Product inhibition in nucleophilic aromatic substitution through DPPPent-supported π-arene catalysis

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Supporting Information

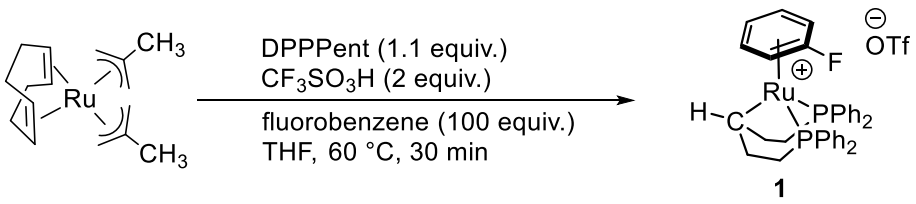
I. General Information

General Considerations. All syntheses and manipulations were carried out using standard vacuum, Schlenk, cannula, or glovebox techniques under N_2 unless otherwise specified. Tetrahydrofuran, dichloromethane, and pentane were degassed with argon and dried over activated alumina using a solvent purification system. Fluorobenzene and morpholine were degassed with nitrogen and stored over activated 4 Å molecular sieves. The following chemicals were purchased from commercial vendors and used as received: Ru(cod)(methallyl)$_2$, 1,5-bis(diphenylphosphino)pentane, trifluoromethanesulfonic acid, bis[4-(trifluoromethyl)phenyl]chlorophosphine and *N*-phenylmorpholine.

Spectroscopy. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded on Bruker NMR spectrometers at ambient temperature unless otherwise noted. ^{1}H and ^{13}C chemical shifts are referenced to residual solvent signals; ^{31}P chemical shifts are referenced to an external H_3PO_4 standard. ^{13}C assignments were made with the assistance of 2D methods.

Elemental Analysis. Elemental analyses of complexes **1**-**3** are of the bulk samples for which yields are reported. No additional purification operations are carried out prior to packaging for analysis, but samples are dried under vacuum for *ca.* 2 days to remove residual or co-crystalized solvent. Elemental analyses were performed at the University of Rochester CENTC Elemental Analysis Facility or by Midwest Microlab.

II. Synthesis and Characterization



1

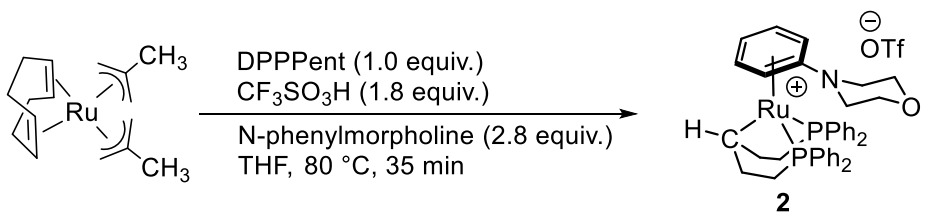
Preparation of [(κ³-bis(diphenylphosphino)pentane)(η⁶-fluorobenzene)ruthenium] trifluoromethanesulfonate (1). In an inert-atmosphere glovebox a 40 mL glass vial was charged with Ru(cod)(methallyl)$_2$ (0.064 g, 0.20 mmol) and 1,5-bis(diphenylphosphino)pentane (0.097 g, 0.22 mmol, 1.1 equiv.) in 6 mL THF. While stirring, trifluoromethanesulfonic acid (35 μL, 0.40 mmol) was added via microsyringe, followed by fluorobenzene (1.87 mL, 20.0 mmol, 100 equiv.). The solution was heated at 60 °C for 30 minutes after which it was cooled to room temperature and evaporated to dryness. The resulting residue was suspended in 1 mL THF, then was filtered and washed with two 1 mL portions of THF after which it was dried under vacuum. The resulting solid was dissolved in 3 mL of dichloromethane and filtered through a 0.45 μm PTFE syringe filter which was rinsed with an additional 3 mL of dichloromethane. The combined filtrate was dried under vacuum to give the solid product. Yield: 0.065 g (42%). Single crystals were obtained by vapor diffusion of pentane into a solution of THF at room temperature. Elemental Analysis for $C_{36}H_{34}F_4O_3P_2RuS$: C, 55.03; H, 4.36. Found C, 52.12; H, 3.86.

^{1}H NMR (400 MHz, 23 °C, $CDCl_3$): δ 2.00-2.20 (m, 4H, C*H*$_2$ of DPPPent), 2.29-2.39 (m, 2H, C*H*$_2$ of DPPPent), 2.43-2.50 (m, 2H, C*H*$_2$ of DPPPent), 5.03 (t, $^2J_{HP}$ = 6.8 Hz, 1H, C-*H* of DPPPent), 5.29 (dd, $^3J_{HH}$ = 5.6 Hz, $^4J_{HH}$ = 4.8 Hz , 2H, o-C-*H* of arene), 5.46 (apparent q, $^3J_{HH}$ = 3.7 Hz, 2H, *m*-C-*H* of arene), 6.32 (td, $^3J_{HH}$ = 5.9 Hz, $^4J_{HH}$ = 2.6 Hz, 1H, *p*-C-*H* of arene), 7.11-7.21 (m, 12H, C-*H* of PPh_2), 7.29-7.35 (m, 8H, C-*H* of PPh_2).

^{19}F{^{1}H} NMR (376 MHz, 23 °C, $CDCl_3$): δ -132.72 (s, C-*F*), -78.00 (s, S-C*F*$_3$).

^{31}P{^{1}H} NMR (202 MHz, 23 °C, $CDCl_3$): δ 65.45 (s).

^{13}C{^{1}H,^{31}P} NMR (126 MHz, 23 °C, CD_2Cl_2): δ 33.2 (*C*H$_2$ of DPPPent), 40.2 (*C*H$_2$ of DPPPent), 46.2 (*C*H of DPPPent), 79.8 (d, $^2J_{CF}$ = 20.0 Hz, *o*-*C*-H of arene), 88.1 (*p*-C-H of arene), 98.6 (d, $^3J_{CF}$ = 6.7 Hz, *m*-*C*-H of arene), 129.1 (*m*-*C*-H of PPh_2), 129.2 (*m*-*C*-H of PPh_2), 130.8 (*o*-*C*-H of PPh_2), 130.9 (*o*-*C*-H of PPh_2), 131.0(*o*-*C*-H of PPh_2), 132.2 (*p*-*C*-H of PPh_2), 138.5 (*C* of DPPPent), 143.2 (d, $^1J_{CF}$ = 278.3, *C*-F of arene).
*Triflate carbon was observed only by ^{13}C{^{1}H} NMR at δ 121.6 (q, $^1J_{CF}$ = 321.4 Hz).



2

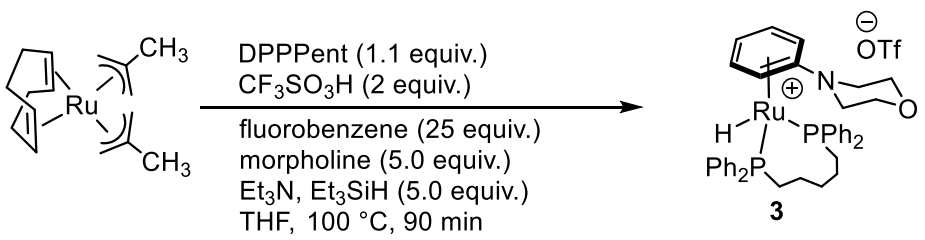
Preparation of [(κ³-bis(diphenylphosphino)pentane)(η⁶-(N-phenylmorpholine)) ruthenium]trifluoromethanesulfonate (2). In an inert-atmosphere glove box a 40 mL glass vial was charged with Ru(cod)(methallyl)$_2$ (0.070 g, 0.22 mmol, 1.0 equiv.) and 1,5-bis(diphenylphosphino)pentane (0.097 g, 0.22 mmol, 1.0 equiv.) in 6 mL THF. While stirring, trifluoromethanesulfonic acid (35 μL, 0.40 mmol, 1.8 equiv.) was added via microsyringe, followed by N-phenylmorpholine (0.100 g, 0.605 mmol, 2.8 equiv.). The solution was heated at 80 °C for 35 minutes. After cooling to room temperature, the volume was reduced to approximately 3 mL under vacuum. The resulting suspension was filtered and washed with three 1 mL portions of THF. The filtered solid was dried under vacuum to give the product as a yellow solid. Yield: 0.129 g (76%). Single crystals were obtained by vapor diffusion of pentane into a solution of dichloromethane at room temperature. Elemental Analysis for $C_{40}H_{42}F_3NO_4P_2RuS$: C, 56.33; H, 4.96; N, 1.64. Found C, 55.81; H, 4.82; N 1.59.

^{1}H NMR (500 MHz, 23 °C, CD_2Cl_2): δ 2.02-2.21 (m, 4H, C*H*$_2$ of DPPPent), 2.29-2.38 (m, 2H, C*H*$_2$ of DPPPent), 2.47-2.51 (m, 2H, C*H*$_2$ of DPPPent), 3.42 (t, $^3J_{HH}$ = 4.9 Hz , 4H, N-C*H*$_2$ of morpholine), 3.81 (t, $^3J_{HH}$ = 4.9 Hz , 4H, O-C*H*$_2$ of morpholine), 4.68 (d, $^3J_{HH}$ = 6.5 Hz, 2H, *o*-C-*H* of arene), 4.68 (bs, 1H, C-*H* of DPPPent), 5.01 (apparent t, $^3J_{HH}$ = 5.0 Hz, 2H, *m*-C-*H* of arene), 5.87 (t, $^3J_{HH}$ = 5.5 Hz, 1H, *p*-C-*H* of arene), 7.08-7.12 (m, 12H, C-*H* of PPh$_2$), 7.29-7.35 (m, 8H, C-*H* of PPh$_2$).

^{31}P{^{1}H} NMR (202 MHz, 23 °C, CD_2Cl_2): δ 67.65 (s).

^{13}C{^{1}H,^{31}P} NMR (126 MHz, 23 °C, CD_2Cl_2): δ 34.0 (*C*H$_2$ of DPPPent), 41.1 (*C*H$_2$ of DPPPent), 46.3 (N-*C*H$_2$ of morpholine), 47.0 (*C*-H of DPPPent), 66.8 (O-*C*H$_2$ of morpholine), 70.0 (*o*-*C*-H of arene), 82.0 (*p*-*C*-H of arene), 98.6 (*m*-*C*-H of arene), 128.8 (*m*-*C*-H of PPh$_2$), 128.9 (*m*-*C*-H of PPh$_2$), 130.3 (*o*-*C*-H of PPh$_2$), 130.6 (*o*-*C*-H of PPh$_2$), 132.2 (*p*-*C*-H of PPh$_2$), 139.5 (*C* of arene), 139.7 (*C* of PPh$_2$).

*Triflate carbon was observed only by ^{13}C{^{1}H} NMR at δ 121.5 (q, $^1J_{CF}$ = 320.0 Hz).



