Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Electronic supplementary information

Effect of the bulkiness of indenylidene moieties on the catalytic initiation and efficiency of second generation ruthenium-based olefin metathesis catalysts

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General Information

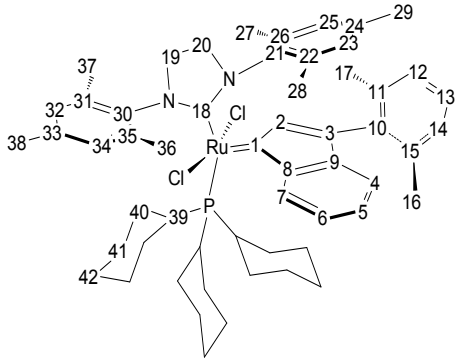
All reactions were carried out under an argon atmosphere using Schlenk tube technique. Solvents were dried and freshly distilled prior to use. Dichloromethane used CaH_2; toluene used sodium and used benzophenone as indicator. *n*-Hexane, *n*-pentane, ethyl acetate, dichloromethane, methanol, toluene were purchased from Fiers. Complexes **1b**, **2**, **3a**, Diethyl 2,2-diallylmalonate (**6**), *cis,cis*-cycloocta-1,5-diene (**COD**) and 1,3-bis(mesityl)-imidazolidine-2-ylidene (SIMes) were purchased from Sigma Aldrich. Complex **3c**,[1] complexes **4a-d**,[2] Diethyl 2-allyl-2-(2-methylallyl)malonate (**7**),[2] (1-(allyloxy)prop-2-yne-1,1-diyl)dibenzene (**8**) [3] and bis(3,5-dimethoxyphenyl)methanone[4] were prepared according to literature procedures.

^1H, ^{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 (^1H, ^{13}C) or external H_3PO_4 (^{31}P). 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. Elemental analyses were performed on a CHNS-O 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) and ω scans. All images were interpreted and integrated with the program CrysAlisPro (Agilent Technologies).[5] Using Olex2[6], the structures were solved by direct methods using the ShelXS structure solution program[7] and refined by full-matrix least-squares on F^2 using the ShelXL program[8]. 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). Also GPC measurements were done using an Agilent (Polymer Laboratories) PLGPC 50 plus instrument, which uses a RI detector and 2 PL gel 5 mm MIXED-D columns thermostated at 40 °C. Calibration was performed with Polystyrene and PMMA standards (780 g.mol-1 to 371100 g.mol-1) where THF was used as eluens with a flow rate of 1 mL.min^{-1}. Samples were injected with a PL-AS RT autosampler.

Synthesis of the ruthenium complexes

To a Schlenk flask, ruthenium complexes **4a-d** (1 eq., 0.42 mmol) and SIMes (2 eq., 0.26 g, 0.84 mmol) were added together with dry toluene (3 mL). The result solution was vigorously stirred for three hours at room temperature. Thereafter, the solvent was dried under vacuum and the solid was washed with cold methanol (2 x 2 mL) and cold *n*-pentane (2 x 2 mL) affording an orange brown powder **5a-d**.

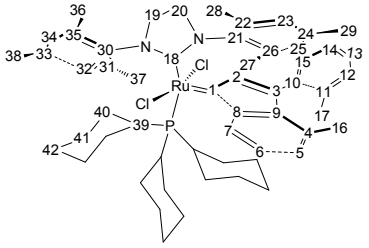
$RuCl_2$(3-2,6-xylyl-1-indenylidene)(SIMes)(PCy_3) (5a)



0.369 g (yield, 90%). Red brown crystals, suitable for X-ray diffraction analysis, of complex **5a** were obtained by slow evaporation of the solution of the complex in *n*-hexane/ethyl acetate/dichloromethane solution. ^1H-NMR (500 MHz, $CDCl_3$, TMS, 20 °C): δ 8.30 (d, $^3J_{H,H}$ = 7.3 Hz, 1 H, H-7), 7.14-7.16 (m, 2 H, H-2, H-13), 7.06-7.08 (m, 3 H, H-5, H-12, H-34), 7.02-7.04 (m, 2 H, H-6, H-32), 6.95 (d, $^3J_{H,H}$ = 7.3 Hz, 1 H, H-14), 6.53 (s, 1 H, H-25), 6.31 (d, $^3J_{H,H}$ = 6.7 Hz, 1 H, H-4), 6.20 (s, 1 H, H-23), 4.03-4.11 (m, 1 H, H-19), 3.85-3.96 (m, 2 H, H-19, H-20), 3.76-3.85 (m, 1 H, H-20), 2.85 (s, 3 H, H-36), 2.60 (s, 3 H, H-37), 2.53 (s, 3 H, H-17), 2.43 (s, 3 H, H-28), 2.33 (s, 3 H, H-38), 2.12-2.15 (m, 6 H, H-27, H-39), 1.95 (s, 3 H, H-16), 1.76 (s, 3 H, H-29), 1.62 (3 H, H_{eq}-40), 1.40-1.51 (m, 12 H, H_{eq}-40, H_{eq}-41, H_{eq}-42), 1.03-1.12 (m, 6 H, H_{ax}-40, H_{ax}-42), 0.93-0.99 (m, 6 H, H_{ax}-40, H_{ax}-41), 0.86-0.91 (m, 3 H, H_{ax}-41); $^{13}C\{^1H\}$NMR (126 MHz, $CDCl_3$, 20 °C): δ 292.3 (d, $^2J_{C,P}$ = 7.6 Hz, C-1), 216.6 (d, $^2J_{C,P}$ = 71.7 Hz, C-18), 142.3 (C-9), 142.0 (C-8), 139.8 (C-2), 139.6 (C-31), 139.0 (C-3), 138.4 (C-35), 138.3 (C-33), 137.1 (C-21), 136.5 (C-24), 135.8 (C-22), 135.8 (C-30), 135.5 (C-26), 135.3 (C-10), 134.7 (C-15), 134.5 (C-11), 130.1 (C-34), 130.0 (C-32), 129.8 (C-23), 129.3 (C-25), 128.7 (C-7), 127.7 (C-14), 127.54 (C-6), 127.45 (C-12), 127.0 (C-5), 126.9 (C-13), 116.1 (H-4), 53.0 (C-19), 52.0 (C-20), 33.1 (C-39), 33.0 (C-39), 29.4, 29.2 (C-40), 27.6, 27.5 (C-41), 26.1 (C-42), 21.9 (C-17), 21.3 (C-16), 21.2 (C-38), 20.7 (C-29), 20.3 (C-37),

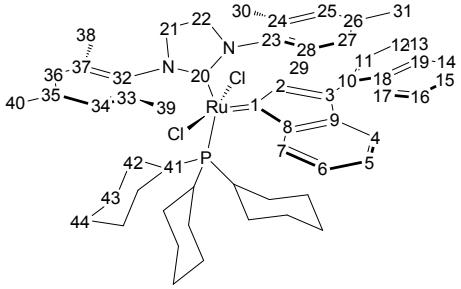
20.1 (C-36), 18.9 (C-28), 18.7 (C-27). ^{31}P&^{1}H}NMR (202 MHz, $CDCl_3$, 20 °C): δ 27.2 (s). IR (Neat): ν = 2953, 2935, 2924, 2915, 2872, 2854, 2837, 1485, 1476, 1462, 1440, 1420, 1377, 1353, 1268, 1252, 1232, 1207, 1174, 1157, 1037, 1028, 1012, 1006, 997, 901, 868, 859, 853, 846, 771, 760, 732, 730 cm^{-1}. Anal. calcd. for $C_{56}H_{73}Cl_2N_2PRu$ (976.39): C 68.83, H 7.53, N 2.87; found: C 68.98, H 7.33, N, 3.03. ESI-MS: $[M\text{-}Cl]^+$ calcd for $C_{56}H_{73}ClN_2PRu$, 941.4243; found: 941.4266.

