Electronic Supplementary Material (ESI) for Dalton Transactions.

Ruthenium Indenylidene Complexes Bearing *N*-Alkyl/*N*-Mesityl Substituted *N*-Heterocyclic Carbenes Ligands

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Supporting information

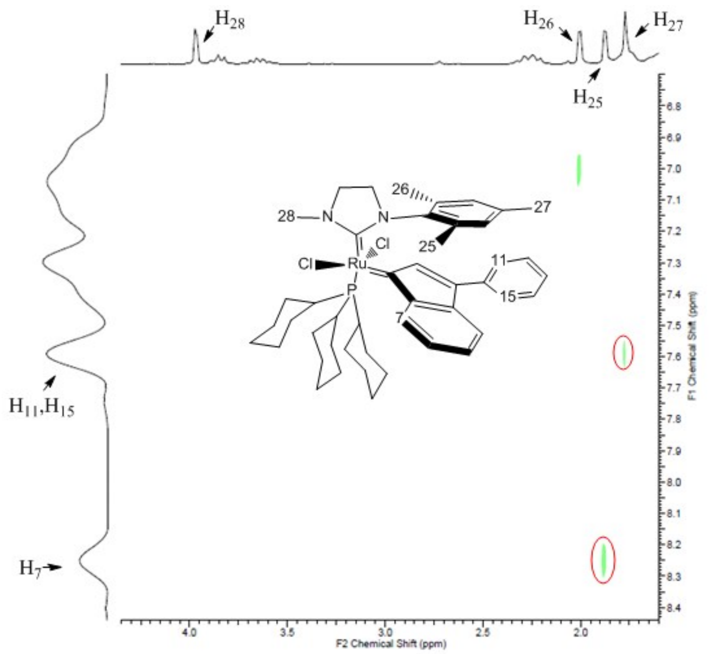


Fig. S1 NOESY spectrum of **8a**, chemical shift of ^{1}H-NMR range from 1.0 to 5.0 ppm (horizontal) and ^{1}H-NMR range from 5.0 to 8.5 ppm (vertical).

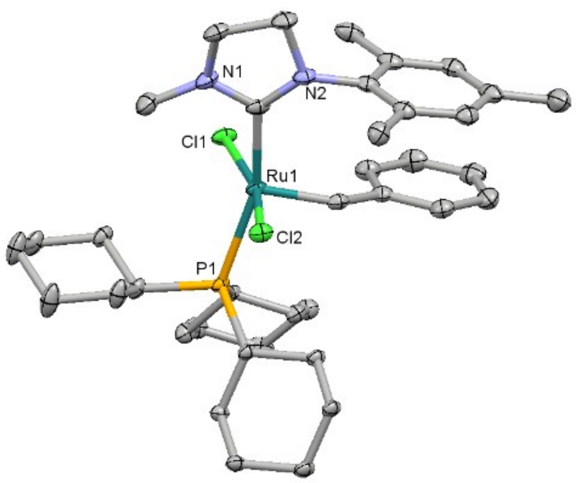
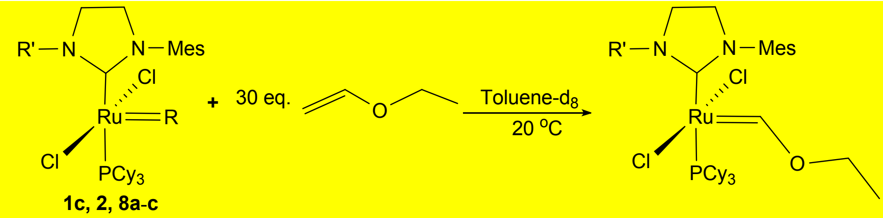


Fig. S2 ORTEP representation of the structure of complex **1c** (thermal ellipsoids are drawn at the 30% probability level), showing the atom labeling scheme of the heteroatoms. The hydrogen atoms are omitted for clarity.

Crystals of complex **1c** were obtained by evaporation of the complex solution in hexane/EtOAc/CH_2Cl_2 and analyzed by single crystal X-ray analysis. **1c** crystallized in the triclinic centro-symmetric space group *P*-1 with one $RuCl_2$(benzylidene)(1-mesityl-3-methyl-4,5-dihydroimidazol-2-ylidene)(PCy_3) molecule (Fig. S2) in the asymmetric unit. The bond length between the ruthenium and $C_{Benzylidene}$ is 1.840(3) Å. The Ru-Cl bond lengths are 2.3793(8) and 2.4061(8) Å as well as the Ru-P bond length is 2.4243(9) Å. The C_{NHC}-Ru-P and C_{NHC}-Ru=$C_{Benzylidene}$ angles are 160.6(1) and 100.7(1)°, respectively. The Cl-Ru-Cl angle is equal to 164.29(3)°.

Initiation studies of complexes 1c, 2 and 8a-c



1c, R = Benzylidene. R' = Methyl

2, R = 3-phenyl-indenylidene, R' = Mes

8a, R = 3-phenyl-indenylidene, R' = Methyl

8b, R = 3-phenyl-indenylidene, R' = Octyl

8c, R = 3-phenyl-indenylidene, R' = Cyclohexyl

Scheme S1. Reaction of complexes **1c**, **2** and **8a-c** with 30 eq. of ethyl vinyl ether to obtain the relative ruthenium ethoxymethylene complexes.

It is known that a reaction of ruthenium alkylidene complexes with vinyl ether could generate Fisher-carbene complexes, which are inert to metathesis reaction.[1] This method is often used for catalysts initiation studies[2] and the quenching of metathetic reactions.[3] Here, initiation studies were carried out by using the ruthenium complexes (10 mmol) to react with 30 eq. of ethyl vinyl ether in Toluene-d_8 at 20 °C (Scheme S1).[2a,2c] The kinetic plots of conversion of the initial complexes to the formed relative ruthenium ethoxymethylidene complexes are shown in Fig. S3. In the figure, it is shown that the benzylidene complex **1c** exhibits the fastest initiation rate, followed by complex **8a**, then the complexes **8b** and **8c**. However, for the reference complex **2**, after 5 hours no detectable amount of desired ruthenium ethoxymethylidene complex was observed from the reaction mixture. Actually, only 18% of complex **2** was found to convert after 24 hours.

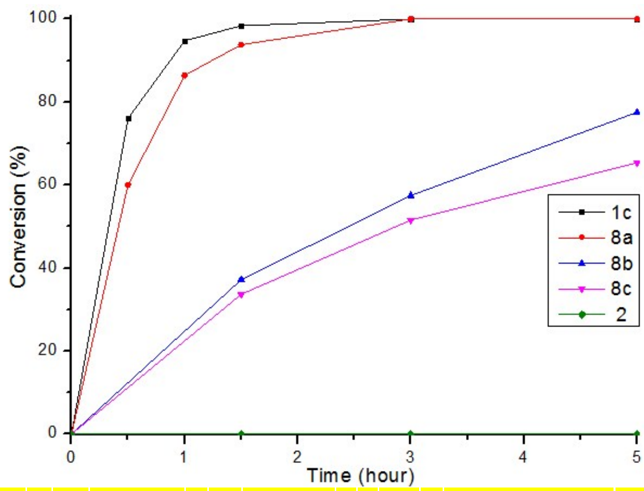


Fig. S3 The conversion of the complexes **1**, **2**, **8a-c** to Fisher-carbene-type ruthenium ethoxymethylidene complexes in toluene-d_8 (6 ml) at 20 °C. The lines are intended as a visual aid.

