

Supporting Information

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**Carbon(sp³)–Fluorine Bond-Forming Reductive Elimination from
Palladium(IV) Complexes****

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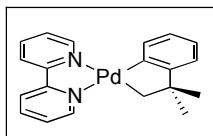
General Procedures

NMR spectra were obtained on a Varian vnmrs 700 (699.76 MHz for ^1H ; 175.95 MHz for ^{13}C), a Varian Inova 400 (399.96 MHz for ^1H ; 376.34 MHz for ^{19}F ; 100.57 MHz for ^{13}C), a Varian vnmr500 (500.09 MHz for ^1H ; 470.56 MHz for ^{19}F ; 125.75 MHz for ^{13}C), or a Varian MR400 (400.53 MHz for ^1H ; 376.87 MHz for ^{19}F ; 100.71 MHz for ^{13}C) spectrometer. ^1H , ^{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 ^1H NMR spectrum.¹ ^1H 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

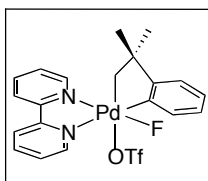
Bipyridine (bpy) and 2-methyl-2-phenylpropyl magnesium chloride were obtained from Aldrich. 1-Fluoro-2,4,6-trimethylpyridinium triflate (NFTPT) and 1-fluoro-2,4,6-trimethylpyridinium tetrafluoroborate (NFTPB) were obtained from TCI America. Unless otherwise noted, all reagents were used as received. 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

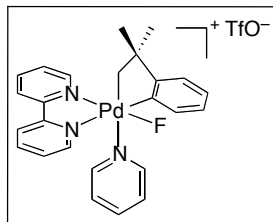


Pd^{II}(CH₂CMe₂-*o*-C₆H₄)(COD)² (720 mg, 2.08, 1.0 equiv) was combined with 2,2'-bipyridine (325 mg, 2.08 mmol, 1.0 equiv) in CH₂Cl₂ (200 mL), and the reaction mixture allowed to stir for 30 min. The solution was concentrated under vacuum (to 5 mL), and hexanes (30 mL) was added to precipitate the product. Complex **1** was isolated as a bright yellow solid (737 mg, 90% yield). ¹H NMR (500 MHz [D₃]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). ¹³C NMR (125 MHz [D₃]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 C₂₀H₂₀N₂Pd, 395.0734; Found, 395.0746.

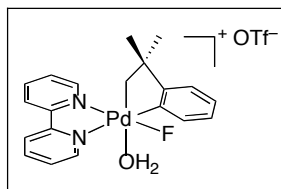
Synthesis of Pd^{IV} Complexes 2-5



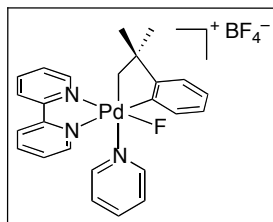
Compound **1** (70 mg, 0.18 mmol, 1.0 equiv) and NFTPT (52 mg, 0.18 mmol, 1.0 equiv) were combined in CH₂Cl₂ (15 mL), and this mixture was stirred for 15 min. The solvent was removed by rotary evaporation, and the resulting yellow oil was washed with diethyl ether (15 mL). The solid material was then dissolved in CH₂Cl₂ (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). ¹H NMR (400 MHz [D₃]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). ¹⁹F NMR (376 MHz [D₃]acetonitrile, 25 °C): δ = -79.11 (s, 3F), -336.17 (d, *J* = 15 Hz, 1F). ¹³C 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 C₂₀H₂₀FN₂Pd 413.0640; Found, 413.0644.



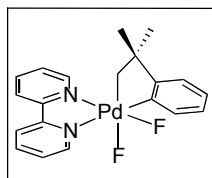
Compound **1** (120 mg, 0.3 mmol, 1.0 equiv), NFTPT (88 mg, 0.3 mmol, 1.0 equiv), and C_5H_5N (49 μ L, 0.6 mmol, 2.0 equiv) were combined in CH_2Cl_2 (15 mL), and this mixture was stirred for 15 min. The solvent was removed by rotary evaporation, and the resulting yellow oil was washed with diethyl ether (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). 1H NMR (700 MHz [D_2]dichloromethane, 25 $^\circ$ 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 $^\circ$ 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 $^\circ$ C 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). 1H NMR (500 MHz [D_6]dimethyl sulfoxide, 25 $^\circ$ 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 $^\circ$ 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.

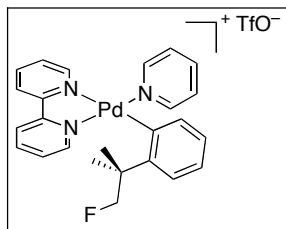


Compound **1** (552 mg, 1.4 mmol, 1.0 equiv), NFTPB (259 mg, 1.4 mmol, 1.0 equiv), and C₅H₅N (225 μ L, 2.8 mmol, 2.0 equiv) were combined in CH₂Cl₂ (50 mL), and this mixture was stirred for 15 min. The solvent was removed by rotary evaporation, and the resulting yellow oil was washed with diethyl ether (20 mL). The solid material was then dissolved in CH₂Cl₂ (3 mL), and diethyl ether (25 mL) was added to precipitate the product. The precipitate was collected and dried under vacuum to afford **3-BF₄** as an off-white solid (486 mg, 58% yield). ¹H NMR (400 MHz [D₂]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). ¹⁹F NMR (376 MHz [D₂]dichloromethane, 25 °C): δ = -152.48 (s, 4F), -324.80 (d, *J* = 15 Hz, 1F). ¹³C 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 – pyridine – BF₄]⁺ calcd for C₂₀H₂₀FN₂Pd 413.0640; Found, 413.0645.

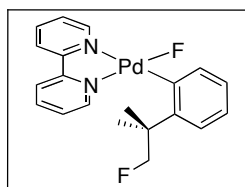


Compound **2** (310 mg, 0.54 mmol, 1.0 equiv) and Me₄NF (52 mg, 0.86 mmol, 1.6 equiv) were combined in dry CH₂Cl₂ (15 mL), and this mixture was stirred for 15 min in the glovebox. The solution turned dark orange with a dark solid precipitate. The reaction was filtered through celite, and the solvent 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 % Me₄NBF₄ as determined by ¹H NMR). ¹H NMR (500 MHz [D₂]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). ¹⁹F NMR (470 MHz [D₂]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 C₂₀H₂₀FN₂Pd 413.0645; Found, 413.0640.

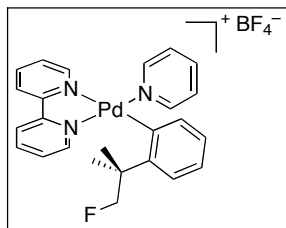
Synthesis of Pd^{II} Reductive Elimination Products



Compound **3** (30 mg, 0.06 mmol) was dissolved 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** as a tacky yellow solid (28 mg, 93% yield). ^1H NMR (500 MHz $[\text{D}_3]$ 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 $[\text{D}_3]$ chloroform, 25 °C): δ = -78.99 (s, 1F), -217.01 (t, J = 48 Hz, 1F). ^{13}C NMR (125 MHz $[\text{D}_3]$ 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): $[\text{M} - \text{C}_5\text{H}_5\text{N} - \text{OTf}]^+$ calcd for $\text{C}_{20}\text{H}_{20}\text{FN}_2\text{Pd}$ 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 °C. 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). ^1H NMR (700 MHz $[\text{D}_2]$ 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 $[\text{D}_2]$ dichloromethane, 25 °C): δ = -151.89 (s, 1F), -214.87 (t, J = 49 Hz, 1F). ^{13}C NMR (175 MHz $[\text{D}_3]$ chloroform, 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): $[\text{M} - \text{F}]^+$ calcd for $\text{C}_{20}\text{H}_{20}\text{FN}_2\text{Pd}$ 413.0640; Found, 413.0641.

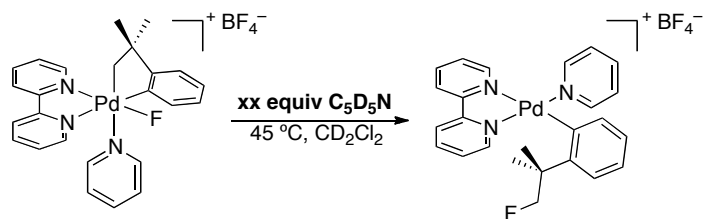


Compound **3-BF₄** (30 mg, 0.05 mmol) dissolved combined in CH₂Cl₂ (10 mL). The reaction was stirred for 30 min at 80 °C. The solvent was removed by rotary evaporation, and the resulting yellow oil was dissolved in CH₂Cl₂ (1 mL), and precipitated with pentane (15 mL). The precipitate was collected and dried under vacuum to afford **6-BF₄** as a tacky yellow solid (26 mg, 87% yield). ¹H NMR (700 MHz [D₂]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). ¹⁹F NMR (376 MHz [D₃]chloroform, 25 °C): δ = -152.42 (s, 1F), -216.08 (t, *J* = 48 Hz, 1F). ¹³C NMR (125 MHz [D₃]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 - C₅H₅N - BF₄]⁺ calcd for C₂₀H₂₀FN₂Pd 413.0645; Found, 413.0655.

