Supporting Information

Mechanism of C−F Reductive Elimination from Palladium(IV) Fluorides

Takeru Furuya, Diego Benitez, Ekaterina Tkatchouk, Alexandra E. Strom, Pingping Tang, William A. Goddard, III and Tobias Ritter*

Department of Chemistry and Chemical Biology, Harvard University
Cambridge, Massachusetts 02138

Materials and Process Simulation Center, California Institute of Technology
Pasadena, California 91125

E-mail: ritter@chemistry.harvard.edu

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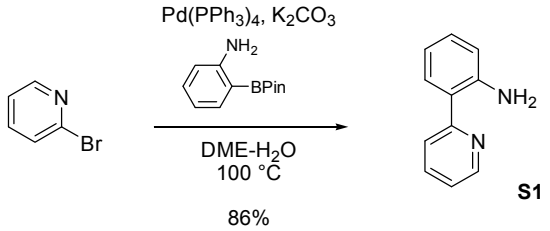
Materials and Methods

All reactions were carried out under an inert nitrogen atmosphere unless otherwise indicated. Solvents other than methanol 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 eluent 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). NMR spectra were recorded on a Varian Mercury 400 (400 MHz for ^{1}H, 100 MHz for ^{13}C, 375 MHz for ^{19}F, and 126 MHz for ^{31}P acquisitions), Unity/Inova 500 (500 MHz for ^{1}H, 125 MHz for ^{13}C acquisitions), or Unity/Inova 600 (600 MHz for ^{1}H acquisitions) spectrometer. ^{13}C NMR spectra were recorded ^{1}H decoupled. ^{19}F NMR spectra were recorded ^{1}H coupled. Chemical shifts are reported in ppm with the solvent resonance as the internal standard. Data are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, h = heptet, m = multiplet, br = broad; 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. Chemicals were purchased from Aldrich, Alfa Aesar, Frontier Scientific, Matrix Scientific, or Boron Molecular and used as received. NMR spectroscopic data of known compounds correspond to the data given in the appropriate references.

Experimental Data

Synthesis of palladium(IV) fluoride complexes 1−3

2-(2-Pyridinyl)aniline (S1)



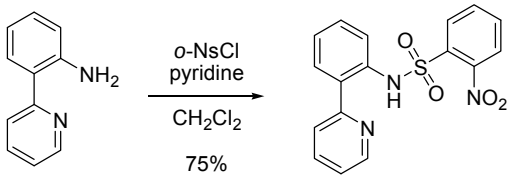
[1] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.

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

Under air, to 2-bromopyridine (4.54 g, 28.7 mmol, 1.00 equiv) in DME–H_2O (1:1, 100 mL) at 23 ºC was added K_2CO_3 (5.96 g, 43.1 mmol, 1.50 equiv), 2-aminophenylboronic acid pinacol ester (6.30 g, 28.7 mmol, 1.00 equiv), and tetrakis(triphenylphosphine)palladium (1.66 g, 1.44 mmol, 5.00 mol%). The reaction mixture was stirred at 100 °C for 3.0 h. After cooling to 23 ºC, the phases were separated and the aqueous phase was extracted with EtOAc (3 × 50 mL). The combined organic phases were washed with brine (100 mL) and dried (Na_2SO_4). The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel eluting with hexanes/EtOAc 4:1 (v/v) to afford 4.20 g of the title compound as a red-brown oil (86% 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): 159.5, 147.9, 146.6, 136.9, 129.9, 129.4, 122.2, 122.2, 121.0, 117.6, 117.2.[3]

2-(2-Pyridinyl)-2-nitrobenzenesulfonanilide (S2)

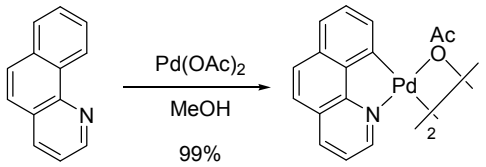


To 2-(2-pyridinyl)aniline (**S1**) (851 mg, 5.00 mmol, 1.00 equiv) in CH_2Cl_2 (10 mL) at 0 ºC was added pyridine (1.60 mL, 20.0 mmol, 4.00 equiv) and 2-nitrobenzenesulfonyl chloride (2.20 g, 10.0 mmol, 2.00 equiv). The reaction mixture was warmed to 23 ºC and stirred for 2.0 hr before the addition of water (10 mL). The phases were separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 8 mL). The combined organic phases were washed with brine (30 mL) and dried (Na_2SO_4). The filtrate was concentrated in vacuo and the residue was 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], 356.06995. Found, 356.07008.[3]

[3] Furuya, T.; Ritter, T. *J. Am. Chem. Soc.* **2008**, *130*, 10060−10061.

Benzo[*h*]quinolinyl palladium acetate dimer (S3)

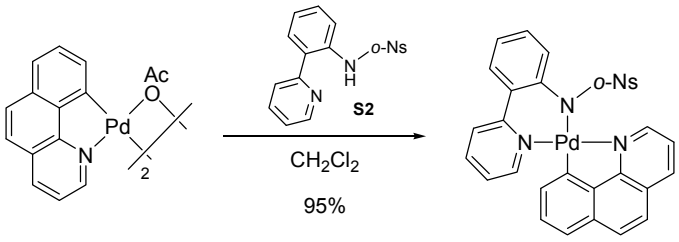


S3

To benzo[*h*]quinoline (1.79 g, 10.0 mmol, 1.00 equiv) in MeOH (100 mL) at 23 ºC was added palladium acetate (2.25 g, 10.0 mmol, 1.00 equiv). After stirring for 17 h, the suspension was 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.[3]

Benzo[*h*]quinolinyl palladium(II) pyrdine-sulfonamido complex S4[4]



S3 **S4**

To benzo[*h*]quinolinyl palladium acetate dimer (**S3**) (342 mg, 0.500 mmol, 1.00 equiv) in CH_2Cl_2 (1 mL) at 23 ºC was added 2-(2-pyridinyl)phenyl-2-nitrobenzenesulfonanilide (**S2**) (342 mg, 1.00 mmol, 2.00 equiv). After stirring for 20 min the reaction mixture was concentrated in vacuo. The resulting residue was triturated with Et_2O (3 × 1 mL) to afford 606 mg of the title compound as a colorless solid (95% yield).

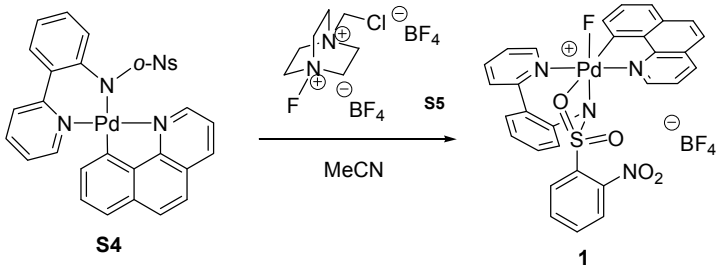
Melting Point: >260 ºC (decomp.). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 9.55 (dd,

[4] Compound **S4** and **11** are identical, but labeled like this for clarity.

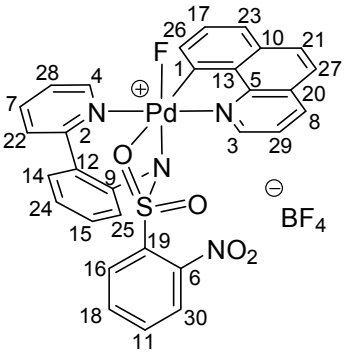
J = 5.5 Hz, 1.5 Hz, 1H), 8.99 (dd, *J* = 5.5 Hz, 1.0 Hz, 1H), 8.30 (dd, *J* = 8.5 Hz, 1.5 Hz, 1H), 7.76–7.71 (m, 2H), 7.64–7.54 (m, 5H), 7.49 (ddd, *J* = 9.5 Hz, 8.5 Hz, 1.5 Hz, 1H), 7.41 (dd, *J* = 7.5 Hz, 1.5 Hz, 1H), 7.36 (dd, *J* = 8.0 Hz, 8.0 Hz, 1H), 7.26–7.13 (m, 5H), 7.04 (dd, *J* = 8.0 Hz, 1.5 Hz, 1H), 7.00 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ)[5]: 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.[3]

Structure Assignment of Palladium(IV) fluoride complexes

Monofluoro palladium(IV) complex 1



To benzo[*h*]quinolinyl palladium(II) pyridine-sulfonamido complex **S4** (12.8 mg, 0.0200 mmol, 1.00 equiv) in acetonitrile-*d3* (0.6 mL) at 23 ºC was added 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo [2.2.2]octane bis(tetrafluoroborate) (**S5**) (7.1 mg, 0.020 mmol, 1.0 equiv). After stirring for 10 min at 23 ºC, the colorless suspension formed a dark purple solution. Compound **1** was characterized by NMR in acetonitrile solution without purification.



NMR Spectroscopy: ^{1}H NMR (500 MHz, acetonitrile-*d3*, 23 ºC, δ)[6]: 9.60 (d, *J* = 6.0 Hz, 1H, H-3), 9.46

[5] The ^{13}C NMR spectrum of **S4** has a low signal-to-noise ratio due to the low solubility of **S4** in common organic solvents.

[6] The numbering scheme is based on the ^{13}C chemical shifts, and is not IUPAC standard.

(d, *J* = 6.0 Hz, 1H, H-4), 8.89 (dd, *J* = 8.0 Hz, 1.0 Hz, 1H, H-8), 8.48 (dd, *J* = 7.5 Hz, 7.5 Hz, 1H, H-7), 8.40 (d, *J* = 8.0 Hz, 1H, H-22), 8.06 (d, *J* = 8.5 Hz, 1H, H-27), 8.05 (dd, *J* = 8.5 Hz, 6.0 Hz, 1H, H-29), 8.06 (d, *J* = 8.5 Hz, 1H, H-21), 7.95 (dd, *J* = 7.0 Hz, 6.5 Hz, 1H, H-28), 7.78 (d, *J* = 7.5 Hz, 1H, H-14), 7.78 (d, *J* = 7.5 Hz, 1H, H-23), 7.61 (ddd, *J* = 8.0 Hz, 8.0 Hz, 1.0 Hz, 1H, H-11), 7.60 (d, *J* = 8.5 Hz, 1H, H-16), 7.46 (d, *J* = 8.5 Hz, 1H, H-30), 7.42 (dd, *J* = 7.0 Hz, 7.0 Hz, 1H, H-18), 7.20 (dd, *J* = 7.5 Hz, 7.5 Hz, 1H, H-24), 7.06 (dd, *J* = 8.0 Hz, 8.0 Hz, 1H, H-17), 6.89 (dd, *J* = 8.0 Hz, 7.5 Hz, 1H, H-15), 6.78 (d, *J* = 8.0 Hz, 1H, H-25), 6.31 (d, *J* = 9.0 Hz, 1H, H-26). ^{13}C NMR (125 MHz, acetonitrile-*d3*, 23 ºC, δ): 166.98 (s, C-1), 154.52 (s, C-2), 153.81 (s, C-3), 151.56 (d, $J_{C\text{-}F}$ = 16.4 Hz, C-4), 150.81 (s, C-5), 148.56 (s, C-6), 144.06 (s, C-7), 142.32 (s, C-8), 139.58 (s, C-9), 136.71 (s, C-10), 135.80 (s, C-11), 135.24 (s, C-12), 134.87 (s, C-13), 133.24 (s, C-14), 132.58 (s, C-15), 132.48 (s, C-16), 132.20 (s, C-17), 132.11 (s, C-18), 131.19 (s, C-19), 130.04 (s, C-20), 129.37 (s, C-21), 127.77 (s, C-22), 127.45 (s, C-23), 127.12 (s, C-24), 127.08 (s, C-25), 126.63 (s, C-26), 126.62 (s, C-27), 126.34 (d, $J_{C\text{-}F}$ = 2.5 Hz, C-28), 125.52 (s, C-29), 124.92 (s, C-30). ^{19}F NMR (375 MHz, acetonitrile-*d3*, 23 ºC, δ): –152.0 (s), –278.0 (br s).[3]

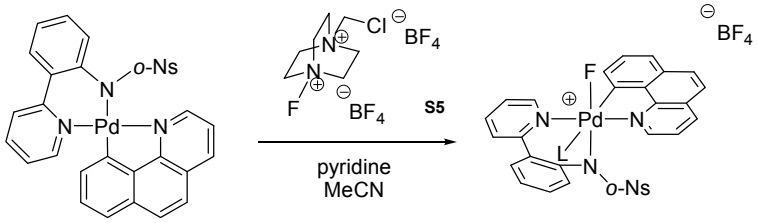
^{1}H, ^{13}C, ^{1}H-^{1}H COSY, HSQC, HMBC, NOESY spectra are attached in the spectroscopic data section.

The relative configuration was assigned as follows:

1) the nOe signal between H-26 and H-14 is most consistent with the above configuration of the two bidentate ligands

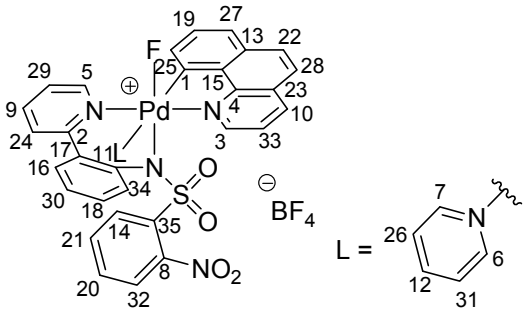
2) the lack of trans C−F coupling indicates the fluoride is not trans to C-1

Monofluoro palladium(IV) pyridine complex 2



S4 **2** L = py

To benzo[*h*]quinolinyl palladium(II) pyrdine-sulfonamido complex **S4** (12.8 mg, 0.0200 mmol, 1.00 equiv) in acetonitrile-*d3* (0.6 mL) at 23 ºC was added 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo [2.2.2]octane bis(tetrafluoroborate) (**S5**) (7.1 mg, 0.020 mmol, 1.0 equiv). After stirring for 10 min at 23 ºC, pyridine (2.1 μL, 0.026 mmol, 1.3 equiv) was added to the reaction mixture. Compound **2** was characterized by NMR as acetonitrile solution without purification.



NMR Spectroscopy: ^{1}H NMR (500 MHz, acetonitrile-*d3*, 23 ºC, δ)[7]: 9.34 (d, *J* = 5.5 Hz, 1H, H-7), 8.88 (d, *J* = 6.0 Hz, 1H, H-3), 8.75 (d, *J* = 8.0 Hz, 1H, H-10), 8.62 (d, *J* = 6.5 Hz, 1H, H-5), 8.58 (d, *J* = 8.0 Hz, 1H, H-24), 8.52 (d, *J* = 5.0 Hz, 1H, H-6), 8.38 (dd, *J* = 8.0 Hz, 8.0 Hz, 1H, H-9), 8.24 (dd, *J* = 8.5 Hz, 7.5 Hz, 1H, H-12), 8.03 (d, *J* = 9.0 Hz, 1H, H-22), 7.98 (d, *J* = 9.0 Hz, 1H, H-28), 7.98−7.96 (m, 1H, H-26), 7.86−7.81 (m, 3H, H-16, H-27, H-33), 7.60−7.53 (m, 3H, H-14, H-20, H-31), 7.49 (ddd, *J* = 8.0 Hz, 7.5 Hz, 1.5 Hz, 1H, H-29), 7.45 (dd, *J* = 7.5 Hz, 1.0Hz, 1H, H-32), 7.32−7.26 (m, 1H, H-21), 7.21 (dd, *J* = 7.5 Hz, 7.5 Hz, 1H, H-30), 7.15 (dd, *J* = 8.0 Hz, 7.5 Hz, 1H, H-19), 6.89 (dd, *J* = 8.0 Hz, 8.0 Hz, 1H, H-18), 6.78 (d, *J* = 8.0 Hz, 1H, H-34), 6.42 (d, *J* = 8.0 Hz, 1H, H-25). ^{13}C NMR (125 MHz, acetonitrile-*d3*, −15 ºC, δ): 164.89 (s, C-1), 154.31 (s, C-2), 153.42 (s, C-3), 152.20. (s, C-4), 150.59 (d, $J_{C\text{-}F}$ = 17.3 Hz, C-5), 150.30 (s, C-6), 148.69 (s, C-7), 148.67 (s, C-8), 143.65 (s, C-9), 142.12 (s, C-10), 141.37 (s, C-11), 141.24 (s, C-12), 136.18 (s, C-13), 135.47 (s, C-14), 134.95 (s, C-15), 133.89 (s, C-16), 133.33 (s, C-17), 132.37 (s, C-18), 132.05 (s, C-19), 131.88 (s, C-20), 130.85 (s, C-21), 129.63 (s, C-22), 129.56 (s, C-23), 128.27 (s, C-24), 127.93 (s, C-25), 127.65 (s, C-26), 126.91 (s, C-27), 126.20–126.04 (m, C-28, C-29, C-30, C-31), 125.64 (s, C-32), 125.33 (s, C-33), 124.74 (s, C-34), 124.28 (s, C-35). ^{19}F NMR (375 MHz, acetonitrile-*d3*, 23 ºC, δ): –152.0 (s), –264.3 (br s).

^{1}H, ^{13}C, ^{1}H-^{1}H COSY, HSQC, HMBC, NOESY spectra were attached in the spectroscopic data section.

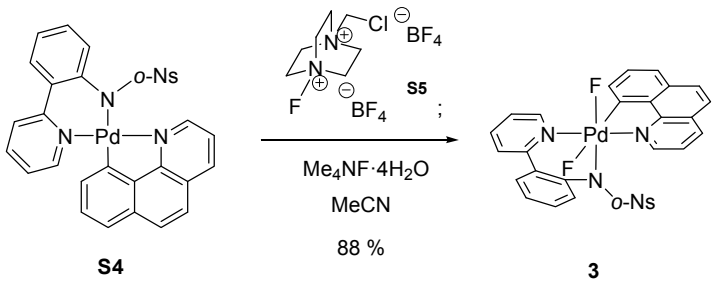
The relative configuration was assigned as follows:

1) the nOe signal between H-25 and H-16 is most consistent with the above configuration of the two bidentate ligands

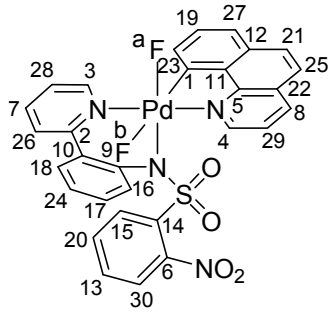
2) the lack of trans C−F coupling indicates the fluoride is not trans to C-1

[7] The numbering scheme is based on the ^{13}C chemical shifts, and is not IUPAC standard.

Difluoro palladium(IV) complex 3



To benzo[*h*]quinolinyl palladium(II) pyrdine-sulfonamido complex **S4** (128 mg, 0.200 mmol, 1.00 equiv) in MeCN (2.0 mL) at 23 ºC was added 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (**S5**) (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) was added to the reaction mixture. After stirring for 20 min at 23 ºC, the precipitate was filtered off and washed with acetone (5 × 2 mL). The solid was dissolved in CH_2Cl_2 and filtered through a pad of celite. The filtrate was concentrated in vacuo to afford 119 mg of the title compound as an orange solid (88% yield).



NMR Spectroscopy: ^{1}H NMR (500 MHz, DMSO-*d6*, 23 ºC, δ)[8]: 9.72 (d, *J* = 5.0 Hz, 1H, H-4), 9.28 (d, *J* = 5.0 Hz, 1H, H-3), 9.18 (dd, $J_{H\text{-}F}$ = 17.5 Hz, $J_{H\text{-}H}$ = 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, $J_{H\text{-}H}$ = 7.5 Hz, $J_{H\text{-}F}$ = 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,

[8] The numbering scheme is based on the ^{13}C chemical shifts, and is not IUPAC standard.

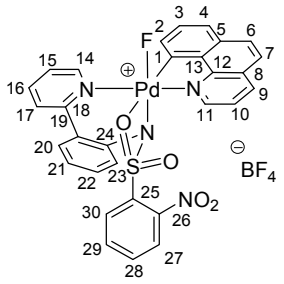
C-16), 131.7 (s, C-17), 131.4 (s, C-18), 131.0 (d, *J* = 6.4 Hz, C-19), 130.9 (s, C-20), 129.2 (s, C-21), 128.7 (s, C-22), 127.7 (d, *J* = 3.6 Hz, C-23), 127.5 (s, C-24), 125.5 (s, C-25), 125.4 (s, C-26), 125.4 (s, C-27), 125.2 (s, C-28,), 124.1 (s, C-29), 122.6 (s, C-30). ^{19}F NMR (375 MHz, DMSO-*d6*, 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.

^{1}H, ^{13}C, ^{1}H-^{1}H COSY, ^{19}F-^{19}F COSY, HSQC, HMBC, NOESY, HOM2DJ spectra are attached in the spectroscopic data section. For the details of the crystal structure see the previous publication.[3]

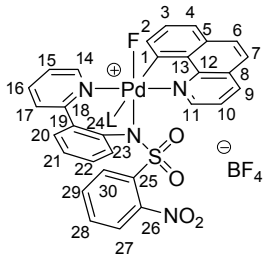
The relative configuration was assigned as follows:

1) the C-F coupling between C-1 and F-b dictates F-b to be trans to C-1
2) in order to accommodate the bidentate pyridylsulfonamide ligand, F-a cannot be in the same plane as the benzoquinoline ligand
3) in order to explain the doublet of doublets in C-3, the pyridyl moiety needs to be trans to the benzoquinoline nitrogen ligand. Also the nOe signal between H-23 and H-18 is most consistent with the above configuration of the two bidentate ligands

Comparison of ^{13}C NMR chemical shift between 1 and 2



1



2

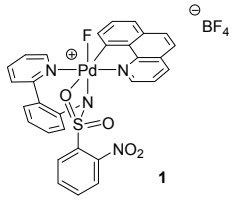
L = py

	1	2	Δδ
C1	126.6	127.9	1.3
C2	132.2	132.1	0.1
C3	127.5	126.9	0.6
C4	136.7	136.2	0.5
C5	129.4	129.6	0.2
C6	126.6	126.2	0.4
C7	130.0	129.6	0.4
C8	142.3	142.1	0.2
C9	125.5	125.3	0.2
C10	153.8	153.4	0.4
C11	150.8	152.2	1.4
C12	134.9	135.0	0.1
C13	167.0	164.9	2.1
C14	151.6	150.6	1.0
C15	126.3	126.2	0.1
C16	144.1	143.7	0.4
C17	127.8	128.3	0.5
C18	154.5	154.3	0.2
C19	135.2	133.3	1.9
C20	133.2	133.9	0.7
C21	127.1	126.2	0.9
C22	132.6	132.4	0.2
C23	127.1	124.7	2.4
C24	139.6	141.4	1.8
C25	***131.2***	***124.3***	***6.9***
C26	148.6	148.7	0.1
C27	124.9	125.6	0.7
C28	135.8	131.9	3.9
C29	132.1	130.9	1.2
C30	132.5	135.5	3.0
		AVERAGE:	1.1

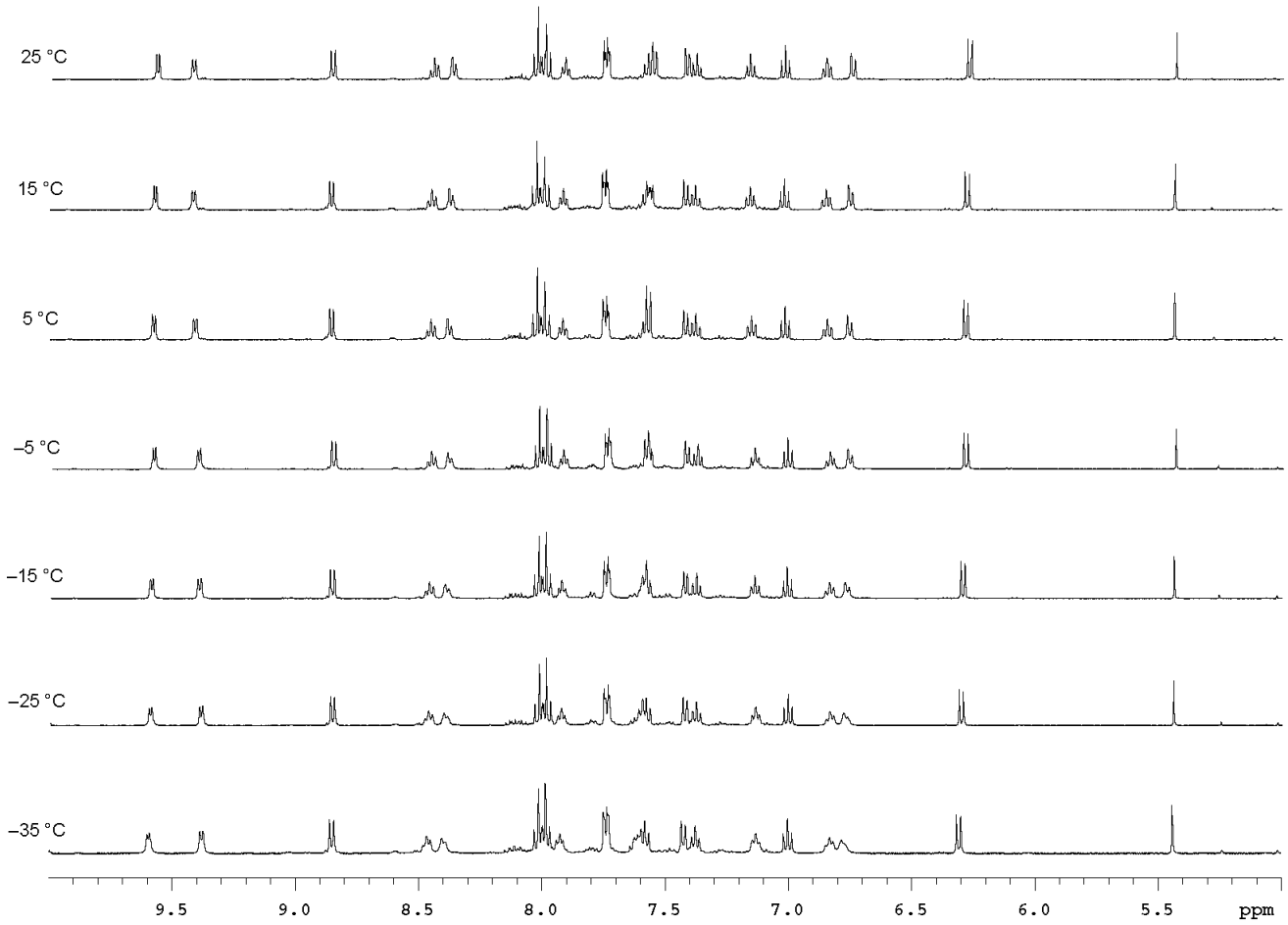
Line-shape analysis of complexes 1 and 2

Line-shape analysis of 1

A Solution (16.7 mM) of compound **1** was prepared by reacting compound **S4** (6.4 mg, 0.010 mmol, 1.0 equiv) with 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo [2.2.2]octane bis(tetrafluoroborate) (**S5**) (3.5 mg, 0.010 mmol, 1.0 equiv) in acetonitrile-*d3* (0.6 mL) in an NMR tube under nitrogen. ^{1}H NMR spectra were taken at –35, –25, –15, –5, 5, 15, 25 ºC.

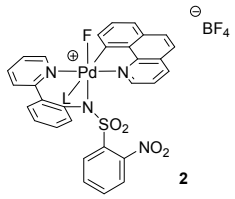


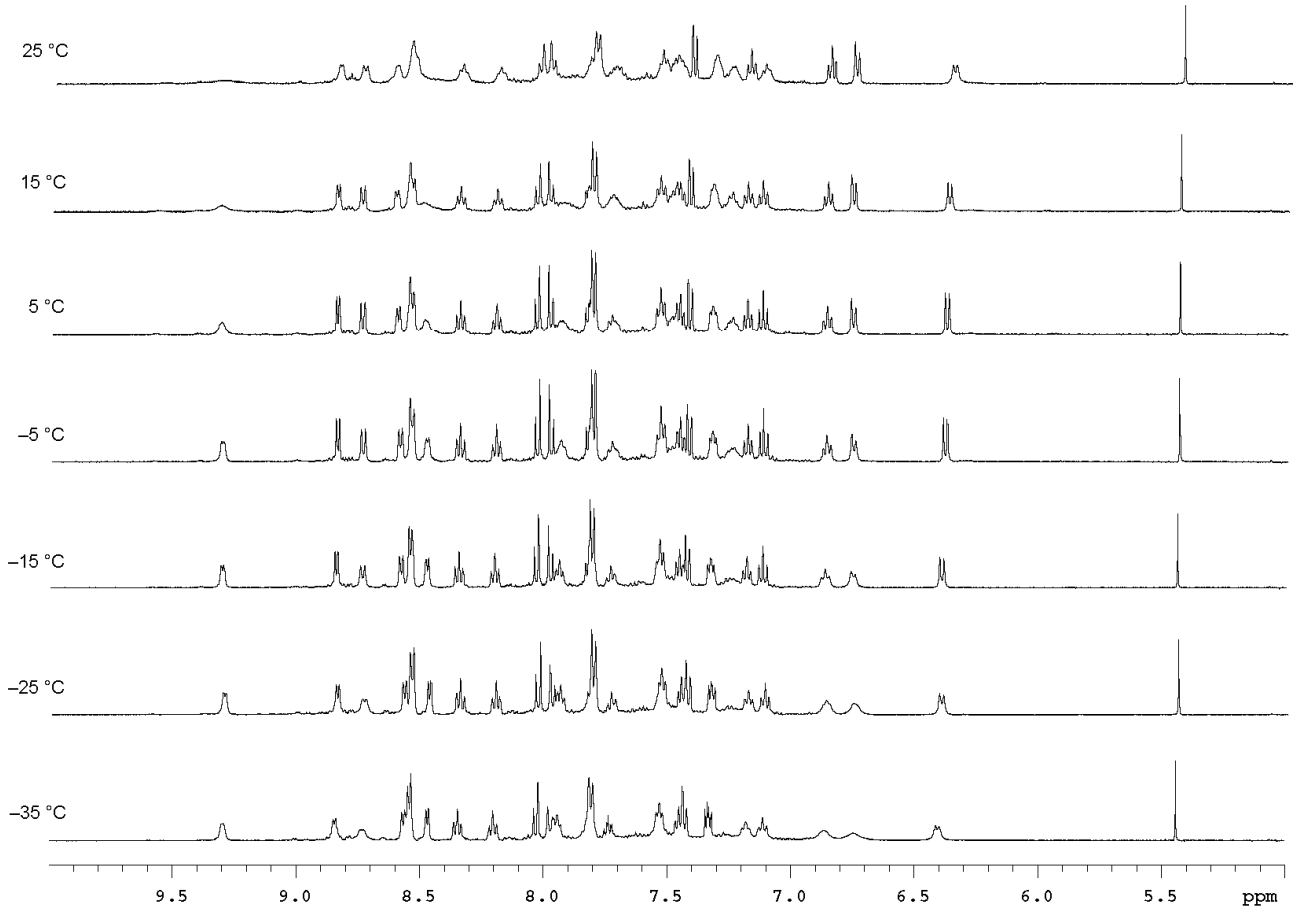
1



Line-shape analysis of 2

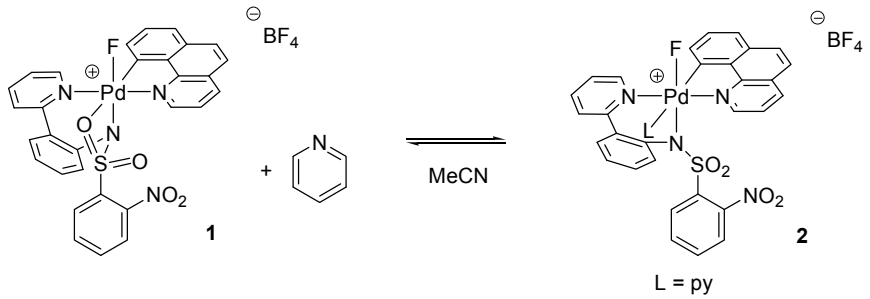
Solutions (16.7 mM) of compound **2** was prepared by reacting compound **S4** (6.4 mg, 0.010 mmol, 1.00 equiv) with 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo [2.2.2]octane bis(tetrafluoroborate) (**S5**) (3.5 mg, 0.010 mmol, 1.0 equiv) and pyridine (1.2 μL, 0.015 mmol, 1.5 equiv) in acetonitrile-*d3* (0.6 mL) in an NMR tube under nitrogen. ^{1}H NMR spectra were taken at –35, –25, –15, –5, 5, 15, 25 ºC.





Determination of equilibrium constant and rate of exchange between 1 and 2

Dependence of equilibrium constant on temperature

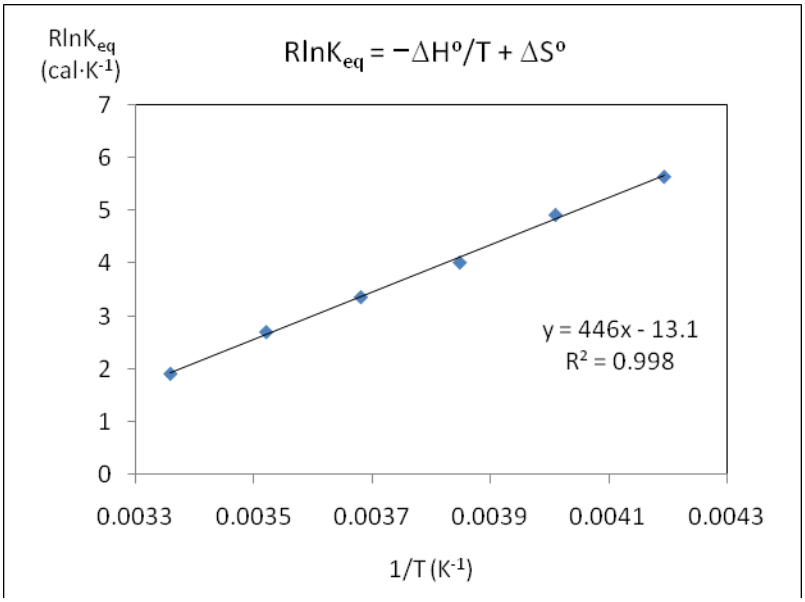


A solution of a mixture of compounds **1** and **2** was prepared by reacting compound **S4** (12.8 mg, 0.0200 mmol, 1.00 equiv) with 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo [2.2.2]octane bis(tetrafluoroborate) (**S5**) (7.1 mg, 0.020 mmol, 1.0 equiv) and pyridine (1.6 μL, 0.020 mmol, 1.0 equiv) in acetonitrile-*d3* in an NMR tube under nitrogen. The equilibrium constant was measured by integrating the peak at 6.42 ppm (complex **2**) and 6.31 ppm (complex **1**). Using the same sample, the rate of exchange was measured by line-shape analysis of the peak at 6.31 ppm. ($k = \pi\cdot(\Delta\upsilon-\Delta\upsilon_{ref})$,[9] where $\Delta\upsilon$ is a peak width at half height (6.31 ppm) and $\Delta\upsilon_{ref}$ is a peak width at half height of non-exchangeable peak (4.91 ppm, 1-chloromethyl-1,4-diazoniabicyclo [2.2.2]octane (tetrafluoroborate))). $\Delta\upsilon$ was not measured at 24.8 ºC due to the merging of two peaks at 6.31 ppm and 6.42 ppm. $\Delta\upsilon$ at −34.6 ºC was not measured because line-broadening that does not correspond to the exchange between **1** and **2**, presumably due to the sluggish bond rotation at this temperature, was observed at −34.6 ºC.

T (ºC)	1/T(K^{-1})	K_{eq}	RlnKeq ($cal\cdot K^{-1}$)	$\Delta\upsilon$	$\Delta\upsilon_{ref}$	k (s^{-1})	Rln(kh/kbT) ($cal\cdot K^{-1}\cdot mol^{-1}$)
−34.6	0.0042	17.2	5.65	—	—	—	—
−23.7	0.00401	11.9	4.92	1.78	1.65	0.393	-60
−13.2	0.00385	7.56	4.02	1.97	1.52	1.41	-57.6
−1.31	0.00368	5.43	3.36	2.87	1.47	4.4	-55.4
11.1	0.00352	3.89	2.7	6.3	1.69	14.5	-53.1
24.8	0.00336	2.61	1.91	—	—	—	—

[9] Sandstrom, J. *Dynamic NMR spectroscopy*, London: New York, 1982.

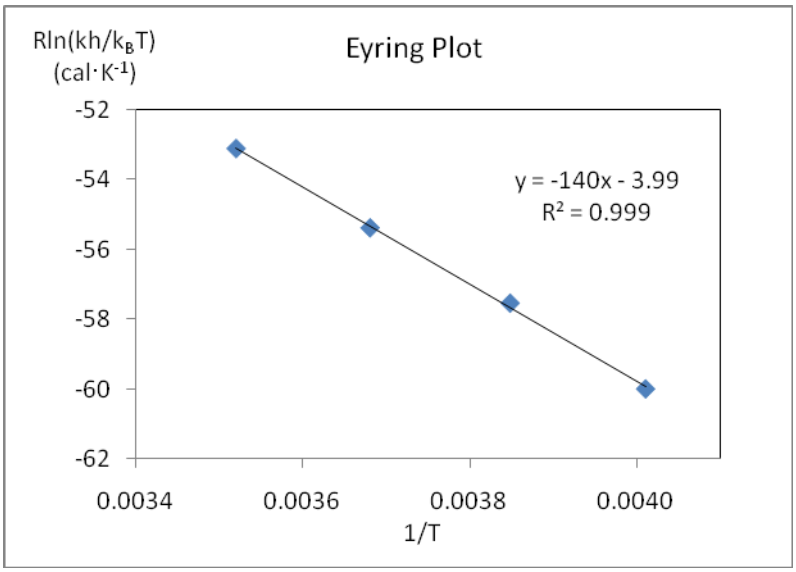
Determination of ΔH^o, ΔS^o and ΔG^o



Error analysis

	ΔH^o (kcal·mol^{-1})	Difference	ΔS^o (cal·K^{-1}·mol^{-1})	Difference	ΔG_{298}^o (kcal·mol^{-1})	Difference
calcd + error	–4.74	–0.28	–12.02	–1.05	0.605	0.03
calcd	–4.46	–	–13.07	–	0.570	–
calcd - error	–4.19	0.28	–14.11	1.05	0.535	–0.03

Eyring plot for rate of exchange

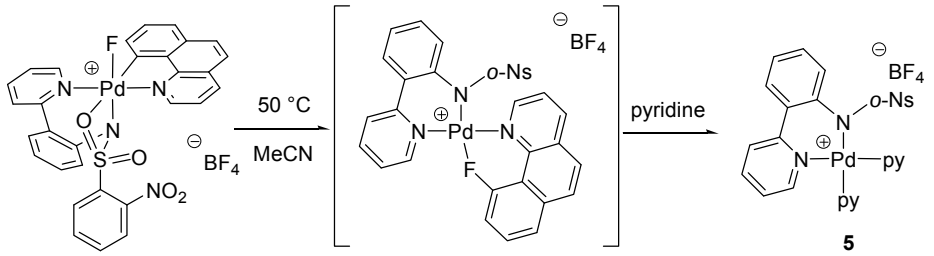


Error analysis of the Eyring plot

	$\Delta H^{\ddagger}$ (kcal·mol^{-1})	Difference	$\Delta S^{\ddagger}$ (cal·K^{-1}·mol^{-1})	Difference	$\Delta G_{298}^{\ddagger}$ (kcal·mol^{-1})	Difference
calcd + error	15.2	1.27	-8.78	–4.79	15.3	0.16
calcd	14.0	–	-3.99	–	15.1	–
calcd - error	12.7	–1.27	0.80	4.79	15.0	–0.16

Isolation of Pd^{II} product from C−F reductive elimination reaction of 1

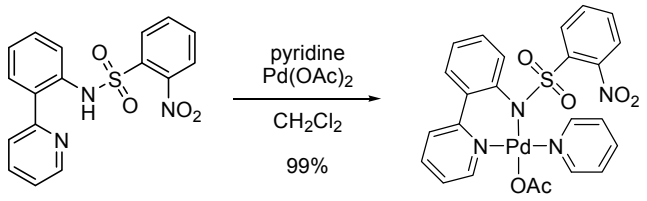
Observation of 5 from C−F reductive elimination reaction of 1



Compound **1** (0.030 mmol) in MeCN (2.0 mL) prepared by above described procedure was warmed to 50 ºC and stirred for 30 min. After cooled to 23 ºC, pyridine (9.7 μL, 0.12 mmol, 4.0 equiv) was added to the reaction mixture. The presence of compound **5** was comfirmed by comparing ^{1}H and ^{13}C NMR spectra with those of the authentic sample synthesized as shown below.

Independent synthesis of cationic Pd^{II} bispyridinium complex 5

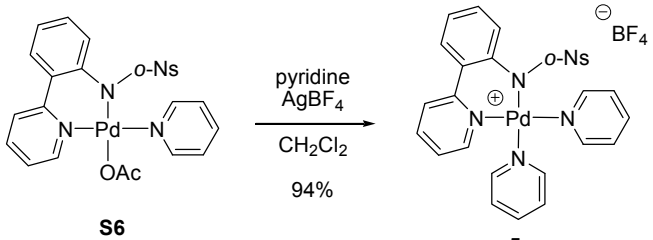
Acetato palladium complex S6



To palladium acetate (448 mg, 2.00 mmol, 1.00 equiv) in CH_2Cl_2 (20 mL) at 23 ºC was added pyridine (485 μL, 6.00 mmol, 3.00 equiv) and 2-(2-pyridinyl)phenyl-2-nitrobenzenesulfonamide (**S2**) (711 mg, 2.00 mmol, 1.00 equiv). After stirring for 20 min, the solution was concentrated in vacuo. The resulting residue was 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 [$C_{24}H_{20}N_4O_6PdS + NH_4$], 616.04760. Found, 616.04730. 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.[3]

Bis(pyridinium)palladium(II) tetrafluoroborate complex 5



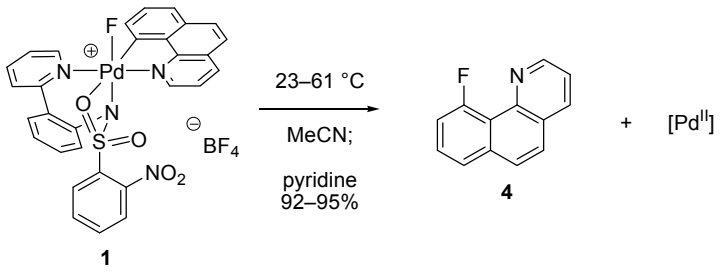
S6 **5**

To acetato palladium complex **S6** (30.0 mg, 0.0501 mmol, 1.00 equiv) in CH_2Cl_2 (1.0 mL) at 23 ºC was added pyridine (4.1 μL, 0.050 mmol, 1.0 equiv) and silver tetrafluoroborate (9.7 mg, 0.050 mmol, 1.0 equiv). After stirring for 30 min at 23 ºC, the reaction mixture was filtered through a pad of celite. The filtrate was 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 [$C_{27}H_{22}BF_4N_5O_4PdS - BF_4$], 618.04327. Found, 618.04334. [3]

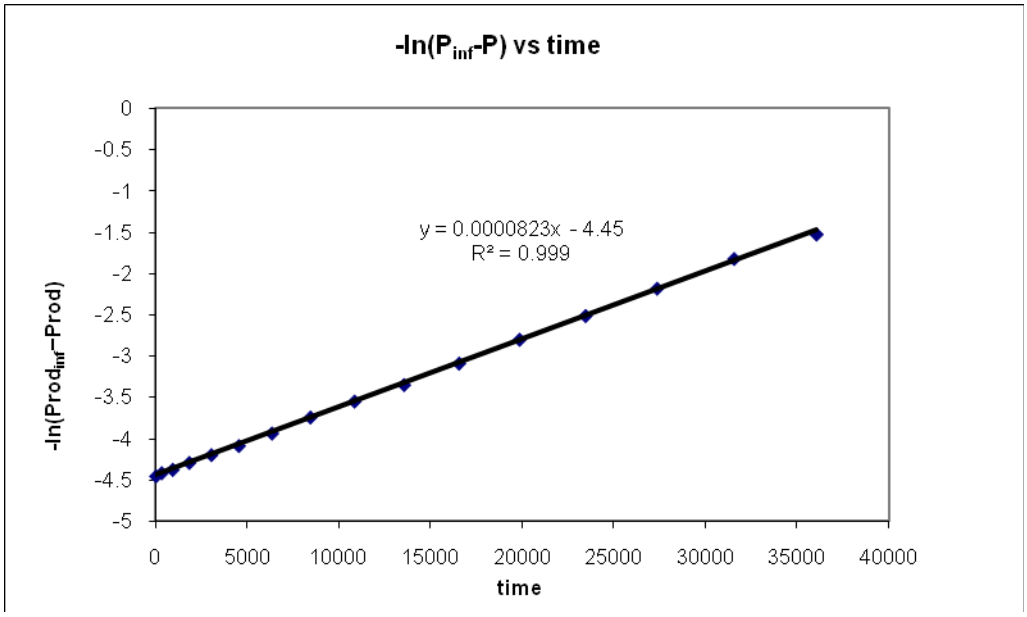
Determination of activation parameters

C−F reductive elimination from monofluoro Pd(IV) complex 1

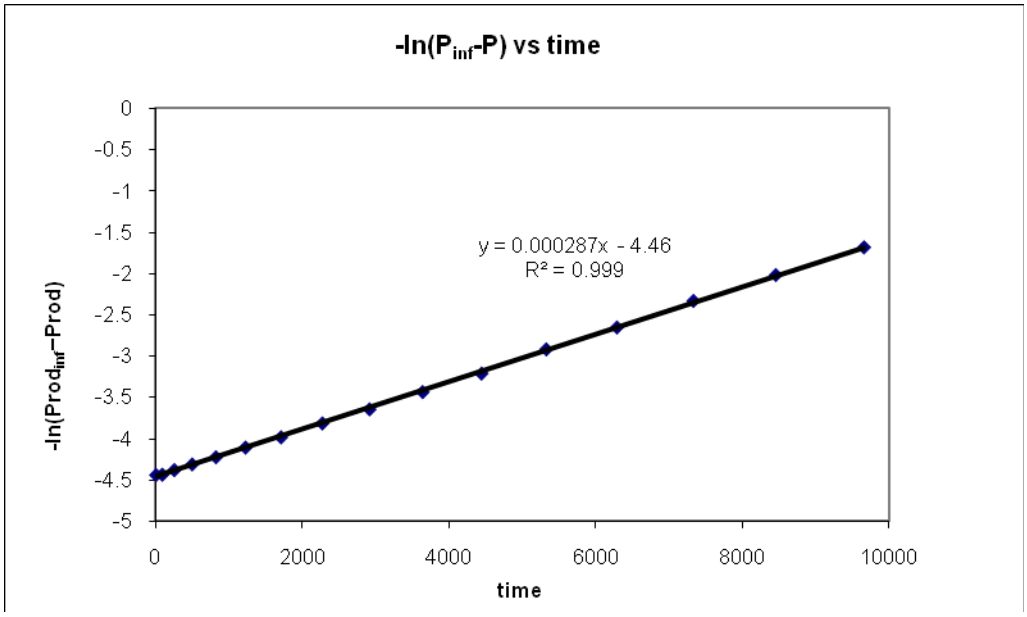


Solutions (33.3 mM) of compound **1** were prepared by reacting compound **S4** (12.8 mg, 0.0200 mmol, 1.00 equiv) with 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo [2.2.2]octane bis(tetrafluoroborate) (**S5**) (7.1 mg, 0.020 mmol, 1.0 equiv) in NMR tubes under nitrogen. NMR samples were placed in the preheated NMR machine and the disappearance of compound **1** and formation of the product **4** were monitored by integrating the peaks, at 6.33 ppm and 9.07 ppm respectively, relative to the peak of 1-chloromethyl-1,4-diazoniabicyclo [2.2.2]octane (tetrafluoroborate) at 4.91 ppm.

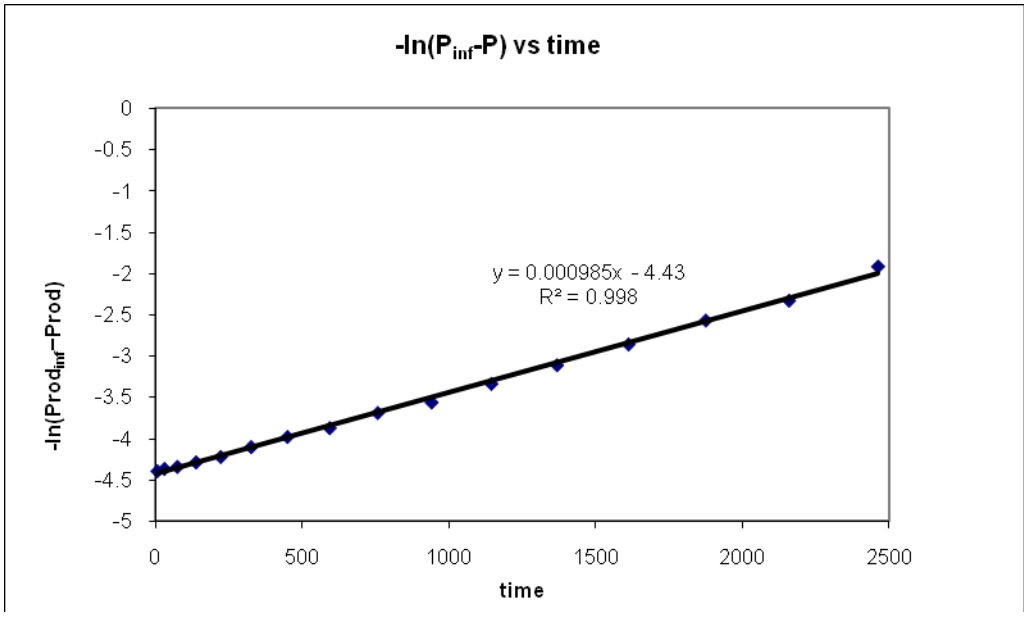
Kinetic data at 23.3 ºC



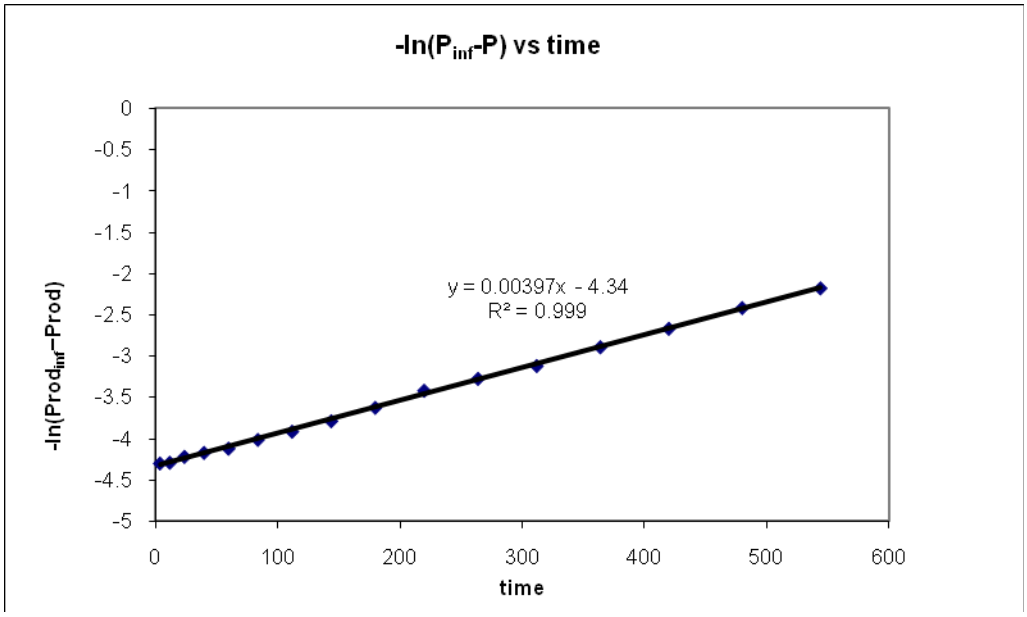
Kinetic data at 31.7 ºC



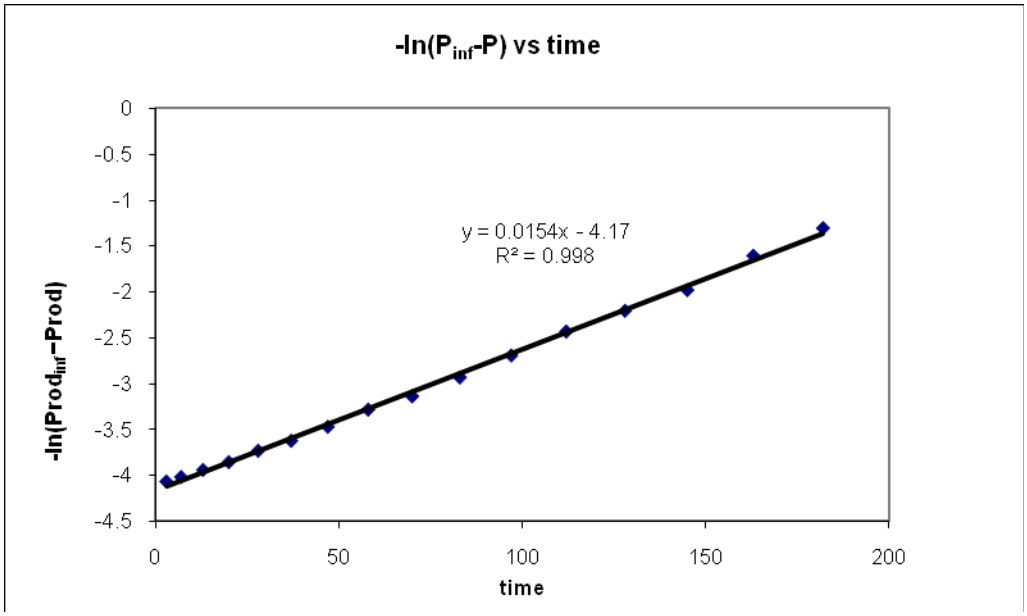
Kinetic data at 40.0 ºC



Kinetic data at 50.6 ºC

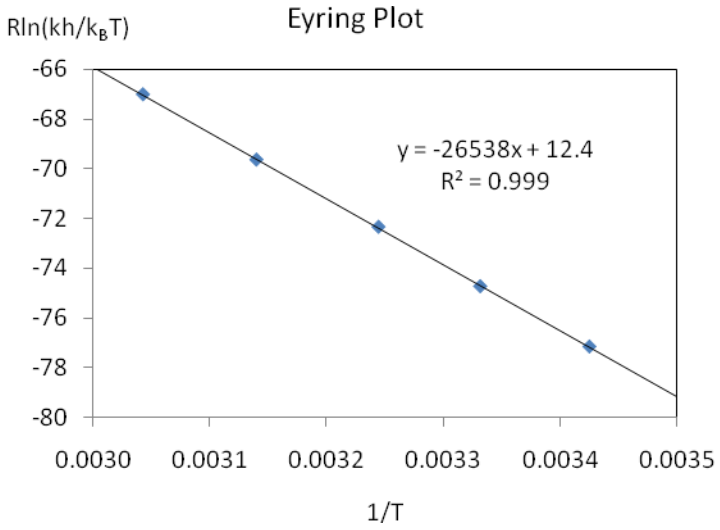


Kinetic data at 61.1 ºC



Eyring plot

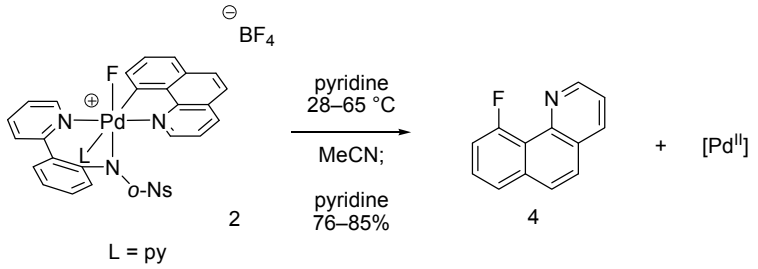
T (ºC)	T (K)	k (s^{-1})	1/T (K^{-1})	Rln(kh/k_bT) ($cal \cdot K^{-1} \cdot mol^{-1}$)	Yield of **4** (%)
23.3	296.3	0.0000823	0.003376	–77.2	92
31.7	304.7	0.000287	0.003282	–74.8	95
40.0	313.0	0.000985	0.003195	–72.4	94
50.6	323.6	0.00397	0.003090	–69.7	95
61.1	334.1	0.0154	0.002993	–67.0	94



Error analysis of the Eyring plot

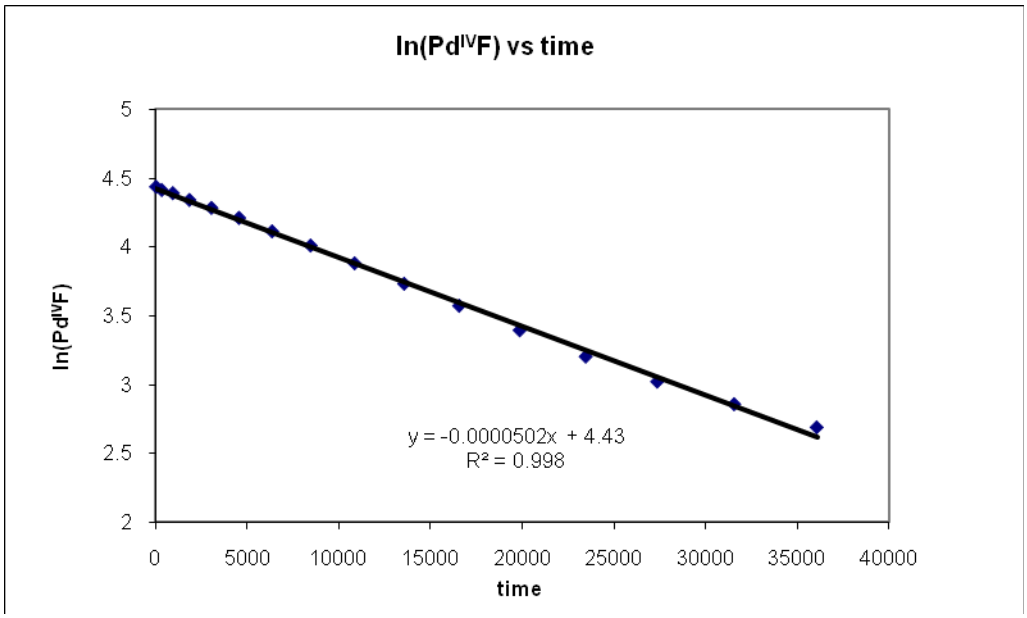
	$\Delta H^{‡}$ ($kcal \cdot mol^{-1}$)	Difference	$\Delta S^{‡}$ ($cal \cdot K^{-1} \cdot mol^{-1}$)	Difference	$\Delta G_{298}^{‡}$ ($kcal \cdot mol^{-1}$)	Difference
calcd + error	27.0	0.42	11.1	–1.33	22.8	–0.02
calcd	26.5	–	12.4	–	22.9	–
calcd - error	26.1	–0.42	13.7	1.33	22.9	0.02

C−F reductive elimination from monofluoro Pd(IV) pyridine complex 2

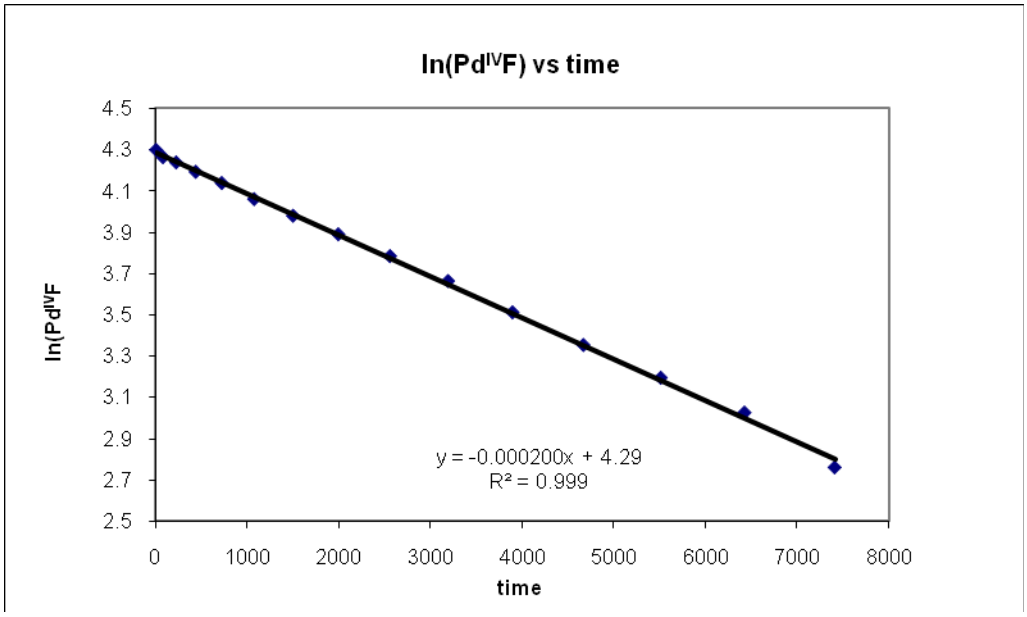


Solutions (33.3 mM) of compound **2** were prepared by reacting compound **S4** (12.8 mg, 0.0200 mmol, 1.00 equiv) with 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo [2.2.2]octane bis(tetrafluoroborate) (**S5**) (7.1 mg, 0.020 mmol, 1.0 equiv) and pyridine (2.4 μL, 0.030 mmol, 1.5 equiv) in NMR tubes under nitrogen. NMR samples were placed in the preheated NMR machine and the disappearance of the compound **2** was monitored by integrating the peak at 6.40 ppm relative to the peak of 1-chloromethyl-1,4-diazoniabicyclo [2.2.2]octane (tetrafluoroborate) at 4.91 ppm. Monitoring product formation was difficult because the competing coordination of pyridine and 10-fluorobenzo[*h*]quinoline complicated the ^{1}H NMR spectra. Addition of excess pyridine for monitoring the product formation was unsuccessful because in the presence of excess pyridine, the fluorination yield was significantly lower. The yield of **4** was 83% and 43% for 1.5 equiv and 3.0 equiv of pyridine, respectively at 50 ºC.

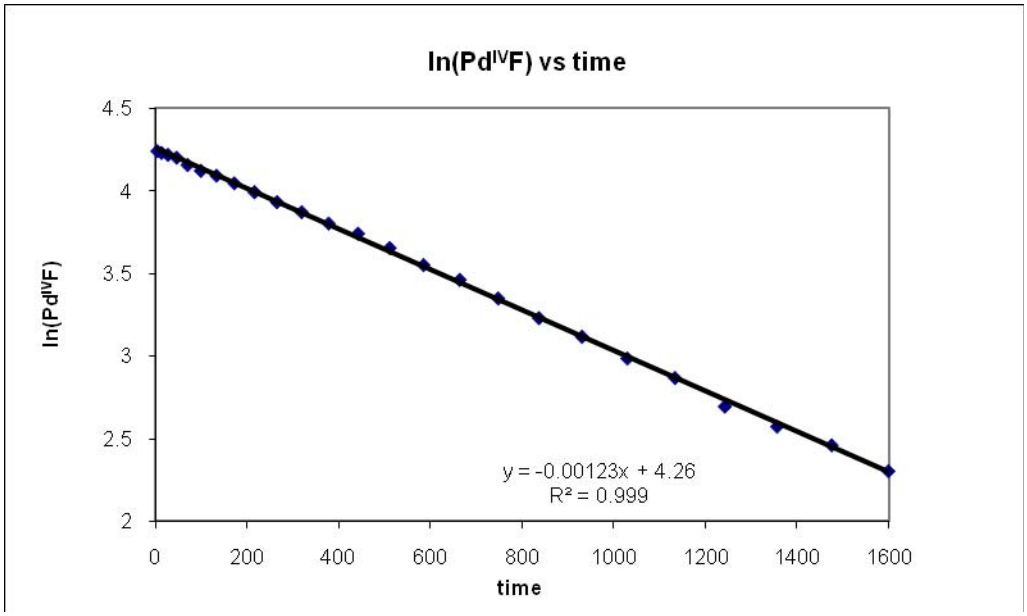
Kinetic data at 27.9 ºC



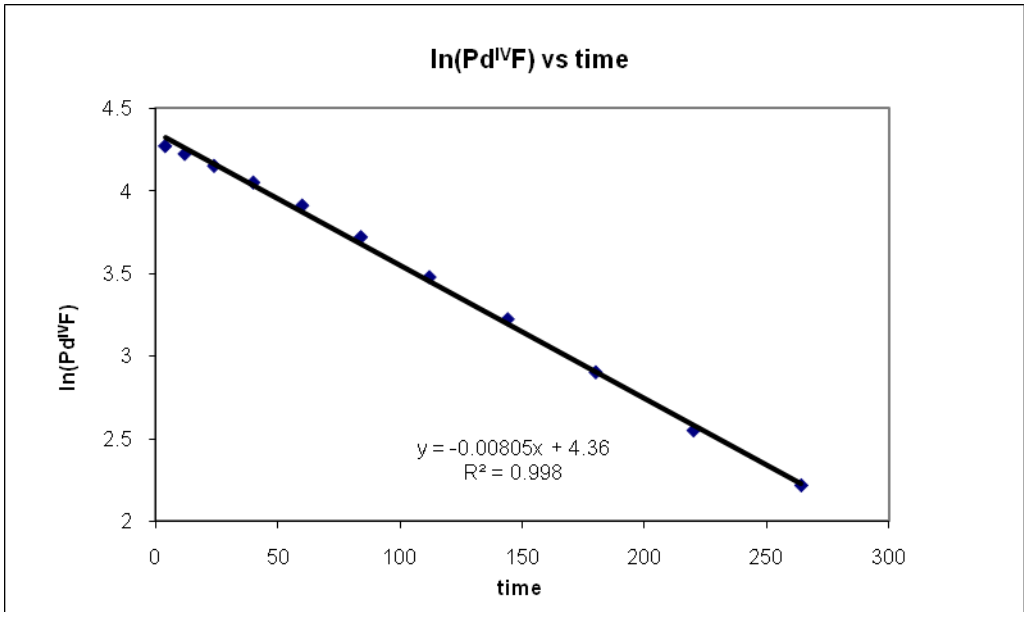
Kinetic data at 37.3 ºC



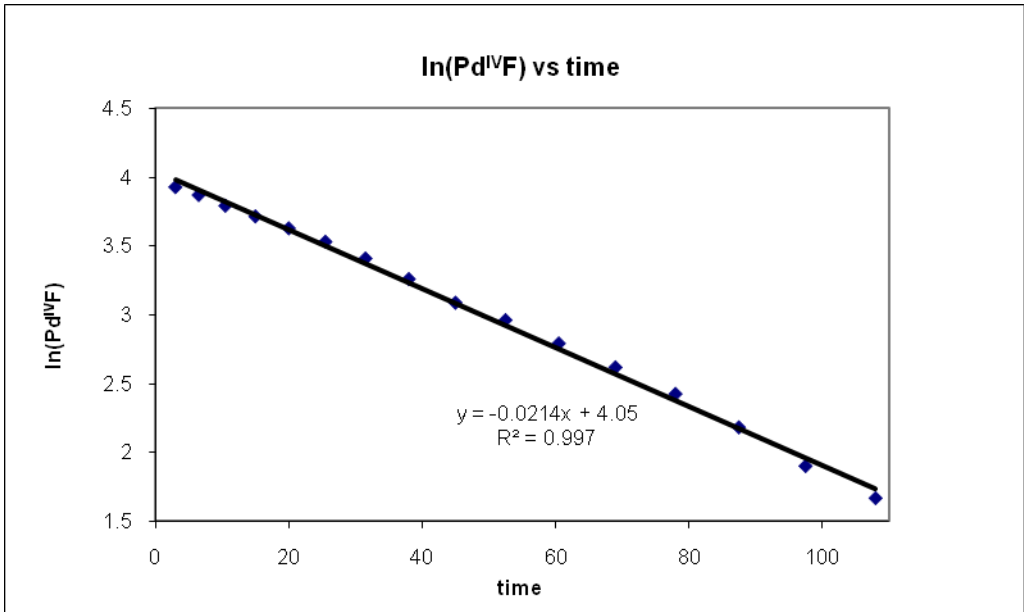
Kinetic data at 47.0 ºC



Kinetic data at 58.6 ºC

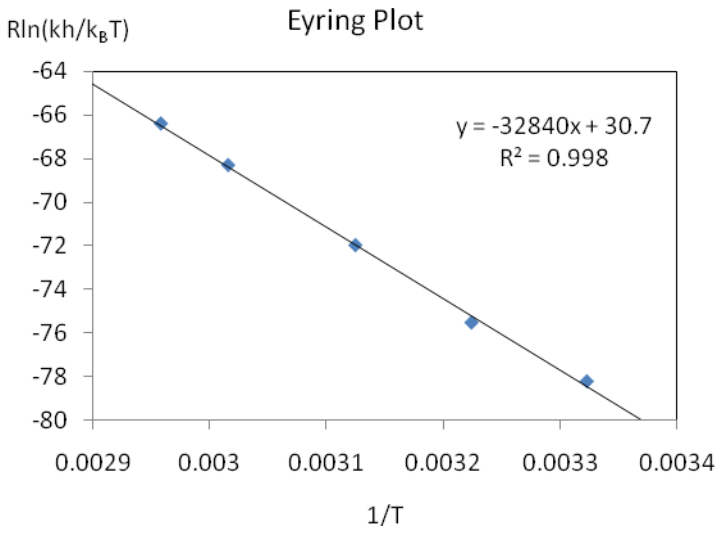


Kinetic data at 65.0 ºC



Eyring plot

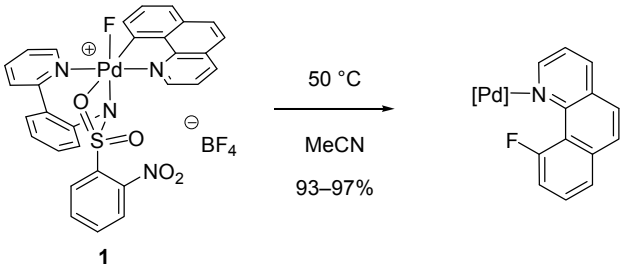
T (ºC)	T (K)	k (s^{-1})	1/T (K^{-1})	Rln(kh/k_bT) ($cal \cdot K^{-1} \cdot mol^{-1}$)	Fluorination Yield (%)
27.9	300.9	0.0000502	0.003323	–78.2	76
37.2	310.2	0.000201	0.003224	–75.5	80
47.0	320.0	0.00123	0.003125	–72.0	84
58.6	331.6	0.00805	0.003016	–68.3	84
65.0	338.0	0.0214	0.002958	–66.4	85



Error analysis of the Eyring plot

	$\Delta H^{‡}$ ($kcal \cdot mol^{-1}$)	Difference	$\Delta S^{‡}$ ($cal \cdot K^{-1} \cdot mol^{-1}$)	Difference	$\Delta G_{298}^{‡}$ ($kcal \cdot mol^{-1}$)	Difference
calcd + error	35.3	2.49	22.9	–7.79	23.5	–0.17
calcd	32.8	–	30.7	–	23.7	–
calcd - error	30.4	–2.49	38.5	7.79	23.9	0.17

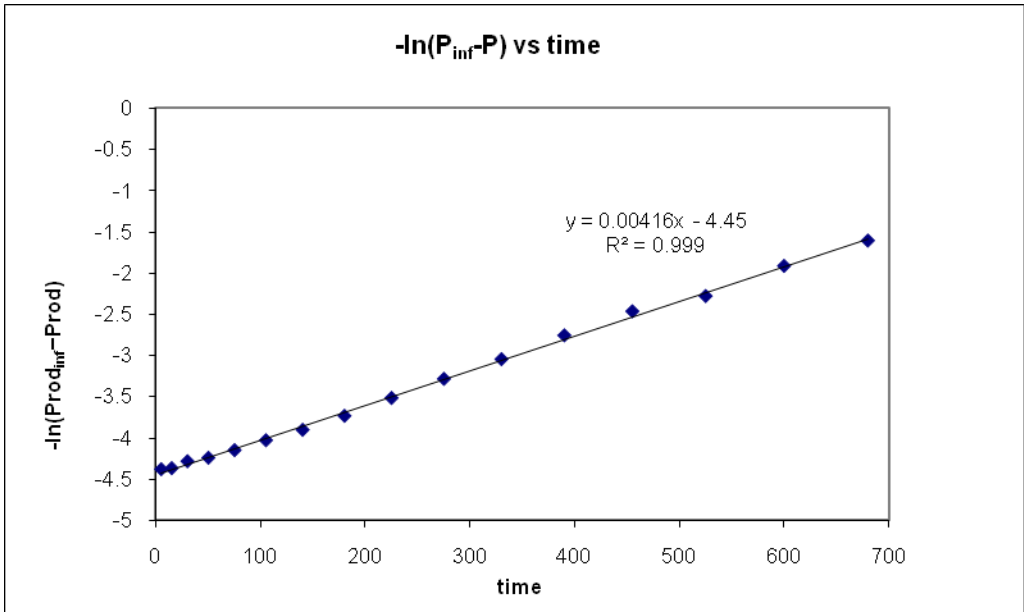
Dependence on acetonitrile concentration



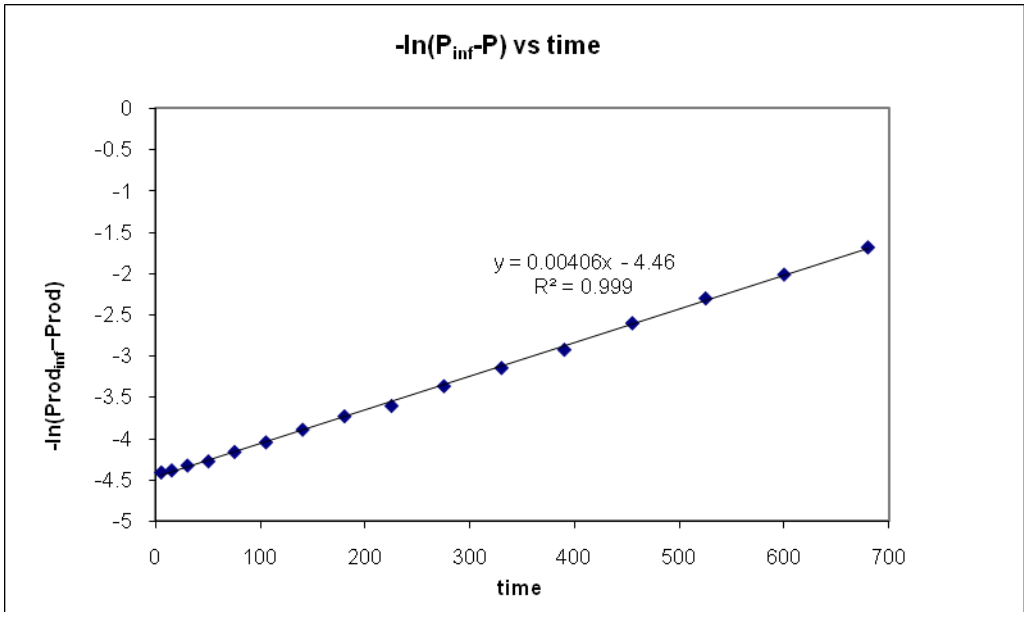
1

Solutions of compound **1** in various concentration (8.33─41.6 mM) were prepared by reacting compound **S4** (1.0 equiv) with 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo [2.2.2]octane bis-(tetrafluoroborate) (**S5**) (1.0 equiv) in NMR tubes under nitrogen. NMR samples were placed in the preheated NMR machine and the disappearance of compound **1** and formation of product **4** were monitored by integrating the peaks, at 6.33 ppm and 9.07 ppm respectively, relative to the peak of 1-chloromethyl-1,4-diazoniabicyclo [2.2.2]octane (tetrafluoroborate) at 4.91 ppm.

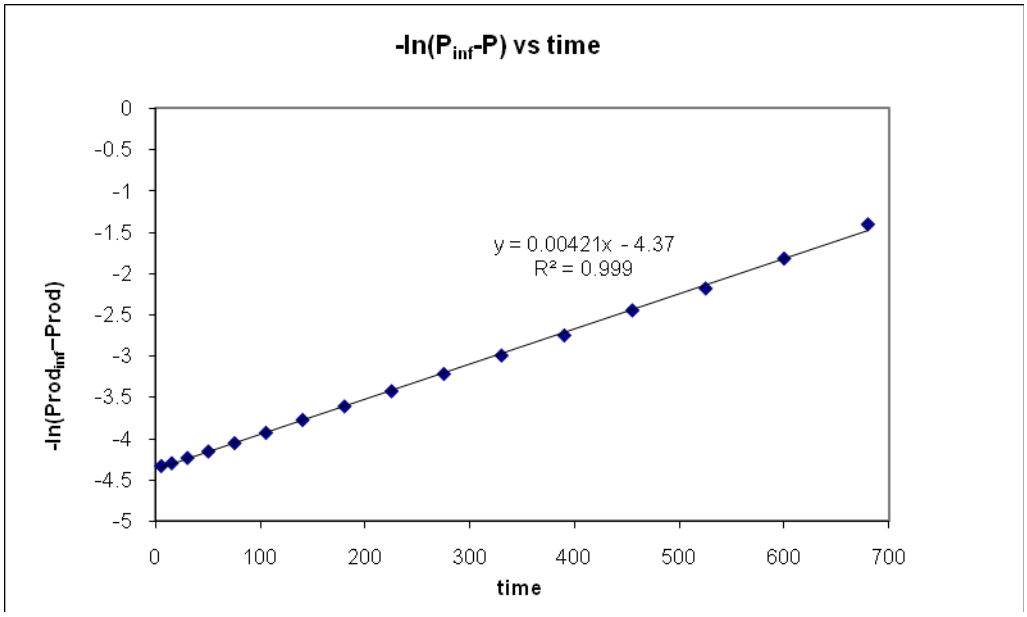
$Pd^{IV}F$ vs MeCN concentration = 1:2298



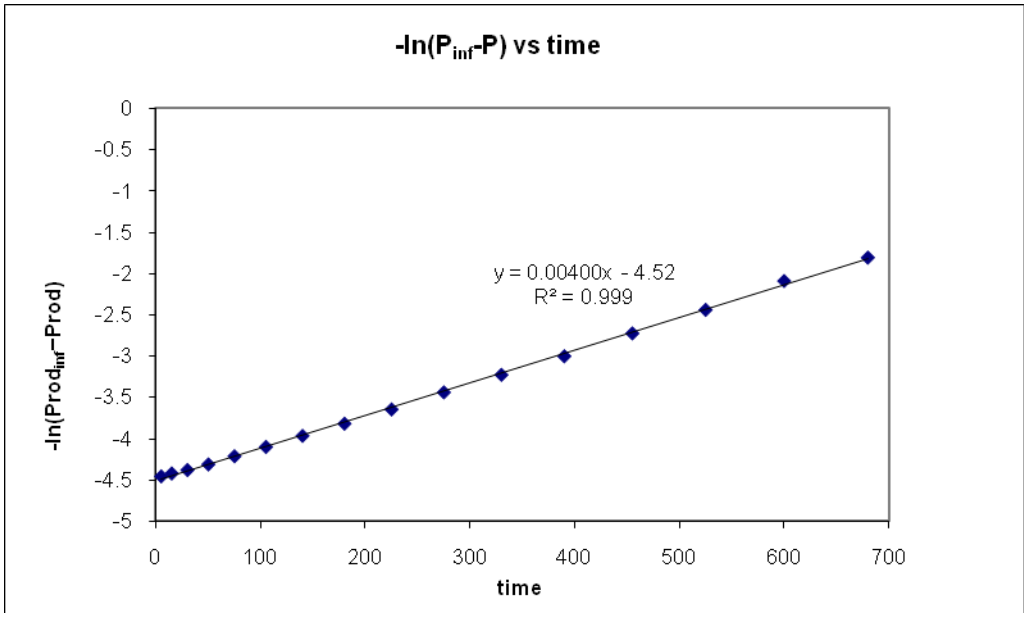
$Pd^{IV}F$ vs MeCN concentration = 1:1532



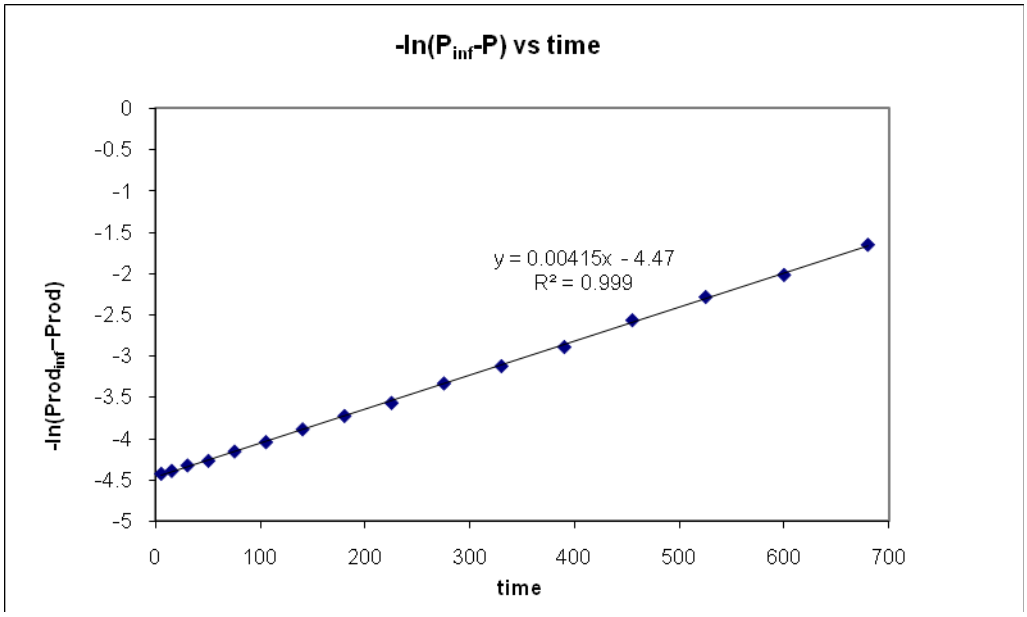
$Pd^{IV}F$ vs MeCN concentration = 1:1149



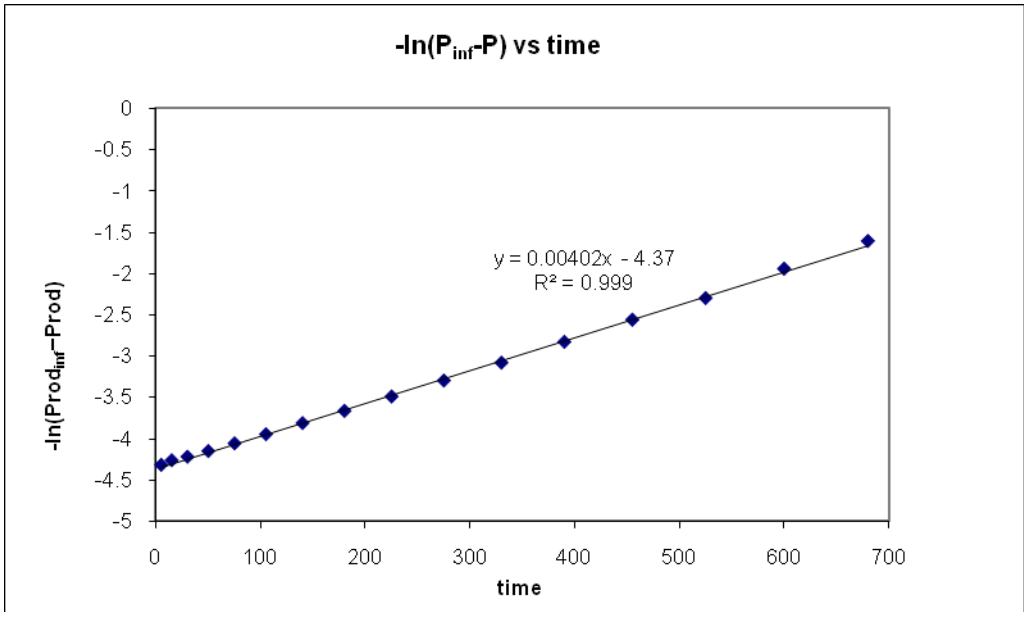
$Pd^{IV}F$ vs MeCN concentration = 1:766



$Pd^{IV}F$ vs MeCN concentration = 1:574

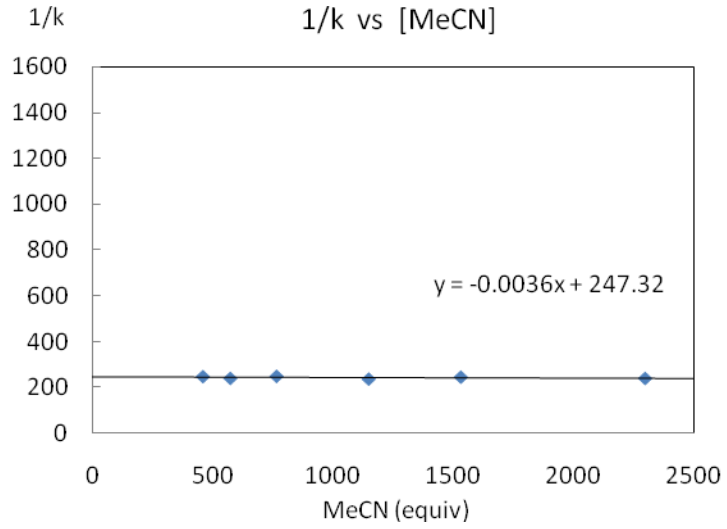


$Pd^{IV}F$ vs MeCN concentration = 1:460

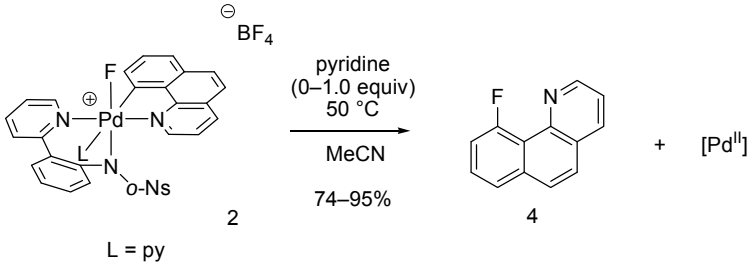


Relationship of rate vs. pyridine concentration

MeCN (equiv) (vs. $Pd^{IV}F$)	k (s^{-1})	1/k (s)	Fluorination Yield (%)
460	0.00402	249	95
574	0.00415	241	96
766	0.00400	250	95
1149	0.00421	237	97
1532	0.00406	246	94
2298	0.00416	240	93

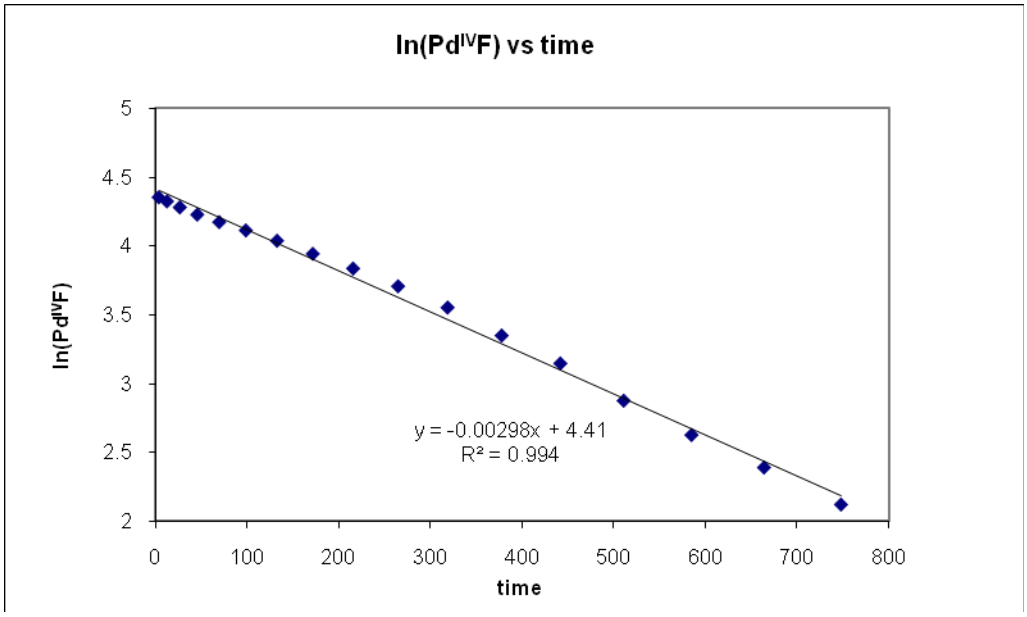


Dependence on pyridine concentration

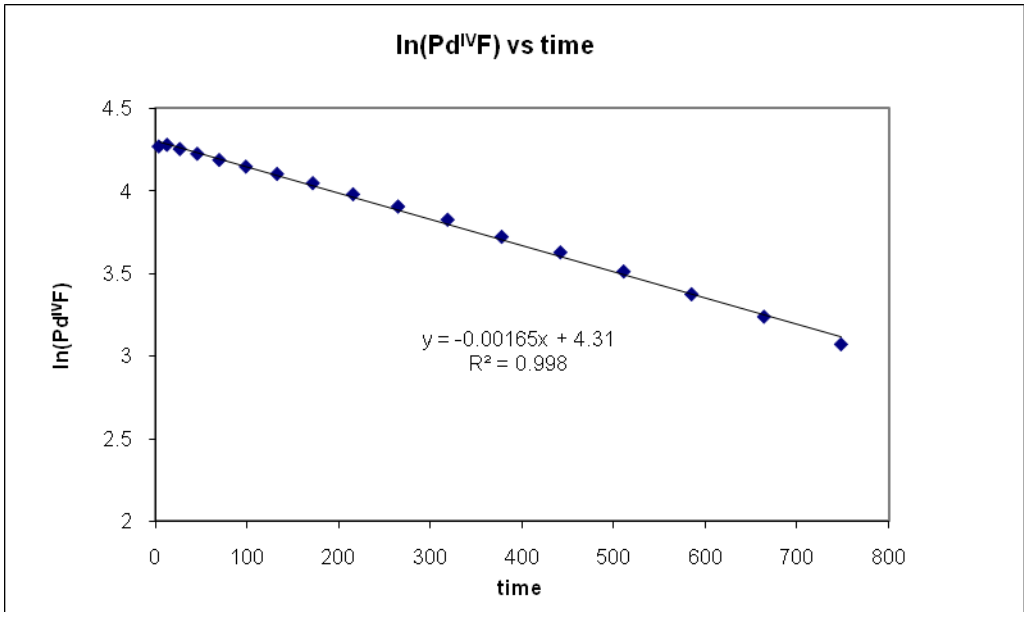


Solutions (33.3 mM) of compound **2** were prepared by reacting compound **S4** (12.8 mg, 0.0200 mmol, 1.00 equiv) with 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo [2.2.2]octane bis(tetrafluoroborate) (**S5**) (7.1 mg, 0.020 mmol, 1.0 equiv) and pyridine (1.00−2.00 equiv) in NMR tubes under nitrogen. NMR samples were placed in a preheated NMR machine and the disappearance of compound **2** was monitored by integrating the peak at 6.40 ppm relative to the peak of 1-chloromethyl-1,4-diazoniabicyclo [2.2.2]octane (tetrafluoroborate) at 4.91 ppm. Monitoring product formation was difficult because the competing coordination of pyridine and 10-fluorobenzo[*h*]quinoline complicated the ^{1}H NMR spectra. Further addition of pyridine resulted in significant decrease in fluorination yield. For example, when complex **2** was heated at 50 ºC in the presence of 2.0 equiv of additional pyridine, the yield of **4** was 43%. One of the side reaction observed by ^{1}H NMR was reduction of **2** to Pd(II) complex **13** similar to the thermal decomposition of **3**.

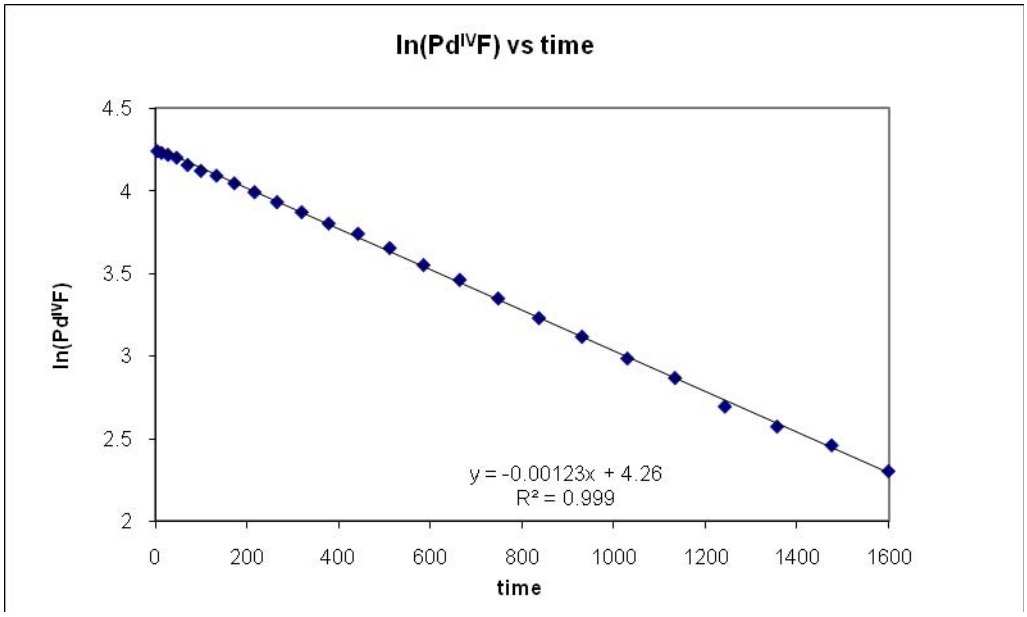
Kinetic data with 0 equiv of pyridine



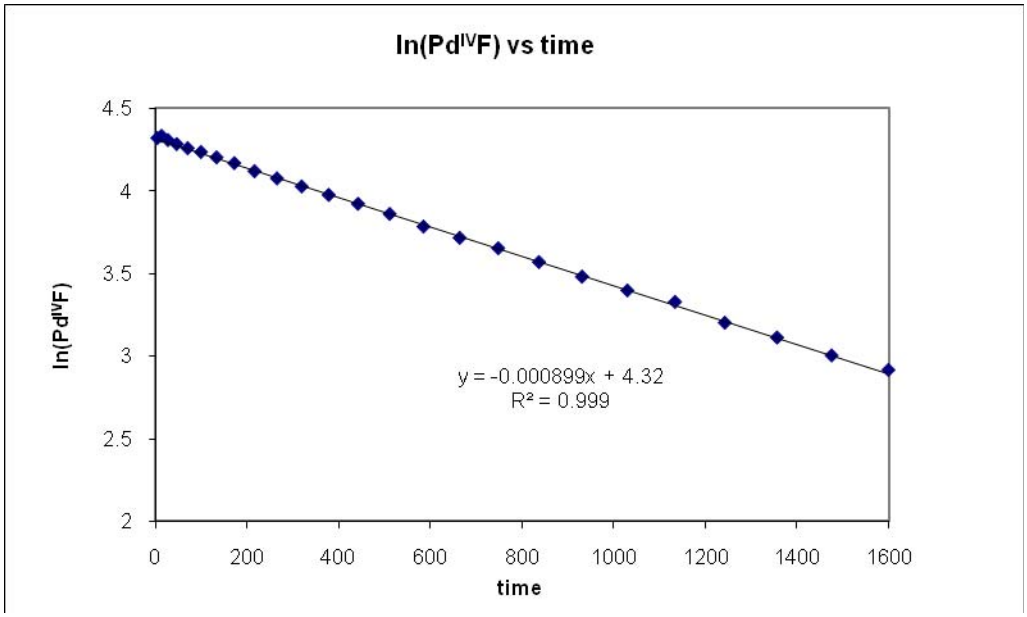
Kinetic data with 0.25 equiv of pyridine



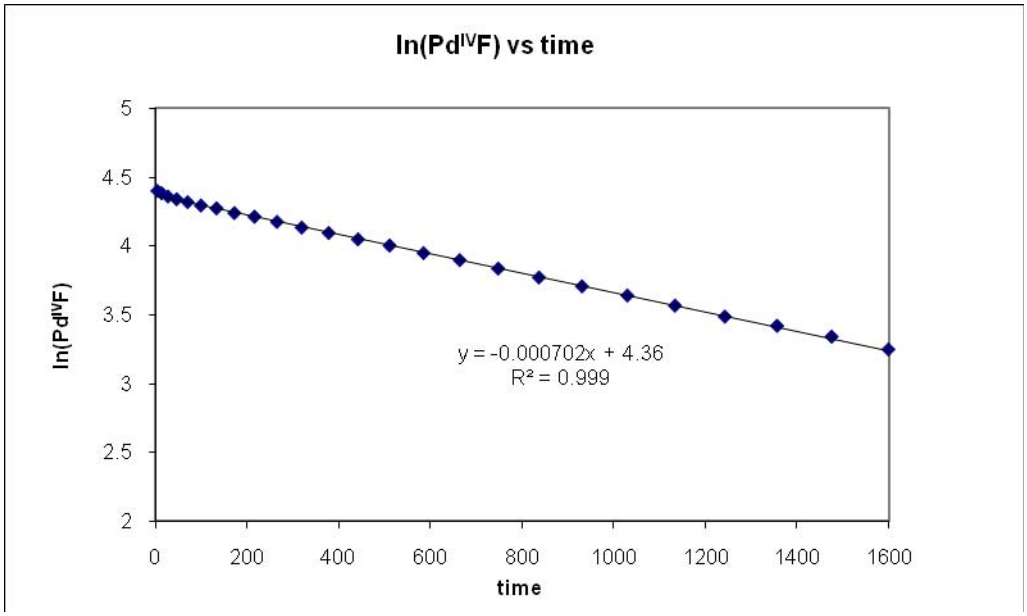
Kinetic data with 0.50 equiv of pyridine



Kinetic data with 0.75 equiv of pyridine

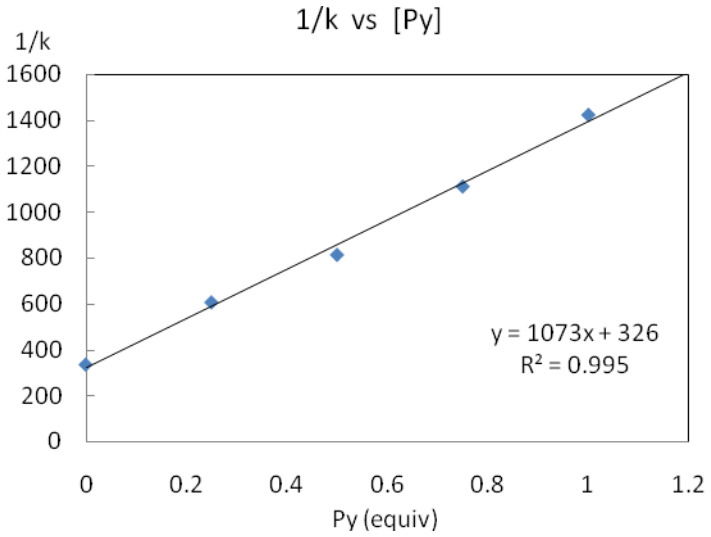


Kinetic data with 1.00 equiv of pyridine

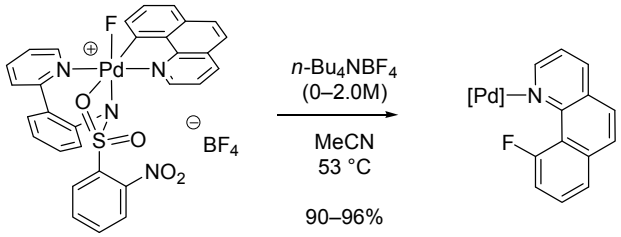


Relationship of rate vs pyridine concentrateion

py (equiv)	k (s^{-1})	1/k (s)	Fluorination Yield (%)
0	0.00298	336	95
0.25	0.00165	608	90
0.50	0.00123	814	86
0.75	0.000899	1112	80
1.00	0.000702	1425	74



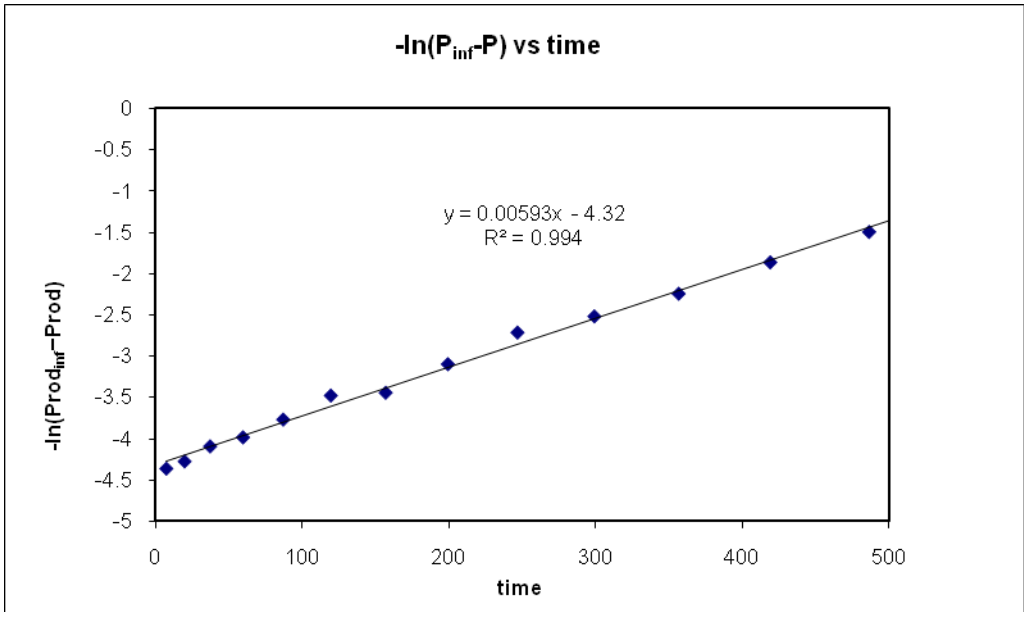
Rate dependence on *n*-Bu_4NBF_4



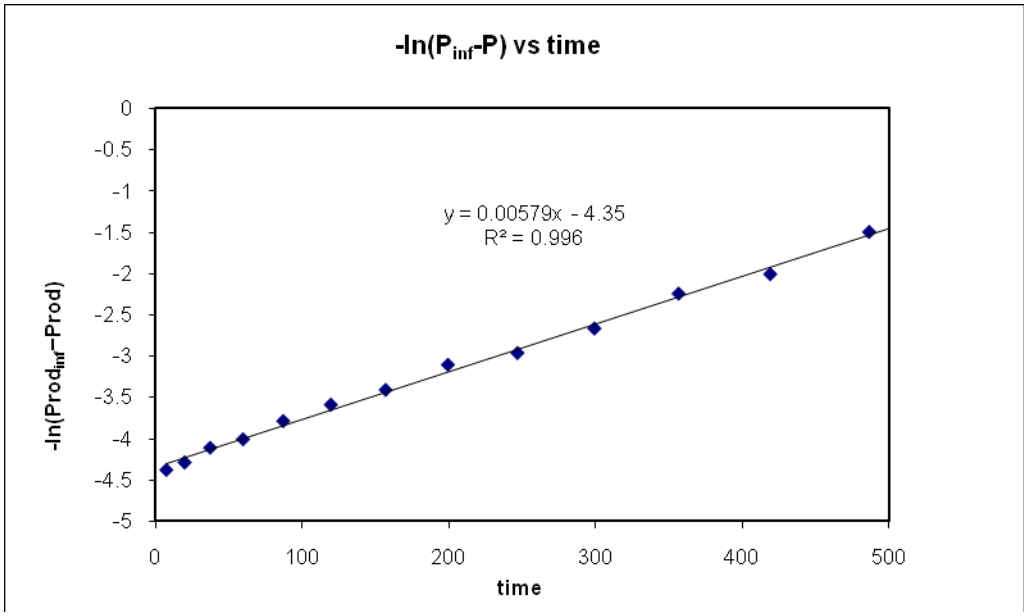
1

Solutions (16.7 mM) of compound **1** in acetonitrile (0.6 mL) were prepared by reacting compound **S4** (6.4 mg, 0.010 mmol, 1.0 equiv) with 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo [2.2.2]octane bis(tetrafluoroborate) (**S5**) (3.5 mg, 0.010 mmol, 1.0 equiv) and *n*-$BuNBF_4$ (0−2.0 M) in NMR tubes under nitrogen. NMR samples were placed in a preheated NMR machine (53 ºC) and the formation of the product was monitored by integrating the peak at −109 ppm (10-fluoro[*h*]benzoquinoline coordinated to Pd^{II}) relative to the peak at −115 ppm (4-fluorotoluene, internal standard, 1.1 μL, 0.010 mmol) in ^{19}F NMR.

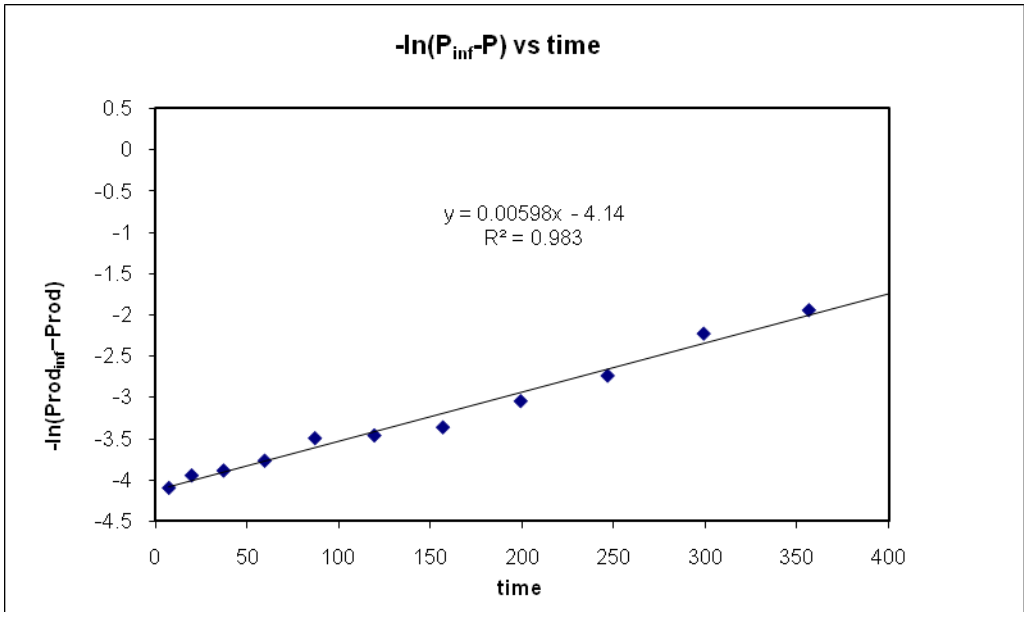
Kinetic data with 0 M of *n*-Bu_4NBF_4



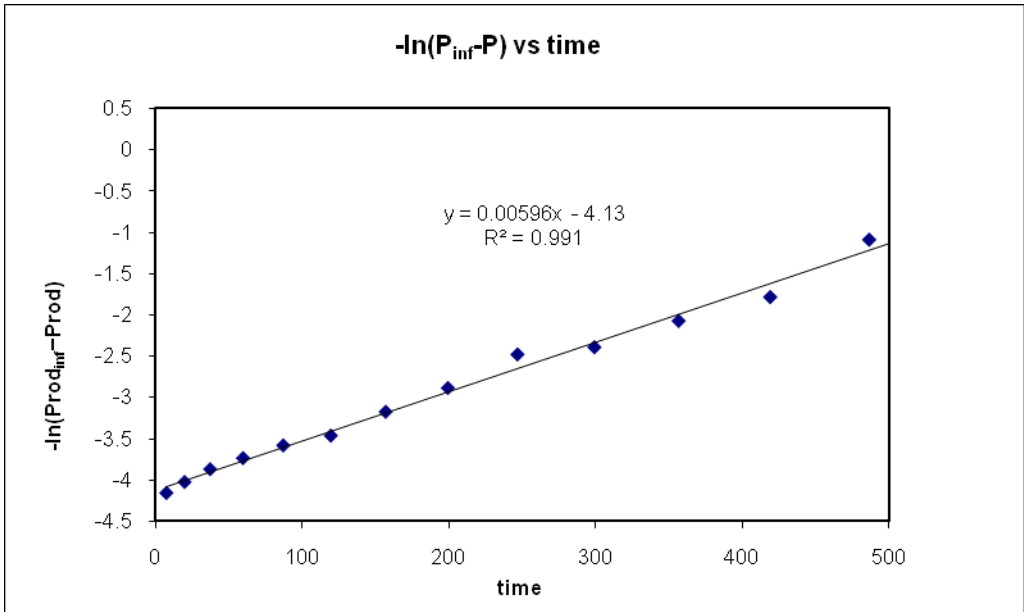
Kinetic data with 0.5 M of *n*-Bu_4NBF_4



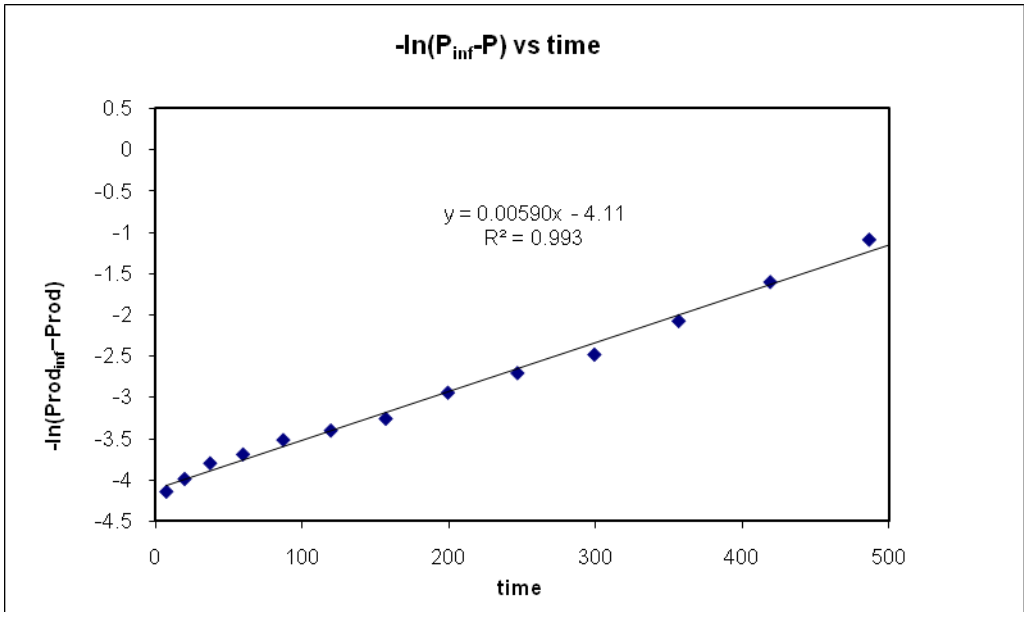
Kinetic data with 1.0 M of *n*-Bu_4NBF_4



Kinetic data with 1.5 M of *n*-Bu_4NBF_4

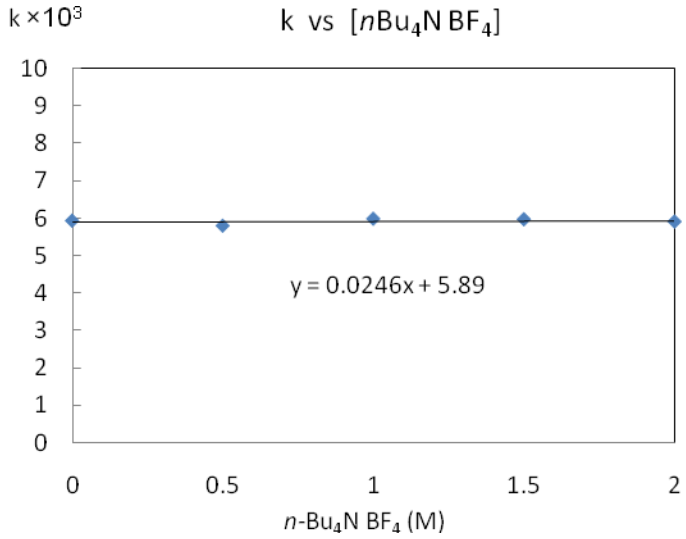


Kinetic data with 2.0 M of *n*-Bu_4NBF_4



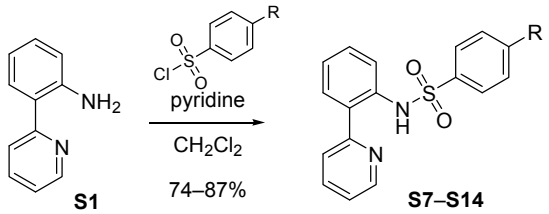
Relationship of rate vs *n*-Bu_4NBF_4 concentration

n-Bu_4NBF_4 (M)	k (s^{-1})	Fluorination Yield (%)
0	0.00593	96
0.5	0.00579	93
1.0	0.00598	93
1.5	0.00596	93
2.0	0.00590	90



Hammett plot for sulfonanilide substitution

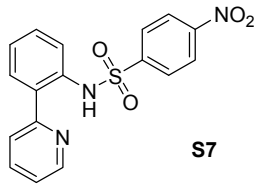
Synthesis of pyridinylsulfonanilide ligands with different sulfonanilide substitution



(R = NO_2, CN, Cl, F, Ph, H, Me, *t*-Bu)

To 2-(2-pyridinyl)aniline (**S1**) (1.00 mmol, 1.00 equiv) in CH_2Cl_2 (3 mL) at 0 ºC was added pyridine (121 µL, 1.50 mmol, 1.50 equiv) and a substituted sulfonyl chloride (1.40 mmol, 1.40 equiv). The reaction mixture was warmed to 23 ºC and stirred for 2.0 hr before the addition of water (3 mL). The phases were separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 2 mL). The combined organic phases were washed with brine (5 mL) and dried (Na_2SO_4). The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel to afford the correspondingly substituted 2-(2-pyridinyl)benzenesulfonanilide (74−87% yield).

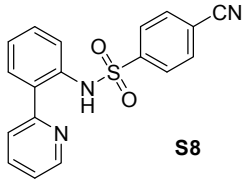
2-(2-Pyridinyl)-4-nitrobenzenesulfonanilide (S7)



S7

R_f = 0.12 (hexanes/EtOAc 7:3 (v/v)). 87% yield. NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 12.47 (br s, 1H), 8.60 (dd, *J* = 4.0 HZ, *J* = 1.0 Hz, 1H), 7.97 (d, *J* = 8.5 Hz, 2H), 7.73–7.68 (m, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.55 (dd, *J* = 7.5 Hz, *J* = 1.0 Hz, 1H), 7.41–7.37 (m, 2H), 7.28 (dd, *J* = 5.0 Hz, *J* = 2.5 Hz, 1H), 7.22 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 156.6, 149.6, 147.3, 144.8, 137.8, 135.7, 130.4, 128.5, 127.8, 127.6, 125.7, 124.0, 123.6, 122.4, 122.2. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{17}H_{13}N_3O_4S$ + Na], 378.05190. Found, 378.05196.

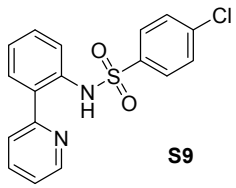
2-(2-Pyridinyl)-4-cyanobenzenesulfonanilide (S8)



S8

R_f = 0.25 (hexanes/EtOAc 4:1 (v/v)). 75% yield. NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 12.39 (br s, 1H), 7.73 (ddd, *J* = 8.0 Hz, *J* = 8.0 Hz, *J* = 2.0 Hz, 1H), 7.70 (dd, *J* = 8.5 Hz, *J* = 1.5 Hz, 1H), 7.56–7.52 (m, 3H), 7.44–7.36 (m, 5H), 7.29–7.27 (m, 1H), 7.21 (ddd, *J* = 7.5 Hz, *J* = 7.5 Hz, *J* = 1.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 156.5, 147.3, 143.2, 137.8, 135.8, 132.2, 130.3, 128.5, 127.6, 127.2, 125.6, 124.0, 122.3, 122.1, 117.2, 115.7. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{18}H_{13}N_3O_2S$ + Na], 358.06207. Found, 358.06245.

