Supporting information

Polarized Au(I)/Rh(I) Bimetallic Pairs Cooperatively Trigger Ligand non-Innocence and Bond Activation

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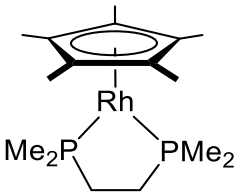
1. Experimental procedures

General considerations

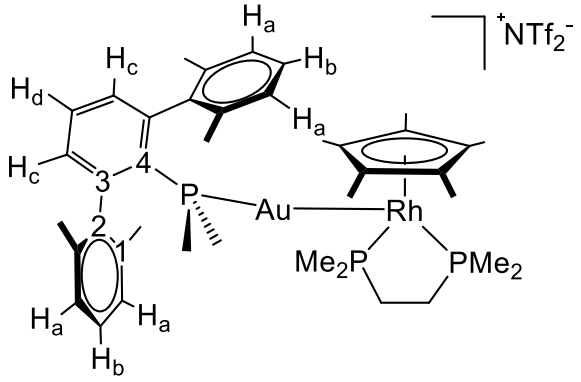
All preparations and manipulations were carried out using standard Schlenk and glove-box techniques, under argon or high-purity nitrogen atmosphere, respectively. All solvents were dried, stored over 4 Å molecular sieves, and degassed prior to use. Toluene (C_7H_8) and *n*-pentane (C_5H_{12}) were distilled under nitrogen over sodium. Benzene-d_6 and toluene-d_8 were dried over molecular sieves (4 Å). THF-d_8 was distilled under nitrogen over sodium/benzophenone. [Au(THT)Cl], **1a**[1], $\mathbf{2^{Me}}$ and $\mathbf{2^{Cyp}}$ were prepared according to previously reported procedures[2]. Other chemicals were commercially available and used as received. Solution NMR spectra were recorded on Bruker AMX-300, DRX-400 and DRX-500 spectrometers. Spectra were referenced to external SiMe4 (δ: 0 ppm) using the residual proton solvent peaks as internal standards (^{1}H NMR experiments), or the characteristic resonances of the solvent nuclei (^{13}C{^{1}H} NMR experiments), while ^{31}P was referenced to H_3PO_4. Spectral assignments were made by routine one- and two-dimensional NMR experiments where appropriate. For elemental analyses a LECO TruSpec CHN elementary analyzer was utilized. For mass spectroscope we use an Ion Trap Bruker Esquire 6000 with ESI sources.

Synthesis and characterization of new compounds



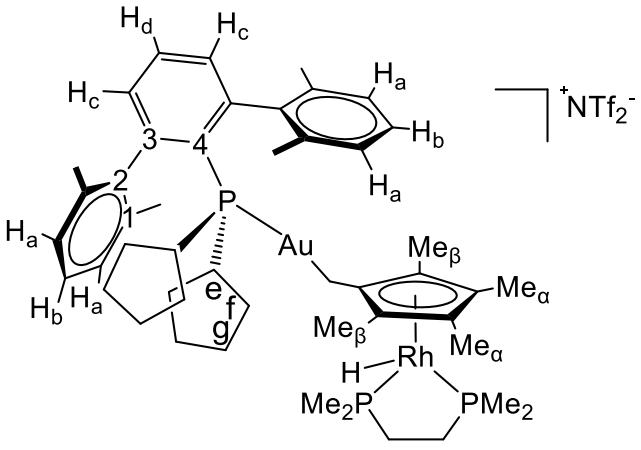
Compound 1b. Sodium amalgam was prepared by adding sodium (58 mg, 2.5 mmol) to mercury (1.5 mL, 102 mmol) under argon atmosphere. The mixture was suspended in diethyl ether (20 mL) to which a solution of dmpe (0.2 mL, 1.13 mmol) was added first and $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2$ (309 mg, 0.5 mmol) in toluene (5 mL) afterwards. The mixture was stirred for 8 hours, after which it was filtered, the solvent evaporated under reduced pressure and the residue extracted with pentane (20 mL). The solution volume was reduced to 5 mL and stored at −78 °C to crystallize. Rhombic pink crystals were obtained after 5 days (750 mg, 60 %). Anal. Calcd. for $C_{16}H_{31}P_2Rh$: C, 49.5; H, 8.1. Found: C, 49.6; H, 8.0.

^{1}H NMR (400 MHz, C_6D_6, 25 °C) δ: 2.17 (s, 15H, C_5Me_5), 1.19 (vt, 12H, $^2J_{HP}$ = 4 Hz, PMe_2), 1.13 (d, 4H, $^2J_{HP}$ = 16 Hz, CH_2). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 25 °C) δ: 94.9 (m, C_5Me_5), 31.8 (vtd, $^1J_{CP}$ = 27, $^2J_{CRh}$ = 4 Hz, CH_2), 20.4 (vt, $^1J_{CP}$ = 9 Hz, PMe_2), 12.4 (C_5Me_5). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 25 °C) δ: 42.2 (d, $^1J_{PRh}$ = 220 Hz).



Compound 3b^{Me}. A solid mixture of compounds **1b** (33 mg, 0.085 mmol) and **2^{Me}** (70 mg, 0.085 mmol) was dissolved in toluene (5 mL) and stirred at room temperature for 5 minutes. NMR spectroscopy reaction monitoring revealed that formation of **3b^{Me}** was immediate and proceeded quantitatively. The solution was concentrated to half its volume and precipitated with pentane. The orange residue was then filtered and dried under vacuum (77 mg, 64%). Anal. Calcd. for $C_{44}H_{66}AuF_6NO_4P_3RhS_2$: C, 42.4; H, 5.4; N, 1.1; S, 5.2. Found: C, 41.9; H, 5.2; N, 1.3; S, 5.2.

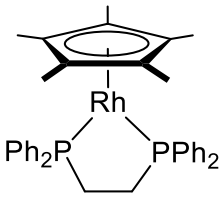
^{1}H NMR (500 MHz, C_6D_6, 25 °C) δ: 7.20 (t, 2H, $^3J_{HH}$ = 7.7 Hz, H_b), 7.02 (d, 4H, $^3J_{HH}$ = 7.7 Hz, H_a), 6.98 (td, 1H, $^3J_{HH}$ = 7.6, $^5J_{HP}$ = 1.6 Hz, H_d), 6.63 (dd, 2H, $^3J_{HH}$ = 7.6, $^4J_{HP}$ = 3.0 Hz, H_c), 2.09 (s, 12H, Me_{Xyl}), 1.76 (d, 4H, $^2J_{HP}$ = 12.4 Hz, CH_2), 1.64 (s, 15H, C_5Me_5), 1.25 (d, 6H, $^2J_{HP}$ = 9.5 Hz, P*Me*Me (dmpe)), 1.13 (d, 6H, $^2J_{HP}$ = 9.5 Hz, PMe*Me*(dmpe)), 0.77 (d, 6H, $^2J_{HP}$ = 8.6 Hz, P*Me*$_2$Ar^{Xyl2}). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 25 °C) δ: 144.8 (d, $^2J_{CP}$ = 9 Hz, C_3), 141.7 (d, $^3J_{CP}$ = 3 Hz, C_2), 135.9 (C_1), 131.5 (d, $^1J_{CP}$ ≈ 40Hz, C_4), 130.5 (overlapped CH_c and CH_d), 128.5 (CH_a), 127.2 (CH_b), 121.3 (q, $^1J_{CF}$ = 324 Hz, CF_3), 98.7 (C_5Me_5), 34.1 (CH_2), 22.4 (PMe*Me* (dmpe)), 21.7 (Me_{Xyl}), 17.7-17.4 (overlapped P*Me*$_2$Ar^{Xyl2} and P*Me*Me (dmpe)), 11.2 (C_5Me_5). ^{19}F{^{1}H} NMR (471 MHz, C_6D_6, 25 °C) δ: −78.3. ^{31}P{^{1}H} NMR (202 MHz, C_6D_6, 25 °C) δ: 45.5 (dd, $^1J_{PRh}$ = 154, $^3J_{PP}$ = 9 Hz, dmpe), 14.6 (dt, $^2J_{PRh}$ = 12, $^3J_{PP}$ = 9 Hz, PMe_2Ar^{Xyl2}).



Compound 4b^{Cyp}. A solid mixture of compounds **1b** (21 mg, 0.054 mmol) and **2^{Cyp}** (50 mg, 0.054 mmol) was dissolved in toluene (5 mL) and stirred at room temperature for 5 minutes. NMR spectroscopy reaction monitoring revealed that formation of **4b^{Cyp}** was immediate and proceeded quantitatively. The solution was concentrated to half volume and precipitated with pentane. The brown residue was then filtered and dried under vacuum (40 mg, 30%). To increase purity, compound **4b^{Cyp}** was crystallized by slow diffusion of pentane over a benzene solution to provide

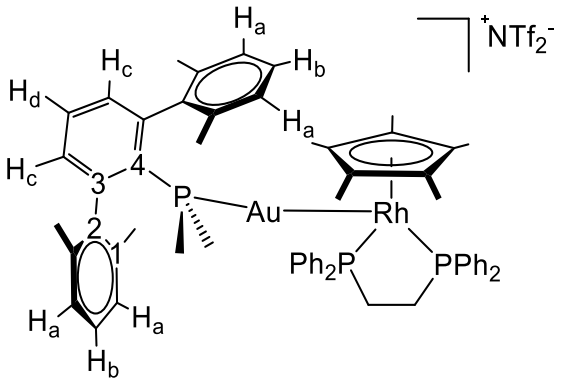
a yellow/brownish crystalline material. Anal. Calcd. for $C_{50}H_{75}AuF_6NO_4P_3RhS_2$: C, 45.3; H, 5.7; N, 1.1; S, 4.8. Found: C, 44.6; H, 5.7; N, 1.1; S, 4.9.

^{1}H NMR (400 MHz, C_6D_6, 25 °C) δ: 7.23 (t, 2H, $^3J_{HH}$ = 7.4 Hz, H_b), 7.08 to 7.05 (m, 5H, H_a and H_d), 6.68 (brd, 2H, $^3J_{HH} \approx$ 7.4 Hz, H_c), 2.18 (m, 2H, H_e), 1.99 (s, 12H, Me_{Xyl}), 1.74 (s, 6H, Me_α), 1.69 (s, 6H, Me_β), 1.65 (m, 8H, H_g), 1.43 (d, 4H, $^2J_{HP}$ = 9 Hz, C*H*$_2$dmpe), 1.35 (m, 8H, H_f), 1.28 (d, 6H, $^2J_{HP}$ = 9.8 Hz, P*Me*Me), 1.21 (d, 2H, $^2J_{HP}$ = 7.7 Hz, CH_2Au), 1.12 (d, 6H, $^2J_{HP}$ = 9.8 Hz, PMe*Me*), −13.6 (td, 1H, $^2J_{HP}$ = 34, $^1J_{HRh}$ = 26 Hz, RhH). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 25 °C) δ: 148.4.0 (d, $^2J_{CP}$ = 8 Hz, C_3), 142.2 (C_2), 136.3 (br s, C_1) , 131.7 (br, CH_c), 131.4 (d, $^1J_{CP} \approx$ 30Hz, C_4) 130.8 (CH_d), 127.9 and 127.7 (CH_a and CH_b, overlapped with C_6D_6), 120.9 (q, $^1J_{CF}$ = 324 Hz, CF_3), 98.8 (*C*Me$_\beta$), 90.9 (*C*Me$_\alpha$), 37.8 (d, $^1J_{CP}$ = 31 Hz, CH_e), 34.4 (CH_g), 31.9 (CH_f), 27.1 (d, $^2J_{CP}$ = 75 Hz, CH_2Au), 25.4 (vdd, $^2J_{CRh}$ = 28, $^1J_{CP}$ = 9 Hz, *C*H$_2$dmpe), 21.4 (Me_{Xyl}), 18.9 (vt, $^1J_{CP}$ = 22 Hz, PMe*Me*), 13.4 (vt, $^1J_{CP}$ = 18 Hz, P*Me*Me), 10.6 and 10.5 (Me_α and Me_β). ^{19}F{^{1}H} NMR (376 MHz, C_6D_6, 25 °C) δ: −78.3. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 25 °C) δ: 57.0 (t, $^3J_{PP}$ = 10 Hz), 42.9 (dd, $^1J_{PRh}$ = 137, $^3J_{PP}$ = 10 Hz).



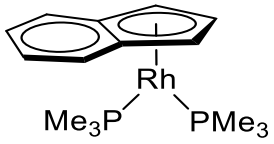
Compound 1c. Sodium amalgam was prepared by adding sodium (173 mg, 7.5 mmol) to mercury (4.5 mL, 306 mmol) under argon atmosphere. The mixture was suspended in ether (20 mL), dppe (1343 mg, 2.25 mmol) was added first and [(η^5-C_5Me_5)$RhCl_2$]$_2$ (907 mg, 1.4 mmol) in toluene (5 mL) second. The mixture was stirred for 8 hours, after which time was filtrated, the solvent evaporated under reduced pressure and the residue extracted with pentane (20 mL). The solution volume was reduced to 5 mL and stored at −78 °C to crystallize. Rhombic pink crystals were obtained after 5 days (950 mg, 66 %). Anal. Calcd. for $C_{36}H_{39}P_2Rh$: C, 67.9; H, 6.2. Found: C, 67.9; H, 6.4.

^{1}H NMR (400 MHz, C_6D_6, 25 °C) δ: 7.68 (m, 8H, *o*-Ph_2), 7.17 (m, 8H, *m*-Ph_2), 7.09 (m, 4H, *p*-Ph_2), 1.85 (d, 4H, $^2J_{HP}$ = 19 Hz, CH_2), 1.79 (s, 15H, C_5Me_5). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 25 °C) δ: 139.6 (vt, $^1J_{CP}$ = 16 Hz, $C_{ipso}Ph_2$), 132.9 (vt, $^2J_{CP}$ = 6 Hz, C_oPh_2), 128.3 (overlapped, C_mPh_2 and C_pPh_2), 95.4 (m, *C*$_5$Me$_5$), 32.2 (vtd, $^1J_{CP}$ = 27, $^2J_{CRh}$ = 2 Hz, CH_2), 10.8 (C_5*Me*$_5$). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 25 °C) δ: 81.2 (d, $^1J_{PRh}$ = 219 Hz).

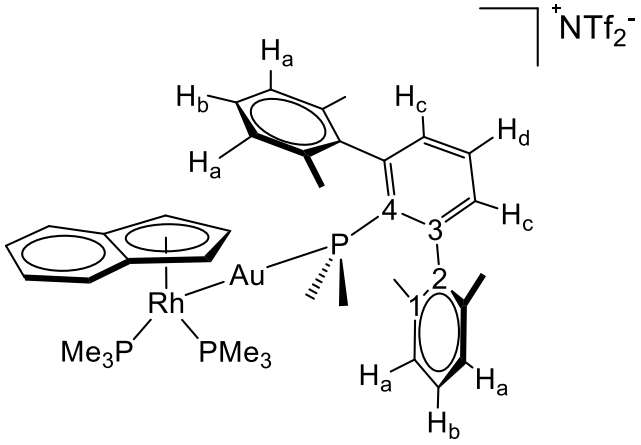


Compound 3c^{Me}. A solid mixture of compounds **1c** (38.7 mg, 0.061 mmol) and **2^{Me}** (50 mg, 0.061 mmol) was dissolved in toluene (5 mL) and stirred at room temperature for 5 minutes. Reaction monitoring revealed that formation of **3c^{Me}** was immediate and proceeded quantitatively by NMR spectroscopy. The solution was concentrated to half volume and precipitated with pentane. The green residue was then filtered and dried under vacuum (40 mg, 45 %). Anal. Calcd. for $C_{62}H_{66}AuF_6NO_4P_3RhS_2$: C, 51.0; H, 4.6; N, 1.0; S, 4.4. Found: C, 50.6; H, 4.7; N, 1.2; S, 4.8.

^{1}H NMR (500 MHz, C_6D_6, 25 °C) δ: 7.57 (m, 4H, *o*-Ph_2), 7.38 (m, 4H, *o*-Ph_2), 7.32 (m, 2H, H_b), 7.13 to 7.03 (m, 16H, overlapping *m*-Ph_2, *p*-Ph_2, H_a), 6.90 (m, 1H, H_d), 6.52 (dd, 2H, $^3J_{HH}$ = 7.3, $^4J_{HP}$ = 2.4 Hz, H_c), 2.62 (m, 4H, CH_2(dmpe)), 1.86 (s, 12H, Me_{Xyl}), 1.54 (s, 15H, C_5Me_5), 0.37 (d, 6H, $^2J_{HP}$ = 8.8 Hz, P*Me*$_2$) . ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 25 °C) δ: 144.9 (d, $^1J_{CP}$ = 8 Hz, C_3), 141.2 (d, $^1J_{CP}$ = 2 Hz, C_2), 137.4 (m, $C_{ipso}Ph_2$), 136.1 (C_1), 132.5 (m, C_oPh_2)), 131.5 (m, C_mPh_2), 130.5 (overlapped C_4 and CH_c), 130.4 (CH_d), 128.8 (m, C_pPh_2), 128.4 (CH_a), 127.2 (CH_b), 121.5 (q, $^1J_{CF}$ = 324 Hz, CF_3), 100.5 (C_5Me$_5$), 34.1 (CH_2), 21.4 (Me_{Xyl}), 17.5 (d, $^1J_{CP}$ = 32 Hz, P*Me*$_2$Ar^{Xyl2}), 10.9 (C_5*Me*$_5$). ^{19}F{^{1}H} NMR (471 MHz, C_6D_6, 25 °C) δ: −77.9. ^{31}P{^{1}H} NMR (202 MHz, C_6D_6, 25 °C) δ: 74.1 (dd, $^1J_{PRh}$ = 164, $^3J_{PP}$ = 6 Hz), 12.1 (q, $^1J_{PRh}$ = $^3J_{PP}$ = 6 Hz).



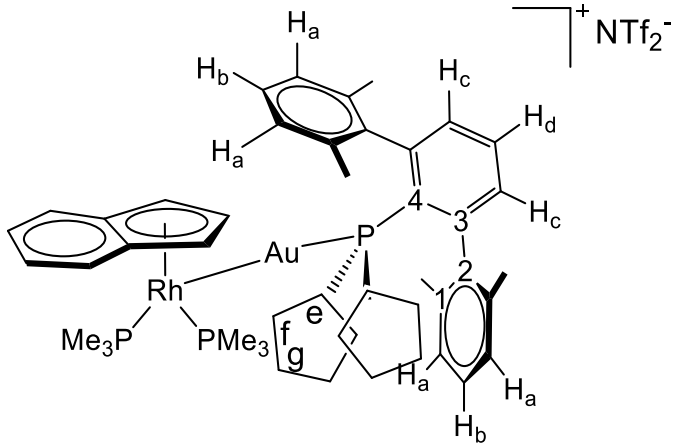
Compound 6a. Following a previously reported procedure,[3] (C_9H_7)Li (120 mg, 0.962 mmol) was added to a solution of [RhCl(COE)$_2$]$_2$ (332 mg, 0.461 mmol) in toluene (10 mL). The solution was stirred at room temperature overnight, filtered through celite and solvent was is removed under vacuum. PMe_3 (1.25 mL, 1.23 mmol) was slowly added to a solution of the resulting product (268 mg, 0.616 mmol) in THF at −80 °C, stirring overnight. Solvent was removed under vacuum and the resulting green solid was coevaporated with pentane (329 mg, 72%).



Compound 7a^{Me}. A solid mixture of compounds **6a** (32 mg, 0.085 mmol) and **2^{Me}** (70 mg, 0.085 mmol) was dissolved in toluene (5 mL) and stirred at room temperature for 5 minutes. Reaction monitoring revealed that formation of **7a^{Me}** was immediate and proceeded quantitatively by NMR spectroscopy. The solution was concentrated to half volume and precipitated with pentane. The brown residue was then filtered and dried under vacuum (58 mg, 57 %). Anal. Calcd. for $C_{41}H_{53}AuF_6NO_4P_3RhS_2$: C, 41.2; H, 4.5; N, 1.2; S, 5.4. Found: C, 41.0; H, 4.3; N, 1.2; S, 5.5.

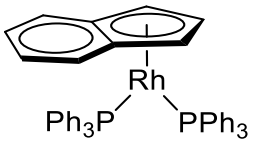
^{1}H NMR (500 MHz, C_6D_6, 25 °C) δ: 7.20 (m, 2H, H_b), 7.04 (m, 4H, H_a), 6.93-6.87 (m, 5H, overlapping Ind and H_d), 6.65 (dd, 2H, $^3J_{HH}$ = 7.6, $^4J_{HP}$ = 3.3 Hz, H_c), 5.79 (m, 1 H, Ind), 4.89

(m, 2H, Ind), 2.09 (s, 12H, Me_{Xyl}), 1.07 (vt, dar *J* del vt, 18H, PMe_3), 0.88 (d, 6H, $^2J_{HP}$ = 9.6 Hz, P*Me*$_2$Ar^{Xyl2}) . $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6, 25 °C) δ: 145.9 (br , C_3), 140.5 (d $^3J_{CP}$ = 9 Hz, C_2), 135.9 (C_1), 131.9 (CH_d), 130.8 (CH_c), 128.8 (d,$^1J_{CP}$ = 24 Hz, C_4), 127.9 and 127.8 (CH_a and CH_b, overlapped with C_6D_6), 124.9 (Ind), 119.6 (q, $^1J_{CF}$ = 326 Hz, CF_3), 115.8 (Ind), 94.6 (Ind), 82.8 (Ind), 74.0 (Ind), 22.5 (m, PMe_3), 21.3 (Me_{Xyl}), 16.3 (d, $^1J_{CP}$ = 16 Hz, P*Me*$_2$Ar^{Xyl2}). $^{19}F\{^1H\}$ NMR (471 MHz, C_6D_6, 25 °C) δ: −78.4. $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 25 °C) δ: 4.6 (d, $^2J_{PRh}$ = 18 Hz), −3.9 (d, $^1J_{PRh}$ = 158 Hz).



Compound 7a^{Cyp}. A solid mixture of compounds **6a** (40 mg, 0.107 mmol) and **2^{Cyp}** (100 mg, 0.107 mmol) was dissolved in toluene (5 mL) and stirred at room temperature for 5 minutes. Reaction monitoring revealed that formation of **7a^{Cyp}** was immediate and proceeded quantitatively by NMR spectroscopy. The solution was concentrated to half volume and precipitated with pentane. The green residue was then filtered and dried under vacuum (80 mg, 57 %). Anal. Calcd. for $C_{49}H_{67}AuF_6NO_4P_3RhS_2$: C, 45.1; H, 5.2; N, 1.1; S, 5.9. Found: C, 45.1; H, 5.0; N, 1.3; S, 5.8.

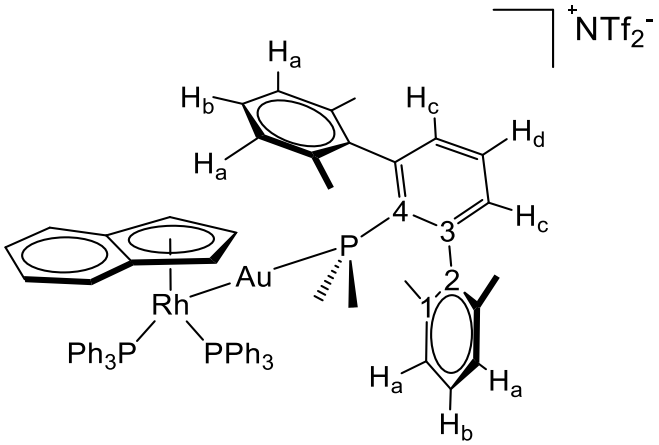
^1H NMR (500 MHz, C_6D_6, 25 °C) δ: 7.12 (m, 2H, H_b), 6.99 (m, 4H, H_a), 6.94 to 6.91 (m, 5H, H_d and Ind), 6.48 (dd, 2H, $^3J_{HH}$ = 7.5, $^4J_{HP}$ = 3.3 Hz, H_c), 5.75 (m, 1H, Ind), 4.86 (m, 2H, Ind), 2.30 (m, 2H, H_e), 1.99 (s, 12H, Me_{Xyl}), 1.65 to 1.57 (m, 8H, H_f), 1.42 (m, 8H, H_g), 1.13 (vt, 18H, PMe_3). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6, 25 °C) δ: 147.5 (d,$^2J_{CP}$ = 9 Hz, C_3), 142.1 (d $^3J_{CP}$ = 4 Hz, C_2), 137.5 (C_1), 132.7 (d,$^1J_{CP}$ = 30 H, C_4), 132.3 (CH_d), 131.9 (CH_c), 128.9 (CH_a), 128.1 (CH_b), 125.2 (Ind), 121.3 (q, $^1J_{CF}$ = 326 Hz, CF_3), 119.1 (Ind), 116.5 (Ind), 94.2 (Ind), 73.3 (Ind), 39.1 (d, $^1J_{CP}$ = 28 Hz, CH_e), 34.1 (CH_f), 31.9 (CH_g), 21.3 (Me_{Xyl}), 21.5 (m, PMe_3). $^{19}F\{^1H\}$ NMR (471 MHz, C_6D_6, 25 °C) δ: −78.3. $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 25 °C) δ: 43.3 (d, $^2J_{PRh}$ = 19 Hz), −6.2 (d, $^1J_{PRh}$ = 159 Hz).



