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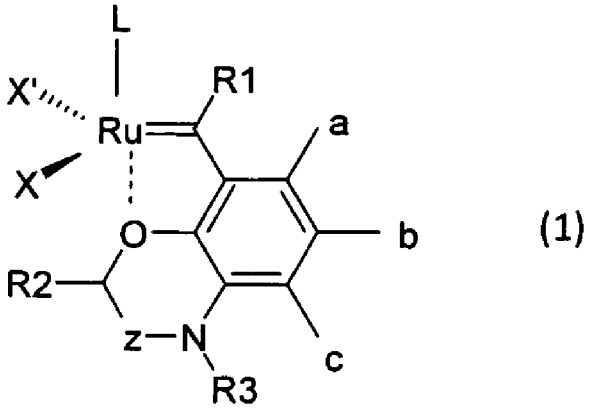
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WO 2012/013208 A1

(54) Title: NOVEL STABLE AND HIGHLY TUNABLE METATHESIS CATALYSTS



(1)

(57) Abstract: The present invention relates to catalytically active compounds of the general formula (1) that are highly tunable, as well as to a method of their preparation and their use in any type metathesis reaction. The new compounds of the present invention comprise activation sites that allow for specific catalyst design. Particularly, side chains and ligands allow efficient activity and specificity control of the catalysts of the present invention.

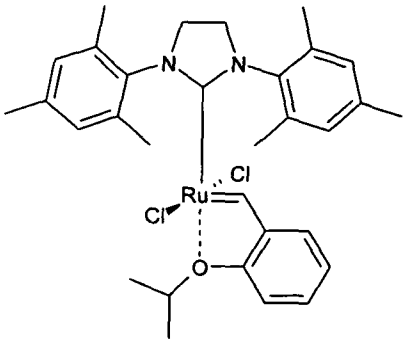
NOVEL STABLE AND HIGHLY TUNABLE METATHESIS CATALYSTS

The present invention concerns novel ruthenium compounds and the use thereof as catalyst in olefin metathesis reactions. The present invention also concerns a method for the preparation of said ruthenium compounds.

Ruthenium compounds or complexes, as well as their use as catalysts are well known in prior art. Methods for their preparation are vastly studied and can be found in a great number of scientific publications.

For instance, the compounds called *Grubbs III*, *Schrock catalyst*, *Piers-Grubbs II* are well known as highly active catalysts for olefins metathesis and are respectively described in the following scientific publications: *Angew. Chem. Int. Ed.* 2002, 41, 4035-4038; *J. Am. Chem. Soc.* 1990, 112, 3875-3886; *Angew. Chem. Int. Ed.*, 2004, 43, 6161-6165.

The ruthenium complex of the formula **A**, known as Hoveyda-Grubbs catalyst, is disclosed in WO 02/14376 A2 and in the original paper: *J. AM. CHEM. SOC., 2000, 122, 8168-8179.*



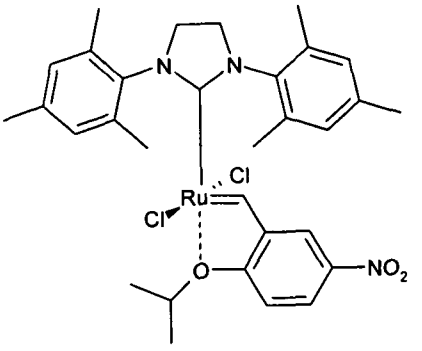
(A)

The Hoveyda-Grubbs catalyst is considered in prior art as an active, air stable and recoverable metathesis catalyst. In order to enhance and improve the activity towards olefin metathesis transformations, several structural modifications have been achieved through the styrenylether benzylidene ligand.

These structural modifications have led to other well-known catalysts, showing a higher catalytic activity than the classic Hoveyda-Grubbs catalyst of formula **A**.

For instance, WO 2004/035596, *Angew. Chem. Int. Ed. 2002, 41, 4038-4040* and *J. Am. Chem. Soc. 2004, 126, 9318-9325* disclose a catalyst of formula **B** (also referred to as *Grela* catalyst):

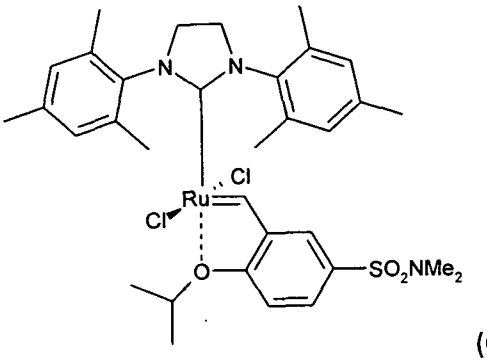
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(B)

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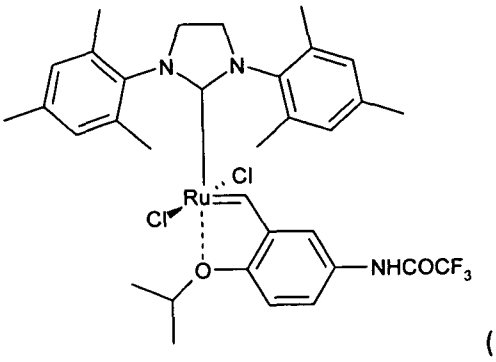
WO 2007/003135 discloses a catalyst of formula **C** (also referred to as *Zannan* catalyst):



(C)

;

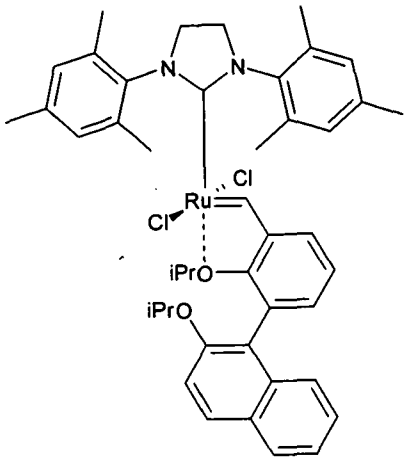
WO 2008/065187 A1 and *Eur. J. Org. Chem. 2009, 4254-4265* disclose a catalyst of formula **D**:



(D)

;

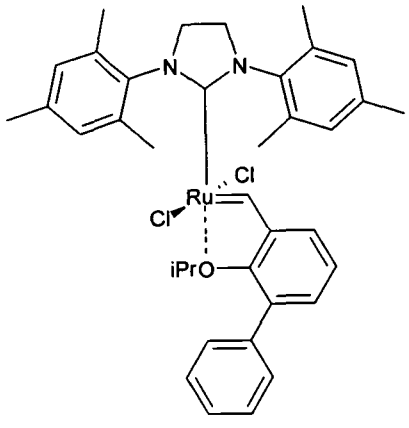
Angew. Chem. Int. Ed. 2002, 41, 794-796 discloses a catalyst of formula **E:**



(E)

;

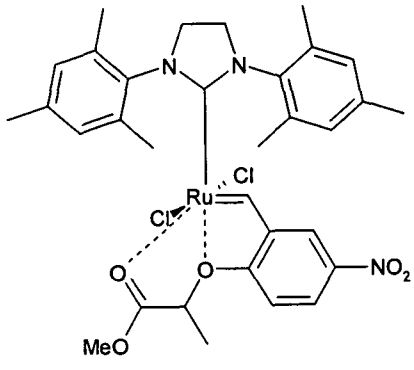
Angew. Chem. Int. Ed. 2002, 41, 2403-2405 discloses a catalyst of formula **F** (also referred to as *Blechert* catalyst),



(F)

;

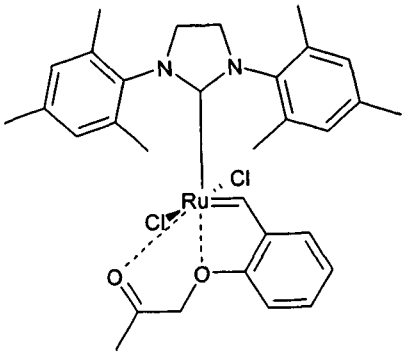
J. Am. Chem. Soc. 2006, 128, 13652-13653 discloses a catalyst of formula **G**:



(G)

;

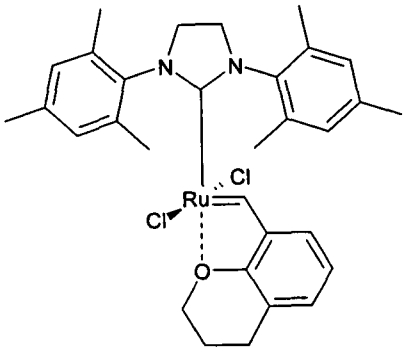
US 2010/0113795 A1 discloses a catalyst of formula **H**:



(H)

;

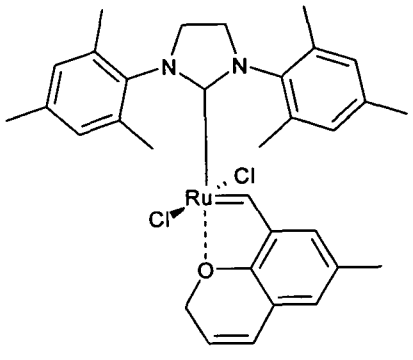
Adv. Synth. Catal. 2007, 349, 193-203 discloses a catalyst of formula **I**:



(I)

; and

J. Organomet. Chem. 2010, 695, 1265-1270 discloses a catalyst of formula **J**:



(J)

.

The improvement in the activity of **B**, **C**, **D** compared to **A** is attributed to the electronic effects of the substituents on the styrenylether benzylidene ligand (respectively NO_2, SO_2NMe_2 and $NHCOCF_3$).

The improvement in the activity of **E** and **F** compared to **A** is attributed to the steric effects of the ortho-substituents on the styrenylether benzylidene ligand (respectively a naphtol and a phenyl).

The improvement in the activity of **G** and **H** compared to **A** is attributed to the additional coordinating functions on the styrenylether benzylidene ligand (respectively an ester and a ketone). An additional electronic effect can be involved, as showed in **G** with a NO_2 substituent.

The improvement in the activity of **I** and **J** compared to **A** is attributed to the conformational constraints of the chelating ether into the styrenylether benzylidene ligand (respectively a chroman and chromenyl ring).

One between other problems of prior art catalysts is that catalytic activity goes along with complex instability. In fact, generally the more a catalyst is active the less said catalyst is stable.

The present invention improves the situation.

For this purpose, the invention proposes ruthenium compounds having a novel backbone structure.

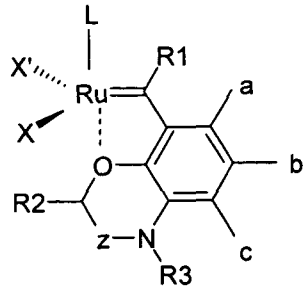
In fact, the applicant surprisingly found that ruthenium compounds comprising an oxazinone or oxazine function in their backbone show a significant activity increase compared to prior art catalysts such as those of formula **A, B, C, D, E, F, G, H, I** or **J**.

The oxazinone or oxazine function is set as new coordinating alkoxy ligand into the benzylidene fragment of the prior art catalysts.

Moreover, in the present invention the applicant identified three different activation sites within the new chelating benzylidene ligand. These activation sites allow efficient and specific control of the catalytic activity of the ruthenium complexes in olefin metathesis transformation.

Further, the improvement of the catalytic activity does not occur at the detriment of the complex stability. Indeed, the complex of the invention remains remarkably stable towards moisture, air and solvents.

To this end, the invention proposes compound of the general formula 1,



(1)

wherein,

X and X' are anionic ligands;

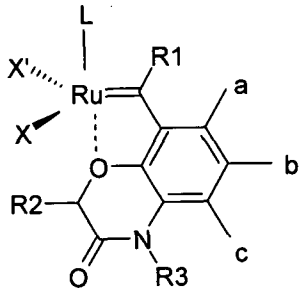
L is an uncharged ligand;

z is a methylene or a carbonyl group;

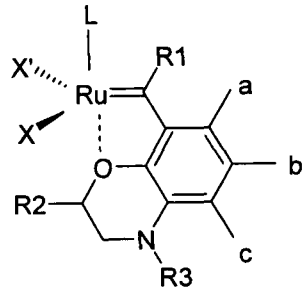
a, b and c are each, independently of one another, H, or a substituted or unsubstituted, charged or uncharged side chain comprising up to 20 carbon atoms and optionally comprising one or more functional groups;

R1, R2 and R3 are each, independently of one another, H or a substituted or unsubstituted, charged or uncharged side chain comprising up to 20 carbon atoms and optionally comprising one or more functional groups.

When z is carbonyl, general formula 1 can be represented by following formula 1^a; and when z is methylene general formula 1 can be represented by following formula 1^b.



(1^a)



(1^b)

Preference is given here to the compounds of general formula 1 in which X and X' are halogen and particularly to the compounds in which said halogen are selected from the group consisting of Cl and Br.

In the above mentioned compounds of general formula 1, preference is given to those in which a, b and c are each selected from the group consisting of H; $-NO_2$; C_{1-12}-alkyl; C_{5-12}-cycloalkyl; C_{1-12}-alkoxy; cyano; aryl or heteroaryl, preferentially phenyl optionally substituted by a radical selected from the group consisting of C_{1-6}-alkyl and C_{1-6}-alkoxy; monohalogenated or polyhalogenated aryl radicals or hetero-aryl radicals; monohalogenated or polyhalogenated C_{1-6}-alkyl radicals; monohalogenated or polyhalogenated C_{1-6}-alkyl-substituted aryl radicals; C_{1-6}-alkylcarbonyl radicals; monohalogenated or polyhalogenated C_{1-6}-alkylcarbonyl radicals; C_{1-6}-alkoxycarbonyl radicals; monohalogenated or polyhalogenated C_{1-6}-alkoxycarbonyl radicals; arylcarbonyl radicals; monohalogenated or polyhalogenated arylcarbonyl radicals; aryloxycarbonyl radicals; monohalogenated or polyhalogenated aryloxycarbonyl radicals; $-(C=O)-N(R^a)_2$ radicals wherein R^a is a C_{1-6}-alkyl or aryl radical; $-NH-(C=O)-R^a$ radicals wherein R^a is a C_{1-6}-alkyl or aryl radical; C_{1-6}-alkylsulfonyl radicals; C_{1-6}-alkylsulfinyl radicals; $-P(=O)(R^a)_2$ radicals wherein R^a is a C_{1-6}-alkyl or aryl radical; $-NH-SO_2-R^a$ radicals wherein R^a is a C_{1-6}-alkyl or aryl radical; $(SO_2)NR^a_2$ radicals wherein R^a is a C_{1-6}-alkyl or aryl radical; $P(=O)(OR^a)(R^a)$ radicals wherein R^a is a C_{1-6}-alkyl or aryl radical.

In a particular preferred embodiment a, b and c are each H.

Further, preference is given here to the compounds of general formula 1 in which R1 is selected from the group consisting of H, C_{2-12}-alkenyl, C_{2-12}-alkynyl or aryl.

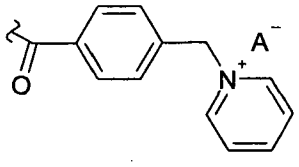
In a particular preferred embodiment R1 is H.

Furthermore, preference is given here to the compounds of general formula 1 in which R2 is selected from the group consisting of H, C_{1-12}-alkyl, C_{5-12}-cycloalkyl, C_{7-18}-aralkyl or aryl.

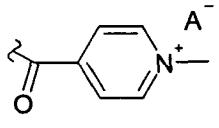
In a particular preferred embodiment R2 is a methyl-, ethyl- or isopropyl-group.

Furthermore, preference is given to the compounds of general formula 1 in which R3 is selected from the group consisting of H, C_{1-12}-alkyl, C_{5-12}-cycloalkyl, C_{7-18}-aralkyl, aryl, C_{1-12}-halogeno-alkyl, C_{1-12}-ammonium-alkyl, C_{1-12}-pyridinum-alkyl, C_{1-12}-aldehyde-alkyl, C_{1-12}-nitro-alkyl, nitrile or a radical selected from the group consisting of ketones COR4, esters CO_2R4, oxalates $COCO_2R4$, sulfones SO_2R4 or amides CONHR4 wherein R4 is selected from the group consisting of H, C_{1-12}-alkyl, C_{5-12}-cycloalkyl, C_{7-18}-aralkyl, aryl, C_{1-12}-halogeno-alkyl, C_{1-12}-ammonium-alkyl, C_{1-12}-pyridinum-alkyl, C_{1-12}-aldehyde-alkyl, C_{1-12}-nitro-alkyle, nitrile.

Particular preference is given to the compounds of general formula 1 in which z is methylene, and R3 is a side chain of following formula $R3^a$ or $R3^b$:



($R3^a$)

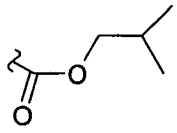


($R3^b$)

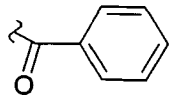
;

in this preferred embodiment, A^- is selected from the group consisting of F^-, Cl^-, Br^-, I^-, tetrafluoroborate BF_4^-, hexafluorophosphate PF_6^- and bis(trifluoromethylsulfonyl)amide NTf_2^-.

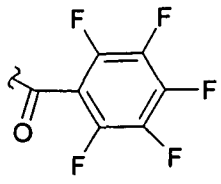
In another preferred embodiment, R3 is a side chain of following formula $R3^c$, $R3^d$, $R3^e$, $R3^f$, $R3^g$, $R3^h$, $R3^i$, $R3^j$, $R3^k$, $R3^l$, $R3^m$, $R3^n$, $R3^o$ or $R3^p$:



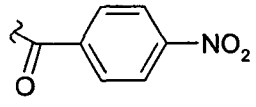
($R3^c$)

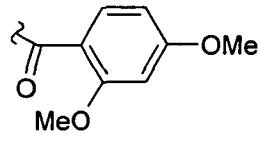


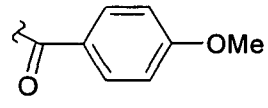
($R3^d$)

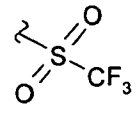

(R3[e])

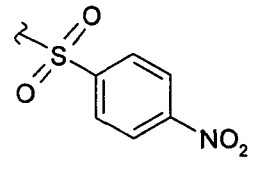

(R3[f])

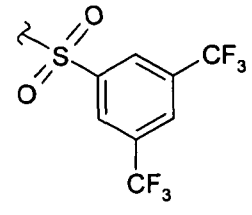

(R3[g])

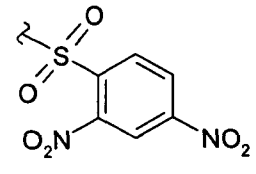

(R3[h])

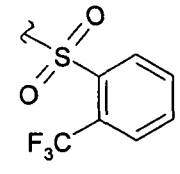

(R3[i])

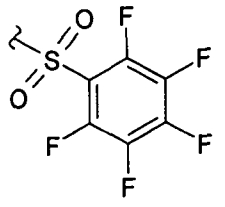

(R3[j])


(R3[k])

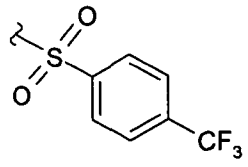

(R3[l])


(R3[m])


(R3[n])



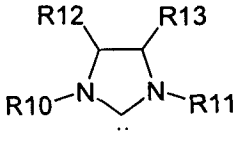
(R3°)



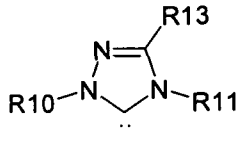
(R3ᵖ)

Preference is given to the compounds of general formula 1 in which L is a phosphine $P(R8)_3$ or a phosphate $P(OR9)_3$ and wherein R8 and R9 are each independently of one another C_{1-6}-alkyl, C_{5-12}-cycloalkyl or aryl.

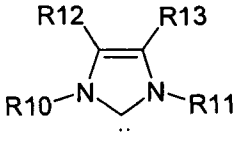
Another preference is given to the compounds of general formula 1 in which L is a ligand of following formula L1, L2, L3 or L4:



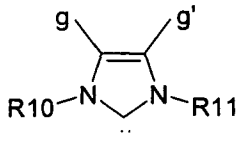
(L1)



(L2)



(L3)



(L4)

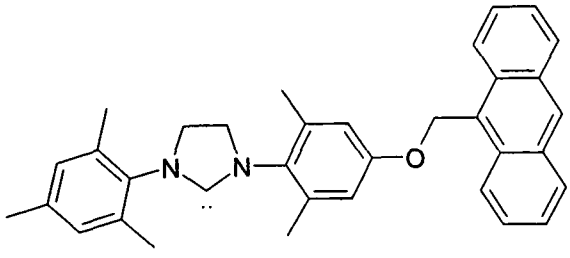
;

in this embodiment, R10 and R11 are each, independently of one another a substituted or an unsubstituted side chain comprising 1 to 30 carbon atoms and optionally comprising one or more functional groups. Further, in this embodiment R12 and R13 are each, independently of

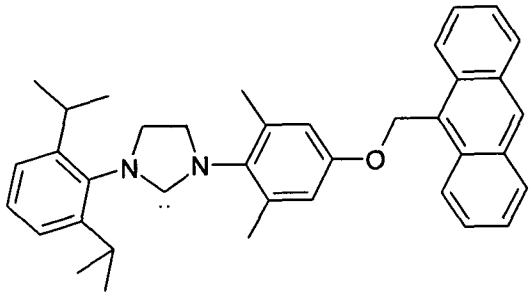
one another, H, C_{1-6}-alkyl optionally substituted by a alkoxy radical OR15, or aryl optionally substituted by a alkoxy radical OR15, or form a 3- or 4-membered alkylene bridge, and wherein R15 is selected from the group consisting of C_{1-20}-alkyl, aryl and C_{7-18}-aralkyl, and wherein g and g' are each halogen. In a particular preferred embodiment g and g' are either Cl or Br atoms.

Furthermore, in the above mentioned embodiment, particular preference is given to the compounds in which R10 and R11 are each, independently of one another, C_{1-30}-alkyl optionally substituted by a alkoxy radical OR15, C_{2-30}-alkenyl optionally substituted by a alkoxy radical OR15, aryl optionally substituted by a alkoxy radical OR15, aminoalkyl or aminocycloalkyl.

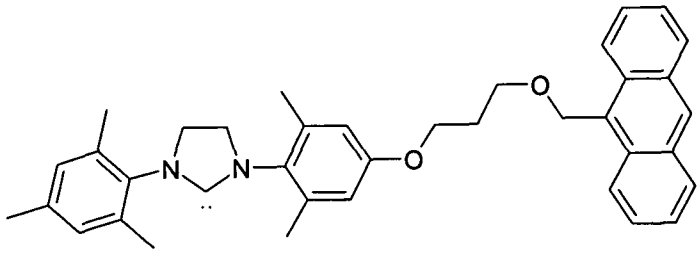
Particular preference is given to the compounds of general formula 1 in which L is a ligand of following formula $L1^a$, $L1^b$, $L1^c$, $L1^d$, $L1^e$, $L1^f$ or $L1^g$:



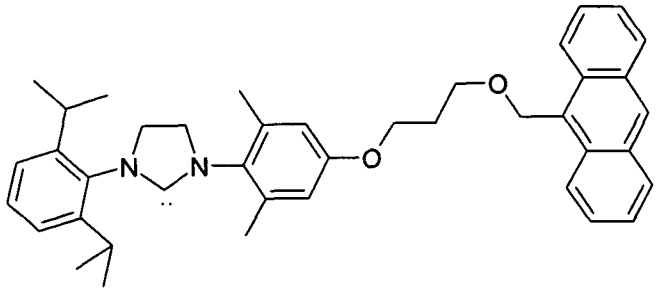
($L1^a$)



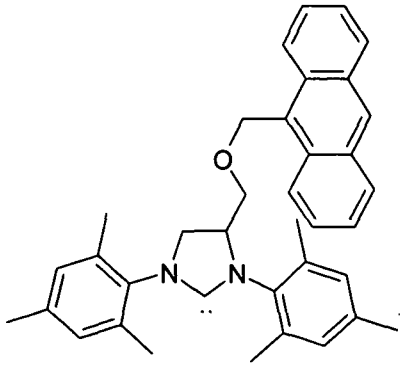
($L1^b$)



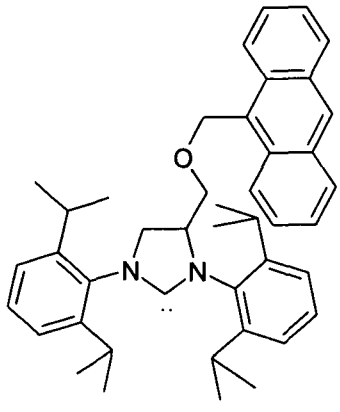
($L1^c$)



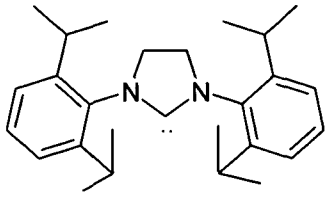
($L1^d$)



(L1^e)



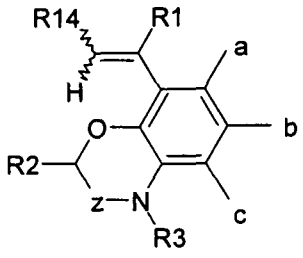
(L1^f)



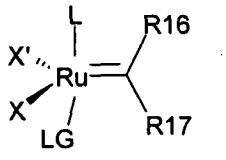
(L1^g)

An additional aspect of the present invention is the use of the compound described above as a catalyst for a chemical reaction. More particularly, said chemical reaction is a metathesis reaction such as ring-closing metathesis (RCM), cross-metathesis (CM) and ring-opening metathesis polymerization (ROMP).

An additional aspect of the present invention is a method for preparing the new compounds of general formula 1 disclosed hereinabove. The method of the present invention comprises a step of reacting a compound of the below general formula (2) with a ruthenium complex of the below general formula (3):



(2)



(3)

wherein

X and X' are anionic ligands;

L is an uncharged ligand;

z is a methylene or a carbonyl group;

a, b and c are each, independently of one another, H, or a substituted or unsubstituted, charged or uncharged side chain comprising up to 20 carbon atoms and optionally comprising one or more functional groups;

R1, R2 and R3 are each, independently of one another, H or a substituted or unsubstituted, charged or uncharged side chain comprising up to 20 carbon atoms and optionally comprising one or more functional groups,

and wherein,

LG is a leaving group, preferentially LG is a phosphine $P(R8)_3$ wherein R8 is selected from the group consisting of C_{1-6}-alkyl; C_{5-12}-cycloalkyl preferentially cyclohexyl; aryl; more preferentially LG is a pyridine wherein pyridine is unsubstituted or substituted by a charged or uncharged side chain comprising up to 20 carbon atoms,

R14 is selected from the group consisting of H; C_{1-12}-alkyl, preferentially a methyl group; C_{5-12}-cycloalkyl,

R16 and R17 are each independently of one another H, C_{1-6}-alkyl, optionally substituted by one or more halogens or by aryl, optionally substituted by one or more halogens or by C_{1-6}-alkyl; or R16 and R17 form together a 5- to 12-membered aliphatic and/or aromatic ring system, optionally substituted by one or more halogens, C_{1-6}-alkyl or by aryl; and preferentially R16 and R17 form an indenylidene system.

Preference is given here to the method in which X and X' are halogen. In this embodiment, X and X' are preferably selected from the group consisting of Cl and Br.

Further, preference is given to the method in which, a, b and c are each selected from the group consisting of H; $-NO_2$; C_{1-12}-alkyl; C_{5-12}-cycloalkyl; C_{1-12}-alkoxy; cyano; aryl or heteroaryl, preferentially phenyl optionally substituted by a radical selected from the group consisting of C_{1-6}-alkyl and C_{1-6}-alkoxy; monohalogenated or polyhalogenated aryl radicals or hetero-aryl radicals; monohalogenated or polyhalogenated C_{1-6}-alkyl radicals; monohalogenated or

polyhalogenated C_{1-6}-alkyl-substituted aryl radicals; C_{1-6}-alkylcarbonyl radicals; monohalogenated or polyhalogenated C_{1-6}-alkylcarbonyl radicals; C_{1-6}-alkoxycarbonyl radicals; monohalogenated or polyhalogenated C_{1-6}-alkoxycarbonyl radicals; arylcarbonyl radicals; monohalogenated or polyhalogenated arylcarbonyl radicals; aryloxycarbonyl radicals; monohalogenated or polyhalogenated aryloxycarbonyl radicals; -(C=O)-N(R^a)$_2$ radicals wherein R^a is a C_{1-6}-alkyl or aryl radical; -NH-(C=O)-R^a radicals wherein R^a is a C_{1-6}-alkyl or aryl radical; C_{1-6}-alkylsulfonyl radicals; C_{1-6}-alkylsulfinyl radicals; -P(=O)(R^a)$_2$ radicals wherein R^a is a C_{1-6}-alkyl or aryl radical; -NH-SO_2-R^a radicals wherein R^a is a C_{1-6}-alkyl or aryl radical; (SO_2)NR^a_2 radicals wherein R^a is a C_{1-6}-alkyl or aryl radical; P(=O)(OR^a)(R^a) radicals wherein R^a is a C_{1-6}-alkyl or aryl radical.

Particular preference is given to the method in which a, b and c are each H.

Another preference is given to the method in which R1 is selected from the group consisting of H, C_{2-12}-alkenyl, C_{2-12}-alkynyl or aryl.

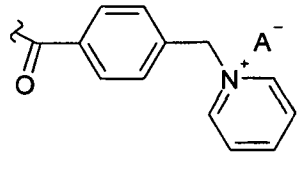
Particular preference is given to the method in which R1 is H.

Another preference is given to the method in which R2 is selected from the group consisting of H, C_{1-12}-alkyl, C_{5-12}-cycloalkyl, C_{7-18}-aralkyl or aryl.

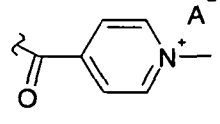
Particular preference is given to the method in which R2 is a methyl-, ethyl- or isopropyl-group.

Another preference is given to the method in which R3 is selected from the group consisting of H, C_{1-12}-alkyl, C_{5-12}-cycloalkyl, C_{7-18}-aralkyl, aryl, C_{1-12}-halogeno-alkyl, C_{1-12}-ammonium-alkyl, C_{1-12}-pyridinum-alkyl, C_{1-12}-aldehyde-alkyl, C_{1-12}-nitro-alkyle, nitrile or a radical selected from the group consisting of ketones COR4, esters CO_2R4, oxalates $COCO_2$R4, sulfones SO_2R4 or amides CONHR4 wherein, R4 is selected from the group consisting of H, C_{1-12}-alkyl, C_{5-12}-cycloalkyl, C_{7-18}-aralkyl, aryl, C_{1-12}-halogeno-alkyl, C_{1-12}-ammonium-alkyl, C_{1-12}-pyridinum-alkyl, C_{1-12}-aldehyde-alkyl, C_{1-12}-nitro-alkyle, nitrile.

In a preferred embodiment of the method, z is methylene, and R3 is a side chain of following formula $R3^a$ or $R3^b$:



($R3^a$)

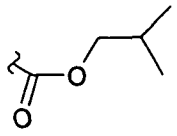


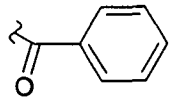
($R3^b$)

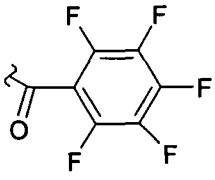
;

in this embodiment, A^- is selected from the group consisting of F^-, Cl^-, Br^-, I^-, tetrafluoroborate BF_4^-, hexafluorophosphate PF_6^- and bis(trifluoromethylsulfonyl)amide NTf_2^-.

