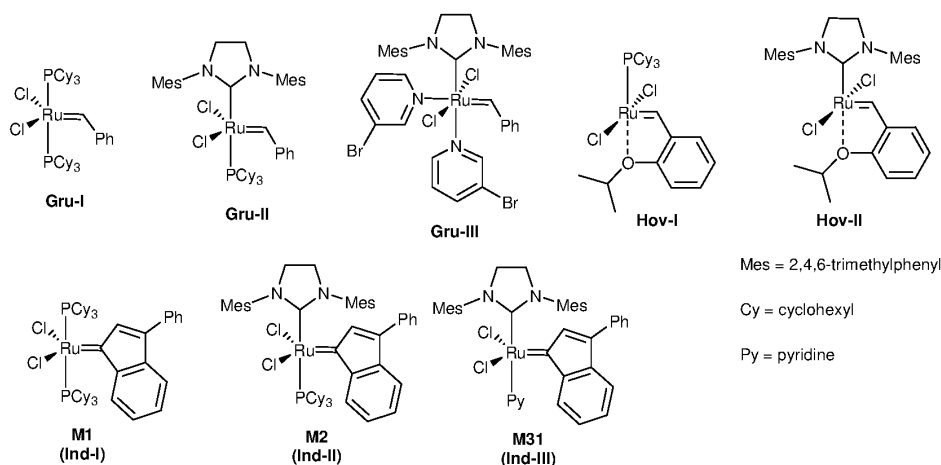


Process for producing ruthenium complexes and intermediates thereof and their use in olefin metathesis

The invention provides a new process for producing ruthenium complexes and their use in olefin metathesis as precatalysts and/or catalysts. This invention finds its application in the broadly defined organic synthesis using olefin cross-metathesis (CM), ring-closing metathesis (RCM), ring closing enyne metathesis (RCEYM) reactions, in a diastereoselective ring-rearrangement metathesis (DRRM) reaction, in polymerization of olefins in ring-opening metathesis polymerization (ROMP) reactions and an acyclic diene metathesis (ADMET).

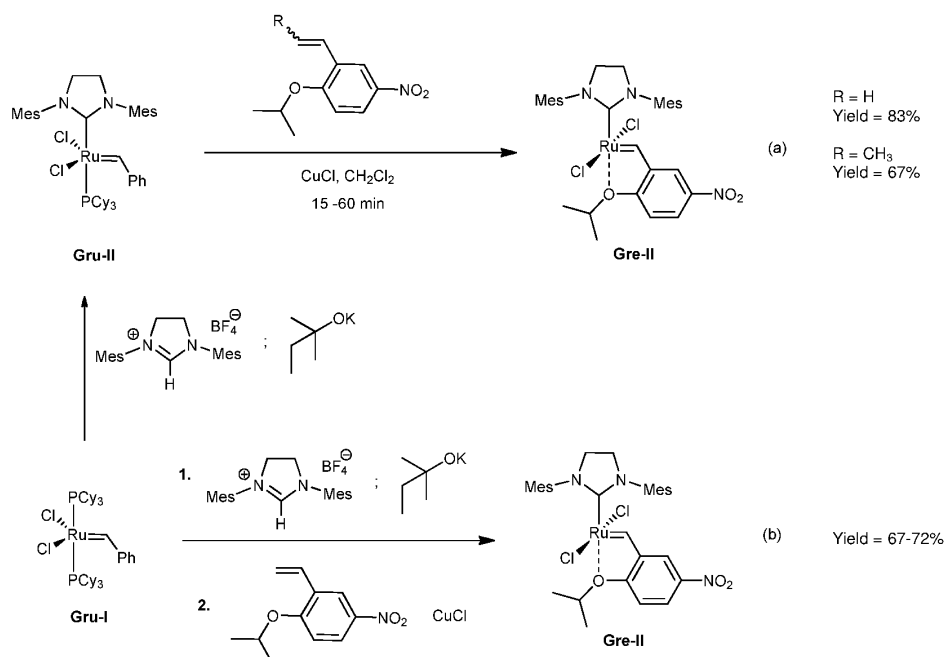
Over the last few years a great progress has been made in olefin metathesis applications in organic synthesis [R. H. Grubbs (ed.), A. G. Wenzel (ed.), D. J. O'Leary (ed.), E. Khosravi (ed.), *Handbook of Olefin Metathesis*, 2nd. ed., 3 volumes **2015**, John Wiley & Sons, Inc., 1608 pages].



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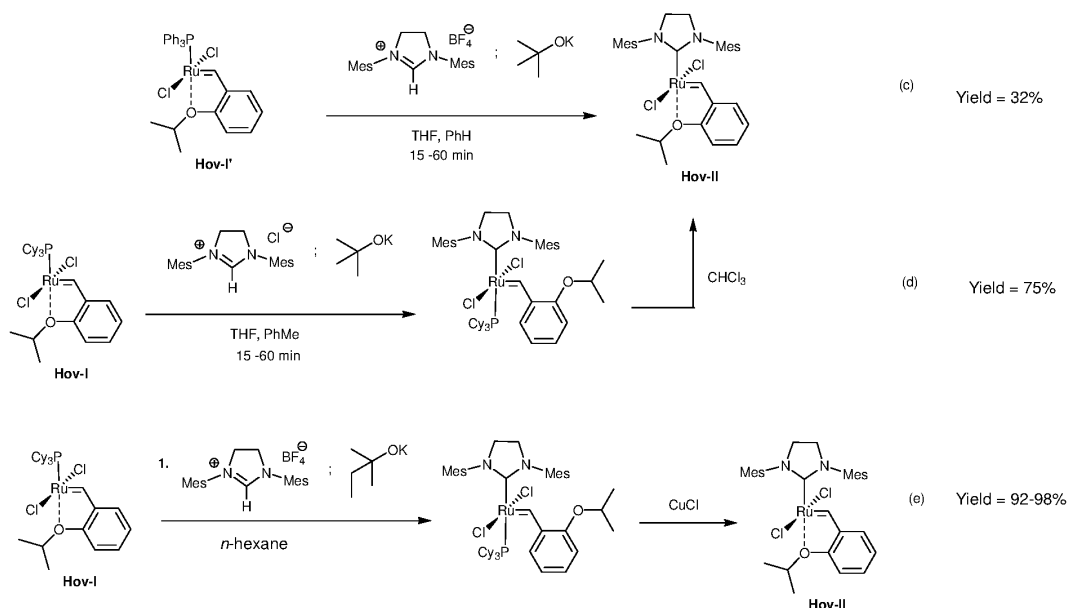
In the prior art there are known dozens of commercially available ruthenium carbene complexes acting as precatalysts and/or catalysts, characterised by both high activity in various types of metathesis reactions, and a broad tolerance of functional groups. The above combination of properties determines the suitability of this type of precatalysts and/or catalysts in the organic synthesis. The most prevalent in the literature ruthenium complexes in olefin metathesis reactions are 1st, 2nd and 3rd generation Grubbs-type ruthenium complexes (**Gru-I**, **Gru-II** and **Gru-III**), Hoveyda-type complexes (**Hov-I** and **Hov-II**) and indenylidene complexes (**Ind-I**, **Ind-II** and **Ind-III**), [Grubbs *et al. Chem. Rev.* **2010**, 110, 1746-1787; Nolan *et al. Chem. Commun.* **2014**, 50, 10355-10375]. In other cases, the majority of olefin metathesis catalyst structures are derived from the above-mentioned ruthenium complexes.



In the prior art there are known few methods of second generation Hoveyda-type precatalyst preparation [K. Grela, *et al.*, *Organometallics*, **2007**, 26, 1096-1099]. They involve contacting second generation Grubbs-type complexes (**Gru-II**) with 1-isopropoxy-5-nitrostyrene, or 1-isopropoxy-4-nitro-2-propenylbenzene in the presence of a copper(I) salt, Path (a). Another method of second generation Hoveyda-type complex preparation is a three-step one-pot procedure, Path (b). It involves *in situ* N-heterocyclic carbene (NHC) ligand generation, and contacting it with **Gru-I** complex and then addition of 1-isopropoxy-5-nitrostyrene in the presence of copper(I) chloride. Unfortunately, the use of styrene derivatives in large-scale synthesis is undesirable. Such compounds are obtained using cumbersome Wittig reaction or Stille coupling reaction. Much more desirable on an industrial scale is the use of propenyl derivatives such as 1-isopropoxy-4-nitro-2-propenylbenzene. Propenyl derivatives are obtained in a sequence of reactions: alkylation of a suitable phenol derivative with an allyl halide, Claisen rearrangement [3,3], and C=C bond isomerisation.

Alternative synthesis routes of the second generation Hoveyda-type complexes (**Hov-II**) involve contacting the first generation Hoveyda-type complexes (**Hov-I**) with NHCs, generated *in situ*, or provided to the reaction medium in another way, Paths (c), (d), and (e). These methods are complementary to the previously presented but they are not free of important industrial flaws.

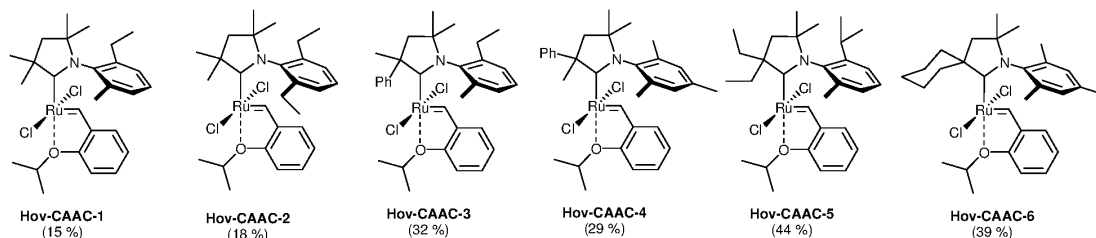
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The most important of them is the first generation Hoveyda-type catalyst synthesis (**Hov-I**) which requires the use of a diazo compound [A. H. Hoveyda *et al.*, *J. Am. Chem. Soc.* **1999**, 121, 791-799]. Alternatively, **Hov-I** may be obtained in a reaction of the first generation catalyst containing two phosphine ligands (e.g. **Gru-I** or **Ind-I**) with 2-isopropoxystyrene, which synthesis, as mentioned above, is cumbersome. What is important, the first generation catalysts containing two phosphine ligands do not react neither with the easily obtained 2-isopropoxypropenylbenzene not with its substituted in the aromatic ring derivatives.

In practical terms, the use of olefin metathesis reaction particularly on an industrial scale the most important parameters are the turn over number (TON) and the reaction selectivity. One type of olefin metathesis reaction of a huge industrial potential is a cross metathesis with ethylene (i.e. ethenolysis), particularly the ethenolysis of unsaturated fatty acid derivatives.

The first generation catalysts show relatively good selectivity in the ethenolysis reaction but unsatisfactory efficiency (low TON). On the other hand, the second generation catalysts containing NHC ligands show good efficiency (high TON) but low selectivity. The best ethenolysis reaction results are obtained with complexes containing both CAAC (Cyclic Alkyl Amino Carbene) ligands and Hoveyda-type benzylidene ligand (**Hov-CAAC**).

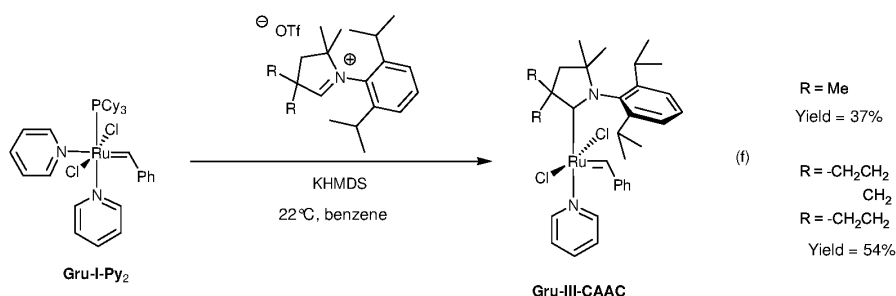


Known in the prior art **Hov-CAAC** complex synthesis method involves contacting CAAC ligand (in its pure form or generated *in situ*) with **Hov-I** complex, synthesis similar to Paths (c), (d), and (e). This method is unfavourable not only because of cumbersome **Hov-I** complex synthesis [A. H. Hoveyda *et al.*, *J. Am. Chem. Soc.* **1999**, 121, 791-799], but also due to its low yields and the use of a glovebox

[US2014309433A1; G. Bertrand, and R. H. Grubbs *et al.*, *Angew. Chem. Int. Ed.*, **2015**, 54, 1919-1923]. The disadvantage of this synthetic approach is a difficult benzylidene ligand modification, which may affect the activity and efficiency of the target ruthenium complex. Obtaining the second generation Hoveyda-type complexes containing CAAC ligand and modified benzylidene ligand according to a method known in the prior art would require each time a synthesis of a properly modified 2-isopropoxystyrene and then respective first generation Hoveyda-type complex.

In the prior art, there is also known a problem with preparation of precatalysts containing both CAAC-type ligand and modified benzylidene ligand. French patent [FR2947189B1] provides a cumbersome method of the non-activated benzylidene ($=CH-C_6H_4-OCH(CH_3)_2$) ligand replacement in the **Hov-CAAC**-type precatalyst, which for this reason was contacted with 5 molar equivalents of 1-isopropoxy-5-diethylamino-2-propenylbenzene in the presence of ethylene gas, which served as a reaction activator.

Known is also in the prior art a CAAC carbene reaction with Grubbs-type complex containing both tricyclohexylphosphine and two pyridine ligands **Gru-I-Py₂**, Path (f). Such reaction leads to a phosphine ligand substitution with CAAC carbene and formation of a respective third generation **Gru-III-CAAC** complex which had unexpectedly low activities in the standard RCM reaction of diene ring closing [G. Bertrand and R. H. Grubbs *et al.*, *Angew. Chem.*, **2007**, 119, 7400-7403].



Above-described most preferable synthesis method of the second generation Hoveyda-type complexes containing NHC ligands in which ruthenium precursor is the first generation complex containing two phosphine ligands never was employed in the **Hov-CAAC**-type complex synthesis.

Synthesis of the **Hov-CAAC**-type complexes from the first generation complexes containing two phosphine ligands would be advantageous particularly from the large-scale production aspect. Moreover, it would be particularly advantageous if this three-step synthesis could be performed in a single reaction vessel (one-pot synthesis).

During laboratory studies on the ruthenium complexes it has been surprisingly found that CAAC-type ligands react with the first generation complexes containing two phosphine ligands causing replacement of the both phosphines leading to a complex containing two CAAC ligands. With 1.25 to 2 molar equivalents of the CAAC ligand by TLC analysis one can observe formation of only small amounts of complex containing both one CAAC ligand and one phosphine ligand. It has been surprisingly found that in the presence of a compound which can form complexes with carbenes (e.g. CuCl or other phosphine and/or NHC ligand scavenger) complexes containing two CAAC ligands react with respective propenylbenzene derivatives providing **Hov-CAAC**-type complexes. Moreover, it has been noted that this reaction can be conducted without isolating the complex containing two CAAC ligands, that is **Hov-CAAC**-type complex may be easily obtained by multi-step one-pot type procedure, starting from the first

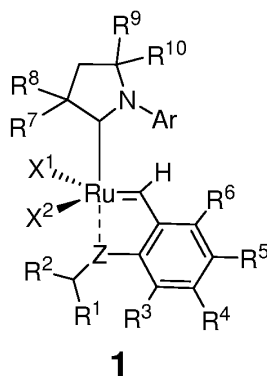
generation complex containing two phosphine ligands. The method according to the invention allows avoiding cumbersome **Hov-I** complex synthesis and allows a simple modification of the benzylidene ligand. Catalytic properties of the complexes obtained could be modulated by choosing the right CAAC ligand, benzylidene ligand or anionic ligands. During studies it has also been noted, that the activity and efficiency of the complexes containing two CAAC ligands depend strongly on structure of the CAAC ligand. Relatively fast-initiating complexes containing two CAAC ligands showed to be perfect catalysts for olefin metathesis.

The present application provides a general and economically advantageous method of **Hov-CAAC**-type complex synthesis in which ruthenium precursor is any first generation complex containing two phosphine ligands e.g. **Gru-I**, **Ind-I**, or Umicore **M10TM**. The invention provides also complexes containing two CAAC ligands, which may serve as precursors in the **Hov-CAAC** complex synthesis, and also as olefin metathesis catalysts.

The invention will be described in more detail in the preferred embodiment and in embodiments of the invention with reference to the accompanying drawing, in which:

Fig. 1 summarizes commercially available olefin metathesis precatalysts and catalysts, and novel precatalysts and catalysts of the present invention.

Therefore, the present invention provides a process for producing compound represented by the Formula 1,



wherein:

X¹ and X² are each independently an anionic ligand selected from halogen atoms, -CN, -SCN, -OR', -SR', -O(C=O)R', -O(SO₂)R', and -OSi(R')₃ group, wherein R' is C₁-C₁₂ alkyl, C₃-C₁₂ cycloalkyl, C₂-C₁₂ alkenyl, C₅-C₂₀ aryl, which are optionally substituted with at least one C₁-C₁₂ alkyl, C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, or a halogen atom;

Z is an atom selected from a group of O, S, NR', wherein R' is C₁-C₁₂ alkyl, C₃-C₁₂ cycloalkyl, C₂-C₁₂ alkenyl, C₅-C₂₀ aryl, which are optionally substituted with at least one C₁-C₁₂ alkyl, C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, or a halogen atom;

Ar is an aryl group substituted with hydrogen atoms or optionally substituted with at least one C₁-C₁₂ alkyl, C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy, and C₅-C₂₀ heteroaryloxy group, or a halogen atom;

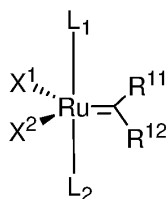
R¹ and R² are each independently hydrogen atom, C₁-C₂₅ alkyl group, C₁-C₂₅ alkoxy group, C₂-C₂₅ alkenyl group, C₁-C₁₂ perfluoroalkyl, C₅-C₂₀ aryl, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, or can be combined together to form substituted or unsubstituted C₄-C₁₀ cyclic or C₄-C₁₂ polycyclic system, can be also an

ester (-COOR'), amide (-CONR'₂), formyl (-CHO), ketone (-COR'), and hydroxamic (-CON(OR')(R')) group or a halogen atom, in which R' is C₁-C₁₂ alkyl, C₃-C₁₂ cycloalkyl, C₂-C₁₂ alkenyl, C₅-C₂₀ aryl, which are optionally substituted with at least one C₁-C₁₂ alkyl, C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, or a halogen atom;

- 5 R³, R⁴, R⁵, R⁶ are each independently hydrogen atom, C₁-C₂₅ alkyl group, C₁-C₂₅ alkoxy group, or C₂-C₂₅ alkenyl group, wherein R³, R⁴, R⁵, R⁶ substituents can be combined together to form substituted or unsubstituted C₄-C₁₀ cyclic or C₄-C₁₂ polycyclic system, can also independently be an alkoxy (-OR'), sulphide (-SR'), sulfoxide (-S(O)R'), sulphonium (-S⁺R'₂), sulphone (-SO₂R'), sulphonamide (-SO₂NR'₂), amine (-NR'₂), ammonium (-N⁺R'₃), nitro (-NO₂), cyano (-CN), phosphonate (-P(O)(OR')₂), phosphinate (-P(O)R'(OR')), phosphoninim (-P(OR')₂), phosphine (-PR'₂), phosphine oxide (-P(O)R'₂), phosphonium (-P⁺R'₃), carboxy (-COOH), ester (-COOR'), amide (-CONR'₂, or -NR'C(O)R'), formyl (-CHO), and ketone (-COR') group, wherein R' is C₁-C₅ alkyl, C₁-C₅ perfluoroalkyl, C₅-C₂₄ aryl, C₇-C₂₄ aralkyl, C₅-C₂₄ perfluoroaryl;

- 10 R⁷, R⁸, R⁹, and R¹⁰ are each independently hydrogen atom, or C₁-C₂₅ alkyl group, R⁷ and/or R⁸ can be combined with R⁹ and/or R¹⁰ to form cyclic system, are also independently C₁-C₁₂ alkyl group, C₃-C₁₂ cycloalkyl, C₂-C₁₂ alkenyl, C₅-C₂₀ aryl, C₁-C₅ perfluoroalkyl, C₇-C₂₄ aralkyl, C₅-C₂₄ perfluoroaryl, which are optionally substituted with at least one C₁-C₁₂ alkyl, C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, or a halogen atom;

characterised in that the alkylidene ruthenium complex represented by the Formula 2



2

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wherein:

- L¹, L² are each a neutral ligand selected from a group including phosphine, in particular P(R')₃, wherein each R' is independently C₁-C₁₂ alkyl, C₃-C₁₂ cycloalkyl, C₅-C₂₀ aryl, C₇-C₂₄ aralkyl, C₅-C₂₄ perfluoroaryl, 5-12-membered heteroaryl; two R' can be combined together to form cycloalkyl ring containing phosphorus atom in the ring.

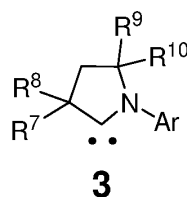
- 25 X¹, X² are each an anionic ligand selected independently from a group including halide anions, -CN, -SCN, -OR', -SR', -O(C=O)R', -O(SO₂)R', and -OSi(R')₃ group, wherein R' is C₁-C₁₂ alkyl, C₃-C₁₂ cycloalkyl, C₂-C₁₂ alkenyl, or C₅-C₂₀ aryl, which is optionally substituted with at least one C₁-C₁₂ alkyl, C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, or a halogen atom;

- 30 R¹¹, R¹² are each independently hydrogen atom, halogen atom, optionally substituted C₁-C₂₅ alkyl, optionally substituted C₁-C₂₅ perfluoroalkyl, optionally substituted C₂-C₂₅ alkene, optionally substituted C₃-C₇ cycloalkyl, optionally substituted C₂-C₂₅ alkenyl, optionally substituted C₃-C₂₅ cycloalkenyl, optionally substituted C₂-C₂₅ alkynyl, optionally substituted C₃-C₂₅ cycloalkynyl, optionally substituted C₁-C₂₅ alkoxy, optionally substituted C₅-C₂₄ aryloxy, optionally substituted C₅-C₂₀ heteroaryloxy, optionally substituted

C₅-C₂₄ aryl, optionally substituted C₅-C₂₀ heteroaryl, optionally substituted C₇-C₂₄ aralkyl, optionally substituted C₅-C₂₄ perfluoroaryl, optionally substituted 3-12-membered heterocycle;

wherein R¹¹ and R¹² substituents can be combined together to form a ring selected from a group including C₃-C₇ cycloalkyl, C₃-C₂₅ cycloalkenyl, C₃-C₂₅ cycloalkynyl, C₅-C₂₄ aryl, C₅-C₂₀ heteroaryl, C₅-C₂₄ perfluoroaryl, 3-12-membered heterocycle, which can be substituted independently with one and/or more substituents selected from a group including hydrogen atom, halogen atom, C₁-C₂₅ alkyl, C₁-C₂₅ perfluoroalkyl, C₂-C₂₅ alkene, C₃-C₇ cycloalkyl, C₂-C₂₅ alkenyl, C₃-C₂₅ cycloalkenyl, C₂-C₂₅ alkynyl, C₃-C₂₅ cycloalkynyl, C₁-C₂₅ alkoxy, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, C₅-C₂₄ aryl, C₅-C₂₀ heteroaryl, C₇-C₂₄ aralkyl, C₅-C₂₄ perfluoroaryl, 3-12-membered heterocycle;

is reacted with carbene represented by the Formula 3

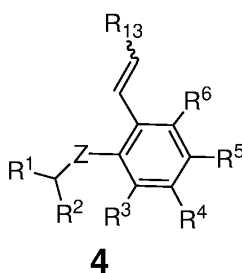


wherein:

Ar is an aryl group substituted with hydrogen atoms or optionally substituted with at least one C₁-C₁₂ alkyl, C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy group, or a halogen atom;

R⁷, R⁸, R⁹, and R¹⁰ are each independently hydrogen atom, or C₁-C₂₅ alkyl group, R⁷ and/or R⁸ can be combined with R⁹ and/or R¹⁰ to form cyclic system, can be also independently C₁-C₁₂ alkyl, C₃-C₁₂ cycloalkyl, C₂-C₁₂ alkenyl, C₅-C₂₀ aryl, C₁-C₅ perfluoroalkyl, C₇-C₂₄ aralkyl, and C₅-C₂₄ perfluoroaryl group, which are optionally substituted with at least one C₁-C₁₂ alkyl, C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, or a halogen atom;

thus formed reaction mixture is then contacted with the compound represented by the Formula 4



wherein:

Z is an atom selected from the group of O, S, NR', wherein R' is C₁-C₁₂ alkyl, C₃-C₁₂ cycloalkyl, C₂-C₁₂ alkenyl, C₅-C₂₀ aryl, which are optionally substituted with at least one C₁-C₁₂ alkyl, C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, or a halogen atom;

R¹ and R², are each independently hydrogen atom, C₁-C₂₅ alkyl group, C₁-C₂₅ alkoxy group, C₂-C₂₅ alkenyl group, C₁-C₁₂ perfluoroalkyl, C₅-C₂₀ aryl, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, or can be combined together to form substituted or unsubstituted C₄-C₁₀ cyclic or C₄-C₁₂ polycyclic system, can also be an ester (-COOR'), amide (-CONR'₂), formyl (-CHO), ketone (-COR'), and hydroxamic (-CON(OR')(R')) group or a halogen atom, wherein R' is C₁-C₁₂ alkyl, C₃-C₁₂ cycloalkyl, C₂-C₁₂ alkenyl, C₅-C₂₀ aryl, which

are optionally substituted with at least one C₁-C₁₂ alkyl, C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, or a halogen atom;

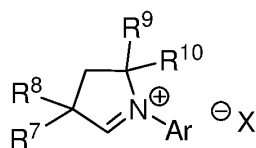
R³, R⁴, R⁵, R⁶ are each independently hydrogen atom, C₁-C₂₅ alkyl group, C₁-C₂₅ alkoxy group, or C₂-C₂₅ alkenyl group, wherein R³, R⁴, R⁵, R⁶ substituents can be combined together to form substituted or unsubstituted C₄-C₁₀ cyclic or C₄-C₁₂ polycyclic system; can independently also be alkoxy (-OR'), sulphide (-SR'), sulfoxide (-S(O)R'), sulphonium (-S⁺R'₂), sulphone (-SO₂R'), sulphonamide (-SO₂NR'₂), amine (-NR'₂), ammonium (-N⁺R'₃), nitro (-NO₂), cyano (-CN), phosphonate (-P(O)(OR')₂), phosphinate (-P(O)R'(OR')), phosphoninim (-P(OR')₂), phosphine (-PR'₂), phosphine oxide (-P(O)R'₂), phosphonium (-P⁺R'₃), carboxy (-COOH), ester (-COOR'), amide (-CONR'₂, or -NR'C(O)R'), formyl (-CHO), ketone (-COR') group, wherein R' is C₁-C₅ alkyl, C₁-C₅ perfluoroalkyl, C₅-C₂₄ aryl, C₇-C₂₄ aralkyl, C₅-C₂₄ perfluoroaryl;

R¹³ is a hydrogen atom, C₁-C₂₅ alkyl group, C₁-C₂₅ alkoxy group, C₂-C₂₅ alkenyl group, C₁-C₁₂ perfluoroalkyl, C₅-C₂₀ aryl, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, or can be combined together to form substituted or unsubstituted C₄-C₁₀ cyclic or C₄-C₁₂ polycyclic system or a halogen atom;

to form the compound represented by the Formula 1.

Preferably, the reaction mixture is contacted with the compound represented by the Formula 4 in the presence of phosphine ligand PR'₃ scavenger and/or CAAC ligand scavenger.

Preferably, carbenes represented by the Formula 3 are provided in the reaction medium by their generation *in situ* from suitable carbene precursors, CAAC salts represented by the Formula 3a,



3a

wherein:

Ar is an aryl group substituted with hydrogen atoms or optionally substituted with at least one C₁-C₁₂ alkyl group, C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, or a halogen atom;

R⁷, R⁸, R⁹, and R¹⁰ are each independently hydrogen atom or C₁-C₂₅ alkyl group, R⁷ and/or R⁸ can be combined with R⁹ and/or R¹⁰ to form cyclic system, can be also independently C₁-C₁₂ alkyl, C₃-C₁₂ cycloalkyl, C₂-C₁₂ alkenyl, C₅-C₂₀ aryl, C₁-C₅ perfluoroalkyl, C₇-C₂₄ aralkyl, and C₅-C₂₄ perfluoroaryl group, which are optionally substituted with at least one C₁-C₁₂ alkyl, C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, or a halogen atom;

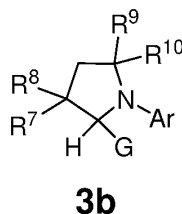
X⁻ is a halide anion, or BF₄⁻, PF₆⁻, ClO₄⁻, CF₃SO₂O⁻.

involving contacting the compound represented by the Formula 3a with a suitable base selected from potassium *N,N'*-bis(trimethylsilyl)amide, lithium *N,N'*-bis(trimethylsilyl)amide, sodium *N,N'*-bis(trimethylsilyl)amide, potassium *tert*-amylate, potassium *tert*-butoxide, and sodium hydride.

Preferably, carbenes represented by the Formula 3 are provided in the reaction medium by their generation *in situ* from suitable carbene precursors represented by the Formula 3a, which are contacted

with a base such as alkali metal *N,N'*-bis(trimethylsilyl)amide.

Preferably, carbenes represented by the Formula **3** are provided in the reaction medium by their thermal generation *in situ* from suitable carbene precursors represented by the Formula **3b** which are chloroform or alcohol adducts,

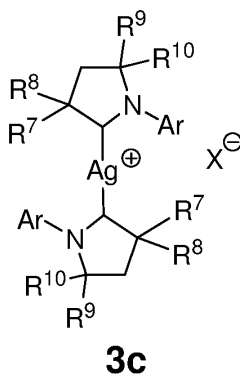


5 wherein:

G is CCl_3 or OR' , wherein R' is $\text{C}_1\text{-C}_{12}$ alkyl, $\text{C}_3\text{-C}_{12}$ cycloalkyl, $\text{C}_2\text{-C}_{12}$ alkenyl, or $\text{C}_5\text{-C}_{20}$ aryl, which is optionally substituted with at least one $\text{C}_1\text{-C}_{12}$ alkyl, $\text{C}_1\text{-C}_{12}$ perfluoroalkyl, $\text{C}_1\text{-C}_{12}$ alkoxy, $\text{C}_5\text{-C}_{24}$ aryloxy, $\text{C}_5\text{-C}_{20}$ heteroaryloxy or a halogen atom;

- Ar is an aryl group substituted with hydrogen atoms or optionally substituted with at least one $\text{C}_1\text{-C}_{12}$ alkyl, $\text{C}_1\text{-C}_{12}$ perfluoroalkyl, $\text{C}_1\text{-C}_{12}$ alkoxy, $\text{C}_5\text{-C}_{24}$ aryloxy, and $\text{C}_5\text{-C}_{20}$ heteroaryloxy group, or a halogen atom;
- 10 R^7 , R^8 , R^9 , and R^{10} are each independently hydrogen atom or $\text{C}_1\text{-C}_{25}$ alkyl group, R^7 and/or R^8 can be combined with R^9 and/or R^{10} to form cyclic system, can be also independently $\text{C}_1\text{-C}_{12}$ alkyl, $\text{C}_3\text{-C}_{12}$ cycloalkyl, $\text{C}_2\text{-C}_{12}$ alkenyl, $\text{C}_5\text{-C}_{20}$ aryl, $\text{C}_1\text{-C}_5$ perfluoroalkyl, $\text{C}_7\text{-C}_{24}$ aralkyl, and $\text{C}_5\text{-C}_{24}$ perfluoroaryl group, which are optionally substituted with at least one $\text{C}_1\text{-C}_{12}$ alkyl, $\text{C}_1\text{-C}_{12}$ perfluoroalkyl, $\text{C}_1\text{-C}_{12}$ alkoxy, $\text{C}_5\text{-C}_{24}$
- 15 aryloxy, $\text{C}_5\text{-C}_{20}$ heteroaryloxy, or a halogen atom.

Preferably, alkylidene ruthenium complex represented by the Formula **2**, is contacted with the compound represented by the Formula **3c**, which acts as CAAC carbene ligand donor represented by the Formula **3**,

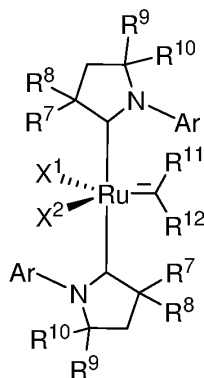


wherein:

- 20 Ar is an aryl group substituted with hydrogen atoms or optionally substituted with at least one $\text{C}_1\text{-C}_{12}$ alkyl, $\text{C}_1\text{-C}_{12}$ perfluoroalkyl, $\text{C}_1\text{-C}_{12}$ alkoxy, $\text{C}_5\text{-C}_{24}$ aryloxy, and $\text{C}_5\text{-C}_{20}$ heteroaryloxy group, or a halogen atom;
- R^7 , R^8 , R^9 , and R^{10} are each independently hydrogen atom or $\text{C}_1\text{-C}_{25}$ alkyl group, R^7 and/or R^8 can be combined with R^9 and/or R^{10} to form cyclic system, can be also independently $\text{C}_1\text{-C}_{12}$ alkyl, $\text{C}_3\text{-C}_{12}$ cycloalkyl, $\text{C}_2\text{-C}_{12}$ alkenyl, $\text{C}_5\text{-C}_{20}$ aryl, $\text{C}_1\text{-C}_5$ perfluoroalkyl, $\text{C}_7\text{-C}_{24}$ aralkyl, and $\text{C}_5\text{-C}_{24}$ perfluoroaryl group,
- 25 which are optionally substituted with at least one $\text{C}_1\text{-C}_{12}$ alkyl, $\text{C}_1\text{-C}_{12}$ perfluoroalkyl, $\text{C}_1\text{-C}_{12}$ alkoxy, $\text{C}_5\text{-C}_{24}$ aryloxy, $\text{C}_5\text{-C}_{20}$ heteroaryloxy, or a halogen atom;
- X is a halide anion or BF_4^- , PF_6^- , ClO_4^- , CF_3SO_3^- .

