, C₁-C₁₅ alkoxy carbonyl, C₆-C₁₅ arylcarbonyl, C₆-C₁₅ aryloxycarbonyl, C₁-C₁₅ alkylmino, C₁-C₁₅ alkylamino, C₆-C₁₅ arylamino or C₂-C₁₅ heterocyclic amino group; “Y―X” is either single bond or double bond.

When n = 0, p = 0 or 1; when n = 1, p = 0.

When n = 0 and p = 1, L₃ is one or more substituted pyridine at the ortho-position, meta-position and/or para-position, and the nitrogen atom of the substituted pyridine donates a pair of electron to the transition metal cation, wherein the substituents at the ortho-position, meta-position and/or para-position of pyridine are each selected from halogen, nitro, cyano, C₁-C₁₅ alkyl, C₁-C₁₅ alkoxy, C₁-C₁₅ alkylthio, C₂-C₁₅ alkenyloxy, C₁-C₁₅ silanyl, C₁-C₁₅ alkylsilyloxy, C₆-C₁₅ aryl, C₆-C₁₅ aryloxy, C₁-C₁₅ alkylcarbonyl, C₆-C₁₅ arylcarbonyl, C₁-C₁₅ alkoxy carbonyl, C₆-C₁₅ aryloxycarbonyl, C₃-C₁₅ alkylaminocarbonyl, C₆-C₁₅ arylaminocarbonyl, C₁-C₁₅ alkenamido, C₆-C₁₅ arylamido, C₁-C₁₅ alkylaminosulfonyle, C₆-C₁₅ arylaminosulfonyle, C₁-C₁₅ sulfonylamido, C₃-C₁₅ heteroaryl or C₂-C₁₅ heterocyclic group; each optionally substituted with an alkyl, alkoxy, alkylthio, aryl, aryloxy, halogen atom or heterocyclic group.

When n = 1 and p = 0, X¹ and Y¹ are each oxygen, nitrogen, sulfur, carbonyl, imino, CH, CH₂, C₁-C₁₅ alkyl, C₆-C₁₅ aryl, C₆-C₁₅ aryloxy, C₂-C₁₅ heterocyclic aryl, C₁-C₁₅ alkylamino, C₆-C₁₅ arylamino or C₂-C₁₅ heterocyclic amino group;

10. The transition metal complex according to claim 9, wherein the structure IIa
or IIb,

When \( m = 0 \), \( Y \) is oxygen, nitrogen, carbonyl, imino, \( C_1-C_8 \) alkoxy, \( C_6-C_{12} \) aryloxy, \( C_1-C_8 \) alkoxy carbonyl, \( C_6-C_{12} \) aryl oxy carbonyl, \( C_1-C_8 \) alkylimino, \( C_1-C_8 \) alkylamino, \( C_6-C_{12} \) aryl amino or \( C_2-C_8 \) heterocyclic amino group;

When \( m = 1 \), \( X \) is oxygen, nitrogen, sulfur, \( CH, CH_2 \), carbonyl; \( Y \) is nitrogen, oxygen, \( CH, CH_2 \), imino, \( C_1-C_8 \) alkoxy, \( C_6-C_{12} \) aryl, \( C_6-C_{12} \) aryloxy, \( C_3-C_{12} \) heteroaryl, \( C_1-C_8 \) alkyl carbonyl, \( C_1-C_8 \) alkoxy carbonyl, \( C_6-C_{12} \) aryl carbonyl, \( C_6-C_{12} \) aryloxy carbonyl, \( C_1-C_8 \) alkyl imino, \( C_1-C_8 \) alky amino, \( C_6-C_{12} \) aryl amino or \( C_2-C_8 \) heterocyclic amino group; “\( Y=\equiv X \)” is either single bond or double bond.

When \( n = 0 \), \( p = 0 \) or 1; when \( n = 1 \), \( p = 0 \).

