Supplementary Information

Palladium(III)-Catalyzed Fluorination of Arylboronic Acid Derivatives

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Materials and Methods

Reactions were carried out under ambient atmosphere unless otherwise noted. Purified compounds were further dried under high vacuum (0.01–0.05 Torr). Yields refer to purified and spectroscopically pure compounds. Thin layer chromatography (TLC) was performed using EMD TLC plates pre-coated with 250 μm thickness silica gel 60 F_{254} plates and visualized by fluorescence quenching under UV light and $KMnO_4$ stain. Flash chromatography was performed using silica gel (230-400 mesh) purchased from Silicycle Inc. Melting points were measured on a Thomas Scientific Uni-Melt capillary melting point apparatus. All melting points were measured in open capillaries and are uncorrected. NMR spectra were recorded on either a Varian Unity/Inova 600 spectrometer operating at 600 MHz for ^{1}H acquisitions, a Varian Unity/Inova 500 spectrometer operating at 500 MHz and 125 MHz for ^{1}H and ^{13}C acquisitions, respectively, or a Varian Mercury 400 spectrometer operating at 400 HMz and 375 MHz for ^{1}H and ^{19}F acquisitions, respectively. Chemical shifts are reported in ppm with the solvent resonance as the internal standard (^{1}H: $CDCl_3$, δ 7.26; $(CD_3)_2SO$, δ 2.50; CD_3CN, δ 1.94; $(CD_3)_2CO$, δ 2.05), (^{13}C: $CDCl_3$, δ 77.16; CD_3CN, δ 1.32, $(CD_3)_2SO$, δ 39.52; $(CD_3)_2CO$, δ 29.84, 206.26).[1] Data is reported as follows: s = singlet, br = broad, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet; coupling constants in Hz; integration. All deuterated solvents were purchased from Cambridge Isotope Laboratories. Solution-state magnetic susceptibility measurements were obtained using the Evans method[2] and are reported as follows: (field strength, solvent, temperature): μ_{eff} (concentration in mg/mL). EPR spectra were recorded on a Bruker ElexSys E500 EPR spectrometer operating at X-band frequency (9 GHz). UV-vis/NIR spectra were measured on a PerkinElmer Lambda 750 spectrophotometer. Electrochemical measurements were made using a CH Instruments Model 600E Series Electrochemical Analyzer/Workstation. High-resolution mass spectra were obtained using an Agilent ESI-TOF (6210) mass spectrometer or a Bruker q-TOF Maxis Impact mass spectrometer. LC/MS data were obtained using a Shimadzu LCMS-2020. $Pd(OAc)_2$ was purchased from Strem. HBF_4•OEt_2 was purchased from Alfa Aesar. 1-Chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (Selectfluor) and 2,2′:6′,2″-terpyridine (terpy) were purchased from Strem or SigmaAldrich. All chemicals were used as received. DMF was ACS Reagent grade, purchased from SigmaAldrich; MeCN was ACS grade, purchased from BDH. These solvents were used as received without further purification.

Acknowledgement:

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[1] Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallics* **2010**, *29*, 2176-2179.

[2] Evans, D. F. *J. Chem. Soc.* **1959**, 2003–2005.

possible in part by the American Recovery and Reinvestment Act of 2009. The DOE SCGF program is administered by the Oak Ridge Institute for Science and Education for the DOE. ORISE is managed by Oak Ridge Associated Universities (ORAU) under DOE contract number DE-AC05-06OR23100. All opinions expressed in this paper are the authors' and do not necessarily reflect the policies and views of DOE, ORAU, or ORISE.

Experimental Data

Experimental Procedures and Compound Characterization

I. Representative Procedure for the Pd-Catalyzed Fluorination Reaction

Representative Procedure A: Electron Poor Substrates (MeCN)

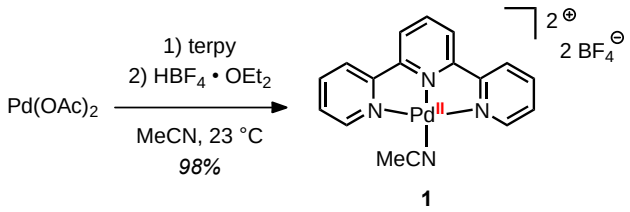
Palladium precatalyst **1** (307 mg, 554 µmol, 0.010 equiv), terpy (258 mg, 1.11 mmol, 0.040 equiv), aryl trifluoroborate (55.4 mmol, 1.00 equiv), Selectfluor (23.5 g, 66.4 mmol, 1.20 equiv), and sodium fluoride (2.32 g, 55.4 mmol, 1.00 equiv) were added to a round-bottom flask (200 mL), followed by acetonitrile (55.4 mL, 1.0 M) at 23 °C. An air-cooled reflux condenser was fitted to the round bottom flask. The reaction mixture was stirred for 15 hours open to air at 40 °C, allowed to cool to 23 °C, and then transferred to a separatory funnel, rinsing the reaction flask with additional acetonitrile (2 × 50 mL). Pentane (250 mL) was added and the organic layer was washed with water (350 mL). The aqueous layer was extracted with dichloromethane (4 × 300 mL). The combined organic layers were washed with brine (500 mL), dried over sodium sulfate, filtered, and concentrated *in vacuo*. The residue was purified by chromatography on silica gel to afford the aryl fluoride product.

Representative Procedure B: Electron Neutral or Electron Rich Substrates (DMF)

Palladium precatalyst **1** (201 mg, 362 µmol, 0.010 equiv), terpy (169 mg, 724 µmol, 0.040 equiv), aryl trifluoroborate (36.2 mmol, 1.00 equiv), Selectfluor (14.1 g, 39.8 mmol, 1.10 equiv), and sodium fluoride (1.52 g, 36.2 mmol, 1.00 equiv) were added to a round-bottom flask (100 mL), followed by DMF (36 mL, 1.0 M) at 23 °C. An air-cooled reflux condenser was fitted to the round bottom flask. The reaction mixture was stirred for 15 hours open to air at 23 °C, and then transferred to a separatory funnel. Pentane (250 mL) was added and the organic layer was washed with a 5% aqueous lithium chloride solution (250 mL). The aqueous layer was extracted with pentane (4 × 150 mL). For aryl fluorides that are poorly soluble in pentane, diethyl ether was used as the extraction solvent. The combined organic layers were dried over sodium sulfate, filtered, and concentrated *in vacuo*. The residue was purified by chromatography on silica gel to afford the aryl fluoride product.

II. Synthesis and Characterization of Palladium Complexes

[(terpy)Pd(MeCN)][BF_4]$_2$ (1)



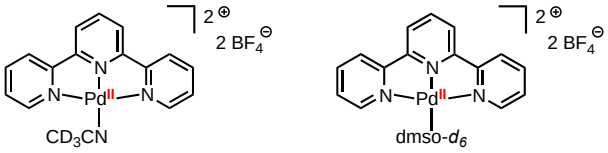
1

To $Pd(OAc)_2$ (5.00 g, 20.4 mmol, 1.00 equiv) in MeCN (250 mL) at 23 ºC was added terpy (4.77 g, 20.4 mmol, 1.00 equiv). The reaction mixture was stirred for 20 minutes, affording a pink/orange slurry. To this slurry was added HBF_4•OEt_2 (6.05 mL, 7.20 g, 41.9 mmol, 2.05 equiv) via syringe. The reaction mixture was stirred vigorously for 30 min, at which point a suspension of tan solids was observed. The solids were collected by filtration and washed with Et_2O (100 mL). Further precipitation was observed from the filtrate at this point, and the precipitate was collected by a second filtration. The combined solids were washed with additional Et_2O (50 mL), and then dried under vacuum to afford 10.8 g of the title compound as a pale tan solid (98% yield).

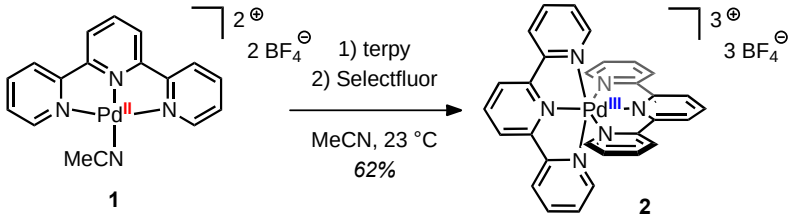
X-ray quality crystals were grown as follows: a saturated solution of **1** in MeCN was prepared by dissolving approximately 5 mg of **1** in 1 mL MeCN at 23 °C, and filtering over a celite plug to remove any remaining solids. A 4 mL glass vial containing the solution was placed, uncapped, into a 20 mL glass vial containing approximately 4 mL of Et_2O. The 20 mL vial was capped, and vapor diffusion of Et_2O into the MeCN solution of **1** at 23 °C gave orange crystals after 24 hours.

mp: 273–275 °C (decomp). NMR spectroscopy: ^{1}H-NMR (400 MHz, CD_3CN, 23 ºC, δ): 8.57 (d, *J* = 5.6 Hz, 2H), 8.51 (t, *J* = 8.2 Hz, 1H), 8.43 (t, *J* = 7.8 Hz, 2H), 8.34 (d, *J* = 8.0 Hz, 2H), 8.28 (d, *J* = 8.4 Hz, 2H), 7.84 (td, *J* = 6.6 Hz, 1.5 Hz, 2H), 1.96 (s, 3H). ^{1}H-NMR (400 MHz, dmso-d_6, 23 ºC, δ): 8.67–8.60 (m, 5H), 8.54–8.49 (m, 4H), 7.92 (td, *J* = 6.8 Hz, 1.0 Hz, 2H), 2.06 (s, 3H). ^{13}C-NMR (125 MHz, dmso-d_6, 23 ºC, δ): 157.0, 155.2, 150.5, 143.5, 143.2, 129.0, 125.5, 124.7, 118.1, 1.2. ^{19}F-NMR (375 MHz, CD_3CN, 23 ºC, δ): –151.7 (s). UV-VIS Spectroscopy (DMF, 23 ˚C): 526 nm (ε = 144 M^{-1} cm^{-1}); 367 nm (ε = 1.16 × 10^4 M^{-1} cm^{-1}); 349 nm (ε = 1.29 × 10^4 M^{-1} cm-1); 333 nm (ε = 1.07 × 104 M-1 cm-1). FT-IR Spectroscopy (neat, cm^{-1}): 2323, 1606, 1574, 1483, 1452, 1323, 1029, 828, 781, 724, 517. Anal: calcd for $C_{17}H_{14}B_2F_8N_4Pd$: C, 36.83; H, 2.55; N, 10.11; found: C, 37.11; H, 2.56; N, 9.97. X-ray data included in X-Ray Data Analysis section.

The acetonitrile ligand in **1** is displaced by either CD_3CN or dmso-d_6 upon dissolution; as a result, free CH_3CN is observed in the ^{1}H and ^{13}C NMR spectra (^{13}C-NMR signals were not observed in CD_3CN due to low solubility). Compound **1** is poorly soluble in non-coordinating solvents. Accordingly, the solution structures corresponding to the NMR data reported above should be considered as:



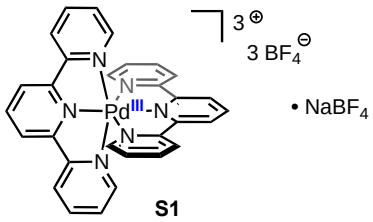
[(terpy)$_2$Pd][BF$_4$]$_3$ (2)



To a suspension of [(terpy)Pd(MeCN)][BF$_4$]$_2$ (**1**) (250. mg, 0.451 mmol, 1.00 equiv) in MeCN (10 mL) at 23 ºC was added terpy (105 mg, 0.451 mmol, 1.00 equiv) and the mixture was stirred for 1 minute, affording a homogeneous orange solution. To this solution was added Selectfluor (168 mg, 0.474 mmol, 1.05 equiv), and the reaction mixture was stirred vigorously at 23 °C for 20 minutes, at which point a homogeneous deep red solution was observed. The solution was transferred to a 20 mL glass vial, and the vial was placed, uncapped, into a jar containing approximately 50 mL of Et_2O. The jar was capped, and vapor diffusion of Et_2O into the MeCN solution at 23 °C resulted in the growth of large red needle crystals after 24 hours. The following purification procedure was performed to remove residual Selectfluor and TEDA-BF$_4$: the supernatant from crystallization was decanted, and the crystallized material was dissolved in MeCN (15 mL), filtered over a celite plug, and crystallized again by vapor diffusion of Et_2O (50 mL) into the MeCN solution. The supernatant from crystallization was decanted, and the crystallized material was again dissolved in MeCN (15 mL), filtered over a celite plug, and crystallized once more by vapor diffusion of Et_2O (50 mL) into the MeCN solution. The final batch of crystals was isolated and dried under vacuum to afford 233 mg of the title compound as deep red needle crystals (62% yield). Crystals grown in this manner were found to be suitable for X-ray diffraction.

mp: 220 °C (decomp). NMR Spectroscopy: ^{19}F-NMR (375 MHz, CD_3CN, 23 ºC, δ): –151.3 (s). UV-VIS Spectroscopy (MeCN, 23 ˚C): 1002 nm (ε = 95.9 M^{-1} cm^{-1}); 419 nm (ε = 1.52 × 10^3 M^{-1} cm^{-1}); 340 nm (ε = 2.36 × 10^4 M^{-1} cm^{-1}). Magnetic susceptibility (500 MHz, CD_3CN, 23 ºC): μ_{eff} = 1.74 μ_B (14.3 mg/mL). FT-IR Spectroscopy (neat, cm^{-1}): 3102, 1603, 1502, 1479, 1315, 1245, 1026, 780, 644, 519. Anal: calcd for $C_{30}H_{22}B_3F_{12}N_6Pd$: C, 43.24; H, 2.66; N, 10.08; found: C, 43.05; H, 2.51; N, 9.85. EPR spectra included in EPR Data section. X-ray data included in X-Ray Data Analysis section. ^{1}H-NMR and ^{13}C-NMR signals were not observed.

Crystallization of $[(terpy)_2Pd][BF_4]_3 \cdot [NaBF_4]$ (S1)



S1

Due to the high level of disorder in the X-ray crystal structure of $[(terpy)_2Pd][BF_4]_3$ (**2**) (see X-ray data section), we felt that this structure was not suitable to satisfactorily determine the structural metrics or Pd oxidation state. Therefore, compound **2** was derivatized as its $NaBF_4$ adduct, which allowed us to unambiguously characterize the Pd(III) cation.

To a solution of **2** (15. mg, 0.018 mmol, 1.0 equiv) in MeCN (1 mL) was added $NaBF_4$ (4.0 mg, 0.036 mmol, 2.0 equiv). The mixture was allowed to stir for 30 minutes at 23 °C, and was then transferred to a 4 mL glass vial. The vial was placed, uncapped, into a 20 mL glass vial containing approximately 4 mL of Et_2O. The 20 mL vial was capped, and vapor diffusion of Et_2O into the MeCN solution at 23 °C gave dark red plate crystals of **S1** after 24 hours, which were suitable for X-ray analysis. Full details are presented in the X-ray crystallographic data section.

Solutions prepared by dissolving crystals of **S1** in MeCN displayed spectroscopic properties (^{19}F-NMR, UV-vis/NIR, EPR) identical to **2**.

The X-ray structure of **S1** allows a determination of the (+III) oxidation state at Pd, and the Pd(III) cation displays a Jahn-Teller distored octahedral geometry, consistent with the d^7 electronic configuration (Pd–N_1 and Pd–N_3 *vs.* Pd–N_4 and Pd–N_6, Fig. S1).

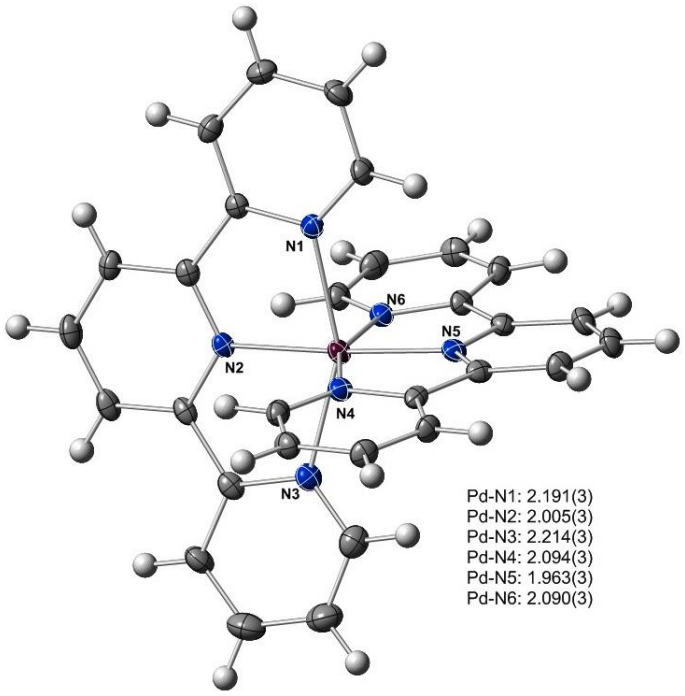
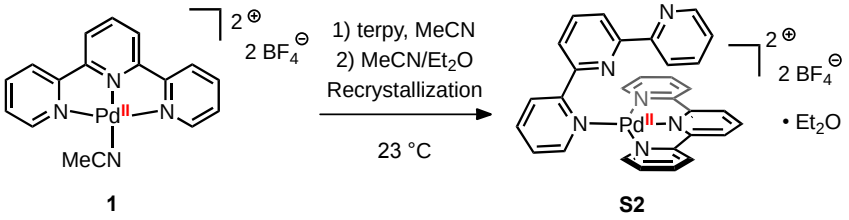


Figure S1. X-ray crystal structure of the Pd(III) cation of complex **S1**, with Pd–N distances (in Å), displaying a Jahn-Teller distorted octahedral structure. Thermal ellipsoids are plotted at the 50% probability level.

Crystallization of $[(terpy)_2Pd][BF_4]_2$ (S2)



To a suspension of $[(terpy)Pd(MeCN)][BF_4]_2$ (**1**) (20. mg, 0.036 mmol, 1.0 equiv) in MeCN (1 mL) at 23 ºC was added terpy (8.4 mg, 0.036 mmol, 1.0 equiv), and the mixture was stirred for 5 minutes, affording an orange solution. The mixture was transferred to a 4 mL glass vial, and the vial was placed, uncapped, into a 20 mL glass vial containing approximately 4 mL of Et_2O. The 20 mL vial was capped, and vapor diffusion of Et_2O into the MeCN solution at 23 °C resulted in the growth of orange/yellow crystals after 24 hours, which were suitable for X-ray diffraction.

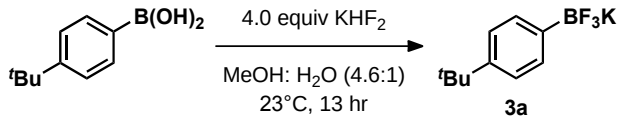
mp: 260–266 °C (decomp). NMR spectroscopy: ^{1}H-NMR (400 MHz, CD_3CN, 23 ºC, δ): 8.8 (br s), 8.5–7.8 (br m), 7.5 (br s). ^{19}F-NMR (375 MHz, CD_3CN, 23 ºC, δ): –151.9 (s). UV-VIS Spectroscopy (MeCN, 23 ˚C): 526 nm ($\varepsilon = 102\ M^{-1}\ cm^{-1}$); 364 nm ($\varepsilon = 1.15 \times 10^4\ M^{-1}\ cm^{-1}$); 347 nm ($\varepsilon = 1.08 \times 10^4\ M^{-1}\ cm^{-1}$); 331 nm ($\varepsilon = 7.52 \times 10^3\ M^{-1}\ cm^{-1}$). FT-IR Spectroscopy (neat, cm^{-1}): 3086, 1605, 1563, 1451, 1321, 1249, 1028, 771 520. Anal: calcd for $C_{30}H_{22}B_2F_8N_6Pd \bullet 0.5\ Et_2O$:

C, 49.01; H, 3.45; N, 10.75; found: C, 49.06; H, 3.27; N, 10.73. X-ray data included in X-Ray Data Analysis section. ^{13}C-NMR signals were not observed due to low solubility of **S2**. The broad ^{1}H-NMR signals suggest fluxional behavior, likely due to rotation of the unligated pyridyl groups on the NMR timescale. X-ray crystallographic analysis, along with the ^{1}H-NMR spectrum of crystals of **S2** dissolved in CD_3CN, shows that compound **S2** crystallizes with Et_2O as a solvent of crystallization (1:1 ratio of **S2**:Et_2O).

Please see the discussion in the Reaction Kinetics section regarding the relevance of **S2** vs. **5** to the Pd-catalyzed fluorination reaction.

III. Synthesis and Characterization of Non-Commerically Available Starting Materials

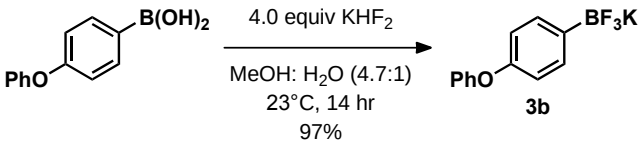
Potassium 4-*tert*-butylphenyl trifluoroborate (3a)



To a vigorously stirred suspension of 4-*tert*-butylphenylboronic acid (1.00 g, 5.62 mmol, 1.00 equiv) in methanol (25 mL, c = 0.2 M) was added a solution of potassium bifluoride (1.76 g, 22.5 mmol, 4.00 equiv) in water (5 mL) at 23 °C. The reaction mixture was stirred for 13 hours at 23 °C and then concentrated *in vacuo* to afford a colorless solid that was further dried at 80 °C at 100 mtorr. The solid was stirred in refluxing acetone (50 mL) and the hot supernatant was filtered through celite. The product was further extracted with acetone (2 × 50 mL) at 23 °C and the supernatant was filtered through celite. The combined filtrates were concentrated *in vacuo* to afford the title compound (1.22 g, 5.09 mmol, 91% yield) as a colorless crystalline solid.

NMR Spectroscopy: ^{1}H NMR (500 MHz, acetone-d_6, 23 °C, δ): 7.39 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 7.6 Hz, 2H), 1.25 (s, 9H). ^{13}C NMR (125 MHz, DMSO-d_6, 23 °C, δ): 146.9, 131.1, 122.9, 33.9, 31.4. ^{19}F NMR (375 MHz, acetone-d_6, 23 °C, δ): –143.1 (bs). HRMS-FIA(m/z) calcd for $C_{10}H_{13}BF_3K$ $[M–K]^-$, 201.1070; found, 201.1070.

Potassium 4-phenoxyphenyl trifluoroborate (3b)

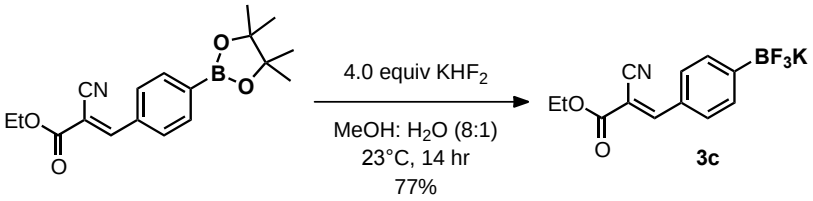


To a vigorously stirred suspension of 4-phenoxyphenylboronic acid (15.0 g, 70.1 mmol, 1.00 equiv) in methanol (280 mL, c = 0.3 M) was added a solution of potassium bifluoride (21.9 g, 280 mmol, 4.00 equiv) in water (60 mL) at 23 °C. The reaction mixture was stirred for 14 hours at 23 °C and then concentrated *in vacuo* to afford a colorless solid that was further dried at 80 °C

at 100 mtorr. The solid was suspended in acetone (1 × 180 mL, 4 × 60 mL), stirred vigorously, and the supernatant was filtered through celite. The combined filtrates were concentrated *in vacuo* to afford the title compound (18.7 g, 67.8 mmol, 97% yield) as a colorless crystalline solid.

NMR Spectroscopy: ^{1}H NMR (500 MHz, acetone-d_6, 23 °C, δ): 7.48 (d, J = 8.2 Hz, 2H), 7.31-7.27 (m, 2H), 7.00 (tt, J = 7.4, 1.0 Hz, 1H), 6.91-6.89 (m, 2H), 6.78-6.77 (m, 2H). ^{13}C NMR (125 MHz, acetone-d_6, 23 °C, δ): 159.5, 155.5, 133.8, 133.8, 130.3, 122.9, 118.4, 118.4. ^{19}F NMR (375 MHz, acetone-d_6, 23 °C, δ): –143.1 (bs). HRMS-FIA(m/z) calcd for $C_{12}H_9BF_3OK$ $[M–K]^-$, 237.0706; found, 237.0712.

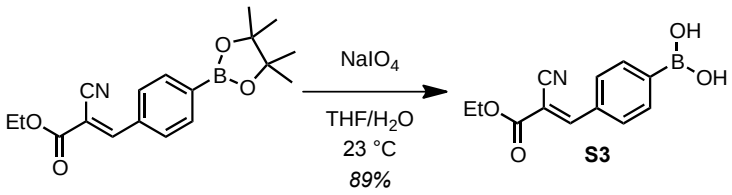
Potassium (*E*)-4-(2-cyano-2-ethoxycarbonylvinyl)phenyl trifluoroborate (3c)



To a vigorously stirred suspension of [(*E*)-4-(2-cyano-2-ethoxycarbonylvinyl)phenyl]boronic acid pinacol ester (25.0 g, 76.4 mmol, 1.00 equiv) in methanol (560 mL, c = 0.1 M) was added a solution of potassium bifluoride (23.9 g, 306 mmol, 4.00 equiv) in water (70 mL) at 23 °C. The reaction mixture was stirred for 14 hours at 23 °C and then concentrated *in vacuo* to afford a colorless solid that was further dried at 80 °C at 100 mtorr. The solid was suspended in acetone (1 × 500 mL, 4 × 100 mL), stirred vigorously, and the supernatant was filtered through celite. The combined filtrates were concentrated *in vacuo* to afford a colorless solid. The solid was purified by the following procedure: the solid was dissolved in refluxing acetone (300 mL) and the solution was allowed to cool to 23 °C. Pentane (300 mL) was layered on top of the cooled acetone solution at 23 °C. Slow diffusion of the pentane into the acetone solution resulted in the growth of colorless crystals, which were isolated by filtration. The colorless crystals were dissolved in refluxing acetone (300 mL) and the hot solution was filtered through celite. The filtrate was concentrated *in vacuo* to afford a colorless solid. The solid was purified by crystallization using the layering procedure detailed above to afford the title compound (18.1 g, 58.9 mmol, 77% yield) as a colorless crystalline solid.

NMR Spectroscopy: ^{1}H NMR (600 MHz, DMSO-d_6, 23 °C, δ): 8.27 (s, 1H), 7.83 (d, J = 7.9 Hz, 2H), 7.51 (d, J = 8.0 Hz, 2H), 4.29 (q, J = 7.1 Hz, 2H), 1.29 (d, J = 14.2 Hz, 3H). ^{13}C NMR (125 MHz, DMSO-d_6, 23 °C, δ): 162.4, 156.3, 132.2, 129.4, 128.4, 116.1, 99.5, 62.1, 14.0. ^{19}F NMR (375 MHz, acetone-d_6, 23 °C, δ): –144.6 (bs). HRMS-FIA(m/z) calcd for $C_{12}H_{10}BF_3NO_2K$ $[M–K]^-$, 268.0764; found, 268.0770.

[(*E*)-4-(2-cyano-2-ethoxycarbonylvinyl)phenyl]boronic acid (S3)

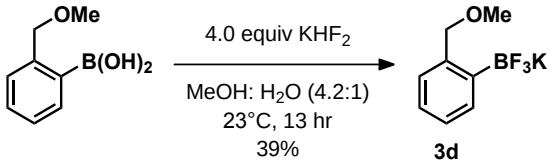


A 50 mL round-bottom flask was charged with [(*E*)-4-(2-cyano-2-ethoxycarbonylvinyl)phenyl]boronic acid pinacol ester (1.00 g, 3.06 mmol, 1.00 equiv), followed by THF (6 mL) and H_2O (6 mL) at 23 ºC. To this mixture was added $NaIO_4$ (1.96 g, 9.18 mmol, 3.00 equiv), and the reaction mixture was stirred for 1 hour at 23 °C, affording a thick white slurry. To this slurry was added 1.0 N HCl (10 mL), and the mixture was allowed to stir for an additional 4 hours. The reaction mixture was transferred to a separatory funnel, and the product was extracted from the aqueous mixture with EtOAc (4 × 50 mL). The combined organic phases were washed with brine (2 × 50 mL), dried over Na_2SO_4, filtered, and concentrated under vacuum to give an off-white solid. The solid was triturated with hexanes (2 × 30 mL), and then dried under vacuum to afford 668 mg of the title compound as an off-white solid (89% yield).

NMR spectroscopy: ^{1}H-NMR (400 MHz, dmso-d_6, 23 ºC, δ): 8.37 (s, 1H), 8.31 (br s, 2H), 7.99–7.91 (m, 4H), 4.30 (q, J = 7.2 Hz, 2H), 1.29 (t, J = 7.0 Hz, 3H). ^{13}C-NMR (125 MHz, dmso-d_6, 23 ºC, δ): 161.8, 155.1, 140.3, 134.6, 132.5, 129.6, 115.6, 102.9, 62.4, 14.0. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $[C_{12}H_{12}BNO_4 + Na]^+$, 268.0757. Found, 268.0744.

The ^{1}H-NMR spectrum of **S3** in dmso-d_6 displays a minor set of aromatic peaks, the presence of which are concentration-dependent, corresponding to the boroxine of **S3**: arylboronic acids are well known to equilibrate with the boroxine form in solution.[3] The presence of the boroxine did not have an observable impact on the Pd-catalyzed fluorination of **S3** (*vide infra*).

Potassium 2-(methoxymethyl)phenyl trifluoroborate (3d)



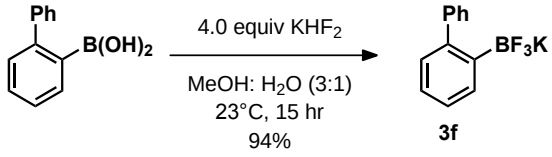
To a vigorously stirred suspension of 2-(methoxymethyl)phenylboronic acid (1.00 g, 6.02 mmol,

[3] Hall, D.G. Boronic Acids: Preparation and Applications in Organic Synthesis and Medicine. Wiley-VCH 2005. doi: 10.1002/3527606548

1.00 equiv) in methanol (25 mL, c = 0.2 M) was added a solution of potassium bifluoride (1.88 g, 24.1 mmol, 4.00 equiv) in water (6 mL) at 23 °C. The reaction mixture was stirred for 13 hours at 23 °C and then concentrated *in vacuo* to afford a colorless solid that was further dried at 80 °C at 100 mtorr. The solid was stirred in refluxing acetone (3 × 50 mL) and the hot supernatant was filtered through celite. The combined filtrates were concentrated *in vacuo* to afford the title compound (535 mg, 2.35 mmol, 39% yield) as a colorless crystalline solid.

NMR Spectroscopy: ^{1}H NMR (600 MHz, acetone-d_6, 23 °C, δ): 7.51 (d, J = 7.1 Hz, 1H), 7.24 (d, J = 7.5 Hz, 1H), 7.01 (td, J = 7.4, 1.4 Hz, 1H), 6.96 (t, J = 7.2 Hz, 1H), 4.68 (s, 2H), 3.29 (s, 3H). ^{13}C NMR (125 MHz, acetone-d_6, 23 °C, δ): 142.2, 133.0, 133.0, 126.9, 126.2, 126.0, 74.9, 57.6. ^{19}F NMR (375 MHz, acetone-d_6, 23 °C, δ): –140.2 (bs). HRMS-FIA(m/z) calcd for $C_8H_9BF_3OK$ $[M–K]^-$, 189.0706; found, 189.0706.

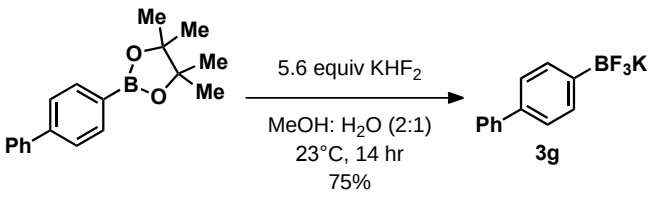
Potassium 2-biphenyl trifluoroborate (3f)



To a vigorously stirred suspension of 2-biphenylboronic acid (250 mg, 1.26 mmol, 1.00 equiv) in methanol (3 mL, c = 0.4 M) was added a solution of potassium bifluoride (394 mg, 5.05 mmol, 4.00 equiv) in water (1 mL) at 23 °C. The reaction mixture was stirred for 15 hours at 23 °C and then concentrated *in vacuo* to afford a colorless solid that was further dried at 80 °C at 100 mtorr. The solid was suspended in acetone (3 × 20 mL), stirred vigorously, and the supernatant was filtered through celite. The combined filtrates were concentrated *in vacuo* to afford the title compound (310 mg, 1.19 mmol, 94% yield) as a colorless crystalline solid.

NMR Spectroscopy: ^{1}H NMR (600 MHz, acetone-d_6, 23 °C, δ): δ 7.70 (dd, J = 6.2, 2.5 Hz, 1H), 7.54-7.52 (m, 2H), 7.25-7.22 (m, 2H), 7.16-7.13 (m, 1H), 7.10-7.06 (m, 2H), 7.04-7.01 (m, 1H). ^{13}C NMR (125 MHz, DMSO-d_6, 23 °C, δ): 146.0, 145.3, 133.0, 133.0, 129.2, 128.8, 126.8, 125.3, 125.1, 125.0. ^{19}F NMR (375 MHz, acetone-d_6, 23 °C, δ): –136.5 (bs). HRMS-FIA(m/z) calcd for $C_{12}H_9BF_3K$ $[M–K]^-$, 221.0757; found, 221.0761.

Potassium 4-biphenyl trifluoroborate (3g)

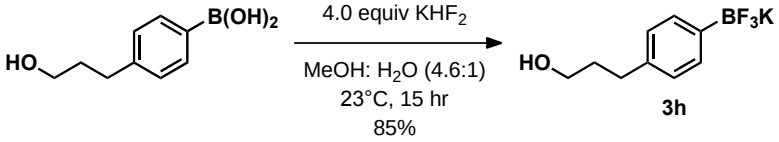


To a vigorously stirred suspension of 4-biphenylboronic acid pinacol ester (1.00 g, 3.57 mmol, 1.00 equiv) in methanol (10 mL, c = 0.4 M) was added a solution of potassium bifluoride (1.56 g,

20.0 mmol, 5.60 equiv) in water (5 mL) at 23 °C. The reaction mixture was stirred for 14 hours at 23 °C and then concentrated *in vacuo* to afford a colorless solid that was further dried at 80 °C at 100 mtorr. The solid was suspended in water (40 mL) and the suspension was filtered. The filter cake was washed with methanol (2 × 40 mL), diethyl ether (40 mL), and pentane (40 mL). The residue was dried under vacuum to afford the title compound (699 mg, 2.69 mmol, 75% yield) as a colorless crystalline solid.

NMR Spectroscopy: ^{1}H NMR (600 MHz, DMSO-d_6, 23 °C, δ): 7.59 (dd, J = 8.2, 1.1 Hz, 2H), 7.42-7.37 (m, 6H), 7.28 (tt, J = 7.3, 1.1 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6, 23 °C, δ): 141.5, 136.9, 132.0, 128.8, 126.6, 126.3, 124.7. ^{19}F NMR (375 MHz, DMSO-d_6, 23 °C, δ): –141.1. HRMS-FIA(m/z) calcd for $C_{12}H_9BF_3K$ $[M–K]^-$, 221.0757; found, 221.0761.

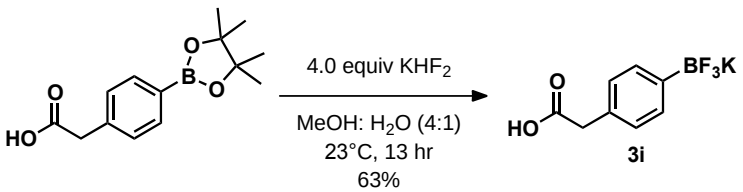
Potassium 4-(3-hydroxypropyl)phenyl trifluoroborate (3h)



To a vigorously stirred suspension of 4-(3-hydroxypropyl)phenylboronic acid (1.00 g, 5.56 mmol, 1.00 equiv) in methanol (23 mL, c = 0.2 M) was added a solution of potassium bifluoride (1.74 g, 22.2 mmol, 4.00 equiv) in water (5 mL) at 23 °C. The reaction mixture was stirred for 15 hours at 23 °C and then concentrated *in vacuo* to afford a colorless solid that was further dried at 80 °C at 100 mtorr. The solid was stirred in refluxing acetone (4 × 20 mL) and the hot supernatant was filtered through celite. The combined filtrates were concentrated *in vacuo* to afford the title compound (1.14 g, 4.72 mmol, 85% yield) as a colorless crystalline solid.

NMR Spectroscopy: ^{1}H NMR (600 MHz, acetone-d_6, 23 °C, δ): 7.37 (d, J = 7.7 Hz, 2H), 6.94 (d, J = 7.5 Hz, 2H), 3.55-3.52 (m, 2H), 3.41 (t, J = 5.3 Hz, 1H), 2.57 (t, J = 7.7 Hz, 2H), 1.79-1.74 (m, 2H). ^{13}C NMR (125 MHz, DMSO-d_6, 23 °C, δ): 138.4, 131.4, 126.4, 60.4, 34.7, 31.7. ^{19}F NMR (375 MHz, acetone-d_6, 23 °C, δ): –142.9 (bs). HRMS-FIA(m/z) calcd for $C_9H_{11}BF_3OK$ $[M–K]^-$, 203.0862; found, 203.0862.

Potassium 4-(carboxymethyl)phenyl trifluoroborate (3i)

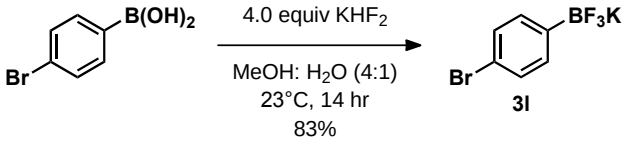


To a vigorously stirred suspension of 4-(carboxymethyl)phenylboronic acid pinacol ester (1.00 g, 3.82 mmol, 1.00 equiv) in methanol (16 mL, c = 0.2 M) was added a solution of potassium bifluoride (1.19 g, 15.3 mmol, 4.00 equiv) in water (4 mL) at 23 °C. The reaction mixture was

stirred for 13 hours at 23 °C and then concentrated *in vacuo* to afford a yellow solid that was further dried at 80 °C at 100 mtorr. The solid was purified by continuous soxhlet extraction for 72 hours with acetone (200 mL). The filtrate was concentrated *in vacuo* and the residue was triturated with diethyl ether (3 × 10 mL) to afford the title compound (577 mg, 2.38 mmol, 63% yield) as a colorless crystalline solid.

NMR Spectroscopy: ^{1}H NMR (600 MHz, DMSO-d_6, 23 °C, δ): 12.38 (s, 1H), 7.23 (d, J = 7.7 Hz, 1H), 6.95 (d, J = 7.5 Hz, 1H), 3.38 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6, 23 °C, δ): 173.4, 131.5, 131.3, 127.2, 41.3. ^{19}F NMR (375 MHz, DMSO-d_6, 23 °C, δ): –140.9. HRMS-FIA(m/z) calcd for $C_8H_7BF_3O_2K$ $[M–K]^-$, 203.0498; found, 203.0496.

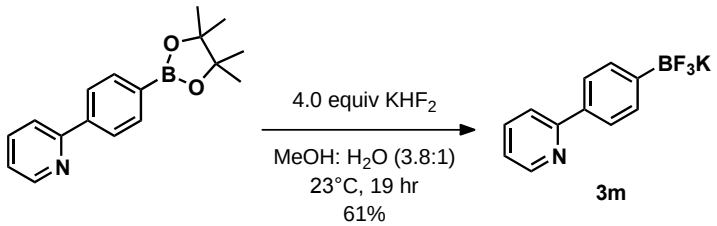
Potassium 4-bromophenyl trifluoroborate (3l)



To a vigorously stirred suspension of 4-bromophenylboronic acid (1.00 g, 4.98 mmol, 1.00 equiv) in methanol (20 mL, c = 0.2 M) was added a solution of potassium bifluoride (1.56 g, 19.9 mmol, 4.00 equiv) in water (5 mL) at 23 °C. The reaction mixture was stirred for 14 hours at 23 °C and then concentrated *in vacuo* to afford a colorless solid that was further dried at 80 °C at 100 mtorr. The solid was suspended in acetone (4 × 25 mL), stirred vigorously, and the supernatant was filtered through celite. The combined filtrates were concentrated *in vacuo* to afford the title compound (1.09 g, 4.15 mmol, 83% yield) as a colorless crystalline solid.

NMR Spectroscopy: ^{1}H NMR (600 MHz, DMSO-d_6, 23 °C, δ): 7.28-7.20 (m, 2H). ^{13}C NMR (125 MHz, acetone-d_6, 23 °C, δ): 134.6, 129.9, 119.7. ^{19}F NMR (375 MHz, acetone-d_6, 23 °C, δ): –143.8 (bs). HRMS-FIA(m/z) calcd for $C_6H_4BBrF_3L$ $[M–K]^-$, 222.9548; found, 222.9547.

Potassium 4-(pyridin-2-yl)phenyl trifluoroborate (3m)

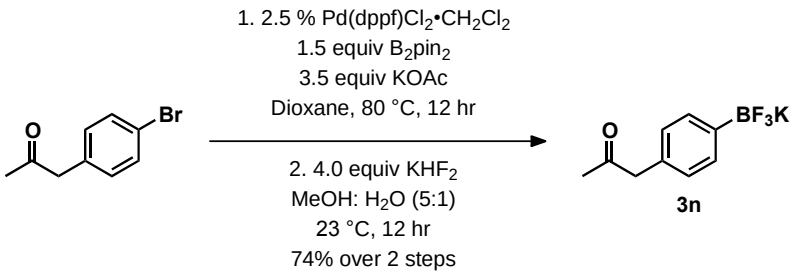


To a vigorously stirred suspension of 4-(pyridine-2-yl)phenylboronic acid pinacol ester (1.00 g, 3.56 mmol, 1.00 equiv) in methanol (15 mL, c = 0.2 M) was added a solution of potassium bifluoride (1.11 g, 14.2 mmol, 4.00 equiv) in water (4 mL) at 23 °C. The reaction mixture was stirred for 19 hours at 23 °C and then concentrated *in vacuo* to afford a yellow solid that was further dried at 80 °C at 100 mtorr. The solid was stirred in refluxing acetone (4 × 30 mL) and

the hot supernatant was filtered through celite. The combined filtrates were concentrated *in vacuo* to afford a yellow solid. The solid was purified by the following procedure: the solid was dissolved in refluxing acetone (10 mL) and the solution was allowed to cool to 23 °C. Layering of pentane (10 mL) on top of the cooled acetone solution at 23 °C resulted in the growth of yellow crystals, which were isolated by filtration of the suspension. This layering procedure was repeated twice more to afford the title compound (563 mg, 2.16 mmol, 61% yield) as a colorless crystalline solid.

NMR Spectroscopy: ^{1}H NMR (600 MHz, acetone-d_6, 23 °C, δ): 8.58 (dq, J = 4.8, 1.2 Hz, 1H), 7.86 (d, J = 7.7 Hz, 2H), 7.82 (dt, J = 8.4, 1.2 Hz, 1H), 7.76 (td, J = 7.7, 1.9 Hz, 1H), 7.58 (d, J = 8.0 Hz, 2H), 7.19 (ddd, J = 7.3, 4.8, 1.1 Hz, 1H). ^{13}C NMR (125 MHz, acetone-d_6, 23 °C, δ): 159.0, 150.2, 137.3, 137.2, 132.8, 135.6, 122.2, 120.4. ^{19}F NMR (375 MHz, acetone-d_6, 23 °C, δ): –143.4 (bs). HRMS-FIA(m/z) calcd for $C_{11}H_8BF_3NK$ $[M–K]^-$, 222.0709; found, 222.0710.

Potassium 4-(2-oxopropyl)phenyl trifluoroborate (3n)



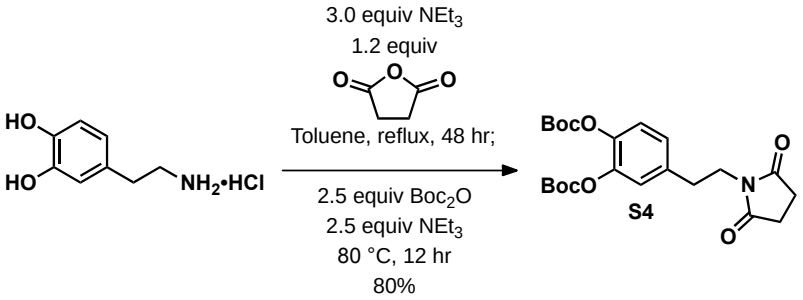
To a flame-dried Schlenk tube was added bis(pinacolato)diboron (3.58 g, 14.1 mmol, 1.5 equiv) and potassium acetate (3.22 g, 32.9 mmol, 3.5 equiv). The Schlenk tube was evacuated and backfilled with dinitrogen (process repeated three times). Dioxane (40 mL anhydrous, degassed) was added followed by 1-(4-bromophenyl)propan-2-one (2.00 g, 9.39 mmol, 1.00 equiv). The reaction mixture was submitted to two freeze-pump-thaw cycles, followed by the addition of [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium complex in dichloromethane (192 mg, 0.235 mmol, 0.025 equiv). The reaction mixture was submitted to another freeze-pump-thaw cycle and heated at 80 °C for 12 hours. The reaction was allowed to cool to 23 °C and water (30 mL) was added dropwise under a dinitrogen atmosphere. The reaction mixture was transferred to separatory funnel and the aqueous layer was extracted with dichloromethane (3 × 30 mL). The combined organic layers were dried over magnesium sulfate, filtered, and concentrated *in vacuo* to afford an orange oil. The residue was purified by chromatography on silica gel eluting with a solvent mixture of hexanes/dichloromethane (1:4 (v/v)) to afford a yellow oil (3.48 g) containing 4-(2-oxopropyl)phenylboronic acid pinacol ester (2.37 g, 9.10 mmol, 97% yield), dioxane, and pinacol. The purity of the residue was determined by integration of the ^{1}H NMR spectrum of the mixture. This mixture was carried through to the next reaction without further purification.

The yellow oil obtained from the previous step was diluted with methanol (40 mL, c = 0.2). To this vigorously stirred solution was added a solution of potassium bifluoride (2.84 g, 36.4 mmol,

4.00 equiv) in water (8 mL) at 23 °C. The reaction mixture was stirred for 12 hours at 23 °C and then concentrated *in vacuo* to afford a yellow solid that was further dried at 80 °C at 100 mtorr. The solid was stirred in refluxing acetone (3 × 150 mL) and the hot supernatant was filtered through celite. The filtrate was concentrated *in vacuo* and the residue was triturated with tetrahydrofuran (5 × 12 mL) to afford the title compound (1.65 g, 6.89 mmol, 74% yield for 2 steps) as a colorless crystalline solid.

NMR Spectroscopy: ^{1}H NMR (600 MHz, DMSO-d_6, 23 °C, δ): 7.26 (d, J = 7.7 Hz, 2H), 6.91 (d, J = 7.5 Hz, 2H), 3.57 (s, 2H), 2.04 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6, 23 °C, δ): 206.8, 131.6, 131.1, 127.5, 50.2, 29.0. ^{19}F NMR (375 MHz, DMSO-d_6, 23 °C, δ): –141.0 (bs). HRMS-FIA(m/z) calcd for $C_9H_9BF_3OK$ $[M–K]^-$, 201.0706; found, 201.0705.

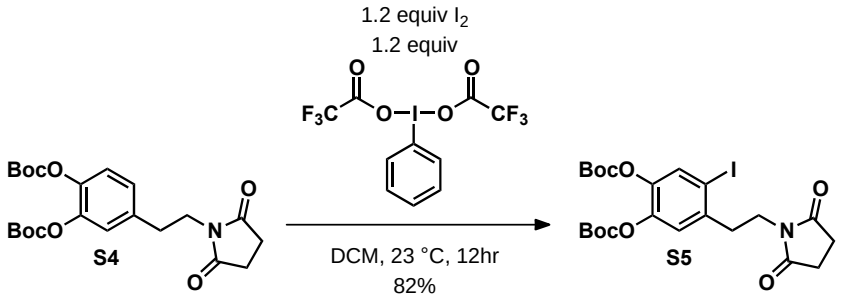
Protected dopamine (S4)



To a vigorously stirred suspension of dopamine hydrochloride (5.00 g, 26.4 mmol, 1.00 equiv) in toluene (100 mL, 0.3 M) was added triethylamine (10.9 mL, 79.1 mmol, 3.00 equiv) and succinic anhydride (3.17 g, 31.6 mmol, 1.20 equiv) at 23 °C. The reaction mixture was stirred for 48 hours at reflux and allowed to cool to 23 °C. Boc anhydride (15.2 mL, 65.9 mmol, 2.50 equiv) and triethylamine (9.11 mL, 65.9 mmol, 2.50 equiv) were added to the reaction mixture at 23 °C. The reaction mixture was stirred for 12 hours at 80 °C, allowed to cool to 23 °C, and then transferred to a separatory funnel. The organic layer was washed with brine (3 × 50 mL). The combined aqueous layers were extracted with ethyl acetate (50 mL). The combined organic layers were dried over magnesium sulfate, filtered, and concentrated *in vacuo*. The residue was purified by chromatography on silica gel eluting with a solvent mixture of hexanes/ethyl acetate (1:1 (v/v)) to afford the title compound (9.15 g, 21.0 mmol, 80% yield) as a colorless crystalline solid.

R_f = 0.37 (hexanes/ethyl acetate 1:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$, 23 °C, δ): 7.17 (d, J = 8.3 Hz, 1H), 7.11 (dd, J = 8.3, 2.0 Hz, 1H), 7.08 (d, J = 2.0 Hz, 1H), 3.73 (dd, J = 8.5, 7.0 Hz, 2H), 2.88 (t, J = 7.7 Hz, 2H), 2.65 (s, 4H), 1.54 (s, 9H), 1.53 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 °C, δ): 177.0, 150.6, 150.6, 142.2, 141.1, 136.1, 126.6, 123.5, 123.0, 83.6, 83.5, 39.3, 32.6, 27.9, 27.5, 27.5. HRMS-FIA(m/z) calcd for $C_{22}H_{29}NO_8$ $[M+NH_4]^+$, 453.2231; found, 453.2246.

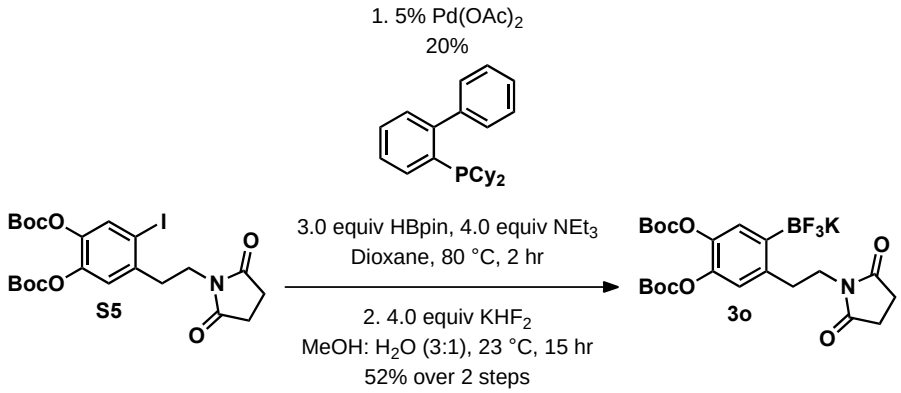
Aryl iodide S5



To a vigorously stirred solution of [bis(trifluoroacetoxy)iodo]benzene (2.15 g, 4.99 mmol, 1.20 equiv) and iodine (1.27 g, 4.99 mmol, 1.20 equiv) in dichloromethane (80 mL, c = 0.06 M) was added compound **S4** (1.81 g, 4.16 mmol, 1.00 equiv) at 23 °C. The reaction mixture was stirred for 12 hours at 23 °C, followed by the addition of a saturated aqueous sodium thiosulfate solution (approx. 30 mL) at 23 °C. The reaction mixture was transferred to a separatory funnel and extracted with dichloromethane (3 × 40 mL). The combined organic layers were dried over magnesium sulfate, filtered, and concentrated *in vacuo*. The residue was purified by chromatography on silica gel eluting with a solvent mixture of hexanes/ethyl acetate (2:1 (v/v)) to afford the title compound (1.90 g, 3.39 mmol, 82% yield) as a yellow oil.

R_f = 0.43 (hexanes/ethyl acetate 1:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$, 23 °C, δ): 7.67 (s, 1H), 7.05 (s, 1H), 3.77 (t, *J* = 7.2 Hz, 2H), 3.01 (t, *J* = 7.1 Hz, 2H), 2.65 (s, 4H), 1.52 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$-d_6, 23 °C, δ): 177.1, 150.4, 150.2, 142.5, 141.3, 138.9, 133.5, 124.0, 94.7, 84.1, 84.1, 37.8, 37.5, 28.0, 27.6, 27.5. HRMS-FIA(m/z) calcd for $C_{22}H_{28}INO_8$ $[M+NH_4]^+$, 579.1198; found, 579.1204.

Aryl trifluoroborate 3o



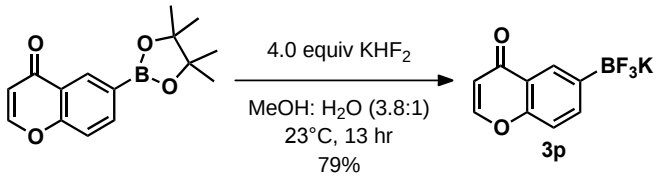
To a flame-dried Schlenk tube was added aryl iodide **S5** (1.00 g, 1.78 mmol, 1.00 equiv). The Schlenk tube was evacuated and backfilled with dinitrogen (process repeated three times). Dioxane (5 mL anhydrous, degassed) was added followed by triethylamine (985 μL, 7.13 mmol,

4.00 equiv) and pinacolborane (775 μL, 5.35 mmol, 3.00 equiv). The reaction mixture was submitted to three freeze-pump-thaw cycles, followed by the addition of palladium acetate (20.0 mg, 89.1 μmol, 0.0500 equiv) and (2-biphenyl)dicyclohexylphosphine (125 mg, 356 μmol, 0.200 equiv). The reaction mixture was submitted to another freeze-pump-thaw cycle and heated to 80 °C for 2 hours. The reaction was allowed to cool to 23 °C and a saturated aqueous ammonium chloride solution (5 mL) was added dropwise under a dinitrogen atmosphere. The reaction mixture was transferred to a separatory funnel and the aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over magnesium sulfate, filtered, and concentrated *in vacuo*. The residue was purified by chromatography on silica gel eluting with a solvent mixture of hexanes/ethyl acetate (3:1 (v/v)) to afford a yellow oil (1.00 g).

An aliquot of the yellow oil obtained in the previous step (400 mg) was diluted with methanol (3 mL). To this vigorously stirred solution was added a solution of potassium bifluoride (223 mg, 2.85 mmol, 4.00 equiv) in water (1 mL) at 23 °C. The reaction mixture was stirred for 18 hours at 23 °C and then concentrated *in vacuo* to afford a yellow solid that was further dried at 80 °C at 100 mtorr. The solid was suspended in acetone (4 × 20 mL), stirred vigorously, and the supernatant was filtered through celite. The combined filtrates were concentrated *in vacuo* to afford a yellow solid. The solid was purified by the following procedure: the solid was dissolved in acetone (4 mL) and the resulting solution was layered with pentane (15 mL). Slow diffusion of pentane into the acetone solution afforded colorless crystals, which were isolated and dried under vacuum to give the title compound (200 mg, 370 μmol, 52% yield over 2 steps) as a colorless crystalline solid.

NMR Spectroscopy: ^{1}H NMR (600 MHz, DMSO-d_6, 23 °C, δ): 7.08 (s, 1H), 6.76 (s, 1H), 3.57 (t, J = 7.3 Hz, 2H), 2.88 (t, J = 7.3 Hz, 2H), 2.58 (s, 4H), 1.46 (s, 18H). ^{13}C NMR (125 MHz, DMSO-d_6, 23 °C, δ): 177.5, 150.7, 150.6, 140.2, 139.5, 138.9, 125.6, 121.7, 82.8, 82.6, 31.6, 27.9, 27.2. ^{19}F NMR (375 MHz, DMSO-d_6, 23 °C, δ): –138.9 (bs). HRMS-FIA(m/z) calcd for $C_{22}H_{28}BF_3NO_8K$ $[M–K]^-$, 502.1870; found, 502.1879.

Potassium 4-oxo-4*H*-chromen-6-yl trifluoroborate (3p)



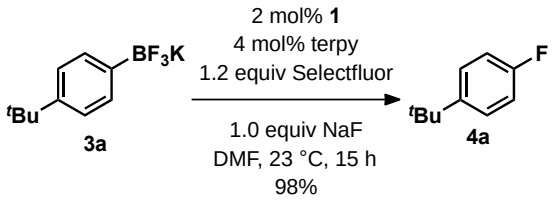
To a vigorously stirred suspension of 4-oxo-4*H*-chromen-6-ylboronic acid pinacol ester (1.00 g, 3.68 mmol, 1.00 equiv) in methanol (15 mL, c = 0.2 M) was added a solution of potassium bifluoride (1.15 g, 14.7 mmol, 4.00 equiv) in water (4 mL) at 23 °C. The reaction mixture was stirred for 13 hours at 23 °C and then concentrated *in vacuo* to afford an orange solid that was further dried at 80 °C at 100 mtorr. The solid was purified by continuous soxhlet extraction for 40 hours with acetone (250 mL). Subsequently, the hot extract was filtered through celite, which

was rinsed with hot acetone (3 × 20 mL). The filtrate was concentrated *in vacuo* and the residue was triturated with tetrahydrofuran (4 × 5 mL) to afford the title compound (732 mg, 2.90 mmol, 79% yield) as a colorless crystalline solid.

NMR Spectroscopy: ^{1}H NMR (600 MHz, DMSO-d_6, 23 °C, δ): 8.18 (d, J = 6.0 Hz, 1H), 8.02 (s, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.34 (d, J = 8.1 Hz, 1H), 6.24 (d, J = 5.9 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6, 23 °C, δ): 177.3, 156.2, 155.0, 137.8, 127.0, 127.0, 122.9, 115.7, 112.1. ^{19}F NMR (375 MHz, acetone-d_6, 23 °C, δ): –143.4. HRMS-FIA(m/z) calcd for $C_9H_5BF_3O_2$ $[M–K]^-$, 213.0342; found, 213.0340.

IV. Synthesis and Characterization of Aryl Fluorides

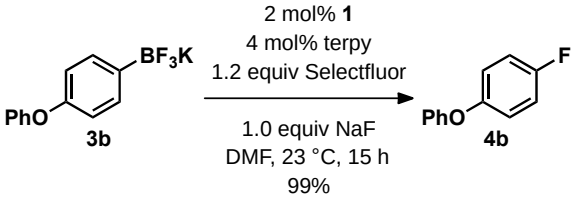
1-(*tert*-Butyl)-4-fluorobenzene (4a)



To a mixture of palladium precatalyst **1** (7.8 mg, 14 μmol, 0.020 equiv), terpy (6.5 mg, 28 μmol, 0.040 equiv), aryl trifluoroborate **3a** (168 mg, 700 μmol, 1.00 equiv), Selectfluor (298 mg, 840 μmol, 1.20 equiv), and sodium fluoride (29.4 mg, 700 μmol, 1.00 equiv) was added dimethylformamide (7.0 mL, 0.1 M) at 23 °C. The reaction mixture was stirred for 15 hours at 23 °C and then transferred to a separatory funnel. Pentane (20 mL) was added and the organic layer was washed with a 5% aqueous lithium chloride solution (3 × 20 mL). The organic layer was dried over sodium sulfate. The organic layer was filtered through silica gel (approx. 20 g) eluting with pentane (approx. 200 mL) and concentrated *in vacuo* at 0 °C to afford a colorless oil (166 mg) containing the title compound (105 mg, 687 μmol, 98% yield), water, and pentane. The remaining solvent was not removed from the sample due to volatility of the product. The solvent content of the residue was determined by integration of the ^{1}H NMR spectrum of the mixture. Azeotropic evaporation of the trace solvent with $CDCl_3$ was performed prior to ^{1}H and ^{13}C NMR characterization.

R_f = 0.79 (pentane). NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$, 23 °C, δ): 7.35–7.32 (m, 2H), 6.99–6.95 (m, 2H), 1.31 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 °C, δ): 160.9 (d, J = 242 Hz), 146.7 (d, J = 1.8 Hz), 126.7 (d, J = 7.3 Hz), 114.6 (d, J = 20.0 Hz), 34.3, 31.5. ^{19}F NMR (375 MHz, $CDCl_3$, 23 °C, δ): –121.7. HRMS-FIA(m/z) calcd for $C_{10}H_{13}F$ $[M–CH_3]^+$, 137.0761; found, 137.0760.

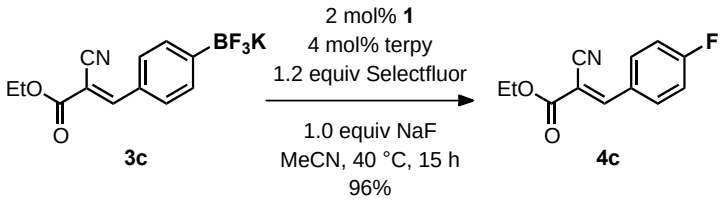
1-Fluoro-4-phenoxybenzene (4b)



To a mixture of palladium precatalyst **1** (7.8 mg, 14 μmol, 0.020 equiv), terpy (6.5 mg, 28 μmol, 0.040 equiv), aryl trifluoroborate **3b** (193 mg, 700 μmol, 1.00 equiv), Selectfluor (298 mg, 840 μmol, 1.20 equiv), and sodium fluoride (29.4 mg, 700 μmol, 1.00 equiv) was added dimethylformamide (7.0 mL, 0.1 M) at 23 °C. The reaction mixture was stirred for 15 hours at 23 °C and then transferred to a separatory funnel. Pentane (20 mL) was added and the organic layer was washed with a 5% aqueous lithium chloride solution (20 mL). The aqueous layer was extracted with pentane (3 × 20 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated *in vacuo* at 0 °C to afford a colorless oil. The residue was purified by chromatography on silica gel eluting with pentane to afford a colorless oil (142 mg) containing the title compound (99.2 mg, 700 μmol, >99% yield), water, pentane, diethyl ether, and acetone. The remaining solvent was not removed from the sample due to volatility of the product. The solvent content of the residue was determined by integration of the ^{1}H NMR spectrum of the mixture. Azeotropic evaporation of the trace solvent with $CDCl_3$ was performed prior to ^{1}H and ^{13}C NMR characterization.

R_f = 0.35 (pentane). NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$, 23 °C, δ): 7.34–7.31 (m, 2H), 7.09 (tt, *J* = 7.4, 1.0 Hz, 1H), 7.05–7.01 (m, 2H), 7.00–6.97 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 °C, δ): 158.8 (d, *J* = 240 Hz), 157.7, 152.9, 129.8, 123.1, 120.5 (d, *J* = 8.3 Hz), 118.2, 116.3 (d, *J* = 23.8 Hz). ^{19}F NMR (375 MHz, $CDCl_3$, 23 °C, δ): –123.2. HRMS-FIA(m/z) calcd for $C_{12}H_9FO$ $[M]^+$, 188.0632; found, 188.0633.

(*E*)-Ethyl 2-cyano-3-(4-fluorophenyl)acrylate (4c) (milligram scale)



To a mixture of palladium precatalyst **1** (4.4 mg, 8.0 μmol, 0.020 equiv), terpy (3.7 mg, 16 μmol, 0.040 equiv), aryl trifluoroborate **3a** (123 mg, 400 μmol, 1.00 equiv), Selectfluor (170 mg, 480 μmol, 1.20 equiv), and sodium fluoride (16.8 mg, 400 μmol, 1.00 equiv) was added acetonitrile (4.0 mL, 0.1 M) at 23 °C. The reaction mixture was stirred for 15 hours at 40 °C, allowed to cool to 23 °C, and then transferred to a separatory funnel, rinsing the reaction vial with additional

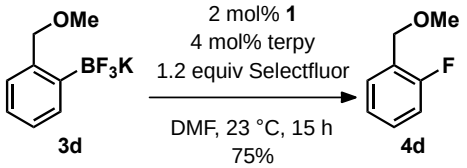
acetonitrile (2 × 4 mL). Pentane (20 mL) was added and the organic layer was washed with water (20 mL). The aqueous layer was extracted with pentane (5 × 20 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated *in vacuo* to afford a colorless solid. The solid was purified by chromatography on silica gel eluting with a solvent mixture of pentane/Et_2O (17:3 (v/v)) to afford the title compound (84.5 mg, 385 μmol, 96% yield) as a colorless crystalline solid. Purity of the product was confirmed via ^1H and ^{19}F NMR spectroscopy. The spectra were identical to those obtained from the large-scale reaction below.

(*E*)-Ethyl 2-cyano-3-(4-fluorophenyl)acrylate (4c) (decagram scale).

To a mixture of palladium precatalyst **1** (307 mg, 554 μmol, 0.010 equiv), terpy (258 mg, 1.11 mmol, 0.040 equiv), aryl trifluoroborate **3a** (17.0 g, 55.4 mmol, 1.00 equiv), Selectfluor (23.5 g, 66.4 mmol, 1.20 equiv), and sodium fluoride (2.32 g, 55.4 mmol, 1.00 equiv) were added to a round-bottom flask (200 mL), followed by acetonitrile (55.4 mL, 1.0 M) at 23 °C. An air-cooled reflux condenser was fitted to the round bottom flask. The reaction mixture was stirred for 15 hours open to air at 40 °C, allowed to cool to 23 °C, and then transferred to a separatory funnel, rinsing the reaction vial with additional acetonitrile (2 × 50 mL). Pentane (250 mL) was added and the organic layer was washed with water (350 mL). The aqueous layer was extracted with dichloromethane (4 × 300 mL). The combined organic layers were extracted with brine (500 mL), dried over sodium sulfate, filtered, and concentrated *in vacuo* to afford a yellow solid. The solid was purified by chromatography on silica gel eluting with a solvent mixture of pentane/Et_2O (9:1 (v/v)) to afford the title compound (10.6 g, 48.6 mmol, 88% yield) as a colorless crystalline solid.

R_f = 0.38 (pentane/Et_2O 9:1 (v/v)). NMR Spectroscopy: ^1H NMR (500 MHz, $CDCl_3$, 23 °C, δ): 8.21 (s, 1H), 8.05–8.01 (m, 2H), 7.22–7.17 (m, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 °C, δ): 165.2 (d, *J* = 256 Hz), 162.2, 153.2, 133.4 (d, *J* = 9.1 Hz), 127.7 (d, *J* = 3.6 Hz), 116.5 (d, *J* = 21.9 Hz), 115.3, 102.4 (d, *J* = 2.8 Hz), 62.6, 14.0. ^{19}F NMR (375 MHz, $CDCl_3$, 23 °C, δ): –106.0. HRMS-FIA(m/z) calcd for $C_{12}H_{10}FNO_2$ $[M+H]^+$, 220.0768; found, 220.0769.

1-Fluoro-2-(methoxymethyl)benzene (4d)

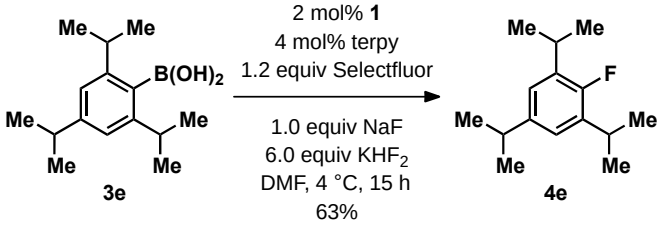


To a mixture of palladium catalyst **1** (7.8 mg, 14 μmol, 0.020 equiv) and terpy (6.5 mg, 28 μmol, 0.040 equiv) was added dimethylformamide (7.0 mL, 0.1 M) at 23 °C. This suspension was swirled for approx. 20 seconds until it became homogenous. This solution was transferred via syringe to a mixture of aryl trifluoroborate **3d** (160 mg, 700 μmol, 1.00 equiv) and Selectfluor

(298 mg, 840 μmol, 1.20 equiv). The reaction mixture was stirred for 15 hours at 23 °C and then transferred to a separatory funnel. Pentane (20 mL) was added and the organic layer was washed with a 5% aqueous lithium chloride solution (1 × 20 mL, 2 × 10 mL). The organic layer was dried over sodium sulfate. The organic layer was filtered through silica gel (approx. 20 g) eluting with a solvent mixture of pentane/Et_2O (9:1 (v/v), approx. 200 mL) and concentrated *in vacuo* at 0 °C to afford a yellow oil (86.3 mg) containing the title compound (74.0 mg, 528 μmol, 75% yield), water, diethyl ether, and pentane. The remaining solvent was not removed from the sample due to volatility of the product. The solvent content of the residue was determined by integration of the ^{1}H NMR spectrum of the mixture. Azeotropic evaporation of the trace solvent with $CDCl_3$ was performed prior to ^{1}H and ^{13}C NMR characterization. The ^{1}H NMR and LRMS data correspond to the data reported in reference 4.[4] High resolution mass spectrometry could only identify [(M+H)-F], therefore low resolution mass spectrometry was used to confirm the molecular ion of the title compound.

R_f = 0.67 (pentane/Et_2O 9:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C, δ): 7.41 (t, *J* = 7.0 Hz, 1H), 7.28 (q, *J* = 7.5 Hz, 1H), 7.14 (t, *J* = 7.0 Hz, 1H), 7.05 (t, *J* = 9.0 Hz, 1H), 4.53 (s, 2H), 3.42 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 °C, δ): 160.8 (d, *J* = 246 Hz), 130.0 (d, *J* = 3.6 Hz), 129.3 (d, *J* = 8.3 Hz), 125.2 (d, *J* = 14.6 Hz), 124.0 (d, *J* = 3.6 Hz), 115.2 (d, *J* = 21.9 Hz), 68.0 (d, *J* = 3.6 Hz), 58.3. ^{19}F NMR (375 MHz, $CDCl_3$, 23 °C, δ): –122.2. LRMS-FIA(m/z) calcd for C_8H_9FO $[M]^+$, 140.1; found, 140.1. HRMS-FIA(m/z) calcd for C_8H_9FO [(M+H)-F], 123.0760; found, 123.0756.

2-Fluoro-1,3-5-triisopropylbenzene (4e)



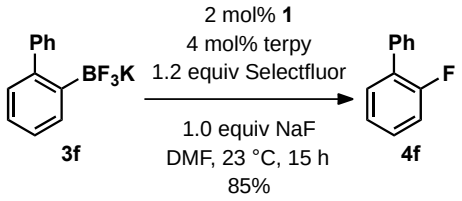
To a mixture of palladium precatalyst **1** (7.8 mg, 14 μmol, 0.020 equiv), terpy (6.5 mg, 28 μmol, 0.040 equiv), arylboronic acid **3e** (175 mg, 700 μmol, 1.00 equiv), Selectfluor (298 mg, 840 μmol, 1.20 equiv), sodium fluoride (29.4 mg, 700 μmol, 1.00 equiv), and potassium bifluoride (328 mg, 4.20 mmol, 6.00 equiv) at 4 °C was added cold dimethylformamide (7.0 mL, 0.1 M) at 4 °C. The reaction mixture was stirred for 15 hours at 4 °C and then transferred cold to a separatory funnel. Pentane (20 mL) was added and the organic layer was washed with a 5% aqueous lithium chloride solution (20 mL). The aqueous layer was extracted with pentane (3 ×

[4] Ortiz, B.; Walls, F.; Yuste, F.; Barrios, H.; Sanchez-Obregon, R. Pinelo, L. *Synth. Commun.* **1993**, 23(6), 749-756.

20 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated *in vacuo* at 0 °C to afford a yellow oil. The residue was purified by preparative thin layer chromatography on silica gel eluting with perfluorohexanes to afford a colorless oil (148 mg) containing the title compound (98.6 mg, 443 μmol, 63% yield), water, pentane, and dichloromethane. The remaining solvent was not removed from the sample due to volatility of the product. The solvent content of the residue was determined by integration of the ^{1}H NMR spectrum of the mixture. Azeotropic evaporation of the trace solvent with $CDCl_3$ was performed prior to ^{1}H and ^{13}C NMR characterization.

R_f = 0.10 (perfluorohexanes). NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$, 23 °C, δ): 6.91 (d, *J* = 6.8 Hz, 2H), 3.22 (hept, *J* = 6.9 Hz, 2H), 2.86 (hept, *J* = 7.1 Hz, 1H), 1.26 (d, *J* = 7.0 Hz, 12H), 1.24 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 °C, δ): 156.6 (d, *J* = 240 Hz), 143.8 (d, *J* = 3.6 Hz), 134.5 (d, *J* = 15.4 Hz), 122.2 (d, *J* = 5.5 Hz), 33.9, 27.4 (d, *J* = 2.6 Hz), 24.3, 22.8. ^{19}F NMR (375 MHz, $CDCl_3$, 23 °C, δ): –133.4. HRMS-FIA(m/z) calcd for $C_{15}H_{23}F$ $[M]^+$, 222.1778; found, 222.1773.

2-Fluoro-1,1'-biphenyl (4f)

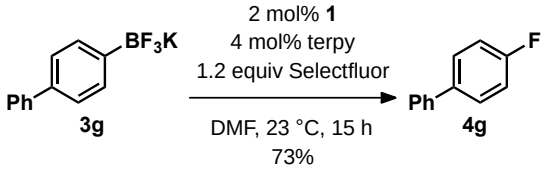


To a mixture of palladium catalyst **1** (7.8 mg, 14 μmol, 0.020 equiv) and terpy (6.5 mg, 28 μmol, 0.040 equiv) was added dimethylformamide (7.0 mL, 0.1 M) at 23 °C. This suspension was swirled for approx. 20 seconds until it became homogenous. This solution was transferred via syringe to a mixture of aryl trifluoroborate **3f** (182 mg, 700 μmol, 1.00 equiv), Selectfluor (298 mg, 840 μmol, 1.20 equiv), and sodium fluoride (29.4 mg, 700 μmol, 1.00 equiv). The reaction mixture was stirred for 15 hours at 23 °C and then transferred to a separatory funnel. Pentane (20 mL) was added and the organic layer was washed with a 5% aqueous lithium chloride solution (20 mL). The aqueous layer was extracted with pentane (4 × 20 mL). The combined organic layers were dried over sodium sulfate. The organic layer was filtered through silica gel (approx. 20 g) eluting with pentane (approx. 200 mL) and concentrated *in vacuo* at 0 °C to afford a colorless solid (106.6 mg) containing the title compound (102 mg, 592 μmol, 85% yield) and biphenyl (4.6 mg, 29.8 μmol, 4% yield). Purity of the residue was determined by integration of the ^{1}H NMR spectrum of the mixture.

R_f = 0.62 (pentane). NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$, 23 °C, δ): 7.57–7.54 (m, 2H), 7.46–7.43 (m, 3H), 7.39 (tt, *J* = 7.5, 1.4 Hz, 1H), 7.32 (dddd, *J* = 8.2, 7.3, 5.2, 1.9 Hz, 1H), 7.21 (td, *J* = 7.5, 1.2 Hz, 1H), 7.16 (ddd, *J* = 10.8, 8.2, 1.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 °C, δ): 159.7 (d, *J* = 247 Hz), 135.8, 130.7 (d, *J* = 3.6 Hz), 129.1 (d, *J* = 5.3 Hz), 129.0 (d, *J* =

2.8 Hz), 128.9 (d, *J* = 8.3 Hz), 128.4, 127.6, 124.3 (d, *J* = 3.6 Hz), 116.0 (d, *J* = 22.8 Hz). ^{19}F NMR (375 MHz, $CDCl_3$, 23 °C, δ): –121.1. HRMS-APCI(m/z) calcd for $C_{12}H_9F$ $[M]^+$, 172.0683; found, 172.0688.

