Aggregation induced emission in BF_2-hydrazone (BODIHY) complexes

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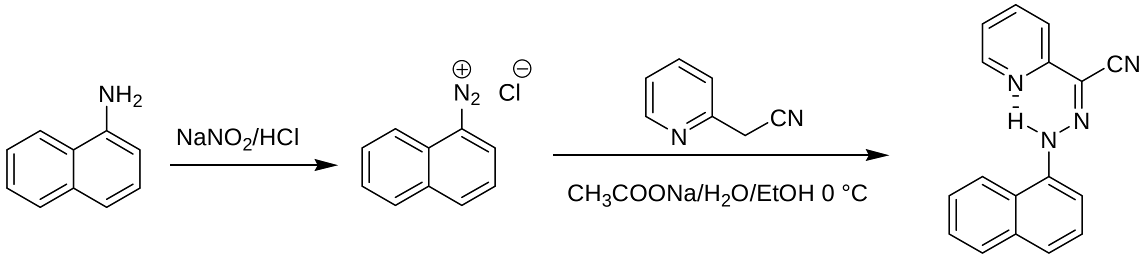
Table of Contents

General Information

All reagents and starting materials were purchased from commercial vendors and used without further purification. Column chromatography was performed on silica gel (Silicycle, 230-400 mesh). The melting points were measured on an Electrothermal 9100 instrument in open capillary tubes without thermometer correction. Deuterated solvents were purchased from Cambridge Isotope Laboratories and used as received. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 500 MHz spectrometer, with working frequencies of 499.87 MHz for ^{1}H nuclei and 125.7 MHz for ^{13}C nuclei, respectively. ^{19}F NMR spectra were recorded on a 300 MHz spectrometer, with working frequency of 282.2 MHz for ^{19}F nuclei. Chemical shifts are expressed in ppm relative to tetramethylsilane, using the residual solvent peak as a reference standard. Hi-Res mass spectra were measured on a Micromass Q-Tof Ultima. GC-MS spectra were measured on a Shimadzu Gas Chromatograph/Mass Spectrometer (GCMS-QP2010Plus). UV-Vis spectra were recorded on a Shimadzu UV-Vis spectrophotometer (UV-1800). Solid state fluorescence excitation and emission data were acquired with a Horiba Jobin-Yvon FluoroMax-4 fluorescence spectrophotometer equipped with an integrating sphere for PLQYs and a Hamamatsu R2658P photomultiplier tube. Spectra were corrected for integrating sphere scatter and background fluorescence by subtraction within the HJY operating system. All slit widths were held constant at 3.5/3.5 nm. Films were spin-coated or drop-casted from solvents to yield a maximum absorbance of 0.1 au. The poly(methylmethacrylate) (PMMA) film was spin-coated from 0.1 wt% PMMA/methylene chloride solution containing 10 wt% of the BF2-complex relative to PMMA. Fluorescence excitation and emission data in solution were recorded on a Shimadzu spectrofluorophotometer (RF-1501) using anthracene in EtOH as a standard. The quantum yields in solution were calculated using the following equation: $\Phi = \Phi_{st} \frac{I}{I_{st}} \frac{A_{st}}{A} \frac{\eta^2}{\eta_{st}{}^2}, \Phi_{st} = 0.27, \eta_{st} = 1.36, \eta = 1.424$, where A is the absorbance at the excitation wavelength and *I* is the integrated emission.[S1] For the solid-state sensing experiment a sheet of TLC plate (TLC Silica gel 60, 5748/7, Merck KGaA, Darmstadt, Germany) was cut into a "D" shape, and the extra silica gel was scratched off from the plate. The plate was then soaked in a DCM solution of **2**, and dried in air. The bare plastic substrate of the plate was masked with two small pieces of TLC.

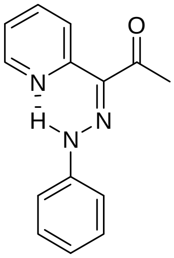
Synthesis



Hydrazone 1

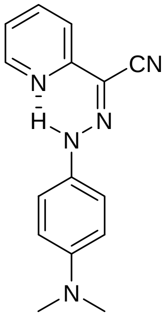
Scheme S1. Synthesis of **Hydrazone 1**.

Hydrazone 1: 1-Naphthylamine (1.0 g, 7.0 mmol) was dissolved in a mixture of 10 mL water and 4 mL conc. HCl, and was let to stir in an ice-bath for 30 min. A precooled solution of $NaNO_2$ (1 equiv, 0.483 g, 7.0 mmol) was then added dropwise over a period of 30 min to the naphthylamine solution. The diazonium salt solution was then added dropwise to a suspension of 2-pyridylacetonitrile (1 equiv, 0.78 mL, 7.0 mmol) and sodium acetate (6.4 equiv, 3.7 g, 44.8 mmol) in a cooled and well stirred 40 mL ethanol/water (4:1) mixture. The resulting reaction mixture was left to stir overnight at room temperature. The precipitated compound was then collected by filtration, dissolved in methylene chloride, washed with saturated potassium bicarbonate solution and dried over magnesium sulfate. The crude product was purified by silica gel column chromatography (hexane/ethyl acetate 7:1) to give **Hydrazone 1** as a dark orange powder (1.42 g, 75%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 15.88 (s, 1H), 8.82 (d, J = 6.5 Hz, 1H), 8.03 (d, J = 9.0 Hz, 1H), 7.96 (t, J = 8.5 Hz, 1H), 7.89 (m, 3H), 7.62 (m, 2H), 7.54 (m, 2H), 7.41 (t, J = 6.0 Hz, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.45, 149.79, 147.54, 138.11, 136.88, 134.38, 129.09, 126.71, 126.46, 126.32, 124.14, 123.23, 122.59, 120.04, 119.10, 111.49, 110.69 ppm; mp 216.2-217.1 $^\circ$C; GC-MS: calcd for $C_{17}H_{12}N_4$, 272.1; m/z (rel. inten.) 272 (62%, M^+), 141 (25%), 127 (100%), 115 (62%), 77 (22%).



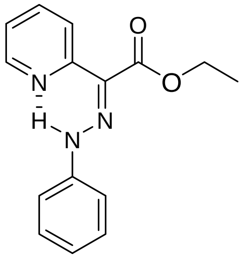
Hydrazone 2

Hydrazone 2: The compound was synthesized in a similar manner as described above for **Hydrazone 1** using the corresponding aniline and 2-pyridylacetone[S2] to afford **Hydrazone 2** as a yellow powder with a yield of 54%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 14.86 (s, 1H), 8.630 (d, J = 7.5 Hz, 1H), 8.43 (d, J = 10.5 Hz, 1H), 7.82 (t, J = 9.0 Hz, 1H), 7.38 (m, 4H), 7.28 (t, J = 7.0 Hz, 1H), 7.07 (t, J = 8.5 Hz, 1H), 2.64 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.48, 152.44, 146.50, 143.29, 137.04, 132.99, 129.64, 125.52, 123.45, 122.73, 115.18, 27.07 ppm; mp 110.1-111.0 °C; GC-MS: calcd for $C_{14}H_{13}N_3O$, 239.1; m/z (rel. inten.) 239 (43%, M^+), 106 (100%), 92 (55%), 78 (62%), 65 (43%).



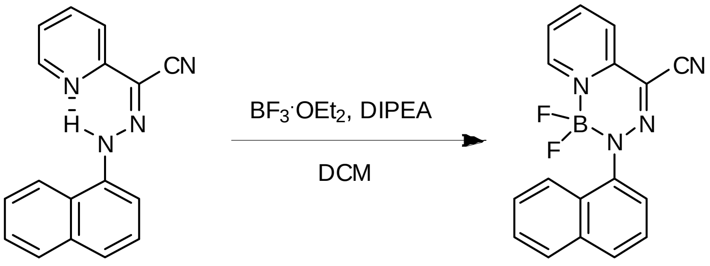
Hydrazone 3

Hydrazone 3: The compound was synthesized in a similar manner as described above for **Hydrazone 1** using *N*,*N*-dimethyl-1,4-phenylenediamine and 2-pyridylacetonitrile, to afford **Hydrazone 3** as a dark red powder with a yield of 70%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 15.04 (s, 1H), 8.58 (d, J = 6.0 Hz, 1H), 7.84 (t, J = 8.5 Hz, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.26 (m, 3H), 6.75 (m, 2H), 2.96 (s, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.10, 148.21, 147.12, 137.51, 133.29, 122.12, 121.60, 118.60, 116.51, 113.63, 109.05, 41.14 ppm; mp 109.5-111.0 °C; GC-MS: calcd for $C_{15}H_{15}N_5$, 265.1; *m*/*z* (rel. inten.) 265 (29%, M^+), 135 (100%), 78 (46%).



Hydrazone 4

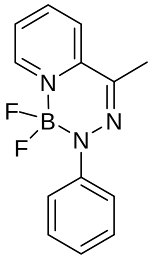
Hydrazone 4: The compound was synthesized in a similar manner as described above for **Hydrazone 1** using the corresponding aniline and ethyl-2-pyridylacetate, to afford **Hydrazone 4** as a yellow powder with a yield of 72%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 14.80 (s, 1H), 8.63 (d, *J* = 7.0 Hz, 1H), 7.81 (d, *J* = 9.5 Hz, 1H), 7.36 (m, 4H), 7.26 (t, *J* = 6.0 Hz, 1H), 7.03 (t, *J* = 6.5 Hz, 1H), 4.40 (q, 2H), 1.45 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.96, 153.01, 146.58, 143.53, 136.98, 129.54, 124.50, 123.04, 122.42, 115.09, 114.69, 61.21, 14.60 ppm; mp 78.2-79.0 °C; GC-MS: calcd for $C_{15}H_{15}N_3O_2$, 269.1; *m*/*z* (rel. inten.) 269 (36%, M^+), 195 (32%), 105 (62%), 91 (100%).



5

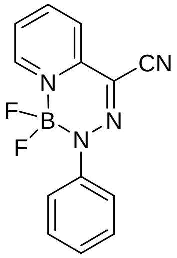
Scheme S2. Synthesis of BODIHY complex **5**.

5: *N*,*N*-Diisopropylethylamine (DIPEA, 7 equiv, 0.33 mL, 2.0 mmol) was added to a solution of **Hydrazone 1** (80 mg, 0.29 mmol) in dry methylene chloride at room temperature. After 2 hours, boron trifluoride diethyl ether complex (10 equiv, 0.36 mL, 2.9 mmol) was added dropwise. The reaction mixture was stirred at room temperature overnight. The reaction mixture was quenched with water and extracted by methylene chloride. The organic layer was washed three times with 10 mL water and dried over magnesium sulfate. After solvent concentration, the crude product was subjected to silica gel column chromatography (hexane/ethyl acetate 8:1) to give **5** as a bright orange powder (22 mg, 30%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72 (d, J = 6.0 Hz, 1H), 8.34 (t, J = 8.5 Hz, 1H), 8.04 (d, J = 8.5 Hz, 1H), 7.91 (d, J = 8.5 Hz, 2H), 7.80 (d, J = 9.5 Hz, 1H), 7.73 (t, J = 7.3 Hz, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.52 (m, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.29, 141.67, 140.38, 140.07, 134.85, 130.22, 129.34, 128.44, 127.07, 126.55, 125.33, 124.23, 123.98, 123.38, 121.01, 115.27, 109.05 ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ -136.43 (q, J = 28.3 Hz, 2F) ppm; mp 167.6-168.0 °C; Hi-Res MS (ESI): m/z calcd for $C_{17}H_{11}BF_2N_4$, 320.1123; found [M-H$^+$]: $C_{17}H_{12}BF_2N_4^+$, 321.1125.