When \( n = 0 \) and \( p = 1 \), \( L_3 \) is one or more substituted pyridine at the ortho-position, meta-position and/or para-position, and the nitrogen atom of the substituted pyridine donates a pair of electron to the transition metal cation, where in the substituents at the ortho-position, meta-position and/or para-position of pyridine are each selected from halogen, nitro, cyano, \( C_1-C_8 \) alkyl, \( C_1-C_8 \) alkoxy, \( C_1-C_8 \) alkyl thi o, \( C_2-C_8 \) alkenyloxy, \( C_1-C_8 \) silanyl, \( C_1-C_8 \) alkyl silyloxy, \( C_6-C_{12} \) aryl, \( C_6-C_{12} \) aryloxy, \( C_1-C_8 \) alky carbonyl, \( C_6-C_{12} \) aryl carbonyl, \( C_1-C_8 \) alkoxy carbonyl, \( C_6-C_{12} \) aryloxy carbonyl, \( C_1-C_{12} \) alkylaminocarbonyl, \( C_6-C_{12} \) arylaminocarbonyl, \( C_1-C_8 \) alkyl amido, \( C_6-C_{12} \) aryl amido, \( C_1-C_8 \) alkylaminosulfonyl, \( C_6-C_{12} \) arylaminosulfonyl, \( C_1-C_8 \) sulfon ylamido, \( C_3-C_{12} \) heteroaryl or \( C_2-C_8 \) heterocyclic group; each optionally substituted with an alkyl, alkoxy, alkylthio, aryl, aryloxy, halogen atom or heterocyclic group;

When \( n = 1 \) and \( p = 0 \), \( X^1 \) and \( Y^1 \) are each oxygen, nitrogen, sulfur, carbonyl, imino, \( CH, CH_2 \), \( C_1-C_8 \) alkyl, \( C_6-C_{12} \) aryl, \( C_6-C_{12} \) aryloxy, \( C_2-C_{12} \) heterocyclic aryl, \( C_1-C_8 \) alky lamino, \( C_6-C_{12} \) aryl amino or \( C_2-C_8 \) heterocyclic amino group;

\( R^1 \) is \( H, C_1-C_8 \) alkyl, \( C_2-C_8 \) alkenyl, \( C_6-C_{12} \) aryl or \( C_6-C_{12} \) aryl enyl;

\( R^2 \) is methyl, ethyl, isopropyl, \( C_1-C_8 \) alkyl or \( C_6-C_{12} \) aryl;

\( E, E^1, E^2, E^3, E^4, E^5, E^6 \) and \( E^7 \) are each independently selected from the group consisting of \( H \), halogen atom, nitro, \( C_1-C_8 \) alkyl, \( C_1-C_8 \) alkoxy, \( C_1-C_8 \) alkylthio, \( C_2-C_8 \) alkenyloxy, \( C_1-C_8 \) silanyl, \( C_1-C_8 \) alkylsilyloxy, \( C_6-C_{12} \) aryl, \( C_6-C_{12} \) aryloxy, \( C_1-C_8 \) sulfonylamido, \( C_3-C_{12} \) heteroaryl or \( C_2-C_8 \) heterocyclic group; each optionally substituted with an alkyl, alkoxy, alkylthio, aryl, aryloxy, halogen atom or heterocyclic group;
alkylcarbonyl, C₆-C₁₂ arylcarbonyl, C₁-C₈ alkoxy carbonyl, C₆-C₁₂ aryl oxycarbonyl, C₁-C₈ alkylaminocarbonyl, C₆-C₁₂ arylaminocarbonyl, C₁-C₈ alkylamido, C₆-C₁₂ aryl amido, C₁-C₈ alkylaminosulfanyl, C₆-C₁₂ arylaminosulfonyl, C₁-C₈ sulfonylamido, C₃-C₁₂ heteroaryl or C₂-C₈ heterocyclic group; each optionally substituted with an alkyl, alkoxy, alkylthio, aryl, aryloxy, halogen atom or heterocyclic group. 

11. The transition metal complex according to claim 10, wherein the structure IIa or IIb:

M is ruthenium;

L is IIIa or IIIId; and in IIIa, q = 1, R⁴ and R⁵ each is 2,4,6-trimethylphenyl, R⁶ and R⁷ each is H, or in IIIId, R⁸ and R⁹ each is cyclohexyl (Cy).

L¹ and L² each is chloride anion;

m = 0 or 1, and n = 0 or 1;

When m = 0, Y is CH₂, NH, C₁-C₄ alkoxy, C₁-C₄ alkylamino or C₆-C₉ arylamino group;

When m = 1, X is nitrogen, C₁-C₃ alkylamino, CH, CH₂, or carbonyl; Y is oxygen, nitrogen, imino, NH, C₁-C₄ alkyl, C₁-C₄ alkoxy, C₁-C₄ alkylamino, or C₆-C₉ arylamino; "Y≡X" is either single bond or double bond;

When n = 0, p = 0 or 1; when n = 1, p = 0;