Preferably, carbenes represented by the Formula 3 are provided in the reaction medium by their direct adding to the reaction mixture.

Preferably, the alkylidene ruthenium complex represented by the Formula 2 is reacted with the carbene represented by the Formula 3 to form an intermediate compound represented by the Formula 5



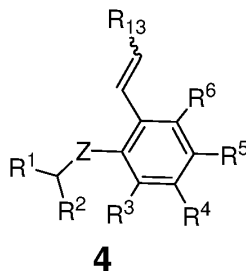
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wherein:

- X^1 and X^2 are each independently an anionic ligand selected from halogen atoms, -CN, -SCN, -OR', -SR', -O(C=O)R', -O(SO₂)R', and -OSi(R')₃ group, wherein R' is C₁-C₁₂ alkyl, C₃-C₁₂ cycloalkyl, C₂-C₁₂ alkenyl, C₅-C₂₀ aryl, which are optionally substituted with at least one C₁-C₁₂ alkyl, C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, or a halogen atom;
- Ar is an aryl group substituted with hydrogen atoms or optionally substituted with at least one C₁-C₁₂ alkyl, C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy, and C₅-C₂₀ heteroaryloxy group, or a halogen atom;
- R⁷, R⁸, R⁹, and R¹⁰ are each independently hydrogen atom or C₁-C₂₅ alkyl group, R⁷ and/or R⁸ can be combined with R⁹ and/or R¹⁰ to form cyclic system, can be also independently C₁-C₁₂ alkyl, C₃-C₁₂ cycloalkyl, C₂-C₁₂ alkenyl, C₅-C₂₀ aryl, C₁-C₅ perfluoroalkyl, C₇-C₂₄ aralkyl, and C₅-C₂₄ perfluoroaryl group, which are optionally substituted with at least one C₁-C₁₂ alkyl, C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, or a halogen atom;
- R¹¹, R¹² are each independently hydrogen atom, halogen atom, optionally substituted C₁-C₂₅ alkyl, optionally substituted C₁-C₂₅ perfluoroalkyl, optionally substituted C₂-C₂₅ alkene, optionally substituted C₃-C₇ cycloalkyl, optionally substituted C₂-C₂₅ alkenyl, optionally substituted C₃-C₂₅ cycloalkenyl, optionally substituted C₂-C₂₅ alkynyl, optionally substituted C₃-C₂₅ cycloalkynyl, optionally substituted C₁-C₂₅ alkoxy, optionally substituted C₅-C₂₄ aryloxy, optionally substituted C₅-C₂₀ heteroaryloxy, optionally substituted C₅-C₂₄ aryl, optionally substituted C₅-C₂₀ heteroaryl, optionally substituted C₇-C₂₄ aralkyl, optionally substituted C₅-C₂₄ perfluoroaryl, optionally substituted 3-12-membered heterocycle;
- wherein R¹¹ and R¹² substituents can be combined together to form a ring selected from a group including C₃-C₇ cycloalkyl, C₃-C₂₅ cycloalkenyl, C₃-C₂₅ cycloalkynyl, C₅-C₂₄ aryl, C₅-C₂₀ heteroaryl, C₅-C₂₄ perfluoroaryl, 3-12-membered heterocycle, which can be substituted independently with one and/or more substituents selected from a group including hydrogen atom, halogen atom, C₁-C₂₅ alkyl, C₁-C₂₅ perfluoroalkyl, C₂-C₂₅ alkene, C₃-C₇ cycloalkyl, C₂-C₂₅ alkenyl, C₃-C₂₅ cycloalkenyl, C₂-C₂₅ alkynyl, C₃-C₂₅ cycloalkynyl, C₁-C₂₅ alkoxy, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, C₅-C₂₄ aryl, C₅-C₂₀ heteroaryl, C₇-C₂₄ aralkyl, C₅-C₂₄ perfluoroaryl, 3-12-membered heterocycle;

which is then contacted with the compound represented by the Formula 4



wherein:

Z is an atom selected from a group of O, S, NR', wherein R' is C₁-C₁₂ alkyl, C₃-C₁₂ cycloalkyl, C₂-C₁₂ alkenyl, C₅-C₂₀ aryl, which are optionally substituted with at least one C₁-C₁₂ alkyl, C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, or a halogen atom;

R¹ and R² are each independently hydrogen atom, C₁-C₂₅ alkyl group, C₁-C₂₅ alkoxy group, C₂-C₂₅ alkenyl group, C₁-C₁₂ perfluoroalkyl, C₅-C₂₀ aryl, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, or can be combined together to form substituted or unsubstituted C₄-C₁₀ cyclic or C₄-C₁₂ polycyclic system, can also be an ester (-COOR'), amide (-CONR'₂), formyl (-CHO), ketone (-COR'), and hydroxamic (-CON(OR')(R')) group or a halogen atom, wherein R' is C₁-C₁₂ alkyl, C₃-C₁₂ cycloalkyl, C₂-C₁₂ alkenyl, C₅-C₂₀ aryl, which are optionally substituted with at least one C₁-C₁₂ alkyl, C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, or a halogen atom;

R³, R⁴, R⁵, R⁶ are each independently hydrogen atom, C₁-C₂₅ alkyl group, C₁-C₂₅ alkoxy group, or C₂-C₂₅ alkenyl group, wherein R³, R⁴, R⁵, R⁶ substituents can be combined together to form substituted or unsubstituted C₄-C₁₀ cyclic or C₄-C₁₂ polycyclic system; can also independently be an alkoxy (-OR'), sulphide (-SR'), sulfoxide (-S(O)R'), sulphonium (-S⁺R'₂), sulphone (-SO₂R'), sulphonamide (-SO₂NR'₂), amine (-NR'₂), ammonium (-N⁺R'₃), nitro (-NO₂), cyano (-CN), phosphonate (-P(O)(OR')₂), phosphinate (-P(O)R'(OR')), phosphoninim (-P(OR')₂), phosphine (-PR'₂), phosphine oxide (-P(O)R'₂), phosphonium (-P⁺R'₃), carboxy (-COOH), ester (-COOR'), amide (-CONR'₂, or -NR'C(O)R'), formyl (-CHO), and ketone (-COR') group, wherein R' is C₁-C₅ alkyl, C₁-C₅ perfluoroalkyl, C₅-C₂₄ aryl, C₇-C₂₄ aralkyl, C₅-C₂₄ perfluoroaryl;

R¹³ is a hydrogen atom, C₁-C₂₅ alkyl group, C₁-C₂₅ alkoxy group, C₂-C₂₅ alkenyl group, C₁-C₁₂ perfluoroalkyl, C₅-C₂₀ aryl, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, or can be combined together to form substituted or unsubstituted C₄-C₁₀ cyclic or C₄-C₁₂ polycyclic system or a halogen atom;

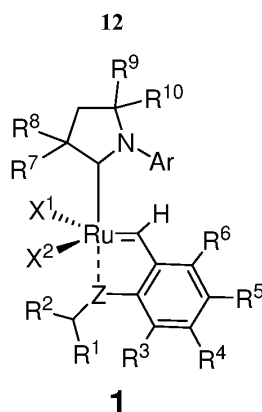
to form the compound represented by the Formula 1.

Preferably, Compound 5 is reacted with the Compound 4 in the presence of the phosphine ligand scavenger PR'₃ and/or CAAC ligand scavenger.

Preferably, as the phosphine ligand scavenger PR'₃ and/or the CAAC ligand scavenger a compound selected from copper(I) salts and/or HCl is used.

Preferably, all reaction steps are conducted in a polar and/or nonpolar solvent, preferably in aliphatic or aromatic hydrocarbons, over a period of 1 minute to 24 hours.

The invention provides also a compound represented by the Formula 1,

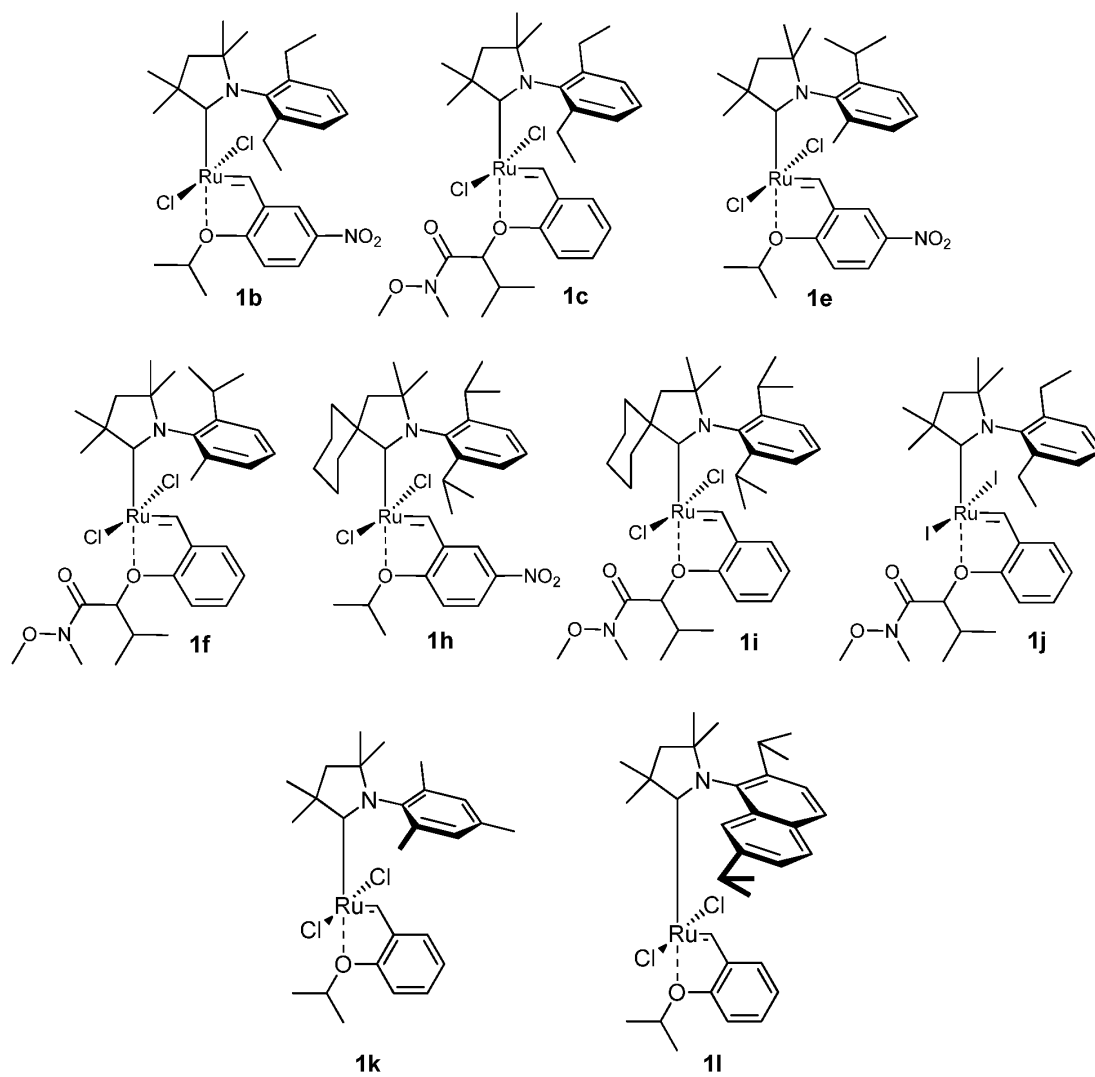


wherein:

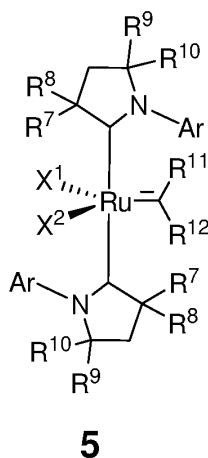
- X¹ and X² are each independently an anionic ligand selected from halogen atoms, -CN, -SCN, -OR', -SR', -O(C=O)R', -O(SO₂)R', and -OSi(R')₃ group, wherein R' is C₁-C₁₂ alkyl, C₃-C₁₂ cycloalkyl, C₂-C₁₂ alkenyl, C₅-C₂₀ aryl, which are optionally substituted with at least one C₁-C₁₂ alkyl, C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, or a halogen atom;
- Z is an atom selected from a group of O, S, NR', wherein R' is C₁-C₁₂ alkyl, C₃-C₁₂ cycloalkyl, C₂-C₁₂ alkenyl, C₅-C₂₀ aryl, which are optionally substituted with at least one C₁-C₁₂ alkyl, C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, or a halogen atom;
- Ar is an aryl group substituted with hydrogen atoms or optionally substituted with at least one C₁-C₁₂ alkyl, C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy group, or a halogen atom;
- R¹ and R² are each independently hydrogen atom, C₁-C₂₅ alkyl group, C₁-C₂₅ alkoxy group, C₂-C₂₅ alkenyl group, C₁-C₁₂ perfluoroalkyl, C₅-C₂₀ aryl, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, or can be combined together to form substituted or unsubstituted C₄-C₁₀ cyclic or C₄-C₁₂ polycyclic system, can also be an ester (-COOR'), amide (-CONR'₂), formyl (-CHO), ketone (-COR'), and hydroxamic (-CON(OR')(R')) group or a halogen atom, in which R' is C₁-C₁₂ alkyl, C₃-C₁₂ cycloalkyl, C₂-C₁₂ alkenyl, C₅-C₂₀ aryl, which are optionally substituted with at least one C₁-C₁₂ alkyl, C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, or a halogen atom;
- R³, R⁴, R⁵, R⁶ are each independently hydrogen atom, sulfoxide group (-S(O)R'), sulphonamide group (-SO₂NR'₂), phosphonate group (-P(O)(OR')₂), phosphinate group (-P(O)R'(OR')), phosphonium group (-P(OR')₂), phosphine group (-PR'₂), nitro group (-NO₂), nitroso group (-NO), carboxy group (-COOH), ester group (-COOR'), formyl group (-CHO), and ketone group (-COR'), wherein R' is C₁-C₅ alkyl, C₁-C₅ perfluoroalkyl, C₅-C₂₄ aryl, C₇-C₂₄ aralkyl, C₅-C₂₄ perfluoroaryl;
- wherein, when R¹ and R² are -CH₃ group, then at least one of R³, R⁴, R⁵, R⁶ substituents is not hydrogen atom;
- R⁷, R⁸, R⁹, and R¹⁰ are each independently hydrogen atom or C₁-C₂₅ alkyl group, R⁷ and/or R⁸ can be combined with R⁹ and/or R¹⁰ to form cyclic system, are also independently C₁-C₁₂ alkyl, C₃-C₁₂ cycloalkyl, C₂-C₁₂ alkenyl, C₅-C₂₀ aryl, C₁-C₅ perfluoroalkyl, C₇-C₂₄ aralkyl, and C₅-C₂₄ perfluoroaryl group, which are optionally substituted with at least one C₁-C₁₂ alkyl, C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, or halogen.

Preferably, the invention provides a compound of a structure represented by the formula selected from **1b**, **1c**, **1e**, **1f**, **1h**, **1i**, **1j**, **1k**, **1l**:

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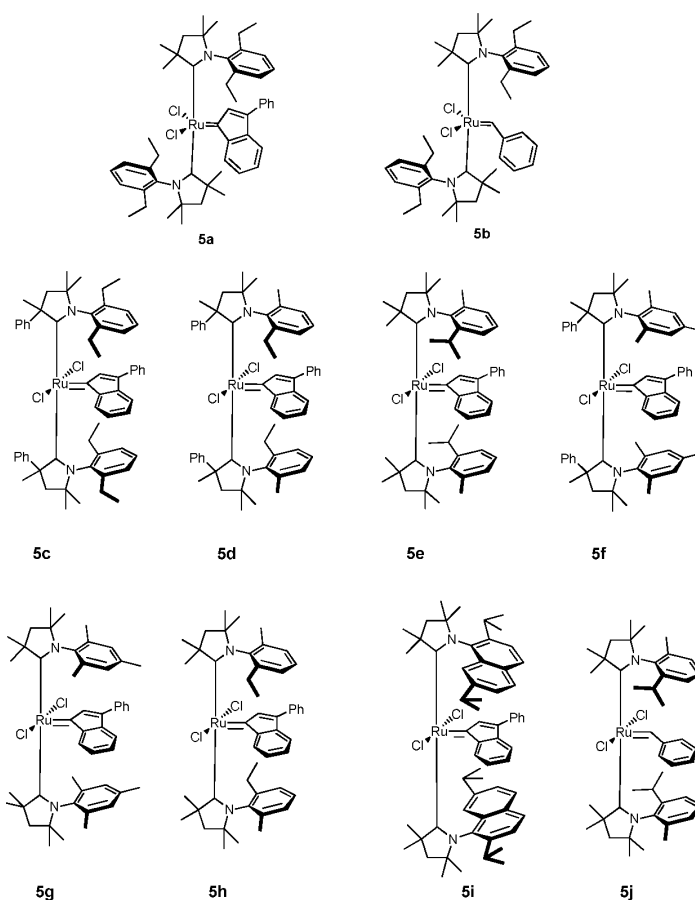
The invention provides also a compound represented by the Formula 5,



wherein:

- 5 X¹ and X² are each independently an anionic ligand selected from halogen atoms, -CN, -SCN, -OR', -SR', -O(C=O)R', -O(SO₂)R', and -OSi(R')₃ group, wherein R' is C₁-C₁₂ alkyl, C₃-C₁₂ cycloalkyl, C₂-C₁₂ alkenyl, C₅-C₂₀ aryl, which are optionally substituted with at least one C₁-C₁₂ alkyl, C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, or a halogen atom;
Ar is an aryl group substituted with hydrogen atoms or optionally substituted with at least one C₁-C₁₂ alkyl,
 - 10 C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy, and C₅-C₂₀ heteroaryloxy group, or a halogen atom;
R⁷, R⁸, R⁹, and R¹⁰ are each independently hydrogen atom or C₁-C₂₅ alkyl group, R⁷ and/or R⁸ can be combined with R⁹ and/or R¹⁰ to form cyclic system, can be also independently C₁-C₁₂ alkyl, C₃-C₁₂ cycloalkyl, C₂-C₁₂ alkenyl, C₅-C₂₀ aryl, C₁-C₅ perfluoroalkyl, C₇-C₂₄ aralkyl, C₅-C₂₄ perfluoroaryl, which are optionally substituted with at least one C₁-C₁₂ alkyl, C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy,
 - 15 and C₅-C₂₀ heteroaryloxy group, or a halogen atom;
R¹¹, R¹² are each independently hydrogen atom, halogen atom, optionally substituted C₁-C₂₅ alkyl, optionally substituted C₁-C₂₅ perfluoroalkyl, optionally substituted C₂-C₂₅ alkene, optionally substituted C₃-C₇ cycloalkyl, optionally substituted C₂-C₂₅ alkenyl, optionally substituted C₃-C₂₅ cycloalkenyl, optionally substituted C₂-C₂₅ alkynyl, optionally substituted C₃-C₂₅ cycloalkynyl, optionally substituted C₁-C₂₅ alkoxy,
 - 20 optionally substituted C₅-C₂₄ aryloxy, optionally substituted C₅-C₂₀ heteroaryloxy, optionally substituted C₅-C₂₄ aryl, optionally substituted C₅-C₂₀ heteroaryl, optionally substituted C₇-C₂₄ aralkyl, optionally substituted C₅-C₂₄ perfluoroaryl, optionally substituted 3-12-membered heterocycle;
- wherein R¹¹ and R¹² substituents can be combined together to form a ring selected from a group including C₃-C₇ cycloalkyl, C₃-C₂₅ cycloalkenyl, C₃-C₂₅ cycloalkynyl, C₅-C₂₄ aryl, C₅-C₂₀ heteroaryl, C₅-C₂₄
- 25 perfluoroaryl, 3-12-membered heterocycle, which can be substituted independently with one and/or more substituents selected from a group including hydrogen atom, halogen atom, C₁-C₂₅ alkyl, C₁-C₂₅ perfluoroalkyl, C₂-C₂₅ alkene, C₃-C₇ cycloalkyl, C₂-C₂₅ alkenyl, C₃-C₂₅ cycloalkenyl, C₂-C₂₅ alkynyl, C₃-C₂₅ cycloalkynyl, C₁-C₂₅ alkoxy, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, C₅-C₂₄ aryl, C₅-C₂₀ heteroaryl, C₇-C₂₄ aralkyl, C₅-C₂₄ perfluoroaryl, 3-12-membered heterocycle.

Preferably, invention relates to a compound of a structure represented by the formula selected from **5a-5j**, (wherein these compounds may be in a rotamer form):



- 5 The invention provides also the use of a compound represented by the Formula **1**, obtained by the above-mentioned method, as a precatalyst and/or catalyst in olefin metathesis reactions, particularly in ring-closing metathesis (RCM), homometathesis, cross-metathesis (CM), ethenolysis, and isomerisation reactions, in reaction of diastereoselective ring-rearrangement metathesis (DRRM), in „alkene-alkyne” (en-yn) type metathesis or ROMP type polymerisation reactions.
- 10 Preferably, compound represented by the Formula **1** is used as the precatalyst and/or catalyst in a reaction mixture over a period of 1 minute to 24 hours in organic solvents or without solvent.
The invention relates also to the use of compound represented by the Formula **1**, obtained as described above, as a substrate for the synthesis of other ruthenium complex compounds which are precatalysts and/or catalysts for olefin metathesis.
- 15 The present invention provides also the use of the compound represented by the Formula **5** as the precatalyst and/or catalyst in olefin metathesis reactions, particularly in ring-closing metathesis (RCM), homometathesis, cross-metathesis (CM), ethenolysis, and isomerisation reactions, in reaction of diastereoselective ring-rearrangement metathesis (DRRM), in “alkene-alkyne” (en-yn) type metathesis or ROMP type polymerisation reactions, and also the use of the compound represented by the Formula **5** as
- 20 the precatalyst and/or catalyst in olefin metathesis reactions in the presence of a CAAC ligand scavenger.

The present invention and its advantageous effects are shown in the figures, wherein:

Fig. 1 shows structures of the compounds of the present invention;

Fig. 2 shows graphs depicting relationship between area under the peak (AUP) on the chromatogram and the concentration (mg/mL) of the analysed compound for reaction of the Example XXXX;

- 5 Fig. 3 shows graphs depicting relationship between area under the peak (AUP) on the chromatogram and the concentration (mg/mL) of the analysed compound for reaction of the Example XXXXI;

Fig. 4 shows standard curve for product **P9** of the Example XXXXVI.

Terms used the present specification have the following meanings:

The term "*halogen atom*" or "*halogen*" means an element selected from F, Cl, Br, I.

- 10 The term "*carbene*" means a particle containing a neutral carbon atom of a valence number two and two unpaired (triplet state) or paired (singlet state) valence electrons. The term "*carbene*" encompasses also carbene analogues, wherein the carbon atom is replaced by other chemical element such as boron, silicon, germanium, tin, lead, nitrogen, phosphorus, sulphur, selenium, and tellurium.

- The term "*alkyl*" refers to a saturated, straight, or branched hydrocarbon substituent with an indicated carbon atom number. Examples of an alkyl substituent are -methyl, -ethyl, -*n*-propyl, -*n*-butyl, -*n*-pentyl, -*n*-hexyl, -*n*-heptyl, -*n*-octyl, -*n*-nonyl, and -*n*-decyl. Representative branched -(C1-C10)alkyls include -isopropyl, -*sec*-butyl, -isobutyl, -*tert*-butyl, -isopentyl, -neopentyl, -1-methylbutyl, -2-methylbutyl, -3-methylbutyl, -1,1-dimethylpropyl, -1,2-dimethylpropyl, -1-methylpentyl, -2-methylpentyl, -3-methylpentyl, -4-methylpentyl, -1-ethylbutyl, -2-ethylbutyl, -3-ethylbutyl, -1,1-dimethylbutyl, -1,2-dimethylbutyl, -1,3-dimethylbutyl, -2,2-dimethylbutyl, -2,3-dimethylbutyl, -3,3-dimethylbutyl, -1-methylhexyl, -2-methylhexyl, -3-methylhexyl, -4-methylhexyl, -5-methylhexyl, -1,2-dimethylpentyl, -1,3-dimethylpentyl, -1,2-dimethylhexyl, -1,3-dimethylhexyl, -3,3-dimethylhexyl, -1,2-dimethylheptyl, -1,3-dimethylheptyl, and -3,3-dimethylheptyl, and the like.
- 15
- 20

The term "*alkoxy*" refers to an alkyl substituent as described above connected by an oxygen atom.

- 25 The term "*perfluoroalkyl*" means an alkyl group as described above, in which all hydrogen atoms were replaced with the same or different type of halogen atoms.

The term "*cycloalkyl*" refers to a saturated mono- or polycyclic hydrocarbon substituent with an indicated carbon atom number. Examples of a cycloalkyl substituent are -cyclopropyl, -cyclobutyl, -cyclopentyl, -cyclohexyl, -cycloheptyl, -cyclooctyl, -cyclononyl, -cyclodecyl, and the like.

- 30 The term "*alkenyl*" refers to a saturated, straight, or branched acyclic hydrocarbon substituent with an indicated carbon atom number and containing at least one carbon-carbon double bond. Examples of an alkenyl substituent are -vinyl, -allyl, -1-butenyl, -2-butenyl, -isobutylenyl, -1-pentenyl, -2-pentenyl, -3-methyl-1-butenyl, -2-methyl-2-butenyl, -2,3-di-methyl-2-butenyl, -1-hexenyl, -2-hexenyl, -3-hexenyl, -1-heptenyl, -2-heptenyl, -3-heptenyl, -1-octenyl, -2-octenyl, -3-octenyl, -1-nonenyl, -2-nonenyl, -3-nonenyl, -1-decenyl, -2-decenyl, -3-decenyl, and the like.
- 35

- The term "*cycloalkenyl*" refers to a saturated mono- or polycyclic hydrocarbon substituent with an indicated carbon atom number and containing at least one carbon-carbon double bond. Examples of cycloalkenyl substituent are -cyclopentenyl, -cyclopentadienyl, -cyclohexenyl, -cyclohexadienyl, -cycloheptenyl, -cycloheptadienyl, -cycloheptatrienyl, -cyclooctenyl, -cyclooctadienyl, -cyclooctatrienyl, -cyclooctatetraenyl, -cyclononenyl, -cyclononadienyl, -cyclodecenyl, -cyclodecadienyl, and the like.
- 40

The term "*alkynyl*" refers to a saturated, straight, or branched acyclic hydrocarbon substituent with an indicated carbon atom number and containing at least one carbon-carbon triple bond. Examples of an alkynyl substituent are -acetylenyl, -propynyl, -1-butylnyl, -2-butylnyl, -1-pentylnyl, -2-pentylnyl, -3-methyl-1-butylnyl, -4-pentylnyl, -1-hexynyl, -2-hexynyl, -5-hexynyl, and the like.

- 5 The term "*cycloalkynyl*" refers to a saturated mono- or polycyclic hydrocarbon substituent with an indicated carbon atom number and containing at least one carbon-carbon triple bond. Examples of cycloalkynyl substituent are -cyclohexynyl, -cycloheptynyl, -cyclooctynyl, and the like.

The term "*aryl*" refers to an aromatic mono- or polycyclic hydrocarbon substituent with an indicated carbon atom number. Examples of an aryl substituent are -phenyl, -tolyl, -xylyl, -naphthyl, -2,4,6-
10 trimethylphenyl, -2-fluorophenyl, -4-fluorophenyl, -2,4,6-trifluorophenyl, -2,6-difluorophenyl, -4-nitrophenyl, and the like.

The term "*aralkyl*" refers to an alkyl substituent, as described above, substituted with at least one aryl as described above. Examples of an aralkyl substituent are -benzyl, -diphenylmethyl, -triphenylmethyl, and the like.

- 15 The term "*heteroaryl*" refers to an aromatic mono- or polycyclic hydrocarbon substituent with an indicated carbon atom number, wherein at least one carbon atom was replaced with a heteroatom selected from O, N and S atoms. Examples of heteroaryl substituent are -furyl, -thienyl, -imidazolyl, -oxazolyl, -thiazolyl, -isoxazolyl, triazolyl, -oxadiazolyl, -thiadiazolyl, -tetrazolyl, -pyridyl, -pyrimidyl, -triazinyl, -indolyl, -benzo[b]furyl, -benzo[b]thienyl, -indazolyl, -benzimidazolyl, -azaindolyl, -quinolyl, -isoquinolyl, -carbazolyl,
20 and the like.

The term "*heterocycle*" refers to a saturated or partly unsaturated, mono- or polycyclic hydrocarbon substituent with an indicated carbon atom number, wherein at least one carbon atom was replaced with a heteroatom selected from O, N and S atoms. Examples of a heterocyclic substituent are furyl, thiophenyl, pyrrolyl, oxazolyl, imidazolyl, thiazolyl, isoxazolyl, pyrazolyl, isothiazolyl, triazinyl, pyrrolidinonyl,
25 pyrrolidinyl, hydantoinyl, oxiranyl, oxetanyl, tetrahydrofuranyl, tetrahydrothiophenyl, quinoliny, isoquinoliny, chromonyl, coumariny, indolyl, indoliziny, benzo[b]furanyl, benzo[b]thiophenyl, indazolyl, puriny, 4H-quinoliziny, isoquinolyl, quinolyl, phthalaziny, naphthyridiny, carbazolyl, β -carboliny, and the like.

The term "*neutral ligand*" refers to an uncharged substituent, which is able to form a coordinate bond with a metal centre (ruthenium atom). Examples of such ligands may be: amines, phosphines and their oxides,
30 alkyl and aryl phosphites and phosphates, arsines and their oxides, ethers, alkyl and aryl sulphides, coordinated hydrocarbons, alkyl and aryl halides.

The term "*indenylidene*" refers to an unsaturated hydrocarbon substituent with an indene (benzocyclopentadiene) backbone linked via a double bond to a metal atom.

- 35 The term "*heteroindenylidene*" refers to an indenylidene substituent, defined above, wherein at least one carbon atom was replaced with heteroatom from a group including nitrogen, oxygen, sulphur.

The term "*anionic ligand*" refers to a substituent, which is able to form a coordinate bond with a metal centre (ruthenium atom) having a charge which is able to partially or totally compensate the charge of the metal centre. Examples of such ligands may be fluorine, chloride, bromide, iodide, cyanide, cyanate, and
40 thiocyanate anions, carboxylic acid anions, alcohol anions, phenol anions, thiol and thiophenol anions,

- anions of hydrocarbons with a delocalised charge (e.g. cyclopentadiene), anions of (organo)sulphuric and (organo)phosphoric acids and esters thereof (such as e.g. anions of alkylsulphonic and arylsulphonic acids, anions of alkylphosphoric and arylphosphoric acids, anions of sulphuric acid alkyl and aryl esters, anions of phosphoric acid alkyl and aryl esters, anions of alkylphosphoric and arylphosphoric acid alkyl and aryl esters). Optionally, anionic ligand may have L^1 , L^2 and L^3 group, linked in the same way as catechol anion, acetylacetone anion, and salicylaldehyde anion. Anionic ligands (X^1 , X^2) and neutral ligands (L^1 , L^2 , L^3) can be combined together to form polydentate ligands, for example bidentate ligand (X^1 - X^2), tridentate ligand (X^1 - X^2 - L^1), tetradentate ligand (X^1 - X^2 - L^1 - L^2), bidentate ligand (X^1 - L^1), tridentate ligand (X^1 - L^1 - L^2), tetradentate ligand (X^1 - L^1 - L^2 - L^3), bidentate ligand (L^1 - L^2), tridentate ligand (L^1 - L^2 - L^3).
- 5 Examples of such ligands are: catechol anion, acetylacetone anion, and salicylaldehyde anion.

The term "*heteroatom*" means an atom selected from a group of oxygen, sulphur, nitrogen, phosphorus, and others.

- The term "*chlorinated solvent*" means a solvent containing in its structure at least one atom of fluorine, chlorine, bromine, or iodine; more preferably more than one. Examples of such solvents are
- 15 dichloromethane, chloroform, tetrachloromethane (carbon tetrachloride), 1,2-dichloroethane, chlorobenzene, perfluorobenzene, perfluorotoluene, freons, and others.

- The term "*nonpolar solvent*" means a solvent characterised by a zero or very small dipole moment. Examples of such solvents are pentane, hexane, octane, nonane, decane, benzene, toluene, tetrahydrofuran (THF) and its derivatives, diethyl ether, dichloromethane, ethyl acetate, chloroform, and
- 20 others.

The term "*DEDAM*" means diethyl diallylmalonate, used as a model diene in RCM reactions comparing activities of available precatalysts and catalysts for olefin metathesis reactions.

The term "*GC*" means gas chromatography.

- The term "*HPLC*" means high pressure liquid chromatography, and solvents designated as solvents for
- 25 "*HPLC*" are solvents of suitable purity for HPLC analysis.

The term "*NMR*" means nuclear magnetic resonance.

The term "*NHC*" means *N*-heterocyclic carbene.