Preparation of [(κ²-bis(diphenylphosphino)pentane)(η⁶-(N-phenylmorpholine)) hydridoruthenium]trifluoromethanesulfonate (3). In an inert-atmosphere glove box a 20 mL glass vial was charged with Ru(cod)(methallyl)$_2$ (0.190 g, 0.595 mmol, 1.0 equiv.) and 1,5-bis(diphenylphosphino)pentane (0.288 g, 0.654 mmol, 1.1 equiv.) in 5.0 mL THF. While stirring, the following reagents were added in order: trifluoromethanesulfonic acid (105 µL, 1.19 mmol, 2.0 equiv.), fluorobenzene (1,395 µL, 14.86 mmol, 25.0 equiv.), morpholine (257 µL, 2.98 mmol, 5.0 equiv.), triethylamine (415 µL, 2.98 mmol, 5.0 equiv.), and triethylsilane (475 µL, 2.98 mmol, 5.0 equiv.). The reaction mixture was heated at 100 °C for 90 minutes, then allowed to cool to room temperature before being filtered through a 0.45 µm PTFE syringe filter. Crystallization of the separated filtrate was accomplished by vapor diffusion of pentane at room temperature overnight. The crude product obtained by crystallization was separated by decanting off the mother liquor and the resulting crystals were washed with 5 mL of pentane. The crystals were then dried under vacuum. The crystals were treated with 5.5 mL THF and the resulting suspension was stirred for 15 minutes, filtered, and washed with THF (3 x 1 mL). The resulting solid was dried under vacuum to give the product as an off-white solid. Yield: 0.150 g (25%). Single crystals were obtained by vapor diffusion of pentane into a solution of THF at room temperature. Elemental Analysis for $C_{40}H_{44}F_3NO_4P_2RuS$: C, 56.20; H, 5.19; N, 1.64. Found C, 55.90; H, 5.48; N 1.52.

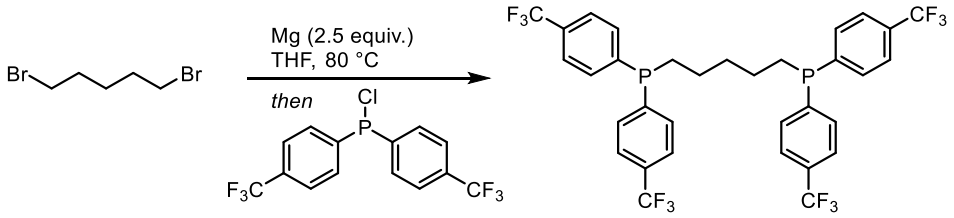
^{1}H NMR (500 MHz, 23 °C, acetone-d_6): δ -9.53 (t, $^2J_{HP}$ = 39.0 Hz, 1H, Ru-*H*), 1.03-1.09 (m, 1H, C*H*$_2$ of DPPPent), 1.28-1.33 (m, 1H, C*H*$_2$ of DPPPent), 1.37-1.45 (m, 2H, C*H*$_2$ of DPPPent), 1.74-1.85 (m, 2H, C*H*$_2$ of DPPPent), 2.52 (t, $^3J_{HH}$ = 4.8 Hz , 4H, N-C*H*$_2$ of morpholine), 2.64-2.72 (m, 2H, C*H*$_2$ of DPPPent), 2.97-3.04 (m, 2H, C*H*$_2$ of DPPPent), 3.65 (t, $^3J_{HH}$ = 4.8 Hz , 4H, O-C*H*$_2$ of morpholine), 3.73 (d, $^3J_{HH}$ = 6.5 Hz, 2H, *o*-C-*H* of arene), 5.64 (t, $^3J_{HH}$ = 5.5 Hz, 2H, *m*-C-*H* of arene), 6.60 (t, $^2J_{Hh}$ = 5.6 Hz, 1H, *p*-C-*H* of arene), 7.33-7.96 (m, 20H, C-*H* of PPh$_2$).

^{31}P{^{1}H} NMR (202 MHz, 23 °C, acetone-d_6): δ 44.74 (s).

^{13}C{^{1}H,^{31}P} NMR (151 MHz, 23 °C, acetone-d_6): δ 24.2 (*C*H$_2$ of DPPPent), 24.9 (*C*H$_2$ of DPPPent), 32.6 (*C*H$_2$ of DPPPent), 48.4 (N-*C*H$_2$ of morpholine), 66.1 (O-*C*H$_2$ of

morpholine), 73.9 (*o*-*C*-H of arene), 88.9 (*p*-*C*-H of arene), 98.9 (*m*-*C*-H of arene), 129.2 (*m*-*C*-H of PPh_2), 129.6 (*m*-*C*-H of PPh_2), 130.3 (*o*-*C*-H of PPh_2), 132.0 (*o*-*C*-H of PPh_2), 134.0 (*C* of PPh_2), 135.2 (*p*-*C*-H of PPh_2), 137.6 (*C* of arene), 145.0 (*C* of PPh_2).

*Triflate carbon was observed only by $^{13}C\{^1H\}$ NMR at δ 122.7 (q, $^1J_{CF}$ = 321.7 Hz).



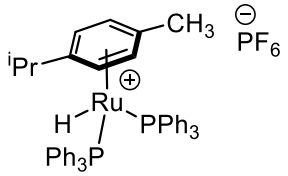
Preparation of 1,5-bis(bis(4′-(trifluoromethyl)phenyl)phosphino)pentane (^{CF_3}DPPPent). A flame-dried 100 mL three neck flask equipped with a reflux condenser was charged with magnesium turnings (0.157 g, 6.46 mmol, 2.3 equiv.) and a few small crystals of iodine, followed by 10 mL of dry THF under nitrogen. 1,5-dibromopentane (0.645 g, 2.80 mmol, 1.0 equiv.) was added slowly while heating to 80 °C. Once initiation had occurred, the addition rate was controlled to maintain the reaction at reflux. After addition, the reaction was heated in an 80 °C oil bath for 1.5 hours, at which point little residual magnesium was observed. Upon cooling to room temperature, the resulting cloudy solution was added dropwise by syringe to a solution of bis(4-trifluoromethylphenyl)chlorophosphine (2.02 g, 5.66 mmol, 2.02 equiv.) in 6 mL of dry THF. The solution was allowed to stir for 5 days, during which time a white precipitate slowly appeared, followed by removal of the solvent under vacuum. The resulting white solid was extracted with 10 mL of diethyl ether, which was removed under vacuum to yield a clear oil. The oil solidified upon standing overnight. This white solid was washed with pentane (6 x 5 mL) and dried under vacuum to give a white solid. This material was dissolved in 6 mL of 1,4-dioxane, flushed through a short plug of silica, and eluted with CH_2Cl_2. The resulting solution was dried under vacuum at 50 °C to give the solid product. Yield: 0.286 g (14%) HRMS (ESI) m/z $[M-H]^+$ Calcd for $C_{33}H_{26}F_{12}P_2H^+$: 713.1391, Found: 713.1375

^1H NMR (500 MHz, 23 °C, $CDCl_3$): δ 1.39-1.47 (m, 4H, C*H*$_2$ of DPPPent), 1.56-1.62 (m, 2H, C*H*$_2$ of DPPPent), 2.01-2.09 (m, 4H, C*H*$_2$ of DPPPent), 7.44-7.51 (m, 8H, C-*H* of P-Ar), 7.55-7.61 (m, 8H, C-*H* of P-Ar).

$^{19}F\{^1H\}$ NMR (471 MHz, 23 °C, $CDCl_3$): δ -61.19 (s).

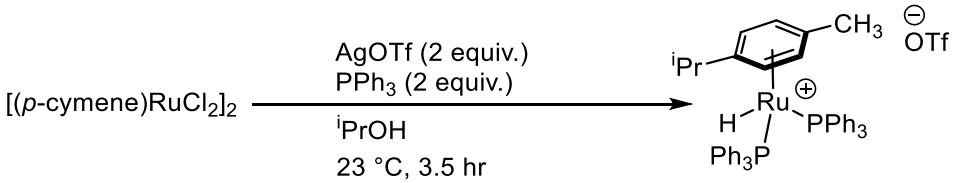
$^{31}P\{^{1}H\}$ NMR (202 MHz, 23 °C, $CDCl_3$): δ -14.60 (s).

$^{13}C\{^{1}H\}$ NMR (126 MHz, 23 °C, $CDCl_3$): δ 25.5 (d, $^{2}J_{CP}$ = 15.9 Hz, CH_2 of DPPPent), 27.6 (d, $^{1}J_{CP}$ = 12.3 Hz, CH_2 of DPPPent), 32.5 (t, $^{3}J_{CP}$ = 12.9 Hz, CH_2 of DPPPent), 124.1 (q, $^{1}J_{CF}$ = 272.4 Hz, CF_3), 125.4 (m, *C*-H of P-Ar), 131.1 (q, $^{2}J_{CF}$ = 32.7 Hz, *C*-CF_3), 133.1 (d, $^{2}J_{CP}$ = 18.5 Hz, *C*-H of P-Ar), 143.2 (d, $^{1}J_{CP}$ = 16.7 Hz, *C* of P-Ar).



4-PF$_6$

Preparation of [bis(triphenylphosphino)(η^6-(1-isopropyl-4-methylbenzene)) hydridoruthenium] trifluoromethanesulfonate (4-PF$_6$). Compound **4-PF$_6$** was synthesized according a reported procedure[1] from [(*p*-cymene)$RuCl_2$)]$_2$.[2]



4-OTf

Preparation of [bis(triphenylphosphino)(η^6-(1-isopropyl-4-methylbenzene)) hydridoruthenium] trifluoromethanesulfonate (4-OTf). Compound **4-OTf** was prepared by a variant of the procedure for **4-PF$_6$.** AgOTf was substituted for $AgPF_6$, two molar equivalents of PPh_3 were used per ruthenium, and isopropanol was substituted for methanol. Single crystals were obtained by storage of a concentrated Et_2O/methanol solution of **4-OTf** at -35 °C.

^{1}H NMR (500 MHz, 23 °C, $CDCl_3$): δ -9.69 (t, $^{2}J_{HP}$ = 37.8 Hz, 1H, Ru-*H*), 1.38 (d, $^{3}J_{HH}$ = 6.9 Hz, 6 H, CH-(CH_3)$_2$), 2.30 (s, 3 H, CH_3), 2.85 (quint, $^{3}J_{HH}$ = 6.9 Hz, 1H, C*H*-(CH_3)$_2$), 4.50 (d, $^{3}J_{HH}$ = 5.9 Hz, 2H, C-H of arene), 4.88 (d, $^{3}J_{HH}$ = 5.9 Hz, 2H, C-H of arene), 7.17-7.43 (m, 30H, C-*H* of PPh_3).

$^{31}P\{^{1}H\}$ NMR (202 MHz, 23 °C, CD_2Cl_2): δ 52.6 (s).

