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Supporting Information

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Carbon(sp^3)–Fluorine Bond-Forming Reductive Elimination from Palladium(IV) Complexes**

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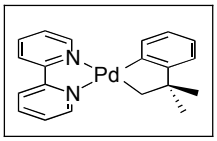
General Procedures

NMR spectra were obtained on a Varian vnmrs 700 (699.76 MHz for ^{1}H; 175.95 MHz for ^{13}C), a Varian Inova 400 (399.96 MHz for ^{1}H; 376.34 MHz for ^{19}F; 100.57 MHz for ^{13}C), a Varian vnmr500 (500.09 MHz for ^{1}H; 470.56 MHz for ^{19}F; 125.75 MHz for ^{13}C), or a Varion MR400 (400.53 MHz for ^{1}H; 376.87 MHz for ^{19}F; 100.71 MHz for ^{13}C) spectrometer. ^{1}H, ^{19}F and ^{13}C chemical shifts are reported in parts per million (ppm) relative to TMS, with the residual solvent peak used as an internal reference. ^{19}F NMR spectra are referenced on a unified scale, where the single primary reference is the frequency of the residual solvent peak in the ^{1}H NMR spectrum.[1] ^{1}H and ^{19}F multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), quartet (q), multiplet (m), and broad resonance (br). Mass spectral data were obtained on a Micromass magnetic sector mass spectrometer or on a Micromass LCT mass spectrometer in electrospray ionization mode.

Materials and Methods

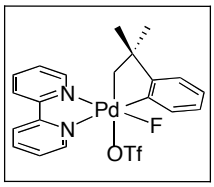
Bipyridine (bpy) and 2-methyl-2-phenylpropyl magnesium chloride were obtained from Aldrich. 1-Fluoro-2,4,6-trimethylpyridinium triflate (NFTPT) and 1-fluoro-2,4,6-trimethylpyridinium tetrafluoroborate (NFTPB) were obtained from TCI America. Unless otherwise noted, all reagents were used as received. NMR solvents were obtained from Cambridge Isotope Laboratories. All other solvents were obtained from Fisher Chemicals. Tetrahydrofuran was purified using an Innovative Technologies (IT) solvent purification system consisting of a copper catalyst, activated alumina, and molecular sieves.

Synthesis of Pd^{II} Complex 1

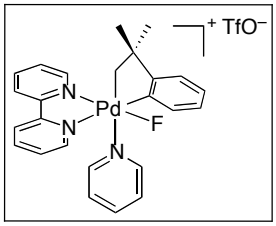


$Pd^{II}(CH_2CMe_2\text{-}o\text{-}C_6H_4)(COD)$[2] (720 mg, 2.08, 1.0 equiv) was combined with 2,2′-bipyridine (325 mg, 2.08 mmol, 1.0 equiv) in CH_2Cl_2 (200 mL), and the reaction mixture allowed to stir for 30 min. The solution was concentrated under vacuum (to 5 mL), and hexanes (30 mL) was added to precipitate the product. Complex **1** was isolated as a bright yellow solid (737 mg, 90% yield). ^{1}H NMR (500 MHz [D_3]chloroform, 25 °C): δ = 9.25 (d, *J* = 5 Hz, 1H), 8.80 (d, *J* = 5 Hz, 1H), 8.07-8.05 (multiple peaks, 2H), 7.99-7.93 (multiple peaks, 2H), 7.56-7.53 (multiple peaks, 2H), 7.47 (t, *J* = 7 Hz, 1H), 7.01-6.99 (multiple peaks, 2H), 6.87 (t, *J* = 5 Hz, 1H), 2.46 (s, 2H), 1.43 (s, 6H). ^{13}C NMR (125 MHz [D_3]chloroform, 25 °C): δ = 168.71, 158.54, 154.73, 154.21, 150.43, 149.37, 137.11, 134.35, 128.18, 125.42, 125.13, 123.72, 122.76, 121.34, 121.04, 121.00, 46.96, 44.97, 33.35 (two overlapping carbons). HRMS-electrospray (m/z): $[M + H]^+$ calcd for $C_{20}H_{20}N_2Pd$, 395.0734; Found, 395.0746.

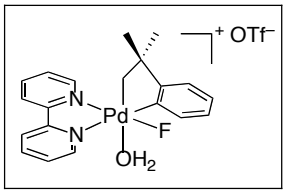
Synthesis of Pd^{IV} Complexes 2-5



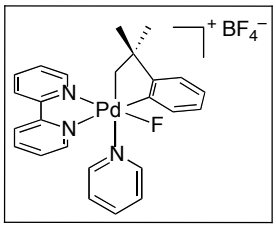
Compound **1** (70 mg, 0.18 mmol, 1.0 equiv) and NFTPT (52 mg, 0.18 mmol, 1.0 equiv) were combined in CH_2Cl_2 (15 mL), and this mixture was stirred for 15 min. The solvent was removed by rotary evaporation, and the resulting yellow oil was washed with diethyl ether (15 mL). The solid material was then dissolved in CH_2Cl_2 (1 mL), and diethyl ether (10 mL) was added to precipitate the product. The precipitate was collected and dried under vacuum to afford **2** as a light yellow solid (96 mg, 94% yield). ^{1}H NMR (400 MHz [D_3]acetonitrile, 25 °C): δ = 8.96 (d, *J* = 5 Hz, 1H), 8.58-8.56 (multiple peaks, 2H), 8.43 (t, *J* = 8 Hz, 1H), 8.34 (t, *J* = 8 Hz, 1H), 8.03-7.99 (multiple peaks, 2H), 7.78 (d, *J* = 8 Hz, 1H), 7.61 (t, *J* = 6 Hz, 1H), 7.34 (d, *J* = 8 Hz, 1H), 7.29 (d, *J* = 8 Hz, 1H), 7.13 (d, *J* = 8 Hz, 1H), 4.80 (dd, *J* = 15, 5 Hz, 1H), 4.24 (app. br. s, 1H), 1.45 (s, 3H), 1.12 (s, 3H). ^{19}F NMR (376 MHz [D_3]acetonitrile, 25 °C): δ = –79.11 (s, 3F), –336.17 (d, *J* = 15 Hz, 1F). ^{13}C NMR data could not be obtained due to the instability of the complex over the timescale required for the experiment. HRMS-ESI (m/z): $[M – OTf]^+$ calcd for $C_{20}H_{20}FN_2Pd$ 413.0640; Found, 413.0644.



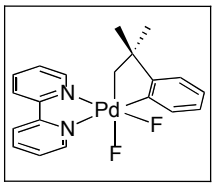
Compound **1** (120 mg, 0.3 mmol, 1.0 equiv), NFTPT (88 mg, 0.3 mmol, 1.0 equiv), and C_5H_5N (49 μL, 0.6 mmol, 2.0 equiv) were combined in CH_2Cl_2 (15 mL), and this mixture was stirred for 15 min. The solvent was removed by rotary evaporation, and the resulting yellow oil was washed with diethyl ether (10 mL). The solid material was then dissolved in CH_2Cl_2 (2 mL), and diethyl ether (25 mL) was added to precipitate the product. The precipitate was collected and dried under vacuum to afford **3** as an off-white solid (125 mg, 63% yield). ^{1}H NMR (700 MHz [D_2]dichloromethane, 25 °C): δ = 8.93-8.91 (multiple peaks, 2H), 8.72 (d, *J* = 8 Hz, 1H), 8.48 (t, *J* = 8 Hz, 1H), 8.29 (t, *J* = 8 Hz, 1H), 8.24 (app. br. s, 2H), 8.07 (d, *J* = 6 Hz, 1H), 7.88 (t, *J* = 8 Hz, 1H), 7.77 (t, *J* = 6 Hz, 1H), 7.64 (t, *J* = 6 Hz, 1H), 7.47-7.44 (multiple peaks, 2H), 7.24 (t, *J* = 7 Hz, 1H), 7.05 (d, *J* = 8 Hz, 1H), 7.01 (t, *J* = 8 Hz, 1H), 6.66 (d, *J* = 8 Hz, 1H), 4.72 (dd, *J* = 15, 6 Hz, 1H), 3.89 (app. br. s, 1H), 1.50 (s, 3H), 1.13 (s, 3H). ^{19}F NMR (376 MHz [D_2]dichloromethane, 25 °C):: δ = –78.97 (s, 3F), –324.80 (d, *J* = 15 Hz, 1F). ^{13}C NMR data could not be obtained due to the instability of the complex over the timescale required for the experiment. HRMS-ESI (m/z): $[M + H]^+$ calcd for $C_{26}H_{24}F_4N_3O_3PdS$ 642.0660; Found, 642.0669.



Compound 2 (11 mg, 0.02 mmol) was dissolved in acetone (1.5 mL) in a 3 mL vial. The vial was then placed in a 20 mL vial containing pentane and sealed with a Teflon-lined cap. The vial was placed in a –35 ºC freezer until yellow crystals formed. The solvent was decanted, and the crystals were washed with pentanes (3 mL), CH_2Cl_2 (3 mL), and acetone (3 mL). The crystals were then collected and dried under vacuum to afford 4 as a bright yellow solid (5.2 mg, 53% yield). ^{1}H NMR (500 MHz [D_6]dimethyl sulfoxide, 25 °C): δ = 9.04 (d, *J* = 5 Hz, 1H), 8.91-8.89 (multiple peaks, 2H), 8.56 (t, *J* = 8 Hz, 1H), 8.47 (t, *J* = 8 Hz, 1H), 8.10 (t, *J* = 6 Hz, 1H), 7.86 (d, *J* = 7 Hz, 1H), 7.78 (t, *J* = 6 Hz, 1H), 7.72 (d, *J* = 7 Hz, 1H), 7.31 (d, *J* = 8 Hz, 1H), 7.27 (d, *J* = 8 Hz, 1H), 7.14 (d, *J* = 7 Hz, 1H), 4.61 (dd, *J* = 15, 5 Hz, 1H), 4.23 (d, *J* = 5 Hz, 1H), 3.31 (broad s) 1.45 (s, 3H), 1.13 (s, 3H). ^{19}F NMR (376 MHz [D_6]dimethyl sulfoxide, 25 °C): δ = –77.91 (s, 3F), –328.96 (d, *J* = 15 Hz, 1F). ^{13}C NMR data could not be obtained due to the instability of the complex over the timescale required for the experiment. HRMS-ESI (m/z): $[M – H_2O – OTf]^+$ calcd for $C_{20}H_{20}FN_2Pd$ 413.0640; Found, 413.0656.

