Supporting information for

P–C Reductive Elimination in Ru(II) Complexes to Convert Triaryl Phosphine Ligands into Five- or Six-membered Phosphacycles Fused with Aromatic Systems

Takuya Kuwabara, Takahiro Kato, Kouichi Takano, Shintaro Kodama, Keiko Takano, Noriko Tsuchida, Yasunori Minami, Tamejiro Hiyama, and Youichi Ishii*

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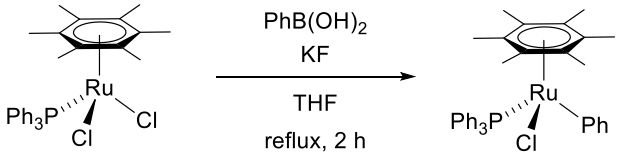
1. General considerations

All manipulations were carried out under an argon atmosphere by using standard Schlenk techniques unless otherwise stated. 1,2-Dichloroethane ($C_2H_4Cl_2$) and dichloromethane (CH_2Cl_2) were dried and distilled over P_4O_{10}, degassed, and stored under argon. The other solvents (anhydrous grade) were purchased from Sigma-Aldrich and purged with argon before use. Diphenylacetylene and 3-hexyne (Sigma-Aldrich), 2-butyne and KF (Wako Chemical), NaOAc (Kanto Chemical) and phenylboronic acid (TCI) were purchased and used as received. $[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$,[1] $[(\eta^6\text{-}C_6Me_6)RuCl_2(PPh_3)]$,[2] $[(\eta^6\text{-}C_6Me_6)RuCl(Ph)(PPh_3)]$,[2] $NaBAr^F{}_4\cdot 2H_2O$,[3] $P(1\text{-Naph})Ph_2$,[4] were synthesized according to the literature. ^{1}H (500 MHz), $^{13}C\{^1H\}$ (126 MHz), and $^{31}P\{^1H\}$ (202 MHz) NMR spectra were recorded on a JEOL ECA-500 spectrometer at 20 °C unless otherwise stated. Chemical shifts are reported in δ and referenced to residual ^{1}H and ^{13}C signals of deuterated solvents as internal standards or to the ^{31}P signal of PPh_3 (δ −5.65) as an external standard. IR spectra were recorded on a JASCO FT/IR-4200 spectrometer by using KBr pellets. Elemental analyses were performed on a Perkin Elmer 2400 series II CHN analyzer. X-ray crystallographic analyses were performed on a Rigaku/MSC VariMax/Saturn CCD diffractometer. Amounts of the solvent molecules in the crystals were determined not only by elemental analyses but also by ^{1}H NMR spectroscopy. Diffraction data for **2a**, **g**-**i**, **3** were collected on a VariMax Saturn CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71070 Å) at –160 °C. Intensity data were corrected for Lorenz-polarization effects and for empirical absorption (REQAB).[5] The structures were solved by a direct method (SIR-2014)[6] and refined by a full-matrix-least-square method on F^2 for all reflections using SHELXL-2014 program.[7] All hydrogen atoms were placed at the calculated positions with fixed isotropic parameters.

2. Synthesis and analytical data for 1-7

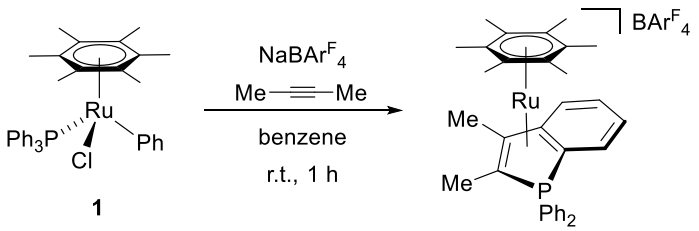
Synthesis of $[(\eta^6\text{-}C_6Me_6)RuCl(Ph)(PPh_3)]$ (1)



1 (36%)

A mixture of $[(\eta^6\text{-}C_6Me_6)RuCl_2(PPh_3)]$ (52.5 mg, 0.088 mmol), $PhB(OH)_2$ (53.7 mg, 0.440 mmol) and KF (25.9 mg, 0.517 mmol) in THF (4 mL) and CH_2Cl_2 (5 mL) was refluxed for 2 h. The resulting yellow suspension was filtered through a short pad of Celite, and the pad was rinsed with CH_2Cl_2 (*ca*. 5 mL). The combined filtrate was dried in vacuo, and the residue was purified by column chromatography on silica gel (CH_2Cl_2). The eluate was dried up in vacuo and recrystallized from benzene/hexane to afford **1** (20.2 mg, 0.032 mmol, 36% yield) as orange crystals. **1**: ^{1}H NMR (CD_2Cl_2): δ 7.58 (br, 3H, Ph), 7.39 (br, 7H, Ph), 7.21 (br, 2H, Ph), 7.05 (br, 2H, Ph), 6.92–6.83 (br, 4H, Ph), 6.69 (t, $^3J_{HH}$ = 7.0 Hz, 1H, Ph), 6.51 (br, 1H, Ph), 1.66 (s, 18H, C_6Me_6). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 41.6 (s). Selected $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 100.2 (d, $^2J_{PH}$ = 3.3 Hz, C_6Me_6), 15.4 (s, $C_6\mathit{Me}_6$). Anal. Calcd for $C_{36}H_{38}ClPRu$ (**1**): C, 67.75; H, 6.00. Found: C, 67.47; H, 6.00.

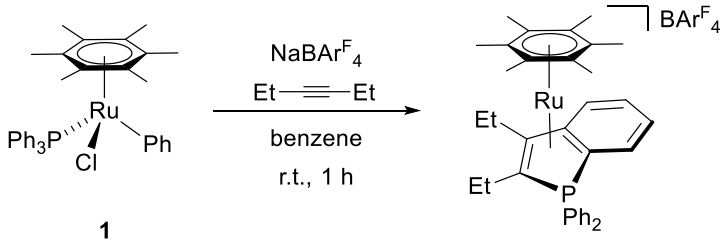
Synthesis of $[(\eta^6\text{-}C_6Me_6)Ru\{\eta^4\text{-}PPh_2(C_8H_4Me_2)\}][BAr^F{}_4]$ (2a)



1 **2a** (53%)

A mixture of **1** (29.3 mg, 0.046 mmol), 2-butyne (14.4 mg, 0.266 mmol) and $NaBAr^F_4 \cdot 2H_2O$ (47.5 mg, 0.052 mmol) in benzene (2 mL) was stirred at room temperature for 1 h. The resulting orange suspension was filtered through a short pad of Celite, and the pad was rinsed with sufficient amount of benzene (up to 10 mL). The combined filtrate was dried in vacuo, and the residue was purified by column chromatography on silica (CH_2Cl_2 : Et_2O = 1 : 1). The eluate was dried up in vacuo and recrystallized from benzene/hexane to afford **2a** (34.9 mg, 0.024 mmol, 53% yield) as orange crystals. **2a**: ^{1}H NMR (CD_2Cl_2): δ 7.93 (dd, $^3J_{PH}$ = 12.5 Hz, $^3J_{HH}$ = 7.0 Hz, 2H, *o*-H of Ph), 7.88–7.80 (m, 3H, *m*, *p*-H of Ph), 7.72 (br, 8H, BAr^F_4), 7.56 (br, 4H, BAr^F_4), 7.40 (td, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, *p*-H of Ph), 7.26 (td, $^3J_{HH}$ = 7.5 Hz, $^4J_{PH}$ = 2.0 Hz, 2H, *m*-H of Ph), 7.23 (d, $^3J_{HH}$ = 9.5 Hz, 1H, C_6H_4), 7.12 (dd, $^3J_{PH}$ = 9.0 Hz, $^3J_{HH}$ = 6.0 Hz, 1H, C_6H_4), 6.92–6.86 (m, 2H, C_6H_4), 6.68 (dd, $^3J_{PH}$ = 9.5 Hz, $^3J_{HH}$ = 7.5 Hz, 2H, *o*-H of Ph), 2.14 (s, 3H, CH_3), 1.64 (s, 18H, C_6Me_6), 1.53 (d, $^3J_{PH}$ = 16.0 Hz, 3H, CH_3). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 24.5 (s). Selected ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 96.4 (s, C_6Me_6), 89.8 (d, $^2J_{CP}$ = 20.4 Hz, C_β), 79.2 (d, $^2J_{CP}$ = 19.3 Hz, C_β), 45.3 (d, $^1J_{CP}$ = 108.1 Hz, C_α), 30.6 (d, $^1J_{CP}$ = 108.1 Hz, C_α), 15.1 (s, C_6Me_6), 11.1 (d, $^3J_{CP}$ = 3.5 Hz, CH_3), 10.2 (d, $^2J_{CP}$ = 7.2 Hz, CH_3). Anal. Calcd for $C_{66}H_{50}BF_{24}PRu$ (**2a**): C, 54.98; H, 3.50. Found: C, 55.03; H, 3.24.

Synthesis of [(η^6-C_6Me_6)Ru{η^4-$PPh_2(C_8H_4Et_2)$}][BAr^F_4] (2b)

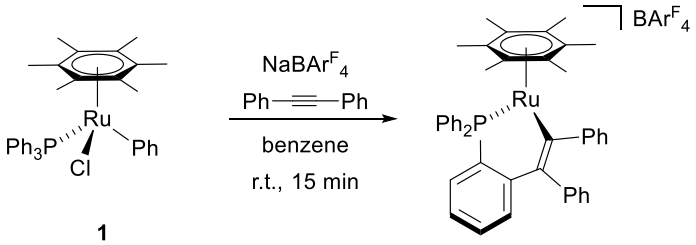


1 **2b** (50%)

A mixture of **1** (30.0 mg, 0.047 mmol), 3-hexyne (20.3 mg, 0.247 mmol) and $NaBAr^F_4 \cdot 2H_2O$ (47.7 mg, 0.052 mmol) in benzene (2 mL) was stirred at room temperature for 3 h. The resulting orange suspension was filtered through a short pad of Celite, and the pad was rinsed with sufficient amount of benzene (up to 10 mL). The combined filtrate was dried in vacuo, and the residue was purified by column chromatography on silica gel (CH_2Cl_2 : Et_2O = 1 : 1). The eluate was dried up in vacuo and recrystallized from benzene/hexane to afford **2b** (34.7 mg, 0.024 mmol, 50% yield) as orange crystals. **2b**: ^{1}H NMR (CD_2Cl_2): δ 7.95 (ddd, $^3J_{PH}$ = 12.5 Hz, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 2.0 Hz, 2H, *o*-H of Ph), 7.90–7.83 (m, 3H, *m*, *p*-H of Ph), 7.73 (br, 8H, BAr^F_4), 7.56 (br, 4H, BAr^F_4), 7.38 (td, $^3J_{HH}$ = 7.5 Hz, $^4J_{PH}$ = 2.0 Hz, 1H, *p*-H of Ph), 7.27 (d, $^3J_{HH}$ = 9.0 Hz, 1H, C_6H_4), 7.23 (td, $^3J_{HH}$ = 7.5 Hz, $^4J_{PH}$ = 2.0 Hz, 2H, *m*-H of Ph), 7.15 (dd, $^3J_{HH}$ = 9.0 Hz, $^3J_{HH}$ = 5.5 Hz, 1H, C_6H_4), 6.92 (m, 1H, C_6H_4), 6.84 (dd, $^3J_{PH}$ = 9.0 Hz, $^3J_{HH}$ = 6.3 Hz, 1H, C_6H_4), 6.67 (dd, $^3J_{PH}$ = 10.0 Hz, $^3J_{HH}$ = 8.0 Hz, 2H, *o*-H of Ph), 2.61 (dqd, $^2J_{HH}$ = 14.5 Hz, $^3J_{HH}$ = 7.5

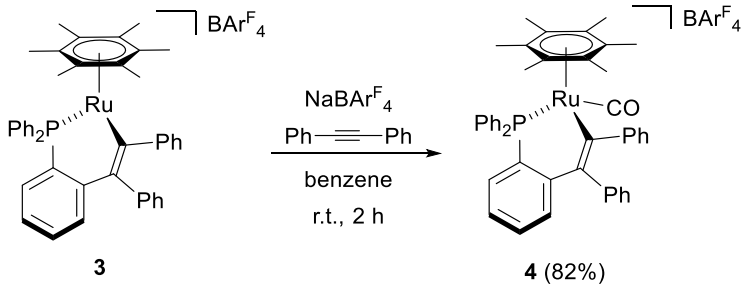
Hz, $^4J_{PH}$ = 2.0 Hz, 1H, CH_2CH$_3$), 2.27 (dq, $^2J_{HH}$ = 15.0 Hz, $^3J_{HH}$ = 7.5 Hz, 1H, CH_2CH$_3$), 2.19 (ddq, $^2J_{HH}$ = 15.0 Hz, $^3J_{HH}$ = 7.5 Hz, $^3J_{PH}$ = 2.0 Hz, 1H, CH_2CH$_3$), 1.84 (ddq, $^3J_{PH}$ = 33.0 Hz, $^2J_{HH}$ = 15.0 Hz, $^3J_{HH}$ = 7.5 Hz, 1H, CH_2CH$_3$), 1.61 (s, 18H, C$_6$Me$_6$), 1.44 (t, $^3J_{HH}$ = 8.0 Hz, 3H, CH$_2$CH_3), 0.88 (t, $^3J_{HH}$ = 7.0 Hz, 3H, CH$_2$CH_3). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 21.2 (s). Selected ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 96.5 (s, *C*$_6$Me$_6$), 89.7 (d, $^2J_{CP}$ = 22.9 Hz, C$_\beta$), 83.5 (d, $^2J_{CP}$ = 18.0 Hz, C$_\beta$), 44.9 (d, $^1J_{CP}$ = 98.5 Hz, C$_\alpha$), 39.4 (d, $^1J_{CP}$ = 72.1 Hz, C$_\alpha$), 21.1 (d, $^2J_{CP}$ = 8.3 Hz, *C*H$_2$CH$_3$), 20.1 (d, $^3J_{CP}$ = 3.7 Hz, *C*H$_2$CH$_3$), 15.9 (d, $^3J_{CP}$ = 6.0 Hz, CH$_2$*C*H$_3$), 15.7 (s, CH$_2$*C*H$_3$), 15.1 (s, C$_6$*M*e$_6$). Anal. Calcd for $C_{68}H_{54}BF_{24}PRu$ (**2b**): C, 55.56; H, 3.70. Found: C, 55.75; H, 3.45.

Synthesis of [(η^6-C$_6$Me$_6$)Ru(PPh$_2${C$_6$H$_4$C(Ph)=CPh})][BAr$^F_4$] (3)



A mixture of **1** (24.9 mg, 0.039 mmol), diphenylacetylene (35.2 mg, 0.197 mmol) and NaBAr$^F_4$·2H$_2$O (39.0 mg, 0.042 mmol) in benzene (2 mL) was stirred at room temperature for 15 min. The resulting black blue suspension was filtered through a short pad of Celite, and the pad was rinsed with benzene (*ca*. 1 mL). The eluate was dried up in vacuo and recrystallized from benzene/hexane to afford **3** (51.4 mg, 0.033 mmol, 84% yield) as black green crystals. **3**: ^{1}H NMR ($CDCl_3$): δ 7.93 (d, $^3J_{HH}$ = 7.4 Hz, 2H, Ar), 7.79 (t, $^3J_{HH}$ = 7.4 Hz, 1H, Ar), 7.70 (br, 8H, BAr$^F_4$), 7.56–7.41 (m, 15H, BAr$^F_4$ and Ar), 7.37–7.28 (m, 5H, Ar), 7.25–7.15 (m, 3H, Ar), 7.08 (m, 1H, Ar), 6.71 (d, $^3J_{HH}$ = 7.4 Hz, 1H, Ar), 1.63 (s, 18H, C$_6$Me$_6$). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 73.5 (s). Selected ^{13}C{^{1}H} NMR ($CDCl_3$): δ 110.8 (s, *C*$_6$Me$_6$), 16.0 (s, C$_6$*M*e$_6$). Anal. Calcd for $C_{76}H_{54}BF_{24}PRu$ (**3**): C, 58.29; H, 3.48. Found: C, 57.95; H, 3.22.