2-(2-Pyridinyl)-4-chlorobenzenesulfonanilide (S9)

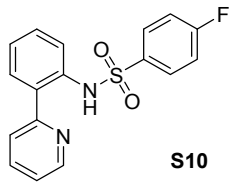


S9

R_f = 0.20 (hexanes/EtOAc 7:3 (v/v)). 87% yield. NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 12.13 (br s, 1H), 8.58 (d, *J* = 5.0 Hz, 1H), 7.74–7.69 (m, 2H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.39–7.34 (m,

4H), 7.26 (dd, *J* = 6.5 Hz, *J* = 6.5 Hz, 1H) 7.20 (dd, *J* = 7.5 Hz, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 156.8, 147.3, 138.6, 137.6, 137.5, 136.2, 130.2, 128.6, 128.5, 128.0, 128.0, 125.3, 124.1, 122.3, 122.2. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{17}H_{13}ClN_2O_2S$ + Na], 367.02785. Found, 367.02687.

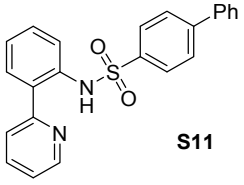
2-(2-Pyridinyl)-4-fluorobenzenesulfonanilide (S10)



S10

R_f = 0.12 (hexanes/EtOAc 7:3 (v/v)). 74% yield. NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 12.15 (br s, 1H), 8.59 (dd, *J* = 5.5 Hz, *J* = 1.0 Hz, 1H), 7.74–7.70 (m, 2H), 7.53 (dd, *J* = 9.0 Hz, *J* = 1.0 Hz, 1H), 7.45–7.35 (m, 5H), 7.26–7.24 (m, 1H), 7.20 (ddd, *J* = 7.5 Hz, *J* = 7.5 Hz, *J* = 1.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 164.7 (d, *J* = 253.0 Hz), 156.8, 147.3, 137.6, 136.3. 135.2 (d, *J* = 3.6 Hz), 130.2, 129.3 (d, *J* = 9.2 Hz), 128.5, 127.8. 125.2, 124.0. 122.2, 122.2, 115.6 (d, *J* = 22.0 Hz). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –106.2. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{17}H_{13}FN_2O_2S$ + H], 329.07545. Found, 329.07554.

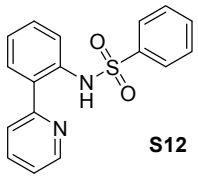
2-(2-Pyridinyl)-4-phenylbenzenesulfonanilide (S11)



S11

R_f = 0.25 (hexanes/EtOAc 4:1 (v/v)). 83% yield. NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 12.15 (br s, 1H), 8.59 (dd, *J* = 5.5 Hz, *J* = 1.0 Hz, 1H), 7.77 (dd, *J* = 8.0 Hz, *J* = 1.5 Hz, 1H), 7.63 (ddd, *J* = 8.0 Hz, *J* = 8.0 Hz, *J* = 2.0 Hz, 1H), 7.52–7.31 (m, 11H), 7.23 (ddd, *J* = 4.5 Hz, *J* = 7.0 *J* = 1.0 Hz, 1H), 7.18 (ddd, *J* = 7.5 Hz, *J* = 7.5 Hz, *J* = 1.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 156.8, 147.2, 144.9, 139.1, 137.5, 137.4, 136.4, 130.0, 128.9, 128.4, 128.3, 128.0, 127.0, 127.0, 126.9, 125.0, 124.0, 122.2, 122.0. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{23}H_{18}N_2O_2S$ + Na], 409.09812. Found, 409.09709.

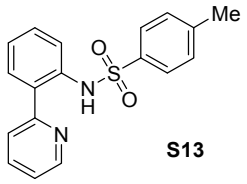
2-(2-Pyridinyl)-4-benzenesulfonanilide (S12)



S12

R_f = 0.25 (hexanes/EtOAc 7:3 (v/v)). 74% yield. NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 12.20 (br s, 1H), 8.59 (d, *J* = 5.5 Hz, 1H), 7.72–7.67 (m, 2H), 7.52 (d, *J* = 8.5 Hz, 1H), 7.46–7.45 (m, 2H), 7.37–7 .31 (m, 3H) 7.23 (dd, *J* = 7.5 Hz, *J* = 5.0 Hz, 1H), 7.18–7.14 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 156.9, 147.3, 139.1, 137.6, 136.6, 132.1, 130.1, 128.5, 128.5, 127.6, 126.6, 124.8, 123.6, 122.2, 122.0. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{17}H_{14}N_2O_2S$ + Na], 333.06682. Found, 333.06713.

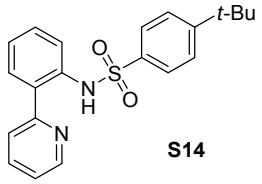
2-(2-Pyridinyl)-4-toluenesulfonanilide (S13)



S13

R_f = 0.30 (hexanes/EtOAc 7:3 (v/v)). 80% yield. NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 12.17 (s, 1H), 8.61 (d, *J* = 4.5 Hz, 1H), 7.74–7.71 (m, 2H), 7.54 (d, *J* = 7.5 Hz, 1H), 7.42–7.34 (m, 4H), 7.28–7.25 (m, 1H), 7.17 (dd, *J* = 8.5 Hz, *J* = 8.5 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 2H), 2.28 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 157.0, 147.3, 142.9, 137.4, 136.7, 136.3, 130.1, 129.1, 128.4, 127.4, 126.7, 124.6, 123.3, 122.2, 122.0, 21.3. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{18}H_{16}N_2O_2S$ + Na], 347.08247. Found, 347.08296.

2-(2-Pyridinyl)-4-*tert*-butylbenzeneesulfonanilide (S14)

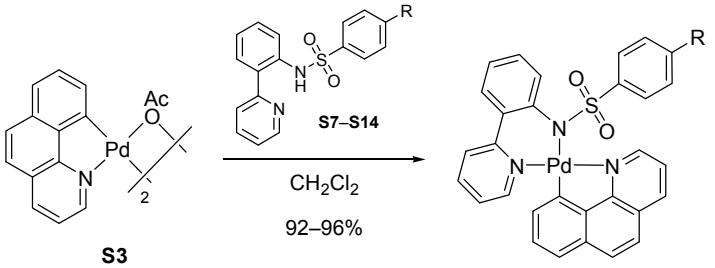


S14

R_f = 0.25 (hexanes/EtOAc 4:1 (v/v)). 86% yield. NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 12.02 (s, 1H), 8.57 (dd, *J* = 5.0 Hz, *J* = 1.0 Hz, 1H), 7.71 (dd, *J* = 7.5 Hz, *J* = 1.0 Hz, 1H), (ddd, *J* = 8.0 Hz, *J* = 8.0 Hz, *J* = 2.0 Hz, 1H), 7.50 (dd, *J* = 7.5 Hz, *J* = 1.0 Hz, 1H), 7.38–7.28 (m, 4H), 7.23–7.13

(m, 3H), 1.21 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 156.9, 155.8, 147.3, 137.4, 136.6, 136.1, 130.0, 128.4, 128.0, 126.4,3, 125.4, 124.9, 124.1, 122.1, 121.9, 34.8, 30.9. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{21}H_{22}N_2O_2S$ + H], 367.14748. Found, 367.14798.

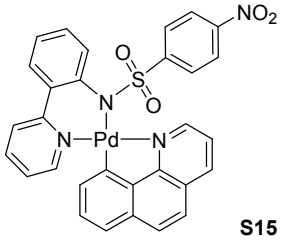
Synthesis of Pd(II) complexes with different sulfonanilide substitution



(R = NO_2, CN, Cl, F, Ph, H, Me, *t*-Bu)

To benzo[*h*]quinolinyl palladium acetate dimer (**S3**) (100 mg, 0.145 mmol, 1.00 equiv) in CH_2Cl_2 (2 mL) at 23 ºC was added a substituted pyridinylsulfonanilide ligand **S7**–**S14** (0.291 mmol, 2.00 equiv). After stirring for 1.0 hr the reaction mixture was concentrated in vacuo. The resulting residue was triturated with Et_2O (3 × 1 mL) to afford the corresponding substituted palladium(II) complex (92−96% yield).

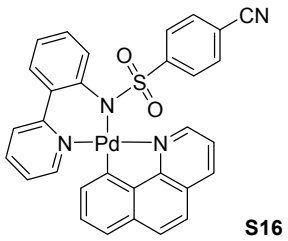
4-Nitrobenzenesulfonanilido palladium(II) complex S15



S15

92% yield. NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 9.59 (dd, *J* = 5.5 Hz, *J* = 1.5 Hz, 1H), 8.89 (dd, *J* = 6.0 Hz, *J* = 1.5 Hz, 1H), 8.33 (dd, *J* = 8.0 Hz, *J* = 1.5 Hz, 1H), 7.81–7.74 (m, 3H), 7.68–7.58 (m, 5H), 7.52–7.50 (m, 3H), 7.38–7.35 (m, 2H), 7.30 (dd, *J* =7.0 Hz, *J* =7.0 Hz, 1H), 7.22 (ddd, *J* = 8.0 Hz, *J* = 8.0 Hz, *J* = 1.0 Hz, 1H), 7.06 (d, *J* = 10.5, 1H), 6.95 (d, *J* = 6.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 157.9, 155.3, 154.4, 153.7, 150.8, 149.8, 147.9, 142.2, 142.2, 138.4, 137.5, 135.7, 133.2, 131.9, 130.9, 130.3, 129.3, 128.8, 128.3, 126.7, 126.6, 124.8, 124.7, 123.6, 123.4, 123.3, 123.2, 121.7. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{30}H_{20}N_4O_4PdS$ + H], 639.03183. Found, 639.03155.

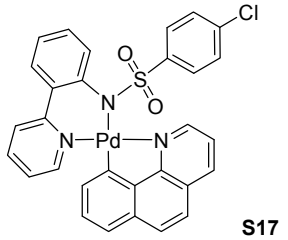
4-Cyanobenzenesulfonanilido palladium(II) complex S16



S16

93% yield. NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 9.58 (dd, *J* = 1.5 Hz, *J* = 5.5 Hz, 1H), 8.88 (dd, *J* = 1.0 Hz, *J* = 5.5 Hz, 1H), 8.32 (dd, *J* = 1.5 Hz, *J* = 8.0 Hz, 1H), 7.80–7.73 (m, 3H), 7.66 (dd, *J* = 5.0 Hz, *J* = 8.0 Hz, 1H), 7.60 (dd, *J* = 8.5 Hz, *J* = 12.5 Hz, 2H), 7.50 (dd, *J* = 7.5 Hz, *J* = 7.5 Hz, 1H), 7.43 (d, *J* = 7.0 Hz, 2H), 7.38–7.33 (m, 3H), 7.26–7.20 (m, 3H), 7.08 (d, *J* = 8.0 Hz, 1H), 6.96 (d, *J* = 7.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 157.8, 155.4, 154.4, 153.7, 150.8, 148.1, 142.3, 142.1, 138.5, 137.4, 135.7, 133.2, 131.9, 131.7, 130.9, 130.3, 129.2, 128.8, 128.3, 126.7, 126.3, 124.8, 124.6, 123.5, 123.4, 123.3, 121.6, 118.1, 112.7. Anal: calcd for $C_{31}H_{20}N_4O_2PdS$: C, 60.15; H, 3.26; N, 9.05; found: C, 59.89; H, 3.09; N, 8.94.

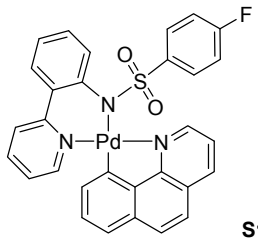
4-Chlorobenzenesulfonanilido palladium(II) complex S17



S17

94% yield. NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 9.63 (dd, *J* = 1.5 Hz, *J* = 5.5 Hz, 1H), 8.88 (dd, *J* = 2.0 Hz, *J* = 5.5 Hz, 1H), 8.31 (dd, *J* = 1.5 Hz, *J* = 8.0 Hz, 1H), 7.80–7.72 (m, 3H), 7.63 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H), 7.60 (dd, *J* = 5.5 Hz, *J* = 8.0 Hz, 1H), 7.59 (dd, *J* = 9.0 Hz, *J* = 12.5 Hz, 2H), 7.48 (dd, *J* = 7.5 Hz, *J* = 7.5 Hz, 1H), 7.38–7.33 (m, 3H), 7.32 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H), 7.19 (dd, *J* = 7.5 Hz, *J* = 7.5 Hz, 1H), 7.08 (d, *J* = 3.0, 1H), 6.99 (d, *J* = 7.0 Hz, 1H), 6.90–6.89 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 157.8, 155.4, 154.9, 153.6, 150.9, 142.8, 142.4, 142.2, 138.4, 137.3, 136.2, 135.3, 133.2, 131.7, 130.9, 130.5, 129.2, 128.7, 128.3, 128.0, 127.1, 126.6, 124.9, 124.3, 123.5, 123.4, 123.2, 121.6. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{30}H_{20}ClN_3O_2PdS$ + H], 628.00723. Found, 628.00483.

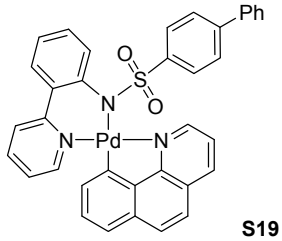
4-Fluorobenzenesulfonanilido palladium(II) complex S18



S18

94% yield. NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 9.64 (dd, *J* = 1.5 Hz, *J* = 5.5 Hz, 1H), 8.90 (dd, *J* = 1.0 Hz, *J* = 6.0 Hz, 1H), 8.30 (dd, *J* = 1.5 Hz, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.75–7.71 (m, 2H), 7.64 (dd, *J* = 8.0 Hz, *J* = 5.5 Hz, 1H), 7.58 (dd, *J* = 8.5 Hz, *J* = 8.5 Hz, 2H), 7.47 (ddd, *J* = 8.0 Hz, *J* = 8.0 Hz, *J* = 1.5, 1H), 7.38–7.28 (m, 5H), 7.19 (td, *J* = 7.5 Hz, *J* = 1.0 Hz, 1H), 7.08 (d, *J* = 8.5, 1H), 6.99 (d, *J* = 7.0 Hz, 1H), 6.61 (dd, *J* = 8.5 Hz, *J* = 8.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 163.1 (d, *J* = 248.5 Hz), 157.9, 155.4, 154.9, 153.6, 150.9, 142.9, 142.2, 140.1 (d, *J* = 2.8 Hz), 138.4, 137.3, 136.2, 133.1, 131.7, 130.9, 130.4, 129.1, 128.7, 128.2, 127.9 (d, *J* = 8.3 Hz), 126.6, 124.8, 124.2, 123.5, 123.3, 123.1, 121.6, 114.7 (d, *J* = 21.9 Hz). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –111.7. Anal: calcd for $C_{30}H_{20}FN_3O_2PdS$: C, 58.88; H, 3.29; N, 6.87; found: C, 58.64; H, 3.15; N, 6.69.

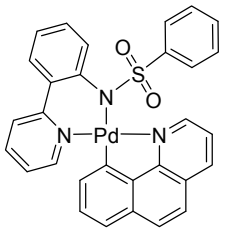
4-Phenylbenzenesulfonanilido palladium(II) complex S19



S19

96% yield. NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 9.68 (dd, *J* = 5.5 Hz, *J* = 1.5 Hz, 1H), 8.87 (d, *J* = 5.5 Hz, 1H), 8.27 (dd, *J* = 8.0 Hz, *J* = 1.5 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 9.0 Hz, 1H), 7.63 (dd, *J* = 8.0 Hz, *J* = 5.0 Hz, 1H), 7.58–7.45 (m, 8H), 7.39–7.33 (m, 3H), 7.26–7.14 (m, 5H), 7.02 (d, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 160.3, 155.4, 155.1, 153.6, 150.9, 143.1, 142.6, 142.2, 141.9, 140.1, 138.2, 137.2, 136.3, 133.1, 131.6, 130.9, 130.6, 129.1, 128.9, 128.6, 128.2, 127.8, 126.9, 126.6, 126.5, 126.1, 124.8, 124.2, 123.5, 123.1, 123.1, 121.6. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{36}H_{25}N_3O_2PdS$ + H], 670.07661. Found, 670.07661.

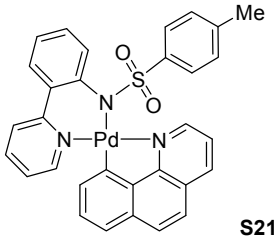
Benzenesulfonanilido palladium(II) complex S20



S20

92% yield. NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 9.67 (d, *J* = 5.0 Hz, 1H), 8.87 (d, *J* = 5.5 Hz, 1H), 8.27 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.71–7.55 (m, 5H), 7.47 (dd, *J* = 7.5 Hz, *J* = 7.5 Hz, 1H), 7.36–7.21 (m, 5H), 7.16 (dd, *J* = 7.5 Hz, *J* = 7.5 Hz, 1H), 7.06–6.98 (m, 3H), 6.95–6.92 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 157.8, 155.4, 155.1, 153.5, 151.0, 143.9, 143.2, 142.2, 138.4, 137.2, 136.3, 133.1, 131.5, 130.9, 130.3, 129.2, 129.0, 128.7, 128.2, 127.9, 126.6, 125.6, 124.7, 124.1, 123.5, 123.2, 123.1, 121.6. Anal: calcd for $C_{30}H_{21}N_3O_2PdS$: C, 60.66; H, 3.56; N, 7.07; found: C, 60.88; H, 3.39; N, 6.96.

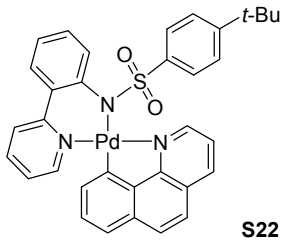
4-Toluenesulfonanilido palladium(II) complex S21



S21

93% yield. NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 9.68 (dd, *J* = 5.5 Hz, *J* = 1.5 Hz, 1H), 8.88 (dd, *J* = 6.0 Hz, *J* = 1.5 Hz, 1H), 8.29 (dd, *J* = 8.5 Hz, *J* = 1.5 Hz, 1H), 7.80 (dd, *J* = 8.5 Hz, *J* = 1.5 Hz, 1H), 7.71 (dd, *J* = 8.5 Hz, *J* = 1.5 Hz, 1H), 7.72 (d, *J* = 8.5 Hz, 1H), 7.66–7.63 (m, 2H), 7.60–7.56 (m, 2H), 7.46–7.44 (m, 1H), 7.37–7.33 (m, 2H), 7.27–7.14 (m, 4H), 7.04 (d, *J* = 8.5 Hz, 1H), 7.00 (d, *J* = 5.0 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 2H), 2.21 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 158.1, 155.7, 155.5, 153.8, 151.3, 143.6, 142.5, 141.3, 139.4, 138.2, 137.4, 136.6, 133.3, 131.8, 131.2, 130.7, 129.3, 128.9, 128.7, 128.4, 126.8, 125.9, 124.9, 124.2, 123.7, 123.4, 123.3, 121.8, 21.4. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{31}H_{23}N_3O_2PdS$ + H], 608.06186. Found, 608.05922.

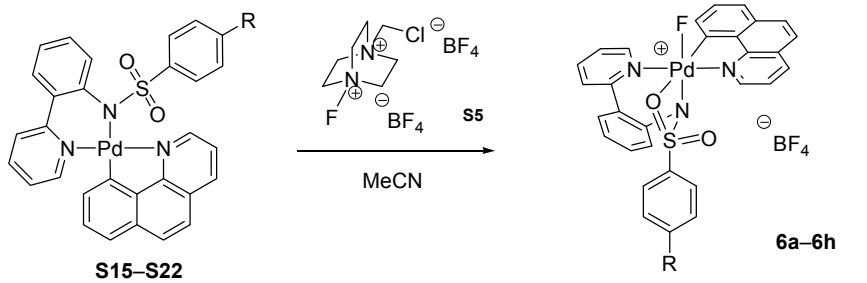
4-*tert*-Butylbenzenesulfonanilido palladium(II) complex S22



S22

92% yield. NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 9.68 (d, *J* = 5.5 Hz, 1H), 8.90 (d, *J* = 5.5 Hz, 1H), 8.29 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 7.5 Hz, 1H), 7.72 (d, *J* = 8.5 Hz, 1H), 7.66–7.55 (m, 4H), 7.47 (dd, *J* = 7.5 Hz, *J* = 7.5 Hz, 1H), 7.38–7.32 (m, 2H), 7.25–7.20 (m, 3H), 7.16 (dd, *J* = 7.5 Hz, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 8.5 Hz, 1H), 7.00 (d, *J* = 5.0 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 2H), 1.23 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 157.9, 155.5, 155.3, 153.6, 152.2, 151.0, 143.3, 142.2, 141.1, 138.2, 137.2, 136.3, 133.1, 131.6, 130.9, 130.5, 129.0, 128.6, 128.2, 126.6, 125.4, 124.8, 124.5, 124.0, 123.5, 123.0, 123.0, 121.6, 34.5, 31.2. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{34}H_{29}N_3O_2PdS$ + H], 650.10936. Found, 650.10911.

Synthesis of monofluoro Pd(IV) complexes with different sulfonanilide substitution

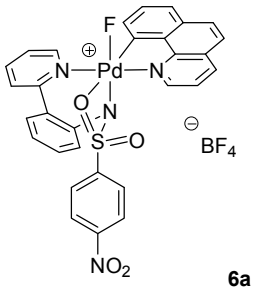


S15–S22 **6a–6h**

(R = NO_2, CN, Cl, F, Ph, H, Me, *t*-Bu)

To benzo[*h*]quinolinyl palladium(II) pyrdine-sulfonamido complex **S15**–**S22** (0.020 mmol, 1.0 equiv) in acetonitrile-*d3* (0.6 mL) at 23 ºC was added 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo [2.2.2]octane bis(tetrafluoroborate) (**S5**) (7.1 mg, 0.020 mmol, 1.0 equiv). After stirring for 10 min at 23 ºC, the colorless suspension formed a dark purple solution. Compounds **6a**–**6h** were characterized by NMR spectroscopy in acetonitrile solution without purification.

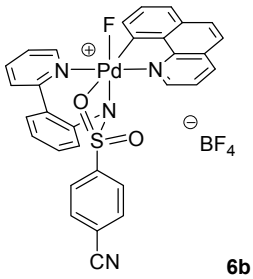
4-Nitrobenzenesulfonanilido palladium(IV) complex 6a



6a

NMR Spectroscopy: ^{1}H NMR (600 MHz, acetonitrile-*d3*, 25 ºC, δ): 9.66 (d, *J* = 6.0 Hz, 1H), 9.33 (d, *J* = 6.0 Hz, 1H), 8.89 (d, *J* = 7.8 Hz, 1H), 8.25 (dd, *J* = 8.4 Hz, *J* = 8.4 Hz, 1H), 8.07–7.96 (m, 6H), 7.83–7.78 (m, 2H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.66 (dd, *J* = 7.8 Hz, *J* = 1.8 Hz, 1H), 7.40 (d, *J* = 9.0 Hz, 1H), 7.28 (ddd, *J* = 9.0 Hz, *J* = 9.0 Hz, *J* = 1.2 Hz, 1H), 7.03–7.00 (m, 2H), 6.74 (d, *J* = 7.8 Hz, 1H), 6.22 (d, *J* = 8.4 Hz, 1H). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –152.0 (s), –281.1 (br, s).

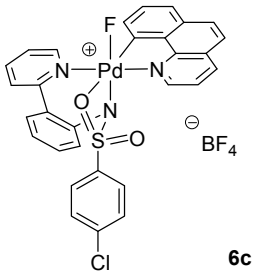
4-Cyanobenzenesulfonanilido palladium(IV) complex 6b



6b

NMR Spectroscopy: ^{1}H NMR (600 MHz, acetonitrile-*d3*, 25 ºC, δ): 9.65 (d, *J* = 5.4 Hz, 1H), 9.32 (d, *J* = 5.4 Hz, 1H), 8.88 (d, *J* = 8.4 Hz, 1H), 8.30 (dd, *J* = 7.8 Hz, *J* = 7.8, 1H), 8.06–8.04 (m, 3H), 7.99 (d, *J* = 8.4 Hz, 1H), 8.82 (ddd, *J* = 7.8 Hz, *J* = 7.8 Hz, *J* = 1.8 Hz, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.66 (dd, *J* = 7.8 Hz, *J* = 1.2 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.34–7.31 (m, 2H), 7.27 (ddd, *J* = 7.8 Hz, *J* = 7.8 Hz, *J* = 1.2 Hz, 1H), 7.02–6.98 (m, 2H), 6.72 (d, *J* = 6.72 Hz, 1H), 6.21 (d, *J* = 8.4 Hz, 1H). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –152.1 (s), –280.7 (br, s).

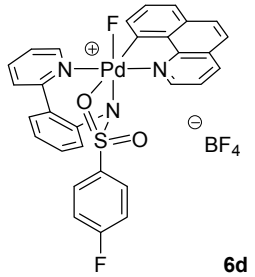
4-Chlorobenzenesulfonanilido palladium(IV) complex 6c



6c

NMR Spectroscopy: ^{1}H NMR (600 MHz, acetonitrile-*d3*, 25 ºC, δ): 9.65 (d, *J* = 5.4, 1H), 9.36 (d, *J* = 6.0 Hz, 1H), 8.87 (dd, *J* = 8.4 Hz, *J* = 1.2 Hz, 1H), 8.31 (dd, *J* = 7.2 Hz, *J* = 7.2 Hz, 1H), 8.05–8.03 (m, 2H), 7.98 (d, *J* = 9.0, 1H), 7.83 (ddd, *J* = 7.2 Hz, *J* = 7.2 Hz, *J* = 1.2 Hz, 1H), 7.74 (d, *J* = 7.2 Hz, 1H), 7.66 (dd, *J* = 7.8 Hz, *J* = 1.8 Hz, 1H), 7.24 (ddd, *J* = 7.8 Hz, *J* = 7.8 Hz, *J* = 0.6 Hz, 1H), 7.20–7.19 (m, 5H), 7.02–6.95 (m, 2H), 6.73 (d, *J* = 8.4 Hz, 1H), 6.21 (d, *J* = 8.4 Hz, 1H). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –152.0 (s), –279.1 (br, s).

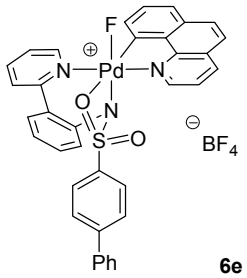
4-Fluorobenzenesulfonanilido palladium(IV) complex 6d



6d

NMR Spectroscopy: ^{1}H NMR (600 MHz, acetonitrile-*d3*, 25 ºC, δ): 9.66 (d, *J* = 5.4 Hz, 1H), 9.37 (d, *J* = 6.0 Hz, 1H), 8.87 (d, *J* = 7.8 Hz, 1H), 8.31 (dd, *J* = 7.8 Hz, *J* = 7.8 Hz, 1H), 8.10 (d, *J* = 7.8 Hz, 1H), 8.05–8.03 (m, 2H), 7.98 (d, *J* = 9.0 Hz, 1H), 7.83 (dd, *J* = 7.2 Hz, *J* = 7.2 Hz, 1H), 7.66 (dd, *J* = 8.4 Hz, *J* = 4.8 Hz, 1H), 7.27 (dd, *J* = 8.4 Hz, *J* = 8.4 Hz, 2H), 7.23 (dd, *J* = 7.2 Hz, *J* = 7.2 Hz, 1H), 7.01 (dd, *J* = 7.2 Hz, *J* = 7.2 Hz, 1H), 6.97–6.90 (m, 4H), 6.73 (d, *J* = 7.8 Hz, 1H), 6.21 (d, *J* = 7.8 Hz, 1H). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –107.9 (s), –152.1 (s), –278.6 (br, s).

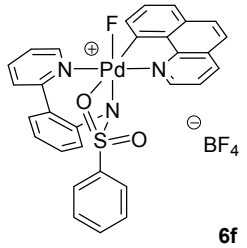
4-Phenylbenzenesulfonanilido palladium(IV) complex 6e



6e

NMR Spectroscopy: ^{1}H NMR (600 MHz, acetonitrile-*d3*, 25 ºC, δ): 9.76 (d, *J* = 6.0 Hz, 1H), 9.43 (d, *J* = 6.0 Hz, 1H), 8.94 (d, *J* = 7.8 Hz, 1H), 8.27 (dd, *J* = 7.2 Hz, *J* = 7.2 Hz, 1H), 8.13–8.09 (m, 3H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.87 (dd, *J* = 6.0 Hz, *J* = 6.0 Hz, 1H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.61 (d, *J* = 7.2 Hz, 2H), 7.56–7.53 (m, 2H), 7.51–7.48 (m, 3H), 7.34–7.30 (m, 3H), 7.09– 7.04 (m, 2H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.28 (d, *J* = 8.4 Hz, 1H). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –152.1 (s), –278.5 (br, s).

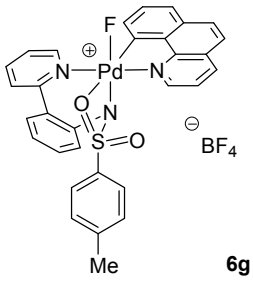
Benzenesulfonanilido palladium(IV) complex 6f



6f

NMR Spectroscopy: ^{1}H NMR (600 MHz, acetonitrile-*d3*, 25 ºC, δ): 9.74 (d, *J* = 5.4 Hz, 1H), 9.44 (d, *J* = 6.0 Hz, 1H), 8.94 (d, *J* = 7.2 Hz, 1H), 8.36 (dd, *J* = 7.8 Hz, *J* = 7.8 Hz, 1H), 8.14–8.10 (m, 3H), 8.05 (d, *J* = 9.0 Hz, 1H), 7.89 (dd, *J* = 7.2 Hz, *J* = 1.2 Hz, 1H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.71 (dd, *J* = 8.4 Hz, *J* = 1.8 Hz, 1H), 7.45 (dd, *J* = 7.2 Hz, *J* = 7.2 Hz, 1H), 7.32–7.24 (m, 5H), 7.07 (t, *J* = 8.4 Hz, 1H), 7.01 (ddd, *J* = 7.2 Hz, *J* = 7.2 Hz, *J* = 1.2 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 6.23 (d, *J* = 8.4 Hz, 1H). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –152.1 (s), –278.2 (br, s).

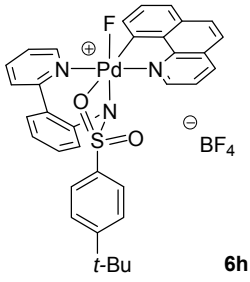
4-Toluenesulfonanilido palladium(IV) complex 6g



6g

NMR Spectroscopy: ^{1}H NMR (600 MHz, acetonitrile-*d3*, 25 ºC, δ): 9.73 (dd, *J* = 5.4 Hz, *J* = 0.6 Hz, 1H), 9.45 (d, *J* = 6.6 Hz, 1H), 8.93 (dd, *J* = 8.4 Hz, *J* = 1.2 Hz, 1H), 8.37 (dd, *J* = 7.8 Hz, *J* = 7.8 Hz, 1H), 8.13–8.09 (m, 3H), 8.04 (d, *J* = 9.0 Hz, 1H), 7.89 (dd, *J* = 7.8 Hz, *J* = 1.8 Hz, 1H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.70 (dd, *J* = 7.8 Hz, *J* = 1.2 Hz, 1H), 7.26 (dd, *J* = 7.2 Hz, *J* = 7.2 Hz, 1H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.08–7.04 (m, 3H), 6.99 (ddd, *J* = 8.4 Hz, *J* = 8.4 Hz, *J* = 1.8 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.27 (d, *J* = 9.0 Hz, 1H), 2.37 (s, 3H). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –152.0 (s), –277.6 (br, s).

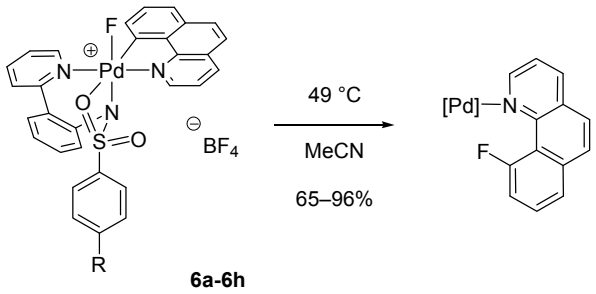
4-*tert*-Butylbenzenesulfonanilido palladium(IV) complex 6h



6h

NMR Spectroscopy: ^{1}H NMR (500 MHz, acetonitrile-*d3*, 25 ºC, δ): 9.67 (d, *J* = 5.5 Hz, 1H), 9.34 (d, *J* = 6.0 Hz, 1H), 8.86 (d, *J* = 8.0 Hz, 1H), 8.24 (dd, *J* = 7.0 Hz, *J* = 7.0 Hz, 1H), 8.05–7.96 (m, 4H), 7.78 (dd, *J* = 6.0 Hz, *J* = 6.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.38–7.29 (m, 3H), 7.10 (d, *J* = 8.5 Hz, 2H), 7.03–6.95 (m, 2H), 6.73 (d, *J* = 8.5 Hz, 1H), 6.19 (d, *J* = 8.0 Hz, 1H), 1.22 (s, 9H). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –152.0 (s), –278.1 (br, s).

Kinetic experiment of C−F reductive elimination from monofluoro palladium(IV) complexes

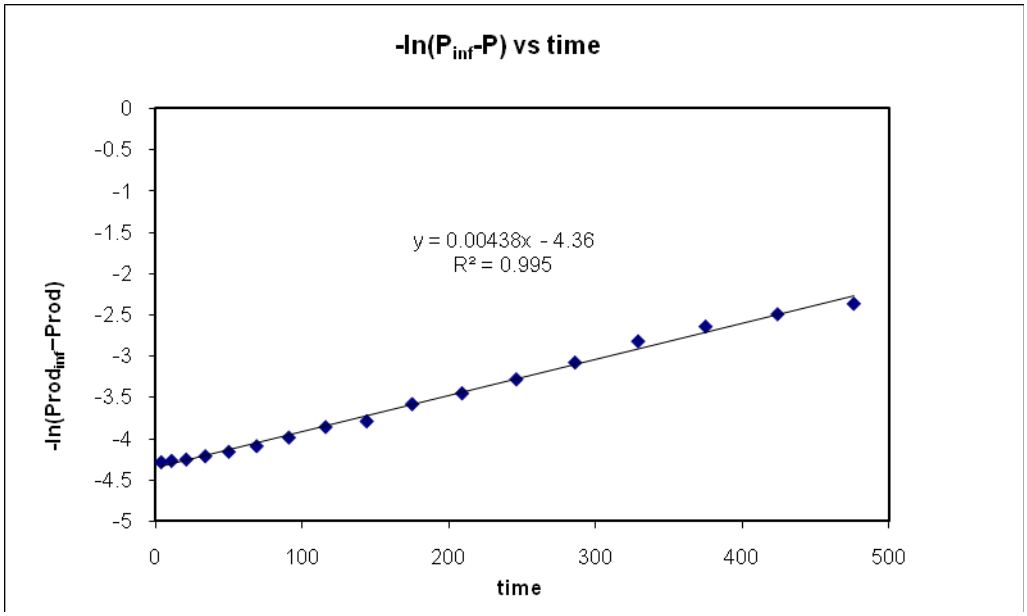


6a-6h

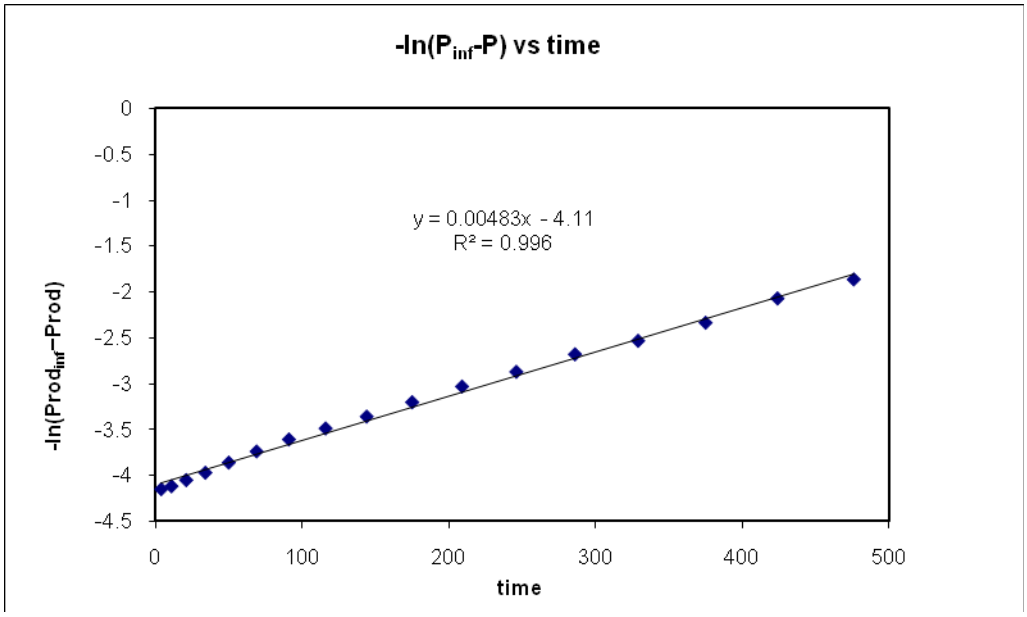
(R = NO_2, CN, Cl, F, Ph, H, Me, *t*-Bu)

Solutions (33.3 mM) of compound **6a-6h** were prepared by reacting compounds **S15-S22** (0.020 mmol, 1.0 equiv) with 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo [2.2.2]octane bis(tetrafluoroborate) (**S5**) (7.1 mg, 0.020 mmol, 1.0 equiv) in NMR tubes under nitrogen. NMR samples were placed in the preheated NMR machine (49 ºC) and the disappearance of the compounds **6a-6h** and the formation of the product were monitored by integrating the peak at around 6.3 ppm and 9.1 ppm, respectively, relative to the peak of 1-chloromethyl-1,4-diazoniabicyclo [2.2.2]octane (tetrafluoroborate) at 4.91 ppm. Rates of starting material decomposition and rates of product formation corrected for the appropriate yield at time infinity were identical. The plots for product formation are shown below.

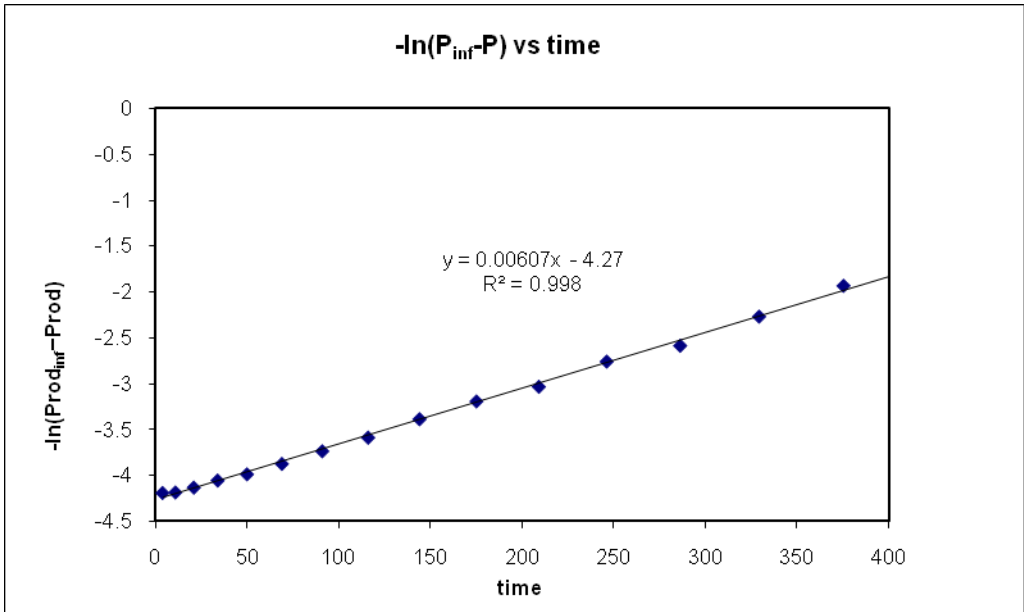
R = NO_2



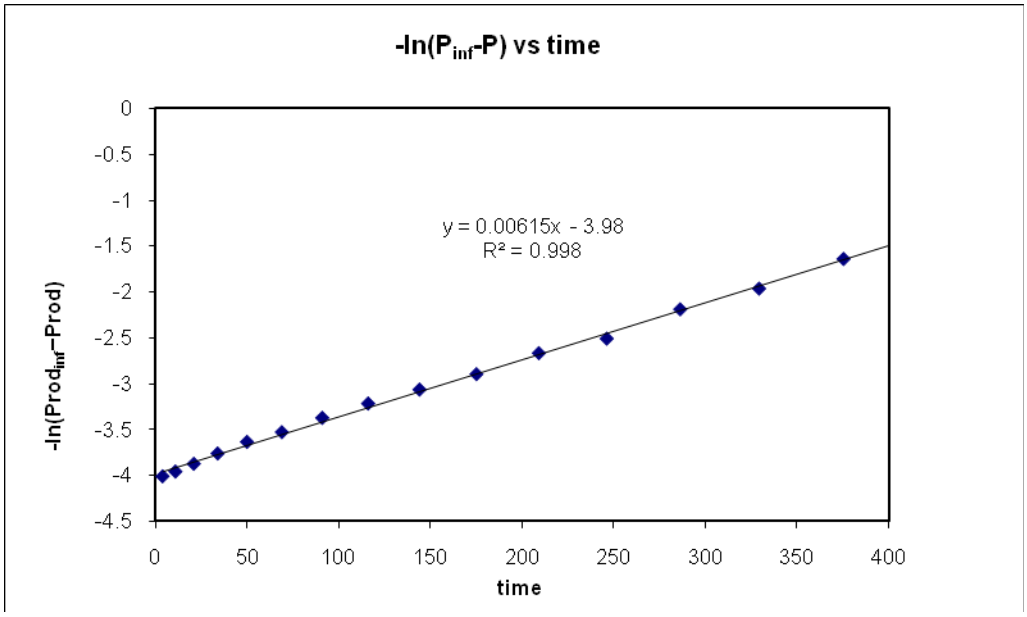
R = CN


-ln(P$_{inf}$-P) vs time
y = 0.00483x - 4.11
R² = 0.996
-ln(Prod$_{inf}$–Prod)
time
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
-4
-4.5
0
100
200
300
400
500

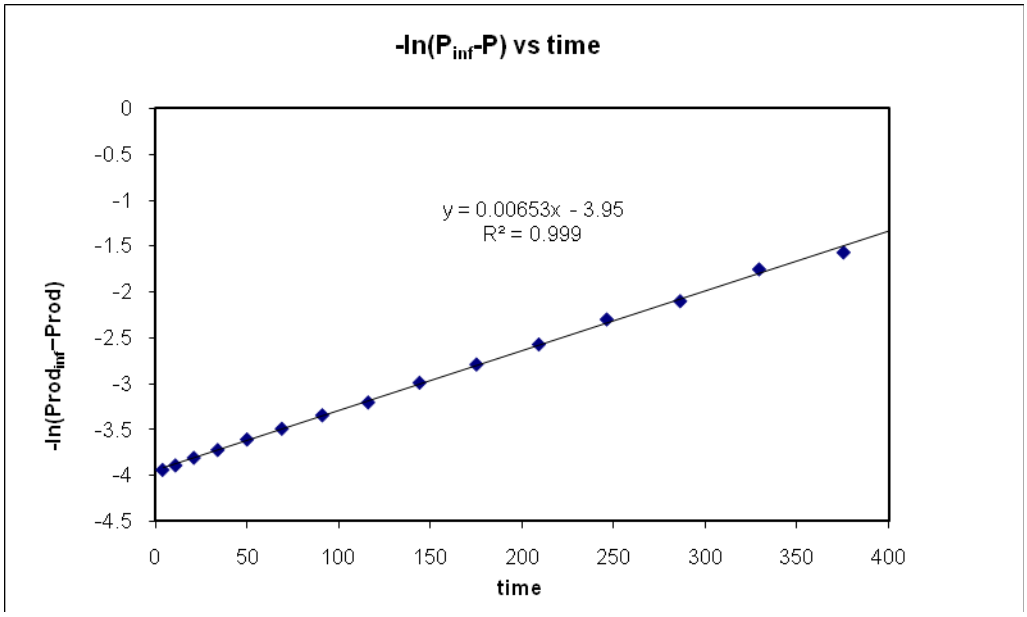
R = Cl


-ln(P$_{inf}$-P) vs time
y = 0.00607x - 4.27
R² = 0.998
-ln(Prod$_{inf}$–Prod)
time
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
-4
-4.5
0
50
100
150
200
250
300
350
400

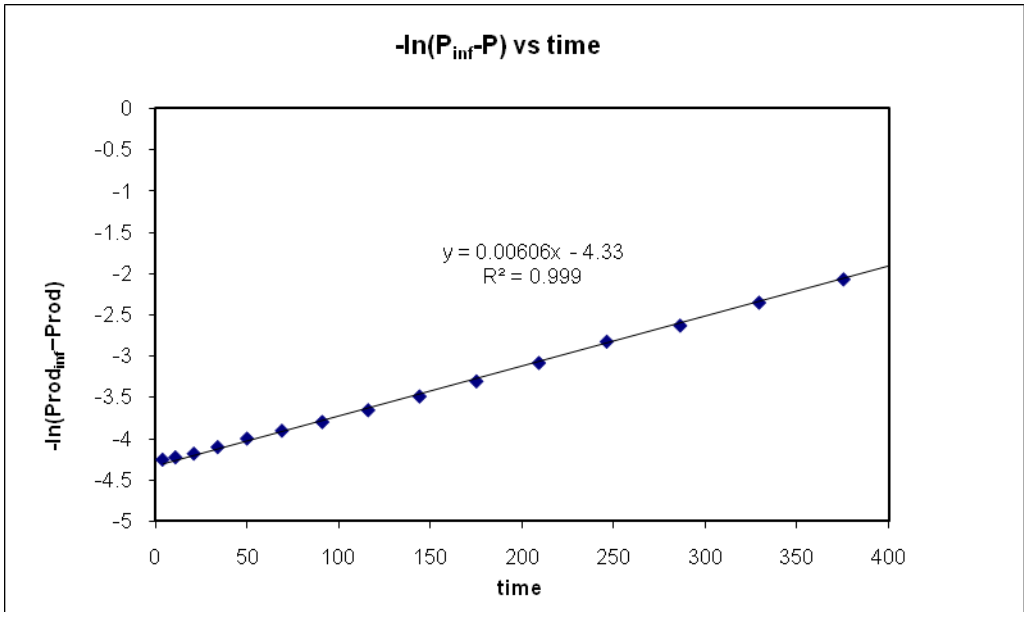
R = F


-ln(P_inf-P) vs time
y = 0.00615x - 3.98
R² = 0.998
-ln(Prod_inf−Prod)
time
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
-4
-4.5
0
50
100
150
200
250
300
350
400

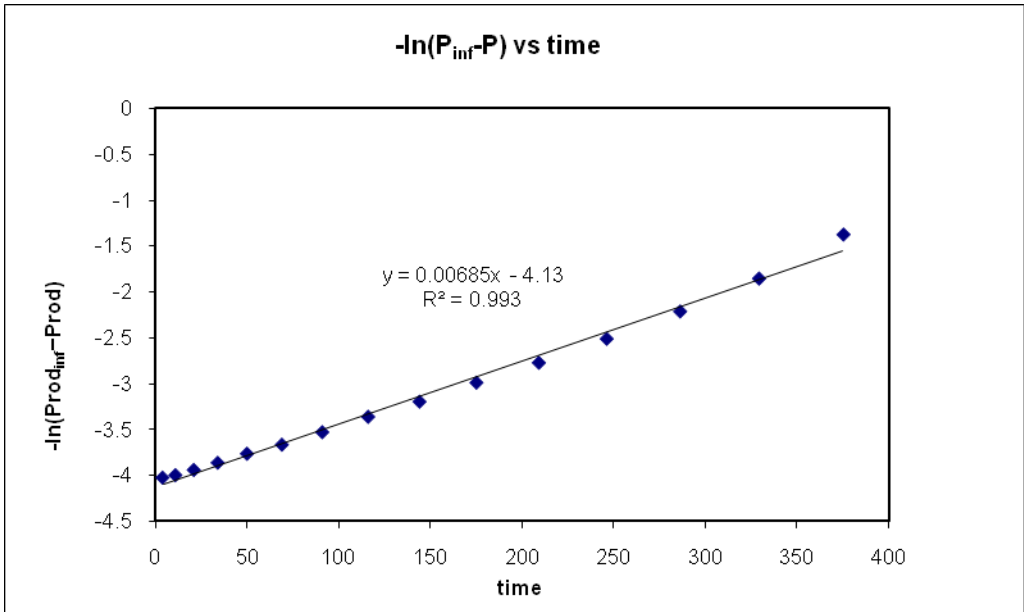
R = Ph


-ln(P_inf-P) vs time
y = 0.00653x - 3.95
R² = 0.999
-ln(Prod_inf−Prod)
time
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
-4
-4.5
0
50
100
150
200
250
300
350
400

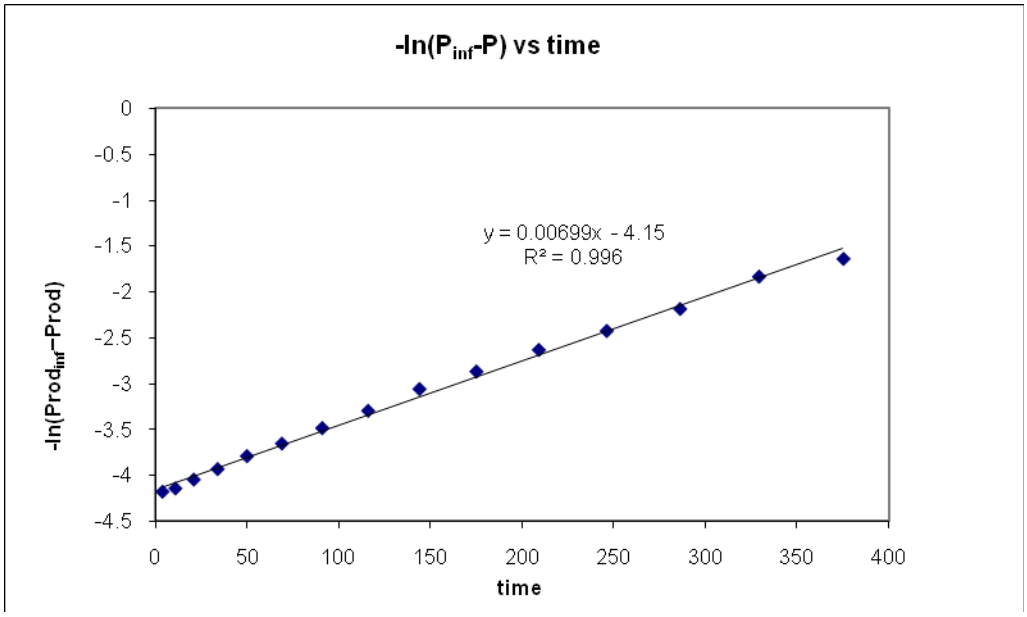
R = H


-ln(P$_{inf}$-P) vs time
y = 0.00606x - 4.33
R² = 0.999
-ln(Prod$_{inf}$–Prod)
time
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
-4
-4.5
-5
0
50
100
150
200
250
300
350
400

R = Me


-ln(P$_{inf}$-P) vs time
y = 0.00685x - 4.13
R² = 0.993
-ln(Prod$_{inf}$–Prod)
time
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
-4
-4.5
0
50
100
150
200
250
300
350
400

R = *t*-Bu



R	σ	k	ln(k_X/k_H)	Fluorination Yield (%)
NO_2	0.78	0.00438	-0.325	96
CN	0.66	0.00483	-0.228	92
Cl	0.23	0.00607	0.00150	85
F	0.15	0.00615	0.0134	87
Ph	-0.01	0.00653	0.0736	89
H	0	0.00606	0.0000	75
Me	-0.17	0.00685	0.122	71
t-Bu	-0.20	0.00699	0.142	65

A lower fluorination yield was observed for more electron-donating substituents. This may be due to the competing N−F reductive elimination because more nucleophilic amides undergo reductive elimination more readily (for example, see: Hartwig, J. F. *Synlett* **2006**, 1283−1294). From the reaction of **6h**, free ligand **S14** was isolated in ca. 10%, whereas no free ligand **S7** was observed from the reaction of **6a**. The formation of the free ligand may be due to the N−F reductive eliminateon and subsequent decomposition of *N*-fluoro compounds.

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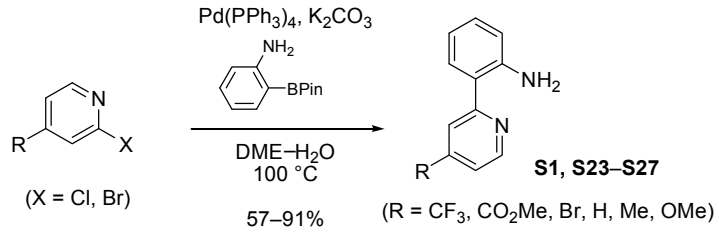
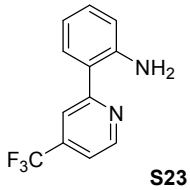
Hammett plot for pyridine substitution

Synthesis of pyridinylsulfonanilide ligands with different pyridine substitution



Under air, to a substituted 2-bromopyridine[10] (1.00 mmol, 1.00 equiv) in DME−H_2O (1:1, 5 mL) at 23 ºC was added K_2CO_3 (207 mg, 1.50 mmol, 1.50 equiv), 2-aminophenylboronic acid pinacol ester (219 mg, 1.00 mmol, 1.00 equiv), and tetrakis(triphenylphosphine)palladium (57.8 mg, 0.0500 mmol, 5.00 mol%). The reaction mixture was stirred at 100 °C for 3.0 h. After cooling to 23 ºC, the phases were separated and the aqueous phase was extracted with EtOAc (3 × 2 mL). The combined organic phases were washed with brine (5 mL) and dried (Na_2SO_4). The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel to afford the correspondingly substituted 2-(2-pyridinyl)aniline (57−91% yield).

2-(2-(4-trifluoromethylpyridinyl)aniline (S23)

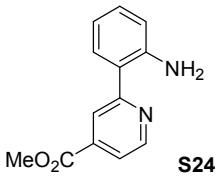


S23

R_f = 0.20 (hexanes/EtOAc 85:15 (v/v)). 91% yield. NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 8.77 (d, *J* = 6.5 Hz, 1H), 7.91 (s, 1H), 7.58 (d, *J* = 9.5 Hz, 1H), 7.38 (d, *J* = 6.0 Hz, 1H), 7.23 (dd, *J* = 5.0 Hz, 5.0 Hz, 1H), 6.84–6.77 (m, 2H) 5.80 (br s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 160.6, 148.7, 146.8, 138.9 (q, 33.5 Hz), 130.74, 129.3, 122.9 (q, 273 Hz), 120.4, 117.7, 117.5 (q, *J* = 3.6 Hz) 117.4, 116.0 (q, *J* = 3.6 Hz). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –65.2. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{12}H_9F_3N_2$ + H], 239.07906. Found, 239.07887.

[10] 2-Chloro-4-methoxylpyridine was used for the synthesis of **S27**

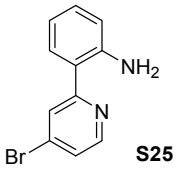
Methyl 2-(2-aminophenyl)pyridine-4-carboxylate (S24)



S24

R_f = 0.50 (hexanes/EtOAc 7:3 (v/v)). 57% yield. NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 8.74 (d, *J* = 5.5 Hz, 1H), 8.26 (s, 1H), 7.70 (dd, *J* = 5.0 Hz, *J* = 1.5 Hz, 1H), 7.62 (dd, *J* = 8.0 Hz, *J* = 1.5 Hz, 1H), 7.20 (ddd, *J* = 7.5 Hz, *J* = 7.5 Hz, *J* = 1.0 Hz, 1H), 6.82–6.76 (m, *2*H), 5.79 (br s, 2H), 3.98 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 165.7, 160.4, 148.5, 146.7, 138.1, 130.4, 129.4, 121.4, 121.0, 119.7, 117.6, 117.3, 52.7. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{13}H_{12}N_2O_2$ + H], 229.09715. Found, 229.09741.

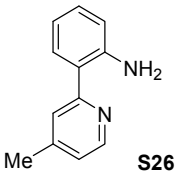
2-(2-(4-bromopyridinyl)aniline (S25)



S25

R_f = 0.20 (hexanes/EtOAc 9:1 (v/v)). 80% yield. NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 8.41 (d, *J* = 5.0 Hz, 1H), 7.85 (d, *J* = 1.5 Hz, 1H), 7.50 (dd, *J* = 8.0 Hz, *J* = 1.5 Hz, 1H), 7.33 (dd, *J* = 5.5 Hz, *J* = 2.0 Hz, 1H), 7.19 (ddd, *J* = 8.5 Hz, *J* = 7.0 Hz, *J* = 1.5 Hz, 1H) 6.80–6.74 (m, *2*H), 5.74 (br s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 160.6, 148.4, 146.7, 133.4, 130.4, 129.2, 125.1, 123.9, 120.4, 117.5, 117.2. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{11}H_9BrN_2$ + H], 249.00219. Found, 249.00219.

2-(2-(4-methylpyridinyl)aniline (S26)

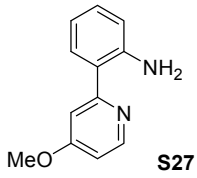


S26

R_f = 0.15 (hexanes/EtOAc 9:1 (v/v)). 65% yield. NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 8.48 (d, *J* = 5.0 Hz, 1H), 7.52 (dd, *J* = 8.0 Hz, *J* = 1.5 Hz, 1H), 7.47 (s, 1H), 7.18 (ddd, *J* = 6.5 Hz, *J* = 6.5 Hz, *J* = 1.0 Hz, 1H), 7.00 (d, *J* = 5.0 Hz, 1H), 6.82–6.75 (m, 2H), 5.79 (br s, 2H), 2.39 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 159.1, 147.7, 147.5, 146.5, 129.6, 129.2, 122.9, 122.3, 121.9, 117.4,

117.0, 21.1. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{12}H_{12}N_2$ + H], 185.10732. Found, 185.10766.

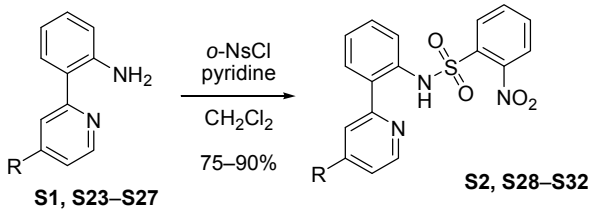
2-(2-(4-methoxylpyridinyl)aniline (S27)



S27

R_f = 0.20 (hexanes/EtOAc 7:3 (v/v)). 80% yield. NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 8.42 (d, *J* = 6.0 Hz, 1H), 7.46 (d, *J* = 7.5 Hz, 1H), 7.16 (dd, *J* = 7.5 Hz, *J* = 7.5 Hz, 1H), 7.12 (d, *J* = 2.0 Hz, 1H), 6.80–6.72 (m, 3H), 5.50 (br s, 2H), 3.88 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 166.4, 161.0, 149.2, 146.3, 129.8, 129.3, 122.6, 117.6, 117.0, 108.0, 107.7, 55.0. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{12}H_{12}N_2O$ + H], 201.10224. Found, 201.10255.

Synthesis of pyridinylsulfonanilide ligands with different pyridine substitution

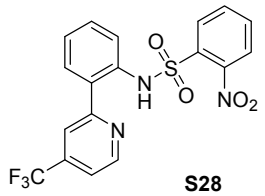


S1, S23–S27 **S2, S28–S32**

(R = CF_3, CO_2Me, Br, H, Me, OMe)

To a substituted 2-(2-pyridinyl)aniline **S1**, **S23**−**S26** (1.00 mmol, 1.00 equiv) in CH_2Cl_2 (3 mL) at 0 ºC was added pyridine (119 mg, 121 μL, 1.50 mmol, 1.50 equiv) and a 2-nitrobenzenesulfonyl chloride (310 mg, 1.40 mmol, 1.40 equiv). The reaction mixture was warmed to 23 ºC and stirred for 2.0 hr before the addition of water (3 mL). The phases were separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 2 mL). The combined organic phases were washed with brine (5 mL) and dried (Na_2SO_4). The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel to afford the corresponding substituted 2-(2-pyridinyl)-2-nitrobenzenesulfonanilide (75−90% yield).

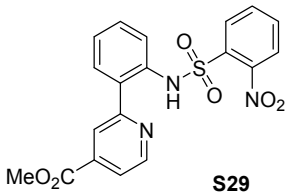
2-(2-(4-trifluoromethylpyridinyl)-2-nitrobenzenesulfonanilide (S28)



S28

R_f = 0.35 (hexanes/EtOAc 7:3 (v/v)). 90% yield. NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 12.00 (s, 1H), 8.92 (d, *J* = 5.5 Hz, 1H), 7.87–7.85 (m, 2H), 7.64 (s, 1H), 7.61–7.54 (m, 4H), 7.48–7.44 (m, 2H), 7.26 (ddd, *J* = 6.5 Hz, *J* = 6.5 Hz, *J* = 1.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 158.0, 149.3, 147.6, 139.8 (q, *J* = 16.8), 135.8, 133.6, 132.7, 132.0, 131.0, 130.8, 129.1, 127.0, 125.2, 124.7, 123.6, 122.9, 121.4, 117.6. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{18}H_{12}F_3N_3O_4S$ + Na], 446.03928. Found, 446.03807.

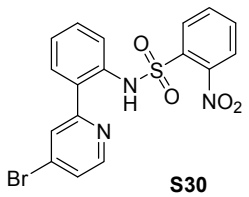
Methyl 2-(2-(2-nitrobenzenesulfonylamidophenyl)pyridine-4-carboxylate (S29)



S29

R_f = 0.12 (hexanes/EtOAc 7:3 (v/v)). 83% yield. NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 12.48 (s, 1H), 8.87 (d, *J* = 5.0 Hz, 1H), 8.07 (s, 1H), 7.91 (dd, *J* = 6.5 Hz, *J* = 3.0 Hz, 1H), 7.84 (d, *J* = 8.5 Hz, 1H), 7.77 (dd, *J* = 5.0 Hz, *J* = 1.5 Hz, 1H), 7.67 (dd, *J* = 8.0 Hz, *J* = 1.5 Hz, 1H), 7.57–7.54 (m, 3H), 7.41 (ddd, *J* = 8.8 Hz, *J* = 8.8 Hz, *J* = 1.5 Hz, 1H), 7.22 (ddd, *J* = 8.0 Hz, *J* = 8.0 Hz, *J* = 1.0 Hz, 1H), 3.97 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 165.1, 157.6, 148.8, 147.6, 138.8, 135.8, 135.9, 133.5, 132.9, 132.0, 130.6, 129.1, 126.6, 124.8, 124.8, 121.9, 121.3, 121.1, 52.9. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{19}H_{15}N_3O_6S$ + H], 414.07543. Found, 414.07512.

2-(2-(4-bromopyridinyl)-2-nitrobenzenesulfonanilide (S30)

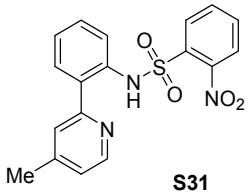


S30

R_f = 0.30 (hexanes/EtOAc 7:3 (v/v)). 80% yield. NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC,

δ): 12.22 (s, 1H), 8.54 (d, *J* = 5.5 Hz, 1H), 7.87 (d, *J* = 7.5 Hz, 1H), 7.83 (dd, *J* = 8.5 Hz, *J* = 1.0 Hz, 1H), 7.62–7.53 (m, 5H), 7.44–7.40 (m, 2H), 7.21 (ddd, *J* = 8.0 Hz, *J* = 8.0 Hz, *J* = 1.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 157.8, 148.8, 147.6, 135.9, 134.2, 133.5, 132.9, 132.0, 130.8, 130.7, 128.9, 126.7, 125.4, 125.2, 125.0, 124.8, 122.6. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{17}H_{12}BrN_3O_4S$ + H], 433.98047. Found, 433.98002.

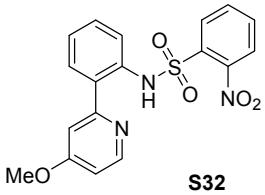
2-(2-(4-methylpyridinyl)-2-nitrobenzenesulfonanilide (S31)



S31

R_f = 0.15 (hexanes/EtOAc 7:3 (v/v)). 75% yield. NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 13.18 (s, 1H), 8.52 (d, *J* = 5.0 Hz, 1H), 7.90 (dd, *J* = 7.0 Hz, *J* = 1.5 Hz, 1H), 7.78 (dd, *J* = 8.5 Hz, *J* = 1.5 Hz, 1H), 7.62–7.52 (m, 4H), 7.37–7.33 (m, 2H), 7.16 (ddd, *J* = 7.5 Hz, *J* = 7.5 Hz, *J* = 1.5 Hz, 1H), 7.05 (dd, *J* = 5.5 Hz, *J* = 1.5 Hz, 1H), 3.35 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 156.3, 149.0, 147.7, 147.3, 136.2, 133.2, 133.1, 131.9, 130.6, 129.9, 128.6, 126.8, 124.6, 124.4, 123.2, 122.4, 121.5, 21.3. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{18}H_{15}N_3O_4S$ + Na], 392.06755. Found, 392.06758.

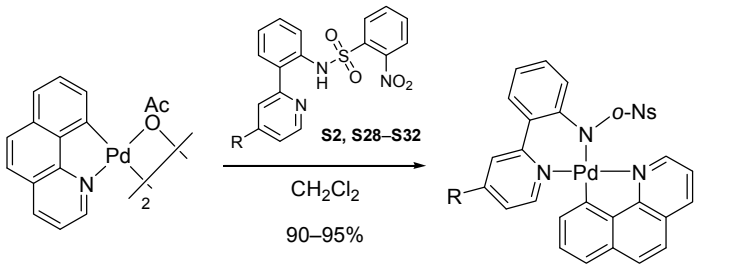
2-(2-(4-methoxylpyridinyl)-2-nitrobenzenesulfonanilide (S32)



S32

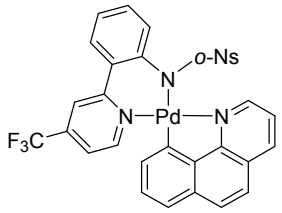
R_f = 0.15 (hexanes/EtOAc 7:3 (v/v)). 70% yield. NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 13.22 (s, 1H), 8.54 (d, *J* = 6.0 Hz, 1H), 7.93 (dd, *J* = 7.0 Hz, *J* = 1.5 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.63–7.53 (m, 4H), 7.36 (dd, *J* = 7.5 Hz, *J* = 7.5 Hz, 1H), 7.16 (dd, *J* = 7.5 Hz, *J* = 7.5 Hz, 1H), 7.01 (d, *J* = 2.0 Hz, 1H), 6.78 (dd, *J* = 7.0 Hz, *J* = 2.0 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 166.8, 158.2, 149.2, 147.8, 136.4, 133.4, 133.2, 131.9, 130.7, 130.2, 128.6, 126.8, 124.7, 124.3, 121.5, 108.2, 107.9, 55.3. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{18}H_{15}N_3O_5S$ + H], 386.08052. Found, 386.08000.

Synthesis of Pd(II) complexes with different pyridine substitution



To benzo[*h*]quinolinyl palladium acetate dimer (**S3**) (100 mg, 0.145 mmol, 1.00 equiv) in CH_2Cl_2 (2 mL) at 23 ºC was added a substituted pyridinylsulfonanilide ligand **S2**, **S28**–**S32** (0.291 mmol, 2.00 equiv). After stirring for 1.0 hr the reaction mixture was concentrated in vacuo. The resulting residue was triturated with Et_2O (3 × 1 mL) to afford the corresponding substituted palladium(II) complex (90−95% yield).

4-Trifluoromethylpyridinyl palladium(II) complex S33

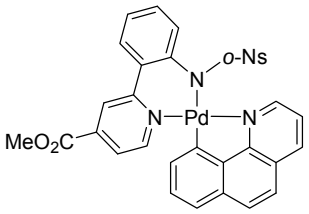


S33

90% yield. NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 9.52 (dd, *J* = 5.0 Hz, *J* = 1.0 Hz, 1H), 9.23 (d, *J* = 6.0 Hz, 1H), 8.32 (dd, *J* = 8.0 Hz, *J* = 1.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.5 Hz, 1H), 7.64–7.57 (m, 3H), 7.47–7.42 (m, 2H), 7.39–7.34 (m, 3H), 7.30–7.21 (m, 3H), 7.16 (ddd, *J* = 7.5 Hz, *J* = 7.5 Hz, *J* = 1.0 Hz, 1H), 7.03 (dd, *J* = 6.5 Hz, *J* = 6.5 Hz, 1H), 6.93 (d, *J* = 7.0 Hz, 1H). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –65.2. Anal: calcd for $C_{31}H_{19}F_3N_4O_2PdS$: C, 52.66; H, 2.71; N, 7.92; found: C, 52.41; H, 2.48; N, 7.73.[11]

[11] The ^{13}C NMR spectrum of this compound has a low signal-to-noise ratio due to the low solubility in common organic solvents.

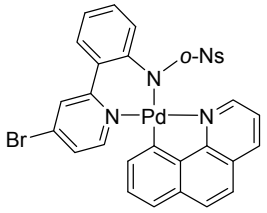
4-Methoxycarbonylpyridinyl palladium(II) complex S34



S34

93% yield. NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 9.56 (dd, *J* = 5.5 Hz, *J* = 1.0 Hz, 1H), 9.15 (d, *J* = 7.0 Hz, 1H), 8.30 (dd, *J* = 8.5 Hz, *J* = 1.0 Hz, 1H), 7.76–7.72 (m, 2H), 7.69–7.68 (m, 2H), 7.63–7.58 (m, 3H), 7.53 (ddd, *J* = 8.5 Hz, *J* = 8.5 Hz, *J* = 1.0 Hz, 1H), 7.47–7.45 (m, 2H), 7.36 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H), 7.28–7.27 (m, 1H), 7.15–7.12 (m, 2H), 7.01–6.99 (m, 1H), 6.96 (d, *J* = 7.0 Hz, 1H), 4.02 (s, 3H). Anal: calcd for $C_{32}H_{22}N_4O_6PdS$: C, 55.14; H, 3.18; N, 8.04; found: C, 55.28; H, 3.06; N, 7.99.[11]

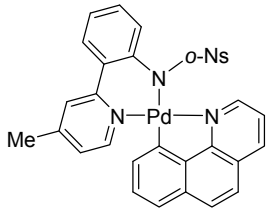
4-Bromopyridinyl palladium(II) complex S35



S35

95% yield. NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 9.51 (d, *J* = 5.5 Hz, 1H), 8.83 (d, *J* = 6.0 Hz, 1H), 8.30 (d, *J* = 8.0 Hz, 1H), 7.74–7.72 (m, 2H), 7.62–7.58 (m, 3H), 7.50 (dd, *J* = 7.5 Hz, *J* = 7.5 Hz, 1H), 7.39–7.34 (m, 3H), 7.23–7.19 (m, 2H), 7.15 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H), 7.05–7.02 (m, 2H), 6.98–6.97 (m, 2H). Anal: calcd for $C_{30}H_{19}BrN_4O_4PdS$: C, 50.19; H, 2.67; N, 7.80; found: C, 49.95; H, 2.39; N, 7.69. [11]

4-Methylpyridinyl palladium(II) complex S36

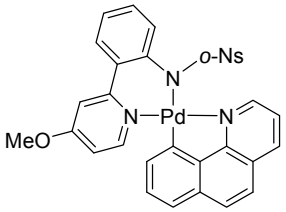


S36

91% yield. NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 9.54 (d, *J* = 5.5 Hz, 1H), 8.82 (d, *J* = 5.5 Hz, 1H), 8.29 (d, *J* = 8.0 Hz, 1H), 7.74–7.71 (m, 2H), 7.63–7.54 (m, 4H), 7.48 (dd, *J* = 7.0 Hz, *J* = 7.0 Hz, 1H), 7.39–7.34 (m, 2H), 7.23–7.19 (m, 2H), 7.15 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H), 7.05–7.02 (m,

2H), 6.98–6.97 (m, 2H), 2.30 (s, 3H). Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{31}H_{22}N_4O_4PdS$ + H], 653.04748. Found, 653.04758. [11]

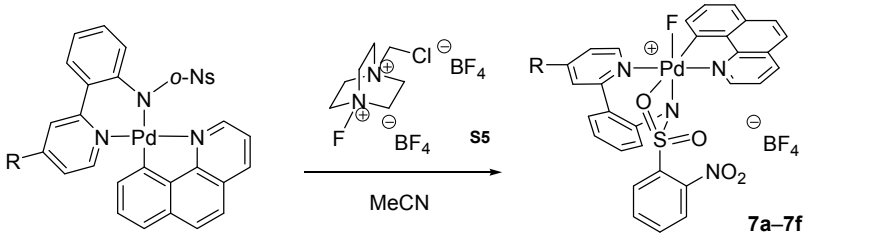
4-Methoxylpyridinyl palladium(II) complex S37



S37

90% yield. NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 9.54 (d, *J* = 5.0 Hz, 1H), 8.77 (d, *J* = 6.5 Hz, 1H), 8.28 (d, *J* = 8.0 Hz, 1H), 7.74–7.71 (m, 2H), 7.61–7.55 (m, 4H), 7.49 (dd, *J* = 8.0 Hz, *J* = 7.5 Hz, 1H), 7.38–7.34 (m, 2H), 7.23–7.14 (m, 3H), 7.07–7.02 (m, 2H), 6.68 (dd, *J* = 6.5 Hz, *J* = 3.0 Hz, 1H), 6.60 (d, *J* = 3.0 Hz, 1H), 3.84 (s, 3H). Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{31}H_{22}N_4O_5PdS$ + H], 669.04240. Found, 669.04260. [11]

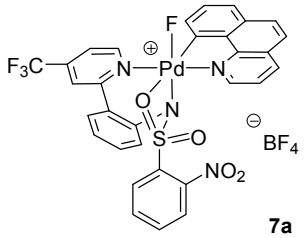
Synthesis of monofluoro Pd(IV) complexes with different pyridine substitution



To benzo[*h*]quinolinyl palladium(II) pyrdine-sulfonamido complex **S4, S33**–**S37** (0.020 mmol, 1.0 equiv) in acetonitrile-*d3* (0.6 mL) at 23 ºC was added 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo [2.2.2]octane bis(tetrafluoroborate) (**S5**) (7.1 mg, 0.020 mmol, 1.0 equiv). After stirring for 10 min at 23 ºC, the colorless suspension formed a dark purple solution. Compounds **7a**–**7f** were characterized by NMR spectroscopy as acetonitrile solution without purification.[12]

[12] Compound **7d** and **1** are identical, but labeled like this for clarity.

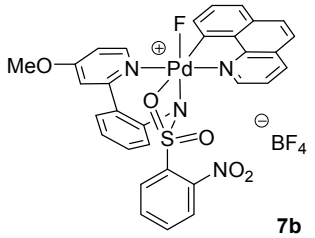
4-Trifluoromethylpyridinyl palladium(IV) complex 7a



7a

NMR Spectroscopy: ^{1}H NMR (600 MHz, acetonitrile-*d3*, 25 ºC, δ): 9.65 (d, *J* = 6.0 Hz, 1H), 9.58 (d, *J* = 5.4 Hz, 1H), 8.87 (d, *J* = 7.8 Hz, 1H), 8.68 (s, 1H), 8.19 (d, *J* = 6.0 Hz, 1H), 8.04–7.98 (m, 3H), 7.82 (dd, *J* = 7.8 Hz, *J* = 1.2 Hz, 1H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.60–7.58 (m, 2H), 7.43–7.38 (m, 2H), 7.19 (dd, *J* = 7.8 Hz, *J* = 7.8 Hz, 1H), 7.03 (dd, *J* = 8.4 Hz, *J* = 8.4 Hz, 1H), 6.90 (ddd, *J* = 9.0 Hz, *J* = 9.0 Hz, *J* = 1.2 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 6.30 (d, *J* = 8.4 Hz, 1H). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –65.9 (s), –152.3 (s), –278.4 (br s).

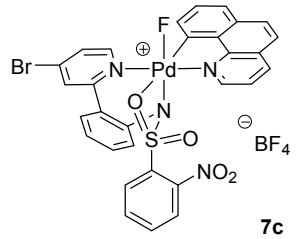
4-Methoxycarbonylpyridinyl palladium(IV) complex 7b



7b

NMR Spectroscopy: ^{1}H NMR (600 MHz, acetonitrile-*d3*, 25 ºC, δ): 9.66–9.64 (m, 2H), 8.94 (d, *J* = 8.4 Hz, 1H), 8.86 (d, *J* = 1.2 Hz, 1H), 8.38 (dd, *J* = 6.6 Hz, *J* = 1.8 Hz, 1H), 8.12–8.06 (m, 3H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.66–7.64 (m, 2H), 7.49–7.45 (m, 2H), 7.25 (dd, *J* = 7.8 Hz, *J* = 7.8 Hz, 1H), 7.10 (dd, *J* = 7.8 Hz, *J* = 7.8 Hz, 1H), 6.95 (dd, *J* = 7.8 Hz, *J* = 7.8 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.35 (d, *J* = 8.4 Hz, 1H), 4.18 (s, 3H). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –152.3 (s), –278.6 (br s).

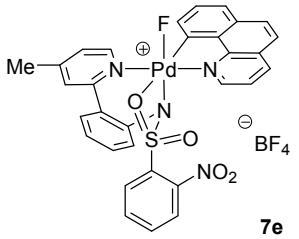
4-Bromopyridinyl palladium(II) complex 7c



7c

NMR Spectroscopy: ^{1}H NMR (600 MHz, acetonitrile-*d3*, 25 ºC, δ): 9.63 (d, *J* = 5.4 Hz, 1H), 9.33 (d, *J* = 7.2 Hz, 1H), 8.93 (d, *J* = 7.8 Hz, 1H), 8.67 (s, 1H), 8.18–8.17 (m, 2H), 8.11–8.05 (m, 2H), 7.84–7.80 (m, 2H), 7.69–7.63 (m, 2H), 7.52–7.46 (m, 2H), 7.23 (dd, *J* = 7.8 Hz, *J* = 7.8 Hz, 1H), 7.10 (dd, *J* = 7.8 Hz, *J* = 7.8 Hz, 1H), 6.94 (dd, *J* = 7.8 Hz, *J* = 7.8 Hz, 1H), 6.82 (d, *J* = 9.0 Hz, 1H), 6.37 (d, *J* = 9.0 Hz, *J* = 9.0 Hz, 1H). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –152.3 (s), –279.8 (br s).

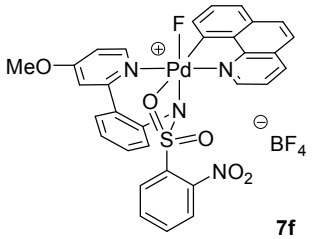
4-Methylpyridinyl palladium(II) complex 7e



7e

NMR Spectroscopy: ^{1}H NMR (600 MHz, acetonitrile-*d3*, 25 ºC, δ): 9.61 (d, *J* = 5.4 Hz, 1H), 9.29 (d, *J* = 6.6 Hz, 1H), 8.92 (d, *J* = 7.8 Hz, 1H), 8.25 (s, 1H), 8.11–8.04 (m, 3H), 7.83 (dd, *J* = 6.0 Hz, *J* = 6.0 Hz, 1H), 7.78 (d, *J* = 6.0 Hz, 1H), 7.66 (d, *J* = 7.8 Hz, *J* = 7.8 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.46 (dd, *J* = 7.8 Hz, *J* = 7.8 Hz, 1H), 7.25 (dd, *J* = 7.2 Hz, *J* = 7.2 Hz, 1H), 7.10 (dd, *J* = 7.8 Hz, *J* = 7.8 Hz, 1H), 6.93 (dd, *J* = 7.8 Hz, *J* = 7.8 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 6.32 (d, *J* = 8.4 Hz, 1H), 2.78 (s, 3H). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –152.1 (s), –278.5 (br s).

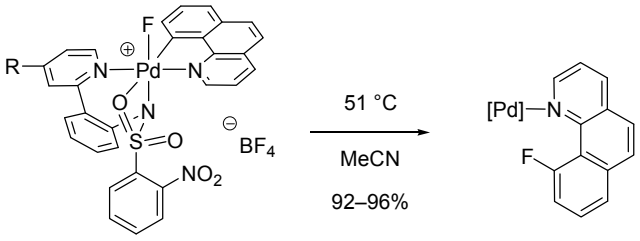
4-Methoxylpyridinyl palladium(II) complex 7f



7f

NMR Spectroscopy: ^{1}H NMR (500 MHz, acetonitrile-*d3*, 25 ºC, δ): 9.53 (d, *J* = 5.5 Hz, 1H), 9.17 (d, *J* = 7.0 Hz, 1H), 8.85 (d, *J* = 8.0 Hz, 1H), 8.05–7.98 (m, 3H), 7.80–7.73 (m, 3H), 7.59 (dd, *J* = 8.0 Hz, *J* = 7.5 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.46 (dd, *J* = 7.8 Hz, *J* = 7.8 Hz, 1H), 7.43–7.36 (m, 2H), 7.17 (dd, *J* = 7.5 Hz, *J* = 7.5 Hz, 1H), 7.04 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H), 6.87 (dd, *J* = 7.5 Hz, *J* = 7.0 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 6.29 (d, *J* = 9.0 Hz, 1H), 4.17 (s, 3H). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –152.1 (s), –280.0 (br s).

Kinetic experiment of C−F reductive elimination from monofluoro Pd(IV) complexes

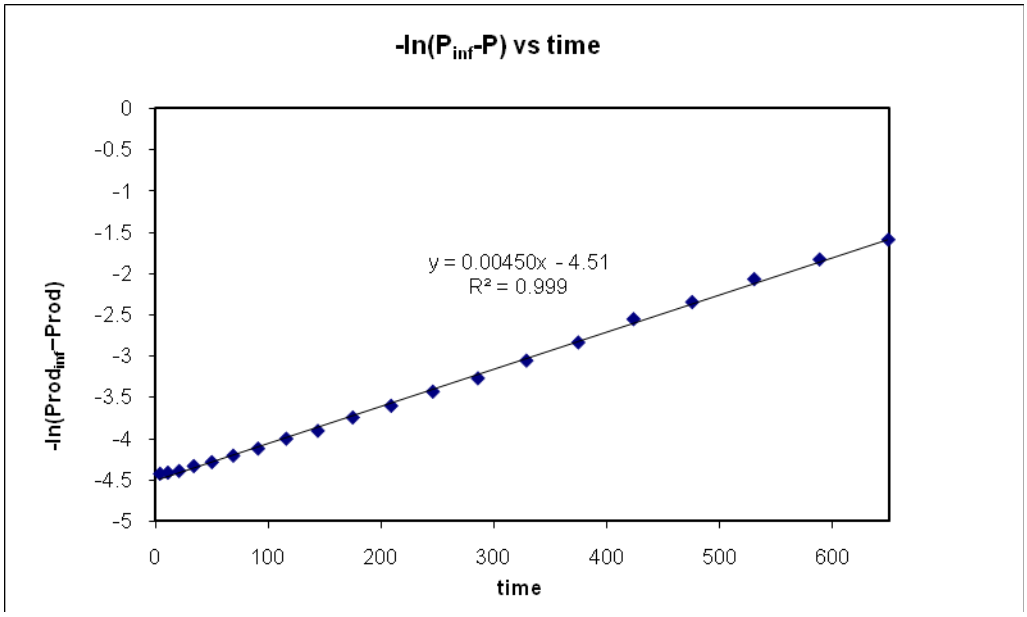


7a–7f

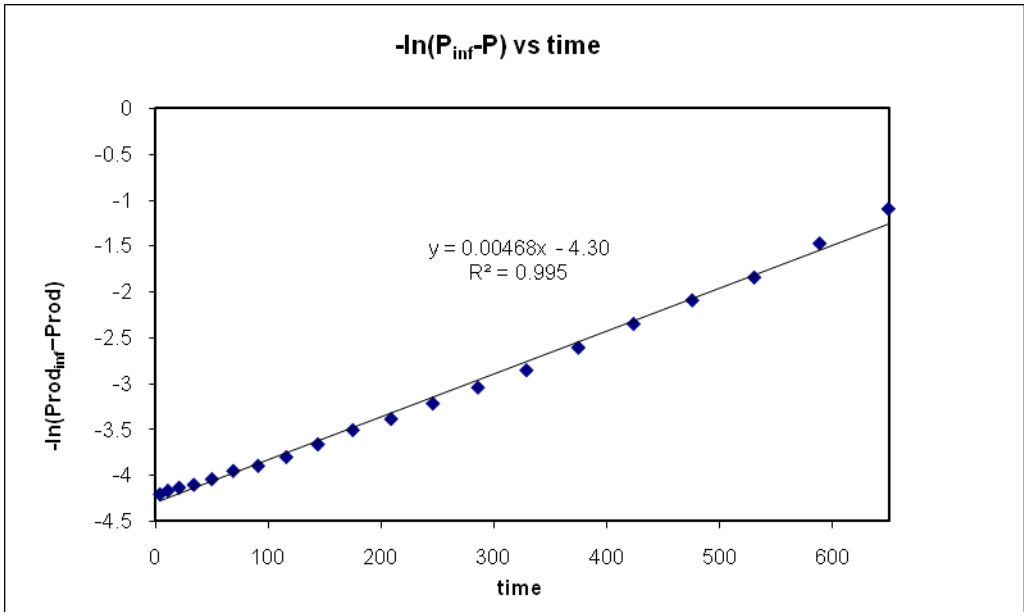
(R = CF_3, CO_2Me, Br, H, Me, OMe)

Solutions (33.3 mM) of compounds **7a**–**7f** were prepared by reacting compound **S4, S33**–**S37** (0.020 mmol, 1.0 equiv) with 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo [2.2.2]octane bis(tetrafluoroborate) (**S5**) (7.1 mg, 0.020 mmol, 1.0 equiv) in NMR tubes under nitrogen. NMR samples were placed in the preheated NMR machine (51 ºC) and the disappearance of the compounds **7a**–**7f** and the formation of product were monitored by integrating the peak at around 6.3 ppm and 9.1 ppm, respectively, relative to the peak of 1-chloromethyl-1,4-diazoniabicyclo [2.2.2]octane (tetrafluoroborate) at 4.91 ppm.

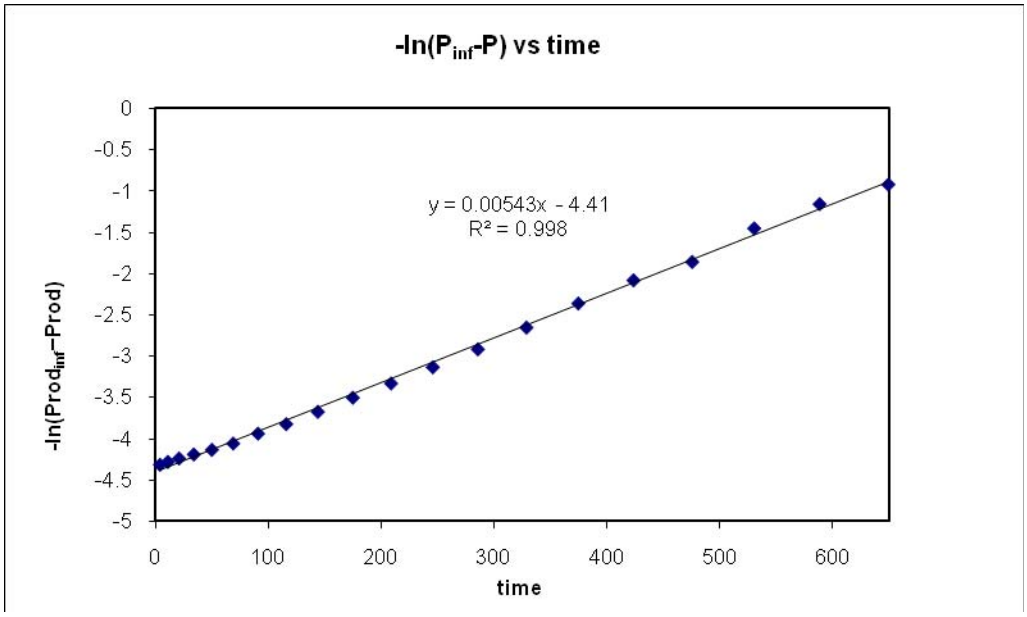
R = CF_3


-ln(P_inf-P) vs time
y = 0.00450x - 4.51
R² = 0.999
-ln(Prod_inf−Prod)
time
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
-4
-4.5
-5
0
100
200
300
400
500
600

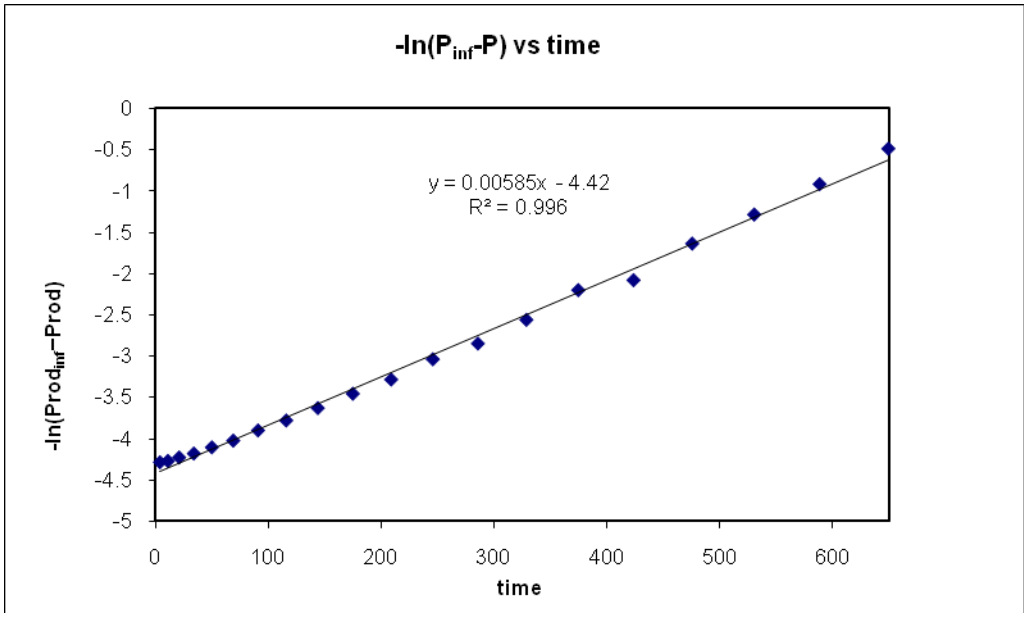
R = CO_2Me


-ln(P_inf-P) vs time
y = 0.00468x - 4.30
R² = 0.995
-ln(Prod_inf−Prod)
time
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
-4
-4.5
0
100
200
300
400
500
600

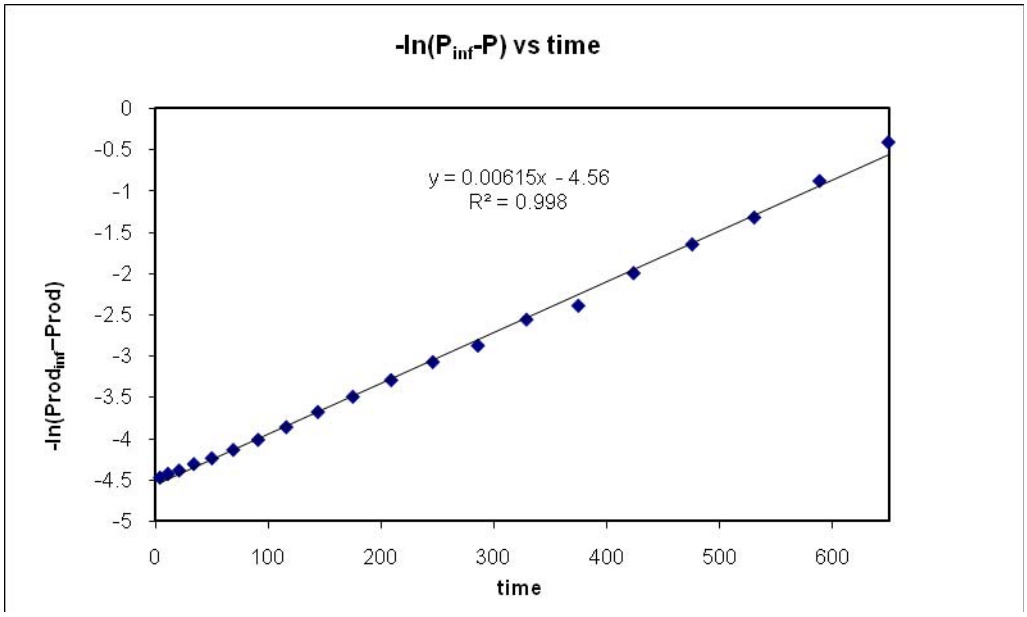
R = Br


-ln(P_inf-P) vs time
y = 0.00543x - 4.41
R² = 0.998
-ln(Prod_inf−Prod)
time
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
-4
-4.5
-5
0
100
200
300
400
500
600

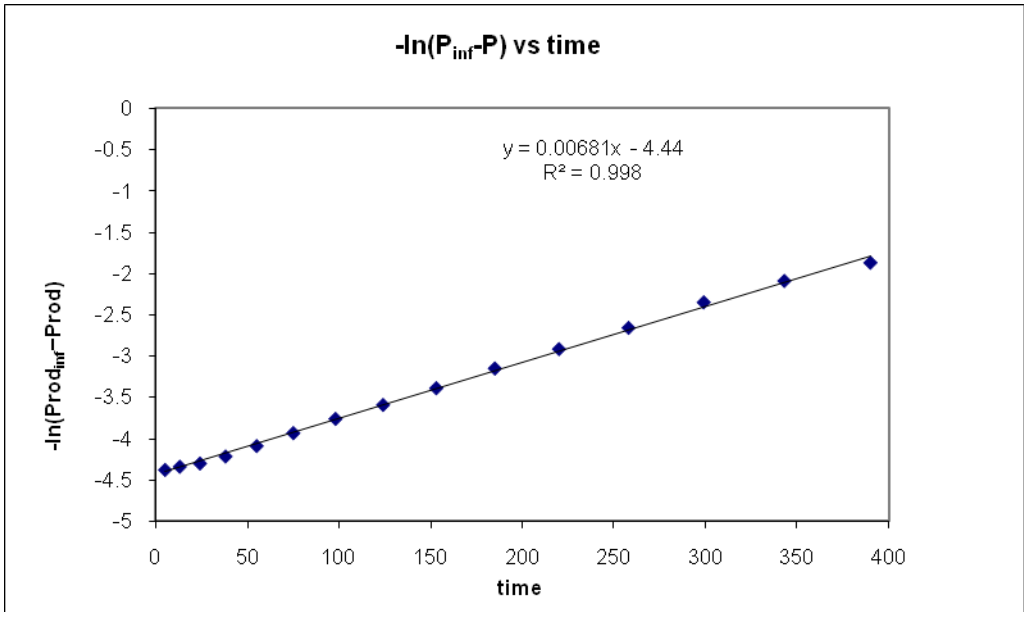
R = H


-ln(P_inf-P) vs time
y = 0.00585x - 4.42
R² = 0.996
-ln(Prod_inf−Prod)
time
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
-4
-4.5
-5
0
100
200
300
400
500
600

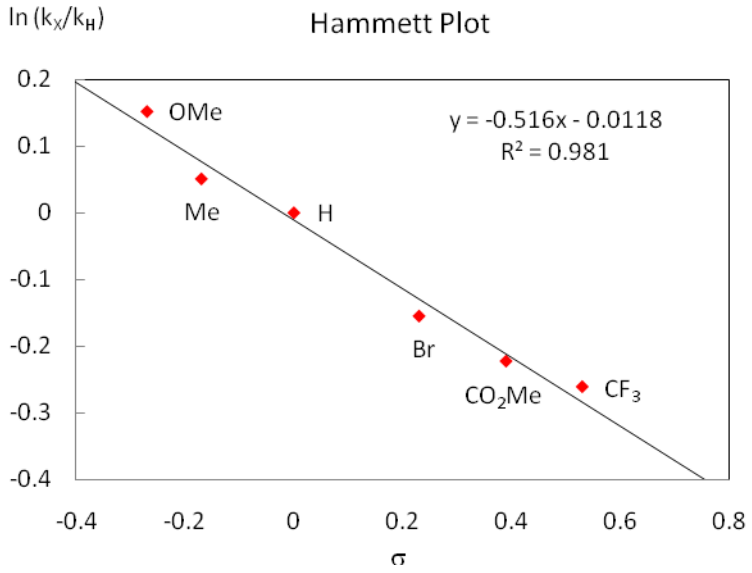
R = Me


-ln(P_inf-P) vs time
y = 0.00615x - 4.56
R² = 0.998
-ln(Prod_inf−Prod)
time
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
-4
-4.5
-5
0
100
200
300
400
500
600

R = OMe


-ln(P_inf-P) vs time
y = 0.00681x - 4.44
R² = 0.998
-ln(Prod_inf−Prod)
time
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
-4
-4.5
-5
0
50
100
150
200
250
300
350
400

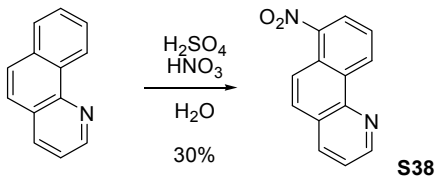
R	σ	k	$\ln(k_X/k_H)$	Fluorination Yield (%)
CF_3	0.53	0.00450	–0.262	94
CO_2Me	0.39	0.00468	–0.223	96
Br	0.23	0.00543	–0.0747	95
H	0	0.00585	0.0000	95
Me	–-0.17	0.00615	0.0510	92
OMe	–0.27	0.00681	0.152	93



Hammett plot for benzo[*h*]quinoline substitution

Synthesis of substituted benzo[*h*]quinolines

7-Nitrobenzo[*h*]quinoline (S38)



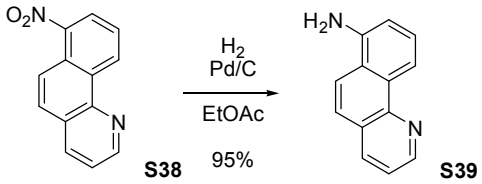
S38

Under air, benzo[*h*]quinoline (5.00 g, 27.9 mmol, 1.00 equiv) was dissolved in conc. H_2SO_4 (10 mL) at 23 ºC. The reaction mixture was cooled to 0 ºC and the mixture of conc. H_2SO_4 (3.3 mL) and HNO_3 (5.3 mL) (prepared with cooling) was added dropwise over 20 min. The reaction mixture was stirred at 0 °C

for 15 min and was subsequently poured onto water (300 mL). The precipitate was filtered, dried and purified by chromatography on silica gel eluting with CH_2Cl_2/hexanes 1:1 (v/v) to afford 1.88 g of the title compound as a pale yellow solid (30% yield).

R_f = 0.78 (CH_2Cl_2). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 9.65 (d, *J* = 8.0 Hz, 1H), 9.03 (dd, *J* = 4.5 Hz, *J* = 2.0 Hz, 1H), 8.43 (d, *J* = 9.5 Hz, 1H), 8.32 (dd, *J* = 7.5 Hz, *J* = 1.0 Hz, 1H), 8.21 (dd, *J* = 8.0 Hz, *J* = 1.5 Hz, 1H), 7.88 (d, *J* = 9.0 Hz, 1H), 7.77 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H), 7.61 (dd, *J* = 8.0 Hz, *J* = 4.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 149.9, 146.9, 145.3, 135.9, 132.9, 130.4, 129.0, 125.9, 125.6, 125.6, 125.1, 123.0, 121.3. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{13}H_8N_2O_2$ + H], 225.06585. Found, 225.06650.[13]

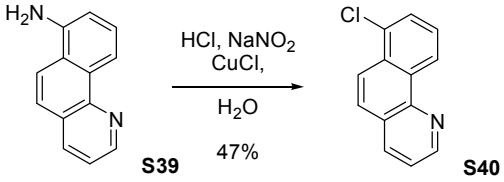
7-Aminobenzo[*h*]quinoline (S39)



To 7-nitrobenzo[*h*]quinoline (**S38**) (1.00 g, 4.46 mmol, 1.00 equiv) in EtOAc (45 mL) at 23 ºC was added 10% Pd/C (446 mg). H_2 gas (1 atm) was introduced using a balloon and the reaction mixture was stirred for 1.0 hr at 23 ºC. The reaction mixture was filtered through a pad of celite and the filtrate was concentrated to afford 820 mg of the title compound as a brown solid (95% yield).

R_f = 0.30 (CH_2Cl_2). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ) : 8.99 (dd, *J* =4.0 Hz, *J* = 1.5 Hz, 1H), 8.79 (d, *J* = 8.5 Hz, 1H), 8.13 (dd, *J* = 8.0 Hz, 1.5 Hz, 1H), 7.82 (d, *J* = 9.0 Hz, 1H), 7.62 (d, *J* = 9.5 Hz, 1H), 7.54 (dd, *J* = 7.5 Hz, *J* = 7.5 Hz, 1H), 7.49 (dd, *J* = 8.0 Hz, *J* = 4.5 Hz, 1H), 7.02 (dd, *J* = 7.5 Hz, *J* = 1.0 Hz, 1H), 4.19 (br s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 146.8, 146.7, 142.4, 135.7, 132.5, 127.5, 126.1, 124.0, 122.4, 121.7, 120.5, 115.3, 113.5. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{13}H_{10}N_2$ + H], 195.09222. Found, 195.09235.

7-Chlorobenzo[*h*]quinoline (S40)

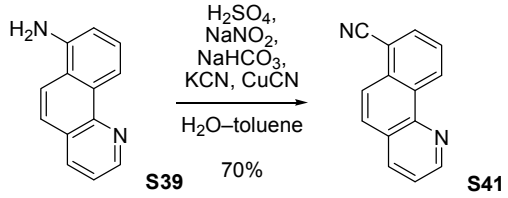


[13] Barltrop, J. A.; MacPhee, K. E. *J. Chem. Soc.* **1952**, 638–642.

Under air, 7-aminobenzo[*h*]quinoline (**S39**) (39.0 mg, 0.200 mmol, 1.00 equiv) was dissolved in 2N HCl (1.2 mL) at 0 ºC. To the reaction mixture was added a solution of $NaNO_2$ (16.6 mg, 0.240 mmol, 1.20 equiv) in H_2O (0.5 mL) dropwise over 2 min. The reaction mixture was stirred for 30 min at 0 ºC and a solution of CuCl (19.8 mg, 0.200 mmol, 1.00 equiv) in conc. HCl (0.5 mL) was added dropwise over 2 min. The reaction mixture was warmed to 23 ºC and further stirred for 1.0 hr before aqueous $NaHCO_3$ (3.0 mL) was added. To the reaction mixture was added CH_2Cl_2 (2.0 mL) and the phases were separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 2 mL). The combined organic phases were washed with brine (5 mL) and dried (Na_2SO_4). The filtrate was concentrated in vacuo and the residue was purified by preparative TLC eluting with hexanes/CH_2Cl_2 1:2 (v/v) to afford 20 mg of the title compound as a pale-yellow solid (47% yield).

R_f = 0.79 (CH_2Cl_2). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 9.26 (d, *J* = 8.5 Hz, 1H), 9.02 (dd, *J* = 4.5 Hz, *J* = 2.0 Hz, 1H), 8.27 (d, *J* = 9.5 Hz, 1H), 8.19 (dd, *J* = 8.0 Hz, *J* = 2.0 Hz, 1H), 7.79–7.76 (m, 2H), 7.64 (dd, *J* = 8.5 Hz, *J* = 8.5 Hz, 1H), 7.55 (dd, *J* = 8.0 Hz, *J* = 4.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 149.3, 146.1, 135.9, 133.1, 131.9, 130.8, 128.6, 127.0, 126.5, 126.2, 123.4, 123.4, 122.3. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{13}H_8ClN$ + H], 214.04235. Found, 214.04200.

7-Cyanobenzo[*h*]quinoline (S41)

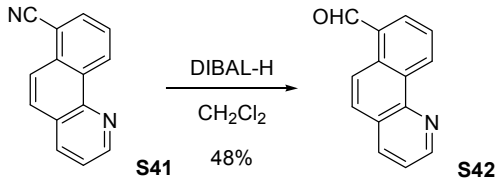


Under air, to 7-aminobenzo[*h*]quinoline (**S39**) (194 mg, 1.00 mmol, 1.00 equiv) in H_2O (4.0 mL), sulfuric acid (106 μL, 2.00 mmol, 2.00 equiv) was added dropwise at 0 ºC. After stirring for 10 min, a solution of $NaNO_2$ (83.0 mg, 1.20 mmol, 1.20 equiv) in H_2O (2.0 mL) was added dropwise and the reaction mixture was stirred for 30 min at 0 ºC. $NaHCO_3$ (336 mg, 4.00 mmol, 4.00 equiv), H_2O (5.0 mL), and toluene (5.0 mL) were added and the reaction mixture was warmed to 23 ºC over 15 min. A solution of KCN (446 mg, 6.85 mmol, 6.85 equiv) and CuCN (224 mg, 2.50 mmol, 2.50 equiv) in H_2O (2.0 mL) was added dropwise. The reaction mixture was warmed to 70 ºC, stirred for 2.0 hr, and cooled to 23 ºC. The cooled mixture was extracted with EtOAc (3 x 15 mL). The combined organic phases were washed with brine, dried ($MgSO_4$), and concentrated in vacuo. The crude product was purified by chromatography on silica gel eluting with EtOAc/hexanes 1:9 (v/v) to afford 143 mg of the title compound as a brown solid (70% yield).

R_f = 0.15 (hexanes/EtOAc 14 :1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 9.55 (d, *J* = 8.5 Hz, 1H), 9.05 (d, *J* = 4.5 Hz, 1H), 8.24 (d, *J* = 8.0 Hz, 1H), 8.20 (d, *J* = 9.0 Hz, 1H), 8.07 (d, *J* = 7.5 Hz, 1H), 7.90 (d, *J* = 9.0 Hz, 1H), 7.77 (ddd, *J* = 8.0 Hz, *J* = 8.0 Hz, *J* = 1.0 Hz, 1H), 7.61 (ddd, *J* =

8.0 Hz, *J* = 4.0 Hz, *J* = 2.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 149.8, 145.7, 136.1, 133.8, 133.4, 131.7, 129.6, 128.5, 126.4, 126.3, 123.9, 122.8, 117.9, 110.1. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{14}H_8N_2$ + H], 205.07657. Found, 205.07669.

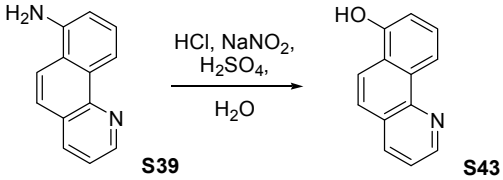
7-Formylbenzo[*h*]quinoline (S42)



S41 **S42**

To 7-cyanobenzo[*h*]quinoline (**S41**) (84.6 mg, 0.414 mmol, 1.00 equiv) in CH_2Cl_2 (5.0 mL) at –78 ºC, diisobutylaluminum hydride (1.0 M in hexanes, 0.83 mL, 0.83 mmol, 2.0 equiv) was added dropwise and the reaction mixture was stirred for 1.5 hr. An additional equivalent of diisobutylaluminum hydride (1.0 M in hexanes, 0.42 mL, 0.42 mmol, 2.0 equiv) was added dropwise. The reaction mixture was stirred for 30 min and warmed to 23 ºC. The reaction was quenched with 1N HCl (5.0 mL), and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phases were washed with $NaHCO_3$ (aq) and brine, dried ($MgSO_4$), and concentrated in vacuo. The crude mixture was filtered through a plug of silica gel eluting with CH_2Cl_2 and concentrated in vacuo to afford 41.3 mg of the title compound as a tan solid (48 % yield). R_f = 0.33 (hexanes/EtOAc 5:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 10.51 (s, 1H), 9.68 (d, *J* = 8.5 Hz, 1H), 9.26 (d, *J* = 9.5 Hz, 1H), 9.05 (dd, *J* = 4.5 Hz, *J* = 1.5 Hz, 1H), 8.25 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 8.19 (dd, *J* = 7.0 Hz, *J* = 1.0 Hz, 1H), 7.93–7.89 (m, 2H), 7.60 (dd, *J* = 8.0 Hz, *J* = 4.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 193.6, 149.4, 145.8, 137.2, 135.8, 132.2, 131.7, 131.2, 131.1, 128.7, 126.3, 126.2, 123.5, 122.5. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{14}H_9NO$ + H], 208.07624. Found, 208.07655.

7-Hydroxybenzo[*h*]quinoline (S43)

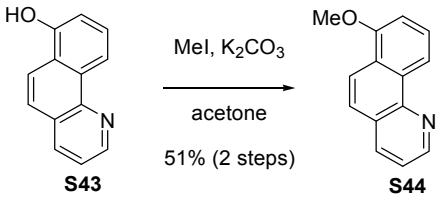


S39 **S43**

Under air, to 7-aminobenzo[*h*]quinoline (**S39**) (400 mg, 2.06 mmol, 1.00 equiv) in 2N HCl (3.8 mL) and water (5.8 mL) at 0 ºC was added sodium nitrite (156 mg, 2.27 mmol, 1.10 equiv) in H_2O (1.4 mL). The reaction mixture was stirred at 0 ºC for 1.0 hr. The reaction mixture was added dropwise to a stirring solution of sulfuric acid (3.3 mL) in H_2O (7.9 mL) at 88 ºC, and subsequently heated to 100 ºC for 1.0 hr. The reaction was cooled to 23 ºC and neutralized to pH 7 with 3N NaOH (aq), and extracted with EtOAc

(3 × 150 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated in vacuo to afford a crude solid (370 mg), which was used in the next step without further purification.[14]

7-Methoxybenzo[*h*]quinoline (S44)

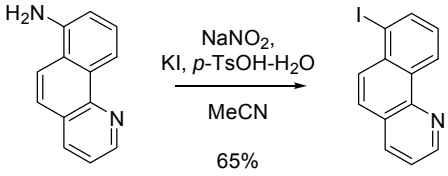


S43 **S44**

Under air, to crude 7-hydroxybenzo[*h*]quinoline (**S43**) (370 mg, 1.90 mmol, 1.00 equiv) in acetone (50 mL) were added potassium carbonate (524 mg, 3.79 mmol, 2.00 equiv) and iodomethane (0.180 mL, 2.84 mmol, 1.50 equiv). The mixture was heated at reflux and stirred for 11 hr. The reaction mixture was cooled to 23 ºC and concentrated in vacuo. The concentrate was diluted with EtOAc (15 mL), washed with H_2O (10 mL) and brine (10 mL), and the aqueous phase was extracted with EtOAc (2 × 15 mL). The combined organic phases were dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by chromatography on silica gel eluting with hexanes/EtOAc 9:1 (v/v) to afford 218 mg of the title compound as a light yellow solid (51% yield, 2 steps).

R_f = 0.34 (hexanes/EtOAc 9:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 9.00 (dd, *J* = 4.5 Hz, *J* = 1.5 Hz, 1H), 8.89 (d, *J* = 8.0 Hz, 1H), 8.30 (d, *J* = 9.0 Hz, 1H), 8.18 (dd, *J* = 8.0 Hz, *J* = 1.5 Hz, 1H), 7.69–7.65 (m, 2H), 7.52 (dd, *J* = 8.0 Hz, *J* = 4.5 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 1H), 4.05 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 155.6, 148.9, 146.4, 136.0, 132.8, 127.4, 126.7, 125.0, 124.5, 122.0, 121.6, 116.6, 107.5, 55.9. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{14}H_{11}NO$ + H], 210.09189. Found, 210.09207.

7-Iodobenzo[*h*]quinoline (S45)



S39 **S45**

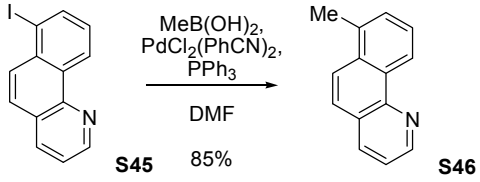
To a solution of *p*–toluenesulfonic acid monohydrate (588 mg, 3.09 mmol, 3.00 equiv) in acetonitrile (4.0 mL) under air was added 7-aminobenzo[*h*]quinoline (**S39**) (200 mg, 1.03 mmol, 1.00 equiv). The reaction mixture was cooled to 10 ºC and a solution of $NaNO_2$ (142 mg, 2.06 mmol, 2.00 equiv) and KI

[14] Aramoto, H.; Obora, Y..; Ishii, Y. *J. Org. Chem.*. **2009**, *74*, 628–633.

(427 mg, 2.57 mmol, 2.50 equiv) in H_2O (0.6 mL) was added dropwise, and the reaction was stirred for 10 min, warmed to 23 ºC, and stirred for an additional 1.5 hr. H_2O (15 mL), $Na_2S_2O_3$ (2 mL) and sat $NaHCO_3$ (aq) were added to basify the solution. The reaction mixture was extracted with EtOAc (10 mL) and CH_2Cl_2 (2 × 10 mL). The combined organic phases were dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by chromatography on silica gel eluting with CH_2Cl_2/ hexanes 2:1 (v/v) to afford 204 mg of the title compound as a light yellow crystalline solid (65% yield).

R_f = 0.52 (CH_2Cl_2/hexanes 2:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 9.37 (dd, *J* = 9.5 Hz, *J* = 1.0 Hz, 1H), 9.03 (dd, *J* = 4.5 Hz, *J* = 1.5 Hz, 1H), 8.28 (dd, *J* = 7.5 Hz, *J* = 1.5 Hz, 1H), 8.22 (dd, *J* = 8.0 Hz, *J* = 1.5 Hz, 1H), 8.13 (d, *J* = 9.5 Hz, 1H), 7.79 (d, *J* = 9.5 Hz, 1H), 7.57 (dd, *J* = 8.5 Hz, *J* = 4.5 Hz, 1H), 7.44 (dd, *J* = 7.5 Hz, *J* = 7.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 149.5, 146.2, 139.7, 136.0, 134.7, 132.9, 131.5, 128.2, 127.2, 126.2, 125.3, 122.5, 99.4. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{13}H_8IN$ + H], 305.97797. Found, 305.97765.

7-Methylbenzo[*h*]quinoline (S46)

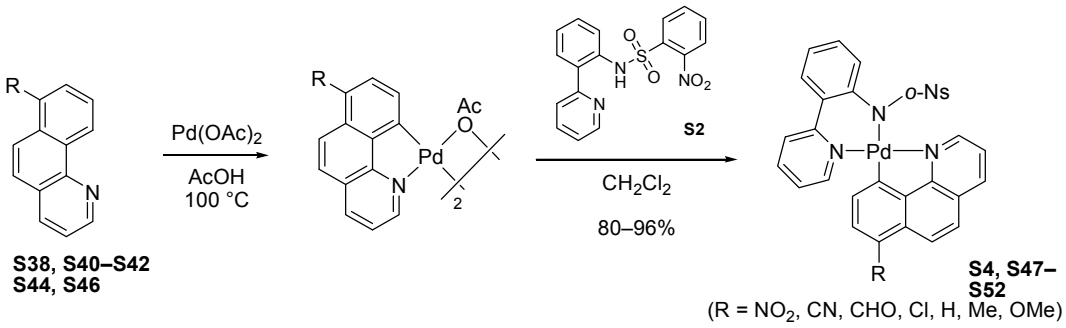


S45 **S46**

Under air, to 7-iodobenzo[*h*]quinoline (**S45**) (289 mg, 0.950 mmol, 1.00 equiv), methylboronic acid (623 mg, 2.84 mmol, 3.00 equiv), $PdCl_2(PhCN)_2$ (36.0 mg, 0.095 mmol, 10.0 mol%), PPh_3 (50.0 mg, 0.190 mmol, 20.0 mol%), and potassium carbonate (393 mg, 2.84 mmol, 3.00 equiv), was added DMF (7.2 mL). The reaction mixture was heated to 110 ºC for 5.5 hr. After cooling to 23 ºC, the reaction mixture was diluted with H_2O and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were dried with Na_2SO_4 and concentrated in vacuo. The crude product was purified by chromatography on silica gel eluting with CH_2Cl_2 to afford 155 mg of the title compound as a light yellow solid (85% yield).

