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Preparation, Characterization and Reactivity of Trifluoromethoxy Palladium(II) Complexes

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General information

All glassware was oven or flame dried for several hours prior to use. Solvents were freshly degassed according to the procedures in *Purification of Laboratory Chemicals* prior to use. Tetrahydrofuran, Toluene, Diethyl ether, pentane and benzene were distilled from Na^0/benzophenone. All syntheses were conducted using standard Schlenk techniques or in an inert atmosphere glovebox. (1,5-COD)Pd($CH_2TMS)_2$ was prepared according to a procedure reported in the literature[1] and stored at -35 °C in an argon filled glovebox when not in use. Unless otherwise noted, all other reagents and starting materials were purchased from commercial sources and used without further purification. ^{1}H NMR spectra were recorded on a 600 MHz, 500 MHz or 400 MHz spectrometer. ^{19}F NMR spectra were recorded on a 564 MHz, 470 MHz or 376 MHz spectrometer. ^{31}P NMR spectra were recorded on a 243 MHz, 202 MHz or 162 MHz spectrometer. ^{1}H NMR chemical shifts are reported in parts per million (ppm) relative to TMS, with the residual NMR solvent peak used as an internal reference. ^{19}F NMR chemical shifts are reported in ppm and are referenced to the solvent lock. ^{31}P NMR spectra were calibrated to an external standard of neat H_3PO_4 (δ 0.0 ppm).Coupling constants are reported in hertz. The following abbreviations were used to explain the multiplicities: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; br = broad.

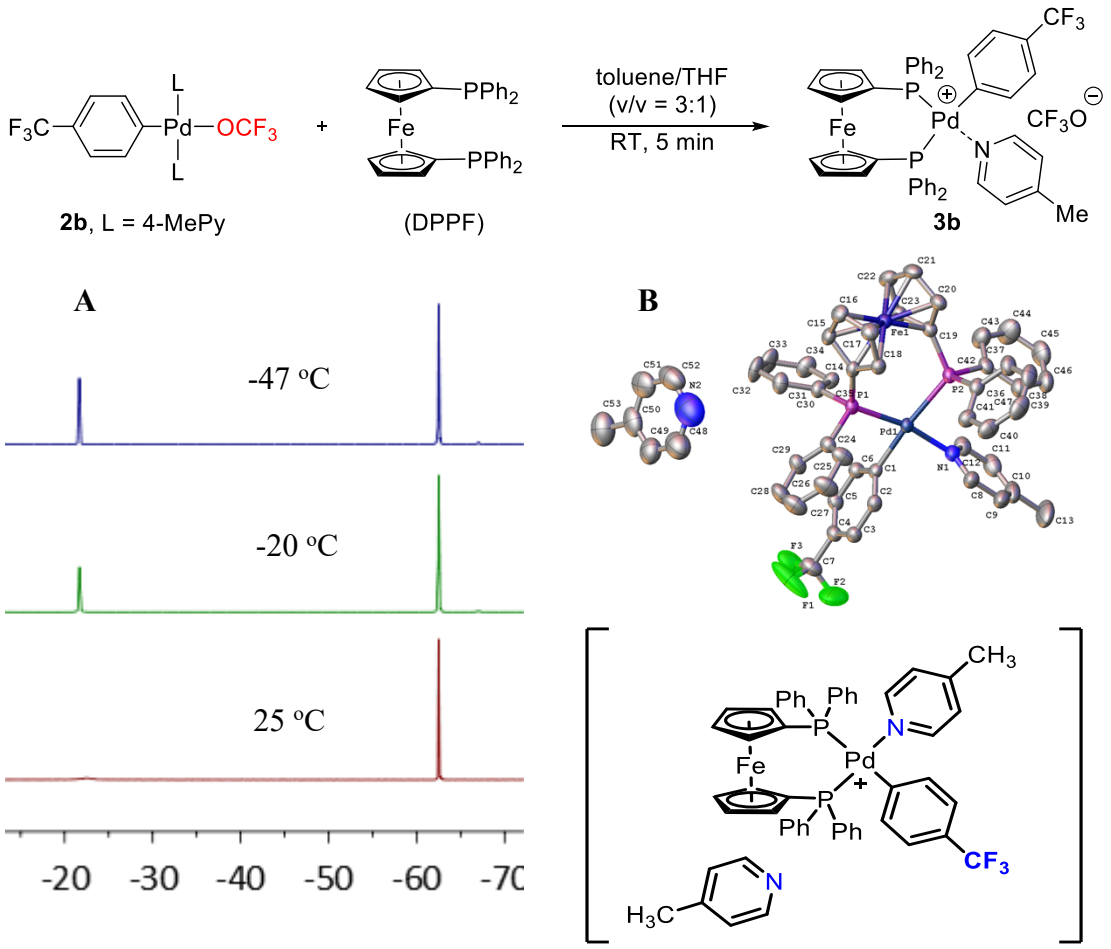


Figure S1. (a) Variable temperature ^{19}F NMR of **3b**. (b) X-ray structure of **3b'**.

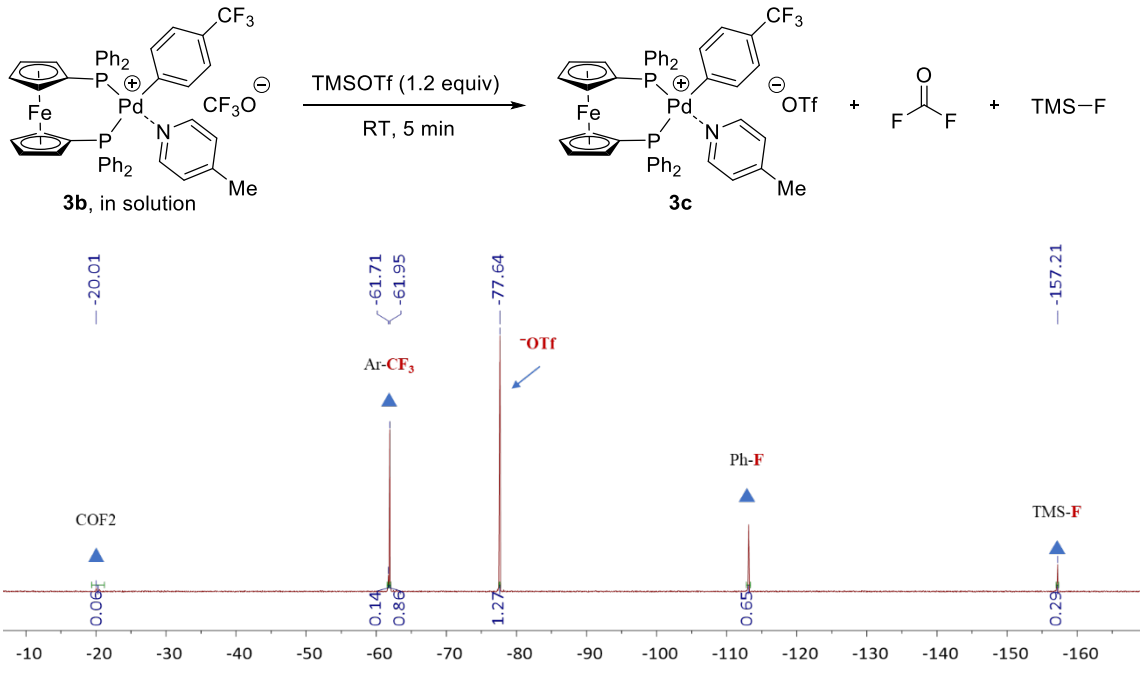
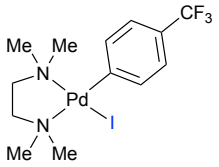


Figure S2. ^{19}F NMR of the anion exchange reaction using PhF as an internal standard.

General procedure for preparation of [L_2Pd(Aryl)(I)]

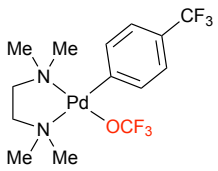
Synthesis of [(TMEDA)Pd(4-CF_3-Ph)(I)] 1a. [(Tmeda)Pd(Aryl)(I)] was synthesized via a modified literature procedure.[2] Under nitrogen, $Pd(dba)_2$ (11.5 g, 20.0 mmol) was weighed into a 250 mL round bottom flask and THF (150 mL) was added. TMEDA (3.50 g, 30.0 mmol) was added, and the resulting mixture was stirred at 25 ºC for 15 min. The appropriate aryl iodide (36.0 mmol, 1.80 equiv.) was added, and the mixture was heated at 60 ºC for 30 min. The mixture was filtered through a plug of Celite, and the solvent was removed under reduced pressure. The residue was washed with hexane (20 mL × 3) and then diethyl ether (50 mL × 3) to remove all residual dibenzylidene acetone (dba). The target complex was then dried *in vacuo* and used without further purification.



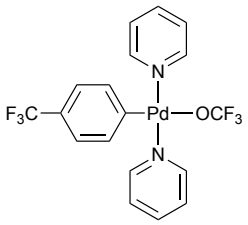
[(TMEDA)Pd(4-CF_3-Ph)(I)] 1a. Complex **1a** was obtained according to the general procedure as a yellow solid (20.0 mmol scale, 6.8 g, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 7.8 Hz, 2 H), 7.15 (d, J = 7.9 Hz, 2 H), 2.74 (t, J = 5.5 Hz, 2 H), 2.69 (s, 6 H), 2.57 (t, J = 5.5 Hz, 2 H), 2.32 (s, 6 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.74 (s) ppm. ^{1}H and ^{19}F NMR were consistent with those reported in the literature.[2]

Synthesis of [(4-CH_3-Py)$_2$Pd(4-CF_3-Ph)(I)] 1b. [(4-CH_3-Py)$_2$Pd(4-CF_3-Ph)(I)] was synthesized via a modified literature procedure.[3] $Pd(dba)_2$ (5.70 g, 10.0 mmol) was added to a solution of 4-iodobenzotrifluoride (6.80 g, 25.0 mmol) and 4-methylpyridine (9.30 g, 100 mmol) in THF (20.0 mL) at room temperature. The mixture was stirred at room temperature. After 15 min, a yellow precipitate was formed. The thick suspension was stirred at room temperature for another 30 min, and then hexane (30 mL) was added. The precipitate was filtered and washed with diethyl ether (50 mL × 4) and hexane (50 mL × 4) to give complex **1b** as yellow crystals (2.7 g, 48% yield). The complex was used directly without further purification.

General procedure for the synthesis of [L_2Pd(Aryl)(OCF_3)] 2a/b. In a glovebox under an argon atmosphere, a 20 mL scintillation vial equipped with an oven-dried stirring bar was charged with [L_2Pd(Ar)(I)] (1.0 mmol, 1.0 equiv), and THF (3.0 mL). To the orange solution, $AgOCF_3$ (1.0 M in acetonitrile, stored under an argon atmosphere at -35 °C) (1.1 mL, 1.1 mmol, 1.0 equiv.) was added slowly by a plastic syringe. The mixture was stirred violently at room temperature, and the color of the mixture turned from orange to yellow. Upon completion, the crude was filtered through a 0.22 μm microfiltration membrane® using THF (2.0 mL) as eluent. The filtrate was collected, concentrated to ~0.5 mL, then Et_2O (30 mL) was added. An off-white colored precipitate was formed. The mixture was stored in a -35 °C freezer for 1 h. The precipitate was collected by filtration and washed with Et_2O (10 mL × 2), and dried under vacuum to give [L_2Pd(Ar)(OCF_3)] as a solid.



[(TMEDA)Pd(4-CF_3-Ph)(OCF_3)] 2a. Complex **2a** was obtained according to the general procedure as a yellow solid (1.5 mmol scale, 461.9 mg, 68% yield). ^{1}H NMR (400 MHz, THF-d_8) δ 7.53 (d, J = 7.7 Hz, 2 H), 7.13 (d, J = 7.7 Hz, 2 H), 2.78 (t, J = 5.6 Hz, 2 H), 2.61 (t, J = 5.6 Hz, 2 H), 2.57 (s, 6 H), 2.42 (s, 6 H); ^{19}F NMR (376 MHz, THF-d_8) δ -31.98 (s, 3 F), -62.46 (s, 3 F) ppm. Anal. Calcd. for $C_{14}H_{20}F_6N_2OPd$: C, 37.14; H, 4.45; N, 6.19. Found: C, 37.18; H, 4.63; N, 6.35.

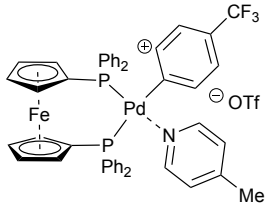


[*trans*-(4-CH_3-Py)$_2$Pd(4-CF_3-Ph)(OCF_3)] 2b. Complex **2b** was obtained according to the general procedure as a white solid (1.0 mmol scale, 315.3 mg, 60% yield). ^{1}H NMR (400 MHz, THF-d_8) δ 8.46 (d, J = 6.2 Hz, 4 H), 7.42 (d, J = 7.9 Hz, 2 H), 7.18 (d, J = 6.2 Hz, 4 H), 7.10 (d, J = 8.1 Hz, 2 H), 2.32 (s, 6 H); ^{19}F NMR (376 MHz, THF-d_8) δ -

31.40 (br, 3 F), -62.77 (s, 3 F); ^{19}F NMR (565 MHz, THF-d_8, 253 K) δ -31.34 (s, 3 F), -62.52 (s, 3 F) ppm. Anal. Calcd. for $C_{22}H_{18}F_6N_2OPd$: C, 45.95; H, 3.47; N, 5.36. Found: C, 45.93; H, 3.58; N, 5.35.

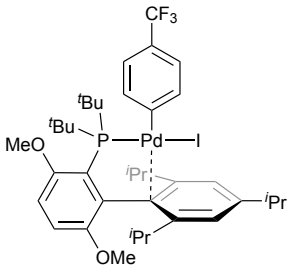
4-(Trifluoromethyl)benzoyl fluoride 2c. The yield (98%) and chemical shift were determined by ^{19}F NMR spectroscopy using (trifluoromethoxy)benzene (-58.0 ppm) as reference. Characterization of **2c** in reaction solution: ^{19}F NMR (unlocked) δ 18.81 (s, 1 F) -63.72 (s, 3 F) ppm. GC-MS (EI): 192 $[M]^+$.

Synthesis of [(DPPF)Pd(4-CH$_3$-Py)(4-CF$_3$-Ph)][OTf] 3c. In a glovebox under an argon atmosphere, a 25 mL round-bottom flask equipped with an oven-dried stirring bar was charged with **2b** (156.6 mg, 0.3 mmol), DPPF (166.3 mg, 0.3 mmol), toluene (3.0 mL) and THF (1.0 mL). After stirred at room temperature for 5 min, TMSOTf (80.0 mg, 0.36 mmol) was added. The mixture was stirred violently at room temperature for another 5 min, resulted in a yellow suspend. Upon completion, Et_2O (20 mL) was added and a precipitate was formed. The solvent was decanted and the residue was washed by a mixed solvent of Et_2O/THF (22 ml, v/v = 10:1) twice. Complex **3c** (270.3 mg, 87%) was obtained as a yellow solid.

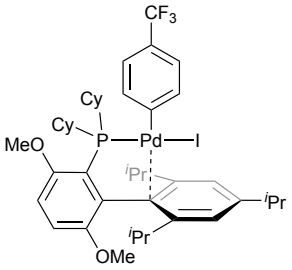


^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.94 (d, J = 5.7 Hz, 2 H), 7.60 – 7.39 (m, 20 H), 7.06 – 7.02 (m, 2 H), 6.77 – 6.72 (m, 2 H), 4.46 – 4.41 (m, 8 H), 2.14 (s, 3 H); ^{19}F NMR (376 MHz, CD_2Cl_2) δ -62.73 (s, 3 F), -78.85 (s, 3 F); ^{31}P NMR (162 MHz, CD_2Cl_2) δ 28.81 (d, J = 26.8 Hz), 16.30 (d, J = 26.9 Hz) ppm. Anal. Calcd. for $C_{48}H_{39}F_6FeNO_3P_2PdS$: C, 55.01; H, 3.75; N, 1.34; Found: C, 54.91; H, 3.95; N, 1.54. Single crystals of complex **3c** were obtained by layering a solution of complex **3c** in dichloromethane with ether at -35 °C.

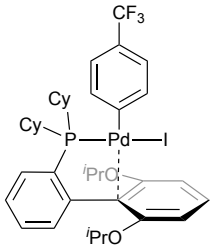
General procedure for the synthesis of complex [(L)Pd(Ar)(I)].[4] In an argon-filled glovebox, an oven-dried scintillation vial (20 mL) equipped with a magnetic stir bar was charged with ligand (1.1 equiv) and ArX (3.0 equiv). Cyclohexane was added dropwise with stirring until the ligand was dissolved. [(COD)Pd(CH_2SiMe_3)$_2$] (1.0 equiv) was added rapidly in one portion. The mixture was allowed to stir overnight at room temperature. Pentane (10.0 mL) was added and the mixture was placed into a -20 °C freezer for 1 h. The vial was then taken outside of the glovebox, and the precipitate was filtered through a sintered glass frit, washed with pentane for three times, and dried under reduced pressure to afford complex [(L)Pd(Ar)(I)].



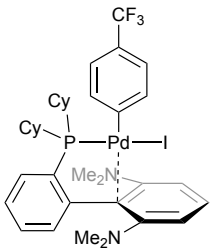
[(*t*Bu-BrettPhos)Pd(4-CF_3-Ph)(I)] 4a. Following the general procedure, a mixture containing *t*Bu-BrettPhos (1.07 g, 2.2 mmol), 4-iodobenzotrifluoride (1.63 g, 6.00 mmol), and [(COD)Pd(CH_2SiMe_3)$_2$] (0.78 g, 2.0 mmol) was stirred at room temperature in cyclohexane (7.0 mL) to afford complex **4a** (0.83 g, 40% yield) as a yellow solid. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.29 – 7.25 (m, 2 H), 7.11 – 7.07 (m, 2 H), 6.98 – 6.92 (m, 3 H), 6.85 (d, *J* = 8.8 Hz, 2 H), 3.79 (s, 3 H), 3.30 (s, 3 H), 3.12 – 3.08 (m, 1 H), 2.62 – 2.56 (m, 2 H), 1.60 (d, *J* = 6.7 Hz, 6 H), 1.46 – 1.29 (m, 24 H), 0.80 (d, *J* = 6.6 Hz, 6 H); ^{19}F NMR (376 MHz, CD_2Cl_2) δ -61.90 (s); ^{31}P NMR (162 MHz, CD_2Cl_2) δ 65.33 (s) ppm. Anal. Calcd. for $C_{38}H_{53}F_3IO_2PPd$: C, 52.88; H, 6.19; Found: C, 52.46; H, 6.05.



[(BrettPhos)Pd(4-CF_3-Ph)(I)] 4b. Following the general procedure, a mixture containing BrettPhos (1.18 g, 2.20 mmol), 4-iodobenzotrifluoride (1.63 g, 6.00 mmol), and [(COD)Pd(CH_2SiMe_3)$_2$] (0.78 g, 2.0 mmol) was stirred at room temperature in cyclohexane (5.0 mL) to afford complex **4b** (1.22 g, 67%) as a yellow solid. Clean ^{1}H NMR spectra for complex **4b** could not be obtained due to its very rapid isomerization in solution (1:1). ^{19}F NMR (376 MHz, CD_2Cl_2) δ -60.05 (s, 3 F), -60.25 (s, 3 F); ^{31}P NMR (162 MHz, CD_2Cl_2) δ 43.56 (s, 1 P), 34.05 (s, 1 P) ppm. Anal. Calcd. for $C_{42}H_{57}F_3IO_2PPd$: C, 55.12; H, 6.28; Found: C, 55.15; H, 6.27.

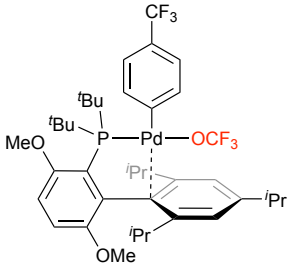


[(RuPhos)Pd(4-CF_3-Ph)(I)] 4c. Following the general procedure, a mixture containing RuPhos (1.0 g, 2.2 mmol), 4-iodobenzotrifluoride (1.63 g, 6.00 mmol), and [(COD)Pd(CH_2SiMe_3)$_2$] (0.78 g, 2.0 mmol) was stirred at room temperature in cyclohexane (4.0 mL) to afford complex **4c** (1.52 g, 90%) as a bright yellow solid. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.64 (d, *J* = 8.4 Hz, 1 H), 7.61 (d, *J* = 5.6 Hz, 1 H),7.45 (t, *J* = 7.5 Hz, 1 H), 7.38 (t, *J* = 7.5 Hz, 1 H), 7.25 (d, *J* = 7.8 Hz, 2 H), 7.14 (d, *J* = 8.1 Hz, 2H), 6.85 (dd, *J* = 7.7, 2.0 Hz, 1 H), 6.68 (d, *J* = 8.4 Hz, 2 H), 4.60 (hept, *J* = 6.0 Hz, 2 H), 2.16 – 2.09 (m, 2 H), 1.77 – 1.75 (m, 6 H), 1.67 – 1.64 (m, 4 H), 1.59 – 1.51 (m, 2 H), 1.39 (d, *J* = 6.0 Hz, 6 H), 1.24 – 1.16 (m, 4 H), 1.12 – 1.07 (m, 2 H), 1.02 (d, *J* = 6.1 Hz, 6 H), 0.72 – 0.66 (m, 2 H); ^{19}F NMR (471 MHz, CD_2Cl_2) δ -62.03 (s); ^{31}P NMR (202 MHz, CD_2Cl_2) δ 27.10 (s) ppm. Anal. Calcd. for $C_{37}H_{47}F_3IO_2PPd$: C, 52.59; H, 5.61; Found: C, 52.31; H, 5.62.

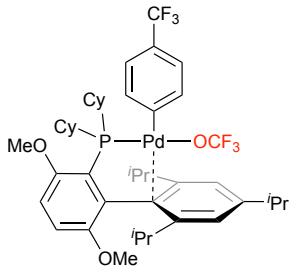


[(CPhos)Pd(4-CF_3-Ph)(I)] 4d. Following the general procedure, a mixture containing CPhos (0.44 g, 1.10 mmol), 4-iodobenzotrifluoride (1.36 g, 5.00 mmol), and [(COD)Pd(CH_2SiMe_3)$_2$] (0.39 g, 1.00 mmol) was stirred at room temp-erature in cyclohexane (7.0 mL) to afford complex **4d** (0.48 g, 59%) as a light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (t, *J* = 7.1 Hz, 1 H), 7.56 (t, *J* = 8.1 Hz, 1 H), 7.43 (t, *J* = 7.5 Hz, 1 H), 7.35 – 7.28 (m, 3 H), 7.13 (d, *J* = 7.9 Hz, 2 H), 7.05 (d, *J* = 6.5 Hz, 1 H), 6.88 (d, *J* = 8.1 Hz, 2 H), 2.60 (s, 12 H), 2.35 – 2.27 (m, 2 H), 2.02 – 1.98 (m, 2 H), 1.73 – 1.64 (m, 8 H), 1.50 (t, *J* = 15.7 Hz, 2 H), 1.29 – 1.02 (m, 6 H), 0.87 – 0.84 (m, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.87 (s); ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.63 (s) ppm. HRMS (ESI) calcd for $[M-I]^+$ $C_{35}H_{45}F_3N_2PPd$: 687.2307, found: 687.2289.

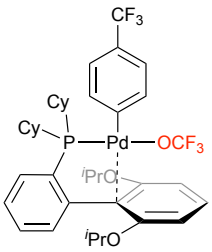
General procedure for the synthesis of complex [(L)Pd(Ar)(OCF$_3$)]. In an argon-filled glovebox, an oven-dried scintillation vial (10 mL) equipped with a magnetic stir bar was charged with complex [(L)Pd(Ar)(I)] (0.2 mmol, 1.0 equiv.). Toluene was then added dropwise by syringes with stirring until palladium complex was fully dissolved. A solution of AgOCF$_3$ in acetonitrile (1.0 M, 0.24 mL, 0.24 mmol, 1.2 eq) was added dropwise. The suspension was stirred rapidly for another 3.0 min. The mixture was filtered through a 0.22 μm microfiltration membrane® to a 50 mL round-bottom flask. The orange solution was then layered with n-pentane (30 mL). The solution was stored in a freezer for 12 h, and the resulted solid was collected, washed with n-pentane (10 mL × 3), dried under vacuum and stored in a freezer.