$RuCl_2$(3-*o*-tolyl-1-indenylidene)(SIMes)(PCy_3)(5b)



0.377 g (yield, 92%). Red crystals, suitable for X-ray diffraction, of complex **5b** were obtained by evaporation of the complex in methanol/ dichloromethane solution. ^{1}H-NMR (500 MHz, $CDCl_3$, TMS, 20 °C): δ (major isomer) 8.46 (d, $^{3}J_{H,H}$ = 7.3 Hz, 1 H, H-7), 7.44 (d, $^{3}J_{H,H}$ = 6.7 Hz, 1 H, H-15), 7.22-7.25 (m, 2 H, H-13, H-14), 7.10 (d, $^{3}J_{H,H}$ = 6.7 Hz, 1 H, H-12), 7.05 (s, 1 H, H-32/34), 7.04 (s, 1 H, H-32/34), 7.00 (t, $^{3}J_{H,H}$ = 7.3 Hz, 1 H, H-6), 6.92 (s, 1 H, H-2), 6.88 (d, $^{3}J_{H,H}$ = 7.3 Hz, 1 H, H-5), 6.81 (s, 1 H, H-23), 6.05 (s, 1 H, H-25), 3.94-4.06 (m, 2 H, H-19), 3.74-3.87 (m, 2 H, H-20), 2.74 (s, 3 H, H-36/37), 2.68 (s, 3 H, H-36/37), 2.38 (s, 3 H, H-28), 2.33 (s, 3 H, H-38), 2.09-2.14 (s, 6 H, H-27, H-39), 2.02 (s, 3 H, H-17), 1.87 (s, 3 H, H-29), 1.64-1.66 (m, 3 H, H_{eq}-40), 1.61 (s, 3 H, H-16), 1.43-1.51 (m, 12 H, H_{eq}-40, H_{eq}-41, H_{eq}-42), 1.03-1.15 (m, 6 H, H_{ax}-40, H_{ax}-42), 0.84-1.00 (m, 9 H, Hax-40, H_{ax}-41); ^{13}C&^{1}H}NMR (126 MHz, $CDCl_3$, 20 °C): δ 294.0 (d, $^{2}J_{C,P}$ = 6.1 Hz, C-1), 216.7 (d, $^{2}J_{C,P}$ = 73.2 Hz, C-18), 143.9 (C-8), 140.1 (C-2), 139.8 (C-10), 139.6 (C-9), 139.41 (C-3), 139.39 (C-31/35), 138.8 (C-31/35), 138.3 (C-33), 136.94 (C-21, C-24), 136.85 (C-26), 136.3 (C-22), 135.7 (C-30), 134.1 (C-11), 130.7 (C-5), 130.0 (C-32/34), 129.9 (C-32/34), 129.6 (C-12), 129.0 (C-23), 128.6 (C-25), 128.1 (C-6), 127.3 (C-7), 127.1 (C-13), 126.3 (C-4), 125.3 (C-14), 125.1 (C-15), 52.7 (d, J = 3.1 Hz, C-19), 52.3 (C-20), 33.1, 33.0 (C-39), 29.5, 29.3 (C-40), 27.7, 27.6 (C-41), 26.2 (C-42), 21.2 (C-38), 20.9 (C-29), 20.3 (C-36/37), 20.2 (C-36/37), 19.4 (C-17), 19.0 (C-27), 18.9 (C-28), 18.4 (C-16). ^{31}P&^{1}H}NMR (202 MHz, $CDCl_3$, 20 °C): δ 26.7 (s, major), 23.2 (s, minor). IR (Neat): ν = 2921, 2849, 1482, 1445, 1417, 1404, 1379, 1352, 1262, 1246, 1231, 1212, 1173, 1033, 1006, 856, 845, 780, 763, 754, 730, 725 cm^{-1}. Anal. calcd. for $C_{56}H_{73}Cl_2N_2PRu$ (76.39): C 68.83, H 7.53, N 2.87; found: C 69.06, H 7.49, N, 2.62. ESI-MS: $[M\text{-}Cl]^+$ calcd for $C_{56}H_{73}ClN_2PRu$, 941.4; found: 941.4, calcd: 941.4243; found: 941.4231.

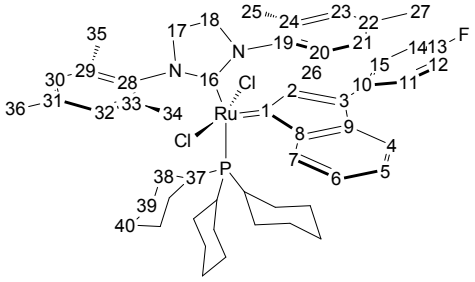
$RuCl_2$(3-1-naphthyl-1-indenylidene)(SIMes)(PCy_3)(5c)



0.390 g (yield, 93%). ^{1}H-NMR (500 MHz, $CDCl_3$, TMS, 20 °C): (major isomer) δ 8.60 (d, $^{3}J_{H,H}$ = 7.0 Hz, 1 H, H-7), 7.94 (d, $^{3}J_{H,H}$ = 8.2 Hz, 1 H, H-13), 7.87-7.91 (m, 2 H, H-14, H-17), 7.74 (d, $^{3}J_{H,H}$ = 7.0 Hz, 1 H, H-11), 7.53 (t, $^{3}J_{H,H}$ = 7.6 Hz, 1 H, H-12), 7.46 (t, $^{3}J_{H,H}$ = 7.0 Hz, 1 H, H-15), 7.42 (s, 1 H, H-2), 7.37 (t, $^{3}J_{H,H}$ = 7.6 Hz, 1 H, H-16), 7.09-7.15 (m, 2 H, H-5, H-6), 7.06 (s, 1 H, H-34/36), 7.05 (s, 1 H, H-34/36), 6.68 (s, 1 H, H-25), 6.51 (d, $^{3}J_{H,H}$ = 6.7 Hz, 1 H, H-4), 6.04 (s, 1 H, H-27), 3.99-4.06 (m, 2 H, H-21), 3.80-3.92 (m, 2 H, H-22), 2.76 (s, 3 H, H-38/39), 2.69 (s, 3 H, H-38/39), 2.36 (s, 3 H, H-30), 2.34 (s, 3 H, H-40), 2.21 (s, 3 H, H-29), 1.77 (s, 3 H, H-31), 2.16 (m, 3 H, H-41), 1.55-1.62 (m, 6 H, H_{eq}-42), 1.41-1.46 (m, 9 H, H_{eq}-43, H_{eq}-44), 0.84-1.16 (m, 15 H, H_{ax}-42, H_{ax}-43, H_{ax}-44); ^{13}C&^{1}H}NMR (125.78 MHz, $CDCl_3$, 20 °C): δ 293.0 (d, $^{2}J_{C,P}$ = 9.2 Hz, C-1), 216.9 (d, $^{2}J_{C,P}$ = 73.2 Hz, C-20), 143.6 (C-8), 142.5 (C-9), 139.6 (C-2), 139.3 (C-33/37), 139.0 (C-33/37), 138.4 (C-35), 137.5 (C-3), 137.0 (C-23), 136.9 (C-26), 136.7 (C-28), 136.3 (C-24), 135.5 (C-32), 134.9 (C-10), 134.1 (C-19), 130.1 (C-18), 130.0 (C-34/36), 129.9 (C-34/36), 129.1 (C-25), 128.9 (C-7), 128.7 (C-27), 128.11(C-14), 128.06 (C-6), 128.0 (C-13), 127.1 (C-17), 127.0 (C-5), 125.8 (C-15), 125.5 (C-12), 125.1 (C-16), 123.8 (C-11), 116.9 (C-4), 52.7 (d, J = 4.6 Hz, C-21), 52.0 (C-22), 33.47, 33.33 (C-41), 29.31 (C-42), 27.68, 27.66, 27.61, 27.58 (C-43), 26.2 (C-44), 21.2 (C-40), 20.9 (C-31), 20.3 (C-38/39), 20.2 (C-38/39), 19.0 (C-29), 18.9 (C-30). ^{31}P&^{1}H}NMR (202 MHz, $CDCl_3$, 20 °C): δ 27.6 (s, minor), 24.7 (s, major). IR (Neat): ν = 3052, 3004, 2925, 2850, 1941, 1608, 1590, 1529, 1504, 1483, 1444, 1420, 1378, 1355, 1328, 1265, 1242, 1207, 1183, 1174, 1129, 1075, 1035, 1018, 1006, 963, 914, 889, 849, 816,

801, 777, 764, 754, 734 cm^{-1}. Anal. calcd. for $C_{58}H_{71}Cl_2N_2PRu$ (998.38): C 69.72, H 7.16, N 2.80; found: C 69.36, H 7.17, N, 2.81. ESI-MS: $[M-Cl]^+$ calcd for $C_{58}H_{71}ClN_2PRu$, 963.4; found: 963.4, calcd: 963.4087; found: 963.4075.

