IPr* vs IPr in ruthenium olefin metathesis

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Supporting Information

General informations:

All reagents were used as received. Dichloromethane and toluene were dispensed from a solvent purification system from Innovative Technology. Catalyst syntheses were performed in a MBraun glovebox containing dry Ar and less than 1 ppm oxygen. ^{1}H, ^{31}P, and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker Avance 300 or Bruker Avance II 400 Ultrashield NMR spectrometers. Elemental analyses were performed at the London Metropolitan University. Substrates **5**, **7**, **9**, **11**, **13**, **15**, **18**, **21** and products **6**, **8**, **10**, **12**, **14**, **16**, **19, 20**, **22** and **23** have previously been described in the literature.[1-3]

Synthesis of [$RuCl_2$(IPr*)(PPh_3)(3-phenylindenylidene)](1):

In the glovebox, $\mathbf{M_{10}}$ (1.00 g, 1.13 mmol) and IPr* (914 mg, 1.2 mmol)) were charged to a Schlenk flask and dissolved in toluene (3 mL). The reaction was taken out of the glovebox and stirred at 40 °C for 10 h under Ar. After this time, the mixture was allowed to cool to RT and the solvent was removed under vacuum. The remaining solid was recrystallised in a mixture of dichloromethane / pentane. The mixture was filtered, washed with cold methanol (2 x 5 mL) and cold hexane (8 x 25 mL), affording [$RuCl_2$(IPr*)(PPh_3)(3-phenylindenylidene)] (**1**) (750 mg, 0.49 mmol, 44%) as a microcrystalline solid. ^{1}H NMR (C_6D_6, 400MHz): δ = 8.13 (d, J=7.3 Hz, 1 H), 7.67 - 8.00 (m, 7 H), 7.57 (t, J=7.8 Hz, 5 H), 6.55 - 7.42 (m, 60 H), 6.24 (s, 1 H), 6.03 (s, 1 H), 5.90 (s, 1 H), 4.93 (s, 1 H), 4.51 (s, 1 H), 2.05 (s, 2 H), 1.77 (s, 3 H) ppm, ^{13}C NMR (CD_2Cl_2 ,75MHz): δ = 301.02, 185.1, 183.8, 146.9, 146.7, 145.7, 145.2, 144.1, 141.0, 138.2, 135,8, 135.0, 134.8, 132.1, 131.6, 130.0, 129.3, 129.0, 128.6, 128.3, 128.1, 128.1, 126.5, 123.6, 116.7, 50.8, 50.4, 22.5, 21.9, ppm, ^{31}P NMR (162MHz, C_6D_6) δ = 27.54 ppm Anal. Calcd for $C_{103}H_{85}Cl_2N_2PRu$ C, 79.62; H, 5.51; N 1.80; Found: C, 79.77; H, 5.25; N, 1.73.

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Synthesis of [$RuCl_2$(IPr*)(Py)(3-phenylindenylidene)](2):

In the glovebox, $\mathbf{M_{10}}$ (1.00 g, 1.13 mmol) and IPr* (914 mg, 1.2 mmol) were weighed to a Schlenk flask and dissolved in toluene (3 mL), taken out of the glovebox, connected to a Schlenk

line and stirred at 40 °C for 10 h under Ar. Pyridine (0.45 mL) was then added by syringe, the resulting solution was left stirring for 0.5 h, after which time pentane was added (35 mL) and the reaction left stirring for another 0.5 h. The resulting suspension was then cooled to -40°C, filtered and recrystalsed from dichloromethane/pentane. The mixture was filtered, washed with cold methanol (1 x 10 mL) and cold hexane (3 x 10 mL) affording compound [$RuCl_2$(IPr*)(Py)(3-phenylindenylidene)](**2**) (940 mg, 0.69 mmol, 73% yield).^{1}H NMR (CD_2Cl_2 ,400MHz): TM δ = 8.12 (d, J=7.2 Hz, 1 H), 7.85 (br. s., 2 H), 7.77 (d, J=5.1 Hz, 2 H), 6.42 - 7.57 (m, 60 H), 6.31 (br. s., 2 H), 6.09 - 6.19 (m, 1 H), 5.95 (s, 1 H), 5.72 - 5.86 (m, 1 H), 5.69 (s, 1 H), 4.97 - 5.01 (m, 1 H), 4.93 (d, J=1.9 Hz, 1 H), 4.08 (d, J=1.7 Hz, 1 H), 2.24 (s, 3 H), 2.10 - 2.18 (m, 1 H), 1.22 ppm (s, 3 H) ^{13}C NMR (CD_2Cl_2 ,75MHz): TM δ = 153.6, 146.3, 143.1, 142.7, 142.0, 140.7, 140.2, 140.0, 139.8, 137.3, 136.5, 135.6, 133.8, 131.7, 130.7, 130.0, 129.3, 128.6, 128.0, 126.8, 126.4, 126.2, 124.6, 124.5, 123.9, 118.1, 22.7, 22.0, 20.8 ppm Anal. Calcd for $C_{89}H_{71}Cl_2N_3Ru$ C, 78.86; H, 5.35; N 3.10; Found: C, 78.81; H, 5.16; N, 3.05.