[(*t*Bu-BrettPhos)Pd(4-CF$_3$-Ph)(OCF$_3$)] 5a. Following the standard procedure, complex [(*t*Bu-BrettPhos)Pd(4-CF$_3$-Ph)(I)] **4a** (173 mg, 0.200 mmol, 1.00 equiv.) in toluene (5.0 mL) was reacted with a solution of AgOCF$_3$ in acetonitrile (1.0 M, 0.24 mL, 0.24 mmol) to afford complex **5a** (64 mg, 39 %) as a bright yellow solid. ^{1}H NMR (600 MHz, C$_6$D$_6$) δ 7.58 (d, *J* = 7.0 Hz, 2 H), 7.40 (s, 2 H), 7.17 (d, *J* = 10.1 Hz, 2 H), 6.33 (d, *J* = 8.8 Hz, 1 H), 6.25 (d, *J* = 6.3 Hz, 1 H), 3.28 – 3.25 (m, 1 H), 3.02 (s, 3 H), 2.84 (s, 3 H), 2.68 (hept, *J* = 6.6 Hz, 1 H), 1.86 (d, *J* = 6.2 Hz, 6 H), 1.44 (d, *J* = 6.8 Hz, 6 H), 1.25 (s, 9 H), 1.22 (s, 9 H), 0.94 (d, *J* = 6.3 Hz, 6 H); ^{19}F NMR (565 MHz, C$_6$D$_6$, **298 K)** δ -27.29 (br, 3 F), -61.39 (s, 3 F); ^{19}F NMR (565 MHz, C$_6$D$_6$, **283 K**) δ -27.18 (s, 3 F), -61.29 (s, 3 F); ^{31}P NMR (243 MHz, C$_6$D$_6$) δ 77.30 (s) ppm. Anal. Calcd. for C$_{39}$H$_{53}$F$_6$O$_3$PPd: C, 57.04; H, 6.51; Found: C, 57.20; H, 6.66.

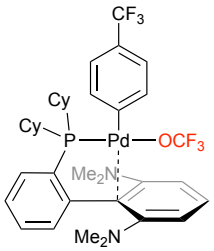


[(BrettPhos)Pd(4-CF_3-Ph)(OCF_3)] 5b. Following the standard procedure, complex [(BrettPhos)Pd(4-CF_3-Ph)(I)] **4b** (183 mg, 0.200 mmol, 1.00 equiv.) in toluene (6.0 mL) was reacted with a solution of $AgOCF_3$ in acetonitrile (1.0 M, 0.24 mL, 0.24 mmol) to afford the desired complex **5b** (88 mg, 51 %) as a bright yellow solid. The desired complex was obtained as a mixture of two rotamers *O*-bound and *C*-bound in a ratio of 5:1. ^{1}H NMR (600 MHz, C_6D_6, majority) δ 7.59 (d, *J* = 7.7 Hz, 2 H), 7.47 (s, 2 H), 7.29 – 7.25 (m, 2 H), 6.33 (d, *J* = 8.9 Hz, 1 H), 6.28 (dd, *J* = 8.9, 3.1 Hz, 1 H), 3.11 (s, 3 H), 2.85 (s, 3 H), complex spectrum due to its isomerization in solution; ^{19}F NMR (565 MHz, C_6D_6, 283 K) δ -28.01 (s, 3 F), -30.27 (s, 0.6 F), -61.32 (s, 3 F), -61.39 (s, 0.6 F); ^{31}P NMR (243 MHz, C_6D_6) δ 51.38 (s, 0.2 P), 42.42 (s, 1 P) ppm. Anal. Calcd. for $C_{43}H_{57}F_6O_3PPd$•(n-pentane)$_{0.23}$: C, 59.59; H, 6.77; Found: C, 59.80; H, 6.83.



[(RuPhos)Pd(4-CF_3-Ph)(OCF_3)] 5c. Following the standard procedure, complex [(RuPhos)Pd(4-CF_3-Ph)(I)] **4c** (169 mg, 0.200 mmol, 1.00 equiv.) in toluene (5.0 mL) was reacted with a solution of $AgOCF_3$ in acetonitrile (1.0 M, 0.24 mL, 0.24 mmol) to afford the desired complex **5c** (71 mg, 44 %) as a white solid. ^{1}H NMR (600 MHz, C_6D_6) δ 7.73 (t, *J* = 8.5 Hz, 1 H), 7.53 (d, *J* = 7.4 Hz, 2 H), 7.25 (d, *J* = 5.5 Hz, 2 H), 7.18 (d, *J* = 7.6 Hz, 1 H), 7.07 (t, *J* = 7.5 Hz, 1 H), 6.94 (t, *J* = 7.6 Hz, 1 H), 6.70 (d, *J* = 7.6 Hz, 1 H), 6.57 (d, *J* = 5.2 Hz, 2 H), 4.30 – 4.26 (m, 2 H), 1.97 (q, *J* = 12.0 Hz, 2 H), 1.86 – 1.84 (m, 2 H), 1.61 – 1.54 (m, 6 H), 1.51 – 1.45 (m, 4 H), 1.32 (d, *J* = 5.5 Hz, 6 H), 1.10 – 1.03 (m, 2 H), 1.00 – 0.90 (m, 4 H), 0.80 (d, *J* = 6.1 Hz, 6 H), 0.77 –

0.70 (m, 2 H); ^{19}F NMR (565 MHz, C_6D_6, **298K**) δ -27.52 (br, 3 F), -61.51 (s, 3 F); ^{19}F NMR (565 MHz, C_6D_6, **283 K**) δ -27.41 (s, 3 F), -61.38 (s, 3 F); ^{31}P NMR (243 MHz, C_6D_6) δ 37.98 (s) ppm. Anal. Calcd. for $C_{38}H_{47}F_6O_3PPd$•$(Toluene)_{0.16}(n\text{-}pentane)_{0.4}$: C, 58.33; H, 6.32; Found: C, 58.40; H, 6.44. The residual solvent was difficult to remove completely due to the week coordination.



[(CPhos)Pd(4-CF_3-Ph)(OCF_3)] 5d. Following the standard procedure, complex [(CPhos)Pd(4-CF_3-Ph)(I)] **4d** (163 mg, 0.200 mmol, 1.00 equiv.) in toluene (3.0 mL) was reacted with a solution of $AgOCF_3$ in acetonitrile (1.0 M, 0.24 mL, 0.24 mmol) to afford the desired complex **5d** (85 mg, 55 %) as a bright yellow solid. ^{1}H NMR (400 MHz, C_6D_6) δ 7.77 – 7.62 (m, 1 H), 7.53 (d, *J* = 5.5 Hz, 2 H), 7.28 – 7.23 (m, 3 H), 6.98 – 6.90 (m, 4 H), 6.85 – 6.80 (m, 1 H), 2.42 (s, 12 H), 2.16 – 2.09 (m, 2 H), 1.87 – 1.81 (m, 2 H), 1.64 – 1.61 (m, 2H), 1.57 – 1.40 (m, 6 H), 1.38 – 1.26 (m, 2H), 1.01 – 0.85 (m 6 H), 0.81 – 0.65 (m, 2 H); ^{19}F NMR (376 MHz, C_6D_6) δ -27.57 (s, 3 F), -61.54 (s, 3 F); ^{31}P NMR (162 MHz, C_6D_6) δ 34.73 (s) ppm. Anal. Calcd. for $C_{36}H_{45}F_6N_2OPPd$: C, 55.93; H, 5.87; N, 3.62; Found: C, 56.16; H, 5.99; N, 3.83.

Computational details. DFT calculations were performed using Gaussian 16.[5] Geometry optimizations and frequencies were performed at the B3LYP-D3(BJ)[6]/6-31G(d,p)-LANL2DZ[7](Pd) level of theory at 403.15 K. Frequency calculations confirmed that optimized structures are minima (no imaginary frequency) or transition structures (one imaginary frequency). To obtain more accurate electronic energies, single-point energy calculations were performed at the B97X-D[8]/6-311G(2d,p)-SDD[9](Pd) level of theory with the optimized structures. The SMD[10] model was used to account for the solvation effects of toluene when calculating the single-point energies.

B3LYP-D3(BJ)/6-31G(d,p)-LANL2DZ(Pd) calculated cartesian coordinates

int1.log

Pd	0.42764	0.18623	0.32692
O	0.96319	2.12965	0.87045
C	1.69041	2.91952	0.17067
F	3.04743	2.78137	0.32779
F	1.4926	2.82264	-1.20379
F	1.44717	4.2452	0.4653
C	2.4098	-0.10309	0.20584
C	3.02065	0.02138	-1.04609
C	3.211	-0.17813	1.34699
C	4.40967	0.00543	-1.16224
H	2.42709	0.14825	-1.9429
C	4.60008	-0.19943	1.23531
H	2.76561	-0.18928	2.33356
C	5.20231	-0.11916	-0.02125
H	4.87551	0.10416	-2.13685
H	5.21659	-0.25479	2.12632
C	6.69167	-0.22015	-0.14776
F	7.15856	0.43678	-1.23363
F	7.33172	0.27759	0.93457
F	7.09771	-1.51088	-0.27464
P	-0.25147	-2.05562	0.06879
C	0.49808	-2.9061	-1.4774
C	0.03488	-3.12853	1.65006
C	0.35356	-1.88854	-2.62045
H	-0.69088	-1.79001	-2.92415
H	0.72206	-0.90252	-2.34554
H	0.92195	-2.23925	-3.489

C	1.99326	-3.17689	-1.21661
H	2.14831	-4.00044	-0.51917
H	2.45947	-3.46497	-2.1657
H	2.52071	-2.30284	-0.84438
C	-0.15805	-4.21252	-1.95237
H	0.38852	-4.5477	-2.84214
H	-0.10956	-5.00768	-1.2111
H	-1.19949	-4.06383	-2.23939
C	1.27895	-2.56144	2.35031
H	1.47249	-3.14439	3.25823
H	2.16928	-2.6059	1.72162
H	1.12372	-1.52081	2.63774
C	-1.16582	-2.9474	2.59237
H	-2.0808	-3.37765	2.18462
H	-0.9435	-3.45721	3.53681
H	-1.33989	-1.89803	2.82311
C	0.25726	-4.63384	1.42529
H	0.39635	-5.09844	2.40858
H	-0.59468	-5.10705	0.94711
H	1.15525	-4.84448	0.84521
C	-2.09544	-1.9379	-0.18782
C	-2.70514	-0.66802	-0.23637
C	-2.92293	-3.08564	-0.29717
C	-4.10776	-0.57422	-0.4349
C	-4.28758	-2.97093	-0.53471
C	-4.88261	-1.71318	-0.60977
H	-4.90719	-3.85196	-0.6383
H	-5.94924	-1.64346	-0.78044
C	-2.03543	0.66899	-0.04682

C	-1.78691	1.48526	-1.18956
C	-2.1142	1.29277	1.23411
C	-1.59965	2.85451	-1.02691
C	-1.91333	2.66651	1.33568
C	-1.67272	3.47155	0.22232
H	-1.39203	3.45418	-1.90318
H	-1.94741	3.13052	2.31661
O	-2.3212	-4.29607	-0.11162
O	-4.62328	0.69189	-0.43132
C	-3.06687	-5.47875	-0.3452
H	-3.89852	-5.57683	0.36265
H	-3.45523	-5.51061	-1.3702
H	-2.3707	-6.30524	-0.1971
C	-6.01848	0.85208	-0.62253
H	-6.20258	1.92549	-0.57507
H	-6.33756	0.47234	-1.6016
H	-6.5934	0.34888	0.16522
C	-1.79092	0.91174	-2.59595
H	-1.78016	-0.17548	-2.50486
C	-0.55059	1.34162	-3.39741
H	-0.46551	0.74832	-4.31374
H	-0.61441	2.39372	-3.69182
H	0.36318	1.2296	-2.81175
C	-3.07724	1.29548	-3.35025
H	-3.15097	2.3828	-3.45654
H	-3.07627	0.85699	-4.35408
H	-3.96671	0.95106	-2.81949
C	-2.49411	0.51541	2.4827
H	-2.6013	-0.53353	2.1995

C	-3.85998	0.97514	3.02152
H	-4.1643	0.35932	3.87466
H	-3.82147	2.01701	3.35535
H	-4.62642	0.90111	2.24553
C	-1.4031	0.61294	3.56108
H	-1.28076	1.64242	3.91018
H	-1.65688	-0.00801	4.42716
H	-0.43531	0.28925	3.1662
C	-1.53039	4.97336	0.40434
H	-0.8129	5.11555	1.2206
C	-0.97971	5.70132	-0.82564
H	-1.68658	5.66522	-1.66295
H	-0.81044	6.75605	-0.58818
H	-0.03058	5.26721	-1.14382
C	-2.88023	5.57978	0.83398
H	-3.26828	5.10576	1.74045
H	-2.77684	6.65246	1.02825
H	-3.62739	5.44873	0.04296

Zero-point correction= 0.856360 (Hartree/Particle)

Thermal correction to Energy= 0.952254

Thermal correction to Enthalpy= 0.953530

Thermal correction to Gibbs Free Energy= 0.710302

SP-E = -2812.18609175 hartree

int2.log

Pd	0.51435	0.43556	0.32675
C	2.49824	0.22246	0.19326
C	3.10589	0.42202	-1.05292
C	3.31486	0.11059	1.32261

C	4.49407	0.43977	-1.17944
H	2.50203	0.56783	-1.94143
C	4.70419	0.12567	1.20381
H	2.87709	0.02846	2.30961
C	5.29853	0.27851	-0.05005
H	4.95172	0.58942	-2.15176
H	5.32721	0.03499	2.08762
C	6.78757	0.21226	-0.19016
F	7.2355	0.93607	-1.24243
F	7.42661	0.66526	0.91336
F	7.22081	-1.06043	-0.38839
P	-0.16823	-1.7978	0.05525
C	0.57819	-2.6107	-1.51171
C	0.13633	-2.90895	1.60337
C	0.40901	-1.57253	-2.63163
H	-0.64224	-1.45914	-2.9058
H	0.79314	-0.59686	-2.34071
H	0.95309	-1.908	-3.52175
C	2.08187	-2.8469	-1.26814
H	2.26664	-3.66522	-0.57136
H	2.5458	-3.12298	-2.22207
H	2.58895	-1.95777	-0.90059
C	-0.05621	-3.92014	-2.00624
H	0.492	-4.2336	-2.90308
H	0.00542	-4.72653	-1.27815
H	-1.10106	-3.78313	-2.28716
C	1.38213	-2.34011	2.30158
H	1.59066	-2.93309	3.19982
H	2.26683	-2.36672	1.66331

H	1.22074	-1.30382	2.60143
C	-1.05779	-2.76341	2.56009
H	-1.96839	-3.20237	2.15139
H	-0.81994	-3.28513	3.49437
H	-1.24876	-1.72144	2.80918
C	0.37183	-4.4066	1.3453
H	0.53283	-4.89076	2.31591
H	-0.4839	-4.87859	0.87175
H	1.26107	-4.59632	0.74452
C	-2.01581	-1.68706	-0.1968
C	-2.6298	-0.41737	-0.22484
C	-2.84029	-2.83448	-0.32138
C	-4.03325	-0.32433	-0.40839
C	-4.20739	-2.71998	-0.54662
C	-4.8067	-1.46271	-0.59469
H	-4.82547	-3.60076	-0.66157
H	-5.87516	-1.3937	-0.75399
C	-1.94665	0.90982	-0.01974
C	-1.68815	1.74975	-1.14761
C	-1.95349	1.49096	1.28091
C	-1.37618	3.08557	-0.94042
C	-1.62827	2.84071	1.42677
C	-1.31177	3.64608	0.33963
H	-1.14535	3.7083	-1.79791
H	-1.591	3.27058	2.42279
O	-2.23179	-4.04619	-0.16551
O	-4.55288	0.9409	-0.37593
C	-2.97595	-5.22648	-0.41276
H	-3.80019	-5.3405	0.30155

H	-3.37513	-5.24123	-1.4341
H	-2.27574	-6.05331	-0.28711
C	-5.95211	1.09679	-0.5388
H	-6.1418	2.16795	-0.46692
H	-6.28719	0.73463	-1.51926
H	-6.50977	0.57451	0.24896
C	-1.77574	1.22507	-2.57101
H	-1.80993	0.13511	-2.5167
C	-0.55059	1.62623	-3.40997
H	-0.52525	1.05957	-4.34646
H	-0.57899	2.68884	-3.6708
H	0.3793	1.4481	-2.8656
C	-3.06976	1.69477	-3.26045
H	-3.09309	2.78775	-3.32633
H	-3.12989	1.29298	-4.27786
H	-3.95273	1.37569	-2.70457
C	-2.37584	0.7055	2.51088
H	-2.51905	-0.33372	2.2083
C	-3.7298	1.21164	3.0389
H	-4.0671	0.60061	3.88316
H	-3.65284	2.24858	3.38182
H	-4.48944	1.17459	2.25387
C	-1.29916	0.74125	3.60714
H	-1.16322	1.75315	4.00006
H	-1.57756	0.09298	4.44503
H	-0.33309	0.41346	3.21196
C	-0.89237	5.08856	0.53237
H	-0.86327	5.27383	1.61359
C	0.52361	5.32214	-0.02334

H	0.52507	5.26129	-1.11767
H	0.88494	6.31829	0.25433
H	1.20285	4.55429	0.35105
C	-1.91218	6.0595	-0.08599
H	-2.91029	5.91568	0.34039
H	-1.61067	7.09793	0.08749
H	-1.98647	5.91188	-1.16901
F	1.08606	2.31504	0.61944

Zero-point correction= 0.839244 (Hartree/Particle)

Thermal correction to Energy= 0.929162

Thermal correction to Enthalpy= 0.930438

Thermal correction to Gibbs Free Energy= 0.700025

SP-E = -2499.13354140 hartree

COF2.log

C	0.	0.14302	0.
O	-0.00007	1.32317	0.
F	-1.06862	-0.6358	0.
F	1.06868	-0.63569	0.

Zero-point correction= 0.014136 (Hartree/Particle)

Thermal correction to Energy= 0.019161

Thermal correction to Enthalpy= 0.020437

Thermal correction to Gibbs Free Energy= -0.022606

SP-E = -313.022909842 hartree

LnPd.log

Pd	0.48751	-1.7759	0.38634
P	-1.58978	-0.99916	-0.23316
C	-2.0146	-1.29514	-2.06705

C	-2.97196	-1.6795	0.92639
C	-0.7974	-0.74957	-2.83022
H	-0.7159	0.3339	-2.7159
H	0.12935	-1.20019	-2.46397
H	-0.90083	-0.97063	-3.89953
C	-2.07549	-2.81932	-2.27348
H	-2.95036	-3.26909	-1.79735
H	-2.13452	-3.03869	-3.34634
H	-1.18002	-3.30291	-1.8709
C	-3.27518	-0.63464	-2.6429
H	-3.35861	-0.90548	-3.7034
H	-4.18767	-0.95668	-2.14243
H	-3.2175	0.45306	-2.58016
C	-2.48357	-3.0863	1.33922
H	-3.19614	-3.52013	2.05229
H	-2.41196	-3.75956	0.48086
H	-1.49495	-3.04221	1.80361
C	-3.01189	-0.79979	2.18697
H	-3.43606	0.18412	1.9831
H	-3.63421	-1.28782	2.94693
H	-2.01377	-0.66855	2.6122
C	-4.38848	-1.83989	0.35382
H	-5.0334	-2.269	1.13111
H	-4.8169	-0.8919	0.04405
H	-4.41028	-2.52866	-0.49398
C	-1.50071	0.88176	-0.04981
C	-0.25513	1.53768	0.16777
C	-2.66902	1.68364	-0.07441
C	-0.24008	2.93073	0.41996

C	-2.62107	3.05999	0.1233
C	-1.40542	3.68593	0.38306
H	-3.52296	3.65737	0.09618
H	-1.38888	4.75378	0.55885
C	1.07841	0.84195	0.1666
C	1.96429	0.93991	-0.91796
C	1.4271	0.03669	1.30989
C	3.14168	0.1625	-0.91612
C	2.59616	-0.76318	1.23626
C	3.44709	-0.72027	0.11092
H	3.80954	0.23188	-1.76765
H	2.90981	-1.32775	2.10862
O	-3.85402	1.03395	-0.28687
O	0.98539	3.47075	0.71801
C	-5.03546	1.79723	-0.44266
H	-5.28705	2.34841	0.47213
H	-4.95076	2.5033	-1.278
H	-5.8294	1.08024	-0.65689
C	1.04912	4.8521	1.02469
H	2.09563	5.05943	1.25124
H	0.73484	5.47084	0.17425
H	0.43265	5.09998	1.89821
C	1.72262	1.86421	-2.10683
H	0.67747	2.18975	-2.07482
C	1.96944	1.19083	-3.46956
H	1.62181	1.8428	-4.27823
H	3.03706	1.01452	-3.63601
H	1.45738	0.23261	-3.55741
C	2.61497	3.11741	-2.00591

H	3.67143	2.83434	-2.07126
H	2.40255	3.81108	-2.82767
H	2.461	3.63206	-1.05849
C	0.77567	0.30748	2.66629
H	-0.24362	0.65472	2.47534
C	1.53525	1.44724	3.37254
H	1.04116	1.71658	4.31293
H	2.55902	1.13343	3.6054
H	1.58988	2.33283	2.73664
C	0.68651	-0.92073	3.57972
H	1.67728	-1.26474	3.89501
H	0.12461	-0.67565	4.48741
H	0.18624	-1.74964	3.06896
C	4.64884	-1.64503	0.03846
H	4.77164	-2.09637	1.03197
C	4.38614	-2.78696	-0.96048
H	4.25223	-2.38894	-1.97204
H	5.22233	-3.49496	-0.98027
H	3.47476	-3.33136	-0.69363
C	5.95083	-0.90352	-0.30078
H	6.1407	-0.09327	0.40958
H	6.80365	-1.59035	-0.27612
H	5.91018	-0.46598	-1.30367

Zero-point correction= 0.738946 (Hartree/Particle)

Thermal correction to Energy= 0.811364

Thermal correction to Enthalpy= 0.812640

Thermal correction to Gibbs Free Energy= 0.622209

SP-E = -1830.56575062 hartree

phf.log

C	-2.39643	0.	0.00371
C	-1.73038	-1.21976	-0.00567
C	-0.33819	-1.21384	-0.02464
C	0.35541	-0.00003	-0.03671
C	-0.33817	1.21381	-0.02464
C	-1.73036	1.21976	-0.00567
H	-2.29459	-2.14529	-0.00129
H	0.20469	-2.152	-0.0355
H	0.20474	2.15196	-0.03552
H	-2.29454	2.1453	-0.00129
C	1.85325	-0.00001	-0.00147
F	2.33542	0.00038	1.26862
F	2.37975	1.08895	-0.6087
F	2.37979	-1.0893	-0.60807
F	-3.74731	0.00002	0.01972

Zero-point correction= 0.097033 (Hartree/Particle)

Thermal correction to Energy= 0.110097

Thermal correction to Enthalpy= 0.111279

Thermal correction to Gibbs Free Energy= 0.049558

SP-E = -668.533149047 hartree

TS1.log

Pd	-0.30921	-0.45829	0.51118
P	-0.31623	1.86687	0.22934
C	-1.45753	2.39063	-1.21386
C	-0.78673	2.83053	1.83541
C	-1.11081	1.44341	-2.37284
H	-0.09487	1.6152	-2.73585

