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New olefin metathesis catalysts with fluorinated unsymmetrical imidazole-based ligands

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Experimental Section

General remarks: All solvents were freshly distilled from appropriate drying agents before use. All other reagents were recrystallized or distilled as necessary. Syntheses of ruthenium complexes were performed under argon atmosphere using a standard Schlenk technique. Analytical TLC was performed with Merck silica gel 60 F254 plates. Visualization was accomplished by UV light (254 and 366 nm), spraying by $Ce(SO_4)_2$ solution in 5% H_2SO_4 or $KMnO_4$ solution in water. Column chromatography was carried out using Merck silica gel 60 (230−400 mesh ASTM) and ethyl acetate/petroleum ether as eluent. NMR spectra were recorded at room temperature unless otherwise stated on Bruker AV-300, AV-400, AV-600 spectrometers operating at 300, 400, and 500 MHz for ^{1}H; 75, 101, and 126 MHz for ^{13}C; 282, 376, and 471 MHz for ^{19}F ($CFCl_3$ as reference), and 162 MHz for ^{31}P (85% H_3PO_4 as reference), respectively. The chemical shifts are frequency referenced relative to the residual undeuterated solvent peaks. 1-(2-(1,1,1,3,3,3-hexafluoro-2-hydroxypropan-2-yl)-4,6-dimethylphenyl)-3-mesityl-1*H*-imidazol-3-ium tetrafluoroborate (**1**)[1], diethyl diallylmalonate[2], diethyl 2-allyl-2-methallylmalonate[3] were synthesized according to literature procedures. All crystals suitable for X-ray were grown by slow diffusion of hexane vapors in $CHCl_3$ solution.

Dichloro(1,3-dimesityl-1*H*-imidazol-2-ylidene)(2-isopropoxybenzylidene)ruthenium(II) (uHG-II). In a flame-dried Schlenk flask, **uG-II** (85 mg, 0.1 mmol) was dissolved in anhydrous CH_2Cl_2 under argon atmosphere, then 2-isopropoxystyrene (16 mg, 0.1 mmol) and CuCl (24 mg, 0.25 mmol) were added. The reaction mixture was stirred for 1.5 h at 40°C. Once it was

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complete (TLC-control), the solvents were removed under reduced pressure, and the resulting residue was purified by column chromatography using petroleum ether/ethyl acetate 8:1 as eluent under argon atmosphere. The resulting solid was recrystallized from MeOH to yield 38 mg of complex **uHG-II** as dark-green solid. Yield: 60%. ^{1}H NMR (400 MHz, C_6D_6): δ = 16.83 (s, 1H, C*H*Ar), 7.20 (dd, $J_{H,H}$ = 7.5, 1.6 Hz, 1H, H_{Ar}), 7.14-7.09 (m, 1H, H_{Ar}), 6.90 (s, 4H, H_{Ar}), 6.69 (t, $J_{H,H}$ = 7.4 Hz, 1H, H_{Ar}), 6.34 (d, $J_{H,H}$ = 8.3 Hz, 1H, H_{Ar}), 6.26 (s, 2H, H_{Im}), 4.48 [hept, $^{3}J_{H,H}$ = 5.6 Hz, 1H, OC*H*(CH_3)$_2$], 2.40 (s, 12H, CH_3), 2.25 (s, 6H, CH_3), 1.38 ppm [d, $^{3}J_{H,H}$ = 6.1 Hz, 6H CH(CH_3)$_2$]; ^{13}C NMR (101 MHz, C_6D_6): δ = 288.2 (Ru=*C*H), 177.6 (N*C*N), 152.8 (C_{Ar}), 146.1 (C_{Ar}), 139.3 (C_{Ar}), 138.5 (C_{Ar}), 136.7 (C_{Ar}), 129.4 (C_{Ar}), 124.6 (C_{Ar}), 122.3 (C_{Ar}), 121.9 (C_{Ar}), 113.3 (C_{Ar}), 75.3 [O*C*H(CH_3)$_2$], 21.5 (*C*H$_3$), 21.2 (*C*H$_3$), 19.5 ppm (*C*H$_3$). Elemental analysis calcd for $C_{31}H_{36}Cl_2N_2ORu$ (%): C, 59.61; H, 5.81; N, 4.48; found C, 59.81; H, 6.19; N, 4.33.

General procedure for synthesis of Grubbs-type complexes 5. In a flame-dried Schlenk flask, imidazolium tetrafluoroborate **2** (0.32 mmol) was mixed with anhydrous toluene (15 mL). The resulting mixture was cooled to 0°C and deaerated three times, and then KHMDS (0.34 mL of 1 *M* solution in THF, 0.34 mmol) was added under argon. The mixture was stirred for 1 min at r.t.; then Grubbs' catalyst 1-st generation **G-I** (0.2 g, 0.24 mmol) was added, and the mixture was stirred for 1 h. During this time, the colour changed from violet to red-brown. Once complete (TLC-control), the solvents were removed under reduced pressure, and the resulting substance was purified by column chromatography using petroleum ether/ethyl acetate 20:1 as eluent under an argon atmosphere. The resulting solid was recrystallized from MeOH to yield complex **3** as a brown solid.

Benzylidene(dichloro){3-[2-(1,1,1,3,3,3-hexafluoro-2-methoxypropan-2-yl)-4,6-dimethyl-phenyl]-1-mesityl-1*H*-imidazol-2-ylidene}(tricyclohexylphosphine)ruthenium(II) (5a). Yield: 53%. ^{1}H NMR (500 MHz, C_6D_6): δ = 20.46 (s, 1H, C*H*Ph), 9.29 (s, 1H, H_{Ar}), 7.33 (s, 2H, H_{Ar}), 7.14 (t, $J_{H,H}$ = 7.0 Hz, 1H, H_{Ar}), 7.08-6.79 (m, 3H, H_{Ar}), 6.64 (s, 1H, H_{Ar}), 6.25 (s, 1H, H_{Ar}), 5.94 (s, 1H, H_{Ar}), 3.72 (s, 3H, OCH_3), 2.84 (s, 3H, CH_3), 2.59-2.50 (m, 3H, PCy$_3$), 2.45 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 1.75-0.94 ppm (m, 33H, PCy$_3$); ^{13}C NMR (126 MHz, C_6D_6): δ = 298.4 (Ru=*C*Ph), 190.4 (d, *J* = 85 Hz, N*C*N), 152.8 (C_{Ph}), 141.7 (C_{Ar}), 139.9 (C_{Ar}), 139.1 (C_{Ar}), 138.1 (C_{Ar}), 137.4 (C_{Ar}), 137.3 (C_{Ar}), 136.3 (C_{Ar}), 133.9 (C_{Ar}), 131.9 (C_{Ar}), 130.0 (C_{Ar}), 128.4 (C_{Ar}), 127.7 (C_{Ar}), 127.4 (C_{Ar}), 126.6 (C_{Ar}), 125.5 (C_{Ar}), 124.5 (q, $^{1}J_{C,F}$ = 295 Hz, *C*F$_3$), 123.1 (C_{Ar}), 123.6 (q, $^{1}J_{C,F}$ = 293 Hz, *C*F$_3$), 84.7-83.4 [m, *C*(CF_3)$_2$], 56.5 (O*C*H$_3$), 32.0 (d, $^{1}J_{C,P}$ = 17 Hz, PCy$_3$), 30.0 (PCy$_3$), 29.6 (PCy$_3$), 28.2 (dd, *J* = 9.8, 5.5 Hz, PCy$_3$), 26.7 (PCy$_3$), 21.2 (*C*H$_3$), 21.1 (*C*H$_3$), 20.5 (*C*H$_3$), 20.2 (*C*H$_3$), 20.0 ppm (*C*H$_3$); ^{19}F NMR (376 MHz, C_6D_6) δ -

65.13 (C*F*$_3$), -68.19 ppm (C*F*$_3$); ^{31}P NMR (162 MHz, C_6D_6): δ = 29.19 ppm. Elemental analysis calcd for $C_{49}H_{63}Cl_2F_6N_2OPRu$ (%): C, 58.10; H, 6.27; N, 2.77; found C, 58.21; H, 6.17; N, 2.65.

