Supplemetary Information

Efficient one-pot synthesis of dan-substituted organo- and silyl-boron compounds

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1. General remarks

All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under an argon atmosphere. Nuclear magnetic resonance spectra were taken on a Varian System 500 (^{1}H, 500 MHz; ^{13}C, 125 MHz; ^{11}B, 160 MHz; ^{119}Sn, 186 MHz) spectrometer using residual chloroform (^{1}H, δ = 7.26), $CDCl_3$ (^{13}C, δ = 77.16), residual benzene (^{1}H, δ = 7.16), C_6D_6 (^{13}C, δ = 128.06) or tetramethylsilane (^{1}H and ^{13}C, δ = 0.00) as an internal standard, and boron trifluoride diethyl etherate (^{11}B, δ = 0.00) or tetramethytin (^{119}Sn, δ = 0.00) as an external standard (solvent: $CDCl_3$). ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sext = sextet, m = multiplet), coupling constants (Hz), integration. GC analysis was performed on a Shimadzu GC-2014 (GC conditions: Column: TC-1 (GL Science), 30 m × 0.25 mm, film 0.25 μm; Flow rate: 1.89 mL/min; Injector temperature: 250 °C; Oven temperature: 100 °C to 250 °C at 20 °C/min, hold at 250 °C for 10 min; FID temperature: 250 °C). High-resolution mass spectra were obtained with a Thermo Fisher Scientific LTQ Orbitrap XL spectrometer or a JEOL JMS-T100GCV spectrometer. Melting points were measured with Yanaco Micro Melting Point apparatus and uncorrected. Column chromatography on silica gel was carried out using Merck Kieselgel 60. Column chromatography on florisil was carried out using KANTO CHEMICAL 16231-08. 2,5-Bis(tributylstannyl)thiophene (**1p**)[1] was prepared according to a literature procedure. Unless otherwise noted, commercially available reagents were used without purification. All solvents were dried over activated molecular sieves 4Å.

Abbreviations

Å: Angstrom

equiv: Equivalent

sat.: Saturated

aq.: Aqueous

mp: Melting point

THF: Tetrahydrofuran

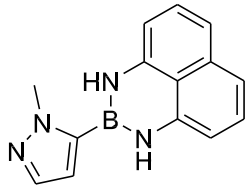
DMF: *N*,*N*-Dimethylformamide

2. Synthesis of dan (or aam)-substituted boron compounds

2-1. Synthesis of 5-pyrazolyl–B(dan) (2a)

A flame-dried 50 mL of two-necked flask equipped with a magnetic stirring bar was charged with 1-methyl-1*H*-pyrazole (**1a**) (411 mg, 5 mmol) and THF (10 mL) under an argon atmosphere. The resulting mixture was cooled to -78 °C and *n*-BuLi (1.6 M in Hexane, 3.75 mL, 6 mmol) was dropped into this slowly. After stirring at this temperature for 1.5 hours, triethylborate (876 mg, 6 mmol) was added dropwise at -78 °C. The resulting mixture was then warmed to room temperature and stirred overnight. Then, 1,8-diaminonaphthalene (791 mg, 5 mmol) dissolved in THF (2 mL) was added dropwise to the reaction mixture. After stirring at this temperature for 10 minutes, acetic acid was added dropwise until the pH of the reaction mixture became about 3. The reaction mixture was quenched with sat. $NaHCO_3$ aq. The organic layer was allowed to separate, and the aqueous layer was extracted with ethyl acetate. The organic solution was washed with brine and dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude material was purified by column chromatography on silica gel (Hexane/EtOAc = 1:1 as an eluent) to give 5-pyrazolyl–B(dan) (**2a**) (1.0929 g, 88% yield).

2-(1-Methyl-1*H*-pyrazol-5-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2a)



White solid: mp 202–206 °C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 1.9 Hz, 1H), 7.15 (dd, *J* = 8.3, 7.2 Hz, 2H), 7.09 (dd, *J* = 8.4, 1.1 Hz, 2H), 6.53 (d, *J* = 1.9 Hz, 1H), 6.40 (dd, *J* = 7.2, 1.1 Hz, 2H), 5.93 (s, 2H), 4.04 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 140.39, 138.89, 136.36, 127.72, 119.98, 118.56, 112.64, 106.51, 39.41. The signal of the boron-bound carbon atom was obscure due to the quadrupolar boron nucleus.

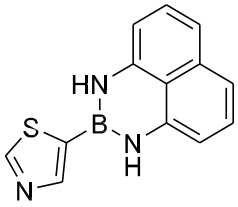
^{11}B NMR (160 MHz, $CDCl_3$) δ 26.58.

HRMS (APCl) Calcd for $C_{14}H_{13}N_4B$: $[M+H]^+$, 249.13060. Found: *m/z* 249.13094.

2-2. Synthesis of 5-thiazolyl–B(dan) (2b)

A flame-dried 50 mL of two-necked flask equipped with a magnetic stirring bar was charged with 2-(trimethylsilyl)thiazole (**1b**) (787 mg, 3 mmol) and THF (6 mL) under an argon atmosphere. The resulting mixture was cooled to -78 °C and *n*-BuLi (1.6 M in Hexane, 3.75 mL, 6 mmol) was dropped into this slowly. After stirring at this temperature for 1 hour, triethylborate (526 mg, 3.6 mmol) was added dropwise at -78 °C. The resulting mixture was stirred at this temperature for 1 hour, then warmed to room temperature and stirred overnight. Then, 1,8-diaminonaphthalene (570 mg, 3.6 mmol) was added to the reaction mixture. After stirring at this temperature for 10 minutes, acetic acid (541 mg, 9 mmol) was added to the reaction mixture. The reaction mixture was quenched with sat. $NaHCO_3$ aq. The organic layer was allowed to separate, and the aqueous layer was extracted with ethyl acetate. The organic solution was washed with brine and dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude material was purified by column chromatography on silica gel (Hexane/EtOAc = 1:1 as an eluent) to give 5-thiazolyl–B(dan) (**2b**) (0.5400 g, 72% yield).

5-(1*H*-Naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)thiazole (2b)



White solid: mp 164–168 °C

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.04 (s, 1H), 8.25 (s, 1H), 7.15 (dd, *J* = 8.3, 7.2 Hz, 2H), 7.09 (dd, *J* = 8.3, 1.0 Hz, 2H), 6.43 (dd, *J* = 7.2, 1.1 Hz, 2H), 6.01 (s, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 156.52, 148.57, 140.36, 136.39, 127.74, 120.02, 118.58, 106.54. The signal of the boron-bound carbon atom was obscure due to the quadrupolar boron nucleus.

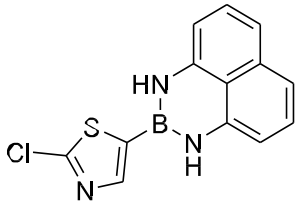
^{11}B NMR (160 MHz, $CDCl_3$) δ 26.95.

HRMS (APCl) Calcd for $C_{13}H_{10}N_3BS$: $[M+H]^+$, 252.07612. Found: *m/z* 252.07613.

2-3. Synthesis of 2-chloro-5-thiazolyl–B(dan) (2c)

A flame-dried 50 mL of two-necked flask equipped with a magnetic stirring bar was charged with 2-chlorothiazole (**1c**) (598 mg, 5 mmol) and THF (10 mL) under an argon atmosphere. The resulting mixture was cooled to -78 °C and *n*-BuLi (1.6 M in Hexane, 3.75 mL, 6 mmol) was dropped into this slowly. After stirring at this temperature for 1 hour, triethylborate (876 mg, 6 mmol) was added dropwise at -78 °C. The resulting mixture was stirred at this temperature for 1 hour, then warmed to room temperature and stirred for another 1 hour. Then, 1,8-diaminonaphthalene (791 mg, 5 mmol) dissolved in THF (2 mL) was added dropwise to the reaction mixture. After stirring at this temperature for 10 minutes, acetic acid (450 mg, 7.5 mmol) was added to the reaction mixture. The reaction mixture was quenched with sat. $NaHCO_3$ aq. The organic layer was allowed to separate, and the aqueous layer was extracted with ethyl acetate. The organic solution was washed with brine and dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude material was purified by column chromatography on silica gel (Hexane/EtOAc = 5:1 as an eluent) to give 2-chloro-5-thiazolyl–B(dan) (**2c**) (0.8161 g, 57% yield).

2-Chloro-5-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)thiazole (2c)



Yellow solid: mp 197–200 °C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.14 (t, *J* = 7.7 Hz, 2H), 7.09 (d, *J* = 8.2 Hz, 2H), 6.40 (d, *J* = 7.2 Hz, 2H), 5.88 (s, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 155.70, 146.44, 140.05, 136.35, 127.72, 120.03, 118.78, 106.67. The signal of the boron-bound carbon atom was obscure due to the quadrupolar boron nucleus.

^{11}B NMR (160 MHz, $CDCl_3$) δ 26.29.

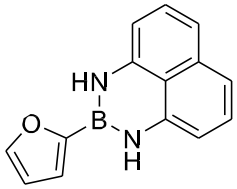
HRMS (APCl) Calcd for $C_{13}H_9N_3BClS$: $[M+H]^+$, 286.03715. Found: *m/z* 286.03738.

2-4. Synthesis of 2-furyl–B(dan) (2d)

A flame-dried Schlenk tube equipped with a magnetic stirring bar was charged with furan (**1d**) (68.1 mg, 1 mmol) and THF (2 mL) under an argon atmosphere. The

resulting mixture was cooled to -10 °C and *n*-BuLi (1.6 M in Hexane, 0.75 mL, 1.2 mmol) was dropped into this slowly. After stirring at 0 °C for 1 hour, triethylborate (175 mg, 1.2 mmol) was added dropwise at -78 °C. The resulting mixture was stirred at this temperature for 30 minutes, then warmed to room temperature and stirred for another 30 minutes. Then, 1,8-diaminonaphthalene (190 mg, 1.2 mmol) was added to the reaction mixture. After stirring at this temperature for 10 minutes, acetic acid (180 mg, 3 mmol) was added to the reaction mixture. The reaction mixture was quenched with sat. $NaHCO_3$ aq. The organic layer was allowed to separate, and the aqueous layer was extracted with ethyl acetate. The organic solution was washed with brine and dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude material was purified by column chromatography on silica gel (Hexane/EtOAc = 9:1 as an eluent) to give 2-furyl–B(dan) (**2d**) (0.1759 g, 75% yield).

2-(Furan-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2d)



White solid: mp 82–85 °C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 1.7 Hz, 1H), 7.14 (dd, *J* = 8.3, 7.2 Hz, 2H), 7.05 (dd, *J* = 8.3, 1.0 Hz, 2H), 6.91 (d, *J* = 3.3 Hz, 1H), 6.50 (dd, *J* = 3.3, 1.6 Hz, 1H), 6.41 (dd, *J* = 7.3, 1.0 Hz, 2H), 6.07 (s, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 146.34, 140.76, 136.47, 127.71, 119.91, 118.78, 118.01, 110.65, 106.19. The signal of the boron-bound carbon atom was obscure due to the quadrupolar boron nucleus.

^{11}B NMR (160 MHz, $CDCl_3$) δ 24.88.

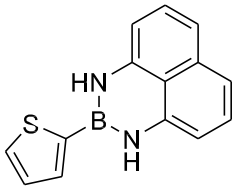
HRMS (APCl) Calcd for $C_{14}H_{11}ON_2B$: $[M+H]^+$, 235.10372. Found: *m/z* 235.10374.

2-5. Synthesis of 2-thienyl–B(dan) (2e)

A flame-dried 50 mL of two-necked flask equipped with a magnetic stirring bar was charged with thiophene (**1e**) (252 mg, 3 mmol) and THF (6 mL) under an argon atmosphere. The resulting mixture was cooled to -78 °C and *n*-BuLi (1.6 M in Hexane, 2.25 mL, 3.6 mmol) was dropped into this slowly. After stirring at this temperature for 1

hour, the reaction mixture was warmed to -20 °C. After cooling to -78 °C again, triethylborate (526 mg, 3.6 mmol) was added dropwise at -78 °C. The resulting mixture was stirred at this temperature for 1 hour, then warmed to room temperature and stirred for another 1 hour. Then, 1,8-diaminonaphthalene (570 mg, 3.6 mmol) was added to the reaction mixture. After stirring at this temperature for 10 minutes, acetic acid (541 mg, 9 mmol) was added to the reaction mixture. The reaction mixture was quenched with sat. $NaHCO_3$ aq. The organic layer was allowed to separate, and the aqueous layer was extracted with ethyl acetate. The organic solution was washed with brine and dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude material was purified by column chromatography on silica gel (Hexane/EtOAc = 9:1 as an eluent) to give 2-thieyl–B(dan) (**2e**) as a white solid (0.5282 g, 70% yield).

2-(Thiophen-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2e)[2]



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 4.7, 0.8 Hz, 1H), 7.47 (dd, *J* = 3.4, 0.9 Hz, 1H), 7.23 (dd, *J* = 4.8, 3.3 Hz, 1H), 7.13 (dd, *J* = 8.3, 7.3 Hz, 2H), 7.08−7.01 (m, 2H), 6.39 (dd, *J* = 7.3, 1.0 Hz, 2H), 5.94 (s, 2H).

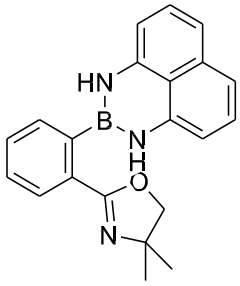
^{13}C NMR (125 MHz, $CDCl_3$) δ 140.82, 136.41, 132.97, 130.22, 128.68, 127.71, 119.86, 118.10, 106.25. The signal of the boron-bound carbon atom was obscure due to the quadrupolar boron nucleus.