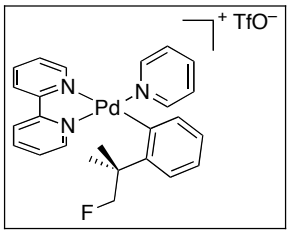


Compound **1** (552 mg, 1.4 mmol, 1.0 equiv), NFTPB (259 mg, 1.4 mmol, 1.0 equiv), and C_5H_5N (225 μL, 2.8 mmol, 2.0 equiv) were combined in CH_2Cl_2 (50 mL), and this mixture was stirred for 15 min. The solvent was removed by rotary evaporation, and the resulting yellow oil was washed with diethyl ether (20 mL). The solid material was then dissolved in CH_2Cl_2 (3 mL), and diethyl ether (25 mL) was added to precipitate the product. The precipitate was collected and dried under vacuum to afford **3-BF$_4$** as an off-white solid (486 mg, 58% yield). ^{1}H NMR (400 MHz [D_2]dichloromethane, 25 °C): δ = 8.91 (d, *J* = 5 Hz, 1H), 8.79 (d, *J* = 8 Hz, 1H), 8.62 (d, *J* = 8 Hz, 1H), 8.47 (d, *J* = 8 Hz, 1H), 8.29 (d, *J* = 8 Hz, 1H), 8.23 (app. br. s, 2H), 8.07 (d, *J* = 6 Hz, 1H), 7.88 (t, *J* = 8 Hz, 1H), 7.77 (t, *J* = 5 Hz, 1H), 7.64 (t, *J* = 7 Hz, 1H), 7.45 (t, *J* = 7 Hz, 2H), 7.24 (t, *J* = 7 Hz, 1H), 7.05 (d, *J* = 7 Hz, 1H), 7.01 (t, *J* = 8 Hz, 1H), 6.65 (d, *J* = 8 Hz, 1H), 4.72 (dd, *J* = 15, 6 Hz, 1H), 3.88 (app. br. s, 1H), 1.49 (s, 3H), 1.13 (s, 3H). ^{19}F NMR (376 MHz [D_2]dichloromethane, 25 °C): δ = –152.48 (s, 4F), –324.80 (d, *J* = 15 Hz, 1F). ^{13}C NMR data could not be obtained due to the instability of the complex over the timescale required for the experiment. HRMS-ESI (m/z): $[M - \text{pyridine} - BF_4]^+$ calcd for $C_{20}H_{20}FN_2Pd$ 413.0640; Found, 413.0645.

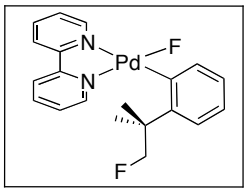


Compound **2** (310 mg, 0.54 mmol, 1.0 equiv) and Me_4NF (52 mg, 0.86 mmol, 1.6 equiv) were combined in dry CH_2Cl_2 (15 mL), and this mixture was stirred for 15 min in the glovebox. The solution turned dark orange with a dark solid precipitate. The reaction was filtered through celite, and the solvent was removed under vacuum. The resulting yellow oil was dissolved in DCE (4 mL), and pentane (30 mL) was added to precipitate the product. The precipitate was collected and dried under vacuum to afford **5** as a light yellow solid (190 mg, 77% yield, along with 19 % Me_4NBF_4 as determined by ^{1}H NMR). ^{1}H NMR (500 MHz [D_2]dichloromethane, 25 °C): δ = δ 9.06 (d, *J* = 5 Hz, 1H), 8.43 (d, *J* = 8 Hz, 1H), 8.40 (d, *J* = 8 Hz, 1H), 8.14-8.08 (multiple peaks, 2H), 8.01 (t, *J* = 8 Hz, 1H), 7.95 (d, *J* = 8 Hz, 1H), 7.74 (d, *J* = 6 Hz, 1H), 7.31 (t, *J* = 6 Hz, 1H), 7.24-7.16 (multiple peaks, 2H), 6.95 (d, *J* = 8 Hz, 1H), 4.11 (m, 1H), 3.51 (dd, *J* = 6, 3 Hz, 1H), 1.39 (s, 3H), 1.02 (s, 3H). ^{19}F NMR (470 MHz [D_2]dichloromethane, 25 °C): δ = –201.42 (d, *J* = 51 Hz, 1F), –336.71 (dd, *J* = 51, 14 Hz, 1F). HRMS-ESI (m/z): $[M - F]^+$ calcd for $C_{20}H_{20}FN_2Pd$ 413.0645; Found, 413.0640.

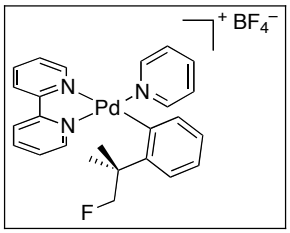
Synthesis of Pd^{II} Reductive Elimination Products



Compound **3** (30 mg, 0.06 mmol) was dissolved CH_2Cl_2 (10 mL). The reaction was stirred for 30 min at 80 °C. The solvent was removed by rotary evaporation, and the resulting yellow oil was dissolved in CH_2Cl_2 (1 mL), and precipitated with pentane (15 mL). The precipitate was collected and dried under vacuum to afford **6** as a tacky yellow solid (28 mg, 93% yield). ^{1}H NMR (500 MHz [D_3]chloroform, 25 °C): δ = 8.88 (d, *J* = 8 Hz, 2H), 8.56 (d, *J* = 8 Hz, 1H), 8.53 (d, *J* = 8 Hz, 1H), 8.22 (t, *J* = 8 Hz, 1H), 8.16 (t, *J* = 8 Hz, 1H), 8.04-7.99 (multiple peaks, 2H), 7.77 (d, *J* = 5 Hz, 1H), 7.68-7.61 (multiple peaks, 2H), 7.56 (d, *J* = 6 Hz, 1H), 7.32 (t, *J* = 6 Hz, 1H), 7.22 (t, *J* = 8 Hz, 1H), 7.11-7.08 (multiple peaks, 2H), 4.69 (dd, *J* = 48, 9 Hz, 1H), 4.53 (dd, *J* = 48, 9 Hz, 1H), 1.68 (s, 3H), 1.61 (s, 3H). ^{19}F NMR (470 MHz [D_3]chloroform, 25 °C): δ = –78.99 (s, 1F), –217.01 (t, *J* = 48 Hz, 1F). ^{13}C NMR (125 MHz [D_3]chloroform, 25 °C): δ = 156.40, 153.70, 152.45, 152.25, 150.41, 148.29, 148.13, 141.10, 140.82, 139.70, 132.91, 128.34, 128.07, 126.94, 126.86, 126.48 (q, *J* = 322 Hz, 1C), 126.38, 125.27, 124.04, 124.01, 92.21 (d, *J* = 177 Hz, 1C), 40.91, 40.76, 27.60. HRMS-ESI (m/z): $[M - C_5H_5N - OTf]^+$ calcd for $C_{20}H_{20}FN_2Pd$ 413.0645; Found, 413.0643.



Compound **7** (20 mg, 0.04 mmol, 1.0 equiv) was dissolved in dry CH_2Cl_2 (6 mL) under N_2. The reaction was stirred for 15 min at 80 ºC. The solvent was removed by rotary evaporation, the resulting yellow oil was dissolved in CH_2Cl_2 (1 mL), and the product was precipitated with pentane (15 mL). The precipitate was collected and dried under vacuum to afford **8** as a tacky yellow solid (18 mg, 90% yield). ^{1}H NMR (700 MHz [D_2]dichloromethane, 25 °C): δ = 9.16 (d, *J* = 5 Hz, 1H), 8.75 (d, *J* = 5 Hz, 1H), 8.15-8.13 (multiple peaks, 2H), 8.06-8.01 (multiple peaks, 2H), 7.61 (t, *J* = 5 Hz, 1H), 7.53 (d, *J* = 6 Hz, 1H), 7.51 (d, *J* = 8 Hz, 1H), 6.99 (t, *J* = 7 Hz, 1H), 6.95 (t, *J* = 8 Hz, 1H), 6.86 (d, *J* = 7 Hz, 1H), 4.54 (dd, *J* = 49, 9 Hz, 1H), 4.51 (dd, *J* = 49, 9 Hz, 1H), 1.39 (s, 3H), 1.38 (s, 3H). ^{19}F NMR (376 MHz [D_2]dichloromethane, 25 °C): δ = –151.89 (s, 1F), –214.87 (t, *J* = 49 Hz, 1F). ^{13}C NMR (175 MHz [D_3]chlorodorm, 25 °C): δ = 163.45, 160.98, 155.59, 155.19, 151.02, 150.11, 138.42, 138.37, 135.29, 126.46, 126.24, 125.22, 123.63, 123.25, 122.27, 122.20, 95.39 (d, *J* = 176 Hz, 1C), 36.62, 36.60, 25.63. HRMS-APCI (m/z): $[M - F]^+$ calcd for $C_{20}H_{20}FN_2Pd$ 413.0640; Found, 413.0641.

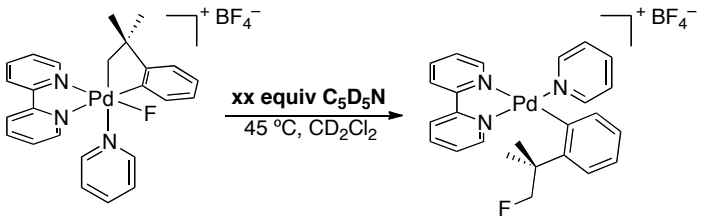


Compound **3-BF$_4$** (30 mg, 0.05 mmol) dissolved combined in CH_2Cl_2 (10 mL). The reaction was stirred for 30 min at 80 °C. The solvent was removed by rotary evaporation, and the resulting yellow oil was dissolved in CH_2Cl_2 (1 mL), and precipitated with pentane (15 mL). The precipitate was collected and dried under vacuum to afford **6-BF$_4$** as a tacky yellow solid (26 mg, 87% yield). ^{1}H NMR (700 MHz [D_2]dichloromethane, 25 °C): δ = 8.85-8.83 (multiple peaks, 2H), 8.48-8.45 (multiple peaks, 2H), 8.16-8.11 (multiple peaks, 2H), 8.01-7.96 (multiple peaks, 2H), 7.75 (d, *J* = 5 Hz, 1H), 7.63 (d, *J* = 7 Hz, 1H), 7.62-7.58 (multiple peaks, 2H), 7.52 (d, *J* = 6 Hz, 1H), 7.27 (t, *J* = 6 Hz, 1H), 7.19 (d, *J* = 8 Hz, 1H), 7.08-7.05 (multiple peaks, 2H), 4.68 (dd, *J* = 48 Hz, *J* = 9 Hz, 1H), 4.50 (dd, *J* = 48 Hz, *J* = 9 Hz, 1H), 1.64 (s, 3H), 1.40 (s, 3H). ^{19}F NMR (376 MHz [D_3]chloroform, 25 °C): δ = –152.42 (s, 1F), –216.08 (t, *J* = 48 Hz, 1F). ^{13}C NMR (125 MHz [D_3]chloroform, 25 °C): δ = 156.03, 153.23, 151.87 (two overlapping carbon's), 150.16, 147.91, 140.67, 140.49, 139.35, 132.58, 127.94, 127.74, 126.60 (two overlapping carbon's), 126.42, 126.00, 124.87, 123.55, 123.47, 93.31 (d, *J* = 176 Hz, 1C), 40.53, 40.40, 27.19. HRMS-ESI (m/z): $[M - C_5H_5N - BF_4]^+$ calcd for $C_{20}H_{20}FN_2Pd$ 413.0645; Found, 413.0655.

