Supporting Information

Carbon–Fluorine Reductive Elimination from a High–Valent Palladium Fluoride

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Materials and Methods

All reactions were carried out under an ambient atmosphere unless otherwise indicated. Solvents were dried by passage through alumina[1]. Except as indicated otherwise, reactions were magnetically stirred and monitored by thin layer chromatography (TLC) using EMD TLC plates pre-coated with 250 μm thickness silica gel 60 F254 plates and visualized by fluorescence quenching under UV light. In addition, TLC plates were stained using ceric ammonium molybdate or potassium permanganate stain. Flash chromatography was performed on Dynamic Adsorbents Silica Gel 40–63 μm particle size using a forced flow of eluant at 0.3–0.5 bar pressure.[2] Concentration under reduced pressure was performed by rotary evaporation at 25–30 ºC at appropriate pressure. Purified compounds were further dried under high vacuum (0.01–0.05 Torr). Melting points were measured on a Buchi 510 apparatus. All melting points were measured in open capillaries and are uncorrected. NMR spectra were recorded on a Varian Unity/Inova 500 spectrometer operating at 500 MHz and 125 MHz for ^{1}H and ^{13}C acquisitions, respectively, or on a Varian Mercury 400 spectrometer operating at 375 MHz for ^{19}F acquisition. ^{13}C NMR spectra are recorded ^{1}H decoupled. ^{19}F NMR spectra are recorded ^{1}H coupled. Chemical shifts are reported in ppm with the solvent resonace as the internal standard. Data is reported as follows: s = singlet, br = broad, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constants in Hz; integration. High-resolution mass spectra were obtained on Jeol AX-505 or SX-102 spectrometers at the Harvard University Mass Spectrometry Facilities. Triethylamine was distilled over calcium hydride. Benzo[*h*]quinoline was purchased from TCI America. 2-Nitrobenzenesulfonyl chloride, 2-bromoaniline, pinacolborane, [1,1'-biphenyl]-2-yldicyclohexylphosphine, barium hydroxide octahydrate, 2-bromopyridine, tetramethylammonium fluoride tetrahydrate, anhydrous dioxane were purchased from Aldrich. 1-Chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) was purchased from Alfar Aesar. Palladium acetate and silver tetrafluoroborate were purchased from Strem. Xenone difluoride was purchased from Matrix Scientific. 4-*tert*-Butylphenylboronic acid was purchased from Frontier Scientific and used as received.

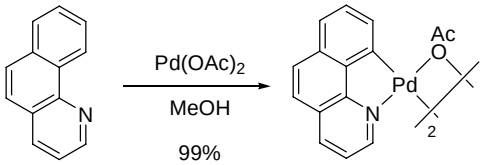
[1] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.

[2] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2925–2927.

Experimental Data

Experimental Procedures and Compound Characterization

Benzo[*h*]quinolinyl palladium acetate dimer (7)[3]

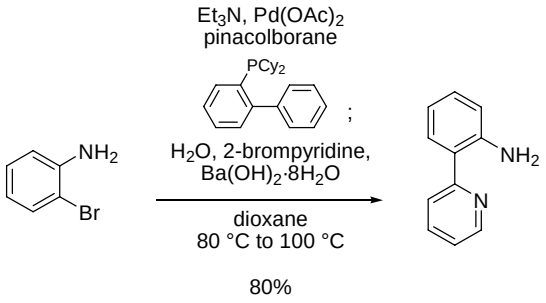


7

To benzo[*h*]quinoline (1.79 g, 10.0 mmol, 1.00 equiv) in MeOH (100 mL) at 23 ºC is added palladium acetate (2.25 g, 10.0 mmol, 1.00 equiv). After stirring for 17 h, the suspension is filtered off and washed with MeOH (50 mL) and Et_2O (50 mL) to afford 3.19 g of the title compound as a yellow solid (99% yield).

NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.80 (dd, *J* = 5.5 Hz, 1.5 Hz, 1H), 7.43 (dd, *J* = 8.0 Hz, 1.5 Hz, 1H), 7.24–7.18 (m, 3H), 7.08 (dd, *J* = 7.0 Hz, *J* = 1.5 Hz, 1H), 6.97 (d, *J* = 9.0 Hz, 1H), 6.46 (dd, *J* = 7.5 Hz, 5.0 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 182.5, 153.2, 148.9, 148.8, 140.0, 135.3, 132.4, 129.0, 127.9, 127.7, 125.0, 122.9, 122.1, 119.8, 25.2. These spectroscopic data correspond to the reported data in reference 3.

2-(2-Pyridyl)aniline[4]



Under nitrogen atmosphere, to 2-bromoaniline (1.50 g, 1.55 mL, 8.72 mmol, 1.00 equiv) in anhydrous dioxane (18 mL) at 23 ºC is added Et_3N (4.06 mL, 34.9 mmol, 4.00 equiv), palladium acetate (97.9 mg, 0.440 mmol, 5.00 mol%), [1,1'-biphenyl]-2-yldicyclohexylphosphine (458 mg, 1.31 mmol, 15.0 mol%)

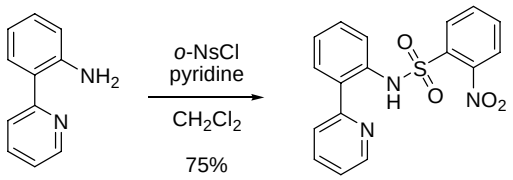
[3] Dick, A. R.; Hull , K. L.; Sanford, M. S. *J. Am. Chem. Soc.* **2004**, *126*, 2300–2301.

[4] Rebstock, A. S.; Mongin, F.; Trecourt, F.; Queguiner, G. *Org. Biomol. Chem.* **2003**, *1*, 3064–3068.

and pinacolborane (3.83 mL, 26.2 mmol, 3.00 equiv). The reaction mixture is stirred at 80 °C for 1.0 h before the addition of water (3.80 mL), $Ba(OH)_2 \cdot 8H_2O$ (8.25 g, 26.2 mmol, 3.00 equiv), and 2-bromopyridine (1.38g, 0.850 mL, 8.72 mmol, 1.00 equiv). The suspension is heated at 100 °C for 4.0 h. After cooling to 23 ºC, the reaction mixture is filtered through celite and brine (50 mL) is added to the filtrate. The phases are separated and the aqueous phase is extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phases are washed with brine (30 mL) and dried (Na_2SO_4). The filtrate is concentrated in vacuo and the residue is purified by chromatography on silica gel eluting with hexanes/EtOAc 3:1 (v/v) to afford 1.18 g of the title compound as red-brown oil (80% yield).

R_f = 0.38 (hexanes/EtOAc 3:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 8.61–8.60 (m, 1H), 7.78–7.75 (m, 1H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.51 (dd, *J* = 7.6 Hz, 1.4 Hz, 1H), 7.19–7.16 (m, 2H), 6.80–6.76 (m, 2H), 5.72 (br s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 159.2, 147.6, 146.3, 136.6, 129.6, 129.1, 121.9, 120.7, 117.3, 116.9. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{11}H_{10}N_2$ + H], 171.0917. Found, 171.0923. This spectroscopic data corresponds to the reported data in reference 4.

2-(2-Pyridinyl)phenyl-2-nitrobenzenesulfonamide (2)

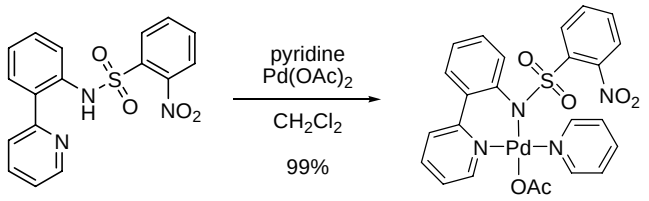


2

To 2-(2-Pyridyl)aniline (851 mg, 5.00 mmol, 1.00 equiv) in CH_2Cl_2 (10 mL) at 0 ºC is added pyridine (1.60 mL, 20.0 mmol, 4.00 equiv) and 2-nitrobenzenesulfonyl chloride (2.20 g, 10.0 mmol, 2.00 equiv). The reaction mixture is warmed to 23 ºC and stirred for 2.0 hr before the addition of water (10 mL). The phases are separated and the aqueous layer is extracted with CH_2Cl_2 (3 × 8 mL). The combined organic phases are washed with brine (30 mL) and dried (Na_2SO_4). The filtrate is concentrated in vacuo and the residue is purified by chromatography on silica gel eluting with hexanes/EtOAc 3:7 (v/v) to afford 1.33 g of the title compound as a pale-yellow solid (75% yield).

R_f = 0.12 (hexanes/EtOAc 7:3 (v/v)). Melting Point: 91–94 ºC. NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 8.73 (d, *J* = 5.0 Hz, 1H), 7.94 (dd, *J* = 7.5 Hz, 2.0 Hz, 1H), 7.82 (dd, *J* = 8.0 Hz, 1.0 Hz, 1H), 7.74 (ddd, *J* = 7.5 Hz, 7.5 Hz, 2.0 Hz, 1H), 7.63–7.52 (m, 5H), 7.38 (ddd, *J* = 7.5 Hz, 7.5 Hz, 1.5 Hz, 1H), 7.27–7.24 (m, 1H), 7.18 (ddd, *J* = 7.5 Hz, 7.5 Hz, 1.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 156.9, 156.2, 148.0, 137.9, 136.4, 133.6, 132.2, 131.0, 130.0, 129.0, 127.1, 125.0, 124.7, 122.4, 121.9, 121.9, 110.9. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{17}H_{13}N_3O_4S$ + H], 356.0700. Found, 356.0701. Anal: calcd for $C_{17}H_{13}N_3O_4S$: C, 57.45; H, 3.69; N, 11.83; found: C, 57.14; H, 3.66; N, 11.64.

Acetato palladium complex 3

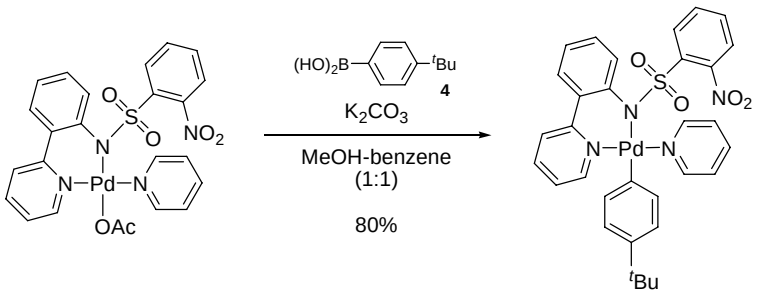


2 **3**

To palladium acetate (448 mg, 2.00 mmol, 1.00 equiv) in CH_2Cl_2 (20 mL) at 23 ºC is added pyridine (485 µL, 6.00 mmol, 3.00 equiv) and 2-(2-pyridinyl)phenyl-2-nitrobenzenesulfonamide (**2**) (711 mg, 2.00 mmol, 1.00 equiv). After stirring for 20 min, the solution is concentrated in vacuo. The resulting residue is triturated with Et_2O (3 × 1 mL) to afford 1.19 g of the title compound as a pale-yellow solid (99% yield).

Melting Point: 195 ºC (decomp.). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 8.79 (d, *J* = 6.5 Hz, 2H), 8.58 (d, *J* = 5.5 Hz, 1H), 7.80 (dd, *J* = 7.5 Hz, 7.5 Hz, 1H), 7.61 (d, *J* = 7.5 Hz, 2H), 7.57–7.52 (m, 2H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.39–7.33 (m, 3H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.21–7.15 (m, 2H), 7.06–7.03 (m, 2H), 1.85 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 177.6, 154.7, 151.8, 151.1, 146.9, 139.9, 138.6, 138.4, 136.3, 134.8, 131.7, 131.1, 130.3, 129.9, 129.6, 125.8, 124.8, 123.3, 122.8, 122.3, 110.7, 23.5. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{24}H_{20}N_4O_6PdS + NH_4$], 616.0476. Found, 616.0473. Anal: calcd for $C_{24}H_{20}N_4O_6PdS$: C, 48.13; H, 3.37; N, 9.36; found: C, 47.88; H, 3.27; N, 9.20.

Aryl palladium complex 5



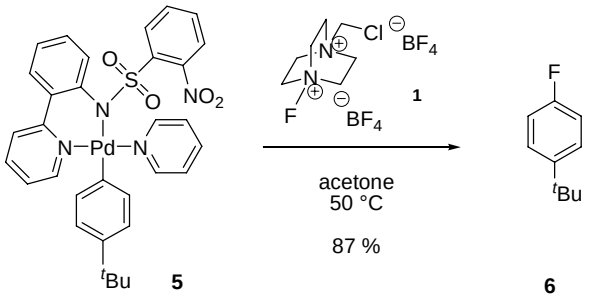
3 **5**

To the acetato palladium complex **3** (300 mg, 0.501 mmol, 1.00 equiv) in MeOH (5.0 mL) and benzene (5.0 mL) at 23 ºC is added 4-*tert*-butylphenylboronic acid (98.0 mg, 0.551 mmol, 1.10 equiv) and K_2CO_3 (138 mg, 1.00 mmol, 2.00 equiv). The reaction mixture is stirred at 23 ºC for 3.0 h, and the solvent is removed in vacuo. To the solid residue is added $CHCl_3$ (5 mL) and water (5 mL). The phases are separated and the aqueous phase is extracted with $CHCl_3$ (3 × 5 mL). The combined organic phases are washed with brine (5 mL) and dried (Na_2SO_4). The filtrate is concentrated in vacuo and the residue is

purified by chromatography on silica gel eluting with hexanes/EtOAc 2:3 (v/v) to afford 270 mg of the title compound as a colorless solid (80% yield).

R_f = 0.13 (hexanes/EtOAc 1:1). Melting Point: 145 ºC (decomp.). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.85 (dd, *J* = 6.0 Hz, 1.5 Hz, 2H), 8.18 (d, *J* = 5.5 Hz, 1H), 7.66 (dd, *J* = 8.0 Hz, 8.0 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.48–7.42 (m, 2H), 7.38 (dd, *J* = 7.5 Hz, 1.5 Hz, 1H), 7.29 (d, *J* = 7.0 Hz, 1H), 7.26–7.20 (m, 3H), 7.18–7.12 (m, 3H), 7.10–7.00 (m, 3H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.79 (dd, J = 7.5 Hz, 6.0 Hz, 1H), 1.21 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 157.6, 153.2, 153.1, 149.7, 147.2, 146.2, 143.1, 138.0, 137.7, 136.5, 136.3, 134.1, 131.4, 130.4, 130.2, 129.8, 129.5, 129.4, 124.9, 124.8, 124.2, 124.1, 122.6, 122.3, 34.1, 31.7. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{32}H_{30}N_4O_4PdS$ + H], 673.1101. Found, 673.1111. Anal: calcd for $C_{32}H_{30}N_4O_4PdS$: C, 57.10; H, 4.49; N, 8.33; found: C, 57.16; H, 4.38; N, 8.21.

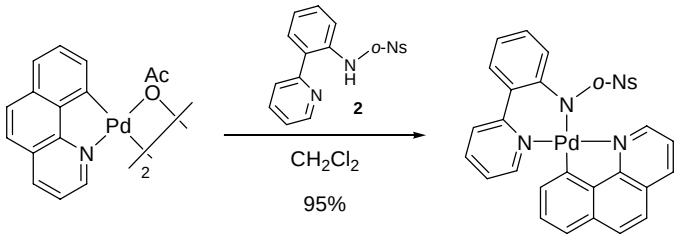
1-*tert*-Butyl-4-fluorobenzene (6)



To 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (**1**) (4.3 mg, 0.012 mmol, 1.2 equiv) in acetone-*d*6 (0.3 mL) at 50 ºC is added aryl palladium complex **5** (6.7 mg, 0.010 mmol, 1.0 equiv) in 10 portions over 10 min. The reaction mixture is stirred at 50 ºC for 10 min. The reaction mixture is cooled to 23 ºC, at which temperature 3-nitrofluorobenzene (2.65 mg, 2.00 μL, 0.0188 mmol) is added. The yield is determined by comparing the integration of the ^{19}F NMR (375 MHz, acetone-*d*6, 23 ºC) resonance of 1-*tert*-butyl-4-fluorobenzene (–120.6 ppm) and that of 3-nitro-fluorobenzene (–111.8 ppm) (87% yield). The ^{19}F NMR chemical shift of the product corresponds to that of reported data.[5]

[5] Laali, K. K.; Okazaki, T.; Bunge, S. D. *J. Org. Chem.* **2007**, *72*, 6758–6762.

Benzo[*h*]quinolinyl palladium(II) pyrdine-sulfonamido complex 8

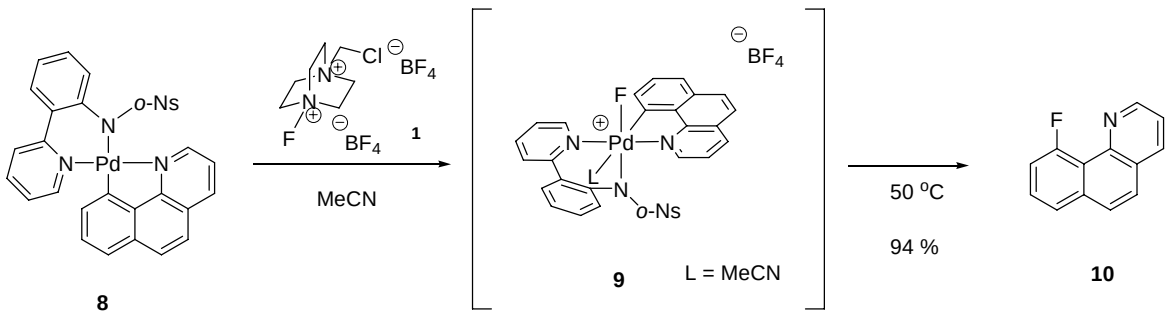


7 **8**

To the benzo[*h*]quinolinyl palladium acetate dimer (**7**) (342 mg, 1.00 mmol, 1.00 equiv) in CH_2Cl_2 (100 mL) at 23 ºC is added 2-(2-pyridinyl)phenyl-2-nitrobenzenesulfonamide (**2**) (342 mg, 1.00 mmol, 1.00 equiv). After stirring for 20 min the reaction mixture is concentrated in vacuo. The resulting residue is triturated with Et_2O (3 × 1 mL) to afford 606 mg of the title compound as a colorless solid (95% yield).

Melting Point: >260 ºC (decomp.). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 9.55 (dd, *J* = 5.5 Hz, 1.5 Hz, 1H), 8.99 (dd, *J* = 5.5 Hz, 1.0 Hz, 1H), 8.30 (dd, *J* = 8.5 Hz, 1.5 Hz, 1H), 7.76–7.71 (m, 2H), 7.64–7.54 (m, 5H), 7.49 (ddd, *J* = 9.5 Hz, 8.5 Hz, 1.5 Hz, 1H), 7.41 (dd, *J* = 7.5 Hz, 1.5 Hz, 1H), 7.36 (dd, *J* = 8.0 Hz, 8.0 Hz, 1H), 7.26–7.13 (m, 5H), 7.04 (dd, *J* = 8.0 Hz, 1.5 Hz, 1H), 7.00 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ)[6]: 176.0, 174.7, 168.4, 162.3, 160.4, 158.3, 155.5, 154.3, 151.3, 144.2, 142.3, 138.4, 137.5, 136.4, 134.9, 132.0, 131.1, 130.4, 130.1, 129.3, 128.9, 128.4, 126.9, 124.8, 124.6, 123.8, 123.4, 123.3, 122.6, 122.0. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{30}H_{20}N_4O_4S$ + H], 639.0313. Found, 639.0331. Anal: calcd for $C_{30}H_{20}N_4O_4PdS$: C, 56.39; H, 3.16; N, 8.77; found: C, 56.13; H, 2.99; N, 8.44.

10-fluorobenzo[*h*]quinoline (10)[7]



8 **9** **10**

– 0.0100 mmol scale –

[6] The ^{13}C NMR spectrum of **8** has a low signal-to-noise ratio due to its low solubility to common organic solvents.

[7] Saeki, K; Tomomitsu, M; Kawazoe, Y; Momota, K; Kimoto, H. *Chem Pharma Bull*, **1996**, *44*, 2254–2258.

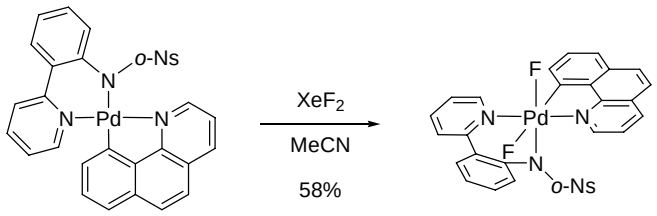
To the benzo[*h*]quinolinyl palladium(II) pyrdine-sulfonamido complex **8** (6.39 mg, 0.0100 mmol, 1.00 equiv) in MeCN (0.5 mL) at 23 ºC is added 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (**1**) (3.90 mg, 0.0110 mmol, 1.10 equiv). After stirring for 10 min at 23 ºC, the reaction mixture has a dark purple color. The reaction mixture is warmed to 50 ºC and stirred for 30 min. After cooling to 23 ºC, the reaction mixture is concentrated in vacuo. The resulting solid is purified by preparative TLC eluting with hexanes/EtOAc 7:3 (v/v) to afford 1.86 mg of the title compound as a colorless solid (94% yield, average of two runs).

– 0.200 mmol scale –

To the benzo[*h*]quinolinyl palladium(II) pyrdine-sulfonamido complex **8** (128 mg, 0.200 mmol, 1.00 equiv) in MeCN (2.0 mL) at 23 ºC is added 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (**1**) (77.9 mg, 0.220 mmol, 1.10 equiv). After stirring for 10 min at 23 ºC, the reaction mixture has a dark purple color. The reaction mixture is warmed to 50 ºC and stirred for 1.5 hr. After cooling to 23 ºC, the reaction mixture is concentrated in vacuo. The resulting solid is dissolved in CH_2Cl_2 and filtered through a pad of celite. The filtrate is concentrated in vacuo and the residue is purified by chromatography on silica gel eluting with hexanes/EtOAc 9:1 (v/v) to afford 27.4 mg of the title compound as a colorless solid (70% yield). [8]

R_f = 0.79 (hexanes/EtOAc 7:3 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 9.12 (dd, *J* = 4.0 Hz, 1.0 Hz, 1H), 8.17 (d, *J* = 7.5 Hz, 1H), 7.79 (d, *J* = 9.0 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.36 (ddd, *J* = 8.0 Hz, 7.5 Hz, 4.5 Hz, 1H), 7.54 (dd, *J* = 7.0 Hz, 4.5 Hz, 1H), 7.44 (dd, *J* = 13.0 Hz, 8.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 161.4 (d, *J* = 259 Hz), 149.4, 146.3 (d, *J* = 7.4 Hz), 136.5, 136.0, 128.6 (d, *J* = 9.1 Hz), 127.8, 127.4, 126.9, 124.4, 121.9, 120.5 (d, *J* = 6.4 Hz), 114.8 (d, *J* = 24 Hz). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –109.4 (d, *J* = 11 Hz). Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{13}H_8FN$ + H], 198.0714. Found, 198.0719. These spectroscopic data correspond to the reported data in reference 7.