2-6. Synthesis of (2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)phenyl)–B(dan) (2f)

A flame-dried Schlenk tube equipped with a magnetic stirring bar was charged with 4,4-dimethyl-2-phenyl-4,5-dihydrooxazole (**1f**) (175 mg, 1 mmol) and THF (2 mL) under an argon atmosphere. The resulting mixture was cooled to -78 °C and *n*-BuLi (1.6 M in Hexane, 0.75 mL, 1.2 mmol) was dropped into this slowly. The reaction mixture was stirred at -78 °C for 1 hour, then warmed to 0 °C and stirred for 30 minutes. After the reaction mixture was cooled to -78 °C, triethylborate (175 mg, 1.2 mmol) was added dropwise at -78 °C. The reaction mixture was stirred at -78 °C for 1 hour, then warmed to room temperature and stirred for another 1 hour. Then, 1,8-diaminonaphthalene (190

mg, 1.2 mmol) was added to the reaction mixture. After stirring at this temperature for 10 minutes, acetic acid (180 mg, 3 mmol) was added to the reaction mixture. The reaction mixture was quenched with sat. $NaHCO_3$ aq. The organic layer was allowed to separate, and the aqueous layer was extracted with ethyl acetate. The organic solution was washed with brine and dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude material was purified by column chromatography on silica gel (Hexane/EtOAc = 3:1 as an eluent) to give (2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)phenyl)–B(dan) (**2f**) (0.2185 g, 64% yield).

2-(2-(1*H*-Naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)phenyl)-4,4-dimethyl-4,5-dihydrooxazole (2f)



White solid: mp 126–129 °C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84−7.80 (m, 1H), 7.61−7.56 (m, 1H), 7.52−7.41 (m, 2H), 7.12 (dd, *J* = 8.3, 7.3 Hz, 2H), 7.03 (dd, *J* = 8.3, 1.0 Hz, 2H), 6.32 (dd, *J* = 7.3, 1.0 Hz, 2H), 6.17 (s, 2H), 4.06 (s, 2H), 1.35 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.79, 141.59, 136.53, 132.80, 131.96, 130.43, 129.20, 129.01, 127.75, 119.92, 117.53, 105.79, 79.69, 68.17, 28.47. The signal of the boron-bound carbon atom was obscure due to the quadrupolar boron nucleus.

^{11}B NMR (160 MHz, $CDCl_3$) δ 29.98.

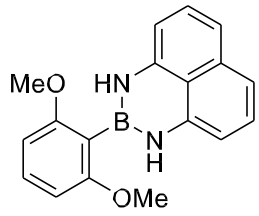
HRMS (APCl) Calcd for $C_{21}H_{20}ON_3B$: $[M+H]^+$, 342.17722. Found: *m/z* 342.17786.

2-7. Synthesis of 2,6-dimethoxyphenyl–B(dan) (2g)

A flame-dried Schlenk tube equipped with a magnetic stirring bar was charged with 1,3-dimethoxybenzene (**1g**) (132 mg, 1 mmol) and THF (2 mL) under an argon atmosphere. The resulting mixture was cooled to 0 °C and *n*-BuLi (1.6 M in Hexane, 0.75 mL, 1.2 mmol) was dropped into this slowly. After stirring at 0 °C for 4 hours, triethylborate (175 mg, 1.2 mmol) was added dropwise at -78 °C. The resulting mixture

was then warmed to room temperature and stirred overnight. Then, 1,8-diaminonaphthalene (190 mg, 1.2 mmol) was added to the reaction mixture. After stirring at this temperature for 10 minutes, acetic acid (180 mg, 3 mmol) was added to the reaction mixture. The reaction mixture was quenched with sat. $NaHCO_3$ aq. The organic layer was allowed to separate, and the aqueous layer was extracted with ethyl acetate. The organic solution was washed with brine and dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude material was purified by column chromatography on silica gel (Hexane/EtOAc = 5:1 as an eluent) to give 2,6-dimethoxyphenyl–B(dan) (**2g**) (0.1570 g, 52% yield).

2-(2,6-Dimethoxyphenyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2g)



White solid: mp 132–139 °C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (t, *J* = 8.3 Hz, 1H), 7.20 (s, 2H), 7.10 (ddd, *J* = 8.3, 7.3, 0.9 Hz, 2H), 6.98 (dt, *J* = 8.3, 1.0 Hz, 2H), 6.62 (d, *J* = 8.3 Hz, 2H), 6.32 (dt, *J* = 7.3, 0.9 Hz, 2H), 3.90 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 165.56, 142.15, 136.59, 131.93, 127.74, 120.19, 116.78, 105.59, 104.30, 55.94. The signal of the boron-bound carbon atom was obscure due to the quadrupolar boron nucleus.

^{11}B NMR (160 MHz, $CDCl_3$) δ 28.31.

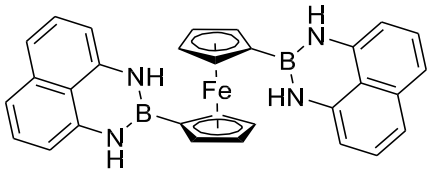
HRMS (APCl) Calcd for $C_{18}H_{17}O_2N_2B$: $[M+H]^+$, 305.14558. Found: *m/z* 305.14590.

2-8. Synthesis of 1,1'-bis(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)ferrocene (2h)

A flame-dried Schlenk tube equipped with a magnetic stirring bar was charged with ferrocene (**1h**) (186 mg, 1 mmol), tetramethylethylenediamine (279 mg, 2.4 mmol) and Hexane (2 mL) under an argon atmosphere. *n*-BuLi (1.6 M in Hexane, 1.50 mL, 2.4 mmol) was slowly added dropwise to the resulting mixture at room temperature and stirred at this temperature overnight. After the reaction mixture was cooled to -78 °C,

triethylborate (350 mg, 2.4 mmol) was added dropwise at -78 °C. The resulting mixture was then warmed to room temperature and stirred overnight. Then, 1,8-diaminonaphthalene (380 mg, 2.4 mmol) was added to the reaction mixture. After stirring at this temperature for 10 minutes, acetic acid (721 mg, 12 mmol) was added to the reaction mixture. The reaction mixture was quenched with sat. $NaHCO_3$ aq. The organic layer was allowed to separate, and the aqueous layer was extracted with ethyl acetate. The organic solution was washed with brine and dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude material was purified by column chromatography on silica gel (Hexane/EtOAc = 3:1 as an eluent) to give 1,1'-bis(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)ferrocene (**2h**) (0.3033 g, 59% yield).

1,1'-Bis(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)ferrocene (2h)



Orange solid: mp 276–280 °C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (t, *J* = 7.7 Hz, 2H), 7.05 (d, *J* = 8.2 Hz, 2H), 6.30 (d, *J* = 7.2 Hz, 2H), 5.75 (s, 2H), 4.46 (t, *J* = 1.8 Hz, 2H), 4.32 (t, *J* = 1.8 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 141.06, 136.47, 127.71, 119.57, 117.75, 106.14, 72.55, 72.15. The signal of the boron-bound carbon atom was obscure due to the quadrupolar boron nucleus.

^{11}B NMR (160 MHz, $CDCl_3$) δ 30.44.

HRMS (APCl) Calcd for $C_{30}H_{24}N_4B_2Fe$: $[M+H]^+$, 519.16093. Found: *m/z* 519.16174.

2-9. Synthesis of phenylethynyl–B(dan) (2i)

・With triethylborate

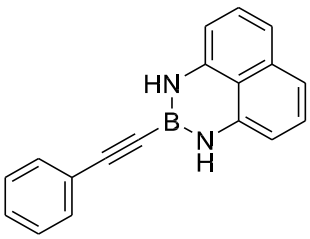
A flame-dried Schlenk tube equipped with a magnetic stirring bar was charged with phenylacetylene (**1i**) (102 mg, 1 mmol) and THF (2 mL) under an argon atmosphere. The resulting mixture was cooled to -78 °C and *n*-BuLi (1.6 M in Hexane, 0.63 mL, 1 mmol) was dropped into this slowly. After stirring at this temperature for 1 hour, triethylborate (146 mg, 1 mmol) was added dropwise at -78 °C. The resulting mixture

was stirred at this temperature for 2 hours, then warmed to room temperature and stirred for 1 hours. Then, 1,8-diaminonaphthalene (158 mg, 1 mmol) was added to the reaction mixture. After stirring at this temperature for 10 minutes, acetic acid (180 mg, 3 mmol) was added to the reaction mixture. The reaction mixture was quenched with sat. $NaHCO_3$ aq. The organic layer was allowed to separate, and the aqueous layer was extracted with ethyl acetate. The organic solution was washed with brine and dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude material was purified by column chromatography on silica gel (Hexane/EtOAc = 9:1 as an eluent) to give phenylethynyl–B(dan) (**2i**) as a white solid (0.0791 g, 30% yield).

・With trimethylborate

A flame-dried Schlenk tube equipped with a magnetic stirring bar was charged with phenylacetylene (**1i**) (1.02 g, 10 mmol) and THF (20 mL) under an argon atmosphere. The resulting mixture was cooled to -78 °C and *n*-BuLi (1.6 M in Hexane, 6.3 mL, 10 mmol) was dropped into this slowly. After stirring at this temperature for 1 hour, trimethylborate (1.04 g, 10 mmol) was added dropwise at -78 °C. The resulting mixture was stirred at this temperature for 2 hours, then warmed to room temperature and stirred for 4 hours. Then, 1,8-diaminonaphthalene (1.58 g, 10 mmol) was added to the reaction mixture. After stirring at this temperature for 10 minutes, acetic acid (1.80 g, 30 mmol) was added to the reaction mixture. The reaction mixture was quenched with sat. $NaHCO_3$ aq. The organic layer was allowed to separate, and the aqueous layer was extracted with ethyl acetate. The organic solution was washed with brine and dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude material was purified by column chromatography on silica gel (Hexane/EtOAc = 9:1 as an eluent) to give phenylethynyl–B(dan) (**2i**) as a white solid (1.2054 g, 45% yield).

2-(Phenylethynyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2i)[3]



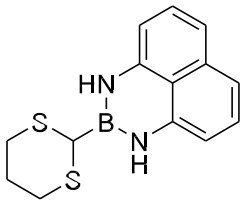
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54−7.50 (m, 2H), 7.40−7.32 (m, 3H), 7.10 (dd, *J* = 8.3,

7.3 Hz, 2H), 7.03 (dd, *J* = 8.3, 1.0 Hz, 2H), 6.32 (dd, *J* = 7.3, 1.0 Hz, 2H), 5.91 (s, 2H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 140.76, 136.44, 132.24, 129.27, 128.57, 127.70, 122.49, 120.08, 118.20, 106.06, 102, 54. The signal of the boron-bound carbon atom was obscure due to the quadrupolar boron nucleus.

2-10. Synthesis of 1,3-dithian-2-yl–B(dan) (2j)

A flame-dried Schlenk tube equipped with a magnetic stirring bar was charged with 1,3-dithiane (**1j**) (120 mg, 1 mmol) and THF (2 mL) under an argon atmosphere. The resulting mixture was cooled to -78 °C and *n*-BuLi (1.6 M in Hexane, 0.63 mL, 1 mmol) was dropped into this slowly. The reaction mixture was stirred at -78 °C for 3 hours, then warmed to 0 °C and stirred for 30 minutes. After the reaction mixture was cooled to -78 °C, triethylborate (146 mg, 1 mmol) was added dropwise at -78 °C. The reaction mixture was stirred at -78 °C for 1 hour, then warmed to room temperature and stirred overnight. Then, 1,8-diaminonaphthalene (158 mg, 1 mmol) was added to the reaction mixture. After stirring at this temperature for 10 minutes, acetic acid (180 mg, 3 mmol) was added to the reaction mixture. The reaction mixture was quenched with sat. $NaHCO_3$ aq. The organic layer was allowed to separate, and the aqueous layer was extracted with ethyl acetate. The organic solution was washed with brine and dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude material was purified by column chromatography on silica gel (Hexane/EtOAc = 3:1 as an eluent) to give 1,3-dithian-2-yl–B(dan) (**2j**) (0.0659 g, 23% yield).

2-(1,3-Dithian-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2j)



White solid: mp 135–141 °C
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 (dd, *J* = 8.3, 7.2 Hz, 2H), 7.04 (dd, *J* = 8.4, 1.0 Hz, 2H), 6.35 (dd, *J* = 7.3, 1.1 Hz, 2H), 6.06 (s, 2H), 3.80 (s, 1H), 2.92−2.80 (m, 4H), 2.18−2.00 (m, 2H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 140.61, 136.41, 127.69, 120.12, 118.32, 106.44, 30.25, 29.85, 26.22.

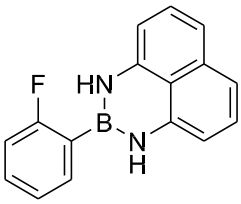
^{11}B NMR (160 MHz, $CDCl_3$) δ 29.37.

HRMS (APCl) Calcd for $C_{14}H_{15}N_2BS_2$: $[M+H]^+$, 287.08425. Found: *m/z* 287.08459.

2-11. Synthesis of 2-fluorophenyl–B(dan) (2k)

A flame-dried Schlenk tube equipped with a magnetic stirring bar was charged with 1-bromo-2-fluorobenzene (**1k**) (435 mg, 3 mmol) and THF (3 mL) under an argon atmosphere. The resulting mixture was cooled to -78 °C and *n*-BuLi (1.6 M in Hexane, 2.25 mL, 3.6 mmol) was dropped into this slowly. After stirring at this temperature for 1 hour, triethylborate (526 mg, 3.6 mmol) was added dropwise at -78 °C. The resulting mixture was stirred at this temperature for 1 hour, then warmed to room temperature and stirred for 30 minutes. Then, 1,8-diaminonaphthalene (475 mg, 3 mmol) was added to the reaction mixture. After stirring at this temperature for 10 minutes, acetic acid was added dropwise until the pH of the reaction mixture became about 3. The reaction mixture was quenched with sat. $NaHCO_3$ aq. The organic layer was allowed to separate, and the aqueous layer was extracted with ethyl acetate. The organic solution was washed with brine and dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude material was purified by column chromatography on silica gel (Hexane/EtOAc = 9:1 as an eluent) to give 2-fluorophenyl–B(dan) (**2k**) as a white solid (0.5581 g, 71% yield).