Benzylidene(dichloro){3-[2-[2-ethoxy-1,1,1,3,3,3-hexafluoropropan-2-yl)-4,6-dimethyl-phenyl]-1-mesityl-1*H*-imidazol-2-ylidene}(tricyclohexylphosphine)ruthenium(II) (5b). Yield: 52%. ^{1}H NMR (500 MHz, C_6D_6): δ = 20.39 (s, 1H, C*H*Ph), 9.10 (s, 1H, *H*$_{\mathrm{Ar}}$), 7.50 (s, 1H, *H*$_{\mathrm{Ar}}$), 7.38 (s, 1H, *H*$_{\mathrm{Ar}}$), 7.13 (t, $J_{\mathrm{H,H}}$ = 7.2 Hz, 1H, *H*$_{\mathrm{Ar}}$), 7.02 (s, 1H, *H*$_{\mathrm{Ar}}$), 6.93 (s, 1H, *H*$_{\mathrm{Ar}}$), 6.87 (s, 2H, *H*$_{\mathrm{Ar}}$), 6.73-6.72 (m, 1H, *H*$_{\mathrm{Ar}}$), 6.22-6.22 (m, 1H, *H*$_{\mathrm{Ar}}$), 6.03 (s, 1H, *H*$_{\mathrm{Ar}}$), 4.48-4.40 (m, 1H, OC*H*$_2$), 4.08-3.99 (m, 1H, OC*H*$_2$), 2.82 (s, 3H, C*H*$_3$), 2.57-2.48 (m, 3H, PCy$_3$), 2.45 (s, 3H, C*H*$_3$), 2.20 (s, 3H, C*H*$_3$), 2.06 (s, 3H, C*H*$_3$), 1.72 (s, 3H, C*H*$_3$), 1.70-0.96 ppm (m, 33H, PCy$_3$, CH$_2$C*H*$_3$); ^{13}C NMR (126 MHz, C_6D_6): δ = 298.2 (Ru=*C*Ph), 191.5 (d, *J* = 85 Hz, N*C*N), 152.9 (*C*$_{\mathrm{Ar}}$), 141.9 (*C*$_{\mathrm{Ar}}$), 139.7 (*C*$_{\mathrm{Ar}}$), 138.9 (*C*$_{\mathrm{Ar}}$), 138.0 (*C*$_{\mathrm{Ar}}$), 137.4 (*C*$_{\mathrm{Ar}}$), 137.1 (*C*$_{\mathrm{Ar}}$), 136.4 (*C*$_{\mathrm{Ar}}$), 134.1 (*C*$_{\mathrm{Ar}}$), 131.7 (*C*$_{\mathrm{Ar}}$), 130.1 (*C*$_{\mathrm{Ar}}$), 130.1 (*C*$_{\mathrm{Ar}}$), 128.4 (*C*$_{\mathrm{Ar}}$), 127.8 (*C*$_{\mathrm{Ar}}$), 126.6 (*C*$_{\mathrm{Ar}}$), 126.5 (*C*$_{\mathrm{Ar}}$), 123.9 (q, $^1J_{\mathrm{C,F}}$ = 295 Hz, *C*F$_3$), 123.3 (*C*$_{\mathrm{Ar}}$), 85.1-83.9 [m, *C*(CF$_3$)$_2$], 65.3 (O*C*H$_2$), 32.0 (d, $^1J_{\mathrm{C,P}}$ = 17 Hz, PCy$_3$), 29.9 (PCy$_3$), 29.6 (PCy$_3$), 28.2 (dd, $J_{\mathrm{C,P}}$ = 9.8, 5.5 Hz, PCy$_3$), 26.7 (PCy$_3$), 21.2 (*C*H$_3$), 21.1 (*C*H$_3$), 20.7 (*C*H$_3$), 20.5 (*C*H$_3$), 20.3 (*C*H$_3$), 15.9 ppm (CH$_2$*C*H$_3$); ^{19}F NMR (376 MHz, C_6D_6): δ = -64.18 (C*F*$_3$), -69.11 ppm (C*F*$_3$); ^{31}P NMR (162 MHz, C_6D_6): δ = 28.94 ppm. Elemental analysis calcd for $C_{50}H_{65}Cl_2F_6N_2OPRu$ (%): C, 58.47; H, 6.38; N, 2.73; found C, 58.64; H, 6.41; N, 2.46.

Benzylidene(dichloro)(3-{2-[1,1,1,3,3,3-hexafluoro-2-(3-methylbutyloxy)propan-2-yl]-4,6-dimethylphenyl}-1-mesityl-1*H*-imidazol-2-ylidene)(tricyclohexylphosphine)ruthenium(II) (5c). Yield: 46%. ^{1}H NMR (500 MHz, C_6D_6): δ = 20.43 (s, 1H, C*H*Ph), 9.13 (s, 1H, *H*$_{\mathrm{Ar}}$), 7.48 (s, 1H, *H*$_{\mathrm{Ar}}$), 7.44 (s, 1H, *H*$_{\mathrm{Ar}}$), 7.13 (t, $J_{\mathrm{H,H}}$ = 7.2 Hz, 1H, *H*$_{\mathrm{Ar}}$), 7.02 (s, 1H, *H*$_{\mathrm{Ar}}$), 6.94 (s, 1H, *H*$_{\mathrm{Ar}}$), 6.88 (s, 2H, *H*$_{\mathrm{Ar}}$), 6.74 (s, 1H, *H*$_{\mathrm{Ar}}$), 6.22 (s, 1H, *H*$_{\mathrm{Ar}}$), 6.05 (s, 1H, *H*$_{\mathrm{Ar}}$), 4.57-4.44 (m, 1H, OC*H*$_2$), 4.21-4.09 (m, 1H, OC*H*$_2$), 2.84 (s, 3H, C*H*$_3$), 2.57-2.49 (q, *J* = 11.4 Hz, 3H, PCy$_3$), 2.46 (s, 3H, CH$_3$), 2.21 (s, 3H, CH$_3$), 2.07 (s, 3H, CH$_3$), 1.73 (s, 3H, CH$_3$), 1.71-0.95 [m, 33H, PCy3, C*H*$_2$C*H*(CH$_3$)$_2$], 0.91 [d, $^3J_{\mathrm{H,H}}$ = 5.8 Hz, 3H, CH(C*H*$_3$)$_2$], 0.87 ppm [d, $^3J_{\mathrm{H,H}}$ = 5.9 Hz, 3H, CH(C*H*$_3$)$_2$]; ^{13}C NMR (126 MHz, C_6D_6): δ = 298.2 (Ru=*C*Ph), 191.8 (d, *J* = 85 Hz, N*C*N), 152.9 (*C*$_{\mathrm{Ar}}$), 142.0 (*C*$_{\mathrm{Ar}}$), 139.6 (*C*$_{\mathrm{Ar}}$), 138.9 (*C*$_{\mathrm{Ar}}$), 138.0 (*C*$_{\mathrm{Ar}}$), 137.4 (*C*$_{\mathrm{Ar}}$), 137.2 (*C*$_{\mathrm{Ar}}$), 136.4 (*C*$_{\mathrm{Ar}}$), 134.2 (*C*$_{\mathrm{Ar}}$), 131.7 (*C*$_{\mathrm{Ar}}$), 130.1 (*C*$_{\mathrm{Ar}}$), 130.0 (*C*$_{\mathrm{Ar}}$), 128.4 (*C*$_{\mathrm{Ar}}$), 127.8 (*C*$_{\mathrm{Ar}}$), 126.6 (*C*$_{\mathrm{Ar}}$), 124.0 (q, $^1J_{\mathrm{C,F}}$ = 293 Hz, *C*F$_3$), 123.8 (q, $^1J_{\mathrm{C,F}}$ = 294 Hz, *C*F$_3$), 123.2 (*C*$_{\mathrm{Ar}}$), 85.2-83.8 [m, *C*(CF$_3$)$_2$], 68.4 (O*C*H$_2$), 38.64 (CH$_2$*C*H$_2$CH), 32.0 (d, $^1J_{\mathrm{C,P}}$ = 17 Hz, PCy$_3$), 29.9 (PCy$_3$), 29.6 (PCy$_3$), 28.4-28.1 (m, PCy$_3$), 26.68 (PCy$_3$), 25.3 [CH$_2$*C*H(CH$_3$)$_2$], 22.9 (*C*H$_3$), 22.8 (*C*H$_3$), 21.2 (*C*H$_3$), 21.1 (*C*H$_3$), 21.0 (*C*H$_3$), 20.5 (*C*H$_3$), 20.3 ppm (*C*H$_3$); ^{19}F NMR (376 MHz, C_6D_6): δ = -64.80 (C*F*$_3$), -68.28

ppm (CF_3); ^{31}P NMR (162 MHz, C_6D_6) : δ = 28.85 ppm. Elemental analysis calcd for $C_{53}H_{71}Cl_2F_6N_2OPRu$ (%): C, 59.54; H, 6.69; N, 2.62; found C, 59.77; H, 6.63; N, 2.54.

General procedure for synthesis of Hoveyda–Grubbs-type complexes 6. In a flame-dried Schlenk flask, imidazolium tetrafluoroborate **2** (0.43 mmol) was mixed with anhydrous toluene (15 mL). The resulting mixture was cooled to 0°C and deaerated three times, and then KHMDS (0.47 mL of 1 *M* solution in THF, 0.47 mmol) was added under argon. The mixture was stirred for 1 min at r.t.; then Hoveyda–Grubbs' catalyst 1-st generation **HG-I** (0.2 g, 0.33 mmol) was added, and the mixture was stirred for 1 h. During this time, the colour changed from brown to dark-green. Once complete (TLC-control), the solvents were removed under reduced pressure, and the resulting substance was purified by column chromatography using petroleum ether/ethyl acetate 5:1 as eluent under an argon atmosphere.

Dichloro{3-[2-(1,1,1,3,3,3-hexafluoro-2-methoxypropan-2-yl)-4,6-dimethylphenyl]-1-mesityl-1*H*-imidazol-2-ylidene}(2-isopropoxybenzylidene)ruthenium(II) (6a). Yield: 57%. ^1H NMR (500 MHz, C_6D_6): δ = 16.98 (s, 1H, $CHAr$), 7.73 (s, 1H, H_{Ar}), 7.20 (dd, $J_{H,H}$ = 7.6, 1.5 Hz, 1H, H_{Ar}), 7.10 (ddd, $J_{H,H}$ = 8.3, 7.5, 1.6 Hz, 1H, H_{Ar}), 7.00 (s, 2H, H_{Ar}), 6.70 (td, $J_{H,H}$ = 8.1, 7.5, 0.6 Hz, 1H, H_{Ar}), 6.69-6.66 (m, 2H, H_{Ar}), 6.36-6.33 (m, 2H, H_{Ar}), 4.48 [hept, $^3J_{H,H}$ = 6.2 Hz, 1H, $OCH(CH_3)_2$], 3.53 (s, 3H, OCH_3), 2.58 (s, 3H, CH_3), 2.55 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 1.41 [d, $^1J_{H,H}$ = 6.1 Hz, 3H, $CH(CH_3)_2$], 1.35 ppm [d, $^1J_{H,H}$ = 6.1 Hz, 3H, $CH(CH_3)_2$]; ^{13}C NMR (126 MHz, C_6D_6): δ = 286.1 (d, *J* = 21 Hz, Ru=*C*H), 179.45 (N*C*N), 153.2 (C_{Ar}), 145.6 (C_{Ar}), 142.7 (C_{Ar}), 139.5 (C_{Ar}), 139.3 (C_{Ar}), 139.3 (C_{Ar}), 139.1 (C_{Ar}), 138.4 (C_{Ar}), 135.5 (C_{Ar}), 135.1 (C_{Ar}), 129.6 (C_{Ar}), 129.5 (C_{Ar}), 128.6 (C_{Ar}), 126.7 (C_{Ar}), 123.9 (q, $^1J_{C,F}$ = 294 Hz, CF_3), 123.4 (q, $^1J_{C,F}$ = 291 Hz, CF_3), 123.2 (C_{Ar}), 122.3 (C_{Ar}), 121.8 (C_{Ar}), 113.5 (C_{Ar}), 84.4 [hept, $^2J_{C,F}$ = 28 Hz, $C(CF_3)_2$], 75.4 [$OCH(CH_3)_2$], 57.0 (OCH_3), 21.5 (CH_3), 21.4 (CH_3), 21.1 (CH_3), 21.00 (CH_3), 20.95 (CH_3), 20.7 (CH_3), 20.0 ppm (CH_3); ^{19}F NMR (471 MHz, C_6D_6): δ = -66.83 (CF_3), -69.44 ppm (CF_3). Elemental analysis calcd for $C_{34}H_{36}Cl_2F_6N_2O_2Ru$ (%): C, 51.65; H, 4.59; N, 3.54; found C, 51.61; H, 4.85; N, 3.78. CCDC 1847041 contains the supplementary crystallographic data for this complex. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