When n = 0 and p = 1, L³ is one substituted pyridine at the meta-position or para-position, and the nitrogen atom of the substituted pyridine donates a pair of electron to ruthenium cation, wherein the substituents at the meta-position or para-position of pyridine are each selected from halogen, nitro, C₁-C₃ alkyl, C₁-C₃ alkoxy, C₁-C₆ alkylamino, unsubstituted or substituted C₆-C₁₂ aryl;

When n = 1, X¹ is CH₂, substituted or unsubstituted phenyl, or carbonyl; Y¹ is oxygen or carbonyl;

R¹ is H;

when n = 1, R² is methyl, ethyl, or isopropyl; when n = 0, R² is H, halogen, C₁-C₄ alkyl or C₁-C₄ alkoxy in structure IIa.

E is H, halogen, nitro, C₁-C₄ alkyl, C₁-C₄ alkoxy, C₁-C₄ alkoxy carbonyl, C₁-C₈ alkylaminosulfanyl, C₆-C₁₂ arylaminosulfonyl;
E¹ and E² are each H, halogen, C₁-C₄ alkyl or C₁-C₄ alkoxy;
E³ is H;
E⁴ is H or C₁-C₄ alkyl;
E⁵ and E⁶ is H, halogen, C₁-C₄ alkyl or C₁-C₆ alkoxy;
E⁷ is H or C₁-C₄ alkyl.

12. A method of carrying out a metathesis reaction with olefin substrate, comprising intramolecular ring-closing metathesis (RCM), intermolecular cross metathesis (CM), acyclic diene metathesis (ADMET) or ring-opening metathesis polymerization (ROMP) of cyclo-olefin substrate in the presence of one or more catalysts of claim 5.

13. The method according to claim 12, wherein cyclo-olefin substrate for ROMP is selected from dicyclopentadiene (DCPD), norbornene, cyclooctene, or a kind of tensional cycloolefin; each is optionally substituted or unsubstituted with one or more of F, Cl, Br, C₁-C₁₅ alkyl, C₁-C₁₅ alkoxy, C₁-C₁₅ alkylthio, C₂-C₁₅ alkenyloxy, C₁-C₁₅ silanyl, C₁-C₁₅ alkylsilyloxy, C₆-C₁₅ aryl, C₆-C₁₅ aryloxy, C₁-C₁₅ alkylcarbonyl, C₆-C₁₅ arylcarbonyl, C₁-C₁₅ alkoxy carbonyl, C₆-C₁₅ aryloxycarbonyl, C₁-C₁₅ alkylaminocarbonyl, C₆-C₁₅ arylaminocarbonyl, C₁-C₁₅ alkylamido, C₆-C₁₅ arylamido, C₁-C₁₅ alkylaminosulfonyl, C₆-C₁₅ arylaminosulfonyl, C₁-C₁₅ sulfonlamido, C₃-C₁₅ heteroaryl or C₂-C₁₅ heterocyclic group.

14. A cycloolefin substrate having the following structure VIa-VIc;

Wherein, r = 1, 2, 3 or 4; s = 1, 2, 3 or 4;
A is O, S, C₁-C₁₅ alkyl, C₁-C₁₅ alkoxy, C₁-C₁₅ aryloxy, C₁-C₁₅ alkylthio, C₁-C₁₅ alkoxy carbonyl, C₁-C₁₅ alkyaminocarbonyl, C₆-C₁₅ arylamino, C₁-C₁₅ arylaminocarbonyl, C₁-C₁₅ alkylamido, C₆-C₁₅ arylamido, or C₁-C₁₅ heterocyclic amido group;
G is a group of compounds with specific properties and uses; each is optionally selected from commercial drugs or liquid crystal monomers;

R^{10} and R^{11} are each H, halogen, C_{1}-C_{15} alkyl, C_{1}-C_{15} alkoxy, C_{1}-C_{15} alkylthio, C_{1}-C_{15} alkysiloxyo, C_{6}-C_{15} aryloxy, C_{6}-C_{15} aryl, C_{2}-C_{15} heterocyclic, C_{3}-C_{15} heterocyclic aryl, C_{1}-C_{15} alkylcarbonyl, C_{1}-C_{15} alkoxy carbonyl, C_{6}-C_{15} aryloxy carbonyl, C_{1}-C_{15} alkylaminocarbonyl, C_{6}-C_{15} arylaminocarbonyl, C_{1}-C_{15} alkylamido, C_{1}-C_{15} alkylsulfonyl, C_{1}-C_{15} alkylsulfonamido, liquid crystal monomer or modified pro-drug;