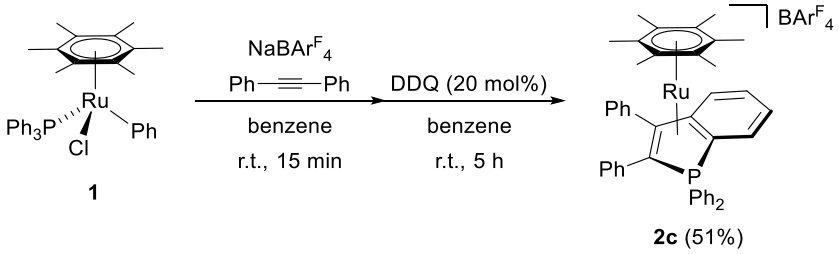
Synthesis of [η^6-(C$_6$Me$_6$)Ru(CO)(PPh$_2${C$_6$H$_4$C(Ph)=CPh})][BAr$^F_4$] (4)



Under a CO atmosphere, a solution of **3** (24.8 mg, 0.016 mmol) in benzene (2 mL) was stirred at room temperature for 2 h. After removal of the solvent, the residue was recrystallized from benzene/hexane to afford **4** (30.8 mg, 0.020 μmol, 82% yield) as yellow crystals. **4**: ^{1}H NMR (CD_2Cl_2): δ 7.71 (m, 10H, Ar and BAr$^F_4$), 7.63–7.49 (m, 11H, Ar and BAr$^F_4$), 7.44–7.21 (m, 7H, Ar), 7.09–6.74 (m, 8H, Ar), 2.06 (s, 18H, C$_6$Me$_6$). ^{31}P{^{1}H} NMR

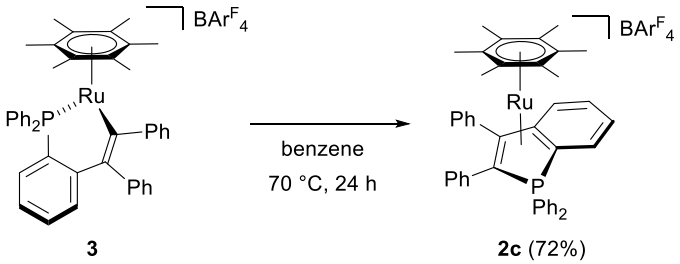
(CD_2Cl_2): δ 55.5 (s). Selected $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 199.5 (d, $^2J_{CP}$ = 24.1 Hz, CO), 17.4 (s, C_6Me_6). IR (KBr, cm^{-1}): 1981 ($\nu_{C=O}$). Anal. Calcd for $C_{77}H_{54}BF_{24}OPRu$ (**4**): C, 58.02; H, 3.41. Found: C, 58.39; H, 3.37.

Synthesis of [(η^6-C_6Me_6)Ru{η^4-$PPh_2(C_8H_4Ph_2)$}][BAr^F_4] (2c) (with DDQ)



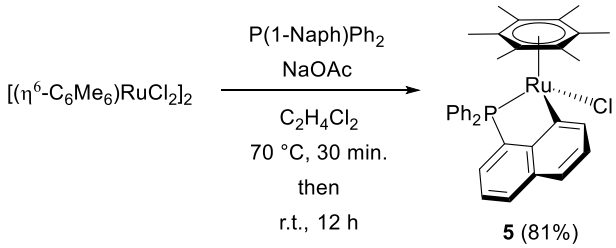
A mixture of **1** (24.9 mg, 0.039 mmol), $NaBAr^F_4 \cdot 2H_2O$ (39.4 mg, 0.043 mmol) and diphenylacetylene (35.3 mg, 0.196 mmol) in benzene (2 mL) was stirred at room temperature for 15 min. Then DDQ (*ca*. 0.1 M benzene solution, 75.0 µL, *ca*. 20 mol%) was added and stirring was continued for additional 5 h. Purification by column chromatography on silica gel (CH_2Cl_2) followed by recrystallization from CH_2Cl_2/hexane afforded **2c** (31.4 mg, 0.020 mmol, 51% yield) as orange crystals. **2c**: ^1H NMR ($CDCl_3$): 7.91 (dd, $^3J_{PH}$ = 12.5 Hz, $^3J_{HH}$ = 7.3 Hz, 2H, Ph), 7.83 (t, $^3J_{HH}$ = 6.9 Hz, 1H, Ph), 7.76–7.73 (m, 10H, BAr^F_4 and Ph), 7.53 (br, 4H, BAr^F_4), 7.47 (t, $^3J_{HH}$ = 6.9 Hz, 1H, Ph), 7.39–7.28 (m, 6H, Ph and C_6H_4), 7.21 (dd, $^3J_{HH}$ = 9.0 Hz, $^3J_{HH}$ = 6.0 Hz, 1H, C_6H_4), 7.16 (t, $^3J_{HH}$ = 7.5 Hz, 1H, Ph), 7.10–7.05 (m, 5H, Ph and C_6H_4), 6.86 (t, $^3J_{PH}$ = 8.9 Hz, $^3J_{HH}$ = 6.0 Hz, 1H, C_6H_4), 6.72 (t, $^3J_{HH}$ = 8.5 Hz, 2H, Ph), 6.66 (d, $^3J_{HH}$ = 8.0 Hz, 2H, Ph), 1.66 (s, 18H, C_6Me_6). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 30.6 (s). Selected $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 97.1 (s, C_6Me_6), 90.5 (d, $^2J_{CP}$ = 20.4 Hz, C_β), 85.4 (d, $^2J_{CP}$ = 16.9 Hz, C_β), 44.4 (d, $^1J_{CP}$ = 96.1 Hz, C_α), 39.8 (d, $^1J_{CP}$ = 75.7 Hz, C_α), 15.5 (s, C_6Me_6). Anal. Calcd for $C_{76}H_{54}BF_{24}PRu$ (**2c**): C, 58.29; H, 3.48. Found: C, 58.69; H, 3.15.

Synthesis of 2c (without DDQ)



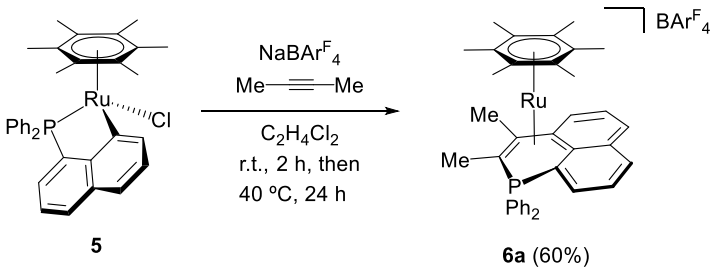
A solution of **3** (15.3 mg, 9.77 µmol) in benzene (2 mL) was heated at 70 °C for 24 h. After removal of the solvent, the residue was recrystallized from benzene/hexane to afford **2c** (11.0 mg, 7.02 µmol, 72% yield) as orange crystals.

Synthesis of [(η⁶-C₆Me₆)RuCl{PPh₂(C₁₀H₆)}] (5)



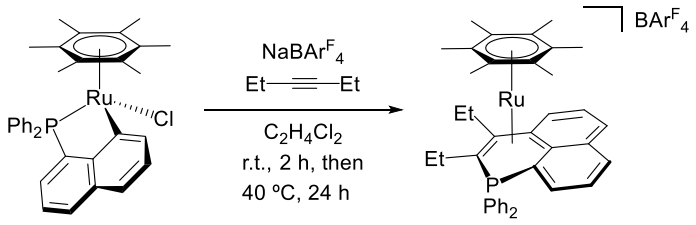
A mixture of $[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$ (178.3 mg, 0.267 mmol) and $P(1\text{-Naph})Ph_2$ (178 mg, 0.570 mmol) in $C_2H_4Cl_2$ (2 mL) was heated at 70 °C for 30 min. NaOAc (267.2 mg, 3.26 mmol) was added to the mixture and the solution was further stirred at the same temperature for 12 h. The resulting reddish brown suspension was filtered through a short pad of Celite, and the pad was rinsed with $C_2H_4Cl_2$ (*ca*. 10 mL). The combined filtrate was dried in vacuo, and the residue was purified by column chromatography on silica gel (AcOEt). The eluate was dried up in vacuo and recrystallized from CH_2Cl_2/hexane to afford **5** (264.2 mg, 0.433 mmol, 81% yield) as yellow crystals. **5**: ^{1}H NMR (CD_2Cl_2): δ 8.05 (m, 2H, Ph), 7.93 (d, $^3J_{HH}$ = 6.3 Hz, 1H, $C_{10}H_6$), 7.76 (d, $^3J_{HH}$ = 8.0 Hz, 1H, $C_{10}H_6$), 7.56–7.48 (m, 4H, Ph and $C_{10}H_6$), 7.41 (d, $^3J_{HH}$ = 8.0 Hz, 1H, $C_{10}H_6$), 7.35–7.27 (m, 3H, Ph and $C_{10}H_6$), 7.19 (t, $^3J_{HH}$ = 7.5 Hz, 2H, Ph), 6.94 (dd, $^3J_{PH}$ = 9.8 Hz, $^3J_{HH}$ = 7.8 Hz, 2H, Ph), 1.85 (s, 18H, C_6Me_6). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 69.6 (s). Selected ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 100.5 (d, $^2J_{PC}$ = 3.5 Hz, *C*$_6$Me$_6$), 15.8 (s, C$_6$*Me*$_6$). Anal. Calcd for $C_{34}H_{34}ClPRu$ (**5**): C, 66.93; H, 5.62. Found: C, 67.28; H, 5.47.

Synthesis of [(η⁶-C₆Me₆)Ru{η⁴-PPh₂(C₁₂H₆Me₂)}][BAr$^F_4$] (6a)



A mixture of **5** (30.2 mg, 0.050 mmol), 2-butyne (13.5 mg, 0.250 mmol) and $NaBAr^F_4 \cdot 2H_2O$ (49.9 mg, 0.054 mmol) in $C_2H_4Cl_2$ (2 mL) was stirred at room temperature for 2 h, then heated at 40 °C for 24 h. The resulting black green suspension was filtered through a short pad of Celite, and the pad was rinsed with $C_2H_4Cl_2$ (*ca*. 1 mL). The combined filtrate was dried in vacuo, and the residue was purified by column chromatography on silica gel (CH_2Cl_2 : Et_2O = 1 : 2). The eluate was dried up in vacuo and recrystallized from CH_2Cl_2/hexane to afford **6a** (45.0 mg, 0.030 mmol, 60% yield) as black green crystals. **6a**: ^{1}H NMR (CD_2Cl_2): δ 7.85 (td, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, Ar), 7.74–7.72 (br, 10H, Ar and BAr$^F_4$), 7.65 (br, 2H, Ar), 7.56–7.49 (m, 6H, Ar and BAr$^F_4$), 7.40 (td, $^3J_{HH}$ = 8.0 Hz, $^4J_{PH}$ = 3.0 Hz, 2H, Ar), 7.34–7.26 (m, 4H, Ar), 7.16 (d, $^3J_{HH}$ = 7.5 Hz, 1H, Ar), 6.91 (br, 1H, Ar), 6.06 (dd, $^3J_{PH}$ = 13.0 Hz, $^3J_{HH}$ = 7.0 Hz, 1H, Ar), 2.30 (s, 3H, CH_3), 1.63 (s, 18H, C_6Me_6), 1.41 (d, $^3J_{PH}$ = 16.0 Hz, 3H, CH_3). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 10.2 (s). Selected ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 95.2 (s, *C*$_6$Me$_6$), 15.3 (br, C$_6$*Me*$_6$). Anal. Calcd for $C_{70}H_{52}BF_{24}PRu$ (**6a**): C, 56.35; H, 3.51. Found: C, 56.31; H, 3.26.

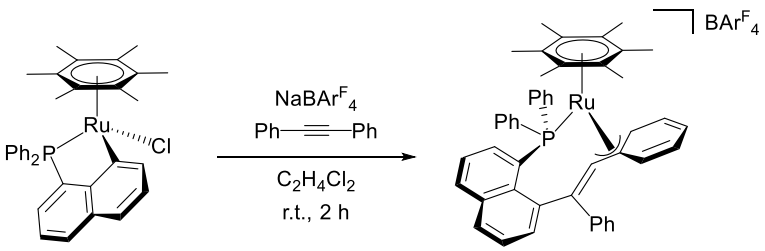
Synthesis of [(η⁶-C₆Me₆)Ru{η⁴-PPh₂(C₁₂H₆Et₂)}][BAr$^F_4$] (6b)



5 **6b** (59%)

A mixture of **5** (60.0 mg, 0.098 mmol), 3-hexyne (43.4 mg, 0.528 mmol) and NaBAr$^F_4$·2H$_2$O (99.7 mg, 0.108 mmol) in C$_2$H$_4$Cl$_2$ (4 mL) was stirred at room temperature for 2 h, then heated at 40 °C for 24 h. The resulting black green suspension was filtered through a short pad of Celite, and the pad was rinsed with C$_2$H$_4$Cl$_2$ (*ca*. 1 mL). The combined filtrate was dried in vacuo, and the residue was purified by column chromatography on silica gel (CH$_2$Cl$_2$: Et$_2$O = 1 : 2). The eluate was dried up in vacuo and recrystallized from CH$_2$Cl$_2$/hexane to afford **6b** (88.9 mg, 0.058 mmol, 59% yield) as black green crystals. **6b**: ^{1}H NMR (−80 °C, CD$_2$Cl$_2$): δ 7.90 (t, $^3J_{HH}$ = 8.0 Hz, 1H, Ar), 7.84–7.81 (m, 1H, Ar), 7.78–7.75 (br, 9H, Ar and BAr$^F_4$), 7.61–7.59 (m, 2H, Ar), 7.54–7.42 (m, 8H, Ar and BAr$^F_4$), 7.33 (t, $^3J_{HH}$ = 7.5 Hz, 2H, Ar), 7.26 (d, $^3J_{HH}$ = 8.0 Hz, 1H, Ar), 7.13 (d, $^3J_{HH}$ = 8.0 Hz, 1H, Ar), 7.06 (d, $^3J_{HH}$ = 7.0 Hz, 1H, Ar), 6.86 (br, 1H, Ar), 5.89 (br, 1H, Ar), 2.74 (br, 1H, *CH$_2$*CH$_3$), 2.44 (br, 1H, *CH$_2$*CH$_3$), 1.74 (t, $^3J_{HH}$ = 7.0 Hz, 3H, CH$_2$*CH$_3$*), 1.61 (br, 1H, *CH$_2$*CH$_3$), 1.47 (s, 18H, C$_6$Me$_6$), 1.27 (br, 1H, *CH$_2$*CH$_3$), 1.03 (t, $^3J_{HH}$ = 7.0 Hz 3H, CH$_2$*CH$_3$*). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 8.26 (s). Selected ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): 15.3 (s, C$_6$*Me$_6$*). Anal. Calcd for C$_{72}$H$_{56}$BF$_{24}$PRu (**6b**): C, 56.89; H, 3.71. Found: C, 56.77; H, 3.54.

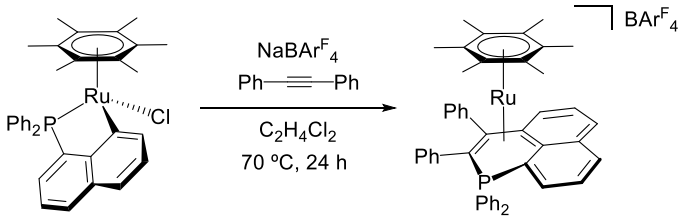
Synthesis of [(η⁶-C₆Me₆)Ru(PPh₂{C₁₀H₆C(Ph)=CPh})][BAr$^F_4$] (7)



5 **7** (88%)

A mixture of **5** (30.0 mg, 0.049 mmol), diphenylacetylene (43.9 mg, 0.246 mmol) and NaBAr$^F_4$·2H$_2$O (50.0 mg, 0.054 mmol) in C$_2$H$_4$Cl$_2$ (2 mL) was stirred at room temperature for 2 h. The resulting red suspension was filtered through a short pad of Celite, and the pad was rinsed with C$_2$H$_4$Cl$_2$ (*ca*. 1 mL). The filtrate was dried up in vacuo and recrystallized from CH$_2$Cl$_2$/hexane to afford 7 (70.1 mg, 0.043 mmol, 88% yield) as red crystals. 7: ^{1}H NMR (CD$_2$Cl$_2$): 8.28 (d, $^3J_{HH}$ = 8.0 Hz, 1H, Ar), 8.20–8.16 (m, 2H, Ar), 8.11–8.04 (m, 3H, Ar), 7.84 (t, $^3J_{HH}$ = 7.5 Hz, 1H, Ar), 7.73–7.66 (m, 11H, Ar and BAr$^F_4$), 7.63–7.54 (m, 9H, Ar and BAr$^F_4$), 6.94 (m, 3H, Ar), 6.82 (d, $^3J_{HH}$ = 7.4 Hz, 2H, Ar), 6.76 (m, 1H, Ar), 6.51 (m, 5H, Ar), 1.30 (s, 18H, C$_6$Me$_6$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 41.4 (s). Selected ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 102.5 (s, *C$_6$*Me$_6$), 15.6 (s, C$_6$*Me$_6$*). Anal. Calcd for C$_{80}$H$_{56}$BF$_{24}$PRu (7): C, 59.45; H, 3.49. Found: C, 59.19; H, 3.22.