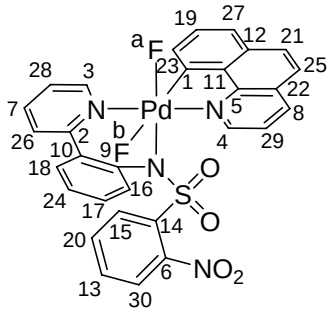
Difluoro palladium(IV) complex 11 by XeF_2 oxidation



8 **11**

[8] The fluorination yield is temperature-dependent and afforded lower yields at lower temperature. The lower yield on 0.200 mmol scale may be explicable due to slower heating on larger scale.

Under nitrogen atmosphere, to the benzo[*h*]quinolinyl palladium(II) pyrdine-sulfonamido complex **8** (128 mg, 0.200 mmol, 1.00 equiv) in anhydrous MeCN (2.0 mL) at 23 ºC is added xenone difluoride (81.1 mg, 0.480 mmol, 2.40 equiv). After stirring for 1.0 hr at 23 ºC, the precipitate is filtered off and washed with acetone (5 × 1 mL). The solid is dissolved in CH_2Cl_2 and filtered through a pad of celite. The filtrate is concentrated in vacuo to afford 79.1 mg of the title compound as an orange solid (58% yield).



Melting Point: 143 ºC (decomp.). NMR Spectroscopy: ^{1}H NMR (500 MHz, DMSO-*d6*, 23 ºC, δ): 9.72 (d, *J* = 5.0 Hz, 1H, H-4), 9.28 (d, *J* = 5.0 Hz, 1H, H-3), 9.18 (dd, *J* = 17.5 Hz, 8.0 Hz, 1H, H-15), 8.94 (d, *J* = 8.0 Hz, 1H, H-8), 8.20 (dd, *J* = 8.0 Hz, 8.0 Hz, 1H, H-7), 8.12 (dd, *J* = 8.0 Hz, 5.5 Hz, 1H, H-29), 8.07 (d, *J* = 9.0 Hz, 1H, H-25), 8.03 (d, *J* = 9.0 Hz, 1H, H-21), 7.89 (dd, *J* = 7.0 Hz, 7.0 Hz, 1H, H-28), 7.86 (d, *J* = 8.0 Hz, 1H, H-26), 7.75 (d, *J* = 7.5 Hz, 1H, H-18), 7.73 (d, *J* = 8.0 Hz, 1H, H-27), 7.44 (dd, *J* = 7.5 Hz, 7.5 Hz, 1H, H-13), 7.35 (d, *J* = 8.0 Hz, 1H, H-30), 7.31 (dd, *J* = 7.5 Hz, 7.5 Hz, 1H, H-24), 7.14 (dd, *J* = 8.0 Hz, 8.0 Hz, 1H, H-20), 7.07 (dd, *J* = 8.0 Hz, 7.5 Hz, 1H, H-19), 7.01 (dd, *J* = 7.5 Hz, 7.5 Hz, 1H, H-17), 6.36 (d, *J* = 8.0 Hz, 1H, H-16), 6.21 (dd, *J* = 7.5 Hz, 5.0 Hz, 1H, H-23). ^{13}C NMR (125 MHz, DMSO-*d6*, 23 ºC, δ):160.8 (d, *J* = 63 Hz, C-1), 152.8 (s, C-2), 152.0 (dd, *J* = 13.5 Hz, 6.3 Hz, C-3), 151.3 (d, *J* = 2.1 Hz, C-4), 151.0 (s, C-5), 148.3 (s, C-6), 142.9 (s, C-7), 141.0 (s, C-8), 139.6 (s, C-9), 136.7 (s, C-10), 135.3 (s, C-11), 135.0 (d, *J* = 3.6 Hz, C-12), 133.4 (s, C-13), 133.1 (s, C-14), 132.1 (d, *J* = 31 Hz, C-15), 131.9 (s, C-16), 131.7 (s, C-17), 131.4 (s, C-18), 131.0 (d, *J* = 6.4 Hz, C-19), 130.9 (s, C-20), 129.2 (s, C-21), 128.7 (s, C-22), 127.7 (d, *J* = 3.6 Hz, C-23), 127.5 (s, C-24), 125.5 (s, C-25), 125.4 (s, C-26), 125.4 (s, C-27), 125.2 (s, C-28,), 124.1 (s, C-29), 122.6 (s, C-30). ^{19}F NMR (375 MHz, DMSO-*d6*, 23 ºC, δ): –169.2 (d, *J* = 113 Hz 1F, F-b), –277.8 (d, *J* = 113 Hz, 1F, F-a). Anal: calcd for $C_{30}H_{20}F_2N_4O_4PdS$: C, 53.22; H, 2.98; N, 8.28; found: C, 53.17; H, 2.99; N, 8.17. The crystal structure is shown in the X-ray Crystallographic Analysis section.

The $^2J_{C–F}$ coupling constant of 63 Hz in **11** is similar in size to a coupling constant reported for an arylpalladium (II) fluoride (51.7 Hz).[9] The chemical shift of –169 ppm in the ^{19}F NMR differs from the ^{19}F chemical shifts of palladium (II) fluorides, which are typically found in the range of –274 ppm – –323 ppm.[9,10] Varying ^{19}F chemical shifts have, however, been observed for platinum complexes.[11]

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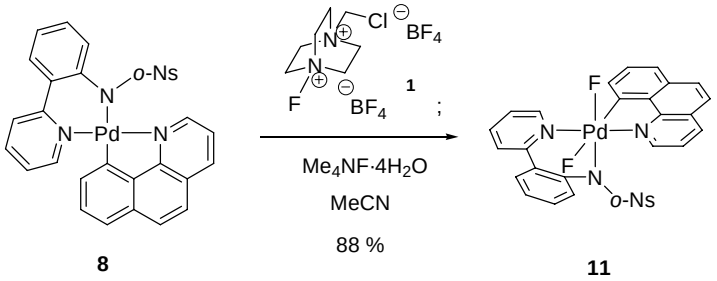
[9] Marshall, W. J.; Thorn, D. L.; Grushin, V. V. *Organometallics* **1998**, *17*, 5427–5430.

[10] a) Jasim, N. A.; Perutz, R. N.; Whitwood, A. C.; Braun, T.; Izundu, J.; Neumann, B.; Rothfeld, S.; Stammler, H.-G. *Organometallics* **2004**, *23*,

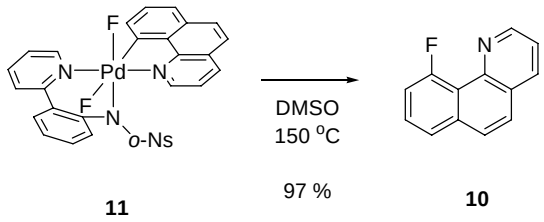
Difluoro palladium(IV) complex 11 by Selectfluor™ (1) oxidation



8 **11**

To the benzo[*h*]quinolinyl palladium(II) pyrdine-sulfonamido complex **8** (128 mg, 0.200 mmol, 1.00 equiv) in MeCN (2.0 mL) at 23 ºC is added 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (**1**) (77.9 mg, 0.220 mmol, 1.10 equiv). After stirring for 10 min at 23 ºC, tetramethylammonium fluoride tetrahydrate (72.6 mg, 0.440 mmol, 2.20 equiv) is added to the reaction mixture. After stirring for 20 min at 23 ºC, the precipitate is filtered off and washed with acetone (5 × 2 mL). The solid is dissolved in CH_2Cl_2 and filtered through a pad of celite. The filtrate is concentrated in vacuo to afford 119 mg of the title compound as an orange solid (88% yield).

Decomposition of palladium(IV) difluoride 11



11 **10**

– 0.0100 mmol scale –

To DMSO-*d6* (0.5 mL) at 150 ºC is added palladium(IV) difluoride complex **11** (6.76 mg, 0.0100 mmol, 1.00 equiv) in 5 portions over 5 min. After stirring for 10 min at 150 ºC, the reaction mixture is cooled to 23 ºC, at which temperature fluorobenzene (2.05 mg, 2.00 μL, 0.0213 mmol) is added. The yield is determined by comparing the integration of the ^{19}F NMR (375 MHz, DMSO-*d*6, 23 ºC) resonance of 10-

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6140–6149; b) Fraser, S. L.; Antipin, M. Y.; Khroustalyov, V. N.; Grushin, V. V. *J. Am. Chem. Soc.* **1997**, *119*, 4769–4770; c) Grushin, V. V.; Marshall, W. J. *J. Am. Chem. Soc.* **2006**, *128*, 12644–12645.

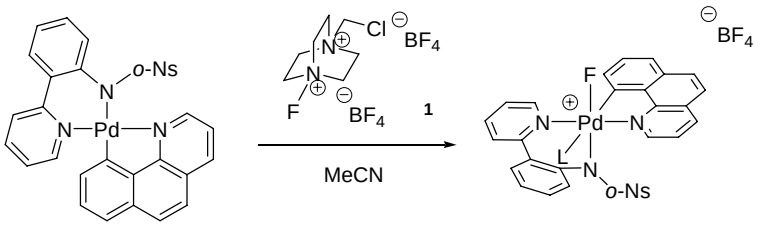
[11] a) For a ^{19}F chemical shift at –107.6, see Nilsson, P.; Plamper, F.; Wendt, O. F. *Organometallics* **2003**, *22*, 5235–5242; b) for a collection of 16 different ^{19}F chemical shifts from –116 ppm to – 456 ppm, see Yahav, A.; Goldberg, I.; Vigalok, A. *Inorg. Chem.* **2005**, *44*, 1547–1553.

fluorobenzo[*h*]quinoline (–108.2 ppm) and that of fluorobenzene (–113.4 ppm) (97% yield, average of three runs).

– 0.100 mmol scale –

To DMSO (5.0 mL) at 150 ºC is added palladium(IV) difluoride complex **11** (67.6 mg, 0.100 mmol, 1.00 equiv) in 20 portions over 10 min. After stirring for 10 min at 150 ºC, the reaction mixture is cooled to 23 ºC and half of the solvent is removed in vacuo. To the solution is added water (5.0 mL) and the aqueous phase is extracted with Et_2O (7 × 3 mL). The combined organic phases are washed with brine (3 mL) and dried (Na_2SO_4). The filtrate is concentrated in vacuo and the residue is purified by preparative TLC eluting with hexanes/EtOAc 4:1 (v/v) to afford 14.1 mg of the title compound as a colorless solid. (71% yield).

Fluoro palladium(IV) tetrafluoroborate complex 9

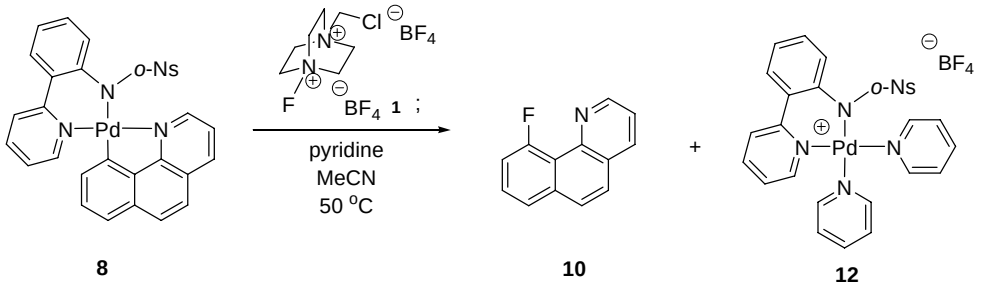


8 **9** L = MeCN

To the benzo[*h*]quinolinyl palladium(II) pyrdine-sulfonamido complex **8** (6.4 mg, 0.010 mmol, 1.0 equiv) in acetonitrile-*d3* (0.5 mL) at 23 ºC is added 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (**1**) (3.9 mg, 0.011 mmol, 1.1 equiv). After stirring for 10 min at 23 ºC, the colorless suspension forms a dark purple solution. Compound **9** was characterized by NMR in acetonitrile solution without purification.

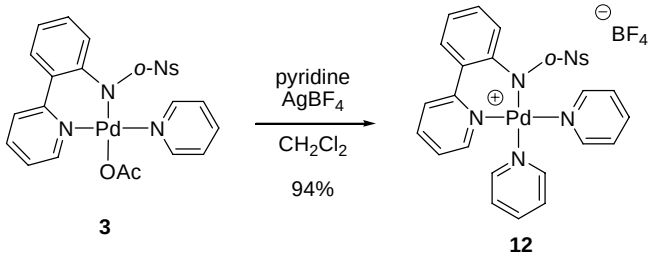
NMR Spectroscopy: ^{1}H NMR (500 MHz, acetonitrile-*d3*, 23 ºC, δ): 9.60 (d, *J* = 6.0 Hz, 1H), 9.46 (d, *J* = 6.0 Hz, 1H), 8.89 (dd, *J* = 8.0 Hz, 1.0 Hz, 1H), 8.48 (dd, *J* = 7.5 Hz, 7.5 Hz, 1H), 8.40 (d, *J* = 8.0 Hz, 1H), 8.10–8.00 (m, 3H), 7.95 (dd, *J* = 7.0 Hz, 6.5 Hz, 1H), 7.80–7.75 (m, 2H), 7.66–7.56 (m, 2H), 7.47–7.40 (m, 2H), 7.20 (dd, *J* = 7.5 Hz, 7.5 Hz, 1H), 7.06 (dd, *J* = 8.0 Hz, 8.0 Hz, 1H), 6.89 (dd, *J* = 8.0 Hz, 7.5 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.31 (d, *J* = 9.0 Hz, 1H). ^{13}C NMR (125 MHz, acetonitrile-*d3*, 23 ºC, δ): 153.8, 153.2, 151.1, 151.0, 150.1, 148.0, 147.3, 143.5, 141.7, 138.9, 136.1, 135.2, 134.7, 134.3, 132.7, 132.0, 131.8, 131.6, 131.5, 130.6, 129.4, 128.7, 127.2, 126.9, 126.6, 126.1, 126.0, 125.9, 125.0, 124.3. ^{19}F NMR (375 MHz, acetonitrile-*d3*, 23 ºC, δ): –152.0 (s, 8H), –278.0 (brs, 1H). Given that the reactive intermediate **9** is not purified from the Selectfluor residue, the BF_4^- counteranion of **9** and the BF_4^- counteranion of the Selectfluor residue overlap in the ^{19}F NMR spectrum. The integral ratio of the ^{19}F NMR resonances at –278 ppm (Pd(IV)F) and –152 ppm (BF_4^-) of 1:8 is consistent with the expected ratio of **9** : BF_4^- of 1:1.

Bis(pyridinium)palladium(II) tetrafluoroborate complex 12 from compound 8



To the benzo[*h*]quinolinyl palladium(II) pyrdine-sulfonamido complex **8** (19.2 mg, 0.0300 mmol, 1.00 equiv) in acetonitrile-*d3* (0.5 mL) at 23 ºC is added 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (**1**) (10.6 mg, 0.0300 mmol, 1.00 equiv). After stirring for 10 min at 23 ºC, the reaction mixture has a dark purple color. The reaction mixture is warmed to 50 ºC and stirred for 30 min. After cooling to 23 ºC, to the reaction mixture is added pyridine (9.7 uL, 0.12 mmol, 4.0 equiv). The presence of compound **12** was comfirmed by comparing ^{1}H and ^{13}C spectra with those of the authentic sample synthesized as below.

Bis(pyridinium)palladium(II) tetrafluoroborate complex 12



To acetato palladium complex **3** (30.0 mg, 0.501 mmol, 1.00 equiv) in CH_2Cl_2 (1.0 mL) at 23 ºC is added pyridine (4.1 μL, 0.050 mmol, 1.0 equiv) and silver tetrafluoroborate (19.5 mg, 0.100 mmol, 2.00 equiv). After stirring for 30 min at 23 ºC, the reaction mixture is filtered through a pad of celite. The filtrate is concentrated in vacuo to afford 33.2 mg of the title compound as yellow oil (94% yield)

NMR Spectroscopy: ^{1}H NMR (500 MHz, acetonitrile-*d3*, 23 ºC, δ): 8.84–8.78 (m, 4H), 7.98–7.93 (m, 2H), 7.76 (dd, *J* = 6.0 Hz, 1.0 Hz, 1H), 7.74–7.68 (m, 2H), 7.60 (ddd, *J* = 7.5 Hz, 7.5 Hz, 1.5 Hz, 1H), 7.54–7.48 (m, 6H), 7.45 (dd, *J* = 8.0 Hz, 1.0 Hz, 1H), 7.32 (ddd, *J* = 8.0 Hz, 7.0 Hz, 2.0 Hz, 1H), 7.26 (dd, *J* = 7.5 Hz, 1.0 Hz, 1H), 7.18–7.12 (m, 2H), 7.32 (ddd, *J* = 7.5 Hz, 5.5 Hz, 1.5 Hz, 1H). ^{13}C NMR (125 MHz, acetonitrile-*d3*, 23 ºC, δ): 154.8, 151.9, 151.6, 151.0, 147.1, 141.1, 140.9, 140.5, 139.0, 137.0, 133.4, 132.9, 132.1, 131.7, 130.9, 130.5, 129.1, 127.5, 126.8, 126.5, 125.4, 124.9, 123.3. ^{19}F NMR (375 MHz, acetonitrile-*d3*, 23 ºC, δ): –152.0 (s). Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{27}H_{22}BF_4N_5O_4PdS - BF_4$], 618.0427. Found, 618.0434.

X-ray Crystallographic Analysis

Difluoro palladium(IV) complex 11 (CCDC 686490)

Experimental

The compound was crystallized from an acetonitrile solution as orange prisms. A crystal 0.025 mm x 0.050 mm x 0.075 mm in size was selected, mounted on a nylon loop with Paratone-N oil, and transferred to a Bruker SMART APEX II diffractometer equipped with an Oxford Cryosystems 700 Series Cryostream Cooler and Mo Kα radiation (λ = 0.71073 Å). A total of 2147 frames were collected at 193 (2) K to θ_{max} = 22.49° with an oscillation range of 0.5°/frame, and an exposure time of 15 s/frame using the APEX2 suite of software. (Bruker AXS, 2006a) Data were collected to θ_{max} = 22.49° rather than the routine value of θ_{max} = 27.50° because the crystal examined did not exhibit usable diffraction beyond 22.49°. Unit cell refinement on all observed reflections, and data reduction with corrections for Lp and decay were performed using SAINT. (Bruker AXS, 2006b) Scaling and a multi-scan absorption correction were done using SADABS. (Bruker AXS, 2004) The minimum and maximum transmission factors were 0.9421 and 0.9802, respectively. A total of 34170 reflections were collected, 3643 were unique (R_{int} = 0.147), and 2584 had $I > 2\sigma(I)$. Systematic absences were consistent with the compound having crystallized in the monoclinic space group $P2_1/n$. The observed mean $|E^2-1|$ value was 0.912 (versus the expectation values of 0.968 and 0.736 for centric and noncentric data, respectively).

The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL. (Bruker AXS, 2001) The asymmetric unit was found to contain one molecule of (Benzo[*h*]quinolinato){(2-nitrophenyl-sulfonyl)[(2-(pyridin-2-yl)phenyl)amido]difluoro-palladium(IV) and one molecule of acetonitrile. All of the nonhydrogen atoms were refined with anisotropic displacement coefficients. The hydrogen atoms were assigned isotropic displacement coefficients $U(H) = 1.2U(C)$ or $1.5U(C_{methyl})$, and their coordinates were allowed to ride on their respective carbons. The acetonitrile was treated with a two-site disorder model consisting of partial atoms with fixed site occupancy factors of a half. The atoms associated with one of the two sites were specified with an asterisk, e.g. N1S and N1S*, and included in the least-squares refinement with 1,2-distance, rigid-bond and similar U_{ij} restraints. The refinement converged to $R(F)$ = 0.0383, $wR(F^2)$ = 0.0703, and S = 1.042 for 2584 reflections with I > 2σ(I), and $R(F)$ = 0.0728, $wR(F^2)$ = 0.0829, and S = 1.042 for 3643 unique reflections, 424 parameters, and 58 restraints. The maximum $|\Delta/\sigma|$ in the final cycle of least-squares was 0.001, and the residual peaks on the final difference-Fourier map ranged from -0.505 to 0.392 eÅ^{-3}. Scattering factors were taken from the International Tables for Crystallography, Volume C. (Maslen et al., 1992, and Creagh & McAuley, 1992)

References

Bruker AXS (2001). *SHELXTL v6.12*. Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, USA.

Bruker AXS (2004). *SADABS*. Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, USA.