2-(2-Fluorophenyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2k)[4]



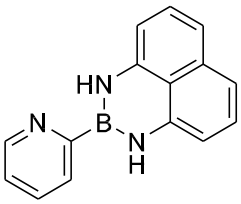
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (td, *J* = 7.0, 1.8 Hz, 1H), 7.45 (tdd, *J* = 7.5, 5.8, 1.8 Hz, 1H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.17−7.03 (m, 5H), 6.42 (d, *J* = 7.3 Hz, 2H), 6.27 (s, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 167.03 (d, J_{CF} = 245.0 Hz), 141.00,136.44, 133.39 (d, J_{CF} = 8.5 Hz), 132.42 (d, J_{CF} = 9.2 Hz), 127.74, 124.36 (d, J_{CF} = 2.7 Hz), 120.05, 118.00, 115.72 (d, J_{CF} = 25.2 Hz), 106.25. The signal of the boron-bound carbon atom was obscure due to the quadrupolar boron nucleus.

2-12. Synthesis of 2-pyridyl–B(dan) (2l)

A flame-dried 50 mL of two-necked flask equipped with a magnetic stirring bar was charged with 2-bromopyridine (**1l**) (474 mg, 3 mmol) and THF (6 mL) under an argon atmosphere. The resulting mixture was cooled to -78 °C and *n*-BuLi (1.6 M in Hexane, 2.30 mL, 3.6 mmol) was dropped into this slowly. After stirring at this temperature for 1 hour, triethylborate (526 mg, 3.6 mmol) was added dropwise at -78 °C. The resulting mixture was stirred at this temperature for 1.5 hours, then warmed to room temperature and stirred for 30 minutes. Then, 1,8-diaminonaphthalene (475 mg, 3 mmol) was added to the reaction mixture. After stirring at this temperature for 10 minutes, acetic acid was added dropwise until the pH of the reaction mixture became about 3. The reaction mixture was quenched with sat. $NaHCO_3$ aq. The organic layer was allowed to separate, and the aqueous layer was extracted with ethyl acetate. The organic solution was washed with brine and dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude material was purified by column chromatography on florisil (Hexane/EtOAc = 9:1 as an eluent) to give 2-pyridyl–B(dan) (**2l**) as a white solid (0.3739 g, 51% yield).

2-(Pyridin-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2l)[2]



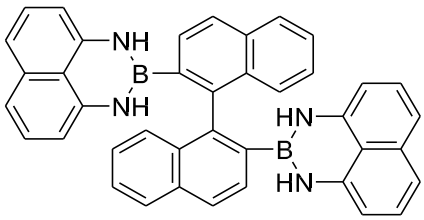
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.80 (dt, *J* = 4.8, 1.3 Hz, 1H), 7.73 (td, *J* = 7.6, 1.7 Hz, 1H), 7.66 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.35 (ddd, *J* = 7.6, 4.8, 1.3 Hz, 1H), 7.14 (dd, *J* = 8.3, 7.3 Hz, 2H), 7.06 (dd, *J* = 8.4, 1.0 Hz, 2H), 6.56 (s, 2H), 6.46 (dd, *J* = 7.3, 1.0 Hz, 2H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 150.23, 141.11, 136.56, 135.09, 127.77, 126.87, 124.62, 120.51, 118.05, 106.36. The signal of the boron-bound carbon atom was obscure due to the quadrupolar boron nucleus.

2-13. Synthesis of 2,2'-bis(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)-1,1'-binaphthalene (2m)

A flame-dried Schlenk tube equipped with a magnetic stirring bar was charged with 2,2'-dibromo-1,1'-binaphthalene (**1m**) (412 mg, 1 mmol) and THF (2 mL) under an

argon atmosphere. The resulting mixture was cooled to -78 °C and *n*-BuLi (1.6 M in Hexane, 1.50 mL, 2.4 mmol) was dropped into this slowly. After stirring at this temperature for 1 hour, triethylborate (350 mg, 2.4 mmol) was added dropwise at -78 °C. The resulting mixture was warmed to room temperature and stirred overnight. Then, 1,8-diaminonaphthalene (380 mg, 2.4 mmol) was added to the reaction mixture. After stirring at this temperature for 10 minutes, acetic acid (360 mg, 6 mmol) was added to the reaction mixture. The reaction mixture was quenched with sat. $NaHCO_3$ aq. The organic layer was allowed to separate, and the aqueous layer was extracted with ethyl acetate. The organic solution was washed with brine and dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude material was purified by column chromatography on silica gel (Hexane/EtOAc = 9:1 as an eluent) to give 2,2'-bis(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)-1,1'-binaphthalene (**2m**) (0.2137 g, 36% yield).

2,2'-Bis(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)-1,1'-binaphthalene (2m)



White solid: mp 233–239 °C

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (t, *J* = 8.4 Hz, 4H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.58 (ddd, *J* = 8.2, 5.2, 2.7 Hz, 2H), 7.44−7.36 (m, 4H), 6.99−6.88 (m, 8H), 5.75 (dd, *J* = 7.0, 1.4 Hz, 4H), 5.31 (s, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 143.32, 140.95, 136.12, 133.83, 133.24, 129.26, 128.53, 127.95, 127.61, 127.14, 126.86, 126.66, 119.50, 117.45, 105.78. The signal of the boron-bound carbon atom was obscure due to the quadrupolar boron nucleus.

^{11}B NMR (160 MHz, $CDCl_3$) δ 29.69.

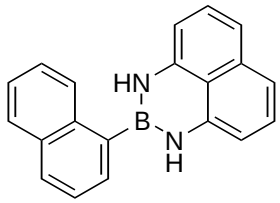
HRMS (APCl) Calcd for $C_{40}H_{28}N_4B_2$: $[M+H]^+$, 587.25728. Found: *m/z* 587.25861.

2-14. Synthesis of 1-naphthyl–B(dan) (2n)

A Schlenk tube was charged with a magnetic stirring bar and magnesium turnings (29.2 mg, 1.2 mmol). After the Schlenk tube was heated under vacuum for 5 minutes with the

aid of a heating gun, the Schlenk tube was cooled to room temperature and back-filled with argon. THF (2 mL) and iodine (trace) were then added. After stirring for 15 minutes at room temperature, 1-bromonaphthalene (**1n**) (207 mg, 1 mmol) was added. After stirring at this temperature for 1 hour, triethylborate (175 mg, 1.2 mmol) was added dropwise at -78 °C. The resulting mixture was stirred at this temperature for 1 hour, then warmed to room temperature and stirred overnight. Then, 1,8-diaminonaphthalene (190 mg, 1.2 mmol) was added to the reaction mixture. After stirring at this temperature for 10 minutes, acetic acid (180 mg, 3 mmol) was added to the reaction mixture. The reaction mixture was quenched with sat. $NaHCO_3$ aq. The organic layer was allowed to separate, and the aqueous layer was extracted with ethyl acetate. The organic solution was washed with brine and dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude material was purified by column chromatography on silica gel (Hexane/EtOAc = 9:1 as an eluent) to give 1-naphthyl–B(dan) as a white solid (**2n**) (0.2680 g, 91% yield).

2-(naphthalen-1-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2n)[2]



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (dd, *J* = 6.2, 3.4 Hz, 1H), 7.93−7.87 (m, 2H), 7.70 (dd, *J* = 6.8, 1.3 Hz, 1H), 7.56−7.47 (m, 3H), 7.17 (dd, *J* = 8.3, 7.2 Hz, 2H), 7.13−7.07 (m, 2H), 6.45−6.34 (m, 2H), 6.02 (s, 2H).

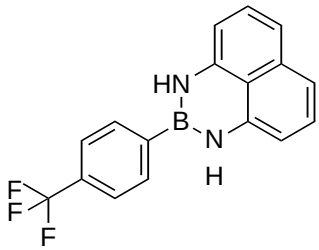
^{13}C NMR (125 MHz, $CDCl_3$) δ 141.23, 136.55, 135.53, 133.39, 130.79, 129.65, 128.91, 128.02, 127.79, 126.36, 125.97, 125.53, 120.08, 118.12, 106.17. The signal of the boron-bound carbon atom was obscure due to the quadrupolar boron nucleus.

2-15. Synthesis of 4-(trifluoromethyl)phenyl–B(dan) (2o)

A Schlenk tube was charged with a magnetic stirring bar and magnesium turnings (29.2 mg, 1.2 mmol). After the Schlenk tube was heated under vacuum for 5 minutes with the aid of a heating gun, the Schlenk tube was cooled to room temperature and back-filled with argon. THF (2 mL) and iodine (trace) were then added. After stirring for 15 minutes at room temperature, 1-bromo-4-(trifluoromethyl)benzene (**1o**) (225 mg, 1

mmol) was added. After stirring at this temperature for 1 hour, triethylborate (175 mg, 1.2 mmol) was added dropwise at -78 °C. The resulting mixture was stirred at this temperature for 1 hour, then warmed to room temperature and stirred overnight. Then, 1,8-diaminonaphthalene (190 mg, 1.2 mmol) was added to the reaction mixture. After stirring at this temperature for 10 minutes, acetic acid (180 mg, 3 mmol) was added to the reaction mixture. The reaction mixture was quenched with sat. $NaHCO_3$ aq. The organic layer was allowed to separate, and the aqueous layer was extracted with ethyl acetate. The organic solution was washed with brine and dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude material was purified by column chromatography on silica gel (Hexane/EtOAc = 9:1 as an eluent) to give 4-(trifluoromethyl)phenyl–B(dan) as a white solid (**2o**) (0.2706 g, 87% yield).

2-(4-(trifluoromethyl)phenyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2o)[2]



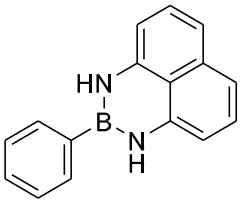
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.7 Hz, 2H), 7.69 (d, *J* = 7.8 Hz, 2H), 7.16 (t, *J* = 7.8 Hz, 2H), 7.09 (d, *J* = 8.2 Hz, 2H), 6.44 (d, *J* = 7.2 Hz, 2H), 6.01 (s, 2H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 140.74, 136.44, 132.09 (q, J_{CF} = 32.3 Hz), 131.86, 127.77, 125.00 (q, J_{CF} = 3.8 Hz), 124.23 (q, J_{CF} = 271.3 Hz), 120.06, 118.36, 106.42. The signal of the boron-bound carbon atom was obscure due to the quadrupolar boron nucleus.

2-16. Synthesis of phenyl–B(dan) (2p)

A 50 mL of two-necked flask was charged with a magnetic stirring bar and magnesium turnings (146 mg, 6 mmol). After the flask was heated under vacuum for 5 minutes with the aid of a heating gun, the flask was cooled to room temperature and back-filled with argon. THF (10 mL) and iodine (trace) were then added. After stirring for 15 minutes at room temperature, bromobenzene (**1p**) (785 mg, 5 mmol) was added. After stirring at this temperature for 1 hour, triethylborate (876 mg, 6 mmol) was added dropwise at

-78 °C. The resulting mixture was stirred at this temperature for 1 hour, then warmed to room temperature and stirred for another 1 hour. Then, 1,8-diaminonaphthalene (949 mg, 6 mmol) was added to the reaction mixture. After stirring at this temperature for 10 minutes, acetic acid (900 mg, 15 mmol) was added to the reaction mixture. The reaction mixture was quenched with sat. $NaHCO_3$ aq. The organic layer was allowed to separate, and the aqueous layer was extracted with ethyl acetate. The organic solution was washed with brine and dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude material was purified by column chromatography on silica gel (Hexane/EtOAc = 9:1 as an eluent) to give phenyl–B(dan) as a white solid (**2p**) (1.1005 g, 90% yield).

2-Phenyl-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2p)[2]



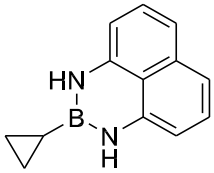
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69−7.63 (m, 2H), 7.52−7.42 (m, 3H), 7.15 (dd, *J* = 8.3, 7.3 Hz, 2H), 7.07 (dd, *J* = 8.3, 1.0 Hz, 2H), 6.43 (dd, *J* = 7.3, 1.0 Hz, 2H), 6.04 (s, 2H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 141.19, 136.48, 131.55, 130.42, 128.41, 127.76, 119.97, 117.97, 106.16. The signal of the boron-bound carbon atom was obscure due to the quadrupolar boron nucleus.

2-17. Synthesis of cyclopropyl–B(dan) (2q)

A Schlenk tube was charged with a magnetic stirring bar and magnesium turnings (58.3 mg, 2.4 mmol). After the Schlenk tube was heated under vacuum for 5 minutes with the aid of a heating gun, the Schlenk tube was cooled to room temperature and back-filled with argon. THF (2 mL) and iodine (trace) were then added. After stirring for 15 minutes at room temperature, bromocyclopropane (**1q**) (242 mg, 2 mmol) was added and then stirred for 4 h at reflux temperature. After cooling to -78 °C, triethylborate (350 mg, 2.4 mmol) was added dropwise at -78 °C. The resulting mixture was stirred at this temperature for 1 hour, then warmed to room temperature and stirred overnight. Then, 1,8-diaminonaphthalene (380 mg, 2.4 mmol) was added to the reaction mixture. After stirring at this temperature for 10 minutes, acetic acid (360 mg, 6 mmol) was

added to the reaction mixture. The reaction mixture was quenched with sat. $NaHCO_3$ aq. The organic layer was allowed to separate, and the aqueous layer was extracted with ethyl acetate. The organic solution was washed with brine and dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude material was purified by column chromatography on silica gel (Hexane/EtOAc = 9:1 as an eluent) to give cyclopropyl–B(dan) (**2q**) as a white solid (0.1519 g, 37% yield).