Determining Order in Pyridine with 3-BF₄ at 45 °C in CD₂Cl₂

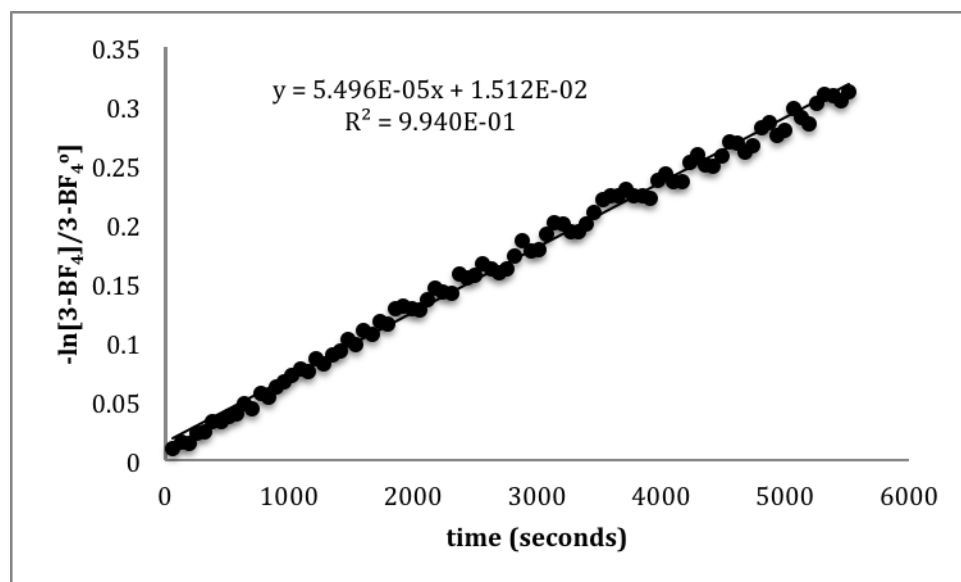
Complex **3-BF₄** (4.4 mg, 0.00758 mmol, 1.0 equiv) and C₅D₅N (0.001895 to 0.0114 mmol, 3.8 mM to 20.0 mM) were combined in a screw cap NMR tube and dissolved in CD₂Cl₂ (0.5 mL). An internal standard (2-nitrobenzotrifluoride) was added (20 μl of a stock solution in CD₂Cl₂, 0.00758, 1 equiv) and the tube was sealed with a Teflon®-lined cap. The tube was immediately placed in an NMR spectrometer with the temperature pre-equilibrated to 45 °C, and the reaction was allowed to equilibrate for 2 min. The rate of reductive elimination was monitored by ¹⁹F 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-BF₄**/**3-BF₄**^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-BF₄** in the Presence of 5.68 mM C_5D_5N)



Study of the Appearance of 7 at 40 °C in CD₂Cl₂

Complex **5** (4.9 mg, 0.0113 mmol, 1.0 equiv) and NMe₄NF (2.5 mg, 0.0269 mmol, 2.4 equiv) or NBu₄PF₆ (10.4 mg, 0.0269 mmol, 2.4 equiv) were combined in a screw cap NMR tube and dissolved in CD₂Cl₂ (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-equilibrated 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	<i>k</i>_{obs}
none	5.75 x 10 ⁻⁴
NMe ₄ F	3.26 x 10 ⁻⁴
NBu ₄ PF ₆	3.30 x 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 $-35\text{ }^{\circ}\text{C}$. A crystal of dimensions $0.10 \times 0.10 \times 0.10\text{ mm}$ 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 ($\lambda = 0.71073\text{ \AA}$) 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 ϕ 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 $\text{C}_{33}\text{H}_{26}\text{BN}_3\text{F}_4\text{Cl}_2\text{Pd}$. 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 $I > 2\sigma(I)$], $R1 = 0.0232$ 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**.

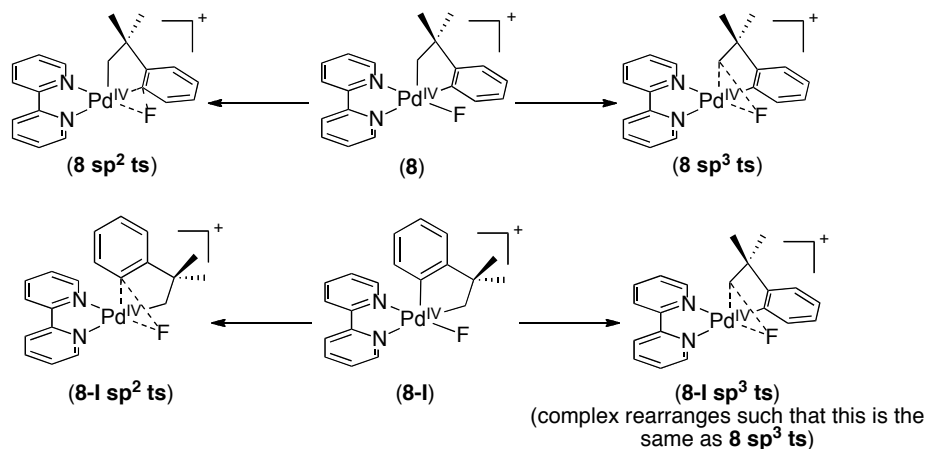
Empirical formula	C ₂₁ H ₂₂ F ₄ N ₂ O ₄ Pd S
Formula weight	580.87
Temperature	85(2) K
Wavelength	1.54178 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 9.3652(2) Å alpha = 94.404(7) deg. b = 11.5602(3) Å beta = 108.848(8) deg. c = 11.9928(8) Å gamma = 111.654(8) deg.
Volume	1113.33(8) Å 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 Å).
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 > 2σ(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.Å ⁻³

Computational Methods

Using the Gaussian 09 suite of programs,³ all density functional theory (DFT) calculations were performed with the M06 functional⁴ 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: $\xi_d = 0.8$ 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 model⁹ with default settings at the optimized geometries from gas phase calculations.

Energy Comparisons

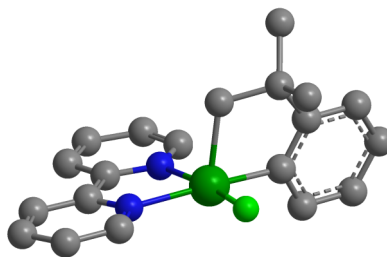
Calculated energies of the intermediates and transition states calculated are shown below. All energies have been solvent corrected using dichloromethane. All energies are listed in kcal/mol and complex **8** has been set to 0.0 for reference.



Complex	Electronic (SCF)	Enthalpy	Free Energy
8	0.0	0.0	0.0
8-I	3.2	3.2	2.3
8 sp³ ts	17.0	15.2	16.5
8 sp² ts	29.5	28.0	27.0
8-I sp² ts	22.7	21.1	23.3

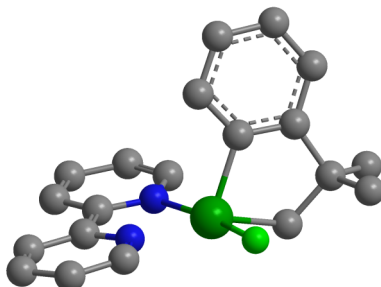
XYZ coordinates – Calculated Structures

Complex 8



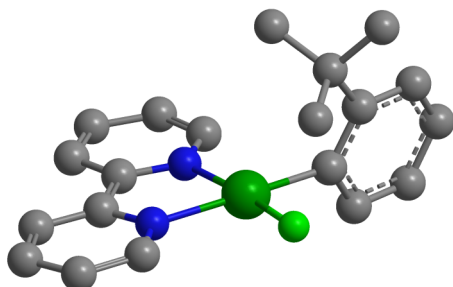
Pd	-0.01303000	-0.49412300	-0.47371000
C	-2.90262500	0.11813800	0.04593100
C	-2.68542400	-2.16451800	-0.48770600
C	-4.30416700	-0.00718600	0.18973400
C	-4.07856300	-2.37707200	-0.36317600
H	-1.97891300	-2.96082900	-0.75867300
C	-4.89326000	-1.27589400	-0.01894600
H	-4.93064500	0.85006400	0.45408300
H	-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
H	5.54882300	1.34566900	-1.13148400
F	0.44466500	-2.31081800	-0.98194500
N	-0.79792500	1.37219900	0.04124500
N	-2.13535800	-0.95441400	-0.28449700

Complex 8-I



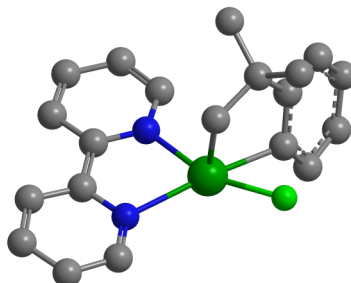
Pd	-0.04392300	-0.64474800	-0.51992000
C	2.16487600	1.30209800	-0.24363600
C	0.15217800	2.40685100	-0.77416400
C	2.85615800	2.53600600	-0.22539700
C	0.77700100	3.67041700	-0.77222500
H	-0.92332200	2.31192600	-0.96697900
C	2.15996800	3.73214800	-0.49768900
H	3.92427700	2.56385500	0.00804200
H	0.18732800	4.56730700	-0.97778700
H	2.68727700	4.69108600	-0.48621500
C	2.50027700	-2.31228500	0.34309700
C	2.84036900	0.00052800	0.06158700
C	3.86960800	-2.52867700	0.62463900
H	1.75808600	-3.12152900	0.31890600
C	4.22349300	-0.12800700	0.32744200
C	4.73756100	-1.41442500	0.61322700
H	4.23487100	-3.53626800	0.83985600
H	4.89123300	0.73867100	0.30986100
H	5.80486600	-1.54069400	0.82132700
C	-1.36602300	-0.00253400	0.87490400
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
C	-1.73873100	-0.31168100	-1.68097600
H	-1.54432400	0.68562300	-2.12310100
H	-1.61825400	-1.10985600	-2.43696100
C	-3.06433800	-0.38217000	-0.89680500
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
C	-4.09129000	0.54540000	-1.58227500
H	-4.23286200	0.24687400	-2.63730100
H	-5.07619000	0.47133600	-1.08551100
H	-3.76997400	1.60457900	-1.55660400
F	-0.57020100	-2.50996400	-0.47008400
N	0.82408700	1.25764600	-0.53748600
N	2.02128300	-1.08396400	0.07819600