IV. Experimental Procedures

General procedure for catalytic reactions. A 4 mL vial was charged with Ru(cod)(methallyl)$_2$ (6.3 mg, 0.020 mmol), DPPPent (12.5 mg, 0.028 mmol) and 1,4-dioxane (0.4 mL). Trifluoromethanesulfonic acid (3.5 μL, 0.040 mmol) was then added to the stirred mixture. To this solution was added fluorobenzene (187 μL, 2.00 mmol), morpholine (35 μL, 0.40 mmol), triethylamine (56 μL, 0.40 mmol), and triethylsilane (64 μL, 0.40 mmol). The reaction mixture was heated at 100 °C in an oil bath for 24 hours, at which point the vessel was removed from the oil bath and allowed to cool to room temperature. A portion of dodecane (3.0 μL, 0.013 mmol) was then added as an internal standard for analysis by flame ionization gas chromatography.

Note on product quantitation: GC-FID allows for detection of product bound to ruthenium. For instance, analysis of 1 equiv. complex **2** by GC-FID leads to detection of 0.90 eq. N-phenyl morpholine, presumably due to liberation of the arene in the GC inlet (300 °C).

Safety note: Glass etching by liberated fluoride ions in conventional (non-catalyzed) S$_N$Ar reactions has been reported, which has led to issues on scale-up.[3-5] Additionally, these experiments have the potential to generate HF, therefore care should be taken in all cases to minimize risk from fluoride ion or HF to laboratory equipment and personnel.

Quantification of precipitate in additive-free catalytic reaction. A catalytic reaction was set up according to the general procedure, omitting triethylamine and triethylsilane additives. A yellow precipitate deposited during the reaction. After 24 hours, the vessel was removed from the oil bath and allowed to cool to room temperature. The reaction was returned to the glove box and filtered. The filtered solid was washed with dioxane (0.5 mL) and was then dissolved in a mixture of DMF/$CDCl_3$ (1.5:1) containing trimethyl phosphate (20 μL, 0.170 mmol) as an internal standard. The quantity of **2** was quantified by ^{31}P NMR.

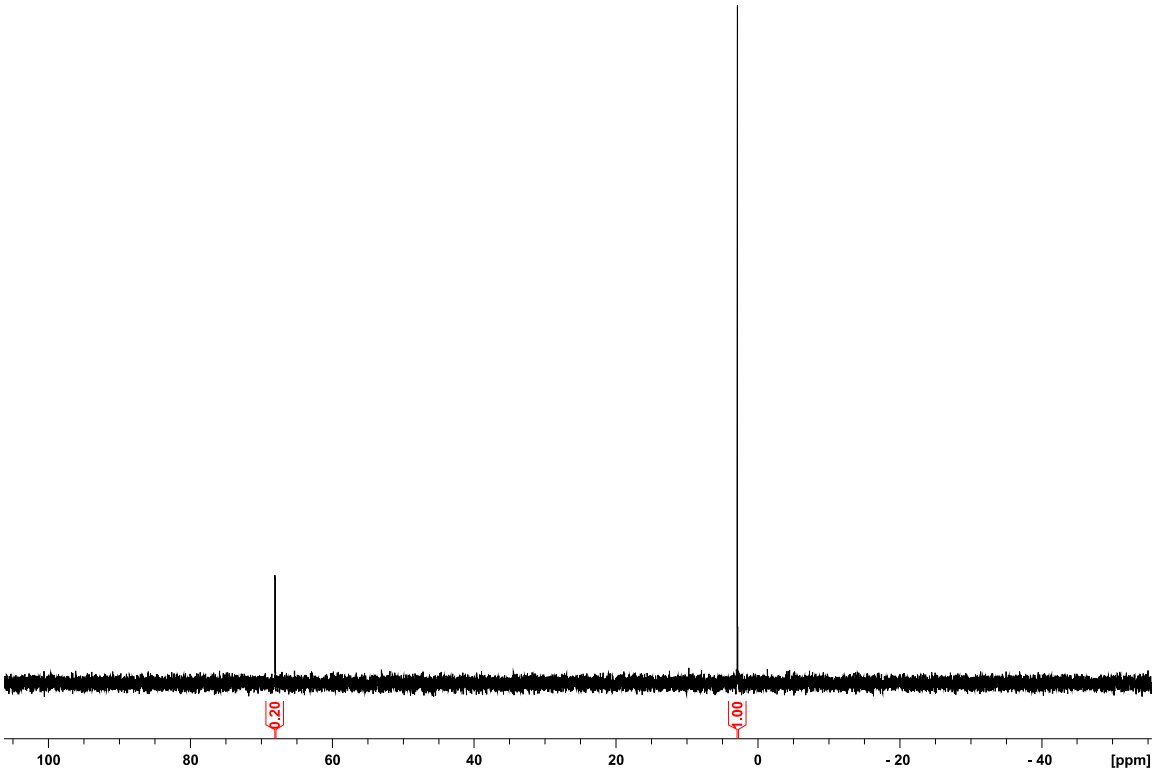


Figure S1: ^{31}P NMR of **2** (67.7 ppm) after precipitation at the end of a catalytic reaction.

Kinetic analysis of formation of 2 from 1 (Figure 3). In a nitrogen-filled glove box, a screw-cap NMR tube was charged with complex **1** (0.0050 g, 6.36 μmol) in a solution of 0.1 mL of DMF (for solubility), followed by 0.4 mL of dioxane. A sealed capillary containing a C_6D_6 solution of trimethyl phosphate was added as a standard. Immediately prior to kinetic analysis, a portion of morpholine (5.5 μL, 64 μmol) was added via a syringe through the septum cap. The sample was mixed by inversion and then analyzed by ^{31}P NMR every 60 seconds. The experiment was conducted in triplicate.

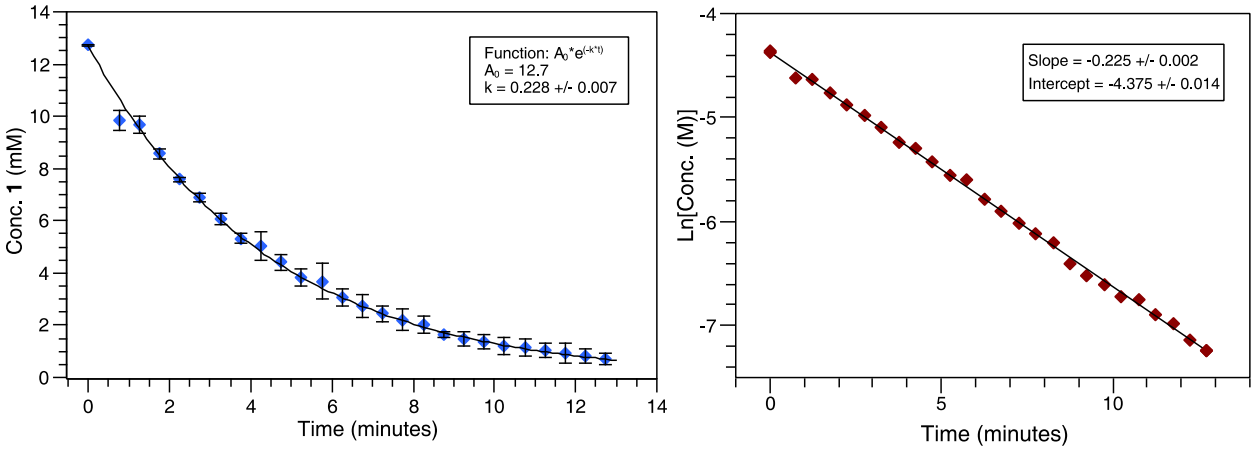


Figure S2: Consumption of **1** over time.

Determination of equilibrium constant of arene exchange. In a nitrogen-filled glove box, a screw-cap NMR tube was charged with 500 μL of a saturated solution of **1** in fluorobenzene, followed by N-phenylmorpholine (2.5 μmol as stock solution in fluorobenzene). The temperature of the NMR spectrometer was raised to 373 K, and the sample monitored by ^{31}P until a stable equilibrium was reached (< 15 min). This equilibrium ratio was stable on cooling, suggesting a moderate kinetic barrier to arene exchange. Relative concentrations of **1** and **2** were measured both at 373K and at *ca*. 323K. Both measurements gave results consistent with one another but the lower temperature measurement gave an improved signal-to-noise ratio. Finally, the sample was cooled to room temperature and trimethyl phosphate (2.0 μL, 17 μmol) was added as an internal standard to aid in quantifying absolute concentrations.

Kinetic analysis of arene displacement in 2 by fluorobenzene to give 1 (Table 3). In a nitrogen-filled glove box, a screw-cap NMR tube was charged with complex **2** (0.0038 g, 4.5 μmol) in a solution of 0.3 mL of 1,2-dichloroethane, followed by 0.3 mL of fluorobenzene. A sealed capillary containing a C_6D_6 solution of PPh_3 was added as a standard. The NMR spectrometer sample bore was preheated to the temperature required for kinetic analysis and the sample was then analyzed by ^{31}P NMR. Initial rate constants were obtained using kinetic data in the range from [**2**] = 7.5 mM to [**2**] = 6.0 mM. The activation energy was calculated from the slope of the Arrhenius plot.