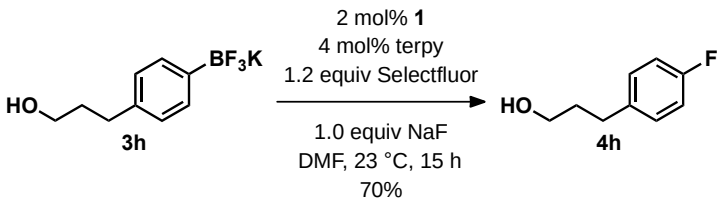
4-Fluoro-1,1'-biphenyl (4g)



To a mixture of palladium catalyst **1** (7.8 mg, 14 μmol, 0.020 equiv) and terpy (6.5 mg, 28 μmol, 0.040 equiv) was added dimethylformamide (7.0 mL, 0.1 M) at 23 °C. This suspension was swirled for approx. 20 seconds until it became homogenous. This solution was transferred via syringe to a mixture of aryl trifluoroborate **3g** (182 mg, 700 μmol, 1.00 equiv) and Selectfluor (298 mg, 840 μmol, 1.20 equiv). The reaction mixture was stirred for 15 hours at 23 °C and then transferred to a separatory funnel. Pentane (20 mL) was added and the organic layer was washed with a 5% aqueous lithium chloride solution (20 mL). The aqueous layer was extracted with pentane (4 × 20 mL). The combined organic layers were dried over sodium sulfate. The organic layer was filtered through silica gel (approx. 20 g) eluting with pentane (approx. 200 mL) and concentrated *in vacuo* at 0 °C to afford the title compound (88.4 mg, 513 μmol, 73% yield) as a colorless crystalline solid.

R_f = 0.62 (pentane). NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$, 23 °C, δ): 7.56–7.53 (m, 4H), 7.45–7.42 (tm, *J* = 7.8 Hz, 2H), 7.36–7.33 (m, 1H), 7.15–7.11 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 °C, δ): 162.4 (d, *J* = 246 Hz), 140.2, 137.3 (d, *J* = 3.6 Hz), 128.8, 128.6 (d, *J* = 8.3 Hz), 127.2, 127.0, 115.6 (d, *J* = 21.9 Hz). ^{19}F NMR (375 MHz, $CDCl_3$, 23 °C, δ): –118.9. HRMS-FIA(m/z) calcd for $C_{12}H_9F$ $[M]^+$, 172.0683; found, 172.0685.

3-(4-Fluorophenyl)propan-1-ol (4h)

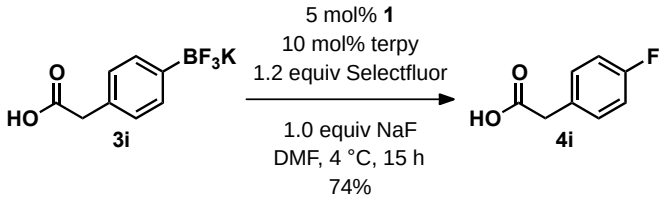


To a mixture of palladium precatalyst **1** (5.5 mg, 10 μmol, 0.020 equiv), terpy (4.7 mg, 20 μmol, 0.040 equiv), aryl trifluoroborate **3h** (121 mg, 500 μmol, 1.00 equiv), Selectfluor (213 mg, 600 μmol, 1.20 equiv), and sodium fluoride (21.0 mg, 500 μmol, 1.00 equiv) was added dimethylformamide (5.0 mL, 0.1 M) at 23 °C. The reaction mixture was stirred for 15 hours at 23 °C and then transferred to a separatory funnel. Diethyl ether (20 mL) was added and the

organic layer was washed with a 5% aqueous lithium chloride solution (20 mL). The aqueous layer was extracted with diethyl ether (2 × 20 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated *in vacuo* at 0 °C to afford a yellow oil. The residue was purified by chromatography on silica gel eluting with a solvent mixture of pentane/Et_2O (11:9 (v/v)) to afford a colorless oil (97.2 mg) containing the title compound (54.7 mg, 355 μmol, 71% yield), water, pentane, diethyl ether, and dichloromethane. The remaining solvent was not removed from the sample due to volatility of the product. The solvent content of the residue was determined by integration of the ^{1}H NMR spectrum of the mixture. Azeotropic evaporation of the trace solvent with $CDCl_3$ was performed prior to ^{1}H and ^{13}C NMR characterization. The ^{1}H and ^{13}C NMR spectroscopic data correspond to the data reported in reference 5.[5] High resolution mass spectrometry could only identify [(M+H)-F], therefore low resolution mass spectrometry was used to confirm the molecular ion of the title compound.

R_f = 0.24 (pentane/Et_2O 11:9 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C, δ): 7.17–7.13 (m, 2H), 6.99–6.94 (m, 2H), 3.67 (t, *J* = 6.4 Hz, 2H), 2.69 (t, *J* = 7.7 Hz, 2H), 1.90–1.84 (tdd, *J* = 8.6, 6.8, 5.3 Hz, 2H), 1.32 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 °C, δ): 161.2 (d, *J* = 242 Hz), 137.4 (d, *J* = 2.8 Hz), 129.7 (d, *J* = 7.4 Hz), 115.0 (d, *J* = 20.9 Hz), 62.0, 34.2, 31.2. ^{19}F NMR (375 MHz, $CDCl_3$, 23 °C, δ): –120.7. LRMS-FIA(m/z) calcd for $C_9H_{11}FO$ $[M]^+$, 154.1; found, 154.1. HRMS-FIA(m/z) calcd for $C_9H_{11}FO$ [(M+H)-F], 136.0883; found, 136.0882.

2-(4-Fluorophenyl)acetic acid (4i)



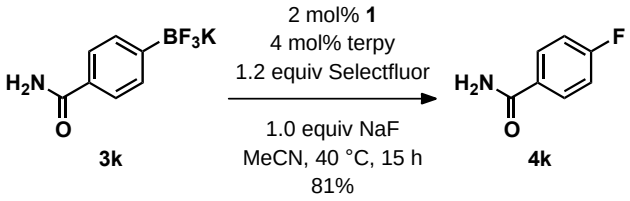
To a mixture of palladium precatalyst **1** (13.9 mg, 25.0 μmol, 0.0500 equiv), terpy (11.7 mg, 50.0 μmol, 0.100 equiv), aryl trifluoroborate **3i** (121 mg, 500 μmol, 1.00 equiv), Selectfluor (213 mg, 600 μmol, 1.20 equiv), and sodium fluoride (21.0 mg, 500 μmol, 1.00 equiv) was added dimethylformamide (5.0 mL, 0.1 M) at 23 °C. The reaction mixture was stirred for 15 hours at 4 °C and then transferred to a separatory funnel. Diethyl ether (20 mL) was added and the organic layer was washed with a 1 N aqueous HCl solution (20 mL). The aqueous layer was extracted with diethyl ether (3 × 20 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated *in vacuo* to afford a yellow solid. The solid was purified by chromatography on silica gel eluting with a solvent mixture of pentane/Et_2O/AcOH (70:30:1 (v/v)) to afford a colorless solid (60.1 mg) containing the title compound (57.1 mg, 370 μmol,

[5] Szostak, M.; Spain, M.; Procter, D. J. *Org. Let.* **2012**, 14(3), 840-843.

74% yield) and dichloromethane. The remaining solvent was not removed from the sample due to volatility of the product. The solvent content of the residue was determined by integration of the ^{1}H NMR spectrum of the mixture. Azeotropic evaporation of the trace solvent with $CDCl_3$ was performed prior to ^{1}H and ^{13}C NMR characterization.

R_f = 0.36 (pentane/Et_2O/AcOH 70:30:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$, 23 °C, δ): 10.31 (bs, 1H), 7.27–7.24 (m, 2H), 7.05–7.01 (m, 2H), 3.64 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 °C, δ): 178.1, 162.1 (d, J = 245 Hz), 130.9 (d, J = 8.3 Hz), 128.9 (d, J = 3.6 Hz), 115.5 (d, J = 21.9 Hz), 40.2. ^{19}F NMR (375 MHz, $CDCl_3$, 23 °C, δ): –118.2. HRMS-FIA(m/z) calcd for $C_8H_7FO_2$ $[M–H]^-$, 153.0357; found, 153.0353.

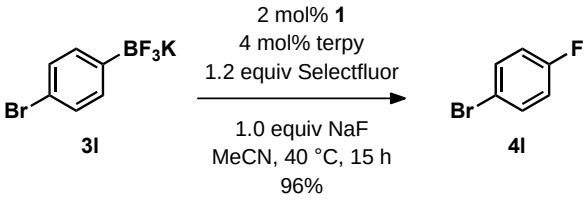
4-Fluorobenzamide (4k)



To a mixture of palladium precatalyst **1** (5.5 mg, 10 μmol, 0.020 equiv), terpy (4.7 mg, 20 μmol, 0.040 equiv), aryl trifluoroborate **3k** (114 mg, 500 μmol, 1.00 equiv), Selectfluor (213 mg, 600 μmol, 1.20 equiv), and sodium fluoride (21.0 mg, 500 μmol, 1.00 equiv) was added acetonitrile (5.0 mL, 0.1 M) at 23 °C. The reaction mixture was stirred for 15 hours at 40 °C, allowed to cool to 23 °C, and then transferred to a separatory funnel. Dichloromethane (20 mL) was added and the organic layer was washed with water (20 mL). The aqueous layer was extracted with dichloromethane (3 × 20 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated *in vacuo* to afford a yellow solid. The solid was purified by chromatography on silica gel eluting with a solvent mixture of dichloromethane/methanol (99:1 (v/v)) ramping to a solvent mixture of dichloromethane/methanol (97:3 (v/v)) to afford a colorless solid (64.2 mg) containing the title compound (56.0 mg, 403 μmol, 81% yield), 3-fluorobenzamide (3.88 mg, 27.9 μmol, 6% yield), 2-fluorobenzamide (2.22 mg, 15.9 μmol, 3% yield), water, pentane, and dichloromethane. The remaining solvent was not removed from the sample due to volatility of the product. The solvent content of the residue was determined by integration of the ^{1}H NMR spectrum of the mixture. Azeotropic evaporation of the trace solvent with $CDCl_3$ was performed prior to ^{1}H and ^{13}C NMR characterization.

R_f = 0.20 (dichloromethane/methanol 19:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$, 23 °C, δ): 7.85–7.81 (m, 2H), 7.15–7.11 (m, 2H), 5.98 (bs, 1H), 5.67 (bs, 1H). ^{13}C NMR (100 MHz, DMSO-d_6, 23 °C, δ): 167.2, 163.9 (d, J = 249 Hz) , 130.3, 129.8 (d, J = 9.1 Hz), 114.6 (d, J = 21.4 Hz). ^{19}F NMR (375 MHz, $CDCl_3$, 23 °C, δ): –110.3. HRMS-FIA(m/z) calcd for C_7H_6FNO $[M+H]^+$, 140.0506; found, 140.0508.

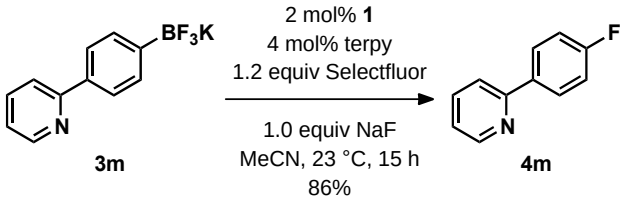
1-Bromo-4-fluorobenzene (4l)



To a mixture of palladium precatalyst **1** (5.5 mg, 10 μmol, 0.020 equiv), terpy (4.7 mg, 20 μmol, 0.040 equiv), aryl trifluoroborate **3l** (131 mg, 500 μmol, 1.00 equiv), Selectfluor (213 mg, 600 μmol, 1.20 equiv), and sodium fluoride (21.0 mg, 500 μmol, 1.00 equiv) was added acetonitrile (5.0 mL, 0.1 M) at 23 °C. The reaction mixture was stirred for 15 hours at 40 °C, allowed to cool to 23 °C, and then transferred to a separatory funnel. Pentane (20 mL) was added and the organic layer was washed with water (20 mL). The aqueous layer was extracted with pentane (3 × 20 mL). The combined organic layers were dried over sodium sulfate. The organic layer was filtered through silica gel (approx. 20 g) eluting with pentane (approx. 200 mL) and concentrated *in vacuo* at 0 °C to afford a colorless oil (130 mg) containing the title compound (84.4 mg, 482 μmol, 96% yield), pentane, and water. The remaining solvent was not removed from the sample due to volatility of the product. The solvent content of the residue was determined by integration of the ^{1}H NMR spectrum of the mixture.

R_f = 0.84 (pentane). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C, δ): 7.47–7.42 (m, 1H), 6.98–6.93 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 °C, δ): 161.8 (d, J = 245 Hz), 132.9 (d, J = 7.4 Hz), 117.2 (d, J = 22.8 Hz), 116.5 (d, J = 3.6 Hz). ^{19}F NMR (375 MHz, $CDCl_3$, 23 °C, δ): –118.4. HRMS-FIA(m/z) calcd for C_6H_4BrF $[M]^+$, 175.9455; found, 175.9452.

2-(4-Fluorophenyl)pyridine (4m)

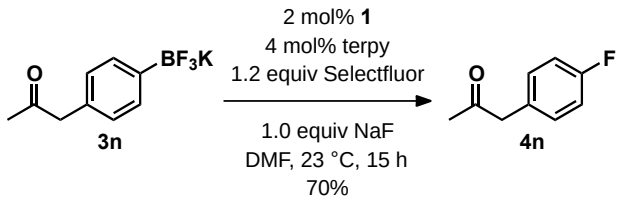


To a mixture of palladium precatalyst **1** (5.5 mg, 10 μmol, 0.020 equiv), terpy (4.7 mg, 20 μmol, 0.040 equiv), aryl trifluoroborate **3m** (131 mg, 500 μmol, 1.00 equiv), Selectfluor (213 mg, 600 μmol, 1.20 equiv), and sodium fluoride (21.0 mg, 500 μmol, 1.00 equiv) was added acetonitrile (5.0 mL, 0.1 M) at 23 °C. The reaction mixture was stirred for 15 hours at 23 °C and then transferred to a separatory funnel, rinsing the reaction vial with additional acetonitrile (2 × 4 mL). Pentane (20 mL) was added and the organic layer was washed with water (20 mL). The aqueous layer was extracted with pentane (6 × 20 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated *in vacuo* to afford a yellow solid. The solid was

purified by chromatography on silica gel eluting with a solvent mixture of pentane/Et_2O (4:1 (v/v)) to afford a colorless solid (78.0 mg) containing the title compound (74.9 mg, 432 μmol, 86% yield), water, and pentane. The remaining solvent was not removed from the sample due to volatility of the product. The solvent content of the residue was determined by integration of the ^1H NMR spectrum of the mixture. Azeotropic evaporation of the trace solvent with $CDCl_3$ was performed prior to ^1H and ^{13}C NMR characterization.

R_f = 0.41 (pentane/diethyl ether 4:1 (v/v)). NMR Spectroscopy: ^1H NMR (600 MHz, $CDCl_3$, 23 °C, δ): 8.68 (ddd, *J* = 4.8, 1.7, 0.9 Hz, 1H), 7.98 (q, *J* = 7.5 Hz, 2H), 7.75 (td, *J* = 7.7, 1.8 Hz, 1H), 7.23 (ddd, *J* = 7.4, 4.8, 1.1 Hz, 1H), 7.18–7.14 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 °C, δ): 163.4 (d, *J* = 249 Hz), 156.4, 149.6, 136.7, 135.5, 128.6 (d, *J* = 7.3), 122.0, 120.1, 115.6 (d, *J* = 20.0 Hz). ^{19}F NMR (375 MHz, $CDCl_3$, 23 °C, δ): –116.2. HRMS-FIA(m/z) calcd for $C_{11}H_8FN$ $[M+H]^+$, 174.0714; found, 174.0722.

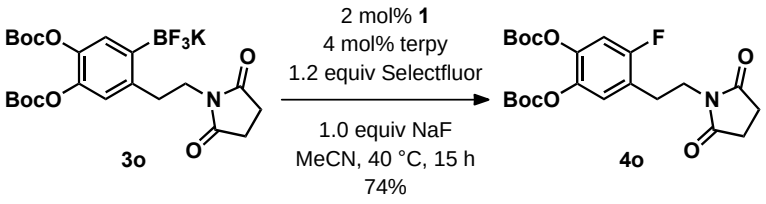
1-(4-Fluorophenyl)propan-2-one (4n)



To a mixture of palladium precatalyst **1** (7.8 mg, 14 μmol, 0.020 equiv), terpy (6.5 mg, 28 μmol, 0.040 equiv), aryl trifluoroborate **3n** (168 mg, 700 μmol, 1.00 equiv), Selectfluor (298 mg, 840 μmol, 1.20 equiv), and sodium fluoride (29.4 mg, 700 μmol, 1.00 equiv) was added dimethylformamide (7.0 mL, 0.1 M) at 23 °C. The reaction mixture was stirred for 15 hours at 23 °C and then transferred to a separatory funnel. Pentane (20 mL) was added and the organic layer was washed with a 5% aqueous lithium chloride solution (20 mL). The aqueous layer was extracted with pentane (3 × 20 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated *in vacuo* at 0 °C to afford a yellow oil. The residue was purified by chromatography on silica gel eluting with a solvent mixture of pentane/Et_2O (17:3 (v/v)) to afford a colorless oil (104 mg) containing the title compound (74.9 mg, 493 μmol, 70% yield), dichloromethane, pentane, and water. The remaining solvent was not removed from the sample due to volatility of the product. The solvent content of the residue was determined by integration of the ^1H NMR spectrum of the mixture. Azeotropic evaporation of the trace solvent with $CDCl_3$ was performed prior to ^1H and ^{13}C NMR characterization.

R_f = 0.28 (pentane/diethyl ether 17:3 (v/v)). NMR Spectroscopy: ^1H NMR (600 MHz, $CDCl_3$, 23 °C, δ): 7.18–7.14 (m, 2H), 7.04–7.00 (m, 2H), 3.68 (s, 2H), 2.17 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 °C, δ): 206.0, 161.9 (d, *J* = 244 Hz), 130.9 (d, *J* = 8.3 Hz), 129.9 (d, *J* = 3.6 Hz), 115.5 (d, *J* = 21.0 Hz), 49.8, 29.2. ^{19}F NMR (375 MHz, $CDCl_3$, 23 °C, δ): –118.8. HRMS-FIA(m/z) calcd for C_9H_9FO $[M+H]^+$, 153.0710; found, 153.0709.

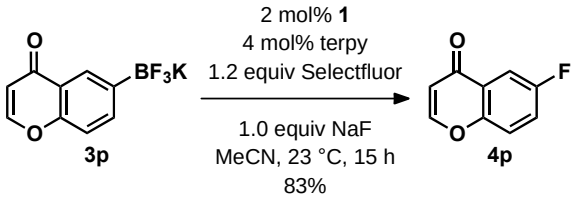
Aryl Fluoride 4o



To a mixture of palladium precatalyst **1** (2.2 mg, 4.0 μmol, 0.020 equiv), terpy (1.9 mg, 8.0 μmol, 0.040 equiv), aryl trifluoroborate **3o** (108 mg, 200 μmol, 1.00 equiv), Selectfluor (85.0 mg, 240 μmol, 1.20 equiv), and sodium fluoride (8.40 mg, 200 μmol, 1.00 equiv) was added acetonitrile (2.0 mL, 0.1 M) at 23 °C. The reaction mixture was stirred for 15 hours at 40 °C, allowed to cool to 23 °C, and then transferred to a separatory funnel. Dichloromethane (20 mL) was added and the organic layer was washed with water (20 mL). The aqueous layer was extracted with dichloromethane (4 × 20 mL). The combined organic layers were washed with brine (20 mL), dried over sodium sulfate, filtered, and concentrated *in vacuo* to afford a yellow solid. The solid was purified by chromatography on silica gel eluting with a solvent mixture of hexanes/ethyl acetate (1:1 (v/v)) to afford the title compound (67.1 mg, 148 μmol, 74% yield) as a colorless crystalline solid.

R_f = 0.44 (hexanes/ethyl acetate 1:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$, 23 °C, δ): 7.02 (d, *J* = 7.1 Hz, 1H), 7.00 (d, *J* = 9.6 Hz, 1H), 3.77 (t, *J* = 7.2 Hz, 2H), 2.93 (t, *J* = 7.2 Hz, 2H), 2.65 (s, 4H), 1.54 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 °C, δ): 177.0, 158.0 (d, *J* = 245 Hz), 150.8, 150.1, 141.7 (d, *J* = 11.0 Hz), 138.3 (d, *J* = 3.6 Hz), 124.7 (d, *J* = 6.4 Hz), 122.7 (d, *J* = 18.3 Hz), 110.6 (d, *J* = 26.4 Hz), 84.1, 83.8, 37.9, 28.0, 27.5, 27.5, 26.7. ^{19}F NMR (375 MHz, $CDCl_3$, 23 °C, δ): –121.3. HRMS-FIA(m/z) calcd for $C_{22}H_{28}FNO_8$ $[M+NH_4]^+$, 471.2137; found, 471.2155.

6-Fluoro-4*H*-chromen-4-one (4p)

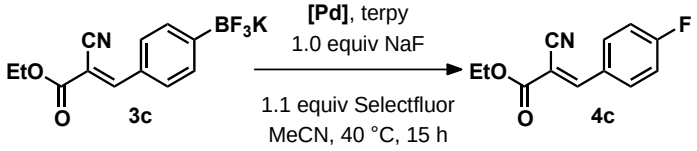


To a mixture of palladium precatalyst **1** (5.5 mg, 10 μmol, 0.020 equiv), terpy (4.7 mg, 20 μmol, 0.040 equiv), aryl trifluoroborate **3p** (126 mg, 500 μmol, 1.00 equiv), Selectfluor (213 mg, 600 μmol, 1.20 equiv), and sodium fluoride (21.0 mg, 500 μmol, 1.00 equiv) was added acetonitrile (5.0 mL, 0.1 M) at 23 °C. The reaction mixture was stirred for 15 hours at 23 °C and then transferred to a separatory funnel. Pentane (20 mL) was added and the organic layer was washed with water (20 mL). The aqueous layer was extracted with pentane (9 × 20 mL). The combined

organic layers were dried over sodium sulfate, filtered, and concentrated *in vacuo* to afford a yellow solid. The solid was purified by chromatography on silica gel eluting with a solvent mixture of pentane/diethyl ether (7:3 (v/v)) to afford a colorless solid (72.8 mg) containing the title compound (67.9 mg, 413 μmol, 83% yield), dichloromethane, pentane, and water. The remaining solvent was not removed from the sample due to volatility of the product. The solvent content of the residue was determined by integration of the ^{1}H NMR spectrum of the mixture. Azeotropic evaporation of the trace solvent with $CDCl_3$ was performed prior to ^{1}H and ^{13}C NMR characterization.

R_f = 0.20 (pentane/diethyl ether 7:3 (v/v)). NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$, 23 °C, δ): 7.87 (d, *J* = 6.1 Hz, 1H), 7.85 (dd, *J* = 8.2, 3.1 Hz, 1H), 7.48 (dd, *J* = 9.2, 4.2 Hz, 1H), 7.40 (ddd, *J* = 9.2, 7.6, 3.1 Hz, 1H), 6.34 (d, *J* = 6.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 °C, δ): 176.7, 159.4 (d, *J* = 245 Hz), 155.4, 152.7 (d, *J* = 1.8 Hz), 125.9 (d, *J* = 7.3 Hz), 121.9 (d, *J* = 25.5 Hz), 120.3 (d, *J* = 7.3 Hz), 112.1, 110.5 (d, *J* = 23.6 Hz). ^{19}F NMR (375 MHz, $CDCl_3$, 23 °C, δ): –117.9. HRMS-FIA(m/z) calcd for $C_9H_5FO_2$ $[M+H]^+$, 165.0346; found, 165.0351.

Evaluation of other [Pd] pre-catalysts (Data pertaining to Table 2)



General Procedure:

To aryl trifluoroborate **3c** (31 mg, 0.10 mmol, 1.0 equiv), Selectfluor (39 mg, 0.11 mmol, 1.1 equiv), NaF (4.2 mg, 0.10 mmol, 1.0 equiv), the [Pd] source (2.0×10^{-3} mmol, 0.020 equiv), and terpy (1.0 mg, 4.0×10^{-3} mmol, 0.040 equiv) in a 4 mL glass vial was added MeCN (1.0 mL). The vial was sealed with a teflon-lined cap, and the reaction mixture was heated at 40 ºC with vigorous stirring. After 15 hours, the reaction mixture was cooled to room temperature, and then transferred to a separatory funnel, rinsing the reaction vial with additional MeCN (2 × 0.5 mL). H_2O (15 mL) was added, and the product was extracted from the aqueous mixture with CH_2Cl_2 (3 × 4 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated under vacuum to give an off-white solid. To the solid was added 2 mL of a 10% (v/v) Et_2O/pentane mixture, and the mixture was agitated using an ultrasonic bath. The resulting suspension was filtered over a plug of SiO_2 (~1.5" in a Pasteur pipette), eluting with an additional 15 mL of 10% Et_2O/pentane. The filtrate was concentrated, and the product was further dried under vacuum, affording aryl fluoride **4c** as a colorless crystalline solid. Purity of the product was confirmed in each case via ^{1}H and ^{19}F NMR spectroscopy.

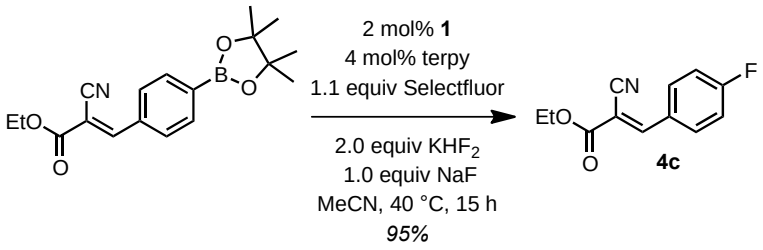
Specific details for each [Pd] source used are given in Table S1 below:

Table S1. Evaluation of Palladium Pre-Catalysts

[Pd] Source	Commercial Supplier	Additive	Yield ArF 4c
$[(terpy)_2Pd][BF_4]_3$ (**2**) (1.7 mg, 2 mol%)	*N/A*	None	21 mg, 95%
$[Pd(MeCN)_4][BF_4]_2$ (0.9 mg, 2 mol%)	Strem	None	21 mg, 95%
$Pd(OAc)_2$ (1.2 mg, 5 mol%)	Strem	$NaBF_4$ (22 mg, 2.0 equiv)	20 mg, 91%
$Pd(O_2CCF_3)_2$ (0.7 mg, 2 mol%)	Strem	$NaBF_4$ (11 mg, 1.0 equiv)	20 mg, 91%
$PdCl_2(MeCN)_2$ (1.3 mg, 5 mol%)	Sigma-Aldrich	$NaBF_4$ (22 mg, 2.0 equiv)	19 mg, 86% (as a mixture with ~10% ArCl)
$PdBr_2$ (1.3 mg, 5 mol%)	Sigma-Aldrich	$NaBF_4$ (22 mg, 2.0 equiv)	17 mg, 78% (as a mixture with ~10% ArBr)

Evaluation of other arylboron reagents (Data pertaining to eq 1–3)

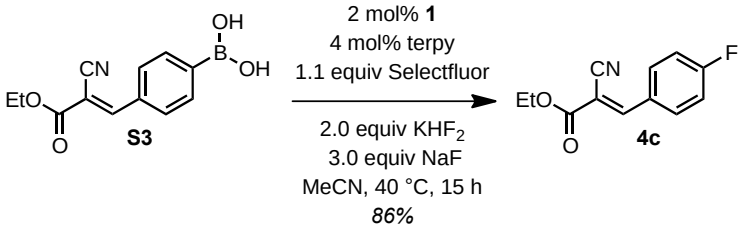
Fluorination of [(*E*)-4-(2-cyano-2-ethoxycarbonylvinyl)phenyl]boronic acid pincol ester



To [(*E*)-4-(2-cyano-2-ethoxycarbonylvinyl)phenyl]boronic acid pinacol ester (33 mg, 0.10 mmol, 1.0 equiv), Selectfluor (39 mg, 0.11 mmol, 1.1 equiv), KHF_2 (16 mg, 0.20 mmol, 2.0 equiv), NaF (4.2 mg, 0.10 mmol, 1.0 equiv), Pd complex **1** (1.1 mg, 2.0×10^{-3} mmol, 0.020 equiv), and terpy (1.0 mg, 4.0×10^{-3} mmol, 0.040 equiv) in a 4 mL glass vial was added MeCN (1.0 mL). The vial was sealed with a teflon-lined cap, and the reaction mixture was heated at 40 ºC with vigorous stirring. After 15 hours, the reaction mixture was cooled to room temperature, and then transferred to a separatory funnel, rinsing the reaction vial with additional MeCN (2 × 0.5 mL). H_2O (15 mL) was added, and the product was extracted from the aqueous mixture with CH_2Cl_2 (3 × 4 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated under

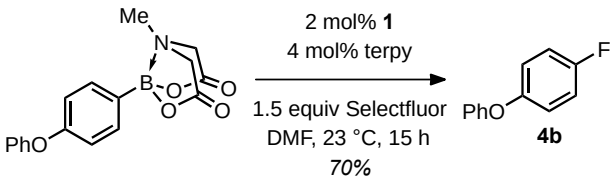
vacuum to give an off-white solid. To the solid was added 2 mL of a 10% (v/v) Et_2O/pentane mixture, and the mixture was agitated using an ultrasonic bath. The resulting suspension was filtered over a plug of SiO_2 (~1.5" in a Pasteur pipette), eluting with an additional 15 mL of 10% Et_2O/pentane. The filtrate was concentrated, and the product was further dried under vacuum, affording 21 mg of aryl fluoride **4c** as a colorless crystalline solid (95% yield). Purity of the product was confirmed via ^1H and ^{19}F NMR spectroscopy.

Fluorination of [(*E*)-4-(2-cyano-2-ethoxycarbonylvinyl)phenyl]boronic acid (S3)



To [(*E*)-4-(2-cyano-2-ethoxycarbonylvinyl)phenyl]boronic acid (**S3**) (25 mg, 0.10 mmol, 1.0 equiv), Selectfluor (39 mg, 0.11 mmol, 1.1 equiv), KHF_2 (16 mg, 0.20 mmol, 2.0 equiv), NaF (13 mg, 0.30 mmol, 3.0 equiv), Pd complex **1** (1.1 mg, 2.0×10^{-3} mmol, 0.020 equiv), and terpy (1.0 mg, 4.0×10^{-3} mmol, 0.040 equiv) in a 4 mL glass vial was added MeCN (1.0 mL). The vial was sealed with a teflon-lined cap, and the reaction mixture was heated at 40 ºC with vigorous stirring. After 15 hours, the reaction mixture was cooled to room temperature, and then transferred to a separatory funnel, rinsing the reaction vial with additional MeCN (2 × 0.5 mL). H_2O (15 mL) was added, and the product was extracted from the aqueous mixture with CH_2Cl_2 (3 × 4 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated under vacuum to give an off-white solid. To the solid was added 2 mL of a 10% (v/v) Et_2O/pentane mixture, and the mixture was agitated using an ultrasonic bath. The resulting suspension was filtered over a plug of SiO_2 (~1.5" in a Pasteur pipette), eluting with an additional 15 mL of 10% Et_2O/pentane. The filtrate was concentrated, and the product was further dried under vacuum, affording 19 mg of aryl fluoride **4c** as a colorless crystalline solid (86% yield). Purity of the product was confirmed via ^1H and ^{19}F NMR spectroscopy.

Fluorination of 4-phenoxyphenylboronic acid MIDA ester

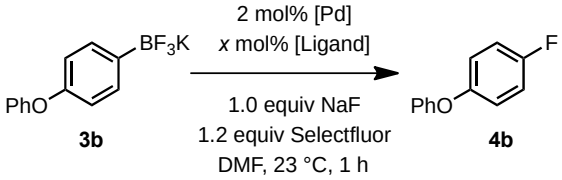


To 4-phenoxyphenylboronic acid MIDA ester (65 mg, 0.20 mmol, 1.0 equiv), Selectfluor (110 mg, 0.30 mmol, 1.5 equiv), Pd complex **1** (2.2 mg, 4.0×10^{-3} mmol, 0.020 equiv), and terpy (1.9

mg, 8.0×10^{-3} mmol, 0.040 equiv) in a 4 mL glass vial was added DMF (2.0 mL). The vial was sealed with a teflon-lined cap, and the reaction mixture was stirred at 23 ºC. After 15 hours, the reaction mixture was transferred to a separatory funnel. Brine (15 mL) was added, and the product was extracted from the resulting aqueous mixture with pentane (5 × 5 mL). The combined organic phases were dried over Na_2SO_4, and then filtered over a short pad of SiO_2 (~1 cm in a fritted funnel), eluting with an additional 20 mL of pentane. The filtrate was concentrated under vacuum at 0 °C, affording a colorless oil containing 27 mg of aryl fluoride **4b** (70% yield), along with water and pentane. The residual solvents were not further removed due to volatility of the product. The yield of **4b** was confirmed via ^{19}F and ^{1}H NMR spectroscopy using 1-fluoro-3-nitrobenzene (10. μL, 9.4×10^{-5} mol) as an internal standard.

No formation of aryl fluoride **4b** was observed in the reaction between 4-phenoxyphenylboronic acid MIDA ester and Selectfluor in the absence of Pd complex **1**.

Evaluation of other nitrogenous ligands



To a mixture of the [Pd] catalyst (14 μmol, 0.020 equiv) and nitrogenous ligand (see Table S2) was added DMF (1 mL, 0.1 M) at 23 °C. This suspension was stirred for approximately 10 minutes, at which point the solution was homogenous. This solution was transferred via syringe to a 4 mL glass vial containing aryl trifluoroborate **3b** (28 mg, 100 μmol, 1.0 equiv), Selectfluor (43 mg, 120 μmol, 1.2 equiv), and sodium fluoride (4.2 mg, 100 μmol, 1.0 equiv). The reaction mixture was stirred for 1 hour at 23 °C, at which point the remaining Selectfluor was quenched by the addition of triphenylphosphine (32 mg, 120 μmol, 1.2 equiv), and 1-fluoro-3-nitrobenzene (10. μL, 94 μmol) was added as an internal standard. The yield of the aryl fluoride product was determined via ^{19}F NMR spectroscopy, integrating against the internal standard peak at –112 ppm.

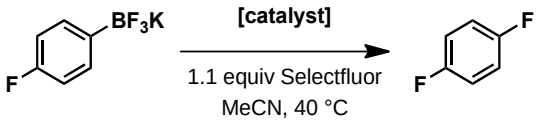
Table S2. Evaluation of other nitrogenous ligands

[Pd] pre-catalyst	Ligand	Yield ArF
1	terpy (4 mol%)	48%
1	none	<1%
1	pyridine (12 mol%)	<1%

$Pd(MeCN)_4(BF_4)_2$	2,2'-bipyridine (9 mol%)	7%
$Pd(MeCN)_4(BF_4)_2$	1,10-phenanthroline (9 mol%)	28%

The results indicate that while other nitrogenous chelating ligands, such as phenanthroline, are effective in the Pd-catalyzed fluorination reaction, use of terpy provides optimal results.

Evaluation of other single-electron redox catalysts



The proposed mechanism for the Pd-catalyzed fluorination reaction suggests the possiblity that other catalysts, capable of single-electron redox chemistry, may also be competent in the fluorination reaction. Therefore, we have performed a preliminary evaluation of other potential catalysts, summarized in Table S3 below. The results indicate that other metal complexes are indeed competent to catalyze the fluorination reaction, but that the combination of Pd complex **1** and terpyridine is uniquely effective in providing high yields and selectivity.

General Procedure:

To the aryl trifluoroborate (25 mg, 0.11 mmol, 1.0 equiv), Selectfluor (50. mg, 0.14 mmol, 1.1 equiv), and the catalyst (see Table S3) in a 4 mL glass vial was added MeCN (1.2 mL). The vial was sealed with a teflon-lined cap, and the reaction mixture was heated at 40 ºC with vigorous stirring. After 15 hours, the reaction mixture was cooled to room temperature, and then 1-fluoro-3-nitrobenzene (10. μL, 9.4×10^{-5} mol) was added as an internal standard. The yield of the aryl fluoride product, as well as unconsumed aryl trifluoroborate and protodeborylated product, was determined via ^{19}F NMR spectroscopy, integrating against the internal standard peak at –112 ppm.

Specific details for each catalyst are given in Table S3 below:

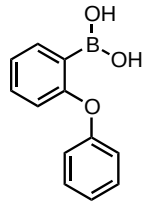
Table S3. Evaluation of other single-electron redox catalysts

Catalyst	**Additive**	**Yield ArF**	**Remaining $ArBF_3K$**	**Yield of Protodeborylation**
$[(terpy)_2Ni][OTf]_2$ (2 mol%)	terpy (2 mol%)	19%	35%	22%
$[Ni(bpy)_3][BF_4]_2$ (2 mol%)	none	17%	51%	*not observed*

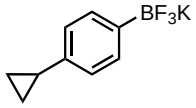
$[Ni(phen)_3][BF_4]_2$ (2 mol%)	none	13%	56%	< 2%
$[(terpy)Pt(MeCN)][BF_4]_2$ (2 mol%)	terpy (4 mol%)	17%	51%	*not observed*
Ferrocene (5 mol%)	none	9.5%	28%	42%

Evaluation of radical clock substrates

In order to probe the possibility of radical intermediates, we performed the Pd-catalyzed fluorination reaction on substrates **S6** and **S8**. Substrate **S6** probes the intermediacy of an aryl radical formed by homolysis of the C–B bond, and is known to undergo radical cyclization to afford dibenzofuran.[6] Substrate **S8** can undergo cyclopropane ring opening if a long-lived radical intermediate is formed via SET from the arene π-system. Both **S6** and **S8** underwent Pd-catalyzed fluorination to give a single major aryl fluoride product, in 54% and 62% yields, respectively (aryl fluoride yields determined by ^{19}F NMR spectroscopy, using 1-fluoro-3-nitrobenzene as internal standard). In the case of **S6**, radical cyclization was not observed; in the case of **S8**, no cyclopropane ring-opening was observed (the crude product mixtures were analyzed by ^{1}H NMR spectroscopy).



S6



S8

The lack of radical cyclization observed for **S6** is consistent with our mechanistic hypothesis, in which the C–F bond is formed prior to C–B bond cleavage. We note that the lack of cyclopropane ring opening for **S8** does not exclude the possibility of a radical mechanism, as the lifetime of the delocalized radical intermediate may be significantly shorter than the timescale of ring opening. In previous mechanistic investigations regarding SET reactivity with Selectfluor, computational evidence suggests that the lifetime of such intermediates are significantly shorter than the ring opening/closing timescale for radical clock substrates.[7]

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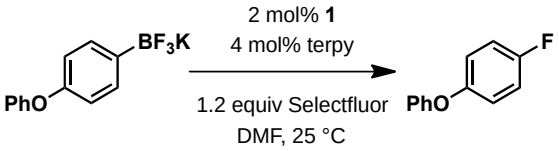
[6] Lockner, J. W.; Dixon, D. D.; Risgaard, R.; Baran, P. S. *Org. Lett.* **2011**, *13*, 5628–5631.

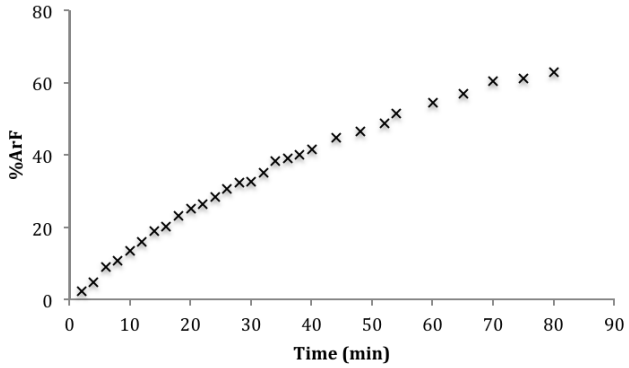
[7] Nyffeler, P. T.; Dur n, S. G.; Burkart, M. D.; Vincent, S. P. P.; Wong, C.-H. *Angew. Chem. Int. Ed***. 2005**, *44*, 192–212; and references therein.

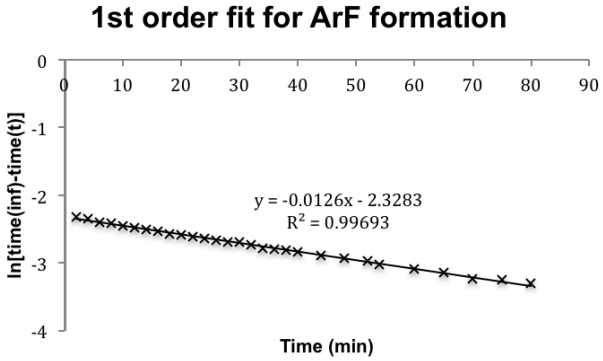
Reaction Kinetics

Kinetic Profile of Catalytic Reaction

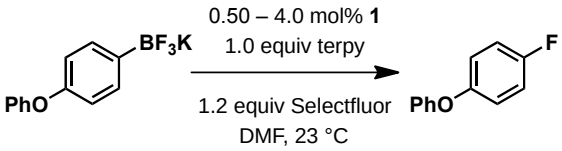


Solution A was prepared containing the aryl trifluoroborate (28 mg, 0.10 mmol, 1.0 equiv), Selectfluor (43 mg, 0.12 mmol, 1.2 equiv), and 1-fluoro-3-nitrobenzene (5.0 μL, 4.7×10^{-5} mol) as internal standard, in 0.80 mL DMF. Solution B was prepared containing Pd(II) complex **1** (1.1 mg, 2.0×10^{-3} mmol, 0.020 equiv) and terpy (1.0 mg, 4.0×10^{-3} mmol, 0.040 equiv) in 0.20 mL DMF. Solution A was added to an NMR tube, followed by solution B, and the tube was shaken rapidly to mix the reagents. The reaction was monitored via ^{19}F NMR spectroscopy at 25 °C, following evolution of the product signal at –123 ppm and integrating against the internal standard peak at –112 ppm. The reaction was followed to greater than three half-lives, as determined by disappearance of the ^{19}F NMR signal corresponding to the aryl trifluoroborate. Because evolution of product was measured, linear natural log plots were obtained by using an infinite time point set to 100% yield. Data were fitted to a first order regression, shown below.

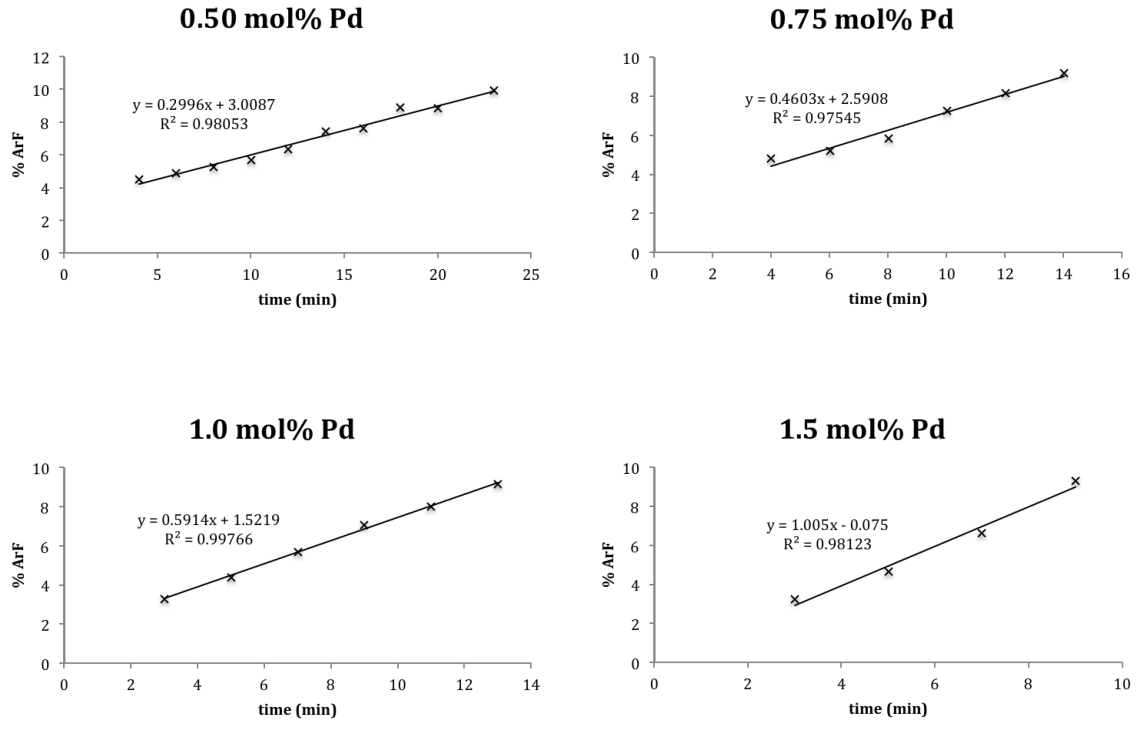


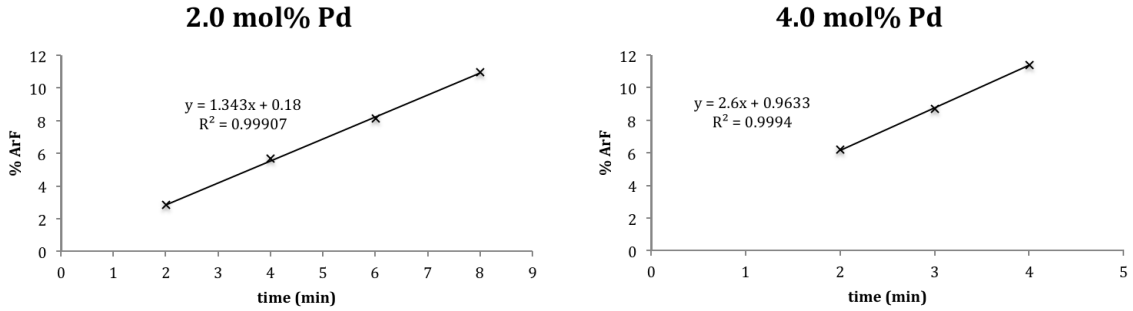


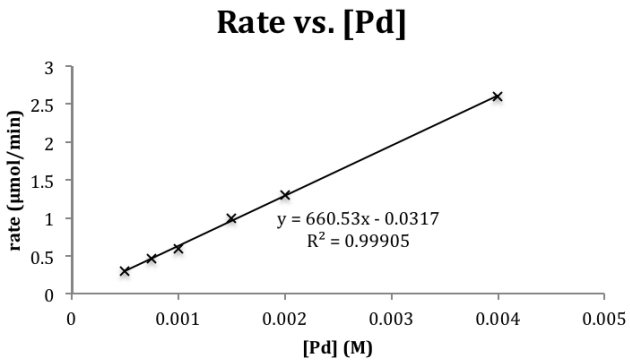
Initial Rate Kinetics of Pd Dependence

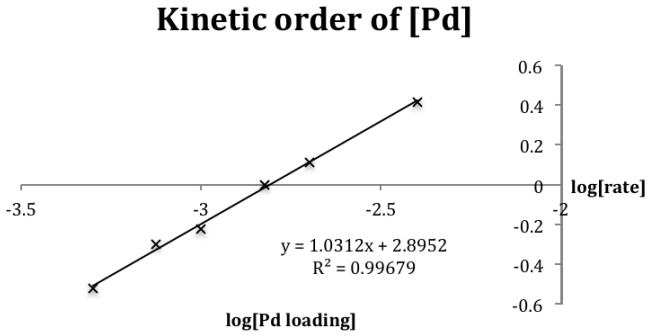


Three stock solutions were prepared: solution A, containing the aryl trifluoroborate (166 mg, 0.601 mmol), Selectfluor (255 mg, 0.720 mmol), and 1-fluoro-3-nitrobenzene (30.0 μL, 2.82 × 10^{-4} mol) as internal standard, in 3.00 mL DMF; solution B, containing Pd(II) complex **1** (5.5 mg, 1.0 × 10^{-2} mmol) in 0.50 mL DMF; and solution C, containing terpy (116 mg, 0.497 mmol) in 2.00 mL DMF. For each reaction, solution A (0.50 mL) was added to an NMR tube, followed by solution C (0.40 mL), DMF (100 – *x* μL), and finally solution B (*x* μL). Pd loadings in the range of 0.50–4.0 mol% were used. The tube was shaken rapidly to mix the reagents, and then the reaction was monitored via ^{19}F NMR spectroscopy at 25 °C, following evolution of the product signal at –123 ppm and integrating against the internal standard peak at –112 ppm. Product formation was monitored up to ~10% yield, and data in the 3–10% yield range was used to determine the initial rates.

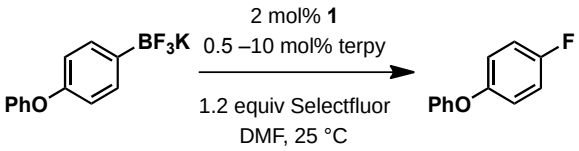






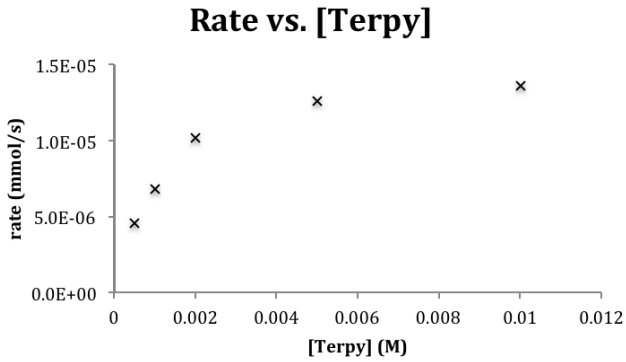


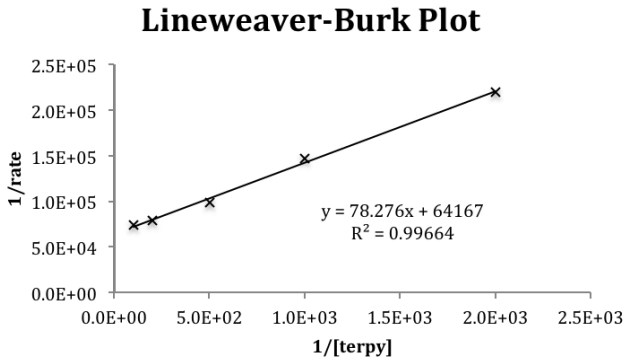
Initial Rate Kinetics of Terpyridine Dependence



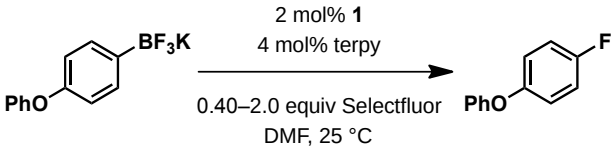
Three stock solutions were prepared: solution A, containing the aryl trifluoroborate (166 mg, 0.601 mmol), Selectfluor (255 mg, 0.720 mmol), and 1-fluoro-3-nitrobenzene (30.0 µL, 2.82×10^{-4} mol) as internal standard, in 3.00 mL DMF; solution B, containing Pd(II) complex **1** (3.3 mg, 6.0×10^{-3} mmol) in 0.60 mL DMF; and solution C, containing terpy (9.0 mg, 0.039 mmol) in 0.75

mL DMF. For each reaction, solution A (0.50 mL) was added to an NMR tube, followed by DMF (400 – *x* μL), solution C (*x* μL), and finally solution B (100 μL). Terpy loadings in the range of 0.5–10 mol% were used. The tube was shaken rapidly to mix the reagents, and then the reaction was monitored via ^{19}F NMR spectroscopy at 25 °C, following evolution of the product signal at –123 ppm and integrating against the internal standard peak at –112 ppm. Each reaction was monitored to approximately 5% yield, and yield was converted to an initial rate by dividing by the reaction time. The data obtained are presented below, along with a Lineweaver-Burk plot, indicating saturation kinetics with respect to terpyridine.



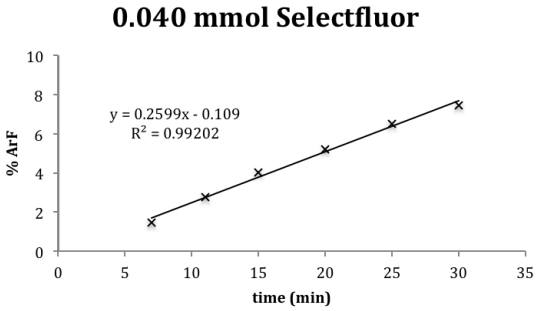


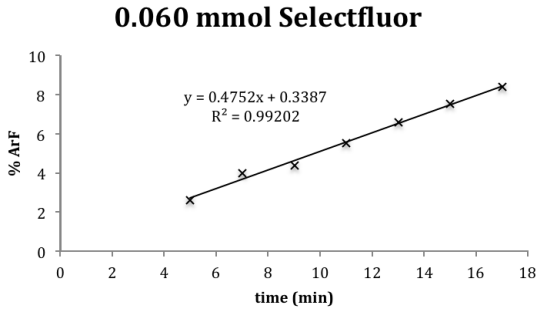
Initial Rate Kinetics of Selectfluor Dependence

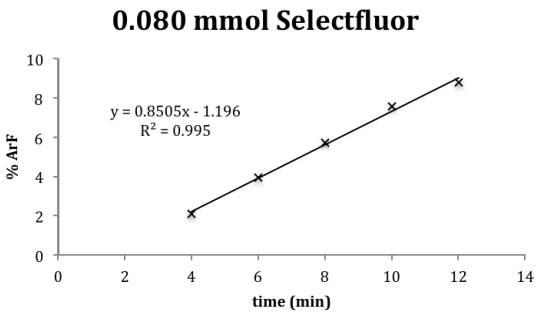


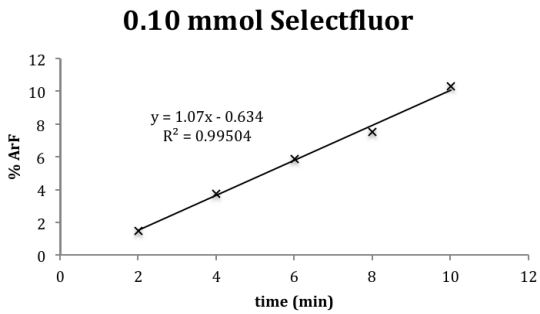
Three stock solutions were prepared: solution A, containing the aryl trifluoroborate (166 mg, 0.601 mmol) and 1-fluoro-3-nitrobenzene (30.0 μL, 2.82×10^{-4} mol) as internal standard, in 2.40 mL DMF; solution B, containing Pd(II) complex **1** (6.7 mg, 1.2×10^{-2} mmol) and terpy (5.6 mg, 2.4×10^{-2} mmol) in 1.20 mL DMF; and solution C, containing Selectfluor (176 mg, 0.500 mmol)

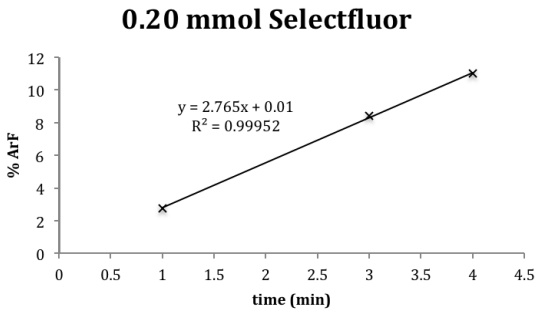
in 1.00 mL DMF. For each reaction, solution A (0.40 mL) was added to an NMR tube, followed by DMF (400 – *x* μL), solution C (*x* μL), and finally solution B (0.20 mL). Selectfluor concentrations in the range of 0.040–0.20 M were used. The tube was shaken rapidly to mix the reagents, and then the reaction was monitored via ^{19}F NMR spectroscopy at 25 °C, following evolution of the product signal at –123 ppm and integrating against the internal standard peak at –112 ppm. Product formation was monitored up to ~10% yield, and data in the 2–10% yield range was used to determine the initial rates. The data obtained are presented below.

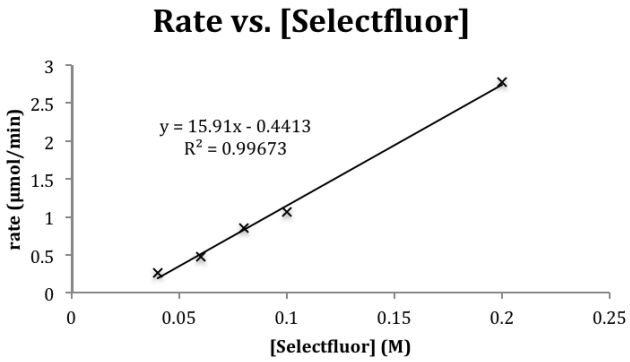


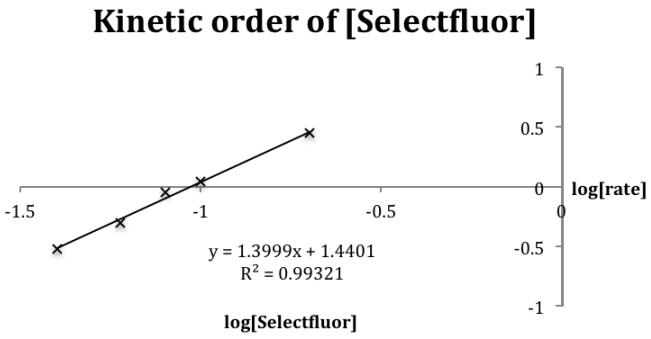




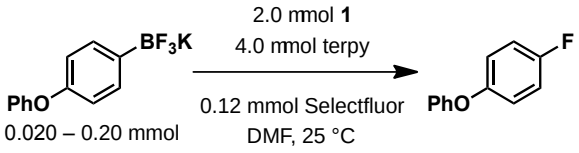




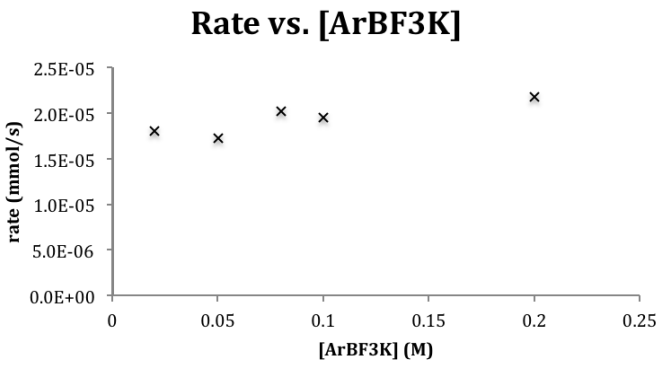


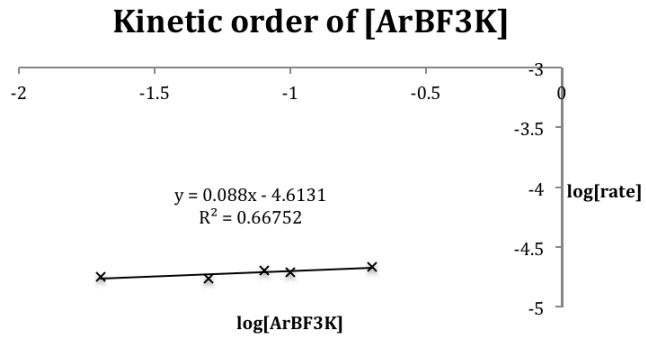


Initial Rate Kinetics of Aryl Trifluoroborate Dependence



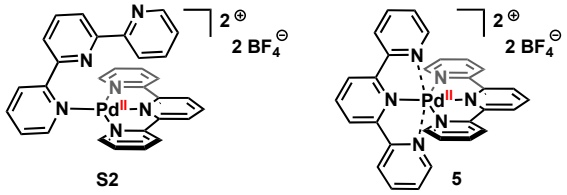
Three stock solutions were prepared: solution A, containing the aryl trifluoroborate (166 mg, 0.601 mmol) in 0.900 mL DMF; solution B, containing Pd(II) complex **1** (6.7 mg, 1.2×10^{-2} mmol) and terpy (5.6 mg, 2.4×10^{-2} mmol) in 1.20 mL DMF; and solution C, containing Selectfluor (255 mg, 0.720 mmol) and 1-fluoro-3-nitrobenzene (30.0 µL, 2.82×10^{-4} mol) as internal standard, in 3.00 mL DMF. For each reaction, solution A (x µL) was added to an NMR tube, followed by DMF (300 – x µL), solution C (500 µL), and finally solution B (200 µL). Aryl trifluoroborate concentrations in the range of 0.020–0.20 M were used. The tube was shaken rapidly to mix the reagents, and then the reaction was monitored via ^{19}F NMR spectroscopy at 25 °C, following evolution of the product signal at –123 ppm and integrating against the internal standard peak at –112 ppm. Each reaction was monitored to approximately 6% yield, and yield was converted to an initial rate by dividing by the reaction time. The data obtained are presented below.



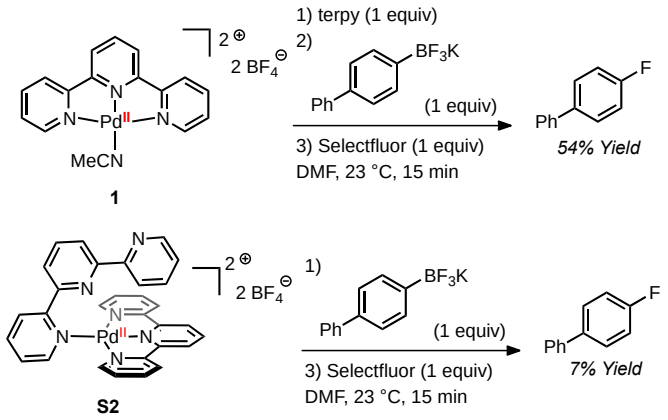


Discussion of the structure of $[(terpy)_2Pd][BF_4]_2$ (5)

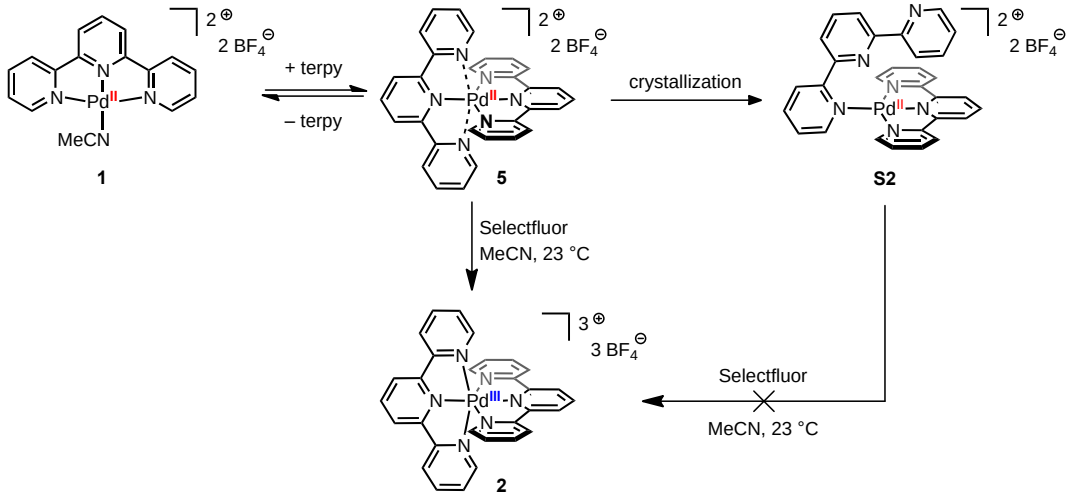
It is challenging to characterize the structure of the initial adduct formed between Pd(II) complex **1** and terpyridine due to rapid equilibria in solution. As described in the Experimental Procedures section, crystallization from a mixture of **1** and terpy affords compound **S2**, the structure of which was determined using X-ray crystallography. However, experimental and theoretical data indicate that **S2** is not the structure of the initial adduct between **1** and terpy, and is not relevant to the Pd-catalyzed fluorination reaction. Data suggest that the relevant structure is likely the pseudo-octahedral Pd(II) complex **5**:



When the reactivity of isolated **S2** was compared with a freshly prepared solution of **1** and terpy, it was found that **S2** is not chemically competent in the fluorination of aryl trifluoroborates with Selectfluor (yields determined by ^{19}F NMR spectroscopy vs 1-fluoro-3-nitrobenzene as internal standard):



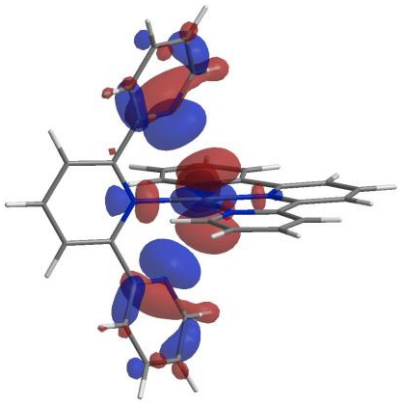
Additionally, **S2** does not react with Selectfluor to form Pd(III) complex **2**. The observed reactivity is summarized in Scheme S1, in which **S2** is a thermodynamically more stable product than **5**, but is not relevant in the catalytic fluorination reaction with Selectfluor:



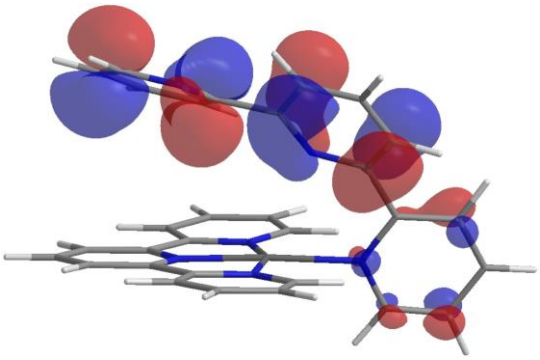
Scheme S1. Reactivity of bis-terpyridyl Pd(II) complexes **5** and **S2** with Selectfluor.

DFT calculations are consistent with the observed chemical reactivity difference between **5** and **S2** (see DFT Calculations section for details): the optimized structure of **5** displays a pseudo-octahedral geometry, in which the apical pyridyl ligands are rotated away from the *z*-axis to avoid interaction with the filled d_{z^2} orbital on Pd. The calculated HOMO is primarily of d_{z^2} parentage with respect to Pd, and antibonding with respect to the apical pyridyl ligands. Removal of one electron from this orbital via oxidation would be expected to give a distorted octahedral d^7 Pd(III) complex (e.g. **2**), as is indeed observed when **1** is treated with terpyridine and Selectfluor. The optimized structure of **S2** has a calculated HOMO which is primarily based on the π-system of the monodentate terpyridine ligand: this is consistent with the observation that **S2** is not oxidized to Pd(III) **2**. The calculations indicate that **S2** is thermodynamically favored by 2.3 kcal/mol as compared to **5**. Based on the observed reactivity, however, we believe that **S2** is not kinetically

accessible during the Pd-catalyzed fluorination reaction.



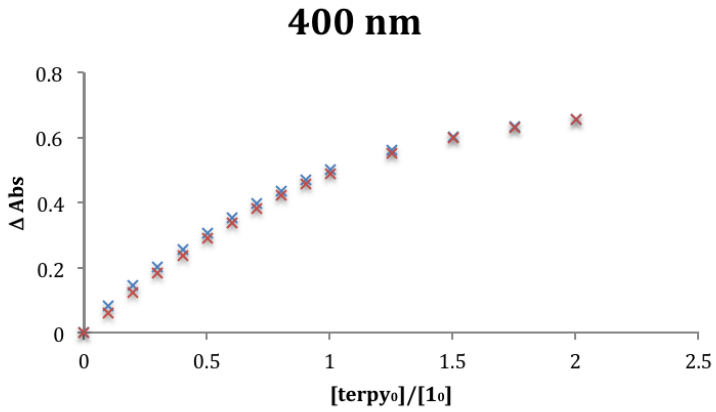
Calculated HOMO of **5**



Calculated HOMO of **S2**

Binding Constant Analysis

The equilibrium between **1** and **5** was probed experimentally using UV-vis spectroscopy. Exogenous terpy was added to a solution of **1** in DMF, and absorbance at 400 nm was measured. 400 nm was chosen based on the fact that neither **1** nor terpy display a significant absorption feature at this wavelength (see UV-vis data section), but the absorption value at 400 nm displayed a notable increase when terpy was added to **1**. A titration experiment was carried out, and the measured binding isotherm is shown below (the plot shows overlaid data from two separate experiments):



Fitting of the binding isotherm was performed using a 1:1 binding model between **1** and

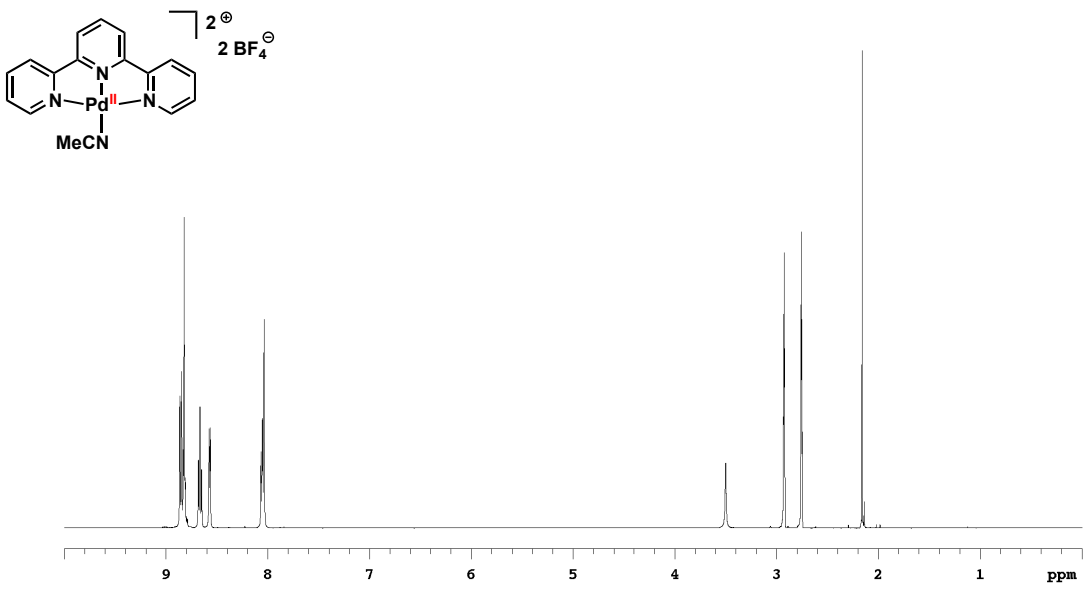
terpyridine,[8] which provided satisfactory results. The fitting gave an association constant (K_a) of 3×10^3 (± 19%). The output from the fitting program is given below, with K_a and the associated error analysis highlighted in red.

Results from 1:1 fitting

sum of squares (ss)	Standard error (SEy)	covariance of fit
0.001395689	0.007189728	0.001107889
Results for Ka	Results for other fitted parameters	
2711.11372	441.678802	432.3025342
%confidence interval on parameters (from asymptotic error):		
19.49414486	3.812721295	3.817393058

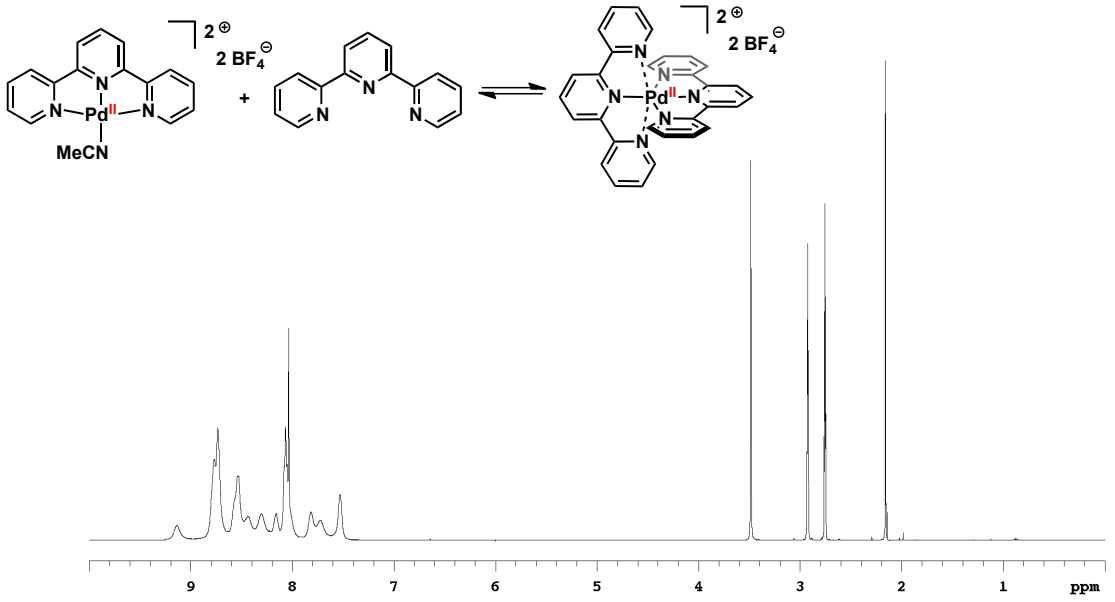
In-Situ ^{1}H NMR of Pd-Catalyzed Fluorination Reaction

The broad signals for the [Pd] catalyst observed during catalysis are also consistent with the catalyst resting state consisting of a rapid equilibrium involving **1** and **5**:

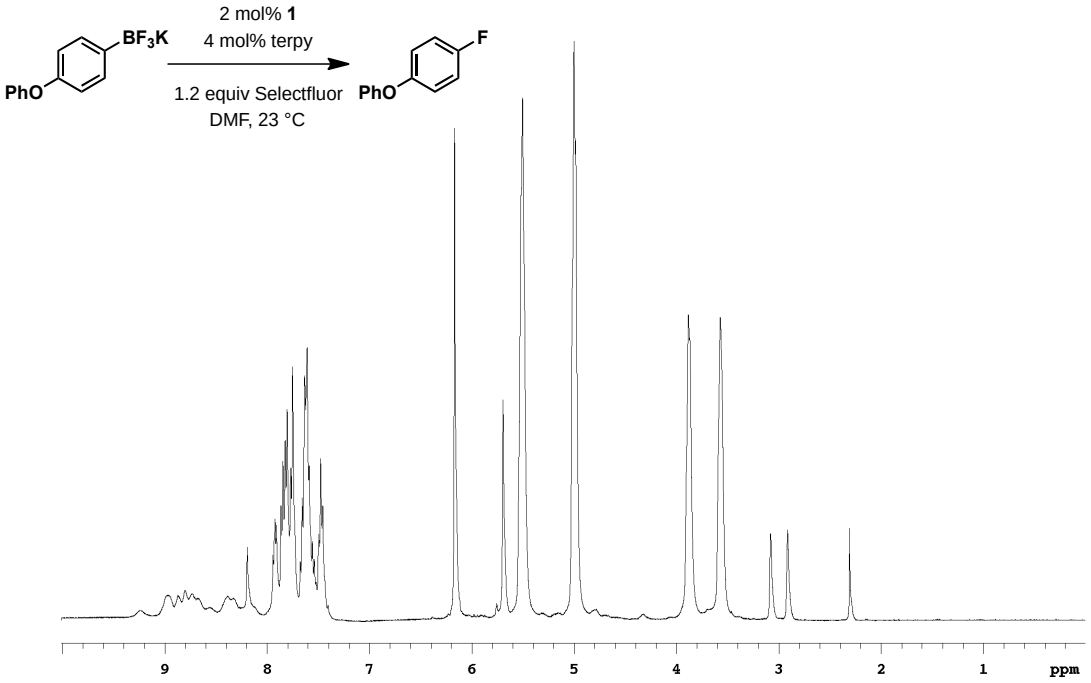


^{1}H NMR of **1**. DMF-d_7, 500 MHz, 23 °C

[8] Thordarson, P. *Chem. Soc. Rev.* **2011**, *40*, 1305.