Dichloro{3-[2-(2-ethoxy-1,1,1,3,3,3-hexafluoropropan-2-yl)-4,6-dimethylphenyl]-1-mesityl-1*H*-imidazol-2-ylidene}(2-isopropoxybenzylidene)ruthenium(II) (6b). Yield: 51%. ^1H NMR (500 MHz, C_6D_6): δ = 16.91 (s, 1H, $CHAr$), 7.85 (s, 1H, H_{Ar}), 7.12 (ddd, $J_{H,H}$ = 14.9, 8.4, 1.5 Hz, 2H, H_{Ar}), 7.01 (s, 2H, H_{Ar}), 6.74-6.68 (m, 3H, H_{Ar}), 6.37 (d, $J_{H,H}$ = 8.3 Hz, 1H, H_{Ar}), 6.32 (d, $J_{H,H}$ = 2.0 Hz, 1H, H_{Ar}), 4.49 [hept, $^3J_{H,H}$ = 6.0 Hz, 1H, $OCH(CH_3)_2$], 3.84-3.69 (m, 2H, OCH_2), 2.60

(s, 3H, C*H*$_3$), 2.59 (s, 3H, C*H*$_3$), 2.27 (s, 3H, C*H*$_3$), 2.19 (s, 3H, C*H*$_3$), 2.08 (s, 3H, C*H*$_3$), 1.44 [d, $^3J_{H,H}$ = 6.1 Hz, 3H, CH(C*H*$_3$)$_2$], 1.37 [d, $^3J_{H,H}$ = 6.1 Hz, 3H, CH(C*H*$_3$)$_2$], 0.99 ppm (t, $^3J_{H,H}$ = 7.0 Hz, 3H, CH$_2$C*H*$_3$); ^{13}C NMR (126 MHz, C$_6$D$_6$): δ = 283.9 (d, *J* = 19 Hz, Ru=*C*H), 180.1 (N*C*N), 153.3 (*C*$_{Ar}$), 145.5 (*C*$_{Ar}$), 143.0 (*C*$_{Ar}$), 139.8 (*C*$_{Ar}$), 139.4 (*C*$_{Ar}$), 139.4 (*C*$_{Ar}$), 138.8 (*C*$_{Ar}$), 138.2 (*C*$_{Ar}$), 135.4 (*C*$_{Ar}$), 129.6 (*C*$_{Ar}$), 129.4 (*C*$_{Ar}$), 129.1 (*C*$_{Ar}$), 128.6 (*C*$_{Ar}$) 123.4 (*C*$_{Ar}$), 123.3 (q, $^1J_{C,F}$ = 292 Hz, *C*F$_3$), 123.1 (q, $^1J_{C,F}$ = 290 Hz, *C*F$_3$), 122.3 (*C*$_{Ar}$), 121.5 (*C*$_{Ar}$), 113.7 (*C*$_{Ar}$), 84.46 [hept, $^2J_{C,F}$ = 29 Hz, *C*(CF$_3$)$_2$], 75.5 [O*C*H(CH$_3$)$_2$], 64.3 (O*C*H$_3$), 21.5 (*C*H$_3$), 21.5 (*C*H$_3$), 21.1 (*C*H$_3$), 21.0 (*C*H$_3$), 20.8 (*C*H$_3$), 20.7 (*C*H$_3$), 20.2 (*C*H$_3$), 15.4 ppm (CH$_2$*C*H$_3$); ^{19}F NMR (376 MHz, C$_6$D$_6$) δ -66.2 (C*F*$_3$), -70.0 ppm (C*F*$_3$). Elemental analysis calcd for $C_{35}H_{38}Cl_2F_6N_2O_2Ru$ (%): C, 52.24; H, 4.76; N, 3.48; found C, 52.20; H, 4.95; N, 3.31. CCDC 1847042 contains the supplementary crystallographic data for this complex. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

Dichloro(3-{2-[1,1,1,3,3,3-hexafluoro-2-(3-methylbutyloxy)propan-2-yl]-4,6-dimethylphenyl}-1-mesityl-1*H*-imidazol-2-ylidene)(2-isopropoxybenzylidene)ruthenium(II) (6c). Yield: 50%. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 16.92 (s, 1H, C*H*Ar), 7.92 (s, 1H, *H*$_{Ar}$), 7.15-7.09 (m, 2H, *H*$_{Ar}$), 7.01 (s, 2H, *H*$_{Ar}$), 6.78-6.68 (m, 3H, *H*$_{Ar}$), 6.35 (d, $J_{H,H}$ = 8.3 Hz, 1H, *H*$_{Ar}$), 6.30 (d, $J_{H,H}$ = 2.0 Hz, 1H, *H*$_{Ar}$), 4.48 [hept, $^3J_{H,H}$ = 6.4 Hz, 1H, OC*H*(CH$_3$)$_2$], 3.94-3.71 (m, 1H, OC*H*$_2$), 2.62 (s, 3H, C*H*$_3$), 2.60 (s, 3H, C*H*$_3$), 2.27 (s, 3H, C*H*$_3$), 2.19 (s, 3H, C*H*$_3$), 2.12 (s, 3H, C*H*$_3$), 1.59 [hept, $^3J_{H,H}$ = 6.4 Hz, 1H, CH$_2$C*H*(CH$_3$)$_2$], 1.45 [d, $^3J_{H,H}$ = 6.1 Hz, 3H, OCH(C*H*$_3$)$_2$], 1.41 (q, $J_{H,H}$ = 6.8 Hz, 2H, CH$_2$C*H*$_2$CH), 1.35 [d, $^3J_{H,H}$ = 6.1 Hz, 3H, OCH(C*H*$_3$)$_2$], 0.80 [d, $^3J_{H,H}$ = 6.6 Hz, 3H, CH$_2$CH(C*H*$_3$)$_2$], 0.74 ppm [d, $^3J_{H,H}$ = 6.6 Hz, 3H, CH$_2$CH(C*H*$_3$)$_2$]; ^{13}C NMR (101 MHz, CDCl$_3$) δ 283.3 (Ru=*C*H), 180.4 (N*C*N), 153.3 (*C*$_{Ar}$), 145.5 (*C*$_{Ar}$), 143.2 (*C*$_{Ar}$), 140.1 (*C*$_{Ar}$), 139.5 (*C*$_{Ar}$), 139.4 (*C*$_{Ar}$), 138.6 (*C*$_{Ar}$), 138.2 (*C*$_{Ar}$), 135.6 (*C*$_{Ar}$), 135.3 (*C*$_{Ar}$), 129.6 (*C*$_{Ar}$), 129.5 (*C*$_{Ar}$), 129.3 (*C*$_{Ar}$), 128.6 (*C*$_{Ar}$), 123.4 (*C*$_{Ar}$), 123.1 (d, $^1J_{C,F}$ = 293 Hz, *C*F$_3$), 122.9 (d, $^1J_{C,F}$ = 288 Hz, *C*F$_3$), 122.1 (*C*$_{Ar}$), 121.6 (*C*$_{Ar}$), 113.7 (*C*$_{Ar}$), 84.2 [hept, $^2J_{C,F}$ = 30 Hz, *C*(CF$_3$)$_2$], 75.5 [O*C*H(CH$_3$)$_2$], 68.0 (O*C*H$_2$), 38.8 [CH$_2$*C*H(CH$_3$)$_2$], 24.8 (CH$_2$*C*H$_2$CH), 22.8 (*C*H$_3$), 22.6 (*C*H$_3$), 21.5 (*C*H$_3$), 21.5 (*C*H$_3$), 21.1 (*C*H$_3$), 21.0 (*C*H$_3$), 20.9 (*C*H$_3$), 20.7 (*C*H$_3$), 20.2 ppm (*C*H$_3$); ^{19}F NMR (376 MHz, C$_6$D$_6$): δ = -64.32 (C*F*$_3$), -71.75 ppm (C*F*$_3$). Elemental analysis calcd for $C_{38}H_{44}Cl_2F_6N_2O_2Ru$ (%): C, 53.90; H, 5.24; N, 3.31; found C, 54.07; H, 5.44; N, 3.13.

Ring-closing metathesis of diethyl diallylmalonate (DEDAM).

A solution of DEDAM in CD$_2$Cl$_2$ (0.11 *M*, 0.5 mL, 0.055 mmol) was added into an NMR tube under argon atmosphere. Once spectrum of pure DEDAM was recorded, a solution of catalyst in CD$_2$Cl$_2$ (0.011 *M*, 0.05 mL, 0.55 μmol, 1 mol. %) was syringed, and data points were collected by recording NMR spectra of the sample at 30°C on Bruker AC-200. The conversion of

DEDAM was determined by comparing the integral ratio of the methylene protons in the starting material (*δ* = 2.61 ppm) with those in the product (*δ* = 2.98 ppm).

Ring-closing metathesis of diethyl allylmethallylmalonate (DEAMM).

A solution of DEAMM in CD_2Cl_2 (0.11 *M*, 0.5 mL, 0.055 mmol) was added into an NMR tube under argon atmosphere. Once spectrum of pure DEAMM was recorded, a solution of catalyst in CD_2Cl_2 (0.011 *M*, 0.05 mL, 0.55 µmol, 1 mol. %) was syringed, and data points were collected by recording NMR spectra of the sample at 30°C on Bruker AC-200. The conversion of DEAMM was determined by comparing the ration of integrals of the methylene protons in starting material (*δ* = 2.67, 2.64 ppm) with those in the product (*δ* = 2.93, 2.88 ppm).