R_f = 0.57 (CH_2Cl_2). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 9.22 (d, *J* = 8.0 Hz, 1H), 9.01 (dd, *J* = 4.5 Hz, *J* = 2.0 Hz, 1H), 8.18 (dd, *J* = 8.0 Hz, 1.5 Hz, 1H), 8.03 (d, *J* = 9.5 Hz, 1H), 7.73 (d, *J* = 9.5 Hz, 1H), 7.64 (dd, *J* = 8.0 Hz, *J* = 7.0 Hz, 1H), 7.56–7.51 (m, 2H), 2.78 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 149.0, 147.0, 135.9, 134.4, 132.6, 131.8, 129.5, 126.8, 126.1, 125.2, 124.0, 122.7, 121.8, 19.9. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{14}H_{11}N$ + H], 194.09697. Found, 194.09667.

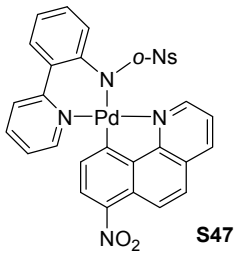
Synthesis of Pd(II) complexes with different benzo[*h*]quinoline substitution



To a substituted benzo[*h*]quinoline **S38**, **S40**−**S42**, **S44**, **S46** (0.100 mmol, 1.00 equiv) in AcOH (1 mL) at 23 ºC was added $Pd(OAc)_2$ (22.4 mg, 0.100 mmol, 1.00 equiv) and the reaction mixture was heated to 100 ºC for 10 min. After being cooled to 23 ºC, the reaction mixture was concentrated in vacuo and triturated with Et_2O (3 × 1 mL) to afford the corresponding cyclopalladation product, which was used in the next step without further purification.

To the crude benzo[*h*]quinoline palladium(II) acetate dimer in CH_2Cl_2 (1 mL) at 23 ºC was added pyridinylsulfonanilide ligand **S2** (35.5 mg, 0.100 mmol, 1.00 equiv). After stirring for 1.0 hours the reaction mixture was concentrated in vacuo. The resulting residue was triturated with Et_2O (3 × 1 mL) to afford the corresponding substituted palladium(II) complex (80−96% yield).

7-Nitrobenzo[*h*]quinolinyl palladium(II) complex S47

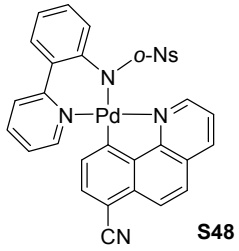


92% yield. NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 9.66 (d, *J* = 5.0 Hz, 1H), 8.74 (d, *J* = 5.5 Hz, 1H), 8.50 (d, *J* = 9.5 Hz, 1H), 8.29 (d, *J* = 7.5 Hz, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.71–7.65 (m, 2H), 7.53 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H), 7.34–7.22 (m, 5H), 7.11–7.06 (m, 2H), 6.99–6.94 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ)[15]: 167.5, 157.6, 153.9, 153.1, 151.7, 143.2, 142.7, 142.0, 141.9, 138.9, 137.6, 136.2, 131.8, 130.2, 130.0, 129.5, 129.2, 128.0, 127.5, 126.4, 125.6, 125.3, 125.0, 124.9, 124.5, 124.0, 123.7, 122.9. Mass Spectrometry: HRMS-FIA (m/z): Calcd for

[15] Due to the low solubility of the palladium complex, only 28 carbon resonances were observed in the ^{13}C spectrum.

$[C_{30}H_{19}N_5O_6PdS + H]$, 684.01636. Found, 684.01552.

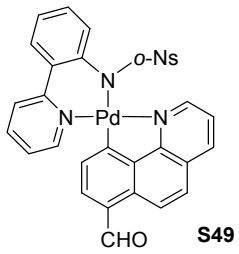
7-Cyanobenzo[*h*]quinolinyl palladium(II) complex S48



S48

90% yield. NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 9.55 (d, *J* = 5.5 Hz, 1H), 8.99 (d, *J* = 5.0 Hz, 1H), 8.30 (d, *J* = 7.5 Hz, 1H), 7.75–7.72 (m, 2H), 7.63–7.55 (m, 4H), 7.49 (dd, *J* = 7.0 Hz, *J* = 7.0 Hz, *J* = 1.0 Hz, 1H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.36 (dd, *J* = 7.0 Hz, *J* = 7.0 Hz, 1H), 7.24–7.14 (m, 5H), 7.04 (d, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 7.5 Hz, 1H). Mass Spectrometry: HRMS-FIA (m/z): Calcd for $[C_{31}H_{19}N_5O_4PdS + H]$, 664.02653. Found, 664.02440.[10]

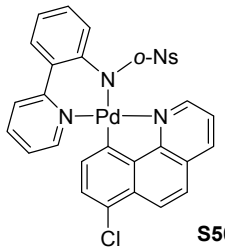
7-Formylbenzo[*h*]quinolinyl palladium(II) complex S49



S49

88% yield. NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 10.30 (s, 1H), 9.63 (d, *J* = 5.5 Hz, 1H), 9.14 (d, *J* = 9.0 Hz, 1H), 8.96 (d, *J* = 6.0 Hz, 1H), 8.39 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 9.0 Hz, 1H), 7.78–7.76 (m, 2H), 7.71 (dd, *J* = 8.0 Hz, *J* = 5.5 Hz, 1H), 7.66 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H), 7.52–7.44 (m, 3H), 7.28–7.21 (M, 5H), 7.15 (d, *J* = 7.0 Hz, 1H), 7.06 (d, *J* = 8.5 Hz, 1H). Mass Spectrometry: HRMS-FIA (m/z): Calcd for $[C_{31}H_{20}N_4O_5PdS + H]$, 667.02620. Found, 667.02289.[10]

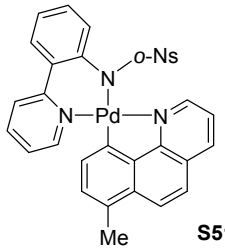
7-Chlorobenzo[*h*]quinolinyl palladium(II) complex S50



S50

96% yield. NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 9.71 (d, *J* = 5.5, 1H), 8.82 (d, *J* = 5.5, 1H), 8.33 (d, *J* = 8.0, 1H), 8.10 (d, *J* = 8.5, 1H), 7.83 (d, *J* = 8.5, 1H), 7.71–7.68 (m, 2H), 7.64 (ddd, *J* = 8.5 Hz, *J* = 8.5 Hz, *J* = 1.5 Hz, 1H), 7.48 (ddd, *J* = 9.0 Hz, *J* = 9.0 Hz, 1.5 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.35 (dd, *J* = 7.5 Hz, *J* = 1.5 Hz, 1H), 7.31 (d, *J* = 7.0 Hz, 1H), 7.25–7.23 (m, 2H), 7.18 (dd, *J* = 7.5 Hz, *J* = 7.5 Hz, 1H), 7.09–7.02 (m, 2H), 6.96–6.89 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ)[16]: 157.8, 154.9, 153.7, 153.3, 151.5, 143.7, 138.5, 137.5, 136.2, 131.7, 131.3, 130.4, 130.3, 129.3, 129.1, 127.9, 127.5, 126.8, 126.0, 125.7, 125.0, 124.8, 124.7, 124.2, 123.3, 122.3. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{30}H_{19}ClN_4O_4PdS$ + H], 672.99231. Found, 672.99188.[10]

7-Methylbenzo[*h*]quinolinyl palladium(II) complex S51

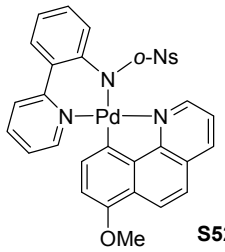


S51

80% yield. NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 9.56 (d, *J* = 5.0 Hz, 1H), 8.97 (d, *J* = 6.0 Hz, 1H), 8.30 (d, *J* = 8.5 Hz, 1H), 7.91 (d, *J* = 9.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.65–7.56 (m, 4H), 7.49 (dd, *J* = 7.0 Hz, *J* = 7.0 Hz, 1H), 7.41 (d, *J* = 7.5 Hz, *J* = 7.5 Hz, 1H), 7.26–7.14 (m, 6H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.88 (d, *J* = 7.5 Hz, 1H), 2.65 (s, 3H). Anal: calcd for $C_{31}H_{22}N_4O_4PdS$: C, 57.02; H, 3.40; N, 8.58; found: C, 56.75; H, 3.23; N, 8.41.[10]

[16] Due to the low solubility of the palladium complex, only 26 carbon resonances were observed in the ^{13}C spectrum.

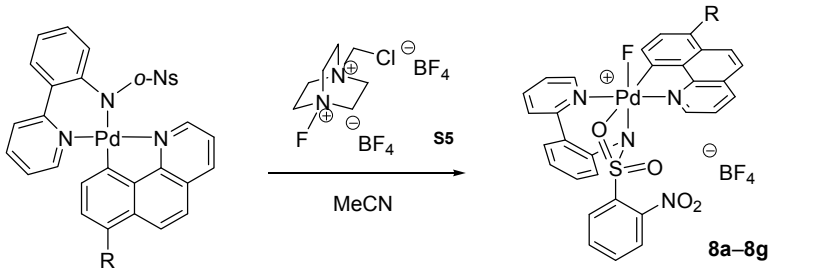
7-Methoxybenzo[*h*]quinolinyl palladium(II) complex S52



S52

95% yield. NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 9.55 (d, *J* = 5.0 Hz, 1H), 8.99 (d, *J* = 5.5 Hz, 1H), (d, *J* = 8.5 Hz, 1H), 8.13 (d, *J* = 9.0 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.64–7.58 (m, 4H), 7.49 (dd, *J* = 7.0 Hz, *J* = 7.0 Hz, 1H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.24–7.13 (m, 5H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 3.96 (s, 3H). Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{31}H_{22}N_4O_5PdS$ + H], 669.04240. Found, 669.04268.[10]

Synthesis of monofluoro Pd(IV) complexes with different benzo[*h*]quinoline substitution



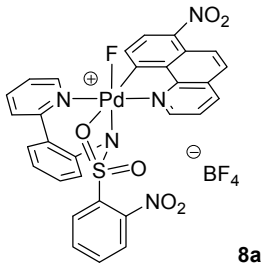
S4, S47–S52 **8a–8g**

(R = NO_2, CN, CHO, Cl, H, Me, OMe)

To benzo[*h*]quinolinyl palladium(II) pyridine-sulfonamido complex **S4**, **S47**–**S52** (0.020 mmol, 1.0 equiv) in acetonitrile-*d3* (0.6 mL) at 23 ºC was added 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo [2.2.2]octane bis(tetrafluoroborate) (**S5**) (7.1 mg, 0.020 mmol, 1.0 equiv). After stirring for 10 min at 23 ºC, the colorless suspension formed a dark purple solution. Compounds **8a**–**8g** were characterized by NMR spectroscopy in acetonitrile solution without purification.[17]

[17] Compound **8e** and **1** are identical, but labeled like this for clarity.

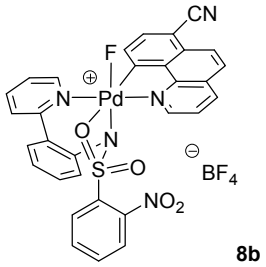
7-Nitrobenzo[*h*]quinolinyl palladium(IV) complex 8a



8a

NMR Spectroscopy: ^{1}H NMR (500 MHz, acetonitrile-*d3*, 25 ºC, δ): 9.69 (d, *J* = 5.5 Hz, 1H), 9.45 (d, *J* = 6.0 Hz, 1H), 8.97 (d, *J* = 8.0 Hz, 1H), 8.64 (d, *J* = 9.5 Hz, 1H), 8.50 (d, *J* = 8.0 Hz, 1H), 8.43 (d, *J* = 7.5 Hz, 1H), 8.29 (d, *J* = 9.5 Hz, 1H), 8.14 (dd, *J* = 8.5 Hz, *J* = 6.0 Hz, 1H), 7.96 (d, *J* = 6.5 Hz, 1H), 7.79–7.74 (m, 2H), 7.61–7.56 (m, 2H), 7.43–7.37 (m, 2H), 7.18 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H), 6.85 (dd, *J* = 7.5 Hz, *J* = 7.5 Hz, 1H), 6.71 (d, *J* = 8.5 Hz, 1H), 6.48 (d, *J* = 9.0 Hz, 1H). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –151.8 (s), –277.4 (br s).

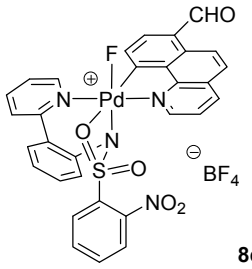
7-Cyanobenzo[*h*]quinolinyl palladium(IV) complex 8b



8b

NMR Spectroscopy: ^{1}H NMR (500 MHz, acetonitrile-*d3*, 25 ºC, δ): 9.57 (d, *J* = 5.5 Hz, 1H), 9.42 (d, *J* = 6.5 Hz, 1H), 8.85 (d, *J* = 7.5 Hz, 1H), 8.45 (dd, *J* = 7.5 Hz, 1H), 8.37 (d, *J* = 7.5 Hz, 1H), 8.04–7.97 (m, 2H), 7.92 (ddd, *J* = 7.5 Hz, *J* = 7.5 Hz, *J* = 1.5 Hz, 1H), 7.76–7.74 (m, 2H), 7.60–7.54 (m, 2H), 7.43–7.37 (m, 2H), 7.17 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H), 7.02 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H), 6.86 (ddd, *J* = 8.5 Hz, *J* = 8.5 Hz, *J* = 1.5 Hz, 1H), 6.75 (d, *J* = 8.5 Hz, 1H), 6.27 (d, *J* = 8.5 Hz, 1H). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –152.0 (s), –278.5 (br s).

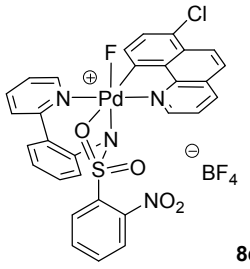
7-Formylbenzo[*h*]quinolinyl palladium(IV) complex 8c



8c

NMR Spectroscopy: ^{1}H NMR (500 MHz, acetonitrile-*d3*, 25 ºC, δ): 10.22 (s, 1H), 9.65 (d, *J* = 5.5 Hz, 1H), 9.45 (d, *J* = 6.0 Hz, 1H), 9.07 (d, *J* = 9.5 Hz, 1H), 8.93 (d, *J* = 7.5 Hz, 1H), 8.49 (d, *J* = 7.5 Hz, 1H), 8.42 (d, *J* = 6.5 Hz, 1H), 8.23 (d, *J* = 9.5 Hz, 1H), 8.09 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H), 7.96 (ddd, *J* = 8.0 Hz, *J* = 8.0 Hz, *J* = 1.5 Hz, 1H), 7.76 (dd, *J* = 7.5 Hz, *J* = 0.5 Hz, 1H), 7.60–7.52 (m, 3H), 7.43–7.37 (m, 2H), 7.17 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H), 6.82 (ddd, *J* = 8.5 Hz, *J* = 8.5 Hz, *J* = 1.0 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 6.51 (d, *J* = 9.0 Hz, 1H). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –151.9 (s), –278.2 (br s).

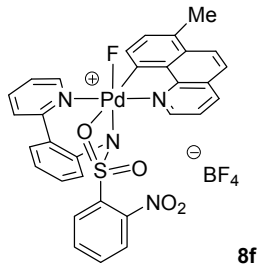
7-Chlorobenzo[*h*]quinolinyl palladium(IV) complex 8d



8d

NMR Spectroscopy: ^{1}H NMR (500 MHz, acetonitrile-*d3*, 25 ºC, δ): 9.62 (d, *J* = 5.0 Hz, 1H), 9.42 (d, *J* = 6.0 Hz, 1H), 8.91 (d, *J* = 8.0 Hz, 1H), 8.46 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H), 8.39 (d, *J* = 8.5 Hz, 1H), 8.21–8.15 (m, 2H), 8.07 (dd, *J* = 8.0 Hz, *J* = 5.5 Hz, 1H), 7.93 (dd, *J* = 5.5 Hz, *J* = 5.5 Hz, 1H), 7.74 (dd, *J* = 8.0 Hz, *J* = 1.0 Hz, 1H), 7.60–7.55 (m, 2H), 7.43–7.37 (m, 2H), 7.19 (dd, *J* = 7.5 Hz, *J* = 7.5 Hz, 1H), 7.12 (d, *J* = 8.5 Hz, 1H), 6.88 (ddd, *J* = 9.0 Hz, *J* = 9.0 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 6.26 (d, *J* = 9.0 Hz, 1H). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –151.8 (s), –277.9 (br s).

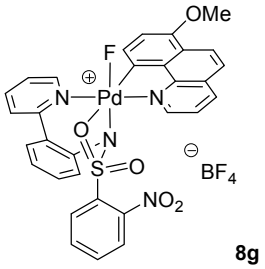
7-Methylbenzo[*h*]quinolinyl palladium(IV) complex 8f



8f

NMR Spectroscopy: ^{1}H NMR (500 MHz, acetonitrile-*d3*, 25 ºC, δ): 9.57 (d, *J* = 6.0 Hz, 1H), 9.41 (d, *J* = 6.0 Hz, 1H), 8.84 (d, *J* = 8.0 Hz, 1H), 8.43 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H), 8.35 (d, *J* = 7.5 Hz, 1H), 8.08–7.98 (m, 3H), 7.90 (ddd, *J* = 7.5 Hz, *J* = 7.5 Hz, *J* = 1.5 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.59–7.54 (m, 2H), 7.43–7.36 (m, 2H), 7.17 (dd, *J* = 7.5 Hz, *J* = 7.5 Hz, 1H), 6.89–6.84 (m, 2H), 6.75 (d, *J* = 8.5 Hz, 1H), 6.16 (d, *J* = 8.5 Hz, 1H), 2.59 (s, 3H). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –151.9 (s), –276.8 (br s).

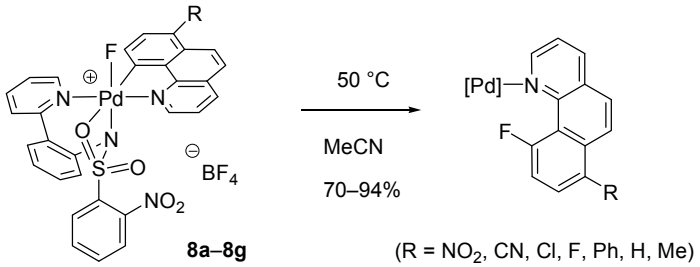
7-Methoxybenzo[*h*]quinolinyl palladium(IV) complex 8g



8g

NMR Spectroscopy: ^{1}H NMR (500 MHz, acetonitrile-*d3*, 25 ºC, δ): 9.55 (d, *J* = 5.5 Hz, 1H), 9.41 (d, *J* = 5.5 Hz, 1H), 8.83 (d, *J* = 8.0 Hz, 1H), 8.44 (dd, *J* = 8.0 Hz, 1H), 8.35 (d, *J* = 7.5 Hz, 1H), 8.14 (d, *J* = 9.0 Hz, 1H), 8.01–7.97 (m, 2H), 7.91 (ddd, *J* = 8.0 Hz, *J* = 8.0 Hz, *J* = 1.5 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.59–7.52 (m, 2H), 7.43–7.36 (m, 2H), 7.18 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H), 6.90 (dd, *J* = 7.0 Hz, *J* = 7.0 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H), 6.48 (d, *J* = 9.0 Hz, 1H), 6.19 (d, *J* = 9.0 Hz, 1H), 3.86 (s, 3H). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –151.9 (s), –276.3 (br s).

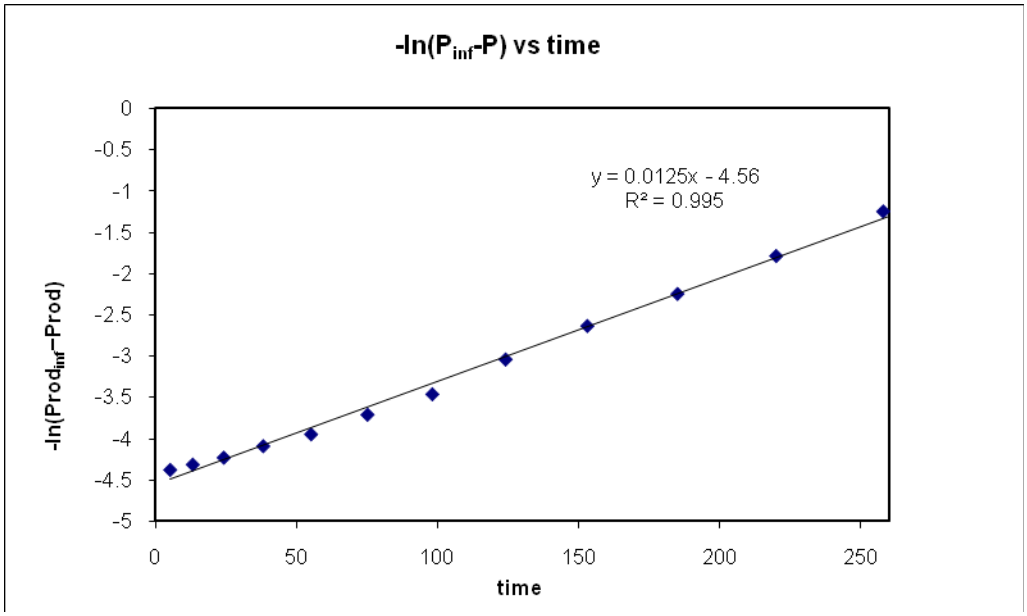
Kinetic experiments of C−F reductive elimination from Pd(IV) complexes



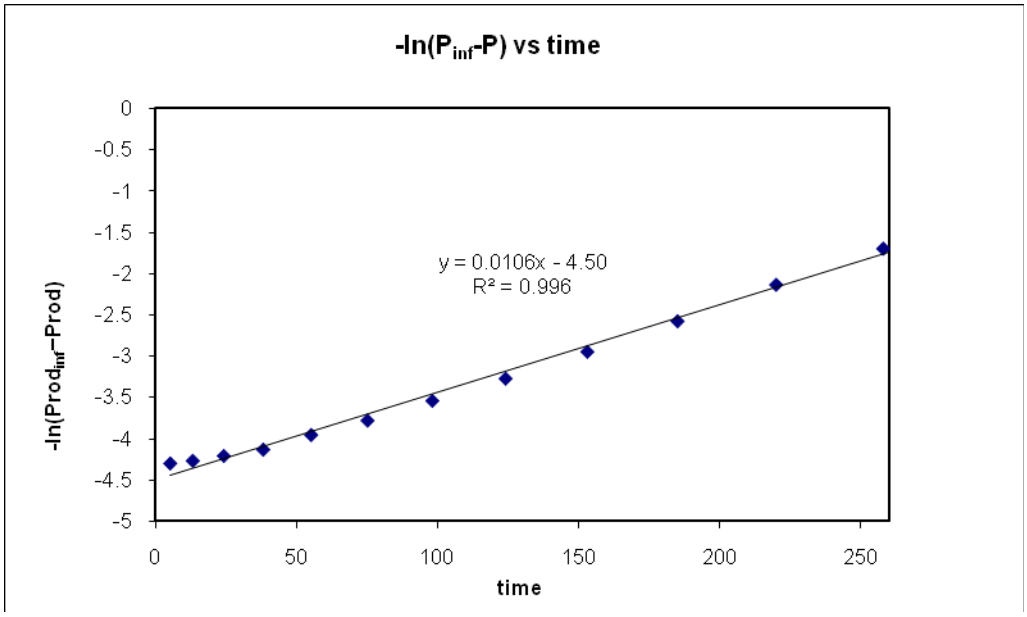
8a–8g (R = NO_2, CN, Cl, F, Ph, H, Me)

Solutions (33.3 mM) of compound **8a**–**8g** were prepared by reacting compound **S4**, **S42**–**S47** (0.020 mmol, 1.0 equiv) with 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo [2.2.2]octane bis(tetrafluoroborate) (**S5**) (7.1 mg, 0.020 mmol, 1.0 equiv) in NMR tubes under nitrogen. NMR samples were placed in the preheated NMR machine (50 ºC) and the disappearance of the compounds **8a**–**8g** and formation of the product were monitored by integrating the peak at around 6.3 ppm and 9.1 ppm, respectively, relative to the peak of 1-chloromethyl-1,4-diazoniabicyclo [2.2.2]octane (tetrafluoroborate) at 4.91 ppm.

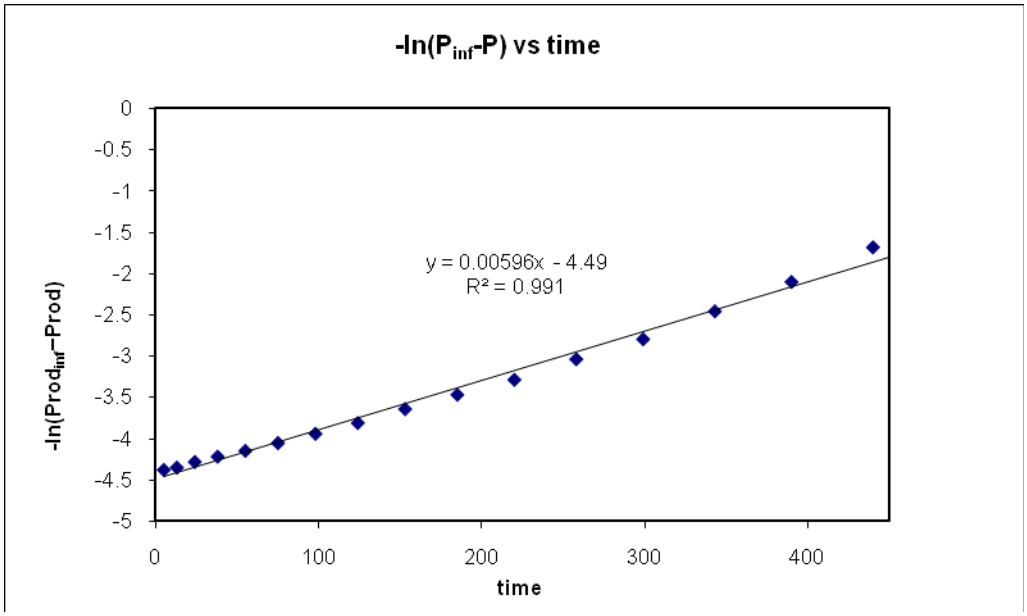
R = NO_2



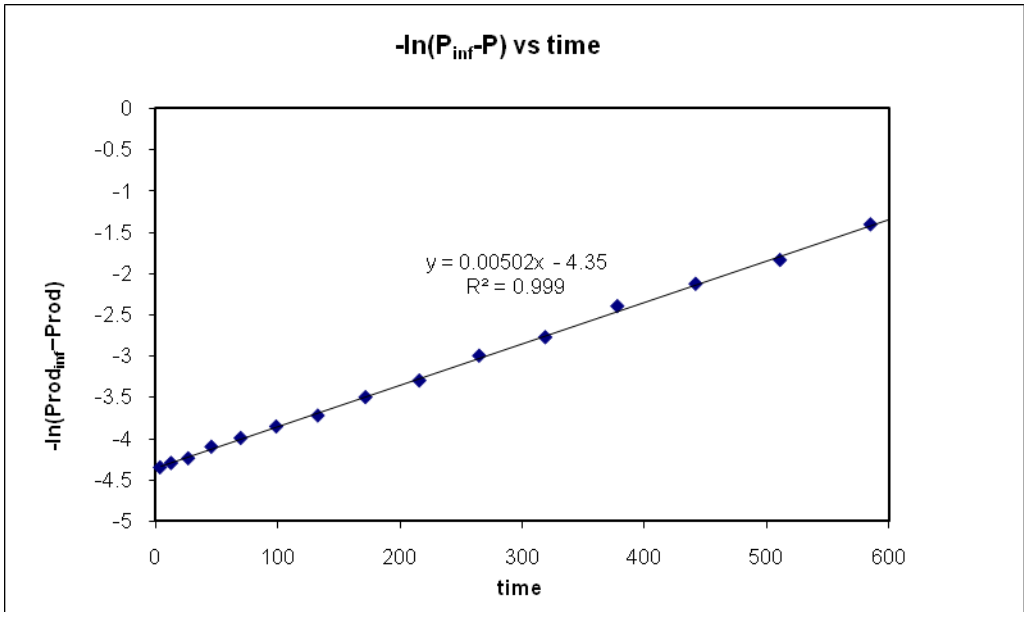
R = CN


-ln(P_inf-P) vs time
y = 0.0106x - 4.50
R² = 0.996
-ln(Prod_inf−Prod)
time
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
-4
-4.5
-5
0
50
100
150
200
250

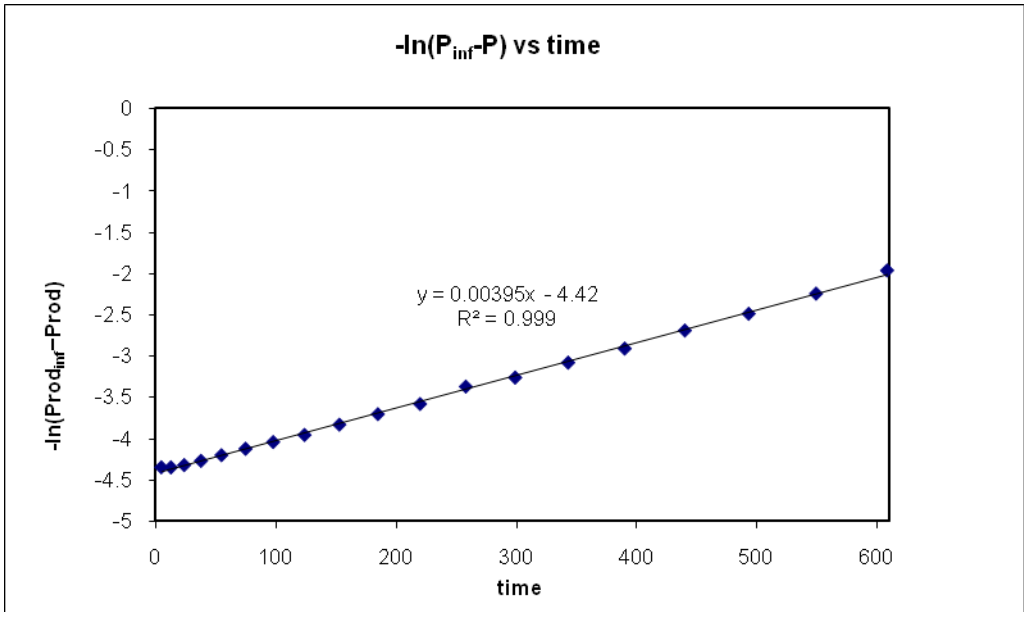
R = CHO


-ln(P_inf-P) vs time
y = 0.00596x - 4.49
R² = 0.991
-ln(Prod_inf−Prod)
time
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
-4
-4.5
-5
0
100
200
300
400

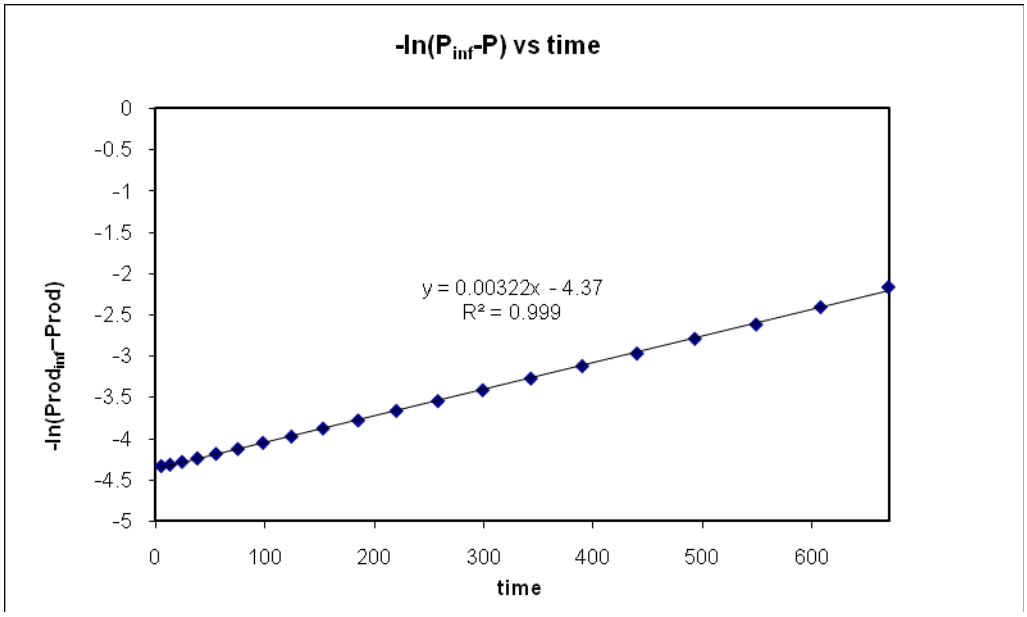
R = Cl


-ln(P$_{inf}$-P) vs time
y = 0.00502x - 4.35
R² = 0.999
-ln(Prod$_{inf}$–Prod)
time
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
-4
-4.5
-5
0
100
200
300
400
500
600

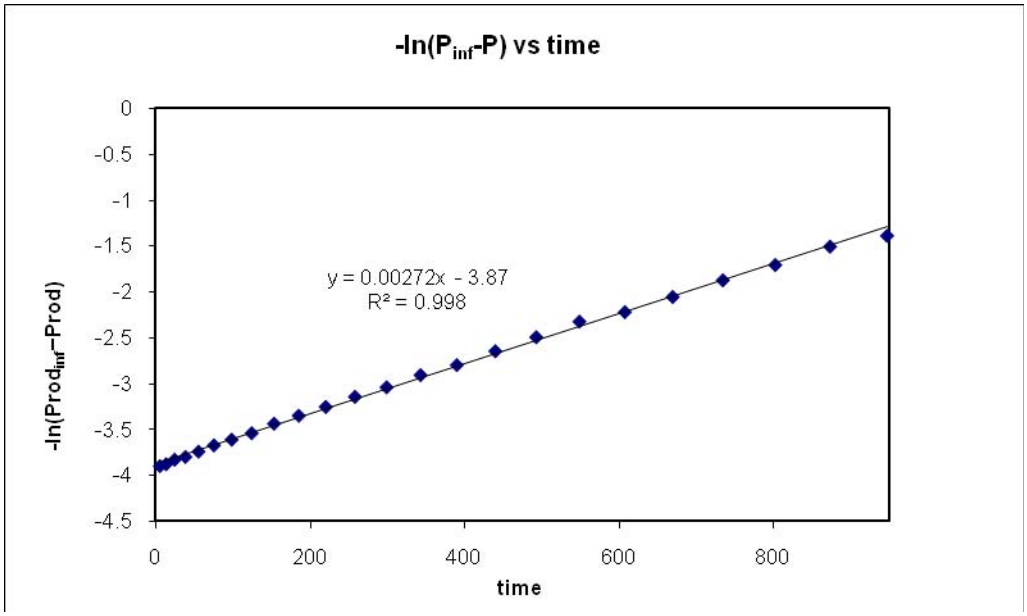
R = H


-ln(P$_{inf}$-P) vs time
y = 0.00395x - 4.42
R² = 0.999
-ln(Prod$_{inf}$–Prod)
time
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
-4
-4.5
-5
0
100
200
300
400
500
600

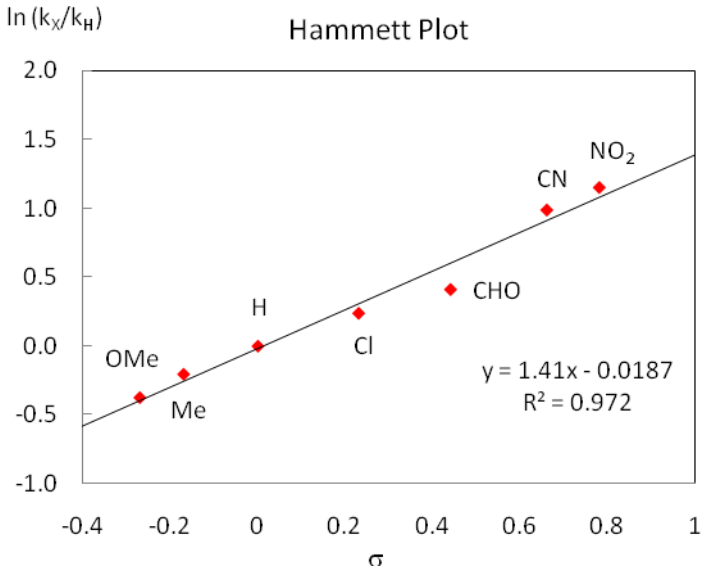
R = Me


-ln(P_inf-P) vs time
y = 0.00322x - 4.37
R² = 0.999
-ln(Prod_inf−Prod)
time
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
-4
-4.5
-5
0
100
200
300
400
500
600

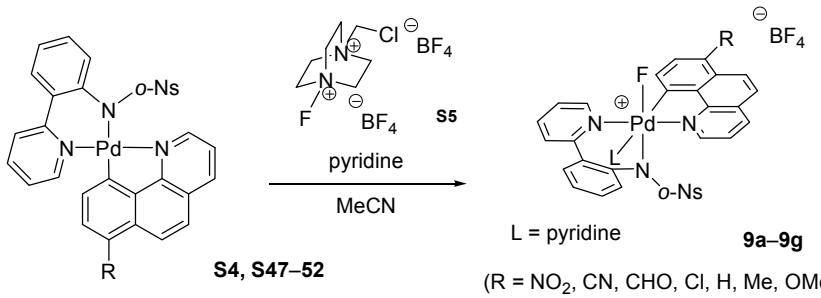
R = OMe


-ln(P_inf-P) vs time
y = 0.00272x - 3.87
R² = 0.998
-ln(Prod_inf−Prod)
time
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
-4
-4.5
0
200
400
600
800

	σ	k	$\ln(k_X/k_H)$	Fluorination Yield (%)
NO_2	0.78	0.0125	1.15	94
CN	0.66	0.0106	0.990	92
CHO	0.44	0.00596	0.412	91
Cl	0.23	0.00502	0.239	71
H	0	0.00395	0	94
Me	–0.17	0.00322	–0.204	86
OMe	–0.27	0.00272	–0.374	70



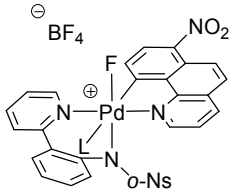
Synthesis of monofluoro Pd(IV) pyridine complexes with different benzo[*h*]quinoline substitution



Solutions (33.3 mM) of compound **9a**–**9g** were prepared by reacting compound **S4**, **S47**–**S52** (0.020 mmol, 1.0 equiv) with 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo [2.2.2]octane bis(tetrafluoroborate) (**S5**) (7.1 mg, 0.020 mmol, 1.0 equiv) and pyridine (2.4 μL, 0.030 mmol, 1.50 equiv) in NMR tubes under

nitrogen. Compounds **9a**–**9g** were characterized by NMR spectroscopy in acetonitrile solution without purification.[18]

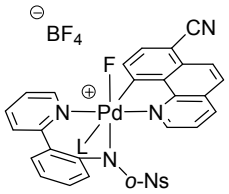
7-Nitrobenzo[*h*]quinolinyl palladium(IV) pyridine complex 9a



L = pyridine **9a**

NMR Spectroscopy: ^{1}H NMR (500 MHz, acetonitrile-*d3*, 25 ºC, δ): 8.96 (d, *J* = 6.0 Hz, 1H), 8.89 (d, *J* = 8.0 Hz, 1H), 8.72 (d, *J* = 9.0 Hz, 1H), 8.61–8.58 (m, 2H), 8.38 (dd, *J* = 7.5 Hz, *J* = 7.5 Hz, 1H), 8.28 (d, *J* = 9.0 Hz, 1H), 7.98 (dd, *J* = 7.5 Hz, *J* = 5.5 Hz, 1H), 7.87 (d, *J* = 9.0 Hz, 1H), 7.81 (d, *J* = 7.0 Hz, 1H), 7.60–7.57 (m, 2H), 7.50 (dd, *J* = 7.5 Hz, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 7.5 Hz, 1H), 7.35 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H), 7.22 (dd, *J* = 7.5 Hz, *J* = 7.5 Hz, 1H), 6.87 (dd, *J* = 7.5 Hz, *J* = 7.5 Hz, 1H), 6.75 (d, *J* = 8.5 Hz, 1H), 6.55 (d, *J* = 9.0 Hz, 1H). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –151.8 (s), –264.1 (br s).

7-Cyanobenzo[*h*]quinolinyl palladium(IV) pyridine complex 9b

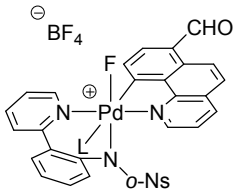


L = pyridine **9b**

NMR Spectroscopy: ^{1}H NMR (500 MHz, acetonitrile-*d3*, 25 ºC, δ): 8.93 (d, *J* = 5.5 Hz, 1H), 8.89 (d, *J* = 7.5 Hz, 1H), 8.60–8.56 (m, 2H), 8.38 (dd, *J* = 7.5 Hz, *J* = 7.5 Hz, 1H), 8.27–8.22 (m, 2H), 7.96 (dd, *J* = 8.0 Hz, *J* = 6.0 Hz, 1H), 7.80 (d, *J* = 7.5 Hz, 1H), 7.59–7.53 (m, 3H), 7.49 (dd, *J* = 6.0 Hz, *J* = 6.0 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.34 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H), 7.21 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H), 6.87 (dd, *J* = 6.5 Hz, *J* = 6.5 Hz, 1H), 6.74 (d, *J* = 8.5 Hz, 1H), 6.50 (d, *J* = 8.0 Hz, 1H). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –151.8 (s), –264.9 (br s).

[18] Compound **9e** and **2** are identical, but labeled like this for clarity

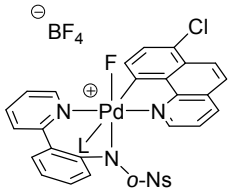
7-Formylbenzo[*h*]quinolinyl palladium(IV) pyridine complex 9c



L = pyridine **9c**

NMR Spectroscopy: ^{1}H NMR (500 MHz, acetonitrile-*d3*, 25 ºC, δ): 10.28 (s, 1H), 9.17 (d, *J* = 9.5 Hz, 1H), 8.92 (d, *J* = 6.5 Hz, 1H), 8.84 (d, *J* = 7.5 Hz, 1H), 8.61 (d, *J* = 6.0 Hz, 1H), 8.58 (d, *J* = 8.0 Hz, 1H), 8.38 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H), 8.21 (d, *J* = 8.5 Hz, 1H), 7.92 (d, *J* = 7.5 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.5 Hz, 1H), 7.58–7.54 (m, 2H), 7.49 (dd, *J* = 6.5 Hz, *J* = 6.5 Hz, 1H), 7.43 (d, *J* = 7.5 Hz, 1H), 7.31 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H), 7.20 (dd, *J* = 7.5 Hz, *J* = 7.5 Hz, 1H), 6.84 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H), 6.74 (d, *J* = 8.0 Hz, 1H), 6.60 (d, *J* = 8.0, 1H). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –151.8 (s), –264.6 (br s).

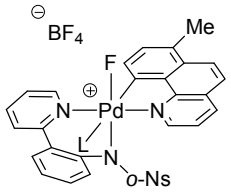
7-Chlorobenzo[*h*]quinolinyl palladium(IV) pyridine complex 9d



L = pyridine **9d**

NMR Spectroscopy: ^{1}H NMR (500 MHz, acetonitrile-*d3*, 25 ºC, δ): 8.90 (d, *J* = 5.5 Hz, 1H), 8.82 (d, *J* = 8.0 Hz, 1H), 8.60 (d, *J* = 6.0 Hz, 1H), 8.55 (d, *J* = 7.5 Hz, 1H), 8.36 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H), 8.28 (d, *J* = 9.0 Hz, 1H), 8.14 (d, *J* = 9.5 Hz, 1H), 7.90 (dd, *J* = 7.0 Hz, *J* = 7.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.57–7.52 (m, 3H), 7.47 (dd, *J* = 6.0 Hz, *J* = 6.0 Hz, 1H), 7.43 (d, *J* = 7.5 Hz, 1H), 7.30 (dd, *J* = 7.5 Hz, *J* = 7.5 Hz, 1H), 7.21 (dd, *J* = 9.5 Hz, *J* = 9.5 Hz, 1H), 6.89 (dd, *J* = 7.0 Hz, *J* = 7.0 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.35 (d, *J* = 8.0 Hz, 1H). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –151.8 (s), –264.3 (br s).

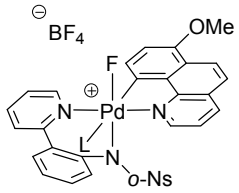
7-Methylbenzo[*h*]quinolinyl palladium(IV) pyridine complex 9f



L = pyridine **9f**

NMR Spectroscopy: ^{1}H NMR (500 MHz, acetonitrile-*d3*, 25 ºC, δ): 8.84 (d, *J* = 4.0 Hz, 1H), 8.73 (d, *J* = 7.5 Hz, 1H), 8.62 (s, 1H), 8.54 (d, *J* = 8.0 Hz, 1H), 8.34 (dd, *J* = 7.0 Hz, *J* = 7.0 Hz, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 9.0 Hz, 1H), 7.83–7.81 (m, 2H), 7.53 (dd, *J* = 7.5 Hz, *J* = 7.5 Hz, 1H), 7.45–7.41 (m, 3H), 7.22–7.19 (m, 2H), 6.97 (d, *J* = 8.0 Hz, 1H), 6.90 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H), 6.79 (d, *J* = 7.5 Hz, 1H), 6.27 (d, *J* = 8.5 Hz, 1H), 2.65 (s, 3H). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –151.8 (s), –263.1 (br s).

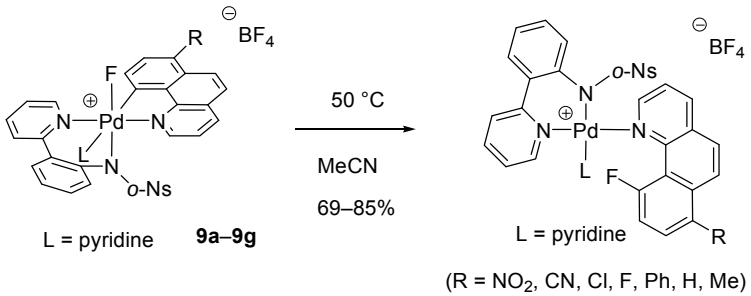
7-Methoxybenzo[*h*]quinolinyl palladium(IV) pyridine complex 9g



L = pyridine **9g**

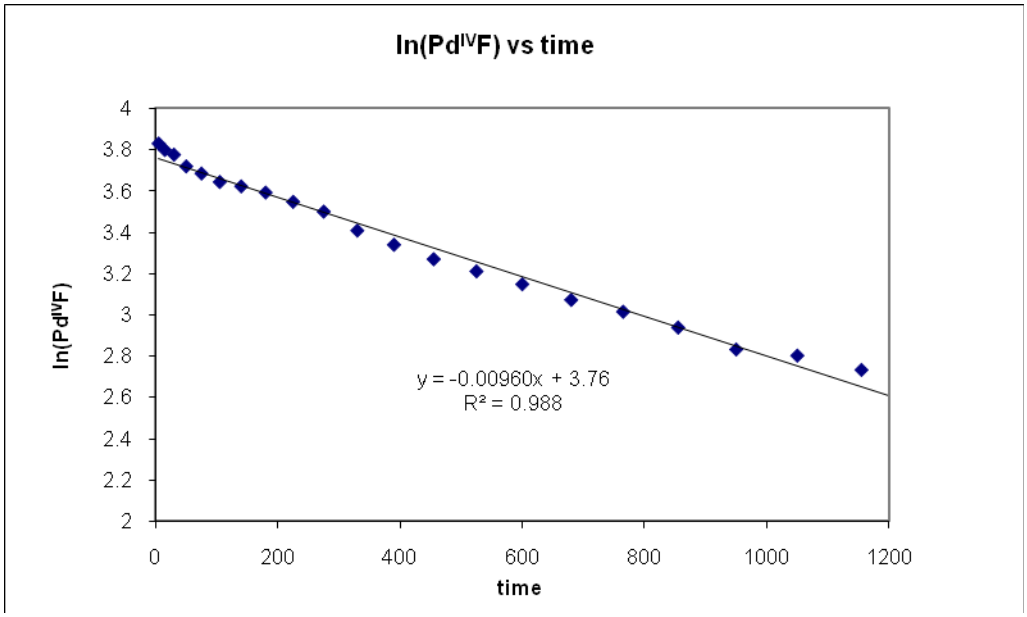
NMR Spectroscopy: ^{1}H NMR (500 MHz, acetonitrile-*d3*, 25 ºC, δ): 8.83 (d, *J* = 5.5 Hz, 1H), 8.72 (d, *J* = 7.0 Hz, 1H), 8.60 (s, 1H), 8.54 (dd, *J* = 7.0 Hz, *J* = 7.0 Hz, 1H), 8.34 (dd, *J* = 7.0 Hz, *J* = 7.0 Hz, 1H), 8.23 (d, *J* = 9.5 Hz, 1H), 7.95 (d, *J* = 8.5 Hz, 1H), 7.83–7.81 (m, 2H), 7.52 (dd, *J* = 12.5 Hz, *J* = 7.5 Hz, 1H), 7.47–7.41 (m, 3H), 7.23–7.20 (m, 2H), 6.92 (dd, *J* = 8.0 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.61 (d, *J* = 8.5 Hz, 1H), 6.29 (d, *J* = 8.5 Hz, 1H), 3.96 (s, 3H). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –151.8 (s), –262.8 (br s).

Kinetic experiments of C−F reductive elimination from Pd(IV) pyridine complexes with different benzo[*h*]quinoline substitution

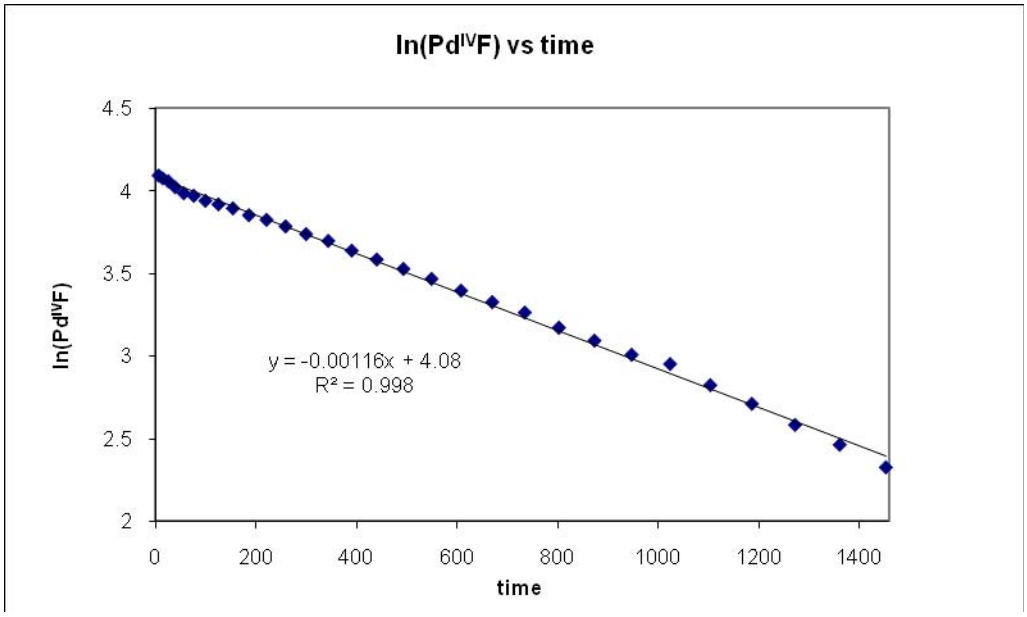


Solutions (33.3 mM) of compound **9a**–**9g** were prepared by reacting compound **S4**, **S47**–**S52** (0.020 mmol, 1.0 equiv) with 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo [2.2.2]octane bis(tetrafluoroborate) (**S5**) (7.1 mg, 0.020 mmol, 1.0 equiv) and pyridine (2.4 μL, 0.030 mmol, 1.50 equiv) in NMR tubes under nitrogen. NMR samples were placed in a preheated NMR machine and using array program, disappearance of the compound **9a**–**9g** was monitored by integrating the peak at around 6.40 ppm relative to the peak of 1-chloromethyl-1,4-diazoniabicyclo [2.2.2]octane (tetrafluoroborate) at 4.91 ppm. Monitoring product formation was difficult because the competing coordination of pyridine and 10-fluorobenzo[*h*]quinoline derivatives complicates the ^{1}H NMR spectra.

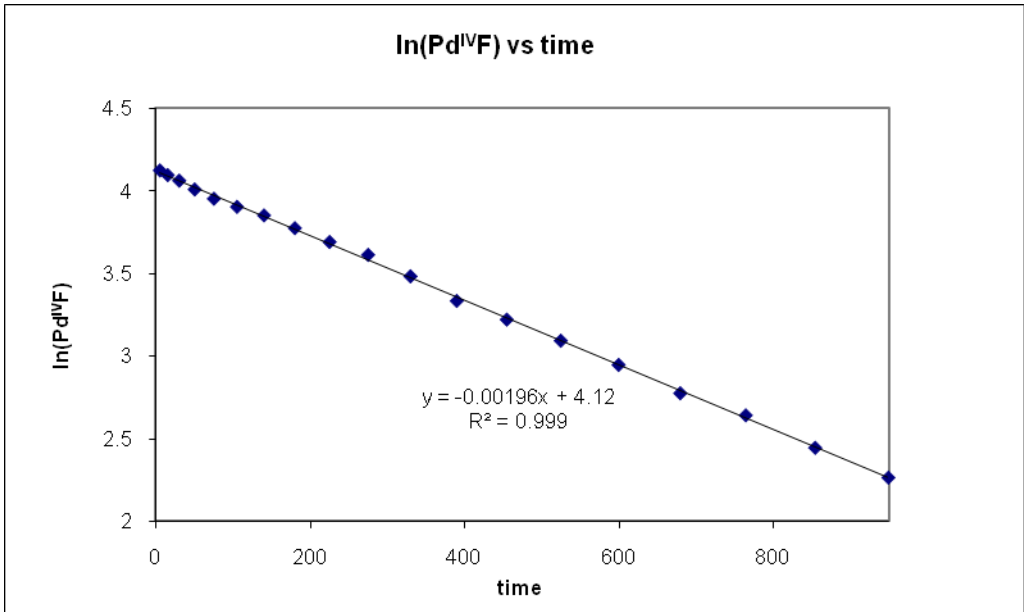
R = NO_2



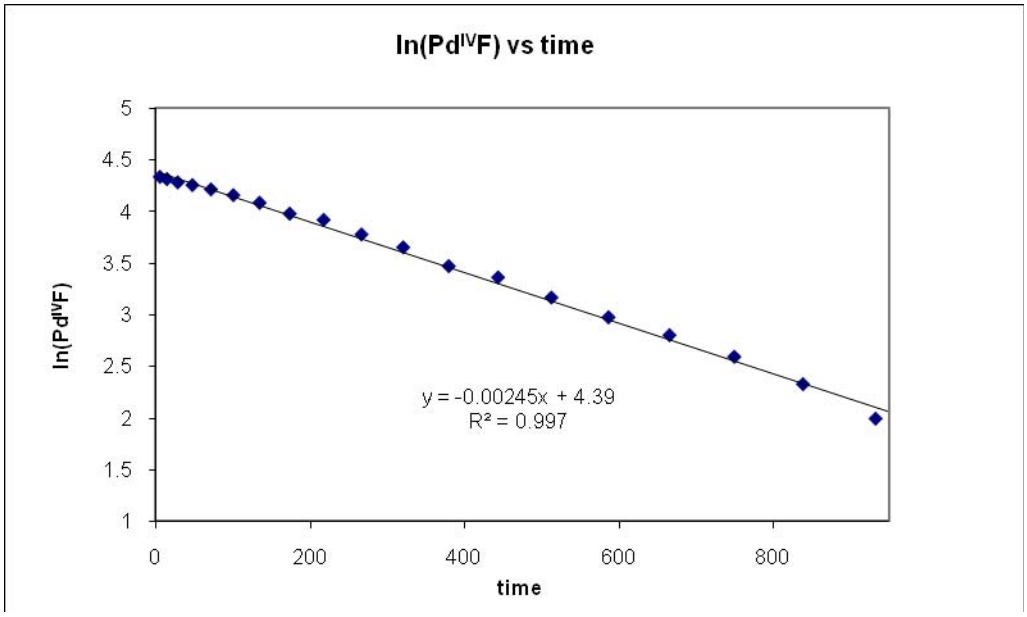
R = CN


ln(Pd^{IV}F) vs time
4.5
4
3.5
3
2.5
2
ln(Pd^{IV}F)
y = -0.00116x + 4.08
R² = 0.998
0
200
400
600
800
1000
1200
1400
time

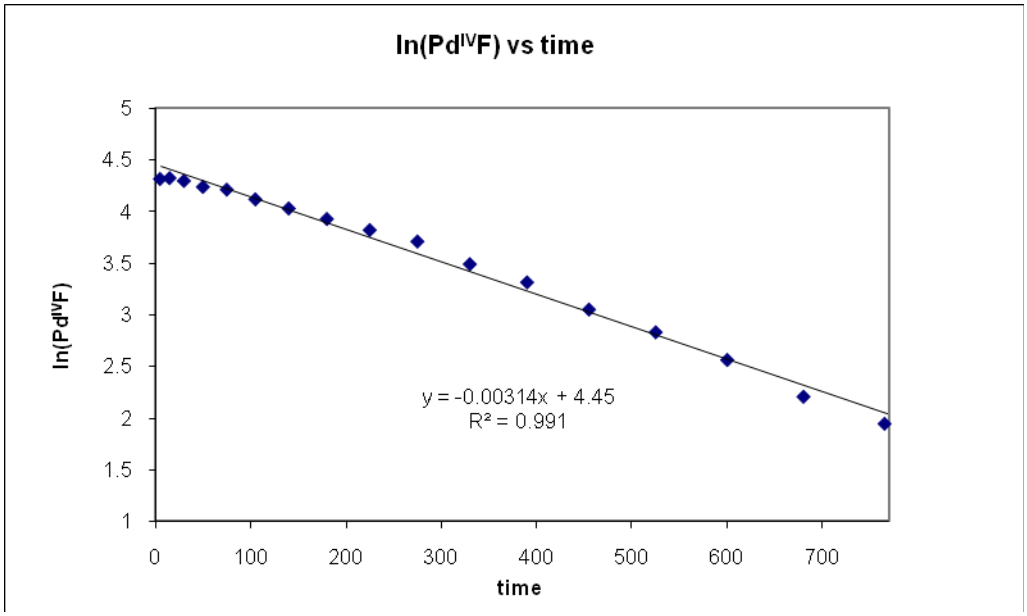
R = CHO


ln(Pd^{IV}F) vs time
4.5
4
3.5
3
2.5
2
ln(Pd^{IV}F)
y = -0.00196x + 4.12
R² = 0.999
0
200
400
600
800
time

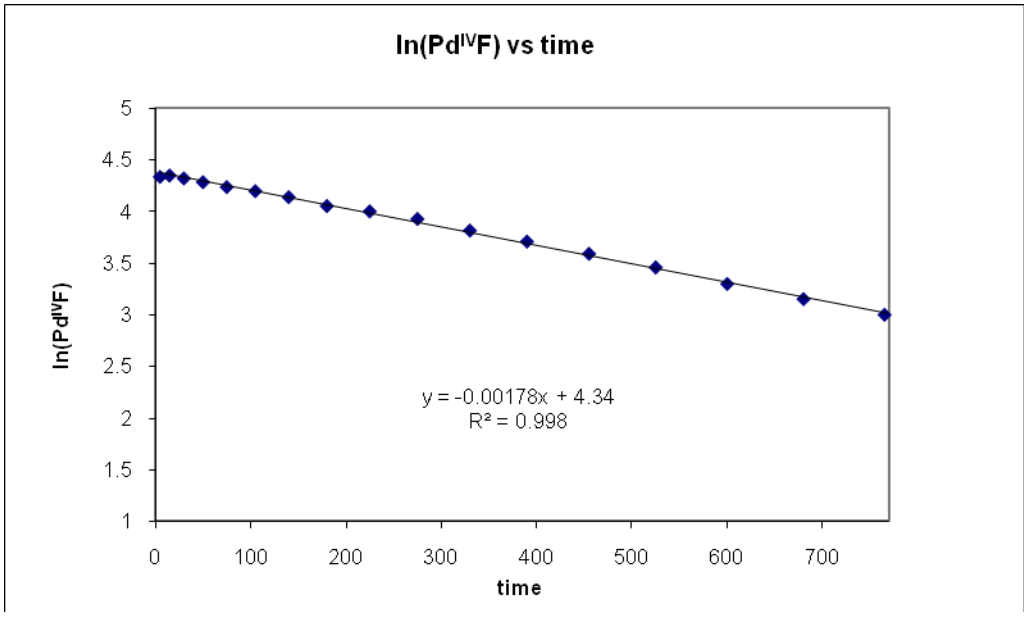
R = Cl


ln(Pd^{IV}F) vs time
ln(Pd^{IV}F)
time
y = -0.00245x + 4.39
R² = 0.997
5
4.5
4
3.5
3
2.5
2
1.5
1
0
200
400
600
800

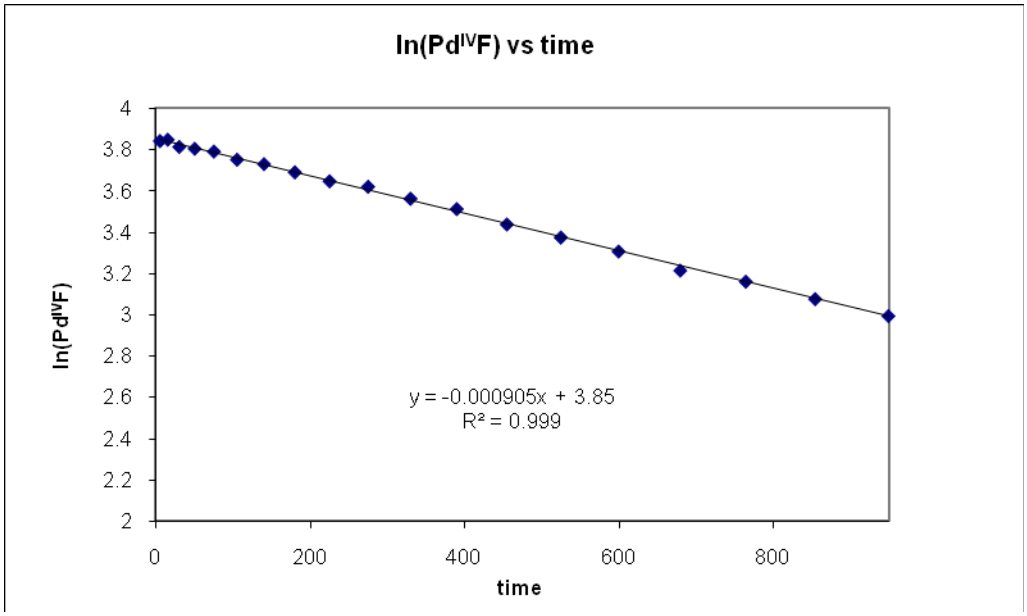
R = H


ln(Pd^{IV}F) vs time
ln(Pd^{IV}F)
time
y = -0.00314x + 4.45
R² = 0.991
5
4.5
4
3.5
3
2.5
2
1.5
1
0
100
200
300
400
500
600
700

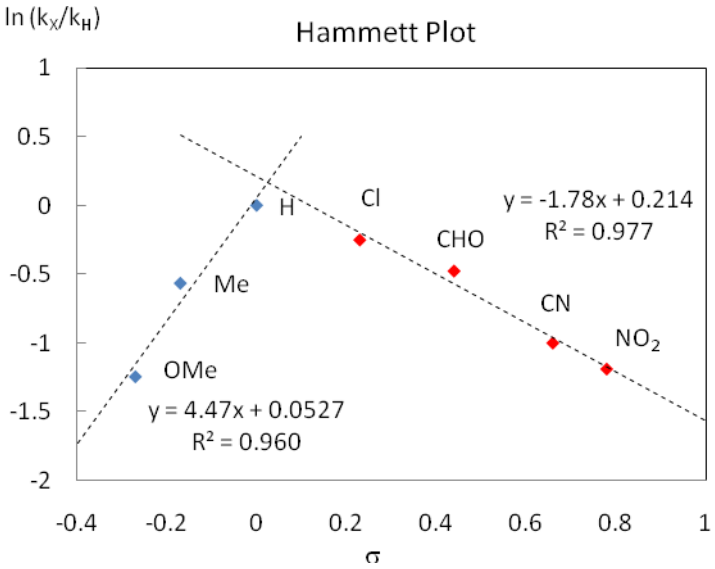
R = Me


ln(Pd^{IV}F) vs time
ln(Pd^{IV}F)
time
y = -0.00178x + 4.34
R² = 0.998
5
4.5
4
3.5
3
2.5
2
1.5
1
0
100
200
300
400
500
600
700

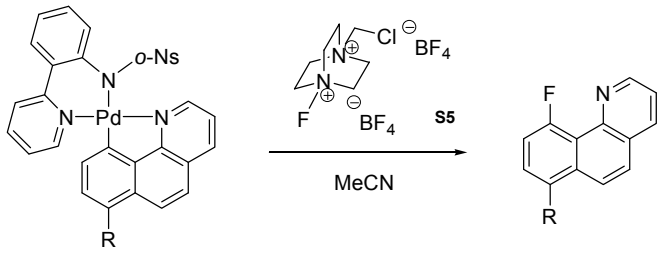
R = OMe


ln(Pd^{IV}F) vs time
ln(Pd^{IV}F)
time
y = -0.000905x + 3.85
R² = 0.999
4
3.8
3.6
3.4
3.2
3
2.8
2.6
2.4
2.2
2
0
200
400
600
800

	σ	k	$\ln(k_X/k_H)$	Fluorination Yield (%)
NO_2	0.78	0.00960	–1.19	85
CN	0.66	0.00116	–0.996	83
CHO	0.44	0.00196	–0.474	83
Cl	0.23	0.00245	-0.248	69
H	0	0.00314	0	85
Me	–0.17	0.00179	–0.565	80
OMe	–0.27	0.000905	–1.24	72



Synthesis of substituted 10-fluorobenzo[*h*]quinolines



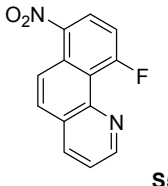
S47–S52 **S53–S58**

(R = NO_2, CN, CHO, Cl, Me, OMe)

To benzo[*h*]quinolinyl palladium(II) pyridine-sulfonamido complex **S47**–**S52** (0.0500 mmol, 1.00 equiv) in acetonitrile (1.5 mL) at 23 ºC was added 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo [2.2.2]octane bis(tetrafluoroborate) (**S5**) (17.8 mg, 0.0500 mmol, 1.00 equiv). After being stirred for 10 min at 23 ºC, the reaction mixture was warmed to 50 ºC and further stirred for 1.0 hr. After being cooled to 23 ºC, the

reaction mixture was added pyridine (19.8 mg, 20.0 μL, 0.250 mmol, 5.00 equiv) and concentrated in vacuo. The resulting solid was dissolved in CH_2Cl_2 (2 mL) and was added H_2O (2 mL). The phases were separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 1 mL). The combined organic phases were washed with brine (3 mL) and dried (Na_2SO_4). The filtrate was concentrated in vacuo and the residue was purified by preparative TLC.

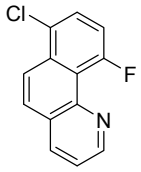
7-Nitro-10-fluorobenzo[*h*]quinoline (S53)



S53

R_f = 0.10 (EtOAc/hexanes 1:9 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 9.20–9.19 (m, 1H), 8.48 (dd, *J* = 11.5 Hz, *J* = 2.0 Hz, 1H), 8.34 (dd, *J* = 11.0 Hz, *J* = 5.0 Hz, 1H), 8.29 (dd, *J* = 10.0 Hz, *J* = 2.5 Hz, 1H), 7.97 (d, *J* = 9.2 Hz, 1H), 7.68 (dd, *J* = 8.4 Hz, *J* = 4.4 Hz, 1H), 7.52 (dd, *J* = 12.0 Hz, *J* = 8.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 163.8 (d, *J* = 271.4), 150.3, 145.2 (d, *J* = 8.3 Hz), 143.4, 136.0, 130.4, 129.0, 126.9, 126.3, 126.2, 123.0, 121.2, 113.7 (d, *J* = 12.8). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –96.0 (d, *J* = 12.4 Hz). Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{13}H_7FN_2O_2$ + H], 243.05643. Found, 243.05637.

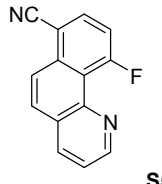
7-Chloro-10-fluorobenzo[*h*]quinoline (S54)



S54

R_f = 0.25 (EtOAc/hexanes 1:9 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$ 25 ºC, δ): 9.16 (m, 1H), 8.30 (dd, *J* = 9.2 Hz, *J* = 2.0 Hz, 1H), 8.25 (dd, *J* = 8.4 Hz, *J* = 2.0 Hz, 1H), 7.85 (d, *J* = 9.2 Hz, 1H), 7.73 (dd, *J* = 8.4 Hz, *J* = 4.0 Hz, 1H), 7.61 (dd, *J* = 8.0 Hz, *J* = 4.0 Hz, 1H), 7.40 (dd, *J* = 12.4 Hz, *J* = 8.4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 160.0 (d, *J* = 260.2 Hz, 1H), 149.7, 145.7 (d, *J* = 8.4 Hz), 135.9, 132.8 (d, *J* = 2.3 Hz), 128.7 (d, *J* = 9.1 Hz), 128.0, 127.1, 127.1, 123.6 (d, *J* = 2.3 Hz), 122.3 (d, *J* = 2.3 Hz), 121.6 (d, *J* = 6.8 Hz), 114.7 (d, *J* = 25.0 Hz). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –109.4 (d, *J* = 12.0 Hz). Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{13}H_7ClFN$ + H], 232.03238. Found, 232.03256.

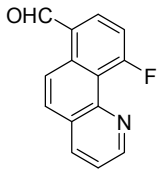
7-Cyano-10-fluorobenzo[*h*]quinoline (S55)



S55

R_f = 0.10 (EtOAc/hexanes 1:9 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 9.20–9.19 (m, 1H), 8.30 (dd, *J* = 8.0 Hz, *J* = 2.0 Hz, 1H), 8.26 (dd, *J* = 9.0 Hz, *J* = 2.0 Hz, 1H), 8.07 (dd, *J* = 8.0 Hz, *J* = 4.5 Hz, 1H), 7.97 (d, *J* = 9.0 Hz, 1H), 7.66 (dd, *J* = 8.0 Hz, *J* = 4.5 Hz, 1H), 7.52 (dd, *J* = 12.0 Hz, *J* = 8.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 163.9 (d, *J* = 271.3 Hz), 150.2, 145.5 (d, *J* = 8.3 Hz), 137.0, 136.2, 134.5 (d, *J* = 10.9 Hz), 130.0, 127.3, 124.0, 122.8, 120.9, 117.4, 114.7 (d, *J* = 24.5 Hz), 106.5. ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –96.8 (d, *J* = 3.6 Hz). Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{14}H_7FN_2$ + H], 223.06660. Found, 223.06637.

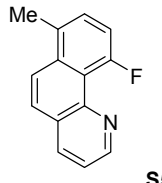
7-Formyl-10-fluorobenzo[*h*]quinoline (S56)



S56

R_f = 0.08 (EtOAc/hexanes 1:9 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 10.54 (s, 1H), 9.34 (dd, *J* = 9.0 Hz, *J* = 2.0 Hz, 1H), 9.18–9.17 (m, 1H), 8.27 (dd, *J* = 8.0 Hz, *J* = 1.5 Hz, 1H), 8.18 (dd, *J* = 8.0 Hz, *J* = 4.5 Hz, 1H), 7.96 (d, *J* = 9.5 Hz, 1H), 7.65–7.57 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 192.1, 165.0 (d, *J* = 272.1 Hz) 149.9, 138.1, 138.0, 135.8, 135.3, 130.1, 127.1, 123.1, 123.1, 122.5, 120.7, 114.2 (d, *J* = 24.5 Hz). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –95.4. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{14}H_8FNO$ + H], 226.06627. Found, 226.06605.

7-Methyl-10-fluorobenzo[*h*]quinoline (S57)

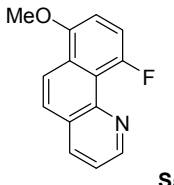


S57

R_f = 0.25 (EtOAc/hexanes 1:9 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 9.14–9.12 (m, 1H), 8.20 (dd, *J* = 8.0 Hz, *J* = 1.5 Hz, 1H), 7.98 (dd, *J* = 9.0 Hz, *J* = 2.0 Hz, 1H), 7.75 (d, *J* = 8.0

Hz, 1H), 7.55 (dd, *J* = 8.0 Hz, *J* = 5.5 Hz, 1H), 7.48 (ddd, *J* = 8.0 Hz, *J* = 4.5 Hz, *J* = 0.5 Hz, 1H), 7.35 (dd, *J* = 13.0 Hz, *J* = 8.0 Hz, 1H), 2.73 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 159.9 (d, *J* = 256.8 Hz), 149.2, 146.3 (d, *J* = 8.3 Hz), 135.6, 134.4, 130.1 (*J* = 4.6 Hz), 129.4 (d, *J* = 9.0 Hz), 126.8, 126.4, 123.9 (d, *J* = 2.8 Hz), 121.6 (d, *J* = 2.8 Hz), 120.3 (5.4 Hz), 113.9 (*J* = 22.8 Hz). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –112.1 (d, *J* = 4.4 Hz). Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{14}H_{10}FN$ + H], 212.08700. Found, 212.08709.

7-Methoxy-10-fluorobenzo[*h*]quinoline (S58)

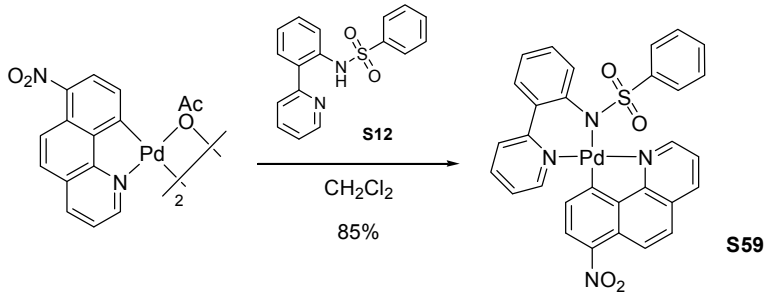


S58

R_f = 0.20 (EtOAc/hexanes 1:9 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 9.13–9.12 (m, 1H), 8.31 (dd, *J* = 8.5 Hz, *J* = 1.5 Hz, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, *J* = 4.5 Hz, 1H), 7.38 (dd, *J* = 13.0 Hz, *J* = 8.5 Hz, 1H), 7.04 (dd, *J* = 8.5 Hz, *J* = 3.0 Hz, 1H), 4.04 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 155.5 (*J* = 256.3 Hz), 151.7, 149.4, 146.0, 136.0, 127.7, 126.6, 126.0, 122.0, 121.7, 121.1, 114.0 (*J* = 25.5 Hz), 107.6 (*J* = 9.1 Hz), 56.4. ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –120.0. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{14}H_{10}FNO$ + H], 228.08192. Found, 228.08238.

Synthesis of Pd(II) complexes with mixed ligands

7-Nitrobenzoquinolinyl-benzenesulfonanilido palladium(II) complex (S59)

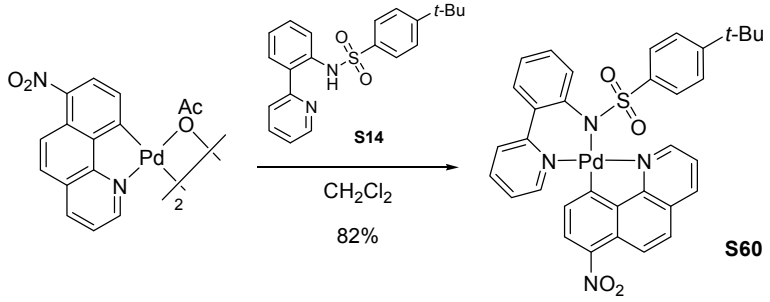


S59

To 7-nitrobenzo[*h*]quinolinyl palladium acetate dimer (38.9 mg, 0.100 mmol, 1.00 equiv) in CH_2Cl_2 (1 mL) at 23 ºC was added the substituted pyridinylsulfonanilide ligand **S12** (31.0 mg, 0.100 mmol, 1.00 equiv). After stirring for 1.0 hr the reaction mixture was concentrated in vacuo. The resulting residue was triturated with Et_2O (3 × 1 mL) to afford 54 mg of palladium(II) complex **S59** (85% yield).

NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 9.62 (d, *J* = 5.0 Hz, 1H), 8.72 (d, *J* = 5.5 Hz, 1H), 8.42 (d, *J* = 9.0 Hz, 1H), 8.24 (d, *J* = 7.5 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 9.0 Hz, 1H), 7.71–7.60 (m, 3H), 7.53 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.35–7.22 (m, 4H), 7.11–7.05 (m, 2H), 6.98–6.92 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 167.5, 157.5, 153.7, 153.1, 151.6, 143.2, 142.8, 141.8, 141.7, 138.9, 137.6, 136.2, 131.8, 130.2, 130.0, 129.5, 129.2, 128.0, 127.4, 126.7, 125.6, 125.3, 125.0, 124.7, 124.5, 124.0, 123.7, 122.8. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{34}H_{28}N_4O_4PdS$ + H], 695.09443. Found, 695.09488.

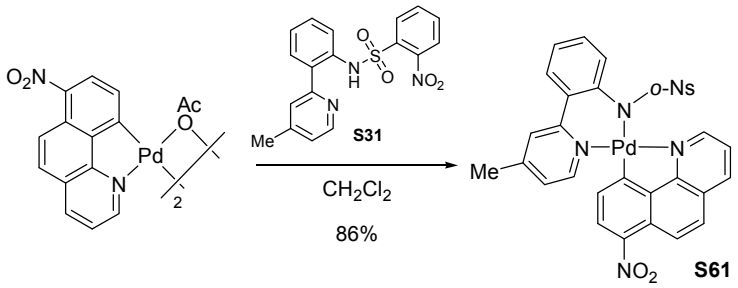
7-Nitrobenzoquinolinyl-4-*tert*-butylbenzenesulfonanilido palladium(II) complex (S60)



To 7-nitrobenzo[*h*]quinolinyl palladium acetate dimer (38.9 mg, 0.100 mmol, 1.00 equiv) in CH_2Cl_2 (1 mL) at 23 ºC was added the substituted pyridinylsulfonanilide ligand **S14** (32.4 mg, 0.100 mmol, 1.00 equiv). After stirring for 1.0 hr the reaction mixture was concentrated in vacuo. The resulting residue was triturated with Et_2O (3 × 1 mL) to afford 57 mg of palladium(II) complex **S60** (82% yield).

NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 9.64 (d, *J* = 5.0 Hz, 1H), 8.75 (d, *J* = 5.5 Hz, 1H), 8.44 (d, *J* = 9.0 Hz, 1H), 8.26 (d, *J* = 7.5 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 9.0 Hz, 1H), 7.67–7.61 (m, 3H), 7.53 (dd, *J* = 8.0 Hz, *J* = 7.5 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.32 (dd, *J* = 7.0 Hz, *J* = 6.5 Hz, 1H), 7.26–7.19 (m, 3H), 7.08 (d, *J* = 8.0 Hz, 1H), 6.99–6.93 (m, 3H), 1.23 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 167.7, 157.6, 153.8, 153.2, 151.7, 142.9, 141.9, 141.8, 140.5, 138.7, 137.6, 136.2, 131.8, 130.4, 130.0, 129.2, 127.4, 126.4, 125.4, 125.3, 124.9, 124.8, 124.4, 124.0, 123.5, 122.8, 34.6, 31.2. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{34}H_{28}N_4O_4PdS$ + H], 695.09443. Found, 695.09488.

7-Nitrobenzoquinolinyl-4-methylpyridylsulfonanilido palladium(II) complex (S61)

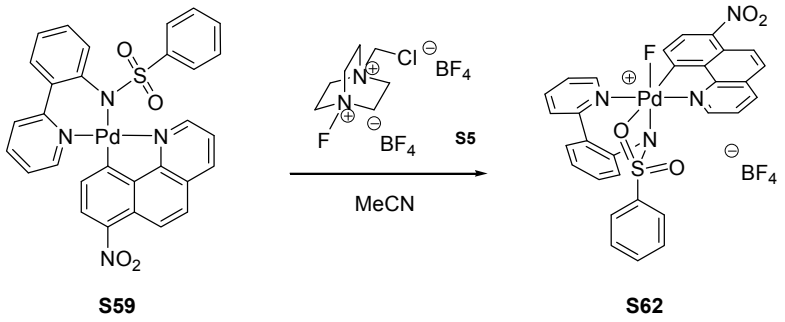


To 7-nitrobenzo[*h*]quinolinyl palladium acetate dimer (38.9 mg, 0.100 mmol, 1.00 equiv) in CH_2Cl_2 (1 mL) at 23 ºC was added the substituted pyridinylsulfonanilide ligand **S31** (36.9 mg, 0.100 mmol, 1.00 equiv). After stirring for 1.0 hr the reaction mixture was concentrated in vacuo. The resulting residue was triturated with Et_2O (3 × 1 mL) to afford 60 mg of palladium(II) complex **S61** (86% yield).

NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 9.65 (d, *J* = 5.0 Hz, 1H), 8.74 (d, *J* = 3.0 Hz, 1H), 8.73 (s, 1H), 8.40 (d, *J* = 9.0 Hz, 1H), 8.20 (d, *J* = 8.5 Hz, 1H), 7.88 (d, *J* = 9.0 Hz, 1H), 7.77–7.72 (m, 2H), 7.52 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H), 7.45–7.40 (m, 2H), 7.30–7.22 (m, 2H), 7.18–7.13 (m, 2H), 7.08–6.98 (m, 3H), 2.33 (s, 3H). Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{14}H_{10}FNO$ + H], 698.03256. Found, 698.03190.[19]

Synthesis of Pd(IV) complexes with mixed ligands

7-Nitrobenzoquinolinyl-benzenesulfonanilido palladium(IV) complex (S62)

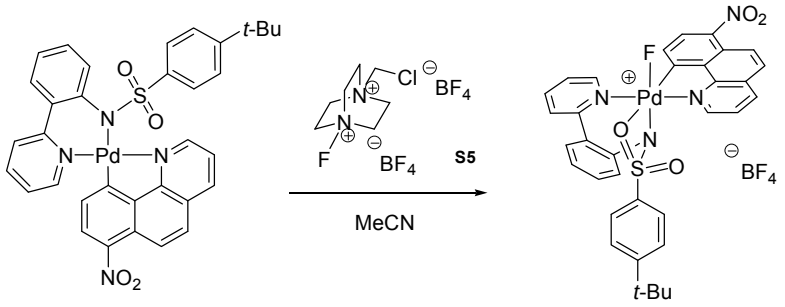


A solution (33.3 mM) of compound **S62** was prepared by reacting compound **S59** (12.8 mg, 0.0200 mmol, 1.00 equiv) with 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo [2.2.2]octane bis(tetrafluoroborate) (**S5**) (7.1 mg, 0.020 mmol, 1.0 equiv) in NMR tubes under nitrogen. Compound **S62** was characterized by NMR spectroscopy in acetonitrile solution without purification.

[19] The ^{13}C NMR spectrum of this compound has a low signal-to-noise ratio due to the low solubility in common organic solvents.

NMR Spectroscopy: ^{1}H NMR (500 MHz, acetonitrile-*d3*, 5 ºC, δ): 9.83 (d, *J* = 6.0 Hz, 1H), 9.42 (d, *J* = 6.0 Hz, 1H), 9.03 (d, *J* = 8.0 Hz, 1H), 8.69 (d, *J* = 9.0 Hz, 1H), 8.35(d, *J* = 9.0 Hz, 1H), 8.24–8.15 (m, 2H), 7.90 (dd, *J* = 8.0 Hz, *J* = 7.5 Hz, 1H), 7.82 (d, *J* = 9.0 Hz, 1H), 7.70 (d, *J* = 7.5 Hz, 1H), 7.45–7.40 (m, 1H), 7.33–7.20 (m, 4H), 7.12–7.05 (m, 2H), 6.99 (dd, *J* = 8.0 Hz, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 8.5 Hz, 1H), 6.48 (d, *J* = 9.0 Hz, 1H). ^{19}F NMR (375 MHz, acetonitrile-*d3*, 5 ºC, δ): –152.0 (s), –276.2 (s).

7-Nitrobenzoquinolinyl-4-*tert*-butylbenzenesulfonanilido palladium(IV) complex (S63)

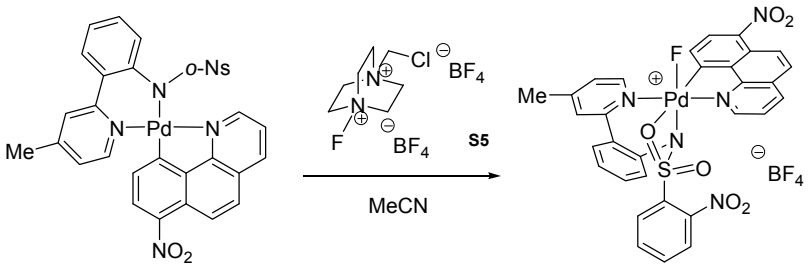


S60 **S63**

Solution (33.3 mM) of compound **S63** was prepared by reacting compound **S60** (13.9 mg, 0.0200 mmol, 1.00 equiv) with 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo [2.2.2]octane bis(tetrafluoroborate) (**S5**) (7.1 mg, 0.020 mmol, 1.0 equiv) in NMR tubes under nitrogen. Compound **S63** was characterized by NMR spectroscopy in acetonitrile solution without purification.

NMR Spectroscopy: ^{1}H NMR (500 MHz, acetonitrile-*d3*, 25 ºC, δ): 9.77 (d, *J* = 6.0 Hz, 1H), 9.35 (d, *J* = 6.0 Hz, 1H), 8.98 (d, *J* = 8.0 Hz, 1H), 8.64 (d, *J* = 9.0 Hz, 1H), 8.32 (d, *J* = 9.0 Hz, 1H), 8.28 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H), 8.17 (dd, *J* = 8.0 Hz, *J* = 6.0 Hz, 1H), 8.04 (d, *J* = 7.0 Hz, 1H), 7.82–7.75 (m, 2H), 7.65 (d, *J* = 6.5 Hz, 1H), 7.30–7.20 (m, 3H), 7.11 (d, *J* = 8.5 Hz, 2H), 6.99 (dd, *J* = 8.0 Hz, *J* = 7.5 Hz, 1H), 6.73 (d, *J* = 8.5 Hz, 1H), 6.41 (d, *J* = 9.0 Hz, 1H), 1.22 (s, 9H). ^{19}F NMR (375 MHz, acetonitrile-*d3*, 23 ºC, δ): –152.0 (s), –276.4 (br s).

7-Nitrobenzoquinolinyl-4-methylpyridylsulfonanilido palladium(IV) complex (S64)

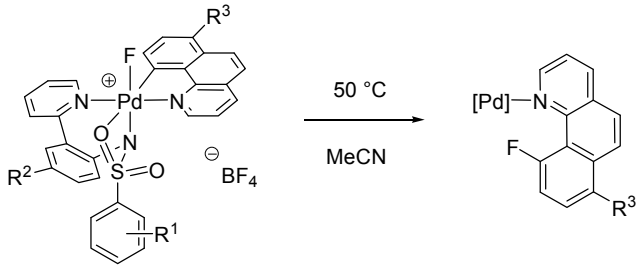


S61 **S64**

Solution (33.3 mM) of compound **S64** was prepared by reacting compound **S61** (14.0 mg, 0.0200 mmol, 1.00 equiv) with 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo [2.2.2]octane bis(tetrafluoroborate) (**S5**) (7.1 mg, 0.020 mmol, 1.0 equiv) in NMR tubes under nitrogen. Compound **S64** was characterized by NMR spectroscopy in acetonitrile solution without purification.

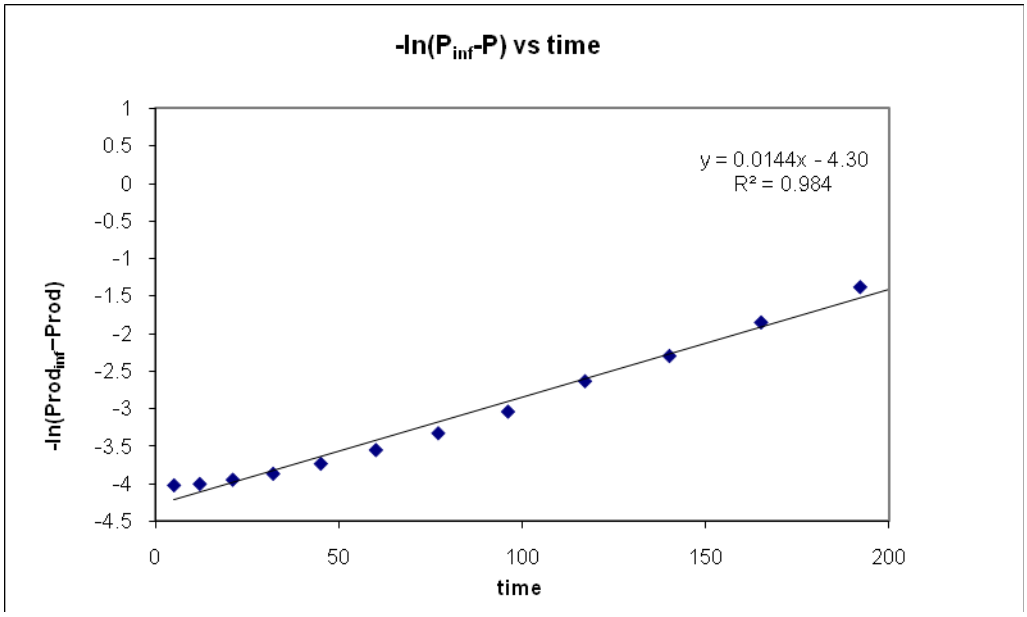
NMR Spectroscopy: ^{1}H NMR (500 MHz, acetonitrile-*d3*, 25 ºC, δ): 9.68 (d, *J* = 6.0 Hz, 1H), 9.25 (d, *J* = 6.0 Hz, 1H), 8.98 (d, *J* = 7.0 Hz, 1H), 8.66 (d, *J* = 9.0 Hz, 1H), 8.32 (d, *J* = 9.0 Hz, 1H), 8.26 (s, 1H), 8.14 (dd, *J* = 8.0 Hz, *J* = 6.0 Hz, 1H), 7.81–7.75 (m, 3H), 7.60 (dd, *J* = 7.5 Hz, *J* = 7.5 Hz, 1H), 7.54 (d, *J* = 8.5 Hz, 1H), 7.43 (d, *J* = 7.0 Hz, 1H), 7.39 (dd, *J* = 7.5 Hz, *J* = 7.5 Hz, 1H), 7.19 (dd, *J* = 7.5 Hz, *J* = 7.5 Hz, 1H), 6.85 (dd, *J* = 8.0 Hz, *J* = 7.5 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 6.46 (d, *J* = 9.0 Hz, 1H), 2.73 (s, 3H). ^{19}F NMR (375 MHz, acetonitrile-*d3*, 23 ºC, δ): –152.0 (s), –278.1 (br s).

Kinetic experiments of C−F reductive elimination from Pd(IV) complexes with mixed ligands

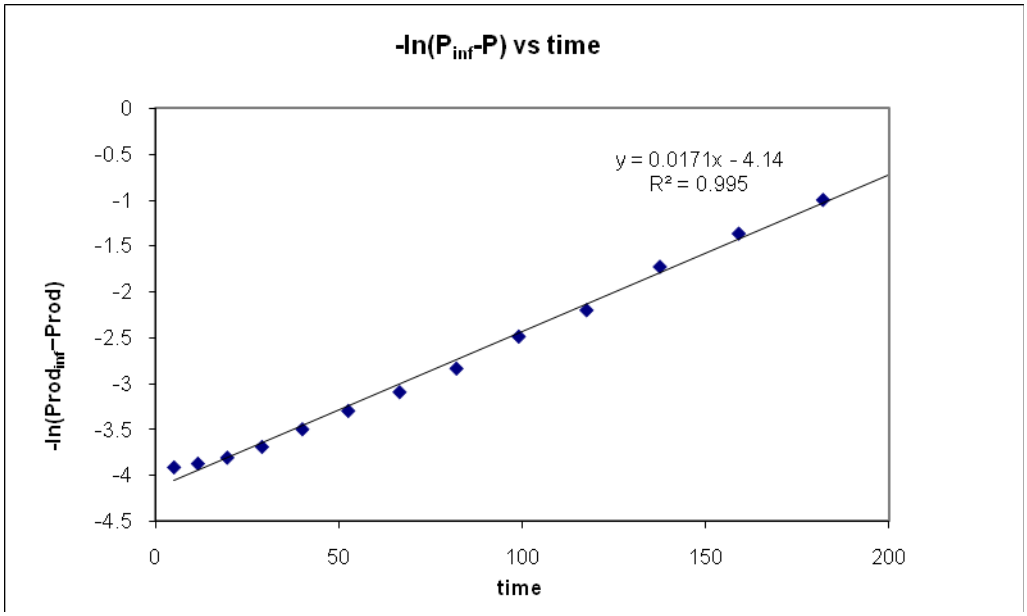


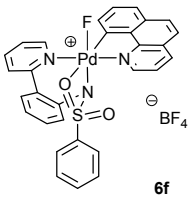
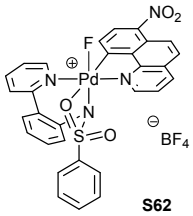
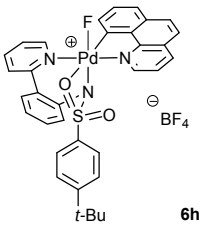
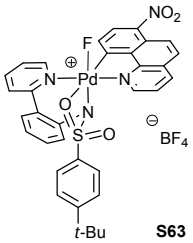
Solutions (16.7 mM) of compound **S62−S64** were prepared by reacting compound **S59−S61** (0.010 mmol, 1.0 equiv) with 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo [2.2.2]octane bis(tetrafluoroborate) (**S5**) (3.5 mg, 0.010 mmol, 1.0 equiv) in NMR tubes under nitrogen. NMR samples were placed in the preheated NMR machine (50 ºC) and the disappearance of the compounds **S62−S64** and formation of the product were monitored by integrating the peak at around 6.3 ppm and 9.1 ppm, respectively, relative to the peak of 1-chloromethyl-1,4-diazoniabicyclo [2.2.2]octane (tetrafluoroborate) at 4.91 ppm.

Kinetic data of S62

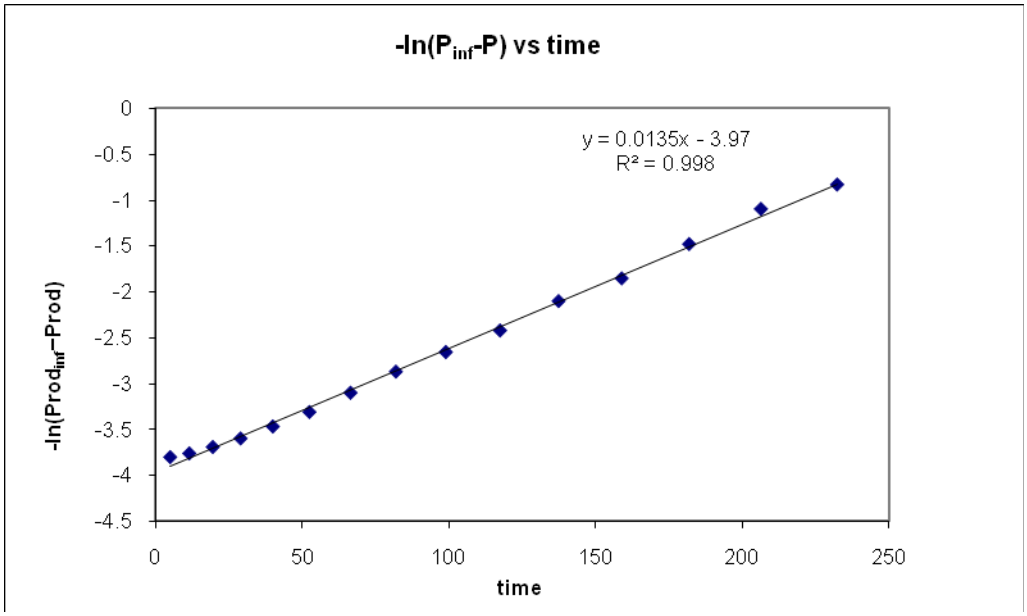


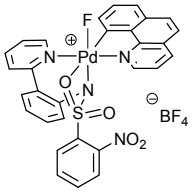
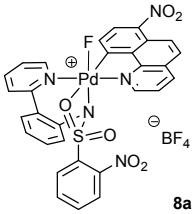
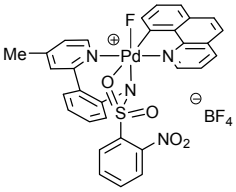
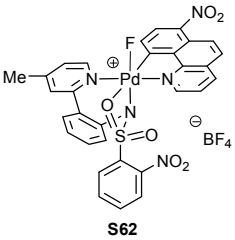
Kinetic data of S63



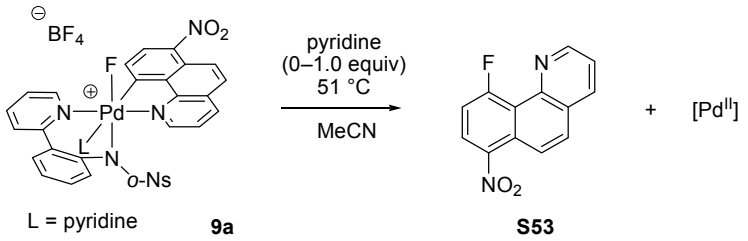
Pd(IV) complex	 6f	 S62	 6h	 S63
rate (s^{-1}) at 49.5 ºC	0.00536	0.0144	0.00611	0.0171
relative rate at 49.5 ºC	1.00	2.69	1.14	3.19

Kinetic data of S64



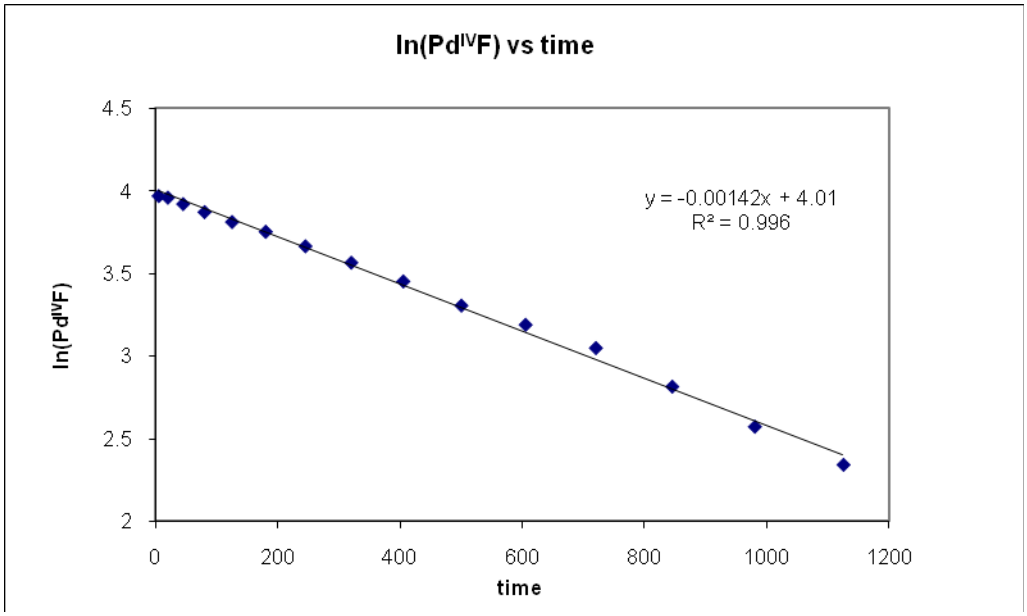
Pd(IV) complex	 1	 8a	 7e	 S62
rate (s^{-1}) at 49.5 ºC	0.00343	0.0115	0.00389	0.0135
relative rate at 49.5 ºC	1.00	3.35	1.13	3.94

Dependence on pyridine concentration for 7-nitrobenzoquinolynyl Pd(IV) fluoride complex 9a

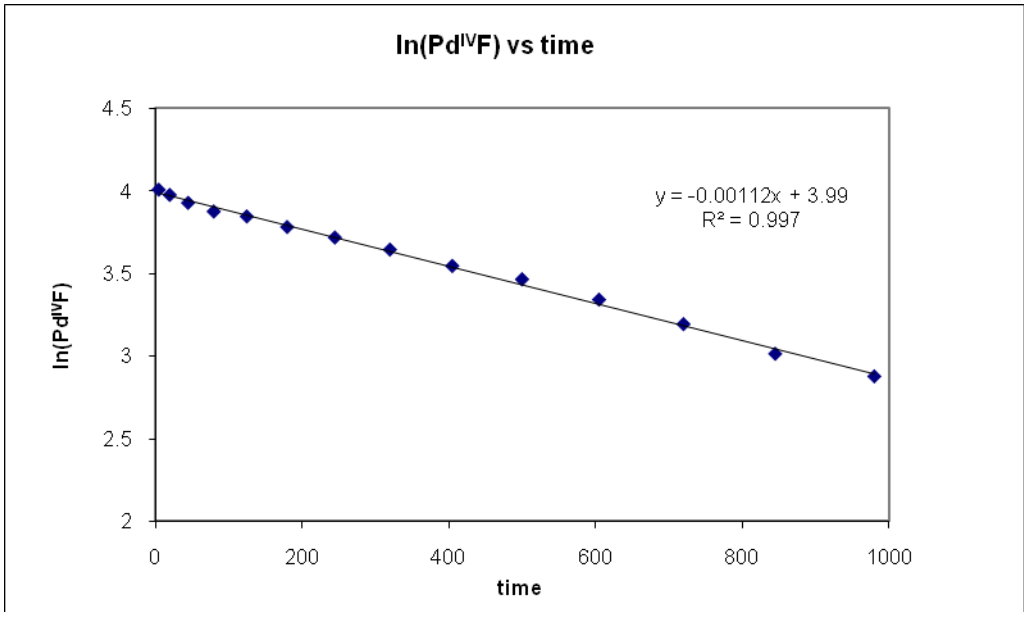


Solutions (33.3 mM) of compound **9a** were prepared by reacting compound **S47** (14 mg, 0.020 mmol, 1.0 equiv) with 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo [2.2.2]octane bis(tetrafluoroborate) (**S5**) (7.1 mg, 0.020 mmol, 1.0 equiv) and pyridine (1.0−2.0 equiv) in NMR tubes under nitrogen. NMR samples were placed in a preheated NMR machine and the disappearance of compound **9a** was monitored by integrating the peak at 6.60 ppm relative to the peak of 1-chloromethyl-1,4-diazoniabicyclo [2.2.2]octane (tetrafluoroborate) at 4.91 ppm.

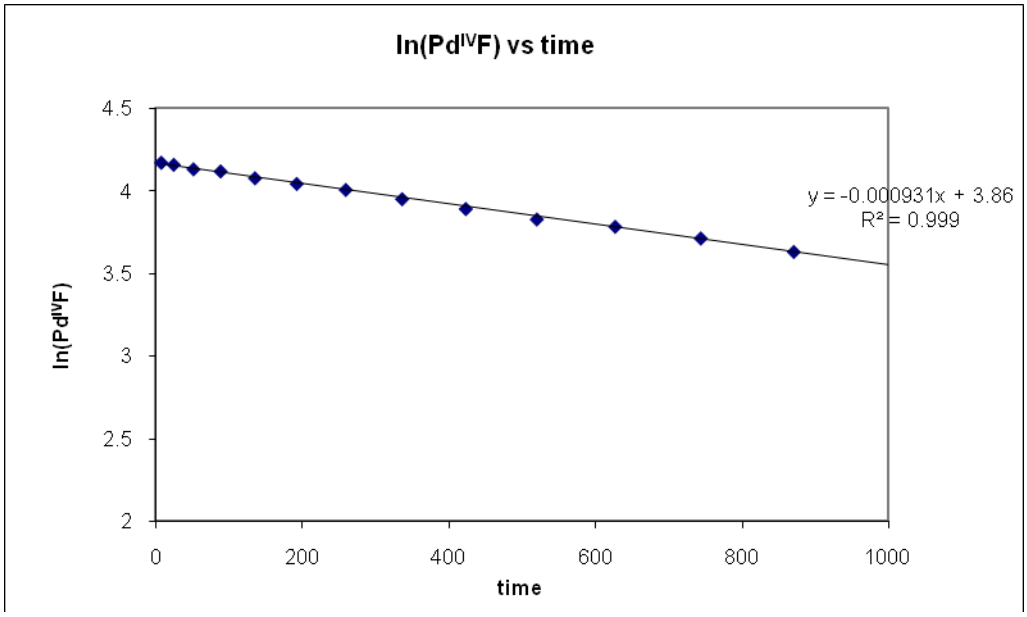
Kinetic data with 0 equiv of pyridine



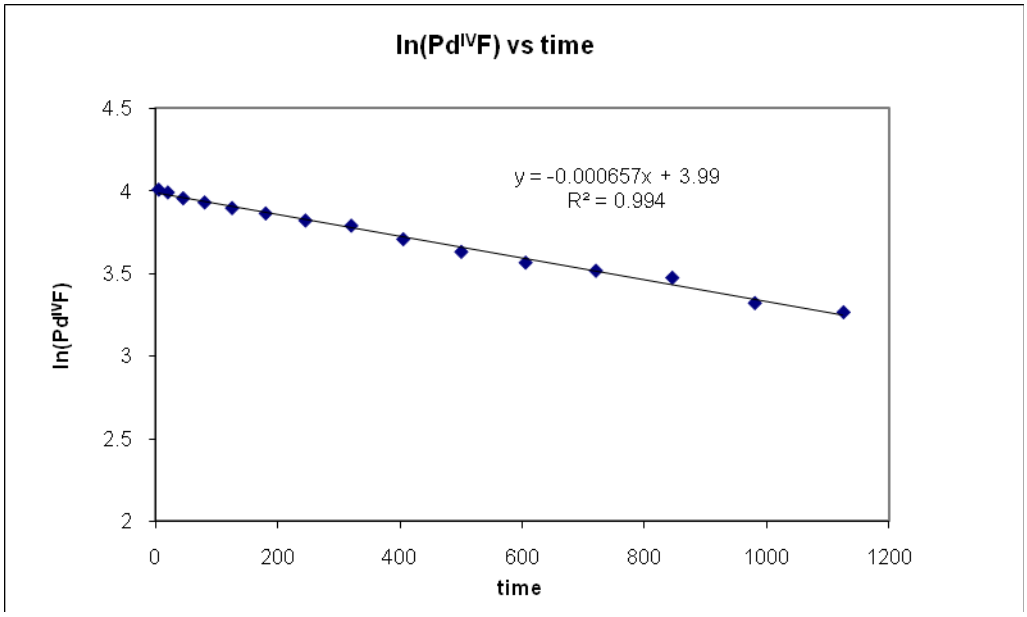
Kinetic data with 0.25 equiv of pyridine



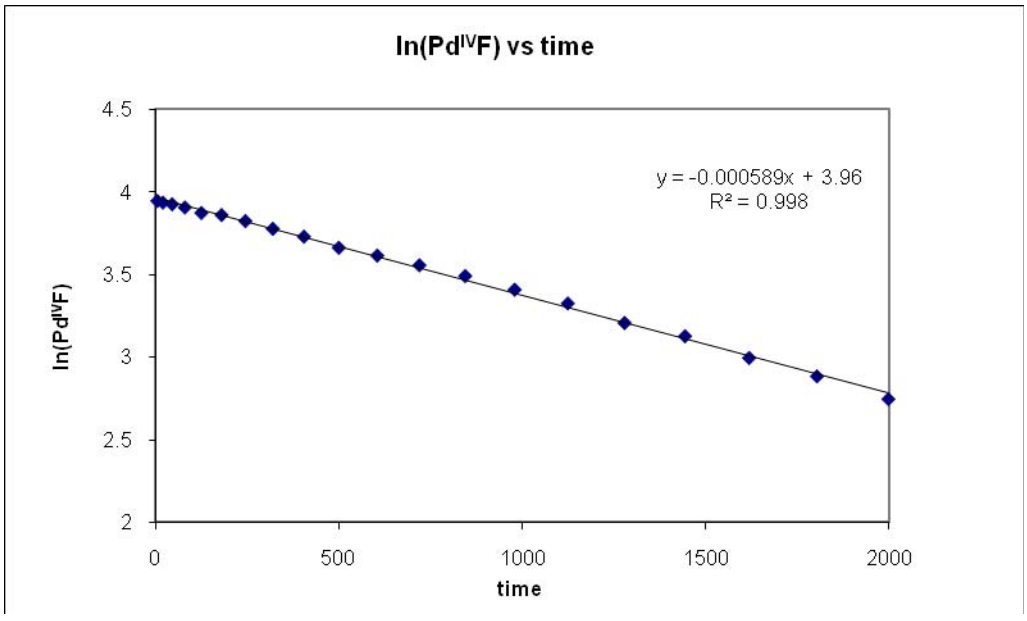
Kinetic data with 0.50 equiv of pyridine



Kinetic data with 0.75 equiv of pyridine

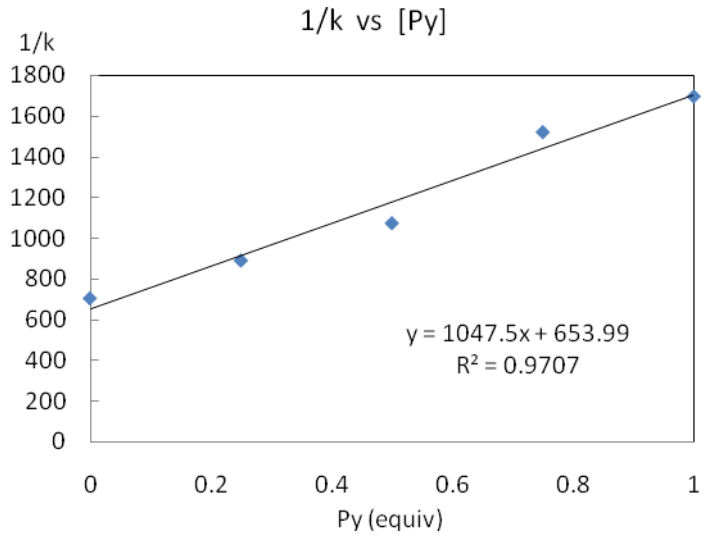


Kinetic data with 1.00 equiv of pyridine

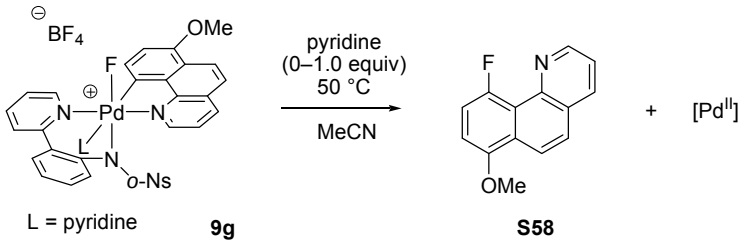


Relationship of rate vs pyridine concentrateion

py (equiv)	k (s^{-1})	1/k (s)
0	0.00142	704
0.25	0.00112	890
0.50	0.000931	1074
0.75	0.000657	1522
1.00	0.000589	1698



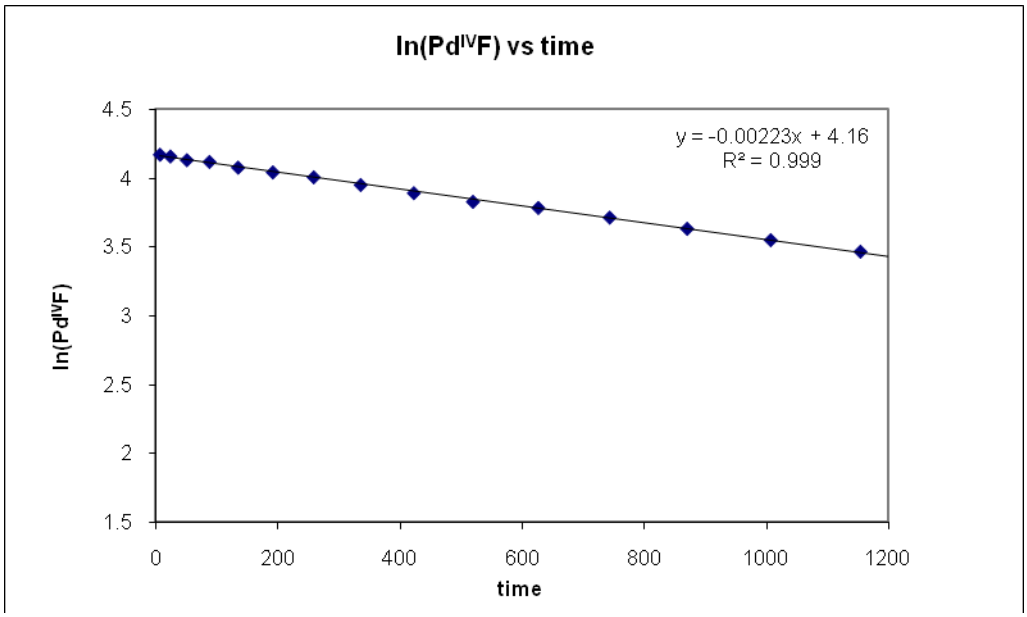
Dependence on pyridine concentration for 7-methoxybenzoquinolinyl Pd(IV) fluoride complex 9g



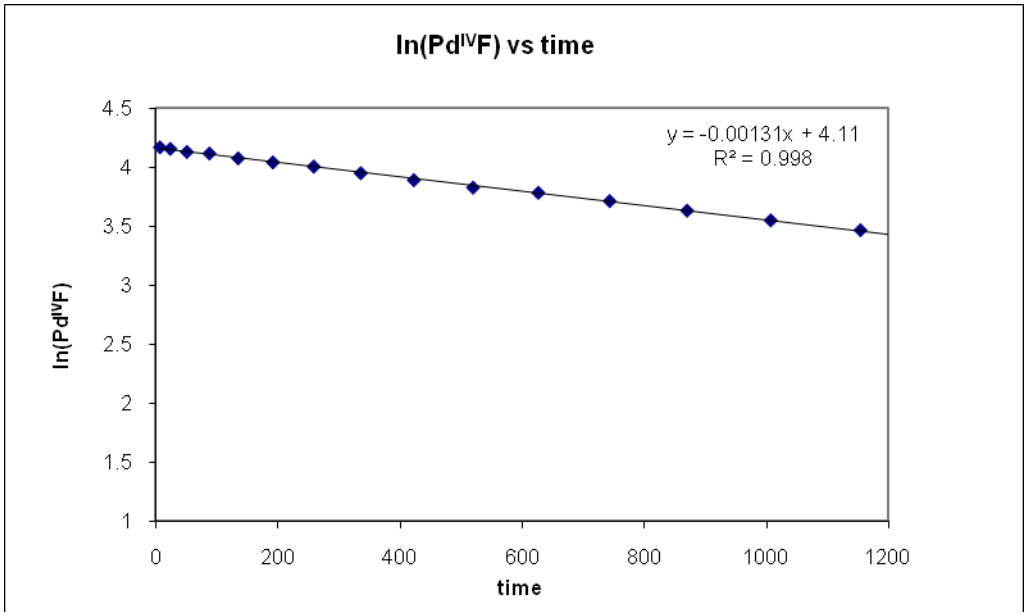
Solutions (33.3 mM) of compound **9g** were prepared by reacting compound **S52** (13 mg, 0.020 mmol, 1.0 equiv) with 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo [2.2.2]octane bis(tetrafluoroborate) (**S5**) (7.1 mg, 0.020 mmol, 1.0 equiv) and pyridine (1.0−2.0 equiv) in NMR tubes under nitrogen. NMR samples were placed in a preheated NMR machine and the disappearance of compound **9g** was monitored by integrating

the peak at 6.30 ppm relative to the peak of 1-chloromethyl-1,4-diazoniabicyclo [2.2.2]octane (tetrafluoroborate) at 4.91 ppm.