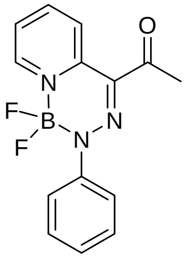
1

1: The compound was synthesized in a similar way as described for **5** using the appropriate hydrazone[S3] to afford **1** as a bright yellow powder with a yield of 38%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.74 (d, J = 6.0 Hz, 1H), 8.14 (t, J = 8.8 Hz, 1H), 7.65 (m, 3H), 7.57 (t, J = 7.3 Hz, 1H), 7.35 (t, J = 10.0 Hz, 2H), 7.08 (t, J = 7.3 Hz, 1H), 2.52 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.74, 141.71, 140.31, 140.26, 128.90, 123.47, 122.76, 121.04, 119.42, 119.37, 19.31 ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ -136.95 (q, J = 33.3 Hz, 2F) ppm; mp 120.2-120.8 °C; Hi-Res MS (ESI): m/z calcd for $C_{13}H_{12}BF_2N_3$, 259.1171; found [M-H$^+$]: $C_{13}H_{13}BF_2N_3^+$, 260.1172.



2

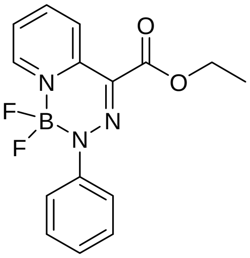
2: The compound was synthesized in a similar way as described for **5** using the appropriate hydrazone[S4] to afford **2** as a greenish yellow powder with a yield of 41%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (d, J = 6.0 Hz, 1H), 8.27 (t, J = 8.8 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.73 (m, 2H), 7.67 (t, J = 7.5 Hz, 1H), 7.43 (m, 2H), 7.28 (t, J = 7.5 Hz, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.84, 143.21, 141.58, 140.44, 129.25, 126.87, 123.84, 120.86, 120.78, 115.50, 108.69 ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ -134.10 (q, J = 50.0 Hz, 2F) ppm; mp 201.3-201.7 °C; Hi-Res MS (ESI): *m/z* calcd for $C_{13}H_9BF_2N_4$, 270.0967; found [M-H$^+$]: $C_{13}H_{10}BF_2N_4^+$, 271.0969.



3

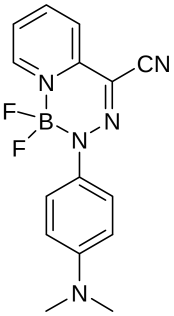
3: The compound was synthesized in a similar way as described for **5** using **Hydrazone 2** to afford **3** as a bright yellow powder with a yield of 35%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.26 (d, J = 8.5 Hz, 1H), 8.71 (d, J = 5.5 Hz, 1H), 8.20 (t, J = 8.0 Hz, 1H), 7.78 (d, J = 8.5 Hz, 2H), 7.63 (t, J = 6.8 Hz, 1H), 7.44 (m, 2H), 7.27 (t, J = 7.3 Hz, 1H), 2.69 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.25, 145.52, 142.49, 141.21, 139.75, 129.20, 126.09, 123.89, 123.55, 120.61, 120.57, 27.45 ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ -137.29 (q, J = 32.1 Hz, 2F) ppm; mp

121.7-122.1 °C; Hi-Res MS (ESI): *m/z* calcd for $C_{14}H_{12}BF_2N_3O$, 287.1120; found [M-H$^+$]: $C_{14}H_{13}BF_2N_3O^+$, 288.1122.



4

4: The compound was synthesized in a similar way as described for **5** using **Hydrazone 4** to afford **4** as a light brown solid with a yield of 23%. ^{1}H NMR (500 MHz, CDCl$_3$) δ 9.03 (d, *J* = 8.5 Hz, 1H), 8.70 (d, *J* = 6.0 Hz, 1H), 8.17 (t, *J* = 9.0 Hz, 1H), 7.78 (d, *J* = 8.5 Hz, 2H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.42 (t, *J* = 8.3 Hz, 2H), 7.23 (t, *J* = 7.8 Hz, 1H), 4.43 (q, *J* = 7.0 Hz, 2H), 1.45 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (126 MHz, CDCl$_3$) δ 164.64, 145.61, 142.08, 141.74, 139.84, 129.12, 125.90, 123.20, 123.03, 120.72, 120.68, 61.51, 14.62 ppm; ^{19}F NMR (282 MHz, CDCl$_3$) δ -136.84 (q, *J* = 33.3 Hz, 2F) ppm; mp 103.3-103.9 °C; Hi-Res MS (ESI): *m/z* calcd for $C_{15}H_{14}BF_2N_3O_2$, 317.1225; found [M-H$^+$]: $C_{15}H_{15}BF_2N_3O_2^+$, 318.1224.



6

6: The compound was synthesized in a similar way as described for **5** using **Hydrazone 3** to afford **6** as a dark purple powder with a yield of 52%. ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.58 (d, *J* = 6.0 Hz, 1H), 8.16 (t, *J* = 8.5 Hz, 1H), 7.85 (d, *J* = 8.5 Hz, 1H), 7.61 (d, *J* = 9.0 Hz, 2H), 7.54 (t, *J*

= 7.3 Hz, 1H), 6.74 (m, 2H), 3.00 (s, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.70, 142.28, 141.90, 139.79, 135.15, 122.57, 122.01, 121.97, 120.40, 116.23, 112.53, 40.77 ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ -134.78 (q, *J* = 31.0 Hz, 2F) ppm; mp 215.3-215.8 $^{\circ}$C; Hi-Res MS (ESI): *m*/*z* calcd for $C_{15}H_{14}BF_2N_5$, 313.1389; found [M-H$^+$]: $C_{15}H_{15}BF_2N_5^+$, 314.1389.

UV/Vis and Fluorescence Spectra

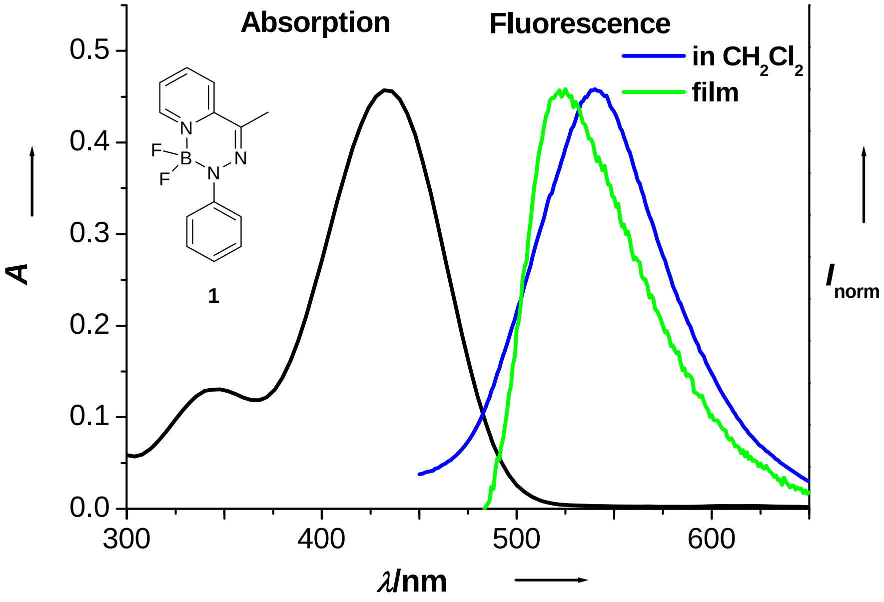


Figure S1. Absorption (left, 5.0 × 10^{-5} M in CH_2Cl_2) and normalized fluorescence (right) spectra of **1** in solution (1.0 × 10^{-5} M in CH_2Cl_2, excited at 432 nm) and the solid state (excited at 363 nm).

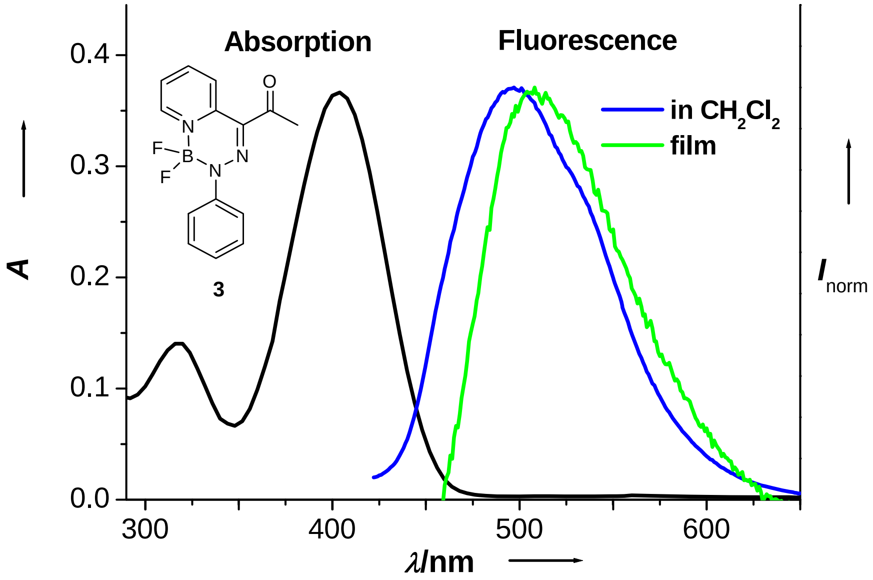


Figure S2. Absorption (left, 5.0 × 10^{-5} M in CH_2Cl_2) and normalized fluorescence (right) spectra of **3** in solution (1.0 × 10^{-5} M in CH_2Cl_2, excited at 404 nm) and the solid state (excited at 363 nm).