H	-1.20322	0.39984	-2.07447
H	-1.80026	1.62525	-3.20541
C	-2.90401	2.10829	-0.76451
H	-3.27984	2.86339	-0.07279
H	-3.56318	2.11401	-1.63887
H	-3.00027	1.1344	-0.29303
C	-1.35512	3.82868	-1.7416
H	-2.09842	3.94573	-2.54005
H	-1.56179	4.5778	-0.97946
H	-0.37186	4.03194	-2.16904
C	-1.73865	1.90567	2.61687
H	-2.00834	2.38685	3.56482
H	-2.65868	1.70166	2.06676
H	-1.26511	0.94584	2.83479
C	0.4819	3.03934	2.67668
H	1.18518	3.72166	2.19699
H	0.19532	3.47242	3.64222
H	0.9893	2.0974	2.88009
C	-1.48347	4.19004	1.65863
H	-1.70232	4.58991	2.6563
H	-0.8526	4.90555	1.13935
H	-2.43472	4.10875	1.13275
C	1.44257	2.32411	-0.21188
C	2.42431	1.31328	-0.33541
C	1.84841	3.67245	-0.38047
C	3.7641	1.67684	-0.63088
C	3.15691	4.0026	-0.71485
C	4.11871	3.00292	-0.84119
H	3.44992	5.03447	-0.85788

H	5.13669	3.27821	-1.08523
C	2.23188	-0.17196	-0.15239
C	2.14298	-1.01554	-1.29146
C	2.48128	-0.75881	1.11745
C	2.29687	-2.39462	-1.13839
C	2.60337	-2.14858	1.21616
C	2.54092	-2.98533	0.10225
H	2.22811	-3.02202	-2.01847
H	2.78742	-2.59074	2.19119
O	0.89757	4.62643	-0.16049
O	4.66308	0.64445	-0.68286
C	1.20204	5.97994	-0.44709
H	1.99671	6.36227	0.20513
H	1.49804	6.11043	-1.49502
H	0.28438	6.53892	-0.25953
C	6.01923	0.94886	-0.95869
H	6.54779	-0.00455	-0.9375
H	6.13737	1.40619	-1.94954
H	6.44493	1.61772	-0.19982
C	1.94739	-0.45568	-2.69179
H	1.65747	0.59257	-2.58957
C	0.83205	-1.18712	-3.45668
H	0.58358	-0.64897	-4.37718
H	1.14018	-2.19828	-3.74064
H	-0.07199	-1.27509	-2.85144
C	3.25987	-0.49559	-3.49591
H	3.59924	-1.52885	-3.62618
H	3.11471	-0.0599	-4.49048
H	4.05224	0.05317	-2.98435

C	2.7366	0.08576	2.35544
H	2.51473	1.12285	2.0969
C	4.2233	0.02598	2.74941
H	4.42696	0.69522	3.59236
H	4.50794	-0.98874	3.04727
H	4.85732	0.31757	1.90831
C	1.83124	-0.31648	3.52938
H	2.05003	-1.3315	3.87516
H	1.97537	0.3607	4.37809
H	0.77821	-0.28801	3.23277
C	2.81352	-4.47202	0.26988
H	2.30641	-4.78504	1.19011
C	2.28203	-5.34309	-0.87326
H	2.82457	-5.15361	-1.80641
H	2.41719	-6.40158	-0.63034
H	1.22044	-5.16358	-1.04977
C	4.32571	-4.69918	0.46246
H	4.71187	-4.12314	1.3087
H	4.54121	-5.75822	0.64083
H	4.8749	-4.38587	-0.43254
C	-2.26673	-1.2593	0.46792
C	-2.74458	-1.4662	-0.84509
C	-4.06479	-1.15862	-1.14454
C	-4.94092	-0.71055	-0.15153
C	-4.48683	-0.6222	1.17387
C	-3.17656	-0.93305	1.49588
H	-2.07984	-1.82724	-1.61766
H	-4.41598	-1.25862	-2.16616
H	-5.17219	-0.31144	1.95543

H	-2.83021	-0.88879	2.52063
C	-6.29786	-0.21842	-0.51815
F	-6.28158	1.10456	-0.85386
F	-7.18485	-0.33722	0.49771
F	-6.81369	-0.86916	-1.58761
O	-1.14108	-2.42771	1.06852
C	-1.05507	-3.57942	0.41665
F	-0.55658	-3.45774	-0.85016
F	-2.24461	-4.20631	0.2943
F	-0.22812	-4.4193	1.0808

Zero-point correction= 0.854155 (Hartree/Particle)

Thermal correction to Energy= 0.949563

Thermal correction to Enthalpy= 0.950839

Thermal correction to Gibbs Free Energy= 0.709177

SP-E = -2812.13102136 hartree

TS2.log

Pd	-0.42946	0.18716	-0.29143
O	-1.03181	1.46198	-2.29093
C	-1.53051	2.47431	-1.76274
F	-2.88143	2.67239	-1.89863
F	-1.37571	2.43629	-0.28259
F	-0.96945	3.70099	-2.0706
C	-2.36926	-0.22002	-0.01646
C	-2.85836	-0.19016	1.29272
C	-3.26811	-0.24149	-1.08482
C	-4.23162	-0.22403	1.53663
H	-2.18657	-0.14312	2.1392
C	-4.64021	-0.28668	-0.84092

H	-2.91127	-0.16367	-2.10102
C	-5.12511	-0.28844	0.46775
H	-4.60326	-0.19777	2.55538
H	-5.3349	-0.29355	-1.67402
C	-6.59613	-0.41562	0.72648
F	-6.96279	0.18021	1.8844
F	-7.33788	0.12824	-0.26328
F	-6.97539	-1.71589	0.82507
P	0.34153	-1.99846	-0.18917
C	-0.31862	-3.10474	1.22911
C	0.09393	-2.83234	-1.91128
C	-0.16623	-2.27035	2.51077
H	0.88756	-2.15619	2.77701
H	-0.60077	-1.27927	2.40925
H	-0.66806	-2.78449	3.33796
C	-1.80742	-3.40571	0.97069
H	-1.94856	-4.08524	0.12914
H	-2.21798	-3.89836	1.85937
H	-2.39149	-2.50785	0.78957
C	0.41116	-4.43713	1.47202
H	-0.09798	-4.93927	2.30336
H	0.38417	-5.10308	0.61214
H	1.44962	-4.28346	1.76623
C	-1.20297	-2.26164	-2.50788
H	-1.36211	-2.71679	-3.49231
H	-2.07561	-2.48314	-1.89098
H	-1.13631	-1.18035	-2.63675
C	1.25652	-2.40182	-2.81844
H	2.21914	-2.77876	-2.47056

H	1.07776	-2.8033	-3.82235
H	1.30409	-1.31747	-2.90868
C	-0.01182	-4.36622	-1.91311
H	-0.15265	-4.68574	-2.95211
H	0.88649	-4.84274	-1.53328
H	-0.87351	-4.72719	-1.35063
C	2.16951	-1.79564	0.13029
C	2.69479	-0.52225	0.43572
C	3.05838	-2.90103	0.10222
C	4.05987	-0.40372	0.80214
C	4.38519	-2.76778	0.49543
C	4.88465	-1.51984	0.86105
H	5.04964	-3.62179	0.49949
H	5.92321	-1.43256	1.15315
C	1.97356	0.7929	0.2992
C	1.56834	1.51521	1.4649
C	2.084	1.48909	-0.94007
C	1.23963	2.85911	1.34936
C	1.72245	2.84106	-0.99461
C	1.30499	3.54325	0.12823
H	0.91962	3.39583	2.23567
H	1.76515	3.3562	-1.94665
O	2.55675	-4.07893	-0.36814
O	4.49679	0.86563	1.06096
C	3.35689	-5.24697	-0.29085
H	4.2552	-5.16	-0.91312
H	3.64886	-5.46386	0.74371
H	2.73619	-6.06023	-0.66882
C	5.8676	1.05714	1.36915

H	5.99245	2.131	1.50877
H	6.15053	0.53622	2.29268
H	6.51369	0.71867	0.54941
C	1.52673	0.86336	2.83799
H	1.64301	-0.21258	2.69435
C	0.18609	1.11079	3.54922
H	0.09254	0.46604	4.42922
H	0.10328	2.14723	3.891
H	-0.65732	0.92317	2.88269
C	2.68762	1.34265	3.72867
H	2.62339	2.42337	3.89384
H	2.64652	0.84953	4.70599
H	3.65293	1.1315	3.26791
C	2.73007	0.86059	-2.16666
H	2.75602	-0.21927	-2.01311
C	4.19147	1.33523	-2.29056
H	4.675	0.85215	-3.14644
H	4.22872	2.41832	-2.4474
H	4.76609	1.1087	-1.39058
C	1.96354	1.1455	-3.46793
H	2.0844	2.18895	-3.7766
H	2.36125	0.52262	-4.2765
H	0.89271	0.96903	-3.35321
C	0.97819	5.02101	0.03656
H	0.87634	5.25842	-1.02751
C	-0.34952	5.38115	0.71898
H	-0.29858	5.22884	1.80293
H	-0.58397	6.43703	0.54878
H	-1.16046	4.77	0.32323

C	2.14228	5.85128	0.60778
H	3.08086	5.62823	0.09037
H	1.93978	6.92285	0.50699
H	2.28771	5.63515	1.67235

Zero-point correction= 0.855131 (Hartree/Particle)

Thermal correction to Energy= 0.950603

Thermal correction to Enthalpy= 0.951879

Thermal correction to Gibbs Free Energy= 0.710264

SP-E = -2812.16766748 hartree

TS3.log

Pd	-0.35734	-0.6131	0.69834
P	-0.09747	1.64511	0.22105
C	-1.21938	2.21698	-1.2161
C	-0.38748	2.7374	1.78309
C	-1.00863	1.18306	-2.33138
H	0.01198	1.21813	-2.71897
H	-1.21649	0.17471	-1.97645
H	-1.69148	1.40189	-3.16037
C	-2.67563	2.11267	-0.72191
H	-2.93626	2.91231	-0.02637
H	-3.35211	2.19361	-1.57954
H	-2.87561	1.15918	-0.23942
C	-0.97519	3.60958	-1.81469
H	-1.72453	3.77244	-2.59915
H	-1.07497	4.41094	-1.08483
H	0.01153	3.68263	-2.27468
C	-1.42265	1.98106	2.63802
H	-1.60456	2.54448	3.56118

H	-2.37555	1.8618	2.11934
H	-1.06506	0.98283	2.90029
C	0.92909	2.81947	2.57157
H	1.68416	3.40616	2.0461
H	0.73309	3.30438	3.53506
H	1.33707	1.83064	2.77978
C	-0.9156	4.16292	1.55313
H	-1.04547	4.63842	2.53297
H	-0.22179	4.76586	0.97453
H	-1.88941	4.17343	1.06222
C	1.693	1.85303	-0.29486
C	2.54089	0.72291	-0.38717
C	2.25865	3.13018	-0.53768
C	3.90931	0.90154	-0.70901
C	3.59342	3.27815	-0.89941
C	4.42314	2.16241	-0.9835
H	4.00937	4.25756	-1.09641
H	5.46397	2.29794	-1.24789
C	2.13321	-0.70808	-0.14979
C	1.81732	-1.55129	-1.25328
C	2.27421	-1.28028	1.14167
C	1.56308	-2.90095	-1.02096
C	2.00978	-2.64851	1.31411
C	1.62761	-3.46784	0.25764
H	1.29503	-3.53328	-1.86026
H	2.08471	-3.07778	2.30823
O	1.43518	4.20404	-0.36226
O	4.67061	-0.23787	-0.71985
C	1.90271	5.49474	-0.71278

H	2.74483	5.80446	-0.08194
H	2.20264	5.53924	-1.76671
H	1.06322	6.17131	-0.54806
C	6.05138	-0.11739	-1.01781
H	6.45811	-1.1271	-0.9559
H	6.21293	0.27664	-2.02938
H	6.56471	0.52686	-0.29285
C	1.79629	-1.03251	-2.68407
H	1.70795	0.0561	-2.63985
C	0.61484	-1.57701	-3.50337
H	0.52635	-1.03063	-4.44779
H	0.75607	-2.63336	-3.75325
H	-0.32937	-1.48423	-2.96419
C	3.11893	-1.36272	-3.4028
H	3.25052	-2.44798	-3.47349
H	3.11497	-0.95512	-4.41965
H	3.97537	-0.95795	-2.86321
C	2.78638	-0.47551	2.32755
H	2.77879	0.57838	2.03872
C	4.24582	-0.85485	2.63834
H	4.64219	-0.23256	3.44806
H	4.31478	-1.90198	2.95211
H	4.87529	-0.7265	1.75493
C	1.90084	-0.63236	3.57346
H	1.94482	-1.65035	3.97258
H	2.23161	0.04675	4.36635
H	0.85453	-0.41519	3.33865
C	1.27944	-4.92683	0.47882
H	1.32088	-5.10755	1.5604

C	-0.15359	-5.23062	0.00717
H	-0.2306	-5.15057	-1.0833
H	-0.44079	-6.25076	0.28345
H	-0.85819	-4.52201	0.44737
C	2.30259	-5.85622	-0.1957
H	3.3162	-5.66414	0.17018
H	2.05945	-6.90614	-0.00115
H	2.30589	-5.71077	-1.28159
C	-2.33839	-1.17752	0.64252
C	-2.78161	-1.53022	-0.6501
C	-4.08402	-1.2412	-1.02877
C	-4.9825	-0.67105	-0.1172
C	-4.56658	-0.44088	1.20143
C	-3.26586	-0.72061	1.59789
H	-2.09005	-1.99285	-1.34488
H	-4.41129	-1.45893	-2.04026
H	-5.26946	-0.03172	1.91983
H	-2.94851	-0.54164	2.61735
C	-6.32226	-0.21396	-0.57784
F	-6.28234	1.05129	-1.08866
F	-7.23451	-0.18515	0.423
F	-6.82643	-0.99604	-1.56329
F	-1.34376	-2.4443	1.26029

Zero-point correction= 0.837414 (Hartree/Particle)

Thermal correction to Energy= 0.926622

Thermal correction to Enthalpy= 0.927898

Thermal correction to Gibbs Free Energy= 0.700553

SP-E = -2499.09196060 hartree

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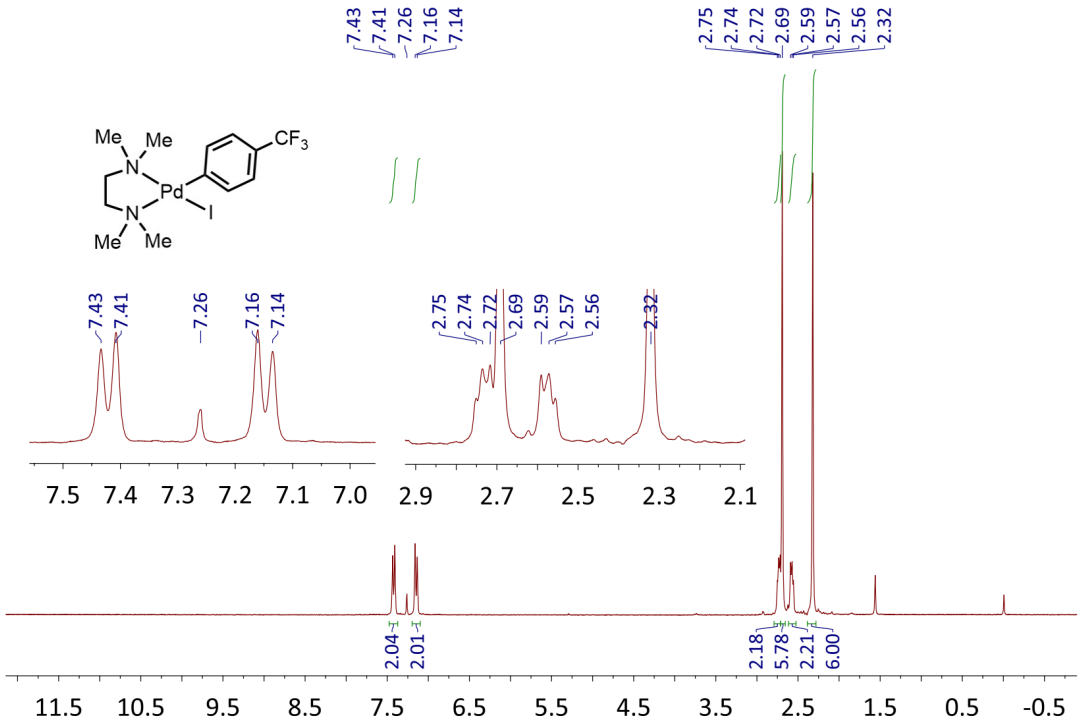
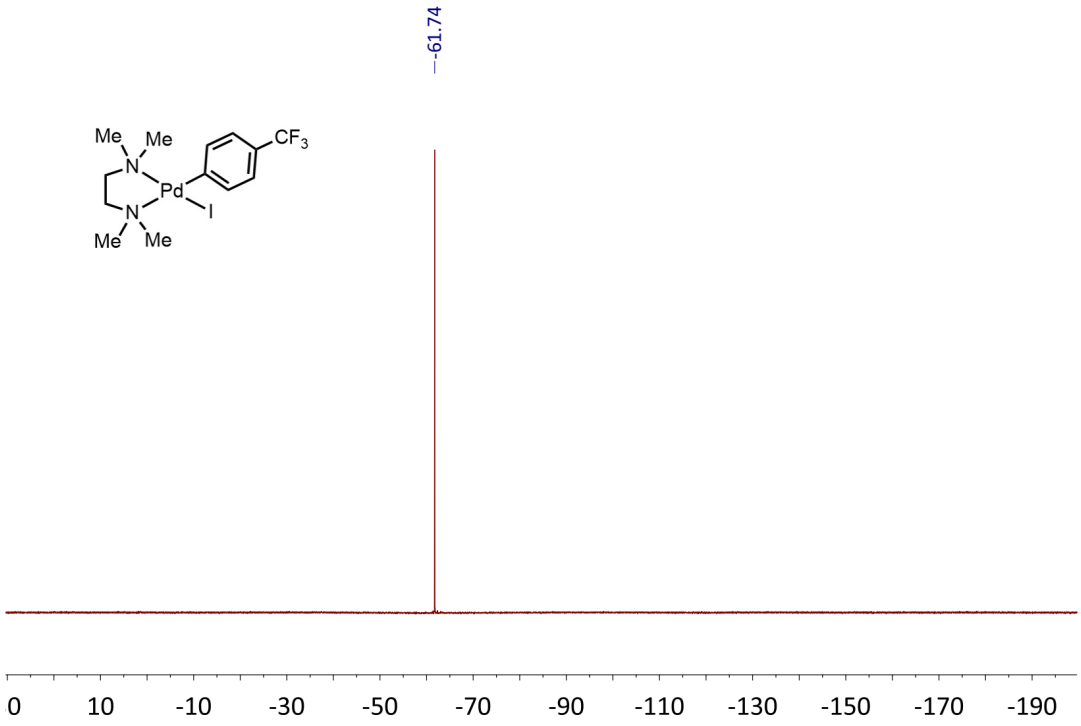
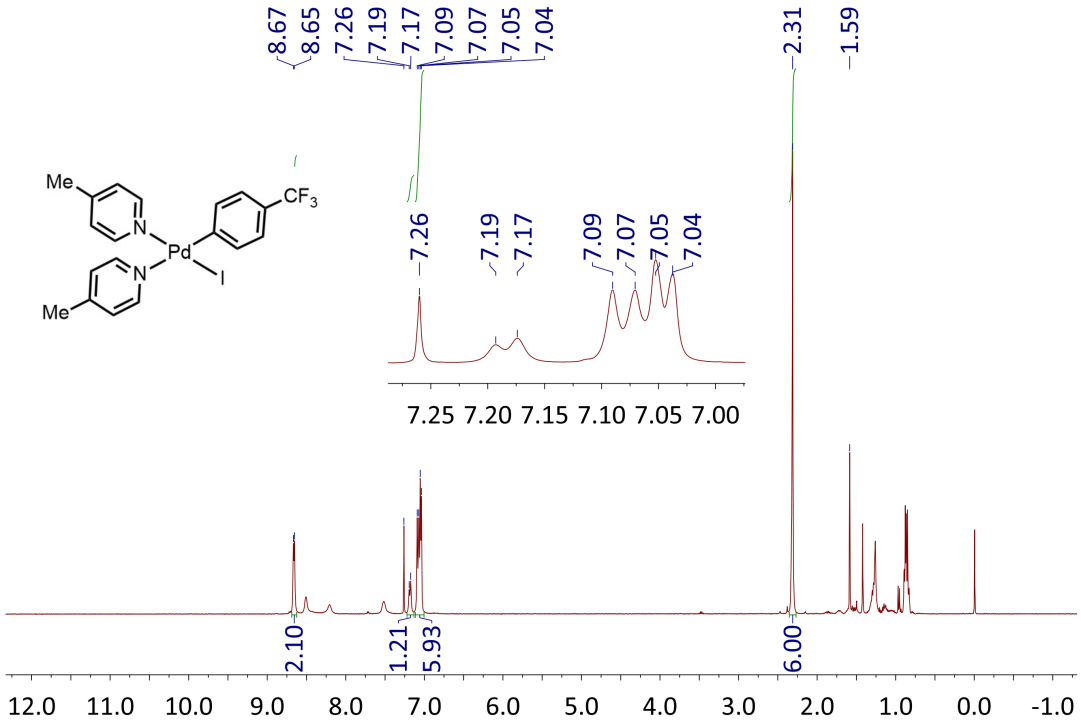
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of [(TMEDA)Pd(4-CF_3Ph)(I)] 1a



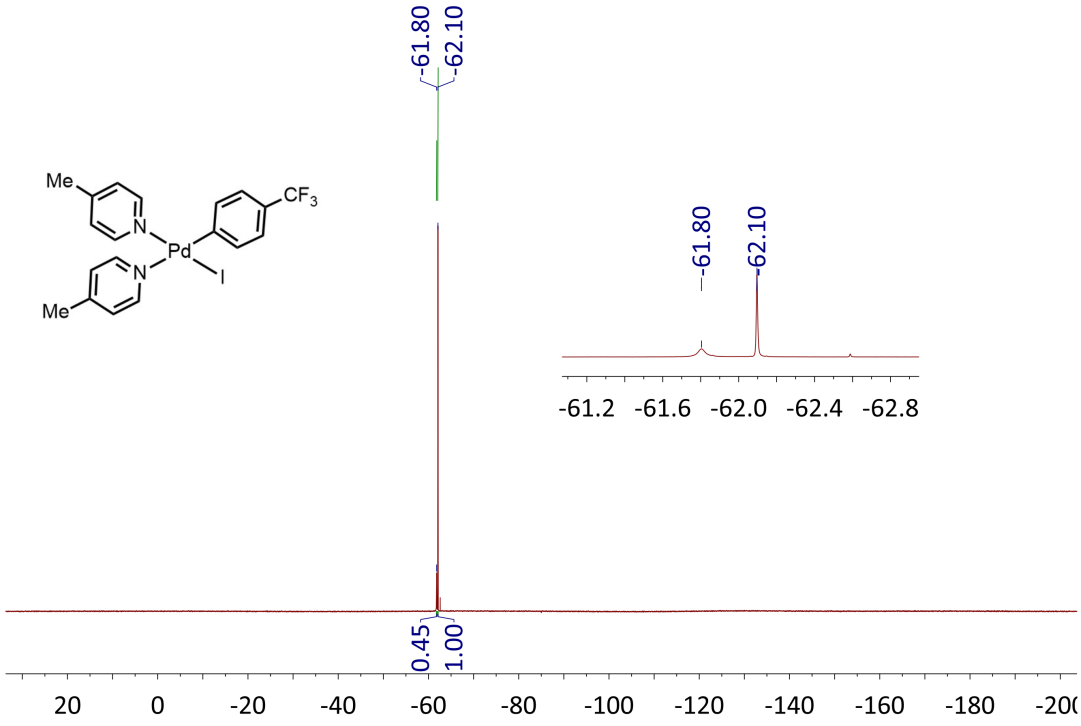
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of [(TMEDA)Pd(4-CF_3Ph)(I)] 1a