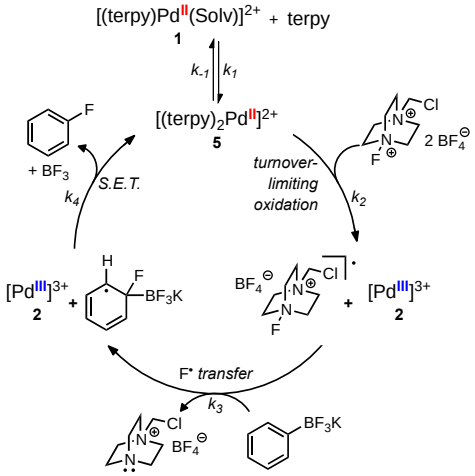


^{1}H NMR of **1** with added terpyridine. DMF-d_7, 500 MHz, 23 °C



^{1}H NMR of Pd-catalyzed fluorination reaction. DMF-d_7, 400 MHz, 23 °C

Derivation of the Rate Law for the Catalytic Reaction



A proposed mechanism for the Pd-catalyzed fluorination reaction (as depicted in Scheme 2) is shown above. Based on the kinetics data, oxidation of [Pd] by Selectfluor is turnover-limiting during catalysis. The observed saturation kinetics with respect to terpyridine, along with the measurement of a fast equilibrium between **5** and [**1** + terpy] (*vide supra*: binding constant analysis in Discussion of the Structure of **5**), supports a catalyst resting state consisting of an equilibrium between **1** and **5**. The mechanism shown above would result in zero-order dependence on the aryl trifluoroborate, first-order dependence on palladium, saturation behavior with respect to terpyridine, and first-order dependence on Selectfluor (rate law derivation given below):

$$\text{rate} = \frac{d[\text{ArF}]}{dt} = k_2[\text{Selectfluor}][\mathbf{5}]$$

Applying steady state approximation:

$$\frac{d[\mathbf{5}]}{dt} = 0 = k_1[\mathbf{1}][\text{terpy}] - k_{-1}[\mathbf{5}] - k_2[\text{Selectfluor}][\mathbf{5}]$$

$$= k_1([\text{Pd}]_0 - [\mathbf{5}])[\text{terpy}] - k_{-1}[\mathbf{5}] - k_2[\mathbf{5}][\text{Selectfluor}]$$

$$\left([\text{Pd}]_0 = \text{total concentration of Pd} = [\mathbf{1}] + [\mathbf{5}]\right)$$

$$k_1[\text{Pd}]_0[\text{terpy}] = k_1[\mathbf{5}][\text{terpy}] + k_{-1}[\mathbf{5}] + k_2[\mathbf{5}][\text{Selectfluor}]$$

$$k_1[\text{Pd}]_0[\text{terpy}] = [\mathbf{5}](k_1[\text{terpy}] + k_{-1} + k_2[\text{Selectfluor}])$$

$$[\mathbf{5}] = \frac{k_1[\text{Pd}]_0[\text{terpy}]}{k_{-1} + k_2[\text{Selectfluor}] + k_1[\text{terpy}]}$$

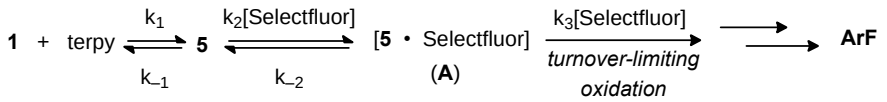
$$\text{rate} = \frac{k_1k_2[\text{Pd}]_0[\text{terpy}][\text{Selectfluor}]}{k_{-1} + k_2[\text{Selectfluor}] + k_1[\text{terpy}]}$$

if $k_{-1} + k_1[\text{terpy}] >> k_2[\text{Selectfluor}]$, then

$$\boxed{\text{rate} = \frac{k_1k_2[\text{Pd}][\text{Selectfluor}][\text{terpy}]}{k_{-1} + k_1[\text{terpy}]}}$$

Due to k_1/k_{-1} being a fast equilibrium, and k_2 being the rate of the turnover-limiting step, assuming $k_{-1} + k_1[\text{terpy}] >> k_2[\text{Selectfluor}]$ is reasonable, and consistent with the measured data.

The observation of a non-integer kinetic order for Selectfluor (1.4), along with the observation that oxidation of Pd(II) complex **5** to Pd(III) **2** does not occur via outer-sphere S.E.T. (see Electrochemical data section), suggests the formation of an initial adduct between **5** and Selectfluor. If an equilibrium involving such an adduct (**A**) is incorporated into the mechanism proposal outlined above, a rate law can be derived that is consistent with all measured data:



$$\text{rate} = \frac{d[\text{ArF}]}{dt} = k_3[\text{Selectfluor}][\mathbf{A}]$$

Applying steady state approximation for **A**:

$$\frac{d[\mathbf{A}]}{dt} = 0 = k_2[\mathbf{5}][\text{Selectfluor}] - k_{-2}[\mathbf{A}] - k_3[\text{Selectfluor}][\mathbf{A}]$$

$$[\mathbf{A}] = \frac{k_2[\mathbf{5}][\text{Selectfluor}]}{k_{-2} + k_3[\text{Selectfluor}]}$$

Applying steady state approximation for **5**:

$$\frac{d[\mathbf{5}]}{dt} = 0 = k_1[\mathbf{1}][\text{terpy}] - k_{-1}[\mathbf{5}] - k_2[\text{Selectfluor}][\mathbf{5}]$$

$$\left([\text{Pd}]_0 = \text{total concentration of Pd} = [\mathbf{1}] + [\mathbf{5}] \right)$$

$$[\mathbf{5}] = \frac{k_1[\text{Pd}]_0[\text{terpy}]}{k_{-1} + k_2[\text{Selectfluor}] + k_1[\text{terpy}]}$$

Incorporating [**5**] into [**A**]:

$$[\mathbf{A}] = \left(\frac{k_2[\text{Selectfluor}]}{\underbrace{k_{-2} + k_3[\text{Selectfluor}]}_{\approx k_{-2}}} \right) \bullet \left(\frac{k_1[\text{Pd}]_0[\text{terpy}]}{k_{-1} + k_2[\text{Selectfluor}] + k_1[\text{terpy}]} \right)$$

$$[\mathbf{A}] = \frac{k_1 k_2[\text{Pd}]_0[\text{terpy}][\text{Selectfluor}]}{k_{-1}k_{-2} + k_2 k_{-2}[\text{Selectfluor}] + k_1 k_{-2}[\text{terpy}]}$$

$$\boxed{\text{rate} = \frac{k_1 k_2 k_3[\text{Pd}]_0[\text{terpy}][\text{Selectfluor}]^2}{k_{-1}k_{-2} + k_2 k_{-2}[\text{Selectfluor}] + k_1 k_{-2}[\text{terpy}]}}$$

While the nature of the adduct between **5** and Selectfluor (**A**) is not known at this point, the data suggest that the interaction between **5** and Selectfluor that occurs prior to turnover-limiting oxidation is critical to the success of the Pd-catalyzed fluorination reaction.

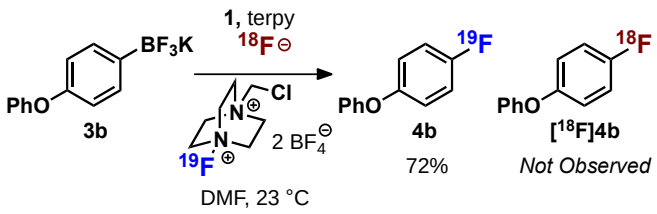
Isotopic Labeling Experiment

Radiochemistry General Methods and Procedures

No-carrier-added [^{18}F]fluoride was produced from water 97% enriched in ^{18}O (Sigma-Aldrich®) by the nuclear reaction ^{18}O(p,n)^{18}F using a Siemens Eclipse HP cyclotron and a silver-bodied target at MGH Athinoula A. Martinos Center for Biomedical Imaging. The produced [^{18}F]fluoride in water was transferred from the cyclotron target by helium push. In the analysis of the ^{18}F-labeled compounds, isotopically unmodified reference substances were used for identification. Radioactivity was measured in a Capintec, Inc. CRC-25PET ion chamber. *Solvents and reagents for radiochemical experiments:* Acetonitrile, extra dry, (AcroSeal®) was purchased from Acros® and used as received. *N*,*N*-dimethylformamide was distilled from 4Å molecular sieves and stored under inert atmosphere. Water was obtained from a Millipore Milli-Q Integral Water Purification System. 18-crown-6 was sublimed. Potassium carbonate (≥99.99%) was purchased from Sigma-Aldrich® and used as received.

[^{18}F]Fluoride solution obtained from a cyclotron was loaded onto a Macherey-Nagel SPE Chromafix 30-PS-HCO3 cartridge that had been previously washed with 2.0 mL of 5.0 mg/mL K_2CO_3 in Millipore Milli-Q water and then 20 mL of Millipore Milli-Q water. After loading, the cartridge was washed with 2 mL of Millipore Milli-Q water. [^{18}F]Fluoride was eluted with 2.0 mL of a 5.0 mg/mL K_2CO_3 in Millipore Milli-Q water solution. The solution was diluted with 8.0 mL of acetonitrile providing 10 mL of 4:1 MeCN:H_2O solution containing 1.0 mg/mL K_2CO_3. 1.0 mL of this solution was then put in a conical vial that had been washed with acetone and deionized water and dried at 150 °C prior to use. 0.50 mL of a stock solution containing 18-crown-6 (26.2 mg/mL MeCN) was then added. The solution was evaporated at 108 °C with a constant nitrogen gas stream. At dryness, 0.5 mL of acetonitrile was added and evaporated at 108 °C with a constant nitrogen gas stream. Another 0.5 mL of acetonitrile was added and evaporated at 108 °C with a constant nitrogen gas stream to leave a white precipitate around the bottom and sides of the vial. The vial was purged with nitrogen, and sealed with a cap fitted with a septum. 0.4 mL of *N*,*N*-dimethylformamide was added and the conical vial was sonicated for 30 seconds before the solution was taken up in a syringe.

Procedure for Labeling Experiment



A 4 mL vial was charged with aryl trifluoroborate **3b** (5.0 mg, 0.018 mmol, 1.0 equiv), Selectfluor (6.4 mg, 0.018 mmol, 1.0 equiv), Pd(II) complex **1** (2.5 mg, 4.5×10^{-3} mmol, 0.25

equiv) and terpy (2.1 mg, 9.1×10^{-3} mmol, 0.50 equiv), and sealed with a cap fitted with a septum. A DMF solution (0.4 mL) of [^{18}F]fluoride, prepared and dried as described above, was added to the vial via the septum. The mixture was allowed to stir for 15 minutes at 23 °C, and then a capillary tube was used to spot the solution on a silica gel TLC plate. The TLC plate was eluted with a 10% (v/v) mixture of Et_2O/pentane. The TLC plate was scanned with a Bioscan AR-2000 Radio TLC Imaging Scanner to determine [^{18}F]fluoride incorporation into the aryl fluoride product (**4b**), using an authentic sample of **4b** as a reference. The radio TLC scan is shown in Figure S2, and indicates no [^{18}F]fluoride incorporation into the organic product:

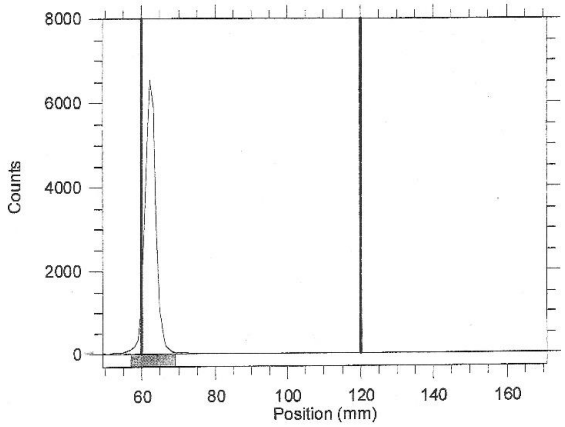


Figure S2. Radio TLC scan for the isotopic labeling experiment. The position at 60 mm corresponds to the baseline of the TLC plate, and no [^{18}F] incorporation into aryl fluoride **4b** is observed.

The radioactivity was allowed to decay over the course of 3 days, and then 1-fluoro-3-nitrobenzene (5.0 μL, 4.7×10^{-5} mol) was added to the vial as internal standard. The mixture was transferred to an NMR tube, and then the yield of aryl fluoride **4b** was determined to be 0.013 mmol (72%) via ^{19}F NMR spectroscopy, integrating against the internal standard peak at –112 ppm.

The result of the isotopic labeling experiment suggests that C–F bond formation in the Pd-catalyzed fluorination reaction does not occur via nucleophilic attack by fluoride.

DFT Calculations

Density functional theory (DFT) calculations were performed using Gaussian09[9] at the Odyssey cluster at Harvard University. Geometry optimizations were carried out using the atomic coordinates from the crystal structures of **2** and **S2** as starting points. The unrestricted wave function was used for ground state optimizations. BS I includes SDD quasirelativistic pseudopotentials on Pd (MWB28) with basis sets (Pd: (8s7p6d)/[6s5p3d][10]) extended by polarization functions (Pd: f, 1.472[11]) and 6-31G(d,p)[12] on H, C, N. All geometry optimizations were performed using the M06 functional with the BS I basis set. Molecular orbitals were generated using an isosurface value of 0.03 with M06/BS I. Atomic contributions to the frontier molecular orbitals (Mulliken contribution) were calculated using Chemissian.[13] Images were generated using Chem3D or GaussView5.[14]

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[9] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; , J. A. Montgomery, J.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd; J. J. Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Normand; J. Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Cossi, J. M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adam, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels; A. D. Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski; J. Fox, D. J. *Gaussian 09, Revision A.02*; Gaussian, Inc.: Wallingford CT, 2009.

[10] (a) Andrae, D.; Häussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123-141. (b) Andrae, D.; Häussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1991**, *78*, 247-266.

[11] Ehlers, A. W.; Böhme, M.; Dapprich, S.; Gobbi, A.; Höllwarth, A.; Jonas, V.; Köhler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking, G. *Chem. Phys. Lett*. **1993**, *208*, 111-114.

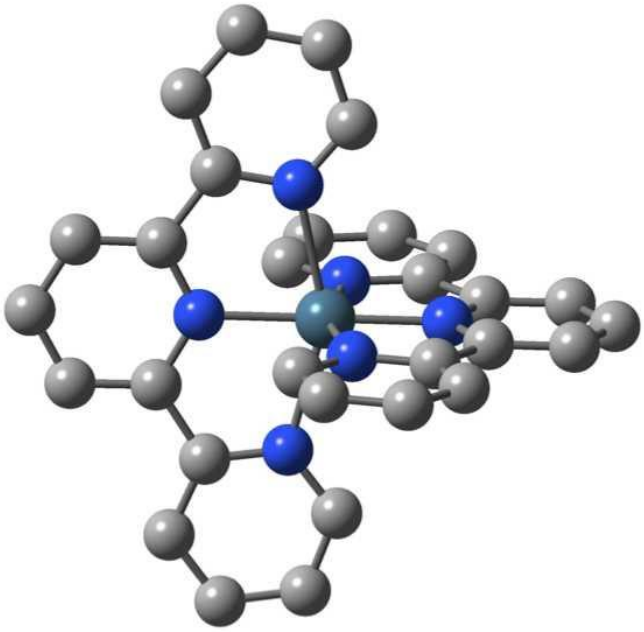
[12] Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213-222.

[13] *Chemissian*, Version 3.3; © Skripnikov Leonid 2005-2012; www.chemissian.com

[14] Dennington, R., II; Keith, T. A.; Millam, J. M. *GaussView*, Version 5.0.8; Semichem, Inc.

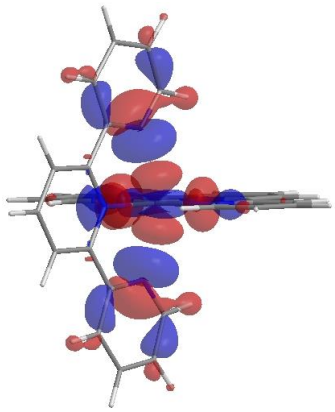
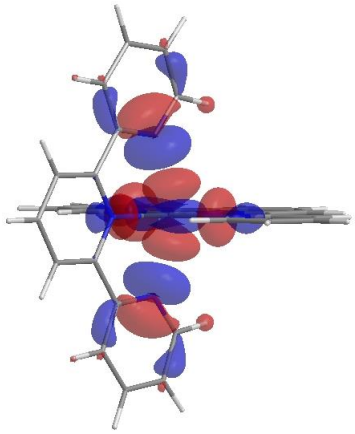
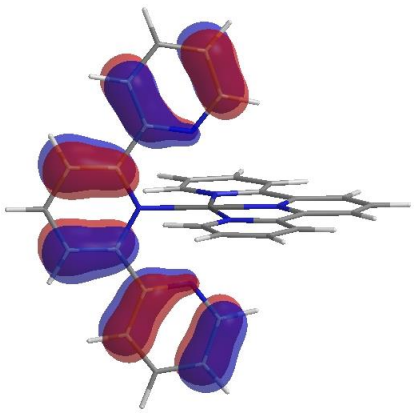
The optimized structure of 2 with M06/BS I and Cartesian coordinates (Å)

Atom	X	Y	Z
C	-0.3859153	3.2601299	-0.0029228
C	-0.3857447	-3.2601528	0.0019591
C	0.0749534	4.5719638	-0.0034432
C	2.3121468	-3.6971685	0.0016506
C	0.4476814	0.0021814	3.0558466
C	4.0094389	-1.2029189	0.0003614
C	4.0093664	1.2031441	-0.0008604
C	-2.6877253	-0.0006931	-1.192966
C	0.0689162	-0.0031507	-4.3937792
C	-4.0783461	0.0006164	1.2113523
C	-1.2825659	0.0027586	4.7051837
C	2.617441	1.1889604	-0.000864
C	-4.7661917	-0.0000914	0.0007202
C	-2.6873867	0.0006932	1.1938355
C	-2.2215526	0.0020336	3.6762028
C	1.7840977	-2.4094761	0.0011341
C	4.7035311	0.0001317	-0.0002461
C	0.0701654	0.0028601	4.3938717
C	-1.7896499	-0.0014654	-2.3576439
C	2.3119621	3.6972918	-0.0021118
C	1.7839918	2.4095668	-0.0016692
C	-2.2226056	-0.0022002	-3.6754755
C	-1.7889781	0.0014154	2.3582497
C	-1.2839048	-0.0030426	-4.7047146
C	2.617507	-1.1888313	0.0004109
C	0.075195	-4.5719595	0.0025213
C	1.4467682	-4.7876582	0.0023481
C	-4.0786848	-0.0007564	-1.210108
C	0.4468136	-0.0023419	-3.0558676
C	1.4465141	4.7877305	-0.0029804
N	1.9655339	0.0000444	-0.0001979
N	-0.454182	0.0014689	2.0713335
N	0.4455376	2.2196481	-0.0020462
N	-0.4547851	-0.0015077	-2.0711077
N	-2.0544249	0.0000673	0.0003476
N	0.4456386	-2.219611	0.0012816
Pd	-0.078421	0.0000568	0.00007
H	-1.4519024	3.035544	-0.0032291
H	-1.451744	-3.0356108	0.0020361
H	-0.6289514	5.398267	-0.0041901
H	3.3848868	-3.863958	0.0015167
H	1.4944928	0.0022054	2.7600832

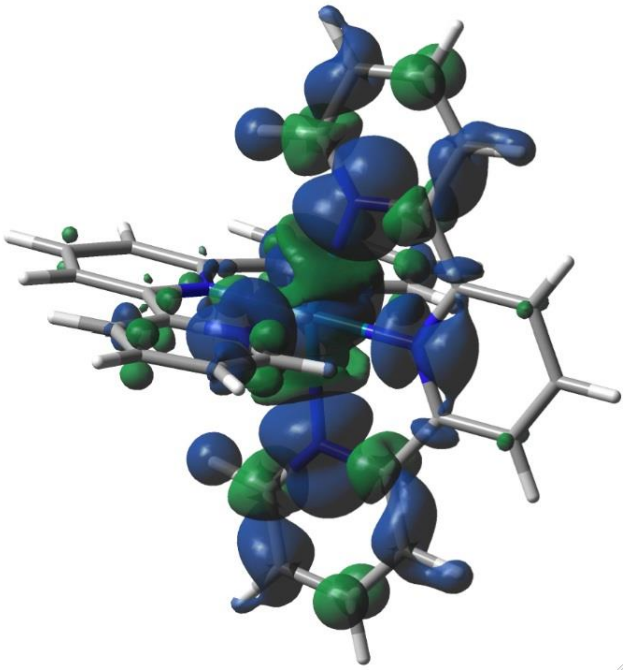


H	4.5528592	-2.1421546	0.0008089
H	4.552729	2.1424121	-0.0013659
H	0.8289274	-0.0038667	-5.1687552
H	-4.6257985	0.0011238	2.1490569
H	-1.6102158	0.0032461	5.7410615
H	-5.8526973	-0.0001385	0.0008748
H	-3.2824799	0.0019567	3.9091442
H	5.789947	0.0001609	-0.0002564
H	0.8303937	0.0034749	5.1686352
H	3.3846921	3.8641521	-0.0017851
H	-3.2835994	-0.0021268	-3.908108
H	-1.6118354	-0.0036112	-5.7405035
H	-0.6286718	-5.3982962	0.0030784
H	1.8463331	-5.7979485	0.0027505
H	-4.6263964	-0.0013346	-2.1476614
H	1.4937014	-0.0023422	-2.7603681
H	1.846039	5.798039	-0.0032914

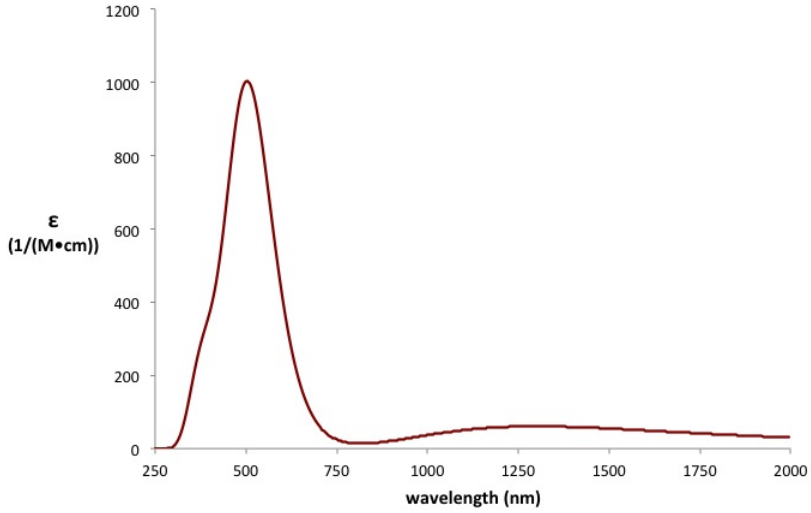
Table S4. Selected Frontier MOs for 2, with Atomic Contributions

MO # **(Energy, eV)**	**MO** **(isosurface value 0.03)**	**Atomic** **Contributions**
α HOMO (130) (-15.003)		Pd: 38% N(axial): 32% N(equitorial): 13%
β LUMO (130) (-12.239)		Pd: 52% N(axial): 26% N(equitorial): 12%
α HOMO–1 (129) (-15.408)		C: 98% N: 2%

Spin Density Plot for 2



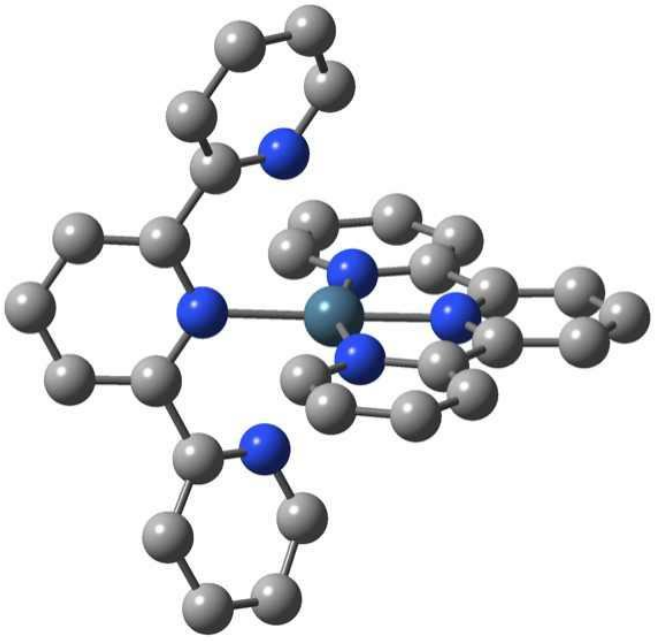
Calculated UV-vis/NIR spectrum for 2



The simulated UV-vis/NIR spectrum reproduces the characteristic absorption features observed for **2**: the predicted absorbances at 505 nm ($\varepsilon = 1.00 \times 10^3$ M^{-1} cm^{-1}) and 1300 nm ($\varepsilon = 60.8$ M^{-1} cm^{-1}) correspond to the experimental values of 419 nm ($\varepsilon = 1.52 \times 10^3$ M^{-1} cm^{-1}) and 1002 nm ($\varepsilon = 95.9$ M^{-1} cm^{-1}); see UV-vis Data section for the measured spectrum of **2**.

The optimized structure of 5 with M06/BS I and Cartesian coordinates (Å)

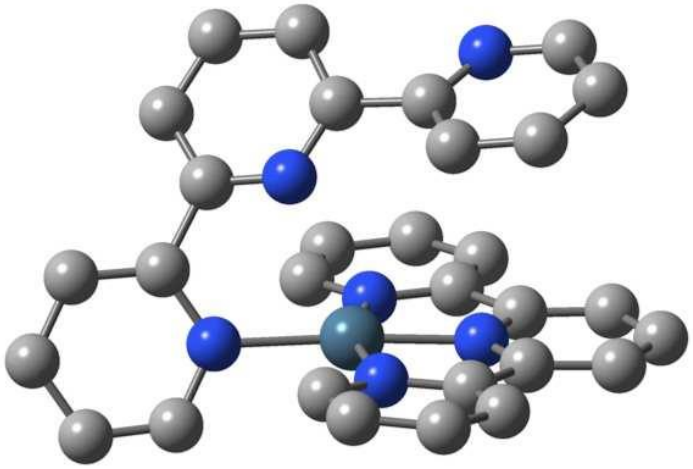
Atom	X	Y	Z
C	0.6367384	3.5915343	-0.5571764
C	-0.4092436	-3.6275313	-0.8690596
C	0.2489311	4.7901551	0.0341997
C	-2.9132926	-3.1896287	0.0994121
C	0.438609	0.0247059	-3.0541408
C	-4.0304378	-0.6201965	-0.8954269
C	-3.6902368	1.7391194	-0.8116021
C	2.3998737	-0.3474722	1.7951073
C	-1.0797925	-0.099027	4.1696253
C	4.3454509	-0.4691316	-0.1732299
C	2.5043847	-0.1402174	-4.2449078
C	-2.3459085	1.5158806	-0.5204391
C	4.7009456	-0.5422825	1.1693875
C	3.0003728	-0.3324553	-0.5031404
C	3.1630231	-0.253179	-3.0241812
C	-2.1396403	-2.1789349	-0.4724075
C	-4.54014	0.6630501	-1.0076797
C	1.1244777	0.0001091	-4.2630157
C	1.2325406	-0.2623459	2.6873673
C	-1.9239596	3.8301277	0.3285001
C	-1.4470976	2.6733698	-0.2897865
C	1.3046114	-0.3290338	4.0706598
C	2.4218969	-0.2240583	-1.8518804
C	0.1360343	-0.2464523	4.8210575
C	-2.6794525	-0.8040779	-0.6067273
C	-1.108897	-4.7021617	-0.3275453
C	-2.3830757	-4.47246	0.172962
C	3.7325778	-0.4805648	2.167514
C	-1.0903819	-0.0352949	2.7821991
C	-1.0565325	4.9041703	0.4914246
N	-1.849639	0.255564	-0.4426617
N	1.0687017	-0.0843372	-1.886924
N	-0.1838288	2.5546103	-0.717257
N	0.0297283	-0.1136408	2.0593275
N	2.0885199	-0.2821511	0.4863751
N	-0.9028404	-2.3920202	-0.9398719
Pd	0.2035015	-0.0495035	0.0056335
H	1.6535658	3.461162	-0.9289463
H	0.5937563	-3.7681855	-1.2720815
H	0.9552576	5.6086616	0.1324626
H	-3.9033526	-2.9790151	0.4953752
H	-0.6415445	0.1346014	-3.0078707



H	-4.6620699	-1.4867707	-1.0644232
H	-4.0519772	2.757396	-0.9140718
H	-2.0129445	-0.0327262	4.7193608
H	5.1068262	-0.515981	-0.9454747
H	3.069808	-0.1614733	-5.1719583
H	5.7469411	-0.6463543	1.4426218
H	4.2428818	-0.3633042	-2.9926673
H	-5.5852825	0.8231095	-1.2569854
H	0.5773716	0.0904912	-5.1956851
H	-2.9455756	3.8894489	0.6942778
H	2.264378	-0.4483654	4.5645762
H	0.1800991	-0.2989152	5.9048353
H	-0.6618357	-5.6911054	-0.3003971
H	-2.9596643	-5.2797221	0.6157613
H	4.0195175	-0.5336568	3.2130481
H	-2.0163403	0.0801182	2.2240089
H	-1.3996492	5.8172747	0.9697538

The optimized structure of S2 with M06/BS I and Cartesian coordinates (Å)

Symbol	X	Y	Z
C	-3.0261131	0.1805551	2.4284873
C	-3.8334569	-0.949817	2.4004544
C	-3.2215828	-2.1949354	2.2704261
N	-1.9038685	-2.3572554	2.1689944
C	-1.1329236	-1.2637255	2.1970498
C	0.3259579	-1.502365	2.1077504
C	0.8847812	-2.6918256	2.5880434
C	2.2545495	-2.8709977	2.4863268
C	3.0283277	-1.8862164	1.8771136
C	2.3846471	-0.7471392	1.3987057
C	3.113317	0.2704353	0.6093542
C	4.4474228	0.5886391	0.8588966
C	5.1010645	1.5135713	0.0587764
C	4.411195	2.1084318	-0.9929591
C	3.0872071	1.7606851	-1.1910177
C	1.5288533	-2.1704033	-1.7209617
C	1.4197215	-3.4673626	-2.2058719
C	0.1625667	-3.9545616	-2.5313733
C	-0.948842	-3.1339088	-2.3669356
C	-0.7779646	-1.8465217	-1.8821727
C	-1.8780224	-0.8910173	-1.6836664
C	-3.2269261	-1.0965527	-1.9522849
C	-4.1194287	-0.0547979	-1.7213739
C	-3.6767226	1.1628254	-1.2140184
C	-2.3220023	1.3192866	-0.942645
C	-1.6651572	2.4935901	-0.3484956
C	-2.3400083	3.6362341	0.0538
C	-1.633575	4.6702745	0.6602766
C	-0.2678218	4.5317921	0.8607958
C	0.3548729	3.3654137	0.4341539
C	-1.6486188	0.0284051	2.3210866
N	1.0678012	-0.5500749	1.5345102
N	2.4483416	0.8697158	-0.4083708
N	0.4641694	-1.3797153	-1.5634779
N	-1.4819711	0.3003693	-1.20075
N	-0.3175022	2.379032	-0.1646444
Pd	0.4139481	0.5371455	-0.7719112
H	-3.4646519	1.1676134	2.5629737
H	-4.9122779	-0.877125	2.5018326



H	-3.8220465	-3.1037632	2.2551148
H	0.2353115	-3.4408131	3.0302497
H	2.7206851	-3.7765498	2.8647792
H	4.0984033	-2.0241959	1.7465657
H	4.9563801	0.1257718	1.699472
H	6.1377759	1.7714788	0.2562439
H	4.8850945	2.8290519	-1.6512434
H	2.5031833	2.1946891	-2.0002319
H	2.4921938	-1.7421964	-1.456609
H	2.3113092	-4.0738168	-2.325989
H	0.0429813	-4.9637552	-2.9144523
H	-1.940365	-3.4988595	-2.6170573
H	-3.5808912	-2.0456275	-2.3422987
H	-5.1744823	-0.1943361	-1.9382572
H	-4.3813811	1.9684244	-1.0330696
H	-3.4119013	3.7223836	-0.0979128
H	-2.1509459	5.570996	0.9776006
H	0.3163635	5.30986	1.3409926
H	1.4210479	3.2084031	0.5762145
H	-0.9741022	0.8812221	2.3628366

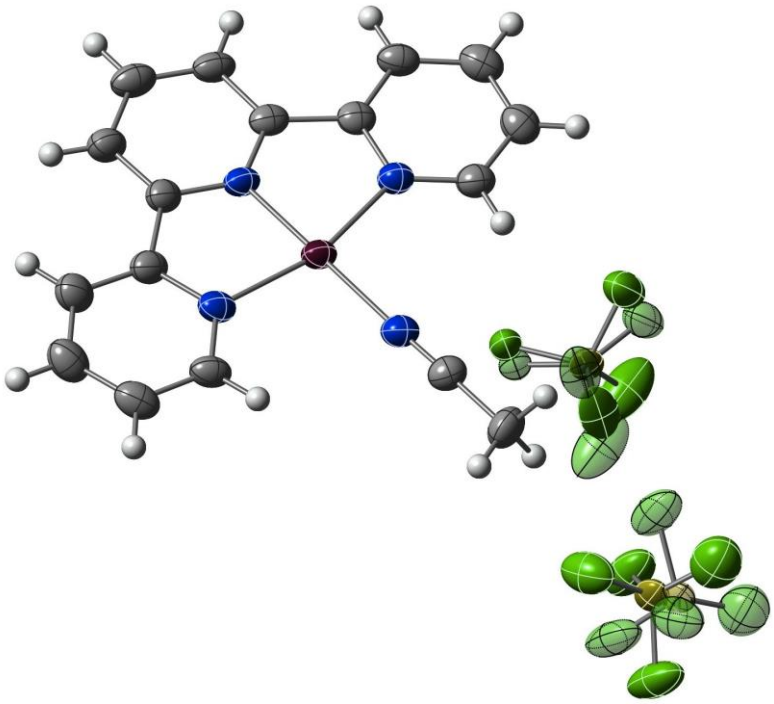
X-ray Crystallographic Analysis

[(terpy)Pd(MeCN)][BF_4]$_2$ (1) (CCDC 935776)

Experimental

Compound **1** was crystallized from MeCN/Et_2O as orange prisms. A crystal was mounted on a nylon loop using Paratone-N oil, and transferred to a Bruker APEX II CCD diffractometer (MoK_α radiation, λ=0.71073 Å) equipped with an Oxford Cryosystems nitrogen flow apparatus. The sample was held at 100 K during the experiment. The collection method involved 0.5° scans in ω at 28° in 2θ. Data integration down to 0.82 Å resolution was carried out using SAINT V7.46 A (Bruker diffractometer, 2009) with reflection spot size optimisation. Absorption corrections were made with the program SADABS (Bruker diffractometer, 2009). The structure was solved by the direct methods

procedure and refined by least-squares methods again F_2 using SHELXS-97 and SHELXL-97 (Sheldrick, 2008). Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were allowed to ride on the respective atoms. Restraints on bond lengths and constraints of the atomic displacement parameters on each pair of disorder fragments (SADI and EADP instructions of SHELXL97), as well as the restraints of the atomic displacement parameters (SIMU/DELU instructions of SHELXL97) if necessary, have been applied for the disorder refinement. Crystal data as well as details of data collection and refinement are summarized in Table S5. Graphics were produced using the CystalMaker 8.6 software program (©1994-2012 CrystalMaker Software Ltd.)



X-ray structure of **1**. Thermal ellipsoids are drawn at the 50% probability level; the disorder model is depicted using transparent ellipsoids.

Table S5. Experimental Details

	Compound **1**
Crystal data	
Chemical formula	$C_{17}H_{14}B_2F_8N_4Pd$
M_r	554.34
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100

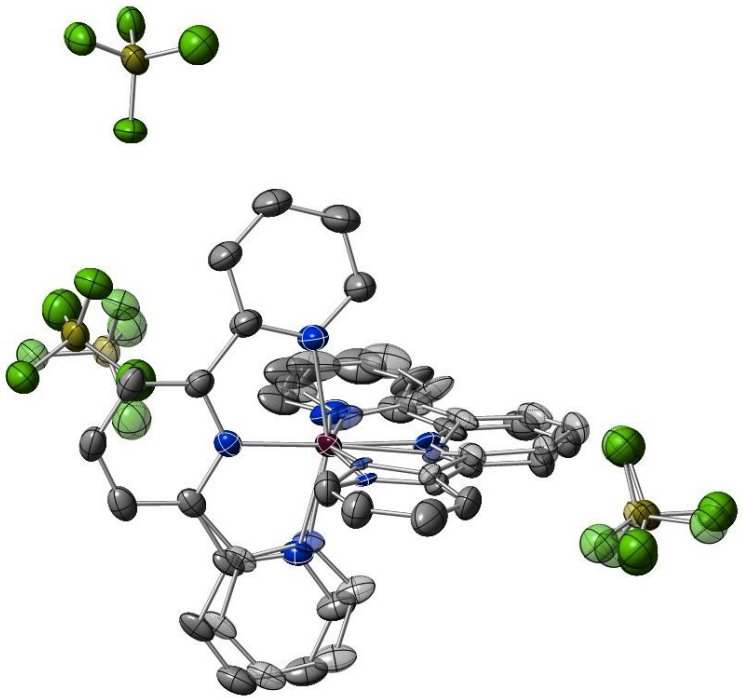
a, *b*, *c* (Å)	13.490 (4), 11.504 (3), 13.834 (4)
β (°)	113.793 (4)
V (Å^3)	1964.4 (10)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	1.03
Crystal size (mm)	0.30 × 0.25 × 0.20
Data collection	
Diffractometer	CCD area detector diffractometer
Absorption correction	Multi-scan *SADABS* (Sheldrick, 2009)
T_{min}, T_{max}	0.747, 0.820
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	15857, 3717, 3105
R_{int}	0.039
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.610
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.050, 0.140, 1.05
No. of reflections	3717
No. of parameters	312
No. of restraints	10
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.26, -1.03

Computer programs: *APEX2* v2009.3.0 (Bruker-AXS, 2009), *SAINT* 7.46A (Bruker-AXS, 2009), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008), Bruker *SHELXTL*.

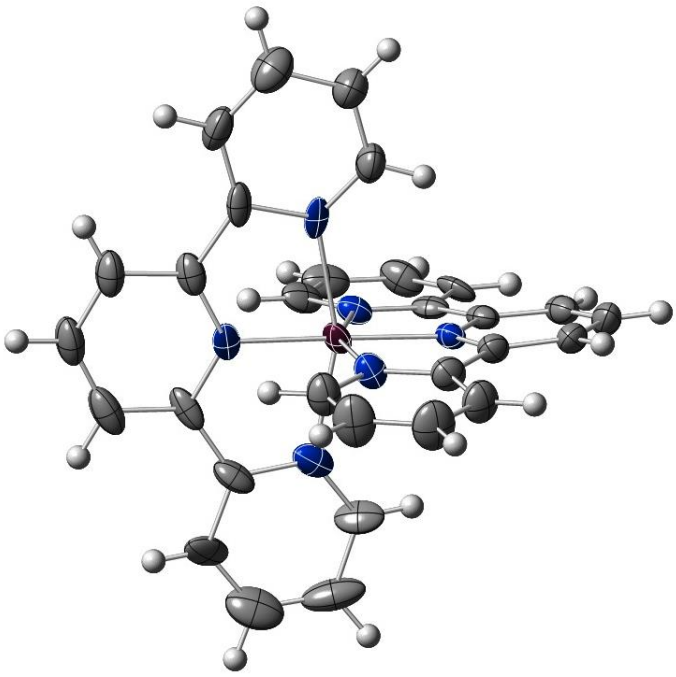
$[(terpy)_2Pd][BF_4]_3$ (2) (CCDC 935777)

Experimental

Compound **2** was crystallized from $MeCN/Et_2O$ as red needles. A crystal was mounted on a nylon loop using Paratone-N oil, and transferred to a Bruker APEX II CCD diffractometer ($Mo_{K\alpha}$ radiation, λ=0.71073 Å) equipped with an Oxford Cryosystems nitrogen flow apparatus. The sample was held at 100 K during the experiment. The collection method involved 0.5° scans in ω at 28° in 2θ. Data integration down to 0.82 Å resolution was carried out using SAINT V7.46 A (Bruker diffractometer, 2009) with reflection spot size optimisation. Absorption corrections were made with the program SADABS (Bruker diffractometer, 2009). The structure was solved by the direct methods procedure and refined by least-squares methods again F_2 using SHELXS-97 and SHELXL-97 (Sheldrick, 2008). Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were allowed to ride on the respective atoms. Restraints on bond lengths and constraints of the atomic displacement parameters on each pair of disorder fragments (SADI and EADP instructions of SHELXL97), as well as the restraints of the atomic displacement parameters (SIMU/DELU instructions of SHELXL97) if necessary, have been applied for the disorder refinement. A solvent mask was implemented in the Olex 2 software due to a non-integer number of highly disordered MeCN solvent molecules. Crystal data as well as details of data collection and refinement are summarized in Table S6. Graphics were produced using the CystalMaker 8.6 software program (©1994-2012 CrystalMaker Software Ltd.)



X-ray structure of **2**. Thermal ellipsoids are drawn at the 50% probability level; the disorder model is depicted using transparent ellipsoids. H-atoms have been omitted for clarity.



Structure of the Pd(III) cation of **2**, with disorder omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

Table S6. Experimental Details

	Compound **2**
Crystal data	
Chemical formula	$C_{30}H_{22}B_3F_{12}N_6Pd$
M_r	833.37
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	100
a, *b*, *c* (Å)	15.0771 (6), 17.6720 (7), 15.6002 (6)
β (°)	99.830 (1)
V (Å^3)	4095.5 (3)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	0.54
Crystal size (mm)	1.0 × 0.43 × 0.29

Data collection	
Diffractometer	CCD area detector diffractometer
Absorption correction	Numerical *SADABS* (Sheldrick, 2009)
T_{min}, T_{max}	0.587, 0.862
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7791, 7791, 6585
R_{int}	0.0000
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.611
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.077, 0.209, 1.04
No. of reflections	7791
No. of parameters	513
No. of restraints	72
H-atom treatment	H-atom parameters constrained
	$w = 1/[\sigma^2(F_o^2) + (0.096P)^2 + 29.5516P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	3.06, -2.05

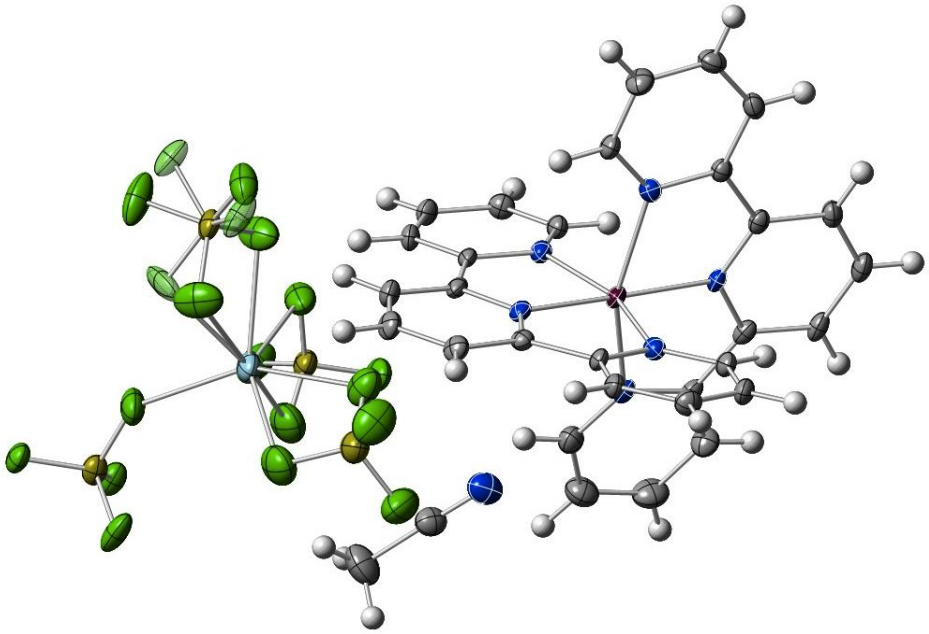
Computer programs: *APEX2* v2009.3.0 (Bruker-AXS, 2009), *SAINT* 7.46A (Bruker-AXS, 2009), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008), Bruker *SHELXTL*.

$[(terpy)_2Pd][BF_4]_3$•$[NaBF_4]$ (S1) (CCDC 935778)

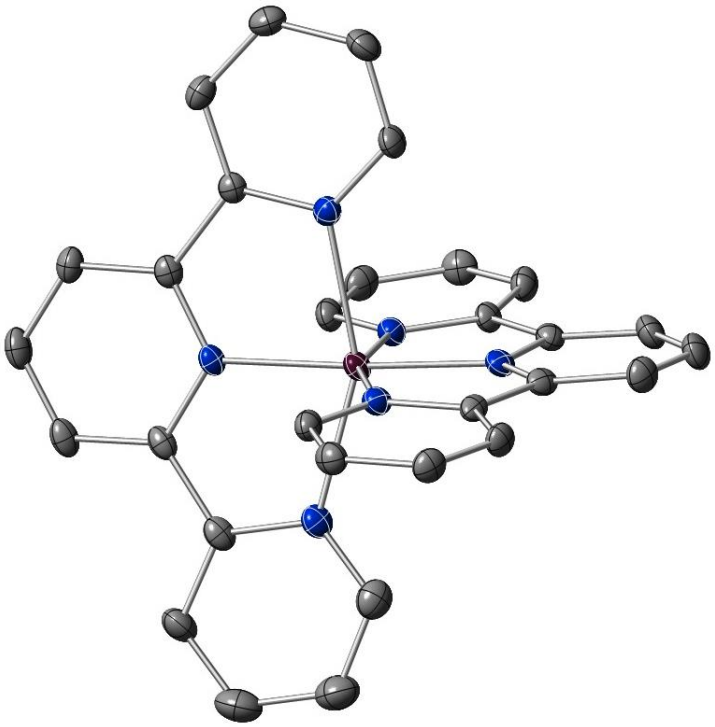
Experimental

Compound **S1** was crystallized from MeCN/Et_2O as red plates. A crystal was mounted on a nylon loop using Paratone-N oil, and transferred to a Bruker APEX II CCD diffractometer ($Mo_{K\alpha}$ radiation, λ=0.71073 Å) equipped with an Oxford Cryosystems nitrogen flow apparatus. The sample was held at 100 K during the experiment. The collection method involved 0.5° scans in ω at 28° in 2θ. Data integration down to 0.82 Å resolution was carried out using SAINT V7.46 A (Bruker diffractometer, 2009) with reflection spot size optimisation. Absorption corrections were made with the program SADABS (Bruker diffractometer, 2009). The structure was solved by the direct methods procedure

and refined by least-squares methods again F_2 using SHELXS-97 and SHELXL-97 (Sheldrick, 2008). Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were allowed to ride on the respective atoms. Restraints on bond lengths and constraints of the atomic displacement parameters on each pair of disorder fragments (SADI and EADP instructions of SHELXL97), as well as the restraints of the atomic displacement parameters (SIMU/DELU instructions of SHELXL97) if necessary, have been applied for the disorder refinement. Crystal data as well as details of data collection and refinement are summarized in Table S7. Graphics were produced using the CystalMaker 8.6 software program (©1994-2012 CrystalMaker Software Ltd.)



X-ray structure of **S1**. Thermal ellipsoids are drawn at the 50% probability level; the disorder model is depicted using transparent ellipsoids.



Structure of the Pd(III) cation of **S1**, with H-atoms omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

Table S7. Experimental Details

	Compound **S1**
Crystal data	
Chemical formula	$C_{32}H_{25}B_4F_{16}N_7NaPd$
M_r	984.22
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	100
a, *b*, *c* (Å)	9.7835 (14), 12.3525 (17), 16.842 (2)
α, β, γ (°)	104.147 (2), 103.269 (2), 100.107 (2)
V (Å^3)	1862.2 (4)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	0.63

Crystal size (mm)	0.28 × 0.16 × 0.12
Data collection	
Diffractometer	CCD area detector diffractometer
Absorption correction	Numerical *SADABS* (Sheldrick, 2009)
T_{min}, T_{max}	0.844, 0.928
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	21336, 7078, 6045
R_{int}	0.044
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.611
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.046, 0.117, 1.06
No. of reflections	7078
No. of parameters	573
No. of restraints	0
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.32, -1.37

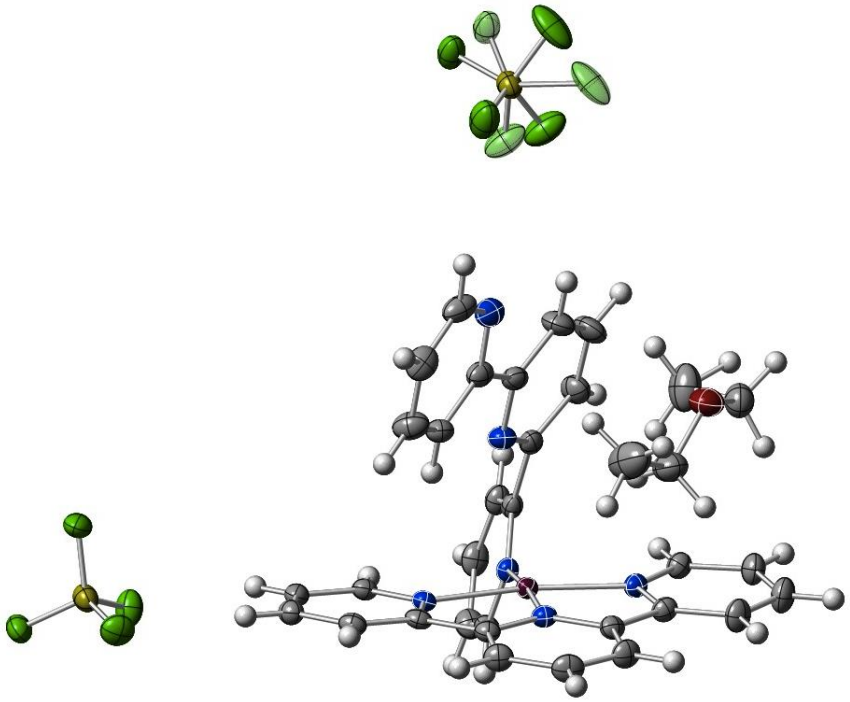
Computer programs: *APEX2* v2009.3.0 (Bruker-AXS, 2009), *SAINT* 7.46A (Bruker-AXS, 2009), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008), Bruker *SHELXTL*.

$[(terpy)_2Pd][BF_4]_2$ (S2) (CCDC 935779)

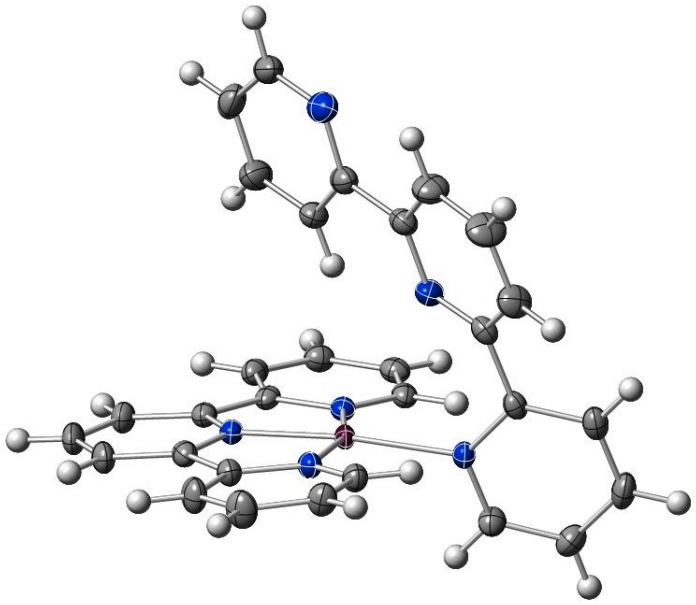
Experimental

Compound **S2** was crystallized from MeCN/Et_2O as yellow prisms. A crystal was mounted on a nylon loop using Paratone-N oil, and transferred to a Bruker APEX II CCD diffractometer (Mo$K\alpha$ radiation, λ=0.71073 Å) equipped with an Oxford Cryosystems nitrogen flow apparatus. The sample was held at 100 K during the experiment. The collection method involved 0.5° scans in ω at 28° in 2θ. Data integration down to 0.82 Å resolution was carried out using SAINT V7.46 A (Bruker diffractometer, 2009) with reflection spot size optimisation. Absorption corrections were made with the program SADABS (Bruker diffractometer, 2009). The structure was solved by the direct methods procedure and refined by least-squares methods again F^2 using SHELXS-97 and SHELXL-97

(Sheldrick, 2008). Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were allowed to ride on the respective atoms. The crystal exhibits pseudo-merohedral twinning, but satisfactory refinement was achieved by applying the twin law that was found by using Platon/TwinRotMat. Restraints on bond lengths and constraints of the atomic displacement parameters on each pair of disorder fragments (SADI and EADP instructions of SHELXL97), as well as the restraints of the atomic displacement parameters (SIMU/DELU instructions of SHELXL97) if necessary, have been applied for the disorder refinement. Crystal data as well as details of data collection and refinement are summarized in Table S8. Graphics were produced using the CystalMaker 8.6 software program (©1994-2012 CrystalMaker Software Ltd.)



X-ray structure of **S2**. Thermal ellipsoids are drawn at the 50% probability level; the disorder model is depicted using transparent ellipsoids.



Structure of the Pd(II) cation of **S2**. Thermal ellipsoids are drawn at the 50% probability level.

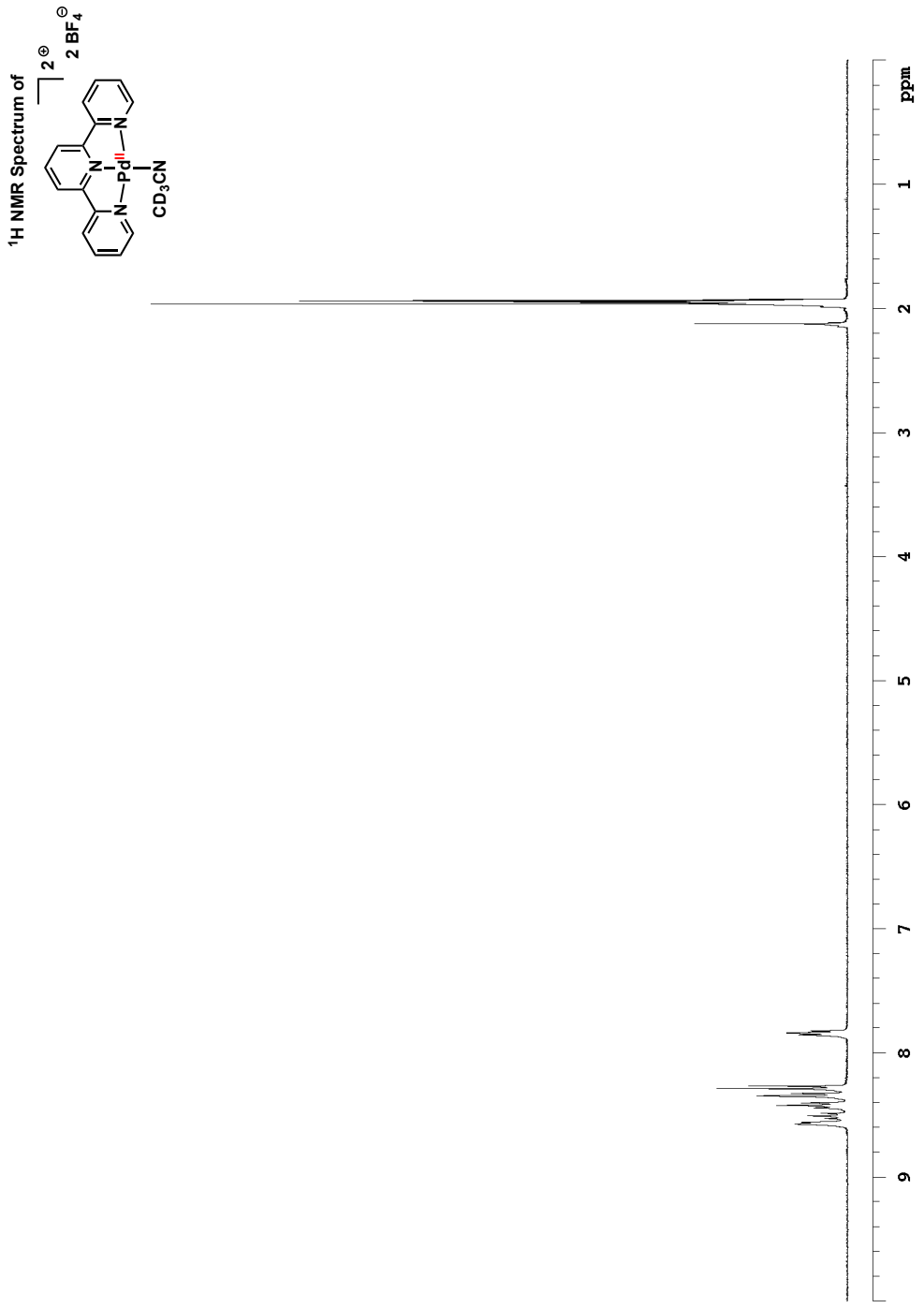
Table S8. Experimental Details

	Compound **S2**
Crystal data	
Chemical formula	$C_{34}H_{32}B_2F_8N_6OPd$
M_r	820.68
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	100
a, *b*, *c* (Å)	12.1099 (7), 12.6815 (8), 20.7558 (13)
β (°)	90.080 (1)
V (Å^3)	3187.5 (3)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.67
Crystal size (mm)	0.49 × 0.39 × 0.33
Data collection	
Diffractometer	CCD area detector

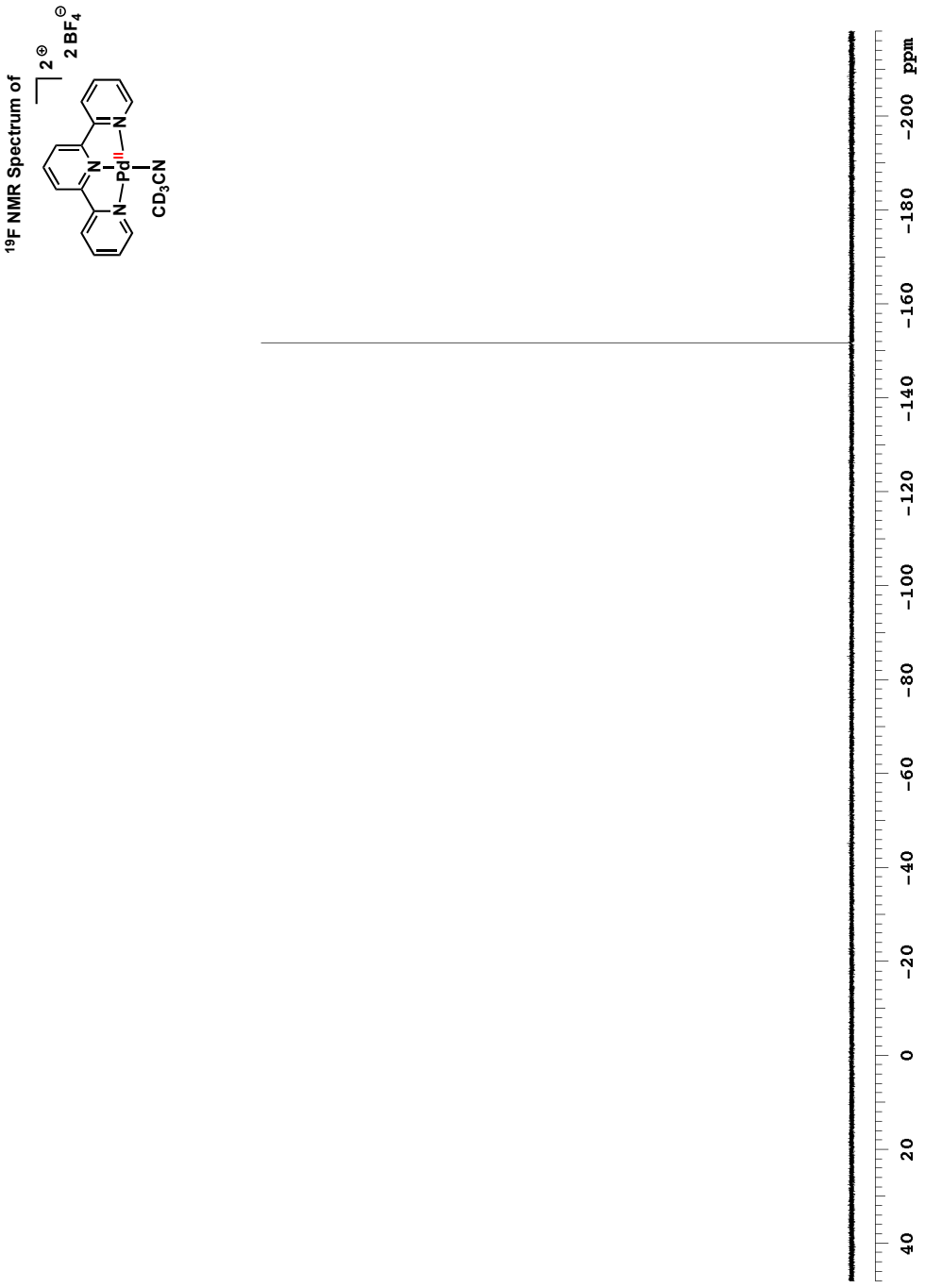
	diffractometer
Absorption correction	Multi-scan *SADABS* (Sheldrick, 2009)
T_{min}, T_{max}	0.735, 0.809
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	49913, 7077, 6487
R_{int}	0.032
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.643
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.024, 0.060, 1.03
No. of reflections	7077
No. of parameters	470
No. of restraints	6
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.52, -0.55

Computer programs: *APEX2* v2009.3.0 (Bruker-AXS, 2009), *SAINT* 7.46A (Bruker-AXS, 2009), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008), Bruker *SHELXTL*.

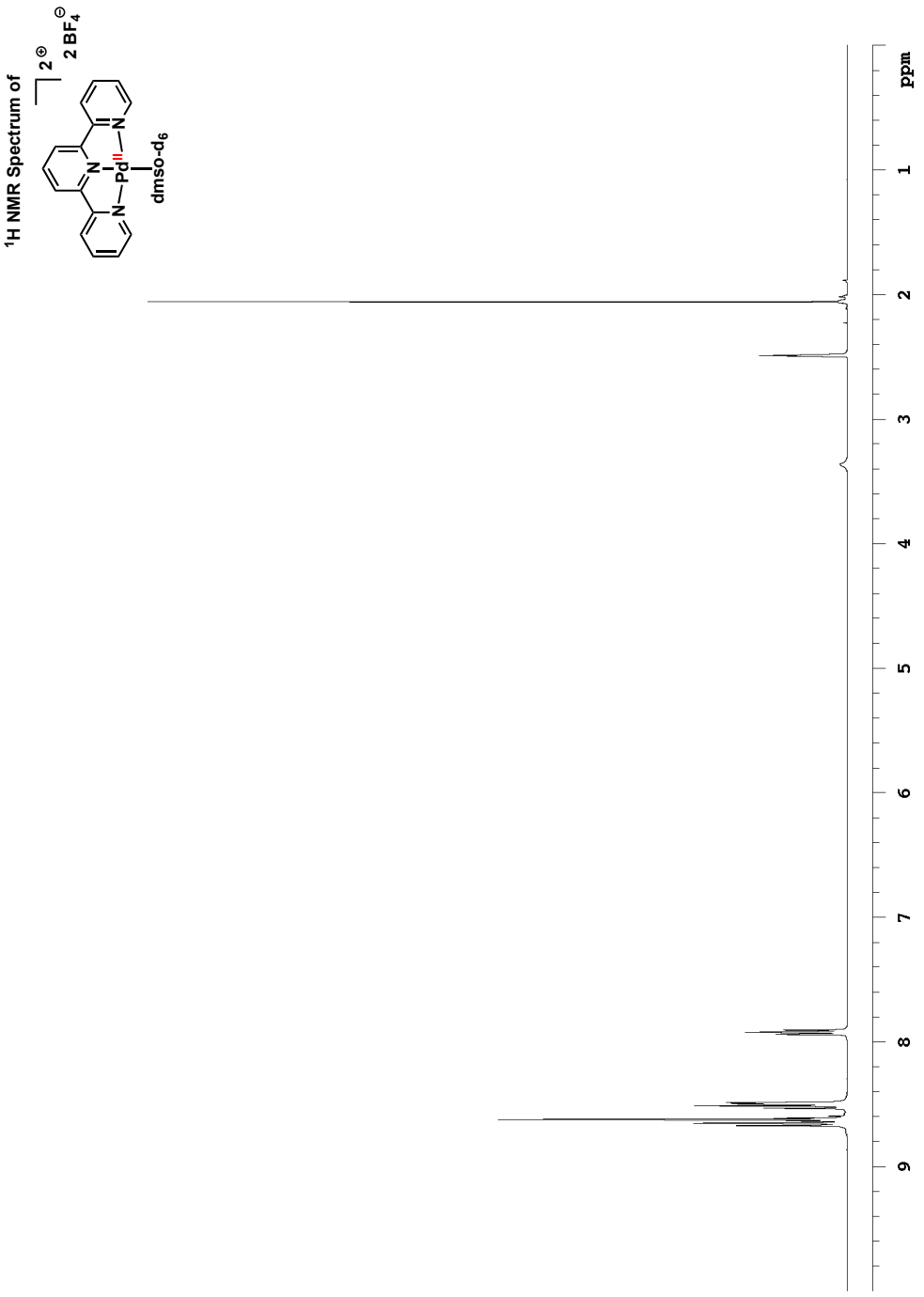
NMR Data



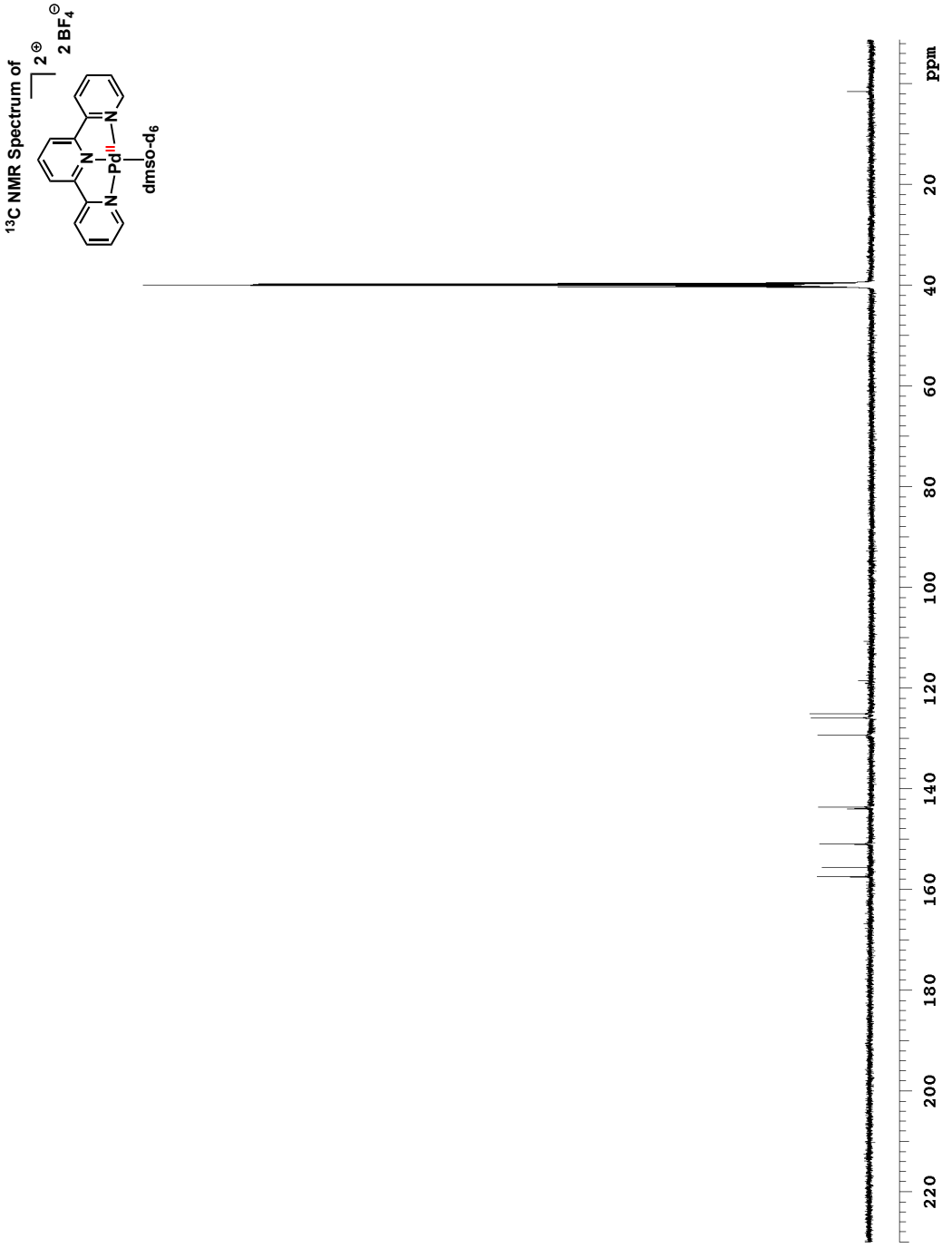
^{1}H NMR of **1**. CD_3CN, 400 MHz, 23 °C



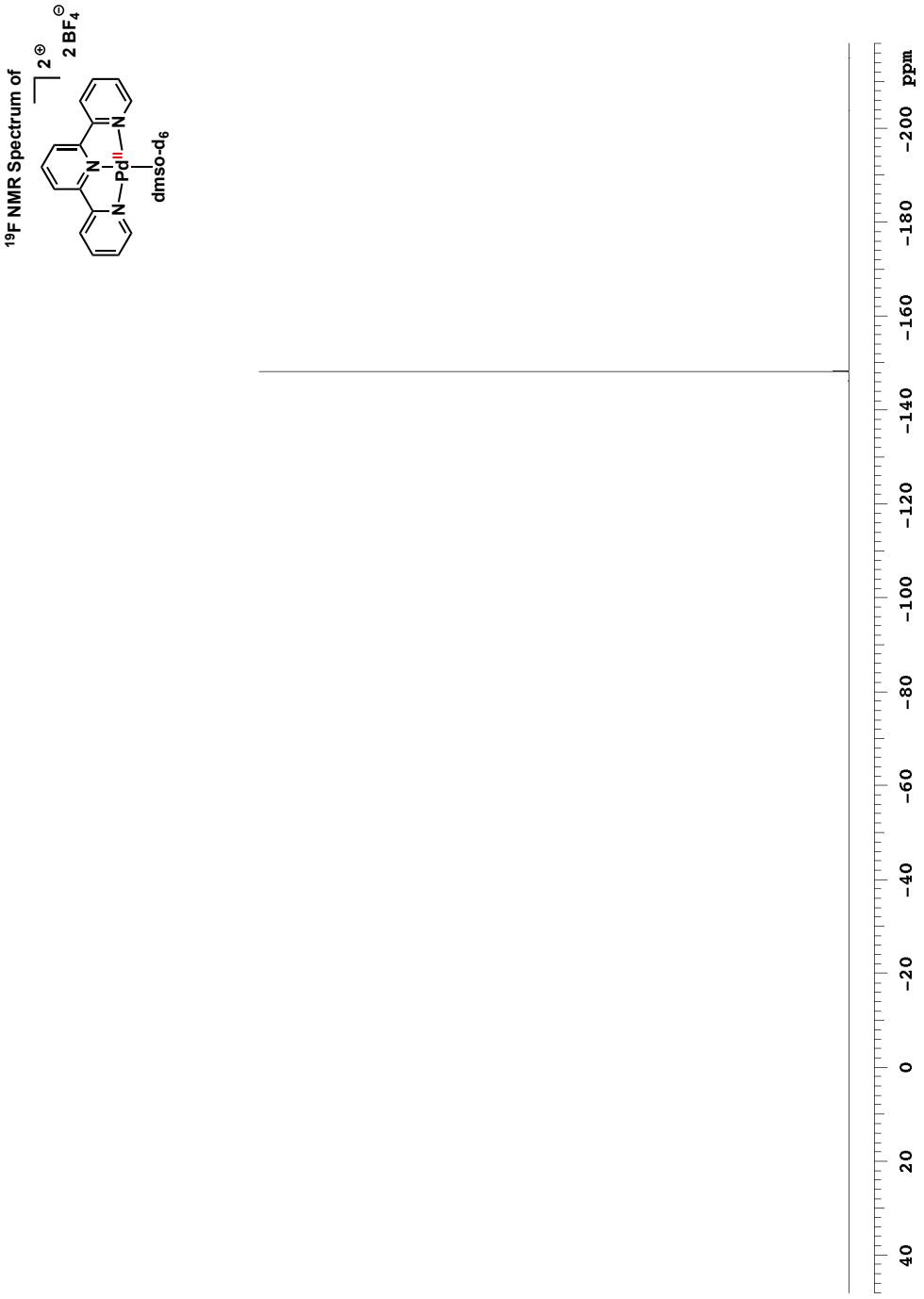
^{19}F NMR of **1**. CD_3CN, 375 MHz, 23 °C



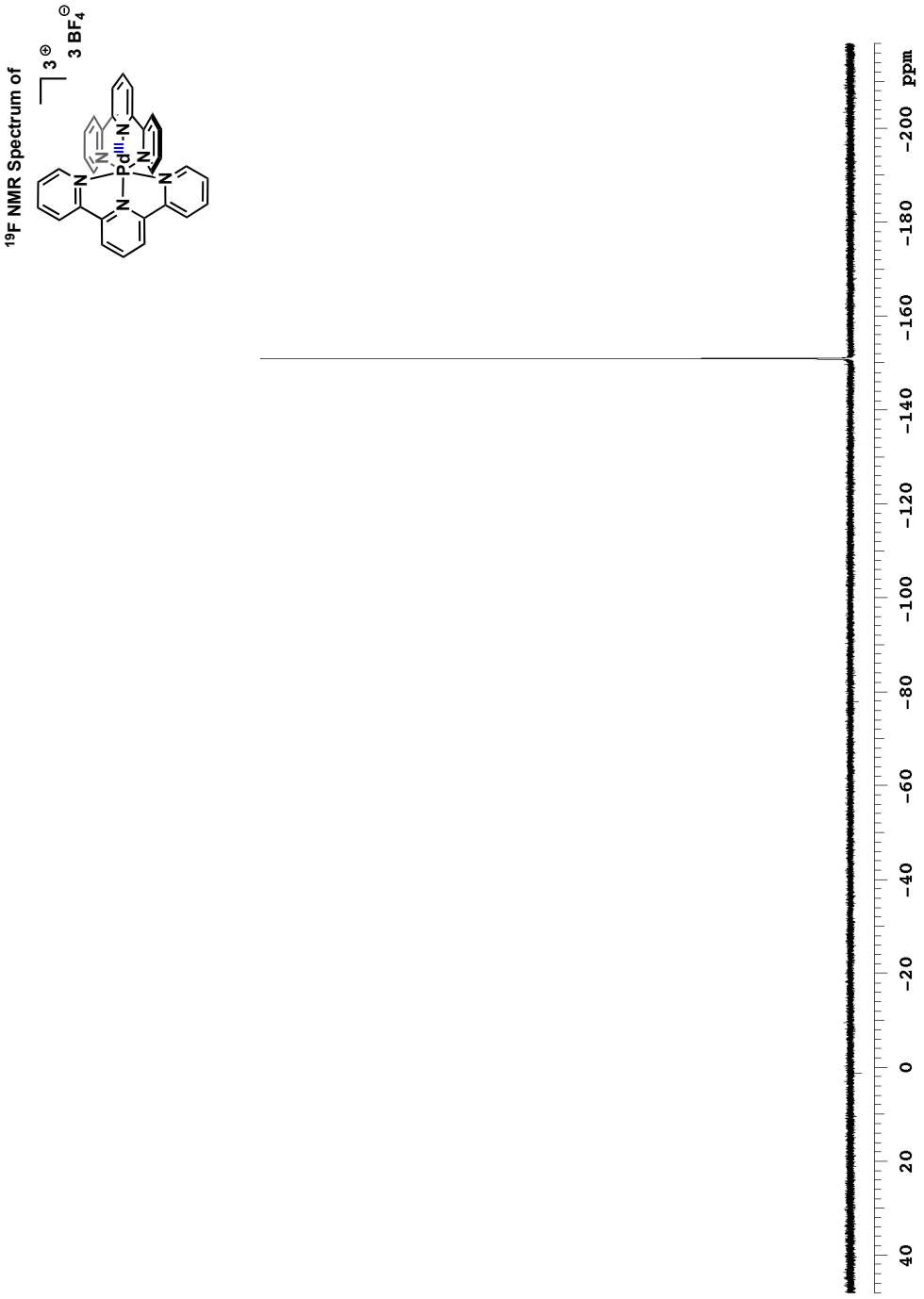
^{1}H NMR of **1**. dmso-d_6, 400 MHz, 23 °C