Complex 8-sp³-ts



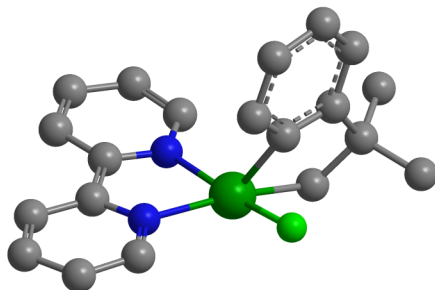
Pd	-0.06868900	-0.53774700	-0.51850100
C	-2.89075400	0.17759900	0.08919500
C	-2.77360100	-2.10237500	-0.47248800
C	-4.29333600	0.10282700	0.26112500
C	-4.17030600	-2.26467300	-0.32126100
H	-2.10766900	-2.92313000	-0.77113700
C	-4.93610500	-1.13851300	0.05336200
H	-4.88129300	0.98140800	0.54319300
H	-4.63277000	-3.24003800	-0.49497700
H	-6.02055900	-1.21997900	0.17844800
C	0.01803200	2.46216000	0.16586500
C	-2.09788200	1.43478900	0.26752500
C	-0.51122800	3.71355700	0.54421300
H	1.08736400	2.33497500	-0.04527900
C	-2.69628000	2.65750500	0.65248200
C	-1.89682200	3.81077300	0.79452200
H	0.15353800	4.57660700	0.63321400
H	-3.77265300	2.70909400	0.83994400
H	-2.34818500	4.76234200	1.09245000
C	1.51239600	-2.14893200	0.88433100
H	2.00127200	-2.81780900	0.17027800
H	0.67085600	-2.57227100	1.45279000
C	2.31958600	-1.02272800	1.42754900
C	3.47262600	-1.84988000	2.10180000
H	4.10160400	-2.36778700	1.35879700
H	4.09967900	-1.13860500	2.66969300
H	3.07971600	-2.58301800	2.82997700
C	1.60017700	-0.19619400	2.50767900
H	0.71142600	0.31298100	2.09405900
H	1.27610700	-0.83628700	3.34965700
H	2.28573800	0.57413500	2.90330500
C	1.84515900	0.03991100	-0.78596300
C	2.79745700	-0.18776600	0.24668000
C	2.20120800	0.77700500	-1.93791400
C	4.10102500	0.36315800	0.13534600
C	3.50643200	1.32416200	-2.04375300
H	1.47529900	0.92732700	-2.74799100
C	4.44800800	1.12789500	-1.00318900
H	4.84821400	0.19506600	0.92196300
H	3.78410300	1.89825800	-2.93500200
H	5.45391600	1.55306600	-1.08765500
F	0.33051700	-2.43542200	-0.98605800
N	-0.74755500	1.35402400	0.03252400
N	-2.16893300	-0.91872200	-0.26578400

Complex 8-sp²-ts



Pd	0.02088200	-0.73309400	-0.50230600
C	-2.94785200	0.20403000	-0.02576700
C	-3.06064800	-2.09249300	-0.40495700
C	-4.31931100	0.25614500	0.32684400
C	-4.43665900	-2.14141800	-0.07997600
H	-2.51775300	-3.00067700	-0.69823100
C	-5.07214800	-0.93856300	0.29827900
H	-4.79281700	1.19397400	0.63365800
H	-4.98024300	-3.08933600	-0.12072100
H	-6.13241400	-0.92747600	0.57028100
C	0.10358600	2.28805200	-0.26156000
C	-2.07863100	1.42877900	-0.04638200
C	-0.34427900	3.62093700	-0.15607200
H	1.16930600	2.04662400	-0.39525000
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
H	1.34946900	0.58390800	3.61345600
H	2.90240400	1.15602200	2.96373600
C	2.11785900	-0.64218100	-0.74595400
C	2.66669600	-0.15573800	0.46043600
C	2.64519300	-0.45436100	-2.03418200
C	3.83939200	0.63062500	0.31946200
C	3.79964000	0.36461300	-2.12685300
H	2.19344500	-0.93582800	-2.90785700
C	4.40209300	0.88855200	-0.95621600
H	4.30683700	1.06032800	1.21528500
H	4.23957700	0.55422600	-3.11191900
H	5.30951400	1.49592200	-1.03282900
F	1.40420900	-2.27976000	-0.69311500
N	-0.74001400	1.23286400	-0.20491100
N	-2.33980200	-0.95600800	-0.38020700

Complex 8-I-sp²-ts



Pd	-0.06845700	-0.12734500	-0.80944000
C	2.33664100	1.19685500	0.29158200
C	0.58167300	2.74931600	0.11408300
C	3.17598000	2.18484500	0.85865700
C	1.35758300	3.78371900	0.67666000
H	-0.45513100	2.93510500	-0.18920000
C	2.68608900	3.49274900	1.05253200
H	4.19745900	1.93500000	1.15833500
H	0.92233100	4.77740700	0.81048800
H	3.32767800	4.26212400	1.49311800
C	2.16203600	-2.37337800	-0.57413500
C	2.80028700	-0.21239300	0.08162300
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
H	-4.35623500	0.28650000	1.79774600
H	-3.65554300	-1.20732100	3.67894100
C	-1.72152200	0.87210500	-1.52904700
H	-1.44767400	1.94356900	-1.57738600
H	-1.77311000	0.46145000	-2.55579900
C	-3.02281000	0.61156100	-0.71817000
C	-4.02992000	-0.19012400	-1.57923100
H	-4.94872400	-0.40364200	-1.00173400
H	-4.31334300	0.39540800	-2.47359100
H	-3.59442700	-1.14953000	-1.90795400
C	-3.65098400	1.96147700	-0.31425900
H	-3.82922900	2.57525900	-1.21627200
H	-4.62798500	1.82504600	0.18374200
H	-2.99240200	2.52723400	0.37306200
F	-1.12082700	-1.80027300	-1.21165600
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

JMRVIII-190.characterization

Sample Name:

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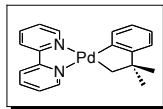
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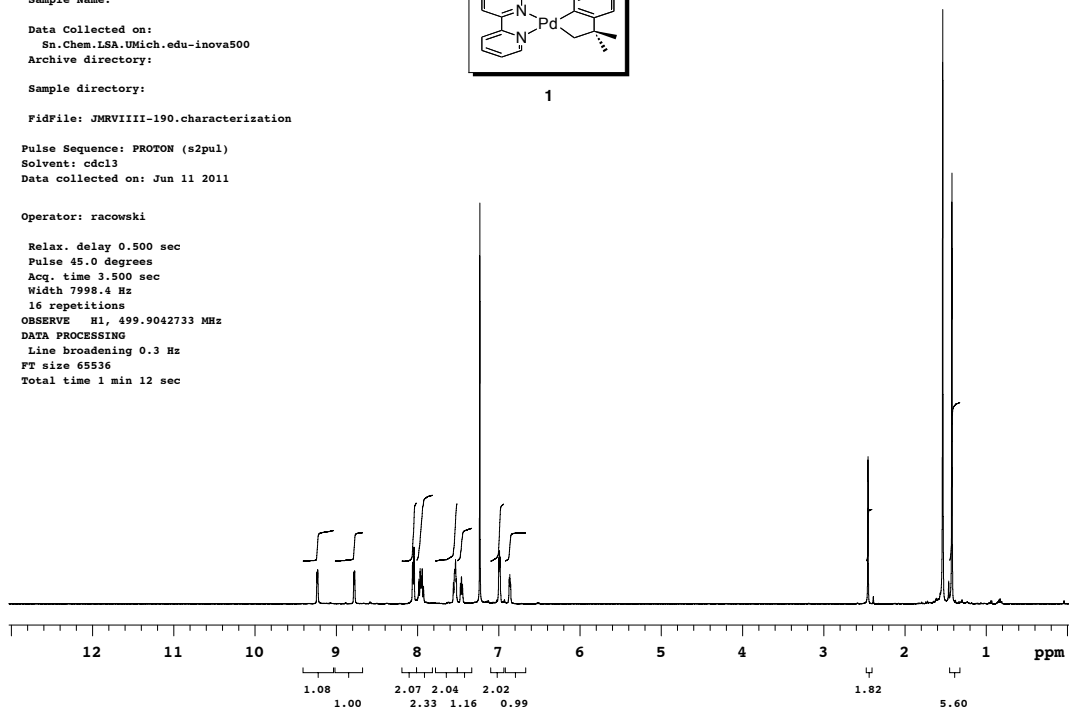
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Solvent: cdcl3
Data collected on: Jun 11 2011