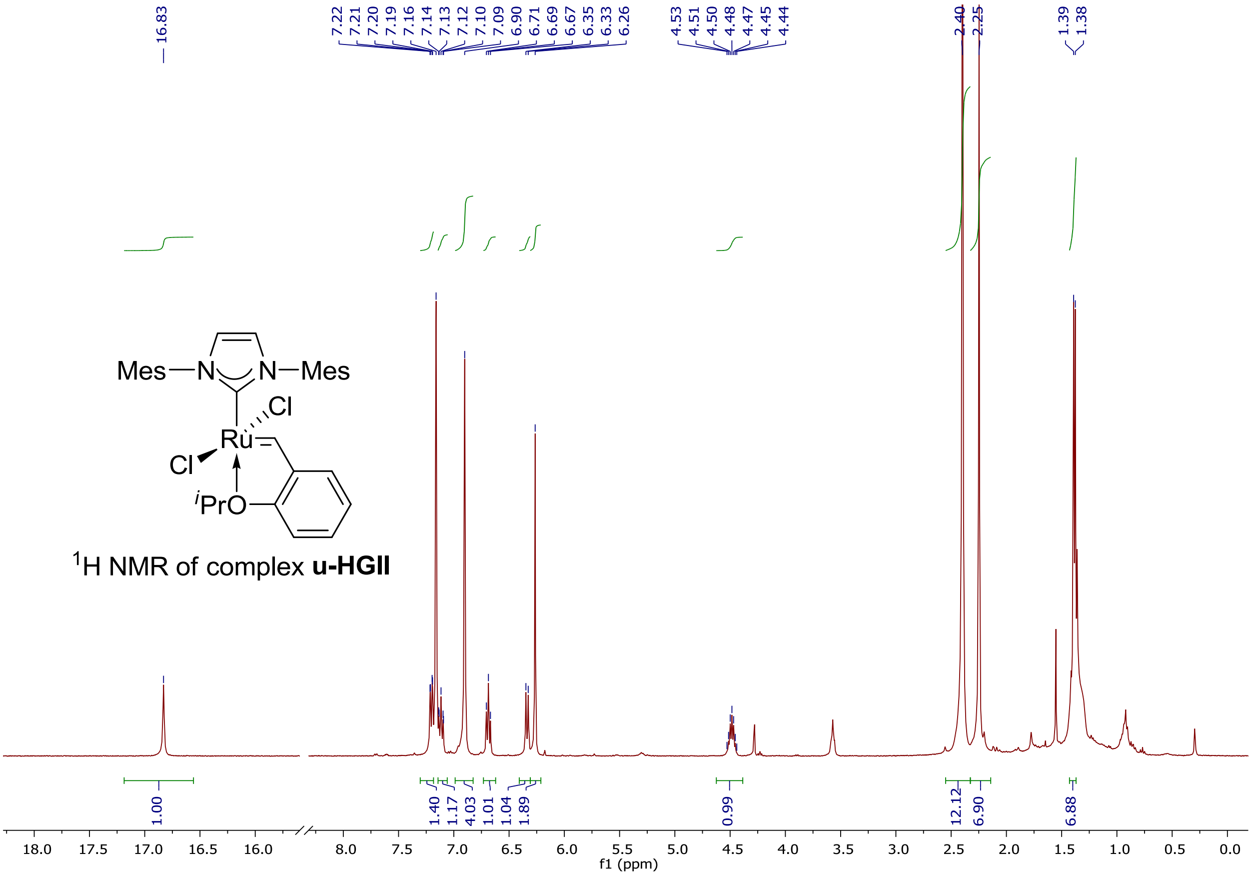

Figure S1. ^{1}H NMR spectrum of complex **u-HGII** in C_6D_6.

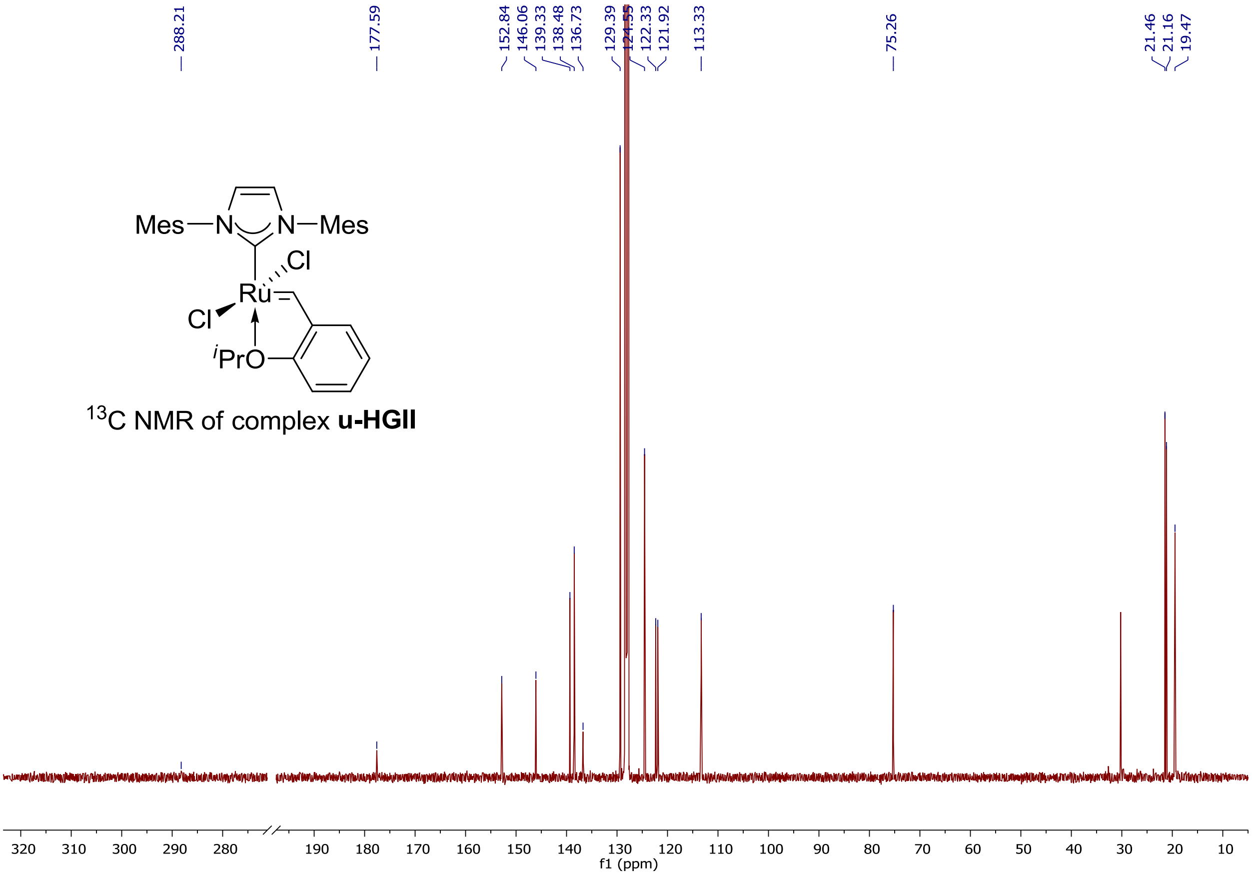

Figure S2. ^{13}C NMR spectrum of complex **u-HGII** in C_6D_6.

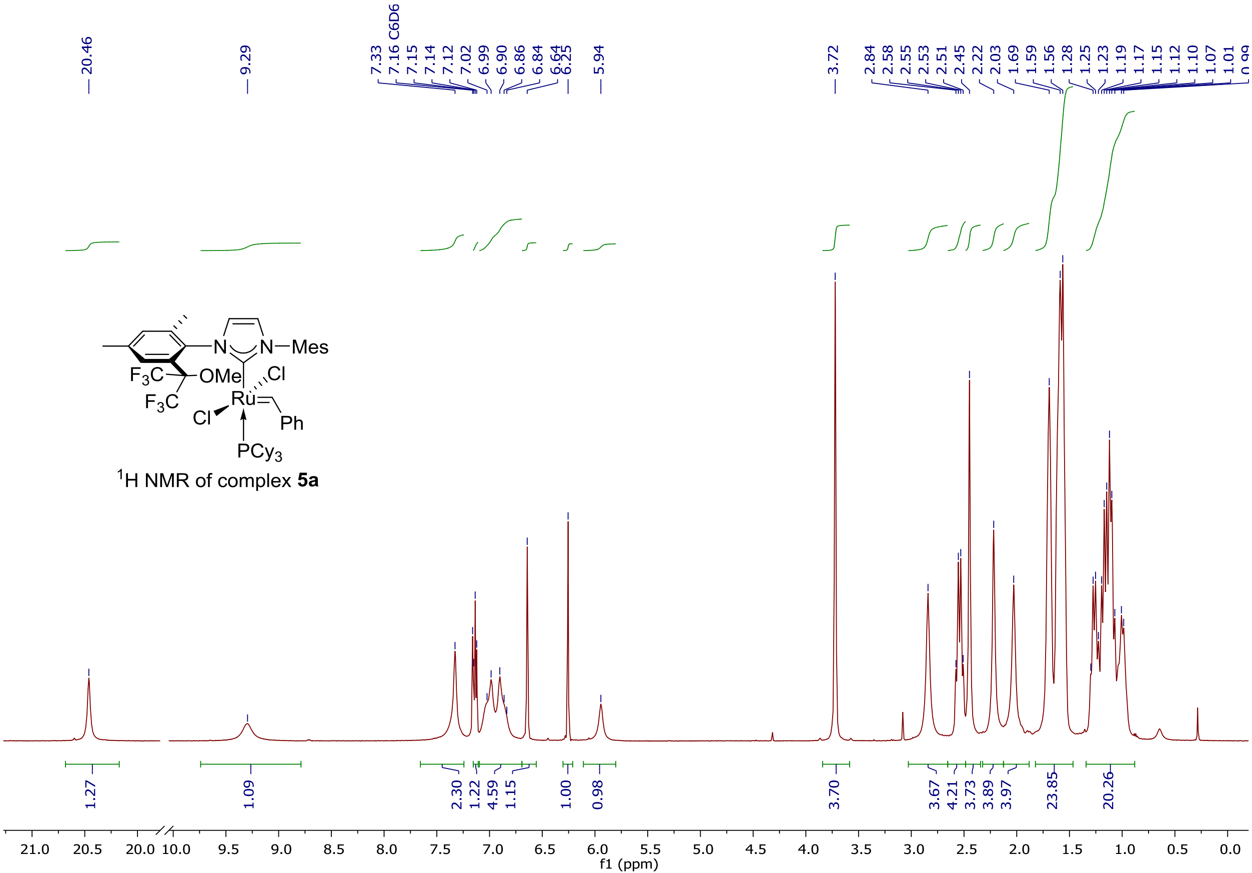

Figure S3. ^{1}H NMR spectrum of complex **5a** in C_6D_6.