$RuCl_2$(3-*p*-fluorophenyl-1-indenylidene)(SIMes)(PCy_3) (5d)



0.365 g, (yield, 90%). Red crystals, suitable for X-ray diffraction, of complex **5d** were obtained by slow evaporation of the complex in a toluene solution. ^{1}H-NMR (500 MHz, $CDCl_3$, TMS, 20 °C): δ 8.63 (d, $^3J_{H,H}$ = 7.0 Hz, 1 H, H-7), 7.66-7.69 (m, 2 H, H-11, H-15), 7.27 (s, 1 H, H-2), 7.20 (t, $^3J_{H,H}$ = 7.0 Hz, 1 H, H-5), 7.17 (t, $^3J_{H,H}$ = 7.0 Hz, 1 H, H-6), 7.09 (t, *J* = 8.5 Hz, 2 H, H-12, H-14), 7.05 (s, 2 H, H-30, H-32), 6.98 (d, $^3J_{H,H}$ = 6.7 Hz, 1 H, H-4), 6.41 (s, 1 H, H-23), 5.99 (s, 1 H, H-21), 3.99 (t, $^3J_{H,H}$ = 10.4 Hz, 2 H, H-17), 3.85 (q, $^{2\text{-}3}J_{H,H}$ = 10.4 Hz, 1 H, H-18), 3.77 (q, $^{2\text{-}3}J_{H,H}$ = 10.4 Hz, 1 H, H-18), 2.70 (s, 3 H, H-34/35), 2.69 (s, 3 H, H-34/35), 2.34 (s, 3 H, H-36), 2.24 (s, 3 H, H-25), 2.15-2.18 (m, 3 H, H-37), 2.06 (s, 3 H, H-26), 1.84 (s, 3 H, H-27), 1.58 (3 H, H_{eq}-38), 1.50-1.52 (m, 6 H, H_{eq}-39, H_{eq}-40), 1.44 (m, 6 H, H_{eq}-38, H_{eq}-39), 0.95-1.08 (m, 15 H, H_{ax}-38, H_{ax}-39, H_{ax}-40); ^{13}C&^{1}H}NMR (125.78 MHz, $CDCl_3$, 20 °C): δ 291.8 (d, $^2J_{P,C}$ = 7.6 Hz, C-1), 216.9 (d, $^2J_{C,P}$ = 73.2 Hz, C-16), 161.9 (d, $^1J_{C,F}$ = 247.2 Hz, C-13), 144.8 (C-8), 140.7 (C-9), 139.2 (C-29/33), 139.0 (C-29/33), 138.4 (C-31), 137.8 (C-2), 137.0 (C-20), 136.9 (C-19), 136.8 (C-24), 136.7 (C-22), 135.4 (C-3, C-28), 133.1 (d, $^4J_{F,C}$ = 3.0 Hz, C-10), 129.9 (C-30, C32), 129.3 (C-7), 128.9 (C-23), 128.6 (C-21), 128.2 (C-6), 127.9 (d, $^3J_{F,C}$ = 7.6 Hz, C-11, C-15), 126.9 (C-5), 116.0 (d, $^2J_{F,C}$ = 21.4 Hz, C-12, C-14), 115.6 (C-4), 52.6 (d, *J* = 3.1 Hz, C-17), 52.0 (C-18), 32.92, 32.79 (C-37), 29.38, 29.38 (C-28), 27.85, 27.78, 27.71, 27.63 (C-39), 26.2 (C-40), 21.2 (C-36), 21.0 (C-27), 20.3 (C-34/35), 20.2 (C-34/35), 18.8 (C-26), 18.7 (C-25). ^{31}P&^{1}H}NMR (202 MHz, $CDCl_3$, 20 °C): δ 26.5 (s). IR (Neat): ν = 2934, 2919, 2849, 1603, 1500, 1484, 1475, 1444, 1420, 1408, 1378, 1357, 1303, 1278, 1264, 1246, 1228, 1208, 1175, 1160, 1039, 1024, 1015, 1005, 974, 862, 842, 818, 775, 762, 754, 736 cm^{-1}. Anal. calcd. for $C_{54}H_{68}Cl_2FN_2PRu$ (966.35): C 67.07, H 7.09, N 2.90; found: C 66.72, H 7.06, N, 2.97. ESI-MS: $[M-Cl]^+$ calcd for $C_{54}H_{68}ClFN_2PRu$, 931.4; found: 931.4, calcd: 931.3836; found: 931.3837.

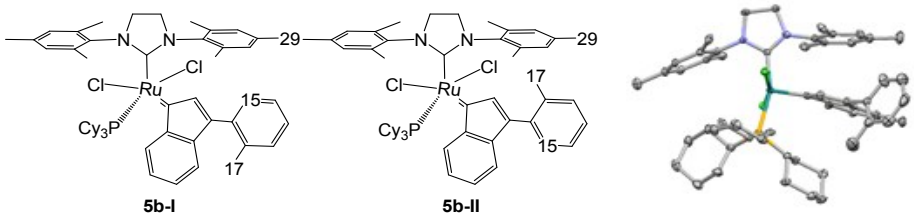


Fig. S1 The proposed two conformers (**5b-I** and **5b-II**) of complex **5b** and representation of the structure of complex **5b** obtained by single crystal X-ray diffraction analysis.

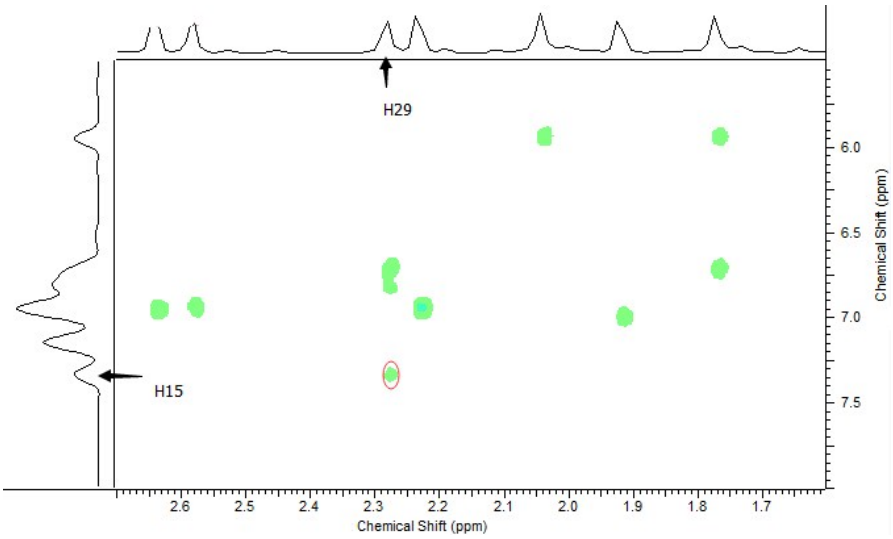


Fig. S2 The NOESY spectrum of complex **5b** in $CDCl_3$. Horizontal (1.6 ppm to 2.7 ppm) and vertical (5.5 ppm to 7.5 ppm).

Both $^{31}P\{^{1}H\}$NMR and ^{1}H-NMR spectra of complexes **5b** and **5c** feature two sets of peaks and indicate the presence of some isomers/conformers. Whereas, these were not observed for complexes **3a**, **5a** and **5d** which bear a symmetrical 3-aryl group. So, we envisaged the formation of the conformers is due to the orientation of the asymmetrical 3-aryl group on complexes **5b** and **5d**. First of all, taking complex **5b** as an example, we estimated two conformers existing in two forms as **5b-I** and **5b-II** (Figure S1). The existence of **5b-I** is proven by the obtained solid-state crystal structure (Figure S1 and Figure 2). According to the assigned proton peaks for the major conformer of **5b**, proton to proton NOE correlations involving H15–H29 on a NOESY spectrum (Figure S2) allowed to determine the relative position of the protons. Considering the resonance of H17, there is no NOE correlation between H17 and any methyl groups of the SIMes ligand. So the form of **5b-I** was believed to be the major conformer of **5b**. Therefore, the configuration of complex **5b** that was obtained from the single crystal analysis represents the major conformer of complex **5b**, as that observed from NMR spectra.