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



Agilent Technologies



JMRXII-139.CNMR

Sample Name:

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

Sample directory:

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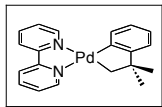
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jun 11 2011

Operator: racowski

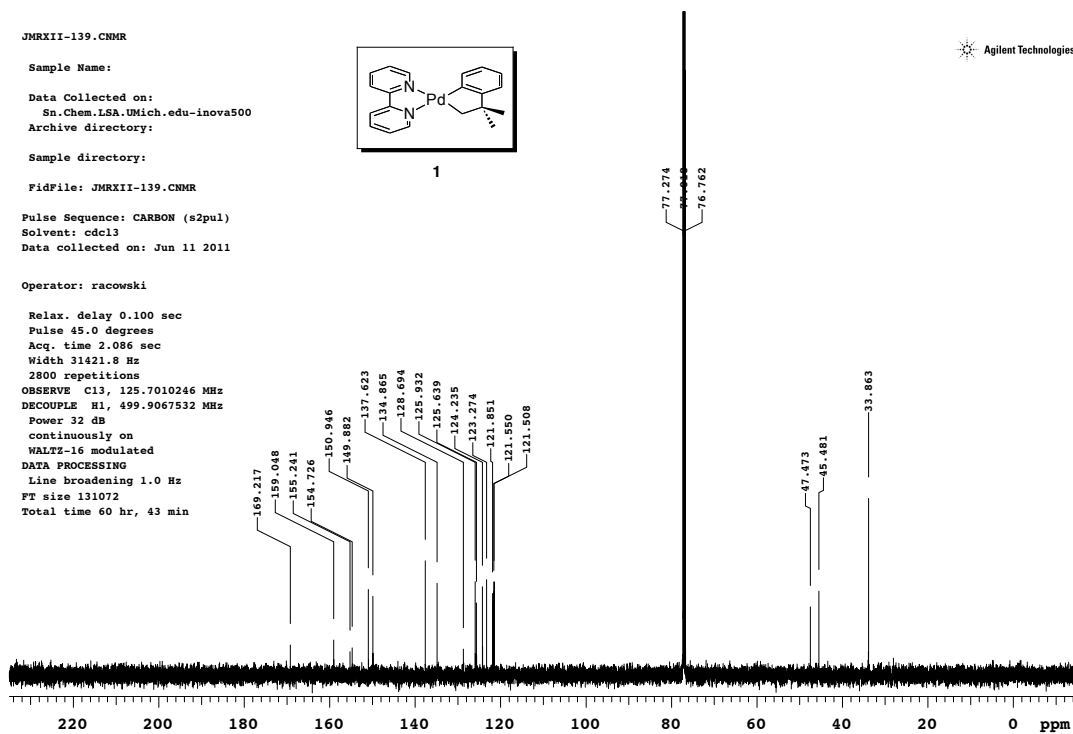
Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 2.086 sec
Width 31421.8 Hz
2800 repetitions

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



Agilent Technologies



JMRX-110.001

Sample Name:

Data Collected on:
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Archive directory:

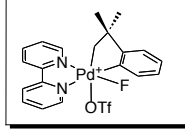
Sample directory:

FidFile: JMRX-110.001

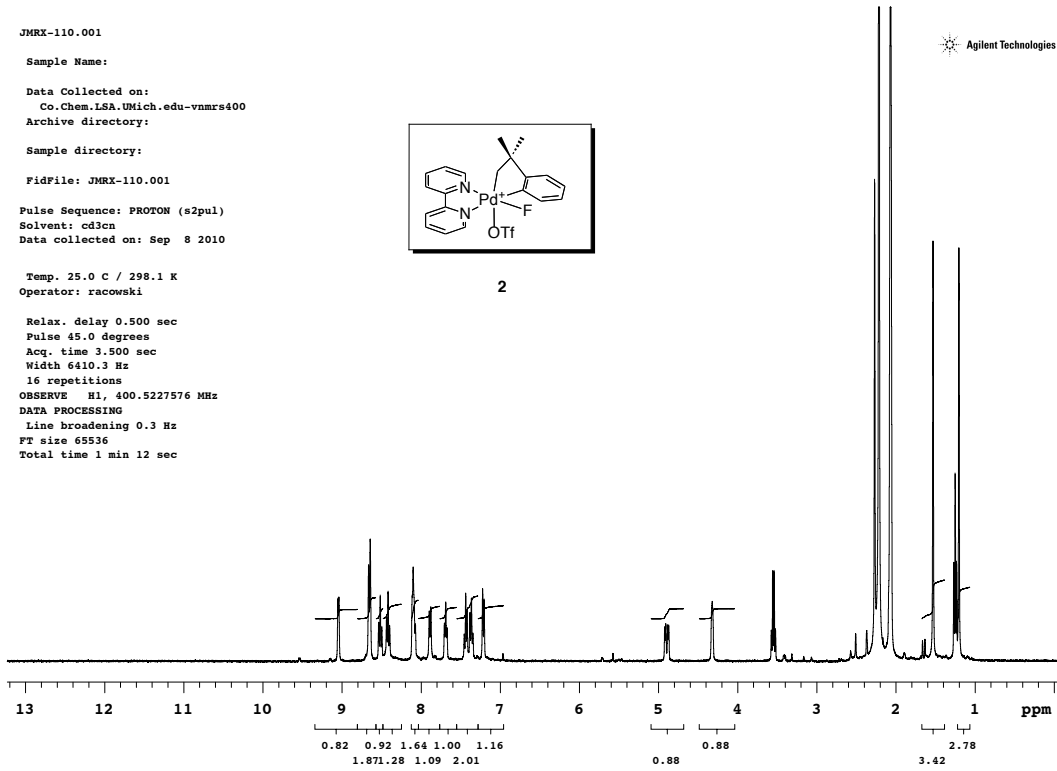
Pulse Sequence: PROTON (s2pul)
Solvent: cd3cn
Data collected on: Sep 8 2010

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, 400.522756 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 1 min 12 sec



Agilent Technologies



JMRX-110.001FNMR

Agilent Technologies

Sample Name:

Data Collected on:
Co.Chem.LSA.UMich.edu-vmrs400

Archive directory:

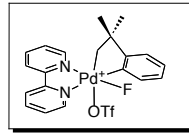
Sample directory:

Fidfile: JMRX-110.001FNMR

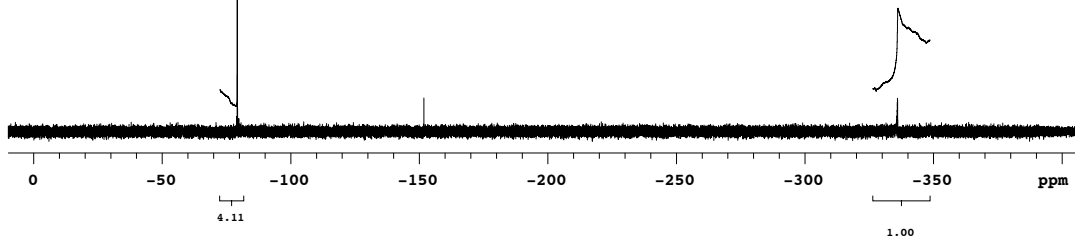
Pulse Sequence: FLUORINE (s2pul)
Solvent: cd3cn
Data collected on: Sep 8 2010

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



2



JMRX-111.characterization

Agilent Technologies

Sample Name:

Data Collected on:
Yb-vnmrs700
Archive directory:

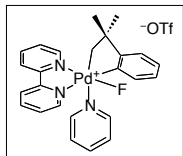
Sample directory:

FidFile: JMRX-111.characterization

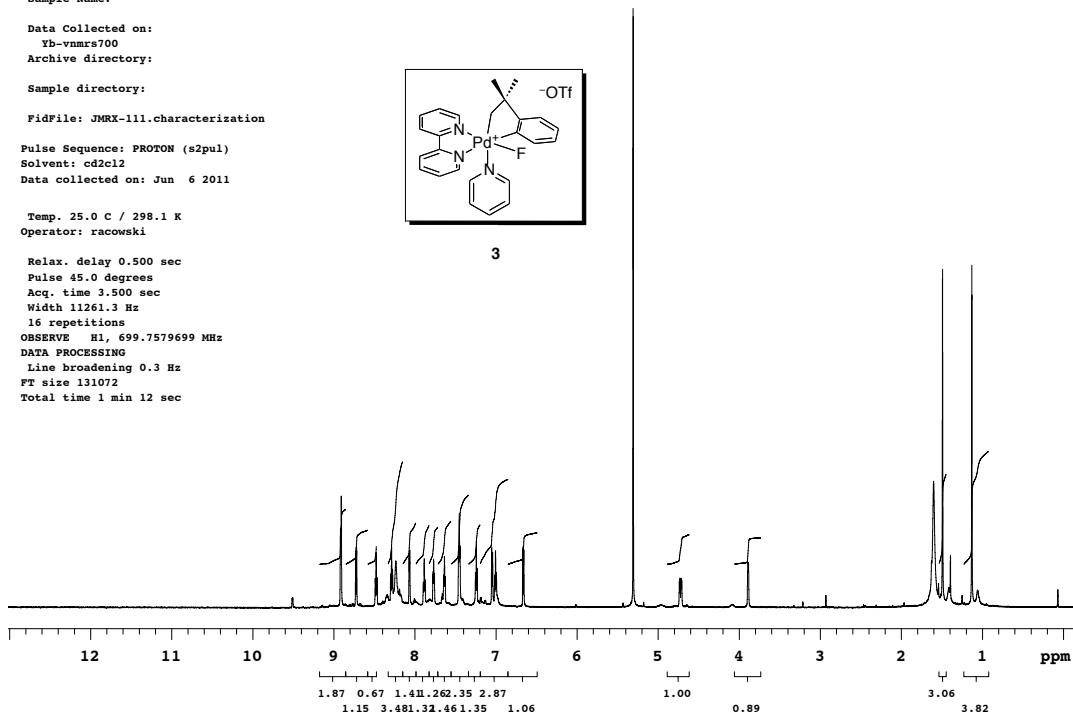
Pulse Sequence: PROTON (s2pul)
Solvent: cd2cl2
Data collected on: Jun 6 2011