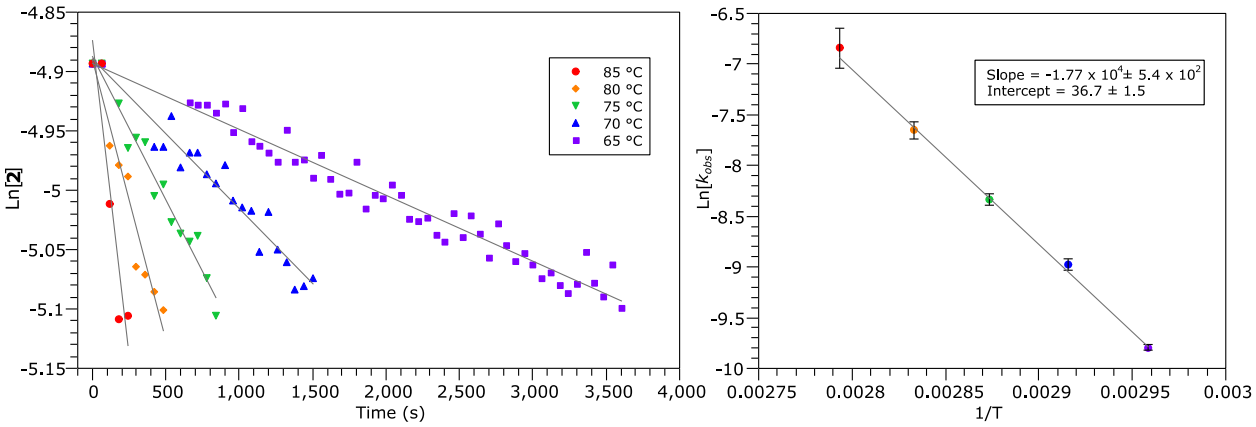


Figure S3: Temperature dependence of arene exchange in **2**

IV. NMR Spectra

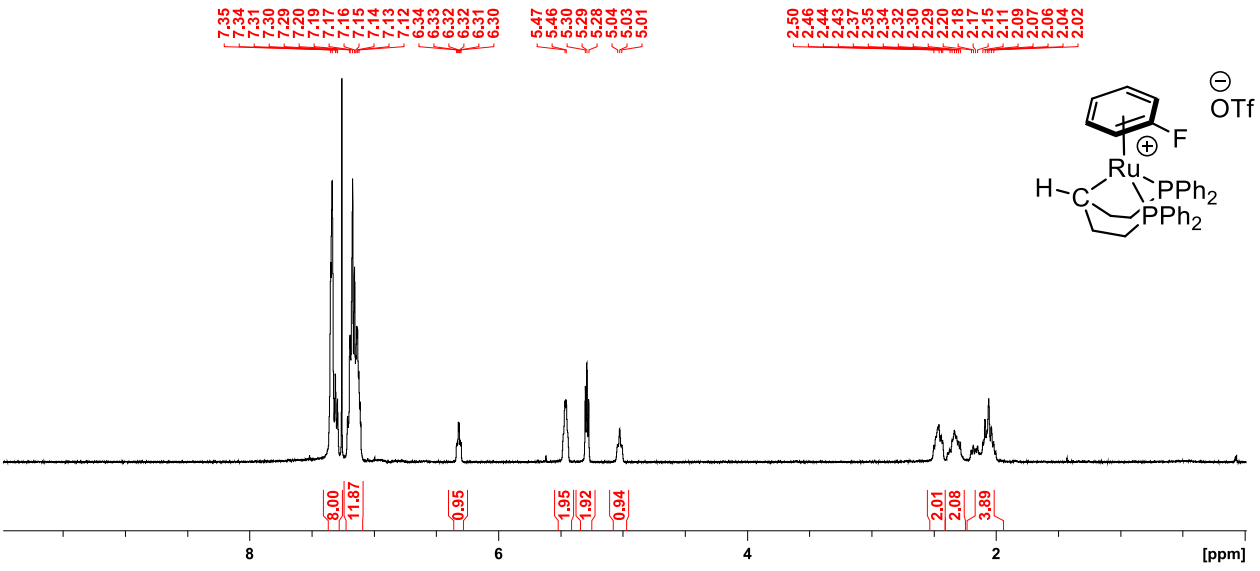


Figure S4. ^{1}H NMR Spectrum of **1**. (400 MHz, $CDCl_3$)

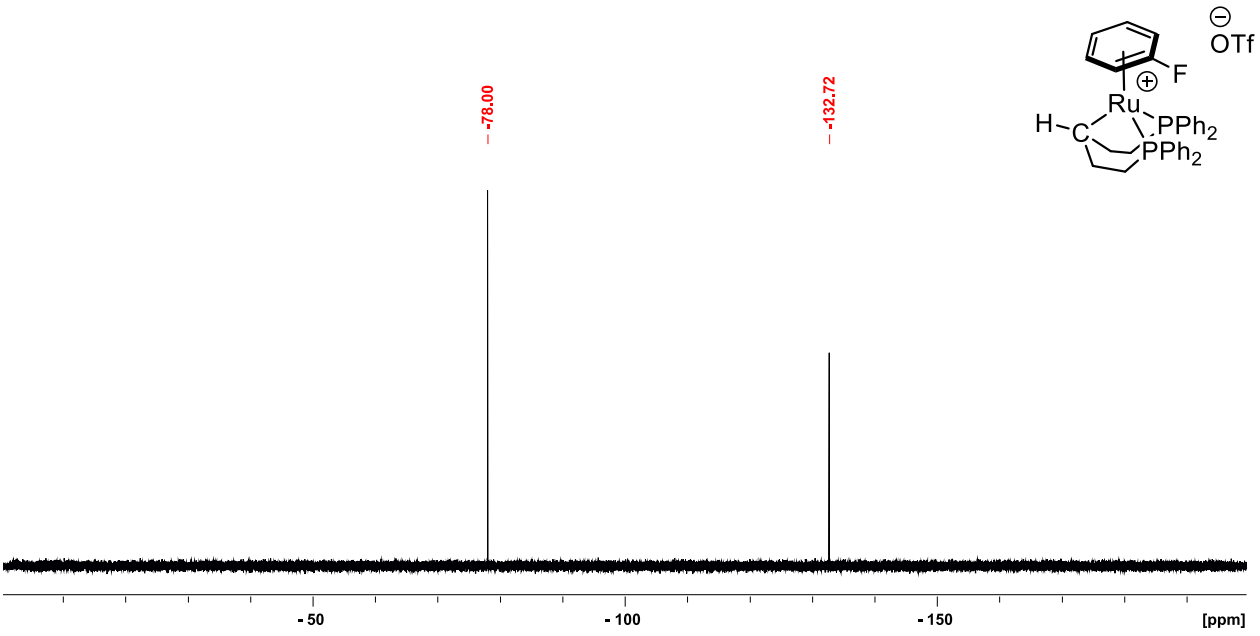


Figure S5. $^{19}F\{^{1}H\}$ NMR Spectrum of **1**. (376 MHz, $CDCl_3$)

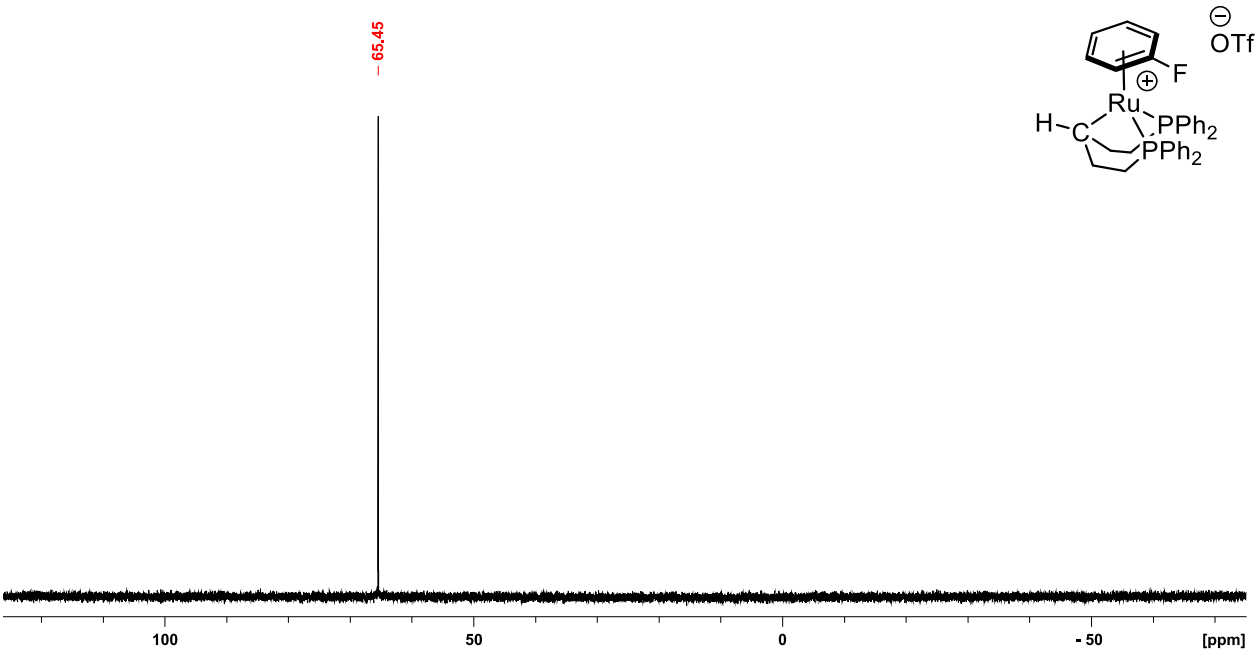


Figure S6. $^{31}P\{^{1}H\}$ NMR Spectrum of **1**. (202 MHz, $CDCl_3$)

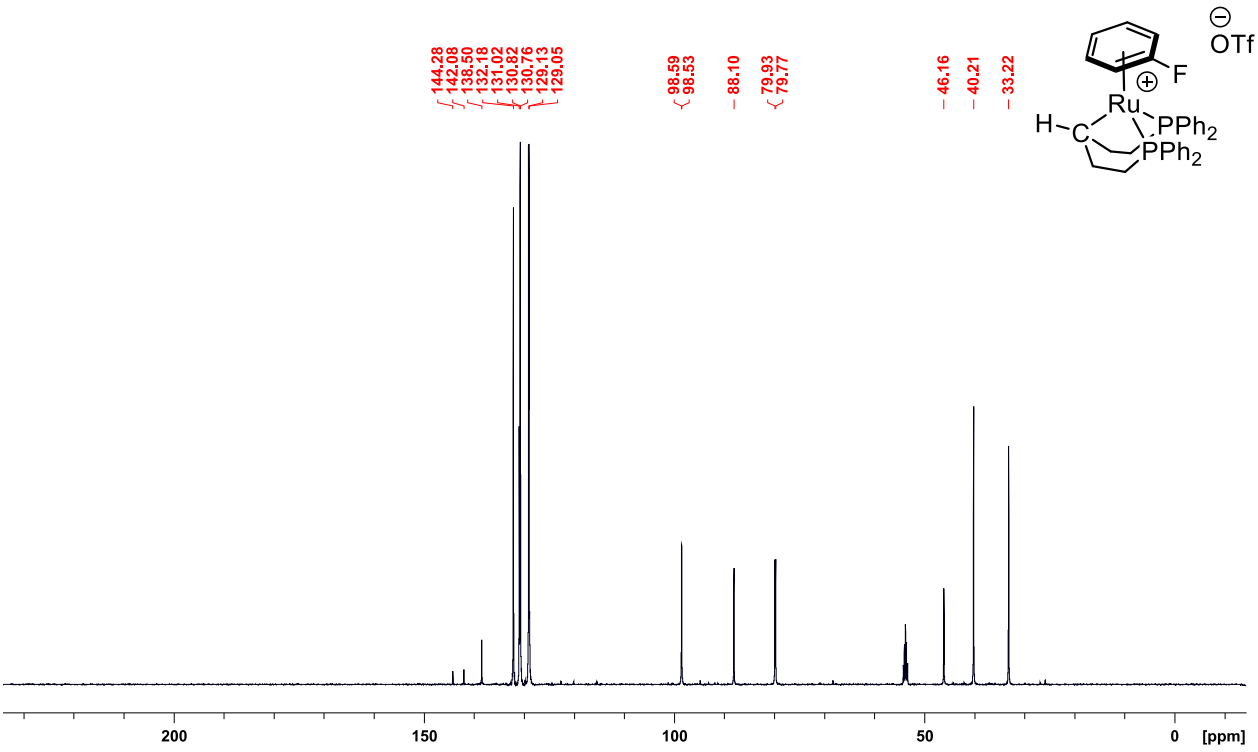


Figure S7. $^{13}C\{^{1}H,^{31}P\}$ NMR Spectrum of **1**. (126 MHz, CD_2Cl_2)