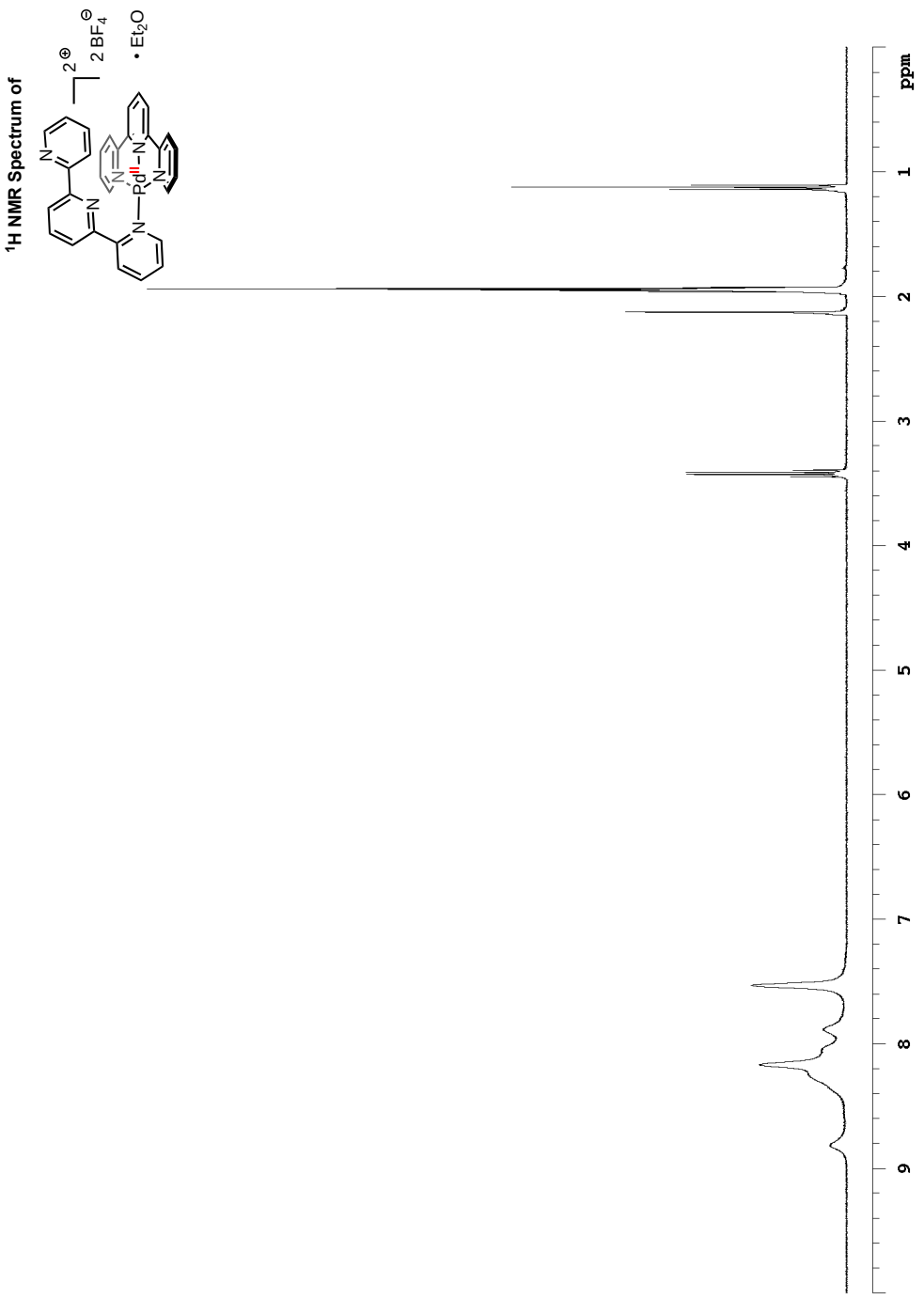
^{13}C NMR of **1**. dmso-d_6, 125 MHz, 23 °C



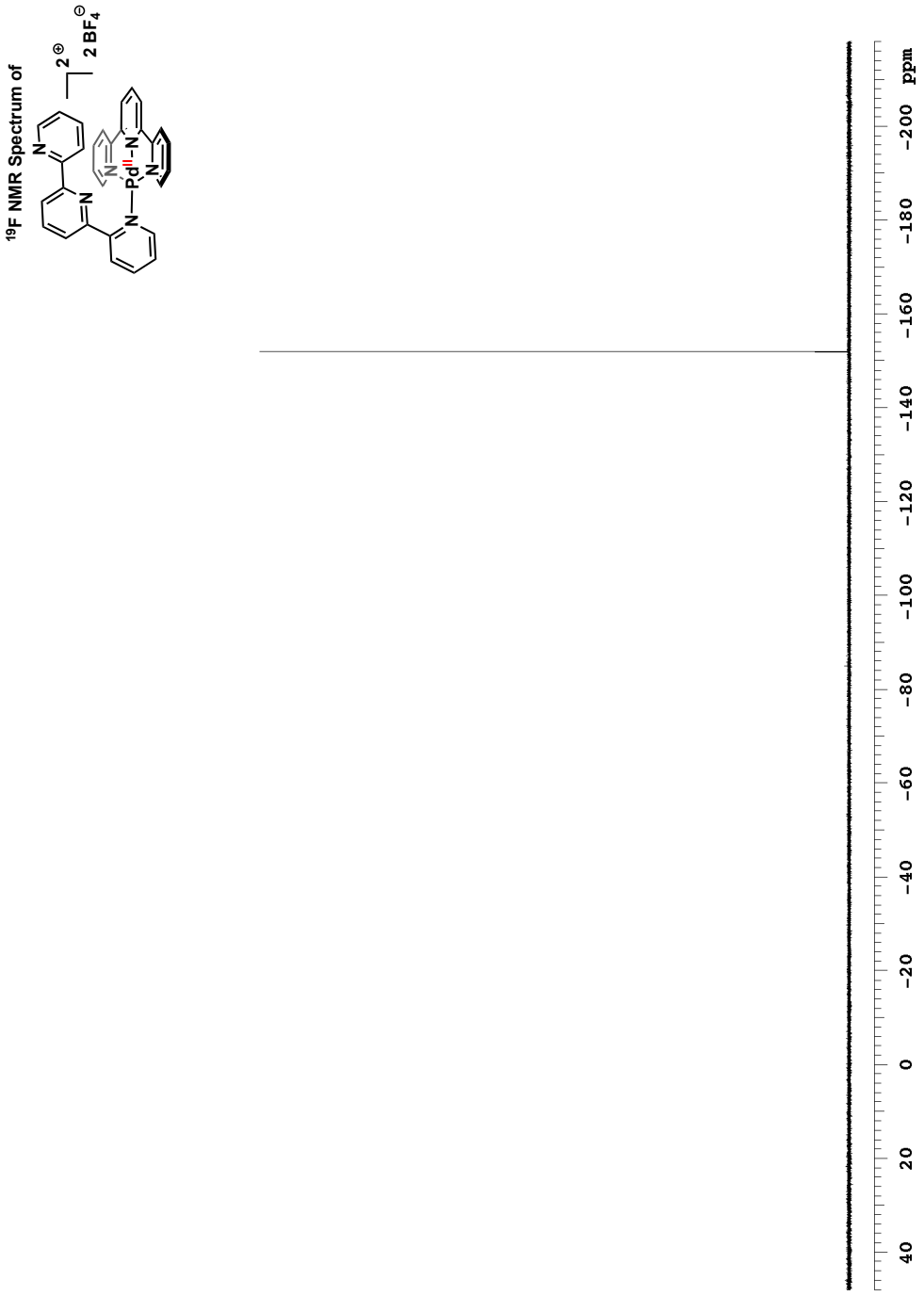
^{19}F NMR of **1**. dmso-d_6, 375 MHz, 23 °C



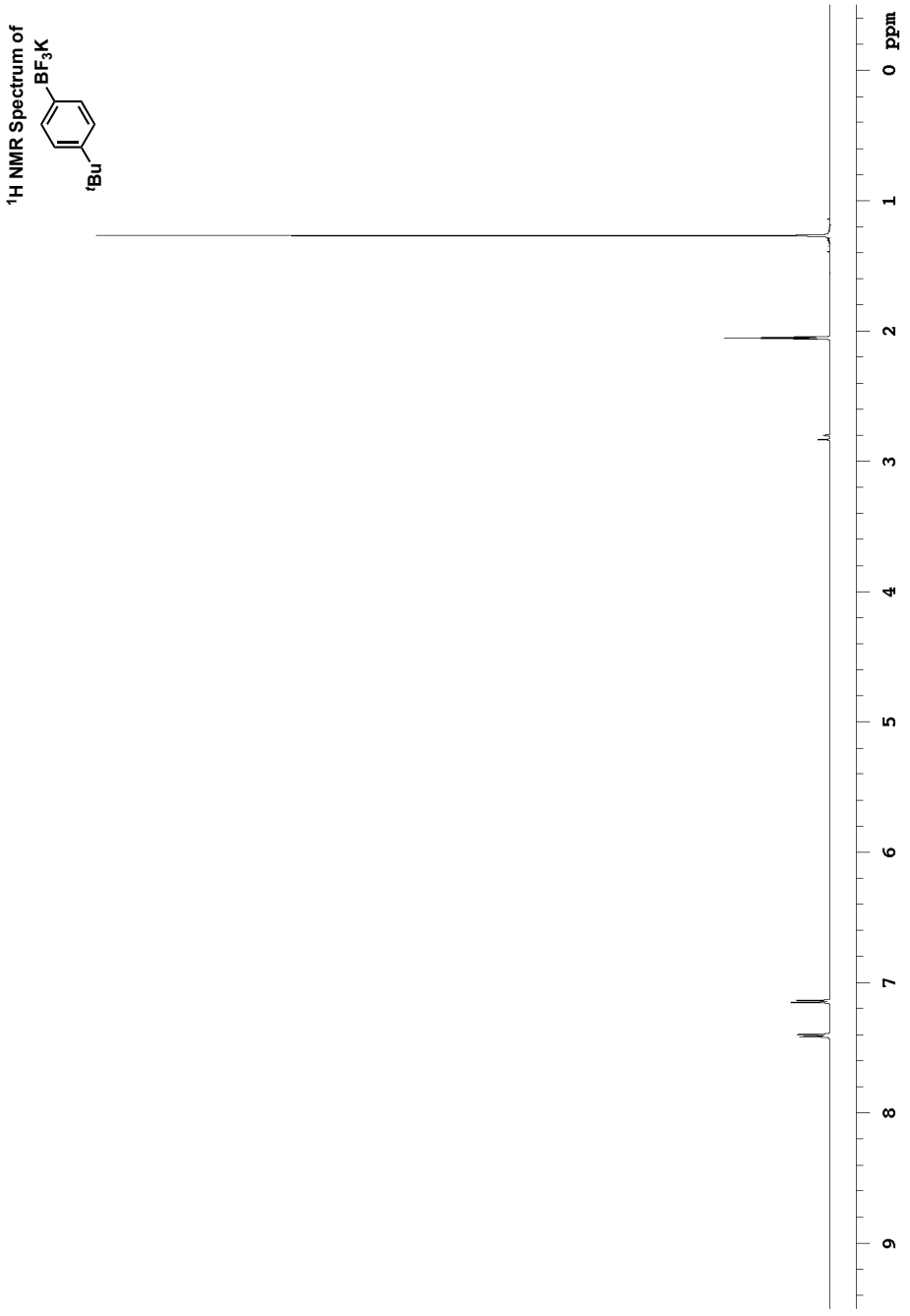
^{19}F NMR of **2**. CD_3CN, 375 MHz, 23 °C



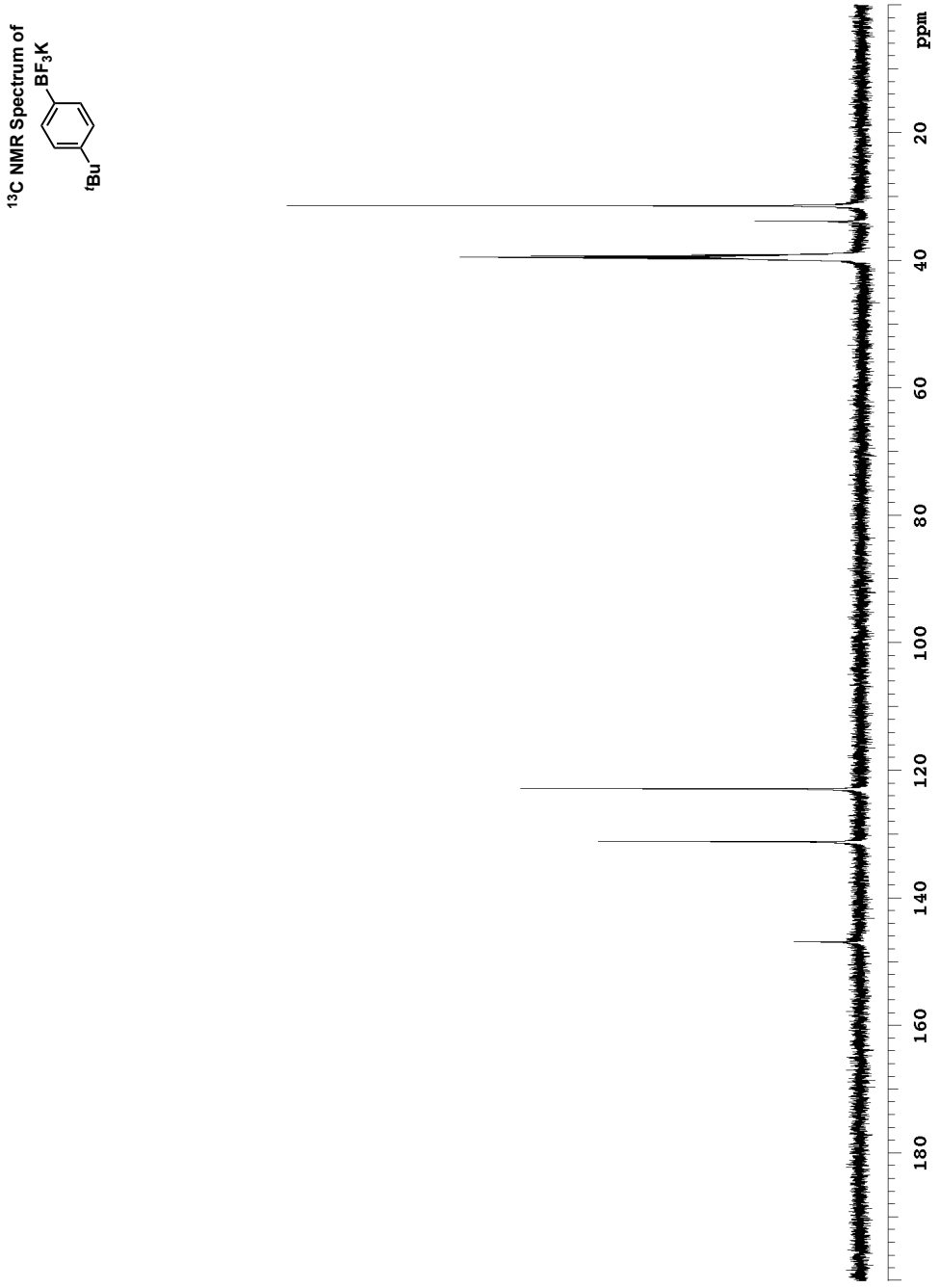
^{1}H NMR of **S2**. CD_3CN, 400 MHz, 23 °C



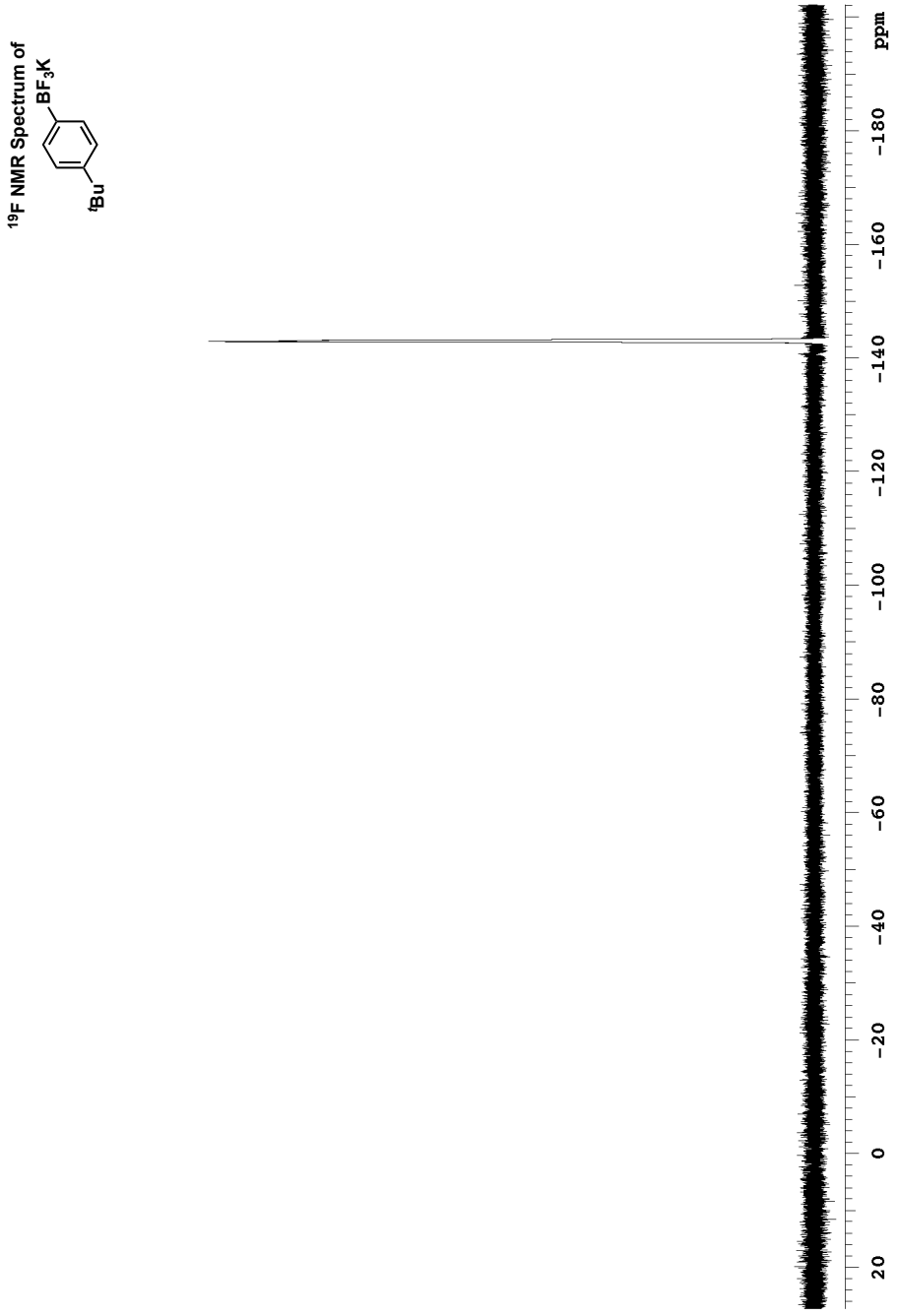
^{19}F NMR of **S2**. CD_3CN, 375 MHz, 23 °C



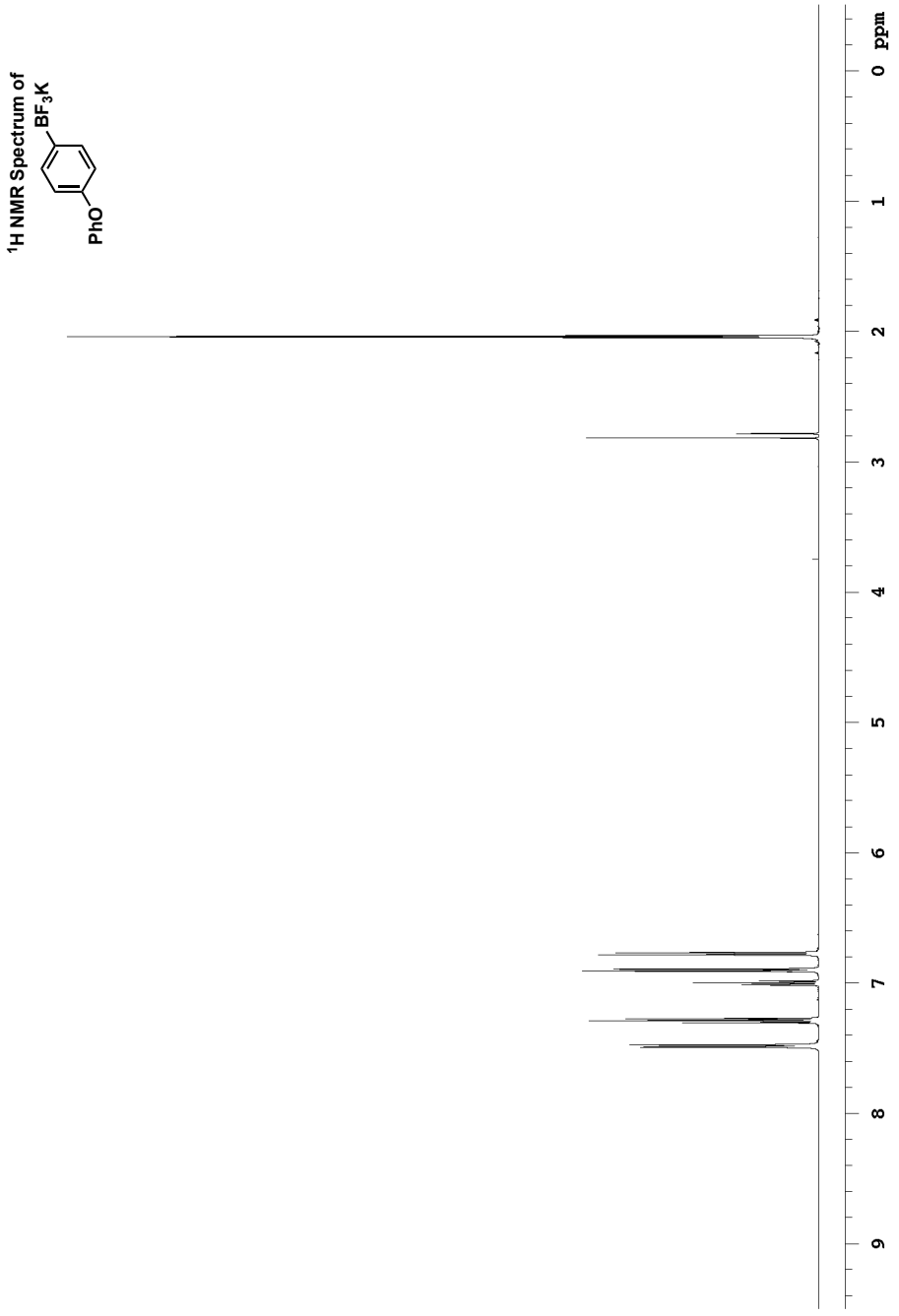
^{1}H NMR of **3a**. acetone-d_6, 500 MHz, 23 °C



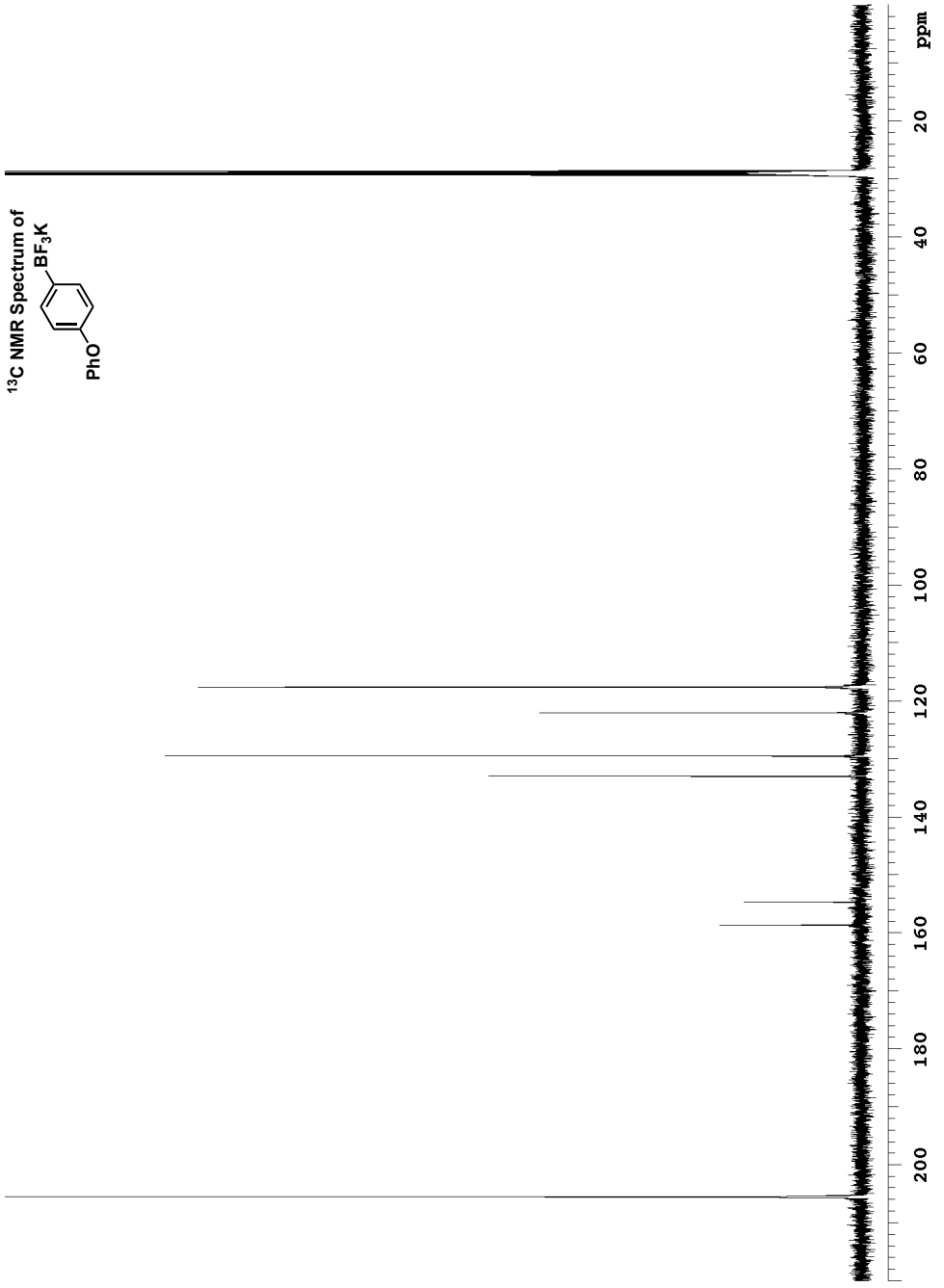
^{13}C NMR of **3a**. DMSO-d_6, 125 MHz, 23 °C



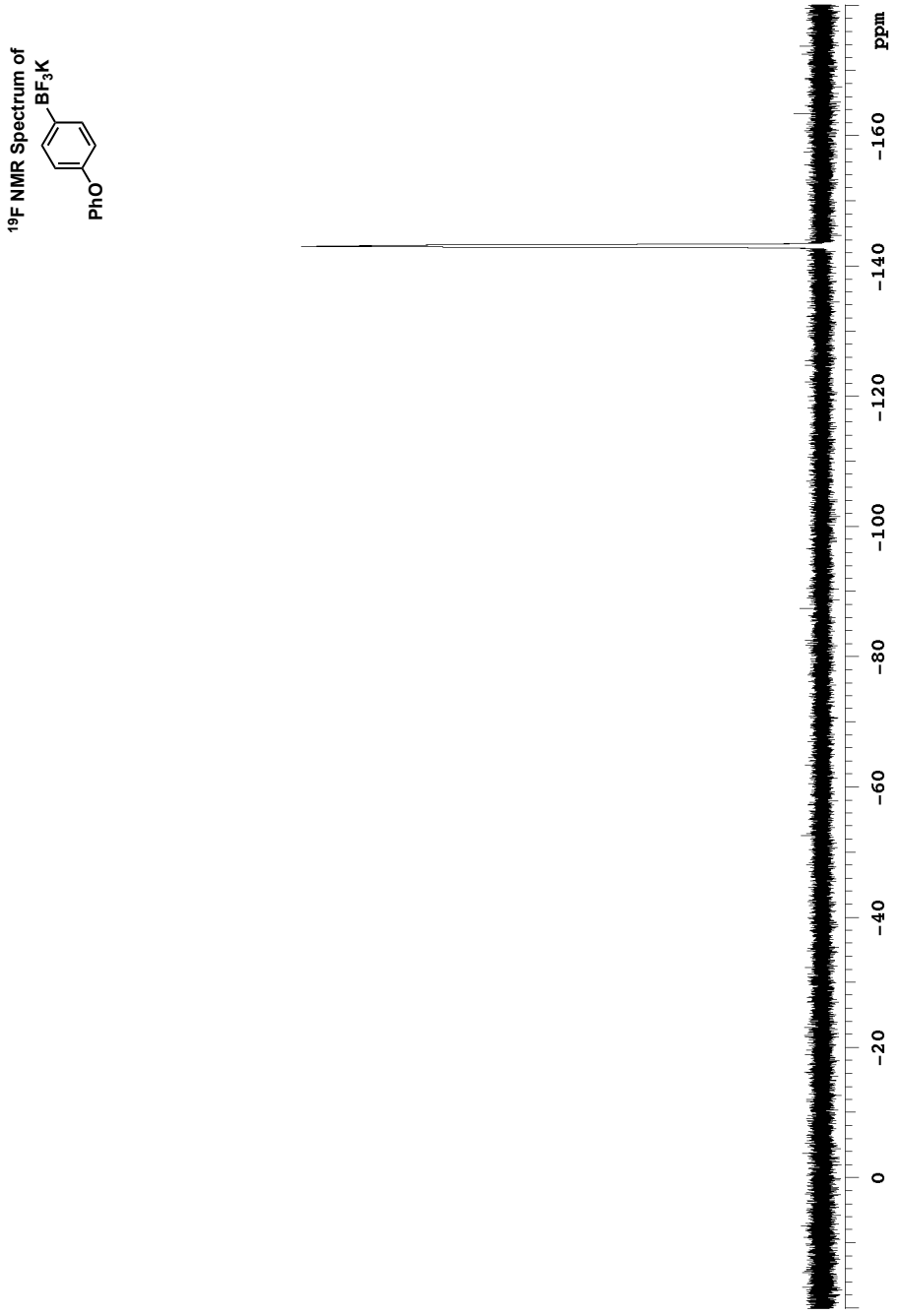
^{19}F NMR of **3a**. acetone-d_6, 375 MHz, 23 °C



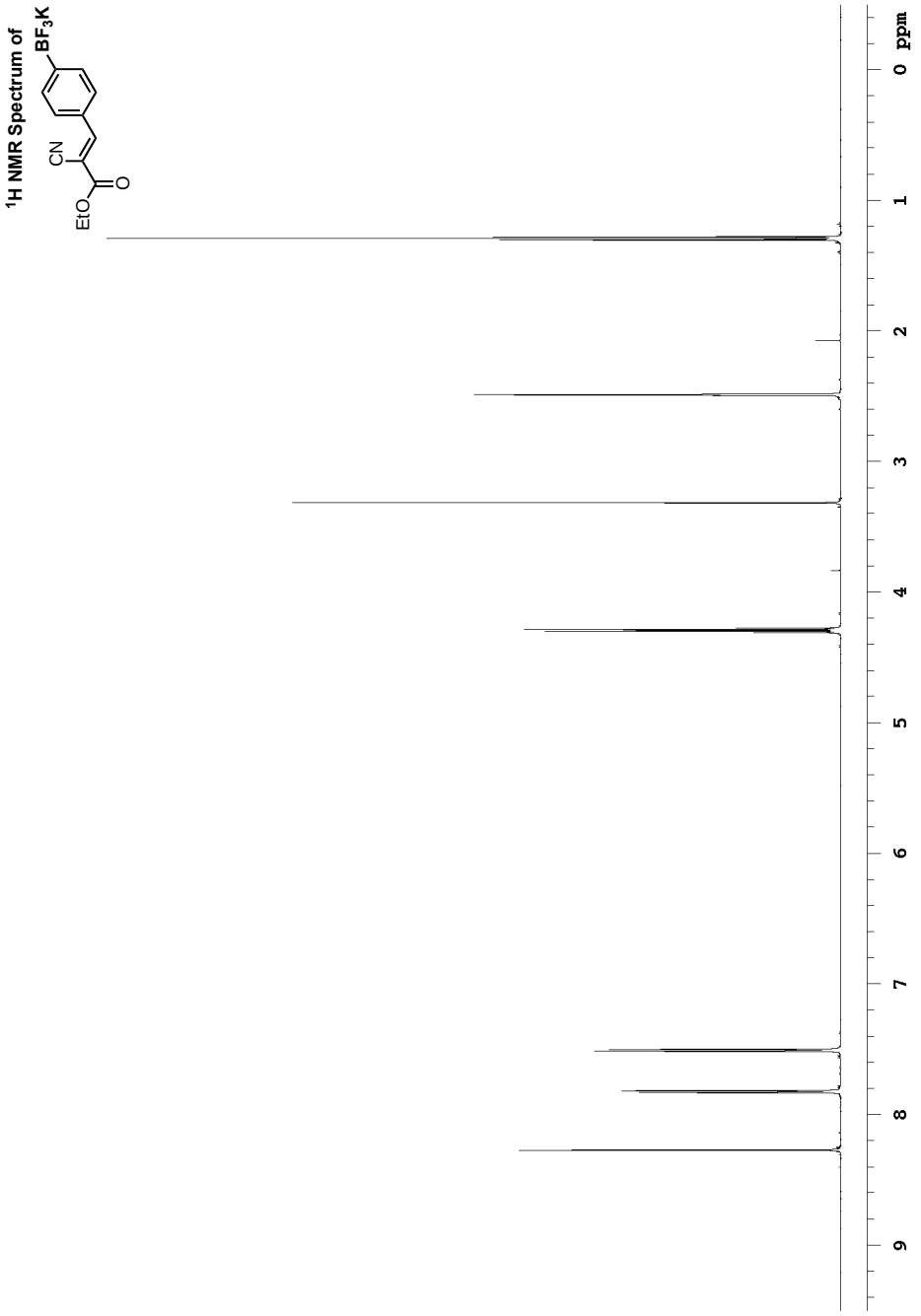
^{1}H NMR of **3b**. acetone-d_6, 500 MHz, 23 °C



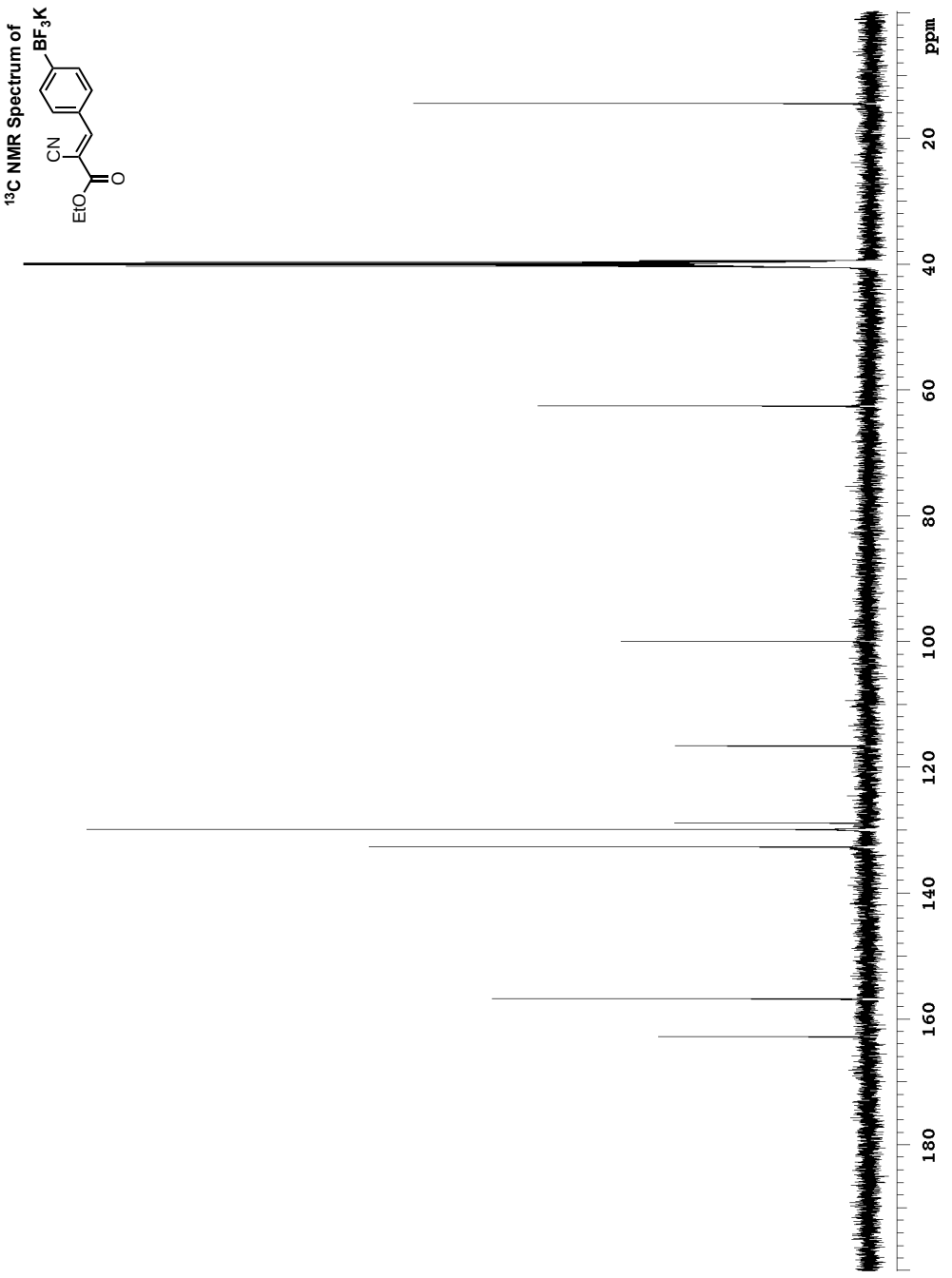
^{13}C NMR of **3b**. acetone-d_6, 125 MHz, 23 °C



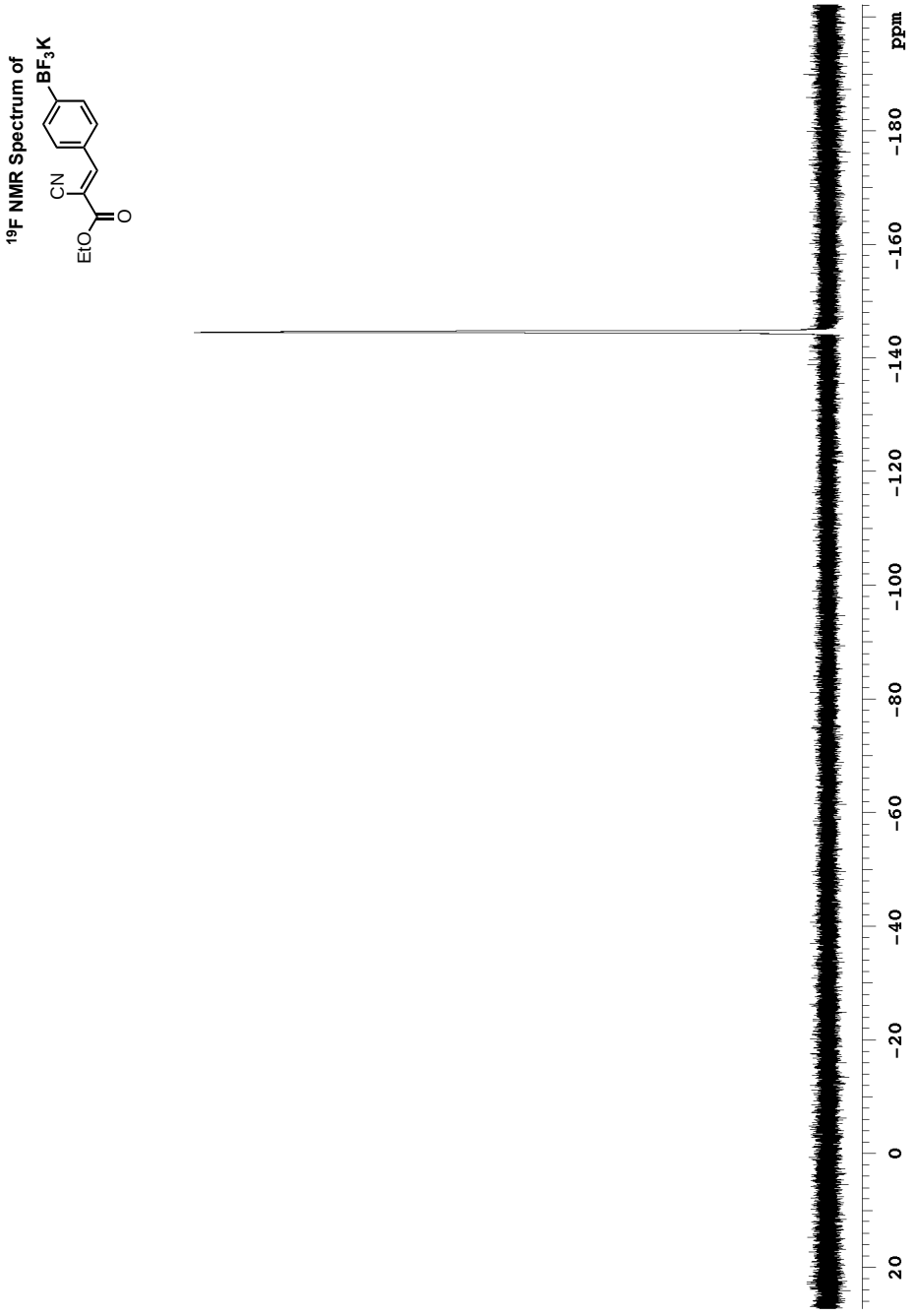
^{19}F NMR of **3b**. acetone-d_6, 375 MHz, 23 °C



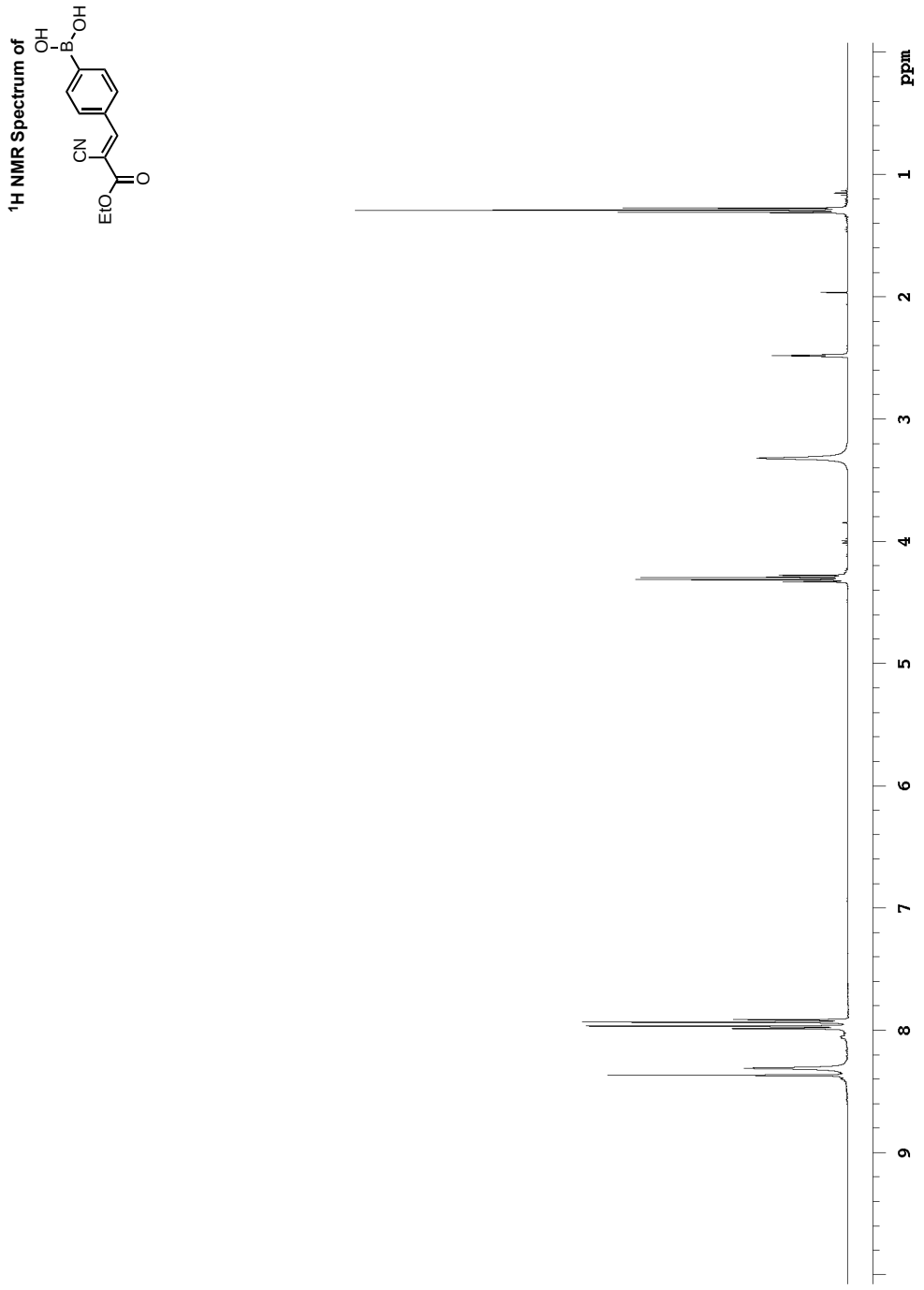
^{1}H NMR of **3c**. DMSO-d_6, 600 MHz, 23 °C



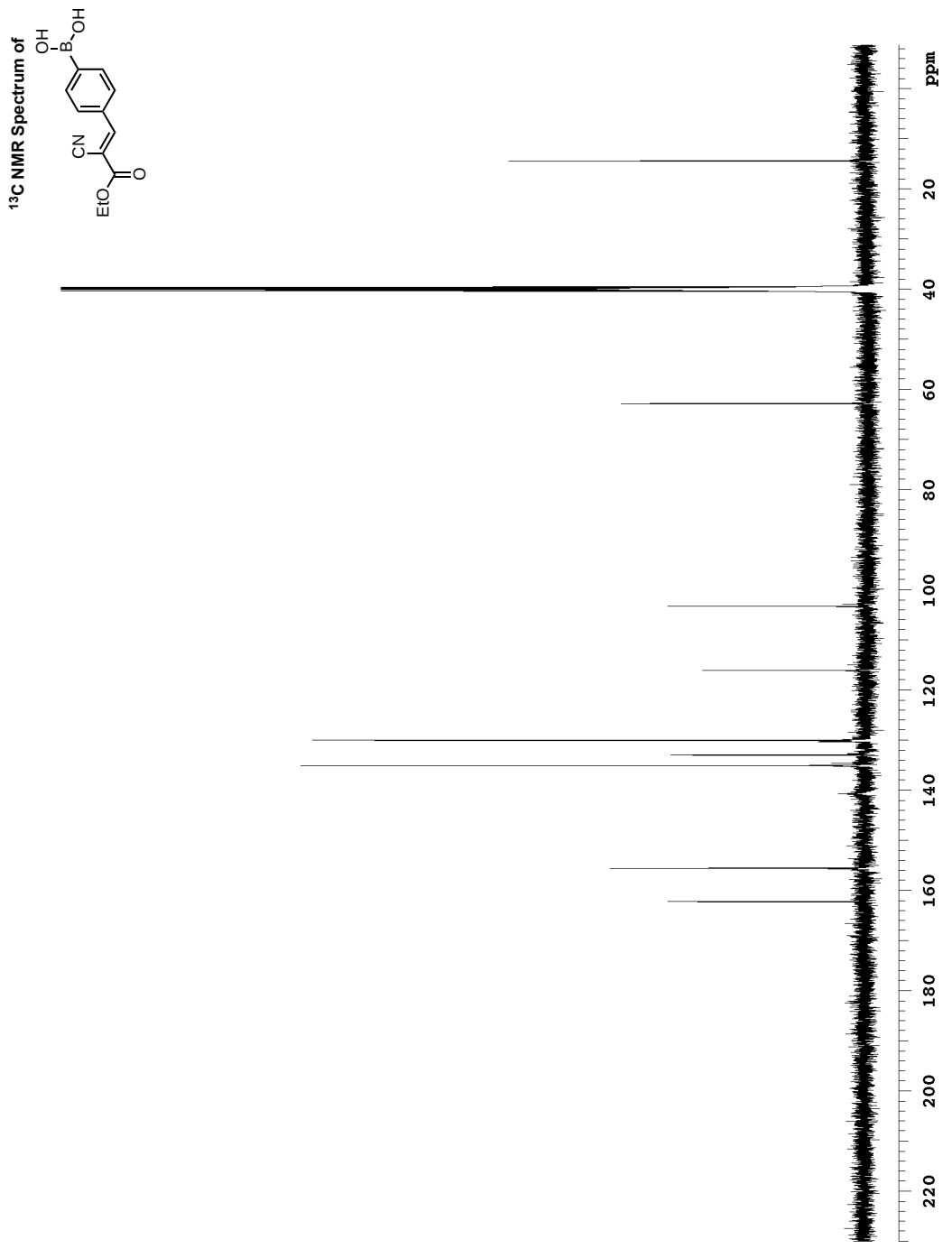
^{13}C NMR of **3c**. DMSO-d_6, 125 MHz, 23 °C



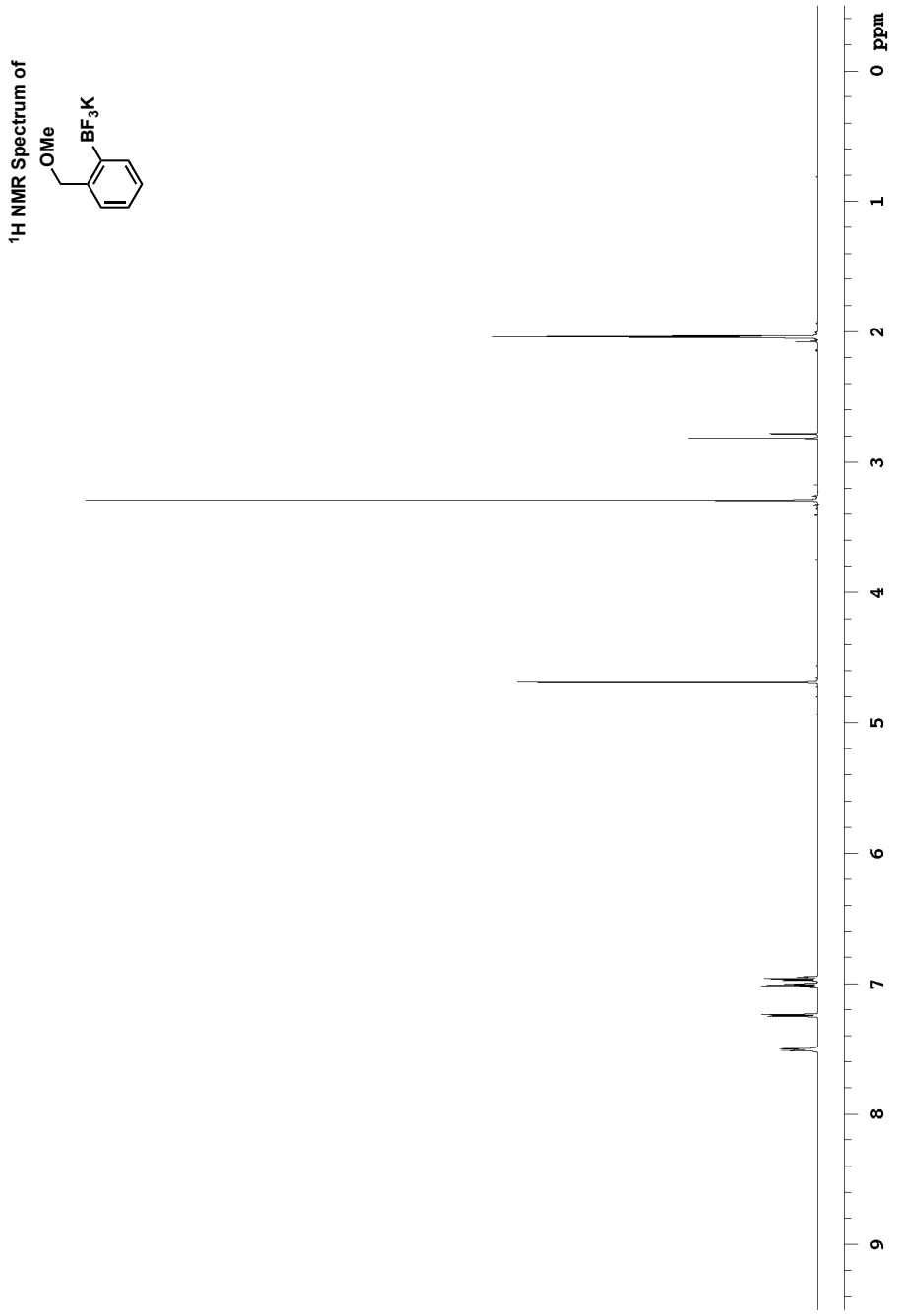
^{19}F NMR of **3c**. DMSO-d_6, 375 MHz, 23 °C



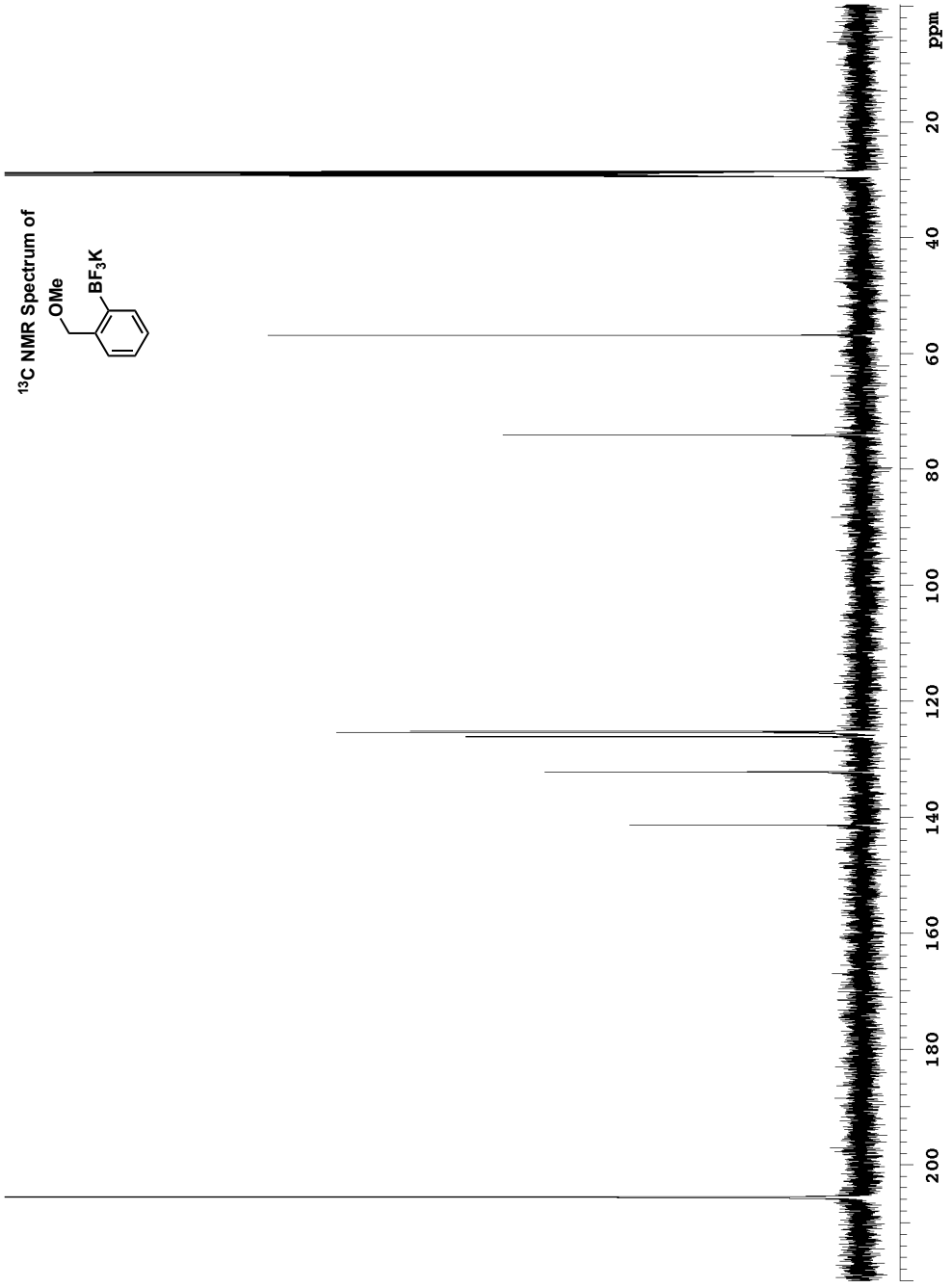
^{1}H NMR of **S3**. dmso-d_6, 400 MHz, 23 °C



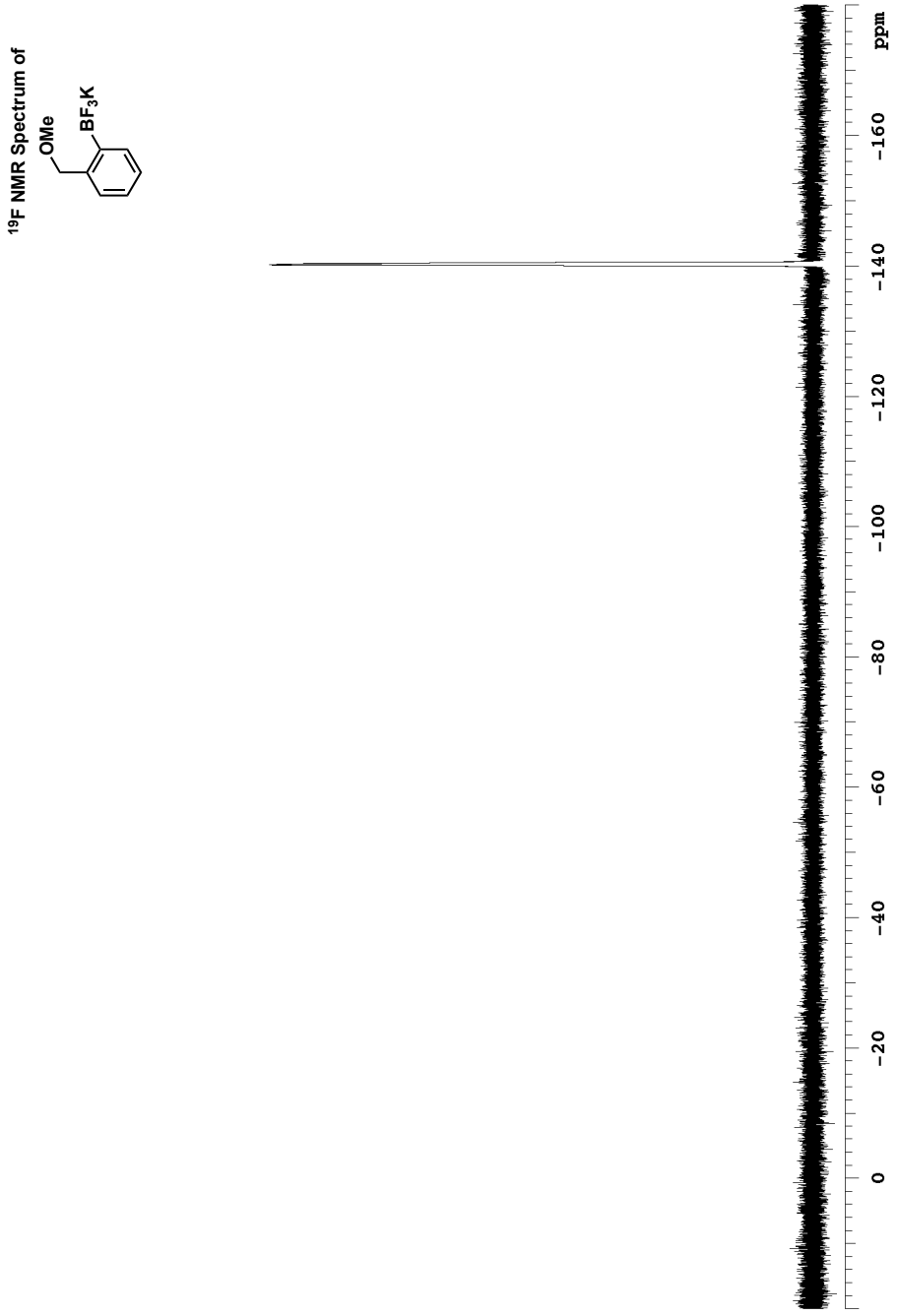
^{13}C NMR of **S3**. dmso-d_6, 125 MHz, 23 °C



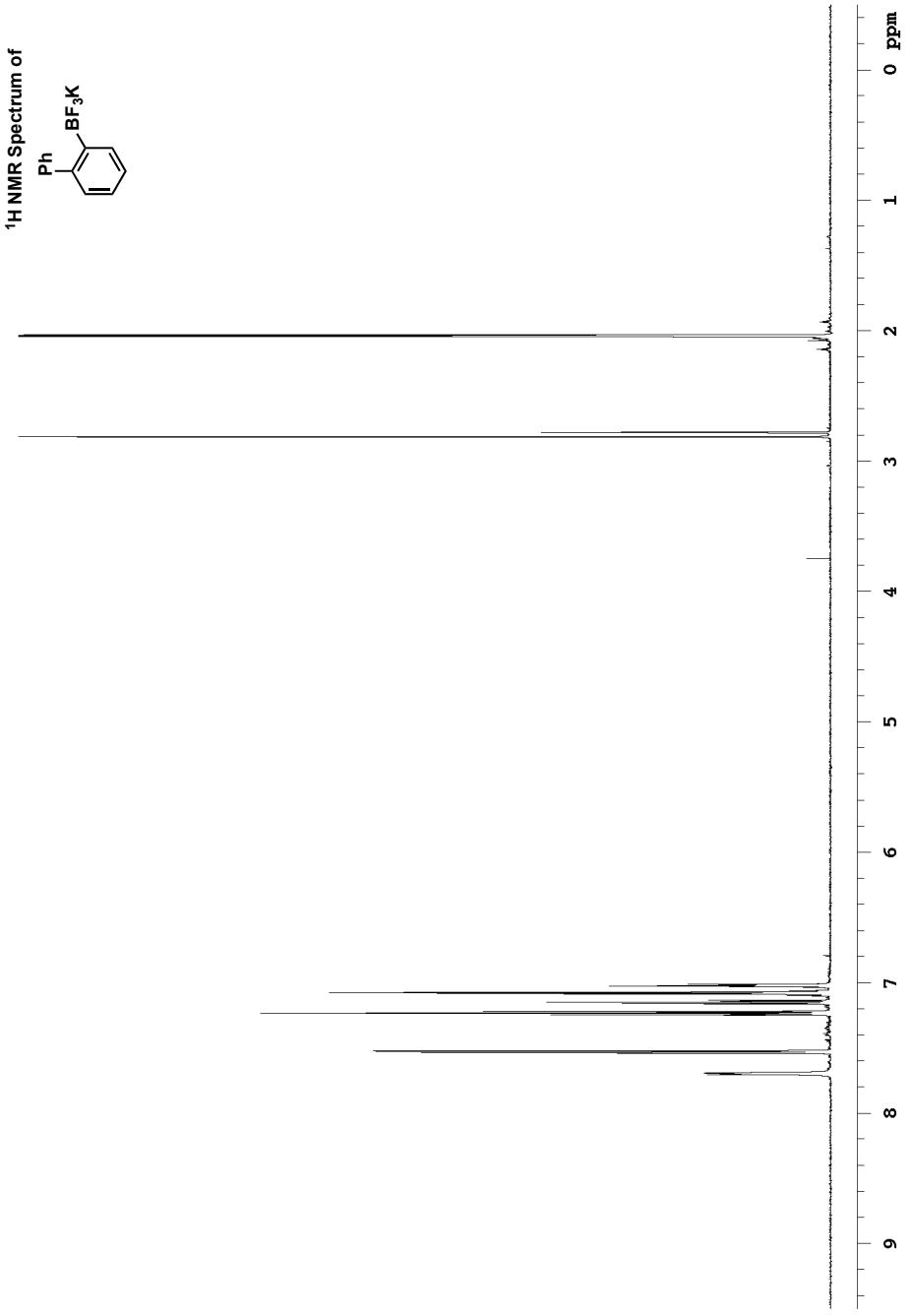
^{1}H NMR of **3d**. acetone-d_6, 600 MHz, 23 °C



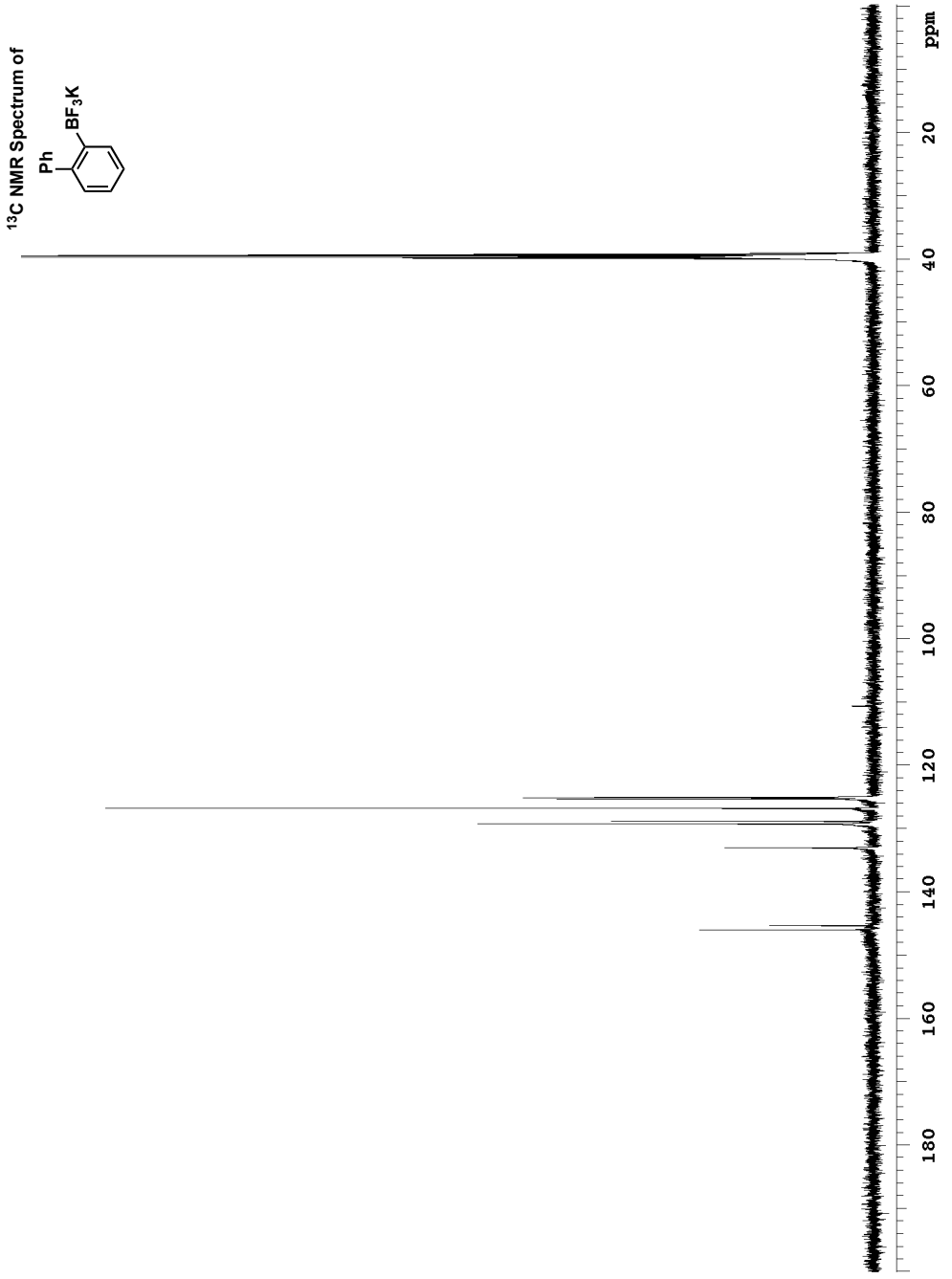
^{13}C NMR of **3d**. acetone-d_6, 125 MHz, 23 °C



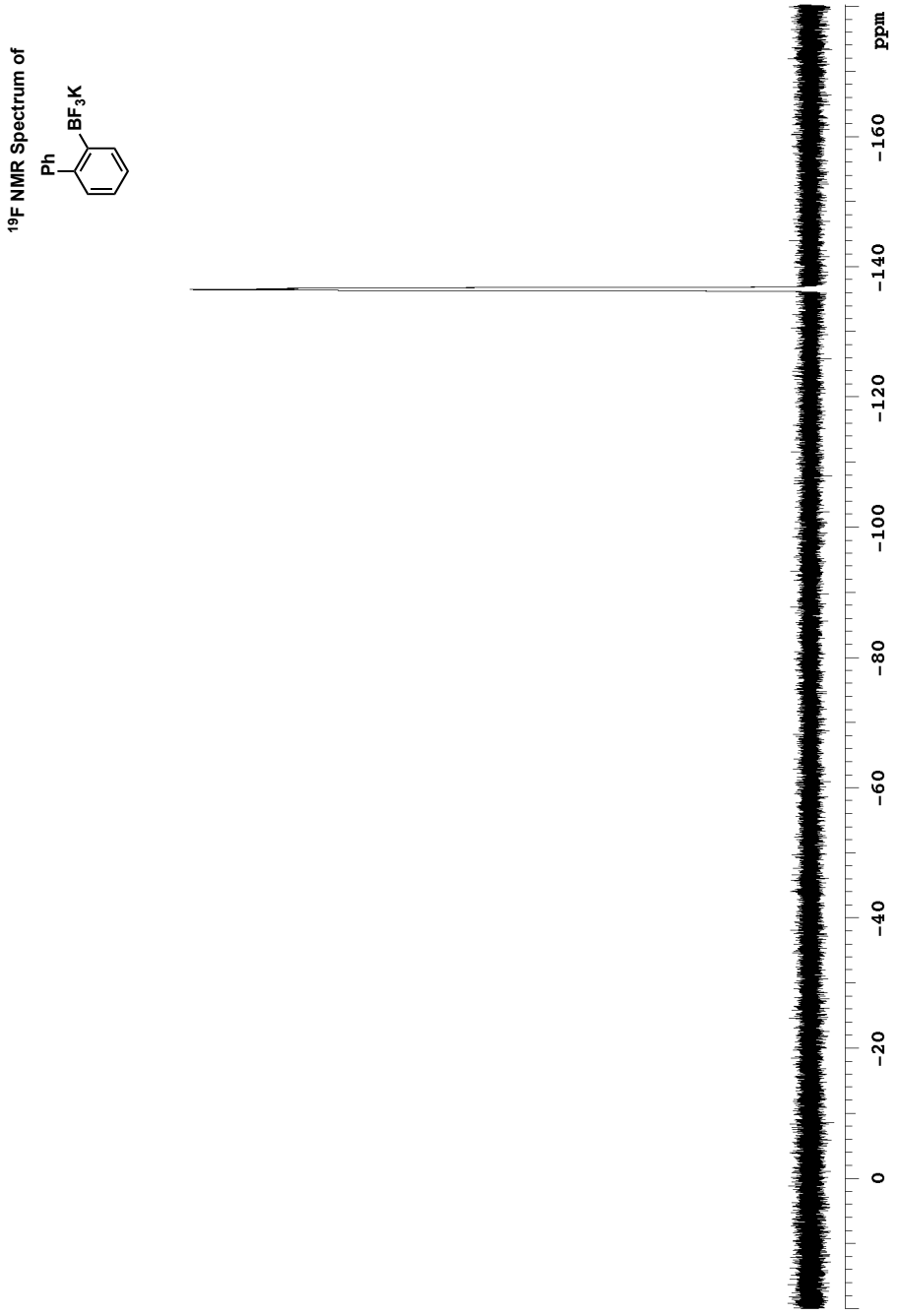
^{19}F NMR of **3d**. acetone-d_6, 375 MHz, 23 °C



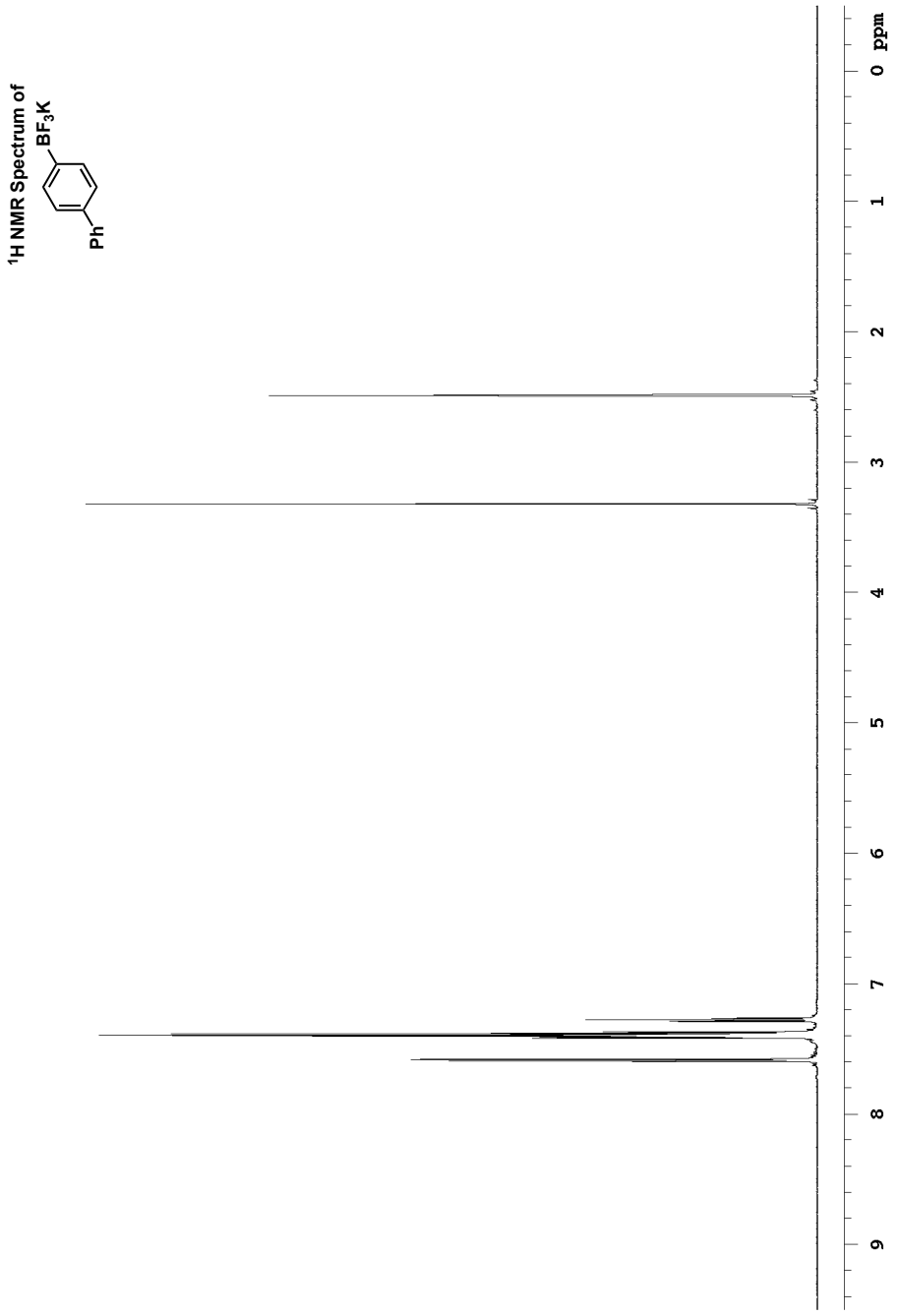
^{1}H NMR of **3f**. acetone-d_6, 600 MHz, 23 °C