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

Agilent Technologies

Sample Name:

Data Collected on:
Co.Chem.LSA.UMich.edu-vmrs500
Archive directory:

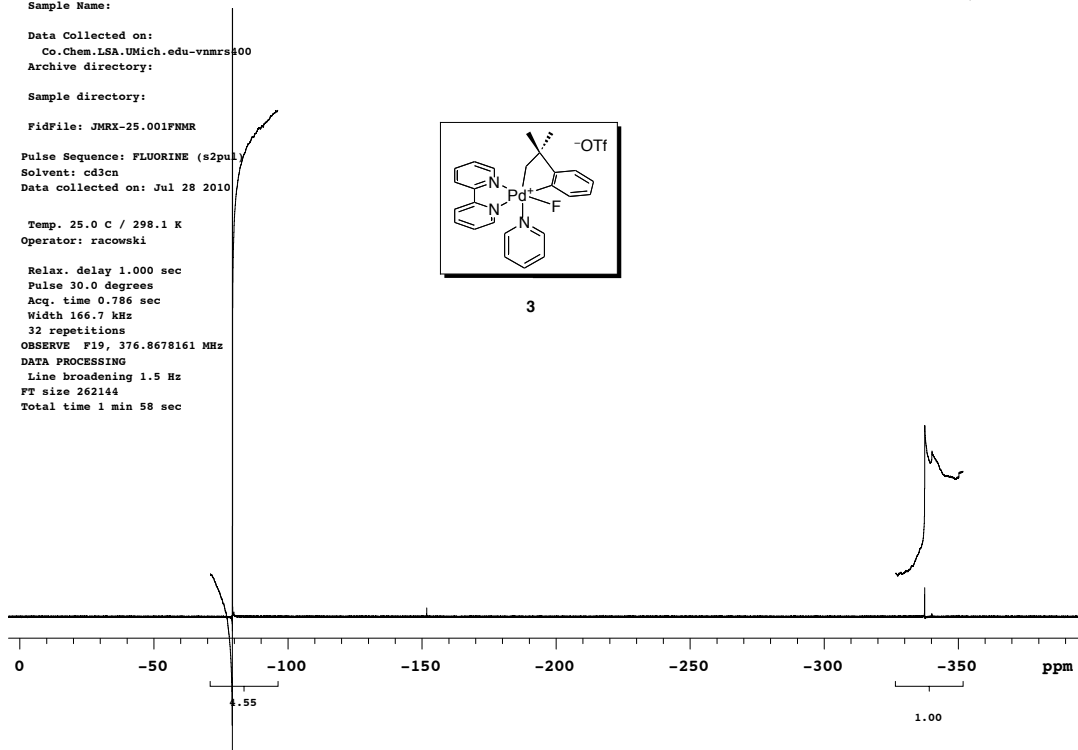
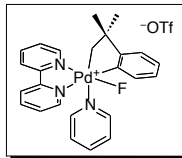
Sample directory:

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



JMRX-28.001

Agilent Technologies

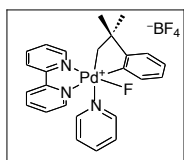
Sample Name:

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

Sample directory:

FidFile: JMRX-28.001

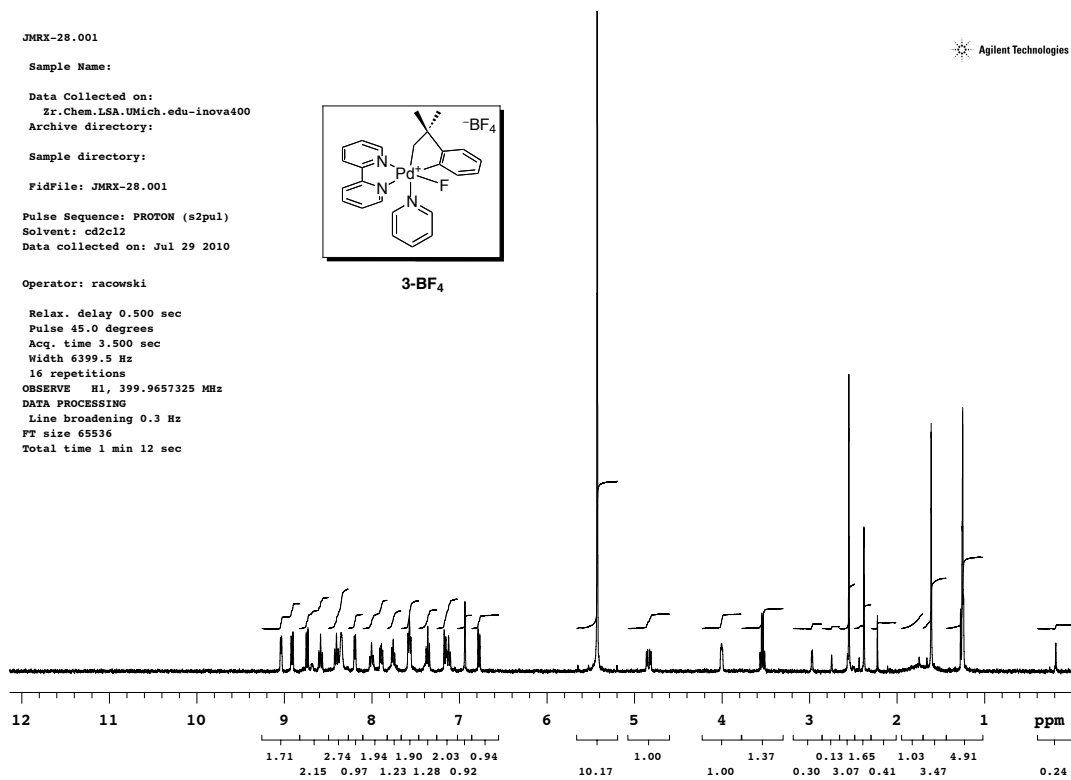
Pulse Sequence: PROTON (s2pul)
Solvent: cd2cl2
Data collected on: Jul 29 2010



3-BF₄

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



JMRX-28.001FNMR

Agilent Technologies

Sample Name:

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

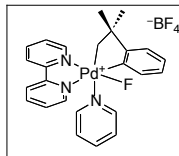
Sample directory:

FidFile: JMRX-28.001FNMR

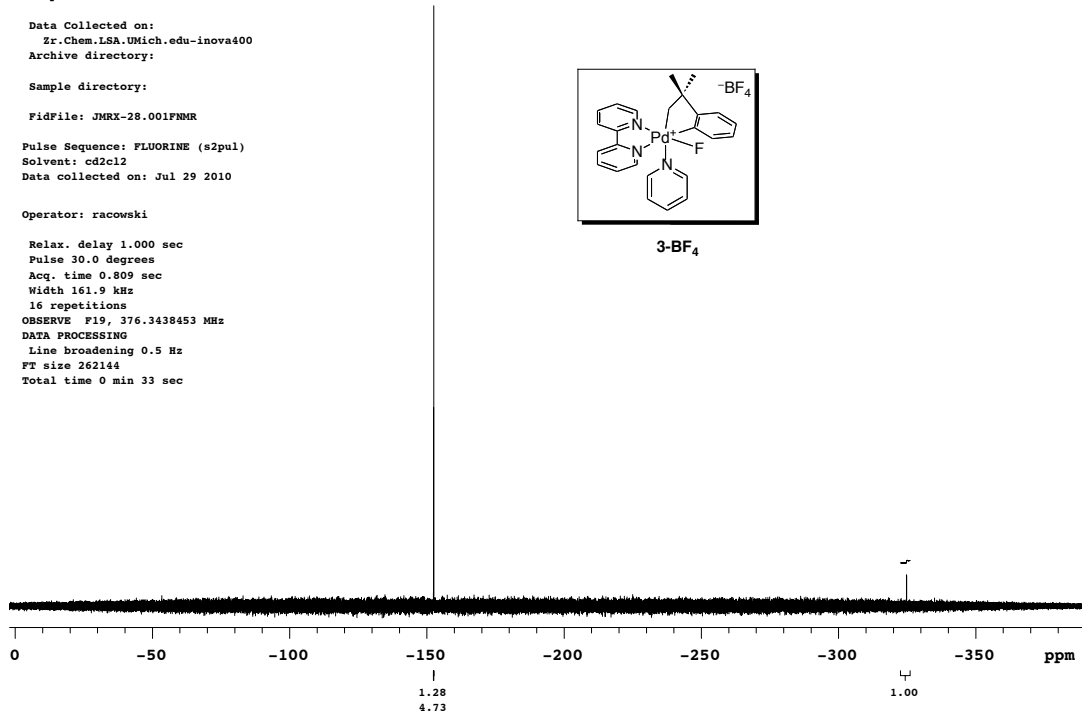
Pulse Sequence: FLUORINE (s2pul)
Solvent: cd2cl2
Data collected on: Jul 29 2010