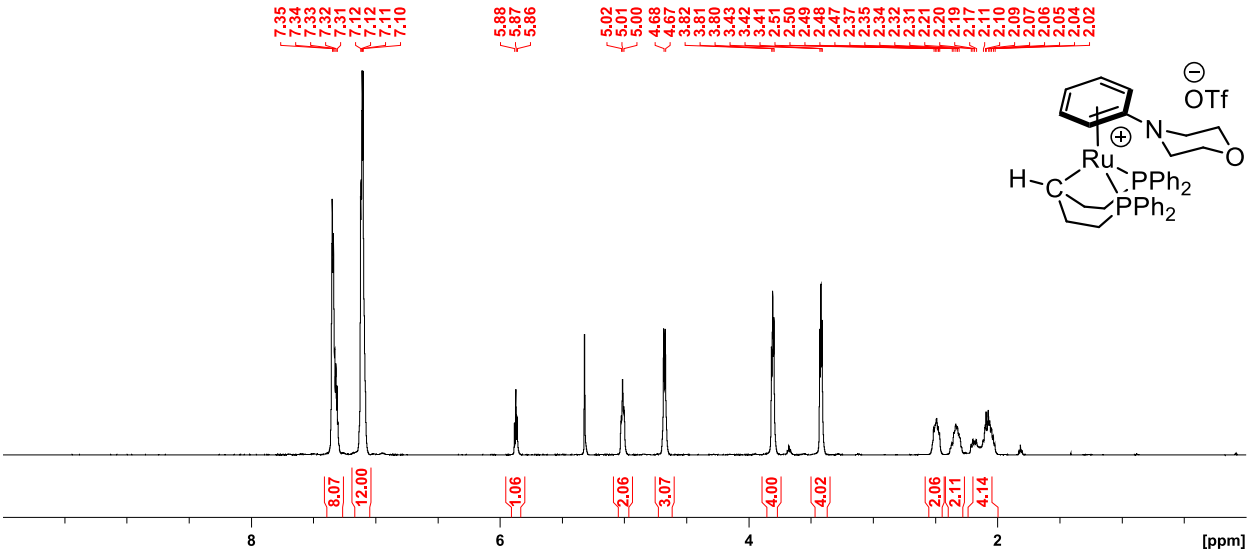


Figure S8. ^{1}H NMR Spectrum of **2**. (500 MHz, CD_2Cl_2)

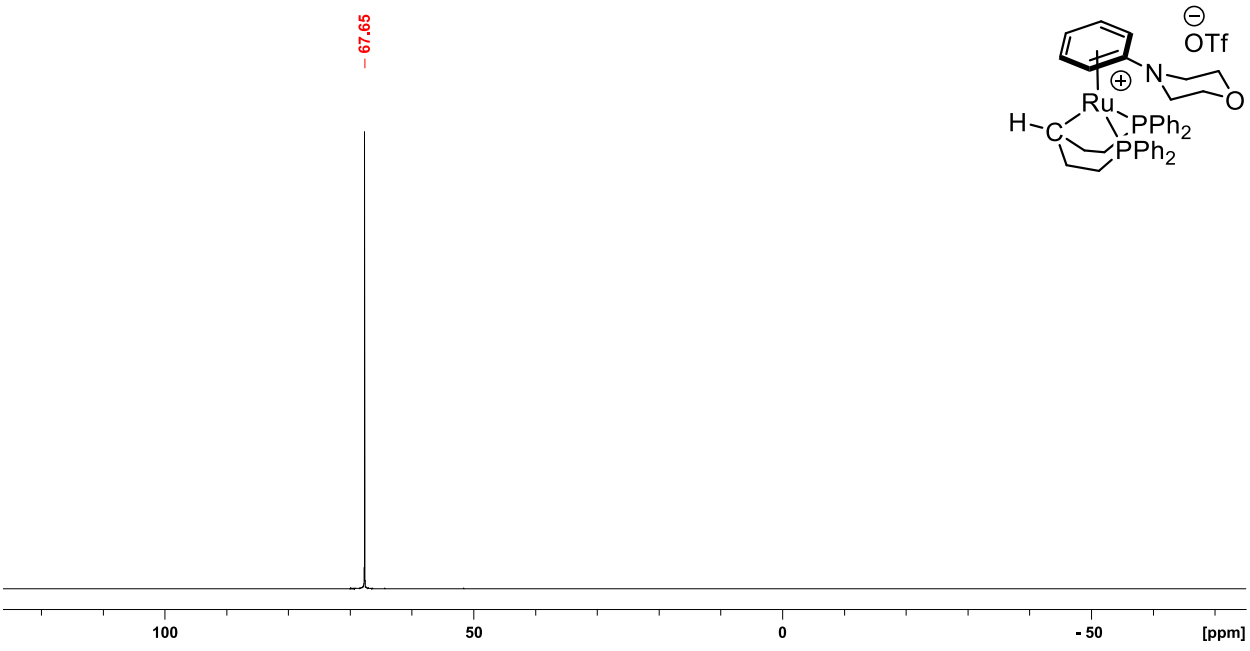


Figure S9. $^{31}P\{^{1}H\}$ NMR Spectrum of **2**. (202 MHz, CD_2Cl_2)

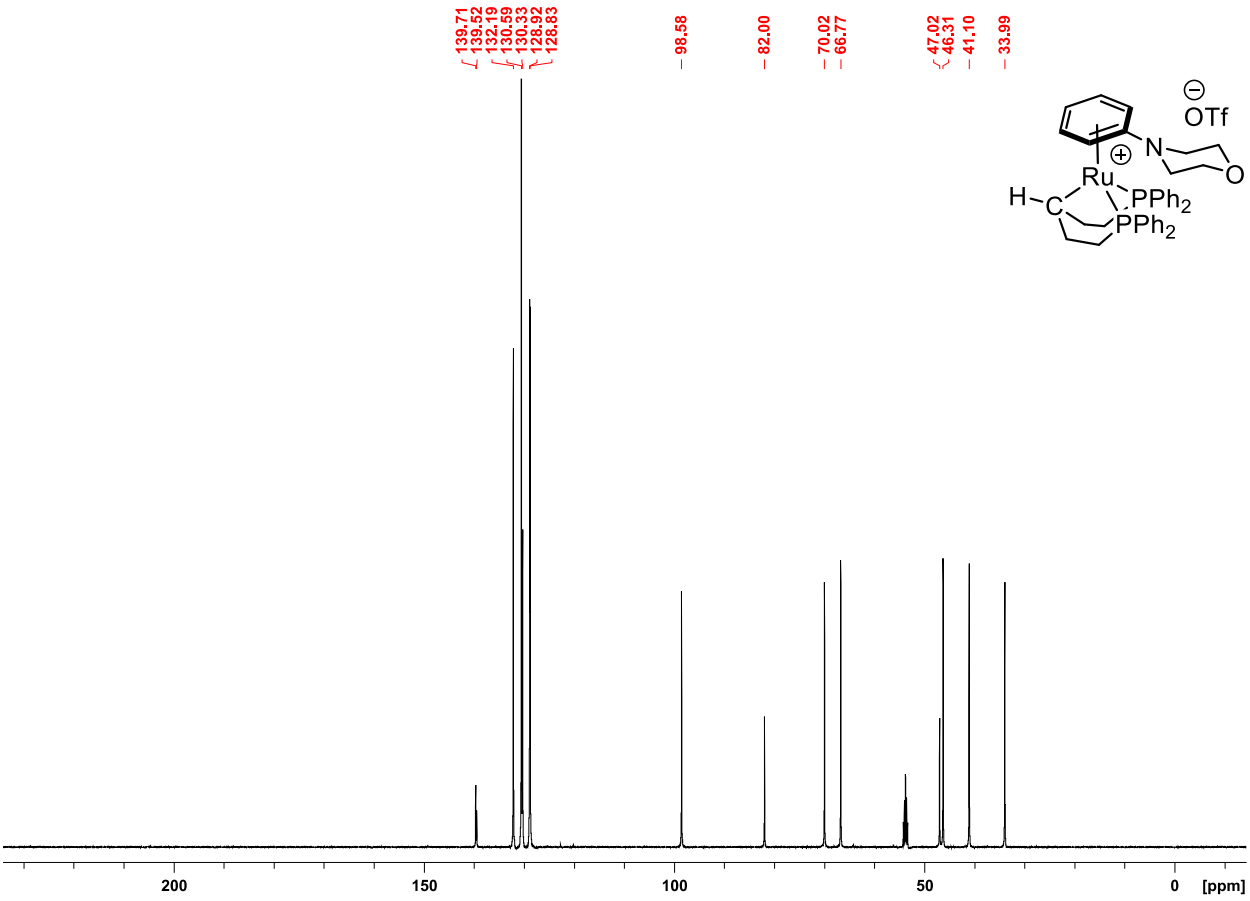


Figure S10. $^{13}C\{^{1}H,^{31}P\}$ NMR Spectrum of **2**. (126 MHz, CD_2Cl_2)

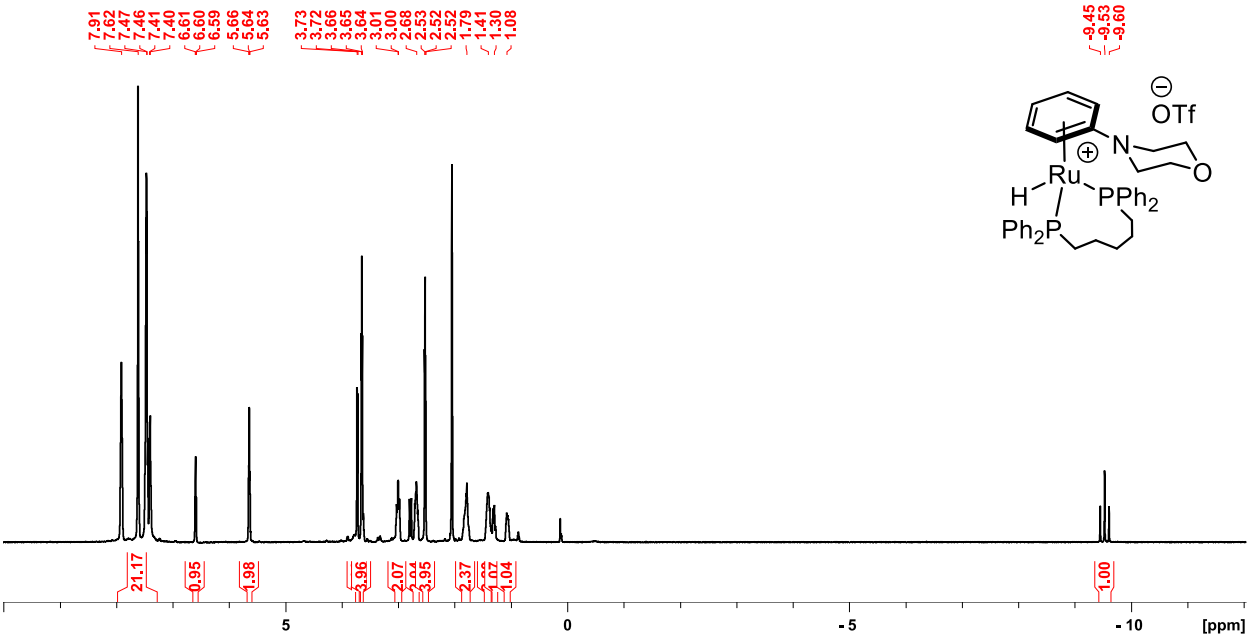


Figure S11. ^{1}H NMR Spectrum of **3**. (500 MHz, acetone-d_6)