Compound 6d. $(C_9H_7)Li$ (360 mg, 2.8 mmol) is added to a solution of $[RhCl(COE)_2]_2$ (1 g, 1.4 mmol) in toluene (10 mL), stirred at room temperature overnight and filtered through celite. The solvent was removed under vacuum and PMe_3 (738 mg, 2.8 mmol) was slowly added to a solution of the resulting product (600 mg, 1.4 mmol) in THF at −80 °C, stirring the solution upon warming to room temperature and heating at 60 °C overnight. Solvent was removed under vacuum and the

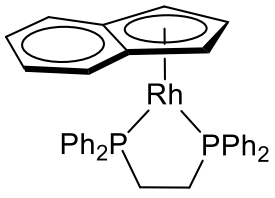
resulting red solid was coevaporated with pentane (840 mg, 84 %). ^{1}H NMR resonances are in agreement with prior literature data(REF).

^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 25 °C) δ: 50.9 (d, $^{2}J_{PRh}$ = 223 Hz).



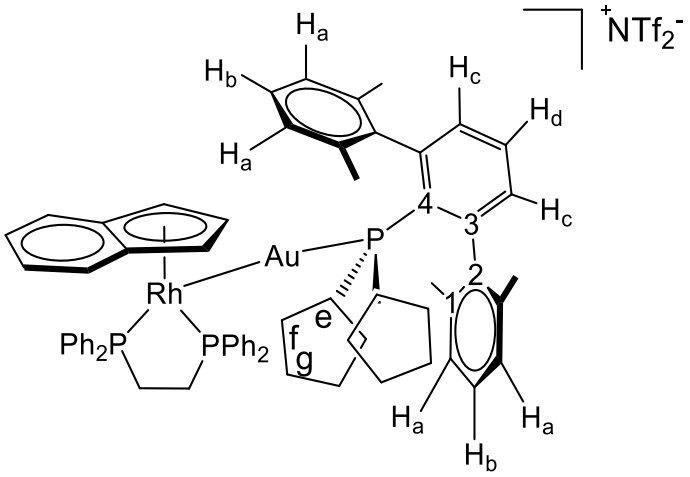
Compound 7d^{Me}. A solid mixture of compound **6d** (61 mg, 0.085 mmol) and **2^{Me}** (70 mg, 0.085 mmol) was dissolved in toluene (5 mL) and stirred at room temperature for 5 minutes. Reaction monitoring revealed that formation of **7d^{Me}** was immediate and proceeded quantitatively by NMR spectroscopy. The solution was concentrated to half volume and precipitated with pentane. The yellow residue was then filtered and dried under vacuum (40 mg, 31 %). Anal. Calcd. for $C_{71}H_{65}AuF_6NO_4P_3RhS_2$: C, 54.4; H, 4.2; N, 0.9; S, 4.1. Found: C, 54.4; H, 4.2; N, 1.0; S, 4.2.

^{1}H NMR (500 MHz, THF-d_8, 25 °C) δ: 7.74 (m, 1H, H_d), 7.44 to 7.41 (m, 8H, overlapped *p*-Ph_3 and H_b), 7.23 to 7.20 (m , 18H, overlapped *m*-Ph_3, H_c and H_a), 7.06 to 7.01 (m, 3H, overlapping Ind), 6.90 (m, 12H, *o*-Ph_3), 5.83 (m, 2H, Ind), 5.00 (m, 2H, Ind), 2.22 (s, 12 H, Me_{Xyl}), 0.77 (d, 6H, $^{2}J_{HP}$ = 10.0 Hz, P*Me*$_2$Ar^{Xyl2}). ^{13}C{^{1}H} NMR (125 MHz, THF-d_8, 25 °C) δ: 145.3 (d, $^{2}J_{CP}$ = 9 Hz, C_3), 141.3 (d, $^{3}J_{CP}$ = 4 Hz, C_2), 136.4 (C_1), 135.8 (d, $^{1}J_{CP}$ = 47 Hz, C_4), 133.6 (t, $^{2}J_{CP}$ = 5 Hz, C_oPh$_3$), 131.8 (CH_d), 131.3 (d, $^{3}J_{CP}$ = 8 Hz, CH_c), 130.2 (C_pPh$_3$), 128.4 (CH_b), 128.1 (t, $^{3}J_{CP}$ = 5 Hz, C_mPh$_3$; overlapped with CH_a), 127.9 (Ind), 120.2 (Ind), 119.9 (q, $^{1}J_{CF}$ = 330 Hz, CF_3), 94.9 (br, Ind), 79.6 (br, Ind), 21.5 (Me_{Xyl}), 17.4 (d, $^{1}J_{CP}$ = 35 Hz, P*Me*$_2$Ar^{Xyl2}). ^{19}F{^{1}H} NMR (471 MHz, THF-d_8, 25 °C) δ: −78.3. ^{31}P{^{1}H} NMR (202 MHz, THF-d_8, 25 °C) δ: 40.1 (d, $^{1}J_{PRh}$ = 168 Hz), 1.6 (d, $^{1}J_{PRh}$ = 15 Hz).



Compound 6c (C_9H_7)Li (360 mg, 2.8 mmol) is added to a solution of [RhCl(COE)$_2$]$_2$ (1 g, 1.4 mmol) in toluene (10 mL), stirred at room temperature overnight and filtered through celite. Solvent was removed under vacuum and dppe (273 mg, 0.69 mmol) was slowly added to a solution of the resulting product (300 mg, 0.69 mmol) in THF (5 mL) at −80 °C, stirring the solution upon warming to room temperature and heating at 60 °C overnight. Solvent was removed under vacuum yielding a yellow solid (320 mg, 77 %). Anal. Calcd. for $C_{35}H_{31}P_2Rh$: C, 68.2; H, 5.1. Found: C, 68.2; H, 5.4.

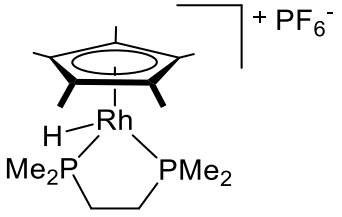
^{1}H NMR (500 MHz, C_6D_6, 25 °C) δ: 7.45 (m, 8H, *o*-Ph_2), 7.11 (m, 8H, *m*-Ph_2), 7.07 (m, 4H, *p*-Ph_2), 7.05 to 6.92 (m, 4H, Ind), 6.14 (m, 1H, Ind), 5.52 (m, 2H, Ind), 1.63 (d, 4H, $^{2}J_{HP}$ = 18 Hz, CH_2).^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 25 °C) δ: 139.9 (m, $C_{ipso}Ph_2$), 132.6 (m, C_oPh_2), 128.8 (C_pPh_2), 127.7 (overlapped with C_6D_6, C_mPh_2) 120.5 (Ind), 117.2 (Ind), 116.5 (Ind), 95.1 (m, Ind), 73.1 (m, Ind), 28.9 (vt, $^{1}J_{CP}$ = 25 Hz, CH_2). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6, 25 °C) δ: 75.9 (d, $^{1}J_{PRh}$ = 223 Hz).



Compound 7c^{Cyp}. A solid mixture of compound **6c** (10 mg, 0.0816 mmol) and **2^{Cyp}** (8 mg, 0.0816 mmol) was dissolved in toluene (5 mL) and stirred at room temperature for 5 minutes. Reaction monitoring revealed that formation of **7c^{Cyp}** was immediate and proceeded quantitatively by NMR spectroscopy. The solution was concentrated to half volume and precipitated with pentane. The brown residue was then filtered and dried under vacuum (57.5 mg, 57 %). Anal. Calcd. for $C_{69}H_{70}AuF_6NO_4P_3RhS_2$: C, 53.6; H, 4.6; N, 0.9; S, 4.4. Found: C, 53.6; H, 4.3; N, 1.1; S, 4.5.

^{1}H NMR (400 MHz, THF-d_8, 25 °C) δ:7.88 (br, 2H, Hb), 7.59 (br, 4H, Ha), 7,39 (m, 1H, Hd), 7.28 (m, 5H, overlapped *p*-PPh_3 and Ind), 7.24 (m, 6H, PPh_3), 7.15 (m, 10H, PPh_3), 7.07 (m,1H, Ind), 6.92 (m, 2H, H_c), 6.83 (m, 1H, Ind), 6.64 (m, 2H, Ind), 6.24 (m, 2H, Ind), 5.92 (br, 2H, Ind), 2.34 (s, 12H, Me_{Xyl}), 2.23 (m, 2H, He), 2.12 (m, 4H, CH_{2dppe}), 1.54 (m, 8H, Hf), 1.39 (m, 8H, Hg). ^{13}C{^{1}H} NMR (100 MHz, THF-d_8, 25 °C) δ: 147.1 (C3) , 142.4 ($CPPh_3$), 137.4 (C2), 128.7 (overlapped PPh_3, Ind, CH_b, CH_a), 127.9 (overlapped PPh_3, CH_c, CH_d), 125.1 (overlapped PPh_3, Ind), 118.9 (Ind), 117.4 (Ind), 39.4 (Ce), 33.7 (Cf), 26.3 (Cg), 20.5 (overlapped CH_{2dppe} and Me_{Xyl}).^{31}P{^{1}H} NMR (162 MHz, THF-d_8, 25 °C) δ: 74.7 (d, , $^{1}J_{PRh}$ = 161 Hz), 47.0 (d, $^{3}J_{PP}$ = 18Hz).

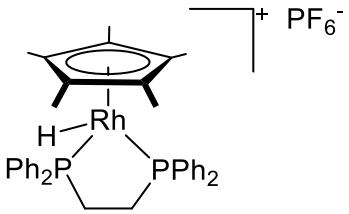
X−H (X = H, C, O, N) bond activation studies using compounds of Rh and Au.



Compound 5b. NH_4PF_6 (42 mg, 0.258 mmol) was added to a solution of **1b** (100 mg, 0.258 mmol) in THF (10 mL) and stirred for 1 hour. Concentration to half volume and precipitation

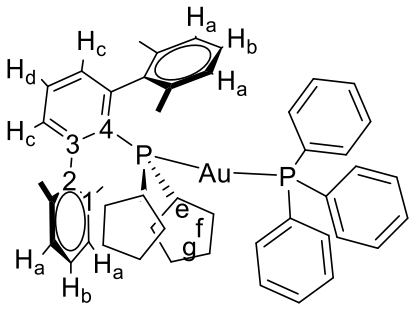
with pentane (20 mL) yielded a solid brown residue (77 mg, 77%). Anal. Calcd. for $C_{16}H_{32}P_2Rh$: C, 49.4; H, 8.3. Found: C, 49.6; H, 8.4.

^{1}H NMR (400 MHz, THF-*d*$_8$, 25 °C) δ: 2.02 (s, 15H, C_5Me_5), 1.92 to 1.75 (br m, 4H, CH_2), 1.62 (dd, 12H, $^3J_{HRh}$ = 15.0, $^2J_{HP}$ = 11.5 Hz, PMe_2), −13.60 (dt, 1H, $^2J_{HP}$ = 31.9, $^1J_{HRh}$ = 27.8 Hz, RhH). ^{13}C{^{1}H} NMR (100 MHz, THF-*d*$_8$, 25 °C) δ: 94.9 (C_5Me_5), 28.8 (m, CH_2), 18.8 and 13.6 (m, PMe_2), 9.72 (C_5Me_5). ^{31}P{^{1}H} NMR (162 MHz, THF-*d*$_8$, 25 °C) δ: 45.9 (d, $^1J_{PRh}$ = 134 Hz, dmpe), -144.2 (q, $^1J_{PF}$ = 710 Hz PF_6)



Compound 5c. NH_4PF_6 (26 mg, 0.157 mmol) was added to a solution of **1c** (100 mg, 0.157 mmol) in THF (10 mL) and stirred for 1 hour. Concentration to half volume and precipitation with pentane (20 mL) yielded a solid brown residue (73 mg, 73%). Anal. Calcd. for $C_{36}H_{40}P_2Rh$: C, 67.8; H, 6.3. Found: C, 67.5; H, 6.7.

^{1}H NMR (400 MHz, THF-d$_8$, 25 °C) δ: 7.74, 7.65, 7.61, 7.45 (m, 20H, overlapped *m*-Ph_2, *o*-Ph_2, *p*-Ph_2), 2.56 (d, 4H, $^2J_{HP}$ = 18.3 Hz, CH_2), 1.60 (s, 15H, C_5Me_5), −12.26 (m, RhH). ^{13}C{^{1}H} NMR (100 MHz, THF-d$_8$, 25 °C) δ: 132.9, 131.4 and 128.9 (C_oPh_2/C_mPh_2/C_pPh_2), 130.0 (d, $^1J_{CP}$ = 43 Hz, $C_{ipso}Ph_2$), 132.9 (vt, $^3J_{CP}$ = 6 Hz, C_oPh_2), 128.3 (C_pPh_2), 95.0 (C_5Me_5), 31.9 (vtd, $^1J_{CP}$ = 27, $^2J_{CRh}$ = 2 Hz, CH_2), 10.7 (C_5Me_5). ^{31}P{^{1}H} NMR (162 MHz, THF-d$_8$, 25 °C) δ: 73.5 (d, $^1J_{PRh}$ = 139 Hz, dppe), -144.2 (q, $^1J_{PF}$ = 690 Hz PF_6)



Compound 8 . PPh_3 (5.62 mg, 0.0.21 mmol) was added to a solution of gold complex (20 mg, 0.021 mmol) in benzene, and stirred for 5 minutes. Solvent was removed under vacuum to yield the desired product (10 mg, 40%).

^{1}H NMR (400 MHz, THF-*d*$_8$, 25 °C) δ: 7.41 to 7.33 (br t, PPh_3), 7.27 to 7.16 (m, PPh_3), 7.06 to 6.9 (m, PPh_3), 6.83 (d, 4H, $^3J_{HH}$ = 7.6 Hz, H_a), 6.61 (br, 1H, H_d) 6.54 (br d, 2H, $^3J_{HH}$= 7.6 Hz, H_c), 2.44 to 2.31 (m, 2H, PCH), 1.98 (s, 12H, Me_{Xyl}), 1.89 to 1.52 (m, 16H, CH_2). ^{13}C{^{1}H} NMR (100 MHz, THF-*d*$_8$, 25 °C) δ: 134.1 (PPh_3), 132.3 (PPh_3), 131.9 (CH_c), 128.3 (CH_a), 37.9 (d, $^1J_{CP}$ = 29 Hz, PCH), 25.7 (d, $^2J_{CP}$ = 10 Hz, CH_2), 25.6 (d, $^3J_{CP}$ = 11 Hz, CH_2), 21.6 (Me_{Xyl}).^{31}P{^{1}H} NMR (162 MHz, THF-*d*$_8$, 25 °C) δ: 59.4 (d, $^1J_{PP}$ = 309 Hz), 44.3 (d, $^1J_{PP}$ = 309Hz).

2. NMR spectra

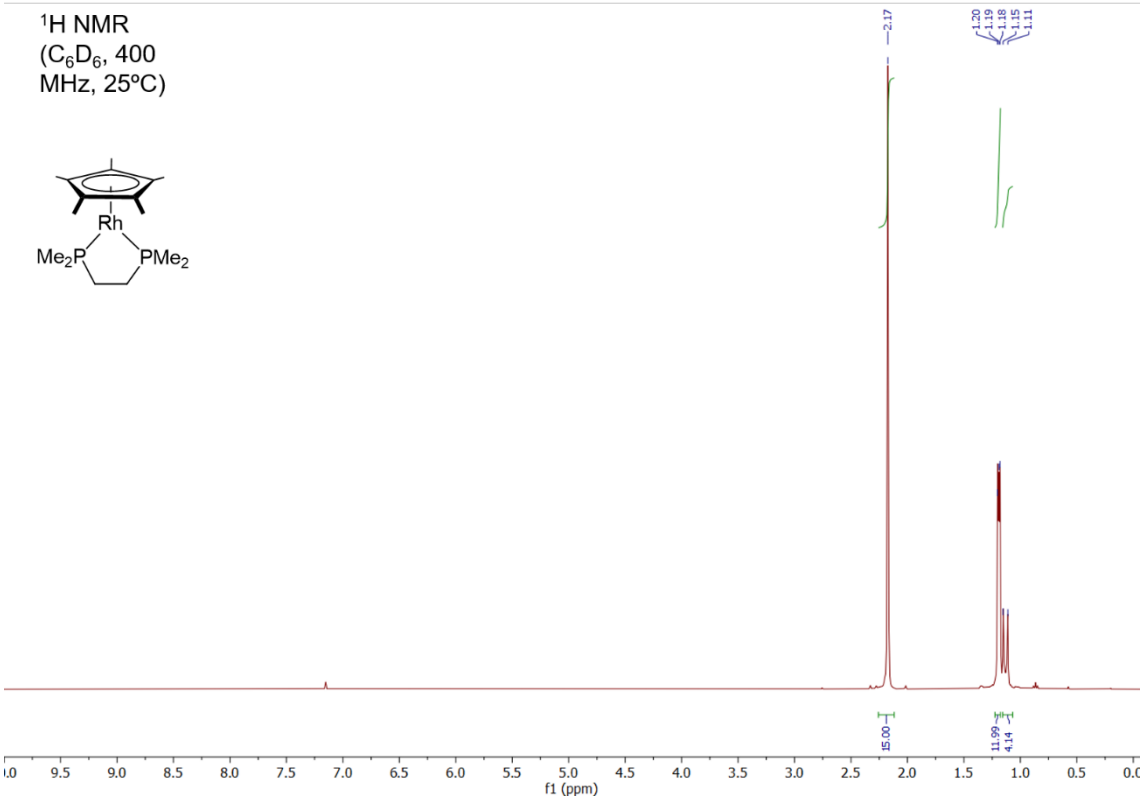


Figure S1. ^{1}H NMR of complex **1b**.

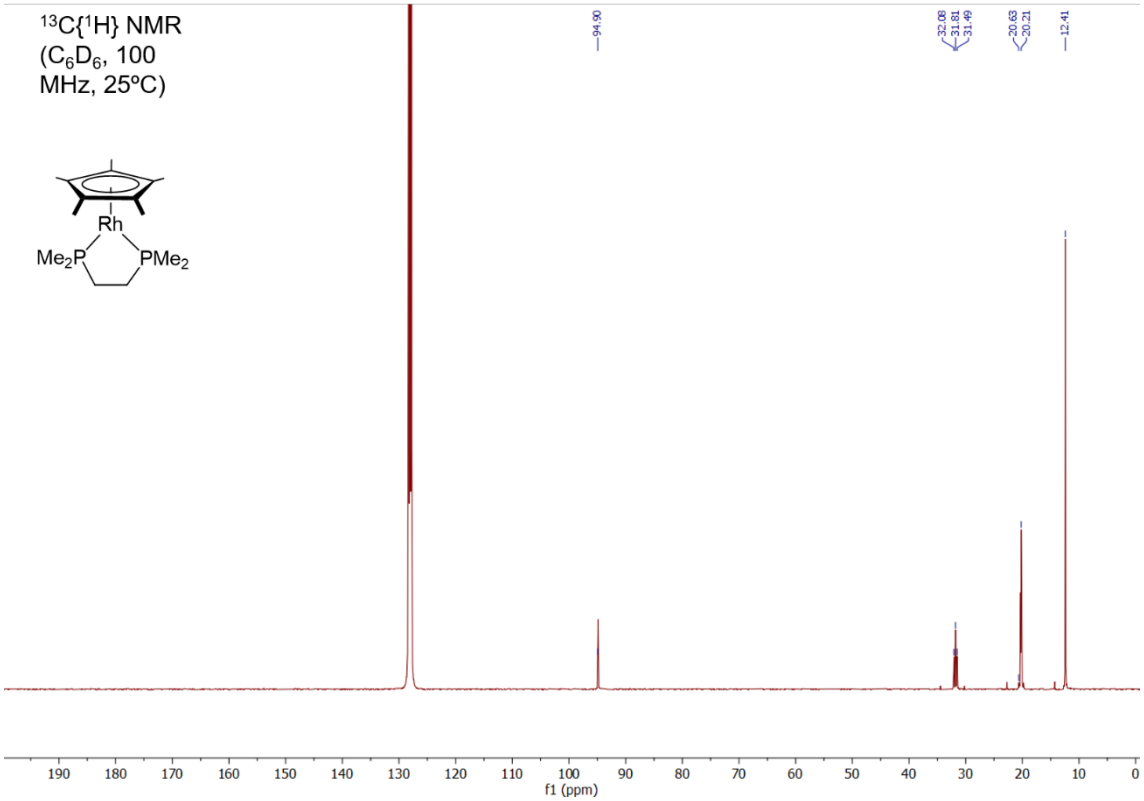


Figure S2. ^{13}C{^{1}H} NMR of complex **1b**.

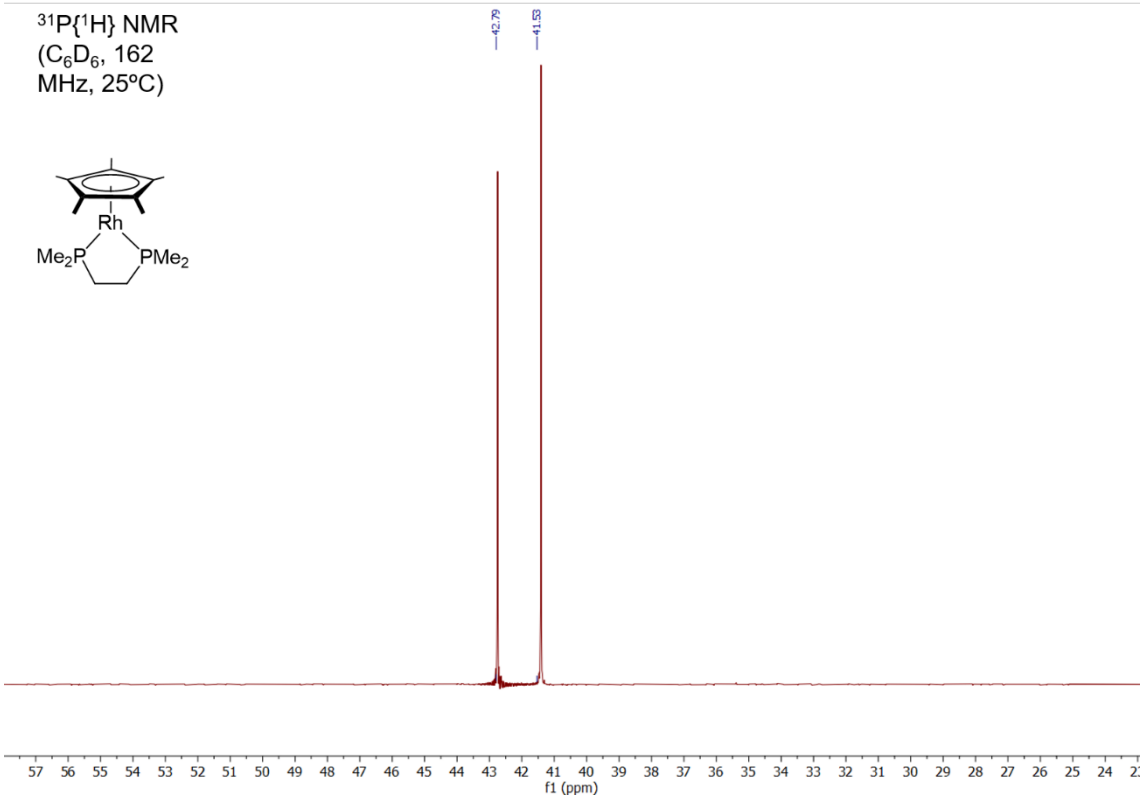


Figure S3. ^{31}P NMR of complex **1b**.