Experimental Section

Unless otherwise stated, all the reactions were carried out under an argon atmosphere by using Shlenck technique and all solvents which involved in reactions were dried and freshly distilled prior to use: dichloromethane (CaH_2), toluene (sodium). Pentane, methanol, dichloromethane and toluene were purchased from Fiers. Flash chromatography was performed using silica gel 60 (230-400 mesh) from Acros Organics. Diethyl 2,2-diallylmalonate, *cis,cis*-cycloocta-1,5-diene, potassium bis(trimethylsilyl)amide (KHMDS), allylbenzene were purchased from Sigma Aldrich. *cis*-1,4-diacetoxy-2-butene was obtained from ABCR. $RuCl_2$(3-phenyl-1-indenylidene)(PCy_3)$_2$ was obtained from Umicore. 1-mesityl-3-methyl-4,5-dihydro-imidazolium chloride, 1-

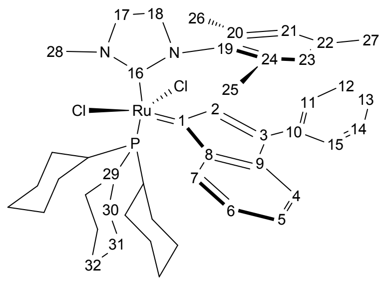
mesityl-3-octyl-4,5-dihydro-imidazolium chloride, 1-mesityl-3-cyclohexyl-4,5-dihydro-imidazolium chloride,[4] diethyl 2-allyl-2-(2-methylallyl)malonate[5] (1-(allyloxy)prop-2-yne-1,1-diyl)dibenzene[6] and bis(3,5-dimethoxyphenyl)methanone[7] were prepared according to literature procedures.

Gas chromatography (GC) was conducted using a Finning Trace GC ultra from Thermo Electron Corporation equipped with a 10 m length, 0.10 mm internal diameter 5% diphenyl/95% polydimethylsiloxane capillary column and a flame ionization detector (FID). For IR, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements were recorded on a Thermo Nicolet 6700 FT-IR spectrometer equipped with a N_2 cooled MCT-A (mercury-cadmium-tellurium) detector and a KBr beam splitter. ^{1}H, ^{13}C, ^{31}P and 2D NMR spectra were recorded on Bruker 300 MHz and 500 MHz spectrometers. Chemical shifts are listed in ppm from tetramethylsilane with the residual solvent resonance as an internal standard (^{1}H, ^{13}C) or external H_3PO_4 (^{31}P). Elemental analyses were performed on a CHNS-0 analyzer from Interscience. HPLC-MS (ESI) was done by Agilent NOD series HPLC with G1946CMSD. Single crystal X-ray diffraction data were collected using an Agilent Supernova Dual Source (Cu at zero) diffractometer equipped with an Atlas CCD detector using CuKα radiation (λ = 1.54178 Å) or MoKα radiation (λ = 0.71073 Å) and ω scans. All images were interpreted and integrated with the program CrysAlisPro (Agilent Technologies).[8] Using Olex2[9], the structures were solved by direct methods using the ShelXS structure solution program[10] and refined by full-matrix least-squares on F^2 using the ShelXL program[11]. Non-hydrogen atoms were anisotropically refined and the hydrogen atoms in the riding mode and isotropic temperature factors fixed at 1.2 times U(eq) of the parent atoms (1.5 times for methyl groups).

General procedure for the preparation of complexes 8a-c

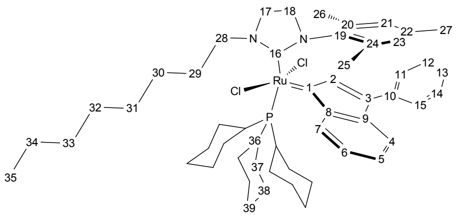
In an oven dried Schlenk vessel, KHMDS (2 eq., 3.2 mL, 1.6 mmol)(0.5 M toluene solution) was added to a suspension of imidazolium salt (1.5 eq., 1.2 mmol) in dry toluene (24 mL) at room temperature. The result solution was vigorously stirred for 30 minutes then was added in a solution of $RuCl_2$(3-phenyl-1-indenylidene)$(PCy_3)_2$ (1 eq., 0.74 g, 0.8 mmol) in toluene (16 mL) in the reactor. The mixture was further stirred overnight. Purification using silica-gel chromatography (hexane:EtOAc, from 60:1 to 20:1) afforded a red-brown colored sludge. Further on, methanol was added to the resulting sludge. The solid suspension was filtrated and was washed several times with methanol and pentane.

$RuCl_2$(3-phenyl-1-indenylidene)(1-mesityl-3-methyl-4,5-dihydroimidazol-2-ylidene)(PCy_3)(8a)