2-Cyclopropyl-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2q)[2]



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (t, *J* = 7.8 Hz, 2H), 7.00 (d, *J* = 8.2 Hz, 2H), 6.28 (d, *J* = 7.3 Hz, 2H), 5.44 (s, 2H), 0.78−0.68 (m, 2H), 0.49−0.40 (m, 2H), -0.09 (tt, *J* = 9.4, 6.3 Hz, 1H).

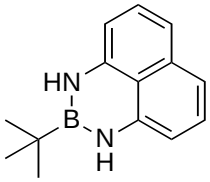
^{13}C NMR (125 MHz, $CDCl_3$) δ 141.27, 136.43, 127.67, 119.55, 117.45, 105.53, 4.08. The signal of the boron-bound carbon atom was obscure due to the quadrupolar boron nucleus.

2-18. Synthesis of *tert*-butyl–B(dan) (2r)

A Schlenk tube was charged with a magnetic stirring bar. After the Schlenk tube was heated under vacuum for 5 minutes with the aid of a heating gun, the Schlenk tube was cooled to room temperature and back-filled with argon. *tert*-Butylmagnesium chloride (1.0 M in THF, 1 mL, 1 mmol) (**1r**) and THF (1 mL) were then added. After stirring for 15 minutes at room temperature, triethylborate (175 mg, 1.2 mmol) was added dropwise at -78 °C. The resulting mixture was stirred at this temperature for 1 hour, then warmed to room temperature and stirred overnight. Then, 1,8-diaminonaphthalene (190 mg, 1.2 mmol) was added to the reaction mixture. After stirring at this temperature for 10 minutes, acetic acid (180 mg, 3 mmol) was added to the reaction mixture. The reaction mixture was quenched with sat. $NaHCO_3$ aq. The organic layer was allowed to separate, and the aqueous layer was extracted with ethyl acetate. The organic solution was washed with brine and dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude material was purified by column chromatography on silica gel

(Hexane/EtOAc = 9:1 as an eluent) to give *tert*-butyl–B(dan) as a white solid (**2r**) (0.1060 g, 47% yield).

2-(*tert*-butyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2r)[2]



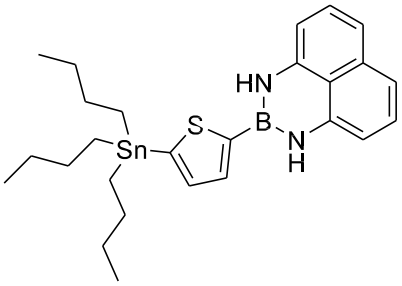
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (dd, *J* = 8.3, 7.3 Hz, 2H), 7.00 (dd, *J* = 8.3, 1.0 Hz, 2H), 6.33 (dt, *J* = 7.3, 0.9 Hz, 2H), 5.61 (s, 2H), 1.02 (s, 9H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 141.38, 136.44, 127.71, 119.60, 117.53, 105.74, 27.84. The signal of the boron-bound carbon atom was obscure due to the quadrupolar boron nucleus.

2-19. Synthesis of 2-(5-(tributylstannyl)thiophen-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2s)

A flame-dried Schlenk tube equipped with a magnetic stirring bar was charged with 2,5-bis(tributylstannyl)thiophene (**1s**) (1.32 g, 2 mmol) and THF (4 mL) under an argon atmosphere. The resulting mixture was cooled to -78 °C and *n*-BuLi (1.6 M in Hexane, 1.50 mL, 2.4 mmol) was dropped into this slowly. After stirring at this temperature for 30 minutes, the reaction mixture was warmed to -20 °C and stirred for another 30 minutes. After cooling to -78 °C again, triethylborate (350 mg, 2.4 mmol) was added dropwise at -78 °C. The resulting mixture was stirred at this temperature for 1 hour, then warmed to room temperature and stirred overnight. Then, 1,8-diaminonaphthalene (380 mg, 2.4 mmol) was added to the reaction mixture. After stirring at this temperature for 10 minutes, acetic acid (144 mg, 2.4 mmol) was added to the reaction mixture. The reaction mixture was quenched with sat. $NaHCO_3$ aq. The organic layer was allowed to separate, and the aqueous layer was extracted with ethyl acetate. The organic solution was washed with brine and dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude material was purified by column chromatography on silica gel (Hexane/EtOAc = 9:1 as an eluent) to give 2-(5-(tributylstannyl)thiophen-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin

e (**2s**) (0.6774 g, 63% yield).

2-(5-(Tributylstannyl)thiophen-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2s)



Purple oil

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66−7.60 (m, 1H), 7.36−7.30 (m, 1H), 7.15 (dd, *J* = 8.3, 7.3 Hz, 2H), 7.07 (dd, *J* = 8.3, 1.0 Hz, 2H), 6.42 (dd, *J* = 7.3, 1.0 Hz, 2H), 6.01 (s, 2H), 1.62 (dddd, *J* = 12.4, 8.1, 7.0, 3.0 Hz, 6H), 1.43−1.34 (m, 6H), 1.24−1.10 (m, 6H), 0.94 (t, *J* = 7.3 Hz, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 143.08, 141.08, 136.82, 136.45, 133.70, 127.72, 119.85, 117.92, 106.15, 29.10, 27.41, 13.82, 11.07. The signal of the boron-bound carbon atom was obscure due to the quadrupolar boron nucleus.

^{11}B NMR (160 MHz, $CDCl_3$) δ 26.89.

^{119}Sn NMR (186 MHz, $CDCl_3$) δ -39.40.

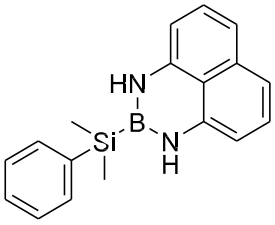
HRMS (APCl) Calcd for $C_{26}H_{37}N_2BSSn$: $[M+H]^+$, 541.18652. Found: *m/z* 541.18677.

2-20. Synthesis of dimethyl(phenyl)silyl–B(dan) (2t)

A flame-dried 50 mL of two-necked flask equipped with a magnetic stirring bar was charged with Li (208 mg, 30 mmol) cut into approximately 1 mm squares and THF (3 mL) under an argon atmosphere. Chlorodimethyl(phenyl)silane (**1t**) (512 mg, 3 mmol) was slowly added dropwise to the resulting mixture at room temperature. After stirring at this temperature for 4 hours, the reaction mixture was transferred via cannula to another flame-dried 50 mL of two-necked flask. After cooling the resulting mixture to -78 °C, triethylborate (438 mg, 3 mmol) was added dropwise at -78 °C. The resulting mixture was warmed to room temperature and stirred overnight. Then, acetic acid (180 mg, 3 mmol) was added to the reaction mixture. Immediately after confirming that the pH of the reaction mixture had reached about 5, 1,8-diaminonaphthalene (475 mg, 3

mmol) was added to the reaction mixture. After stirring at this temperature for 10 minutes, the reaction mixture was quenched with sat. $NaHCO_3$ aq. The organic layer was allowed to separate, and the aqueous layer was extracted with ethyl acetate. The organic solution was washed with brine and dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude material was purified by column chromatography on silica gel (Hexane/EtOAc = 9:1 as an eluent) to give dimethyl(phenyl)silyl–B(dan) (**2t**) as a pale yellow oil (0.3663 g, 40% yield).

2-(Dimethyl(phenyl)silyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2t)[5]



^{1}H NMR (500 MHz, C_6D_6) δ 7.55−7.48 (m, 2H), 7.25−7.19 (m, 3H), 7.08−7.00 (m, 4H), 5.90 (dd, *J* = 7.0, 1.3 Hz, 2H), 4.61 (s, 2H), 0.33 (s, 6H).

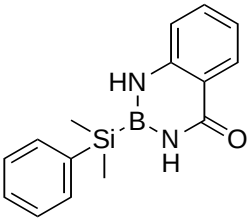
^{13}C NMR (125 MHz, C_6D_6) δ 142.52, 138.41, 136.98, 133.45, 130.32, 128.49, 128.35, 118.65, 117.87, 106.33, -0.06. The signal of the boron-bound carbon atom was obscure due to the quadrupolar boron nucleus.

2-21. Synthesis of dimethyl(phenyl)silyl–B(aam) (2u)

A flame-dried 50 mL of two-necked flask equipped with a magnetic stirring bar was charged with Li (208 mg, 30 mmol) cut into approximately 1 mm squares and THF (3 mL) under an argon atmosphere. Chlorodimethyl(phenyl)silane (**1t**) (512 mg, 3 mmol) was slowly added dropwise to the resulting mixture at room temperature. After stirring at this temperature for 4 hours, the reaction mixture was transferred via cannula to another flame-dried 50 mL of two-necked flask. After cooling the resulting mixture to -78 °C, triethylborate (438 mg, 3 mmol) was added dropwise at -78 °C. The resulting mixture was warmed to room temperature and stirred overnight. Then, anthranilamide (409 mg, 3 mmol) was added to the reaction mixture. After stirring at this temperature for 10 minutes, chlorotrimethylsilane (326 mg, 3 mmol) was added to the reaction mixture. The reaction mixture was quenched with sat. $NaHCO_3$ aq. The organic layer was allowed to separate, and the aqueous layer was extracted with ethyl acetate. The

organic solution was washed with brine and dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude material was purified by column chromatography on florisil (Hexane/EtOAc = 1:1 as an eluent) to give dimethyl(phenyl)silyl–B(aam) (**2u**) (0.1219 g, 15% yield).

2-(dimethyl(phenyl)silyl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (2u)



White solid: mp 172–174 °C

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.56−7.49 (m, 3H), 7.42−7.36 (m, 4H), 7.16 (ddd, *J* = 8.1, 7.1, 1.0 Hz, 1H), 7.01−6.97 (m, 1H), 6.68 (s, 1H), 0.45 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 165.55, 144.00, 137.71, 134.16, 133.90, 129.33, 129.15, 128.41, 122.49, 119.75, 117.60, -3.51. The signal of the boron-bound carbon atom was obscure due to the quadrupolar boron nucleus.

^{11}B NMR (160 MHz, $CDCl_3$) δ 33.87.

HRMS (APCl) Calcd for $C_{15}H_{17}N_2BOSi$: $[M+H]^+$, 281.12760. Found: *m/z* 281.12787.

3. Effect of boron electrophiles on the reaction

By using pentafluorobenzene as a model substate, effect of boron electrophiles on the reaction efficiency was investigated. When $B(OMe)_3$ was used instead of $B(OEt)_3$, the yield of the desired pentafluorophenyl–B(dan) was almost the same as that with $B(OEt)_3$. On the other hand, the yield became lower with $B(OPh)_3$ despite the increasing leaving group ability of the PhO moiety.

・With trimethylborate

A flame-dried Schlenk tube equipped with a magnetic stirring bar was charged with pentafluorobenzene (168 mg, 1 mmol) and THF (2 mL) under an argon atmosphere. The resulting mixture was cooled to -78 °C and *n*-BuLi (1.6 M in Hexane, 0.75 mL, 1.2 mmol) was dropped into this slowly. After stirring at this temperature for 1 hour, trimethylborate (125 mg, 1.2 mmol) was added dropwise at -78 °C. The resulting mixture was stirred at this temperature for 1 hour, then warmed to room temperature and stirred for another 1 hour. Then, 1,8-diaminonaphthalene (190 mg, 1.2 mmol) was added to the reaction mixture. After stirring at this temperature for 10 minutes, acetic acid (180 mg, 3 mmol) was added to the reaction mixture. The reaction mixture was quenched with sat. $NaHCO_3$ aq. The organic layer was allowed to separate, and the aqueous layer was extracted with ethyl acetate. The organic solution was washed with brine and dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude material was purified by column chromatography on silica gel (Hexane/EtOAc = 9:1 as an eluent) to give pentafluorophenyl–B(dan) as a white solid (0.0779 g, 23% yield).

・With triethylborate

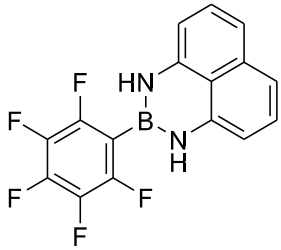
A flame-dried Schlenk tube equipped with a magnetic stirring bar was charged with pentafluorobenzene (168 mg, 1 mmol) and THF (2 mL) under an argon atmosphere. The resulting mixture was cooled to -78 °C and *n*-BuLi (1.6 M in Hexane, 0.75 mL, 1.2 mmol) was dropped into this slowly. After stirring at this temperature for 1 hour, triethylborate (175 mg, 1.2 mmol) was added dropwise at -78 °C. The resulting mixture was stirred at this temperature for 1 hour, then warmed to room temperature and stirred for another 1 hour. Then, 1,8-diaminonaphthalene (190 mg, 1.2 mmol) was added to the

reaction mixture. After stirring at this temperature for 10 minutes, acetic acid (180 mg, 3 mmol) was added to the reaction mixture. The reaction mixture was quenched with sat. $NaHCO_3$ aq. The organic layer was allowed to separate, and the aqueous layer was extracted with ethyl acetate. The organic solution was washed with brine and dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude material was purified by column chromatography on silica gel (Hexane/EtOAc = 9:1 as an eluent) to give pentafluorophenyl–B(dan) as a white solid (0.0642 g, 19% yield).

・With triphenylborate

A flame-dried Schlenk tube equipped with a magnetic stirring bar was charged with pentafluorobenzene (168 mg, 1 mmol) and THF (2 mL) under an argon atmosphere. The resulting mixture was cooled to -78 °C and *n*-BuLi (1.6 M in Hexane, 0.75 mL, 1.2 mmol) was dropped into this slowly. After stirring at this temperature for 1 hour, triphenylborate (348 mg, 1.2 mmol) dissolved in THF (1 mL) was added dropwise at -78 °C. The resulting mixture was stirred at this temperature for 1 hour, then warmed to room temperature and stirred for another 1 hour. Then, 1,8-diaminonaphthalene (190 mg, 1.2 mmol) was added to the reaction mixture. After stirring at this temperature for 10 minutes, acetic acid (180 mg, 3 mmol) was added to the reaction mixture. The reaction mixture was quenched with sat. $NaHCO_3$ aq. The organic layer was allowed to separate, and the aqueous layer was extracted with ethyl acetate. The organic solution was washed with brine and dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude material was purified by column chromatography on silica gel (Hexane/EtOAc = 9:1 as an eluent) to give pentafluorophenyl–B(dan) as a white solid (0.0263 g, 8% yield).