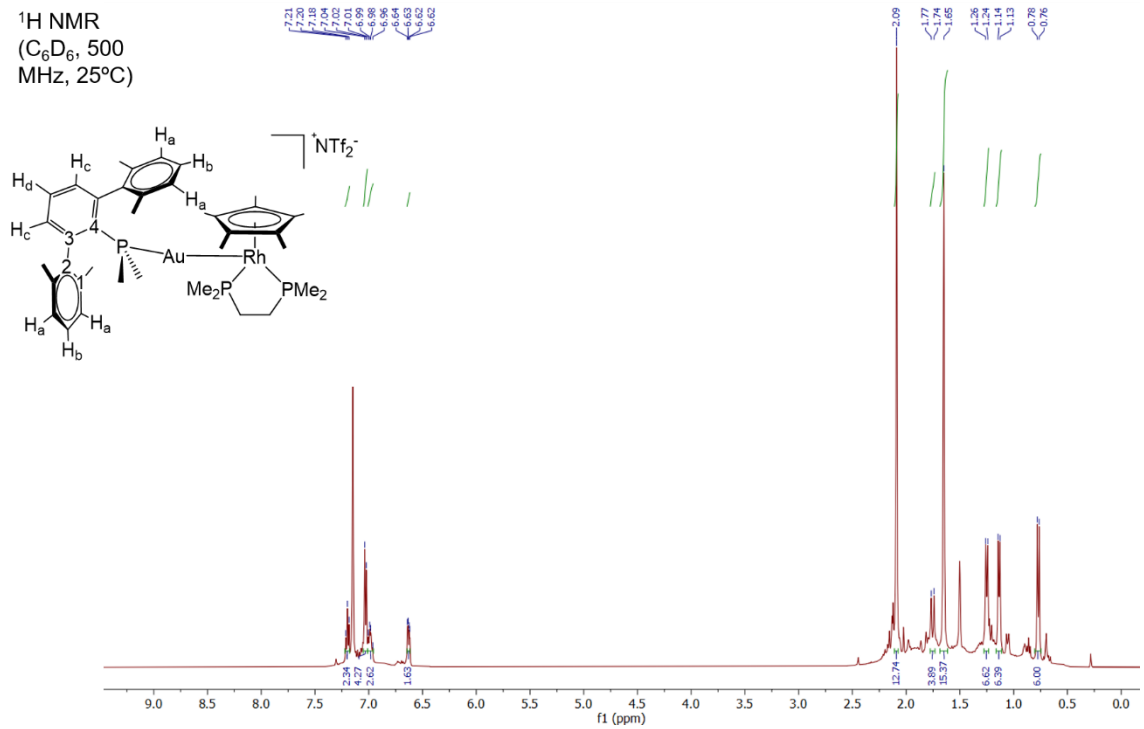


Figure S4. ^{1}H NMR of complex **3b^{Me}**.

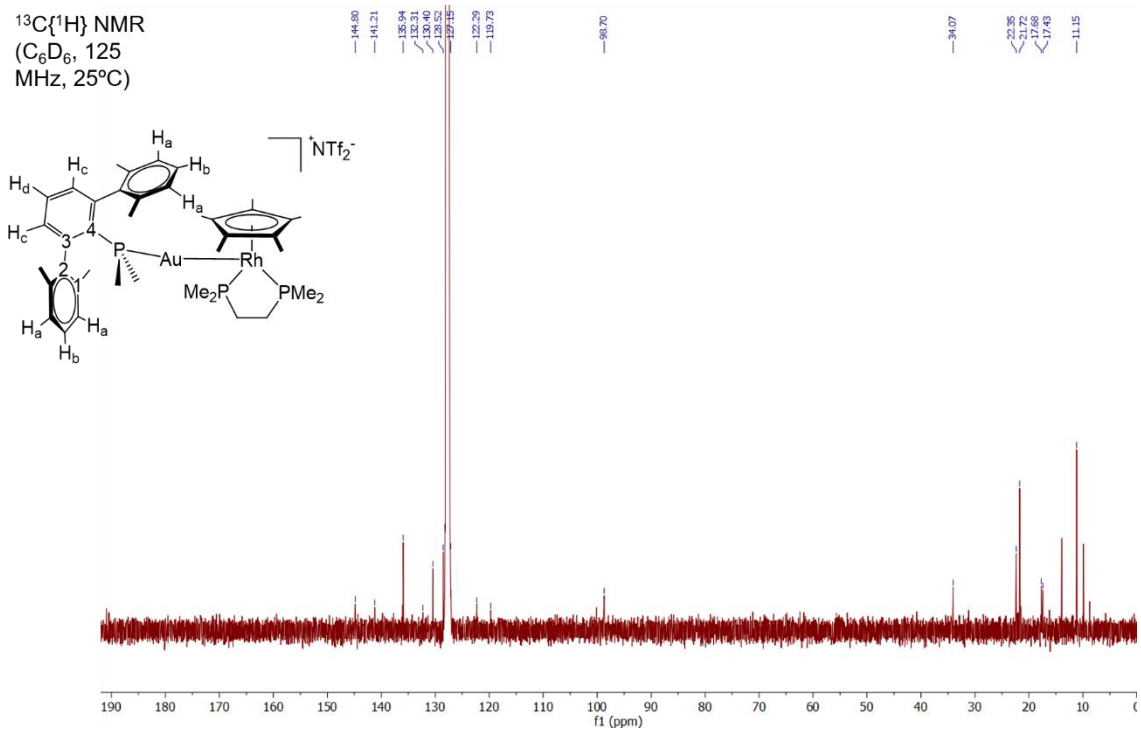


Figure S5. ^{13}C NMR of complex **3b^{Me}**.

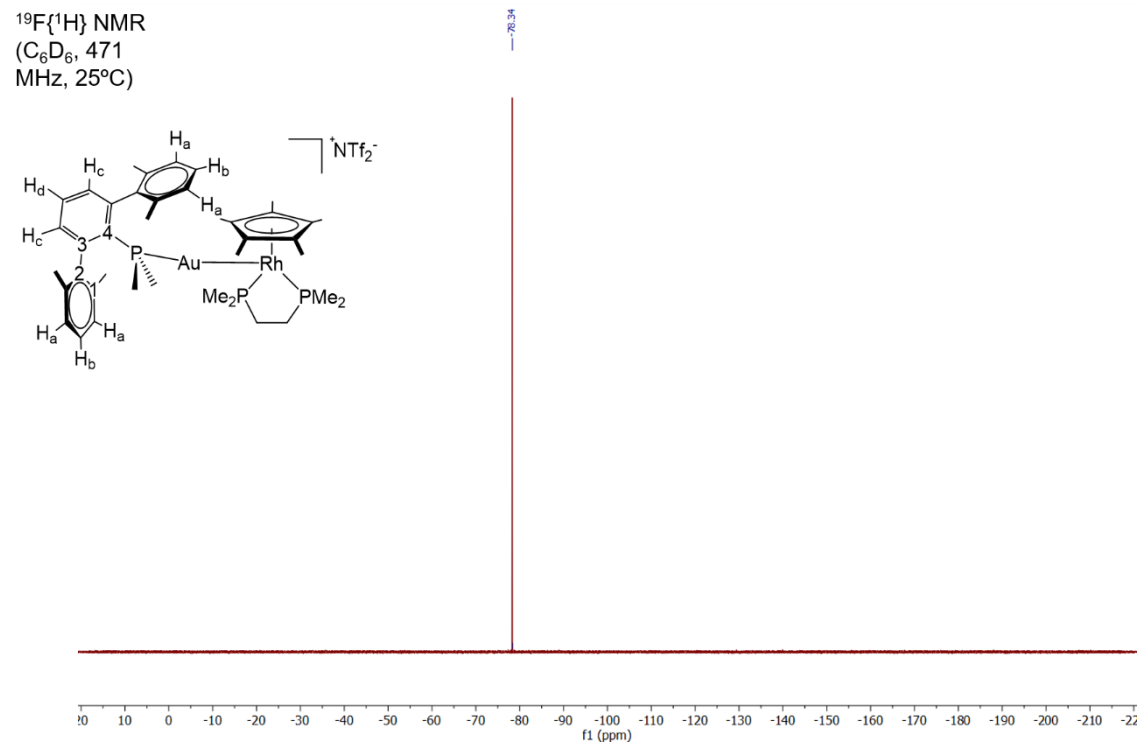


Figure S6. ^{19}F NMR of complex **3b^{Me}**.

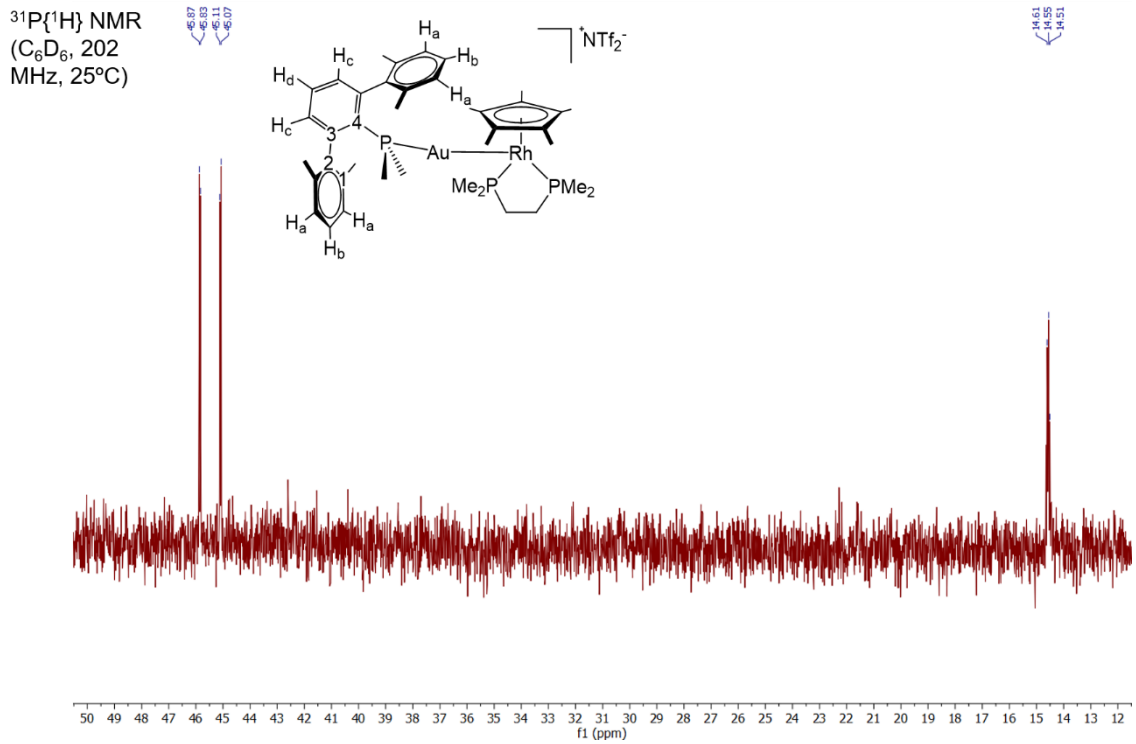


Figure S7. ^{31}P NMR of complex **3b^{Me}**.

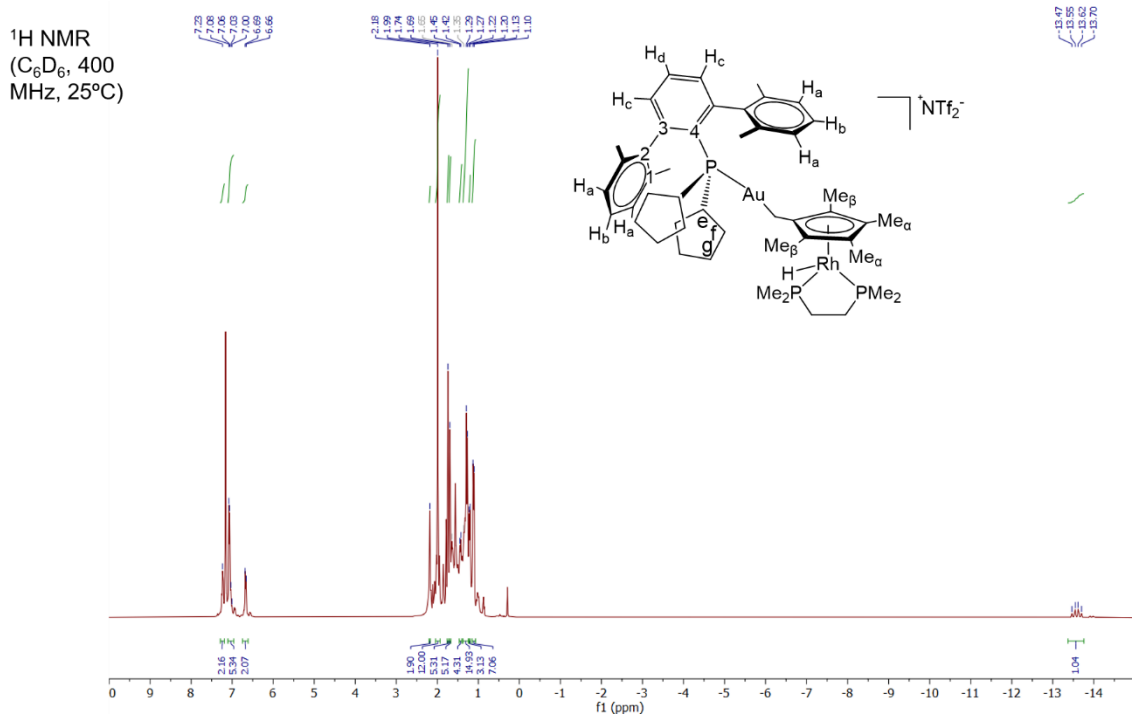


Figure S8. ^{1}H NMR of complex **4b^{Cyp}**.

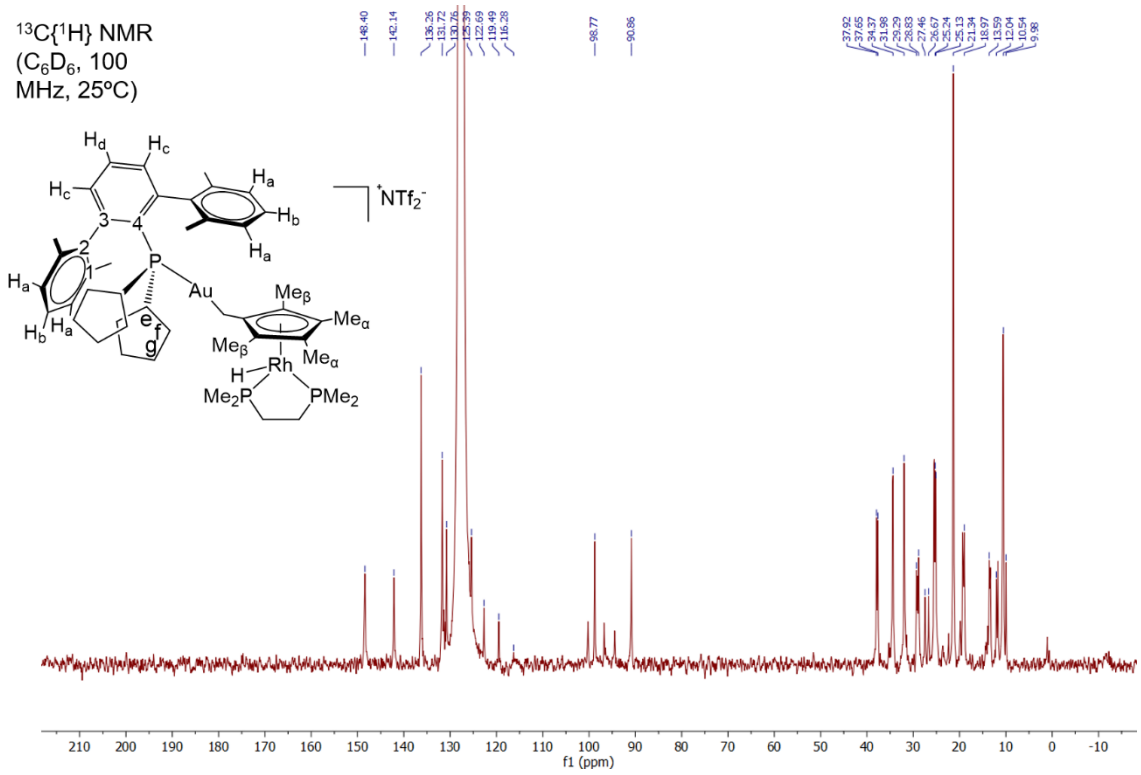


Figure S9. ^{13}C NMR of complex **4b^{Cyp}**.

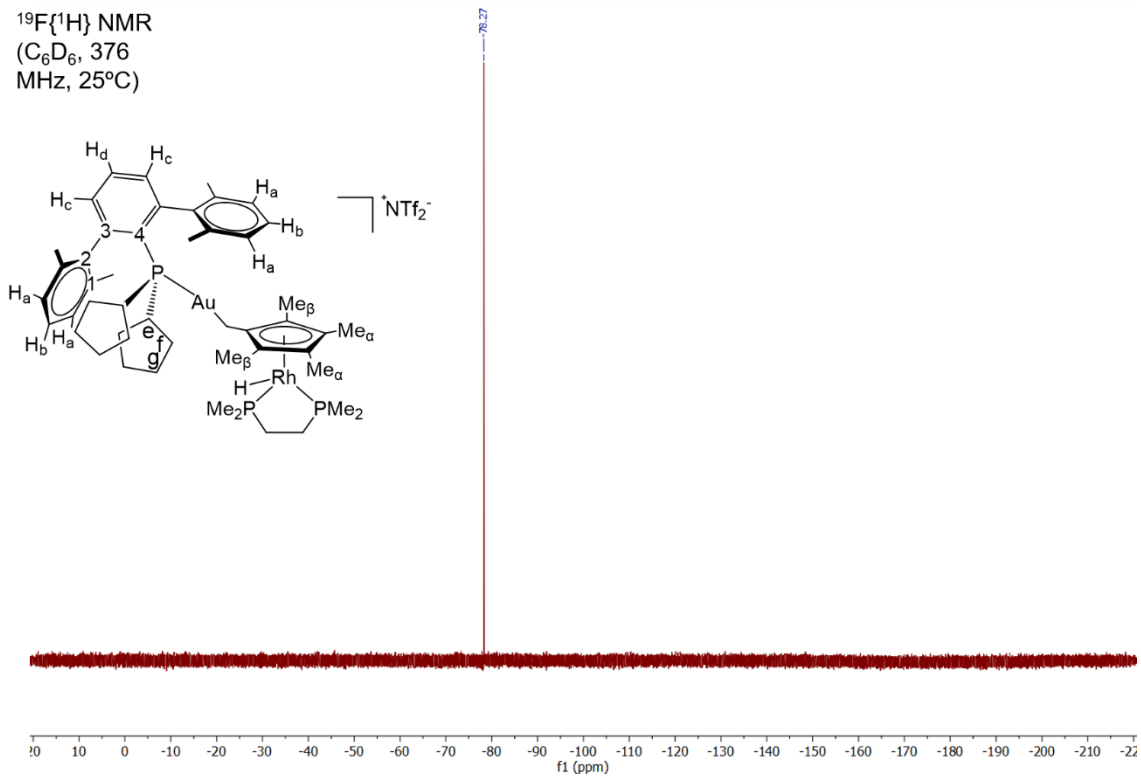


Figure S10. ^{19}F NMR of complex **4b^{Cyp}**.

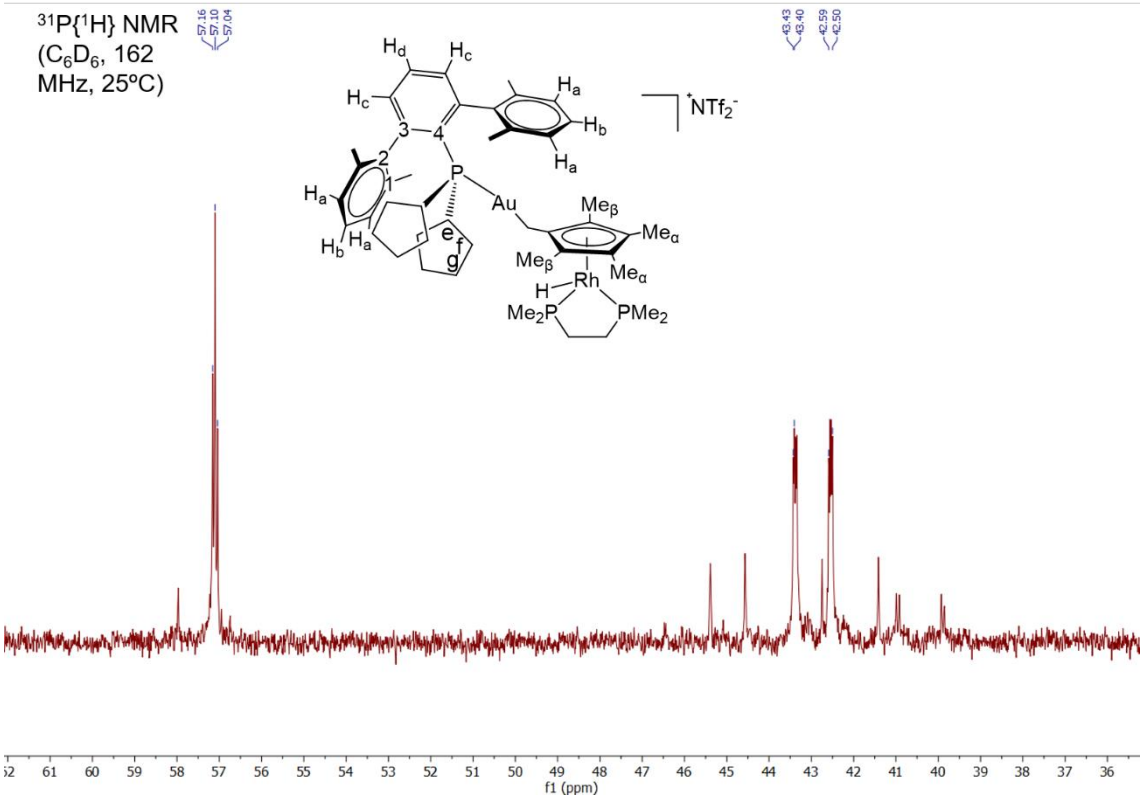


Figure S11. ^{31}P NMR of complex **4b^{Cyp}**.

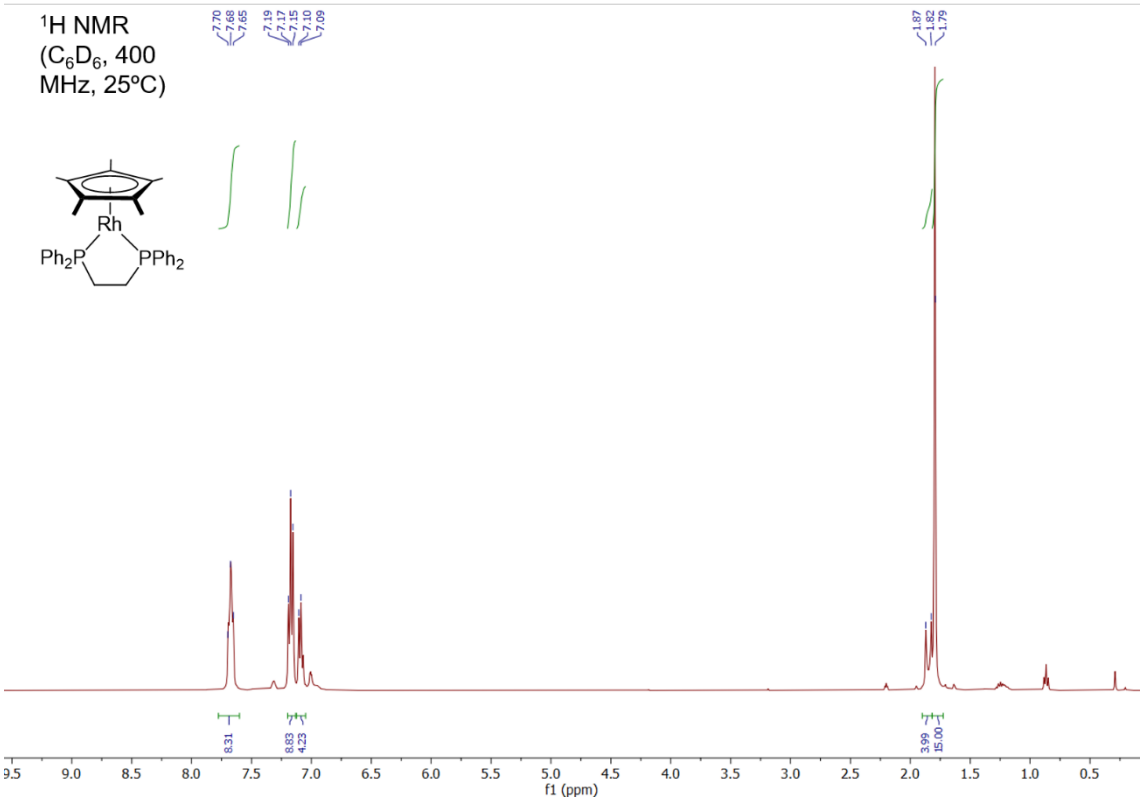


Figure S12. ^{1}H NMR of complex **1c**.