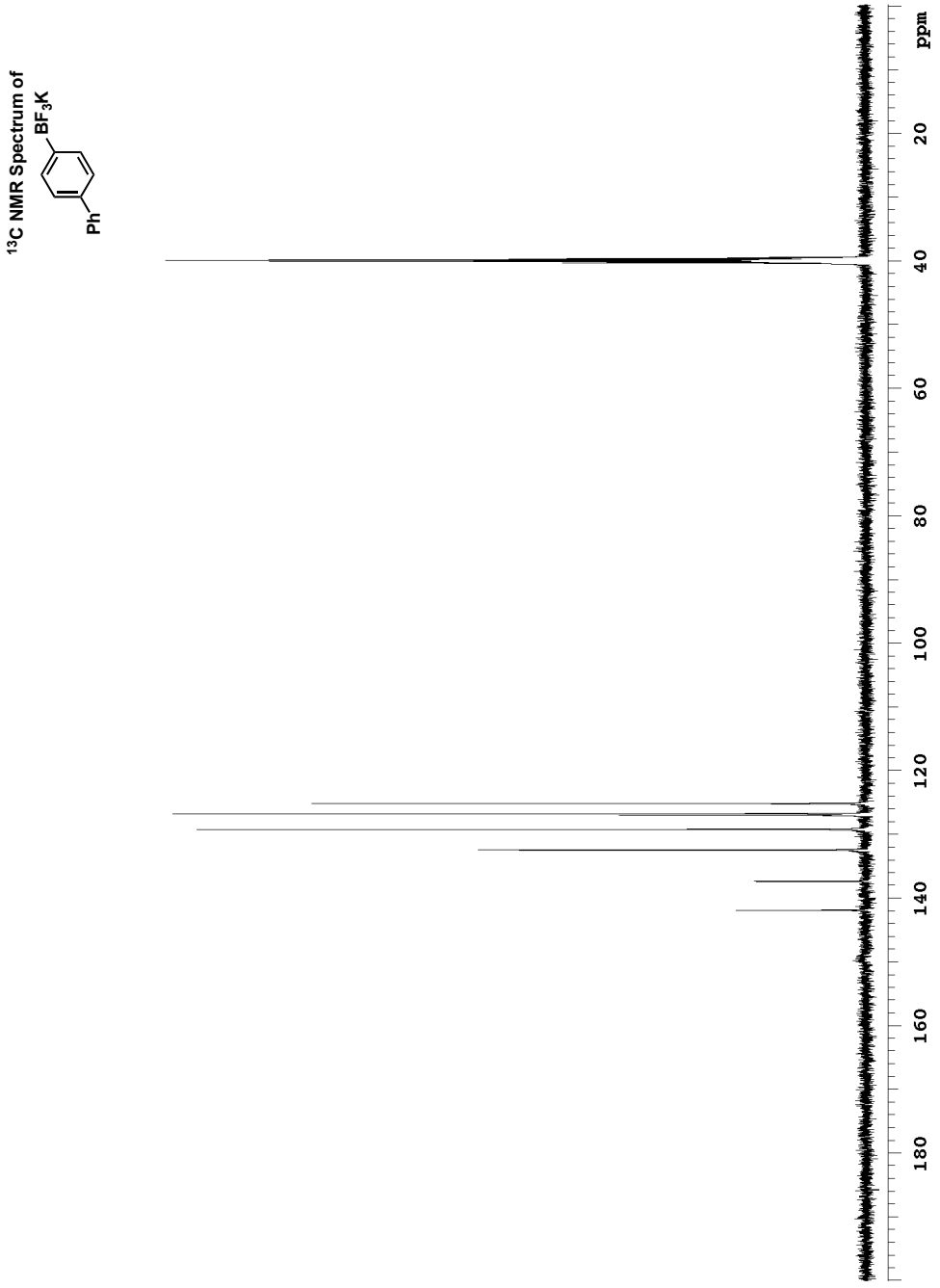
^{13}C NMR of **3f**. DMSO-d_6, 125 MHz, 23 °C



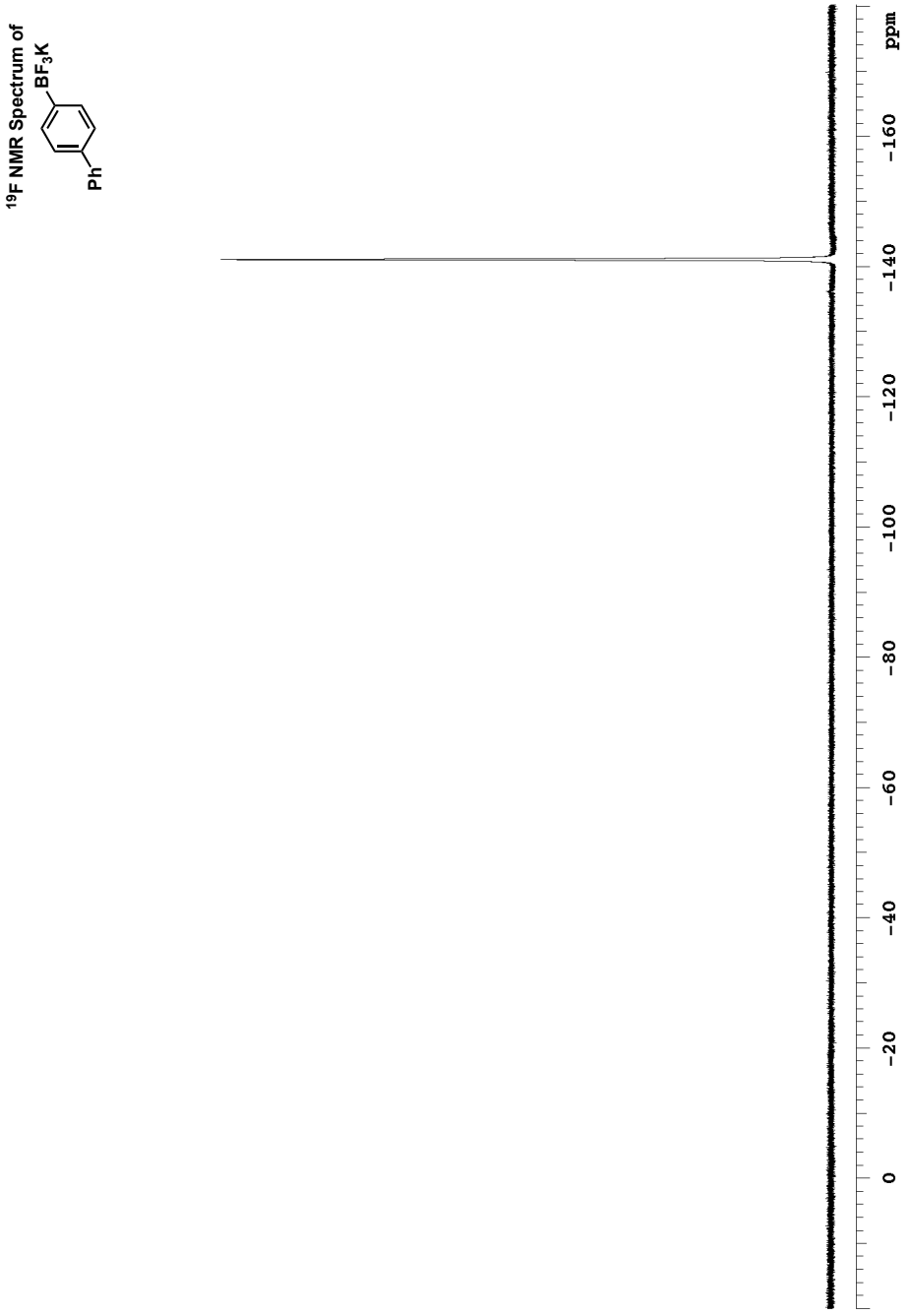
^{19}F NMR of **3f**. acetone-d_6, 375 MHz, 23 °C



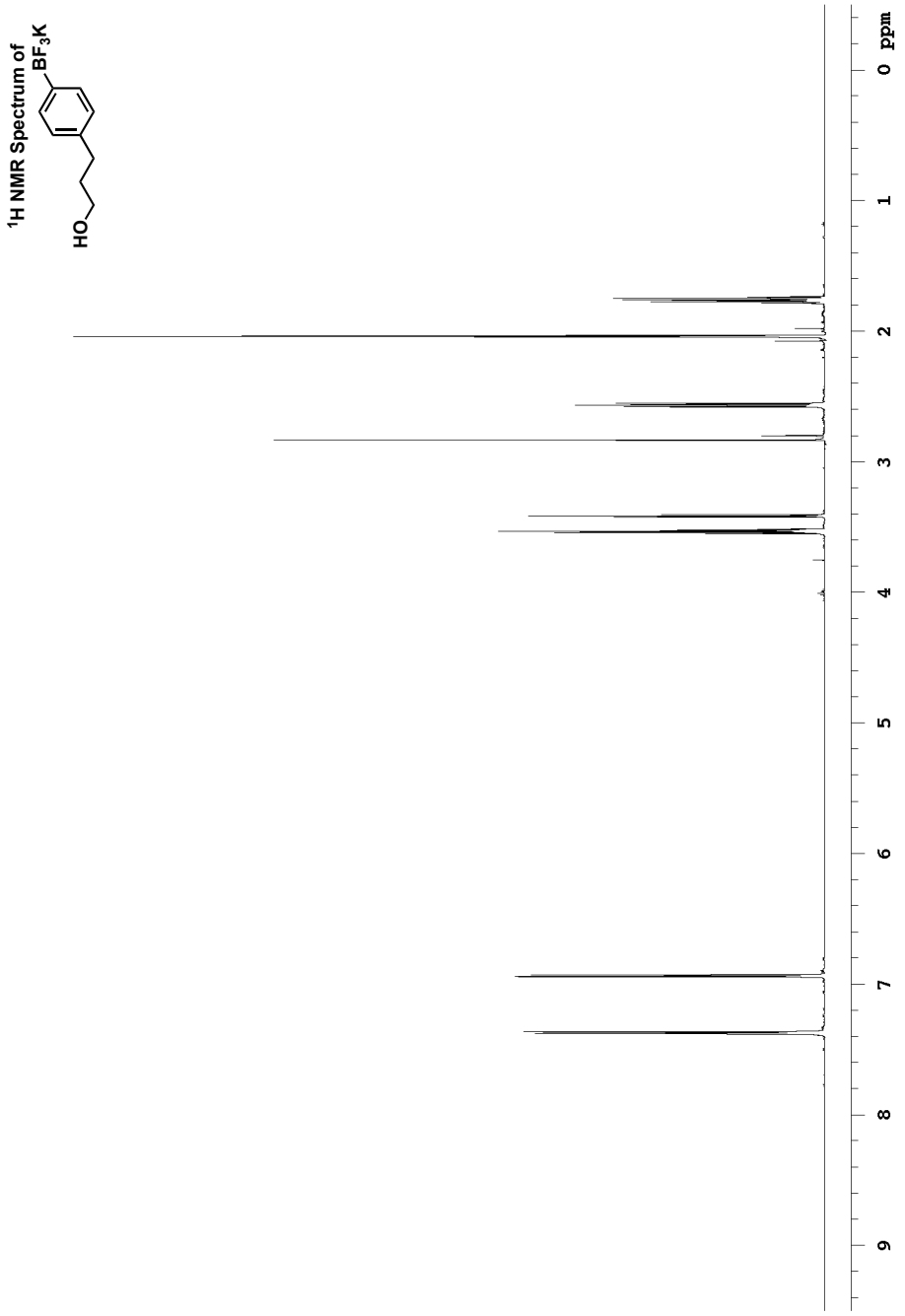
^{1}H NMR of **3g**. DMSO-d_6, 600 MHz, 23 °C



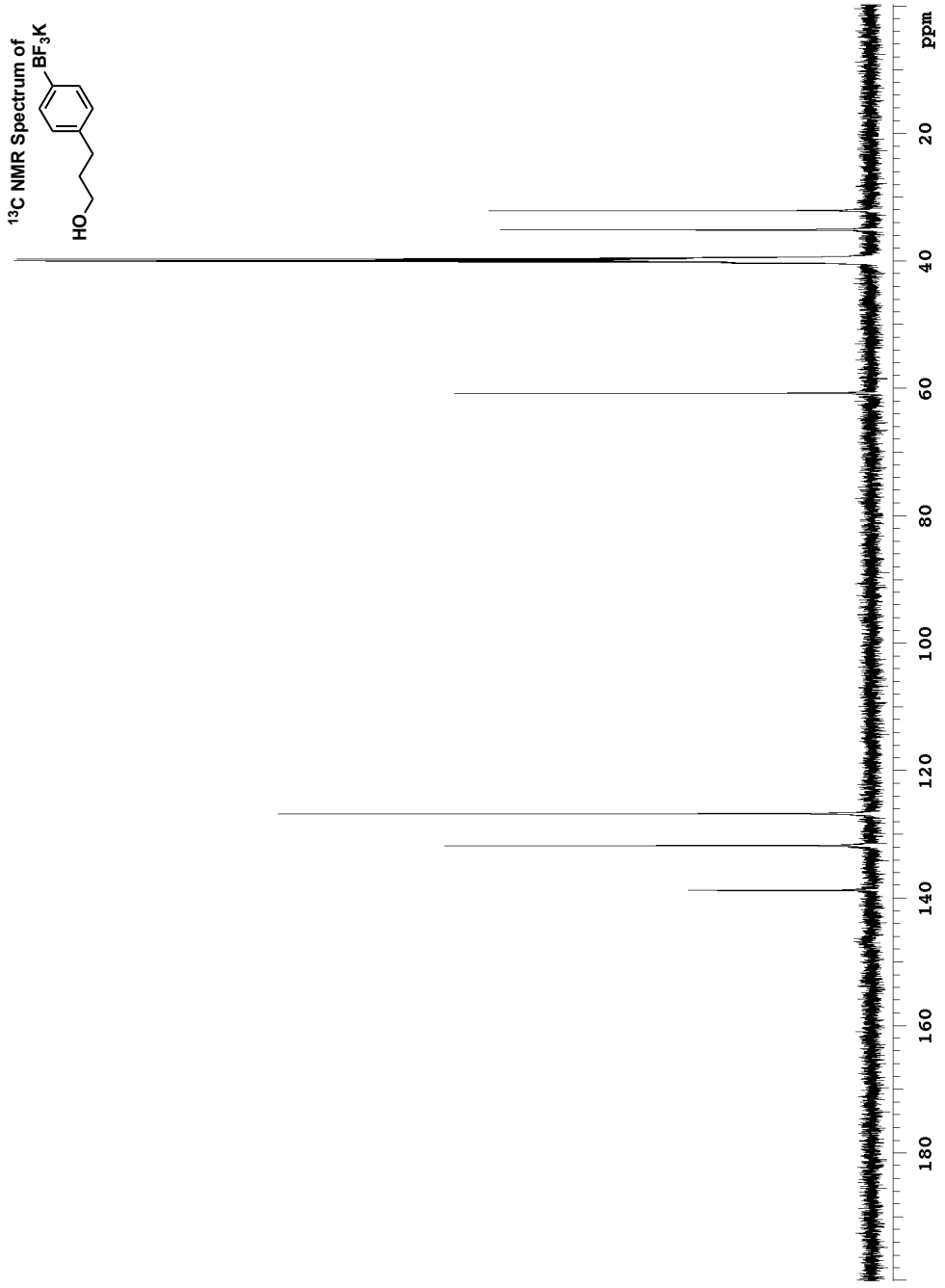
^{13}C NMR of **3g**. DMSO-d_6, 125 MHz, 23 °C



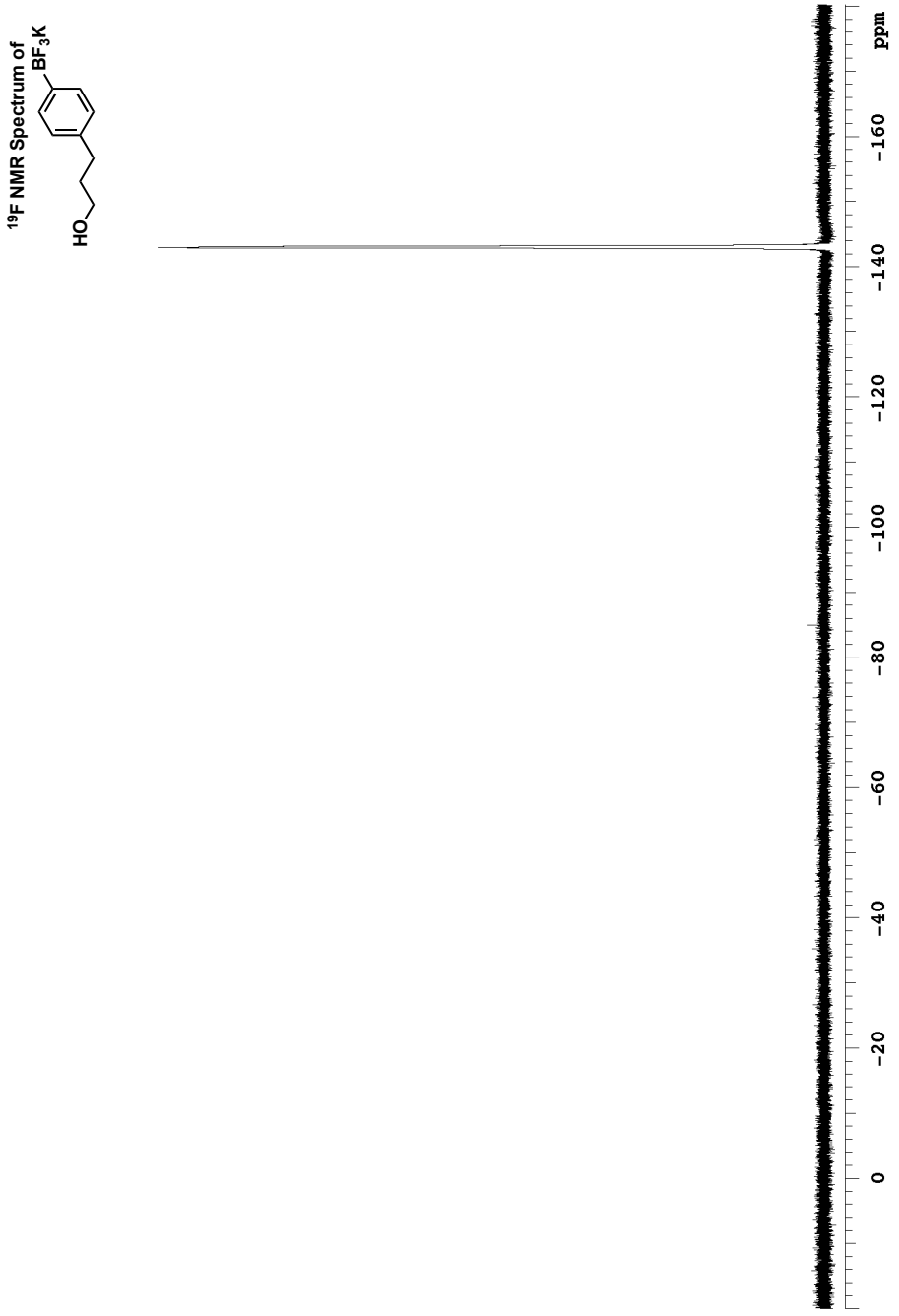
^{19}F NMR of **3g**. DMSO-d_6, 375 MHz, 23 °C



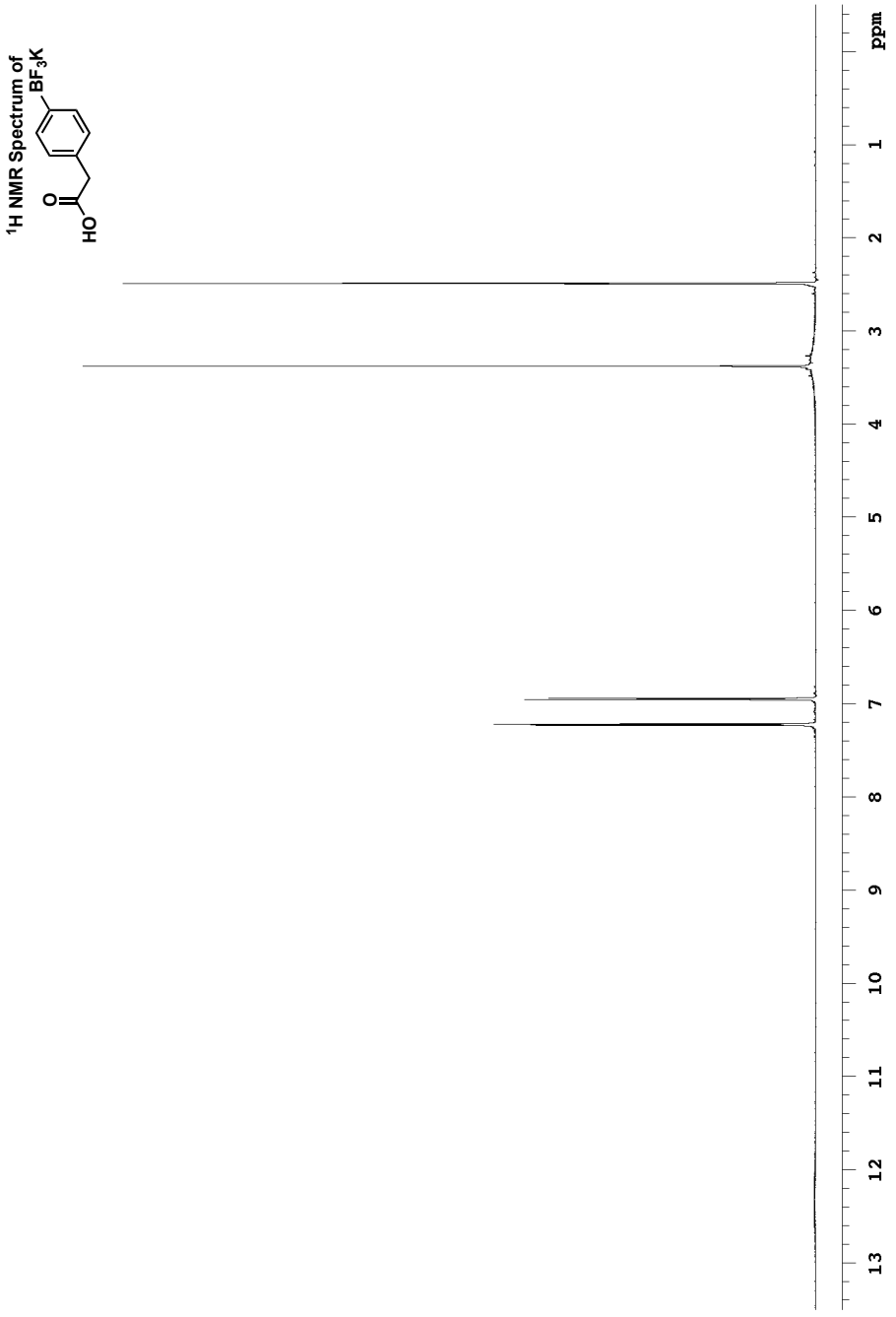
^{1}H NMR of **3h**. acetone-d_6, 600 MHz, 23 °C



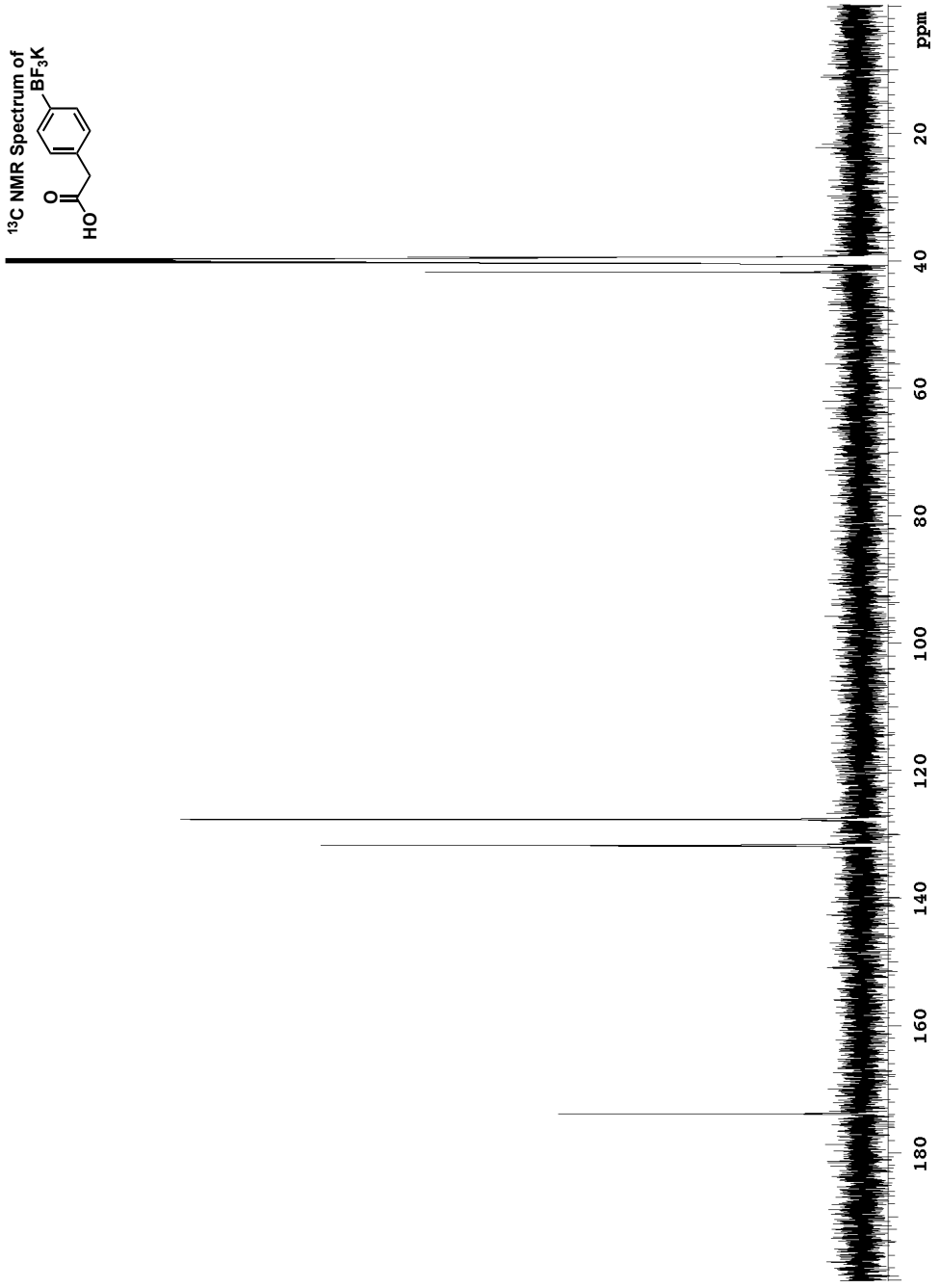
^{13}C NMR of **3h**. DMSO-d_6, 125 MHz, 23 °C



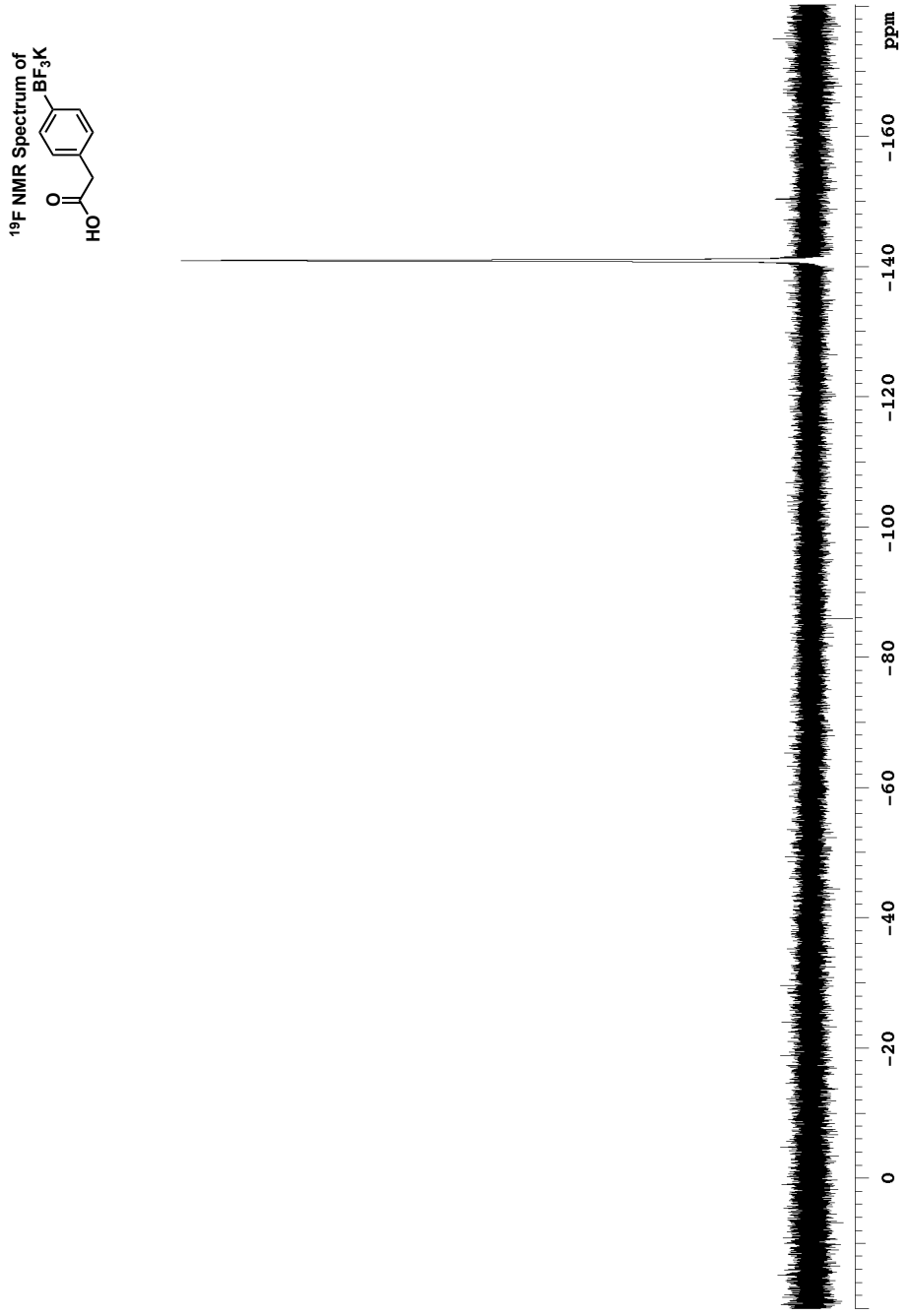
^{19}F NMR of **3h**. acetone-d_6, 375 MHz, 23 °C



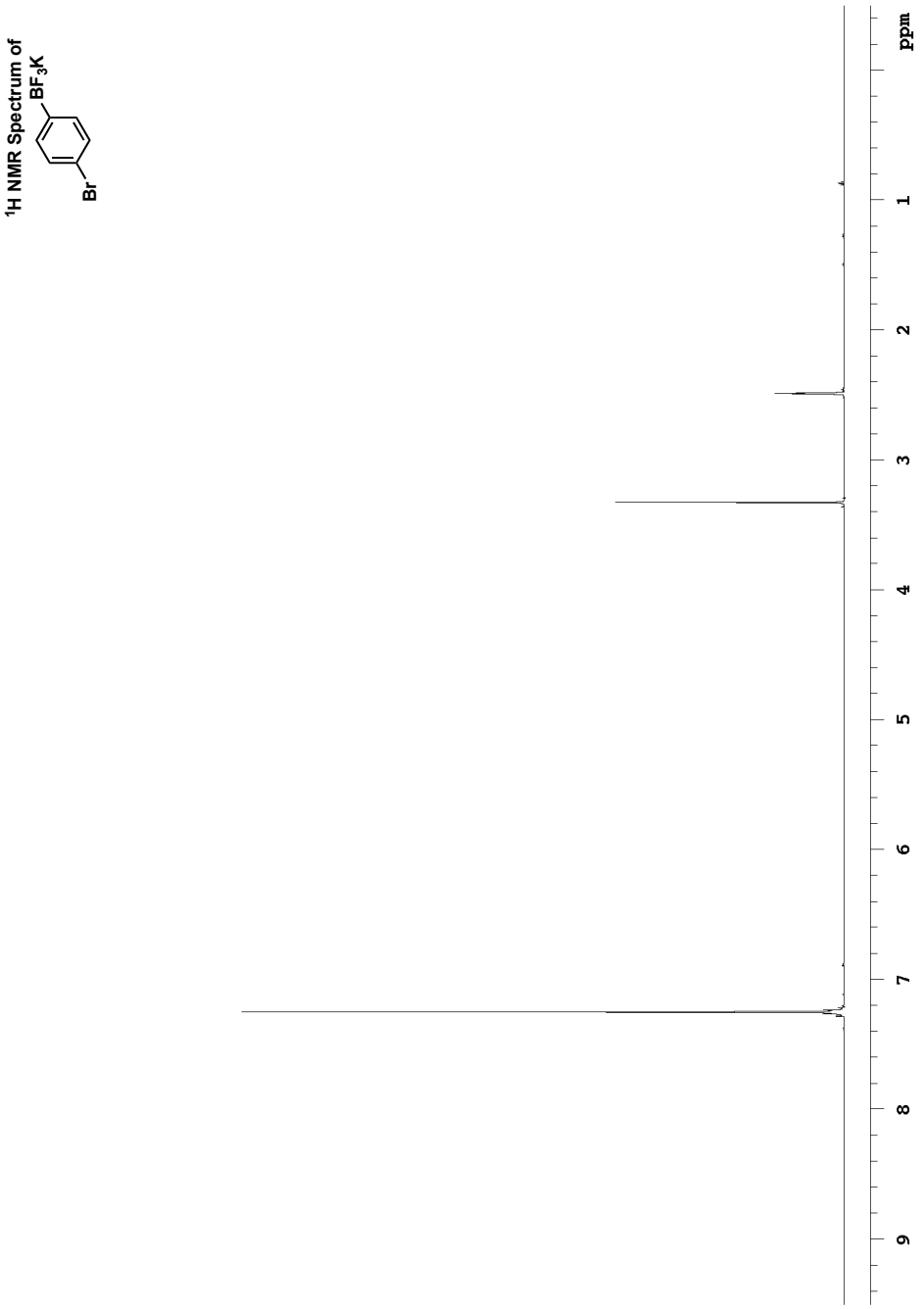
^{1}H NMR of **3i**. DMSO-d_6, 600 MHz, 23 °C



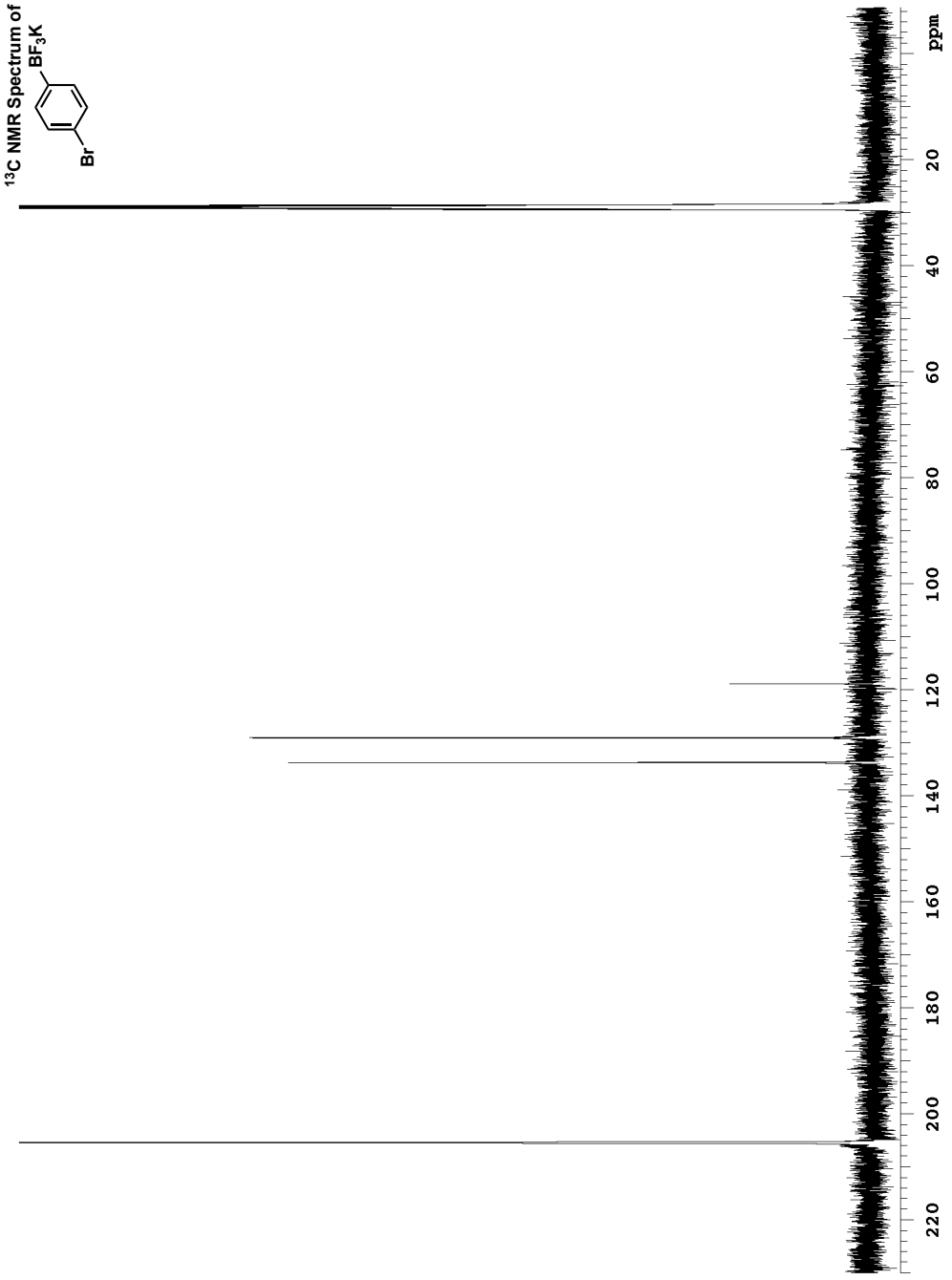
^{13}C NMR of **3i**. DMSO-d_6, 125 MHz, 23 °C



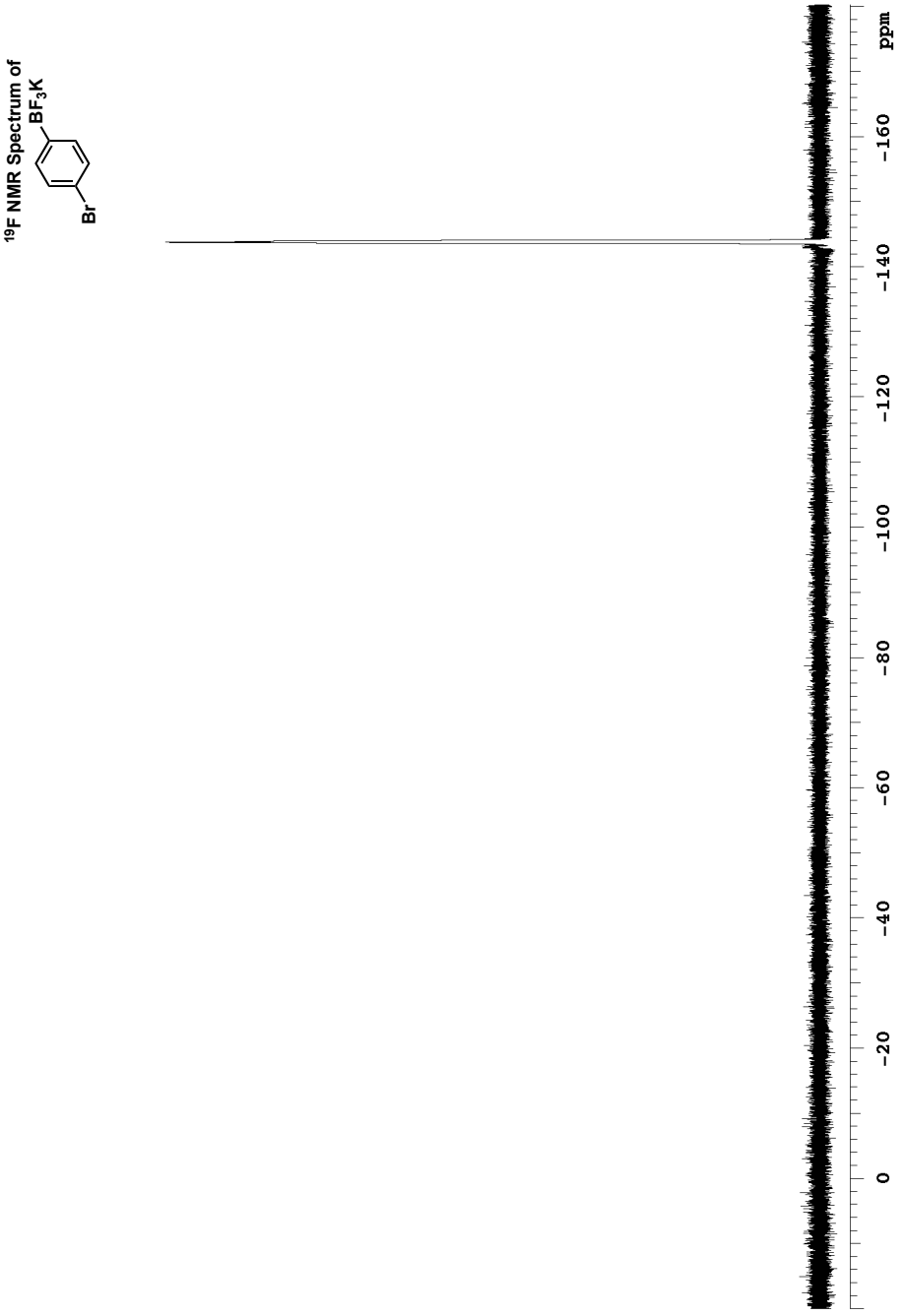
^{19}F NMR of **3i**. DMSO-d_6, 375 MHz, 23 °C



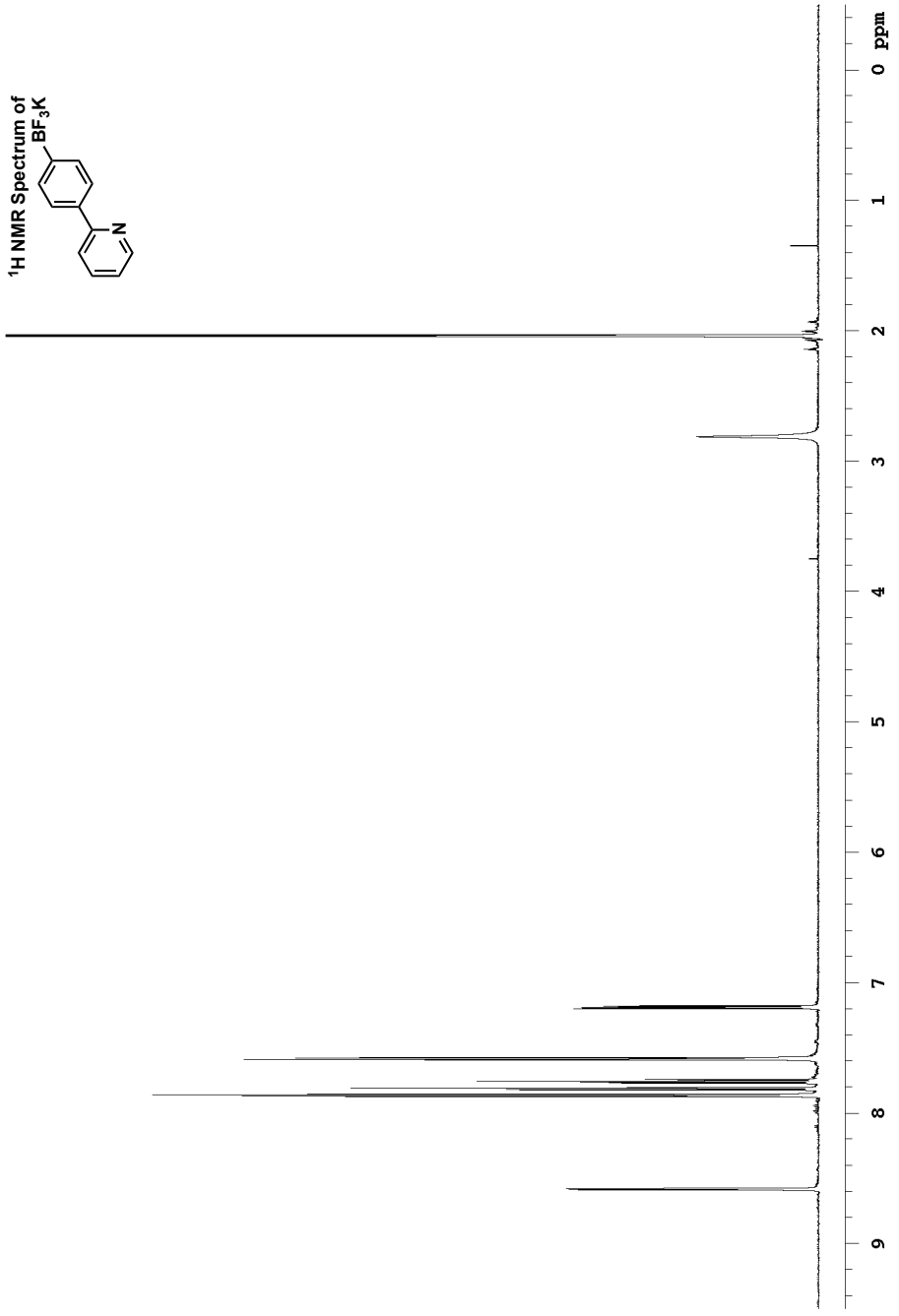
^{1}H NMR of **3l**. $CDCl_3$, 600 MHz, 23 °C



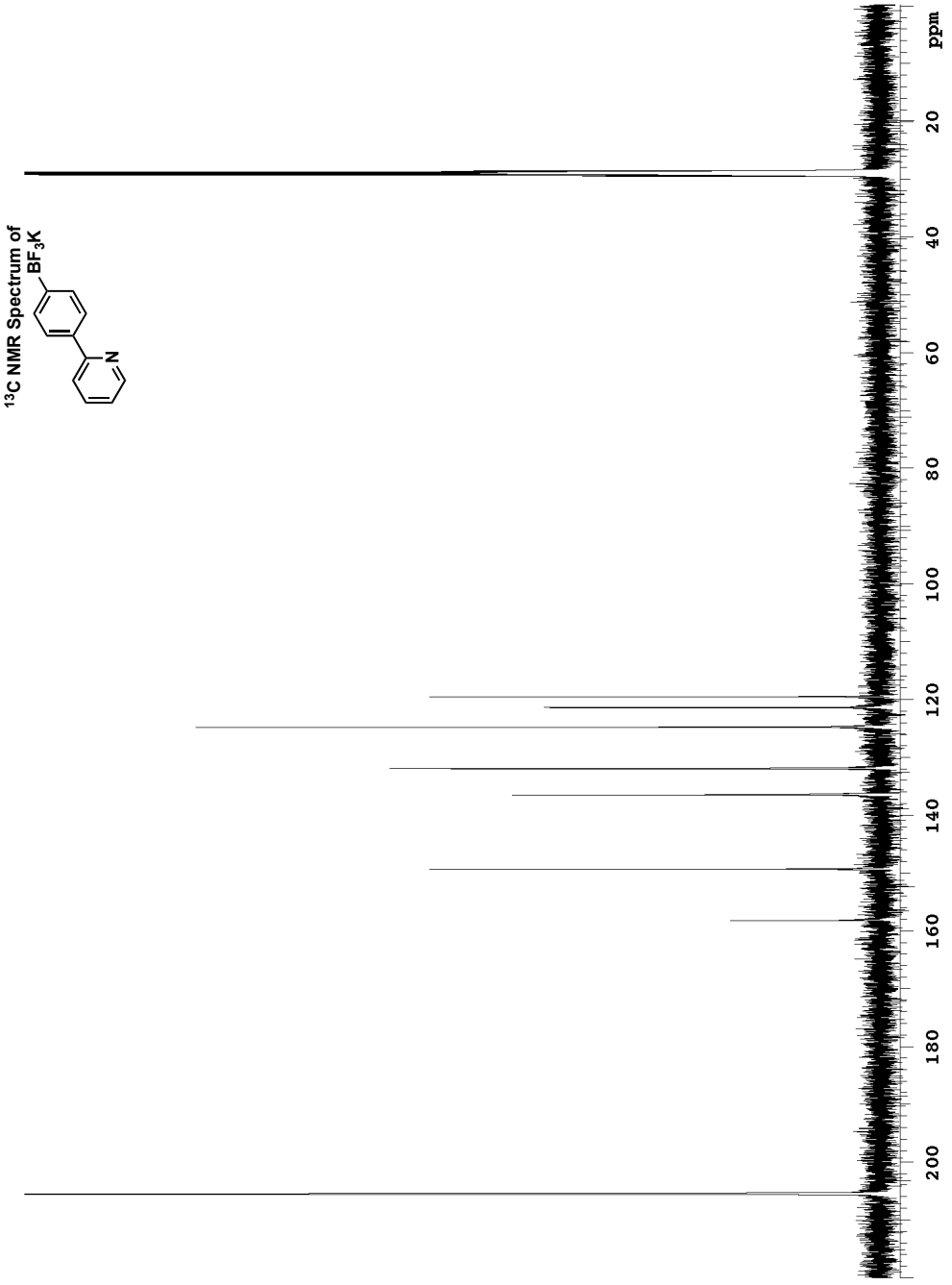
^{13}C NMR of **3l**. acetone-d_6, 125 MHz, 23 °C



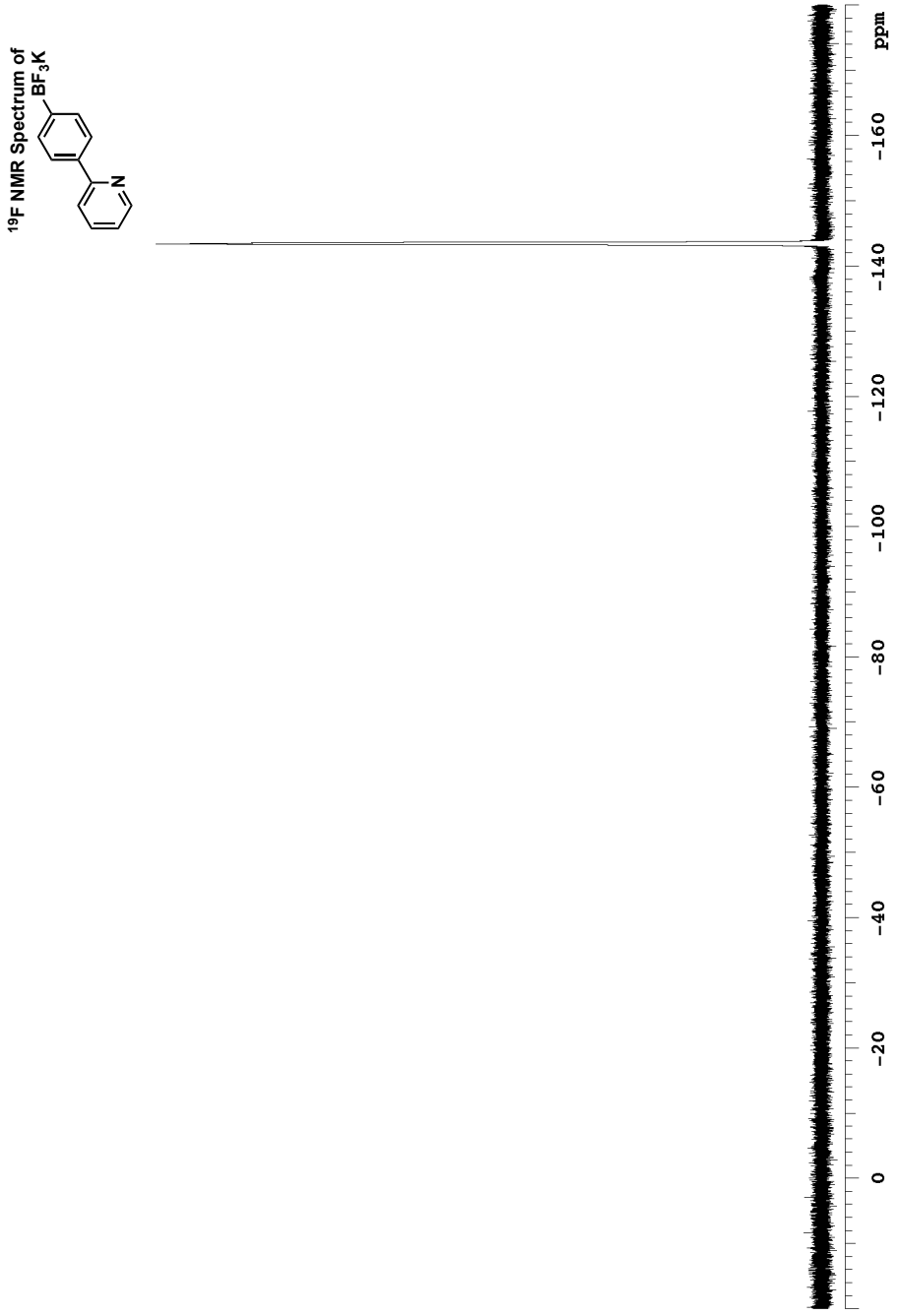
^{19}F NMR of **3l**. acetone-d_6, 375 MHz, 23 °C



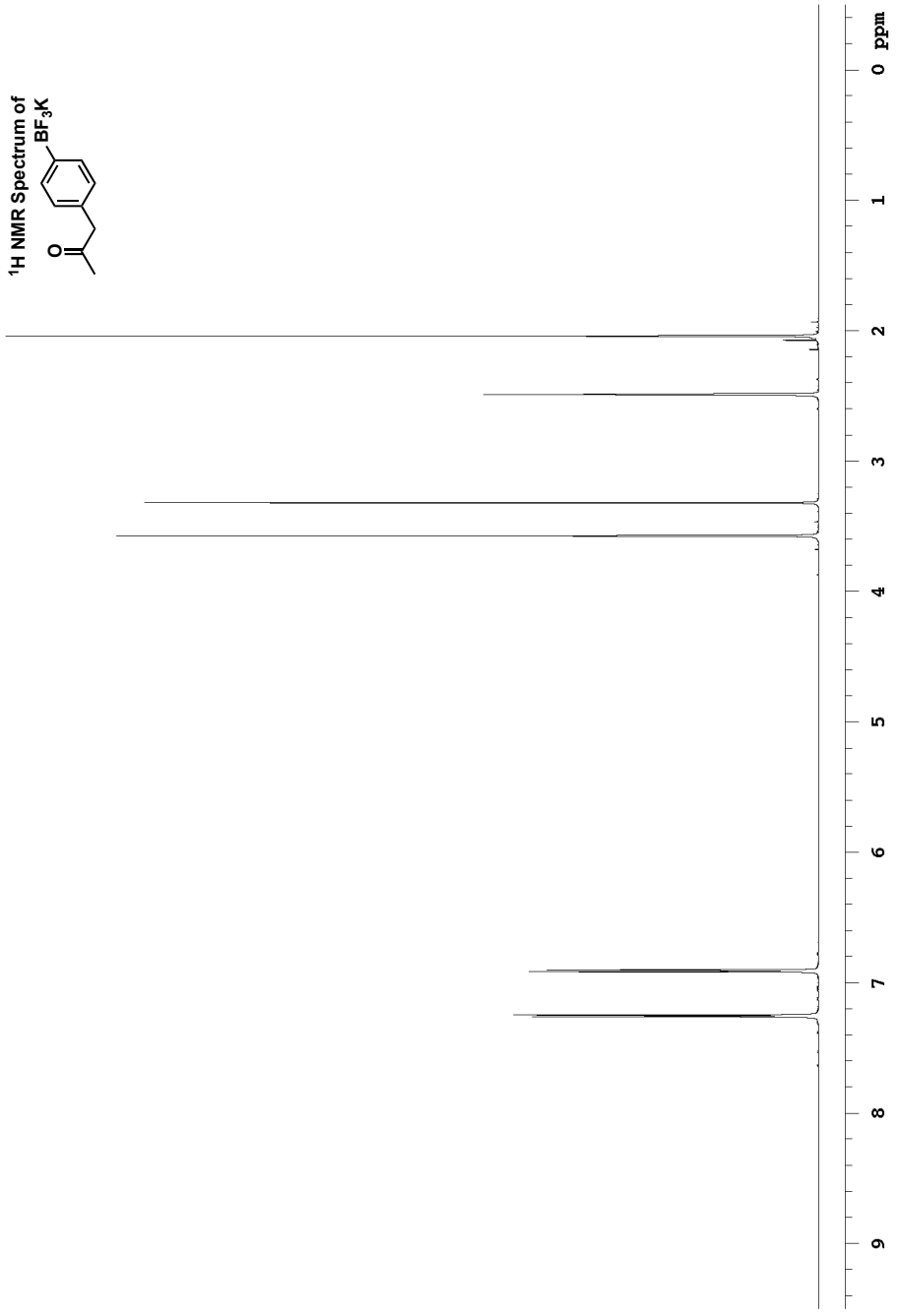
^{1}H NMR of **3m**. acetone-d_6, 600 MHz, 23 °C



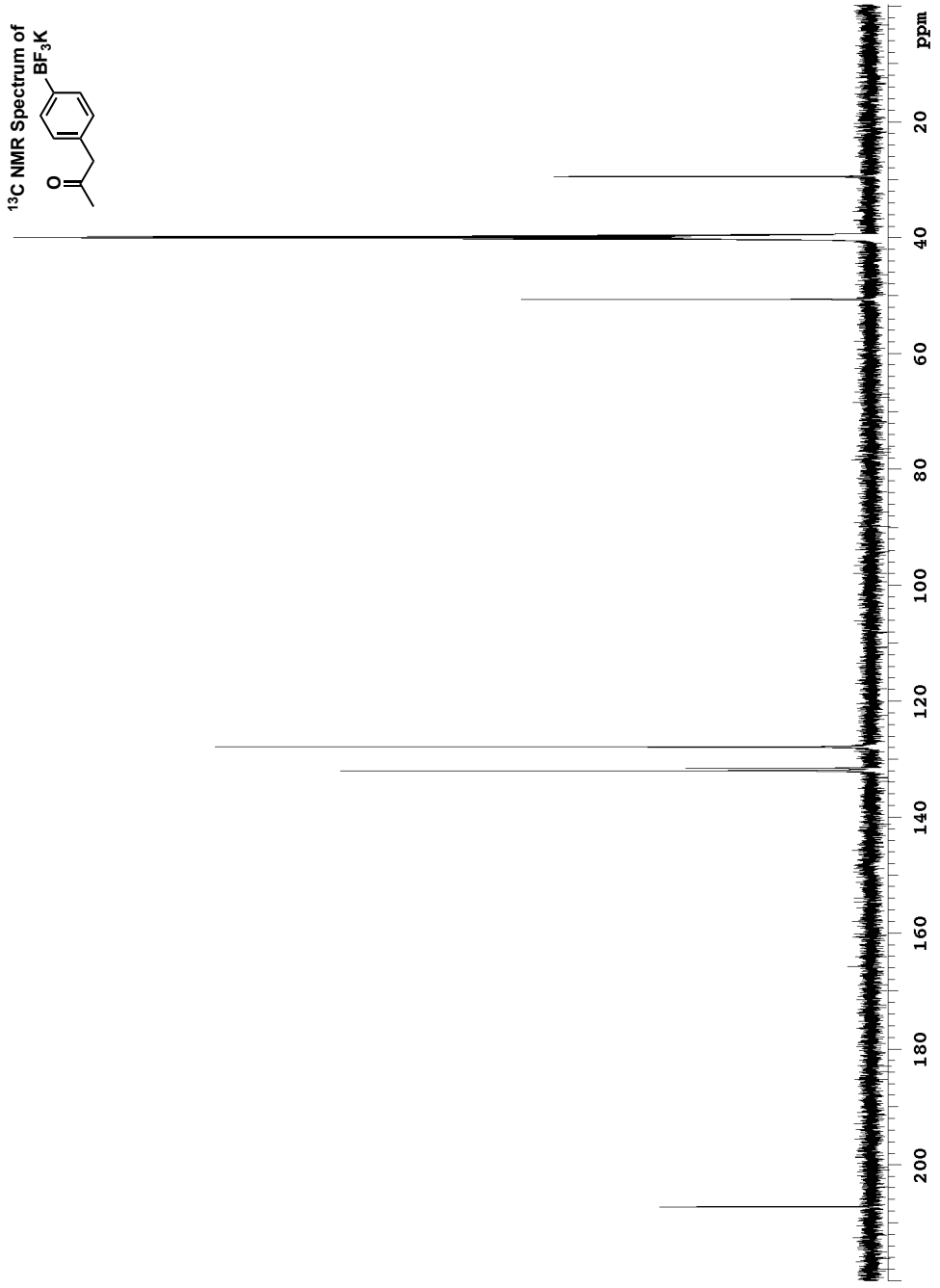
^{13}C NMR of **3m**. acetone-d_6, 125 MHz, 23 °C



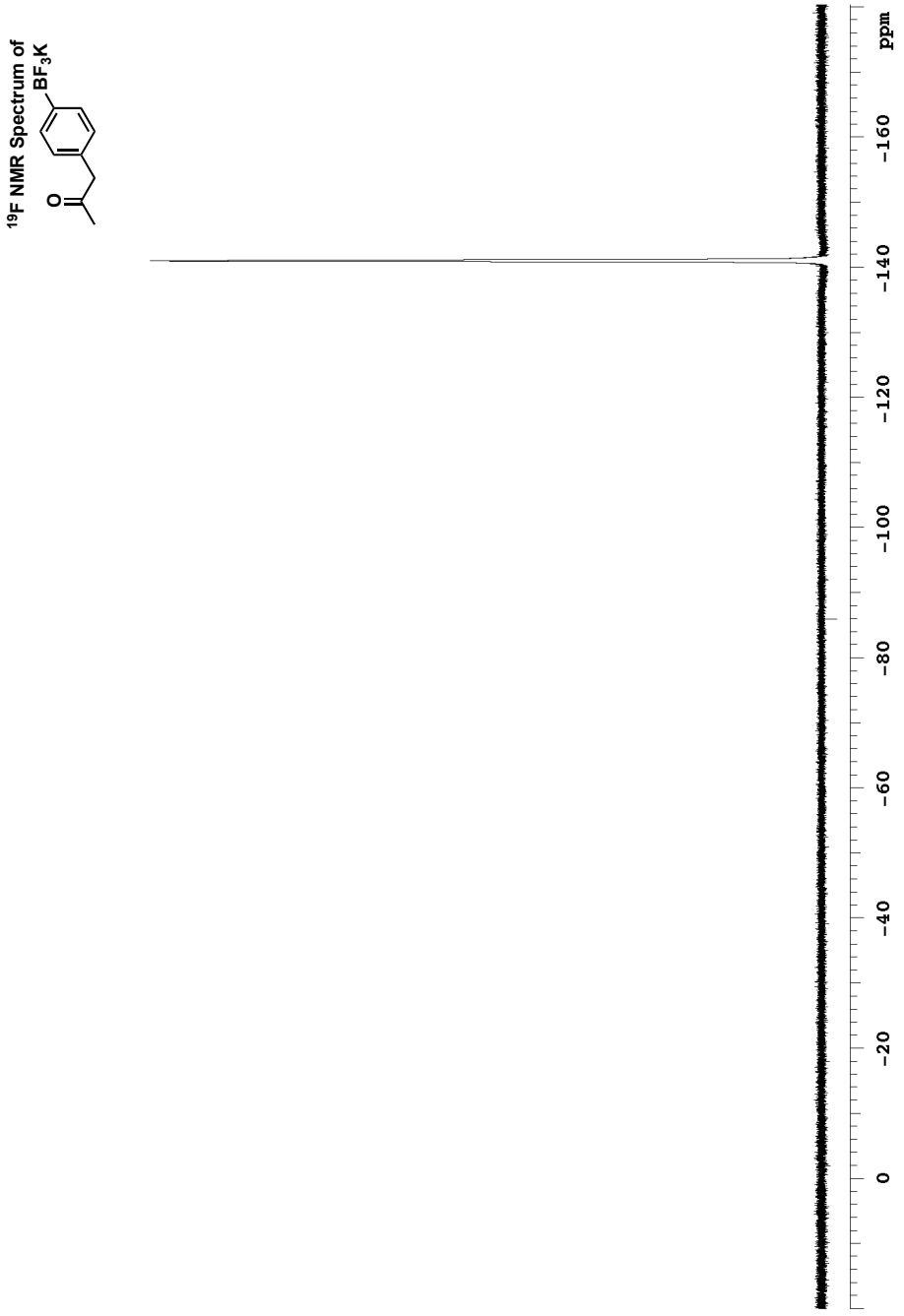
^{19}F NMR of **3m**. acetone-d_6, 375 MHz, 23 °C



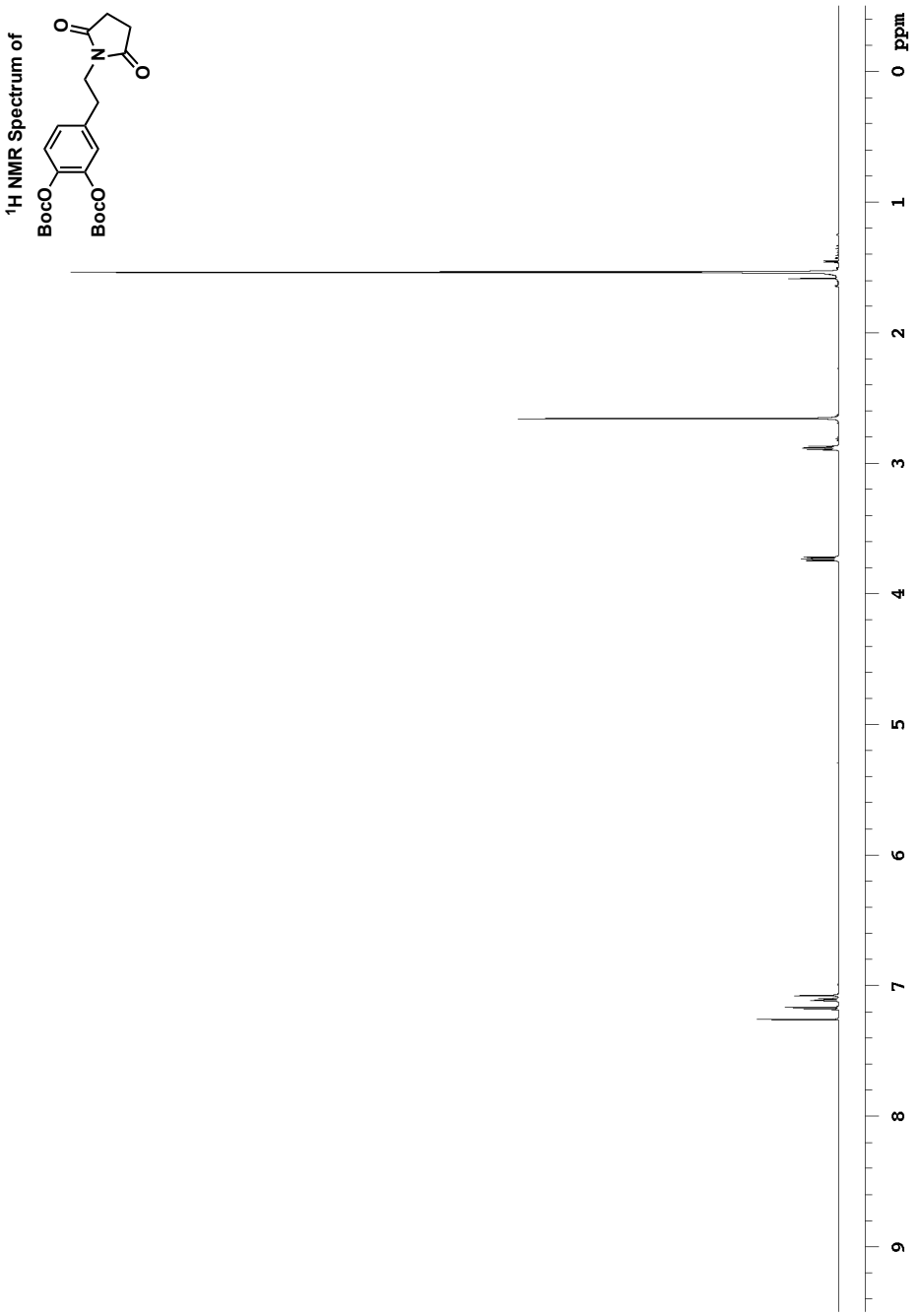
^{1}H NMR of **3n**. DMSO-d_6, 600 MHz, 23 °C



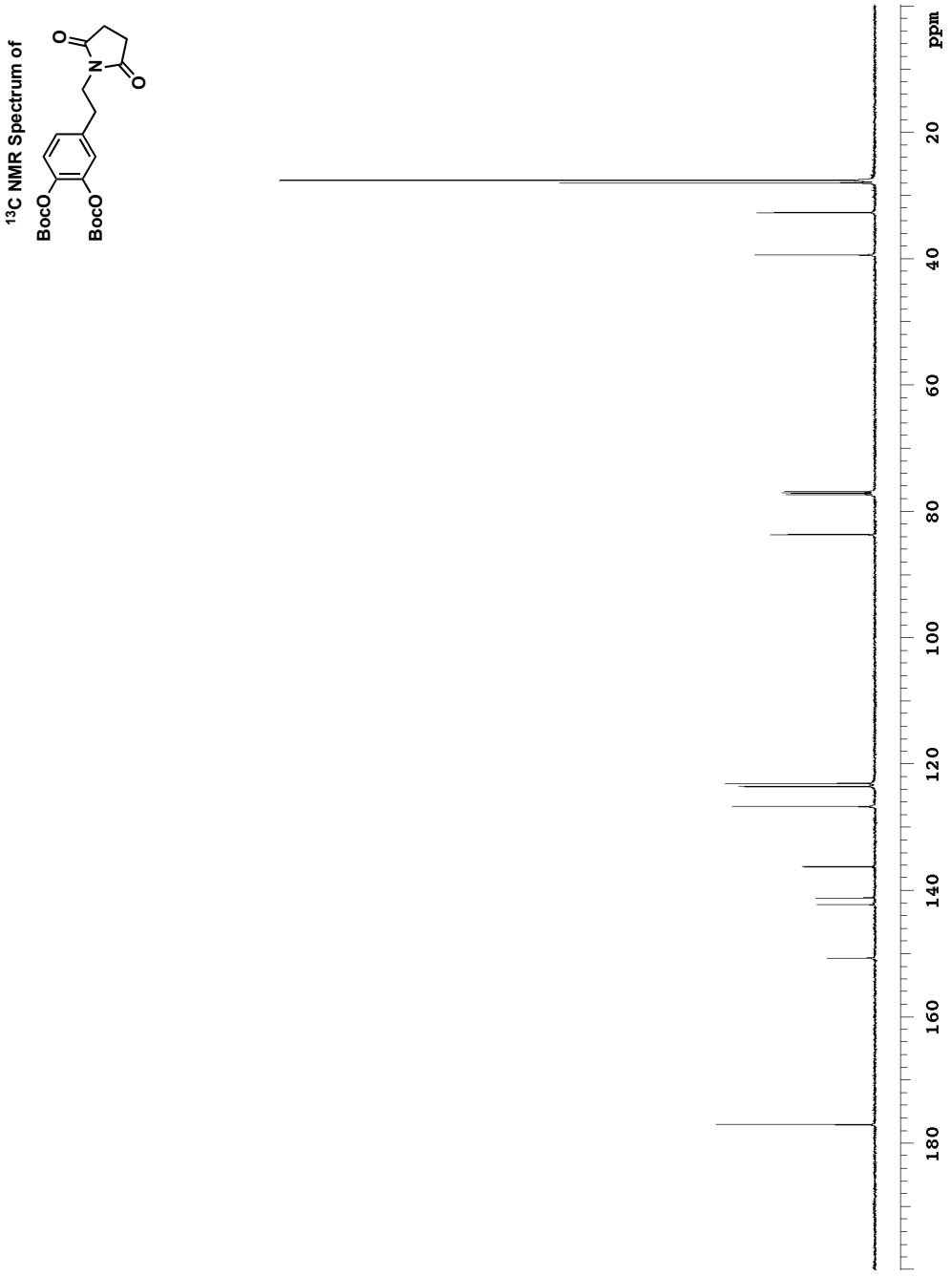
^{13}C NMR of **3n**. DMSO-d_6, 125 MHz, 23 °C



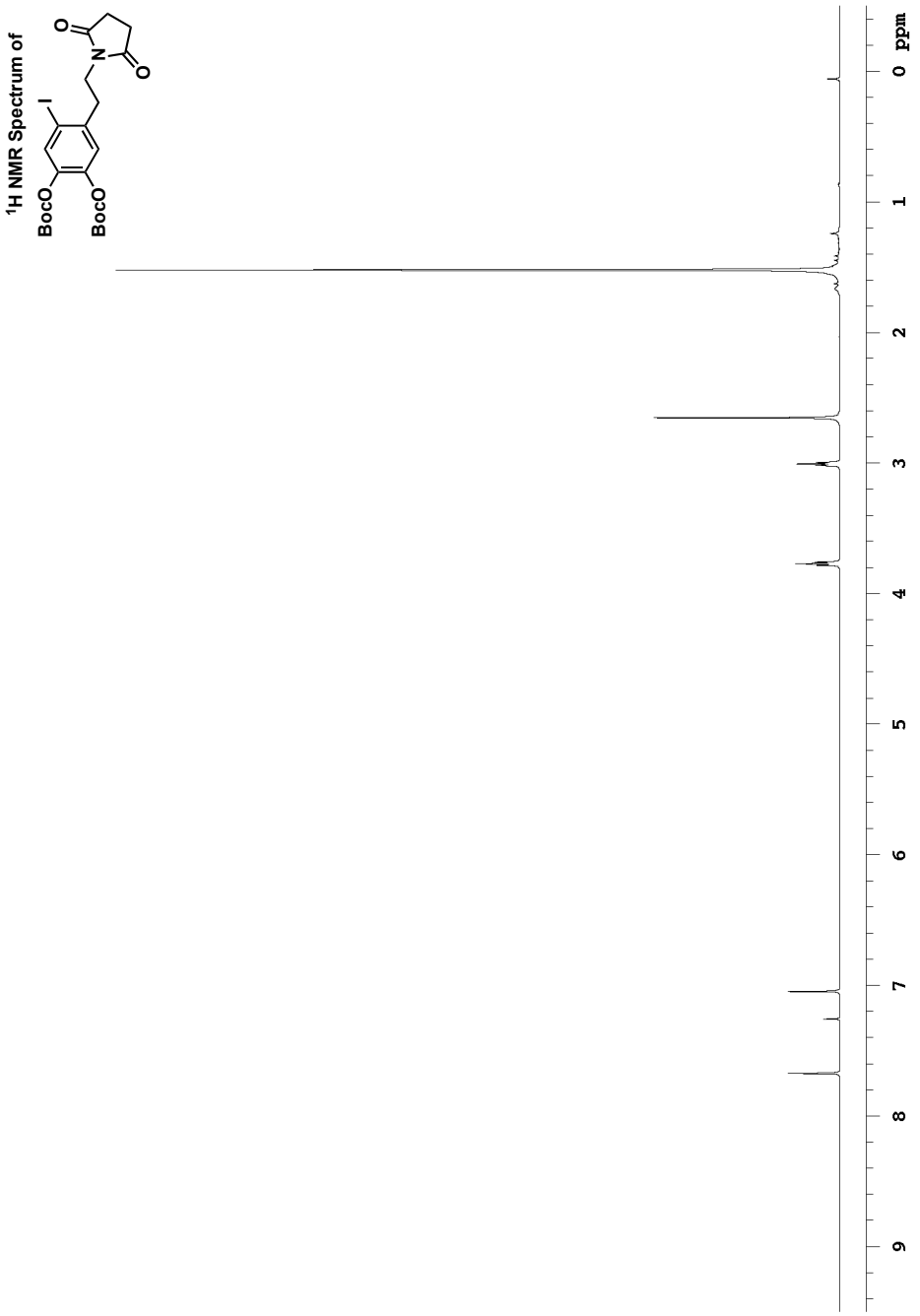
^{19}F NMR of **3n**. DMSO-d_6, 375 MHz, 23 °C