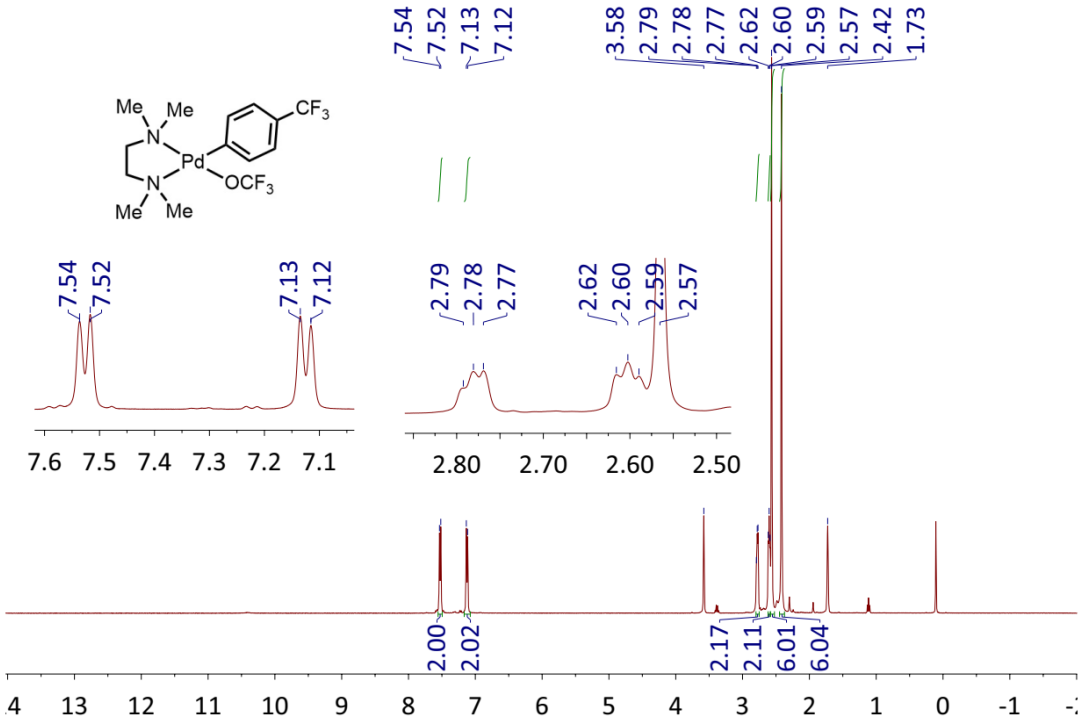
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of [*cis*-(4-MePy)$_2$Pd(4-CF_3Ph)(I)] 1b



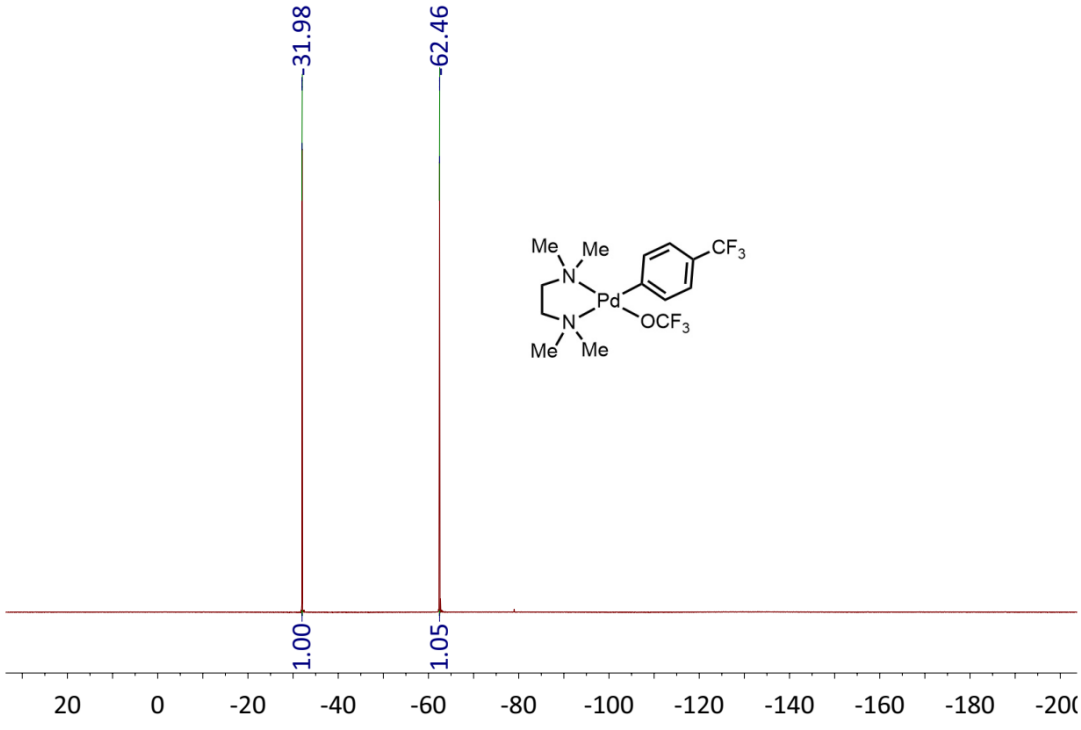
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of [*cis*-(4-MePy)$_2$Pd(4-CF_3Ph)(I)] 1b



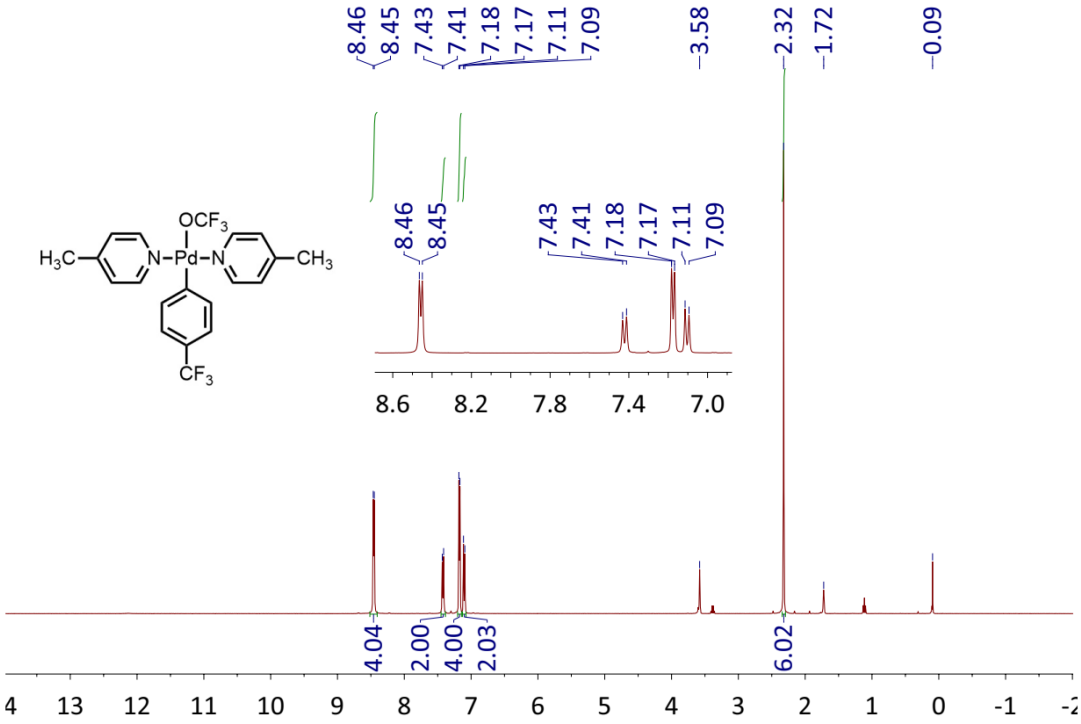
^{1}H NMR spectrum (400 MHz, THF-d_8) of [(TMEDA)Pd(4-CF_3Ph)(OCF_3)] 2a



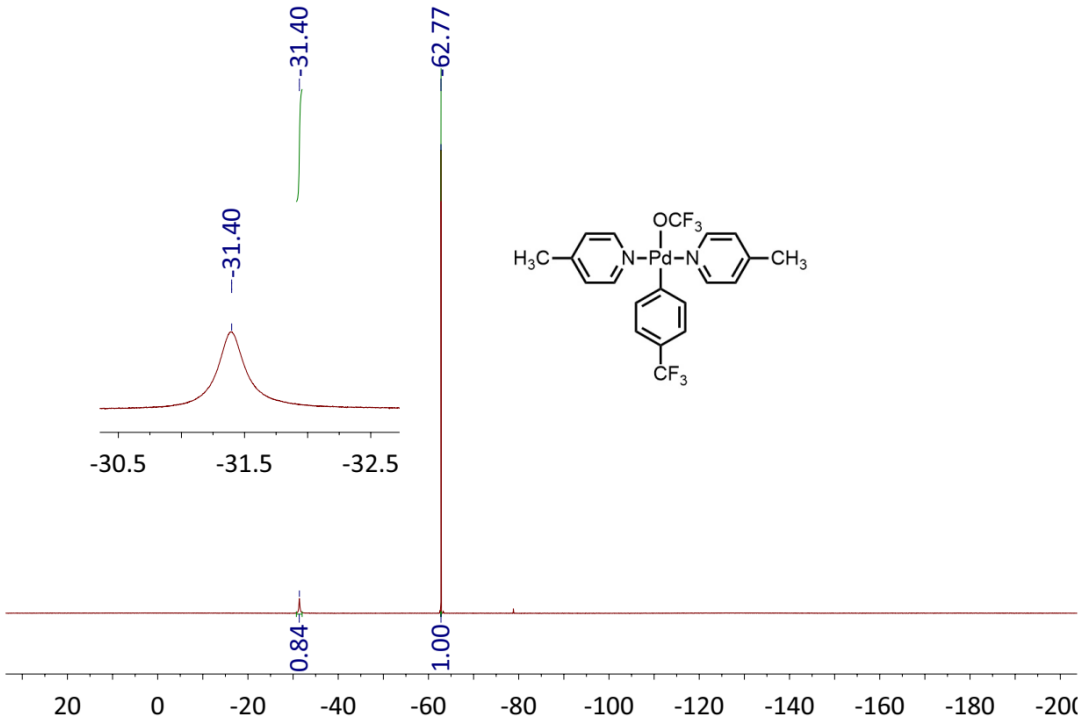
^{19}F NMR spectrum (376 MHz, THF-d_8) of [(TMEDA)Pd(4-CF_3Ph)(OCF_3)] 2a



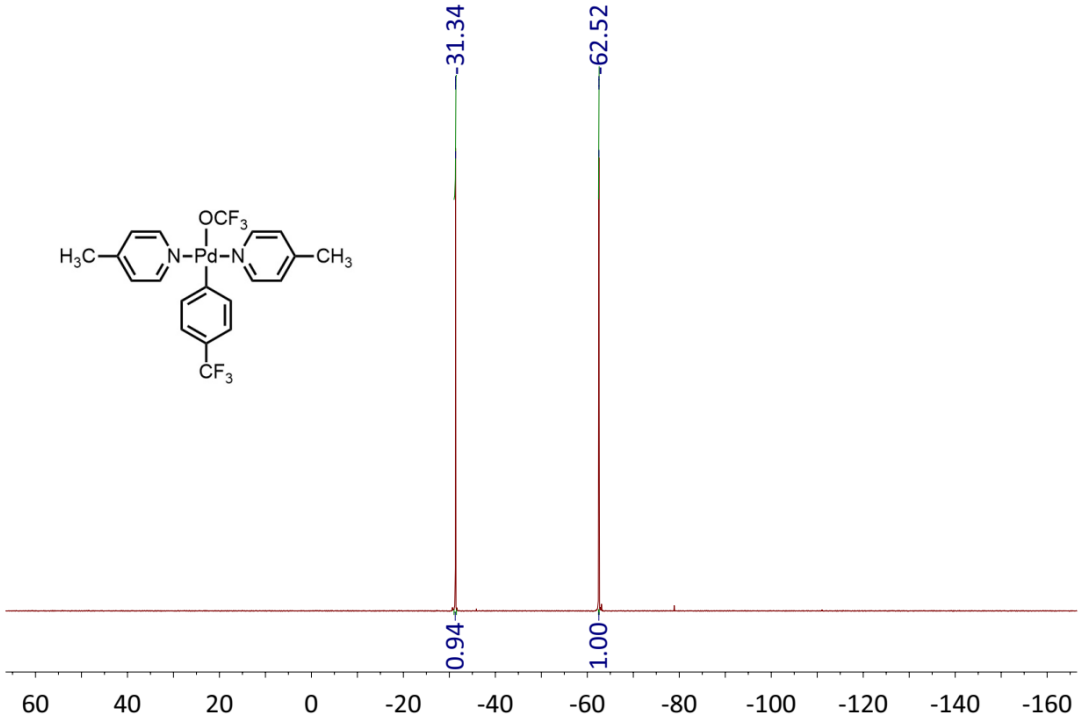
^{1}H NMR spectrum (400 MHz, THF-d_8) of [*trans*-(4-MePy)$_2$Pd(4-CF$_3$Ph)(OCF$_3$)] 2b



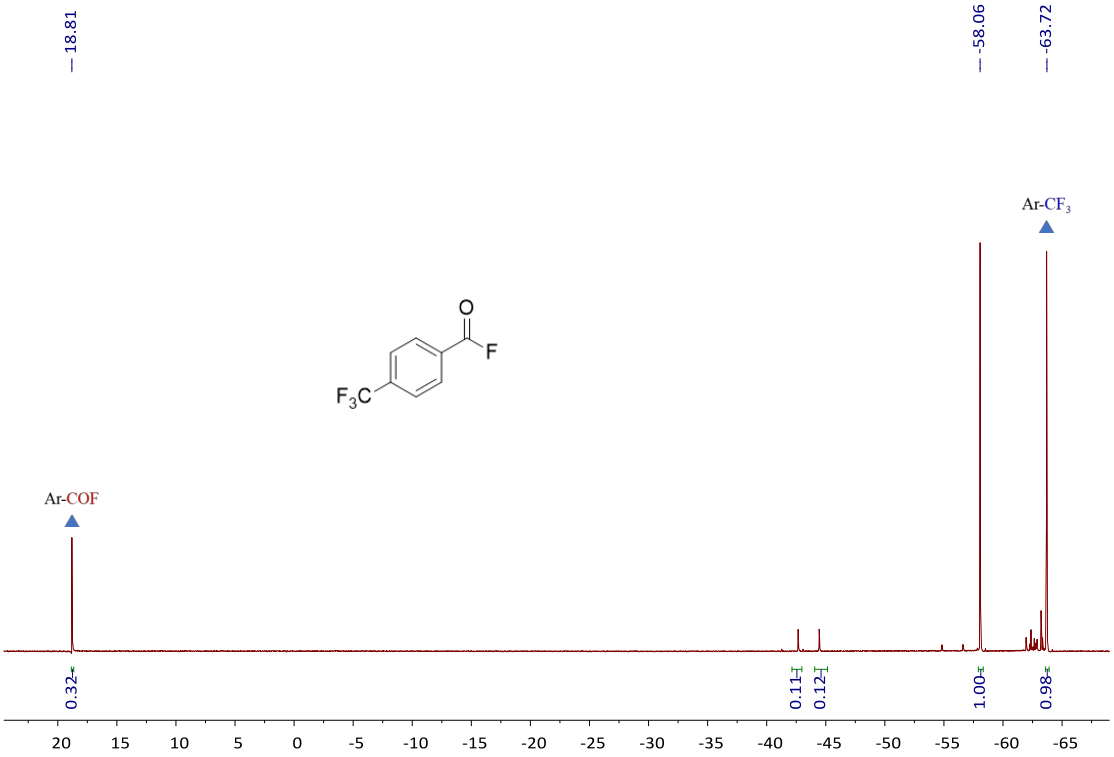
^{19}F NMR spectrum (400 MHz, THF-d_8) of [*trans*-(4-MePy)$_2$Pd(4-CF$_3$Ph)(OCF$_3$)] 2b



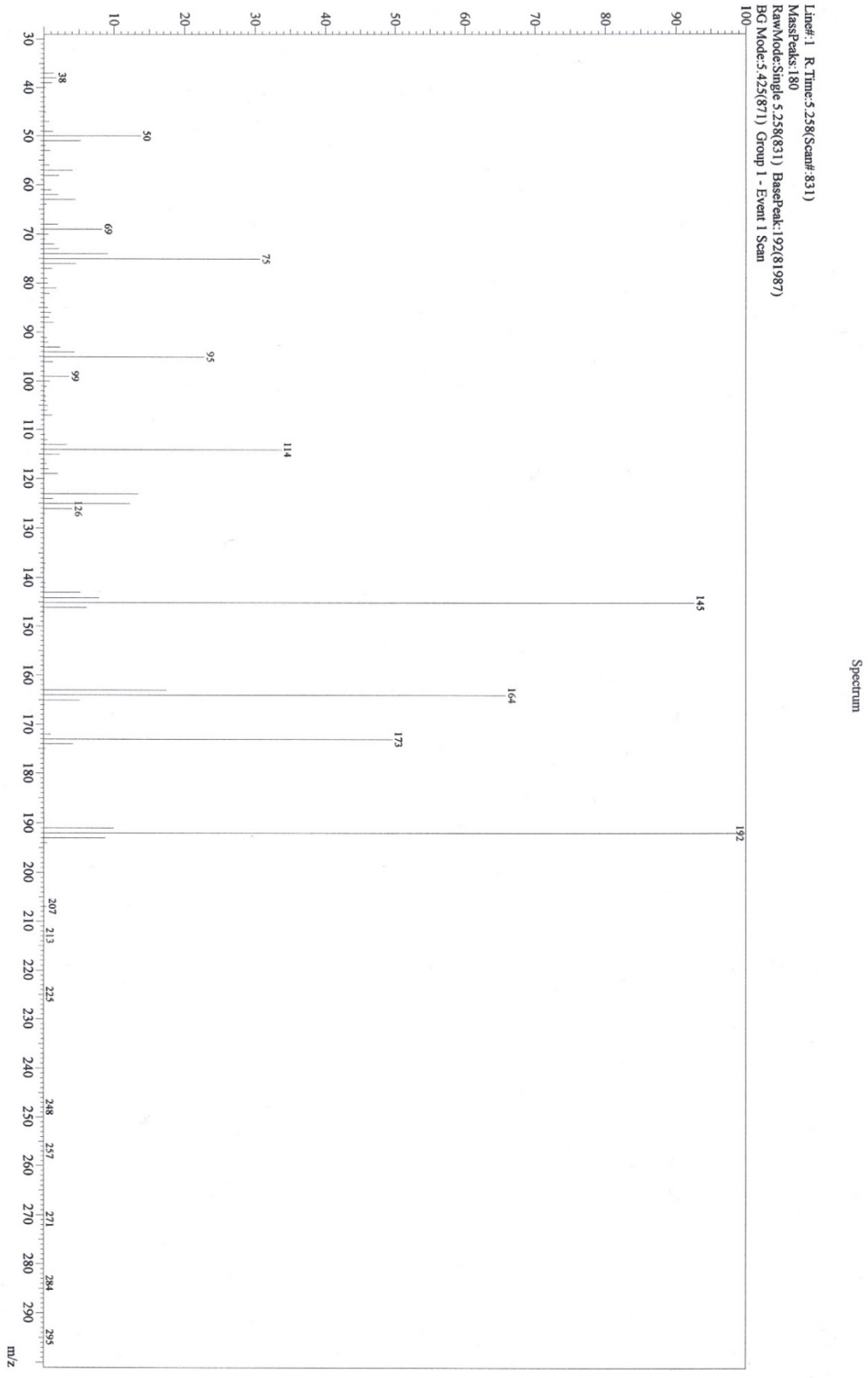
^{19}F NMR spectrum (565 MHz, THF-d_8, 253 K) of [*trans*-(4-MePy)$_2$Pd(4-CF$_3$Ph)(OCF$_3$)] 2b



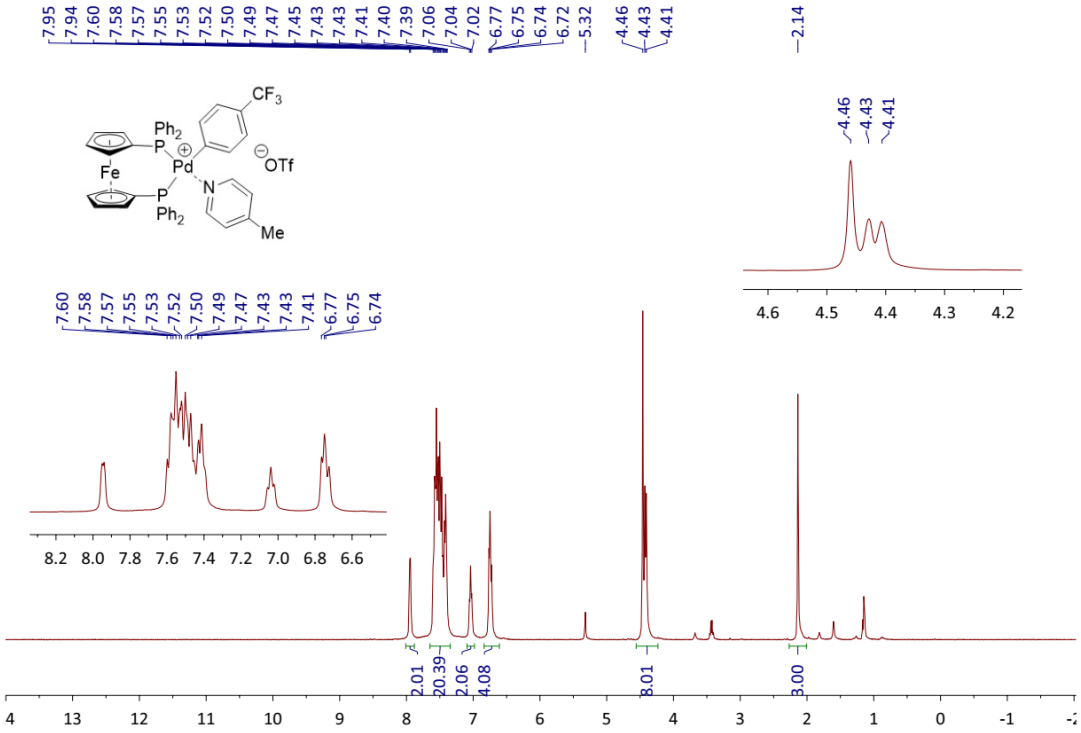
^{19}F NMR spectrum (376 MHz, unlocked) of 4-(trifluoromethyl)benzoyl fluoride 2c in solution.



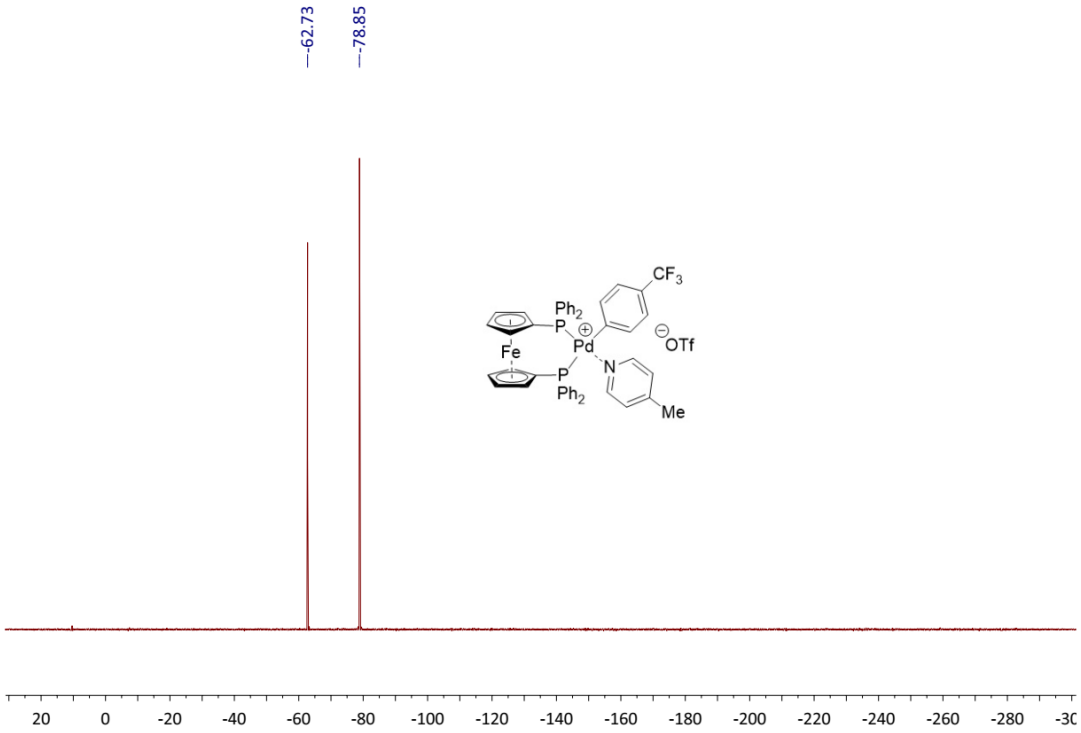
GC-MS of 4-(trifluoromethyl)benzoyl fluoride 2c.