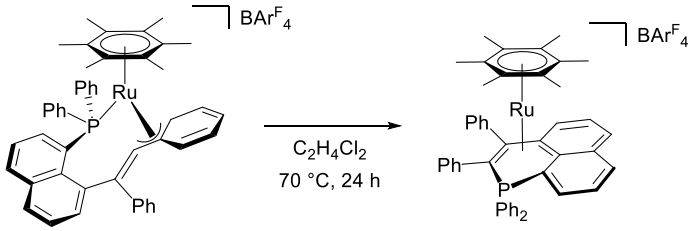
Synthesis of [(η⁶-C₆Me₆)Ru{η⁴-PPh₂(C₁₂H₆Ph₂)}][BAr$^F_4$] (6c)



5 **6c** (71%)

A mixture of **5** (59.9 mg, 0.098 mmol), diphenylacetylene (87.5 mg, 0.491 mmol) and NaBAr$^F_4$·2H₂O (100.0 mg, 0.108 mmol) in $C_2H_4Cl_2$ (4 mL) was heated at 70 °C for 24 h. The resulting black green suspension was filtered through a short pad of Celite, and the pad was rinsed with $C_2H_4Cl_2$ (*ca*. 1 mL). The combined filtrate was dried in vacuo, and the residue was purified by column chromatography on silica gel (CH_2Cl_2 : Et_2O = 1 : 2). The eluate was dried up in vacuo and recrystallized from CH_2Cl_2/hexane. The black green crystals were collected by filtration and dried under vacuum. A part of solvent molecules in the crystals gave off to give a sample with the empirical formula **6c · 0.35 (CH_2Cl_2) · 0.25 (C_6H_{14})** (112.0 mg, 0.069 mmol, 71% yield). The amount of the solvent molecules were determined by ^{1}H NMR as well as Elemental analysis. **6c**: ^{1}H NMR (CD_2Cl_2): 7.81 (t, $^3J_{HH}$ = 7.5 Hz, 1H, Ar), 7.75–7.71 (m, 9H, Ar and BAr$^F_4$), 7.64–7.60 (m, 3H, Ar), 7.57–7.47 (m, 9H, Ar and BAr$^F_4$), 7.43–7.34 (m, 5H, Ar), 7.31–7.27 (m, 2H, Ar), 7.22 (t, $^3J_{HH}$ = 7.0 Hz, 1H, Ar), 7.02–6.96 (m, 2H, Ar), 6.79 (t, $^3J_{HH}$ = 7.0 Hz, 2H, Ar), 6.62 (d, $^3J_{HH}$ = 7.5, 1H, Ar), 6.43 (d, $^3J_{HH}$ = 7.5, 2H, Ar), 6.32 (ddd, $^3J_{PH}$ = 12.5 Hz, $^3J_{HH}$ = 6.5 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, Ar), 1.65 (s, 18H, C_6Me_6). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 6.84 (s). Selected ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 96.3 (s, *C*$_6$Me$_6$), 94.2 (d, $^2J_{CP}$ = 12.5 Hz, Ru–C$_\beta$), 92.1 (d, $^2J_{CP}$ = 12.9 Hz, Ru–C$_\beta$), 78.5 (s, Ru–C$_\gamma$), 41.5 (d, $^1J_{CP}$ = 46.2 Hz, Ru–C$_\alpha$), 15.9 (s, C$_6$*Me*$_6$). Anal. Calcd for $C_{80}H_{56}BF_{24}PRu(CH_2Cl_2)_{0.35}(C_6H_{14})_{0.25}$ (**6c**): C, 58.96; H, 3.64. Found: C, 58.60; H, 3.41.

Synthesis of 6c from 7



7 **6c** (57%)

A solution of **7** (30.0 mg, 0.019 mmol) in $C_2H_4Cl_2$ (4 mL) was heated at 70 °C for 24 h. After removal of the solvent, the residue was purified by column chromatography on silica gel (CH_2Cl_2 : Et_2O = 1 : 2). The eluate was dried up in vacuo and recrystallization from CH_2Cl_2/hexane afforded 6c (17.2 mg, 0.011 mmol, 57% yield) as orange crystals.

3. Solid state structure of 2a and 2c

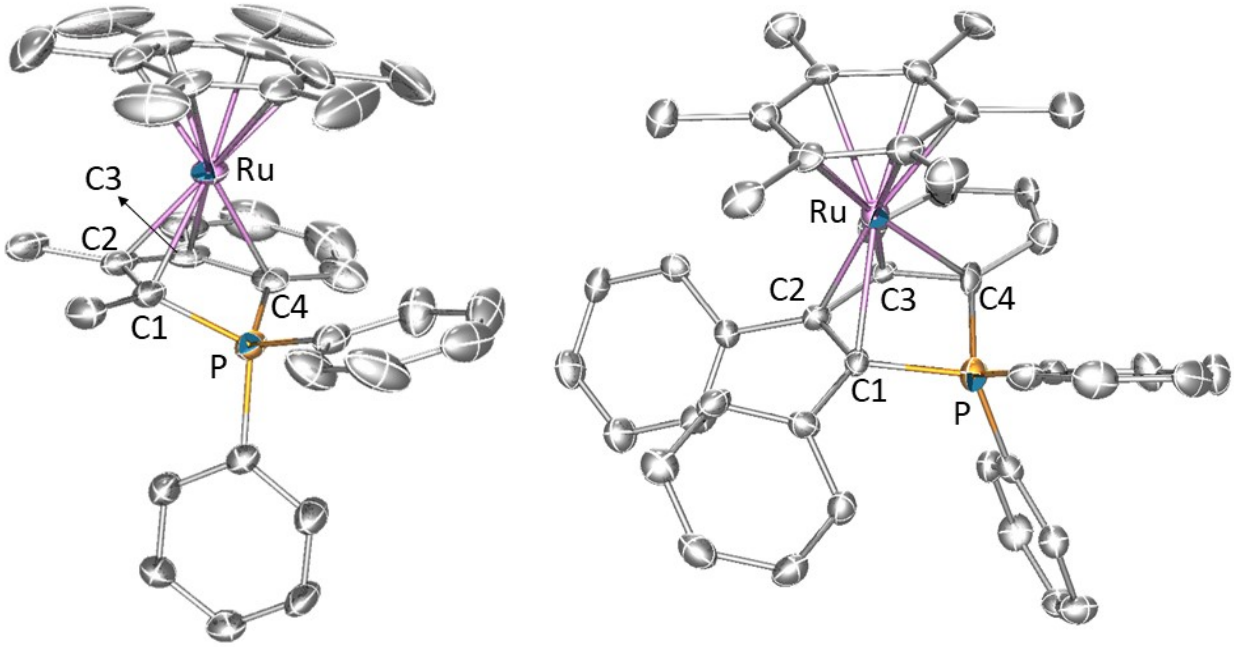


Figure S1. Molecular structure of the cationic part of **2a** (left) and **2c** (right) with 50% probability. All hydrogen atoms were omitted for clarity. Selected bond lengths of **2a** [Å]: C(1)–C(2): 1.460(6), C(2)–C(3): 1.433(7), C(3)–C(4): 1.459(6), Ru–C(1): 2.194(4), Ru–C(2): 2.135(4), Ru–C(3): 2.160(4), Ru–C(4): 2.244(4). Selected bond lengths of **2c** [Å]: C(1)–C(2): 1.459(8), C(2)–C(3): 1.450(8), C(3)–C(4): 1.453(8), Ru–C(1): 2.225(6), Ru–C(2): 2.150(6), Ru–C(3): 2.169(6), Ru–C(4): 2.236(6).

4. Solid state structure of 4

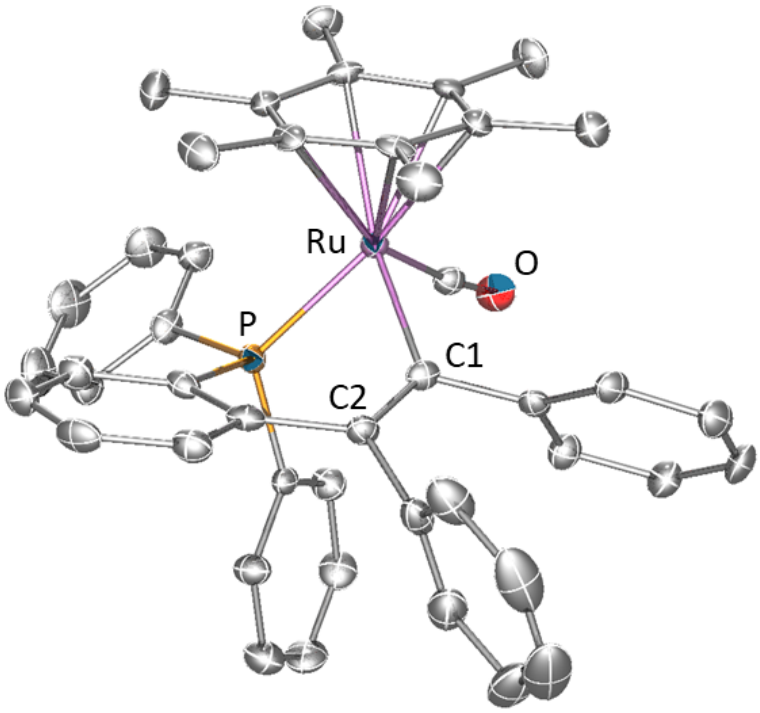


Figure S2. Molecular structure of the cationic part of CO adduct **4** with 50% probability. All hydrogen atoms were omitted for clarity. Selected bond lengths [Å]: Ru–C(1): 2.113(4), C(1)–C(2): 1.349(5).

5. Details for the optimized structure of 3

DFT(B3PW91) calculations were performed for the complex **3** with the Stuttgart/Dresden (SDD) ECP for Ru and 6-31G** for the other atoms using the Gaussian09 program package.[8] Optimized Cartesian coordinates for **3** were summarized in Table S1. All calculations were carried out using the computer facilities at the Research Center for Computational Science in Okazaki, Japan.

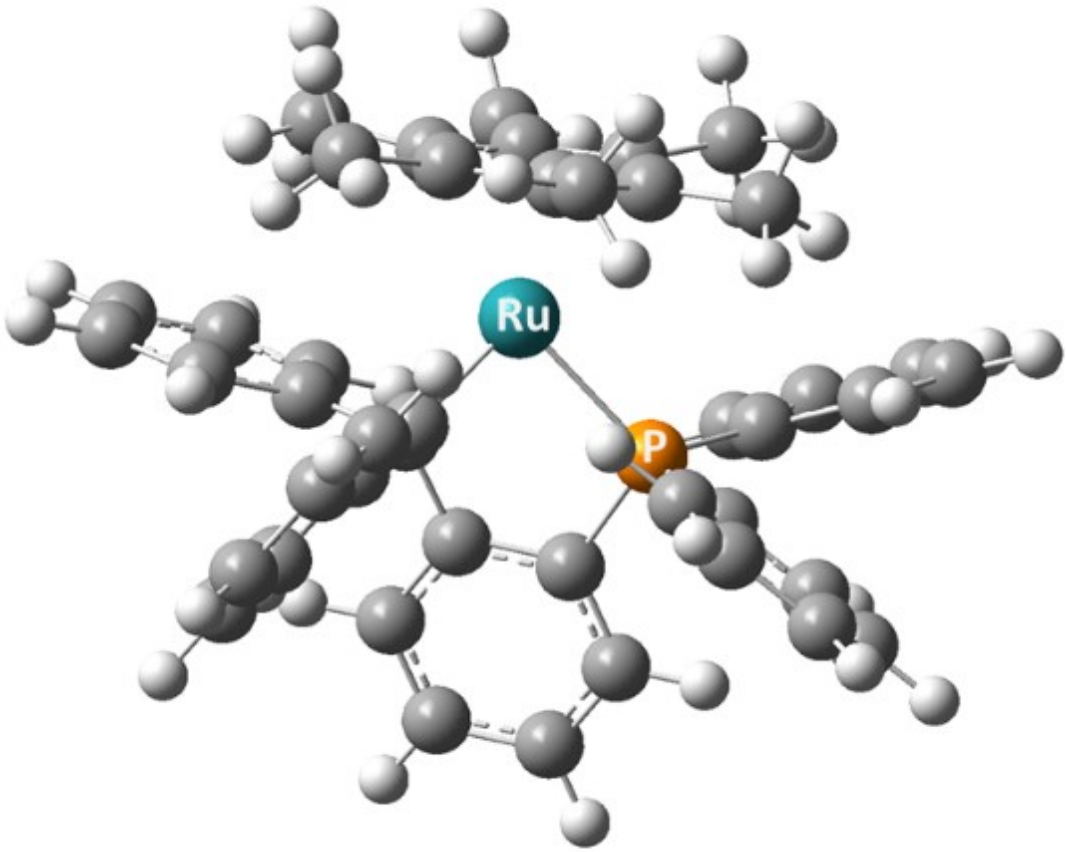


Figure S3. Optimized structure for **3**.

Table S1. Cartesian coordinates for the optimized structure of **3**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.993133	-2.234044	-1.871144
2	6	0	-2.750096	0.365443	-3.181457
3	6	0	2.450266	3.979162	-0.758876
4	6	0	3.663703	4.267394	-0.138449
5	6	0	1.846517	2.738136	-0.565701
6	6	0	-1.633946	-1.632565	-2.107630
7	6	0	-1.496638	-0.373781	-2.782280

8	6	0	4.270082	3.312643	0.677296
9	6	0	2.446907	1.772117	0.250036
10	6	0	-0.671528	-3.815046	-1.239566
11	6	0	-0.481462	-2.444598	-1.829982
12	6	0	3.668207	2.072324	0.872572
13	6	0	0.020645	1.357174	-3.947705
14	6	0	-0.196743	0.122334	-3.108115
15	6	0	4.088482	-0.982480	0.019869
16	6	0	0.799006	-1.984986	-2.204514
17	6	0	-0.489489	0.016028	2.338652
18	6	0	0.946815	-0.656304	-2.738869
19	6	0	5.040073	-1.995620	0.134217
20	6	0	2.873729	-1.068321	0.712957
21	6	0	0.873793	0.315091	2.235947
22	6	0	4.788630	-3.106991	0.935406
23	6	0	-1.073676	0.019116	3.615694
24	6	0	2.629213	-2.191267	1.517595
25	6	0	1.975402	-2.921239	-2.088267
26	6	0	3.580840	-3.202264	1.627190
27	6	0	2.311823	-0.136359	-3.114311
28	6	0	1.633510	0.629247	3.366763
29	6	0	-0.314974	0.320742	4.742023
30	6	0	1.039791	0.633756	4.623666
31	1	0	-3.179321	-3.000108	-2.634794
32	1	0	-3.457080	0.437349	-2.353534
33	1	0	-3.067012	-2.715905	-0.896189
34	1	0	-2.555785	1.380619	-3.519014
35	1	0	1.971890	4.721544	-1.391115
36	1	0	-3.797945	-1.506054	-1.932860
37	1	0	-3.251128	-0.165002	-3.999222
38	1	0	4.137033	5.233147	-0.288633
39	1	0	0.895007	2.505803	-1.034480
40	1	0	-1.379716	-3.788090	-0.409098
41	1	0	-0.909853	1.846765	-4.227675
42	1	0	5.215813	3.533219	1.163395
43	1	0	0.532799	1.089694	-4.878883
44	1	0	0.262678	-4.230097	-0.864891
45	1	0	4.308111	-0.113066	-0.592120