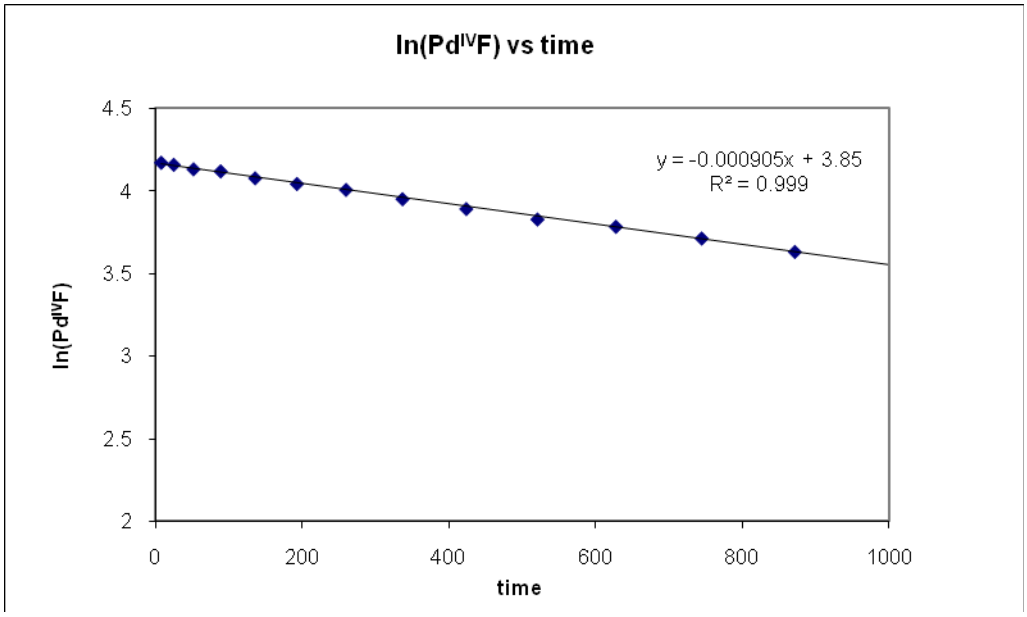
Kinetic data with 0 equiv of pyridine



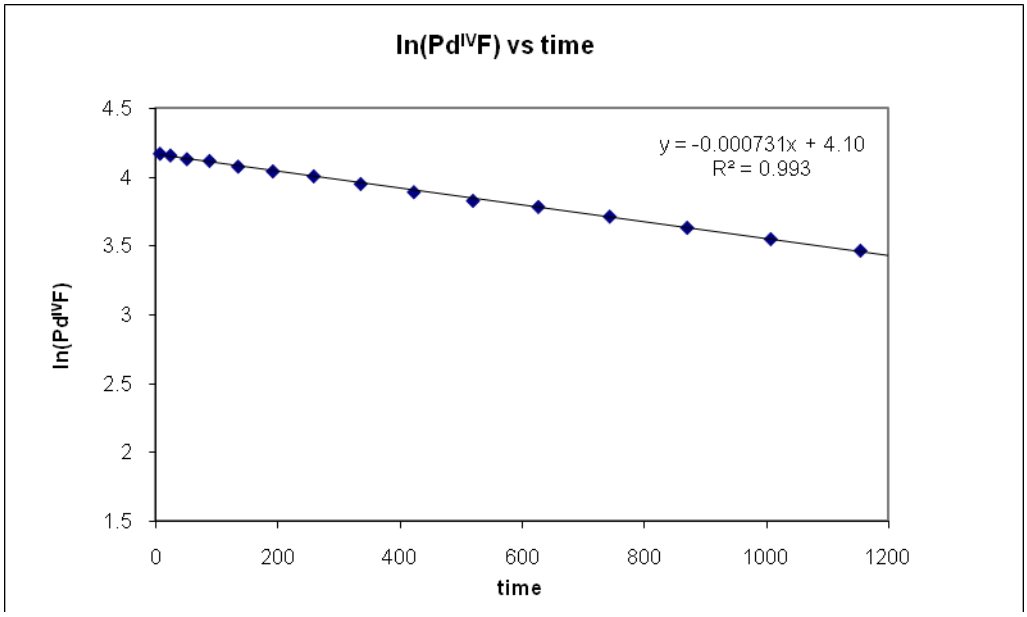
Kinetic data with 0.25 equiv of pyridine



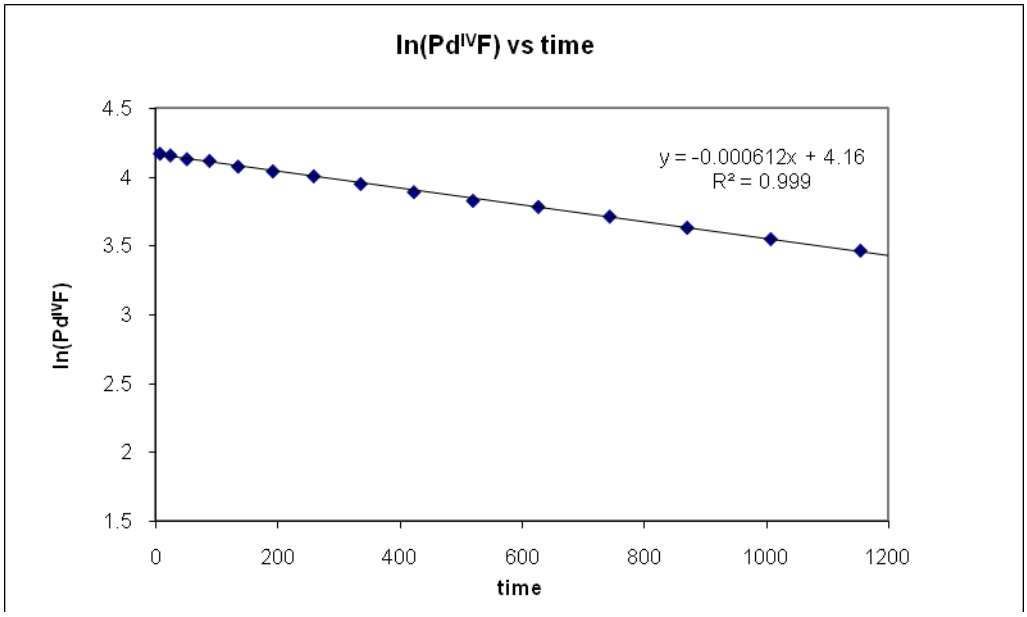
Kinetic data with 0.50 equiv of pyridine



Kinetic data with 0.75 equiv of pyridine

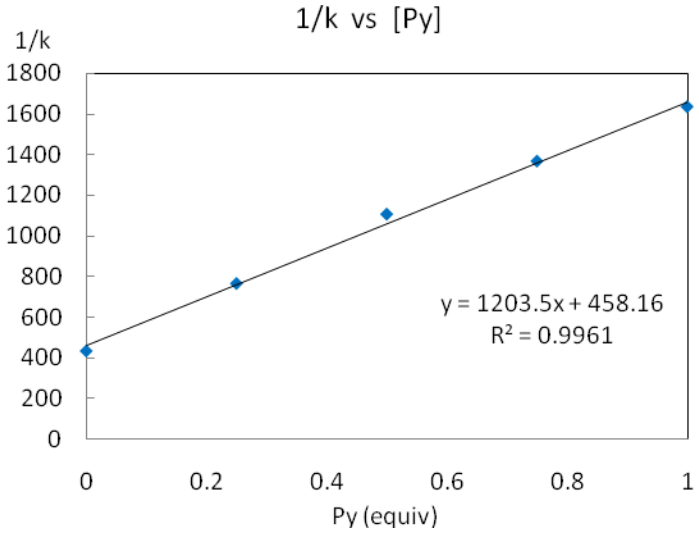


Kinetic data with 1.00 equiv of pyridine

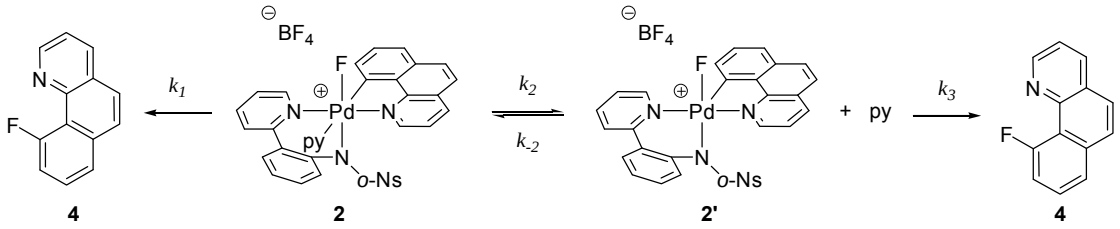


Relationship of rate vs pyridine concentrateion

py (equiv)	k (s^{-1})	1/k (s)
0	0.00232	431
0.25	0.00131	763
0.50	0.000905	1105
0.75	0.000731	1366
1.00	0.000612	1634



Model of reductive elimination from 2



The rate law for reductive elimination from **2** via C−F bond formation with direct mechanism and from a pentacoordinate complex **2'** with pre-equillibrium pyridine dissociation is as follows:

k_1*:* rate of C−F bond formation form hexacoordinate complex **2**

k_2*:* rate of pyridine dissociation to form pentacoordinate complex **2'**

k_{-2}*:* rate of pyridine association to form hexacoordinate complex **2**

k_3*:* rate of C−F bond formation form hexacoordinate complex **2'**

Rate of the reaction is given in eq. 1,

$$\frac{d[P]}{dt} = k_1[2] + k_3[2'] \tag{1}$$

Based on the steady state approximation for **2'**

$$\frac{d[2']}{dt} = 0 \quad \therefore k_2[2] - k_{-2}[2'][py] - k_3[2'] = 0$$

$$\therefore [2'] = \frac{k_2}{k_{-2}[py] + k_3}[2] \tag{2}$$

From eq.1 and eq.2,

$$\frac{d[P]}{dt} = k_1[2] + \frac{k_2 k_3}{k_{-2}[py] + k_3}[2]$$

$$= \left\{ k_1 + \frac{k_2 k_3}{k_{-2}[py] + k_3} \right\}[2]$$

Therefore, the rate expression is

$$\frac{d[P]}{dt} = k_{obs}[2]$$

$$\text{where } k_{obs} = k_1 + \frac{k_2 k_3}{k_{-2}[py] + k_3} \tag{3}$$

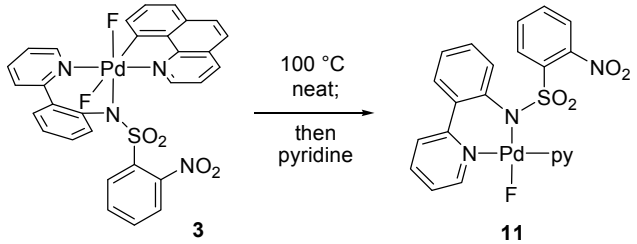
When $k_1 << k_3$, eq. 3 can be simplified to

$$k_{obs} = \frac{k_2 k_3}{k_{-2}[py] + k_3} \tag{4}$$

An alternative form of eq. 4 is eq. 5, which was used to fit the pyridine inhibition data

$$\frac{1}{k_{obs}} = \frac{1}{k_2} + \frac{k_{-2}[py]}{k_2 k_3} \tag{5}$$

C−F Reductive elimination from difluoro Pd(IV) complex 3

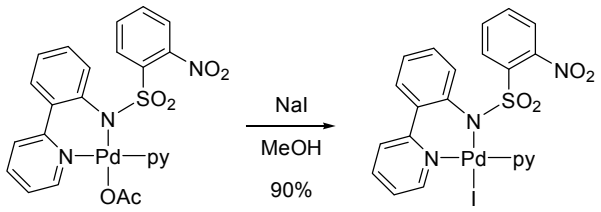


Difluoro palladium(IV) complex **3** (20.3 mg, 0.0300 mmol, 1.00 equiv) was heated at 100 ºC for 6.0 hr without solvent. After cooling to 23 ºC, 1.0 mL of MeCN containing pyridine (2.4 μL, 0.030 mmol, 1.0 equiv) was added to the residue with vigorous stirring. The mixture was concentrated in vacuo and washed with Et_2O (3 × 1.0 mL). The remaining solid was dissolved in CH_2Cl_2 and filtered through a pad of celite. The filtrate was concentrated in vacuo to afford 10 mg of the title compound as a yellow solid (60% yield).

NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 8.84–8.79 (m, 3H), 7.85 (dd, *J* = 7.5 Hz, 7.5 Hz, 1H), 7.67 (d, *J* = 7.5 Hz, 1H), 7.59 (ddd, *J* = 7.5 Hz, 7.5 Hz, 1.5 Hz, 1H), 7.56–7.52 (m, 2H), 7.48 (dd, *J* = 7.5 Hz, 1.5 Hz, 1H), 7.32 (dd, *J* = 7.0 Hz, 7.0 Hz, 2H), 7.38 (t, *J* = 7.0 Hz, 1H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.21 (ddd, *J* = 7.5 Hz, 7.0 Hz, 1.0 Hz, 1H), 7.16–7.11 (m, 2H), 7.05 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 154.2, 151.0 (d, *J* = 13.8 Hz), 150.7 (d, *J* = 6.9 Hz), 147.1, 139.9, 138.8, 138.7, 136.2, 134.0, 131.7, 131.4, 130.4, 130.1, 129.9, 129.5, 126.2, 124.8, 122.9, 122.7, 122.4. ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –323.3. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{22}H_{17}FN_4O_4PdS$ + H], 557.9989Found, 557.9977.

Independent synthesis of monofluoro Pd(II) complex 11

Iodo palladium(II) complex 12

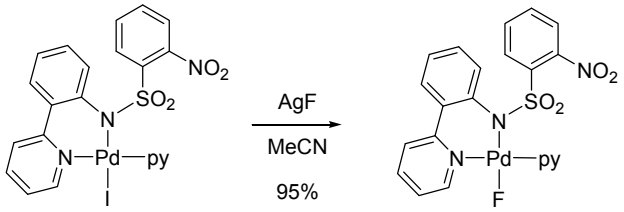


S6 **12**

To acetato palladium complex **S6** (299 mg, 0.500 mmol, 1.00 equiv) in MeOH (5.0 mL) at 23 ºC was added NaI (749 mg, 5.00 mmol, 10.0 equiv). After stirring for 2.0 hr at 23 ºC, the reaction mixture was concentrated in vacuo. The residue was dissolved in CH_2Cl_2 and filtered through a pad of celite. The filtrate was concentrated in vacuo to afford 300 mg of the title compound as a orange solid (90% yield).

NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 9.42 (dd, *J* = 6.0 Hz, 1.0 Hz, 1H), 7.45 (dd, *J* = 6.0 Hz, 1.5 Hz, 2H), 7.79 (dd, *J* = 7.5 Hz, 7.5 Hz, 1H), 7.61–7.50 (m, 3H), 7.79 (dd, *J* = 8.0 Hz, 1.5 Hz, 1H), 7.39–7.33 (m, 4H), 7.25–7.20 (m, 2H), 7.14–7.09 (m, 2H), 6.98 (ddd, *J* = 7.5 Hz, 7.5 Hz, 1.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 157.9, 155.6, 153.8, 146.9, 140.2, 138.7, 138.4, 136.8, 134.9, 131.8, 131.1, 130.3, 129.6, 129.4, 129.2, 125.2, 125.0, 123.7, 122.8, 122.6. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{22}H_{17}IN_4O_4PdS$ + H], 665.9050. Found, 665.9079.

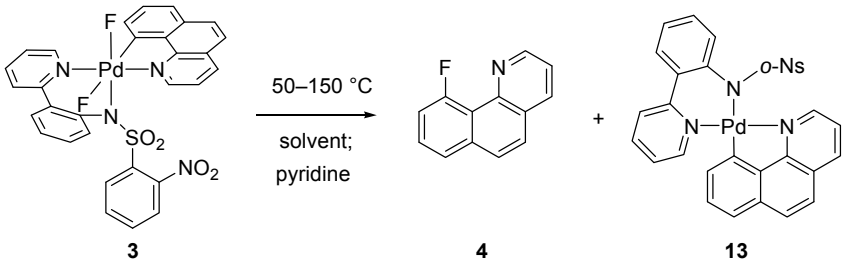
Fluoro palladium(II) complex 11



12 **11**

To iodo palladium complex **12** (200 mg, 0.300 mmol, 1.00 equiv) in MeCN (3.0 mL) at 23 ºC was added AgF (76.1 mg, 0.600 mmol, 2.00 equiv). After stirring for 20 min at 23 ºC, the reaction mixture was concentrated in vacuo. The residue was dissolved in CH_2Cl_2 and filtered through a pad of celite. The filtrate was concentrated in vacuo to afford 159 mg of the title compound as a yellow solid (95% yield).

Temperature and solvent dependency of C−F reductive elimination from 3.

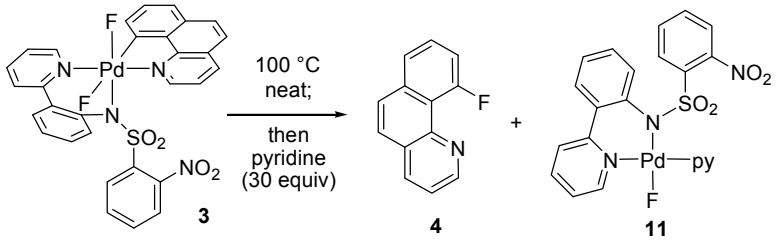


3 **4** **13**

Difluoro palladium(IV) complex **3** (6.8 mg, 0.010 mmol, 1.0 equiv) was heated at 50−150 ºC until complete conversion of the starting material. The yield of **4** and **13** was determined by ^{1}H NMR and ^{19}F NMR using 4-fluorotoluene as a standard. The results are summarized in the table below.

entry	conditions	**4** : **13** (% yield)
1	pyridine, 50 ºC	<1:50
2	pyridine, 75 ºC	<1:57
3	pyridine, 100 ºC	<1:72
4	DMSO, 50 ºC	38:60
5	DMSO, 75 ºC	48:50
6	DMSO, 100 ºC	66:32
7	DMSO, 150 ºC	97:1
8	chloroform, 50 ºC	54:44
9	chloroform, 75 ºC	64:33
10	chloroform, 100 ºC	70:27
11	neat, 75 ºC	95:<1
12	neat, 100 ºC	97: <1
13	neat, 150 ºC	98: <1

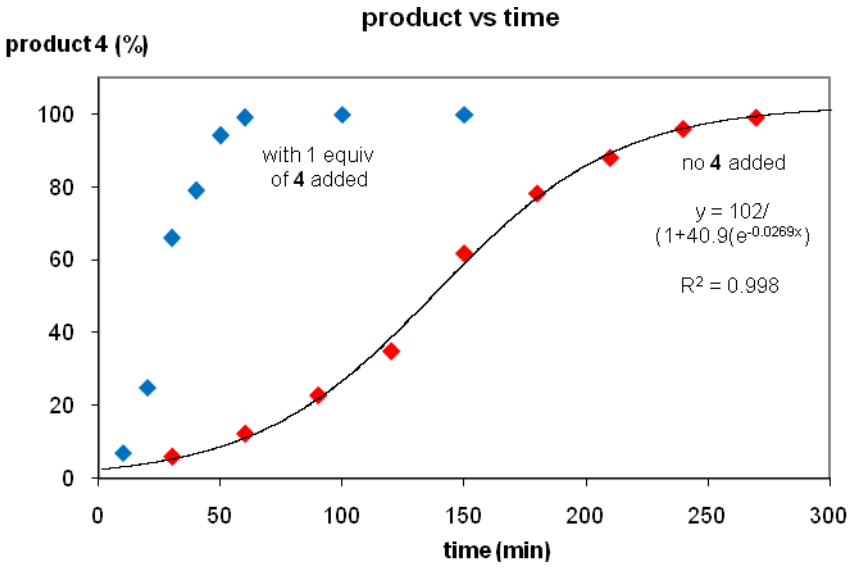
Kinetic experiments for C−F reductive elimination from 3



3 **4** **11**

Nine vials, which contain difluoro palladium(IV) complex **3** (3.4 mg, 0.0050 mmol, 1.0 equiv), were heated at 100 ºC without solvent in the presence/absence of **4** (0.97 mg, 0.0050 mmol, 1.0 equiv). At each data point, one vial was taken and cooled to 23 ºC using a dry ice/isopropanol bath. To each vial was added $CDCl_3$ and pyridine-*d5* (12 μL, 0.15 mol, 30 equiv) and the ratio of **3** and **4** was determined by

^{1}H NMR.



Model of autocatalytic reactions

$$A + B \xrightarrow{k} 2\,B$$

For an autocatalytic model reaction shown above, write $[A] = [A]_0 - x$, $[B] = [B]_0 + x$, when the rate law becomes

$$\frac{dx}{dt} = k([A]_0 - x)([B]_0 + x)$$

Integration by partial fractions using

$$\frac{1}{([A]_0 - x)([B]_0 + x)} = \frac{1}{[A]_0 + [B]_0}\left\{\frac{1}{[A]_0 - x} + \frac{1}{[B]_0 + x}\right\}$$

gives

$$\frac{1}{[A]_0 + [B]_0} ln\left\{\frac{[A]_0([B]_0 + x)}{[B]_0([A]_0 - x)}\right\} = kt$$

hence

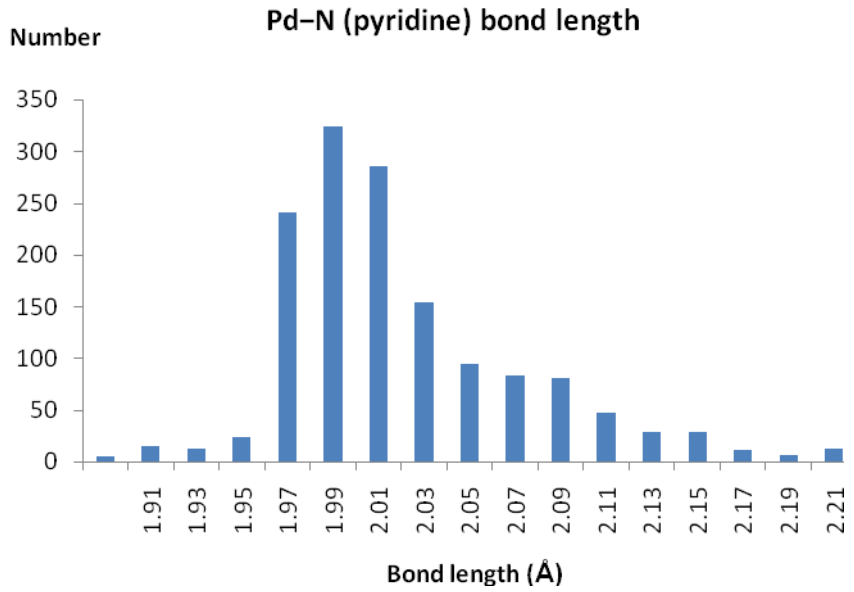
$$x = \frac{[B]_0\,(e^{at} - 1)}{1 + b\,e^{at}} \qquad a = k([A]_0 + [B]_0),\ b = \frac{[B]_0}{[A]_0}$$

$$\therefore \quad [B] = [B]_0 + x = \frac{[A]_0 + [B]_0}{1 + \frac{[A]_0}{[B]_0}\,e^{-([A]_0 + [B]_0)kt}}$$

For the C−F reductive elimination from **3** (= *A*) with no **4** (= *B*) added as shown in red, the data were fitted to $[A]_0 + [B]_0 = 102$, $[A]_0/[B]_0 = 40.9$, $k([A]_0 + [B]_0) = 0.0269$.

Analysis of typical Pd−N (pyridine) bond lengths

Typical Pd−N (pyridine) bond lengths were determined by calculating 95% confidence interval for 1454 samples obtained from Cambridge Crystallographic Database Center. Distribution is shown below.



X-ray Crystallographic Analysis

Difluoro Pd(IV) complex 3 (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 |Δ/σ| 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)

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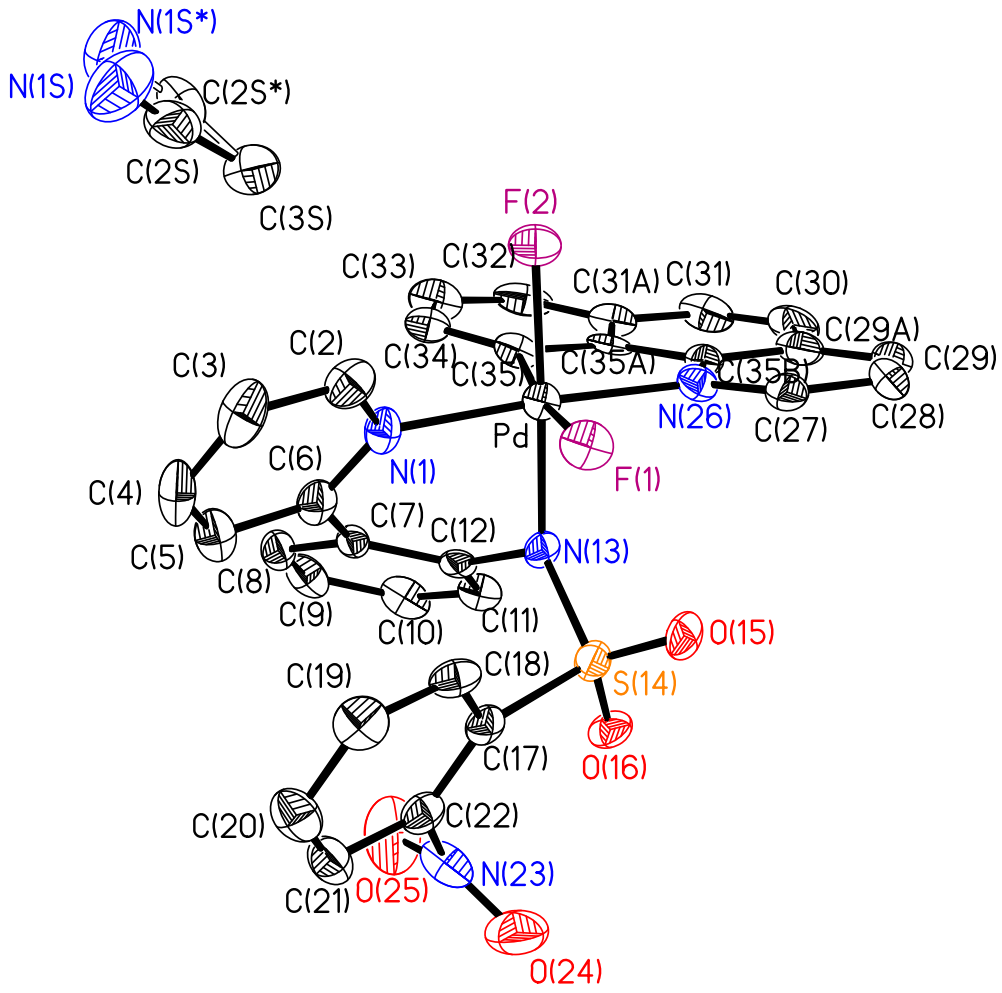
Creagh, D. C. & McAuley, W. J. (1992). *International Tables for Crystallography: Mathematical, Physical and Chemical Tables*, Vol C, edited by A. J. C. Wilson, pp. 206-222. Dordrecht, The Netherlands: Kluwer.

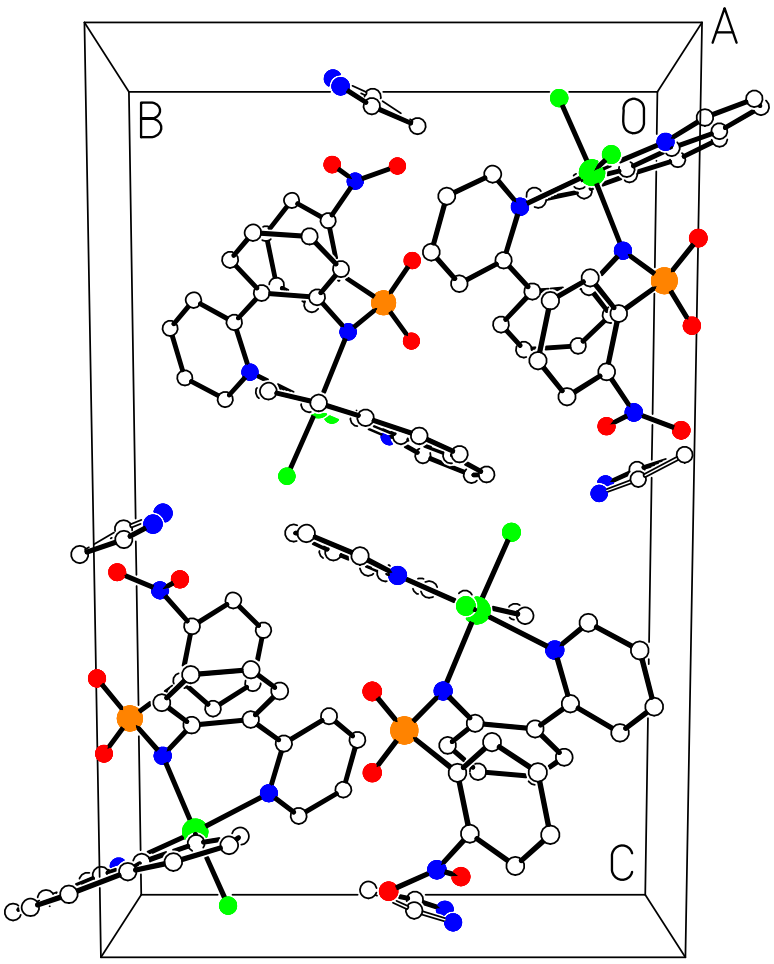
Maslen, E. N., Fox, A. G. & O'Keefe, M. A. (1992). *International Tables for Crystallography: Mathematical, Physical and Chemical Tables*, Vol C, edited by A. J. C. Wilson, pp. 476-516. Dordrecht, The Netherlands: Kluwer.

$R(F) = R1 = \Sigma \, ||F_o|-|F_c|| \, / \, \Sigma|F_o|$, $wR(F^2) = wR2 = [\, \Sigma \, w \, (F_o^2-F_c^2)^2 \, / \, \Sigma \, w \, (F_o^2)^2 \,]^{1/2}$, 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.

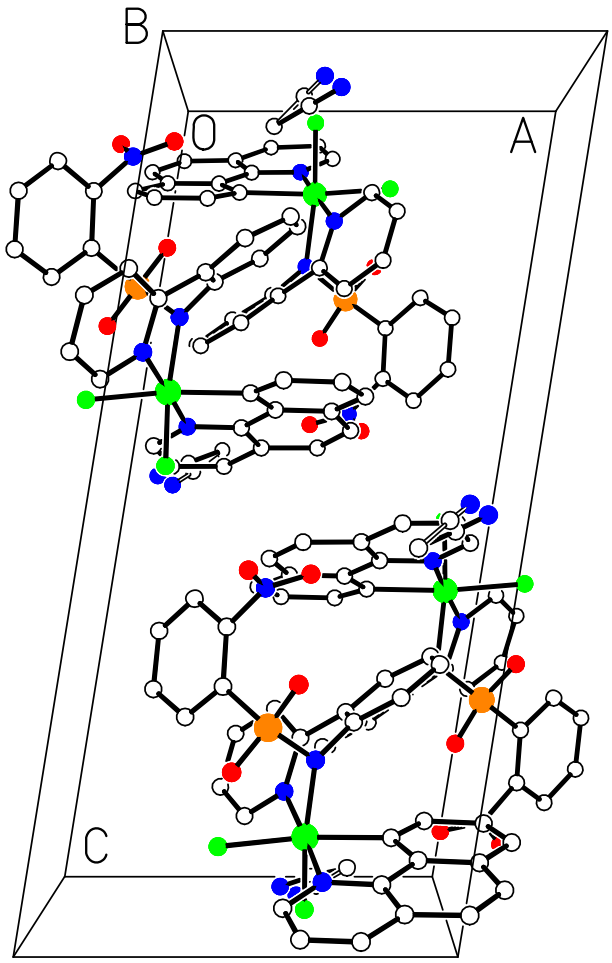


The structure of the difluoro palladium(IV) complex **3** without hydrogens.

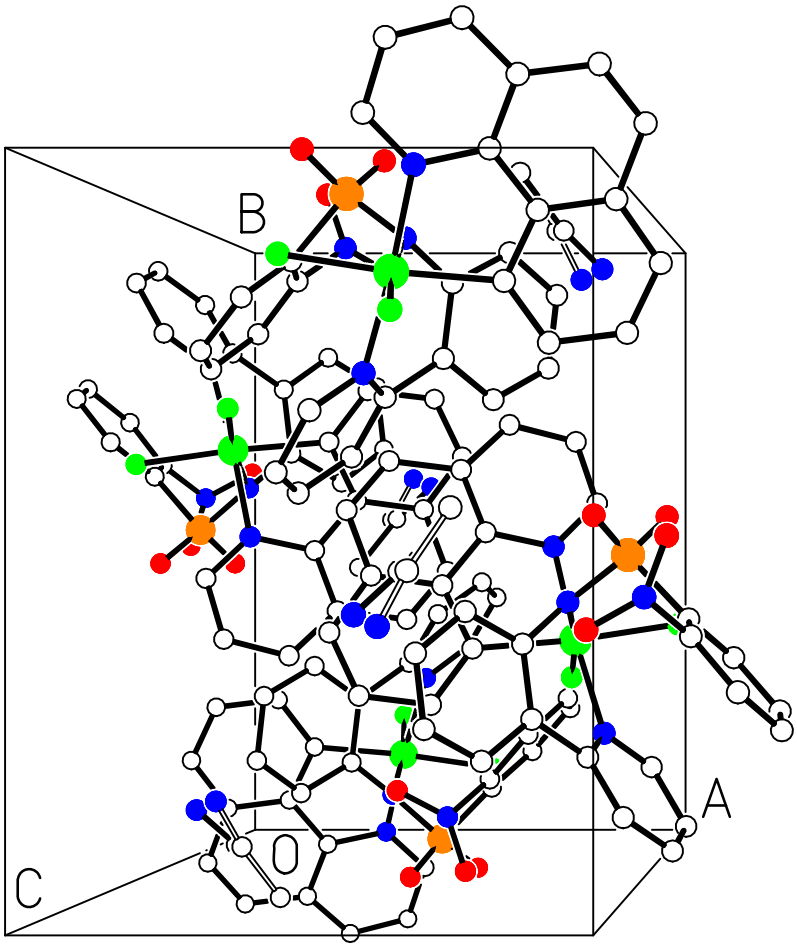
The nonhydrogen atoms are depicted with 50% probability ellipsoids.



A unit cell diagram for the difluoro palladium(IV) complex **3** viewed down the crystallographic *a*-axis. Hydrogen atoms have been removed for clarity.



A unit cell diagram for the difluoro palladium(IV) complex **3** viewed down the crystallographic *b*-axis. Hydrogen atoms have been removed for clarity.



A unit cell diagram for the difluoro palladium(IV) complex **3** viewed down the crystallographic *c*-axis. Hydrogen atoms have been removed for clarity.

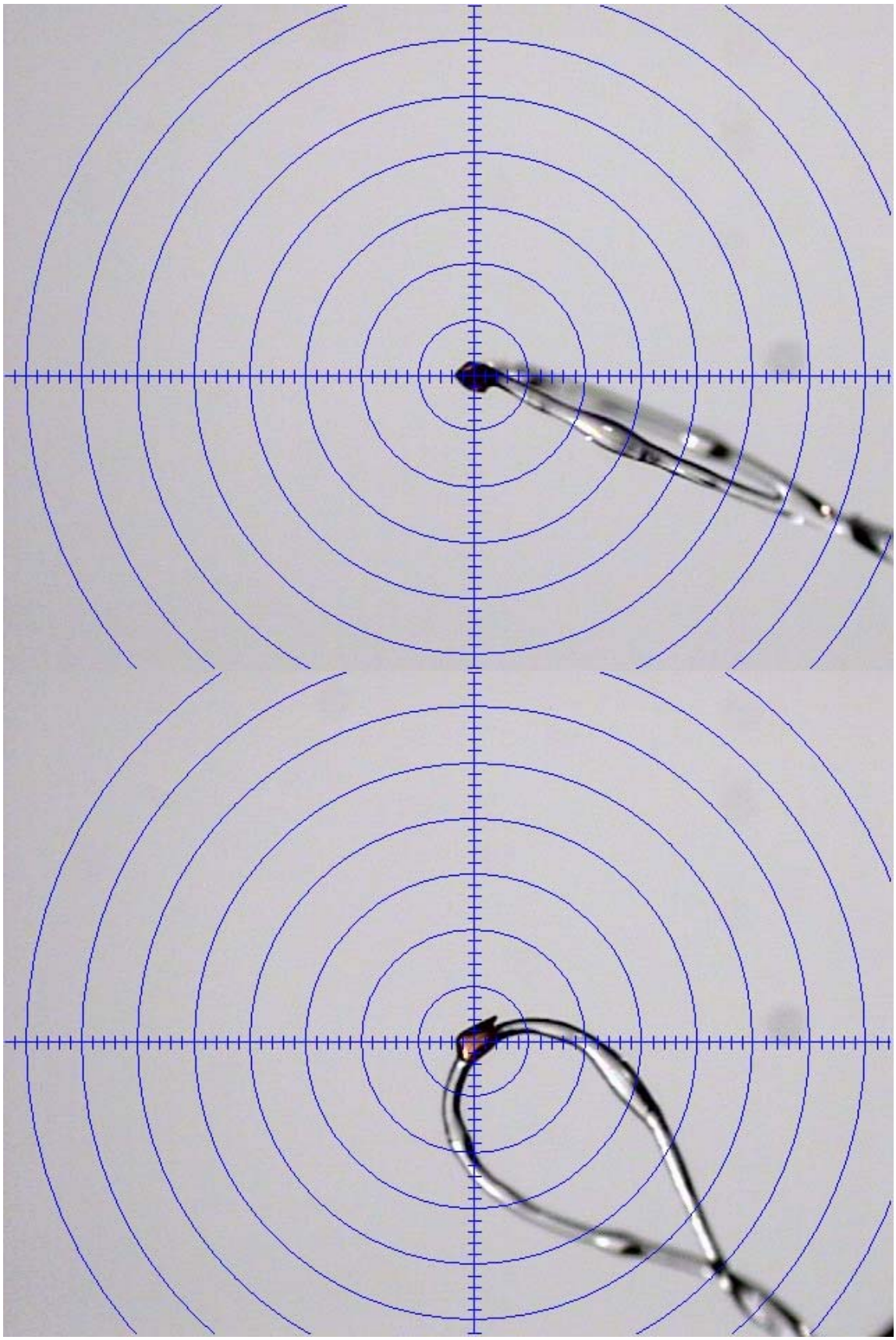


Table 1. Crystal data and structure refinement for the difluoro palladium(IV) complex **3**.

Identification code	difluoro palladium(IV) complex **3 (CCDC 686490)**	
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 **3**. 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 **3**.

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 **3**.

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 **3**.

	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 **3**.

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)

Monofluoro Pd(II) complex 11 (CCDC749260)

Experimental

The compound was crystallized from a dichloromethane / diethyl ether solution as colorless prisms. One of the prisms was cut to 0.120 mm x 0.180 mm x 0.230 mm in size, 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 3064 frames were collected at 193 (2) K to θ_{max} = 27.50° with an oscillation range of 0.5°/frame, and an exposure time of 20 s/frame using the APEX2 suite of software. (Bruker AXS, 2006a) Unit cell refinement on all observed reflections, and data reduction with corrections for Lp and decay were performed using SAINT. (Bruker AXS, 2006b) Scaling was done using SADABS. (Bruker AXS, 2004) The minimum and maximum transmission factors were 0.7875 and 0.8802, respectively. A total of 95236 reflections were collected, 9929 were unique (R_{int} = 0.0382), and 8417 had $I > 2\sigma(I)$. Systematic absences were consistent with the compound having crystallized in the monoclinic space group $P2_1/c$ (No. 14). The observed mean $|E^2-1|$ value was 0.875 (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 [(2-Nitrophenylsulfonyl)(2-(pyridin-2-yl)phenyl)amido](pyridine)palladium(II) fluoride and one molecule of dichloromethane. The pyridine ligand was found to be mildly disordered; this disorder was not treated since treatment of the disorder would not significantly improve the $R(F)$ and $wR(F^2)$ values. All of the nonhydrogen atoms were refined with anisotropic displacement coefficients. The hydrogen atoms were assigned isotropic displacement coefficients $U(H) = 1.2U(C)$ and their coordinates were allowed to ride on their respective carbons. The refinement converged to $R(F) = 0.0257$, $wR(F^2) = 0.0625$, and $S = 1.048$ for 8417 reflections with $I > 2\sigma(I)$, and $R(F) = 0.0347$, $wR(F^2) = 0.0674$, and $S = 1.048$ for 9929 unique reflections, 325 parameters, and 0 restraints. The maximum $|\Delta/\sigma|$ in the final cycle of least-squares was 0.003, and the residual peaks on the final difference-Fourier map ranged from -0.730 to 0.819 eÅ^{-3}. Scattering factors were taken from the International Tables for Crystallography, Volume C. (Maslen *et al.*, 1992, and Creagh & McAuley, 1992)

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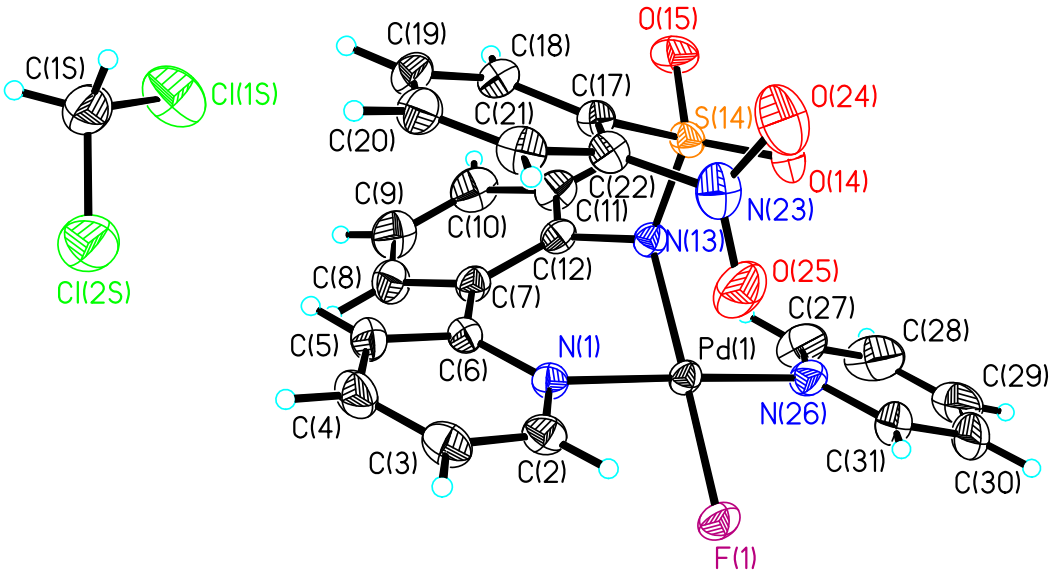
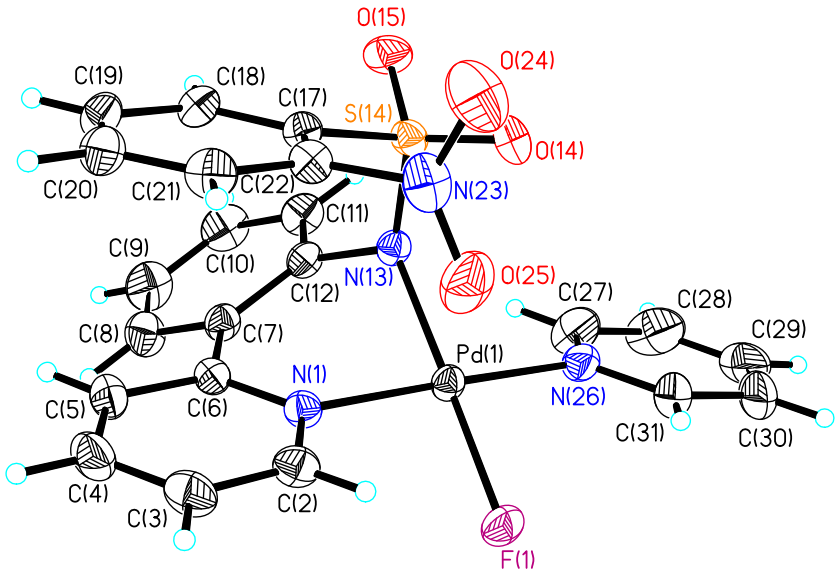
$R(F) = R1 = \Sigma \, ||F_o|-|F_c|| \, / \, \Sigma|F_o|$, $wR(F^2) = wR2 = [\, \Sigma \, w \, (F_o^2-F_c^2)^2 \, / \, \Sigma \, w \, (F_o^2)^2 \,]^{1/2}$, and S = Goodness-of-fit on $F^2 = [\, \Sigma \, w \, (F_o^2-F_c^2)^2 \, / \, (n-p) \,]^{1/2}$, where n is the number of reflections and p is the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



The structure of monofluoro Pd complex **11** dichloromethane solvate with hydrogens and atom labels. The nonhydrogen atoms are depicted with 50% probability ellipsoids.



The structure of complex **11** with hydrogens and atom labels. The nonhydrogen atoms are depicted with 50% probability ellipsoids.

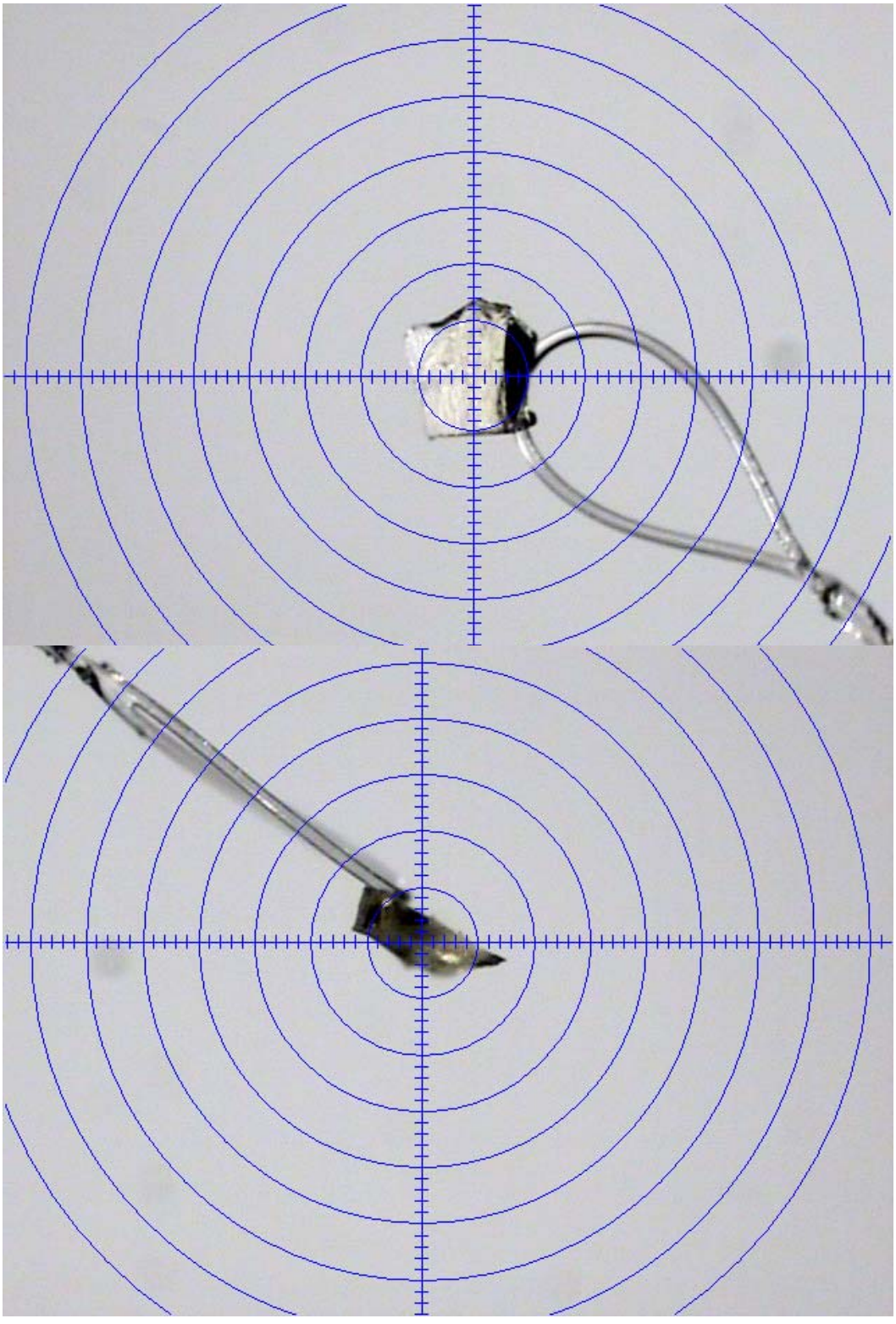


Table 1. Crystal data and structure refinement for compound **11**.

Identification code	compound **11 (CCDC749260)**	
Empirical formula	C23 H19 Cl2 F N4 O4 Pd S	
Formula weight	643.78	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2_1/c	
Unit cell dimensions	a = 15.2325(5) Å	α= 90°
	b = 11.9436(4) Å	β= 101.9750(10)°
	c = 13.9760(5) Å	γ = 90°
Volume	2487.33(15) $Å^3$	
Z	4	
Density (calculated)	1.719 mg/m^3	
Absorption coefficient	1.091 mm^{-1}	
F(000)	1288	
Crystal size	0.230 x 0.180 x 0.120 mm^3	
Theta range for data collection	2.19 to 33.73°.	
Index ranges	-23<=h<=23, -18<=k<=18, -21<=l<=21	
Reflections collected	95236	
Independent reflections	9929 [R(int) = 0.0382]	
Completeness to theta = 33.73°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8802 and 0.7875	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9929 / 0 / 325	
Goodness-of-fit on F^2	1.048	
Final R indices [I>2sigma(I)]	R1 = 0.0257, wR2 = 0.0625	
R indices (all data)	R1 = 0.0347, wR2 = 0.0674	
Largest diff. peak and hole	0.819 and -0.730 $e.Å^{-3}$	

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

	x	y	z	U(eq)
Pd(1)	2696(1)	9893(1)	2172(1)	20(1)
F(1)	3641(1)	10458(1)	1513(1)	31(1)
N(1)	3388(1)	8472(1)	2560(1)	22(1)
C(2)	4289(1)	8544(1)	2808(1)	27(1)
C(3)	4823(1)	7616(1)	3072(1)	33(1)
C(4)	4421(1)	6582(1)	3091(1)	35(1)
C(5)	3497(1)	6510(1)	2847(1)	31(1)
C(6)	2978(1)	7465(1)	2567(1)	23(1)
C(7)	1985(1)	7380(1)	2277(1)	24(1)
C(8)	1608(1)	6379(1)	1856(1)	34(1)
C(9)	690(1)	6220(2)	1624(1)	41(1)
C(10)	122(1)	7058(2)	1799(1)	39(1)
C(11)	472(1)	8071(1)	2194(1)	31(1)
C(12)	1398(1)	8238(1)	2435(1)	23(1)
N(13)	1735(1)	9300(1)	2805(1)	21(1)
S(14)	1739(1)	9579(1)	3927(1)	23(1)
O(14)	2081(1)	10694(1)	4124(1)	32(1)
O(15)	887(1)	9304(1)	4155(1)	33(1)
C(17)	2515(1)	8622(1)	4617(1)	23(1)
C(18)	2227(1)	7517(1)	4679(1)	28(1)
C(19)	2828(1)	6687(1)	5072(1)	32(1)
C(20)	3726(1)	6939(1)	5406(1)	33(1)
C(21)	4024(1)	8033(1)	5386(1)	32(1)
C(22)	3413(1)	8856(1)	4996(1)	25(1)
N(23)	3762(1)	10011(1)	5030(1)	34(1)

O(24)	3747(1)	10546(1)	5768(1)	55(1)
O(25)	4061(1)	10351(1)	4342(1)	47(1)
N(26)	1956(1)	11264(1)	1692(1)	28(1)
C(27)	1082(1)	11173(2)	1287(1)	43(1)
C(28)	593(1)	12071(2)	826(2)	57(1)
C(29)	1009(2)	13085(2)	790(2)	55(1)
C(30)	1895(2)	13183(2)	1220(2)	51(1)
C(31)	2356(1)	12255(1)	1662(1)	37(1)
C(1S)	3028(1)	3293(2)	4461(2)	46(1)
Cl(1S)	2004(1)	3921(1)	3904(1)	62(1)
Cl(2S)	3866(1)	3582(1)	3793(1)	59(1)

Table 3. Bond lengths [Å] and angles [°] for compound **11**.

Pd(1)-F(1)	1.9806(9)	S(14)-O(15)	1.4377(11)
Pd(1)-N(13)	1.9917(11)	S(14)-C(17)	1.7780(13)
Pd(1)-N(1)	2.0112(11)	C(17)-C(22)	1.3888(19)
Pd(1)-N(26)	2.0218(12)	C(17)-C(18)	1.3984(19)
N(1)-C(2)	1.3476(18)	C(18)-C(19)	1.383(2)
N(1)-C(6)	1.3561(16)	C(18)-H(18)	0.9500
C(2)-C(3)	1.380(2)	C(19)-C(20)	1.383(2)
C(2)-H(2)	0.9500	C(19)-H(19)	0.9500
C(3)-C(4)	1.380(2)	C(20)-C(21)	1.385(2)
C(3)-H(3)	0.9500	C(20)-H(20)	0.9500
C(4)-C(5)	1.382(2)	C(21)-C(22)	1.386(2)
C(4)-H(4)	0.9500	C(21)-H(21)	0.9500
C(5)-C(6)	1.3961(19)	C(22)-N(23)	1.4756(18)
C(5)-H(5)	0.9500	N(23)-O(24)	1.217(2)
C(6)-C(7)	1.4862(19)	N(23)-O(25)	1.217(2)
C(7)-C(8)	1.4008(19)	N(26)-C(31)	1.337(2)
C(7)-C(12)	1.4077(19)	N(26)-C(27)	1.339(2)
C(8)-C(9)	1.381(2)	C(27)-C(28)	1.386(2)
C(8)-H(8)	0.9500	C(27)-H(27)	0.9500
C(9)-C(10)	1.378(3)	C(28)-C(29)	1.372(3)
C(9)-H(9)	0.9500	C(28)-H(28)	0.9500
C(10)-C(11)	1.390(2)	C(29)-C(30)	1.363(3)
C(10)-H(10)	0.9500	C(29)-H(29)	0.9500
C(11)-C(12)	1.3937(19)	C(30)-C(31)	1.386(2)
C(11)-H(11)	0.9500	C(30)-H(30)	0.9500
C(12)-N(13)	1.4249(16)	C(31)-H(31)	0.9500
N(13)-S(14)	1.6023(11)	C(1S)-Cl(1S)	1.760(2)
S(14)-O(14)	1.4356(11)	C(1S)-Cl(2S)	1.764(2)

C(1S)-H(2S)	0.9900	C(1S)-H(1S)	0.9900
F(1)-Pd(1)-N(13)	178.59(4)	C(9)-C(8)-H(8)	119.3
F(1)-Pd(1)-N(1)	91.32(4)	C(7)-C(8)-H(8)	119.3
N(13)-Pd(1)-N(1)	88.40(4)	C(10)-C(9)-C(8)	120.08(15)
F(1)-Pd(1)-N(26)	88.78(4)	C(10)-C(9)-H(9)	120.0
N(13)-Pd(1)-N(26)	91.41(5)	C(8)-C(9)-H(9)	120.0
N(1)-Pd(1)-N(26)	175.88(5)	C(9)-C(10)-C(11)	119.93(15)
C(2)-N(1)-C(6)	120.07(12)	C(9)-C(10)-H(10)	120.0
C(2)-N(1)-Pd(1)	117.64(9)	C(11)-C(10)-H(10)	120.0
C(6)-N(1)-Pd(1)	122.28(9)	C(10)-C(11)-C(12)	120.38(15)
N(1)-C(2)-C(3)	122.00(14)	C(10)-C(11)-H(11)	119.8
N(1)-C(2)-H(2)	119.0	C(12)-C(11)-H(11)	119.8
C(3)-C(2)-H(2)	119.0	C(11)-C(12)-C(7)	120.15(12)
C(2)-C(3)-C(4)	119.01(14)	C(11)-C(12)-N(13)	119.03(12)
C(2)-C(3)-H(3)	120.5	C(7)-C(12)-N(13)	120.78(12)
C(4)-C(3)-H(3)	120.5	C(12)-N(13)-S(14)	117.94(9)
C(3)-C(4)-C(5)	118.96(14)	C(12)-N(13)-Pd(1)	113.48(8)
C(3)-C(4)-H(4)	120.5	S(14)-N(13)-Pd(1)	120.48(6)
C(5)-C(4)-H(4)	120.5	O(14)-S(14)-O(15)	118.61(7)
C(4)-C(5)-C(6)	120.47(14)	O(14)-S(14)-N(13)	107.94(6)
C(4)-C(5)-H(5)	119.8	O(15)-S(14)-N(13)	110.43(6)
C(6)-C(5)-H(5)	119.8	O(14)-S(14)-C(17)	108.60(7)
N(1)-C(6)-C(5)	119.47(13)	O(15)-S(14)-C(17)	105.18(7)
N(1)-C(6)-C(7)	120.20(11)	N(13)-S(14)-C(17)	105.27(6)
C(5)-C(6)-C(7)	120.34(12)	C(22)-C(17)-C(18)	117.57(12)
C(8)-C(7)-C(12)	117.94(13)	C(22)-C(17)-S(14)	124.64(10)
C(8)-C(7)-C(6)	118.57(13)	C(18)-C(17)-S(14)	117.32(10)
C(12)-C(7)-C(6)	123.45(11)	C(19)-C(18)-C(17)	120.71(14)
C(9)-C(8)-C(7)	121.50(15)	C(19)-C(18)-H(18)	119.6

C(17)-C(18)-H(18)	119.6	N(26)-C(27)-H(27)	119.2
C(18)-C(19)-C(20)	120.29(14)	C(28)-C(27)-H(27)	119.2
C(18)-C(19)-H(19)	119.9	C(29)-C(28)-C(27)	119.5(2)
C(20)-C(19)-H(19)	119.9	C(29)-C(28)-H(28)	120.3
C(19)-C(20)-C(21)	120.27(14)	C(27)-C(28)-H(28)	120.3
C(19)-C(20)-H(20)	119.9	C(30)-C(29)-C(28)	118.81(17)
C(21)-C(20)-H(20)	119.9	C(30)-C(29)-H(29)	120.6
C(20)-C(21)-C(22)	118.69(14)	C(28)-C(29)-H(29)	120.6
C(20)-C(21)-H(21)	120.7	C(29)-C(30)-C(31)	119.44(19)
C(22)-C(21)-H(21)	120.7	C(29)-C(30)-H(30)	120.3
C(21)-C(22)-C(17)	122.38(13)	C(31)-C(30)-H(30)	120.3
C(21)-C(22)-N(23)	116.25(13)	N(26)-C(31)-C(30)	121.99(18)
C(17)-C(22)-N(23)	121.35(12)	N(26)-C(31)-H(31)	119.0
O(24)-N(23)-O(25)	124.74(15)	C(30)-C(31)-H(31)	119.0
O(24)-N(23)-C(22)	116.70(15)	Cl(1S)-C(1S)-Cl(2S)	110.76(11)
O(25)-N(23)-C(22)	118.53(14)	Cl(1S)-C(1S)-H(2S)	109.5
C(31)-N(26)-C(27)	118.56(14)	Cl(2S)-C(1S)-H(2S)	109.5
C(31)-N(26)-Pd(1)	120.11(11)	Cl(1S)-C(1S)-H(1S)	109.5
C(27)-N(26)-Pd(1)	120.79(11)	Cl(2S)-C(1S)-H(1S)	109.5
N(26)-C(27)-C(28)	121.68(19)	H(2S)-C(1S)-H(1S)	108.1

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for compound **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(1)	18(1)	19(1)	24(1)	1(1)	4(1)	-1(1)
F(1)	26(1)	29(1)	40(1)	4(1)	13(1)	-5(1)
N(1)	20(1)	23(1)	24(1)	0(1)	5(1)	0(1)
C(2)	20(1)	32(1)	30(1)	-2(1)	6(1)	-1(1)
C(3)	22(1)	42(1)	36(1)	-1(1)	6(1)	6(1)
C(4)	32(1)	35(1)	39(1)	2(1)	8(1)	13(1)
C(5)	32(1)	24(1)	38(1)	2(1)	10(1)	5(1)
C(6)	23(1)	22(1)	24(1)	-1(1)	6(1)	1(1)
C(7)	24(1)	22(1)	25(1)	-1(1)	5(1)	-4(1)
C(8)	36(1)	26(1)	39(1)	-7(1)	7(1)	-7(1)
C(9)	40(1)	37(1)	44(1)	-10(1)	3(1)	-18(1)
C(10)	27(1)	45(1)	41(1)	-3(1)	0(1)	-14(1)
C(11)	20(1)	35(1)	35(1)	1(1)	2(1)	-5(1)
C(12)	21(1)	24(1)	23(1)	1(1)	3(1)	-3(1)
N(13)	18(1)	21(1)	24(1)	1(1)	4(1)	-1(1)
S(14)	20(1)	23(1)	26(1)	0(1)	5(1)	3(1)
O(14)	36(1)	22(1)	38(1)	-6(1)	6(1)	3(1)
O(15)	22(1)	44(1)	35(1)	4(1)	11(1)	5(1)
C(17)	21(1)	25(1)	22(1)	1(1)	5(1)	1(1)
C(18)	28(1)	28(1)	27(1)	4(1)	7(1)	-3(1)
C(19)	40(1)	27(1)	29(1)	6(1)	8(1)	0(1)
C(20)	35(1)	34(1)	30(1)	8(1)	5(1)	10(1)
C(21)	25(1)	39(1)	30(1)	2(1)	1(1)	4(1)
C(22)	24(1)	26(1)	25(1)	-2(1)	3(1)	0(1)
N(23)	25(1)	31(1)	41(1)	-5(1)	-3(1)	-4(1)

O(24)	62(1)	47(1)	52(1)	-24(1)	0(1)	-9(1)
O(25)	43(1)	39(1)	61(1)	5(1)	13(1)	-13(1)
N(26)	28(1)	26(1)	31(1)	6(1)	11(1)	4(1)
C(27)	28(1)	48(1)	53(1)	20(1)	10(1)	9(1)
C(28)	39(1)	73(1)	63(1)	30(1)	18(1)	27(1)
C(29)	72(2)	50(1)	53(1)	24(1)	34(1)	37(1)
C(30)	80(2)	26(1)	54(1)	9(1)	31(1)	14(1)
C(31)	49(1)	25(1)	41(1)	2(1)	16(1)	1(1)
C(1S)	56(1)	38(1)	45(1)	1(1)	15(1)	-5(1)
Cl(1S)	40(1)	73(1)	73(1)	-19(1)	11(1)	-6(1)
Cl(2S)	44(1)	66(1)	70(1)	12(1)	18(1)	6(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for compound **11**.

	x	y	z	U(eq)
H(2)	4566	9257	2801	33
H(3)	5458	7686	3237	40
H(4)	4775	5930	3269	42
H(5)	3211	5806	2869	37
H(8)	1993	5797	1727	40
H(9)	451	5532	1343	49
H(10)	-509	6944	1650	46
H(11)	79	8654	2301	37
H(18)	1612	7335	4449	33
H(19)	2623	5941	5112	38
H(20)	4139	6360	5650	40
H(21)	4636	8215	5635	38
H(27)	790	10475	1315	51
H(28)	-25	11986	538	68
H(29)	686	13707	471	66
H(30)	2193	13881	1218	61
H(31)	2976	12327	1952	45
H(2S)	2946	2473	4497	55
H(1S)	3220	3580	5137	55

Table 6. Torsion angles [°] for compound **11**.

F(1)-Pd(1)-N(1)-C(2)	36.39(10)	C(8)-C(7)-C(12)-N(13)	-176.17(13)
N(13)-Pd(1)-N(1)-C(2)	-145.00(10)	C(6)-C(7)-C(12)-N(13)	6.2(2)
F(1)-Pd(1)-N(1)-C(6)	-142.81(10)	C(11)-C(12)-N(13)-S(14)	77.79(14)
N(13)-Pd(1)-N(1)-C(6)	35.81(11)	C(7)-C(12)-N(13)-S(14)	-104.68(13)
C(6)-N(1)-C(2)-C(3)	0.2(2)	C(11)-C(12)-N(13)-Pd(1)	-133.30(11)
Pd(1)-N(1)-C(2)-C(3)	-179.04(11)	C(7)-C(12)-N(13)-Pd(1)	44.23(14)
N(1)-C(2)-C(3)-C(4)	-0.6(2)	N(1)-Pd(1)-N(13)-C(12)	-56.02(9)
C(2)-C(3)-C(4)-C(5)	-0.1(2)	N(26)-Pd(1)-N(13)-C(12)	119.86(9)
C(3)-C(4)-C(5)-C(6)	1.2(2)	N(1)-Pd(1)-N(13)-S(14)	92.02(7)
C(2)-N(1)-C(6)-C(5)	1.0(2)	N(26)-Pd(1)-N(13)-S(14)	-92.10(7)
Pd(1)-N(1)-C(6)-C(5)	-179.84(10)	C(12)-N(13)-S(14)-O(14)	-178.41(10)
C(2)-N(1)-C(6)-C(7)	-178.91(12)	Pd(1)-N(13)-S(14)-O(14)	34.92(9)
Pd(1)-N(1)-C(6)-C(7)	0.26(17)	C(12)-N(13)-S(14)-O(15)	-47.29(11)
C(4)-C(5)-C(6)-N(1)	-1.7(2)	Pd(1)-N(13)-S(14)-O(15)	166.04(7)
C(4)-C(5)-C(6)-C(7)	178.20(14)	C(12)-N(13)-S(14)-C(17)	65.75(11)
N(1)-C(6)-C(7)-C(8)	150.72(14)	Pd(1)-N(13)-S(14)-C(17)	-80.92(8)
C(5)-C(6)-C(7)-C(8)	-29.2(2)	O(14)-S(14)-C(17)-C(22)	-20.39(14)
N(1)-C(6)-C(7)-C(12)	-31.7(2)	O(15)-S(14)-C(17)-C(22)	-148.32(12)
C(5)-C(6)-C(7)-C(12)	148.40(14)	N(13)-S(14)-C(17)-C(22)	95.00(13)
C(12)-C(7)-C(8)-C(9)	-1.6(2)	O(14)-S(14)-C(17)-C(18)	167.70(11)
C(6)-C(7)-C(8)-C(9)	176.07(15)	O(15)-S(14)-C(17)-C(18)	39.76(13)
C(7)-C(8)-C(9)-C(10)	0.4(3)	N(13)-S(14)-C(17)-C(18)	-76.91(12)
C(8)-C(9)-C(10)-C(11)	1.1(3)	C(22)-C(17)-C(18)-C(19)	-2.4(2)
C(9)-C(10)-C(11)-C(12)	-1.4(3)	S(14)-C(17)-C(18)-C(19)	170.11(11)
C(10)-C(11)-C(12)-C(7)	0.1(2)	C(17)-C(18)-C(19)-C(20)	-0.3(2)
C(10)-C(11)-C(12)-N(13)	177.69(14)	C(18)-C(19)-C(20)-C(21)	2.6(2)
C(8)-C(7)-C(12)-C(11)	1.3(2)	C(19)-C(20)-C(21)-C(22)	-2.2(2)
C(6)-C(7)-C(12)-C(11)	-176.26(13)	C(20)-C(21)-C(22)-C(17)	-0.6(2)

C(20)-C(21)-C(22)-N(23)	177.62(14)
C(18)-C(17)-C(22)-C(21)	2.8(2)
S(14)-C(17)-C(22)-C(21)	-169.05(12)
C(18)-C(17)-C(22)-N(23)	-175.30(13)
S(14)-C(17)-C(22)-N(23)	12.8(2)
C(21)-C(22)-N(23)-O(24)	-87.84(18)
C(17)-C(22)-N(23)-O(24)	90.41(18)
C(21)-C(22)-N(23)-O(25)	90.40(18)
C(17)-C(22)-N(23)-O(25)	-91.35(19)
F(1)-Pd(1)-N(26)-C(31)	-37.49(12)
N(13)-Pd(1)-N(26)-C(31)	143.91(12)
F(1)-Pd(1)-N(26)-C(27)	133.99(13)
N(13)-Pd(1)-N(26)-C(27)	-44.60(13)
C(31)-N(26)-C(27)-C(28)	1.1(3)
Pd(1)-N(26)-C(27)-C(28)	-170.47(16)
N(26)-C(27)-C(28)-C(29)	-0.6(3)
C(27)-C(28)-C(29)-C(30)	-0.8(3)
C(28)-C(29)-C(30)-C(31)	1.5(3)
C(27)-N(26)-C(31)-C(30)	-0.4(3)
Pd(1)-N(26)-C(31)-C(30)	171.30(14)
C(29)-C(30)-C(31)-N(26)	-1.0(3)

Computational Method Details

Calculations were performed using density functional theory (DFT) with the M06 functional, as implemented in Jaguar 7.6 release 110.[20] All calculations used the Hay and Wadt small core-valence relativistic effective-core-potential (ECP).[21] The LACV3P** basis set was used for Pd and the 6-311G** basis set was used for F for all geometry optimizations and LACV3P++**(2f) and 6-311++G** basis sets for energies. LACV3P++**(2f) utilizes the LACV3P++** basis set as implemented in Jaguar plus a double-zeta f-shell with exponents from Martin and Sundermann.[22] All electrons were described for all other atoms using the 6-31G** or 6-311++G** basis sets for geometry optimizations and energies, respectively.[23,24] For each optimized structure, the M06 analytic Hessian was calculated to obtain the vibrational frequencies, which in turn were used to obtain the zero point energies and free energy corrections (without translational or rotational components). Solvent corrections were based on single point self-consistent Poisson-Boltzmann continuum solvation calculations for MeCN (ε = 37.5 and R_0= 2.18 Å using the PBF[25] module in Jaguar. Natural population analyses were obtained from NBO 5.0[26] as implemented in Jaguar.

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[20] Jaguar 7.6, Schrodinger, LLC, New York, NY (2006).

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[22] Martin, J. M. L.; Sundermann, A. *J. Chem. Phys.* **2001**, *114*, 3408–3420.

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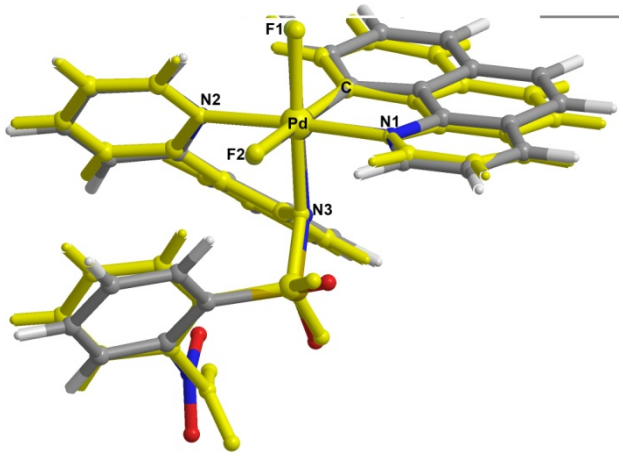
[25] Tannor, D. J. *et al. J. Am. Chem. Soc.* **1994**, *116*, 11875–11882.

[26] (a) *NBO 5.0.* E. D. Glendening, J, K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, and F. Weinhold, Theoretical Chemistry Institute, University of Wisconsin, Madison (2001); (b) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899–926.

Structural Validation for 3. Calculated structure is overlayed in yellow.



Structural Parameter	Experiment (X-ray)	M06 calculated	Deviation
Pd–C	2.008(5) Å	2.035 Å	+0.027 Å
Pd–N1	2.012(5) Å	2.032 Å	+0.020 Å
Pd–F1	1.955(3) Å	2.000 Å	+0.045 Å
Pd–F2	2.039(3) Å	2.089 Å	+0.050 Å
Pd–N2	2.027(5) Å	2.052 Å	+0.025 Å
Pd–N3	2.020(4) Å	2.051 Å	+0.031 Å
F1–Pd–F2	88.3(13)°	87.8°	–0.5°
C–Pd–F1	87.7(18)°	86.5°	–1.2°
C–Pd–F2	173.0(18)°	170.2°	–2.8°
N1–Pd–N2	175.9(18)°	176.0°	+0.1°
N2–Pd–N3	87.7(18)°	87.8°	+0.1°

Natural charges for transition states

Complex	Natural charge on Pd	Natural charge on F1	Natural charge on C
1	1.07	-0.62	-0.13
1‡	0.93	-0.51	0.32
2	1.06	-0.63	0.12
2‡	0.95	-0.51	0.32

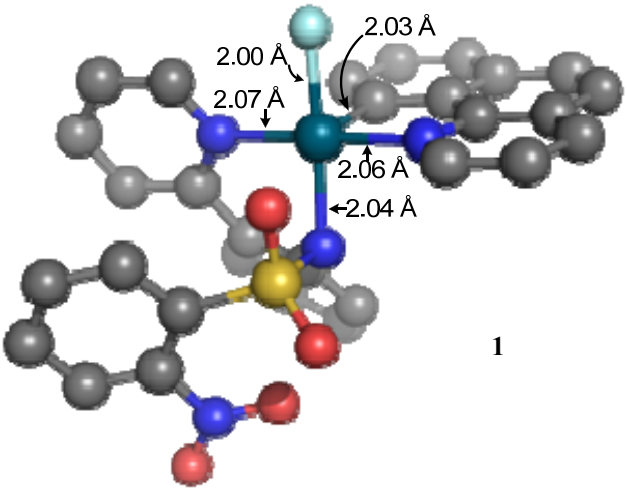
Hammett plot calculations (*values are below the accuracy of the method)

Complex	**($\Delta E^{‡}$ kcal mol^{-1}) relative to unsubstituted complexes 1 and 2**
7a (CF_3)	< − 0.1* relative to **1**
7e (OMe)	+ 0.2* relative to **1**
8a (NO_2)	− 0.6* relative to **1**
8g (OMe)	+ 0.2* relative to **1**
10a (NO_2)	+ 2.7 relative to **2**
10g (OMe)	+ 3.1 relative to **2**

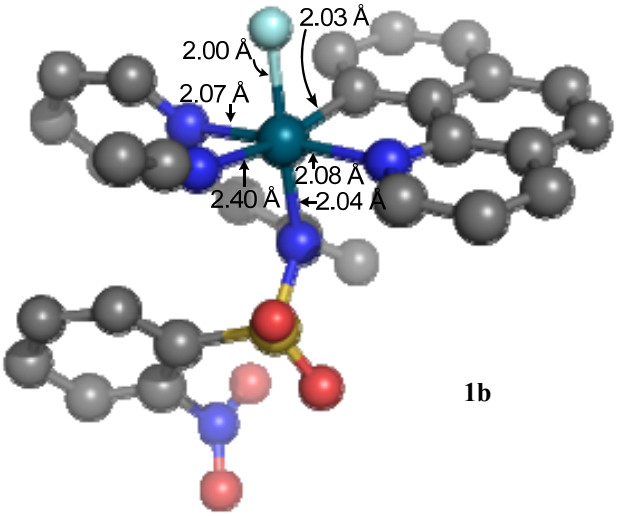
Bond distances in the transition states of reductive elimination from 2, 10a, and 10g.

	2‡	**10a**‡; 7- NO_2	**10g**‡; 7-OMe
Pd–N(py) [Å]	2.47	2.42	2.46
Pd–F [Å]	2.11	2.13	2.11
Pd–C [Å]	2.19	2.15	2.20

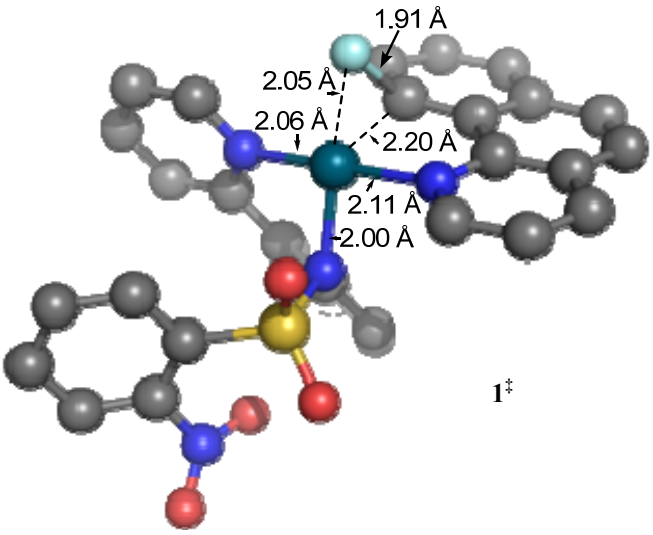
Selected metrical parameters of calculated structures



1



1b


1.91 Å
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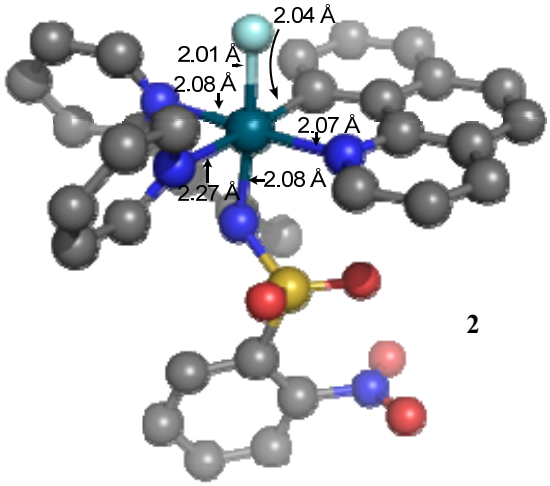
2.11 Å
2.00 Å

1‡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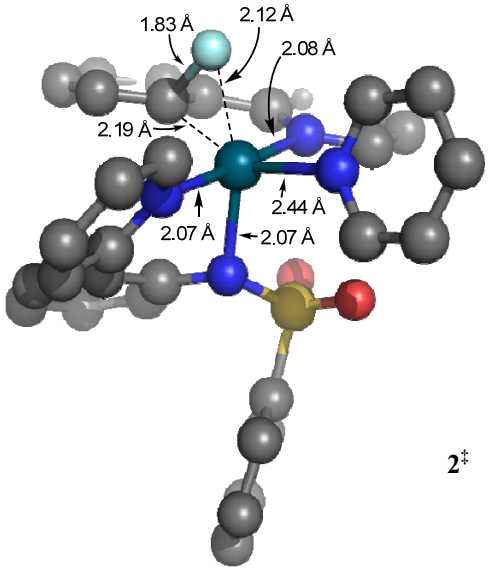
2


1.83 Å
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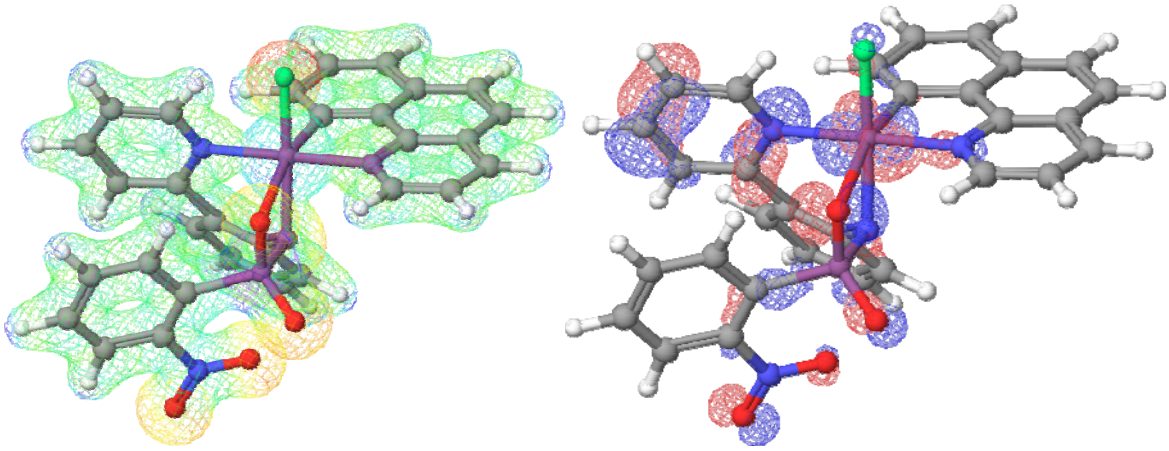
2.08 Å
2.19 Å
2.44 Å
2.07 Å
2.07 Å

2‡

Electrostatic potential (blue is δ^+, red is δ^-) and highest occupied molecular orbital for 1 and $1^{\ddagger}$.



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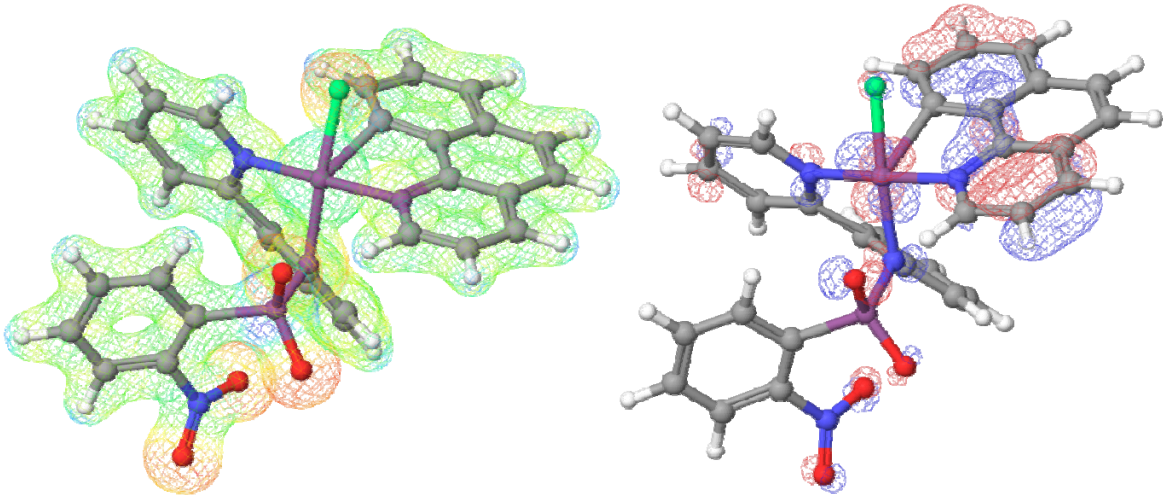
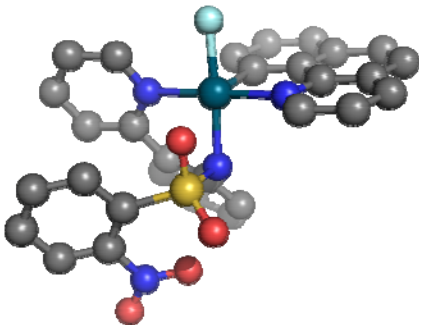


$1^{\ddagger}$

XYZ coordinates from M06 geometry optimizations

1



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C5	4.6677647627	4.2137149947	2.7625933956
H6	4.8368116853	3.8200436526	1.7596832460
C7	5.2272700071	5.3899760115	3.2274120475
H8	5.8832130328	5.9643365322	2.5812736959
C9	4.9278785846	5.7984598510	4.5222540216
H10	5.3663308211	6.7060560183	4.9296610330
C11	4.0683099029	5.0371208698	5.2977564632
H12	3.8460845304	5.3211785726	6.3224479758
C13	3.4981271900	3.8694756101	4.7828113734
C14	2.5081642953	3.1078739599	5.5663482166
C15	1.6156735116	3.8132131459	6.3840068249
H16	1.6782089979	4.8982450524	6.4359080963
C17	0.6120373796	3.1574653406	7.0817925853
H18	-0.0730957682	3.7296198851	7.7014785090
C19	0.4672355527	1.7774275131	6.9642279953
H20	-0.3229432607	1.2611262319	7.5020076304
C21	1.3353923870	1.0613673451	6.1547363470
H22	1.2675842760	-0.0187928606	6.0588717006
C23	2.3699950225	1.7074734514	5.4782664651
N24	3.1964491003	0.9192927199	4.6468765866
S25	4.7902857981	0.5190038239	4.9449785325
O26	5.3622833623	0.7706583154	3.5830069326
O27	4.9691447377	-0.8170317060	5.4635156427
C28	5.6252629628	1.7322381047	6.0096362251
C29	6.6453719286	2.4396717511	5.3791344507
H30	6.8407990179	2.2527820797	4.3273069173
C31	7.4145652032	3.3614080950	6.0852206242
H32	8.2098172869	3.8942250876	5.5701836695
C33	7.1737125094	3.5919869960	7.4319152230
H34	7.7725296225	4.3083583998	7.9871488859
C35	6.1671829750	2.8847120557	8.0790791134
H36	5.9566136612	3.0227863260	9.1352362156
C37	5.4085547372	1.9612866751	7.3775316247
N38	4.3769763513	1.2417810390	8.1420434544
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O40	3.6972461964	0.4399643691	7.5228581524

N41	2.8873016157	-0.2310460348	1.9875116883
C42	3.6850992649	-1.2821206246	1.8618200655
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H45	3.8676199098	-3.3255315749	1.2293274332
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H57	-1.1511431114	4.1624667833	2.2596143647
C58	0.7655634040	3.2110581711	2.5065525981
H59	1.2401995100	4.1038581146	2.9024271283
C60	1.4298552986	2.0310409112	2.3360168262
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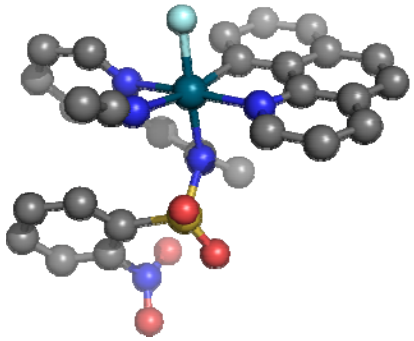
C62	1.5908069171	-0.2858281326	1.6000211060

1b



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C4	4.7069389465	4.5060263057	2.7083244324
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H11	3.7234781998	5.3842662251	6.2896543731
C12	3.4666243348	4.0216800310	4.6561920212
C13	2.4154855193	3.2440463308	5.3268973554
C14	1.4537803530	3.9345197199	6.0749185267
H15	1.5251096614	5.0156747766	6.1773981454
C16	0.3739764818	3.2690395442	6.6341524528
H17	-0.3679081288	3.8258072615	7.2004301978
C18	0.2318779668	1.8970233915	6.4484601268
H19	-0.6154523867	1.3722325707	6.8817402489

C20	1.1701087871	1.1963299332	5.7068778518
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C22	2.2695020840	1.8544351247	5.1555434273
N23	3.1931909129	1.1142671545	4.3892548623
S24	4.3494227078	0.2469968289	5.2001065997
O25	5.2278969578	-0.3125505121	4.1838646459
O26	3.6846178946	-0.5996321925	6.1738915499
C27	5.2999277235	1.4485177392	6.1374517130
C28	6.3043788819	2.1456112201	5.4672821684
H29	6.4919656688	1.9118214881	4.4220326447
C30	7.0589794682	3.1044931413	6.1288433189
H31	7.8355071503	3.6453662053	5.5937344635
C32	6.8367717559	3.3556767139	7.4793249183
H33	7.4348907764	4.0936886000	8.0073432964
C34	5.8618655644	2.6456626297	8.1658944912
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N40	3.0771221966	-0.0232980222	1.7713124476
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C47	1.1737463913	-1.4045243333	1.2228777293
C48	-0.2527184445	-1.4709208707	1.1034571897
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C62	6.8841622389	1.4449135698	1.5707639027

N63	5.8784537520	1.5906250279	2.1256023876
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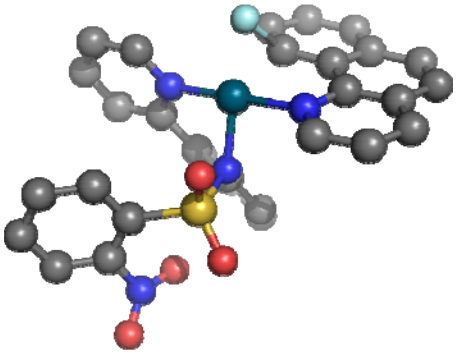
H65	8.7548418205	2.1640747362	0.9686743777
H66	8.6898432692	0.4179931067	1.3064993255
H67	7.9575940819	1.0701309997	-0.1822543039

$\mathbf{1}^{\ddagger}$



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C4	4.4038442373	4.5298696962	3.2691925159
H5	4.7142546854	4.3098683429	2.2501393022
C6	4.7601736436	5.6976490770	3.9147473120
H7	5.3808373729	6.4290047501	3.4074416202
C8	4.3037682463	5.8944810453	5.2153430432
H9	4.5819446610	6.7885734392	5.7673718266
C10	3.4931579021	4.9415213994	5.8067818475
H11	3.1510461543	5.0623836759	6.8303001226
C12	3.1267539444	3.7878306424	5.1039033631
C13	2.2002251676	2.8103102491	5.6936232589
C14	1.1870672371	3.2571645114	6.5482363442
H15	1.0745112760	4.3222292069	6.7404598740
C16	0.2910367283	2.3656459199	7.1202335782
H17	-0.4909929294	2.7360825571	7.7774486831
C18	0.3820843615	1.0063326078	6.8366419081
H19	-0.3176689431	0.3064999740	7.2854644410
C20	1.3660132736	0.5431908114	5.9768533478
H21	1.4790790795	-0.5144064189	5.7530142901
C22	2.2879315667	1.4288349271	5.4223585189
N23	3.2767963308	0.9050304024	4.5700139917
S24	4.7681711039	0.3942700742	5.0763615239
O25	5.5172590384	0.3490917212	3.8142825018
O26	4.6412993338	-0.7840361137	5.9074148448
C27	5.5889950052	1.6760511109	6.0520239668
C28	6.4427803404	2.5204079890	5.3451465267
H29	6.5442510843	2.3803737841	4.2717653367
C30	7.1901951959	3.4900159390	6.0040896507
H31	7.8455917002	4.1420991145	5.4322378214
C32	7.1269116670	3.5978585799	7.3872087221
H33	7.7242449564	4.3394750031	7.9104496864
C34	6.3160436245	2.7331465077	8.1109043487
H35	6.2713091425	2.7687232887	9.1957198089
C36	5.5416496926	1.7956656785	7.4448527661

N37	4.6663362194	0.9787368320	8.3038450002
O38	5.1466831768	0.5713470713	9.3417366270
O39	3.5148642991	0.8316214450	7.9347134768
N40	3.0242005083	0.0475876713	1.7804827103
C41	3.8247229842	-1.0063409476	1.6857171640
H42	4.8131731819	-0.9028601359	2.1269111829
C43	3.3845085901	-2.1960744111	1.0919722216
H44	4.0680104273	-3.0365966277	1.0278498086
C45	2.0831884893	-2.2945738875	0.6483908970
H46	1.7097414983	-3.2260669920	0.2273366505
C47	1.2191762453	-1.1892312161	0.7578101913
C48	-0.1679479990	-1.2028053047	0.4046411647
H49	-0.5870605552	-2.1189630209	-0.0057217243
C50	-0.9570595979	-0.1146654177	0.6129036259
H51	-2.0191569670	-0.1547080871	0.3818382698
C52	-0.4272648408	1.1111239024	1.1324128937
C53	-1.2043881721	2.2615874554	1.3764592502
H54	-2.2702071446	2.2334540066	1.1619846410
C55	-0.6290180413	3.4144355376	1.8687071698
H56	-1.2416293630	4.2945812011	2.0469405971
C57	0.7616362122	3.5107201836	2.0971438672
H58	1.2351230298	4.4462862898	2.3757824803
C59	1.4668042587	2.3653650892	1.8976617203
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2

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N3	3.8185885030	3.9334477872	3.1079095816
C4	4.5334283508	4.6433478637	2.2167706048
H5	4.6355090386	4.1824331962	1.2352576122
C6	5.0678545745	5.8769157676	2.5335250443
H7	5.6259547252	6.4296281767	1.7848586920
C8	4.8810823651	6.3664745950	3.8219705097
H9	5.3207632117	7.3143612405	4.1217828178
C10	4.1227339775	5.6393618606	4.7227156474
H11	3.9677873858	5.9983507198	5.7358070582
C12	3.5571920532	4.4150664757	4.3484356302
C13	2.6049997528	3.7246081143	5.2271524359
C14	1.7044998553	4.5090205157	5.9572869906
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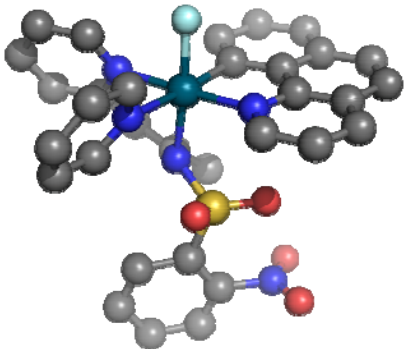

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C20	1.4092614429	1.7507393992	5.9657361862
H21	1.2395591283	0.6790359865	5.9393013032
C22	2.4822254749	2.3146399968	5.2639810638
N23	3.4783490667	1.5704857727	4.6077314336
S24	3.6899090483	-0.0610066930	4.9999802987
O25	4.9817683391	-0.4187511136	4.4315110997
O26	2.5216215667	-0.8777025920	4.6945301357
C27	3.8801617669	0.0111463109	6.7756388435
C28	4.8887205569	0.8225511951	7.2904732976
H29	5.5108857074	1.3925301852	6.6050215522
C30	5.0910534712	0.9026548858	8.6599488606
H31	5.8787458274	1.5382966047	9.0547884659
C32	4.2845559011	0.1696621539	9.5252606191
H33	4.4373678845	0.2322479556	10.5992156588
C34	3.2831714145	-0.6496690095	9.0228749053
H35	2.6465056059	-1.2338647699	9.6827204193
C36	3.0959994479	-0.7312302353	7.6514507481
N37	2.0314379641	-1.6557155898	7.2083582078
O38	2.3805695069	-2.7682627133	6.8822410445
O39	0.8899340006	-1.2347665314	7.2858011595
N40	3.2121678577	-0.0118812068	1.9438855111
C41	4.1252085470	-0.9501343465	1.7244607832
H42	5.1607235118	-0.6906832291	1.9195157889
C43	3.7493274841	-2.2292472864	1.3085179883
H44	4.5189510670	-2.9777984621	1.1512147191
C45	2.4132675188	-2.5230578775	1.1252452186
H46	2.1054553011	-3.5196486250	0.8160679835
C47	1.4407650683	-1.5334073631	1.3405655165
C48	0.0290011561	-1.7142690412	1.1793343839
H49	-0.3329803977	-2.6908992847	0.8655894657
C50	-0.8418102767	-0.6951968062	1.4123390122
H51	-1.9110576782	-0.8497086008	1.2819669614
C52	-0.3896682928	0.6001691347	1.8292403142
C53	-1.2348218948	1.7015249058	2.0659033076
H54	-2.3091280539	1.5862798953	1.9395446845
C55	-0.7056034978	2.9191858418	2.4410432493
H56	-1.3677897496	3.7660369797	2.6058871181
C57	0.6837954401	3.1100210653	2.6171088105
H58	1.0635254201	4.0854223720	2.9081336870
C59	1.4991176803	2.0304570840	2.4148526163

C60	0.9965603939	0.7892999369	2.0070441545
C61	1.8949586896	-0.2724307551	1.7551342725
C62	8.5590296516	1.7737876680	2.2859811838
C63	7.9470646086	1.9854791374	3.5163299133
C64	6.5625813710	2.0052971236	3.5735605479
N65	5.8034186577	1.8343419373	2.4860629787
C66	6.3882556957	1.6531720509	1.2933741340
C67	7.7680860490	1.6077092202	1.1551246392
H68	9.6430675242	1.7437281674	2.2090654548
H69	8.5319337476	2.1278504843	4.4201689264
H70	6.0218869041	2.1607141159	4.5059510607
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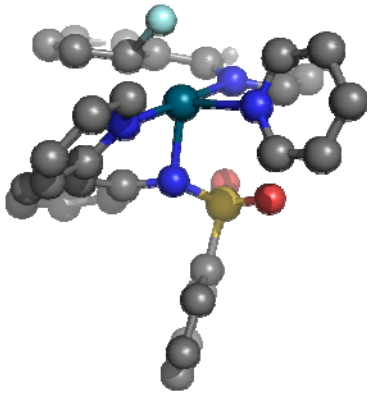

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H5	5.1552535939	4.1804480103	1.7193683527
C6	5.1425438129	5.8927833580	3.0412043525
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C8	4.6155307545	6.3790518613	4.2338644380
H9	4.9002768099	7.3613253120	4.6019483711
C10	3.7245611344	5.6014224595	4.9521488248
H11	3.3191255130	5.9514078518	5.8967763148
C12	3.3495061464	4.3378482643	4.4809475235
C13	2.3112114516	3.5513413918	5.1562806391
C14	1.2248431273	4.2273950687	5.7174170308
H15	1.1851852914	5.3132844061	5.6563516036
C16	0.1735660031	3.5369605502	6.3008762379
H17	-0.6651310245	4.0800160706	6.7277252390
C18	0.1914306190	2.1463465705	6.2998072994
H19	-0.6321466940	1.5852994430	6.7351294114
C20	1.2481911209	1.4497127521	5.7327741367
H21	1.2199794233	0.3650980264	5.7234834572
C22	2.3439124119	2.1338799179	5.1885077583
N23	3.5060183958	1.5178719829	4.6914999388
S24	3.8474323564	-0.0726394804	5.1060321095
O25	5.1868892181	-0.3152381429	4.5882899597
O26	2.7781717087	-1.0071607333	4.7719162001
C27	3.9388979843	0.0754338988	6.8844280591
C28	4.8266577235	1.0166468546	7.4024017385
H29	5.4320281046	1.6038492127	6.7156414487
C30	4.9183820256	1.2090777819	8.7727628022
H31	5.6121693071	1.9443642164	9.1709863967
C32	4.1152838367	0.4673715163	9.6339587873
H33	4.1766787274	0.6227881513	10.7077099296
C34	3.2306601113	-0.4754576102	9.1287040157

H35	2.5956653593	-1.0640542173	9.7861318329
C36	3.1595006274	-0.6741894801	7.7582244199
N37	2.2231847158	-1.7260027065	7.3114599790
O38	2.7053626088	-2.8004340328	7.0296181545
O39	1.0393033259	-1.4346352136	7.3363330304
N40	3.2216099934	0.0164136867	1.9758420450
C41	4.0712538313	-1.0005748713	1.8801327227
H42	5.1096387148	-0.7916875054	2.1215241658
C43	3.6252454804	-2.2858245728	1.5614297769
H44	4.3461812101	-3.0943756569	1.4997001844
C45	2.2743195884	-2.5149511124	1.4012072750
H46	1.9022802044	-3.5208468700	1.2165596078
C47	1.3644223985	-1.4486224051	1.4954973223
C48	-0.0598565185	-1.5813470994	1.4181217944
H49	-0.4767804929	-2.5716465051	1.2485698938
C50	-0.8761105996	-0.5086236896	1.6017835642
H51	-1.9569181982	-0.6335050608	1.5906552173
C52	-0.3506264610	0.8107860889	1.8026041444
C53	-1.1493498835	1.9525737684	2.0077815960
H54	-2.2316369767	1.8465777996	2.0232566932
C55	-0.5705931332	3.1952667474	2.1741841786
H56	-1.2010442353	4.0678438887	2.3280360135
C57	0.8234620585	3.3857696975	2.0869106513
H58	1.2672862124	4.3764303356	2.1035720190
C59	1.5802145554	2.2578897769	1.9376208753
C60	1.0538304501	0.9650937746	1.8026565650
C61	1.8972705554	-0.1714006209	1.7375945876
C62	8.7157158446	1.6531096173	1.5071697389
C63	8.3415272502	1.6614653366	2.8455087869
C64	6.9889394177	1.6941409615	3.1569782501
N65	6.0365805636	1.7241799053	2.2199695618
C66	6.4008984186	1.7201174205	0.9320024726
C67	7.7281938836	1.6822551554	0.5283710676
H68	9.7662686734	1.6221289061	1.2290898064
H69	9.0833686563	1.6354567099	3.6384358860
H70	6.6394135721	1.6744590369	4.1887981730
H71	5.5861213244	1.7501662892	0.2040817536
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3

Pd1	3.3695668195	1.9173722437	2.5536356138
F2	5.4346911601	1.6316120060	2.4155606738
F3	3.4453048155	2.7664130325	0.7439509436
N4	3.7956012707	3.7177655762	3.4403095017
C5	4.7441649072	4.4100431832	2.7912477108
H6	4.9704293214	4.0566870490	1.7874814701
C7	5.3654681363	5.4942009344	3.3849659655
H8	6.1190098956	6.0478886335	2.8343253442
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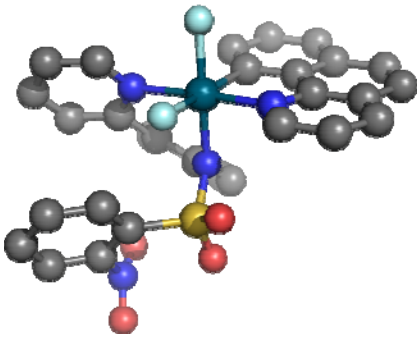

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H12	3.7719889033	5.3063238584	6.3782049195
C13	3.4091249700	4.0350957181	4.6953297900
C14	2.3149722785	3.2984331050	5.3406335882
C15	1.3638362565	4.0115483853	6.0773745044
H16	1.4489528227	5.0948545911	6.1495126970
C17	0.2953840017	3.3618205867	6.6748800497
H18	-0.4430939440	3.9336072584	7.2313206181
C19	0.1660936001	1.9806639447	6.5462268786
H20	-0.6699407966	1.4643274369	7.0113614435
C21	1.0957756328	1.2613867989	5.8123906325
H22	1.0177631579	0.1843357073	5.6955877495
C23	2.1781919907	1.9054024538	5.2092771004
N24	3.0845366405	1.1503861288	4.4343315429
S25	4.2066486694	0.2333749599	5.2344103618
O26	4.8454868531	-0.6319241117	4.2605306932
O27	3.5567442647	-0.3298864145	6.4108107492
C28	5.4714288924	1.3460173222	5.8757843033
C29	6.5180897272	1.6998118186	5.0270392117
H30	6.4797895077	1.3652583737	3.9891567934
C31	7.5493413212	2.5084981614	5.4902125994
H32	8.3491425396	2.7915012568	4.8103461566
C33	7.5695364771	2.9349922048	6.8129882999
H34	8.3855769594	3.5520284552	7.1815792253
C35	6.5460008527	2.5649419987	7.6752538161
H36	6.5435534111	2.8688739579	8.7191269295
C37	5.4969424841	1.7940713242	7.1954752916
N38	4.4275128950	1.5413558322	8.1792597153
O39	4.7211107374	0.8571009288	9.1396537811
O40	3.3717267963	2.1213092749	8.0007964929
N41	3.0736877867	0.0868343991	1.7215752950
C42	4.0374478390	-0.7638182499	1.4167914056
H43	5.0496582170	-0.4171949563	1.6222148443
C44	3.7041526983	-2.0157503341	0.8801618043
H45	4.5003171304	-2.7112007178	0.6348044826
C46	2.3790400666	-2.3496892424	0.6825962916
H47	2.1135574021	-3.3224958910	0.2725305172
C48	1.3592385501	-1.4356272944	1.0080392284
C49	-0.0496305813	-1.6419241997	0.8445641626
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C51	-0.9455345690	-0.6691985677	1.1731308771
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C53	-0.5304155230	0.6021930978	1.6949763449

C54	-1.4009852963	1.6606869468	2.0177265664
H55	-2.4736392393	1.5295106912	1.8907450670
C56	-0.8926817751	2.8605850927	2.4738481735
H57	-1.5741378235	3.6770244131	2.7042877415
C58	0.4922292933	3.0675360976	2.6567662036
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C60	1.3445623341	2.0299966823	2.3839916870
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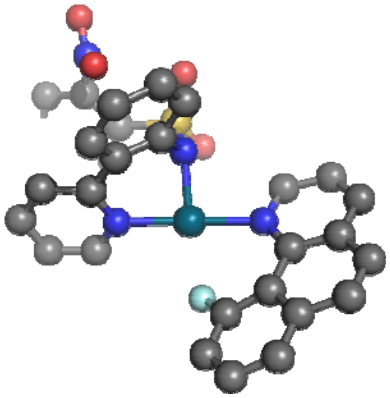

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H6	4.6960447363	4.0869790430	2.3371274135
C7	4.9761381993	5.4191190756	4.0163127341
H8	5.6131466778	6.1111881100	3.4751420991
C9	4.6577343475	5.6096391164	5.3587164541
H10	5.0604865235	6.4587230975	5.9047636753
C11	3.8346208467	4.7006532417	5.9997314936
H12	3.6073362361	4.7983955662	7.0575152882
C13	3.3195480370	3.6033564888	5.3010518560
C14	2.4367358614	2.6383433724	5.9653088106
C15	1.5323160448	3.0702938433	6.9364544242
H16	1.4230522234	4.1346421464	7.1353309169
C17	0.7534224982	2.1573800346	7.6335626321
H18	0.0504765969	2.5092047407	8.3835817270
C19	0.8712435312	0.7966133572	7.3689871542
H20	0.2738276234	0.0791195466	7.9250220179
C21	1.7474024098	0.3497536240	6.3904111975
H22	1.8682223003	-0.7075190976	6.1720290846
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N24	3.4210248752	0.7660107129	4.7052447260
S25	4.9559610386	0.2605400483	5.1032203379
O26	5.5411675961	-0.1594886511	3.8334142176
O27	4.8292309888	-0.6549274952	6.2212507386
C28	6.0218738323	1.6092924063	5.6610848543
C29	6.8233995809	2.2141508667	4.6955066161
H30	6.7120583940	1.9053085171	3.6584327881
C31	7.7909328627	3.1449921811	5.0592476120
H32	8.4061713520	3.6070581020	4.2913854395
C33	8.0023078511	3.4453756163	6.3996352939
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C35	7.2360433379	2.8211756805	7.3765153691
H36	7.3984624184	3.0101629419	8.4342256755
C37	6.2410115781	1.9312720959	7.0024102856
N38	5.4275455224	1.3944492903	8.1065020603
O39	6.0272998886	0.9081820734	9.0408561785
O40	4.2219387800	1.5555424936	8.0233408515
N41	2.4644950062	0.0057260728	1.9606871060
C42	3.1221094815	-1.1313875844	2.1811888270
H43	4.0856416142	-1.0399594968	2.6787006837
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H45	3.1873242663	-3.2732702461	2.0222196630
C46	1.3277123494	-2.4332554539	1.3296406947
H47	0.8483860276	-3.3861255252	1.1153768604
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H50	-1.1935391362	-2.2674206051	0.4702010396
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C54	-1.5420863409	2.2906814485	0.2589284575
H55	-2.5898923557	2.1844749005	-0.0122963939
C56	-0.9479010940	3.5305238261	0.2687555731
H57	-1.5172753283	4.4212799530	0.0214220453
C58	0.4179562693	3.6362852949	0.5622291680
H59	0.9464030298	4.5840708011	0.5223140962
C60	1.1088858065	2.5009145204	0.8854122294
C61	0.5543640157	1.2101395491	0.9653223055
C62	1.2444191483	-0.0056188694	1.3430475105
F62	2.4602441428	2.6709977047	1.0893926430

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Pd1	3.3557410465	1.6697278519	2.6878442071
F2	3.7277566162	2.3719944899	0.8704857672
N3	3.8170458653	3.5194311546	3.5056097298
C4	4.6725426579	4.2454445667	2.7624528323
H5	4.8154604137	3.8808733213	1.7445332712
C6	5.2919206453	5.3694572923	3.2733519191
H7	5.9794035595	5.9443573927	2.6598096393
C8	5.0192612879	5.7281521109	4.5906133562
C10	4.1182947386	4.9917253278	5.3357297184
H11	3.9187406186	5.2496008540	6.3715713874
C12	3.5033249185	3.8670948737	4.7750548596
C13	2.5147681261	3.0989298330	5.5483236012
C14	1.6434085221	3.7939789921	6.3961880396

H15	1.7096576205	4.8780061468	6.4640039622
C16	0.6611594377	3.1252565596	7.1105083697
H17	-0.0086207175	3.6839289464	7.7582332613
C18	0.5245494512	1.7454973983	6.9816189305
H19	-0.2450053647	1.2183590304	7.5386815927
C20	1.3711350634	1.0404051055	6.1398207587
H21	1.3051129568	-0.0391210604	6.0364586817
C22	2.3805166206	1.6990225014	5.4392821519
N23	3.1968736989	0.9263255633	4.5837907112
S24	4.7971136065	0.5328650830	4.8665688496
O25	5.3684297685	0.8342554762	3.5141786520
O26	4.9908615753	-0.8167919114	5.3398166430
C27	5.5849248046	1.7458581131	5.9670605079
C28	6.6446167080	2.4365481285	5.3840648619
H29	6.9197966920	2.2061479672	4.3587841334
C30	7.3382547169	3.4105751368	6.0973765983
H31	8.1630424076	3.9334302597	5.6205834071
C32	6.9730921510	3.7193506825	7.4005071797
H33	7.5053492518	4.4870934236	7.9550548993
C34	5.9255995409	3.0302250203	8.0010824373
H35	5.6174024368	3.2317853171	9.0225849035
C36	5.2475106650	2.0479523129	7.2959819548
N37	4.1677955228	1.3506587656	8.0129489883
O38	3.7778961201	1.8303811046	9.0595993803
O39	3.7382201230	0.3331269617	7.4960682527
N40	2.8992661224	-0.1879316888	1.9241267001
C41	3.7235526340	-1.2138069979	1.7618452185
H42	4.7604523397	-1.0629842366	2.0537702834
C43	3.2466390475	-2.4263569823	1.2483539015
H44	3.9387491574	-3.2533491715	1.1274821232
C45	1.9128604760	-2.5546945935	0.9144159865
H46	1.5321860511	-3.4948136966	0.5200288591
C47	1.0358267905	-1.4680244936	1.0858241545
C48	-0.3645576300	-1.4658779354	0.7815502937
H49	-0.8088050690	-2.3751806941	0.3828681624
C50	-1.1272048648	-0.3554278500	0.9814755326
H51	-2.1880140105	-0.3725161437	0.7413166810
C52	-0.5717965932	0.8597808869	1.5036803958
C53	-1.2970067192	2.0482860605	1.7204229709
C54	-0.6713344330	3.1735437057	2.2142444076
H55	-1.2433860305	4.0859890499	2.3645962733
C56	0.7083488263	3.1893605630	2.5307714388
H57	1.1759340462	4.0962948254	2.9020462577

C58	1.3944450032	2.0262510084	2.3352489732
C59	0.8018678020	0.8677739077	1.8181912284
C60	1.5872021293	-0.2874197397	1.6031908916
H60	-2.3587668240	2.0746337970	1.4852075992
C61	5.7799167889	6.8763055388	5.2055716764
F62	5.2770243499	7.2253372070	6.3860740319
F63	7.0557938683	6.5173902305	5.3882239788
F64	5.7654207078	7.9343109966	4.4025396811

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Pd1	3.3345184059	1.8556211046	2.7936258701
F2	3.1173316584	2.8753003979	1.0224615673
N3	3.5649162705	3.6211607338	3.8541496143
C4	4.3456048053	4.5533724674	3.2750087783
H5	4.6279548247	4.3602252676	2.2424721610
C6	4.7394212616	5.6905190446	3.9480920318
H7	5.3633554373	6.4341329319	3.4613485040
C8	4.3230291875	5.8428474740	5.2696462503
C9	3.4970689722	4.9007875751	5.8485002804
H10	3.1846763114	5.0029396494	6.8832665342
C11	3.0967761003	3.7763573618	5.1140178530
C12	2.1724994373	2.7971379974	5.6984965058
C13	1.1667737453	3.2375298254	6.5649942179
H14	1.0568622150	4.3007238644	6.7695030468
C15	0.2742878150	2.3391700867	7.1315737141
H16	-0.5051092258	2.7019606540	7.7958994001
C17	0.3678168999	0.9822168795	6.8361387967
H18	-0.3280541702	0.2778968275	7.2837090034
C19	1.3497689121	0.5257938738	5.9696020276
H20	1.4661058889	-0.5303743238	5.7411777930
C21	2.2646633542	1.4182406803	5.4144278825
N22	3.2551305647	0.9075901654	4.5556890875
S23	4.7539524612	0.4094636923	5.0663773773
O24	5.5038281718	0.3465513055	3.8064407503
O25	4.6245856870	-0.7543713578	5.9166344167
C26	5.5637524343	1.7149407338	6.0164830095
C27	6.3872060574	2.5753573125	5.2917667492
H28	6.4908144747	2.4202890290	4.2204529673
C29	7.0961947830	3.5855061112	5.9313345932
H30	7.7195162349	4.2583802499	5.3475543468
C31	7.0323723573	3.7145832894	7.3133226860
H32	7.5938295878	4.4956039675	7.8184081992
C33	6.2638732621	2.8269582820	8.0552866090

H34	6.2241047559	2.8777007076	9.1397310920
C35	5.5200946847	1.8525798606	7.4069074683
N36	4.6755330134	1.0190734766	8.2801971056
O37	5.1888271735	0.6003747682	9.2966074411
O38	3.5137688846	0.8736178873	7.9430113421
N39	3.0049082624	0.0558964404	1.7746688431
C40	3.8126059637	-0.9934115633	1.6876450981
H41	4.7995254235	-0.8814312903	2.1293856038
C42	3.3808426931	-2.1908673565	1.1025882192
H43	4.0699111259	-3.0272742469	1.0461359053
C44	2.0812876457	-2.3013928894	0.6577644985
H45	1.7138577040	-3.2380724026	0.2431507691
C46	1.2112631101	-1.1999115249	0.7560165298
C47	-0.1731191683	-1.2236009917	0.3924268389
H48	-0.5847064921	-2.1455531354	-0.0123608758
C49	-0.9689078953	-0.1369617746	0.5810632889
H50	-2.0283185784	-0.1835429329	0.3393407075
C51	-0.4492741800	1.0959259672	1.0929837826
C52	-1.2324244229	2.2470985423	1.3132823576
C53	-0.6679705563	3.4076861950	1.7991502343
H54	-1.2844517940	4.2892136090	1.9556065657
C55	0.7198814460	3.5108258246	2.0461539375
H56	1.1872759902	4.4520119219	2.3156185041
C57	1.4264099295	2.3625927306	1.8745859167
C58	0.9303600000	1.1477121131	1.4015198080
C59	1.7375934636	-0.0141399444	1.2928108292
C60	4.8547561142	7.0083220984	6.0643920798
F61	4.2097114911	7.1586767427	7.2157724588
F62	6.1484095481	6.8047999291	6.3324271412
F63	4.7544560174	8.1363442527	5.3678921097
H64	-2.2948751720	2.2137599447	1.0835821303

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Pd1	3.3840112251	1.6776521791	2.6911852812
F2	3.7579875697	2.3689004803	0.8705285493
N3	3.8436324908	3.5218868832	3.5023554227
C4	4.6998038585	4.2528088523	2.7629712530
H5	4.8443415217	3.8925297915	1.7442468882
C6	5.3155342146	5.3756764705	3.2748154444
H7	5.9973438689	5.9444289304	2.6476214821
C8	5.0670365684	5.7577757895	4.5973122749
C10	4.1641297059	4.9939930286	5.3288723076
H11	3.9620187613	5.2398831286	6.3691873233

C12	3.5420299578	3.8743213458	4.7744084811
C13	2.5451463665	3.1147515061	5.5495707411
C14	1.6732030367	3.8183993136	6.3896658193
H15	1.7485725376	4.9019167834	6.4526485676
C16	0.6813106977	3.1604011561	7.1005152274
H17	0.0122718426	3.7270021404	7.7421630079
C18	0.5320250855	1.7820702136	6.9742733119
H19	-0.2458896092	1.2632312821	7.5272853850
C20	1.3763290887	1.0682229583	6.1378200810
H21	1.2994648236	-0.0105122159	6.0335093880
C22	2.3969388452	1.7167636000	5.4433822902
N23	3.2073562899	0.9366459318	4.5871881392
S24	4.7964758190	0.5209996421	4.8761834000
O25	5.3903512522	0.8296405327	3.5357619708
O26	4.9714244184	-0.8354046170	5.3391515141
C27	5.5934287602	1.7017099279	6.0032737164
C28	6.6744205565	2.3767281689	5.4424759143
H29	6.9413959634	2.1717262306	4.4097863477
C30	7.4047745462	3.2953803449	6.1910676516
H31	8.2558917623	3.7956063279	5.7358780298
C32	7.0503867101	3.5682619133	7.5043964747
H33	7.6172304083	4.2847259430	8.0925844680
C34	5.9687380397	2.9095165344	8.0765190910
H35	5.6621883220	3.0929677330	9.1017925722
C36	5.2576131821	1.9775372731	7.3377182207
N37	4.1490832650	1.3019450976	8.0308742040
O38	3.7517220845	1.7881876781	9.0722438001
O39	3.7069321231	0.2957118513	7.5040158756
N40	2.9391431934	-0.1883296786	1.9331570046
C41	3.7699742240	-1.2081412206	1.7691336531
H42	4.8086372851	-1.0451666541	2.0477129636
C43	3.2979417953	-2.4296789344	1.2730164139
H44	3.9957999195	-3.2515275574	1.1505942892
C45	1.9609777606	-2.5728738136	0.9590910607
H46	1.5833267485	-3.5200642867	0.5791187575
C47	1.0764045572	-1.4927043388	1.1330605967
C48	-0.3282903688	-1.5068031869	0.8503866375
H49	-0.7696040221	-2.4238948565	0.4666679825
C50	-1.0985917087	-0.4022443406	1.0533231616
H51	-2.1628750615	-0.4316758545	0.8305193118
C52	-0.5471811391	0.8226010309	1.5570369663
C53	-1.2817889017	2.0043367473	1.7783476771
C54	-0.6606796209	3.1394273076	2.2552854697