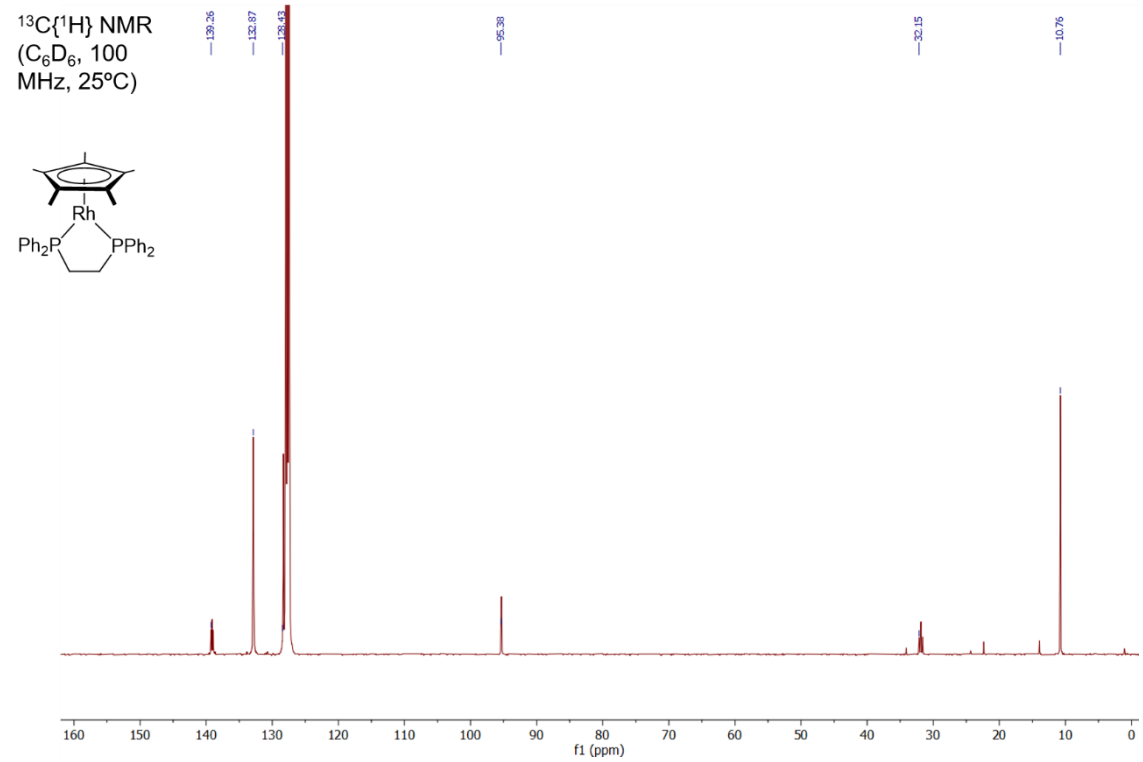


Figure S13. ^{13}C NMR of complex **1c**.

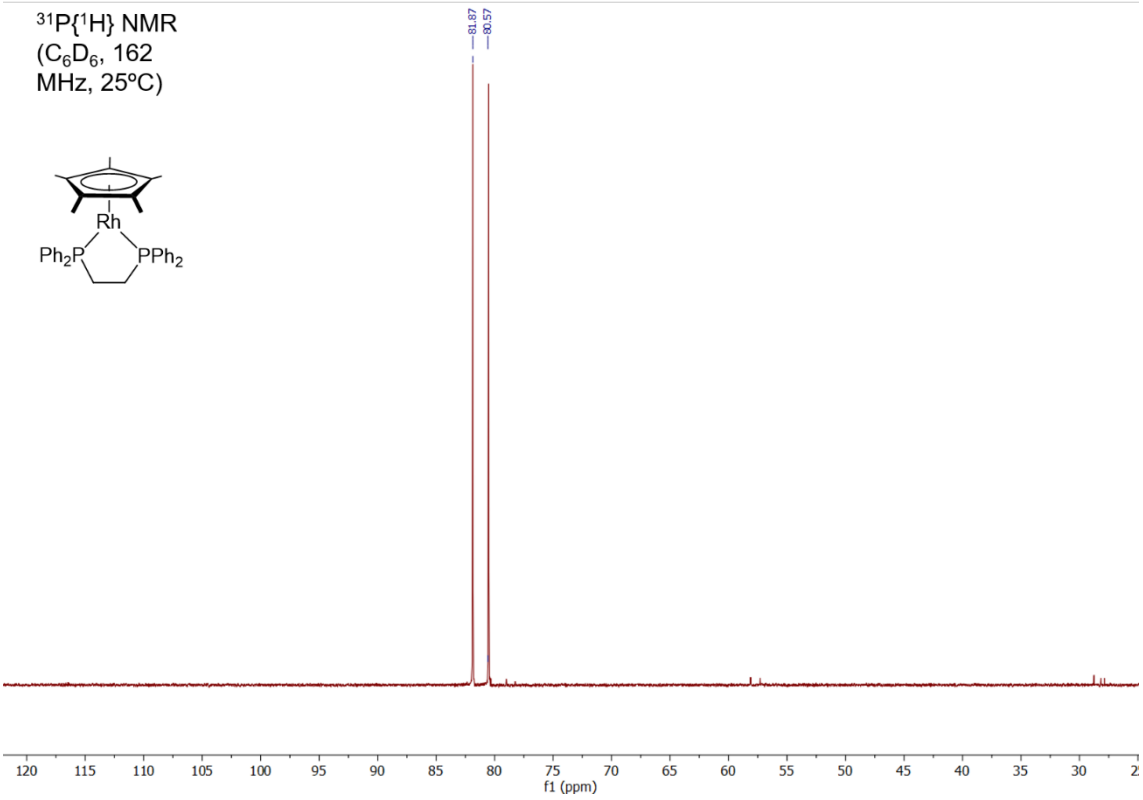


Figure S14. $^{31}P\{^1H\}$ NMR of complex **1c**.

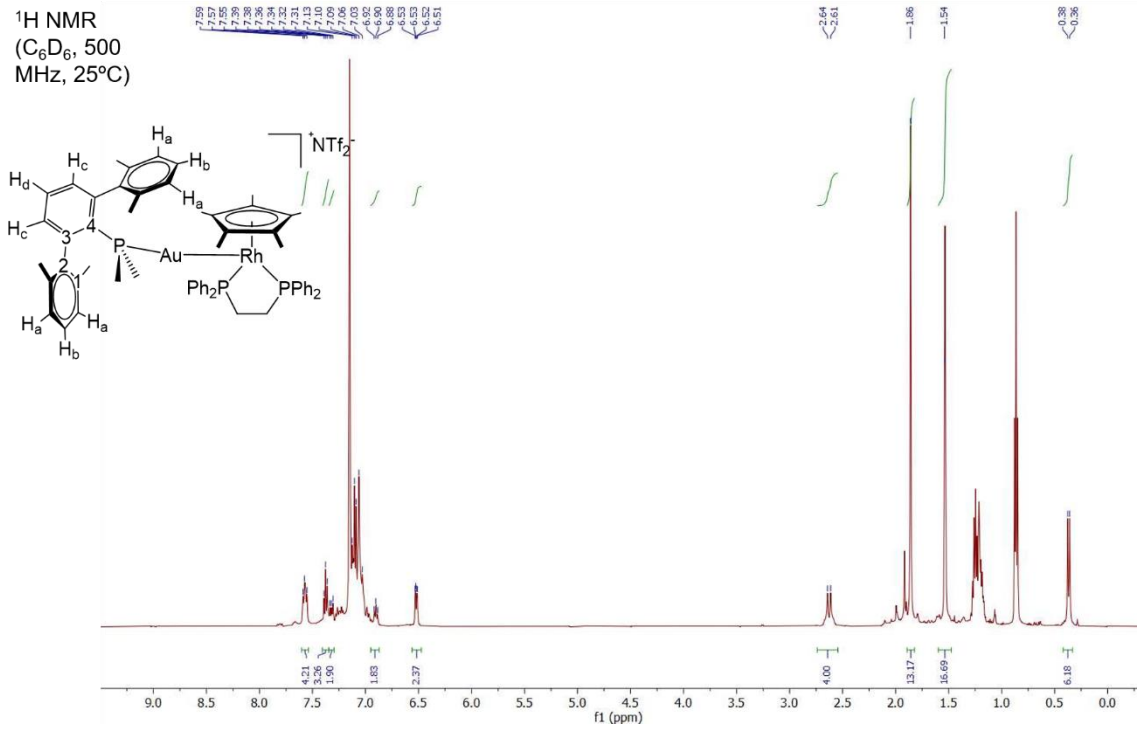


Figure S15. ^{1}H NMR of complex **3c^{Me}**.

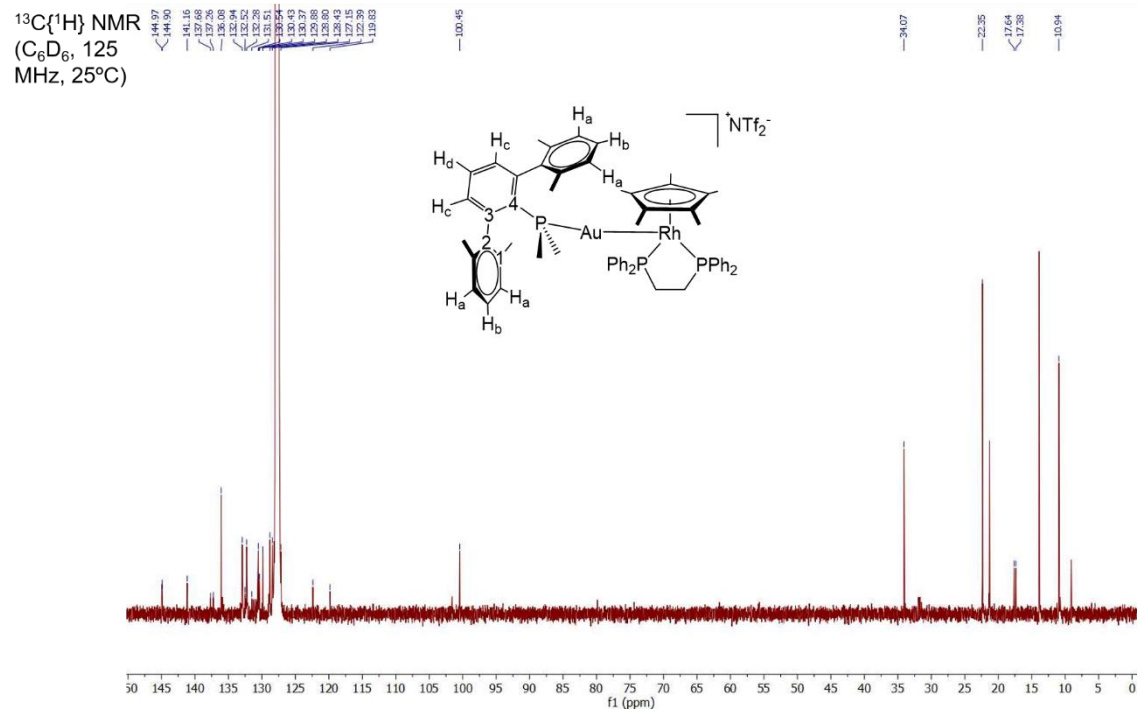


Figure S16. ^{13}C NMR of complex **3c^{Me}**.

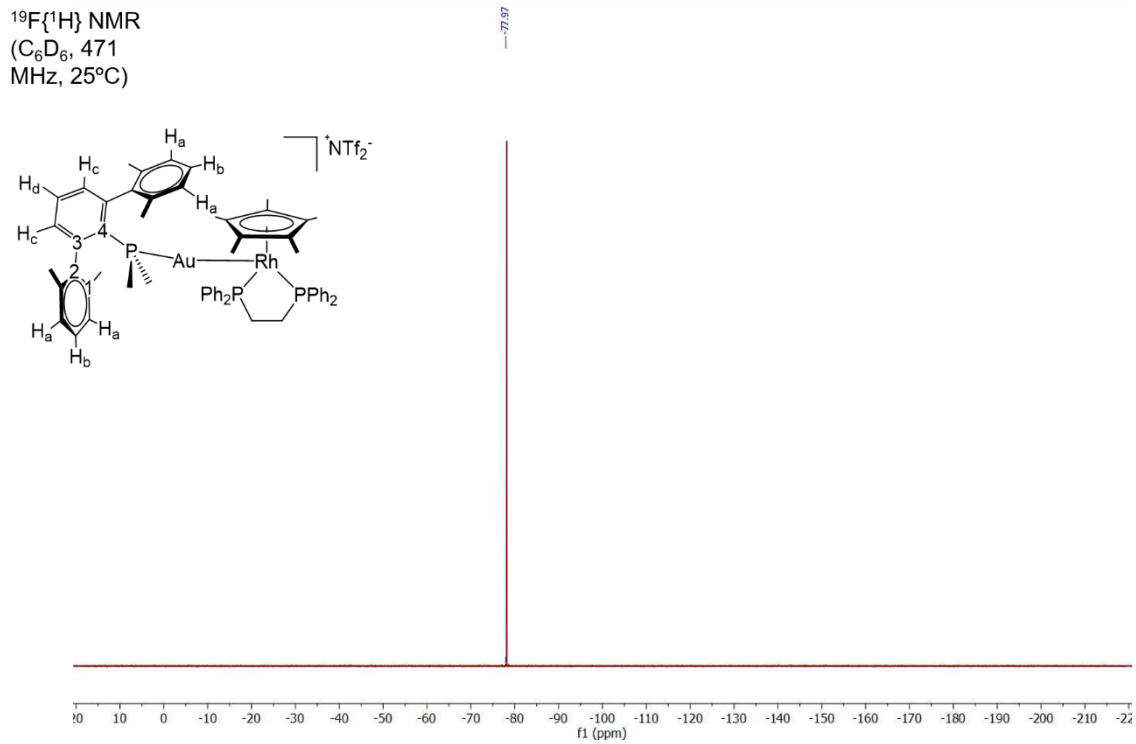


Figure S17. ^{19}F NMR of complex **3c^{Me}**.

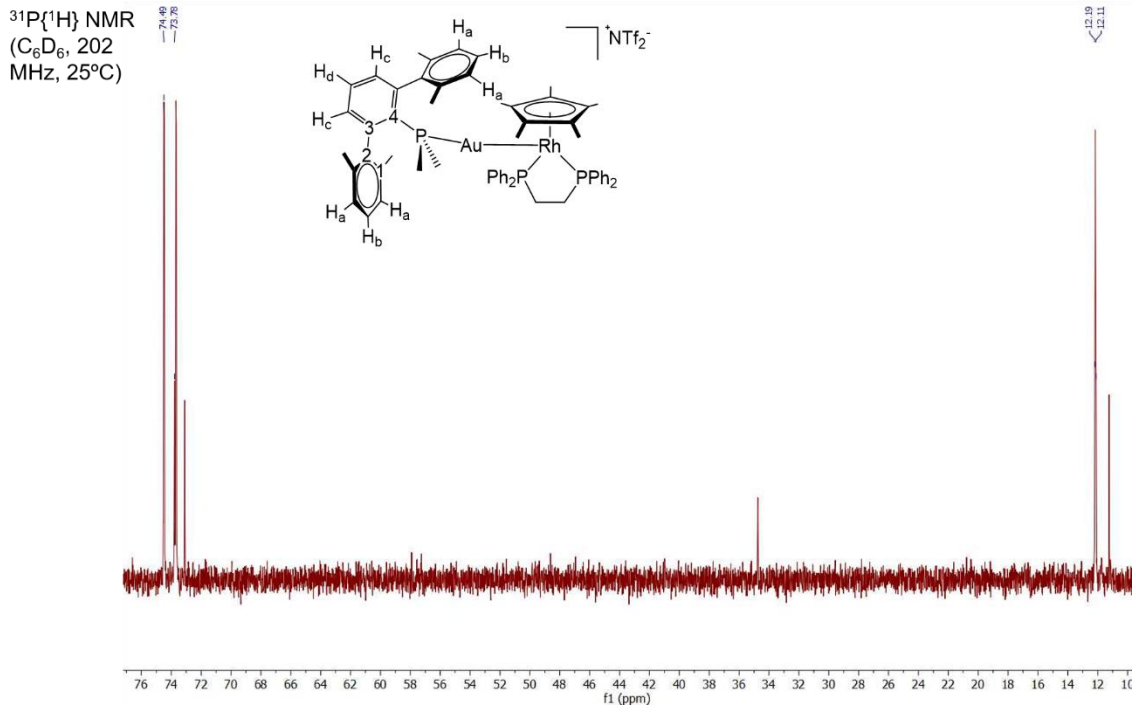


Figure S18. $^{31}P\{^{1}H\}$ NMR of complex **3c^{Me}**.

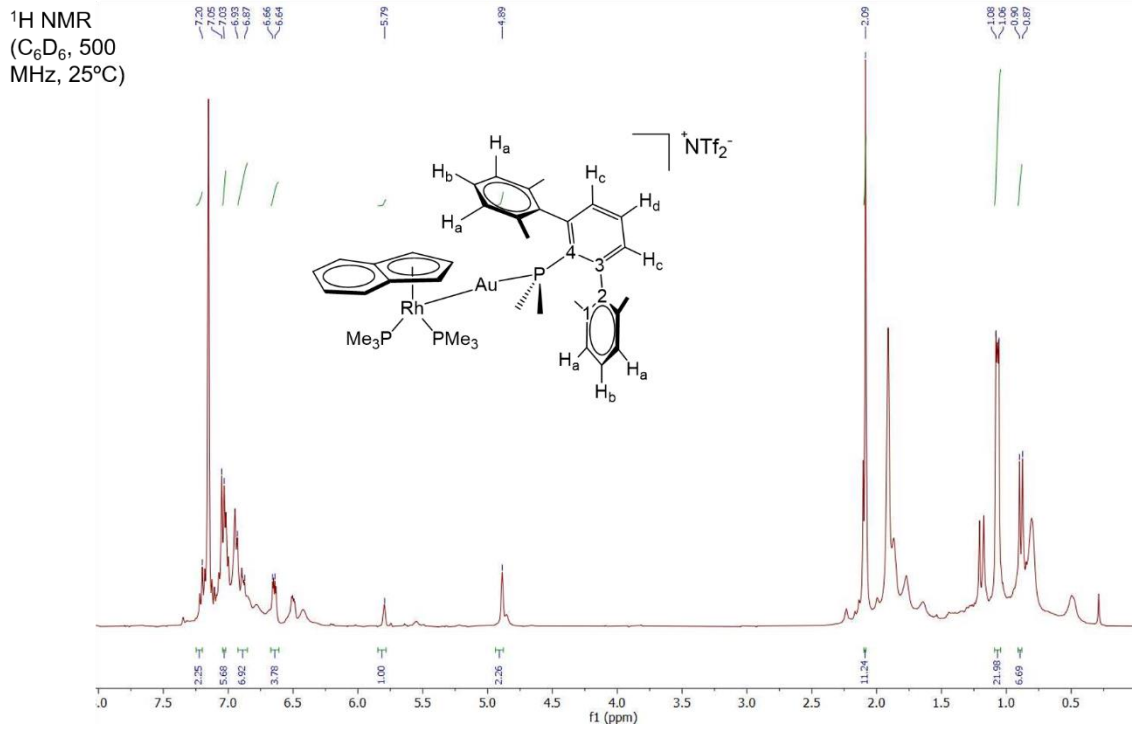


Figure S19. ^{1}H NMR of complex **7a^{Me}**.

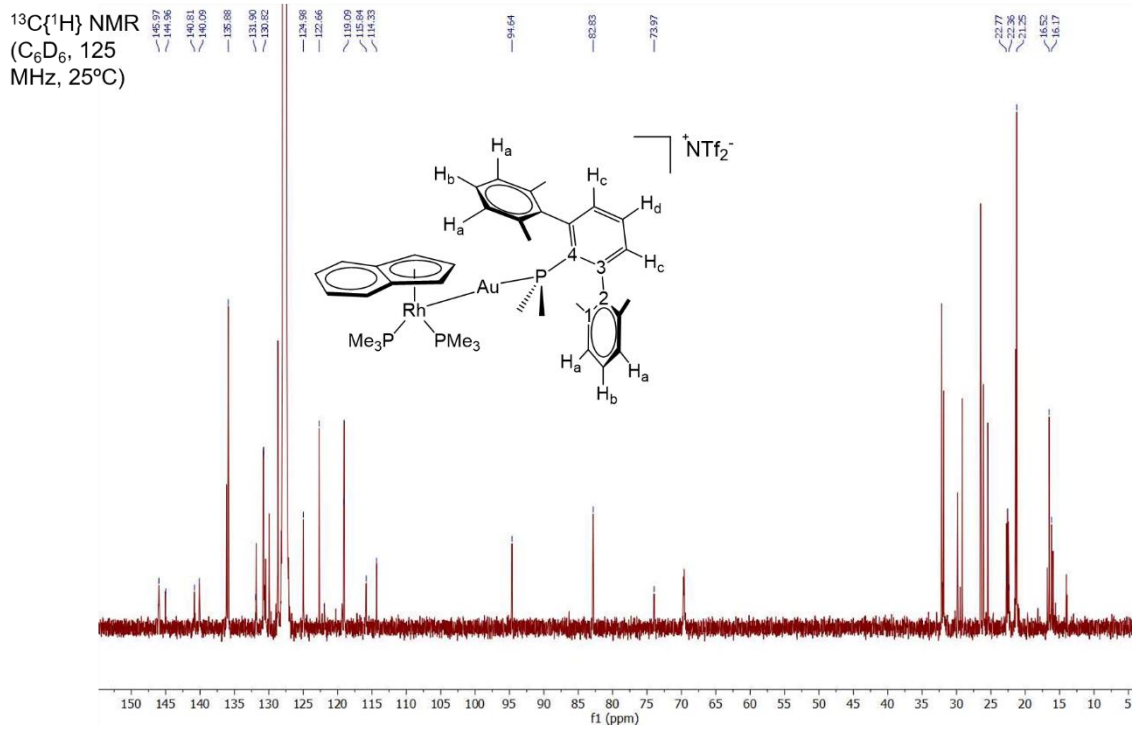


Figure S20. ^{13}C NMR of complex **7a^{Me}**.

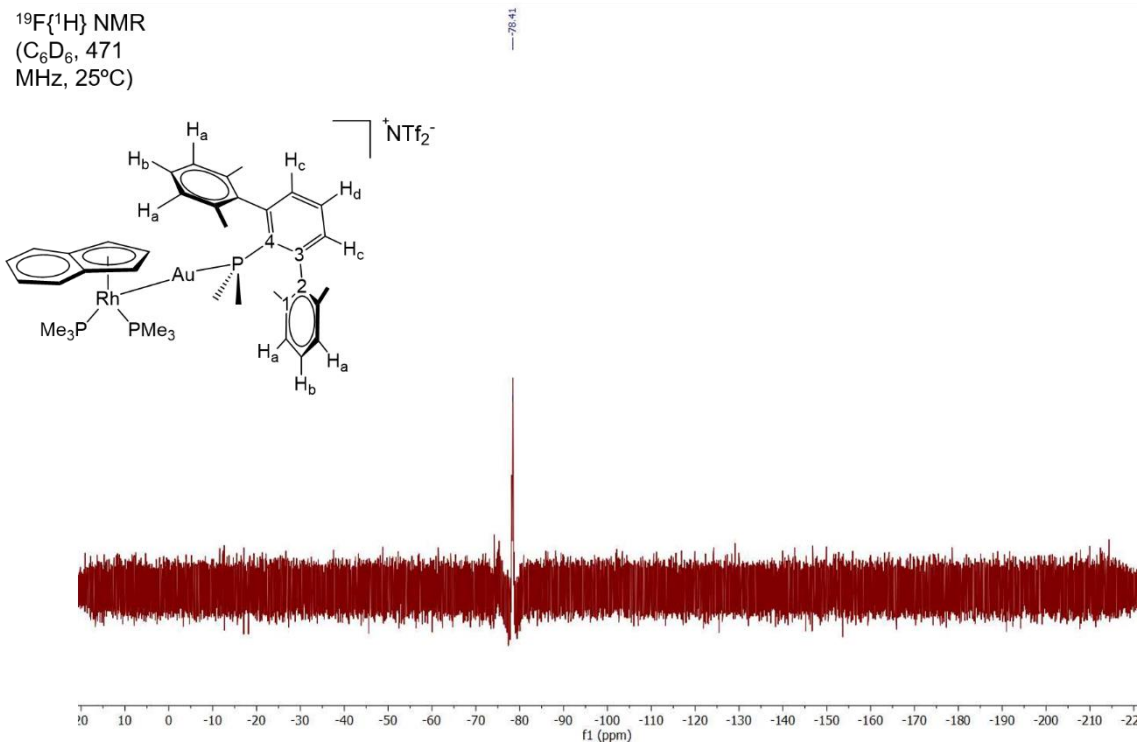


Figure S21. ^{19}F NMR of complex **7a^{Me}**.