Determining Order in Pyridine with 3-BF$_4$ at 45 °C in CD_2Cl_2

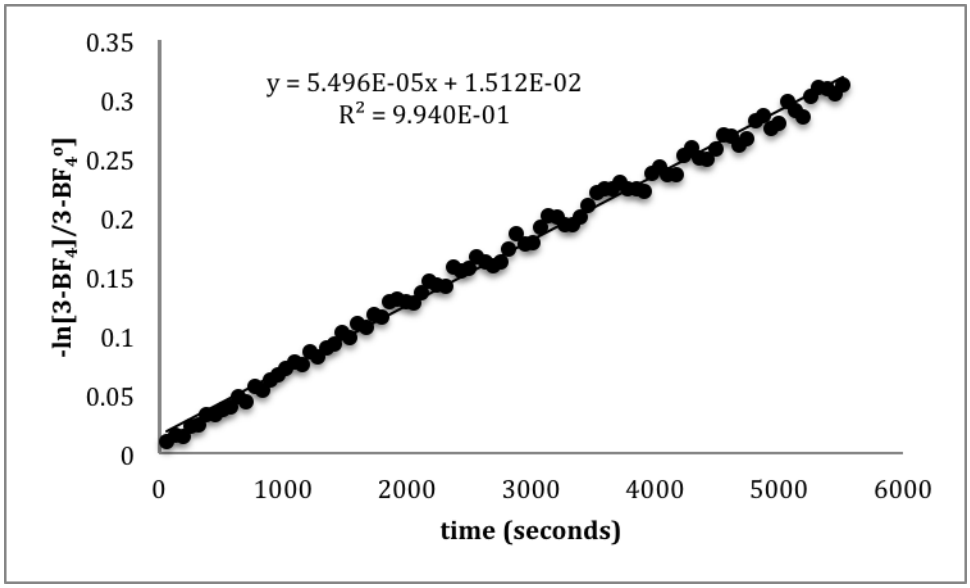
Complex **3-BF$_4$** (4.4 mg, 0.00758 mmol, 1.0 equiv) and C_5D_5N (0.001895 to 0.0114 mmol, 3.8 mM to 20.0 mM) were combined in a screw cap NMR tube and dissolved in CD_2Cl_2 (0.5 mL). An internal standard (2-nitrobenzotrifluoride) was added (20 μl of a stock solution in CD_2Cl_2, 0.00758, 1 equiv) and the tube was sealed with a Teflon®-lined cap. The tube was immediately placed in an NMR spectrometer with the temperature pre-equilbrated to 45 °C, and the reaction was allowed to equilibrate for 2 min. The rate of reductive elimination was monitored by ^{19}F NMR spectroscopy by monitoring the disappearance of the starting material. The reaction was followed to between 2-3 half lives, and the data was plotted as –ln[**3-BF$_4$/3-BF$_4$^{o}**] versus time. A representative kinetics run is shown in **Figure S1**. The values of k_{obs} for each [pyridine] are reported in **Table S1**.

Table S1. Rate as a Function of $[C_5D_5N]$ at 45 °C



equiv C_5D_5N	$[C_5D_5N]$	$[1/C_5D_5N]$	k_{obs}
0.25	0.001895	528	1.60×10^{-4}
0.5	0.00379	264	2.75×10^{-4}
0.75	0.00568	176	5.50×10^{-5}
1	0.00758	132	8.02×10^{-5}
1.5	0.0114	88	2.81×10^{-5}

Figure S1. Representative Rate Data (Reductive Elimination from **3-BF$_4$** in the Presence of 5.68 mM C_5D_5N)



Study of the Appearance of 7 at 40 °C in CD_2Cl_2

Complex **5** (4.9 mg, 0.0113 mmol, 1.0 equiv) and NMe_4NF (2.5 mg, 0.0269 mmol, 2.4 equiv) or NBu_4PF_6 (10.4 mg, 0.0269 mmol, 2.4 equiv) were combined in a screw cap NMR tube and dissolved in CD_2Cl_2 (0.5 mL) from a stock solution that contained the internal standard dichloroethane (0.0057 mmol, 0.5 equiv). The tube was sealed with a Teflon®-lined cap. The tube was immediately placed in an NMR spectrometer with the temperature pre-equilbrated to 40 °C and the reaction was allowed to equilibrate for 2 minutes. The rate of reductive elimination was monitored by ^1H NMR spectroscopy by monitoring the appearance of compound **7**.

Additive	k_{obs}
none	5.75×10^{-4}
NMe_4F	3.26×10^{-4}
NBu_4PF_6	3.30×10^{-3}

X-ray Crystallography Details

Yellow cubes of **4** were grown by diffusion of pentane into a solution of **3** in wet acetone at –35 °C. A crystal of dimensions 0.10 x 0.10 x 0.10 mm was mounted on a Bruker SMART APEX CCD-based X-ray diffractometer equipped with a low temperature device and fine focus Mo-target X-ray tube (l = 0.71073 A) operated at 1500 W power (50 kV, 30 mA). The X-ray intensities were measured at 85(1) K; the detector was placed at a distance 5.055 cm from the crystal. A total of 4717 frames were collected with a scan width of 0.5° in ω and 0.45° in phi with an exposure time of 30 s/frame. The integration of the data yielded a total of 119486 reflections to a maximum 2θ value of 56.64° of which 7429 were independent and 7186 were greater than $2\sigma(I)$. The final cell constants (Table 1) were based on the xyz centroids of 9866 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection; the data were processed with SADABS and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2008/4) software package, using the space group Pca2(1) with Z = 4 for the formula $C_{33}H_{26}BN_3F_4Cl_2Pd$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Full matrix least-squares refinement based on Φ^2 converged at R1 = 0.0219 and wR2 = 0.0533 [based on I > 2sigma(I)], R1 = 0.0232 and wR2 = 0.0542 for all data. Additional details are presented in **Table S2** and are available in the corresponding CIF file (deposited in the Cambridge Structural Database: CCDC 852596).

Sheldrick, G.M. SHELXTL, v. 2008/4; Bruker Analytical X-ray, Madison, WI, 2008.

Saint Plus, v. 7.60A, Bruker Analytical X-ray, Madison, WI, 2009.

Sheldrick, G.M. SADABS, v. 2008/1. Program for Empirical Absorption Correction of Area Detector Data, University of Gottingen: Gottingen, Germany, 2008.

Table S2. Crystal data and structure refinement for **5**.

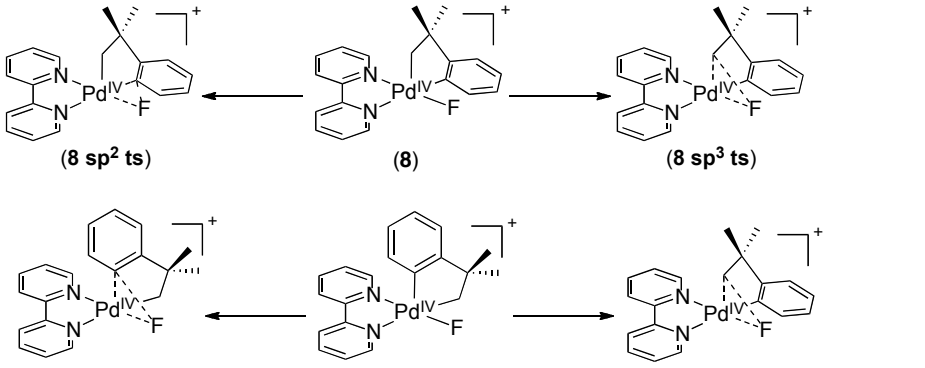
Empirical formula	C21 H22 F4 N2 O4 Pd S
Formula weight	580.87
Temperature	85(2) K
Wavelength	1.54178 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 9.3652(2) A alpha = 94.404(7) deg.
	b = 11.5602(3) A beta = 108.848(8) deg.
	c = 11.9928(8) A gamma = 111.654(8) deg.
Volume	1113.33(8) A^3
Z, Calculated density	2, 1.733 Mg/m^3
Absorption coefficient	8.196 mm^-1
F(000)	584
Crystal size	0.18 x 0.12 x 0.09 mm
Theta range for data collection	4.00 to 68.17 deg.
Limiting indices	-11<=h<=11, -13<=k<=13, -11<=l<=12
Reflections collected / unique	16877 / 3453 [R(int) = 0.0504]
Completeness to theta = 68.17	84.7 % (96% complete to 0.86 A).
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.686 and 0.557
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3453 / 0 / 375
Goodness-of-fit on F^2	1.261
Final R indices [I>2sigma(I)]	R1 = 0.0688, wR2 = 0.2137
R indices (all data)	R1 = 0.0699, wR2 = 0.2141
Largest diff. peak and hole	2.236 and -1.268 e.A^-3

Computational Methods

Using the Gaussian 09 suite of programs,[3] all density functional theory (DFT) calculations were performed with the M06 functional[4] along with the Stevens (CEP-31G) valence basis sets with effective core potentials.[5,6] The CEP-31G basis sets are triple-ξ for Pd and double-ξ for all main group elements. A d-polarization function (see 6-31G*)[7,8] was added to all non-hydrogen main group elements: ξ_d = 0.8 for carbon, nitrogen, oxygen, and fluorine (referred to as CEP-31G(d) level of theory). All geometries were optimized using CEP-31G(d)/M06 without symmetry constraints using the restricted Kohn-Sham formalism for all complexes.. All minima were confirmed by the absence of imaginary frequencies and all transition states were verified by visual inspection of the single imaginary frequency vibration and optimized along the reaction coordinate. Thermochemical data was calculated using unscaled vibrational frequencies and default parameters at 298.15 K and 1 atm. Solvent corrections (CH_2Cl_2) were performed as single point calculations using the SMD model[9] with default settings at the optimized geometries from gas phase calculations.

Energy Comparisons

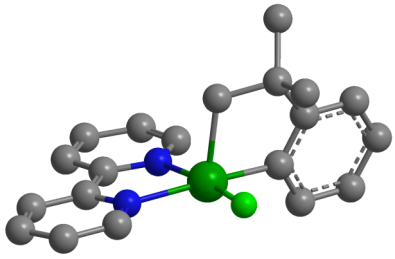
Calculated energies of the intermediates and transition states calculated are shown below. All energies have been solvent corrected using dichloromethane. All energies are listed in kcal/mol and complex **8** has been set to 0.0 for reference.