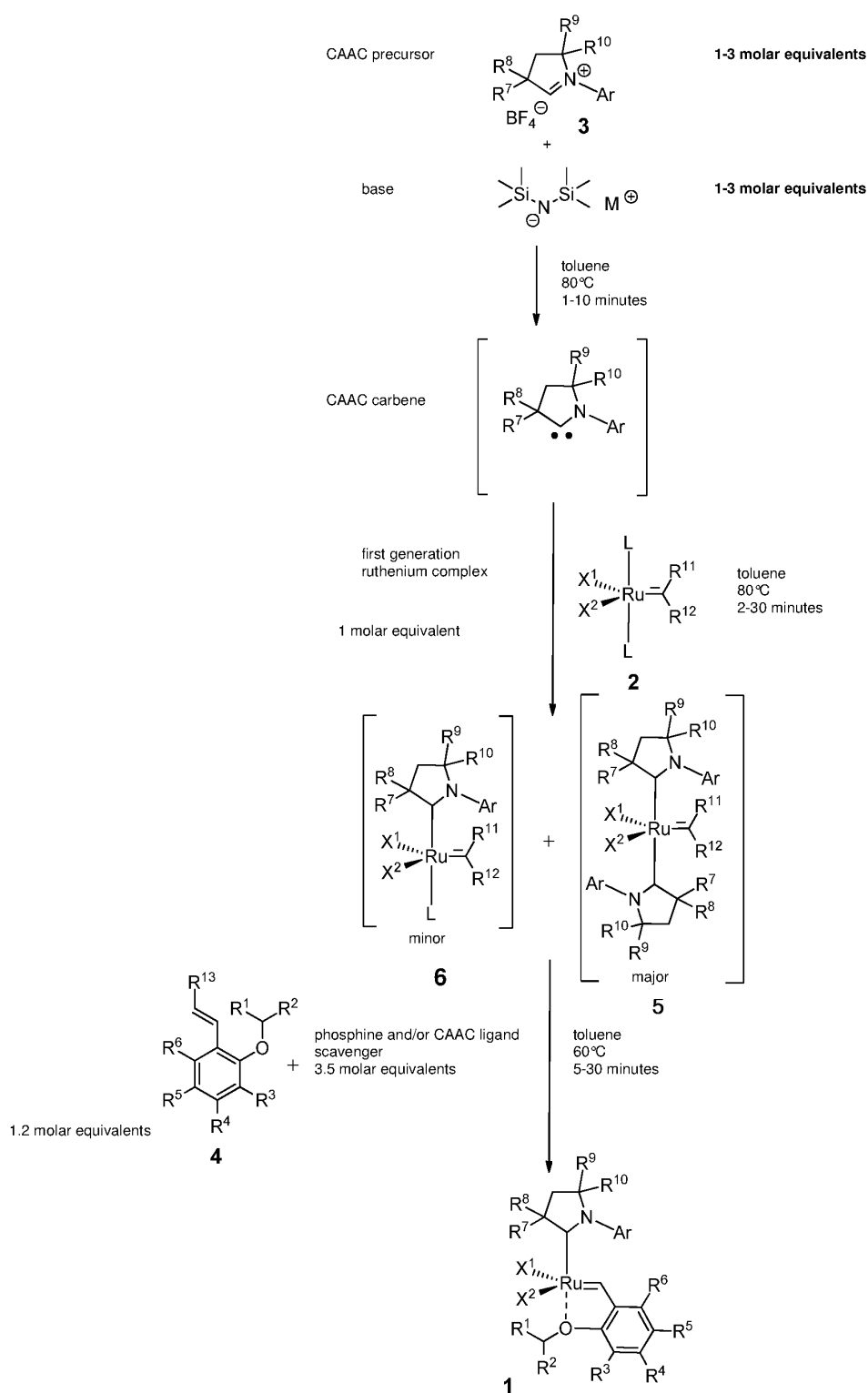
The term "*TLC*" means thin layer chromatography.

The term "*alkenylene*" means a compound having in its structure a double and triple bond (en-yne).

- 30 The term "*precatalyst*" means, in the case of ruthenium complexes, a 16-electrone chemical compound, which after one ligand dissociation or molecular reorganisation step is converted into a proper 14-electrone olefin metathesis catalyst, which takes an active part in the catalytic cycle.

Ruthenium complex compounds of the present invention are prepared by reactions shown on the following general reaction scheme, Scheme 1 and 2.

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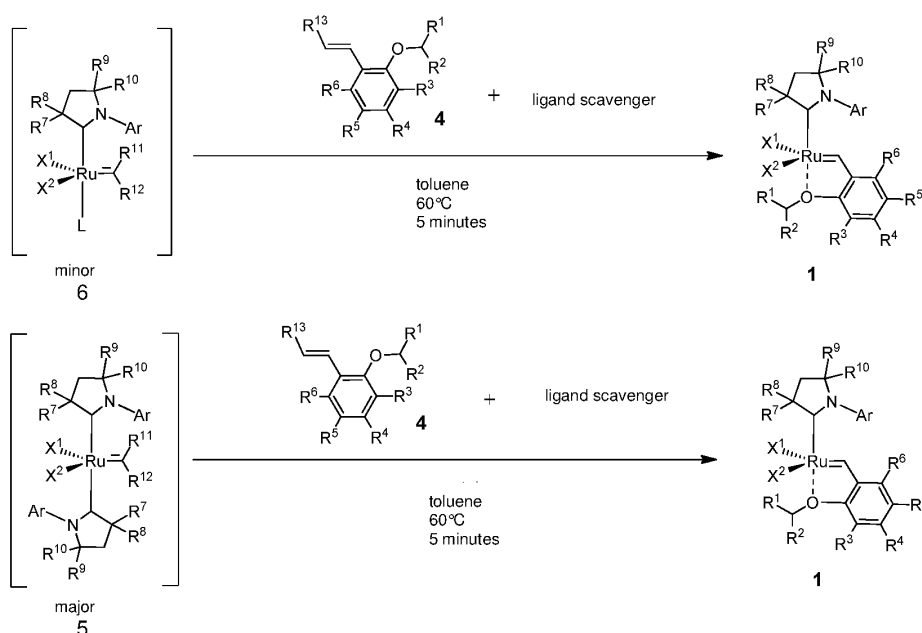


Scheme 1

Scheme 1 shows a general course of reactions in the individual steps of the method of preparation complex compounds represented by the Formula 1 according to the invention. First step is obtaining

CAAC carbene in a deprotonation reaction of the CAAC salt using a suitable base. The most preferable bases are hexamethyldisilazane salts [metal bis(trimethylsilyl)amides] represented by the Formula MHMDS, wherein M is an alkali metal, such as potassium or lithium. Process of deprotonation or contacting together suitable reagents could be conducted in many polar or nonpolar solvents. Preferably toluene is used as a solvent. In the following step, the CAAC carbene formed is contacted with first generation ruthenium complex containing in its structure two phosphine-type ligands.

It has been shown, that the main product of this reaction is a second generation complex containing two CAAC ligands. In the TLC analysis one could observe also small amounts of the other second generation complex, which most probably contains one CAAC ligand and one phosphine ligand, Scheme 1 and 2.

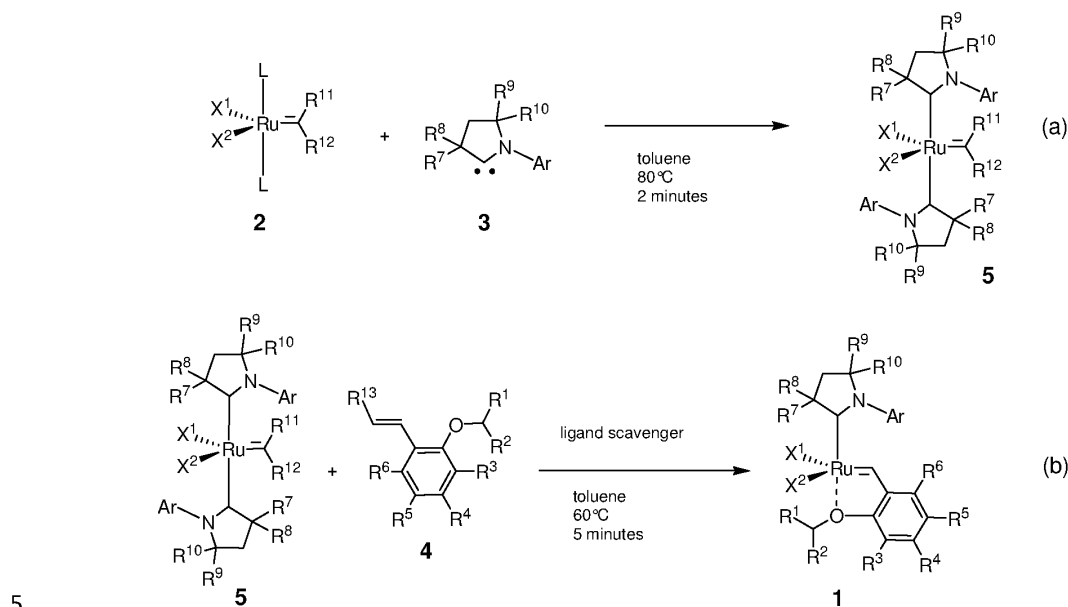


Scheme 2

The last process step is the addition of benzylidene ligand **4** to the mixture of unknown proportion of major and minor intermediates **5**, in the presence of phosphine ligand scavenger and/or CAAC ligand scavenger (Scheme 2). Scheme 2 shows only the proposed course of 16-electron ruthenium complex formation without detailed analysis of the metathesis process mechanism. Preferably, as a benzylidene ligand 2-isopropoxypropenylbenzene derivatives are used. It appeared that the preferable phosphine and/or CAAC ligand scavengers were copper(I) salts, including CuCl. Reactions shown in the Scheme 1 and 2 were conducted in a single reaction vessel without isolation of the intermediates (Embodiments I-XIV).

To confirm that the intermediate compound **5** takes part actively in the preparation process of the precatalysts represented by the Formula **1**, the previous one-pot type process was divided into two independent reaction parts, (a) and (b) in the Scheme 3. Ruthenium complexes represented by the general formula **5** were isolated and characterised with the NMR and MS analysis, confirming lack of phosphine ligand in the structure and presence of the two CAAC ligands. It has been shown, that compounds represented by the structure **5** in the reaction with benzylidene ligand **4** in the presence of CAAC ligand scavenger provide compounds represented by the Formula **1**. Reactions for individual steps

were shown in the Scheme 3 (part (a) in Embodiments **XV**, **XVI** and **XVIII** and part (b) in Embodiments **XVII** and **XIX**). Moreover, the inventors decided to check, whether intermediate compounds represented by the general formula **5** are active precatalysts in the olefin metathesis, what was shown in the Example **XXII**.



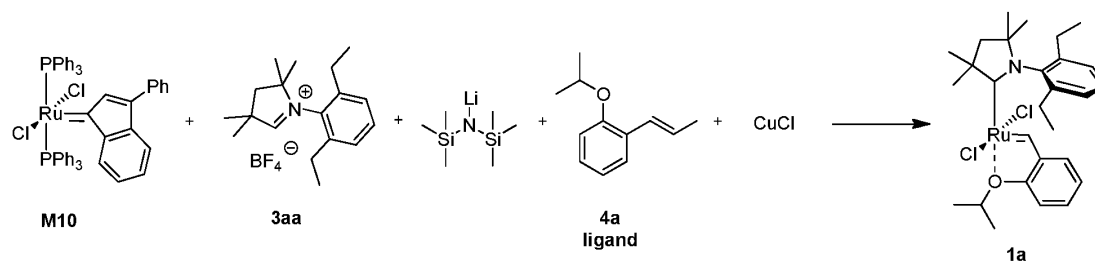
Scheme 3

In the examples described below the preparation methods and use of the new ruthenium complexes of the invention were illustrated. The examples shown below are provided for the better understanding of the invention and they are not intended to limit its scope in any way. Examples of the catalyst preparation of the invention confirm higher process yields and more preferable ruthenium complex preparation parameters on the industrial scale. Comparative Examples with known complexes used confirm that complexes of the invention show different catalytic properties.

EMBODIMENTS OF THE INVENTION

EXAMPLE I

Preparation method of precatalyst **1a**



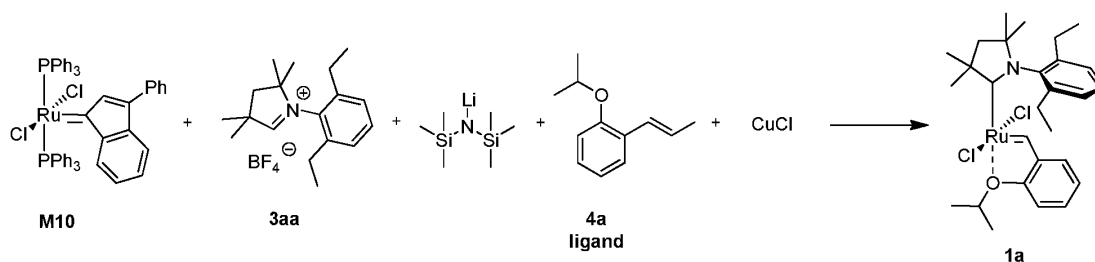
To salt **3aa** (1.73 g, 5.0 mmol, 2 molar equivalents) dry deoxygenated toluene (20 mL) was added in argon atmosphere. The mixture was heated to 80°C and solution of LiHMDS in toluene (1 M, 5.0 mL,

5.0 mmol, 2 molar equivalents) was added. After 1 minute solid complex **M10** (2.22 g, 2.5 mmol, 1 molar equivalent) was added. After 2 minutes the mixture was cooled down to 60°C. Benzyldiene ligand **4a** (0.529 g, 3.0 mmol, 1.2 molar equivalents) and CuCl (0.866 g, 8.75 mmol, 3.5 molar equivalents) were added. Reaction mixture was stirred for 5 minutes at 60°C and cooled down to the room temperature. The crude product was isolated by column chromatography on silica gel (eluent: toluene). Green fraction was collected and concentrated to dryness. The residue was dissolved in ethyl acetate and filtrated. The solvent was evaporated, the residue was washed with isopropanol and dried under high vacuum giving green crystalline solid – precatalyst **1a** (0.584 g, 40%).

¹H NMR (C₆D₆, 500 MHz): δ = 16.41 (s, 1H), 7.33-7.28 (m, 1H), 7.22-7.18 (m, 2H), 7.16-7.11 (m, 1H), 7.01 (dd, *J* = 7.6; 1.6 Hz, 1H), 6.64 (td, *J* = 7.4; 0.8 Hz, 1H), 6.46-6.42 (m, 1H), 4.67 (septet, *J* = 6.1 Hz, 1H), 2.87-2.78 (m, 2H), 2.45-2.35 (m, 2H), 2.23 (s, 6H), 1.77 (s, 2H), 1.70 (d, *J* = 6.1 Hz, 6H), 0.97-0.92 (m, 12H) ppm.

Example II

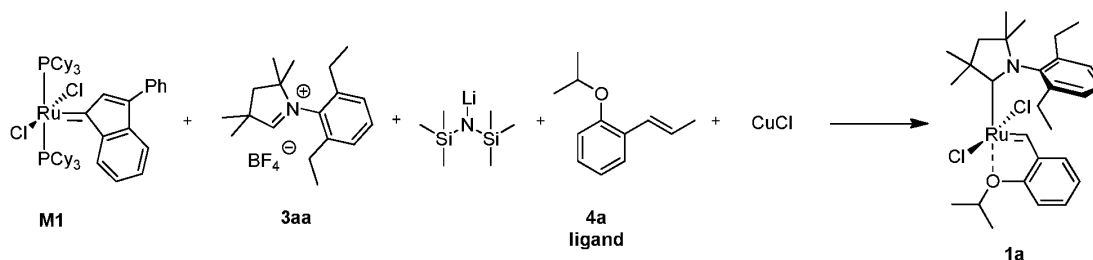
Preparation method of precatalyst **1a**; attempt with a greater amount of CAAC salt **3aa** – here 3 molar equivalents.



To salt **3aa** (1.40 g, 4.05 mmol, 3 molar equivalents) dry deoxygenated toluene (10 mL) was added in argon atmosphere. The mixture was heated to 80°C and solution of LiHMDS in toluene (1 M, 4.05 mL, 4.05 mmol, 3 molar equivalents) was added. After 1 minute solid complex **M10** (1.20 g, 1.35 mmol, 1 molar equivalent) was added. After 2 minutes the mixture was cooled down to 60°C. Ligand **4a** (0.286 g, 1.62 mmol, 1.2 molar equivalents) and CuCl (0.601 g, 6.08 mmol, 4.5 molar equivalents) were added. Reaction mixture was stirred for 5 minutes at 60°C and cooled down to the room temperature. The crude product was isolated by column chromatography on silica gel (eluent: toluene). Green fraction was collected and concentrated to dryness. The residue was dissolved in ethyl acetate and filtrated. The solvent was evaporated, the residue was washed with isopropanol and dried under high vacuum giving green crystalline solid – precatalyst **1a** (0.408 g, 52%). Comparison with **Example I**.

EXAMPLE III

Preparation method of Hoveyda-type precatalyst **1a** using other first generation precursor, here **M1** (Umicore M1™).



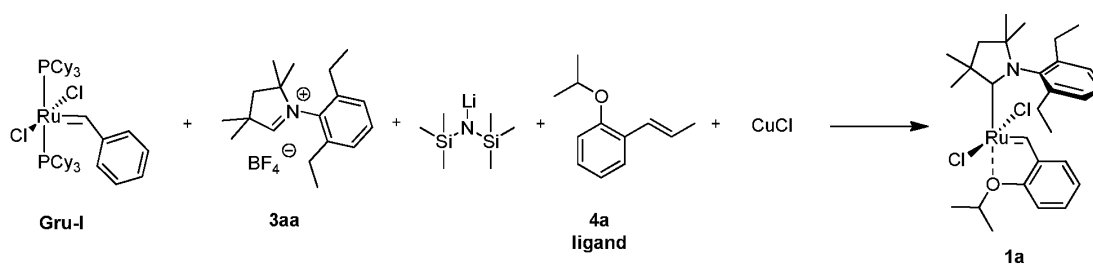
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To salt **3aa** (1.06 g, 3.07 mmol, 2 molar equivalents) dry deoxygenated toluene (12 mL) was added in argon atmosphere. The mixture was heated to 80°C and solution of LiHMDS in toluene (1 M, 3.07 mL, 3.07 mmol, 2 molar equivalents) was added. After 1 minute solid complex **M1** (1.42 g, 1.53 mmol, 1 molar equivalent) was added. After 10 minutes the mixture was cooled down to 60°C. Benzyldiene ligand **4a** (0.325 g, 1.84 mmol, 1.2 molar equivalents) and CuCl (0.532 g, 5.37 mmol, 3.5 molar equivalents) were added. Reaction mixture was stirred for 10 minutes at 60°C and cooled down to the room temperature. The crude product was isolated by column chromatography on silica gel (eluent: toluene). Green fraction was collected and concentrated to dryness. The residue was dissolved in ethyl acetate and filtrated. The solvent was evaporated, the residue was washed with isopropanol and dried under high vacuum giving green crystalline solid – precatalyst **1a** (0.520 g, 58%). Comparison with the **Example I**.

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EXAMPLE IV

Preparation method of precatalyst **1a** using other first generation precursor, here **Gru-I**.



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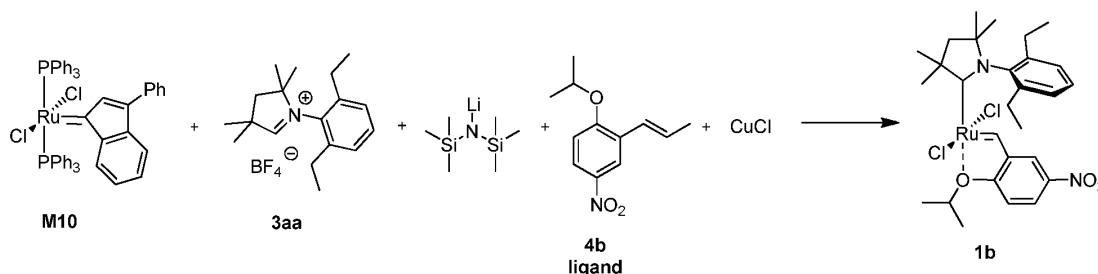
To salt **3aa** (1.04 g, 3.0 mmol, 2 molar equivalents) dry deoxygenated toluene (12 mL) was added in argon atmosphere. The mixture was heated to 80°C and solution of LiHMDS in toluene (1 M, 3.0 mL, 3.0 mmol, 2 molar equivalents) was added. After 1 minute solid complex **Gru-I** (1.23 g, 1.5 mmol, 1 molar equivalent) was added. After 30 minutes the mixture was cooled down to 60°C. Benzyldiene ligand **4a** (0.317 g, 1.8 mmol, 1.2 molar equivalents) and CuCl (0.520 g, 5.25 mmol, 3.5 molar equivalents) were added. Reaction mixture was stirred for 10 minutes at 60°C and cooled down to the room temperature. The crude product was isolated by column chromatography on silica gel (eluent: toluene). Green fraction was collected and concentrated to dryness. The residue was dissolved in ethyl acetate and filtrated. The

25

solvent was evaporated, the residue was washed with isopropanol and dried under high vacuum giving green crystalline solid – precatalyst **1a** (0.409 g, 47%). Comparison with **Example I**.

EXAMPLE V

Preparation method of precatalyst **1b** containing nitro group-activated benzylidene



5

To salt **3aa** (3.45 g, 10.0 mmol, 2 molar equivalents) dry deoxygenated toluene (40 mL) was added in argon atmosphere. The mixture was heated to 80°C and solution of LiHMDS in toluene (1 M, 10.0 mL, 10.0 mmol, 2 molar equivalents) was added. After 1 minute solid complex **M10** (4.43 g, 5.0 mmol, 1 molar equivalent) was added. After 2 minutes the mixture was cooled down to 60°C. Benzylidene ligand **4b** (1.33 g, 6.0 mmol, 1.2 molar equivalents) and CuCl (1.73 g, 17.5 mmol, 3.5 molar equivalents) were added. Reaction mixture was stirred for 5 minutes at 60°C and cooled down to the room temperature. The crude product was isolated by column chromatography on silica gel (eluent: toluene). Green fraction was collected and concentrated to dryness. The residue was dissolved in ethyl acetate and filtrated. The solvent was evaporated, the residue was washed with isopropanol and dried under high vacuum giving green crystalline solid – precatalyst **1b** (1.57 g, 50%).

¹H NMR (CD₂Cl₂, 500 MHz): δ = 16.29 (s, 1H), 8.46 (dd, *J* = 9.1; 2.7 Hz, 1H), 7.72-7.65 (m, 2H), 7.51 (d, *J* = 7.7 Hz, 2H), 7.08 (d, *J* = 8.7 Hz, 1H), 5.26 (septet, *J* = 6.1 Hz, 1H), 2.61-2.49 (m, 4H), 2.21 (s, 2H), 2.07 (s, 6H), 1.77 (d, *J* = 6.2 Hz, 6H), 1.33 (s, 6H), 0.91 (t, *J* = 7.4 Hz, 6H) ppm.

¹³C NMR (CD₂Cl₂, 125 MHz): δ = 290.4, 263.8, 165.6, 157.1, 143.7, 143.4, 138.8, 129.9, 127.7, 125.7, 118.3, 113.7, 79.4, 78.2, 56.5, 52.3, 29.9, 28.9, 25.3, 22.4, 14.9 ppm.

HRMS-ESI calculated for C₂₆H₃₉N₂O₃Ru [M-2Cl+H]⁺: 553.2006; found: 553.2004.

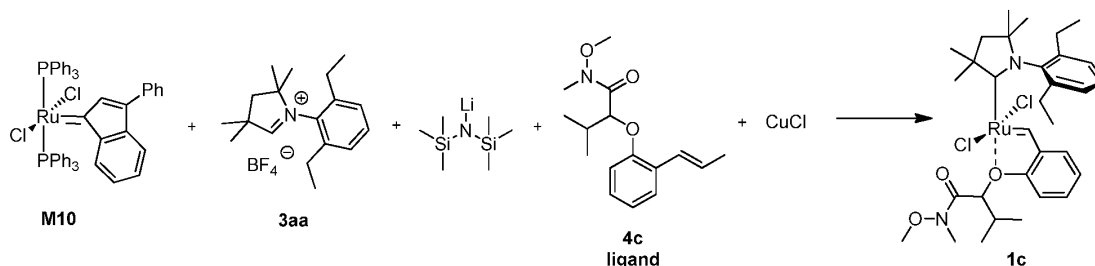
Elemental analysis: calculated for C₂₆H₃₈N₂Cl₂O₃Ru:

C 54.02; H 6.15; N 4.50; Cl 11.39; found: C 54.18; H 6.09; N 4.42; Cl 11.20.

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EXAMPLE VI

Preparation method of precatalyst **1c** containing hydroxamic group-activated benzylidene



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To salt **3aa** (3.45 g, 10.0 mmol, 2 molar equivalents) dry deoxygenated toluene (40 mL) was added in argon atmosphere. The mixture was heated to 80°C and solution of LiHMDS in toluene (1 M, 10.0 mL, 10.0 mmol, 2 molar equivalents) was added. After 1 minute solid complex **M10** (4.43 g, 5.0 mmol, 1 molar equivalent) was added. After 2 minutes the mixture was cooled down to 60°C. Benzylidene ligand **4c** (1.66 g, 6.0 mmol, 1.2 molar equivalents) and CuCl (1.73 g, 17.5 mmol, 3.5 molar equivalents) were added. Reaction mixture was stirred for 5 minutes at 60°C and cooled down to the room temperature. The crude product was isolated by column chromatography on silica gel (eluent: toluene → ethyl acetate/cyclohexane 3:7 v/v). Green fraction was collected and concentrated to dryness. The residue was dissolved in ethyl acetate and filtrated. The solvent was evaporated and the residue was dissolved in a minimal amount of methylene chloride and was added *n*-heptane. Methylene chloride was removed slowly on the evaporator, the resulting crystals were filtered off, washed with a small amount of *n*-heptane and dried under high vacuum giving green crystalline solid – precatalyst **1c** (1.05 g, 31%).

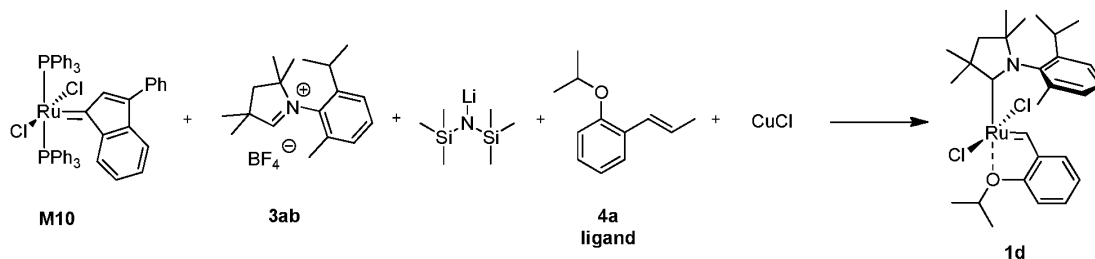
¹H NMR (CD₂Cl₂, 500 MHz): δ = 16.46 (s, 1H), 7.62-7.55 (m, 2H), 7.50-7.46 (m, 1H), 7.43-7.39 (m, 1H), 7.03 (d, *J* = 8.3 Hz, 1H), 6.97 (t, *J* = 7.4 Hz, 1H), 6.92-6.89 (m, 1H), 5.50 (d, *J* = 7.5 Hz, 1H), 3.75 (s, 3H), 3.39 (s, 3H), 2.90 (dq, *J* = 15.0; 7.4 Hz, 1H), 2.66 (dq, *J* = 15.0; 7.4 Hz, 1H), 2.58 (dq, *J* = 14.0; 7.0 Hz, 1H), 2.32 (q, *J* = 7.5 Hz, 2H), 2.28 (s, 3H), 2.25-2.21 (m, 1H), 2.15-2.11 (m, 1H), 1.94 (s, 3H), 1.31 (s, 3H), 1.22 (s, 3H), 1.11 (t, *J* = 7.4 Hz, 3H), 0.98 (dd, *J* = 9.2; 6.9 Hz, 6H), 0.79 (t, *J* = 7.4 Hz, 3H) ppm.

¹³C NMR (CD₂Cl₂, 125 MHz): δ = 305.2, 267.2, 170.0, 154.3, 146.0, 143.8, 143.4, 140.2, 130.0, 129.0, 127.2, 126.9, 123.6, 123.4, 113.2, 79.9, 79.8, 78.2, 62.3, 62.2, 56.3, 53.4, 32.6, 32.5, 31.3, 31.2, 30.9, 29.4, 29.3, 25.6, 25.5, 25.4, 25.1, 25.0, 19.9, 18.2, 14.8, 14.7, 14.6 ppm.

HRMS-ESI calculated for C₃₃H₄₉N₂O₄Ru [M-2Cl+CH₃O]⁺: 639.2740; found: 639.2718.

Elemental analysis: calculated for C₃₂H₄₆N₂Cl₂O₃Ru:

C 56.63; H 6.83; N 4.13; Cl 10.45; found: C 56.63; H 6.73; N 4.01; Cl 10.25.

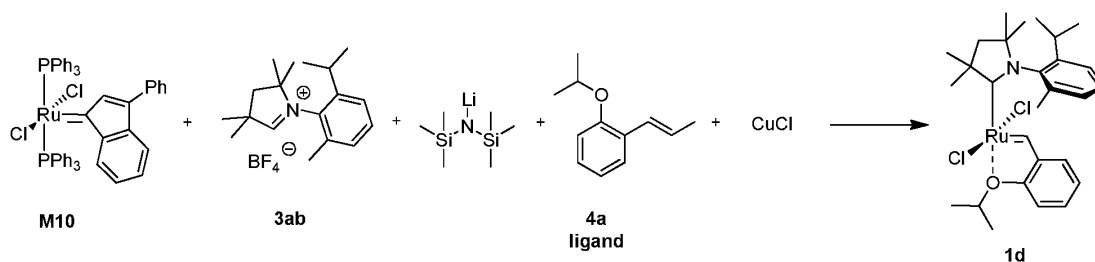
EXAMPLE VIIPreparation method of precatalyst **1d**

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To salt **3ab** (1.73 g, 5.0 mmol, 2 molar equivalents) dry deoxygenated toluene (20 mL) was added in argon atmosphere. The mixture was heated to 80°C and solution of LiHMDS in toluene (1 M, 5.0 mL, 5.0 mmol, 2 molar equivalents) was added. After 1 minute solid complex **M10** (2.22 g, 2.5 mmol, 1 molar equivalent) was added. After 2 minutes the mixture was cooled down to 60°C. Benzylidene ligand **4a** (0.529 g, 3.0 mmol, 1.2 molar equivalents) and CuCl (0.866 g, 8.75 mmol, 3.5 molar equivalents) were added. Reaction mixture was stirred for 5 minutes at 60°C and cooled down to the room temperature. The crude product was isolated by column chromatography on silica gel (eluent: toluene). Green fraction was collected and concentrated to dryness. The residue was dissolved in ethyl acetate and filtrated. The solvent was evaporated, the residue was washed with isopropanol and dried under high vacuum giving green crystalline solid – precatalyst **1d** (0.688 g, 47%).

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¹H NMR (CD₂Cl₂, 500 MHz): δ = 16.20 (s, 1H), 7.60-7.53 (m, 2H), 7.50-7.47 (m, 1H), 7.29 (ddd, *J* = 7.4; 1.7; 0.8 Hz, 1H), 6.97 (d, *J* = 8.3 Hz, 1H), 6.92-6.85 (m, 2H), 5.16 (sept, *J* = 6.1 Hz, 1H), 2.98 (sept, *J* = 6.6 Hz, 1H), 2.24 (s, 3H), 2.23-2.16 (m, 2H), 2.13 (s, 3H), 2.02 (s, 3H), 1.75 (d, *J* = 6.1 Hz, 3H), 1.71 (d, *J* = 6.1 Hz, 3H), 1.40 (s, 3H), 1.36 (s, 3H), 1.28 (d, *J* = 6.7 Hz, 3H), 0.67 (d, *J* = 6.5 Hz, 3H) ppm.

EXAMPLE VIIIPreparation method of precatalyst **1d**; attempt with a reduced amount of CAAC salt **3ab**.

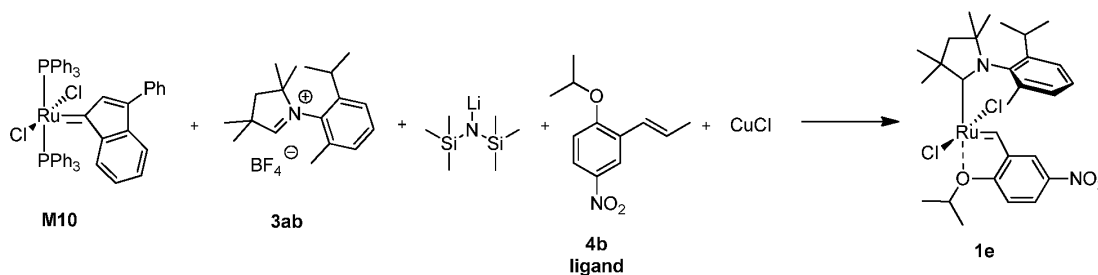
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To salt **3ab** (1.08 g, 3.13 mmol, 1.25 molar equivalents) dry deoxygenated toluene (22 mL) was added in argon atmosphere. The mixture was heated to 80°C and solution of LiHMDS in toluene (1 M, 3.0 mL, 3.0 mmol, 1.2 molar equivalents) was added. After 1 minute solid complex **M10** (2.22 g, 2.5 mmol, 1 molar equivalent) was added. After 2 minutes the mixture was cooled down to 60°C. Benzylidene ligand **4a** (0.529 g, 3.0 mmol, 1.2 molar equivalents) and CuCl (0.619 g, 6.25 mmol, 2.5 molar equivalents) were added. Reaction mixture was stirred for 5 minutes at 60°C and cooled down to the room temperature. The

crude product was isolated by column chromatography on silica gel (eluent: toluene). Green fraction was collected and concentrated to dryness. The residue was dissolved in ethyl acetate and filtrated. The solvent was evaporated, the residue was washed with isopropanol and dried under high vacuum giving green crystalline solid – precatalyst **1d** (0.596 g, 41%). Comparison with **Example VI**.