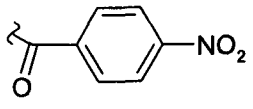
Another preferred embodiment of the method, R3 is a side chain of following formula $R3^c$, $R3^d$,$R3^e$, $R3^f$, $R3^g$, $R3^h$, $R3^i$, $R3^j$, $R3^k$, $R3^l$, $R3^m$, $R3^n$, $R3^o$ or $R3^p$:

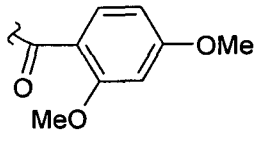

(R3^c)

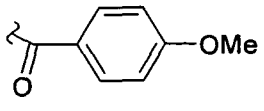

(R3^d)

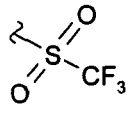

(R3^e)

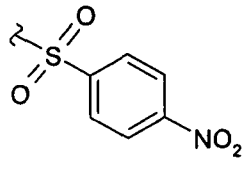

(R3^f)

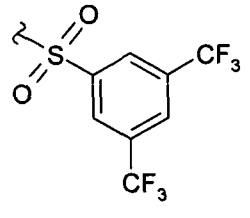

(R3^g)

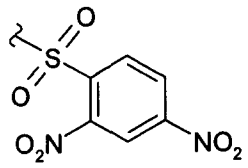

(R3^h)


(R3^i)

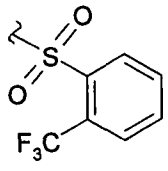

(R3^j)


(R3^k)

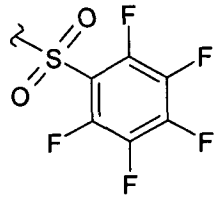

(R3^l)



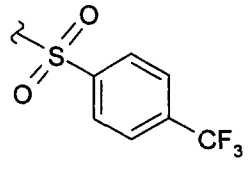
(R3^m)



(R3^n)



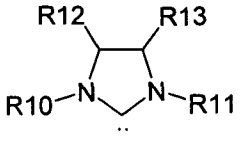
(R3^o)



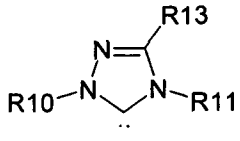
(R3^p)

Preference is given to the method in which L is a phosphine $P(R8)_3$ or a phosphate $P(OR9)_3$ and wherein R8 and R9 are each independently of one another C_{1-6}-alkyl, C_{5-12}-cycloalkyl or aryl.

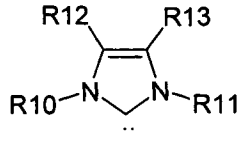
Another preference is given to the method in which L is a ligand of following formula L1, L2, L3 or L4:



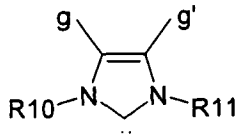
(L1)



(L2)



(L3)

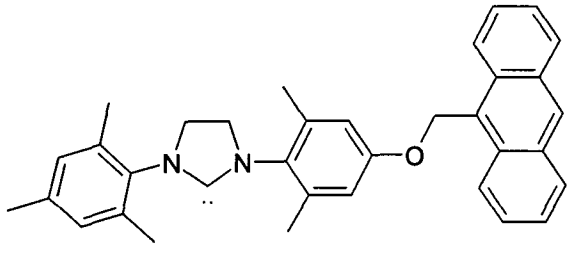


(L4)

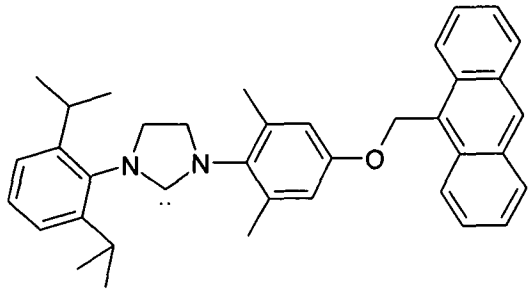
in this embodiment, R10 and R11 are each, independently of one another a substituted or an unsubstituted side chain comprising 1 to 30 carbon atoms and optionally comprising one or more functional groups. Further, in this embodiment R12 and R13 are each, independently of one another, H, C_{1-6}-alkyl optionally substituted by a alkoxy radical OR15, or aryl optionally substituted by a alkoxy radical OR15, or form a 3- or 4-membered alkylene bridge, and wherein R15 is selected from the group consisting of C_{1-20}-alkyl, aryl and C_{7-18}-aralkyl, and wherein g and g' are each halogen. In a particular preferred embodiment g and g' are either Cl or Br atoms.

Furthermore, in the above mentioned embodiment, particular preference is given to the method in which R10 and R11 are each, independently of one another, C_{1-30}-alkyl optionally substituted by a alkoxy radical OR15, C_{2-30}-alkenyl optionally substituted by a alkoxy radical OR15, aryl optionally substituted by a alkoxy radical OR15, aminoalkyl or aminocycloalkyl.

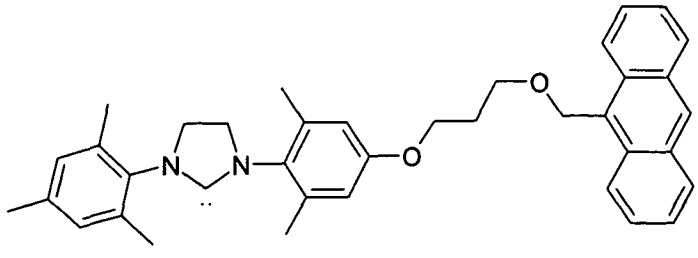
Another particular preference is given to the method in which L is a ligand of following formula $L1^a$, $L1^b$, $L1^c$, $L1^d$, $L1^e$, $L1^f$ or $L1^g$:



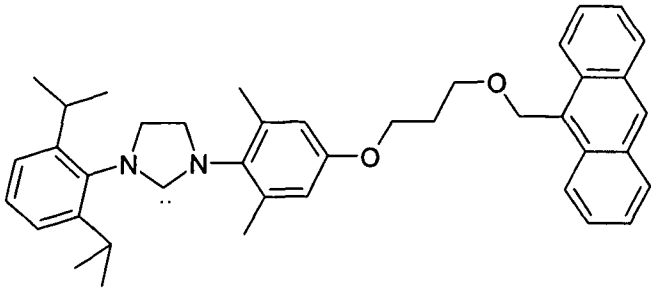
($L1^a$)



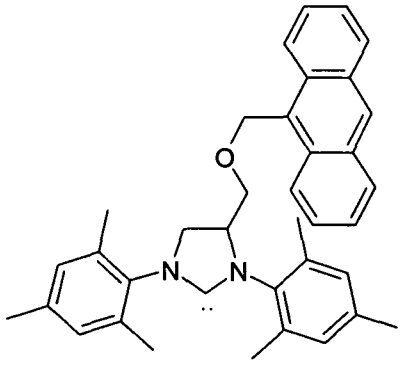
($L1^b$)



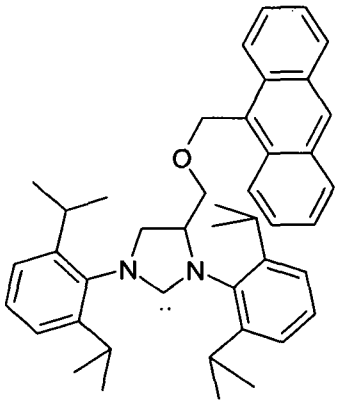
($L1^c$)



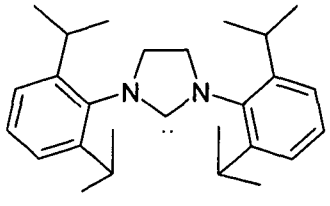
(L1[d])



(L1[e])



(L1[f])



(L1[g])

Other characteristics and advantages of the invention will become apparent upon examination of the upcoming description, examples and the accompanying drawings in which:

- FIG. 1 is a graph showing the conversion rate over time of a product P60 into a product P61 a by metathesis reaction and in the presence of catalysts P32 and P41 according to the present invention,

- FIG. 2 is a graph showing the conversion rate over time of the product P60 into the product P61 a by metathesis reaction and in the presence of catalysts P33, P34, P35, P36 P37, P38, P39 and P40 according to the present invention,
- FIG. 3 is a graph showing the conversion rate over time of the product P60 into the product P61 a by metathesis reaction and in the presence of catalysts P42, P43, P44, P45 and P47 according to the present invention,
- FIG. 4 is a graph showing the conversion rate over time of the product P60 into the product P61 a by metathesis reaction and in the presence of catalysts P48, P49, P50 and P51 according to the present invention,
- FIG. 5 is a graph showing the conversion rate over time of the product P60 into the product P61 by a metathesis reaction and in the presence of catalysts P52, P53, P54, P55, P56 and P57 according to the present invention,
- FIG. 6 is a graph showing the conversion rate over time of the product P60 into the product P61 by metathesis reaction and in the presence of catalysts P58 and P59 according to the present invention,
- FIG. 7 is a graph showing the conversion rate over time of a product P62 into a product P63 by metathesis reaction and in the presence of four different prior art catalysts (*Grubbs III*, *Schrock catalyst*, *Piers-Grubbs II* and compound of formula **G**) in comparison with catalyst P34 according to the present invention,
- FIG. 8 is a graph showing the conversion rate over time of a product P64 into a product P65 by metathesis reaction and in the presence of three different prior art catalysts (*Blechert*, *Umicore M71 SIPr* of formula **D**, *Grela* of formula **B**, *Zannan* of formula **C** and compound of formula **I**) in comparison with catalysts P33 and P34 according to the present invention,
- FIG. 9 is a stability graph showing the degradation rate over time of catalysts P33, P34, P35 and P37 according to the present invention,
- FIG. 10 is a stability graph showing the degradation rate over time of catalysts P42, P43, P44, P45 and P47 according to the present invention,
- FIG. 11 is a stability graph showing the degradation rate over time of catalysts P48, P49, P50, and P51 according to the present invention, and
- FIG. 12 is a stability graph showing the degradation rate over time of catalysts P52, P53, P54 and P55 according to the present invention.

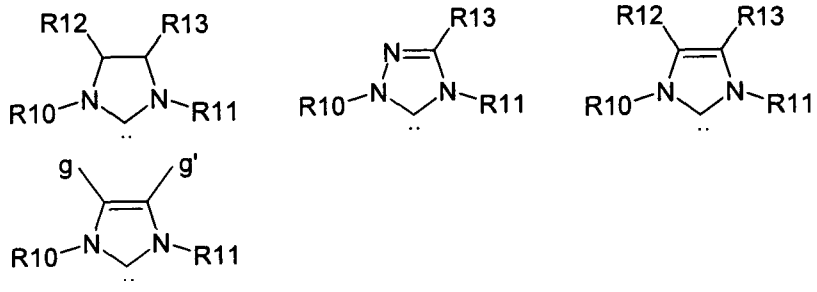
The following description, examples and drawings contain elements of definite nature. They may therefore not only serve to explain and clarify the present invention, but also may serve to contribute to its definition, where appropriate.

TERMINOLOGY AND DEFINITIONS

For the purposes of the present invention, the term "anionic ligand" (X or X') refers to negatively charged molecules or atoms having electron donor properties. Examples which may be mentioned are halogens such as fluorine, chlorine, bromine or iodine.

For the purposes of the present invention, the term "uncharged ligand" (L) refers to uncharged or apparently charge-neutral molecules or atoms having electron donor properties. Examples which may be mentioned are tertiary phosphines containing aliphatic, cycloaliphatic and aromatic hydrocarbon radicals, e.g. trioctylphosphine, tridodecylphosphine, tricyclohexylphosphine, tris(2-methylcyclohexyl)phosphine and tris(o-tolyl)phosphine.

Particularly preferred uncharged ligands (L) are ligands such as the compounds described by the formulae:



(L1) (L2) (L3) (L4)

where R10 and R11 are each, independently of one another a substituted or an unsubstituted side chain comprising 1 to 30 carbon atoms and optionally comprising one or more functional groups, and

where R12 and R13 are each, independently of one another, H, C1-6-alkyl optionally substituted by a alkoxy radical OR15, or aryl optionally substituted by a alkoxy radical OR15, or form a 3- or 4-membered alkylene bridge, and

where R15 is selected from the group consisting of C1-20-alkyl, aryl and C7-18-aralkyl, and

where g and g' are each halogen, preferably Cl or Br

As will be better understood while inspecting the catalyst examples according to the present invention, the ligand (L) is covalently bounded via the carbon atom marked with two dots (carbene radical) to the ruthenium (Ru) metal atom of the general formula 1 backbone.

The term "C_{1-30}-alkyl" refers (also when this is a constituent of other radicals) to branched and unbranched alkyl groups having from 1 to 30 carbon atoms. Correspondingly, the term "C_{1-20}-alkyl" refers to branched and unbranched alkyl groups having from 1 to 20 carbon atoms. The term "C_{1-12}-alkyl" refers to branched and unbranched alkyl groups having from 1 to 12 carbon atoms, the term "C_{1-6}-alkyl" refers to branched and unbranched alkyl groups having from 1 to 6 carbon atoms and the term "C_{1-4}-alkyl" refers to branched and unbranched alkyl groups having from 1 to 4 carbon atoms. Preference is given to alkyl groups having from 1 to 6 carbon atoms, particularly preferably from 1 to 4 carbon atoms. Examples which may be mentioned are: methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl, isopentyl, neopentyl and hexyl. The abbreviations Me, Et, n-Pr, i-Pr, n-Bu, i-Bu, t-Bu, etc., may also be

used for the abovementioned groups. Unless indicated otherwise, in the case of propyl, butyl, pentyl and hexyl, the definitions encompass all conceivable isomeric forms of the respective radicals. Thus, for example, propyl encompasses n-propyl and isopropyl, butyl encompasses isobutyl, sec-butyl and tert-butyl, etc.

The term "C_{1-12}-ammonium-alkyl" refers to an alkyl chain having from 1 to 12 carbon atoms and comprising an ammonium function. The term "C_{1-12}-pyridinium-alkyl" refers to an alkyl chain having from 1 to 12 carbon atoms and comprising a pyridinium function. The term "C_{1-12}-aldehyde-alkyl" refers to an alkyl chain having from 1 to 12 carbon atoms and comprising an aldehyde function. The term "C_{1-12}-nitro-alkyl" refers to an alkyl chain having from 1 to 12 carbon atoms and comprising a nitro function. The term "C_{1-12}-nitrile-alkyl" refers to an alkyl chain having from 1 to 12 carbon atoms and comprising a nitrile function.

The term "C_{2-30}-alkenyl" refers (also when it is a constituent of other radicals) to branched and unbranched alkenyl groups having from 2 to 30 carbon atoms, as long as they have at least one double bond. Correspondingly, the term "C_{2-12}-alkenyl" refers to alkenyl groups having from 2 to 12 carbon atoms and the term "C_{2-6}-alkenyl" refers to branched and unbranched alkenyl groups having from 2 to 6 carbon atoms, the term "C_{2-4}-alkenyl" refers to branched and unbranched alkenyl groups having from 2 to 4 carbon atoms. Preference is given to alkenyl groups having from 2 to 6 carbon atoms, particularly preferably from 2 to 4 carbon atoms. Examples which may be mentioned are: ethenyl and vinyl, propenyl, butenyl, pentenyl and hexenyl. Unless indicated otherwise, in the case of propenyl, butenyl, pentenyl and hexenyl, the definitions encompass all conceivable isomeric forms of the respective radicals. Thus, for example, propenyl encompasses 1-propenyl and 2-propenyl, butenyl encompasses 1-, 2- and 3-butenyl, 1-methyl-1-propenyl, 1-methyl-2-propenyl, etc.

The term "C_{2-12}-alkynyl" refers (also when it is a constituent of other radicals) to branched and unbranched alkynyl groups having from 2 to 12 carbon atoms, as long as they have at least one triple bond. Correspondingly, the term "C_{2-6}-alkynyl" refers to alkynyl groups having from 2 to 6 carbon atoms and the term "C_{2-4}-alkynyl" refers to branched and unbranched alkynyl groups having from 2 to 4 carbon atoms. Preference is given to alkynyl groups having from 2 to 6 carbon atoms, particularly preferably from 2 to 4 carbon atoms. Examples which may be mentioned are: ethynyl, propynyl, butynyl, pentynyl and hexynyl. Unless indicated otherwise, in the case of propynyl, butynyl, pentynyl or hexynyl, the definitions encompass all conceivable isomeric forms of the respective radicals. Thus, for example, propynyl encompasses 1-propynyl and 2-propynyl, butynyl encompasses 1-, 2- and 3-butynyl, 1-methyl-1-propynyl, 1-methyl-2-propynyl, etc.

The term "C_{1-12}-alkoxy" refers (also when it is a constituent of other radicals) to branched and unbranched alkoxy groups having from 1 to 12 carbon atoms; correspondingly, the term "C_{1-6}-alkoxy" refers to branched and unbranched alkoxy groups having from 1 to 6 carbon atoms and the term "C_{1-4}-alkoxy" refers to branched and unbranched alkoxy groups having from 1 to 4 carbon atoms. Preference is given to alkoxy groups having from 1 to 6 carbon atoms, particularly preferably from 1 to 4 carbon atoms. Examples which may be mentioned are: methoxy, ethoxy, propoxy, butoxy and pentoxy. The abbreviations MeO, EtO, PrO, etc., may also be used for the abovementioned groups. Unless indicated otherwise, in the case of

propoxy, butoxy and pentoxy, the definitions encompass all conceivable isomeric forms of the respective radicals. Thus, for example, propoxy encompasses n-propoxy and isopropoxy, butoxy encompasses isobutoxy, sec-butoxy and tert-butoxy, etc.

The term "C_{5-12}-cycloalkyl" refers (even when it is a constituent of other radicals) to cyclic alkyl groups having 5 to 12 carbon atoms. Examples which may be mentioned are: cyclopentyl and cyclohexyl. Unless indicated otherwise, the cyclic alkyl groups can be substituted by one or more radicals selected from the group consisting of methyl, ethyl, isopropyl, tert-butyl, hydroxy, fluorine, chlorine, bromine and iodine. Further, the cyclic alkyl groups can be substituted by one or more functions such as an amino function; they will then be referred to as aminocycloalkyl.

The term "aryl" refers (also when it is a constituent of other radicals) to aromatic ring systems having 6, 10 or more carbon atoms (up to approximately 20 carbon atoms). Examples which may be mentioned are: phenyl and naphthyl; the preferred aryl radical is phenyl. Unless indicated otherwise, the aromatics can be substituted by one or more radicals selected from the group consisting of methyl, ethyl, isopropyl, tert-butyl, hydroxy, fluorine, bromine and iodine. Further the aromatics can comprise one or more functional group; they will then be referred to as "heteroaryl".

The term "C_{7-18}-aralkyl" refers (also when it is a constituent of other radicals) to branched and unbranched alkyl groups which have from 1 to 8 carbon atoms and are substituted by an aromatic ring system having 6 or 10 carbon atoms; correspondingly, the term "C_{7-11}-aralkyl" refers to branched and unbranched alkyl groups which have from 1 to 4 carbon atoms and are substituted by an aromatic ring system having 6 carbon atoms. Examples which may be mentioned are: benzyl, 1- and 2-phenylethyl. Unless indicated otherwise, the aromatics can be substituted by one or more radicals selected from the group consisting of methyl, ethyl, isopropyl, tert-butyl, hydroxy, fluorine, bromine and iodine.

The term "indenylidene system" refers to a divalent radical derived from the cyclopentan ring of an indene wherein said indene consists of a benzene ring fusedto a cyclopentadiene ring.

The sign:



stands for a cutoff in a covalent bond for the purpose of simplicity in representing side chains of compounds of the present invention. For instance, some examples of the present invention refer to a several optional side chains R3. A covalent bond cut by the above sign is actually linked to the Nitrogen (N) atom of the oxazine or oxazinone function.

The signs:



and

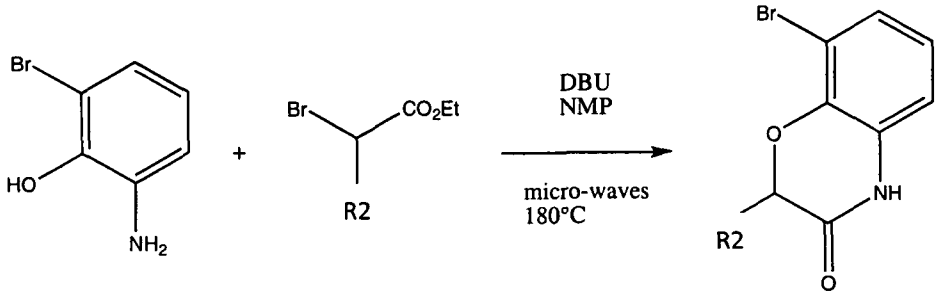


stand for a E or Z configuration of a double bond (E/Z). Accordingly, atoms or atom-groups covalently linked to a double bond via this sign can be in CIS or TRANS position. It has to be understood that for the purpose of the present invention, compounds represented with the above sign can either comprise Z isomeres, E isomeres or a E/Z-mixture of said isomers.

PREPARATION OF COMPOUNDS OF GENERAL FORMULA 1 ACCORDING TO THE INVENTION

The following preparation method encompasses examples of the present invention. A man skilled in the art will know how to prepare other embodiments falling within the scope of the present invention by inspection of the following operations. Particularly, different catalysts according to the invention can be obtained by modification of the side chains R1, R2 and/or R3 and/or a, b and/or c as defined within the present specification.

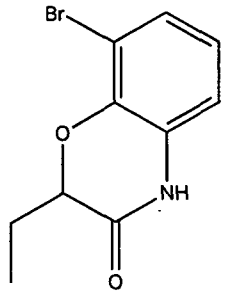
I-A-General procedure for cyclisation.



A mixture of 2-bromo-6-aminophenol, 0,9eq of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and corresponding bromoester (1eq) in 1-Methyl-2-pyrrolidinone (4mL for 1mmol of aminophenol) was warmed in micro-wave at 180°C during 3min. EtOAc (20mL for 1mmol of aminophenol was added. Organic layer was washed with Brine (3X), dried and concentrated. Products were purified on silica gel.

In the present preferred embodiment R1 is selected to be H. However, in other embodiments R1 is selected from the group consisting of H, C_{2-12}-alkenyl, C_{2-12}-alkynyl or aryl.

Depending on the side chain R2, compounds P1, P10 and P16 were obtained (see below). More generally R2 can be chosen to R2 is selected from the group consisting of H, C_{1-12}-alkyl, C_{5-12}-cycloalkyl, C_{7-18}-aralkyl or aryl. More preferentially, R2 is a methyl-, ethyl- or isopropyl-group.

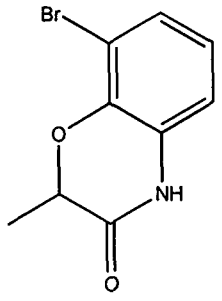


P1

8-bromo-2-ethyl-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one

PROCEDURE & NMR DATA: 1.5g (7.9mmol) of 2-bromo-6-aminophenol, 1.08mL (0,9eq, 7.11mmol) of 1,8-diazabicyclo[5.4.0]undec-7-ene and 3.5mL of DL-Ethyl 2-bromobutyrate (3eq, 23.7mmol)) in 30mL of 1-Methyl-2-pyrrolidinone were mixed. 1.447g of **P1** were obtained, yield 71%.

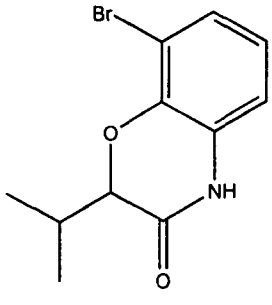
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.14 (dd, *J* = 8.1, 1.4 Hz, 1H), 6.76 (dd, *J* = 8.1, 7.9 Hz, 1H), 6.65 (dd, *J* = 7.9, 1.4 Hz, 1H), 4.54 (dd, *J* = 9.1, 4.2 Hz, 1H), 2.00 – 1.71 (m, 2H), 1.08 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.20, 139.69, 127.75, 127.27, 123.17, 114.43, 111.37, 79.04, 23.95, 9.61.



P10
8-bromo-2-methyl-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one

PROCEDURE & NMR DATA: 1.51g (8mmol) of 2-bromo-6-aminophenol, 1.1mL (0,9eq, 7,2mmol) of 1,8-diazabicyclo[5.4.0]undec-7-ene and 2.1mL (2eq, 1.6mmol) of Methyl 2-bromopropionate in 1-Methyl-2-pyrrolidinone (25ml) were mixed. 1.55g of **P10** were obtained, yield 80%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s broad, 1H), 7.23 (dd, *J* = 8.1, 1.5 Hz, 1H), 6.86 (dd, *J* = 8.1, 7.9 Hz, 1H), 6.76 (dd, *J* = 7.9, 1.5 Hz, 1H), 4.78 (q, *J* = 6.9 Hz, 1H), 1.64 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 140.4, 127.8, 127.4, 123.3, 114.9, 111.1, 73.9, 16.3.



P16
8-bromo-2-isopropyl-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one

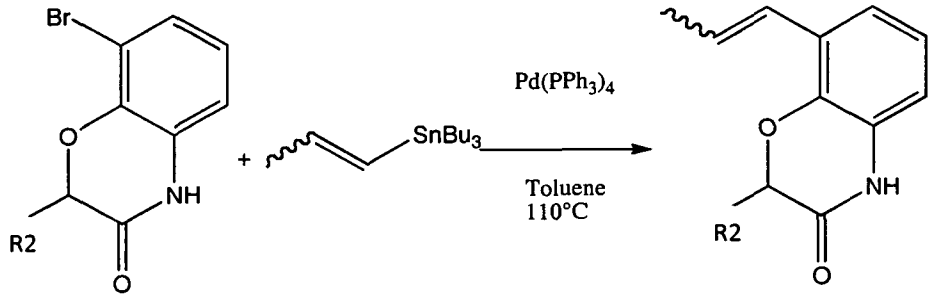
PROCEDURE & NMR DATA : 1.52g (8mmol) of 2-bromo-6-aminophenol, 1.1mL (7.2mmol, 0.9 eq) of 1,8-diazabicyclo[5.4.0]undec-7-ene and 3.35g (2eq, 16mmol) of ethyl 2-bromo-3-methylbutyrate in 1-methyl-2-pyrrolidinone (20mL) were mixed. 1.1g of **P16** were obtained, yield 50%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (s, 1H), 7.12 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.74 (dd, *J* = 8.0, 7.9 Hz, 1H), 6.67 (dd, *J* = 7.9, 1.5 Hz, 1H), 4.39 (d, *J* = 6.2 Hz, 1H), 2.19 (qq, *J* = 6.9, 6.7 Hz, 1H), 1.07 (d, *J* = 6.9 Hz, 3H), 1.00 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.90, 140.59, 127.78, 126.96, 122.95, 114.59, 110.84, 82.49, 29.98, 18.62, 17.58.

In General, it should be noted that according to the invention R1 and R2 can each be, independently of one another, H or a substituted or unsubstituted, charged or uncharged side chain comprising up to 20 carbon atoms and optionally comprising one or more functional groups.

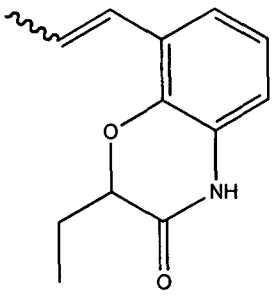
Also, it should be noted that the general procedure begins with z being a carbonyle group (cf. P1, P10 and P16). An amide reduction can be carried out in order to reduce the carbonyle group to a methylene group (see below procedure I-D).

I-B-General procedure for Stille reaction.



To a stirred solution of tetrakis(triphenylphosphine)Palladium (0) (5%) in toluene (1mL for 10mg of tetrakis) was added in solution of toluene (4mL for 1mmol of oxazinone) latter oxazinone. The mixture was degassed during 15min and Propenyl-tributyltin (1.5eq) was added and stirred at 110°C for 12h under nitrogen atmosphere. After filtration and washed on celite the product was purified on silica gel.

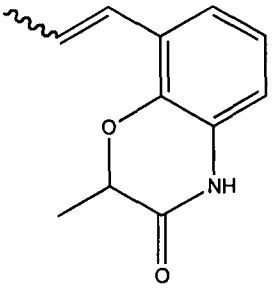
Depending on the side chain R2, compounds P2 (R2 is ethyl), P11 (R2 is methyl) and P17 (R2 is isopropyl) were obtained (see below).



P2
2-ethyl-8-(prop-1-enyl)-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one

PROCEDURE & NMR DATA: 198.5mg (5%, 0.17mmol) of tetrakis(triphenylphosphine)Palladium (0) in toluene (7.5mL) was added in solution of toluene (7.5mL) of oxazinone **P1**. 1.84g (1.5eq, 5.55mmol) of Propenyl-tributyltin were added. 786mg of **P2** was obtained, 98% yield.

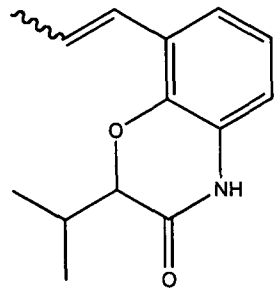
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.04 (dd, *J* = 7.9, 1.3 Hz, 1H), 6.83 (dd, *J* = 7.9, 7.7 Hz, 1H), 6.59 (dq, *J* = 15.9, 1.7 Hz, 1H), 6.53 (dd, *J* = 7.7, 1.3 Hz, 1H), 6.26 (dq, *J* = 15.9, 6.7 Hz, 1H), 4.45 (dd, *J* = 8.7, 4.3 Hz, 1H), 1.97 – 1.71 (m, 5H), 1.11 – 0.99 (m, 3H), 0.85 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.67, 168.65, 140.26, 139.51, 128.31, 127.91, 127.21, 126.71, 126.55, 126.33, 124.29, 123.63, 122.12, 121.53, 114.37, 114.04, 78.22, 78.21, 23.85, 23.79, 18.97, 17.31, 14.80, 13.60, 9.82, 9.69.



P11
2-methyl-8-(prop-1-enyl)-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one

PROCEDURE & NMR DATA: to 370mg (5%, 0.32mmol) of tetrakis(triphenylphosphine)-Palladium (0) in toluene (10mL) was added 1.55g (6.4mmol) of oxazinone **P10** in solution of toluene (40mL). The mixture was degassed during 15min and 3.18g (1.5eq, 9.6mmol) of propenyl-tributyltin were added. 1.27g of **P11** were obtained, yield 98%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 10.4 Hz, 1H), 7.07 – 6.91 (m, 1H), 6.90 – 6.79 (m, 1H), 6.66 – 6.40 (m, 2H), 6.32 – 5.74 (m, 1H), 4.60 (q, *J* = 6.8 Hz, 1H), 1.90 – 1.73 (m, 3H), 1.59 – 1.51 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 168.6, 140.7, 139.9, 128.4, 127.9, 127.2, 126.7, 126.5, 124.9, 124.3, 123.6, 122.2, 121.7, 121.1, 114.3, 113.9, 73.4, 73.3, 18.9, 16.3, 16.2, 14.8.

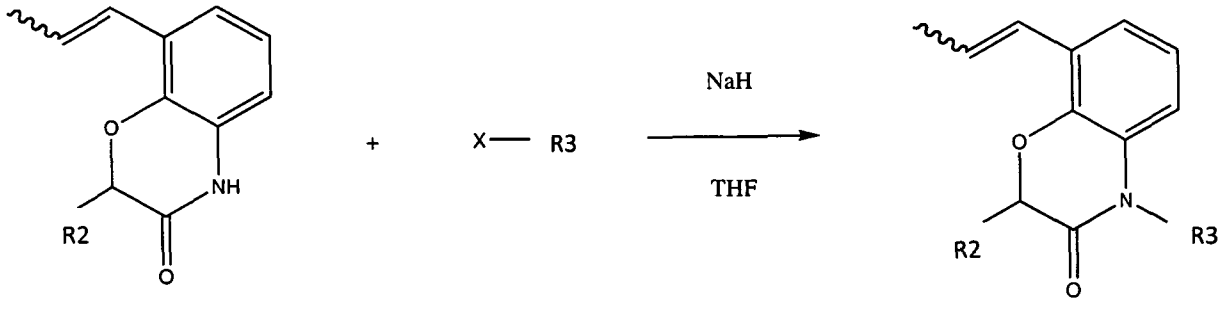


P17
2-isopropyl-8-(prop-1-enyl)-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one

PROCEDURE & NMR DATA : to 235mg (5%, 0.2mmol) of tetrakis(triphenylphosphine)Palladium (0) in toluene (6mL) was added 1,1g (4mmol) of oxazinone **P16** in solution of toluene (24mL). The mixture was degassed during 15min and 2.02g (1.5eq, 6mmol) of propenyl-tributyltin were added. 907mg of **P17** were obtained, yield 98%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.32 (d, *J* = 13.9 Hz, 1H), 6.96 (ddd, *J* = 40.9, 7.9, 1.3 Hz, 1H), 6.80 (dt, *J* = 13.9, 7.9 Hz, 1H), 6.68 – 6.60 (m, 1H), 6.60 – 6.41 (m, 1H), 6.32 – 5.76 (m, 1H), 4.31 (dd, *J* = 6.0, 1.5 Hz, 1H), 2.23 (qq, *J* = 6.9, 6.9 Hz, 1H), 1.80 (ddd, *J* = 29.2, 6.9, 1.8 Hz, 3H), 1.05 (dd, *J* = 9.0, 6.9 Hz, 3H), 0.97 (dd, *J* = 6.9, 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.70, 140.75, 139.99, 128.23, 127.89, 126.84, 126.34, 126.29, 126.06, 124.95, 124.30, 123.67, 121.92, 121.31, 121.20, 114.23, 113.90, 81.81, 81.79, 29.72, 29.63, 26.91.