2-(Perfluorophenyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2w)[6]



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18−7.11 (m, 2H), 7.11−7.05 (m, 2H), 6.40 (dq, *J* = 7.2, 1.5 Hz, 2H), 6.34 (s, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 140.13, 136.35, 127.79, 120.27, 118.74, 106.77. The signal of the boron-bound carbon atom was obscure due to the quadrupolar boron nucleus.

4. Methods for synthesizing $PhMe_2Si$–B(dan) or –B(aam)

$PhMe_2Si$–B(dan) (**2t**) was synthesized according to method A–C; acetic acid was usually added at once to a mixture of 1,8-diaminonaphthalene and a borate intermediate at room temperature (38% yield, **method A**), while slow addition of acetic acid at 0 °C resulted in a slightly lower yield (32% yield, **method B**). On the other hand, the yield was slightly improved when acetic acid was first added to the silylborate before adding 1,8-diaminonaphthalene (40% yield, **method C**). Using a silyl Grignard reagent ($PhMe_2SiMgBr$) instead of $PhMe_2SiLi$ resulted in an almost similar yield (42%, **method D**).

・Method A

A flame-dried 50 mL of two-necked flask equipped with a magnetic stirring bar was charged with Li (208 mg, 30 mmol) cut into approximately 1 mm squares and THF (3 mL) under an argon atmosphere. Chlorodimethyl(phenyl)silane (**1t**) (512 mg, 3 mmol) was slowly added dropwise to the resulting mixture at room temperature. After stirring at this temperature for 4 hours, the reaction mixture was transferred by cannula to another flame-dried 50 mL of two-necked flask. After cooling resulting mixture to -78 °C, triethylborate (438 mg, 3 mmol) was added dropwise at -78 °C. The resulting mixture was warmed to room temperature and stirred overnight. Then, 1,8-diaminonaphthalene (475 mg, 3 mmol) was added to the reaction mixture. After stirring at this temperature for 10 minutes, acetic acid (541 mg, 9 mmol) was added to the reaction mixture. The reaction mixture was quenched with sat. $NaHCO_3$ aq. The organic layer was allowed to separate, and the aqueous layer was extracted with ethyl acetate. The organic solution was washed with brine and dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude material was purified by column chromatography on silica gel (Hexane/EtOAc = 9:1 as an eluent) to give dimethyl(phenyl)silyl–B(dan) (**2t**) as a pale yellow oil (0.3416 g, 38% yield).

・Method B

A flame-dried 50 mL of two-necked flask equipped with a magnetic stirring bar was charged with Li (208 mg, 30 mmol) cut into approximately 1 mm squares and THF (3 mL) under an argon atmosphere. Chlorodimethyl(phenyl)silane (**1t**) (512 mg, 3 mmol)

was slowly added dropwise to the resulting mixture at room temperature. After stirring at this temperature for 4 hours, the reaction mixture was transferred by cannula to another flame-dried 50 mL of two-necked flask. After cooling resulting mixture to -78 °C, triethylborate (438 mg, 3 mmol) was added dropwise at -78 °C. The resulting mixture was warmed to room temperature and stirred overnight. Then, 1,8-diaminonaphthalene (475 mg, 3 mmol) was added to the reaction mixture. After stirring at this temperature for 10 minutes, acetic acid (541 mg, 9 mmol) was slowly added dropwise to the reaction mixture at 0 °C. The reaction mixture was quenched with sat. $NaHCO_3$ aq. The organic layer was allowed to separate, and the aqueous layer was extracted with ethyl acetate. The organic solution was washed with brine and dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude material was purified by column chromatography on silica gel (Hexane/EtOAc = 9:1 as an eluent) to give dimethyl(phenyl)silyl–B(dan) (**2t**) as a pale yellow oil (0.2869 g, 32% yield).

・Method C

See 2-20 on page S22.

・Method D

A flame-dried 50 mL of two-necked flask was charged with a magnetic stirring bar and magnesium turnings (87.5 mg, 3.6 mmol). After the Schlenk tube was heated under vacuum for 5 minutes with the aid of a heating gun, the Schlenk tube was cooled to room temperature and back-filled with argon. THF (3 mL) was then added, and the reaction mixture was heated to 65 °C. 1,2-Dibromoethane (564 mg, 3 mmol) was quickly added and then the reaction mixture was stirred for 3h at this temperature to afford $MgBr_2$. Another flame-dried 50 mL of two-necked flask equipped with a magnetic stirring bar was charged with Li (208 mg, 30 mmol) cut into approximately 1 mm squares and THF (3 mL) under an argon atmosphere. Chlorodimethyl(phenyl)silane (**1t**) (512 mg, 3 mmol) was slowly added dropwise to the resulting mixture at room temperature. After stirring at this temperature for 4 hours, the reaction mixture was slowly transferred by cannula to the reaction mixture containing the prepared $MgBr_2$ at 65 °C. After cooling the resulting mixture to -78 °C, triethylborate (438 mg, 3 mmol) was added dropwise at -78 °C. The resulting mixture was warmed to room temperature and stirred overnight. Then, 1,8-diaminonaphthalene (475 mg, 3 mmol) was added to

the reaction mixture. After stirring at this temperature for 10 minutes, acetic acid (541 mg, 9 mmol) was added to the reaction mixture. The reaction mixture was quenched with sat. $NaHCO_3$ aq. The organic layer was allowed to separate, and the aqueous layer was extracted with ethyl acetate. The organic solution was washed with brine and dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude material was purified by column chromatography on silica gel (Hexane/EtOAc = 9:1 as an eluent) to give dimethyl(phenyl)silyl–B(dan) (**2t**) as a pale yellow oil (0.3764 g, 42% yield).

$PhMe_2Si$–B(aam) (**2u**) was synthesized according to method D–F; chlorotrimethylsilane was added to a mixture of anthranilamide and a borate intermediate (15% yield, **method E**), while the yield was not improved when chlorotrimethylsilane was first added to the silylborate before adding anthranilamide (14% yield, **method F**). On the other hand, the conventional procedure using $PhMe_2Si$–B(N*i*-$Pr_2)_2$ resulted in increase in the yield (65% yield, **method G**).

・Method E

See 2-21 on page S23.

・Method F

A flame-dried 50 mL of two-necked flask equipped with a magnetic stirring bar was charged with Li (208 mg, 30 mmol) cut into approximately 1 mm squares and THF (3 mL) under an argon atmosphere. Chlorodimethyl(phenyl)silane (**1t**) (512 mg, 3 mmol) was slowly added dropwise to the resulting mixture at room temperature. After stirring at this temperature for 4 hours, the reaction mixture was transferred via cannula to another flame-dried 50 mL of two-necked flask. After cooling the resulting mixture to -78 °C, triethylborate (438 mg, 3 mmol) was added dropwise at -78 °C. The resulting mixture was warmed to room temperature and stirred overnight. Then, chlorotrimethylsilane (326 mg, 3 mmol) was added to the reaction mixture before addition of anthranilamide (409 mg, 3 mmol). After stirring at this temperature for 10 minutes, the reaction mixture was quenched with sat. $NaHCO_3$ aq. The organic layer was allowed to separate, and the aqueous layer was extracted with ethyl acetate. The organic solution was washed with brine and dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude material was purified by column

chromatography on florisil (Hexane/EtOAc = 1:1 as an eluent) to give dimethyl(phenyl)silyl–B(aam) (**2u**) (0.1187 g, 14% yield).

・Method G

A flame-dried 50 mL of two-necked flask equipped with a magnetic stirring bar was charged with anthranilamide (136 mg, 1 mmol) and toluene (2.5 mL) under an argon atmosphere. 1-(Dimethyl(phenyl)silyl)-*N*,*N*,*N*',*N*'-tetraisopropylboranediamine (346 mg, 1 mmol) was added to the reaction mixture at room temperature, and then warmed to 125 °C. After stirring at this temperature for 5 hours, the reaction mixture was quenched with brine. The organic layer was allowed to separate, and the aqueous layer was extracted with ethyl acetate. The organic solution was washed with brine and dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude material was purified by column chromatography on florisil (Hexane/EtOAc = 1:1 as an eluent) to give dimethyl(phenyl)silyl–B(aam) (**2u**) (0.1821 g, 65% yield).

5. X-ray crystallographic analysis

General Remarks

Crystals suitable for the X-ray structural determination were mounted on a Bruker SMART APEXII CCD diffractometer and irradiated with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) for data collection. The data were processed using the APEX3 program suite and summarized in a table shown in next page. All structures were solved by an intrinsic phasing method using the SHELXT program (ver. 2014/4– 2014/5).[7] Refinement on F^2 was carried out using full-matrix least-squares with the SHELXL[8] and expanded using Fourier techniques. All nonhydrogen atoms, except those of disordered solvents, were refined using anisotropic thermal parameters. Hydrogen atoms were assigned to idealized geometric positions and included in structure factor calculations. The SHELX was interfaced with SHELXLE GUI for most of the refinement steps.[9] The pictures of the molecules were prepared using Pov-Ray 3.6.[10]

Crystal data and structure refinement for **2u**

Identification code	**2u**
CCDC No.	2121000
Empirical formula	C15 H17 B N2 O Si
Formula weight	280.2
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Pbca
Unit cell dimensions	a = 11.094(10) Å α = 90°. b = 12.199(12) Å β = 90°. c = 22.35(2) Å γ = 90°.
Volume	3024(5) $Å^3$
Z	8
Density (calculated)	1.231 Mg/m^3
Absorption coefficient	0.151 mm^{-1}
F(000)	1184
Crystal size	0.171 x 0.123 x 0.079 mm^3
Theta range for data collection	1.822 to 28.004°.
Index ranges	-14<=h<=14, -16<=k<=16, -29<=l<=29
Reflections collected	33837
Independent reflections	3637 [R(int) = 0.0765]
Completeness to theta = 25.242°	100.00%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3637 / 0 / 183
Goodness-of-fit on F2	1.024
Final R indices [I>2sigma(I)]	R_1 = 0.0420, wR2 = 0.0982
R indices (all data)	R_1 = 0.0697, wR2 = 0.1121
Absolute structure parameter	n/d
Extinction coefficient	n/a
Largest diff. peak and hole	0.459 and -0.294 $e.Å^{-3}$

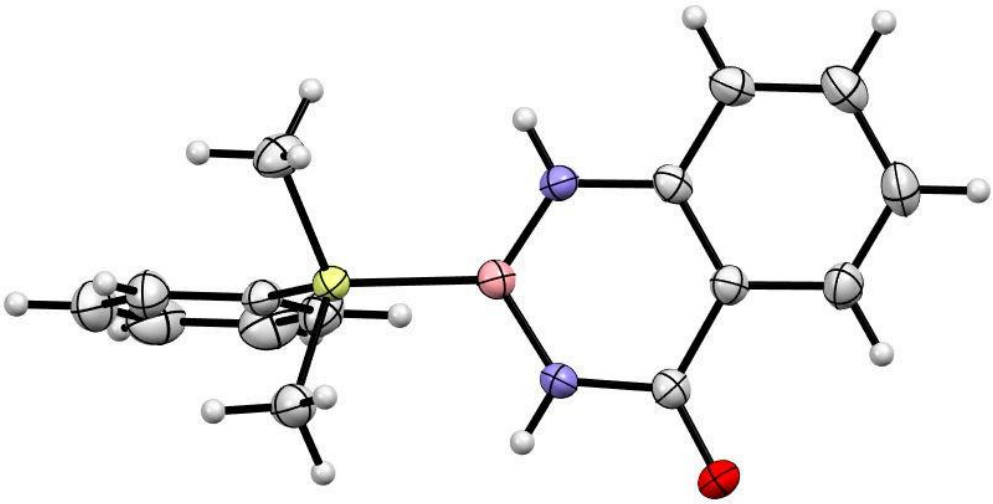


Figure S1 X-ray structure of dimethyl(phenyl)silyl–B(aam) (2u)

6. Mechanistic studies

A flame-dried Schlenk tube equipped with a magnetic stirring bar was charged with *n*-BuLi (1.6 M in Hexane, 0.63 mL, 1 mmol) and THF (2 mL) under an argon atmosphere. The resulting mixture was cooled to -78 °C and triethylborate (146 mg, 1 mmol) was dropped into this slowly. After stirring at this temperature for 1 hour, the reaction mixture was warmed to room temperature and stirred for 3 hours, and then first ^{11}B NMR (160 MHz, THF (no lock)) was measured (**I**).* 1,8-Diaminonaphthalene (158 mg, 1 mmol) was added to the reaction mixture, and then second ^{11}B NMR was measured (**II**). After stirring at this temperature for 10 minutes, acetic acid (180 mg, 3 mmol) was added to the reaction mixture, and third ^{11}B NMR was measured (**III**).

*A portion of the sample was transferred to a flame-dried quartz NMR tube under an argon atmosphere for the ^{11}B NMR measurements.