5 EXAMPLE IX

Preparation method of precatalyst **1e** containing nitro group-activated benzylidene



To salt **3ab** (1.73 g, 5.0 mmol, 2 molar equivalents) dry deoxygenated toluene (20 mL) was added in argon atmosphere. The mixture was heated to 80°C and solution of LiHMDS in toluene (1 M, 5.0 mL, 5.0 mmol, 2 molar equivalents) was added. After 1 minute solid complex **M10** (2.22 g, 2.5 mmol, 1 molar equivalent) was added. After 2 minutes the mixture was cooled down to 60°C. Benzylidene ligand **4b** (0.664 g, 3.0 mmol, 1.2 molar equivalents) and CuCl (0.866g, 8.75 mmol, 3.5 molar equivalents) were added. Reaction mixture was stirred for 5 minutes at 60°C and cooled down to the room temperature. The crude product was isolated by column chromatography on silica gel (eluent: toluene). Green fraction was collected and concentrated to dryness. The residue was dissolved in ethyl acetate and filtrated. The solvent was evaporated, the residue was washed with isopropanol and dried under high vacuum giving green crystalline solid – precatalyst **1e** (0.663 g, 42%).

¹H NMR (CD₂Cl₂, 500 MHz): δ = 16.19 (s, 1H), 8.45 (dd, *J* = 9.1; 2.7 Hz, 1H), 7.70 (d, *J* = 2.7 Hz, 1H), 7.65 (t, *J* = 7.7 Hz, 1H), 7.55 (dd, *J* = 8.0; 1.5 Hz, 1H), 7.35 (ddd, *J* = 7.5; 1.6; 0.7 Hz, 1H), 7.08 (d, *J* = 8.9 Hz, 1H), 5.26 (sept, *J* = 6.2 Hz, 1H), 2.97 (sept, *J* = 6.7 Hz, 1H), 2.26-2.19 (m, 5H), 2.13 (s, 3H), 2.03 (s, 3H), 1.77 (dd, *J* = 16.1; 6.1 Hz, 6H), 1.43 (s, 3H), 1.38 (s, 3H), 1.30 (d, *J* = 6.6 Hz, 3H), 0.68 (d, *J* = 6.5 Hz, 3H) ppm.

¹³C NMR (CD₂Cl₂, 125 MHz): δ = 290.2, 264.6, 157.2, 149.1, 143.5, 143.4, 138.5, 138.4, 130.4, 130.0, 126.5, 125.8, 118.4, 113.7, 79.4, 78.2, 56.6, 52.3, 29.9, 29.7, 29.6, 29.1, 28.9, 26.3, 24.3, 22.4, 22.3, 21.8 ppm.

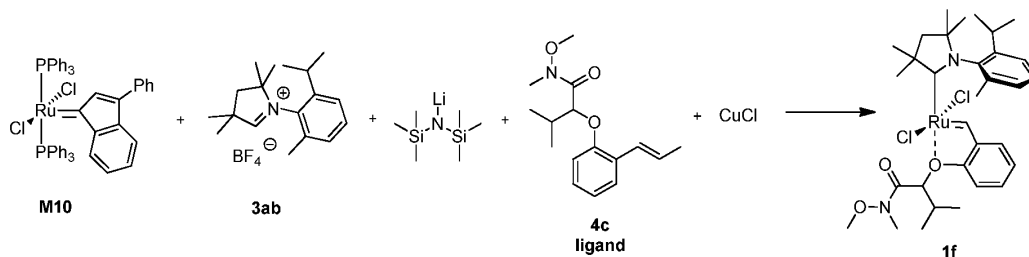
HRMS-ESI calculated for C₂₈H₃₈ClN₂O₃Ru [M-Cl]⁺: 587.1613; found: 587.1636.

Elemental analysis: calculated for C₂₈H₃₈N₂Cl₂O₃Ru:

C 54.02; H 6.15; N 4.50; Cl 11.39; found: C 54.19; H 6.18; N 4.37; Cl 11.21.

EXAMPLE X

Preparation method of precatalyst **1f** containing hydroxamic group-activated benzylidene



- 5 To salt **3ab** (1.73 g, 5.0 mmol, 2 molar equivalents) dry deoxygenated toluene (20 mL) was added in argon atmosphere. The mixture was heated to 80°C and solution of LiHMDS in toluene (1 M, 5.0 mL, 5.0 mmol, 2 molar equivalents) was added. After 1 minute solid complex **M10** (2.22 g, 2.5 mmol, 1 molar equivalent) was added. After 2 minutes the mixture was cooled down to 60°C. Benzylidene ligand **4c** (0.832 g, 3.0 mmol, 1.2 molar equivalents) and CuCl (0.866 g, 8.75 mmol, 3.5 molar equivalents) were added. Reaction mixture was stirred for 5 minutes at 60°C and cooled down to the room temperature. The crude product was isolated by column chromatography on silica gel (eluent: toluene → ethyl acetate/cyclohexane 3:7 v/v). Green fraction was collected and concentrated to dryness. The residue was dissolved in ethyl acetate and filtrated. The solvent was evaporated and the residue was dissolved in a minimal amount of methylene chloride and *n*-heptane was added. Methylene chloride was removed slowly on the evaporator, the resulting crystals were filtered off, washed with a small amount of *n*-heptane and dried under high vacuum giving green crystalline solid – precatalyst **1f** (0.390 g, 23%). A mixture of isomers A:B = 1.8:1.

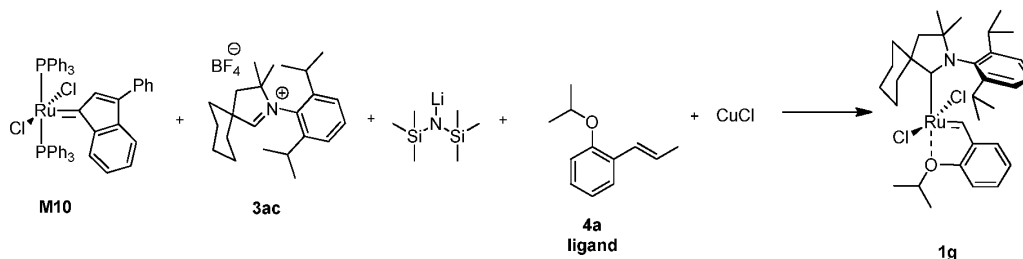
Due to a very complex ^1H NMR spectrum only the characteristic benzylidene proton shifts were given: isomer A: singlet 16.42 ppm, isomer B: singlet 16.45 ppm (CD_2Cl_2).

- 20 ^{13}C NMR (CD_2Cl_2 , 125 MHz): δ = 304.0 (A), 303.5 (B), 268.1 (B), 267.9 (A), 170.0 (A), 169.4 (B), 154.4 (A), 154.3 (B), 149.0 (B), 148.6 (A), 145.4 (B), 145.3 (A), 139.9 (B), 139.8 (A), 138.8 (A), 138.5 (B), 130.2 (A), 130.16 (B), 130.0 (A), 129.9 (B), 129.2 (B), 129.2 (A), 126.2 (B), 125.9 (A), 123.8 (B), 123.8 (A), 123.7 (B), 123.5 (A), 113.3 (B), 113.1 (A), 79.8 (B), 79.6 (A), 78.1 (B), 78.0 (A), 62.4 (A), 62.2 (B), 56.4 (B), 56.3 (A), 53.7 (A), 53.5 (B), 32.6 (A), 32.4 (B), 31.3 (A), 31.1 (B), 30.8 (B), 30.8 (B), 30.7 (A), 30.6 (A), 29.0 (B), 28.9 (A), 28.7 (B), 28.6 (A), 26.9, 24.9 (A), 24.8 (B), 22.3 (A), 21.7 (B), 20.0 (B), 19.9 (A), 18.2 ppm.

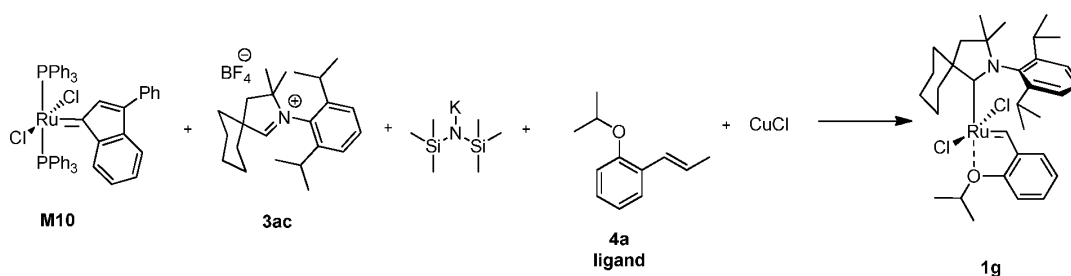
HRMS-ESI calculated for $\text{C}_{33}\text{H}_{49}\text{N}_2\text{O}_4\text{Ru}$ $[\text{M}-2\text{Cl}+\text{CH}_3\text{O}]^+$: 639.2740; found: 639.2756.

Elemental analysis: calculated for $\text{C}_{32}\text{H}_{46}\text{N}_2\text{Cl}_2\text{O}_3\text{Ru}$:

C 56.63; H 6.83; N 4.13; Cl 10.45; found: C 56.69; H 6.80; N 4.07; Cl 10.41.

EXAMPLE XIPreparation method of precatalyst **1g**

- 5 To salt **3ac** (0.413 g, 1.0 mmol, 2 molar equivalents) dry deoxygenated toluene (4 mL) was added in argon atmosphere. The mixture was heated to 80°C and solution of LiHMDS in toluene (1 M, 1.0 mL, 1.0 mmol, 2 molar equivalents) was added. After 1 minute solid complex **M10** (0.443 g, 0.5 mmol, 1 molar equivalent) was added. After 2 minutes the mixture was cooled down to 60°C. Benzylidene ligand **4a** (0.106 g, 0.6 mmol, 1.2 molar equivalents) and CuCl (0.173 g, 1.75 mmol, 3.5 molar equivalents) were added.
- 10 Reaction mixture was stirred for 25 minutes at 60°C and cooled down to the room temperature. The crude product was isolated by column chromatography on silica gel (eluent: toluene). Green fraction was collected and concentrated to dryness. The residue was dissolved in ethyl acetate and filtrated. The solvent was evaporated, the residue was washed with isopropanol and dried under high vacuum giving green crystalline solid – precatalyst **1g** (0.118 g, 37%).
- 15 ¹H NMR (C₆D₆, 500 MHz): δ = 16.56 (s, 1H), 7.38-7.35 (m, 1H), 7.28-7.25 (m, 2H), 7.14-7.11 (m, 1H), 7.03-7.00 (m, 1H), 6.65 (t, *J* = 7.4 Hz, 1H), 6.44 (d, *J* = 8.3 Hz, 1H), 4.66 (sept, *J* = 6.0 Hz, 1H), 3.77 (td, *J* = 13.0; 3.4 Hz, 2H), 3.21 (sept, *J* = 6.4 Hz, 2H), 2.50 (d, *J* = 12.7 Hz, 2H), 1.93 (s, 2H), 1.90-1.85 (m, 2H), 1.74 (d, *J* = 6.1 Hz, 6H), 1.70-1.60 (m, 2H), 1.43-1.34 (m, 2H), 1.16 (d, *J* = 6.6 Hz, 6H), 1.00 (s, 6H), 0.93 (d, *J* = 6.4 Hz, 6H) ppm.

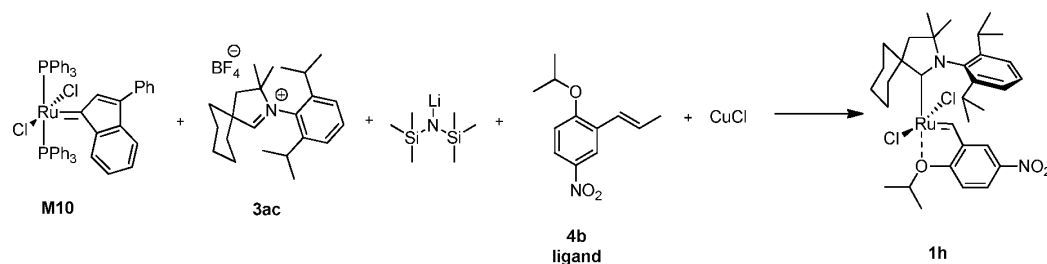
20 Example XIIPreparation method of precatalyst **1g**; attempt with other base to generate CAAC carbene – here KHMDS.

- 25 To salt **3ac** (1.65 g, 4.0 mmol, 2 molar equivalents) dry deoxygenated toluene (12 mL) was added in argon atmosphere. The mixture was heated to 80°C and solution of KHMDS in toluene (0.5M, 8.0 mL, 4.0 mmol, 2 molar equivalents) was added. After 1 minute solid complex **M10** (1.77 g, 2.0 mmol, 1 molar equivalent) was added. After 2 minutes the mixture was cooled down to 60°C. Benzylidene ligand **4a** (0.423 g, 2.4 mmol, 1.2 molar equivalents) and CuCl (0.693 g, 7.0 mmol, 3.5 molar equivalents) were

added. Reaction mixture was stirred for 25 minutes at 60°C and cooled down to the room temperature. The crude product was isolated by column chromatography on silica gel (eluent: toluene). Green fraction was collected and concentrated to dryness. The residue was dissolved in ethyl acetate and filtrated. The solvent was evaporated, the residue was washed with isopropanol and dried under high vacuum giving green crystalline solid – precatalyst **1g** (0.580 g, 45%). Comparison with **Example XI**.

EXAMPLE XIII

Preparation method of precatalyst **1h** containing nitro group-activated benzylidene



To salt **3ac** (1.65 g, 4.0 mmol, 2 molar equivalents) dry deoxygenated toluene (16 mL) was added in argon atmosphere. The mixture was heated to 80°C and solution of LiHMDS in toluene (1 M, 4.0 mL, 4.0 mmol, 2 molar equivalents) was added. After 1 minute solid complex **M10** (1.77 g, 2.0 mmol, 1 molar equivalent) was added. After 2 minutes the mixture was cooled down to 60°C. Benzylidene ligand **4b** (0.531 g, 2.4 mmol, 1.2 molar equivalents) and CuCl (0.693 g, 7.0 mmol, 3.5 molar equivalents) were added. Reaction mixture was stirred for 25 minutes at 60°C and cooled down to the room temperature. The crude product was isolated by column chromatography on silica gel (eluent: toluene). Green fraction was collected and concentrated to dryness. The residue was dissolved in ethyl acetate and filtrated. The solvent was evaporated, the residue was washed with isopropanol and dried under high vacuum giving green crystalline solid – precatalyst **1h** (0.550 g, 40%).

¹H NMR (CD₂Cl₂, 500 MHz): δ = 16.42 (s, 1H), 8.44 (dd, *J* = 9.1; 2.7 Hz, 1H), 7.71 (t, *J* = 7.8 Hz, 1H), 7.65 (d, *J* = 2.7 Hz, 1H), 7.51 (d, *J* = 7.8 Hz, 2H), 7.10-7.07 (m, 1H), 5.25 (sept, *J* = 5.9 Hz, 1H), 3.30-3.21 (m, 2H), 2.96 (sept, *J* = 6.6 Hz, 2H), 2.31 (s, 2H), 2.28-2.22 (m, 2H), 1.96-1.89 (m, 2H), 1.78 (d, *J* = 6.1 Hz, 6H), 1.60-1.46 (m, 4H), 1.35 (s, 6H), 1.26 (d, *J* = 6.6 Hz, 6H), 0.64 (d, *J* = 6.4 Hz, 6H) ppm.

¹³C NMR (CD₂Cl₂, 125 MHz): δ = 288.9, 264.7, 157.5, 148.7, 143.3, 142.9, 136.7, 130.4, 126.5, 125.7, 118.4, 113.8, 79.0, 78.2, 62.8, 44.9, 35.3, 30.8, 28.9, 26.8, 26.1, 24.6, 23.6, 22.5 ppm.

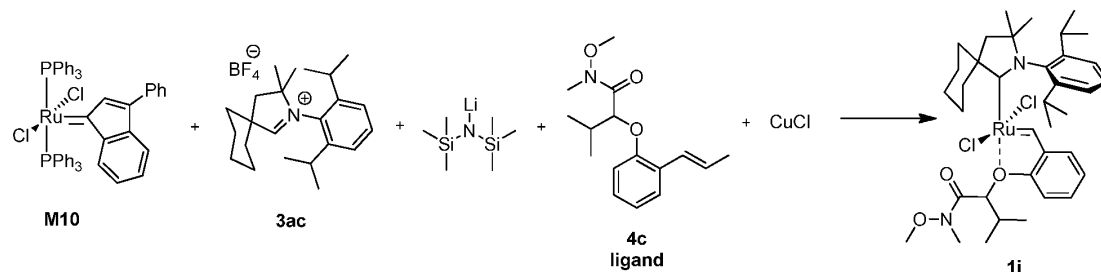
HRMS-ESI calculated for C₃₃H₄₇N₂O₃Ru [M-2Cl+H]⁺: 621.2634; found: 621.2630.

Elemental analysis: calculated for C₃₃H₄₆N₂Cl₂O₃Ru:

C 57.38; H 6.71; N 4.06; Cl 10.27; found: C 57.27; H 6.58; N 4.18; Cl 10.12.

EXAMPLE XIV

Preparation method of precatalyst **1i** containing hydroxamic group-activated benzylidene



- 5 To salt **3ac** (1.16 g, 2.8 mmol, 2 molar equivalents) dry deoxygenated toluene (11 mL) was added in argon atmosphere. The mixture was heated to 80°C and solution of LiHMDS in toluene (1 M, 2.8 mL, 2.8 mmol, 2 molar equivalents) was added. After 1 minute solid complex **M10** (1.24 g, 1.4 mmol, 1 molar equivalent) was added. After 2 minutes the mixture was cooled down to 60°C. Benzylidene ligand **4c** (0.466 g, 1.68 mmol, 1.2 molar equivalents) and CuCl (0.485 g, 4.9 mmol, 3.5 molar equivalents) were
- 10 added. Reaction mixture was stirred for 5 minutes at 60°C and cooled down to the room temperature. The crude product was isolated by column chromatography on silica gel (eluent: toluene → ethyl acetate/cyclohexane 3:7 v/v). Green fraction was collected and concentrated to dryness. The residue was dissolved in ethyl acetate and filtrated. The solvent was evaporated and the residue was dissolved in a minimal amount of methylene chloride and *n*-heptane was added. Methylene chloride was removed
- 15 slowly on the evaporator, the resulting crystals were filtered off, washed with a small amount of *n*-heptane and dried under high vacuum giving green crystalline solid - precatalyst **1i** (0.324 g, 31%).

¹H NMR (CD₂Cl₂, 500 MHz): δ = 16.74 (s, 1H), 7.62-7.55 (m, 1H), 7.48-7.38 (m, 2H), 7.28 (d, *J* = 7.7 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 1H), 6.93 (td, *J* = 7.4; 0.8 Hz, 1H), 6.84 (dd, *J* = 7.5; 1.7 Hz, 1H), 5.51 (d, *J* = 8.3 Hz, 1H), 3.73 (s, 3H), 3.35 (s, 3H), 3.16 (sept, *J* = 6.5 Hz, 1H), 2.80-2.70 (m, 2H), 2.65 (sept, *J* = 6.7 Hz, 1H), 2.22 (t, *J* = 6.3 Hz, 2H), 1.36 (s, 3H), 1.33 (s, 3H), 1.32-1.28 (m, 6H), 1.25 (s, 3H), 1.19 (dd, *J* = 15.4; 6.6 Hz, 6H), 0.98 (dd, *J* = 8.8; 6.8 Hz, 6H), 0.76 (d, *J* = 6.3 Hz, 3H), 0.57 (d, *J* = 6.4 Hz, 3H) ppm.

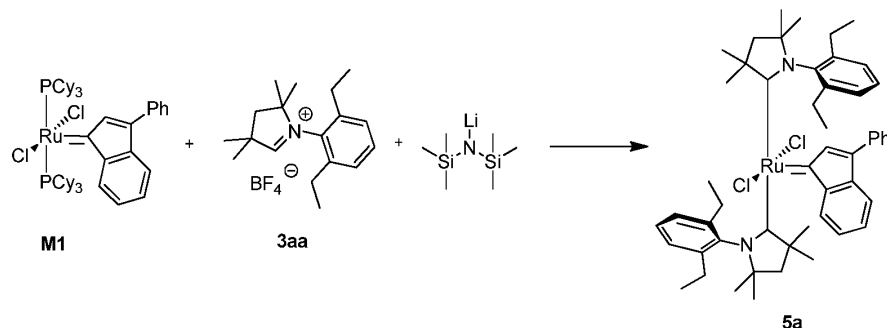
¹³C NMR (CD₂Cl₂, 125 MHz): δ = 299.3, 267.8, 169.1, 154.6, 148.8, 148.6, 145.1, 144.1, 137.8, 132.9, 130.2, 130.0, 129.7, 126.3, 126.0, 125.1, 124.2, 123.4, 113.4, 81.5, 79.5, 78.1, 62.3, 62.1, 58.3, 45.8, 45.5, 37.3, 35.5, 34.6, 32.5, 32.0, 31.7, 30.2, 29.9, 29.6, 29.1, 28.6, 27.5, 27.2, 26.5, 25.8, 25.6, 25.0, 24.8, 24.0, 23.8, 23.7, 22.4, 19.9, 18.3 ppm.

LRMS-ESI calculated for C₃₈H₅₇N₂O₄Ru [M-2Cl+CH₃O]⁺: 707.3; found: 707.3.

HRMS-ESI calculated for C₃₇H₅₄N₂O₃NaCl₂Ru [M+Na]⁺: 769.2453; found 769.2437.

Example XV

Preparation method of intermediate **5a** from first generation precursor **M1**.



- 5 To salt **3aa** (1.20 g, 3.48 mmol, 2 molar equivalents) dry deoxygenated toluene (14 mL) was added in argon atmosphere. The mixture was heated to 80°C and solution of LiHMDS in toluene (1 M, 3.48 mL, 3.48 mmol, 2 molar equivalents) was added. After 1 minute solid complex **M1** (1.60 g, 1.74 mmol, 1 molar equivalent) was added. After 20 minutes the mixture was cooled down to the room temperature. Reaction mixture was filtrated through a small amount of silica gel and washed with toluene. The crude product
- 10 was isolated by column chromatography on silica gel (eluent: ethyl acetate/cyclohexane 1:9 v/v). Red fraction was collected and concentrated to dryness. It was dissolved in *n*-pentane and slowly concentrated to dryness (the product crystallised during solvent removal). Red crystalline solid was obtained – an intermediate compound **5a** (1.07 g, 70%).

- ¹H NMR** (C₆D₆, 500 MHz): δ = 9.74 (d, *J* = 7.7 Hz, 0.25H), 9.09 (d, *J* = 7.3 Hz, 0.5H), 8.16 (s, 0.25H), 7.95-7.75 (m, 2H), 7.55-7.18 (m, 6H), 7.10-6.20 (m, 7H), 3.86-3.66 (m, 1H), 3.30-2.50 (m, 6H), 2.37 (d, *J* = 13.0 Hz, 9H), 1.75-1.22 (m, 12H), 1.10-0.85 (m, 20H) ppm.

- ¹³C NMR** (CD₂Cl₂, 125 MHz): δ = 279.9, 278.5, 277.8, 276.2, 145.5, 144.1, 143.6, 143.5, 141.3, 141.1, 140.8, 140.7, 140.2, 139.0, 138.6, 138.4, 137.9, 137.6, 134.3, 134.1, 130.6, 129.8, 129.4, 129.2, 128.2, 127.9, 127.6, 127.4, 127.0, 126.9, 126.7, 125.7, 125.5, 124.9, 124.7, 116.5, 116.1, 81.3, 79.7, 61.5, 56.9, 56.4, 55.0, 34.7, 32.5, 32.0, 31.5, 31.0, 30.5, 30.3, 30.0, 29.9, 29.6, 29.2, 27.5, 27.4, 25.3, 25.2, 24.7, 22.9, 14.8, 14.7, 14.4, 13.5, 13.2, 12.9 ppm.

LRMS-ESI calculated for C₅₁H₆₄ClN₂Ru [M-Cl]⁺: 841.4; found: 841.4.

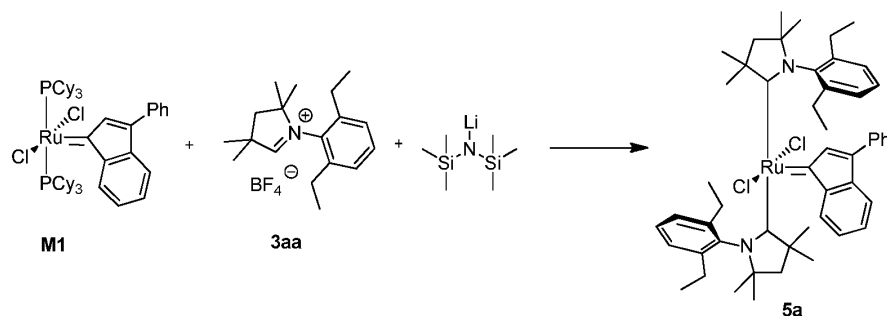
HRMS-ESI calculated for C₅₁H₆₄N₂Cl₂Ru [M]⁺: 876.3490; found 876.3471.

Elemental analysis: calculated for C₅₁H₆₄N₂Cl₂Ru:

- 25 C 69.84; H 7.36; N 3.19; Cl 8.08; found: C 69.88; H 7.22; N 3.21; Cl 8.05.

Example XVI

Preparation method of intermediate **5a** from precursor **M1** – attempt with a greater amount CAAC salt **3aa** – here 3 molar equivalents.

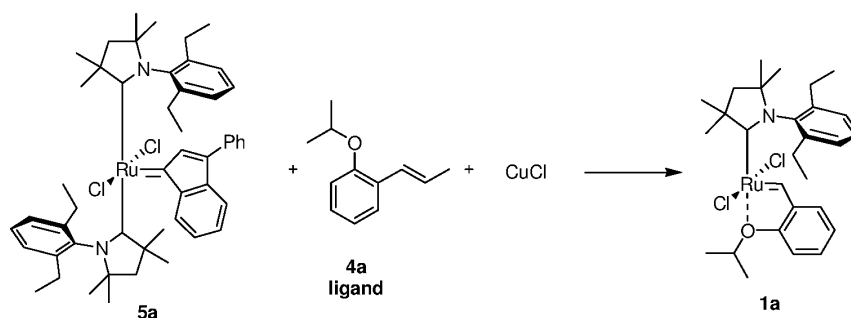


5

To salt **3aa** (1.40 g, 4.05 mmol, 3 molar equivalents) dry deoxygenated toluene (10 mL) was added in argon atmosphere. The mixture was heated to 80°C and solution of LiHMDS in toluene (1 M, 4.05 mL, 4.05 mmol, 3 molar equivalents) was added. After 1 minute solid complex **M1** (1.25 g, 1.35 mmol, 1 molar equivalent) was added. After 5 minutes the mixture was cooled down to the room temperature. Reaction mixture was filtrated through a small amount of silica gel and washed with toluene. The crude product was isolated by column chromatography on silica gel (eluent: ethyl acetate/cyclohexane 1:9 v/v). Red fraction was collected and concentrated to dryness. It was dissolved in *n*-pentane and slowly concentrated to dryness (the product crystallised during solvent removal). Red crystalline solid was obtained – an intermediate compound **5a** (1.02 g, 86%). Comparison with **Example XV**.

15 **Example XVII**

Preparation method of precatalyst **1a** – one-step procedure from intermediate **5a**.

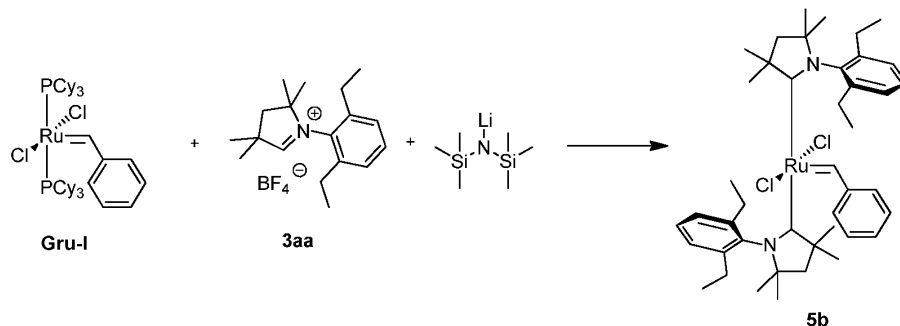


To the solution of an intermediate **5a** (0.948 g, 1.08 mmol, 1 molar equivalent) in dry deoxygenated toluene (10 mL) at 60°C benzylidene ligand **4a** (0.228 g, 1.29 mmol, 1.2 molar equivalents) and CuCl (0.214 g, 2.16 mmol, 2 molar equivalents) were added. Reaction mixture was stirred for 30 minutes and cooled down to the room temperature. The crude product was isolated by column chromatography on silica gel (eluent: toluene). Green fraction was collected and concentrated to dryness. The residue was dissolved in ethyl acetate and filtrated. The solvent was evaporated, the residue was washed with isopropanol and dried under high vacuum giving green crystalline solid – precatalyst **1a** (0.390 g, 62%).

25

Example XVIII

Preparation method of intermediate **5b** from first generation precursor **Gru-I**.



- 5 To salt **3aa** (2.76 g, 8.0 mmol, 2 molar equivalents) dry deoxygenated toluene (32 mL) was added in argon atmosphere. The mixture was heated to 80°C and solution of LiHMDS in toluene (1 M, 8.0 mL, 8.0 mmol, 2 molar equivalents) was added. After 2 minutes solid complex **Gru-I** (3.29 g, 4.0 mmol, 1 molar equivalent) was added. After 25 minutes the mixture was cooled down to the room temperature. Reaction mixture was filtrated through a small amount of silica gel and washed with toluene. The crude product was isolated by column chromatography on silica gel (eluent: ethyl acetate/cyclohexane 1:9 v/v). Brown fraction was collected and concentrated to dryness. It was dissolved in *n*-pentane and slowly concentrated (the product crystallised during solvent removal). It was filtrated off and washed with cold *n*-pentane. Brown crystalline solid was obtained – an intermediate compound **5b** (1.55 g, 50%).

- 15 A mixture of isomers A:B = 3.2:1. Due to a very complex ^1H NMR spectrum only the characteristic benzyldiene proton shifts were given: isomer A: singlet 17.60 ppm, isomer B: singlet 18.52 ppm (CD_2Cl_2).

^{13}C NMR (CD_2Cl_2 , 125 MHz): δ = 283.7, 280.0, 279.9, 278.7, 150.6, 148.3, 143.7, 143.1, 141.6, 141.0, 140.7, 139.7, 139.0, 138.3, 132.5, 131.7, 131.3, 129.7, 128.5, 128.4, 127.7, 127.5, 127.4, 127.3, 127.2, 125.7, 125.5, 125.1, 124.8, 81.0, 79.5, 79.4, 59.0, 56.7, 56.1, 53.7, 53.4, 32.3, 31.7, 31.1, 30.9, 30.6, 30.2, 29.6, 29.0, 28.5, 28.2, 27.3, 27.1, 25.7, 25.4, 24.4, 22.9, 15.2, 14.9, 14.5, 14.4, 12.5, 12.4 ppm.

- 20 LRMS-ESI calculated for $\text{C}_{43}\text{H}_{60}\text{ClN}_2\text{Ru}$ $[\text{M}-\text{Cl}]^+$: 741.3; found: 741.3.

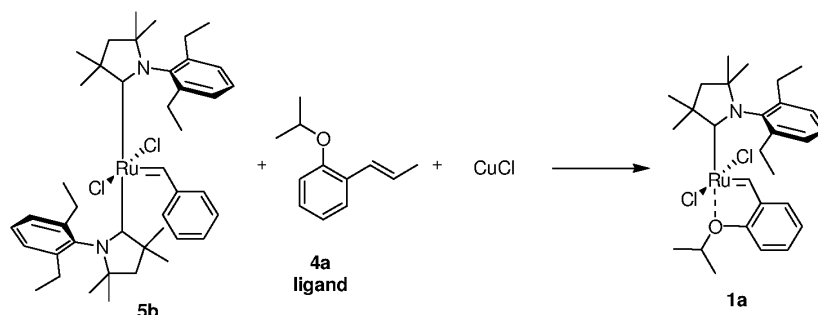
HRMS-ESI calculated for $\text{C}_{43}\text{H}_{60}\text{N}_2\text{Cl}_2\text{Ru}$ $[\text{M}]^+$: 776.3177; found 776.3156.

Elemental analysis: calculated for $\text{C}_{43}\text{H}_{60}\text{N}_2\text{Cl}_2\text{Ru}$:

C 66.47; H 7.78; N 3.61; Cl 9.13; found: C 66.42; H 7.75; N 3.59; Cl 9.18.

Example XIX

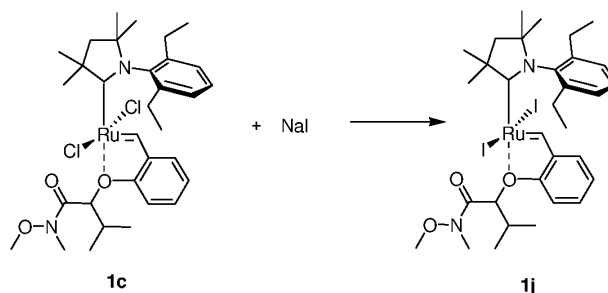
Preparation method of precatalyst **1a** from intermediate **5b**.