H55	-1.2409619311	4.0458908369	2.4105180374
C56	0.7235494565	3.1726041458	2.5492240693
H57	1.1881199758	4.0848547227	2.9115640449
C58	1.4203819633	2.0164637624	2.3479183624
C59	0.8312187963	0.8477486855	1.8490630450
C60	1.6242672563	-0.3024956960	1.6316442286
H60	-2.3475975201	2.0171986546	1.5611720005
C61	5.7624837206	6.9342884634	5.1988814629
H62	5.5285288993	7.0491303626	6.2609764494
H63	6.8493609093	6.8384907360	5.0912735668
H64	5.4750080254	7.8590032561	4.6845977505

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Pd1	3.3935293992	1.8508632770	2.7919465690
F2	3.1607159562	2.8705693403	1.0206223480
N3	3.6283164969	3.6028962850	3.8548676208
C4	4.4103783268	4.5448593522	3.2930025448
H5	4.7385787551	4.3432722101	2.2756116458
C6	4.7423174104	5.7059642170	3.9561633528
H7	5.3625807574	6.4501810963	3.4630932048
C8	4.2792029154	5.9052477737	5.2627543264
C9	3.4646121714	4.9238626074	5.8140568072
H10	3.1043729675	5.0301261614	6.8345497746
C11	3.1190896450	3.7745870328	5.0977592837
C12	2.1922102209	2.7864936913	5.6714885531
C13	1.1623576654	3.2211477714	6.5118622533
H14	1.0364258398	4.2847902892	6.7033721114
C15	0.2686115618	2.3193655692	7.0713189206
H16	-0.5264164323	2.6809030696	7.7178601211
C17	0.3793643009	0.9612556102	6.7891999042
H18	-0.3181428574	0.2534347191	7.2288325860
C19	1.3798164558	0.5096574575	5.9420162197
H20	1.5076314709	-0.5464008762	5.7192228276
C21	2.2973084195	1.4068090400	5.3981423581
N22	3.2986388864	0.8986727731	4.5499672690
S23	4.7800613221	0.3806337270	5.0768853453
O24	5.5476486520	0.3011897602	3.8292414256
O25	4.6267953854	-0.7778004098	5.9313947488
C26	5.5939422347	1.6780893072	6.0357832069
C27	6.4317390516	2.5296707221	5.3184190092
H28	6.5373887894	2.3774247802	4.2470161917
C29	7.1559388390	3.5245771035	5.9652138636
H30	7.7993290415	4.1820702603	5.3855587336

C31	7.0881026077	3.6483114850	7.3474037246
H32	7.6702974918	4.4079769399	7.8621299429
C33	6.2958807630	2.7750870082	8.0814863499
H34	6.2502816559	2.8224768368	9.1658345895
C35	5.5406206164	1.8149199745	7.4257704363
N36	4.6767566837	0.9945462415	8.2934122455
O37	5.1754084242	0.5738452148	9.3172112015
O38	3.5170026892	0.8616111526	7.9460952536
N39	3.0275763098	0.0531915489	1.7785004804
C40	3.8150543969	-1.0111421455	1.6923558652
H41	4.8110990489	-0.9103271721	2.1164246598
C42	3.3531831688	-2.2083365176	1.1304088541
H43	4.0262054308	-3.0576199567	1.0729992897
C44	2.0443840034	-2.3013594073	0.7088891703
H45	1.6538003683	-3.2365227855	0.3123077102
C46	1.1943787849	-1.1846055848	0.8098605085
C47	-0.1974928954	-1.1904447175	0.4743120235
H48	-0.6310563538	-2.1095247753	0.0862784015
C49	-0.9732372081	-0.0905701588	0.6699071221
H50	-2.0380465457	-0.1232792507	0.4503332390
C51	-0.4256814722	1.1382687665	1.1628169478
C52	-1.1885396336	2.3007008270	1.3940228142
C53	-0.5980342586	3.4552155193	1.8639456847
H54	-1.1994388084	4.3453625911	2.0305679160
C55	0.7949786914	3.5393051267	2.0846441126
H56	1.2808050978	4.4730147670	2.3478712424
C57	1.4847064921	2.3820609302	1.9000063104
C58	0.9609512512	1.1726439695	1.4416866825
C59	1.7497758819	-0.0018959367	1.3236549314
C60	4.6724698508	7.1206552997	6.0352322396
H61	4.0773304647	7.2394343266	6.9445135253
H62	5.7280517981	7.0572817617	6.3281933044
H63	4.5648966733	8.0261097496	5.4282451464
H64	-2.2560948368	2.2805956701	1.1873802900

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Pd1	3.4335760063	1.6851874091	2.6396494571
F2	3.8323113367	2.3714609548	0.8215478285
N4	3.9020686812	3.5253477849	3.4556514445
C5	4.7660029097	4.2446101399	2.7173933600
H6	4.9328214547	3.8655099399	1.7088942118
C7	5.3534024070	5.3927891755	3.2164613935
H8	6.0347802361	5.9620104289	2.5926259944

C9	5.0491093921	5.7805934724	4.5167002115
H10	5.5083146647	6.6657758601	4.9495841901
C11	4.1575405152	5.0280732146	5.2644819552
H12	3.9293550348	5.2946267644	6.2926258947
C13	3.5644253803	3.8874679459	4.7169184426
C14	2.5542790927	3.1285270928	5.4752218913
C15	1.6599995678	3.8368348520	6.2880575150
H16	1.7321784676	4.9207351749	6.3474202219
C17	0.6490590246	3.1834436097	6.9763121054
H18	-0.0365730368	3.7540847198	7.5964142693
C19	0.5034872923	1.8039692350	6.8563426902
H20	-0.2881748319	1.2881959806	7.3924604003
C21	1.3682524820	1.0851225561	6.0451172276
H22	1.2917287302	0.0060664029	5.9433386253
C23	2.4055212294	1.7294907875	5.3714770245
N24	3.2238024767	0.9415111817	4.5291341097
S25	4.8123287114	0.5193841549	4.8271176717
O26	5.4184485388	0.8661941869	3.4981767652
O27	4.9780294074	-0.8515584104	5.2467043365
C28	5.5885569574	1.6648865451	5.9965529163
C29	6.7089286890	2.3222576092	5.4955514928
H30	7.0177396599	2.1309385940	4.4717293531
C31	7.4273964417	3.2056995674	6.2969702188
H32	8.3121383725	3.6909962723	5.8934210649
C33	7.0179026572	3.4642691491	7.5972627554
H34	7.5764676917	4.1531016902	8.2248132308
C35	5.8889408897	2.8316354089	8.1043614250
H36	5.5356471849	3.0115124921	9.1153264748
C37	5.1931537596	1.9298054798	7.3163226646
N38	4.0353883340	1.2706501804	7.9377367098
O39	3.5243525561	1.8125550068	8.8986082633
O40	3.6687251650	0.2231366946	7.4329685998
N41	2.9683397514	-0.1647941778	1.8837611318
C42	3.8033798814	-1.1767786209	1.6967252701
H43	4.8482278247	-1.0037807375	1.9450307893
C44	3.3290453910	-2.4040108659	1.2161327378
H45	4.0311979612	-3.2187134841	1.0722996004
C46	1.9848421231	-2.5588520456	0.9453885460
H47	1.6016621046	-3.5087635738	0.5782628725
C48	1.0985707753	-1.4835590875	1.1461580240
C49	-0.3102058258	-1.5033656914	0.9054624665
H50	-0.7590812919	-2.4224527629	0.5352940412
C51	-1.0935947124	-0.4108802477	1.1256033374

H52	-2.1585551703	-0.4651503091	0.9383245302
C53	-0.5429118860	0.8281650871	1.6046391953
C54	-1.2204603453	2.0556542820	1.8303003384
C56	-0.5649721031	3.2016587344	2.2288357539
H57	-1.1514354340	4.1078351272	2.3504180409
C58	0.8189122502	3.2151149164	2.4781458654
H59	1.3102846904	4.1294851933	2.7946859451
C60	1.4817745781	2.0346339393	2.2980625234
C61	0.8497465848	0.8646264190	1.8485116228
C62	1.6455211229	-0.2869288953	1.6224471115
N61	-2.6812945792	2.1861414181	1.6588324441
O62	-3.1241368109	3.3102991546	1.5151425122
O63	-3.3487847854	1.1659659109	1.6967485122

8a‡

Pd1	3.3634349233	1.8603153601	2.7305142532
F2	3.0199851481	2.8034539056	0.9497373388
N3	3.6594444586	3.6453405645	3.7388736893
C4	4.4180359990	4.5479768515	3.0927570948
H5	4.6622411799	4.3101816322	2.0595443484
C6	4.8255723253	5.7198875041	3.7019534139
H7	5.4199681663	6.4388225448	3.1477071031
C8	4.4503330745	5.9388988116	5.0244092285
H9	4.7667531602	6.8397887943	5.5438700436
C10	3.6724494982	4.9993502470	5.6803569548
H11	3.3949738188	5.1358967414	6.7217333623
C12	3.2550782318	3.8420647164	5.0156423820
C13	2.3444522510	2.8825908028	5.6618239091
C14	1.3450167966	3.3722806667	6.5108863811
H15	1.2714532114	4.4422922042	6.6933317963
C16	0.4041706399	2.5213471690	7.0723582131
H17	-0.3698072722	2.9256949351	7.7189496395
C18	0.4340916657	1.1604237939	6.7806414151
H19	-0.3074785837	0.4923404653	7.2099004215
C20	1.4102401233	0.6559712821	5.9360007920
H21	1.4768878369	-0.4048499108	5.7104209313
C22	2.3857950014	1.4965988892	5.3980162420
N23	3.3301168581	0.9230026814	4.5220800632
S24	4.9422343662	0.6036428882	4.8211254860
O25	5.5306859119	1.0755084496	3.5393472378
O26	5.1918816730	-0.7744597515	5.1786511058
C27	5.6035722238	1.7108630128	6.0910637358
C28	6.4892366672	2.6731479043	5.6146272275

H29	6.6988491431	2.7088704847	4.5493798140
C30	7.1126275014	3.5592889189	6.4889991670
H31	7.8017909497	4.3014608753	6.0942713727
C32	6.8657665614	3.4872728219	7.8520659058
H33	7.3512144557	4.1748377535	8.5389697559
C34	6.0048368004	2.5146338952	8.3463571252
H35	5.8050401630	2.4118138852	9.4086318457
C36	5.3835149438	1.6353681579	7.4750960858
N37	4.4833796397	0.6395087104	8.0808509504
O38	4.5219077005	0.5026620087	9.2868214470
O39	3.7501780951	0.0290126421	7.3211228642
N40	3.0132217931	0.0436450523	1.8062081258
C41	3.8496095568	-0.9816383787	1.7108816526
H42	4.8608792392	-0.8252097324	2.0816409898
C43	3.4205826342	-2.2057530967	1.1848782827
H44	4.1256827997	-3.0280675419	1.1204091144
C45	2.1052268955	-2.3540290697	0.7952186254
H46	1.7456241222	-3.3077912800	0.4141856128
C47	1.2125978275	-1.2719978666	0.9063002673
C48	-0.1797791093	-1.3110476354	0.5886108865
H49	-0.5949685694	-2.2363135466	0.1948734377
C50	-0.9937743722	-0.2394232891	0.7944715704
H51	-2.0514895537	-0.3165920787	0.5783176681
C52	-0.4888322589	1.0088622725	1.3007623301
C53	-1.2226842219	2.1965730713	1.5579489193
C55	-0.6140131745	3.3555174472	2.0004937856
H56	-1.2392787383	4.2299578415	2.1553131158
C57	0.7661083745	3.4315401726	2.2226828519
H58	1.2373688085	4.3634712145	2.5162706364
C59	1.4778828203	2.2836975737	2.0045176538
C60	0.9021216404	1.0824219541	1.5568154204
C61	1.7233765959	-0.0663534121	1.4048646704
N61	-2.6845765011	2.2726837764	1.3913668332
O62	-3.1789851154	3.3838850643	1.3293714767
O63	-3.3109724700	1.2259008267	1.3507924882

8g

Pd1	3.4349498772	1.7248672418	2.6354530747
F2	3.8337967576	2.4031751730	0.8159569464
N3	3.9401975672	3.5591855232	3.4443813550
C4	4.8075840291	4.2639242236	2.6962987104
H5	4.9514056286	3.8814744582	1.6853187519
C6	5.4272355126	5.3989496336	3.1886081934

H7	6.1116125629	5.9551516020	2.5566370745
C8	5.1485792557	5.7883415274	4.4941055312
H9	5.6311545092	6.6627035742	4.9236439632
C10	4.2534565857	5.0506785074	5.2529428776
H11	4.0468672776	5.3188802395	6.2852184586
C12	3.6293091804	3.9234243370	4.7115940228
C13	2.6163002812	3.1811996122	5.4838938131
C14	1.7542424020	3.9056652180	6.3172302742
H15	1.8530757608	4.9873498703	6.3796840130
C16	0.7415021660	3.2734747359	7.0220004346
H17	0.0823549478	3.8573250453	7.6585392681
C18	0.5592541568	1.8990862185	6.8957944805
H19	-0.2356780935	1.3993292345	7.4423146902
C20	1.3920841922	1.1649716675	6.0653609486
H21	1.2856080347	0.0893270533	5.9564022812
C22	2.4347915646	1.7861197693	5.3780907105
N23	3.2237479459	0.9812489071	4.5244048026
S24	4.7979677218	0.5110210936	4.8194626114
O25	5.4342103442	0.8746267744	3.5133321153
O26	4.9300870318	-0.8737574824	5.2073350251
C27	5.5687673600	1.6142049178	6.0349292168
C28	6.6828724029	2.3008814216	5.5604109178
H29	6.9967973091	2.1437300104	4.5322112896
C30	7.3855526899	3.1708260192	6.3901152407
H31	8.2642282537	3.6811819567	6.0045503353
C32	6.9662349247	3.3869599001	7.6949891161
H33	7.5099088644	4.0675268396	8.3443440124
C34	5.8462038268	2.7214705886	8.1784579283
H35	5.4858880882	2.8655705072	9.1925772078
C36	5.1662811890	1.8335800278	7.3609461770
N37	4.0161273909	1.1400035891	7.9599991223
O38	3.5262228567	1.6202305510	8.9636593424
O39	3.6319121274	0.1294840512	7.3977259518
N40	2.9433502364	-0.1335607047	1.8986019827
C41	3.7570498008	-1.1662200885	1.7343871120
H42	4.8054472930	-1.0110074092	1.9796748516
C43	3.2548074583	-2.3935688622	1.2826740452
H44	3.9387858178	-3.2271432685	1.1601721642
C45	1.9075760569	-2.5269388503	1.0144481634
H46	1.5073577172	-3.4787217783	0.6706669039
C47	1.0398736728	-1.4312320909	1.1880092678
C48	-0.3705030292	-1.4326942621	0.9467164520
H49	-0.8361156703	-2.3524344548	0.5998791409

C50	-1.1194319183	-0.3096060744	1.1412602455
H51	-2.1887025621	-0.3214415082	0.9503527669
C52	-0.5311010899	0.9130066973	1.5967083999
C53	-1.2542109733	2.1217912045	1.8007280766
C54	-0.5956720220	3.2635144205	2.2338244240
H55	-1.1428665931	4.1897865563	2.3806639879
C56	0.7947171098	3.2668975663	2.4911824714
H57	1.2776935766	4.1837582714	2.8169413319
C58	1.4743749398	2.0993320376	2.3125729605
C59	0.8491281291	0.9314997428	1.8554184700
C60	1.6174182512	-0.2368319294	1.6415603752
O61	-2.5678347502	2.0488873659	1.5390788665
C62	-3.3517173529	3.2183826424	1.6777302880
H63	-4.3687740756	2.9390893430	1.4004787645
H64	-3.3447800901	3.5802725398	2.7142884127
H65	-2.9982207521	4.0132934696	1.0083544689

8g‡

Pd1	3.4936061482	1.9254765238	2.8171812431
F2	2.6346106042	2.9131884612	0.9820339160
N3	3.8584628384	3.5680418841	4.0033746240
C4	4.7459587082	4.4759863831	3.5642607272
H5	5.1431741453	4.3151936477	2.5642924331
C6	5.1276243448	5.5585676076	4.3327131713
H7	5.8422673926	6.2767411628	3.9442373603
C8	4.5825871849	5.6802897075	5.6079190912
H9	4.8799720763	6.4996231837	6.2562370363
C10	3.6699645980	4.7405941797	6.0555041763
H11	3.2721623139	4.7810564545	7.0657863961
C12	3.2979338948	3.6768018520	5.2282692824
C13	2.3392754612	2.6612770568	5.6914876787
C14	1.2594834025	3.0335006137	6.4934374913
H15	1.1102463709	4.0825384619	6.7386076289
C16	0.3718270289	2.0815814911	6.9739198615
H17	-0.4614545510	2.3883934928	7.5990796013
C18	0.5485197000	0.7383257053	6.6533855788
H19	-0.1379193611	-0.0092850604	7.0410621311
C20	1.5949100115	0.3500949397	5.8319200668
H21	1.7657413920	-0.6911655949	5.5767245359
C22	2.4985978814	1.2993210729	5.3554854139
N23	3.5423303512	0.8784092842	4.5079123913
S24	4.9708528523	0.2598871789	5.0691595613
O25	5.8203639927	0.1724596897	3.8838494229

O26	4.6939392871	-0.9277896321	5.8454195316
C27	5.7756556521	1.5102267121	6.1327744839
C28	6.9570364315	2.0179796065	5.5943964631
H29	7.2939755408	1.6260352913	4.6392859984
C30	7.7051146717	2.9834293332	6.2612186185
H31	8.6332580000	3.3379193527	5.8204367696
C32	7.2721189635	3.4829792668	7.4813212488
H33	7.8534532449	4.2299569657	8.0153313355
C34	6.0825061880	3.0146826517	8.0199334930
H35	5.7026845457	3.3928737335	8.9640353338
C36	5.3469453012	2.0367892651	7.3623276854
N37	4.1112218576	1.6382841810	8.0650481104
O38	3.5369688856	2.5222205927	8.6869283283
O39	3.7579120211	0.4794677318	7.9986577682
N40	3.0016307196	0.2445199253	1.6906949842
C41	3.8016485185	-0.8170750490	1.6956723166
H42	4.8078672069	-0.6591982824	2.0794148739
C43	3.3524194110	-2.0818153178	1.3068570015
H44	4.0410584865	-2.9197255298	1.3088718302
C45	2.0178819030	-2.2412836344	1.0208617555
H46	1.6068831176	-3.2253252188	0.8069000978
C47	1.1499457259	-1.1332995082	1.0354182998
C48	-0.2603508123	-1.2772103975	0.8823538373
H49	-0.6639280457	-2.2701939233	0.6986165574
C50	-1.0807349091	-0.2073754857	1.0342067809
H51	-2.1593940980	-0.3218170437	1.0013380993
C52	-0.5497933732	1.1076963712	1.1944944826
C53	-1.4271300641	2.2275516435	1.3068595222
C54	-0.9199137422	3.5134767573	1.3497163580
H55	-1.5755893782	4.3733748095	1.4324152575
C56	0.4590827687	3.7194886532	1.2165525394
H57	0.8764012435	4.7206419361	1.1584906727
C58	1.2944194444	2.6420539976	1.1489439572
C59	0.8544623491	1.3061738758	1.2112902070
C60	1.7015815731	0.1413876982	1.2908979373
O61	-2.7310559587	1.9222221992	1.3710851575
C62	-3.6689387007	2.9771670197	1.4756370323
H63	-4.6503230035	2.5066966594	1.5179540223
H64	-3.5098524715	3.5636636940	2.3900945495
H65	-3.6207597469	3.6395702004	0.6035309984

10a

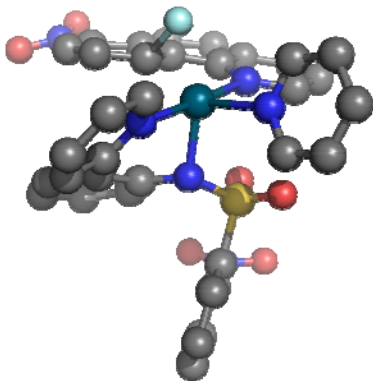
Pd1	3.5578346211	1.9252127171	2.5505600570

F2	3.6715283611	2.4371665189	0.6171448631
N3	3.8315919984	3.9170393061	3.0991433581
C4	4.5430389061	4.6385174491	2.2146829897
H5	4.6555159319	4.1794392773	1.2337219675
C6	5.0574363799	5.8784455624	2.5395303788
H7	5.6121909837	6.4424053540	1.7968051928
C8	4.8521334966	6.3618791592	3.8278303365
H9	5.2742000732	7.3159436946	4.1330924307
C10	4.0951350979	5.6226964957	4.7201505915
H11	3.9221831477	5.9791498987	5.7312335495
C12	3.5497561319	4.3920738366	4.3376287895
C13	2.5864215692	3.6921822429	5.1971152540
C14	1.6570190327	4.4695165522	5.8966030143
H15	1.7174265821	5.5542000896	5.8345742831
C16	0.6228320339	3.8849372614	6.6108828127
H17	-0.0939993635	4.5078035778	7.1383568809
C18	0.4896795292	2.5001017818	6.6038051035
H19	-0.3329859992	2.0222143307	7.1301185939
C20	1.3898509656	1.7074775180	5.9091925367
H21	1.2349488545	0.6334706320	5.8892010029
C22	2.4748123428	2.2815705237	5.2337279718
N23	3.4905889463	1.5480945712	4.5952788960
S24	3.7008284442	-0.0841182359	4.9929514070
O25	4.9962549000	-0.4410576716	4.4326533117
O26	2.5357348724	-0.9011817245	4.6760588671
C27	3.8746491243	-0.0032118780	6.7690784258
C28	4.8746290551	0.8163179539	7.2884408983
H29	5.4985722183	1.3890218641	6.6070541560
C30	5.0657306032	0.9036538190	8.6589719378
H31	5.8468431210	1.5453845229	9.0568732768
C32	4.2562081460	0.1703531655	9.5210125133
H33	4.4000677542	0.2384734437	10.5958294025
C34	3.2619924915	-0.6551748515	9.0143718793
H35	2.6219378021	-1.2379716553	9.6721542428
C36	3.0856176024	-0.7444789196	7.6420031486
N37	2.0258304028	-1.6731586427	7.1955844099
O38	2.3799522049	-2.7838314543	6.8685430223
O39	0.8829386672	-1.2557875901	7.2692063876
N40	3.2251913577	-0.0159089704	1.9372811464
C41	4.1425998145	-0.9490712510	1.7160375761
H42	5.1783867367	-0.6760079980	1.8898426343
C43	3.7736679908	-2.2381098341	1.3225536884
H44	4.5484746753	-2.9804357840	1.1617918371

C45	2.4383090759	-2.5455453400	1.1673827351
H46	2.1300677215	-3.5480716313	0.8778741101
C47	1.4638585042	-1.5577165222	1.3872896977
C48	0.0547849462	-1.7462930428	1.2589786248
H49	-0.3098474974	-2.7299493234	0.9710696609
C50	-0.8316373778	-0.7387139328	1.4853674142
H51	-1.8916462782	-0.9210961423	1.3749980411
C52	-0.3951050539	0.5777667197	1.8668881623
C53	-1.1918387759	1.7310127835	2.1059495120
C55	-0.6339420502	2.9525586466	2.4275747484
H56	-1.3055360548	3.7928800363	2.5741028669
C57	0.7509587226	3.1221938438	2.5681111940
H58	1.1522872685	4.0988152948	2.8196271977
C59	1.5373000331	2.0159864314	2.3919036281
C60	0.9997140122	0.7748634473	2.0202916861
C61	1.9062475204	-0.2873187580	1.7743657198
C62	8.5639821979	1.8051252130	2.2639329882
C63	7.9535047844	1.9611994044	3.5029815201
C64	6.5692243086	1.9622033349	3.5656288136
N65	5.8088981312	1.8252294812	2.4748963868
C66	6.3914199932	1.6970784513	1.2743410467
C67	7.7706925476	1.6728603655	1.1302424414
H68	9.6479110147	1.7925334678	2.1823792341
H69	8.5389566857	2.0758024718	4.4101894675
H70	6.0300937976	2.0753929036	4.5044296689
H71	5.7084612156	1.6405350592	0.4262139042
H72	8.2088904962	1.5597393581	0.1432403797
N72	-2.6681519675	1.7195121005	2.0171877795
O73	-3.2473720979	2.7667715778	2.2444369237
O74	-3.2221998382	0.6725401356	1.7279210375

10a‡

Pd1	3.6312876046	1.8931633385	2.6482978849
F2	2.9454970979	2.5405304505	0.7417178048
N3	3.9099602861	3.8419103343	3.3154367854
C4	4.7677240400	4.6012753726	2.6142055256
H5	5.1611801960	4.1597643203	1.7018238992
C6	5.1130096445	5.8766767763	3.0169997585
H7	5.7919401694	6.4700364688	2.4133865089
C8	4.5692138153	6.3605206639	4.2032417402
H9	4.8354733875	7.3489807420	4.5684855445
C10	3.6827872700	5.5735332958	4.9175773179
H11	3.2618102496	5.9226319725	5.8558090529



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C14	1.1812122331	4.1789675862	5.6471839211
H15	1.1303079142	5.2642179743	5.5817759830
C16	0.1206381666	3.4775752690	6.2019817409
H17	-0.7367874409	4.0122666221	6.6008967457
C18	0.1503668752	2.0865521699	6.2042103188
H19	-0.6803627851	1.5202137942	6.6180190418
C20	1.2286866670	1.3986246105	5.6680100200
H21	1.2159975279	0.3136100406	5.6657987527
C22	2.3301297835	2.0946596191	5.1500701689
N23	3.5078662815	1.4952367153	4.6740470487
S24	3.8715074181	-0.0935268740	5.1024793235
O25	5.2113462118	-0.3171946888	4.5791500166
O26	2.8134298168	-1.0428330259	4.7773927510
C27	3.9671011359	0.0797045021	6.8769991354
C28	4.8543560916	1.0295601034	7.3807339348
H29	5.4521666443	1.6145953601	6.6858009473
C30	4.9580029454	1.2305447536	8.7489379252
H31	5.6517454152	1.9717510453	9.1360585351
C32	4.1689449253	0.4874990940	9.6221715128
H33	4.2423088753	0.6473087688	10.6945280926
C34	3.2839616978	-0.4625677586	9.1308389046
H35	2.6605597853	-1.0525167234	9.7980669947
C36	3.1983445361	-0.6676921165	7.7622476506
N37	2.2623718105	-1.7253916423	7.3297163599
O38	2.7461016509	-2.8058117020	7.0738067624
O39	1.0797772918	-1.4307388155	7.3396068538
N40	3.2101149144	-0.0210124930	1.9712741155
C41	4.0517210889	-1.0450830147	1.8798175441
H42	5.0910236862	-0.8441332678	2.1250612080
C43	3.5976641419	-2.3276600379	1.5607481733
H44	4.3130279221	-3.1415457449	1.5045387222
C45	2.2464190893	-2.5445871287	1.3903122427
H46	1.8656320697	-3.5463397155	1.2017560756
C47	1.3464898622	-1.4685603666	1.4803541451
C48	-0.0743344996	-1.5799573137	1.3976819104
H49	-0.5055428896	-2.5631270163	1.2220403383
C50	-0.8904642711	-0.5062516121	1.5801067645
H51	-1.9648402153	-0.6327163678	1.5530497961
C52	-0.3622656866	0.8132091174	1.7943527334
C53	-1.0962271514	2.0038220159	2.0441304223
C55	-0.4741405911	3.2277592837	2.2197202698

H56	-1.1024055620	4.0930826368	2.4088853796
C57	0.9098145620	3.3761261690	2.1083726686
H58	1.3798587839	4.3538971456	2.1308903372
C59	1.6349654711	2.2231783099	1.9355936445
C60	1.0479464460	0.9492789626	1.8006726262
C61	1.8831157699	-0.1961547656	1.7302945282
C62	8.7019200535	1.7351514243	1.5934221694
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N65	6.0105081203	1.6979719839	2.2558152732
C66	6.3985768103	1.6531917388	0.9750604806
C67	7.7337084726	1.6658797286	0.5974987217
H68	9.7578283436	1.7471520595	1.3352525404
H69	9.0281407311	1.8396897187	3.7292500397
H70	6.5760037562	1.7773488417	4.2353219341
H71	5.5986867583	1.6095248621	0.2319405691
H72	8.0050993002	1.6227573961	-0.4531359903
N72	-2.5618179357	2.0225849182	2.1372202203
O73	-3.0681563518	2.9728165222	2.7107967441
O74	-3.1860460407	1.1023192637	1.6339333950

10g

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C4	4.5696467423	4.6427309212	2.2481641454
H5	4.6835272806	4.1847109712	1.2667208906
C6	5.0900462173	5.8780336017	2.5799711995
H7	5.6528199560	6.4408263407	1.8425908062
C8	4.8806753686	6.3575626362	3.8689195754
H9	5.3064766749	7.3080171980	4.1799473701
C10	4.1161388086	5.6190634005	4.7550905563
H11	3.9419376818	5.9721187252	5.7670371322
C12	3.5652386273	4.3930093050	4.3655711028
C13	2.5996968573	3.6926877062	5.2223613270
C14	1.6806483256	4.4699579589	5.9356280507
H15	1.7479480557	5.5545700458	5.8814123333
C16	0.6502533032	3.8868365687	6.6552893619
H17	-0.0566455154	4.5099163685	7.1956383521
C18	0.5094016344	2.5031952077	6.6395999989
H19	-0.3101436132	2.0257511192	7.1711427426
C20	1.3977537457	1.7102396973	5.9306519909
H21	1.2373809737	0.6370896477	5.9019184428

C22	2.4792571877	2.2829020555	5.2489012842
N23	3.4846995672	1.5469870854	4.5976807974
S24	3.6982769760	-0.0802573541	4.9938157495
O25	4.9889647418	-0.4436085200	4.4264901533
O26	2.5314015823	-0.9023536482	4.6967205761
C27	3.8882299162	0.0076042049	6.7701781619
C28	4.8794857440	0.8435487334	7.2797478807
H29	5.4858787656	1.4267053880	6.5913446001
C30	5.0814597088	0.9370289102	8.6482617210
H31	5.8553454446	1.5925950784	9.0376524660
C32	4.2914809437	0.1932148593	9.5192393418
H33	4.4435854698	0.2662740704	10.5925418676
C34	3.3057229667	-0.6479387665	9.0230219514
H35	2.6796923276	-1.2383565553	9.6873403581
C36	3.1188076462	-0.7425655819	7.6522096444
N37	2.0666763292	-1.6854958070	7.2181577254
O38	2.4316367777	-2.7930482534	6.8907564515
O39	0.9193702918	-1.2834045676	7.3031885491
N40	3.1878187997	0.0041779828	1.9408287456
C41	4.0812732313	-0.9504516365	1.7157908561
H42	5.1242808627	-0.7041837129	1.8867707560
C43	3.6753743112	-2.2287182006	1.3234887756
H44	4.4290702768	-2.9922088889	1.1610425149
C45	2.3319697790	-2.5018859417	1.1704620030
H46	2.0020216923	-3.4971735337	0.8808536734
C47	1.3784720480	-1.4930816728	1.3902987420
C48	-0.0365249063	-1.6489772487	1.2533318082
H49	-0.4230681043	-2.6229050600	0.9619409467
C50	-0.8844193000	-0.6066676430	1.4779969793
H51	-1.9570353965	-0.7340632917	1.3646220218
C52	-0.3952219623	0.6808766287	1.8645518641
C53	-1.2263047094	1.8144082557	2.0792847655
C55	-0.6618983484	3.0333702616	2.4229621470
H56	-1.2901122677	3.9066842481	2.5710782045
C57	0.7334108401	3.1815896878	2.5849841634
H58	1.1320550772	4.1571250638	2.8499067254
C59	1.5293841942	2.0845238670	2.4124550821
C60	0.9898050956	0.8497185311	2.0310652282
C61	1.8620009022	-0.2356057425	1.7810196639
C62	8.5778054496	1.7427615297	2.2510816530
C63	7.9749542922	1.9161210646	3.4916425026
C64	6.5909320911	1.9370221987	3.5590655650
N65	5.8227416673	1.8051107456	2.4738040974

C66	6.3989290534	1.6613660270	1.2727724595
C67	7.7773934104	1.6148757338	1.1220624389
H68	9.6611408922	1.7133649481	2.1649236363
H69	8.5660126498	2.0283978151	4.3956129228
H70	6.0585553494	2.0636248222	4.5002499343
H71	5.7118528969	1.6105158128	0.4276406576
H72	8.2096634894	1.4883963448	0.1339933491
O72	-2.5420729482	1.5993424064	1.9111769811
C73	-3.4278576905	2.6889403068	2.0676045919
H74	-4.4288688729	2.3005097924	1.8761895178
H75	-3.3855799592	3.0936121463	3.0875693253
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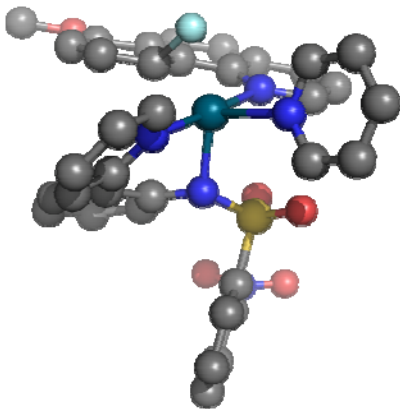
10g‡



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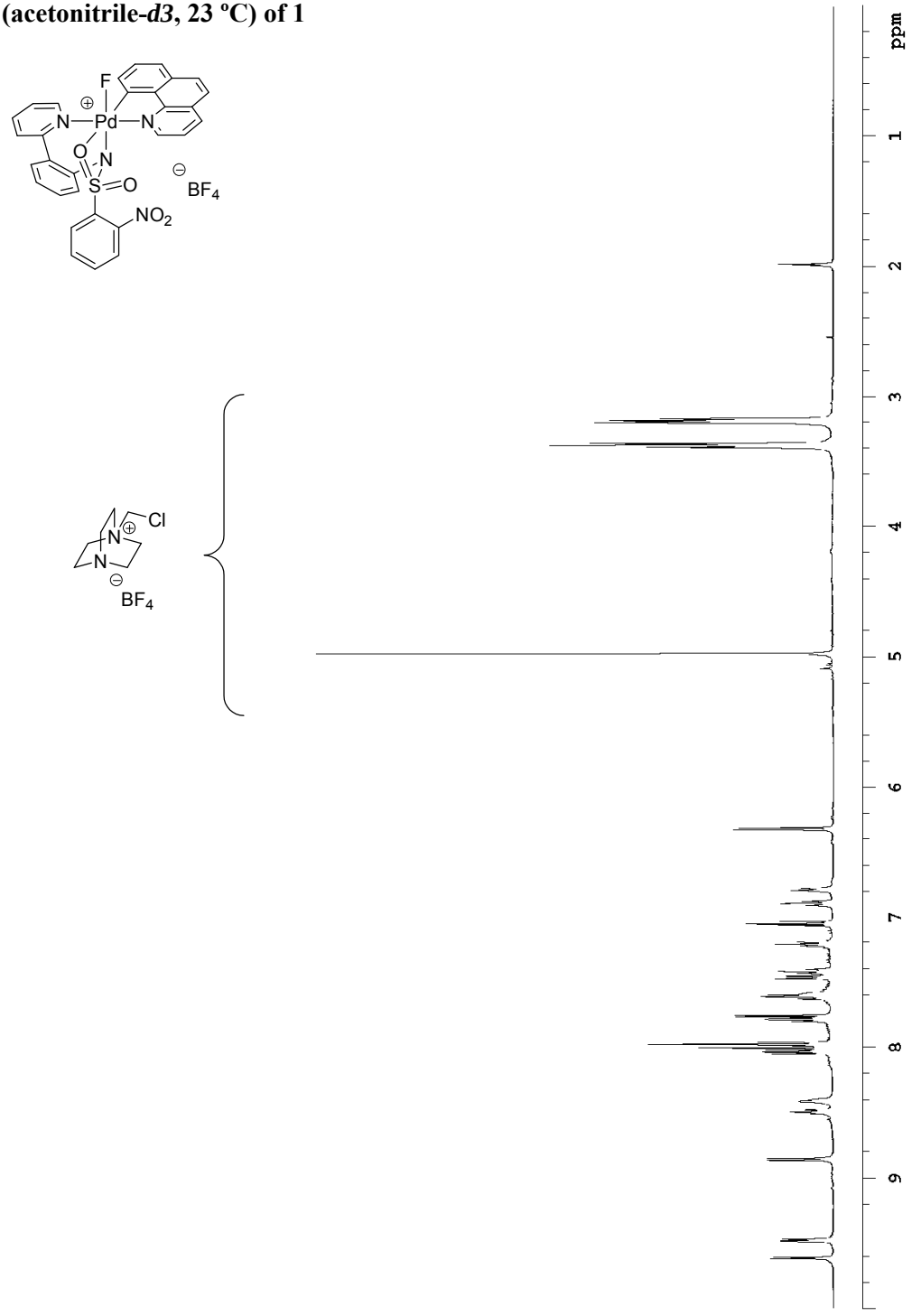
F2	3.0543867289	2.6233436072	0.8086110093
N3	3.9297284702	3.8394820727	3.4106314403
C4	4.8141548194	4.6007297773	2.7469795778
H5	5.2377011464	4.1635223823	1.8463861587
C6	5.1502573703	5.8708368869	3.1744997224
H7	5.8545430690	6.4662177445	2.6026680951
C8	4.5655751564	6.3456814443	4.3445175121
H9	4.8220724698	7.3299314493	4.7280251926
C10	3.6545936090	5.5538897858	5.0218029457
H11	3.2055965156	5.8944176961	5.9500588372
C12	3.3156554903	4.2883151458	4.5302818754
C13	2.2654334105	3.4819264603	5.1647379439
C14	1.1448294208	4.1343221559	5.6835478397
H15	1.0841790440	5.2187444940	5.6188664061
C16	0.0878454953	3.4216306522	6.2295516093
H17	-0.7786208890	3.9468238618	6.6222115862
C18	0.1397241117	2.0318633937	6.2407689824
H19	-0.6845770628	1.4541002412	6.6522336483
C20	1.2337313378	1.3573066970	5.7188666658
H21	1.2384312930	0.2721117235	5.7215920045
C22	2.3262748688	2.0658710445	5.2016704375
N23	3.5083202135	1.4768064764	4.7207660677
S24	3.9007507757	-0.0909112402	5.1565150763
O25	5.2380138370	-0.3087447185	4.6213958916
O26	2.8563548144	-1.0652225444	4.8583262335
C27	4.0214089712	0.0942924786	6.9313161330
C28	4.8984197243	1.0632517407	7.4166112551
H29	5.4689332589	1.6589706486	6.7073581376

C30	5.0271274360	1.2681185241	8.7824997410
H31	5.7142464839	2.0239616142	9.1530827239
C32	4.2728338464	0.5108970220	9.6748884185
H33	4.3655513693	0.6736695811	10.7451677851
C34	3.3978791167	-0.4578211218	9.2014947632
H35	2.8004886068	-1.0605090971	9.8811809007
C36	3.2881663887	-0.6662028560	7.8342761671
N37	2.3661926669	-1.7441268284	7.4212524822
O38	2.8658550745	-2.8178075362	7.1670875434
O39	1.1782706820	-1.4717433070	7.4430817697
N40	3.1709176635	0.0155274604	2.0082381572
C41	3.9834352994	-1.0318398180	1.9372936859
H42	5.0241140013	-0.8583729342	2.1981545758
C43	3.4970820558	-2.3042688171	1.6196302816
H44	4.1897976358	-3.1385471137	1.5774294012
C45	2.1432591790	-2.4848863666	1.4366384507
H46	1.7371884385	-3.4773793228	1.2507378032
C47	1.2702844049	-1.3834013706	1.5040104576
C48	-0.1518224381	-1.4646373284	1.3858466454
H49	-0.6010632404	-2.4412939187	1.2189608234
C50	-0.9339596359	-0.3571108416	1.5179387566
H51	-2.0161846697	-0.4351525279	1.4708848155
C52	-0.3609681087	0.9383355565	1.7085629537
C53	-1.1374161998	2.1240178725	1.8480335048
C55	-0.5170563318	3.3540451883	2.0177446329
H56	-1.1073297581	4.2593070368	2.1222505352
C57	0.8868300546	3.4732646804	1.9894721778
H58	1.3661025901	4.4477145110	1.9959168336
C59	1.6107553464	2.3200917023	1.9228990666
C60	1.0418619396	1.0471856322	1.7706331558
C61	1.8435444945	-0.1236369524	1.7461597099
C62	8.6637271080	1.6254951536	1.3541748572
C63	8.3515651781	1.6105061191	2.7084360104
C64	7.0146087656	1.6317425804	3.0823792121
N65	6.0192828743	1.6726785963	2.1911809790
C66	6.3239860146	1.6918859769	0.8879706350
C67	7.6316719449	1.6659776577	0.4229514628
H68	9.7004464692	1.6042435842	1.0272699459
H69	9.1293405618	1.5756248653	3.4659068519
H70	6.7129911884	1.5928230648	4.1288810884
H71	5.4758026979	1.7352706233	0.1998779511
H72	7.8333280484	1.6774627838	-0.6443613433
O72	-2.4677458273	1.9398652597	1.7957187492

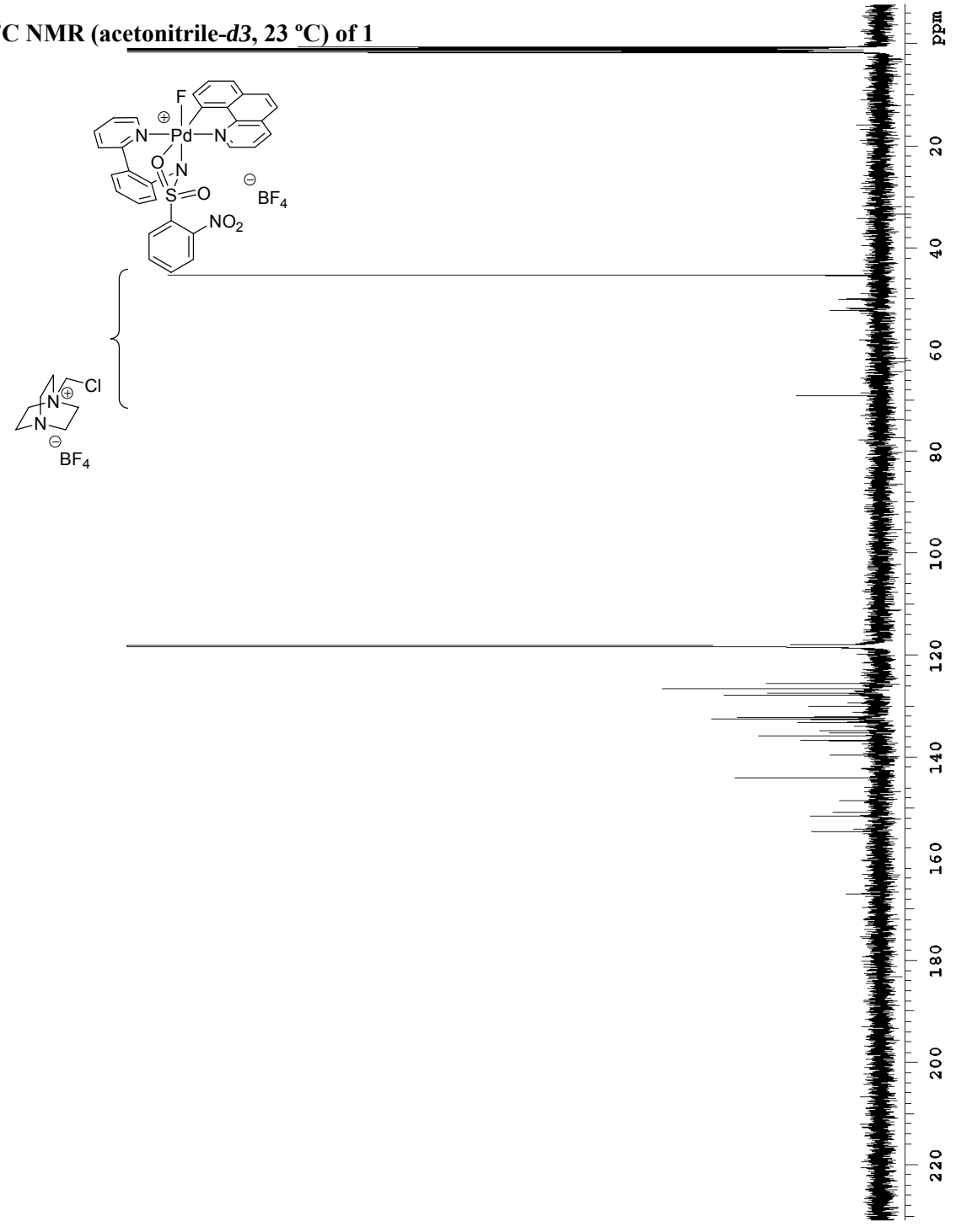
C73	-3.3077358613	3.0746434169	1.8497073402
H74	-4.3298566523	2.7041904202	1.7610624253
H75	-3.1978897404	3.6070521533	2.8041929709
H76	-3.0982332268	3.7634894705	1.0206293105

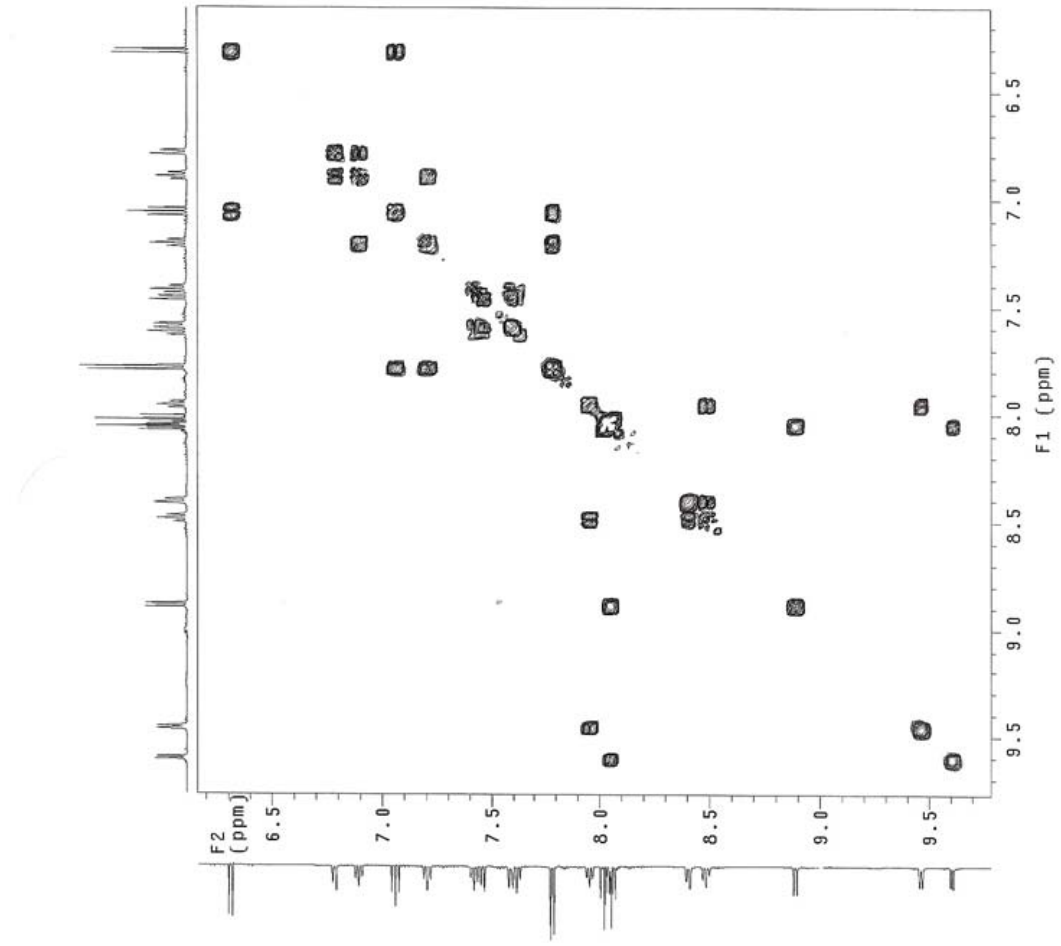
Spectroscopic Data

^{1}H NMR (acetonitrile-*d3*, 23 ºC) of 1



^{13}C NMR (acetonitrile-*d3*, 23 ºC) of 1





STANDARD PROTON PARAMETERS

Data Collected on:
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Archive directory:
/export/home/ds2/vnmrsys/data
Sample directory:

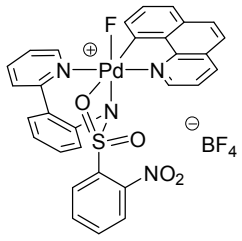
File: Pd4FMeCN_COSY

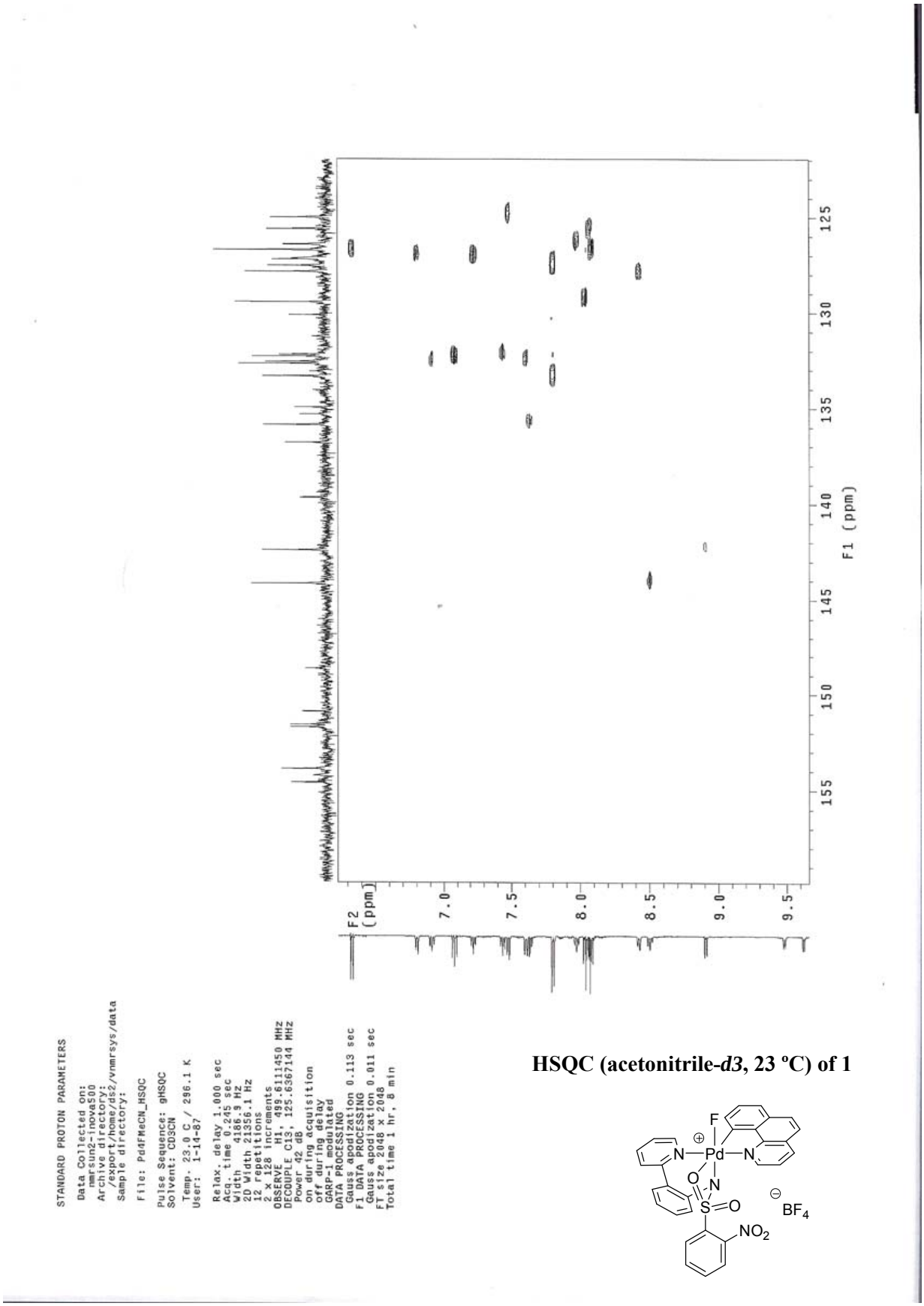
Pulse Sequence: gCOSY
Solvent: CD3CN

Temp. 23.0 C / 296.1 K

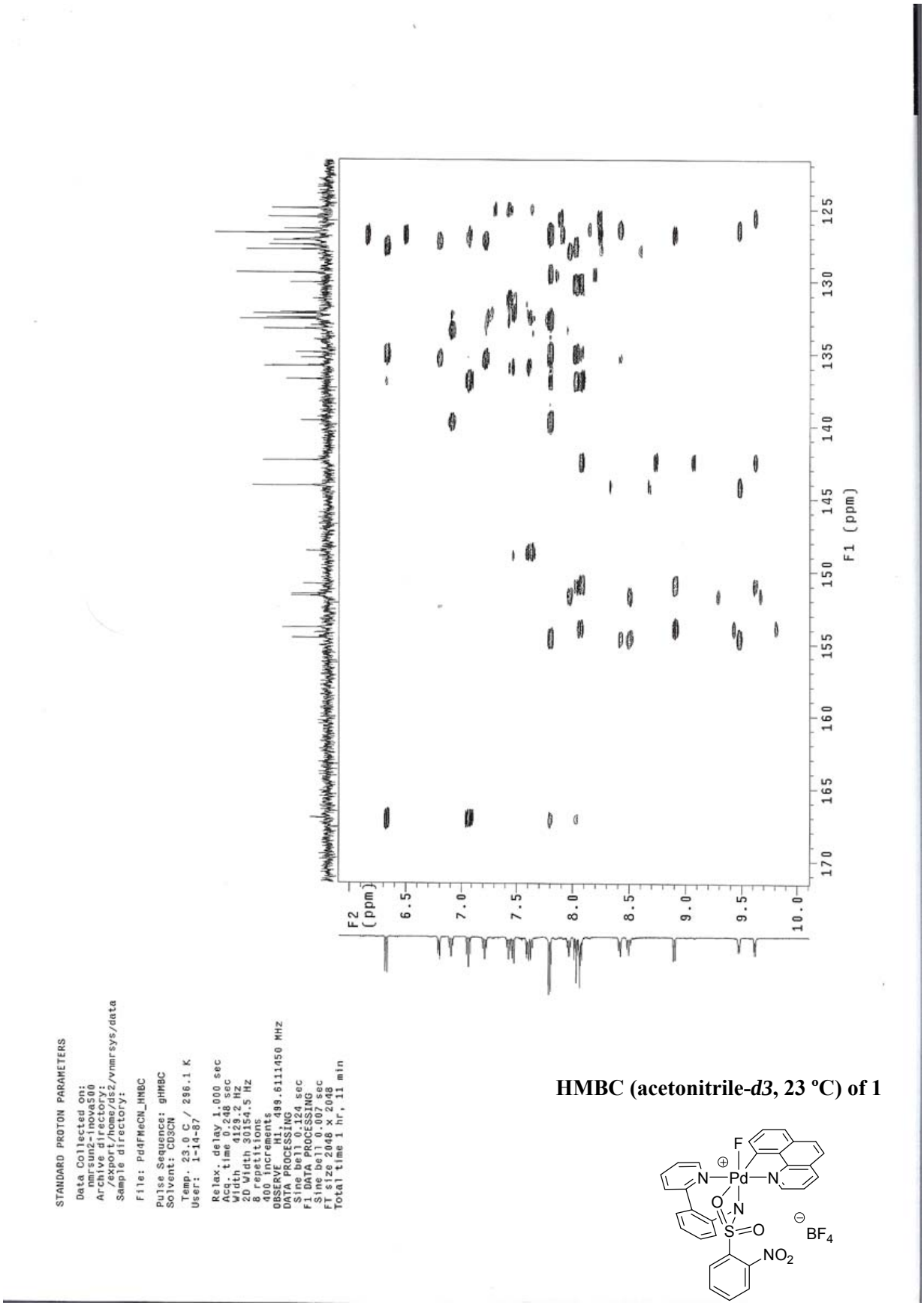
Relax. delay 1.000 sec
Acq. time 0.145 sec
Width 3523.9 HZ
2D Width 3523.9 HZ
Single scan
128 increments
OBSERVE H1, 500.1765938 MHz
DATA PROCESSING
Sq. sine bell 0.073 sec
F1 DATA PROCESSING
Sq. sine bell 0.036 sec
FT size 1024 x 1024
Total time 2 min

^{1}H-^{1}H COSY (acetonitrile-*d3*, 23 ºC) of 1

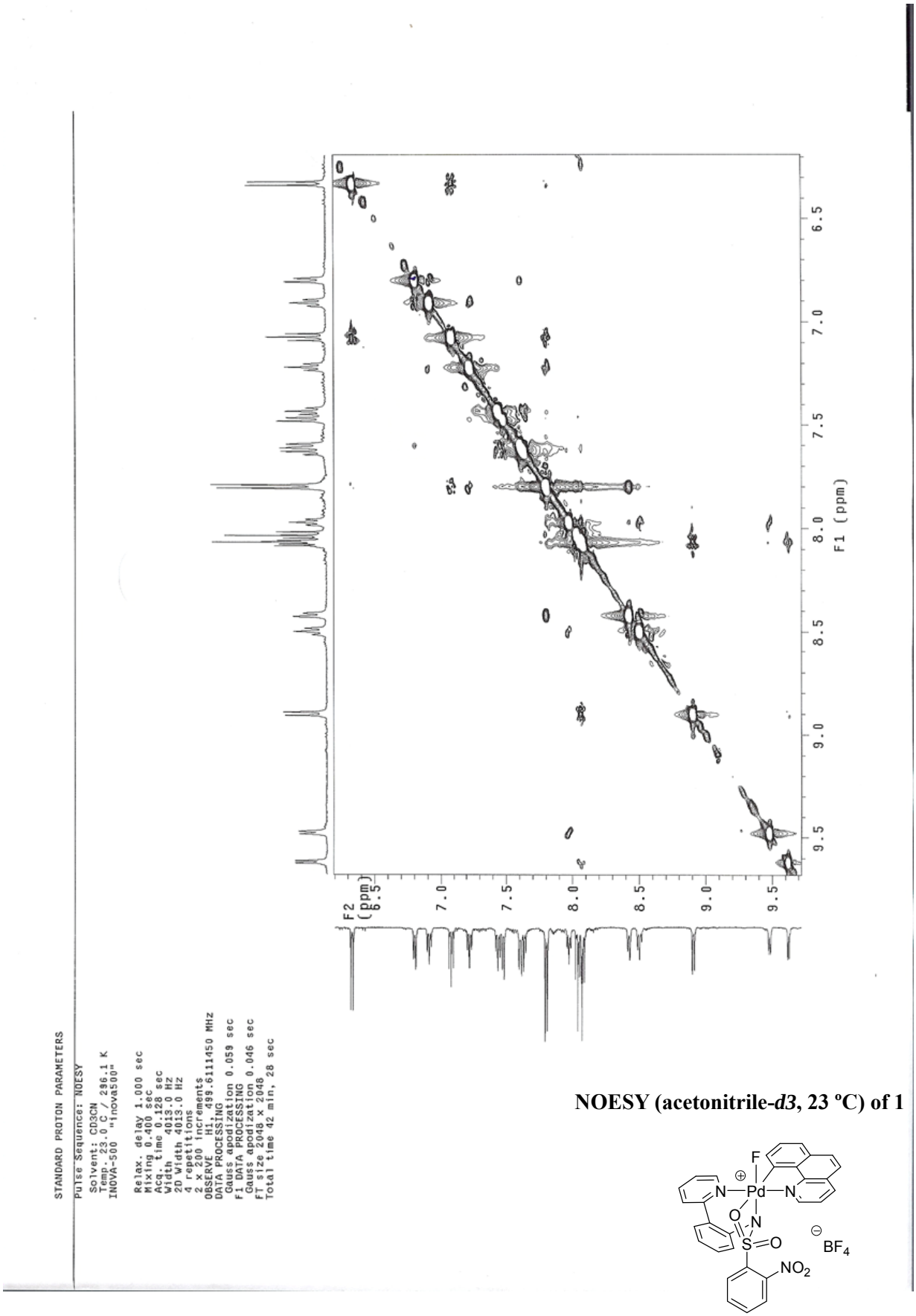




HSQC (acetonitrile-*d3*, 23 ºC) of 1

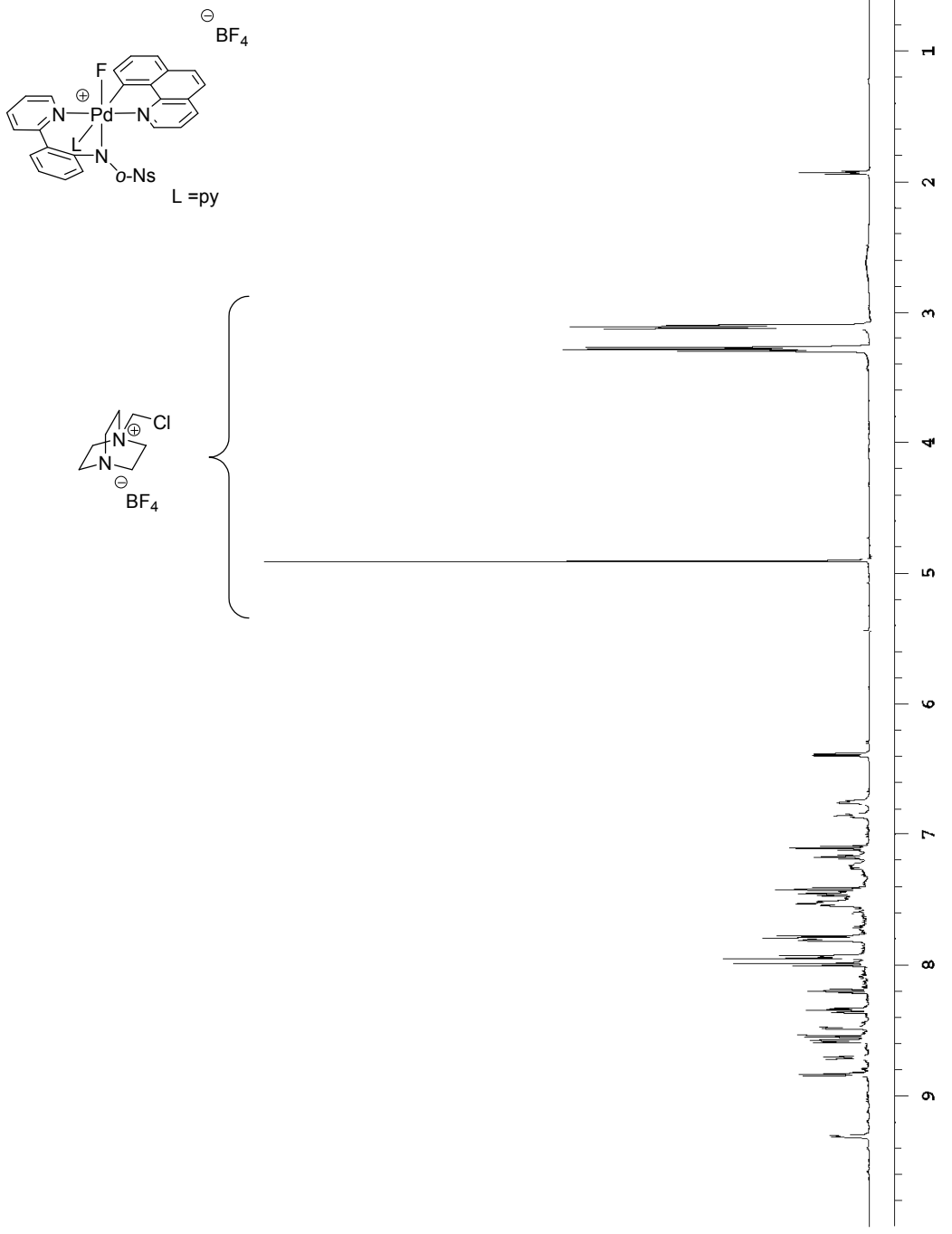


HMBC (acetonitrile-*d3*, 23 ºC) of 1

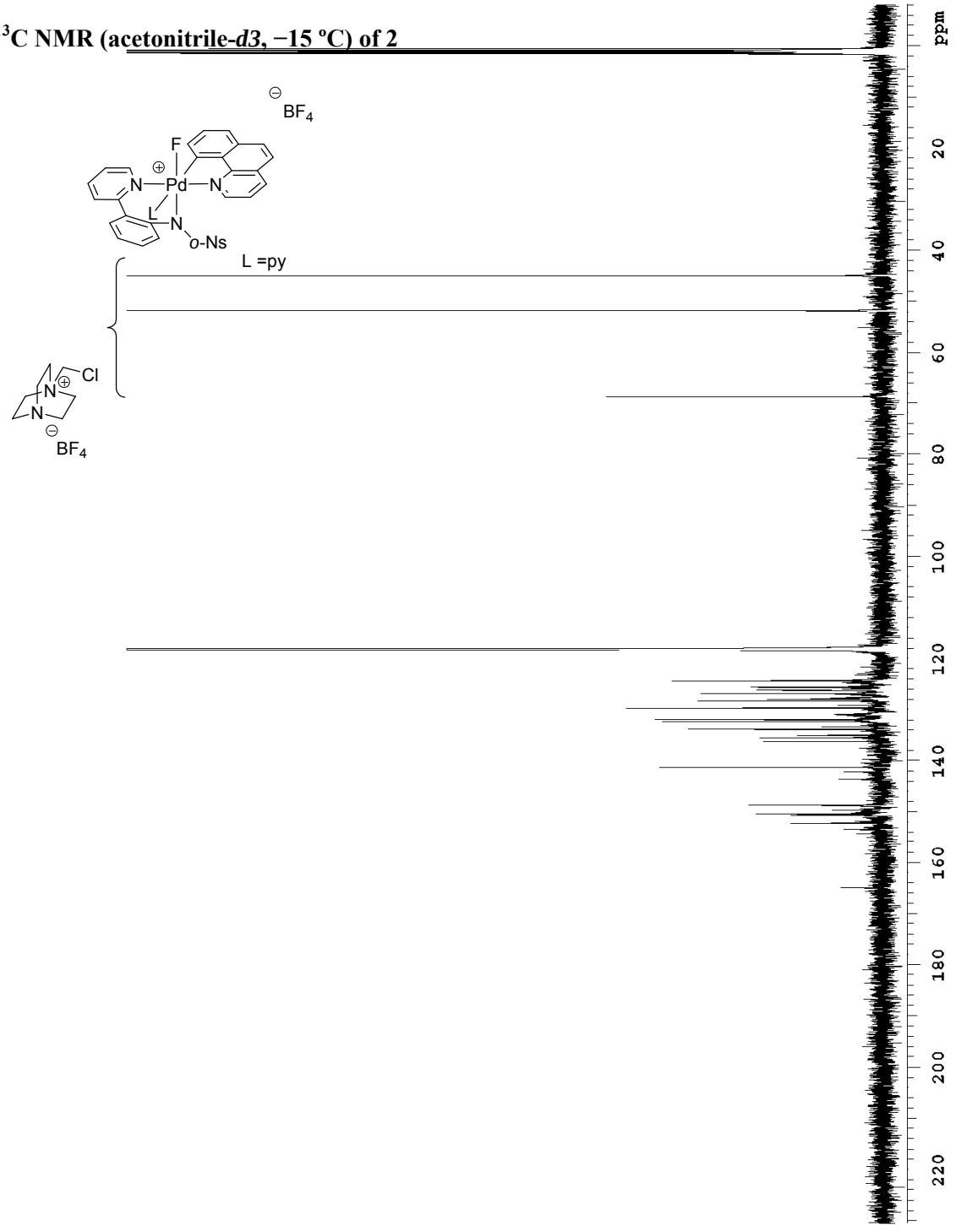


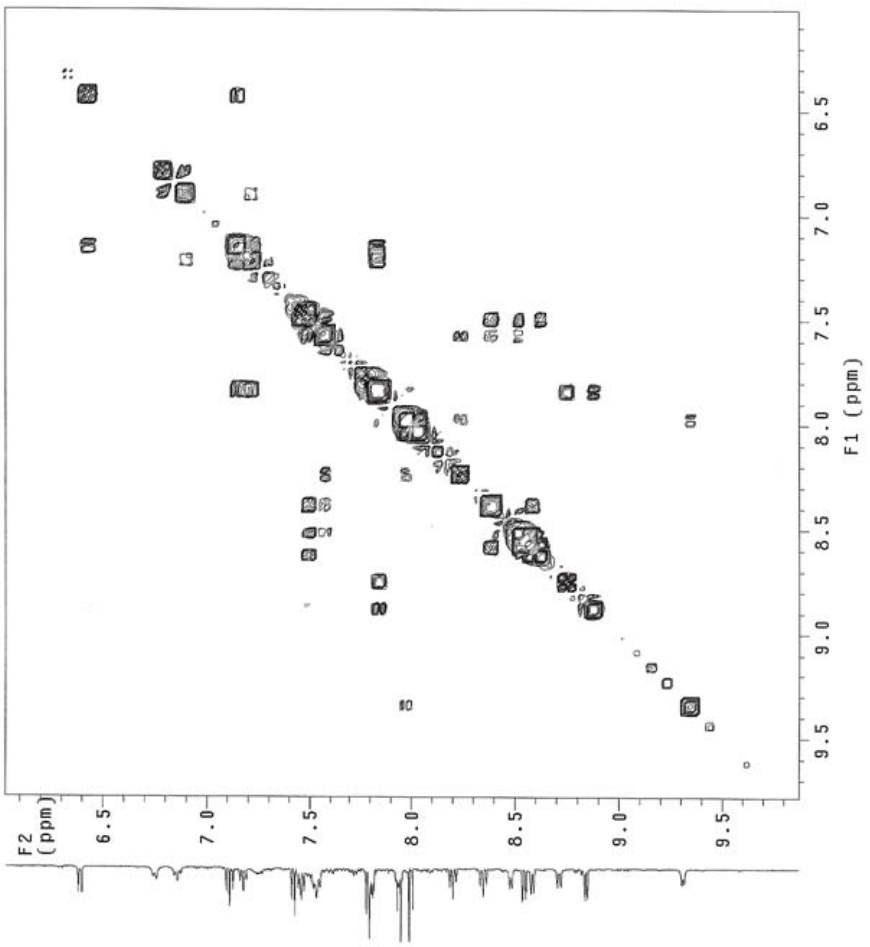
NOESY (acetonitrile-*d3*, 23 ºC) of 1

^{1}H NMR (acetonitrile-*d3*, −15 ºC) of 2



^{13}C NMR (acetonitrile-*d3*, −15 ºC) of 2





Pd4FPy_H

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Export directory:
Sample directory: /home/dsz/vnmrsys/data

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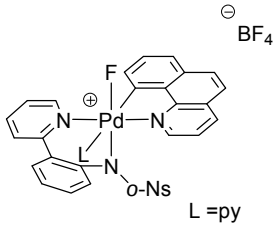
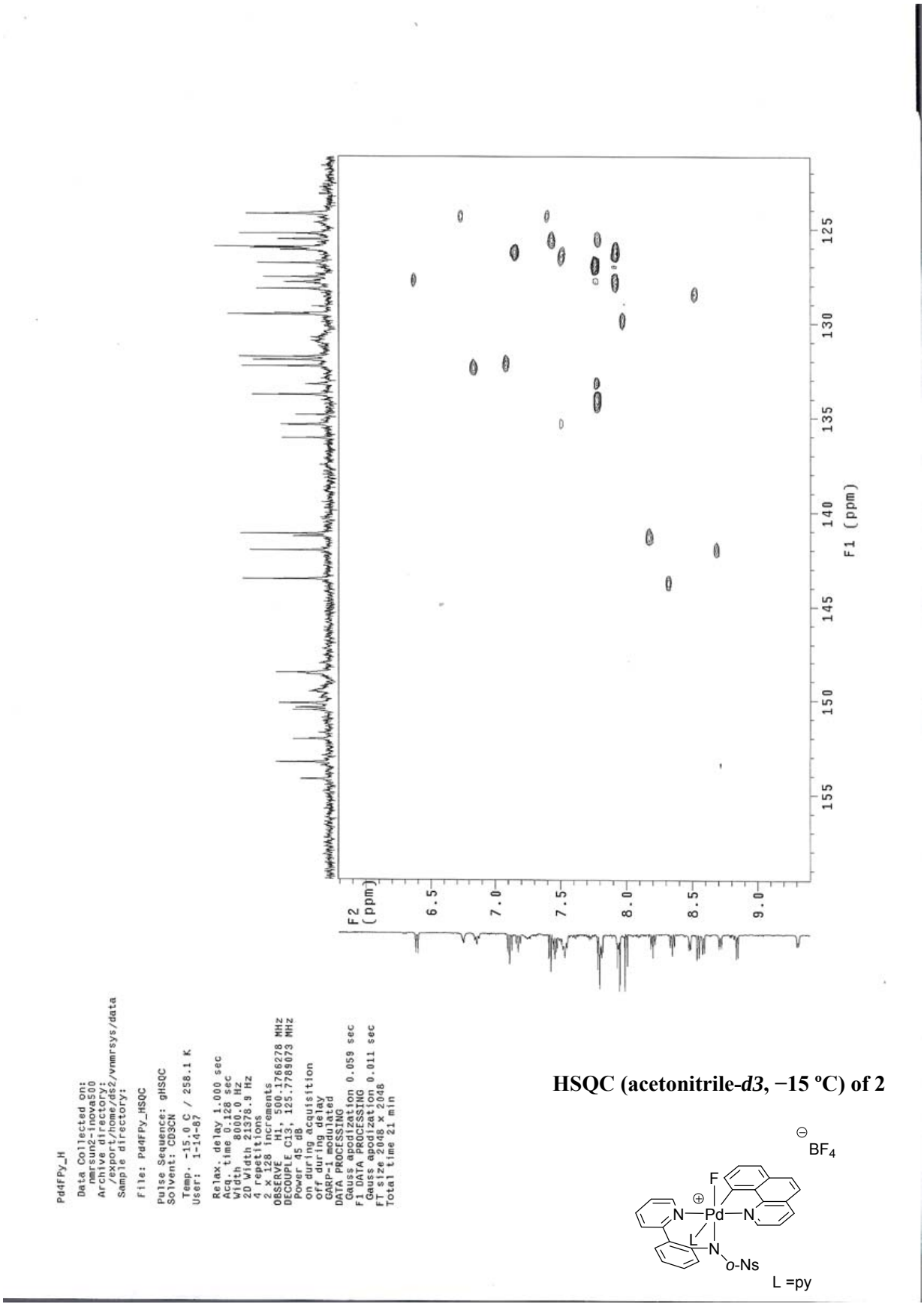
Pulse Sequence: gCOSY
Solvent: CD3CN

Temp. -15.0 C / 258.1 K

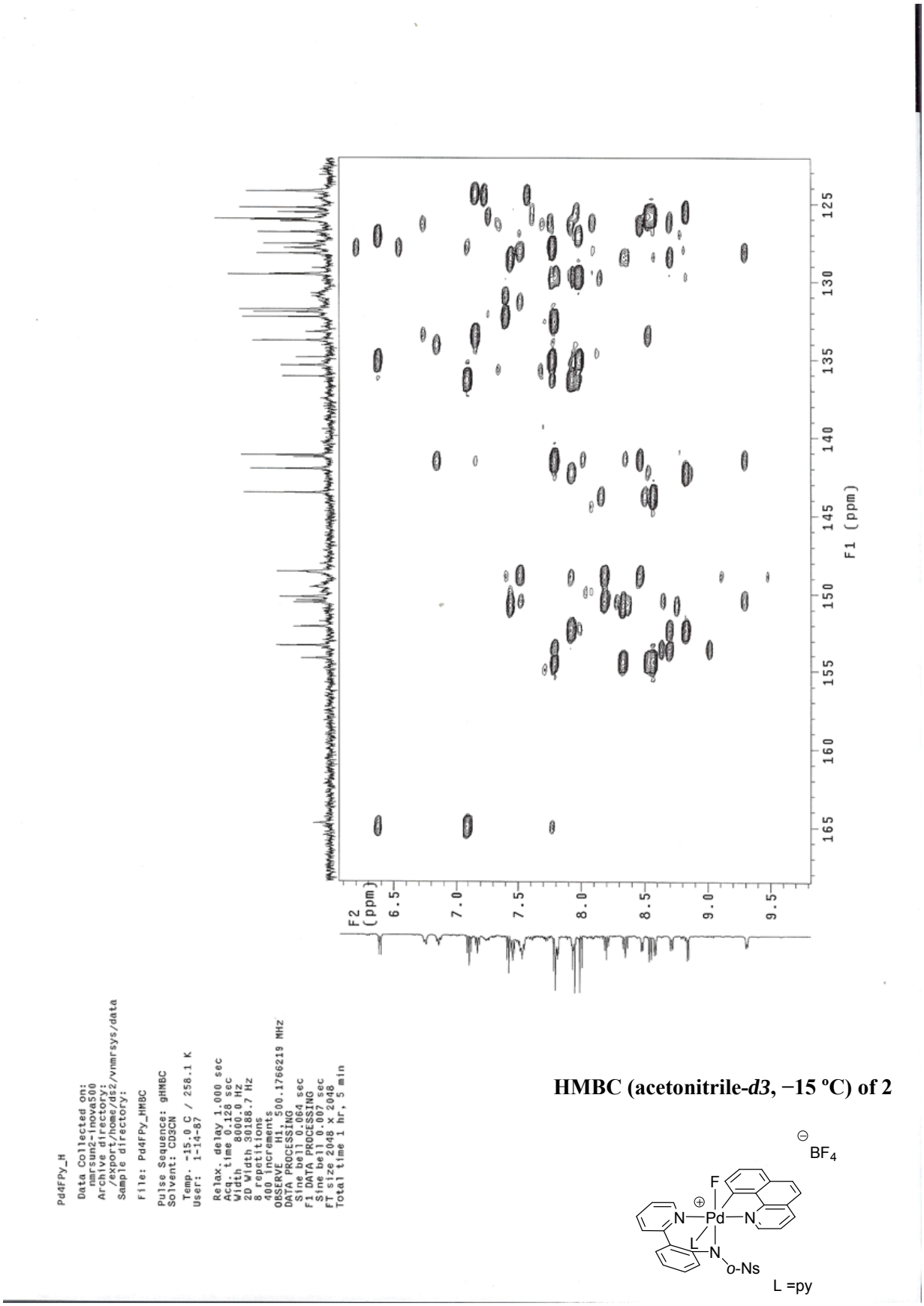
Relax. delay 1.000 sec
Acq. time 0.128 sec
Width 8000.0 Hz
2D Width 8000.0 Hz
Single scan
128 increments
OBSERVE H1, 500.1765938 MHz
DATA PROCESSING
Sq. sine bell 0.064 sec
F1 DATA PROCESSING
Sq. sine bell 0.016 sec
FT size 2048 x 2048
Total time 2 min

^{1}H-^{1}H COSY (acetonitrile-*d3*, −15 ºC) of 2

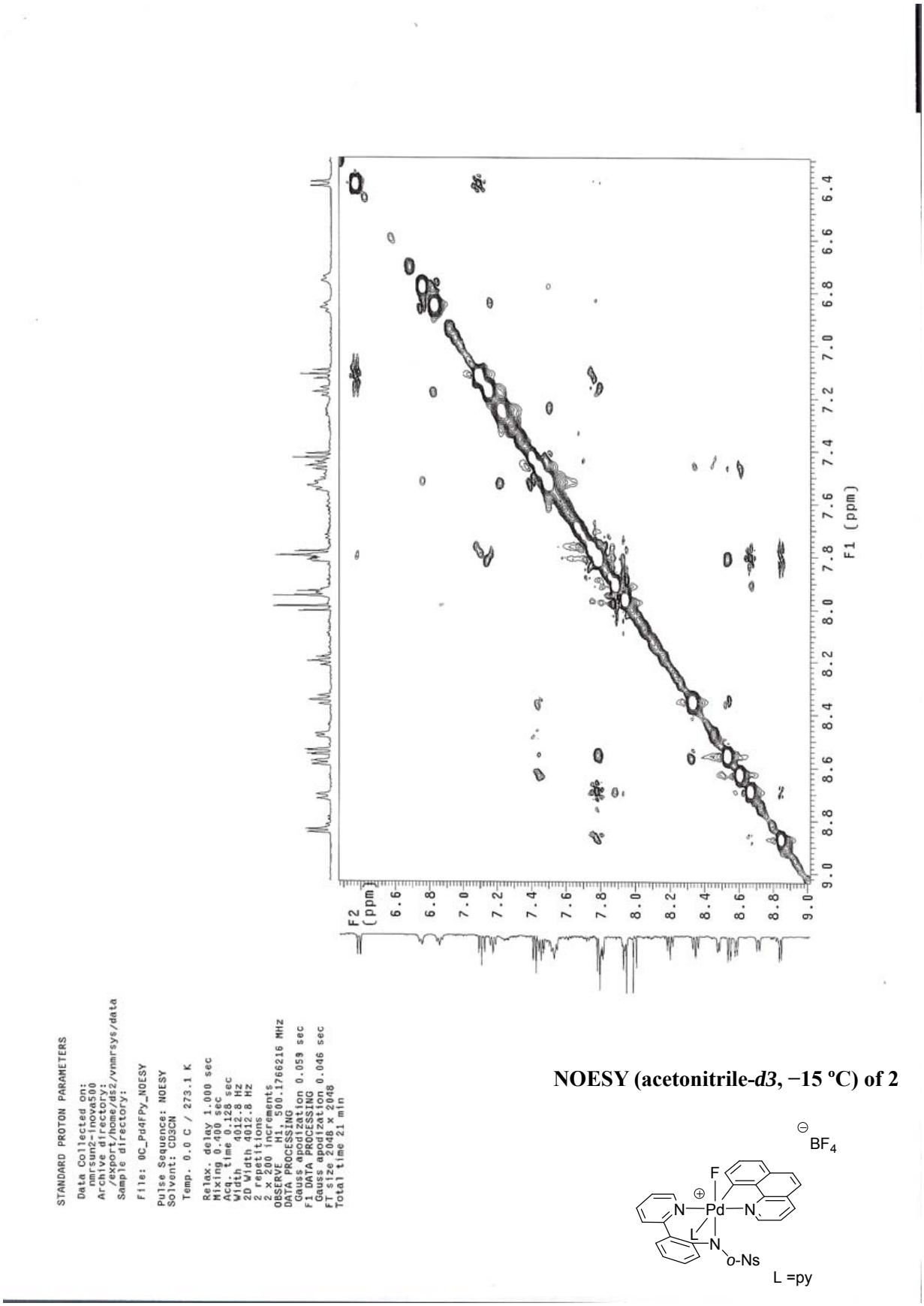




HSQC (acetonitrile-*d3*, −15 ºC) of 2

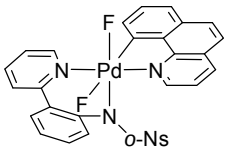


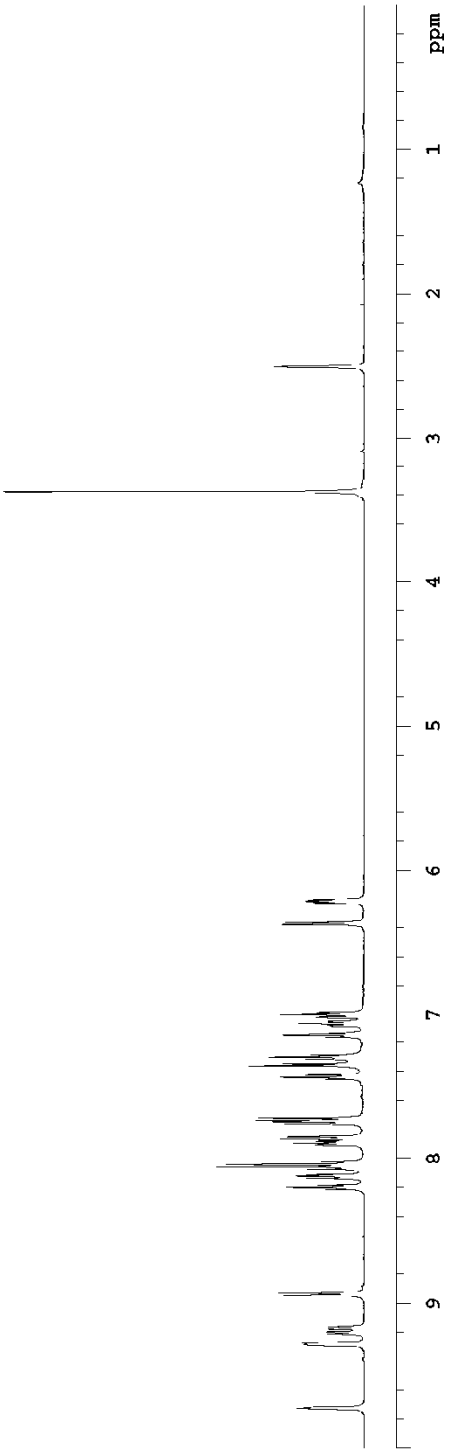
HMBC (acetonitrile-*d3*, −15 ºC) of 2



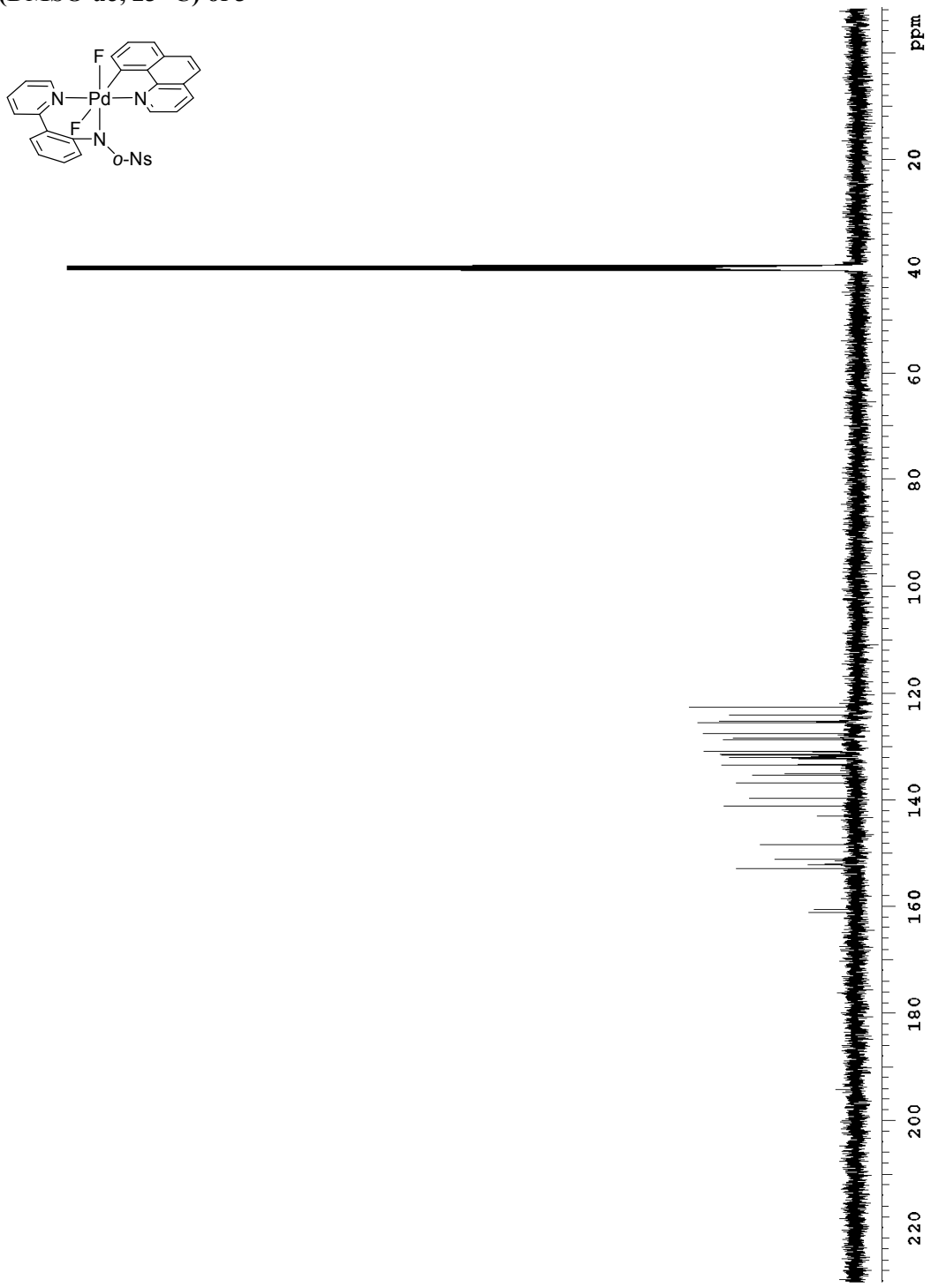
NOESY (acetonitrile-*d3*, −15 ºC) of 2

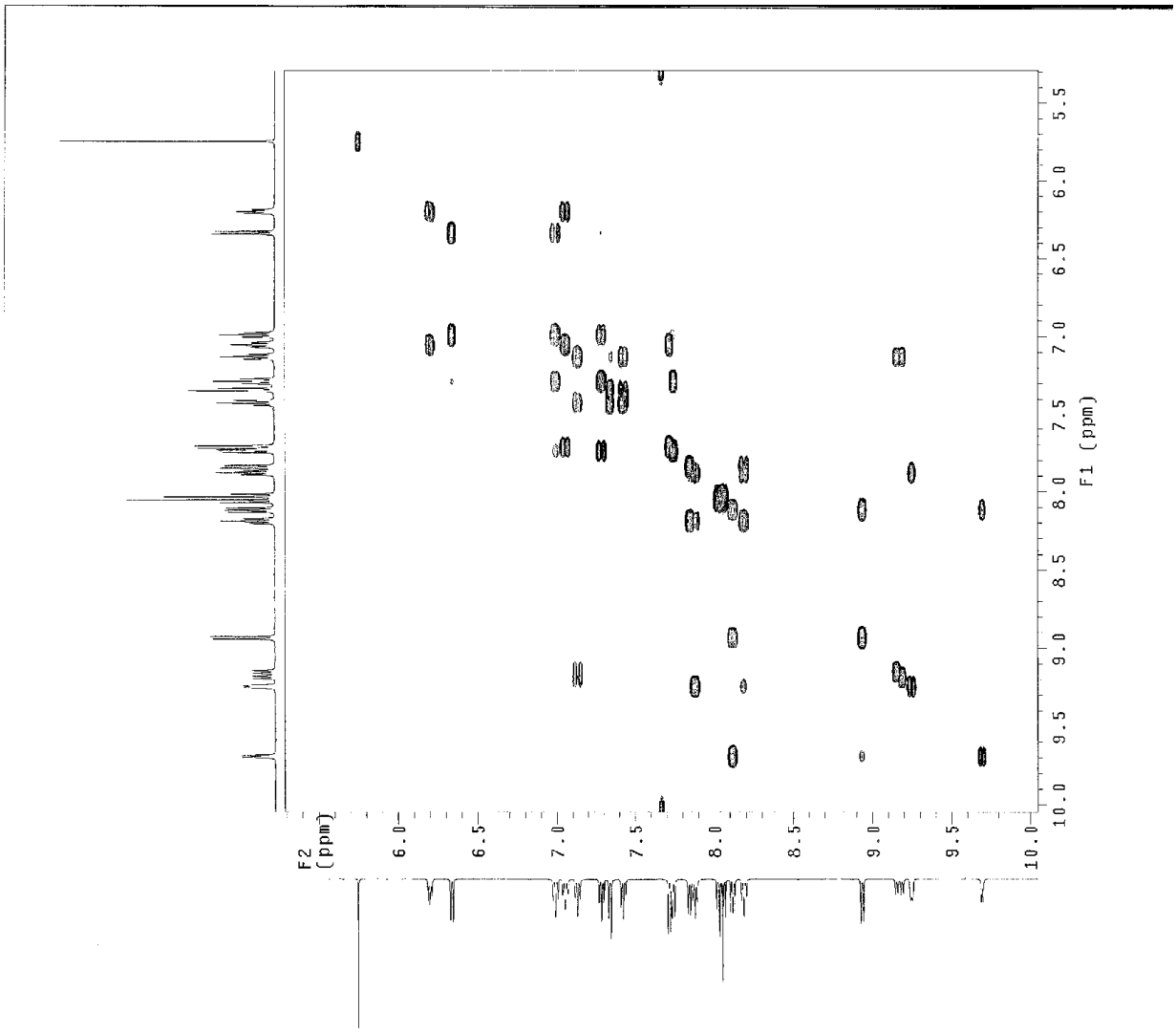
^{1}H NMR (DMSO-*d6*, 23 ºC) of 3





^{13}C NMR (DMSO-*d6*, 23 ºC) of 3



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STANDARD PROTON PARAMETERS

Pulse Sequence: gCOSY

Solvent: DMSO
Temp. 22.0 C / 295.1 K
INOVA-500 "inova500u"

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
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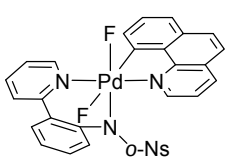
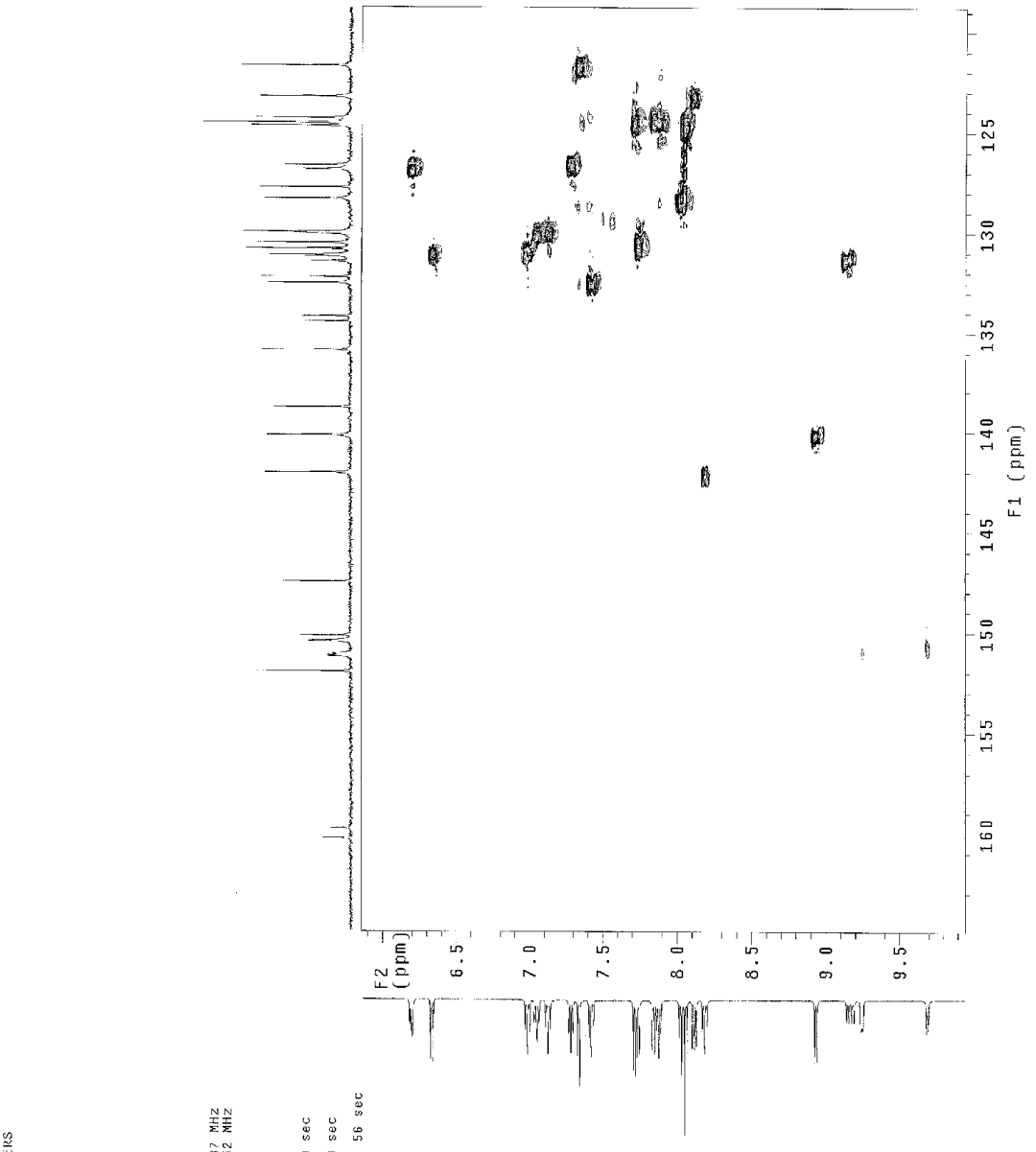
^{1}H-^{1}H COSY (DMSO-*d6*, 23 ºC) of 3



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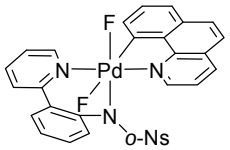
STANDARD PROTON PARAMETERS

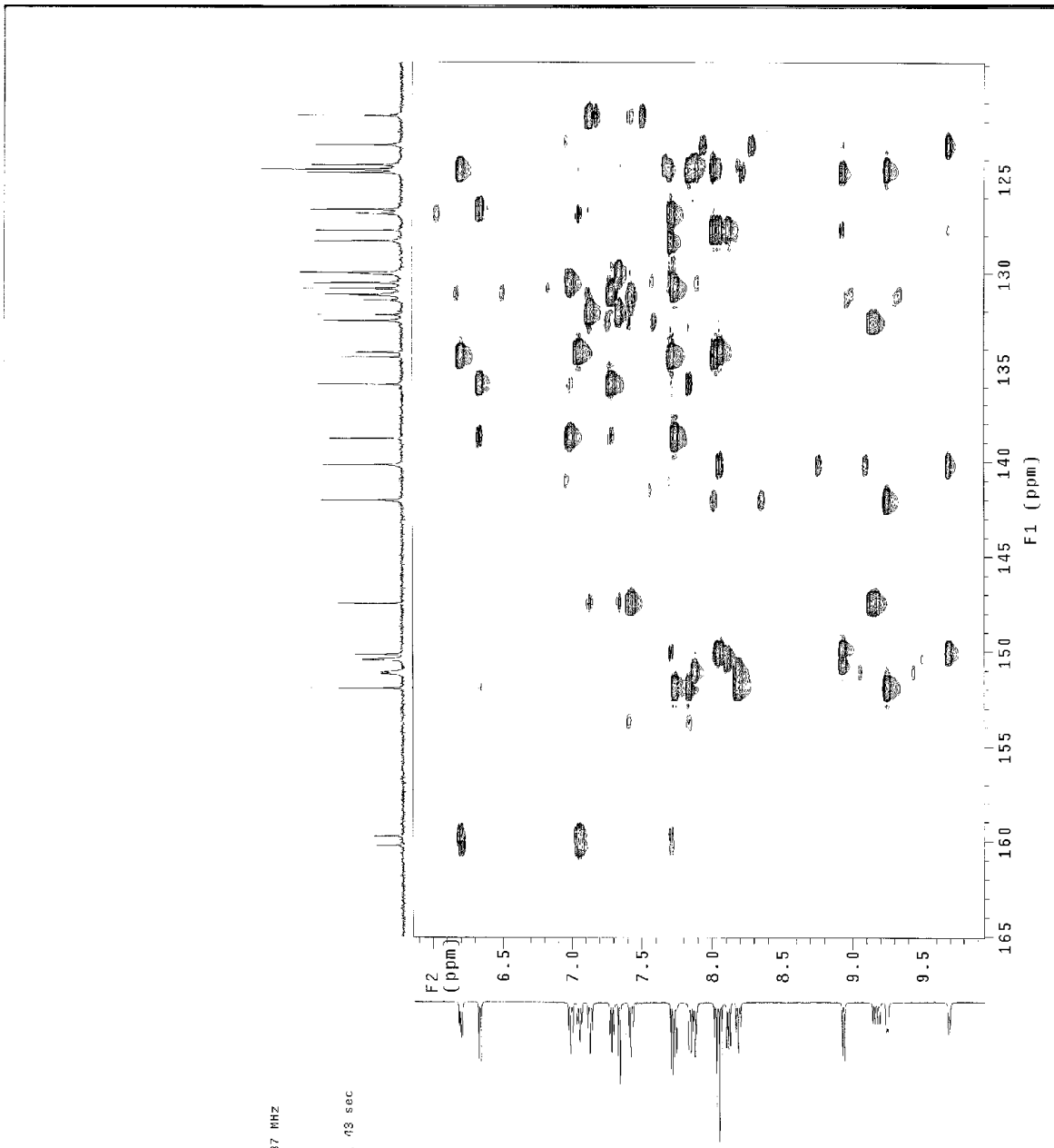
Pulse Sequence:  gHSQC

  Solvent: DMSO
  Temp.  23.0 C / 296.1 K
User:  1-14-87
File:  Pd4F2_HMQC
TNOVA-500  "nmrsun"

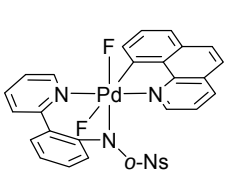
  Relax. delay 1.000 sec
  Acq. time 0.215 sec
  Width   2382.3 Hz
 F2 Width 24001.4 Hz
  16 repetitions
  256 increments
OBSERVE  H1, 500.1783237 MHz
DECOUPLE C13, 125.7813562 MHz
  Power 45 dB
   on during acquisition
   off during delay
   GARP-1 modulated
DATA PROCESSING
  Gauss apodization 0.080 sec
F1 DATA PROCESSING
  Gauss apodization 0.020 sec
FT size 2048 x 2048
Total time 1 hr, 27 min, 56 sec
```

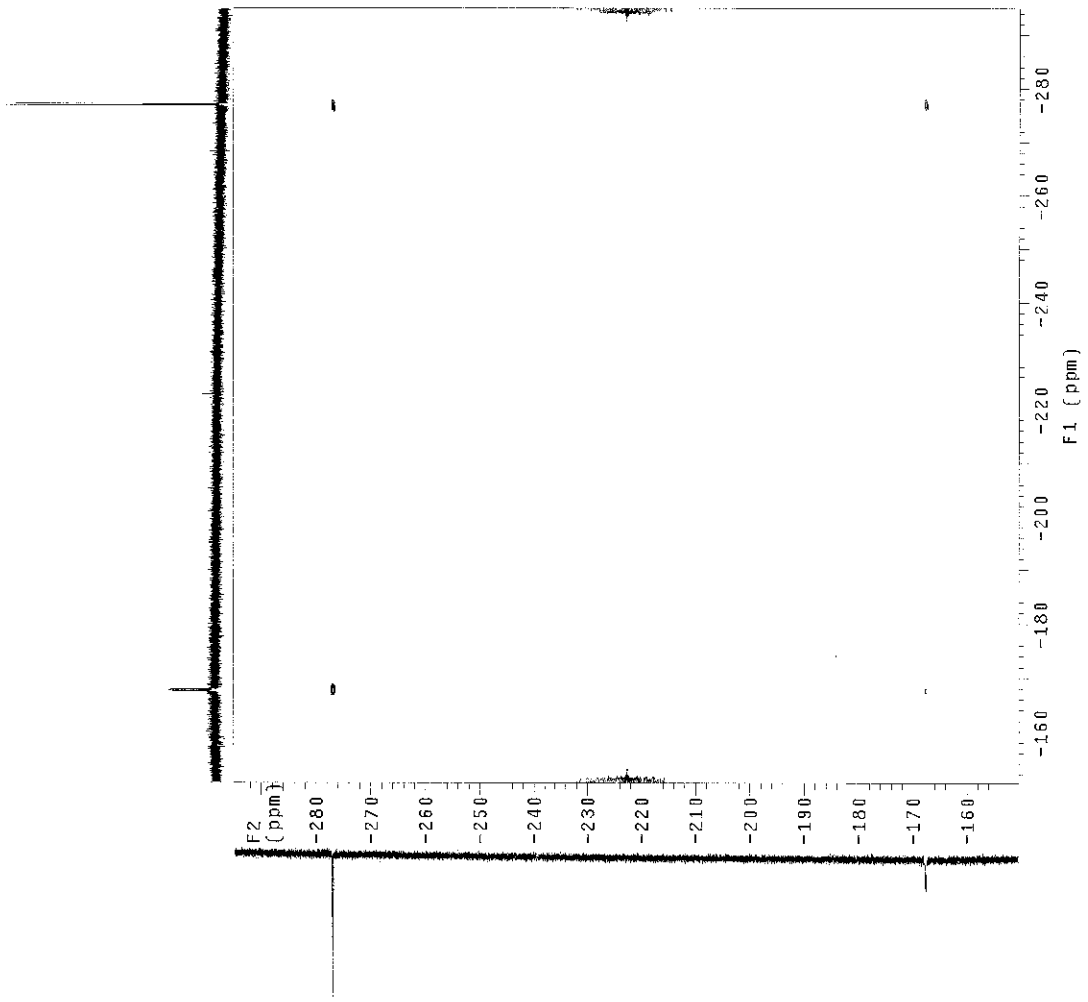
HSQC (DMSO-*d6*, 23 ºC) of 3





HMBC (DMSO-*d6*, 23 ºC) of 3





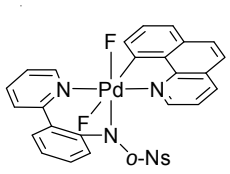
STANDARD CARBON PARAMETERS

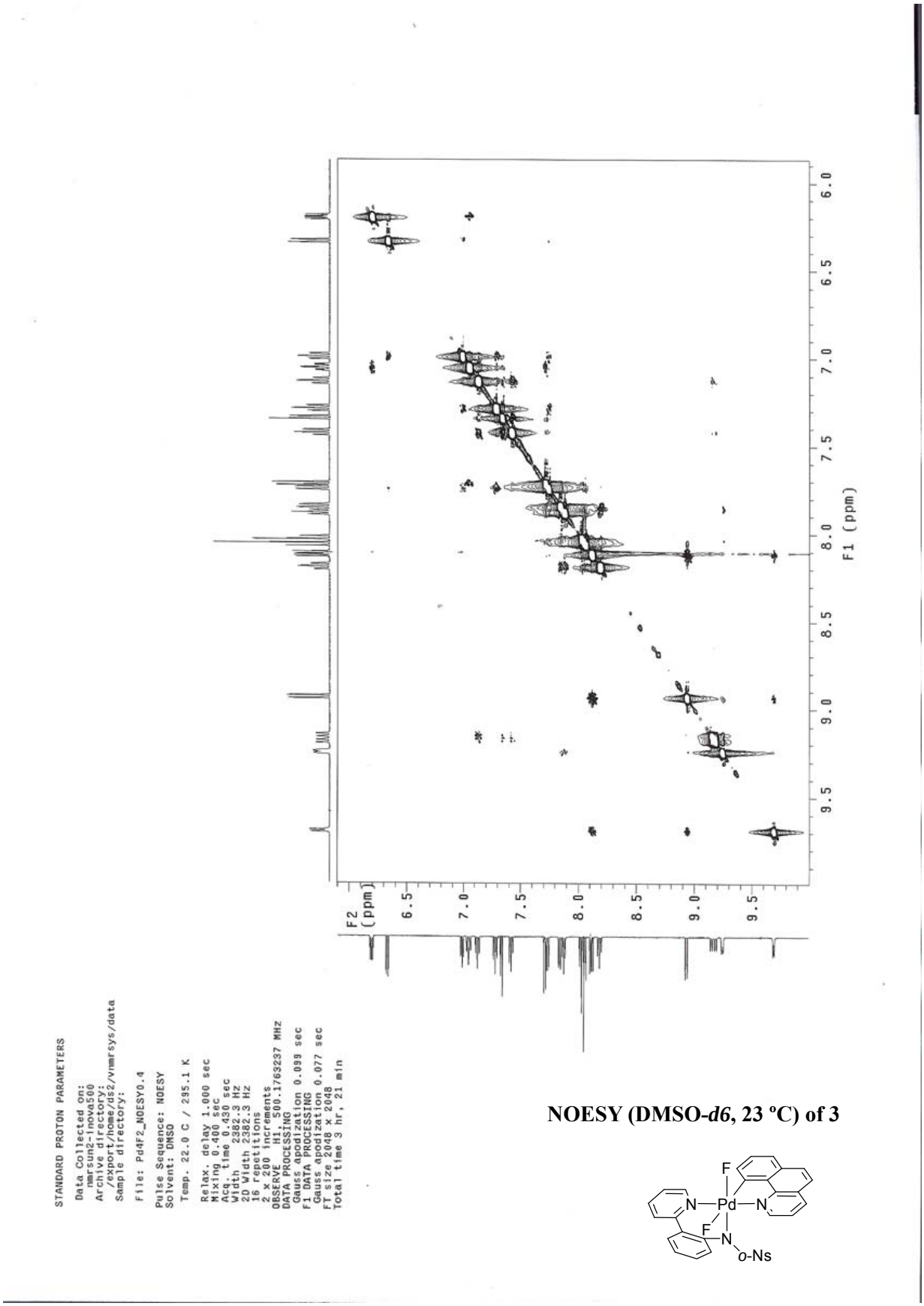
Pulse Sequence: gCOSY

Solvent: DMSO
Ambient temperature
User: lsl
INOVA-500 "inova500b"

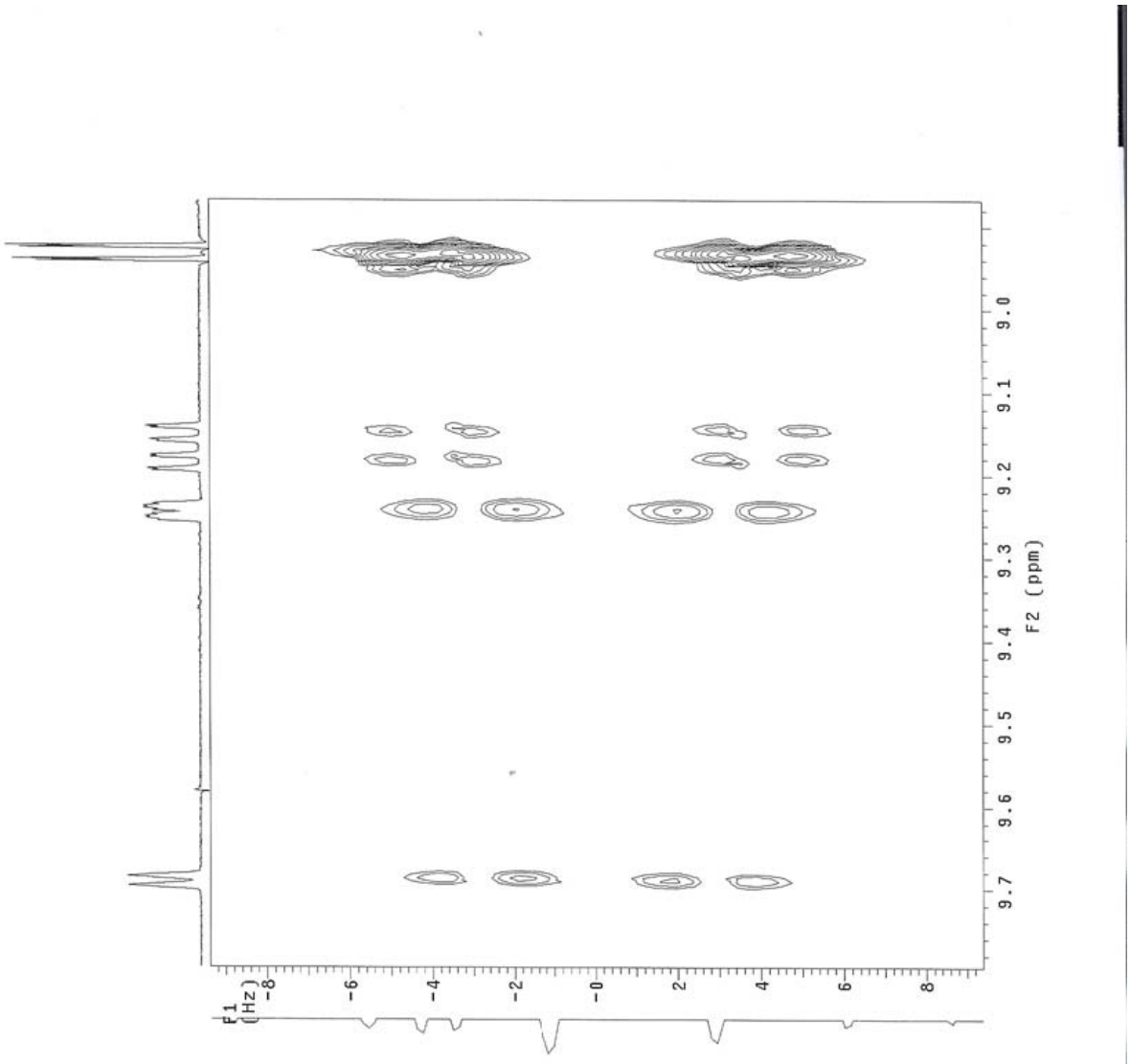
Relax. delay 1.000 sec
Acq. time 0.015 sec
Width 68085.1 HZ
2D Width 68085.1 HZ
Single scan
128 increments
OBSERVE F19, 470.6361483 MHZ
DATA PROCESSING
Sq. sine bell 0.120 sec
F1 DATA PROCESSING
Sq. sine bell 0.002 sec
FT size 2048 x 2048
Total time 2 min, 25 sec

^{19}F-^{19}F COSY (DMSO-*d6*, 23 ºC) of 3





NOESY (DMSO-*d6*, 23 ºC) of 3




```
STANDARD PROTON PARAMETERS

Pulse Sequence: hom2dj

  Solvent: DMSO
  Temp. 22.0 C / 295.1 K
  File: 2dj
  INOVA-500  "nmrsun"