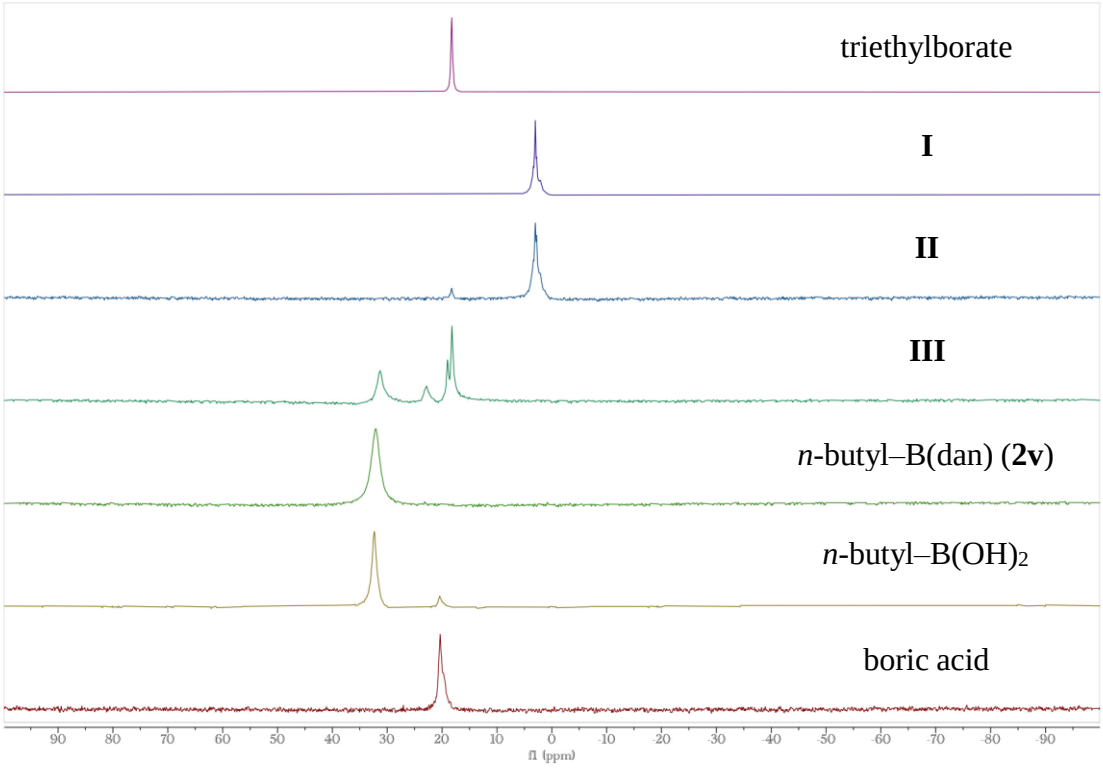


Figure S2. ^{11}B NMR(160 MHz, THF (no lock))

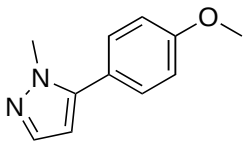
Although three by-products other than *n*-Bu–B(dan) (**2v**) (32.04 ppm) observed in **III** have not yet determined in detail, their chemical shifts and the MS analysis suggest that they may consist of $B(OEt)_3$, $B(OH)_3$, and EtO–B(dan).

7. Direct SMC of heteroaryl–B(dan)

7-1. Direct SMC of 5-pyrazolyl–B(dan) (2a)

A Schlenk tube was charged with a magnetic stirring bar and $Ba(OH)_2$ (51.4 mg, 0.3 mmol). After the Schlenk tube was heated under vacuum for 5 minutes with the aid of a heating gun, the Schlenk tube was cooled to room temperature and back-filled with argon. $Pd(OAc)_2$ (1.7 mg, 7.5 μmol), 1,1'-bis(diphenylphosphino)ferrocene (6.2 mg, 11.3 μmol), 5-pyrazolyl–B(dan) (**2a**) (37.2 mg, 0.15 mmol), 4-bromoanisole (42.1 mg, 0.23 mmol) and DMF (0.3 mL) were then added. The resulting mixture was stirred at 90 °C for 24 h. The reaction mixture was quenched with brine. The organic layer was allowed to separate, and the aqueous layer was extracted with ethyl acetate. The organic solution was washed with brine and dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude material was purified by column chromatography on silica gel (Hexane/EtOAc = 1:1 as an eluent) to give 5-(4-methoxyphenyl)-1-methyl-1*H*-pyrazole (**3a**) as a white solid (0.0281 g, >99% yield).

5-(4-Methoxyphenyl)-1-methyl-1H-pyrazole (3a)[11]



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 1.9 Hz, 1H), 7.36−7.32 (m, 2H), 7.00−6.96 (m, 2H), 6.25 (d, *J* = 1.9 Hz, 1H), 3.87 (s, 3H), 3.86 (s, 3H).

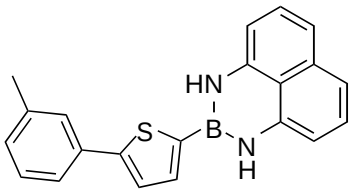
^{13}C NMR (125 MHz, $CDCl_3$) δ 159.83, 143.48, 138.57, 130.16, 123.24, 114.21, 105.80, 55.48, 37.49.

7-2. Migita–Kosugi–Stille cross-coupling of 2-(5-(tributylstannyl)thiophen-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2s)

A flame-dried Schlenk tube equipped with a magnetic stirring bar was charged with $Pd(PPh_3)_4$ (28.9 mg, 25 μmol), 2-(5-(tributylstannyl)thiophen-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (**2s**) (324 mg, 0.6 mmol), 3-bromotoluene (85.5 mg, 0.5 mmol) and toluene (7.1 mL)

under an argon atmosphere. The resulting mixture was stirred at 110 °C for 24 h. The reaction mixture was quenched with brine. The organic layer was allowed to separate, and the aqueous layer was extracted with ethyl acetate. The organic solution was washed with brine and dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude material was purified by column chromatography on silica gel (Hexane/EtOAc = 9:1 as an eluent) to give 2-(5-(*m*-tolyl)thiophen-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (**3b**) (0.1614 g, 95% yield).

2-(5-(*m*-Tolyl)thiophen-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3b)



Green solid: mp 160–162 °C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69−7.65 (m, 1H), 7.51−7.39 (m, 4H), 7.34−7.29 (m, 1H), 7.17−7.13 (m, 2H), 7.07 (dt, *J* = 8.3, 1.1 Hz, 2H), 6.43 (dd, *J* = 7.3, 1.2 Hz, 2H), 5.98 (s, 2H), 2.41 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 140.85, 138.79, 136.45, 133.99, 129.13, 129.02, 128.91, 127.74, 127.02, 126.28, 124.72, 123.41, 119.89, 118.12, 106.27, 21.60. The signal of the boron-bound carbon atom was obscure due to the quadrupolar boron nucleus.

^{11}B NMR (160 MHz, $CDCl_3$) δ 26.88.

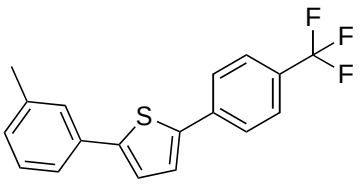
HRMS (APCl) Calcd for $C_{21}H_{17}N_2BS$: $[M+H]^+$, 341.12783. Found: *m/z* 341.12820.

7-3. Direct SMC of 2-(5-(*m*-tolyl)thiophen-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3b)

A Schlenk tube was charged with a magnetic stirring bar and $Ba(OH)_2$ (34.3 mg, 0.2 mmol). After the Schlenk tube was heated under vacuum for 5 minutes with the aid of a heating gun, the Schlenk tube was cooled to room temperature and back-filled with argon. $Pd(OAc)_2$ (1.1 mg, 5 μmol), 1,1'-bis(diphenylphosphino)ferrocene (4.2 mg, 7.5 μmol),

2-(5-(*m*-tolyl)thiophen-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (**3b**) (34.0 mg, 0.1 mmol), 1-bromo-4-(trifluoromethyl)benzene (33.8 mg, 0.15 mmol) and DMF (0.2 mL) were then added. The resulting mixture was stirred at 90 °C for 24 h. The reaction mixture was quenched with brine. The organic layer was allowed to separate, and the aqueous layer was extracted with ethyl acetate. The organic solution was washed with brine and dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude material was purified by column chromatography on silica gel (Hexane as an eluent) to give 2-(*m*-tolyl)-5-(4-(trifluoromethyl)phenyl)thiophene (**3c**) (0.0266 g, 84% yield).

2-(*m*-Tolyl)-5-(4-(trifluoromethyl)phenyl)thiophene (3c)



White solid: mp 152–153 °C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.1 Hz, 2H), 7.63 (d, *J* = 8.1 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.36 (dd, *J* = 4.0, 1.3 Hz, 1H), 7.32−7.27 (m, 2H), 7.13 (d, *J* = 7.5 Hz, 1H), 2.41 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 145.51, 141.54, 138.83, 137.84, 133.96, 129.22 (q, J_{CF} = 32.8 Hz), 129.04, 128.89, 126.61, 126.05 (q, J_{CF} = 3.8 Hz), 125.68, 125.48, 125.38 (t, J_{CF} = 270.8 Hz), 124.24, 123.03, 21.60.

HRMS (EI-MS) Calcd for $C_{18}H_{13}F_3S$: $[M+H]^+$, 318.06901. Found: *m/z* 318.06969.

8. References

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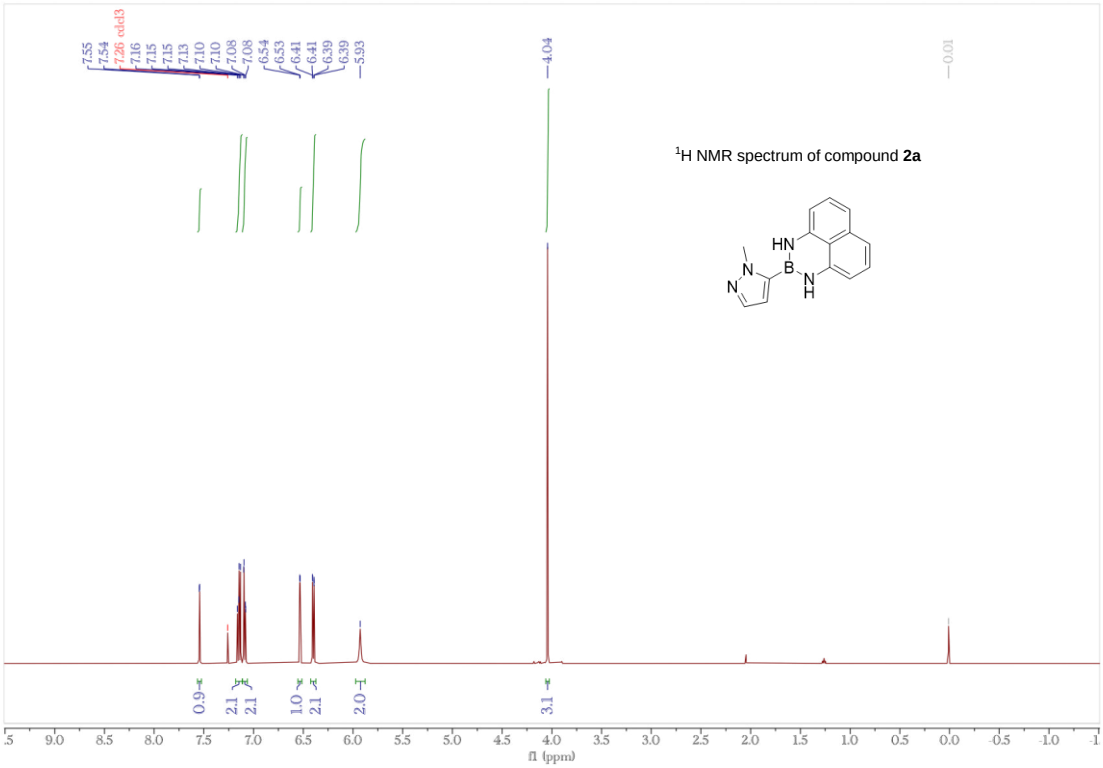
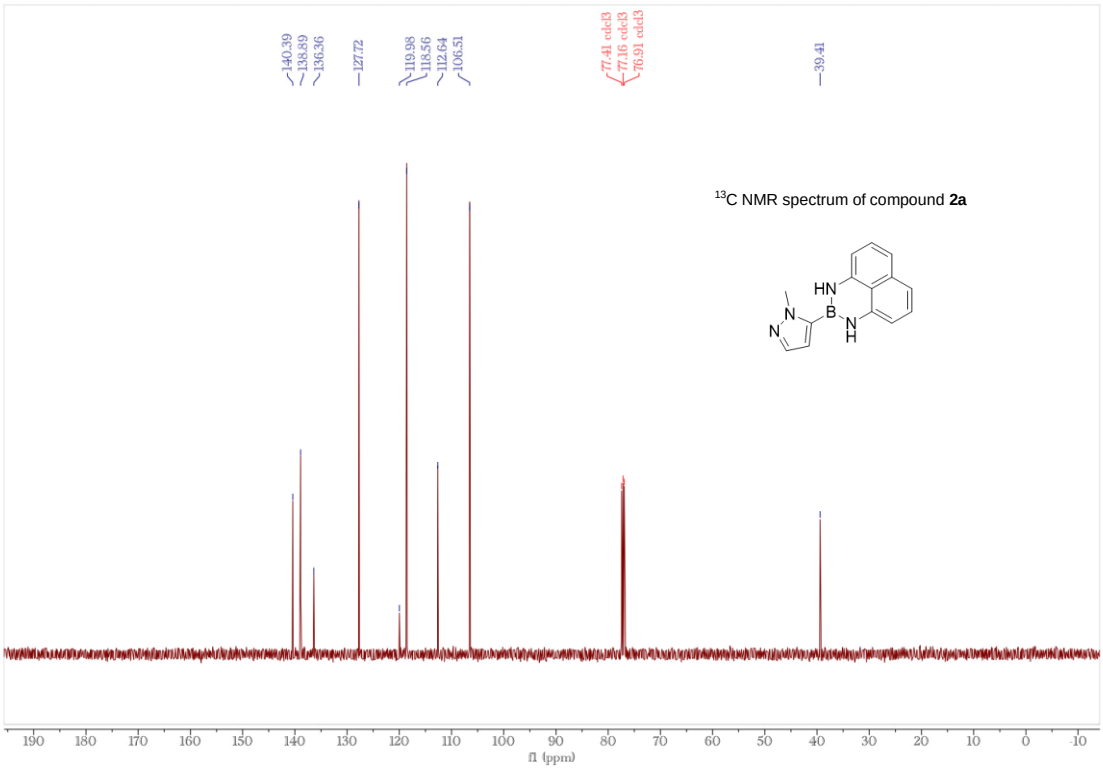
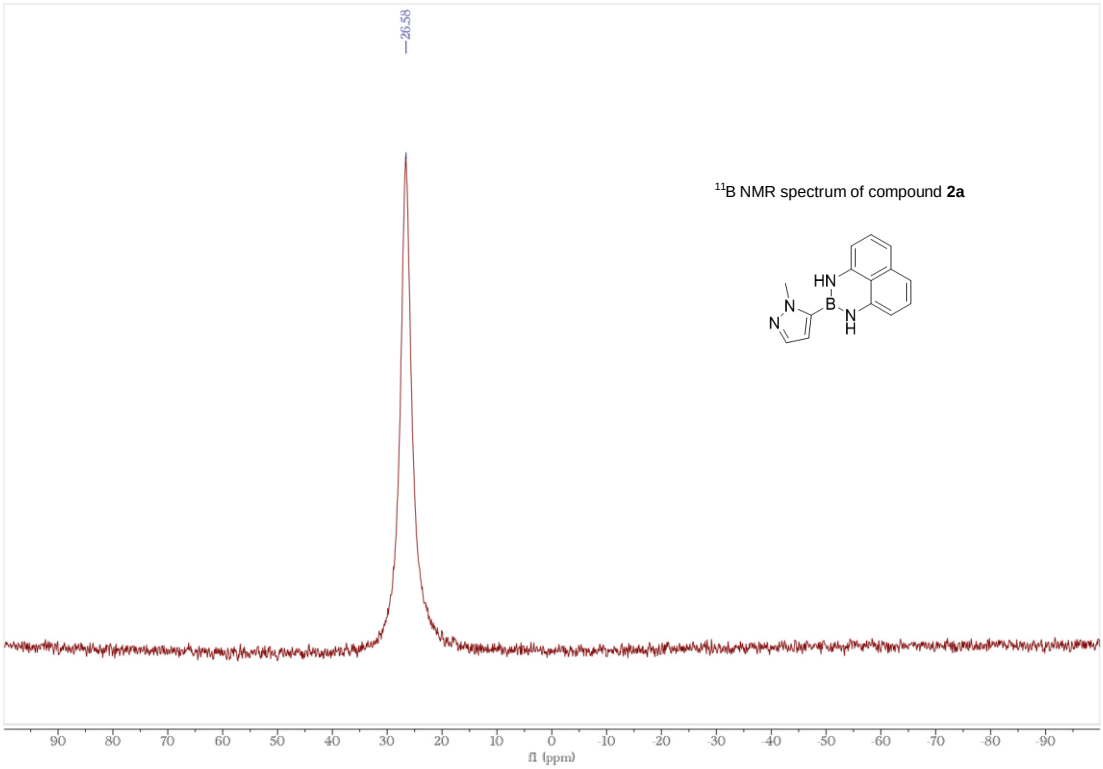
9. NMR spectra