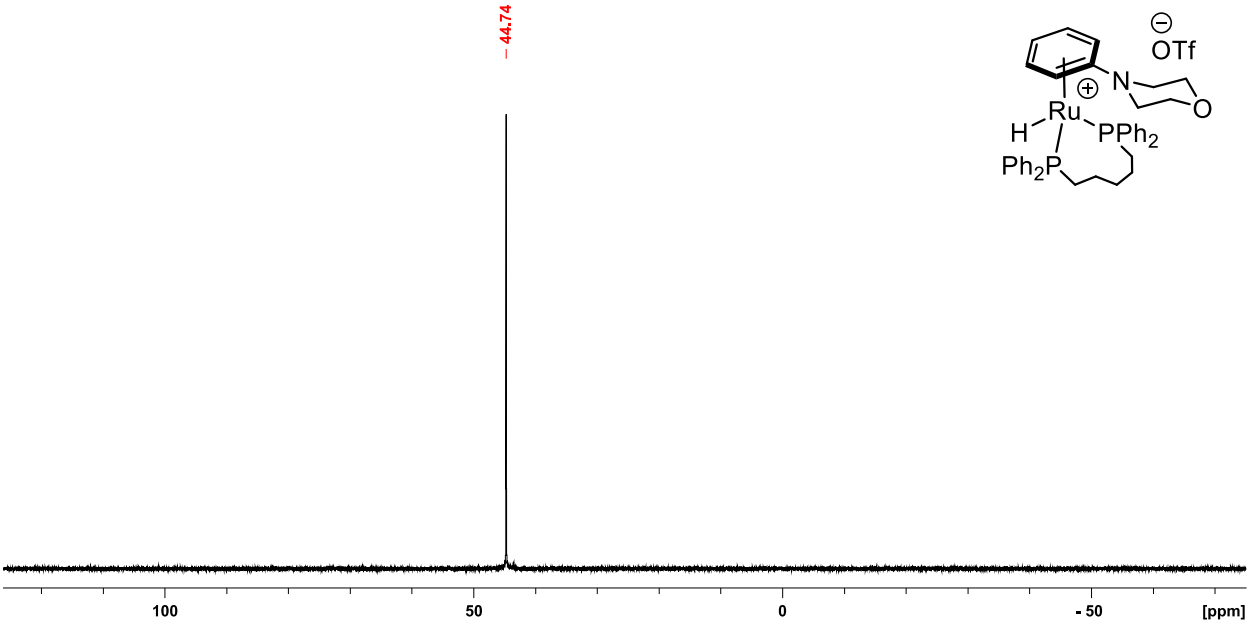


Figure S12. $^{31}P\{^{1}H\}$ NMR Spectrum of **3**. (202 MHz, acetone-d_6)

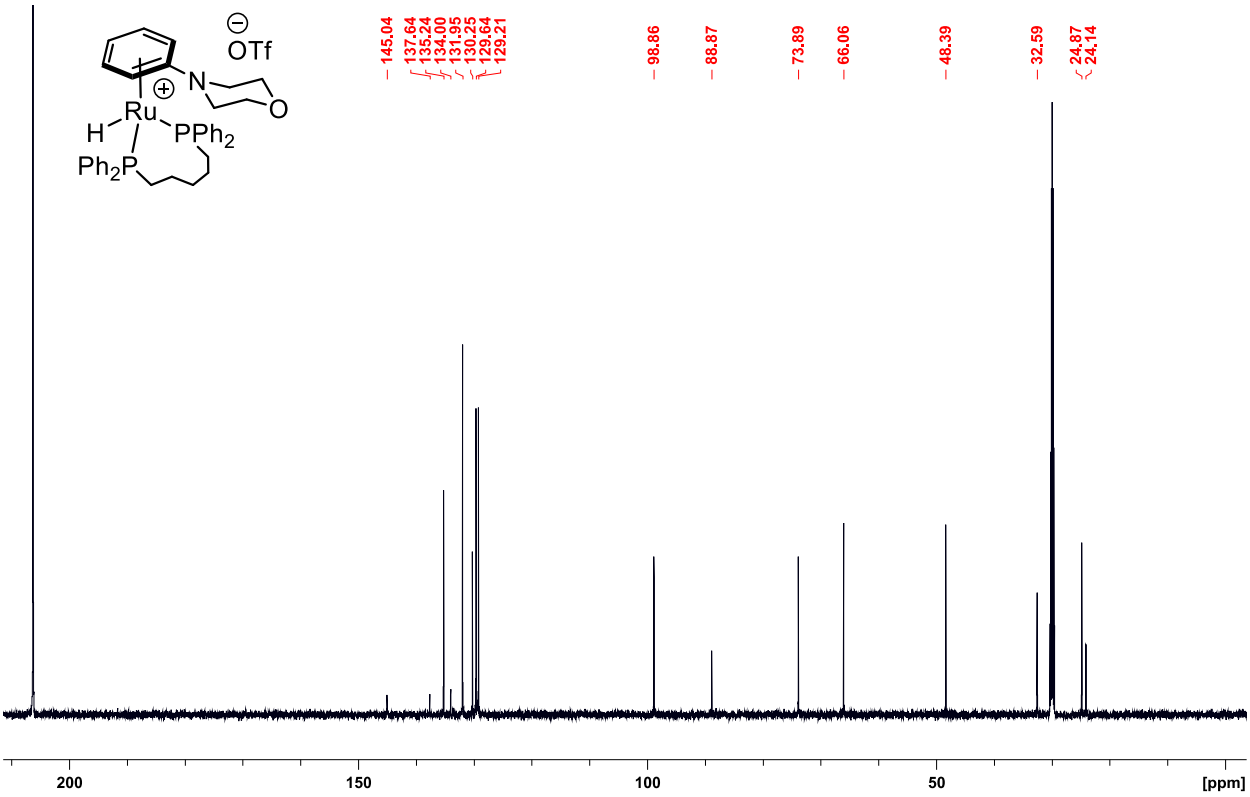


Figure S13. $^{13}C\{^{1}H,^{31}P\}$ NMR Spectrum of **3**. (151 MHz, acetone-d_6)

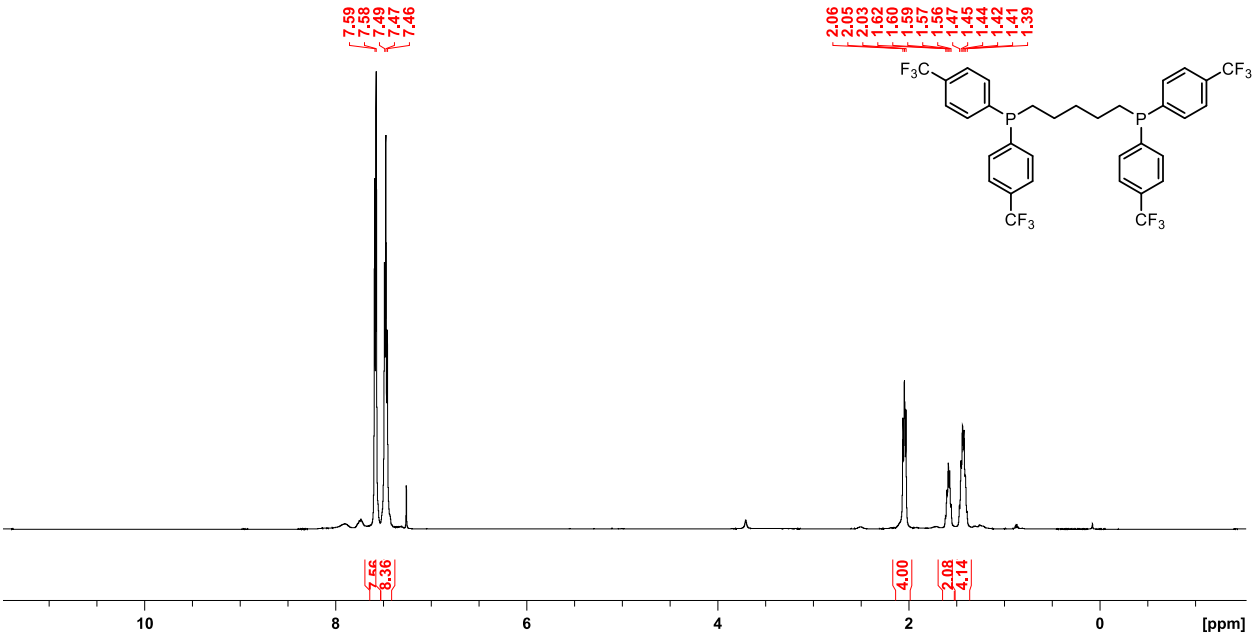


Figure S14. ^{1}H NMR Spectrum of ^{CF3}**DPPPent**. (500 MHz, $CDCl_3$)

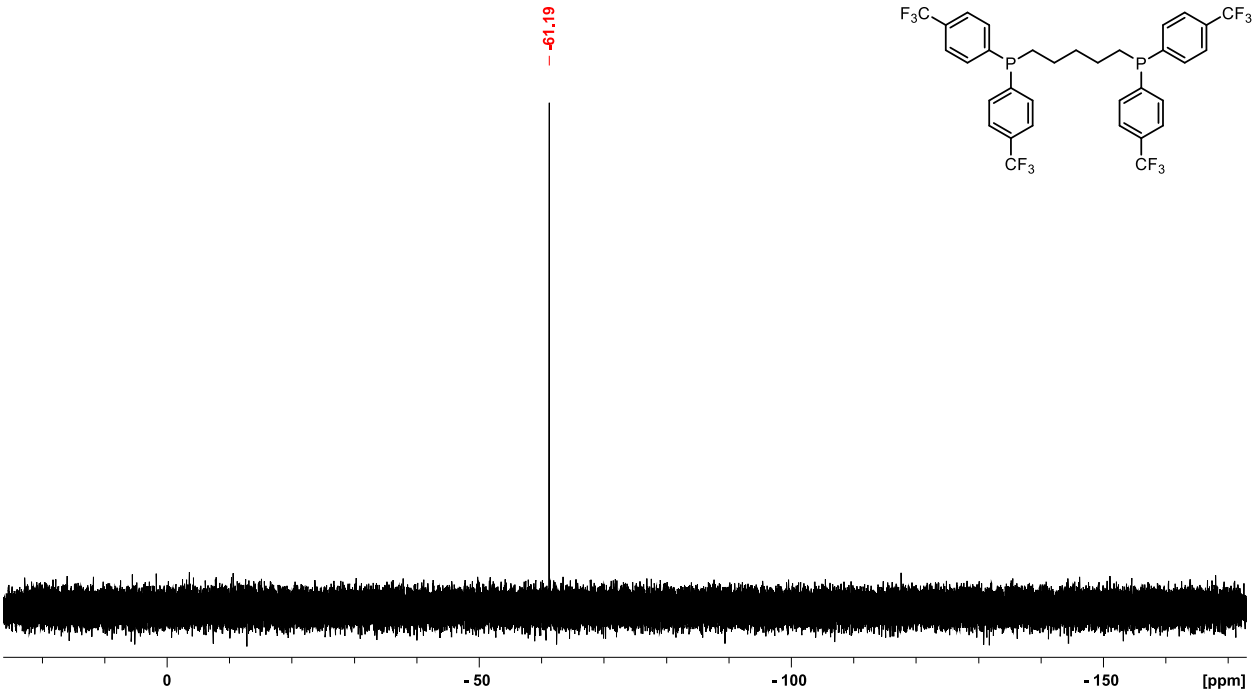


Figure S15. $^{19}F\{^{1}H\}$ NMR Spectrum of ^{CF3}**DPPPent**. (471 MHz, $CDCl_3$)