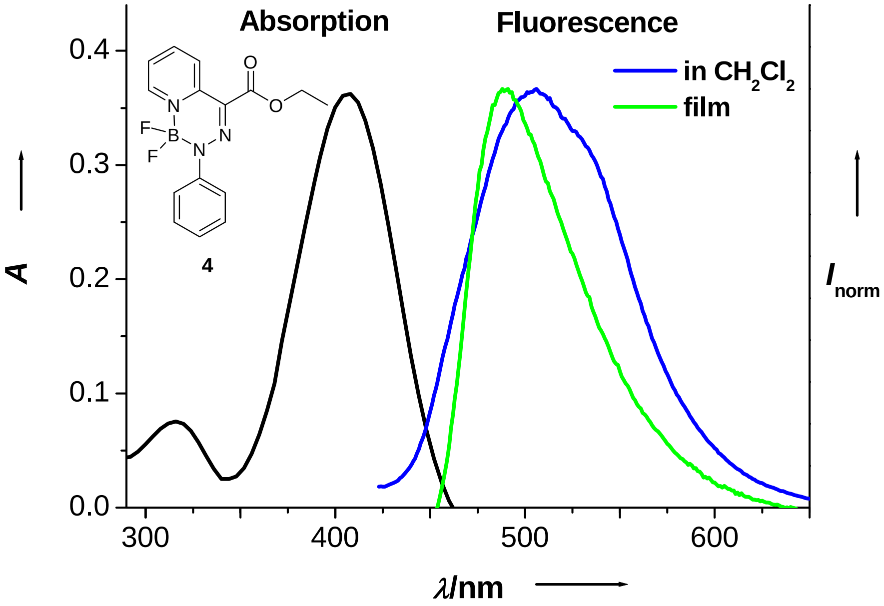


Figure S3. Absorption (left, 5.0 × 10^{-5} M in CH_2Cl_2) and normalized fluorescence (right) spectra of **4** in solution (1.0 × 10^{-5} M in CH_2Cl_2, excited at 408 nm) and the solid state (excited at 363 nm).

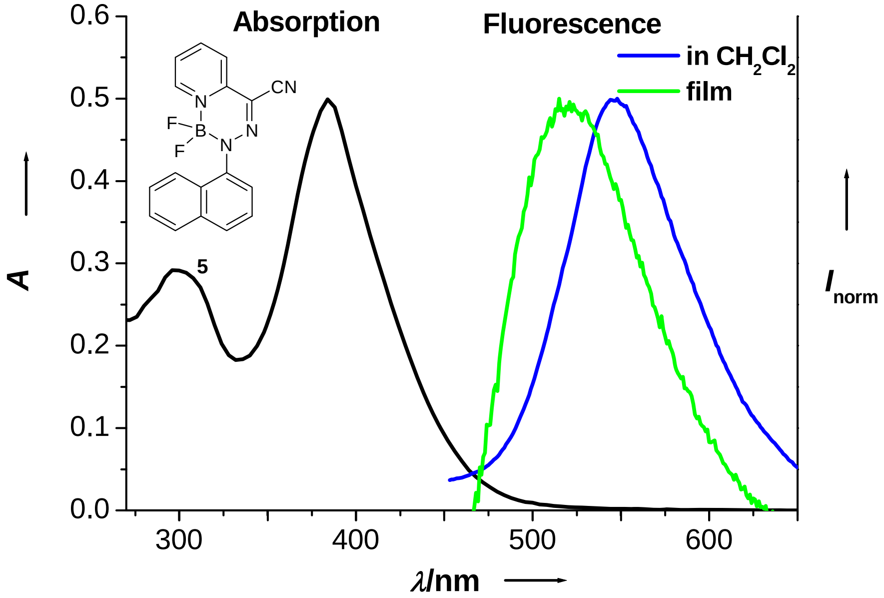


Figure S4. Absorption (left, 5.0 × 10^{-5} M in CH_2Cl_2) and normalized fluorescence (right) spectra of **5** in solution (1.0 × 10^{-5} M in CH_2Cl_2, excited at 384 nm) and the solid state (excited at 363 nm).

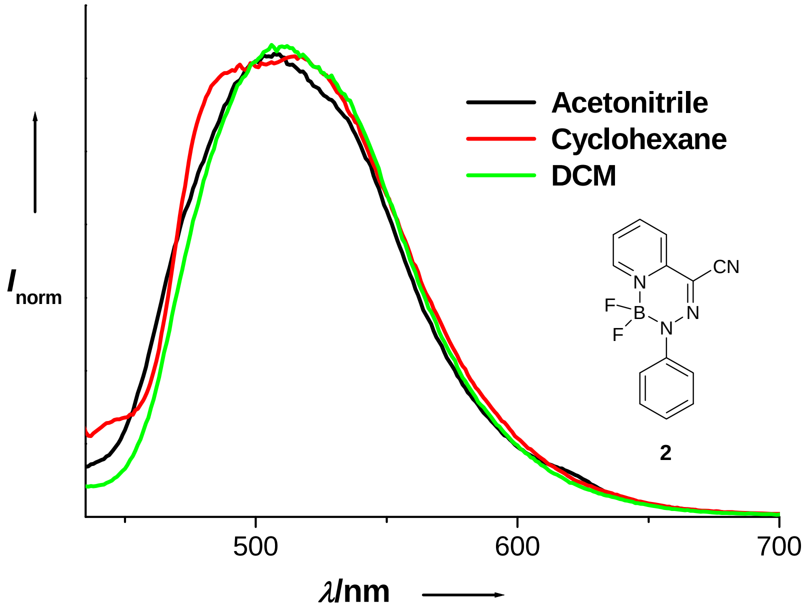


Figure S5. Normalized fluorescence spectra of **2** in various solvents (1.0×10^{-5} M in CH_2Cl_2, excited at 413 nm).

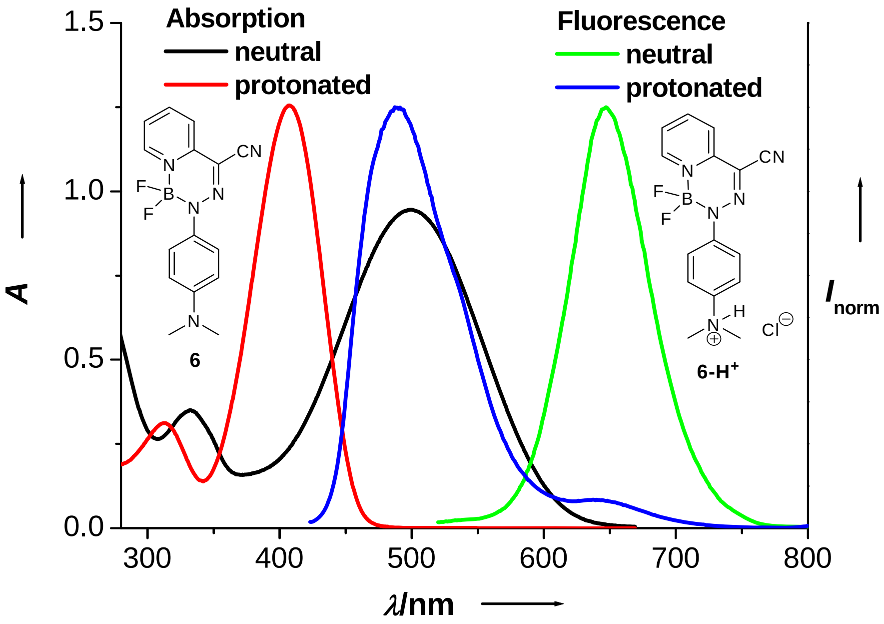


Figure S6. Absorption (5.0×10^{-5} M in CH_2Cl_2) and normalized fluorescence spectra of the switching between **6** and its protonated form **6-H**$^+$ in CH_2Cl_2 (1.0×10^{-5} M, excited at each λ_{abs}).

NMR Spectra

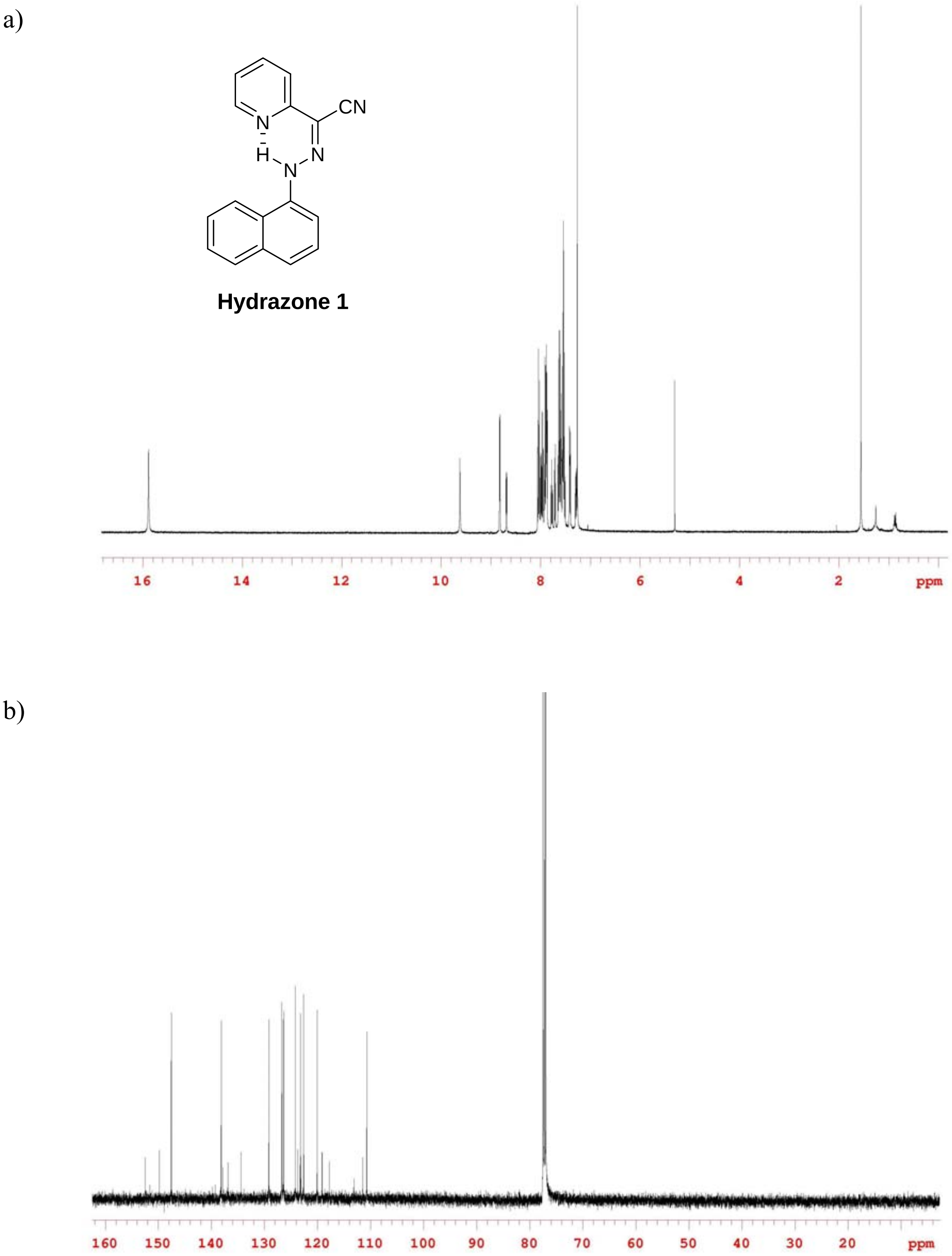


Figure S7. a) ^{1}H NMR and b) ^{13}C NMR spectra of **Hydrazone 1** in $CDCl_3$ at 294 K.