46	1	0	-1.071784	-4.507704	-1.990233
47	1	0	4.160620	1.336838	1.501066
48	1	0	5.982382	-1.909431	-0.398988
49	1	0	0.647188	2.096730	-3.442152
50	1	0	-2.126537	-0.221050	3.725316
51	1	0	5.532794	-3.892430	1.027116
52	1	0	2.231160	-3.147814	-1.049746
53	1	0	2.374391	0.946717	-3.004072
54	1	0	1.698068	-2.266799	2.071542
55	1	0	2.868080	-2.528488	-2.569709
56	1	0	2.537299	-0.378072	-4.160753
57	1	0	3.382523	-4.060919	2.261992
58	1	0	1.733287	-3.866816	-2.583396
59	1	0	3.097639	-0.569502	-2.498412
60	1	0	2.690765	0.854887	3.270116
61	1	0	-0.786158	0.313616	5.720743
62	1	0	1.629186	0.869061	5.504357
63	15	0	1.549744	0.197987	0.549583
64	44	0	-0.280183	-0.307978	-0.801075
65	6	0	-1.322047	-0.202268	1.099296
66	6	0	-1.337422	0.901606	0.166824
67	6	0	-2.006435	2.174152	0.136616
68	6	0	-1.902554	3.030348	-0.979534
69	6	0	-2.738029	2.615154	1.262067
70	6	0	-2.529214	4.267223	-0.983817
71	1	0	-1.320082	2.700535	-1.833147
72	6	0	-3.352724	3.859879	1.259541
73	1	0	-2.804513	1.973050	2.134264
74	6	0	-3.255165	4.683136	0.136174
75	1	0	-2.450502	4.916854	-1.850347
76	1	0	-3.908158	4.192476	2.130963
77	1	0	-3.739168	5.655438	0.135154
78	6	0	-2.532474	-1.064939	1.295475
79	6	0	-3.832029	-0.653331	0.967298
80	6	0	-2.369776	-2.350291	1.842383
81	6	0	-4.926373	-1.493086	1.176105
82	1	0	-3.998378	0.335763	0.552122
83	6	0	-3.460440	-3.189692	2.048706

84	1	0	-1.372066	-2.685261	2.113202
85	6	0	-4.747776	-2.764225	1.715662
86	1	0	-5.923963	-1.145593	0.922078
87	1	0	-3.306797	-4.176528	2.476588
88	1	0	-5.600622	-3.415224	1.882162

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6. X-ray Crystallographic data for 2a-c, 4, 6a, 7

	2a	2b	2c
CCDC	1826396	1826397	1826399
formula	$C_{66}H_{50}BF_{24}PRu$	$C_{68}H_{54}BF_{24}PRu$	$C_{76}H_{54}BF_{24}PRu$
fw	1441.91	1469.96	1566.04
crystal dimension	0.27 × 0.19 × 0.17	0.2 × 0.18 × 0.17	0.22 × 0.09 × 0.04
crystal system	monoclinic	triclinic	monoclinic
space group	*P* $2_1/n$	*P* -1	*P* $2_1/c$
a, Å	13.7640(16)	12.9248(16)	18.038(3)
b, Å	17.7878(19)	13.0190(15)	19.730(4)
c, Å	25.873(3)	19.015(2)	19.271(4)
α, deg	90	82.752(4)	90
β, deg	103.531(2)	84.077(3)	95.329(4)
γ, deg	90	84.036(4)	90
V, Å^3	6158.7(12)	3143.7(7)	6829(2)
Z	4	2	4
σ_{calcd}, g cm^{-3}	1.555	1.553	1.523
F(000)	2904	1484	3160
μ, cm^{-1}	3.95	3.89	3.63
transmission factors range	0.9316 – 0.9597	0.9139 – 0.9322	0.9578 – 0.9868
index range	−16 ≤ h ≤ 16 −21 ≤ k ≤ 21 −31 ≤ l ≤ 24	−15 ≤ h ≤ 12 −15 ≤ k ≤ 15 −23 ≤ l ≤ 23	−20 ≤ h ≤ 22 −24 ≤ k ≤ 24 −21 ≤ l ≤ 23
no. reflections	45157	23489	50216
unique (R_{int})	12045 (0.0572)	12065 (0.0389)	13198 (0.1331)
$I > 2\sigma(I)$	9867	9533	9241
no. parameters	847	864	934
R1 ($I > 2\sigma(I)$)[a]	0.0693	0.0512	0.1018
wR2 (all data)[b]	0.1737	0.1271	0.1907
GOF [c]	1.091	1.052	1.158
max diff peak / hole, e Å^{-3}	1.101/−1.118	0.725/−0.744	0.735/−0.578

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2F_o^2 + (aP)^2 + bP]$ (a and b are constants suggested by the refinement program; $P = [\max(F_o^2,0) + 2F_c^2]/3$). [c] $GOF = [\Sigma w(F_o^2 - F_c^2)^2/(N_{obs} - N_{params})]^{1/2}$.

Table S1. X-ray Crystallographic Data for **2a-c**.

	4	**6a**	**7**
CCDC	1826398	1826401	1826400
formula	$C_{77}H_{54}BF_{24}OPRu$	$C_{70}H_{52}BF_{24}PRu$	$C_{80}H_{56}BF_{24}PRu$
fw	1594.05	1491.96	1616.09
crystal dimension	0.18 × 0.13 × 0.1	0.24 × 0.23 × 0.19	0.22 × 0.12 × 0.01
crystal system	triclinic	triclinic	triclinic
space group	*P* -1	*P* -1	*P* -1
a, Å	12.7071(14)	17.512(2)	12.285(5)
b, Å	15.3471(14)	19.924(3)	15.887(7)
c, Å	19.473(2)	21.061(3)	18.760(8)
α, deg	111.924(4)	109.8153(14)	86.105(14)
β, deg	92.508(5)	93.4840(15)	79.344(16)
γ, deg	99.722(7)	110.4807(13)	84.218(15)
V, Å^3	3448.6(7)	6340.9(15)	3575(3)
Z	2	4	2
ρ_{calcd}, g cm^{-3}	1.535	1.563	1.501
F(000)	1608	3008	1632
μ, cm^{-1}	3.62	3.87	3.49
transmission factors range	0.8764 – 0.9444	0.919 – 0.93	0.9497 – 0.9824
index range	−16 ≤ h ≤ 16 −19 ≤ k ≤ 19 −25 ≤ l ≤ 17	−21 ≤ h ≤ 22 −25 ≤ k ≤ 25 −27 ≤ l ≤ 21	−15 ≤ h ≤ 15 −18 ≤ k ≤ 19 −22 ≤ l ≤ 23
no. reflections	28579	52661	26144
unique (R_{int})	15231 (0.0536)	27980 (0.0517)	13692 (0.0835)
$I > 2\sigma(I)$	9836	18005	8705
no. parameters	951	1803	983
R1 ($I > 2\sigma(I)$)[a]	0.06	0.0687	0.106
wR2 (all data)[b]	0.1617	0.1771	0.2207
GOF [c]	0.996	1.066	1.091
max diff peak / hole, e Å^{-3}	1.856/−0.881	1.045/−0.948	0.707/−0.926

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma\{w(F_o^2 - F_c^2)^2\}7/\Sigma w(F_o^2)^2]^{1/2}$, w = $1/[\sigma^2F_o^2 + (aP)^2 + bP]$ (*a* and *b* are constants suggested by the refinement program; P = $[\max(F_o^2,0) + 2F_c^2]/3$). [c]GOF = $[\Sigma w(F_o^2 - F_c^2)^2/(N_{obs} - N_{params})]^{1/2}$.

Table S2. X-ray Crystallographic Data for **4**, **6a** and **7**.

7. ^{1}H and ^{13}C NMR charts for the new compounds

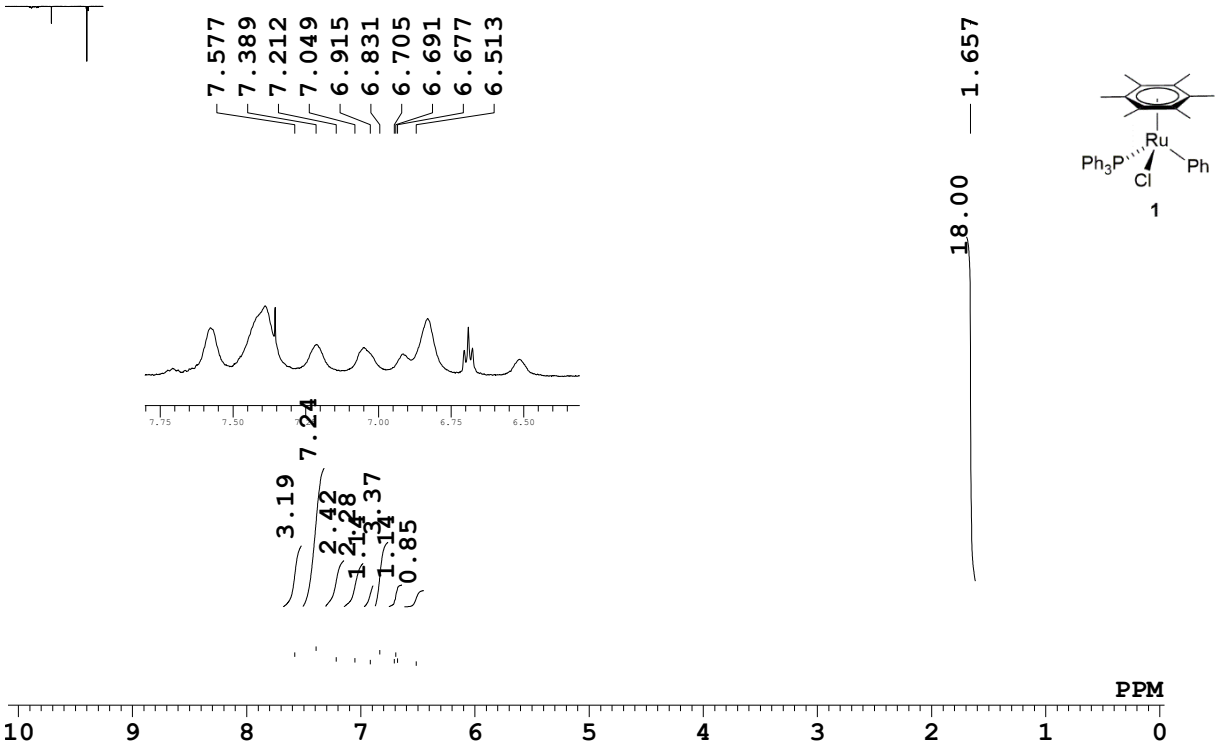

Figure S4. ^{1}H NMR spectra of **1** recorded in CD_2Cl_2.

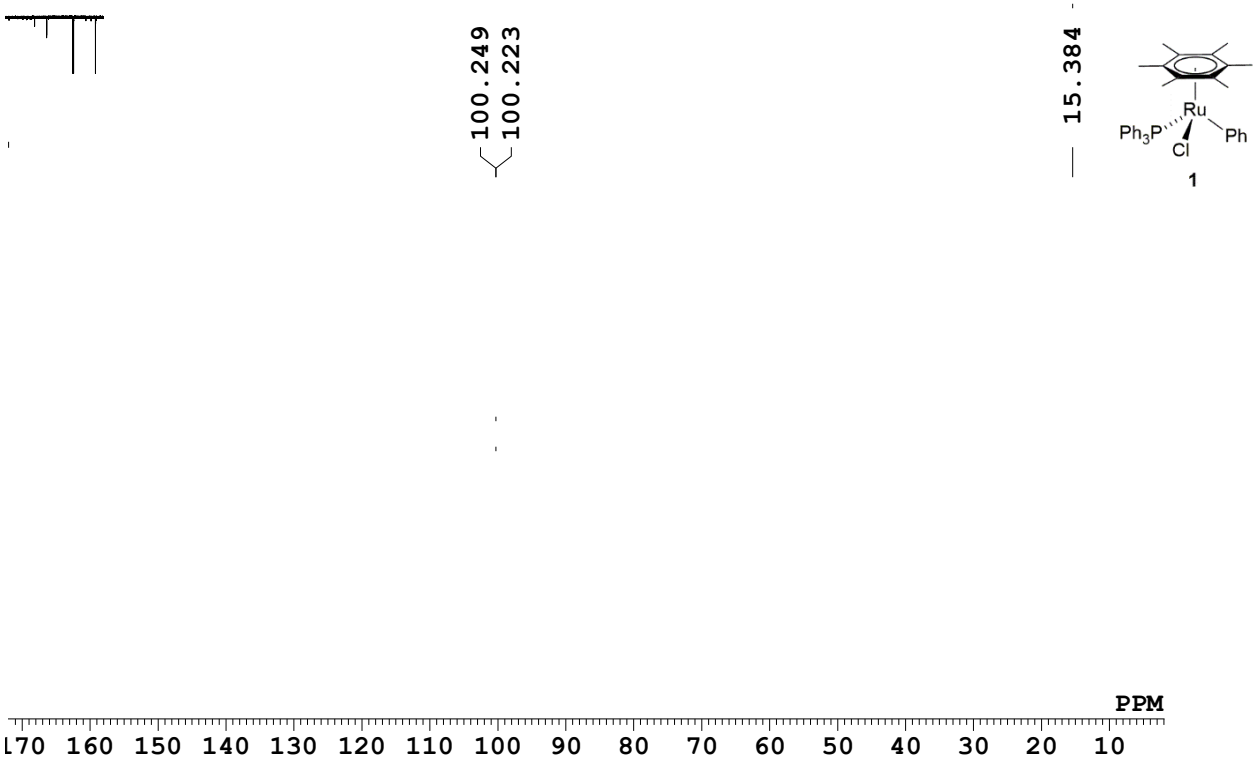

Figure S5. $^{13}C\{^{1}H\}$ NMR spectra of **1** recorded in CD_2Cl_2.

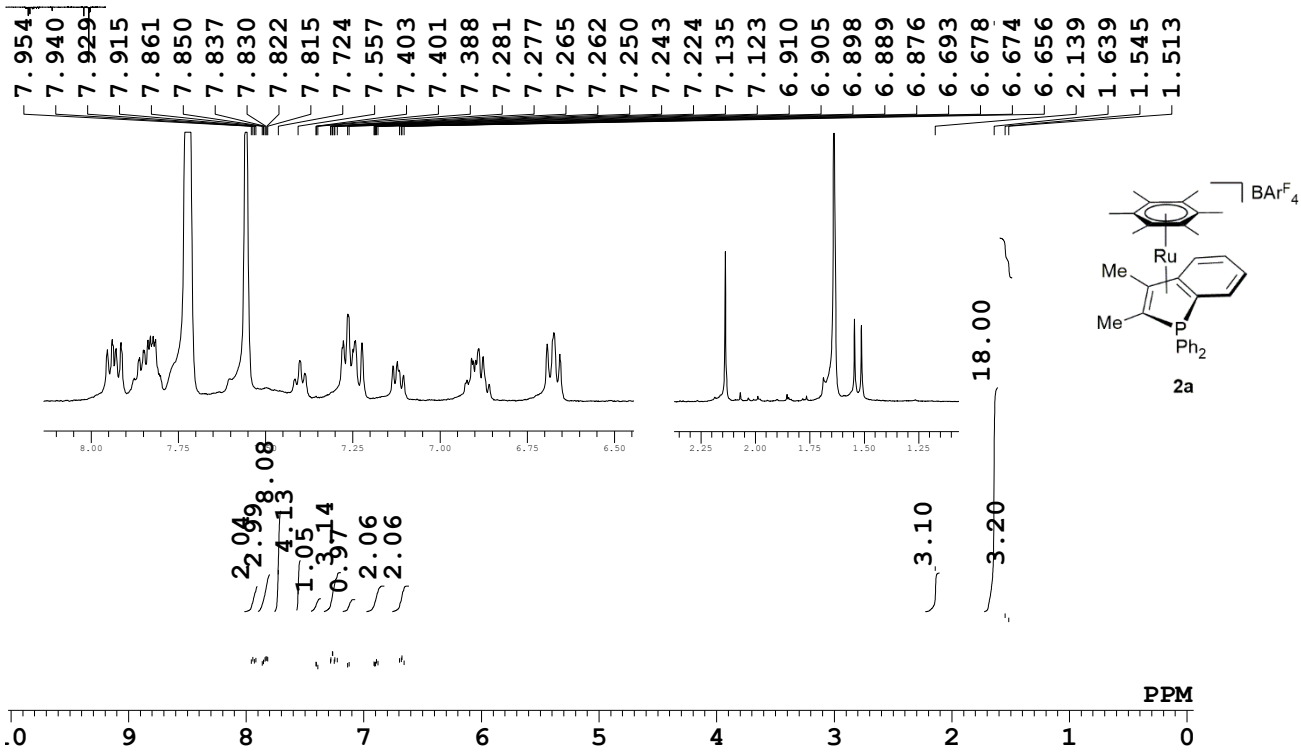

Figure S6. ^{1}H NMR spectra of **2a** recorded in CD_2Cl_2.

