Enolate S_NAr of unactivated arenes via $[(\eta^6\text{-arene})RuCp]^+$ intermediates

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Supporting Information

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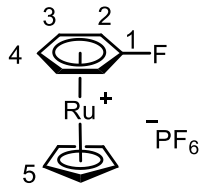
1. Experimental Detail and Product Characterisation

Commercially available reagents were used as received from suppliers. Solvents were laboratory grade and dried using an appropriate drying agent when required. Prior to use, K_2CO_3 was oven dried at 100 °C for 48 h. Reactions requiring anhydrous conditions were carried out under an atmosphere of dry nitrogen using Schlenk-line techniques. Where appropriate, solvents were degassed using the freeze-thaw cycle method. UV Nail lamp used was a Nailstar 36 Watt Professional UV Nail Lamp.

NMR spectra (1H, 13C, 19F) were recorded on a Varian VXR-400 spectrometer (1H at 399.97 Hz, 13 C at 100.57 MHz, 19F at 376.5 MHz) or a Varian VNMRS-500 spectrometer (1H at 499.73 MHz, 13C at 125.95 MHz). Spectra were recorded at 295 K in commercially available deuterated solvents and referenced internally to the residual solvent proton resonances. Electrospray and high-resolution mass spectrometry were performed on an SQD mass spectrometer with Acquity UPLC.

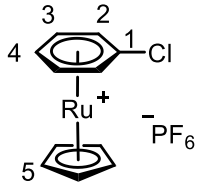
1a. Ru Sandwich Complexes



*$[Ru(\eta^6\text{-fluorobenzene})(\eta^5\text{-cyclopentadienyl})]PF_6$ (**1a**)*

Tris(acetonitrile)cyclopentadienylruthenium(II) hexafluorophosphate (150 mg, 0.357 mmol, 1 eq.) was dissolved in anhydrous 1,2-DCE (8 mL). Fluorobenzene (38 µL, 0.41 mmol, 1.1 eq.) was added and the reaction was stirred at reflux under inert atmosphere overnight. The reaction mixture was cooled to room temperature, filtered and the filtrate dried in *vacuo* to give a brown solid. The crude product was dissolved in a minimum of acetonitrile, then added dropwise to diethyl ether (10 mL). The liquid phase was decanted off and the resulting solid dried to give the title compound as an off-white solid (133 mg, 0.328 mmol, 92%).

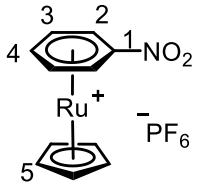
^{1}H (599 MHz, acetone) δ 6.84 – 6.79 (2H, m, H^{2}), 6.46 (2H, tdd, *J* = 5.5, 2.8, 1.3 Hz, H^{3}), 6.26 (1H, td, *J* = 5.7, 3.7 Hz, H^{4}), 5.64 (5H, s, H^{5}); ^{13}C (151 MHz, acetone) δ 137.9 (d, *J* = 275.3 Hz, C^{1}), 86.1 (s, C^{4}), 85.9 (d, *J* = 6.4 Hz, C^{3}), 82.6 (s, C^{5}), 78.5 (d, *J* = 21.2 Hz, C^{2}), ^{19}F{^{1}H} NMR (376 MHz, Acetone) δ -72.4 (d, *J* = 707.9 Hz, F$^{\text{Counter-ion}}$), -137.6, ^{31}P (acetone-D6) δ -144.3 (sept., $J_{P\text{-}F}$ 707 Hz, P$^{\text{Counter-ion}}$); *m/z* (HRMS)$^{+}$ 256.9843 [M-PF_6]$^{+}$ [M-PF6] ($C_{10}H_{11}F^{96}Ru^{+}$ requires 256.9842); Anal. Found (Expected): C 32.26 (32.44); H 2.48 (2.48); N 0.42 (0.00)



*[Ru(η^{6}-chlorobenzene)(η^{5}-cyclopentadienyl)]PF_6 (**1b**)*

Tris(acetonitrile)cyclopentadienylruthenium(II) hexafluorophosphate (150 mg, 0.357 mmol, 1 eq.) was dissolved in anhydrous 1,2-DCE (8 mL). Chlorobenzene (45 µL, 0.40 mmol, 1.1 eq.) was added and the reaction was stirred at reflux under inert atmosphere overnight. The reaction mixture was cooled to room temperature, filtered and the filtrate dried in *vacuo* to give a brown solid. The crude product was dissolved in a minimum of acetonitrile, then added dropwise to diethyl ether (10 mL). The liquid phase was decanted off and the resulting solid dried to give the title compound as an off-white solid (146 mg, 344 mmol, 96%).

^{1}H NMR (599 MHz, acetone) δ 6.83 – 6.80 (2H, m, H^{2}), 6.49 (2H, dd, *J* = 6.4, 5.6 Hz, H^{3}), 6.37 (1H, td, *J* = 5.7, 0.7 Hz, H^{4}), 5.65 (5H, s, H^{5}), ^{13}C NMR (151 MHz, acetone) δ 106.60 (s, C^{1}), 88.74 (s, C^{3}), 87.04 (s, C^{2}), 86.59 (s, C^{4}), 83.47 (s, C^{5}), ^{19}F{^{1}H} NMR (376 MHz, Acetone) δ -72.48 (d, *J* = 707.8 Hz, F$^{\text{Counter-ion}}$), ^{31}P (acetone-D6) δ -144.3 (sept., $J_{P\text{-}F}$ 707 Hz, P$^{\text{Counter-ion}}$); *m/z* (HRMS)$^{+}$ 272.9547 [M-PF6] ($C_{10}H_{11}{}^{35}Cl^{96}Ru^{+}$ requires 272.9510); Anal. Found (Expected): C 31.00 (31.18); H 2.41 (2.38); N 0.52 (0.00)

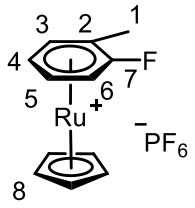


*[Ru(η^{6}-nitrobenzene)(η^{5}-cyclopentadienyl)]PF_6 (**1c**)*

Tris(acetonitrile)cyclopentadienylruthenium(II) hexafluorophosphate (150 mg, 0.357 mmol, 1 eq.) was dissolved in anhydrous 1,2-DCE (8 mL). Nitrobenzene (41 µL, 0.40 mmol, 1.1 eq.) was added and the reaction was stirred at reflux under inert atmosphere overnight. The reaction mixture was cooled to room temperature, filtered and the filtrate dried in *vacuo* to give a brown solid. The crude product was dissolved in a minimum of acetonitrile, then added dropwise to diethyl ether (10 mL). The liquid phase was decanted off and the resulting solid dried to give the title compound as an off-white solid (135 mg, 0.310 mmol, 87%).

^{1}H NMR (599 MHz, acetone) δ 7.46 – 7.44 (2H, m, H^{2}), 6.79 (2H, dd, *J* = 6.7, 5.7 Hz, H^{3}), 6.71 (1H, t, *J* = 5.8 Hz, H^{4}), 5.77 (5H, s, H^{5}), ^{13}C NMR (151 MHz, acetone) δ 111.4 (s, C^{1}), 88.5 (s, C^{4}), 86.4 (s,

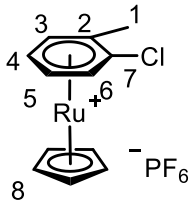
C^3), 83.7 (s, C^5), 82.9 (s, C^2), $^{19}F\{^1H\}$ NMR (376 MHz, Acetone) δ -72.4 (d, *J* = 707 Hz, $F^{Counter\text{-}ion}$), ^{31}P (acetone-D6) δ -144.3 (sept., $J_{P\text{-}F}$ 707 Hz, $P^{Counter\text{-}ion}$); *m/z* (HRMS)$^+$ 283.9788 [M-PF6] ($C_{10}H_{11}NO_2{}^{96}Ru^+$ requires 283.9750); Anal. Found (Expected): C 30.31 (30.43); H 2.33 (2.32); N 3.50 (3.23)



[Ru(η^6-2-fluorotoluene)(η^5-cyclopentadienyl)]PF_6 (***2a***)

Tris(acetonitrile)cyclopentadienylruthenium(II) hexafluorophosphate (100 mg, 0.236 mmol, 1 eq.) was dissolved in anhydrous 1,2-DCE (8 mL). 2-Fluorotoluene (30 µL, 0.260 mmol, 1.1 eq.) was added and the reaction was stirred at reflux under inert atmosphere overnight. The reaction mixture was cooled to room temperature, filtered and the filtrate dried in *vacuo* to give a brown solid. The crude product was dissolved in a minimum of acetonitrile, then added dropwise to diethyl ether (10 mL). The liquid phase was decanted off and the resulting solid dried to give the title compound as an off-white solid (93.5 mg, 0.222 mmol, 94 %).

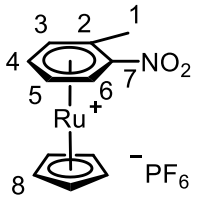
^1H NMR (599 MHz, acetone) δ 6.78 (1H, dd, *J* = 6.1, 4.2 Hz, H^6), 6.52 (1H, td, *J* = 4.4, 2.2 Hz, H^3), 6.34 (1H, tdd, *J* = 6.0, 2.5, 1.1 Hz, H^5), 6.19 (1H, td, *J* = 5.7, 3.1 Hz, H^4), 5.60 (5H, s, H^8), 2.50 (3H, d, *J* = 1.6 Hz, H^1), ^{13}C NMR (151 MHz, acetone) δ 136.2 (d, *J* = 273.3 Hz, C^7), 93.8 (d, *J* = 17.3 Hz, C^2), 86.9 (d, *J* = 4.0 Hz, C^3), 84.5 (s, C^4), 84.1 (d, *J* = 6.5 Hz, C^5), 81.7 (s, C^8), 76.6 (d, *J* = 22.6 Hz, C^6), 13.9 (d, *J* = 1.1 Hz, C^1), $^{19}F\{^1H\}$ NMR (376 MHz, Acetone) δ -72.51 (d, *J* = 707 Hz, $F^{Counter\text{-}ion}$), -142.17 (F^{Arene}),), ^{31}P (acetone-D6) δ -144.3 (sept., $J_{P\text{-}F}$ 707 Hz, $P^{Counter\text{-}ion}$); *m/z* (HRMS)$^+$ 270.9995 [M-PF6] ($C_{12}H_{12}F^{96}Ru^+$ requires 270.9962); Anal. Found (Expected): C 34.09 (34.21); H 2.86 (2.87); N 0.25 (0.00)



[Ru(η^6-2-chlorotoluene)(η^5-cyclopentadienyl)]PF_6 (***2b***)

Tris(acetonitrile)cyclopentadienylruthenium(II) hexafluorophosphate (200 mg, 0.472 mmol, 1 eq.) was dissolved in anhydrous 1,2-DCE (8 mL). 2-chlorotoluene (62 µL, 0.524 mmol, 1.1 eq.) was added and the reaction was stirred at reflux under inert atmosphere overnight. The reaction mixture was cooled to room temperature, filtered and the filtrate dried in *vacuo* to give a brown solid. The crude product was dissolved in a minimum of acetonitrile, then added dropwise to diethyl ether (10 mL). The liquid phase was decanted off and the resulting solid dried to give the title compound as an off-white solid (200 mg, 0.458 mmol, 97 %).

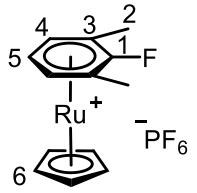
^{1}H NMR (599 MHz, acetone) δ 6.84 – 6.74 (1H, m, H^{6}), 6.59 (1H, dd, *J* = 5.8, 1.0 Hz, H^{3}), 6.38 (1H, td, *J* = 5.8, 1.0 Hz, H^{5}), 6.29 (1H, td, *J* = 5.8, 0.7 Hz, H^{4}), 5.59 (5H, s, H^{8}), 2.60 (3H, s, H^{1}), ^{13}C NMR (151 MHz, acetone) δ 106.7 (s, C^{7}), 102.2 (s, C^{2}), 87.5 (s, $C^{3/6}$), 87.3 (s, $C^{3/6}$), 85.3 (s, $C^{4/5}$), 85.2 (s, $C^{4/5}$), 82.5 (s, C^{8}), 18.5 (s, C^{1}), ^{19}F{^{1}H} NMR (376 MHz, Acetone) δ -72.54 (d, *J* = 707 Hz, $F^{Counter\text{-}ion}$), ^{31}P (acetone-D6) δ -144.3 (sept., $J_{P\text{-}F}$ 707 Hz, $P^{Counter\text{-}ion}$); *m/z* (HRMS)$^{+}$ 286.9703 [M-PF6] ($C_{12}H_{12}{}^{35}Cl^{96}Ru^{+}$ requires 286.9666); Anal. Found (Expected): C 32.96 (32.93); H 2.84 (2.76); N 0.19 (0.00)



*[Ru(η^{6}-2-nitrotoluene)(η^{5}-cyclopentadienyl)]PF_6 (**2c**)*

Tris(acetonitrile)cyclopentadienylruthenium(II) hexafluorophosphate (100 mg, 0.236 mmol, 1 eq.) was dissolved in anhydrous 1,2-DCE (8 mL). 2-Nitrotoluene (31 µL, 0.263 mmol, 1.1 eq.) was added and the reaction was stirred at reflux under inert atmosphere overnight. The reaction mixture was cooled to room temperature, filtered and the filtrate dried in *vacuo* to give a brown solid. The crude product was dissolved in a minimum of acetonitrile, then added dropwise to diethyl ether (10 mL). The liquid phase was decanted off and the resulting solid dried to give the title compound as an off-white solid (94 mg, 0.210 mmol, 89 %).

^{1}H NMR (599 MHz, acetone) δ 7.22 (1H, dd, *J* = 6.0, 0.7 Hz, H^{6}), 6.72 (1H, d, *J* = 5.9 Hz, H^{3}), 6.65 (1H, td, *J* = 6.0, 0.7 Hz, H^{5}), 6.56 (1H, td, *J* = 5.9, 0.7 Hz, H^{4}), 5.74 (5H, s, H^{8}), 2.70 (3H, s, H^{1}), ^{13}C NMR (151 MHz, acetone) δ 110.5 (s, C^{1}), 99. (s, C^{2}), 89.2 (s, C^{3}), 88.6 (s, C^{4}), 86.2 (s, C^{5}), 85.0 (s, C^{8}), 84.2 (s, C^{6}), 18.8 (s, C^{1}), ^{19}F{^{1}H} NMR (376 MHz, Acetone) δ -72.45 (d, *J* = 707 Hz, $F^{Counter\text{-}ion}$), ^{31}P (acetone-D6) δ -144.3 (sept., $J_{P\text{-}F}$ 707 Hz, $P^{Counter\text{-}ion}$); *m/z* (HRMS)$^{+}$ 297.9944 [M-PF6] ($C_{12}H_{12}NO_2{}^{96}Ru^{+}$ requires 9907); Anal. Found (Expected): C 32.00 (32.15); H 2.67 (2.70); N 3.32 (3.12).

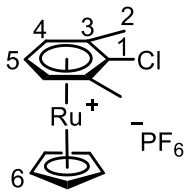


*[Ru(η^{6}-2-fluoro-m-xylene)(η^{5}-cyclopentadienyl)]PF_6 (**3a**)*

Tris(acetonitrile)cyclopentadienylruthenium(II) hexafluorophosphate (100 mg, 0.236 mmol, 1 eq.) was dissolved in anhydrous 1,2-DCE (8 mL). 2-Fluoro-*m*-xylene (33 µL, 0.261 mmol, 1.1 eq.) was added and the reaction was stirred at reflux under inert atmosphere overnight. The reaction mixture was cooled to room temperature, filtered and the filtrate dried in *vacuo* to give a brown solid. The crude product was dissolved in a minimum of acetonitrile, then added dropwise to

diethyl ether (10 mL). The liquid phase was decanted off and the resulting solid dried to give the title compound as an off-white solid (95.6 mg, 0.219 mmol, 94 %)

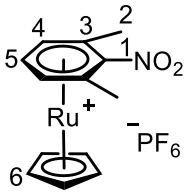
^{1}H NMR (599 MHz, acetone) δ 6.37 (2H, dd, *J* = 5.6, 3.7 Hz, H^{4}), 6.09 (1H, td, *J* = 5.7, 2.5 Hz, H^{5}), 5.54 (5H, s, H^{6}), 2.49 (6H, d, *J* = 1.7 Hz, 6H, H^{2}), ^{13}C NMR (151 MHz, acetone) δ 136.6 (d, *J* = 271.5 Hz, C^{1}), 93.8 (d, *J* = 18.6 Hz, C^{3}), 86.9 (d, *J* = 4.0 Hz, C^{4}), 84.5 (d, *J* = 4.0 Hz, C^{5}), 82.7 (s, C^{6}), 14.9 (d, *J* = 1.4 Hz, C^{2}), ^{19}F{^{1}H} NMR (376 MHz, Acetone) δ -72.46 (d, *J* = 707 Hz, $F^{Counter\text{-}ion}$), -146.72 (1F, s, F^{Arene}), ^{31}P (acetone-D6) δ -144.3 (sept., $J_{P\text{-}F}$ 707 Hz, $P^{Counter\text{-}ion}$); *m/z* (HRMS)$^{+}$ 285.0150 [M-PF6] ($C_{13}H_{14}F^{96}Ru^{+}$ requires 285.0156); Anal. Found (Expected): C 35.70 (35.87); H 3.26 (3.24); N 0.20 (0.00)



*[Ru(η^{6}-2-chloro-m-xylene)(η^{5}-cyclopentadienyl)]PF_6 (**3b**)*

Tris(acetonitrile)cyclopentadienylruthenium(II) hexafluorophosphate (200 mg, 0.472 mmol, 1 eq.) was dissolved in anhydrous 1,2-DCE (8 mL). 2-Chloro-*m*-xylene (69 µL, 0.522 mmol, 1.1 eq.) was added and the reaction was stirred at reflux under inert atmosphere overnight. The reaction mixture was cooled to room temperature, filtered and the filtrate dried in *vacuo* to give a brown solid. The crude product was dissolved in a minimum of acetonitrile, then added dropwise to diethyl ether (10 mL). The liquid phase was decanted off and the resulting solid dried to give the title compound as an off-white solid (201 mg, 0.448 mmol, 95 %).

^{1}H NMR (599 MHz, acetone) δ 6.49 (2H, d, *J* = 5.7 Hz, H^{4}), 6.22 (1H, t, *J* = 5.8 Hz, H^{5}), 5.53 (5H, s, H^{6}), 2.61 (6H, s, H^{2}), ^{13}C NMR (151 MHz, acetone) δ 109.3 (s, C^{1}), 102.6 (s, C^{3}), 87.8 (s, C^{4}), 85.3 (s, C^{5}), 83.6 (s, C^{6}), 20.3 (s, C^{2}), ^{19}F{^{1}H} NMR δ -72.46 (d, *J* = 707 Hz, $F^{Counter\text{-}ion}$), ^{31}P (acetone-D6) δ -144.3 (sept., $J_{P\text{-}F}$ 707 Hz, $P^{Counter\text{-}ion}$); *m/z* (HRMS)$^{+}$ 300.9880 [M-PF6] ($C_{13}H_{14}{}^{35}Cl^{96}Ru^{+}$ requires 300.9860); Anal. Found (Expected): C 34.55 (34.56); H 3.13 (3.12); N 3.23 (3.03)

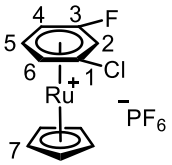


*[Ru(η^{6}-2-nitro-m-xylene)(η^{5}-cyclopentadienyl)]PF_6 (**3c**)*

Tris(acetonitrile)cyclopentadienylruthenium(II) hexafluorophosphate (100 mg, 0.236 mmol, 1 eq.) was dissolved in anhydrous 1,2-DCE (8 mL). 2-Nitro-*m*-xylene (35 µL, 0.260 mmol, 1.1 eq.) was added and the reaction was stirred at reflux under inert atmosphere overnight. The reaction

mixture was cooled to room temperature, filtered and the filtrate dried in *vacuo* to give a brown solid. The crude product was dissolved in a minimum of acetonitrile, then added dropwise to diethyl ether (10 mL). The liquid phase was decanted off and the resulting solid dried to give the title compound as an off-white solid (96 mg, 0.208 mmol, 88 %).

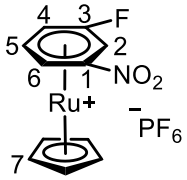
^{1}H NMR (599 MHz, acetone) δ 6.60 (2H, d, *J* = 5.9 Hz, H^{4}), 6.44 (1H, t, *J* = 5.9 Hz, H^{5}), 5.73 (5H, s, H^{6}), 2.53 (6H, s, H^{2}), ^{13}C NMR (151 MHz, acetone) δ 111.4 (s, C^{1}) 96.1 (s, C^{3}), 86.2 (s, C^{5}), 85.9 (s, C^{4}), 84.1 (s, C^{6}), 16.0 (s, C^{2}), ^{19}F{^{1}H} NMR δ -71.45 (d, *J* = 707 Hz, $F^{Counter\text{-}ion}$), ^{31}P (acetone-D6) δ -144.3 (sept., $J_{P\text{-}F}$ 707 Hz, $P^{Counter\text{-}ion}$); *m/z* (HRMS)$^{+}$ 312.0126 [M-PF6] ($C_{13}H_{14}NO_2{}^{96}Ru^{+}$ requires 312.0100); Anal. Found (Expected): C 33.63 (33.78); H 3.04 (3.05); N 0.42 (0.00)



[Ru(η^{6}-1-Chloro-3-fluorobenzene)(η^{5}-cyclopentadienyl)]PF_6

Tris(acetonitrile)cyclopentadienylruthenium(II) hexafluorophosphate (40 mg, 0.092 mmol, 1 eq.) was dissolved in anhydrous 1,2-DCE (8 mL). 1-Chloro-3-fluorobenzene (10 µL, 0.101 mmol, 1.1 eq.) was added and the reaction was stirred at reflux under inert atmosphere overnight. The reaction mixture was cooled to room temperature, filtered and the filtrate dried in *vacuo* to give a brown solid. The crude product was dissolved in a minimum of acetonitrile, then added dropwise to diethyl ether (10 mL). The liquid phase was decanted off and the resulting solid dried to give the title compound as a brown solid (40 mg, 0.82 mmol, 89 %).

^{1}H NMR (599 MHz, Acetone-d_6) δ 7.47 – 7.36 (1H, m, H^{2}), 6.86 (1H, ddd, *J* = 6.1, 3.4, 1.5 Hz, H^{4}), 6.75 (1H, ddd, *J* = 5.9, 3.1, 1.1 Hz, H^{6}), 6.62 (1H, td, *J* = 6.0, 2.9 Hz, H^{5}), 5.77 (5H, s, H^{7}), ^{13}C NMR (151 MHz, Acetone-d_6) δ 137.0 (d, *J* = 279.1 Hz, C^{3}), 104.8 (d, *J* = 7.0 Hz, C^{1}), 87.9 (s, C^{6}), 85.1 (d, *J* = 6.5 Hz, C^{5}), 84.8 (s, C^{7}), 80.5 (d, *J* = 23.6 Hz, C^{2}), 78.2 (d, *J* = 21.4 Hz, C^{4}), ^{19}F{^{1}H} NMR (376 MHz, Acetone-D_6) δ -72.51 (d, *J* = 707 Hz, $F^{Counter\text{-}ion}$), -138.07 (1F, s, F^{Arene}), ^{31}P (acetone-D6) δ -144.3 (sept., $J_{P\text{-}F}$ 707 Hz, $P^{Counter\text{-}ion}$); *m/z* (HRMS)$^{+}$ 290.9451 [M-PF6] ($C_{11}H_9{}^{35}ClF^{96}Ru^{+}$ requires 290.9453).

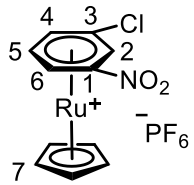


[Ru(η^{6}-1-fluoro-3-nitrobenzene)(η^{5}-cyclopentadienyl)]PF_6)

Tris(acetonitrile)cyclopentadienylruthenium(II) hexafluorophosphate (40 mg, 0.092 mmol, 1 eq.) was dissolved in anhydrous 1,2-DCE (8 mL). 1-fluoro-3-nitrobenzene (12 µL, 0.101 mmol, 1.1 eq.) was added and the reaction was stirred at reflux under inert atmosphere overnight. The reaction mixture was cooled to room temperature, filtered and the filtrate dried in *vacuo* to give a brown solid. The crude product was dissolved in a minimum of acetonitrile, then added dropwise to

diethyl ether (10 mL). The liquid phase was decanted off and the resulting solid dried to give the title compound as a brown solid (35 mg, 0.069 mmol, 75 %).

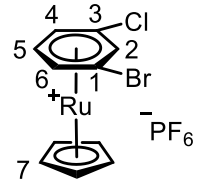
^{1}H NMR (599 MHz, acetone) δ 7.97 (1H, dt, *J* = 3.2, 1.3 Hz, H^{2}), 7.38 (1H, ddd, *J* = 6.1, 2.7, 1.2 Hz, H^{6}), 7.18 (1H, ddd, *J* = 6.2, 3.7, 1.5 Hz, H^{4}), 6.90 (1H, td, *J* = 6.2, 2.8 Hz, H^{5}), 5.90 (5H, s, H^{7}), ^{13}C NMR (151 MHz, acetone) δ 135.8 (d, *J* = 280.5 Hz, C^{3}), 110.2 (s, C^{1}), 85.1 (s, C^{7}), 84.8 (d, *J* = 6.5 Hz, C^{5}), 82.2 (s, C^{6}), 80.2 (d, *J* = 21.5 Hz, C^{4}), 74.2 (d, *J* = 25.6 Hz, C^{2}), ^{19}F{^{1}H} NMR (376 MHz, Acetone-D_6) δ -72.40 (d, *J* = 708 Hz, $F^{Counter\text{-}ion}$), -136.01 (1F, s, F^{Arene}), ^{31}P (acetone-D6) δ -144.3 (sept., $J_{P\text{-}F}$ 708 Hz, $P^{Counter\text{-}ion}$); *m/z* (HRMS)$^{+}$ 301.9701 [M-PF6] ($C_{11}H_9NO_2F^{96}Ru^{+}$ requires 301.9693).



[Ru(η^{6}-1-chloro-3-nitrobenzene)(η^{5}-cyclopentadienyl)]PF_6

Tris(acetonitrile)cyclopentadienylruthenium(II) hexafluorophosphate (40 mg, 0.092 mmol, 1 eq.) was dissolved in anhydrous 1,2-DCE (8 mL). 1-Chloro-3-nitrobenzene (12 µL, 0.101 mmol, 1.1 eq.) was added and the reaction was stirred at reflux under inert atmosphere overnight. The reaction mixture was cooled to room temperature, filtered and the filtrate dried in *vacuo* to give a brown solid. The crude product was dissolved in a minimum of acetonitrile, then added dropwise to diethyl ether (10 mL). The liquid phase was decanted off and the resulting solid dried to give the title compound as a brown solid (36 mg, 0.077 mmol, 83 %).