Monitoring the catalytic process of the ruthenium complexes

Applied procedure for the RCM of diethyl diallymalonate/diethyl 2-allyl-2-(2-methylallyl)malonate:[9]

Diene (1 mmol) and the internal standard dodecane (170 mg, 1 mmol) were dissolved in CH_2Cl_2 (9 mL), then the solution was heated up at 30/35 °C. The ruthenium complex (10 µmol) was dissolved in CH_2Cl_2 (1 mL) and the result ruthenium solution was injected into the substrate solution. Aliquot sampling of the reaction solution were taken at regular time intervals and diluted by a mixture of ethoxyethene and CH_2Cl_2 before being injected into the GC for analysis.

Applied procedure for the RCEYM of (1-(allyloxy)prop-2-yne-1,1-diyl)dibenzene:[9]

(1-(allyloxy)prop-2-yne-1,1-diyl)dibenzene (248 mg, 1 mmol) and the internal standard dodecane (170 mg, 1 mmol) were dissolved in toluene (9 mL), then the solution was heated up at 50 °C. The ruthenium complex (40 µmol) was dissolved in toluene (1 mL) and the result ruthenium solution was injected into the substrate solution. Aliquot sampling of reaction solution were taken at regular time intervals and diluted by a mixture of ethoxyethene and toluene before being injected to the GC for analysis.

Applied procedure for the ROMP of COD:[9-10]

The ruthenium complex (1.63 µmol) was dissolved in $CDCl_3$ (0.6 mL). An NMR tube was filled with COD (0.1 mL) and $CDCl_3$ (0.5 mL) as well as the prepared ruthenium complex solution (0.1 mL). Then, the tube was subjected into ^{1}H-NMR analysis at 40 °C for determination of the conversion.

Single crystal X-ray diffraction

Crystal data for **5a**. CCDC 1043526, $C_{56}H_{73}Cl_2N_2PRu$, M = 977.10, monoclinic, space group $P2_1/n$ (No. 14), a = 11.7833(3) Å, b = 32.7044(10) Å, c = 13.6983(4) Å, β = 111.821(3)°, V = 4900.6(3) Å^3, Z = 4, T = 100 K, ρ_{calc} = 1.324 g cm^{-3}, μ(Cu-Kα) = 4.186 mm^{-1}, F(000) = 2064, 23338 reflections measured, 9380 unique (R_{int} = 0.0909) which were used in all calculations. The final R1 was 0.0560 (I >2σ (I)) and wR2 was 0.1062 (all data).

Crystal data for **5b**. CCDC 1414654, $C_{56}H_{73}N_2Cl_2PRu$, M = 977.10, orthorhombic, space group $P2_12_12_1$ (No. 19), a = 14.1500(4) Å, b = 14.3631(3) Å, c = 24.5735(4) Å, V = 4994.27(19) Å^3, Z = 4, T = 100 K, ρ_{calc} = 1.299 g cm^{-3}, μ(Cu-Kα) = 4.108 mm^{-1}, F(000)

= 2064, 13803 reflections measured, 8245 unique (R_{int} = 0.0683) which were used in all calculations. The final $R1$ was 0.0488 ($I > 2\sigma(I)$) and $wR2$ was 0.0795 (all data).

Crystal data for **5d**. CCDC 1414653, $C_{61}H_{76}N_2FCl_2PRu$, M = 1059.18, monoclinic, space group $P2_1/c$ (No. 14), a = 18.3485(7) Å, b = 16.9164(7) Å, c = 17.4629(8) Å, β = 100.428(4)°, V = 5330.8(4) Å^3, Z = 4, T = 100 K, ρ_{calc} = 1.320 g cm^{-3}, μ(Cu-Kα) = 3.920 mm^{-1}, F(000) = 2232, 26706 reflections measured, 10093 unique (R_{int} = 0.0774) which were used in all calculations. The final $R1$ was 0.0586 ($I > 2\sigma(I)$) and $wR2$ was 0.1688 (all data). The asymmetric unit contains one ruthenium complex molecule and one toluene molecule.

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

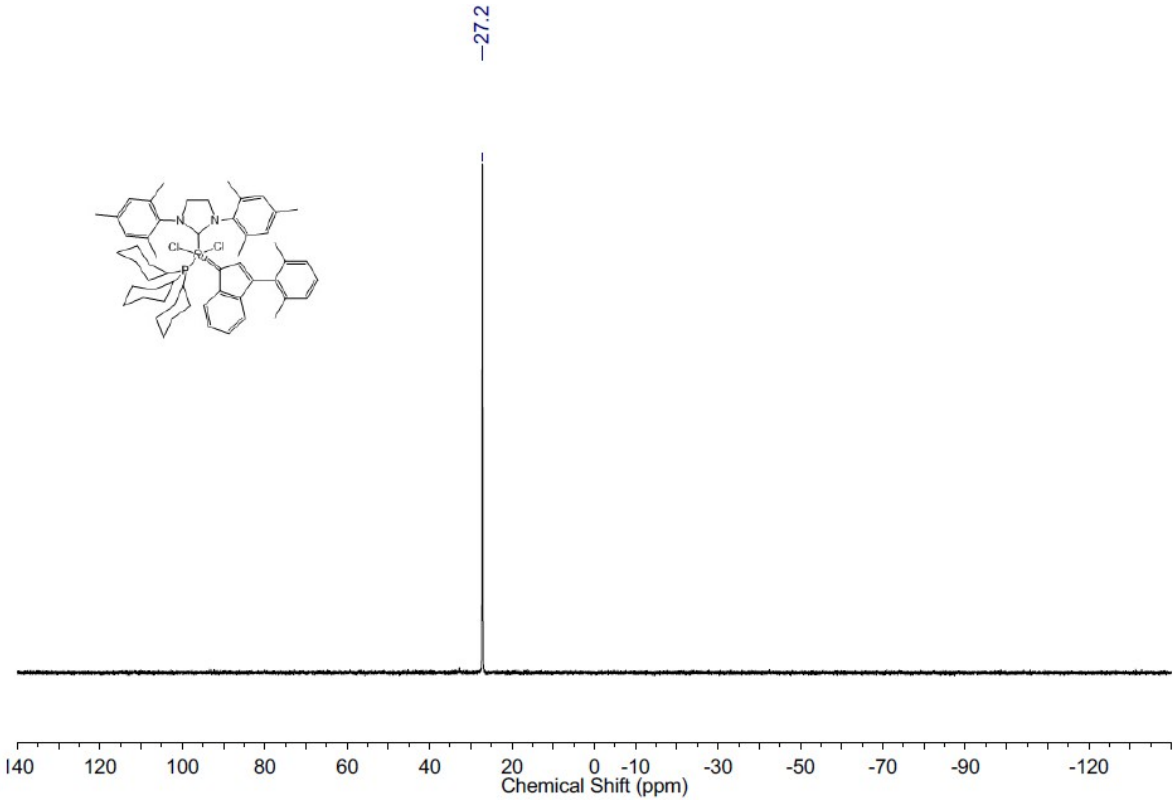


Fig. S3 ^{31}P-NMR spectrum for complex **5a** in $CDCl_3$.