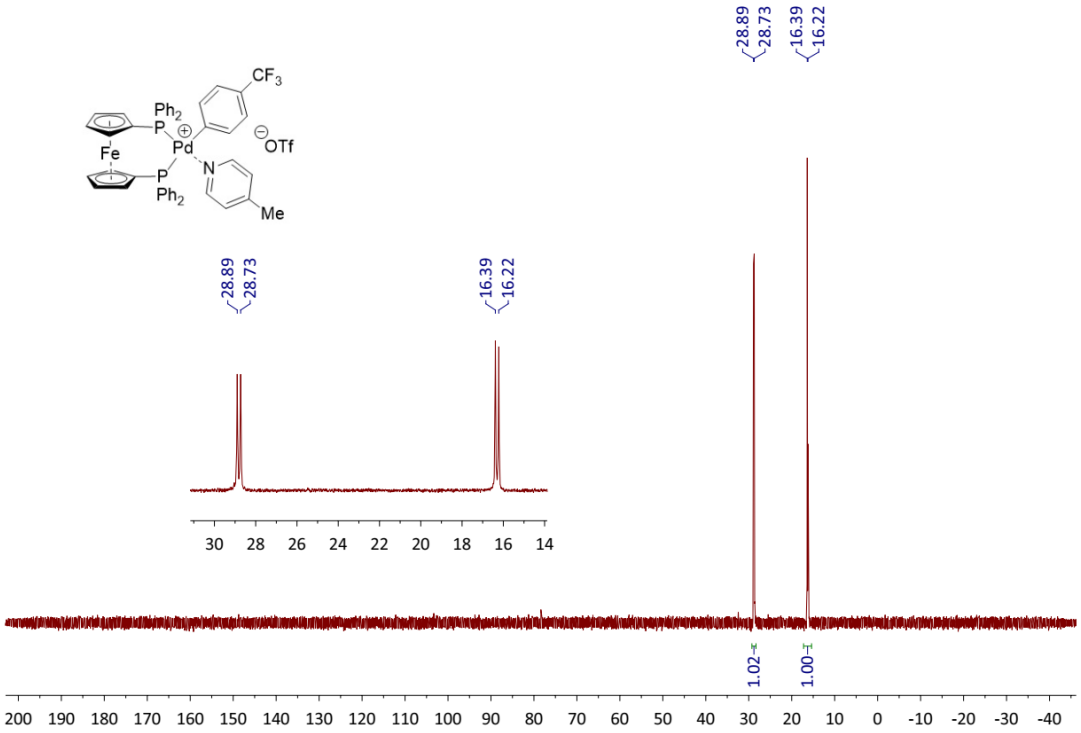
^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of [(DPPF)Pd(4-CH_3-Py)(4-CF_3-Ph)][OTf] 3c



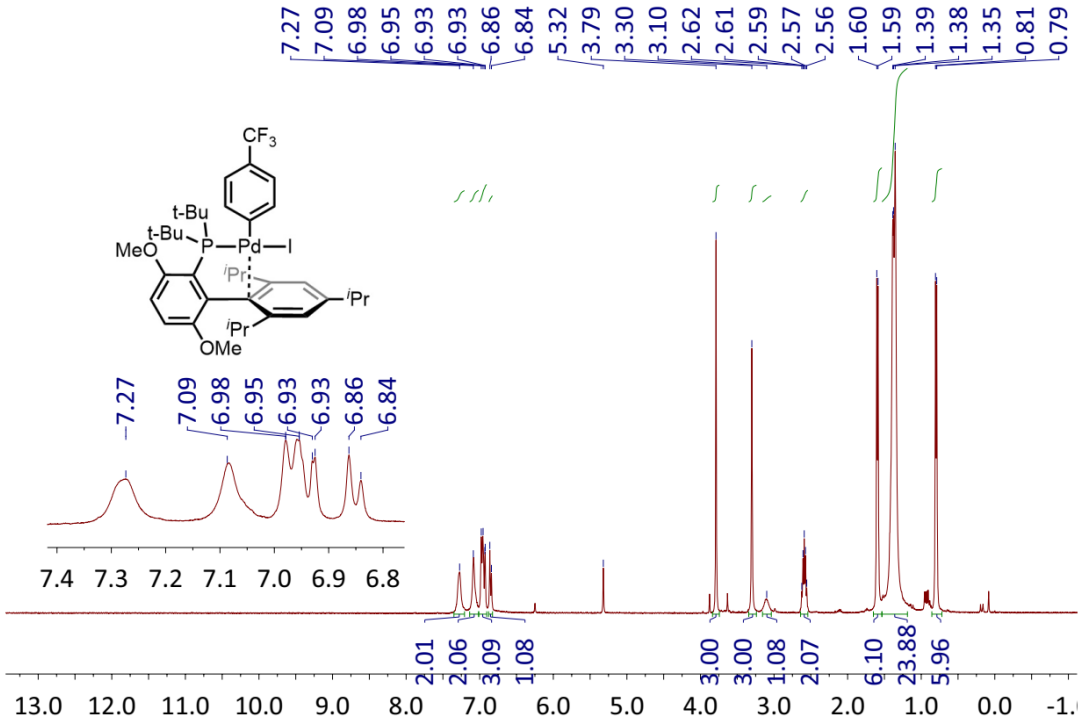
^{19}F NMR spectrum (400 MHz, CD_2Cl_2) of [(DPPF)Pd(4-CH_3-Py)(4-CF_3-Ph)][OTf] 3c



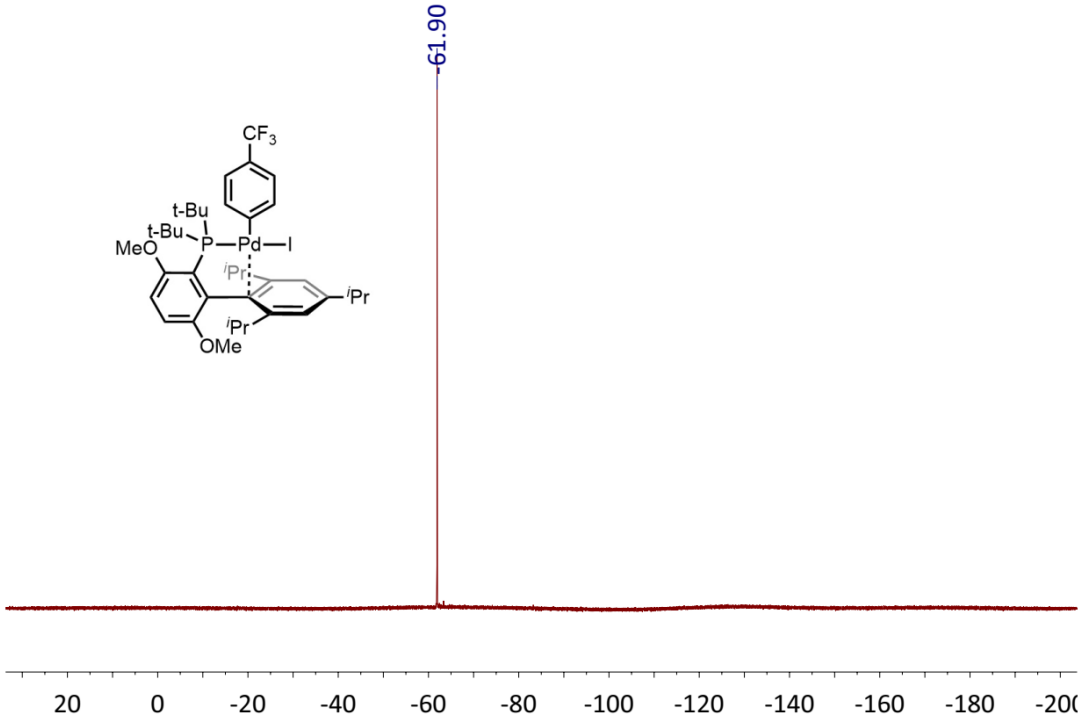
^{31}P NMR spectrum (400 MHz, CD_2Cl_2) of [(DPPF)Pd(4-CH_3-Py)(4-CF_3-Ph)][OTf] 3c



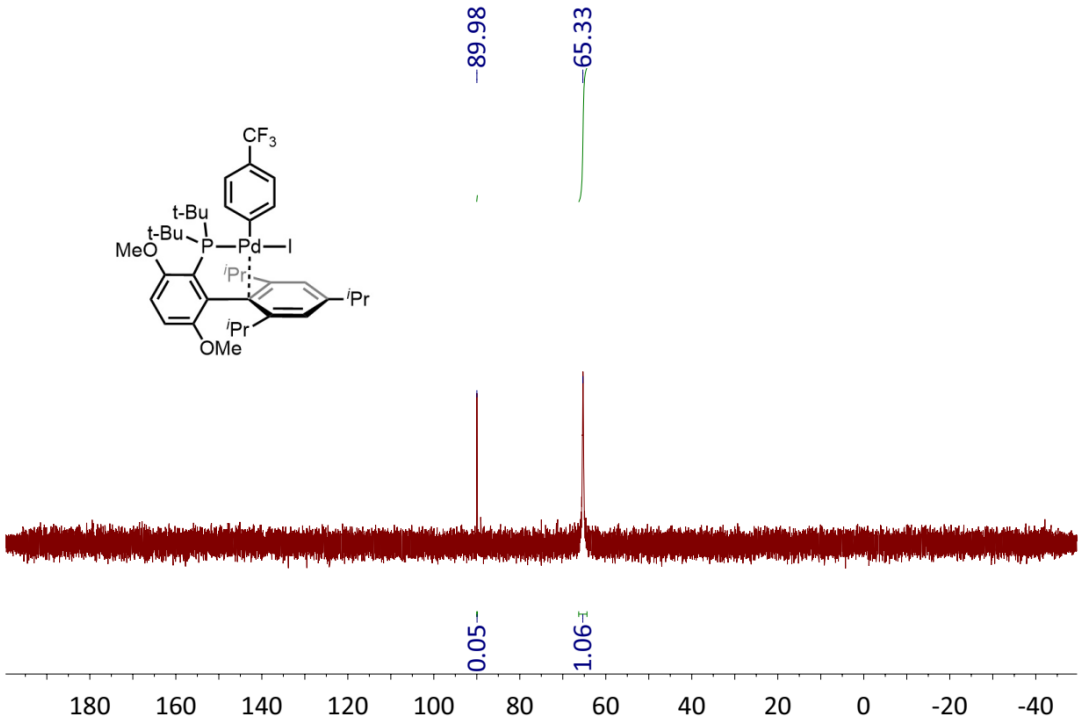
^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of [(^{t}Bu-BrettPhos)Pd(4-CF_3Ph)(I)] 4a



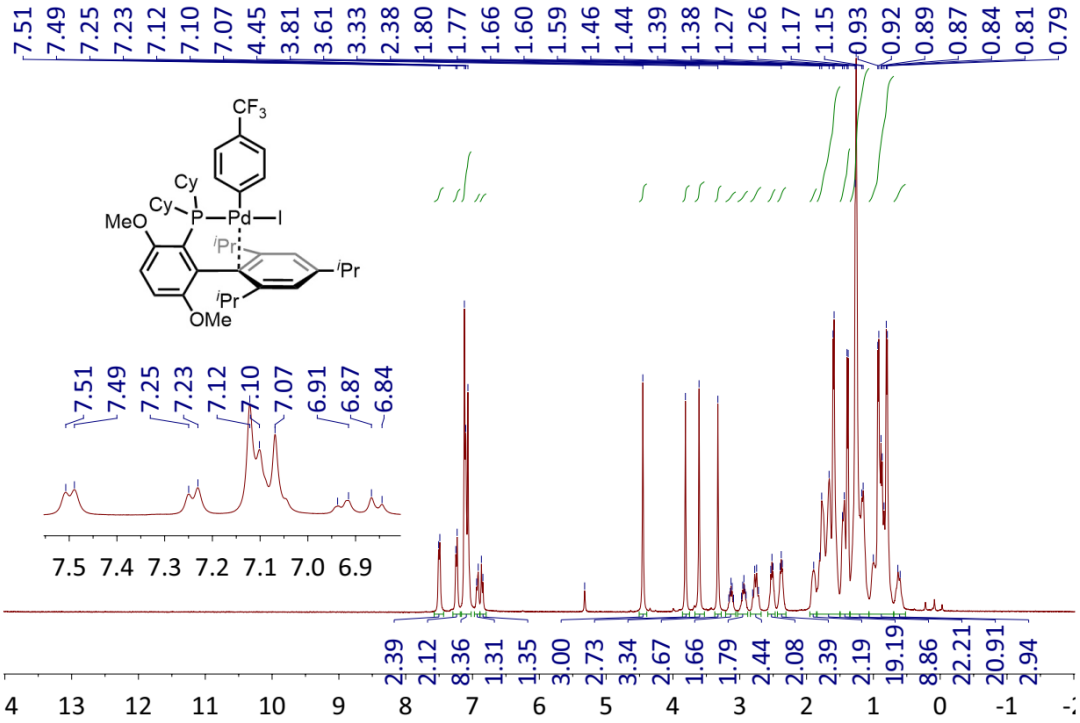
^{19}F NMR spectrum (376 MHz, CD_2Cl_2) of [(^{t}Bu-BrettPhos)Pd(4-CF_3Ph)(I)] 4a



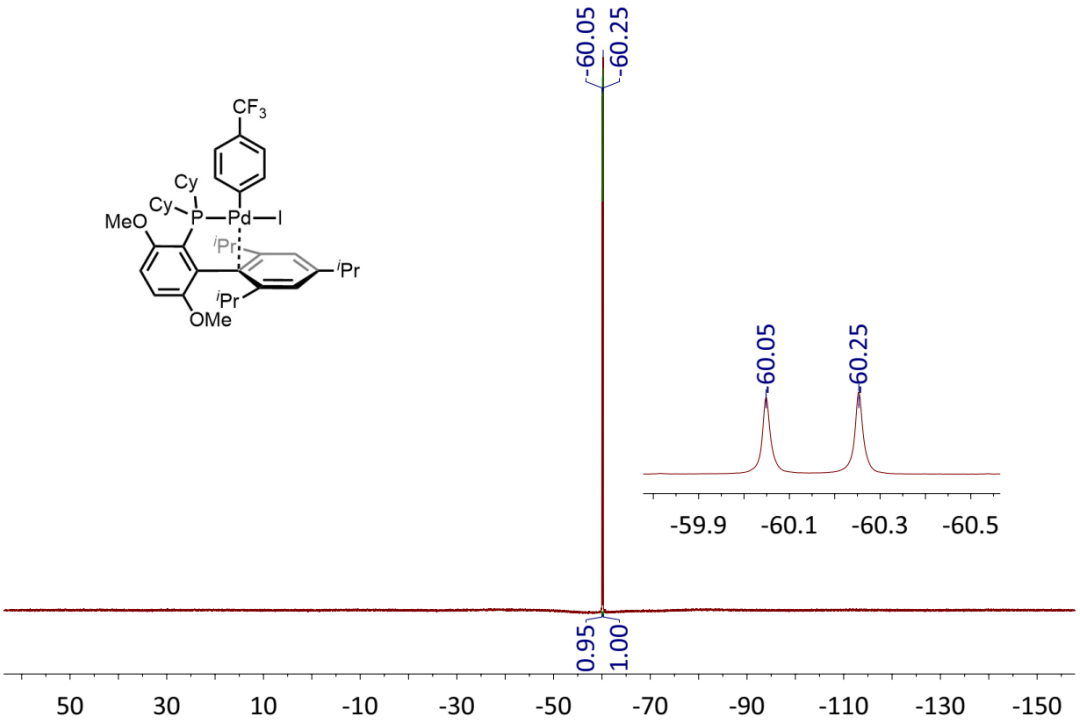
^{31}P NMR spectrum (162 MHz, CD_2Cl_2) of [(^{t}Bu-BrettPhos)Pd(4-CF_3Ph)(I)] 4a



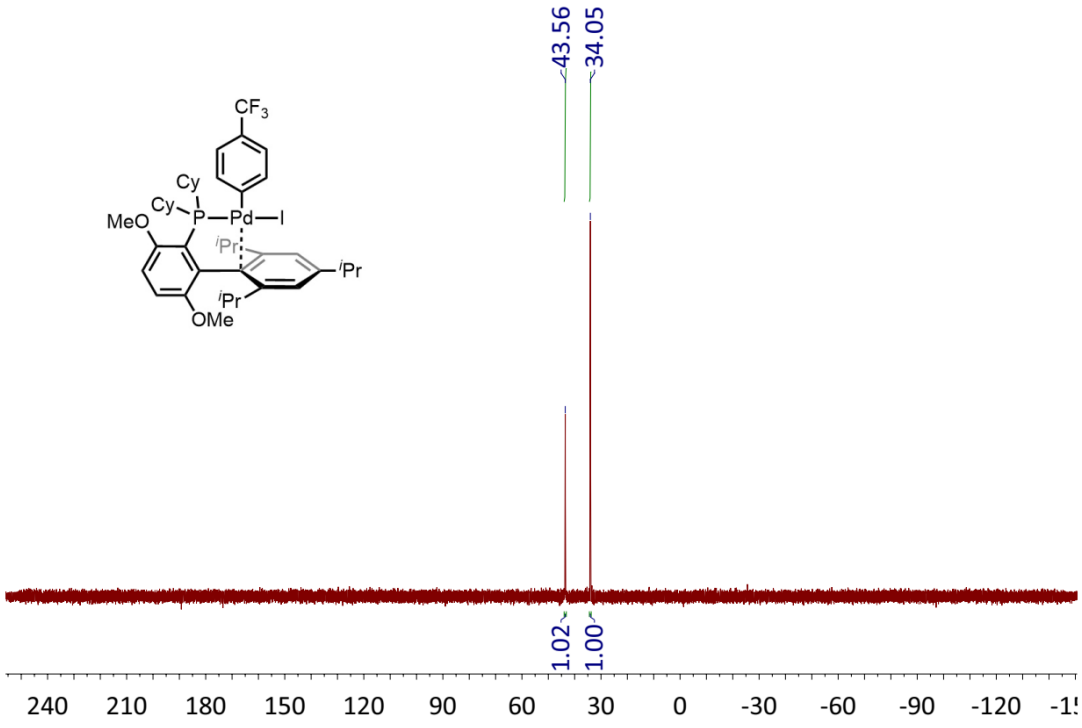
^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of [(BrettPhos)Pd(4-CF_3Ph)(I)] 4b



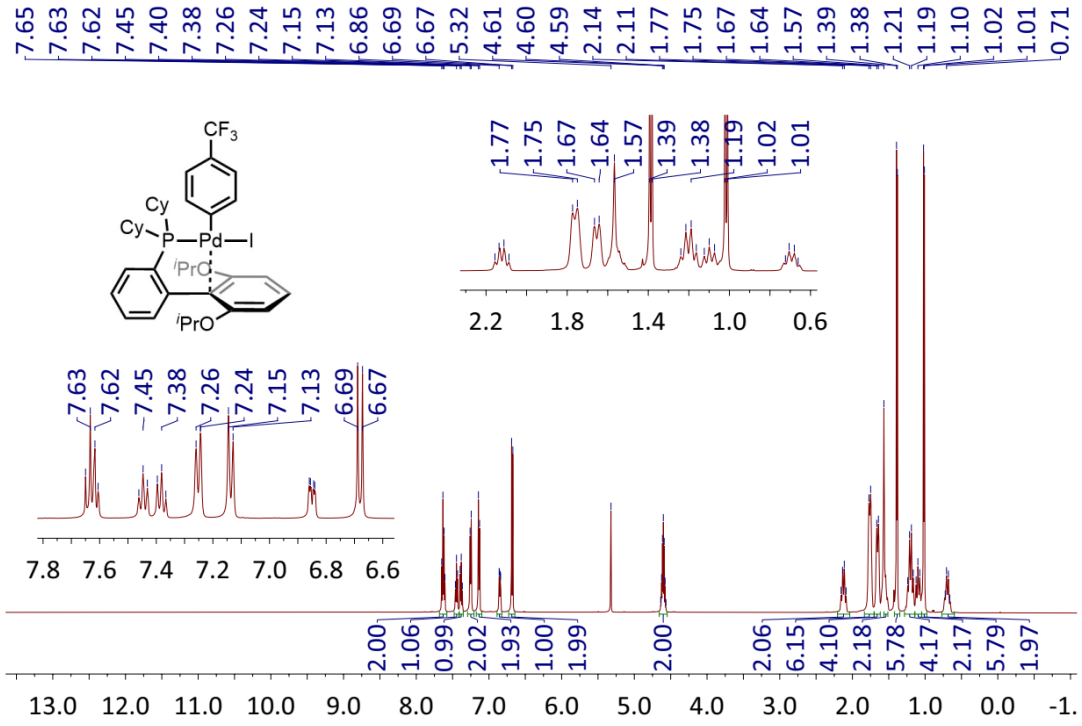
^{19}F NMR spectrum (376 MHz, CD_2Cl_2) of [(BrettPhos)Pd(4-CF_3Ph)(I)] 4b



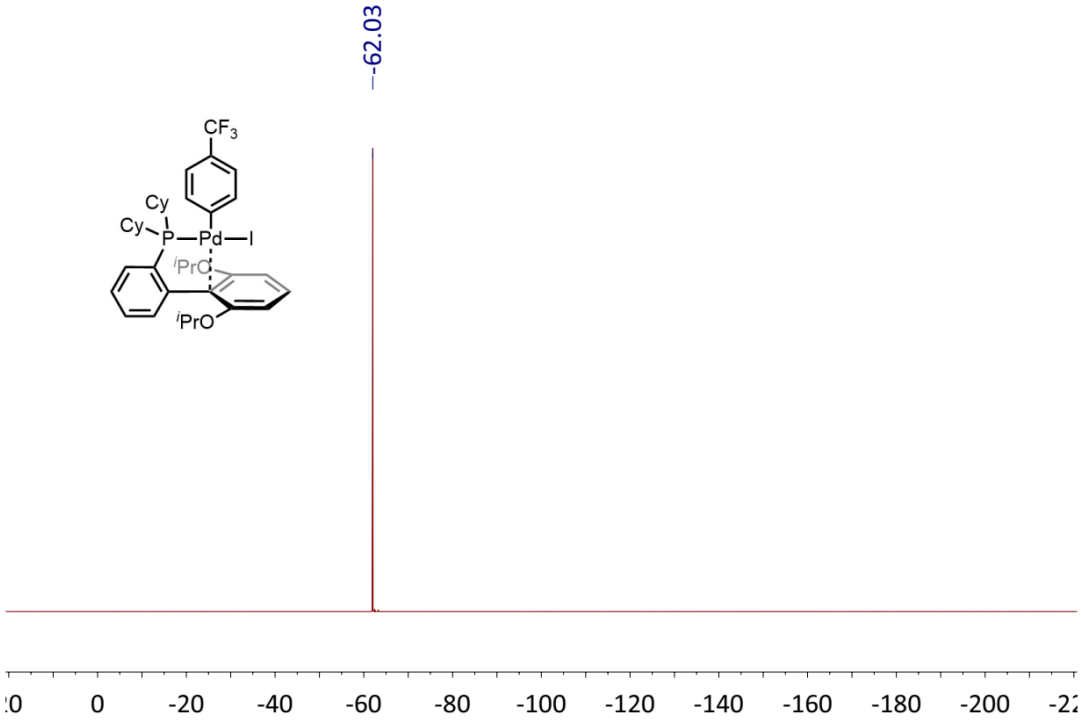
^{31}P NMR spectrum (162 MHz, CD_2Cl_2) of [(BrettPhos)Pd(4-CF_3Ph)(I)] 4b