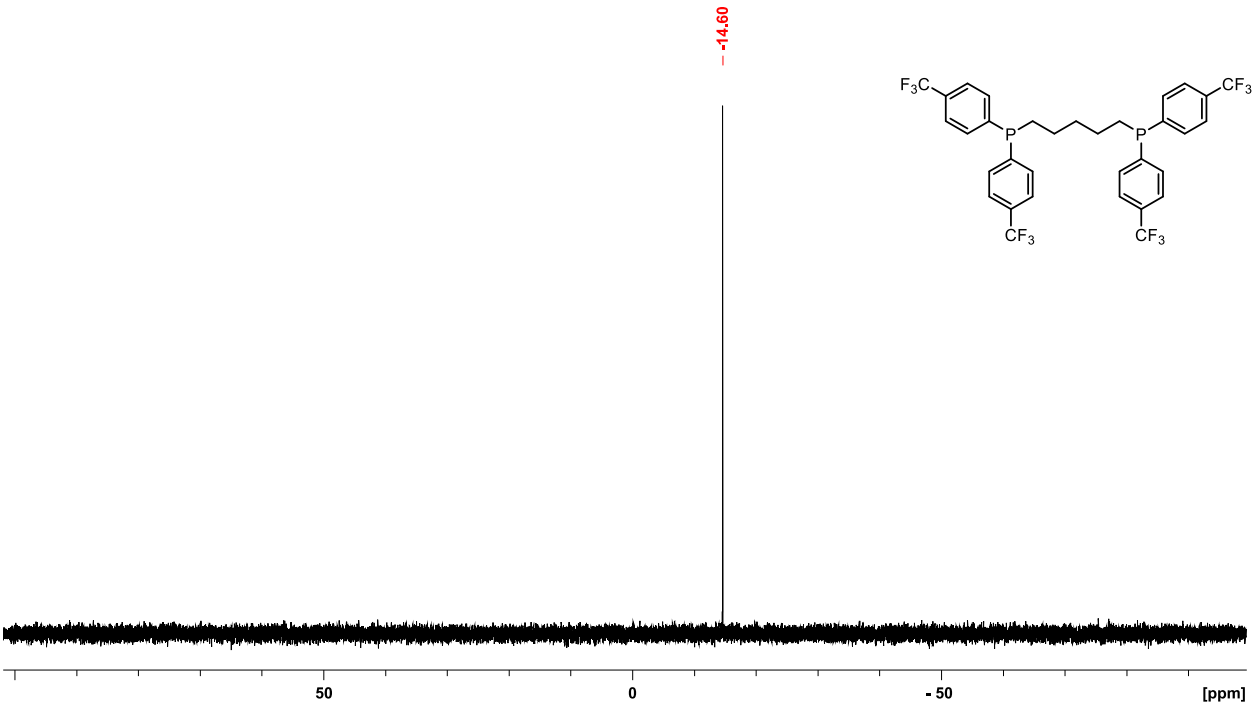


Figure S16. $^{31}P\{^{1}H\}$ NMR Spectrum of ^{CF3}**DPPPent**. (202 MHz, $CDCl_3$)

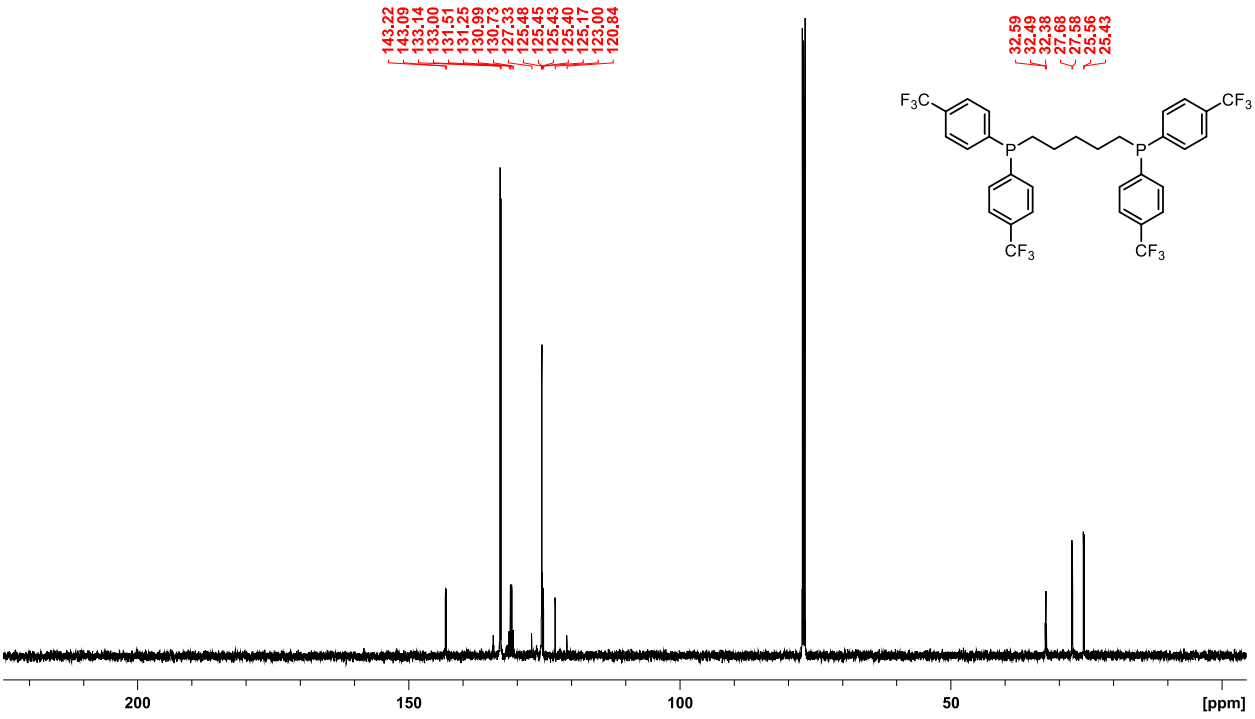


Figure S17. $^{13}C\{^{1}H\}$ NMR Spectrum of ^{CF3}**DPPPent**. (126 MHz, $CDCl_3$)

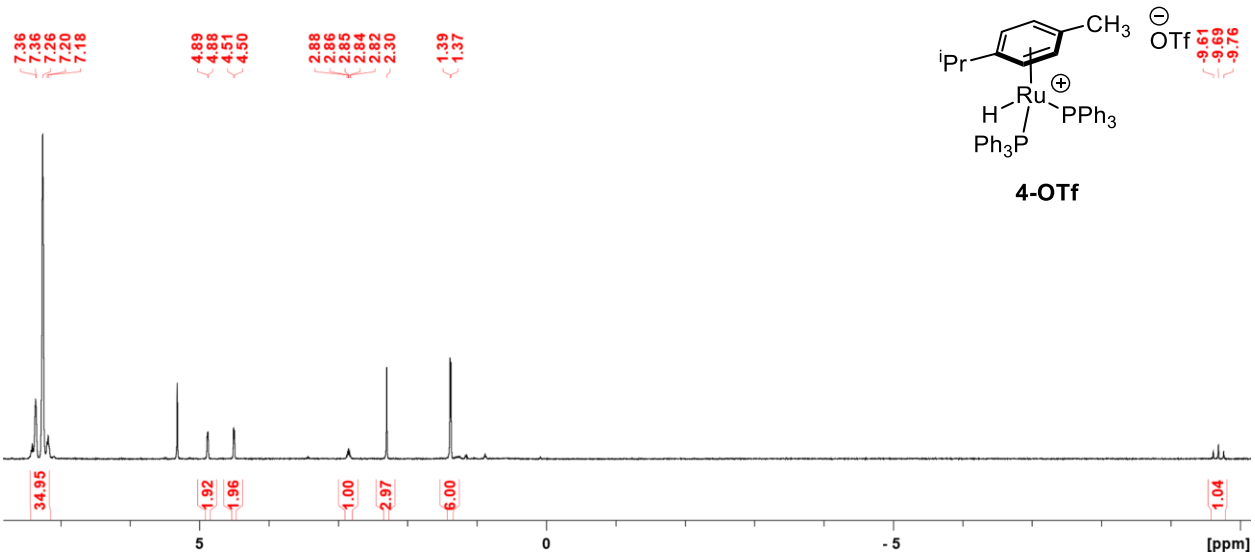


Figure S18. ^{1}H NMR Spectrum of **4-OTf**. (500 MHz, CD_2Cl_2)