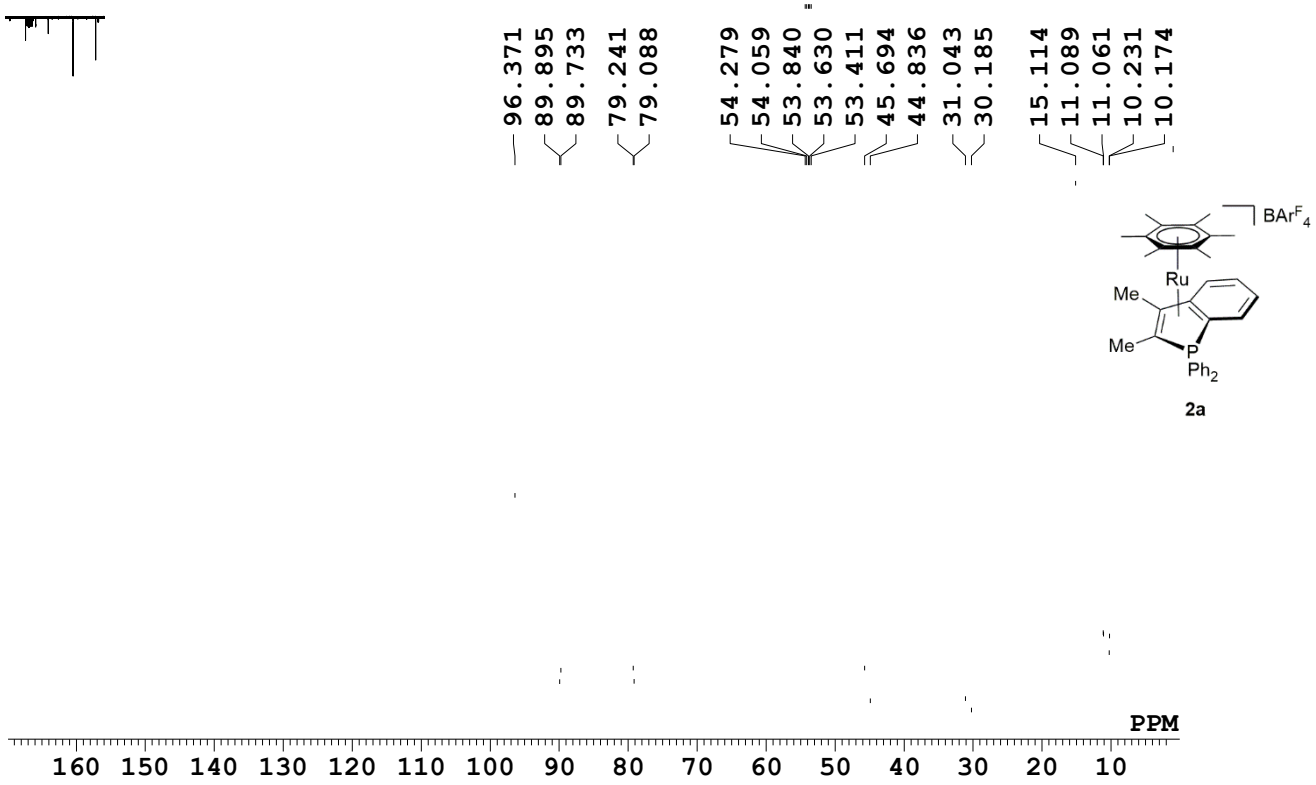

Figure S7. $^{13}C\{^{1}H\}$ NMR spectra of **2a** recorded in CD_2Cl_2.

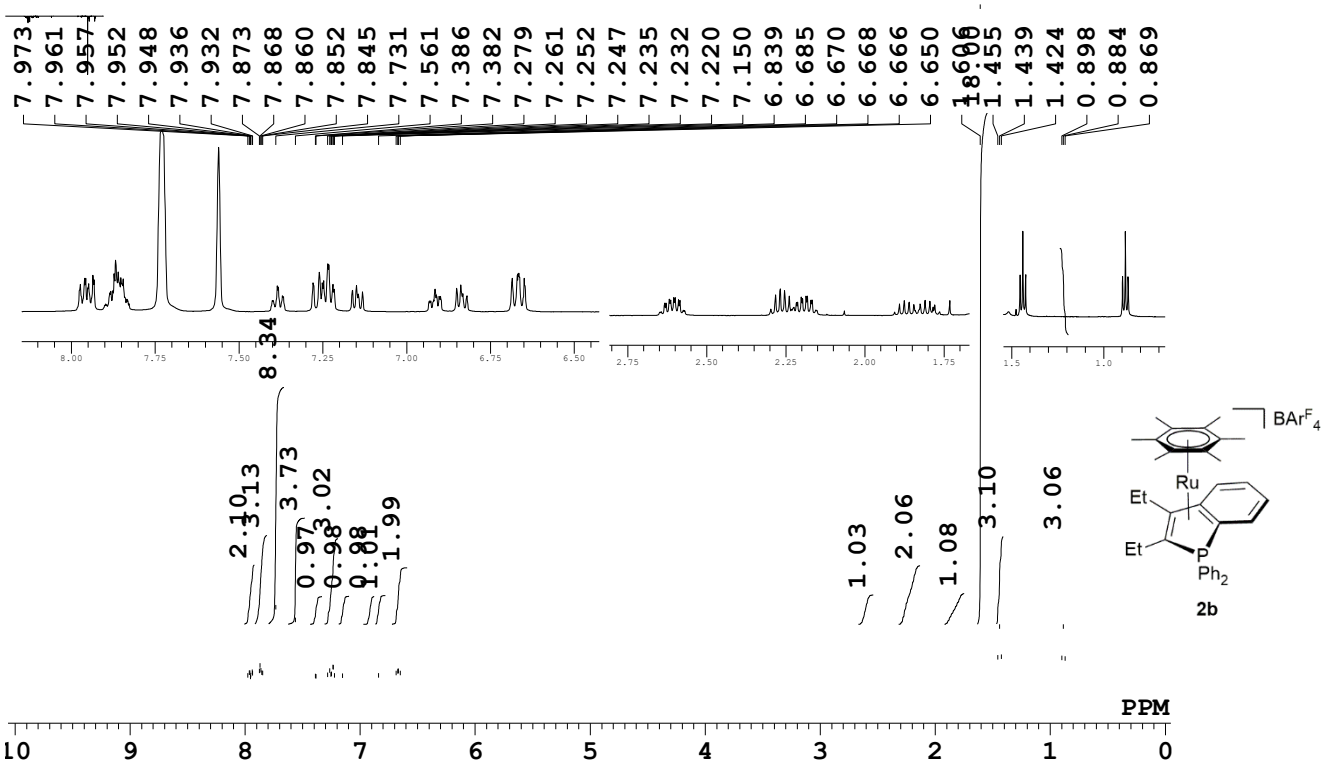

Figure S8. ^{1}H NMR spectra of **2b** recorded in CD_2Cl_2.

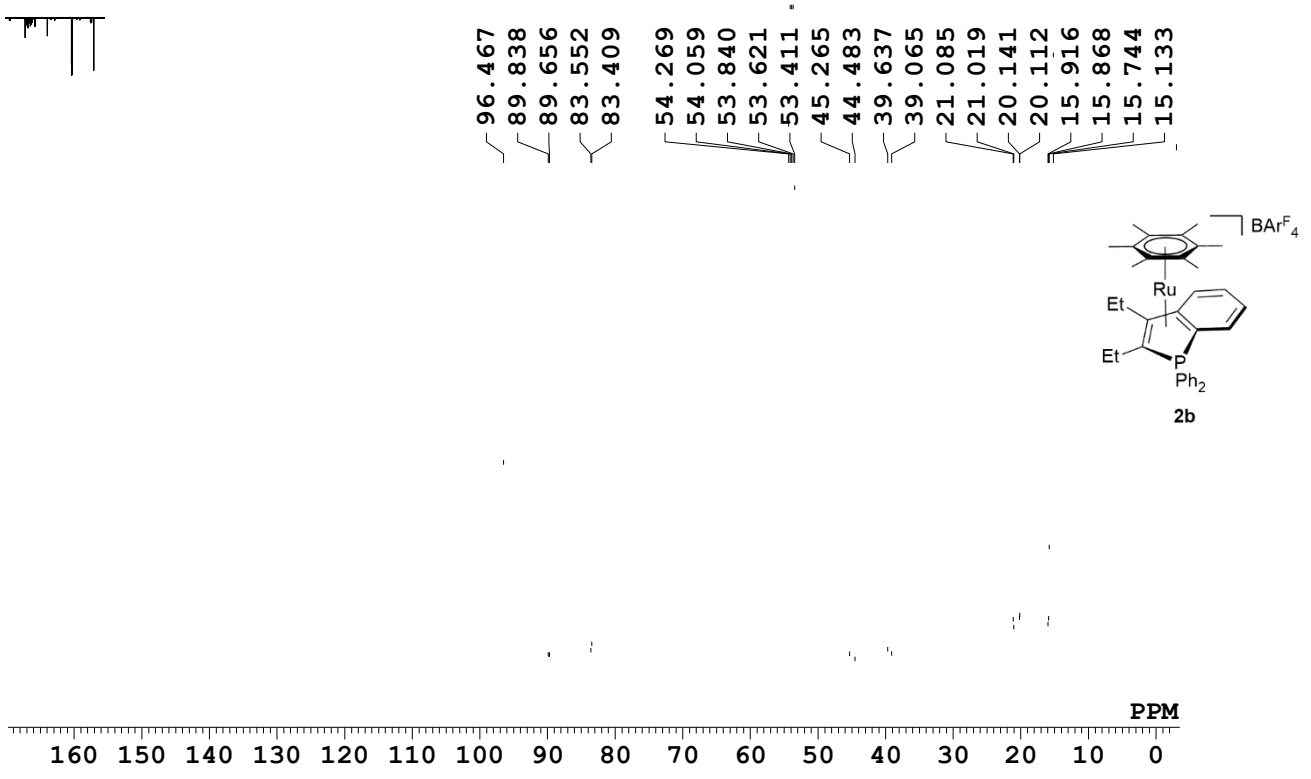

Figure S9. $^{13}C\{^{1}H\}$ NMR spectra of **2b** recorded in CD_2Cl_2.

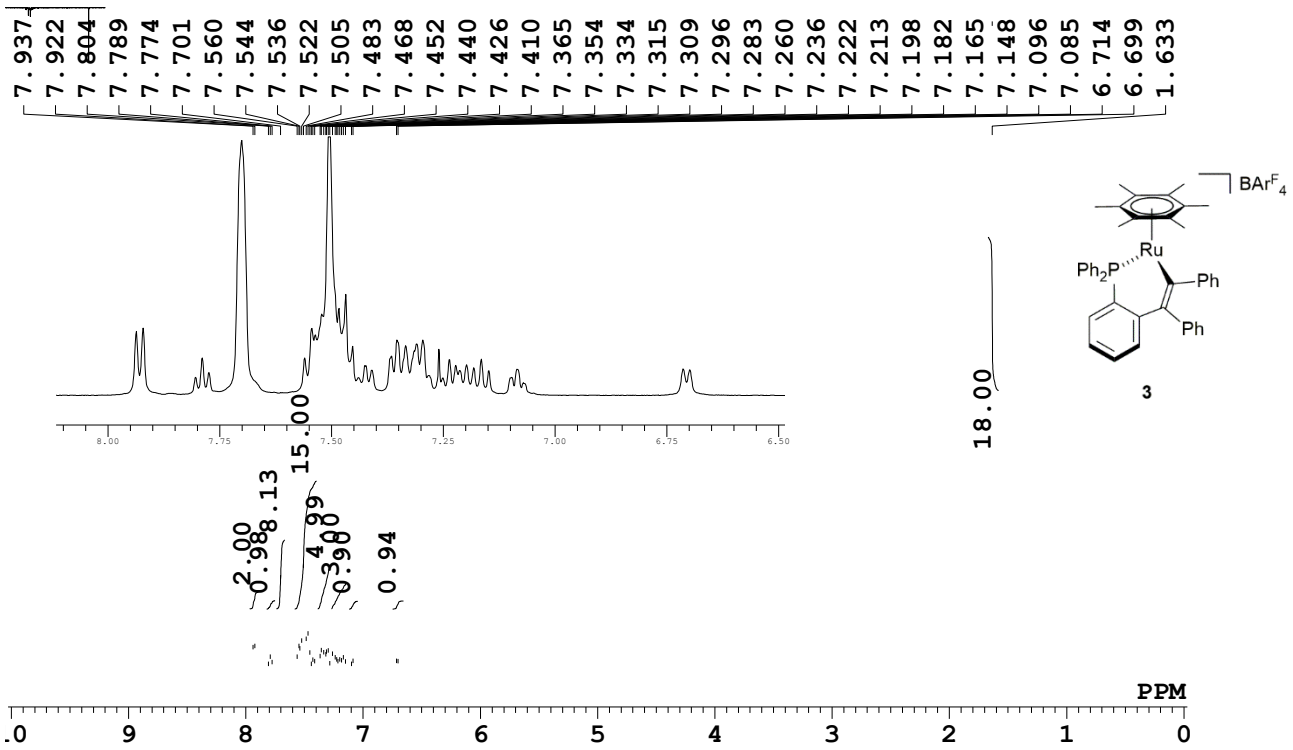

Figure S10. ^{1}H NMR spectra of **3** recorded in $CDCl_3$.

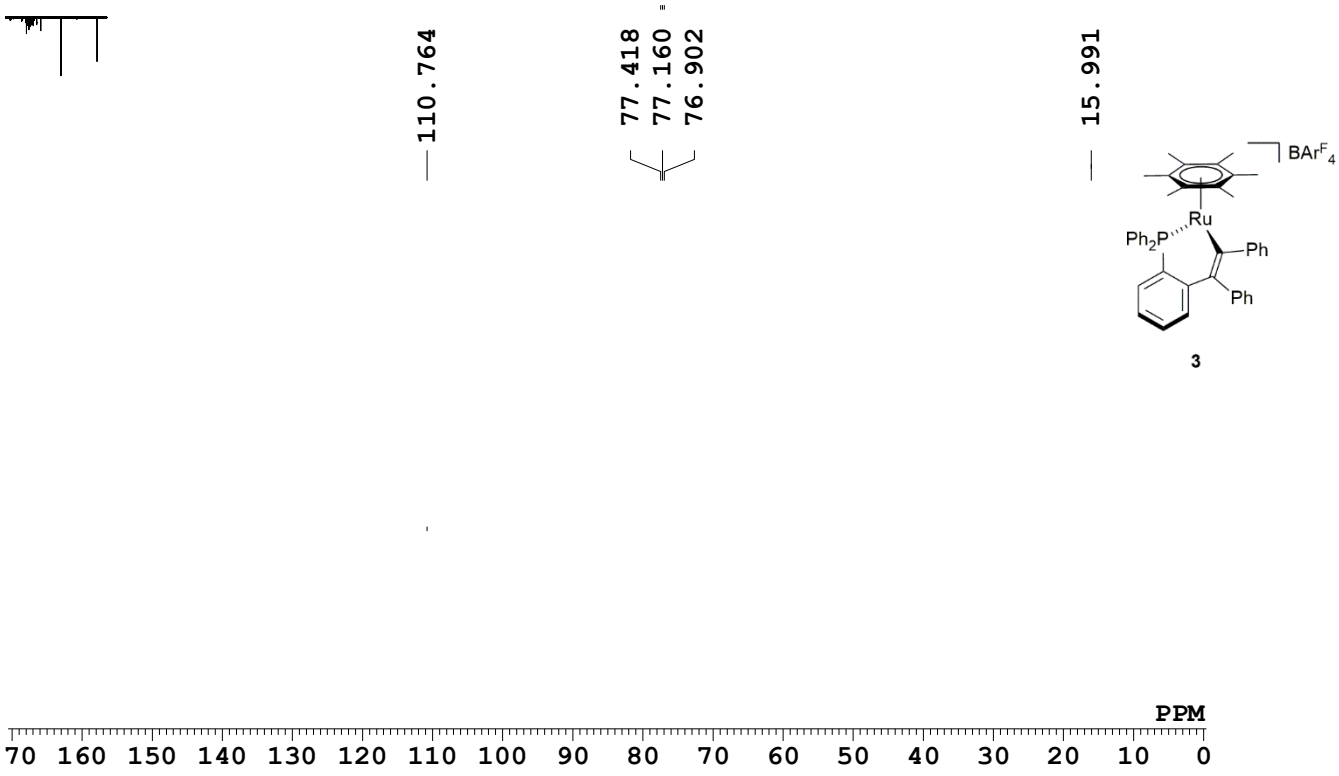

Figure S11. $^{13}C\{^{1}H\}$ NMR spectra of **3** recorded in $CDCl_3$.