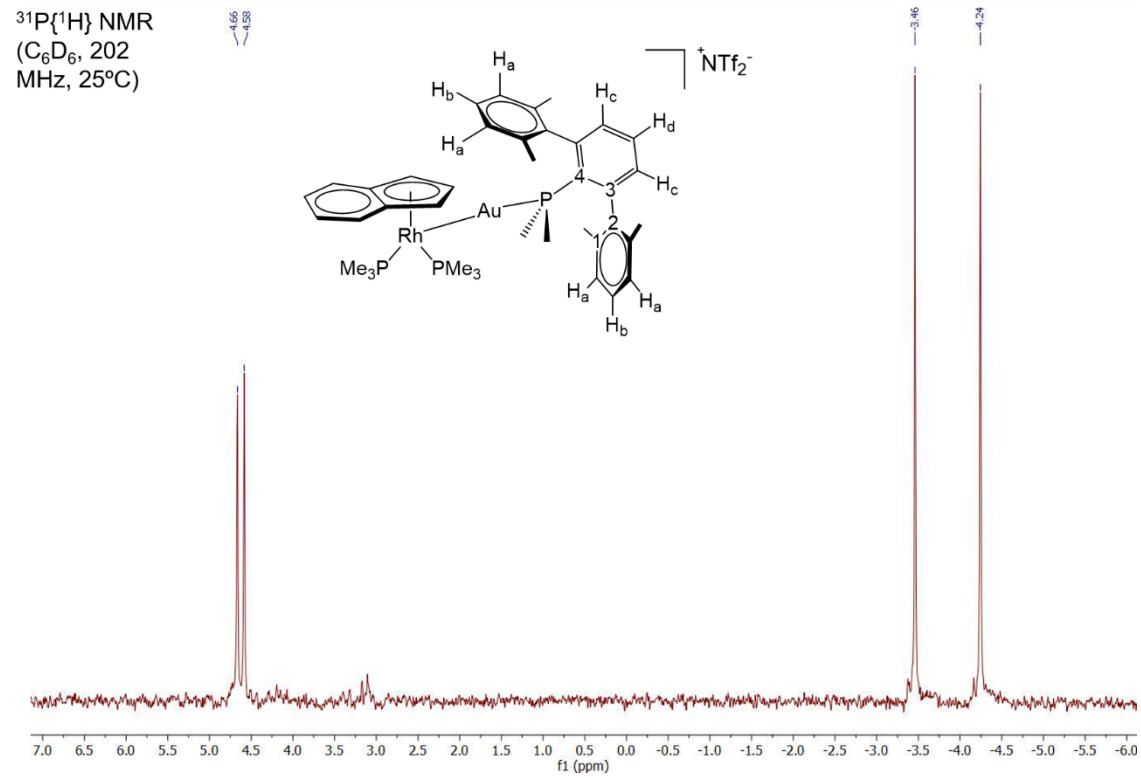


Figure S22. ^{31}P NMR of complex **7a^{Me}**.

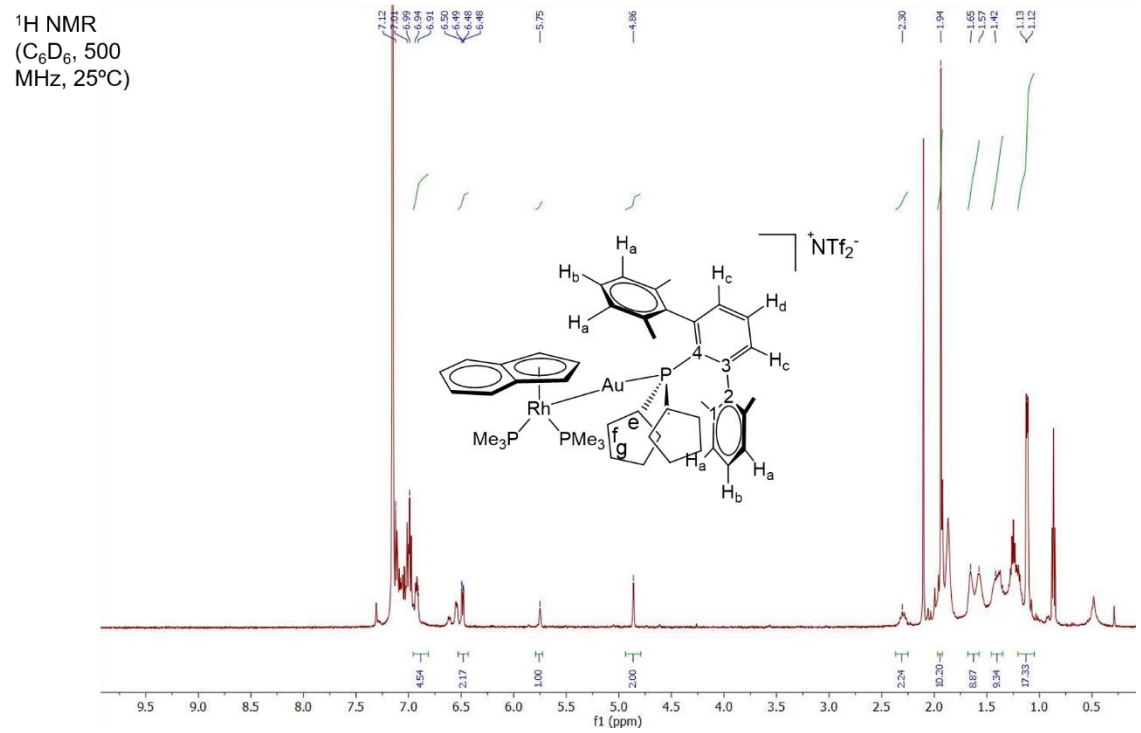


Figure S23. ^{1}H NMR of complex **7a^{Cyp}**.

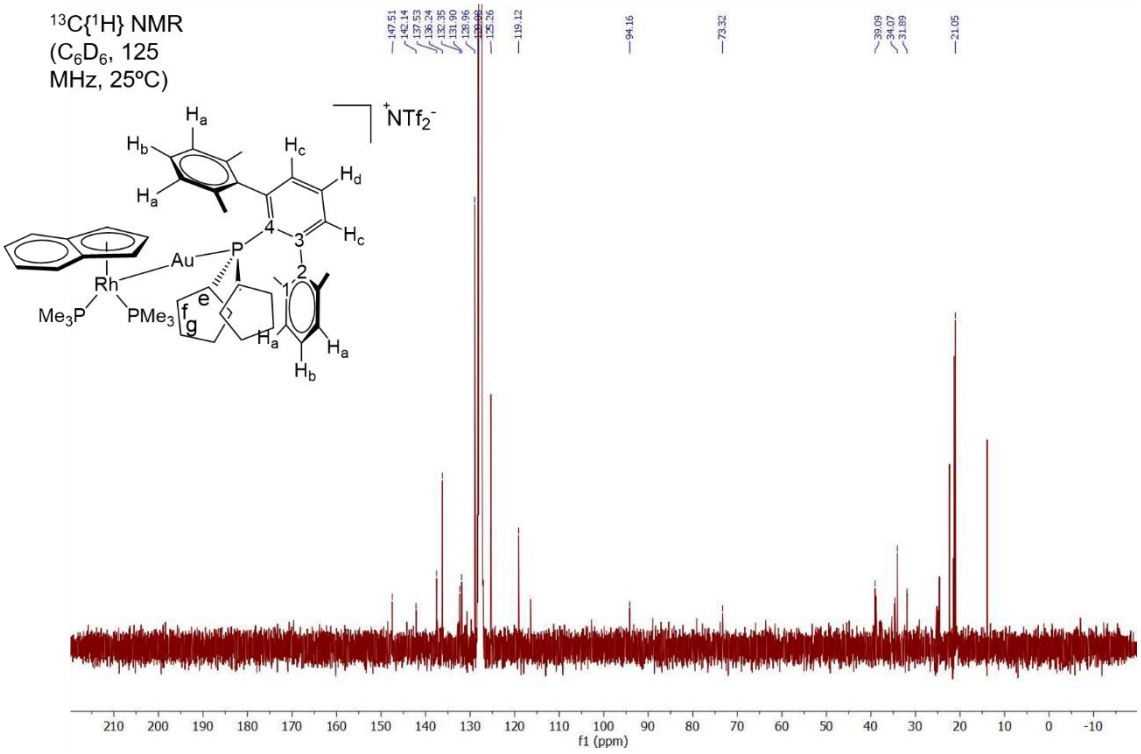


Figure S24. ^{13}C NMR of complex **7a^{Cyp}**.

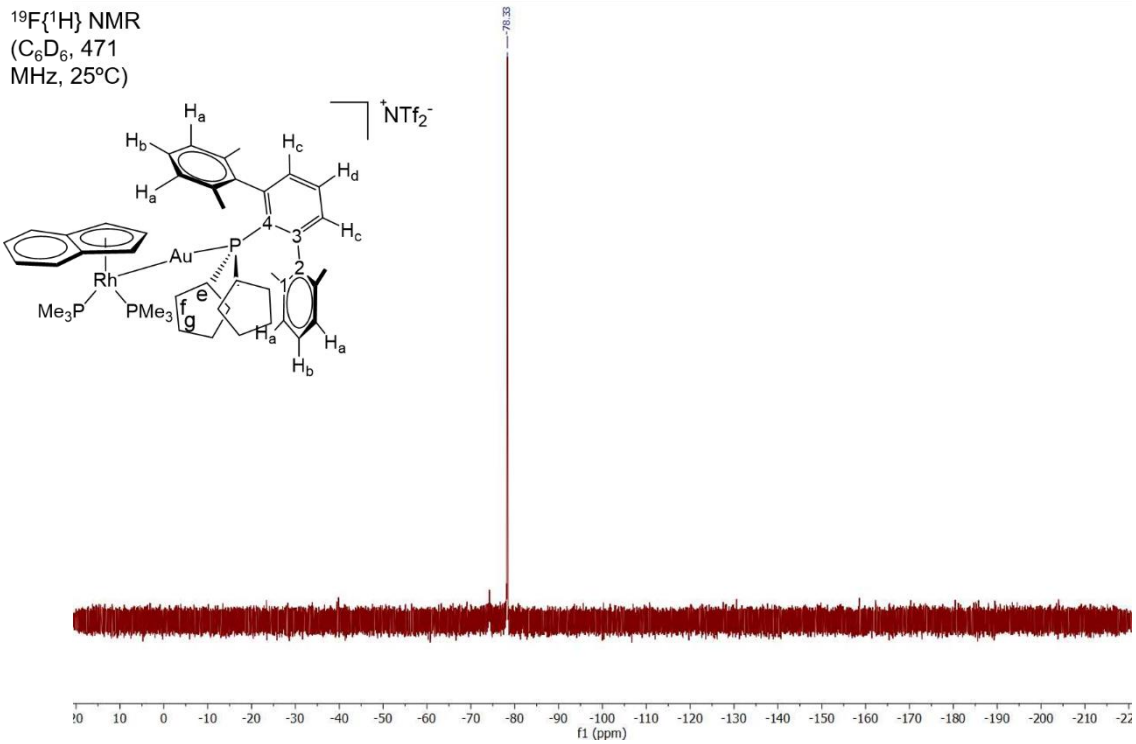


Figure S25. ^{19}F NMR of complex **7a^{Cyp}**.

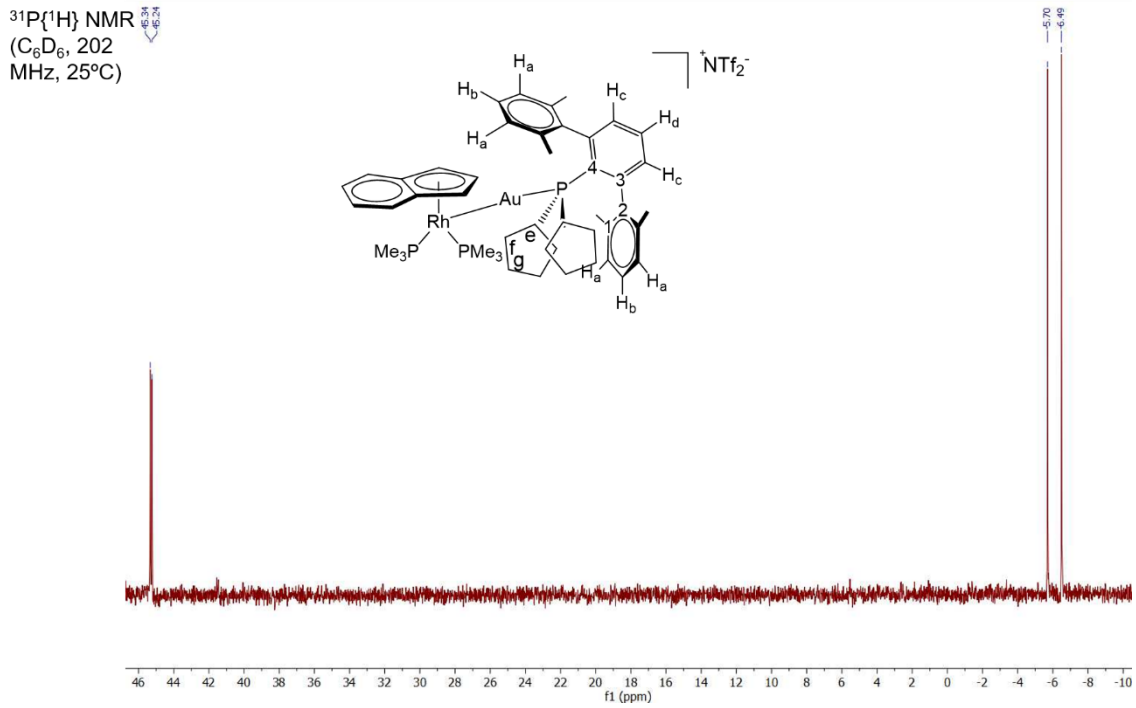


Figure S26. ^{31}P NMR of complex **7a^{Cyp}**.

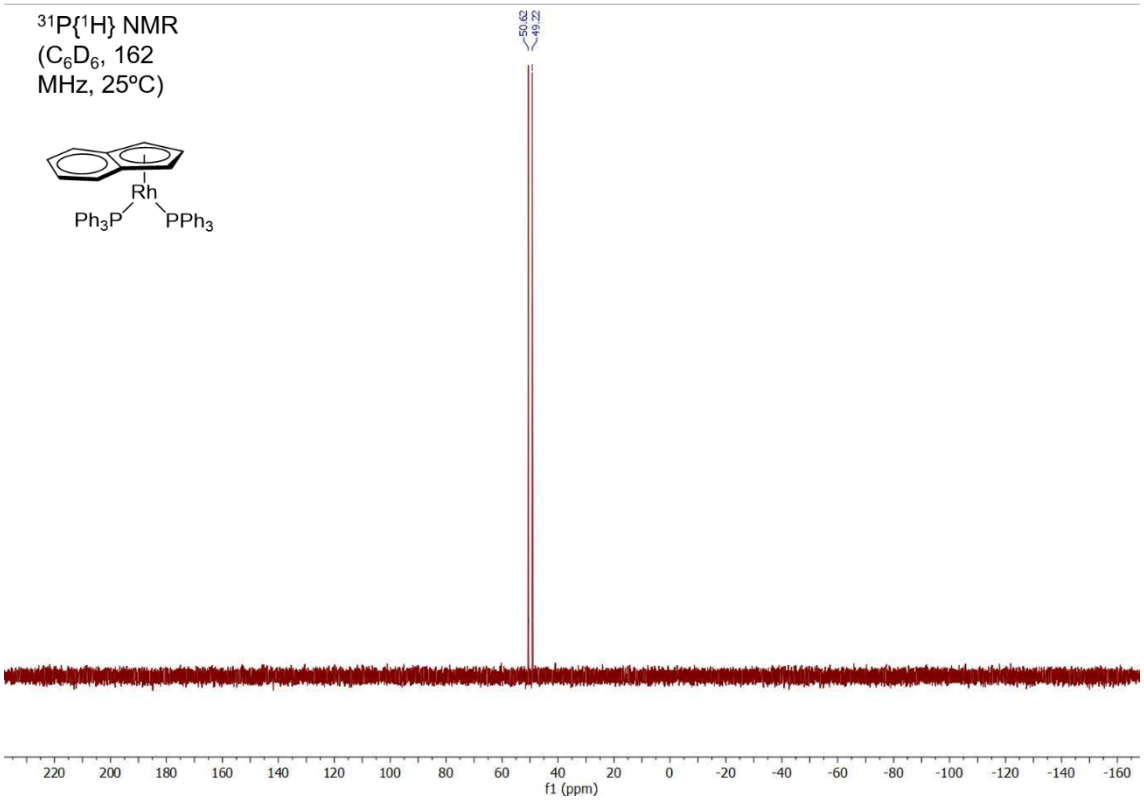


Figure S27. ^{31}P NMR of complex **6d**.

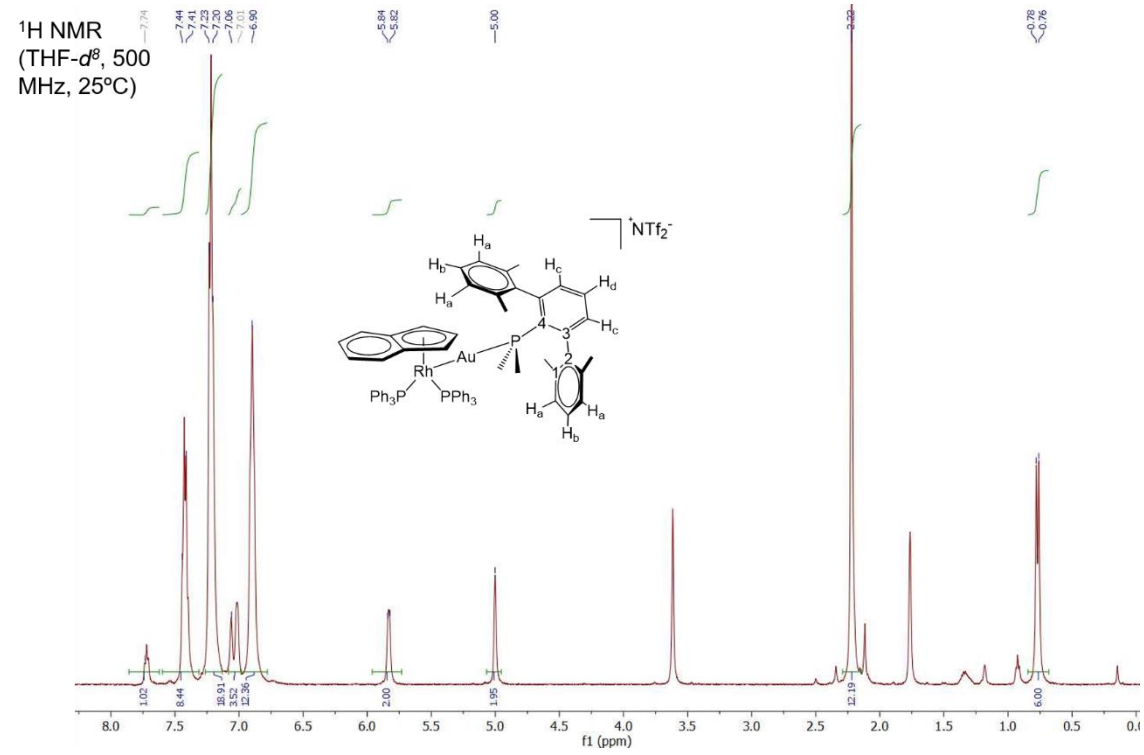


Figure S28. ^{1}H NMR of complex **7d^{Me}**.

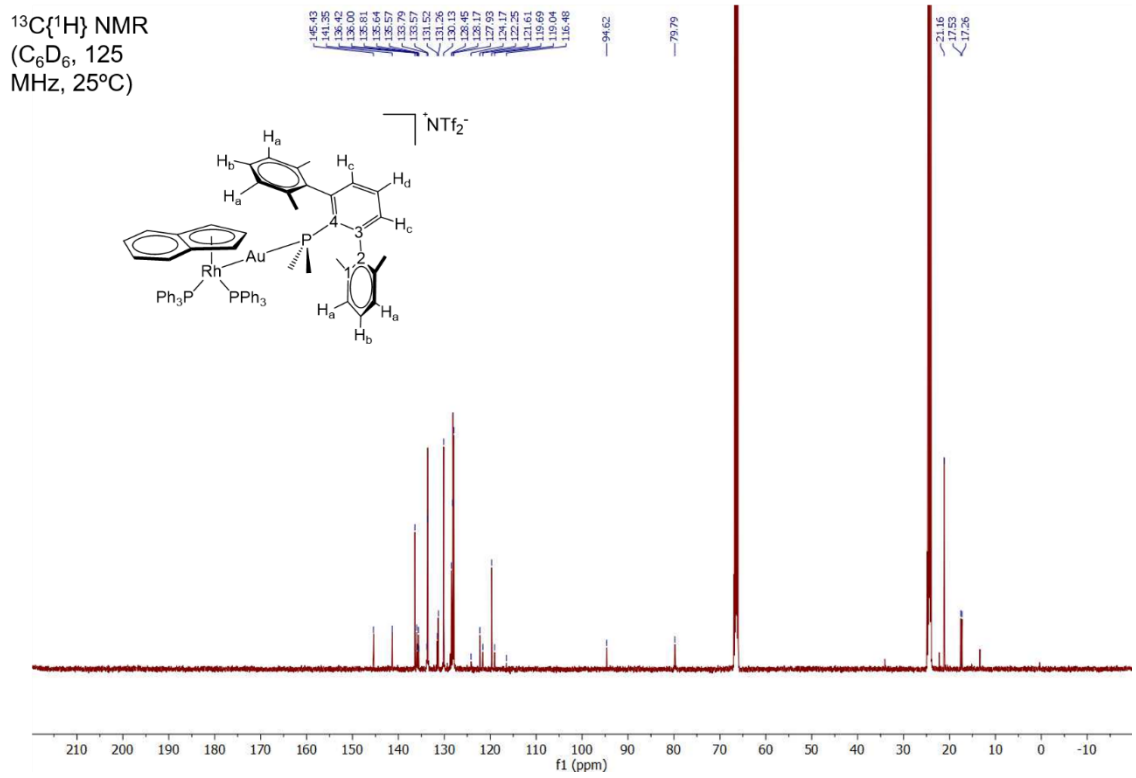


Figure S29. ^{13}C NMR of complex **7d^{Me}**.

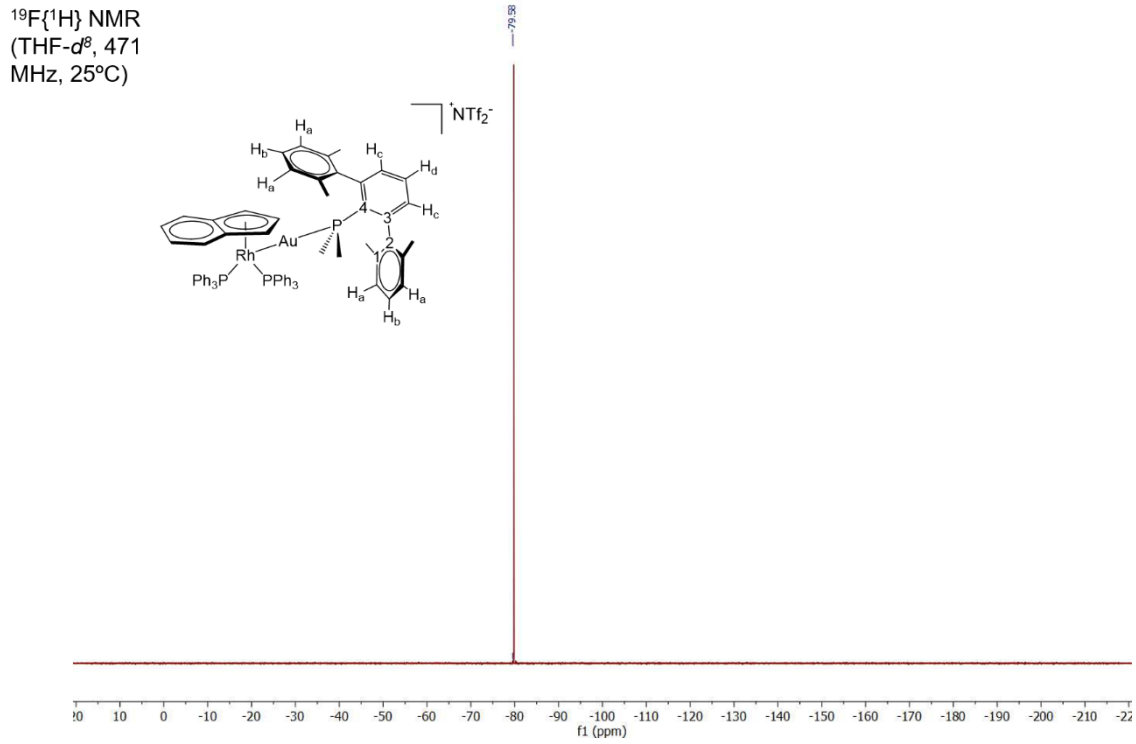


Figure S30. ^{19}F NMR of complex **7d^{Me}**.