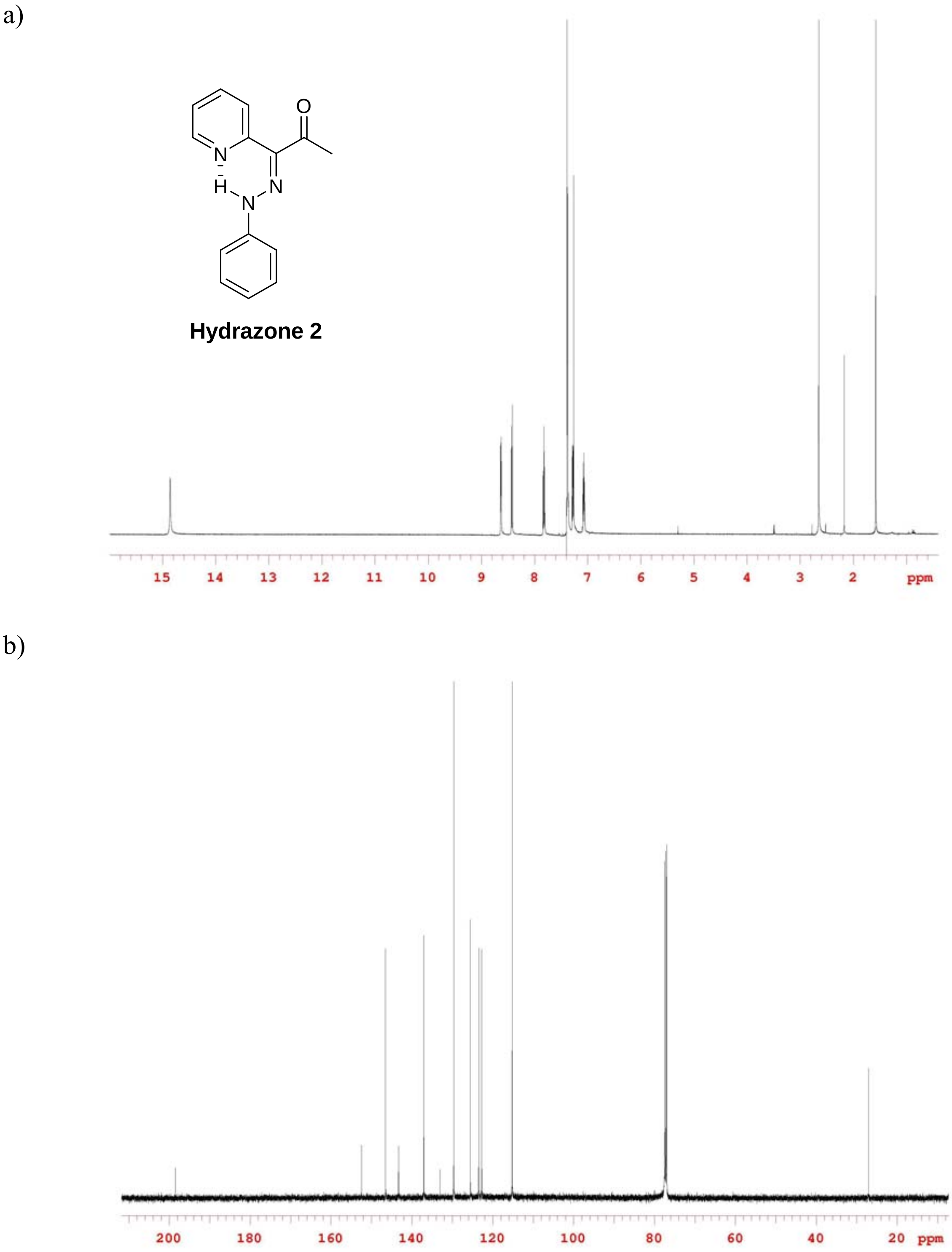


Figure S8. a) ^{1}H NMR and b) ^{13}C NMR spectra of **Hydrazone 2** in $CDCl_3$ at 294 K.

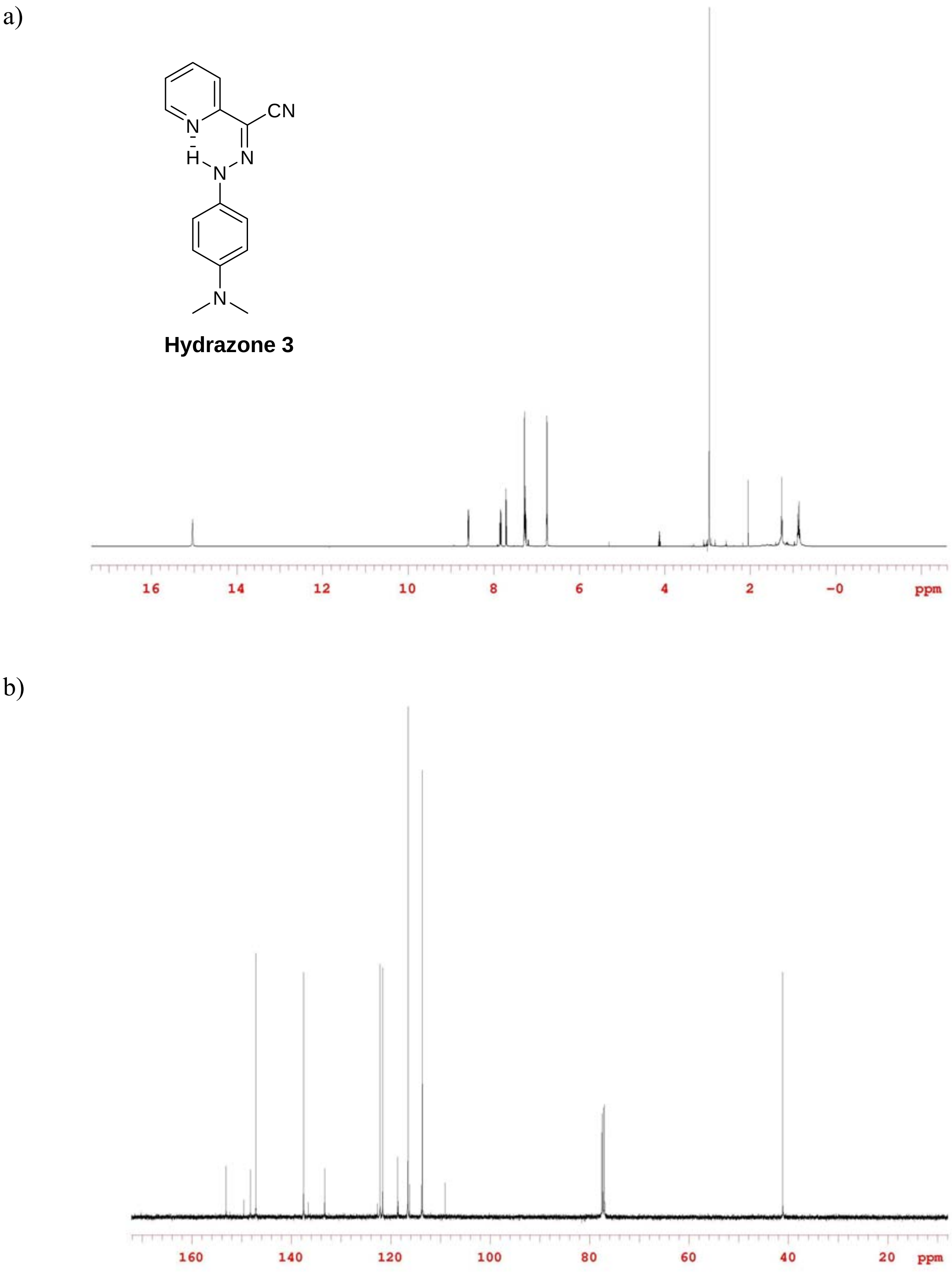


Figure S9. a) ^{1}H NMR and b) ^{13}C NMR spectra of **Hydrazone 3** in $CDCl_3$ at 294 K.

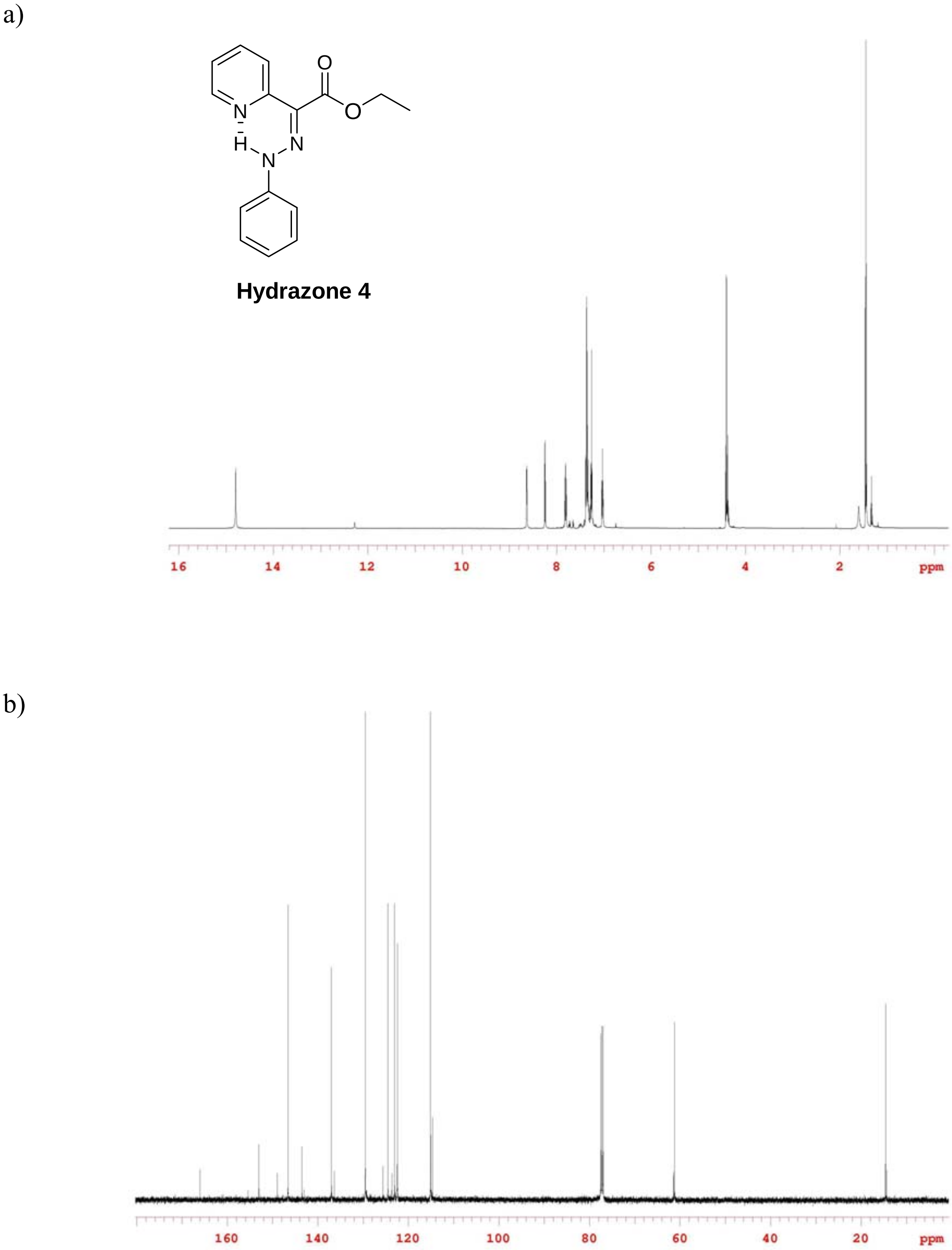


Figure S10. a) ^{1}H NMR and b) ^{13}C NMR spectra of **Hydrazone 4** in $CDCl_3$ at 294 K.