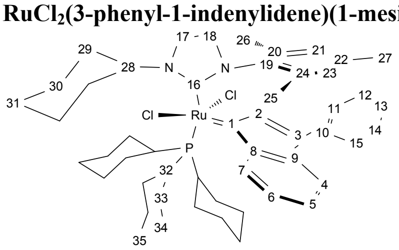
Red-brown powder (0.37 g, Yield: 55%). Red crystals, suitable for X-ray diffraction analysis of **8a** were obtained by slow evaporation of a complex solution in hexane/EtOAc/CH_2Cl_2. The complex consists two rotamers in a ratio of 100: 5 and the NMR data for this major rotamor is presented in following. ^{1}H-NMR (500 MHz, $CDCl_3$, TMS, 20 °C): δ 8.35 (d, 1 H, $^3J_{H,H}$ = 7.3 Hz, H-7), 7.69 (d, 2 H , $^3J_{H,H}$ = 7.3 Hz, H-11, H-15), 7.49 (t, 1 H, $^3J_{H,H}$ = 7.3 Hz, H-13), 7.39 (t, 2 H, $^3J_{H,H}$ = 7.6 Hz, H-12, H-14), 7.21 (t, 1 H, $^3J_{H,H}$ = 7.3 Hz, H-5), 7.14 (t, 1 H, $^3J_{H,H}$ = 7.3 Hz, H-6), 7.10 (s, 1 H, H-2), 7.03 (d, 1 H, $^3J_{H,H}$ = 7.0 Hz, H-4), 6.39 (s, 1 H, H-21), 6.00 (s, 1 H, H-23), 4.06 (s, 3 H, H-28), 3.91-3.99 (m, 2 H, H-17), 3.68-3.80 (m, 2 H, H-18), 2.30-2.40 (m, 3 H, H-29), 2.10 (s, 3 H, H-26), 1.98 (s, 3 H, H-25), 1.85-1.93 (m, 6 H, H-27, Heq-30), 1.66-1.74 (m, 6 H, Heq-30, Heq-31), 1.58-1.62 (m, 6 H, Heq-31, Heq-32), 1.33-1.48 (m, 6 H, Hax-30), 1.02-1.19 (m, 9 H, Hax-31, Hax-32); ^{13}C{^{1}H}NMR (126 MHz, $CDCl_3$, 20 °C): δ 291.3 (d, $^2J_{P,C}$ = 6.1 Hz, C-1), 216.6 (d, $^2J_{P,C}$ = 70.2 Hz, C-16), 143.8 (C-8), 140.5 (C-9), 137.8 (C-3), 137.2 (C-2), 137.1 (C-24), 137.0 (C-20), 136.9 (C-22), 136.7 (C-10), 136.0 (C-19), 128.9 (C-12, C-14), 128.7 (C-21), 128.5 (C-7), 128.4 (C-23), 128.1 (C-6), 127.7 (C-13), 127.2 (C-5), 126.4 (C-11, C-15), 116.1 (C-4), 52.4 (C-17), 51.9 (C-18), 38.1 (C-28), 32.6, 32.5 (C-29), 29.6, 29.5 (C-30), 27.84, 27.77, 27.69, 27.62 (C-31), 26.6 (C-32), 21.0 (C-27), 18.4 (C-25), 18.3 (C-26); ^{31}P{^{1}H}NMR (202 MHz, $CDCl_3$, 20 °C): δ 32.2 (major), 14.7 (minor). IR (Neat): ν = 2927, 2920, 2850, 1510, 1449, 1408, 1358, 1318, 1302, 1270, 1229, 1200, 1173, 1162, 1096, 1028, 1004, 886, 848, 774, 752, 735, 698, 650 cm^{-1}; Anal. Calcd. for $C_{46}H_{61}Cl_2N_2PRu$: C 65.39, H 7.28, N 3.32; Found: C 65.47, H 7.29, N 3.40; ESI-MS: $[M-Cl]^+$ Calcd. for $C_{46}H_{61}ClN_2PRu$, 809.3304; Found: 809.3325.

$RuCl_2$(3-phenyl-1-indenylidene)(1-mesityl-3-octyl-4,5-dihydroimidazol-2-ylidene)(PCy_3)(8b)



Red-brown powder (0.44 g, Yield: 58%). Red crystals, suitable for X-ray diffraction analysis of **8b** were obtained by slow evaporation of a complex solution in hexane/EtOAc/CH_2Cl_2. The complex consists two rotamers in a ratio of 100:2.5 and the NMR data for this major rotamor is presented in following. ^{1}H-NMR (500 MHz, $CDCl_3$, TMS, 20 °C): δ 8.39 (d, 1 H , $^3J_{H,H}$ = 7.3 Hz, H-7), 7.70 (d, 2 H , $^3J_{H,H}$ = 7.3 Hz, H-11, H-15), 7.49 (t, 1 H, $^3J_{H,H}$ = 7.3 Hz, H-13), 7.39 (t, 2 H, $^3J_{H,H}$ = 7.6 Hz, H-12, H-14), 7.20 (t, 1 H, $^3J_{H,H}$ = 7.3 Hz, H-5), 7.14 (t, 1 H, $^3J_{H,H}$ = 7.3 Hz, H-6), 7.11 (s, 1 H, H-2), 7.02 (d, 1 H, $^3J_{H,H}$ = 7.3 Hz, H-4), 6.38 (s, 1 H, H-21), 5.98 (s, 1 H, H-23), 4.45-4.59 (m, 2 H, H-28), 3.85-3.95 (m, 2 H, H-17), 3.64-3.77 (m, 2 H, H-18), 2.27-2.37 (m, 3 H, H-36), 2.10 (s, 3 H, H-26), 1.96-2.02 (m, 5 H, H-25, H-29), 1.85-1.87 (m, 6 H, H-27, Heq-37), 1.71-1.74 (m, 3 H, Heq-37), 1.64-1.67 (m, 3 H, Heq-38), 1.57-1.59 (m, 8 H, Heq-38, Heq-39, H-30), 1.25-1.45 (m, 14 H, H-31, H-32, H-33, H-34, Hax-37), 1.05-1.16 (m, 9 H, Hax-38, Hax-39), 0.89-0.92 (t, 3 H, $^3J_{H,H}$ = 6.7 Hz, H-35); $^{13}C\{^1H\}$NMR (126 MHz, $CDCl_3$, 20 °C): δ 292.3 (d, $^2J_{P,C}$ = 6.1 Hz, C-1), 215.4 (d, $^2J_{P,C}$ = 70.2 Hz, C-16), 144.0 (C-8), 140.7 (C-9), 137.6 (C-3), 137.2 (C-2), 137.1 (C-24), 137.0 (C-20), 136.9 (C-22), 136.8 (C-10), 136.1 (C-19), 128.9 (C-12, C-14), 128.7 (C-21), 128.6 (C-7), 128.4 (C-23), 128.1 (C-6), 127.6 (C-13), 127.1 (C-5), 126.4 (C-11, C-15), 116.0 (C-4), 51.6 (C-18), 51.2 (C-28), 48.2 (d, J = 3.1 Hz, C-17), 33.0, 32.9 (C-36), 31.9 (C-33), 29.8 (C-32), 29.6, 29.4 (C-37), 29.3 (C-31), 28.5 (C-29), 27.79, 27.72, 27.68, 27.60 (C-38), 27.0 (C-30), 26.5 (C-39), 22.7 (C-34), 21.0 (C-27), 18.44 (C-25), 18.39 (C-26), 14.2 (C-35); $^{31}P\{^1H\}$NMR (202 MHz, $CDCl_3$, 20 °C): δ 29.2 (major), 15.0 (minor). IR (Neat): ν = 2931, 2852, 1538, 1494, 1446, 1377, 1325, 1267, 1248, 1204, 1175, 1130, 1074, 1049, 1027, 1006, 977, 889, 845, 775, 753, 735, 700, 651; Anal. Calcd. for $C_{53}H_{75}Cl_2N_2PRu$ (942.41): C 67.50, H 8.02, N 2.97; Found: C 67.27, H 7.94, N 2.99; ESI-MS: $[M-Cl]^+$ Calcd. for $C_{53}H_{75}ClN_2PRu$, 907.4400; Found: 907.4428.