^{1}H NMR (599 MHz, acetone) δ 7.93 (1H, t, *J* = 1.2 Hz, H^{2}), 7.46 (1H, dd, *J* = 6.2, 1.3 Hz, H^{6}), 7.16 (1H, dd, *J* = 6.1, 1.2 Hz, H^{4}), 6.92 (1H, t, *J* = 6.2 Hz, H^{5}), 5.90 (5H, s, H^{7}), ^{13}C NMR (151 MHz, acetone) δ 110.9 (s, C^{1}), 105.50 (s, C^{3}), 90.1 (s, C^{4}), 86.0 (s, C^{5}), 85.8 (s, C^{7}), 83.8 (s, C^{2}), 82.5 (s, C^{6}), ^{19}F{^{1}H} NMR (376 MHz, Acetone) δ -72.5 (d, *J* = 707 Hz, $F^{Counter\text{-}ion}$), -138.0 (1F, s, F^{Arene}), ^{31}P (acetone-D6) δ -144.3 (sept., $J_{P\text{-}F}$ 708 Hz, $P^{Counter\text{-}ion}$); *m/z* (HRMS)$^{+}$ 314.9413 [M-PF6] ($C_{11}H_9{}^{35}ClNO_2{}^{96}Ru^{+}$ requires 314.9398).

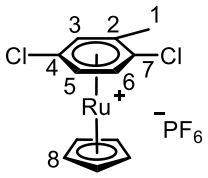


[Ru(η^{6}-1-bromo-3-chlorobenzene)(η^{5}-cyclopentadienyl)]PF_6

Tris(acetonitrile)cyclopentadienylruthenium(II) hexafluorophosphate (60 mg, 0.138 mmol, 1 eq.) was dissolved in anhydrous 1,2-DCE (8 mL). 1-bromo-3-chlorobenzene (18 µL, 0.152 mmol, 1.1 eq.) was added and the reaction was stirred at reflux under inert atmosphere overnight. The reaction mixture was cooled to room temperature, filtered and the filtrate dried in *vacuo* to give a brown solid. The crude product was dissolved in a minimum of acetonitrile, then added dropwise

to diethyl ether (10 mL). The liquid phase was decanted off and the resulting solid dried to give the title compound as a brown solid (57 mg, 0.124 mmol, 90 %).

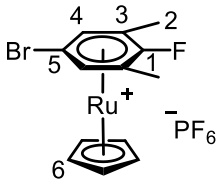
^{1}H NMR (599 MHz, acetone-d_6) δ 7.39 (1H, t, *J* = 1.1 Hz, H^{2}), 6.86 (2H, ddd, *J* = 6.0, 2.5, 1.1 Hz, $H^{4,6}$), 6.58 (1H, t, *J* = 5.9 Hz, H^{5}), 5.74 (5H, s, H^{7}), ^{13}C NMR (151 MHz, acetone-d_6) δ 105.32 (s, C^{3}), 91.12 (s, C^{2}), 89.57 (s, $C^{4/6}$), 89.09 (s, C^{1}), 87.27 (s, $C^{4/6}$), 85.98 (s, C^{5}), 84.73 (s, C^{7}), ^{19}F{^{1}H} NMR (376 MHz, Acetone) δ -72.50 (d, *J* = 707.8 Hz, $F^{Counter\text{-}ion}$), -138.07 (1F, s, F^{Arene}), ^{31}P (acetone-D6) δ -144.3 (sept., $J_{P\text{-}F}$ 708 Hz, $P^{Counter\text{-}ion}$); *m/z* (HRMS)$^{+}$ 350.8658 ($C_{11}H_9{}^{35}Cl^{79}Br^{96}Ru^{+}$ requires 350.8652).



[Ru(η^{6}-2,5-dichlorotoluene)(η^{5}-cyclopentadienyl)]PF$_6$

Tris(acetonitrile)cyclopentadienylruthenium(II) hexafluorophosphate (100 mg, 0.236 mmol, 1 eq.) was dissolved in anhydrous 1,2-DCE (8 mL). 2,5-dichlorotoluene (35 µL, 0.260 mmol, 1.1 eq.) was added and the reaction was stirred at reflux under inert atmosphere overnight. The reaction mixture was cooled to room temperature, filtered and the filtrate dried in *vacuo* to give a brown solid. The crude product was dissolved in a minimum of acetonitrile, then added dropwise to diethyl ether (10 mL). The liquid phase was decanted off and the resulting solid dried to give the title compound as a brown solid (95 mg, 0.210 mmol, 88 %).

^{1}H NMR (599 MHz, Acetone-d_6) δ 7.34 (1H, d, *J* = 1.3 Hz, H^{3}), 6.77 (1H, dd, *J* = 6.0, 1.3 Hz, H^{5}), 6.71 (1H, d, *J* = 6.0 Hz, H^{6}), 5.70 (5H, s, H^{8}), 2.56 (3H, s, H^{1}), ^{13}C NMR (151 MHz, Acetone-d_6) δ 106.9 (s, C^{7}), 105.0 (s, C^{4}), 103.0 (s, C^{2}), 89.3 (s, C^{3}), 87.8 (s, $C^{5/6}$), 87.8 (s, $C^{5/6}$), 85.5 (s, C^{8}), 18.9 (s, C^{1}), ^{19}F{^{1}H} NMR δ -72.52 (d, *J* = 707 Hz, $F^{Counter\text{-}ion}$), ^{31}P (acetone-D6) δ -144.3 (sept., $J_{P\text{-}F}$ 707 Hz, $P^{Counter\text{-}ion}$); *m/z* (HRMS)$^{+}$ 320.9318 ($C_{12}H_{11}{}^{35}Cl_2{}^{96}Ru^{+}$ requires 320.9314).

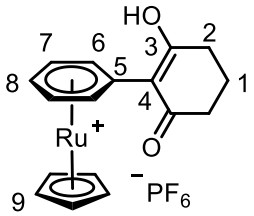


[Ru(η^{6}-5-bromo-2-fluoro-1,3-dimethylbenzene)(η^{5}-cyclopentadienyl)]PF$_6$

Tris(acetonitrile)cyclopentadienylruthenium(II) hexafluorophosphate (100 mg, 0.236 mmol, 1 eq.) was dissolved in anhydrous 1,2-DCE (8 mL). 5-bromo-2-fluoro-1,3-dimethylbenzene (50 µL, 0.253 mmol, 1.1 eq.) was added and the reaction was stirred at reflux under inert atmosphere overnight.

The reaction mixture was cooled to room temperature, filtered and the filtrate dried in *vacuo* to give a brown solid. The crude product was dissolved in a minimum of acetonitrile, then added dropwise to diethyl ether (10 mL). The liquid phase was decanted off and the resulting solid dried to give the title compound as a brown solid (109 mg, 0.212 mmol, 90 %).

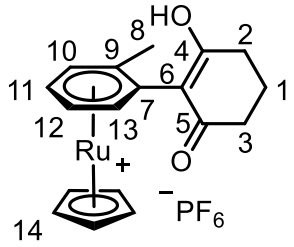
^{1}H NMR (599 MHz, Acetone-d_6) δ 6.91 (2H, d, *J* = 3.0 Hz, H^4), 5.65 (5H, s, H^6), 2.53 (6H, d, *J* = 1.8 Hz, H^2), ^{13}C NMR (151 MHz, Acetone-d_6) δ 135.7 (d, *J* = 272.4 Hz, C^1), 94.5 (d, *J* = 20.2 Hz, C^3), 90.7 (d, *J* = 4.3 Hz, C^4), 87.5 (s, C^5), 85.1 (s, C^6), 14.9 (d, *J* = 1.2 Hz, C^2), ^{19}F{^{1}H} NMR (376 MHz, Acetone) δ -72.41 (d, *J* = 707 Hz, $F^{Counter\text{-}ion}$), -147.26 (1F, s, F^{Arene}), ^{31}P (acetone-D6) δ -144.3 (sept., $J_{P\text{-}F}$ 707 Hz, $P^{Counter\text{-}ion}$); *m/z* (HRMS)$^+$ 362.9268[M-PF6] ($C_{13}H_{13}{}^{79}BrF^{96}Ru^+$ requires 362.9261).



[Ru(η^6-2-phenylcyclohexane-1,3-dione)(η^5-cyclopentadienyl)]PF_6

Potassium carbonate (65.2 mg, 0.472 mmol, 2 eq.), 1,3-cyclohexanedione (29 mg, 0.260 mmol, 1.1 eq.), [CpRu(η^6-chlorobenzene)]PF_6 (**1b**, 100 mg, 0.235 mmol, 1 eq.) and anhydrous DMF were combined in an oven-dried Schlenk flask and stirred at 40 °C for 18 h. The reaction mixture was evaporated to dryness in *vacuo*, then the resulting brown residue was triturated with dichloromethane (3x5 mL) and filtered. The filtrate was dried under reduced pressure, then the brown solid was dissolved in a minimum of dichloromethane and the solution added dropwise to diethyl ether (5 mL). The solvents were decanted and the residue dried to give the title compound as a brown solid (95 mg, 0.191 mmol, 81%).

^{1}H NMR (599 MHz, Acetone-d_6) δ 7.03 (2H, dd, *J* = 7.0, 0.9 Hz, H^6), 6.04 – 5.87 (2H, m, H^7), 5.82 (1H, td, *J* = 5.5, 0.8 Hz, H^8), 5.19 (5H, s, H^9), 2.32 – 2.14 (4H, m, H^2), 1.88 – 1.63 (2H, m, H^1), ^{13}C NMR (151 MHz, Acetone-d_6) δ 190.7 (s, C^3), 109.0 (s, C^5), 102.1 (s, C^4), 85.5 (s, C^6), 83.7 (s, C^7), 81.0 (s, C^8), 78.5 (s, C^9), 38.3 (s, C^2), 20.9 (s, C^1), ^{19}F{^{1}H} NMR δ -72.95 (d, *J* = 707 Hz, $F^{Counter\text{-}ion}$), ^{31}P (acetone-D6) δ -145.74 (sept., $J_{P\text{-}F}$ 707 Hz, $P^{Counter\text{-}ion}$); *m/z* (HRMS)$^+$ 349.0302 [M-PF6] ($C_{17}H_{17}O_2{}^{96}Ru^+$ requires 349.0305).

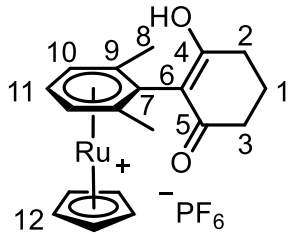


[Ru(η^6-2-(2-tolyl)cyclohexane-1,3-dione)(η^5-cyclopentadienyl)]PF_6

Potassium carbonate (63.0 mg, 0.456 mmol, 2 eq.), 1,3-cyclohexanedione (29 mg, 0.260 mmol, 1.1 eq.), [CpRu(η^6-2-chlorotoluene)]PF_6 (**2b**, 100 mg, 0.228 mmol, 1 eq.) and anhydrous DMF were

combined in an oven-dried Schlenk flask and stirred at 75 °C for 18 h. The reaction mixture was evaporated to dryness in *vacuo*, then the resulting brown residue was triturated with dichloromethane (3x5 mL) and filtered. The filtrate was dried under reduced pressure, then the brown solid was dissolved in a minimum of dichloromethane and the solution added dropwise to diethyl ether (5 mL). The solvents were decanted and the residue dried to give the title compound as a brown solid (80 mg, 0.156 mmol, 69%).

^{1}H NMR (599 MHz, CD_3OD) δ 6.10 (1H, d, *J* = 5.7 Hz, H^{10}), 6.00 – 5.94 (2H. m, $H^{12/13}$), 5.92 (1H, td, *J* = 5.5, 1.2 Hz, H^{11}), 5.27 (5H, s, H^{14}), 2.49 – 2.33 (4H, m, $H^{2/3}$), 2.16 (3H, s, H^{8}), 1.97 (2H, p, *J* = 6.5 Hz, H^{1}), ^{13}C NMR (151 MHz, CD_3OD) δ 193.2 (s, $C^{4/5}$), 191.8 (s, $C^{4/5}$), 105.9 (s, C^{6}), 105.5 (s, C^{7}), 102.5 (s, C^{9}), 88.8 (s, C^{13}), 86.1 (s, C^{10}), 82.9 (s, C^{12}), 82.3 (s, C^{11}), 79.7 (s, C^{14}), 36.4 (s, $C^{2/3}$), 35.8 (s, $C^{2/3}$), 20.8 (s, C^{1}), 18.9 (s, C^{8}), ^{19}F{^{1}H} NMR δ -72.69 (d, *J* = 707 Hz, $F^{Counter\text{-}ion}$); *m/z* (HRMS)$^{+}$ 363.0447 [M-PF6] ($C_{18}H_{19}O_2{}^{96}Ru^{+}$ requires 363.0461).



[Ru(η^{6}-2-(2-m-xylene)cyclohexane-1,3-dione)(η^{5}-cyclopentadienyl)]PF_6

Potassium carbonate (63.0 mg, 0.456 mmol, 2 eq.), 1,3-cyclohexanedione (29 mg, 0.260 mmol, 1.1 eq.), [CpRu(η^{6}-2-chloro-1,3-dimethylbenzene)]PF_6 (**3b**, 100 mg, 0.220 mmol, 1 eq.) and anhydrous DMF were combined in an oven-dried Schlenk flask and stirred at 75 °C for 18 h. The reaction mixture was evaporated to dryness in *vacuo*, then the resulting brown residue was triturated with dichloromethane (3x5 mL) and filtered. The filtrate was dried under reduced pressure, then the brown solid was dissolved in a minimum of dichloromethane and the solution added dropwise to diethyl ether (5 mL). The solvents were decanted and the residue dried to give the title compound as an impure brown solid (77 mg).

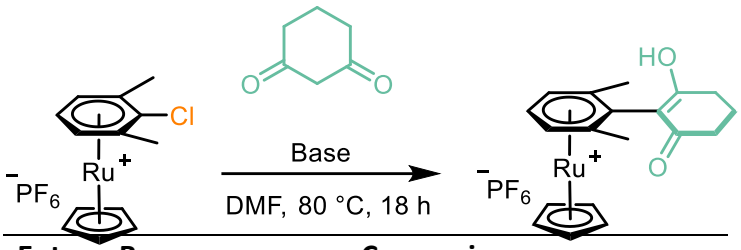
^{1}H NMR (599 MHz, acetone) δ 5.93 (2H, d, *J* = 5.6 Hz, H^{10}), 5.81 (1H, t, *J* = 5.7 Hz, H^{11}), 5.23 (5H, s, H^{12}), 2.22 (4H, ddd, *J* = 24.9, 6.8, 5.8 Hz, $H^{2,3}$), 2.09 (6H, s, H^{8}), 1.89 – 1.82 (2H, m, H^{1}), ^{13}C NMR (151 MHz, acetone) δ 189.2 (s, $C^{4/5}$), 186.6 (s, $C^{4/5}$), 110.0 (s, C^{7}), 102.3 (s, C^{6}), 102.1 (s, C^{9}), 84.9 (s, C^{10}), 81.4 (s, C^{11}), 79.8 (s, C^{12}), 37.6 (s, $C^{2/3}$), 37.4 (s, $C^{2/3}$), 21.7 (s, C^{1}), 19.3 (s, C^{8}), ^{19}F{^{1}H} NMR δ -72.55 (d, *J* = 707 Hz, $F^{Counter\text{-}ion}$), ^{31}P (acetone-D6) δ -145.74 (sept., $J_{P\text{-}F}$ 707 Hz, $P^{Counter\text{-}ion}$); *m/z* (HRMS)$^{+}$ 377.0621 [M-PF6] ($C_{19}H_{21}O_2{}^{96}Ru^{+}$ requires 377.0618).

1b. general Experimental 1 – base, temperature and solvent screening for S_NAr reaction

To an oven dried Schlenk tube were added [Ru] (1 eq.), 1,3-cyclohexanedione (2 eq.), base (3 eq.) and anhydrous solvent (2 mL). The reaction mixture was heated to the desired temperature for 18 hours, then dried under reduced pressure to give a crude brown residue which was triturated with acetonitrile (3x5 mL), then filtered. The filtrate was dried in vacuum, and the resulting brown

residue dissolved in d_6-acetone and analysed by ^{1}H NMR. Conversions were calculated by ^{1}H NMR spectroscopy. Mass spec analysis was used to confirm the presence of any product(s) and/or starting material(s).

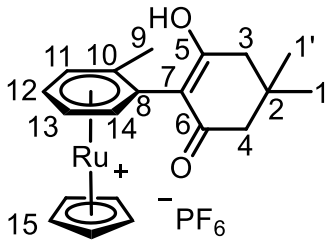
1c. Base Screen for S_NAr



Entry	Base	Conversion
26	DBU	30*
27	NEt_3	Trace
28	Pyridine	Trace
29	DIPEA	Trace
30	NaH	Trace
31	KO^tBu	12
32	NaOH	40
33	$NaHCO_3$	36
34	$(NH_4)_2CO_3$	Trace
35	NaOMe	Trace
36	Na(2,4-di-tert-butylphenoxide)	Trace
37	K_2CO_3	67

General experimental 2 – Dione scope

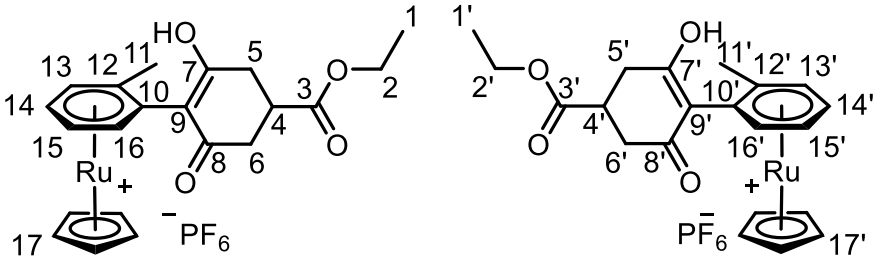
Potassium carbonate (9.5 mg, 0.068 mmol, 2 eq.), dione (0.040 mmol, 1.1 eq.), [CpRu(η^6-2-chlorotoluene)]PF_6 (**2b**, 15 mg, 0.034 mmol, 1 eq.) and anhydrous DMF were combined in an oven-dried Schlenk flask and stirred at 75 °C for 18 h. The reaction mixture was evaporated to dryness in *vacuo*, then the resulting brown residue was triturated with dichloromethane (3x5 mL) and filtered. The filtrate was dried under reduced pressure, then the brown solid was dissolved in a minimum of dichloromethane and the solution added dropwise to diethyl ether (5 mL). The solvents were decanted and the residue dried to give the complex.



[Ru(η^6-2-(2-tolyl)(5,5'-dimethyl)cyclopentane-1,3-dione)(η^5-cyclopentadienyl)]PF_6

Synthesised via general experimental 2, using 5,5'-dimethylcyclohexane1,3-dione (5.4 mg, 0.038 mmol, 1.1 eq.). The title compound was isolated as a brown solid (11.3 mg, 0.021 mmol, 61 %).

^{1}H NMR (599 MHz, CD_3OD) δ 6.10 (1H, d, *J* = 5.6 Hz, H^{11}), 5.98 – 5.95 (1H, m, H^{13}), 5.94 – 5.92 (1H, m, H^{14}), 5.91 (1H, td, *J* = 5.6, 1.0 Hz, H^{12}), 5.26 (5H, s, H^{15}), 2.29 (4H, s, $H^{3,4}$), 2.15 (3H, s, H^9), 1.12 (3H, s, H^1), 1.09 (3H, s, $H^{1'}$), ^{13}C NMR (151 MHz, CD_3OD) δ 193.4 (s, $C^{5/6}$), 192.2 (s, $C^{5/6}$), 106.9 (s, C^8), 106.2 (s, C^7), 103.9 (s, C^{10}), 90.3 (s, C^{14}), 87.6 (s, C^{11}), 84.3 (s, C^{13}), 83.7 (s, C^{12}), 81.1 (s, C^{15}), 51.7 (s, $C^{3/4}$), 51.1 (s, $C^{3/4}$), 32.2 (s, C^2), 29.3 (s, $C^{1/1'}$), 28.5 (s, $C^{1/1'}$), 20.5 (s, C^9), ^{19}F{^{1}H} NMR δ -72.58 (d, *J* = 707 Hz, $F^{Counter\text{-}ion}$); *m/z* (HRMS)$^+$ 391.0772 [M-PF6] ($C_{20}H_{23}O_2{}^{96}Ru^+$ requires 391.0774).

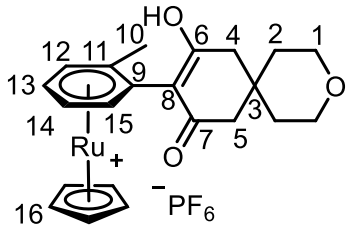


[Ru(η^6-2-(2-tolyl)(5-ethylacetyl)cyclopentane-1,3-dione)(η^5-cyclopentadienyl)]PF_6 (1:1 mixture of diastereomers)

Synthesised via general experimental 2, using 5-(ethylacetyl)cyclohexane1,3-dione (7.1 mg, 0.038 mmol, 1.1 eq.). The title compound was isolated as an impure brown solid (12.5 mg, 0.022 mmol, 63 %).

^{1}H NMR (599 MHz, CD_3OD) δ 6.07 (1H, dd, *J* = 8.7, 5.7 Hz, $H^{13/13'}$), 5.97 – 5.86 (3H, m, $H^{14/14',\ 15/15',\ 16/16'}$), 5.23 (5H, d, *J* = 8.5 Hz, $H^{17/17'}$), 4.14 (2H, dq, *J* = 14.1, 7.1 Hz, $H^{2/2'}$), 3.09 – 3.03 (1H, m, $H^{5/5'\ or\ 6/6'}$), 2.78 – 2.68 (1H, m, $H^{5/5'\ or\ 6/6'}$), 2.63 – 2.54 (3H, m, $H^{4/4',\ 5/5',\ 6/6'}$), 2.10 (3H, d, *J* = 34.2 Hz, $H^{11/11'}$), 1.25 (3H, dt, *J* = 10.5, 7.1 Hz, $H^{1/1'}$), ^{13}C NMR (151 MHz, CD_3OD) δ 190.4 (s, $C^{7/7'\ or\ 8/8'}$), 190.2 (s, $C^{7/7'\ or\ 8/8'}$), 189.2 (s, $C^{7/7'\ or\ 8/8'}$), 189.0 (s, $C^{7/7'\ or\ 8/8'}$), 174.2 (s, $C^{3/3'}$), 174.0 (s, $C^{3/3'}$), 105.7 (s, $C^{9/9'}$), 105.4 (s, $C^{9/9'}$), 104.9 (s, $C^{10/10'}$), 102.5 (s, $C^{12/12'}$), 88.7 (s, $C^{15/15'}$), 88.6 (s, $C^{15/15'}$), 86.4 (s, $C^{13/13'}$), 86.2 (s, $C^{13/13'}$), 83.0 (s, $C^{14/14'}$), 82.5 (s, $C^{16/16'}$), 82.4 (s, $C^{16/16'}$), 79.7 (d, *J* = 2.4 Hz, $C^{17/17'}$), 60.5 (s, $C^{2/2'}$), 60.4 (s, $C^{2/2'}$), 38.3 (s, $C^{4/4'\ or\ 5/5'\ or\ 6/6'}$), 38.2 (s, $C^{4/4'\ or\ 5/5'\ or\ 6/6'}$), 37.9 (s, $C^{4/4'\ or\ 5/5'\ or\ 6/6'}$), 37.8 (s, $C^{4/4'\ or\ 5/5'\ or\ 6/6'}$), 37.7 (s, $C^{4/4'\ or\ 5/5'\ or\ 6/6'}$), 37.5 (s, $C^{4/4'\ or\ 5/5'\ or\ 6/6'}$), 19.0 (s, $C^{11/11'}$), 18.9 (s, $C^{11/11'}$), 13.1 (s, $C^{1/1'}$), 13.1 (s, $C^{1/1'}$), ^{31}P NMR (243 MHz, CD_3OD) δ -132.06 – -156.07 (m, $p^{Counter\text{-}ion}$),

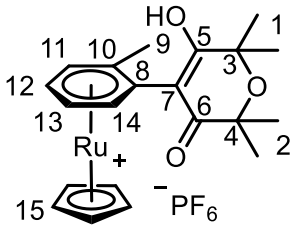
$^{19}F\{^{1}H\}$ NMR δ -74.65 (d, *J* = 707.8 Hz, $F^{Counter\text{-}ion}$); *m/z* (HRMS)$^{+}$ 435.0764 [M-PF6] ($C_{21}H_{23}O_4{}^{96}Ru^{+}$ requires 435.0672)



[Ru(η^6-9-(2-tolyl)-3-oxaspiro[5.5]undecane-8,10-dione)(η^5-cyclopentadienyl)]PF_6

Synthesised via general experimental 2, using 3-oxaspiro[5.5]undecane (6.6 mg, 0.038 mmol, 1.1 eq.). The title compound was isolated as a brown solid (14.4 mg, 0.024 mmol, 70 %).

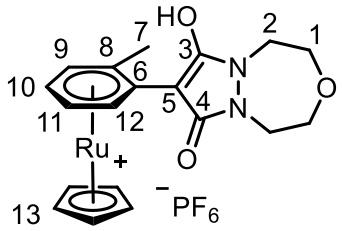
^{1}H NMR (599 MHz, CD_3OD) δ 6.11 (1H, d, *J* = 5.7 Hz, H^{12}), 5.98 (1H, t, *J* = 5.7 Hz, H^{14}), 5.95 – 5.89 (2H, m, $H^{13, 15}$), 5.27 (5H, s, H^{16}), 3.73 (4H, t, *J* = 5.5 Hz, H^{1}), 2.48 (2H, dd, *J* = 16.6, 2.7 Hz, $H^{4/5}$), 2.42 (2H, dd, *J* = 16.4, 2.6 Hz, $H^{4/5}$), 2.14 (3H, s, H^{10}), 1.64 (4H, dt, *J* = 33.9, 5.4 Hz, $H^{2, 2'}$), ^{13}C NMR (151 MHz, CD_3OD) δ 192.1 (s, $C^{5/6}$), 190.9 (s, $C^{5/6}$), 106.5 (s, $C^{8/9}$), 106.5 (s, $C^{8/9}$), 103.8 (s, C^{11}), 90.2 (s, C^{15}), 87.6 (s, C^{12}), 84.4 (s, C^{14}), 83.8 (s, C^{13}), 81.1 (s, C^{16}), 64.7 (s, C^{1}), 64.6 (s, $C^{1'}$), 48.8 (s, $C^{4/5}$), 48.1 (s, $C^{4/5}$), 38.2 (s, C^{2}), 37.5 (s, $C^{2'}$), 32.8 (s, C^{3}), 20.5 (s, C^{10}), $^{19}F\{^{1}H\}$ NMR δ -72.72 (d, *J* = 707 Hz, $F^{Counter\text{-}ion}$); *m/z* (HRMS)$^{+}$ 433.0874 [M-PF6] ($C_{22}H_{25}O_3{}^{96}Ru^{+}$ requires 433.0880).