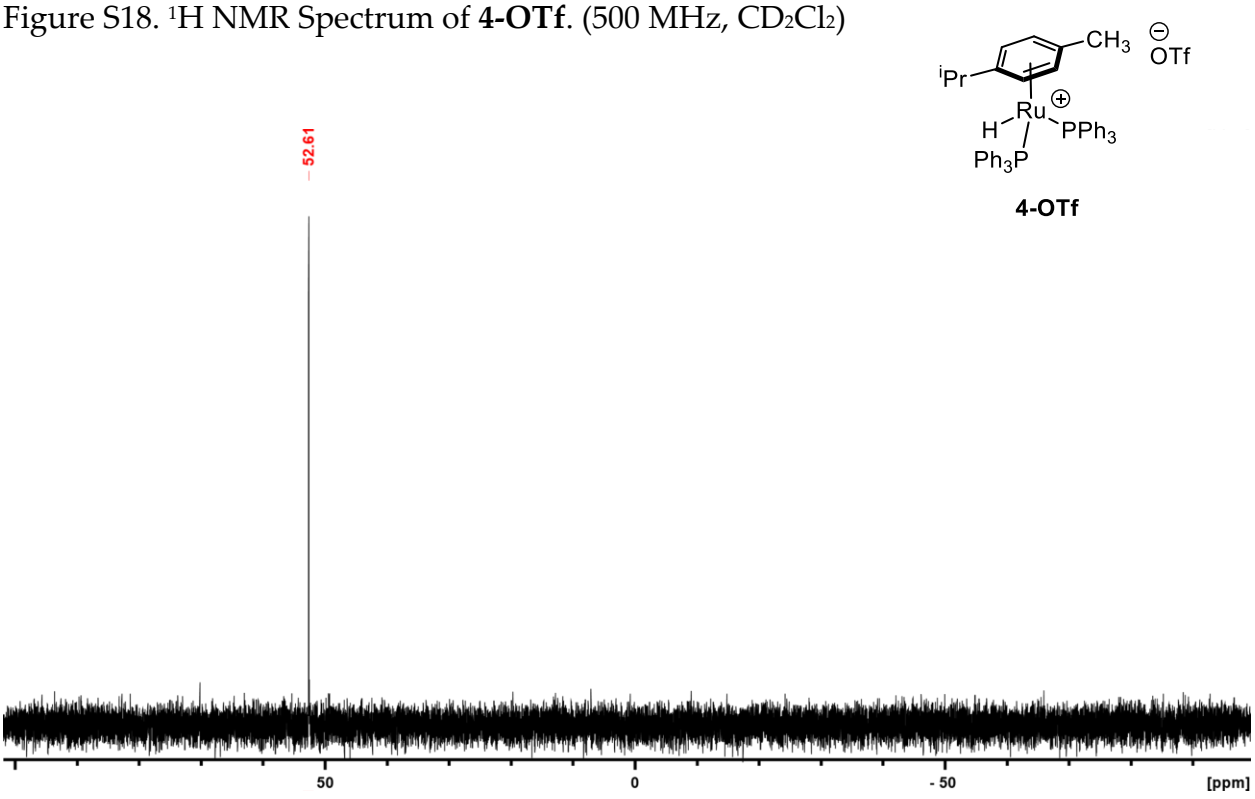


Figure S19. $^{31}P\{^{1}H\}$ NMR Spectrum of **4-OTf**. (202 MHz, CD_2Cl_2)

V. Computational Methods

General Methods. Density functional theory (DFT) calculations were performed using Gaussian 09.[6]

DFT treatment of complexes 1, 2 and 3. Atomic coordinates from the X-ray crystal structures of **1**, **2** and **3** were used as the initial conditions for the optimization of each complex. Calculated free energies at 100 °C were obtained in two steps, with the first being a room temperature optimization of the structure using the M06-L[7] functional with the following basis set (CHN: def2SVP, IrP: def2TZVP).[8] The ECP for Ir was retrieved from the EMSL basis set exchange (http://bse.pnl.gov/).[9]

Keyword. # opt=tight freq m06l/gen geom=connectivity int=ultrafine pseudo=read

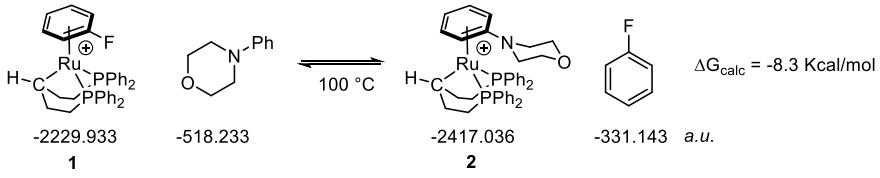
The free energies at 100 °C were then obtained using the optimized structures by inclusion of the temperature keyword.

Keyword. # freq guess=read chkbas genchk geom=allcheck rm06l temperature=373

DFT treatment of fluorobenzene analogue of 3. Optimized coordinates for **3** were used to develop initial conditions for the fluorobenzene analogue. The calculated free energy at 100 °C was determined as above.

Coordinates. The supplemental file "calc_coords.xyz" contains the computed Cartesian coordinates of all of the molecules reported in this study. The file may be opened as a text file to read the coordinates, or opened directly by a molecular modeling program such as Mercury (version 3.3 or later, http://www.ccdc.cam.ac.uk/pages/Home.aspx) for visualization and analysis.

Calculated Energies.



VI. X-Ray Crystallographic Data

*Details of crystallographic refinement for complexes **1**, **2**, **3** and **4-OTf**.*

General Methods. A suitable crystal of each sample was selected for analysis and mounted in a polyimide loop. All measurements were made on a Rigaku Oxford Diffraction Supernova Eos CCD with filtered Cu-Kα radiation at a temperature of 100 K. Using Olex2,[10] the structure was solved with the ShelXT structure solution program using Direct Methods and refined with the ShelXL refinement package[11] using Least Squares minimization.

Complex **1**

Disorder in the trifluoromethyl group of the anion was modeled over two sites using similarity restraints applied to the thermal parameters of the disordered atoms.

Complex **2**

The disordered dichloromethane was modeled over two positions using similarity restraints placed on the atom thermal parameters and C-Cl bond lengths. The disordered triflate anion was modeled over two positions using a fragment-based approach (Guzei, I. A. (2014). *J. Appl. Crystallogr*. 47, 806-809) with similarity restraints placed on the atom thermal parameters.

Complex **3**

The disordered triflate anion was modeled over two positions with similarity restraints placed on the atomic thermal parameters. The disordered tetrahydrofuran molecule was modeled over two positions using the rigid fragment-based approach reported in Guzei, I. A. (2014*). J. Appl. Crystallogr*. 47, 806-809. A similarity restraint was applied to the atomic thermal parameters of the tetrahydrofuran molecule. The metal hydrides were located as the two largest positive electron density peaks in the difference map and their positions freely refined. The metal hydride thermal parameters were fixed to ride on the parent Ru atom.

Complex **4-OTf**

The metal hydride was located in the difference map and refined without restraint.

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

Identification code	Complex **1**	
Empirical formula	$C_{36}H_{34}F_4O_3P_2RuS$	
Formula weight	785.70	
Temperature	100.01(10) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 21.85714(20) Å	α = 90°
	b = 9.81404(12) Å	β = 94.3482(9)°
	c = 30.3186(3) Å	γ = 90°
Volume	6484.84(12) Å^3	
Z	8	
Density (calculated)	1.610 Mg/m^3	
Absorption coefficient	5.970 mm^{-1}	
F(000)	3200	
Crystal size	0.124 x 0.059 x 0.037 mm^3	
Theta range for data collection	2.408 to 73.408°.	
Index ranges	-23<=h<=27, -12<=k<=12, -36<=l<=37	
Reflections collected	42422	
Independent reflections	12620 [R(int) = 0.0421]	
Completeness to theta = 67.684°	98.5 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.940 and 0.664	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12620 / 78 / 884	
Goodness-of-fit on F^2	1.021	
Final R indices [I>2sigma(I)]	R1 = 0.0437, wR2 = 0.1064	
R indices (all data)	R1 = 0.0585, wR2 = 0.1149	
Largest diff. peak and hole	1.823 and -0.601 e/Å^{-3}	

Table S2. Crystal data and structure refinement for **2**.

Identification code	Complex **2**	
Empirical formula	$C_{40}H_{40}F_3NO_4P_2RuS\cdot(CH_2Cl_2)$	
Formula weight	935.72	
Temperature	100.00(10) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 10.27473(16) Å	α = 90°
	b = 15.7066(2) Å	β = 92.2812(14)°
	c = 25.7096(4) Å	γ = 90°
Volume	4145.77(11) $Å^3$	
Z	4	
Density (calculated)	1.499 Mg/m^3	
Absorption coefficient	5.915 mm^{-1}	
F(000)	1912	
Crystal size	0.148 x 0.036 x 0.016 mm^3	
Theta range for data collection	3.298 to 73.240°.	
Index ranges	-12<=h<=12, -19<=k<=14, -31<=l<=29	
Reflections collected	31977	
Independent reflections	8168 [R(int) = 0.0403]	
Completeness to theta = 67.684°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.981 and 0.589	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8168 / 267 / 561	
Goodness-of-fit on F^2	1.081	
Final R indices [I>2sigma(I)]	R1 = 0.0742, wR2 = 0.1997	
R indices (all data)	R1 = 0.0829, wR2 = 0.2066	
Largest diff. peak and hole	2.258 and -1.000 $e/Å^{-3}$	

Table 3. Crystal data and structure refinement for **3**.

Identification code	Complex **3**	
Empirical formula	$C_{40}H_{44}F_3NO_4P_2RuS \cdot \frac{1}{2}(C_4H_8O)$	
Formula weight	890.88	
Temperature	100.01(10) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.87358(18) Å	α = 75.1534(18)°
	b = 16.3420(3) Å	β = 86.1993(16)°
	c = 26.1572(6) Å	γ = 78.7339(16)°
Volume	4000.47(15) $Å^3$	
Z	4	
Density (calculated)	1.479 Mg/m^3	
Absorption coefficient	4.907 mm^{-1}	
F(000)	1840	
Crystal size	0.091 x 0.056 x 0.019 mm^3	
Theta range for data collection	2.846 to 73.397°.	
Index ranges	-12<=h<=12, -16<=k<=20, -32<=l<=31	
Reflections collected	61031	
Independent reflections	15810 [R(int) = 0.0531]	
Completeness to theta = 67.684°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.948 and 0.723	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15810 / 360 / 1089	
Goodness-of-fit on F^2	1.016	
Final R indices [I>2sigma(I)]	R1 = 0.0447, wR2 = 0.1034	
R indices (all data)	R1 = 0.0622, wR2 = 0.1125	
Largest diff. peak and hole	1.313 and -0.739 $e/Å^{-3}$	

Table 4. Crystal data and structure refinement for **4-OTf**.

Identification code	Complex **4-OTf**	
Empirical formula	$C_{47}H_{45}F_3O_3P_2RuS\cdot(C_4H_{10}O)$	
Formula weight	984.02	
Temperature	100.00(10) K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 16.19031(12) Å	α = 90°
	b = 19.05235(16) Å	β = 90°
	c = 29.7018(3) Å	γ = 90°
Volume	9161.92(13) $Å^3$	
Z	8	
Density (calculated)	1.427 Mg/m^3	
Absorption coefficient	4.328 mm^{-1}	
F(000)	4080	
Crystal size	0.195 x 0.091 x 0.026 mm^3	
Theta range for data collection	2.976 to 73.426°.	
Index ranges	-20<=h<=18, -15<=k<=23, -36<=l<=34	
Reflections collected	46582	
Independent reflections	9125 [R(int) = 0.0331]	
Completeness to theta = 67.684°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.563	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9125 / 0 / 567	
Goodness-of-fit on F^2	1.023	
Final R indices [I>2sigma(I)]	R1 = 0.0388, wR2 = 0.0940	
R indices (all data)	R1 = 0.0436, wR2 = 0.0972	
Largest diff. peak and hole	1.865 and -0.768 $e/Å^{-3}$	

VII. References

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