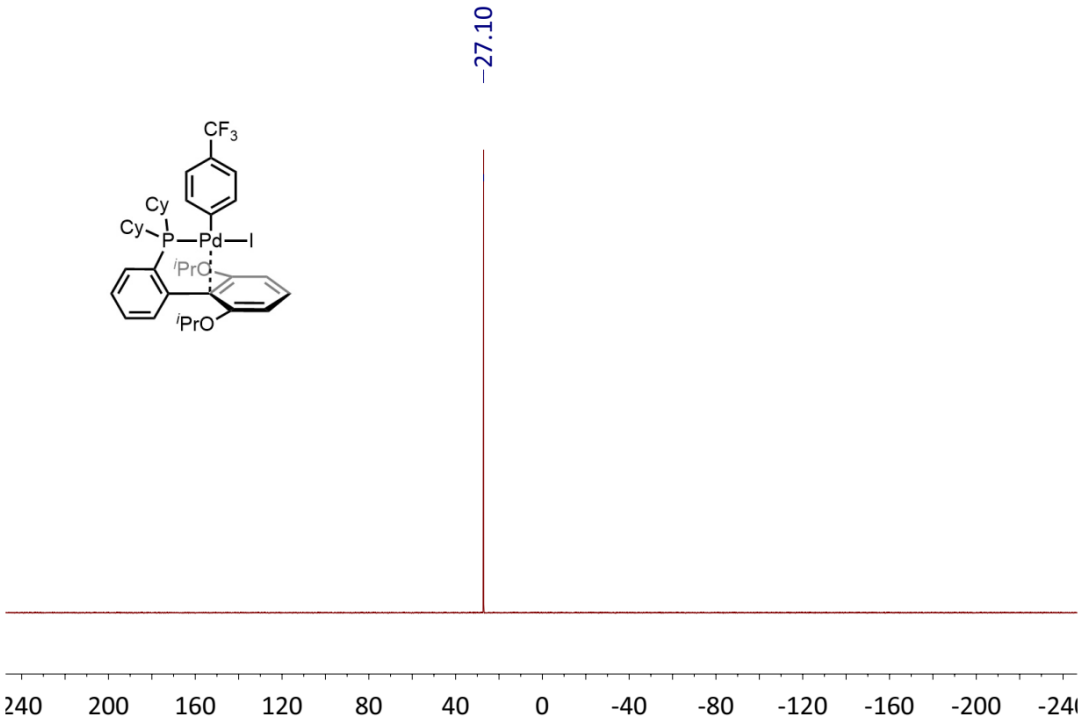
^{1}H NMR spectrum (500 MHz, CD_2Cl_2) of [(RuPhos)Pd(4-CF_3Ph)(I)] 4c



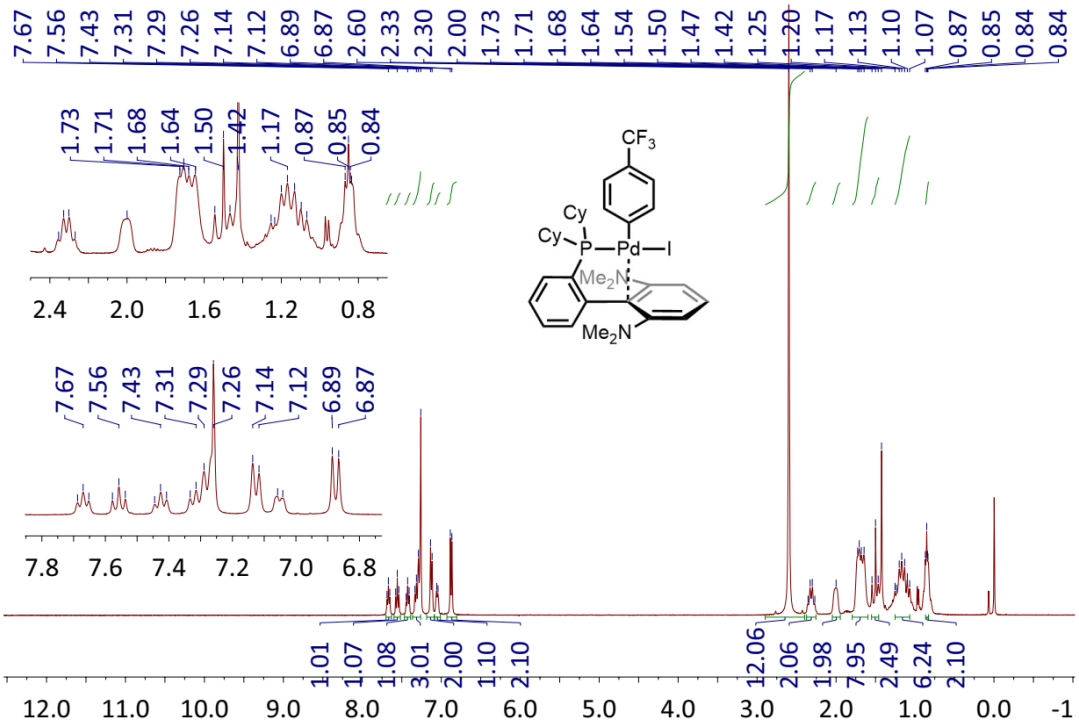
^{19}F NMR spectrum (471 MHz, CD_2Cl_2) of [(RuPhos)Pd(4-CF_3Ph)(I)] 4c



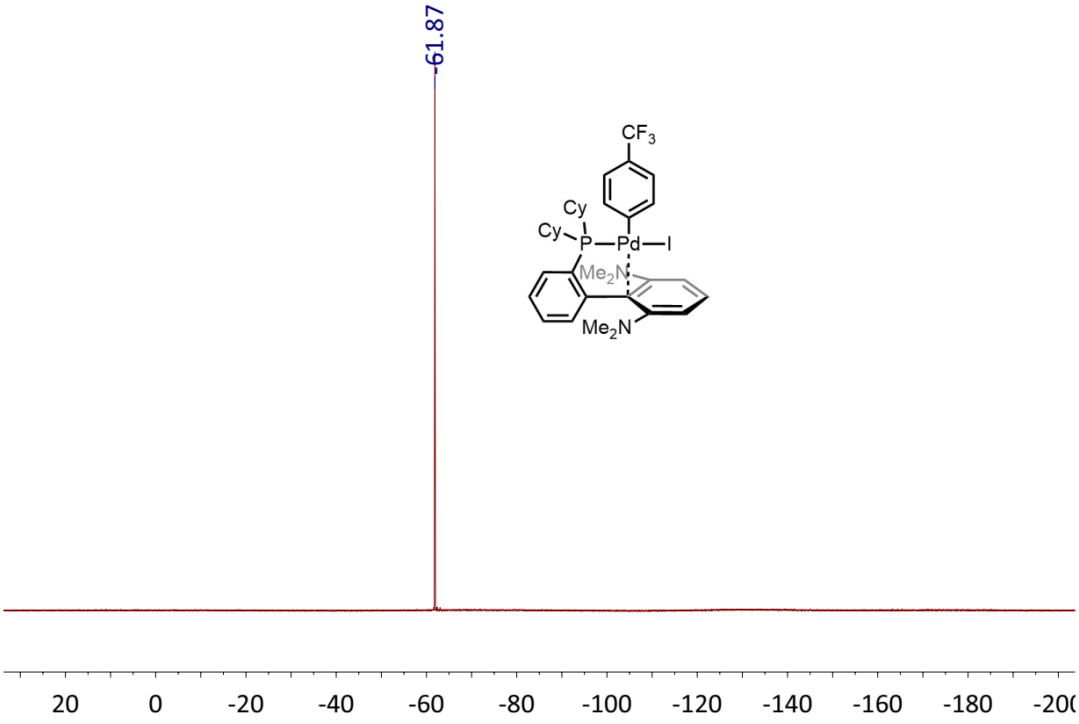
^{31}P NMR spectrum (202 MHz, CD_2Cl_2) of [(RuPhos)Pd(4-CF_3Ph)(I)] 4c



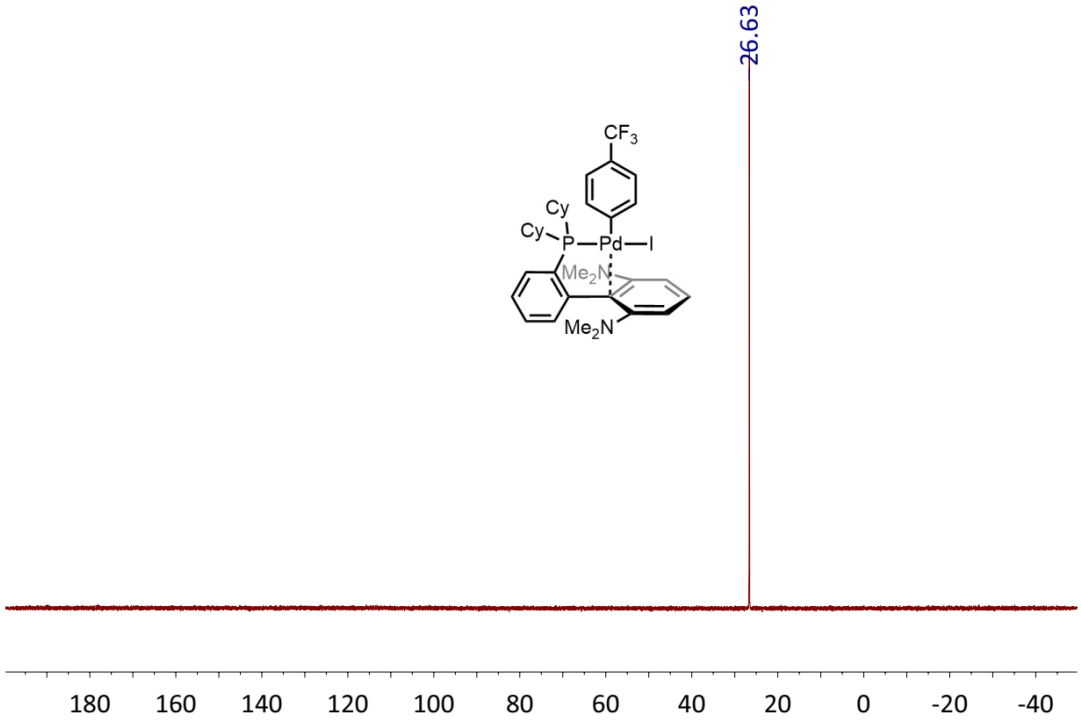
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of [(CPhos)Pd(4-CF_3Ph)(I)] 4d



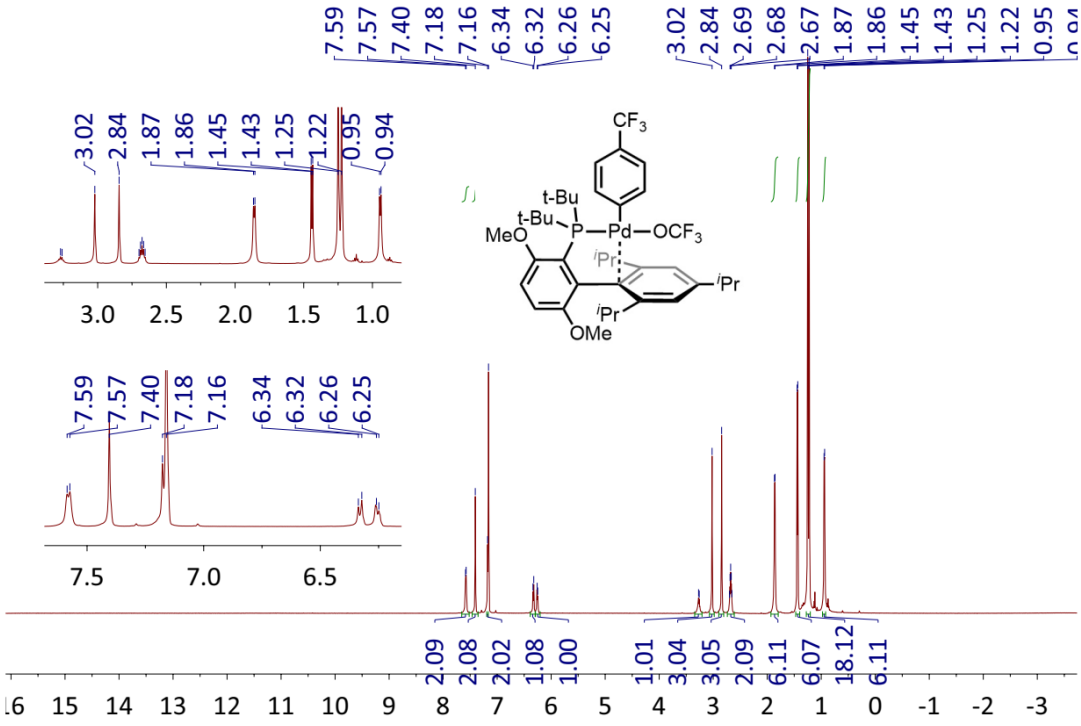
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of [(CPhos)Pd(4-CF_3Ph)(I)] 4d



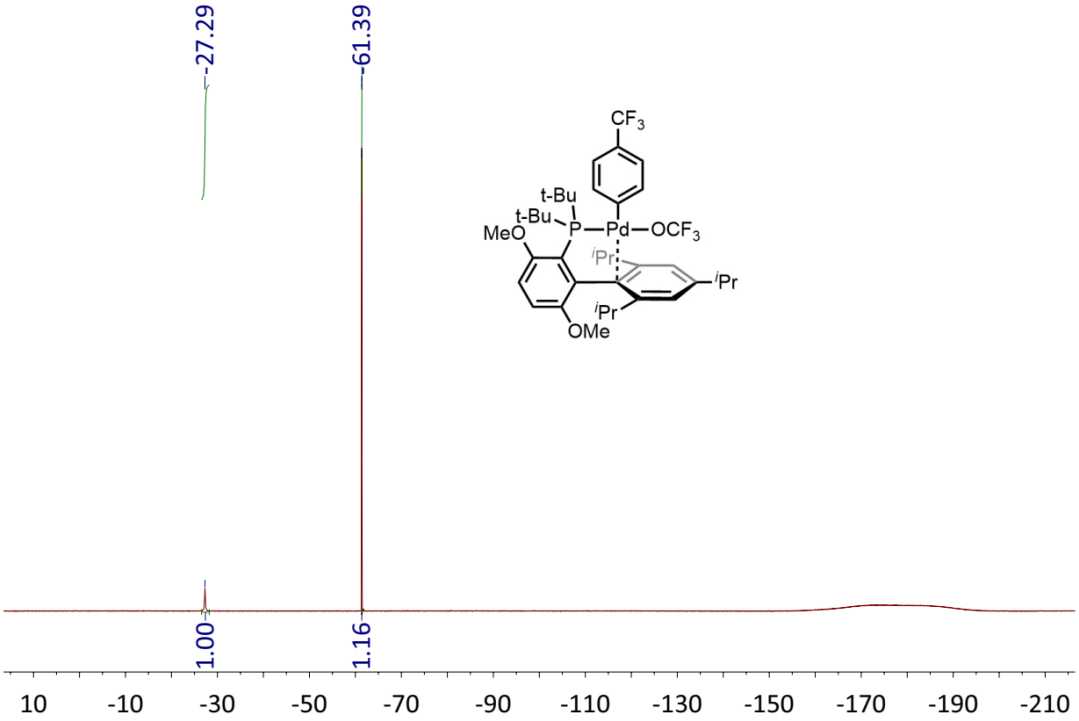
^{31}P NMR spectrum (162 MHz, $CDCl_3$) of [(CPhos)Pd(4-CF_3Ph)(I)] 4d



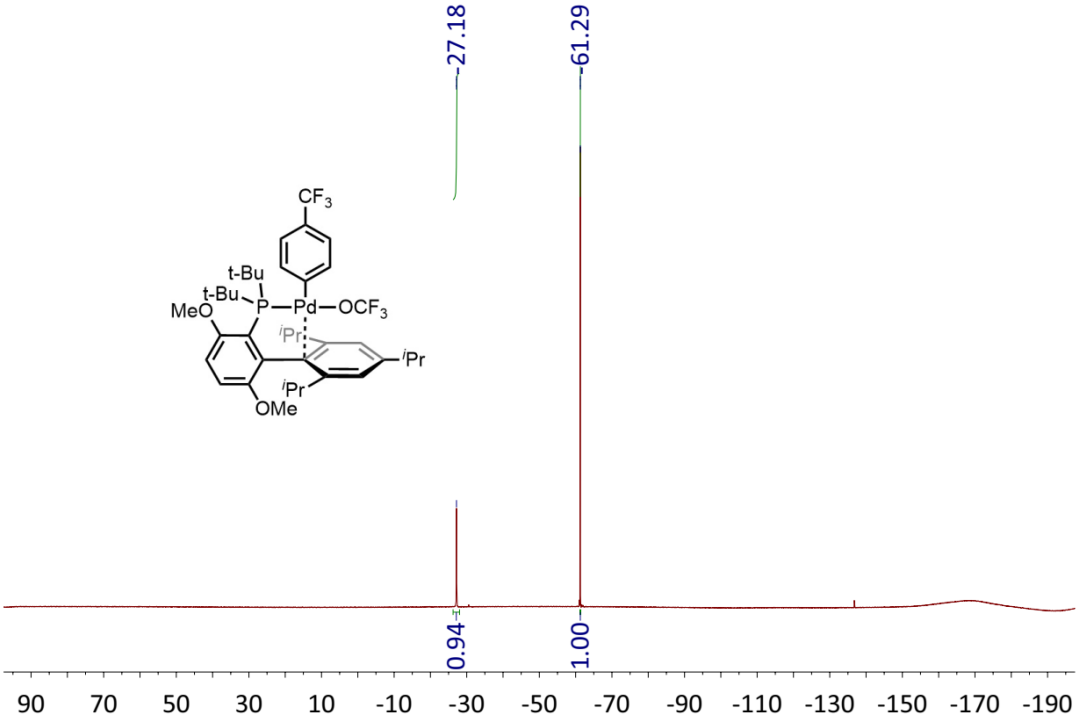
^{1}H NMR spectrum (600 MHz, C_6D_6) of [(^{t}Bu-BrettPhos)Pd(4-CF_3Ph)(OCF_3)] 5a



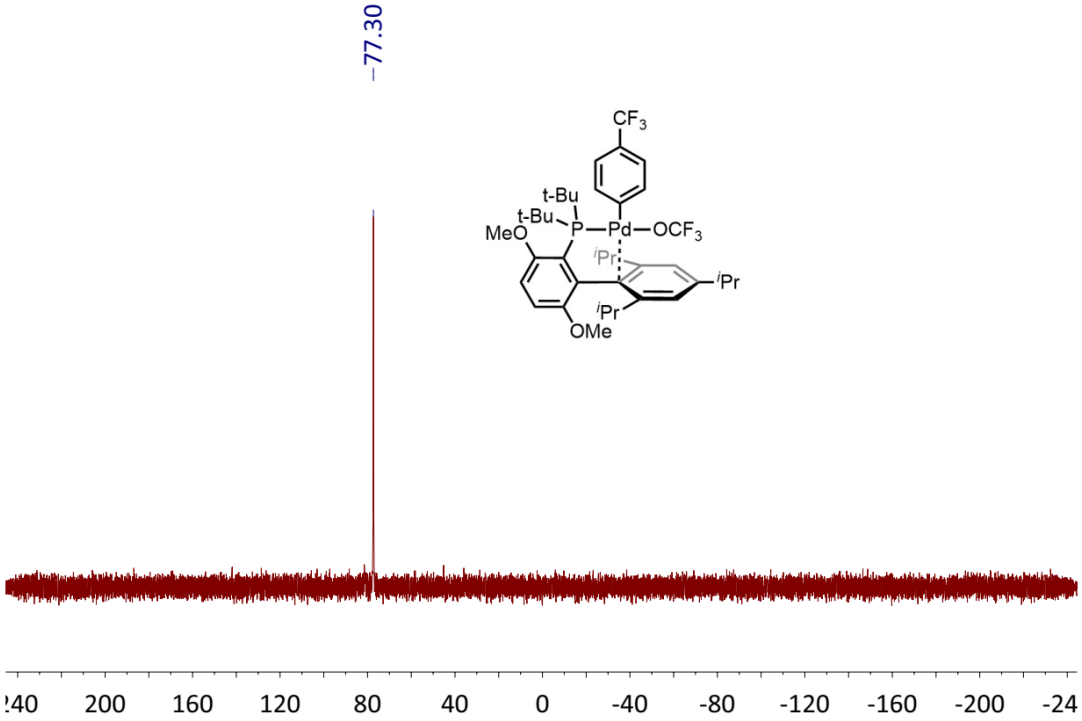
^{19}F NMR spectrum (565 MHz, C_6D_6) of (^{t}Bu-BrettPhos)Pd(4-CF_3Ph)(OCF_3) 5a



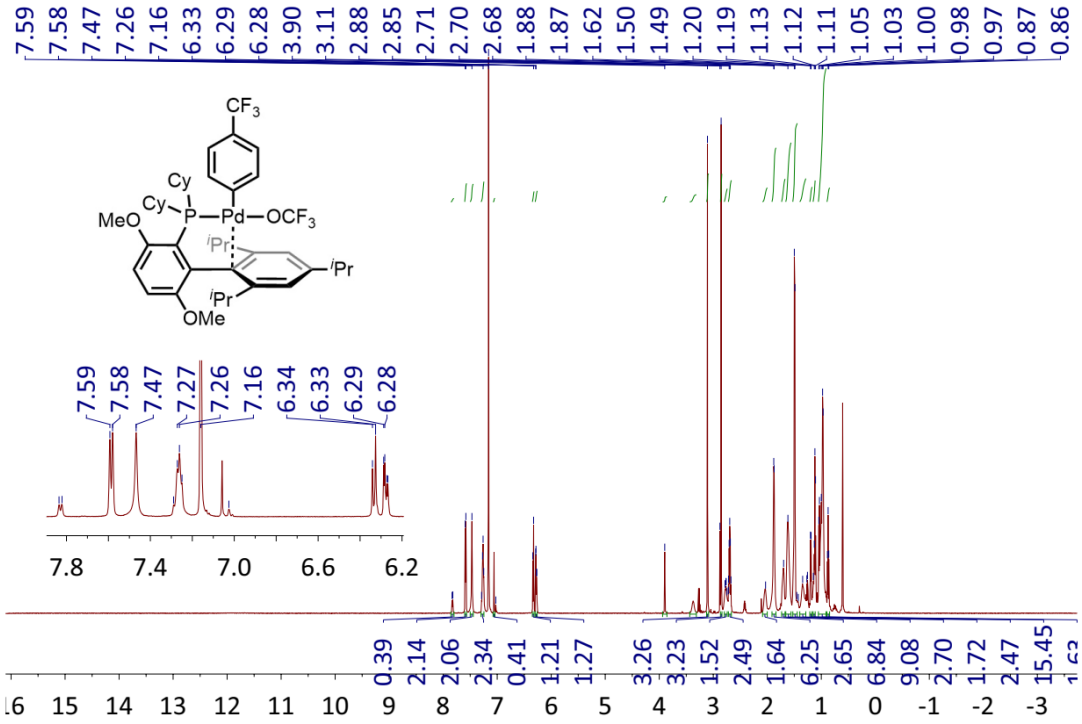
^{19}F NMR spectrum (600 MHz, C_6D_6, 283 K) of [(^{t}-Bu-BrettPhos)Pd(4-CF_3Ph)(OCF_3)] 5a