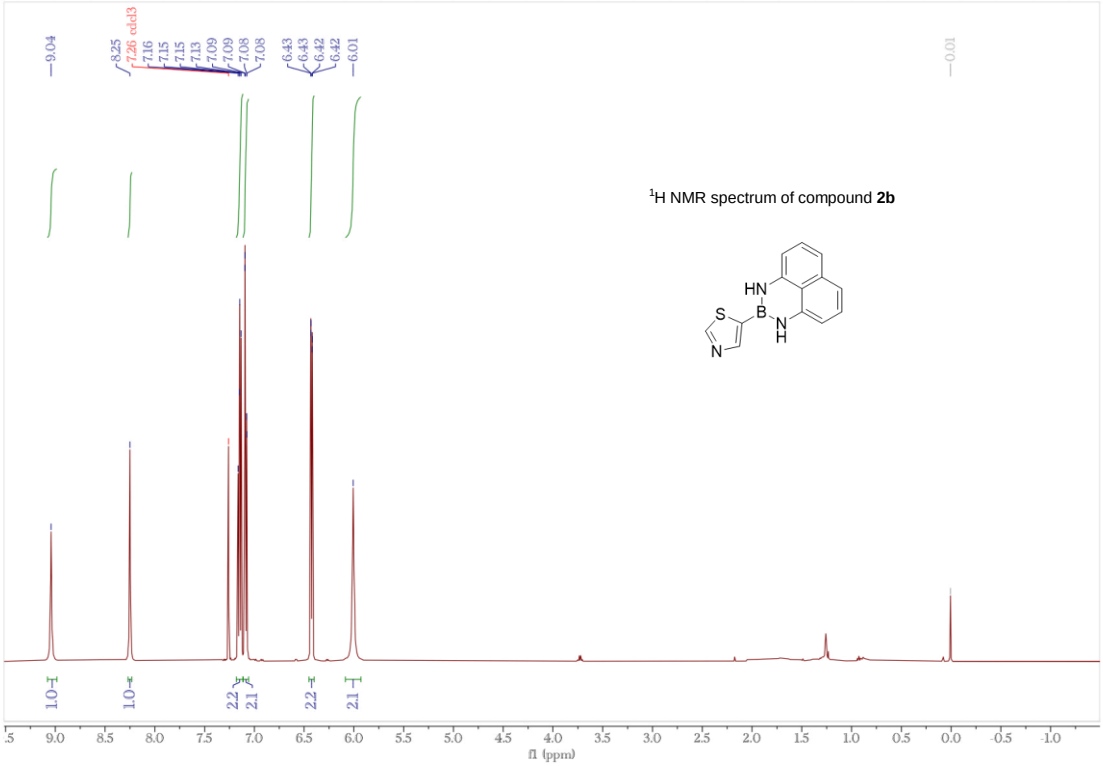
^{1}H NMR spectrum of compound **2a**



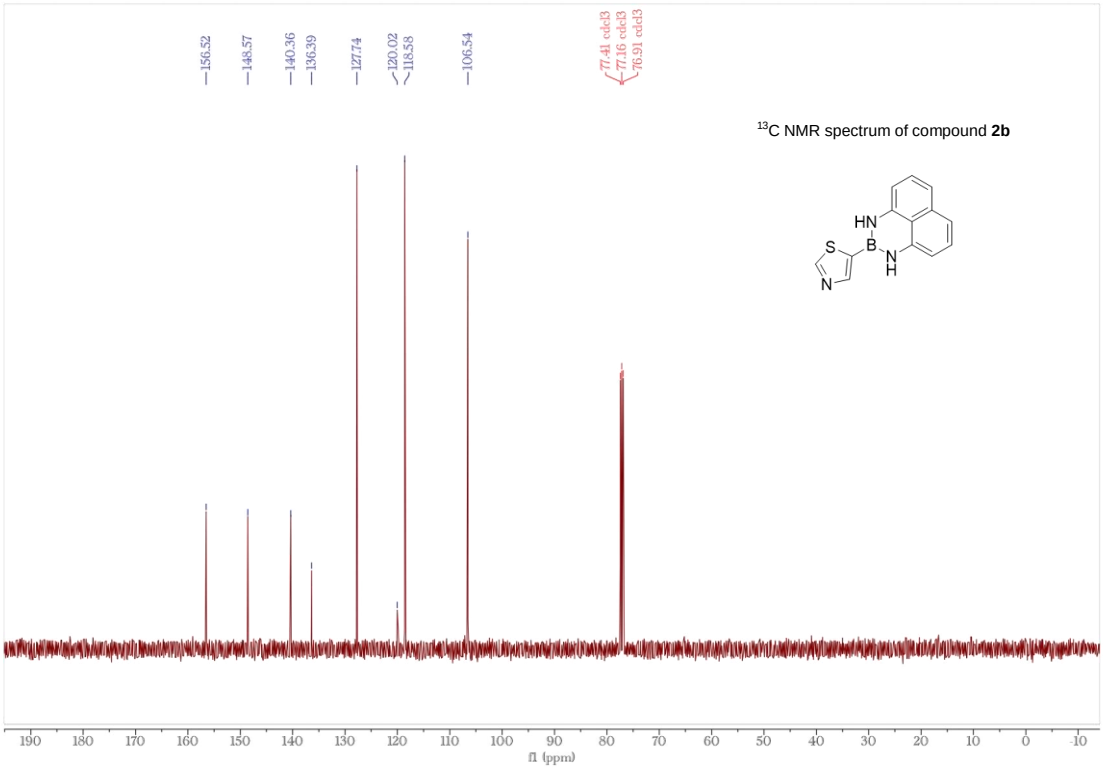
^{13}C NMR spectrum of compound **2a**



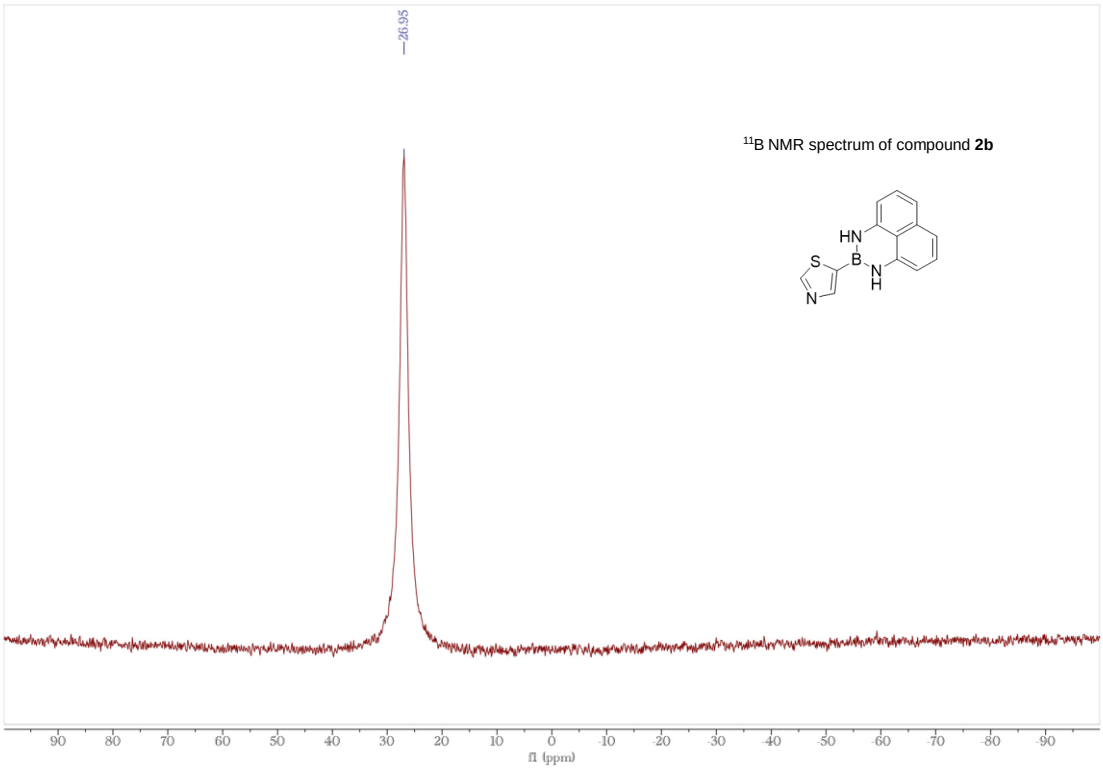
^{11}B NMR spectrum of compound **2a**



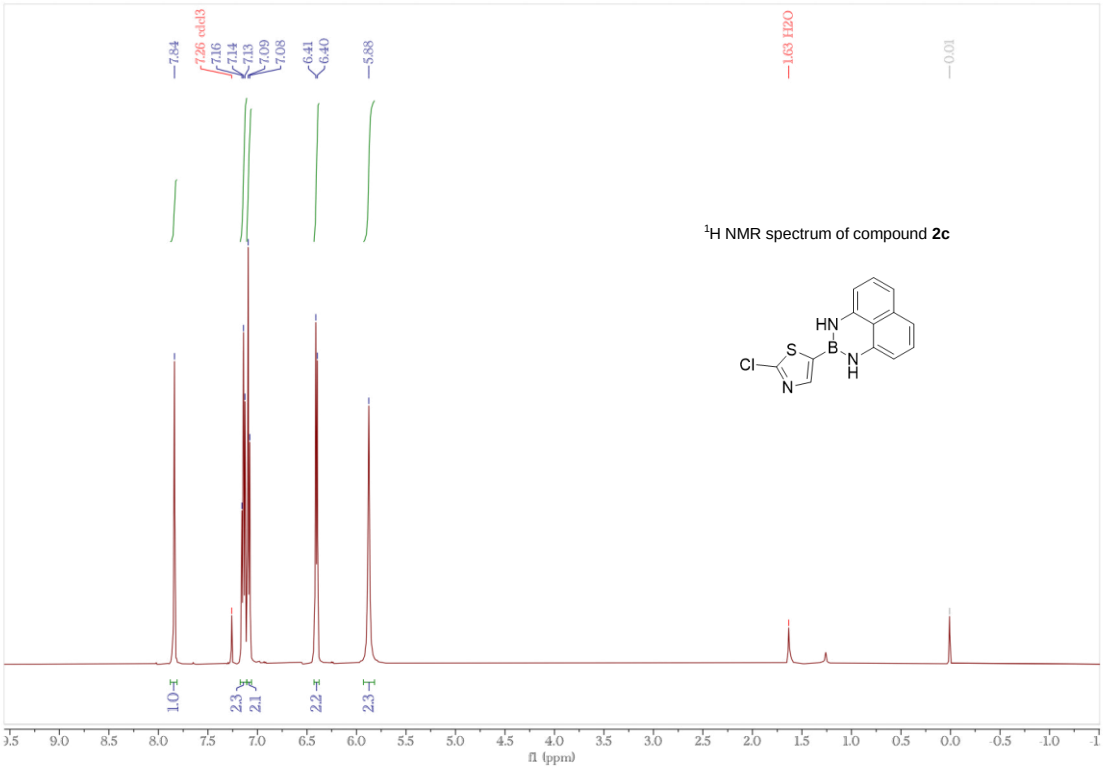
^{1}H NMR spectrum of compound **2b**



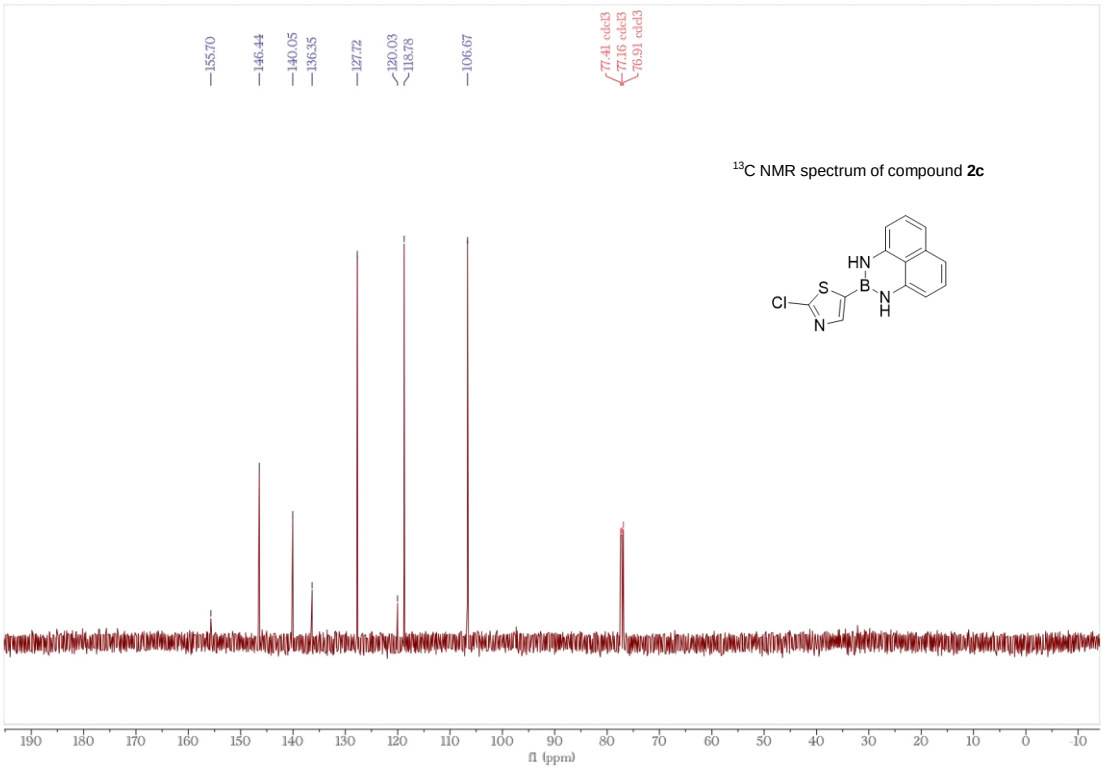