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-BF₄



JMRX-80.005

Sample Name:

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

Sample directory:

FidFile: JMRX-80.005

Pulse Sequence: PROTON (s2pul)
Solvent: dms0
Data collected on: Apr 23 2011

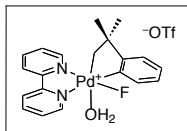
Operator: racowski

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.450 sec
Width 9497.8 Hz
16 repetitions

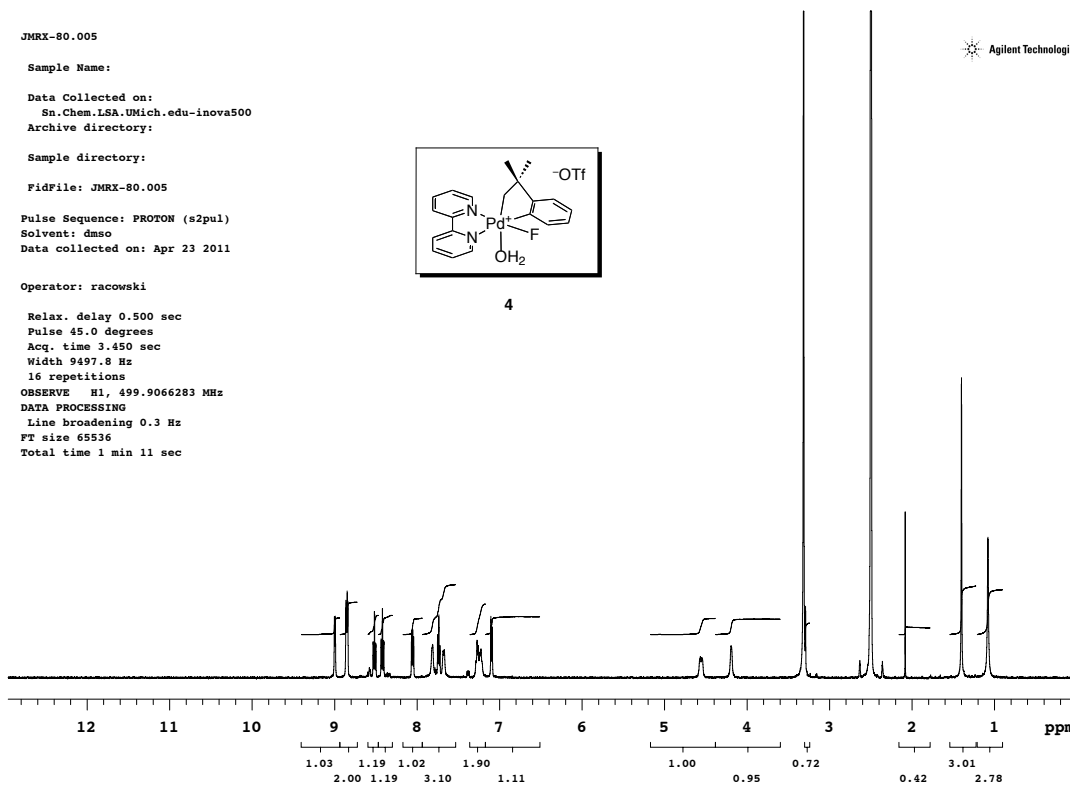
OBSERVE H1, 499.9066283 MHz

DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 1 min 11 sec

Agilent Technologies



4



JMRX-80.FNMR

Agilent Technologies

Sample Name:

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

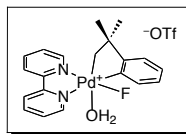
Sample directory:

FidFile: JMRX-80.FNMR

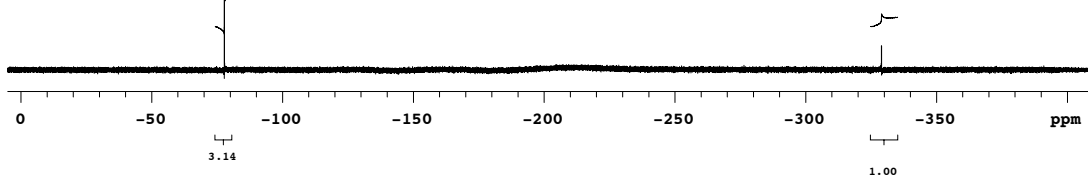
Pulse Sequence: FLUORINE (s2pul)
Solvent: cd2cl2
Data collected on: Aug 16 2011

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



JMRXII-125.001

Agilent Technologies

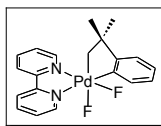
Sample Name:

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

Sample directory:

FidFile: JMRXII-125.001

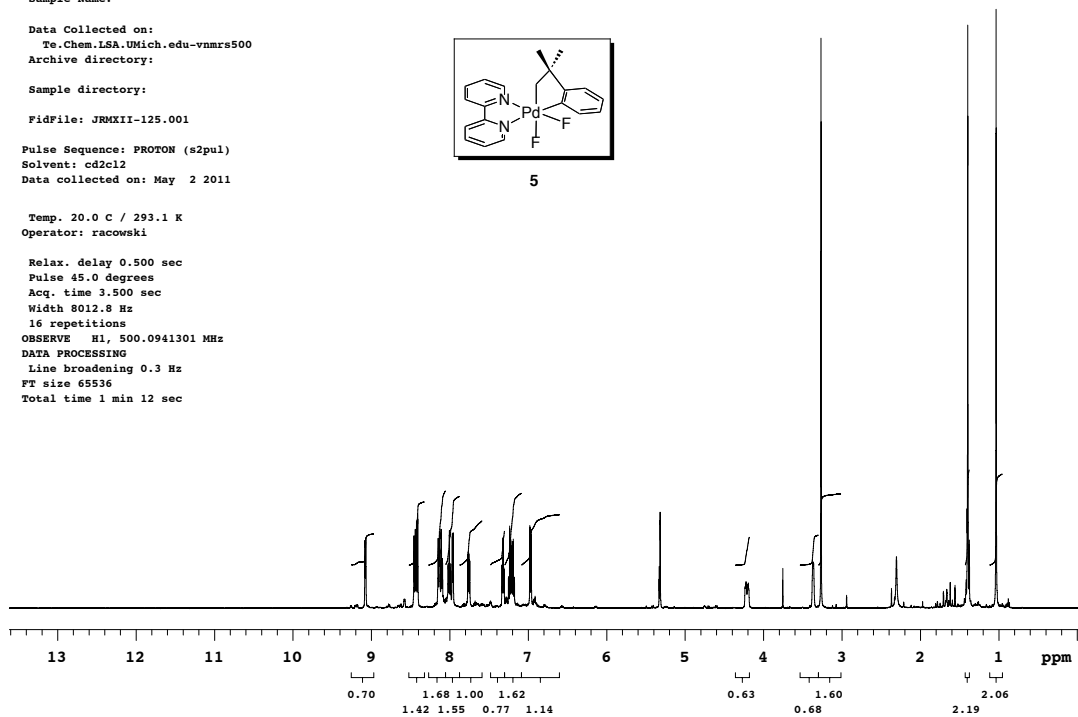
Pulse Sequence: PROTON (s2pul)
Solvent: cd2cl2
Data collected on: May 2 2011



5

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



JMRXII-125.001FNMNR



Sample Name:

Data Collected on:
Te.Chem.LSA.UMich.edu-vmr500
Archive directory:

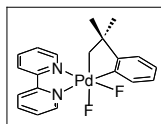
Sample directory:

FidFile: JMRXII-125.001FNMNR

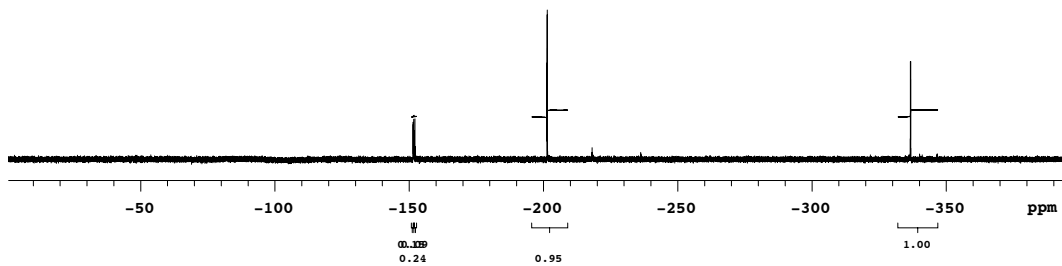
Pulse Sequence: FLUORINE (s2pul)
Solvent: cd2cl2
Data collected on: May 2 2011

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:

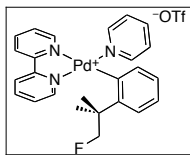
Sample directory:

FidFile: JMRXII-192B.001

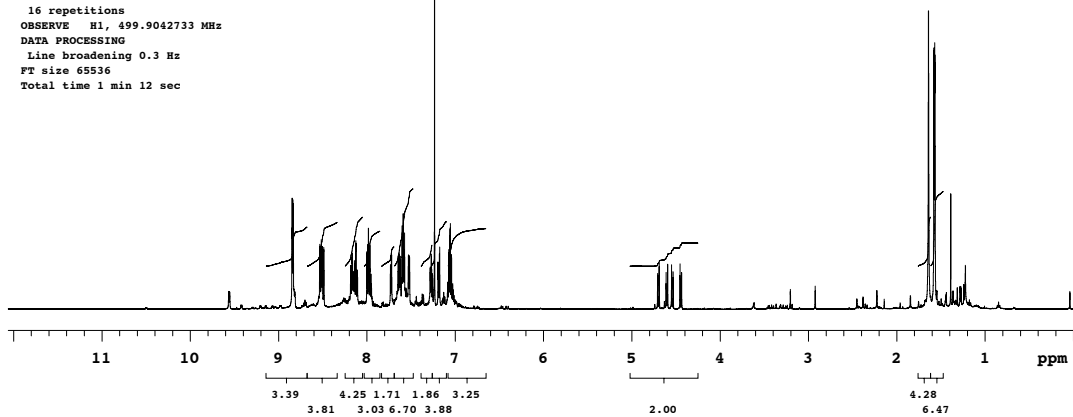
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jun 11 2011

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 (s2pu)

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

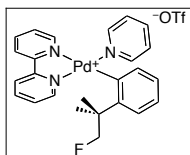
DATA PROCESSING

Line broadening 1.5 Hz

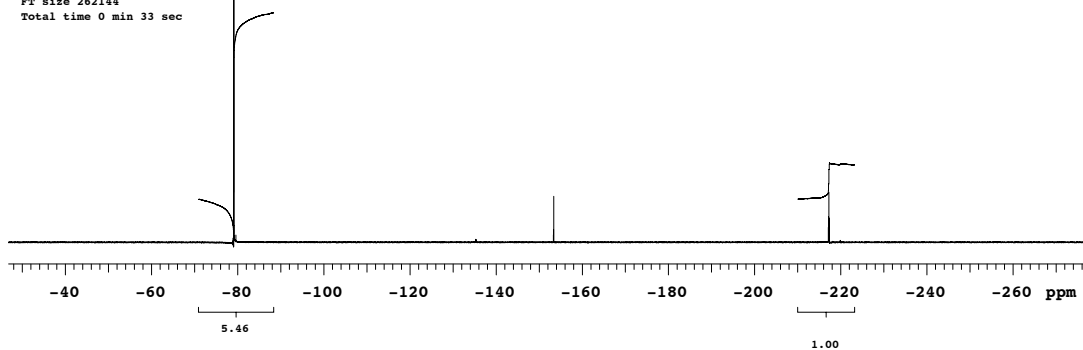
FF size 262144

Total time 0 min 33 sec

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6



JMRXII-192B.CNMR

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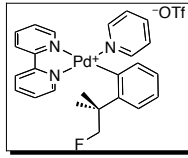
Sample Name:

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



6

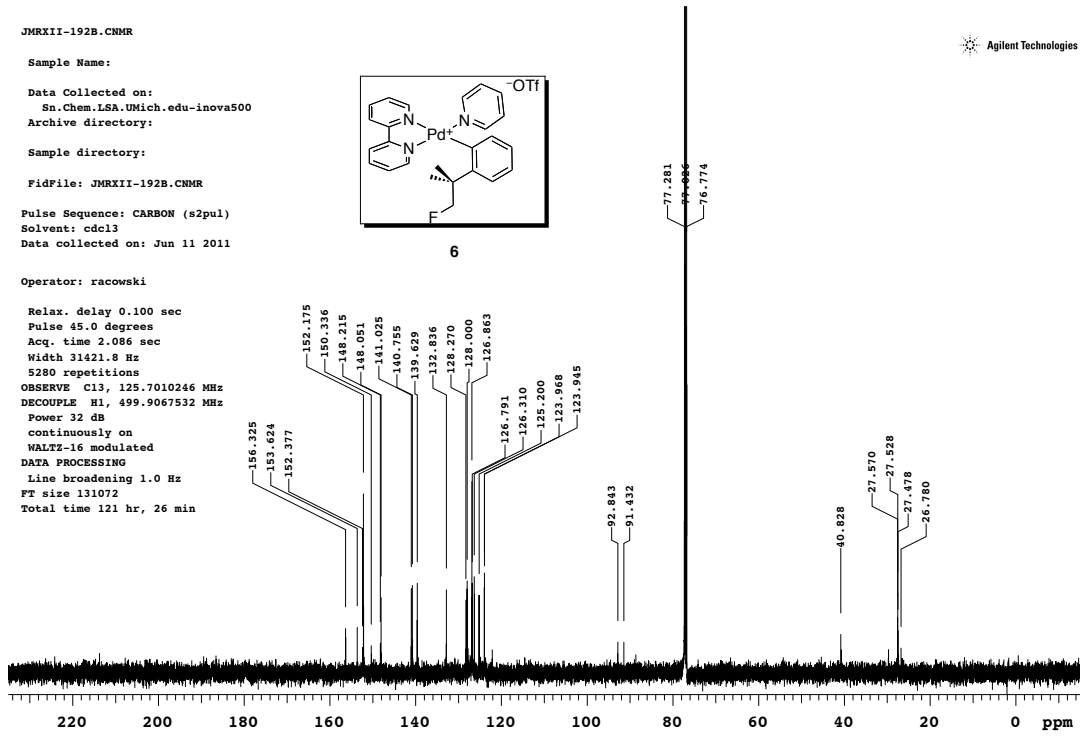
Operator: racowski

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



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

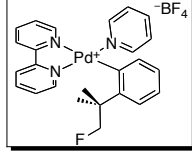
DATA PROCESSING

Line broadening 0.3 Hz

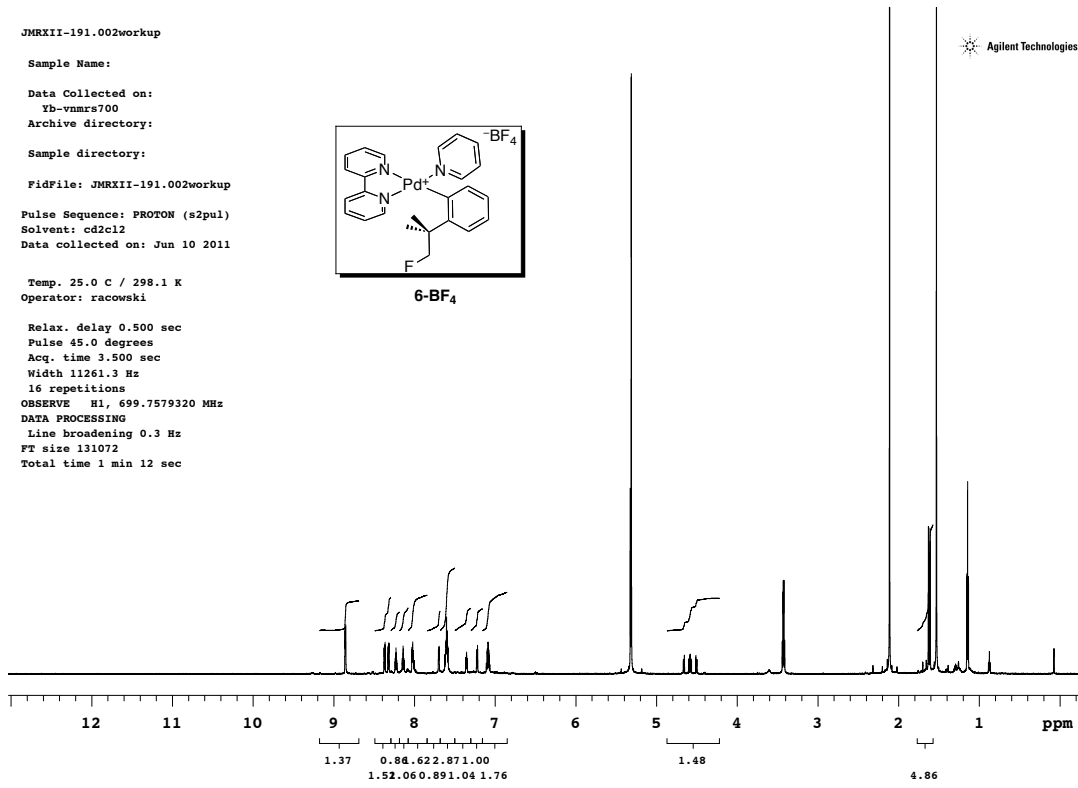
FT size 131072

Total time 1 min 12 sec

Agilent Technologies



6-BF₄



JMRXII-192A.FNMR

Agilent Technologies

Sample Name:

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

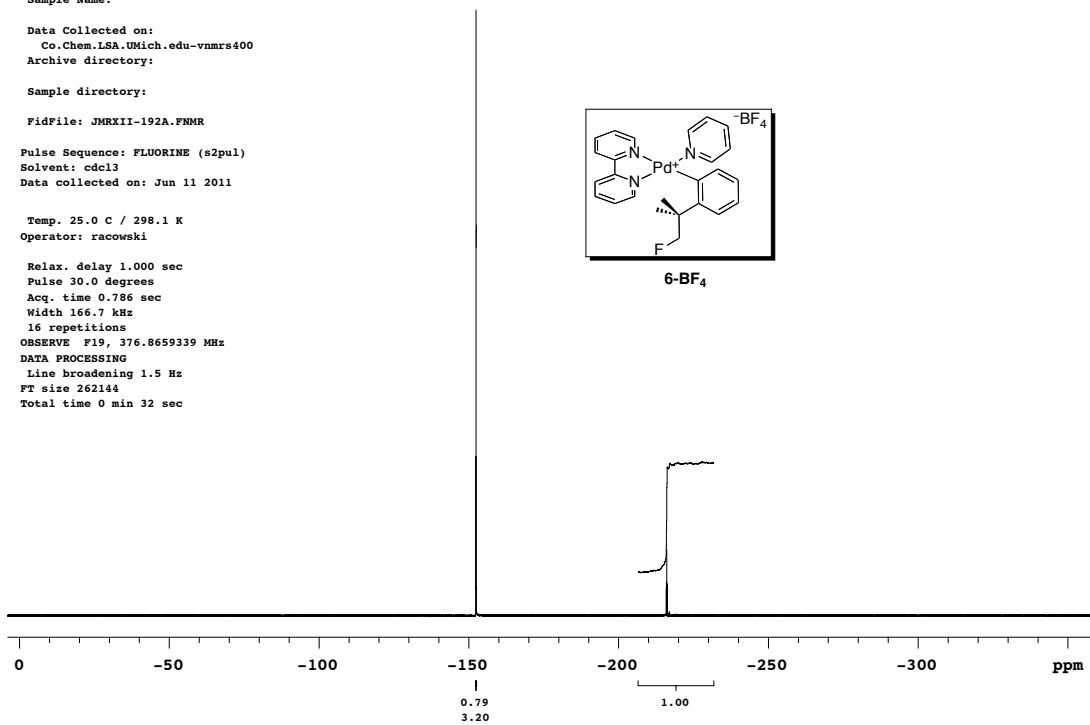
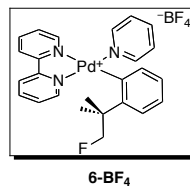
Sample directory:

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



JMRXII-192A.CNMR

Sample Name:

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

Sample directory:

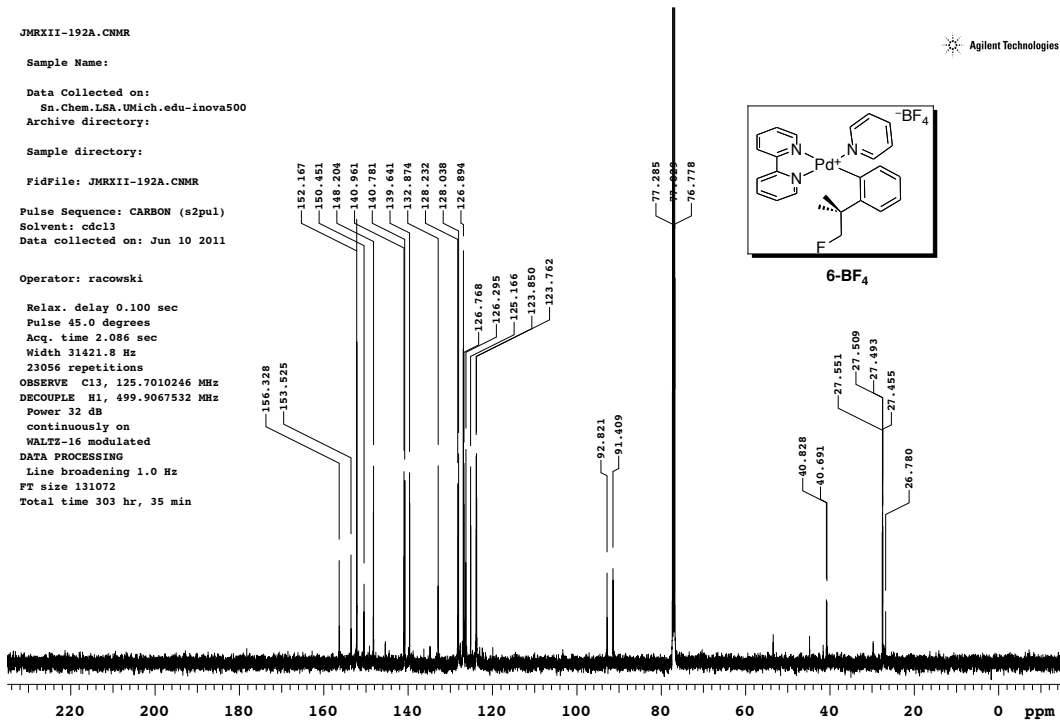
FidFile: JMRXII-192A.CNMR

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



JMRXII-128.004

Sample Name:

Data Collected on:

Yb-vnms700

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

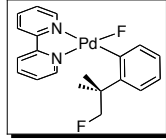
OBSERVE H1, 699.7581182 MHz

DATA PROCESSING

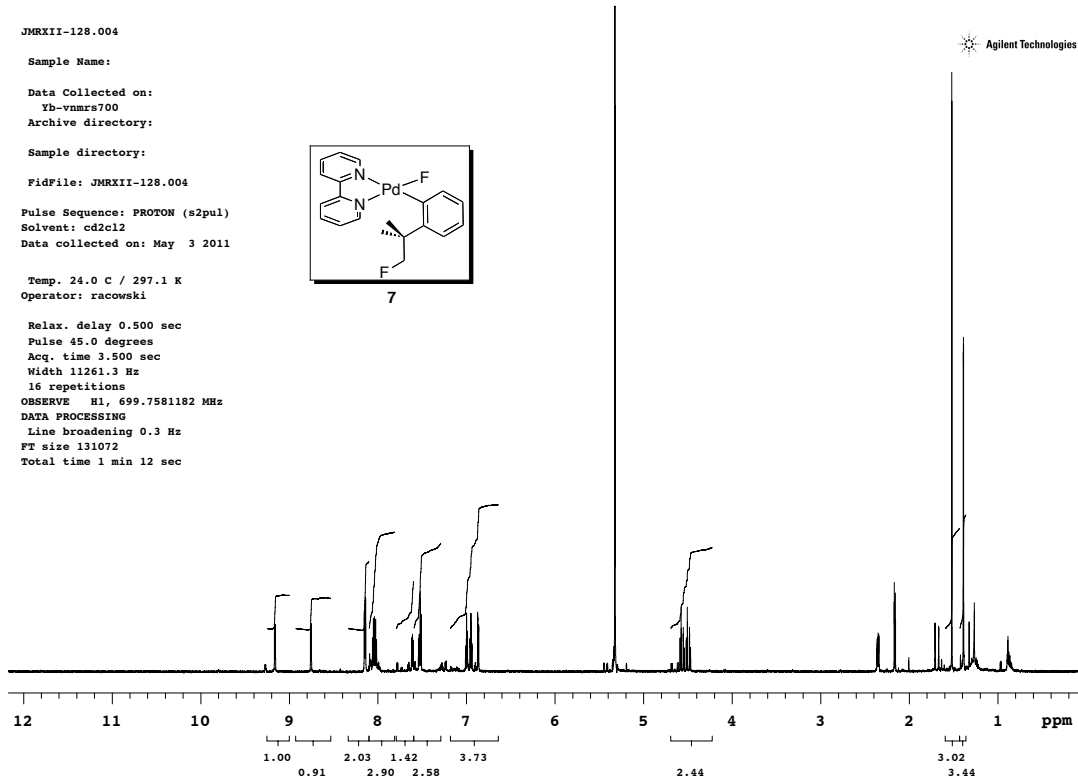
Line broadening 0.3 Hz

FT size 131072

Total time 1 min 12 sec



Agilent Technologies



JMRX-51.filtrateFNMR



Sample Name:

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

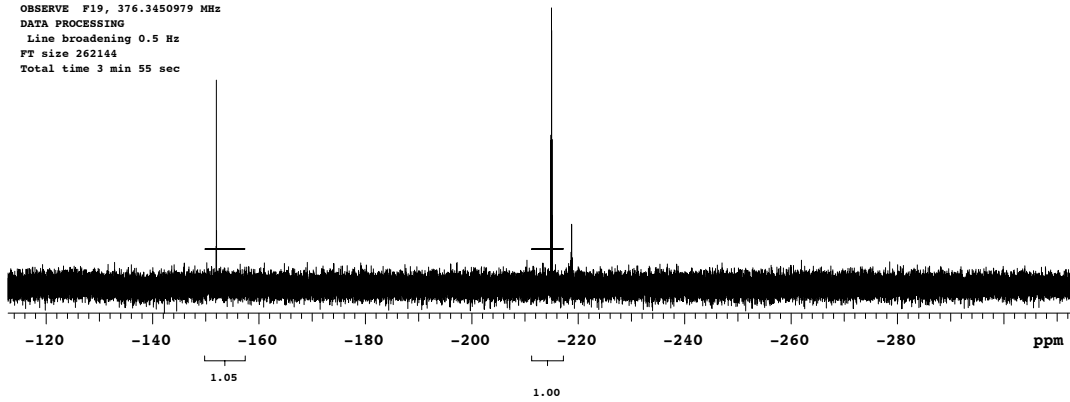
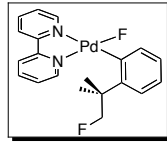
Sample directory:

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



JMRXII-128.3CNMR2

Sample Name:

Data Collected on:

Yb-vnms700

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

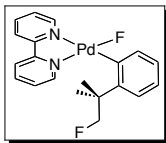
WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 131072

Total time 4 hr, 21 min



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