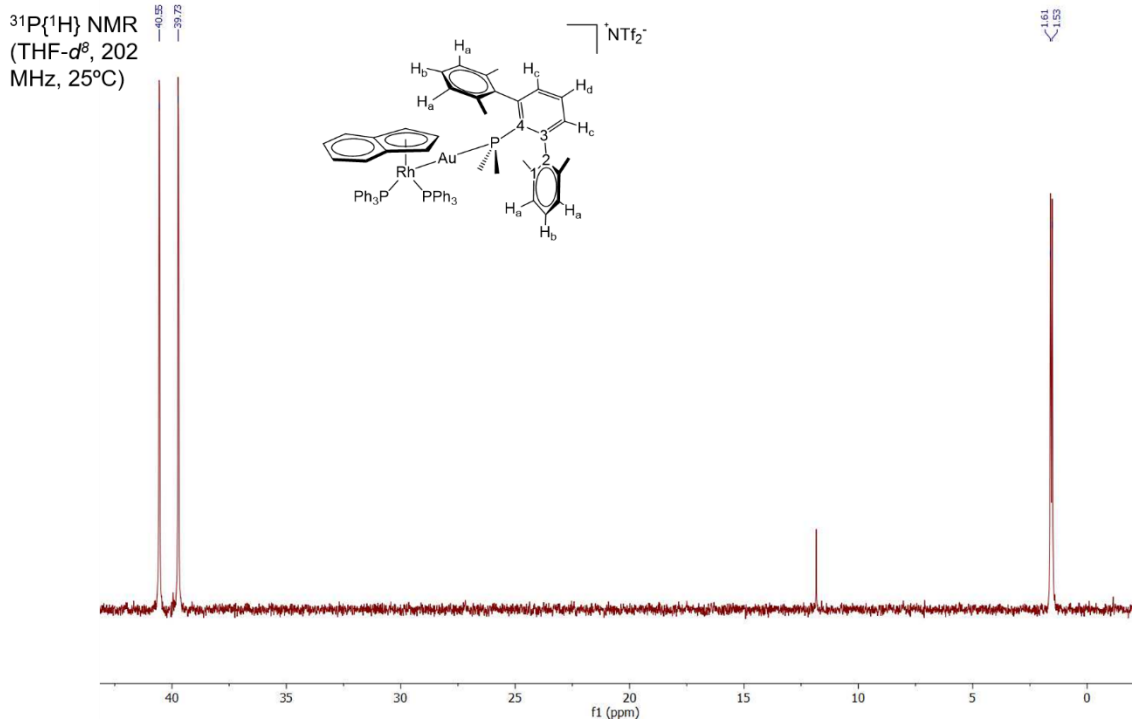


Figure S31. ^{31}P NMR of complex **7d^{Me}**.

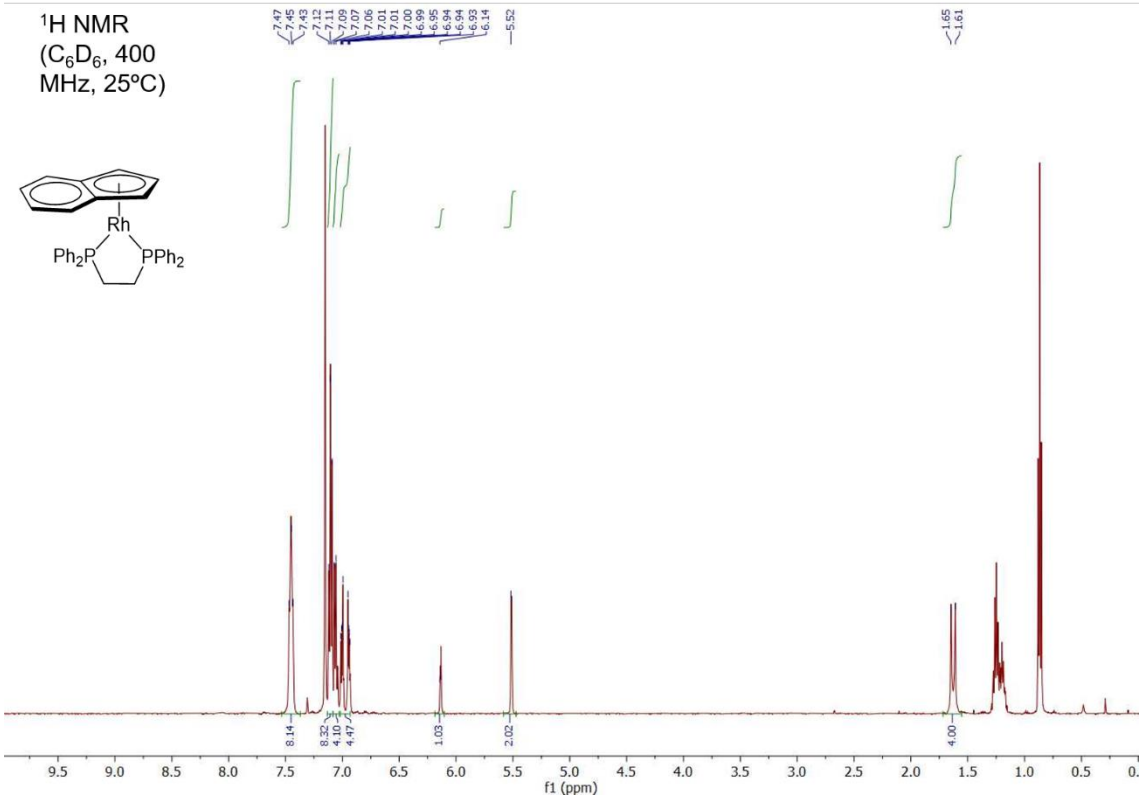


Figure S32. ^{1}H NMR of complex **6c**. There is residual pentane.

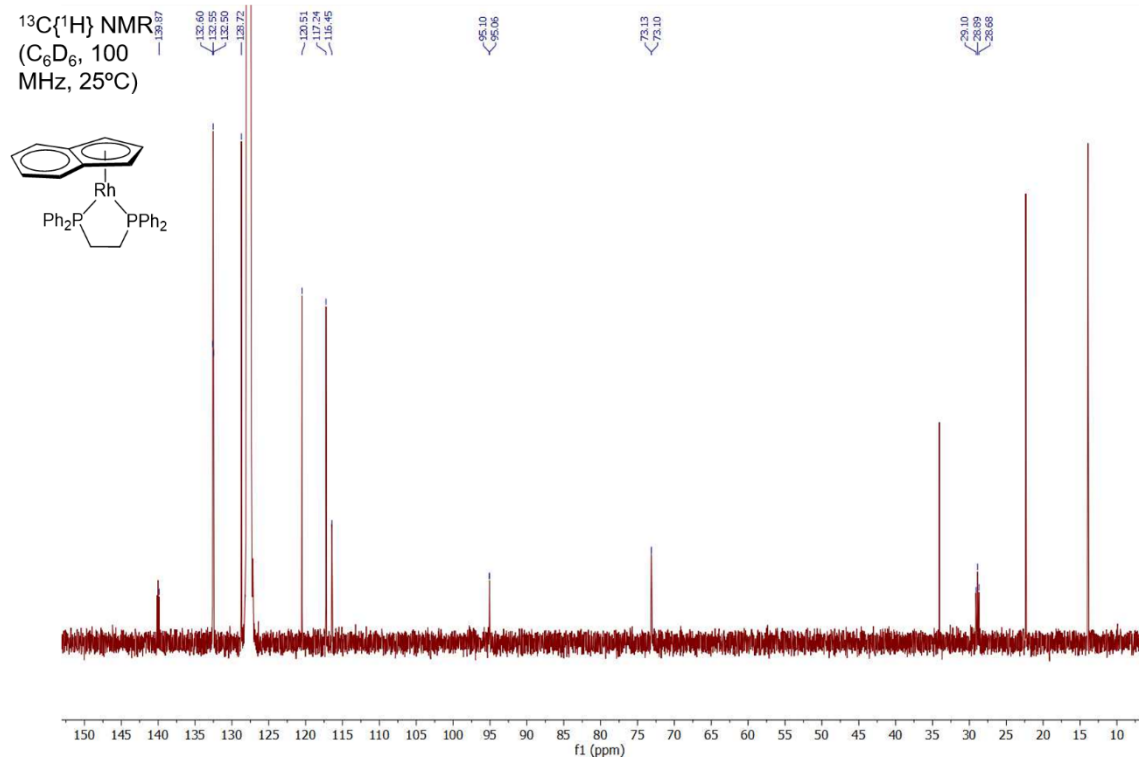


Figure S33. ^{13}C NMR of complex **6c**. There is residual pentane.

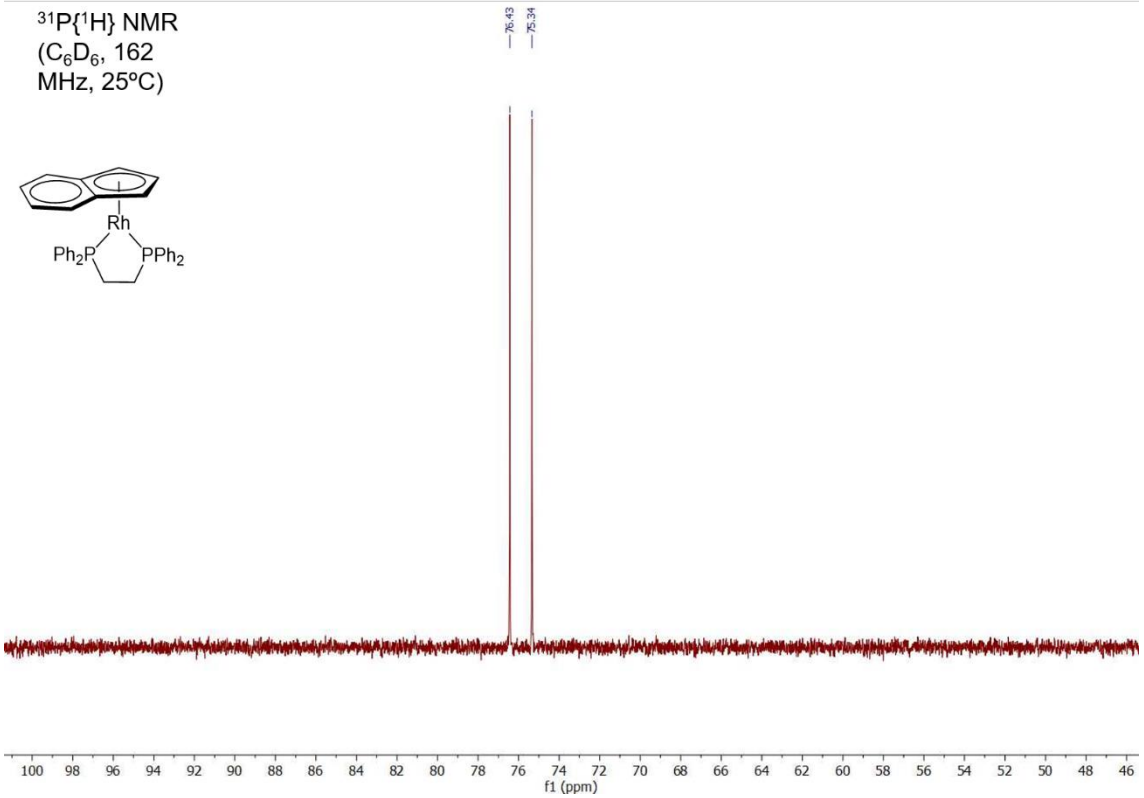


Figure S34. ^{31}P NMR of complex **6c**.

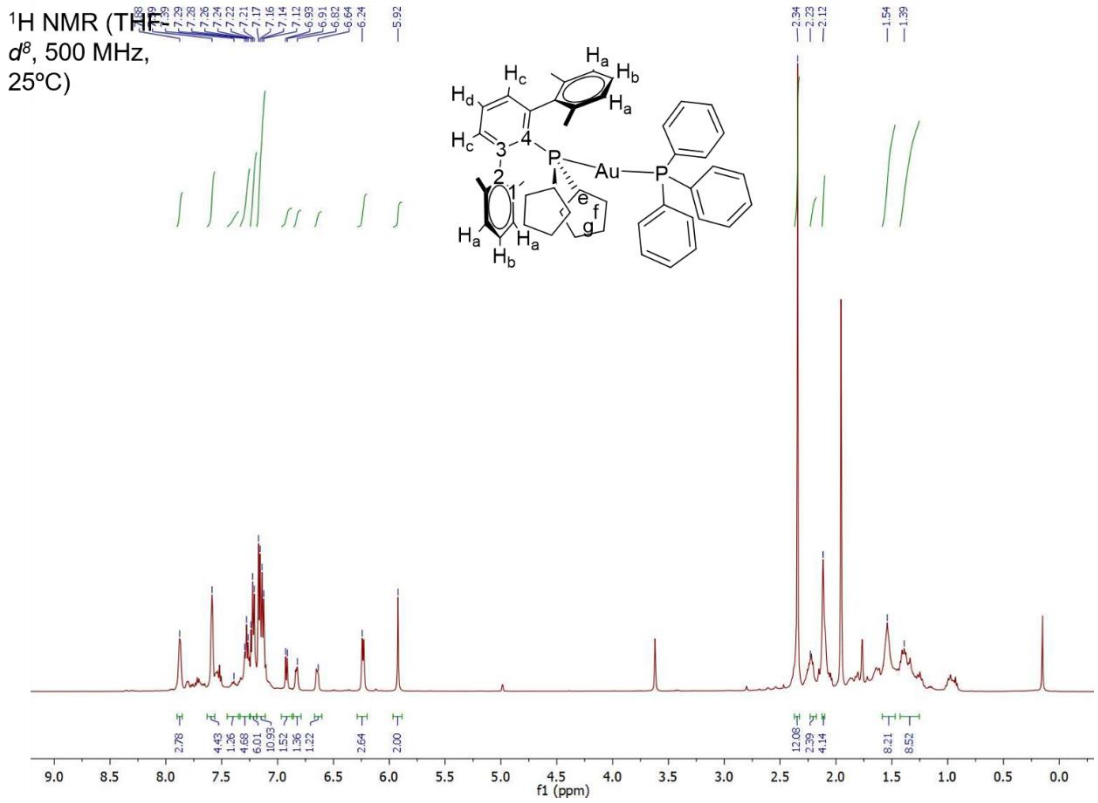


Figure S35. ^{1}H NMR of complex **7c^{Cyp}.**

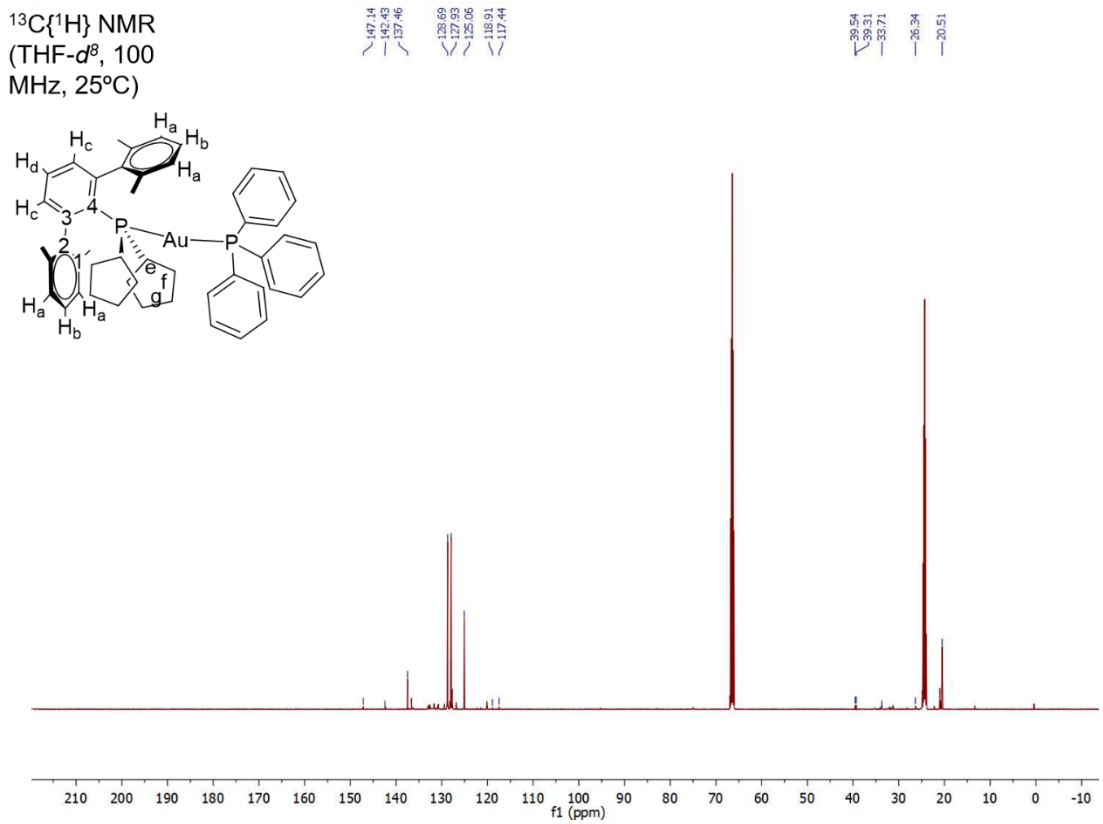


Figure S36. ^{13}C NMR of complex **7c^{Cyp}**.

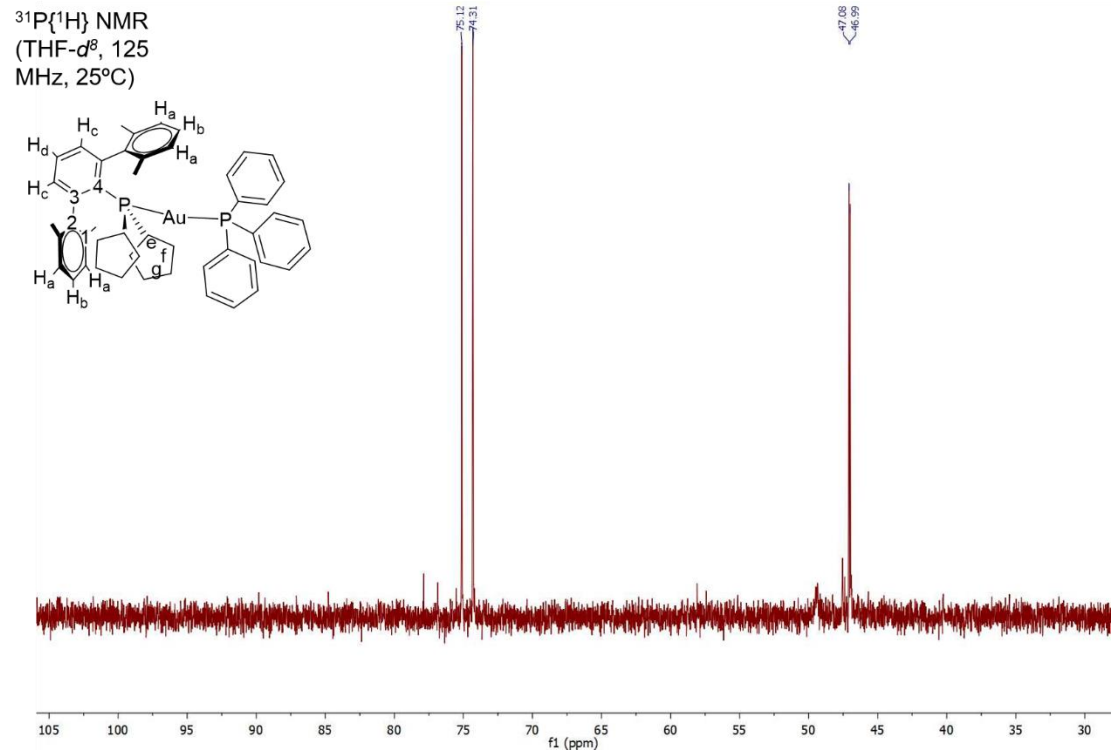


Figure S37. ^{31}P NMR of complex **7c^{Cyp}**.

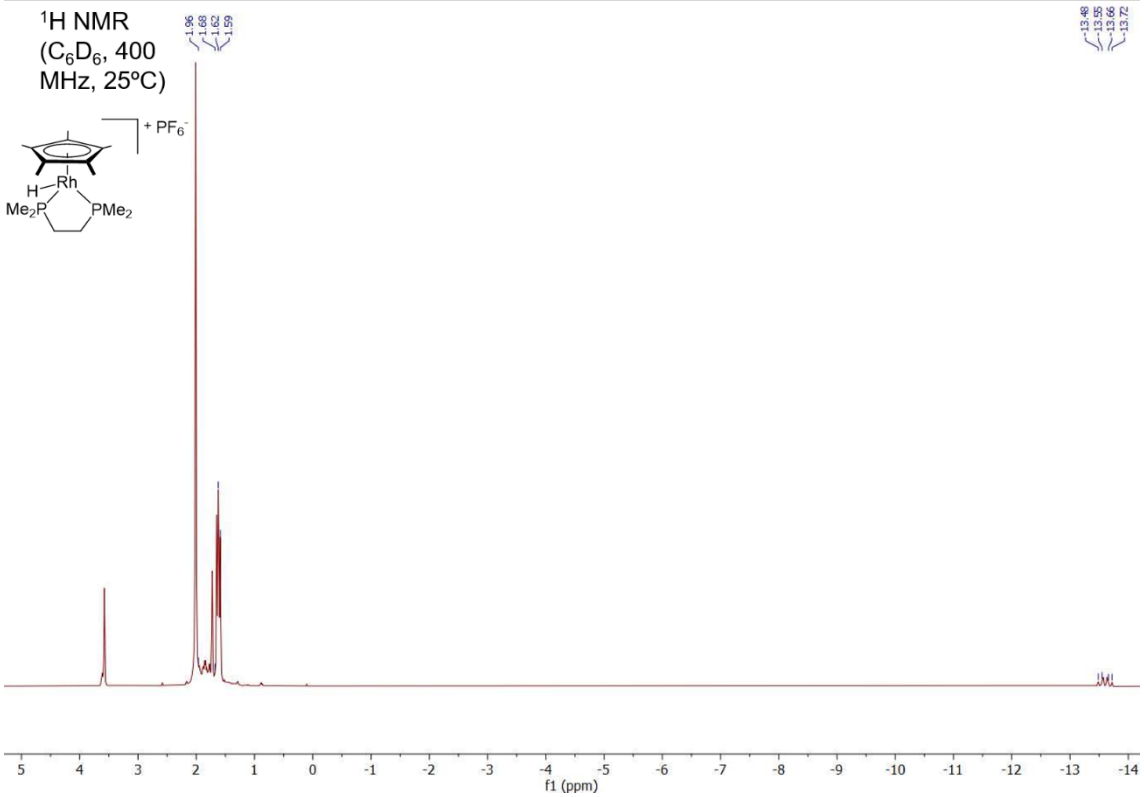


Figure S38. ^{1}H NMR of complex **5b**.

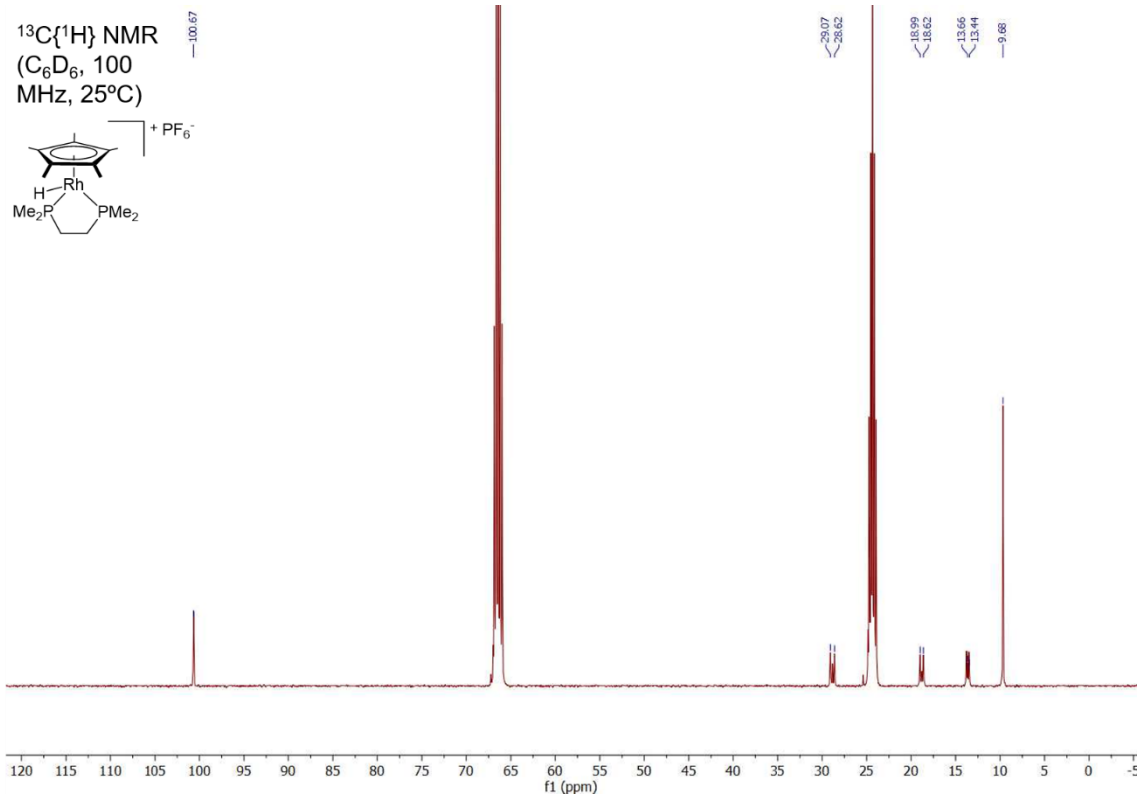


Figure S39. ^{13}C NMR of complex **5b**.