- 5 To the solution of intermediate **5b** (0.801 g, 1.03 mmol, 1 molar equivalent) in dry deoxygenated toluene (10 mL) at 60°C benzylidene ligand **4a** (0.217 g, 1.23 mmol, 1.2 molar equivalents) and CuCl (0.204 g, 2.06 mmol, 2 molar equivalents) were added. Reaction mixture was stirred for 10 minutes and cooled down to the room temperature. The crude product was isolated by column chromatography on silica gel (eluent: toluene). Green fraction was collected and concentrated to dryness. The residue was dissolved in ethyl acetate and filtrated. The solvent was evaporated, the residue was washed with isopropanol and dried under high vacuum giving green crystalline solid – precatalyst **1a** (0.385 g, 65%).

Example XX

Preparation method of precatalyst **1j** containing hydroxamic group-activated benzylidene and iodide ligands.



15

- To suspension of sodium iodide (1.04 g, 6.97 mmol, 30 molar equivalents) in acetone (2.3 mL) solid precatalyst **1c** (0.158 g, 0.232 mmol, 1 molar equivalent) was added. The whole was stirred at room temperature for 3 hours and then concentrated to dryness. The residue was dissolved in methylene chloride and inorganic salts were removed by filtration. The residue was filtrated through a small amount of silica gel (eluent ethyl acetate/cyclohexane 3:7 v/v). The solvent was evaporated and the residue was dissolved in a minimal amount of methylene chloride and *n*-heptane was added. Methylene chloride was removed slowly on the evaporator, the resulting crystals were filtered off, washed with a small amount of *n*-heptane and dried under high vacuum giving green crystalline solid **1j** (0.178 g, 89%).

- ¹H NMR (CD₂Cl₂, 500 MHz): δ = 15.83 (s, 1H), 7.60 (dt, *J* = 8.7; 4.6 Hz, 1H), 7.57-7.52 (m, 1H), 7.47-7.44 (m, 1H), 7.42-7.38 (m, 1H), 7.03 (d, *J* = 8.3 Hz, 1H), 6.95 (d, *J* = 4.5 Hz, 2H), 5.50 (d, *J* = 7.7 Hz, 1H), 3.87 (s, 3H), 3.41 (s, 3H), 3.24 (dq, *J* = 15.1; 7.5 Hz, 1H), 2.80-2.62 (m, 3H), 2.44-2.36 (m, 4H), 2.24-2.20

25

(m, 1H), 2.15 (s, 3H), 2.14-2.10 (m, 1H), 1.35 (s, 3H), 1.26 (s, 3H), 1.20 (t, $J = 7.4$ Hz, 3H), 1.04 (dd, $J = 7.0$; 5.3 Hz, 6H), 0.94 (t, $J = 7.4$ Hz, 3H) ppm.

^{13}C NMR (CD_2Cl_2 , 125 MHz): $\delta = 306.5, 271.3, 170.8, 155.0, 146.3, 144.1, 143.7, 140.3, 130.2, 129.0, 127.3, 127.0, 123.8, 123.3, 113.6, 80.9, 78.4, 62.5, 55.7, 53.2, 35.2, 34.8, 33.4, 32.6, 30.0, 29.5, 27.2, 26.7, 20.8, 18.6, 15.5, 15.3$ ppm.

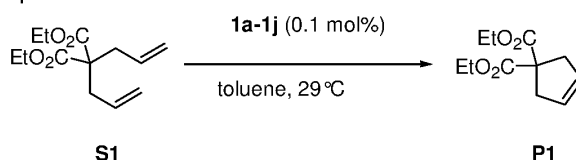
HRMS-ESI calculated for $\text{C}_{32}\text{H}_{46}\text{I}_2\text{N}_2\text{O}_3\text{Ru}$ $[\text{M-I}]^+$: 735.1600; found: 735.1636.

Elemental analysis: calculated for $\text{C}_{32}\text{H}_{46}\text{N}_2\text{I}_2\text{O}_3\text{Ru}$:

C 44.61; H 5.38; N 3.25; I 29.46; found: C 44.47; H 5.37; N 3.21; I 29.29.

EXAMPLE XXI

- 10 Application of precatalysts **1a** - **1j** in ring-closing metathesis (RCM) reactions of diethyl diallylmalonate **S1** leading to a cyclic compound **P1**.



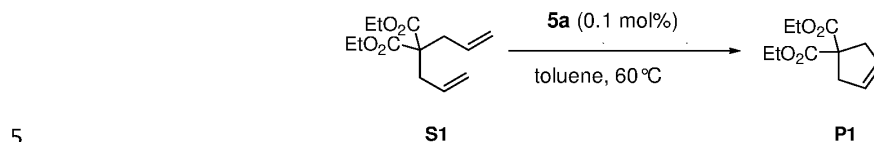
- 15 To the solution of diethyl diallylmalonate **S1** (120.1 mg, 0.5 mmol) in dry deoxygenated toluene (5 mL) at 29°C a solution of respective precatalyst (**1a–1j**), 0.1 mol% in dry deoxygenated toluene (50 μL) was added. It was stirred in argon atmosphere. At certain time intervals 0.1 mL samples of reaction mixture were collected to which one drop of ethyl vinyl ether was added to deactivate the catalyst. The substrate conversion as a function of time was determined by GC analysis. A summary is presented in Table 1.

Table 1. DEDAM conversion as a function of time.

Time (min)	Conversion (%)									
	1a	1b	1c	1d	1e	1f	1g	1h	1i	1j
5	6	10	67	6	9	80	-	-	-	5
10	19	32	87	16	31	94	-	-	-	20
20	43	63	95	38.5	71	98	-	-	-	47
30	62	76	97	54	86	99	-	-	--	60
45	77	85	98	68	93	99.5	-	-	-	71
60	84	90	98.5	77	95	99.5	-	-	-	77
120	92	95	99	88	98	99.5	-	-	-	86
180	-	-	-	91	99	99.6	2.3	5	30	89

EXAMPLE XXII

Application of precatalyst **5a** in ring-closing metathesis (RCM) reactions of diethyl diallylmalonate **S1** leading to cyclic compound **P1**.



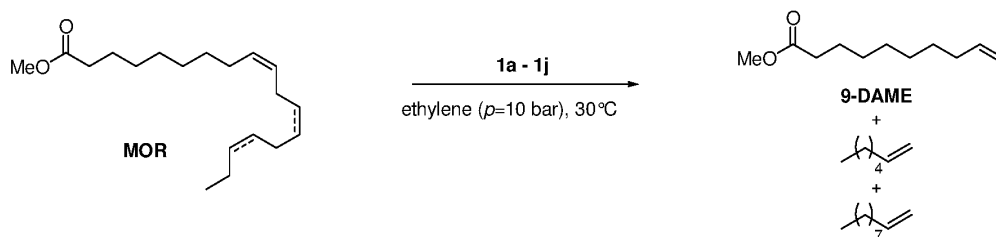
To the solution of diethyl diallylmalonate **S1** (480.6 mg, 2.0 mmol) in dry deoxygenated toluene (20 mL) at 60°C a solution of precatalyst **5a** (1.75 mg, 0.002 mmol, 0.1 mol%) in dry deoxygenated toluene (50 μ L) was added. In case of reaction with CAAC carbene scavenger, CuCl (1.98 mg, 0.02 mmol) was added to the reaction mixture. The whole was stirred in argon atmosphere. At certain time intervals 0.1 mL samples of reaction mixture were collected to which one drop of ethyl vinyl ether was added to deactivate the catalyst. Conversion reaction as a function of time was determined by GC analysis. A summary is presented in Table 2.

Table 2. DEDAM conversion with intermediate **5a** as a function of time.

Time (min)	Conversion (%)	
	5a	5a + CuCl
15	7	>99
30	10	-
60	27	-
120	78	-
240	88	-
360	95	-

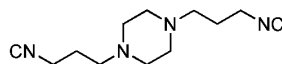
EXAMPLE XXIII

15 Application of precatalysts **1a–1j** in ethenolysis reactions of fatty acid methyl esters which were obtained by rapeseed oil transesterification (**MOR**).



To the reaction, a mixture of fatty acid methyl esters which were obtained by rapeseed oil transesterification (**MOR**), was used, composed of: about 61% methyl oleate, about 21% linoleic acid methyl ester, about 10% α -linolenic acid ester, about 7% saturated fatty acid methyl esters including about 4% methyl palmitate and about 2% methyl stearate.

To degassed **MOR** (610 g) cooled to 0°C a solution of catalyst (0.052 mmol) in dry deoxygenated toluene (5 mL) was added. The mixture was vacuum-pumped to an autoclave and stirred for 2 hours at 30°C at 10 bar of ethylene. After 2 hours the reaction was quenched and to the reaction mixture 6 mL 0.1 M solution of **SnachCat** [CAS: 51641-96-4] was added to deactivate the catalyst.

**SnachCat**

5

The samples were analyzed using gas chromatography. The conversion was determined using methyl palmitate as an internal standard.

Reaction mixtures obtained in reactions catalysed with **1d** and **1e** after filtration through short pad of silica gel were distilled under reduced pressure, giving 173 g and 179 g of 9-decenoic acid methyl ester (**9-DAME**), respectively.

10

Conversion and percentage (GC peak area) of 9-decenoic acid methyl ester (**9-DAME**) were given in the Table 3.

Table 3. MOR conversion in ethenolysis reaction with precatalysts **1a – 1i**

Precatalyst	Conversion (%)	Percentage of 9-DAME (%) in the reaction mixture based on GC	Isolated 9-DAME (g)
1a	77	25	-
1b	71	23	-
1c	69	21	-
1d	83	31	173
1e	79	29	179
1j	27	8	-
1i	21	5 (reaction conducted at 40 °C)	-

15 Analytical data obtained for **9-DAME**:

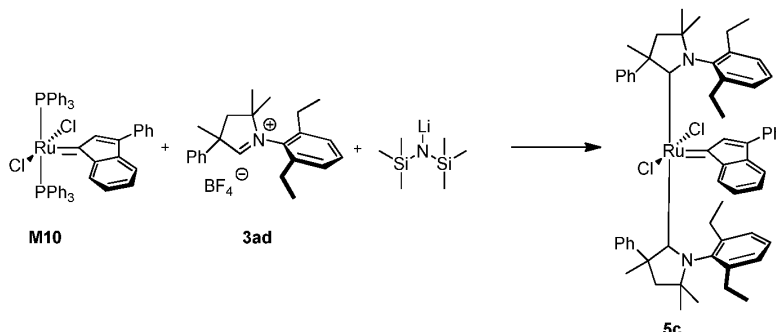
¹H NMR (CDCl₃, 500 MHz): δ = 5.79 (ddt, *J* = 17.0; 10.2; 6.7 Hz, 1H), 4.98 (dq, *J* = 17.1; 1.7 Hz, 1H), 4.92 (ddd, *J* = 11.4; 2.3; 1.2 Hz, 1H), 3.66 (s, 3H), 2.29 (t, *J* = 7.5 Hz, 2H), 2.06-1.99 (m, 2H), 1.66-1.56 (m, 2H), 1.40-1.24 (m, 8H) ppm.

¹³C NMR (CDCl₃, 125 MHz): 174.3, 139.1, 114.2, 51.4, 34.1, 33.7, 29.1, 28.9, 28.8, 24.9 ppm.

20

EXAMPLE XXIV

Preparation method of intermediate **5c** from precursor **M10** and CAAC salt **3ad**.



- 5 To salt **3ad** (6.00 g, 14.73 mmol, 3 molar equivalents) in argon atmosphere dry deoxygenated toluene (35 mL) was added. The mixture was heated to 80°C and solution of LiHMDS in toluene (1 M, 14.73 mL, 14.73 mmol, 3 molar equivalents) was added. After 1 minute solid complex **M10** (4.35 g, 4.91 mmol, 1 molar equivalent) was added. After 2 minutes the mixture was cooled down to the room temperature. Triethylamine (2 mL) was added and filtrated through a short pad of silica gel (deactivated with triethylamine), which was washed with 100 mL toluene/triethylamine mixture (95:5 v/v). Solvents were evaporated under reduced pressure. The crude product was isolated by column chromatography on silica gel (deactivated with triethylamine; eluent: from cyclohexane/triethylamine (95:5 v/v) to cyclohexane/ethyl acetate/triethylamine (90:5:5 v/v/v)). Red brown fraction was collected and concentrated to dryness. The residue was dissolved in *n*-pentane. Solvent was evaporated to 25% of its original amount – precipitate formed during evaporation was filtrated off, washed with a minimal amount of cold *n*-pentane and dried under high vacuum giving an orange brown crystalline solid – compound **5c** (1.73 g, 35%).

- ¹H NMR** (C₆D₆, 500 MHz): δ = 9.59 (d, *J* = 7.5 Hz, 1H), 8.06 (d, *J* = 7.7 Hz, 2H), 7.76 (d, *J* = 7.4 Hz, 2H), 7.49-7.43 (m, 3H), 7.42-7.37 (m, 2H), 7.37-7.23 (m, 6H), 7.22-7.06 (m, 5H), 7.01-6.97 (m, 1H), 6.88 (t, *J* = 7.3 Hz, 1H), 6.81 (d, *J* = 7.6 Hz, 1H), 6.64 (t, *J* = 7.6 Hz, 1H), 6.34 (d, *J* = 7.5 Hz, 1H), 4.14 (dq, *J* = 14.9; 7.2 Hz, 1H), 3.10-2.83 (m, 4H), 2.83-2.73 (m, 1H), 2.73-2.63 (m, 1H), 2.57-2.48 (m, 1H), 2.05 (d, *J* = 12.3 Hz, 1H), 1.94-1.89 (m, 1H), 1.84 (d, *J* = 12.7 Hz, 1H), 1.78 (s, 3H), 1.62 (d, *J* = 12.7 Hz, 1H), 1.48-1.40 (m, 6H), 1.03 (dt, *J* = 14.5; 7.3 Hz, 6H), 0.95 (dt, *J* = 14.5; 7.3 Hz, 3H), 0.77 (s, 3H), 0.71 (s, 3H), 0.63 (s, 3H), 0.50 (s, 3H) ppm.

- ¹³C NMR** (CD₂Cl₂, 125 MHz): δ = 288.1, 279.5, 273.4, 263.3, 150.5, 148.9, 148.1, 147.8, 147.2, 146.6, 144.9, 143.8, 143.8, 143.3, 142.0, 141.6, 141.4, 140.5, 140.2, 139.0, 138.9, 138.6, 138.1, 137.9, 137.5, 136.6, 135.9, 135.0, 131.0, 130.7, 130.4, 130.0, 129.9, 129.7, 129.2, 128.8, 128.7, 128.2, 128.1, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3, 127.3, 127.2, 127.2, 127.2, 127.0, 126.9, 126.8, 126.6, 126.5, 126.4, 126.3, 126.3, 126.1, 125.4, 125.0, 124.7, 118.7, 116.5, 115.7, 96.2, 81.5, 80.5, 79.0, 68.9, 66.0, 65.1, 57.1, 55.4, 52.1, 49.1, 44.4, 32.2, 31.5, 30.2, 29.7, 29.4, 29.1, 28.6, 28.0, 27.7, 27.6, 27.3, 27.2, 26.6, 25.7, 25.5, 24.8, 24.8, 24.4, 16.3, 16.1, 14.5, 14.4, 14.0, 13.6, 13.4, 12.4 ppm.

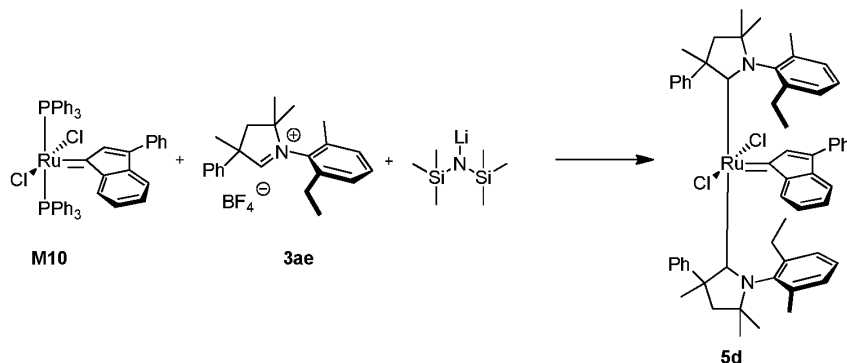
HRMS-ESI calculated for C₆₁H₆₈N₂Cl₂Ru [M]⁺: 1000.3803; found 1000.3798.

Elemental analysis: calculated for C₆₁H₆₈N₂Cl₂Ru:

C 73.18; H 6.85; N 2.80; Cl 7.08; found: C 73.14; H 7.00; N 2.95; Cl 7.10.

EXAMPLE XXV

Preparation method of intermediate **5d** from precursor **M10** and CAAC salt **3ae**.



- 5 To salt **3ae** (2.36 g, 6.0 mmol, 3 molar equivalents) dry deoxygenated toluene (14 mL) was added in argon atmosphere. The mixture was heated to 80°C and solution of LiHMDS in toluene (1 M, 6.0 mL, 6.0 mmol, 3 molar equivalents) was added. After 1 minute solid complex **M10** (1.77 g, 2.0 mmol, 1 molar equivalent) was added. After 2 minutes the mixture was cooled down to the room temperature. Triethylamine (2 mL) was added and filtrated through a short pad of silica gel (deactivated with triethylamine), which was washed with 50 mL toluene/triethylamine mixture (95:5 v/v). Solvents were evaporated under reduced pressure. The crude product was isolated by column chromatography on silica gel (deactivated with triethylamine; eluent: from cyclohexane/triethylamine (95:5 v/v) to cyclohexane/ethyl acetate/triethylamine (90:5:5 v/v/v)). Red brown fraction was collected and concentrated to dryness. The residue was dissolved in *n*-pentane. Solvent was evaporated to 25% of its original amount – precipitate
- 10 formed during evaporation was filtrated off, washed with a minimal amount of cold *n*-pentane and dried under high vacuum giving an orange brown crystalline solid – compound **5d** (0.345 g, 18%).

- ¹H NMR** (C₆D₆, 500 MHz): δ = 9.69-9.49 (m, 1H), 8.17-7.99 (m, 2H), 7.82-7.65 (m, 2H), 7.60-7.23 (m, 9H), 7.23-7.04 (m, 6H), 7.02-6.10 (m, 6H), 3.14-2.76 (m, 4H), 2.74-2.46 (m, 2H), 2.38-2.24 (m, 3H), 2.10-1.35 (m, 12H), 1.31-1.23 (m, 2H), 1.08-0.92 (m, 5H), 0.80-0.59 (m, 10H) ppm.
- 20 **¹³C NMR** (C₆D₆, 125 MHz): δ = 290.2, 289.9, 289.0, 288.6, 280.9, 279.2, 279.1, 274.5, 274.2, 274.0, 149.4, 149.3, 149.3, 149.2, 149.0, 148.3, 145.3, 145.3, 145.2, 144.4, 144.2, 144.1, 144.1, 142.4, 142.1, 141.9, 141.8, 141.8, 141.1, 140.9, 139.6, 139.4, 139.2, 139.1, 139.0, 138.8, 138.6, 138.2, 138.1, 138.1, 136.9, 136.6, 136.0, 136.0, 135.7, 135.6, 135.5, 135.2, 131.1, 131.0, 130.9, 130.8, 130.7, 130.6, 130.4, 130.3, 130.1, 130.0, 129.9, 129.7, 129.6, 129.5, 129.1, 129.1, 129.0, 128.7, 128.3, 128.0, 127.9, 127.8, 127.8, 127.7, 127.7, 127.7, 127.6, 127.6, 127.3, 127.2, 126.8, 126.8, 126.7, 126.5, 126.3, 124.8, 124.6, 116.9, 116.9, 81.7, 81.5, 81.1, 80.9, 80.7, 69.1, 69.0, 65.4, 65.3, 65.2, 56.8, 56.7, 56.6, 55.5, 55.1, 53.9, 53.6, 31.0, 30.7, 30.2, 29.9, 29.9, 29.6, 29.6, 29.5, 29.3, 29.2, 29.0, 28.0, 27.9, 27.6, 27.4, 27.4, 27.3, 27.1, 25.8, 25.5, 25.4, 25.2, 25.1, 25.1, 25.0, 24.2, 24.0, 22.7, 22.6, 14.9, 14.8, 14.0, 13.8, 12.6, 12.6 ppm.

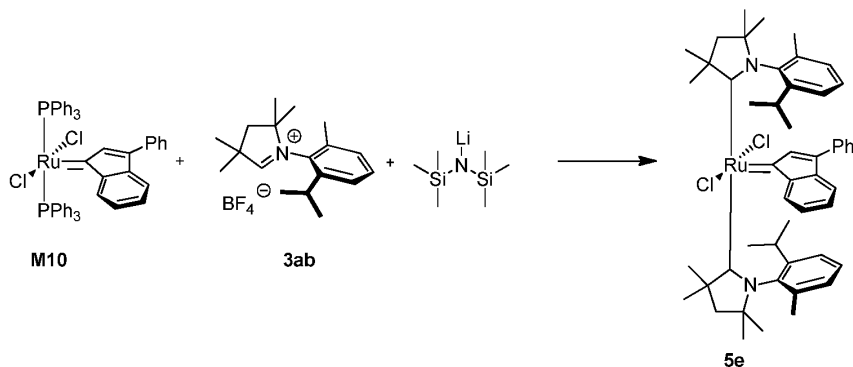
- 30 **HRMS-ESI**: calculated for C₅₉H₆₄N₂Cl₂Ru [M]⁺: 972.3490; found 972.3475.

Elemental analysis: calculated for C₅₉H₆₄N₂Cl₂Ru:

C 72.82; H 6.63; N 2.88; Cl 7.29; found: C 72.69; H 6.68; N 2.71; Cl 7.07.

EXAMPLE XXVI

Preparation method of intermediate **5e** from precursor **M10** and CAAC salt **3ab**.



- 5 To salt **3ab** (8.29 g, 24.0 mmol, 3 molar equivalents) dry deoxygenated toluene (56 mL) was added in argon atmosphere. The mixture was heated to 80°C and solution of LiHMDS in toluene (1 M, 24.0 mL, 24.0 mmol, 3 molar equivalents) was added. After 1 minute solid complex **M10** (7.09 g, 8.0 mmol, 1 molar equivalent) was added. After 2 minutes the mixture was cooled down to the room temperature. Triethylamine (5 mL) was added and filtrated through a short pad of silica gel (deactivated with triethylamine), which was washed with 75 mL toluene/triethylamine mixture (95:5 v/v). Solvents were evaporated under reduced pressure. The crude product was isolated by column chromatography on silica gel (deactivated with triethylamine; eluent: from cyclohexane/triethylamine (95:5 v/v) to cyclohexane/ethyl acetate/triethylamine (90:5:5 v/v/v)). Red brown fraction was collected and concentrated to dryness. The residue was dissolved in *n*-pentane. Solvent was evaporated to 25% of its original amount – precipitate formed during evaporation was filtrated off, washed with a minimal amount of cold *n*-pentane and dried under high vacuum giving an orange brown crystalline solid – compound **5e** (2.89 g, 41%).

- ¹H NMR** (C₆D₆, 500 MHz): δ = 10.05-8.65 (m, 1H), 8.50-7.45 (m, 3H), 7.40-7.15 (m, 7H), 7.05-6.05 (m, 5H), 3.86-3.62 (m, 1H), 3.12-2.89 (m, 1H), 2.86-2.02 (m, 8H), 1.92-1.11 (m, 22H), 1.10-0.65 (m, 14H), 0.44 (s, 2H) ppm.
- 20 **¹³C NMR** (CD₂Cl₂, 125 MHz): δ = 281.7, 281.0, 280.1, 279.1, 278.5, 147.6, 146.3, 142.0, 141.8, 141.1, 140.9, 139.9, 139.8, 139.5, 137.7, 136.7, 136.4, 136.1, 134.0, 131.8, 130.7, 130.0, 129.8, 129.5, 129.4, 129.2, 129.0, 128.7, 127.5, 127.3, 127.2, 127.0, 126.6, 125.8, 125.4, 116.6, 116.5, 80.3, 80.3, 62.7, 61.9, 61.4, 57.3, 56.8, 56.0, 32.0, 31.4, 30.8, 30.0, 28.9, 28.8, 28.6, 28.4, 27.8, 27.5, 27.3, 26.9, 26.5, 26.4, 25.7, 25.4, 24.0, 23.8, 23.2, 22.7 ppm.

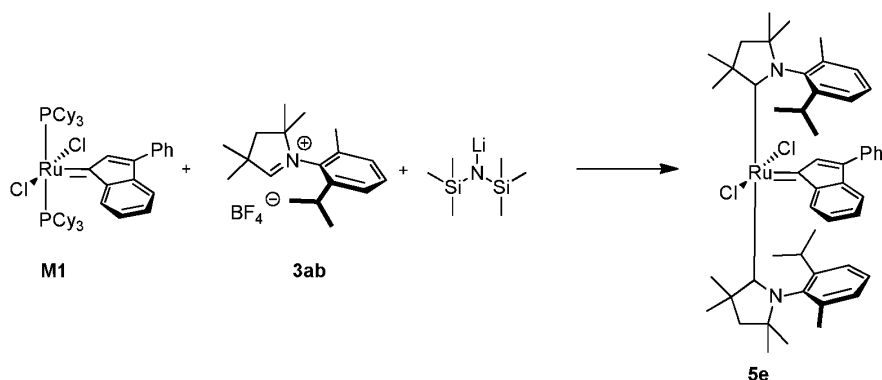
- 25 **HRMS-ESI** calculated for C₅₁H₆₄N₂Cl₂Ru [M]⁺: 876.3490; found 876.3477.

Elemental analysis: calculated for C₅₁H₆₄N₂Cl₂Ru:

C 69.84; H 7.36; N 3.19; Cl 8.08; found: C 69.94; H 7.43; N 3.14; Cl 8.17.

EXAMPLE XXVII

Preparation method of intermediate **5e** from precursor **M1** and CAAC salt **3ab**.

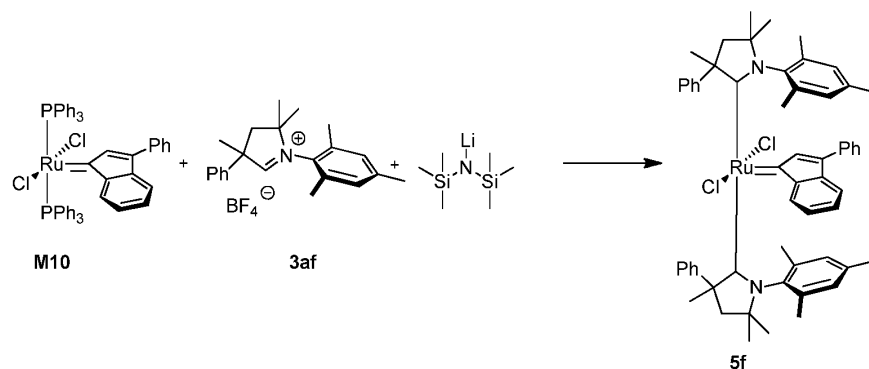


To salt **3ab** (1.04 g, 3.0 mmol, 3 molar equivalents) dry deoxygenated toluene (7 mL) was added in argon atmosphere. The mixture was heated to 80 °C and solution of LiHMDS in toluene (1 M, 3.0 mL, 3.0 mmol, 3 molar equivalents) was added. After 1 minute solid complex **M1** (0.923 g, 1.0 mmol, 1 molar equivalent) was added. After 10 minutes the mixture was cooled down to the room temperature. Triethylamine (1 mL) was added and filtrated through a short pad of silica gel (deactivated with triethylamine), which was washed with 25 mL toluene/triethylamine mixture (95:5 v/v). Solvents were evaporated under reduced pressure. The crude product was isolated by column chromatography on silica gel (deactivated with triethylamine; eluent: from cyclohexane/triethylamine (95:5 v/v) to cyclohexane/ethyl acetate/triethylamine (90:5:5 v/v/v)). Red brown fraction was collected and concentrated to dryness. The residue was dissolved in *n*-pentane. Solvent was evaporated to 25% of its original amount – precipitate formed during evaporation was filtrated off, washed with a minimal amount of cold *n*-pentane and dried under high vacuum giving an orange brown crystalline solid – compound **5e** (0.72 g, 82%).

Analytical data for compound **5e** obtained in this Example were identical as in Example XXVI.

15 EXAMPLE XXVIII

Preparation method of intermediate **5f** from precursor **M10** and CAAC salt **3af**.



To salt **3af** (2.36 g, 6.0 mmol, 3 molar equivalents) dry deoxygenated toluene (14 mL) was added in argon atmosphere. The mixture was heated to 80 °C and solution of LiHMDS in toluene (1 M, 6.0 mL, 6.0 mmol, 3 molar equivalents) was added. After 1 minute solid complex **M10** (1.77 g, 2.0 mmol, 1 molar equivalent) was added. After 2 minutes the mixture was cooled down to the room temperature. Triethylamine (2 mL) was added and filtrated through a short pad of silica gel (deactivated with

triethylamine), which was washed with 50 mL toluene/triethylamine mixture (95:5 v/v). Solvents were evaporated under reduced pressure. The crude product was isolated by column chromatography on silica gel (deactivated with triethylamine; eluent: from cyclohexane/triethylamine (95:5 v/v) to cyclohexane/ethyl acetate/triethylamine (90:5:5 v/v/v)). Red brown fraction was collected and concentrated to dryness. The residue was dissolved in *n*-pentane. Solvent was evaporated to 25% of its original amount – precipitate formed during evaporation was filtrated off, washed with a minimal amount of cold *n*-pentane and dried under high vacuum giving an orange brown crystalline solid – compound **5f** (0.210 g, 11%).

¹H NMR (C₆D₆, 500 MHz): δ = 9.57 (d, *J* = 7.6 Hz, 1H), 8.14 (d, *J* = 7.8 Hz, 2H), 7.73 (d, *J* = 7.6 Hz, 2H), 7.61 (s, 1H), 7.52 (d, *J* = 7.5 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.37-7.16 (m, 5H), 7.15-7.11 (m, 1H), 7.08-6.80 (m, 5H), 6.64 (s, 1H), 6.42 (s, 1H), 5.90 (s, 1H), 2.85 (s, 3H), 2.32 (s, 6H), 2.22 (s, 3H), 2.19 (s, 3H), 2.10 (d, *J* = 12.5 Hz, 1H), 1.95-1.84 (m, 2H), 1.77 (s, 3H), 1.70 (s, 3H), 1.64 (d, *J* = 12.7 Hz, 1H), 1.50 (s, 3H), 0.80 (s, 3H), 0.72 (s, 3H), 0.67 (s, 3H), 0.61 (s, 3H) ppm.

¹³C NMR (CD₂Cl₂, 125 MHz): δ = 286.8, 278.5, 272.1, 148.7, 147.8, 144.8, 141.2, 139.1, 138.8, 138.5, 138.2, 137.7, 137.6, 136.6, 136.1, 136.0, 135.2, 134.3, 131.7, 131.0, 130.3, 130.2, 129.8, 129.6, 128.8, 128.6, 128.1, 127.5, 127.3, 127.3, 127.0, 126.6, 126.4, 116.0, 82.0, 81.9, 68.8, 65.0, 57.0, 55.6, 30.39, 30.16, 29.55, 28.50, 27.86, 27.37, 24.64, 24.30, 21.91, 21.13, 21.0 ppm.

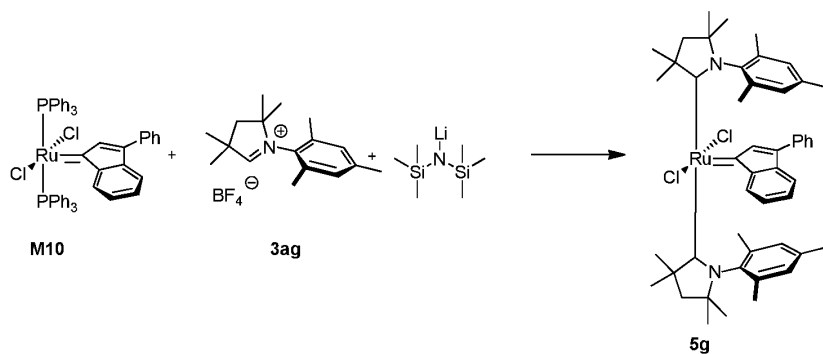
HRMS-ESI calculated for C₅₉H₆₄N₂Cl₂Ru [M]⁺: 972.3490; found 972.3483.

Elemental analysis: calculated for C₅₉H₆₄N₂Cl₂Ru:

C 72.82; H 6.63; N 2.88; Cl 7.29; found: C 72.88; H 6.78; N 2.71; Cl 7.16.

20 EXAMPLE XXIX

Preparation method of intermediate **5g** from precursor **M10** and CAAC salt **3ag**.



To salt **3ag** (1.99 g, 6.0 mmol, 3 molar equivalents) dry deoxygenated toluene (14 mL) was added in argon atmosphere. The mixture was heated to 80 °C and solution of LiHMDS in toluene (1 M, 6.0 mL, 6.0 mmol, 3 molar equivalents) was added. After 1 minute, solid complex **M10** (1.77 g, 2.0 mmol, 1 molar equivalent) was added. After 2 minutes the mixture was cooled down to the room temperature. Triethylamine (2 mL) was added and filtrated through a short pad of silica gel (deactivated with triethylamine), which was washed with 50 mL toluene/triethylamine mixture (95:5 v/v). Solvents were evaporated under reduced pressure. The crude product was isolated by column chromatography on silica gel (deactivated with triethylamine; eluent: from cyclohexane/triethylamine (95:5 v/v) to cyclohexane/ethyl acetate/triethylamine (90:5:5 v/v/v)). Red brown fraction was collected and concentrated to dryness. The

residue was dissolved in *n*-pentane. Solvent was evaporated to 25% of its original amount – precipitate formed during evaporation was filtrated off, washed with a minimal amount of cold *n*-pentane and dried under high vacuum giving an orange brown crystalline solid – compound **5g** (0.561 g, 33%).