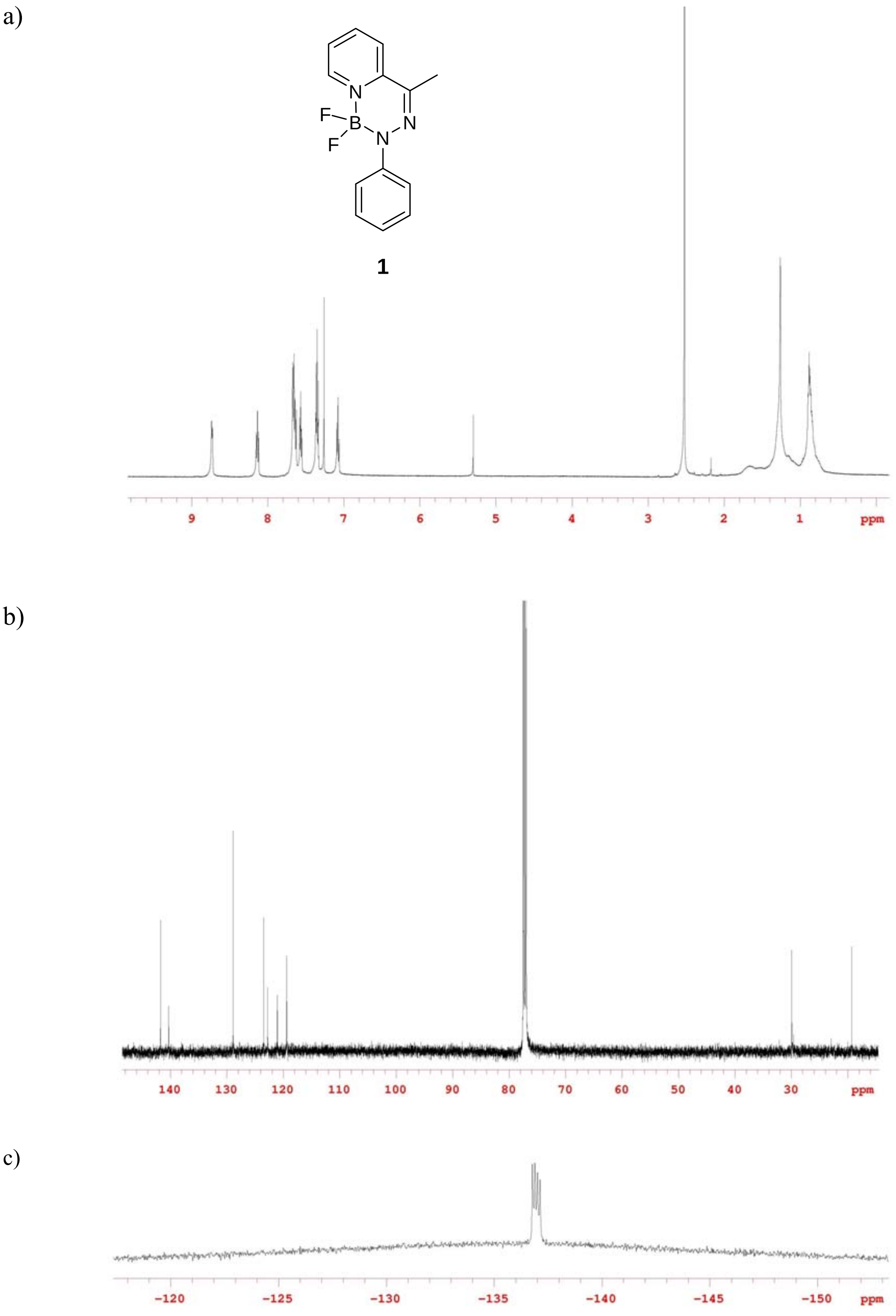


Figure S11. a) ^{1}H NMR and b) ^{13}C NMR c) ^{19}F NMR spectra of **1** in $CDCl_3$ at 294 K.

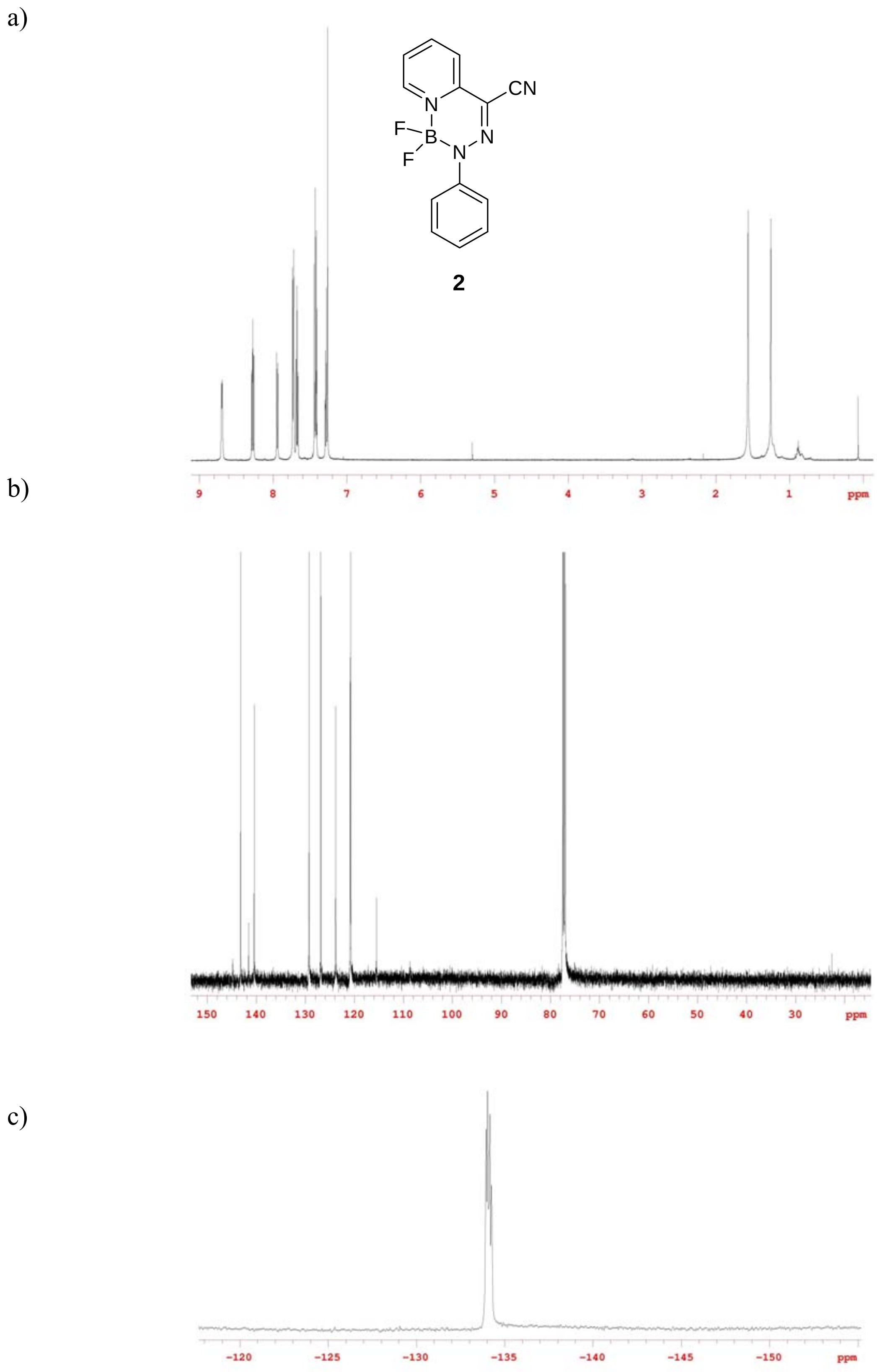


Figure S12. a) ^{1}H NMR and b) ^{13}C NMR c) ^{19}F NMR spectra of **2** in $CDCl_3$ at 294 K.

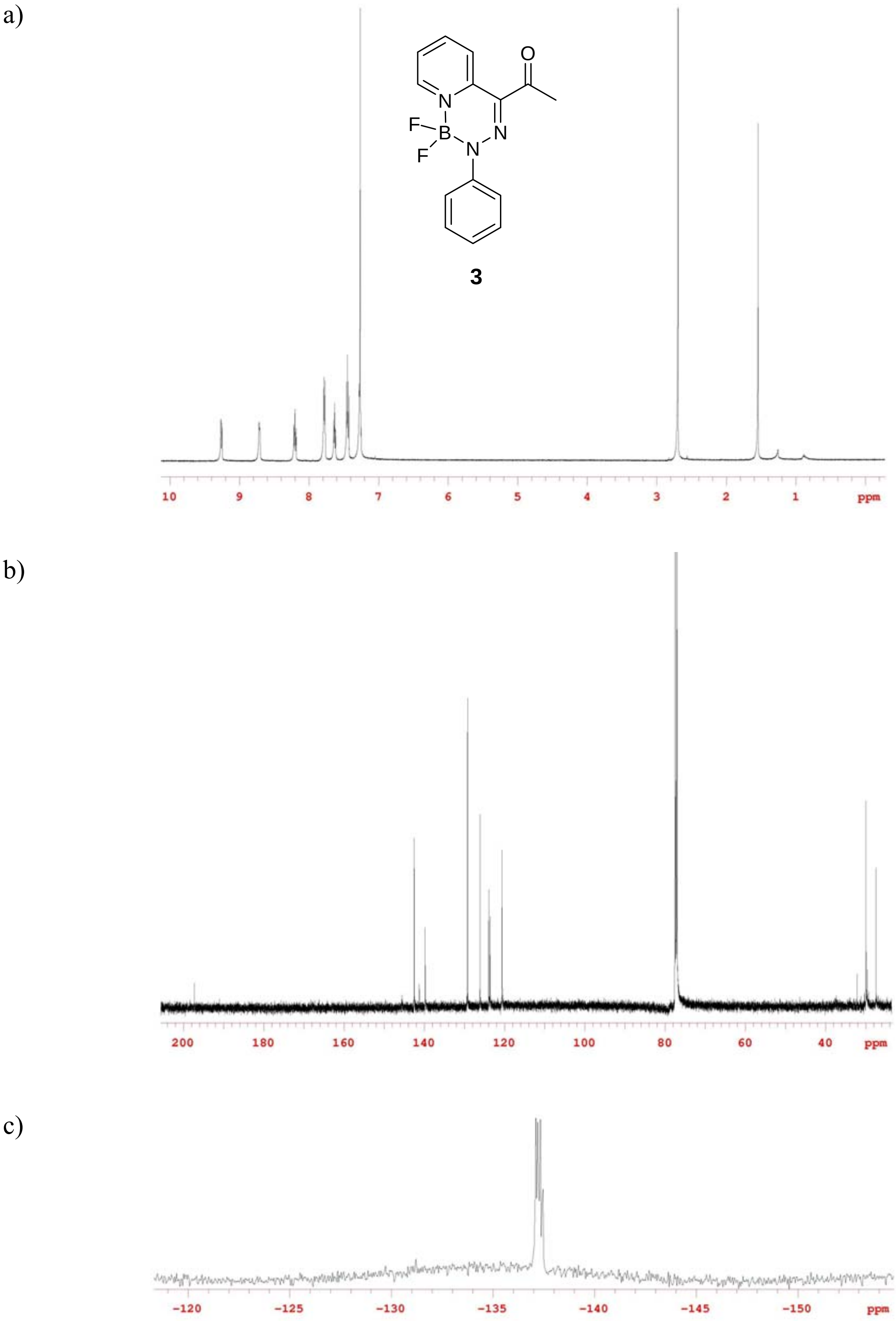


Figure S13. a) ^{1}H NMR and b) ^{13}C NMR c) ^{19}F NMR spectra of **3** in $CDCl_3$ at 294 K.