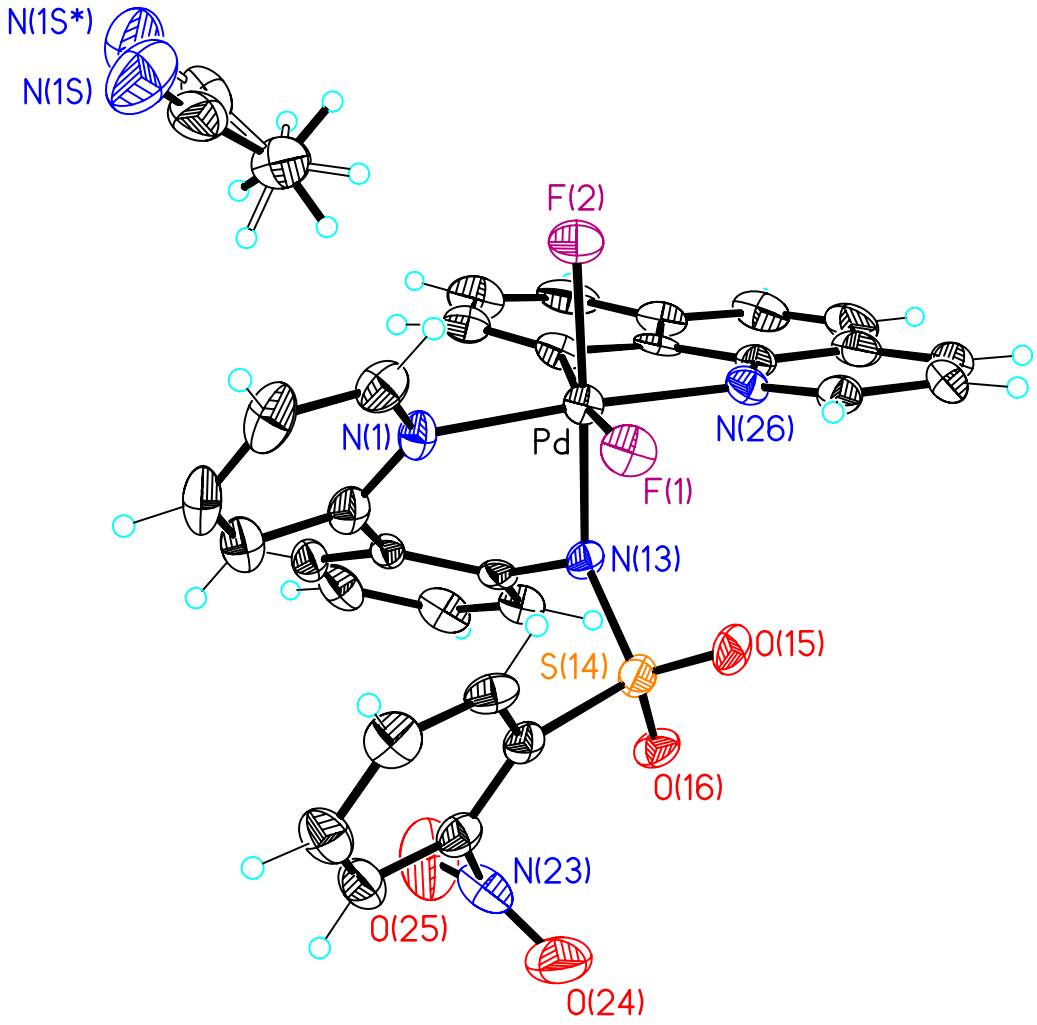
Bruker AXS (2006a). *APEX2 v2.1-0*. Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, USA.

Bruker AXS (2006b). *SAINT V7.34A*. Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, USA.

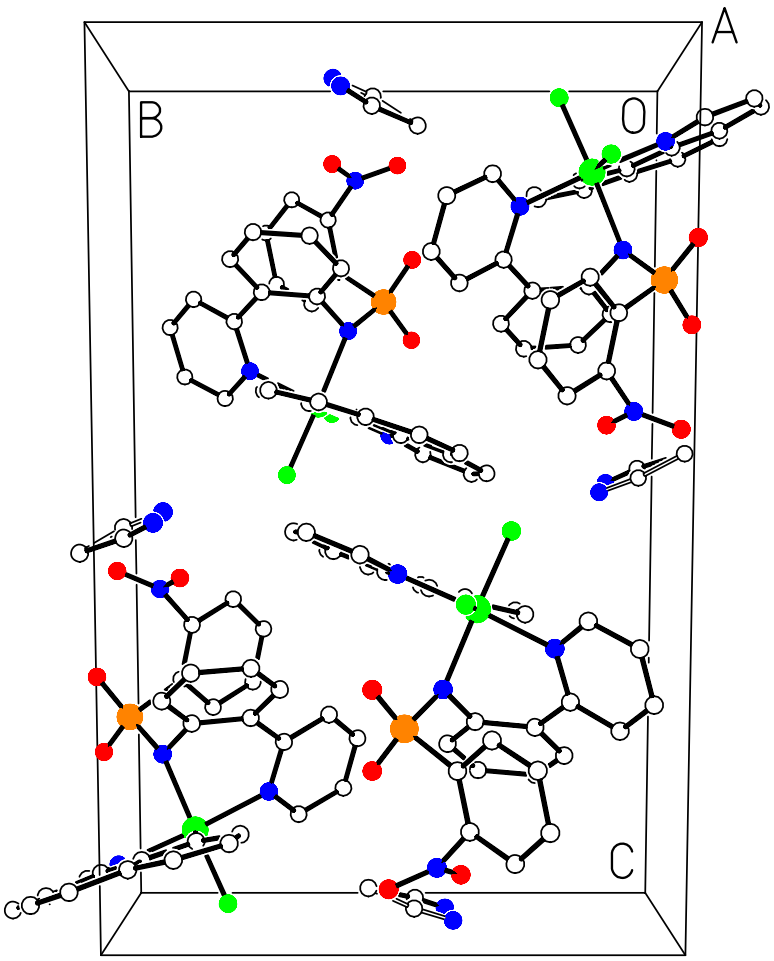
Creagh, D. C. & McAuley, W. J. (1992). *International Tables for Crystallography: Mathematical, Physical and Chemical Tables*, Vol C, edited by A. J. C. Wilson, pp. 206-222. Dordrecht, The Netherlands: Kluwer.

Maslen, E. N., Fox, A. G. & O'Keefe, M. A. (1992). *International Tables for Crystallography: Mathematical, Physical and Chemical Tables*, Vol C, edited by A. J. C. Wilson, pp. 476-516. Dordrecht, The Netherlands: Kluwer.

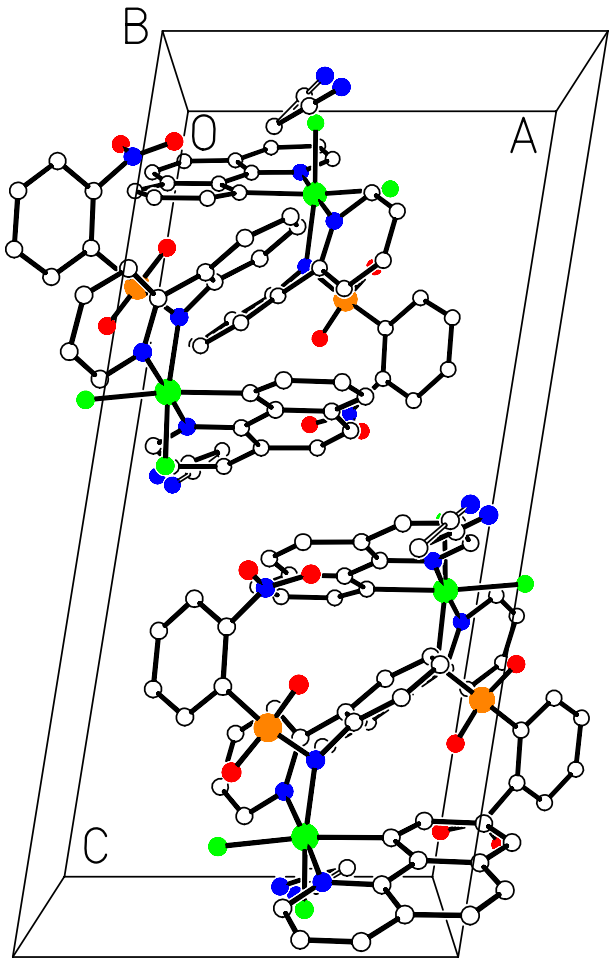
$R(F) = R1 = \Sigma \, ||F_o|-|F_c|| \, / \, \Sigma|F_o|$, $wR(F^2) = wR2 = [\, \Sigma \, w \, (F_o^2-F_c^2)^2 \, / \, \Sigma \, w \, (F_o^2)^2 \,]^{1/2}$, and S = Goodness-of-fit on $F^2 = [\, \Sigma \, w \, (F_o^2-F_c^2)^2 \, / \, (n-p) \,]^{1/2}$, where n is the number of reflections and p is the number of parameters refined.



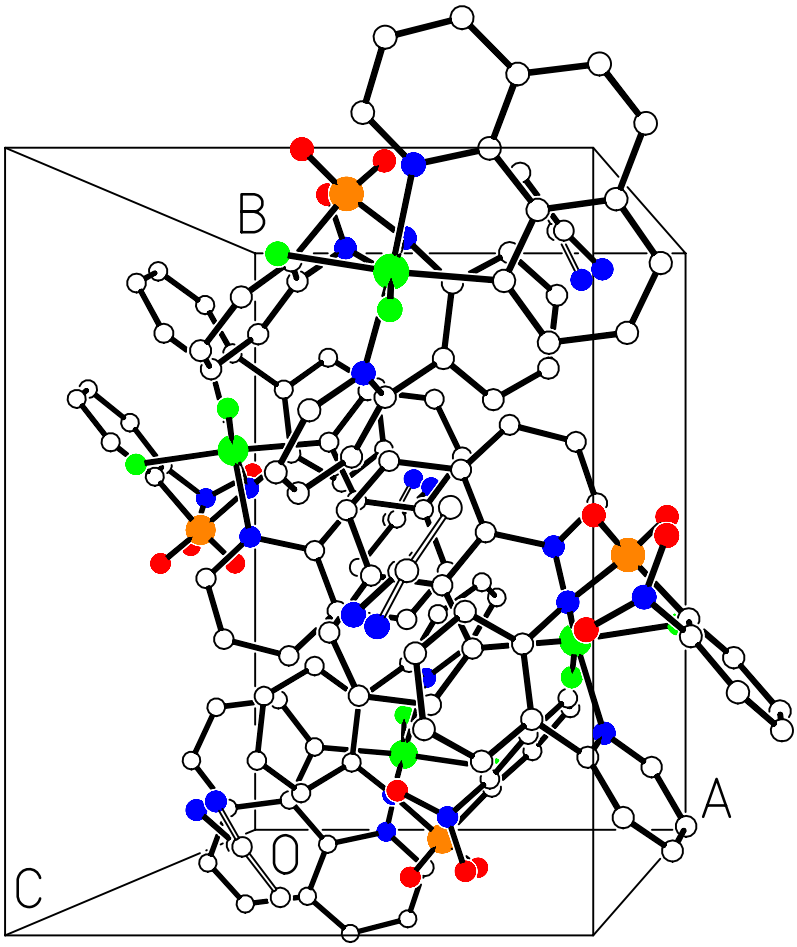
The structure of the difluoro palladium(IV) complex **11** with hydrogens and with selected atom labels. The nonhydrogen atoms are depicted with 50% probability ellipsoids.



A unit cell diagram for the difluoro palladium(IV) complex **11** viewed down the crystallographic *a*-axis. Hydrogen atoms have been removed for clarity.



A unit cell diagram for the difluoro palladium(IV) complex **11** viewed down the crystallographic *b*-axis. Hydrogen atoms have been removed for clarity.



A unit cell diagram for the difluoro palladium(IV) complex **11** viewed down the crystallographic *c*-axis. Hydrogen atoms have been removed for clarity.

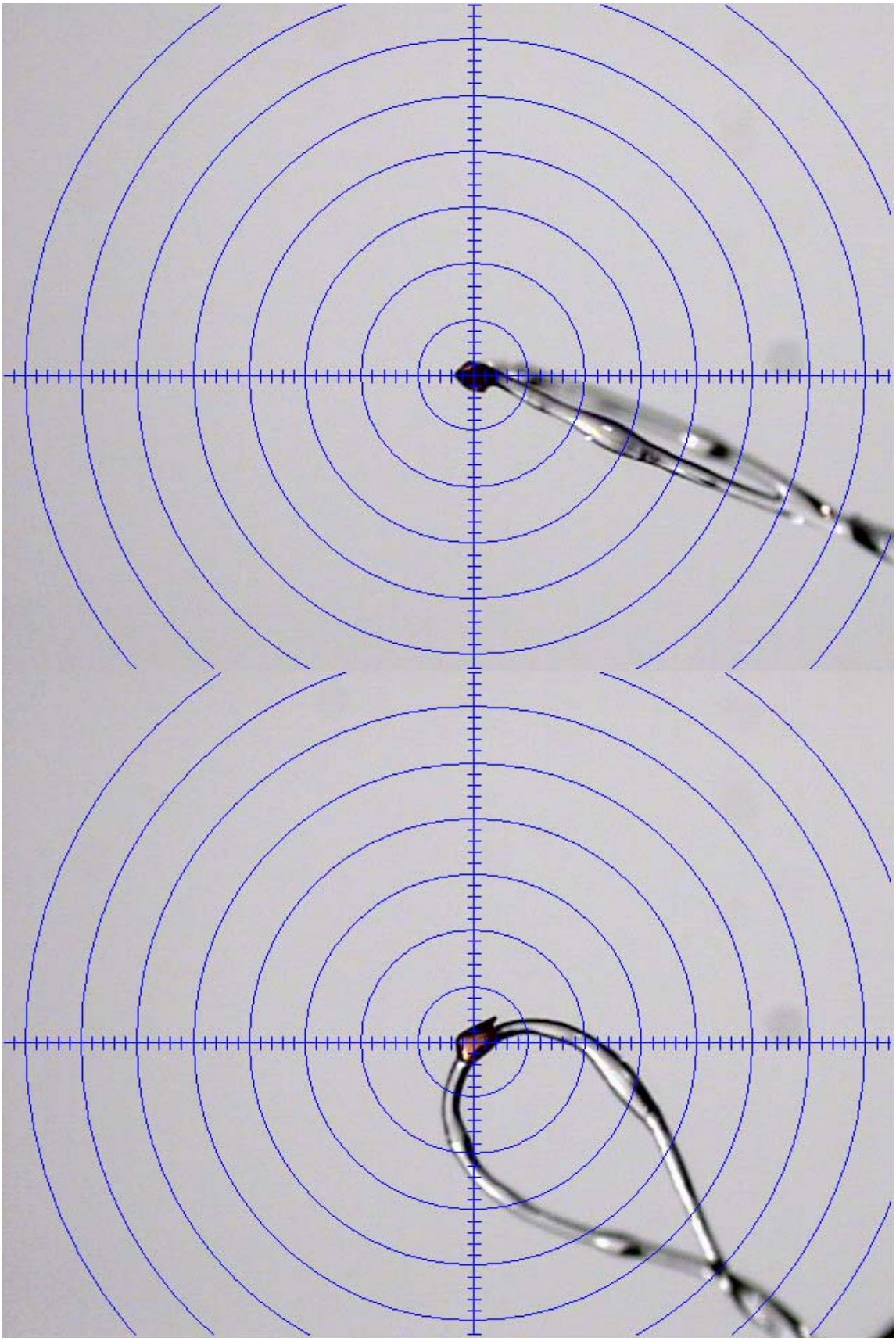


Table 1. Crystal data and structure refinement for the difluoro palladium(IV) complex **11**.

Identification code	difluoro palladium(IV) complex **11**	
Empirical formula	C_{32} H_{23} F_2 N_5 O_4 Pd S	
Formula weight	718.01	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 10.0089(3) Å	α= 90°.
	b = 13.3937(4) Å	β= 99.197(3) °.
	c = 21.0503(7) Å	γ = 90°.
Volume	2785.65(15) Å ^{3}	
Z	4	
Density (calculated)	1.712 Mg/m^3	
Absorption coefficient	0.805 mm^{-1}	
F(000)	1448	
Crystal size	0.075 x 0.050 x 0.025 mm^3	
Theta range for data collection	1.81 to 22.49°.	
Index ranges	-10<=h<=10, -14<=k<=14, -22<=l<=22	
Reflections collected	34170	
Independent reflections	3643 [R(int) = 0.1469]	
Completeness to theta = 22.49∞	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9802 and 0.9421	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3643 / 58 / 424	
Goodness-of-fit on F^2	1.042	
Final R indices [I>2sigma(I)]	R1 = 0.0383, wR2 = 0.0703	

R indices (all data)	R1 = 0.0728, wR2 = 0.0829
Largest diff. peak and hole	0.392 and -0.505 e. $Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for the difluoro palladium(IV) complex **11**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Pd	3838(1)	1424(1)	1183(1)	22(1)
F(1)	5817(3)	1199(2)	1097(1)	32(1)
F(2)	3569(3)	2017(2)	324(1)	34(1)
N(1)	4481(4)	2737(3)	1604(2)	26(1)
C(2)	5333(6)	3254(4)	1286(3)	33(2)
C(3)	6042(6)	4070(5)	1567(4)	41(2)
C(4)	5884(6)	4335(5)	2178(3)	41(2)
C(5)	5021(6)	3826(4)	2496(3)	33(2)
C(6)	4298(5)	3020(4)	2202(3)	27(2)
C(7)	3327(5)	2461(4)	2521(2)	20(1)
C(8)	2497(5)	3008(4)	2879(3)	27(2)
C(9)	1528(6)	2546(5)	3150(3)	33(2)
C(10)	1354(6)	1517(5)	3100(3)	35(2)
C(11)	2160(5)	960(5)	2757(3)	26(2)
C(12)	3140(5)	1421(5)	2464(2)	21(1)
N(13)	3895(4)	854(3)	2075(2)	21(1)
S(14)	5103(1)	186(1)	2466(1)	25(1)
O(15)	5754(4)	-350(3)	2017(2)	31(1)
O(16)	4573(4)	-359(3)	2957(2)	29(1)
C(17)	6294(5)	1061(4)	2875(3)	23(1)
C(18)	7074(5)	1609(4)	2510(3)	26(2)
C(19)	7959(6)	2328(5)	2790(3)	34(2)
C(20)	8057(6)	2534(5)	3443(3)	36(2)
C(21)	7315(6)	1998(5)	3822(3)	34(2)
C(22)	6435(5)	1268(4)	3528(3)	27(2)

N(23)	5678(6)	732(5)	3970(2)	39(1)
O(24)	6112(5)	-78(4)	4178(2)	54(1)
O(25)	4687(5)	1156(4)	4113(2)	63(2)
N(26)	3319(4)	74(3)	802(2)	24(1)
C(27)	4128(6)	-563(5)	580(3)	30(2)
C(28)	3656(6)	-1483(5)	337(3)	34(2)
C(29)	2333(7)	-1735(5)	339(3)	38(2)
C(29A)	1433(6)	-1060(5)	560(3)	34(2)
C(30)	12(7)	-1190(5)	562(3)	41(2)
C(31)	-753(7)	-461(5)	763(3)	38(2)
C(31A)	-199(6)	495(5)	976(3)	32(2)
C(32)	-953(6)	1317(6)	1133(3)	39(2)
C(33)	-330(6)	2224(6)	1277(3)	40(2)
C(34)	1070(6)	2354(5)	1295(3)	28(2)
C(35)	1834(5)	1549(5)	1167(2)	25(1)
C(35A)	1193(5)	636(5)	991(2)	23(1)
C(35B)	1984(6)	-138(4)	791(3)	23(1)
N(1S)	4160(20)	5940(20)	230(20)	65(8)
C(2S)	3430(50)	5390(30)	400(30)	47(8)
C(3S)	2607(7)	4559(5)	577(3)	52(2)
N(1S*)	3720(20)	6080(20)	110(20)	55(7)
C(2S*)	3270(60)	5370(30)	290(30)	48(8)

Table 3. Bond lengths [Å] and angles [°] for the difluoro palladium(IV) complex **11**.