I-C-General procedure for amide alkylation.



Appropriate halogen compound (1.2eq) was added to a mixture of NaH (4eq) and considered oxazinone in THF (1mL for 0.1mmol of oxazinone) at 0°C. The mixture was stirred at room temperature for 2-3h. THF was removed under reduce pressure and EtOAc was added. The organic layer was washed with a saturated solution of $NaHCO_3$ and then with brine, dried over $MgSO_4$ and evaporated to dryness. Products were purified on silica gel.

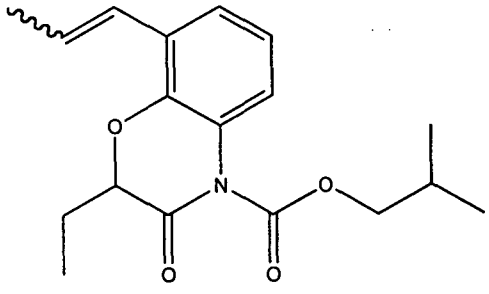
Depending on the side chain R2 and/or the side chain R3, compounds P3 to P9, P12 to P15 and P18 to P21 were obtained (see below).

According to the invention, R3 can be H or a substituted or unsubstituted, charged or uncharged side chain comprising up to 20 carbon atoms and optionally comprising one or more functional groups

Preference is given when R3 is selected from the group consisting of H, C_{1-12}-alkyl, C_{5-12}-cycloalkyl, C_{7-18}-aralkyl, aryl, C_{1-12}-halogeno-alkyl, C_{1-12}-ammonium-alkyl, C_{1-12}-pyridinum-alkyl, C_{1-12}-aldehyde-alkyl, C_{1-12}-nitro-alkyl, nitrile or a radical selected from the group consisting of ketones COR4, esters CO_2R4, oxalates $COCO_2R4$, sulfones SO_2R4 or amides CONHR4 wherein, R4 is selected from the group consisting of H, C_{1-12}-alkyl, C_{5-12}-cycloalkyl, C_{7-18}-aralkyl, aryl, C_{1-12}-halogeno-alkyl, C_{1-12}-ammonium-alkyl, C_{1-12}-pyridinum-alkyl, C_{1-12}-aldehyde-alkyl, C_{1-12}-nitro-alkyle, nitrile.

In particularly preferred embodiments R3 is a side chain of the formula $R3^a$ or $R3^b$ as described above. However, in these embodiments z is chosen to be a methylene as shown in above formula 1^b. For z to become a methylene, one can refer to general procedure I-D that shows a amide reduction.

In other particularly preferred embodiments R3 is a side chain of the formula $R3^c$, $R3^d$, $R3^e$, $R3^f$, $R3^g$, $R3^h$, $R3^i$, $R3^j$, $R3^k$, $R3^l$, $R3^m$, $R3^n$, $R3^o$ or $R3^p$ as described above. In these embodiments z is chosen to be either a methylene as shown in above formula 1^b or a carbonyl as shown in above formula 1^a.

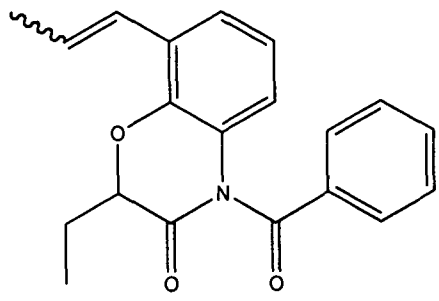


P3

isobutyl 2-ethyl-3-oxo-8-(prop-1-enyl)-2*H*-benzo[*b*][1,4]oxazine-4(3*H*)-carboxylate

PROCEDURE & NMR DATA : 85µL (2.5eq, 0.65mmol) of isobutyl chloroformate was added to a mixture of 42mg (4eq, 1.04mmol) of NaH and oxazinone **P2** (56mg, 0.26mmol) in THF (5mL). 42mg of **P3** were obtained, yield 51%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.96 – 6.84 (m, 2H), 6.63 – 6.56 (m, 1H), 6.25 (dq, *J* = 15.9, 6.6 Hz, 1H), 4.32 (dd, *J* = 8.8, 4.4 Hz, 1H), 4.10 (d, *J* = 6.6 Hz, 2H), 2.07 – 1.74 (m, 6H), 1.04 (t, *J* = 7.4 Hz, 3H), 0.93 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.45, 166.40, 152.04, 142.32, 141.55, 128.69, 128.33, 128.00, 127.45, 126.63, 126.43, 126.38, 123.99, 123.40, 122.51, 122.28, 121.73, 117.47, 117.12, 79.23, 79.22, 74.62, 74.60, 73.94, 69.80, 27.67, 23.14, 23.12, 18.99, 18.94, 18.92, 14.75, 9.72, 9.60. (major signals are double due to two isomers Z/E for the double bond)

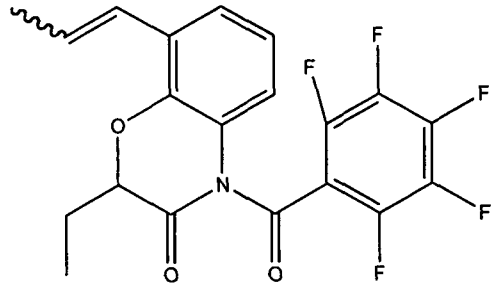


P4

2-ethyl-4-(phenylcarbonyl)-8-(prop-1-enyl)-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one

PROCEDURE & NMR DATA : 142µL (2.5eq, 1.23mmol) of benzoyl chloride was added to a mixture of 78mg of NaH (4eq, 1.96mmol) and 100mg (0.49mmol) of oxazinone **P2** in THF (9.5mL). 58mg of **P4** were obtained, yield 77%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.77 (m, 2H), 7.57 – 7.49 (m, 1H), 7.43 – 7.32 (m, 2H), 7.15 – 6.99 (m, 1H), 6.90 – 6.71 (m, 2H), 6.69 – 6.46 (m, 1H), 6.34 – 5.83 (m, 1H), 4.48 – 4.42 (m, 1H), 2.05 – 1.74 (m, 5H), 1.09 (t, *J* = 7.4 Hz, 3H).

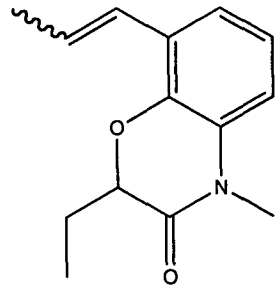


P5

2-ethyl-4-(perfluorophenylcarbonyl)-8-(prop-1-enyl)-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one

PROCEDURE & NMR DATA : 265µL of pentafluorobenzoyl chloride (2eq, 1.84mmol) was added to a mixture of 148mg of NaH (4eq, 3.68mmol) and 200mg (0,92mmol) of oxazinone **P2** in THF (22mL). 240mg of **P5** were obtained, yield 63%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (ddd, *J* = 22.9, 8.2, 1.3 Hz, 1H), 7.22 (ddd, *J* = 43.6, 7.8, 1.2 Hz, 1H), 7.07 – 6.96 (m, 1H), 6.53 (ddd, *J* = 13.8, 13.1, 1.6 Hz, 1H), 6.34 – 5.82 (m, 1H), 4.31 (ddd, *J* = 8.7, 4.5, 3.3 Hz, 1H), 1.94 – 1.73 (m, 2H), 1.03 (dt, *J* = 9.3, 7.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.37, 170.27, 143.98, 143.21, 129.14, 128.79, 128.49, 128.07, 127.94, 125.49, 125.31, 124.15, 123.69, 123.08, 122.66, 122.13, 120.22, 119.92, 79.54, 79.49, 23.12, 18.94, 14.76, 9.55, 9.45. (major signals are double due to two isomers Z/E for the double bond). ^{19}F NMR (376 MHz, $CDCl_3$) δ -142.42 (d, *J* = 21.6 Hz, 2F), -150.02 (d, *J* = 9.9 Hz), -160.44 (dd, *J* = 21,6, 9,9 Hz, 2F).

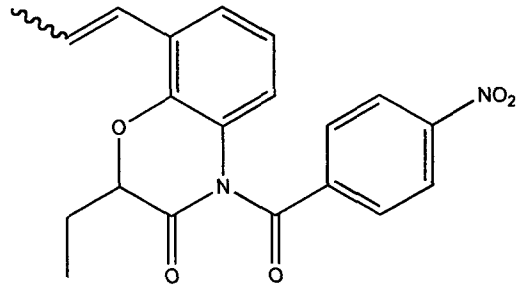


P6

2-ethyl-4-methyl-8-(prop-1-enyl)-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one

PROCEDURE & NMR DATA : 287μL (10eq, 4.6mmol) of Methyl iodide was added to a mixture of 74mg (4eq, 1.84mmol) of NaH and 100mg (0.46mmol) of oxazinone **P2** in THF (10mL). 75mg of 6 were obtained, yield 71%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 – 6.83 (m, 2H), 6.74 (m, 1H), 6.65 – 6.41 (m, 1H), 6.29 – 5.74 (m, 1H), 4.40 (dd, *J* = 9.1, 4.2 Hz, 1H), 3.26 (dd, *J* = 5.8, 0.2 Hz, 3H), 1.92 – 1.66 (m, 5H), 1.00 (dt, *J* = 8.7, 7.4 Hz, 3H).

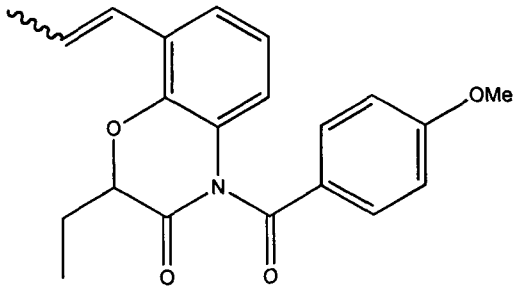


P7

2-ethyl-4-(4-nitrophenylcarbonyl)-8-(prop-1-enyl)-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one

PROCEDURE & NMR DATA : 107mg (2.5eq, 0.58mmol) of 4-Nitrobenzoyl chloride was added to a mixture of 37mg (4eq, 0.92mmol) of NaH and 50mg (0.23mmol) of oxazinone **P2** in THF (10mL). 81mg of **P7** were obtained, yield 96%.

^{1}H NMR (400 MHz, *CDCl*$_3$) δ 8.30 (dd, *J* = 9.0, 3.7 Hz, 2H), 7.95 (dd, *J* = 9.0, 3.5 Hz, 2H), 7.26 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.17 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.07 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.03-6.91 (m, 2H), 6.71 (qd, *J* = 16.2, 1.8 Hz, 1H), 6.56 (qd, *J* = 11.5, 1.8 Hz, 1H), 6.38 (qd, *J* = 15.8, 6.6 Hz, 1H), 5.96 (qd, *J* = 11.5, 7.1 Hz, 1H), 4.48 (ddd, *J* = 8.5, 4.5, 3.7 Hz, 1H), 1.95 (dd, *J* = 6.6, 1.8 Hz, 3H), 2.10-1.89 (m, 2H), 1.87 (dd, *J* = 7.1, 1.9 Hz, 3H), 1.14 (td, *J* = 9.2, 7.4 Hz, 3H). ^{13}C NMR (101 MHz, *CDCl*$_3$) δ 170.0, 170.0, 168.0, 150.4, 142.2, 141.3, 139.3, 139.2, 130.6, 130.3, 130.2, 129.1, 128.9, 128.4, 127.9, 127.0, 126.9, 126.6, 124.0, 123.8, 123.5, 123.2, 123.1, 122.7, 122.2, 118.9, 116.5, 78.9, 78.8, 23.0, 22.9, 18.9, 14.8, 9.6, 9.5. (major signals are double due to two isomers Z/E for the double bond).

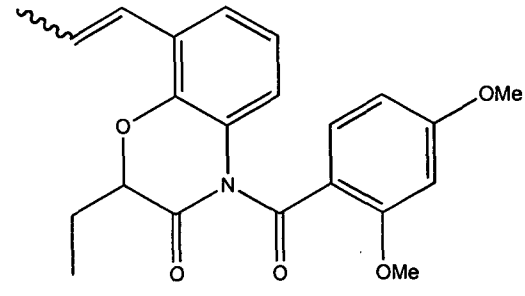


P8

2-ethyl-4-(4-methoxyphenylcarbonyl)-8-(prop-1-enyl)-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one

PROCEDURE & NMR DATA : 137mg (2.5eq, 0.8mmol) of *p*-Anisoyl chloride was added to a mixture of 49mg (4eq, 1.28mmol) of NaH and 73mg (0.32mmol) of oxazinone **P2** in THF (14mL). 73mg of **P8** were obtained, yield 62%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.76 (m, 2H), 7.13 – 6.98 (m, 1H), 6.91 – 6.75 (m, 3H), 6.69 – 6.46 (m, 2H), 6.38 – 5.81 (m, 1H), 4.47 (ddd, *J* = 8.9, 4.4, 2.9 Hz, 1H), 3.79 (d, *J* = 2.7 Hz, 3H), 2.03 – 1.74 (m, 5H), 1.08 (dt, *J* = 14.9, 7.4 Hz, 3H).^{13}C NMR (101 MHz, *CDCl*$_3$) δ 170.5, 166.5, 164.9, 141.0, 140.2, 133.1, 128.7, 128.4, 128.0, 127.4, 127.4, 125.8, 125.0, 124.9, 124.1, 123.4, 122.4, 122.0, 121.9, 115.4, 115.0, 114.5, 78.7, 78.6, 55.6, 23.2, 23.1, 18.9, 14.8, 9.7, 9.6. (major signals are double due to two isomers Z/E for the double bond).

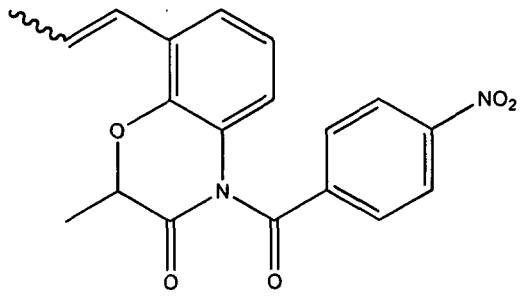


P9

4-(2,4-dimethoxyphenylcarbonyl)-2-ethyl-8-(prop-1-enyl)-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one

PROCEDURE & NMR DATA : 162mg (2.5eq, 0.8mmol) of 2,4-Dimethoxybenzoyl chloride was added to a mixture of 49mg (4eq, 1.28mmol) of NaH and 73mg (0.32mmol) of oxazinone **P2** in THF (14mL). 109mg of **P9** were obtained, yield 84%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 8.8, 1.2 Hz, 1H), 7.14 – 6.97 (m, 1H), 6.97 – 6.75 (m, 2H), 6.69 – 6.42 (m, 2H), 6.34 – 5.78 (m, 2H), 4.40 – 4.32 (m, 1H), 3.78 (d, *J* = 2.3 Hz, 3H), 3.63 (d, *J* = 4.4 Hz, 3H), 1.98 – 1.75 (m, 5H), 1.05 (dt, *J* = 9.5, 7.4 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 166.7, 165.5, 160.5, 160.4, 142.1, 134.7, 134.7, 128.3, 127.9, 127.1, 125.8, 124.3, 123.7, 122.1, 121.9, 121.5, 116.6, 116.3, 105.8, 98.5, 78.9, 55.6, 26.9, 23.0, 18.9, 14.8, 9.9, 9.8. (major signals are double due to two isomers Z/E for the double bond).

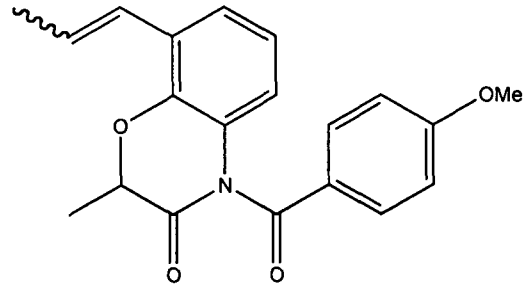


P12

2-methyl-4-(4-nitrophenylcarbonyl)-8-(prop-1-enyl)-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one

PROCEDURE & NMR DATA : 160mg (2.5eq, 0.85mmol) of 4-Nitrobenzoyl chloride was added to a mixture of 53mg (4eq, 1.36mmol) of NaH and 73mg (0,34mmol) of oxazinone **P10** in THF (14mL). 108mg of **P12** were obtained, yield 86%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 – 8.19 (m, 2H), 7.92 – 7.82 (m, 2H), 7.24 – 7.06 (m, 1H), 7.03 – 6.83 (m, 2H), 6.53 (dddd, *J* = 11.5, 3.2, 2.6, 1.6 Hz, 1H), 6.36 – 5.81 (m, 1H), 4.58 (qd, *J* = 6.7, 1.3 Hz, 1H), 1.91 – 1.76 (m, 3H), 1.56 (dd, *J* = 8.2, 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.03, 168.35, 150.47, 142.79, 142.00, 139.34, 139.25, 130.30, 130.25, 129.18, 128.90, 127.73, 127.03, 126.80, 124.05, 123.85, 123.21, 123.14, 122.82, 122.30, 117.12, 116.78, 74.05, 26.91, 18.96, 15.52, 14.82.

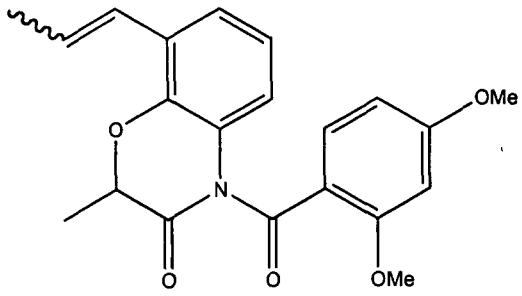


P13

4-(4-methoxyphenylcarbonyl)-2-methyl-8-(prop-1-enyl)-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one

PROCEDURE & NMR DATA : 117µL (2.5eq, 0.85mmol) of *p*-Anisoyl chloride was added to a mixture of 53mg (4eq, 1.36mmol) of NaH and 73mg (0.34mmol) of oxazinone **P10** in THF (14mL). 85mg of **P13** were obtained, yield 69%.

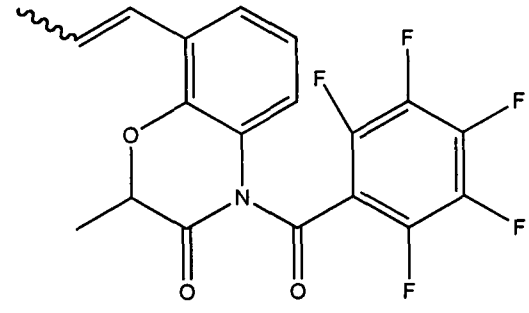
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.73 (m, 2H), 7.05 (ddd, *J* = 42.8, 7.8, 1.2 Hz, 1H), 6.94 – 6.73 (m, 3H), 6.70 – 6.42 (m, 2H), 6.35 – 5.77 (m, 1H), 4.64 (td, *J* = 6.8, 0.7 Hz, 1H), 3.79 (d, *J* = 2.8 Hz, 3H), 1.83 (ddd, *J* = 31.6, 6.9, 1.8 Hz, 3H), 1.58 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.13, 170.02, 166.87, 166.85, 164.94, 141.60, 140.83, 133.08, 133.06, 132.84, 128.78, 128.41, 127.87, 127.79, 127.59, 127.32, 125.86, 124.96, 124.87, 124.14, 123.50, 122.55, 122.01, 115.57, 115.26, 114.46, 114.13, 73.82, 55.64, 26.91, 18.95, 15.76, 14.84.



P14
4-(2,4-dimethoxyphenylcarbonyl)-2-methyl-8-(prop-1-enyl)-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one

PROCEDURE & NMR DATA : 173mg (2.5eq, 0.85mmol) of 2,4-Dimethoxybenzoyl chloride was added to a mixture of 53mg (4eq, 1.36mmol) of NaH and 73mg (0.34mmol) of oxazinone **P10** in THF (14mL). 102mg of **P14** were obtained, yield 76%.

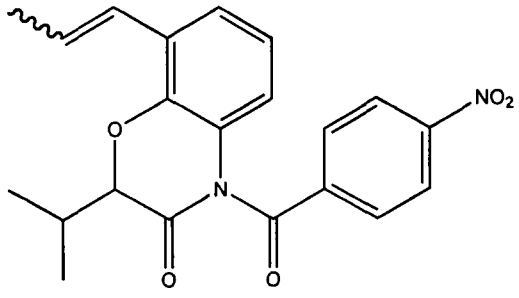
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.16 – 6.71 (m, 3H), 6.68 – 6.39 (m, 2H), 6.34 – 5.74 (m, 2H), 4.52 (q, *J* = 6.8 Hz, 1H), 3.77 (d, *J* = 2.3 Hz, 3H), 3.63 (d, *J* = 4.5 Hz, 3H), 1.82 (ddd, *J* = 32.0, 6.9, 1.8 Hz, 1H), 1.53 (dd, *J* = 8.0, 6.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.20, 168.14, 167.17, 167.16, 165.53, 165.51, 160.41, 160.35, 142.66, 134.73, 134.68, 128.38, 127.82, 127.46, 127.42, 127.23, 126.94, 125.83, 124.29, 123.73, 122.17, 121.91, 121.65, 116.74, 116.37, 116.19, 116.07, 105.87, 105.85, 98.45, 73.92, 55.63, 55.60, 49.43, 30.67, 29.57, 26.90, 18.93, 17.65, 15.68, 15.64, 14.79.



P15
2-methyl-4-(perfluorophenylcarbonyl)-8-(prop-1-enyl)-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one

PROCEDURE & NMR DATA : 124µL (2.5eq, 0.85mmol) of pentafluorobenzoyl chloride was added to a mixture of 53mg (4eq, 1.36mmol) of NaH and 73mg (0.34mmol) of oxazinone **P10** in THF (14mL). 134mg of **P15** were obtained, yield 90%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (ddd, *J* = 23.4, 8.3, 1.4 Hz, 1H), 7.22 (ddd, *J* = 44.7, 7.8, 1.2 Hz, 1H), 7.10 – 6.95 (m, 1H), 6.64 – 6.40 (m, 1H), 6.35 – 5.79 (m, 1H), 4.47 (qd, *J* = 6.8, 1.7 Hz, 1H), 1.82 (ddd, *J* = 32.4, 6.9, 1.8 Hz, 3H), 1.52 (dd, *J* = 8.5, 6.8 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -142.42 (d, *J* = 17.8 Hz, 2F), -149.92 (dd, *J* = 34.2, 20.7 Hz, 1F), -160.38 (td, *J* = 20.7, 6.1 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 170.7, 144.4, 143.7, 129.1, 128.7, 128.3, 128.0, 127.7, 125.5, 125.3, 124.1, 123.7, 123.1, 122.7, 122.2, 120.3, 120.0, 74.8, 74.7, 18.9, 15.5, 14.7, 14.1.

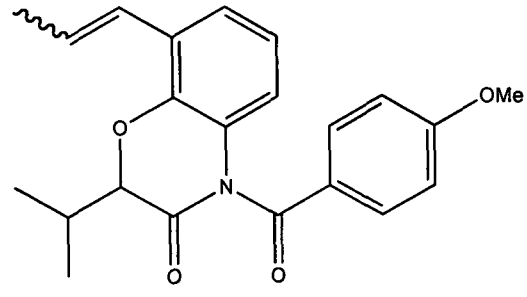


P18

2-isopropyl-4-(4-nitrophenylcarbonyl)-8-(prop-1-enyl)-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one

PROCEDURE & NMR DATA : 151mg (2.5eq, 0.8mmol) of 4-Nitrobenzoyl chloride was added to a mixture of 48mg (4eq, 1.28mmol) of NaH and 74mg (0.32mmol) of oxazinone **P17** in THF (14mL). 100mg of **P18** were obtained, yield 83%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 – 8.20 (m, 2H), 7.95 – 7.85 (m, 2H), 7.25 – 7.06 (m, 1H), 7.03 – 6.82 (m, 2H), 6.71 – 6.42 (m, 1H), 6.39 – 5.71 (m, 1H), 4.33 – 4.14 (m, 1H), 2.30 – 2.17 (m, 1H), 1.84 (ddd, *J* = 31.2, 6.9, 1.8 Hz, 3H), 1.10 – 0.98 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.31, 167.45, 167.41, 150.46, 141.39, 139.53, 130.25, 130.19, 129.08, 128.91, 128.30, 127.76, 126.99, 126.51, 124.05, 123.79, 123.24, 123.09, 122.63, 122.07, 116.73, 116.36, 82.46, 82.43, 28.55, 28.50, 26.91, 19.01, 18.79, 18.72, 17.64, 17.53, 14.82.

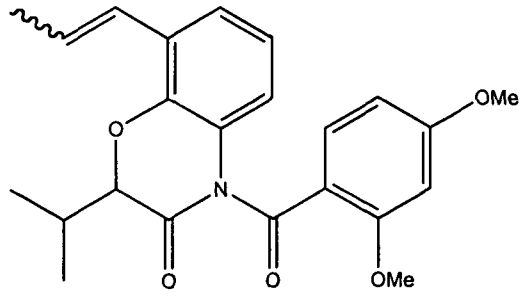


P19

2-isopropyl-4-(4-methoxyphenylcarbonyl)-8-(prop-1-enyl)-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one

PROCEDURE & NMR DATA : 138mg (2.5eq, 0.8mmol) of *p*-Anisoyl chloride was added to a mixture of 48Mg (4eq, 1.28mmol) of NaH and 74mg (0.32mmol) of oxazinone **P17** in THF (14mL). 82mg of **P19** were obtained, yield 65%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 9.0, 6.9 Hz, 2H), 7.04 (ddd, *J* = 41.4, 7.8, 1.2 Hz, 1H), 6.90 – 6.83 (m, 2H), 6.78 (dt, *J* = 10.7, 7.9 Hz, 1H), 6.70 – 6.47 (m, 2H), 6.36 – 5.81 (m, 1H), 4.28 (dd, *J* = 6.8, 3.3 Hz, 1H), 3.79 (d, *J* = 2.8 Hz, 3H), 2.32 – 2.20 (m, 1H), 1.84 (ddd, *J* = 30.2, 6.9, 1.8 Hz, 3H), 1.12 – 0.99 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.15, 170.35, 165.82, 164.92, 141.23, 140.41, 133.05, 133.02, 128.63, 128.38, 127.76, 127.47, 127.24, 125.83, 125.14, 125.03, 124.09, 123.54, 122.31, 121.97, 121.72, 115.25, 114.94, 114.45, 82.29, 82.27, 60.39, 55.63, 28.79, 28.70, 21.04, 19.01, 18.81, 18.74, 17.83, 17.73, 14.83, 14.19.

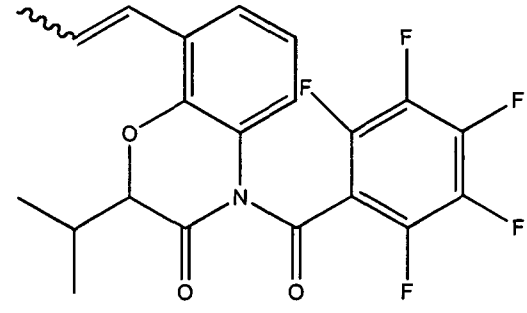


P20

4-(2,4-dimethoxyphenylcarbonyl)-2-isopropyl-8-(prop-1-enyl)-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one

PROCEDURE & NMR DATA : 163mg (2.5eq, 0.8mmol) of 2,4-Dimethoxybenzoyl chloride was added to a mixture of 48mg (4eq, 1.28mmol) of NaH and 74mg (0.32mmol) of oxazinone **P17** in THF (14mL). 106mg of **P20** were obtained, yield 80%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 8.8, 1.0 Hz, 1H), 7.04 (ddd, *J* = 43.6, 7.5, 1.6 Hz, 1H), 6.93 – 6.72 (m, 2H), 6.69 – 6.45 (m, 2H), 6.34 – 5.78 (m, 2H), 4.17 (dd, *J* = 7.0, 4.6 Hz, 1H), 3.77 (d, *J* = 2.3 Hz, 3H), 3.62 (d, *J* = 4.7 Hz, 3H), 2.26 – 2.12 (m, 1H), 1.82 (ddd, *J* = 31.4, 6.9, 1.8 Hz, 3H), 1.09 – 0.95 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.15, 168.45, 165.80, 165.74, 165.53, 165.49, 160.51, 160.43, 142.27, 134.72, 134.66, 128.29, 127.84, 127.38, 127.19, 126.98, 126.89, 125.80, 124.24, 123.76, 121.94, 121.88, 121.37, 116.47, 116.35, 116.20, 116.07, 105.79, 105.77, 98.42, 82.46, 60.39, 55.60, 28.48, 28.43, 21.04, 18.99, 18.85, 18.78, 17.88, 17.78, 14.77, 14.19.



P21

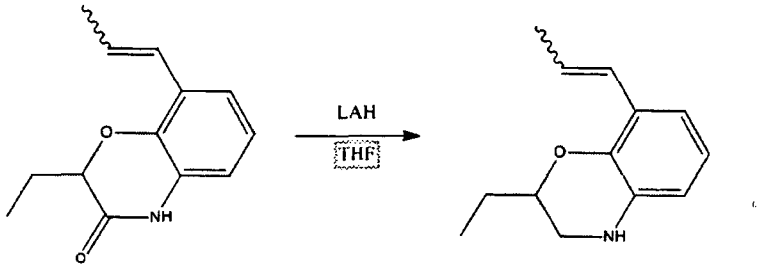
2-isopropyl-4-(perfluorophenylcarbonyl)-8-(prop-1-enyl)-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one

PROCEDURE & NMR DATA : 187mg (2.5eq, 0.8mmol) of pentafluorobenzoyl chloride was added to a mixture of 48mg (4eq, 1.28mmol) of NaH and 74mg (0.32mmol) of oxazinone **P17** in THF (14mL). 133mg of **P21** were obtained, yield 96%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (ddd, *J* = 22.9, 8.2, 1.4 Hz, 1H), 7.22 (ddd, *J* = 44.9, 7.8, 1.2 Hz, 1H), 7.05 – 6.94 (m, 1H), 6.54 (ddq, *J* = 55.1, 11.6, 1.7 Hz, 1H), 6.35 – 5.81 (m, 1H), 4.14 (dd, *J* = 6.3, 4.2 Hz, 1H), 2.20 – 2.09 (m, 1H), 1.83 (ddd, *J* = 31.3, 6.9, 1.8 Hz, 3H), 1.01 (dd, *J* = 8.6, 6.9

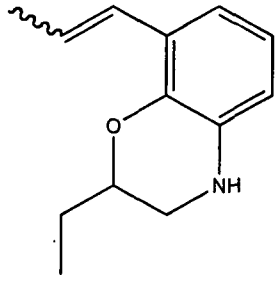
Hz, 3H), 0.95 (dd, *J* = 7.5, 6.8 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -142.33 – -142.68 (m, 2F), -150.12 (t, *J* = 20.4 Hz, 1F), -160.22 – -160.69 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.56, 169.51, 144.02, 143.22, 129.14, 128.80, 128.07, 127.86, 125.31, 125.14, 124.14, 123.69, 123.15, 122.55, 122.00, 120.13, 119.81, 83.13, 83.07, 29.69, 28.66, 26.91, 18.97, 18.75, 18.68, 17.33, 17.22, 14.79.