Complex	Electronic (SCF)	Enthalpy	Free Energy
8	0.0	0.0	0.0
8-I	3.2	3.2	2.3
8 sp^3 ts	17.0	15.2	16.5
8 sp^2 ts	29.5	28.0	27.0
8-I sp^2 ts	22.7	21.1	23.3

XYZ coodinates – Calculated Structures

Complex 8



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C	-4.30416700	-0.00718600	0.18973400
C	-4.07856300	-2.37707200	-0.36317600
H	-1.97891300	-2.96082900	-0.75867300
C	-4.89326000	-1.27589400	-0.01894600
H	-4.93064500	0.85006400	0.45408300
H	-4.50160500	-3.37087300	-0.53212800
H	-5.97613700	-1.39757100	0.08550800
C	-0.06450100	2.49880100	0.19875600
C	-2.15694600	1.40408000	0.23440300
C	-0.64427900	3.73487800	0.55156100
H	1.01508300	2.39558800	0.02845500
C	-2.80199000	2.61109900	0.59171700
C	-2.04091500	3.78837800	0.75152600
H	-0.01041100	4.61843700	0.66115500
H	-3.88485200	2.63308300	0.74369500
H	-2.53170000	4.72707600	1.02705600
C	0.76568700	-0.83288500	1.45904800
H	0.16451700	-1.71578200	1.74141000
H	0.44066200	0.09349300	1.96541700
C	2.28260500	-1.03299500	1.42474200
C	2.65778700	-2.51262300	1.20026800
H	2.24736300	-2.88074900	0.24646200
H	3.75784000	-2.61646700	1.18032600
H	2.26859200	-3.13682900	2.02717600
C	2.80237600	-0.56079100	2.80738400
H	2.62822300	0.52009900	2.96452000
H	2.31704200	-1.12494200	3.62514600
H	3.88860100	-0.75101000	2.87920600
C	1.88298500	0.11885300	-0.74465200
C	2.80486600	-0.17919100	0.28403600
C	2.22343900	0.84642300	-1.90151500
C	4.14038000	0.27506400	0.13667500
C	3.56860700	1.28367000	-2.03545600
H	1.48848900	1.05269500	-2.69116300
C	4.51510000	1.00127800	-1.01914900
H	4.88349700	0.05949200	0.91608000
H	3.86895700	1.83683800	-2.93239300
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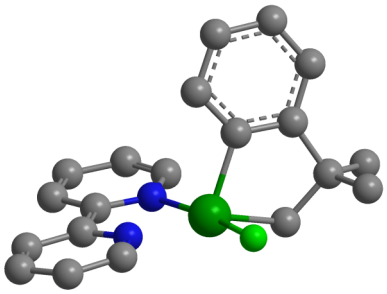
Complex 8-I



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C	0.77700100	3.67041700	-0.77222500
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H	3.92427700	2.56385500	0.00804200
H	0.18732800	4.56730700	-0.97778700
H	2.68727700	4.69108600	-0.48621500
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C	3.86960800	-2.52867700	0.62463900
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C	4.73756100	-1.41442500	0.61322700
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H	4.89123300	0.73867100	0.30986100
H	5.80486600	-1.54069400	0.82132700
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C	-0.83324700	0.30869300	2.13605300
C	-2.72207100	0.07035000	0.50609500
C	-1.76912600	0.71878500	3.12384100
H	0.23576600	0.22453500	2.36560300
C	-3.62428200	0.49206700	1.51863800
C	-3.14801500	0.81198400	2.81188600
H	-1.40981800	0.96006000	4.13043800
H	-4.69603100	0.55914600	1.28912200
H	-3.85466000	1.13299400	3.58458100
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H	-1.54432400	0.68562300	-2.12310100
H	-1.61825400	-1.10985600	-2.43696100
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C	-3.60928300	-1.82693900	-0.85132200
H	-4.53349900	-1.86315900	-0.24538800
H	-3.85395600	-2.16970300	-1.87426700
H	-2.86661600	-2.51610800	-0.41702600
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H	-4.23286200	0.24687400	-2.63730100
H	-5.07619000	0.47133600	-1.08551100
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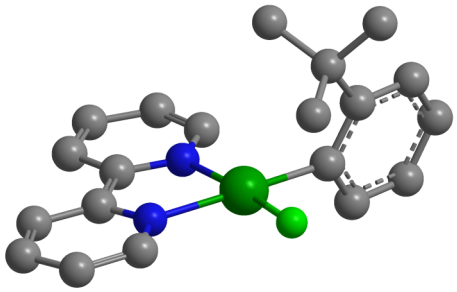
Complex 8-sp^3-ts



Pd	-0.06868900	-0.53774700	-0.51850100
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H	-4.88129300	0.98140800	0.54319300
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C	-2.69628000	2.65750500	0.65248200
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H	0.15353800	4.57660700	0.63321400
H	-3.77265300	2.70909400	0.83994400
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H	2.00127200	-2.81780900	0.17027800
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C	2.31958600	-1.02272800	1.42754900
C	3.47262600	-1.84988000	2.10180000
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H	3.07971600	-2.58301800	2.82997700
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H	1.27610700	-0.83628700	3.34965700
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C	2.79745700	-0.18776600	0.24668000
C	2.20120800	0.77700500	-1.93791400
C	4.10102500	0.36315800	0.13534600
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C	4.44800800	1.12789500	-1.00318900
H	4.84821400	0.19506600	0.92196300
H	3.78410300	1.89825800	-2.93500200
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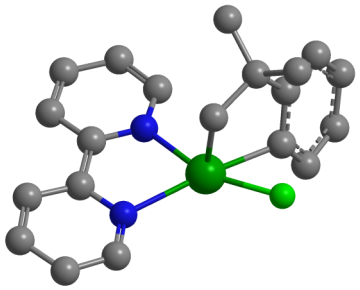
Complex 8-sp^2-ts



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C	0.10358600	2.28805200	-0.26156000
C	-2.07863100	1.42877900	-0.04638200
C	-0.34427900	3.62093700	-0.15607200
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C	-2.60346300	2.73984700	0.07022700
C	-1.72886700	3.84508300	0.01638600
H	0.37186400	4.44485100	-0.21132600
H	-3.68072700	2.89741400	0.17665700
H	-2.12414700	4.86247200	0.09927800
C	0.51022600	-0.92096100	1.49563200
H	0.36505400	-2.01470200	1.56297300
H	-0.28287400	-0.36412900	2.02656800
C	1.95199200	-0.44081200	1.78121300
C	2.69861700	-1.58230500	2.51977500
H	2.75114900	-2.48735900	1.88992700
H	3.73056700	-1.26136900	2.75291700
H	2.19269100	-1.83390300	3.47037500
C	1.89248000	0.81384900	2.67808600
H	1.37386300	1.65112400	2.17245200
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H	2.90240400	1.15602200	2.96373600
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C	2.66669600	-0.15573800	0.46043600
C	2.64519300	-0.45436100	-2.03418200
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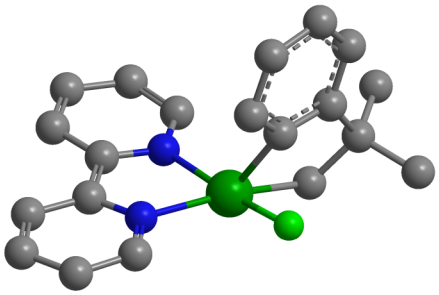
Complex 8-I-sp^2-ts



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C	3.46844500	-2.87820000	-0.38465400
H	1.33562200	-3.00563300	-0.92615000
C	4.13460500	-0.63348800	0.30039400
C	4.46760600	-1.98555600	0.06321900
H	3.68763400	-3.92983300	-0.58814900
H	4.90653700	0.06672000	0.63324400
H	5.49389900	-2.33241200	0.21990300
C	-1.51636500	-0.99955000	0.53486900
C	-1.06993700	-1.89869700	1.50300600
C	-2.67949400	-0.22078000	0.51098700
C	-1.86258900	-1.93558700	2.68126000
H	-0.18591500	-2.52726700	1.36960400
C	-3.44168700	-0.31359100	1.70879800
C	-3.04054200	-1.15499500	2.77484700
H	-1.56205400	-2.59678500	3.50124100
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H	-3.65554300	-1.20732100	3.67894100
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H	-1.44767400	1.94356900	-1.57738600
H	-1.77311000	0.46145000	-2.55579900
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C	-4.02992000	-0.19012400	-1.57923100
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H	-2.99240200	2.52723400	0.37306200
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N	1.05120000	1.49738000	-0.08417400
N	1.84830200	-1.08535300	-0.33899500

References

[1] For further information on using this method to reference NMR spectra, refer to the following website: www.iupac.org/publications/pac/2001/7311/7311x1795.html.

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NMR Spectra of New Compounds

JMRVIIII-190.characterization

Sample Name:

Data Collected on:
Sn.Chem.LSA.UMich.edu-inova500
Archive directory:

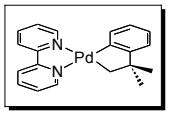
Sample directory:

FidFile: JMRVIIII-190.characterization

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jun 11 2011

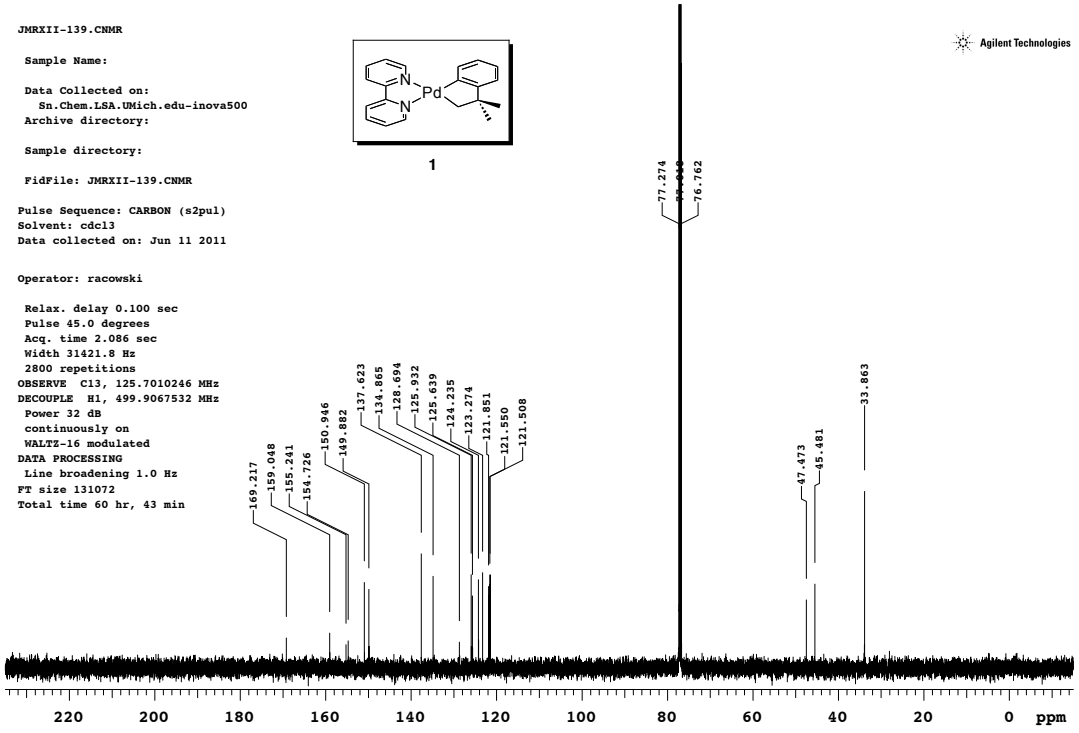
Operator: racowski

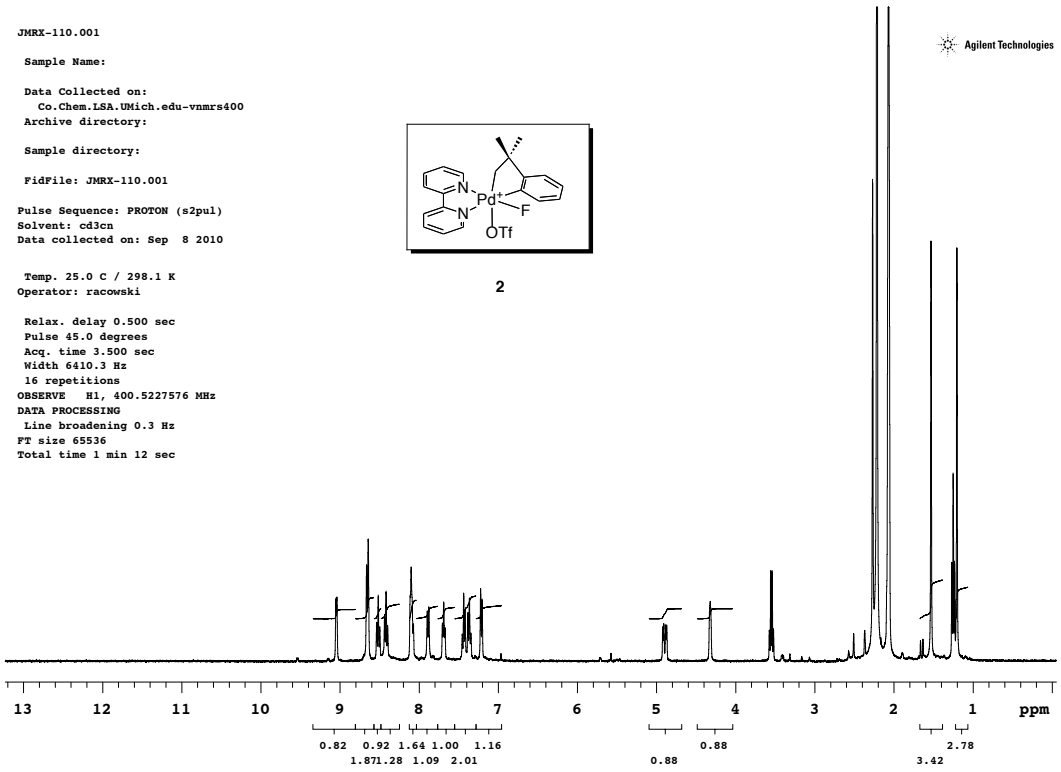
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 7998.4 Hz
16 repetitions
OBSERVE H1, 499.9042733 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 1 min 12 sec



1

Agilent Technologies


JMRXII-139.CNMR
Sample Name:
Data Collected on:
Sn.Chem.LSA.UMich.edu-inova500
Archive directory:
Sample directory:
FidFile: JMRXII-139.CNMR
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jun 11 2011
Operator: racowski
Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 2.086 sec
Width 31421.8 Hz
2800 repetitions
OBSERVE C13, 125.7010246 MHz
DECOUPLE H1, 499.9067532 MHz
Power 32 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 60 hr, 43 min
N
Pd
N
1
Agilent Technologies
169.217
159.048
155.241
154.726
150.946
149.882
137.623
134.865
128.694
125.932
125.639
124.235
123.274
121.851
121.550
121.508
77.274
76.762
47.473
45.481
33.863
220
200
180
160
140
120
100
80
60
40
20
0
ppm


JMRX-110.001
Sample Name:
Data Collected on:
Co.Chem.LSA.UMich.edu-vnmrs400
Archive directory:
Sample directory:
FidFile: JMRX-110.001
Pulse Sequence: PROTON (s2pul)
Solvent: cd3cn
Data collected on: Sep 8 2010
Temp. 25.0 C / 298.1 K
Operator: racowski
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6410.3 Hz
16 repetitions
OBSERVE H1, 400.5227576 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 1 min 12 sec
Agilent Technologies
N
N
Pd
F
OTf
2
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.82
0.92
1.64
1.00
1.16
1.87
1.28
1.09
2.01
0.88
0.88
3.42
2.78

JMRX-110.001FNMR

Sample Name:

Data Collected on:
Co.Chem.LSA.UMich.edu-vnmrs400
Archive directory:

Sample directory:

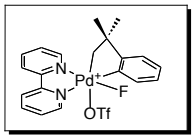
FidFile: JMRX-110.001FNMR

Pulse Sequence: FLUORINE (s2pul)
Solvent: cd3cn
Data collected on: Sep 8 2010

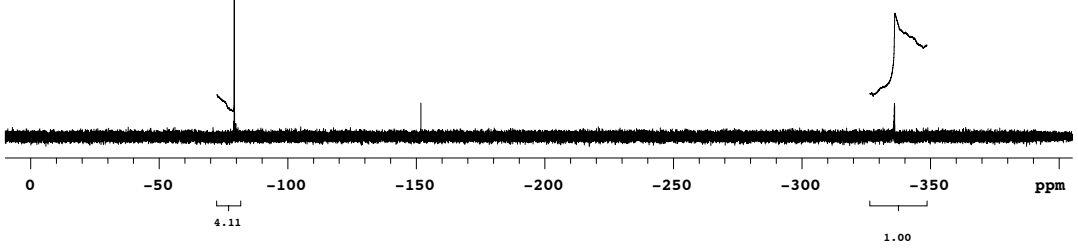
Temp. 25.0 C / 298.1 K
Operator: racowski

Relax. delay 1.000 sec
Pulse 30.0 degrees
Acq. time 0.786 sec
Width 166.7 kHz
16 repetitions
OBSERVE F19, 376.8679276 MHz
DATA PROCESSING
Line broadening 1.5 Hz
FT size 262144
Total time 0 min 32 sec

Agilent Technologies



2



JMRX-111.characterization

Agilent Technologies

Sample Name:

Data Collected on:
Yb-vnmrs700
Archive directory:

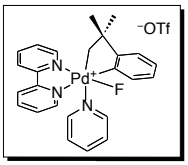
Sample directory:

FidFile: JMRX-111.characterization

Pulse Sequence: PROTON (s2pul)
Solvent: cd2cl2
Data collected on: Jun 6 2011

Temp. 25.0 C / 298.1 K
Operator: racowski

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 11261.3 Hz
16 repetitions
OBSERVE H1, 699.7579699 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 1 min 12 sec



3

JMRX-25.001FNMR

Sample Name:

Data Collected on:
Co.Chem.LSA.UMich.edu-vnmrs400
Archive directory:

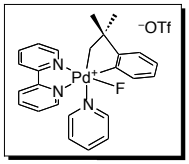
Sample directory:

FidFile: JMRX-25.001FNMR

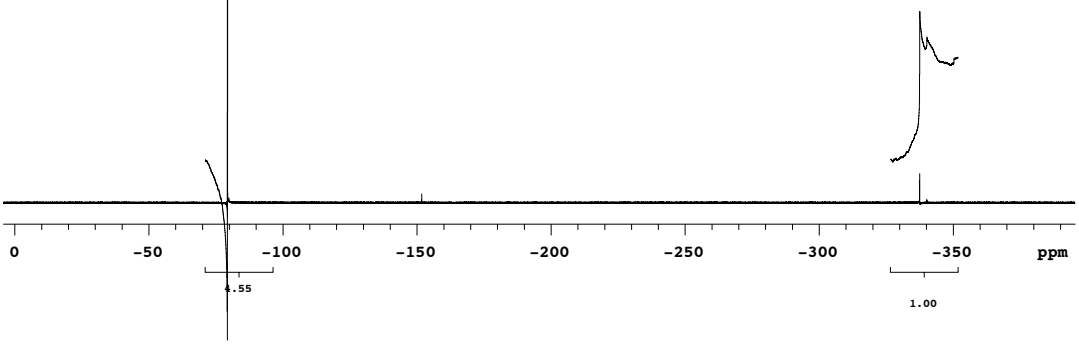
Pulse Sequence: FLUORINE (s2pul)
Solvent: cd3cn
Data collected on: Jul 28 2010

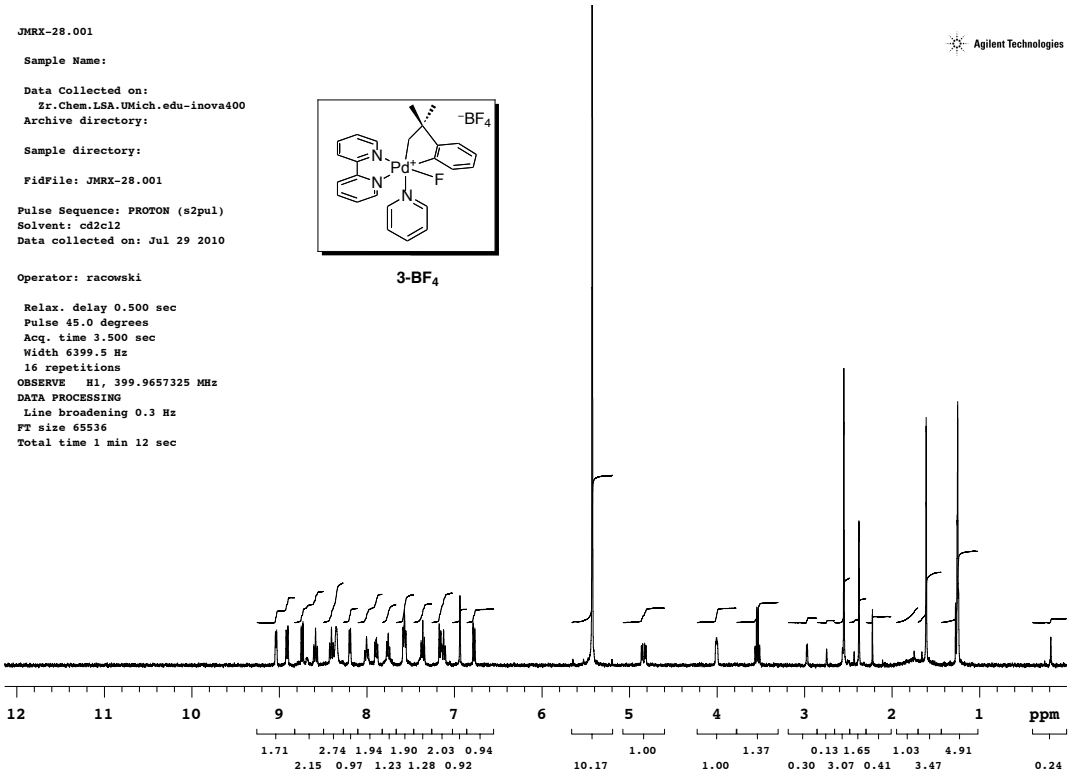
Temp. 25.0 C / 298.1 K
Operator: racowski