“Linker” is C_{1}-C_{15} alkyl, C_{1}-C_{15} alkoxy, C_{1}-C_{15} alkylthio, C_{1}-C_{15} alkysiloxyo, C_{6}-C_{15} aryloxy, C_{6}-C_{15} aryl, C_{1}-C_{15} alkoxy carbonyl, C_{6}-C_{15} aryloxy carbonyl, C_{1}-C_{15} alkylaminocarbonyl, C_{6}-C_{15} arylaminocarbonyl, C_{1}-C_{15} alkylamido, C_{6}-C_{15} arylsulfonamido, C_{3}-C_{15} heteroaryl or C_{2}-C_{15} heterocyclic group.

15. The cycloolefin substrate according to claim 14, wherein r = 1, 2, 3 or 4; s = 1, 2, 3 or 4;

A is O, S, C_{1}-C_{8} alkyl, C_{1}-C_{8} alkoxy, C_{1}-C_{8} aryloxy, C_{1}-C_{15} alkylthio, C_{1}-C_{8} alkoxy carbonyl, C_{1}-C_{8} alkylamino, C_{6}-C_{12} arylamino, C_{1}-C_{8} alkylaminocarbonyl, C_{6}-C_{12} arylaminocarbonyl, C_{1}-C_{8} alkylamido, C_{6}-C_{12} arylamido, or C_{1}-C_{8} heterocyclic amido group;

G is a kind of compounds with specific properties and uses; each is optionally selected from commercial liquid crystal monomers or modified prodrugs;

R^{10} and R^{11} are each H, halogen, C_{1}-C_{8} alkyl, C_{1}-C_{8} alkoxy, C_{1}-C_{8} alkylthio, C_{1}-C_{8} alkysiloxyo, C_{6}-C_{12} aryloxy, C_{6}-C_{12} aryl, C_{2}-C_{8} heterocyclic, C_{3}-C_{12} heterocyclic aryl, C_{1}-C_{8} alkylcarbonyl, C_{1}-C_{8} alkoxy carbonyl, C_{6}-C_{12} aryloxy carbonyl, C_{1}-C_{8} alkylaminocarbonyl, C_{6}-C_{12} arylaminocarbonyl, C_{1}-C_{8} alkylamido, C_{1}-C_{8} alkylsulfonyl, C_{1}-C_{8} alkylsulfonamido, liquid crystal monomer or modified pro-drug;

“Linker” is C_{1}-C_{8} alkyl, C_{1}-C_{8} alkoxy, C_{1}-C_{8} alkylthio, C_{1}-C_{8} alkysiloxyo, C_{6}-C_{12} aryloxy, C_{6}-C_{12} aryl, C_{1}-C_{8} alkoxy carbonyl, C_{6}-C_{12} aryloxy carbonyl, C_{1}-C_{8} alkylaminocarbonyl, C_{6}-C_{12} arylaminocarbonyl, C_{1}-C_{8} alkylamido, C_{6}-C_{12} arylamido,
C₈⁻C₈ alkylsulfonamido, C₆⁻C₁₂ arylsulfonamido, C₃⁻C₁₂ heteroaryl or C₂⁻C₈ heterocyclic group.

16. The cycloolefin substrate according to claim 15, wherein in structure VIa-VIc, r = 1 or 2, and s = 1 or 2;

A is O, CH₂, C₁⁻C₅ alkyl-amino, C₁⁻C₅ alkoxy, C₁⁻C₅ alkyaminocarbonyl or C₁⁻C₅ heterocyclic amido group;

“Linker” is C₁⁻C₆ alkyl, C₁⁻C₅ alkoxy, C₁⁻C₅ alkylthio, C₁⁻C₅ alkoxycarbonyl, C₁⁻C₅ alkyaminocarbonyl, C₆⁻C₁₂ arylaminocarbonyl, C₁⁻C₅ alkylamido or C₆⁻C₁₂ arylamido group;

R¹⁰ and R¹¹ are each H, C₁⁻C₅ alkoxy, C₆⁻C₁₂ aryl, C₁⁻C₅ alkoxy, C₆⁻C₁₂ aryl oxycarbonyl, C₆⁻C₁₂ aryl oxycarbonyl, C₁⁻C₅ alkyaminocarbonyl, C₆⁻C₁₂ arylaminocarbonyl, C₁⁻C₅ alkylamido, C₆⁻C₁₂ arylamido, liquid crystal monomer or modified prodrugs.