I-D-General procedure for amide reduction.



Appropriate oxazinone was added in solution in THF (Tetrahydrofuran) (16.4 mL for 1 mmol) to a suspension of 418mg (2eq, 11mmol) of LAH (Lithium Aluminium Hydride) in THF (5mL for 1.1mmol) at 0°C. The result suspension was stirred at room temperature for 1h. H_2O and a solution af NaOH 1N was slowly added. The precipitate was filtered off on celite and washed with warm THF. No further purification is done for these products. Product **P22** was obtained (NMR DATA are shown below)

In this way, catalysts compounds of the present invention can be obtained where z is methylene. Of course, different preparation of those compounds depend on selected R1, R2 and R3 side chains (see below procedure I-E).



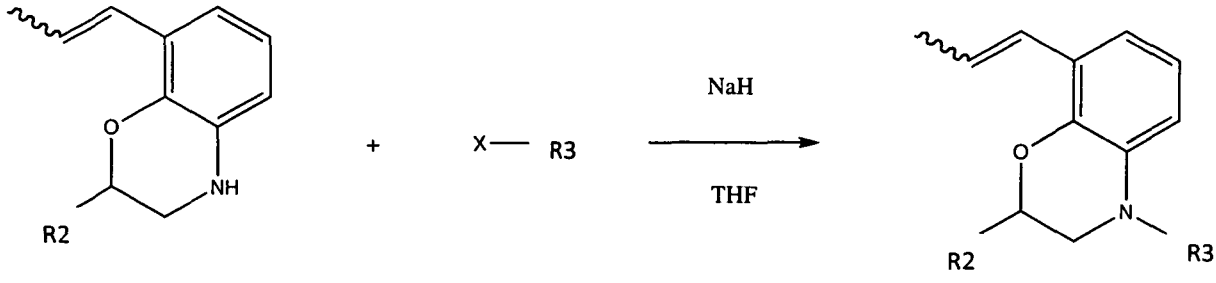
P22
2-ethyl-8-(prop-1-enyl)-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazine

PROCEDURE & NMR DATA : 1.2g (5.5mmol) of oxazinone **P1** was added in solution in THF (90mL) to a suspension of 418mg (2eq, 11mmol) of LAH in THF (50mL) at 0°C. The result suspension was stirred at room temperature for 1h. H_2O and a solution af NaOH 1N was slowly

added. The precipitate was filtered off on celite and washed with warm THF. No further purification is done for these products. 1.1g of **P22** were obtained, yield 99%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.75 – 6.34 (m, 4H), 6.23 – 5.68 (m, 1H), 3.98 – 3.91 (m, 1H), 3.65 (d, *J* = 10.1 Hz, 1H), 3.34 – 3.01 (m, 2H), 2.04 – 1.86 (m, 2H), 1.84 – 1.74 (m, 3H), 1.05 – 0.96 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.48, 140.80, 133.27, 133.12, 126.63, 126.39, 126.15, 125.85, 125.42, 124.84, 120.55, 119.88, 119.86, 116.11, 113.94, 113.64, 107.96, 75.37, 75.35, 67.70, 45.13, 45.11, 29.13, 27.92, 27.17, 25.97, 25.93, 23.92, 18.98, 15.46, 14.89, 14.82, 13.65, 9.85, 9.78.

I-E-General procedure for amine alkylation.



Appropriate halogen compound (1.2eq) was added to a mixture of NaH (4eq) and considered oxazinone in THF (10mL for 0.5mmol of oxazinone) at 0°C. The mixture was stirred at room temperature for 2-3h. THF was removed under reduce pressure and EtOAc was added. The organic layer was washed with a saturated solution of NaHCO3 and then with brine, dried over MgSO4 and evaporated to dryness. Products were purified on silica gel.

Depending on the side chain R2 and/or the side chain R3, compounds P23 to P31 were obtained (see below).

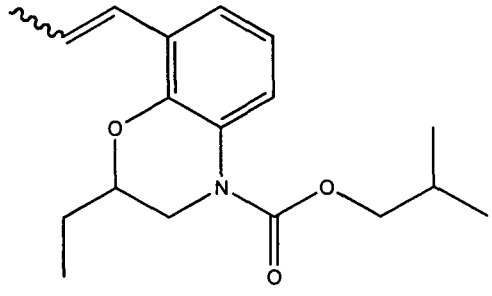
According to the invention, R3 can be H or a substituted or unsubstituted, charged or uncharged side chain comprising up to 20 carbon atoms and optionally comprising one or more functional groups

Preference is given when R3 is selected from the group consisting of H, C_{1-12}-alkyl, C_{5-12}-cycloalkyl, C_{7-18}-aralkyl, aryl, C_{1-12}-halogeno-alkyl, C_{1-12}-ammonium-alkyl, C_{1-12}-pyridinum-alkyl, C_{1-12}-aldehyde-alkyl, C_{1-12}-nitro-alkyl, nitrile or a radical selected from the group consisting of ketones COR4, esters CO_2R4, oxalates $COCO_2R4$, sulfones SO_2R4 or amides CONHR4 wherein, R4 is selected from the group consisting of H, C_{1-12}-alkyl, C_{5-12}-cycloalkyl, C_{7-18}-aralkyl, aryl, C_{1-12}-halogeno-alkyl, C_{1-12}-ammonium-alkyl, C_{1-12}-pyridinum-alkyl, C_{1-12}-aldehyde-alkyl, C_{1-12}-nitro-alkyle, nitrile.

In particularly preferred embodiments R3 is a side chain of the formula $R3^a$ or $R3^b$ as described above. This results in the catalysts according to the invention P30 and P31 respectively. It must

be noted here that P30 and P31 do not follow general procedure I-E. Synthesis details are given below at corresponding products P30 and P31.

In other particularly preferred embodiments R3 is a side chain of the formula $R3^c$, $R3^d$, $R3^e$, $R3^f$, $R3^g$, $R3^h$, $R3^i$, $R3^j$, $R3^k$, $R3^l$, $R3^m$, $R3^n$, $R3^o$ or $R3^p$ as described above. In these embodiments z is chosen to be either a methylene as shown in above formula 1^b or a carbonyl as shown in above formula 1^a.

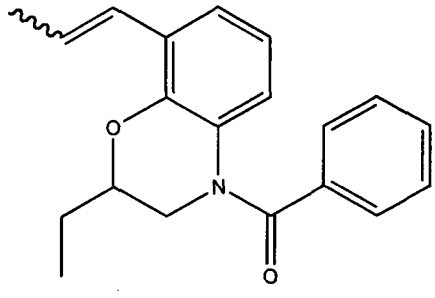


P23

isobutyl 2-ethyl-8-(prop-1-enyl)-2*H*-benzo[*b*][1,4]oxazine-4(3*H*)-carboxylate

PROCEDURE & NMR DATA : 392µL (2.5eq, 3mmol) of isobutyl chloroformate was added to a mixture of 192mg (4eq, 4.8mmol) of NaH and 261mg (1.2mmol) of oxazine **P22** in THF (24mL). 380mg of **P23** were obtained, yield 99%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.49 (m, 1H), 7.01 (ddd, *J* = 47.8, 7.7, 1.5 Hz, 1H), 6.83 – 6.69 (m, 1H), 6.52 (ddd, *J* = 13.7, 13.0, 1.6 Hz, 1H), 6.24 – 5.69 (m, 1H), 4.19 – 3.97 (m, 2H), 3.97 – 3.86 (m, 2H), 3.29 – 3.16 (m, 1H), 2.00 – 1.88 (m, 1H), 1.80 (ddd, *J* = 20.6, 6.9, 1.8 Hz, 3H), 1.02 (dt, *J* = 11.4, 7.5 Hz, 3H), 0.90 (ddd, *J* = 6.7, 3.5, 0.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.83, 143.07, 126.89, 126.64, 126.59, 125.92, 125.56, 125.52, 125.50, 125.25, 124.79, 121.74, 119.49, 118.86, 76.15, 72.39, 45.76, 30.32, 29.70, 27.93, 26.91, 25.66, 25.61, 22.70, 19.20, 19.18, 18.96, 14.77, 9.58, 9.51.

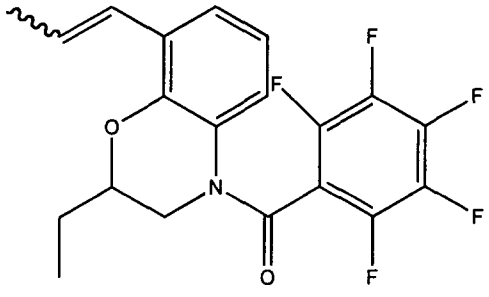


P24

(2-ethyl-8-(prop-1-enyl)-2*H*-benzo[*b*][1,4]oxazin-4(3*H*)-yl)(phenyl)methanone

PROCEDURE & NMR DATA : 348µL (2.5eq, 3mmol) of benzoyl chloride was added to a mixture of 192mg (4eq, 4.8mmol) of NaH and 260mg (1.2mmol) of oxazine **P22** in THF (25mL). 300mg of **P24** were obtained, yield 78%.

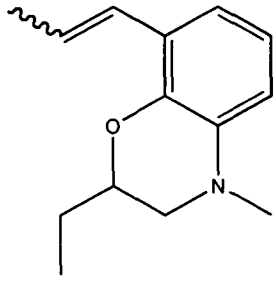
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.38 (m, 2H), 7.38 – 7.31 (m, 1H), 7.31 – 7.22 (m, 2H), 6.98 (ddd, *J* = 42.5, 7.5, 1.2 Hz, 1H), 6.70 – 6.39 (m, 3H), 6.29 – 5.72 (m, 1H), 4.28 – 4.12 (m, 2H), 3.38 (ddd, *J* = 12.8, 7.7, 6.1 Hz, 1H), 1.81 (ddd, *J* = 23.1, 6.9, 1.8 Hz, 3H), 1.76 – 1.53 (m, 2H), 1.01 (dt, *J* = 14.9, 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.31, 135.35, 135.32, 130.61, 130.59, 128.64, 128.60, 128.36, 128.31, 127.27, 127.08, 126.82, 126.27, 126.16, 125.03, 124.47, 123.02, 122.92, 122.56, 119.06, 118.46, 25.99, 18.99, 14.83, 9.59, 9.50.



P25
(2-ethyl-8-(prop-1-enyl)-2*H*-benzo[*b*][1,4]oxazin-4(3*H*)-yl)(perfluorophenyl)methanone

PROCEDURE & NMR DATA : 141µL (2eq, 0.98mmol) of pentafluorobenzoyl chloride was added to a mixture of 78mg (4eq, 1.96mmol) of NaH and 100mg (0.49mmol) of oxazine **P22** in THF (11mL). 118mg of **P25** were obtained, yield 61%.

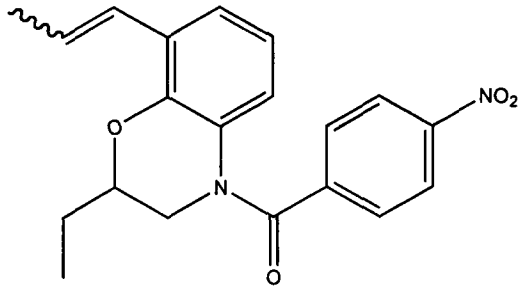
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (ddd, *J* = 45.1, 7.7, 1.2 Hz, 1H), 6.64 – 6.37 (m, 2H), 6.28 (ddd, *J* = 18.8, 8.0, 1.1 Hz, 1H), 6.22 – 5.72 (m, 1H), 4.59 (ddd, *J* = 13.1, 3.1, 1.4 Hz, 1H), 4.28 – 4.04 (m, 1H), 3.38 – 3.17 (m, 1H), 1.87 – 1.64 (m, 5H), 1.06 (dt, *J* = 12.3, 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.94, 145.29, 144.49, 128.11, 127.96, 127.81, 127.61, 127.48, 127.27, 127.22, 126.73, 124.80, 124.57, 124.39, 124.21, 123.96, 123.79, 122.08, 121.90, 120.34, 120.17, 119.98, 119.37, 119.18, 118.58, 75.86, 48.65, 44.13, 26.90, 26.12, 26.08, 25.36, 18.94, 14.78, 9.44, 9.35. ^{19}F NMR (376 MHz, $CDCl_3$) δ -139.59 – -140.69 (m, 2F), -150.30 – -151.23 (m, 1F), -158.61 – -160.29 (m, 2F).



P26
2-ethyl-4-methyl-8-(prop-1-enyl)-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazine

PROCEDURE & NMR DATA : 287µL (10eq, 4.6mmol) of methyl iodide was added to a mixture of 74mg (4eq, 1.84mmol) of NaH and 100mg (0.46mmol) of oxazine **P22** in THF (10mL). 75mg of **P26** were obtained, yield 71%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.77 – 6.64 (m, 2H), 6.63 – 6.49 (m, 1H), 6.48 – 6.42 (m, 1H), 6.20 – 5.65 (m, 1H), 4.03 (tdd, *J* = 7.9, 5.6, 2.5 Hz, 1H), 3.12 (ddd, *J* = 11.3, 3.1, 2.5 Hz, 1H), 2.95 – 2.87 (m, 1H), 2.82 – 2.75 (m, 3H), 1.79 (ddd, *J* = 14.4, 6.9, 1.8 Hz, 3H), 1.75 – 1.50 (m, 2H), 1.02 – 0.95 (m, 1H)

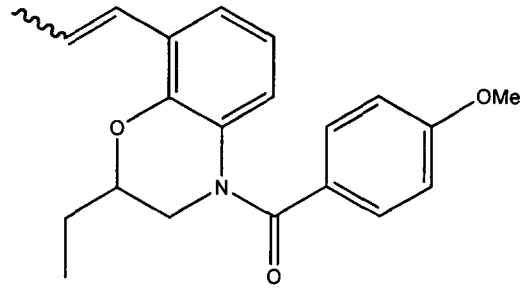


P27

(2-ethyl-8-(prop-1-enyl)-2*H*-benzo[*b*][1,4]oxazin-4(3*H*)-yl)(4-nitrophenyl)methanone

PROCEDURE & NMR DATA : 199mg (2.5eq, 1.08mmol) of 4-Nitrobenzoyl chloride was added to a mixture of 66mg (4eq, 1.72mmol) of NaH and 87mg (0.43mmol) of oxazine **P22** in THF (18mL). 150mg of **P27** were obtained, yield 99%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.04 (m, 2H), 7.65 – 7.48 (m, 2H), 7.02 (dd, *J* = 43.8, 8.9 Hz, 1H), 6.69 – 6.38 (m, 2H), 6.27 – 5.72 (m, 1H), 4.52 – 4.40 (m, 1H), 4.05 (q, *J* = 7.2 Hz, 2H), 3.30 (ddd, *J* = 13.1, 8.3, 6.7 Hz, 1H), 1.81 (ddd, *J* = 27.4, 6.9, 1.8 Hz, 3H), 1.40 (dd, *J* = 11.6, 6.3 Hz, 2H), 1.18 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.12, 148.74, 144.29, 143.52, 141.38, 129.64, 127.81, 127.70, 127.21, 127.13, 126.52, 124.73, 124.18, 123.65, 123.60, 123.39, 122.85, 122.71, 119.30, 118.72, 60.37, 21.03, 18.95, 18.67, 14.82, 14.18.

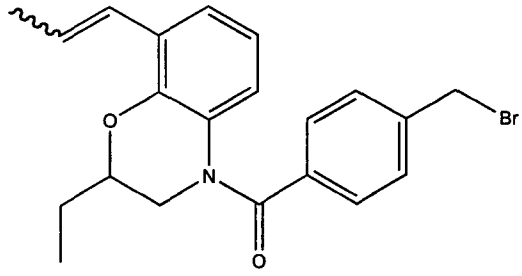


P28

(2-ethyl-8-(prop-1-enyl)-2*H*-benzo[*b*][1,4]oxazin-4(3*H*)-yl)(4-methoxyphenyl)methanone

PROCEDURE & NMR DATA : 133mg (2.5eq, 0.77mmol) of *p*-Anisoyl chloride was added to a mixture of 48mg (4eq, 1.24mmol) of NaH and 63mg (0.31mmol) of oxazine **P22** in THF (12mL). 103mg of **P28** were obtained, yield 98%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.35 (m, 2H), 7.08 – 6.89 (m, 1H), 6.84 – 6.72 (m, 2H), 6.62 (d, *J* = 15.8 Hz, 1H), 6.57 – 6.41 (m, 2H), 6.27 – 5.71 (m, 1H), 4.22 (dd, *J* = 23.3, 8.8 Hz, 2H), 3.76 (d, *J* = 3.8 Hz, 3H), 3.37 (dt, *J* = 12.8, 7.6 Hz, 1H), 1.82 (ddd, *J* = 21.5, 6.9, 1.8 Hz, 3H), 1.75 – 1.56 (m, 2H), 1.01 (dt, *J* = 14.7, 7.5 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 168.61, 161.53, 143.93, 130.90, 130.87, 127.21, 127.03, 126.14, 126.00, 125.07, 124.50, 123.00, 122.90, 122.30, 119.07, 118.46, 113.56, 113.51, 77.48, 77.33, 77.01, 76.69, 55.34, 53.42, 26.91, 25.93, 18.99, 14.85, 9.60, 9.51.

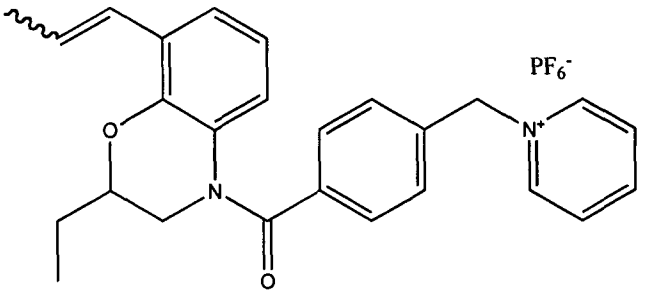


P29

(4-(bromomethyl)phenyl)(2-ethyl-8-(prop-1-enyl)-2*H*-benzo[*b*][1,4]oxazin-4(3*H*)-yl)methanone

PROCEDURE & NMR DATA : 96mg (1.5eq, 0.41mmol) of 4-(bromomethyl)benzoyl chloride was added to a mixture of 33µL (1.5eq, 0.41mmol) of pyridine and oxazine **P22** in DCM (15mL). 53mg of **P29** were obtained, yield 48%.

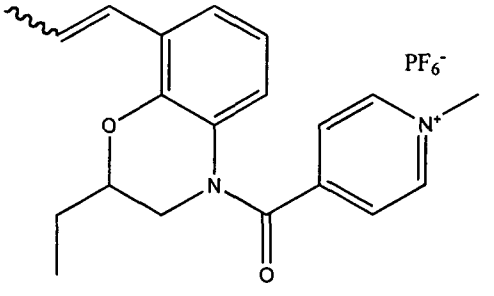
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (q, *J* = 8.30 Hz, 2H), 7.36 (t, *J* = 8.36 Hz, 2H), 7.12 (d, *J* = 9.03 Hz, 1H), 7.01 (d, *J* = 8.68 Hz, 1H), 6.69 (dd, *J* = 15.94, 1.66 Hz, 1H), 6.60 (dd, *J* = 13.96, 6.13 Hz, 1H), 6.53 (dd, *J* = 11.61, 1.63 Hz, 1H), 6.26 (qd, *J* = 15.86, 6.63 Hz, 1H), 5.85 (qd, *J* = 11.61, 7.08 Hz, 1H), 4.47 (s, 2H), 4.37-4.20 (m, 2H), 3.44 (ddd, *J* = 12.82, 7.71, 5.45 Hz, 1H), 1.91 (dd, *J* = 6.66, 1.73 Hz, 3H), 1.85 (dd, *J* = 7.10, 1.85 Hz, 3H), 1.84-1.62 (m, 2H), 1.08 (td, *J* = 14.75, 7.47 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 144.0, 143.2, 140.2, 140.2, 139.8, 135.2, 135.2, 129.1, 129.1, 129.0, 129.0, 128.9, 128.4, 128.4, 127.25.8, 18.9, 14.8, 9.5, 9.5.



P30
1-(4-(2-ethyl-8-(prop-1-enyl)-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazine-4-carbonyl)benzyl)pyridinium hexafluorophosphate(V)

PROCEDURE & NMR DATA : 53mg (0.13mmol) of oxazine **P22** were added to 300µL of pyridine in tolune (15mL). The mixture warm up to reflux for the night. Volatiles were removed then 17mg (1.5eq) of potassium hexafluorophosphate and water (10mL) were added. 30 mg of **P30** were obtained, yield 42%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (d, *J* = 5.54 Hz, 2H), 8.52 (t, *J* = 7.77 Hz, 1H), 8.05 (t, *J* = 7.02 Hz, 2H), 7.51 (t, *J* = 7.86 Hz, 2H), 7.44 (t, *J* = 7.85 Hz, 2H), 7.09 (d, *J* = 7.90 Hz, 1H), 6.97 (d, *J* = 7.96 Hz, 1H), 6.61 (dd, *J* = 15.88, 1.46 Hz, 1H), 6.58-6.48 (m, 1H), 6.44 (dd, *J* = 11.57, 1.43 Hz, 1H), 6.21 (qd, *J* = 15.75, 6.51 Hz, 1H), 5.84-5.73 (m, 3H), 4.32-4.02 (m, 2H), 3.43 (ddd, *J* = 12.93, 7.72, 2.55 Hz, 1H), 1.85 (dd, *J* = 6.62, 1.48 Hz, 3H), 1.78 (dd, *J* = 7.09, 1.73 Hz, 3H), 1.75-1.55 (m, 2H), 1.02 (td, *J* = 14.48, 7.44 Hz, 3H). ^{19}F NMR (376 MHz, CD_2Cl_2) δ -73.3 (d, 6F, *J* = 711Hz) ^{31}P NMR (162 MHz, CDCl3) δ -144.5 (sept, 1P, *J* = 711Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 145.8, 144.1, 143.8, 143.1, 136.5, 134.5, 129.1, 128.7, 128.6, 128.3, 126.8, 126.7, 126.7, 126.4, 126.0, 124.3, 123.8, 122.7, 122.3, 122.2, 118.6, 118.0, 63.7, 77.6, 46.4, 18.1, 13.9, 8.7, 8.6.



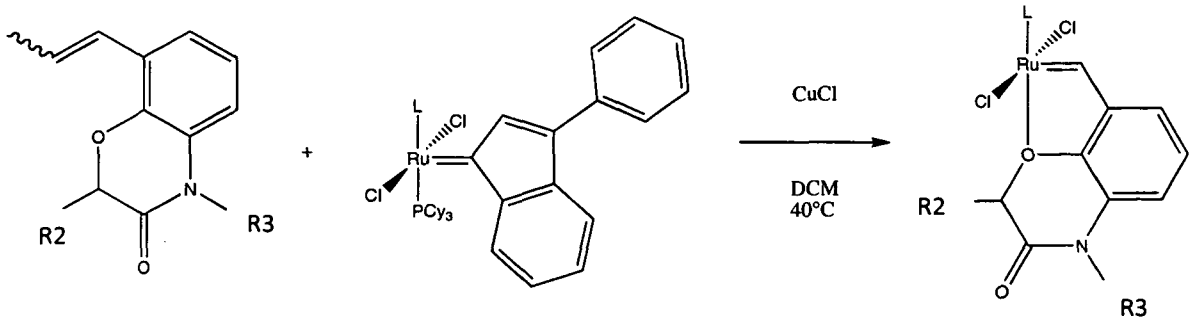
P31
4-(2-ethyl-8-(prop-1-enyl)-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazine-4-carbonyl)-1-methylpyridinium hexafluorophosphate(V)

PROCEDURE & NMR DATA : 123mg (2.5eq, 0.67mmol) of isonicotinoyl chloride was added to a mixture of 42mg (4eq, 1.08mmol) of NaH and 56mg (0.27mmol) of oxazine **P22** in DMF (15mL). 66mg were purified.

This product was added to 500µL of Iodomethane in toluene (15mL). This mixture warm up to reflux for the night then cooled to room temperature then volatiles were removed under reduce pressure. Water (15mL) and 59mg of potassium hexafluorophosphate (1.5eq) were added to crude and stirred for 1h. 62mg of **31** were obtained, yield 62%.

^{1}H NMR (400 MHz, CDCl3) δ 8.78-8.36 (m, 2H), 8.03-7.62 (m, 2H), 7.10 (d, *J* = 7.35 Hz, 1H), 7.02 (d, *J* = 7.25 Hz, 1H), 6.86-6.61 (m, 1H), 6.56 (dd, *J* = 15.78, 1.51 Hz, 1H), 6.42 (dd, *J* = 11.48, 1.48 Hz, 1H), 6.17 (dd, *J* = 15.71, 6.75 Hz, 1H), 6.26-6.03 (m, 1H), 5.89-5.72 (m, 2H), 4.30 (s, 3H), 4.57-3.91 (m, 2H), 3.37-3.13 (m, 1H), 1.83 (dd, *J* = 6.59, 1.52 Hz, 3H), 1.78 (dd, *J* = 7.09, 1.77 Hz, 3H), 1.75-1.37 (m, 2H), 1.16-0.96 (m, 3H). ^{19}F NMR (376 MHz, CDCl3) δ -72.3 (d, 6F, J = 711Hz). ^{31}P NMR (162 MHz, CDCl3) δ -144.9 (sept, 1P, J = 711Hz). ^{13}C NMR (101 MHz, CDCl3) δ 150.7, 146.2, 144.5, 143.7, 127.5, 127.5, 126.1, 124.4, 123.7, 123.6, 119.0, 75.6, 51.0, 48.7, 18.9, 18.4, 14.8, 9.1.

I-F-General procedure for ligand exchange.



To a solution of SIPr (N,N'-bis(2,6-diisopropylphényl)imidazol-2-ylidène) (or SIMes (1,3-dimésityl-4,5-dihydroimidazol-2-ylidène)) containing Ru-indenylidene complex (1.2eq) and copper chloride (1.1eq) in dry DCM (Dichloromethane) (1mL for 0.07mmol of oxazinone), oxazinone in DCM solution (1mL for 0.035mmol of oxazinone) was added. The resulting mixture was stirred at 35°C for 5h. Volatiles were removed under reduce pressure, acetone was added to the residue and the solution is filtered on a plug of Celite. The filtrate was concentrated and purified by chromatography on silica gel.

Depending on R2 and R3 products P32 to P52 are obtained (attention is drawn to the fact that products P52 to P57 were obtained after amide reduction – see below). See below for specific procedure and NMR data for Catalysts according to the invention P32 to P59.

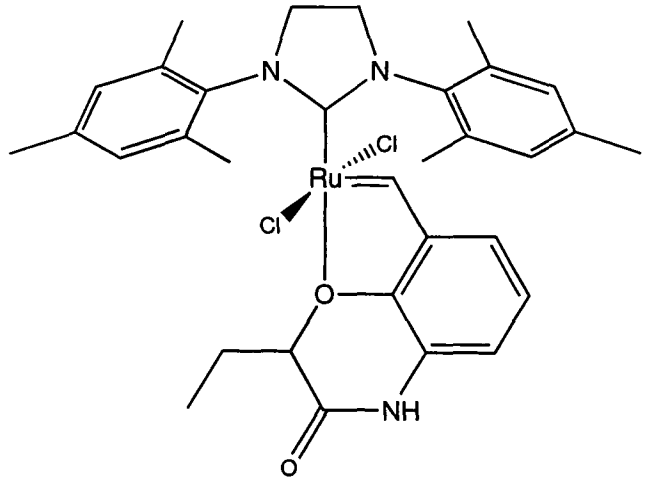
According to a preferred embodiment, L is a phosphine $P(R8)_3$ or a phosphate $P(OR9)_3$, wherein R8 and R9 are each independently of one another C_{1-6}-alkyl, C_{5-12}-cycloalkyl or ary.

According to another preferred embodiment, L is a ligand of the formula L1, L2, L3 or L4 as described above and whereinwherein R10 and R11 are each, independently of one another a substituted or an unsubstituted side chain comprising 1 to 30 carbon atoms and optionally comprising one or more functional groups, and wherein R12 and R13 are each, independently

of one another, H, C_{1-6}-alkyl optionally substituted by a alkoxy radical OR15, or aryl optionally substituted by a alkoxy radical OR15, or form a 3- or 4-membered alkylene bridge, and wherein R15 is selected from the group consisting of C_{1-20}-alkyl, aryl and C_{7-18}-aralkyl, and wherein g and g' are each halogen, preferably Cl or Br. Particular preference is given when R10 and R11 are each, independently of one another, C_{1-30}-alkyl optionally substituted by a alkoxy radical OR15, C_{2-30}-alkenyl optionally substituted by a alkoxy radical OR15, aryl optionally substituted by a alkoxy radical OR15, aminoalkyl or aminocycloalkyl.

In a particular preferred embodiment L is a ligand that respond to one of formulae $L1^a$, $L1^b$, $L1^c$, $L1^d$, $L1^e$, $L1^f$ or $L1^g$ as described above.

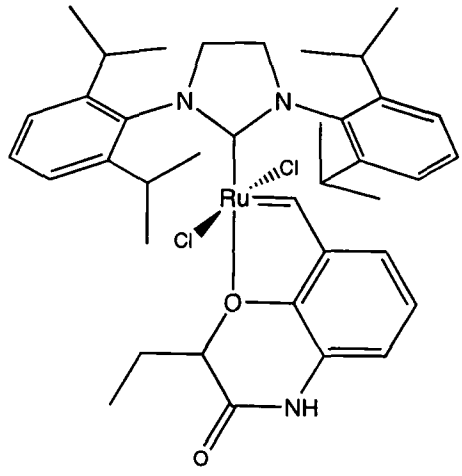
As mentioned above, it must be noted that from products P23 to P28 are respectively obtained the catalysts of the present invention P52 to P57 (where z is methylene). The general procedure when z is methylene is similar to the one shown in I-F where z is carbonyle. For simplicity the reaction mechanism is not shown herein.



P32
(1,3-dimesitylimidazolidin-2-yl)((2-ethyl-3-oxo-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-8-yl)methylene)ruthenium(II) chloride

PROCEDURE & NMR DATA : 50mg (0.23mmol) of **P2** were added to 218mg (1eq, 0.23mmol) of Umicore-M2 and 25mg (1.1eq, 0.25mmol) of copper chloride in dry DCM (4.6mL). 20mg of **P32** were obtained, yield 13%.

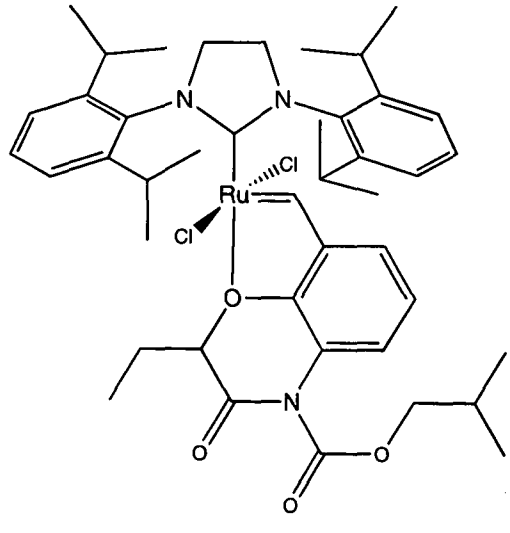
^{1}H NMR (400 MHz, CD_2Cl_2) δ 16.51 (s, 1H), 7.43 (s, 1H), 7.00 (d, *J* = 5.1 Hz, 4H), 6.92 (d, *J* = 7.7 Hz, 1H), 6.85 (dd, *J* = 7.7, 7.6 Hz, 1H), 6.59 (d, *J* = 7.6 Hz, 1H), 4.95 – 4.88 (m, 1H), 4.11 (s, 4H), 2.36 (s, 6H), 2.33 (d, *J* = 5.5 Hz, 12H), 1.93 – 1.69 (m, 2H), 0.84 – 0.64 (m, 3H).