Pd-F(2)	1.955(3)	N(13)-S(14)	1.619(4)
Pd-C(35)	2.008(5)	S(14)-O(15)	1.426(4)
Pd-N(26)	2.012(5)	S(14)-O(16)	1.435(4)
Pd-N(13)	2.019(4)	S(14)-C(17)	1.791(6)
Pd-N(1)	2.027(5)	C(17)-C(22)	1.386(8)
Pd-F(1)	2.040(3)	C(17)-C(18)	1.389(7)
N(1)-C(6)	1.354(7)	C(18)-C(19)	1.376(8)
N(1)-C(2)	1.355(7)	C(18)-H(18)	0.9500
C(2)-C(3)	1.385(8)	C(19)-C(20)	1.389(8)
C(2)-H(2)	0.9500	C(19)-H(19)	0.9500
C(3)-C(4)	1.367(9)	C(20)-C(21)	1.376(8)
C(3)-H(3)	0.9500	C(20)-H(20)	0.9500
C(4)-C(5)	1.357(8)	C(21)-C(22)	1.393(8)
C(4)-H(4)	0.9500	C(21)-H(21)	0.9500
C(5)-C(6)	1.389(8)	C(22)-N(23)	1.477(7)
C(5)-H(5)	0.9500	N(23)-O(25)	1.222(6)
C(6)-C(7)	1.471(8)	N(23)-O(24)	1.224(7)
C(7)-C(12)	1.408(8)	N(26)-C(27)	1.314(7)
C(7)-C(8)	1.412(7)	N(26)-C(35B)	1.363(7)
C(8)-C(9)	1.351(8)	C(27)-C(28)	1.388(8)
C(8)-H(8)	0.9500	C(27)-H(27)	0.9500
C(9)-C(10)	1.390(8)	C(28)-C(29)	1.367(8)
C(9)-H(9)	0.9500	C(28)-H(28)	0.9500
C(10)-C(11)	1.383(8)	C(29)-C(29A)	1.408(8)
C(10)-H(10)	0.9500	C(29)-H(29)	0.9500
C(11)-C(12)	1.385(7)	C(29A)-C(35B)	1.407(8)
C(11)-H(11)	0.9500	C(29A)-C(30)	1.433(8)
C(12)-N(13)	1.421(7)	C(30)-C(31)	1.350(9)

C(30)-H(30)	0.9500	C(35A)-C(35B)	1.408(8)
C(31)-C(31A)	1.438(8)	N(1S)-C(2S)	1.139(10)
C(31)-H(31)	0.9500	C(2S)-C(3S)	1.462(10)
C(31A)-C(35A)	1.401(8)	C(3S)-C(2S*)	1.458(10)
C(31A)-C(32)	1.403(8)	C(3S)-H(3SA)	0.9800
C(32)-C(33)	1.378(9)	C(3S)-H(3SB)	0.9800
C(32)-H(32)	0.9500	C(3S)-H(3SC)	0.9800
C(33)-C(34)	1.406(8)	C(3S)-H(3SD)	0.9800
C(33)-H(33)	0.9500	C(3S)-H(3SE)	0.9800
C(34)-C(35)	1.374(8)	C(3S)-H(3SF)	0.9800
C(34)-H(34)	0.9500	N(1S*)-C(2S*)	1.136(10)
C(35)-C(35A)	1.403(8)		
		C(2)-N(1)-Pd	114.1(4)
F(2)-Pd-C(35)	87.81(18)	N(1)-C(2)-C(3)	120.8(6)
F(2)-Pd-N(26)	90.47(15)	N(1)-C(2)-H(2)	119.6
C(35)-Pd-N(26)	82.8(2)	C(3)-C(2)-H(2)	119.6
F(2)-Pd-N(13)	173.48(15)	C(4)-C(3)-C(2)	118.5(6)
C(35)-Pd-N(13)	85.77(19)	C(4)-C(3)-H(3)	120.7
N(26)-Pd-N(13)	89.85(18)	C(2)-C(3)-H(3)	120.7
F(2)-Pd-N(1)	92.23(17)	C(5)-C(4)-C(3)	120.8(6)
C(35)-Pd-N(1)	100.5(2)	C(5)-C(4)-H(4)	119.6
N(26)-Pd-N(1)	175.84(18)	C(3)-C(4)-H(4)	119.6
N(13)-Pd-N(1)	87.82(18)	C(4)-C(5)-C(6)	119.9(6)
F(2)-Pd-F(1)	88.27(13)	C(4)-C(5)-H(5)	120.1
C(35)-Pd-F(1)	172.95(18)	C(6)-C(5)-H(5)	120.1
N(26)-Pd-F(1)	91.38(16)	N(1)-C(6)-C(5)	119.5(5)
N(13)-Pd-F(1)	98.24(14)	N(1)-C(6)-C(7)	118.7(5)
N(1)-Pd-F(1)	85.54(15)	C(5)-C(6)-C(7)	121.8(5)
C(6)-N(1)-C(2)	120.3(5)	C(12)-C(7)-C(8)	118.5(5)
C(6)-N(1)-Pd	124.6(4)	C(12)-C(7)-C(6)	123.5(5)

C(8)-C(7)-C(6)	117.9(5)	C(17)-C(18)-H(18)	119.6
C(9)-C(8)-C(7)	120.7(6)	C(18)-C(19)-C(20)	120.1(6)
C(9)-C(8)-H(8)	119.6	C(18)-C(19)-H(19)	119.9
C(7)-C(8)-H(8)	119.6	C(20)-C(19)-H(19)	119.9
C(8)-C(9)-C(10)	120.8(6)	C(21)-C(20)-C(19)	120.7(6)
C(8)-C(9)-H(9)	119.6	C(21)-C(20)-H(20)	119.7
C(10)-C(9)-H(9)	119.6	C(19)-C(20)-H(20)	119.7
C(11)-C(10)-C(9)	119.8(6)	C(20)-C(21)-C(22)	118.0(6)
C(11)-C(10)-H(10)	120.1	C(20)-C(21)-H(21)	121.0
C(9)-C(10)-H(10)	120.1	C(22)-C(21)-H(21)	121.0
C(10)-C(11)-C(12)	120.4(6)	C(17)-C(22)-C(21)	122.5(6)
C(10)-C(11)-H(11)	119.8	C(17)-C(22)-N(23)	123.1(5)
C(12)-C(11)-H(11)	119.8	C(21)-C(22)-N(23)	114.3(5)
C(11)-C(12)-C(7)	119.8(5)	O(25)-N(23)-O(24)	125.4(6)
C(11)-C(12)-N(13)	119.9(5)	O(25)-N(23)-C(22)	116.6(6)
C(7)-C(12)-N(13)	120.2(5)	O(24)-N(23)-C(22)	117.9(6)
C(12)-N(13)-S(14)	115.2(3)	C(27)-N(26)-C(35B)	121.2(5)
C(12)-N(13)-Pd	113.3(3)	C(27)-N(26)-Pd	126.2(4)
S(14)-N(13)-Pd	126.1(2)	C(35B)-N(26)-Pd	112.6(4)
O(15)-S(14)-O(16)	118.9(2)	N(26)-C(27)-C(28)	121.0(6)
O(15)-S(14)-N(13)	108.9(2)	N(26)-C(27)-H(27)	119.5
O(16)-S(14)-N(13)	108.4(2)	C(28)-C(27)-H(27)	119.5
O(15)-S(14)-C(17)	108.0(2)	C(29)-C(28)-C(27)	119.4(6)
O(16)-S(14)-C(17)	106.3(3)	C(29)-C(28)-H(28)	120.3
N(13)-S(14)-C(17)	105.6(2)	C(27)-C(28)-H(28)	120.3
C(22)-C(17)-C(18)	117.7(5)	C(28)-C(29)-C(29A)	120.9(6)
C(22)-C(17)-S(14)	124.2(4)	C(28)-C(29)-H(29)	119.5
C(18)-C(17)-S(14)	118.0(4)	C(29A)-C(29)-H(29)	119.5
C(19)-C(18)-C(17)	120.8(5)	C(35B)-C(29A)-C(29)	116.2(6)
C(19)-C(18)-H(18)	119.6	C(35B)-C(29A)-C(30)	116.1(6)

C(29)-C(29A)-C(30)	127.6(6)	N(1S)-C(2S)-C(3S)	171(6)
C(31)-C(30)-C(29A)	121.7(6)	C(2S*)-C(3S)-H(3SA)	99.0
C(31)-C(30)-H(30)	119.2	C(2S)-C(3S)-H(3SA)	109.5
C(29A)-C(30)-H(30)	119.2	C(2S*)-C(3S)-H(3SB)	112.8
C(30)-C(31)-C(31A)	122.2(6)	C(2S)-C(3S)-H(3SB)	109.5
C(30)-C(31)-H(31)	118.9	H(3SA)-C(3S)-H(3SB)	109.5
C(31A)-C(31)-H(31)	118.9	C(2S*)-C(3S)-H(3SC)	116.1
C(35A)-C(31A)-C(32)	117.4(6)	C(2S)-C(3S)-H(3SC)	109.5
C(35A)-C(31A)-C(31)	117.3(6)	H(3SA)-C(3S)-H(3SC)	109.5
C(32)-C(31A)-C(31)	125.2(6)	H(3SB)-C(3S)-H(3SC)	109.5
C(33)-C(32)-C(31A)	120.1(6)	C(2S*)-C(3S)-H(3SD)	109.5
C(33)-C(32)-H(32)	119.9	C(2S)-C(3S)-H(3SD)	99.5
C(31A)-C(32)-H(32)	119.9	H(3SA)-C(3S)-H(3SD)	149.6
C(32)-C(33)-C(34)	121.9(6)	H(3SB)-C(3S)-H(3SD)	49.8
C(32)-C(33)-H(33)	119.0	H(3SC)-C(3S)-H(3SD)	67.5
C(34)-C(33)-H(33)	119.0	C(2S*)-C(3S)-H(3SE)	109.5
C(35)-C(34)-C(33)	118.8(6)	C(2S)-C(3S)-H(3SE)	110.9
C(35)-C(34)-H(34)	120.6	H(3SA)-C(3S)-H(3SE)	69.0
C(33)-C(34)-H(34)	120.6	H(3SB)-C(3S)-H(3SE)	137.3
C(34)-C(35)-C(35A)	119.4(5)	H(3SD)-C(3S)-H(3SE)	109.5
C(34)-C(35)-Pd	130.4(5)	C(2S*)-C(3S)-H(3SF)	109.5
C(35A)-C(35)-Pd	110.2(4)	C(2S)-C(3S)-H(3SF)	117.5
C(31A)-C(35A)-C(35)	122.2(6)	H(3SA)-C(3S)-H(3SF)	48.7
C(31A)-C(35A)-C(35B)	119.9(6)	H(3SB)-C(3S)-H(3SF)	61.5
C(35)-C(35A)-C(35B)	117.7(5)	H(3SC)-C(3S)-H(3SF)	132.5
N(26)-C(35B)-C(29A)	121.2(5)	H(3SD)-C(3S)-H(3SF)	109.5
N(26)-C(35B)-C(35A)	116.0(5)	H(3SE)-C(3S)-H(3SF)	109.5
C(29A)-C(35B)-C(35A)	122.7(5)	N(1S*)-C(2S*)-C(3S)	172(6)

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for the difluoro palladium(IV) complex **11**.

The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U_{11} + ... + 2\ h\ k\ a^*\ b^*\ U_{12}\ ]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd	19(1)	24(1)	22(1)	0(1)	4(1)	0(1)
F(1)	21(2)	42(2)	33(2)	0(2)	8(2)	1(2)
F(2)	36(2)	40(2)	26(2)	6(2)	8(2)	-1(2)
N(1)	23(3)	20(3)	34(3)	-3(2)	5(2)	-2(2)
C(2)	33(4)	31(4)	36(4)	7(3)	13(3)	0(3)
C(3)	27(4)	27(4)	72(6)	4(4)	13(4)	-10(3)
C(4)	38(4)	23(4)	61(5)	-13(4)	10(4)	-2(3)
C(5)	28(4)	31(4)	41(4)	-9(3)	5(3)	-1(3)
C(6)	17(3)	25(4)	38(4)	-2(3)	1(3)	5(3)
C(7)	18(3)	20(4)	19(3)	-3(3)	-1(3)	3(3)
C(8)	23(3)	24(4)	32(4)	-6(3)	-2(3)	3(3)
C(9)	19(3)	46(5)	32(4)	-14(3)	1(3)	2(3)
C(10)	25(3)	52(5)	28(4)	-3(4)	7(3)	-8(4)
C(11)	19(3)	35(4)	25(4)	1(3)	4(3)	-2(3)
C(12)	14(3)	27(3)	19(3)	-1(3)	-5(2)	6(3)
N(13)	15(2)	21(3)	26(3)	0(2)	2(2)	6(2)
S(14)	24(1)	20(1)	31(1)	-1(1)	0(1)	1(1)
O(15)	28(2)	26(2)	39(3)	-6(2)	4(2)	13(2)
O(16)	30(2)	23(2)	31(2)	10(2)	0(2)	-5(2)
C(17)	16(3)	23(4)	31(4)	0(3)	2(3)	6(3)
C(18)	18(3)	35(4)	27(3)	8(3)	5(3)	8(3)
C(19)	18(3)	39(4)	45(4)	2(3)	6(3)	-3(3)
C(20)	24(4)	43(5)	39(4)	-8(4)	1(3)	-7(3)
C(21)	29(4)	38(4)	34(4)	-11(3)	0(3)	1(3)
C(22)	24(3)	27(4)	31(4)	3(3)	7(3)	8(3)

N(23)	38(4)	53(4)	26(3)	-7(3)	3(3)	-11(3)
O(24)	59(3)	54(4)	44(3)	18(3)	-6(2)	-6(3)
O(25)	64(4)	62(4)	77(4)	-13(3)	48(3)	-10(3)
N(26)	25(3)	29(3)	19(3)	-1(2)	5(2)	0(2)
C(27)	39(4)	30(4)	20(3)	3(3)	7(3)	6(3)
C(28)	44(4)	33(4)	22(3)	-7(3)	0(3)	5(4)
C(29)	63(5)	25(4)	22(4)	1(3)	-5(3)	-3(4)
C(29A)	43(4)	34(4)	22(4)	5(3)	-4(3)	-10(3)
C(30)	43(4)	44(5)	29(4)	0(3)	-11(3)	-20(4)
C(31)	33(4)	55(5)	26(4)	5(4)	3(3)	-19(4)
C(31A)	31(4)	44(5)	20(4)	4(3)	1(3)	-1(3)
C(32)	21(3)	74(5)	21(3)	8(4)	1(3)	2(4)
C(33)	28(4)	62(5)	32(4)	-1(4)	7(3)	17(4)
C(34)	23(3)	37(4)	23(3)	2(3)	1(3)	0(3)
C(35)	18(3)	39(4)	18(3)	-1(3)	4(2)	-2(3)
C(35A)	19(3)	40(4)	7(3)	4(3)	-2(2)	1(3)
C(35B)	26(4)	27(4)	16(3)	2(3)	2(3)	2(3)
N(1S)	70(17)	51(11)	80(20)	13(10)	26(17)	23(12)
C(2S)	66(17)	51(13)	26(16)	-3(11)	11(15)	15(10)
C(3S)	66(5)	48(5)	42(4)	4(4)	4(4)	9(4)
N(1S*)	55(14)	42(12)	69(16)	-2(9)	10(14)	6(11)
C(2S*)	58(14)	44(12)	40(20)	-14(11)	-4(11)	-3(10)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for the difluoro palladium(IV) complex **11**.

	x	y	z	U(eq)
H(2)	5444	3054	865	39
H(3)	6627	4439	1341	50
H(4)	6383	4881	2382	49
H(5)	4911	4021	2918	40
H(8)	2622	3708	2930	33
H(9)	957	2928	3376	39
H(10)	684	1198	3301	41
H(11)	2040	258	2723	32
H(18)	6995	1486	2061	32
H(19)	8505	2684	2537	41
H(20)	8643	3050	3630	43
H(21)	7400	2122	4271	41
H(27)	5051	-392	585	36
H(28)	4247	-1934	170	40
H(29)	2017	-2376	190	45
H(30)	-402	-1805	418	49
H(31)	-1687	-583	764	46
H(32)	-1896	1248	1139	47
H(33)	-861	2779	1368	48
H(34)	1479	2987	1394	33
H(3SA)	2038	4302	189	78
H(3SB)	2030	4792	882	78
H(3SC)	3201	4026	776	78
H(3SD)	2798	4616	1047	78
H(3SE)	2951	3919	445	78
H(3SF)	1627	4593	433	78

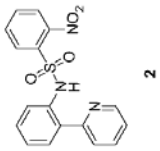
Table 6. Torsion angles [°] for the difluoro palladium(IV) complex **11**.

F(2)-Pd-N(1)-C(6)	149.0(4)	C(10)-C(11)-C(12)-N(13)	-175.5(5)
C(35)-Pd-N(1)-C(6)	60.8(5)	C(8)-C(7)-C(12)-C(11)	-0.1(7)
N(13)-Pd-N(1)-C(6)	-24.5(4)	C(6)-C(7)-C(12)-C(11)	-177.0(5)
F(1)-Pd-N(1)-C(6)	-122.9(4)	C(8)-C(7)-C(12)-N(13)	176.0(4)
F(2)-Pd-N(1)-C(2)	-42.1(4)	C(6)-C(7)-C(12)-N(13)	-0.9(8)
C(35)-Pd-N(1)-C(2)	-130.3(4)	C(11)-C(12)-N(13)-S(14)	-78.2(5)
N(13)-Pd-N(1)-C(2)	144.4(4)	C(7)-C(12)-N(13)-S(14)	105.6(5)
F(1)-Pd-N(1)-C(2)	46.0(4)	C(11)-C(12)-N(13)-Pd	126.1(4)
C(6)-N(1)-C(2)-C(3)	0.8(8)	C(7)-C(12)-N(13)-Pd	-50.0(5)
Pd-N(1)-C(2)-C(3)	-168.6(4)	C(35)-Pd-N(13)-C(12)	-46.7(4)
N(1)-C(2)-C(3)-C(4)	1.1(9)	N(26)-Pd-N(13)-C(12)	-129.5(4)
C(2)-C(3)-C(4)-C(5)	-1.8(10)	N(1)-Pd-N(13)-C(12)	54.0(4)
C(3)-C(4)-C(5)-C(6)	0.7(9)	F(1)-Pd-N(13)-C(12)	139.1(3)
C(2)-N(1)-C(6)-C(5)	-2.0(8)	C(35)-Pd-N(13)-S(14)	160.8(3)
Pd-N(1)-C(6)-C(5)	166.2(4)	N(26)-Pd-N(13)-S(14)	78.0(3)
C(2)-N(1)-C(6)-C(7)	177.8(5)	N(1)-Pd-N(13)-S(14)	-98.5(3)
Pd-N(1)-C(6)-C(7)	-14.0(7)	F(1)-Pd-N(13)-S(14)	-13.4(3)
C(4)-C(5)-C(6)-N(1)	1.2(9)	C(12)-N(13)-S(14)-O(15)	179.1(4)
C(4)-C(5)-C(6)-C(7)	-178.5(5)	Pd-N(13)-S(14)-O(15)	-28.8(4)
N(1)-C(6)-C(7)-C(12)	36.8(8)	C(12)-N(13)-S(14)-O(16)	48.5(5)
C(5)-C(6)-C(7)-C(12)	-143.4(6)	Pd-N(13)-S(14)-O(16)	-159.5(3)
N(1)-C(6)-C(7)-C(8)	-140.1(5)	C(12)-N(13)-S(14)-C(17)	-65.1(4)
C(5)-C(6)-C(7)-C(8)	39.6(8)	Pd-N(13)-S(14)-C(17)	86.9(3)
C(12)-C(7)-C(8)-C(9)	-1.3(8)	O(15)-S(14)-C(17)-C(22)	-139.7(5)
C(6)-C(7)-C(8)-C(9)	175.8(5)	O(16)-S(14)-C(17)-C(22)	-11.0(5)
C(7)-C(8)-C(9)-C(10)	2.2(9)	N(13)-S(14)-C(17)-C(22)	103.9(5)
C(8)-C(9)-C(10)-C(11)	-1.6(9)	O(15)-S(14)-C(17)-C(18)	44.1(5)
C(9)-C(10)-C(11)-C(12)	0.1(8)	O(16)-S(14)-C(17)-C(18)	172.7(4)
C(10)-C(11)-C(12)-C(7)	0.7(8)	N(13)-S(14)-C(17)-C(18)	-72.3(5)

C(22)-C(17)-C(18)-C(19)	0.3(8)	C(29)-C(29A)-C(30)-C(31)	-177.1(6)
S(14)-C(17)-C(18)-C(19)	176.8(4)	C(29A)-C(30)-C(31)-C(31A)	1.2(9)
C(17)-C(18)-C(19)-C(20)	-1.7(9)	C(30)-C(31)-C(31A)-C(35A)	-2.3(9)
C(18)-C(19)-C(20)-C(21)	2.6(9)	C(30)-C(31)-C(31A)-C(32)	173.5(6)
C(19)-C(20)-C(21)-C(22)	-2.0(9)	C(35A)-C(31A)-C(32)-C(33)	1.6(8)
C(18)-C(17)-C(22)-C(21)	0.2(8)	C(31)-C(31A)-C(32)-C(33)	-174.3(6)
S(14)-C(17)-C(22)-C(21)	-176.0(4)	C(31A)-C(32)-C(33)-C(34)	-2.1(9)
C(18)-C(17)-C(22)-N(23)	-179.3(5)	C(32)-C(33)-C(34)-C(35)	-0.3(9)
S(14)-C(17)-C(22)-N(23)	4.5(8)	C(33)-C(34)-C(35)-C(35A)	3.2(8)
C(20)-C(21)-C(22)-C(17)	0.6(9)	C(33)-C(34)-C(35)-Pd	-177.1(4)
C(20)-C(21)-C(22)-N(23)	-179.9(5)	F(2)-Pd-C(35)-C(34)	-81.6(5)
C(17)-C(22)-N(23)-O(25)	-100.3(7)	N(26)-Pd-C(35)-C(34)	-172.3(5)
C(21)-C(22)-N(23)-O(25)	80.1(7)	N(13)-Pd-C(35)-C(34)	97.3(5)
C(17)-C(22)-N(23)-O(24)	81.9(7)	N(1)-Pd-C(35)-C(34)	10.3(5)
C(21)-C(22)-N(23)-O(24)	-97.7(6)	F(2)-Pd-C(35)-C(35A)	98.2(4)
F(2)-Pd-N(26)-C(27)	85.0(4)	N(26)-Pd-C(35)-C(35A)	7.4(4)
C(35)-Pd-N(26)-C(27)	172.8(5)	N(13)-Pd-C(35)-C(35A)	-83.0(4)
N(13)-Pd-N(26)-C(27)	-101.5(5)	N(1)-Pd-C(35)-C(35A)	-170.0(4)
F(1)-Pd-N(26)-C(27)	-3.2(5)	C(32)-C(31A)-C(35A)-C(35)	1.4(8)
F(2)-Pd-N(26)-C(35B)	-94.7(4)	C(31)-C(31A)-C(35A)-C(35)	177.6(5)
C(35)-Pd-N(26)-C(35B)	-7.0(4)	C(32)-C(31A)-C(35A)-C(35B)	-175.1(5)
N(13)-Pd-N(26)-C(35B)	78.7(4)	C(31)-C(31A)-C(35A)-C(35B)	1.0(8)
F(1)-Pd-N(26)-C(35B)	177.0(4)	C(34)-C(35)-C(35A)-C(31A)	-3.8(8)
C(35B)-N(26)-C(27)-C(28)	-1.3(8)	Pd-C(35)-C(35A)-C(31A)	176.4(4)
Pd-N(26)-C(27)-C(28)	179.0(4)	C(34)-C(35)-C(35A)-C(35B)	172.8(5)
N(26)-C(27)-C(28)-C(29)	-1.0(9)	Pd-C(35)-C(35A)-C(35B)	-7.0(6)
C(27)-C(28)-C(29)-C(29A)	2.6(9)	C(27)-N(26)-C(35B)-C(29A)	2.1(8)
C(28)-C(29)-C(29A)-C(35B)	-1.8(8)	Pd-N(26)-C(35B)-C(29A)	-178.1(4)
C(28)-C(29)-C(29A)-C(30)	176.4(6)	C(27)-N(26)-C(35B)-C(35A)	-174.7(5)
C(35B)-C(29A)-C(30)-C(31)	1.2(9)	Pd-N(26)-C(35B)-C(35A)	5.1(6)