Relax. delay 1.000 sec
Pulse 30.0 degrees
Acq. time 0.786 sec
Width 166.7 kHz
32 repetitions
OBSERVE F19, 376.8678161 MHz
DATA PROCESSING
Line broadening 1.5 Hz
FT size 262144
Total time 1 min 58 sec



3




JMRX-28.001
Sample Name:
Data Collected on:
Zr.Chem.LSA.UMich.edu-inova400
Archive directory:
Sample directory:
FidFile: JMRX-28.001
Pulse Sequence: PROTON (s2pul)
Solvent: cd2cl2
Data collected on: Jul 29 2010
Operator: racowski
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6399.5 Hz
16 repetitions
OBSERVE H1, 399.9657325 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 1 min 12 sec
Agilent Technologies
−BF4
N
Pd+
F
N
N
3-BF4
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.71
2.74
1.94
1.90
2.03
0.94
2.15
0.97
1.23
1.28
0.92
10.17
1.00
1.37
1.00
0.13
1.65
0.30
3.07
0.41
1.03
4.91
3.47
0.24

JMRX-28.001FNMR

Agilent Technologies

Sample Name:

Data Collected on:
Zr.Chem.LSA.UMich.edu-inova400
Archive directory:

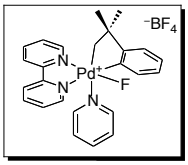
Sample directory:

FidFile: JMRX-28.001FNMR

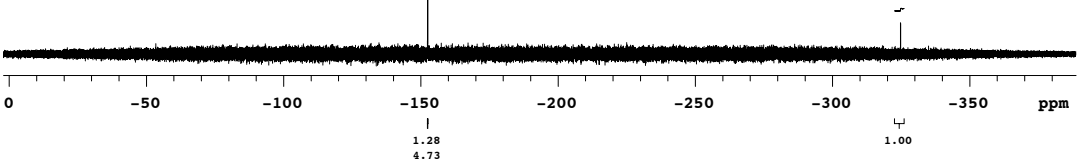
Pulse Sequence: FLUORINE (s2pul)
Solvent: cd2cl2
Data collected on: Jul 29 2010

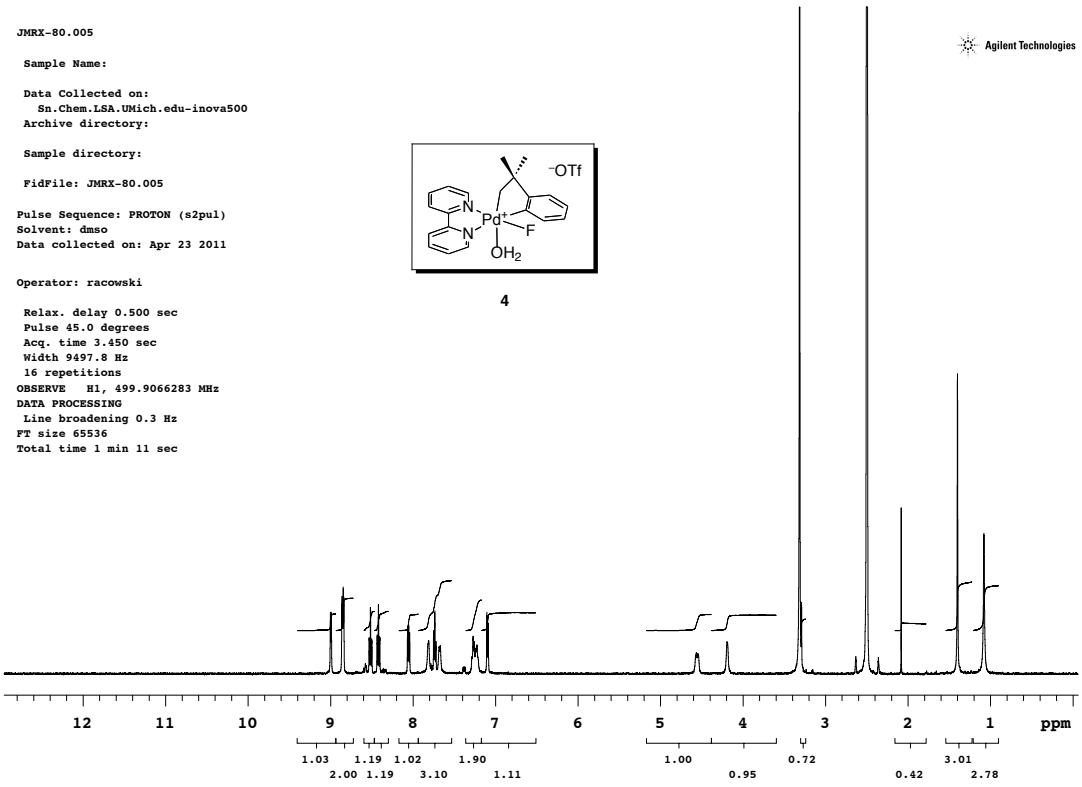
Operator: racowski

Relax. delay 1.000 sec
Pulse 30.0 degrees
Acq. time 0.809 sec
Width 161.9 kHz
16 repetitions
OBSERVE F19, 376.3438453 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 262144
Total time 0 min 33 sec



3-BF_4




JMRX-80.005
Sample Name:
Data Collected on:
Sn.Chem.LSA.UMich.edu-inova500
Archive directory:
Sample directory:
FidFile: JMRX-80.005
Pulse Sequence: PROTON (s2pul)
Solvent: dmso
Data collected on: Apr 23 2011
Operator: racowski
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.450 sec
Width 9497.8 Hz
16 repetitions
OBSERVE H1, 499.9066283 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 1 min 11 sec
Agilent Technologies
⁻OTf
N
Pd
F
OH2
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.03
2.00
1.19
1.19
1.02
3.10
1.90
1.11
1.00
0.95
0.72
0.42
3.01
2.78

4

JMRX-80.FNMR

Agilent Technologies

Sample Name:

Data Collected on:
Co.Chem.LSA.UMich.edu-vnmrs400
Archive directory:

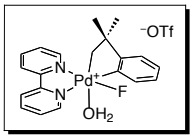
Sample directory:

FidFile: JMRX-80.FNMR

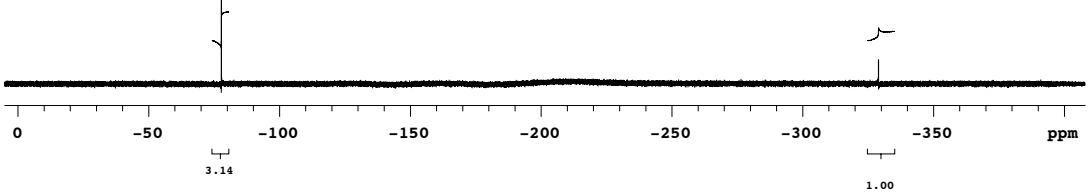
Pulse Sequence: FLUORINE (s2pul)
Solvent: cd2cl2
Data collected on: Aug 16 2011

Operator: racowski

Relax. delay 1.000 sec
Pulse 30.0 degrees
Acq. time 0.786 sec
Width 166.7 kHz
16 repetitions
OBSERVE F19, 376.8675382 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 262144
Total time 0 min 32 sec



4



3.14

1.00

JMRXII-125.001

Sample Name:

Data Collected on:
Te.Chem.LSA.UMich.edu-vnmrs500
Archive directory:

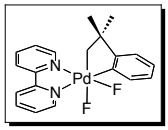
Sample directory:

FidFile: JRMXII-125.001

Pulse Sequence: PROTON (s2pul)
Solvent: cd2cl2
Data collected on: May 2 2011

Temp. 20.0 C / 293.1 K
Operator: racowski

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 8012.8 Hz
16 repetitions
OBSERVE H1, 500.0941301 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 1 min 12 sec



5

JMRXII-125.001FNMR

Agilent Technologies

Sample Name:

Data Collected on:
Te.Chem.LSA.UMich.edu-vnmrs500
Archive directory:

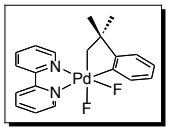
Sample directory:

FidFile: JRMXII-125.001FNMR

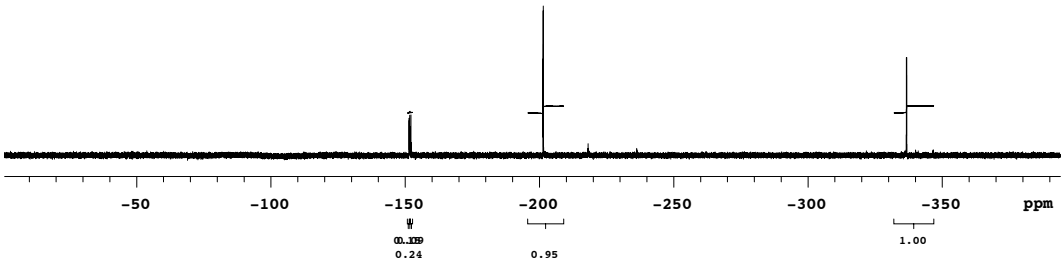
Pulse Sequence: FLUORINE (s2pul)
Solvent: cd2cl2
Data collected on: May 2 2011

Temp. 20.0 C / 293.1 K
Operator: racowski

Relax. delay 1.000 sec
Pulse 30.0 degrees
Acq. time 0.629 sec
Width 208.3 kHz
16 repetitions
OBSERVE F19, 470.5586258 MHz
DATA PROCESSING
Line broadening 1.5 Hz
FT size 262144
Total time 0 min 29 sec



5



JMRXII-192B.001

Agilent Technologies

Sample Name:

Data Collected on:
Sn.Chem.LSA.UMich.edu-inova500
Archive directory:

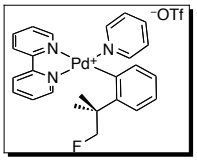
Sample directory:

FidFile: JMRXII-192B.001

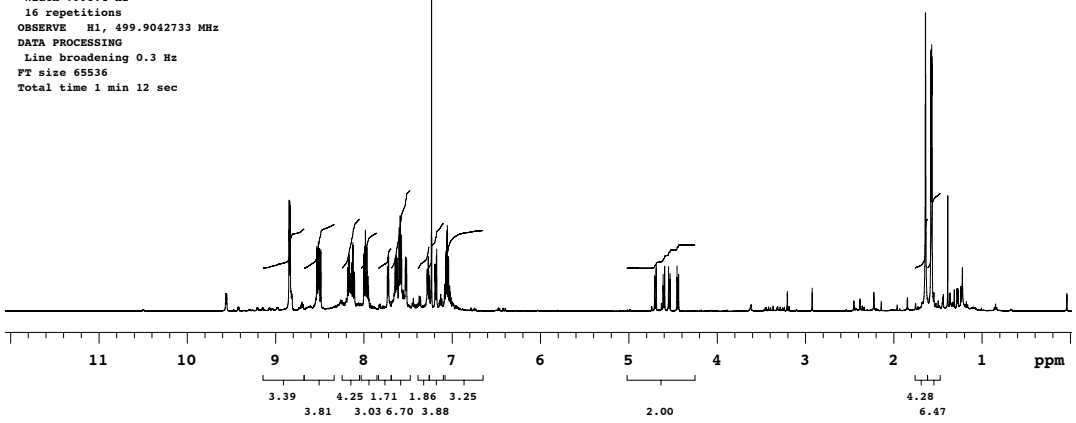
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jun 11 2011