17. The cycloolefin substrate according to claim 15, wherein G is a kind of optionally modified prodrug of commercial drug Lipitor having the following structure VIIa-VIIId:

Wherein R¹² is cyclopropyl, C₁⁻C₁₅ alkyl, C₃⁻C₁₅ cycloalkyl, C₁⁻C₁₅ alkoxy, C₆⁻C₁₅ aryl, C₆⁻C₁₅ alkoxy, C₁⁻C₁₅ alkylamino, C₆⁻C₁₂ arylamino, C₁⁻C₁₅ alkylsulfonamido, C₆⁻C₁₅ arylsulfonamido, C₃⁻C₁₅ heterocyclic aryl or C₂⁻C₁₅ heterocyclic group.

18. The cycloolefin substrate according to claim 17, wherein R¹² is cyclopropyl, C₁⁻C₆ alkyl, C₃⁻C₆ cycloalkyl, C₁⁻C₆ alkoxy, C₆⁻C₁₂ aryl, C₆⁻C₁₂ aryl, C₁⁻C₆
alkylamino, C₆-C₁₂ arylamino, C₁-C₆ alkylsulfonamido, C₆-C₁₂ arylsulfonamido, C₃-C₁₂ heterocyclic aryl or C₂-C₆ heterocyclic group.

19. A method of making a quality-modified polymer having the following structure VIIIa or VIIIb in the presence of one or more mixed catalysts of claim 5.

![Diagram VIIIa and VIIIb](image)

20. A functional polymer, comprising a modified prodrug or functional group G having the following structure IXa-IXc:

![Diagram IXa, IXb, IXc](image)

Wherein: r = 1, 2, 3 or 4; s = 1, 2, 3 or 4;

A is O, S, C₁-C₁₅ alkyl, C₁-C₁₅ alkoxy, C₁-C₁₅ aryloxy, C₁-C₁₅ alkylthio, C₁-C₁₅ alkoxy carbonyl, C₁-C₁₅ arylamino, C₆-C₁₅ arylamino, C₁-C₁₅ alkylaminocarbonyl, C₆-C₁₅ arylaminocarbonyl, C₁-C₁₅ alkylamido, C₆-C₁₅ arylamido, or C₁-C₁₅ heterocyclic amido group;

G is a group of compounds with specific properties and uses; each is optionally selected from commercial liquid crystal monomer or modified prodrugs;

R¹⁰ and R¹¹ are each H, halogen, C₁-C₁₅ alkyl, C₁-C₁₅ alkoxy, C₁-C₁₅ alkylthio, C₁-C₁₅ alkylsiloxy, C₆-C₁₅ aryloxy, C₆-C₁₅ aryl, C₂-C₁₅ heterocyclic, C₃-C₁₅ heterocyclic aryl, C₁-C₁₅ alkylcarbonyl, C₁-C₁₅ alkyloxycarbonyl, C₆-C₁₅ aryloxycarbonyl, C₁-C₁₅ alkylaminocarbonyl, C₆-C₁₅ arylaminocarbonyl, C₁-C₁₅ alkylamido, C₁-C₁₅ alkylsulfonyl, C₁-C₁₅ alkylsulfonamido, liquid crystal monomer or modified prodrug;
“Linker” is C₁-C₁₅ alkyl, C₁-C₁₅ alkoxy, C₁-C₁₅ alkylthio, C₁-C₁₅ alkylsilyloxy, C₆-C₁₅ aryloxy, C₆-C₁₅ aryl, C₁-C₁₅ alkoxycarbonyl, C₆-C₁₅ aryloxycarbonyl, C₁-C₁₅ alkylaminocarbonyl, C₆-C₁₅ arylaminocarbonyl, C₁-C₁₅ alkylamido, C₆-C₁₅ arylamido, C₁-C₁₅ alkylsulfonylamido, C₆-C₁₅ arylsulfonylamido, C₃-C₁₅ heteroaryl or C₂-C₁₅ heterocyclic group.

21. The functional polymer according to claim 20, wherein r, s, A, “Linker”, R¹⁰ and R¹¹ each is as defined in claim 16;

Wherein G is a kind of optionally modified pro-drug of Lipitor having the following structure VIIa-VIIId:

Wherein: R¹² is as defined in claim 18.

22. A method of making a modified nitrile butadiene rubber (NBR) or styrene-butadiene rubber (SBR) by depolymerization in the presence of one or more mixed catalysts of claim 5 at 30-100°C.