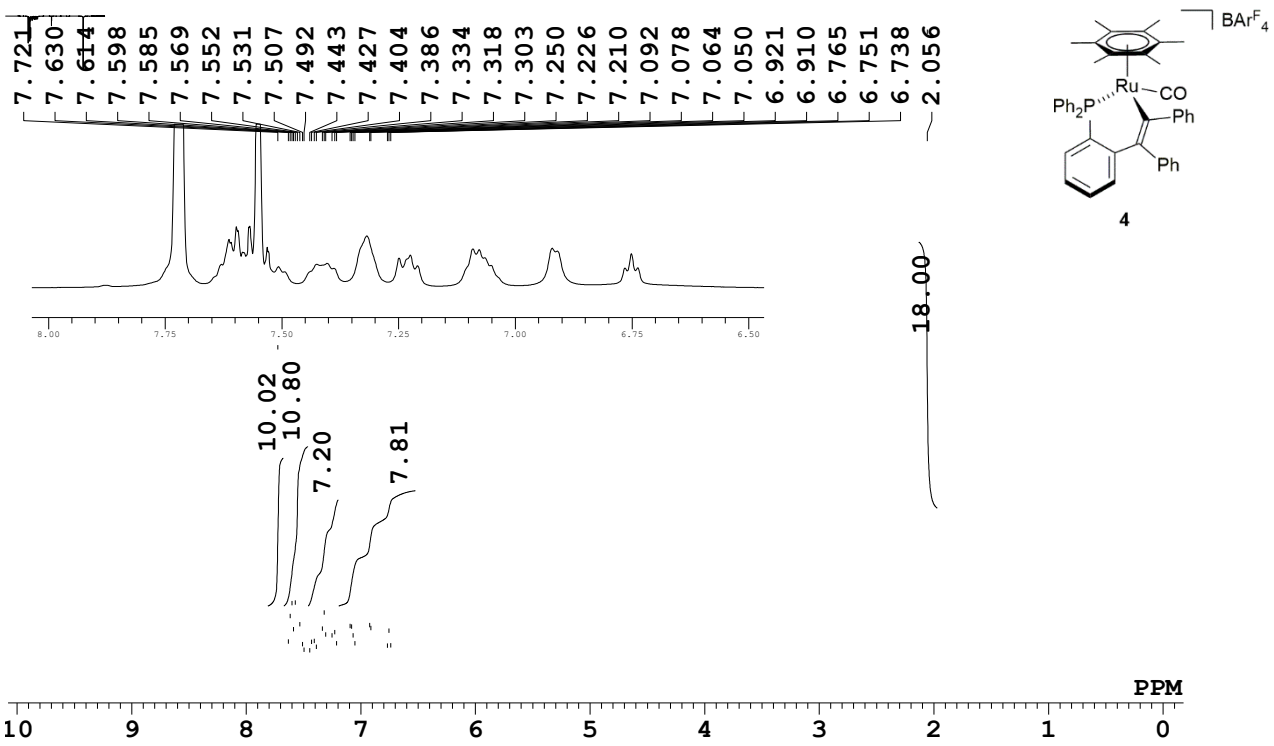

Figure S12. ^{1}H NMR spectra of **4** recorded in CD_2Cl_2.

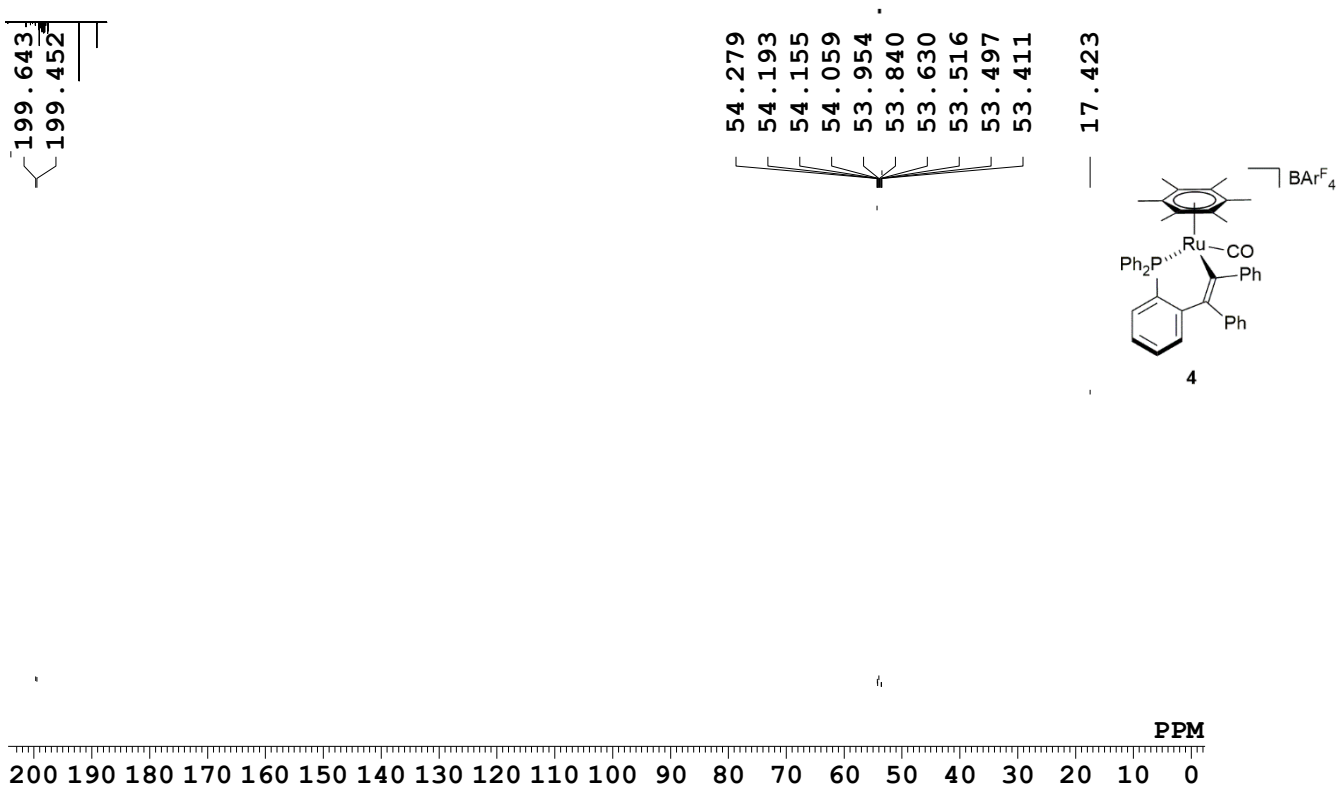

Figure S13. $^{13}C\{^1H\}$ NMR spectra of **4** recorded in CD_2Cl_2.

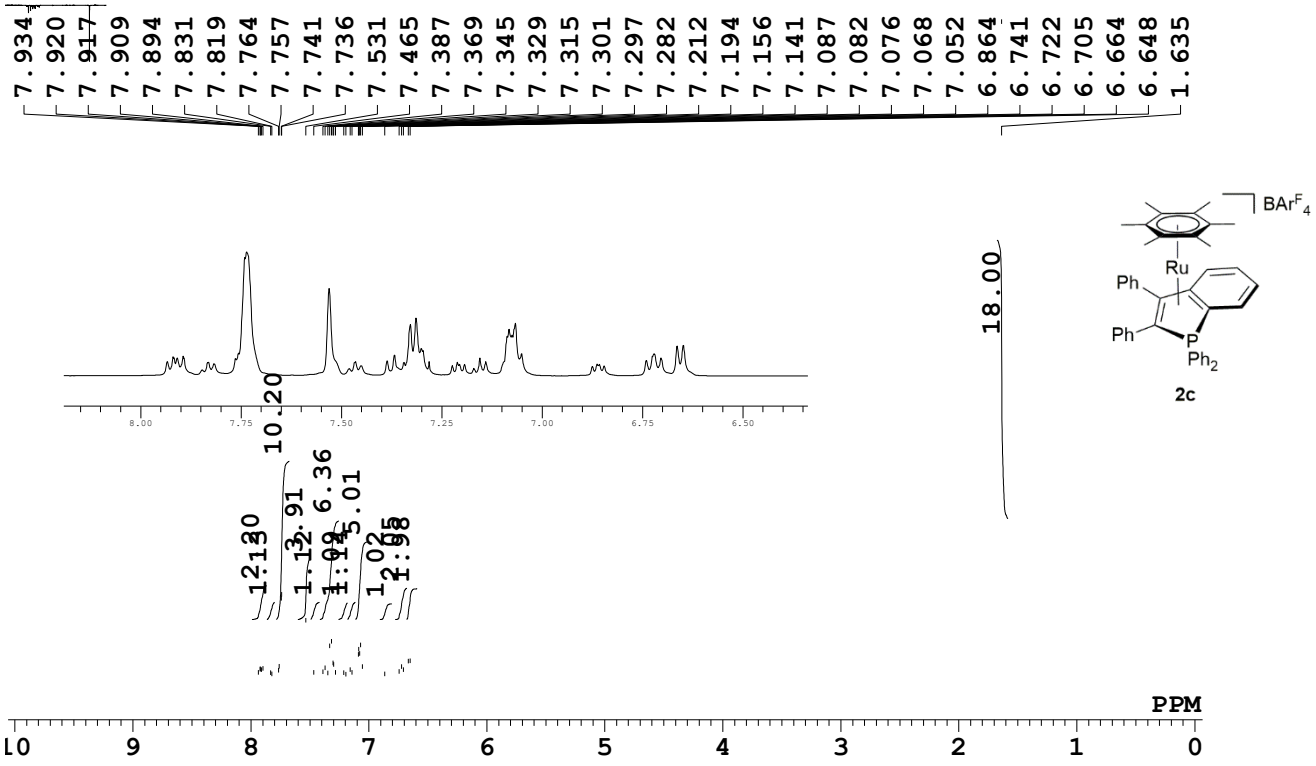

Figure S14. ^{1}H NMR spectra of **2c** recorded in $CDCl_3$.

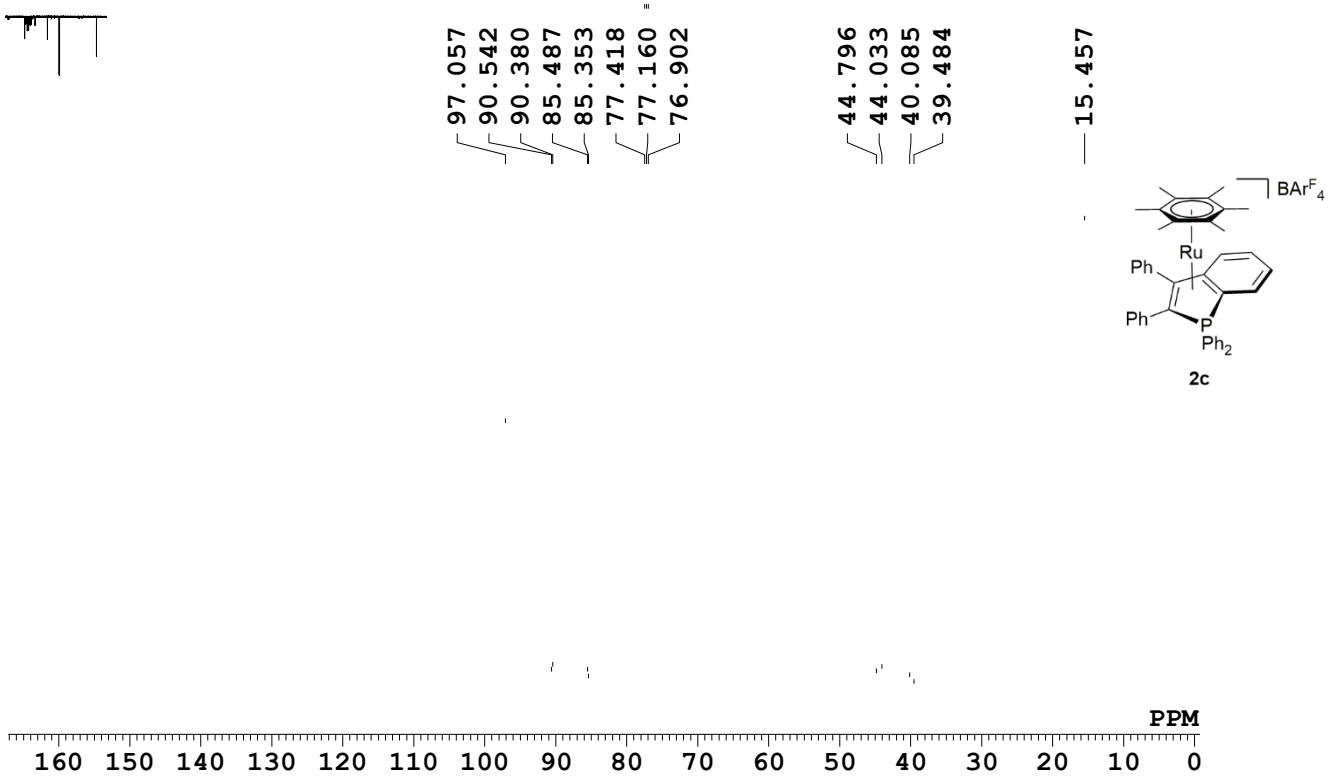

Figure S15. $^{13}C\{^{1}H\}$ NMR spectra of **2c** recorded in $CDCl_3$.

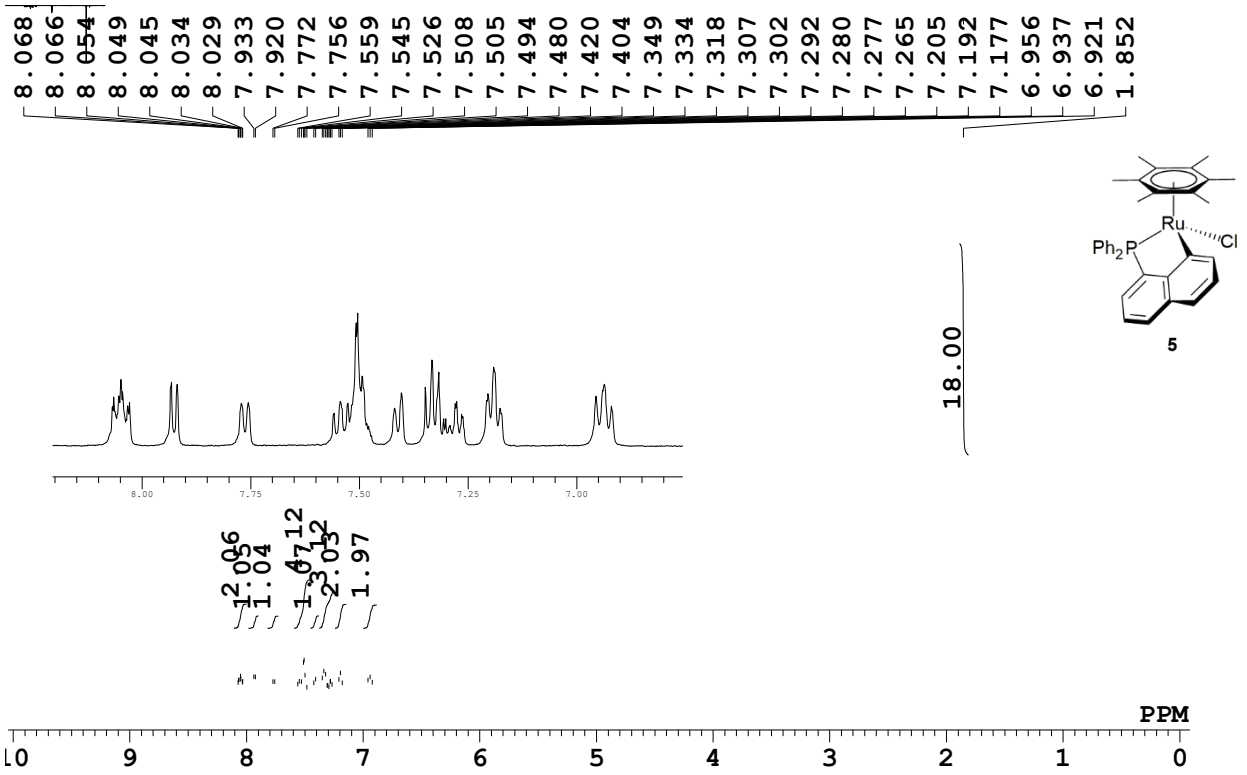

Figure S16. ^{1}H NMR spectra of **5** recorded in CD_2Cl_2.