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Synthesis of [$RuCl_2$(IPr)(PPh_3)(3-phenylindenylidene)](3):

In the glovebox, **M_{10}** (0.500 g, 0.56 mmol) and IPr (240 mg, 0.62 mmol) were charged to a Schlenk flask and dissolved in toluene (3 mL). The reaction was taken out of the glovebox, stirred at 40 °C for 4 h under Ar. After this time, the mixture was allowed to cool to RT and the solvent removed under vacuum. The remaining solid and recrystallised in a mixture of dichloromethane / pentane. The mixture was filtered, washed with cold methanol (2 x 5 mL) and cold hexane (8 x 25 mL), affording [$RuCl_2$(IPr)(PPh_3)(3-phenylindenylidene)] (**3**) (410 mg, 0.41 mmol, 81%) as a microcrystalline solid. Spectroscopic data for the product were in accordance with the literature.[4] Anal. Calcd for $C_{61}H_{65}Cl_2N_2PRu$ C, 71.19; H, 6.37; N, 2.72; Found: C, 71.52; H, 6.19; N, 2.62.

Synthesis of [$RuCl_2$(IPr)(Py)(3-phenylindenylidene)](4):

In the glovebox, **M_{10}** (1.00 g, 1.13 mmol) and IPr (480 mg, 1.2 mmol) were weighed to a Schlenk flask and dissolved in toluene (3 mL), taken out of the glovebox, connected to a Schlenk

line and stirred at 40 °C for 4 h under Ar. Pyridine (0.45 mL) was then added by syringe, the resulting solution was left stirring for 0.5 h, after which time pentane was added (35 mL) and the reaction left stirring for another 0.5 h. The resulting suspension was then cooled to -40°C. Filtration and recrystalysation in dichloromethane/pentane. The mixture was filtered, washed with cold methanol (1 x 10 mL) and cold hexane (3 x 10 mL) affording compound [$RuCl_2$(IPr*)(Py)(3-phenylindenylidene)](**2**) (630 mg, 0.76 mmol, 66% yield). ^{1}H NMR (400 MHz, C_6D_6) δ ~~ppm =~~ 0.66 - 0.94 (m, 4 H) 1.00 - 1.39 (m, 6 H) 1.52 - 1.91 (m, 5 H) 2.80 - 2.97 (m, 1 H) 3.12 - 3.23 (m, 1 H) 3.23 - 3.38 (m, 1 H) 4.63 - 4.81 (m, 1 H) 6.06 (t, *J*=6.9~~2~~ Hz, 1 H) 6.31 - 6.42 (m, 2 H) 6.60 (s, 1 H) 6.64 - 6.75 (m, 1 H) 6.87 - 6.95 (m, 2 H) 7.02 - 7.13 (m, 1 H) 7.32 - 7.45 (m, 2 H) 7.74 (d, *J*=7.5~~2~~ Hz, 1 H) 8.19 (d, *J*=5.1~~2~~ Hz, 1 H) 8.67 (d, *J*=7.2~~17~~ Hz, 1 H) ppm ^{13}C NMR (75 MHz, CD_2Cl_2) δ ~~ppm =~~ 24~~3~~.0~~95~~, 25.2~~02~~, 25.5~~4~~-26.1~~0~~, 26.5~~45~~-26.9~~1~~, 27.6~~2~~, 28.9~~4~~, 29.8~~78~~, 30.1~~06~~-30.7~~2~~, 124.1~~4~~, 127~~6~~.0~~96~~, 127.7~~67~~, 128.44, 129.19, 129.5~~2~~, 130.8~~1~~-131.~~5~~6, 132.4~~2~~, 132.5~~4~~, 132.6~~0~~-132.7~~3~~, 137.2~~4~~, 137.4~~0~~, 140.0~~4~~, 141.2~~0~~, 141.8~~78~~, 142.2~~1~~, 145.7~~1~~, 153.3~~25~~, 181.6~~56~~, 300.7~~65~~ ppm Anal. Calcd for $C_{48}H_{55}Cl_2N_3Ru$ C, 68.15; H, 6.55; N, 4.97; Found: C, 67.68; H, 6.72; N, 5.04.