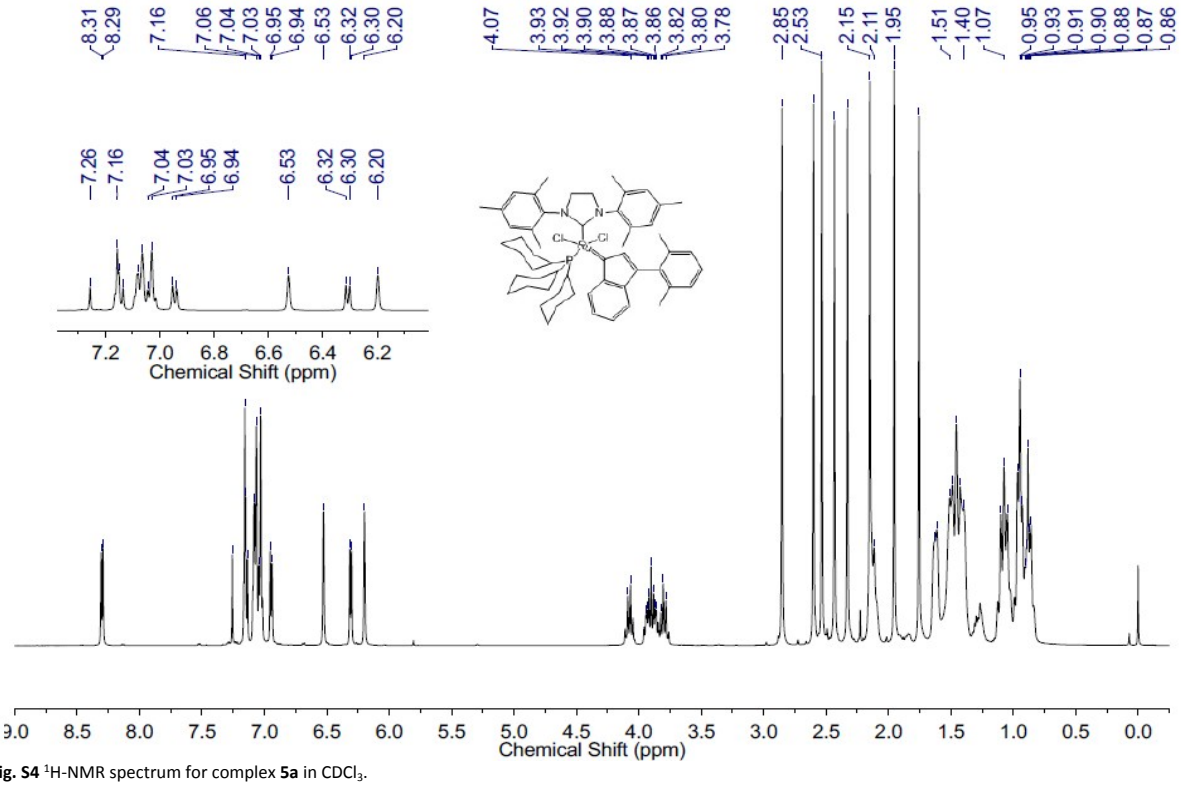


Fig. S4 ^{1}H-NMR spectrum for complex **5a** in $CDCl_3$.

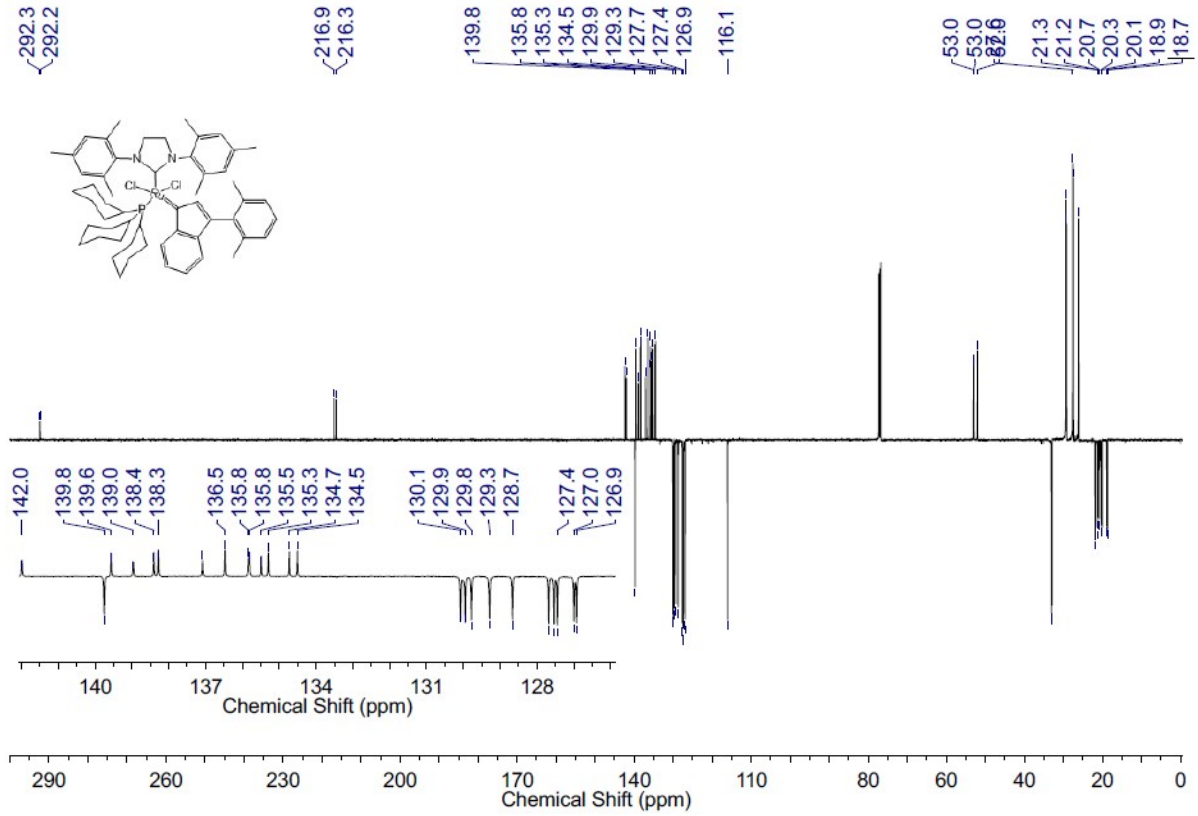


Fig. S5 ^{13}C-NMR spectrum for complex **5a** in $CDCl_3$.

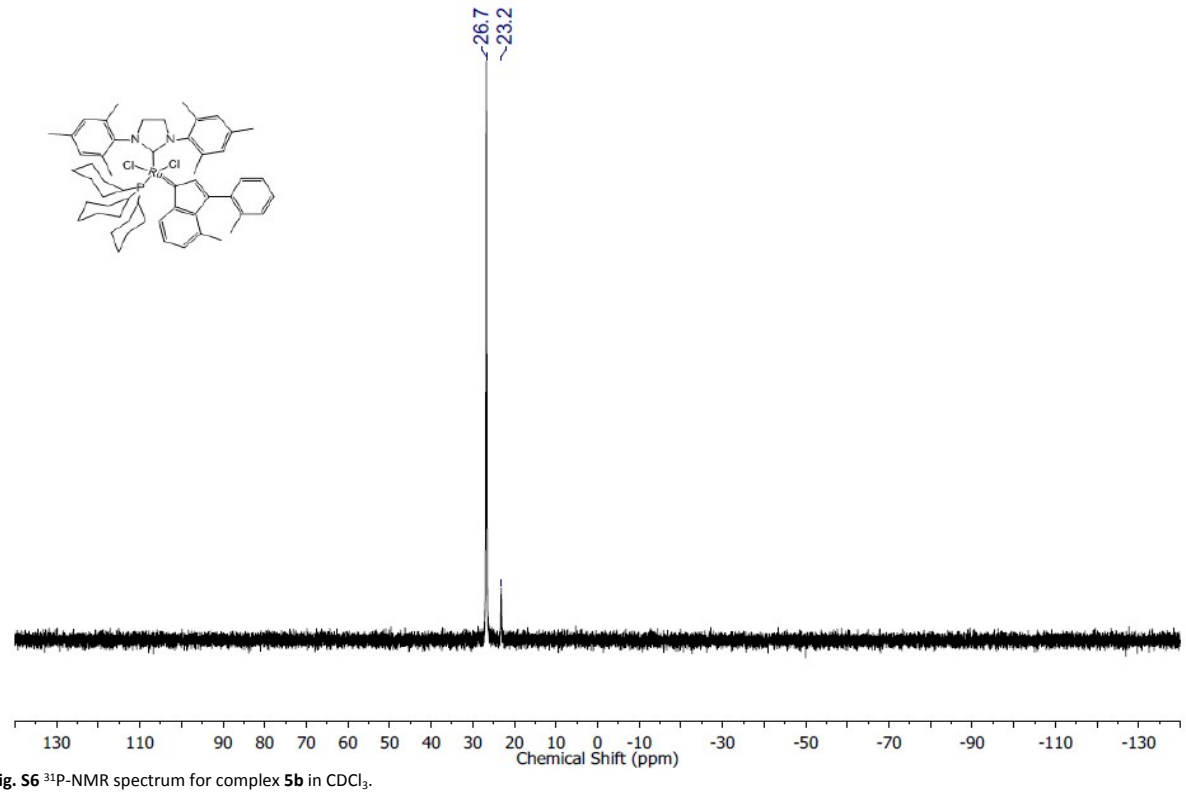


Fig. S6 ^{31}P-NMR spectrum for complex **5b** in $CDCl_3$.