P33
(1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-yl)((2-ethyl-3-oxo-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-8-yl)methylene)ruthenium(II) chloride

PROCEDURE & NMR DATA : 50mg (0.23mmol) of **P2** were added to 238mg (1eq, 0.23mmol) of SIPr-indenylidene and 25mg (1.1eq, 0.25mmol) of copper chloride in dry DCM (6mL). 84mg of **P33** were obtained, yield 49%.

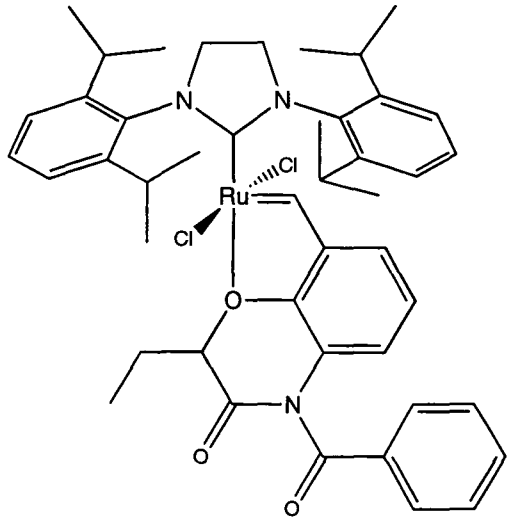
^{1}H NMR (400 MHz, CD_2Cl_2) δ 16.29 (s, 1H), 7.63 (s, 1H), 7.50 – 7.42 (m, 2H), 7.33 – 7.26 (m, 4H), 6.84 (dd, *J* = 7.7, 1.3 Hz, 1H), 6.78 (t, *J* = 7.7 Hz, 1H), 6.47 (dd, *J* = 7.7, 1.3 Hz, 1H), 5.00 (dd, *J* = 5.1, 2.8 Hz, 1H), 4.18 – 4.08 (m, 4H), 3.54 – 3.39 (m, 4H), 1.91 – 1.77 (m, 2H), 1.22 – 1.07 (m, 24H), 0.81 (t, *J* = 7.3 Hz, 3H).



P34
(1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-yl)((2-ethyl-4-(isobutoxycarbonyl)-3-oxo-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-8-yl)methylene)ruthenium(II) chloride

PROCEDURE & NMR DATA : 154mg (0.48mmol) of **P3** were added to 500mg (1eq, 0.48mmol) of SIPr-indenylidene and 52mg (1.1eq, 0.53mmol) of copper chloride in dry DCM (9mL). 262mg of **P34** were obtained, yield 64%.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 16.29 (s, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.40 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.30 (td, *J* = 7.7, 1.4 Hz, 4H), 6.89 (dd, *J* = 7.7, 8.2 Hz, 1H), 6.60 (dd, *J* = 7.7, 1.2 Hz, 1H), 4.95 (dd, *J* = 5.4, 2.6 Hz, 1H), 4.22 – 4.06 (m, 4H), 4.03 (dd, *J* = 6.5, 1.9 Hz, 2H), 3.54 – 3.37 (m, 4H), 1.92 (dt, *J* = 13.5, 6.7 Hz, 1H), 1.88 – 1.66 (m, 2H), 1.23 – 1.09 (m, 24H), 0.86 (d, *J* = 6.7 Hz, 6H), 0.83 (t, *J* = 7.3 Hz, 3H).

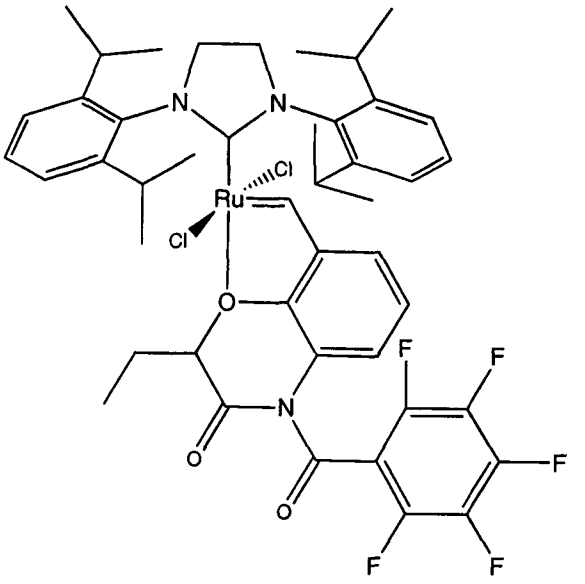


P35

(1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-yl)((2-ethyl-3-oxo-4-(phenylcarbonyl)-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-8-yl)methylene)ruthenium(II) chloride

PROCEDURE & NMR DATA : 58mg (0.18mmol) of **P4** were added to 187mg (1eq, 0.18mmol) of SIPr-indenylidene and 20mg (1.1eq, 0.20mmol) of copper chloride in dry DCM (5.4mL). 74mg of **P35** were obtained, yield 48%.

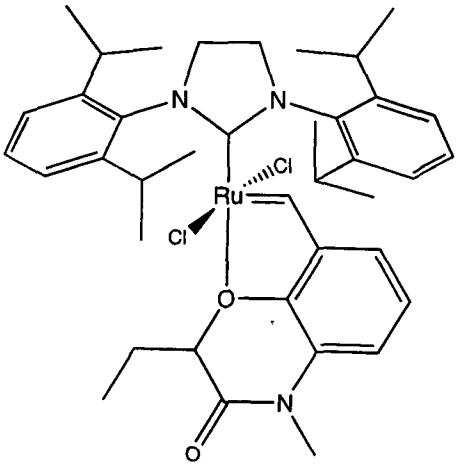
^{1}H NMR (400 MHz, CD_2Cl_2) δ 16.33 (s, 1H), 7.72 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.58 – 7.51 (m, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.41 – 7.34 (m, 2H), 7.31 (td, *J* = 7.7, 1.5 Hz, 4H), 7.13 (dd, *J* = 8.1, 1.2 Hz, 1H), 6.82 (t, *J* = 7.9 Hz, 1H), 6.59 (dd, *J* = 7.7, 1.3 Hz, 1H), 5.11 (dd, *J* = 5.3, 2.7 Hz, 1H), 4.22 – 4.07 (m, 4H), 3.57 – 3.39 (m, 4H), 1.89 – 1.67 (m, 2H), 1.27 – 1.11 (m, 24H), 0.84 (t, *J* = 6.8 Hz, 3H).



P36
(1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-yl)((2-ethyl-3-oxo-4-(perfluorophenylcarbonyl)-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-8-yl)methylene)ruthenium(II) chloride

PROCEDURE & NMR DATA : 50mg (0.12mmol) of **P5** were added to 126mg (1eq, 0.12mmol) of SIPr-indenylidene and 13mg (1.1eq, 0.13mmol) of copper chloride in dry DCM (5.4mL). 68mg of **P36** were obtained, yield 60%.

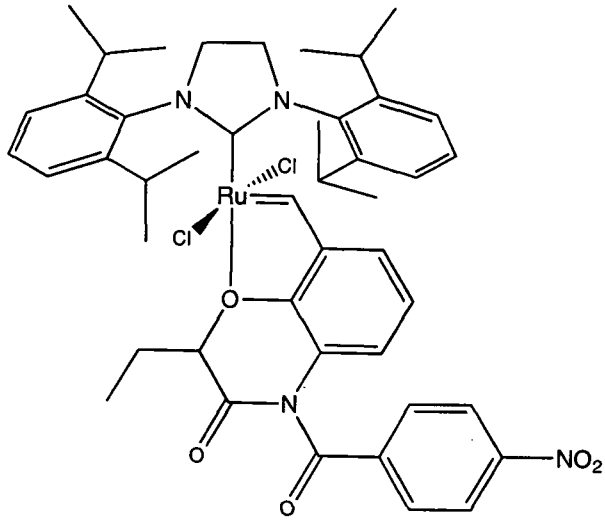
^{1}H NMR (400 MHz, CD_2Cl_2) δ 16.33 (s, 1H), 7.93 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.30 (td, *J* = 7.7, 1.4 Hz, 4H), 7.05 – 6.94 (m, 1H), 6.74 (dd, *J* = 7.7, 1.3 Hz, 1H), 5.01 (dd, *J* = 5.0, 3.2 Hz, 1H), 4.26 – 4.06 (m, 4H), 3.55 – 3.36 (m, 4H), 1.87 – 1.68 (m, 2H), 1.22 – 1.07 (m, 24H), 0.73 (t, *J* = 7.3 Hz, 3H). ^{19}F NMR (376 MHz, CD_2Cl_2) δ -142.62 (2F), -150.67, -161.20 (2F).



P37
(1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-yl)((2-ethyl-4-methyl-3-oxo-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-8-yl)methylene)ruthenium(II) chloride

PROCEDURE & NMR DATA : 75mg (0.33mmol) of **P6** were added to 335mg (1eq, 0.33mmol) of SIPr-indenylidene and 36mg (1.1eq, 0.36mmol) of copper chloride in dry DCM (14mL). 132mg of **P37** were obtained, yield 52%.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 16.30 (s, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.34 – 7.25 (m, 4H), 7.02 (dd, *J* = 8.0, 1.1 Hz, 1H), 6.89 (dd, *J* = 8.0, 7.7 Hz, 1H), 6.50 (dd, *J* = 7.7, 1.1 Hz, 1H), 4.96 (dd, *J* = 5.0, 2.7 Hz, 1H), 4.24 – 4.03 (m, 4H), 3.56 – 3.35 (m, 4H), 3.16 (s, 3H), 1.93 – 1.58 (m, 2H), 1.22 – 1.06 (m, 24H), 0.80 (t, *J* = 7.3 Hz, 3H).

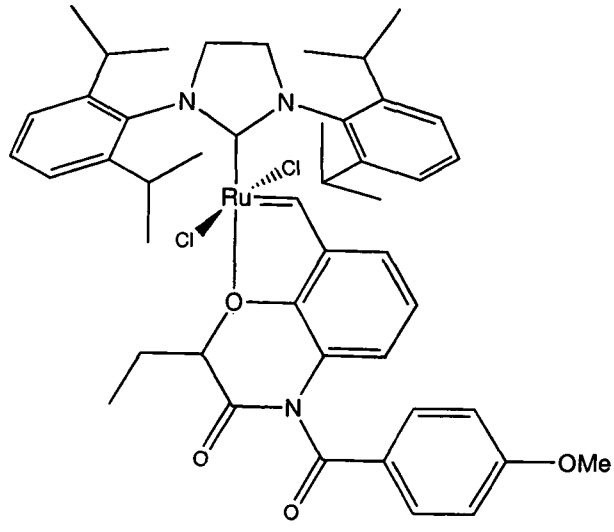


P38

(1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-yl)((2-ethyl-4-(4-nitrophenylcarbonyl)-3-oxo-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-8-yl)methylene)ruthenium(II) chloride

PROCEDURE & NMR DATA : 29mg (0.08mmol) of **P7** were added to 100mg (1.2eq, 0.097mmol) of SIPr-indenylidene and 11mg (1.3eq, 0.11mmol) of copper chloride in dry DCM (10mL). 37mg of **P38** were obtained, yield 52%.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 16.34 (s, 1H), 8.22 – 8.14 (m, 2H), 7.83 – 7.76 (m, 2H), 7.49 – 7.40 (m, 3H), 7.31 (td, *J* = 7.7, 1.5 Hz, 4H), 6.90 (t, *J* = 7.9 Hz, 1H), 6.67 (dd, *J* = 7.7, 1.3 Hz, 1H), 5.10 (dd, *J* = 5.4, 2.8 Hz, 1H), 4.30 – 3.98 (m, 4H), 3.61 – 3.27 (m, 4H), 1.88 – 1.67 (m, 2H), 1.22 – 1.10 (m, 24H), 0.81 (t, *J* = 7.3 Hz, 3H).

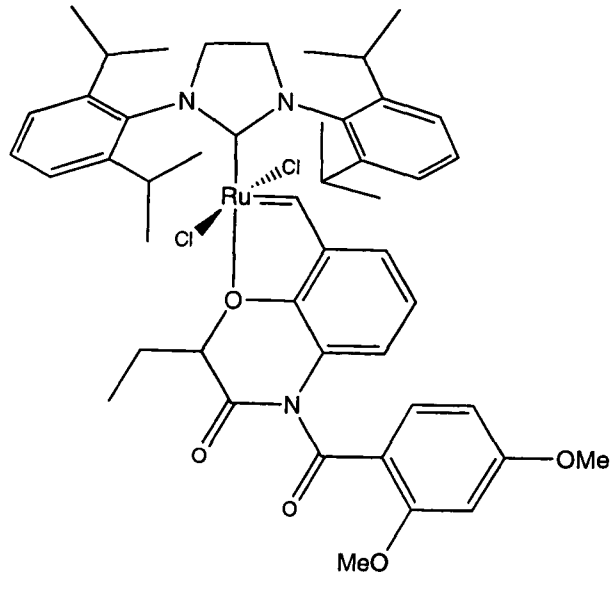


P39

(1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-yl)((2-ethyl-4-(4-methoxyphenylcarbonyl)-3-oxo-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-8-yl)methylene)ruthenium(II) chloride

PROCEDURE & NMR DATA : 28mg (0.08mmol) of **P8** were added to 100mg (1.2eq, 0.097mmol) of SIPr-indenylidene and 11mg (1.3eq, 0.11mmol) of copper chloride in dry DCM (10mL). 61mg of **P39** were obtained, yield 86%.

^{1}H NMR (400 MHz, Acetone) δ 16.32 (s, 1H), 7.87 – 7.75 (m, 2H), 7.50 – 7.40 (m, 2H), 7.35 – 7.25 (m, 3H), 6.98 – 6.89 (m, 4H), 6.84 (t, *J* = 7.9 Hz, 1H), 6.52 (dd, *J* = 7.6, 1.2 Hz, 1H), 5.11 (dd, *J* = 5.0, 3.0 Hz, 1H), 4.31 – 4.15 (m, 4H), 3.77 (s, 3H), 3.62 – 3.43 (m, 4H), 1.83 – 1.73 (m, 2H), 1.18 – 1.05 (m, 24H), 0.80 (t, *J* = 7.3 Hz, 3H).

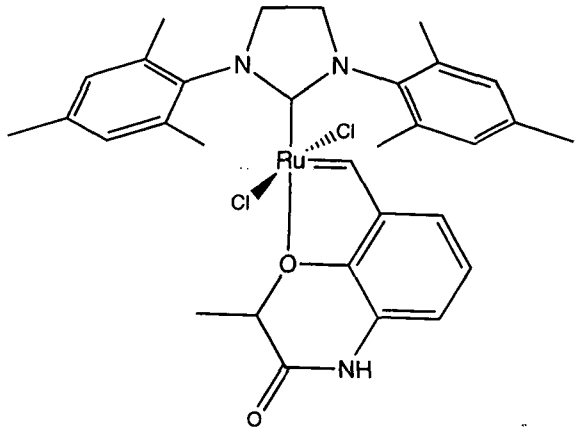


P40

(1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-yl)((4-(2,4-dimethoxyphenylcarbonyl)-2-ethyl-3-oxo-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-8-yl)methylene)ruthenium(II) chloride

PROCEDURE & NMR DATA : 31mg (0.08mmol) of **P9** were added to 100mg (1.2eq, 0.097mmol) of SIPr-indenylidene and 11mg (1.3eq, 0.11mmol) of copper chloride in dry DCM (10mL). 59mg of **P40** were obtained, yield 80%.

^{1}H NMR (400 MHz, Acetone) δ 16.34 (s, 1H), 7.71 (d, *J* = 8.8 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.31 (td, *J* = 7.7, 1.5 Hz, 4H), 7.13 (dd, *J* = 8.1, 1.2 Hz, 1H), 6.81 (t, *J* = 7.9 Hz, 1H), 6.56 – 6.47 (m, 2H), 6.35 (d, *J* = 2.3 Hz, 1H), 4.86 (t, *J* = 4.3 Hz, 1H), 4.28 – 4.19 (m, 4H), 3.74 (s, 3H), 3.60 – 3.50 (m, 4H), 3.49 (s, 3H), 1.80 – 1.71 (m, 2H), 1.18 – 1.07 (m, 24H), 0.78 (t, *J* = 7.3 Hz, 3H).

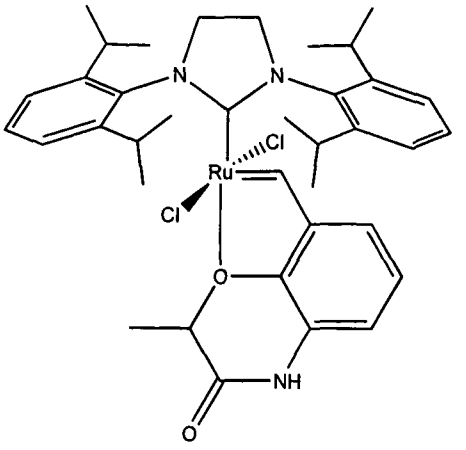


P41

(1,3-dimesitylimidazolidin-2-yl)((2-methyl-3-oxo-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-8-yl)methylene)ruthenium(II) chloride

PROCEDURE & NMR DATA : 50mg (0.25mmol) of **P11** were added to 237mg (1eq, 0.25mmol) of Umicore-M2 and 27mg (1.1eq, 0.27mmol) of copper chloride in dry DCM (4.6mL). 9mg of **P41** were obtained, yield 6%.

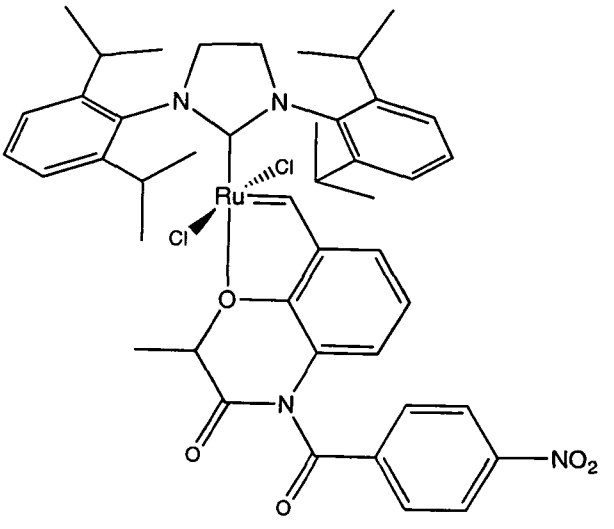
^{1}H NMR (400 MHz, CD_2Cl_2) δ 16.46 (s, 1H), 7.93 (s, 1H), 7.00 (s, 4H), 6.82 (d, *J* = 7.2 Hz, 1H), 6.76 (dd, *J* = 7.3, 7.2 Hz, 1H), 6.53 (d, *J* = 7.3 Hz, 1H), 4.89 (q, *J* = 6.5 Hz, 1H), 4.10 (s, *J* = 9.0 Hz, 4H), 2.35 (d, *J* = 2.9 Hz, 12H), 2.32 (s, 6H), 1.12 (d, *J* = 6.5 Hz, 3H).



P42
(1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-yl)((2-methyl-3-oxo-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-8-yl)methylene)ruthenium(II) chloride

PROCEDURE & NMR DATA : 50mg (0.25mmol) of **P11** were added to 258mg (1eq, 0.25mmol) of SIPr-indenylidene and 27mg (1.1eq, 0.27mmol) of copper chloride in dry DCM (5.4mL). 50mg of **P42** were obtained, yield 27%.

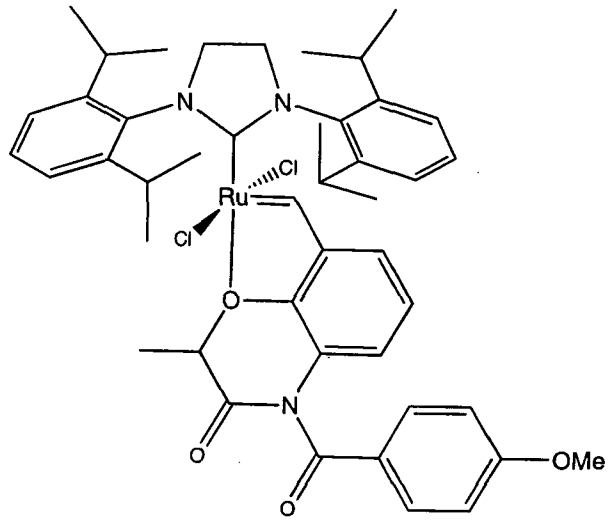
^{1}H NMR (400 MHz, CD_2Cl_2) δ 16.29 (s, 1H), 8.14 (s, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.30 (td, *J* = 7.7, 1.5 Hz, 4H), 6.63 – 6.50 (m, 2H), 6.35 (dd, *J* = 7.4, 1.3 Hz, 1H), 4.81 (q, *J* = 6.6 Hz, 1H), 4.19 – 4.05 (m, 4H), 3.55 – 3.37 (m, 4H), 1.27 (d, *J* = 6.6 Hz, 3H), 1.21 – 1.09 (m, 24H).



P43
(1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-yl)((2-methyl-4-(4-nitrophenylcarbonyl)-3-oxo-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-8-yl)methylene)ruthenium(II) chloride

PROCEDURE & NMR DATA : 47mg (0.14mmol) of **P12** were added to 137mg (1eq, 0.14mmol) of SIPr-indenylidene and 15mg (1.1eq, 0.15mmol) of copper chloride in dry DCM (10mL). 89mg of **P43** were obtained, yield 76%.

^{1}H NMR (400 MHz, Acetone) δ 16.28 (s, 1H), 8.25 – 8.18 (m, 2H), 8.12 – 8.05 (m, 2H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.37 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.31 (td, *J* = 7.7, 1.5 Hz, 4H), 6.99 – 6.90 (m, 1H), 6.62 (dd, *J* = 7.7, 1.1 Hz, 1H), 5.20 (q, *J* = 6.5 Hz, 1H), 4.28 – 4.16 (m, 4H), 3.62 – 3.43 (m, 4H), 1.24 (d, *J* = 6.5 Hz, 3H), 1.19 – 1.05 (m, 24H).

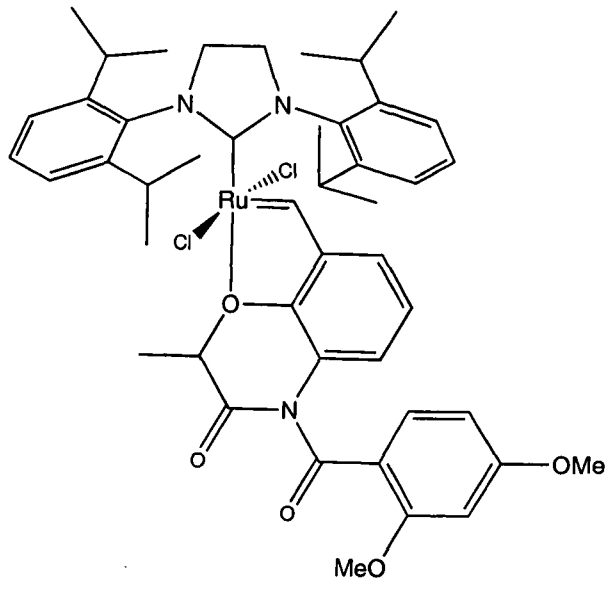


P44

(1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-yl)((4-(4-methoxyphenylcarbonyl)-2-methyl-3-oxo-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-8-yl)methylene)ruthenium(II) chloride

PROCEDURE & NMR DATA : 29mg (0.087mmol) of **P13** were added to 102mg (1.2eq, 0.097mmol) of SIPr-indenylidene and 11mg (1.3eq, 0.11mmol) of copper chloride in dry DCM (10mL). 77mg of **P44** were obtained, yield 90%.

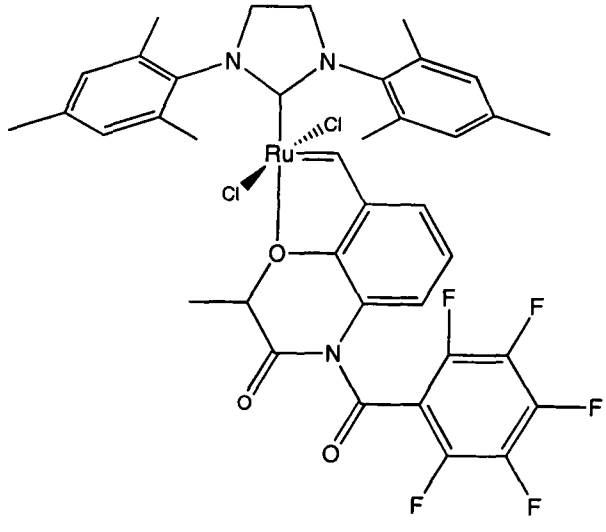
^{1}H NMR (400 MHz, Acetone) δ 16.27 (s, 1H), 7.88 – 7.75 (m, 2H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.31 (td, *J* = 7.7, 1.5 Hz, 4H), 6.97 – 6.89 (m, 3H), 6.89 – 6.82 (m, 1H), 6.54 (dd, *J* = 7.6, 1.2 Hz, 1H), 5.16 (q, *J* = 6.5 Hz, 1H), 4.27 – 4.16 (m, 4H), 3.77 (s, 3H), 3.63 – 3.43 (m, 4H), 1.29 (d, *J* = 6.5 Hz, 3H), 1.18 – 1.04 (m, 24H).



P45
(1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-yl)((4-(2,4-dimethoxyphenylcarbonyl)-2-methyl-3-oxo-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-8-yl)methylene)ruthenium(II) chloride

PROCEDURE & NMR DATA: 32mg (0.087mmol) of **P14** were added to 102mg (1.2eq, 0.097mmol) of SIPr-indenylidene and 11mg (1.3eq, 0.11mmol) of copper chloride in dry DCM (10mL). 79mg of **P45** were obtained, yield 95%.

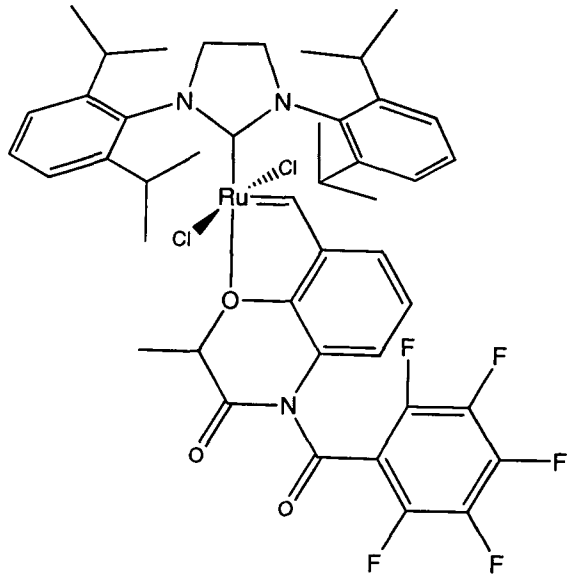
^{1}H NMR (400 MHz, Acetone) δ 16.29 (s, 1H), 7.75 – 7.66 (m, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.33 (dd, *J* = 7.6, 1.3 Hz, 2H), 7.29 (dt, *J* = 7.6, 1.3 Hz, 4H), 6.84 (t, *J* = 7.9 Hz, 1H), 6.57 – 6.49 (m, 2H), 6.35 (d, *J* = 2.3 Hz, 1H), 4.94 (q, *J* = 6.5 Hz, 1H), 4.28 – 4.15 (m, 4H), 3.74 (s, 3H), 3.54 (s, 3H), 3.62 – 3.42 (m, 4H), 1.33 – 1.26 (m, 3H), 1.18 – 1.04 (m, 24H).



P46
(1,3-dimesitylimidazolidin-2-yl)((2-methyl-3-oxo-4-(perfluorophenylcarbonyl)-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-8-yl)methylene)ruthenium(II) chloride

PROCEDURE & NMR DATA : 52mg (0.13mmol) of **P15** were added to 118mg (1eq, 0.13mmol) of Umicore-M2 and 17mg (1.1eq, 0.17mmol) of copper chloride in dry DCM (10mL). 69mg of **P46** were obtained, yield 62%.

^{1}H NMR (400 MHz, Acetone) δ 16.45 (s, 1H), 7.92 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.06 – 6.99 (m, 1H), 6.95 (d, *J* = 9.3 Hz, 4H), 6.80 (dd, *J* = 7.6, 1.0 Hz, 1H), 5.05 (q, *J* = 6.5 Hz, 1H), 4.16 (s, 4H), 2.31 (d, *J* = 10.6 Hz, 12H), 2.26 (s, 6H), 1.07 (d, *J* = 6.5 Hz, 3H). ^{19}F NMR (376 MHz, Acetone) δ 33.47 (2F), 25.58, 14.45 (2F).

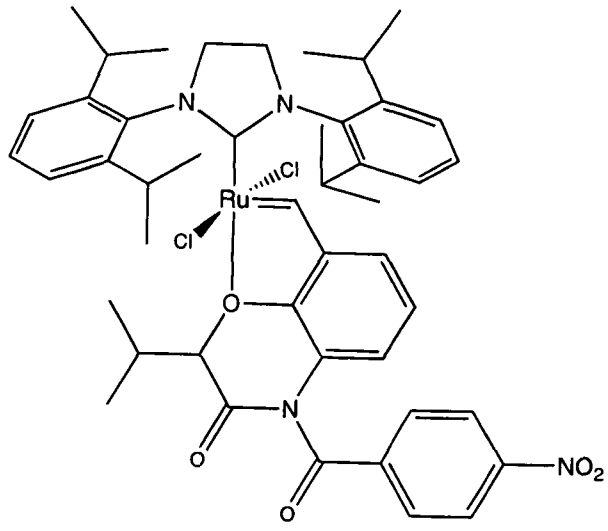


P47

(1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-yl)((2-methyl-3-oxo-4-(perfluorophenylcarbonyl)-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-8-yl)methylene)ruthenium(II) chloride

PROCEDURE & NMR DATA : 50mg (0.13mmol) of **P15** were added to 137mg (1eq, 0.13mmol) of SIPr-indenylidene and 14mg (1.1eq, 0.14mmol) of copper chloride in dry DCM (10mL). 99mg of **P47** were obtained, yield 92%.

^{1}H NMR (400 MHz, Acetone) δ 16.27 (s, 1H), 7.87 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.32 (dd, *J* = 7.7, 1.5 Hz, 2H), 7.27 (dd, *J* = 7.7, 1.5 Hz, 2H), 7.06 – 6.98 (m, 1H), 6.71 (dd, *J* = 7.7, 1.2 Hz, 1H), 5.07 (q, *J* = 6.5 Hz, 1H), 4.33 – 4.14 (m, 4H), 3.64 – 3.39 (m, 4H), 1.26 (d, *J* = 6.5 Hz, 3H), 1.18 – 1.04 (m, 24H). ^{19}F NMR (376 MHz, Acetone) δ 33.56 (2F), 25.62, 14.37 (2F).

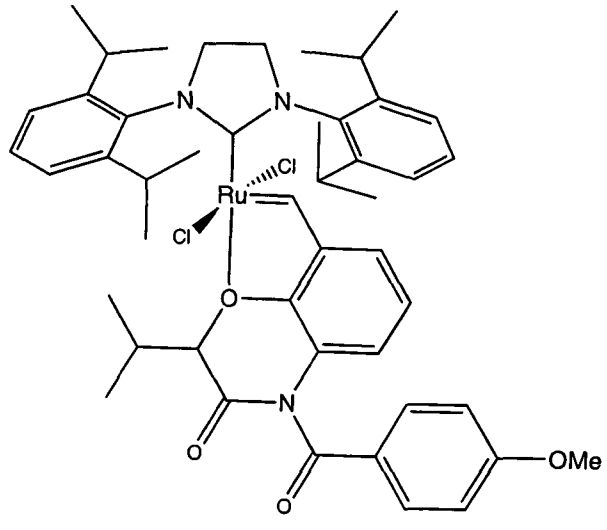


P48

(1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-yl)((2-isopropyl-4-(4-nitrophenylcarbonyl)-3-oxo-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-8-yl)methylene)ruthenium(II) chloride

PROCEDURE & NMR DATA : 19mg (0.05mmol) of **P18** were added to 61mg (1.2eq, 0.059mmol) of SIPr-indenylidene and 11mg (1.3eq, 0.11mmol) of copper chloride in dry DCM (10mL). 39mg of **P48** were obtained, yield 85%.