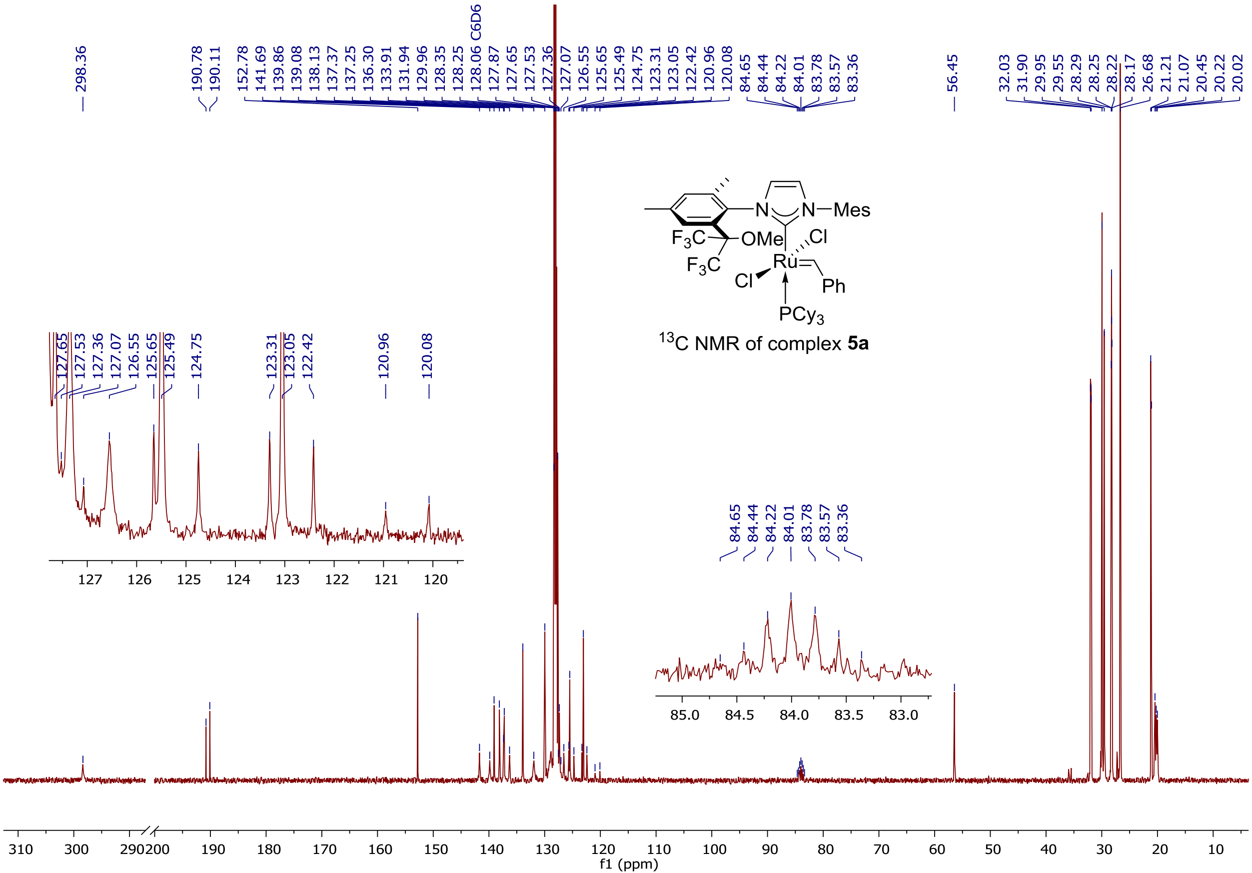

Figure S4. ^{13}C NMR spectrum of complex **5a** in C_6D_6.

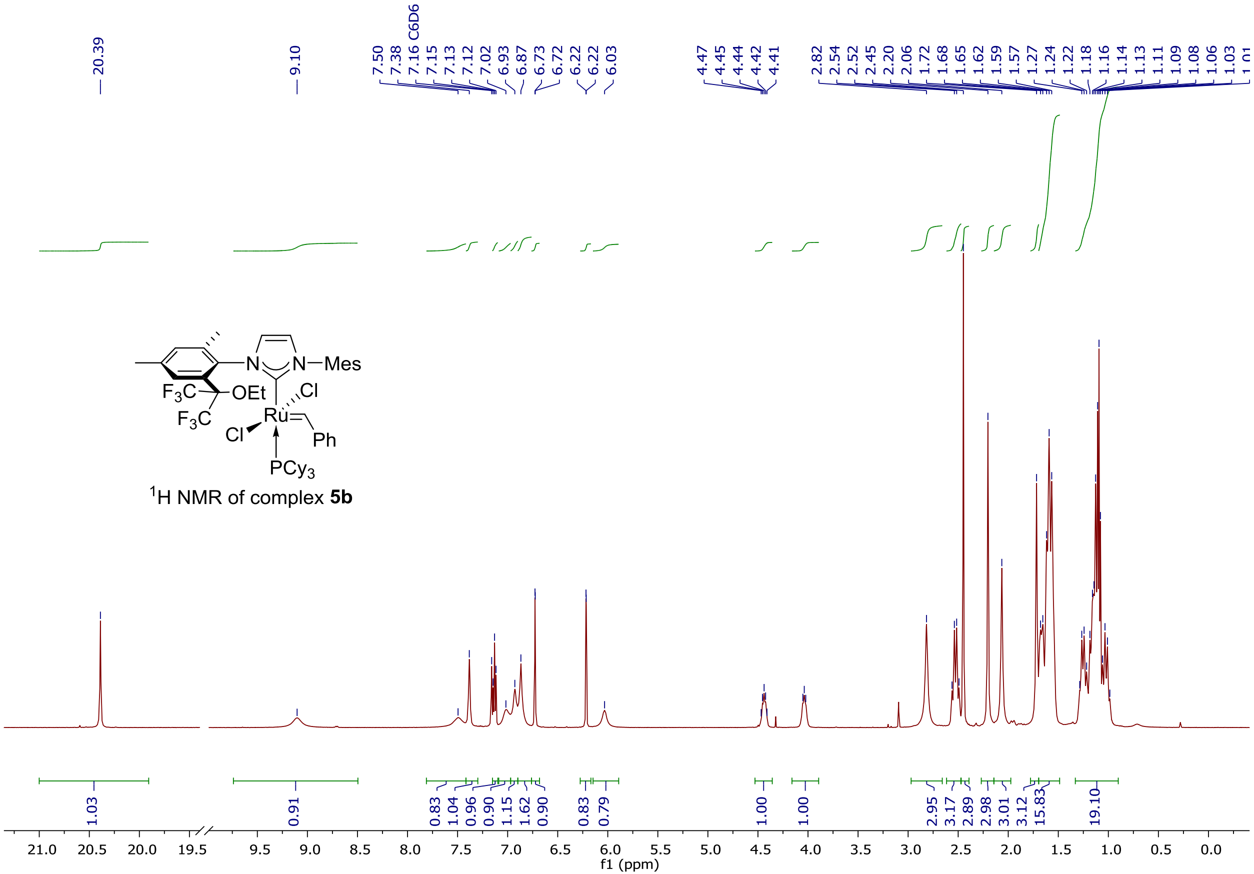

Figure S5. ^{1}H NMR spectrum of complex **5b** in C_6D_6.

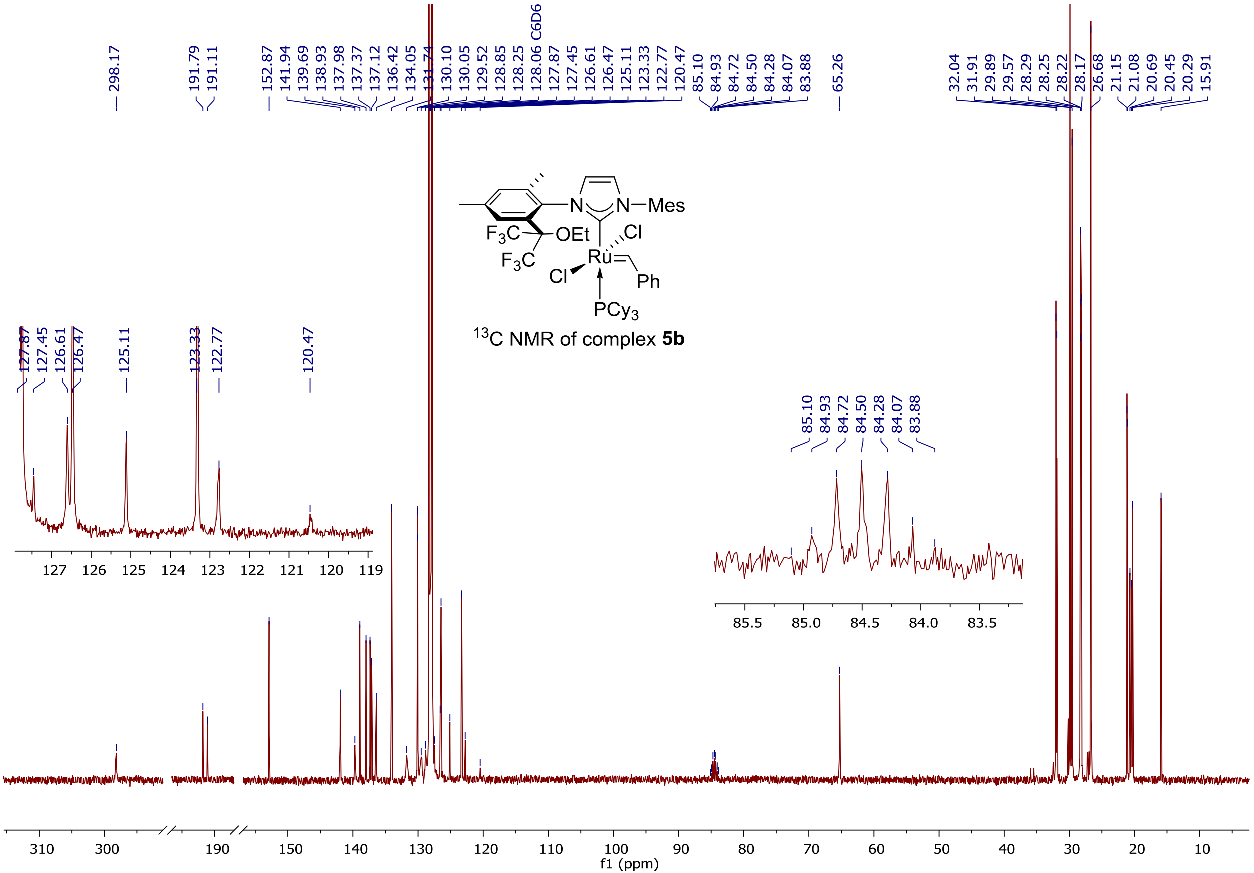

Figure S6. ^{13}C NMR spectrum of complex **5b** in C_6D_6.