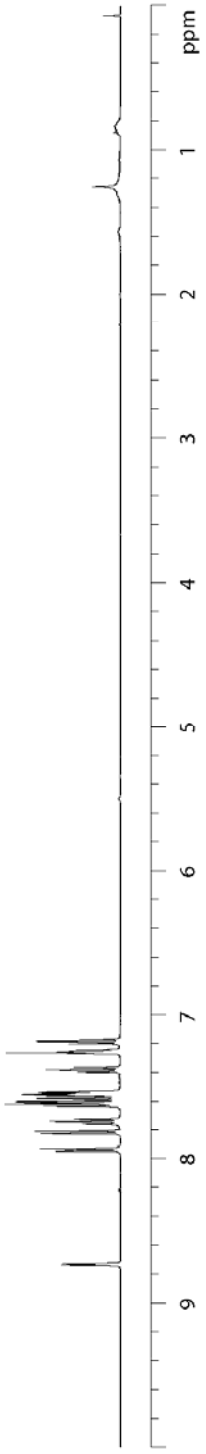
C(29)-C(29A)-C(35B)-N(26)	-0.5(8)
C(30)-C(29A)-C(35B)-N(26)	-178.9(5)
C(29)-C(29A)-C(35B)-C(35A)	176.0(5)
C(30)-C(29A)-C(35B)-C(35A)	-2.4(8)
C(31A)-C(35A)-C(35B)-N(26)	178.0(5)
C(35)-C(35A)-C(35B)-N(26)	1.3(7)
C(31A)-C(35A)-C(35B)-C(29A)	1.3(8)
C(35)-C(35A)-C(35B)-C(29A)	-175.3(5)