^{1}H NMR (400 MHz, Acetone) δ 16.32 (s, 1H), 8.30 – 8.20 (m, 2H), 8.09 – 8.01 (m, 2H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.41 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.34 – 7.28 (m, 4H), 6.94 – 6.85 (m, 1H), 6.60 (dd, *J* = 7.7, 1.2 Hz, 1H), 5.01 (d, *J* = 2.6 Hz, 1H), 4.30 – 4.23 (m, 4H), 3.58 – 3.43 (m, 4H), 2.10 – 2.03 (m, 1H), 1.18 – 1.05 (m, 24H), 0.84 (d, *J* = 7.2 Hz, 3H), 0.80 (d, *J* = 6.8 Hz, 3H).

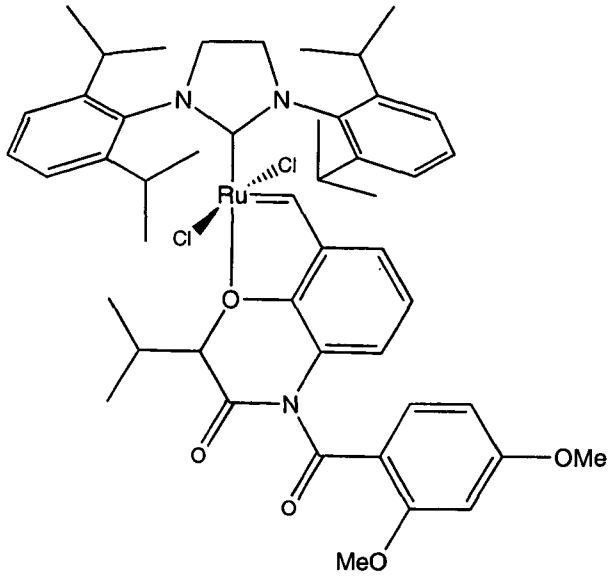


P49

(1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-yl)((2-isopropyl-4-(4-methoxyphenylcarbonyl)-3-oxo-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-8-yl)methylene)ruthenium(II) chloride

PROCEDURE & NMR DATA: 30mg (0.08mmol) of **P19** were added to 100mg (1.2eq, 0.097mmol) of SIPr-indenylidene and 11mg (1.3eq, 0.11mmol) of copper chloride in dry DCM (10 mL). 70mg of **P49** were obtained, yield 98%.

^{1}H NMR (400 MHz, Acetone) δ 16.32 (s, 1H), 7.83 – 7.78 (m, 2H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.33 – 7.27 (m, 4H), 6.96 – 6.91 (m, 3H), 6.83 (t, *J* = 7.9 Hz, 1H), 6.51 (dd, *J* = 7.7, 1.3 Hz, 1H), 4.99 (d, *J* = 2.5 Hz, 1H), 4.29 – 4.19 (m, 4H), 3.78 (s, 3H), 3.58 – 3.45 (m, 4H), 2.10 – 2.04 (m, 1H), 1.18 – 1.05 (m, 24H), 0.91 (d, *J* = 7.1 Hz, 3H), 0.85 (d, *J* = 6.8 Hz, 3H).

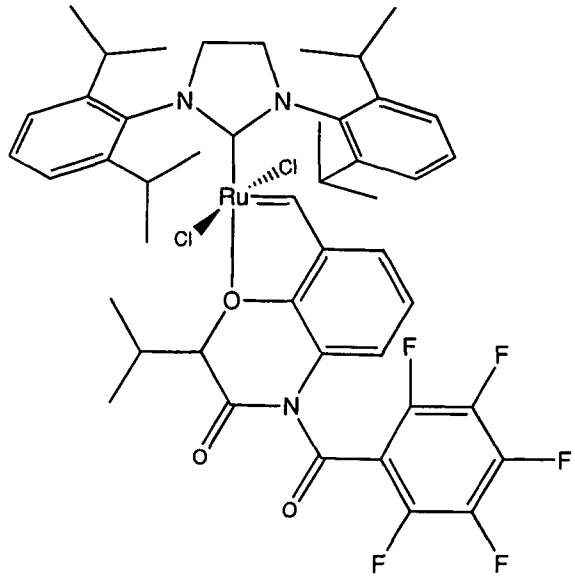


P50

(1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-yl)((4-(2,4-dimethoxyphenylcarbonyl)-2-isopropyl-3-oxo-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-8-yl)methylene)ruthenium(II) chloride

PROCEDURE & NMR DATA: 30mg (0.08mmol) of **P20** were added to 100mg (1.2eq, 0.097mmol) of SIPr-indenylidene and 11mg (1.3eq, 0.11mmol) of copper chloride in dry DCM (10mL). 73mg of **P50** were obtained, yield 98%.

^{1}H NMR (400 MHz, Acetone) δ 16.34 (s, 1H), 7.76 – 7.68 (m, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.34 – 7.28 (m, 4H), 7.00 (dd, *J* = 8.1, 1.2 Hz, 1H), 6.79 (t, *J* = 7.9 Hz, 2H), 6.55 – 6.51 (m, 1H), 6.49 (dd, *J* = 7.7, 1.2 Hz, 1H), 6.35 (d, *J* = 2.3 Hz, 1H), 4.81 (d, *J* = 2.5 Hz, 1H), 4.30 – 4.20 (m, 4H), 3.74 (s, 3H), 3.57 – 3.48 (m, 4H), 3.46 (s, 3H), 2.09 – 2.04 (m, 1H), 1.18 – 1.06 (m, 24H), 0.90 (d, *J* = 7.1 Hz, 3H), 0.83 (d, *J* = 6.8 Hz, 3H).

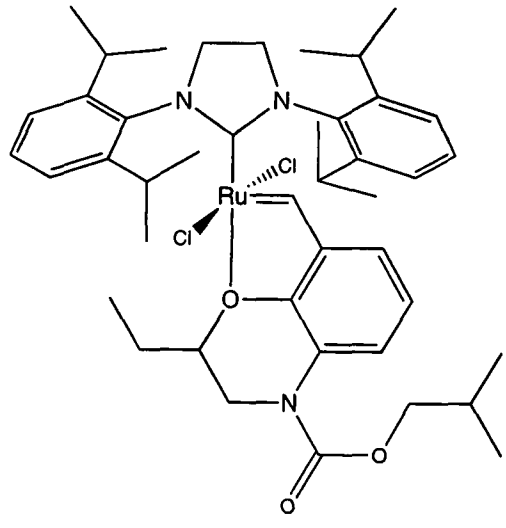


P51

(1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-yl)((2-isopropyl-3-oxo-4-(perfluorophenylcarbonyl)-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-8-yl)methylene)ruthenium(II) chloride

PROCEDURE & NMR DATA: 32mg (0.076mmol) of **P21** were added to 95mg (1.2eq, 0.092mmol) of SIPr-indenylidene and 11mg (1.3eq, 0.11mmol) of copper chloride in dry DCM (10mL). 42mg of **P51** were obtained, yield 59%.

^{1}H NMR (400 MHz, Acetone) δ 16.31 (s, 1H), 7.99 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.31 (ddd, *J* = 13.2, 7.7, 1.4 Hz, 4H), 7.07 – 6.99 (m, 1H), 6.71 (dd, *J* = 7.7, 1.3 Hz, 1H), 4.95 (d, *J* = 2.7 Hz, 1H), 4.29 – 4.16 (m, 4H), 3.58 – 3.39 (m, 4H), 2.12 – 2.02 (m, 1H), 1.18 – 1.04 (m, 24H), 0.81 (d, *J* = 7.1 Hz, 3H), 0.74 (d, *J* = 6.9 Hz, 3H). ^{19}F NMR (376 MHz, Acetone) δ -144.00 (2F), -152.28, -163.04 (2F).

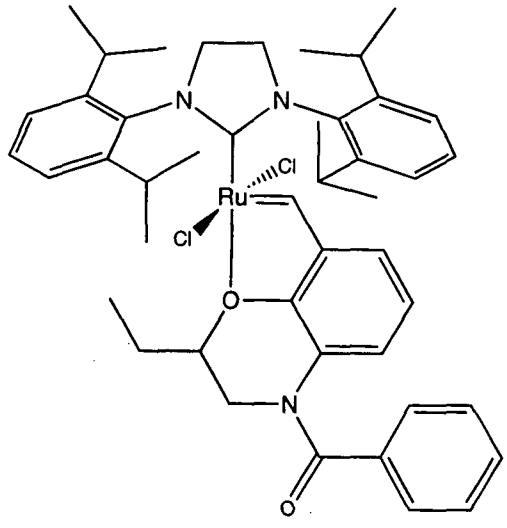


P52

(1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-yl)((2-ethyl-4-(isobutoxycarbonyl)-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-8-yl)methylene)ruthenium(II) chloride

PROCEDURE & NMR DATA : 50mg (0.17mmol) of **P23** were added to 170mg (1eq, 0.17mmol) of SIPr-indenylidene and 18mg (1.1eq, 0.18mmol) of copper chloride in dry DCM (5.2mL). 59mg of **P52** were obtained, yield 43%.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 16.22 (s, 1H), 8.04 – 7.93 (m, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.29 (d, *J* = 7.7 Hz, 4H), 6.82 – 6.73 (m, 1H), 6.53 (dd, *J* = 7.6, 1.3 Hz, 1H), 4.23 (dd, *J* = 13.9, 2.2 Hz, 1H), 4.13 – 4.06 (m, 5H), 3.92 – 3.79 (m, 2H), 3.54 – 3.41 (m, 4H), 3.22 (dd, *J* = 13.9, 8.5 Hz, 1H), 1.92 – 1.75 (m, 2H), 1.17 (d, *J* = 7.0 Hz, 24H), 0.84 (dd, *J* = 6.7, 1.4 Hz, 6H), 0.75 (t, *J* = 7.6 Hz, 3H).

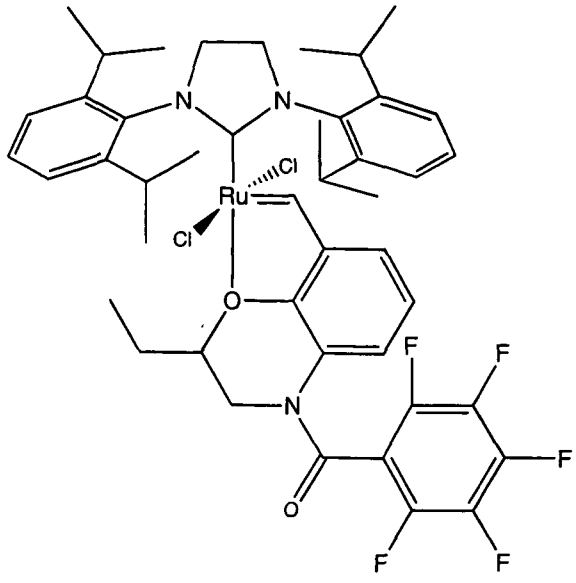


P53

(1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-yl)((2-ethyl-4-(phenylcarbonyl)-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-8-yl)methylene)ruthenium(II) chloride

PROCEDURE & NMR DATA : 50mg (0.16mmol) of **P24** were added to 170mg (1eq, 0.16mmol) of SIPr-indenylidene and 18mg (1.1eq, 0.18mmol) of copper chloride in dry DCM (5.2mL). 30mg of **P53** were obtained, yield 22%.

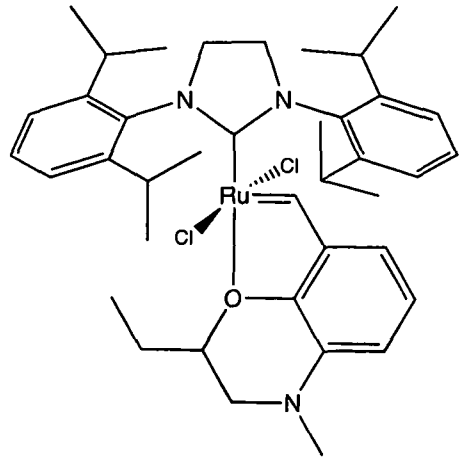
^{1}H NMR (400 MHz, CD_2Cl_2) δ 16.24 (s, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.40 – 7.32 (m, 4H), 7.31 – 7.25 (m, 6H), 6.61 – 6.50 (m, 2H), 4.37 – 4.26 (m, 1H), 4.17 – 4.05 (m, 4H), 4.01 – 3.92 (m, 1H), 3.58 – 3.53 (m, 1H), 3.53 – 3.42 (m, 4H), 1.88 – 1.76 (m, 2H), 1.25 – 1.06 (m, 24H), 0.64 (t, *J* = 7.6 Hz, 3H).



P54
(1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-yl)((2-ethyl-4-(perfluorophenylcarbonyl)-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-8-yl)methylene)ruthenium(II) chloride

PROCEDURE & NMR DATA: 118mg (0.297mmol) of **P25** were added to 307mg (1eq, 0.297mmol) of SIPr-indenylidene and 32mg (1.1eq, 0.32mmol) of copper chloride in dry DCM (13.4mL). 125mg of **P54** were obtained, yield 45%.

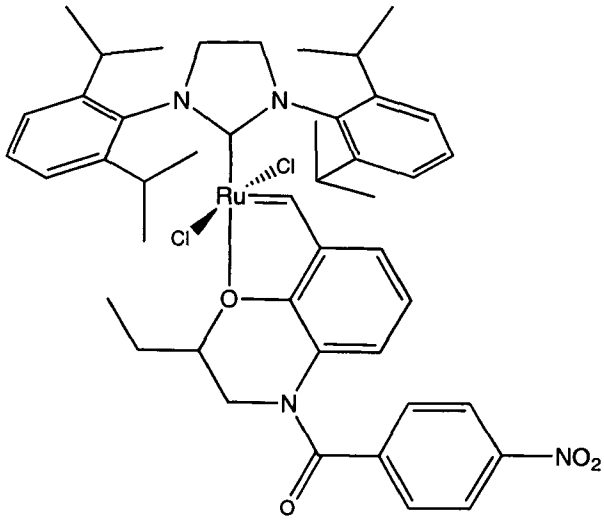
^{1}H NMR (400 MHz, CD_2Cl_2) δ 16.22 (d, *J* = 6.6 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.29 (d, *J* = 7.7 Hz, 4H), 7.22 – 6.82 (m, 1H), 6.72 – 6.59 (m, 1H), 6.57 – 6.44 (m, 1H), 4.33 – 4.21 (m, 1H), 4.16 – 4.04 (m, 4H), 3.70 – 3.59 (m, 1H), 3.57 – 3.41 (m, 4H), 3.41 – 3.29 (m, 1H), 1.96 – 1.71 (m, 2H), 1.27 – 1.02 (m, 24H), 0.60 (t, *J* = 7.6 Hz, 3H). ^{19}F NMR (376 MHz, Acetone) δ -142.94 (2F), -154.00, -161.93,(2F).



P55
(1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-yl)((2-ethyl-4-methyl-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-8-yl)methylene)ruthenium(II) chloride

PROCEDURE & NMR DATA : 39mg (0.18mmol) of **P26** were added to 186mg (1eq, 0.18mmol) of SIPr-indenylidene and 20mg (1.1eq, 0.20mmol) of copper chloride in dry DCM (5.5mL). 34mg of **P55** were obtained, yield 25%.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 16.22 (s, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.28 (dt, *J* = 7.7, 1.5 Hz, 4H), 6.71 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.68 (d, *J* = 7.2 Hz, 1H), 6.14 (dd, *J* = 7.2, 1.7 Hz, 1H), 4.32 – 4.17 (m, 1H), 4.13 – 4.05 (m, 4H), 3.56 – 3.41 (m, 4H), 3.16 (dd, *J* = 12.1, 2.3 Hz, 1H), 3.01 (dd, *J* = 12.1, 9.2 Hz, 1H), 2.74 (s, 3H), 1.80 – 1.68 (m, 2H), 1.20 – 1.06 (m, 24H), 0.70 (t, *J* = 7.6 Hz, 4H).

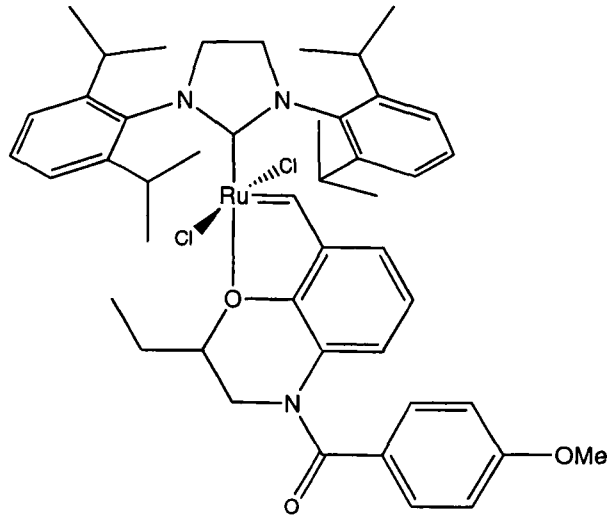


P56

(1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-yl)((2-ethyl-4-(4-nitrophenylcarbonyl)-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-8-yl)methylene)ruthenium(II) chloride

PROCEDURE & NMR DATA : 27mg (0.077mmol) of **P27** were added to 100mg (1.2eq, 0.097mmol) of SIPr-indenylidene and 11mg (1.3eq, 0.11mmol) of copper chloride in dry DCM (10mL). 65mg of **P56** were obtained, yield 92%.

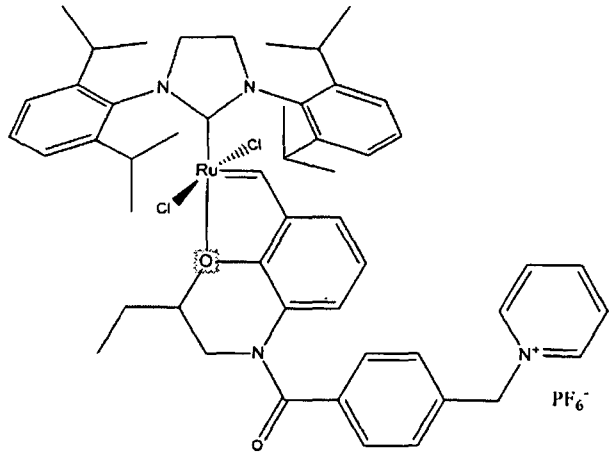
^{1}H NMR (400 MHz, Acetone) δ 16.32 (s, 1H), 8.35 – 8.29 (m, 2H), 7.87 – 7.78 (m, 3H), 7.56 (t, *J* = 7.7 Hz, 2H), 7.46 – 7.39 (m, 4H), 6.82 (t, *J* = 7.7 Hz, 1H), 6.66 (dd, *J* = 7.6, 1.1 Hz, 1H), 4.68 – 4.55 (m, 1H), 4.37 – 4.26 (m, 4H), 4.15 (d, *J* = 13.1 Hz, 1H), 3.73 – 3.62 (m, 4H), 3.59 (dd, *J* = 13.1, 8.6 Hz, 1H), 1.87 – 1.64 (m, 2H), 1.32 – 1.15 (m, 27H).



P57
(1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-yl)((2-ethyl-4-(4-methoxyphenylcarbonyl)-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-8-yl)methylene)ruthenium(II) chloride

PROCEDURE & NMR DATA: 27mg (0.077mmol) of **P28** were added to 100mg (1.2eq, 0.097mmol) of SIPr-indenylidene and 11mg (1.3eq, 0.11mmol) of copper chloride in dry DCM (10mL). 62mg of **P57** were obtained, yield 89%.

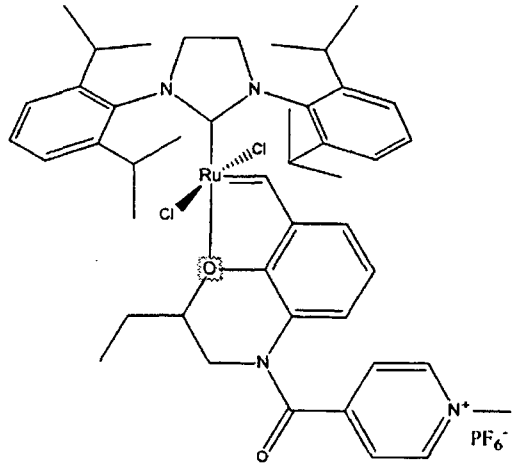
^{1}H NMR (400 MHz, Acetone) δ 16.21 (s, *J* = 9.5 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.38 – 7.32 (m, 3H), 7.31 – 7.24 (m, 4H), 6.86 – 6.79 (m, 2H), 6.60 (t, *J* = 7.9 Hz, 1H), 6.46 (dd, *J* = 7.6, 1.3 Hz, 1H), 4.34 – 4.23 (m, 1H), 4.22 – 4.12 (m, 4H), 3.94 (dd, *J* = 13.7, 2.5 Hz, 1H), 3.75 – 3.68 (m, 4H), 3.62 – 3.48 (m, 4H), 1.73 – 1.50 (m, 2H), 1.19 – 1.03 (m, 24H), 0.60 (t, *J* = 7.6 Hz, 3H).



P58
(1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-yl)((2-ethyl-3-oxo-4-(4-(pyridinium-1-ylmethyl)phenylcarbonyl)-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-8-yl)methylene)ruthenium(II) dichloride hexafluorophosphate(V)

PROCEDURE & NMR DATA : 14mg (0.025mmol) of **P30** were added to 35mg (1.2eq, 0.34mmol) of SIPr-indenylidene and 3.5mg (1.3eq, 0.035mmol) of copper chloride in dry DCM (4mL). 13mg of **P58** were obtained, yield 48%.

^{1}H NMR (400 MHz, CD2Cl2) δ 16.33 (s,1H), 8.69 (d, *J* = 5.62 Hz,2H), 8.47 (t, *J* = 7.81 Hz,1H), 8.01 (dd, *J* = 7.59, 6.74 Hz,2H), 7.74-7.16 (m,13H), 6.64 (s,2H), 4.44-4.33 (m,1H), 4.22-4.15 (m,4H), 4.02 (d, *J* = 13.01 Hz,1H), 3.70-3.60 (m,1H), 3.55 (dt, *J* = 13.48, 6.37 Hz,4H), 1.97-1.77 (m,1H), 1.55-1.45 (m,1H), 1.28-1.14 (m,24H), 0.72 (t, *J* = 7.50 Hz,3H). ^{19}F NMR (376 MHz, CD2Cl2) δ -72.6 (d, 6F, J = 711Hz). ^{31}P NMR (162 MHz, CD2Cl2) δ -144.5 (sept, 1P, *J* = 711Hz)



P59

(1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-yl)((2-ethyl-4-(1-methylpyridin-4-iumcarbonyl)-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-8-yl)methylene)ruthenium(II) dichloride hexafluorophosphate(V)

PROCEDURE & NMR DATA : 23mg (0.05mmol) of **P31** were added to 68mg (1.2eq, 0.066mmol) of SIPr-indenylidene and 6.5mg (1.3eq, 0.065mmol) of copper chloride in dry DCM (7mL). 8mg of **P59** were obtained, yield 15%.

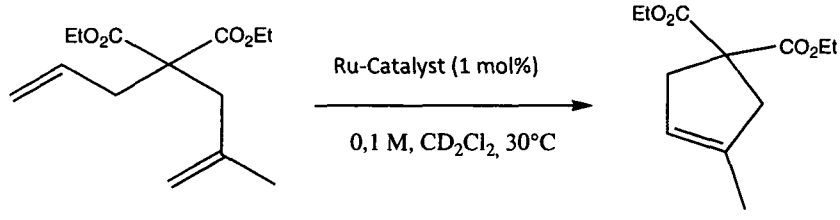
^{1}H NMR (400 MHz CD2Cl2) δ 16.34 (s,1H), 8.52 (s,2H), 7.89 (d, *J* = 5.50 Hz,2H), 7.85-7.56 (m,2H), 7.53 (t, *J* = 7.73, 7.73 Hz,2H), 7.48-7.39 (m,1H), 7.39-7.31 (m,4H), 6.73 (d, *J* = 6.76 Hz,1H), 4.65-4.40 (m,1H), 4.34 (s,3H), 4.19 (qd, *J* = 8.53, 4.26, 4.26, 4.26 Hz,4H), 3.75-3.59 (m,1H), 3.52 (tt, *J* = 13.34, 13.34, 6.72, 6.72 Hz,4H), 3.45-3.29 (m,1H), 1.45-1.27 (m,2H), 1.29-1.10 (m,24H), 0.91 (t, *J* = 7.31, 7.31 Hz,3H). ^{19}F NMR (376 MHz, CD2Cl2) δ -73.0 (d, 6F, *J* = 712Hz). ^{31}P NMR (162 MHz, CD2Cl2) δ -114.8 (sept, 1P, *J* = 711Hz).

KINETIC AND STABILITY STUDIES

Chosen synthesized catalysts according to the invention were tested on performance and stability.

Kinetic studies were performed on diethyl 2-allyl-2-(2-methylallyl)propanedioate **P60** in NMR tube.

A NMR tube equipped with a septum was filled with diethylallylmethallyl malonate **P60** (25.4 mg, 0.1 mmol) and CD_2Cl_2 (0.90 mL) under argon. The sample was equilibrated at 30°C in the NMR probe. The sample was locked and shimmed before the catalyst addition (0,1 mL, 1 µmol, 0.01 M solution of catalyst). The reaction progress was monitored in NMR by the periodical acquisition of data over 1h and integrating the characteristic signals for allylic proton resonances



P60 P61

FIG. 1 is a graph showing the conversion rate over time of a product P60 into a product P61 a by a metathesis reaction and in the presence of catalysts P32 and P41 according to the present invention. The conversion rate of P60 to P61 reflects high catalytic activity of the compounds of the present invention.

FIG. 2 is a graph showing the conversion rate over time of the product P60 into the product P61 by a metathesis reaction and in the presence of catalysts P33, P34, P35, P36 P37, P38, P39 and P40 according to the present invention. The conversion rate of P60 to P61 reflects high catalytic activity of the compounds of the present invention.

FIG. 3 is a graph showing the conversion rate over time of the product P60 into the product P61 by a metathesis reaction and in the presence of catalysts P42, P43, P44, P45 and P47 according to the present invention. The conversion rate of P60 to P61 reflects high catalytic activity of the compounds of the present invention.

FIG. 4 is a graph showing the conversion rate over time of the product P60 into the product P61 by a metathesis reaction and in the presence of catalysts P48, P49, P50 and P51 according to the present invention. The conversion rate of P60 to P61 reflects high catalytic activity of the compounds of the present invention.

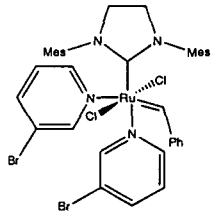
FIG. 5 is a graph showing the conversion rate over time of the product P60 into the product P61 by a metathesis reaction and in the presence of catalysts P52, P53, P54, P55, P56 and P57 according to the present invention. The conversion rate of P60 to P61 reflects high catalytic activity of most compounds of the present invention. It is noted that compounds P52 and P55

show lower activity than P53, P54, P56, P57. These Compounds can be used in appropriate chemical reactions that need to be performed in the presence of moderate catalyst.

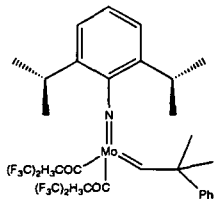
Further, figure 5 clearly reflects how the compounds of the present invention can be designed for performance control. This is mainly due to the side chains (R1, R2, R3, a, b and c). Indeed the compounds of figure 5 show an identical ligand L and greatly differ in their side chain R1. By simply alternating said side chain R1, a significant catalytic activity difference is observed between each compound of figure 5.

FIG. 6 is a graph showing the conversion rate over time of the product P60 into the product P61 by metathesis reaction and in the presence of catalysts P58 and P59 according to the present invention. The conversion rate of P60 to P61 reflects high catalytic activity of the compounds of the present invention. Here again it can be observed how the catalytic activity is controlled by designing side chain R1.

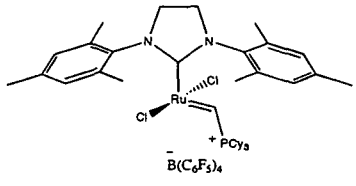
Furthermore, comparative tests between compounds of general formula 1 and prior art catalysts were performed. Prior art catalysts that were used for the tests are defined by following formulae:



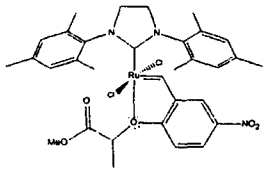
Grubbs III



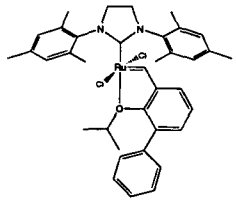
Schrock catalysts



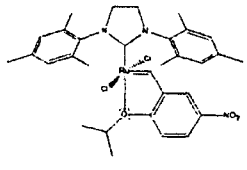
Piers-Grubbs II



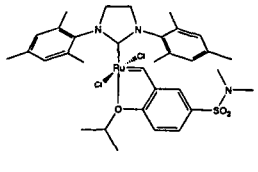
Compound G



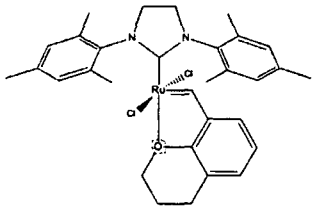
Blechert



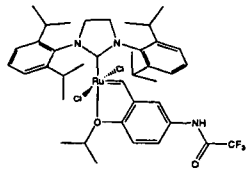
Grela



Zannan

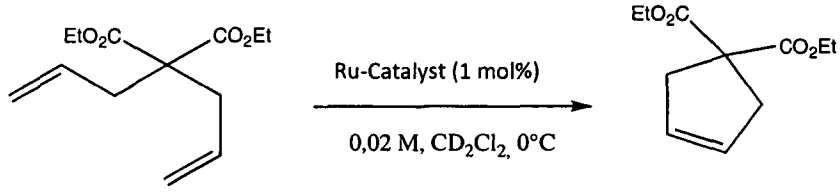


Compound I



Umicore M71 SIPr

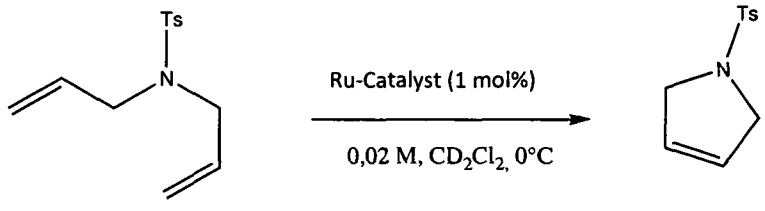
FIG. 7 is a graph showing the conversion rate over time of a product P62 into a product P63 by metathesis reaction and in the presence of four different prior art catalysts (*Grubbs III*; *Schrock catalyst; Piers-Grubbs II*; and compound of formula **G**) in comparison with catalyst P34 according to the present invention.



P62 P63

In figure 7, it is clearly shown that the compound P34 shows higher catalytic activity than the catalysts of the prior art. However, it should be reminded that when desired the catalytic activity can be reduced in selecting appropriate side chains.

FIG. 8 is a graph showing the conversion rate over time of a product P64 into a product P65 by metathesis reaction and in the presence of three different prior art catalysts (*Blechert; Umicore M71 SIPr* of formula **D**; *Grela* of formula **B** - *J. AM. CHEM. SOC. 2006, 128, 13652-13653; Zannan* of formula **C**; and compound of formula **I**) in comparison with catalysts P33 and P34 according to the present invention.



P64 P65

As can be seen on figure 8, catalysts of the present invention can be designed to either show a higher catalytic activity than prior art catalysts, or can be designed to show similar activity than prior art catalysts.

In general it can be noted that the compounds of the present invention according to general formula 1 show high catalytic activity. This activity can be enhanced or allayed when alternating the side chains of general formula 1.

Further to the above kinetic studies, stability studies were performed.