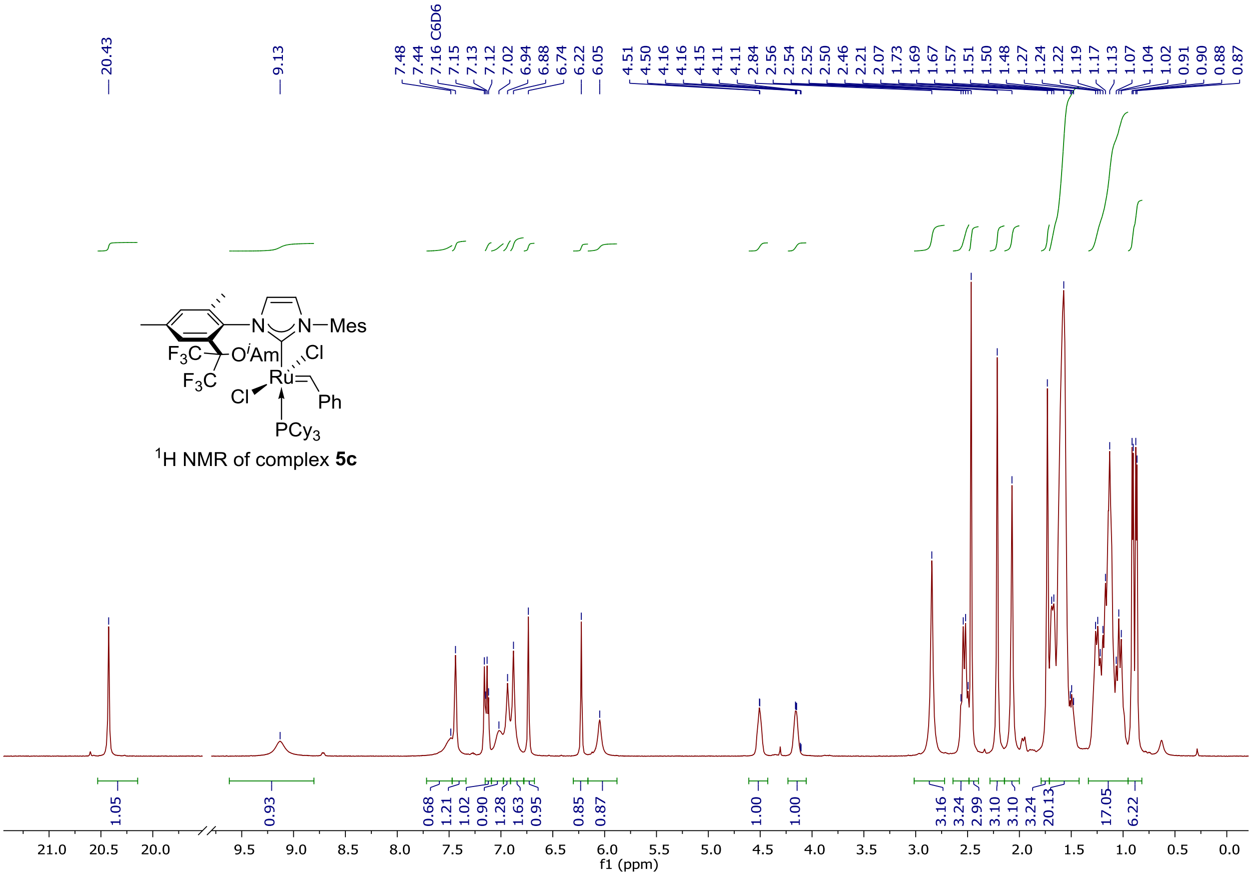

Figure S7. ^{1}H NMR spectrum of complex **5c** in C_6D_6.

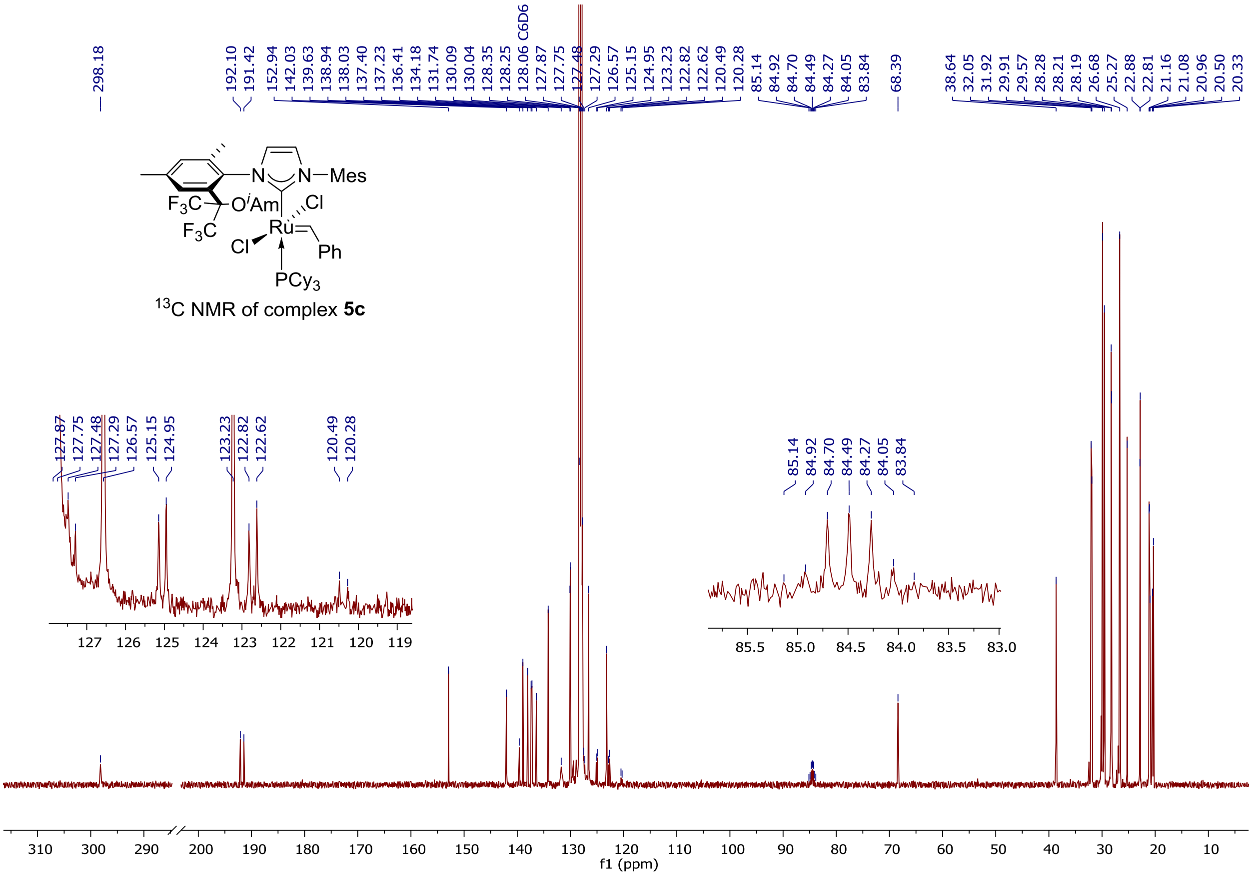

Figure S8. ^{13}C NMR spectrum of complex **5c** in C_6D_6.