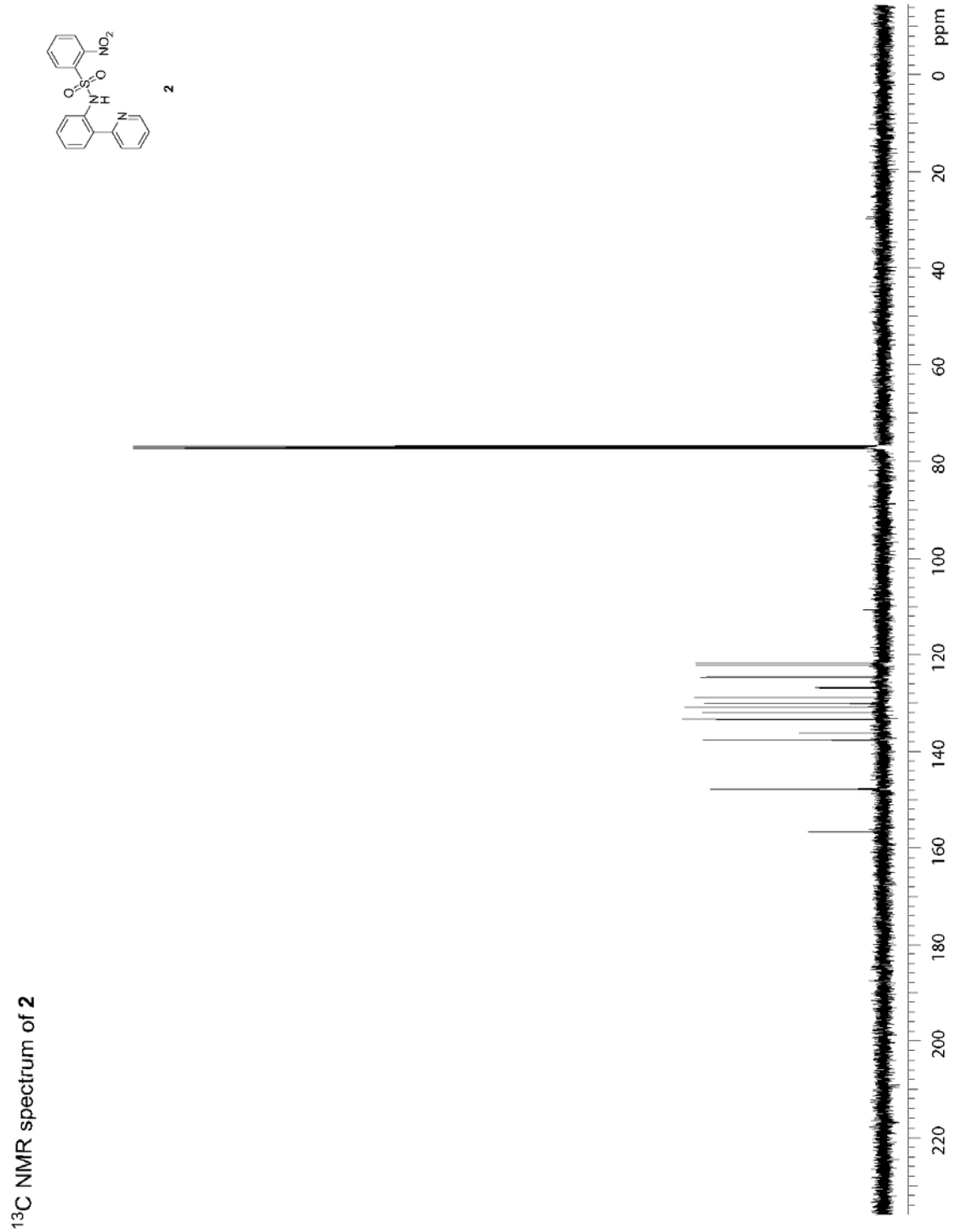
Spectroscopic Data



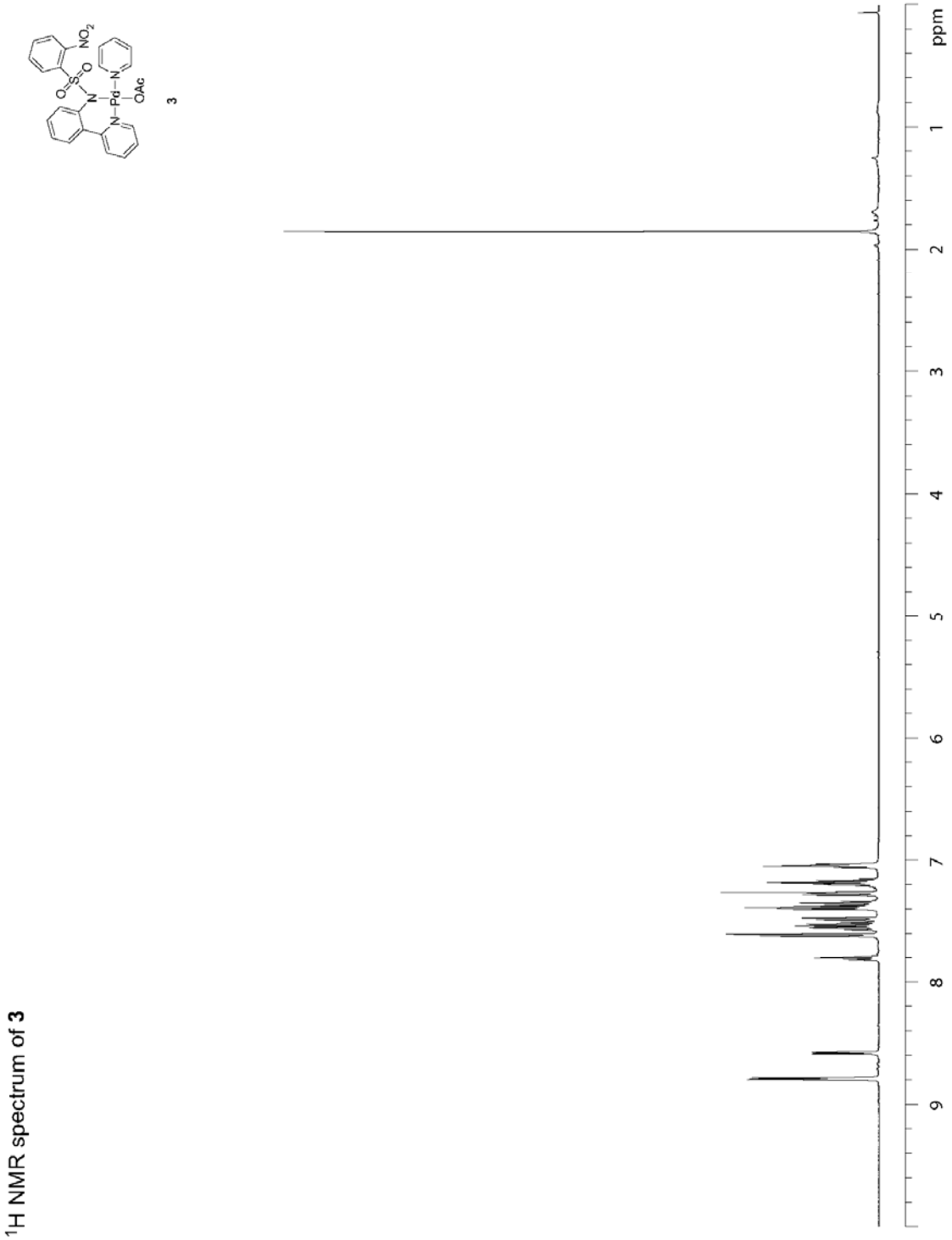
2

^{1}H NMR spectrum of **2**

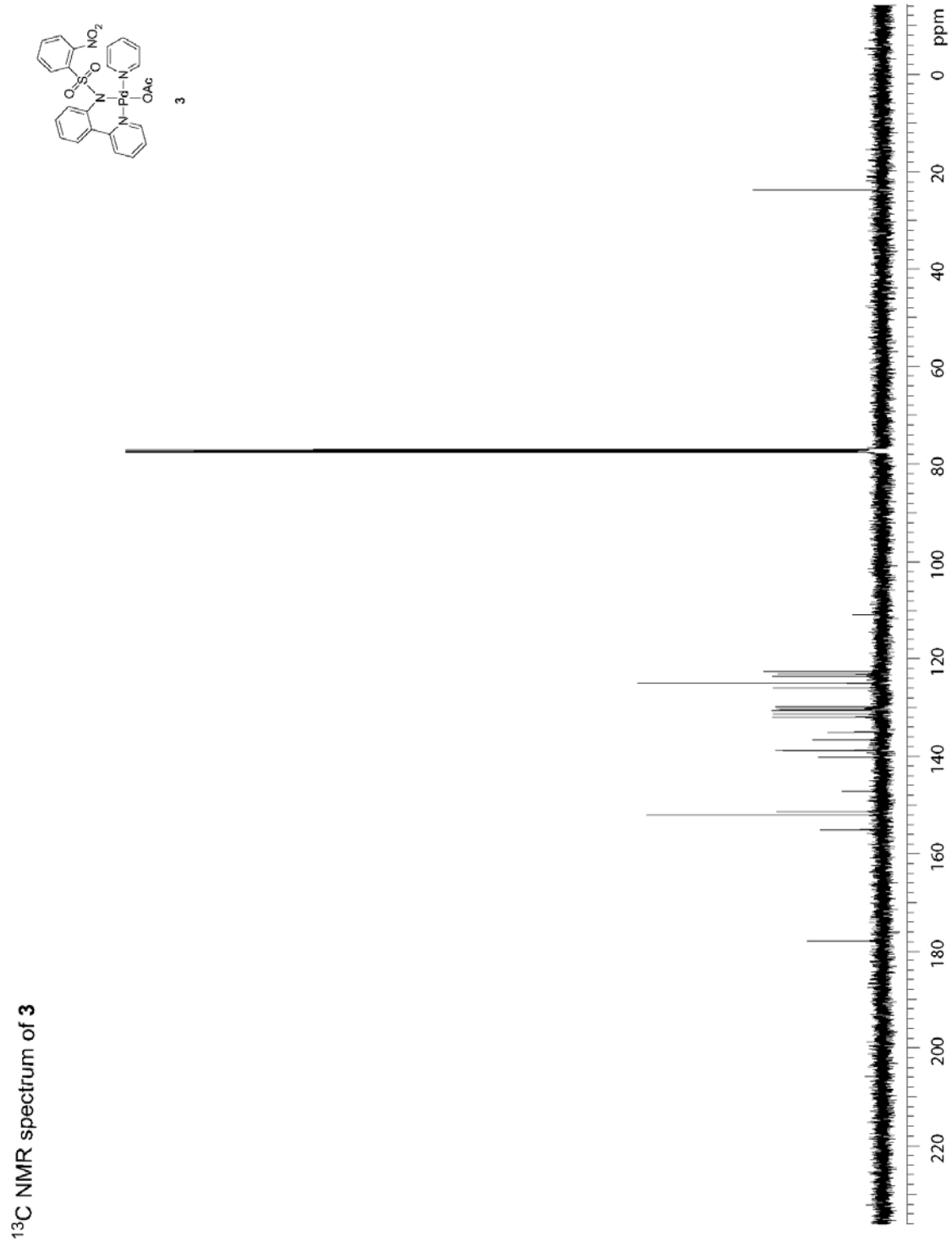




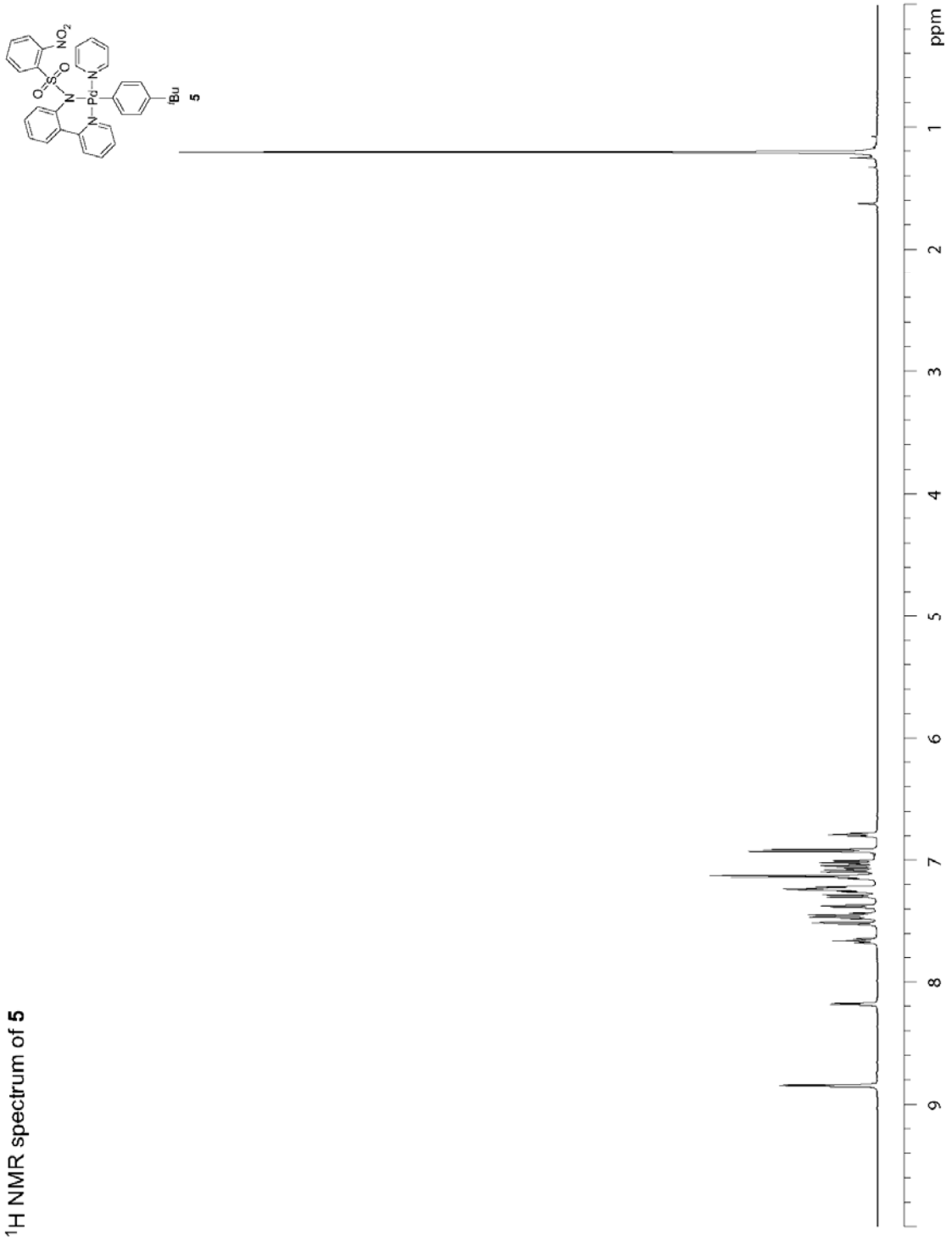
^{13}C NMR spectrum of **2**



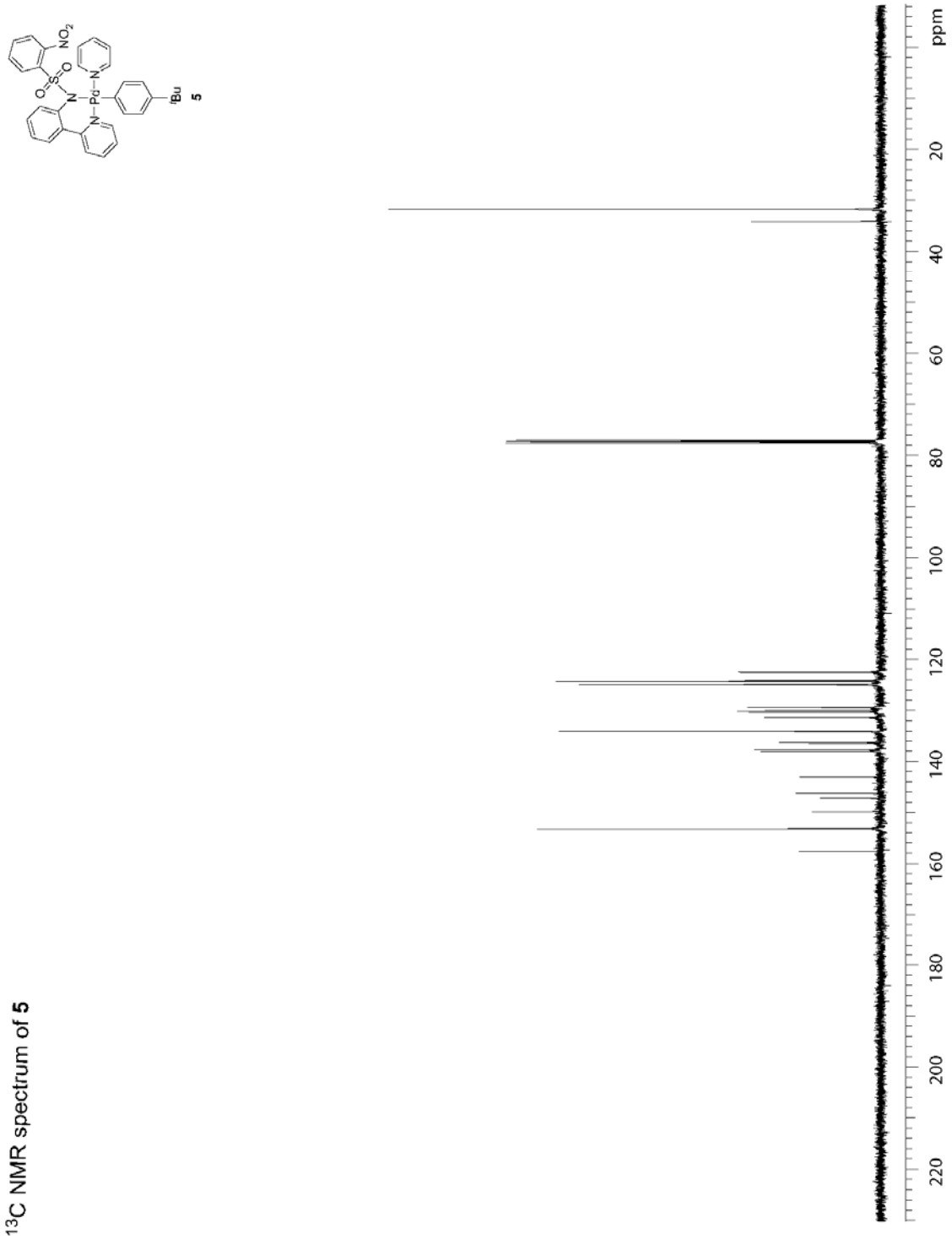
^{1}H NMR spectrum of **3**



^{13}C NMR spectrum of **3**

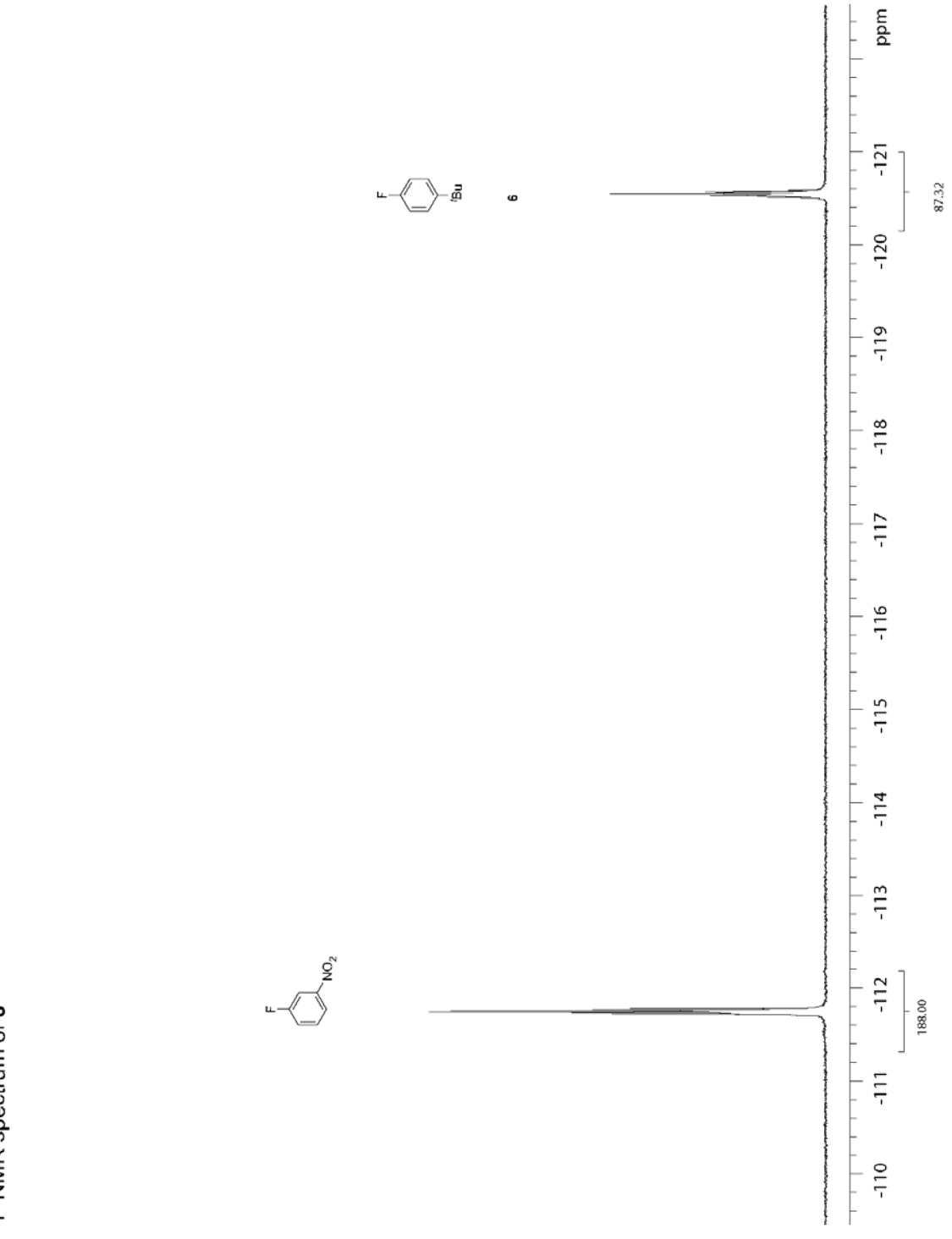


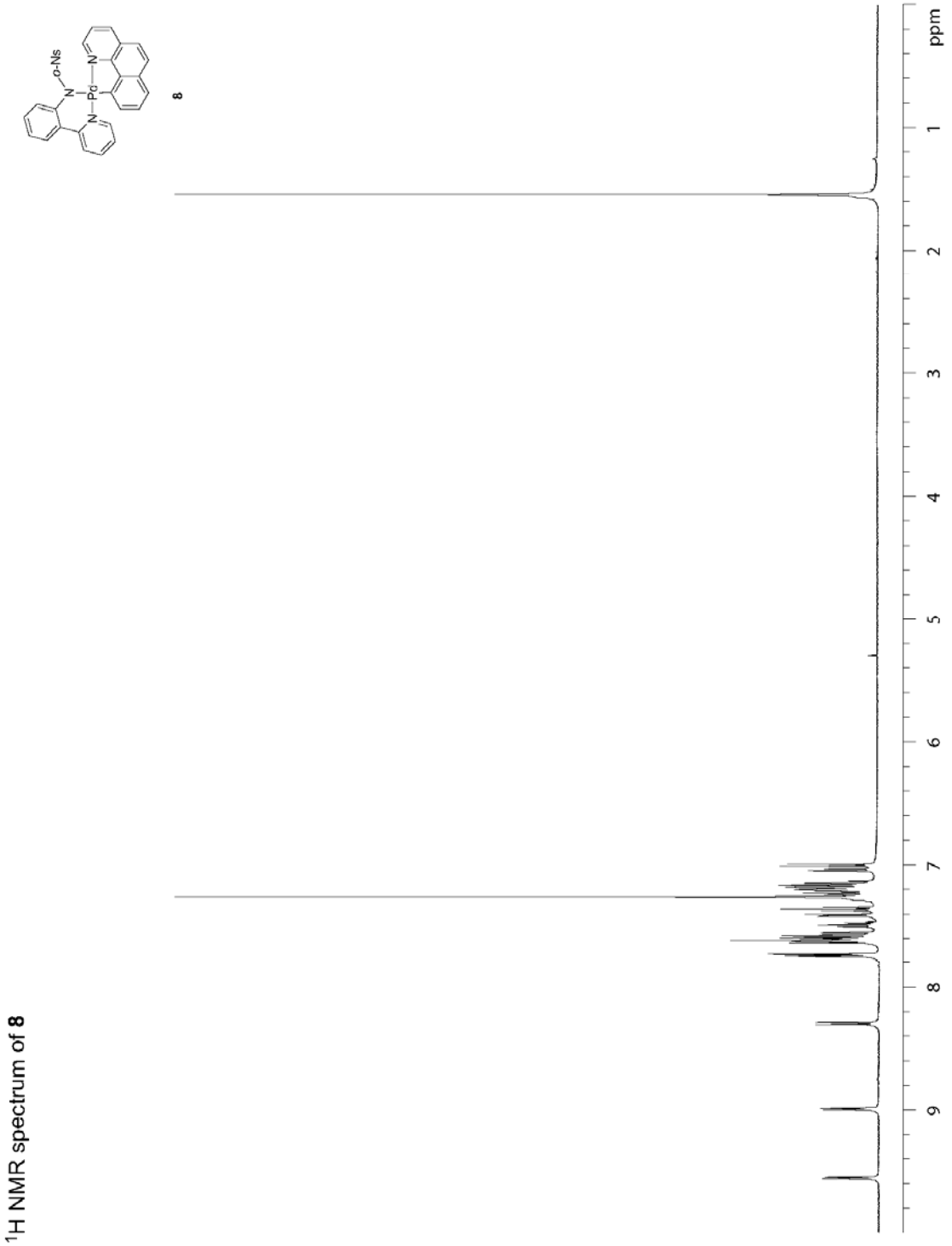
^{1}H NMR spectrum of **5**



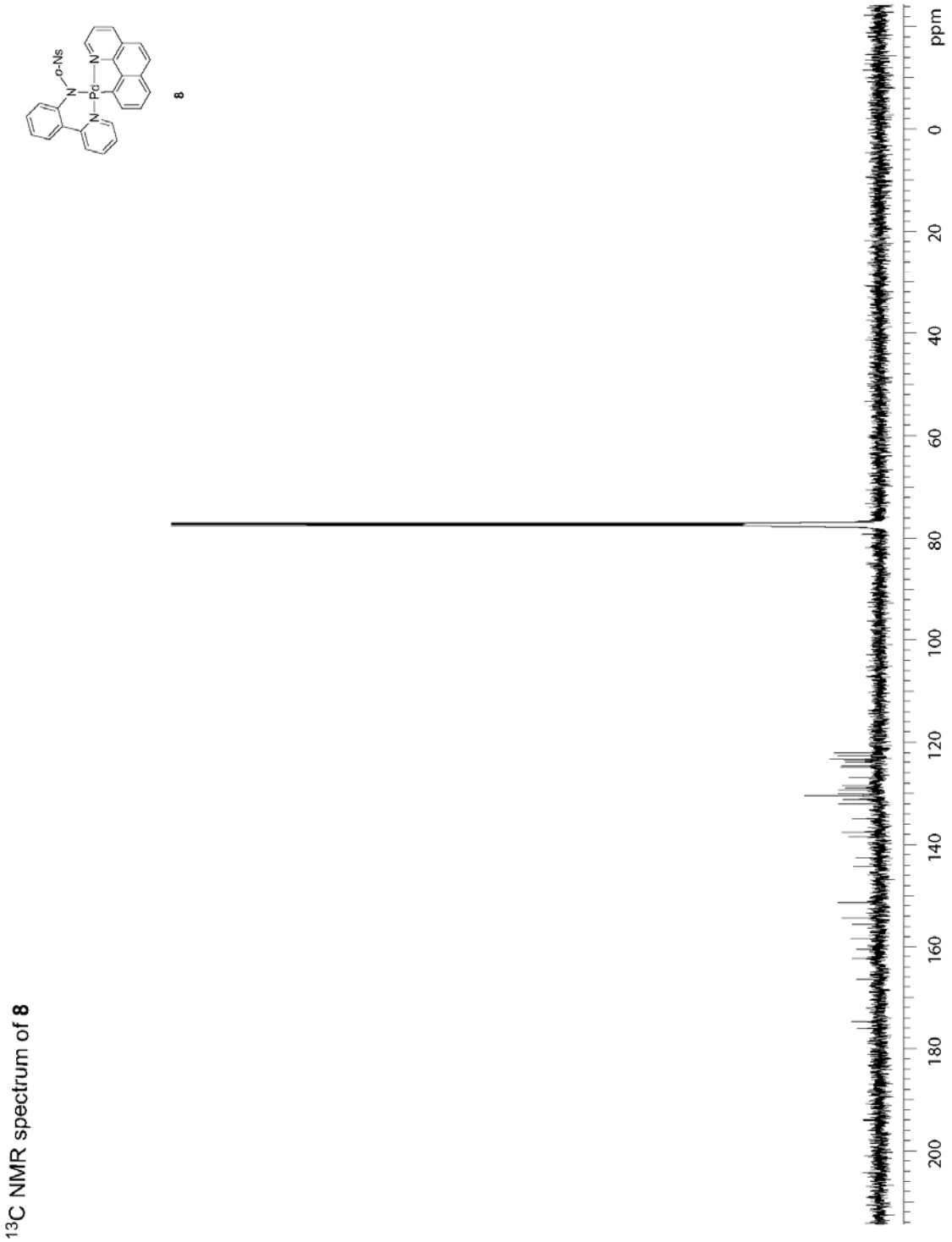
^{13}C NMR spectrum of **5**

^{19}F NMR spectrum of **6**

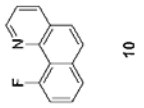




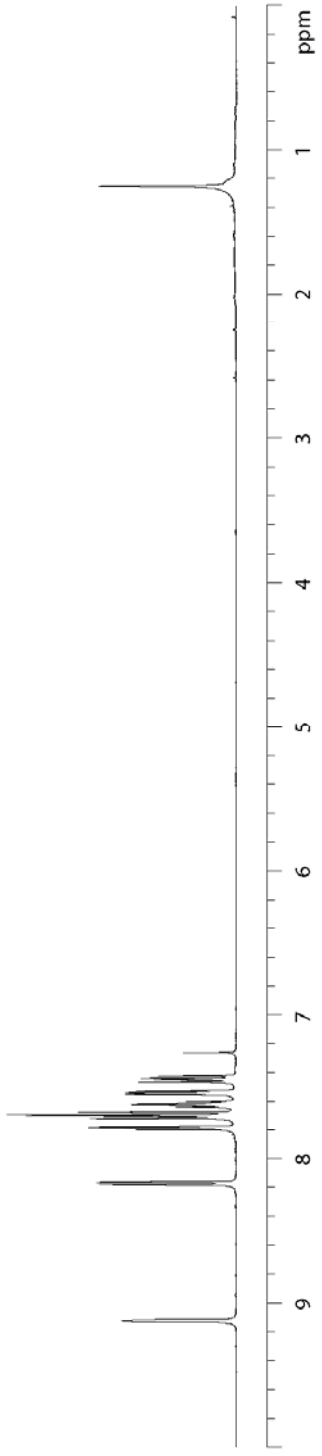
^{1}H NMR spectrum of **8**



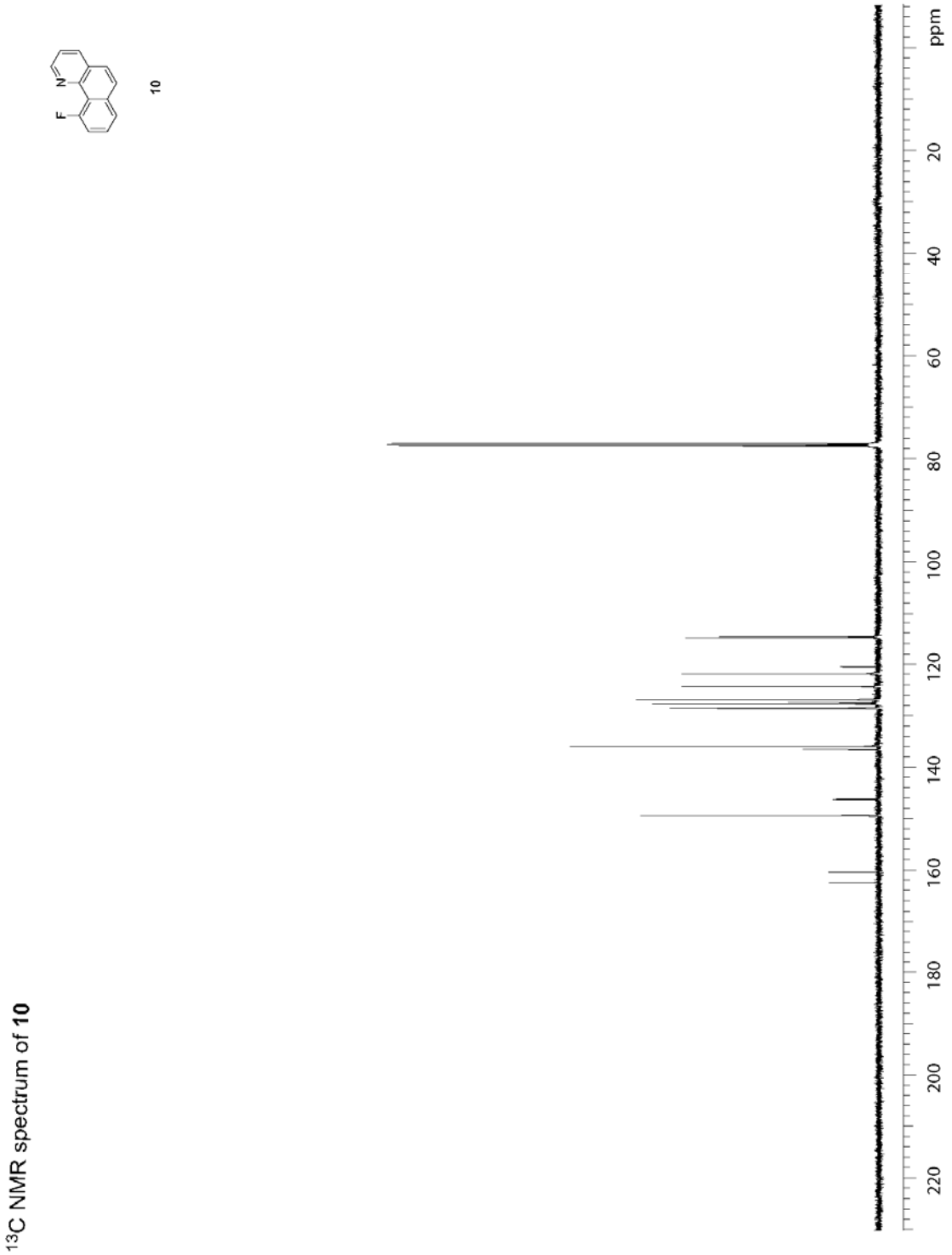
^{13}C NMR spectrum of **8**



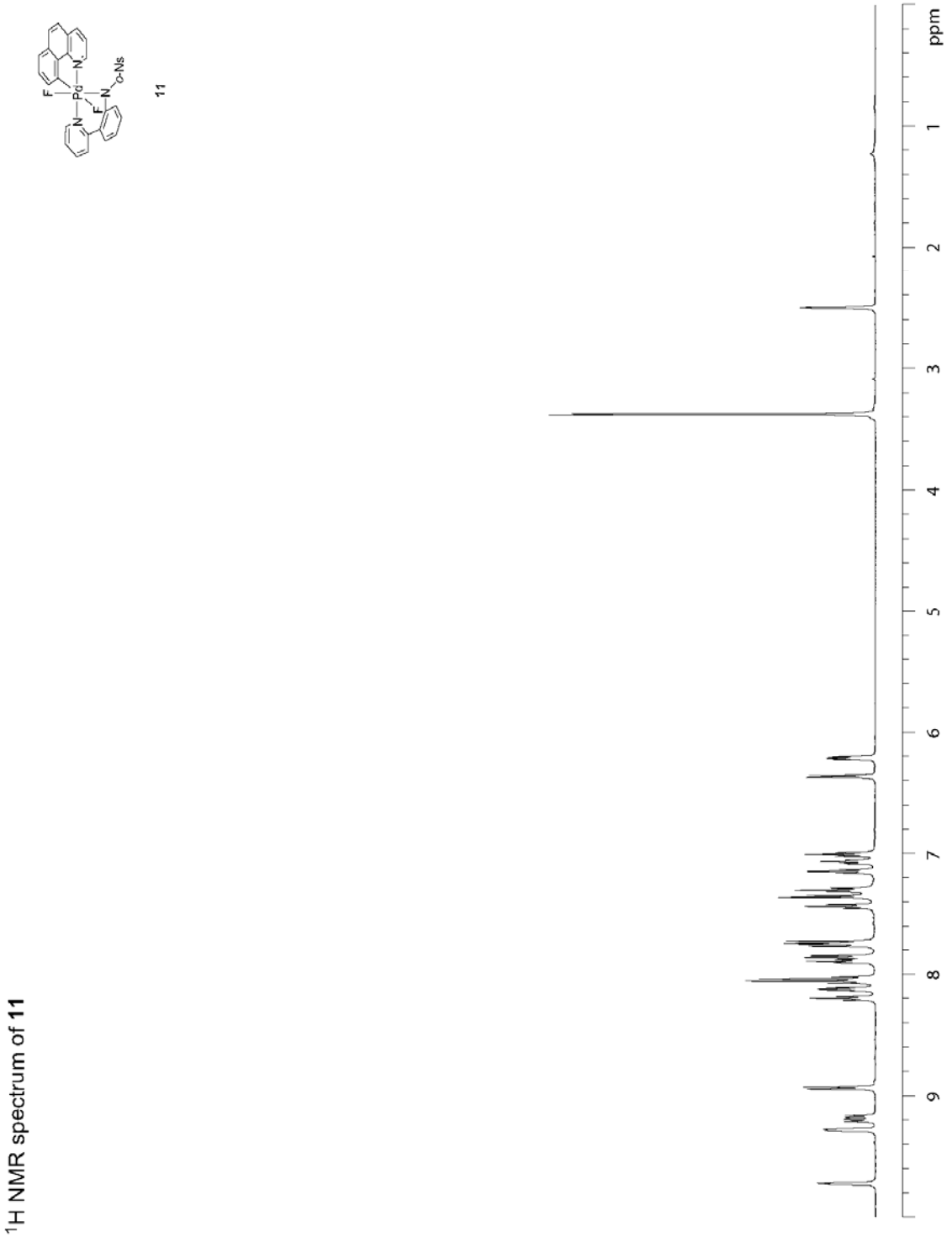
10



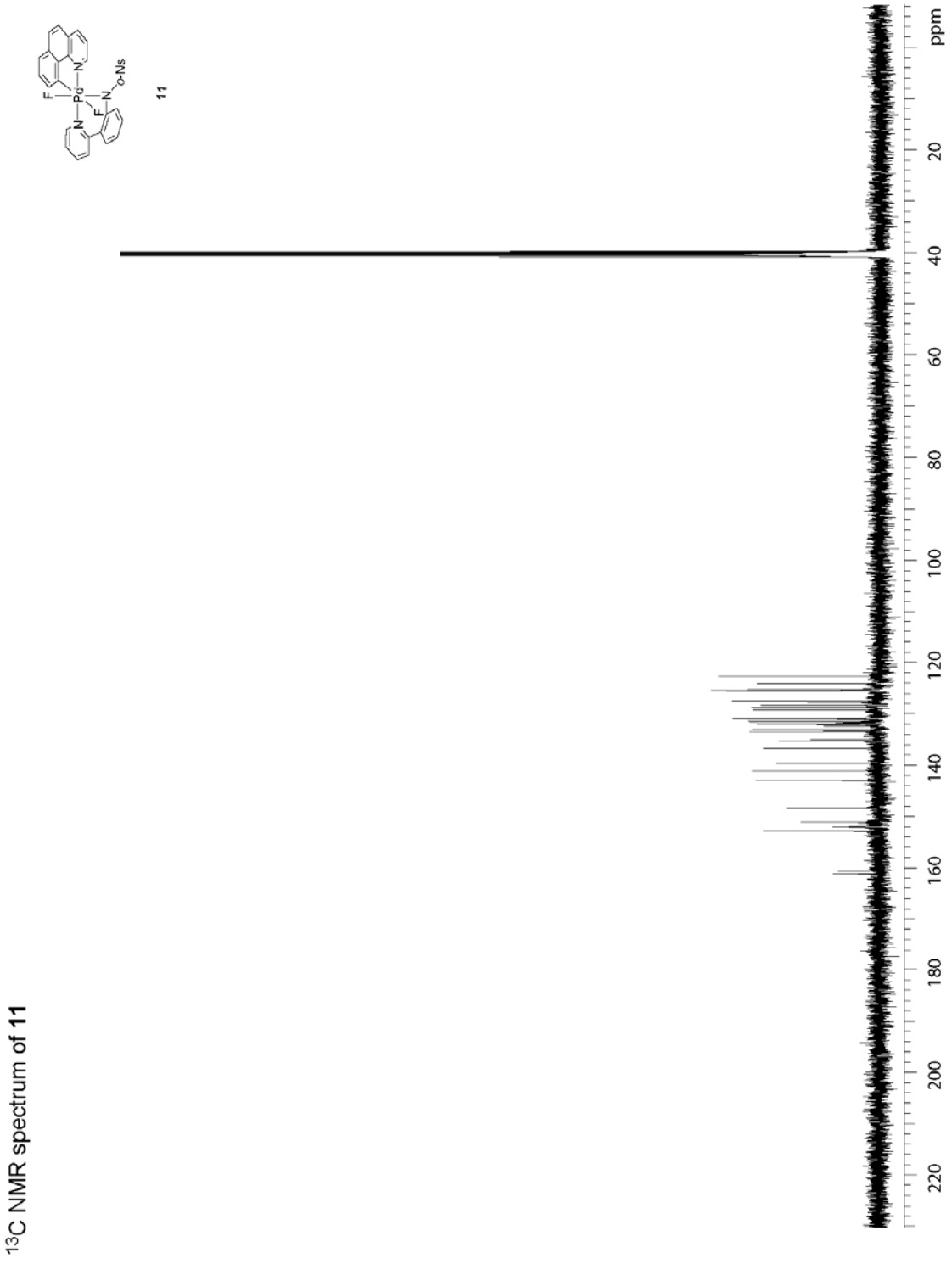
^{1}H NMR spectrum of **10**



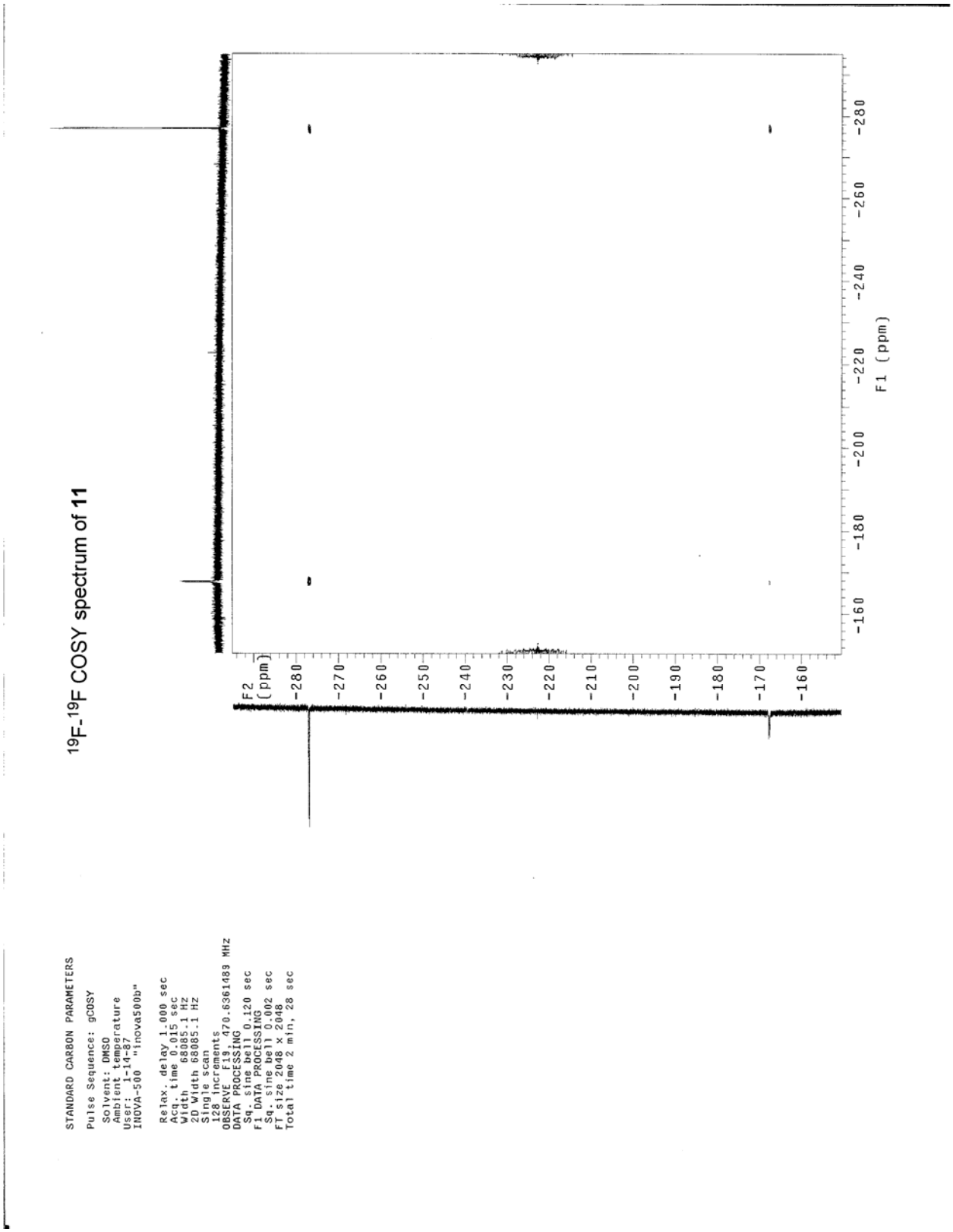
^{13}C NMR spectrum of **10**

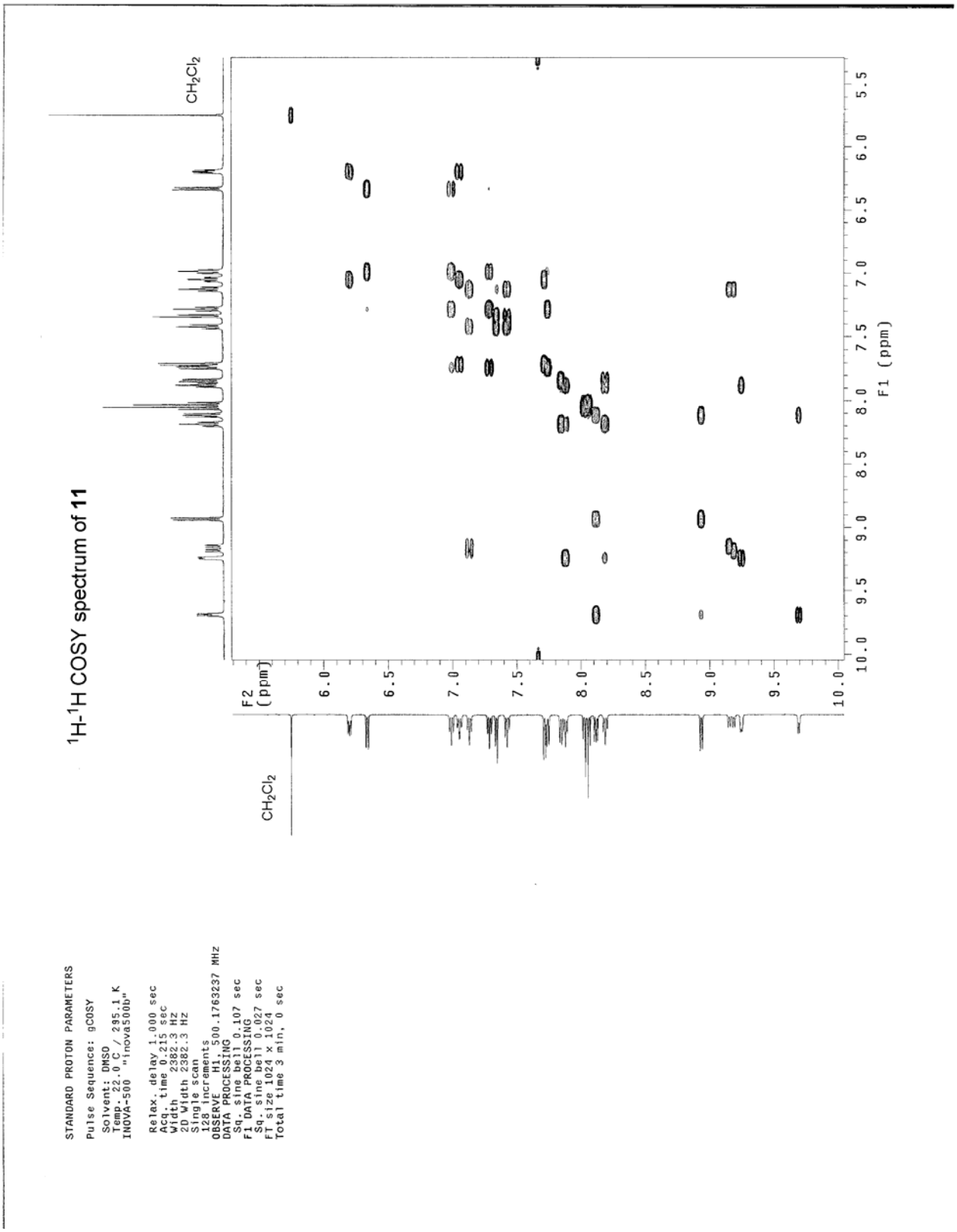


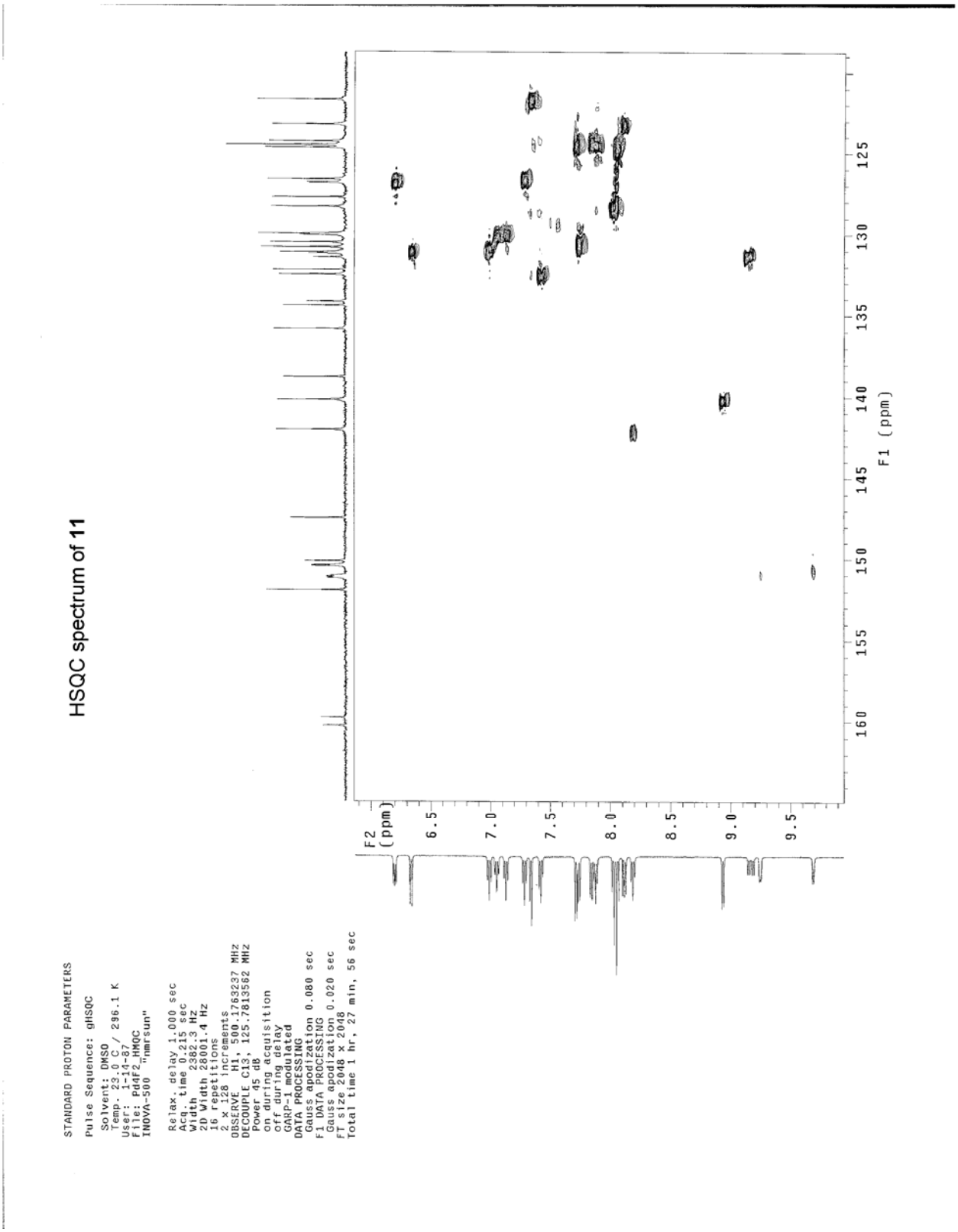
^{1}H NMR spectrum of **11**

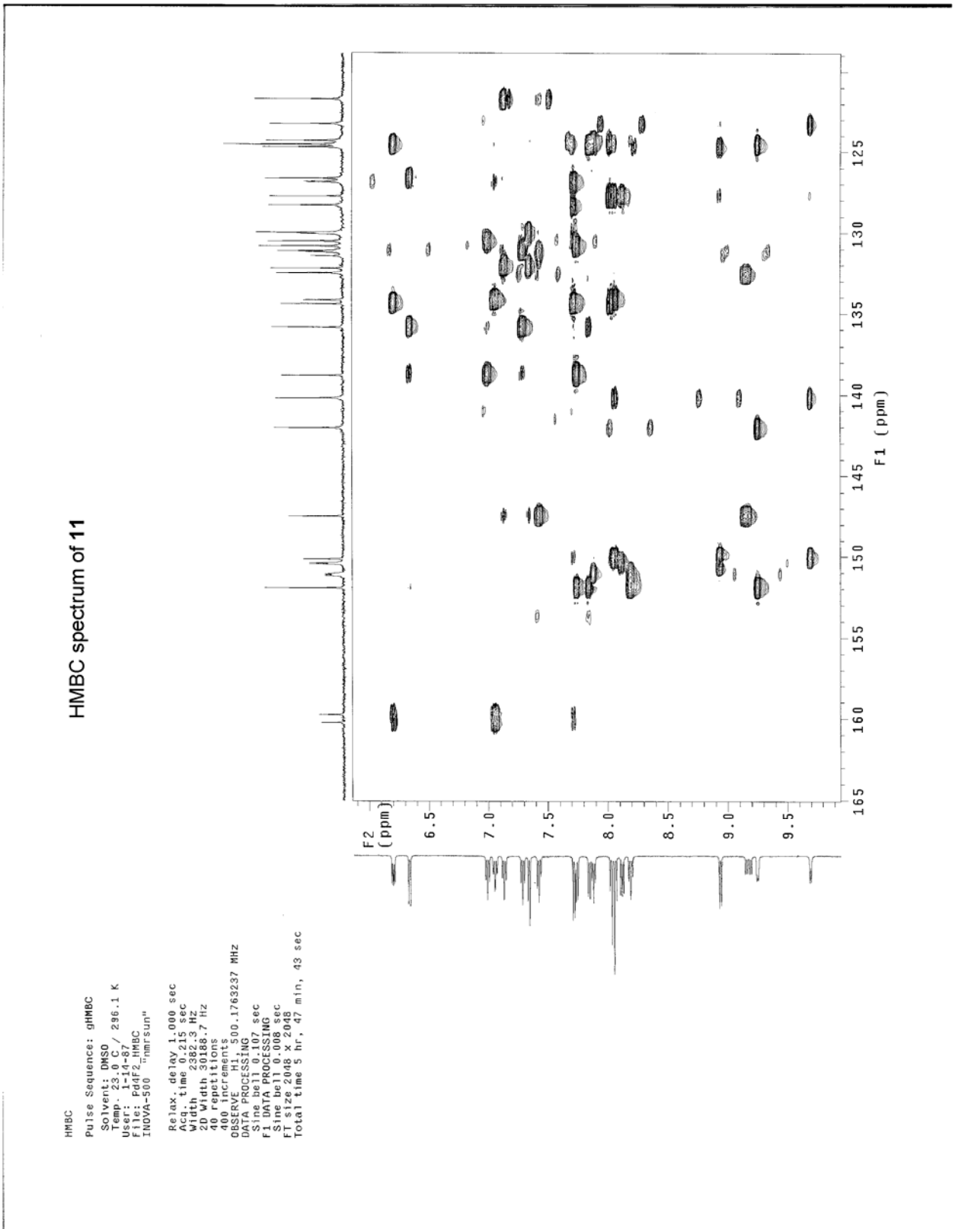


^{13}C NMR spectrum of **11**