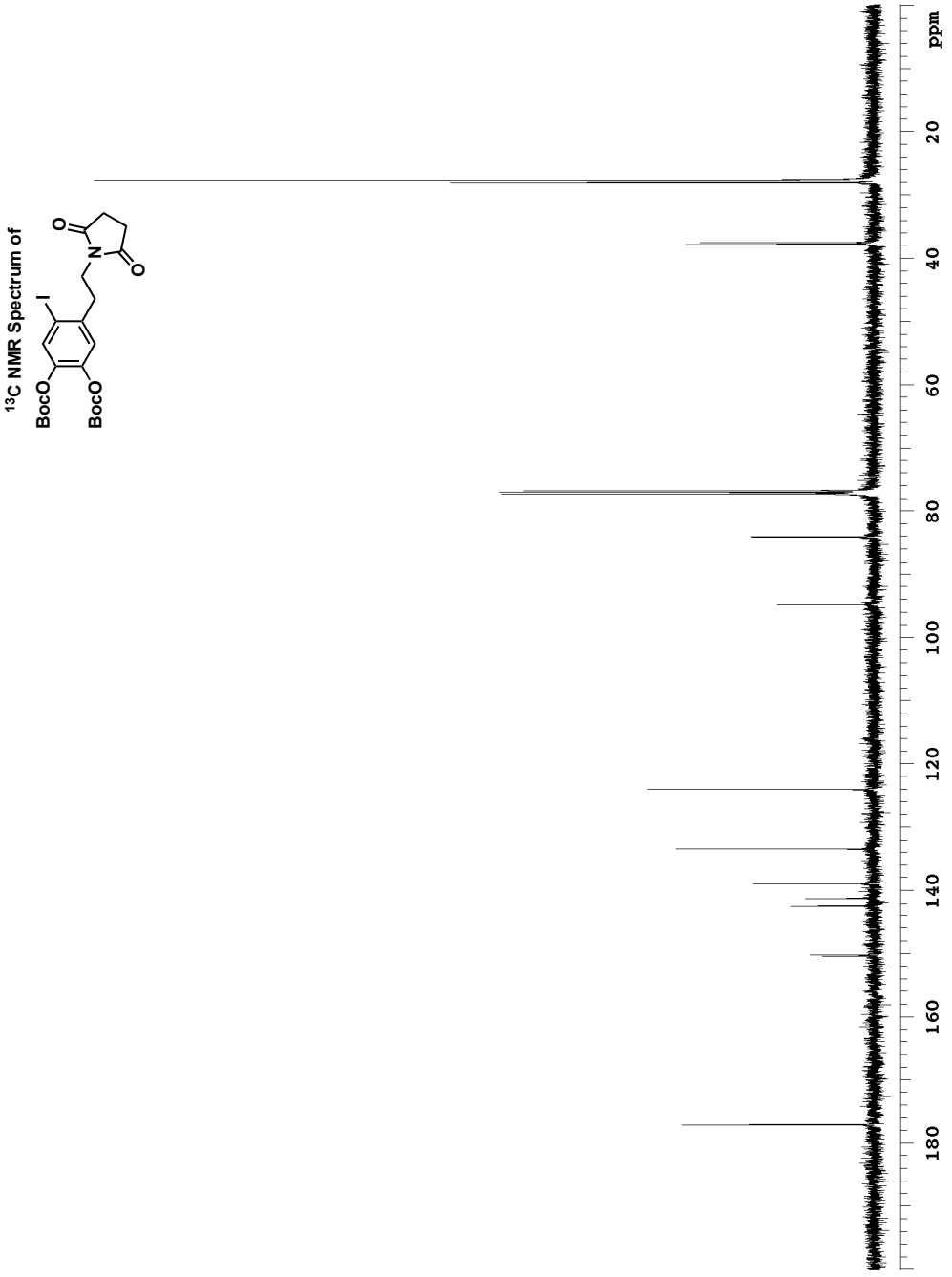
^{1}H NMR of **S4**. $CDCl_3$, 600 MHz, 23 °C



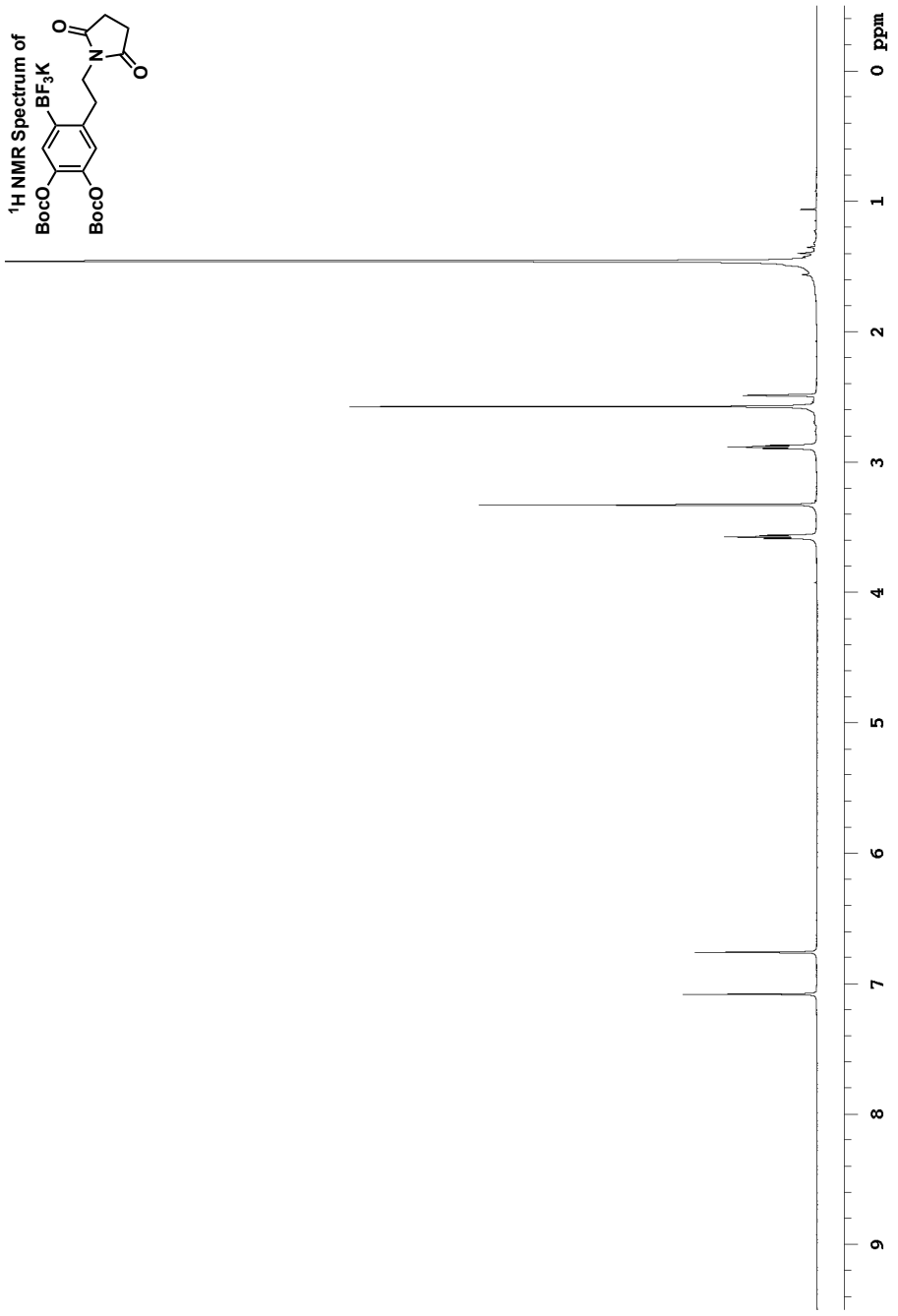
^{13}C NMR of **S4**. $CDCl_3$, 125 MHz, 23 °C



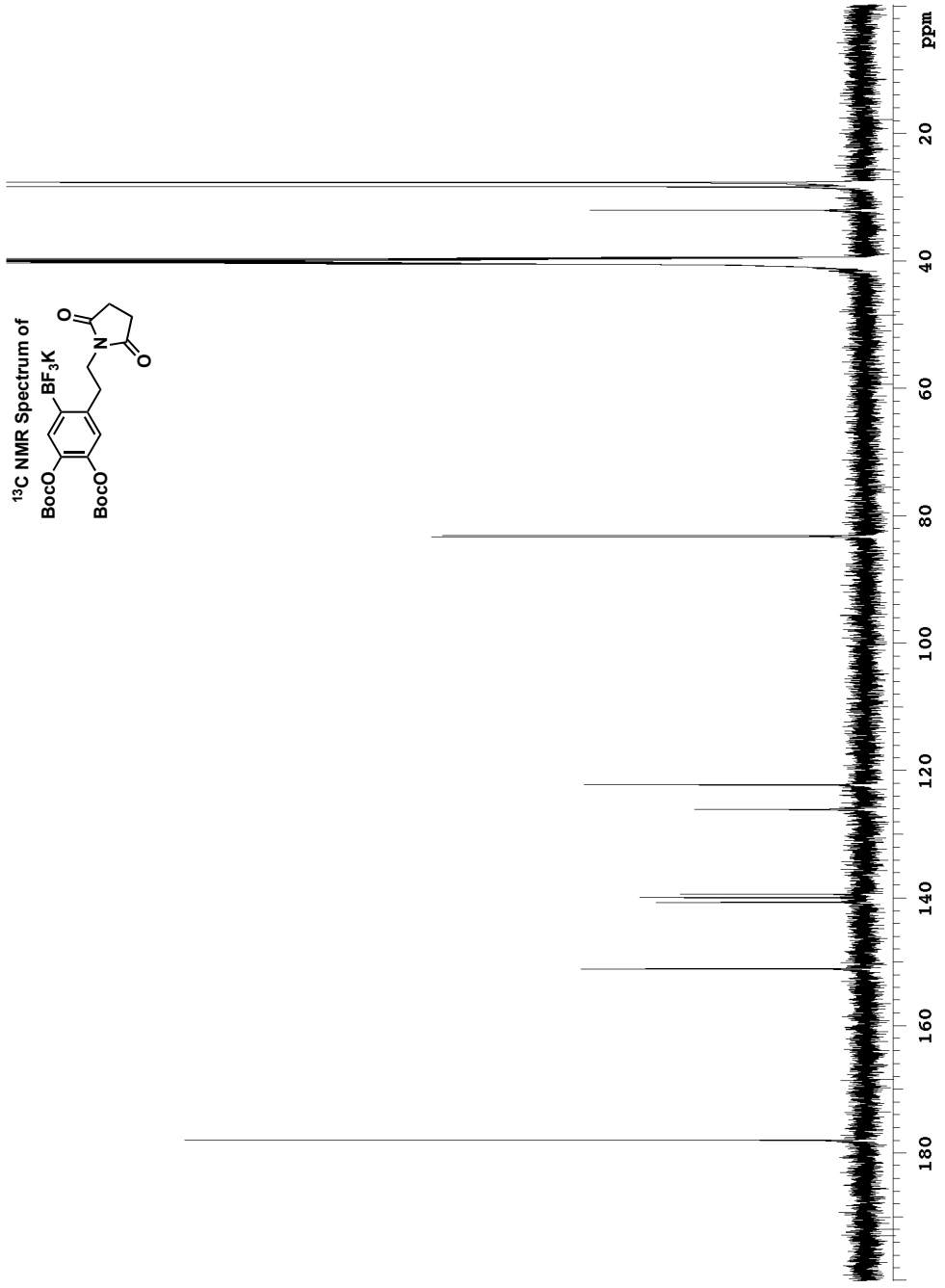
^{1}H NMR of **S5**. $CDCl_3$, 600 MHz, 23 °C



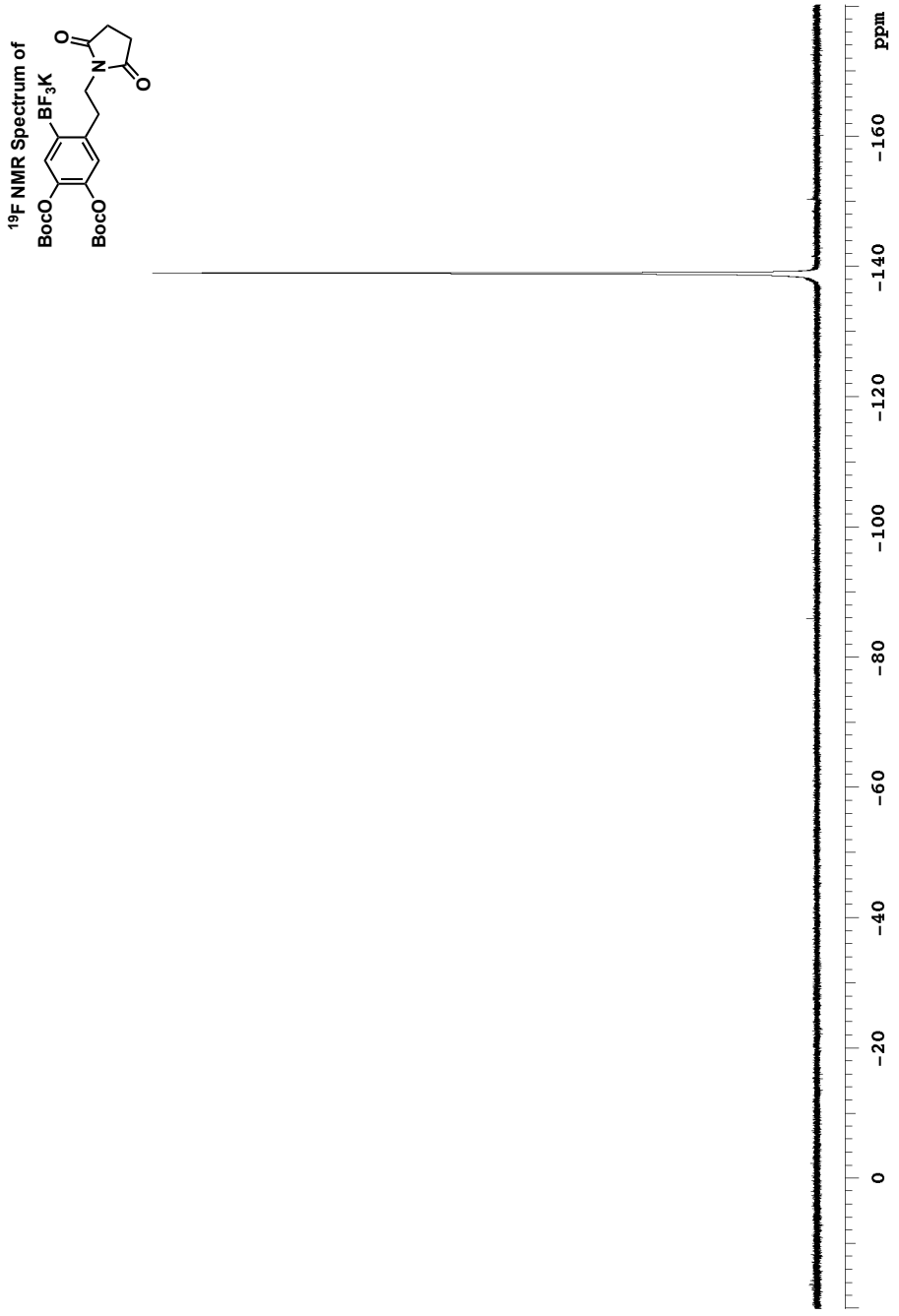
^{13}C NMR of **S5**. $CDCl_3$, 125 MHz, 23 °C



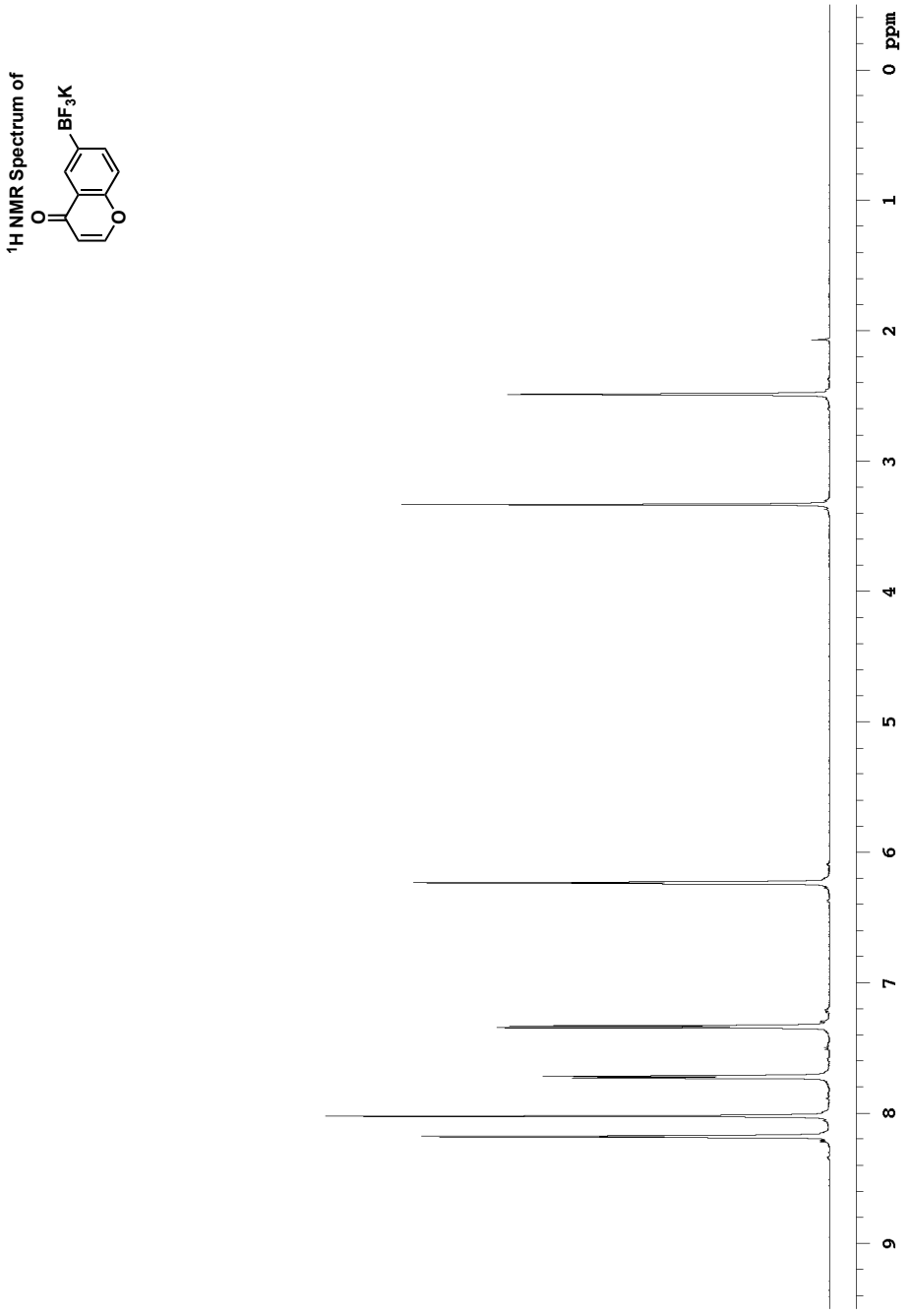
^{1}H NMR of **3o**. DMSO-d_6, 600 MHz, 23 °C



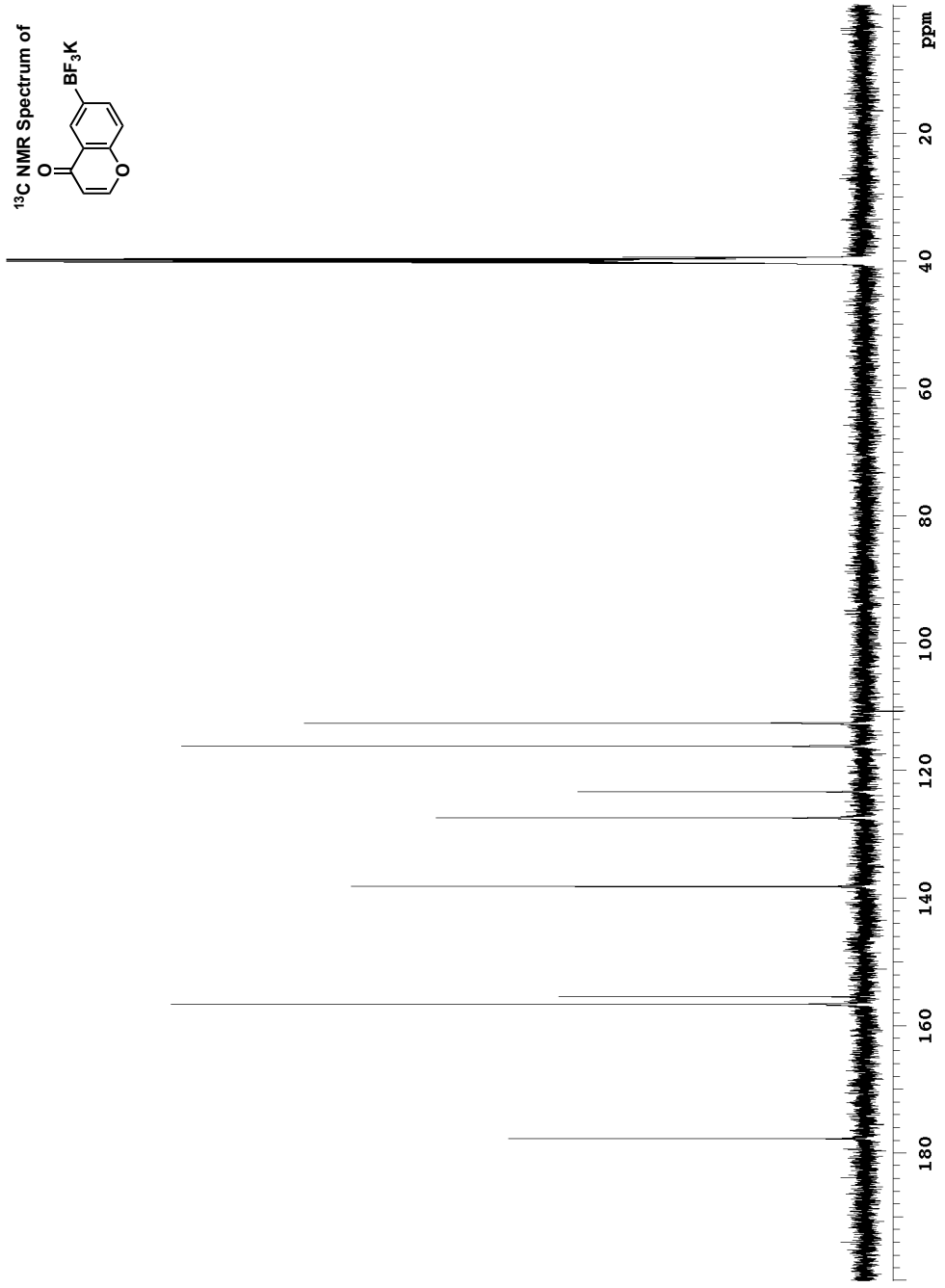
^{13}C NMR of **3o**. DMSO-d_6, 125 MHz, 23 °C



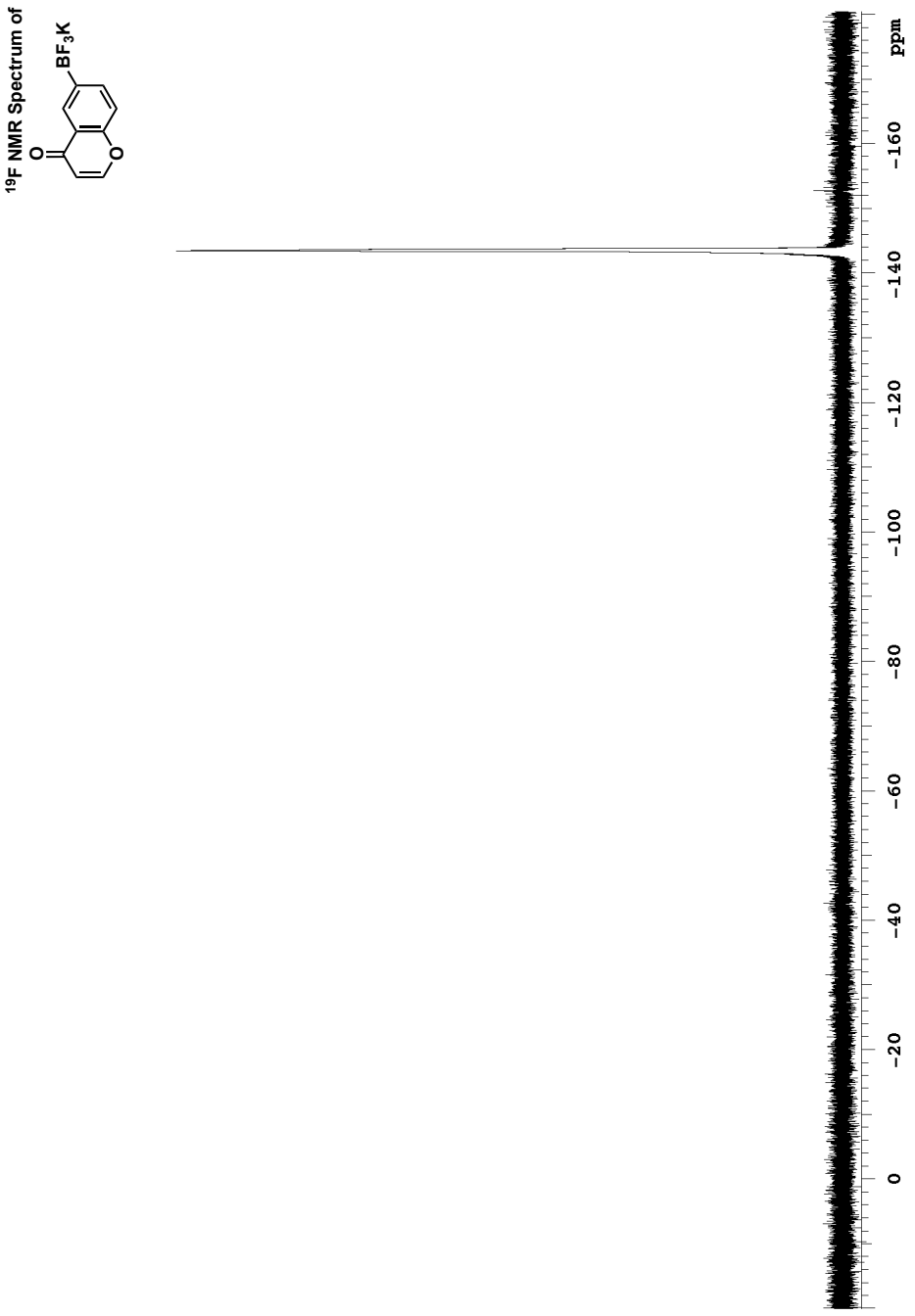
^{19}F NMR of **3o**. DMSO-d_6, 375 MHz, 23 °C



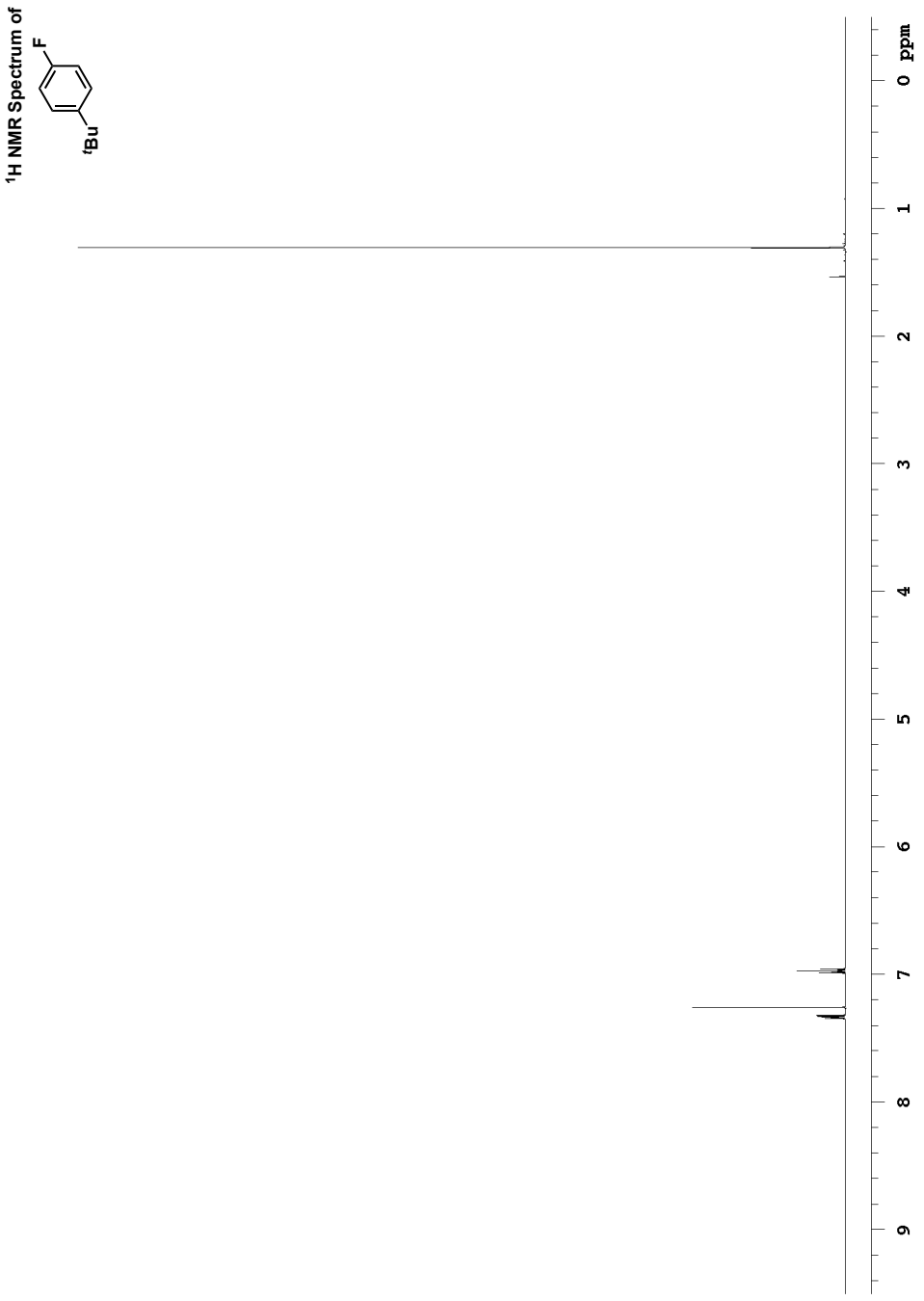
^{1}H NMR of **3p**. DMSO-d_6, 600 MHz, 23 °C



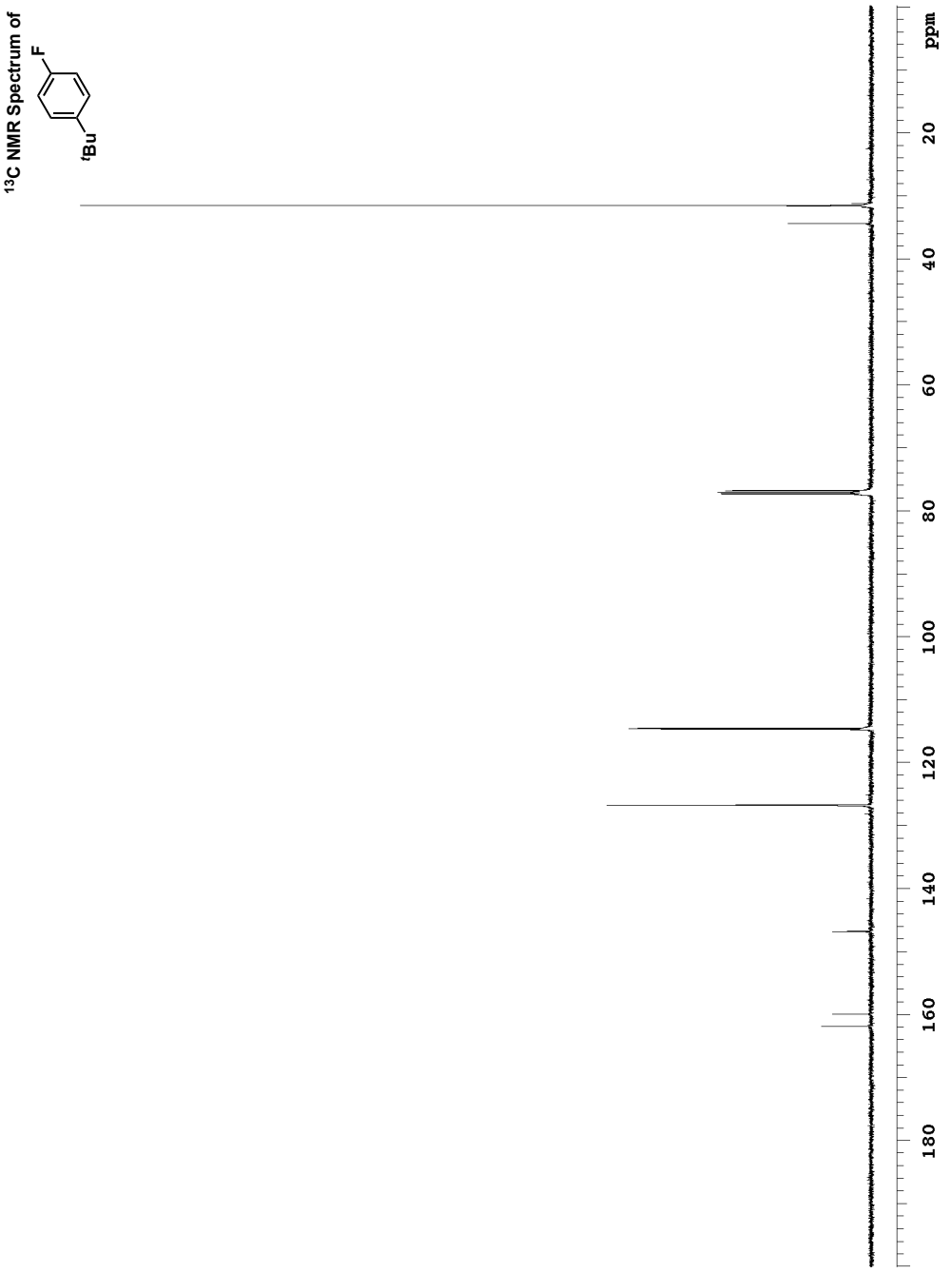
^{13}C NMR of **3p**. DMSO-d_6, 125 MHz, 23 °C



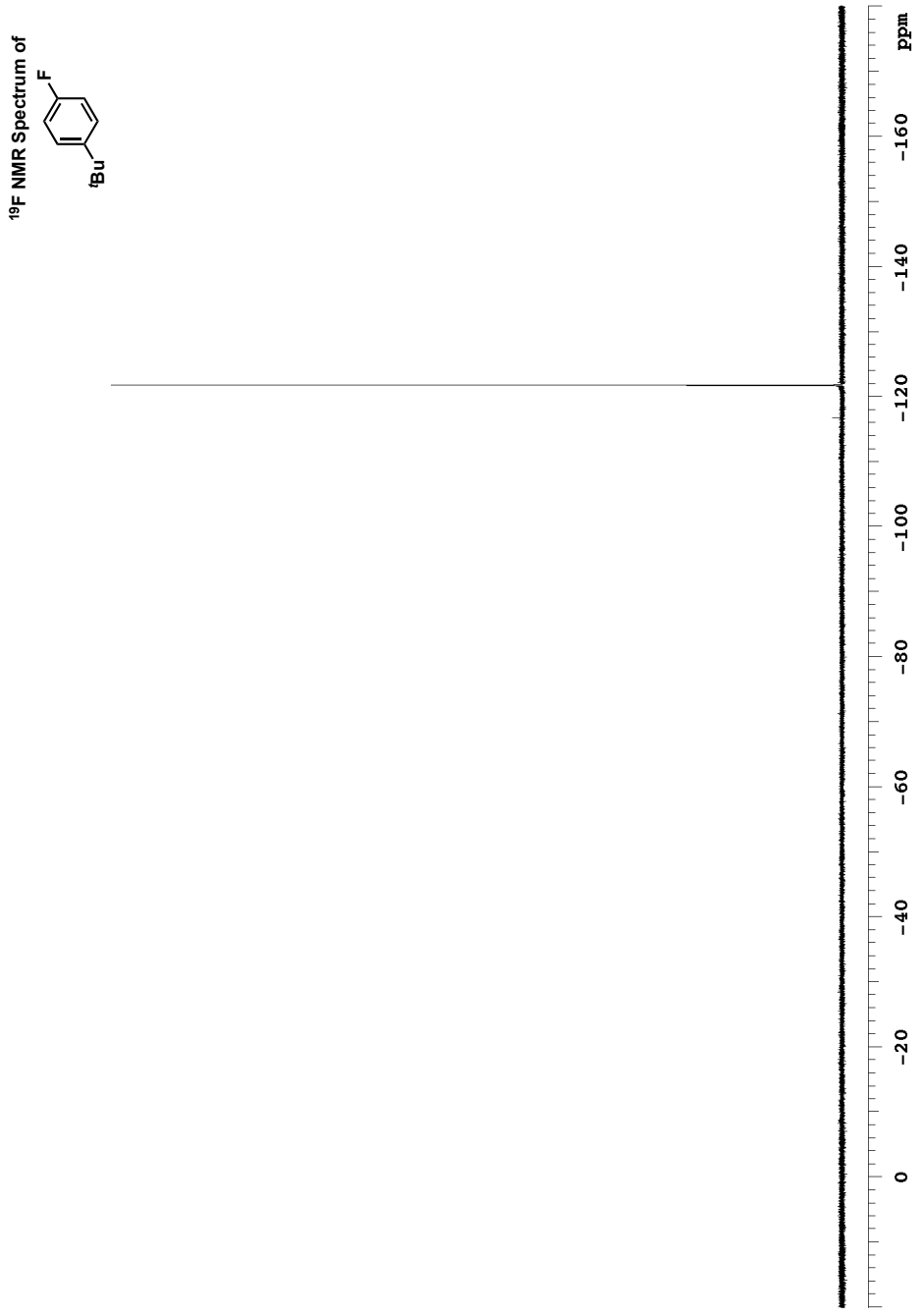
^{19}F NMR of **3p**. DMSO-d_6, 375 MHz, 23 °C



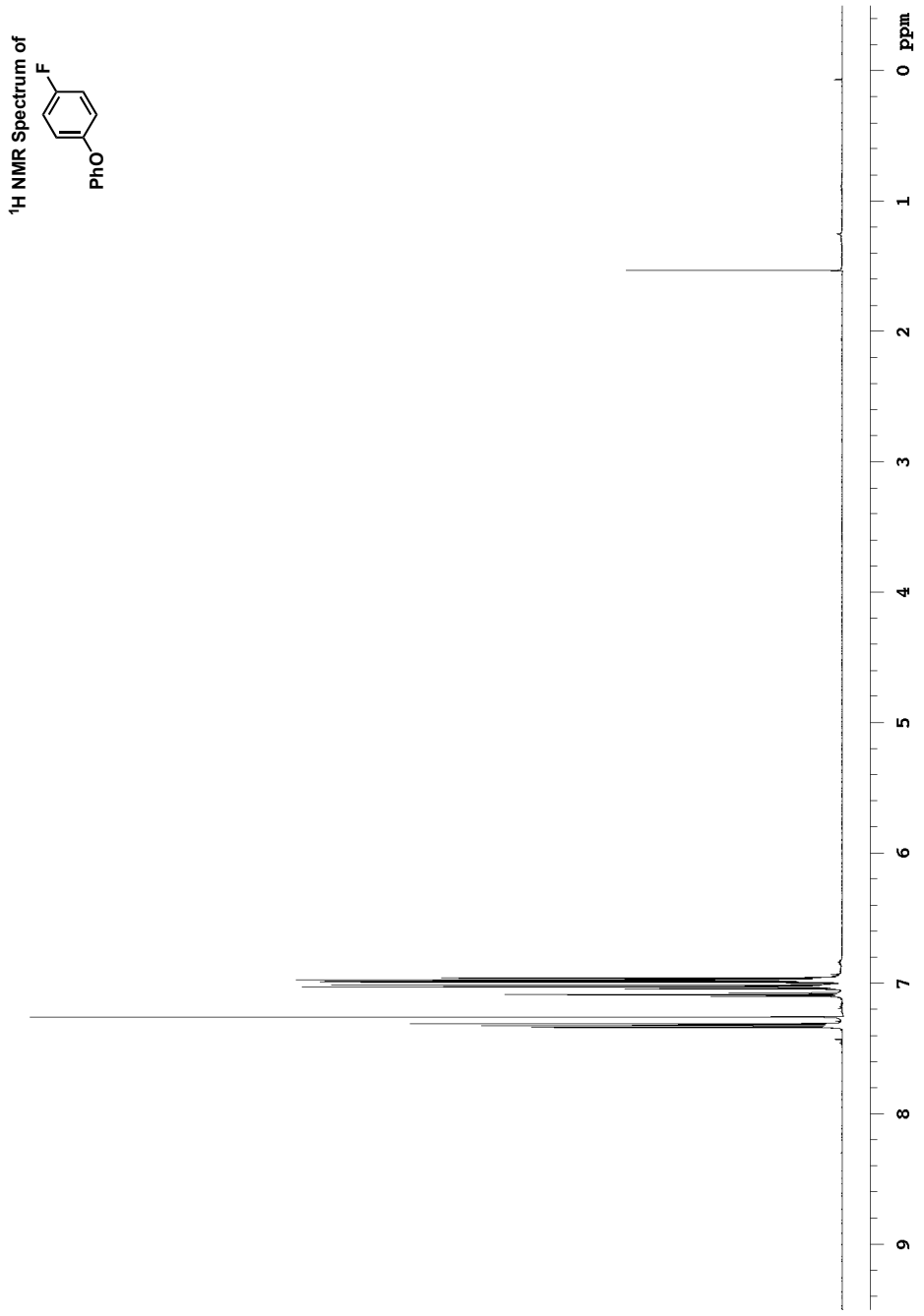
^{1}H NMR of **4a**. $CDCl_3$, 600 MHz, 23 °C



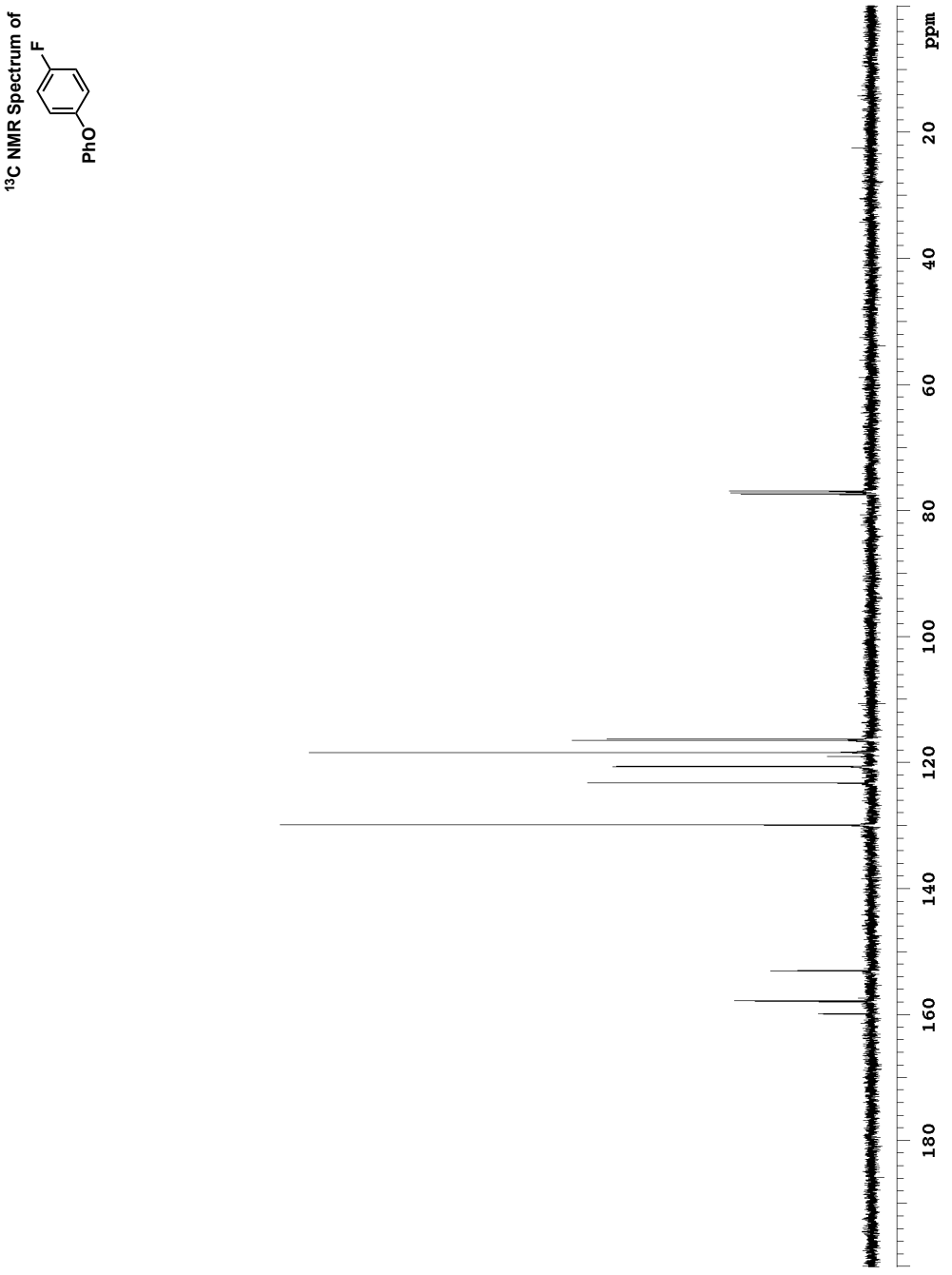
^{13}C NMR of **4a**. $CDCl_3$, 125 MHz, 23 °C



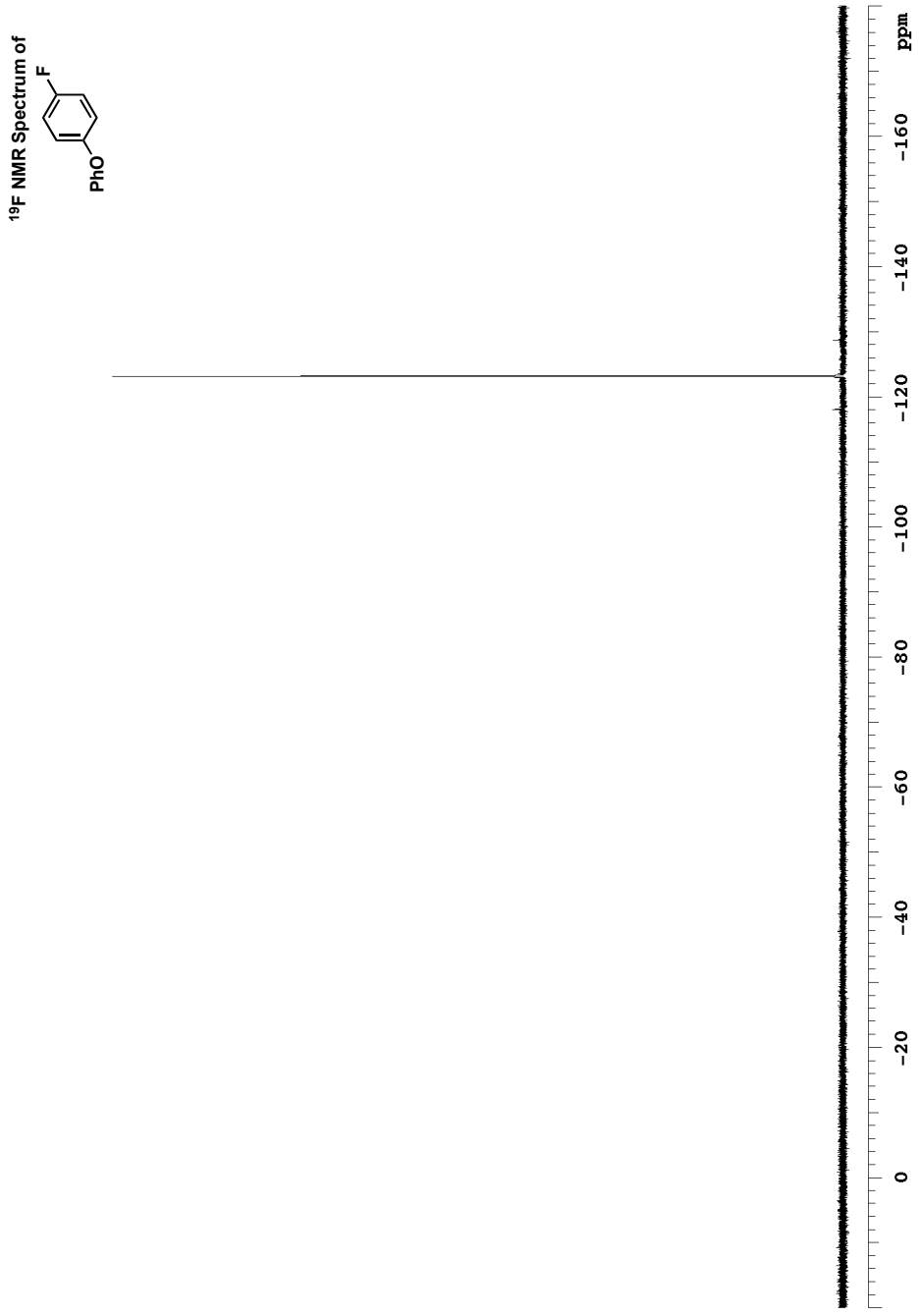
^{19}F NMR of **4a**. $CDCl_3$, 375 MHz, 23 °C



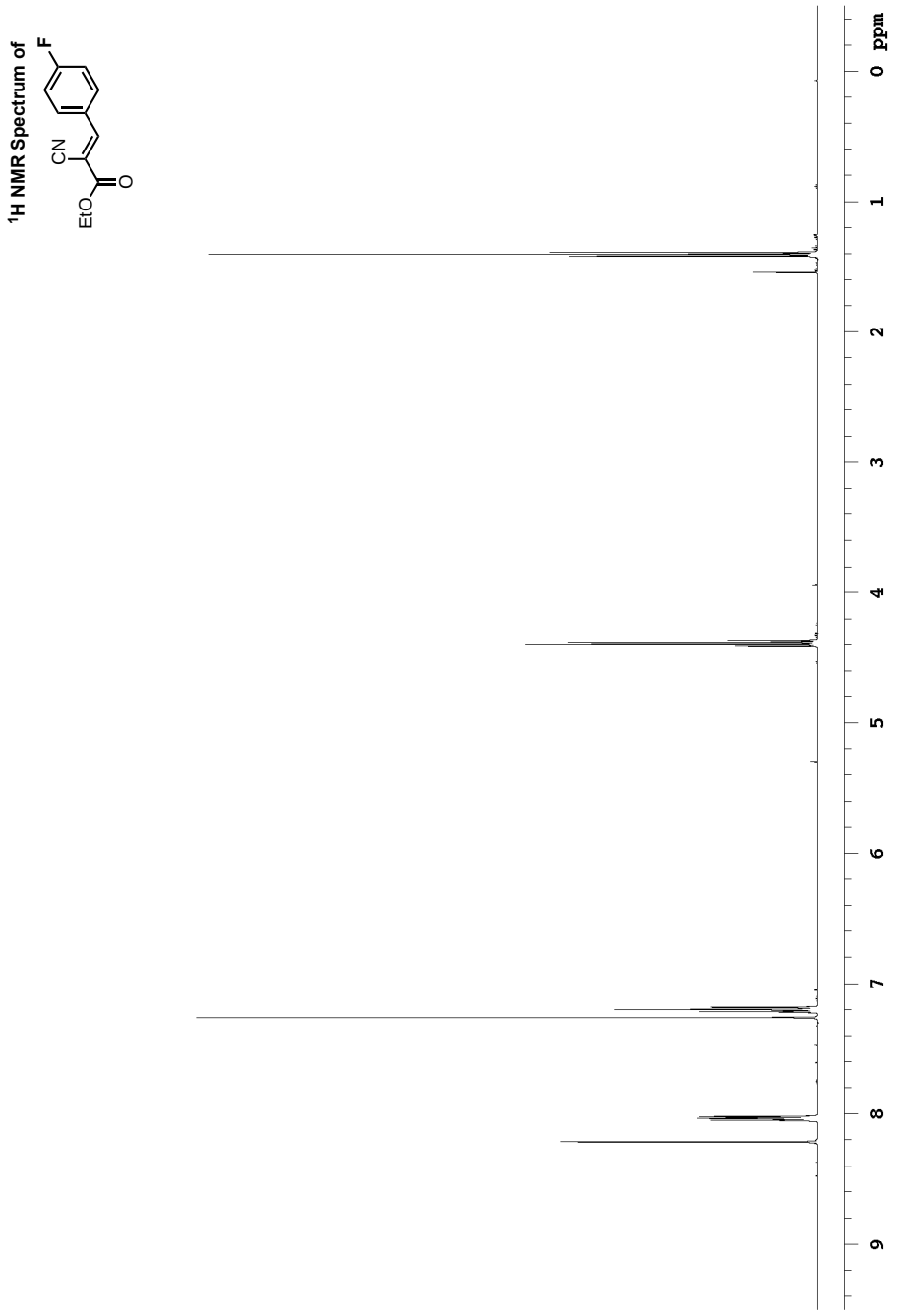
^{1}H NMR of **4b**. $CDCl_3$, 600 MHz, 23 °C



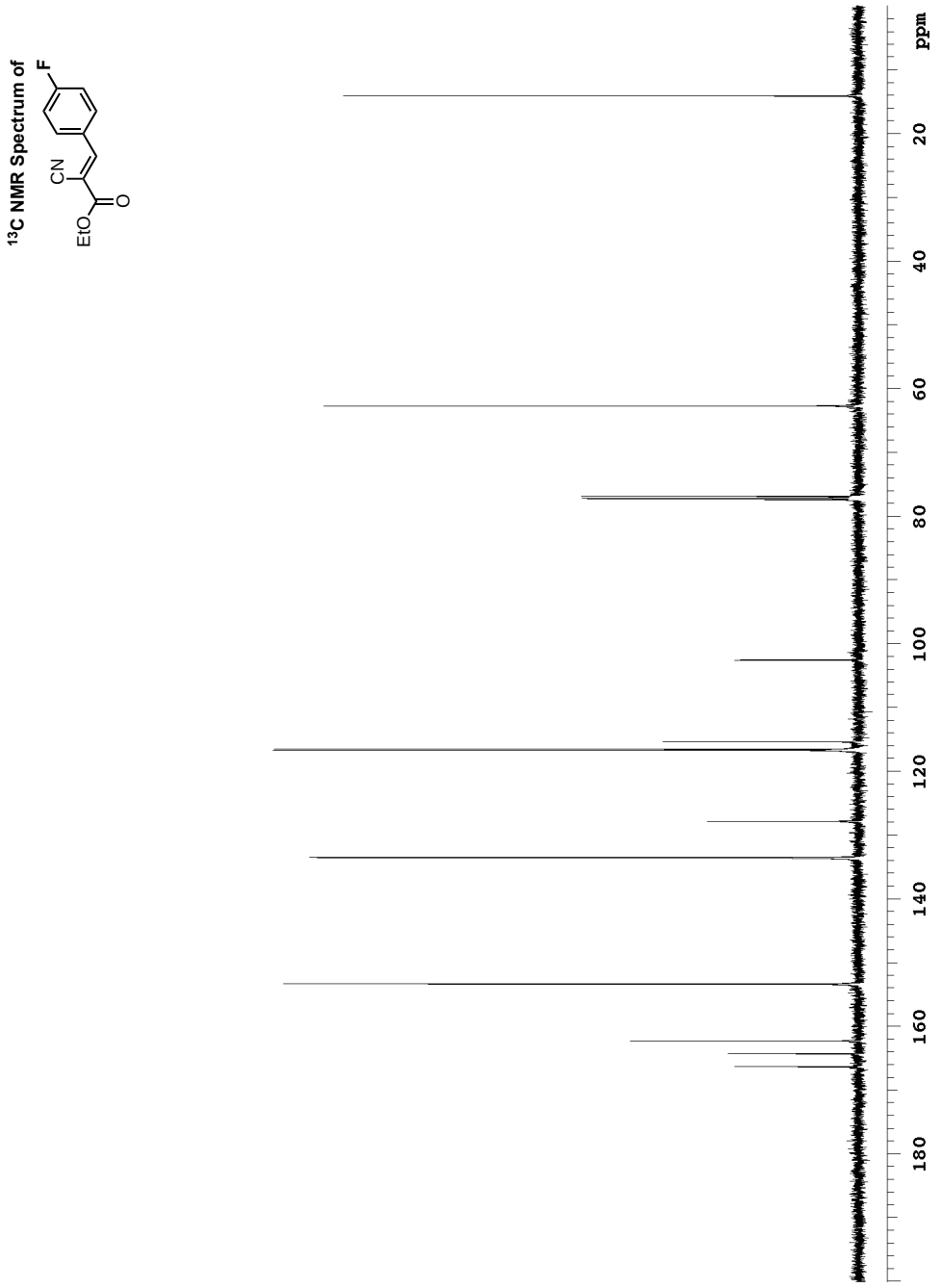
^{13}C NMR of **4b**. $CDCl_3$, 125 MHz, 23 °C



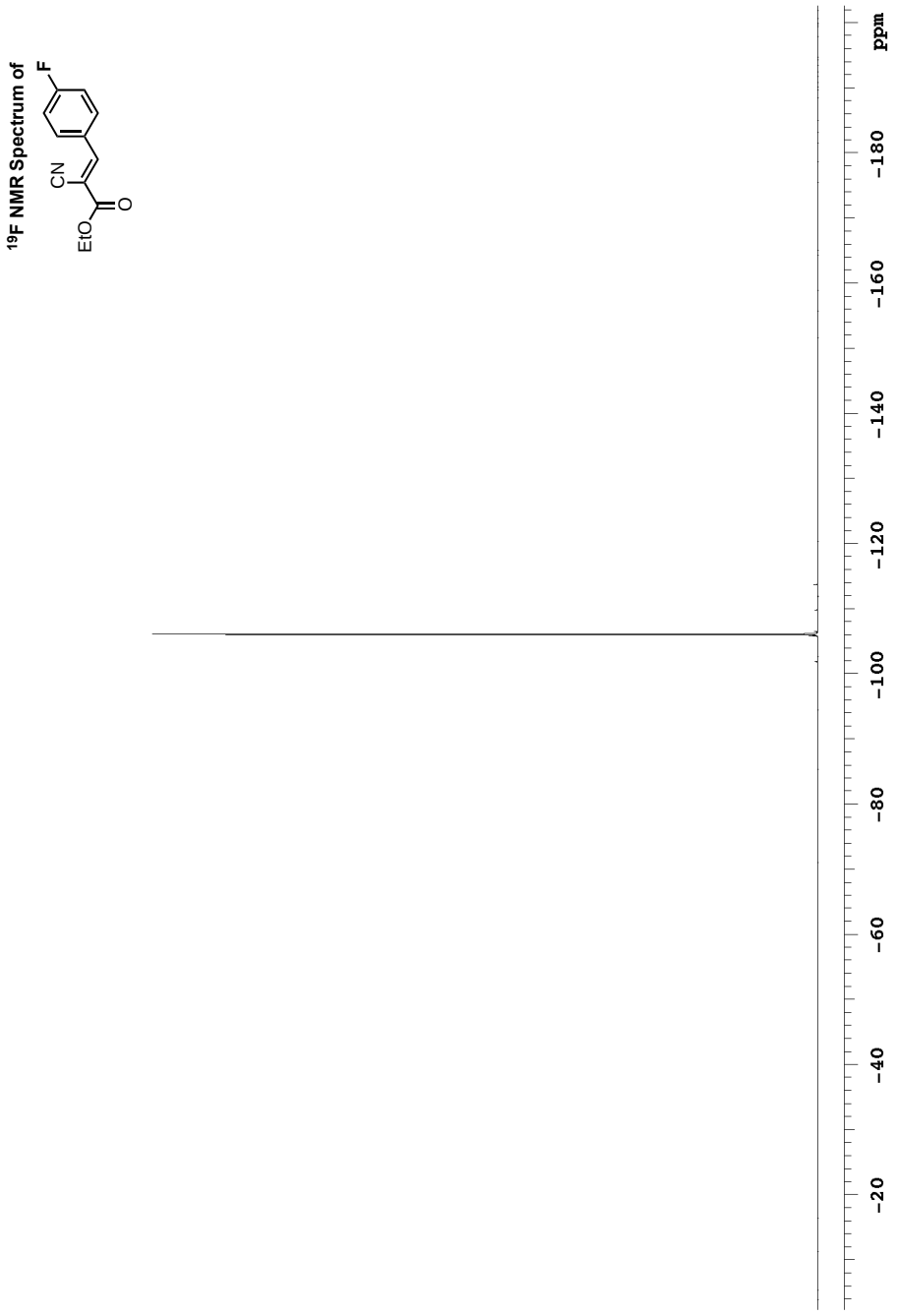
^{19}F NMR of **4b**. $CDCl_3$, 375 MHz, 23 °C



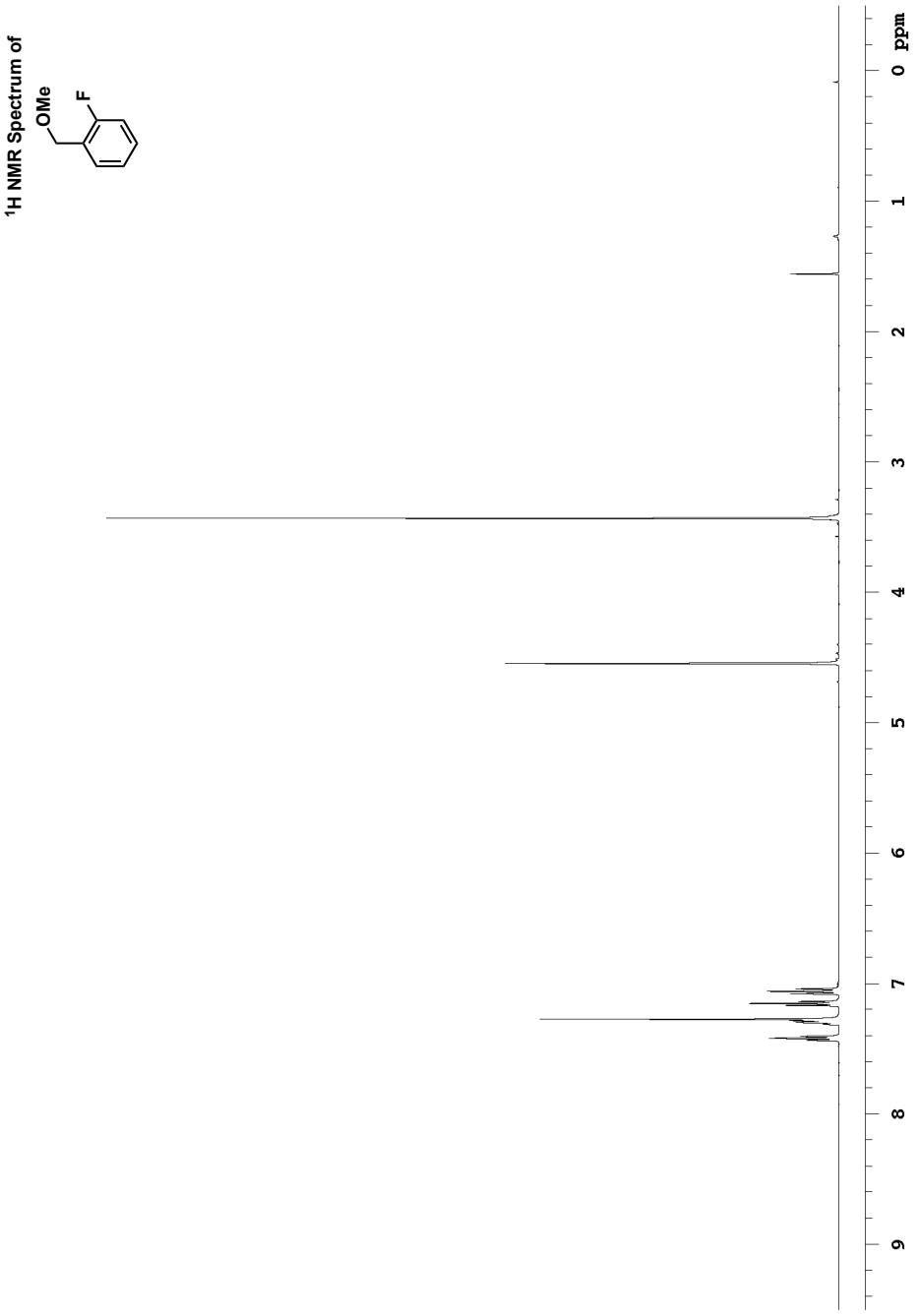
^{1}H NMR of **4c**. $CDCl_3$, 500 MHz, 23 °C



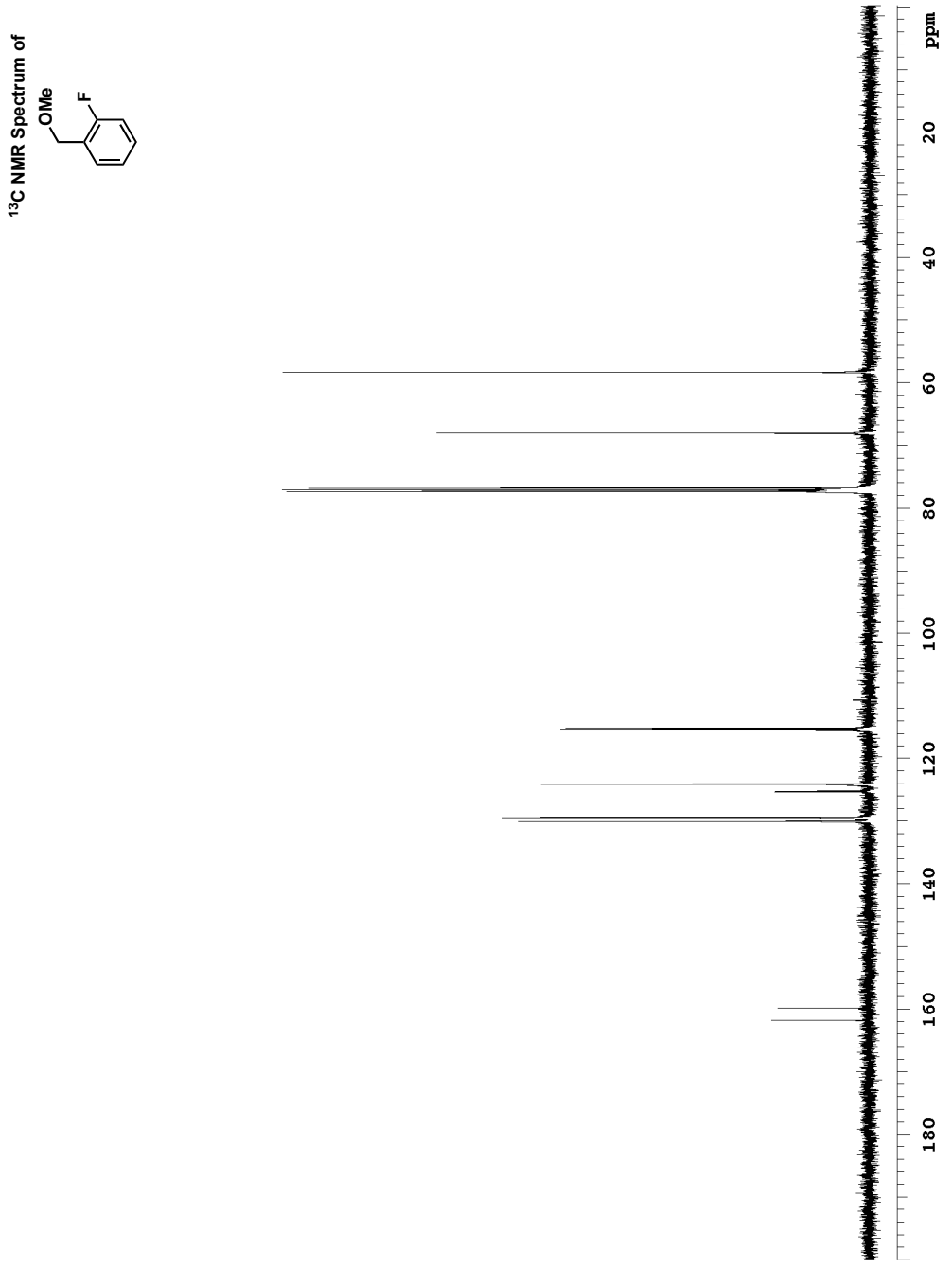
^{13}C NMR of **4c**. $CDCl_3$, 125 MHz, 23 °C



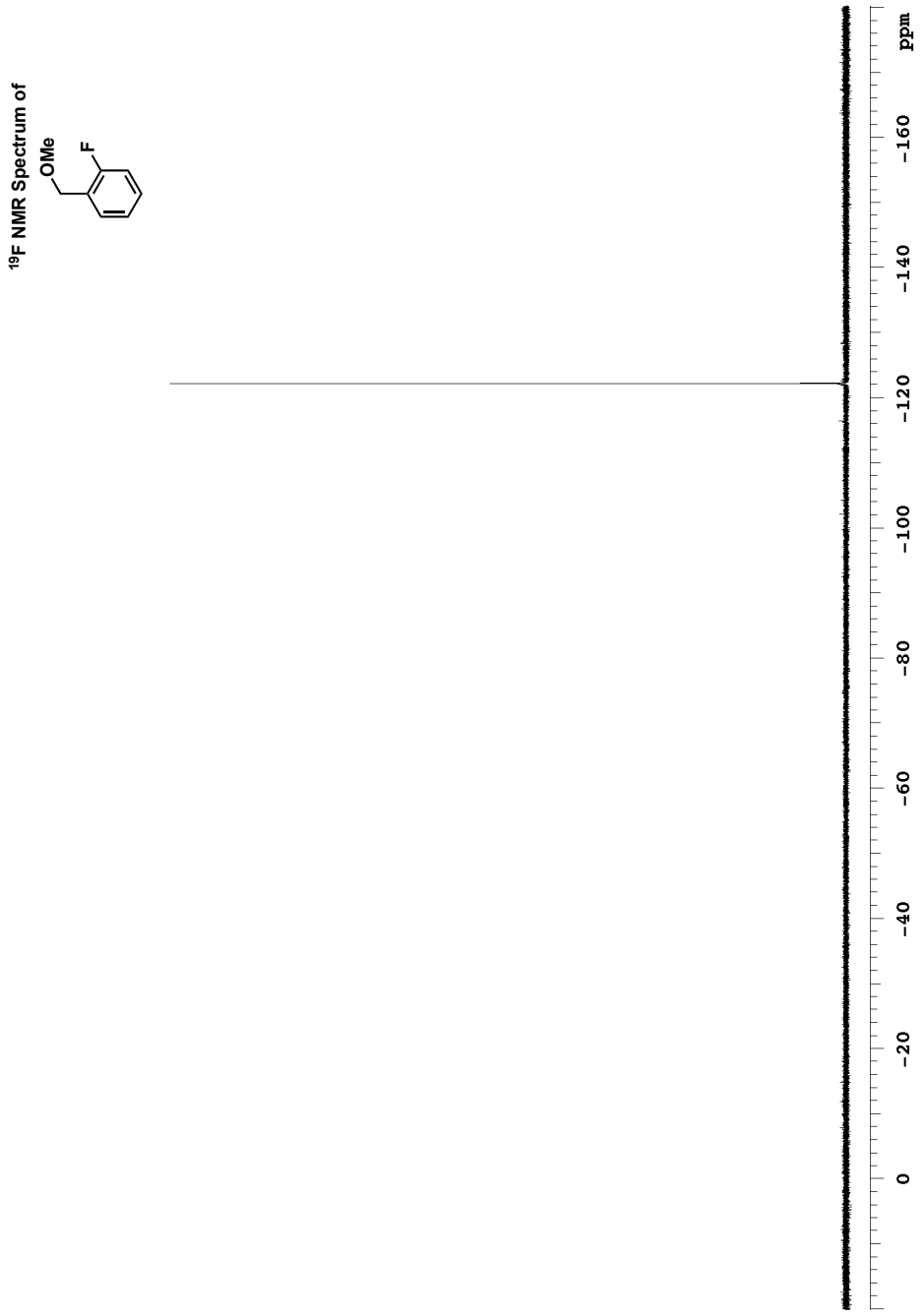
^{19}F NMR of **4c**. $CDCl_3$, 375 MHz, 23 °C



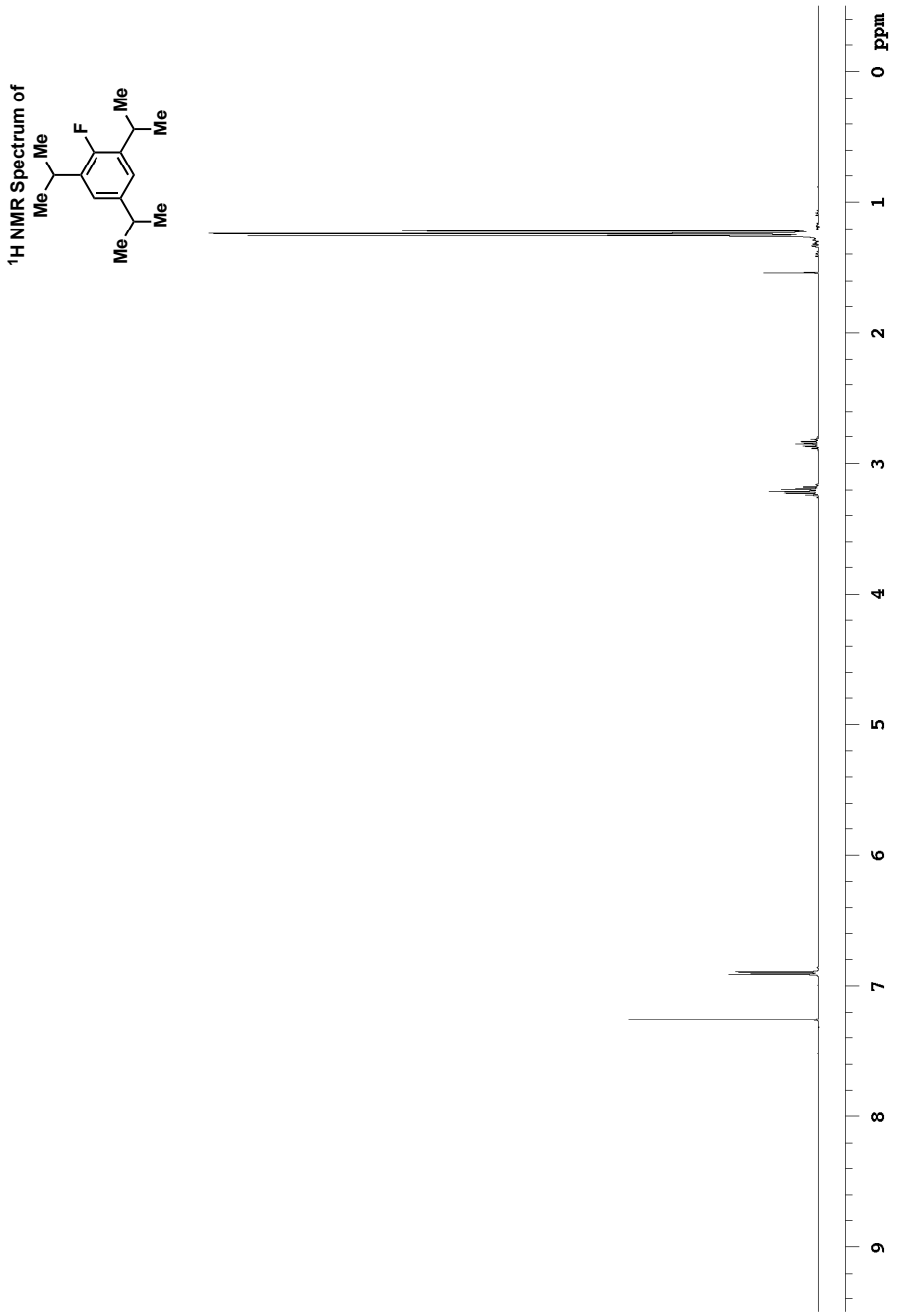
^{1}H NMR of **4d**. $CDCl_3$, 500 MHz, 23 °C