  Relax. delay 1.000 sec
  Mixing 0.400 sec
  Acq. time 0.860 sec
  Width     2382.3 Hz
  2D Width 50.0 Hz
    8 repetitions
   64 increments
  OBSERVE    H1, 500.1763237 MHz
  DATA PROCESSING
   Sine bell 0.107 sec
   F1 DATA PROCESSING
   Sine bell 0.640 sec
  FT size 2048 x 256
  Total time 21 min, 49 sec
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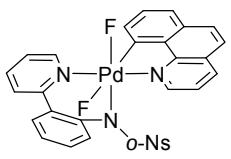
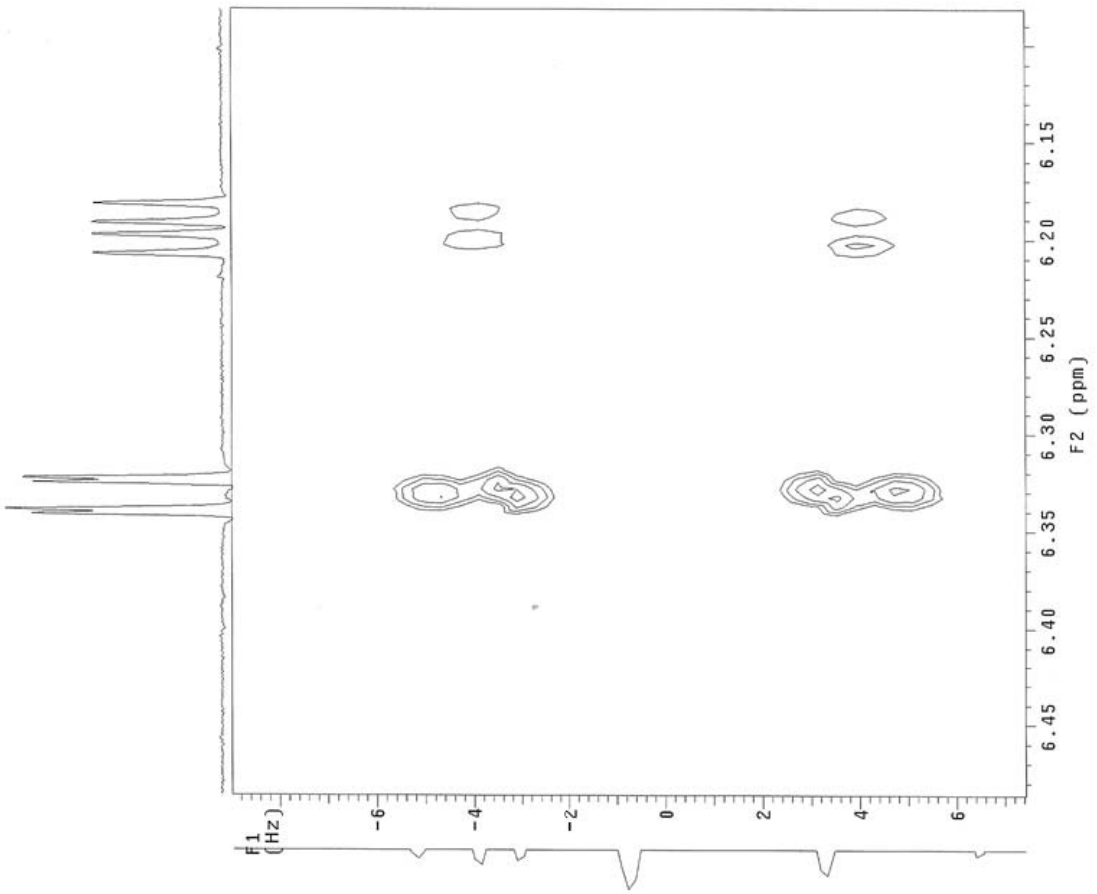
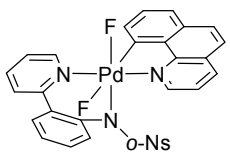
HOM2DJ (DMSO-*d6*, 23 ºC) of 3



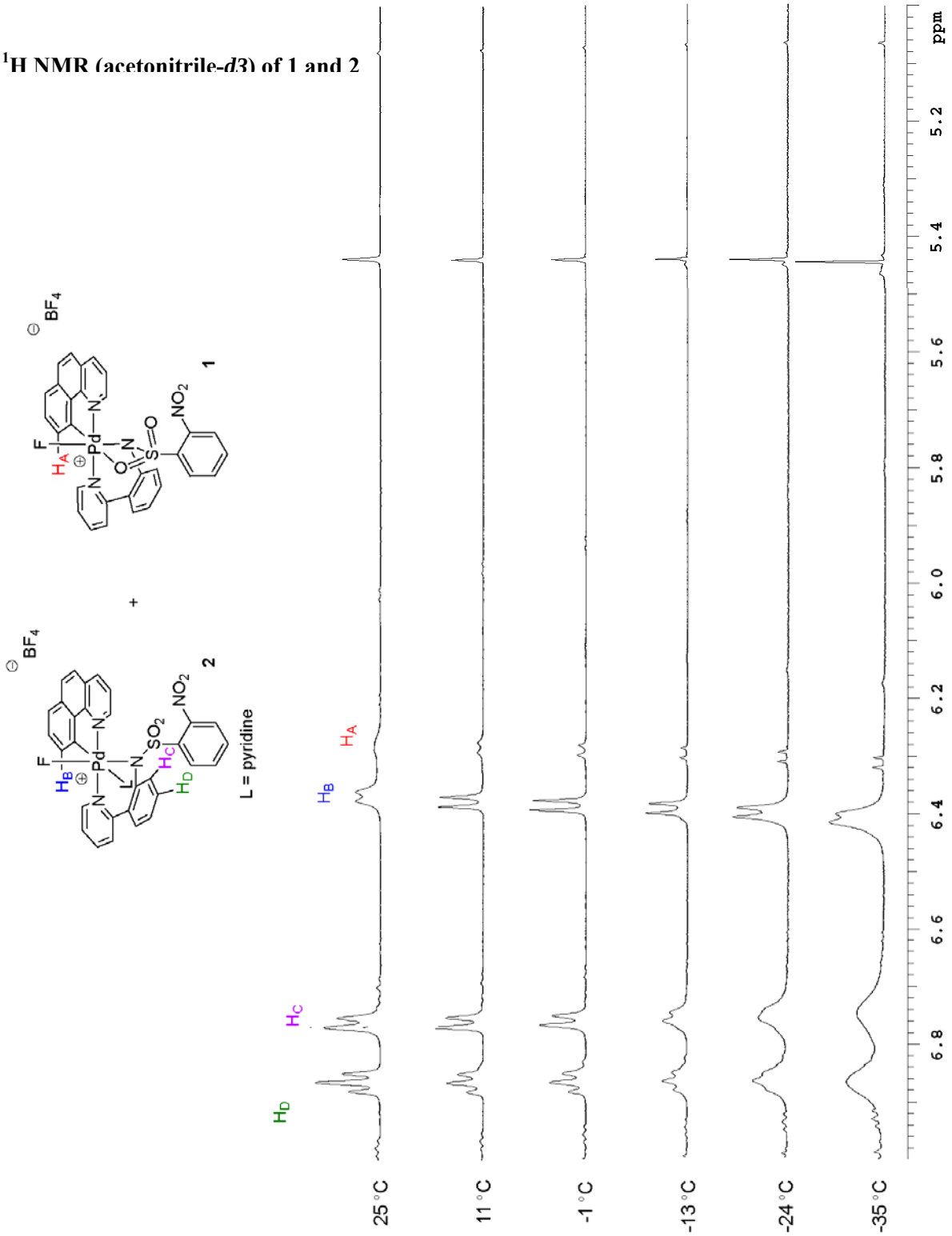



```
STANDARD PROTON PARAMETERS

Pulse Sequence: hom2dj

  Solvent: DMSO
  Temp. 22.0 C / 295.1 K
  File: 2dj
  INOVA-500  "nmrsun"

  Relax. delay 1.000 sec
  Mixing 0.400 sec
  Acq. time 0.860 sec
  Width    2382.3 Hz
  2D Width 50.0 Hz
    8 repetitions
  64 increments
  OBSERVE    H1, 500.1763237 MHz
  DATA PROCESSING
    Sine bell 0.107 sec
  F1 DATA PROCESSING
    Sine bell 0.640 sec
  FT size 2048 x 256
  Total time 21 min, 49 sec
```

HOM2DJ (DMSO-*d6*, 23 ºC) of 3

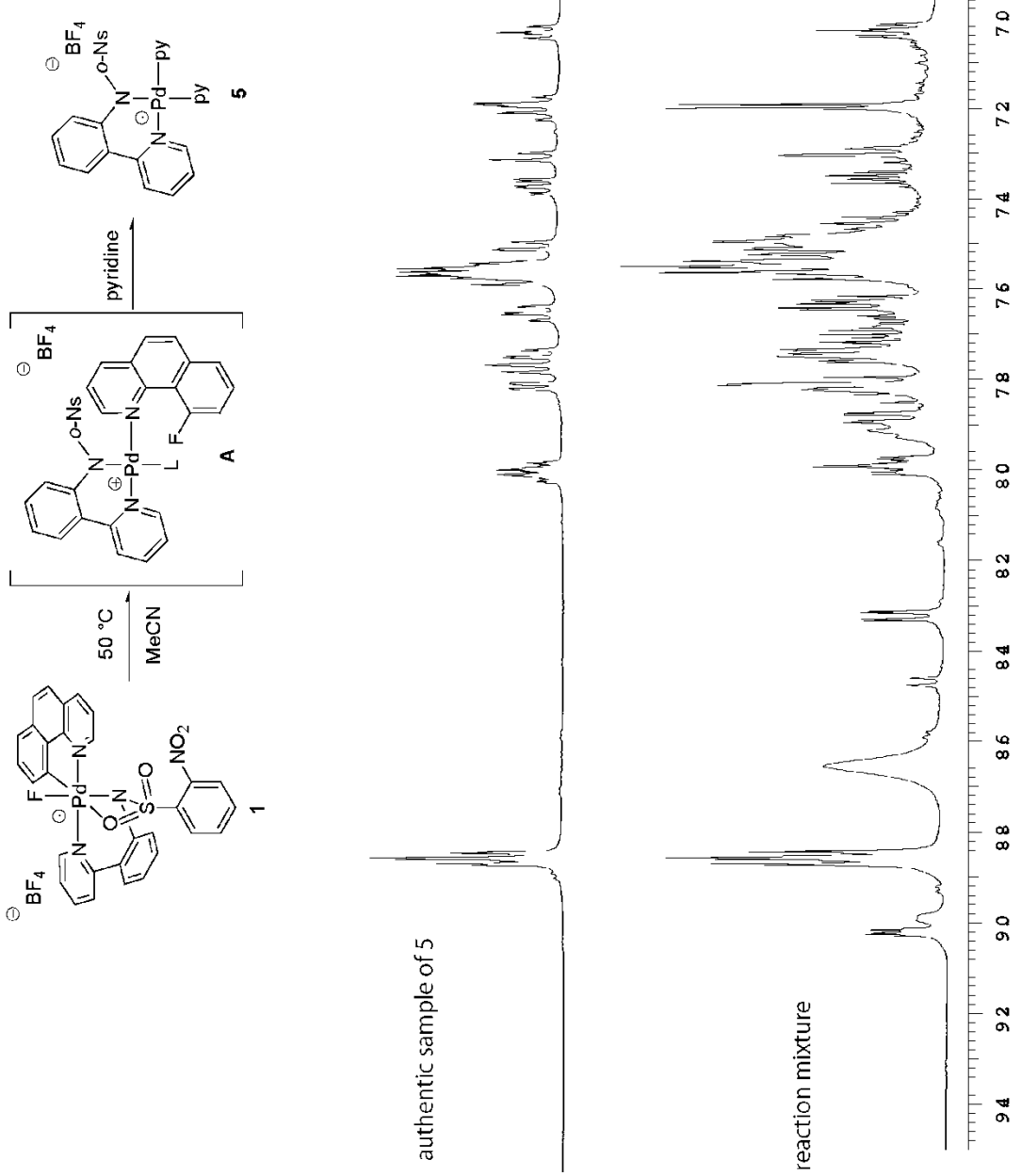


^{1}H NMR (acetonitrile-*d*3) of 1 and 2



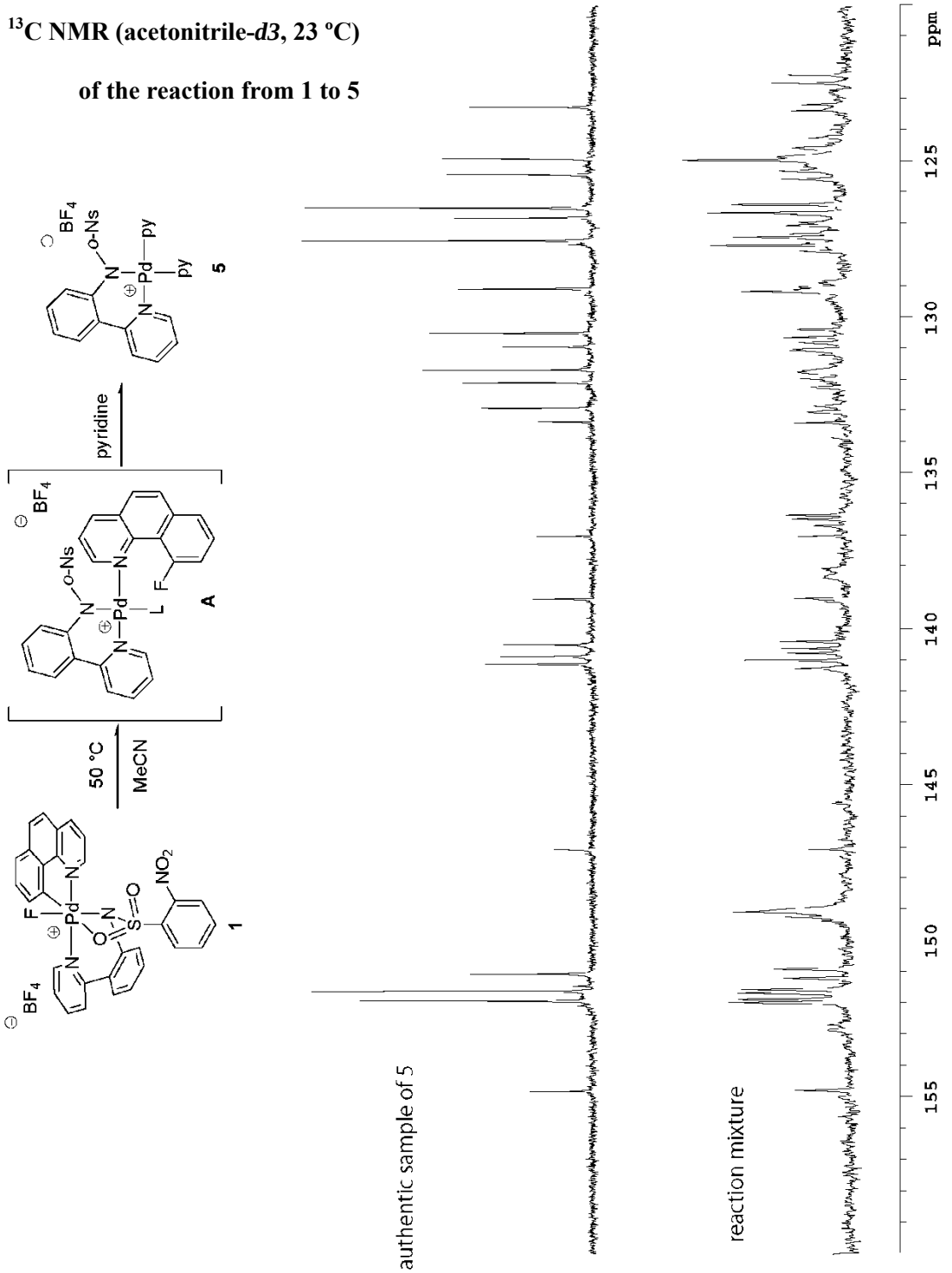
^{1}H NMR (acetonitrile-*d3*, 23 ºC)

of the reaction from 1 to 5

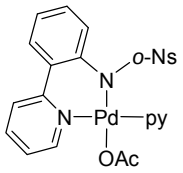


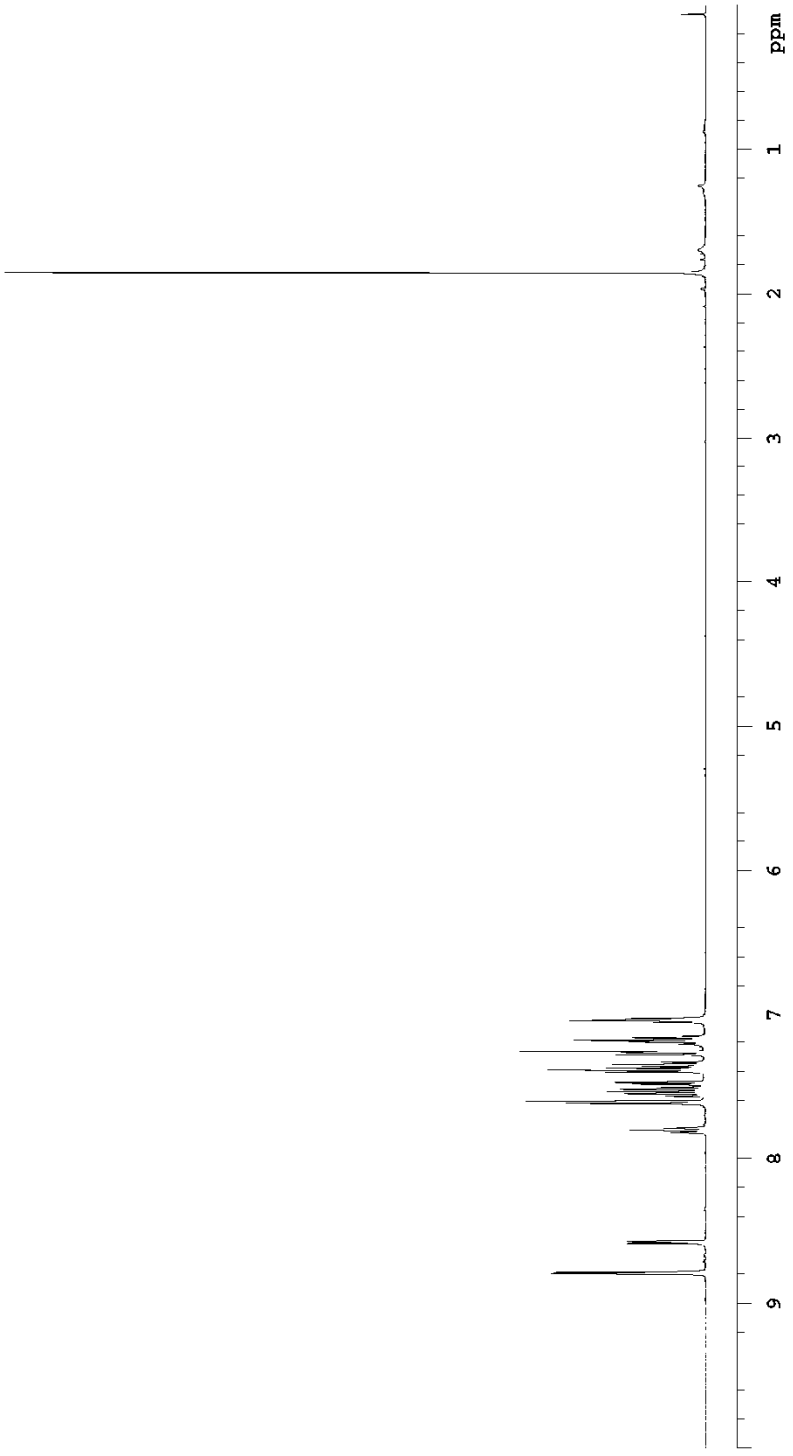
^{13}C NMR (acetonitrile-*d3*, 23 ºC)

of the reaction from 1 to 5

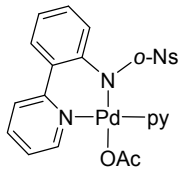


^{1}H NMR ($CDCl_3$, 23 ºC) of S6

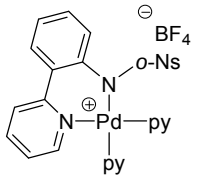


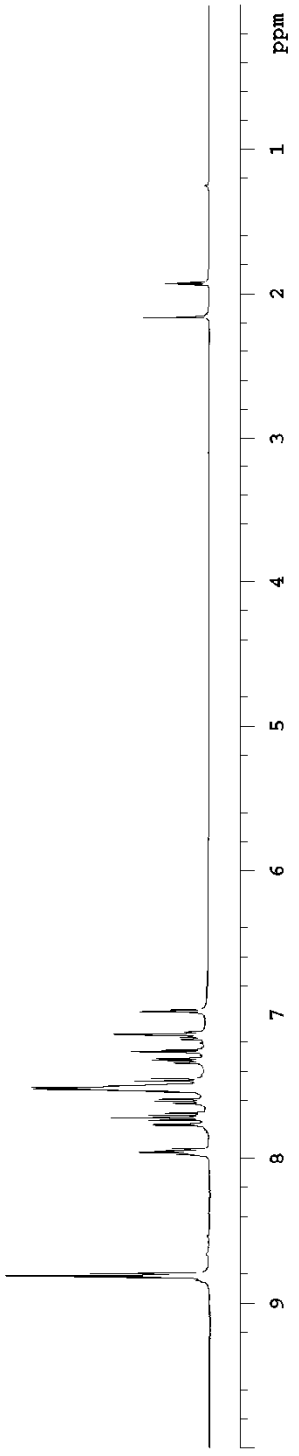


^{13}C NMR ($CDCl_3$, 23 ºC) of S6

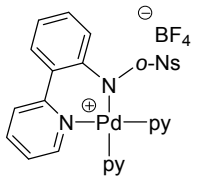


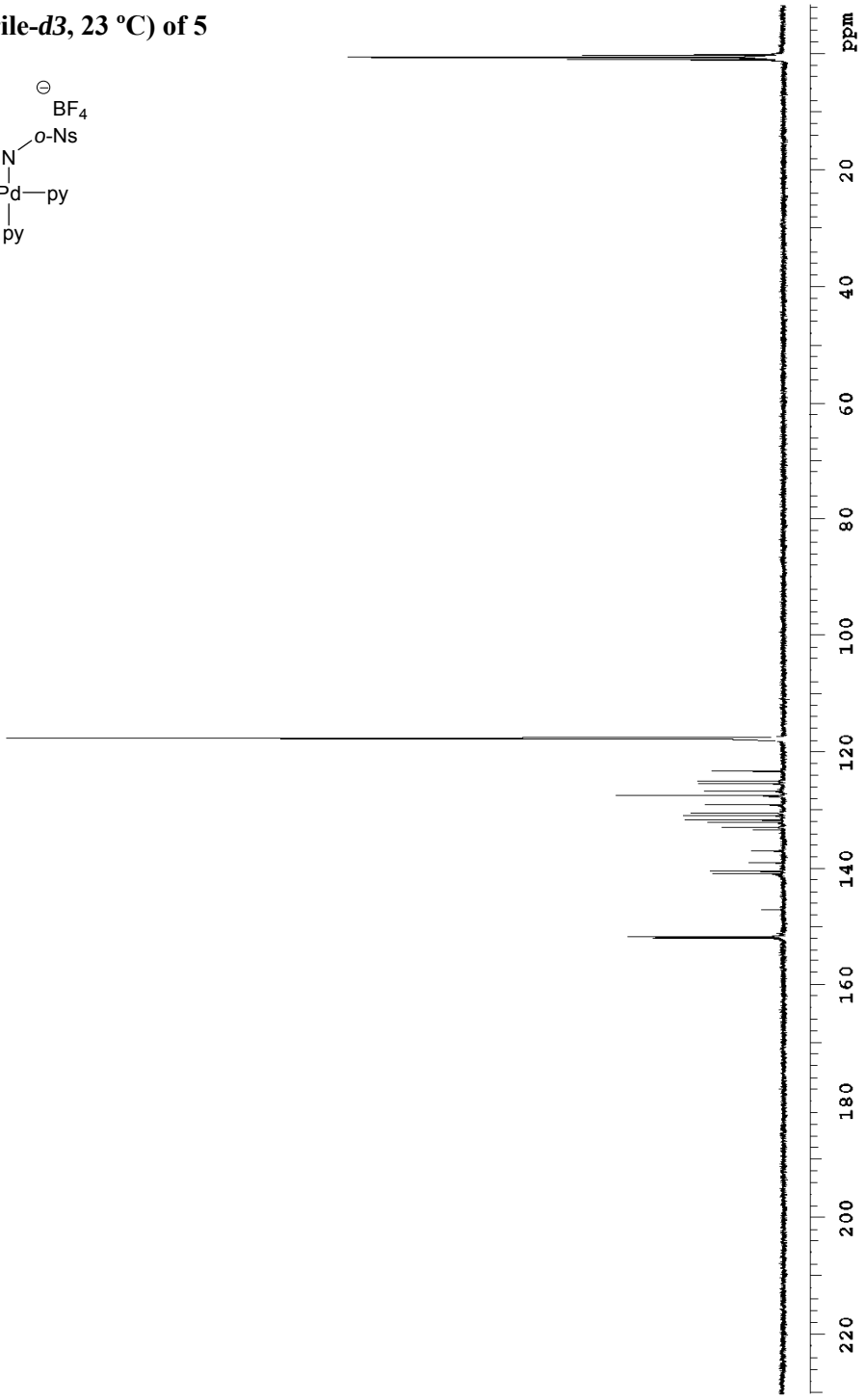
^{1}H NMR (acetonitrile-*d3*, 23 ºC) of 5



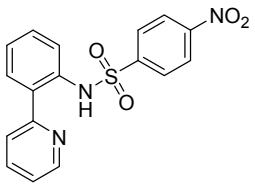


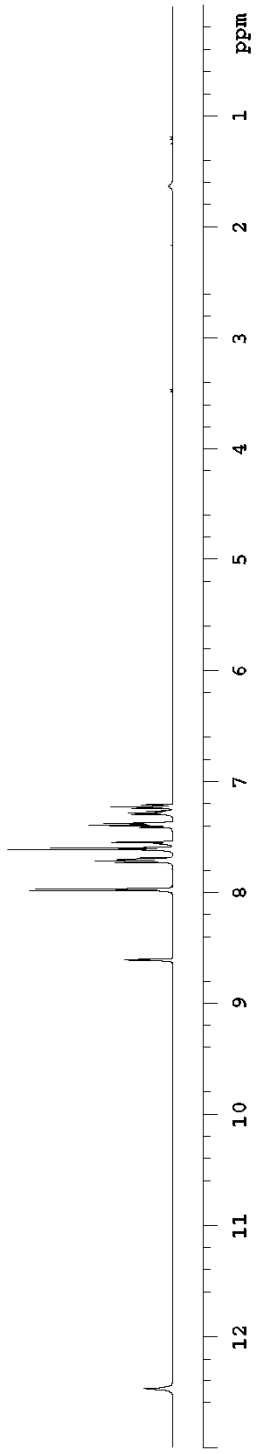
^{13}C NMR (acetonitrile-*d3*, 23 ºC) of 5



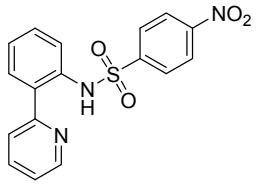


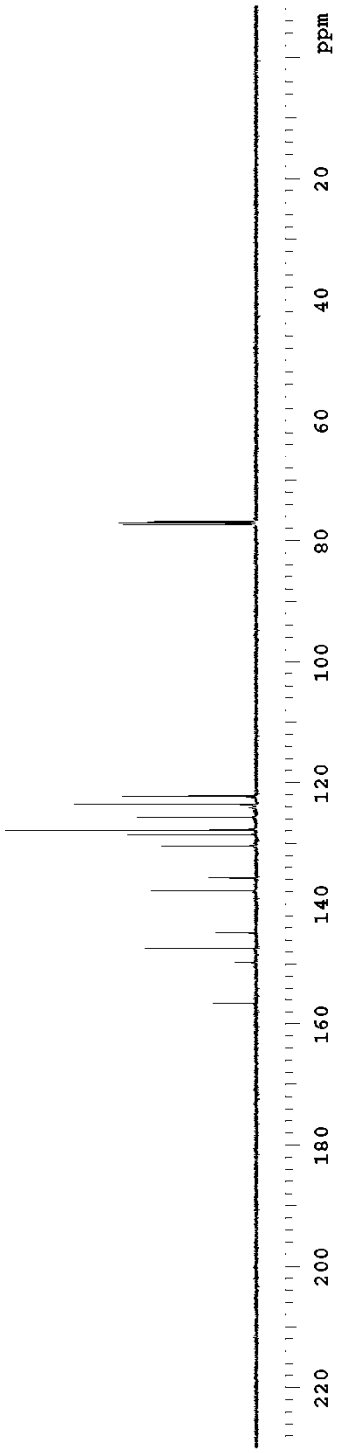
^{1}H NMR ($CDCl_3$, 23 ºC) of S7



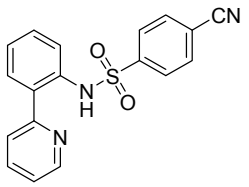


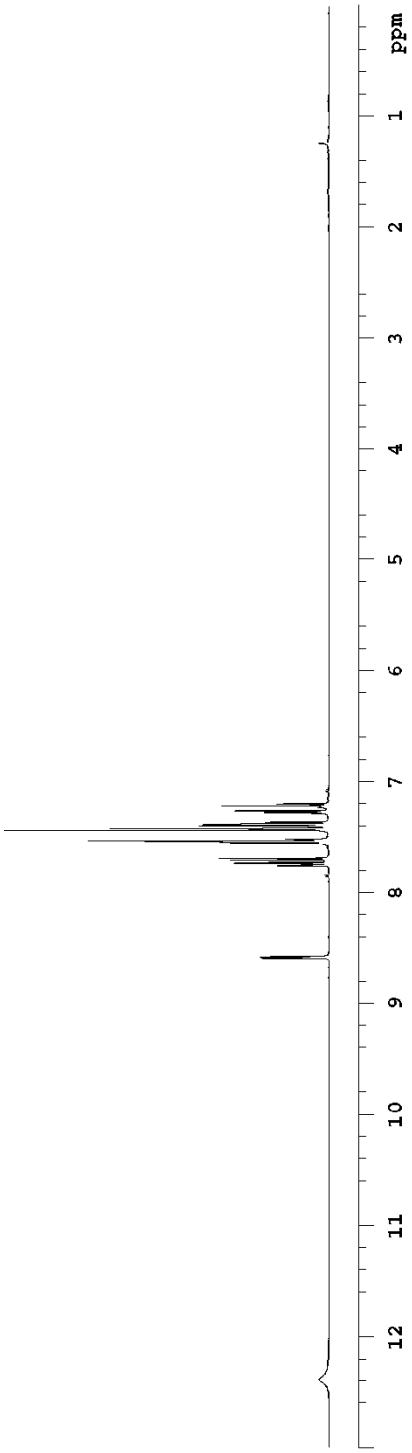
^{13}C NMR ($CDCl_3$, 23 ºC) of S7



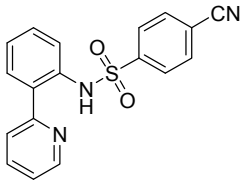


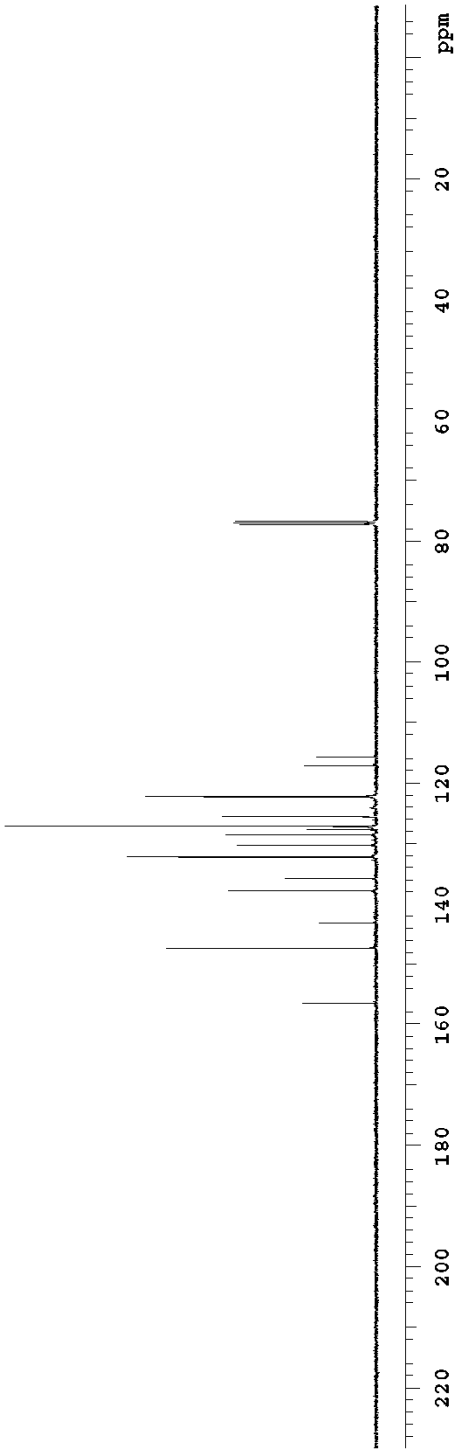
^{1}H NMR ($CDCl_3$, 23 ºC) of S8



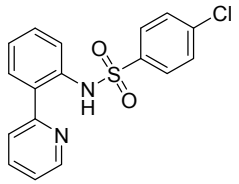


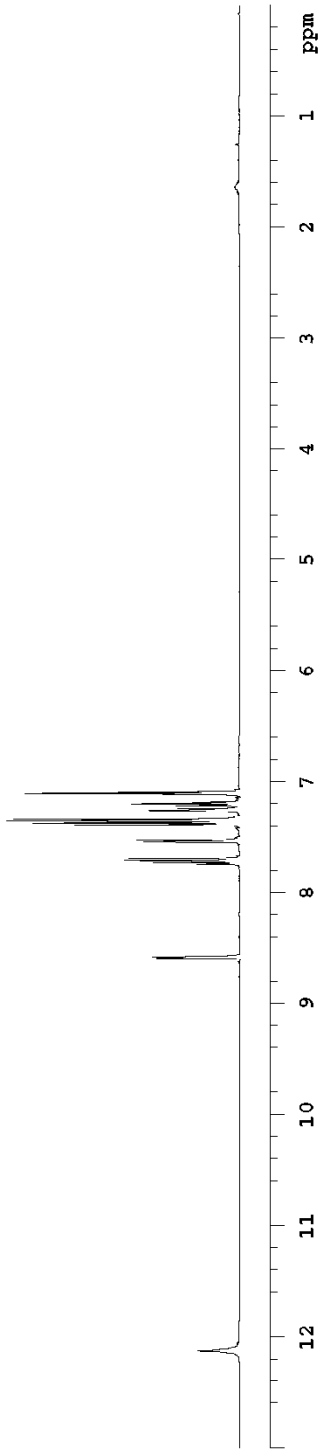
^{13}C NMR ($CDCl_3$, 23 °C) of S8



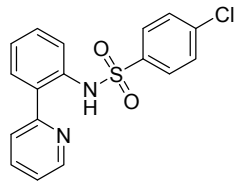


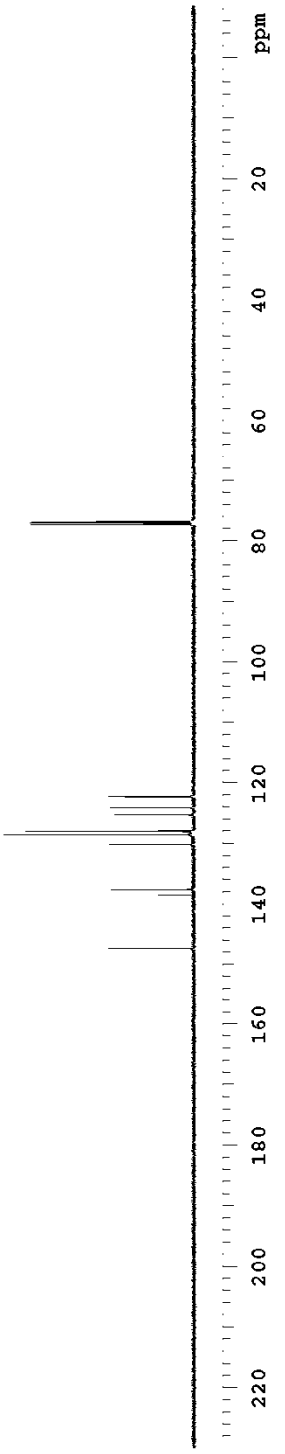
^{1}H NMR ($CDCl_3$, 23 ºC) of S9



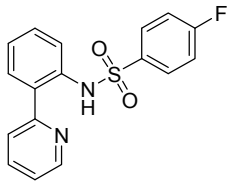


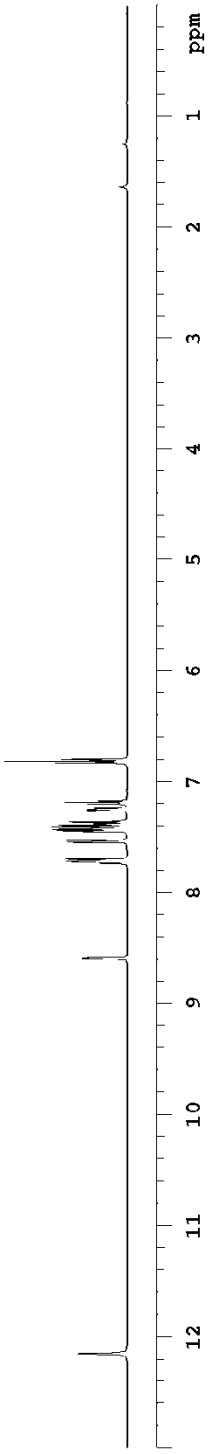
^{13}C NMR ($CDCl_3$, 23 °C) of S9



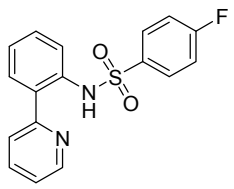


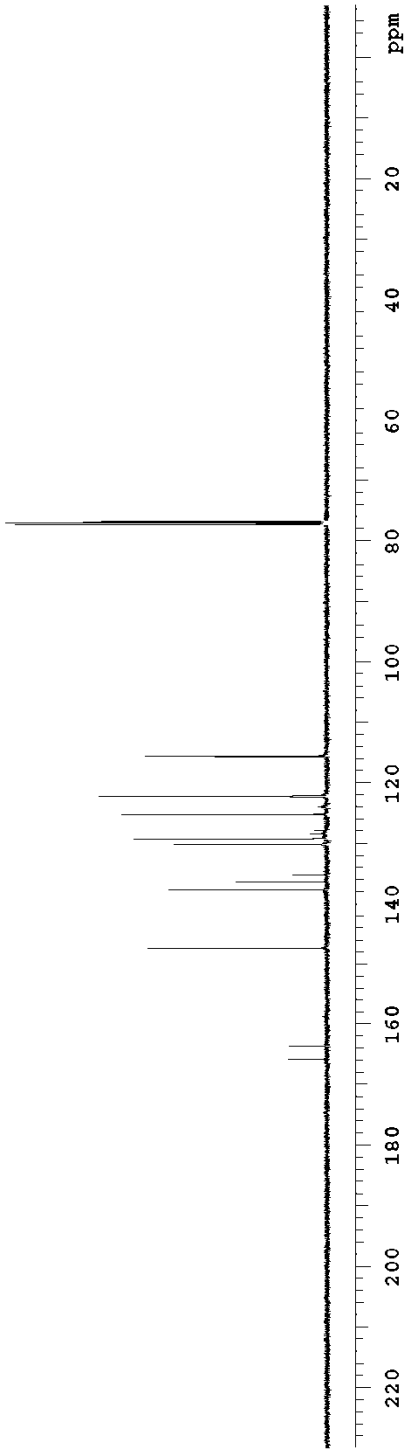
^{1}H NMR ($CDCl_3$, 23 ºC) of S10



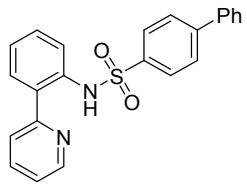


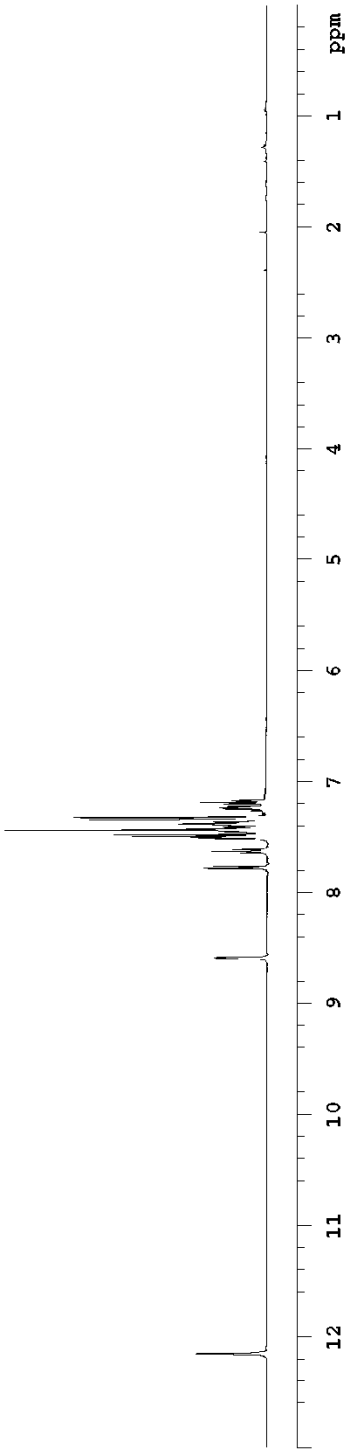
^{13}CNMR ($CDCl_3$, 23 ºC) of S10



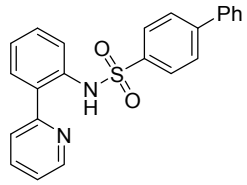


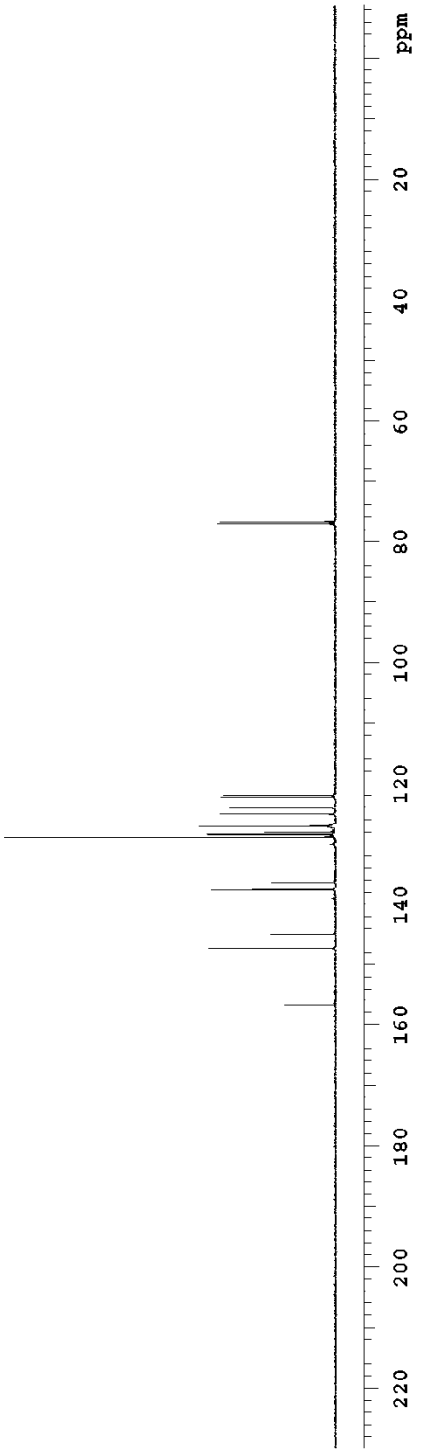
^{1}H NMR ($CDCl_3$, 23 ºC) of S11



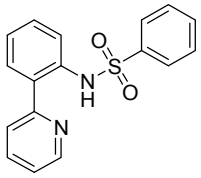


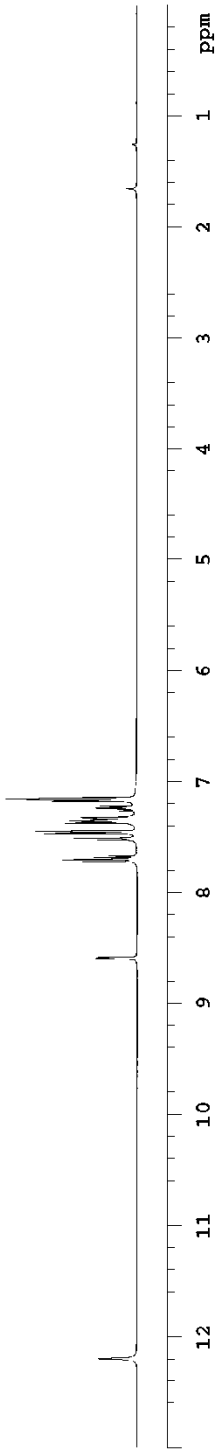
^{13}C NMR ($CDCl_3$, 23 ºC) of S11



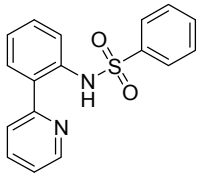


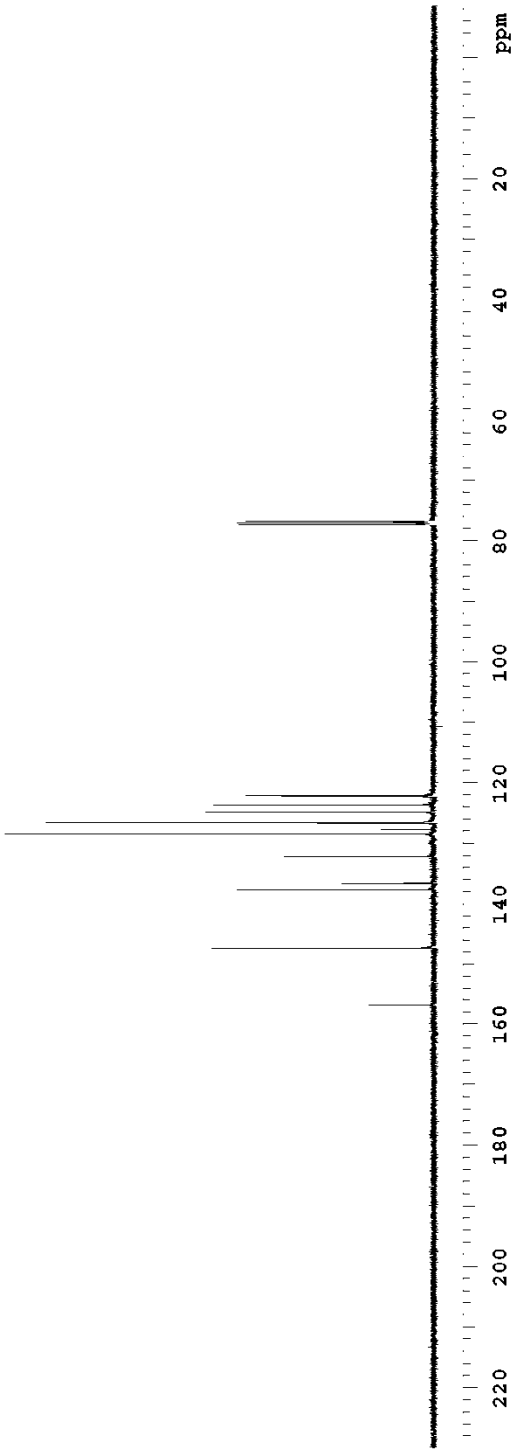
^{1}H NMR ($CDCl_3$, 23 ºC) of S12



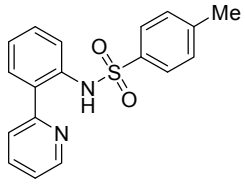


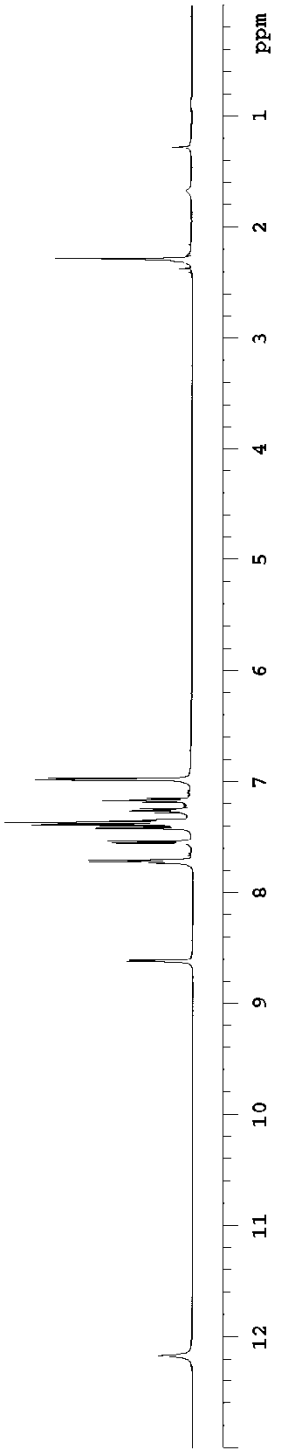
^{13}C NMR ($CDCl_3$, 23 °C) of S12



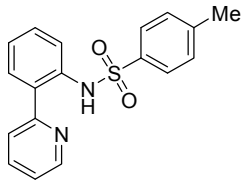


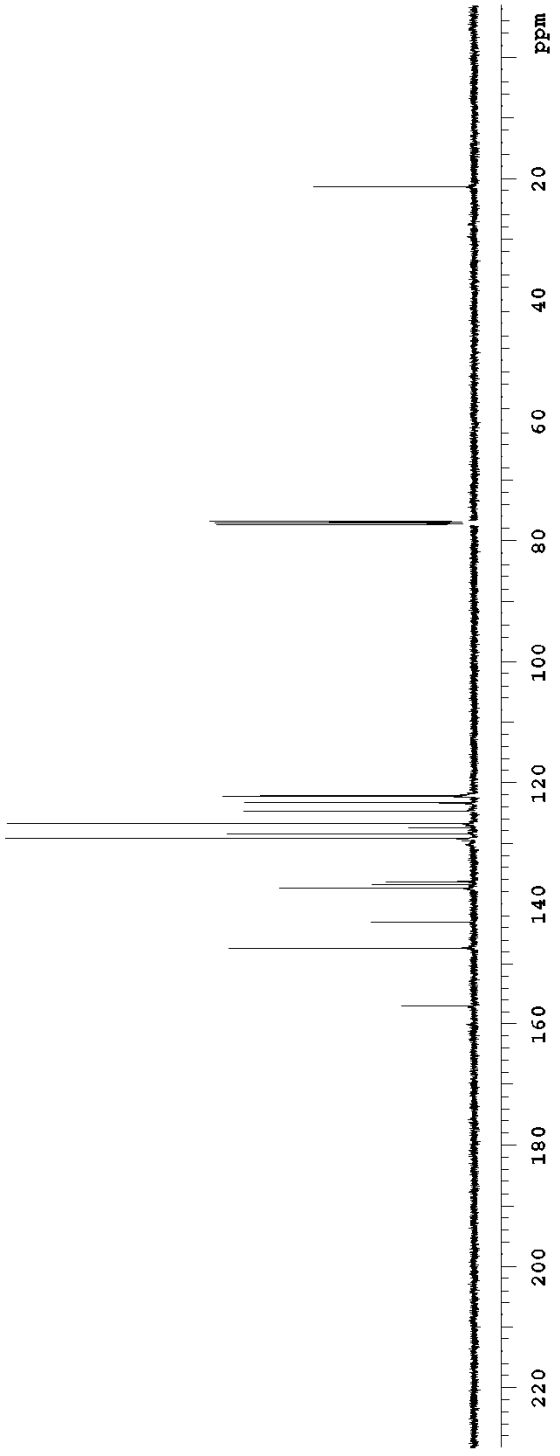
^{1}H NMR ($CDCl_3$, 23 ºC) of S13



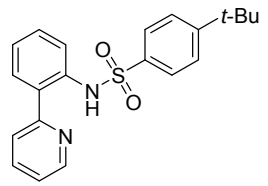


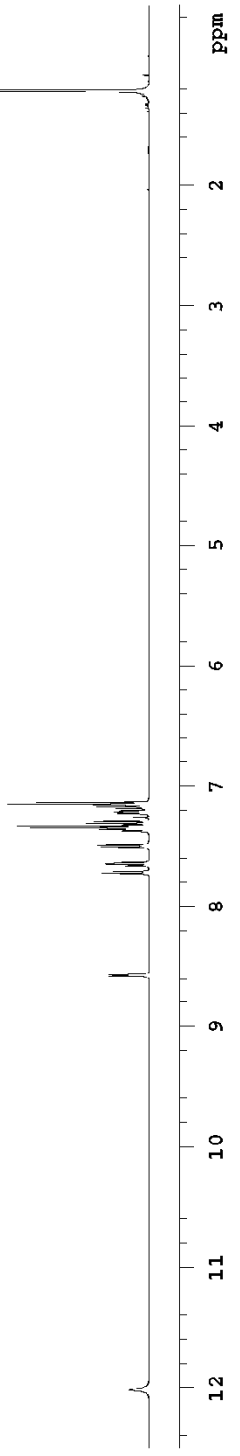
^{13}C NMR ($CDCl_3$, 23 ºC) of S13



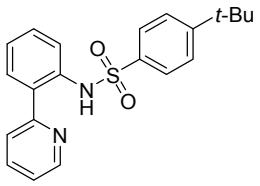


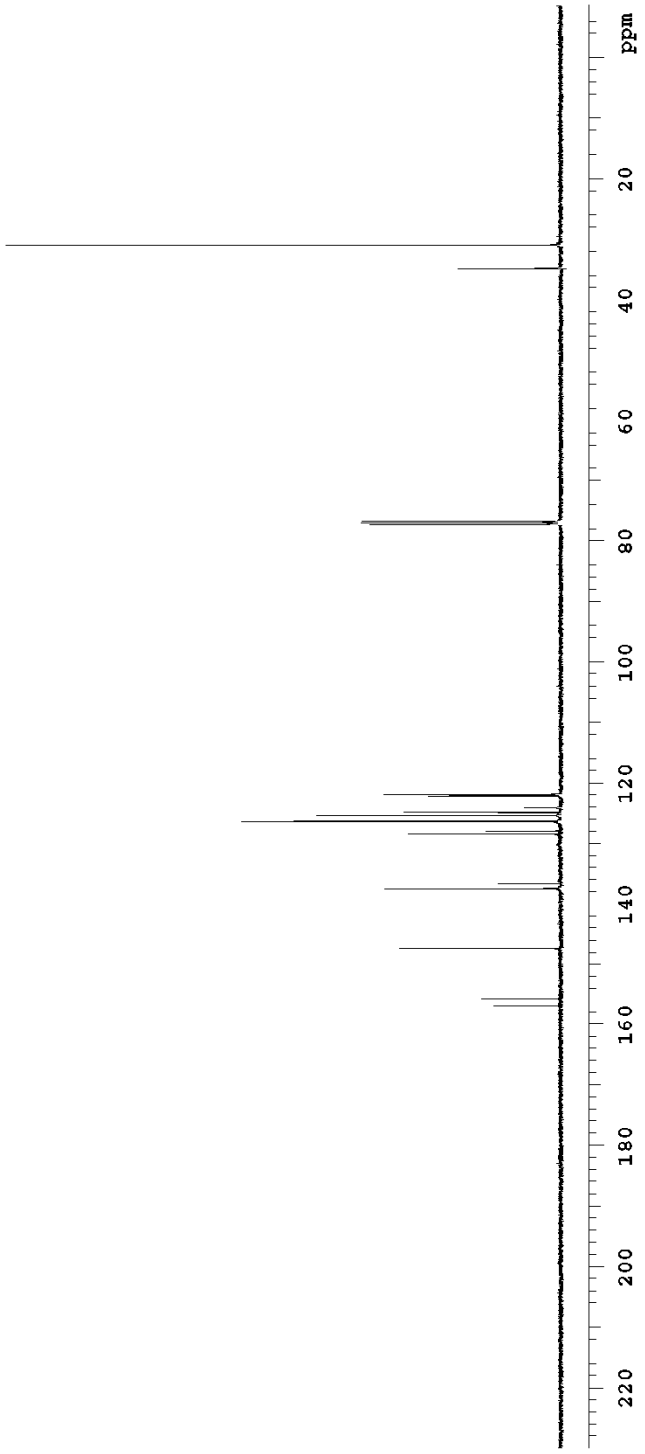
^{1}H NMR ($CDCl_3$, 23 ºC) of S14



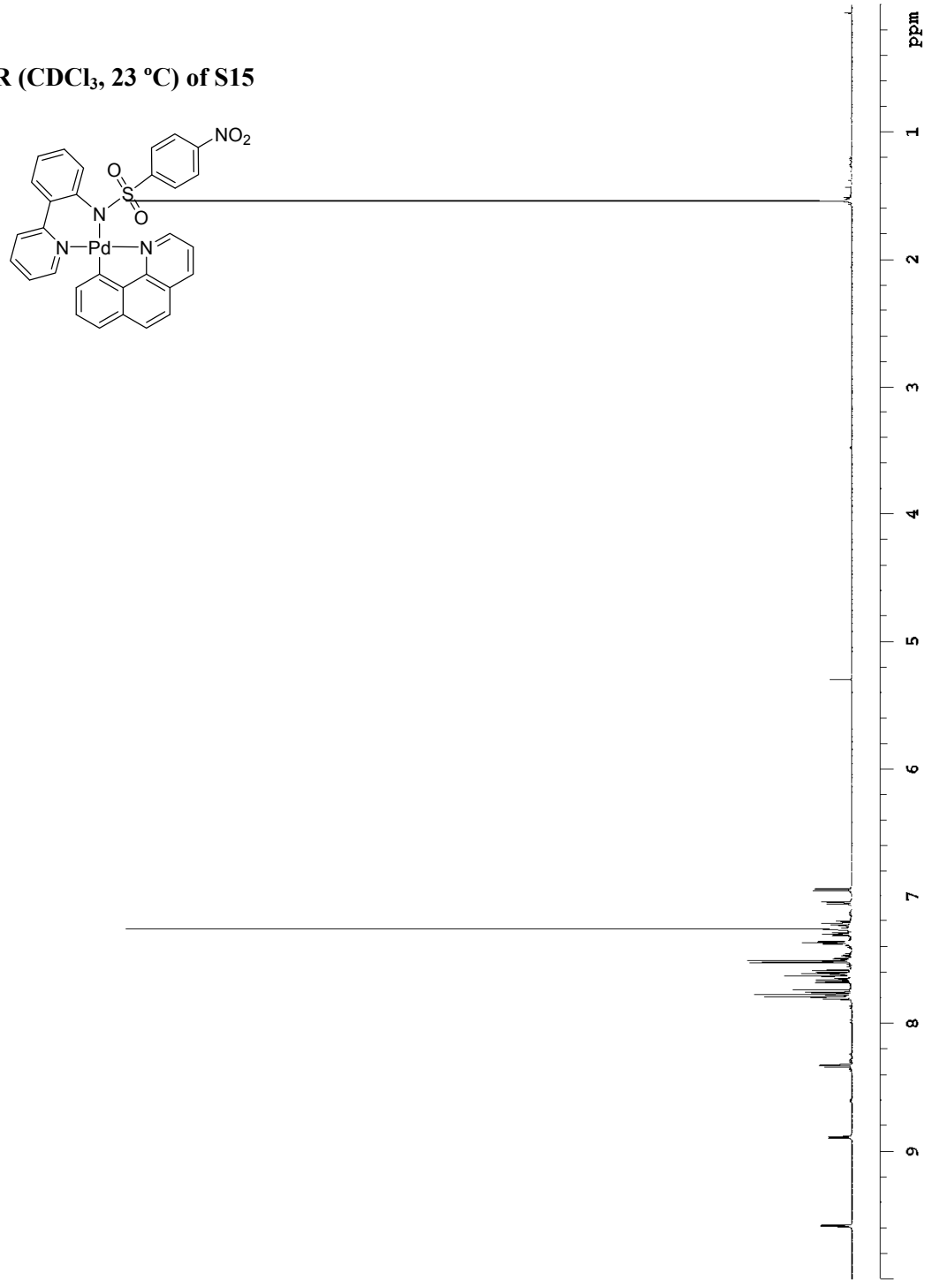


^{13}C NMR ($CDCl_3$, 23 ºC) of S14

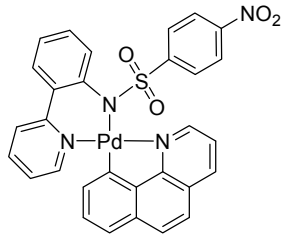




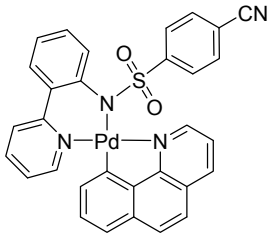
^{1}H NMR ($CDCl_3$, 23 ºC) of S15

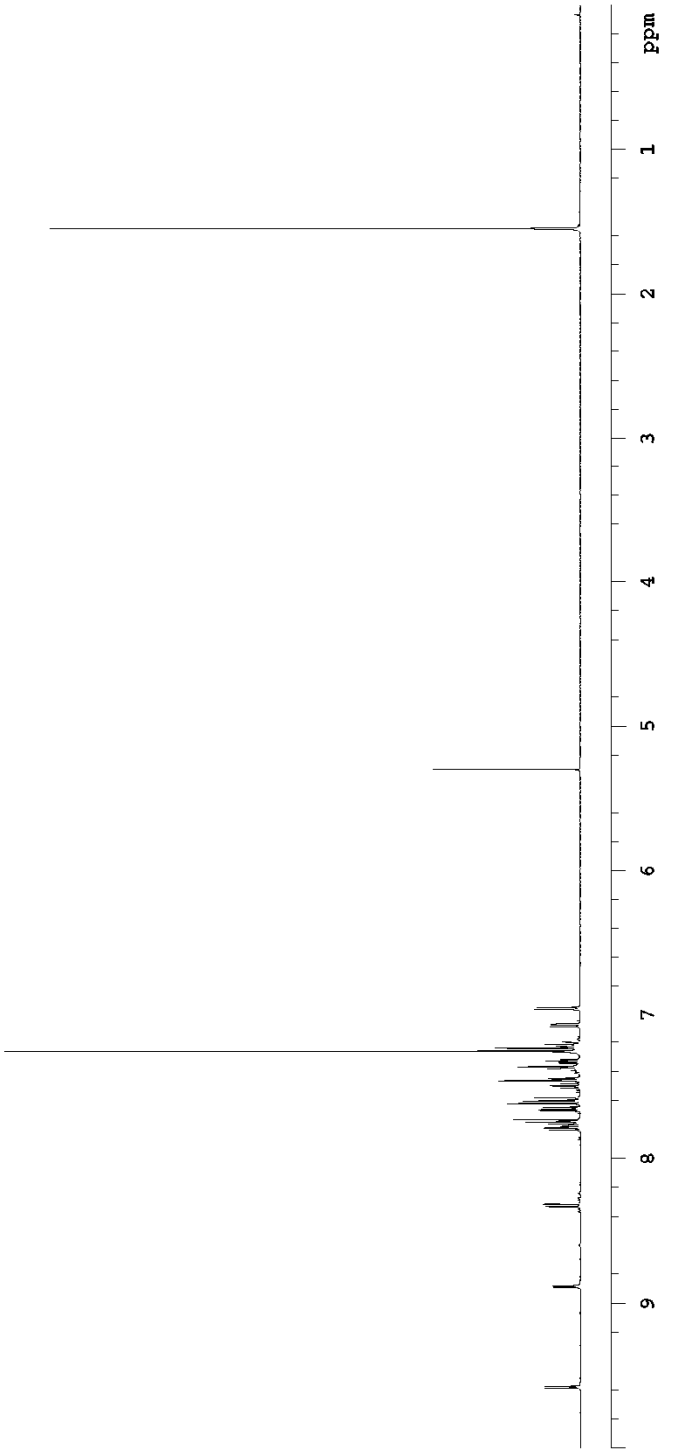


^{13}C NMR ($CDCl_3$, 23 ºC) of S15

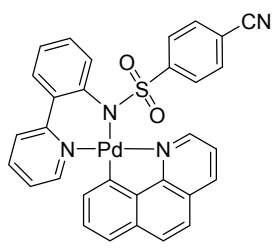


^{1}H NMR ($CDCl_3$, 23 ºC) of S16

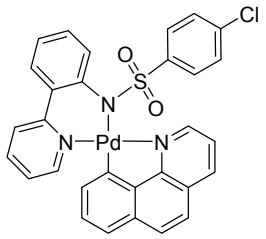


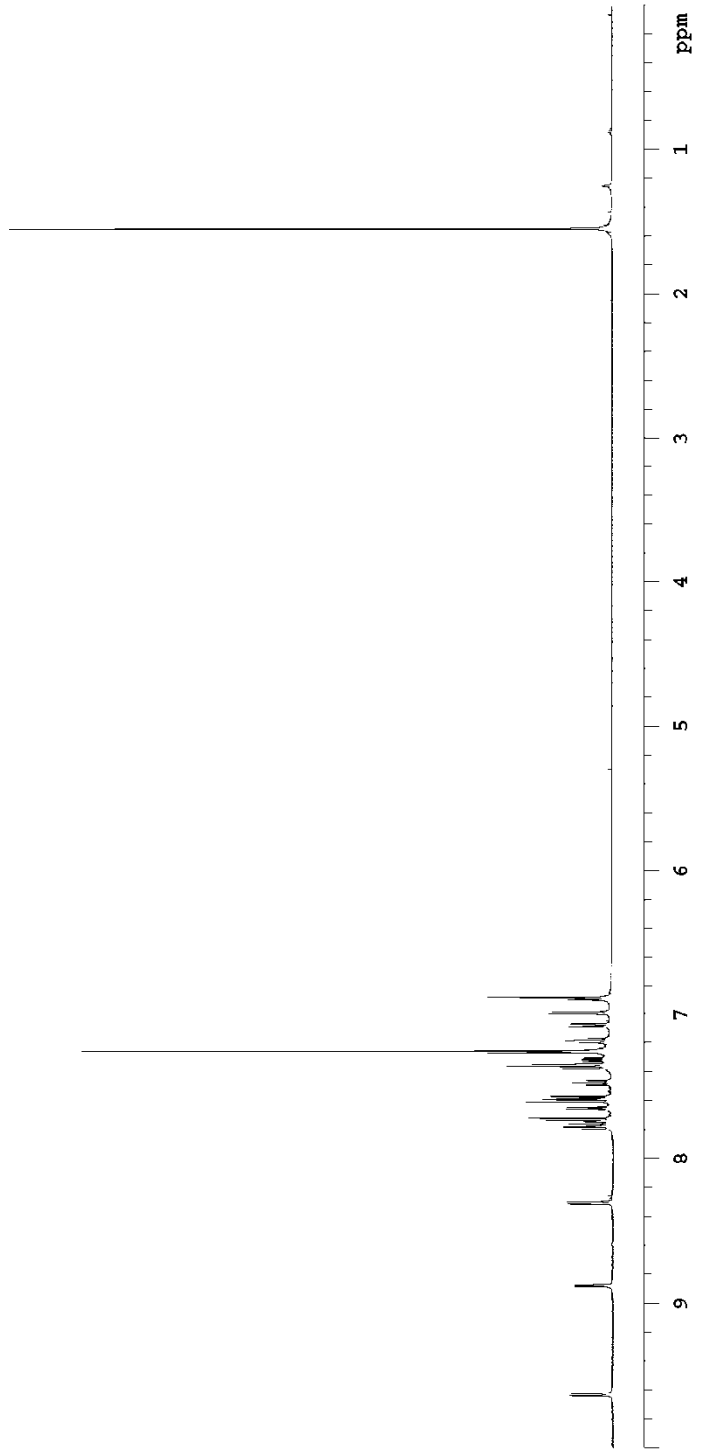


^{13}C NMR ($CDCl_3$, 23 ºC) of S16

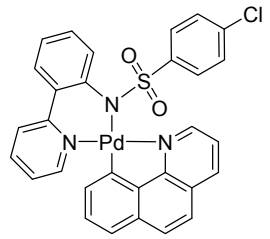


^{1}H NMR ($CDCl_3$, 23 °C) of S17

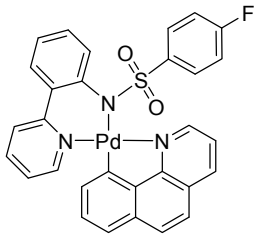


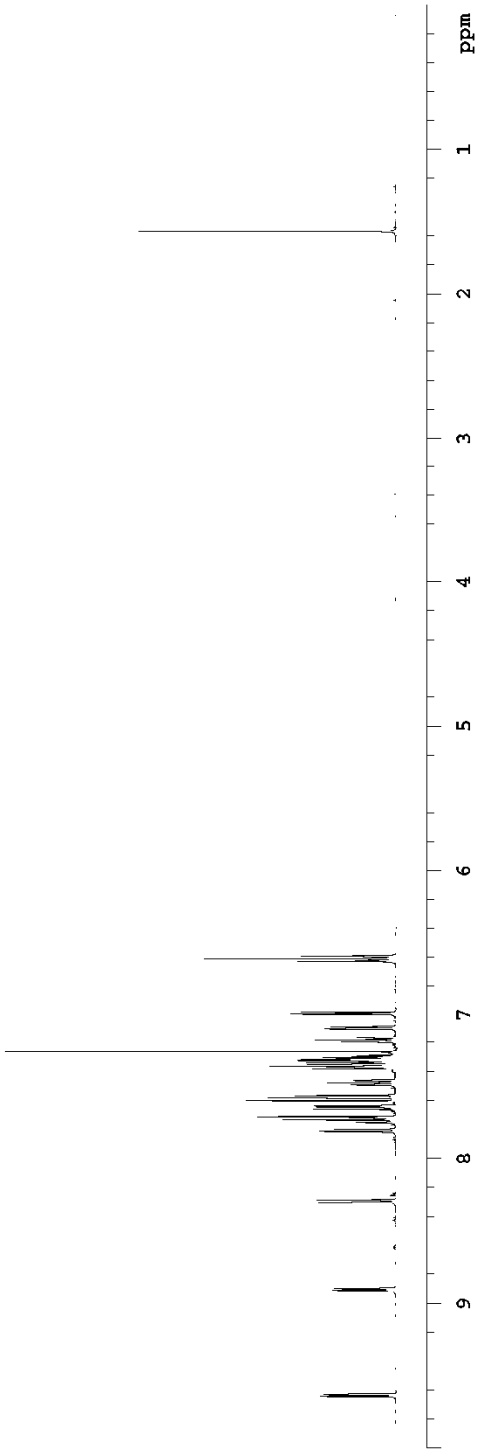


^{13}C NMR ($CDCl_3$, 23 °C) of S17

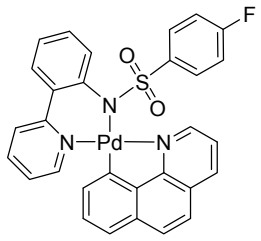


^{1}H NMR ($CDCl_3$, 23 °C) of S18

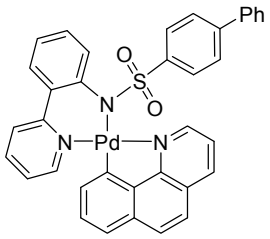


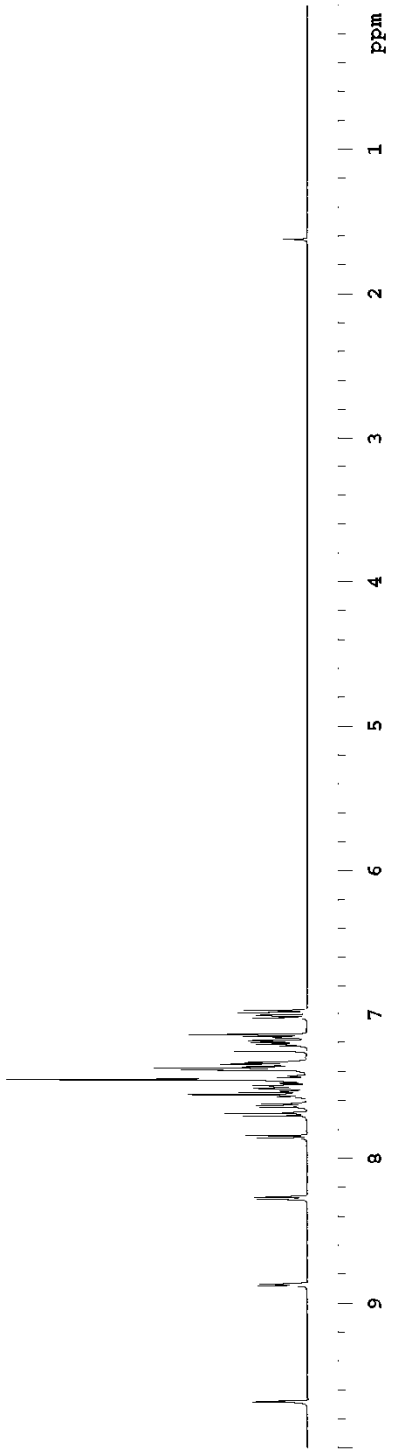


^{13}C NMR ($CDCl_3$, 23 ºC) of S18

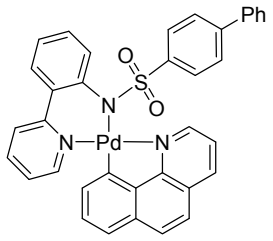


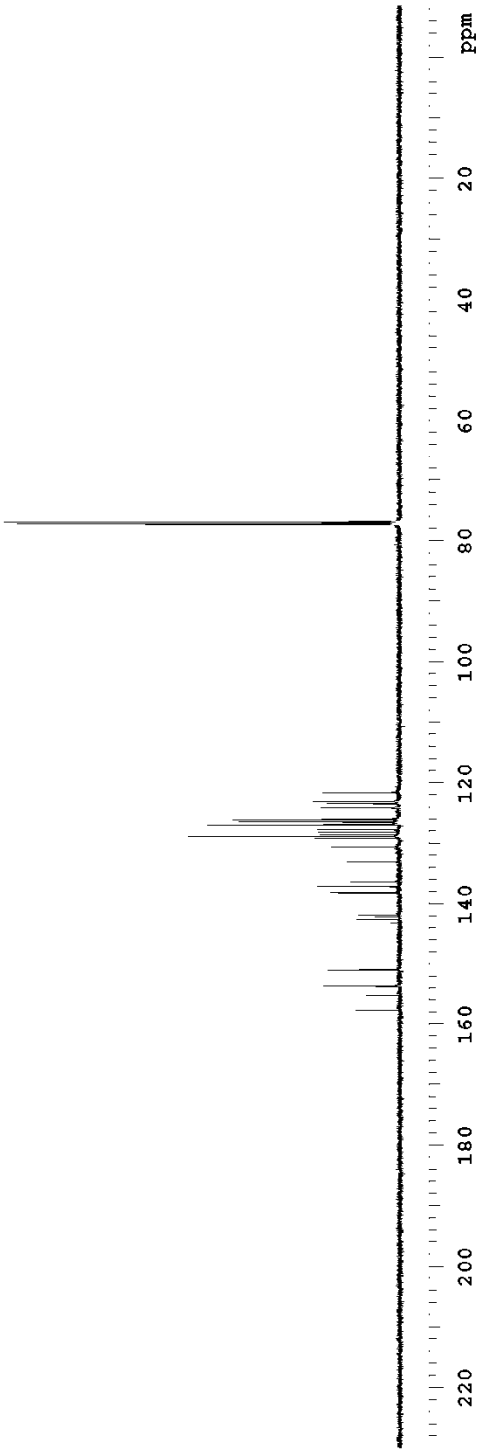
^{1}H NMR ($CDCl_3$, 23 °C) of S19



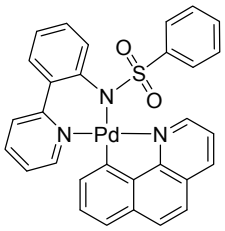


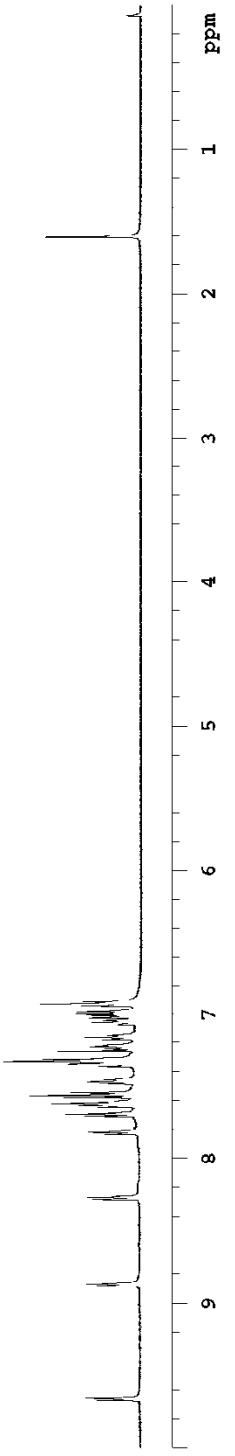
^{13}C NMR ($CDCl_3$, 23 ºC) of S19



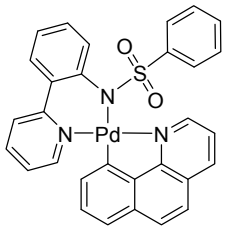


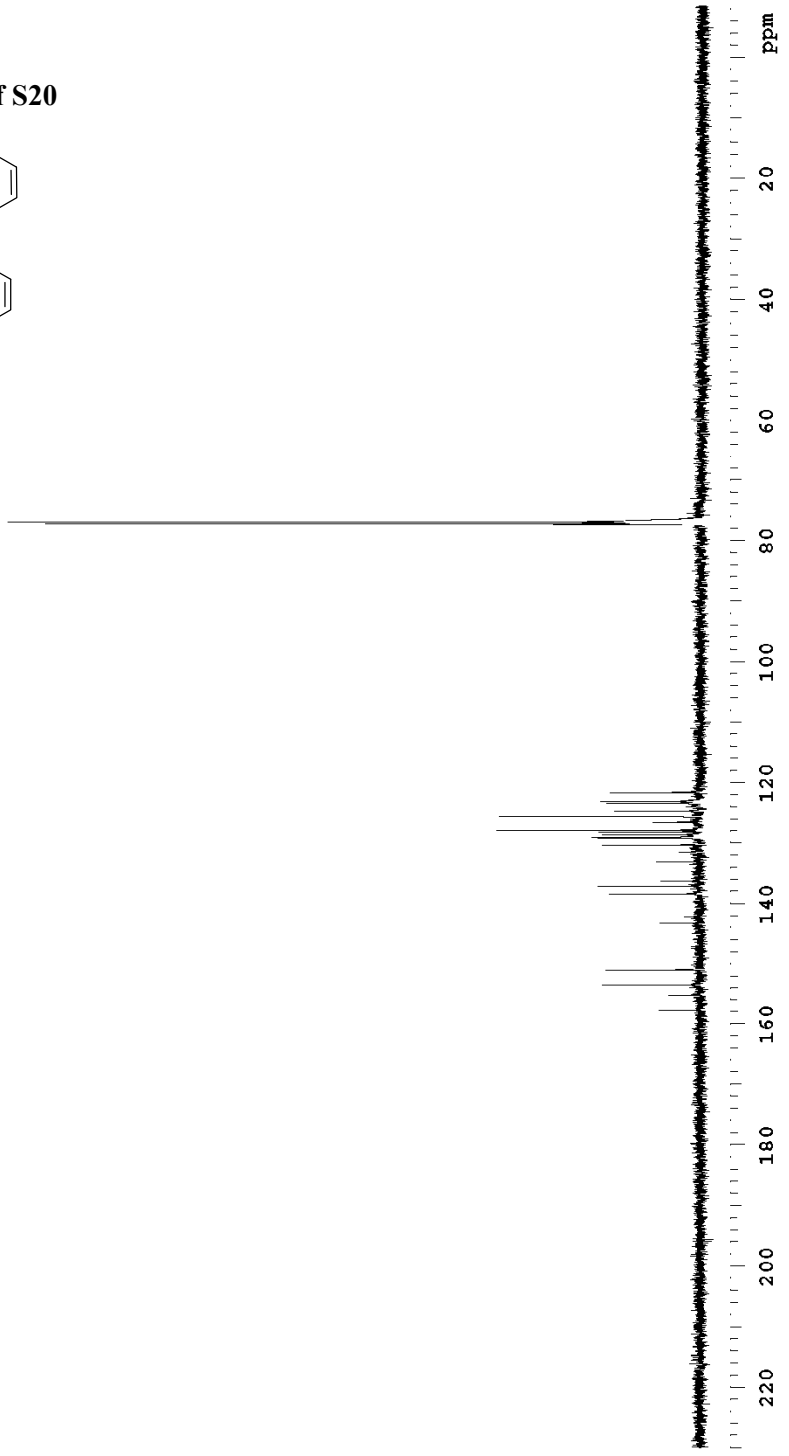
^{1}H NMR ($CDCl_3$, 23 ºC) of S20



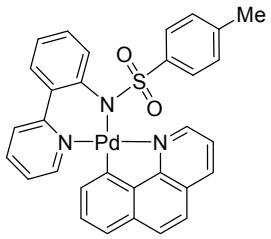


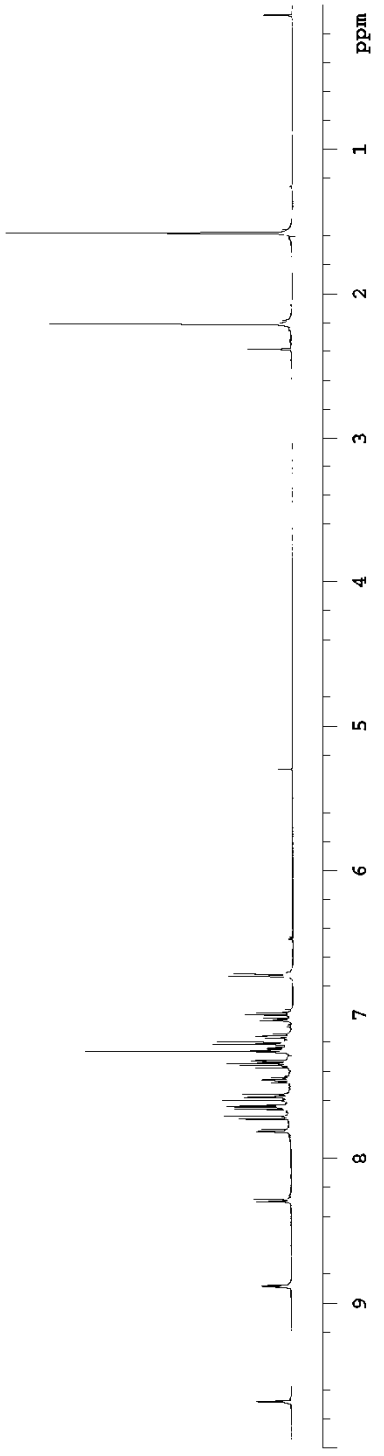
^{13}C NMR ($CDCl_3$, 23 ºC) of S20



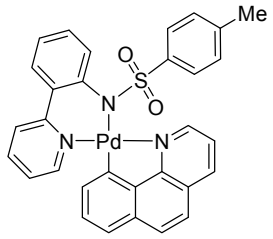


^{1}H NMR ($CDCl_3$, 23 °C) of S21

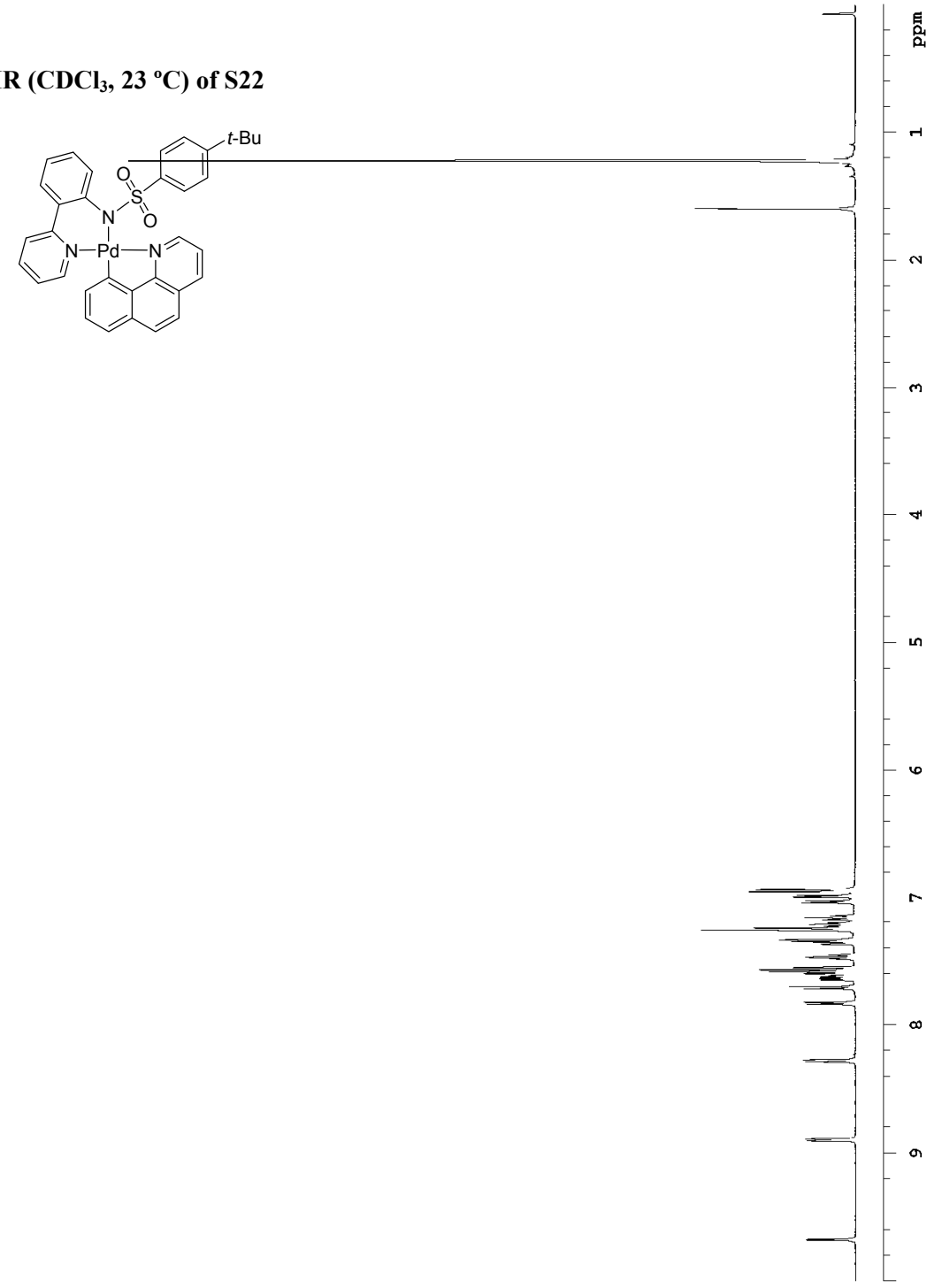




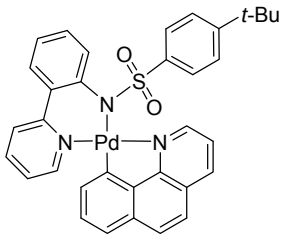
^{13}C NMR ($CDCl_3$, 23 ºC) of S21



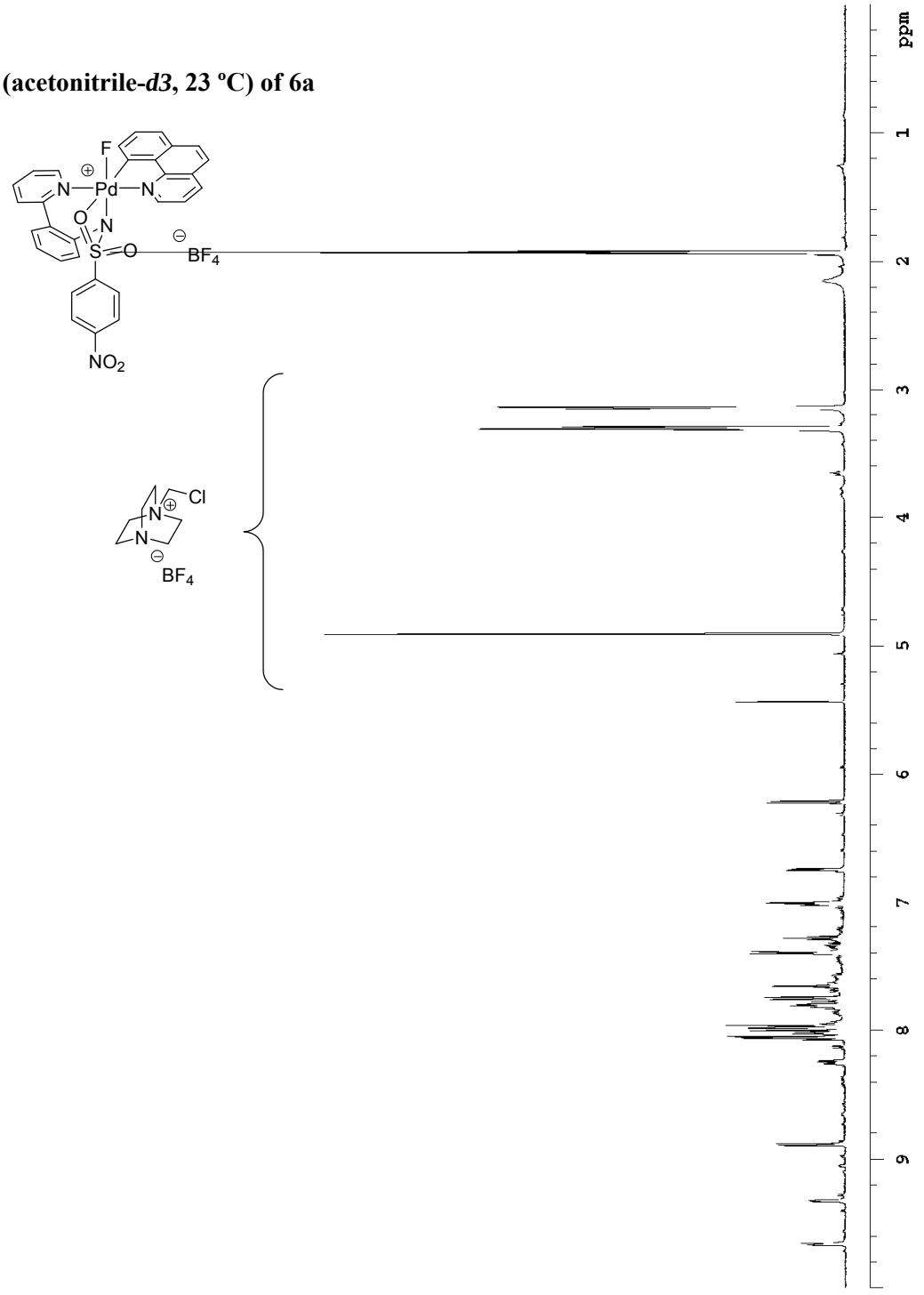
^{1}H NMR ($CDCl_3$, 23 °C) of S22



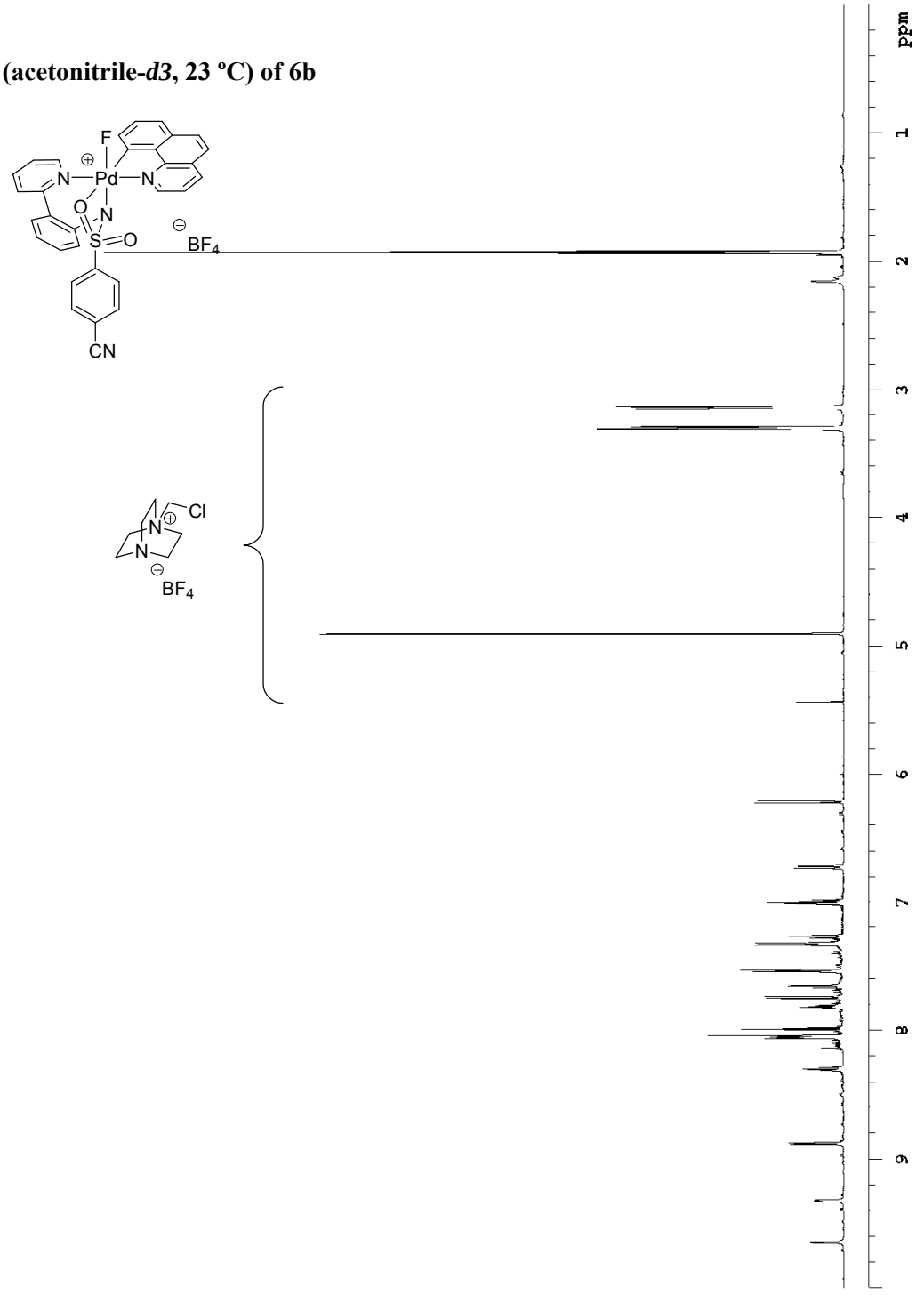
^{13}C NMR ($CDCl_3$, 23 °C) of S22



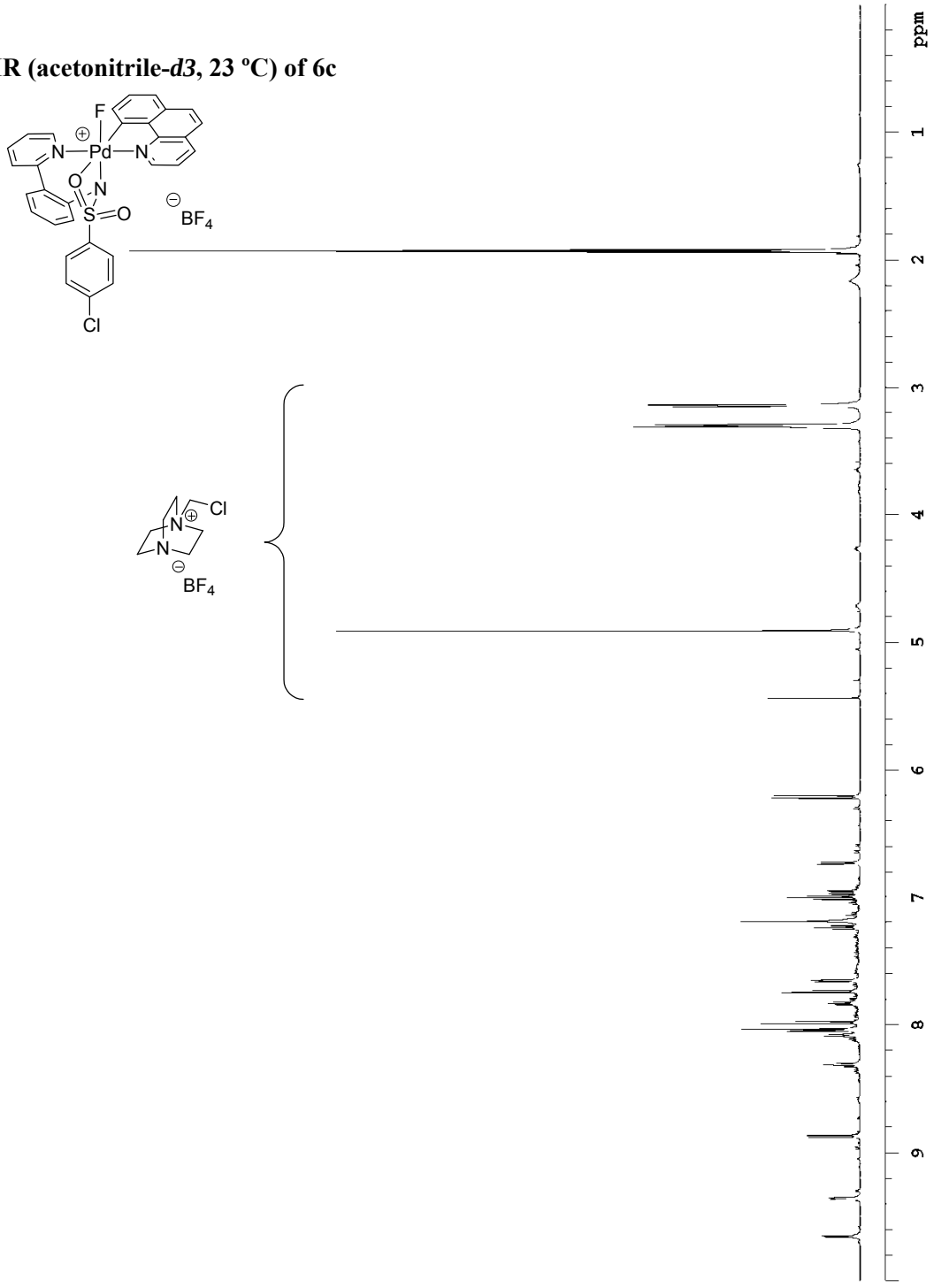
^{1}H NMR (acetonitrile-*d3*, 23 ºC) of 6a



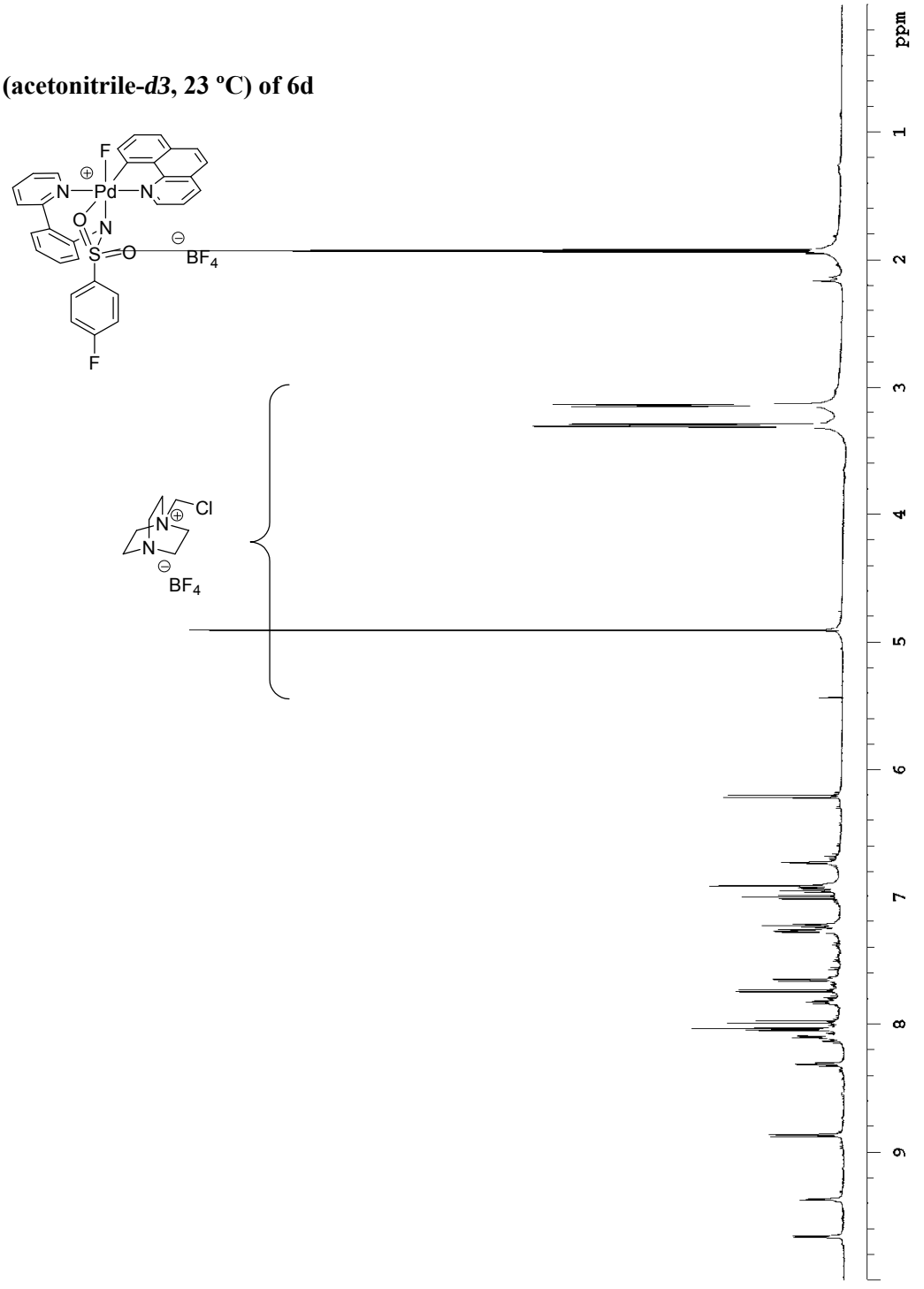
^{1}H NMR (acetonitrile-*d3*, 23 ºC) of 6b



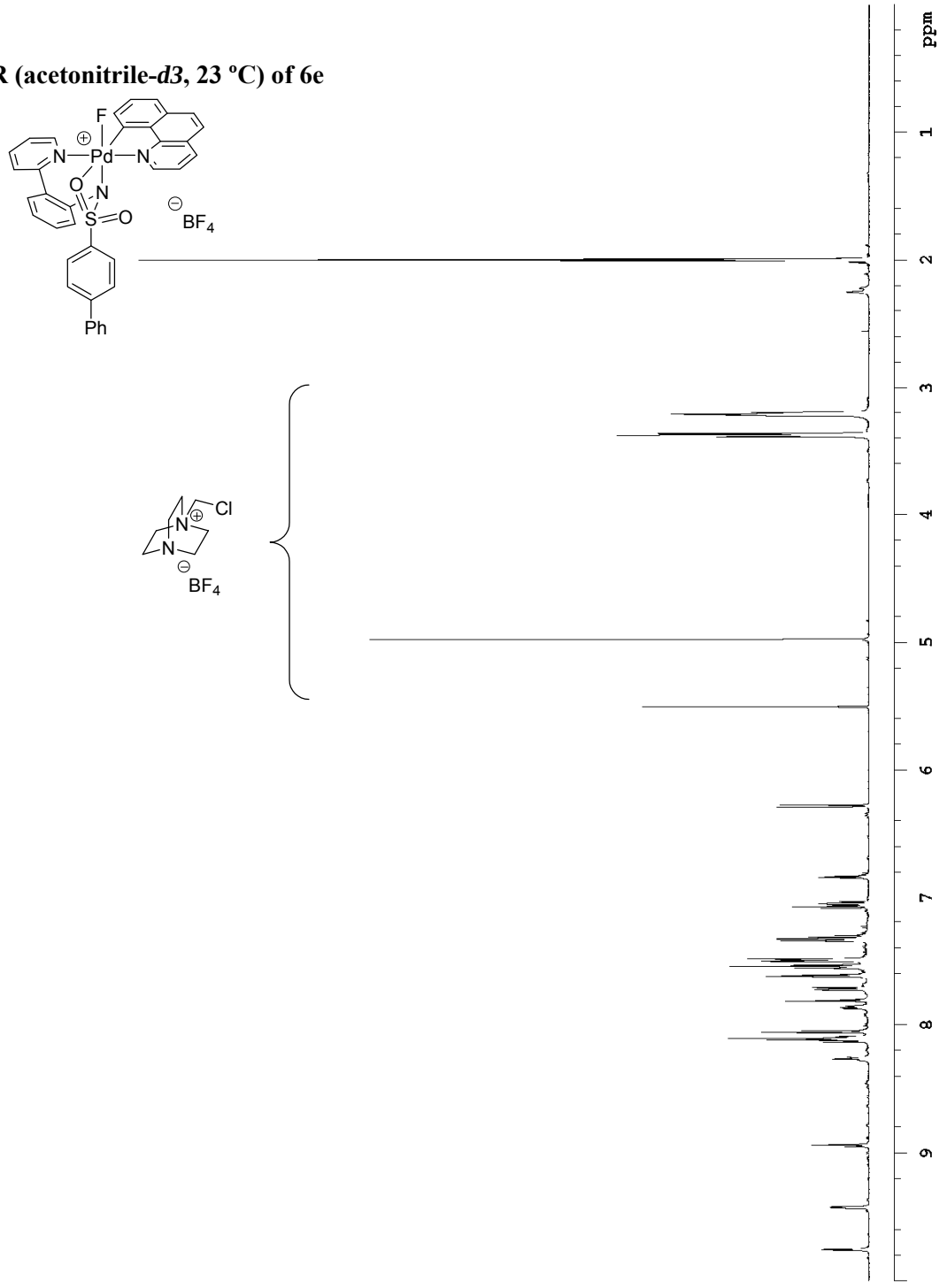
^{1}H NMR (acetonitrile-*d3*, 23 °C) of 6c



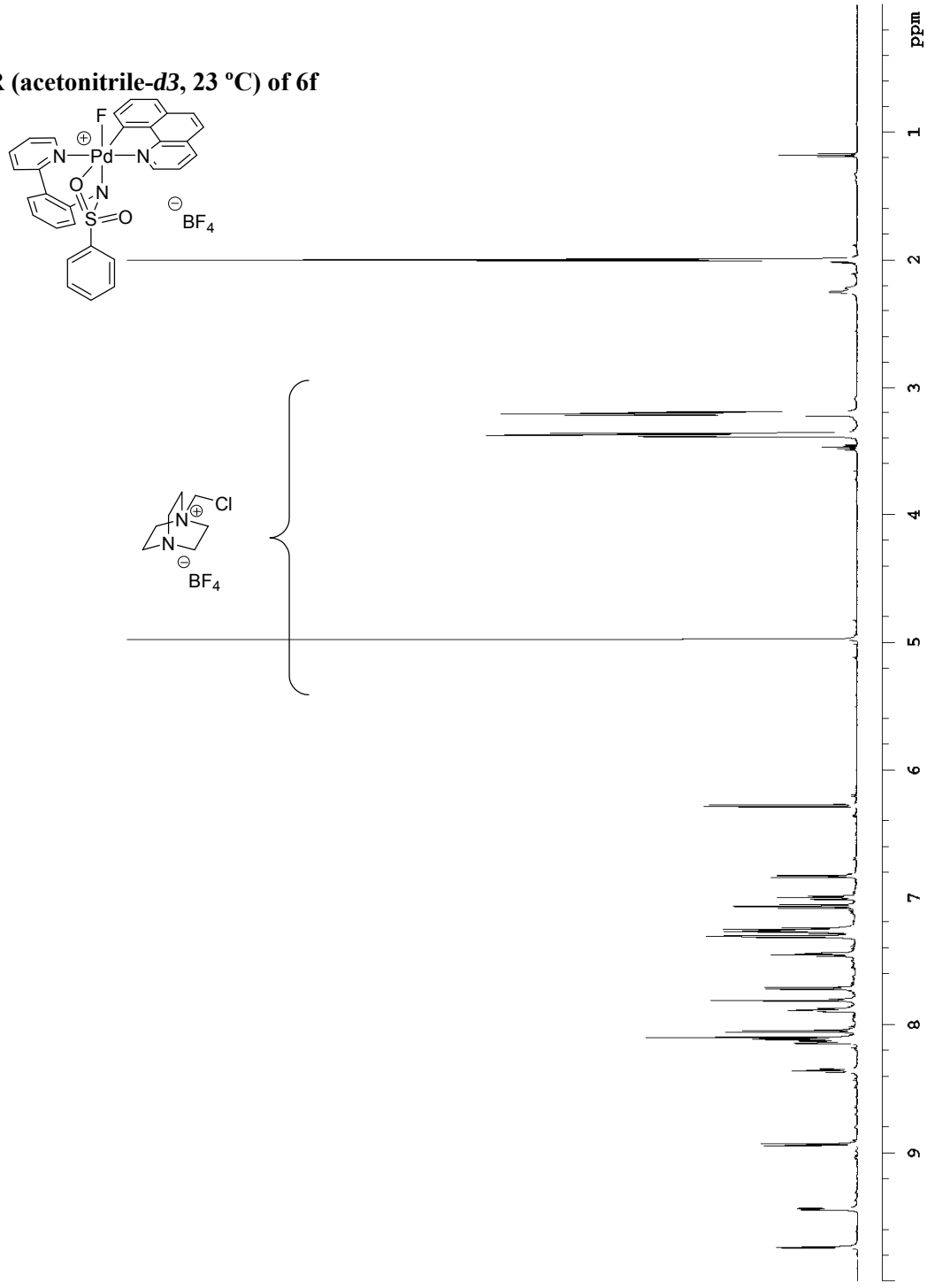
^{1}H NMR (acetonitrile-*d3*, 23 °C) of 6d



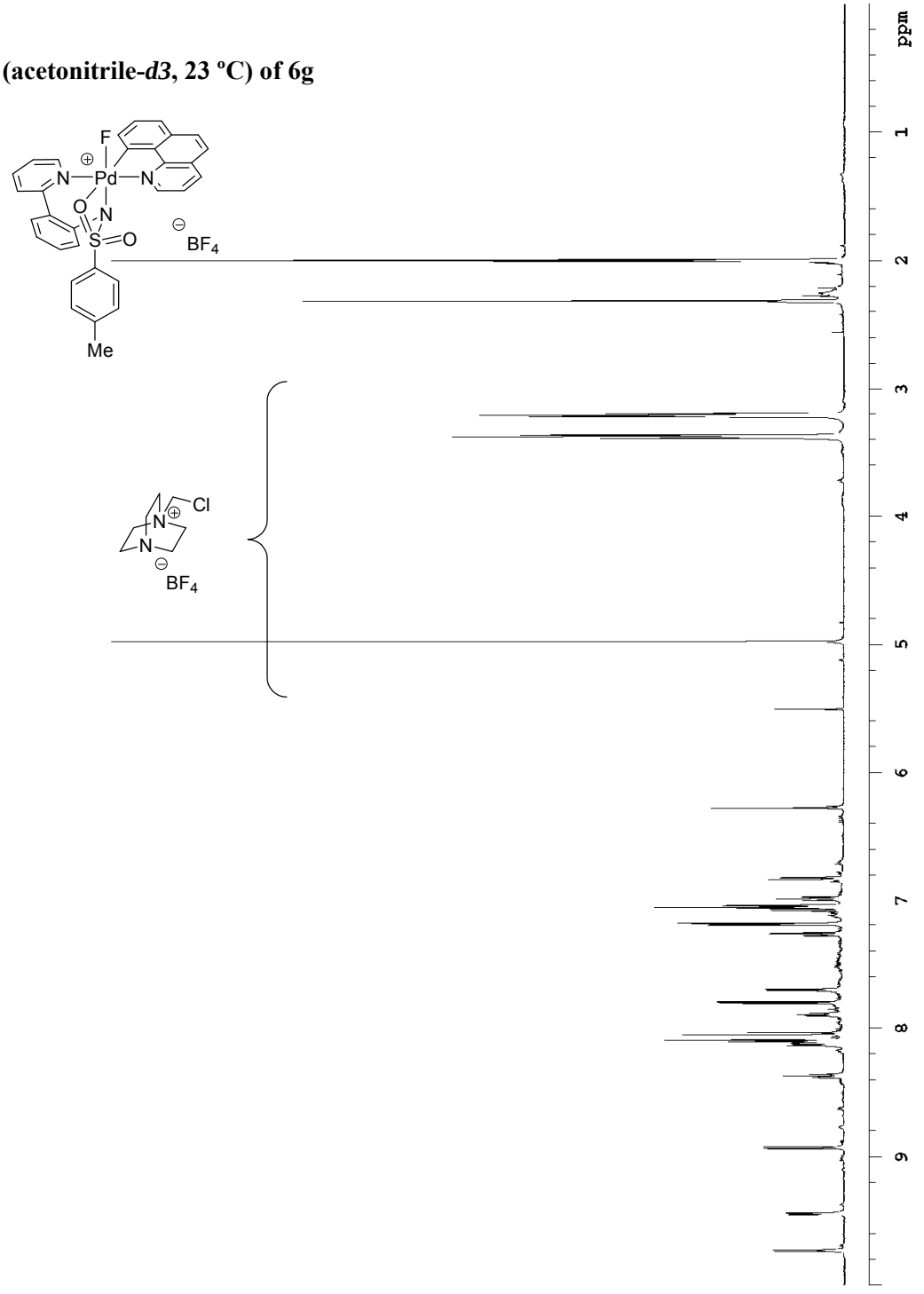
^{1}H NMR (acetonitrile-*d3*, 23 ºC) of 6e



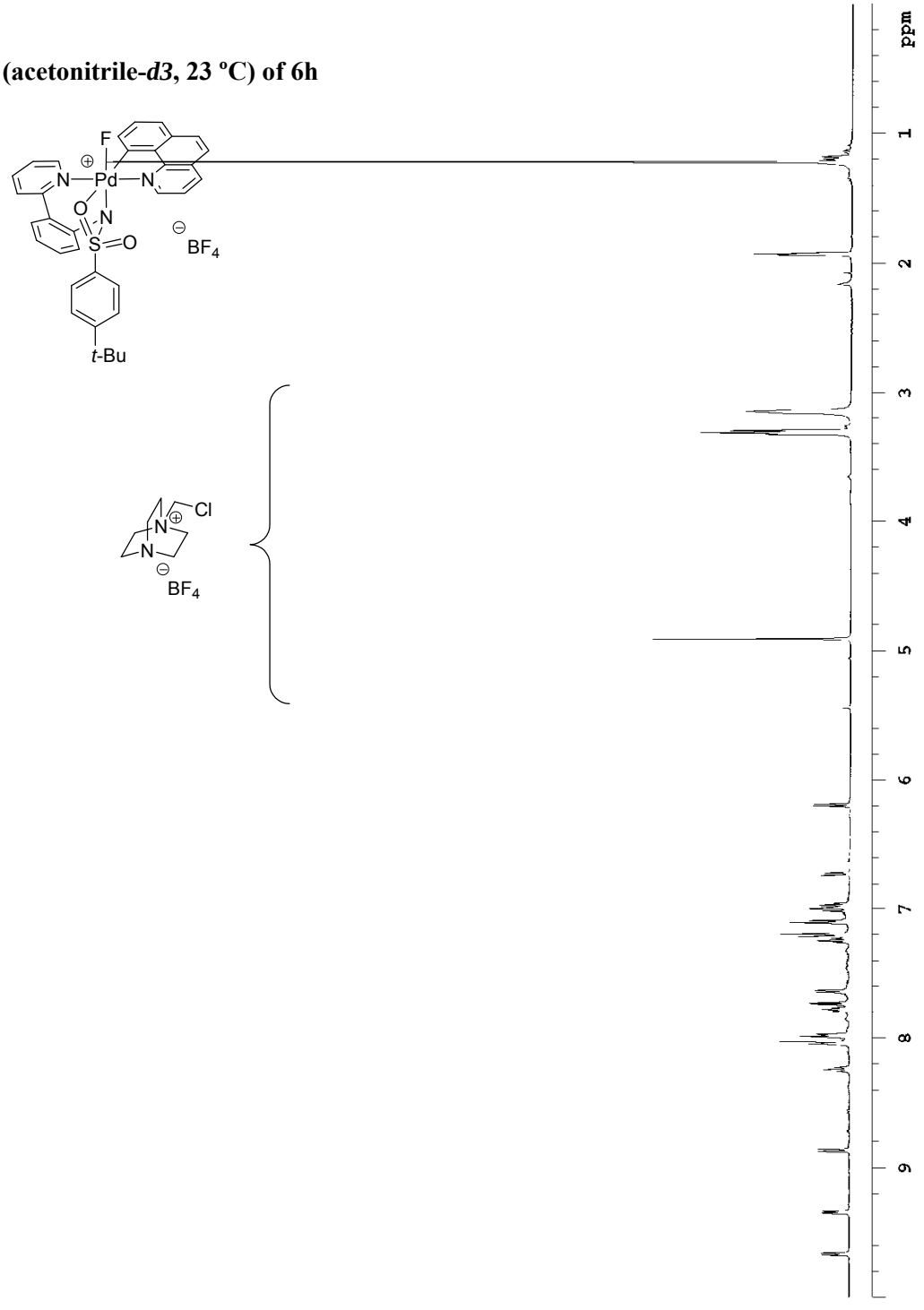
^{1}H NMR (acetonitrile-*d3*, 23 ºC) of 6f