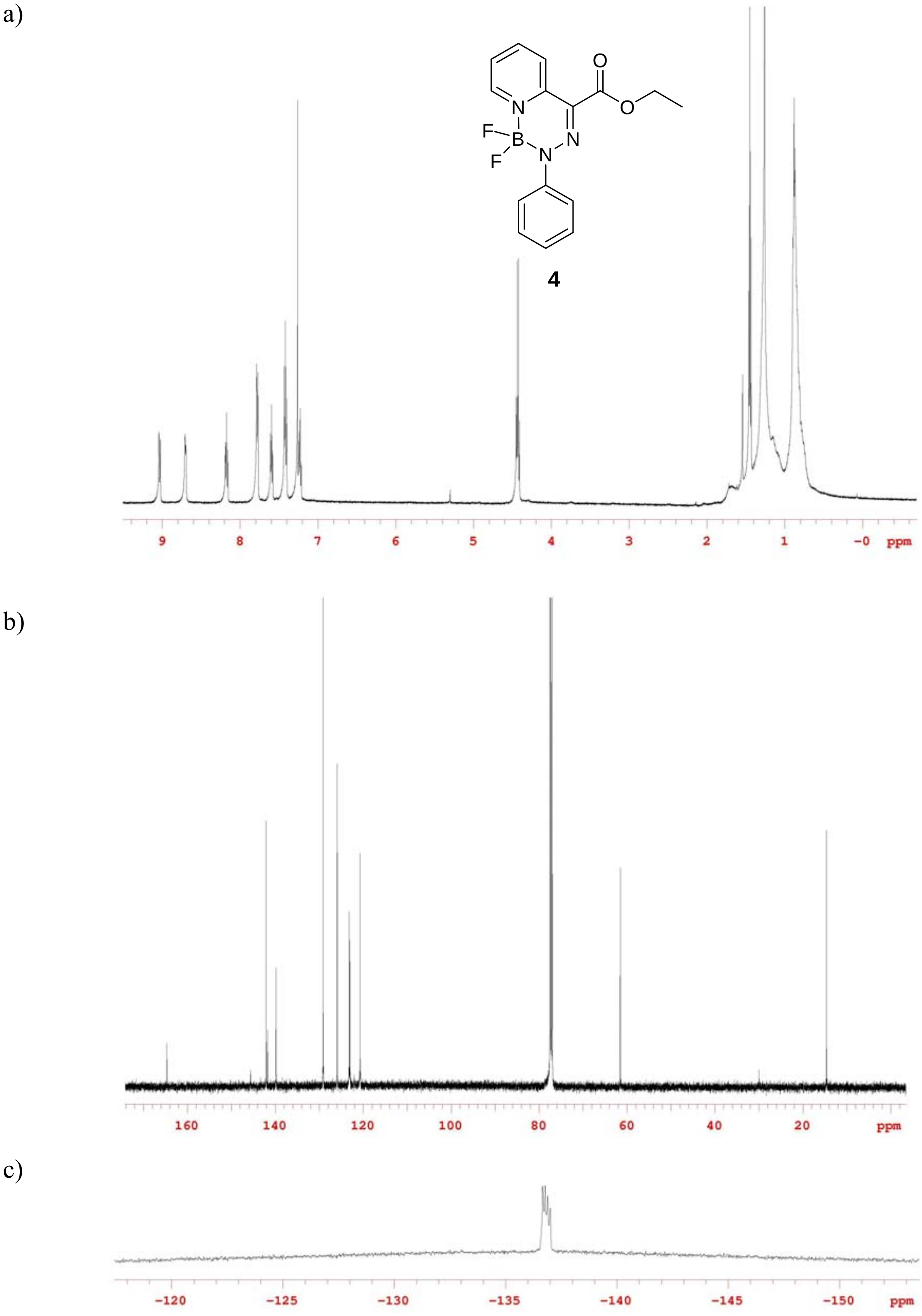


Figure S14. a) ^{1}H NMR and b) ^{13}C NMR c) ^{19}F NMR spectra of **4** in $CDCl_3$ at 294 K.

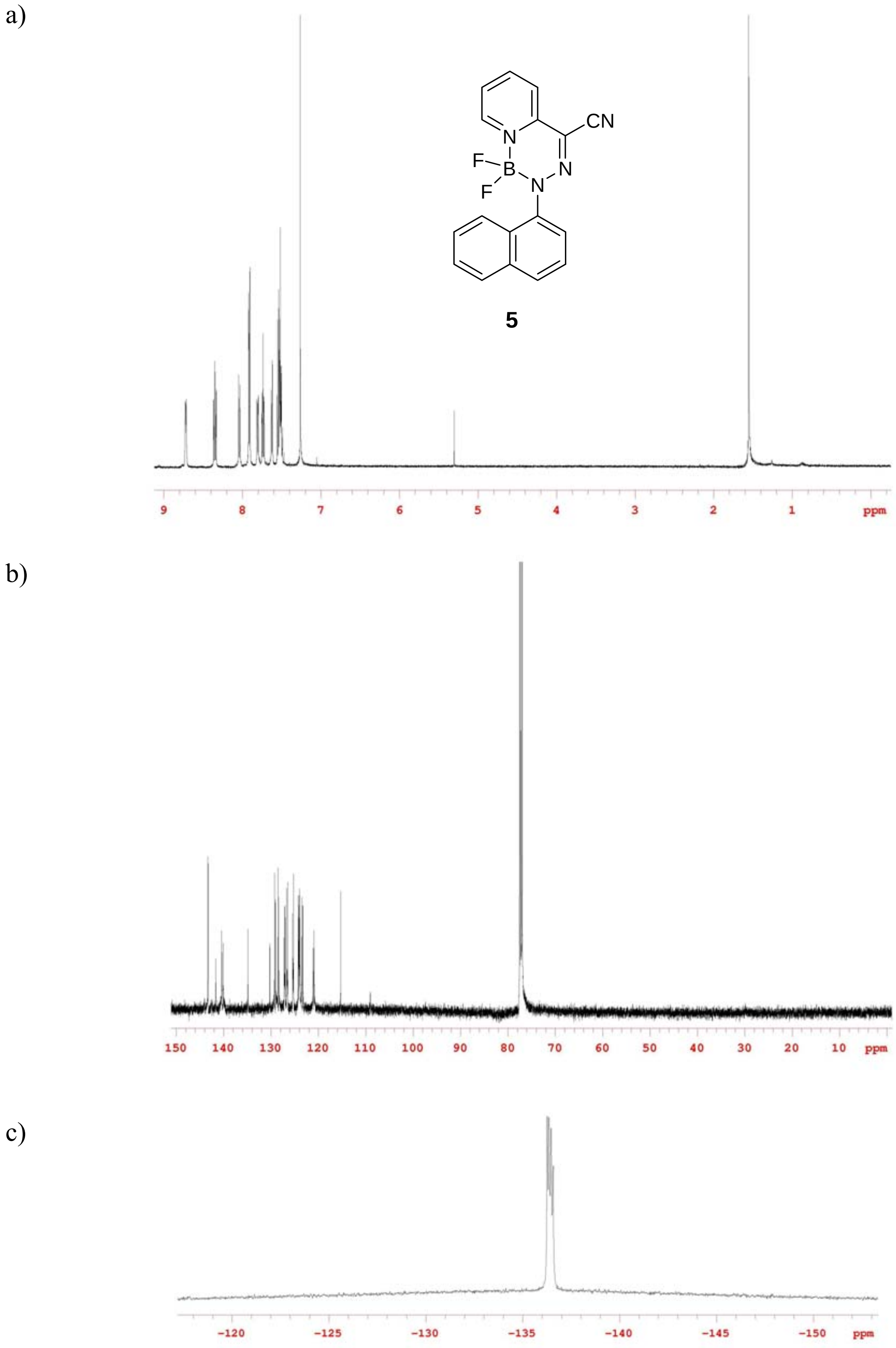


Figure S15. a) ^{1}H NMR and b) ^{13}C NMR c) ^{19}F NMR spectra of **5** in $CDCl_3$ at 294 K.