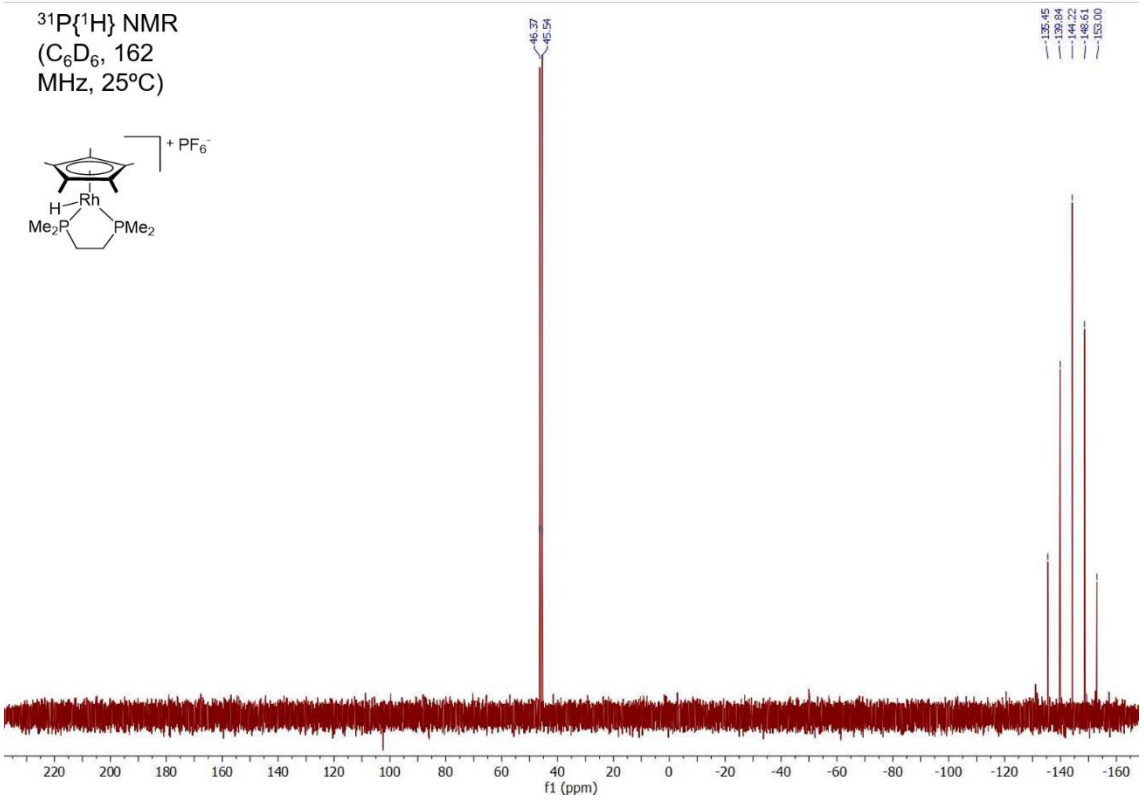


Figure S40. ^{31}P NMR of complex **5b**.

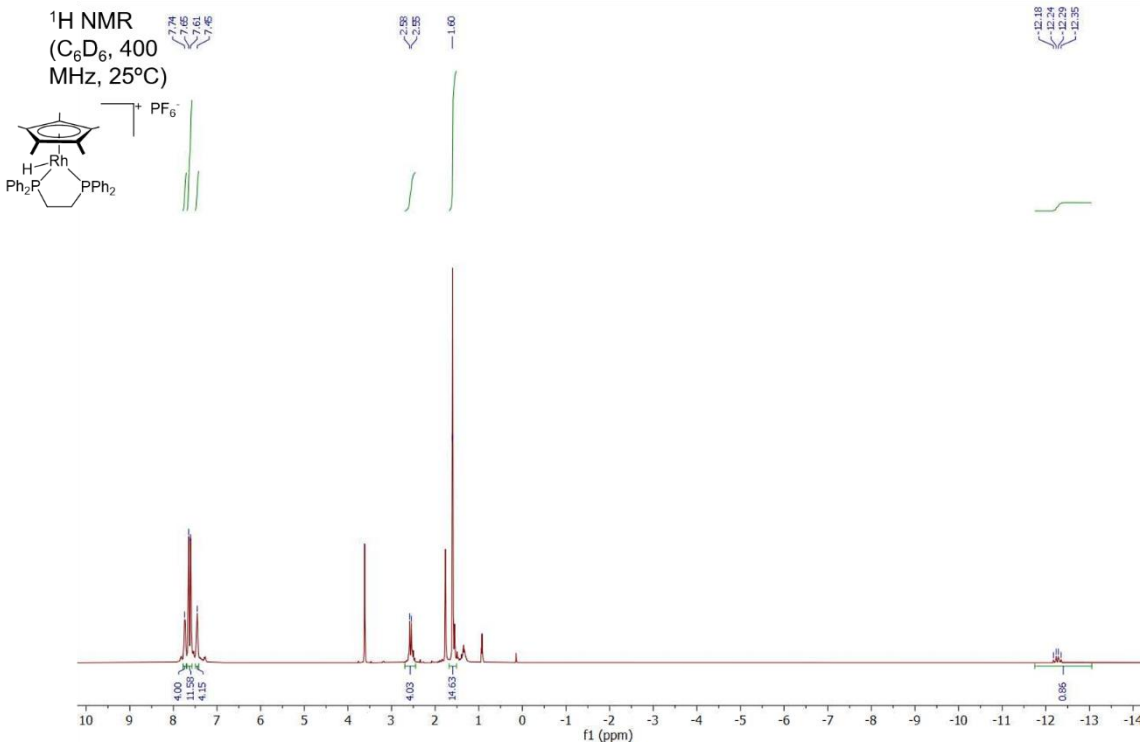


Figure S41. ^{1}H NMR of complex **5c**.

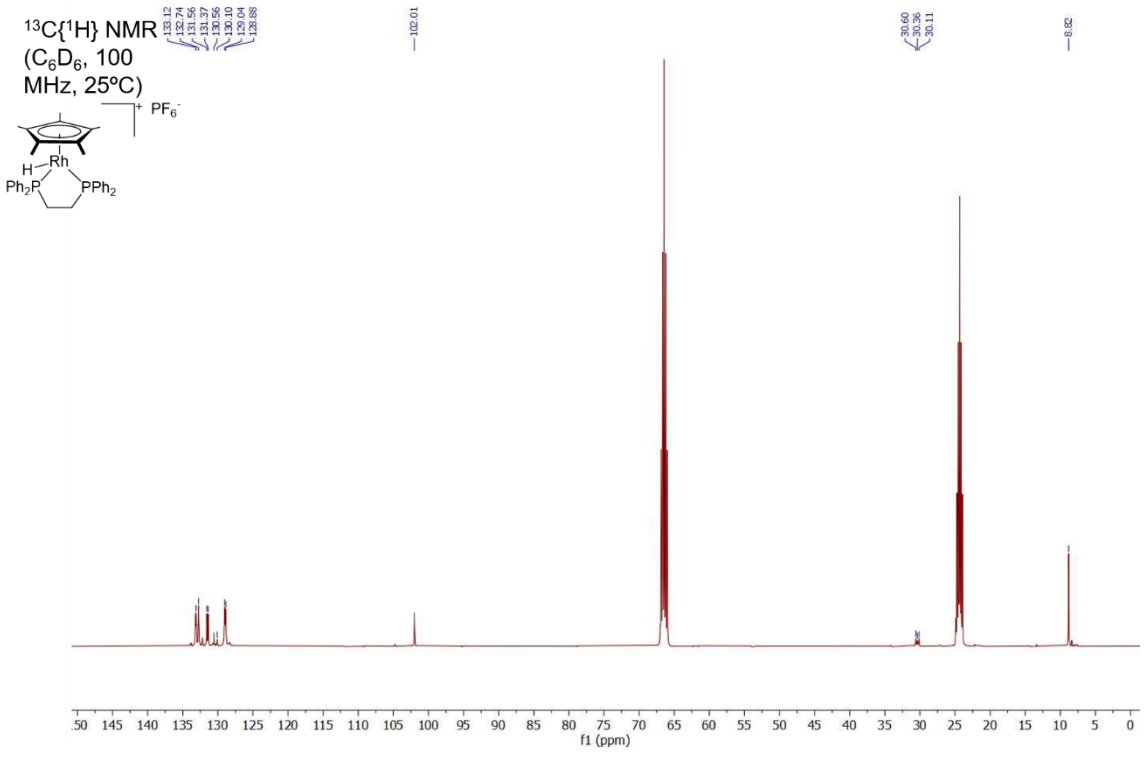


Figure S42. ^{13}C NMR of complex **5c**.

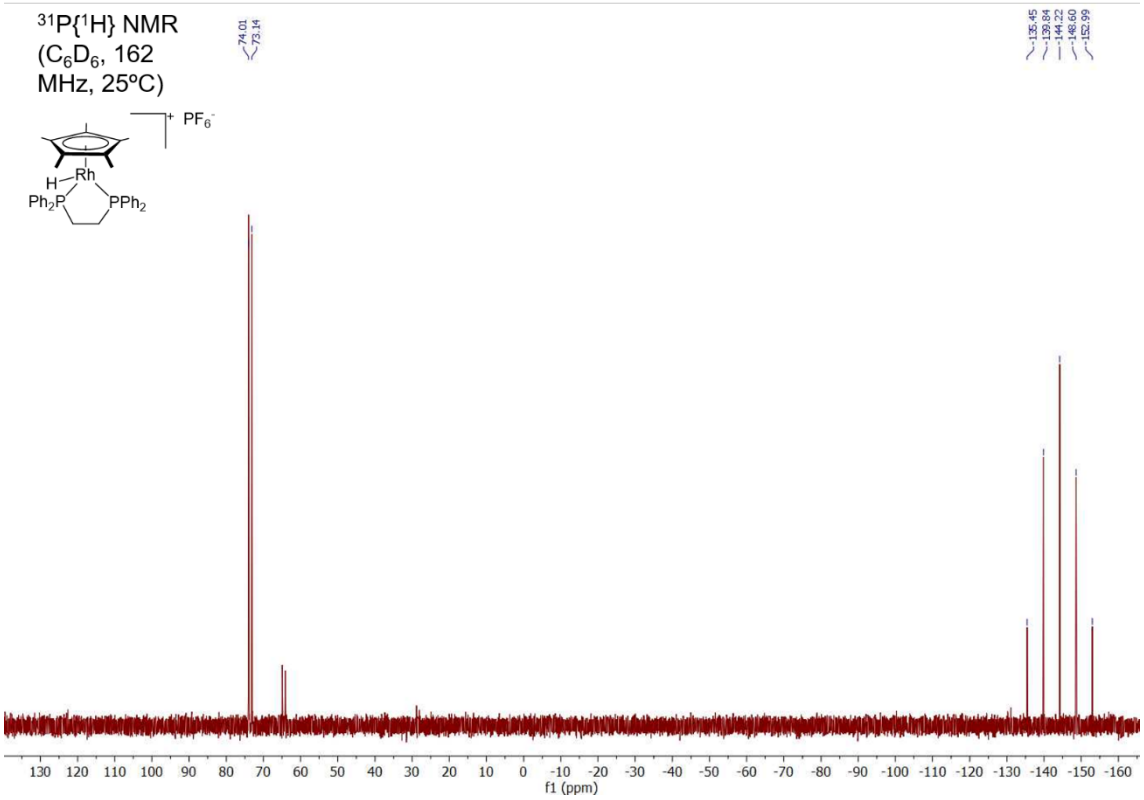


Figure S43. ^{31}P NMR of complex **5c**.

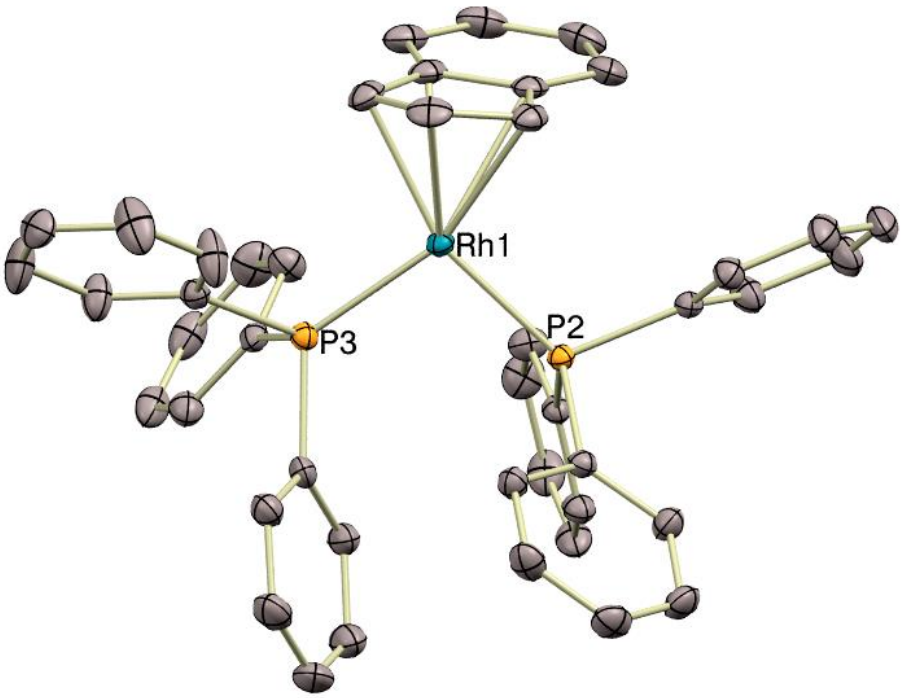
3. Crystal structure determinations

Crystallographic details. Low-temperature diffraction data were collected on a D8 Quest APEX-III single crystal diffractometer with a Photon III detector and a IμS 3.0 microfocus X-ray source (**4b^{Cyp}**, **7a^{Me}**, **7a^{Cyp}**, **6d**, **7d^{Me}**, **6c**, **7c^{Cyp}**, [(η^5-C_9H_8)(PPh_3)(XylNC)Rh→Au($PCyp_2Ar^{Xyl2}$)](NTf_2) and [{($PCyp_2Ar^{Xyl2}$)Au}$_2$(μ-dppe)](NTf_2)$_2$) at the Instituto de Investigaciones Químicas, Sevilla. Data were collected by means of ω and φ scans using monochromatic radiation λ(Mo Kα1) = 0.71073 Å. The diffraction images collected were processed and scaled using APEX-III software. Using Olex2[4], the structures **4b^{Cyp}**, **7c^{Cyp}**, and [{($PCyp_2Ar^{Xyl2}$)Au}$_2$(μ-dppe)](NTf_2)$_2$) were solved with SHELXT and the structures **7a^{Me}, 6c**, **6d, 7a^{Cyp}**, **7d^{Me}**, and [(η^5-C_9H_8)(PPh_3)(XylNC)Rh→Au($PCyp_2Ar^{Xyl2}$)](NTf_2) were solved with olex2.solve1.3 and all was refined against F^2 on all data by full-matrix least squares with SHELXL.[5] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model, excluding H bonded to Rh in complex **4b^{Cyp}**, which was obtained from the Fourier map. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups).

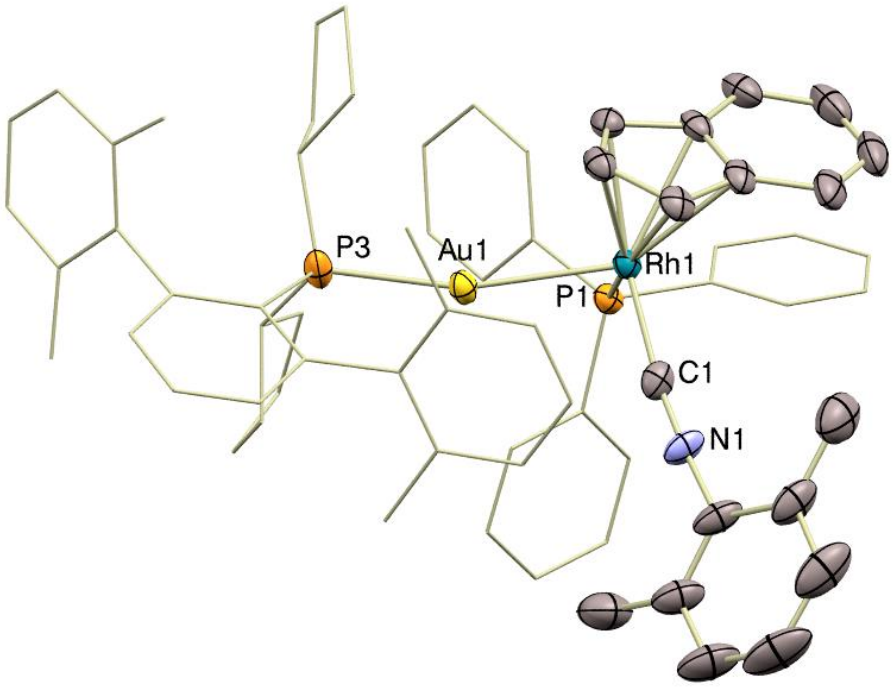
PLATON/SQUEEZE was used for the refinement of **4b^{Cyp}** and **7c^{Cyp}**. When the SQUEEZE recycling converges, 339 electrons were recovered from the difference density map in the unit cell of **4b^{Cyp}**. This is consistent with the presence of one triflimidate anion [$C_2F_6NO_4S_2^-$] and one THF molecule per asymmetric unit which account for (137+28)x2 = 330 electrons per unit cell.

In the case of the structure **7a^{Cyp}**, 215 electrons were found in a void per unit cell. This is consistent with the presence of one toluene molecule (50 electrons) per asymmetric unit.

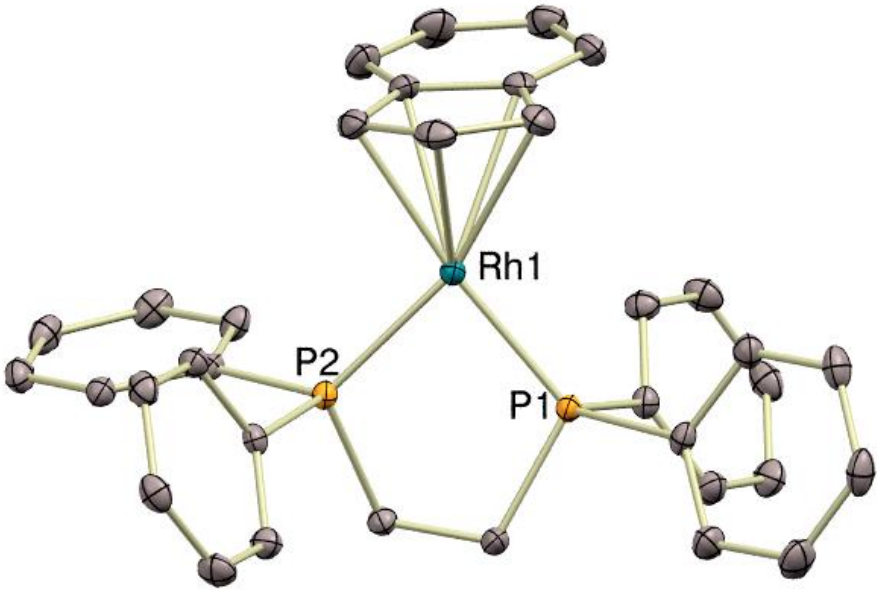
A summary of the fundamental crystal and refinement data are given in Table S1, S2 and S3. Atomic coordinates, anisotropic displacement parameters and bond lengths and angles can be found in the cif files, which have been deposited in the Cambridge Crystallographic Data Centre with no. 2223979 – 2223987. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.



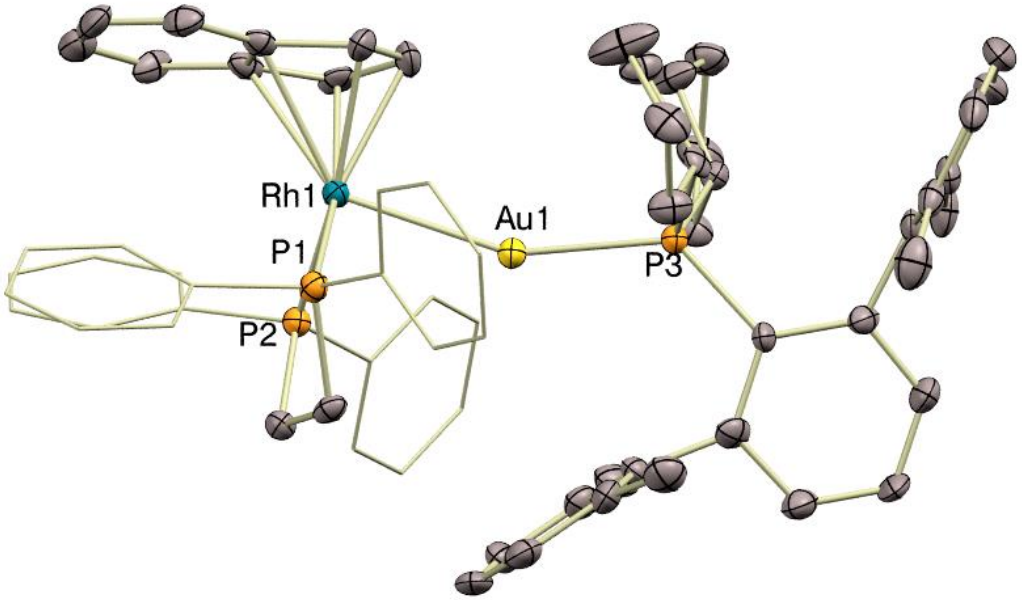
a)



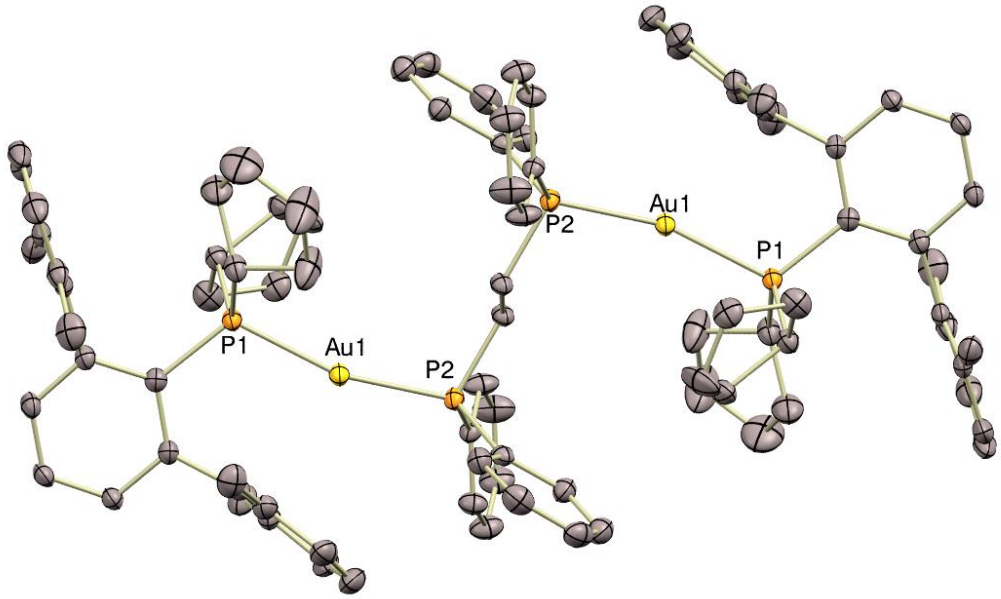
b)



c)



d)



e)

Figure S44. ORTEP of compounds **6d** (a), [(η^5-C_9H_7)(PPh_3)(XylNC)Rh→Au($PCyp_2Ar^{Xyl2}$)](NTf_2) (b), **6c** (c), **7c^{Cyp}** (d) and [{($PCyp_2Ar^{Xyl2}$)Au}$_2$(μ-dppe)](NTf_2)$_2$ (e). For the sake of clarity most hydrogen atoms, as well as solvent molecules and triflimide counteranions are excluded, while some fragments are represented in wireframe format and thermal ellipsoids are set at 50%probability.