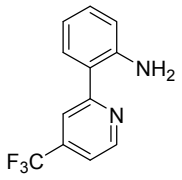
^{1}H NMR (acetonitrile-*d3*, 23 ºC) of 6g

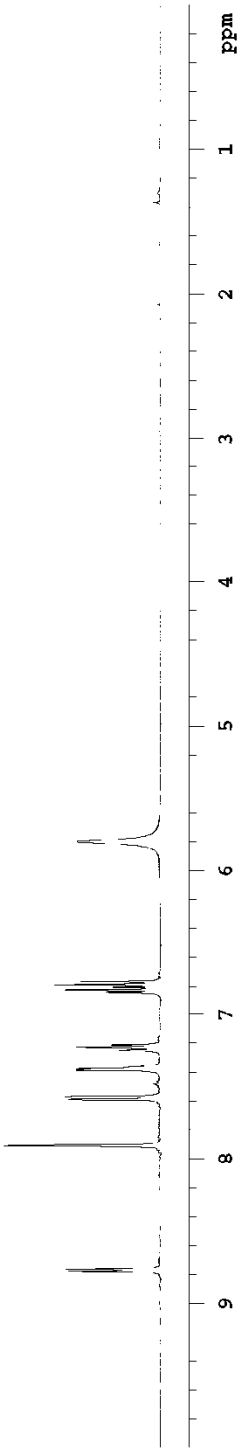


^{1}H NMR (acetonitrile-*d3*, 23 ºC) of 6h

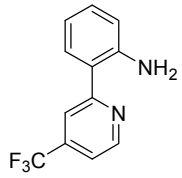


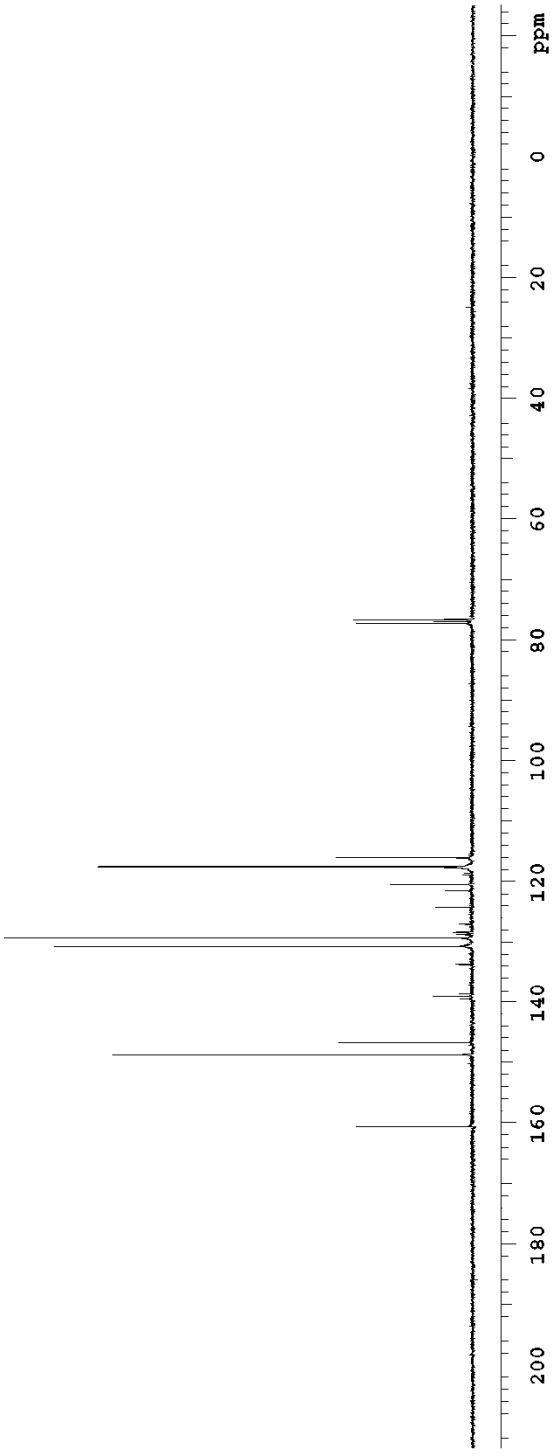
^{1}H NMR ($CDCl_3$, 23 °C) of S23



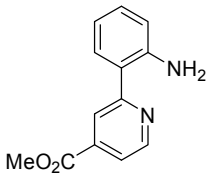


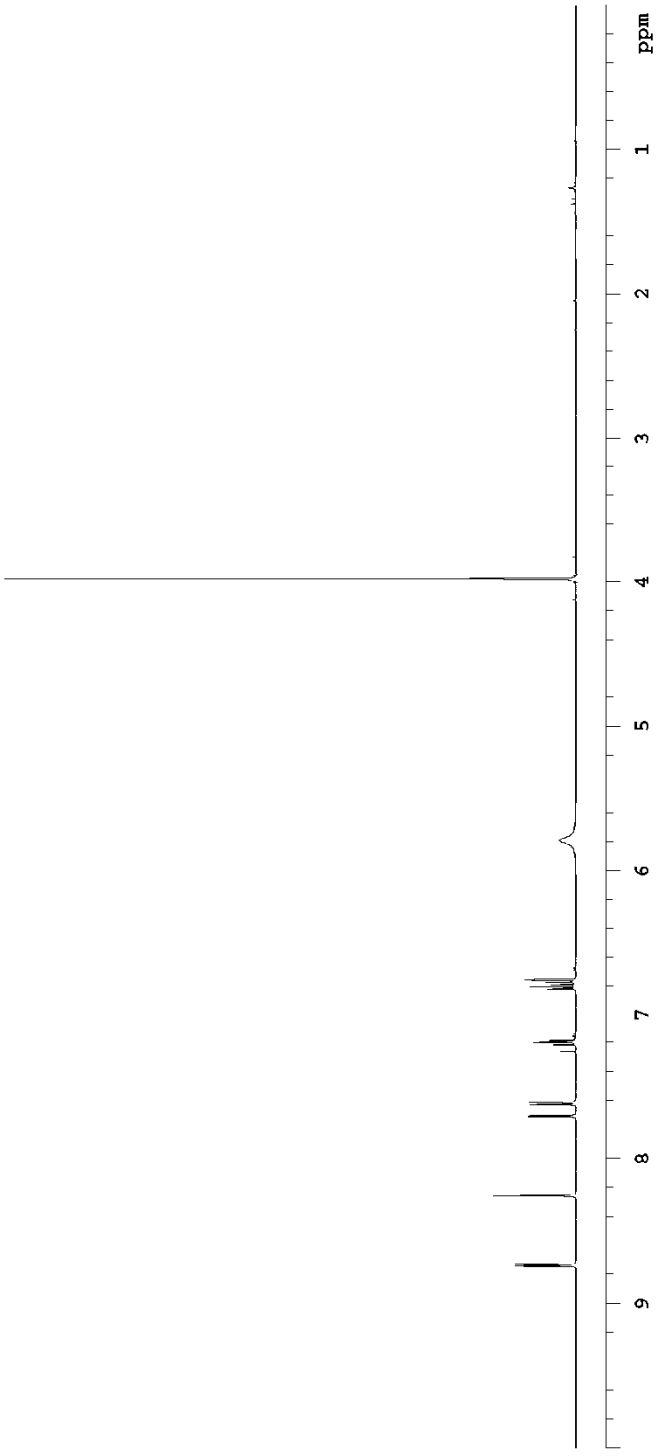
^{13}C NMR ($CDCl_3$, 23 °C) of S23



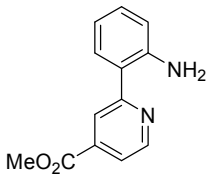


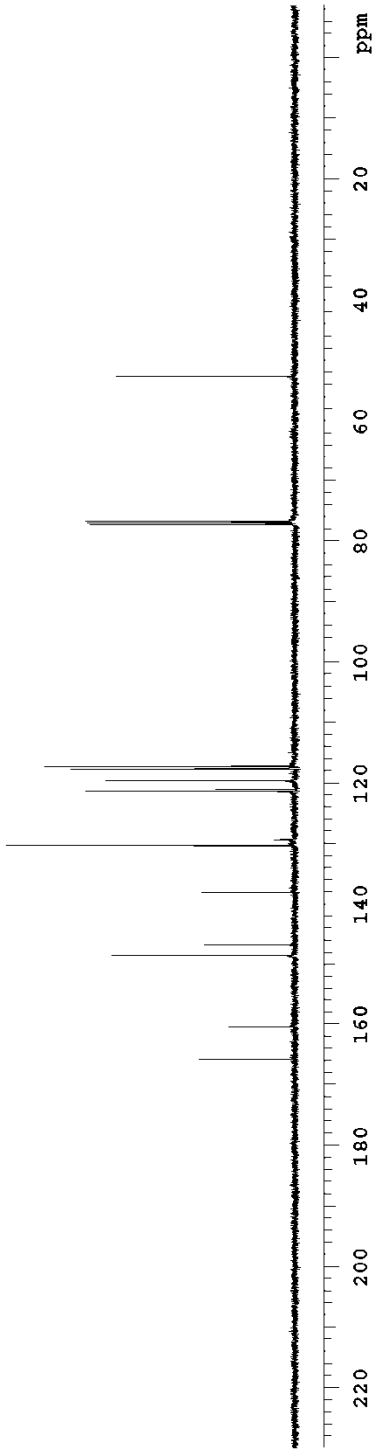
^{1}H NMR ($CDCl_3$, 23 °C) of S24



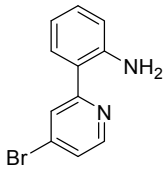


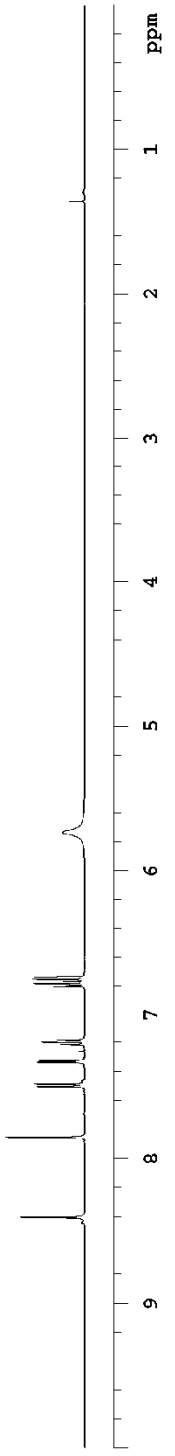
^{13}C NMR ($CDCl_3$, 23 °C) of S24



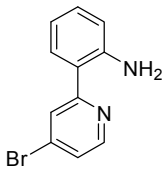


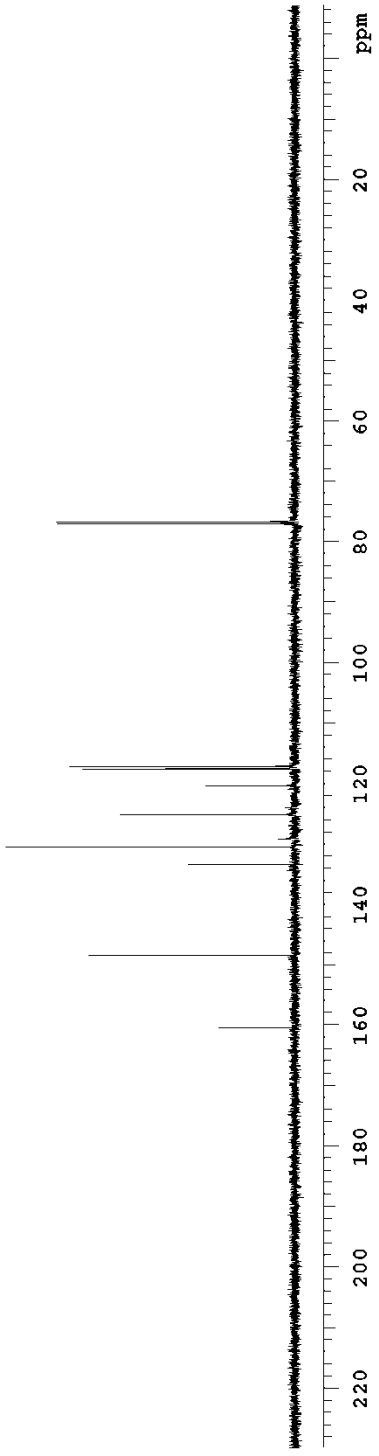
^{1}H NMR ($CDCl_3$, 23 °C) of S25



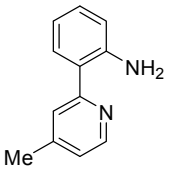


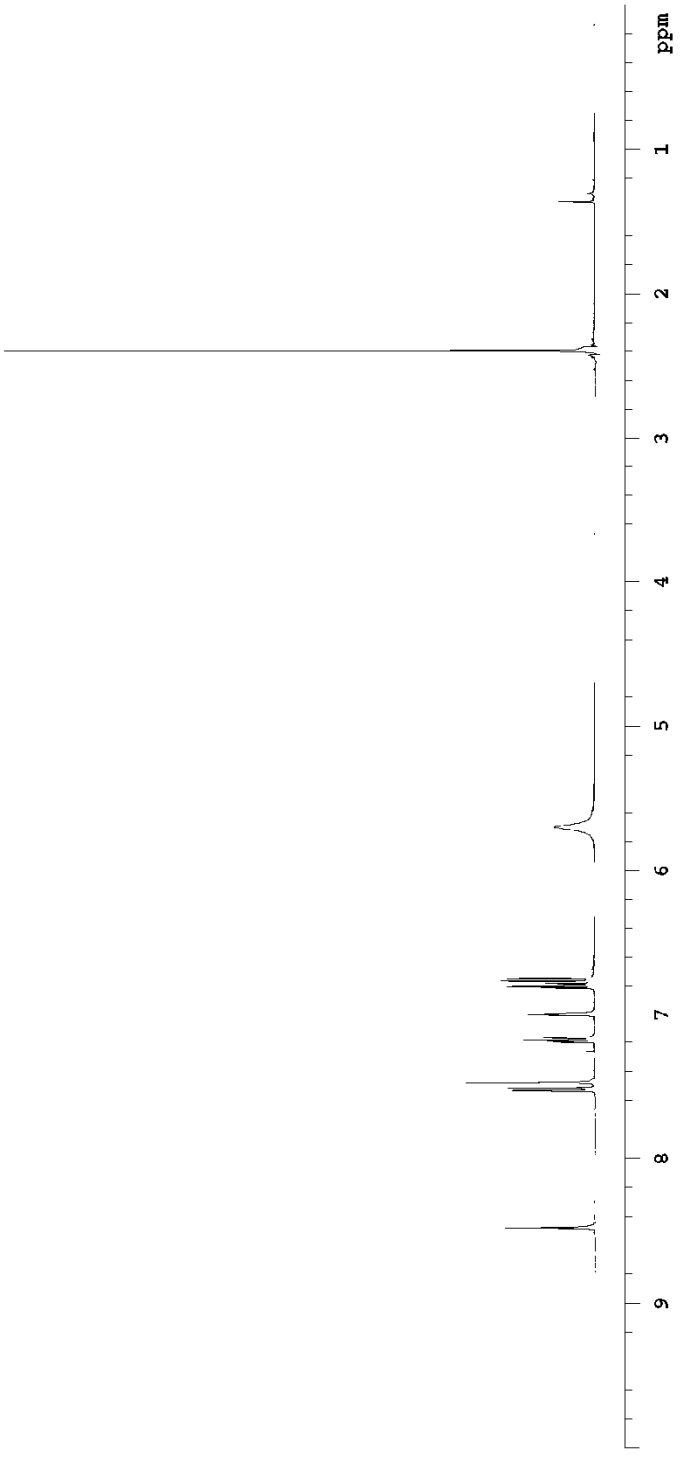
^{13}C NMR ($CDCl_3$, 23 °C) of S25



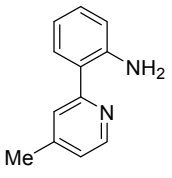


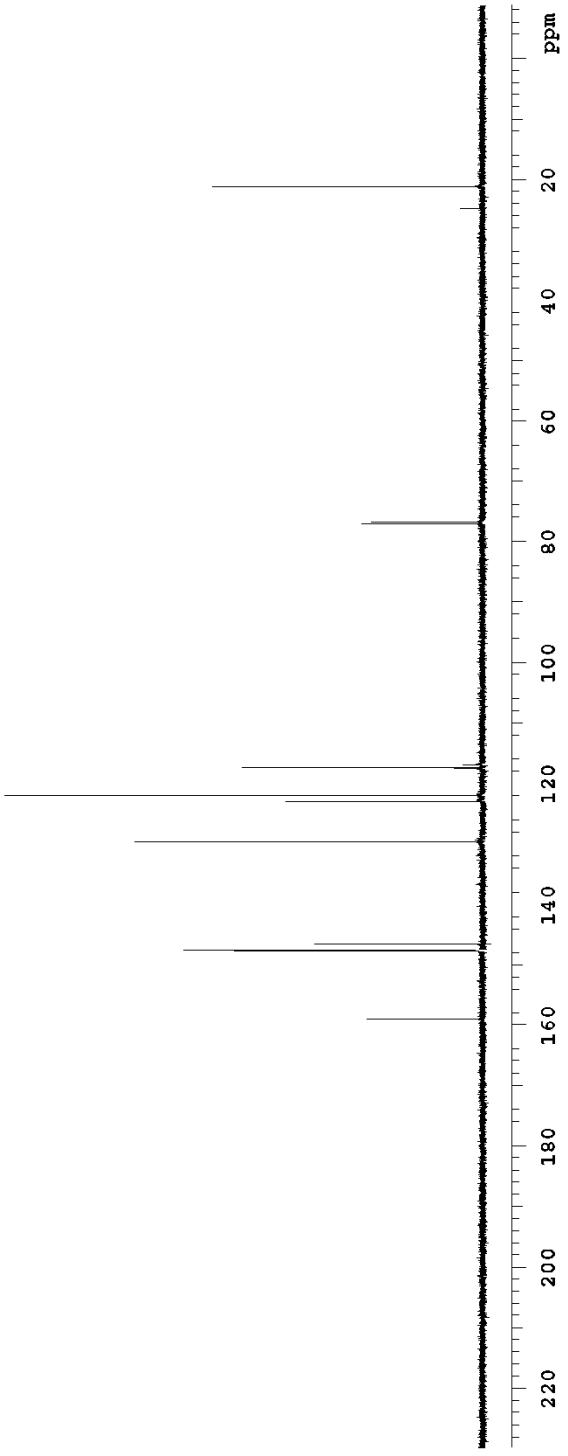
^{1}H NMR ($CDCl_3$, 23 °C) of S26



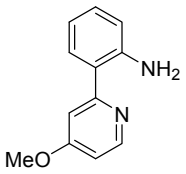


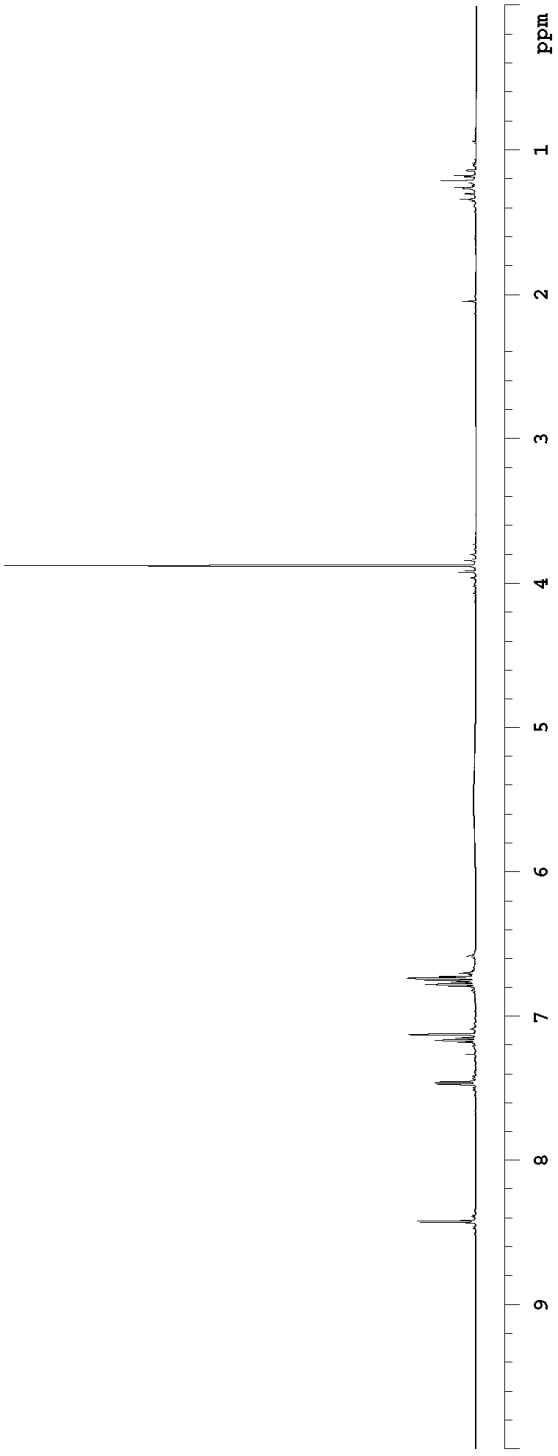
^{13}C NMR ($CDCl_3$, 23 °C) of S26



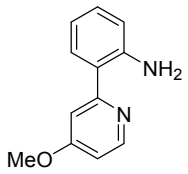


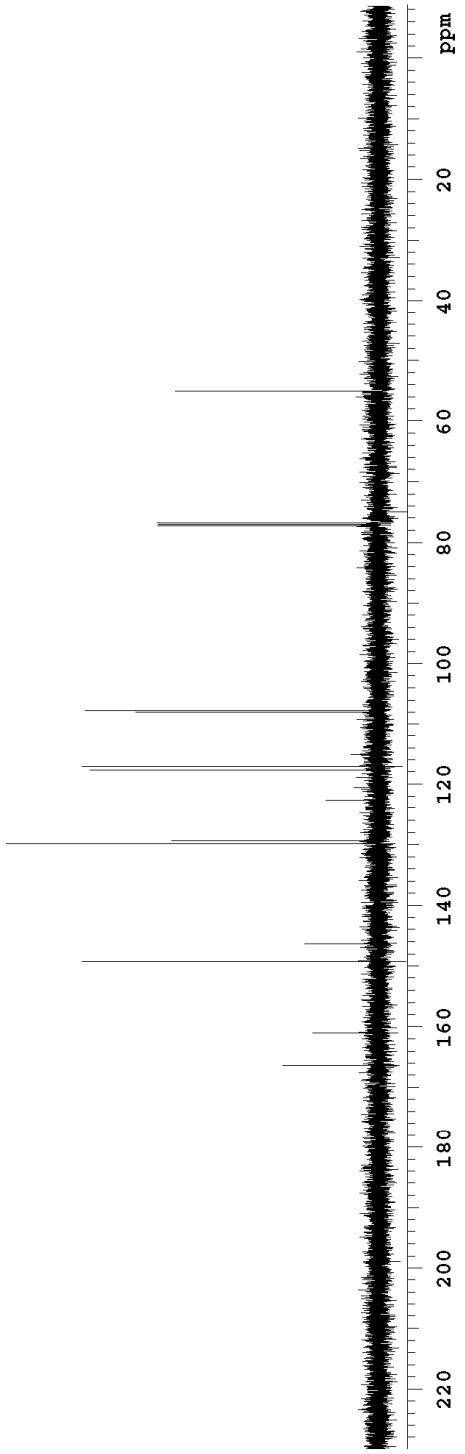
^{1}H NMR ($CDCl_3$, 23 ºC) of S27



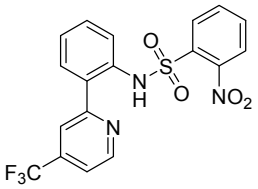


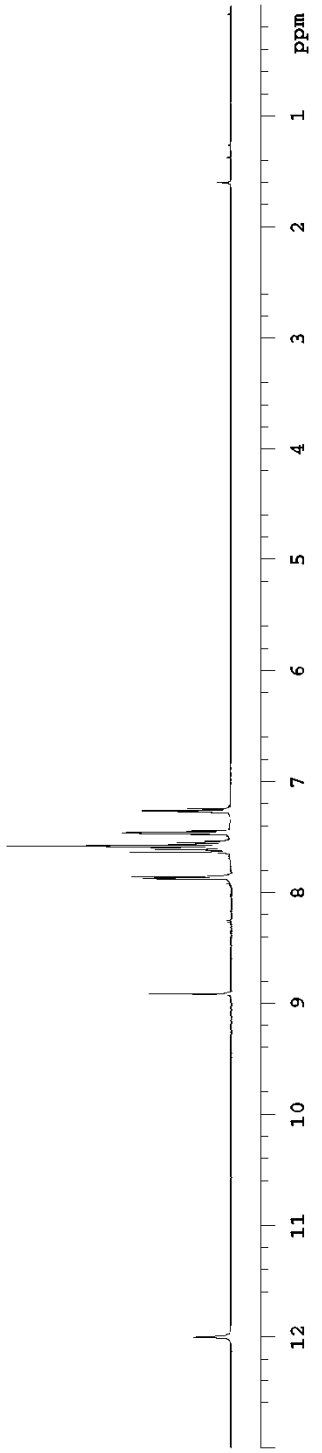
^{13}C NMR ($CDCl_3$, 23 °C) of S27



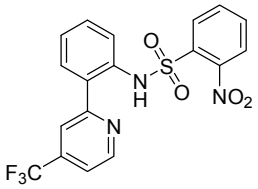


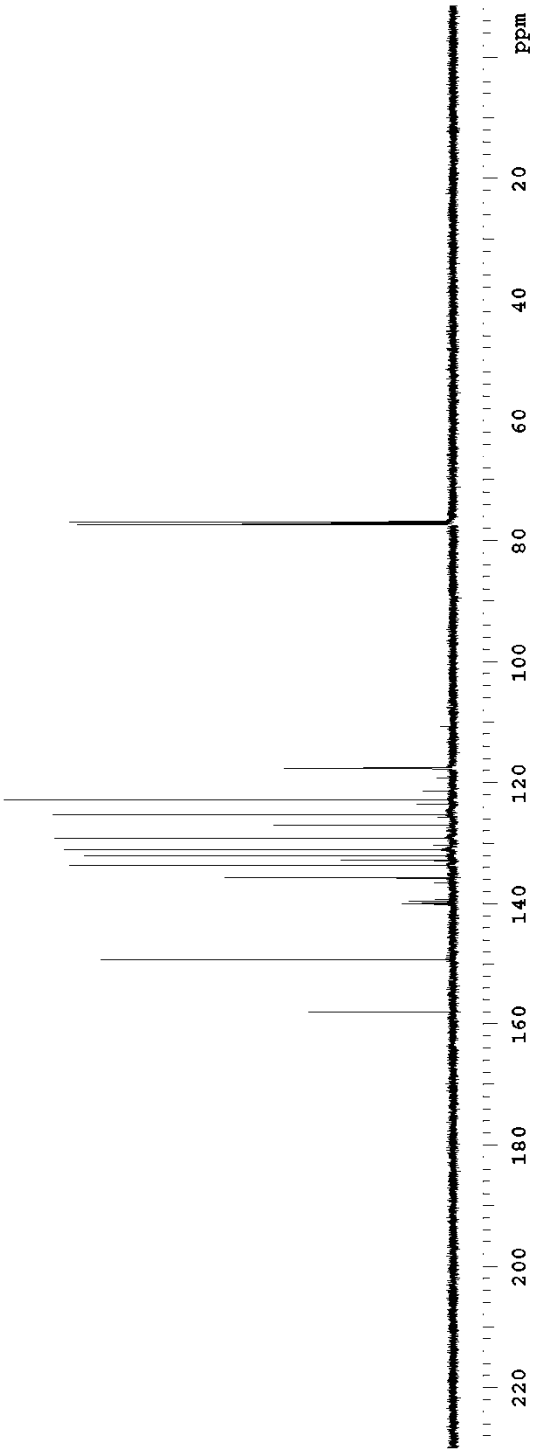
^{1}H NMR ($CDCl_3$, 23 ºC) of S28



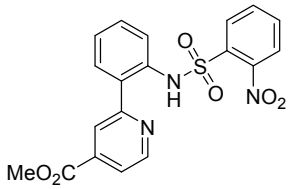


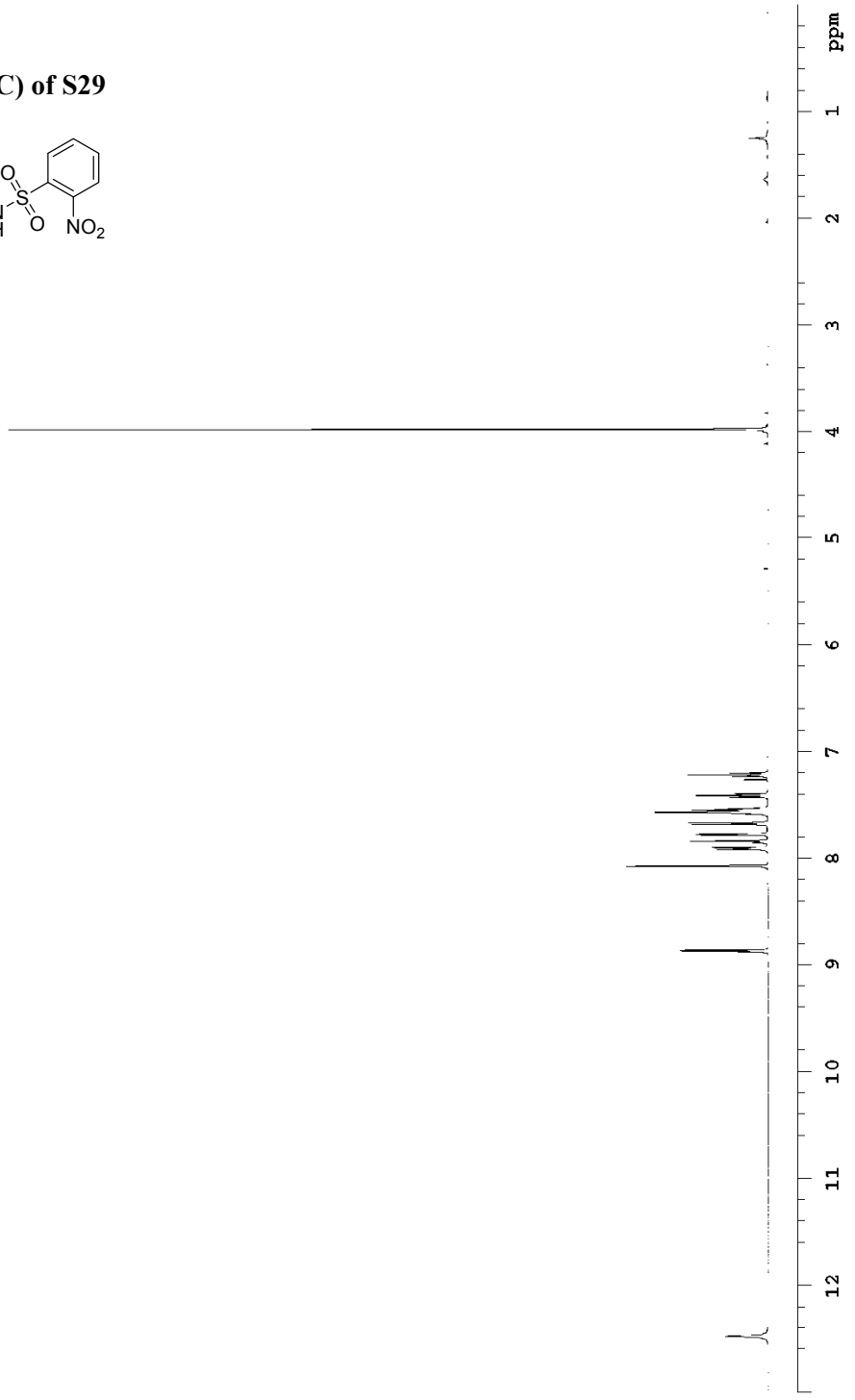
^{13}C NMR ($CDCl_3$, 23 °C) of S28



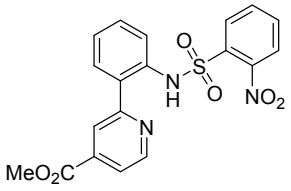


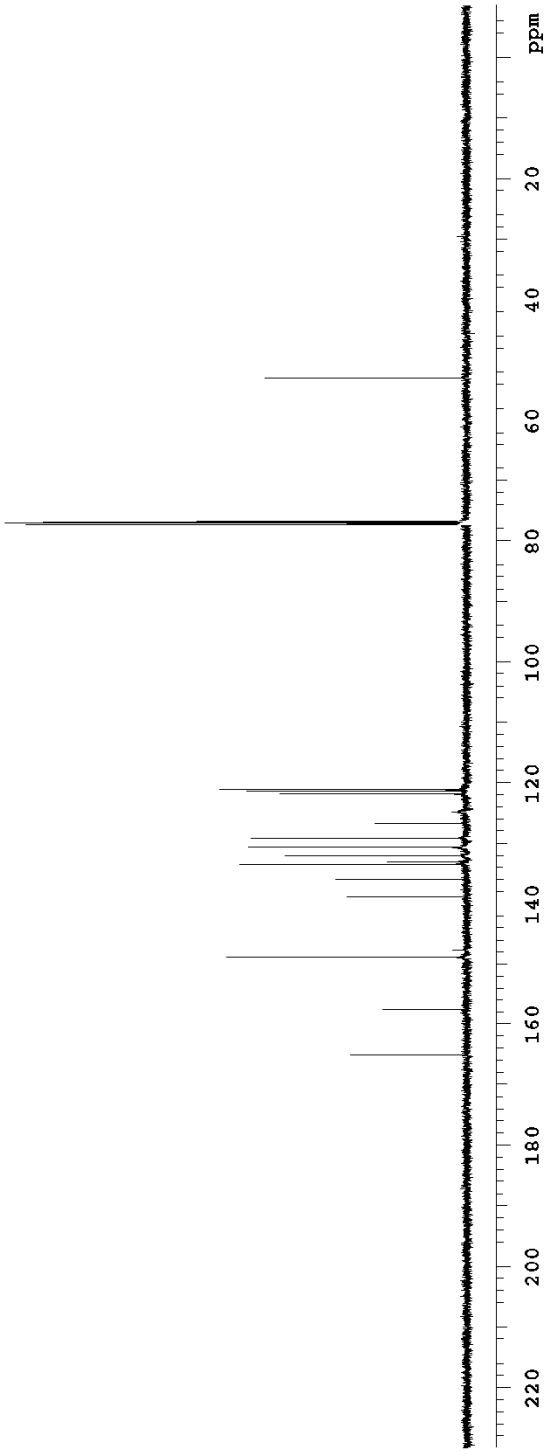
^{1}H NMR ($CDCl_3$, 23 ºC) of S29



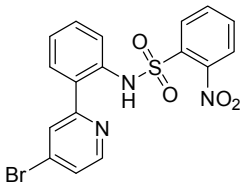


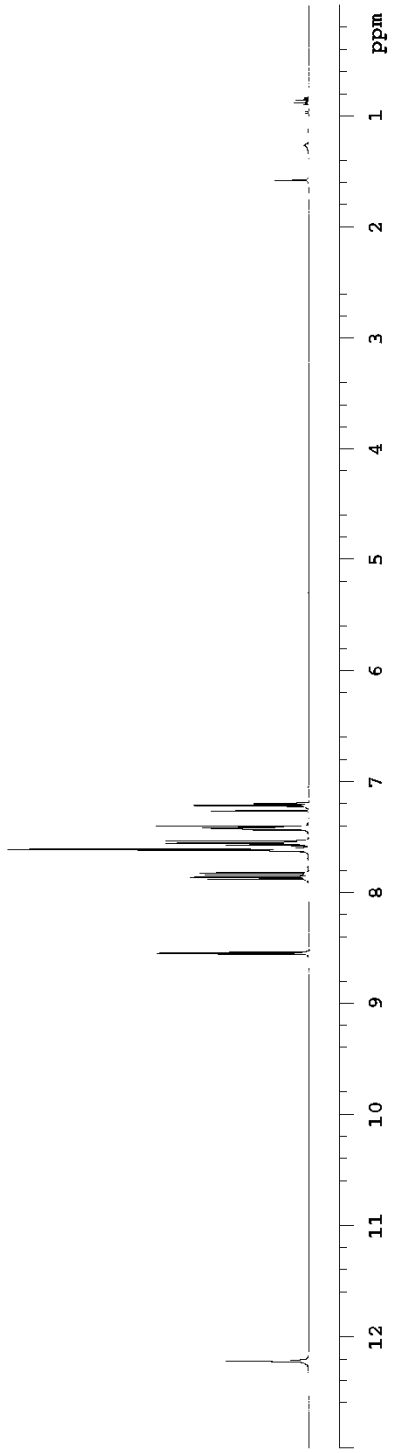
^{13}C NMR ($CDCl_3$, 23 °C) of S29



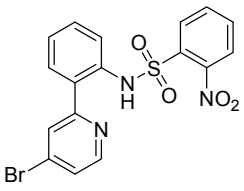


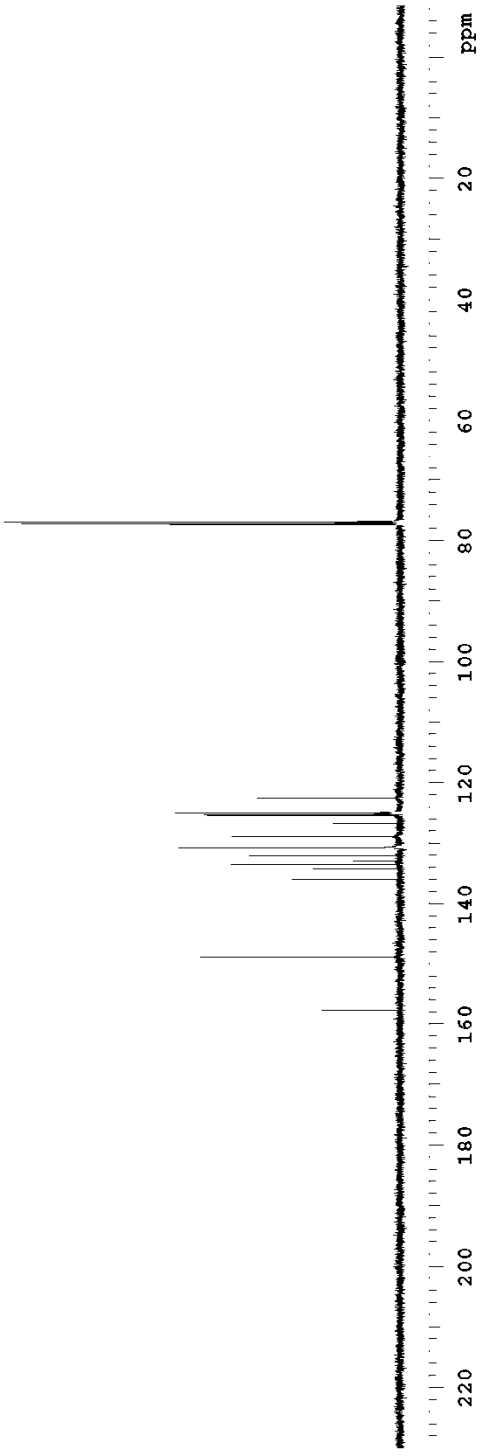
^{1}H NMR ($CDCl_3$, 23 ºC) of S30



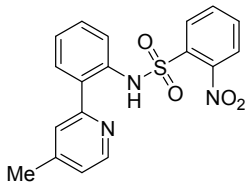


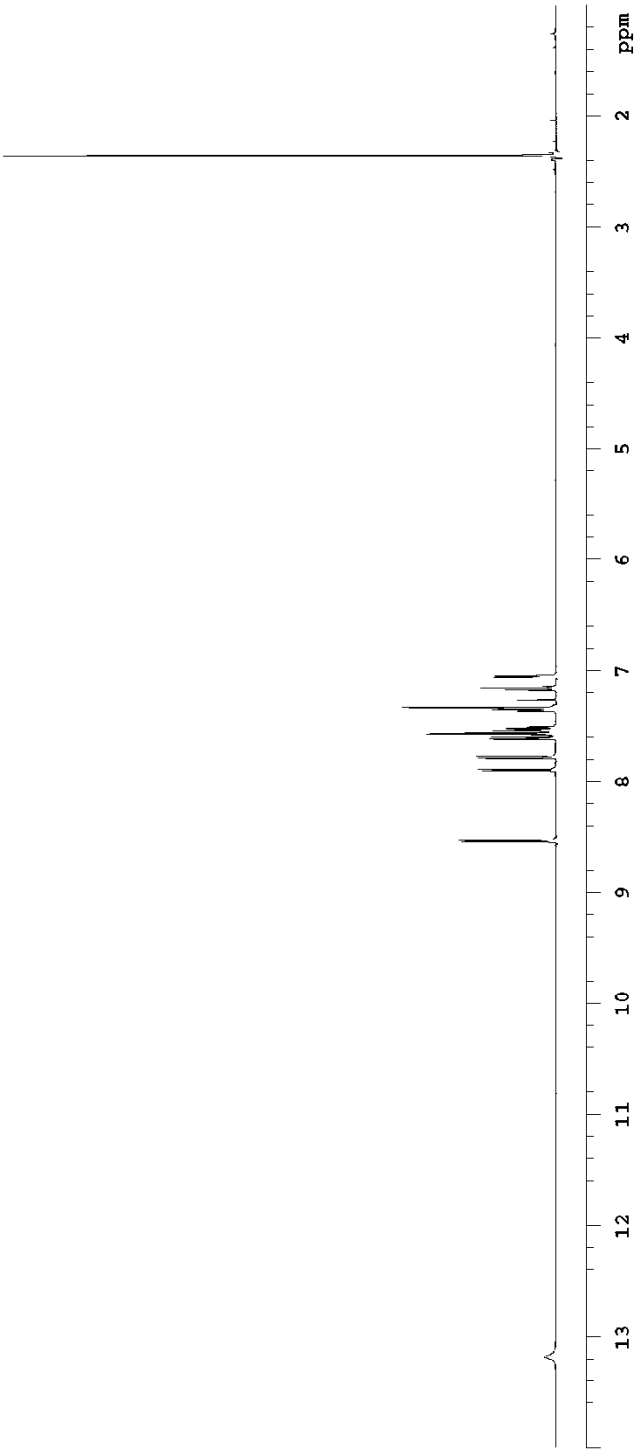
^{13}C NMR ($CDCl_3$, 23 ºC) of S30



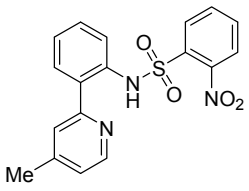


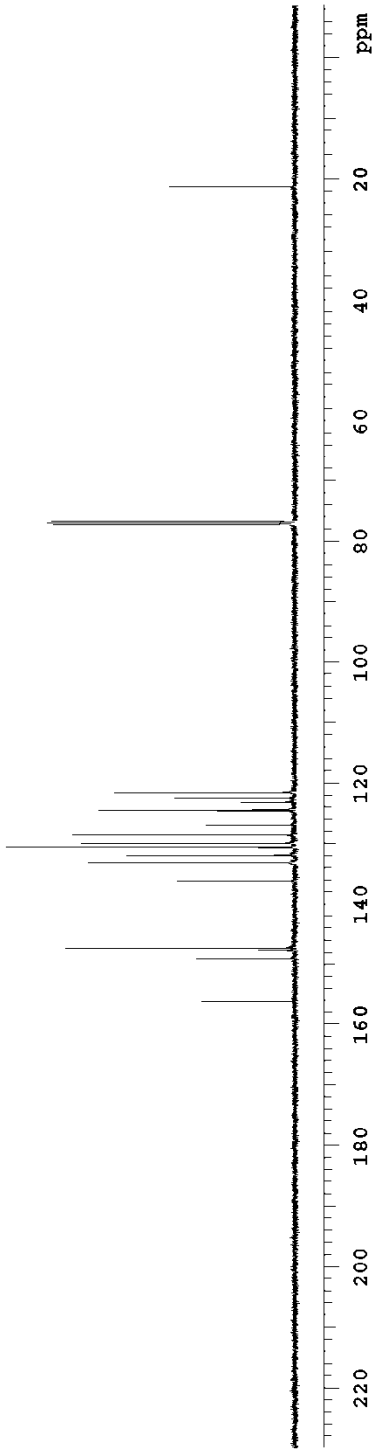
^{1}H NMR ($CDCl_3$, 23 ºC) of S31



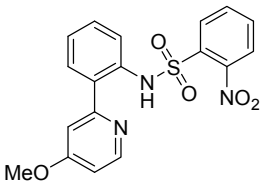


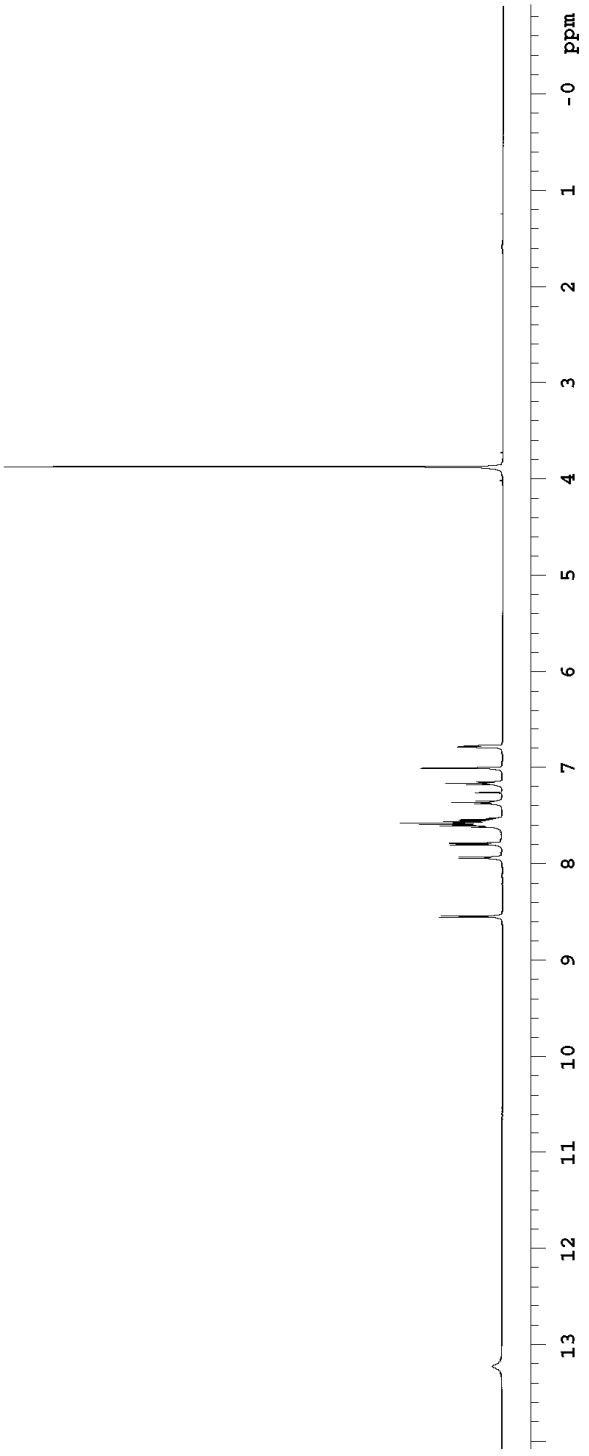
^{13}C NMR ($CDCl_3$, 23 ºC) of S31



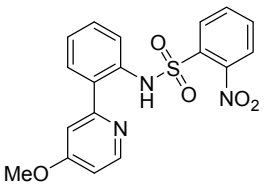


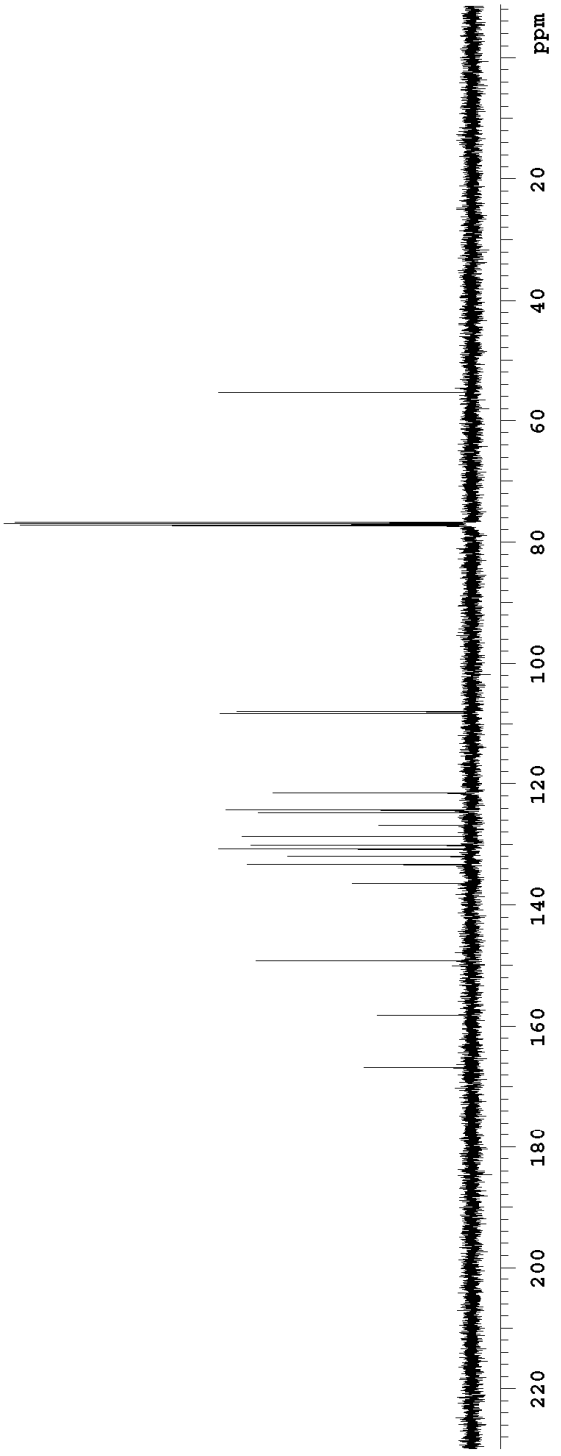
^{1}H NMR ($CDCl_3$, 23 °C) of S32



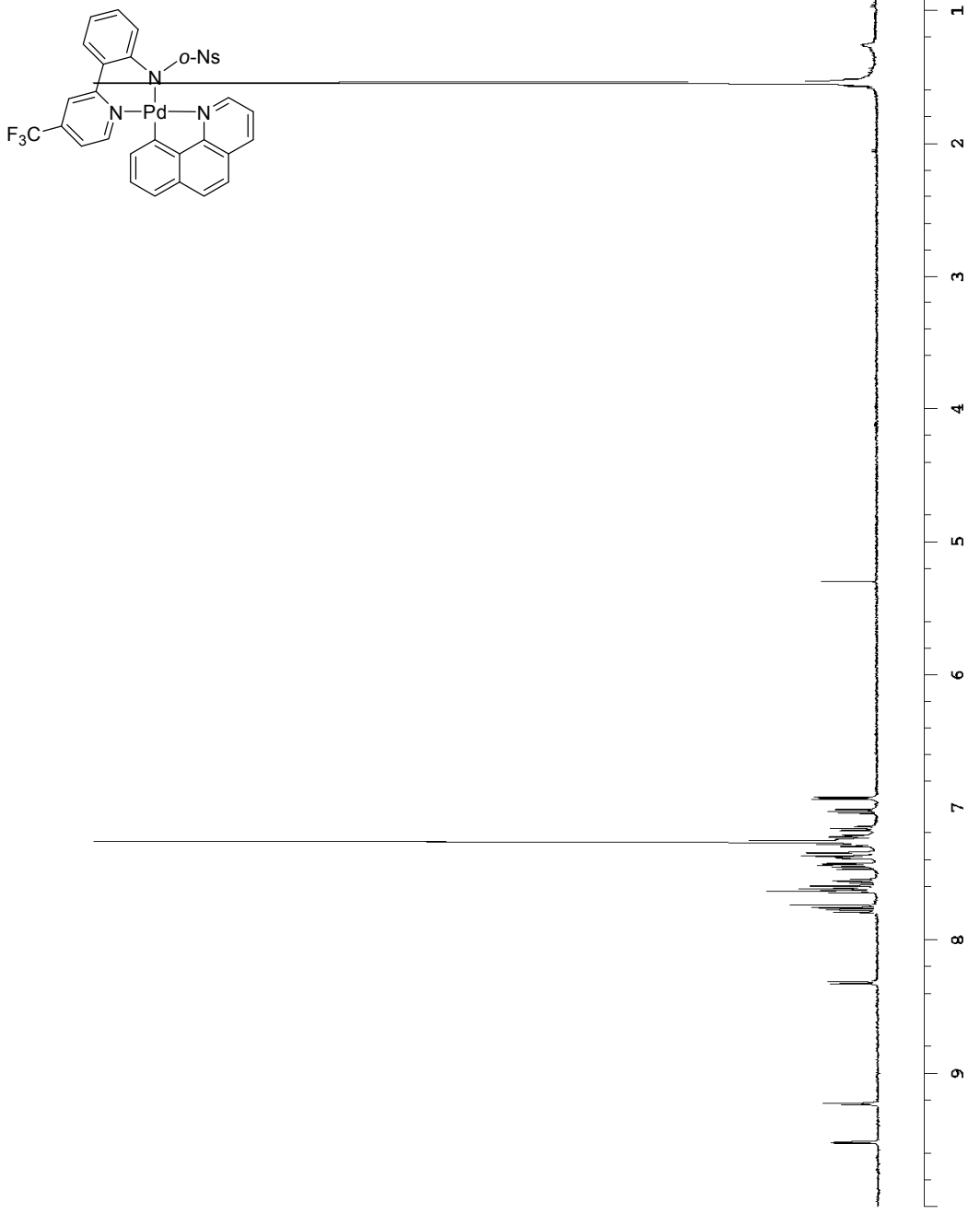


^{13}C NMR ($CDCl_3$, 23 ºC) of S32

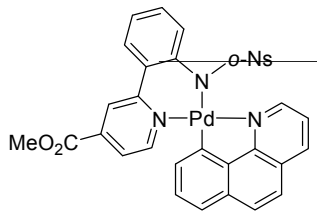


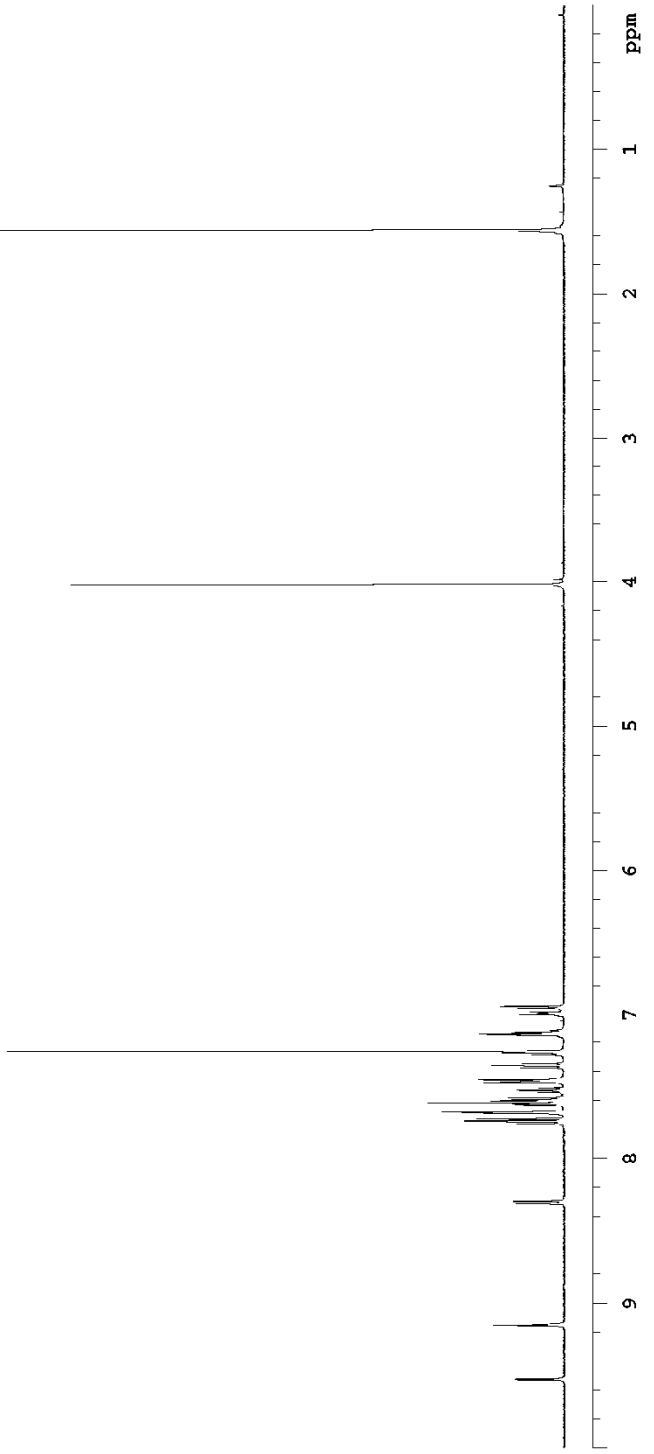


^{1}H NMR ($CDCl_3$, 23 °C) of S33

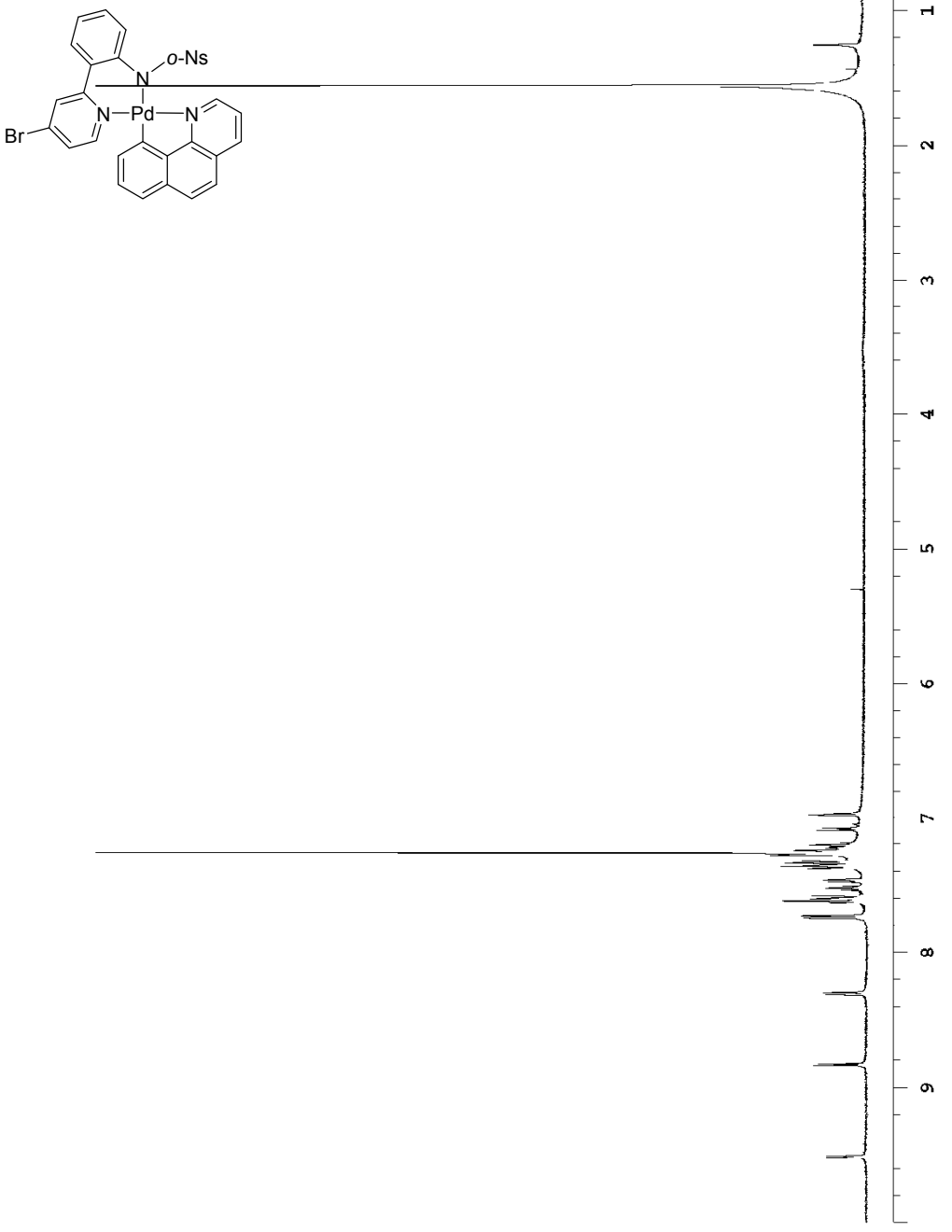


^{1}H NMR ($CDCl_3$, 23 ºC) of S34

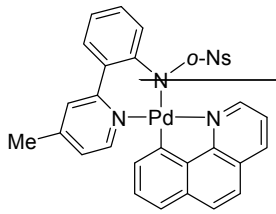




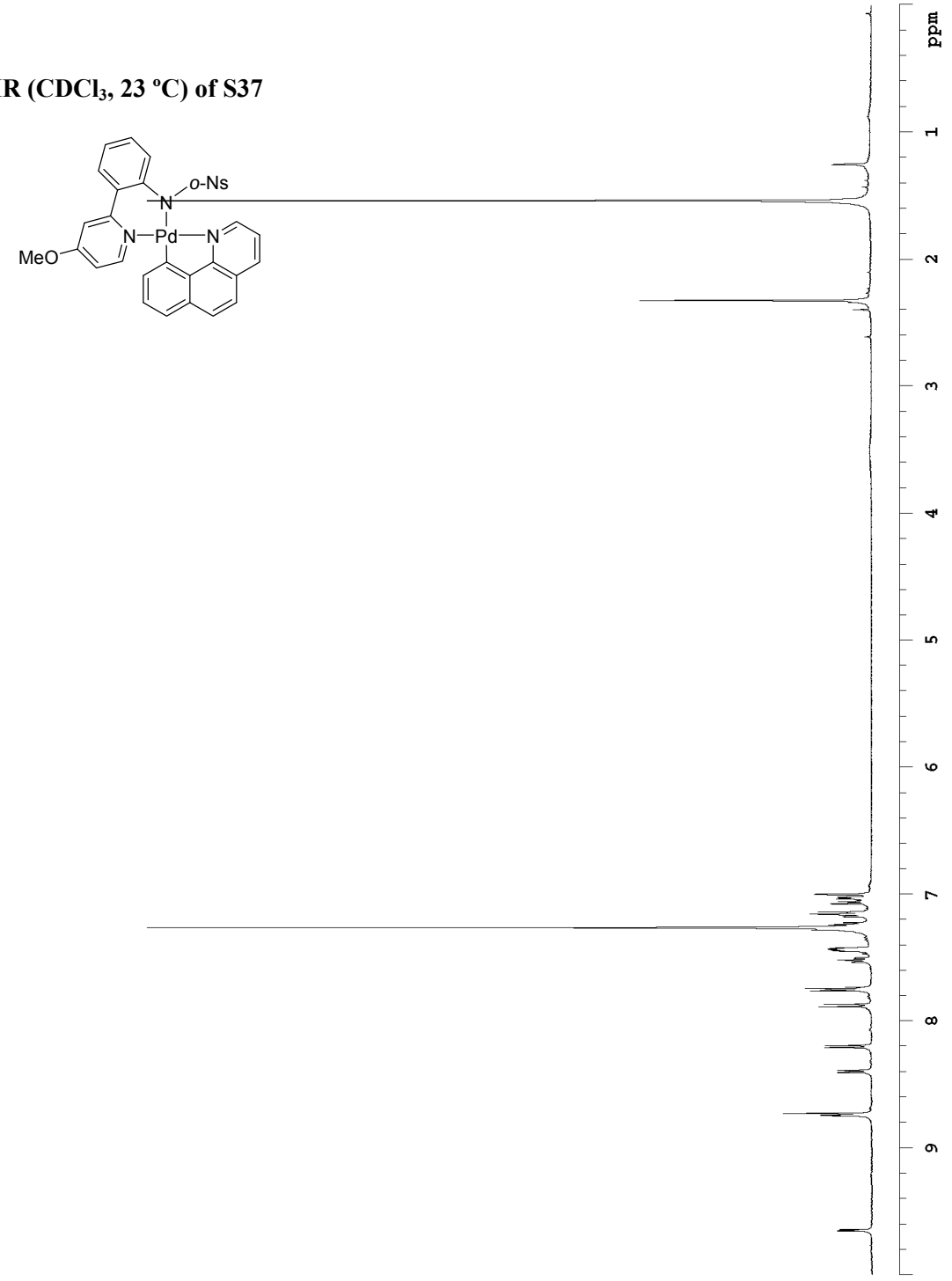
^{1}H NMR ($CDCl_3$, 23 ºC) of S35



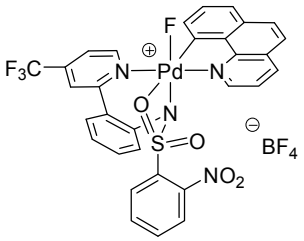
^{1}H NMR ($CDCl_3$, 23 ºC) of S36

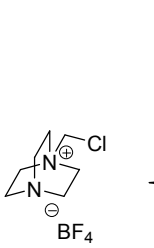


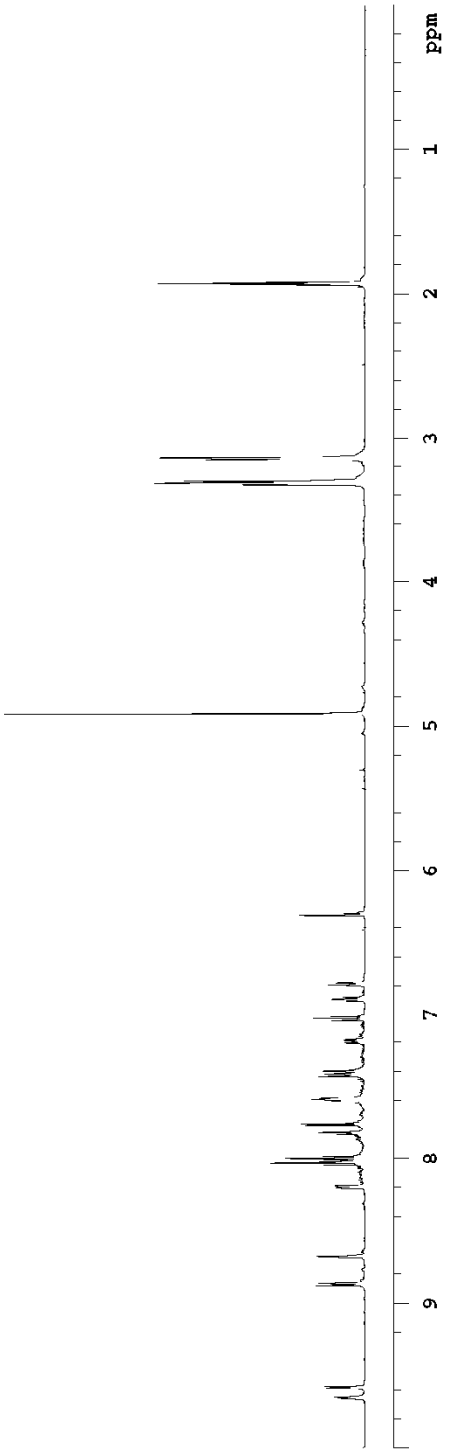
^{1}H NMR ($CDCl_3$, 23 ºC) of S37



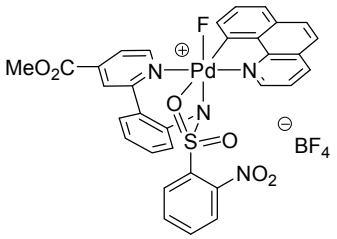
^{1}H NMR ($CDCl_3$, 23 °C) of 7a

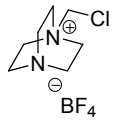


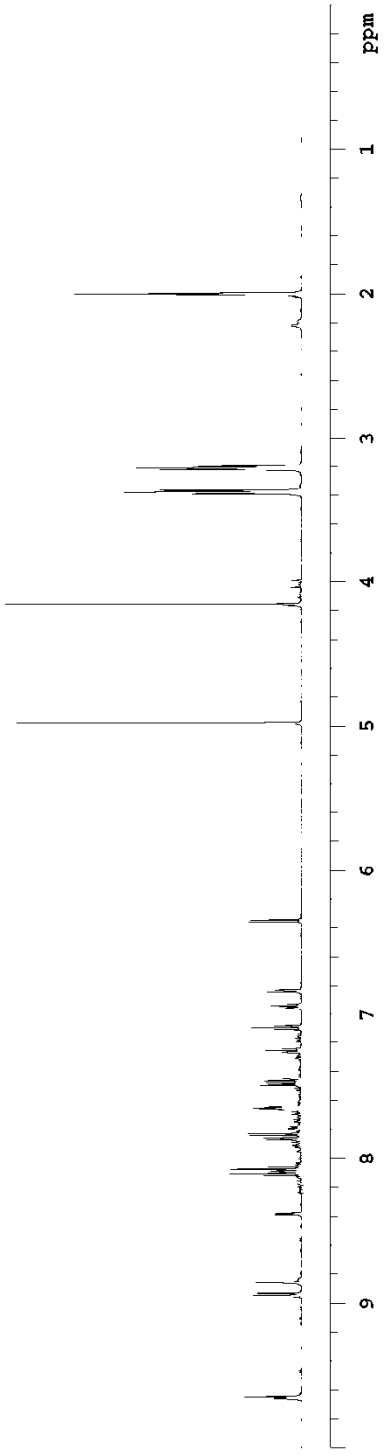




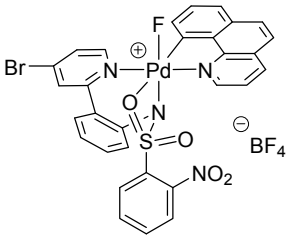
^{1}H NMR ($CDCl_3$, 23 ºC) of 7b

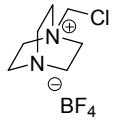


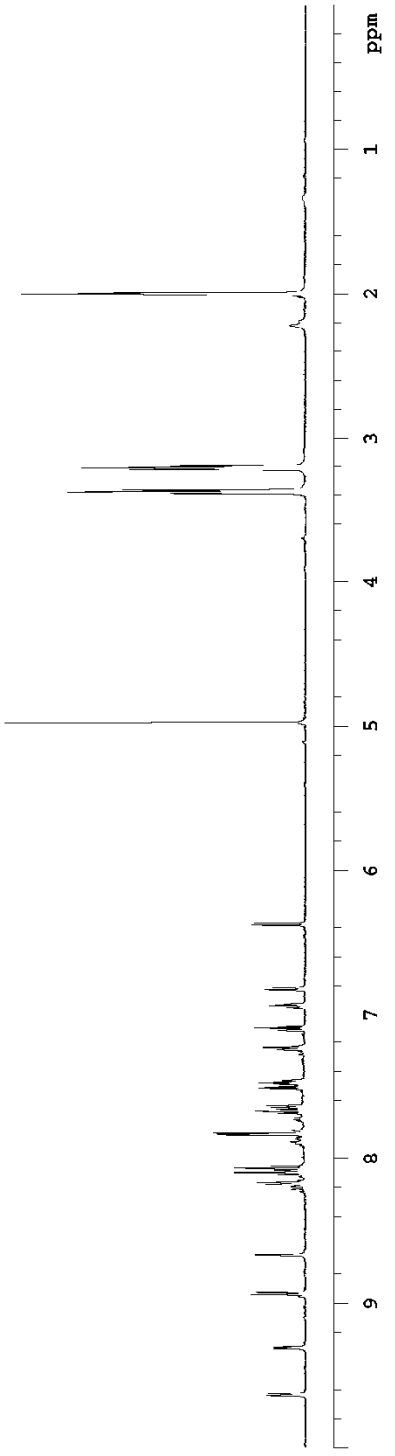




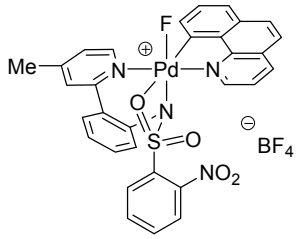
^{1}H NMR ($CDCl_3$, 23 ºC) of 7c

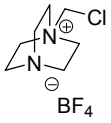


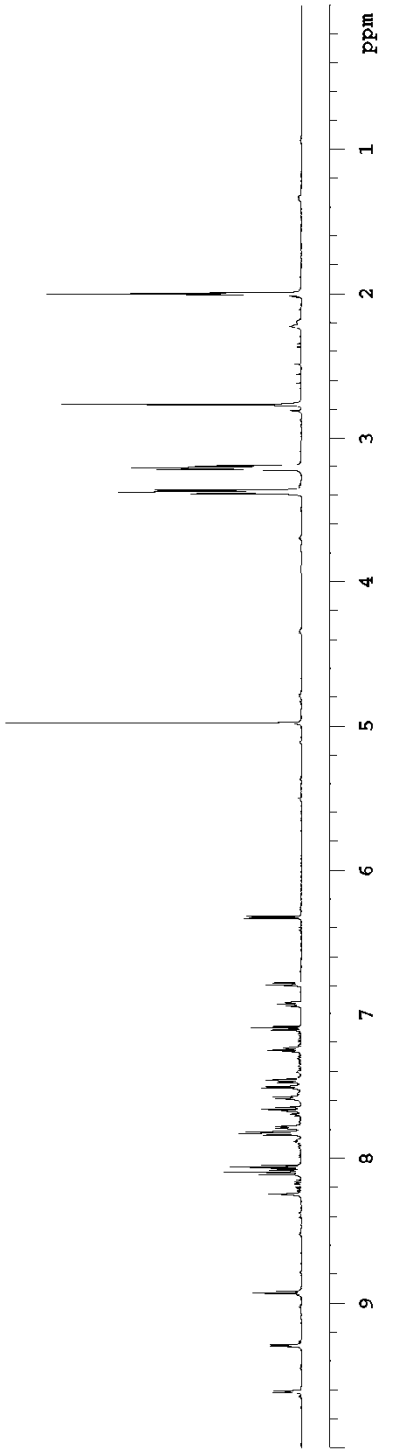




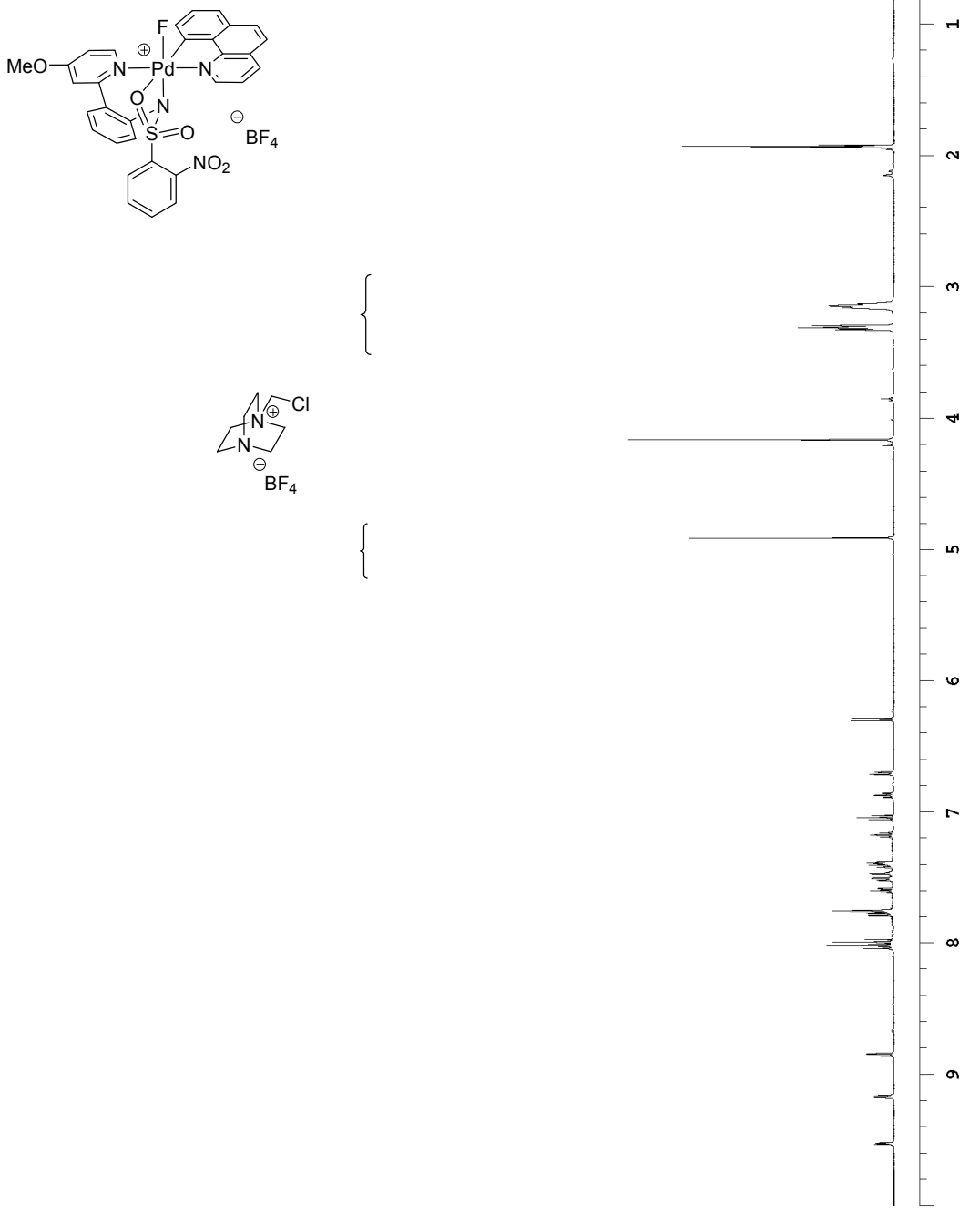
^{1}H NMR ($CDCl_3$, 23 ºC) of 7e



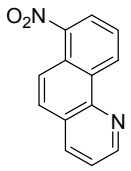


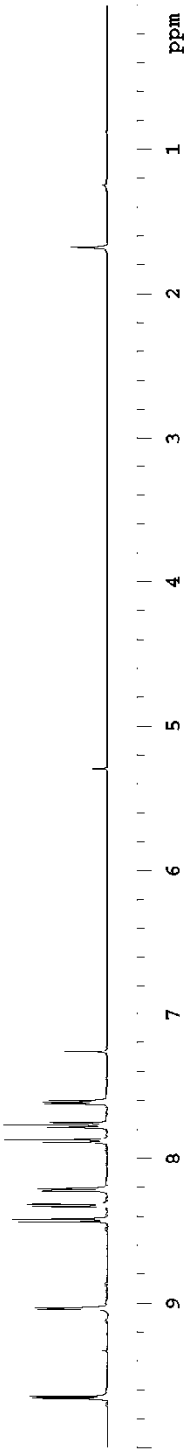


^{1}H NMR ($CDCl_3$, 23 ºC) of 7f

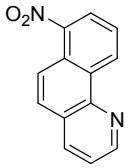


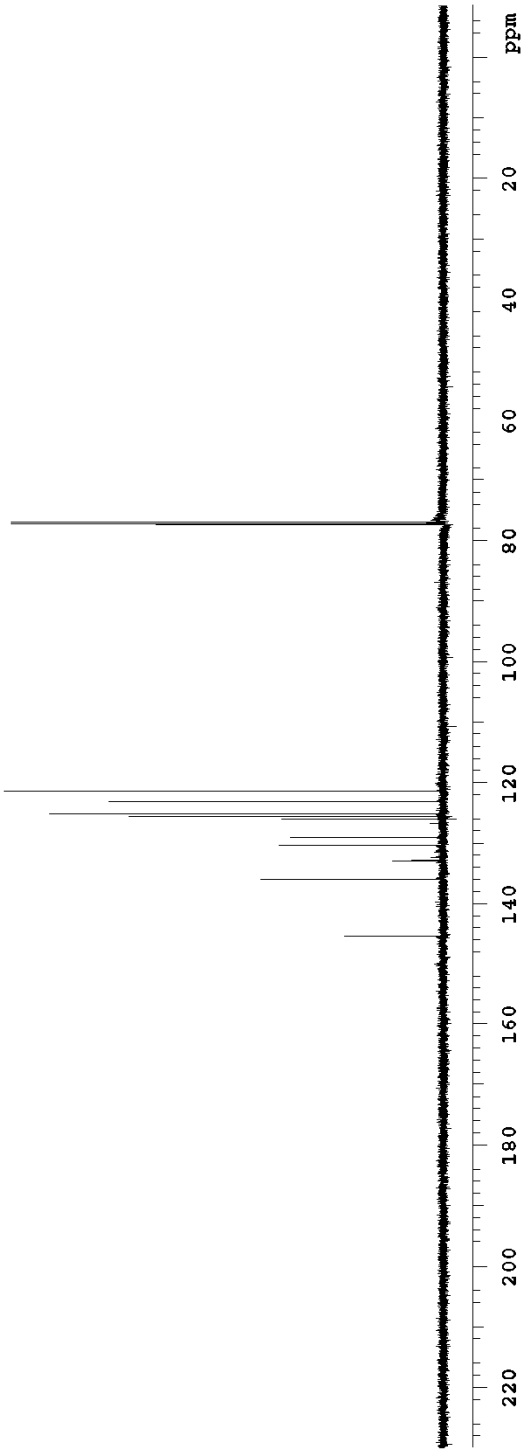
^{1}H NMR ($CDCl_3$, 23 ºC) of S38



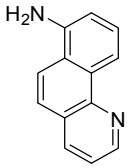


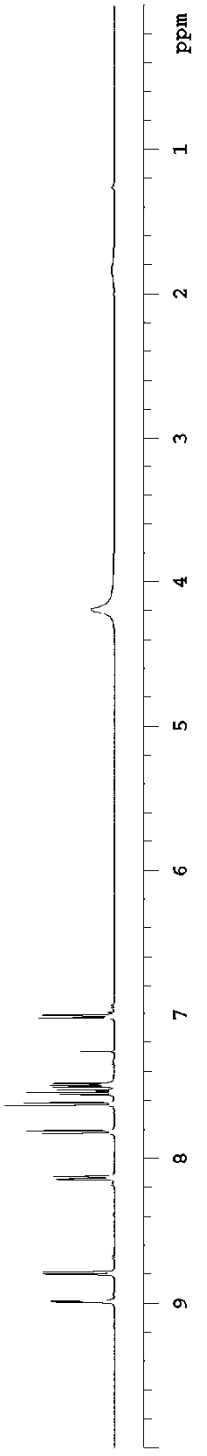
^{13}C NMR ($CDCl_3$, 23 °C) of S38



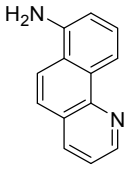


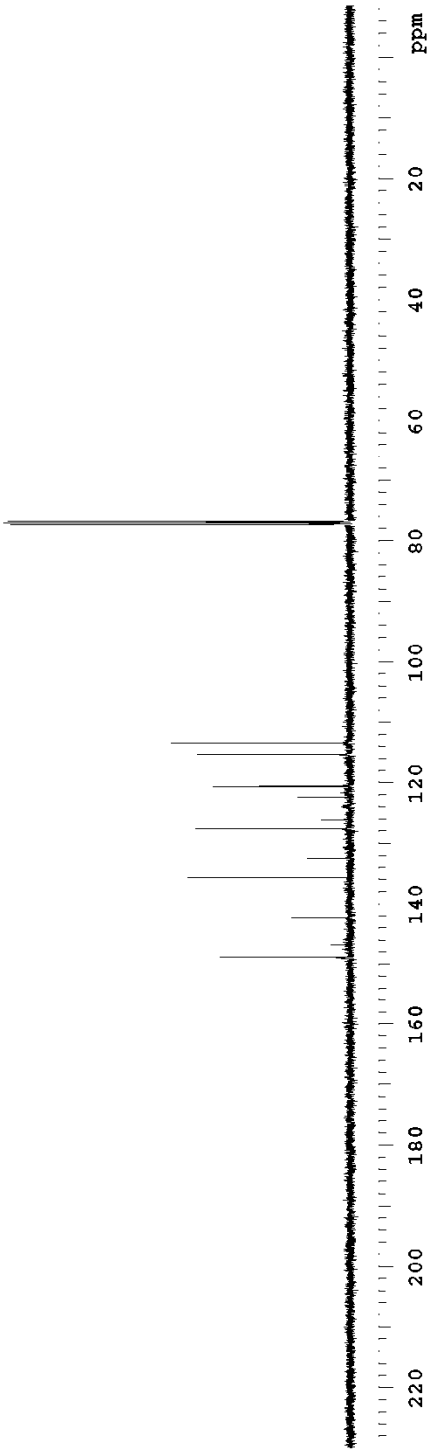
^{1}H NMR ($CDCl_3$, 23 °C) of S39



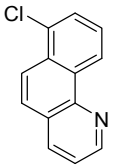


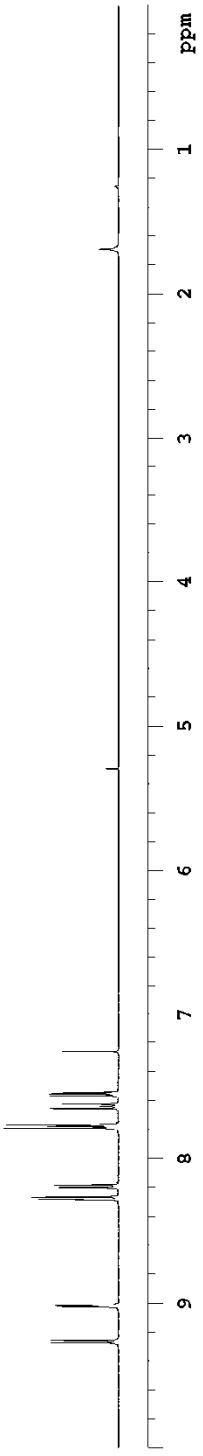
^{13}C NMR ($CDCl_3$, 23 °C) of S39



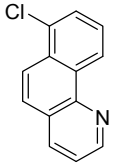


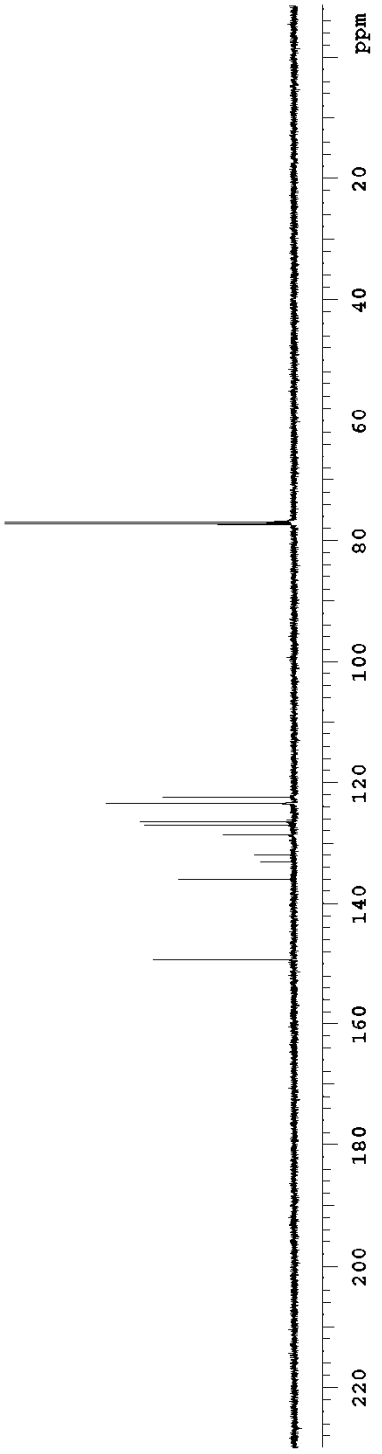
^{1}H NMR ($CDCl_3$, 23 ºC) of S40



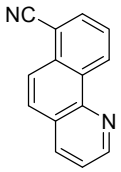


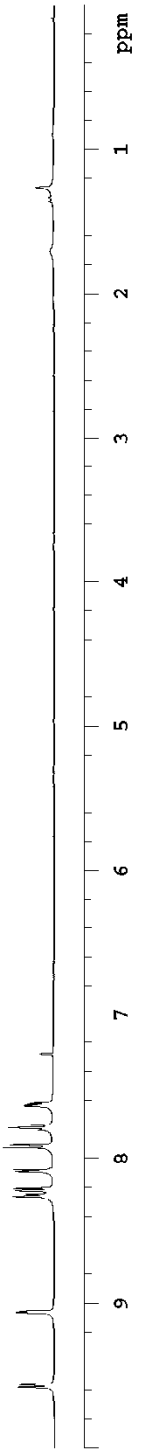
^{13}C NMR ($CDCl_3$, 23 °C) of S40



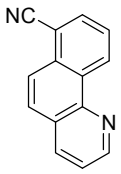


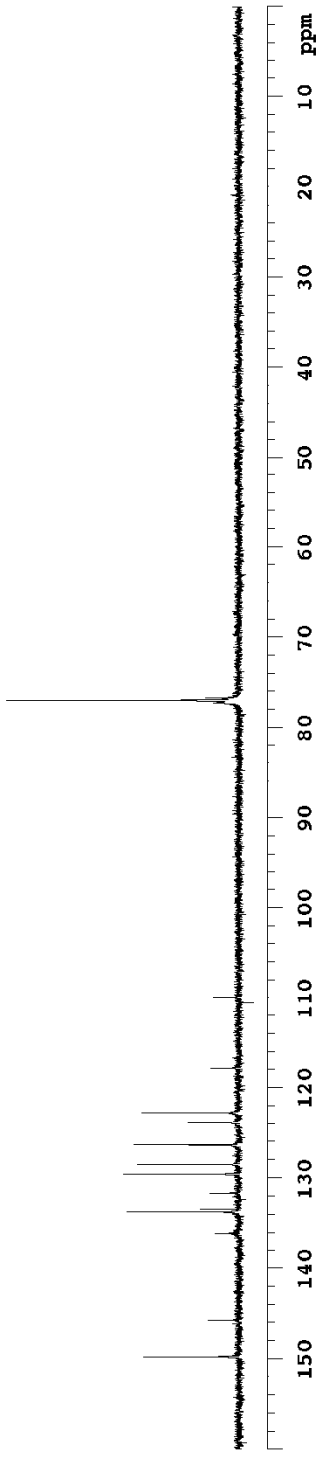
^{1}H NMR ($CDCl_3$, 23 ºC) of S41



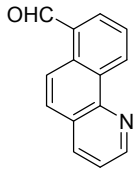


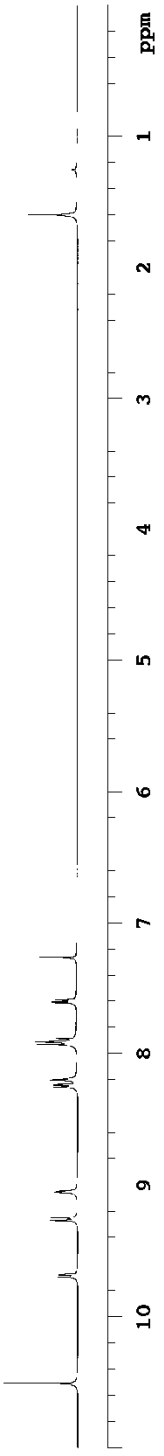
^{13}C NMR ($CDCl_3$, 23 °C) of S41



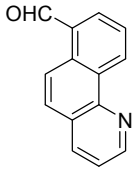


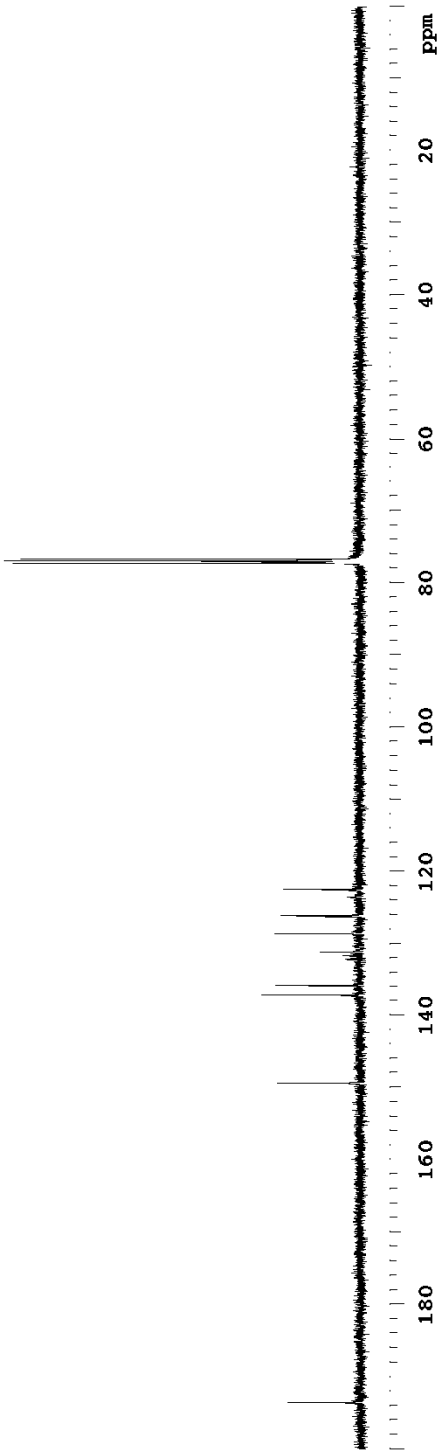
^{1}H NMR ($CDCl_3$, 23 °C) of S42



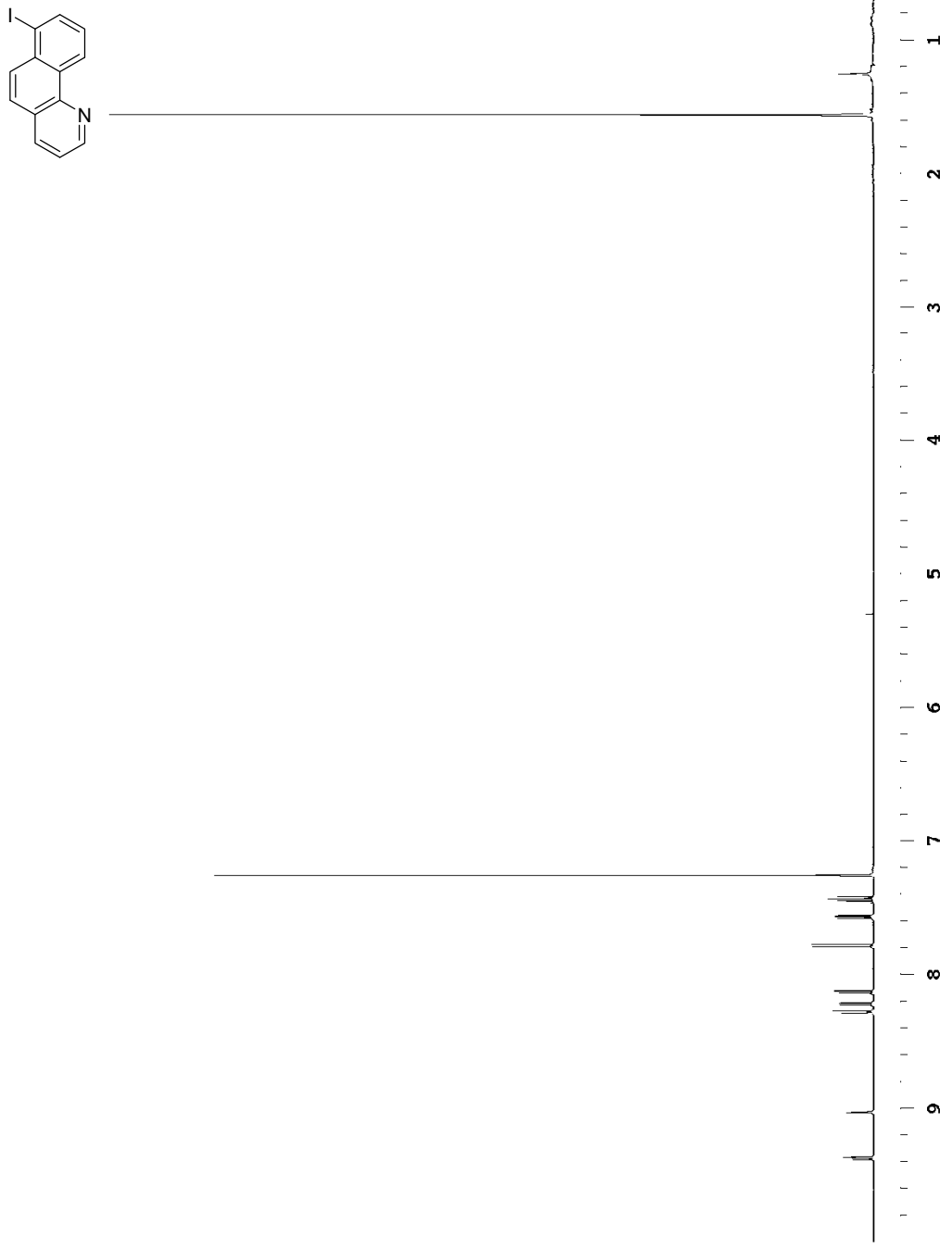


^{13}C NMR ($CDCl_3$, 23 ºC) of S42

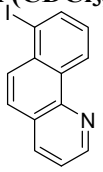


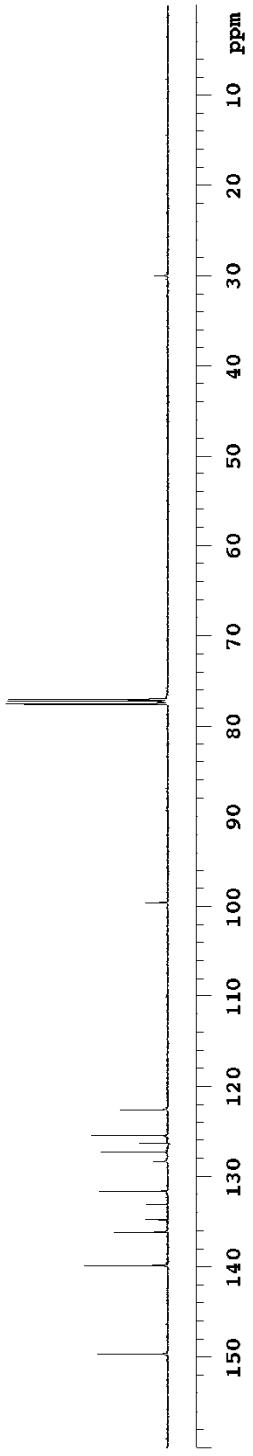


^{1}H NMR ($CDCl_3$, 23 °C) of S45

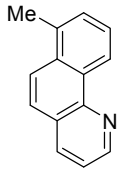


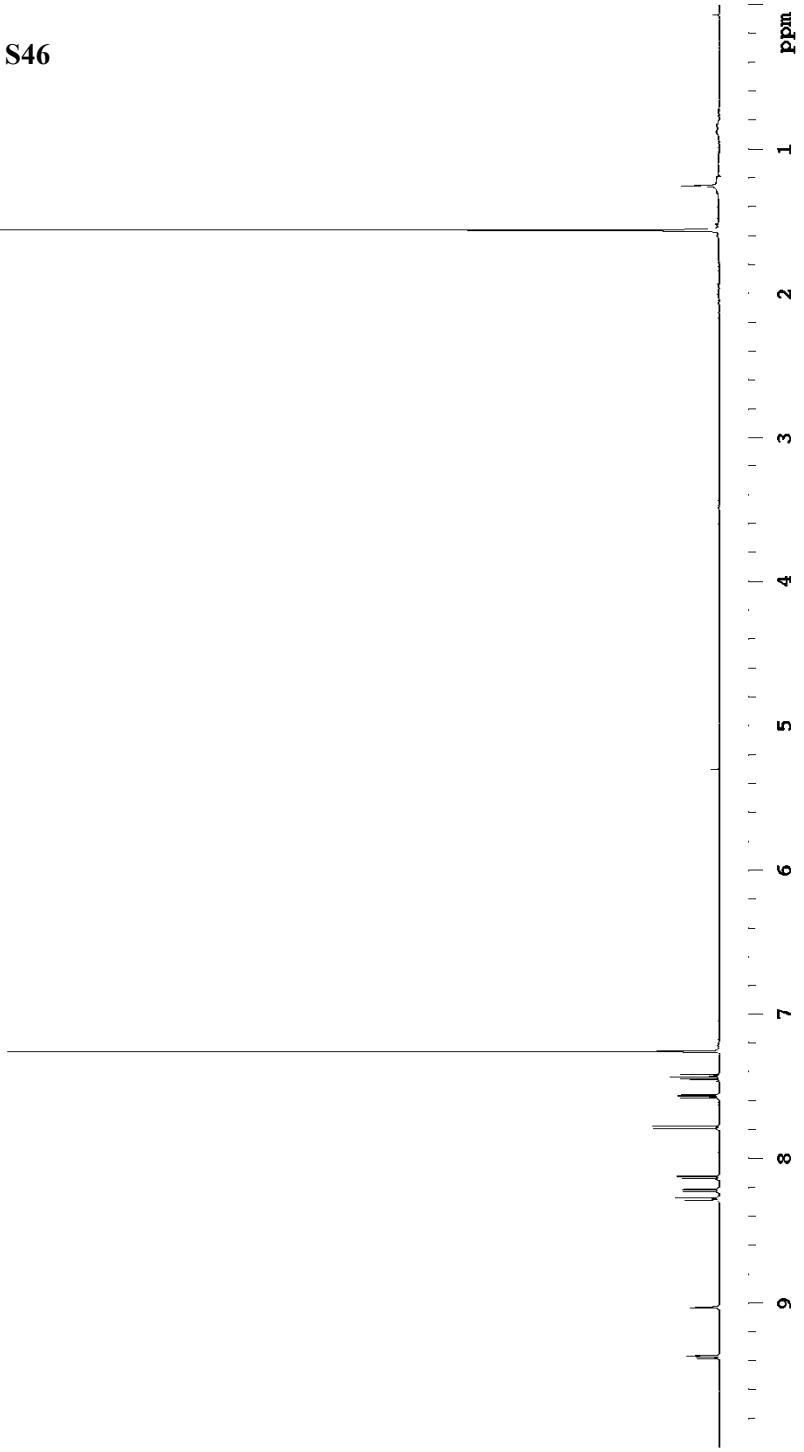
^{13}C NMR ($CDCl_3$, 23 ºC) of S45



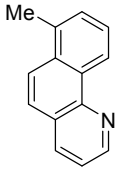


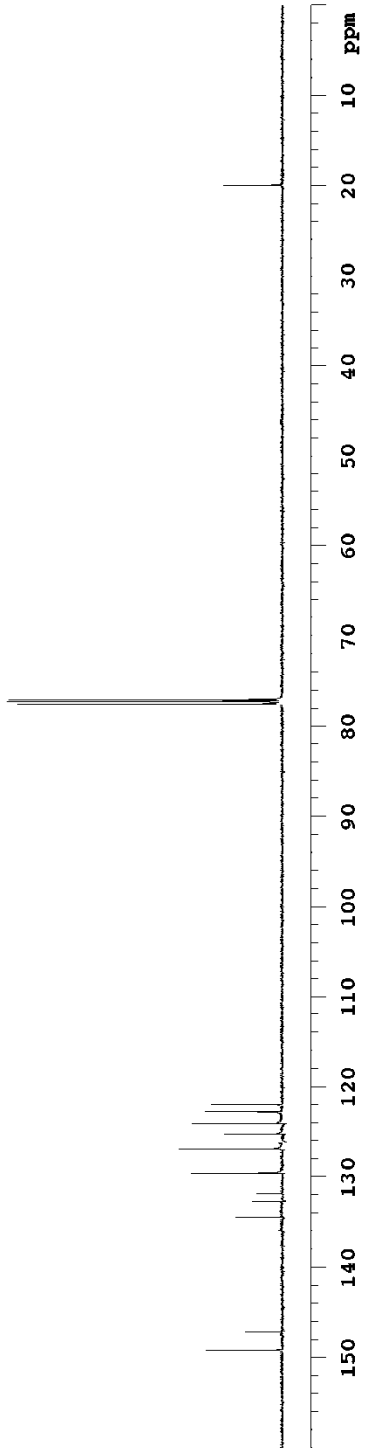
^{1}H NMR ($CDCl_3$, 23 °C) of S46



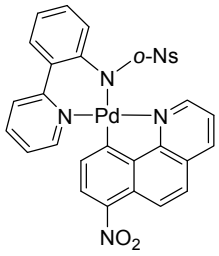


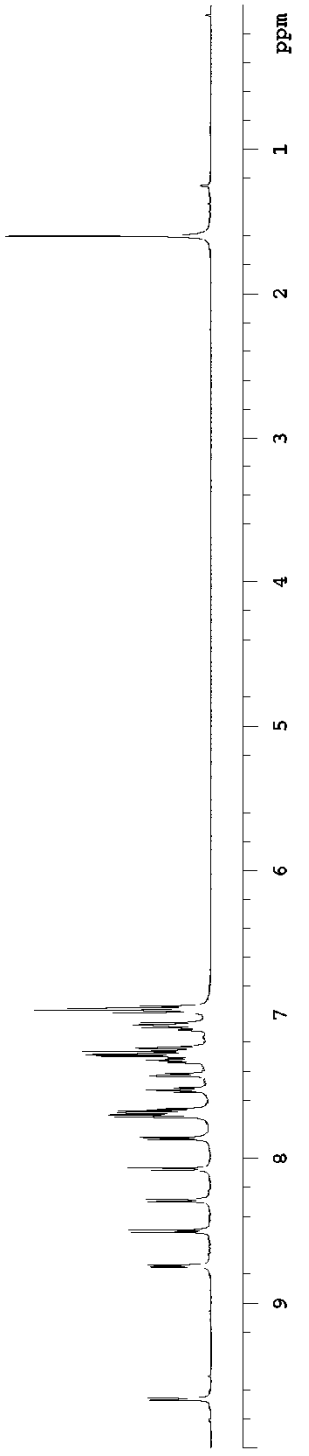
^{13}C NMR ($CDCl_3$, 23 °C) of



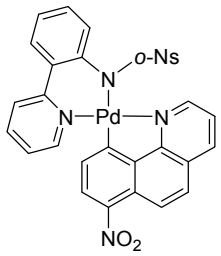


^{1}H NMR ($CDCl_3$, 23 °C) of S47

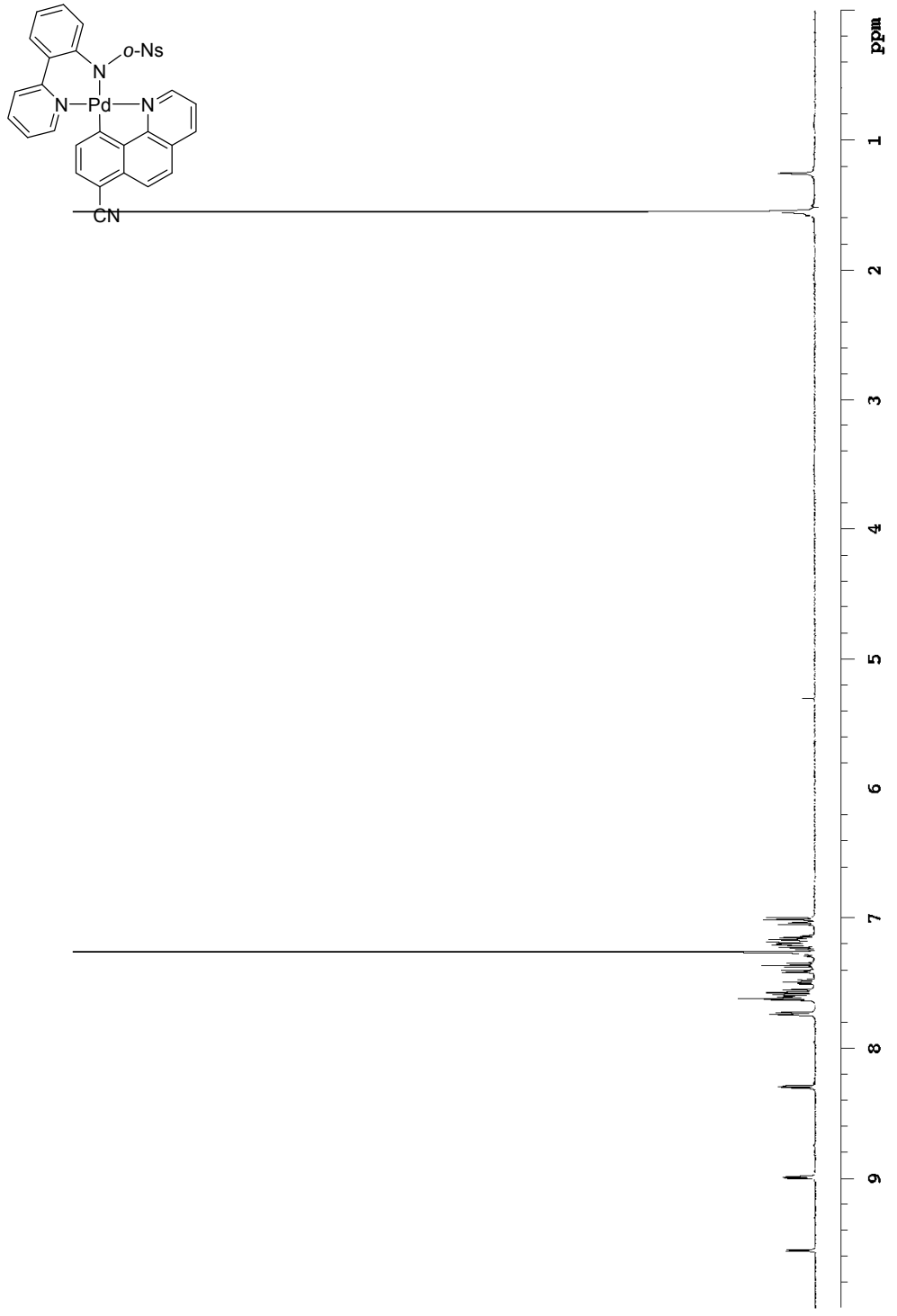




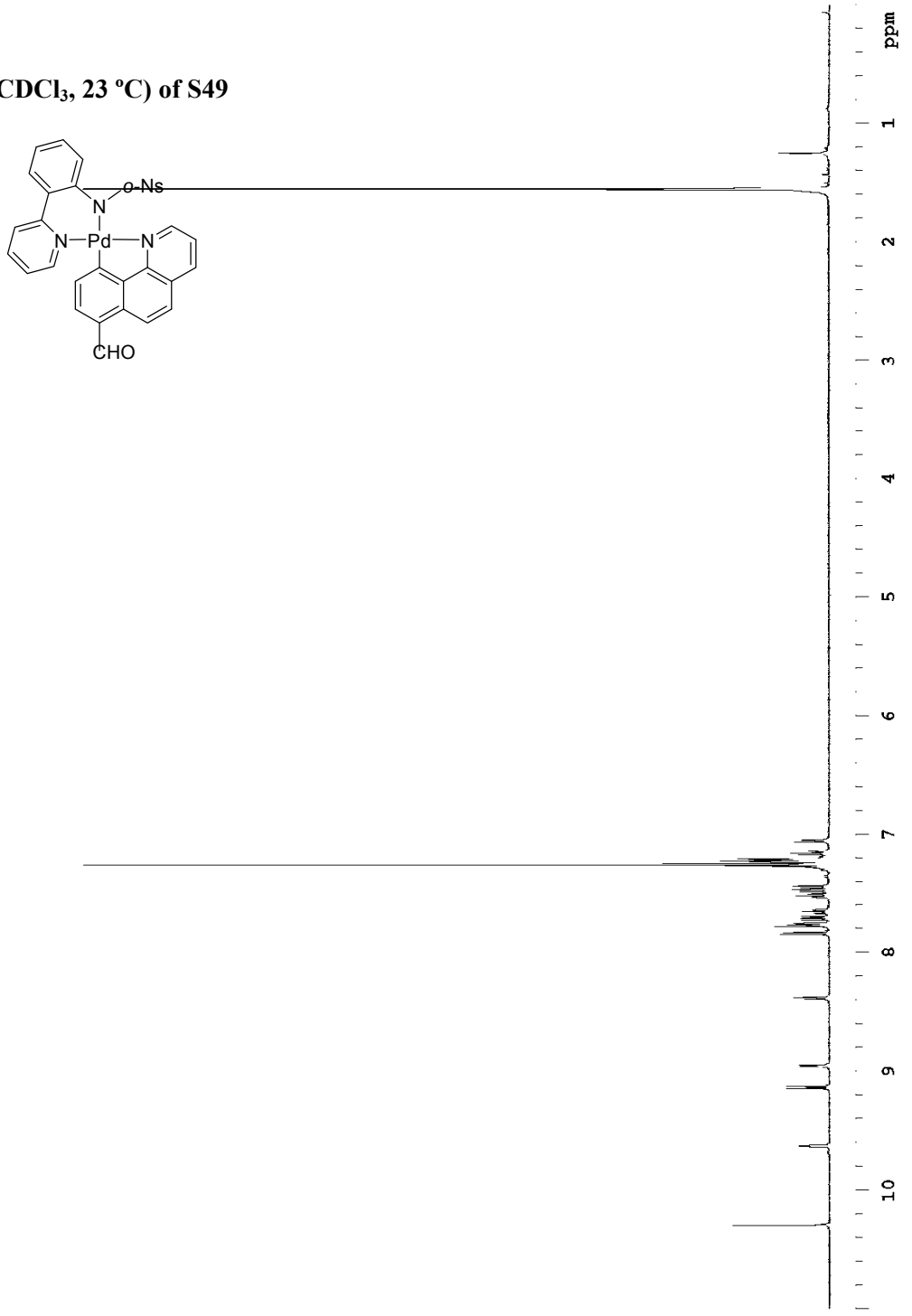
^{13}C NMR ($CDCl_3$, 23 °C) of S47



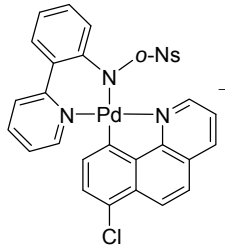
^{13}C NMR ($CDCl_3$, 23 ºC) of S48

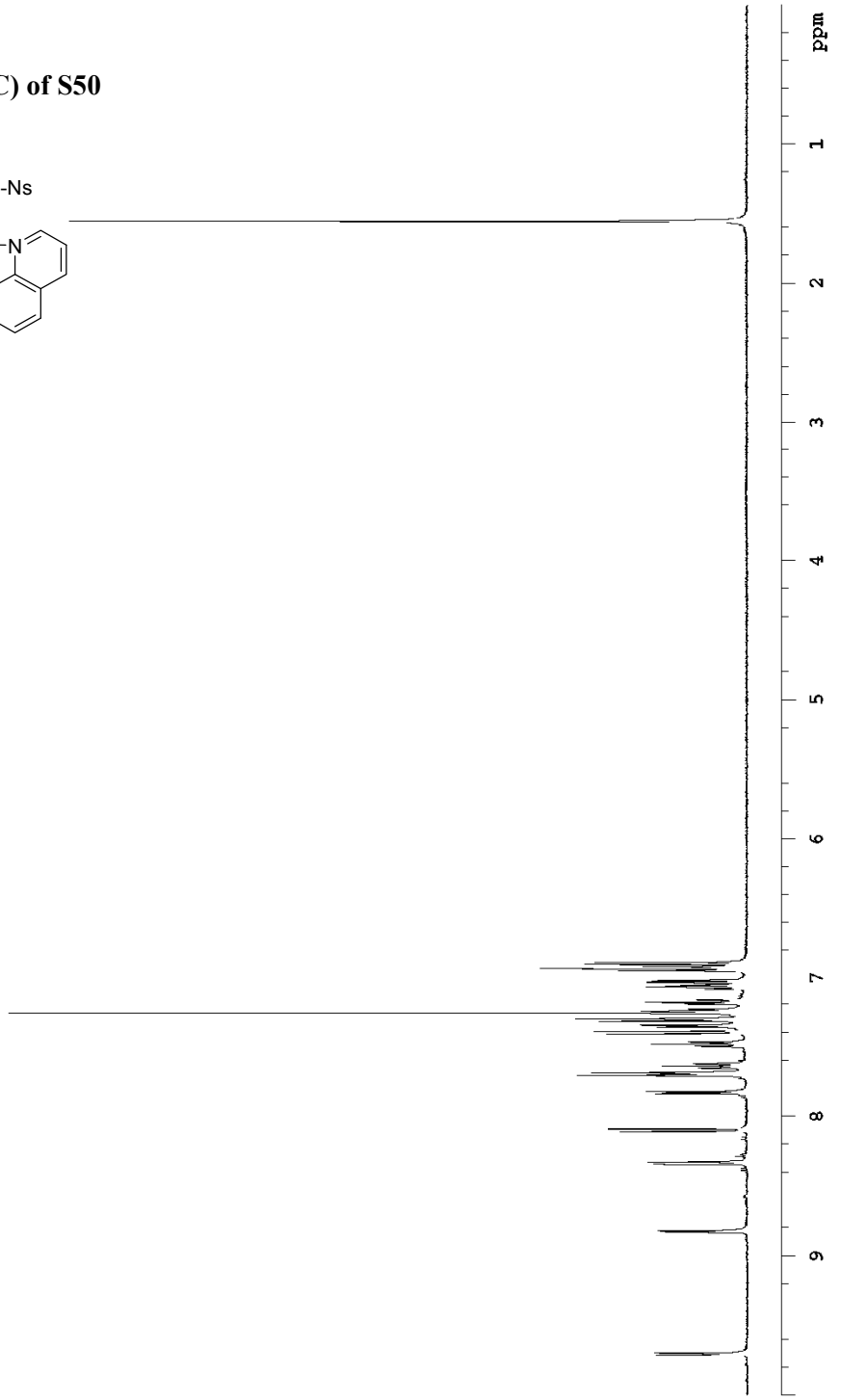


^{1}H NMR ($CDCl_3$, 23 ºC) of S49

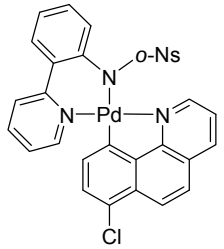


^{1}H NMR ($CDCl_3$, 23 ºC) of S50

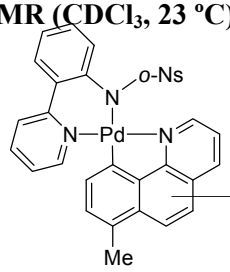


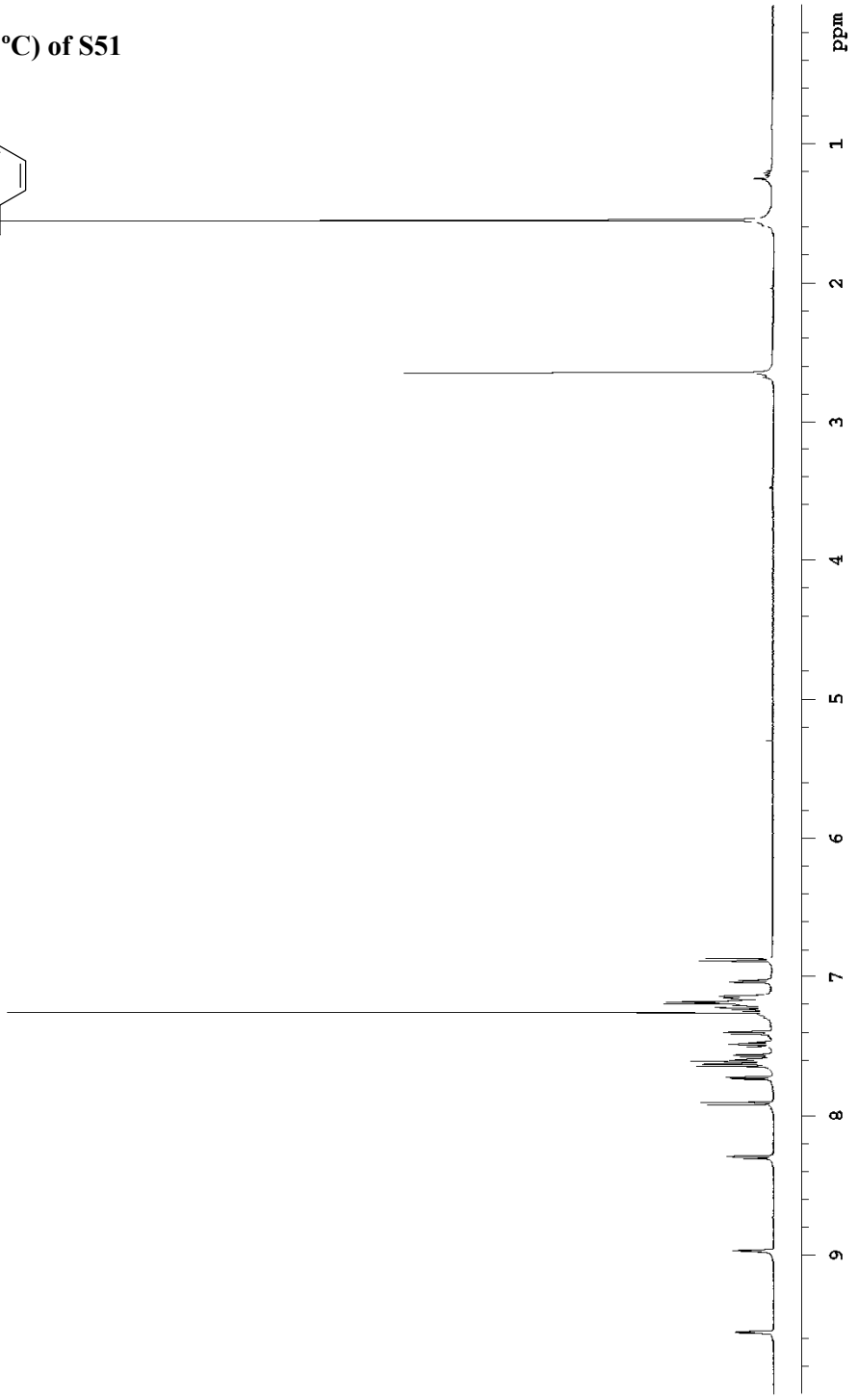


^{13}C NMR ($CDCl_3$, 23 ºC) of S50

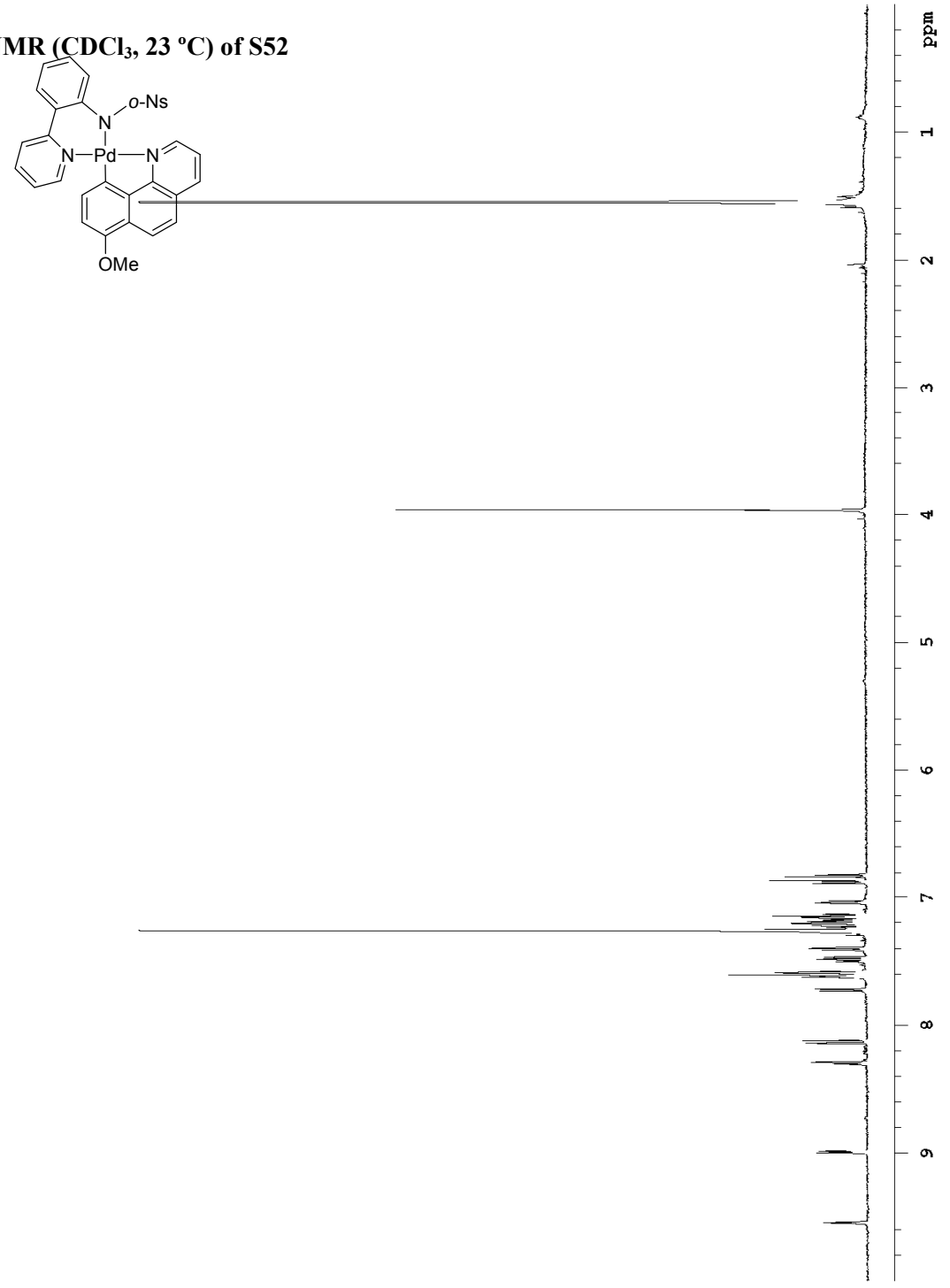


^{1}H NMR ($CDCl_3$, 23 °C) of S51

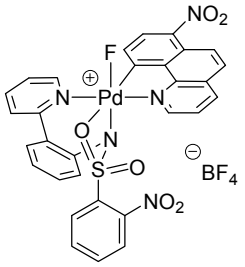


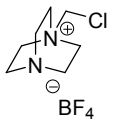


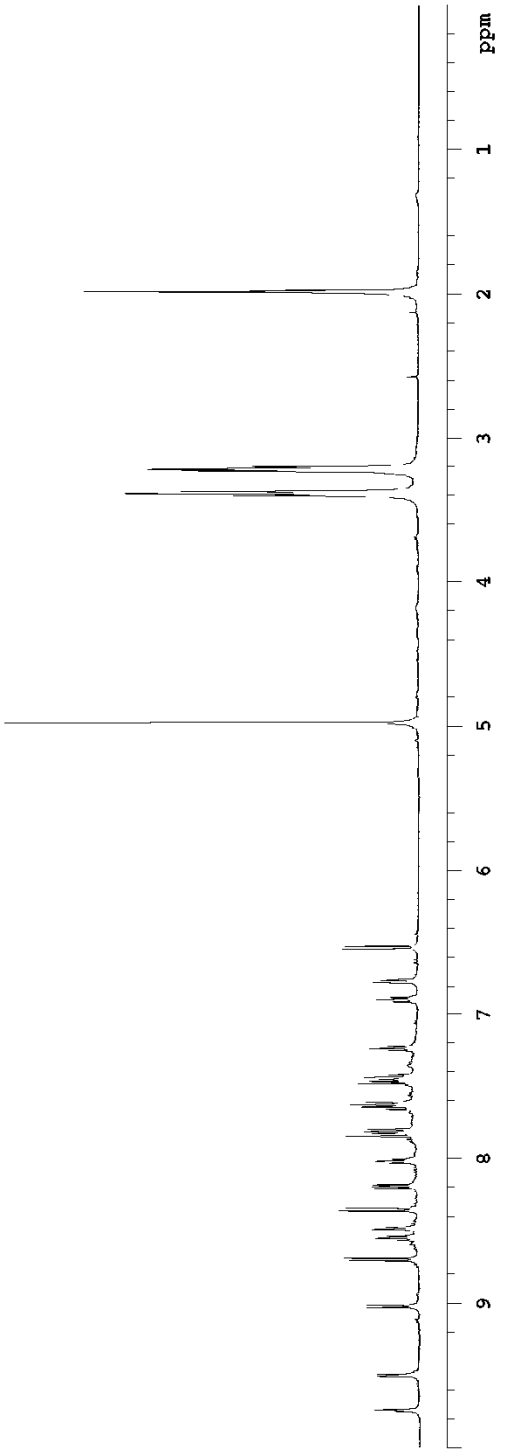
^{1}H NMR ($CDCl_3$, 23 °C) of S52



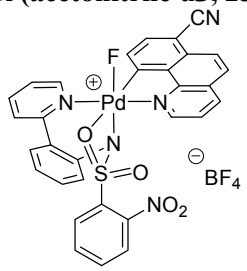
^{1}H NMR (acetonitrile-*d3*, 23 ºC) of 8a