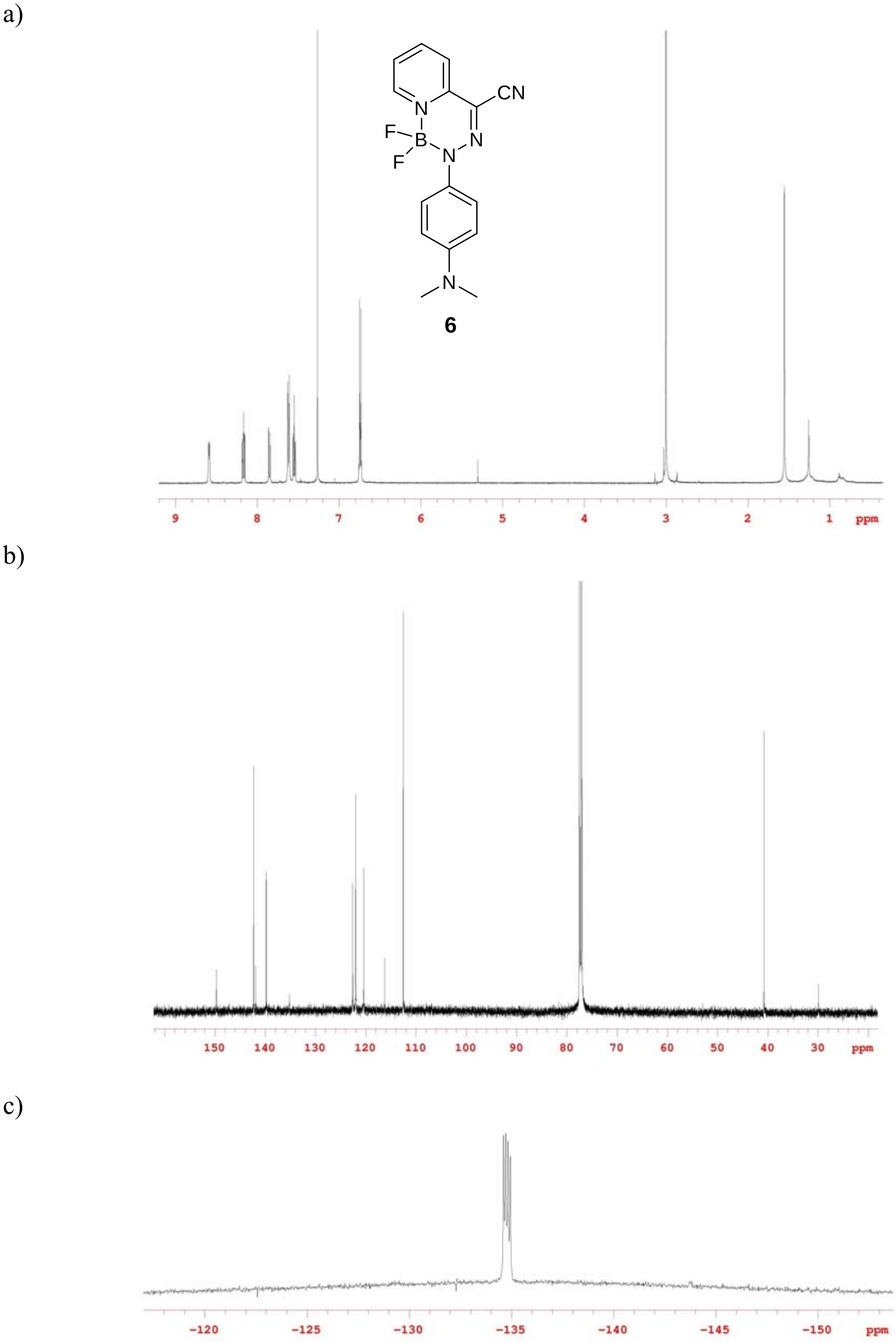


Figure S16. a) ^{1}H NMR and b) ^{13}C NMR c) ^{19}F NMR spectra of **6** in $CDCl_3$ at 294 K.

X-Ray Crystallography

1 (CCDC 841442): 1 (20 mg) was dissolved in 2 mL chloroform and 1 mL hexanes. The solution was filtered and allowed to evaporate over 2 days. Yellow needle crystals were collected.

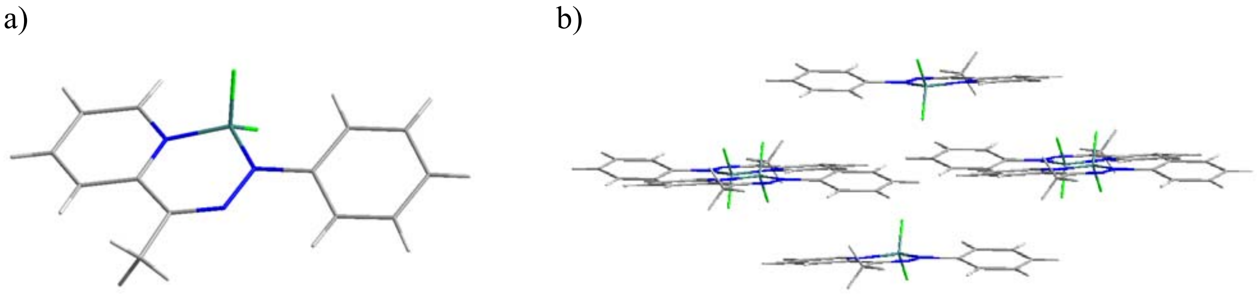


Figure S17. Wire drawing of a) the structure of **1** and b) its crystal packing.

2 (CCDC 841443): 2 (20 mg) was dissolved in 3 mL methylene chloride. The solution was filtered and allowed to evaporate over 2 days. Yellow block crystals were collected.

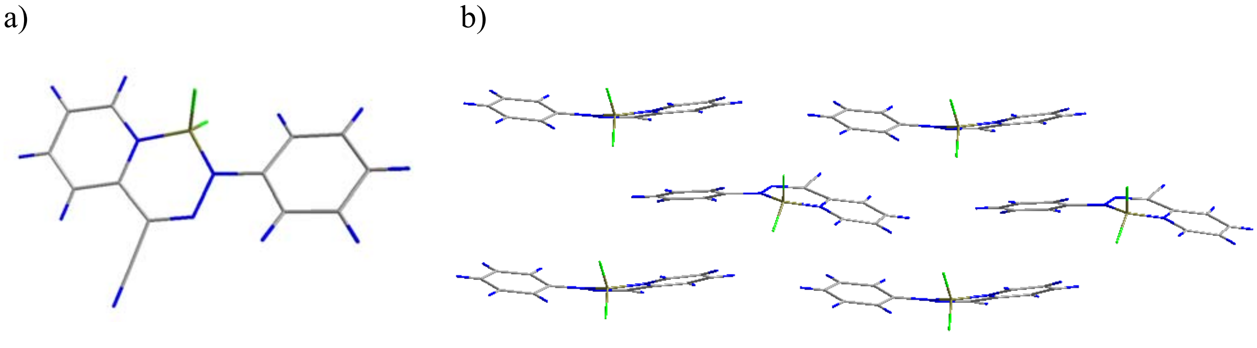


Figure S18. Wire drawing of a) the structure of **2** and b) its crystal packing.

3 (CCDC 841444): 3 (20 mg) was dissolved in 2 mL ethyl acetate and 1 mL hexanes. The solution was filtered and allowed to evaporate over 2 days. Yellow needle crystals were collected.

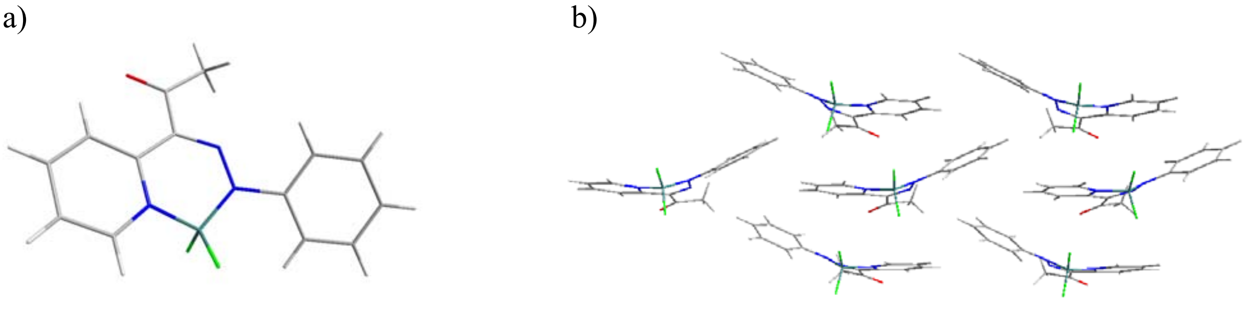


Figure S19. Wire drawing of a) the structure of **3** and b) its crystal packing.

4 (CCDC 841445): 4 (20 mg) was dissolved in 2 mL chloroform and 1 mL hexanes. The solution was filtered and allowed to evaporate over 2 days. Yellow plate crystals were collected.

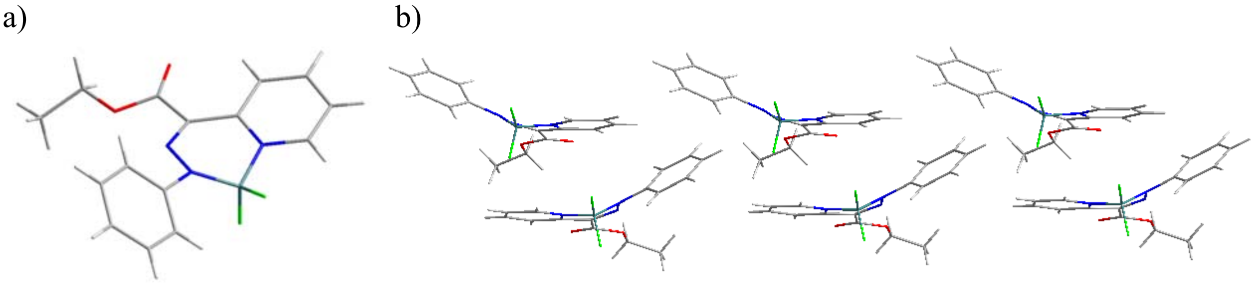


Figure S20. Wire drawing of a) the structure of **4** and b) its crystal packing.

5 (CCDC 841446): 5 (20 mg) was dissolved in 3 mL methanol. Orange plate crystals were obtained by vapor diffusion of diethyl ether into the solution.

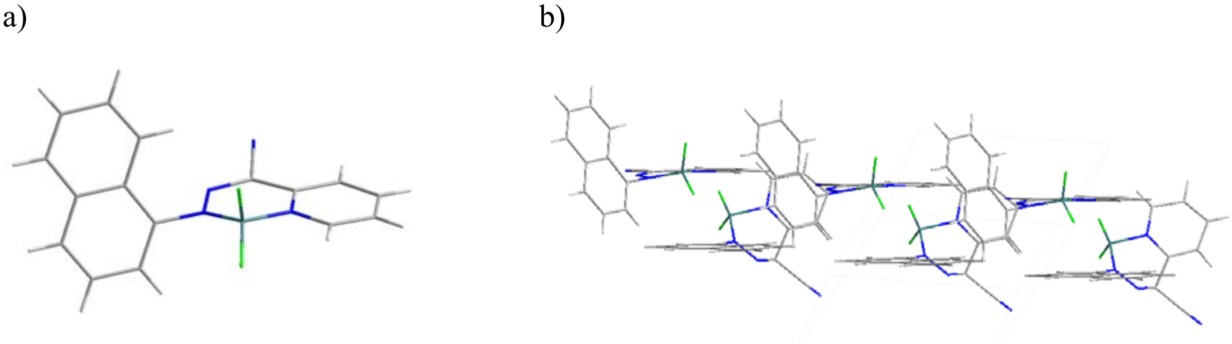


Figure S21. Wire drawing of a) the structure of **5** and b) its crystal packing.

Table S2. Crystal Data and Parameters for BODIHY crystals **1-5**.