$RuCl_2$(3-phenyl-1-indenylidene)(1-mesityl-3-cyclohexyl-4,5-dihydroimidazol-2-ylidene)(PCy_3)(8c)



Red-brown powder (0.46 g, Yield: 63%). Red crystals, suitable for X-ray diffraction analysis of **8c** were obtained by slow evaporation of a complex solution in hexane/EtOAc/CH_2Cl_2. The complex consists two rotamers in a ratio of 100:2.5 and the NMR data for this major rotamor is presented in following. ^{1}H-NMR (500 MHz, $CDCl_3$, TMS, 20 °C): δ 8.43 (d, 1 H , $^3J_{H,H}$ = 7.3 Hz, H-7), 7.70 (d, 2 H , $^3J_{H,H}$ = 7.3 Hz, H-11, H-15), 7.50 (t, 1 H, $^3J_{H,H}$ = 7.0 Hz, H-13), 7.39 (t, 2 H, $^3J_{H,H}$ = 7.3 Hz, H-12, H-14), 7.21 (t, 1 H, $^3J_{H,H}$ = 7.0 Hz, H-5), 7.15 (t, 1 H, $^3J_{H,H}$ = 7.3 Hz, H-6), 7.13 (s, 1 H, H-2), 7.02 (d, 1 H, $^3J_{H,H}$ = 6.7 Hz, H-4), 6.38 (s, 1 H, H-21), 5.96 (s, 1 H, H-23), 5.19 (s, 1 H, H-28), 3.88-3.91 (m, 2 H, H-17), 3.59-3.72 (m, 2 H, H-18), 2.52-2.56 (m, 2 H, Heq-29), 2.20-2.26 (m, 3 H, H-32), 2.10 (s, 3 H, H-26), 1.91-1.95 (m, 8 H, H-25, Heq-30, Heq-33), 1.83 (s, 3 H, H-27), 1.77 (s, 4 H, Heq-31, Heq-33), 1.57-1.63 (m, 13 H, Hax-29, Hax-30, Heq-34, Heq-35), 1.39-1.47 (m, 6 H, Hax-33), 1.25-1.27 (m, 1 H, Hax-31), 1.09 (br, 9 H, Hax-34, Hax-35); $^{13}C\{^1H\}$NMR (126 MHz, $CDCl_3$, 20 °C): δ 294.0 (C-1), 212.4 (d, $^2J_{P,C}$ = 73.2 Hz, C-16), 144.2 (C-8), 140.9 (C-9), 137.49 (C-2), 137.46 (C-3), 137.3 (C-20), 137.2 (C-24), 136.9 (C-22), 136.8 (C-10), 136.3 (C-19), 128.9 (C-12, C14), 128.8 (C-7), 128.7 (C-21), 128.4 (C-23), 128.2 (C-6), 127.6 (C-13), 127.1 (C-5), 126.3 (C-11, C-15), 116.0 (C-4), 58.1 (C-28), 51.1 (C-18), 43.6 (C-17), 33.6, 33.5 (C-32), 30.5, 30.1 (C-29), 29.5, 29.3 (C-33), 27.6, 27.5 (C-34), 26.3 (C-35), 25.4 (C-31), 24.8, 24.7 (C-30), 21.0 (C-27), 18.53 (C-25), 18.47 (C-26); $^{31}P\{^1H\}$NMR (202 MHz, $CDCl_3$, 20 °C): δ 22.7 (major), 16.0 (minor). IR (Neat): ν = 2933, 2850, 1551, 1484, 1479, 1376, 1357, 1334, 1292, 1259, 1236, 1175, 1161, 1073, 1037, 1029, 1010, 991, 888, 850, 837, 778, 700, 756, 701, 654; Anal. Calcd. for $C_{51}H_{69}Cl_2N_2PRu$: C 67.09, H 7.62, N 3.07; Found: C 66.78, H 7.74, N 3.15; ESI-MS: $[M-Cl]^+$ Calcd for $C_{53}H_{75}ClN_2PRu$, 877.3930; Found: 877.3954.

Applied procedure for stability test

An NMR tube was charged with ruthenium catalyst (15 µmol) and internal standard bis(3,5-dimethoxyphenyl)methanone (2.3 mg, 7.5 µmol) together with non-pretreated $CDCl_3$ (0.6 mL), the result solution was kept at 20 °C. The ruthenium complex stability was monitored as a function of time by integrating the ^{1}H-NMR signals every day of the decomposing complex.

Applied procedure for the RCM of diethyl 2-allyl-2-(2-methylallyl)malonate/diethyl 2,2-diallylmalonate[3b,12,13]

A substrate stock solution (0.1 M) was prepared by dissolving the substrate (4 mmol) and the internal standard dodecane (0.68 g, 4 mmol) in CH_2Cl_2 (40 mL). The substrate solution (5 mL) and the ruthenium complex (0.125-1 mol%) were added in a Schlenk tube under argon at 30 °C. The reaction progress was monitored aliquot sampling of the reaction solution and further quenched by ethoxyethene before inject to GC for determination the conversion.

Applied procedure for the ROMP of *cis,cis*-cycloocta-1,5-diene[3b,12,13]
A ruthenium complex solution was made by dissolving the complex (4.07 µmol) in $CDCl_3$ (1 mL). An NMR tube was filled with *cis,cis*-cycloocta-1,5-diene (0.81 mmol, 0.1 mL), $CDCl_3$ (0.5 mL) and complex solution (0.1 mL), then the results solution was subjected into ^{1}H-NMR measurement for determination of the conversion at 40 °C.The conversion was determined by integration of the olefinic ^{1}H-NMR signals of the formed polymer and the consumed monomer.

Applied procedure for the RCEYM of (1-(allyloxy)prop-2-yne-1,1-diyl)dibenzene[13]
The substrate (1-(allyloxy)prop-2-yne-1,1-diyl)dibenzene (0.99 g, 4 mmol) and the internal standard dodecane (0.68 g, 4 mmol) were added in toluene (40 mL) to make a substrate stock solution (0.1 M). A substrate solution (5 mL) and the ruthenium complex (2 mol%) was filled in an Schlenk tube under argon at 50 °C. During the reaction, aliquots were taken out from the reaction mixture and were diluted with CH_2Cl_2 and ethoxyethene before GC analysis.

Applied procedure for the CM between allylbenzene and *cis*-1,4-diacetoxy-2-butene[3b,13-14]
An oven dried flask was added with allylbenzene (0.236 g, 2 mmol) and internal standard *n*-tridecane (0.184 g, 1 mmol) and dry CH_2Cl_2 (10 mL). The flask was further charged with ruthenium complex (50 µmol) and *cis*-1,4-diacetoxy-2-butene (0.69 g, 4 mmol). The reaction mixture was stirred at 35 °C. A sampling of reaction solution (1 mL) and quenched with an ethyl vinyl ether solution (1 mL) as well as further analysed by GC and ^{1}H-NMR.

Applied procedure for initiation test[2a]
An NMR tube was charged with ruthenium catalysts (10 µmol) and toluene-d_8 (0.3 ml). Thereafter, ethyl vinyl ether (30 eq., 0.022 g, 0.3 mmol) in toluene-d_8 (0.3 ml) was added and the resulting solution was kept at 20 °C. The reaction progress was monitored by ^{1}H-NMR signals as a function of time of the intact complex and the new formed complex.

Single crystal X-ray diffraction
Crystal data for compound **1c**. CCDC 1049433, $C_{38}H_{57}Cl_2N_2PRu$, M = 744.80, triclinic, space group P-1 (No. 2), a = 11.9873(5) Å, b = 12.0758(4) Å, c = 13.9907(6) Å, α = 67.575(4)°, β = 84.781(3)°, γ = 74.448(3)°, V = 1803.40(14) Å^3, Z = 2, T = 100 K, ρ_{calc} = 1.372 g cm^{-3}, μ(Cu-Kα) = 5.507 mm^{-1}, F(000) = 784, 20352 reflections measured, 7221 unique (R_{int} = 0.0415) which were used in all calculations. The final R1 was 0.0360 (I >2σ (I)) and wR2 was 0.0933 (all data).