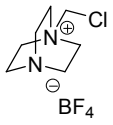


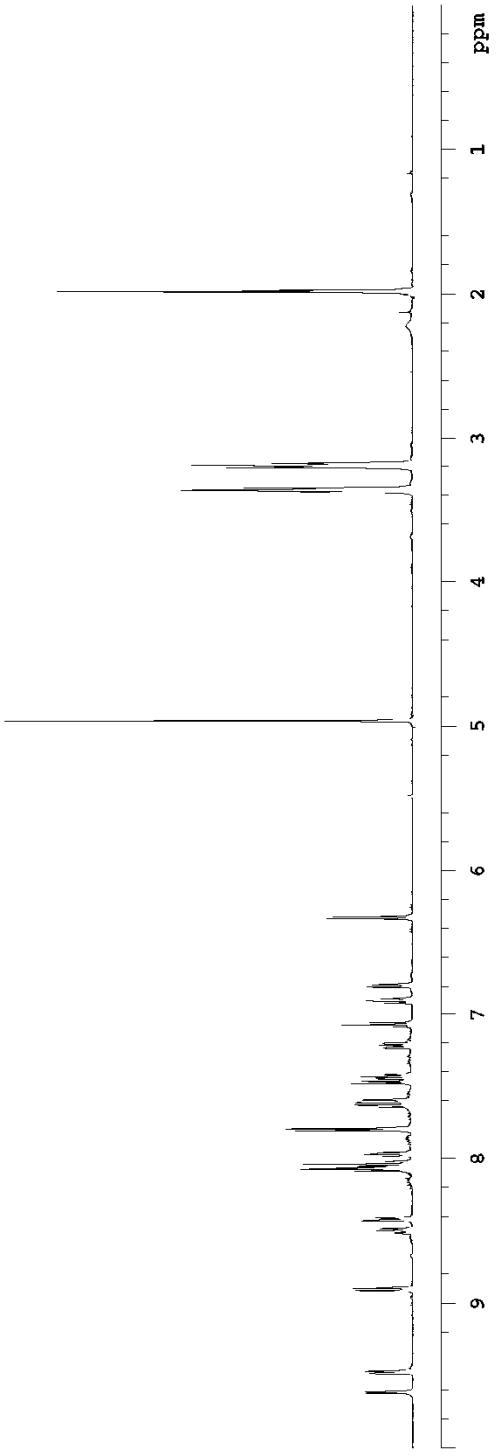




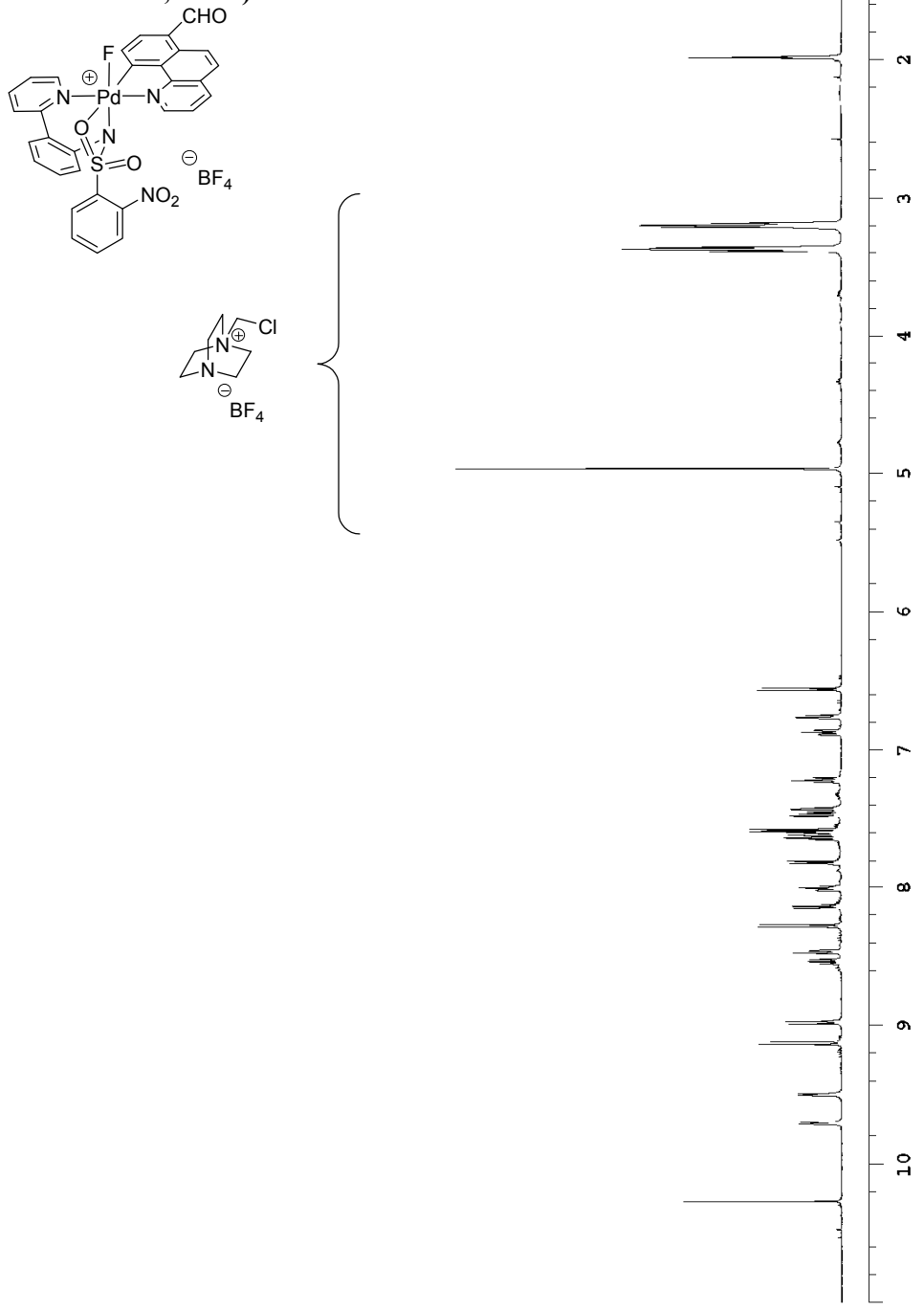
^{1}H NMR (acetonitrile-*d3*, 23 ºC) of 8b



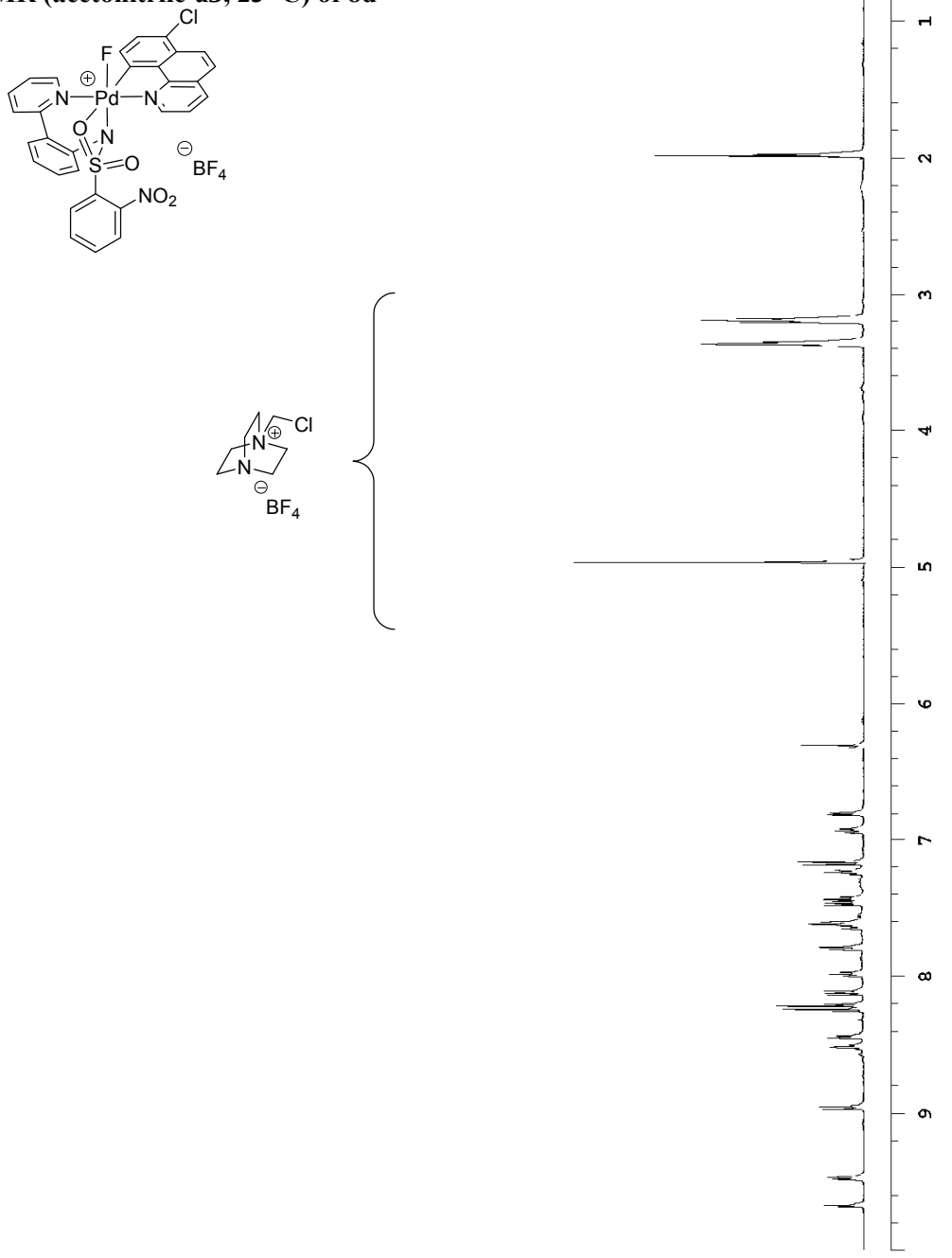




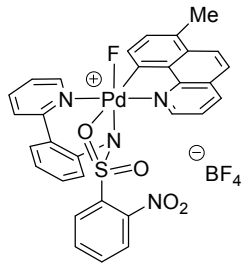
^{1}H NMR (acetonitrile-*d3*, 23 ºC) of 8c

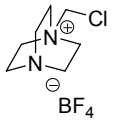


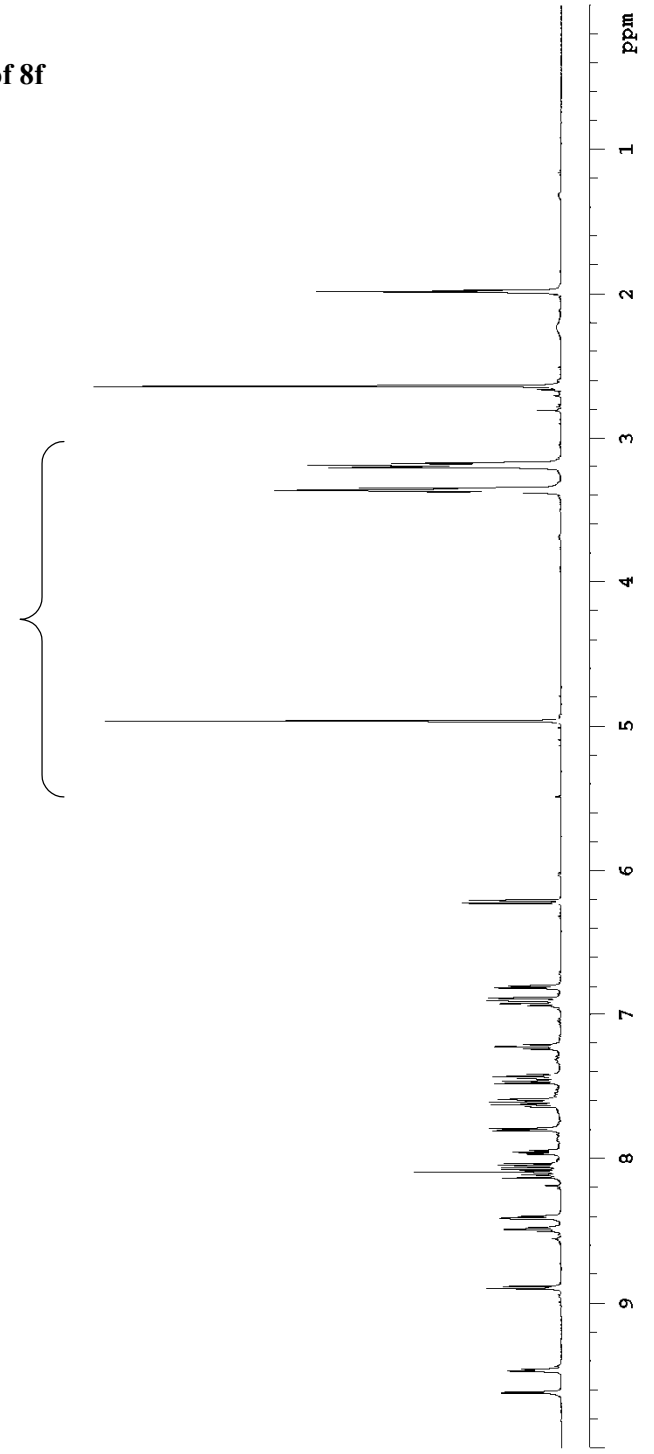
^{1}H NMR (acetonitrile-*d3*, 23 ºC) of 8d



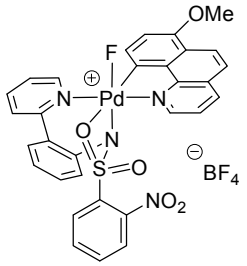
^{1}H NMR (acetonitrile-*d3*, 23 ºC) of 8f

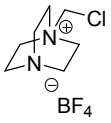


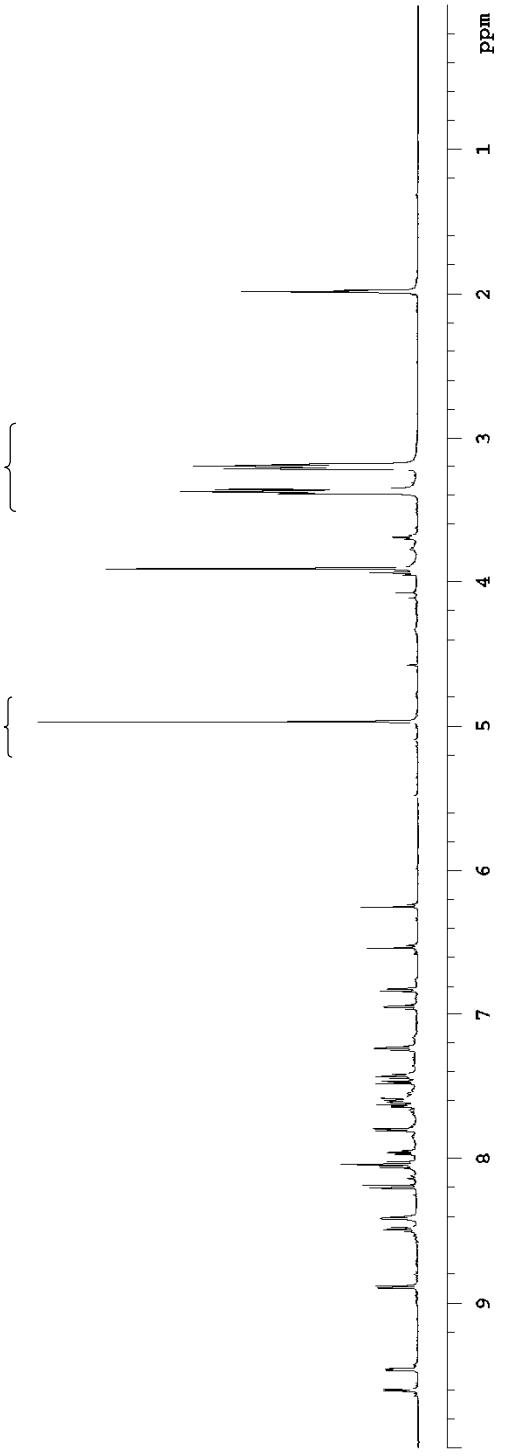




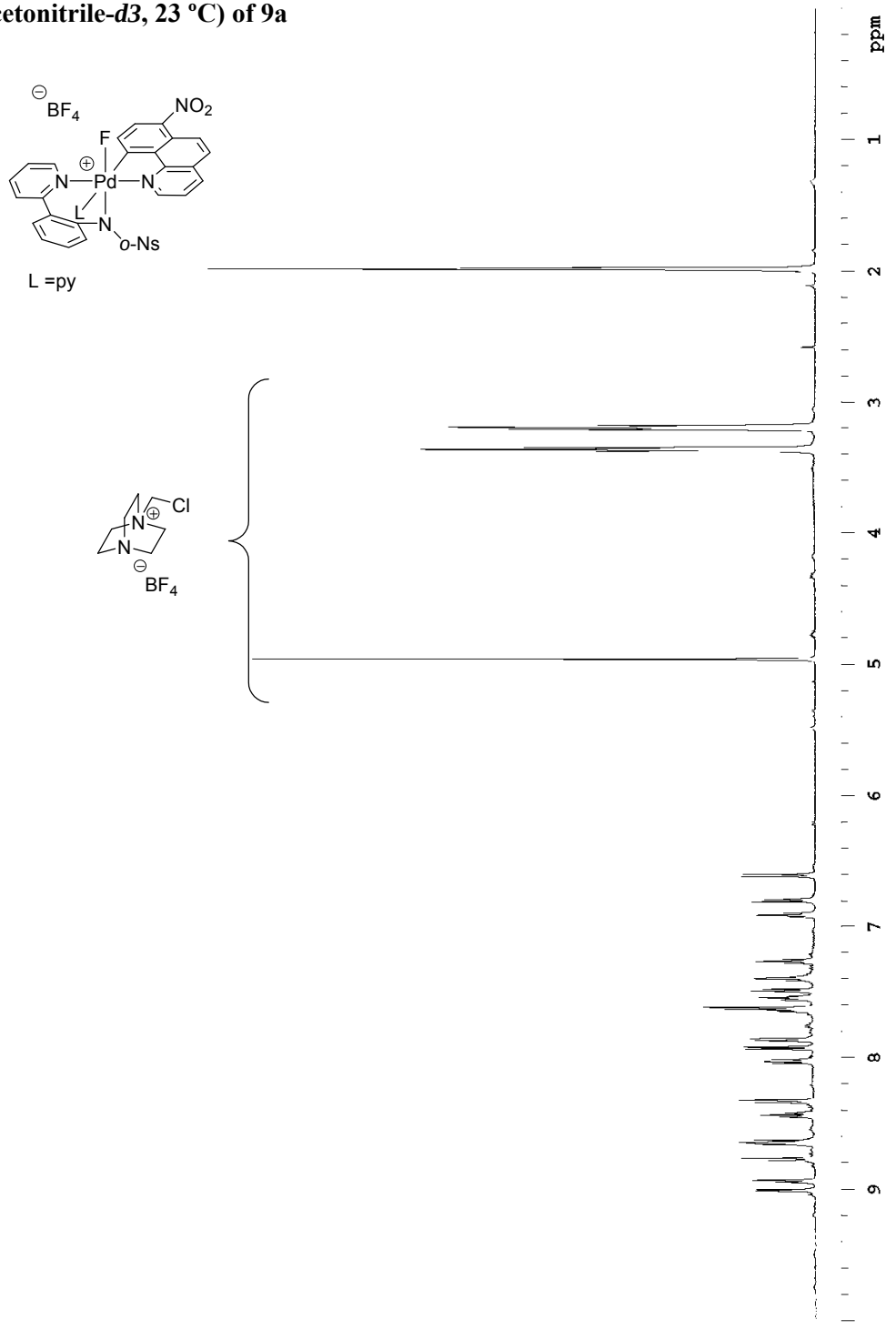
^{1}H NMR (acetonitrile-*d3*, 23 ºC) of 8g



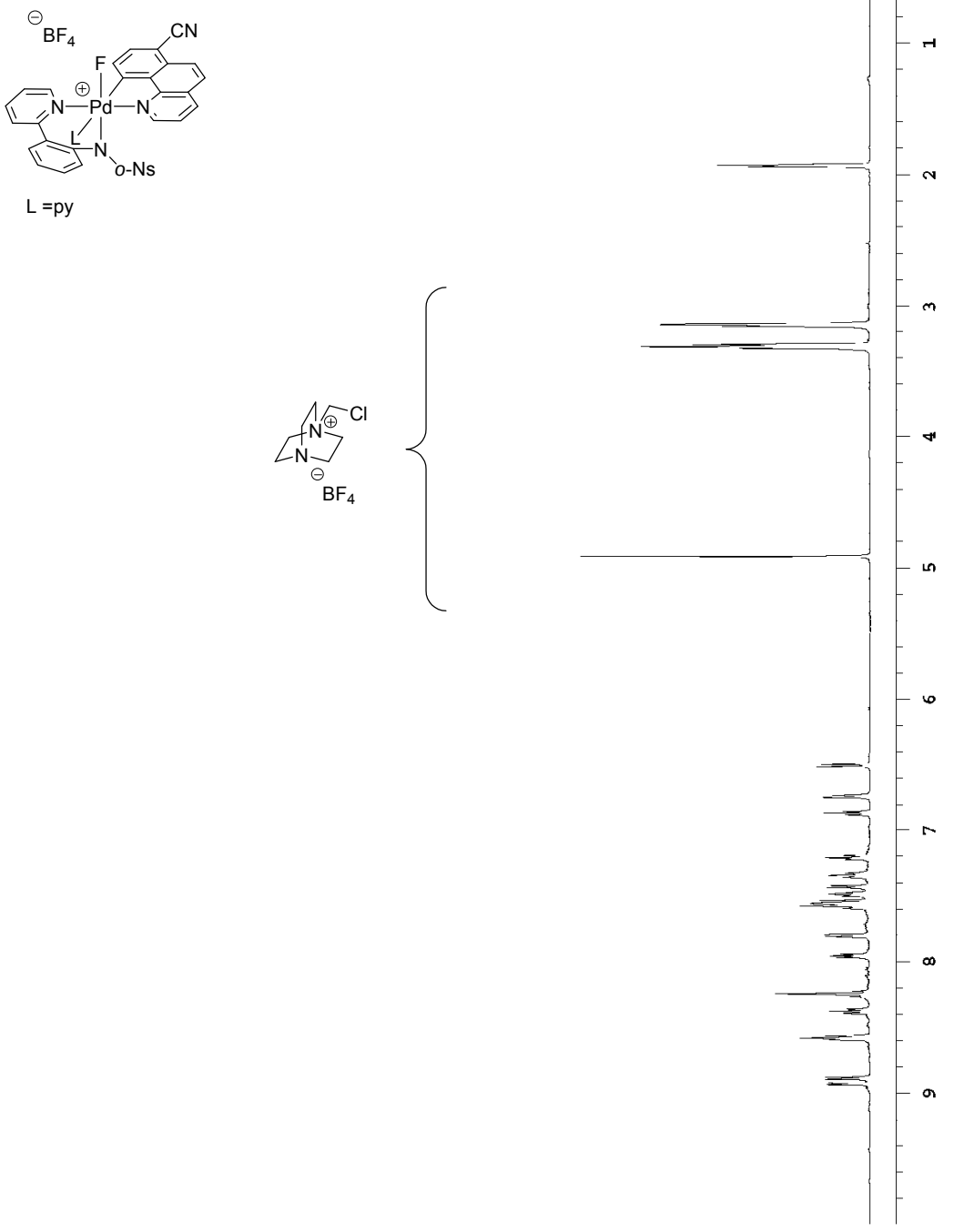




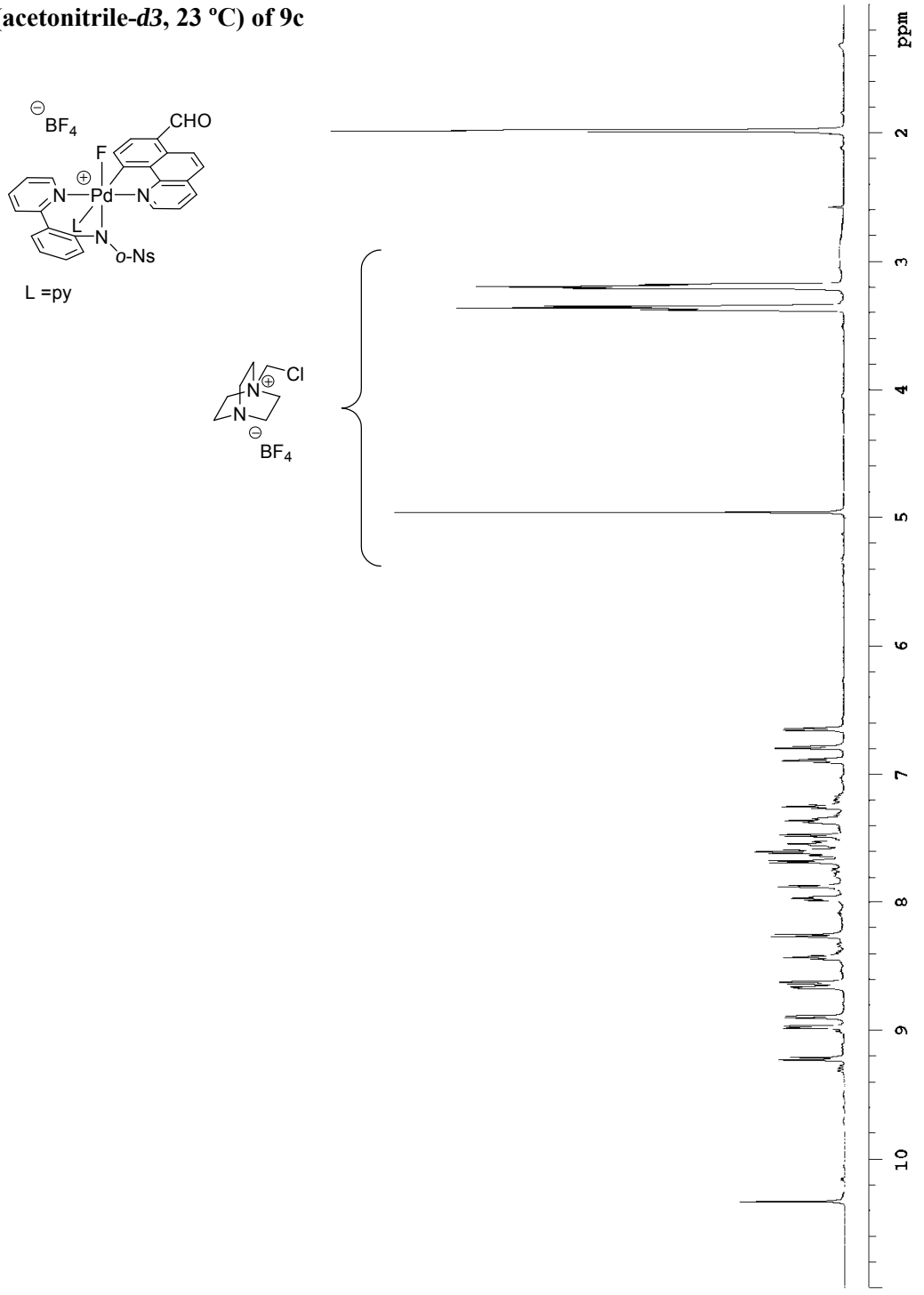
^{1}H NMR (acetonitrile-*d3*, 23 °C) of 9a



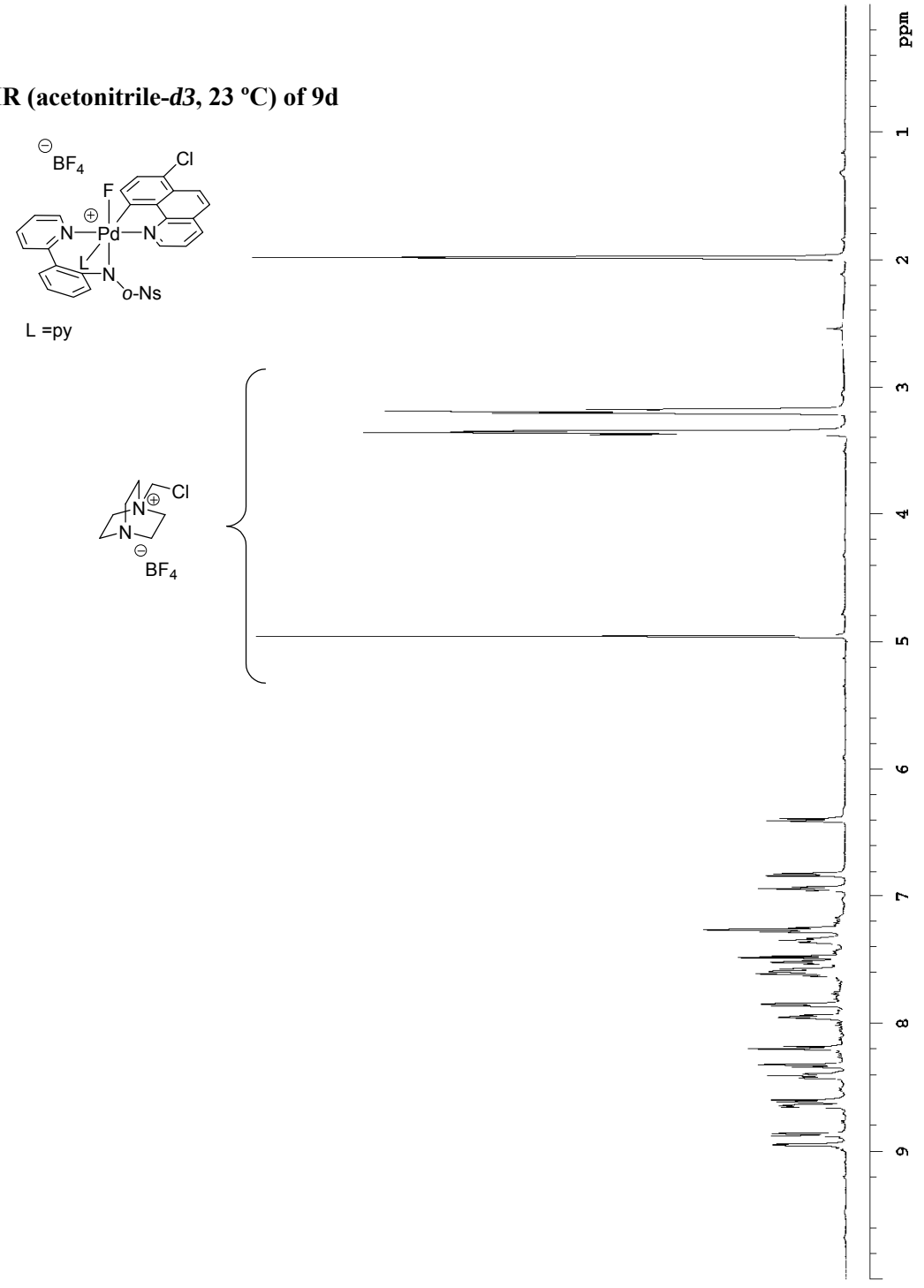
^{1}H NMR (acetonitrile-*d3*, 23 °C) of 9b



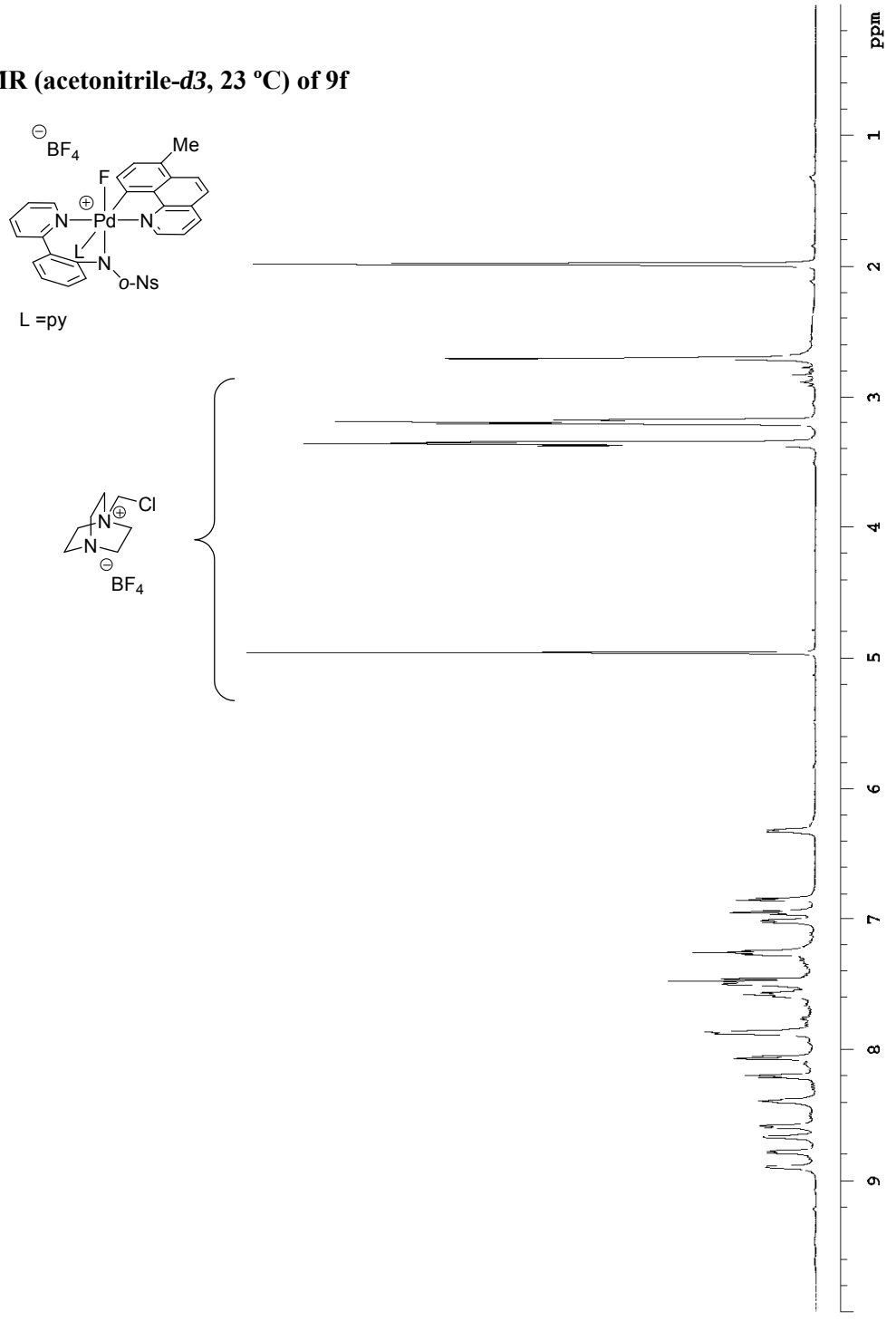
^{1}H NMR (acetonitrile-*d3*, 23 ºC) of 9c



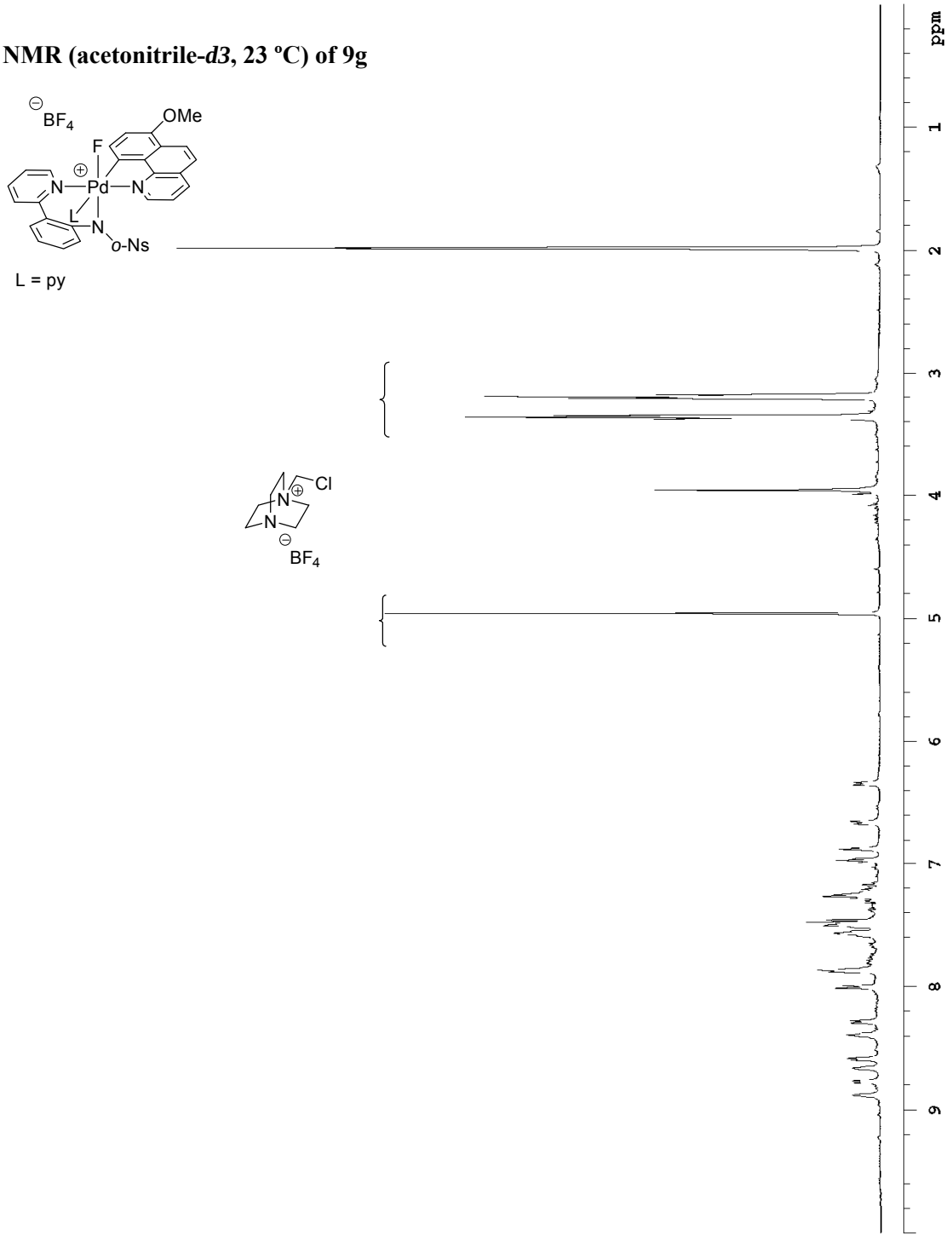
^{1}H NMR (acetonitrile-*d3*, 23 °C) of 9d



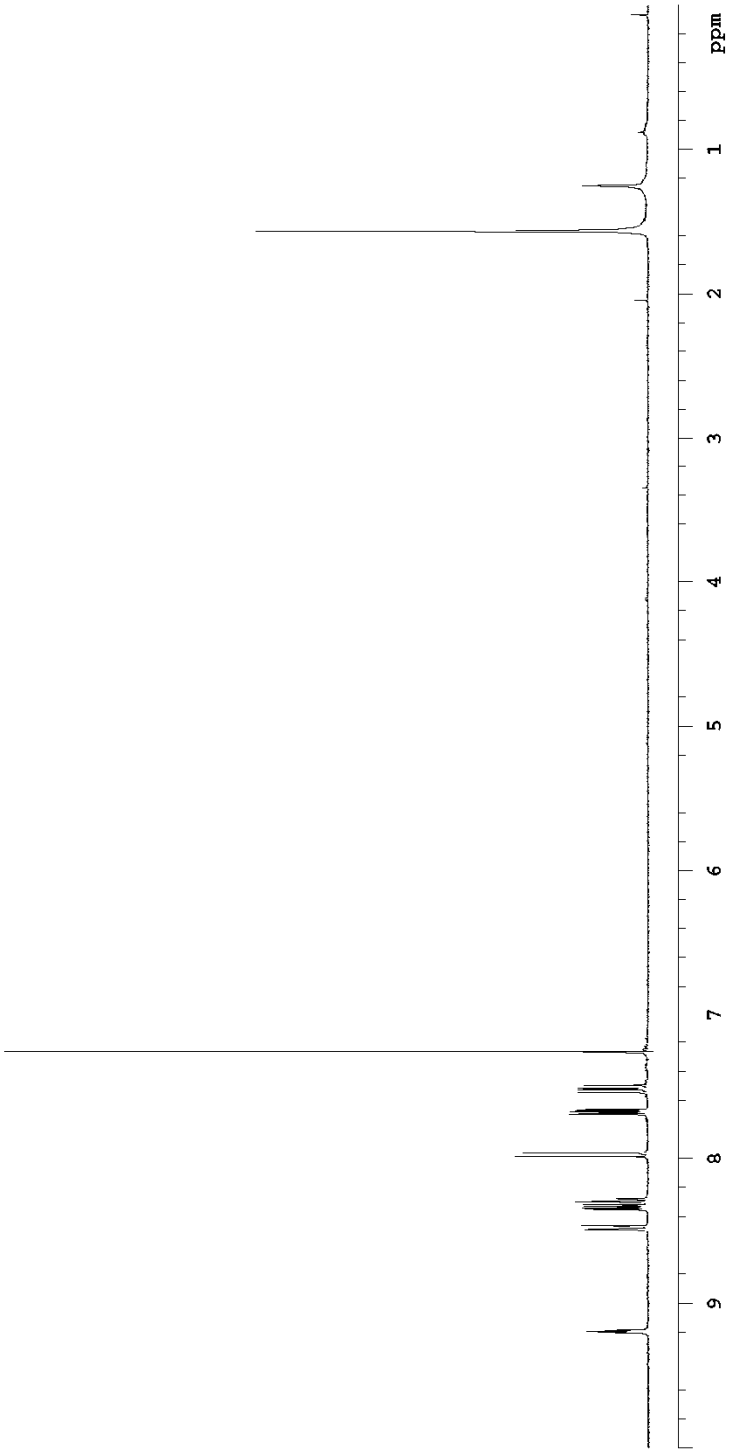
^{1}H NMR (acetonitrile-*d3*, 23 ºC) of 9f



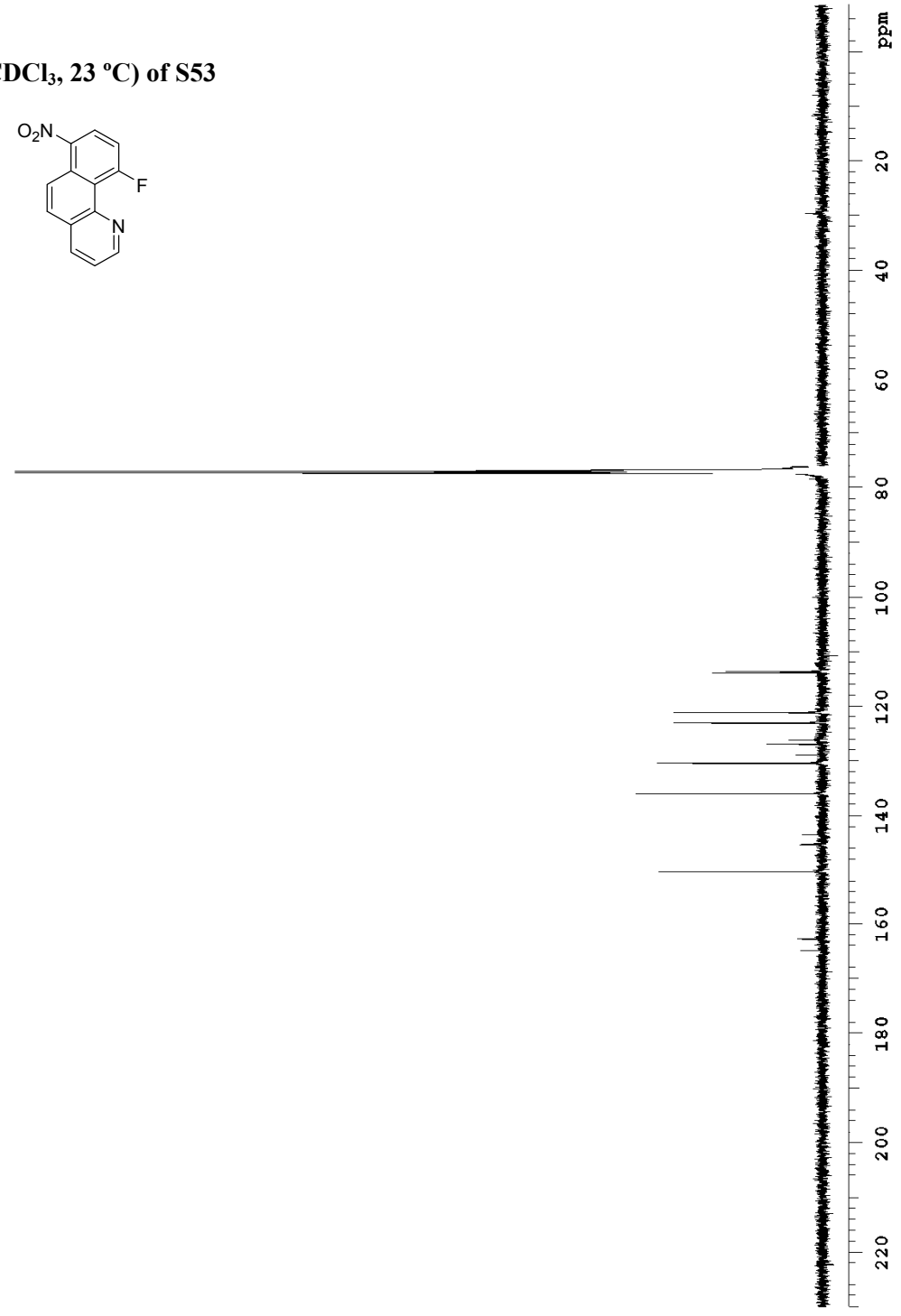
^{1}H NMR (acetonitrile-*d3*, 23 °C) of 9g



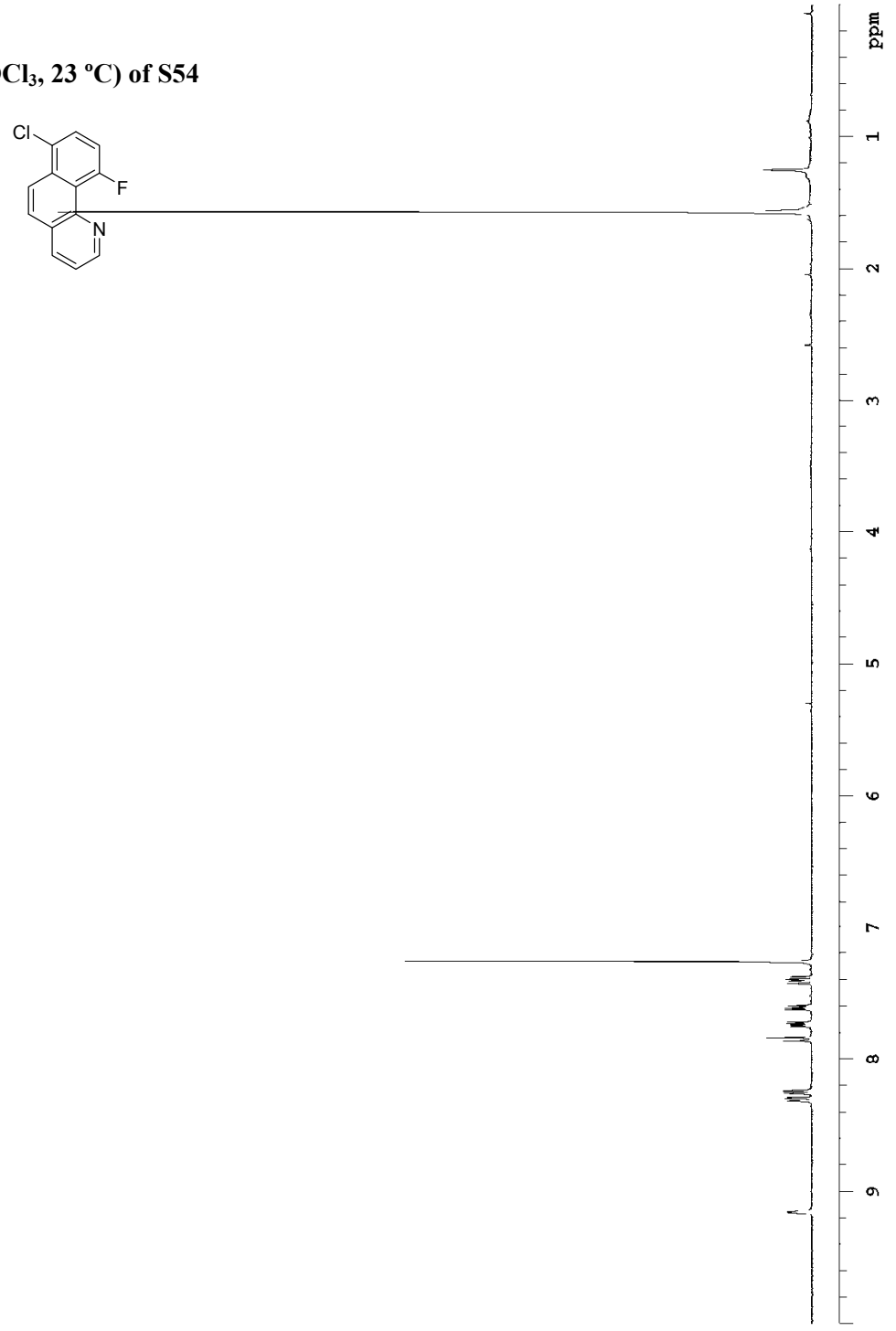
^{1}H NMR ($CDCl_3$, 23 ºC) of S53



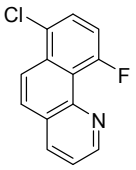
^{13}C NMR ($CDCl_3$, 23 ºC) of S53

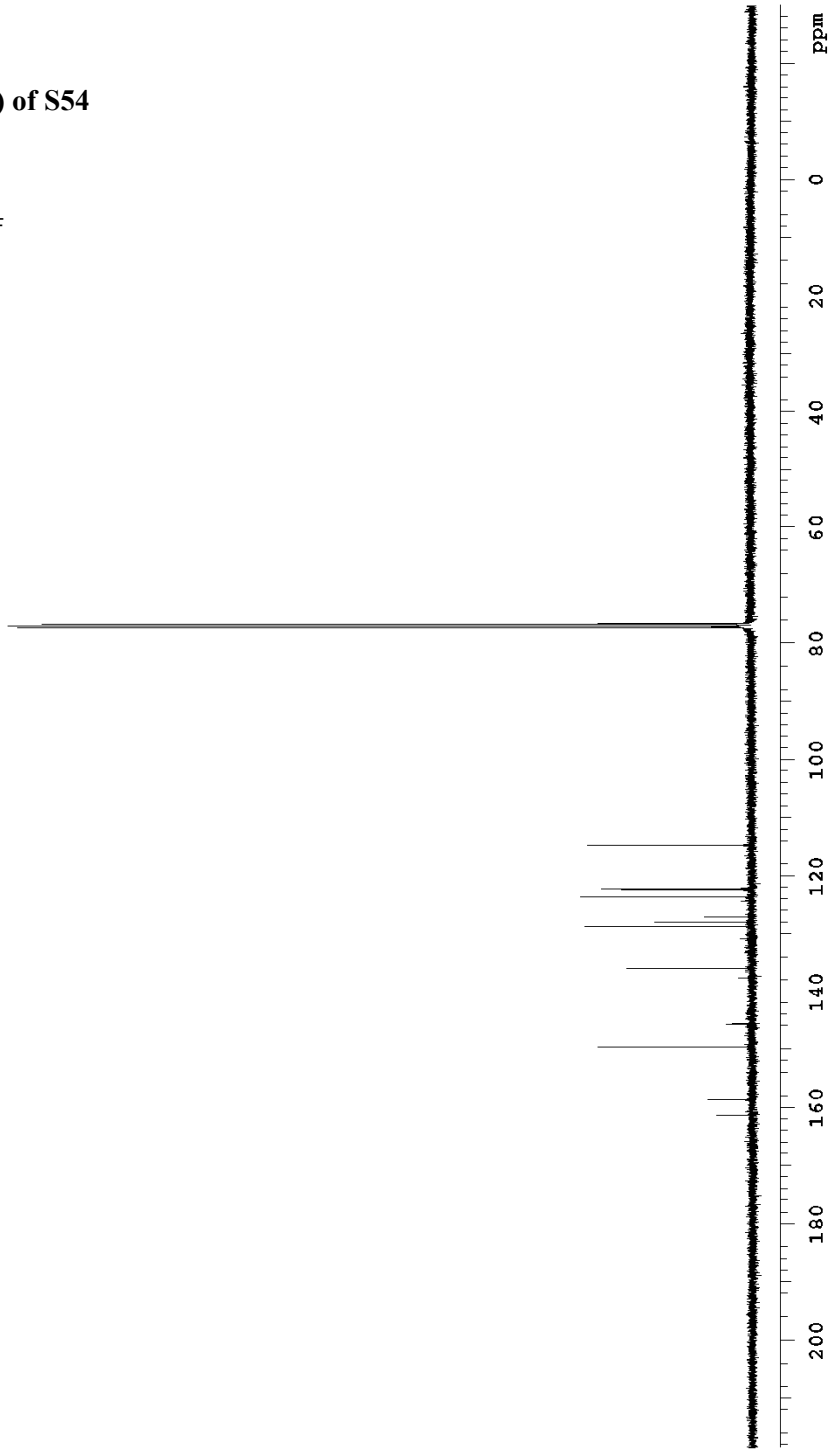


^{1}H NMR ($CDCl_3$, 23 °C) of S54

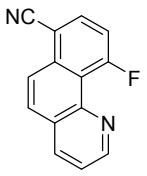


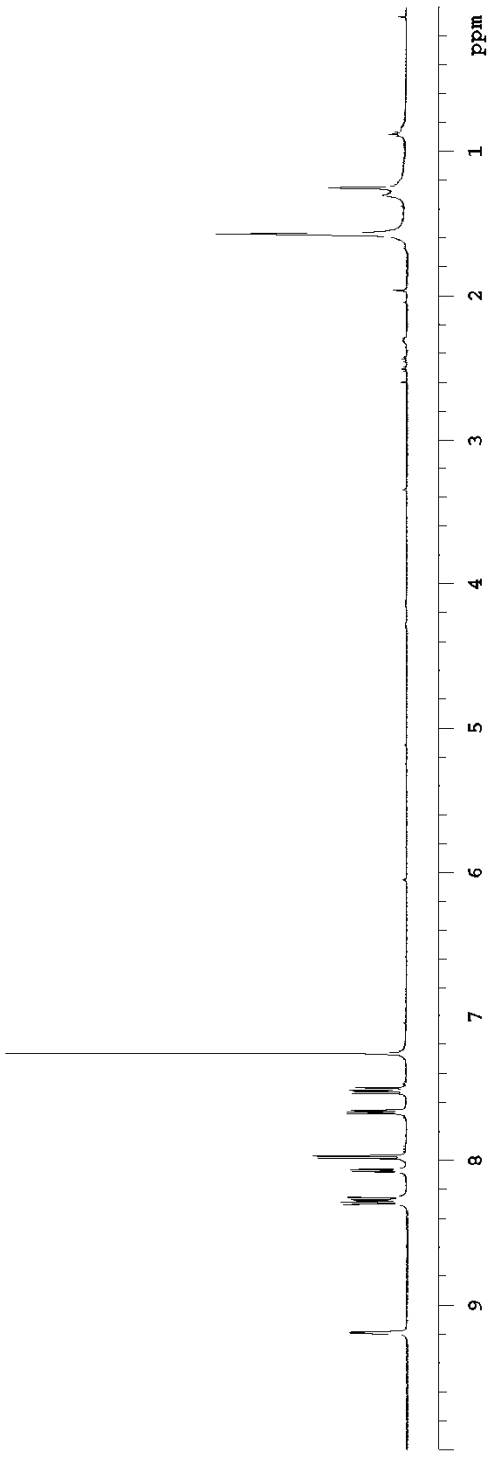
^{13}C NMR ($CDCl_3$, 23 ºC) of S54



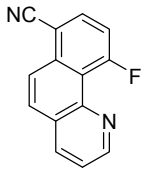


^{1}H NMR ($CDCl_3$, 23 °C) of S55

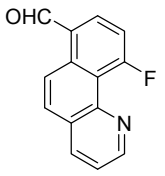


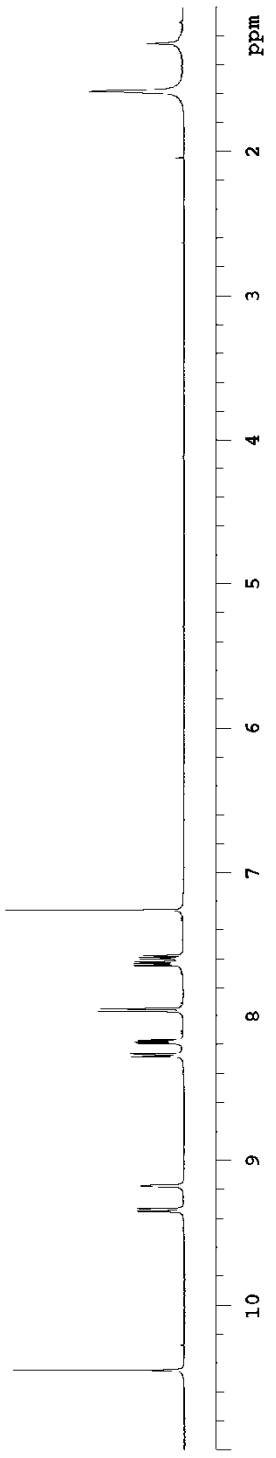


^{13}C NMR ($CDCl_3$, 23 ºC) of S55

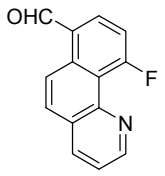


^{1}H NMR ($CDCl_3$, 23 ºC) of S56

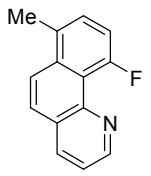


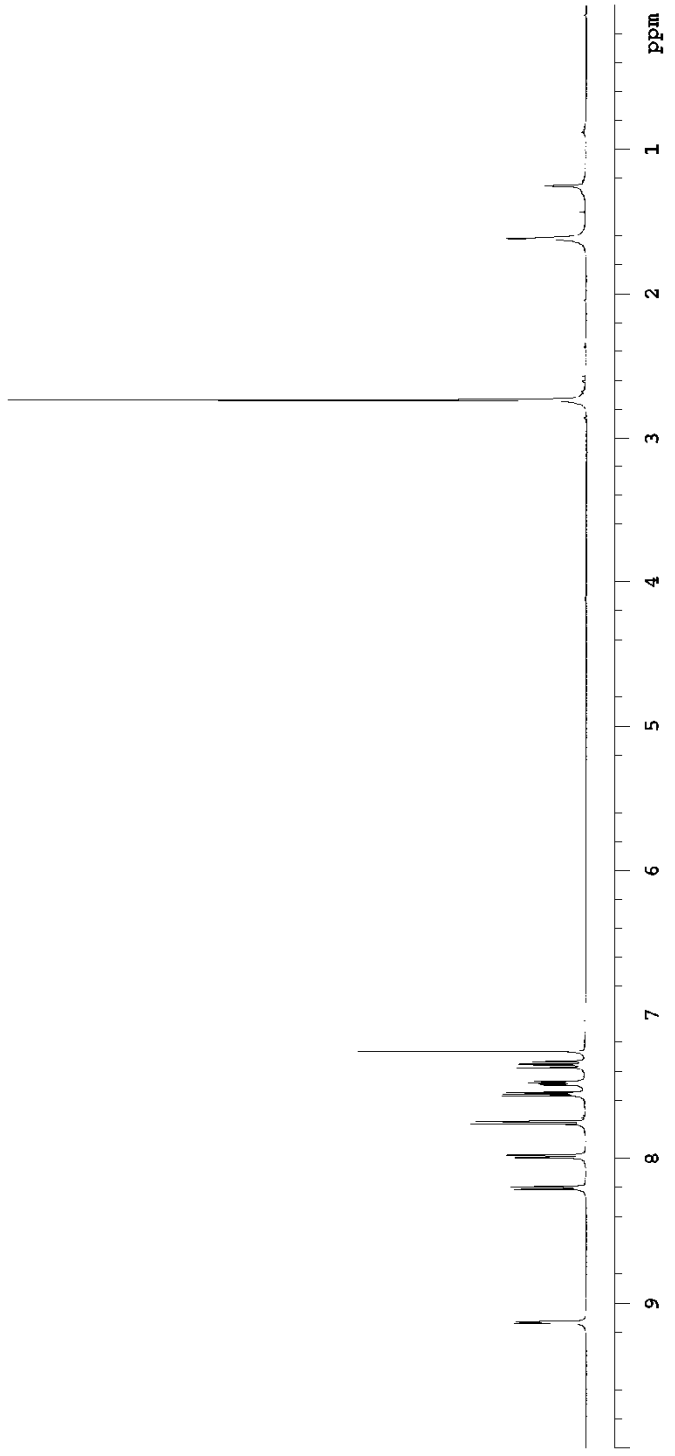


^{13}C NMR ($CDCl_3$, 23 ºC) of S56

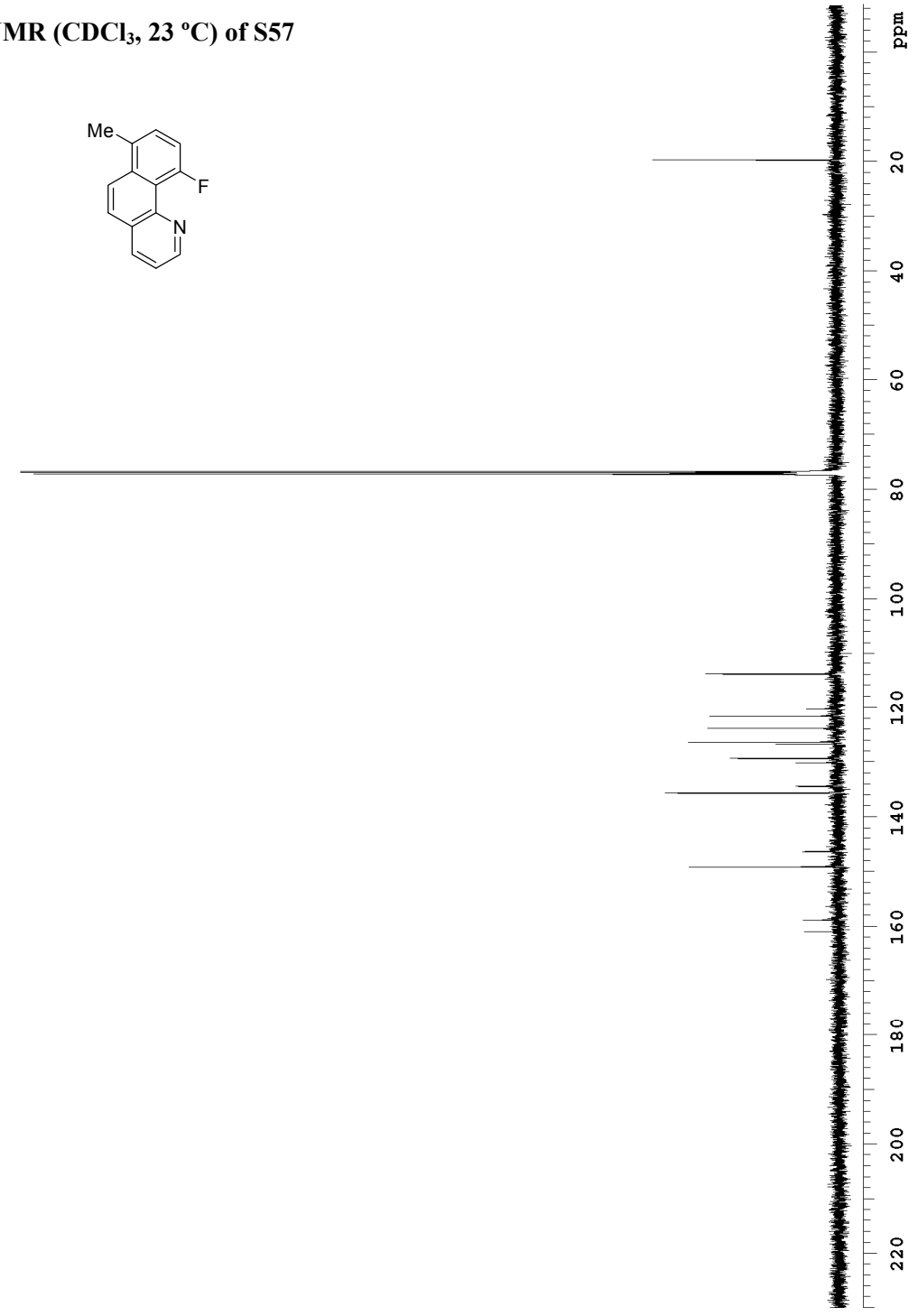


^{1}H NMR ($CDCl_3$, 23 °C) of S57

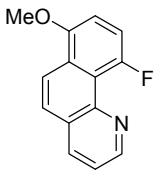


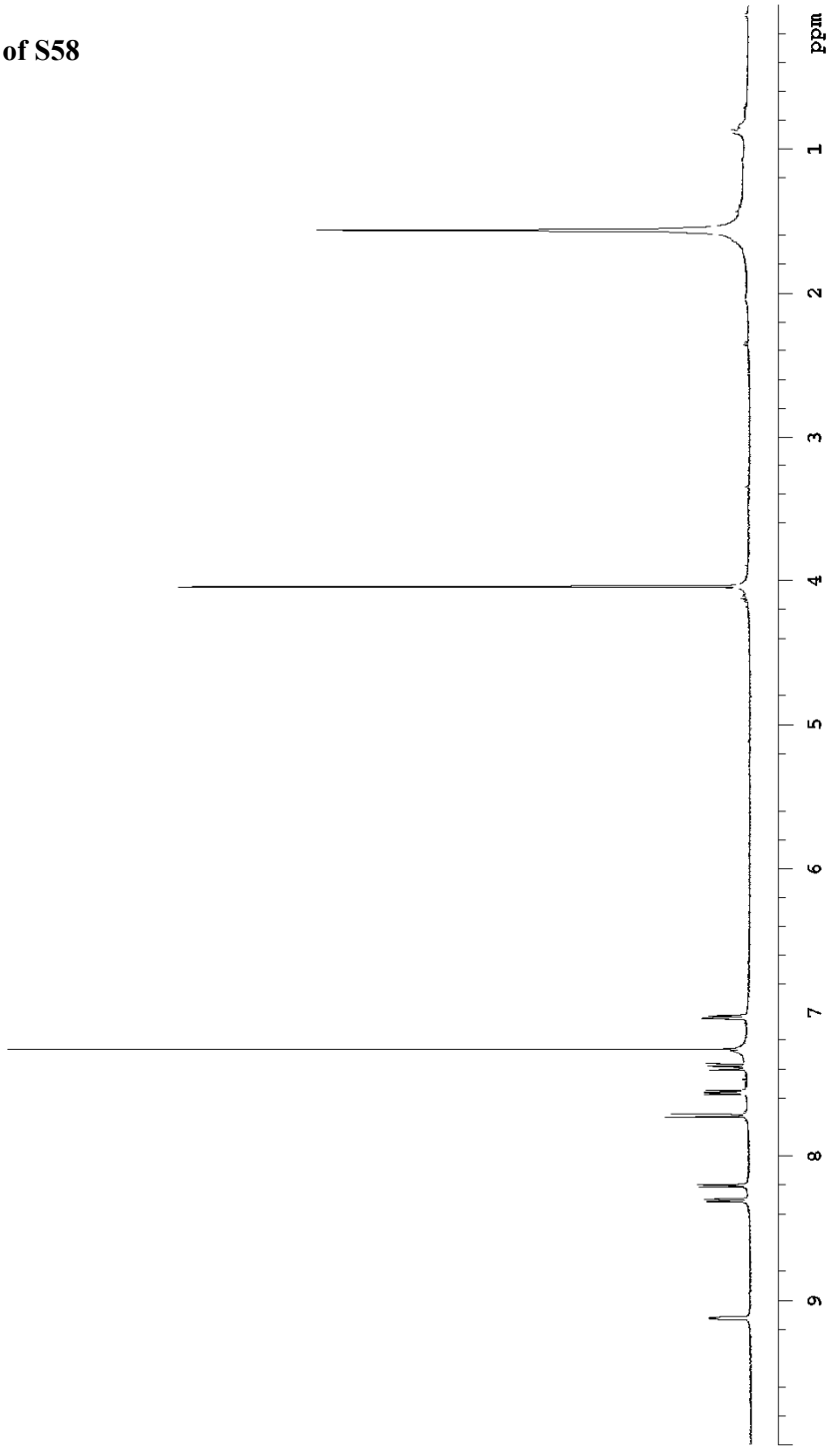


^{13}C NMR ($CDCl_3$, 23 ºC) of S57

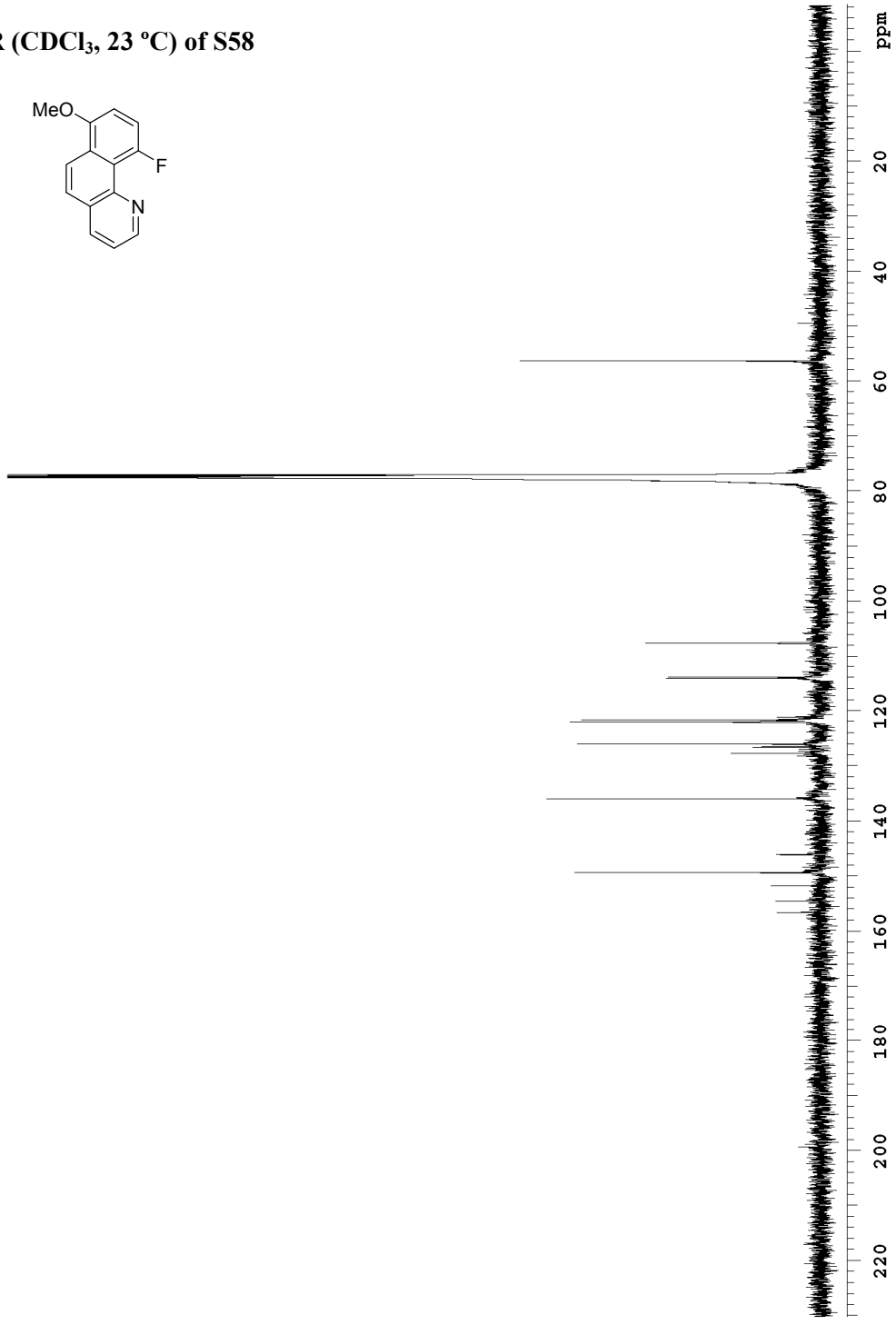


^{1}H NMR ($CDCl_3$, 23 °C) of S58

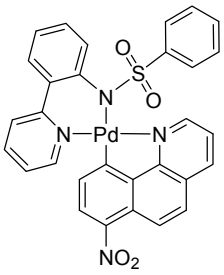


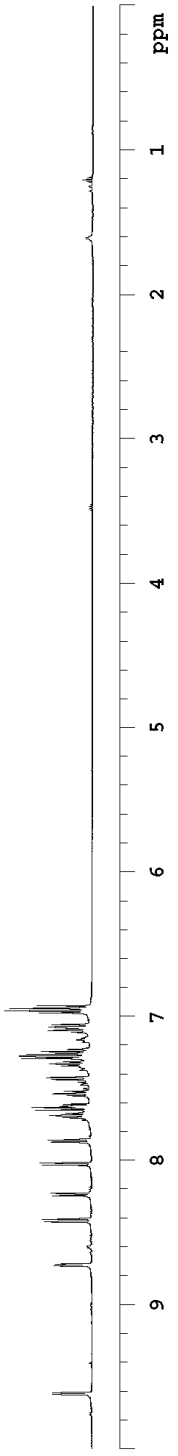


^{13}C NMR ($CDCl_3$, 23 ºC) of S58

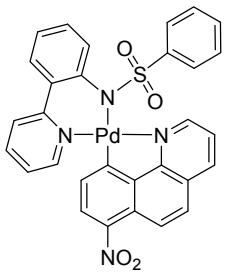


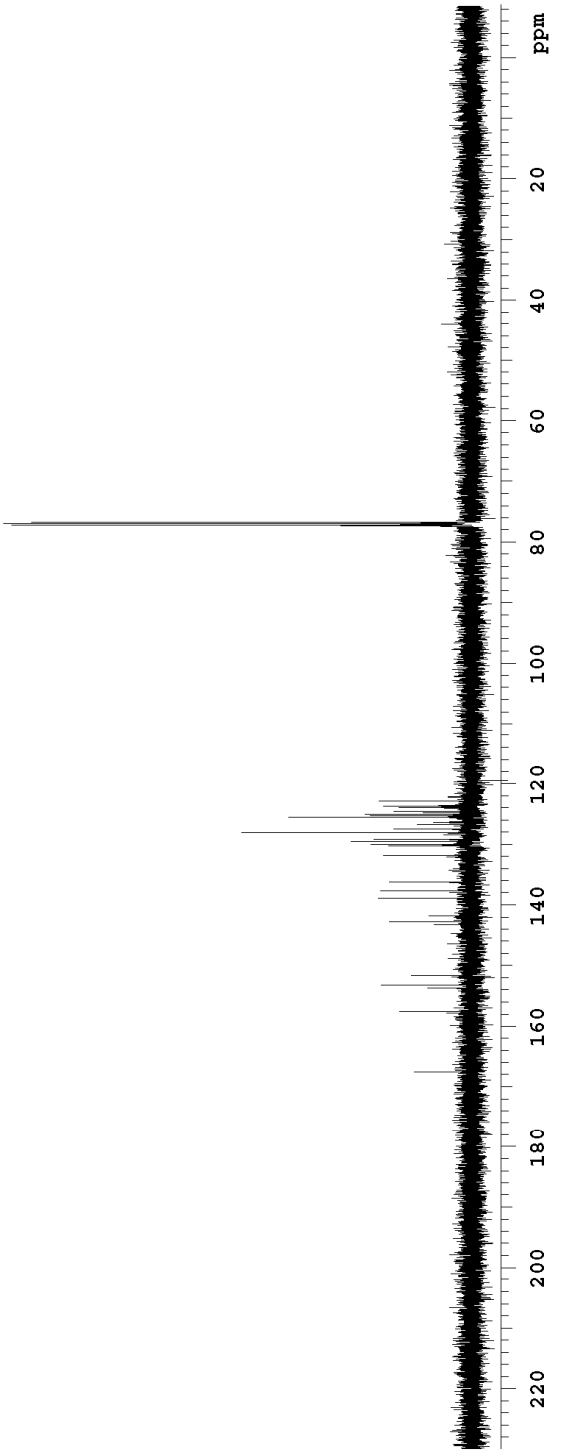
^{1}H NMR ($CDCl_3$, 23 ºC) of S59



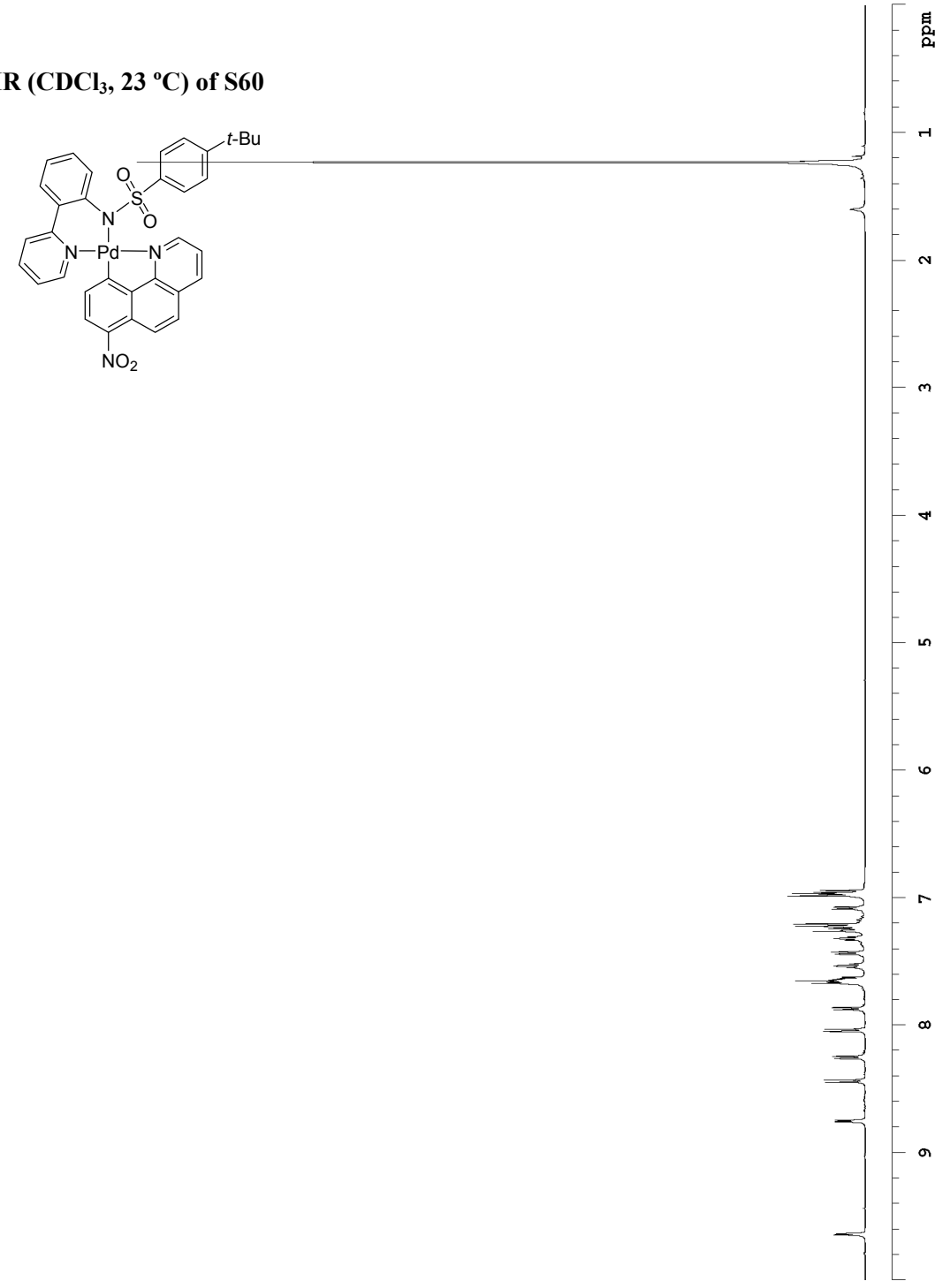


^{13}C NMR ($CDCl_3$, 23 ºC) of S59

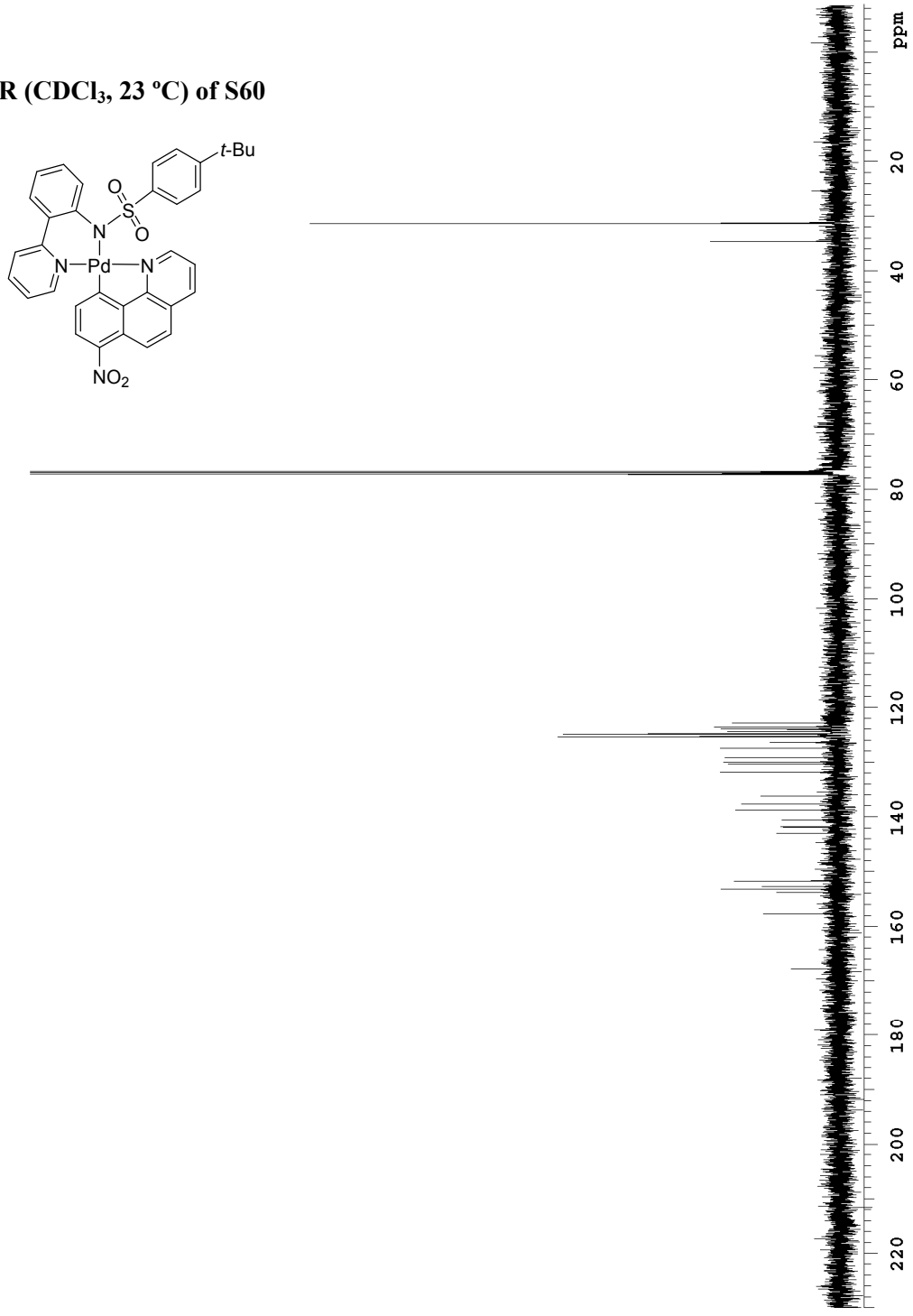




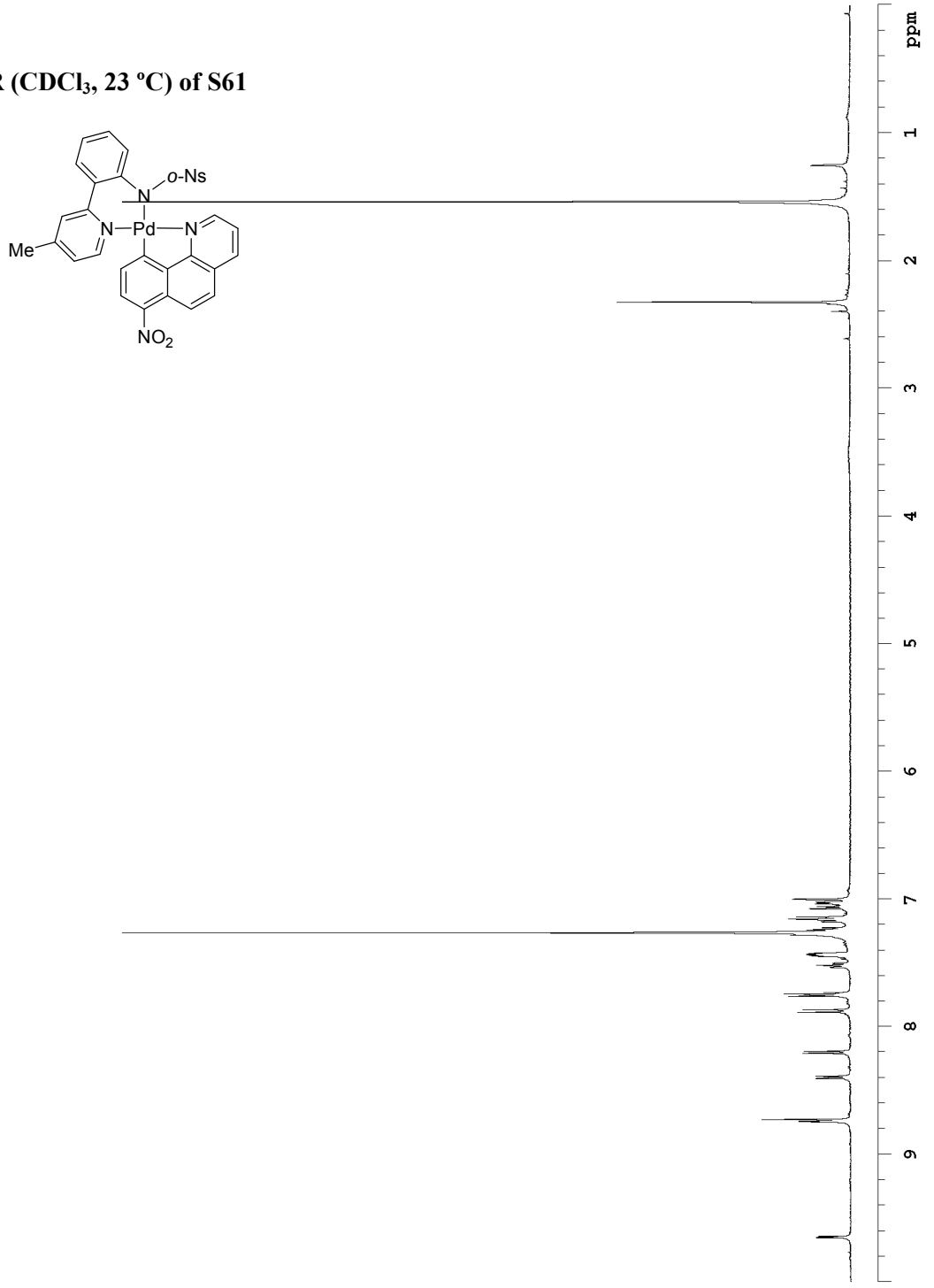
^{1}H NMR ($CDCl_3$, 23 ºC) of S60



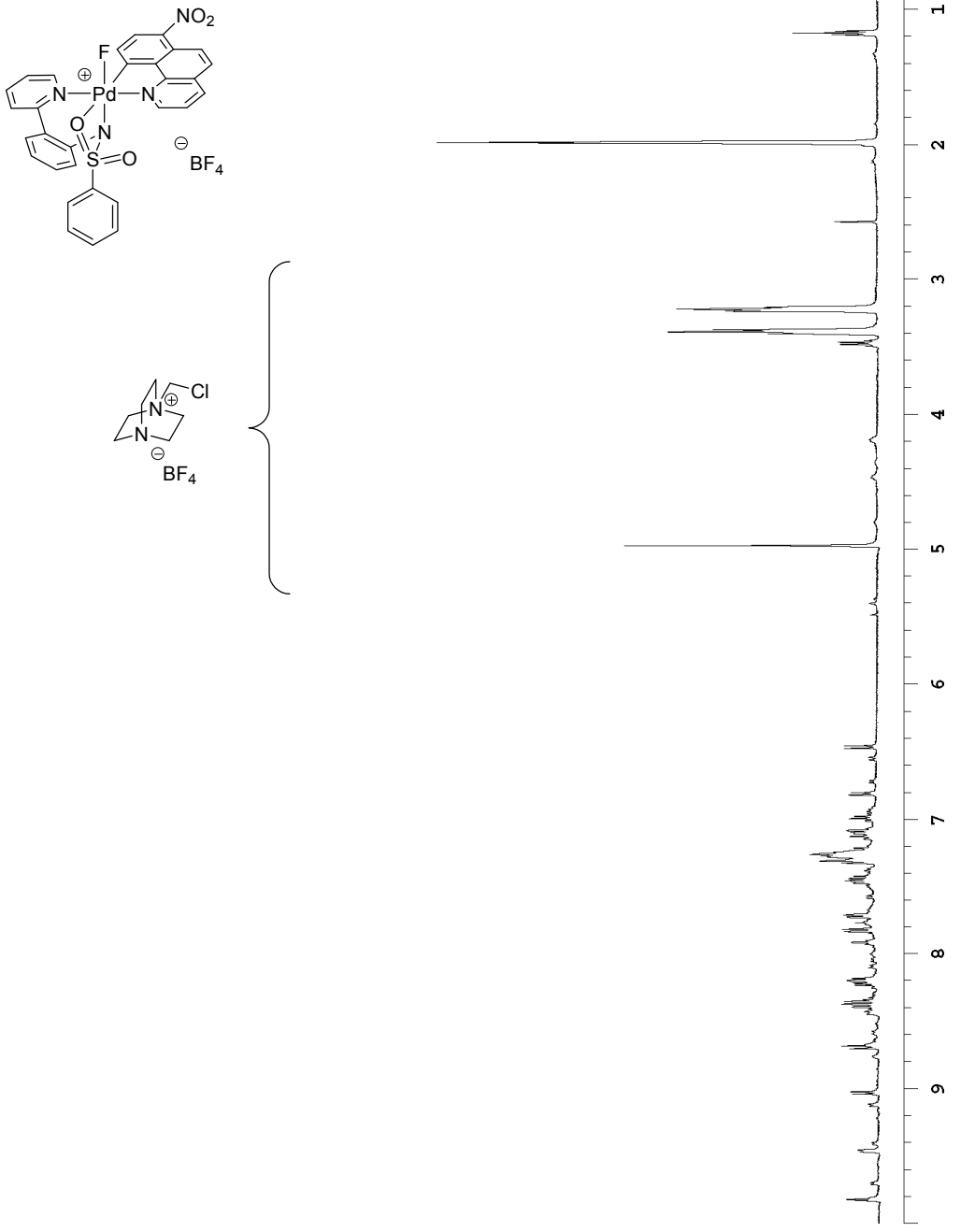
^{13}C NMR ($CDCl_3$, 23 ºC) of S60



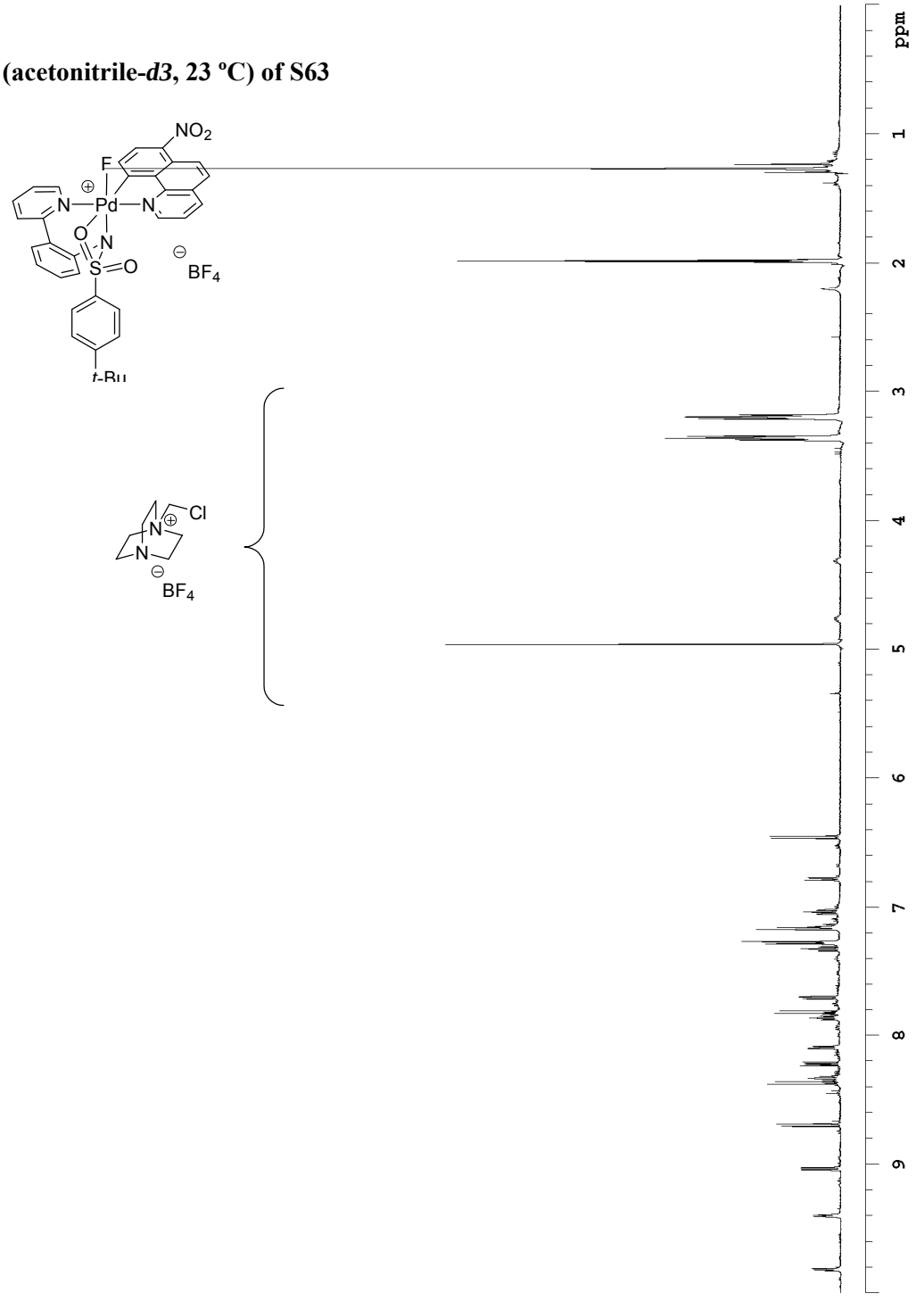
^{1}H NMR ($CDCl_3$, 23 ºC) of S61



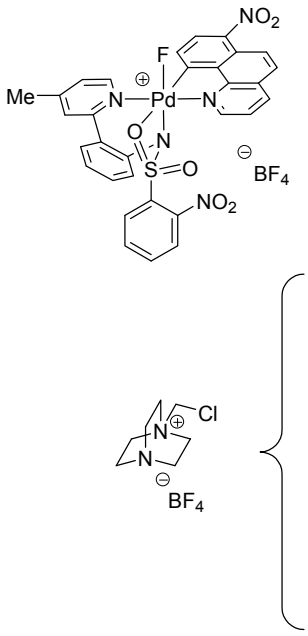
^{1}H NMR (acetonitrile-*d3*, 23 ºC) of S62

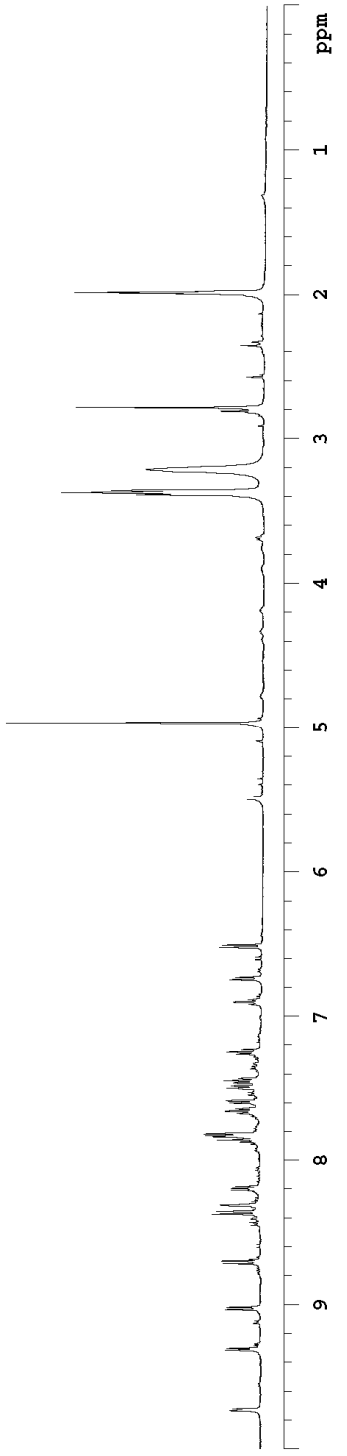


^{1}H NMR (acetonitrile-*d3*, 23 ºC) of S63

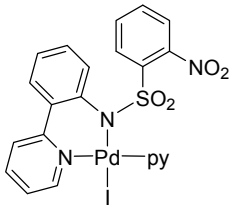


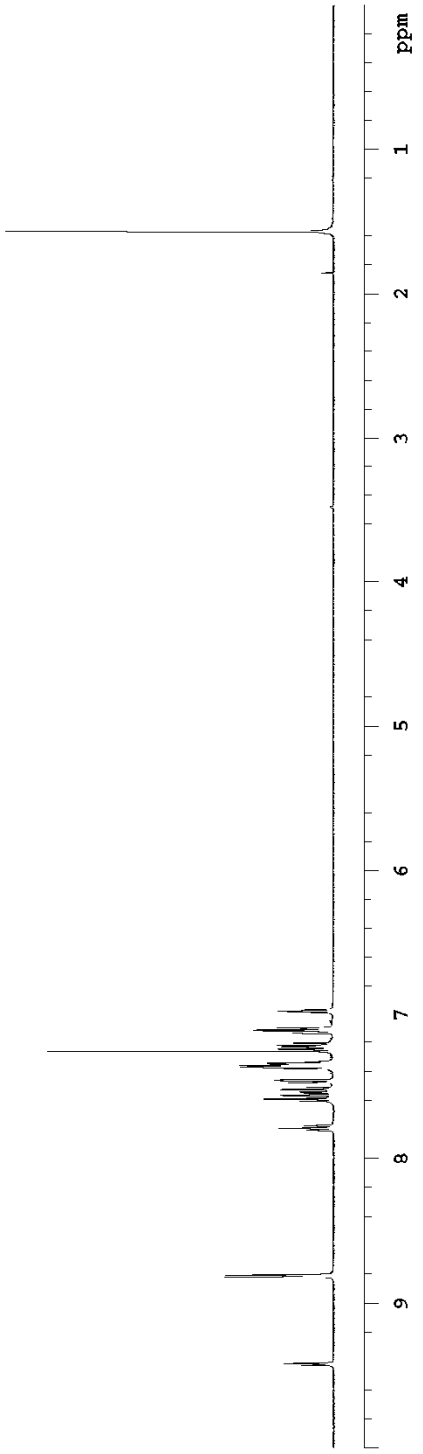
^{1}H NMR (acetonitrile-*d3*, 23 ºC) of S64



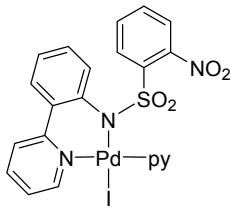


^{1}H NMR ($CDCl_3$, 23 °C) of 12

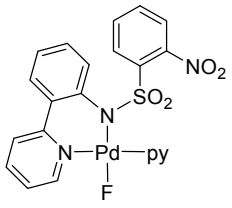


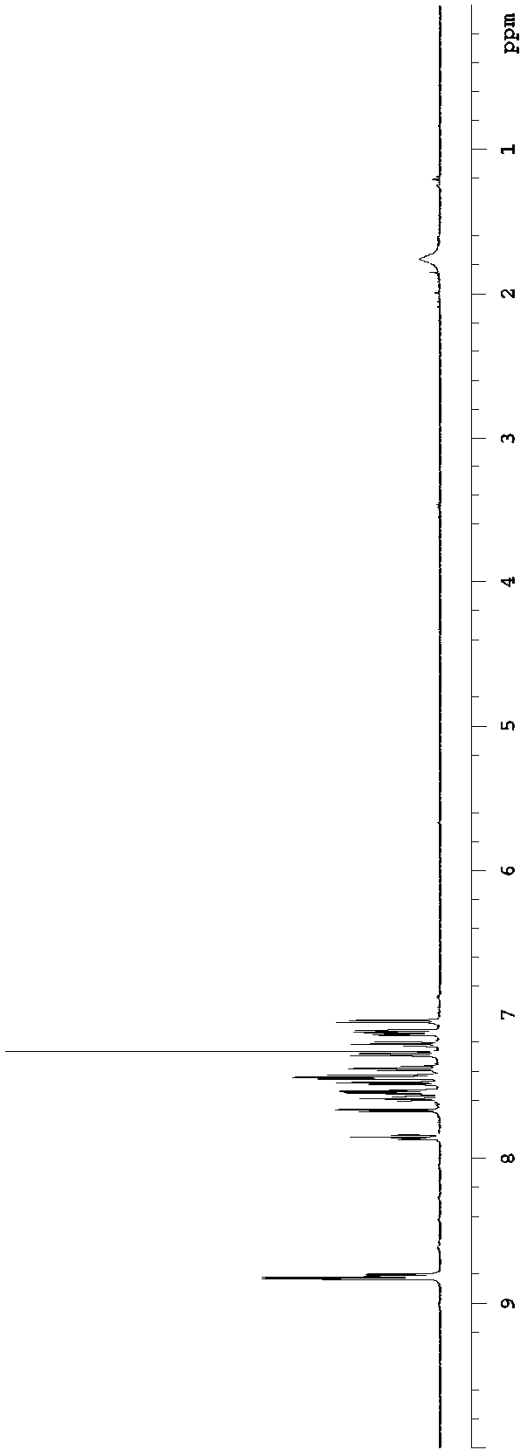


^{13}C NMR ($CDCl_3$, 23 ºC) of 12



^{1}H NMR ($CDCl_3$, 23 ºC) of 11





^{13}C NMR ($CDCl_3$, 23 ºC) of 11