[Ru(η^6-2,2',6,6'-tetramethyl-4-(2-tolyl)-oxane-3,5-dione)(η^5-cyclopentadienyl)]PF_6

Synthesised via general experimental 2, using 2,2',6,6'-tetramethyl-4-(2-tolyl)-oxane-3,5-dione (6.6 mg, 0.038 mmol, 1.1 eq.). The title compound was isolated as an impure brown oil.

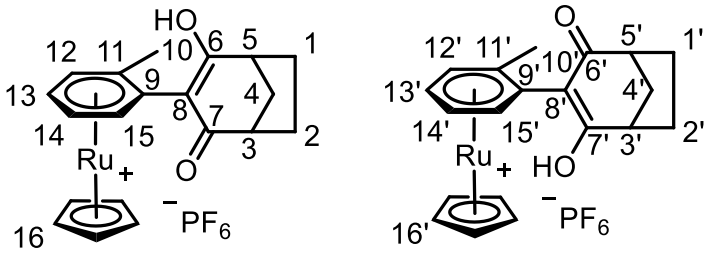
^{1}H NMR (400 MHz, CD_3OD) δ 6.02 (1H, d, *J* = 5.7 Hz, H^{Arene}), 5.89 (2H, dd, *J* = 3.0, 0.9 Hz, H^{Arene}), 5.83 (1H, ddd, *J* = 5.7, 3.9, 2.6 Hz, H^{Arene}), 5.17 (5H, s, H^{15}), 1.30-1.19 (12H, m, $H^{1, 2}$), *m/z* (HRMS)$^{+}$ 421.0875 [M-PF6] ($C_{21}H_{25}O_3{}^{96}Ru^{+}$ requires 421.0880).



[Ru(η^6-8-(2-tolyl)-1,2,4,5-tetrahydropyrazolo[1,2-d][1,4,5]oxadiazepine-7,9-dione)(η^5-cyclopentadienyl)]PF_6

Synthesised via general experimental 2, using 1,2,4,5-tetrahydropyrazolo[1,2-d][1,4,5]oxadiazepine-7,9-dione (6.6 mg, 0.038 mmol, 1.1 eq.). The title compound was isolated as a yellow foam (14.2 mg, 0.023 mmol, 68 %).

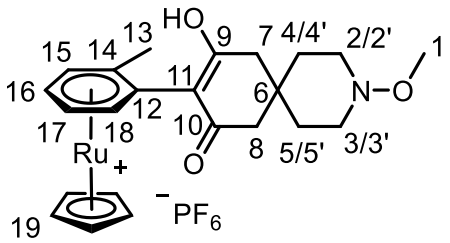
^{1}H NMR (599 MHz, CD_3OD) δ 6.22 (1H, dd, *J* = 6.0, 0.9 Hz, H^{12}), 6.12 (1H, d, *J* = 5.8 Hz, H^9), 6.01 (1H, td, *J* = 5.9, 0.9 Hz, H^{11}), 5.93 (1H, td, *J* = 5.7, 0.9 Hz, H^{10}), 5.32 (5H, s, H^{13}), 3.88 – 3.85 (4H, m, H^1), 3.82 – 3.80 (4H, m, H^2), 2.38 (3H, s, H^7), ^{13}C NMR (151 MHz, CD_3OD) δ 167.1 (s, $C^{3,4}$), 101.8 (s, C^6), 100.5 (s, C^8), 86.7 (s, C^9), 86.3 (s, C^{12}), 83.5 (s, C^{11}), 82.5 (s, C^{10}), 79.5 (s, C^{13}), 79.2 (s, C^5), 69.7 (s, C^1), 47.7 (s, C^2), 19.1 (s, C^7), ^{31}P NMR (243 MHz, CD_3OD) δ -132.06 – -156.07 (m, $p^{Counter\text{-}ion}$), ^{19}F{^{1}H} NMR δ -72.63 (d, *J* = 707 Hz, $F^{Counter\text{-}ion}$); *m/z* (HRMS)$^+$ 421.0261 [M-PF6] ($C_{19}H_{21}N_2O_3{}^{96}Ru^+$ requires 421.0268)



[Ru(η^6-3-(2-tolyl)-1,3-bicyclo[3.2.1]octane-2,4-dione)(η^5-cyclopentadienyl)]PF_6 (1:1 mixture of diastereomers)

Synthesised via general experimental 2, using 1,3-bicyclo[3.2.1]octane-2,4-dione (6.4 mg, 0.038 mmol, 1.1 eq.). The title compound was isolated as an impure brown oil.

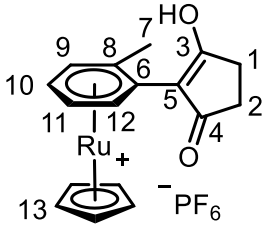
^{1}H NMR (599 MHz, CD_3OD) δ 6.06 (1H, dd, *J* = 9.5, 5.7 Hz, $H^{15/15'}$), 5.93 (1H, q, *J* = 5.6 Hz, $H^{12/12'}$), 5.88 (2H, ddd, *J* = 14.6, 9.4, 5.7 Hz, $H^{13/13',\ 14/14'}$), 5.27 – 5.21 (5H, m, $H^{16/16'}$), 2.83 – 2.74 (2H, m, $H^{1/1'\ or\ 2/2'}$), 2.16 and 2.08 (3H, s, $H^{10/10'}$), 2.13 – 2.07 (3H, m, $H^{4/4'\ and\ 3/3'\ or\ 5/5'}$), 1.74 (2H, dd, *J* = 21.0, 6.6 Hz, $H^{1/1'\ or\ 2/2'}$), 1.55 (1H, ddt, *J* = 23.9, 10.9, 4.3 Hz, $H^{5/5'\ or\ 3/3'}$), ^{13}C NMR (151 MHz, CD_3OD) δ 198.9 (s, $C^{6/6'\ or\ 7/7'}$), 198.3 (s, $C^{6/6'\ or\ 7/7'}$), 197.3 (s, $C^{6/6'\ or\ 7/7'}$), 197.2 (s, $C^{6/6'\ or\ 7/7'}$), 105.2 (s, $C^{8/8'}$), 104.7 (s, $C^{8/8'}$), 102.6 (s, $C^{9/9'}$), 102.2 (s, $C^{9/9'}$), 101.2 (s, $C^{11/11'}$), 100.7 (s, $C^{11/11'}$), 88.9 (s, $C^{13/13'\ or\ 14/14'}$), 88.1 (s, $C^{13/13'\ or\ 14/14'}$), 86.3 (s, $C^{15/15'}$), 86.1 (s, $C^{15/15'}$), 83.0 (s, $C^{12/12'}$), 82.9 (s, $C^{12/12'}$), 82.3 (s, $C^{13/13'\ or\ 14/14'}$), 79.6 (s, $C^{16/16'}$), 79.6 (s, $C^{16/16'}$), 49.5 (s, $C^{1/1'\ or\ 2/2'}$), 49.4 (s, $C^{1/1'\ or\ 2/2'}$), 48.9 (s, $C^{1/1'\ or\ 2/2'}$), 48.8 (s, $C^{1/1'\ or\ 2/2'}$), 36.8 (s, $C^{5/5'\ or\ 3/3'}$), 36.3 (s, $C^{5/5'\ or\ 3/3'}$), 28.1 and 28.1 (s, $C^{1/1'\ or\ 2/2'}$), 27.9 and 27.8 (s, $C^{4/4'}$), 19.0 (s, $C^{10/10'}$), 18.3 (s, $C^{10/10'}$), ^{19}F{^{1}H} NMR δ -72.58 (d, *J* = 707 Hz, $F^{Counter\text{-}ion}$); *m/z* (HRMS)$^+$ 389.0602 [M-PF6] ($C_{22}H_{25}O_3{}^{96}Ru^+$ requires 389.0618).



[Ru(η^6-9-(2-tolyl)-3-methoxy-3-azaspiro[5.5]undecane-8,10-dione)(η^5-cyclopentadienyl)]PF_6

Synthesised via general experimental 2, using 3-methoxy-3-azaspiro[5.5]undecane-8,10-dione (8.3 mg, 0.038 mmol, 1.1 eq.). The title compound was isolated as a brown solid (18 mg, 0.030 mmol, 63 %).

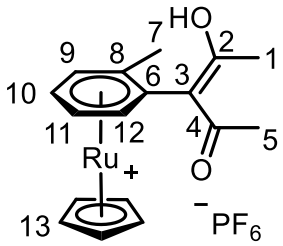
^{1}H NMR (599 MHz, CD_3OD) δ 6.08 (1H, d, *J* = 5.7 Hz, H^{15}), 5.95 (1H, t, *J* = 5.7 Hz, H^{17}), 5.92 – 5.88 (2H, m, $H^{16, 18}$), 5.25 (5H, s, H^{19}), 3.50 (3H, s, H^1), 3.20-3.12 (2H, m, $H^{7/8}$), 2.68-2.60 (2H, m, $H^{7/8}$), 2.54 (1H, d, *J* = 16.5 Hz, H^3), 2.40 (1H, d, *J* = 16.7 Hz, H^2), 2.31-2.24 (2H, m, $H^{2', 3'}$), 2.11 (3H, s, H^{13}), 1.95-1.85 (1H, m, H^4), 1.83-1.74 (1H, m, H^5), 1.60-1.50 (2H, m, $H^{4', 5'}$), ^{13}C NMR (151 MHz, CD_3OD) δ 191.1 (s, $C^{9/10}$), 189.8 (s, $C^{9/10}$), 105.4 (s, $C^{11/12}$), 104.9 (s, $C^{11/12}$), 102.4 (s, C^{14}), 88.8 (s, C^{18}), 86.2 (s, C^{15}), 82.9 (s, C^{17}), 82.4 (s, C^{16}), 79.7 (s, C^{19}), 57.6 (s, C^1), 50.6 (s, $C^{7/8}$), 50.5 (s, $C^{7/8}$), 35.0 (s, C^5), 34.2 (s, C^4), 31.4 (s, C^6), 19.1 (s, C^{13}), ^{19}F{^{1}H} NMR δ -74.76 (d, *J* = 707 Hz, $F^{Counter\text{-}ion}$); *m/z* (HRMS)$^+$ 462.1140 [M-PF6] ($C_{23}H_{28}NO_3{}^{96}Ru^+$ requires 462.1145).



[Ru(η^6-2-(2-tolyl)-cyclopentane-1,3-dione)(η^5-cyclopentadienyl)]PF_6

Synthesised via general experimental 2, using cyclopentane-1,3-dione (3.8 mg, 0.038 mmol, 1.1 eq.). The title compound was isolated as an impure brown solid.

^{1}H NMR (599 MHz, CD_3OD) δ 6.12 (1H, d, *J* = 5.7 Hz, H^9), 6.02-5.96 (2H, m $H^{11, 12}$), 5.95 (1H, t, *J* = 5.6 Hz, H^{10}), 5.32 (5H, s, H^{13}), 2.40 (4H, s, $H^{1, 2}$), 2.23 (3H, s, H^7), ^{13}C NMR (151 MHz, CD_3OD) δ 201.4 (s, $C^{3, 4}$), 106.0 (s, C^5), 101.3 (s, C^6), 101.0 (s, C^8), 87.1 (s, C^{12}), 86.6 (s, C^9), 83.5 (s, C^{11}), 82.9 (s, C^{10}), 79.5 (s, C^{13}), 32.3 (s, $C^{1, 2}$), 18.7 (s, C^7), ^{19}F{^{1}H} NMR δ -72.54 (d, *J* = 707 Hz, $F^{Counter\text{-}ion}$); *m/z* (HRMS)$^+$ 349.0314 [M-PF6] ($C_{17}H_{17}NO_4{}^{96}Ru^+$ requires 349.0305).



[Ru(η^6-3-(2-tolyl)-pentane-2,4-dione)(η^5-cyclopentadienyl)]PF_6

Synthesised via general experimental 2, using acetylacetate (3.8 mg, 0.038 mmol, 1.1 eq.). The title compound was isolated as an impure brown oil (72%).

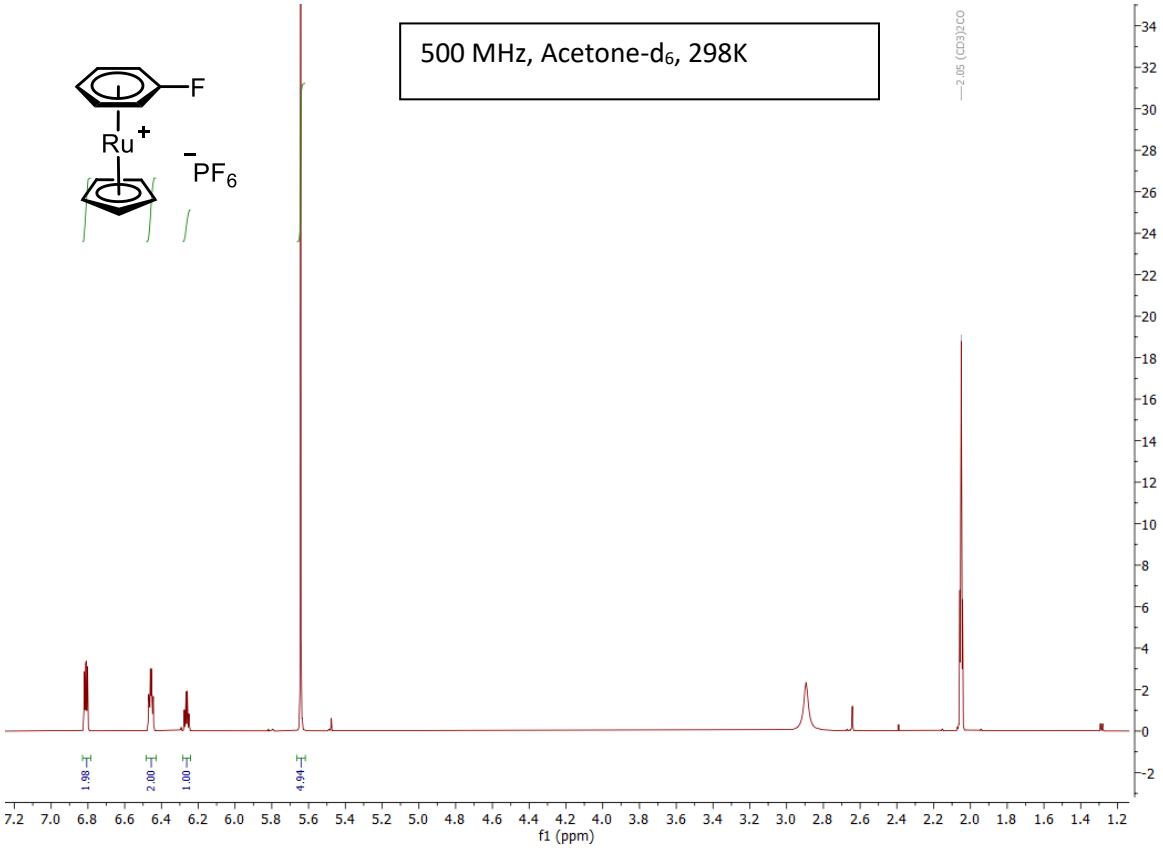
^{1}H NMR (400 MHz, Acetone) δ 6.11 (1H, d, *J* = 5.3 Hz, H^{Arene}), 6.01 (1H, d, *J* = 5.5 Hz, H^{Arene}), 5.98 – 5.90 (2H, m, H^{arene}), 5.29 (5H, s, H^{13}), 2.12 (3H, s, H^7), 2.07 (6H, q, *J* = 2.2 Hz, $H^{1,5}$). m/z (LRMS)$^+$ 351.20 [M-PF6] ($C_{17}H_{19}O_2{}^{96}Ru^+$ requires 351.04).

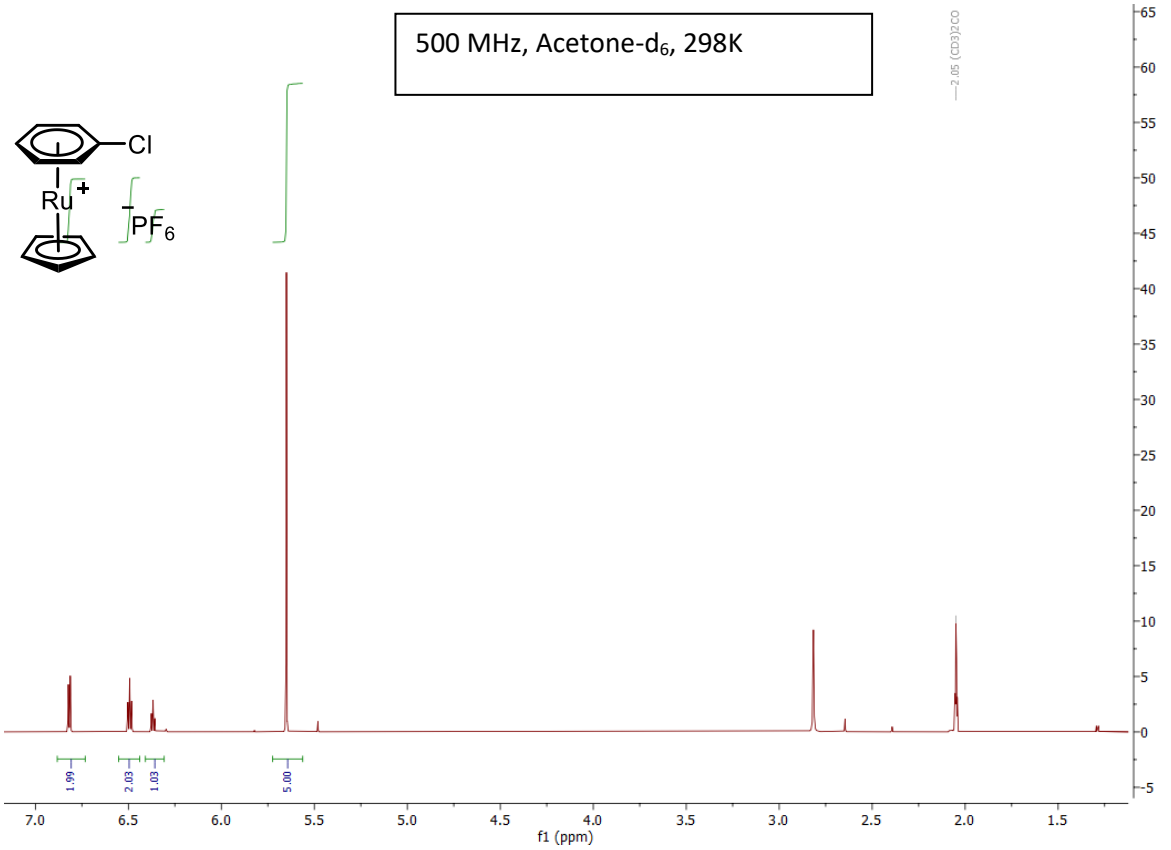
1e. General experimental 3 – Leaving group competition experiments

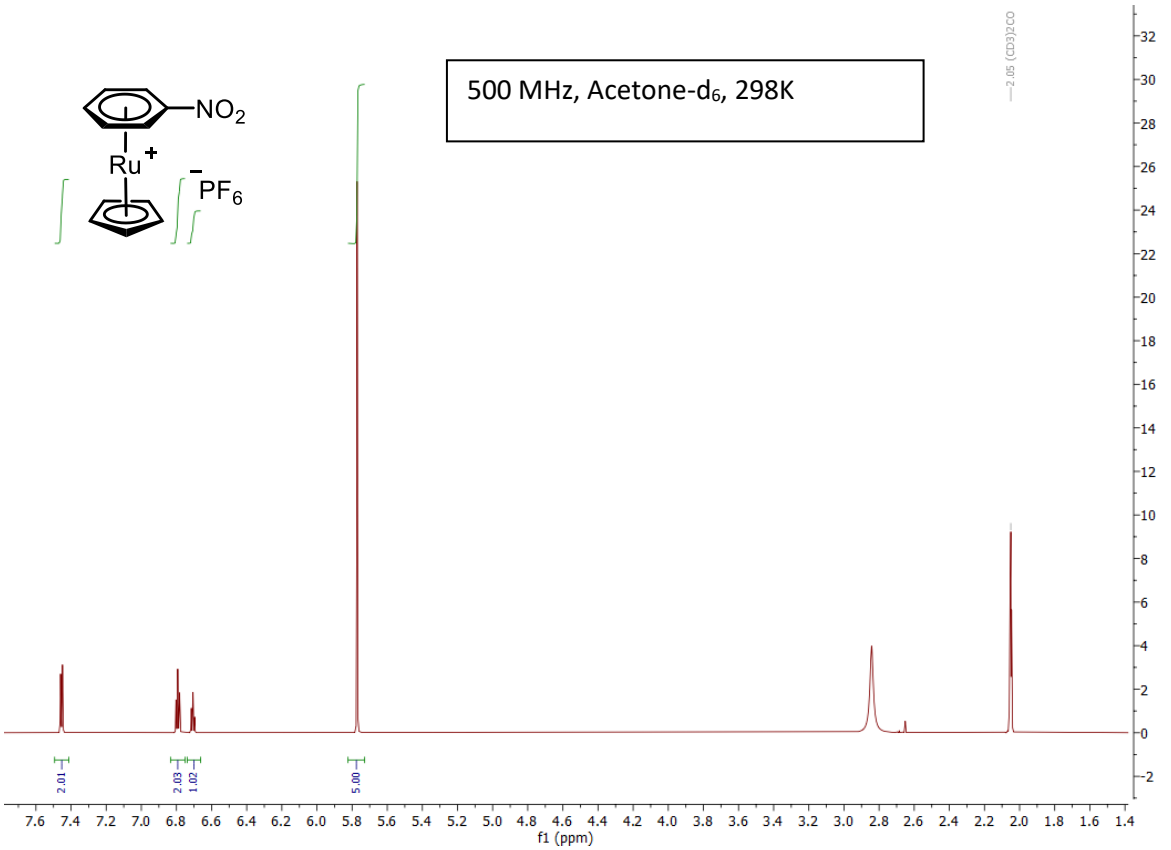
Potassium carbonate (2 eq.), 1,3-cyclohexanedione (1 eq.), [CpRu(η^6-2-chlorotoluene)]PF_6 (1 eq.) and anhydrous DMF were combined in an oven-dried Schlenk flask and stirred at 75 °C for 18 h. The reaction mixture was evaporated to dryness in *vacuo*, then the resulting brown residue was triturated with dichloromethane (3x5 mL) and filtered. The filtrate was dried under reduced pressure, then the brown solid was dissolved in d_6-acetone and analysed by ^{1}H NMR. Ratios of product(s) were calculated via analysis the ^{1}H NMR spectrum and confirmed by analysis of the mass spectrum.