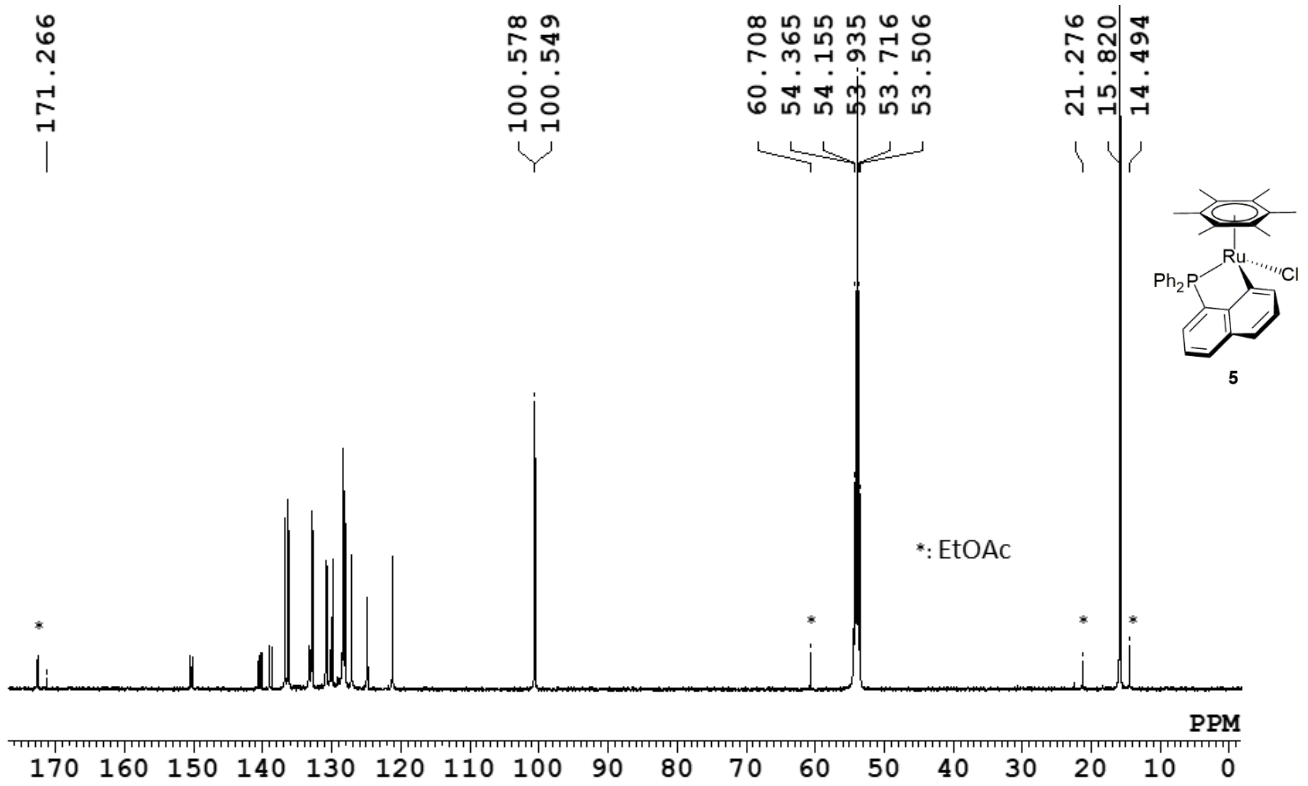

Figure S17. $^{13}C\{^{1}H\}$ NMR spectra of **5** recorded in CD_2Cl_2.

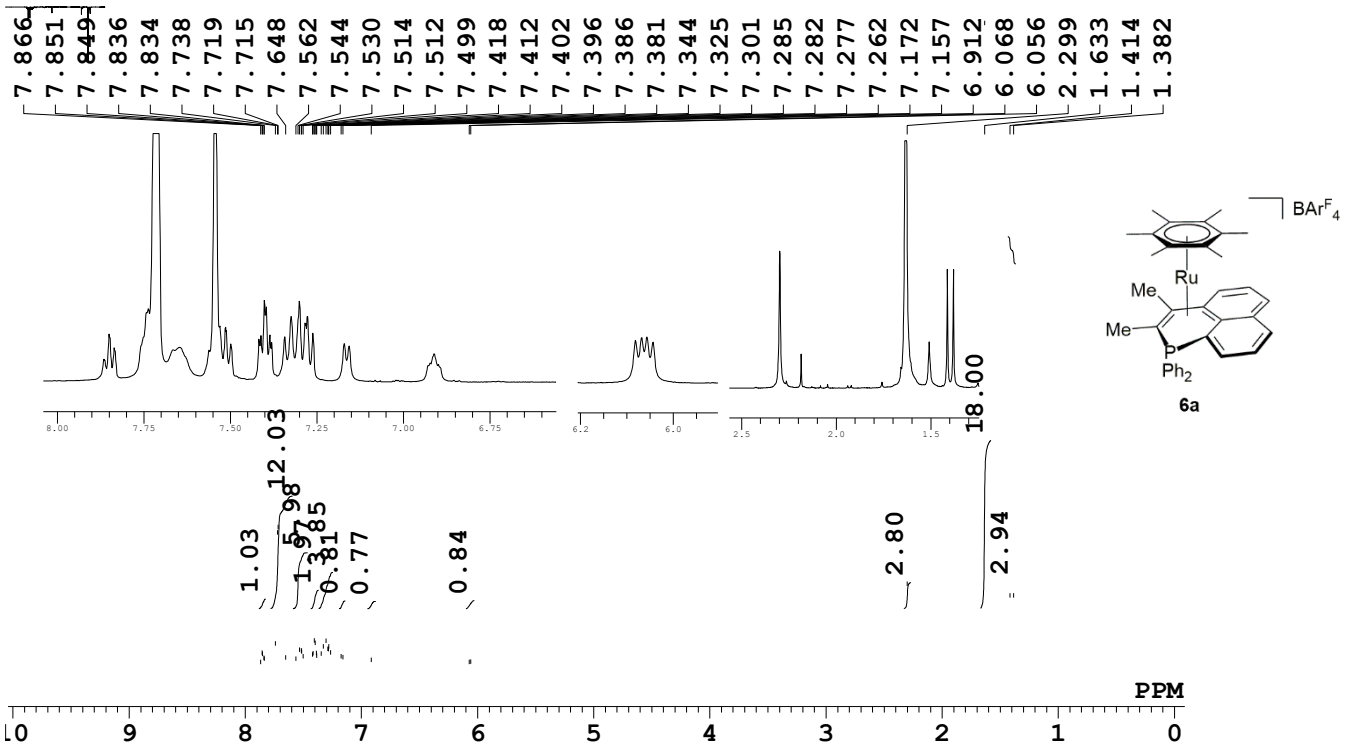

Figure S18. ^{1}H NMR spectra of **6a** recorded in CD_2Cl_2.

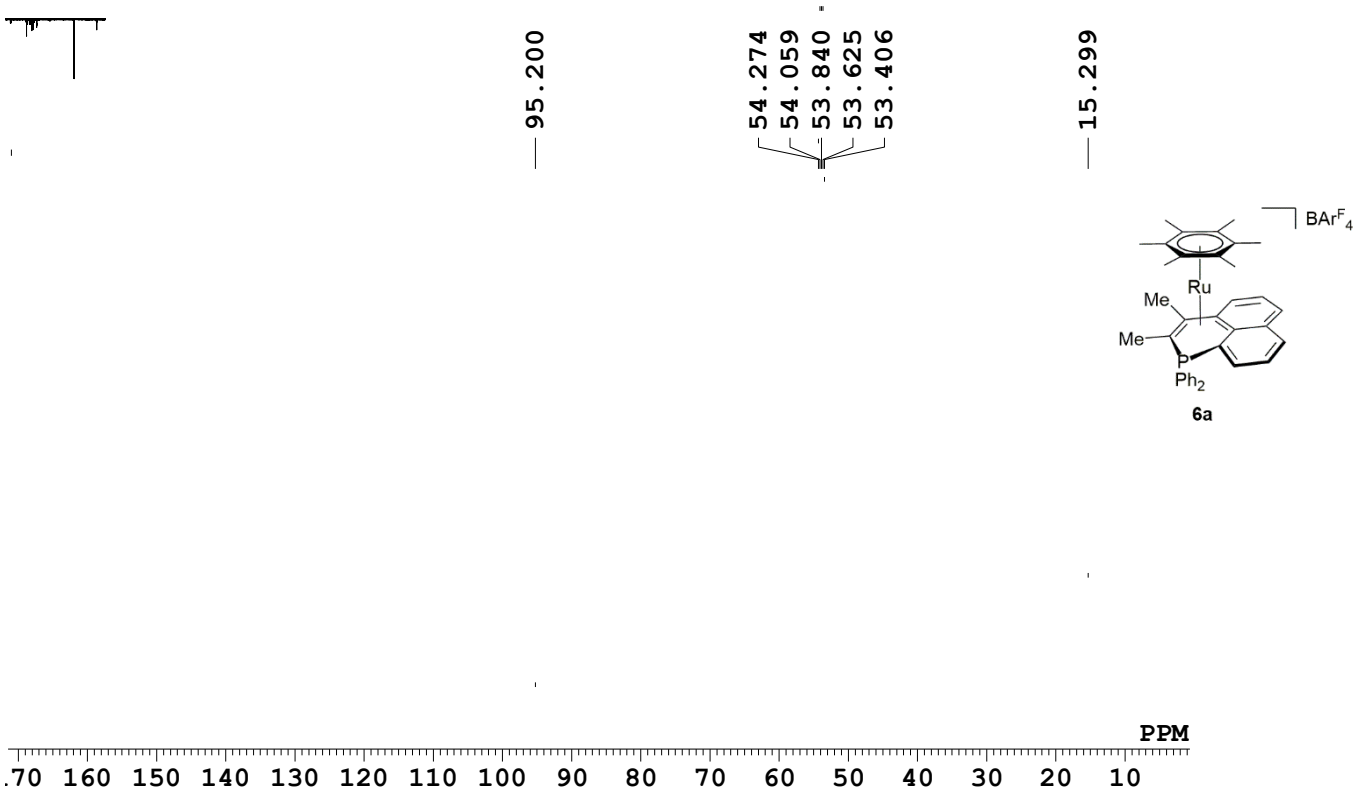

Figure S19. $^{13}C\{^{1}H\}$ NMR spectra of **6a** recorded in CD_2Cl_2.

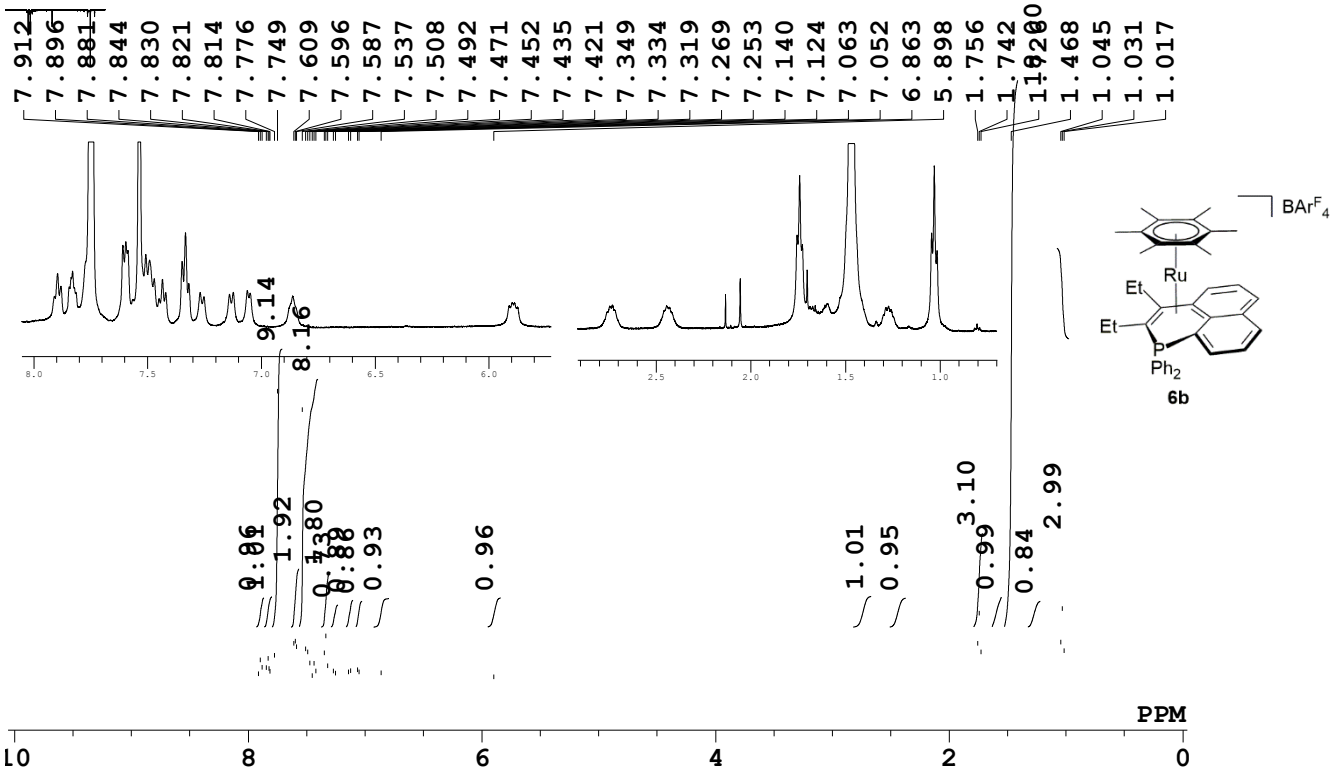

Figure S20. ^{1}H NMR spectra of **6b** recorded in CD_2Cl_2.