Metathesis catalysts according to the present invention were added to a solution of anthracene (1eq) in CD_2Cl_2 (500µL) in NMR tube. Tubes were sealed with paraffin. Anthracene was used as internal standard. Degradation of catalysts was monitored in NMR by the periodical acquisition of data over 14 days. Comparison between characteristic signals for carbene proton resonances and anthracene were performed and are reproduced in figures 9

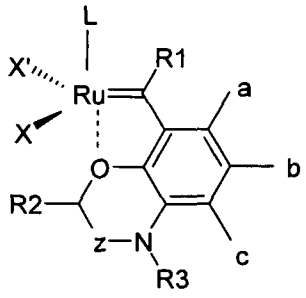
to 12. Figure 9 shows stability of catalysts P33, P34, P35 and P37 according to the present invention. Figure 10 shows stability over time of catalysts P42, P43, P44, P45 and P47 according to the present invention; Figure 11 shows the stability of P48, P49, P50, and P51 according to the present invention; and Figure 12 shows the stability of catalysts P52, P53, P54 and P55 according to the present invention.

In general it is noted that the compounds of the present invention show great stability.

In the present invention the applicant identified a new backbone (or core) for metathesis catalysts. The compounds of the present invention show high catalytic activity and stability. Furthermore, three different activation sites within the new chelating benzylidene ligand were identified. These activation sites allow efficient and specific control of the catalytic activity of the ruthenium complexes in olefin metathesis transformation. Particularly, R2 and R3 show efficient control of the catalysts activity as can be seen in the non-limitative examples of the present specification.

CLAIMS

1. A compound of the general formula 1,



(1)

wherein,

X and X' are anionic ligands;

L is an uncharged ligand;

z is a methylene or a carbonyl group;

a, b and c are each, independently of one another, H, or a substituted or unsubstituted, charged or uncharged side chain comprising up to 20 carbon atoms and optionally comprising one or more functional groups;

R1, R2 and R3 are each, independently of one another, H or a substituted or unsubstituted, charged or uncharged side chain comprising up to 20 carbon atoms and optionally comprising one or more functional groups.

2. The compound of general formula 1 according to claim 1, wherein X and X' are halogen, preferably selected from the group consisting of Cl and Br.

3. The compound of general formula 1 according to one of the preceding claims, wherein a, b and c are each selected from the group consisting of H; $-NO_2$; C_{1-12}-alkyl; C_{5-12}-cycloalkyl; C_{1-12}-alkoxy; cyano; aryl or heteroaryl, preferentially phenyl optionally substituted by a radical selected from the group consisting of C_{1-6}-alkyl and C_{1-6}-alkoxy; monohalogenated or polyhalogenated aryl radicals or hetero-aryl radicals; monohalogenated or polyhalogenated C_{1-6}-alkyl radicals; monohalogenated or polyhalogenated C_{1-6}-alkyl-substituted aryl radicals; C_{1-6}-alkylcarbonyl radicals; monohalogenated or polyhalogenated C_{1-6}-alkylcarbonyl radicals; C_{1-6}-alkoxycarbonyl radicals; monohalogenated or polyhalogenated C_{1-6}-alkoxycarbonyl radicals; arylcarbonyl radicals; monohalogenated or polyhalogenated arylcarbonyl radicals; aryloxycarbonyl radicals; monohalogenated or polyhalogenated aryloxycarbonyl radicals; $-(C=O)-N(R^a)_2$ radicals wherein R^a is a C_{1-6}-alkyl or aryl radical; $-NH-(C=O)-R^a$ radicals wherein R^a is a C_{1-6}-alkyl or aryl radical; C_{1-6}-alkylsulfonyl radicals; C_{1-6}-alkylsulfinyl radicals; $-P(=O)(R^a)_2$ radicals wherein R^a is a C_{1-6}-alkyl or aryl radical; $-NH-SO_2-R^a$ radicals wherein R^a is a C_{1-6}-alkyl or aryl radical; $(SO_2)NR^a_2$ radicals wherein R^a is a C_{1-6}-alkyl or aryl radical; $P(=O)(OR^a)(R^a)$ radicals wherein R^a is a C_{1-6}-alkyl or aryl radical.

4. The compound of general formula 1 according to one of the preceding claims wherein a, b and c are each H.

5. The compound of general formula 1 according to one of the preceding claims wherein R1 is selected from the group consisting of H, C_{2-12}-alkenyl, C_{2-12}-alkynyl or aryl.

6. The compound of general formula 1 according to one of the preceding claims wherein R1 is H.

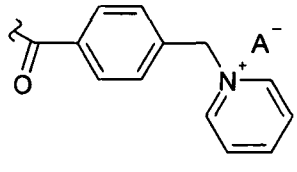
7. The compound of general formula 1 according to one of the preceding claims wherein R2 is selected from the group consisting of H, C_{1-12}-alkyl, C_{5-12}-cycloalkyl, C_{7-18}-aralkyl or aryl.

8. The compound of general formula 1 according to one of the preceding claims wherein R2 is a methyl-, ethyl- or isopropyl-group.

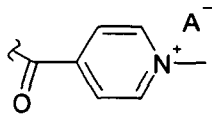
9. The compound of general formula 1 according to one of the preceding claims, wherein R3 is selected from the group consisting of H, C_{1-12}-alkyl, C_{5-12}-cycloalkyl, C_{7-18}-aralkyl, aryl, C_{1-12}-halogeno-alkyl, C_{1-12}-ammonium-alkyl, C_{1-12}-pyridinum-alkyl, C_{1-12}-aldehyde-alkyl, C_{1-12}-nitro-alkyl, nitrile or a radical selected from the group consisting of ketones COR4, esters CO_2R4, oxalates $COCO_2R4$, sulfones SO_2R4 or amides CONHR4 wherein,

R4 is selected from the group consisting of H, C_{1-12}-alkyl, C_{5-12}-cycloalkyl, C_{7-18}-aralkyl, aryl, C_{1-12}-halogeno-alkyl, C_{1-12}-ammonium-alkyl, C_{1-12}-pyridinum-alkyl, C_{1-12}-aldehyde-alkyl, C_{1-12}-nitro-alkyle, nitrile.

10. The compound of general formula 1 according to one of claims 1 to 9, wherein,
z is methylene, and
R3 is a side chain of the formula $R3^a$ or $R3^b$:



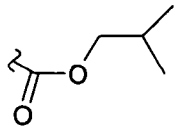
($R3^a$)

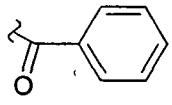


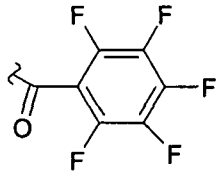
($R3^b$)

wherein A^- is selected from the group consisting of F^-, Cl^-, Br^-, I^-, tetrafluoroborate BF_4^-, hexafluorophosphate PF_6^- and bis(trifluoromethylsulfonyl)amide NTf_2^-.

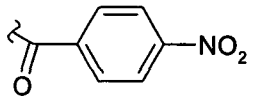
11. The compound of general formula 1 according to one of claims 1 to 9, wherein,
R3 is a side chain of the formula $R3^c$, $R3^d$, $R3^e$, $R3^f$, $R3^g$, $R3^h$, $R3^i$, $R3^j$, $R3^k$, $R3^l$, $R3^m$, $R3^n$, $R3^o$ or $R3^p$:

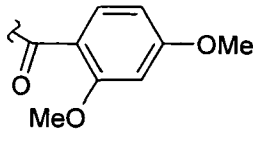

($R3^c$)

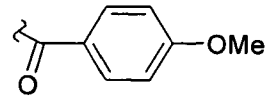

($R3^d$)

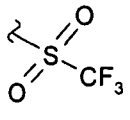

($R3^e$)

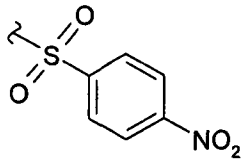

($R3^f$)

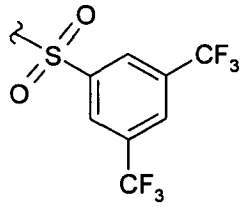

($R3^g$)

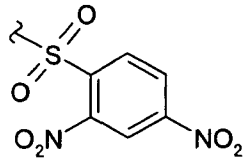

($R3^h$)

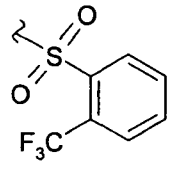

($R3^i$)

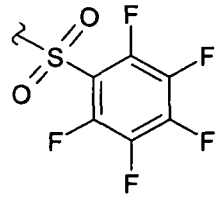

($R3^j$)

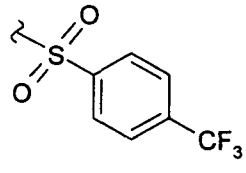

(R3^k)


(R3^l)


(R3^m)

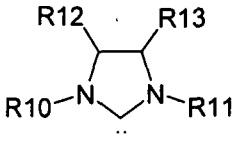

(R3^n)

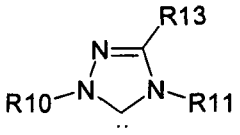

(R3^o)

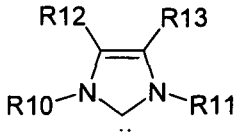

(R3^p)

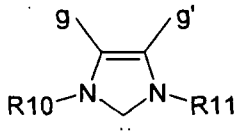
12. The compound of general formula 1 according to one of claims 1 to 11, wherein L is a phosphine $P(R8)_3$ or a phosphate $P(OR9)_3$ and wherein R8 and R9 are each independently of one another C_{1-6}-alkyl, C_{5-12}-cycloalkyl or aryl.

13. The compound of general formula 1 according to one of claims 1 to 11, wherein L is a ligand of the formula L1, L2, L3 or L4:


(L1)


(L2)


(L3)


(L4)

wherein R10 and R11 are each, independently of one another a substituted or an unsubstituted side chain comprising 1 to 30 carbon atoms and optionally comprising one or more functional groups, and

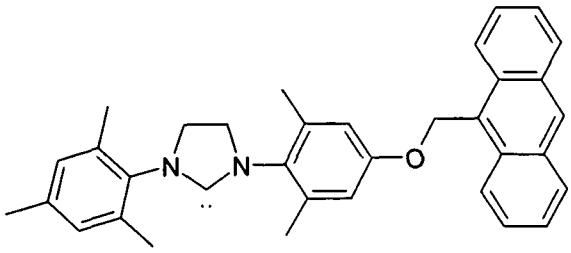
wherein R12 and R13 are each, independently of one another, H, C_{1-6}-alkyl optionally substituted by a alkoxy radical OR15, or aryl optionally substituted by a alkoxy radical OR15, or form a 3- or 4-membered alkylene bridge, and

wherein R15 is selected from the group consisting of C_{1-20}-alkyl, aryl and C_{7-18}-aralkyl, and

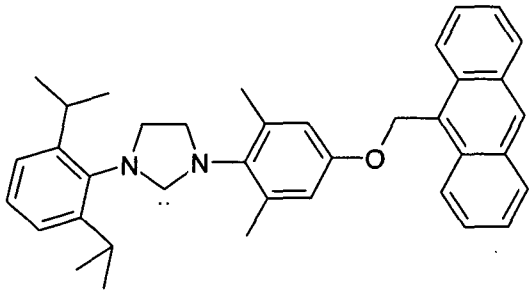
wherein g and g' are each halogen, preferably Cl or Br.

14. The compound of general formula 1 according to Claim 13,
wherein R10 and R11 are each, independently of one another, C_{1-30}-alkyl optionally substituted by a alkoxy radical OR15, C_{2-30}-alkenyl optionally substituted by a alkoxy radical OR15, aryl optionally substituted by a alkoxy radical OR15, aminoalkyl or aminocycloalkyl.

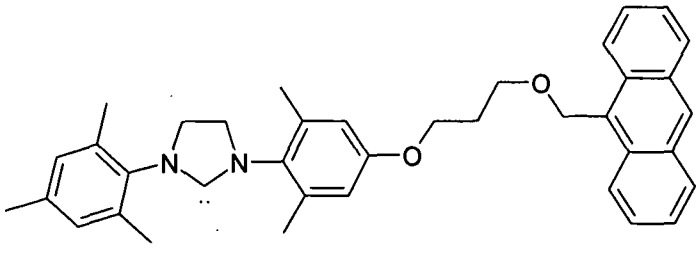
15. The compound of general formula 1 according to one of claims 1 to 11 ,
wherein L is a ligand of the formula $L1^a$, $L1^b$, $L1^c$, $L1^d$, $L1^e$, $L1^f$ or $L1^g$:



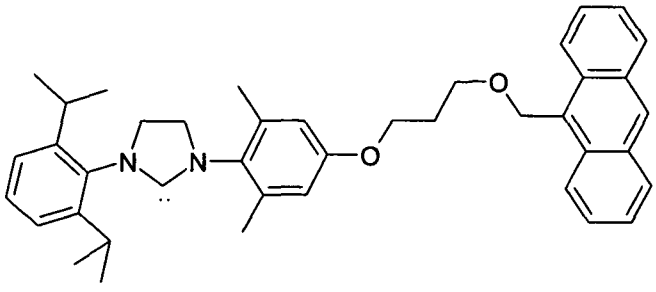
(L1[a])



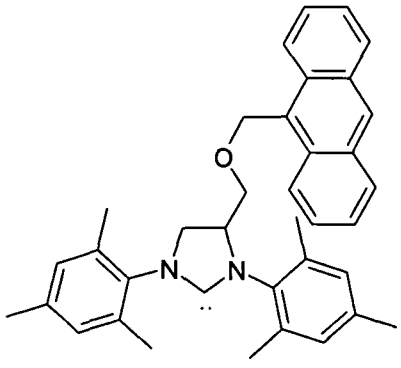
(L1[b])



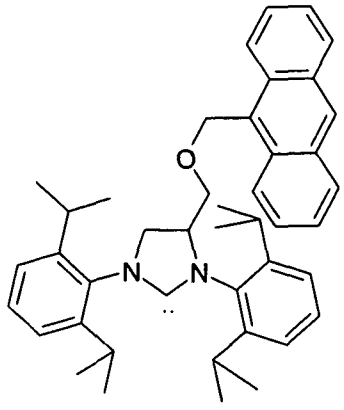
(L1[c])



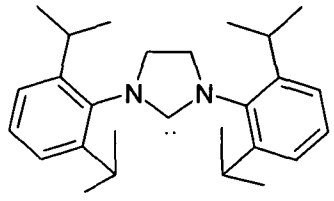
(L1[d])



(L1[e])



(L1[f])

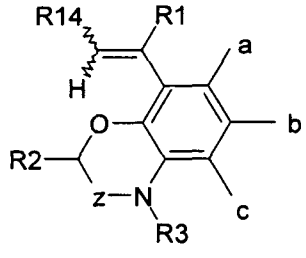


(L1[g])

16. Use of the compound according to one of claims 1 to 15 as a catalyst for a chemical reaction.

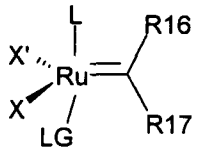
17. Use according to claim 16 wherein said chemical reaction is a metathesis reaction such as ring-closing metathesis (RCM), cross-metathesis (CM), ring-opening metathesis polymerization (ROMP).

18. Method for preparing a compound of the general formula 1 according to claim 1 comprising a step of reacting a compound of the general formula (2)



(2)

with a ruthenium complex of the general formula (3)



(3)

wherein,
X and X' are anionic ligands;
L is an uncharged ligand;

z is a methylene or a carbonyl group;

a, b and c are each, independently of one another, H, or a substituted or unsubstituted, charged or uncharged side chain comprising up to 20 carbon atoms and optionally comprising one or more functional groups;

R1, R2 and R3 are each, independently of one another, H or a substituted or unsubstituted, charged or uncharged side chain comprising up to 20 carbon atoms and optionally comprising one or more functional groups,

and wherein,

LG is a leaving group, preferentially LG is a phosphine $P(R8)_3$ wherein R8 is selected from the group consisting of C_{1-6}-alkyl; C_{5-12}-cycloalkyl preferentially cyclohexyl; aryl; more preferentially LG is a pyridine wherein pyridine is unsubstituted or substituted by a charged or uncharged side chain comprising up to 20 carbon atoms,

R14 is selected from the group consisting of H; C_{1-12}-alkyl, preferentially a methyl group; C_{5-12}-cycloalkyl,

R16 and R17 are each independently of one another H, C_{1-6}-alkyl, optionally substituted by one or more halogens or by aryl, optionally substituted by one or more halogens or by C_{1-6}-alkyl; or R16 and R17 form together a 5- to 12-membered aliphatic and/or aromatic ring system, optionally substituted by one or more halogens, C_{1-6}-alkyl or by aryl; and preferentially R16 and R17 form an indenylidene system.

19. The method according to claim 18,
wherein X and X' are halogen, preferably selected from the group consisting of Cl and Br.

20. The method according to one of claims 18 and 19,
wherein a, b and c are each selected from the group consisting of
H; $-NO_2$; C_{1-12}-alkyl; C_{5-12}-cycloalkyl; C_{1-12}-alkoxy; cyano; aryl or heteroaryl, preferentially phenyl optionally substituted by a radical selected from the group consisting of C_{1-6}-alkyl and C_{1-6}-alkoxy; monohalogenated or polyhalogenated aryl radicals or hetero-aryl radicals; monohalogenated or polyhalogenated C_{1-6}-alkyl radicals; monohalogenated or polyhalogenated C_{1-6}-alkyl-substituted aryl radicals; C_{1-6}-alkylcarbonyl radicals; monohalogenated or polyhalogenated C_{1-6}-alkylcarbonyl radicals; C_{1-6}-alkoxycarbonyl radicals; monohalogenated or polyhalogenated C_{1-6}-alkoxycarbonyl radicals; arylcarbonyl radicals; monohalogenated or polyhalogenated arylcarbonyl radicals; aryloxycarbonyl radicals; monohalogenated or polyhalogenated aryloxycarbonyl radicals; $-(C=O)-N(R^a)_2$ radicals wherein R^a is a C_{1-6}-alkyl or aryl radical; $-NH-(C=O)-R^a$ radicals wherein R^a is a C_{1-6}-alkyl or aryl radical; C_{1-6}-alkylsulfonyl radicals; C_{1-6}-alkylsulfinyl radicals; $-P(=O)(R^a)_2$ radicals wherein R^a is a C_{1-6}-alkyl or aryl radical; $-NH-SO_2-R^a$ radicals wherein R^a is a C_{1-6}-alkyl or aryl radical; $(SO_2)NR^a_2$ radicals wherein R^a is a C_{1-6}-alkyl or aryl radical; $P(=O)(OR^a)(R^a)$ radicals wherein R^a is a C_{1-6}-alkyl or aryl radical.

21. The method according to one of claims 18 to 20,
wherein a, b and c are each H.

22. The method according to one of claims 18 to 21,
wherein R1 is selected from the group consisting of H, C_{2-12}-alkenyl, C_{2-12}-alkynyl or aryl.

23. The method according to one of claims 18 to 22,
wherein R1 is H.

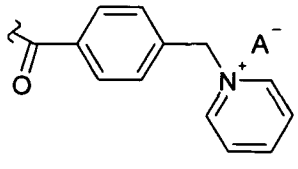
24. The method according to one of claims 18 to 23,
wherein R2 is selected from the group consisting of H, C_{1-12}-alkyl, C_{5-12}-cycloalkyl, C_{7-18}-aralkyl or aryl.

25. The method according to one of claims 18 to 24,
wherein R2 is a methyl-, ethyl- or isopropyl-group.

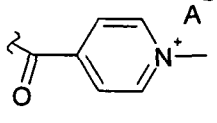
26. The method according to one of claims 18 to 25,
wherein R3 is selected from the group consisting of H, C_{1-12}-alkyl, C_{5-12}-cycloalkyl, C_{7-18}-aralkyl, aryl, C_{1-12}-halogeno-alkyl, C_{1-12}-ammonium-alkyl, C_{1-12}-pyridinum-alkyl, C_{1-12}-aldehyde-alkyl, C_{1-12}-nitro-alkyle, nitrile or a radical selected from the group consisting of ketones COR4, esters CO_2R4, oxalates $COCO_2R4$, sulfones SO_2R4 or amides CONHR4
wherein,

R4 is selected from the group consisting of H, C_{1-12}-alkyl, C_{5-12}-cycloalkyl, C_{7-18}-aralkyl, aryl, C_{1-12}-halogeno-alkyl, C_{1-12}-ammonium-alkyl, C_{1-12}-pyridinum-alkyl, C_{1-12}-aldehyde-alkyl, C_{1-12}-nitro-alkyle, nitrile.

27. The method according to one of claims 18 to 26,
wherein,
z is methylene, and
R3 is a side chain of the formula $R3^a$ or $R3^b$:



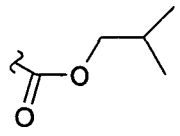
($R3^a$)

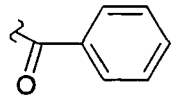


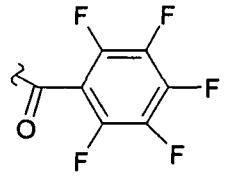
($R3^b$)

wherein A^- is selected from the group consisting of F^-, Cl^-, Br^-, I^-, tetrafluoroborate BF_4^-, hexafluorophosphate PF_6^- and bis(trifluoromethylsulfonyl)amide NTf_2^-.

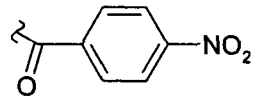
28. The method according to one of claims 18 to 26,
wherein,
R3 is a side chain of the formula $R3^c$, $R3^d$, $R3^e$, $R3^f$, $R3^g$, $R3^h$, $R3^i$, $R3^j$, $R3^k$, $R3^l$, $R3^m$, $R3^n$, $R3^o$ or $R3^p$:

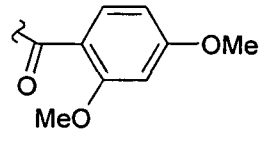

($R3^c$)

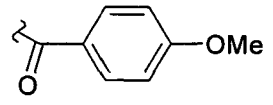

($R3^d$)

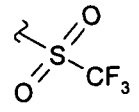

($R3^e$)

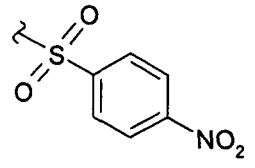

($R3^f$)

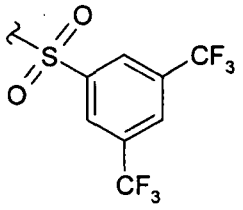

($R3^g$)


($R3^h$)

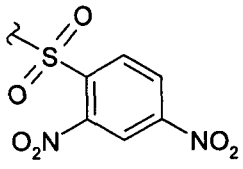

($R3^i$)


($R3^j$)

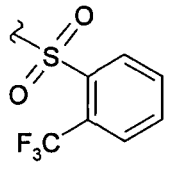

($R3^k$)



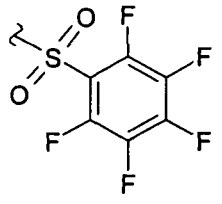
(R3^l)



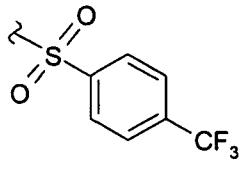
(R3^m)



(R3^n)



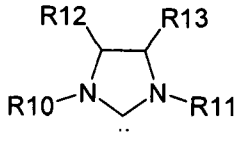
(R3^o)



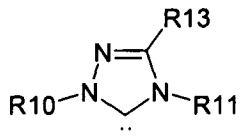
(R3^p)

29. The method according to one of claims 18 to 28,
wherein L is a phosphine $P(R8)_3$ or a phosphate $P(OR9)_3$ and
wherein R8 and R9 are each independently of one another C_{1-6}-alkyl, C_{5-12}-cycloalkyl or aryl.

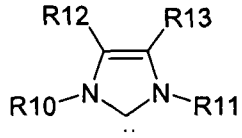
30. The method according to one of claims 18 to 28,
wherein L is a ligand of the formula L1, L2, L3 or L4:



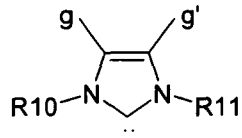
(L1)



(L2)



(L3)



(L4)

wherein R10 and R11 are each, independently of one another a substituted or an unsubstituted side chain comprising 1 to 30 carbon atoms and optionally comprising one or more functional groups, and

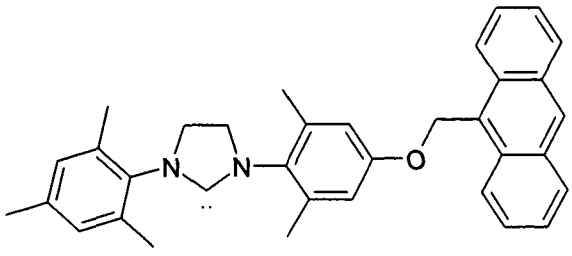
wherein R12 and R13 are each, independently of one another, H, C_{1-6}-alkyl optionally substituted by a alkoxy radical OR15, or aryl optionally substituted by a alkoxy radical OR15, or form a 3- or 4-membered alkylene bridge, and

wherein R15 is selected from the group consisting of C_{1-20}-alkyl, aryl or C_{7-18}-aralkyl, and

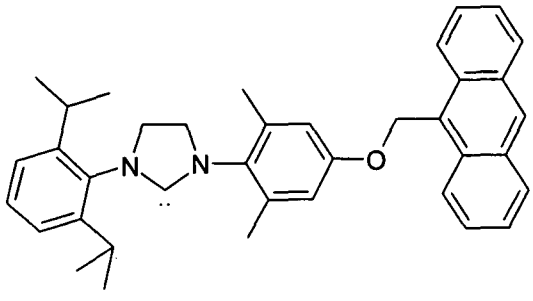
wherein g and g' are each halogen; preferably Cl or Br.

31. The method according to claim 30,
wherein R10 and R11 are each, independently of one another, C_{1-30}-alkyl optionally substituted by a alkoxy radical OR15, C_{2-30}-alkenyl optionally substituted by a alkoxy radical OR15, aryl optionally substituted by a alkoxy radical OR15, aminoalkyl or aminocycloalkyl.

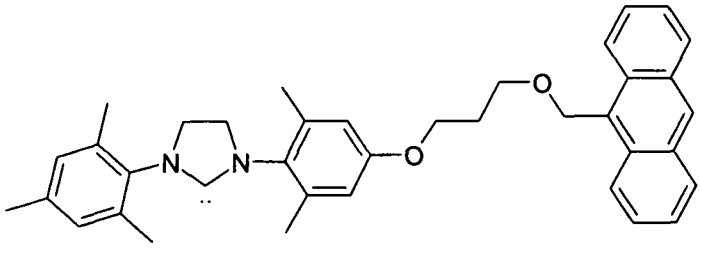
32. The method according to one of claims 18 to 28 ,
wherein L is a ligand of the formula $L1^a$, $L1^b$, $L1^c$, $L1^d$, $L1^e$, $L1^f$ or $L1^g$:



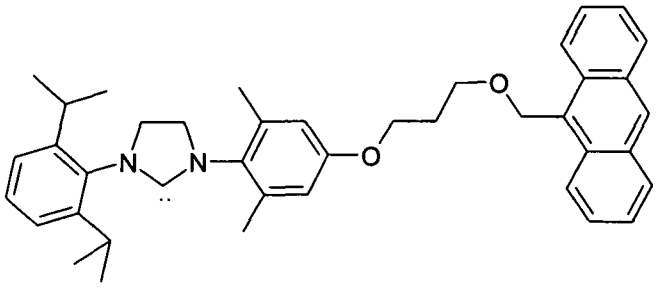
(L1[a])



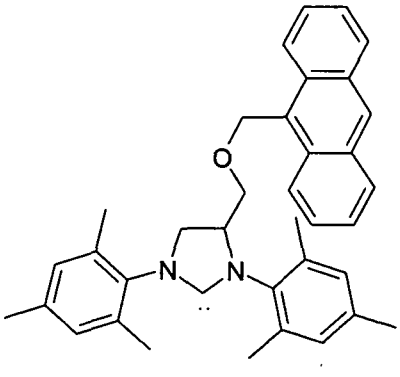
(L1[b])



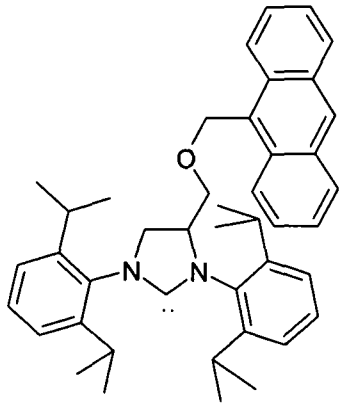
(L1[c])



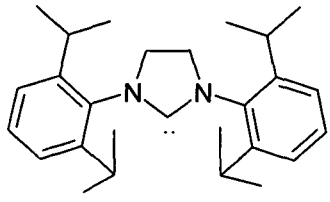
(L1[d])



(L1[e])



(L1^{f})



(L1^{g})