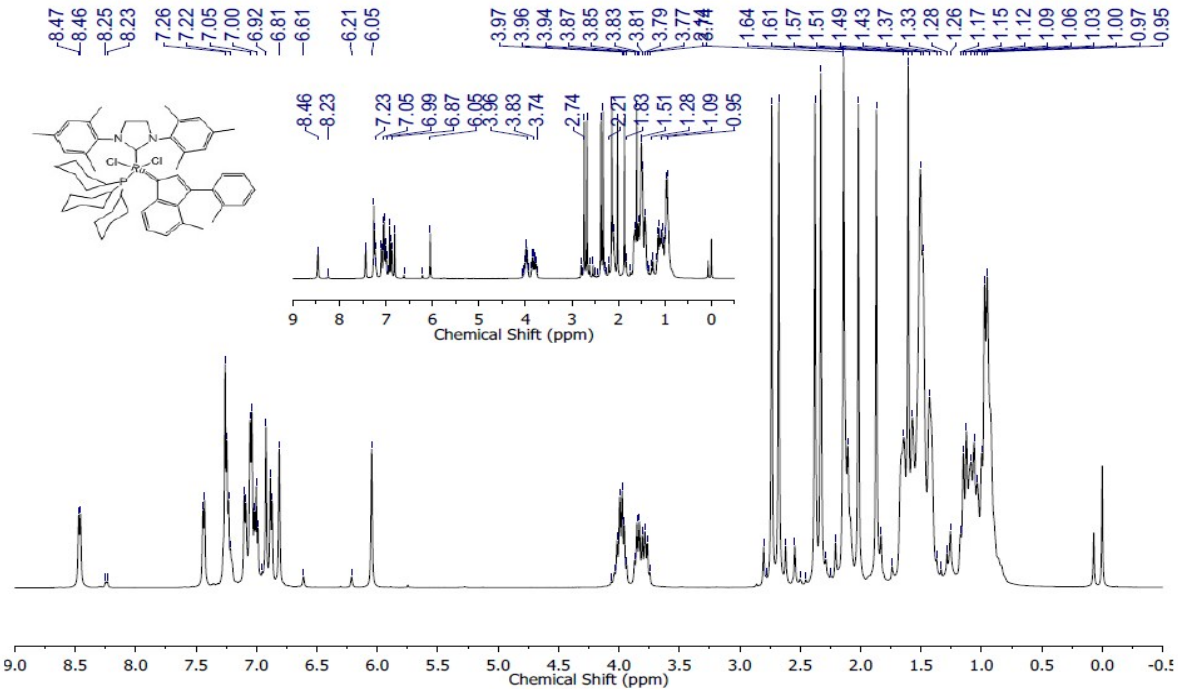


Fig. S7 ^{1}H-NMR spectrum for complex **5b** in $CDCl_3$.

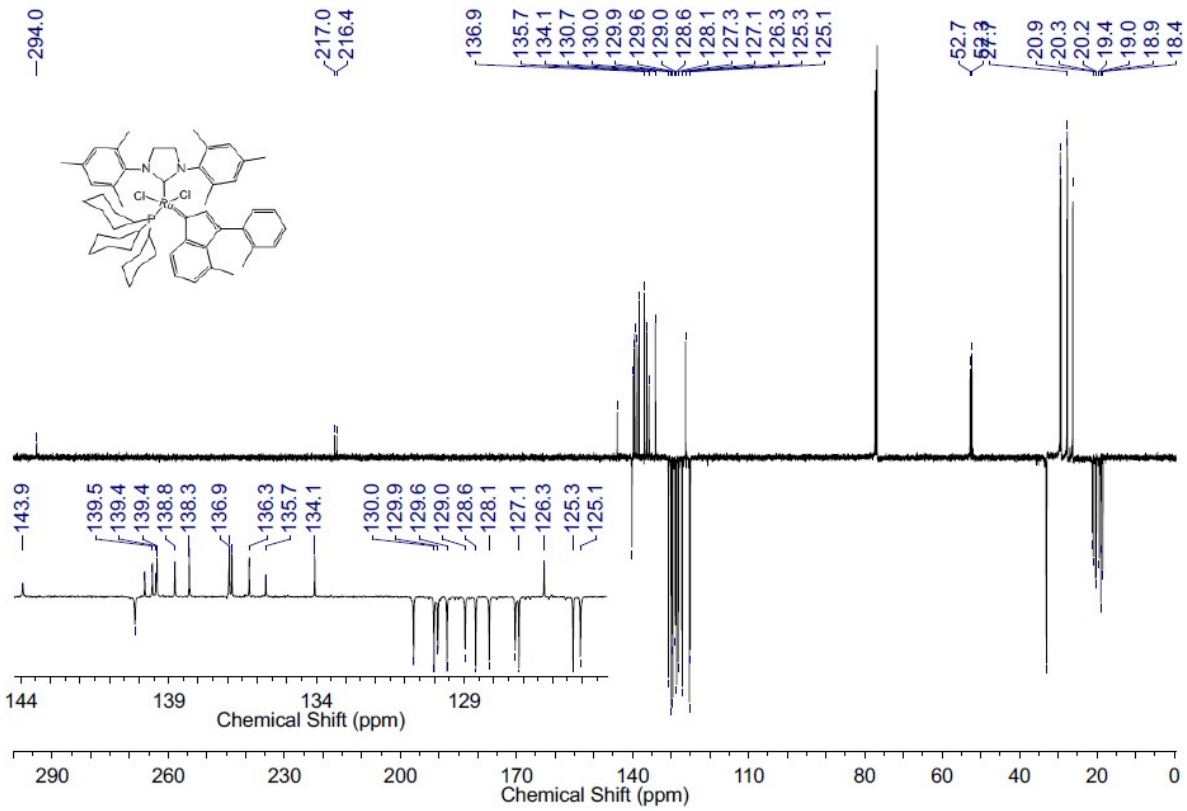


Fig. S8 ^{13}C-NMR spectrum for complex **5b** in $CDCl_3$.

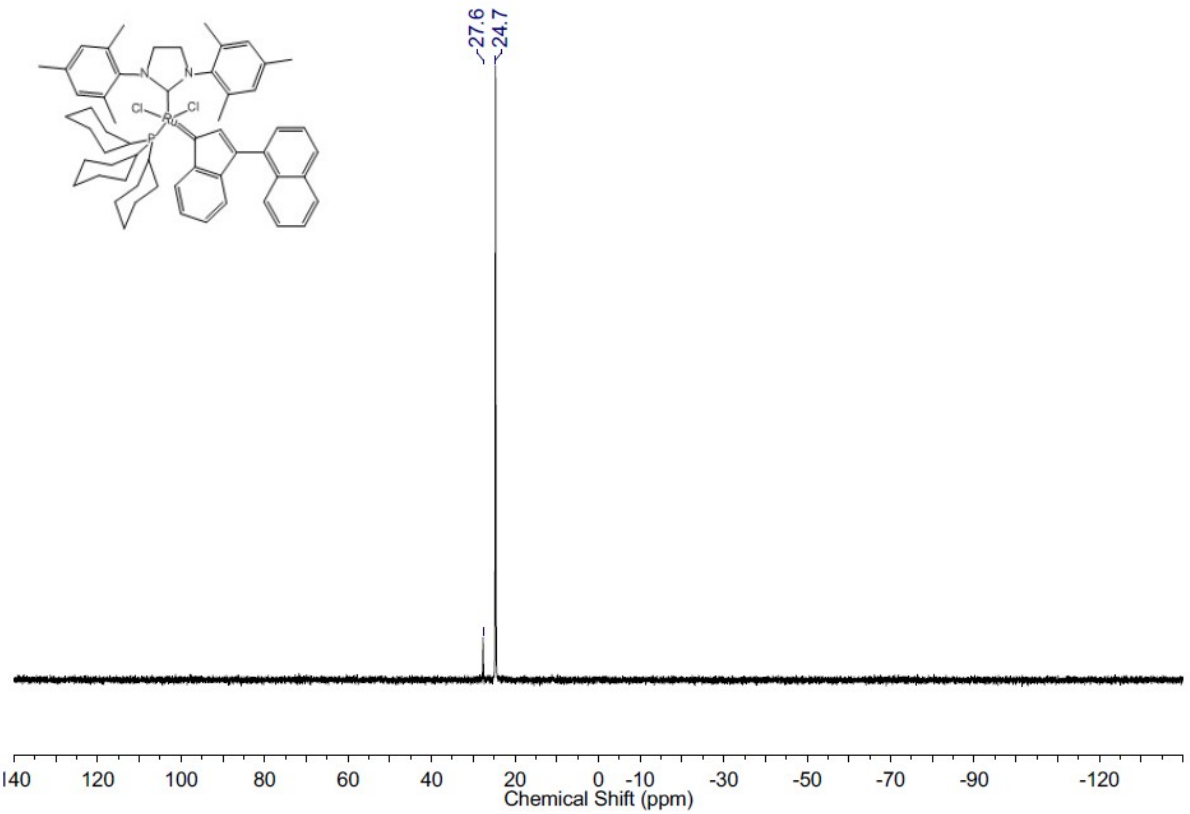


Fig. S9 ^{31}P-NMR spectrum for complex **5c** in $CDCl_3$.