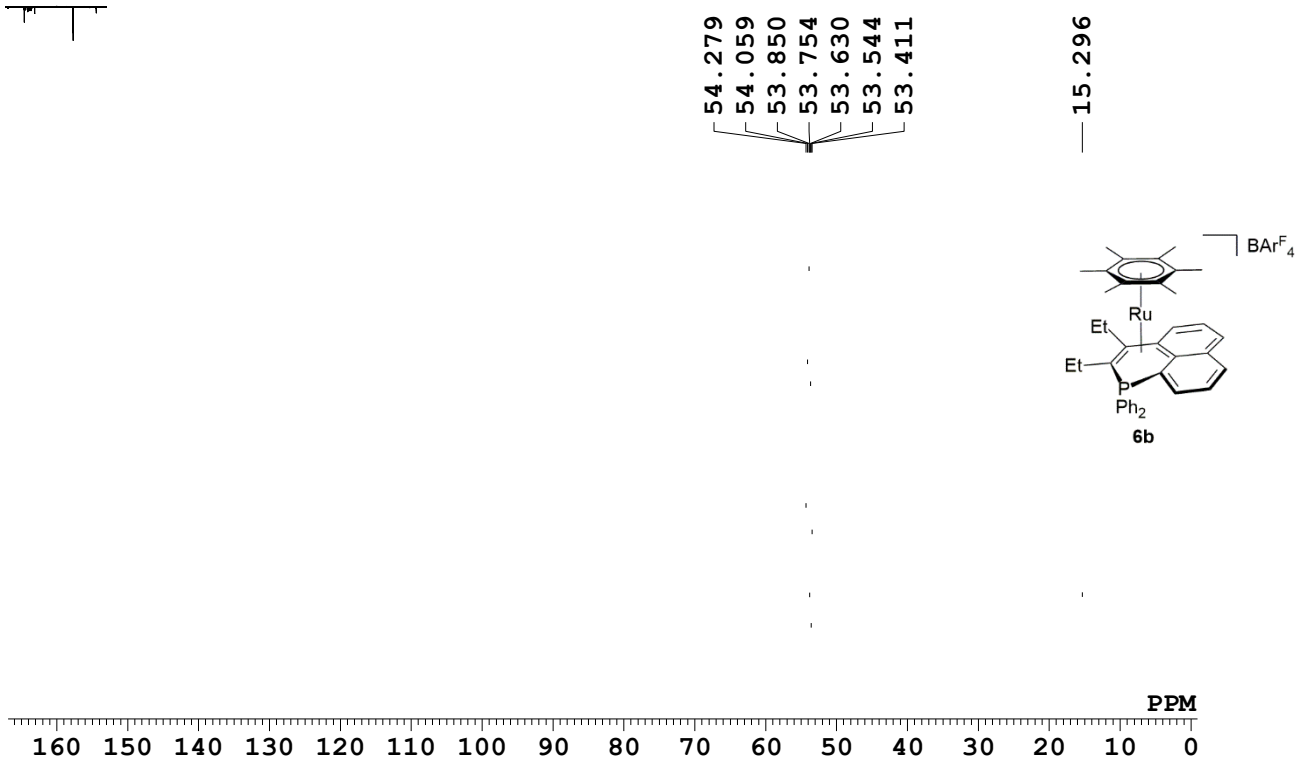

Figure S21. $^{13}C\{^1H\}$ NMR spectra of **6b** recorded in CD_2Cl_2.

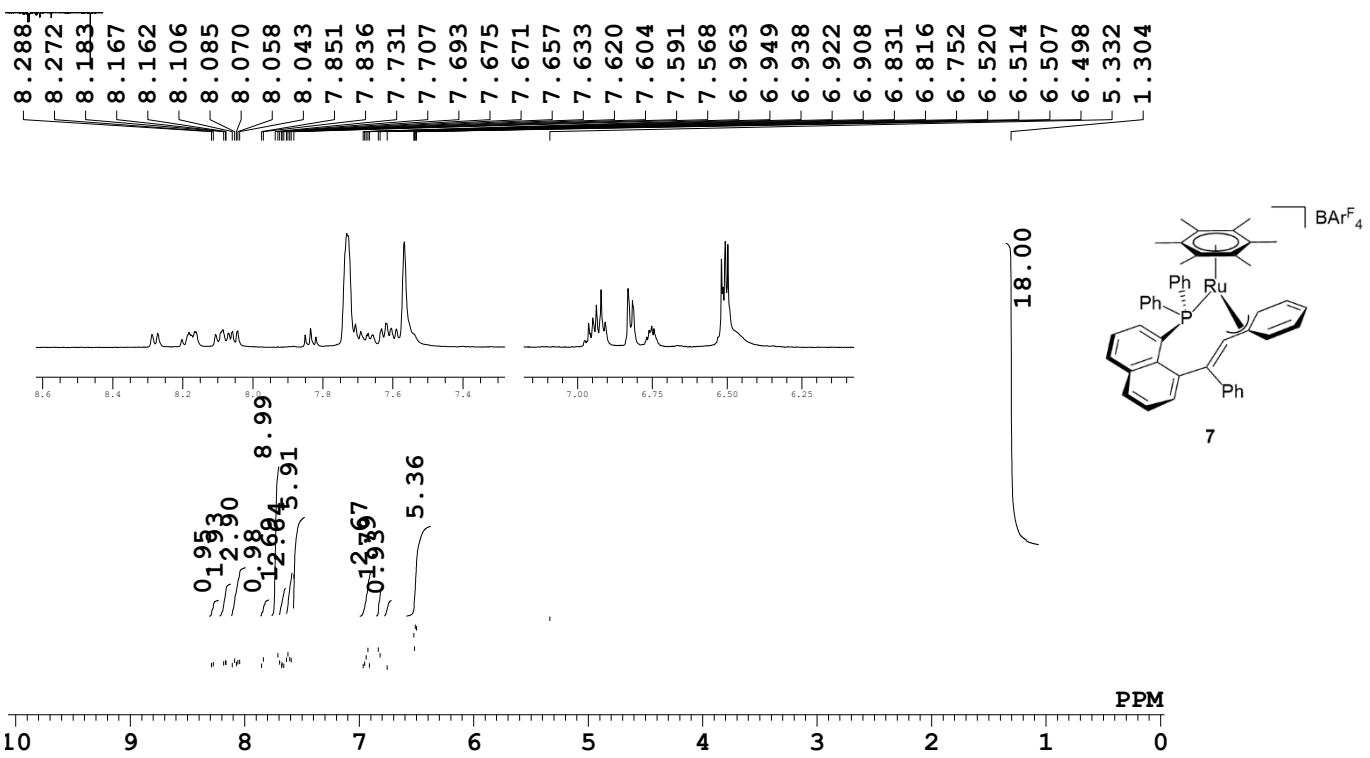

Figure S22. ^{1}H NMR spectra of **7** recorded in CD_2Cl_2.

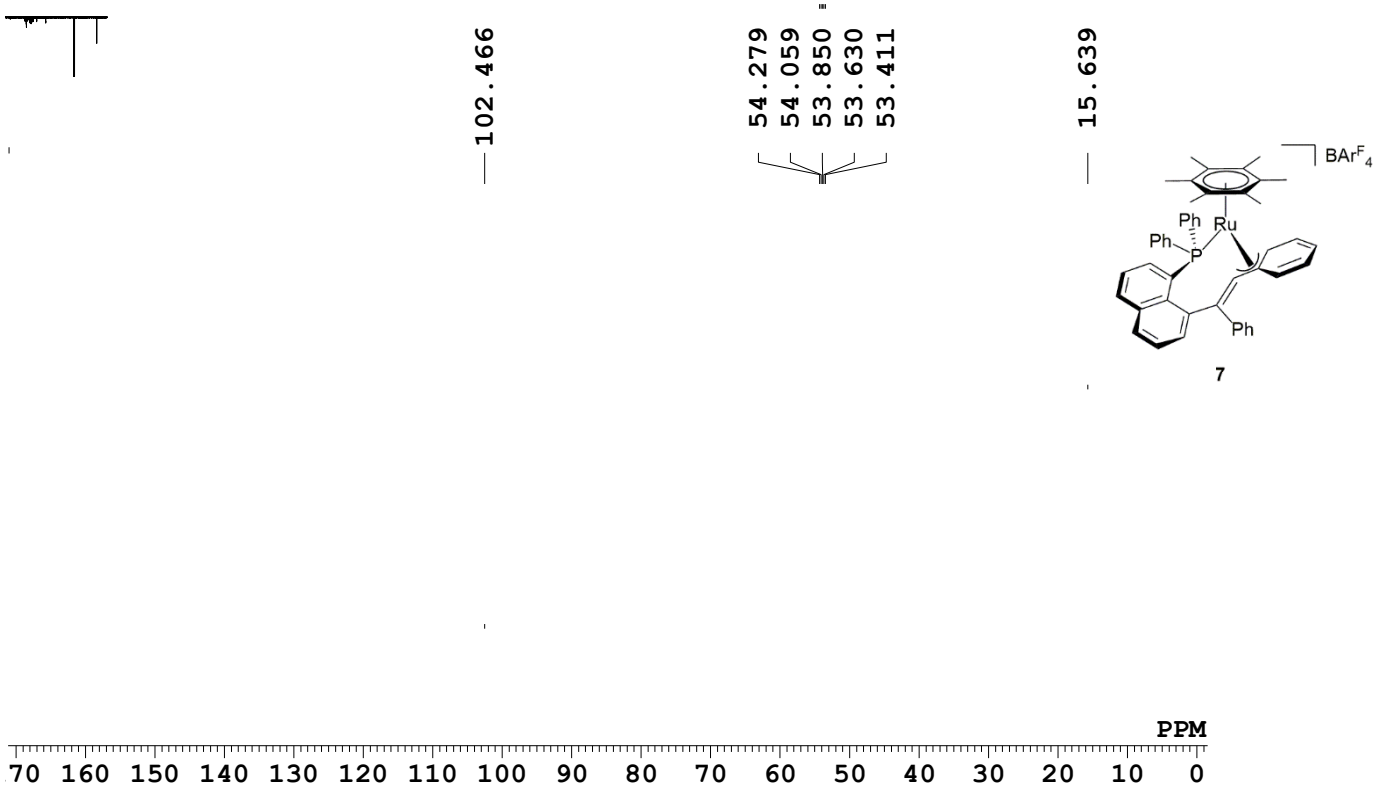

Figure S23. $^{13}C\{^{1}H\}$ NMR spectra of **7** recorded in CD_2Cl_2.

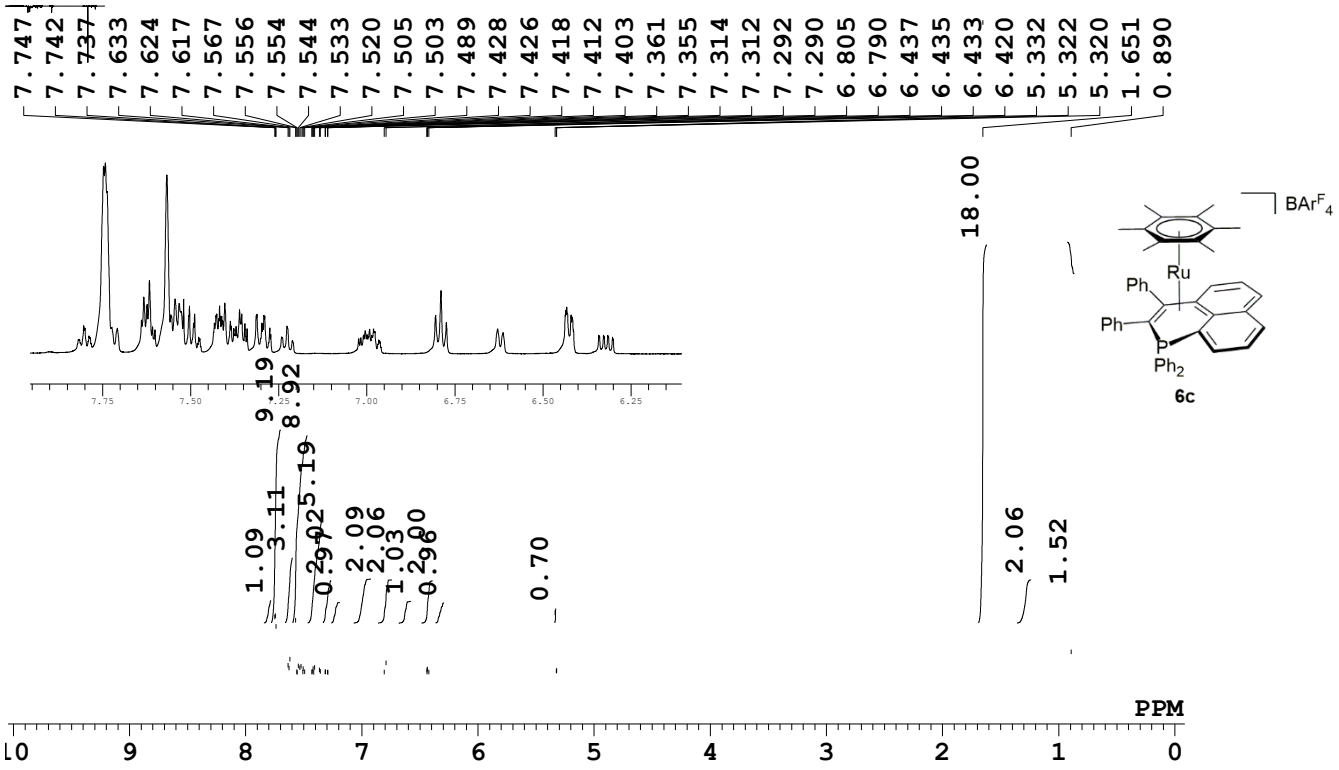

Figure S24. ^{1}H NMR spectra of **6c** recorded in CD_2Cl_2.

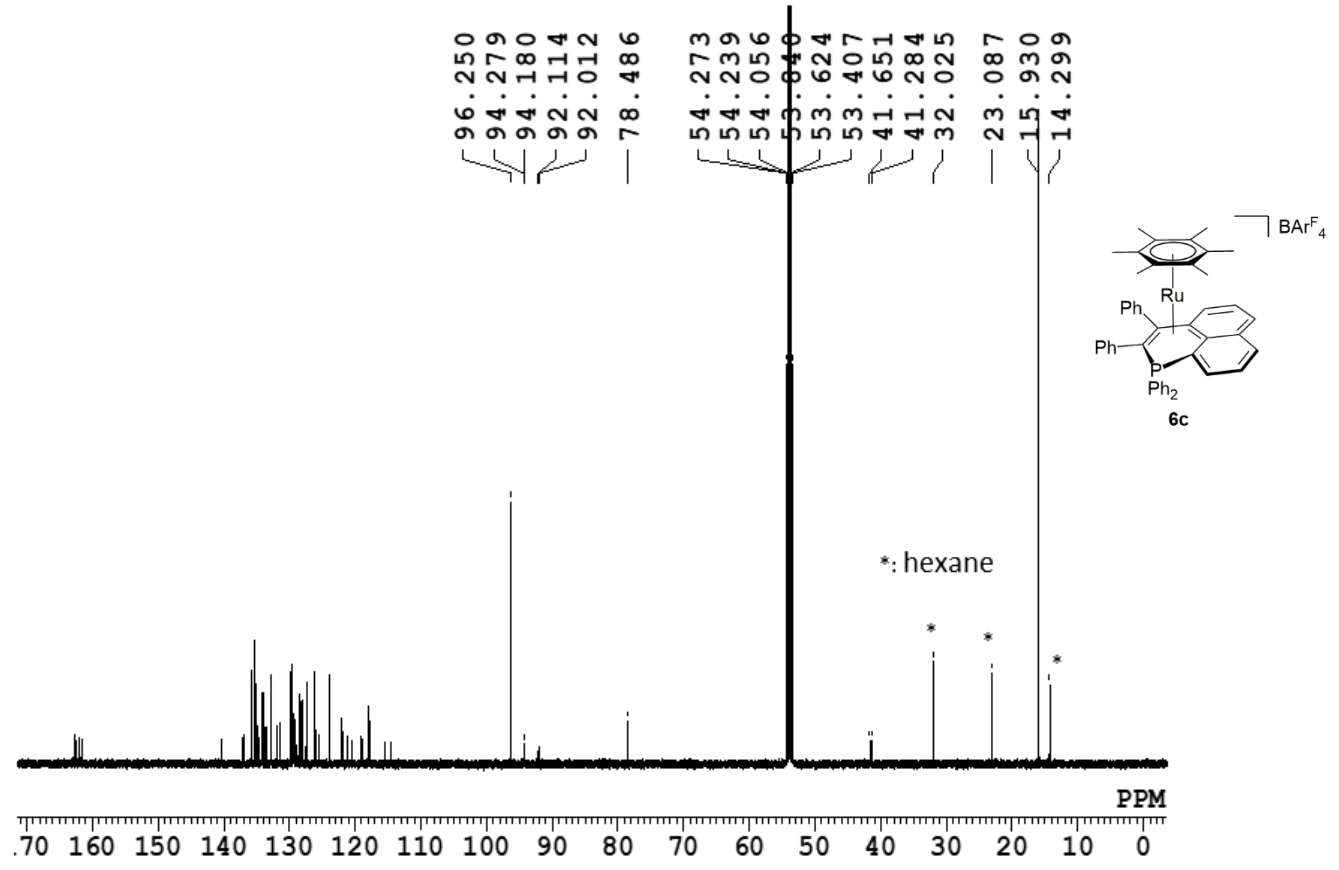

Figure S25. ^{13}C{^{1}H} NMR spectra of **6c** recorded in CD_2Cl_2.

8. References

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