Crystal data for compound **8a**. CCDC 1049431, $C_{46}H_{61}N_2PCl_2Ru$, M = 844.91, triclinic, space group P-1 (No. 2), a = 9.8957(5) Å, b = 12.6238(6) Å, c = 17.6587(6) Å, α = 92.110(3)°, β = 100.964(4)°, γ = 102.538(4)°, V = 2107.00(17) Å^3, Z = 2, T = 100 K, ρ_{calc} = 1.332 g cm^{-3}, μ(Cu-Kα) = 4.782 mm^{-1}, F(000) = 888, 24516 reflections measured, 8618 unique (R_{int} = 0.0630) which were used in all calculations. The final R1 was 0.0533 (I >2σ (I)) and wR2 was 0.1531 (all data). The 3-phenyl-1-indenylidene moiety was found disordered over two positions, rotated about 175° with respect to each other and refined with occupancy factors of 0.819(3) and 0.181(3), respectively.

Crystal data for compound **8b**. CCDC 1049430, $C_{53}H_{75}N_2PCl_2Ru$, M = 943.09, triclinic, space group P-1 (No. 2), a = 13.8813(6) Å, b = 16.8687(7) Å, c = 24.0954(7) Å, α = 70.009(3)°, β = 76.910(3)°, γ = 70.625(4)°, V = 4961.1(4) Å^3, Z = 4, T = 100 K, ρ_{calc} = 1.263 g cm^{-3}, μ(Cu-Kα) = 4.114 mm^{-1}, F(000) = 2000, 33426 reflections measured, 17300 unique (R_{int} = 0.0766) which were used in all calculations. The final R1 was 0.0625 (I >2σ (I)) and wR2 was 0.1674 (all data). The asymmetric unit contains two $RuCl_2$(3-phenyl-1-indenylidene)(1-mesityl-3-octyl-4,5-dihydroimidazol-2-ylidene)(PCy_3) molecules. The octyl group on one of the two ruthenium complexes was found disordered over two positions and was refined with occupancy factors of 0.677(13) and 0.323(13), respectively.

Crystal data for compound **8c**. CCDC 1049495, $C_{103}H_{140}N_4P_2Cl_4Ru_2$, M = 1910.97, monoclinic, space group C2/c (No. 15), a = 33.7446(6) Å, b = 14.6670(3) Å, c = 19.0468(3) Å, β = 94.2889(14)°, V = 9400.5(3) Å^3, Z = 4, T = 100 K, ρ_{calc} = 1.350 g cm^{-3}, μ(Mo-Kα) = 0.575 mm^{-1}, F(000) = 4024, 55212 reflections measured, 11830 unique (R_{int} = 0.0783) which were used in all calculations. The final R1 was 0.0576 (I >2σ (I)) and wR2 was 0.1252 (all data). The asymmetric unit contains one ruthenium complex and one half of dichloromethane molecule on a special position (two-fold rotation axis).

^{1}H-, ^{31}P{^{1}H} and ^{13}C{^{1}H}NMR spectra

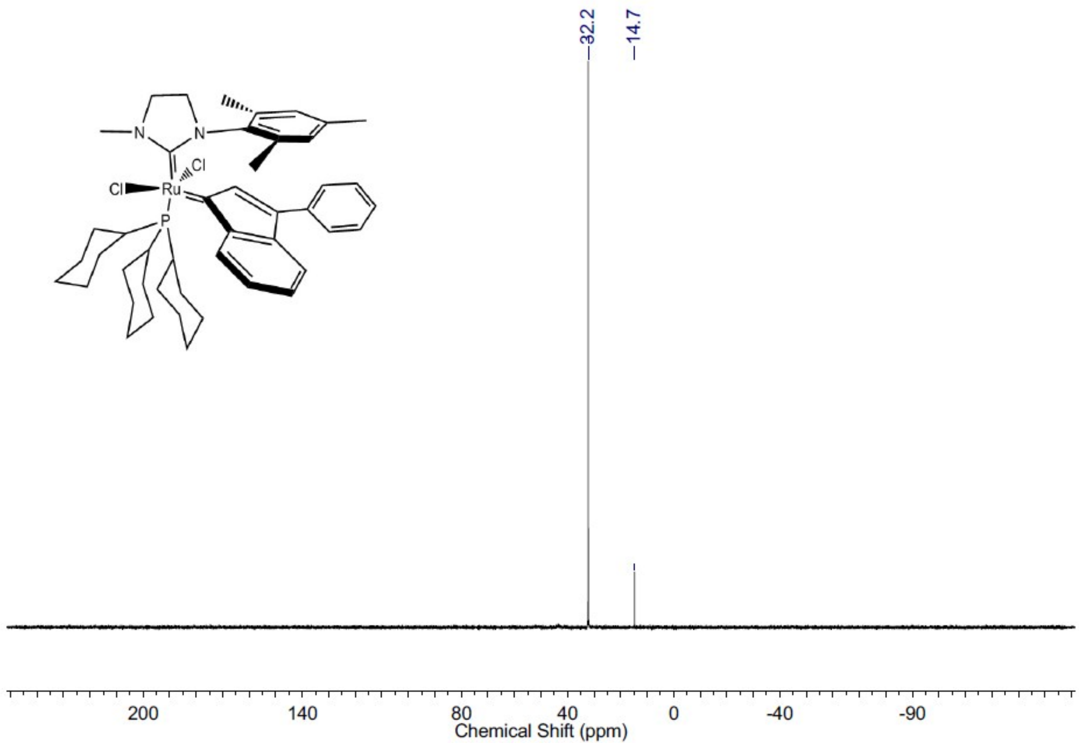


Fig. S4 $^{31}P\{^{1}H\}$NMR spectrum of **8a** in $CDCl_3$.