General procedure for RCM and Enyne reactions:

In a Radley carousel under argon or nitrogen, a reaction tube was charged with the substrate (0.25 mmol) and the solvent (2.5 mL) (CH_2Cl_2 for reaction at RT and 40 °C, toluene for reactions at 80 °C), then precatalyst (0.0025 mmol). The progress of the reaction was monitored by ^{1}H NMR. Conversion determined by ^{1}H NMR spectroscopy by integrating the characteristic signals for allylic proton resonances.

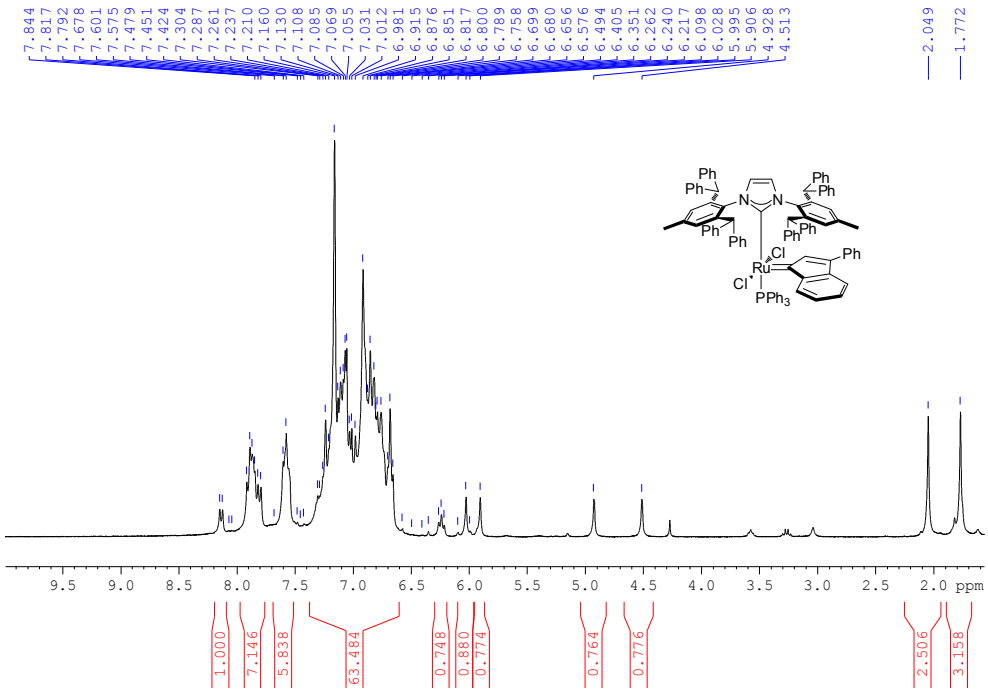
General procedure for CM reactions:

In a Radley carousel under argon or nitrogen, a reaction tube was charged with one equivalent of the electron rich substrates (0.25 mmol) and two equivalents of the electron poor olefin (0.5 mmol) solvent (2.5 mL), then precatalyst (0.0025 mmol). The progress of the reaction was monitored by ^{1}H NMR. At reaction completion solvent was removed under vacuum and the crude residue was