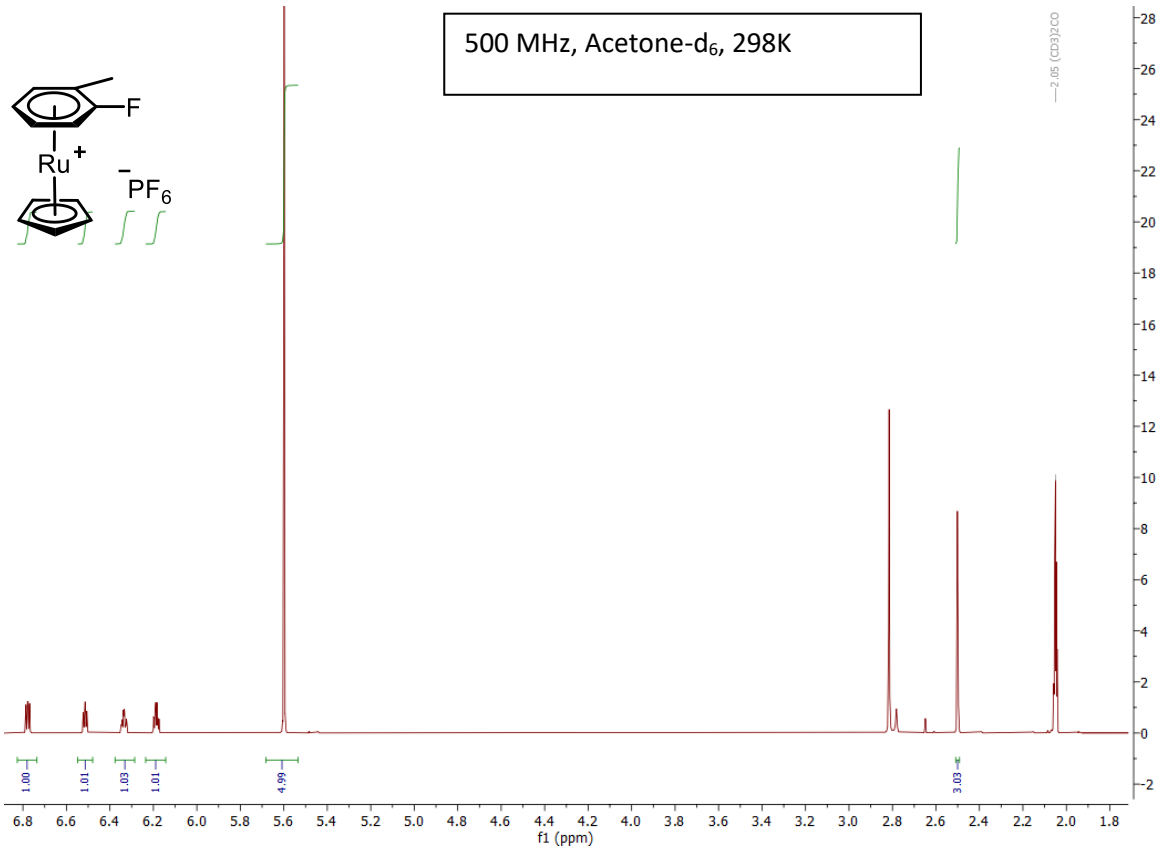
2. NMR Spectra

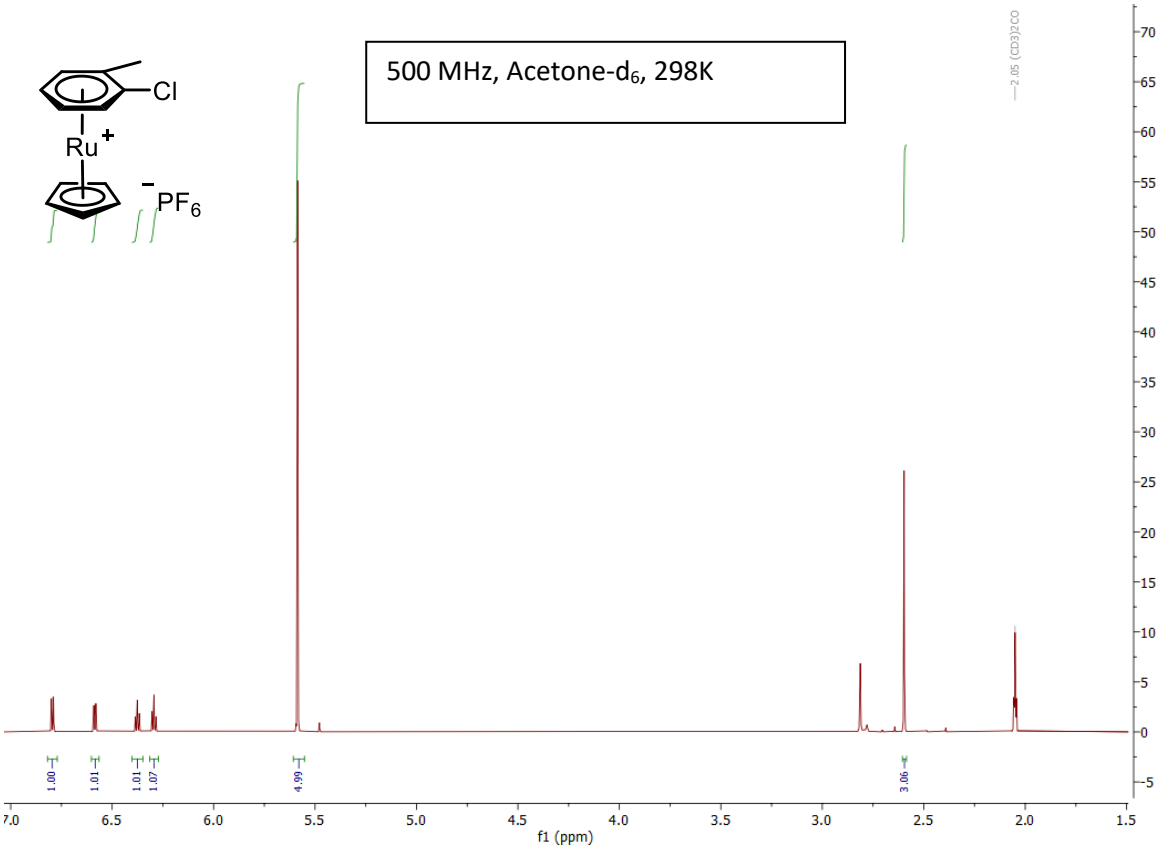
2a. Ru Sandwich complexes

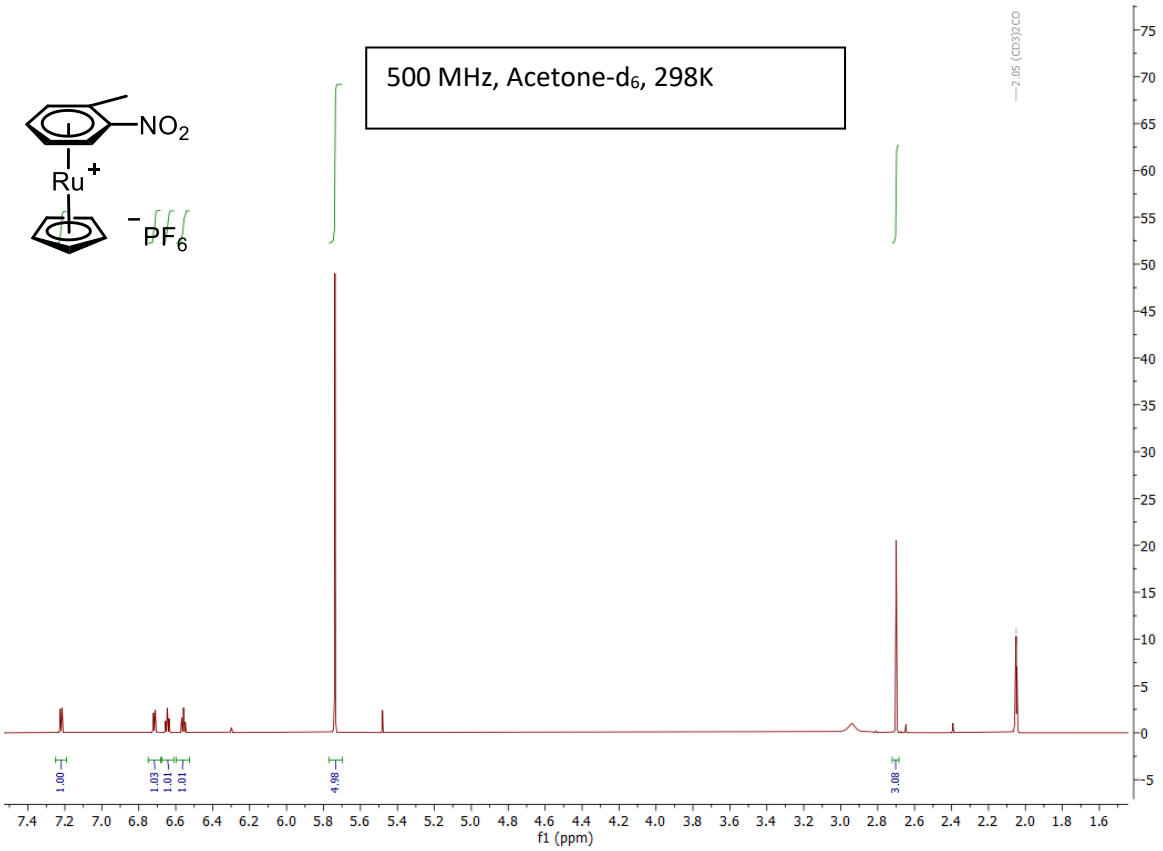


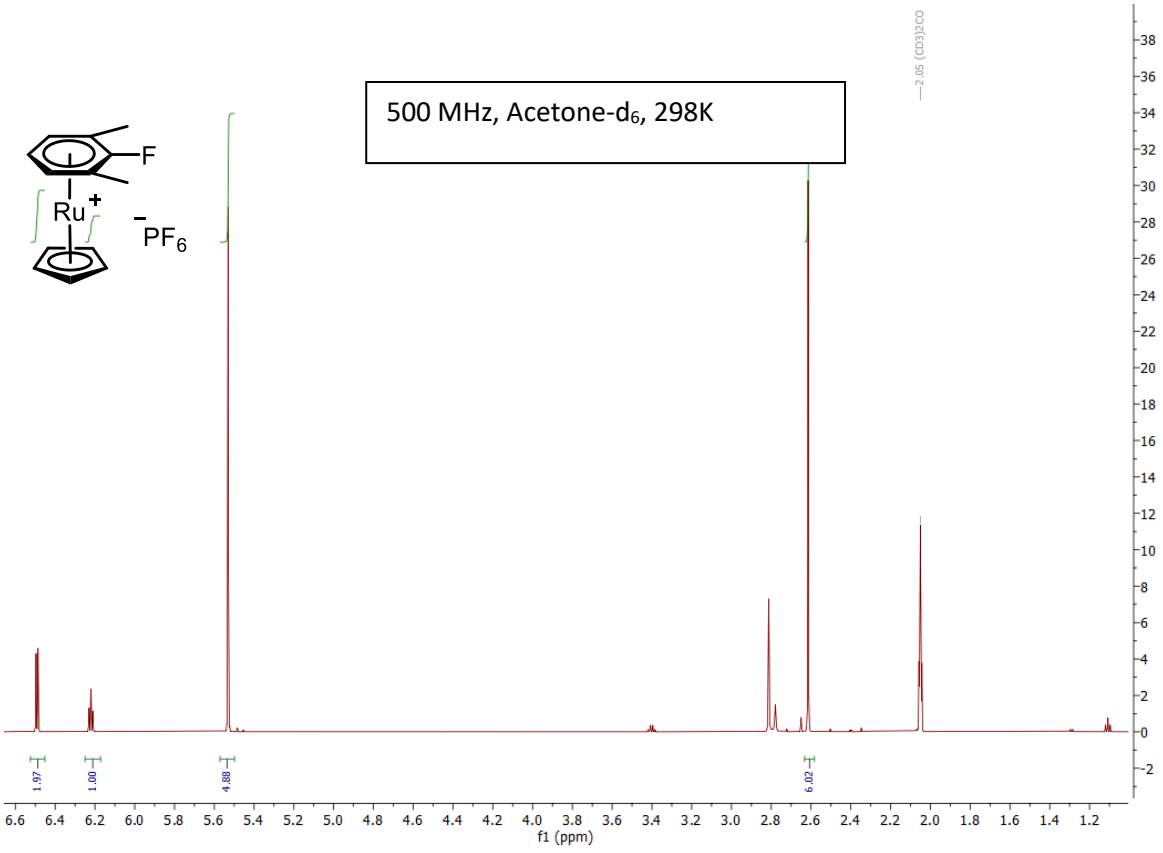

500 MHz, Acetone-d6, 298K
Cl
Ru
PF6
1.99
2.03
1.03
5.00
f1 (ppm)

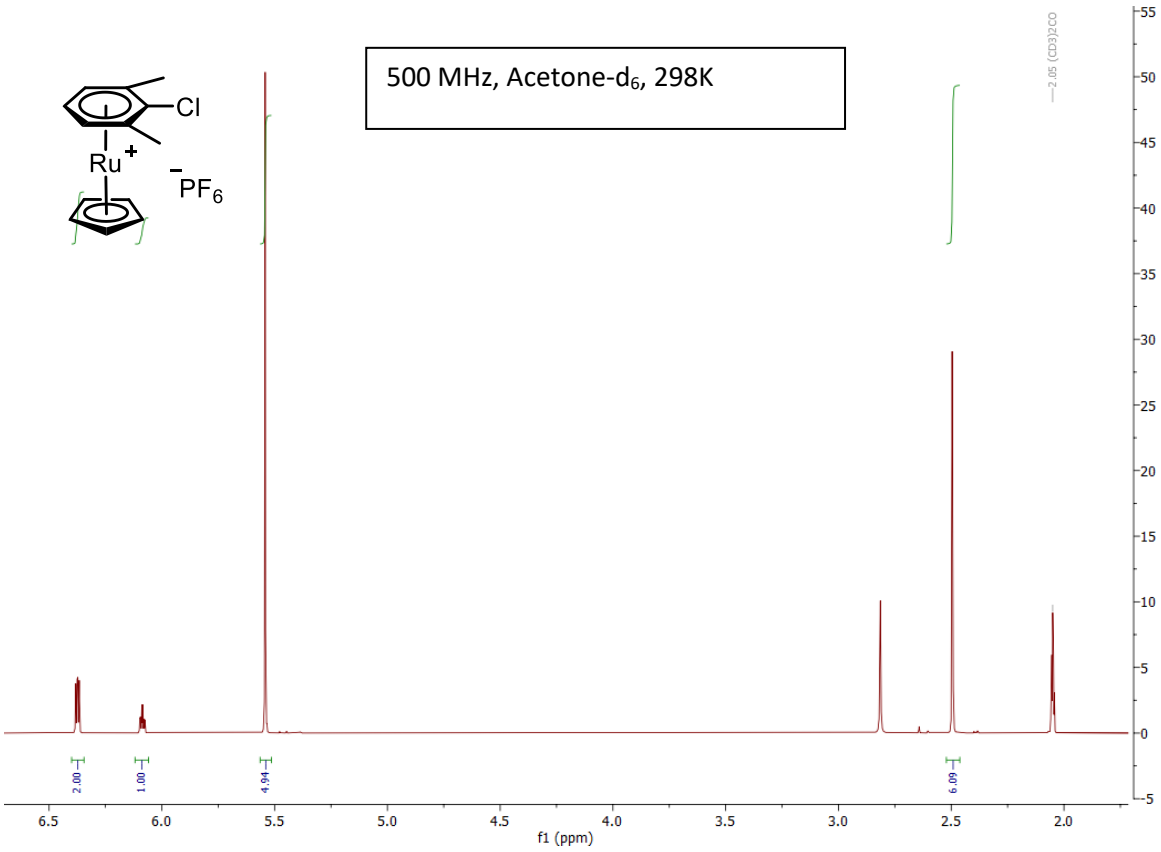

500 MHz, Acetone-d6, 298K
NO2
Ru
PF6
2.01
2.03
1.02
5.00
f1 (ppm)

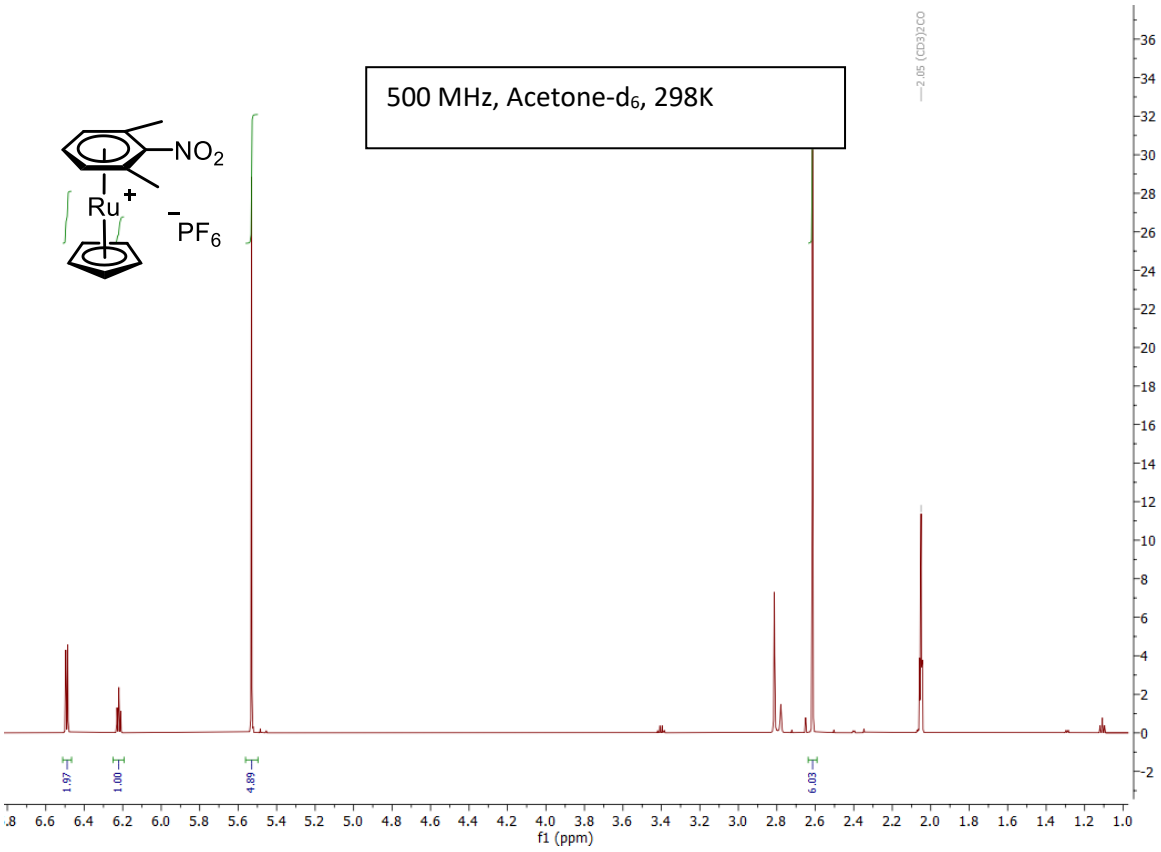

500 MHz, Acetone-d6, 298K
F
Ru+
PF6
f1 (ppm)

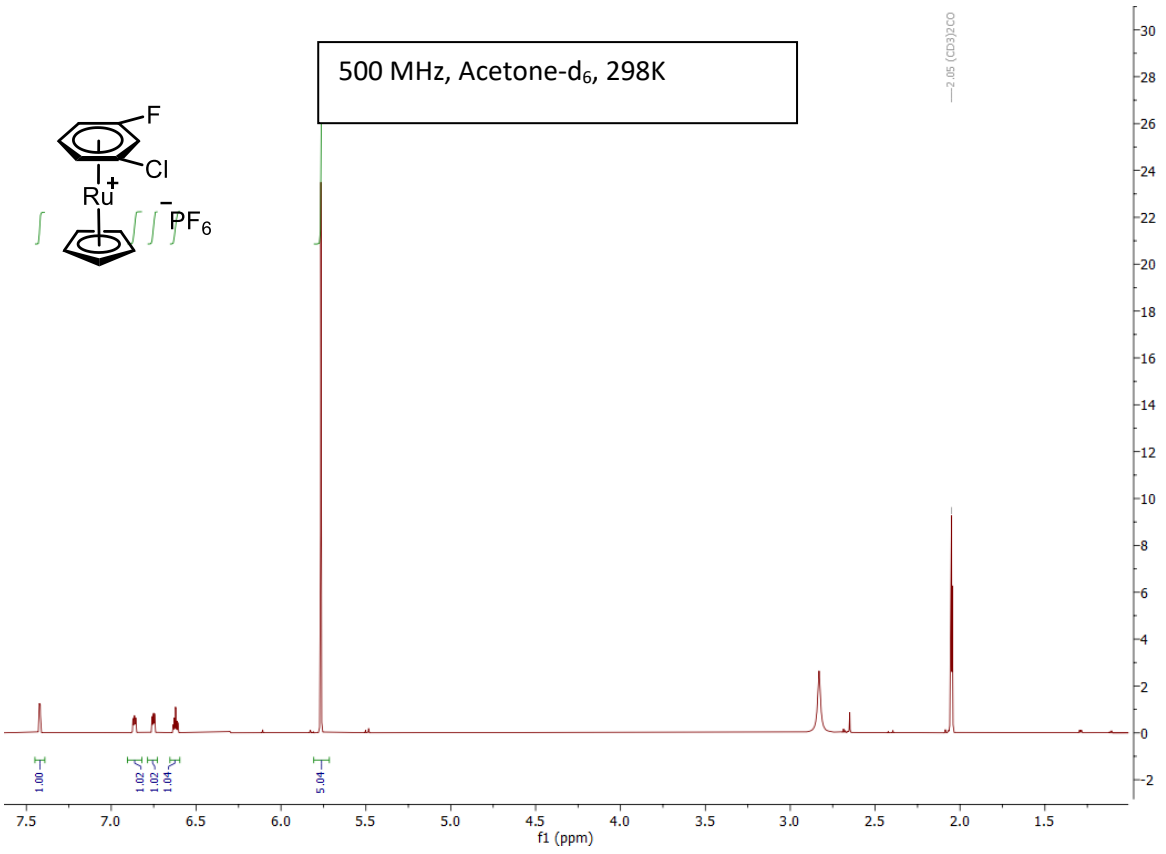

500 MHz, Acetone-d6, 298K
Cl
Ru+
PF6
f1 (ppm)

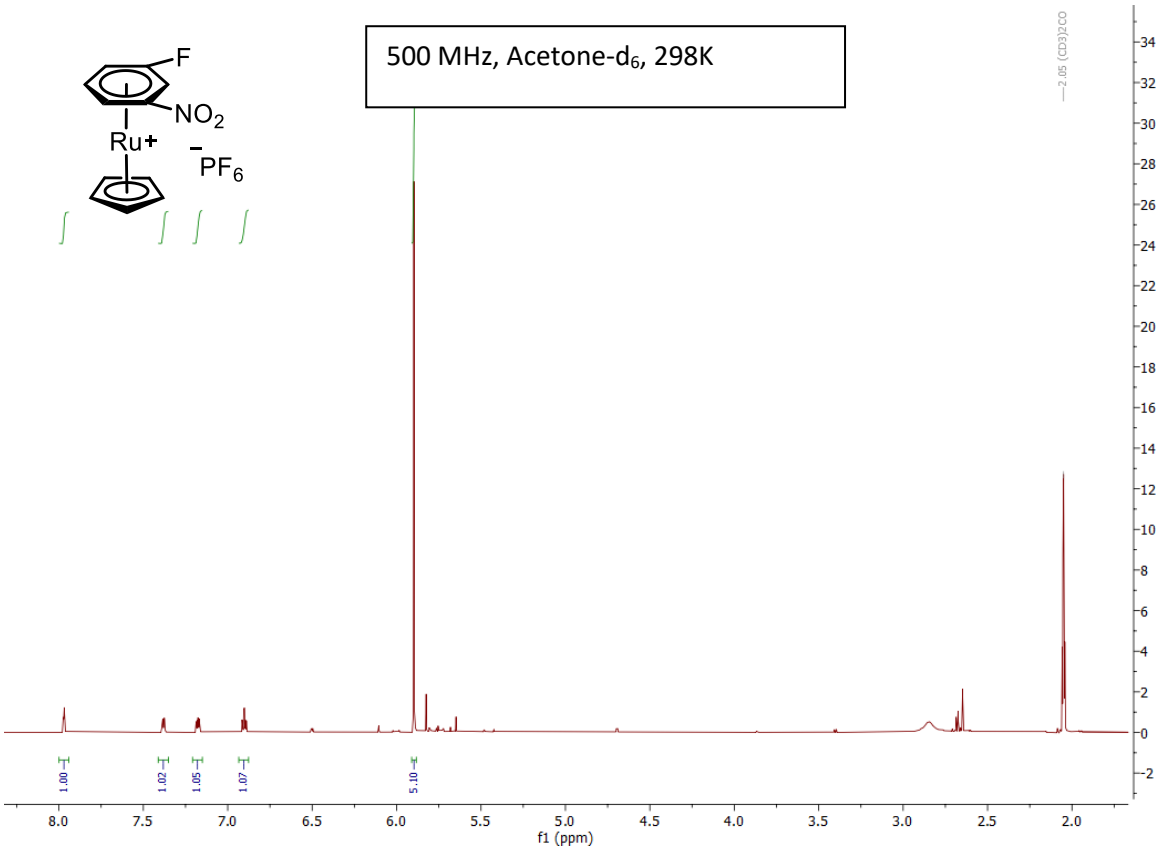

500 MHz, Acetone-d6, 298K
NO2
Ru+
PF6
f1 (ppm)

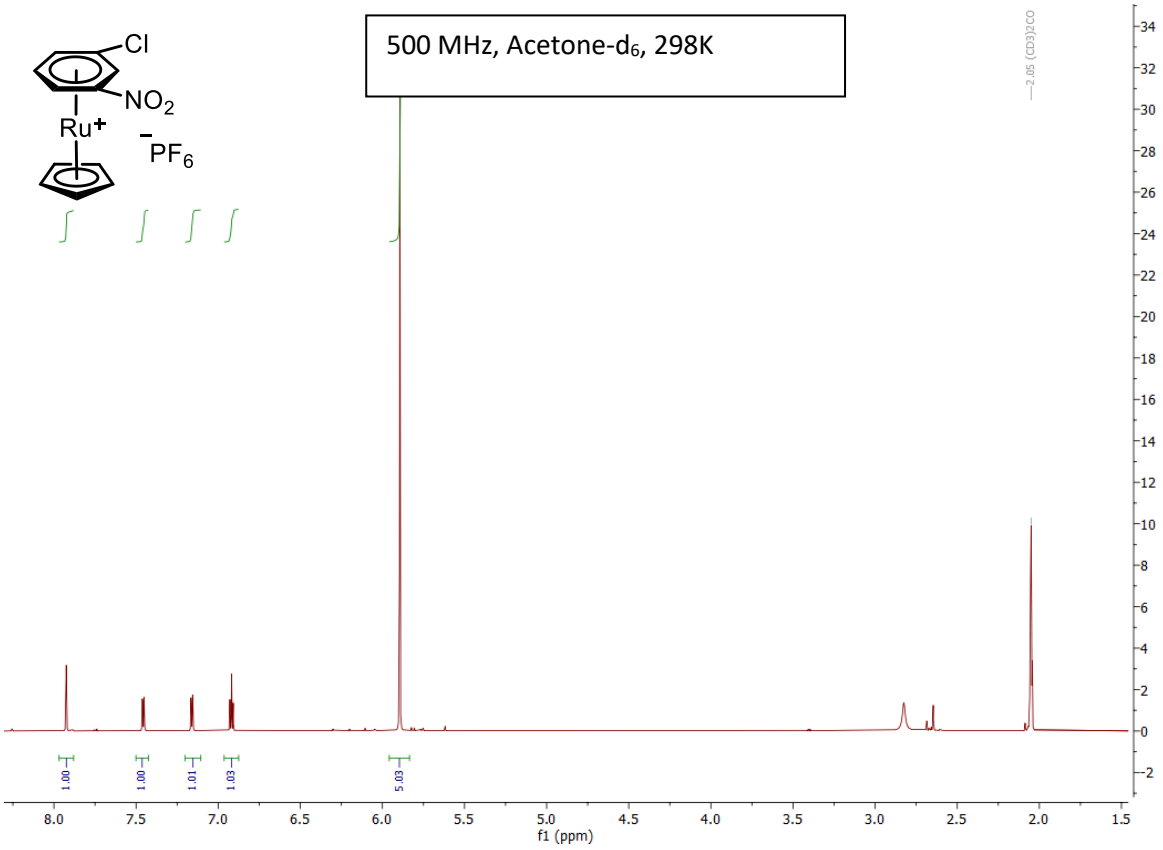

500 MHz, Acetone-d6, 298K
F
Ru+
PF6
f1 (ppm)

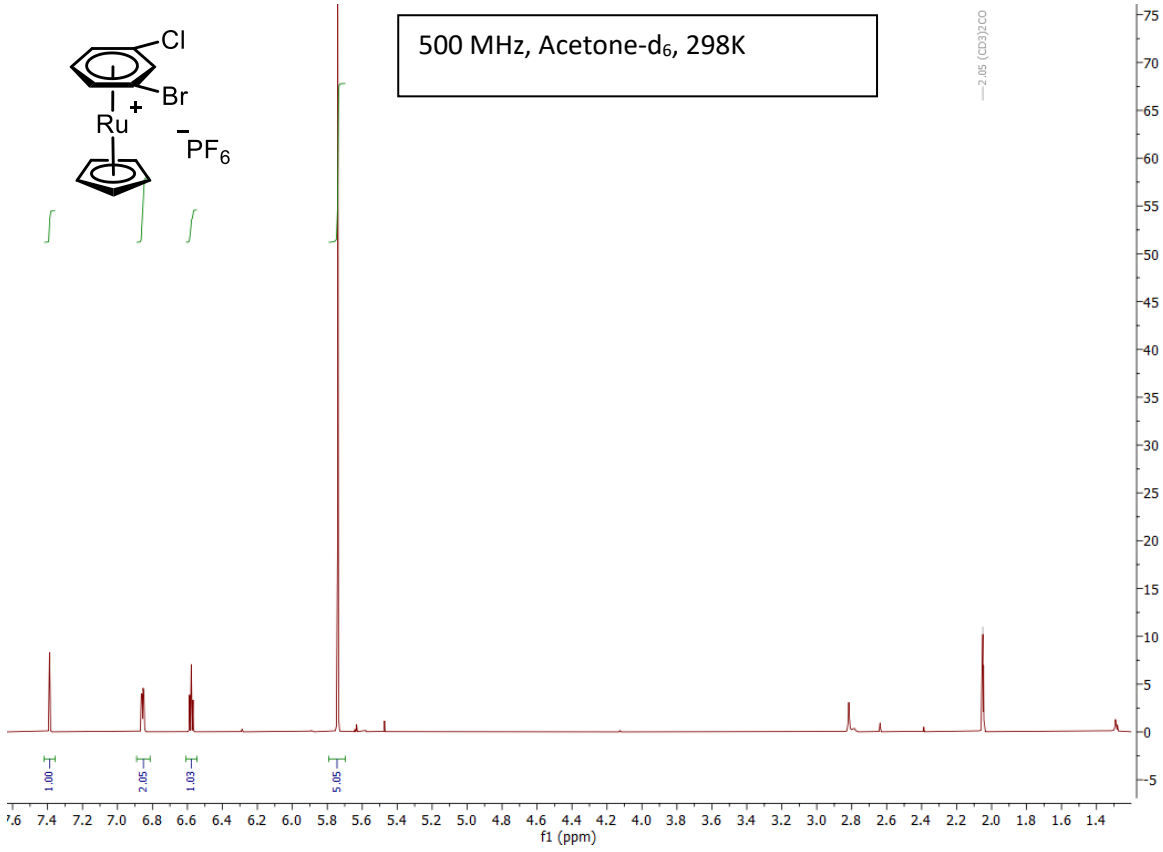

500 MHz, Acetone-d6, 298K
Cl
Ru
+
PF6
2.05 (CD3)2CO
2.00
1.00
4.94
6.09
f1 (ppm)