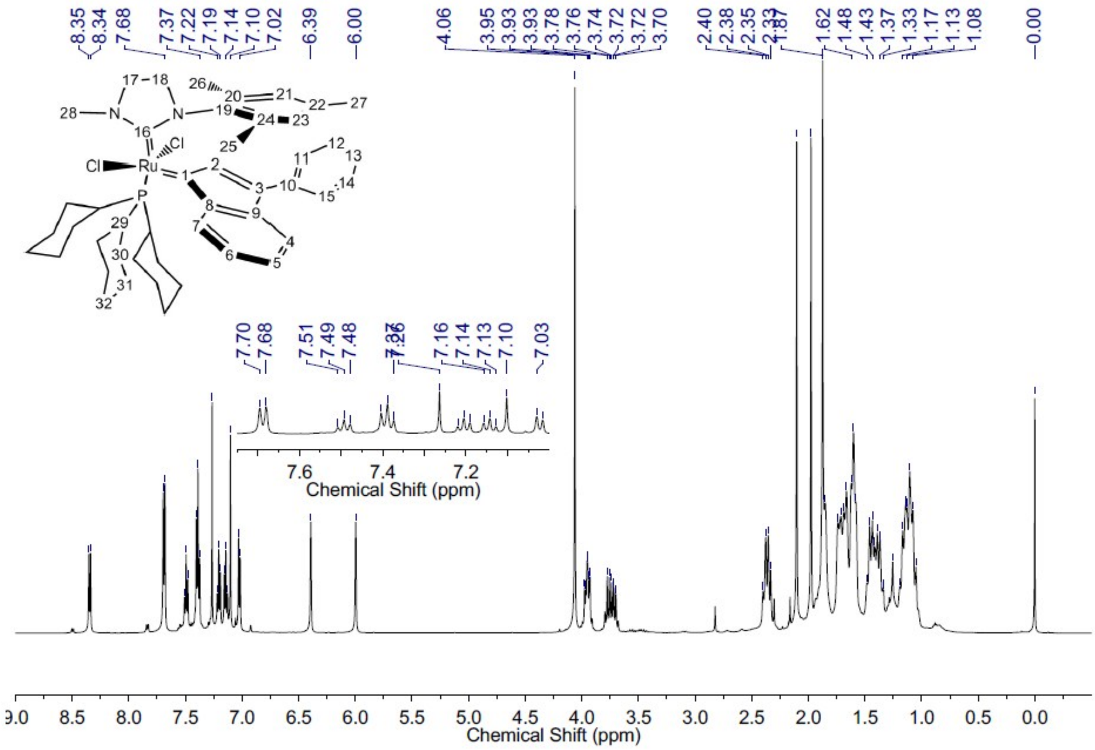


Fig. S5 ^{1}H-NMR spectrum of **8a** in $CDCl_3$.

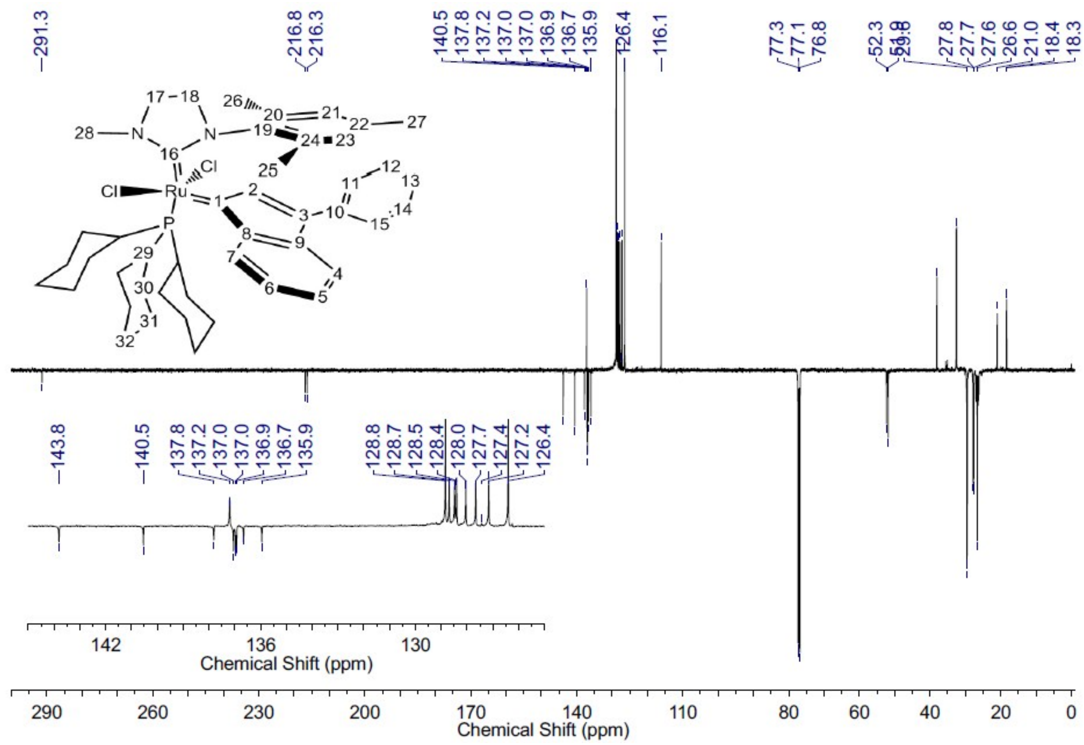


Fig. S6 $^{13}C\{^1H\}$NMR spectrum of **8a** in $CDCl_3$.

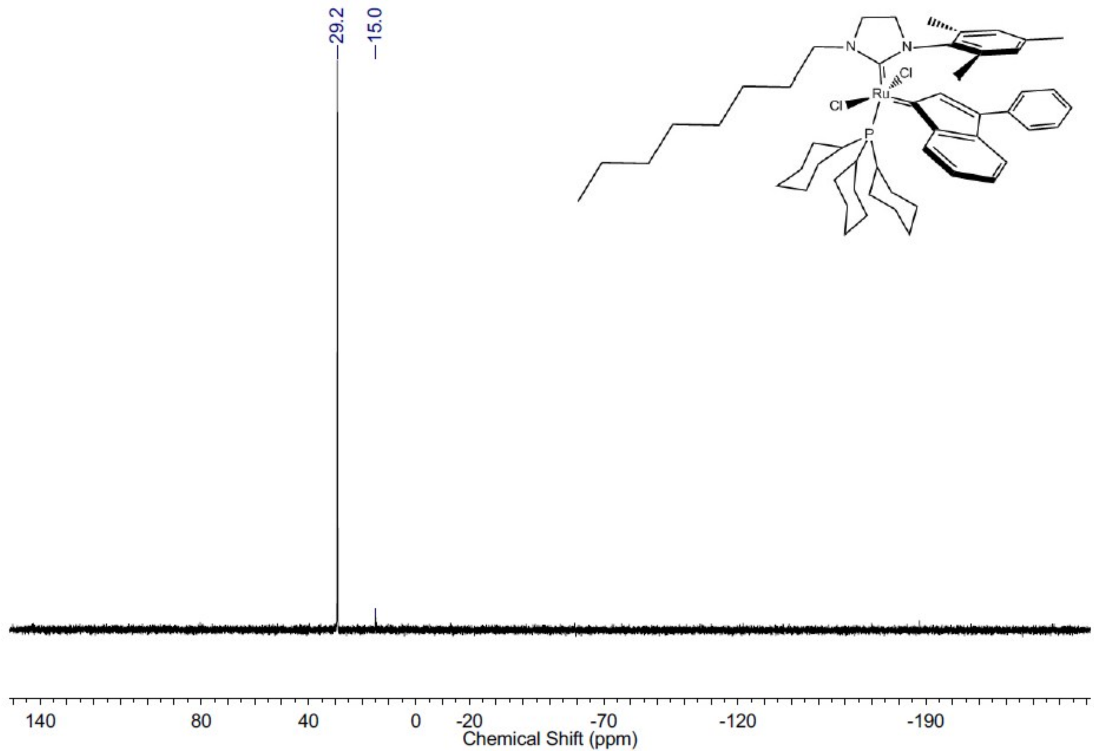


Fig. S7 $^{31}P\{^1H\}$NMR spectrum of **8b** in $CDCl_3$.