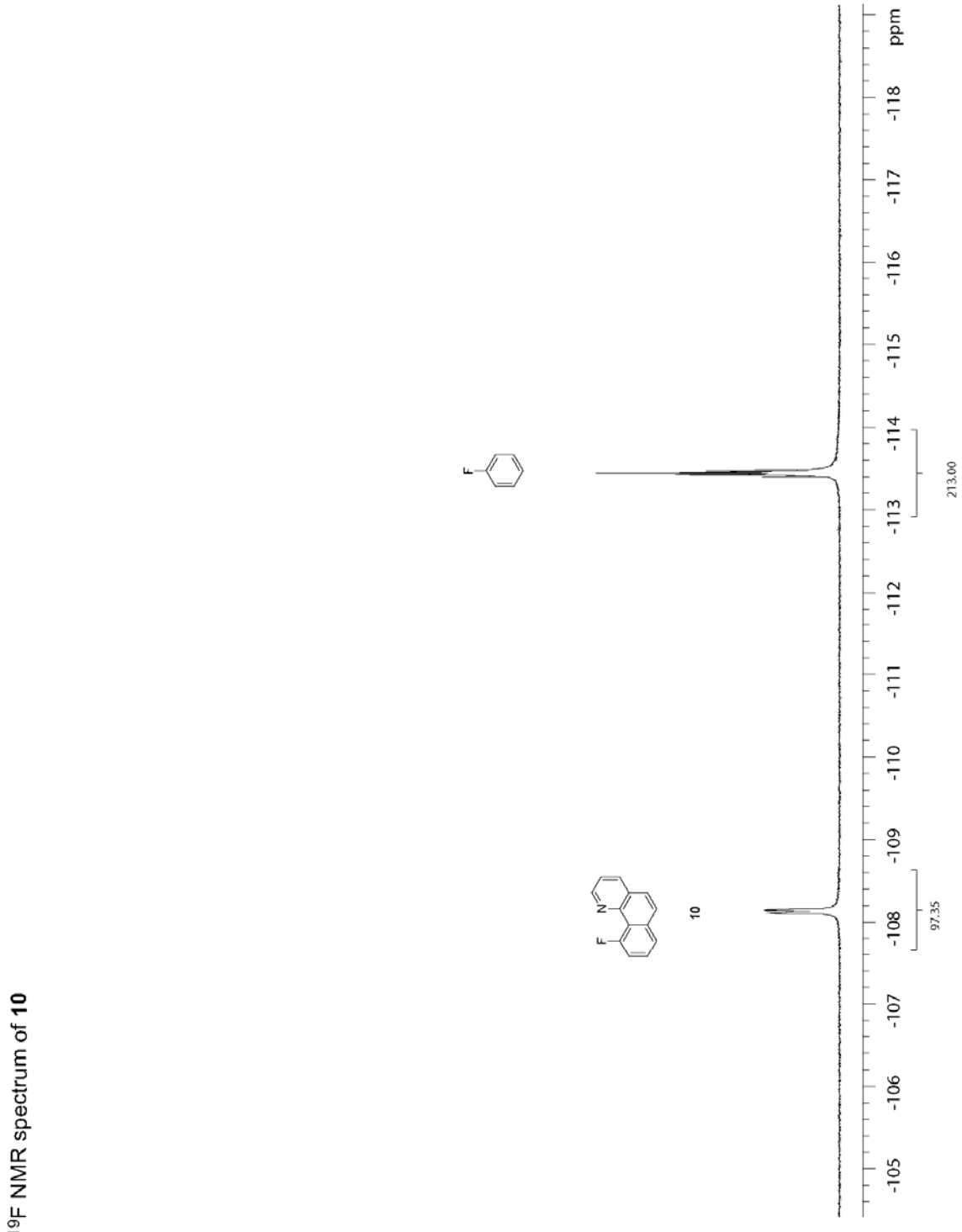

^{19}F-^{19}F COSY spectrum of **11**
F2 (ppm)
-280
-270
-260
-250
-240
-230
-220
-210
-200
-190
-180
-170
-160
-160
-180
-200
-220
-240
-260
-280
F1 (ppm)
STANDARD CARBON PARAMETERS
Pulse Sequence: gCOSY
Solvent: DMSO
Ambient temperature
User: 1-14-87
INOVA-500 "inova500b"
Relax. delay 1.000 sec
Acq. time 0.015 sec
Width 68085.1 Hz
2D Width 68085.1 Hz
Single scan
128 increments
OBSERVE F19, 470.6361489 MHz
DATA PROCESSING
Sq. sine bell 0.120 sec
F1 DATA PROCESSING
Sq. sine bell 0.002 sec
FT size 2048 x 2048
Total time 2 min, 28 sec

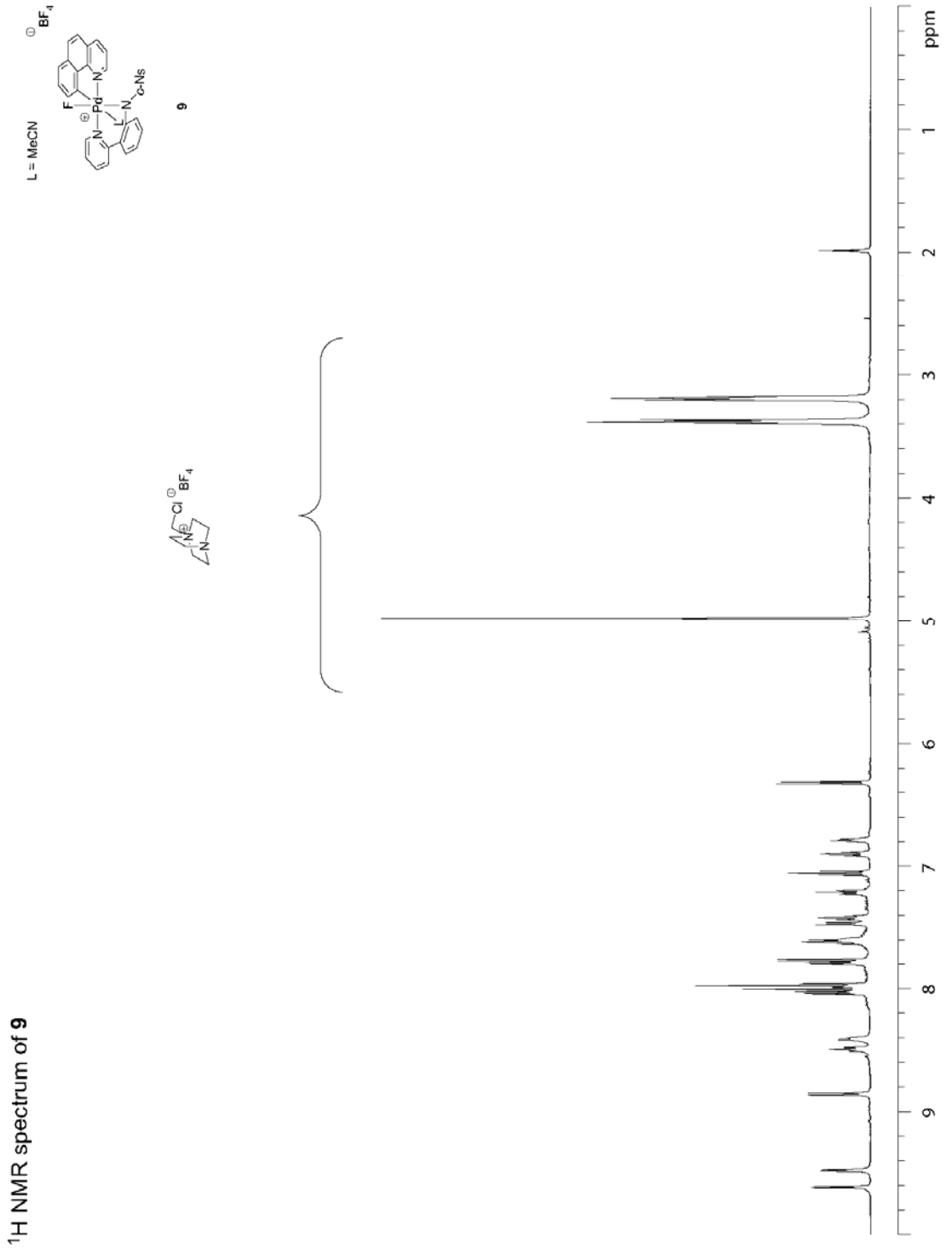

^{1}H-^{1}H COSY spectrum of **11**
CH_2Cl_2
CH_2Cl_2
F2 (ppm)
F1 (ppm)
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
STANDARD PROTON PARAMETERS
Pulse Sequence: gCOSY
Solvent: DMSO
Temp. 22.0 C / 295.1 K
INOVA-500 "inova500b"
Relax. delay 1.000 sec
Acq. time 0.215 sec
Width 2382.3 Hz
2D Width 2382.3 Hz
Single scan
128 increments
OBSERVE H1, 500.1763237 MHz
DATA PROCESSING
Sq. sine bell 0.107 sec
F1 DATA PROCESSING
Sq. sine bell 0.027 sec
FT size 1024 x 1024
Total time 3 min, 0 sec