	1	**2**
CCDC	841442	841443
Empirical formula	$C_{13}H_{12}BF_2N_3$	$C_{13}H_9BF_2N_4$
Formula weight	259.07	270.05
Temperature	173(2) K	173(2) K
Wavelength	1.54178 Å	0.71073 Å
Crystal system	Triclinic	Monoclinic
Space group	P 21/c	P 21/c
Unit cell dimensions	a = 7.41690(10) Å	a = 12.6822(13) Å
	α = 70.2960(10)°	α = 90°
	b = 8.37810(10) Å	b = 6.9729(7) Å
	β = 73.1310(10)°	β = 95.1380(10)°
	c = 11.0339(2) Å	c = 13.8314(14) Å
	γ = 71.4410(10)°	γ = 90°
Volume	598.944(15) Å^3	1218.2(2) Å^3
Z	2	4
Density (calculated)	1.436 Mg/m^3	1.472 Mg/m^3
Absorption coefficient	0.913 mm^{-1}	0.113 mm^{-1}
F(000)	268	552
Theta range for data collection	4.35 to 68.02°	1.61 to 25.39°
Index ranges	-8<=h<=8, -9<=k<=10, -13<=l<=13	-15<=h<=15, -8<=k<=8, -16<=l<=16
Reflections collected	11932	16730
Independent reflections	2112 [*R*(int) = 0.0231]	2249 [*R*(int) = 0.0465]
Goodness-of-fit on F^2	1.049	1.045
Final *R* indices [$I>2\sigma(I)$]	$R_1 = 0.0368$, $\omega R_2 = 0.0968$	$R_1 = 0.0444$, $\omega R_2 = 0.1172$
R indices (all data)	$R_1 = 0.0380$, $\omega R_2 = 0.0981$	$R_1 = 0.0556$, $\omega R_2 = 0.1288$

	3	**4**
CCDC	841444	841445
Empirical formula	$C_{14}H_{12}BF_2N_3O$	$C_{15}H_{14}BF_2N_3O_2$
Formula weight	287.08	317.10
Temperature	173(2) K	173(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	P 21/c	P 21/c
Unit cell dimensions	a = 13.5890(18) Å	a = 14.589(3) Å
	α = 90°	α = 90°
	b = 11.4482(15) Å	b = 11.456(2) Å
	β = 105.5190(10)°	β = 90.271(2)°
	c = 8.7135(11) Å	c = 8.6272(15) Å
	γ = 90°	γ = 90°
Volume	1306.1(3) $Å^3$	1441.8(4) $Å^3$
Z	4	4
Density (calculated)	1.460 Mg/m^3	1.461 Mg/m^3
Absorption coefficient	0.113 mm^{-1}	0.115 mm^{-1}
$F(000)$	592	656
Theta range for data collection	2.36 to 25.28°	2.26 to 25.37°
Index ranges	-16<=h<=16, -13<=k<=13, -10<=l<=10	-17<=h<=17, -13<=k<=13, -10<=l<=10
Reflections collected	8857	11401
Independent reflections	2378 [R(int) = 0.0221]	2656 [R(int) = 0.0616]
Goodness-of-fit on F^2	1.063	1.003
Final R indices [I>2σ(I)]	$R_1 = 0.0315$, $\omega R_2 = 0.0758$	$R_1 = 0.0424$, $\omega R_2 = 0.0921$
R indices (all data)	$R_1 = 0.0400$, $\omega R_2 = 0.0809$	$R_1 = 0.0834$, $\omega R_2 = 0.1099$

	5
CCDC	841446
Empirical formula	$C_{17}H_{11}BF_2N_4$
Formula weight	320.11
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	a = 7.7978(7) Å
	α = 91.862(2)°
	b = 8.4159(11) Å
	β = 95.4460(10)°
	c = 25.529(2) Å
	γ = 117.2480(10)°
Volume	1477.2(3) $Å^3$
Z	4
Density (calculated)	1.439 Mg/m^3
Absorption coefficient	0.106 mm^{-1}
F(000)	656
Theta range for data collection	1.61 to 25.28°
Index ranges	-9<=h<=9, -10<=k<=10, -30<=l<=30
Reflections collected	23953
Independent reflections	5349 [*R*(int) = 0.0412]
Goodness-of-fit on F^2	1.038
Final *R* indices [I>2σ(I)]	R_1 = 0.0492, ωR_2 = 0.1187
R indices (all data)	R_1 = 0.0812, ωR_2 = 0.1350

Computational Methods:

Calculations were performed using density functional theory (DFT) with the B3LYP functional[S5] as implemented in Gaussian 09.[S6] Geometry optimizations and frequency analysis were performed using the 6-311G basis set. Single point calculations (B3LYP/6-311+G(d)) were then run using the optimized structures to calculate the dipole moments.

Optimized Cartesian Coordinates for 1

Atomic No.	Coordinates (Angstroms) X	Y	Z
F1	5.756562	7.140429	4.837879
F2	4.125492	8.459836	3.820660
B3	5.363155	7.780220	3.615764
N4	6.365496	6.593131	1.631665
N5	5.315333	6.797550	2.449013
N6	6.449622	8.868016	3.283019
C7	7.422169	7.391735	1.640166
C8	7.484926	8.598767	2.416611
C9	8.511822	9.562006	2.282377
H10	9.333116	9.359488	1.614535
C11	8.455249	10.748794	2.988103
H12	9.244483	11.479799	2.882445
C13	7.362761	11.006050	3.838440
H14	7.288229	11.928090	4.393116
C15	6.381016	10.048769	3.962160
H16	5.515723	10.162859	4.593449
C17	8.543824	7.013782	0.708141
H18	8.713239	7.765163	-0.068846
H19	9.487734	6.865459	1.239671
H20	8.283479	6.078828	0.218736
C21	4.198315	5.928973	2.231181
C22	3.301235	5.665631	3.277923
H23	3.456637	6.105263	4.249766
C24	2.212592	4.821424	3.059437
H25	1.527296	4.623618	3.872779
C26	2.009288	4.227144	1.811242
H27	1.163682	3.572352	1.649405
C28	2.909296	4.487763	0.773496

H29	2.761962	4.036261	-0.198806
C30	3.996362	5.336613	0.975859
H31	4.693606	5.543486	0.179713

Optimized Cartesian Coordinates for 2

Atomic	Coordinates (Angstroms)		
No.	X	Y	Z
F1	-0.334997	-2.151913	-0.691053
F2	0.021572	-1.671455	1.563057
B3	0.095794	-1.160618	0.230935
N4	-0.704604	0.148085	0.094127
N5	-0.150834	1.351506	0.167843
N6	1.608175	-0.847640	-0.075785
N7	2.095687	3.913652	0.394828
C8	1.175035	1.498745	0.185215
C9	2.116397	0.422751	0.011129
C10	3.505605	0.615173	-0.140671
H11	3.902504	1.615694	-0.067430
C12	4.329374	-0.466568	-0.390109
H13	5.393875	-0.319858	-0.503697
C14	3.776515	-1.756269	-0.504273
H15	4.396048	-2.614995	-0.708869
C16	2.418516	-1.913654	-0.344391
H17	1.917744	-2.864634	-0.414646
C18	1.657585	2.834801	0.300349
C19	-2.136609	0.136539	-0.028122
C20	-2.863216	-0.972016	0.428219
H21	-2.355951	-1.805328	0.886918
C22	-4.252499	-0.978963	0.304268
H23	-4.809896	-1.834996	0.659110
C24	-4.921995	0.108987	-0.261612
H25	-5.999427	0.096813	-0.353895
C26	-4.189920	1.213674	-0.708143
H27	-4.698438	2.060090	-1.149431
C28	-2.800816	1.230757	-0.598066
H29	-2.227414	2.077658	-0.940632

Optimized Cartesian Coordinates for 3

Atomic	Coordinates (Angstroms)		

No.	X	Y	Z
F1	7.145032	1.235026	1.700300
F2	7.149823	1.515878	4.016334
O3	12.448994	3.264241	0.939323
N4	10.336902	0.871309	2.433626
N5	9.146793	0.582300	2.941177
N6	8.514637	2.993690	2.664734
B7	7.951998	1.539023	2.842141
C8	10.646607	2.092387	1.986768
C9	9.767514	3.235700	2.147371
C10	10.133581	4.574676	1.886712
H11	11.108054	4.752062	1.467346
C12	9.252866	5.604978	2.168219
H13	9.542054	6.625937	1.962676
C14	7.993917	5.325641	2.724535
H15	7.294200	6.111712	2.961668
C16	7.655924	4.012357	2.960627
H17	6.712191	3.708504	3.381304
C18	11.995119	2.184051	1.383895
C19	12.830739	0.928745	1.297134
H20	12.327432	0.155870	0.716102
H21	13.014614	0.506323	2.285269
H22	13.775687	1.186569	0.826242
C23	9.005540	-0.738884	3.484718
C24	7.754850	-1.371296	3.456972
H25	6.906042	-0.876621	3.012507
C26	7.622394	-2.653586	3.989603
H27	6.656291	-3.138900	3.964356
C28	8.723928	-3.312127	4.542588
H29	8.613594	-4.306236	4.953883
C30	9.969042	-2.676372	4.563169
H31	10.826585	-3.175437	4.994034
C32	10.112924	-1.391705	4.041361
H33	11.067332	-0.889016	4.062008

Calculated Dipole Moment

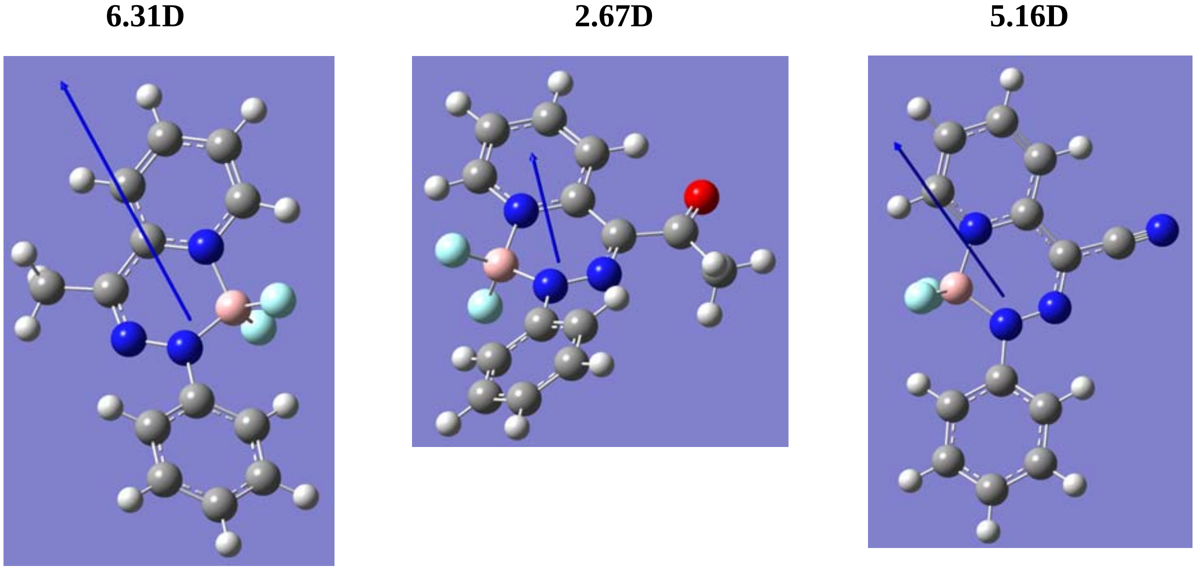


Figure S22. The calculated dipole moments of **1**, **2**, and **3**.

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