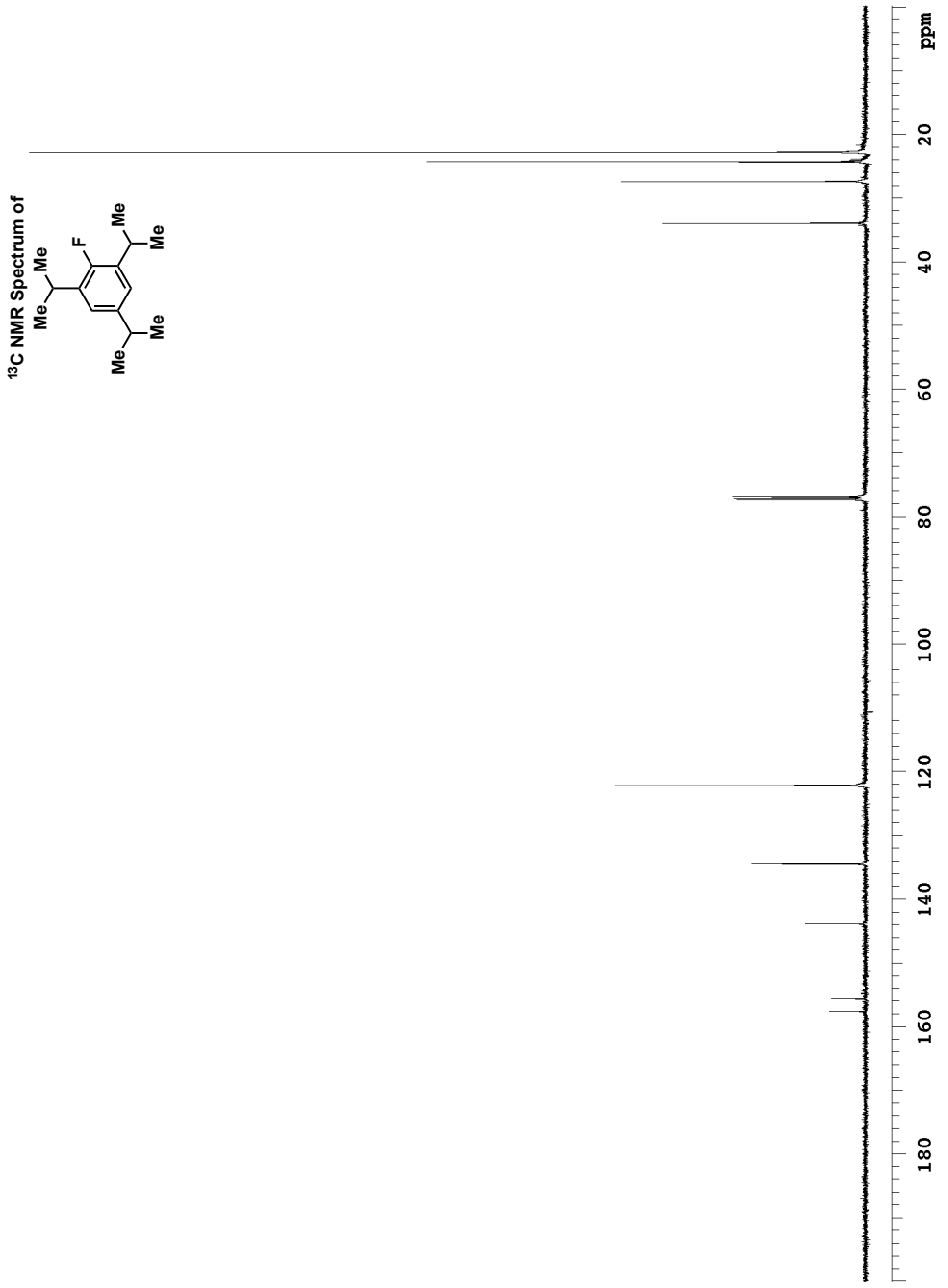
^{13}C NMR of **4d**. $CDCl_3$, 125 MHz, 23 °C



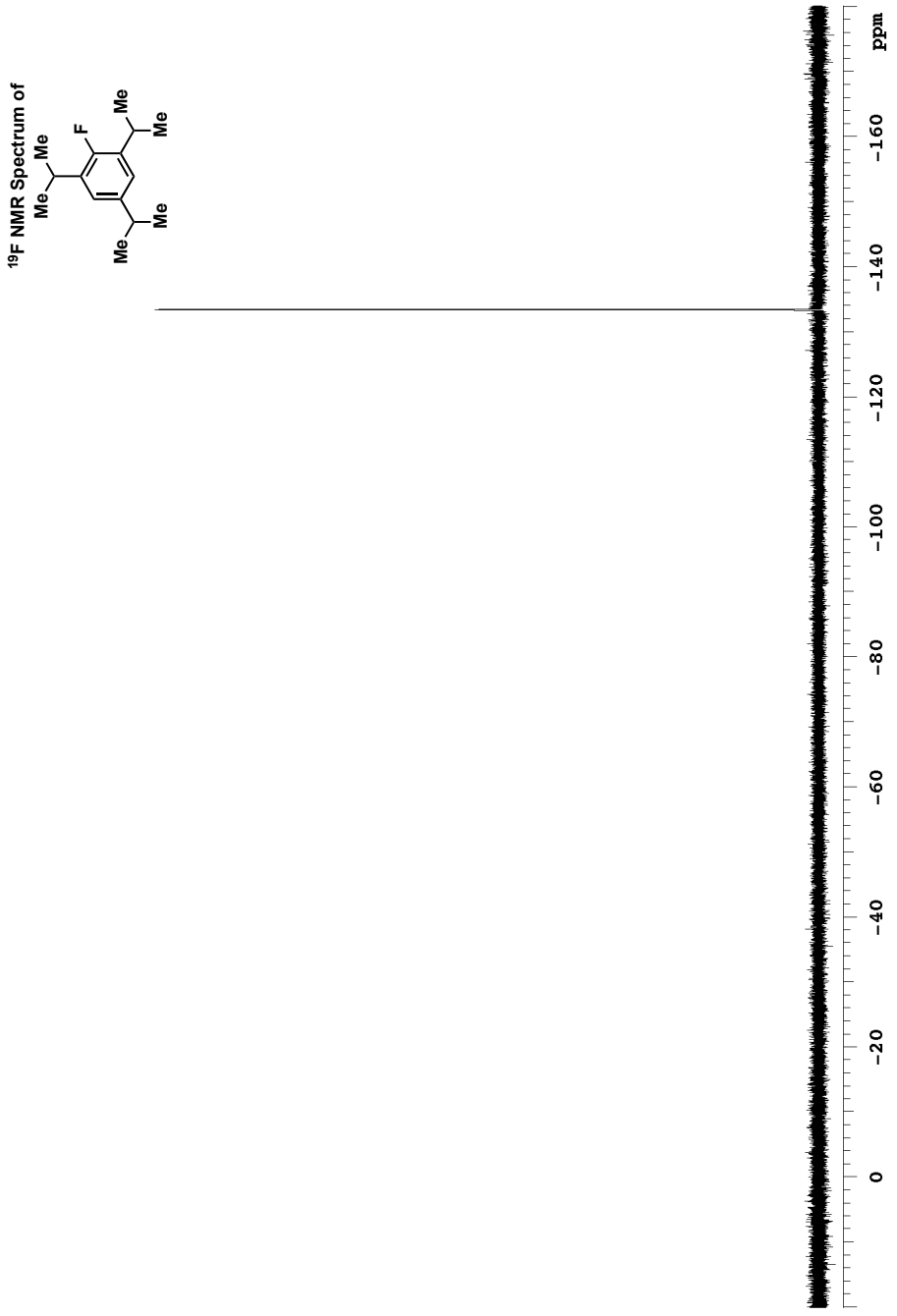
^{19}F NMR of **4d**. $CDCl_3$, 375 MHz, 23 °C



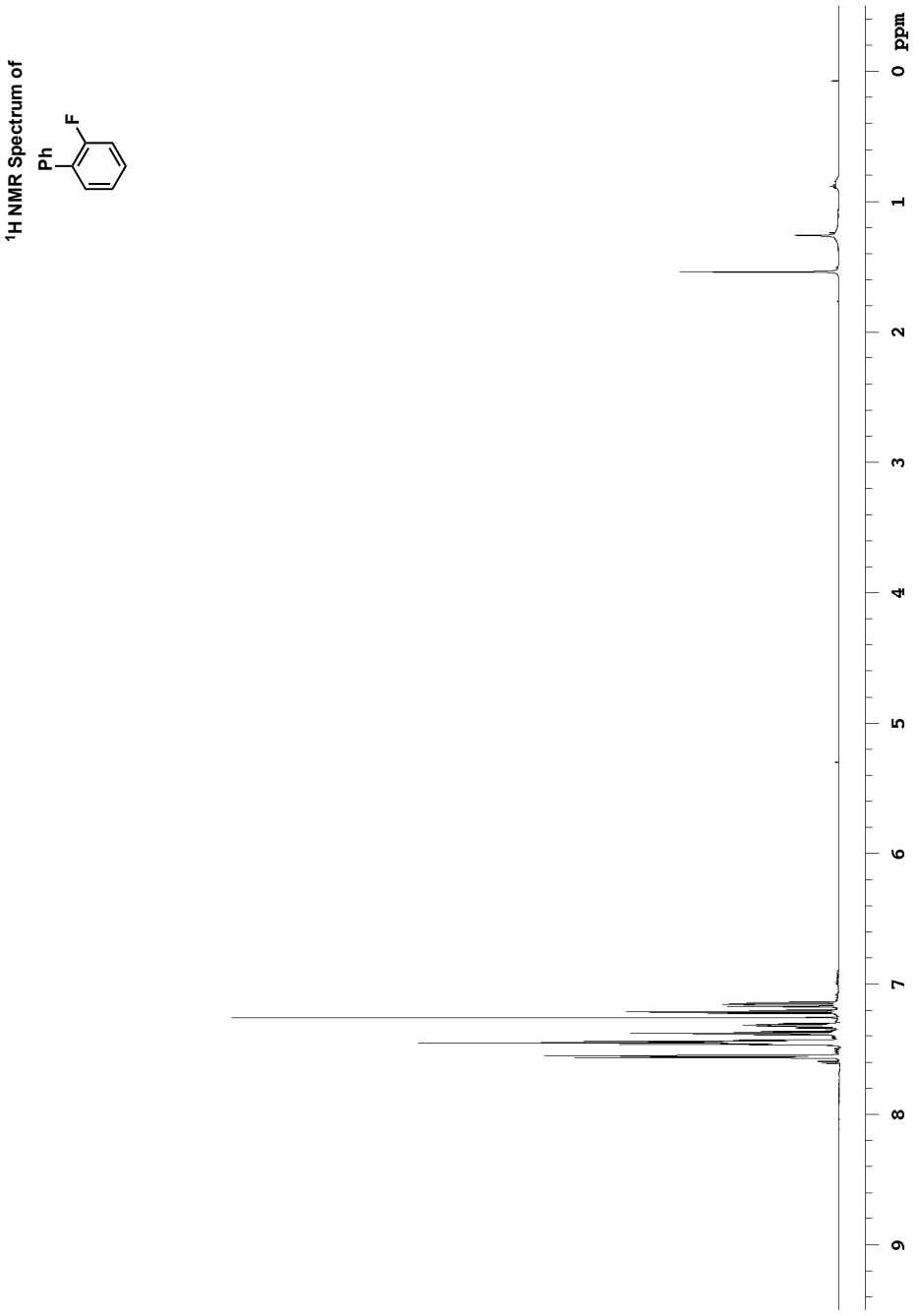
^{1}H NMR of **4e**. $CDCl_3$, 600 MHz, 23 °C



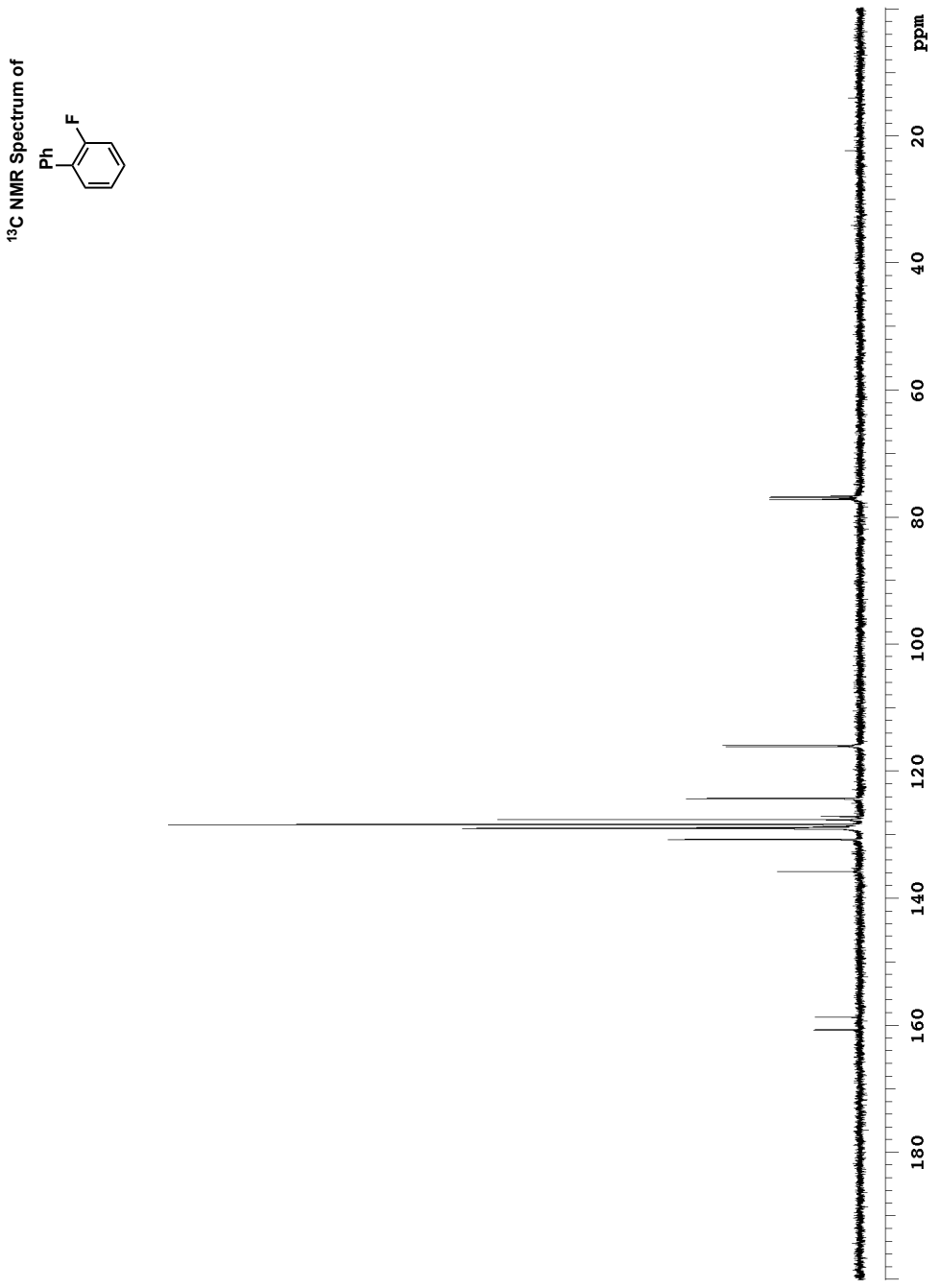
^{13}C NMR of **4e**. $CDCl_3$, 125 MHz, 23 °C



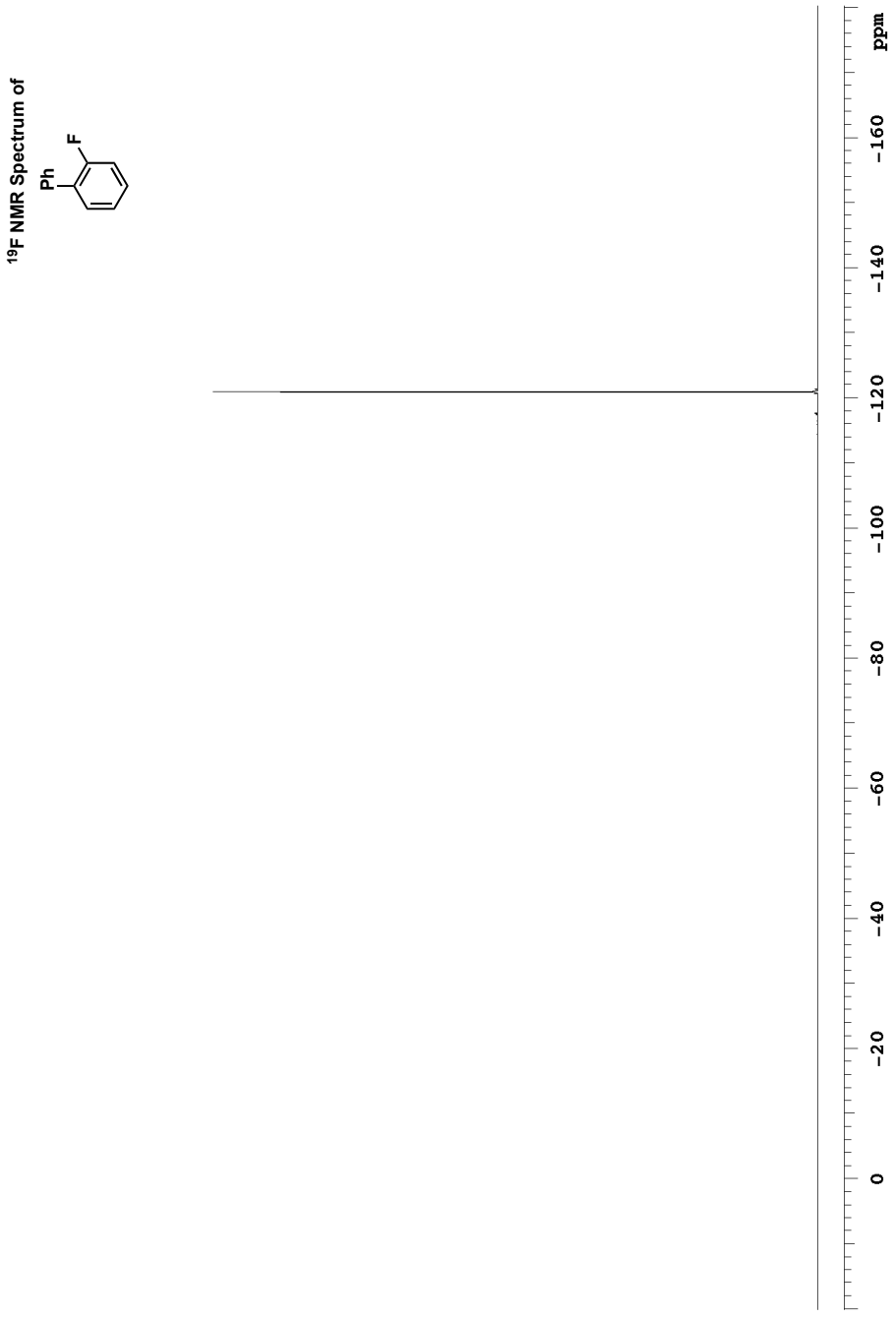
^{19}F NMR of **4e**. $CDCl_3$, 375 MHz, 23 °C



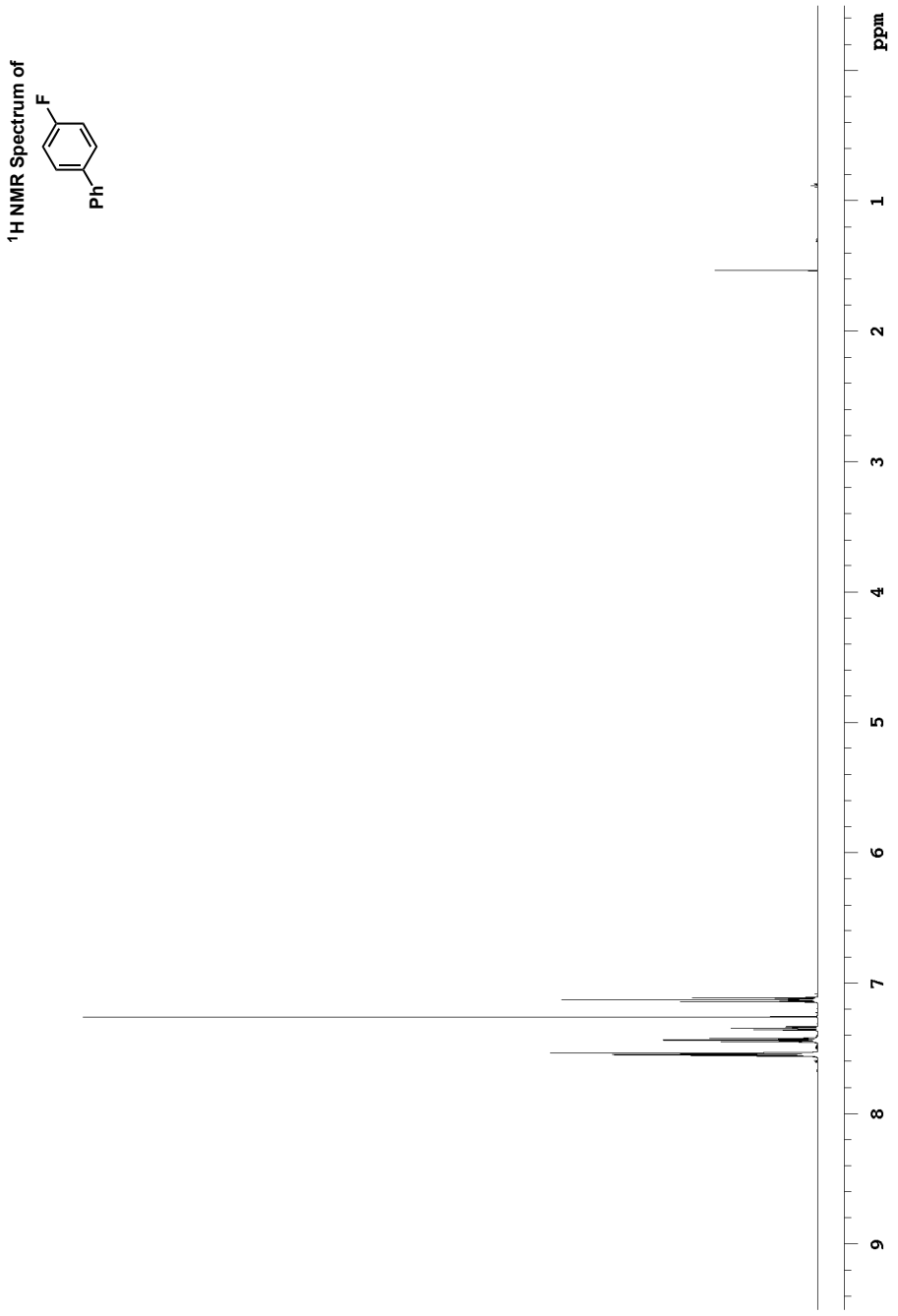
^{1}H NMR of **4f**. $CDCl_3$, 600 MHz, 23 °C



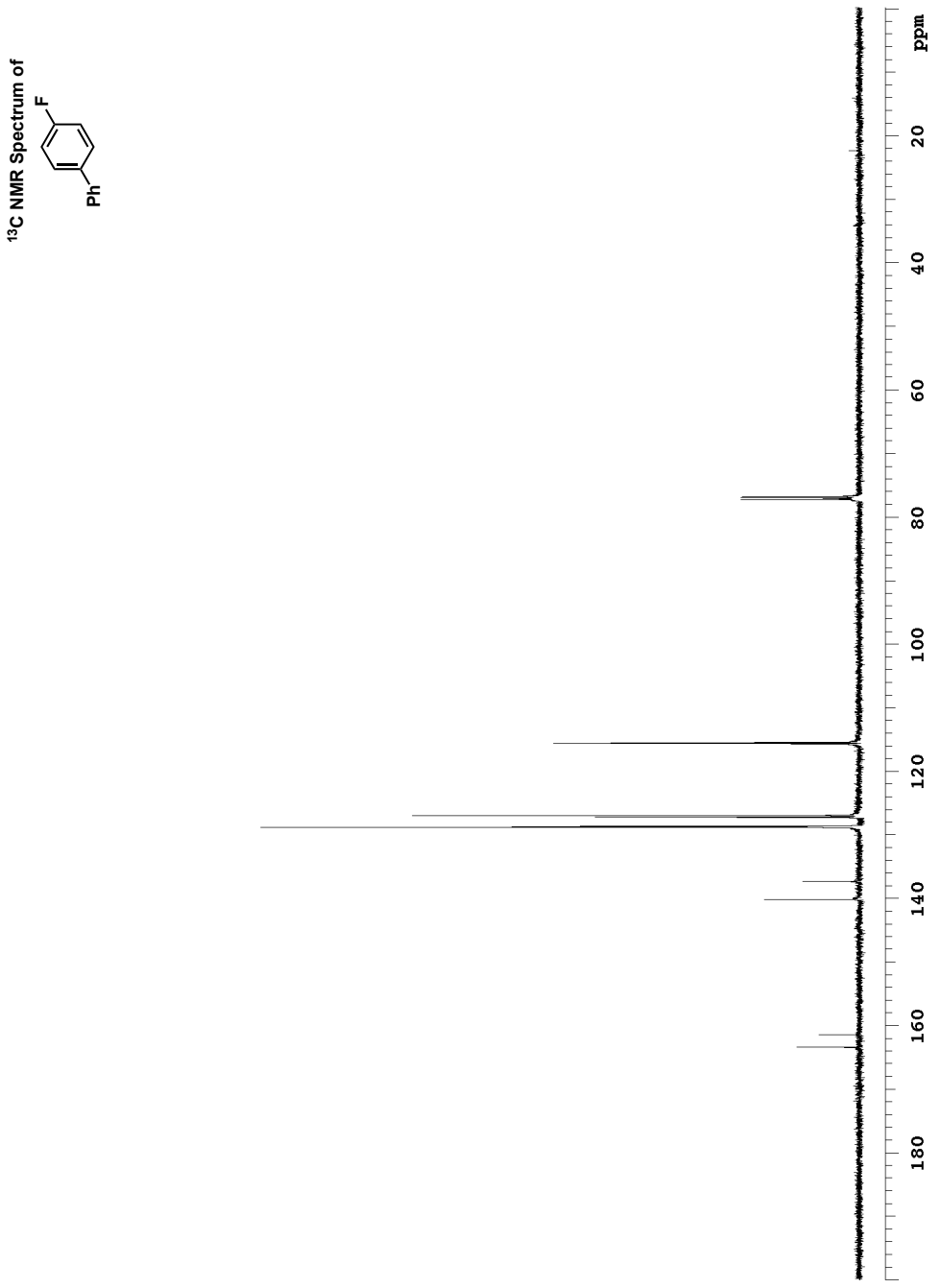
^{13}C NMR of **4f**. $CDCl_3$, 125 MHz, 23 °C



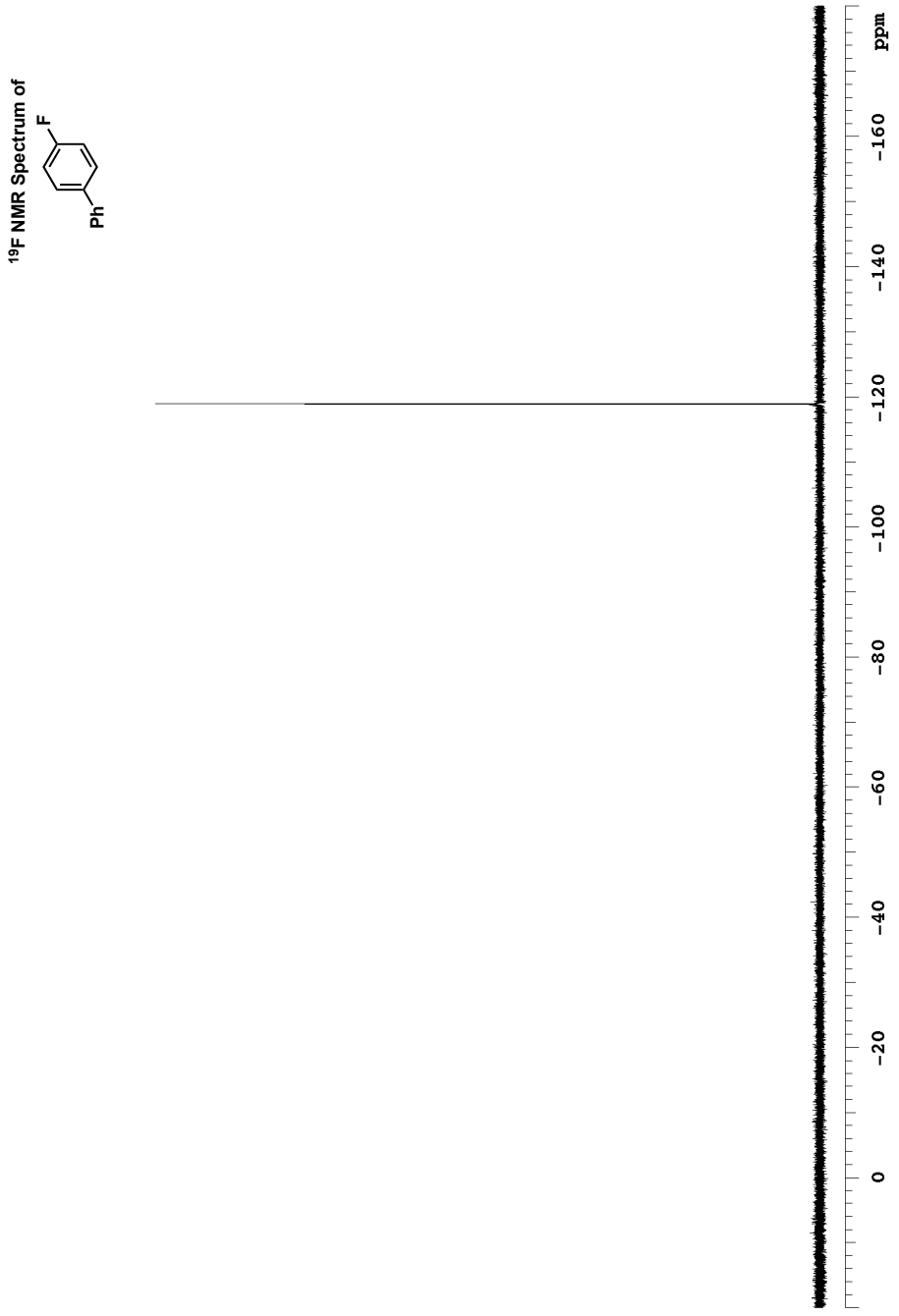
^{19}F NMR of **4f**. $CDCl_3$, 375 MHz, 23 °C



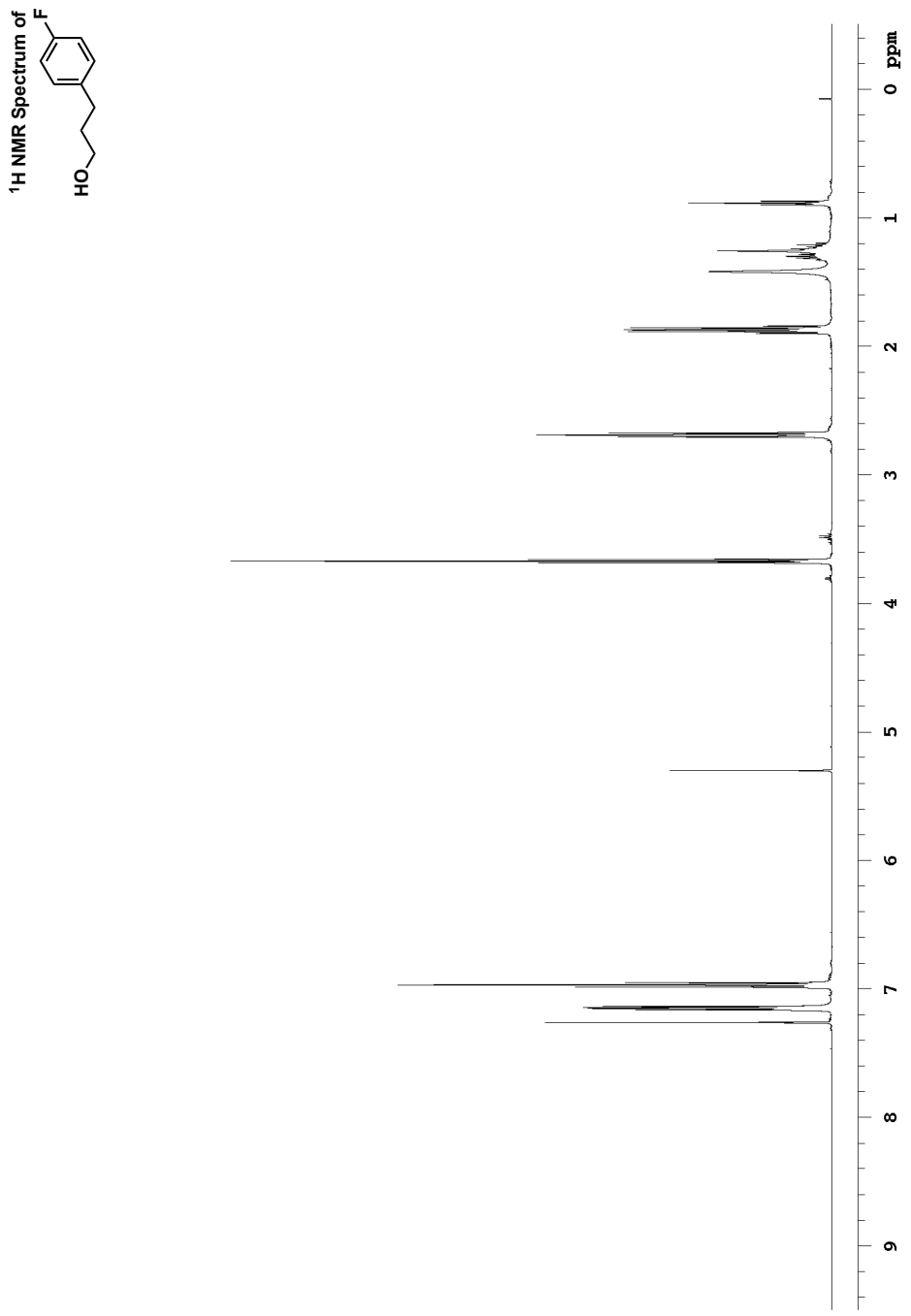
^{1}H NMR of **4g**. $CDCl_3$, 600 MHz, 23 °C



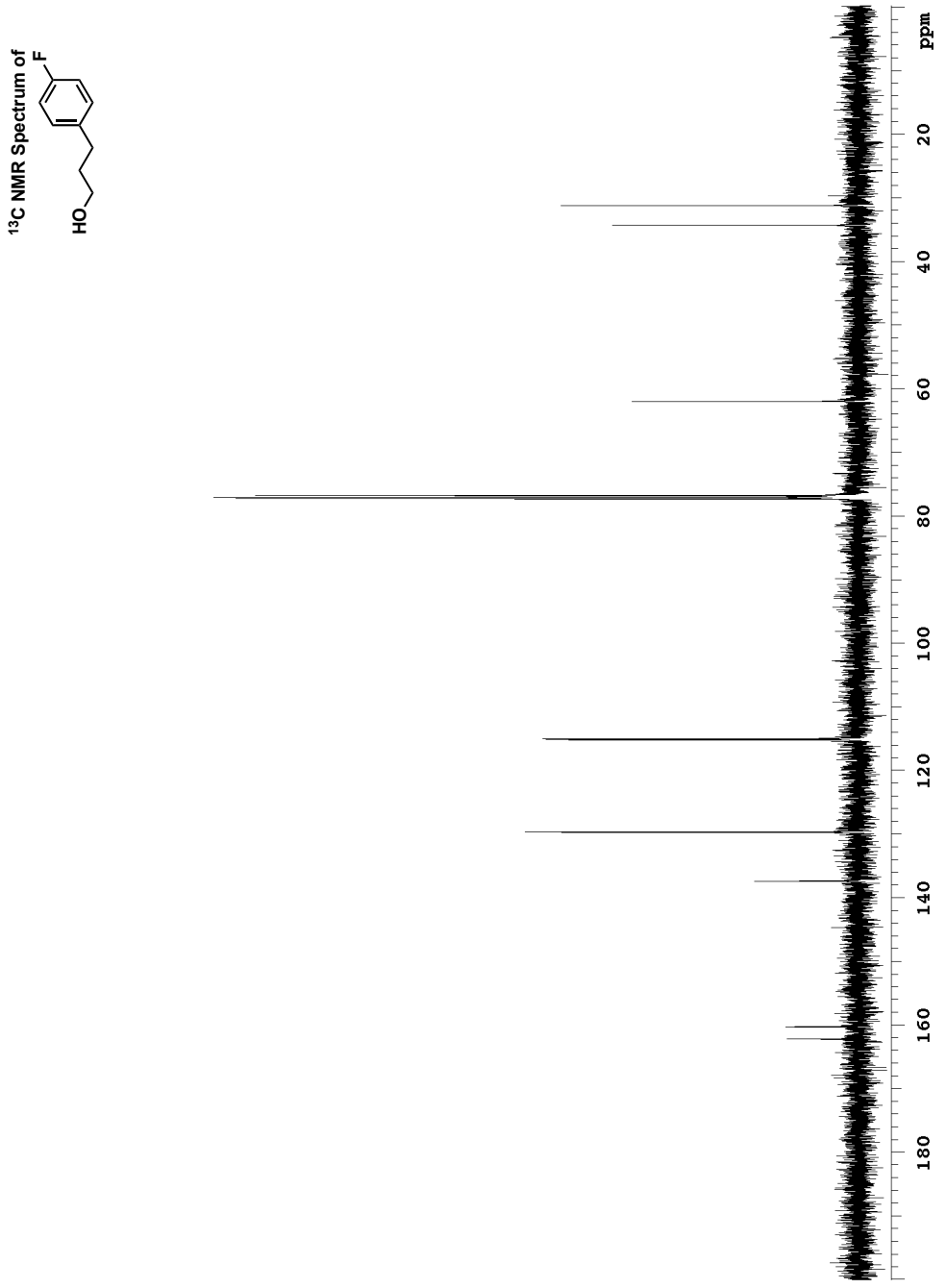
^{13}C NMR of **4g**. $CDCl_3$, 125 MHz, 23 °C



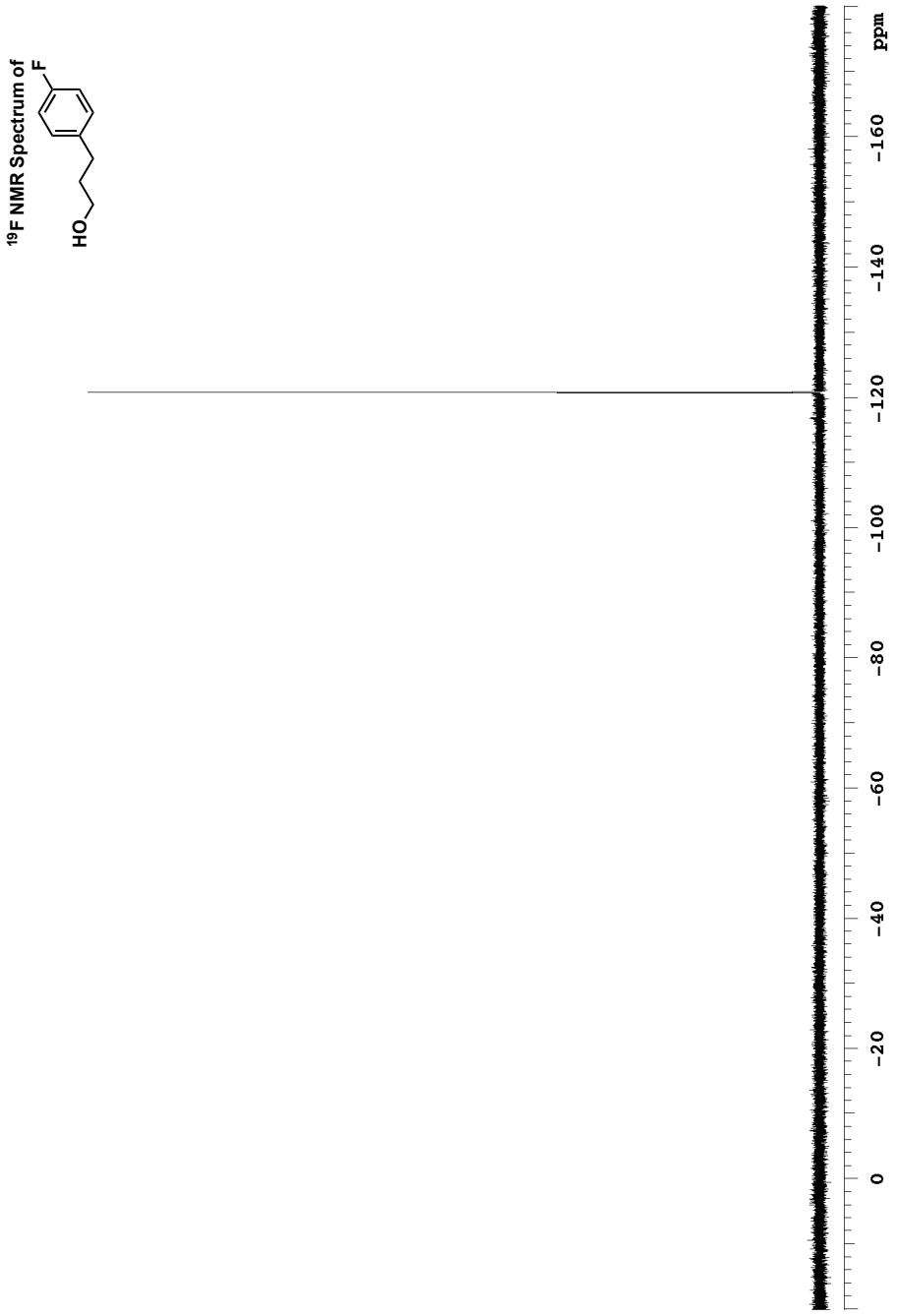
^{19}F NMR of **4g**. $CDCl_3$, 375 MHz, 23 °C



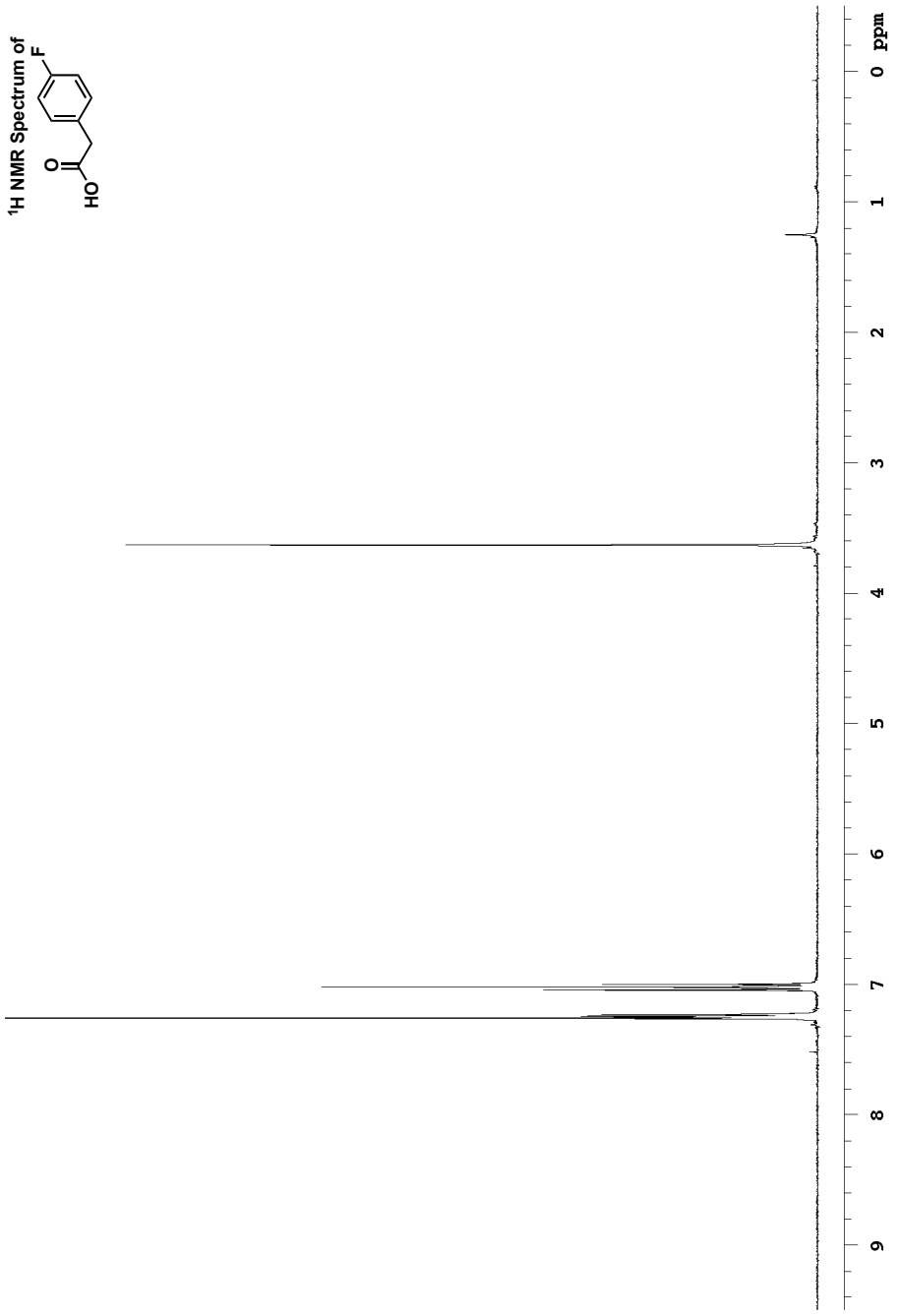
^{1}H NMR of **4h**. $CDCl_3$, 500 MHz, 23 °C



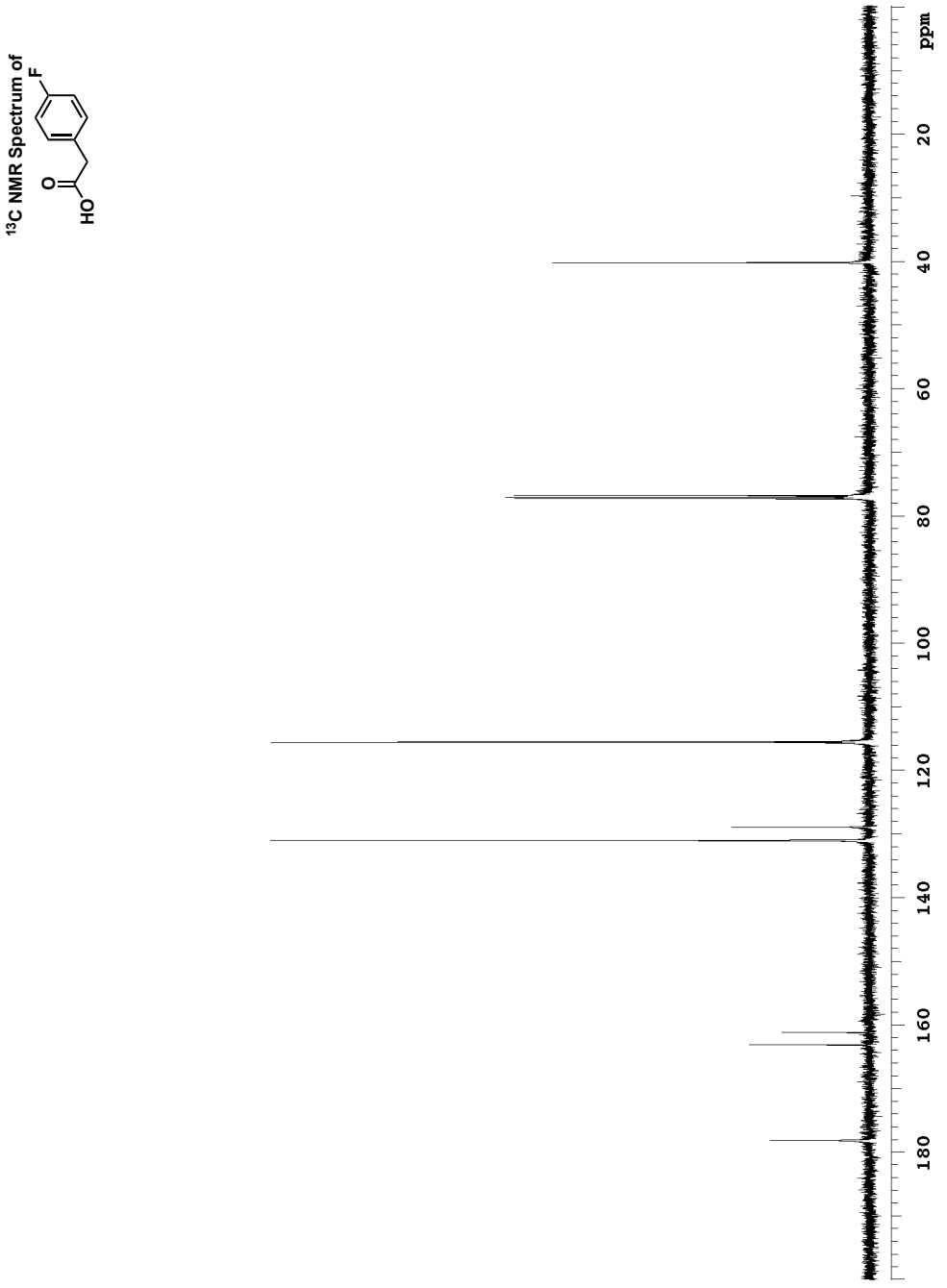
^{13}C NMR of **4h**. $CDCl_3$, 125 MHz, 23 °C



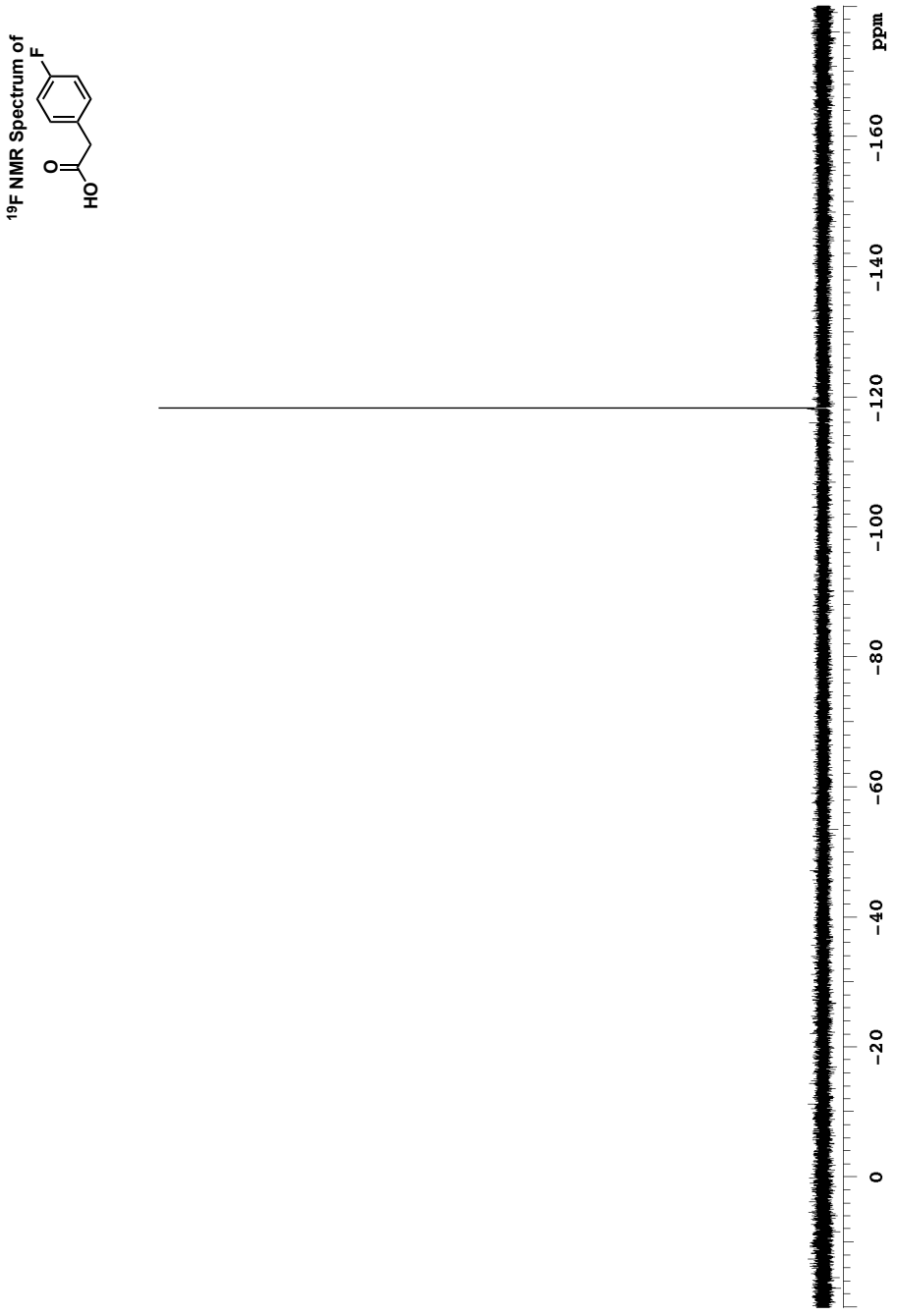
^{19}F NMR of **4h**. $CDCl_3$, 375 MHz, 23 °C



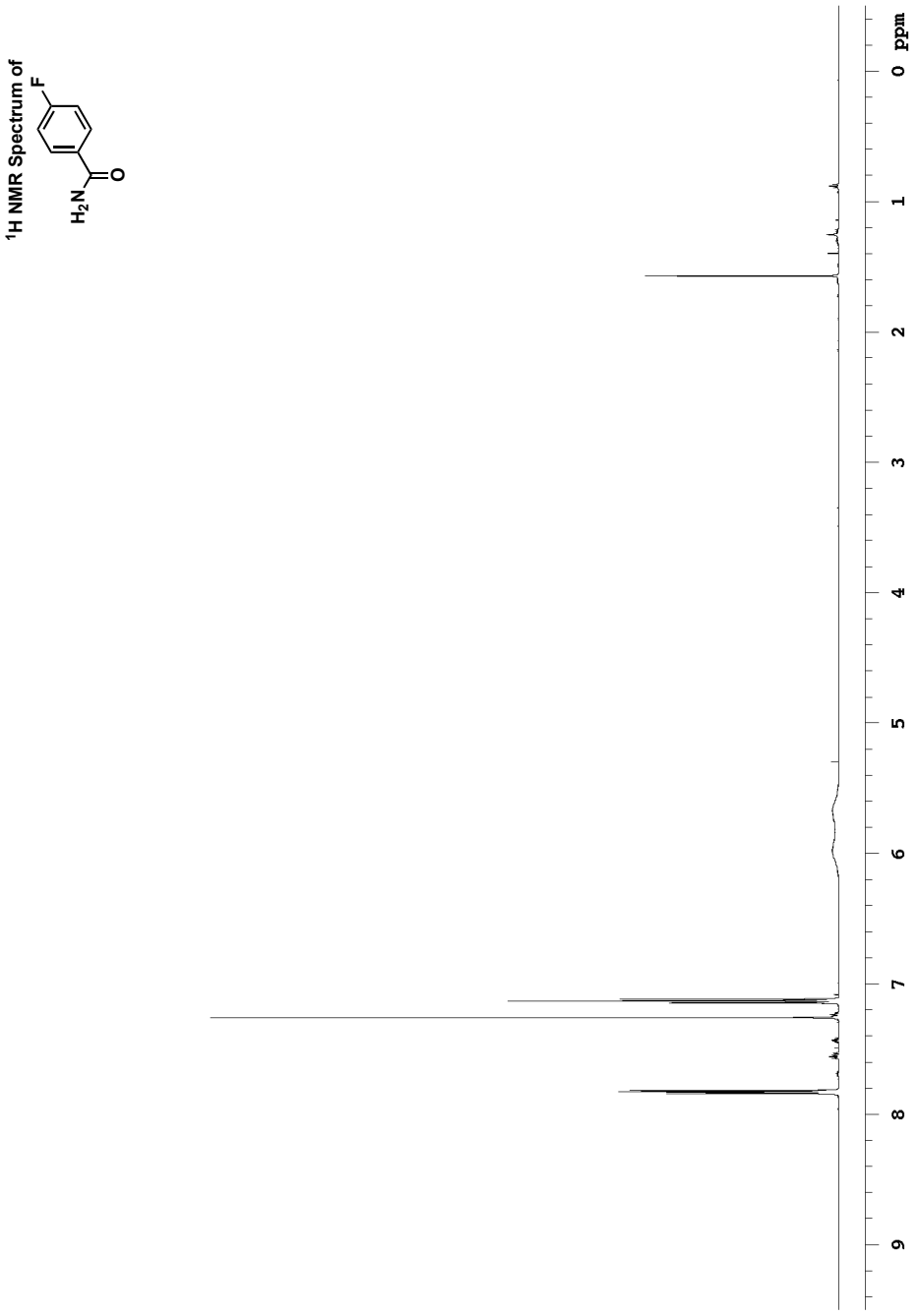
^{1}H NMR of **4i**. $CDCl_3$, 600 MHz, 23 °C



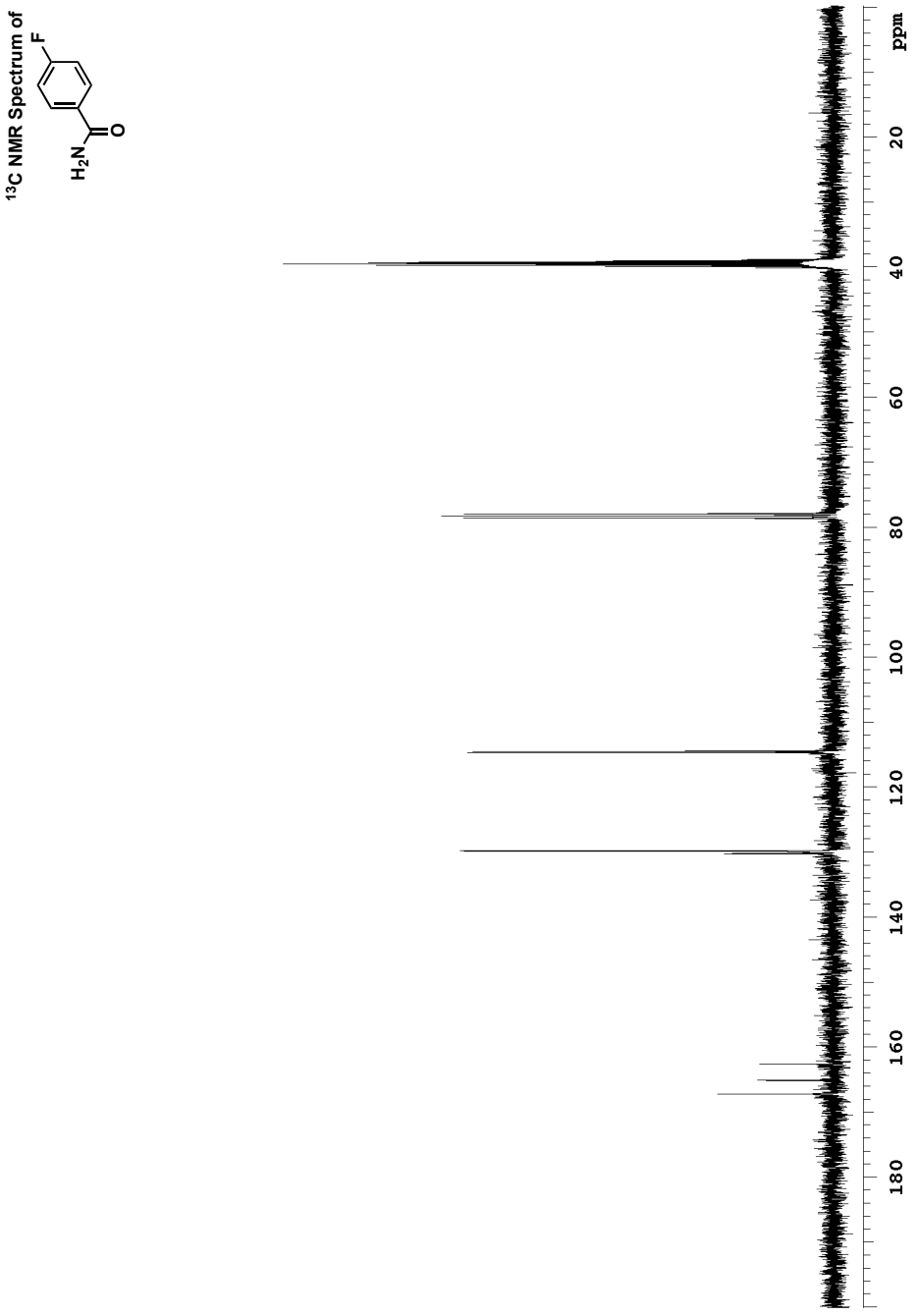
^{13}C NMR of **4i**. $CDCl_3$, 125 MHz, 23 °C



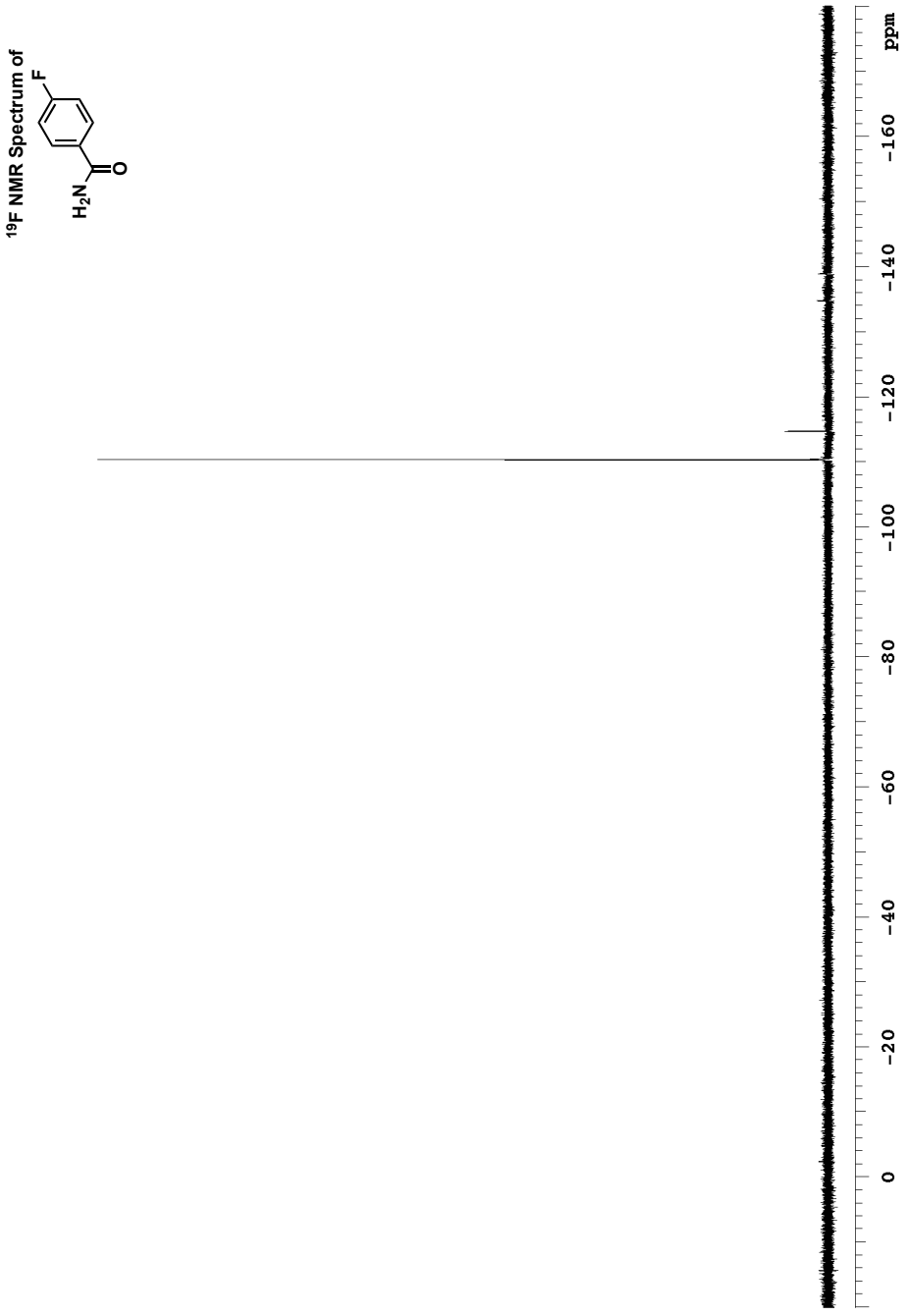
^{19}F NMR of **4i**. $CDCl_3$, 375 MHz, 23 °C



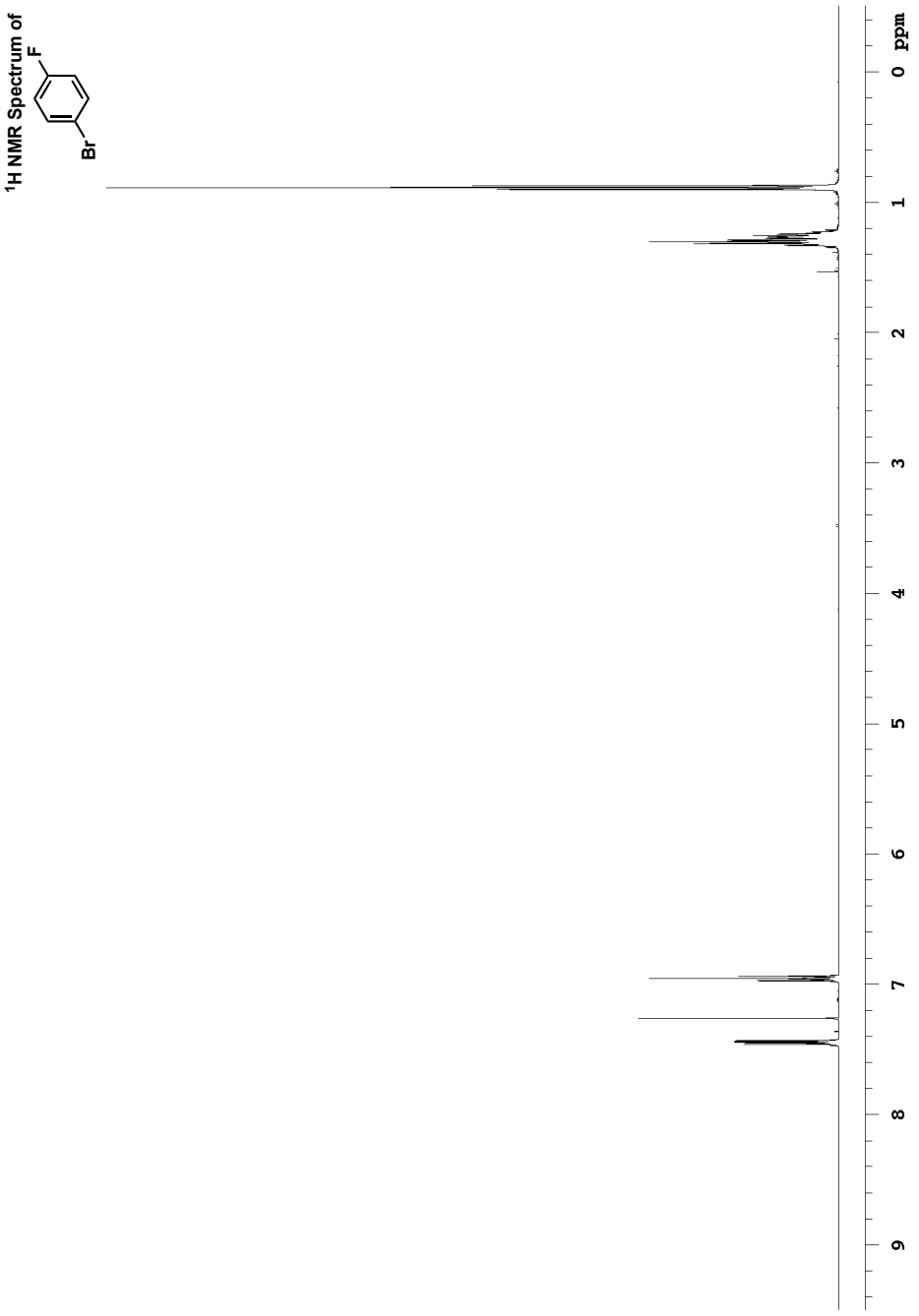
^{1}H NMR of **4k**. $CDCl_3$, 600 MHz, 23 °C



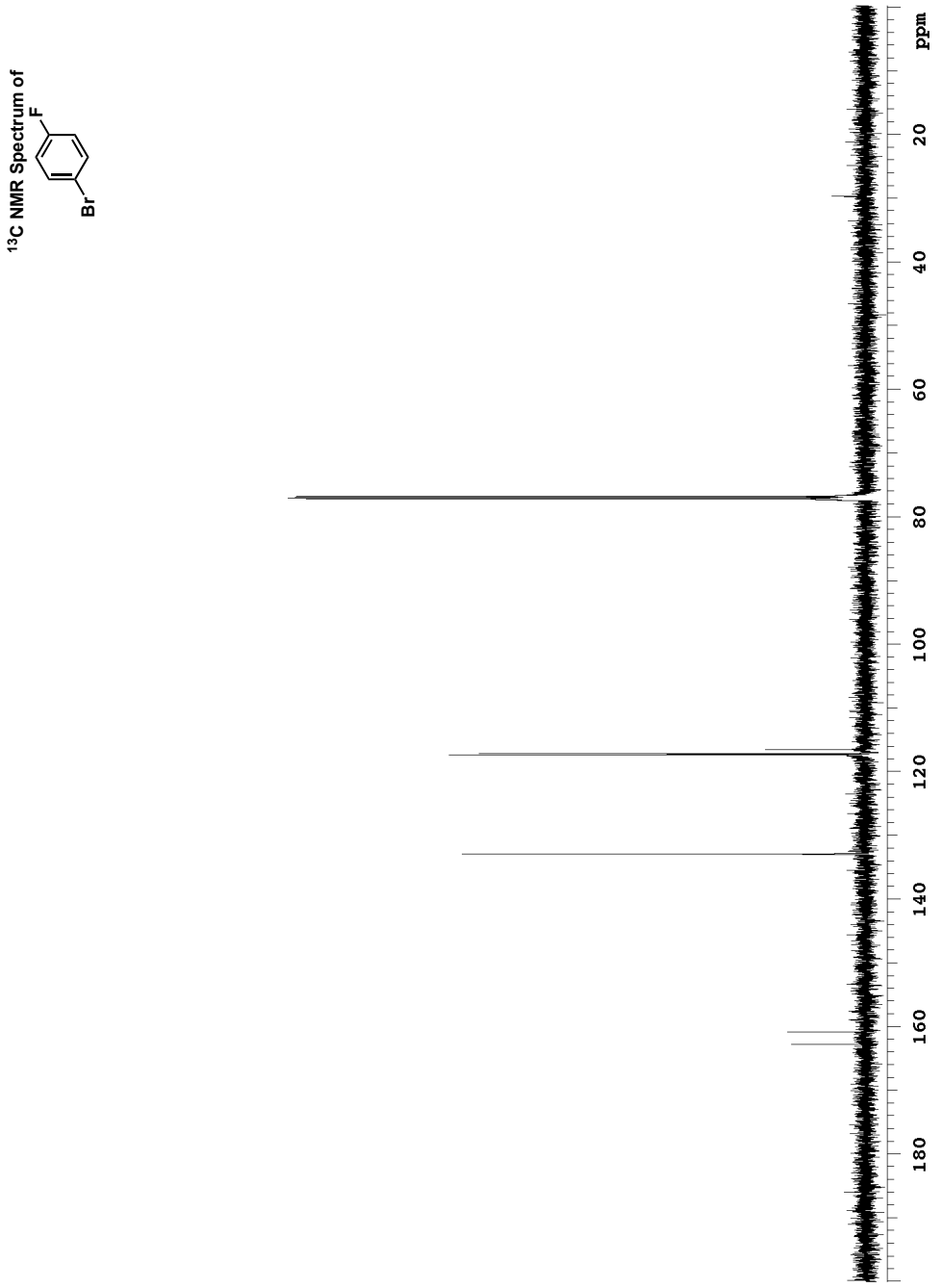
^{13}C NMR of **4k**. $CDCl_3$: DMSO-d_6 (1:1 (v/v)), 100 MHz, 23 °C



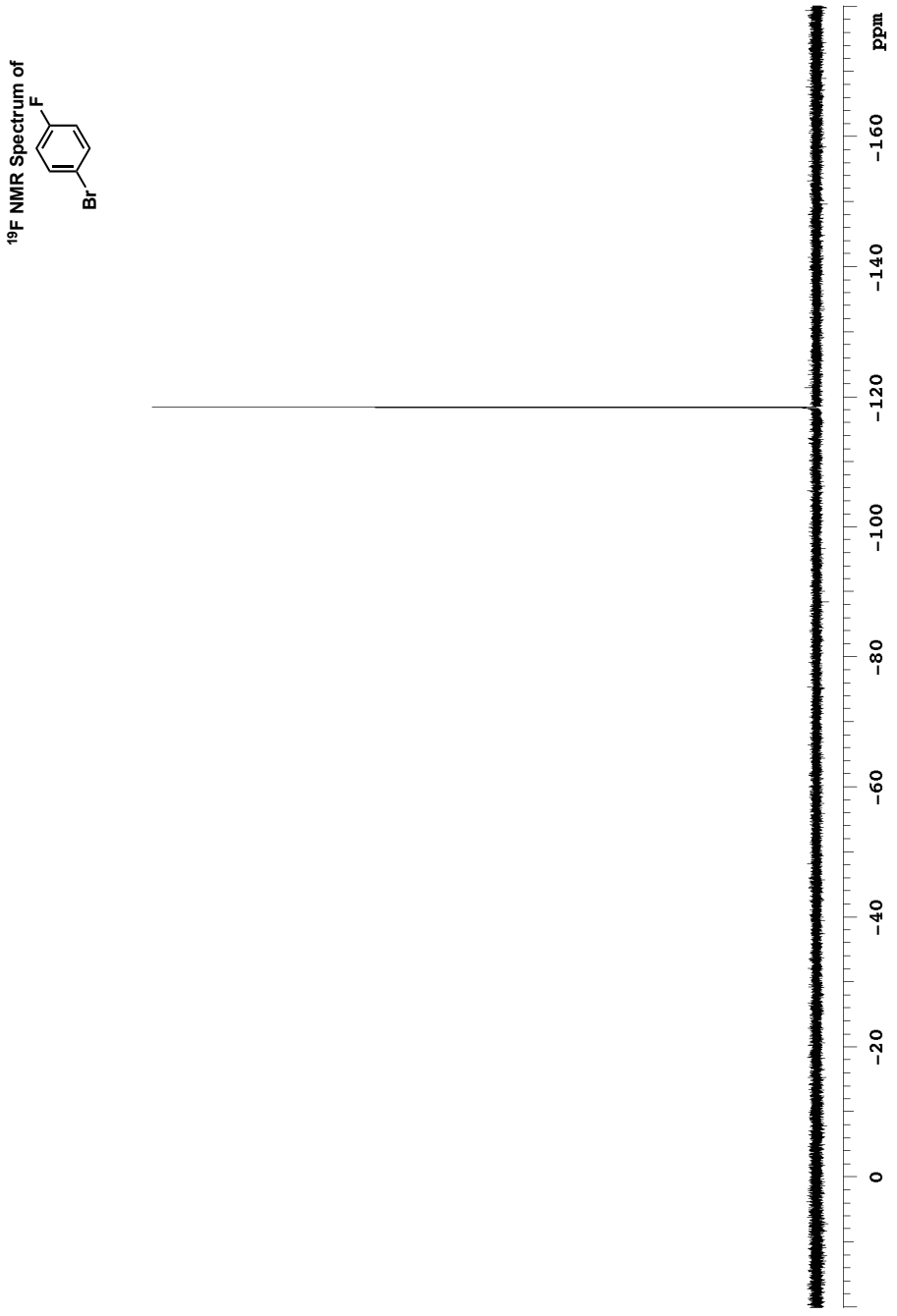
^{19}F NMR of **4k**. $CDCl_3$, 375 MHz, 23 °C