HSQC spectrum of 11
STANDARD PROTON PARAMETERS
Pulse Sequence: gHSQC
Solvent: DMSO
Temp. 23.0 C / 296.1 K
User: 1-14-87
File: Pd4F2_HMQC
INOVA-500 "nmrsun"
Relax. delay 1.000 sec
Acq. time 0.215 sec
Width 2382.3 Hz
2D Width 28001.4 Hz
16 repetitions
2 x 128 increments
OBSERVE H1, 500.1763237 MHz
DECOUPLE C13, 125.7813562 MHz
Power 45 dB
on during acquisition
off during delay
GARP-1 modulated
DATA PROCESSING
Gauss apodization 0.080 sec
F1 DATA PROCESSING
Gauss apodization 0.020 sec
FT size 2048 x 2048
Total time 1 hr, 27 min, 56 sec
F2 (ppm)
6.5
7.0
7.5
8.0
8.5
9.0
9.5
160
155
150
145
140
135
130
125
F1 (ppm)


HMBC spectrum of 11
HMBC
Pulse Sequence: gHMBC
Solvent: DMSO
Temp. 23.0 C / 296.1 K
User: 1-14-87
File: Pd4F2_HMBC
INOVA-500 "nmrsun"
Relax. delay 1.000 sec
Acq. time 0.215 sec
Width 2382.3 Hz
2D Width 30188.7 Hz
40 repetitions
400 increments
OBSERVE H1, 500.1763237 MHz
DATA PROCESSING
Sine bell 0.107 sec
F1 DATA PROCESSING
Sine bell 0.008 sec
FT size 2048 x 2048
Total time 5 hr, 47 min, 43 sec
F2 (ppm)
6.5
7.0
7.5
8.0
8.5
9.0
9.5
165
160
155
150
145
140
135
130
125
F1 (ppm)

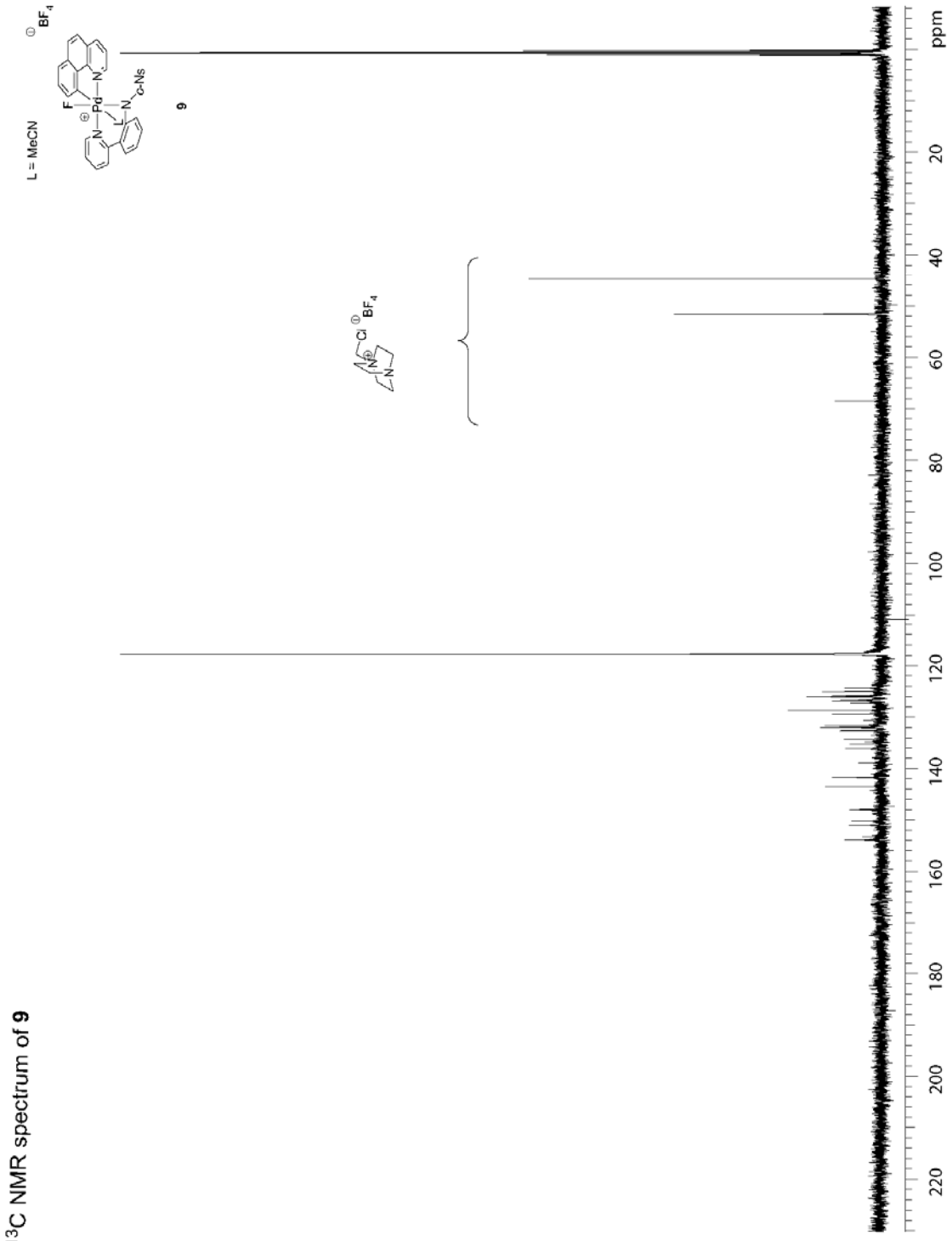
^{19}F NMR spectrum of **10**



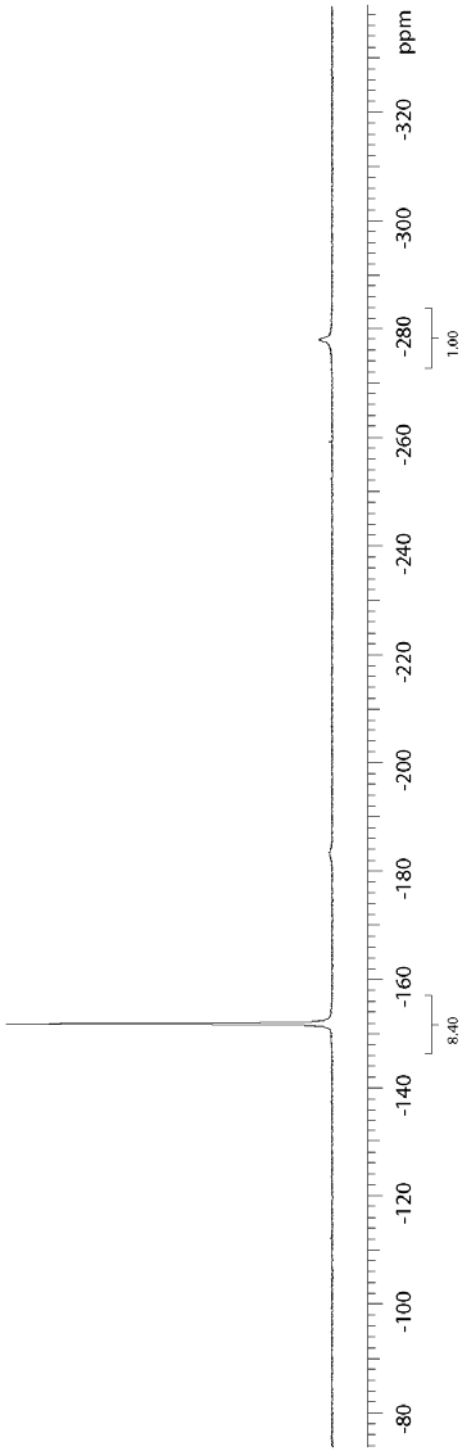


^{1}H NMR spectrum of **9**

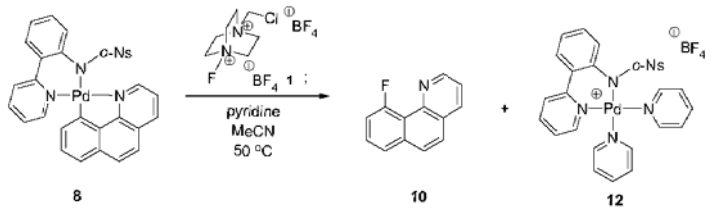
^{13}C NMR spectrum of **9**

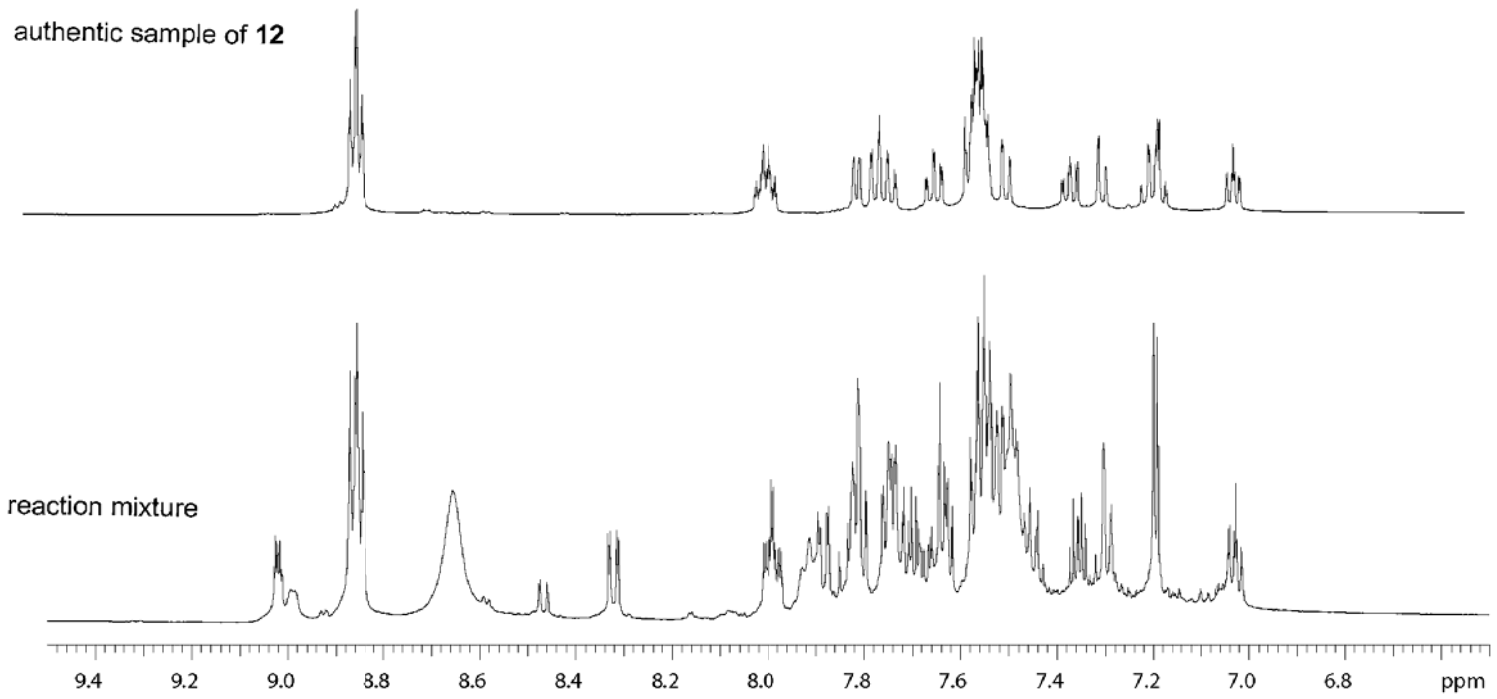


^{19}F NMR spectrum of **9**

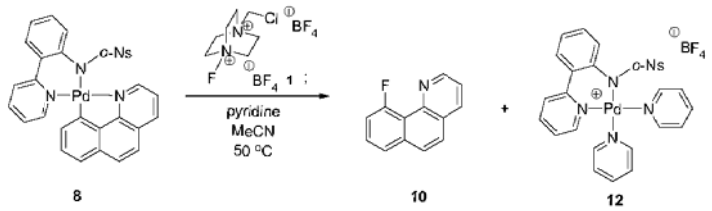


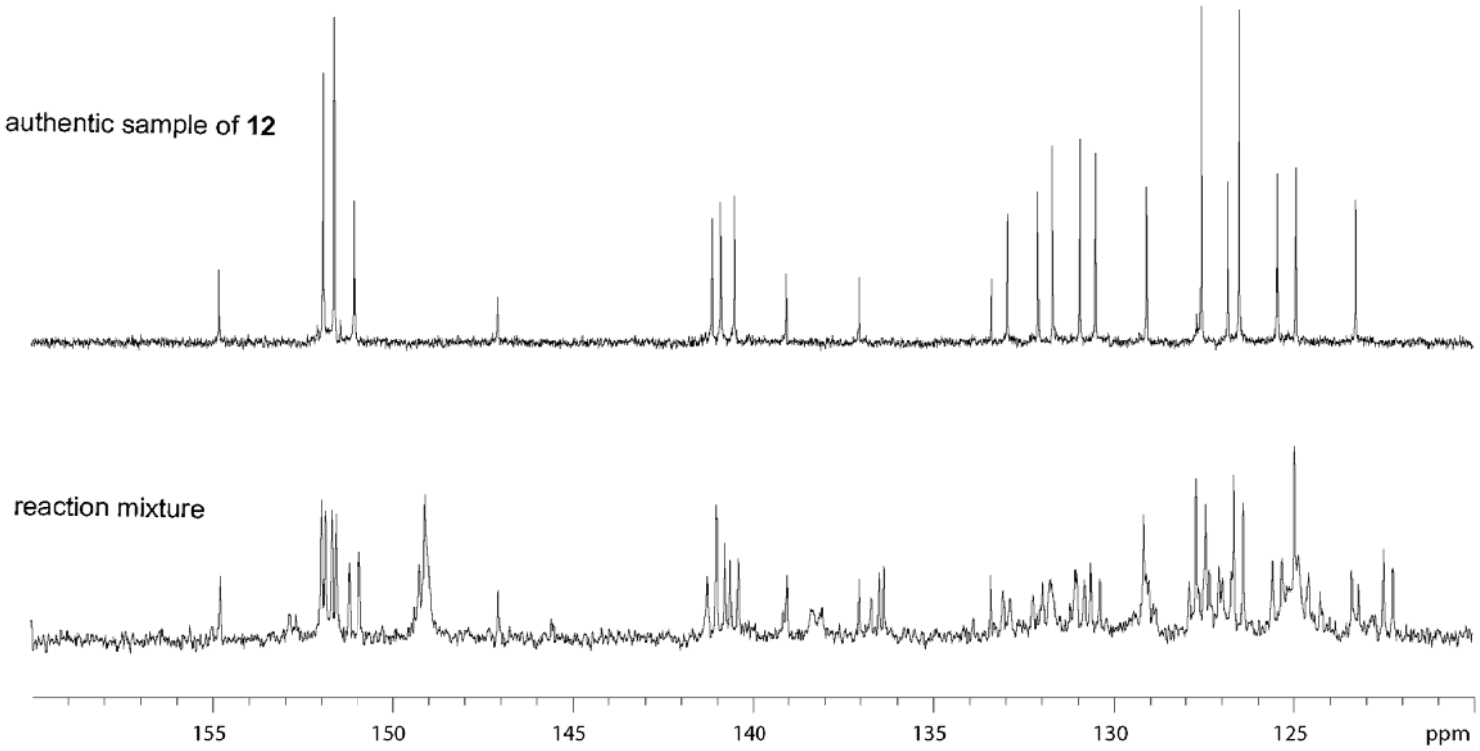
^{1}H NMR spectrum of reaction from **8** to **10** & **12**

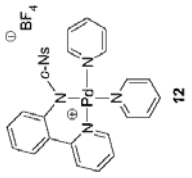




^{13}C NMR spectrum of reaction from **8** to **10** & **12**

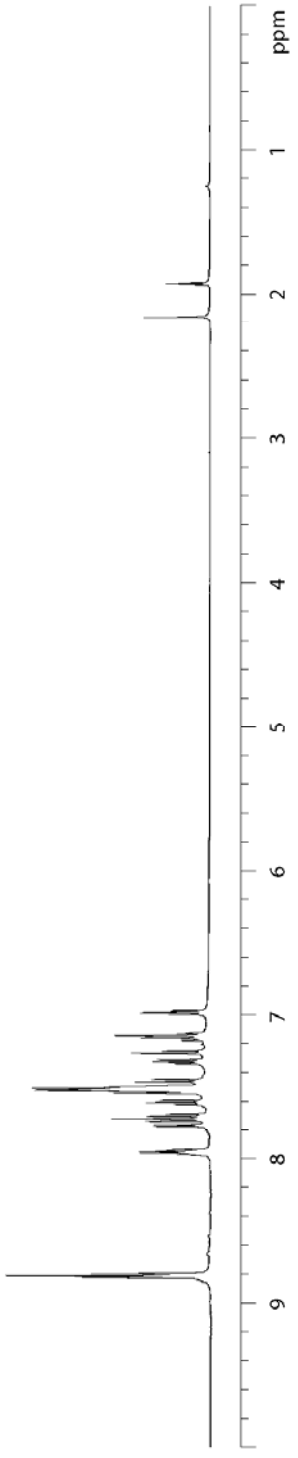


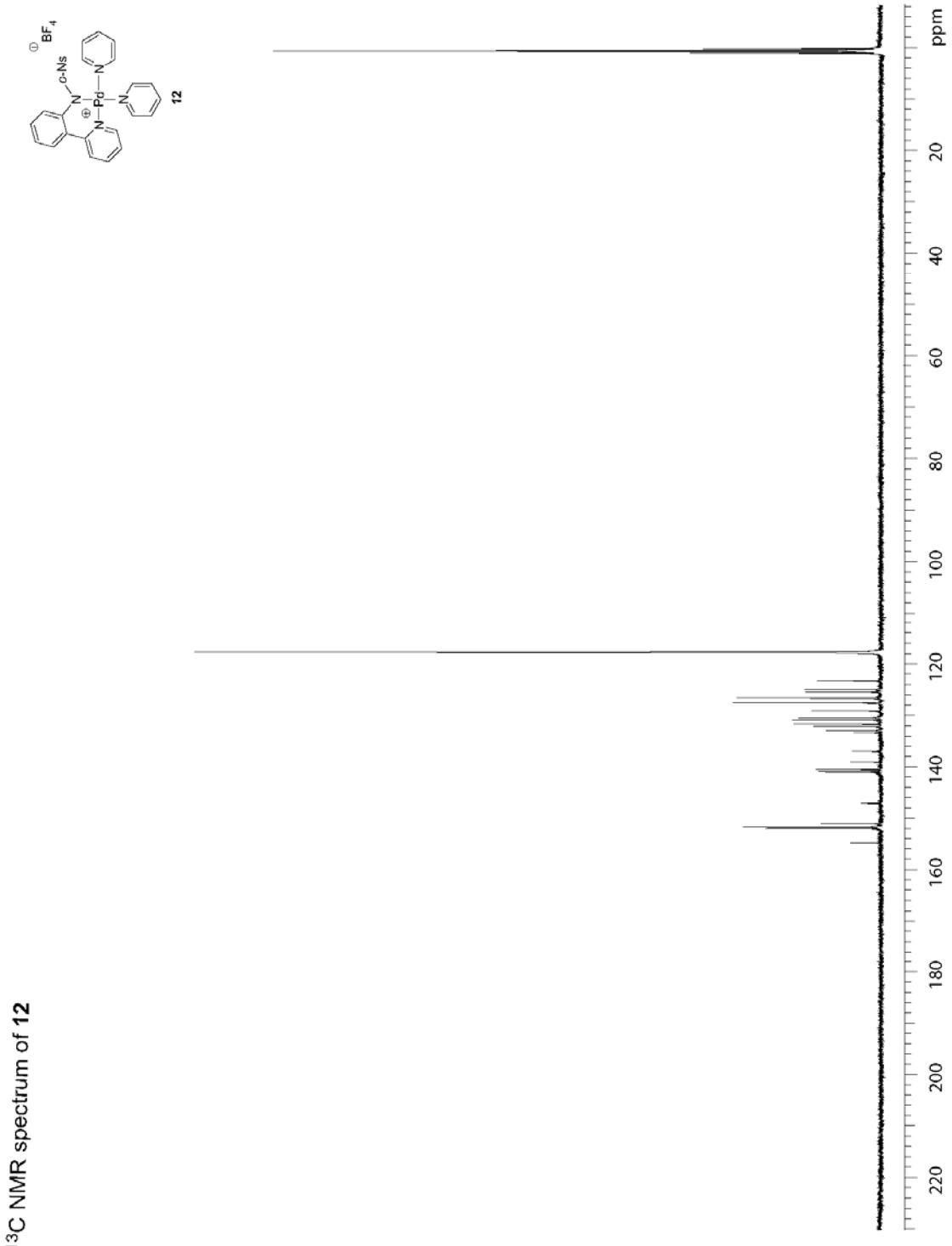




12

^{1}H NMR spectrum of **12**





^{13}C NMR spectrum of **12**