Operator: racowski

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 7998.4 Hz
16 repetitions
OBSERVE H1, 499.9042733 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 1 min 12 sec



6



JMRXIII-192B.FNMR

Sample Name:

Data Collected on:
Te-vnmrs500
Archive directory:

Sample directory:

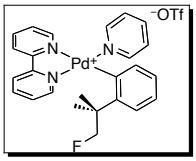
FidFile: JMRXIII-192B.FNMR

Pulse Sequence: FLUORINE (s2pul)
Solvent: cdcl3
Data collected on: Sep 13 2011

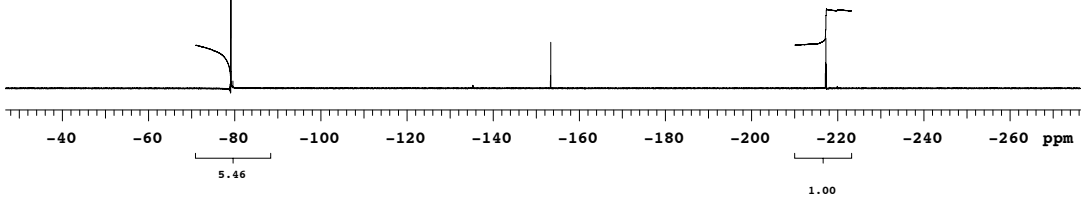
Operator: racowski

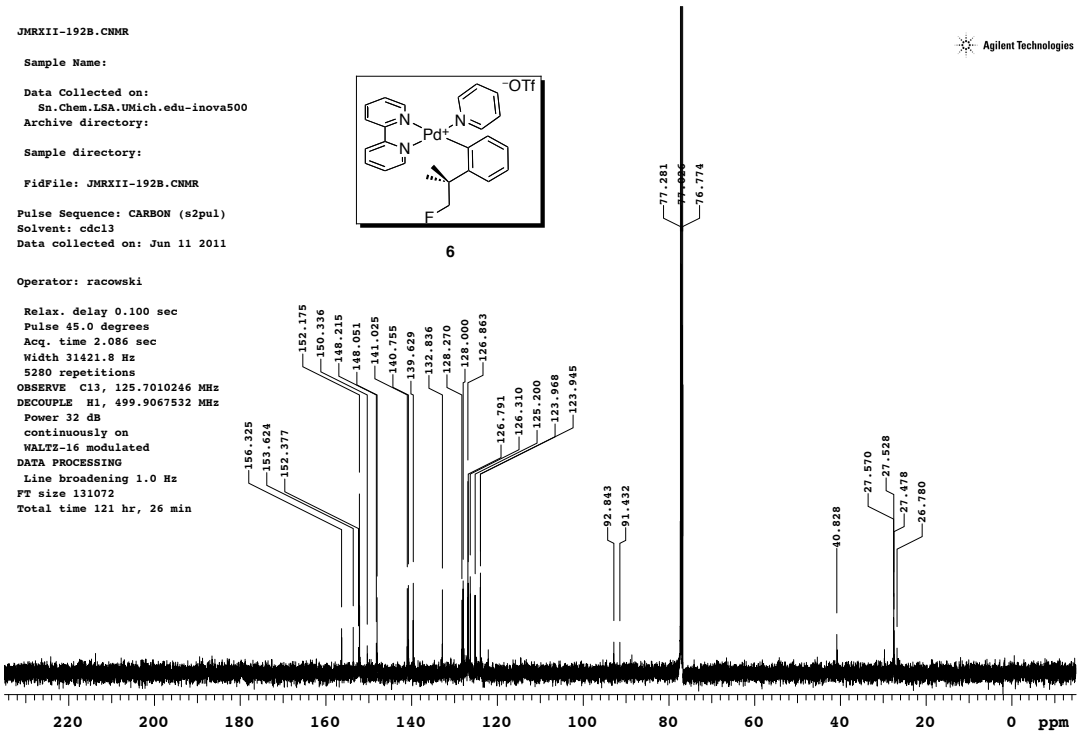
Relax. delay 1.000 sec
Pulse 30.0 degrees
Acq. time 0.839 sec
Width 156.2 kHz
16 repetitions
OBSERVE F19, 470.5581429 MHz
DATA PROCESSING
Line broadening 1.5 Hz
FT size 262144
Total time 0 min 33 sec

Agilent Technologies



6




JMRXII-192B.CNMR
Sample Name:
Data Collected on:
Sn.Chem.LSA.UMich.edu-inova500
Archive directory:
Sample directory:
FidFile: JMRXII-192B.CNMR
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jun 11 2011
Operator: racowski
Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 2.086 sec
Width 31421.8 Hz
5280 repetitions
OBSERVE C13, 125.7010246 MHz
DECOUPLE H1, 499.9067532 MHz
Power 32 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 121 hr, 26 min
Agilent Technologies
−OTf
Pd+
N
F
6
77.281
76.774
152.175
150.336
148.215
148.051
141.025
140.755
139.629
132.836
128.270
128.000
126.863
126.791
126.310
125.200
123.968
123.945
156.325
153.624
152.377
92.843
91.432
40.828
27.570
27.528
27.478
26.780
220
200
180
160
140
120
100
80
60
40
20
0
ppm

JMRXII-191.002workup

Sample Name:

Data Collected on:
Yb-vnmrs700
Archive directory:

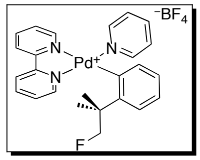
Sample directory:

FidFile: JMRXII-191.002workup

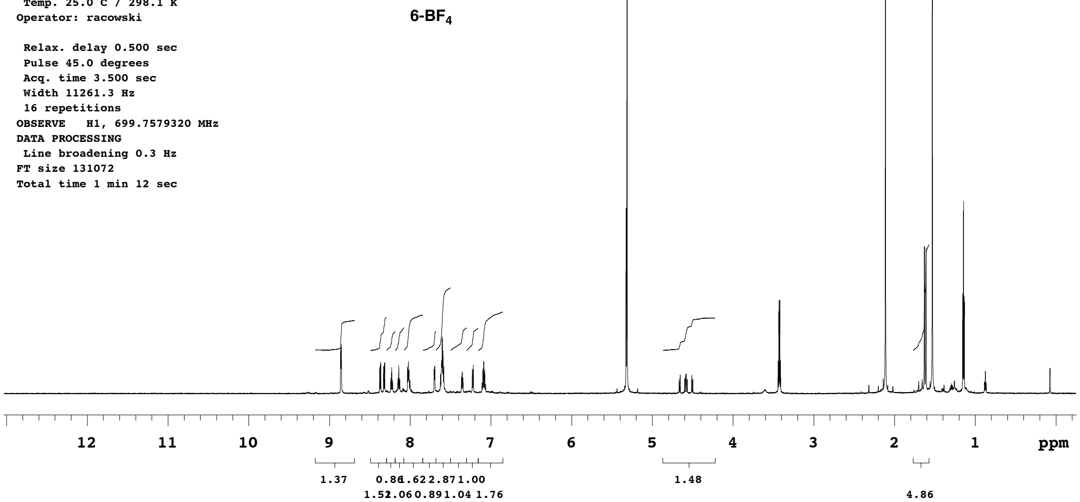
Pulse Sequence: PROTON (s2pul)
Solvent: cd2cl2
Data collected on: Jun 10 2011

Temp. 25.0 C / 298.1 K
Operator: racowski

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 11261.3 Hz
16 repetitions
OBSERVE H1, 699.7579320 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 1 min 12 sec



6-BF_4



JMRXII-192A.FNMR

Agilent Technologies

Sample Name:

Data Collected on:
Co.Chem.LSA.UMich.edu-vnmrs400
Archive directory:

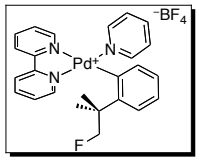
Sample directory:

FidFile: JMRXII-192A.FNMR

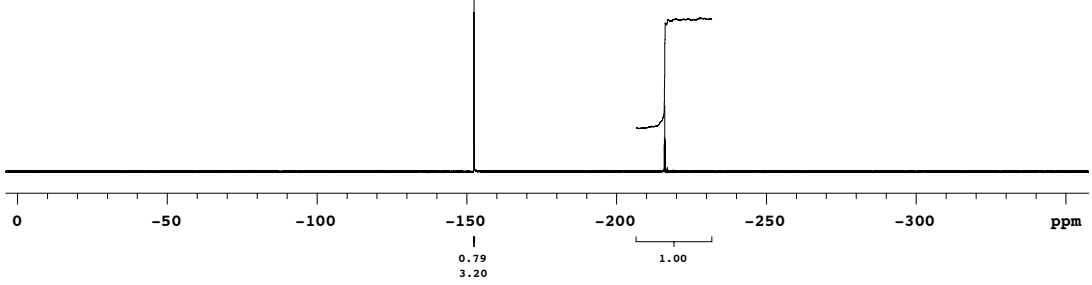
Pulse Sequence: FLUORINE (s2pul)
Solvent: cdcl3
Data collected on: Jun 11 2011

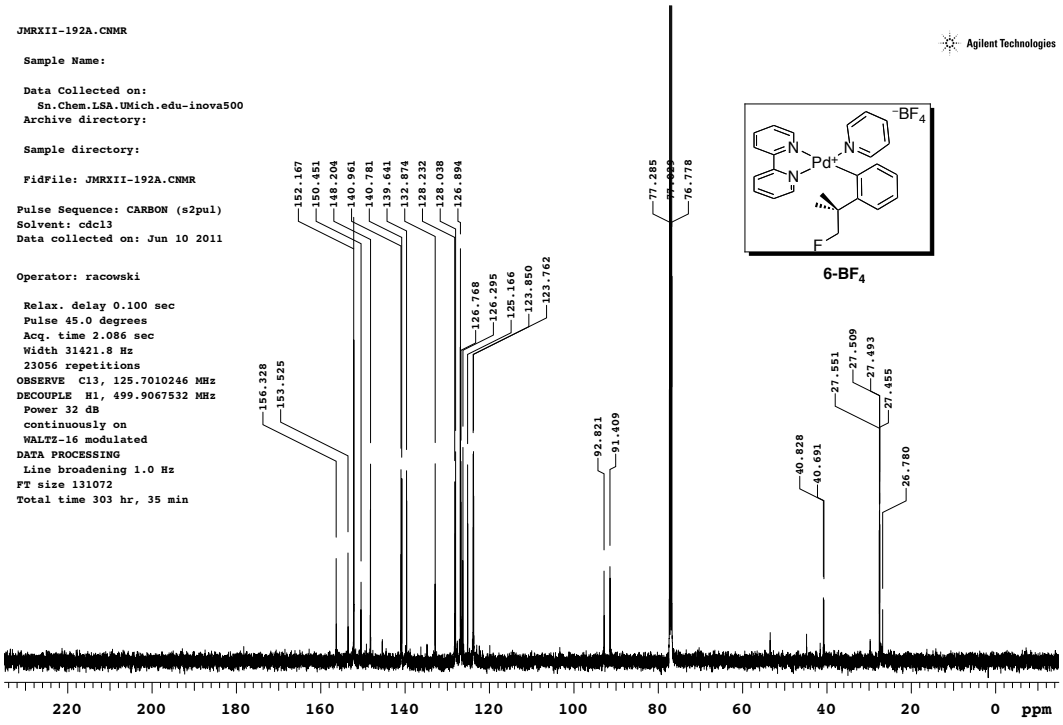
Temp. 25.0 C / 298.1 K
Operator: racowski