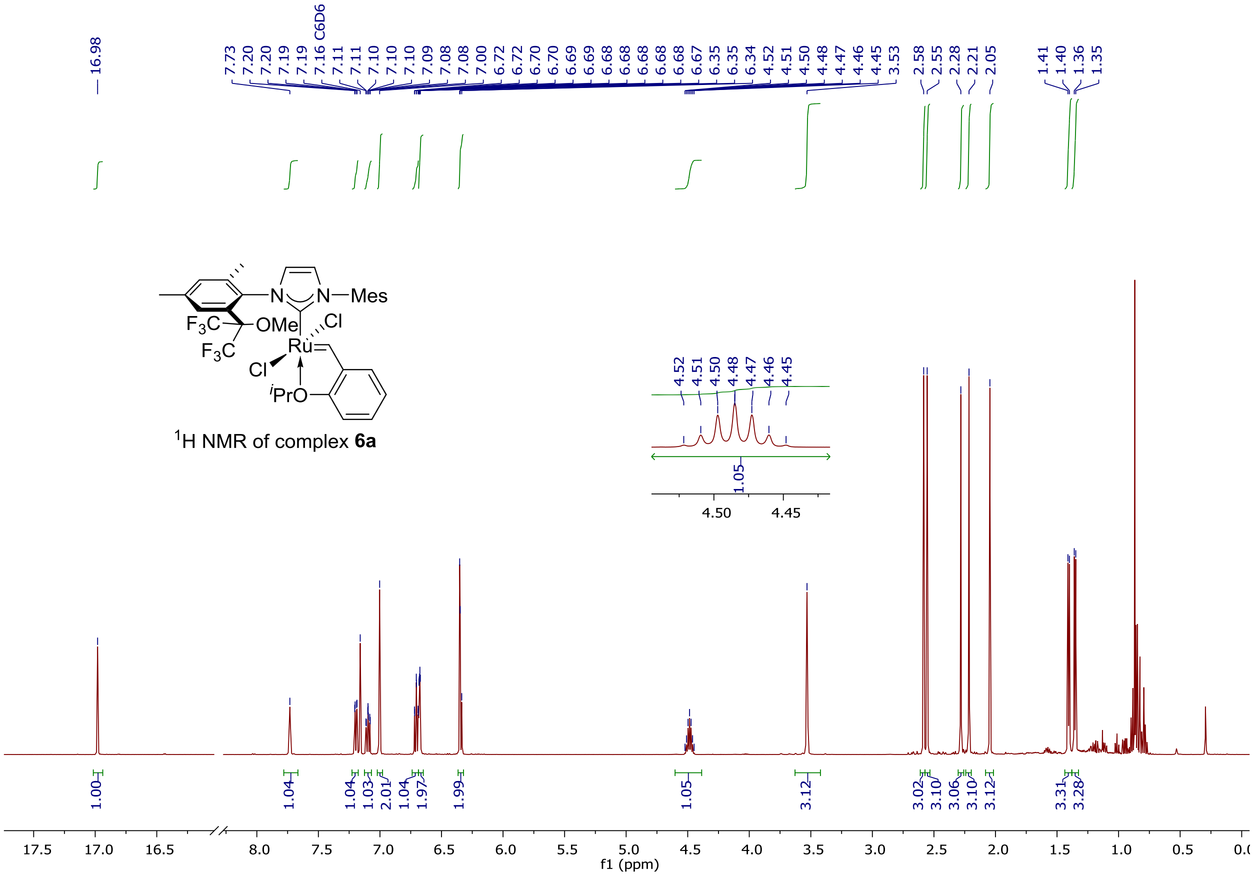

Figure S9. ^{1}H NMR spectrum of complex **6a** in C_6D_6.

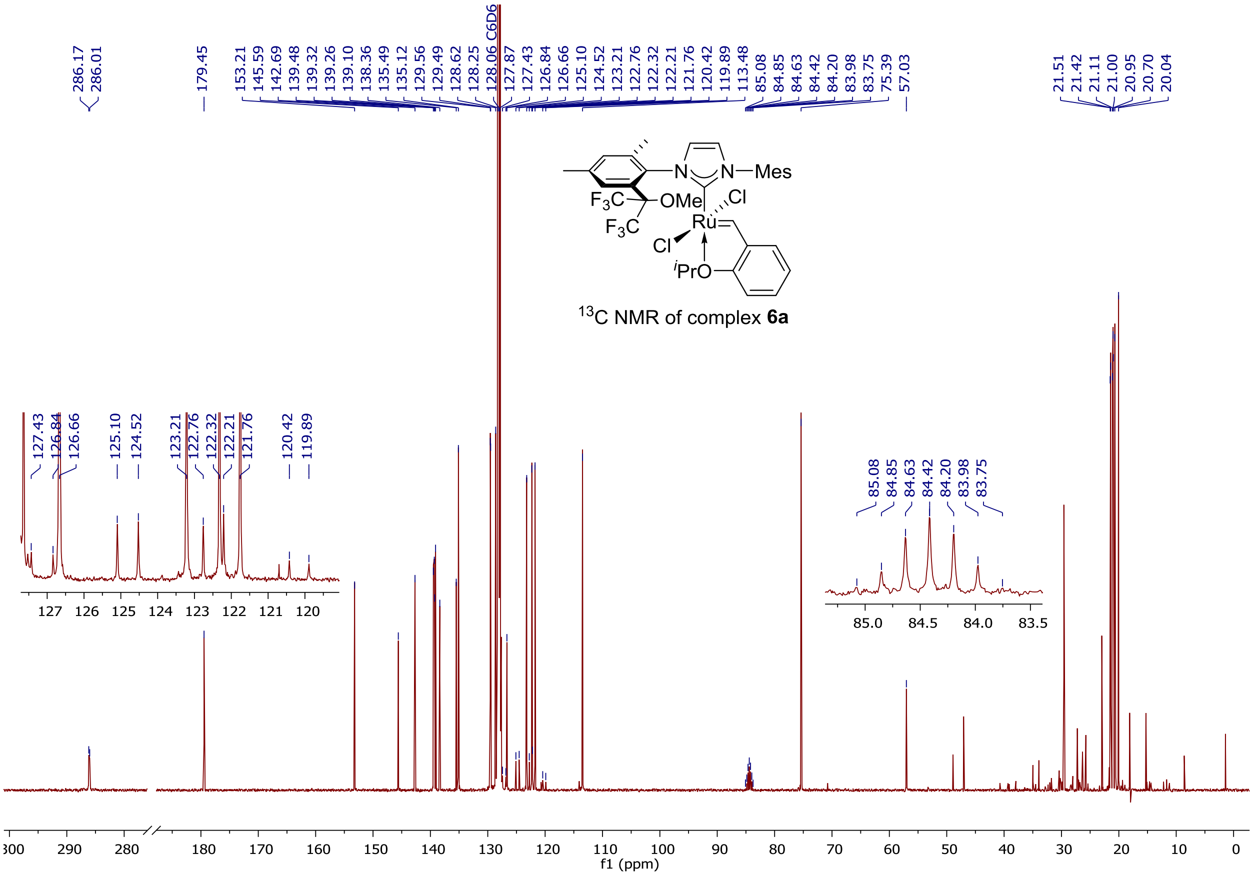

Figure S10. ^{13}C NMR spectrum of complex **6a** in C_6D_6.

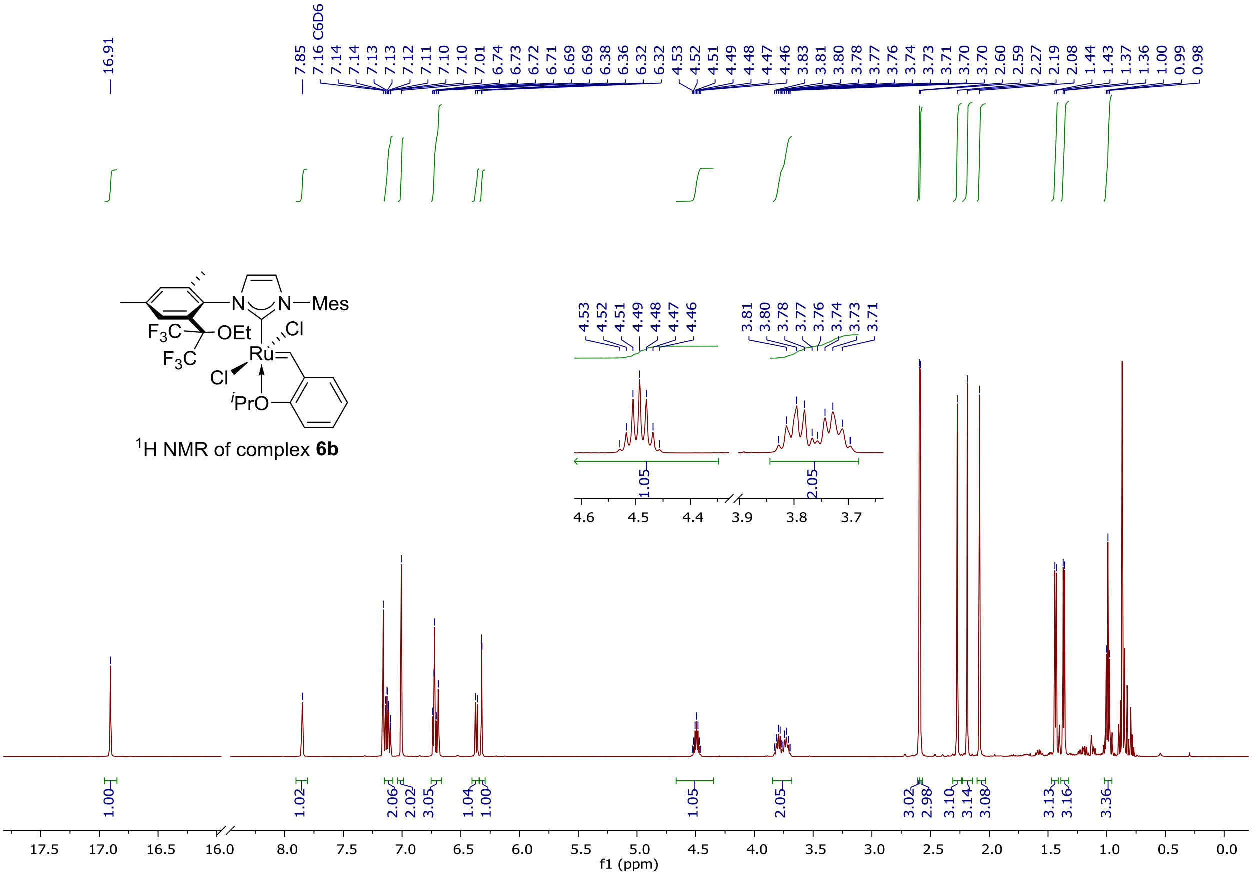

Figure S11. ^{1}H NMR spectrum of complex **6b** in C_6D_6.