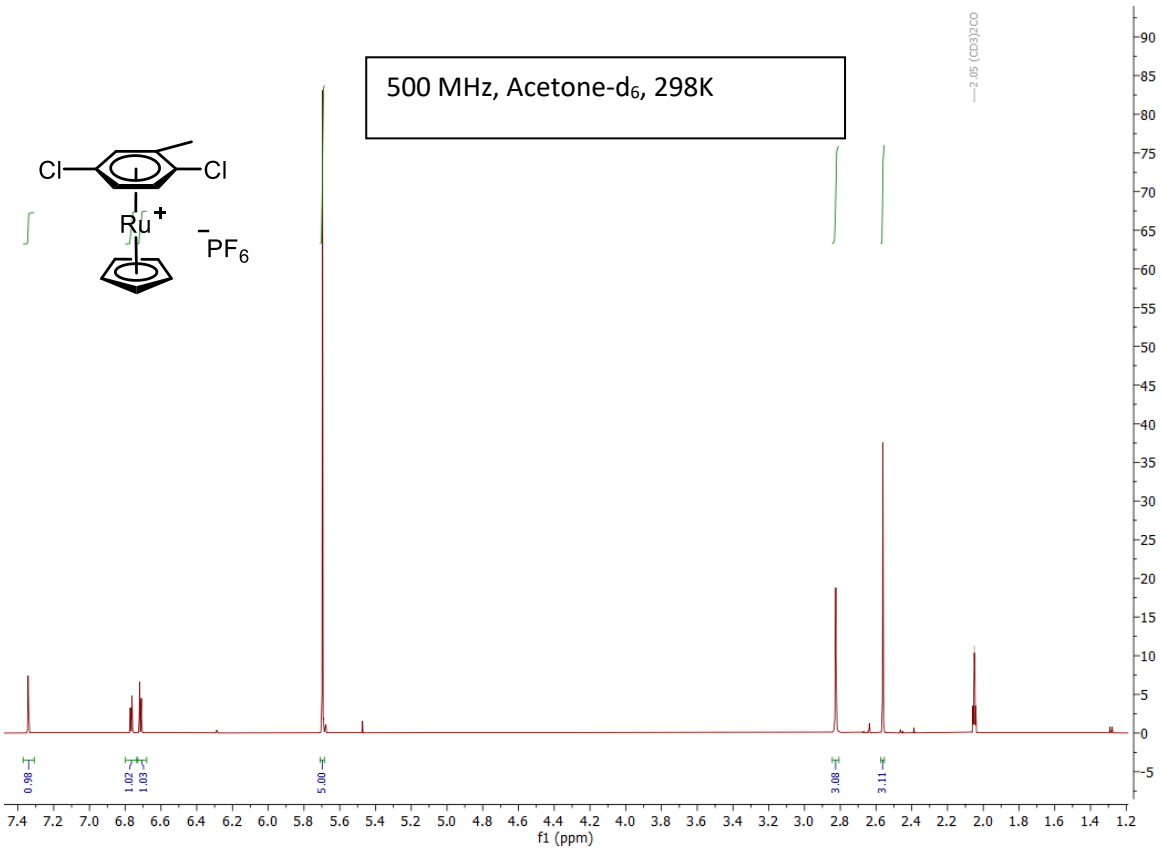

500 MHz, Acetone-d6, 298K
NO2
Ru
+
PF6
2.05 (CD3)2CO
1.97
1.00
4.89
6.03
f1 (ppm)

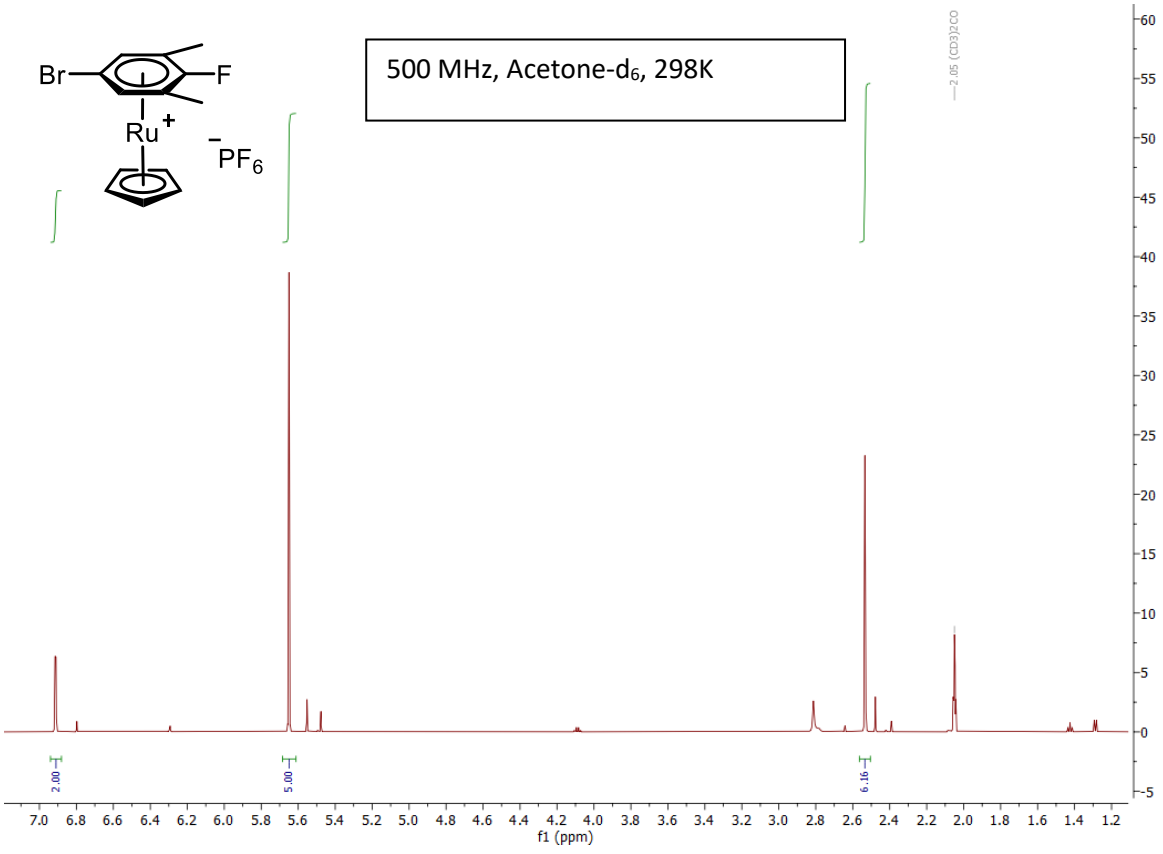

500 MHz, Acetone-d6, 298K
F
Cl
Ru+
PF6
f1 (ppm)

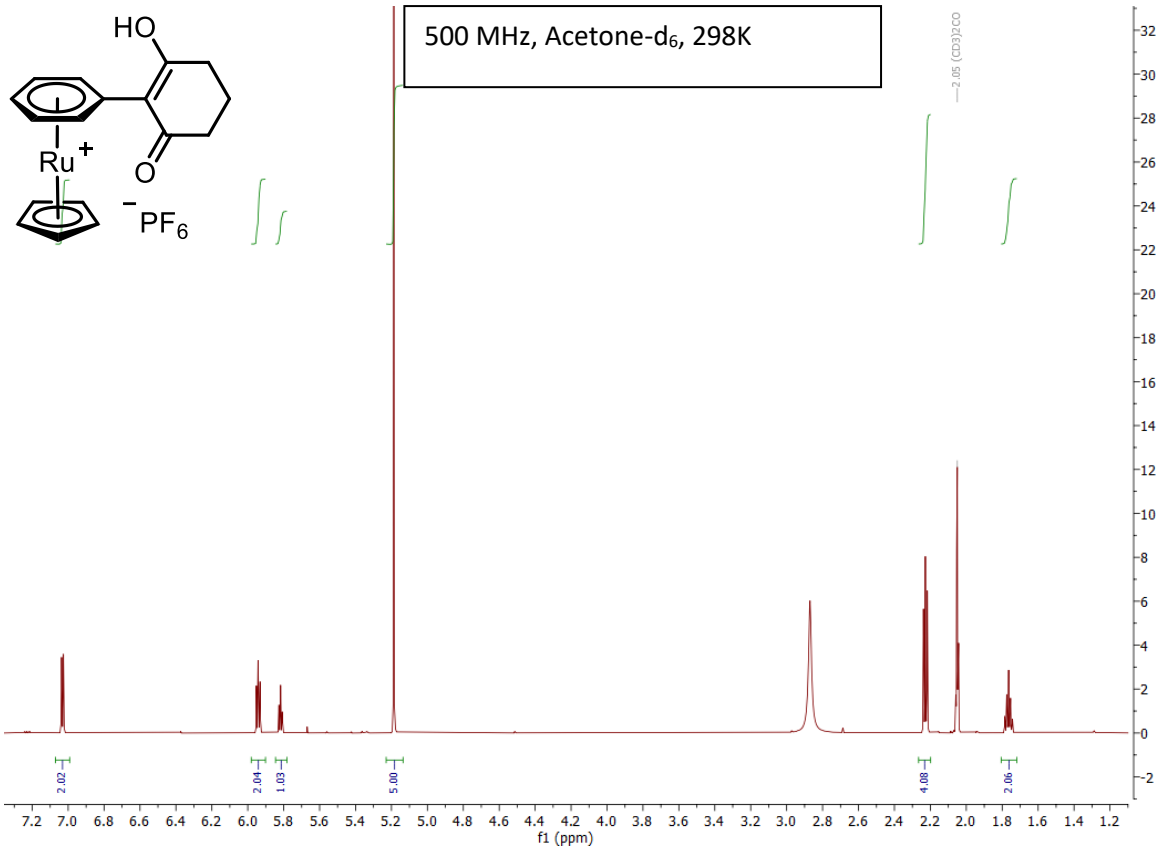

500 MHz, Acetone-d6, 298K
F
NO2
Ru+
PF6
f1 (ppm)

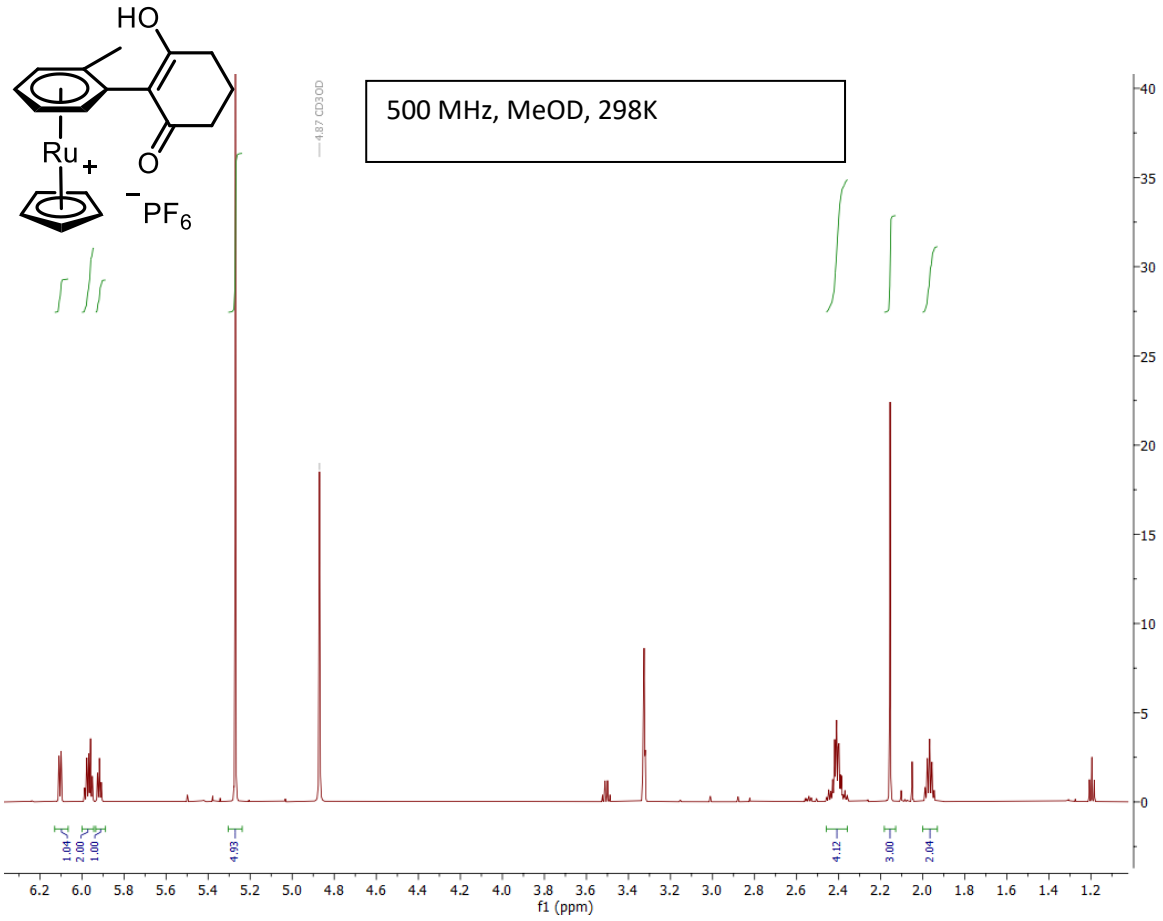

Cl
NO2
Ru+
PF6
500 MHz, Acetone-d6, 298K
2.05 (CD3)2CO
1.00
1.00
1.01
1.03
5.03
f1 (ppm)

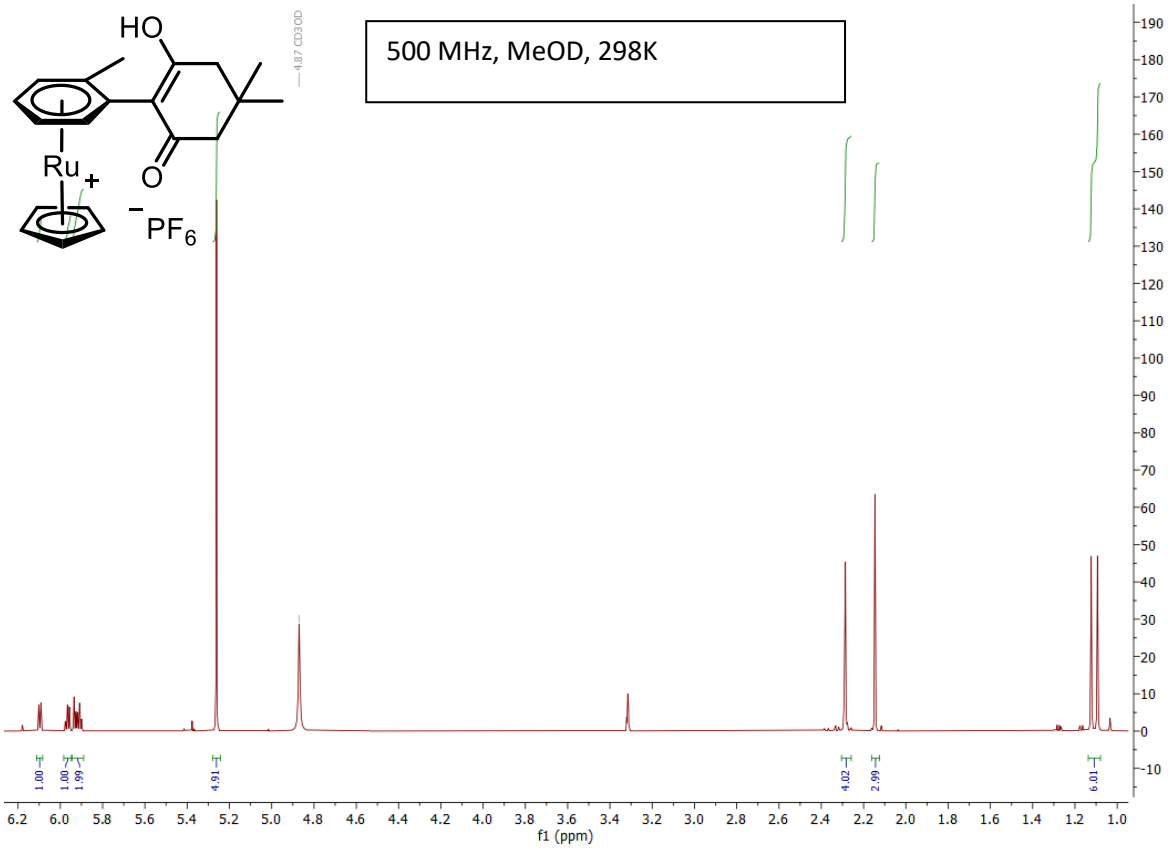

Cl
Br
Ru+
PF6
500 MHz, Acetone-d6, 298K
2.05 (CD3)2CO
1.00
2.05
1.03
5.05
f1 (ppm)

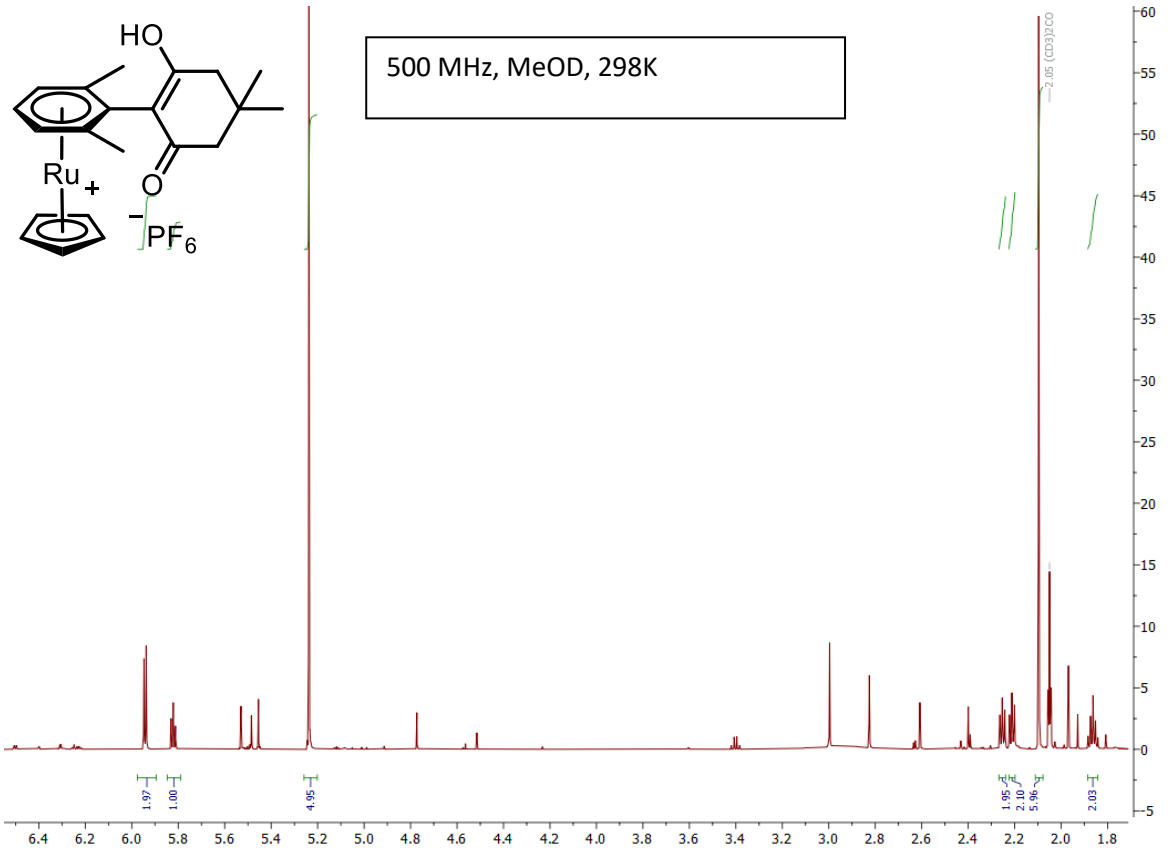

500 MHz, Acetone-d6, 298K
Cl
Cl
Ru+
PF6
f1 (ppm)

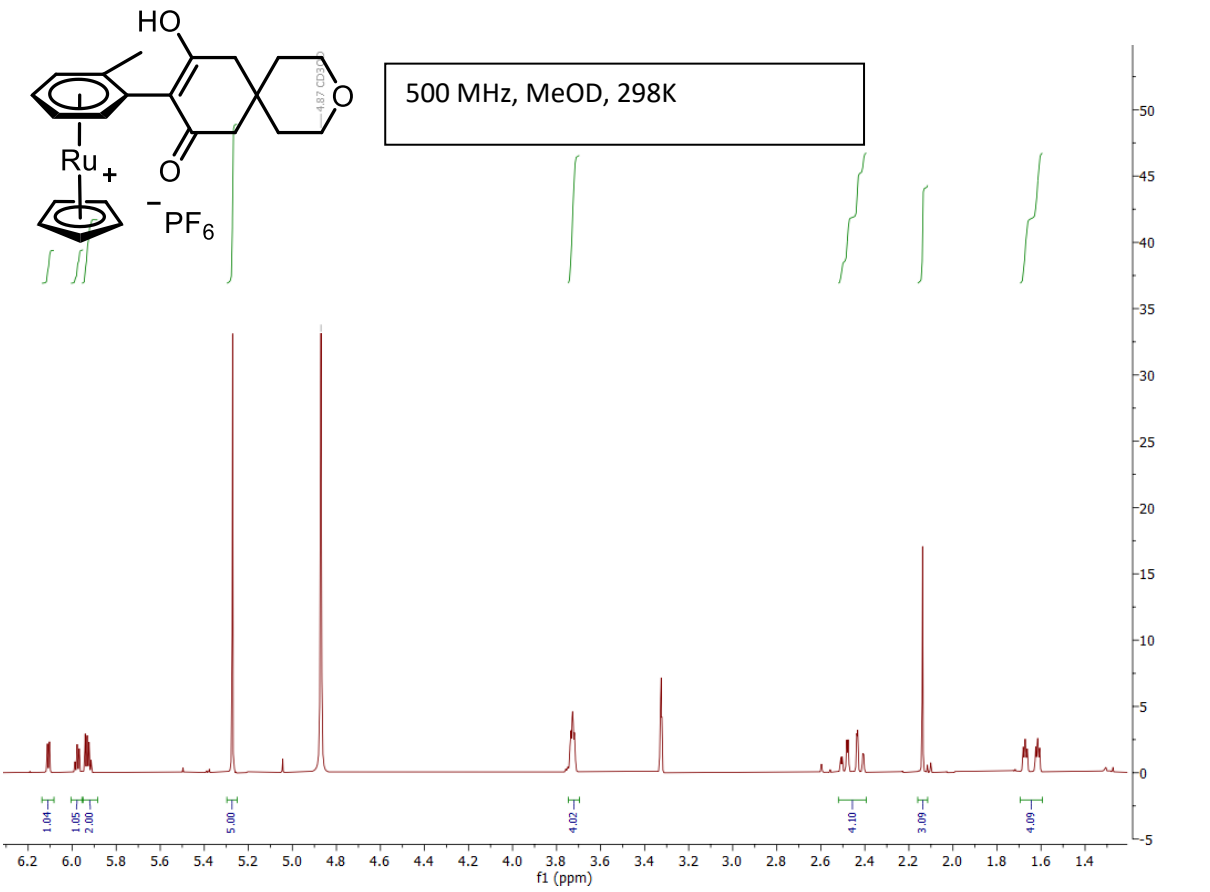

500 MHz, Acetone-d6, 298K
Br
F
Ru+
PF6
f1 (ppm)

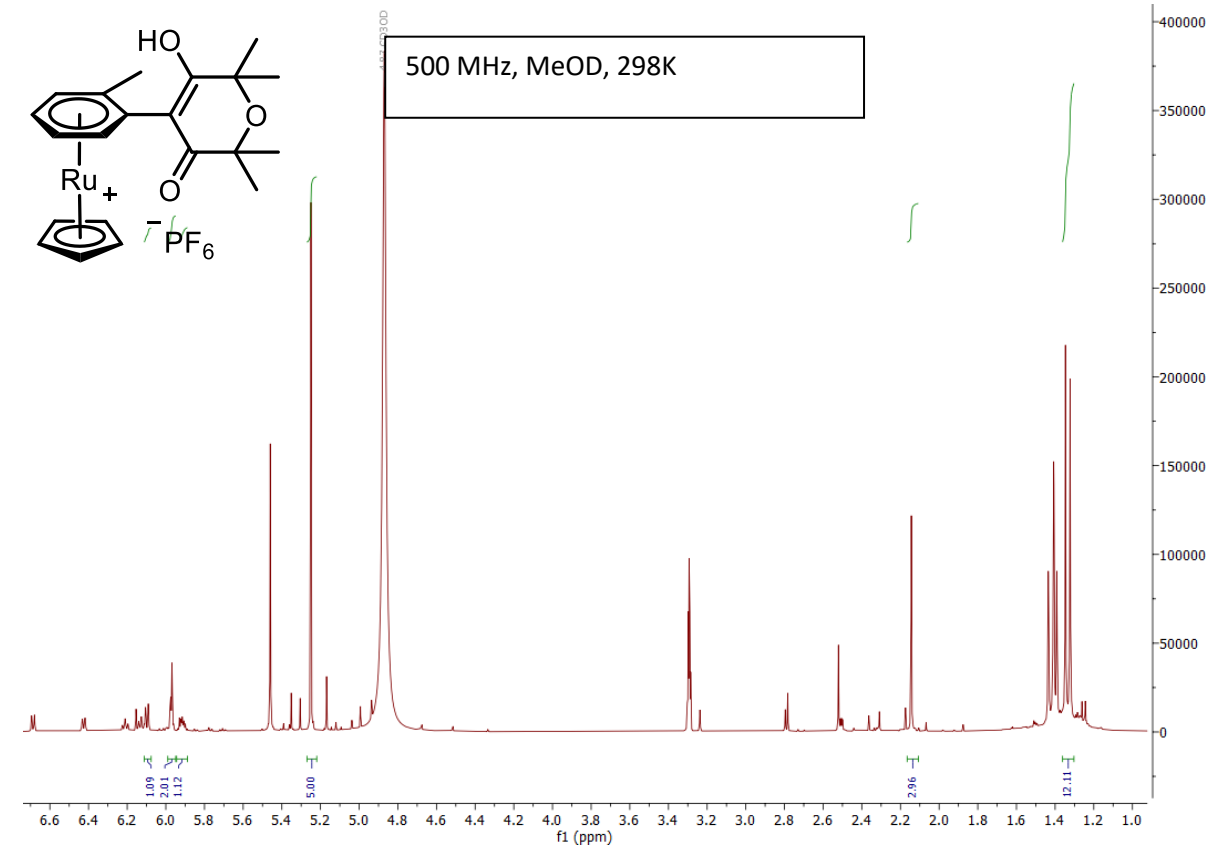

HO
Ru+
O
−PF6
500 MHz, Acetone-d6, 298K
2.05 (CD3)2CO
2.02
2.04
1.03
5.00
4.08
2.06
f1 (ppm)