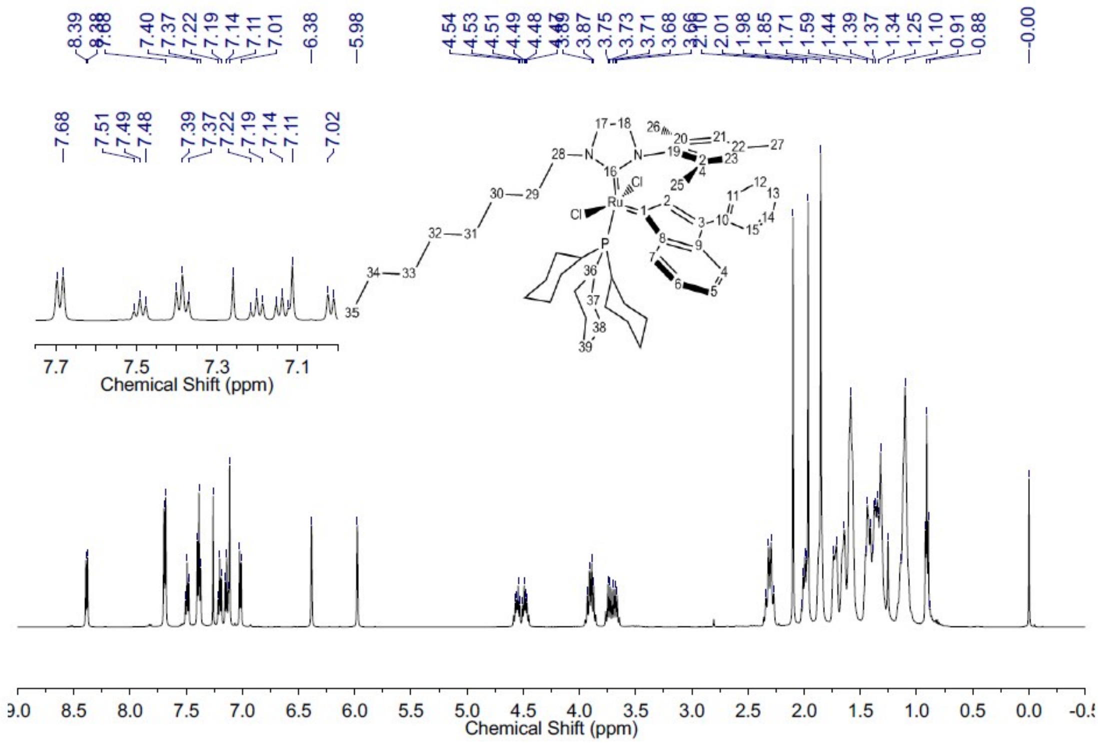


Fig. S8 ^{1}H-NMR spectrum of **8b** in $CDCl_3$.

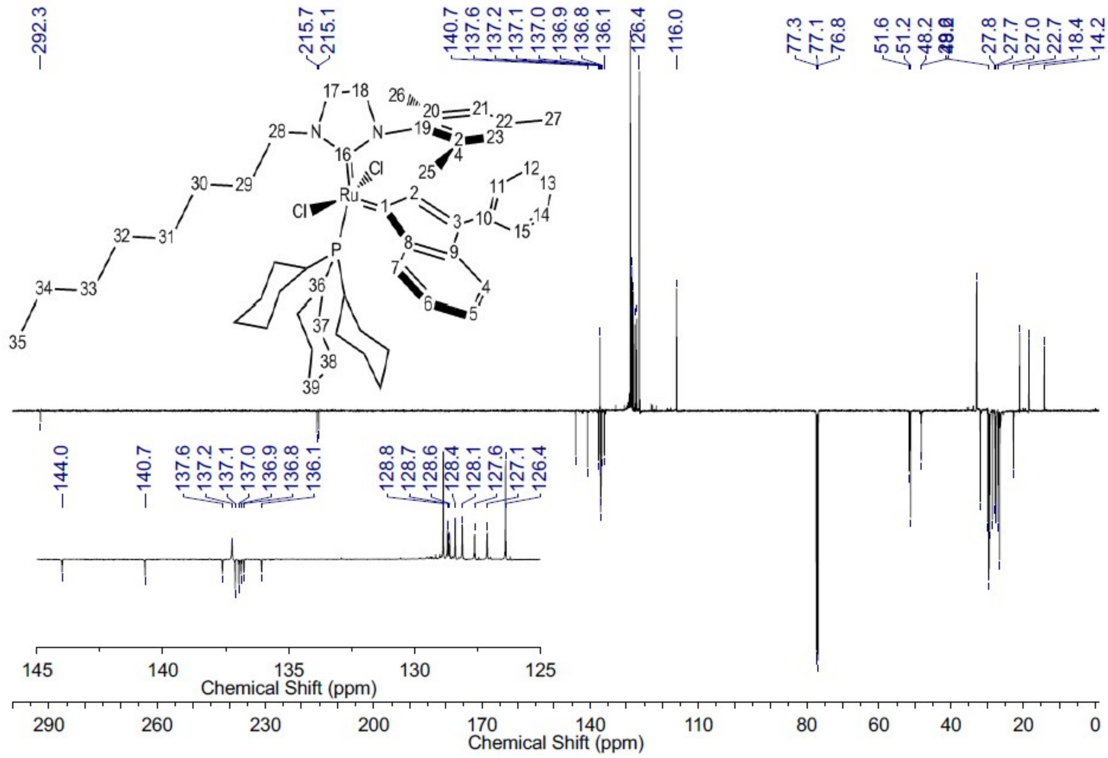


Fig. S9 $^{13}C\{^{1}H\}$NMR spectrum of **8b** in $CDCl_3$.