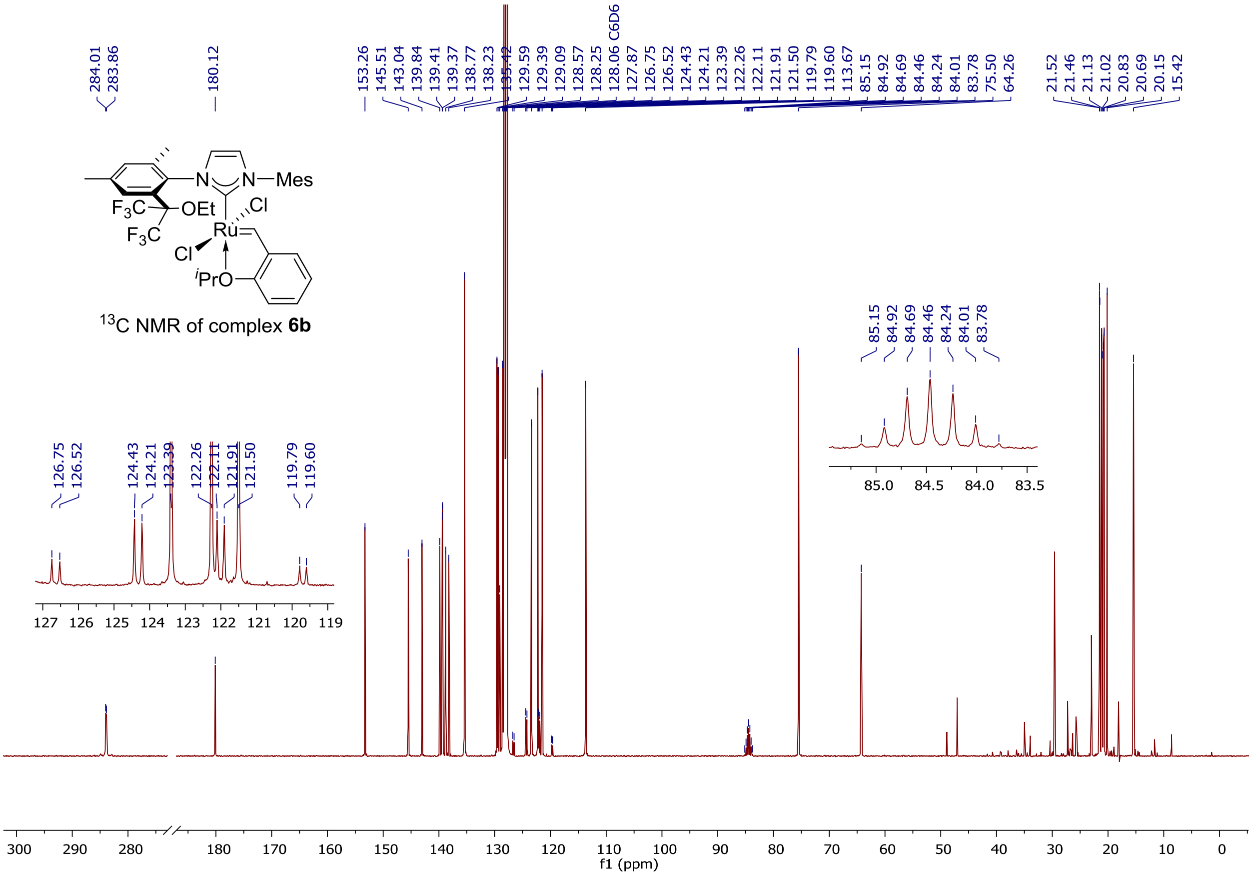

Figure S12. ^{13}C NMR spectrum of complex **6b** in C_6D_6.

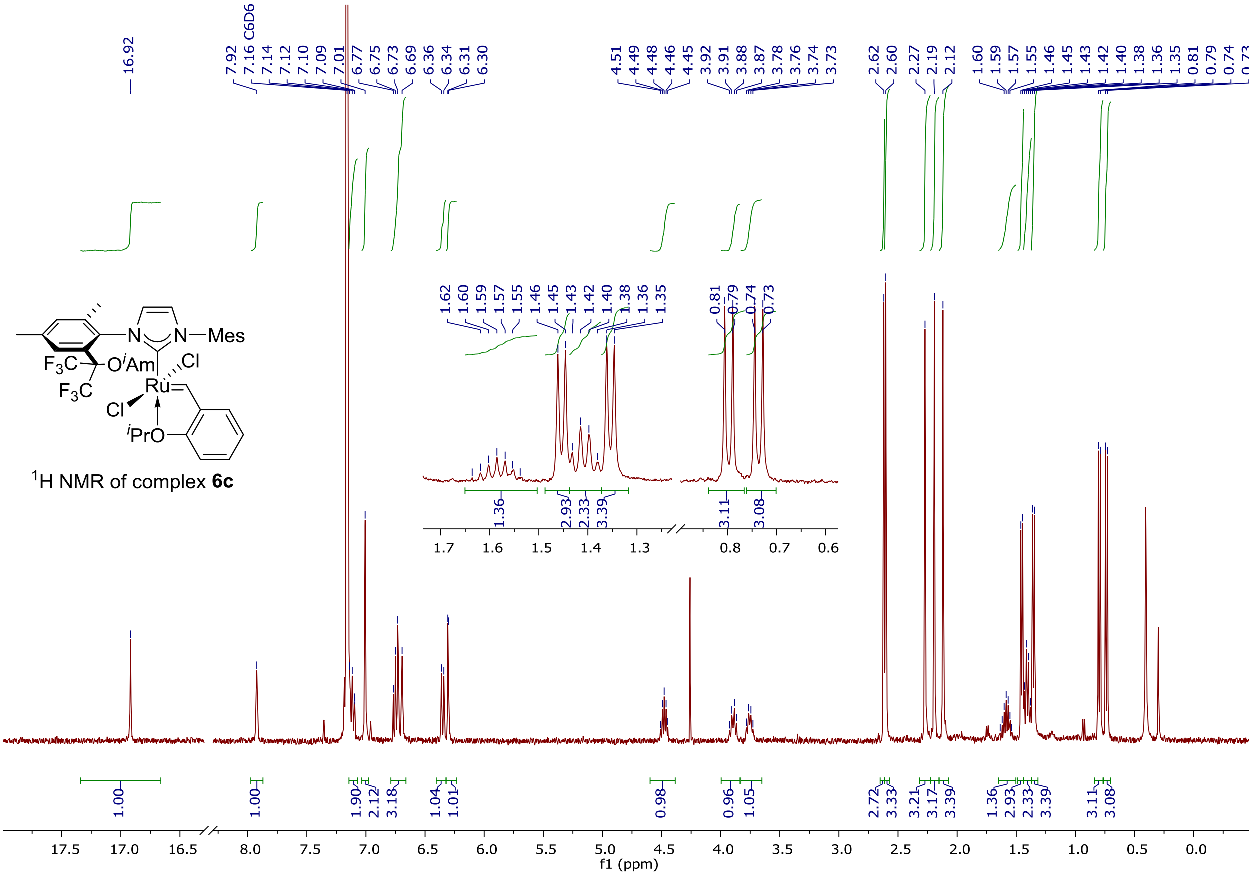

Figure S13. ^{1}H NMR spectrum of complex **6c** in C_6D_6.

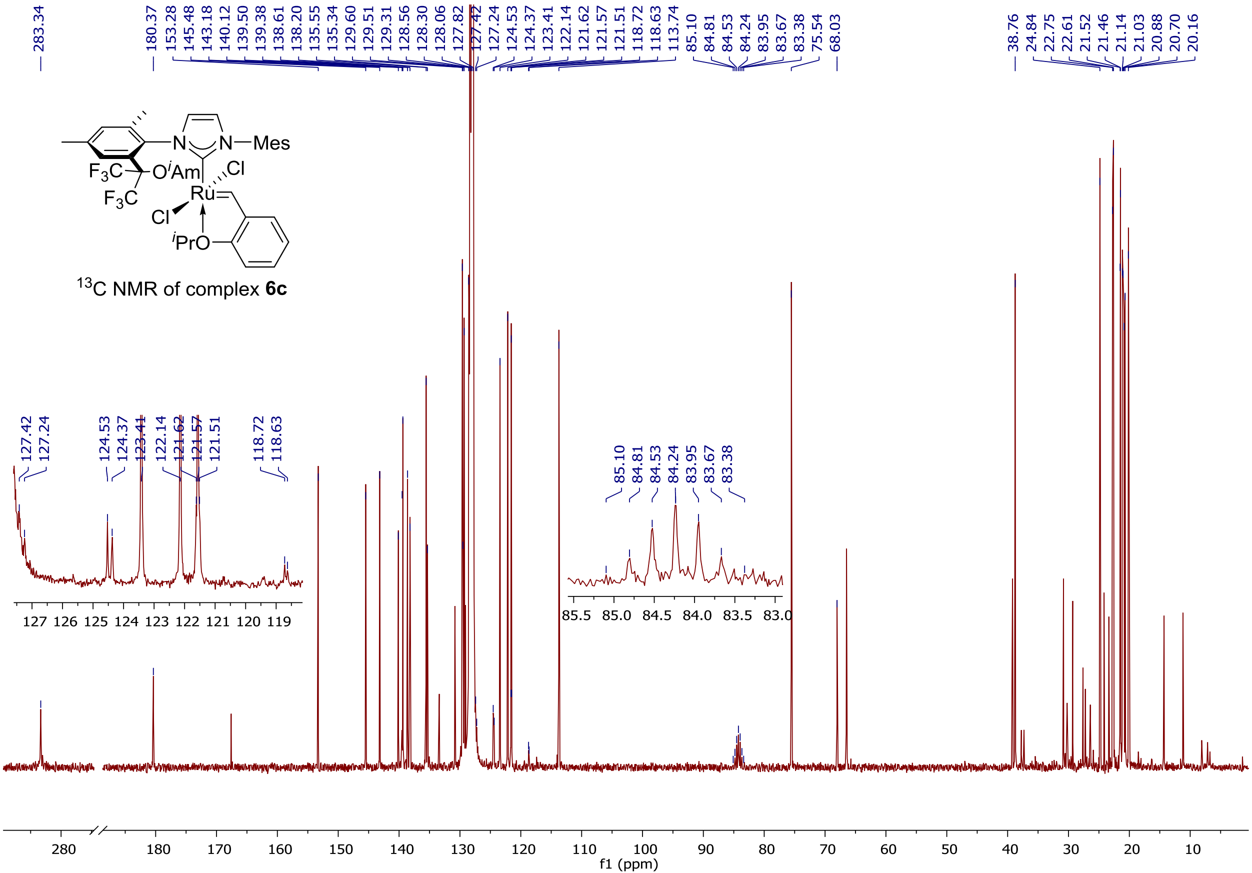

Figure S14. ^{13}C NMR spectrum of complex **6c** in C_6D_6.