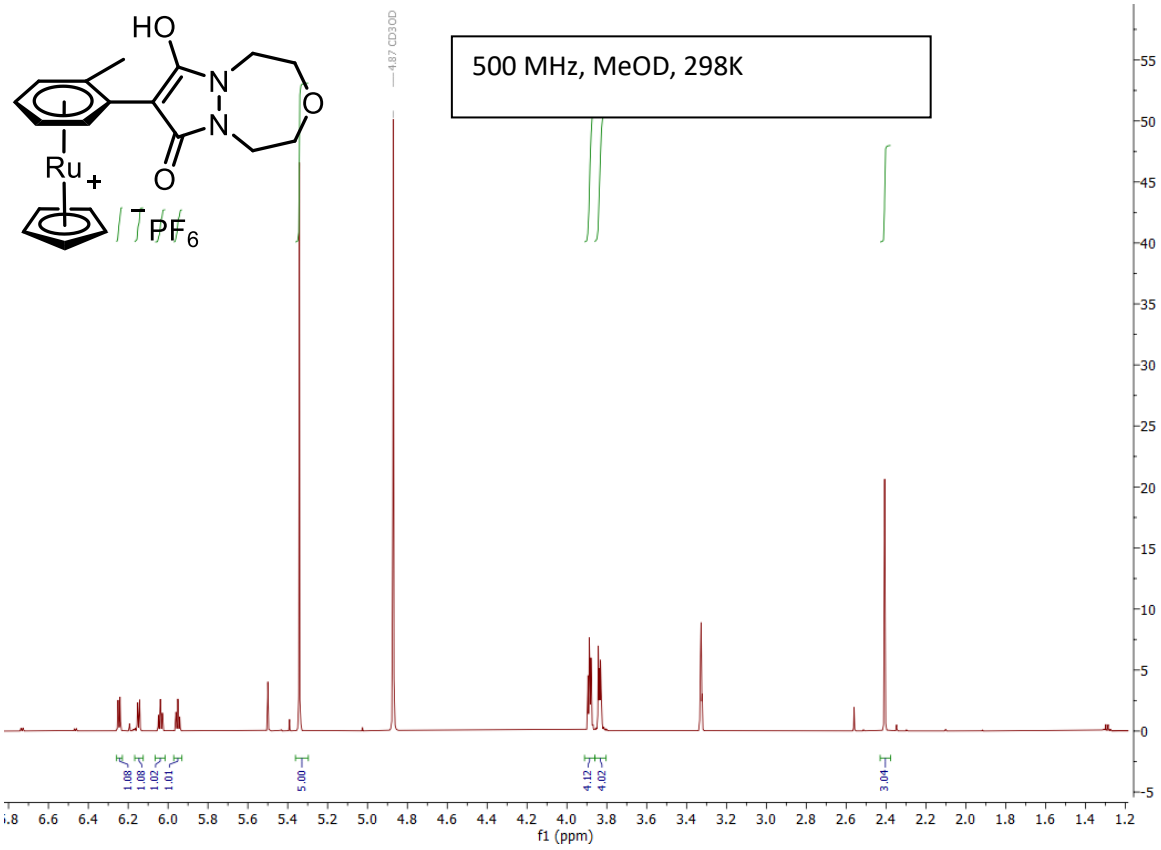

HO
Ru+
O
−PF6
500 MHz, MeOD, 298K
4.87 CD3OD
1.04
2.00
1.00
4.93
4.12
3.00
2.04
f1 (ppm)

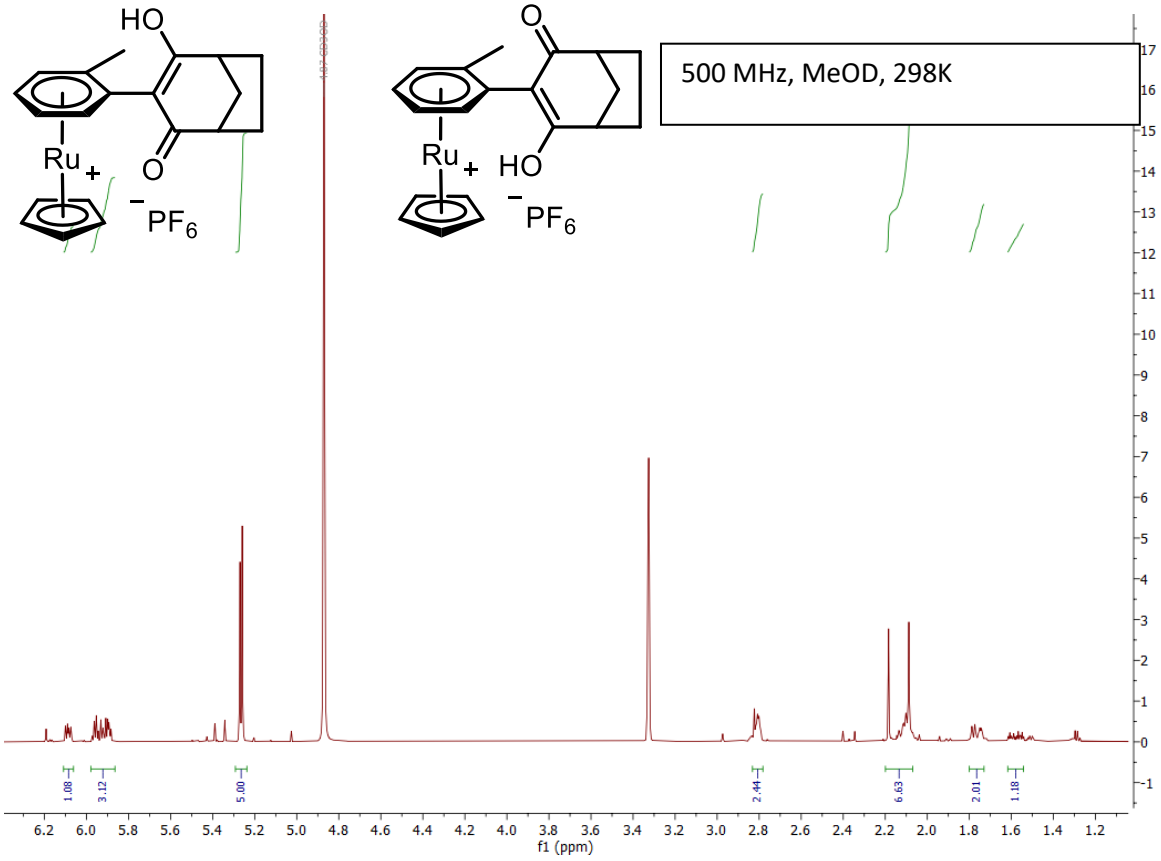

HO
O
Ru
+
PF6
500 MHz, MeOD, 298K
f1 (ppm)

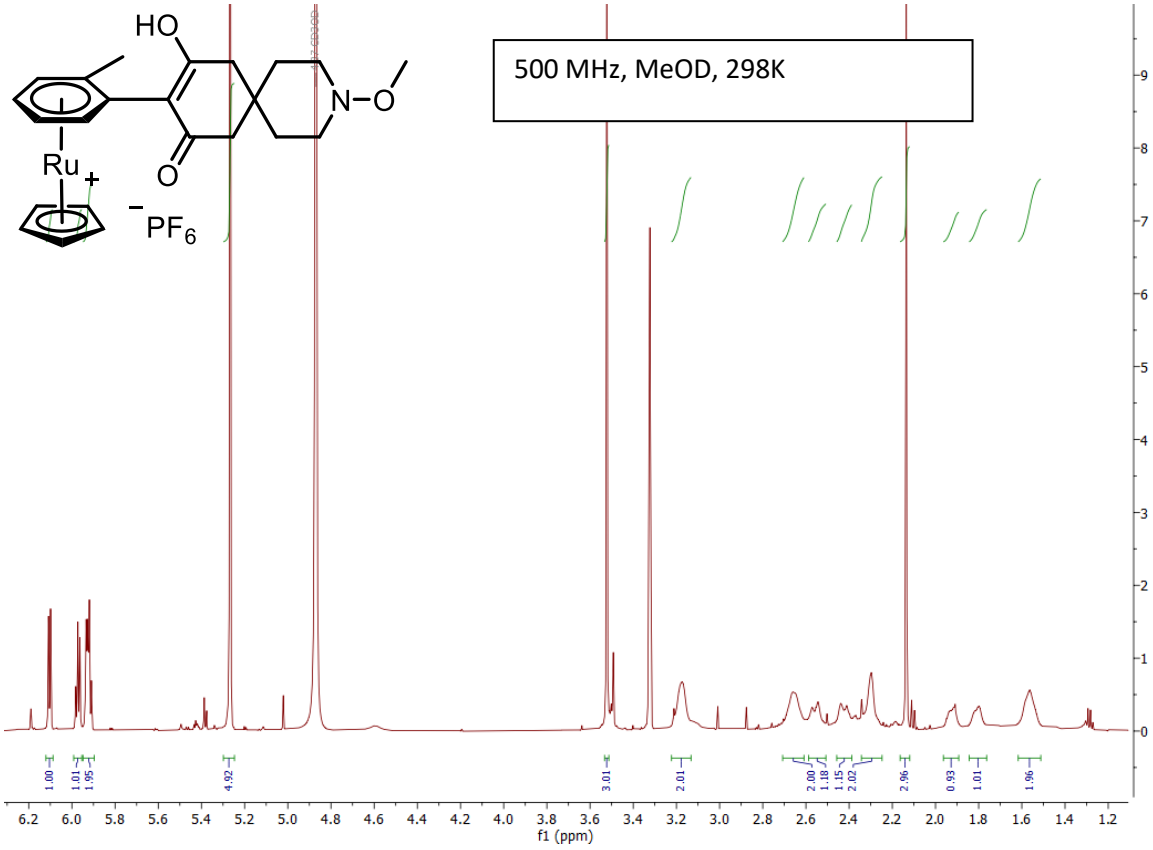

HO
O
Ru
+
PF6
500 MHz, MeOD, 298K

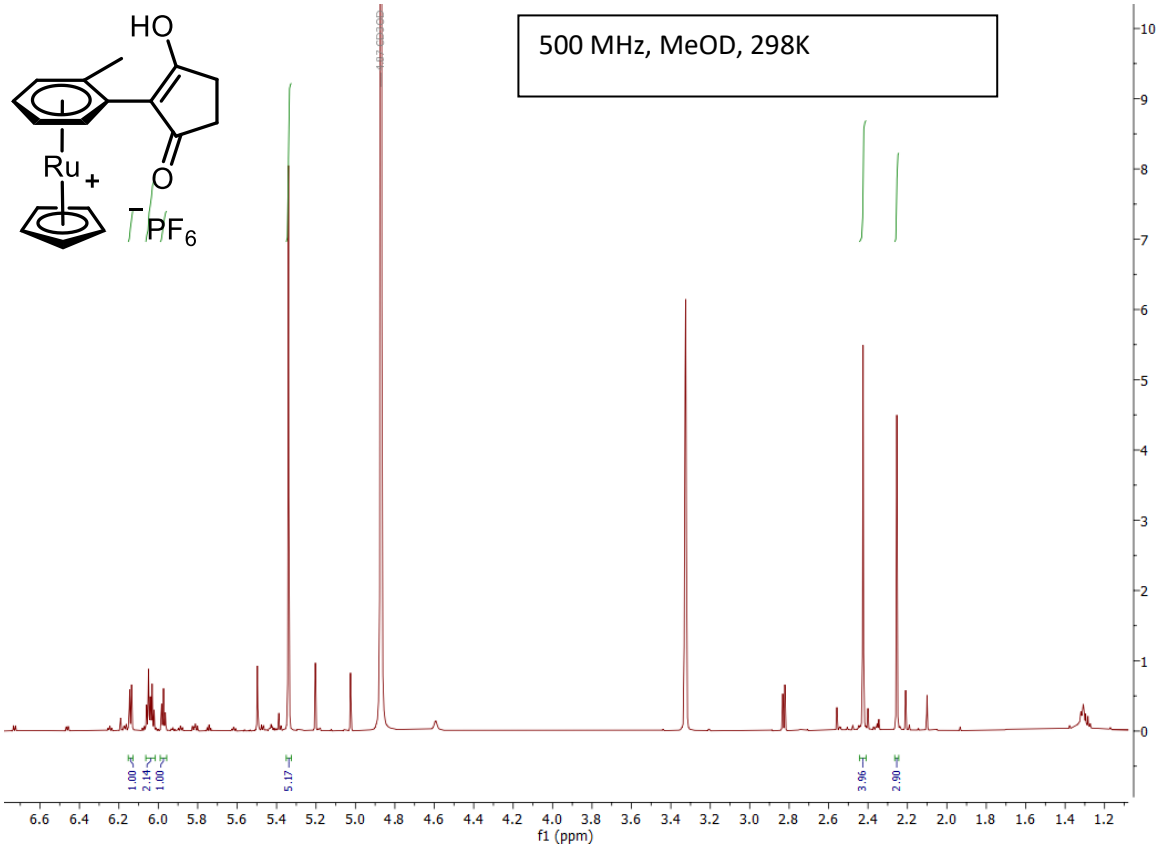

HO
O
Ru
+
O
PF6
500 MHz, MeOD, 298K
f1 (ppm)

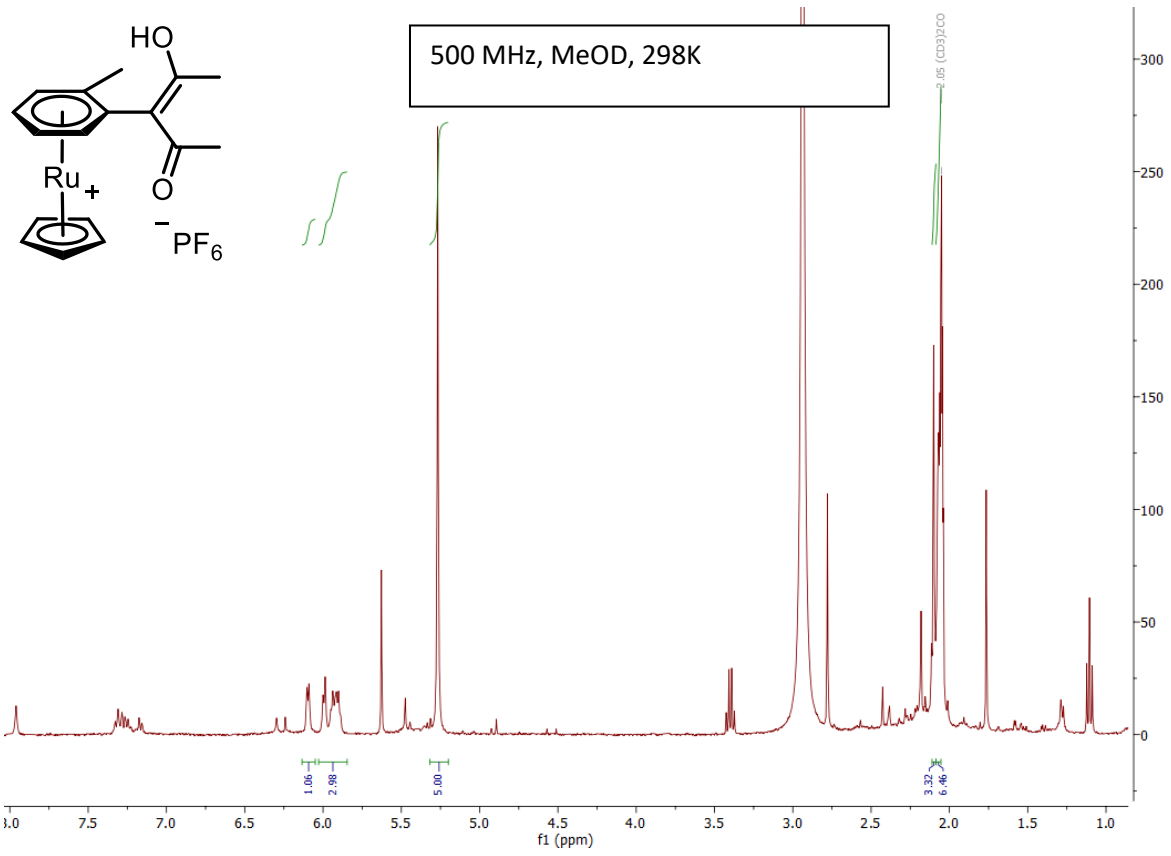

HO
O
Ru
+
O
PF6
500 MHz, MeOD, 298K
f1 (ppm)


HO
N
N
O
O
Ru +
PF6
500 MHz, MeOD, 298K
4.87 CD3OD
1.08
1.08
1.02
1.01
5.00
4.12
4.02
3.04
f1 (ppm)


HO
Ru +
O
PF6
O
Ru +
HO
PF6
500 MHz, MeOD, 298K
1.08
3.12
5.00
2.44
6.63
2.01
1.18
f1 (ppm)


HO
N–O
O
Ru
+
–
PF6
500 MHz, MeOD, 298K
1.00
1.01
1.95
4.92
3.01
2.01
2.00
1.18
1.15
2.02
2.96
0.93
1.01
1.96
f1 (ppm)


HO
Ru +
O
PF6
500 MHz, MeOD, 298K
f1 (ppm)


HO
Ru +
O
PF6
500 MHz, MeOD, 298K
f1 (ppm)

2b. Photolysis of Ru Sandwich Complexes

i. General Experimental

The specified Ru complex (10 mg) was added to a vial and dissolved in 1.5 mL CD_3CN. The vial was placed in a Penn M2 photoreactor and irradiated with UV light (365 nm, 60 Hz) for a specified amount of time. The mixture was analysed by ^1H NMR spectroscopy after 1, 2, 5, 10 and 15 minutes. Formation of free arene was detected by observing disappearance of bound arene signals (ca. 5.8-7 ppm) and emergence of free arene signals (ca. 6.8-8 ppm).

ii. Stacked Photolysis Spectra

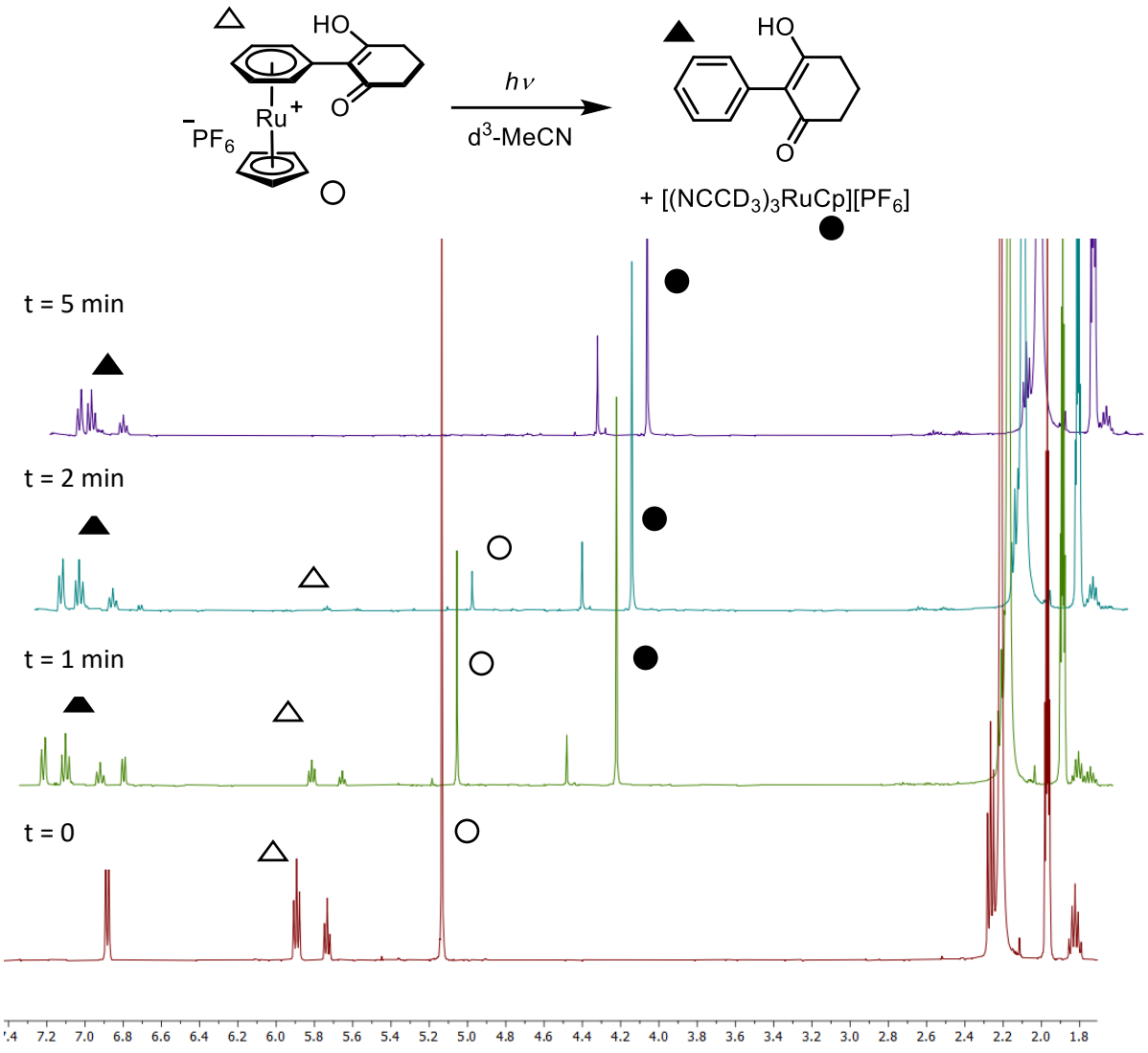


Figure S1. Stacked ^1H NMR spectra (CD_3CN, 298 K, 400 MHz) for the photolysis of the complex [Ru(η^6-2-benzylcyclohexane-1,3-dione)(η^5-cyclopentadienyl)]PF_6

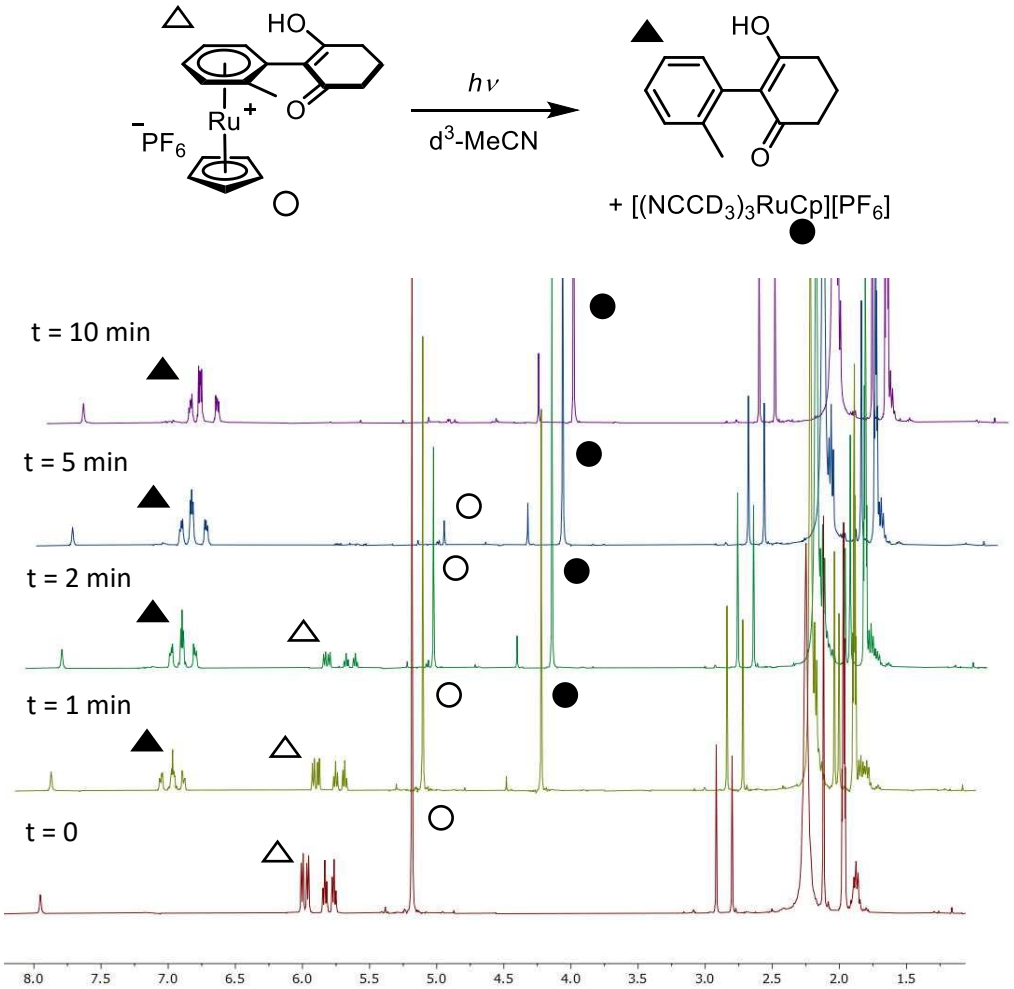


Figure S2. Stacked ^{1}H NMR spectra (CD_3CN, 298 K, 400 MHz) for the photolysis of the complex [Ru(η^6-2-(2-tolyl)cyclohexane-1,3-dione)(η^5-cyclopentadienyl)]PF_6