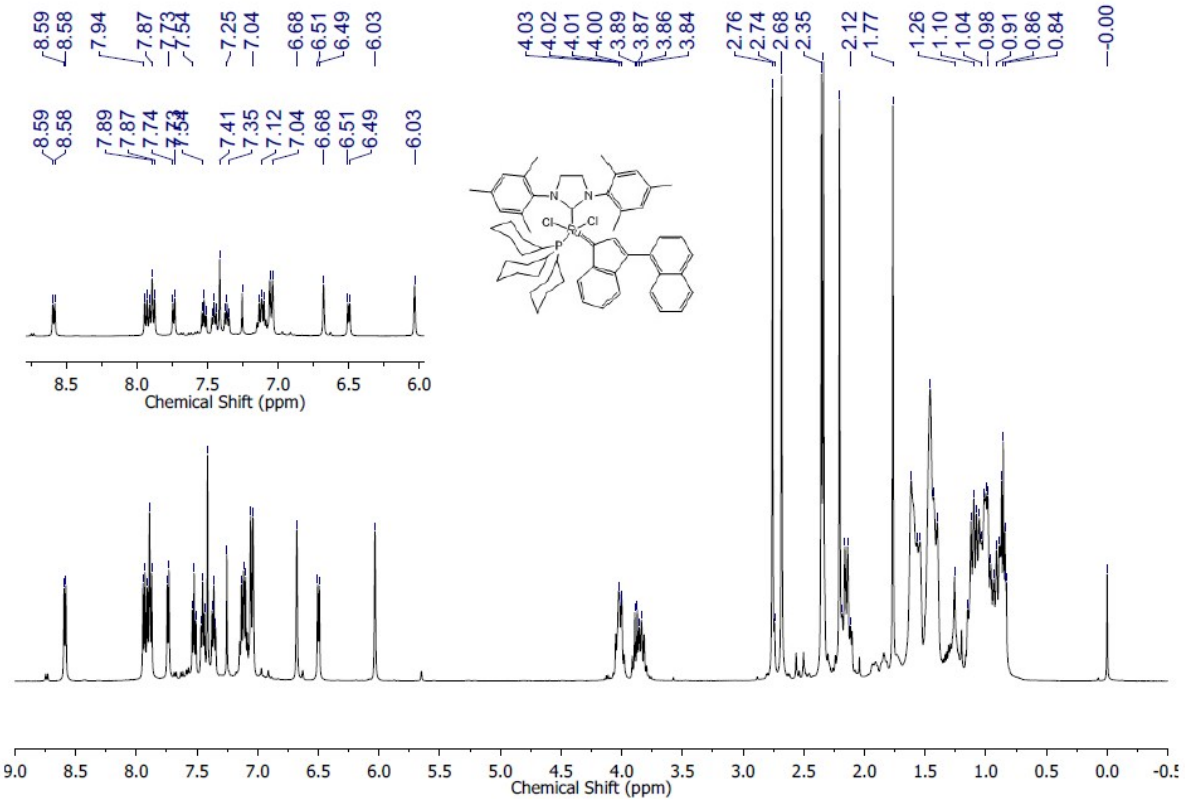


Fig. S10 ^{1}H-NMR spectrum for complex **5c** in $CDCl_3$.

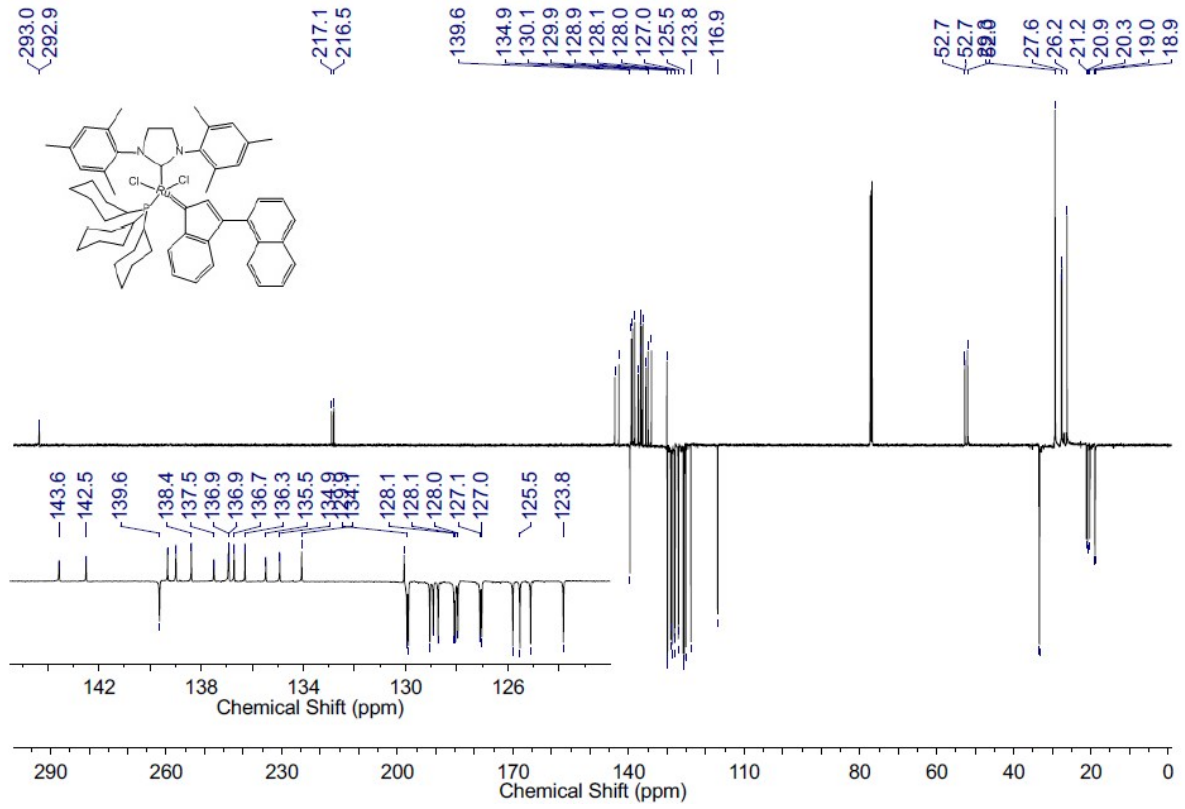


Fig. S11 ^{13}C-NMR spectrum for complex **5c** in $CDCl_3$.