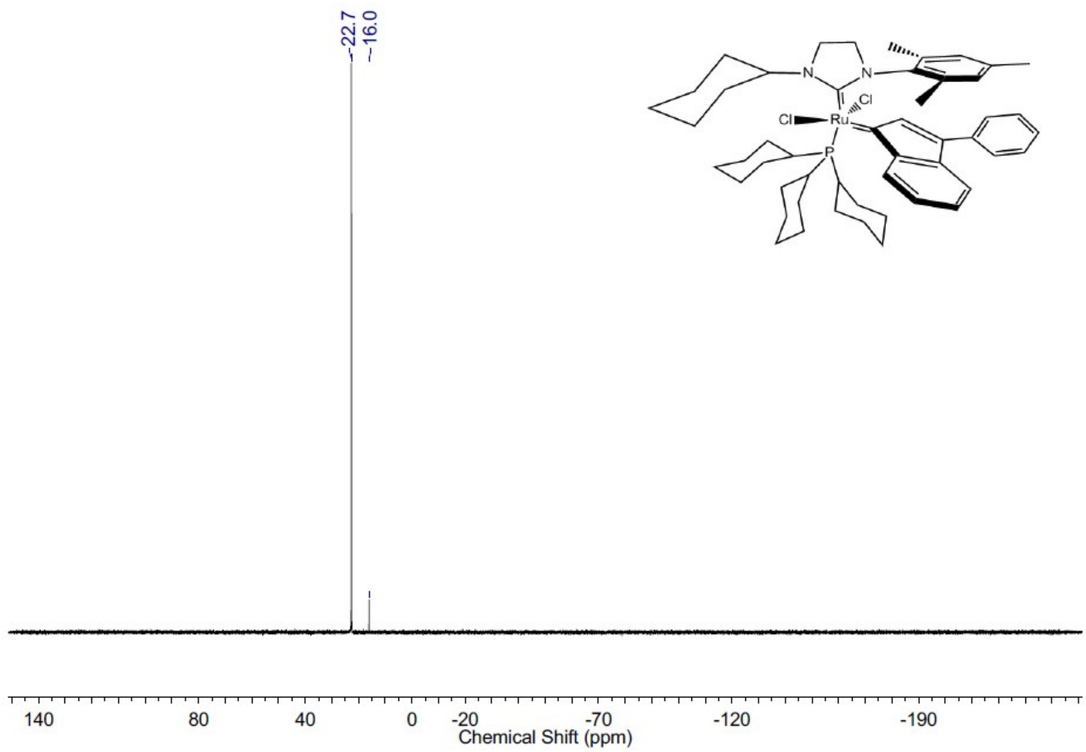


Fig. S10 $^{31}P\{^{1}H\}$NMR spectrum of **8c** in $CDCl_3$.

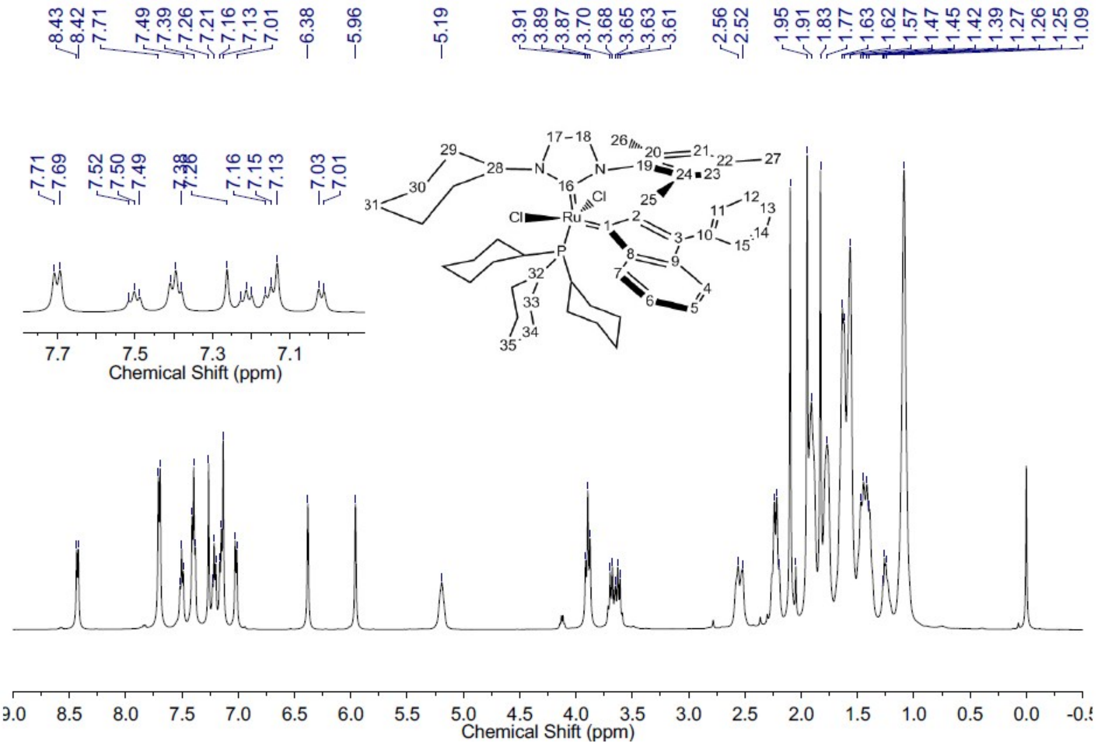


Fig. S11 ^{1}H-NMR spectrum of **8c** in $CDCl_3$.

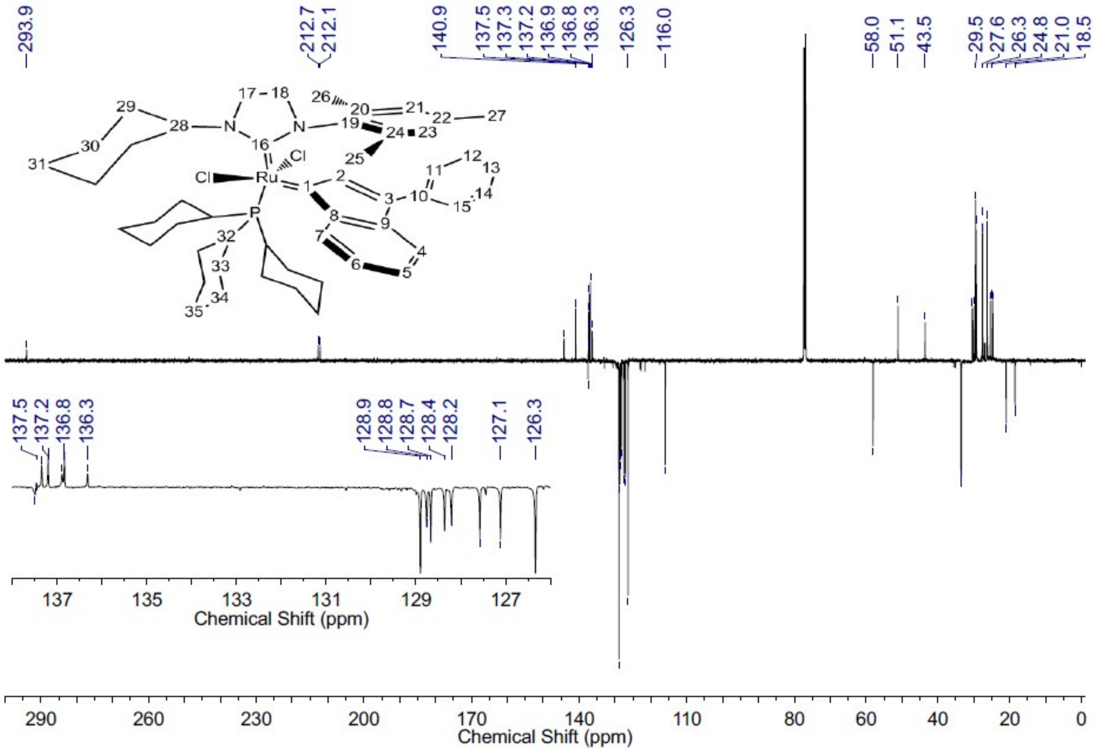


Fig. S12 $^{13}C\{^1H\}$NMR spectrum of **8c** in $CDCl_3$.

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