¹H NMR (CD₂Cl₂, 500 MHz): δ = 8.51 (d, *J* = 7.6 Hz, 1H), 7.75-7.65 (m, 2H), 7.52-7.46 (m, 1H), 7.46-7.39 (m, 2H), 7.14 (s, 1H), 7.11-7.04 (m, 1H), 7.03-6.96 (m, 1H), 6.84 (dd, *J* = 7.2; 1.4 Hz, 1H), 6.23 (s, 2H), 5.79 (s, 2H), 2.16 (s, 6H), 2.11 (s, 6H), 2.06-2.03 (m, 10H), 1.86 (s, 6H), 1.72 (s, 6H), 1.18 (s, 6H), 1.12 (s, 6H) ppm.

¹³C NMR (CD₂Cl₂, 125 MHz): δ = 280.2, 277.9, 144.0, 140.7, 138.2, 137.9, 137.4, 136.4, 135.8, 135.4, 134.1, 129.7, 129.6, 129.3, 129.2, 127.3, 127.0, 126.6, 126.6, 115.5, 80.9, 56.9, 54.5, 32.3, 32.1, 30.2, 29.5, 21.6, 21.4, 21.0 ppm.

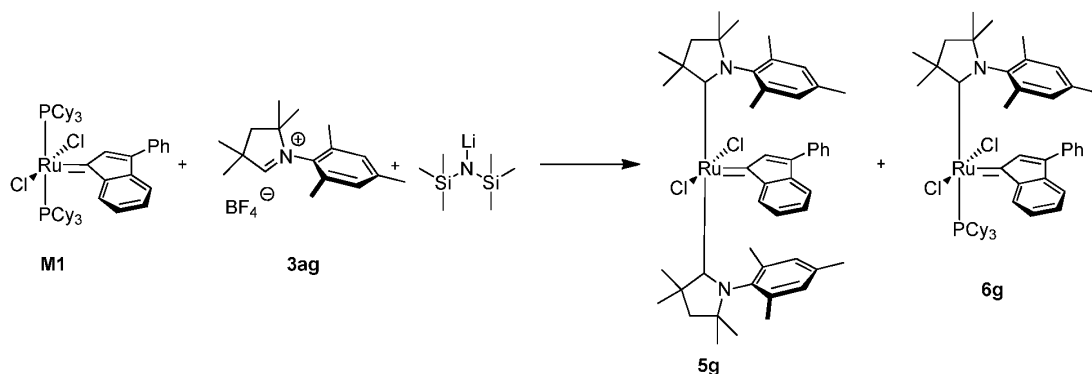
HRMS-ESI calculated for C₄₉H₆₀N₂Cl₂Ru [M]⁺: 848.3177; found 848.3161.

Elemental analysis: calculated for C₄₉H₆₀N₂Cl₂Ru:

C 69.32; H 7.12; N 3.30; Cl 8.35; found: C 69.40; H 7.03; N 3.22; Cl 8.56.

EXAMPLE XXX

Preparation method of intermediate **5g** and minor compound **6g** from precursor **M1** and CAAC salt **3ag**.



To salt **3ag** (1.99 g, 6.0 mmol, 3 molar equivalents) dry deoxygenated toluene (14 mL) was added in argon atmosphere. The mixture was heated to 80 °C and solution of LiHMDS in toluene (1 M, 6.0 mL, 6.0 mmol, 3 molar equivalents) was added. After 1 minute solid complex **M1** (1.85 g, 2.0 mmol, 1 molar equivalent) was added. After 30 minutes the mixture was cooled down to the room temperature. Triethylamine (2 mL) was added and filtrated through a short pad of silica gel (deactivated with triethylamine), which was washed with 50 mL toluene/triethylamine mixture (95:5 v/v). Solvents were evaporated under reduced pressure. Crude products **5g** and **6g** were isolated by column chromatography on silica gel (deactivated with triethylamine; eluent: from cyclohexane/triethylamine (95:5 v/v) to cyclohexane/ethyl acetate/triethylamine (90:5:5 v/v/v)). Two red brown fractions were collected and concentrated to dryness. First fraction residue was dissolved in *n*-pentane. Solvent was evaporated to 25% of its original amount – precipitate formed during evaporation was filtrated off, washed with a minimal amount of cold *n*-pentane and dried under high vacuum giving an orange brown crystalline solid – compound **6g** (0.270 g, 15%). Second fraction residue was dissolved in *n*-pentane. Solvent was evaporated to 25% of its original amount – precipitate formed during evaporation was filtrated off, washed

with a minimal amount of cold *n*-pentane and dried under high vacuum giving an orange brown crystalline solid – compound **5g** (0.350 g, 21%).

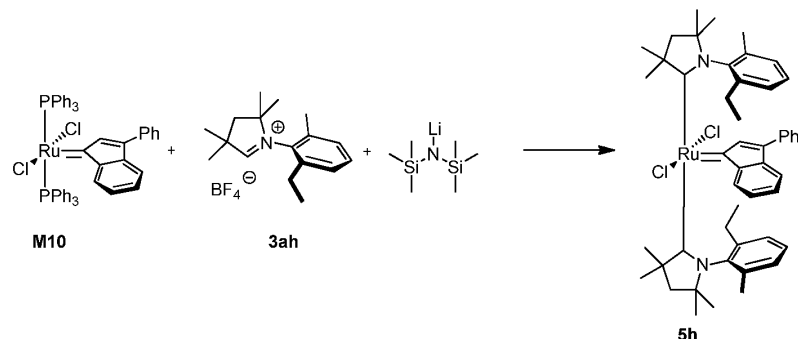
Analytical data for compound **5g** obtained in this Example were identical as in Example XXIX.

Analytical data for compound **6g**:

- 5 ¹H NMR (CD₂Cl₂, 500 MHz): δ = 8.61 (d, *J* = 7.3 Hz, 1H), 7.70 (dd, *J* = 8.2; 1.4 Hz, 2H), 7.54-7.47 (m, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.30 (s, 1H), 7.24-7.18 (m, 1H), 7.17-7.11 (m, 1H), 7.06-7.01 (m, 1H), 6.39 (s, 1H), 6.01 (s, 1H), 2.50-2.38 (m, 3H), 2.31 (s, 3H), 2.17 (s, 3H), 2.14 (d, *J* = 1.8 Hz, 2H), 2.06 (s, 3H), 2.00 (s, 3H), 1.93 (s, 3H), 1.90-1.80 (m, 3H), 1.76-1.54 (m, 12H), 1.53-1.34 (m, 6H), 1.22 (s, 6H), 1.20-1.06 (m, 9H) ppm.
 - 10 ¹³C NMR (CD₂Cl₂, 125 MHz): δ = 287.7, 287.7, 274.7, 274.2, 144.8, 141.4, 138.3, 137.4, 137.3, 137.3, 136.9, 136.5, 136.2, 130.0, 129.9, 129.6, 129.5, 128.1, 128.1, 127.8, 126.8, 116.5, 80.3, 80.3, 57.5, 57.4, 53.5, 53.5, 36.1, 35.6, 32.8, 32.7, 31.9, 31.6, 30.4, 30.1, 29.9, 28.8, 28.6, 28.5, 28.4, 28.3, 27.6, 27.5, 27.2, 27.1, 26.9, 26.9, 26.8, 22.9, 21.7, 21.4, 21.2 ppm.
 - ³¹P NMR (CD₂Cl₂, 202 MHz): δ = 28.7 ppm.
 - 15 HRMS-ESI calculated for C₅₀H₆₈NC₂RuP [M]⁺: 885.3510; found 885.3506.
- Elemental analysis: calculated for C₅₀H₆₈Cl₂NPRu:
C 67.78; H 7.74; N 1.58; Cl 8.00; found: C 67.84; H 7.67; N 1.47; Cl 7.91.

EXAMPLE XXXI

Preparation method of intermediate **5h** from precursor **M10** and CAAC salt **3ah**.



20

- To salt **3ah** (1.99 g, 6.0 mmol, 3 molar equivalents) dry deoxygenated toluene (14 mL) was added in argon atmosphere. The mixture was heated to 80 °C and solution of LiHMDS in toluene (1 M, 6.0 mL, 6.0 mmol, 3 molar equivalents) was added. After 1 minute solid complex **M10** (1.77 g, 2.0 mmol, 1 molar equivalent) was added. After 2 minutes the mixture was cooled down to the room temperature. The crude product was isolated by column chromatography on silica gel (eluent: cyclohexane/ethyl acetate (9:1 v/v)). Red brown fraction was collected and concentrated to dryness. The residue was dissolved in a small amount of methylene chloride and excess of methanol was added. Methylene chloride was removed under reduced pressure – precipitate formed during evaporation was filtrated off, washed with a minimal amount of cold methanol and dried under high vacuum giving an orange brown crystalline solid – compound **5h** (0.589 g, 35%).
- 25
- 30

¹H NMR (C₆D₆, 500 MHz): δ = 9.88-8.08 (m, 1H), 8.02-7.40 (m, 3H), 7.39-7.20 (m, 4H), 7.12-6.85 (m, 3H), 6.75-6.10 (m, 5H), 3.85-2.90 (m, 2H), 2.87-2.67 (m, 1H), 2.66-2.50 (m, 1H), 2.46-2.22 (m, 12H), 2.21-2.01 (m, 3H), 1.80-1.15 (m, 7H), 1.14-0.65 (m, 18H) ppm.

¹³C NMR (CD₂Cl₂, 125 MHz): δ = 280.4, 280.3, 277.9, 277.8, 277.6, 144.2, 144.1, 141.1, 141.0, 140.9, 139.5, 139.4, 139.1, 139.1, 138.8, 137.9, 137.8, 137.8, 137.4, 135.5, 135.0, 134.6, 134.5, 131.0, 130.5, 129.7, 129.3, 129.2, 129.1, 129.0, 128.7, 128.4, 127.8, 127.7, 127.4, 127.3, 127.0, 126.8, 126.7, 126.6, 126.5, 125.2, 124.3, 116.3, 116.2, 116.1, 81.9, 80.6, 80.5, 61.5, 57.0, 56.9, 56.5, 54.9, 54.8, 54.7, 54.6, 32.7, 32.4, 32.4, 32.0, 31.8, 31.0, 30.2, 29.6, 29.5, 29.1, 28.8, 27.4, 25.2, 25.1, 24.6, 22.1, 21.8, 14.7, 13.1, 12.7 ppm.

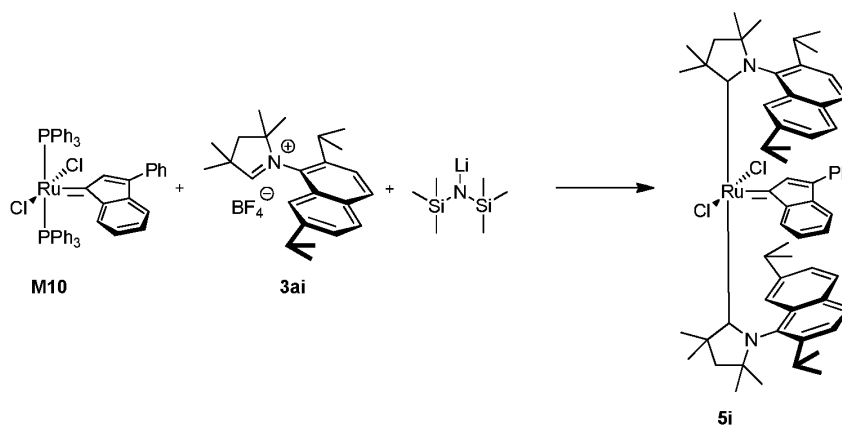
10 HRMS-ESI calculated for C₄₉H₆₀N₂Cl₂Ru [M]⁺: 848.3177; found 848.3159.

Elemental analysis: calculated for C₄₉H₆₀N₂Cl₂Ru:

C 69.32; H 7.12; N 3.30; Cl 8.35; found: C 69.15; H 7.30; N 3.48; Cl 8.40.

EXAMPLE XXXII

Preparation method of intermediate **5i** from precursor **M10** and CAAC salt **3ai**.



15

To salt **3ai** (0.847 g, 2.0 mmol, 2 molar equivalents) dry deoxygenated toluene (8 mL) was added in argon atmosphere. The mixture was heated to 80 °C and solution of LiHMDS in toluene (1 M, 2.0 mL, 2.0 mmol, 2 molar equivalents) was added. After 1 minute solid complex **M10** (0.887 g, 1.0 mmol, 1 molar equivalent) was added. After 2 minutes the mixture was cooled down to the room temperature.

20 Triethylamine (1 mL) was added and filtrated through a short pad of silica gel (deactivated with triethylamine), which was washed with 50 mL toluene/triethylamine mixture (95:5 v/v). Solvents were evaporated under reduced pressure. The crude product was isolated by column chromatography on silica gel (deactivated with triethylamine; eluent: from cyclohexane/triethylamine (95:5 v/v) to cyclohexane/ethyl acetate/triethylamine (90:5:5 v/v/v)). Red brown fraction was collected and concentrated to dryness. The

25 residue was dissolved in *n*-pentane. Solvent was evaporated to 25% of its original amount – precipitate formed during evaporation was filtrated off, washed with a minimal amount of cold *n*-pentane and dried under high vacuum giving an orange brown crystalline solid – compound **5i** (0.147 g, 14%) as a mixture of isomers (isomer A – major and isomer B – minor). The filtrate was evaporated to dryness. It was dissolved in a small amount of methylene chloride and excess of methanol was added. Methylene
30 chloride was evaporated under reduced pressure – precipitate formed during evaporation was filtrated off,

washed with a minimal amount of cold methanol and dried under high vacuum giving red crystalline solid – compound **5i** (0.184 g, 18%) as a mixture of isomers (isomer A – minor and isomer B – major).

¹H NMR (C₆D₆, 500 MHz): δ = 9.86-8.38 (m, 1H), 8.35-7.65 (m, 6H), 7.62-7.53 (m, 1H), 7.51-7.45 (m, 1H), 7.44-7.37 (m, 1H), 7.35-7.25 (m, 5H), 7.10-6.55 (m, 5H), 4.04-3.72 (m, 1H), 3.45-2.75 (m, 3H), 2.08-1.94 (m, 3H), 1.65-1.05 (m, 35H), 0.98-0.71 (m, 14H) ppm (mixture of isomers).

¹³C NMR (CD₂Cl₂, 125 MHz): δ = 282.3, 281.1, 280.2, 279.0, 278.9, 277.5, 145.9, 145.3, 144.5, 144.5, 144.4, 142.8, 142.4, 141.2, 140.6, 140.2, 138.0, 137.5, 135.0, 134.7, 134.4, 134.4, 134.2, 133.2, 132.8, 132.6, 132.6, 132.5, 132.4, 132.4, 132.2, 131.8, 131.8, 131.4, 131.2, 130.6, 130.5, 129.5, 129.4, 129.2, 129.1, 129.0, 128.9, 128.7, 128.4, 128.0, 127.9, 127.6, 127.5, 127.4, 127.3, 127.2, 127.2, 127.1, 126.9, 126.2, 126.0, 125.7, 125.7, 125.6, 125.4, 125.2, 125.1, 124.7, 123.7, 123.6, 116.1, 115.6, 115.3, 81.5, 81.3, 80.8, 80.1, 62.0, 61.5, 56.5, 56.2, 55.8, 55.3, 54.8, 35.5, 35.4, 35.0, 34.3, 33.2, 32.2, 32.2, 31.6, 31.5, 31.3, 31.3, 30.8, 30.7, 30.6, 30.6, 30.5, 30.5, 30.4, 30.2, 30.1, 30.0, 29.9, 29.7, 29.5, 29.5, 28.9, 28.9, 28.8, 28.7, 28.3, 27.6, 27.5, 27.3, 26.8, 26.2, 26.0, 25.7, 25.7, 25.4, 24.9, 24.8, 24.7, 24.6, 24.5, 24.4, 24.3, 24.2, 23.8, 23.3, 23.2, 23.1, 23.1, 23.0, 22.9, 22.5 ppm.

Analytical data for isomer A-enriched mixture:

HRMS-ESI calculated for C₆₃H₇₆N₂Cl₂Ru [M]⁺: 1032.4429; found 1032.4402.

Elemental analysis: calculated for C₆₃H₇₆N₂Cl₂Ru:

C 73.23; H 7.41; N 2.71; Cl 6.86; found: C 73.19; H 7.46; N 2.60; Cl 6.84.

Analytical data for isomer B-enriched mixture:

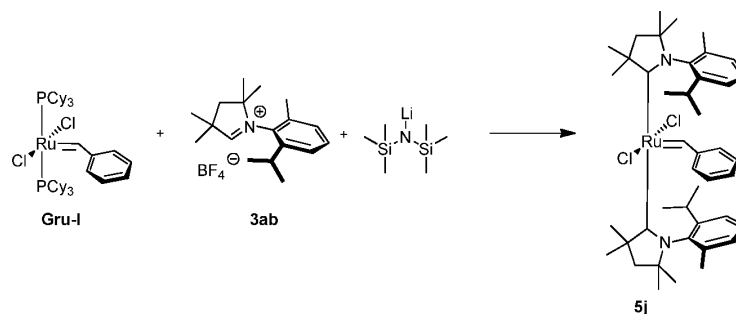
HRMS-ESI calculated for C₆₃H₇₆N₂Cl₂Ru [M]⁺: 1032.4429; found 1032.4426.

Elemental analysis: calculated for C₆₃H₇₆N₂Cl₂Ru:

C 73.23; H 7.41; N 2.71; Cl 6.86; found: C 73.16; H 7.31; N 2.74; Cl 6.97.

EXAMPLE XXXIII

Preparation method of intermediate **5j** from precursor **Gru-I** and CAAC salt **3ab**.



To salt **3ab** (1.04 g, 3.0 mmol, 3 molar equivalents) dry deoxygenated toluene (7 mL) was added in argon atmosphere. The mixture was heated to 80 °C and solution of LiHMDS in toluene (1 M, 3.0 mL, 3.0 mmol, 3 molar equivalents) was added. After 1 minute solid complex **Gru-I** (0.823 g, 1.0 mmol, 1 molar equivalent) was added. After 2 minutes the mixture was cooled down to the room temperature. Triethylamine (1 mL) was added and filtrated through a short pad of silica gel (deactivated with triethylamine), which was washed with 25 mL toluene/triethylamine mixture (95:5 v/v). Solvents were

evaporated under reduced pressure. The crude product was isolated by column chromatography on silica gel (deactivated with triethylamine; eluent: from cyclohexane/triethylamine (95:5 v/v) to cyclohexane/ethyl acetate/triethylamine (90:5:5 v/v/v)). Brown fraction was collected and concentrated to dryness. The residue was dissolved in *n*-pentane. Solvent was evaporated to 25% of its original amount – precipitate
 5 formed during evaporation was filtrated off, washed with a minimal amount of cold *n*-pentane and dried under high vacuum giving dark brown crystalline solid – compound **5j** (0.441 g, 57%).

¹H NMR (C₆D₆, 500 MHz): δ = 18.29 (s, 1H), 9.41 (d, *J* = 8.1 Hz, 1H), 7.12-7.07 (m, 1H), 7.01-6.95 (m, 1H), 6.84 (dd, *J* = 7.9; 1.6 Hz, 2H), 6.67 (td, *J* = 7.6; 1.5 Hz, 1H), 6.42 (t, *J* = 7.7 Hz, 2H), 6.22 (d, *J* = 7.9 Hz, 1H), 5.93 (dd, *J* = 7.5; 1.6 Hz, 2H), 3.23 (hept, *J* = 6.4 Hz, 2H), 2.31 (d, *J* = 4.1 Hz, 12H), 2.21 (s, 6H),
 10 1.74-1.60 (m, 10H), 1.18 (s, 6H), 1.11 (d, *J* = 6.6 Hz, 6H), 0.73 (s, 6H) ppm (main isomer).

¹³C NMR (CD₂Cl₂, 125 MHz): δ = 285.0, 284.9, 281.5, 149.4, 145.3, 139.1, 136.8, 131.9, 130.9, 129.1, 128.3, 127.6, 127.5, 127.3, 124.5, 79.3, 56.5, 55.2, 32.8, 31.8, 31.1, 29.8, 28.9, 28.5, 28.4, 28.3, 26.8, 22.2 ppm.

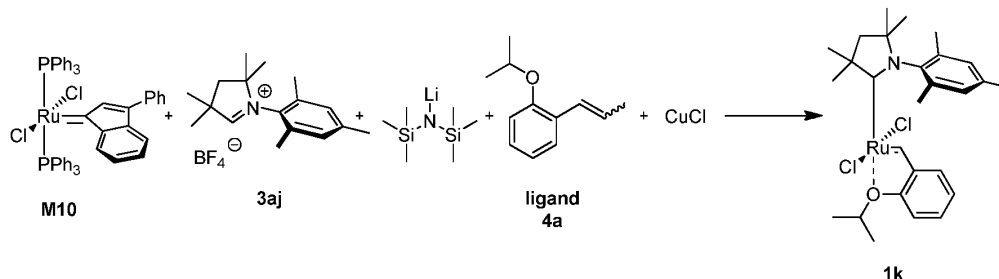
HRMS-ESI calculated for C₄₃H₆₀N₂Cl₂Ru [M]⁺: 776.3177; found 776.3140.

15 **Elemental analysis:** calculated for C₄₃H₆₀N₂Cl₂Ru:

C 66.47; H 7.78; N 3.61; Cl 9.13; found: C 66.24; H 7.75; N 3.46; Cl 9.01.

EXAMPLE XXXIV

Preparation method of precatalyst **1k** from precursor **M10** and CAAC salt **3aj**.



20 To salt **3aj** (0.331 g, 1.0 mmol, 2 molar equivalents) dry deoxygenated toluene (4 mL) was added in argon atmosphere. The mixture was heated to 80°C and solution of LiHMDS in toluene (1 M, 1.0 mL, 1.0 mmol, 2 molar equivalents) was added. After 1 minute solid complex **M10** (0.443 g, 0.5 mmol, 1 molar equivalent) was added. After 2 minutes the mixture was cooled down to 60°C. Benzylidene ligand **4a** (0.106 g, 0.6 mmol, 1.2 molar equivalents) and CuCl (0.173 g, 1.75 mmol, 3.5 molar equivalents) were
 25 added. The whole was stirred for 20 minutes at 60°C and cooled down to the room temperature. The crude product was isolated by column chromatography on silica gel (eluent: toluene). Green fraction was collected and concentrated to dryness. The residue was dissolved in ethyl acetate and filtrated. The solvent was evaporated, the residue was washed with isopropanol and dried under high vacuum giving green crystalline solid – precatalyst **1k** (0.112 g, 40%).

30 **¹H NMR** (CD₂Cl₂, 500 MHz): δ = 16.22 (s, 1H), 7.61 (ddd, *J* = 8.2; 7.1; 2.0 Hz, 1H), 7.15 (s, 2H), 7.01-6.89 (m, 3H), 5.16 (hept, *J* = 6.2 Hz, 1H), 2.48 (s, 3H), 2.20 (s, 8H), 2.07 (s, 6H), 1.71 (d, *J* = 6.1 Hz, 6H), 1.41 (s, 6H) ppm.

¹³C NMR (CD₂Cl₂, 125 MHz): δ = 298.3, 298.1, 266.5, 152.6, 144.9, 139.2, 138.6, 138.2, 131.2, 131.0, 130.9, 123.8, 122.6, 113.6, 79.2, 75.5, 56.5, 52.5, 29.7, 29.3, 22.3, 21.3, 20.9 ppm.

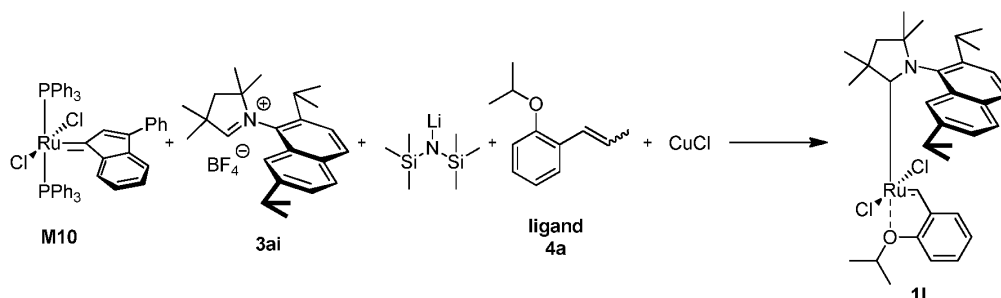
HRMS-ESI calculated for C₂₇H₃₇NONaCl₂Ru [M+Na]⁺: 586.1193; found 586.1185.

Elemental analysis: calculated for C₂₇H₃₇NOCl₂Ru:

- 5 C 57.54; H 6.62; N 2.49; Cl 12.58; found: C 57.51; H 6.62; N 2.39; Cl 12.68.

EXAMPLE XXXV

Preparation method of precatalyst **11** from precursor **M10** and CAAC salt **3ai**.



- To salt **3ai** (1.27 g, 2.0 mmol, 2 molar equivalents) dry deoxygenated toluene (12 mL) was added in argon atmosphere. The mixture was heated to 80°C and solution of LiHMDS in toluene (1 M, 3.0 mL, 3.0 mmol, 2 molar equivalents) was added. After 1 minute solid complex **M10** (1.33 g, 1.0 mmol, 1 molar equivalent) was added. After 2 minutes the mixture was cooled down to 60°C. Benzyldiene ligand **4a** (0.317 g, 1.8 mmol, 1.2 molar equivalents) and CuCl (0.520 g, 5.25 mmol, 3.5 molar equivalents) were added. The whole was stirred for 10 minutes at 60°C and cooled down to the room temperature. The crude product was isolated by column chromatography on silica gel (eluent: toluene). Green fraction was collected and concentrated to dryness. The residue was dissolved in ethyl acetate and filtrated. The solvent was evaporated, the residue was washed with isopropanol and dried under high vacuum giving green crystalline solid – precatalyst **11** (0.517 g, 53%).

- ¹H NMR (CD₂Cl₂, 500 MHz): δ = 15.98 (s, 1H), 8.11 (d, J = 8.7 Hz, 1H), 7.87-7.84 (m, 1H), 7.81 (d, J = 8.4 Hz, 1H), 7.68 (d, J = 8.7 Hz, 1H), 7.47 (ddd, J = 8.3; 7.4; 1.7 Hz, 1H), 7.35 (dd, J = 8.5; 1.7 Hz, 1H), 6.90 (d, J = 8.3 Hz, 1H), 6.76 (td, J = 7.5; 0.9 Hz, 1H), 6.52 (dd, J = 7.6; 1.7 Hz, 1H), 5.12 (hept, J = 6.1 Hz, 1H), 3.23 (hept, J = 6.6 Hz, 1H), 2.97 (hept, J = 6.9 Hz, 1H), 2.38-2.33 (m, 4H), 2.29-2.25 (m, 1H), 2.05 (s, 3H), 1.76 (d, J = 6.1 Hz, 3H), 1.66 (d, J = 6.1 Hz, 3H), 1.45 (s, 3H), 1.39 (d, J = 6.7 Hz, 3H), 1.20 (d, J = 6.9 Hz, 6H), 1.17 (s, 3H), 0.80 (d, J = 6.5 Hz, 3H) ppm.

- ¹³C NMR (CD₂Cl₂, 125 MHz): δ = 296.2, 296.0, 268.5, 152.8, 146.6, 145.4, 143.8, 134.6, 132.1, 131.7, 131.0, 130.1, 127.6, 126.6, 124.4, 124.1, 123.6, 122.3, 113.4, 79.0, 75.5, 56.7, 52.7, 34.8, 31.0, 30.2, 29.6, 29.4, 29.2, 25.4, 24.4, 23.8, 23.4, 22.4, 22.3 ppm.

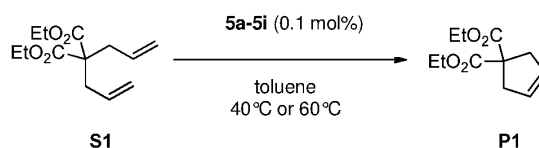
HRMS-ESI calculated for C₃₄H₄₅NOKCl₂Ru [M+K]⁺: 694.1559; found 694.1552.

Elemental analysis: calculated for C₃₄H₄₅NOCl₂Ru:

- 30 C 62.28; H 6.92; N 2.14; Cl 10.81; found: C 62.25; H 6.88; N 1.98; Cl 10.76.

EXAMPLE XXXVI

Application of precatalysts **5a-5i** in ring-closing metathesis (RCM) reactions of diethyl diallylmalonate **S1** leading to a cyclic compound **P1**.



To the solution of diethyl diallylmalonate **S1** (480.6 mg, 2.0 mmol) in dry deoxygenated toluene (20 mL) at 40°C or 60°C a solution of respective precatalyst **5a-5i** (0.002 mmol, 0.1 mol%) in dry deoxygenated toluene (50 μ L) was added. The whole was stirred in argon atmosphere. At certain time intervals 0.1 mL samples of reaction mixture were collected to which one drop of ethyl vinyl ether was added to deactivate the catalyst. Conversion of substrate was determined by gas chromatography. A summary is presented in Table 4 (40°C) and Table 5 (60°C).

10 Table 4. DEDAM conversion as a function of time for a reaction conducted at 40°C.

T=40°C	Conversion (%)								
Time (min)	5a	5c	5d	5h	5e	5g	5f	5i	1d
2	-	14	3	-	2	-		-	6
4	-	25	6	-	7	-		-	22
6	-	37	9	-	14	-		8	42
8	-	49	12	-	21	-		-	60
10	-	60	15	0.2	30	0.7	3	13	73
15	-	81	24	-	48	-		-	90
20	-	92	32	-	63	-		27	95
30	0.6	99	49	-	86	4	9	41	98
60	1	99.6	86	0.6	99	8	19	68	99.2
120	1.8	-	99	1.2	-	12	37	90	-
180	3	-	-	-	-	18	52	96	-

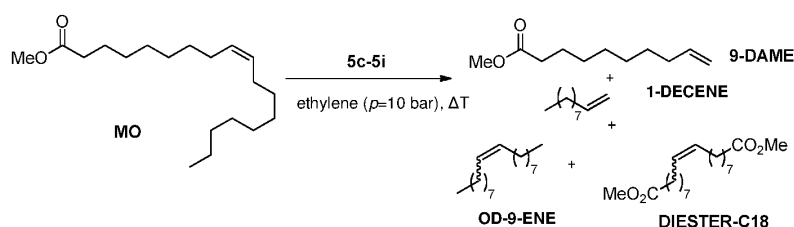
Table 5. DEDAM conversion as a function of time for reaction conducted at 60°C.

T=60°C	Conversion (%)			
Time (min)	5h	5g	5f	5i
2	-	-	10	36
4	-	-	21	69
6	-	4	33	85
8	-	-	44	93

10	1	5	54	97
15	-	-	74	99
20	3	-	86	99.6
30	6	7	96	99.7
60	22	10	99.6	99.8
120	63	20	-	
180	89	38	-	

EXAMPLE XXXVII

Application of precatalysts **5c** – **5i** in ethenolysis reactions of methyl oleate (**MO**).



- 5 To degassed **MO** (35.0 g, 118 mmol) a catalyst (10 ppm or 5 ppm) solution in dry deoxygenated toluene (100 μL) was added. The mixture was vacuum-pumped to an autoclave and stirred for 5 hours in a suitable temperature at 10 bar of ethylene. After 5 hours the reaction was quenched and after removal of ethylene from the reactor to the reaction mixture 0.1 mL 0.1 M **SnatchCat** solution [CAS: 51641-96-4] in methylene chloride was added to deactivate the catalyst. The samples were diluted with methylene
- 10 chloride and analysed by gas chromatography. The conversions were calculated using residual methyl stearate as an internal standard. The results were summarised in Table 6.

In order to determine the FID detector response factors to individual components of the reaction mixture a mixture of substrate - methyl oleate (**MO**), desired reaction products: **1-DECENE** and **9-DAME**, and reaction by-products **OD-9-ENE** and **DIESTER-C18** diester according to the table below was prepared.

- 15 The resulting mixture was diluted with toluene to 10 mL and analysed by gas chromatography. The area under the peak (AUP) for each component (mean of seven injections) was divided by the component mass of the analytical sample taking into account its purity and obtaining absolute response factor of a given component R_f' . Assuming the response factor of methyl oleate (**MO**) equal to $R_f=1$, from the proportions the absolute response factors R_f for remaining components were calculated.

- 20 Table 6.

Component	Analytical sample mass [mg]	Purity according to GC [%]	Area under the peak AUP [μV×s]	Absolute response factor R_f' =AUP/(m×purity)	Response factor for MO R_f
-----------	-----------------------------	----------------------------	--------------------------------	---	-------------------------------------

				[$\mu\text{V}\times\text{s}/\text{mg}$]	
1-DECENE	23.91	99.9	101514.2	4249.9	0.63
9-DAME	28.74	98.0	112831.5	4006.1	0.60
OD-9-ENE	20.65	98.0	145112.4	7170.6	1.07
MO	18.74	96.3	121077.7	6709.2	1.00
DIESTER-C18	19.75	97.4	102791.4	5343.6	0.80

In the further calculations, the area under the peak of a given component on the chromatogram was converted into percentage in the mixture using response factors calculated above.

Reaction selectivity (S) was determined from the formula:

$S = 100 \times (n_{1\text{-DECENE}} + n_{9\text{-DAME}}) / [(n_{1\text{-DECENE}} + n_{9\text{-DAME}}) + 2 \times (n_{\text{OD-9-ENE}} + n_{\text{DIESTER-C18}})]$, where n is the number of moles

Reaction yield (Y) was determined from the formula:

$Y = \text{Conversion} \times \text{Selectivity} / 100$

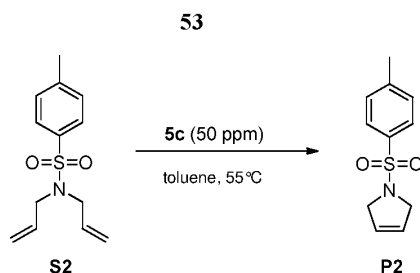
$\text{TON} = \text{Reaction yield} / \text{catalyst amount in ppm} \times 10000$.