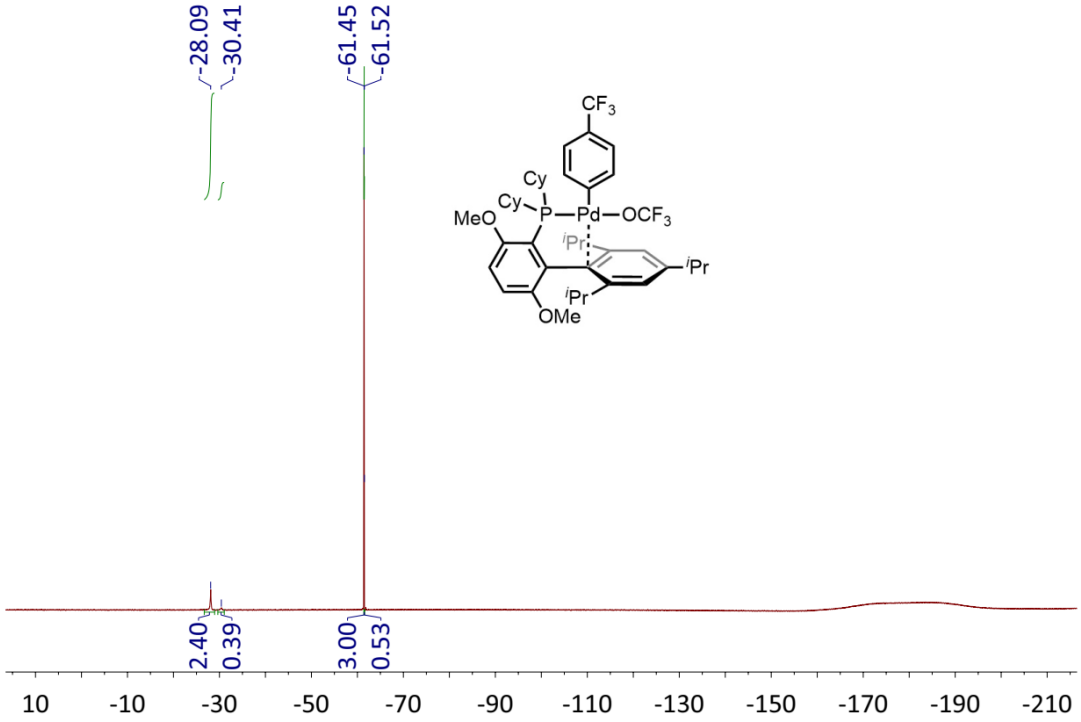
^{31}P NMR spectrum (243 MHz, C_6D_6) of [(^{t}Bu-BrettPhos)Pd(4-CF_3Ph)(OCF_3)] 5a



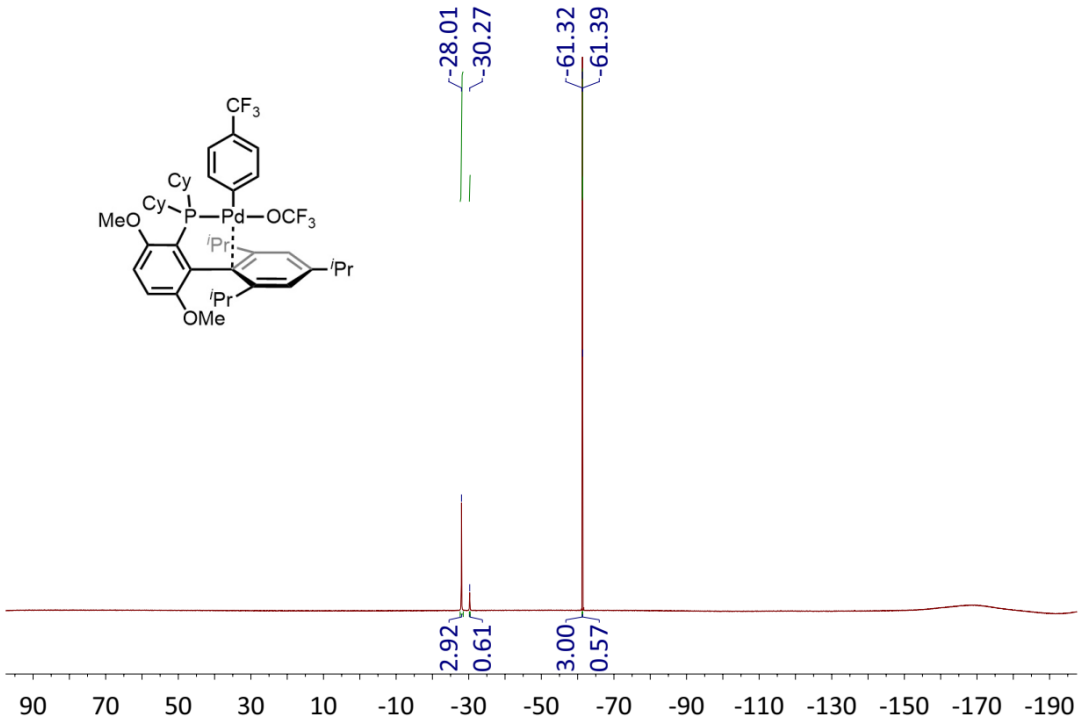
^{1}H NMR spectrum (600 MHz, C_6D_6) of [(BrettPhos)Pd(4-CF_3Ph)(OCF_3)] 5b



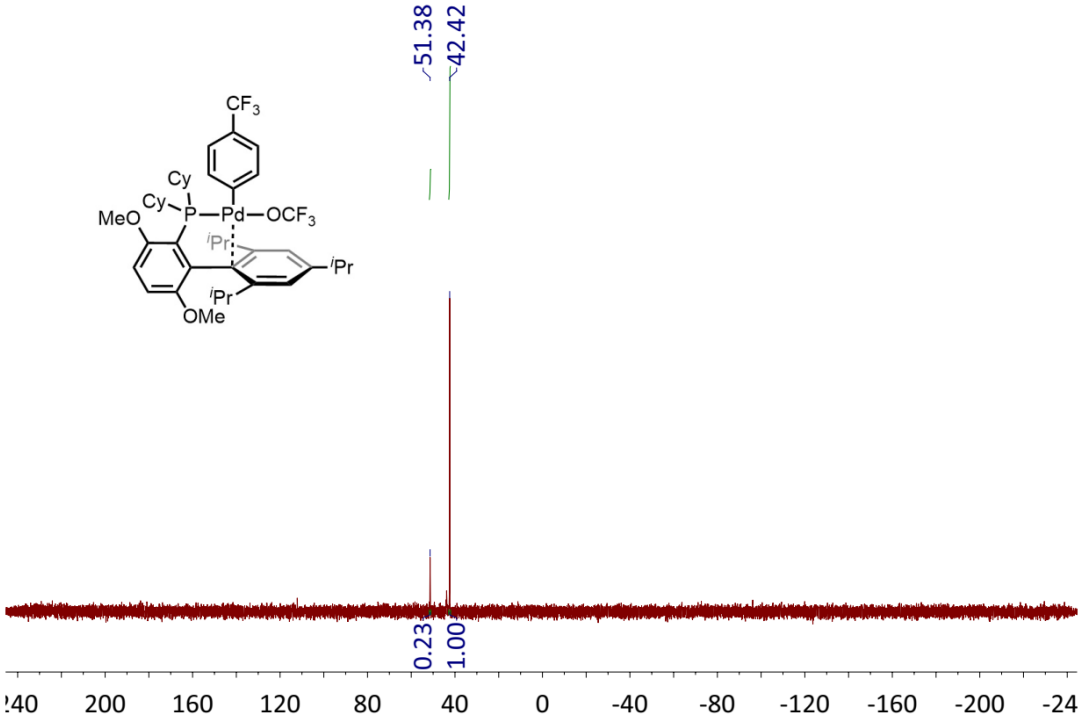
^{19}F NMR spectrum (565 MHz, C_6D_6, 298 K) of [(BrettPhos)Pd(4-CF_3Ph)(OCF_3)] 5b



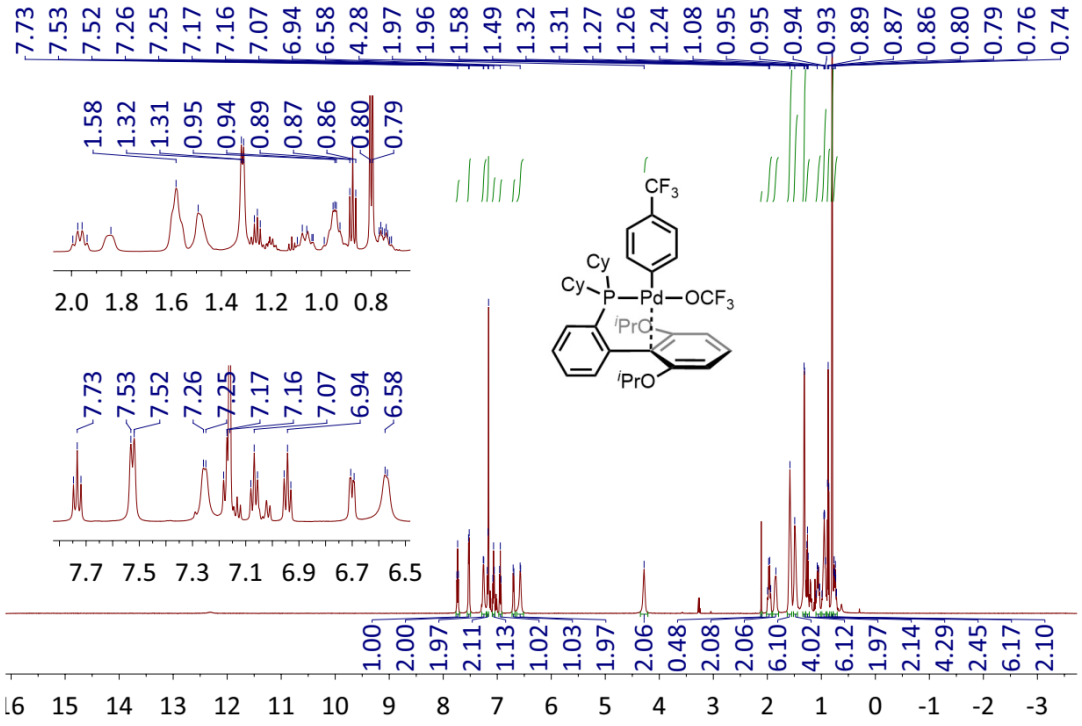
^{19}F NMR spectrum (565 MHz, C_6D_6, 283 K) of [(BrettPhos)Pd(4-CF_3Ph)(OCF_3)] 5b



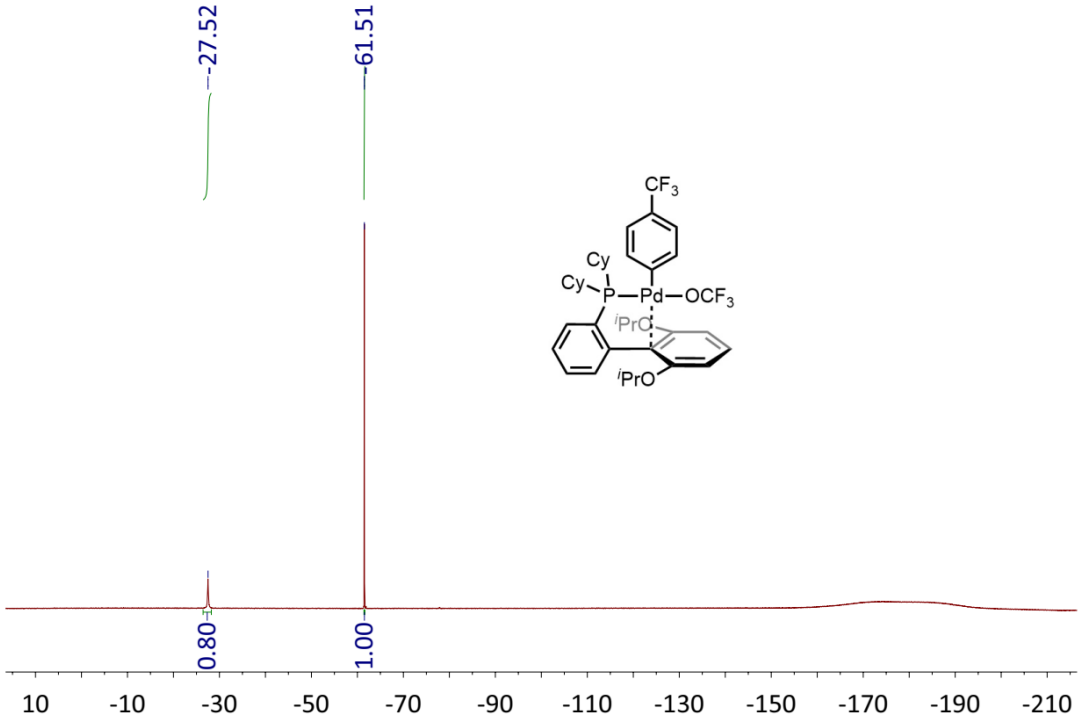
^{31}P NMR spectrum (243 MHz, C_6D_6) of [(BrettPhos)Pd(4-CF_3Ph)(OCF_3)] 5b



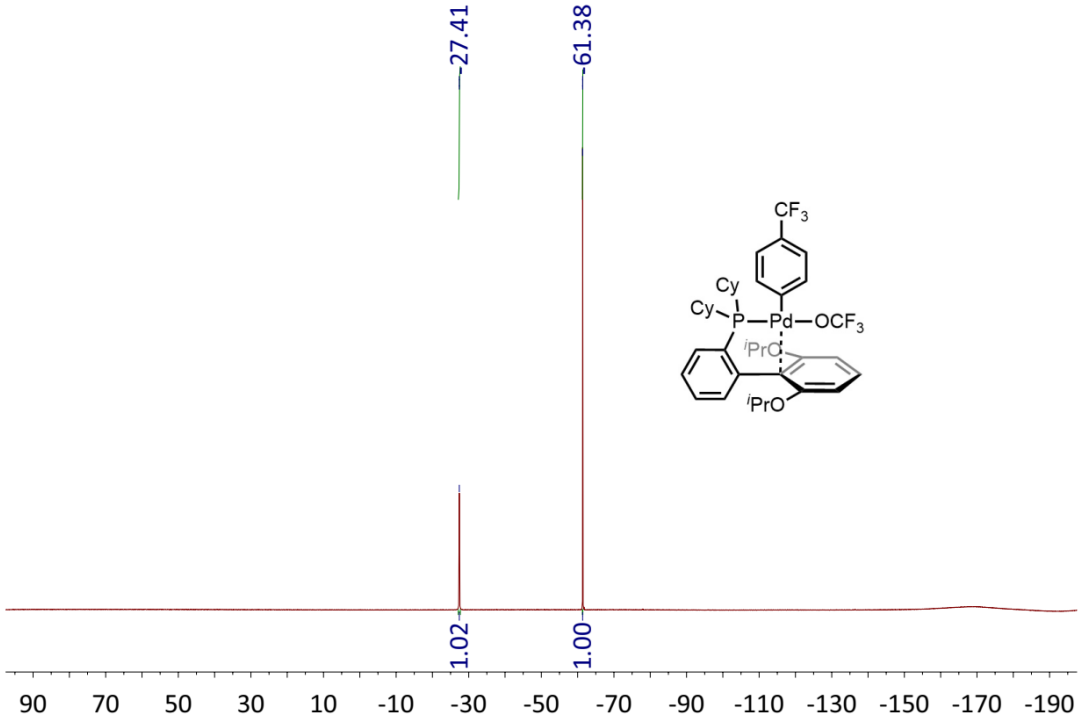
^{1}H NMR spectrum (600 MHz, C_6D_6) of [(RuPhos)Pd(4-CF_3Ph)(OCF_3)] 5c



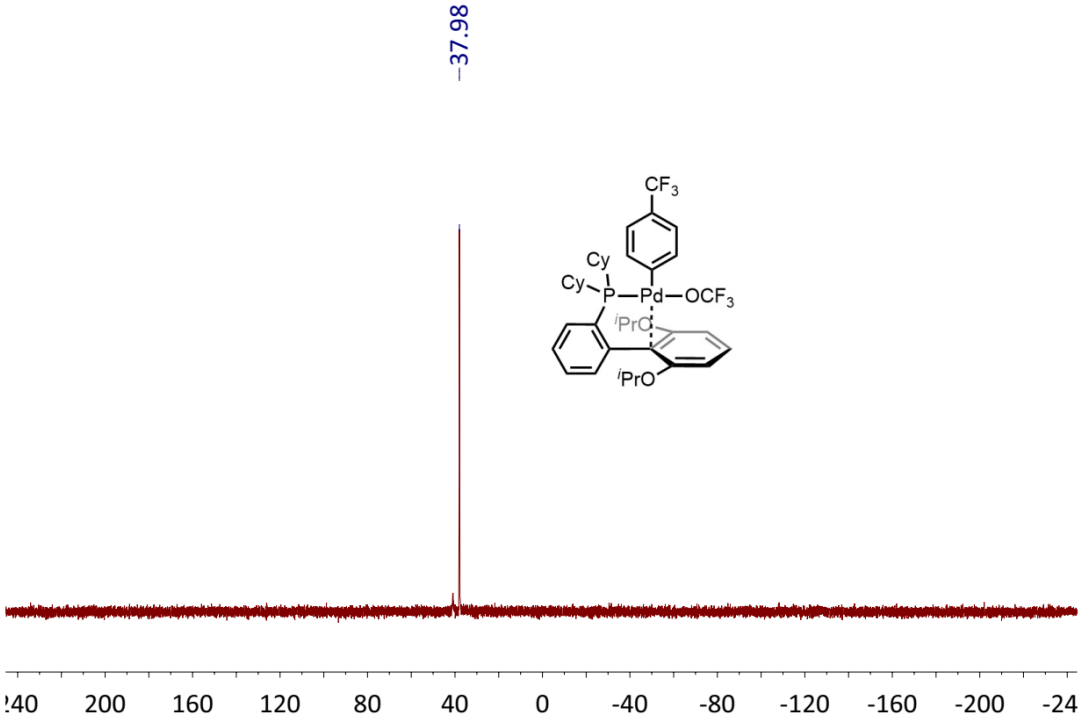
^{19}F NMR spectrum (565 MHz, C_6D_6, 298 K) of [(RuPhos)Pd(4-CF_3Ph)(OCF_3)] 5c



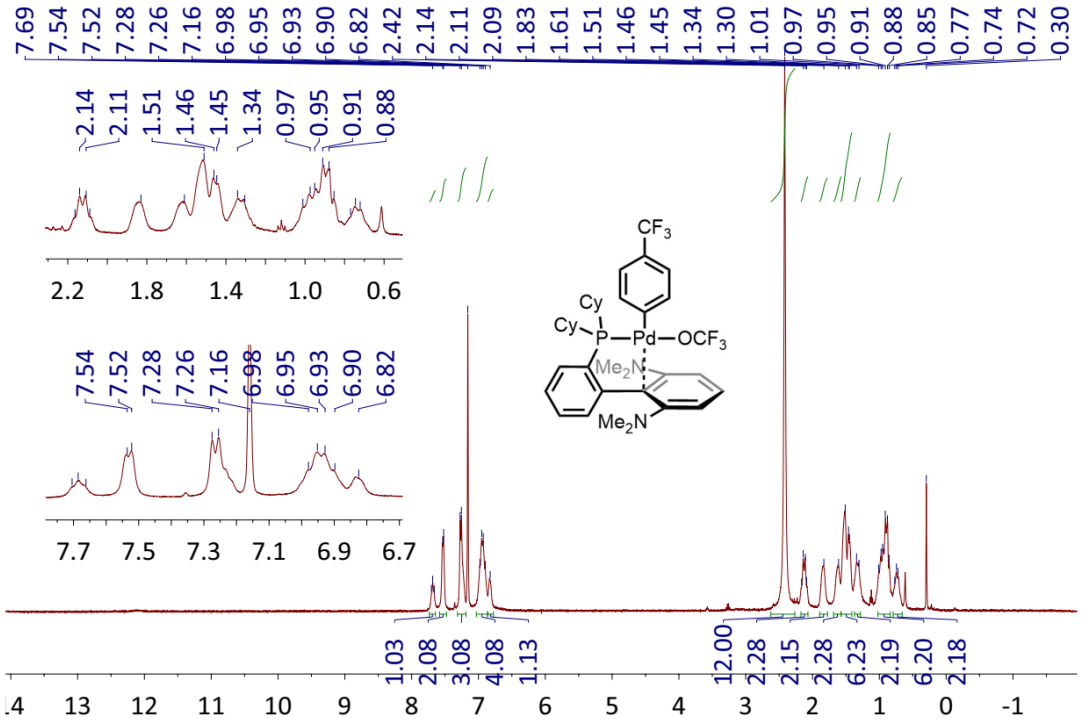
^{19}F NMR spectrum (565 MHz, C_6D_6, 283 K) of [(RuPhos)Pd(4-CF_3Ph)(OCF_3)] 5c



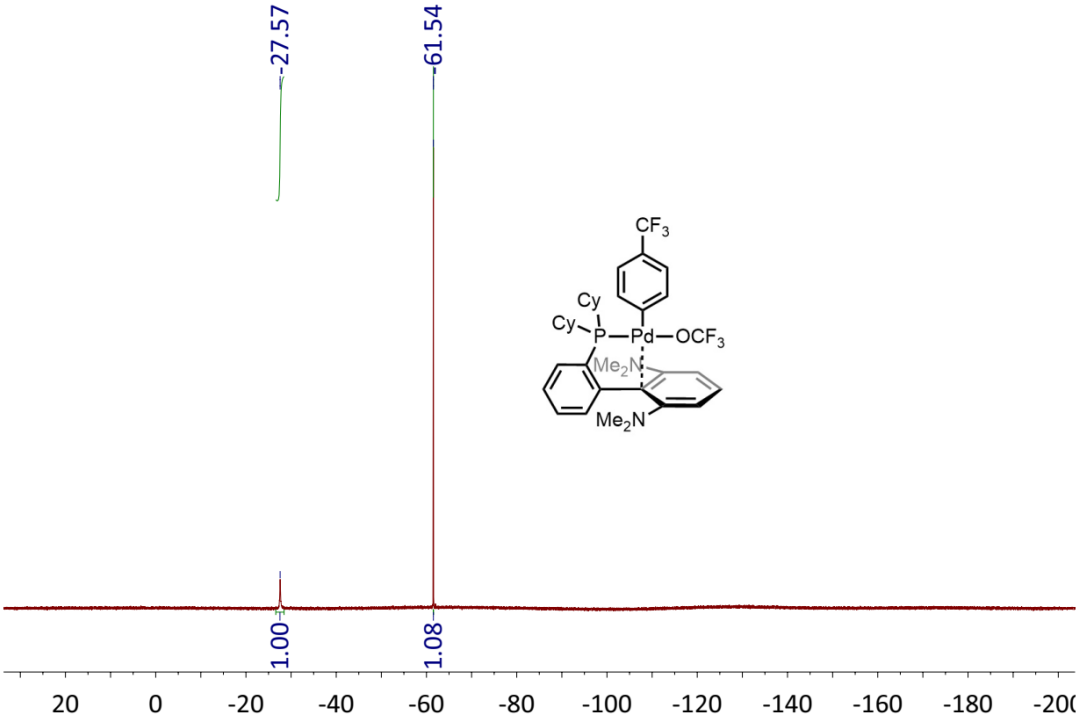
^{31}P NMR spectrum (243 MHz, C_6D_6) of [(RuPhos)Pd(4-CF_3Ph)(OCF_3)] 5c