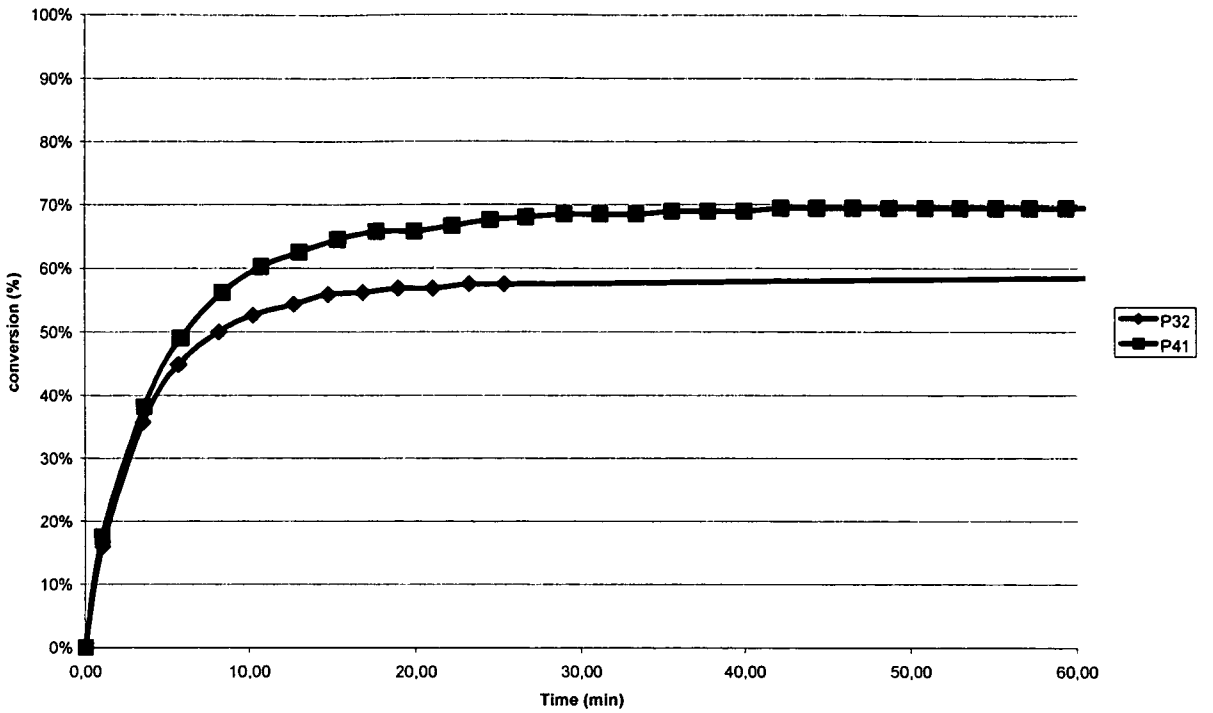


FIGURE 1

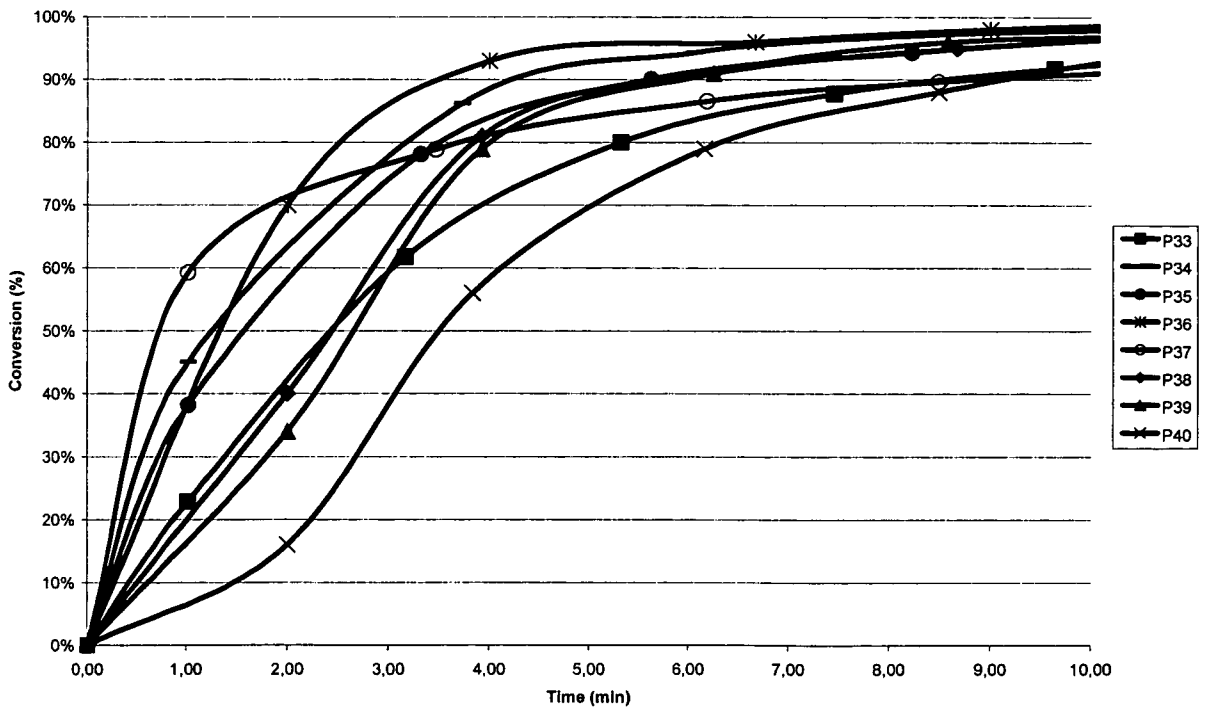


FIGURE 2

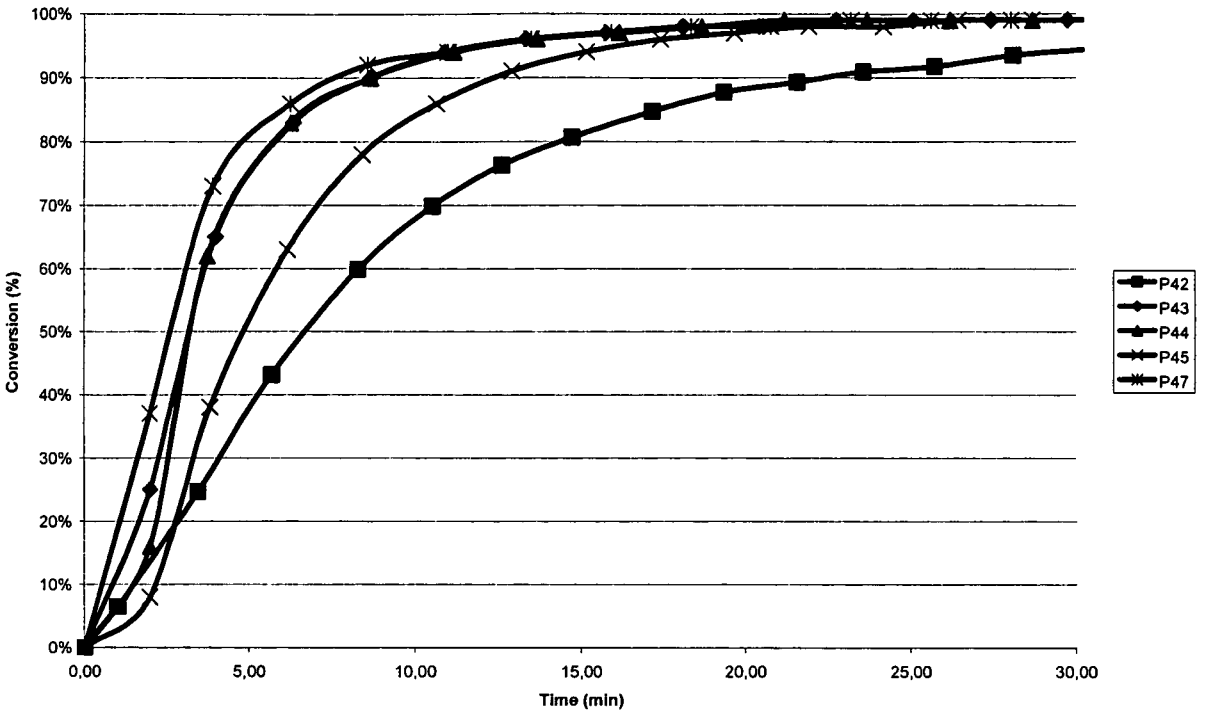


FIGURE 3

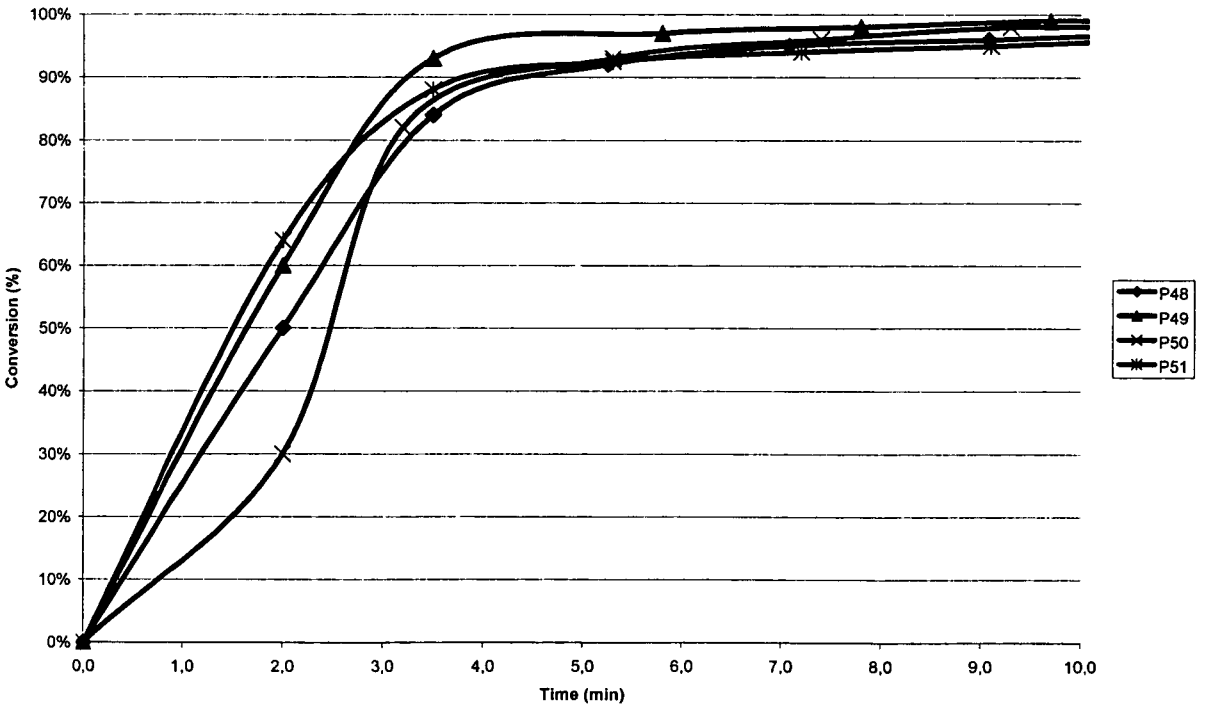


FIGURE 4

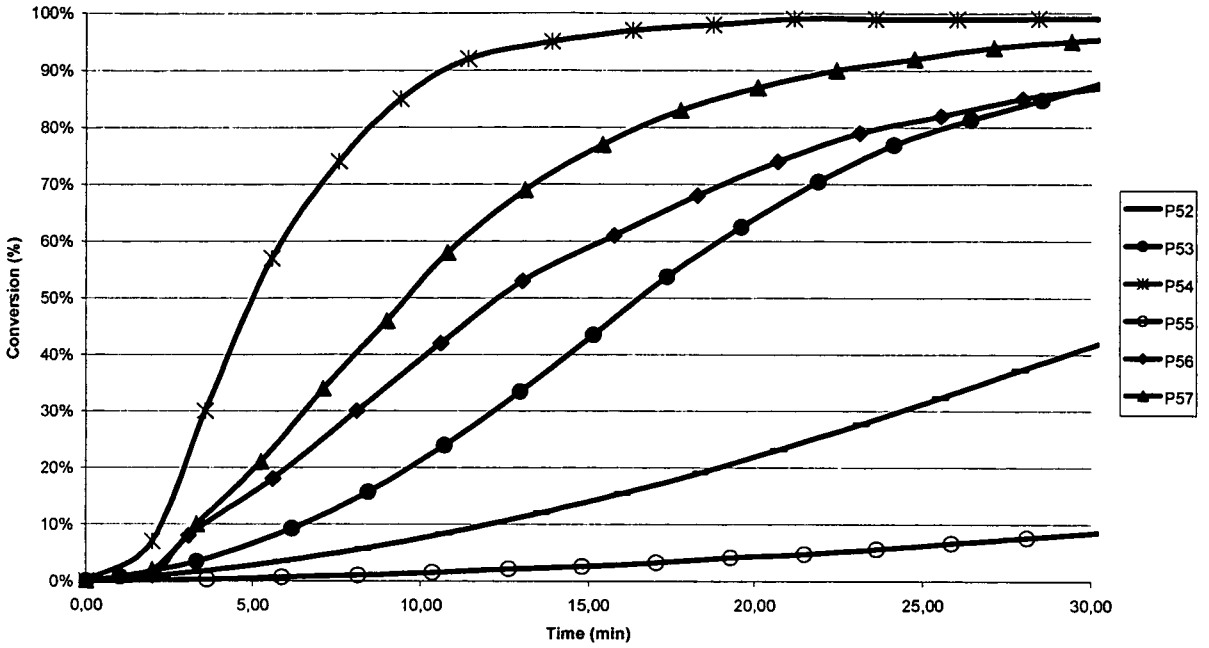


FIGURE 5

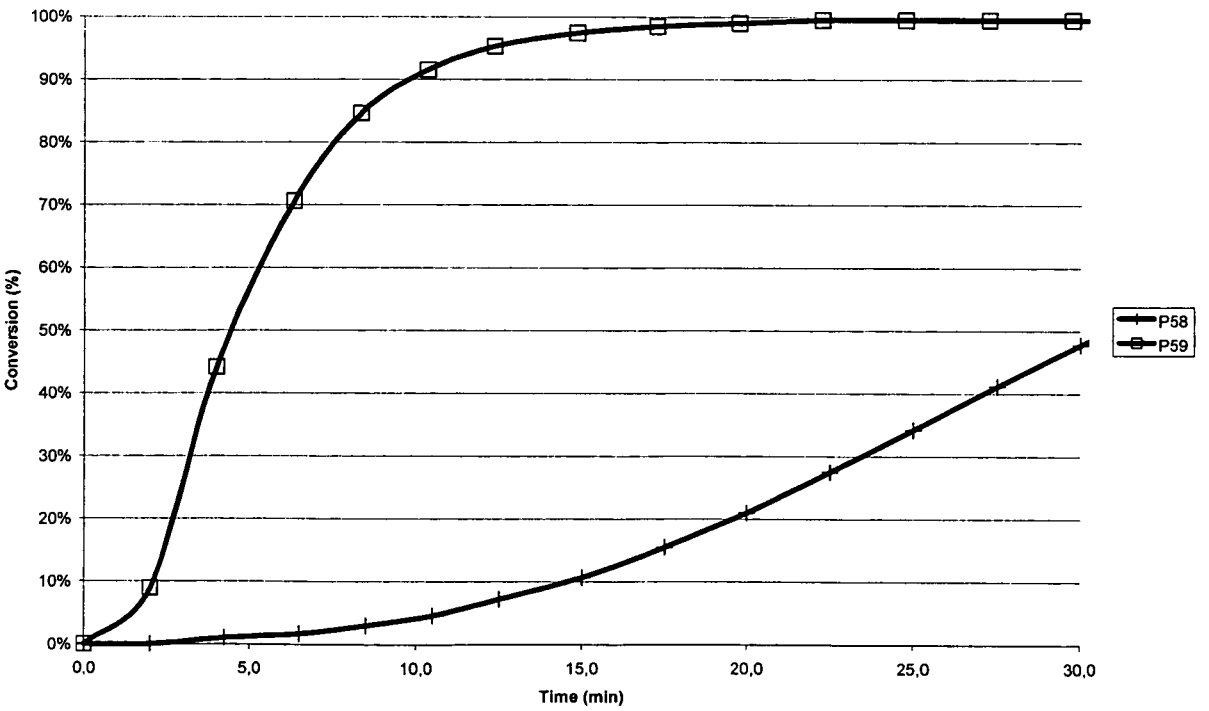


FIGURE 6

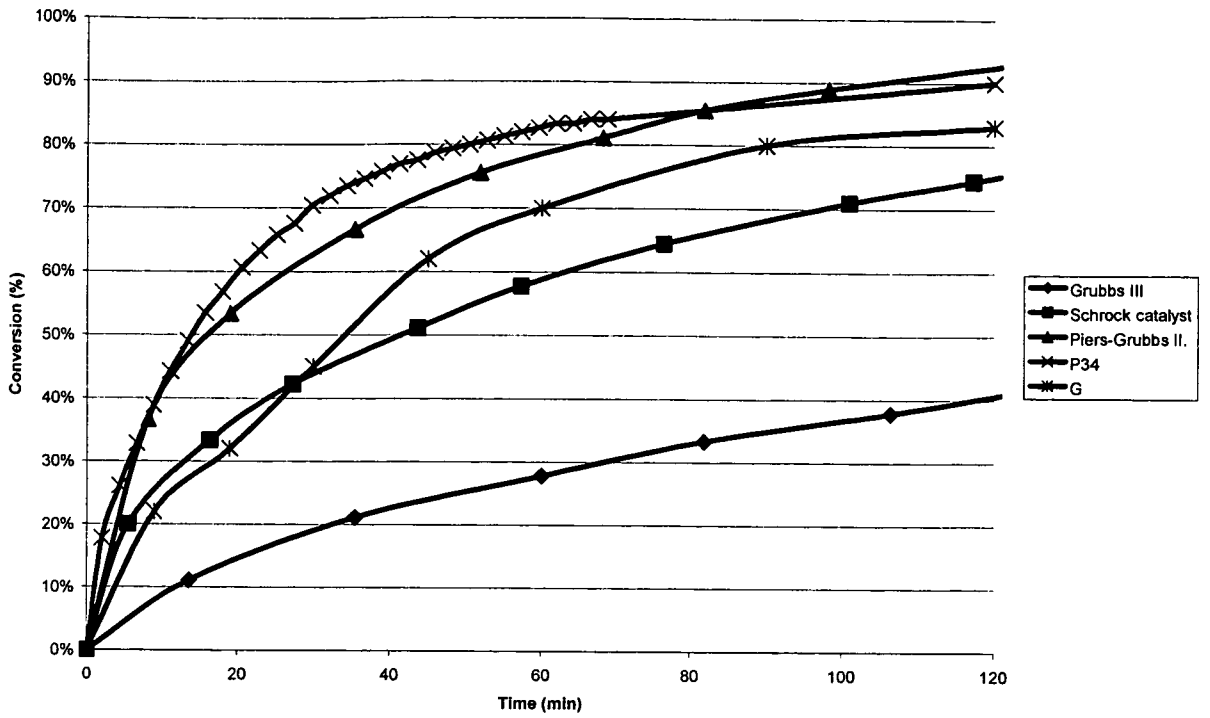


FIGURE 7

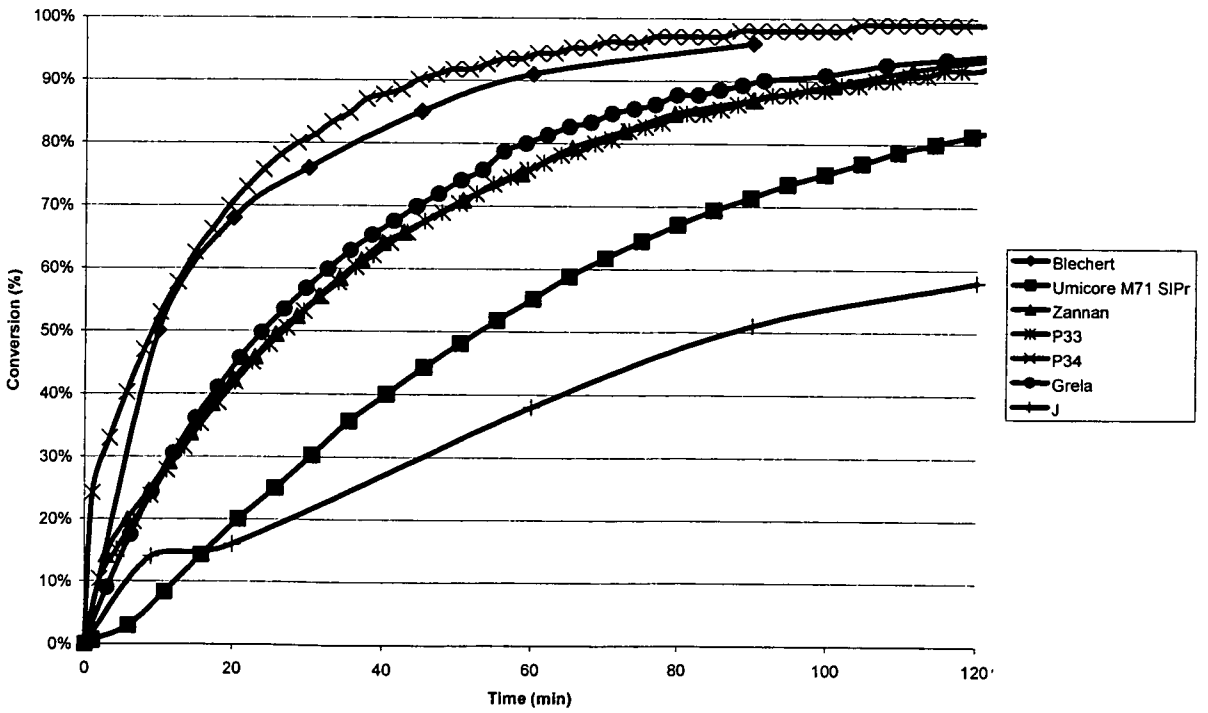


FIGURE 8

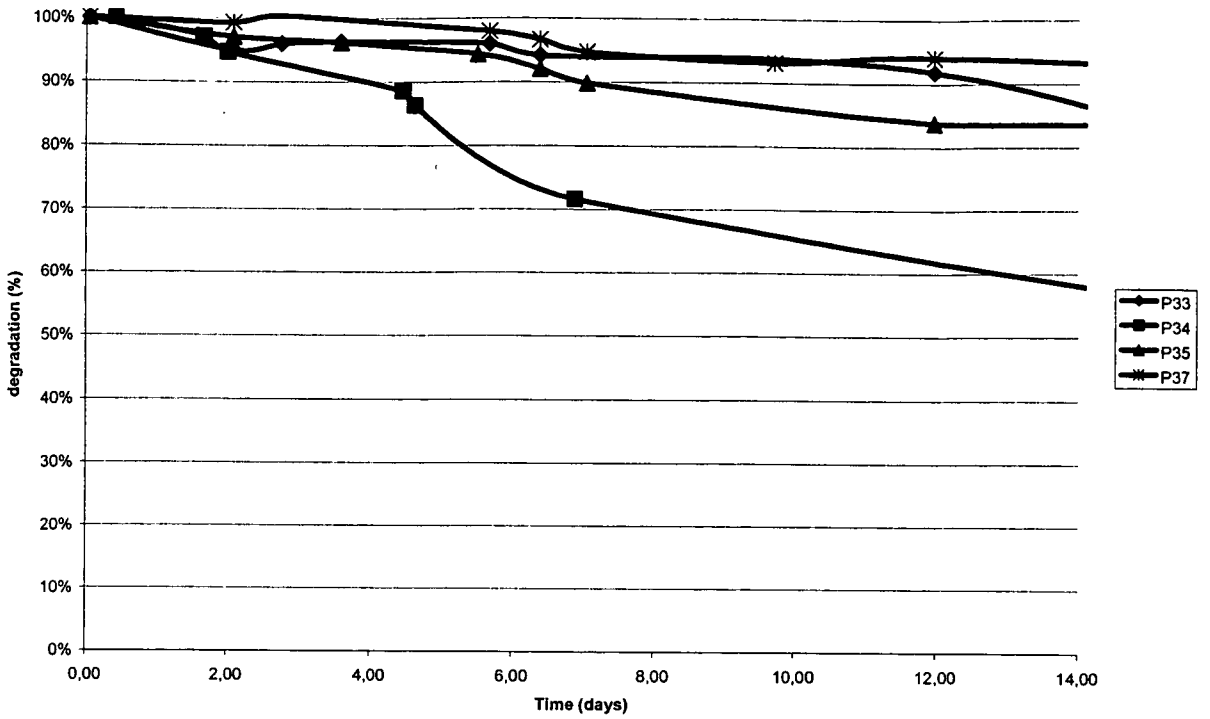


FIGURE 9

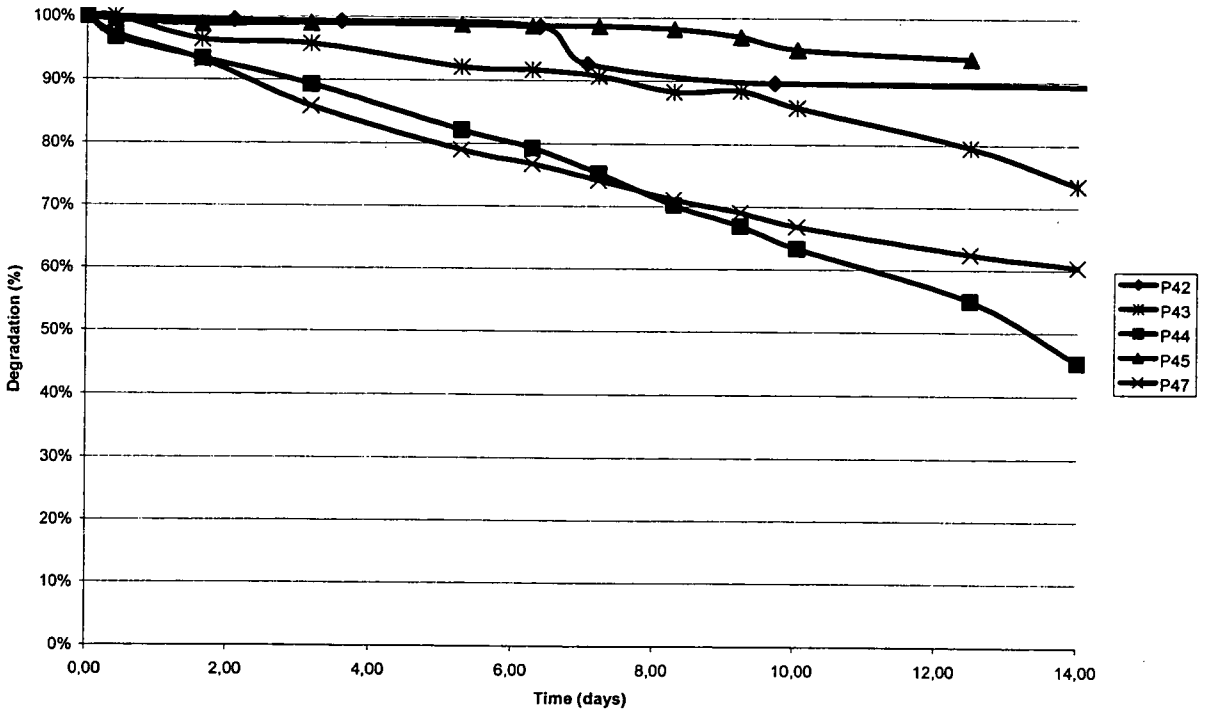


FIGURE 10

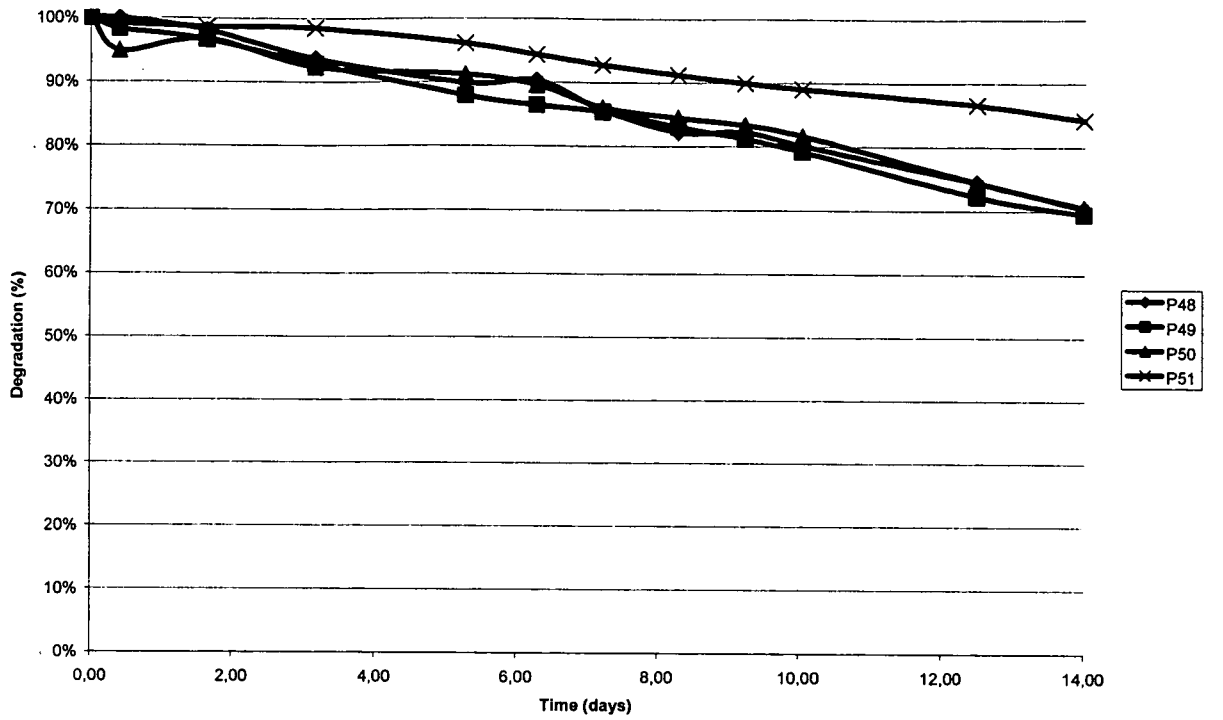


FIGURE 11

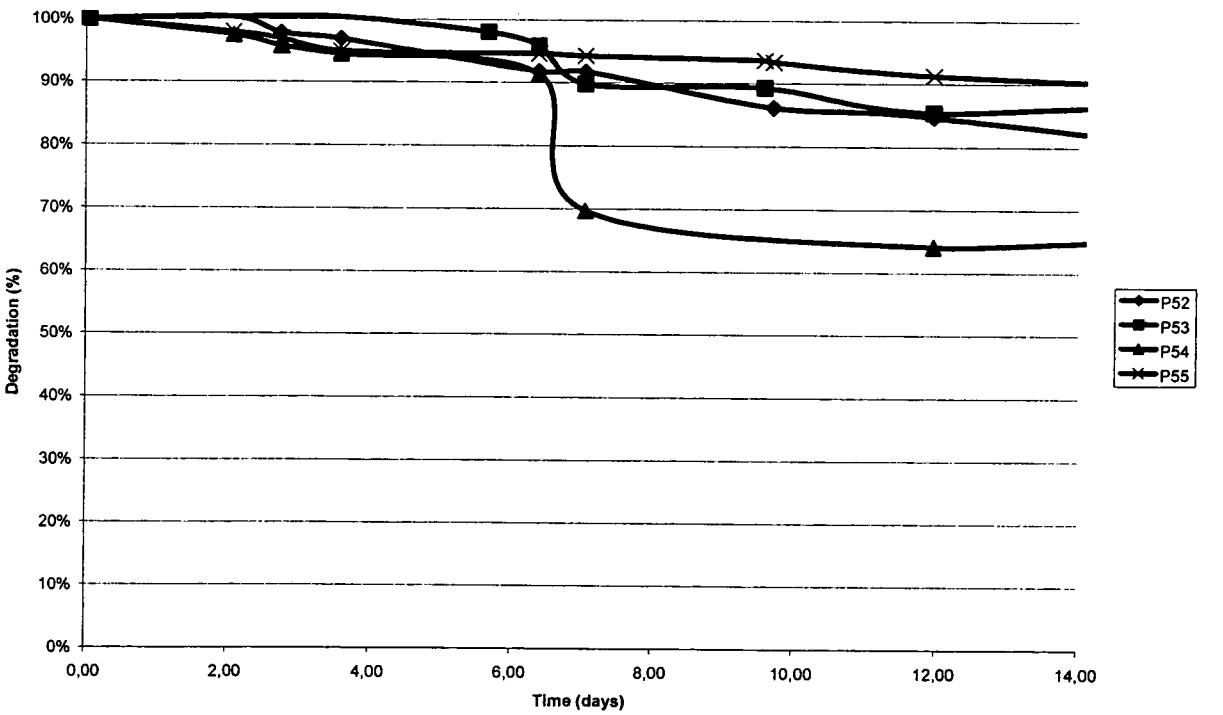


FIGURE 12

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2010/004668

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07F15/00 B01J31/12
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07F B01J

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, CHEM ABS Data, BEILSTEIN Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	HRYNIEWICKA A ET AL: "New efficient ruthenium metathesis catalyst containing chromenyl ligand" JOURNAL OF ORGANOMETALLIC CHEMISTRY, ELSEVIER-SEQUOIA S.A. LAUSANNE, CH, vol. 695, no. 9, 1 May 2010 (2010-05-01), pages 1265-1270, XP026989819 ISSN: 0022-328X [retrieved on 2010-02-24] cited in the application page 1267; figure 3 -----	1-32
Y	WO 2008/046106 A2 (MATERIA INC [US]; SCHRODI YANN [US]; PEDERSON RICHARD L [US]; KAIDO HI) 17 April 2008 (2008-04-17) page 1 - paragraph 1 page 63; claim 36 -----	1-32

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
13 October 2010	27/10/2010

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Jeanjean, Fabien

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2010/004668

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2008/065187 A1 (ECOLE NALE SUP ARTES METIERS [FR]; CNRS CT NAT DE LA RECH SCIENT [FR];) 5 June 2008 (2008-06-05) cited in the application page 29; claim 1	1-32
A	RIX DIANE ET AL: "Aminocarbonyl group containing Hoveyda-Grubbs-type complexes: synthesis and activity in olefin metathesis transformations." THE JOURNAL OF ORGANIC CHEMISTRY 6 JUN 2008 LNKD- PUBMED:18459814, vol. 73, no. 11, 6 June 2008 (2008-06-06), pages 4225-4228, XP002604755 ISSN: 0022-3263 page 4226; compounds 2g-i	1-32
Y	BARBASIEWICZ M., BIENIEK M., MICHROWSKA A., SZADKOWSKA A., MAKAL A., WOZNIAK K., GRELA K.: "Probing of the Ligand Anatomy : Effects of the Chelating Alkoxy Ligand Modifications on the STructure and Catalytic Activity of Ruthenium Carbene Complexes" ADVANCED SYNTHESIS AND CATALYSIS, vol. 349, 2007, pages 193-203, XP002604756 cited in the application page 195; compound 6F	1-32

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2010/004668

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2008046106 A2	17-04-2008	EP 2076484 A2	08-07-2009
		US 2010145086 A1	10-06-2010
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		EP 2097431 A1	09-09-2009
		FR 2909382 A1	06-06-2008
		JP 2010511017 T	08-04-2010
		US 2010087644 A1	08-04-2010