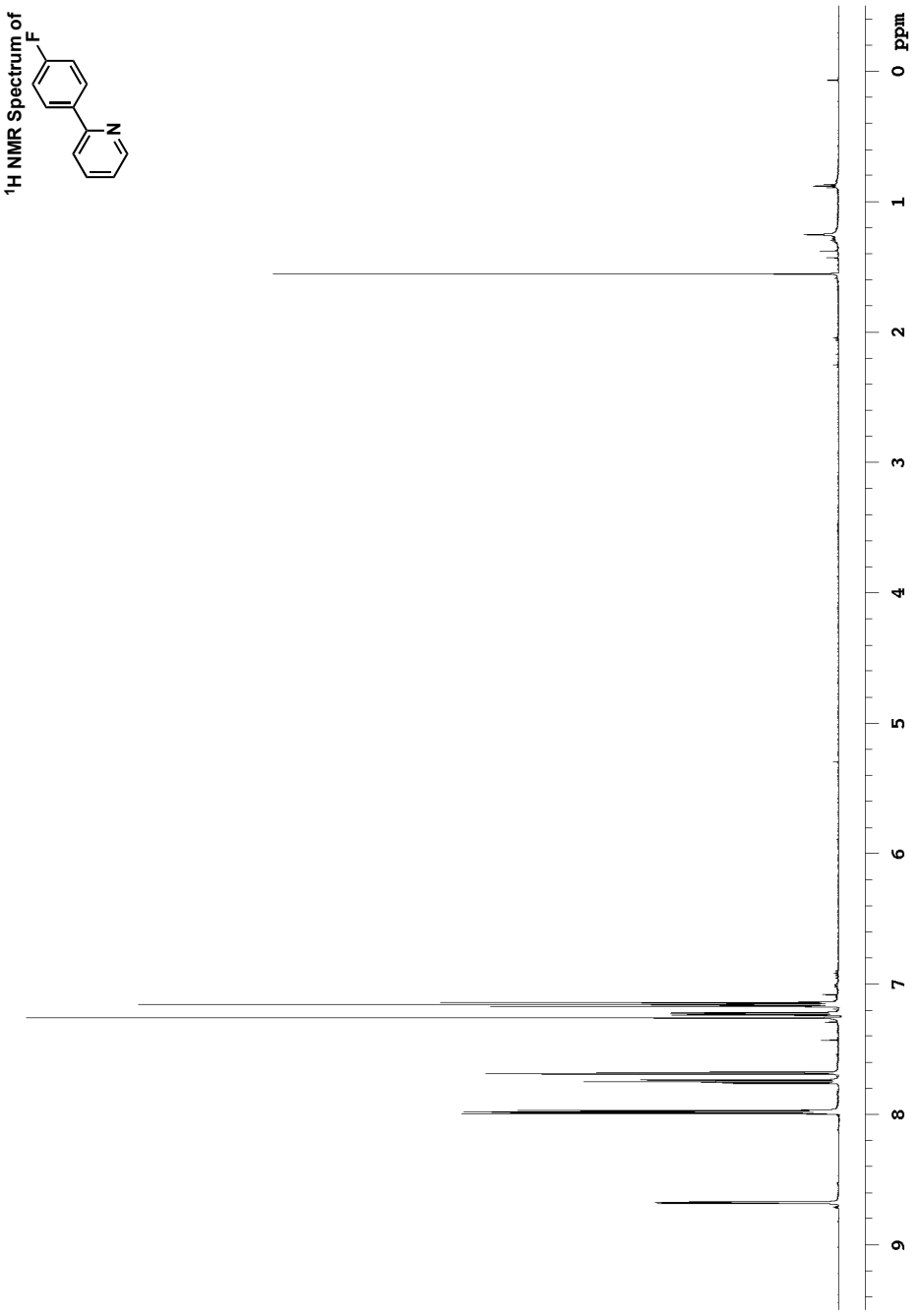
^{1}H NMR of **4l**. $CDCl_3$, 500 MHz, 23 °C



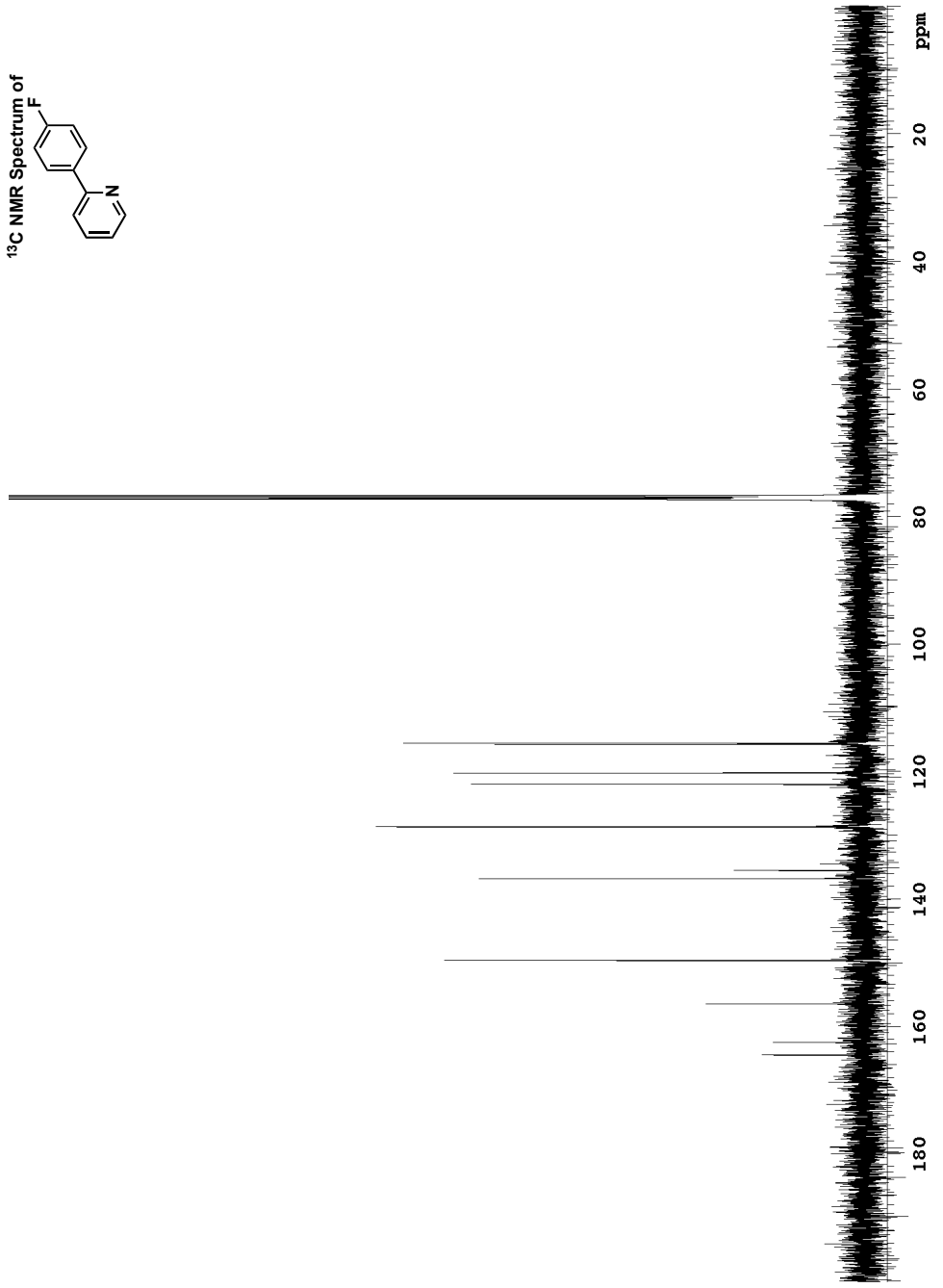
^{13}C NMR of **4l**. $CDCl_3$, 125 MHz, 23 °C



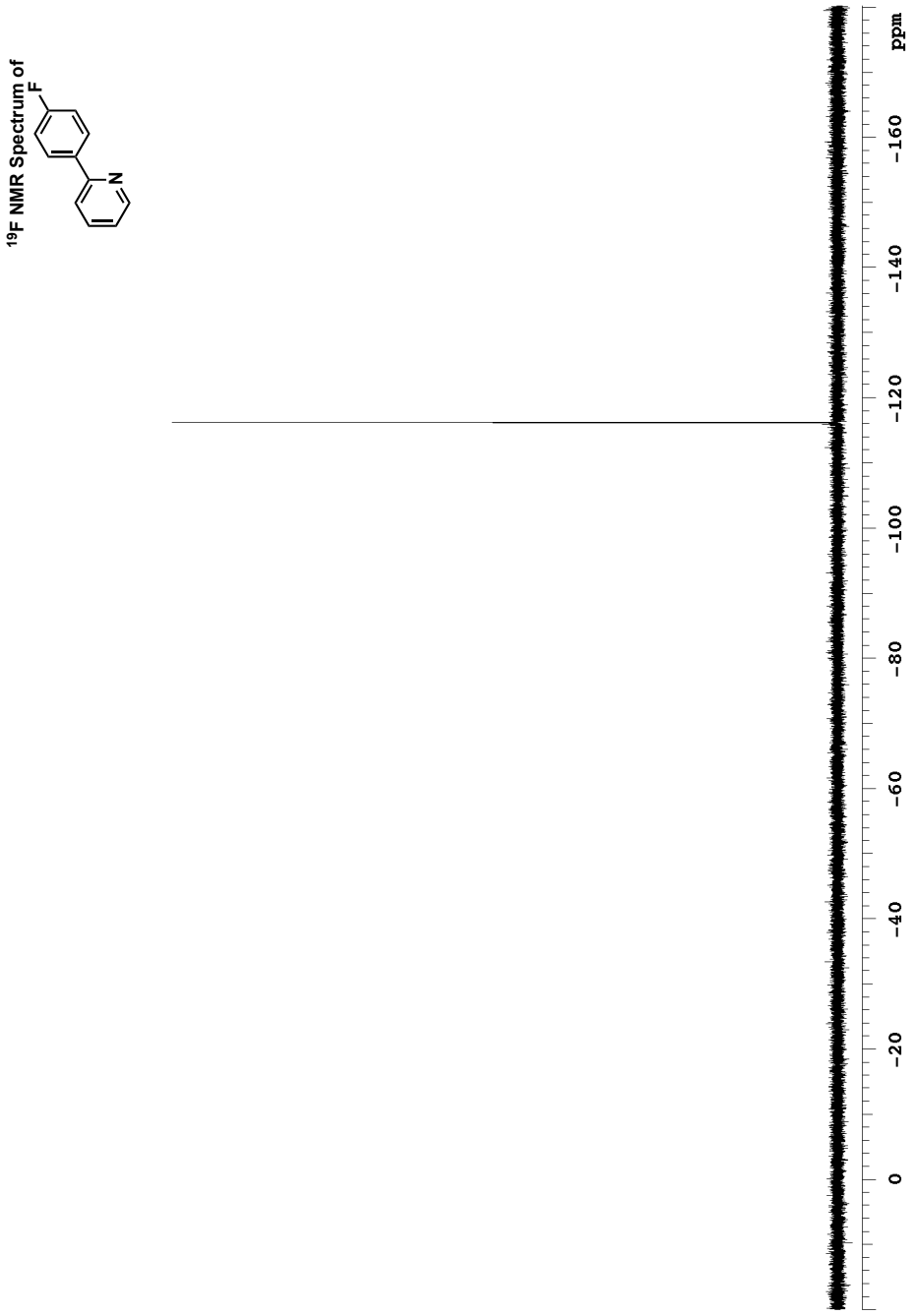
^{19}F NMR of **4l**. $CDCl_3$, 375 MHz, 23 °C



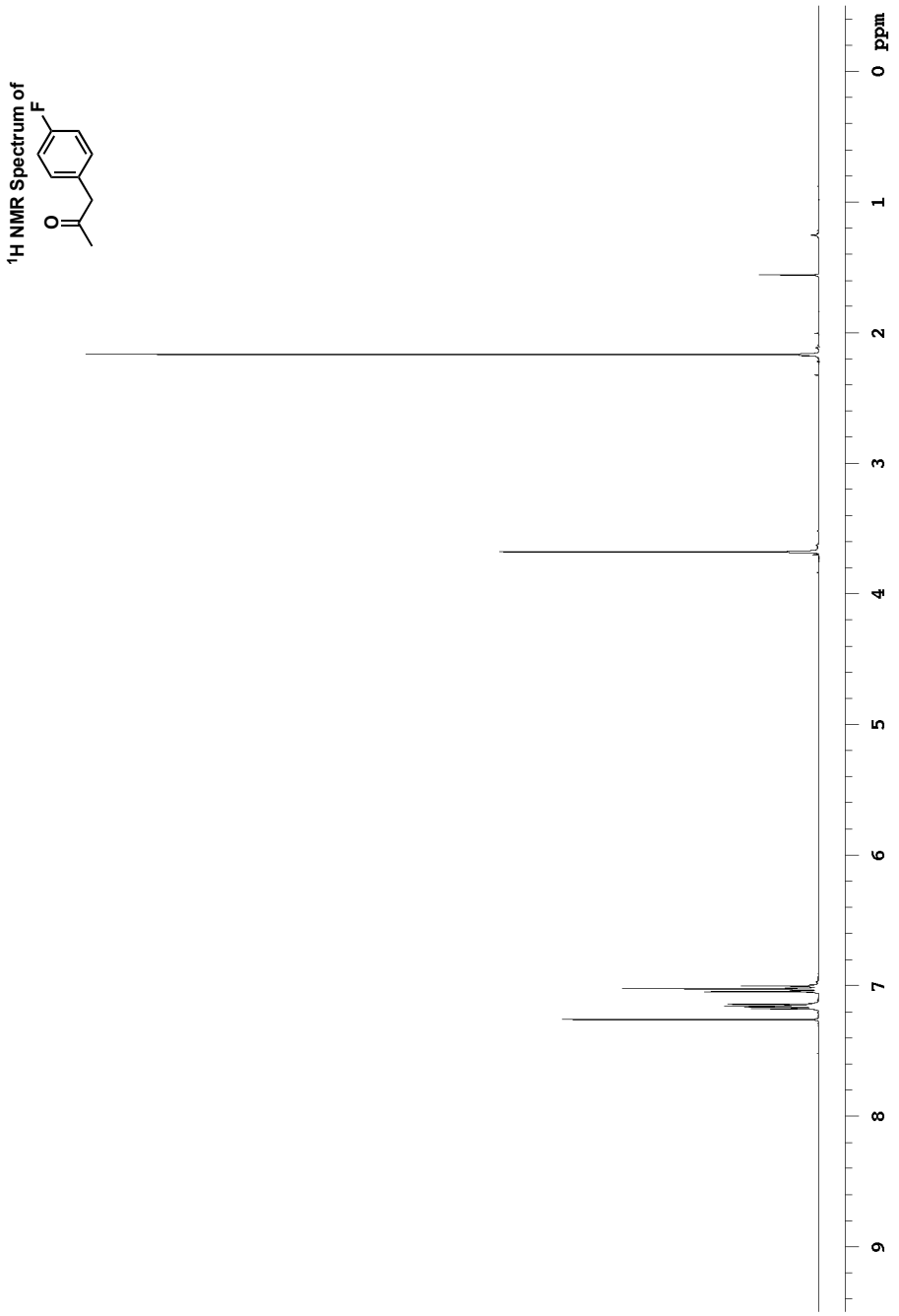
^{1}H NMR of **4m**. $CDCl_3$, 600 MHz, 23 °C



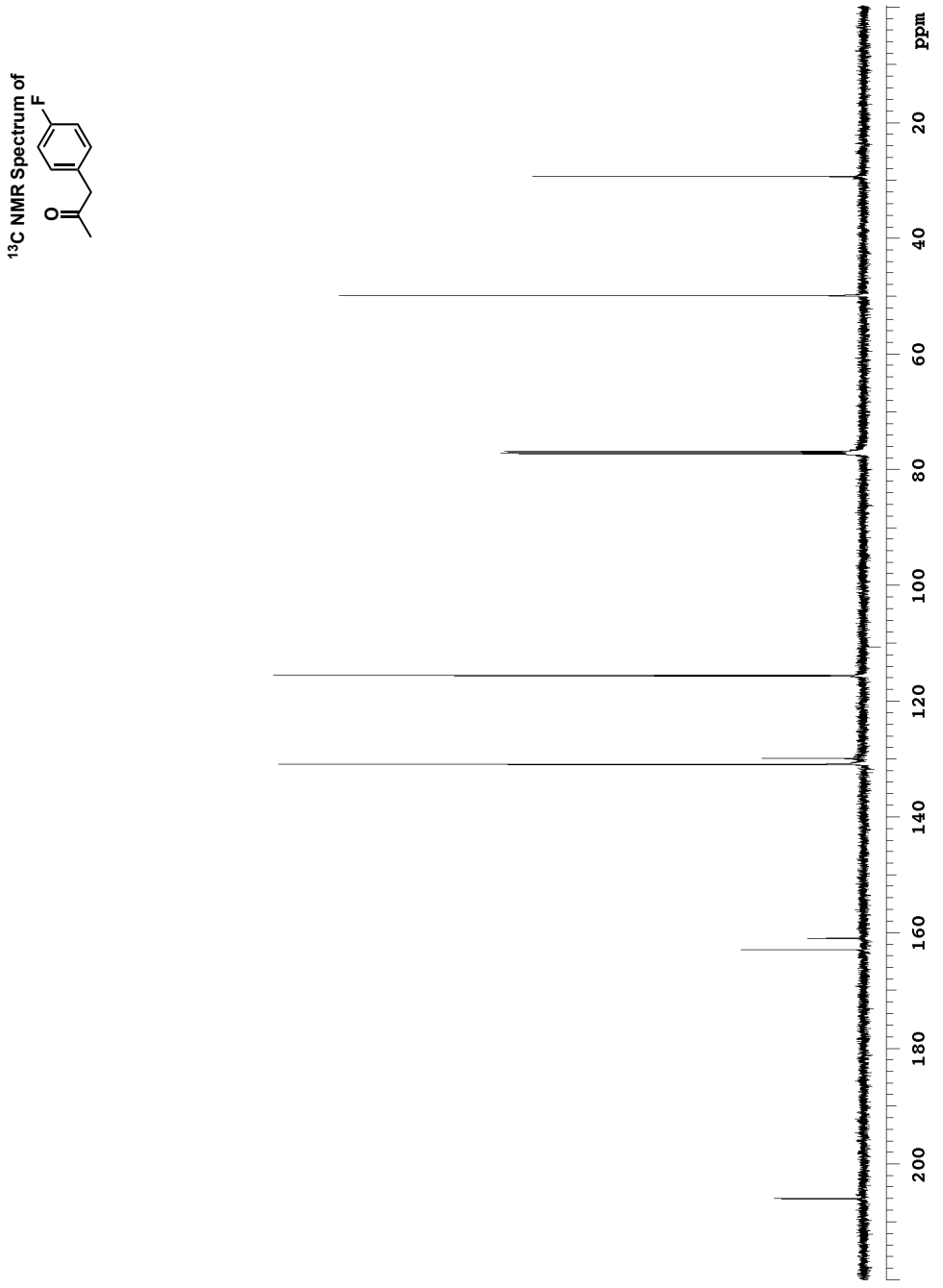
^{13}C NMR of **4m**. $CDCl_3$, 125 MHz, 23 °C



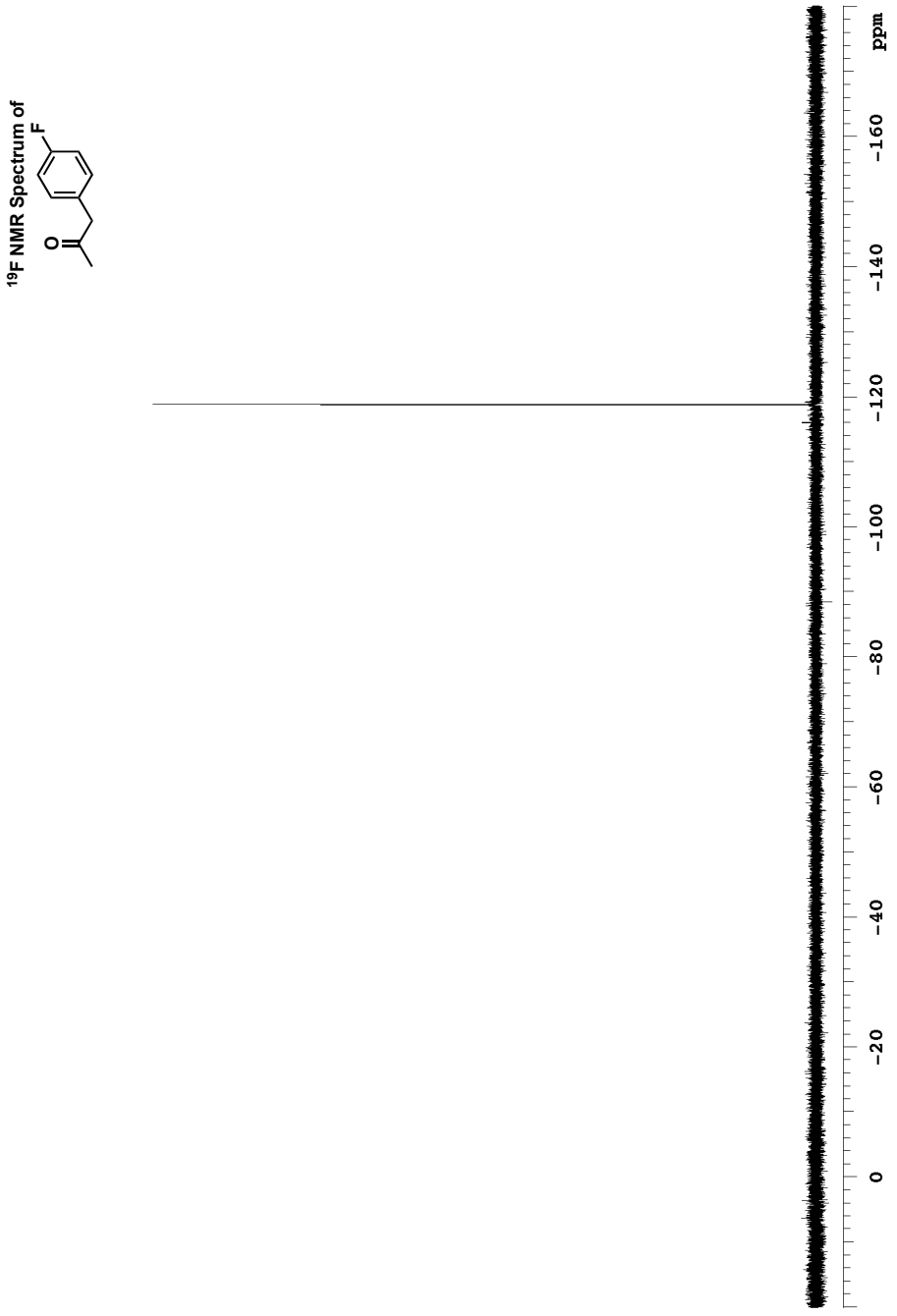
^{19}F NMR of **4m**. $CDCl_3$, 375 MHz, 23 °C



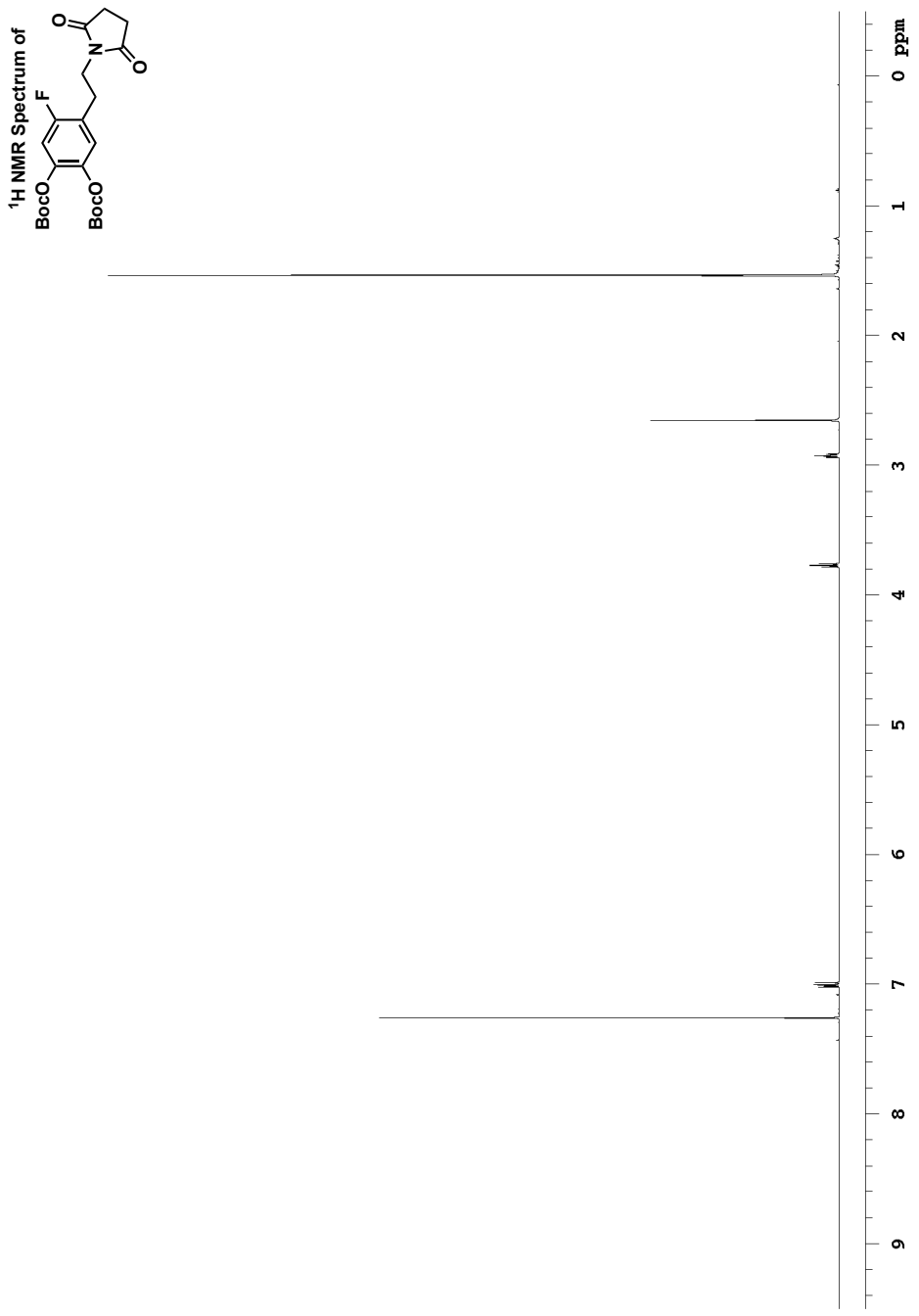
^{1}H NMR of **4n**. $CDCl_3$, 600 MHz, 23 °C



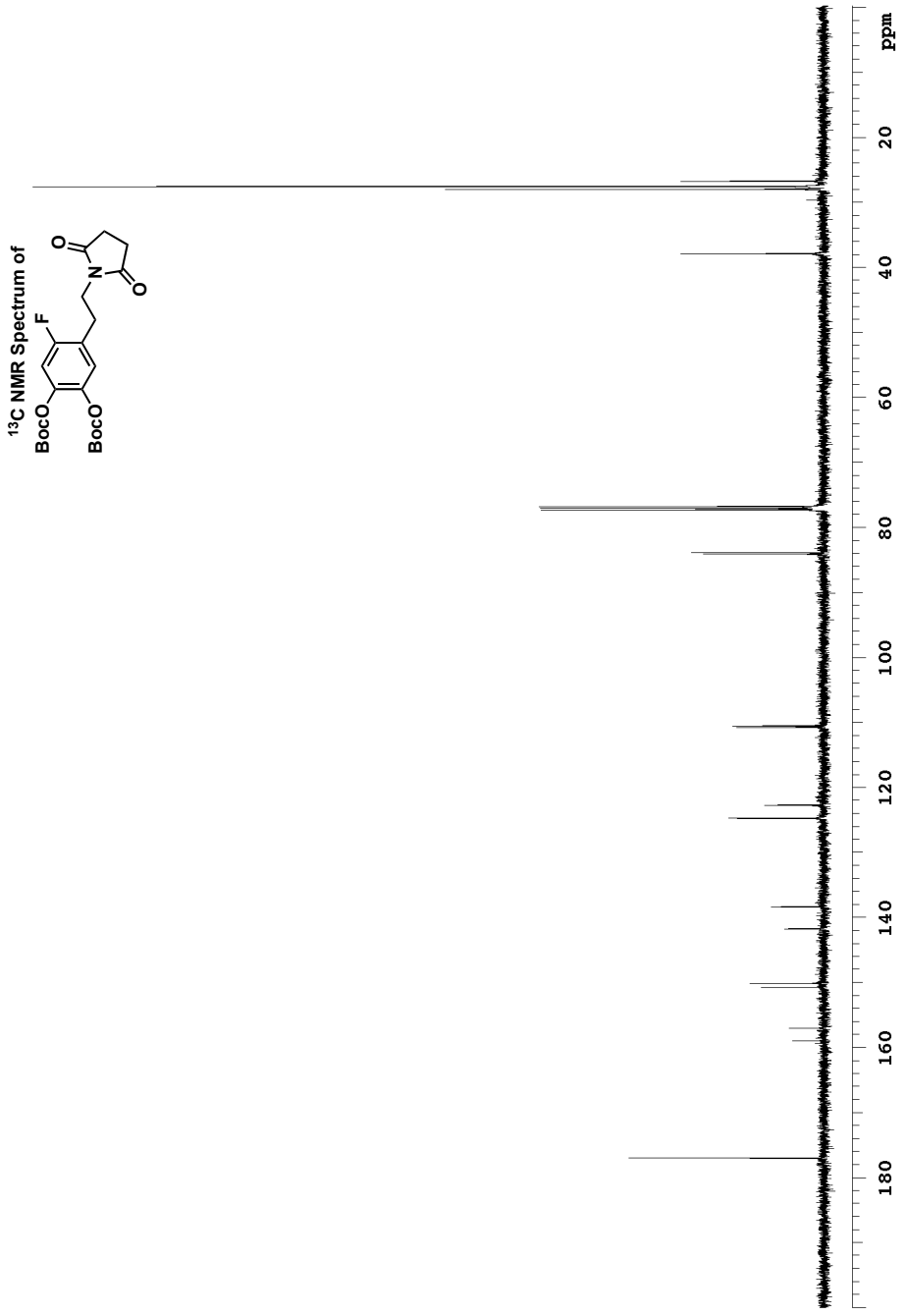
^{13}C NMR of **4n**. $CDCl_3$, 125 MHz, 23 °C



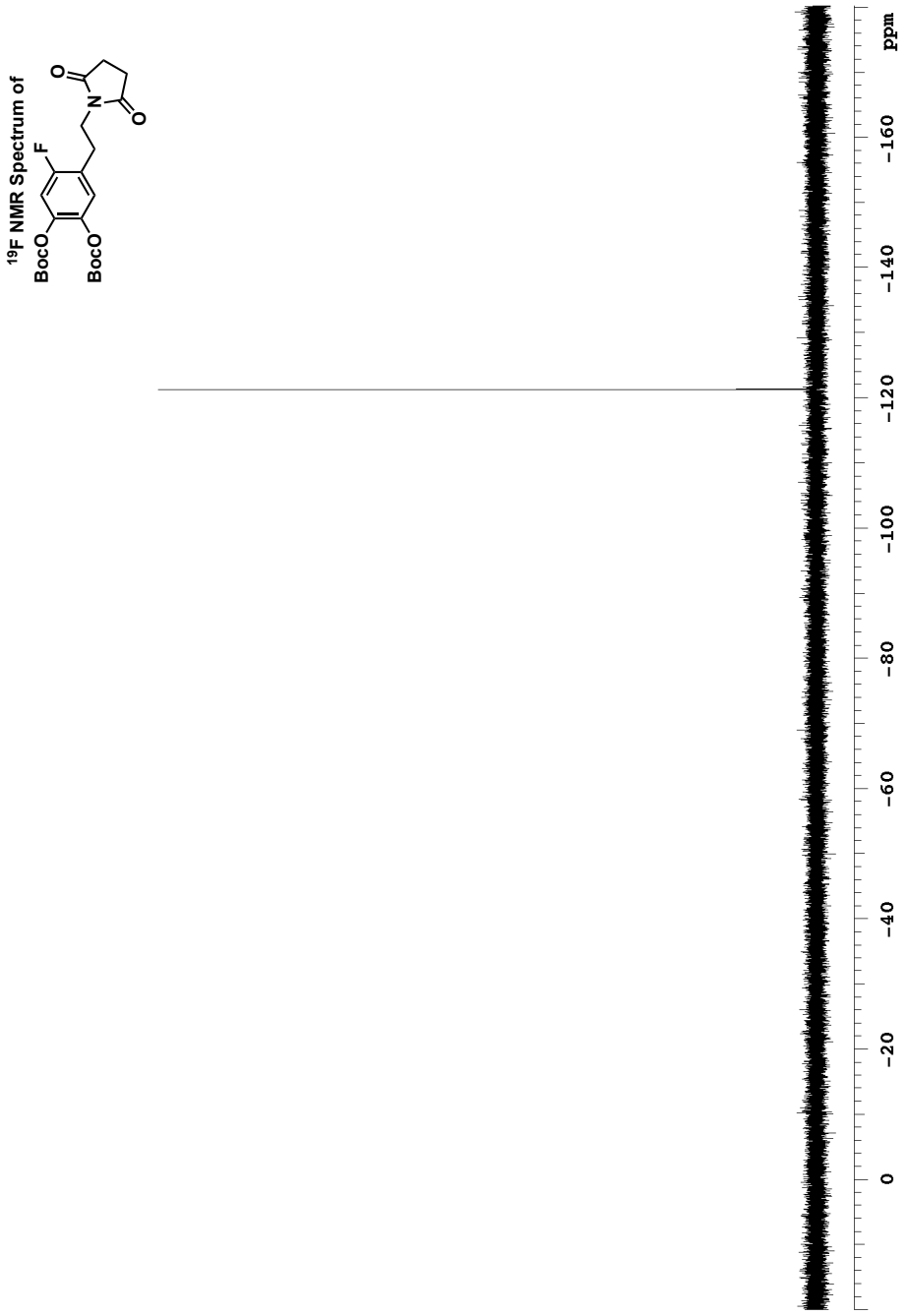
^{19}F NMR of **4n**. $CDCl_3$, 375 MHz, 23 °C



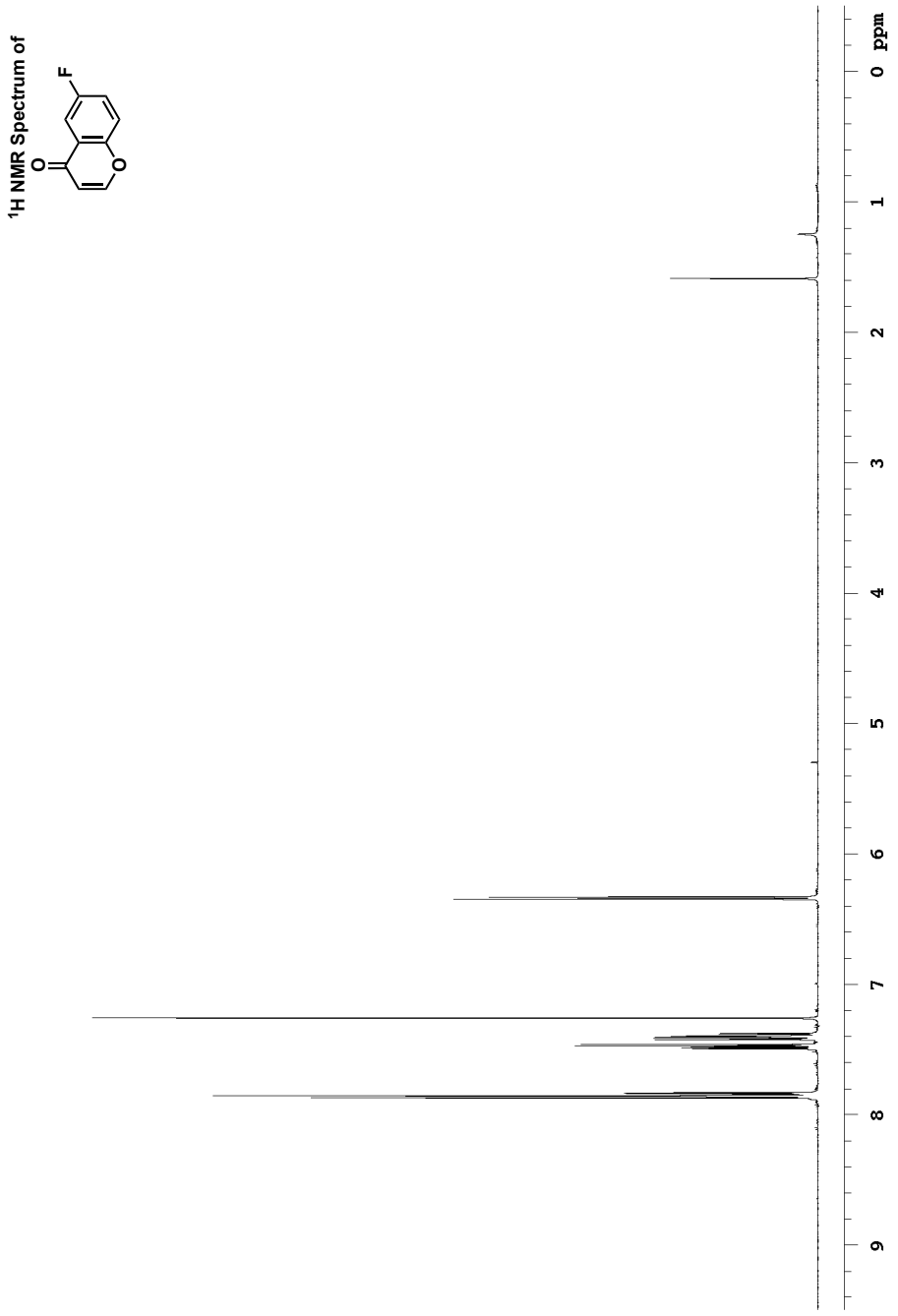
^{1}H NMR of **4o**. $CDCl_3$, 600 MHz, 23 °C



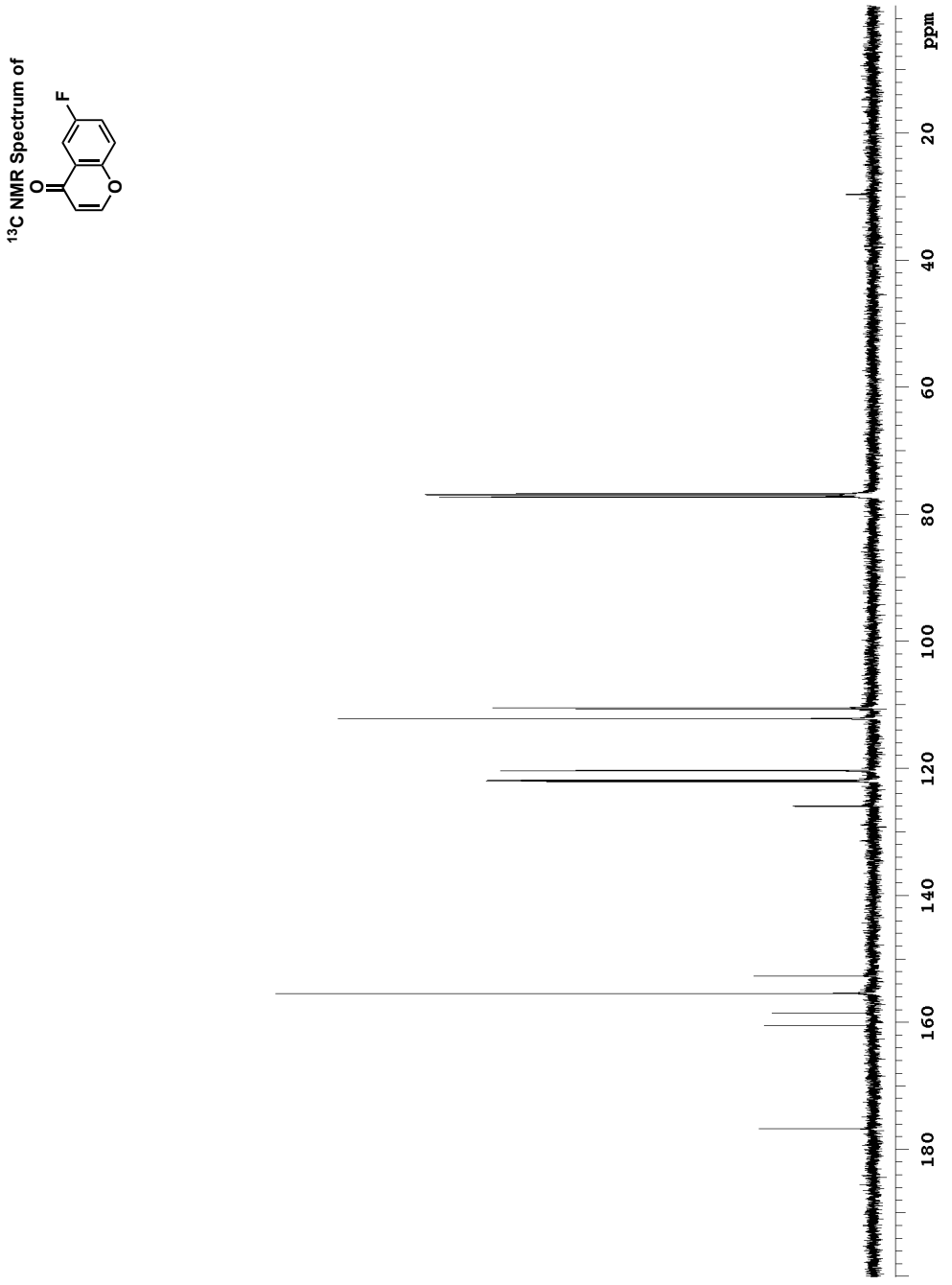
^{13}C NMR of **4o**. $CDCl_3$, 125 MHz, 23 °C



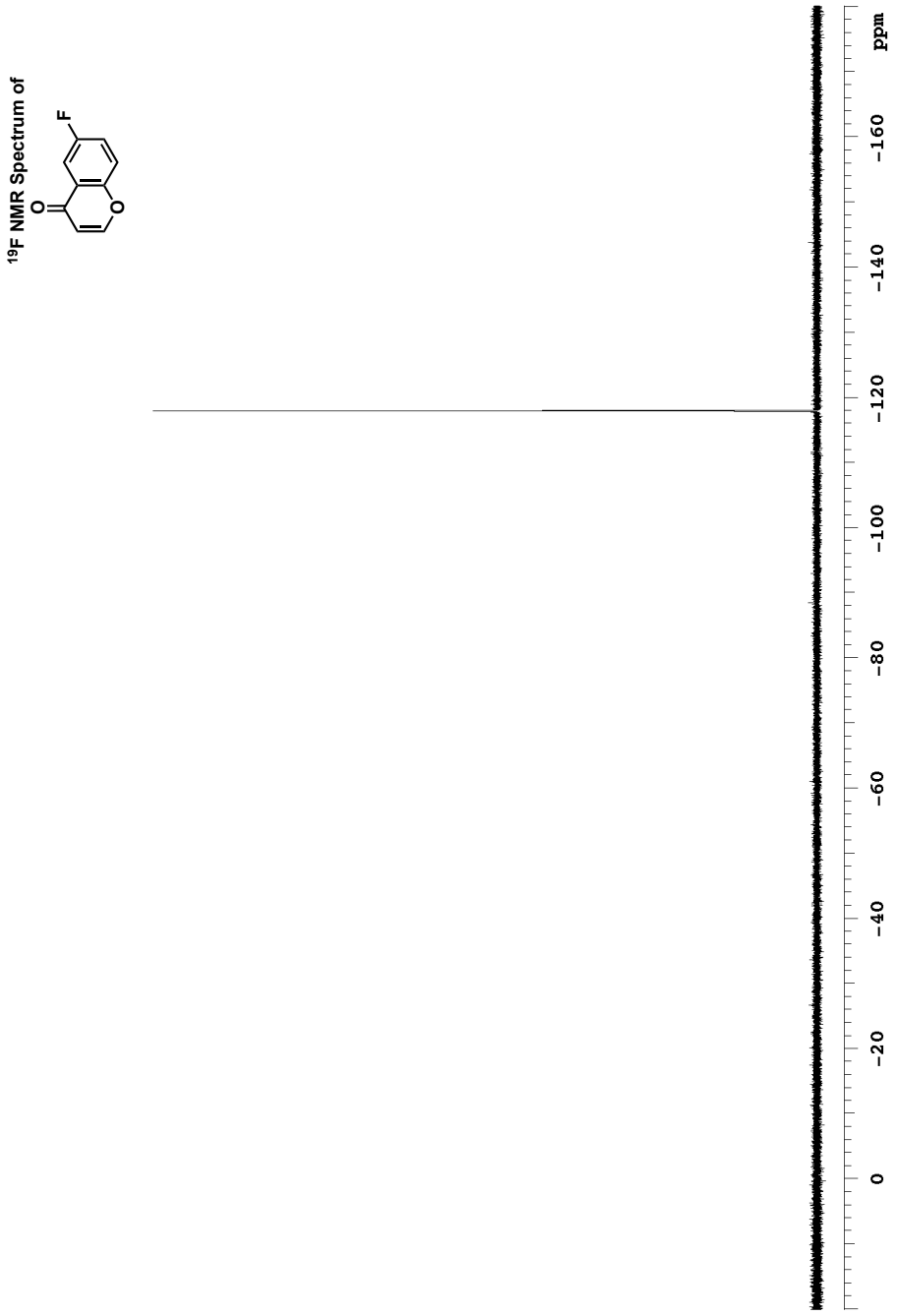
^{19}F NMR of **4o**. $CDCl_3$, 375 MHz, 23 °C



^{1}H NMR of **4p**. $CDCl_3$, 600 MHz, 23 °C

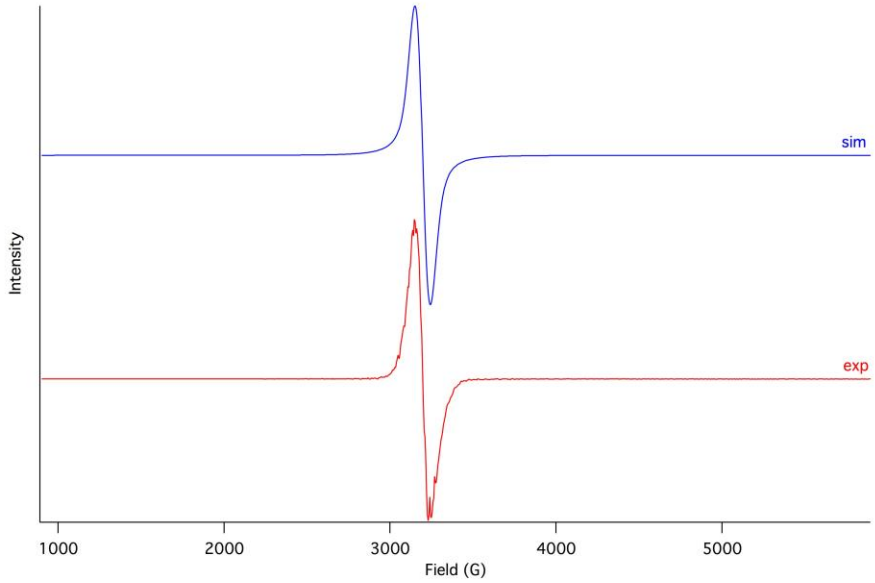


^{13}C NMR of **4p**. $CDCl_3$, 125 MHz, 23 °C



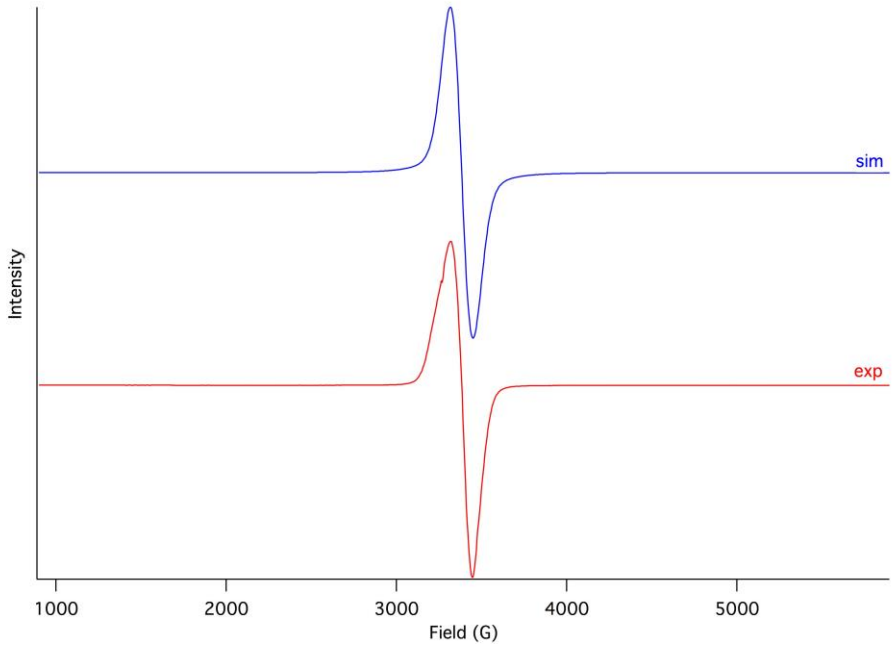
^{19}F NMR of **4p**. $CDCl_3$, 375 MHz, 23 °C

EPR Data



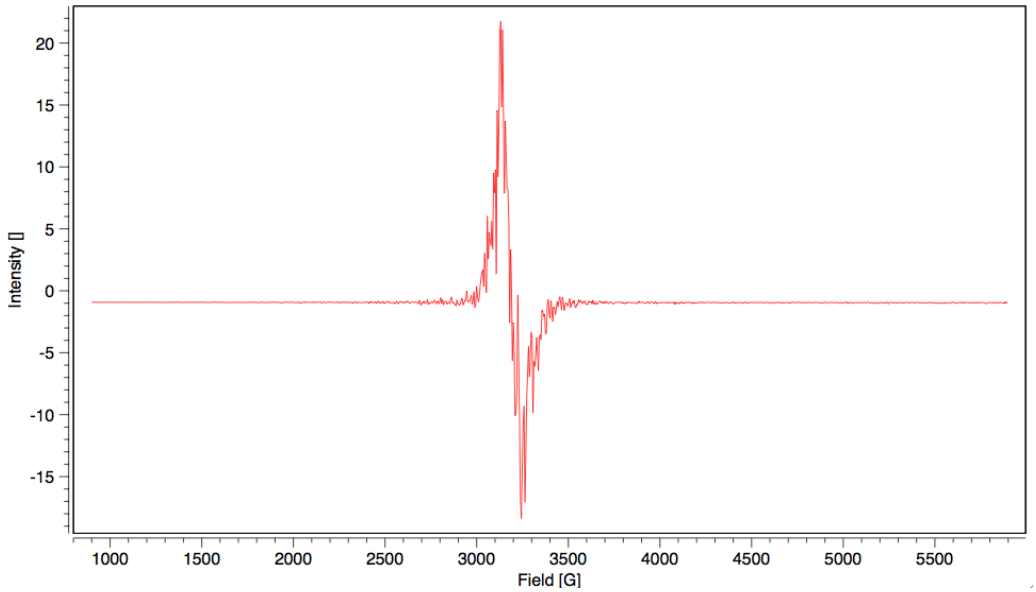
EPR Spectrum of **2** with Simulated Spectum. Frozen MeCN solution, 77 K

(*g*-value: 2.089)



EPR Spectrum of **2** with Simulated Spectum. Single Crystals, 298 K

(*g*-value: 2.082)



EPR Spectrum of **2**. Single Crystals, 77 K

This spectrum is observed to overlay well with the frozen MeCN solution spectrum at 77 K (*g*-value: 2.089).

Discussion of EPR Data

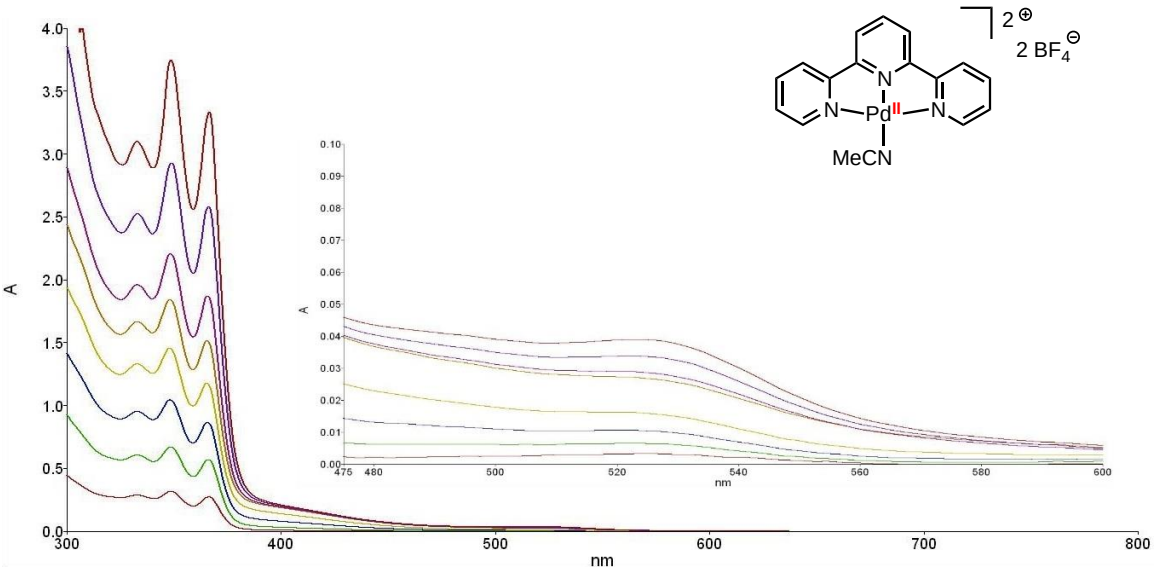
The solid- and solution-state EPR data for Pd(III) complex **2** display isotropic spectra at both 298 K and 77 K, with no observable spectral features due to hyperfine coupling or Jahn-Teller distortion (the fine features seen in the spectra at 77 K are due to vibrations caused by liquid nitrogen bubbling in the finger dewar used for data collection, and are not reproducible spectral features). We hypothesize that the lack of features observed in the EPR spectra may be due to a fluxional Jahn-Teller distortion at the temperatures at which the spectra were measured: fluxional Jahn-Teller distortion is well-precedented for cationic bis-terpyridyl transition metal complexes.[15][16]

[15] Folgado, J. V.; Henke, W.; Allmann, R.; Stratemeier, H.; Beltran-Porter, D.; Rojo, T.; Reinen, D. *Inorg. Chem.* **1990**, *29*, 2035–2042.

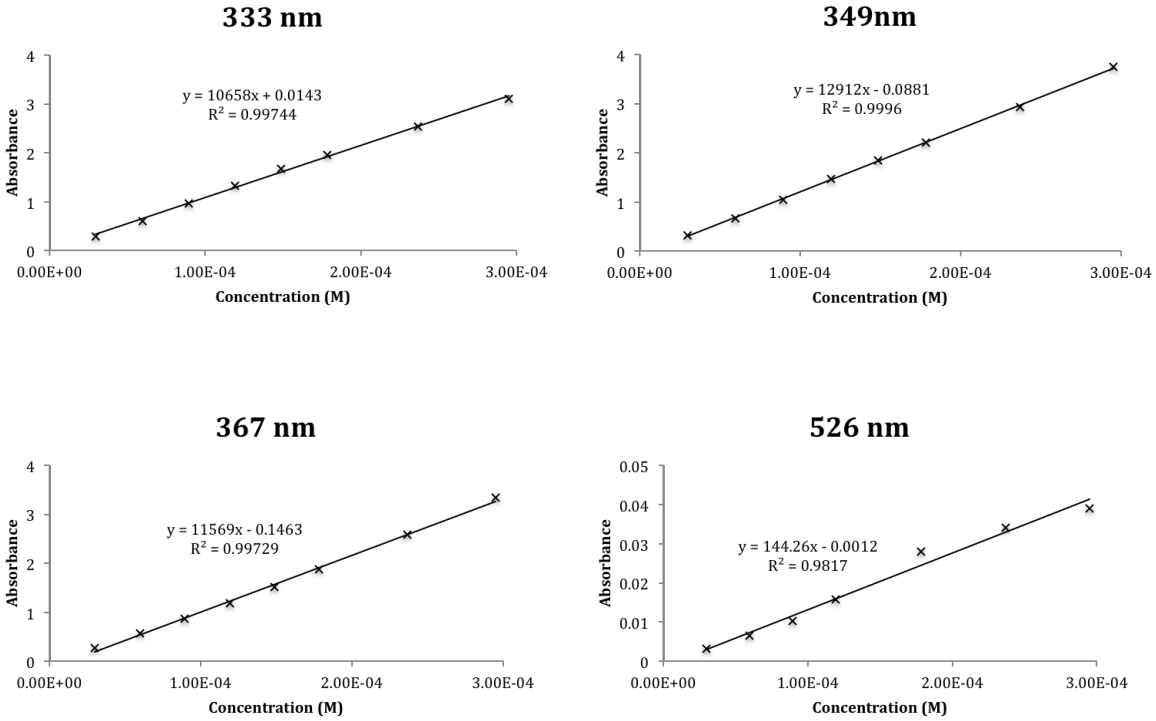
[16] Mack, K.; Wünsche von Leupoldt, A.; Förster, C.; Ezhevskaya, M.; Hinderberger, D.; Klinkhammer, K. W.; Heinze, K. *Inorg. Chem.* **2012**, *51*, 7851–7858.

UV-vis/NIR Data

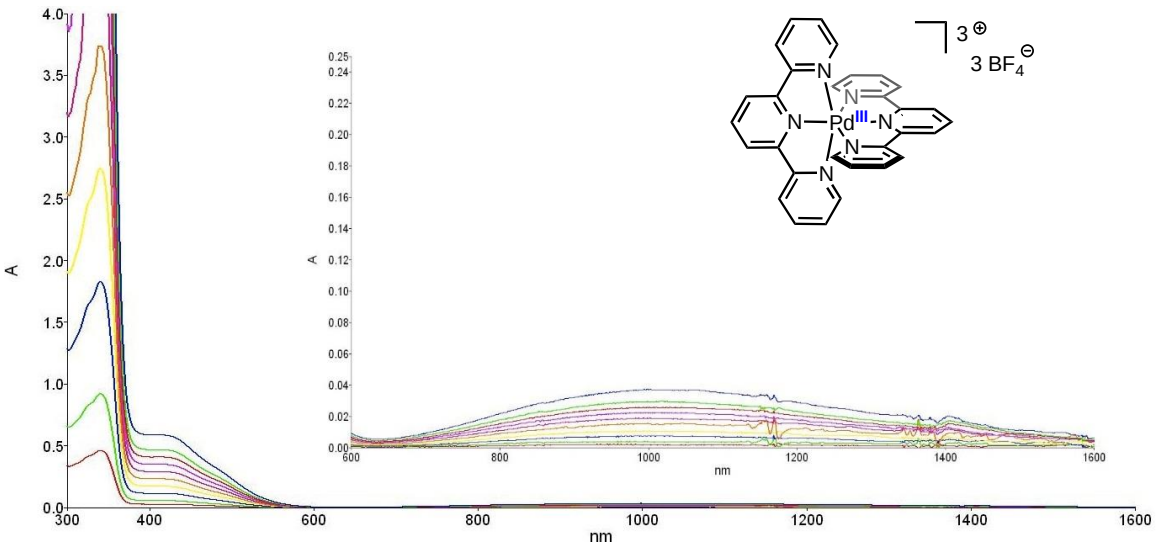
UV-vis Spectrum of 1 (DMF, 23 °C)



Molar Absorptivity Determinations:



UV-vis/NIR Spectrum of 2 (MeCN, 23 °C)



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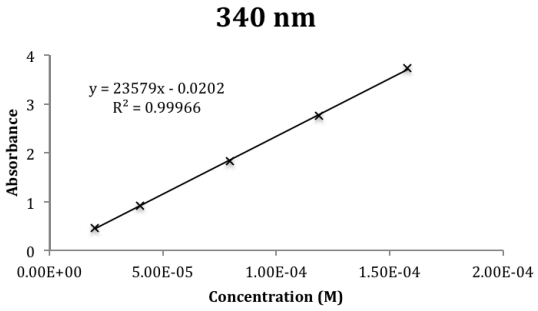
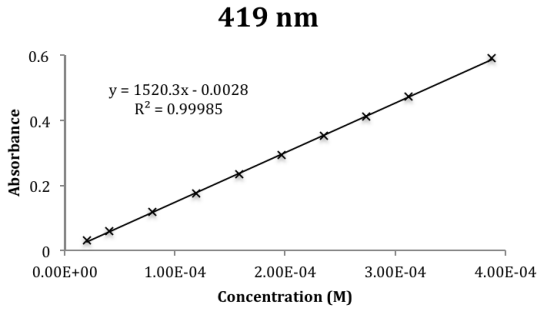
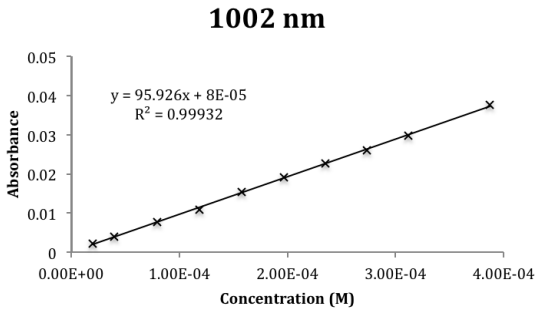
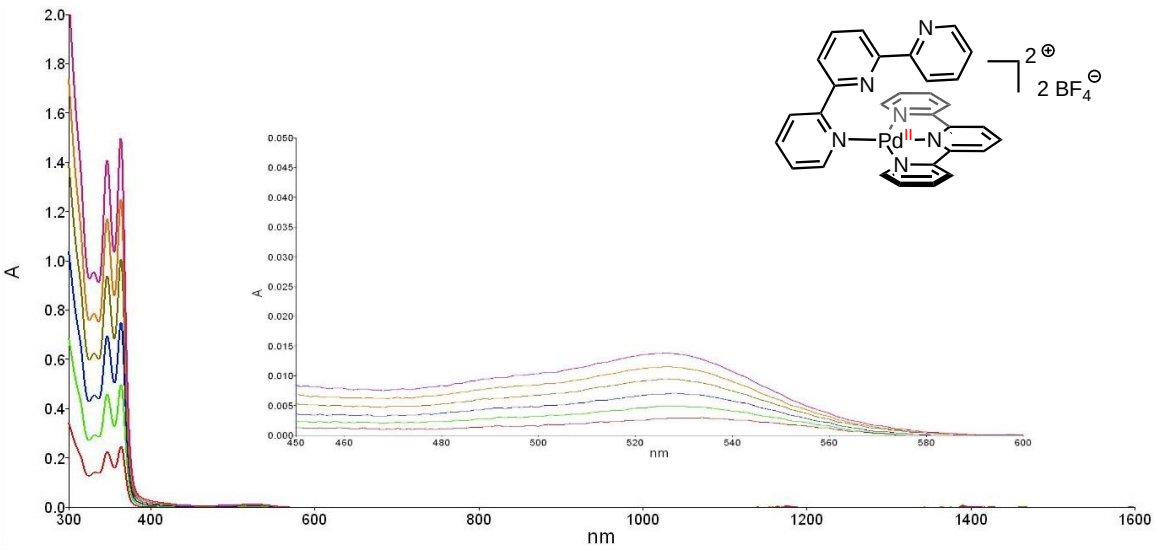


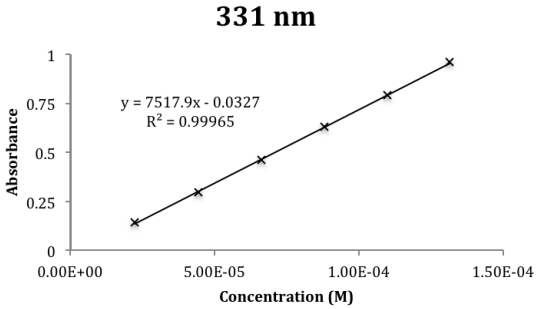


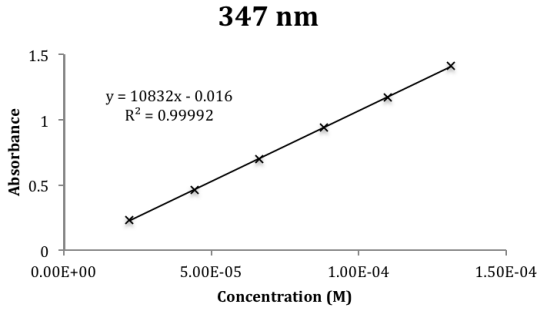


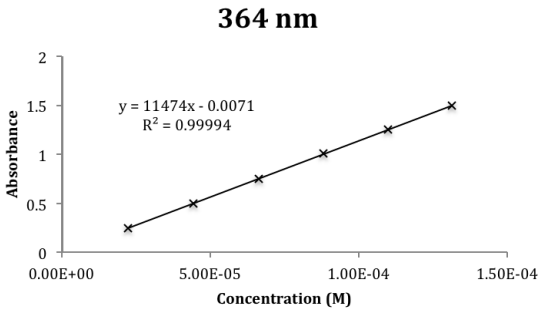
UV-vis/NIR Spectrum of S2 (MeCN, 23 °C)

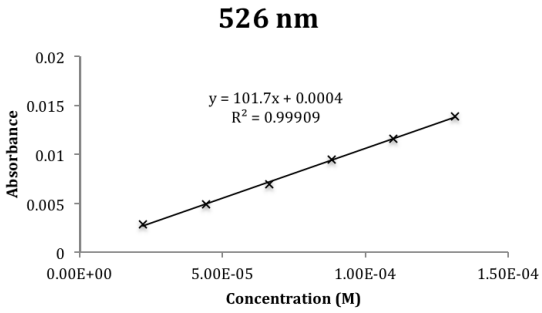


Molar Absorptivity Determinations:







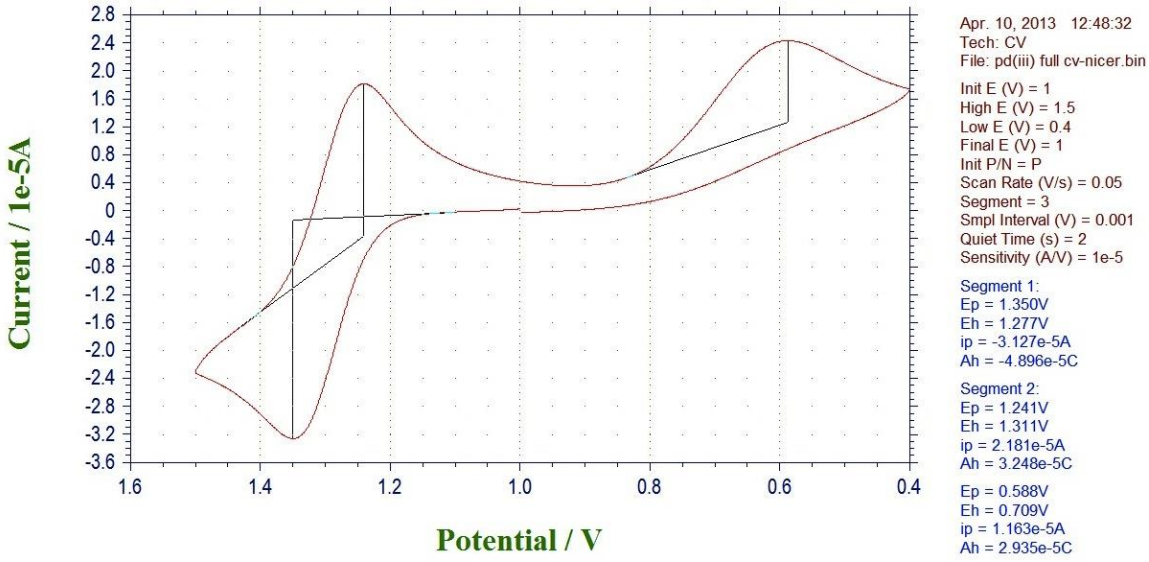


Electrochemical Data

General Methods

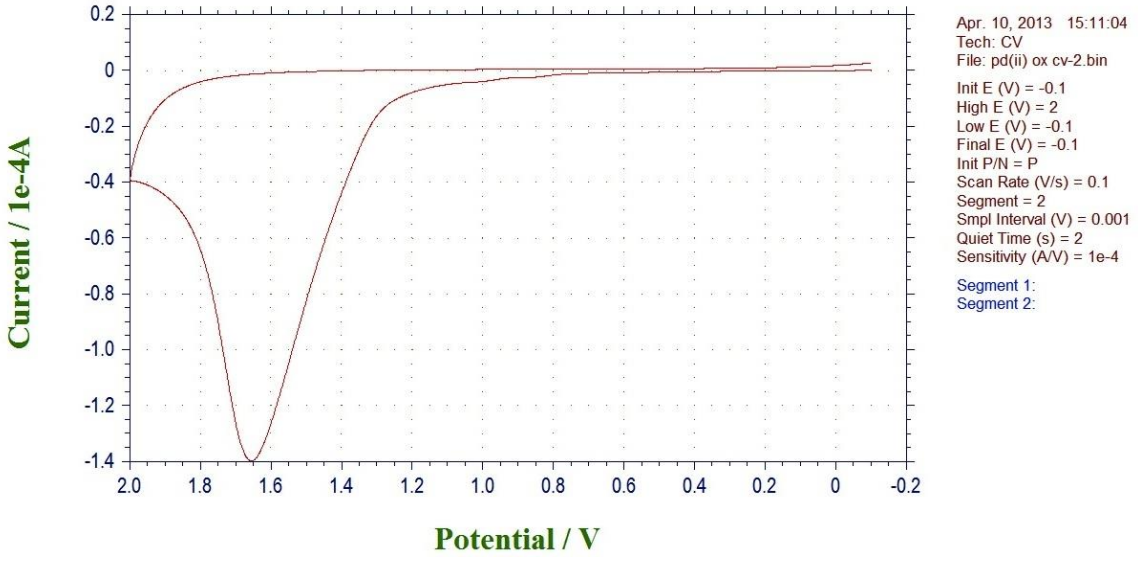
Cyclic Voltammetry (CV) was performed using approximately 2 mg/mL solutions of the analyte in MeCN, with Bu_4NPF_6 (0.1 M) as the electrolyte. A glassy carbon working electrode was used, along with a Pt wire counter electrode and a non-aqueous Ag/Ag^+ reference electrode. CVs were obtained at a scan rate of 0.1 V/s or 0.05 V/s (indicated for each sample), and ferrocene was used as an external reference. All reported potentials are vs Fc/Fc^+ unless otherwise noted.

CV of $[(terpy)_2Pd][BF_4]_3$ (2)



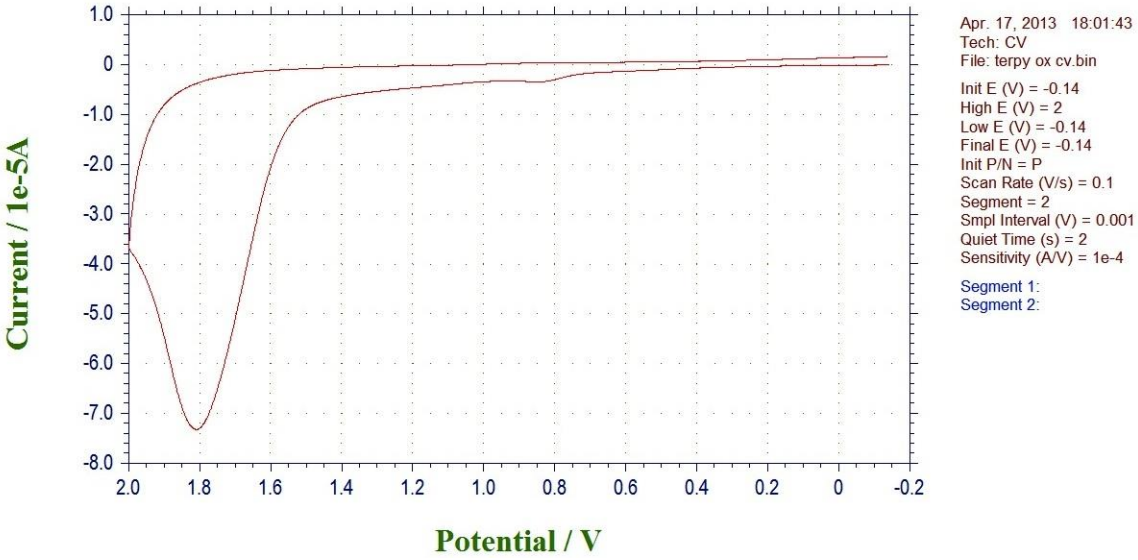
The reversible oxidation at 1.17 V (vs Fc/Fc^+) is assigned as the Pd(III)/Pd(IV) redox couple while the irreversible reduction wave at 460 mV (vs. Fc/Fc^+) is assigned as the Pd(III)/Pd(II) redox couple.

CV of [(terpy)Pd(MeCN)][BF_4]$_2$ (1) with added terpyridine



The only observed feature is an irreversible oxidation wave at 1.5 V (vs. Fc/Fc^+).

CV of terpyridine



The only observed feature is an irreversible oxidation wave at 1.7 V (vs. Fc/Fc^+).

Discussion of electrochemical data

The absence of any reversible oxidation waves for the mixture of $[(terpy)Pd(MeCN)]^{2+}$ (**1**) and terpyridine, and the observation of an irreversible reduction wave at 460 mV for $[(terpy)_2Pd]^{3+}$ (**2**) indicates that the oxidation of **1** to **2** in the presence of terpyridine and Selectfluor does not occur via an outer-sphere S.E.T. pathway.

Additionally, the Pd(III) complex **2** is observed to undergo a reversible one-electron oxidation to the Pd(IV) cation at a potential of 1.17 V. This potential is not accessible under the reaction conditions of the Pd-catalyzed fluorination, and therefore we believe that the intermediacy of Pd(IV) during catalysis is unlikely. It has been notoriously difficult to accurately measure or calculate the reduction potential of Selectfluor:[17] the reduction potential of Selectfluor has been measured at –40 mV vs SCE (–199 mV vs Fc/Fc^+),[18] which is in agreement with our experimental measurements, but this value is inconsistent with the observed chemical reactivity.[19] A better estimate has been provided by chemical means: Gilicinski *et al.* have observed that Selectfluor is capable of oxidizing bromide ion to elemental bromine (690 mV vs Fc/Fc^+), but not of oxidizing chloride ion to elemental chlorine (980 mV Fc/Fc^+).[10] The inability to oxidize chloride ion provides an upper limit for the oxidation potential of Selectfluor at 980 mV, well below the observed Pd(III)/Pd(IV) redox couple at 1.17 V.

[17] Serguchev, Y. A.; Ponomarenko, M. V.; Lourie, L. F.; Fokin, A. A. *J. Phys. Org. Chem.* **2010**, *24*, 407–413.

[18] Gilicinski, A. G.; Pez, G. P.; Syvret, R. G.; Lal, G. S. *J. Fluor. Chem.* **1992**, *59*, 157–162.

[19] Nyffeler, P. T.; Dur n, S. G.; Burkart, M. D.; Vincent, S. P. P.; Wong, C.-H. *Angew. Chem. Int. Ed.* **2005**, *44*, 192–212.