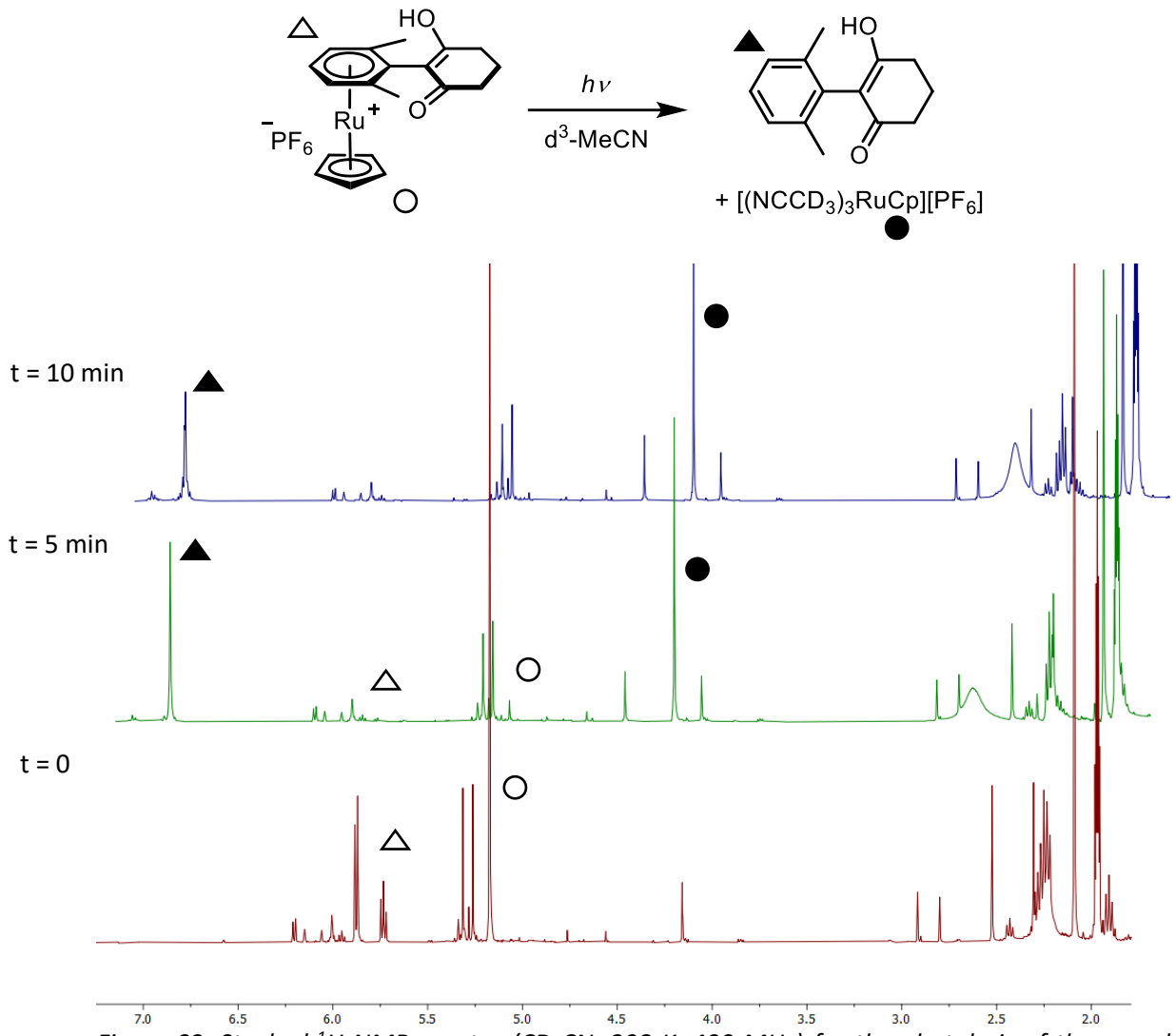


Figure S3. Stacked ^{1}H NMR spectra (CD_3CN, 298 K, 400 MHz) for the photolysis of the complex [Ru(η^6-2-(2-m-xylene)cyclohexane-1,3-dione)(η^5-cyclopentadienyl)]PF_6

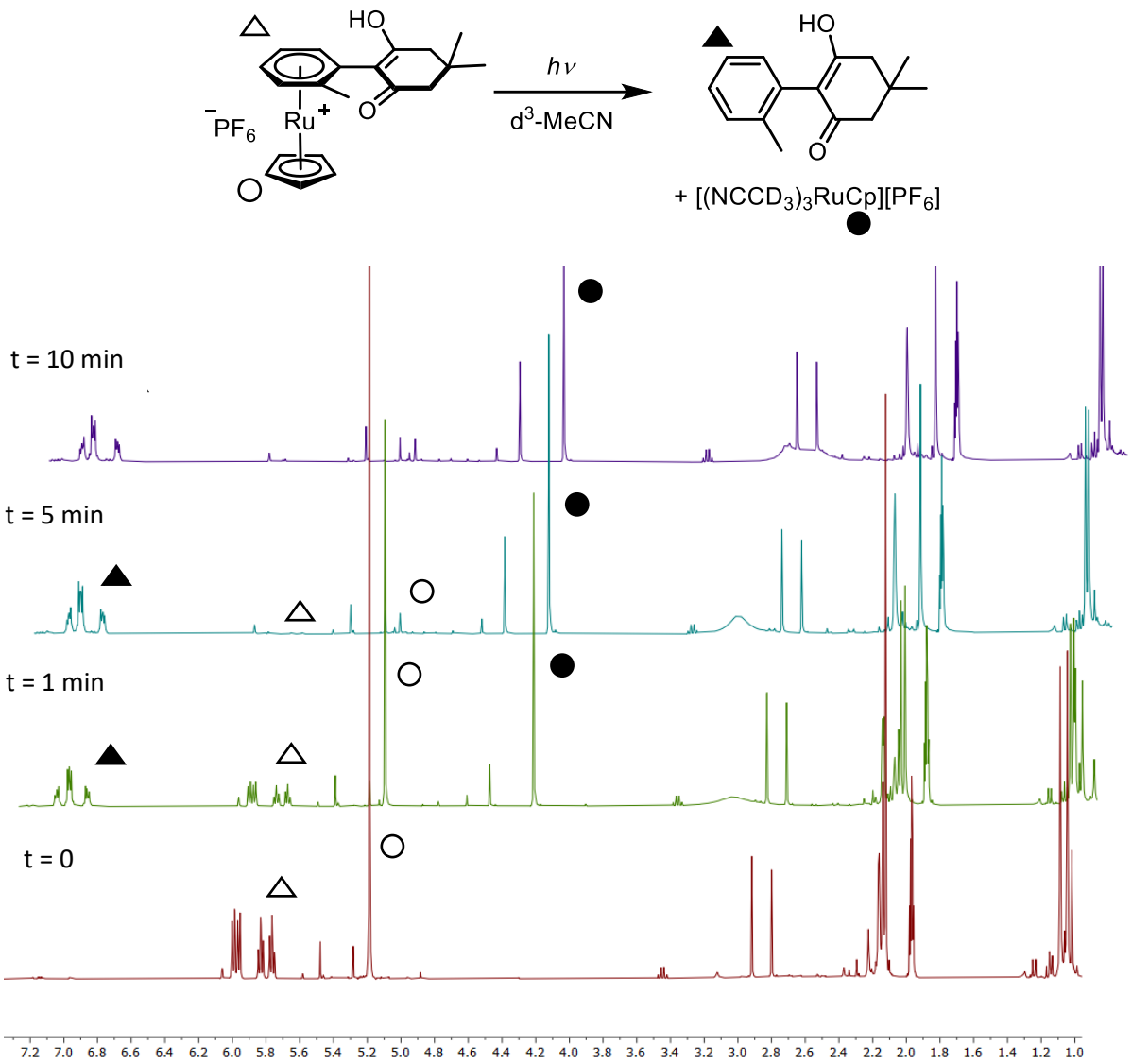


Figure S4. Stacked ^{1}H NMR spectra (CD_3CN, 298 K, 400 MHz) for the photolysis of the complex [Ru(η^6-2-(2-tolyl)-5,5'-dimethylcyclohexane-1,3-dione)(η^5-cyclopentadienyl)]PF_6

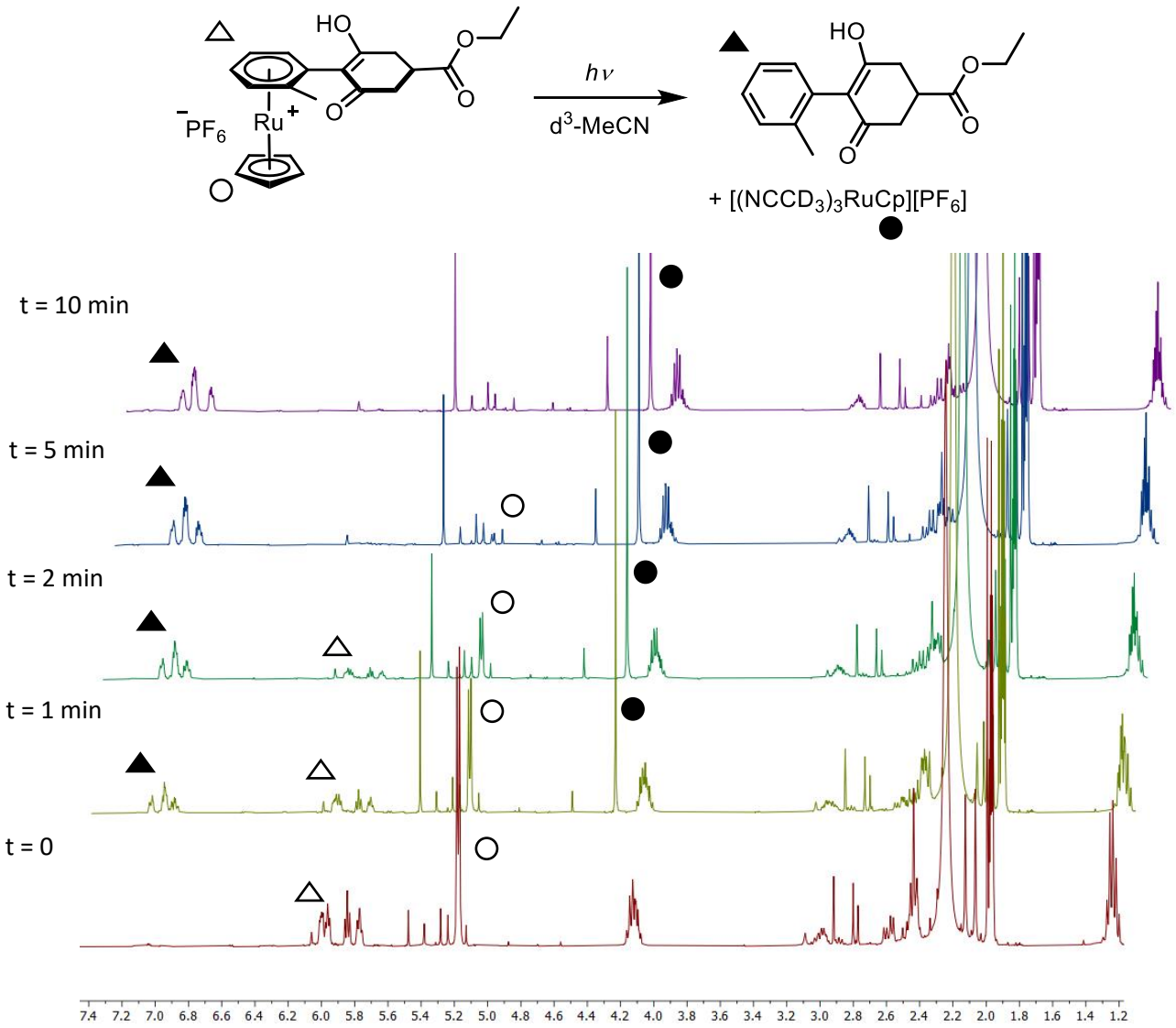


Figure S5. Stacked ^1H NMR spectra (CD_3CN, 298 K, 400 MHz) for the photolysis of the complex [Ru(η^6-2-(2-tolyl)-(5-ethylacetyl)cyclohexane-1,3-dione)(η^5-cyclopentadienyl)]PF_6

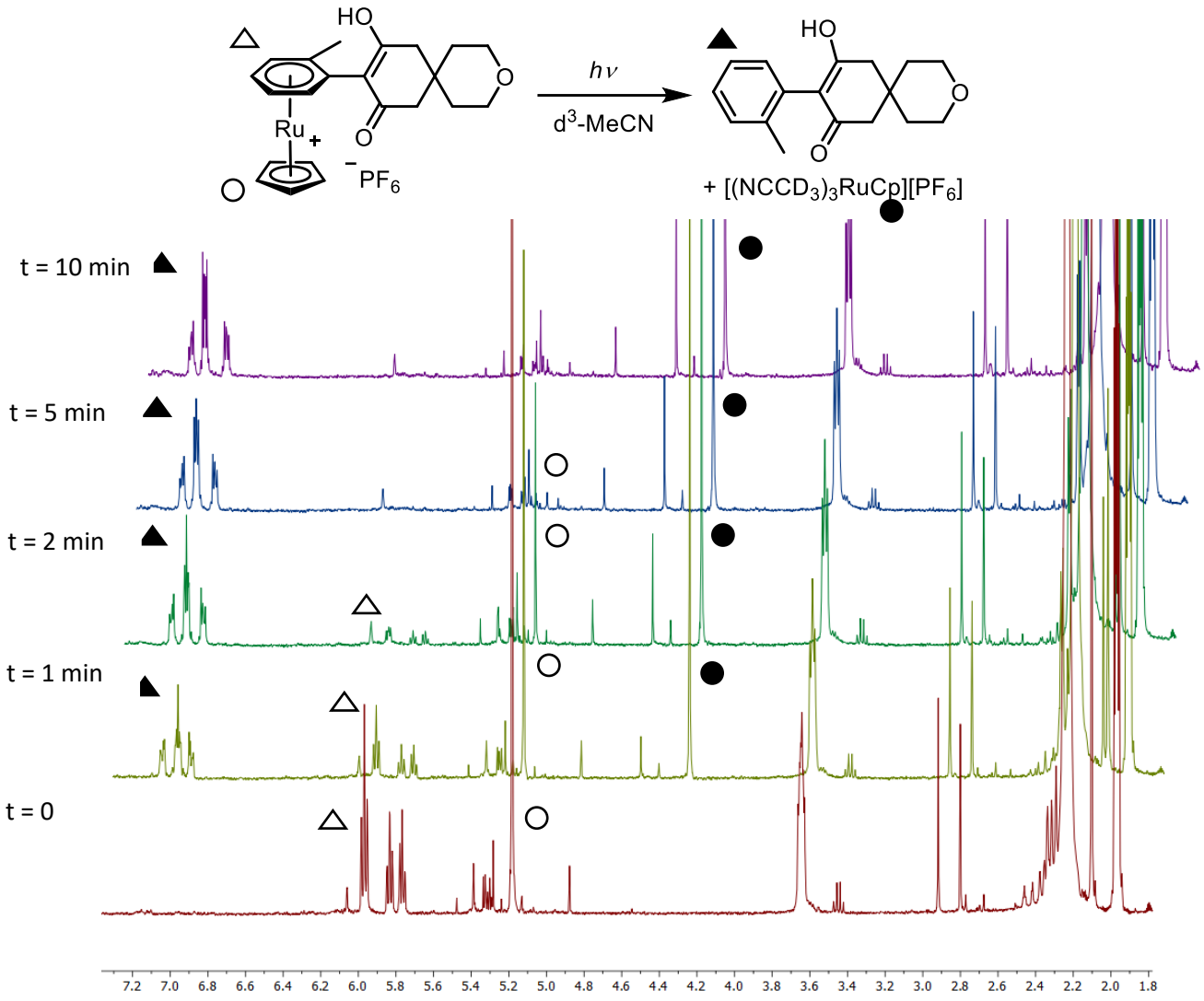


Figure S6. Stacked ^{1}H NMR spectra (CD_3CN, 298 K, 400 MHz) for the photolysis of the complex [Ru(η^6-2-(2-tolyl)- 3-oxaspiro[5.5]undecane-8,10-dione)(η^5-cyclopentadienyl)]PF_6

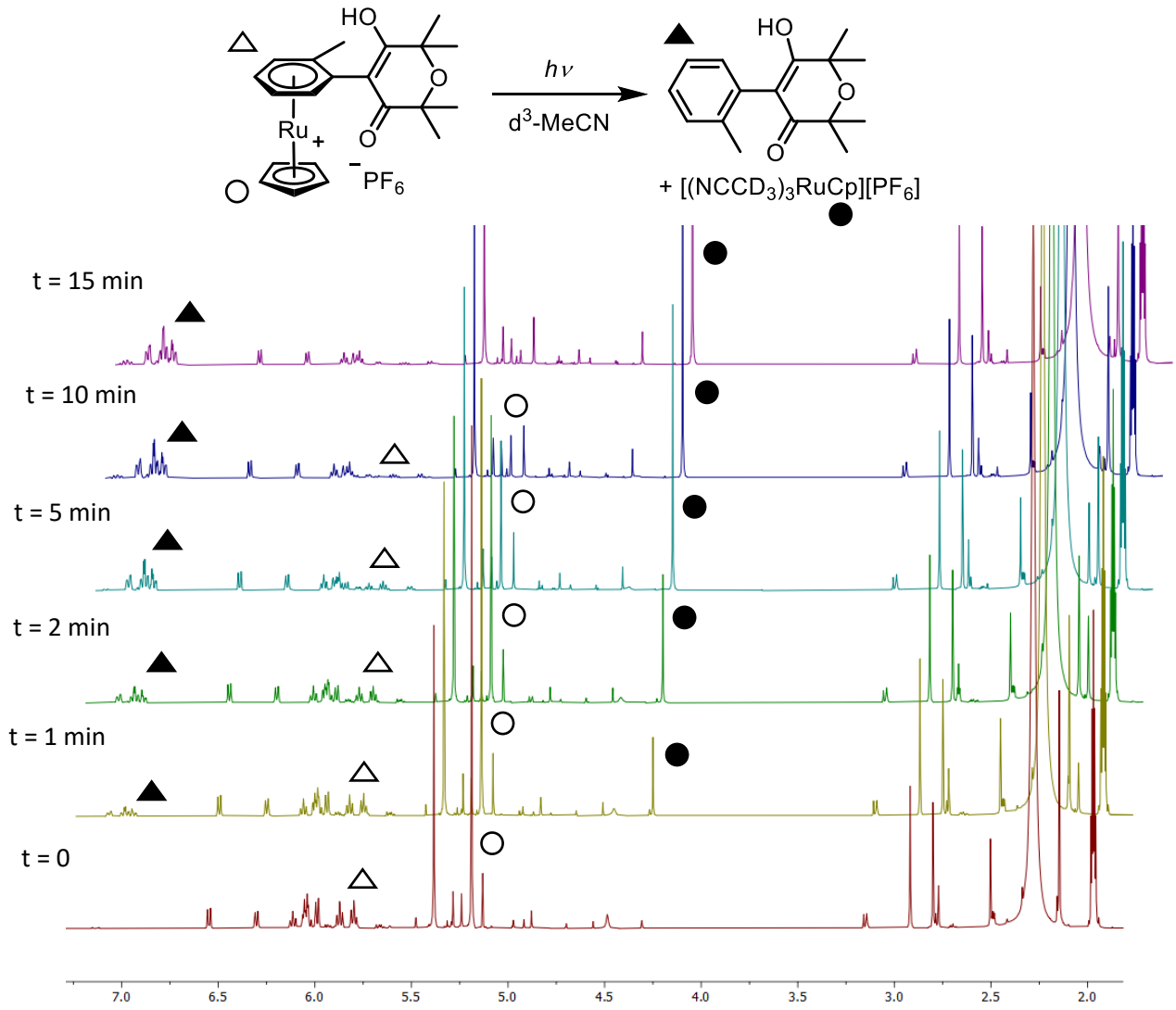


Figure S7. Stacked ^{1}H NMR spectra (CD_3CN, 298 K, 400 MHz) for the photolysis of the complex [Ru(η^6--2,2',6,6'-tetramethyl-4-(2-tolyl)-oxane-3,5-dione)(η^5-cyclopentadienyl)]PF_6

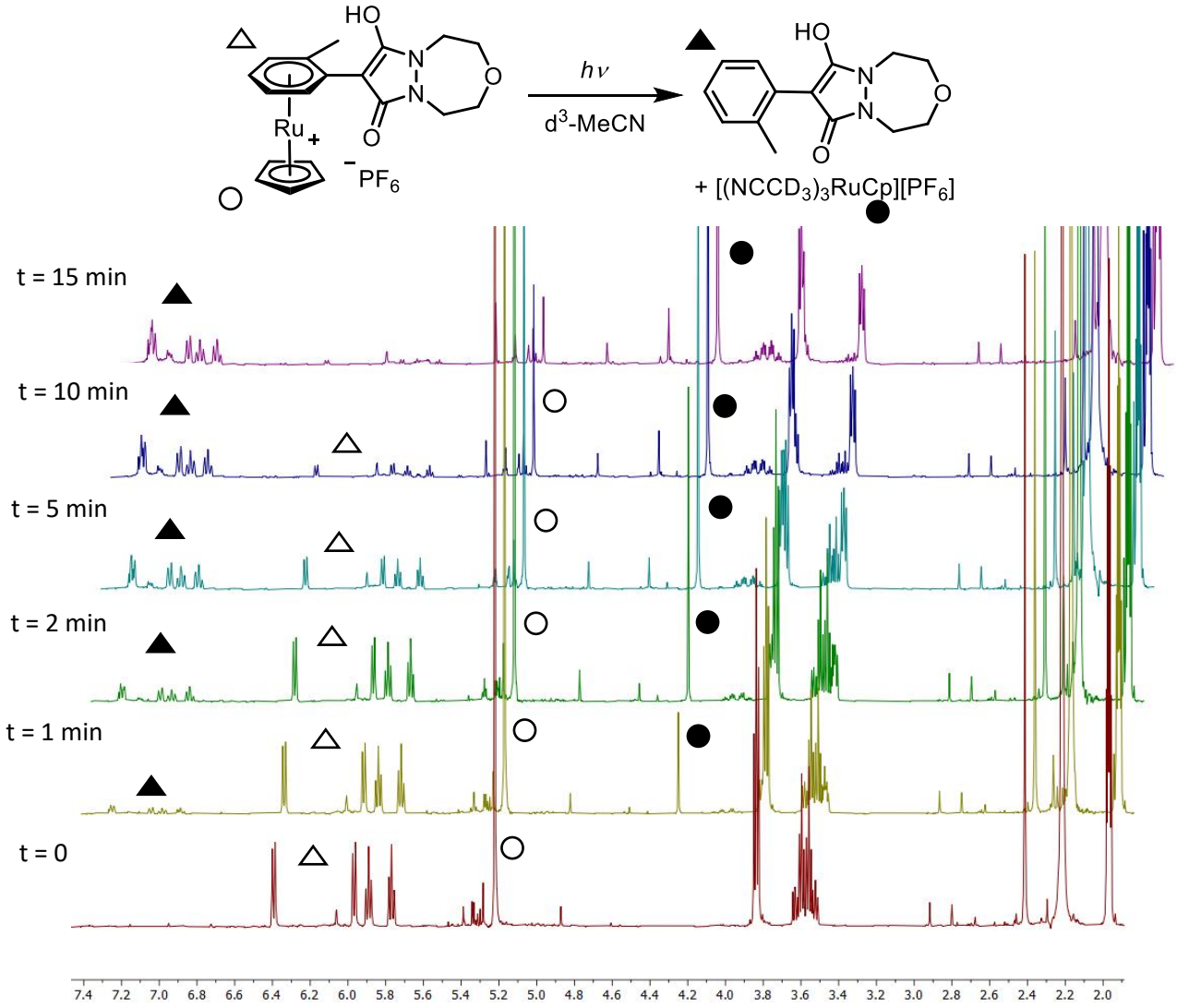


Figure S8. Stacked ^{1}H NMR spectra (CD_3CN, 298 K, 400 MHz) for the photolysis of the complex [Ru(η^6-8-(2-tolyl)-1,2,4,5-tetrahydropyrazolo[1,2-d][1,4,5]oxadiazepine-7,9-dione)(η^5-cyclopentadienyl)]PF_6

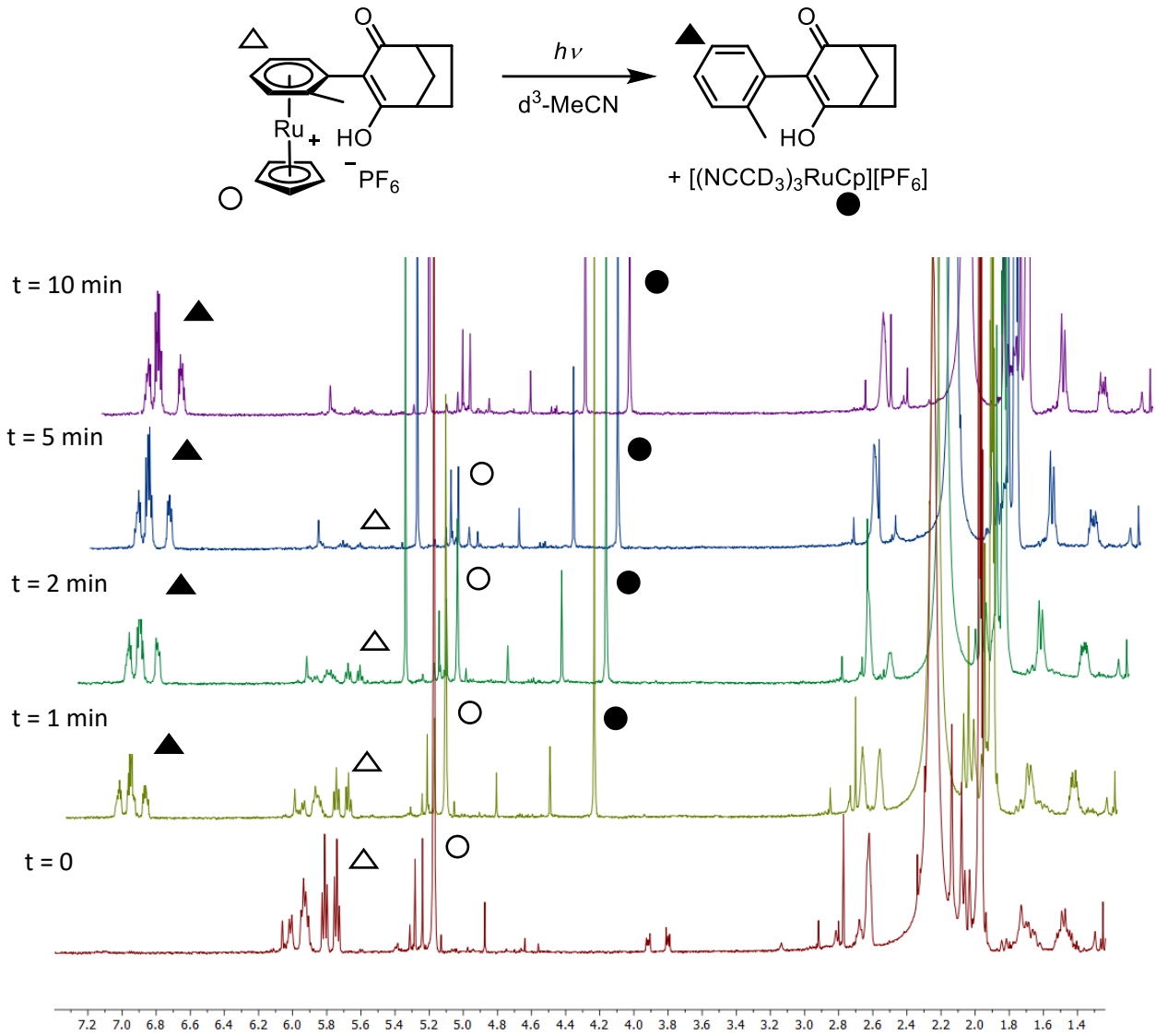


Figure S9. Stacked ^{1}H NMR spectra (CD_3CN, 298 K, 400 MHz) for the photolysis of the complex [Ru(η^6-3-(2-tolyl)-1,3-bicyclo[3.2.1]octane-2,4-dione)(η^5-cyclopentadienyl)]PF_6