Table 7. Methyl oleate (**MO**) ethenolysis with **5c-5i** and **1d** precatalysts application.

Precatalyst	Precatalyst amount (ppm)	T (°C)	Conversion (%)	9-DAME content in the mixture	Selectivity (%)	Yield (%)	TON
5c	10	50	59	34	89	53	52782
5c	5	50	41	28	91	37	73855
5d	10	60	53	31	89	47	46876
5e	10	50	70	40	88	61	61361
5e	5	60	48	31	90	43	86025
5f	10	60	21	16	92	19	18930
5i	10	65	55	34	87	48	47638
1d	10	40	61	34	91	56	56091
1d	5	40	51	33	92	46	92505

EXAMPLE XXXVIII

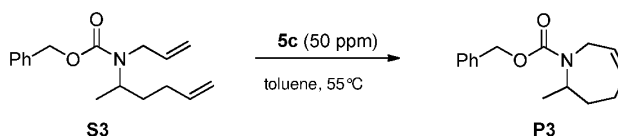
Application of precatalyst **5c** in ring-closing metathesis (RCM) reaction of diallyl tosylamide **S2** leading to a cyclic compound **P2**.



To solution of diallyl tosylamide **S2** (205.0 mg, 0.816 mmol) in dry deoxygenated toluene (3 mL) at 55°C a solution of precatalyst **5c** (0.041 mg, 0.041 μ mol, 50 ppm) in dry deoxygenated toluene (50 μ L) was added. The whole was stirred in argon atmosphere. After 20 minutes a 0.1 mL sample of reaction mixture was collected to which a drop of 0.1 M **SnatchCat** solution was added to deactivate the catalyst. Conversion of substrate determined by gas chromatography was above 99.5%.

EXAMPLE XXXIX

Application of precatalyst **5c** in ring-closing metathesis (RCM) reaction of compound **S3** leading to a cyclic compound **P3**.



10

To solution of compound **S3** (212.0 mg, 0.776 mmol) in dry deoxygenated toluene (3 mL) at 55°C solution of precatalyst **5c** (0.039 mg, 0.039 μ mol, 50 ppm) in dry deoxygenated toluene (50 μ L) was added. The whole was stirred in argon atmosphere. After 1 hour a 0.1 mL sample of reaction mixture was collected to which a drop of 0.1 M **SnatchCat** solution was added to deactivate the catalyst. Conversion of substrate determined by gas chromatography was above 99.5%. No by-products were observed.

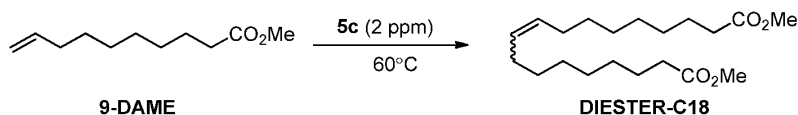
15

¹H NMR (CDCl₃, 500 MHz): δ = 7.39-7.27 (m, 5H), 5.74-5.62 (m, 2H), 5.19-5.10 (m, 2H), 4.46-4.06 (m, 2H), 3.64-3.56 (m, 1H), 2.26-2.08 (m, 2H), 1.93-1.67 (m, 2H), 1.15 (dd, J = 6.4; 4.5 Hz, 3H) ppm.

¹³C NMR (CDCl₃, 125 MHz): δ = 156.04, 155.96, 137.2, 137.1, 131.7, 131.4, 128.4, 128.3, 127.8, 127.7, 127.6, 127.4, 66.9, 66.7, 52.5, 52.3, 39.4, 39.1, 34.0, 33.9, 27.1, 26.9, 19.6, 19.1 ppm.

20 **EXAMPLE XXXX**

Application of precatalyst **5c** in homometathesis reaction of 9-decenoic acid methyl ester **9-DAME** leading to compound **DIESTER-C18**.



To 9-decenoic acid methyl ester **9-DAME** (5.53 g, 30.0 mmol) at 60°C a solution of precatalyst **5c** (0.060 mg, 0.060 μ mol, 2 ppm) in dry deoxygenated toluene (50 μ L) was added. The whole was stirred in argon atmosphere (argon was bubbled through the reaction mixture). After 2 hours the reaction mixture was cooled to the ambient temperature, 5 drops of 0.1 M **SnatchCat** solution were added and reaction mixture was stirred for the next 30 minutes.

25

In order to plot standard curves two analytical samples of substrate and product, respectively, were prepared. Analytical samples were diluted to obtain respective standard solution concentrations. Graphs depicting relationship between area under the peak (AUP) on the chromatogram and the concentration (mg/mL) of the analysed compound were shown in the Fig. 2.

- 5 28.70 mg of the analytical sample of the post-reaction mixture was prepared and diluted to 10 mL (2.87 mg/mL).

On the chromatogram of such obtained solution AUP for the substrate was 166469.8 $\mu\text{V}\times\text{s}$ (mean of three injections) and AUP for product was 47666.1 $\mu\text{V}\times\text{s}$ (mean of three injections), what corresponded to the substrate concentration of 0.89 mg/mL (based on the substrate standard curve) and product concentration of 1.95 mg/mL (based on the product standard curve).

Conversion and yield were determined from the formulas:

$$\text{Conversion} = 100\% \times (1 - (0.89/2.87)) = 68.99\%$$

$$\text{Yield} = 100\% \times 1.95/2.87 = 67.94\%.$$

$$\text{Selectivity} = 100\% \times \text{Yield}/\text{Conversion} = 98.48\%.$$

- 15 TON = 169850.

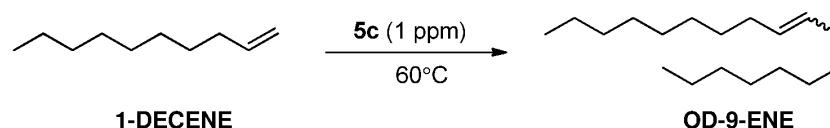
A mixture of *E/Z* isomers (1.5:1).

¹H NMR (CDCl₃, 500 MHz): δ = 5.36 (ddd, *J* = 5.3; 3.7; 1.6 Hz, 2H, *E*), 5.32 (ddd, *J* = 5.7; 4.3; 1.1 Hz, 2H, *Z*), 3.65 (s, 6H), 2.29 (t, *J* = 7.5 Hz, 4H), 2.03-1.90 (m, 4H), 1.68-1.56 (m, 4H), 1.35-1.23 (m, 16H) ppm.

- 20 ¹³C NMR (CDCl₃, 125 MHz): δ = 174.25 (*E*), 174.24 (*Z*), 130.3 (*E*), 129.8 (*Z*), 51.4, 34.1, 32.5, 29.6 (*Z*), 29.5 (*E*), 29.12 (*Z*), 29.08 (*E*), 29.07 (*E*), 29.05 (*Z*), 28.9, 27.1 (*Z*), 24.9 (*E*) ppm.

EXAMPLE XXXXI

Application of precatalyst **5c** in homometathesis reaction of **1-DECENE** leading to octadec-9-ene **E**.



- To **1-DECENE** (5.22 g, 37.2 mmol) at 60°C a solution of precatalyst **5c** (0.037 mg, 0.037 μmol , 1 ppm) in dry deoxygenated toluene (50 μL) was added. The whole was stirred in argon atmosphere (argon was bubbled through the reaction mixture). After 2 hours the reaction mixture was cooled to the ambient temperature, 5 drops of 0.1 M **SnatchCat** solution were added and it was stirred for the next 30 minutes. Then two solutions of reaction mixture with known concentration were prepared separately. Conversion (64%) and yield (63%) were determined by gas chromatography using external standard method (calculations are performed analogously to those shown in Example XXXX). Graphs depicting relationship between area under the peak (AUP) on the chromatogram and the concentration (mg/mL) of the analysed compound were shown in the Fig. 3. Reaction selectivity 98%. TON was 316398.

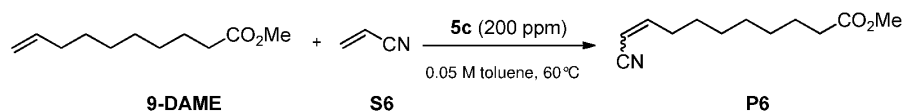
A mixture of *E/Z* isomers (4:1).

- 35 ¹H NMR (CDCl₃, 500 MHz): δ = 5.39 (ddd, *J* = 5.3; 3.7; 1.6 Hz, 2H, *E*), 5.35 (ddd, *J* = 5.7; 4.4; 1.1 Hz, 2H, *Z*), 2.06-1.91 (m, 4H), 1.38-1.18 (m, 24H), 0.88 (t, *J* = 6.9 Hz, 6H) ppm.

¹³C NMR (CDCl₃, 125 MHz): δ = 130.4 (*E*), 129.9 (*Z*), 32.6, 31.9, 29.8 (*Z*), 29.7 (*E*), 29.53 (*Z*), 29.51 (*E*), 29.3, 29.2 (*E*), 27.2 (*Z*), 22.7, 14.1 ppm.

EXAMPLE XXXXII

Application of precatalyst **5c** in cross-metathesis reaction of 9-decenoic acid methyl ester **9-DAME** with acrylonitrile **S6** leading to compound **P6**.



To solution of 9-decenoic acid methyl ester **9-DAME** (184.0 mg, 1.0 mmol) in dry deoxygenated toluene (20 mL) acrylonitrile **S6** (99 μ L, 1.50 mmol, 1.5 molar equivalents) and methyl stearate (10 mg, internal standard) were added at 60°C, following by a solution of precatalyst **5c** (0.1 mg, 0.1 μ mol, 100 ppm) in dry deoxygenated toluene (50 μ L). Reaction mixture was stirred in argon atmosphere. After 1 hour and then after 2 hours further portions of precatalyst **5c** (2x 0.05 mg, 0.05 μ mol, 50 ppm) in dry deoxygenated toluene (50 μ L) were added. Totally 0.2 mg, 0.2 μ mol, 200 ppm precatalyst **5c** was used. After another hour 0.1 mL reaction mixture sample was collected to which a drop of 0.1 M **SnatchCat** solution was added to deactivate the catalyst. Conversion of substrate determined by gas chromatography with internal standard was 87%. Content of the **P6** product on the chromatogram was 75%.

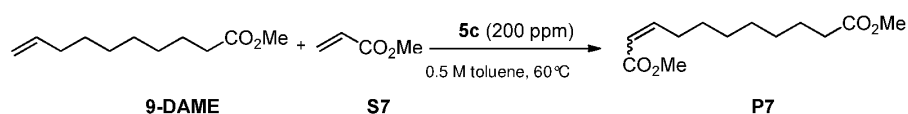
A mixture of E/Z isomers (1:4).

¹H NMR (CDCl₃, 500 MHz): δ = 6.69 (dt, *J* = 16.4; 7.0 Hz, 1H, *E*), 6.46 (dt, *J* = 10.9; 7.7 Hz, 1H, *Z*), 5.30 (dt, *J* = 16.4; 1.7 Hz, 1H, *E*), 5.29 (dt, *J* = 10.9; 1.3 Hz, 1H, *Z*), 3.65 (s, 3H, *E* + 3H, *Z*), 2.40 (dq, *J* = 7.6; 1.3 Hz, 2H, *Z*), 2.29 (t, *J* = 7.5 Hz, 2H, *E* + 2H, *Z*), 2.20 (qd, *J* = 7.1; 1.7 Hz 2H, *E*), 1.64-1.54 (m, 2H, *E* + 2H, *Z*), 1.50-1.39 (m, 2H, *E* + 2H, *Z*), 1.36-1.26 (m, 6H, *E* + 6H, *Z*) ppm.

¹³C NMR (CDCl₃, 125 MHz): δ = 174.12 (*Z*), 174.08 (*E*), 156.0 (*E*), 155.0 (*Z*), 117.5 (*E*), 116.0 (*Z*), 99.6 (*E*), 99.5 (*Z*), 51.39 (*E*), 51.37 (*Z*), 33.95 (*Z*), 33.92 (*E*), 33.2 (*E*), 31.7 (*Z*), 28.87 (*Z*), 28.85 (*E*), 28.83 (*Z+E*), 28.72 (*Z*), 28.68 (*E*), 28.1 (*Z*), 27.5 (*E*), 24.77 (*Z*), 24.75 (*E*) ppm.

EXAMPLE XXXXIII

25 Application of precatalyst **5c** in cross-metathesis reaction of 9-decenoic acid methyl ester **9-DAME** with methyl acrylate **S7** leading to compound **P7**.



To solution of 9-decenoic acid methyl ester **9-DAME** (400.0 mg, 2.17 mmol) in dry deoxygenated toluene (4 mL) methyl acrylate **S7** (0.98 mL, 10.9 mmol, 5 molar equivalents), methyl stearate (20 mg, internal standard) were added at 60 °C, following by a solution of precatalyst **5c** (0.109 mg, 0.109 μmol, 50 ppm) in dry deoxygenated toluene (50 μL). The whole was stirred in argon atmosphere. After 1 hour, 2 hours and 3 hours further portions of precatalyst **5c** (3x 0.109 mg, 0.109 μmol, 50 ppm) in dry deoxygenated toluene (50 μL) were added. Totally 0.436 mg, 0.436 μmol, 200 ppm of precatalyst **5c** was used. After another hour 0.1 mL reaction mixture sample was collected to which a drop of 0.1 M **SnatchCat** solution

was added to deactivate the catalyst. Conversion of substrate determined by gas chromatography with an internal standard was 99%. Content of product **P7** in postreaction mixture was 97%.

A mixture of *E/Z* isomers (87:13).

Isomer *E*:

- 5 ¹H NMR (CDCl₃, 500 MHz): δ = 6.94 (dt, *J* = 15.7; 7.0 Hz, 1H), 5.80 (dt, *J* = 15.6; 1.6 Hz, 1H), 3.71 (s, 3H), 3.65 (s, 3H), 2.28 (t, *J* = 7.5 Hz, 2H), 2.17 (dq, *J* = 7.1; 1.6 Hz, 2H), 1.64-1.56 (m, 2H), 1.47-1.39 (m, 2H), 1.33-1.26 (m, 6H) ppm.

¹³C NMR (CDCl₃, 125 MHz): δ = 174.2, 167.1, 149.6, 133.4, 120.8, 51.4, 51.3, 34.0, 32.1, 29.0, 28.9, 27.9, 24.8 ppm.

- 10 Isomer *Z*:

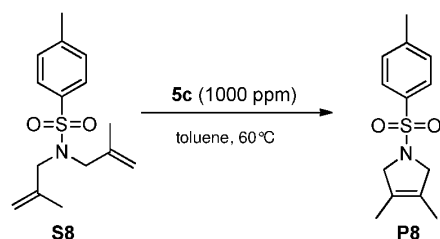
¹H NMR (CDCl₃, 500 MHz): δ = 6.22 (dt, *J* = 11.6; 7.5 Hz, 1H), 5.76 (dt, *J* = 11.5; 1.7 Hz, 1H), 3.70 (s, 3H), 3.66 (s, 3H), 2.64 (dq, *J* = 7.5; 1.7 Hz, 2H), 2.30 (t, *J* = 7.5 Hz, 2H), 1.65-1.56 (m, 2H), 1.47-1.39 (m, 2H), 1.34-1.28 (m, 6H) ppm.

¹³C NMR (CDCl₃, 125 MHz): δ = 174.3, 166.8, 150.8, 119.2, 51.4, 51.0, 34.1, 29.1, 29.0, 28.9, 24.9, 24.8 ppm.

- 15

EXAMPLE XXXXIV

Application of precatalyst **5c** in ring-closing metathesis reaction of **S8** leading to compound **P8** having a tetrasubstituted double bond.



- 20 To solution of compound **S8** (509.0 mg, 1.82 mmol) in dry deoxygenated toluene (6.8 mL) at 60°C, in argon atmosphere every 10 minutes a solution of precatalyst **5c** (0.182 mg, 0.182 μmol, 100 ppm) in dry deoxygenated toluene (50 μL) was added up to a total amount of 1000 ppm of precatalyst **5c** (10 portions). The whole was stirred in argon atmosphere for an additional hour. 0.1 mL of the reaction mixture sample was collected to which a drop of 0.1 M **SnatchCat** solution was added to deactivate the catalyst.
- 25 Conversion of substrate determined by gas chromatography was 90%. The product was isolated by column chromatography on silica gel. White solid, 361 mg (79%).

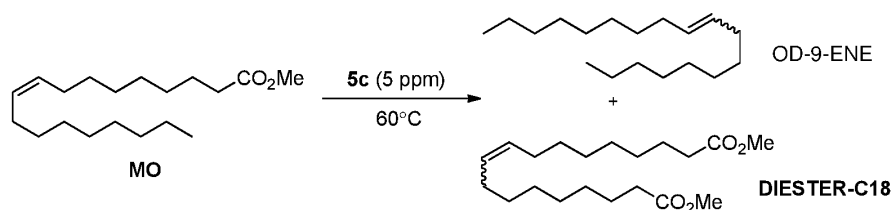
¹H NMR (CDCl₃, 500 MHz): δ = 7.70 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 3.96 (s, 4H), 2.41 (s, 3H), 1.53 (s, 6H) ppm.

¹³C NMR (CDCl₃, 125 MHz): δ = 143.2, 134.2, 129.6, 127.4, 126.1, 58.7, 21.4, 11.0 ppm.

- 30 **EXAMPLE XXXXV**

Application of precatalyst **5c** in homometathesis reaction of methyl oleate **MO** leading to **OD-9-ENE** and **DIESTER-C18** compounds.

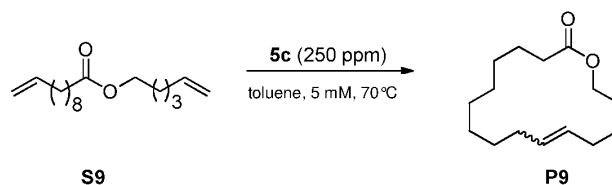
57



- To methyl oleate **MO** (19.52 g, 65.9 mmol) at 60°C in argon atmosphere every 30 minutes a solution of precatalyst **5c** (0.066 mg, 0.066 μ mol, 1 ppm) in dry deoxygenated toluene (50 μ L) was added, up to 5 ppm of precatalyst **5c** (5 portions). The whole was stirred in argon atmosphere for an additional hour. A drop of reaction mixture was collected and diluted with ethyl acetate to 1 mL, and then a drop of 0.1 M **SnatchCat** solution was added to deactivate the catalyst. The sample was analysed by gas chromatography. In the chromatogram obtained the **OD-9-ENE/MO/DIESTER-C18** area ratio was 21%/57%/22%, respectively.

EXAMPLE XXXXVI

- Application of precatalyst **5c** in ring-closing metathesis reaction of compound **S9** leading to macrocyclic lactone **P9**.



- To solution of compound **S9** (213.0 mg, 0.799 mmol) in dry deoxygenated toluene (160 mL, $C_{S9}=5$ mM) at 70°C, in argon atmosphere every 15 minutes a solution of precatalyst **5c** (0.040 mg, 0.040 μ mol, 50 ppm) in dry deoxygenated toluene (50 μ L) was added up to a total amount of (pre)catalyst 250 ppm (5 portions). The whole was stirred in argon atmosphere for an additional hour. 1 mL of the reaction mixture sample was collected to which a drop of 0.1 M **SnatchCat** solution was added to deactivate the catalyst. Conversion of substrate determined by gas chromatography with external standard was 95%. $E/Z = 65:35$. Standard curve for product **P9** was shown in the Fig. 4.

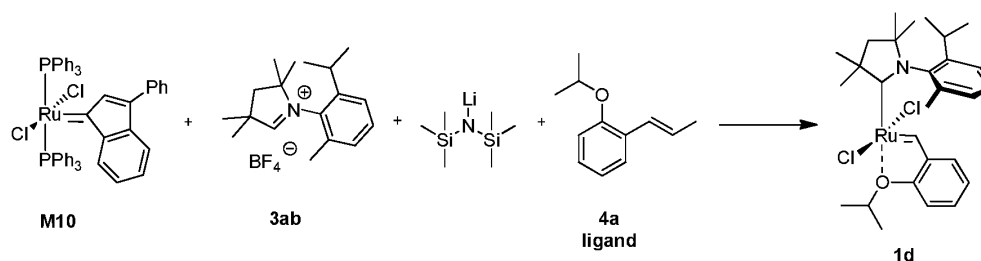
- Postreaction mixture was analysed with GC without further dilutions. Cumulative area under the peaks (E and Z isomers) of the product was 1165868 (mean of three injections). Product concentration in postreaction mixture was 4.56 mM ($C=1165868 / 255756$). Yield GC $Y = 4,56 \text{ mM} \times 100\% / 5 \text{ mM} = 91\%$.

¹H NMR (CDCl₃, 500 MHz): δ = 5.43-5.23 (m, 2H), 4.13 (t, J = 6.3 Hz, 2H, Z), 4.11 (t, J = 7.1 Hz, 2H, E), 2.35-2.27 (m, 2H), 2.07-1.98 (m, 4H), 1.67-1.55 (m, 4H), 1.44-1.16 (m, 12H) ppm.

- ¹³C NMR (CDCl₃, 125 MHz): δ = 173.8, 131.8 (E), 130.3 (E), 130.1 (Z), 129.5 (Z), 64.1 (Z), 63.9 (E), 34.7 (E), 33.8 (Z), 32.0 (E), 31.9 (E), 29.1 (Z), 28.4 (Z), 28.3 (E), 28.3 (E), 28.2 (E), 28.1 (Z), 28.0 (E), 27.9 (Z), 27.6 (Z), 27.21 (E), 27.18 (Z), 27.1 (Z), 26.6 (Z), 26.5 (E), 26.4 (Z), 25.4 (E), 25.20 (Z), 25.18 (E) ppm.

EXAMPLE XXXXVII

Preparation method of precatalyst **1d** without CuCl.

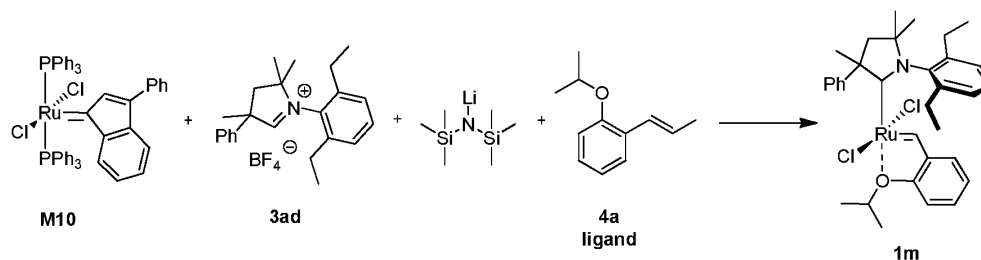


To salt **3ab** (0.345 g, 1.0 mmol, 2 molar equivalents) dry deoxygenated toluene (4 mL) was added in argon atmosphere. The mixture was heated to 80°C and solution of LiHMDS in toluene (1 M, 1.0 mL, 1.0 mmol, 2 molar equivalents) was added. After 1 minute solid complex **M10** (0.443 g, 0.5 mmol, 1 molar equivalent) was added. After 2 minutes benzylidene ligand **4a** (0.176 g, 1.0 mmol, 2.0 molar equivalents) was added. The whole was stirred for 30 minutes at 105°C and cooled down to the room temperature. The crude product was isolated by column chromatography on silica gel (eluent: toluene). Green fraction was collected and concentrated to dryness. The residue was dissolved in ethyl acetate and evaporated and the residue was washed with isopropanol and dried under high vacuum giving green crystalline solid – precatalyst **1d** (0.130 g, 45%).

Analytical data for product **1d** obtained by this method were identical as in Example VII.

EXAMPLE XXXXVIII

Preparation method of precatalyst **1m** without CuCl.



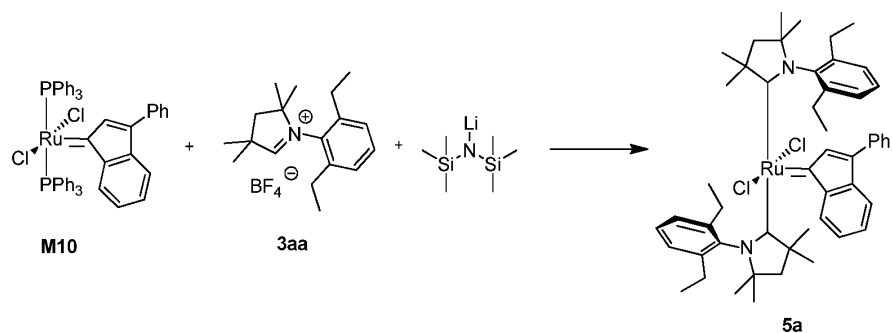
15 To salt **3ad** (0.407 g, 1.0 mmol, 2 molar equivalents) dry deoxygenated toluene (4 mL) was added in argon atmosphere. The mixture was heated to 80°C and solution of LiHMDS in toluene (1 M, 1.0 mL, 1.0 mmol, 2 molar equivalents) was added. After 1 minute solid complex **M10** (0.443 g, 0.5 mmol, 1 molar equivalent) was added. After 2 minutes benzylidene ligand **4a** (0.176 g, 1.0 mmol, 2.0 molar equivalents) was added. The whole was stirred for 30 minutes at 105°C and cooled down to the room temperature.

20 The crude product was isolated by column chromatography on silica gel (eluent: toluene). Green fraction was collected and concentrated to dryness. The residue was dissolved in methylene chloride and excess of isopropanol was added. Methylene chloride was evaporated under reduced pressure, the resulting precipitate was filtrated off and washed with a small amount of isopropanol. It was dried under high vacuum giving green crystalline solid – precatalyst **1m** (0.151 g, 47%). A mixture of A:B isomers = 1:4.

25 Due to a very complex ¹H NMR spectrum only the characteristic benzylidene proton shifts were given: isomer A: singlet 17.88 ppm, isomer B: singlet 16.51 ppm (C₆D₆).

EXAMPLE XXXXIX

Preparation method of intermediate **5a** from first generation precursor **M10**

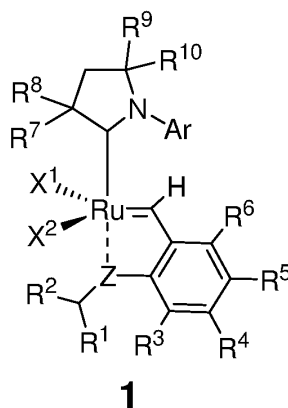


To salt **3aa** (10.00 g, 29.0 mmol, 3 molar equivalents) dry deoxygenated toluene (50 mL) was added in argon atmosphere. The mixture was heated to 80°C and solution of LiHMDS in toluene (1 M, 29.0 mL, 29.0 mmol, 3 molar equivalents) was added. After 1 minute solid complex **M10** (8.56 g, 9.66 mmol, 1 molar equivalent) was added. After 5 minutes the mixture was cooled down to the room temperature. Reaction mixture was filtrated through a small amount of silica gel and washed with toluene. The crude product was isolated by column chromatography on silica gel (eluent: ethyl acetate/cyclohexane 1:9 v/v). Red fraction was collected and concentrated to dryness. It was dissolved in *n*-pentane and slowly concentrated to dryness (the product crystallised during solvent removal). Red crystalline solid was obtained – an intermediate compound **5a** (5.02 g, 59%). Comparison with Example **XV**.

The project leading to this application has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 635405.

Claims

1. A process for producing a compound represented by the Formula 1,



wherein:

X¹ and X² are each independently an anionic ligand selected from halogen atoms, -CN, -SCN, -OR', -SR', -O(C=O)R', -O(SO₂)R', and -OSi(R')₃ group, wherein R' is C₁-C₁₂ alkyl, C₃-C₁₂ cycloalkyl, C₂-C₁₂ alkenyl, C₅-C₂₀ aryl, which are optionally substituted with at least one C₁-C₁₂ alkyl, C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, or a halogen atom;

Z is an atom selected from a group of O, S, NR', wherein R' is C₁-C₁₂ alkyl, C₃-C₁₂ cycloalkyl, C₂-C₁₂ alkenyl, C₅-C₂₀ aryl, which are optionally substituted with at least one C₁-C₁₂ alkyl, C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, or a halogen atom;

Ar is an aryl group substituted with hydrogen atoms or optionally substituted with at least one C₁-C₁₂ alkyl, C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy, and C₅-C₂₀ heteroaryloxy group, or a halogen atom;

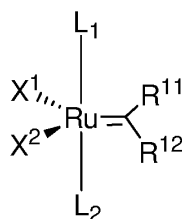
R¹ and R² are each independently hydrogen atom, C₁-C₂₅ alkyl group, C₁-C₂₅ alkoxy group, C₂-C₂₅ alkenyl group, C₁-C₁₂ perfluoroalkyl, C₅-C₂₀ aryl, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, or can be combined together to form substituted or unsubstituted C₄-C₁₀ cyclic or C₄-C₁₂ polycyclic system, can also be an ester (-COOR'), amide (-CONR'₂), formyl (-CHO), ketone (-COR'), and hydroxamic (-CON(OR')(R')) group or a halogen atom, in which R' is C₁-C₁₂ alkyl, C₃-C₁₂ cycloalkyl, C₂-C₁₂ alkenyl, C₅-C₂₀ aryl, which are optionally substituted with at least one C₁-C₁₂ alkyl, C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, or a halogen atom;

R³, R⁴, R⁵, R⁶ are each independently hydrogen atom, C₁-C₂₅ alkyl group, C₁-C₂₅ alkoxy group, or C₂-C₂₅ alkenyl group, wherein R³, R⁴, R⁵, R⁶ substituents can be combined together to form substituted or unsubstituted C₄-C₁₀ cyclic or C₄-C₁₂ polycyclic system, can also independently be an alkoxy (-OR'), sulphide (-SR'), sulfoxide (-S(O)R'), sulphonium (-S⁺R'₂), sulphone (-SO₂R'), sulphonamide (-SO₂NR'₂), amine (-NR'₂), ammonium (-N⁺R'₃), nitro (-NO₂), cyano (-CN), phosphonate (-P(O)(OR')₂), phosphinate (-P(O)R'(OR')), phosphoninim (-P(OR')₂), phosphine (-PR'₂), phosphine oxide (-P(O)R'₂), phosphonium (-

$P^+R'_3$), carboxy (-COOH), ester (-COOR'), amide (-CONR'₂, or -NR'C(O)R'), formyl (-CHO), and ketone (-COR') group, wherein R' is C₁-C₅ alkyl, C₁-C₅ perfluoroalkyl, C₅-C₂₄ aryl, C₇-C₂₄ aralkyl, C₅-C₂₄ perfluoroaryl;

R⁷, R⁸, R⁹, and R¹⁰ are each independently hydrogen atom, or C₁-C₂₅ alkyl group, R⁷ and/or R⁸ can be combined with R⁹ and/or R¹⁰ to form cyclic system, are also independently C₁-C₁₂ alkyl group, C₃-C₁₂ cycloalkyl, C₂-C₁₂ alkenyl, C₅-C₂₀ aryl, C₁-C₅ perfluoroalkyl, C₇-C₂₄ aralkyl, C₅-C₂₄ perfluoroaryl, which are optionally substituted with at least one C₁-C₁₂ alkyl, C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, or a halogen atom;

characterised in that the alkylidene ruthenium complex represented by the Formula 2



2

wherein:

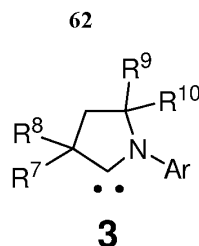
L¹, L² are each a neutral ligand selected from a group including phosphine, in particular P(R')₃, wherein each R' is independently C₁-C₁₂ alkyl, C₃-C₁₂ cycloalkyl, C₅-C₂₀ aryl, C₇-C₂₄ aralkyl, C₅-C₂₄ perfluoroaryl, 5-12-membered heteroaryl; two R' can be combined together to form cycloalkyl ring containing phosphorus atom in the ring.