23. A method of making a depolymerized HNBR (hydrogenated nitrile butadiene rubber) or styrene-butadiene rubber (SBR) by adding one or more mixed catalysts of claim 5 first to carry out depolymerization of NBR, followed by adding hydrogen into the reaction under high pressure for hydrogenation at 60-150°C.

24. A method of making a hydrogenated nitrile butadiene rubber (HNBR) or styrene-butadiene rubber by adding hydrogen under high pressure first, followed by adding one or more mixed catalysts of claim 5 at 60-150°C.

25. A use of catalysts of claim 5 in depolymerization of a rubber comprising at least one carbon-carbon double bond.
26. A use of catalysts of claim 5 in hydrogenation of a rubber comprising at least one carbon-carbon double bond.

27. A process of making a modified polymer VIIIa-VIIIb, functional polymer IXa-IXb in the presence of one or more mixed catalysts of claim 5.

28. A method of making functional polymers, comprising reacting one or more monomers in the presence of one or more mixed catalysts of claim 5.
Figure 1
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: B01J31/--; C07F15/--; C08F4/--

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WPI; EPODOC; CNPAT; CNKI; CAPLUS; MARPAT: complex, ruthenium, carbene, ligand, catalyst, metathesis, ROMP, function, lipitor

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<th>Category*</th>
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<th>Relevant to claim No.</th>
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<td>EVANS, Paul et al. Synthesis of a 6-aryloxymethyl-5-hydroxy-2,3,4,5-tetrahydro-[1H]-2- benzazepin-4-one; a muscarinic (M3) antagonist. Organic &amp; Biomolecular Chemistry, 2008, Vol. 6, p. 2158-2167 see Scheme 1, compound 13</td>
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<td>X</td>
<td>POGOSYAN, G. M. et al. Styrene derivatives. XXII. Synthesis and polymerization of amines of 2-vinylbenzoic acid. Armyanskii Khimicheskii Zhurnal, 1971, Vol. 24, No. 9, p.816-821 see Table 1, the last compound</td>
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Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:
  “A” document defining the general state of the art which is not considered to be of particular relevance
  “E” earlier application or patent but published on or after the international filing date
  “L” document which may throw doubts on priority claim (S) or which is cited to establish the publication date of another citation or other special reason (as specified)
  “O” document referring to an oral disclosure, use, exhibition or other means
  “P” document published prior to the international filing date but later than the priority date claimed

“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

“&” document member of the same patent family

Date of the actual completion of the international search
15 Mar. 2011 (15.03.2011)

Date of mailing of the international search report
07 Apr. 2011 (07.04.2011)

Name and mailing address of the ISA/CN
The State Intellectual Property Office, the P.R.China
6 Xitucheng Rd., Jimen Bridge, Haidian District, Beijing, China
100088
Facsimile No. 86-10-62019451

Form PCT/ISA/210 (second sheet) (July 2009)

Authorized officer
CHEN, Ning
Telephone No. (86-10)82245338
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<td>WO2007003135A1 (ZHAN, Z.) 11 Jan. 2007 (11.01.2007) see examples</td>
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### Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. **☐** Claims Nos.:
   because they relate to subject matter not required to be searched by this Authority, namely:

2. **☐** Claims Nos.:
   because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. **☐** Claims Nos.:
   because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

### Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

I. Claims 1-13, 19, 22-28 relate to the metal complex, its ligand, the method using the catalyst and the use of the catalyst.
II. Claims 14-18, 20-21 relate to the cycloolefin substrate and the obtained functional polymer.

The two groups of inventions relate to the catalyst, the cycloolefin substrate and the functional polymer product, respectively. They are quite different technical proposals, which do not contain any same or corresponding special technical feature, and are not so linked as to form a single general inventive concept. The application, hence does not meet the requirement of unity of invention in the sense of Article 13(1) PCT.

1. **☐** As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. **☒** As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fee.

3. **☐** As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. **☐** No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

**Remark on protest**

- **☐** The additional search fees were accompanied by the applicant’s protest and, where applicable, the payment of a protest fee.
- **☐** The additional search fees were accompanied by the applicant’s protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- **☐** No protest accompanied the payment of additional search fees.
### INTERNATIONAL SEARCH REPORT

Information on patent family members

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Form PCT/ISA/210 (patent family annex) (July 2009)
Continuation of: A. CLASSIFICATION OF SUBJECT MATTER

B01J 31/22 (2006.01)i
C07F 15/00 (2006.01)i
C08F 4/80 (2006.01)i