Table S1. Crystal data and structure refinement for compounds **4b^{Cyp}**, **7a^{Me}** and **7a^{Cyp}**.

	4b^{Cyp}	**7a^{Me}**	**7a^{Cyp}**
formula	$C_{48}H_{69}AuP_3Rh$	$2x(C_{39}H_{52}AuP_3Rh)$ $+2x(C_2F_6NO_4S_2)$	$2x(C_{47}H_{64}AuP_3Rh) + 2x(C_2F_6NO_4S_2) + 2x(C_6H_6)$
Fw	1038.81	2387.48	2760.04
cryst.size, mm	0.34 × 0.07× 0.04	0.30 × 0.10 × 0.05	0.18 × 0.15 × 0.12
crystal system	Triclinic	Monoclinic	Triclinic
space group	*P-1*	*P2$_1$/n*	*P-1*
a, Å	9.4923 (10)	25.8321 (8)	14.1319 (13)
b, Å	17.2690 (18)	8.9867 (3)	17.4134 (15)
c, Å	18.5760 (18)	40.1396 (18)	23.475 (2)
α, deg	104.345 (3)	90	85.692 (4)
β, deg	98.054 (3)	93.4312 (17)	88.744 (4)
γ, deg	90.238 (3)	90	86.622 (4)
V, Å^3	2918.6 (5)	9301.5 (6)	5749.6 (9)
T, K	193	193	193
Z	2	4	2
ρ_{calc}, g cm^{-3}	1.182	1.705	1.594
μ, mm^{-1} (MoKα)	2.900	3.763	3.055
F(000)	1054	4736	2776
absorption corrections	multi-scan, 0.35 – 0.75	multi-scan, 0.48 – 0.75	multi-scan, 0.52 – 0.75
θ range, deg	2.169 – 28.260	2.033 – 25.696	1.808 – 26.434
no. of rflns measd	564417	49516	28874
R_{int}	0.1932	0.0651	0.1328
no. of rflns unique	14378	17159	18490
no. of params / restraints	495/ 0	1100 / 3	1337 / 1
R_1 ($I > 2\sigma(I)$) [a]	0.0666	0.0656	0.0863
R_1 (all data)	0.1607	0.0959	0.1510
wR_2 ($I > 2\sigma(I)$)	0.1396	0.1031	0.1661
wR_2 (all data)	0.1807	0.1109	0.1991
Diff.Fourier.peaks min/max, eÅ^{-3}	-1.555 / 2.104	-1.591 / 1.420	-2.192/ 1.781
CCDC number	2223979	2223980	2223981

Table S2. Crystal data and structure refinement for compounds **6d, 7d^{Me}** and [(η^5-C_9H_7)(PPh_3)(XylNC)Rh→Au($PCyp_2Ar^{Xyl2}$)] (NTf_2) (labelled as **I** in the Table)

	6d	**7d^{Me}**	**I**
formula	$C_{45}H_{37}P_2Rh$	$C_{69}H_{64}AuP_3Rh$ + $C_2F_6NO_4S_2$ + 2x(C_6H_6)	$C_{68}H_{70}AuNP_2Rh$ + $C_3H_{3.5}$
Fw	742.59	1722.35	1302.62
cryst.size, mm	0.19 × 0.14 × 0.11	0.13× 0.1× 0.08	0.20× 0.17× 0.12
crystal system	Monoclinic	Monoclinic	Monoclinic
space group	*P2$_1$/n*	*P2$_1$/c*	*C2/c*
a, Å	10.9920 (4)	22.0242 (17)	24.0998 (7)
b, Å	19.9168 (7)	15.0200 (10)	24.7705 (8)
c, Å	16.4411 (5)	24.1969 (18)	28.1675 (9)
α, deg	90	90	90
β, deg	104.1791 (12)	110.708 (3)	112.8643 (11)
γ, deg	90	90	90
V, Å^3	3489.7 (2)	7487.3 (10)	15493.8 (8)
T, K	193	193	193
Z	4	4	8
ρ_{calc}, g cm^{-3}	1.413	1.528	1.117
μ, mm^{-1} (MoKα)	0.613	2.364	2.179
F(000)	1528	3472	5284
absorption corrections	multi-scan, 0.68 – 0.75	multi-scan, 0.40 – 0.75	multi-scan, 0.65 – 0.75
θ range, deg	2.266– 28.314	1.977–26.421	2.258– 25.037
no. of rflns measd	63448	93036	146359
R_{int}	0.0856	0.0723	0.0538
no. of rflns unique	8672	15320	13710
no. of params / restraints	433/ 9	916/18	692/ 3
R_1 ($I > 2\sigma(I)$) [a]	0.0376	0.0374	0.0364
R_1 (all data)	0.0700	0.0481	0.0462
wR_2 ($I > 2\sigma(I)$)	0.0718	0.0921	0.1109
wR_2 (all data)	0.0893	0.0995	0.1187
Diff.Fourier.peaks min/max, eÅ^{-3}	-0.616/0.844	-1.678/1.270	-0.820/0.884
CCDC number	2223982	2223983	2223984

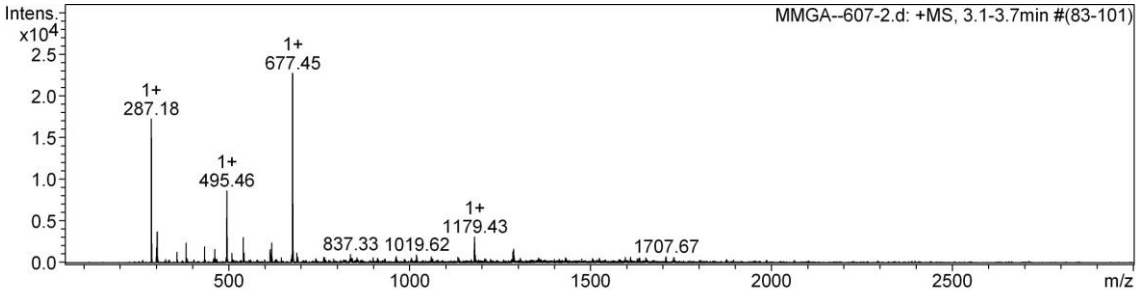
Table S30. Crystal data and structure refinement for compounds **6c**, **7c^{Cyp}** and [{($PCyp_2Ar^{Xyl2}$)Au}$_2$(μ-dppe)](NTf_2)$_2$ (labelled as **II** in the Table).

	6c	**7c^{Cyp}**	**II**
formula	$C_{35}H_{31}P_2Rh$	$C_{67}H_{70}AuP_3Rh$ + $C_2F_6NO_4S_2$	$C_{45}H_{51}AuP_2$
Fw	616.45	1548.16	850.76
cryst.size, mm	0.23 × 0.20 × 0.10	0.10 × 0.05× 0.02	0.17 × 0.13× 0.12
crystal system	Monoclinic	Orthorhombic	Monoclinic
space group	*P2$_1$/n*	*P2$_1$2$_1$2$_1$*	*P2$_1$/n*
a, Å	9.2418 (4)	13.0982(4)	13.5273 (5)
b, Å	8.9282 (4)	17.1018(4)	20.7432 (8)
c, Å	33.9326 (13)	30.9379(9)	16.8019(7)
α, deg	90	90	90
β, deg	92.2885 (12)	90	91.1697(12)
γ, deg	90	90	90
V, Å^3	2783.0 (2)	6930.2(3)	4713.6 (3)
T, K	193	193	193
Z	4	4	4
ρ_{calc}, g cm^{-3}	1.471	1.484	1.199
μ, mm^{-1} (MoKα)	0.752		3.214
F(000)	1264	3112	1720
absorption corrections	multi-scan, 0.64 – 0.75	multi-scan, 0.64 – 0.74	multi-scan, 0.62 – 0.75
θ range, deg	2.233– 27.137	2.36–24.99	1.952–28.298
no. of rflns measd	40098	141393	83091
R_{int}	0.0450	0.1568	0.0790
no. of rflns unique	6171	13158	11695
no. of params / restraints	343/ 0	789/ 0	447/ 0
R_1 ($I > 2\sigma(I)$) [a]	0.0318	0.0459	0.0459
R_1 (all data)	0.0431	0.0825	0.0695
wR_2 ($I > 2\sigma(I)$)	0.0576	0.0954	0.1099
wR_2 (all data)	0.0620	0.1173	0.1237
Diff.Fourier.peaks min/max, eÅ^{-3}	-0.354/0.419	-1.337/1.335	-1.529/3.324
CCDC number	2223985	2223986	2223987

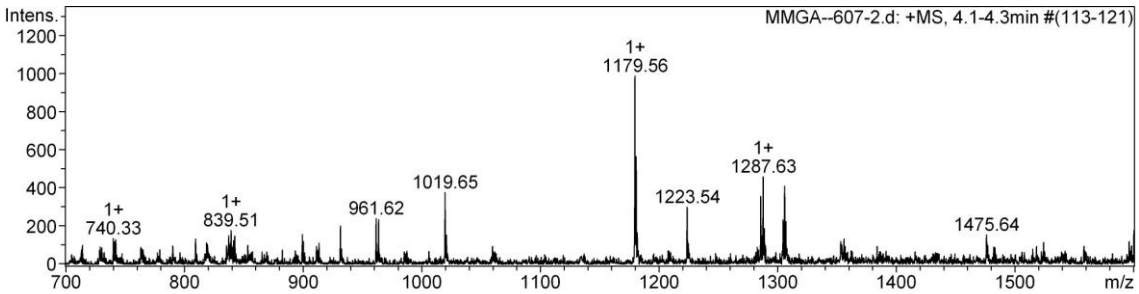
4. Mass spectrometry

Compound [(η^5-C_9H_7)(PPh_3)(C_2H_4)Rh→Au($PCyp_2Ar^{Xyl2}$)](NTf_2)

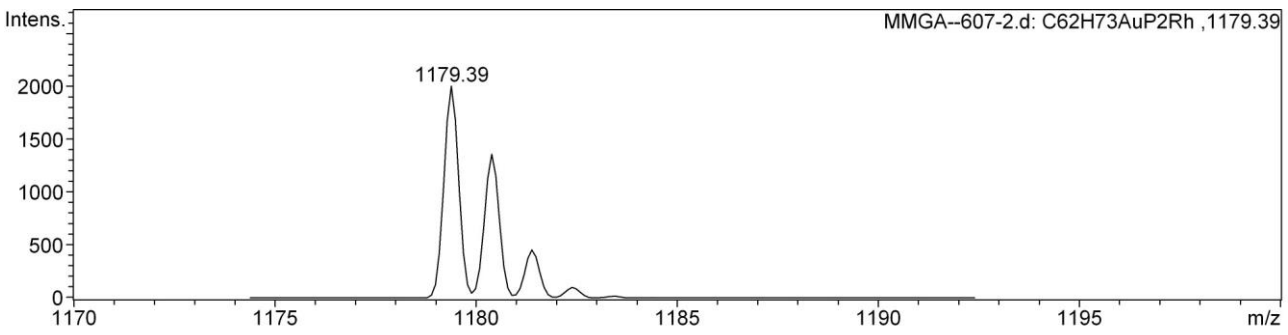
MS (electrospray, m/z): calcd for C62H73P2AuP_2Rh: 1179.36 found 1179.56.



#	m/z	FWHM	S/N
1	287.18	0.39	363.8
2	303.16	0.37	78.4
3	383.32	0.34	50.0
4	495.46	0.41	182.1
5	496.43	0.40	65.0
6	541.22	0.49	63.9
7	619.41	0.39	50.1
8	677.45	0.46	480.0
9	678.43	0.40	147.9
10	1179.43	0.51	65.5

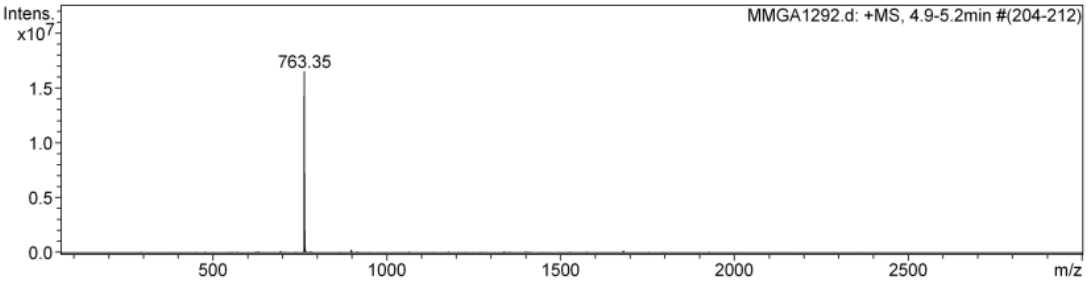


#	m/z	FWHM	S/N
1	961.62	0.39	20.0
2	963.69	0.41	19.6
3	1019.65	0.41	31.4
4	1179.56	0.43	82.3
5	1180.55	0.48	47.1
6	1223.54	0.39	24.9
7	1285.61	0.43	29.7
8	1287.63	0.43	38.3
9	1304.35	0.36	19.4
10	1305.65	0.46	34.2

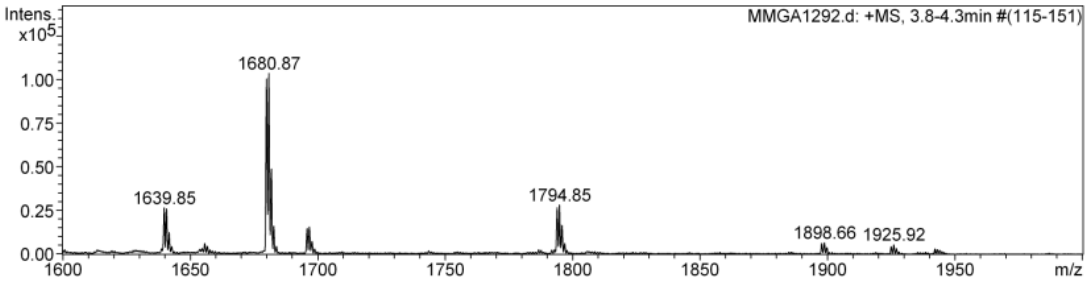


Compound [(η^5-C_9H_8)(PPh_3)(XylNC)Rh→Au($PCyp_2Ar^{Xyl2}$)](NTf_2)

MS (electrospray, m/z): calcd for $C_{78}H_{81}AuF_6N_2O_4P_3RhS_2$: 1680.35 found 1680.87.



#	m/z	FWHM	S/N
1	763.35	0.46	2745.0
2	764.17	0.40	1207.3
3	765.20	0.41	325.6



#	m/z	FWHM	S/N
1	1639.85	0.47	126.1
2	1640.82	0.46	123.7
3	1679.99	0.45	477.0
4	1680.87	0.46	492.1
5	1681.85	0.44	232.1
6	1682.88	0.41	76.6
7	1696.83	0.46	74.5
8	1793.91	0.47	126.8
9	1794.85	0.44	133.6
10	1795.86	0.42	78.2

5. Variable temperatura van´t Hoff study of the equilibrium of 1c and 2^{Cyp} with $3c^{Cyp}$.

Complexes **1c** and $\mathbf{2}^{Cyp}$ were dissolved in benzene-d_6 in a J. Young NMR tube. The reaction was monitored for 24 hours by ^{1}H NMR spectroscopy until disappearance of complex $\mathbf{4c}^{Cyp}$, rendering a mixture comprising complexes **1c**, $\mathbf{2}^{Cyp}$ and $\mathbf{3c}^{Cyp}$. To study the equilibrium between the precursors and the adduct, the tube was inserted into a temperature-controlled NMR probe and ^{1}H NMR spectra were collected at 5 K intervals from 238 K to 298 K, allowing 5 minutes for equilibration at each temperature. Concentrations were determined by NMR. The equilibrium constant of the reaction was calculated according to the expression:

$$K_{obs} = \frac{[\mathbf{3}\boldsymbol{c}]}{[\mathbf{1}\boldsymbol{c}][\mathbf{2}]}$$

The plot of $\ln(K_{obs})$ as a function of T^{-1} was fit by a line according to the expression:

$$\ln(K_{obs}) = \frac{-\Delta H}{RT} + \frac{\Delta S}{R}$$

The enthalpy and entropy of the reaction were extracted from the slope and intercept, respectively.

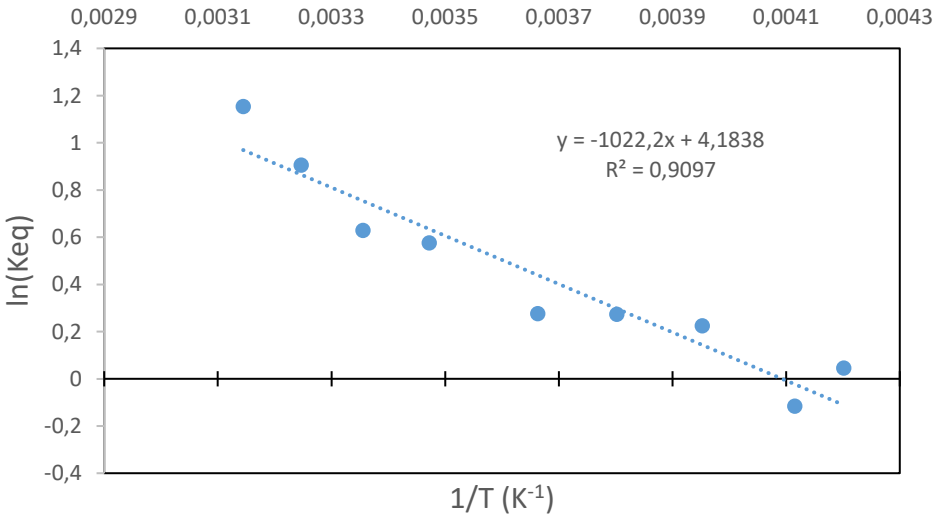


Figure S45. Van't Hoff plot derived from variable temperature ^{1}H NMR spectra of the equilibrium between **1c** and $\mathbf{2}^{Cyp}$ with $\mathbf{3c}^{Cyp}$ from 298 K to 238 K.

6. Computational details

Calculations were performed at the DFT level with the Gaussian 09 (Revision E.01) program.[6] The hybrid functional PBE0[7] was used throughout the computational study, and dispersion effects were accounted for by using Grimme's D3 parameter set with Becke−Johnson (BJ) damping.[8] Geometry optimizations were carried out without geometry constraints, using the 6-31G(d,p)[9] basis set to represent the C, H, P, O, S, F and N atoms and the Stuttgart/Dresden Effective Core Potential and its associated basis set (SDD)[10] to describe the Rh and Au atoms. Bulk solvent effects (dichloromethane) were included at the optimization stage with the SMD continuum model.[11] The stationary points and their nature as minima or saddle points (TS) were characterized by vibrational analysis, which also produced zero-point (ZPE), enthalpy (H), entropy (S) and Gibbs energy (G) data at 298.15 K. The minima connected by a given transition state were determined by perturbing the transition states along the TS coordinate and optimizing to the nearest minimum.

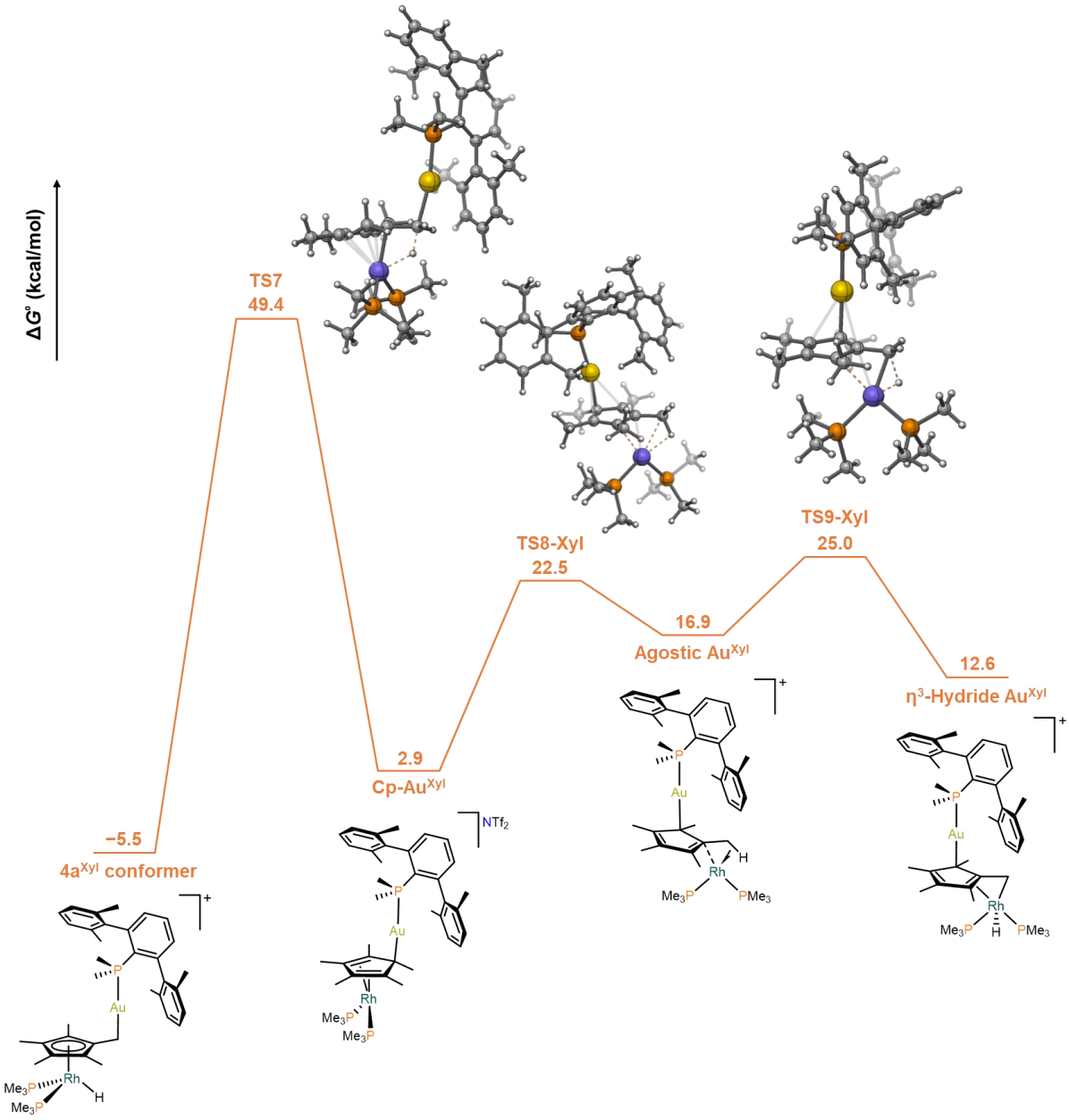


Figure S46. Free energy profile of the direct (left) and stepwise (right) transfer of a hydride from the Cp* to Rh for the Xyl system.

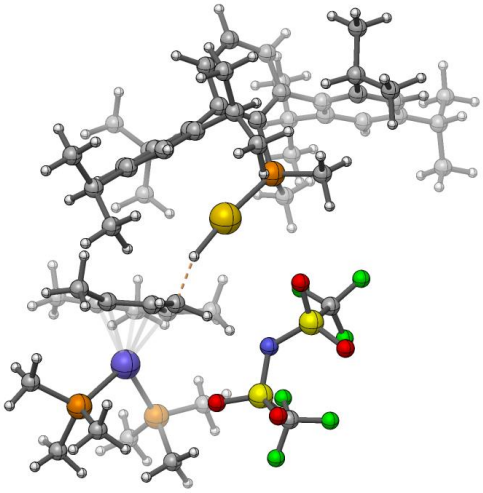


Figure S47. Transition state for the abstraction of a hydride from the Cp* by the gold center for the Tripp system (TS11, 28.1 kcal/mol).

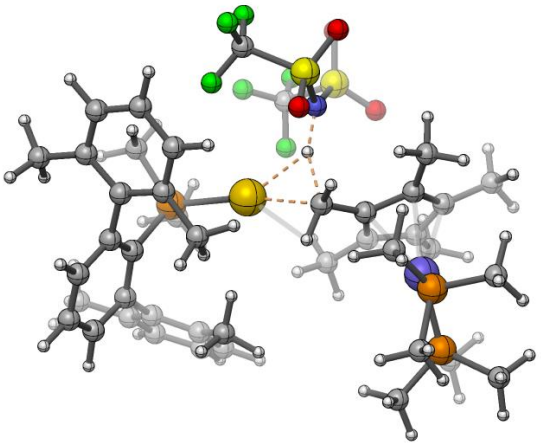


Figure S48. Transition state for the concerted formation of Au−C and N−H bonds for the Xyl system (TS12, 41.2 kcal/mol).

7. Referencias

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