X¹, X² are each an anionic ligand selected independently from a group including halide anions, -CN, -SCN, -OR', -SR', -O(C=O)R', -O(SO₂)R', and -OSi(R')₃ group, wherein R' is C₁-C₁₂ alkyl, C₃-C₁₂ cycloalkyl, C₂-C₁₂ alkenyl, or C₅-C₂₀ aryl, which is optionally substituted with at least one C₁-C₁₂ alkyl, C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, or a halogen atom;

R¹¹, R¹² are each independently hydrogen atom, halogen atom, optionally substituted C₁-C₂₅ alkyl, optionally substituted C₁-C₂₅ perfluoroalkyl, optionally substituted C₂-C₂₅ alkene, optionally substituted C₃-C₇ cycloalkyl, optionally substituted C₂-C₂₅ alkenyl, optionally substituted C₃-C₂₅ cycloalkenyl, optionally substituted C₂-C₂₅ alkynyl, optionally substituted C₃-C₂₅ cycloalkynyl, optionally substituted C₁-C₂₅ alkoxy, optionally substituted C₅-C₂₄ aryloxy, optionally substituted C₅-C₂₀ heteroaryloxy, optionally substituted C₅-C₂₄ aryl, optionally substituted C₅-C₂₀ heteroaryl, optionally substituted C₇-C₂₄ aralkyl, optionally substituted C₅-C₂₄ perfluoroaryl, optionally substituted 3-12-membered heterocycle;

wherein R¹¹ and R¹² substituents can be combined together to form a ring selected from a group including C₃-C₇ cycloalkyl, C₃-C₂₅ cycloalkenyl, C₃-C₂₅ cycloalkynyl, C₅-C₂₄ aryl, C₅-C₂₀ heteroaryl, C₅-C₂₄ perfluoroaryl, 3-12-membered heterocycle, which can be substituted independently with one and/or more substituents selected from a group including hydrogen atom, halogen atom, C₁-C₂₅ alkyl, C₁-C₂₅ perfluoroalkyl, C₂-C₂₅ alkene, C₃-C₇ cycloalkyl, C₂-C₂₅ alkenyl, C₃-C₂₅ cycloalkenyl, C₂-C₂₅ alkynyl, C₃-C₂₅ cycloalkynyl, C₁-C₂₅ alkoxy, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, C₅-C₂₄ aryl, C₅-C₂₀ heteroaryl, C₇-C₂₄ aralkyl, C₅-C₂₄ perfluoroaryl, 3-12-membered heterocycle;

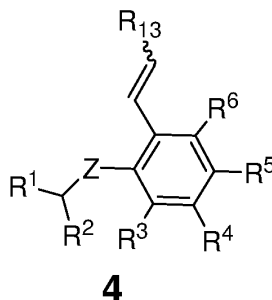
is reacted with carbene represented by the Formula 3



wherein:

Ar is an aryl group substituted with hydrogen atoms or optionally substituted with at least one C₁-C₁₂ alkyl, C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy group, or a halogen atom; R⁷, R⁸, R⁹, and R¹⁰ are each independently hydrogen atom, or C₁-C₂₅ alkyl group, R⁷ and/or R⁸ can be combined with R⁹ and/or R¹⁰ to form cyclic system, can be also independently C₁-C₁₂ alkyl, C₃-C₁₂ cycloalkyl, C₂-C₁₂ alkenyl, C₅-C₂₀ aryl, C₁-C₅ perfluoroalkyl, C₇-C₂₄ aralkyl, and C₅-C₂₄ perfluoroaryl group, which are optionally substituted with at least one C₁-C₁₂ alkyl, C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, or a halogen atom;

thus formed reaction mixture is then contacted with the compound represented by the Formula 4



wherein:

Z is an atom selected from a group of O, S, NR', wherein R' is C₁-C₁₂ alkyl, C₃-C₁₂ cycloalkyl, C₂-C₁₂ alkenyl, C₅-C₂₀ aryl, which are optionally substituted with at least one C₁-C₁₂ alkyl, C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, or a halogen atom;

R¹ and R², are each independently hydrogen atom, C₁-C₂₅ alkyl group, C₁-C₂₅ alkoxy group, C₂-C₂₅ alkenyl group, C₁-C₁₂ perfluoroalkyl, C₅-C₂₀ aryl, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, or can be combined together to form substituted or unsubstituted C₄-C₁₀ cyclic or C₄-C₁₂ polycyclic system, can also be an ester (-COOR'), amide (-CONR'₂), formyl (-CHO), ketone (-COR'), and hydroxamic (-CON(OR')(R')) group or a halogen atom, wherein R' is C₁-C₁₂ alkyl, C₃-C₁₂ cycloalkyl, C₂-C₁₂ alkenyl, C₅-C₂₀ aryl, which are optionally substituted with at least one C₁-C₁₂ alkyl, C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, or a halogen atom;

R³, R⁴, R⁵, R⁶ are each independently hydrogen atom, C₁-C₂₅ alkyl group, C₁-C₂₅ alkoxy group, or C₂-C₂₅ alkenyl group, wherein R³, R⁴, R⁵, R⁶ substituents can be combined together to form substituted or unsubstituted C₄-C₁₀ cyclic or C₄-C₁₂ polycyclic system; can independently also be alkoxy (-OR'), sulphide (-SR'), sulfoxide (-S(O)R'), sulphonium (-S⁺R'₂), sulphone (-SO₂R'), sulphonamide (-SO₂NR'₂), amine (-NR'₂), ammonium (-N⁺R'₃), nitro (-NO₂), cyano (-CN), phosphonate (-P(O)(OR')₂), phosphinate (-P(O)R'(OR')), phosphoninim (-P(OR')₂), phosphine (-PR'₂), phosphine oxide (-P(O)R'₂), phosphonium (-P⁺R'₃), carboxy (-COOH), ester (-COOR'), amide (-CONR'₂, or -NR'C(O)R'), formyl (-CHO), and ketone (-

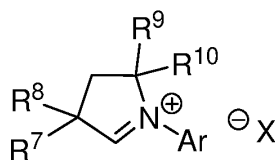
COR') group, wherein R' is C₁-C₅ alkyl, C₁-C₅ perfluoroalkyl, C₅-C₂₄ aryl, C₇-C₂₄ aralkyl, C₅-C₂₄ perfluoroaryl;

R¹³ is a hydrogen atom, C₁-C₂₅ alkyl group, C₁-C₂₅ alkoxy group, C₂-C₂₅ alkenyl group, C₁-C₁₂ perfluoroalkyl, C₅-C₂₀ aryl, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, or can be combined together to form substituted or unsubstituted C₄-C₁₀ cyclic or C₄-C₁₂ polycyclic system or a halogen atom;

to form the compound represented by the Formula 1.

2. A process according to claim 1, **characterised in that** the reaction mixture is contacted with the compound represented by the Formula 4 in the presence of phosphine ligand scavenger PR'₃ and/or CAAC ligand scavenger.

3. A process for producing compound represented by the Formula 1 according to claims 1 or 2, **characterised in that** carbenes represented by the Formula 3 are provided to the reaction medium by their generation *in situ* from suitable carbene precursors, CAAC salts represented by the Formula 3a,



3a

wherein:

Ar is an aryl group substituted with hydrogen atoms or optionally substituted with at least one C₁-C₁₂ alkyl, C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy, and C₅-C₂₀ heteroaryloxy group, or a halogen atom;

R⁷, R⁸, R⁹, and R¹⁰ are each independently hydrogen atom, or C₁-C₂₅ alkyl group, R⁷ and/or R⁸ can be combined with R⁹ and/or R¹⁰ to form cyclic system, can be also independently C₁-C₁₂ alkyl, C₃-C₁₂ cycloalkyl, C₂-C₁₂ alkenyl, C₅-C₂₀ aryl, C₁-C₅ perfluoroalkyl, C₇-C₂₄ aralkyl, and C₅-C₂₄ perfluoroaryl group, which are optionally substituted with at least one C₁-C₁₂ alkyl, C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, or a halogen atom;

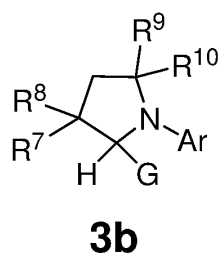
X⁻ is a halide anion, or BF₄⁻, PF₆⁻, ClO₄⁻, CF₃SO₂O⁻.

involving contacting compound represented by the Formula 3a with suitable base selected from potassium *N,N'*-bis(trimethylsilyl)amide, lithium *N,N'*-bis(trimethylsilyl)amide, sodium *N,N'*-bis(trimethylsilyl)amide, potassium *tert*-amylate, potassium *tert*-butoxide, sodium hydride.

4. A process for producing a compound represented by the Formula 1 according to any one of claims 1 to 3, **characterised in that** carbenes represented by the Formula 3 are provided in the reaction medium by their generation *in situ* from suitable carbene precursors represented by the Formula 3a, which are contacted with a base such as alkali metal *N,N'*-bis(trimethylsilyl)amide.

5. A process for producing a compound represented by the Formula 1 according to claim 1 or 2, **characterised in that** the carbenes represented by the Formula 3 are provided in the reaction medium

by their thermal generation *in situ* from suitable carbene precursors represented by the Formula **3b** which are chloroform or alcohol adducts,

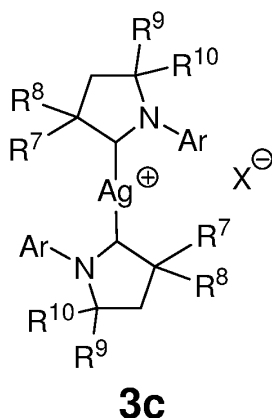


wherein:

G is CCl_3 or OR' , wherein R' is $\text{C}_1\text{-C}_{12}$ alkyl, $\text{C}_3\text{-C}_{12}$ cycloalkyl, $\text{C}_2\text{-C}_{12}$ alkenyl, or $\text{C}_5\text{-C}_{20}$ aryl, which is optionally substituted with at least one $\text{C}_1\text{-C}_{12}$ alkyl, $\text{C}_1\text{-C}_{12}$ perfluoroalkyl, $\text{C}_1\text{-C}_{12}$ alkoxy, $\text{C}_5\text{-C}_{24}$ aryloxy, $\text{C}_5\text{-C}_{20}$ heteroaryloxy or a halogen atom;

Ar is an aryl group substituted with hydrogen atoms or optionally substituted with at least one $\text{C}_1\text{-C}_{12}$ alkyl, $\text{C}_1\text{-C}_{12}$ perfluoroalkyl, $\text{C}_1\text{-C}_{12}$ alkoxy, $\text{C}_5\text{-C}_{24}$ aryloxy, and $\text{C}_5\text{-C}_{20}$ heteroaryloxy group, or a halogen atom; R^7 , R^8 , R^9 , and R^{10} are each independently hydrogen atom or $\text{C}_1\text{-C}_{25}$ alkyl group, R^7 and/or R^8 can be combined with R^9 and/or R^{10} to form cyclic system, can be also independently $\text{C}_1\text{-C}_{12}$ alkyl, $\text{C}_3\text{-C}_{12}$ cycloalkyl, $\text{C}_2\text{-C}_{12}$ alkenyl, $\text{C}_5\text{-C}_{20}$ aryl, $\text{C}_1\text{-C}_5$ perfluoroalkyl, $\text{C}_7\text{-C}_{24}$ aralkyl, $\text{C}_5\text{-C}_{24}$ perfluoroaryl group, which are optionally substituted with at least one $\text{C}_1\text{-C}_{12}$ alkyl, $\text{C}_1\text{-C}_{12}$ perfluoroalkyl, $\text{C}_1\text{-C}_{12}$ alkoxy, $\text{C}_5\text{-C}_{24}$ aryloxy, $\text{C}_5\text{-C}_{20}$ heteroaryloxy, or a halogen atom.

6. A process for producing a compound represented by the Formula **1** according to any one of claims 1 to 5, **characterised in that** the alkylidene ruthenium complex represented by the Formula **2** is contacted with the compound represented by the Formula **3c** which acts as CAAC carbene ligand donor represented by the Formula **3**,



wherein:

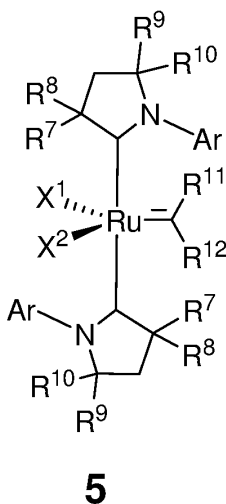
Ar is an aryl group substituted with hydrogen atoms or optionally substituted with at least one $\text{C}_1\text{-C}_{12}$ alkyl, $\text{C}_1\text{-C}_{12}$ perfluoroalkyl, $\text{C}_1\text{-C}_{12}$ alkoxy, $\text{C}_5\text{-C}_{24}$ aryloxy, and $\text{C}_5\text{-C}_{20}$ heteroaryloxy group, or a halogen atom; R^7 , R^8 , R^9 , and R^{10} are each independently hydrogen atom or $\text{C}_1\text{-C}_{25}$ alkyl group, R^7 and/or R^8 can be combined with R^9 and/or R^{10} to form cyclic system, can be also independently $\text{C}_1\text{-C}_{12}$ alkyl, $\text{C}_3\text{-C}_{12}$

cycloalkyl, C₂-C₁₂ alkenyl, C₅-C₂₀ aryl, C₁-C₅ perfluoroalkyl, C₇-C₂₄ aralkyl, and C₅-C₂₄ perfluoroaryl group, which are optionally substituted with at least one C₁-C₁₂ alkyl, C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, or a halogen atom;

X is a halide anion or BF₄⁻, PF₆⁻, ClO₄⁻, CF₃SO₃⁻.

7. A process for producing a compound represented by the Formula 1 according to claim 1 to 2, **characterised in that** the carbenes represented by the Formula 3 are provided to the reaction medium by their direct adding to the reaction mixture.

8. A process for producing a compound represented by the Formula 1 according to any one of claims 1 to 7, **characterised in that** the alkylidene ruthenium complex represented by the Formula 2 is reacted with carbene represented by the Formula 3 to form an intermediate represented by the Formula 5



wherein:

X¹ and X² are each independently an anionic ligand selected from halogen atoms, -CN, -SCN, -OR', -SR', -O(C=O)R', -O(SO₂)R', and -OSi(R')₃ group, wherein R' is C₁-C₁₂ alkyl, C₃-C₁₂ cycloalkyl, C₂-C₁₂ alkenyl, C₅-C₂₀ aryl, which are optionally substituted with at least one C₁-C₁₂ alkyl, C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, or a halogen atom;

Ar is an aryl group substituted with hydrogen atoms or optionally substituted with at least one C₁-C₁₂ alkyl, C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy, and C₅-C₂₀ heteroaryloxy group, or a halogen atom;

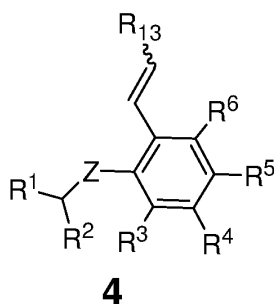
R⁷, R⁸, R⁹, and R¹⁰ are each independently hydrogen atom or C₁-C₂₅ alkyl group, R⁷ and/or R⁸ can be combined with R⁹ and/or R¹⁰ to form cyclic system, can be also independently C₁-C₁₂ alkyl, C₃-C₁₂ cycloalkyl, C₂-C₁₂ alkenyl, C₅-C₂₀ aryl, C₁-C₅ perfluoroalkyl, C₇-C₂₄ aralkyl, and C₅-C₂₄ perfluoroaryl group, which are optionally substituted with at least one C₁-C₁₂ alkyl, C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, or a halogen atom;

R¹¹, R¹² are each independently hydrogen atom, halogen atom, optionally substituted C₁-C₂₅ alkyl, optionally substituted C₁-C₂₅ perfluoroalkyl, optionally substituted C₂-C₂₅ alkene, optionally substituted C₃-C₇ cycloalkyl, optionally substituted C₂-C₂₅ alkenyl, optionally substituted C₃-C₂₅ cycloalkenyl, optionally

substituted C₂-C₂₅ alkynyl, optionally substituted C₃-C₂₅ cycloalkynyl, optionally substituted C₁-C₂₅ alkoxy, optionally substituted C₅-C₂₄ aryloxy, optionally substituted C₅-C₂₀ heteroaryloxy, optionally substituted C₅-C₂₄ aryl, optionally substituted C₅-C₂₀ heteroaryl, optionally substituted C₇-C₂₄ aralkyl, optionally substituted C₅-C₂₄ perfluoroaryl, optionally substituted 3-12-membered heterocycle;

wherein R¹¹ and R¹² substituents can be combined together to form a ring selected from a group including C₃-C₇ cycloalkyl, C₃-C₂₅ cycloalkenyl, C₃-C₂₅ cycloalkynyl, C₅-C₂₄ aryl, C₅-C₂₀ heteroaryl, C₅-C₂₄ perfluoroaryl, 3-12-membered heterocycle, which can be substituted independently with one and/or more substituents selected from a group including hydrogen atom, halogen atom, C₁-C₂₅ alkyl, C₁-C₂₅ perfluoroalkyl, C₂-C₂₅ alkene, C₃-C₇ cycloalkyl, C₂-C₂₅ alkenyl, C₃-C₂₅ cycloalkenyl, C₂-C₂₅ alkynyl, C₃-C₂₅ cycloalkynyl, C₁-C₂₅ alkoxy, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, C₅-C₂₄ aryl, C₅-C₂₀ heteroaryl, C₇-C₂₄ aralkyl, C₅-C₂₄ perfluoroaryl, 3-12-membered heterocycle;

which then is contacted with the compound represented by the Formula 4



wherein:

Z is an atom selected from a group of O, S, NR', wherein R' is C₁-C₁₂ alkyl, C₃-C₁₂ cycloalkyl, C₂-C₁₂ alkenyl, C₅-C₂₀ aryl, which are optionally substituted with at least one C₁-C₁₂ alkyl, C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, or a halogen atom;

R¹ and R², are each independently hydrogen atom, C₁-C₂₅ alkyl group, C₁-C₂₅ alkoxy group, C₂-C₂₅ alkenyl group, C₁-C₁₂ perfluoroalkyl, C₅-C₂₀ aryl, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, or can be combined together to form substituted or unsubstituted C₄-C₁₀ cyclic or C₄-C₁₂ polycyclic system, can also be an ester (-COOR'), amide (-CONR'₂), formyl (-CHO), ketone (-COR'), and hydroxamic (-CON(OR')(R')) group or a halogen atom, wherein R' is C₁-C₁₂ alkyl, C₃-C₁₂ cycloalkyl, C₂-C₁₂ alkenyl, C₅-C₂₀ aryl, which are optionally substituted with at least one C₁-C₁₂ alkyl, C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, or a halogen atom;

R³, R⁴, R⁵, R⁶ are each independently hydrogen atom, C₁-C₂₅ alkyl group, C₁-C₂₅ alkoxy group, or C₂-C₂₅ alkenyl group, wherein R³, R⁴, R⁵, R⁶ substituents can be combined together to form substituted or unsubstituted C₄-C₁₀ cyclic or C₄-C₁₂ polycyclic system; can also independently be an alkoxy (-OR'), sulphide (-SR'), sulfoxide (-S(O)R'), sulphonium (-S⁺R'₂), sulphone (-SO₂R'), sulphonamide (-SO₂NR'₂), amine (-NR'₂), ammonium (-N⁺R'₃), nitro (-NO₂), cyano (-CN), phosphonate (-P(O)(OR')₂), phosphinate (-P(O)R'(OR')), phosphoninim (-P(OR')₂), phosphine (-PR'₂), phosphine oxide (-P(O)R'₂), phosphonium (-P⁺R'₃), carboxy (-COOH), ester (-COOR'), amide (-CONR'₂, or -NR'C(O)R'), formyl (-CHO), and ketone (-COR') group, wherein R' is C₁-C₅ alkyl, C₁-C₅ perfluoroalkyl, C₅-C₂₄ aryl, C₇-C₂₄ aralkyl, C₅-C₂₄ perfluoroaryl;

R^{13} is a hydrogen atom, C_1 - C_{25} alkyl group, C_1 - C_{25} alkoxy group, C_2 - C_{25} alkenyl group, C_1 - C_{12} perfluoroalkyl, C_5 - C_{20} aryl, C_5 - C_{24} aryloxy, C_5 - C_{20} heteroaryloxy, or can be combined together to form substituted or unsubstituted C_4 - C_{10} cyclic or C_4 - C_{12} polycyclic system or a halogen atom;

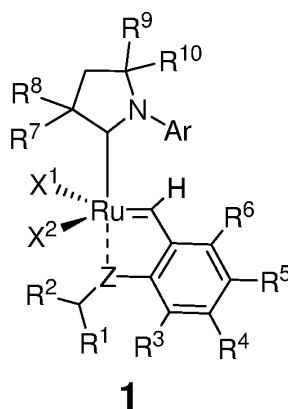
to form the compound represented by the Formula 1.

9. A process according to claim 8, **characterised in that** the reaction of compound 5 with compound 4 is conducted in the presence of phosphine ligand scavenger PR'_3 and/or CAAC ligand scavenger.

10. A process for producing a compound represented by the Formula 1 according to any one of claims 2 to 7 or 9, **characterised in that** as phosphine ligand scavenger PR'_3 and/or CAAC ligand scavenger a compound selected from copper(I) salts and/or HCl is used.

11. A process for producing a compound represented by the Formula 1 according to any one of claims 1 to 10, **characterised in that** all reaction steps are conducted in a polar and/or nonpolar solvent, preferably in aliphatic or aromatic hydrocarbons, over a period of 1 minute to 24 hours.

12. A compound represented by the Formula 1,



wherein:

X^1 and X^2 are each independently an anionic ligand selected from halogen atoms, -CN, -SCN, -OR', -SR', -O(C=O)R', -O(SO₂)R', and -OSi(R')₃ group, wherein R' is C_1 - C_{12} alkyl, C_3 - C_{12} cycloalkyl, C_2 - C_{12} alkenyl, C_5 - C_{20} aryl, which are optionally substituted with at least one C_1 - C_{12} alkyl, C_1 - C_{12} perfluoroalkyl, C_1 - C_{12} alkoxy, C_5 - C_{24} aryloxy, C_5 - C_{20} heteroaryloxy, or a halogen atom;

Z is an atom selected from a group of O, S, NR', wherein R' is C_1 - C_{12} alkyl, C_3 - C_{12} cycloalkyl, C_2 - C_{12} alkenyl, C_5 - C_{20} aryl, which are optionally substituted with at least one C_1 - C_{12} alkyl, C_1 - C_{12} perfluoroalkyl, C_1 - C_{12} alkoxy, C_5 - C_{24} aryloxy, C_5 - C_{20} heteroaryloxy, or a halogen atom;

Ar is an aryl group substituted with hydrogen atoms or optionally substituted with at least one C_1 - C_{12} alkyl, C_1 - C_{12} perfluoroalkyl, C_1 - C_{12} alkoxy, C_5 - C_{24} aryloxy, and C_5 - C_{20} heteroaryloxy group, or a halogen atom;

R^1 and R^2 , are each independently hydrogen atom, C_1 - C_{25} alkyl group, C_1 - C_{25} alkoxy group, C_2 - C_{25} alkenyl group, C_1 - C_{12} perfluoroalkyl, C_5 - C_{20} aryl, C_5 - C_{24} aryloxy, C_5 - C_{20} heteroaryloxy, or can be combined together to form substituted or unsubstituted C_4 - C_{10} cyclic or C_4 - C_{12} polycyclic system, can also be an

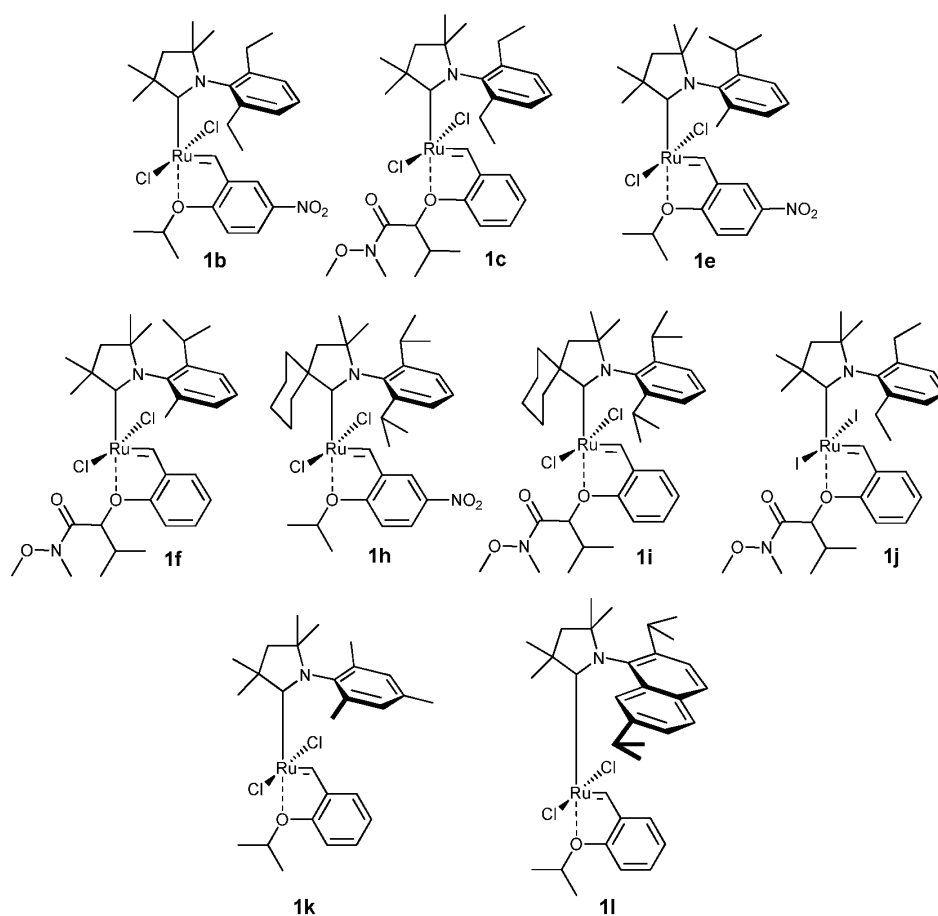
ester (-COOR'), amide (-CONR'₂), formyl (-CHO), ketone (-COR'), and hydroxamic (-CON(OR')(R')) group or a halogen atom, in which R' is C₁-C₁₂ alkyl, C₃-C₁₂ cycloalkyl, C₂-C₁₂ alkenyl, C₅-C₂₀ aryl, which are optionally substituted with at least one C₁-C₁₂ alkyl, C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, or a halogen atom;

R³, R⁴, R⁵, R⁶ are each independently hydrogen atom, sulfoxide group (-S(O)R'), sulphonamide group (-SO₂NR'₂), phosphonate group (-P(O)(OR')₂), phosphinate group (-P(O)R'(OR')), phosphonium group (-P(OR')₂), phosphine group (-PR'₂), nitro group (-NO₂), nitroso group (-NO), carboxy group (-COOH), ester group (-COOR'), formyl group (-CHO), ketone group (-COR'), wherein R' is C₁-C₅ alkyl, C₁-C₅ perfluoroalkyl, C₅-C₂₄ aryl, C₇-C₂₄ aralkyl, C₅-C₂₄ perfluoroaryl;

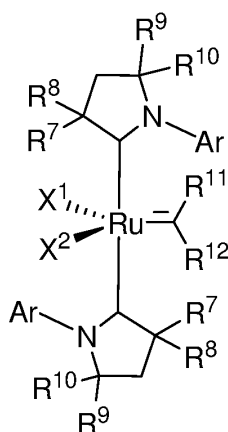
wherein when R¹ and R² are -CH₃ group, then at least one of R³, R⁴, R⁵, R⁶ substituents is not hydrogen atom;

R⁷, R⁸, R⁹, and R¹⁰ are each independently hydrogen atom or C₁-C₂₅ alkyl group, R⁷ and/or R⁸ can be combined with R⁹ and/or R¹⁰ to form cyclic system, are also independently C₁-C₁₂ alkyl, C₃-C₁₂ cycloalkyl, C₂-C₁₂ alkenyl, C₅-C₂₀ aryl, C₁-C₅ perfluoroalkyl, C₇-C₂₄ aralkyl, and C₅-C₂₄ perfluoroaryl group, which are optionally substituted with at least one C₁-C₁₂ alkyl, C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, or a halogen atom.

13. A compound according to claim 12 of a structure represented by the formula selected from **1b**, **1c**, **1e**, **1f**, **1h**, **1i**, **1j**, **1k**, **1l**:



14. A compound represented by the Formula 5,

**5**

wherein:

X¹ and X² are each independently an anionic ligand selected from halogen atoms, -CN, -SCN, -OR', -SR', -O(C=O)R', -O(SO₂)R', and -OSi(R')₃ group, wherein R' is C₁-C₁₂ alkyl, C₃-C₁₂ cycloalkyl, C₂-C₁₂ alkenyl, C₅-C₂₀ aryl, which are optionally substituted with at least one C₁-C₁₂ alkyl, C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, or a halogen atom;

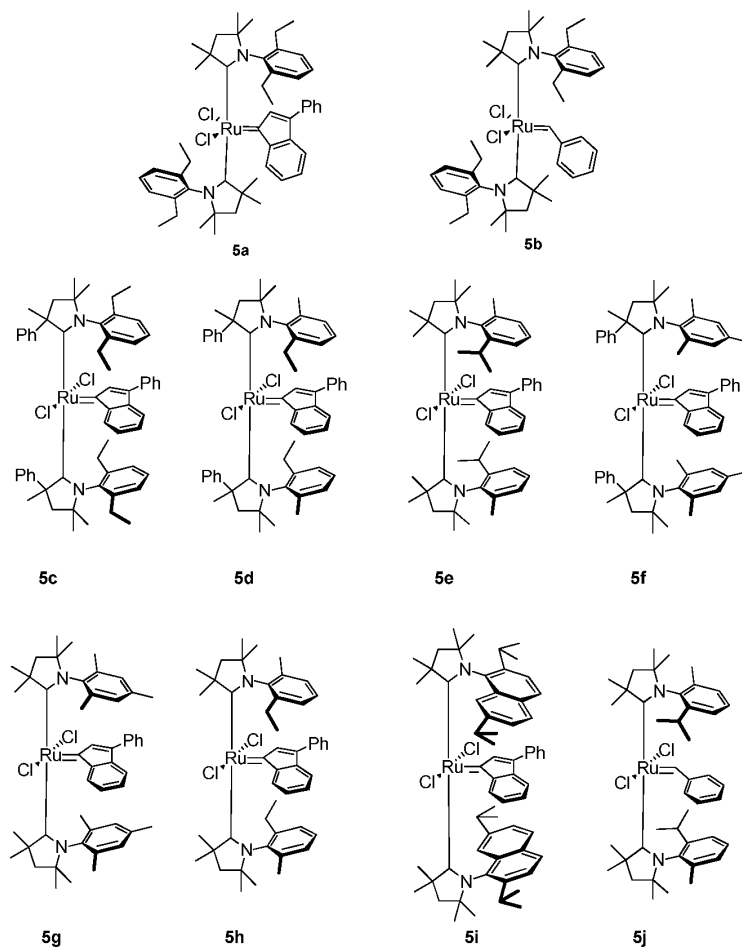
Ar is an aryl group substituted with hydrogen atoms or optionally substituted with at least one C₁-C₁₂ alkyl, C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy group, or a halogen atom;

R⁷, R⁸, R⁹, and R¹⁰ are each independently hydrogen atom or C₁-C₂₅ alkyl group, R⁷ and/or R⁸ can be combined with R⁹ and/or R¹⁰ to form cyclic system, can be also independently C₁-C₁₂ alkyl, C₃-C₁₂ cycloalkyl, C₂-C₁₂ alkenyl, C₅-C₂₀ aryl, C₁-C₅ perfluoroalkyl, C₇-C₂₄ aralkyl, and C₅-C₂₄ perfluoroaryl group, which are optionally substituted with at least one C₁-C₁₂ alkyl, C₁-C₁₂ perfluoroalkyl, C₁-C₁₂ alkoxy, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, or a halogen atom;

R¹¹, R¹² are each independently hydrogen atom, halogen atom, optionally substituted C₁-C₂₅ alkyl, optionally substituted C₁-C₂₅ perfluoroalkyl, optionally substituted C₂-C₂₅ alkene, optionally substituted C₃-C₇ cycloalkyl, optionally substituted C₂-C₂₅ alkenyl, optionally substituted C₃-C₂₅ cycloalkenyl, optionally substituted C₂-C₂₅ alkynyl, optionally substituted C₃-C₂₅ cycloalkynyl, optionally substituted C₁-C₂₅ alkoxy, optionally substituted C₅-C₂₄ aryloxy, optionally substituted C₅-C₂₀ heteroaryloxy, optionally substituted C₅-C₂₄ aryl, optionally substituted C₅-C₂₀ heteroaryl, optionally substituted C₇-C₂₄ aralkyl, optionally substituted C₅-C₂₄ perfluoroaryl, optionally substituted 3-12-membered heterocycle;

wherein R¹¹ and R¹² substituents can be combined together to form a ring selected from a group including C₃-C₇ cycloalkyl, C₃-C₂₅ cycloalkenyl, C₃-C₂₅ cycloalkynyl, C₅-C₂₄ aryl, C₅-C₂₀ heteroaryl, C₅-C₂₄ perfluoroaryl, 3-12-membered heterocycle, which can be substituted independently with one and/or more substituents selected from a group including hydrogen atom, halogen atom, C₁-C₂₅ alkyl, C₁-C₂₅ perfluoroalkyl, C₂-C₂₅ alkene, C₃-C₇ cycloalkyl, C₂-C₂₅ alkenyl, C₃-C₂₅ cycloalkenyl, C₂-C₂₅ alkynyl, C₃-C₂₅ cycloalkynyl, C₁-C₂₅ alkoxy, C₅-C₂₄ aryloxy, C₅-C₂₀ heteroaryloxy, C₅-C₂₄ aryl, C₅-C₂₀ heteroaryl, C₇-C₂₄ aralkyl, C₅-C₂₄ perfluoroaryl, 3-12-membered heterocycle.

15. A compound according to claim 14 of a structure represented by the formula selected from **5a** -**5j**:



16. The use of a compound represented by the Formula **1** produced by the process according to any one of claims 1 to 11 as a precatalyst and/or catalyst in olefin metathesis reactions, particularly in ring-closing metathesis (RCM), homometathesis, cross-metathesis (CM), ethenolysis, isomerisation reactions, in diastereoselective ring-rearrangement metathesis (DRRM) reaction, „alkene-alkyne” (en-yn) type metathesis or ROMP type polymerisation reactions.

17. The use according to claim 16, wherein compound represented by the Formula **1** is used as a precatalyst and/or catalyst in a reaction mixture over a period of 1 minute to 24 hours in an organic solvent, mixture of organic solvents or without solvent.

18. The use of a compound represented by the Formula **1** produced by the process according to any one of claims 1 to 11 as a substrate to synthesis of other ruthenium complex compounds being olefin metathesis precatalysts and/or catalysts.

19. The use of a compound represented by the Formula **5** according to claims 14 or 15 as a precatalyst and/or catalyst in olefin metathesis reactions, particularly in ring-closing metathesis (RCM), homometathesis, cross-metathesis (CM), ethenolysis, isomerisation reactions, in reaction of

diastereoselective ring-rearrangement metathesis (DRRM), „alkene-alkyne” (en-yn) type metathesis or ROMP type polymerisation reactions and in metathetic depolymerisation reaction.

20. The use of a compound represented by the Formula **5** according to claims 14 or 15 as a precatalyst and/or catalyst in olefin metathesis reactions in the presence of CAAC ligand scavenger.