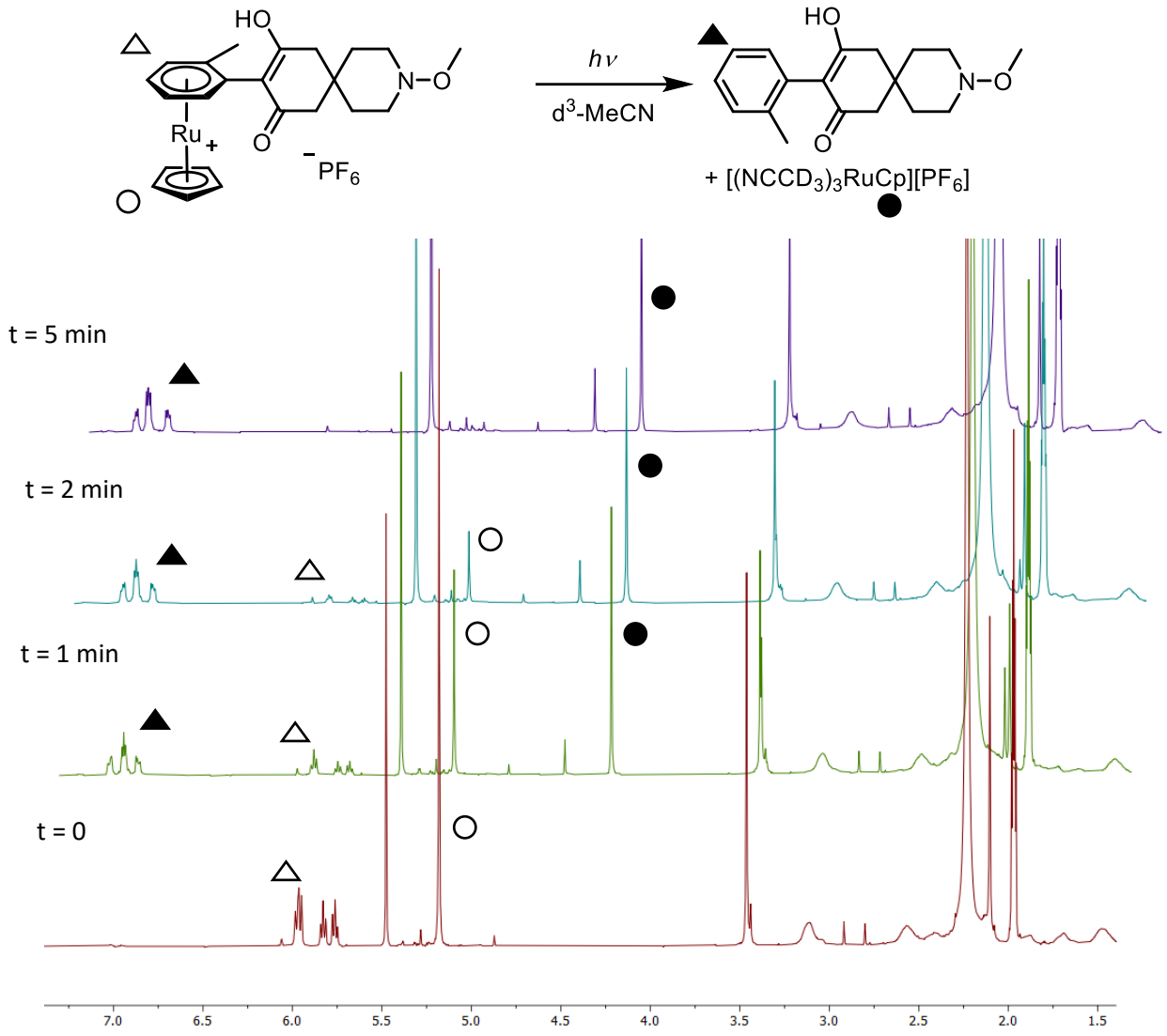


Figure S10. Stacked ^{1}H NMR spectra (CD_3CN, 298 K, 400 MHz) for the photolysis of the complex [Ru(η^6-9-(2-tolyl)-3-methoxy-3-azaspiro[5.5]undecane-8,10-dione)(η^5-cyclopentadienyl)]PF_6

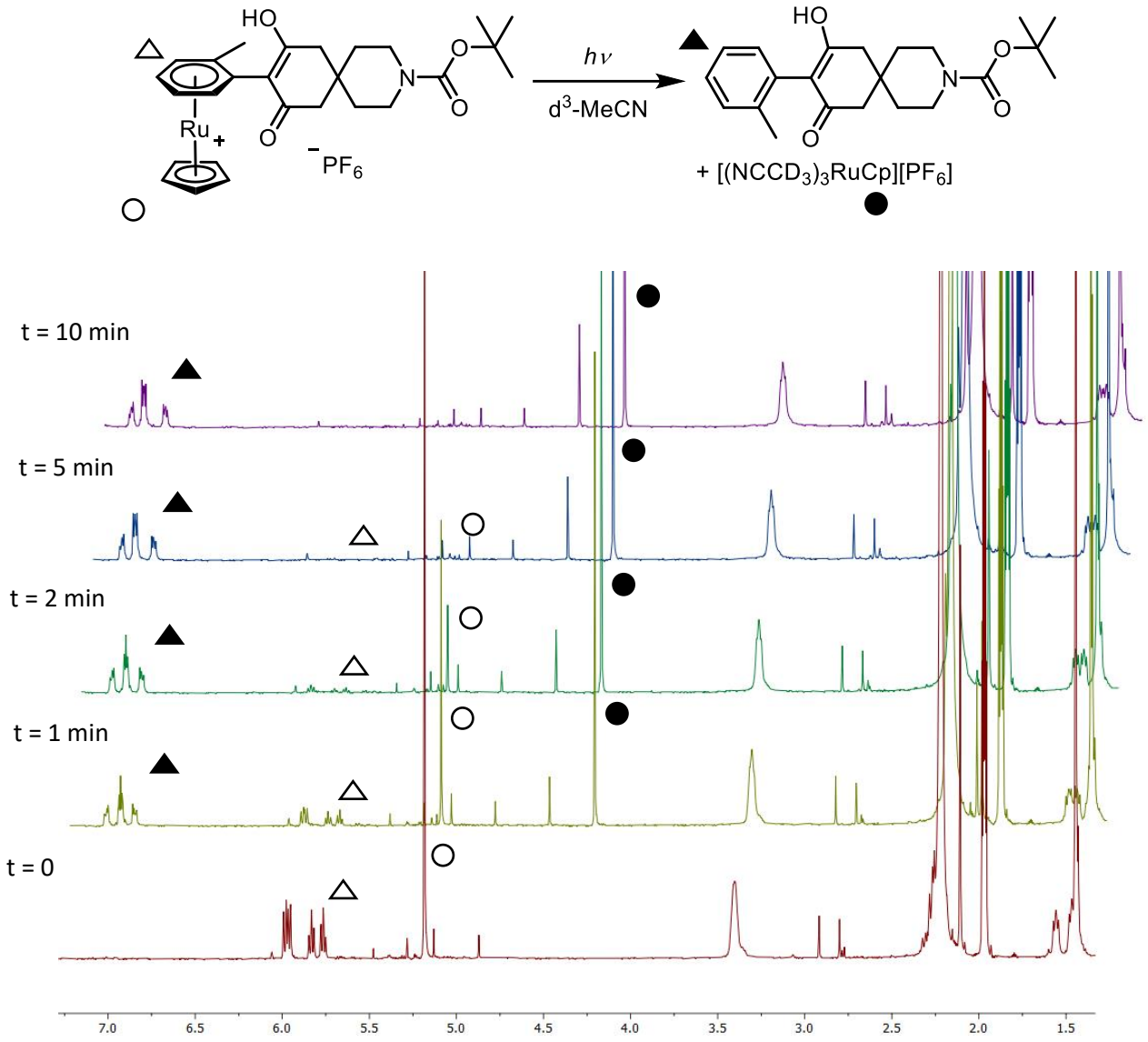


Figure S11. Stacked ^{1}H NMR spectra (CD_3CN, 298 K, 400 MHz) for the photolysis of the complex [Ru(η^6-*9-(2-tolyl)-tert-butyl-8,10-dioxo-3-azaspiro[5.5]undecane-3-carboxylate*)(η^5-cyclopentadienyl)]PF_6

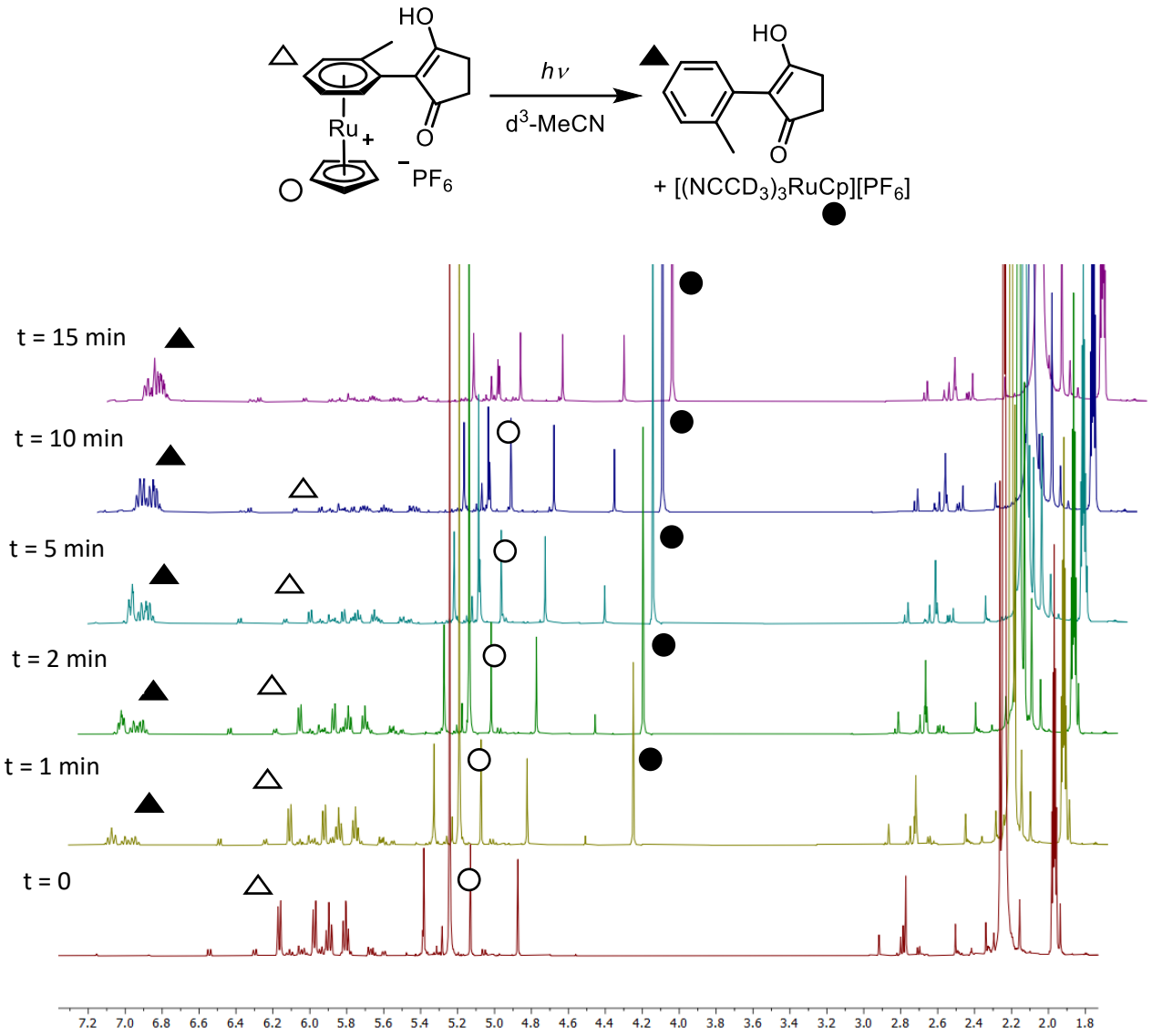


Figure S12. Stacked ^{1}H NMR spectra (CD_3CN, 298 K, 400 MHz) for the photolysis of the complex [Ru(η^6-*2-(2-tolyl)cyclopentanedione*)(η^5-cyclopentadienyl)]PF_6

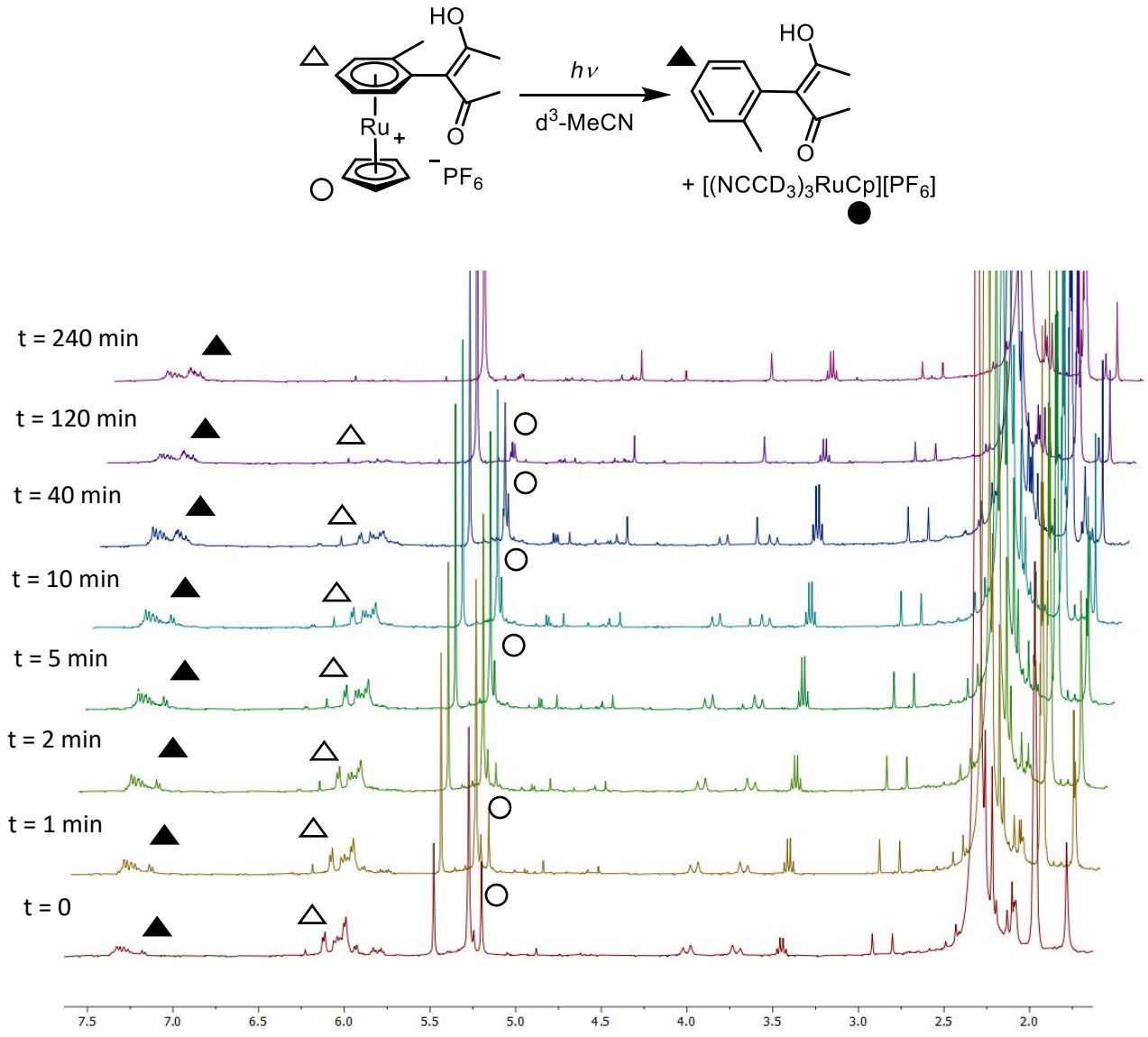


Figure S12. Stacked ^{1}H NMR spectra (CD_3CN, 298 K, 400 MHz) for the photolysis of the complex [Ru(η^6-*2-(2-tolyl)acetylacetone*)(η^5-cyclopentadienyl)]PF_6

Section 3. Crystallographic data

The X-ray single crystal data have been collected using λMoKα radiation (λ =0.71073Å) on an Agilent XCalibur (Sapphire-3 CCD detector, fine-focus sealed tube, graphite monochromator) diffractometer equipped with a Cryostream (Oxford Cryosystems) open-flow nitrogen cryostat at the temperature 120.0(2)K. The structure was solved by direct method and refined by full-matrix least squares on F^2 for all data using Olex2 [3] and SHELXTL [4] software. All non-hydrogen atoms were refined anisotropically, hydrogen atoms were placed in the calculated positions and refined in riding mode. Crystal data and parameters of refinement are listed in Tables S1-S5. Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-1546706.

3a. Complex 1a

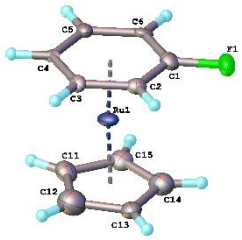


Table S1. Crystal data and structure refinement for Ru complex **1a**

Empirical formula	$C_{11}H_{10}F_7PRu$
Formula weight	407.23
Temperature/K	120.0
Crystal system	monoclinic
Space group	C2
a/Å	8.9922(2)
b/Å	9.5814(3)
c/Å	7.2372(2)
α/°	90
β/°	96.5700(10)
γ/°	90
Volume/Å^3	619.45(3)
Z	2
ρ_{calc}g/cm^3	2.183
μ/mm^{-1}	1.467
F(000)	396.0
Crystal size/mm^3	0.14 × 0.12 × 0.06
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.666 to 59.986
Index ranges	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -10 ≤ l ≤ 10
Reflections collected	6340
Independent reflections	1782 [R_{int} = 0.0196, R_{sigma} = 0.0190]
Data/restraints/parameters	1782/67/126
Goodness-of-fit on F^2	1.089
Final R indexes [I>=2σ (I)]	R_1 = 0.0210, wR_2 = 0.0507
Final R indexes [all data]	R_1 = 0.0215, wR_2 = 0.0511
Largest diff. peak/hole / e Å^{-3}	0.60/-0.43
Flack parameter	0.57(7)

3b. Complex 1b

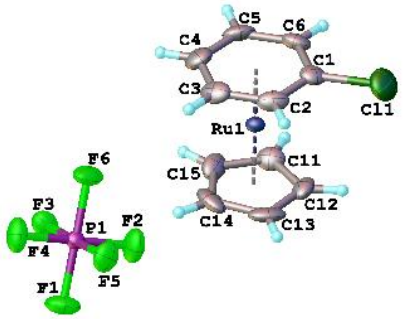


Table S2. Crystal data and structure refinement for Ru complex **1b**

Empirical formula	$C_{11}H_{10}ClRu$ x PF_6
Formula weight	423.68
Temperature/K	120.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.0165(4)
b/Å	13.3485(6)
c/Å	10.9347(5)
α/°	90
β/°	91.0311(18)
γ/°	90
Volume/Å^3	1315.85(10)
Z	4
ρ_{calc}g/cm^3	2.139
μ/mm^{-1}	1.572
F(000)	824.0
Crystal size/mm^3	0.19 × 0.11 × 0.07
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.816 to 58.994
Index ranges	-12 ≤ h ≤ 12, -18 ≤ k ≤ 18, -15 ≤ l ≤ 15
Reflections collected	20662
Independent reflections	3659 [R_{int} = 0.0316, R_{sigma} = 0.0228]
Data/restraints/parameters	3659/0/181
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0189, wR_2 = 0.0398
Final R indexes [all data]	R_1 = 0.0261, wR_2 = 0.0417
Largest diff. peak/hole / e Å^{-3}	0.39/-0.40

3c. Complex 2a

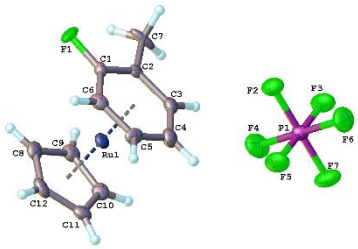


Table S3. Crystal data and structure refinement for Ru complex **2a**

Identification code	22srv023
Empirical formula	$C_{12}H_{12}F_7PRu$
Formula weight	421.26
Temperature/K	120.00
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.0446(3)
b/Å	14.1266(4)
c/Å	10.6960(3)
α/°	90
β/°	90.0265(11)
γ/°	90
Volume/Å^3	1366.62(7)
Z	4
ρ_{calc}g/cm^3	2.047
μ/mm^{-1}	1.334
F(000)	824.0
Crystal size/mm^3	0.14 × 0.09 × 0.06
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.776 to 58.996
Index ranges	-12 ≤ h ≤ 12, -19 ≤ k ≤ 19, -14 ≤ l ≤ 14
Reflections collected	27182
Independent reflections	3817 [R_{int} = 0.0388, R_{sigma} = 0.0251]
Data/restraints/parameters	3817/96/240
Goodness-of-fit on F^2	1.069
Final R indexes [I>=2σ (I)]	R_1 = 0.0292, wR_2 = 0.0676
Final R indexes [all data]	R_1 = 0.0369, wR_2 = 0.0714
Largest diff. peak/hole / e Å^{-3}	0.99/-0.54

3d. Complex 2b

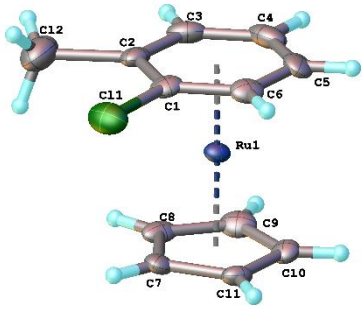


Table S4. Crystal data and structure refinement for Ru complex **2b**

Empirical formula	$C_{12}H_{12}ClF_6PRu$
Formula weight	437.71
Temperature/K	120
Crystal system	triclinic
Space group	P-1
a/Å	13.8713(6)
b/Å	13.8734(6)
c/Å	14.9953(7)
α/°	89.4442(16)
β/°	79.4373(16)
γ/°	89.6981(16)
Volume/Å^3	2836.7(2)
Z	8
ρ_{calc}g/cm^3	2.050
μ/mm^{-1}	1.462
F(000)	1712.0
Crystal size/mm^3	0.208 × 0.132 × 0.124
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.762 to 59.998
Index ranges	-19 ≤ h ≤ 19, -19 ≤ k ≤ 19, -21 ≤ l ≤ 21
Reflections collected	60601
Independent reflections	16458 [R_{int} = 0.0428, R_{sigma} = 0.0439]
Data/restraints/parameters	16458/0/758
Goodness-of-fit on F^2	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0457, wR_2 = 0.1077
Final R indexes [all data]	R_1 = 0.0658, wR_2 = 0.1230
Largest diff. peak/hole / e Å^{-3}	1.06/-1.20

3e. Complex 3a

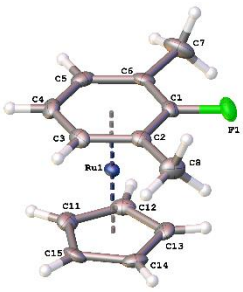


Table S5. Crystal data and structure refinement for Ru complex **3a**

Identification code	22srv007
Empirical formula	$C_{13}H_{14}F_7PRu$
Formula weight	435.28
Temperature/K	120.00
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	7.0290(2)
b/Å	15.3782(5)
c/Å	13.9470(5)
α/°	90
β/°	103.0623(12)
γ/°	90
Volume/Å^3	1468.57(8)
Z	4
ρ_{calc}g/cm^3	1.969
μ/mm^{-1}	1.244
F(000)	856.0
Crystal size/mm^3	0.15 × 0.07 × 0.02
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4 to 59.998
Index ranges	-9 ≤ h ≤ 9, -21 ≤ k ≤ 21, -19 ≤ l ≤ 19
Reflections collected	26106
Independent reflections	4275 [R_{int} = 0.0320, R_{sigma} = 0.0220]
Data/restraints/parameters	4275/24/222
Goodness-of-fit on F^2	1.089
Final R indexes [I>=2σ (I)]	R_1 = 0.0244, wR_2 = 0.0552
Final R indexes [all data]	R_1 = 0.0276, wR_2 = 0.0565
Largest diff. peak/hole / e Å^{-3}	1.35/-0.53

3f. Complex 3b

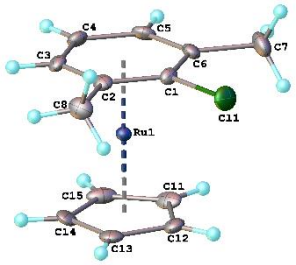


Table S6. Crystal data and structure refinement for Ru complex **3b**

Empirical formula	$C_{13}H_{14}ClF_6PRu$
Formula weight	451.73
Temperature/K	120.0
Crystal system	monoclinic
Space group	$P2_1$
a/Å	6.9414(2)
b/Å	15.3352(4)
c/Å	7.3463(2)
α/°	90
β/°	104.6140(10)
γ/°	90
Volume/Å^3	756.70(4)
Z	2
ρ_{calc}g/cm^3	1.983
μ/mm^{-1}	1.373
F(000)	444.0
Crystal size/mm^3	0.13 × 0.11 × 0.06
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.312 to 57.988
Index ranges	-9 ≤ h ≤ 9, -20 ≤ k ≤ 20, -10 ≤ l ≤ 10
Reflections collected	18388
Independent reflections	3986 [R_{int} = 0.0299, R_{sigma} = 0.0240]
Data/restraints/parameters	3986/1/202
Goodness-of-fit on F^2	1.047
Final R indexes [I>=2σ (I)]	R_1 = 0.0211, wR_2 = 0.0511
Final R indexes [all data]	R_1 = 0.0223, wR_2 = 0.0517
Largest diff. peak/hole / e Å^{-3}	2.02/-0.53
Flack parameter	0.51(4)

3g. Complex 3c

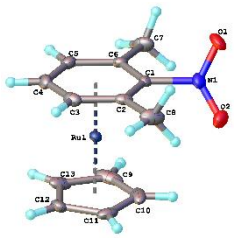


Table S7. Crystal data and structure refinement for Ru complex **3c**

Empirical formula	$C_{13}H_{14}F_6NO_2PRu$
Formula weight	462.29
Temperature/K	120.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	16.7069(7)
b/Å	14.2729(6)
c/Å	14.1391(6)
α/°	90
β/°	112.2030(10)
γ/°	90
Volume/Å^3	3121.6(2)
Z	8
ρ_{calc}g/cm^3	1.967
μ/mm^{-1}	1.179
F(000)	1824.0
Crystal size/mm^3	0.23 × 0.2 × 0.15
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.882 to 60
Index ranges	-23 ≤ h ≤ 23, -20 ≤ k ≤ 20, -19 ≤ l ≤ 19
Reflections collected	52996
Independent reflections	9078 [R_{int} = 0.0295, R_{sigma} = 0.0214]
Data/restraints/parameters	9078/67/470
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0249, wR_2 = 0.0572
Final R indexes [all data]	R_1 = 0.0293, wR_2 = 0.0593
Largest diff. peak/hole / e Å^{-3}	0.85/-0.77