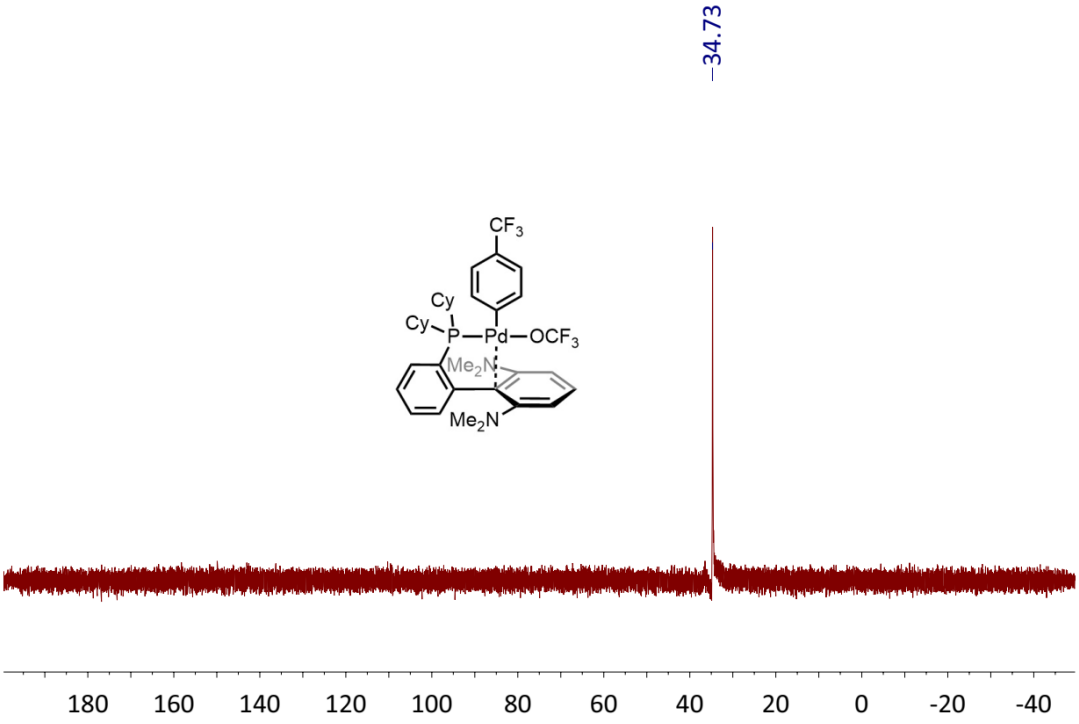
^{1}H NMR spectrum (400 MHz, C_6D_6) of [(CPhos)Pd(4-CF_3Ph)(OCF_3)] 5d



^{19}F NMR spectrum (376 MHz, C_6D_6) of [(CPhos)Pd(4-CF_3Ph)(OCF_3)] 5d



^{31}P NMR spectrum (162 MHz, C_6D_6) of [(CPhos)Pd(4-CF_3Ph)(OCF_3)] 5d



X-ray diffraction data of complexes 2a, 2b, 3b', 3c, 5a

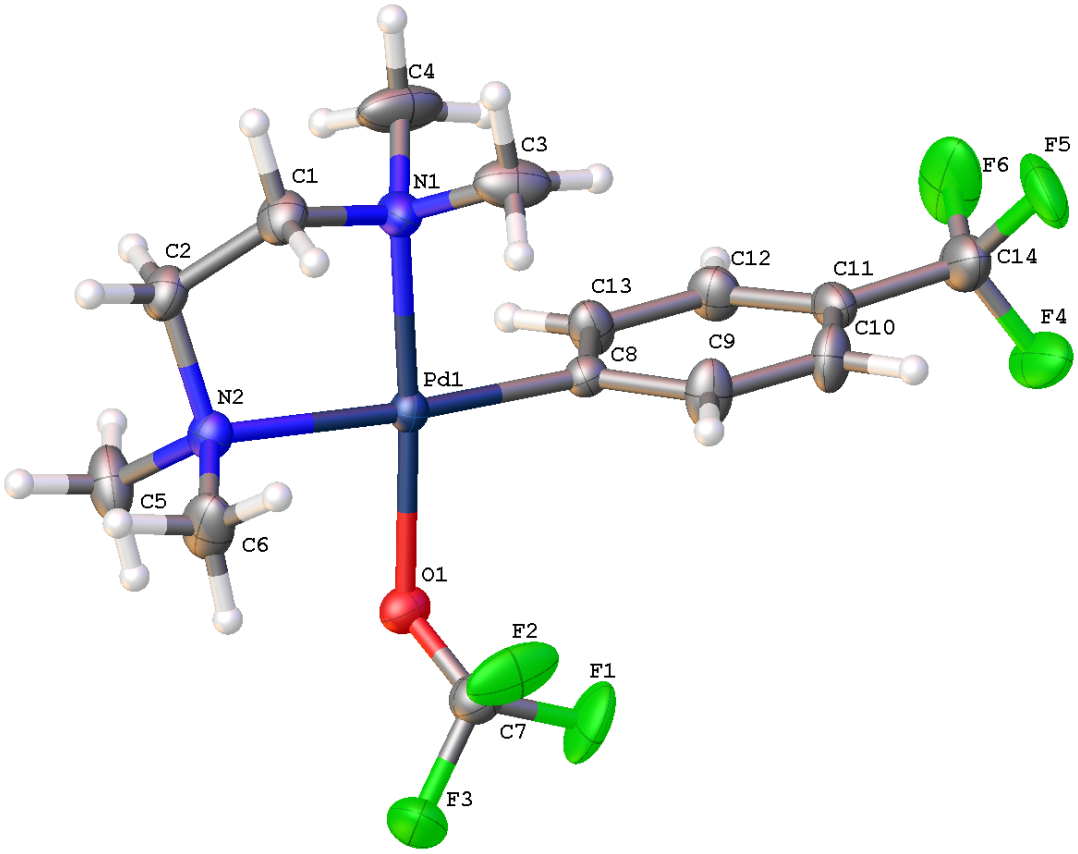


Figure S3. ORTEP diagrams of [(TMEDA)Pd(4-CF_3Ph)(OCF_3)] **2a**.

Table S1-1. Crystal data and structure refinement for **2a**.

Identification code	mo_d8v191192_0m	
Empirical formula	C14 H20 F6 N2 O Pd	
Formula weight	452.72	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	I 41 c d	
Unit cell dimensions	a = 22.1489(5) Å	α= 90°.
	b = 22.1489(5) Å	β= 90°.
	c = 14.1421(3) Å	γ = 90°.
Volume	6937.7(3) $Å^3$	
Z	16	
Density (calculated)	1.734 Mg/m^3	
Absorption coefficient	1.133 mm^{-1}	
F(000)	3616	
Crystal size	0.180 x 0.150 x 0.110 mm^3	
Theta range for data collection	2.510 to 25.996°.	
Index ranges	-27<=h<=23, -22<=k<=27, -17<=l<=17	
Reflections collected	16497	
Independent reflections	3401 [R(int) = 0.0249]	
Completeness to theta = 25.242°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.5885	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3401 / 111 / 293	
Goodness-of-fit on F^2	1.054	
Final R indices [I>2sigma(I)]	R1 = 0.0178, wR2 = 0.0416	
R indices (all data)	R1 = 0.0193, wR2 = 0.0424	
Absolute structure parameter	-0.028(10)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.213 and -0.327 $e.Å^{-3}$	

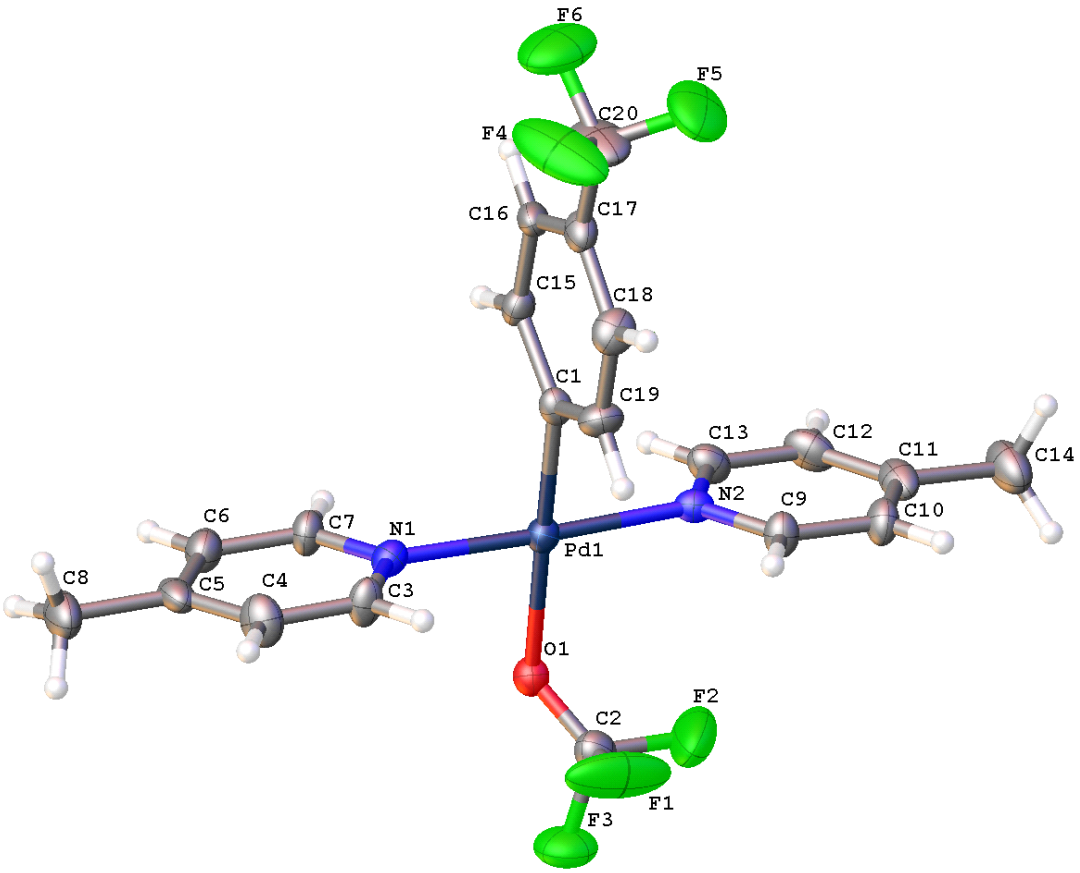


Figure S4. ORTEP diagrams of [*trans*-(4-CH_3-py)$_2$Pd(4-CF_3Ph)(OCF_3)] **2b**.

Table S2-1. Crystal data and structure refinement for **2b**.

Identification code	mj20037_0m	
Empirical formula	C20 H18 F6 N2 O Pd	
Formula weight	522.76	
Temperature	170.0 K	
Wavelength	1.34139 Å	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 13.1935(5) Å	α= 90°.
	b = 11.4522(5) Å	β= 105.432(3)°.
	c = 14.0786(6) Å	γ = 90°.
Volume	2050.51(15) $Å^3$	
Z	4	
Density (calculated)	1.693 Mg/m^3	
Absorption coefficient	5.273 mm^{-1}	
F(000)	1040	
Crystal size	0.05 x 0.03 x 0.02 mm^3	
Theta range for data collection	3.551 to 54.995°.	
Index ranges	-16<=h<=16, -13<=k<=11, -17<=l<=17	
Reflections collected	20044	
Independent reflections	3867 [R(int) = 0.1270]	
Completeness to theta = 53.594°	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7508 and 0.4564	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3867 / 31 / 273	
Goodness-of-fit on F^2	1.059	
Final R indices [I>2sigma(I)]	R1 = 0.0908, wR2 = 0.2048	
R indices (all data)	R1 = 0.1456, wR2 = 0.2376	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.705 and -1.624 $e.Å^{-3}$	

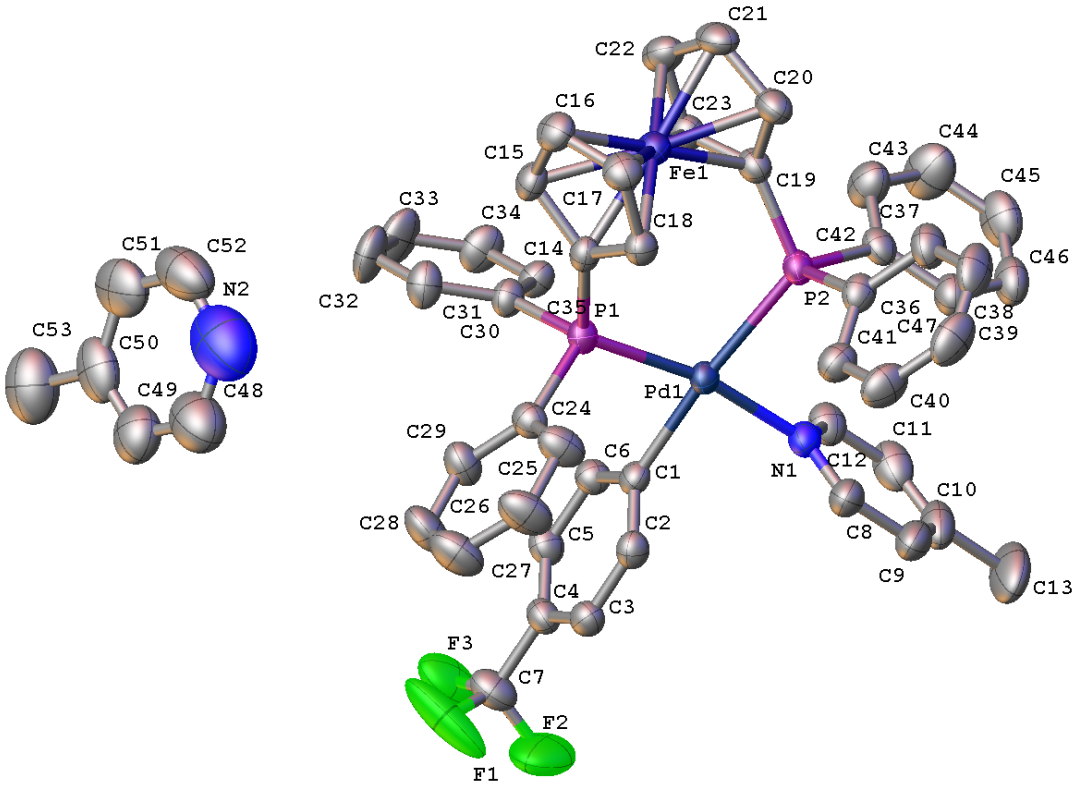


Figure S5. ORTEP diagrams of [(DPPF)Pd(4-CF_3Ph)(4-MePy)•(4-MePy)] **3b'**.

Table S3-1. Crystal data and structure refinement for **3b'**.

Identification code	mj19744_0m	
Empirical formula	C106 H92 F6 Fe2 N4 P4 Pd2	
Formula weight	1984.21	
Temperature	169.96 K	
Wavelength	1.34139 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 10.3574(2) Å	α= 90°.
	b = 17.7893(3) Å	β= 95.5760(10)°.
	c = 27.4578(5) Å	γ = 90°.
Volume	5035.19(16) $Å^3$	
Z	2	
Density (calculated)	1.309 Mg/m^3	
Absorption coefficient	4.116 mm^{-1}	
F(000)	2028	
Crystal size	0.08 x 0.06 x 0.05 mm^3	
Theta range for data collection	3.548 to 54.976°.	
Index ranges	-12<=h<=12, -21<=k<=21, -33<=l<=32	
Reflections collected	65324	
Independent reflections	9569 [R(int) = 0.0553]	
Completeness to theta = 53.594°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7508 and 0.4841	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9569 / 0 / 561	
Goodness-of-fit on F^2	1.018	
Final R indices [I>2sigma(I)]	R1 = 0.0420, wR2 = 0.1032	
R indices (all data)	R1 = 0.0553, wR2 = 0.1105	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.524 and -0.741 $e.Å^{-3}$	

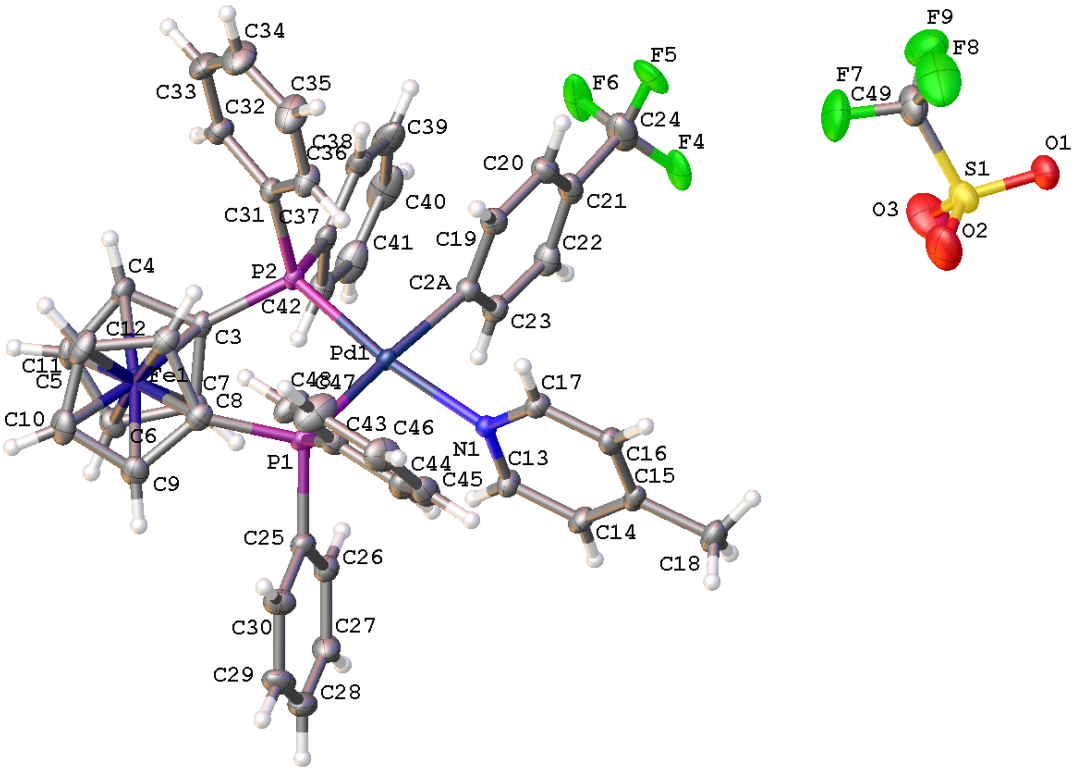


Figure S6. ORTEP diagrams of [(DPPF)Pd(4-CH_3-Py)(4-CF_3-Ph)][OTf] **3c**.

Table S4-1. Crystal data and structure refinement for **3c**.

Identification code	mj22132	
Empirical formula	C48 H39 F6 Fe N O3 P2 Pd S	
Formula weight	1048.05	
Temperature	213.0 K	
Wavelength	1.34139 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 21.6907(5) Å	α= 90°.
	b = 17.7028(4) Å	β= 90°.
	c = 22.6847(5) Å	γ = 90°.
Volume	8710.6(3) $Å^3$	
Z	8	
Density (calculated)	1.598 Mg/m^3	
Absorption coefficient	5.205 mm^{-1}	
F(000)	4240	
Crystal size	0.07 x 0.07 x 0.05 mm^3	
Theta range for data collection	3.276 to 54.877°.	
Index ranges	-26<=h<=26, -21<=k<=21, -27<=l<=26	
Reflections collected	88491	
Independent reflections	8247 [R(int) = 0.0699]	
Completeness to theta = 53.594°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7510 and 0.5513	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8247 / 48 / 587	
Goodness-of-fit on F^2	1.053	
Final R indices [I>2sigma(I)]	R1 = 0.0348, wR2 = 0.0844	
R indices (all data)	R1 = 0.0456, wR2 = 0.0896	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.467 and -0.784 $e.Å^{-3}$	

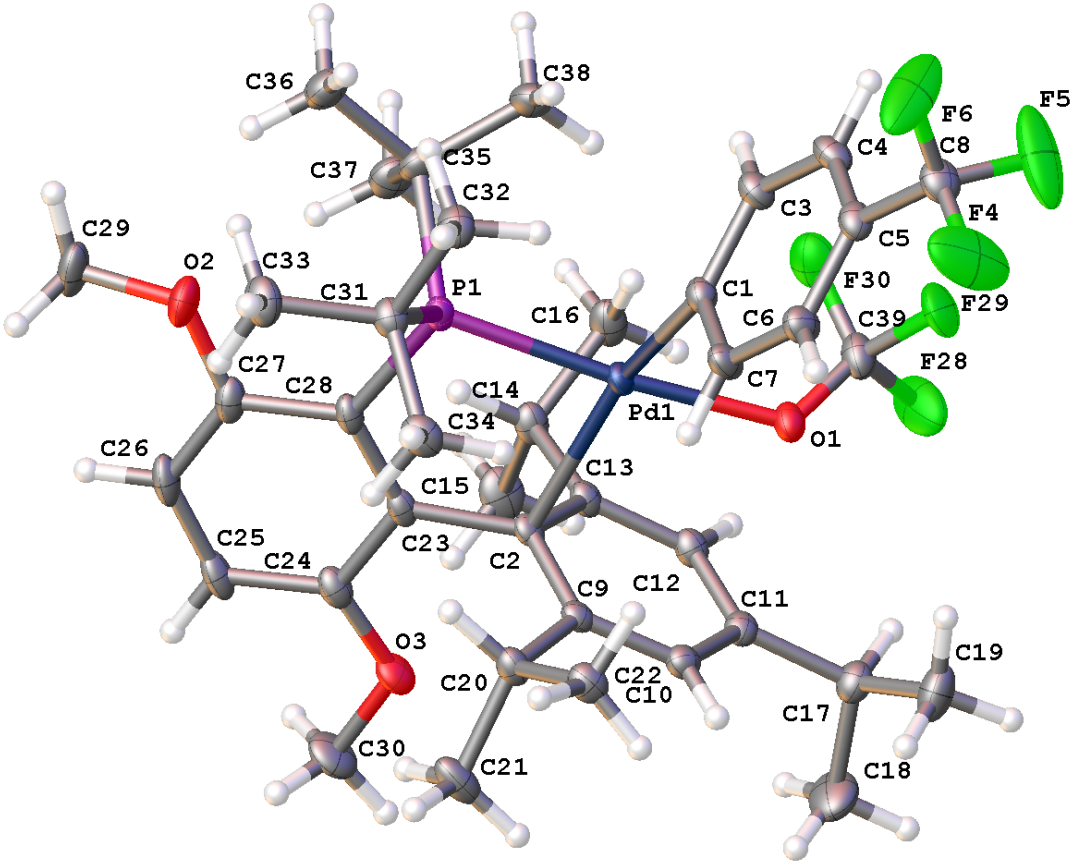


Figure S7. ORTEP diagrams of [(^{t}-Bu-BrettPhos)Pd(4-CF_3Ph)(OCF_3)] **5a**.

Table S5-1. Crystal data and structure refinement for **5a**.

Identification code	mj20146_0m	
Empirical formula	C39 H53 F6 O3 P Pd	
Formula weight	821.18	
Temperature	170.05 K	
Wavelength	1.34139 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.1827(4) Å	α= 87.361(2)°.
	b = 12.7262(4) Å	β= 71.886(2)°.
	c = 13.4392(4) Å	γ = 80.533(2)°.
Volume	1953.34(11) $Å^3$	
Z	2	
Density (calculated)	1.396 Mg/m^3	
Absorption coefficient	3.158 mm^{-1}	
F(000)	852	
Crystal size	0.08 x 0.06 x 0.05 mm^3	
Theta range for data collection	3.010 to 54.996°.	
Index ranges	-14<=h<=14, -15<=k<=14, -16<=l<=16	
Reflections collected	28966	
Independent reflections	7427 [R(int) = 0.0494]	
Completeness to theta = 53.594°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7508 and 0.5105	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7427 / 0 / 465	
Goodness-of-fit on F^2	1.031	
Final R indices [I>2sigma(I)]	R1 = 0.0411, wR2 = 0.1055	
R indices (all data)	R1 = 0.0456, wR2 = 0.1092	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.215 and -1.068 $e.Å^{-3}$	