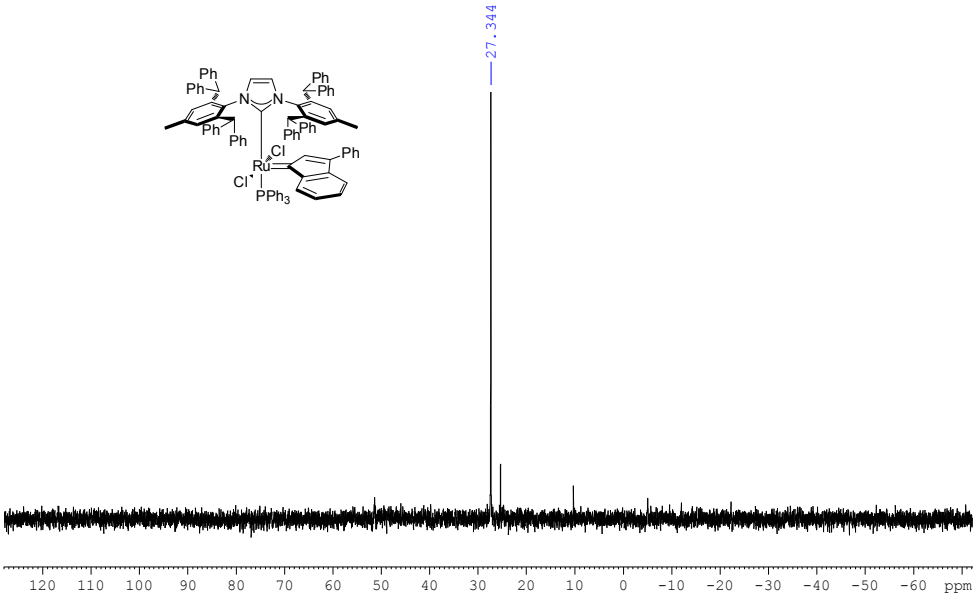
checked by ^{1}H NMR. Conversion determined by ^{1}H NMR spectroscopy by integrating the characteristic signals for allylic proton resonances.

NMR data of [$RuCl_2$(IPr*)(PPh_3)(3-phenylindenylidene)] (1):

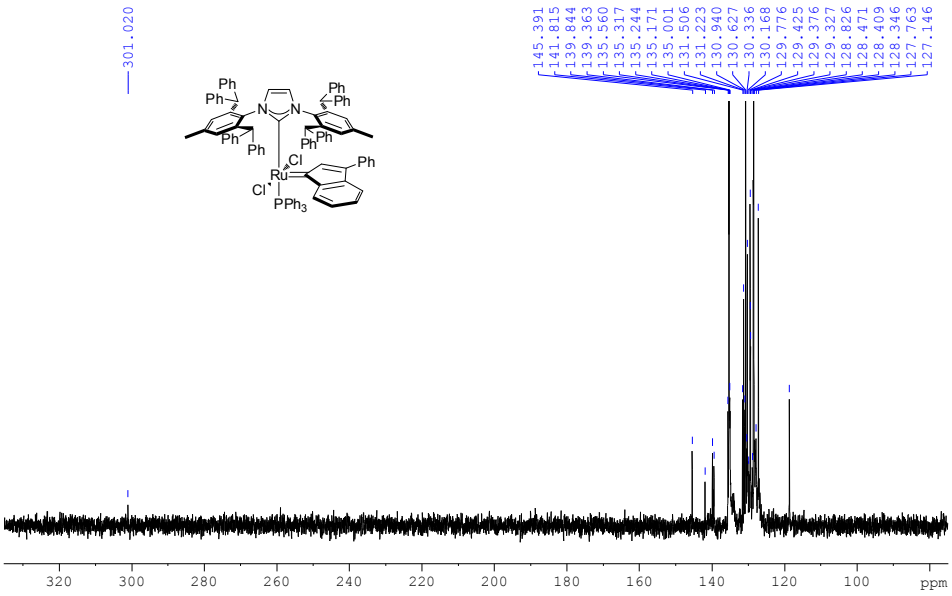
^{1}H NMR of complex **1** in C_6D_6:



^{31}P NMR of complex **1** in C_6D_6:

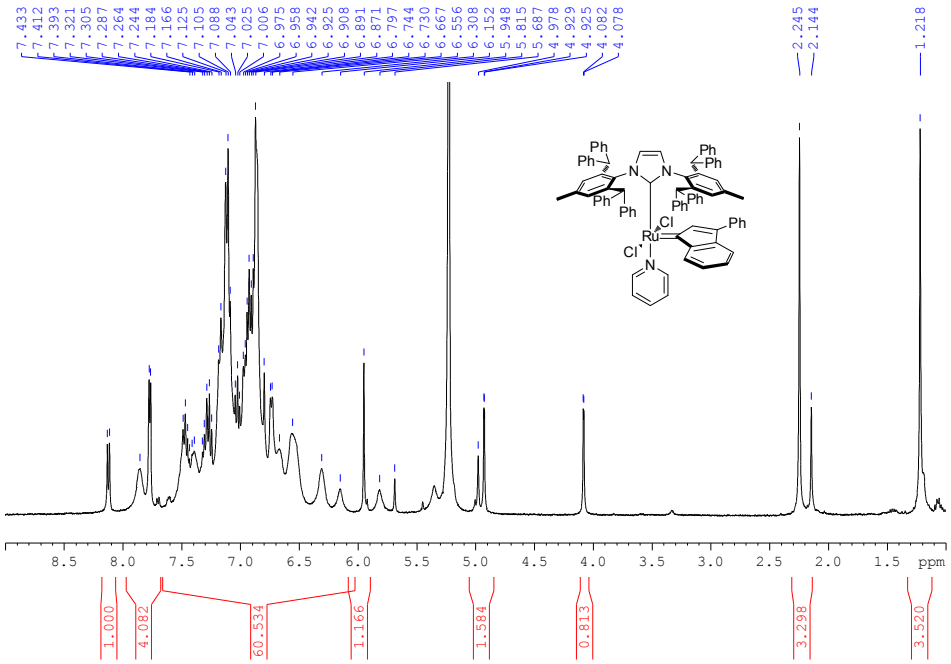


$^{13}C\{^{1}H\}zz$ NMR of complex **1** in CD_2Cl_2

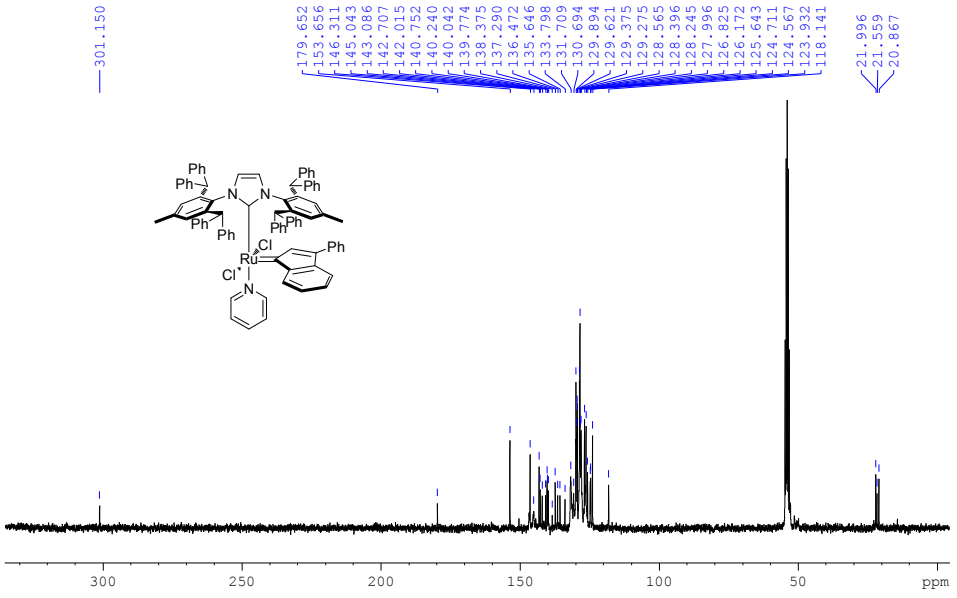


NMR data of [$RuCl_2$(IPr*)(Py)(3-phenylindenylidene)] (2):

^{1}H NMR of complex ~~1~~ 2 in CD_2Cl_2:

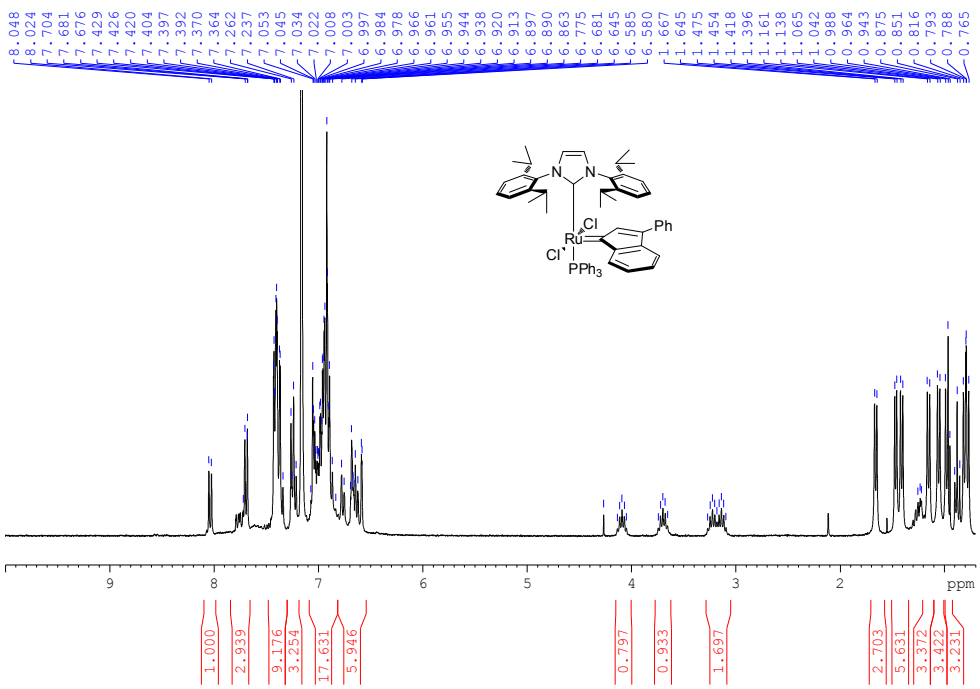


$^{13}C\{^{1}H\}$ NMR of complex ~~2~~ 1 in CD_2Cl_2:

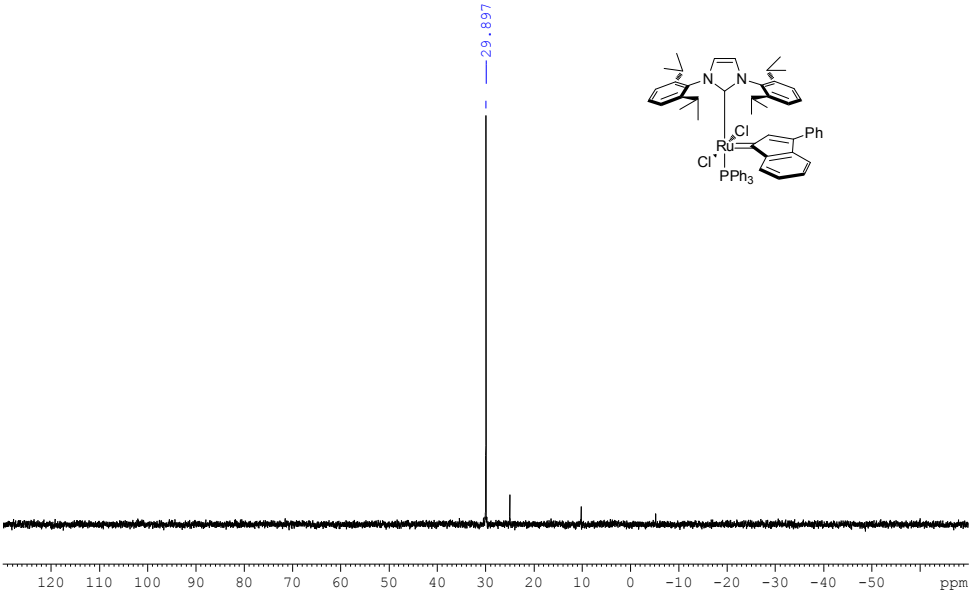


NMR data of [$RuCl_2$(IPr)(PPh_3)(3-phenylindenylidene)] (3):

^{1}H NMR of complex ~~1~~ 3 in C_6D_6:

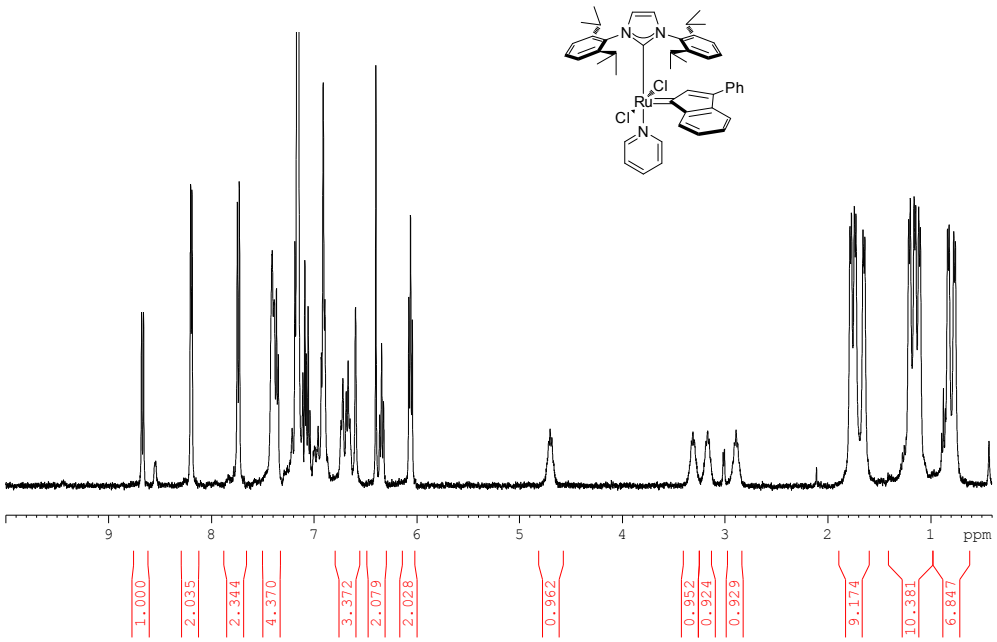


^{31}P NMR of complex ~~1~~ 3 in C_6D_6:

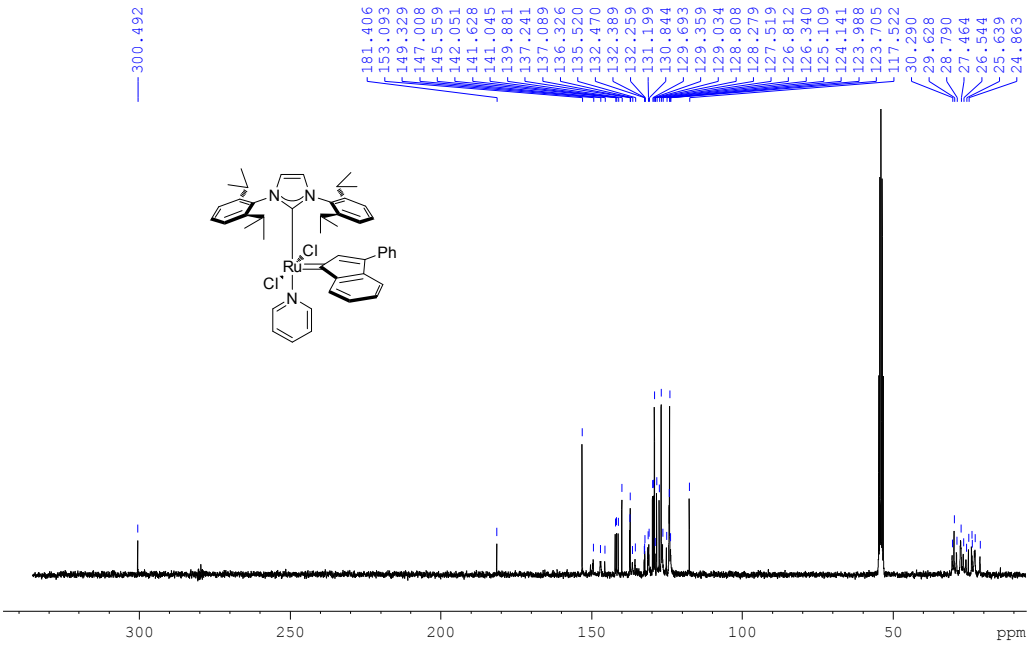


NMR data of [$RuCl_2$(IPr)(Py)(3-phenylindenylidene)] (4):

^{1}H NMR of complex ~~1~~ 4 in C_6D_6:



$^{13}C\{^{1}H\}$ NMR of complex ~~1~~ 4 in C_6D_6:



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