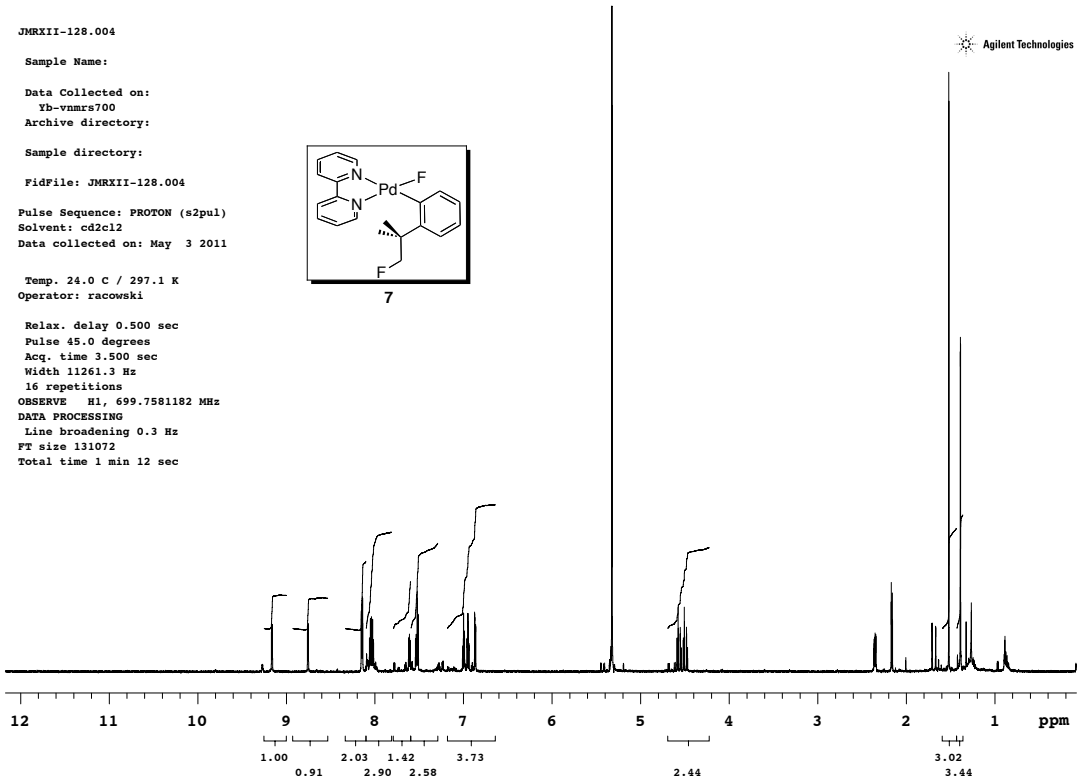
Relax. delay 1.000 sec
Pulse 30.0 degrees
Acq. time 0.786 sec
Width 166.7 kHz
16 repetitions
OBSERVE F19, 376.8659339 MHz
DATA PROCESSING
Line broadening 1.5 Hz
FT size 262144
Total time 0 min 32 sec



6-BF_4




JMRXII-192A.CNMR
Sample Name:
Data Collected on:
Sn.Chem.LSA.UMich.edu-inova500
Archive directory:
Sample directory:
FidFile: JMRXII-192A.CNMR
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jun 10 2011
Operator: racowski
Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 2.086 sec
Width 31421.8 Hz
23056 repetitions
OBSERVE C13, 125.7010246 MHz
DECOUPLE H1, 499.9067532 MHz
Power 32 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 303 hr, 35 min
Agilent Technologies
152.167
150.451
148.204
140.961
140.781
139.641
132.874
128.232
128.038
126.894
126.768
126.295
125.166
123.850
123.762
156.328
153.525
92.821
91.409
77.285
77.000
76.778
27.551
27.509
27.493
27.455
40.828
40.691
26.780
N
N
N
Pd+
−BF4
F
6-BF4
220
200
180
160
140
120
100
80
60
40
20
0
ppm


JMRXII-128.004
Sample Name:
Data Collected on:
Yb-vnmrs700
Archive directory:
Sample directory:
FidFile: JMRXII-128.004
Pulse Sequence: PROTON (s2pul)
Solvent: cd2cl2
Data collected on: May 3 2011
Temp. 24.0 C / 297.1 K
Operator: racowski
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 11261.3 Hz
16 repetitions
OBSERVE H1, 699.7581182 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 1 min 12 sec
Agilent Technologies
N
Pd
F
N
F
7
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
0.91
2.03
2.90
1.42
2.58
3.73
2.44
3.02
3.44

JMRX-51.filtrateFNMR

Sample Name:

Data Collected on:
Zr.Chem.LSA.UMich.edu-inova400
Archive directory:

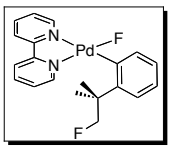
Sample directory:

FidFile: JMRX-51.filtrateFNMR

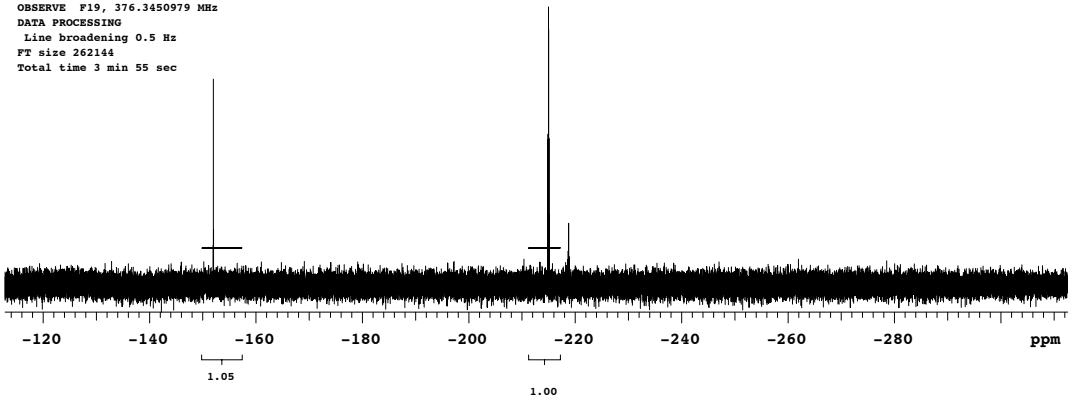
Pulse Sequence: FLUORINE (s2pul)
Solvent: cd2cl2
Data collected on: Aug 11 2010

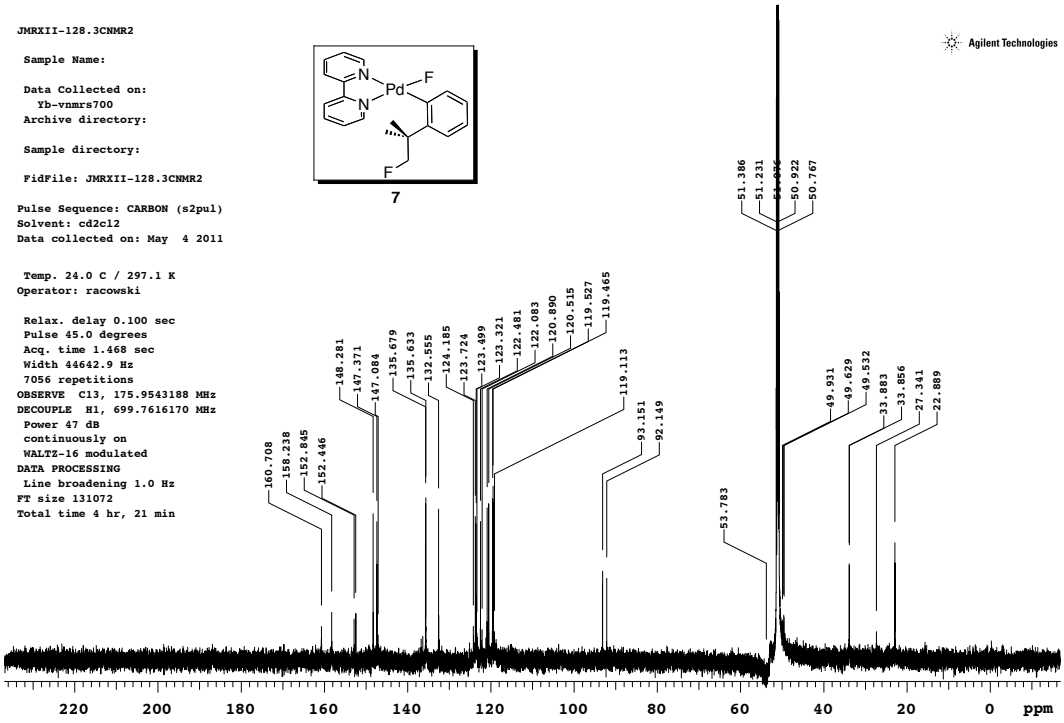
Operator: racowski

Relax. delay 1.000 sec
Pulse 30.0 degrees
Acq. time 0.809 sec
Width 161.9 kHz
16 repetitions
OBSERVE F19, 376.3450979 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 262144
Total time 3 min 55 sec



7




JMRXII-128.3CNMR2
Sample Name:
Data Collected on:
Yb-vnmrs700
Archive directory:
Sample directory:
FidFile: JMRXII-128.3CNMR2
Pulse Sequence: CARBON (s2pul)
Solvent: cd2cl2
Data collected on: May 4 2011
Temp. 24.0 C / 297.1 K
Operator: racowski
Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 1.468 sec
Width 44642.9 Hz
7056 repetitions
OBSERVE C13, 175.9543188 MHz
DECOUPLE H1, 699.7616170 MHz
Power 47 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 4 hr, 21 min
N
Pd
F
N
F
7
Agilent Technologies
160.708
158.238
152.845
152.446
148.281
147.371
147.084
135.679
135.633
132.555
124.185
123.724
123.499
123.321
122.481
122.083
120.890
120.515
119.527
119.465
119.113
93.151
92.149
53.783
51.386
51.231
50.922
50.767
49.931
49.629
49.532
33.883
33.856
27.341
22.889
220
200
180
160
140
120
100
80
60
40
20
0
ppm