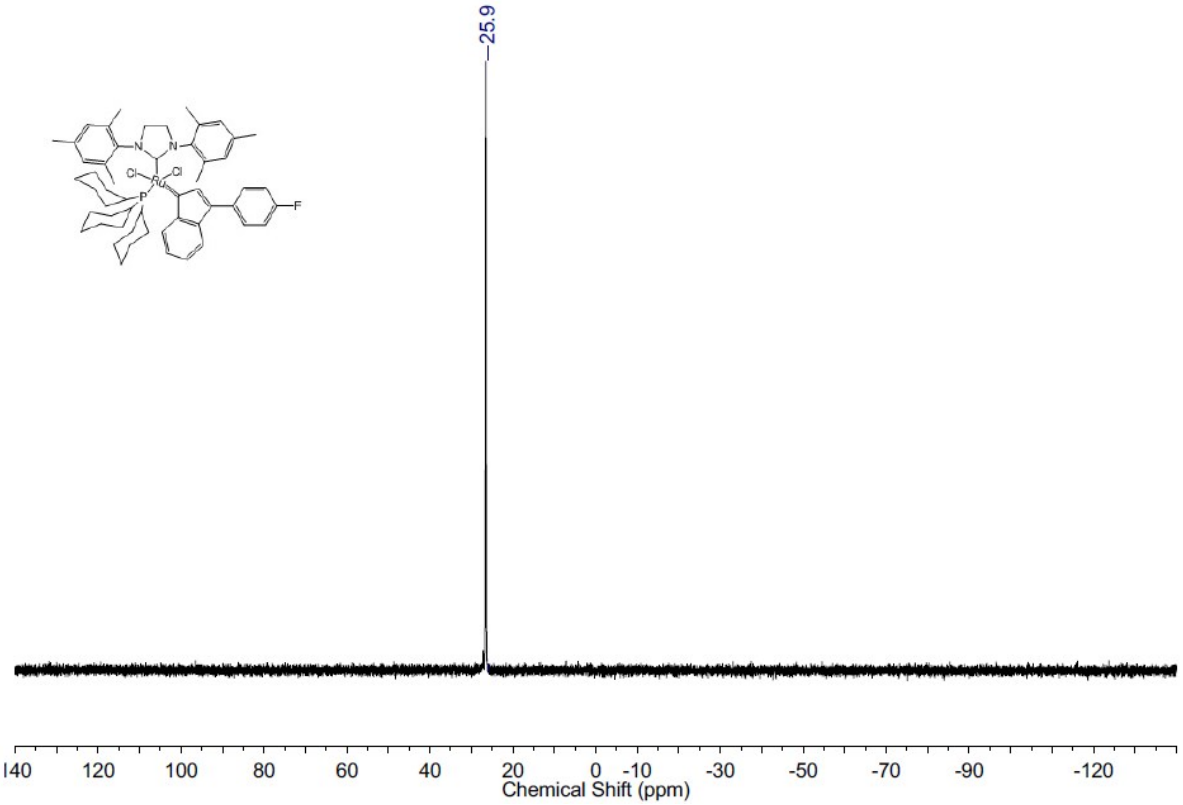


Fig. S12 ^{31}P-NMR spectrum for complex **5d** in $CDCl_3$.

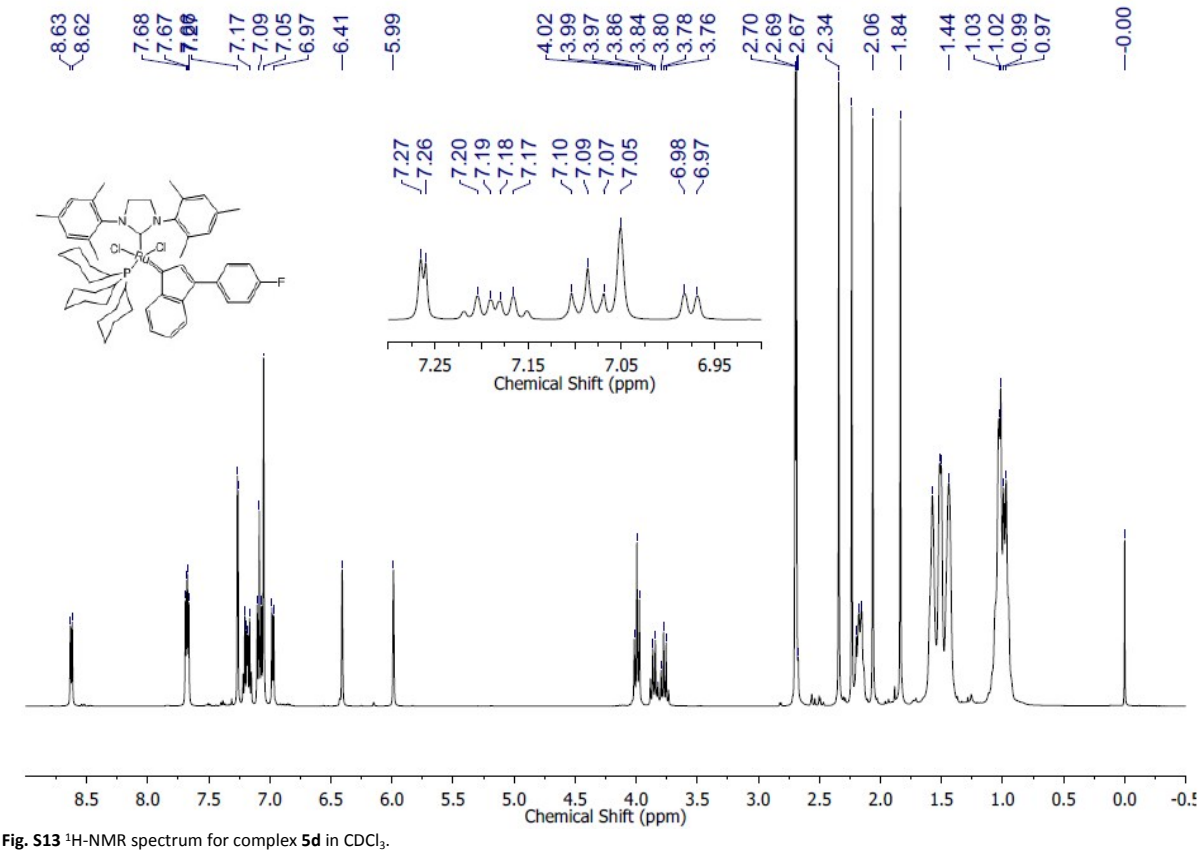


Fig. S13 ^{1}H-NMR spectrum for complex **5d** in $CDCl_3$.

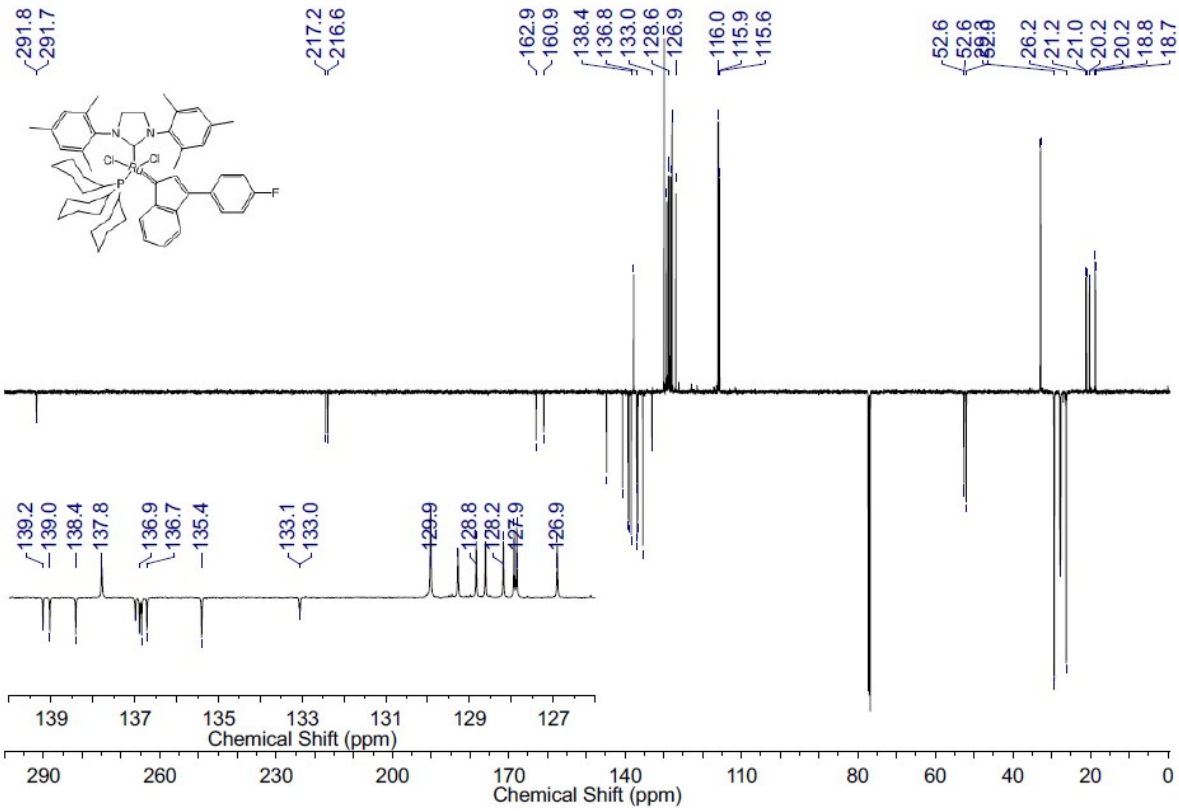


Fig. S14 ^{13}C-NMR spectrum for complex **5d** in $CDCl_3$.

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