^{13}C NMR spectrum of compound **2b**



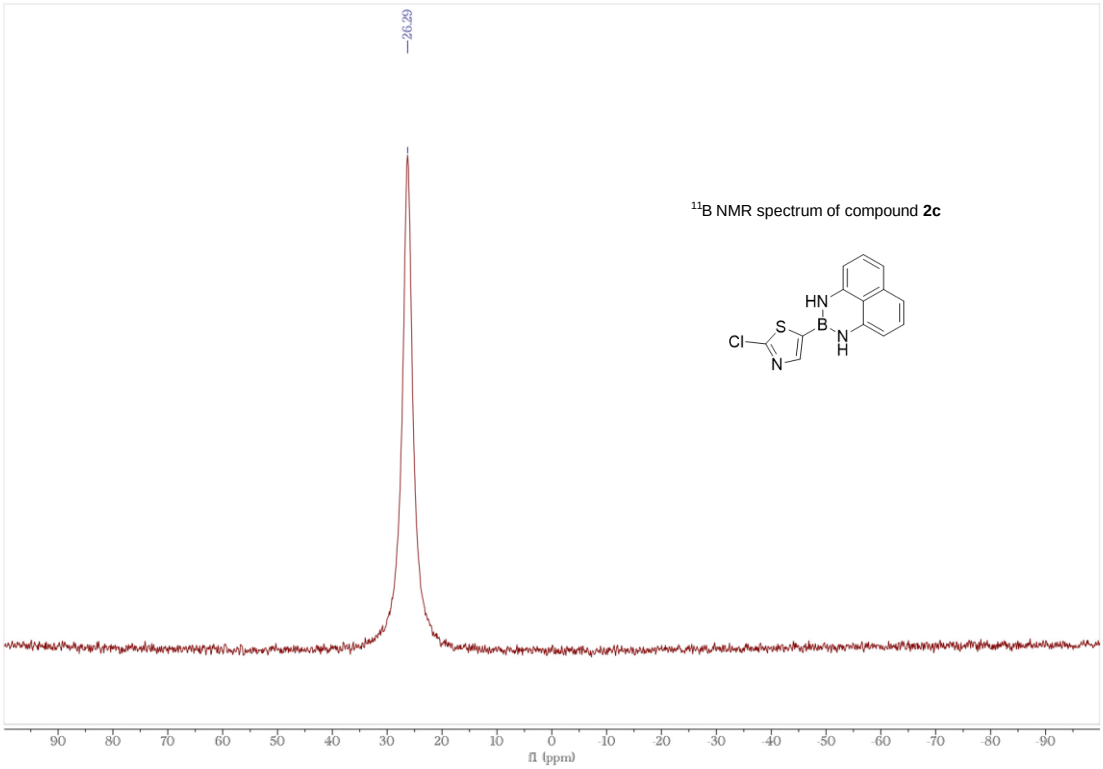
^{11}B NMR spectrum of compound **2b**



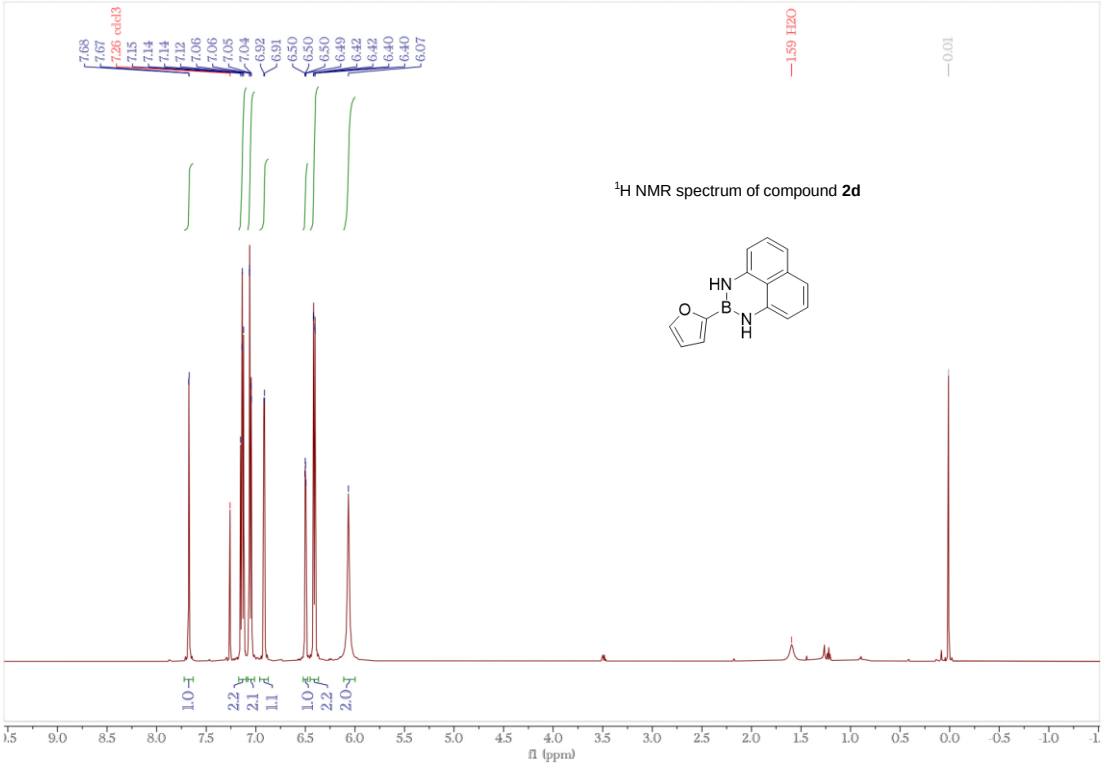
^{1}H NMR spectrum of compound **2c**



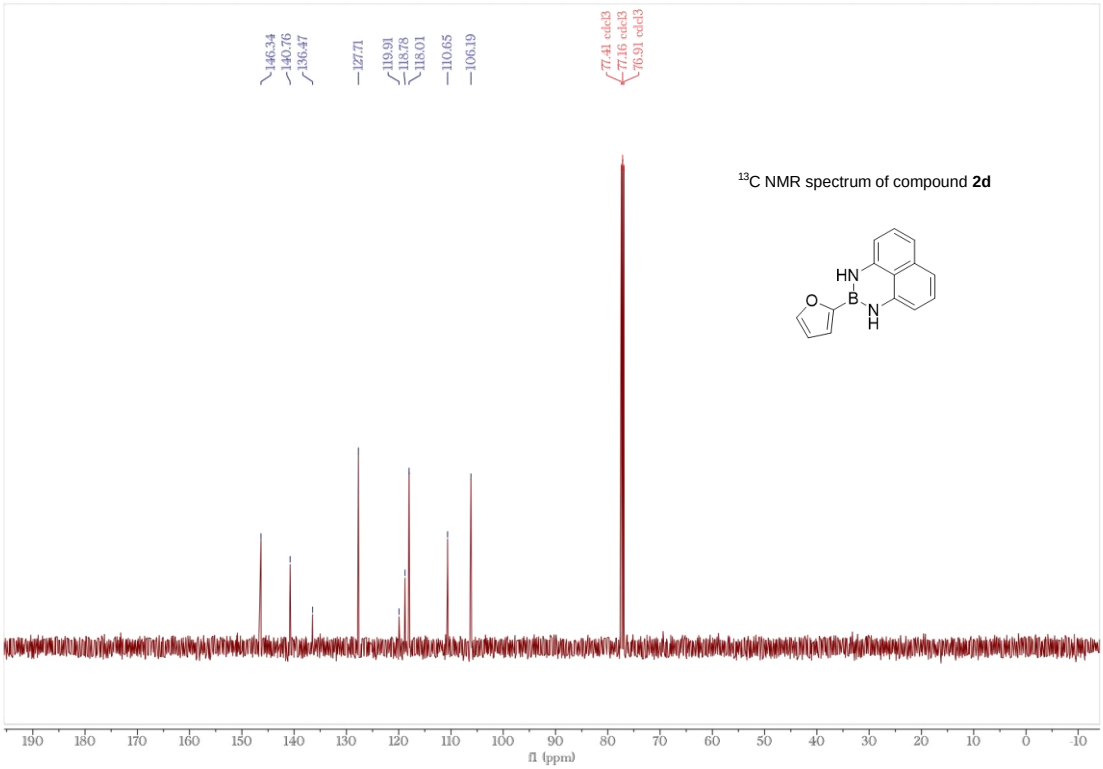
^{13}C NMR spectrum of compound **2c**



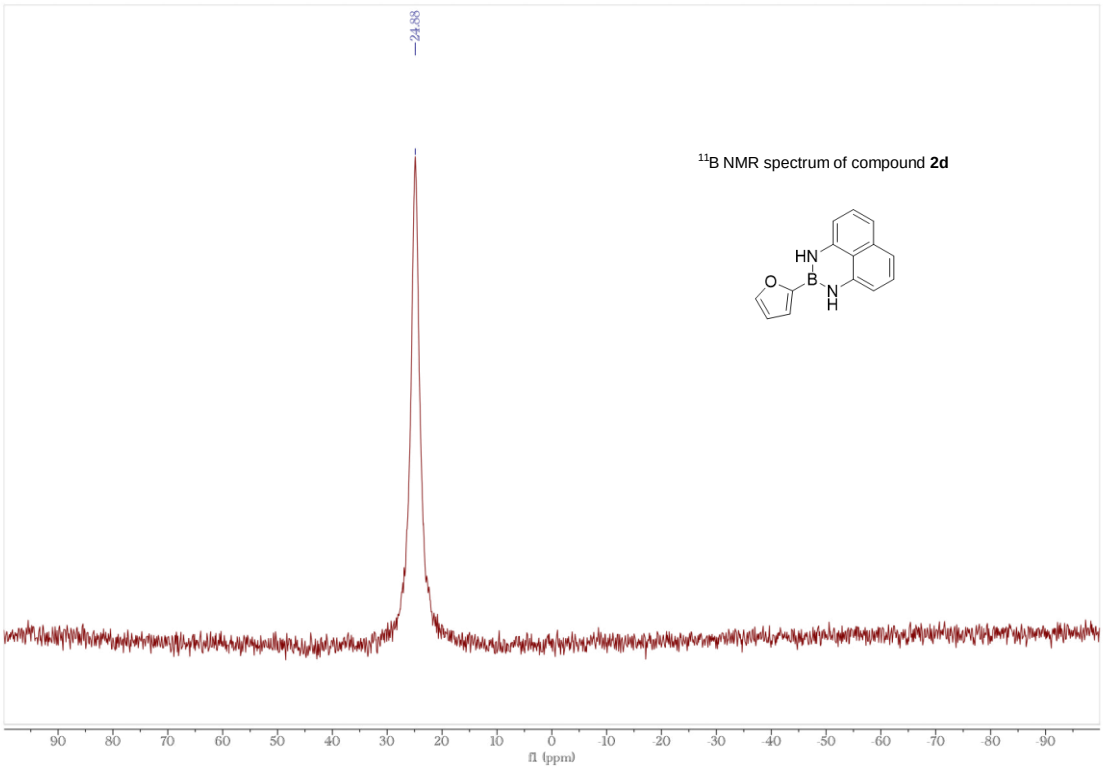
^{11}B NMR spectrum of compound **2c**



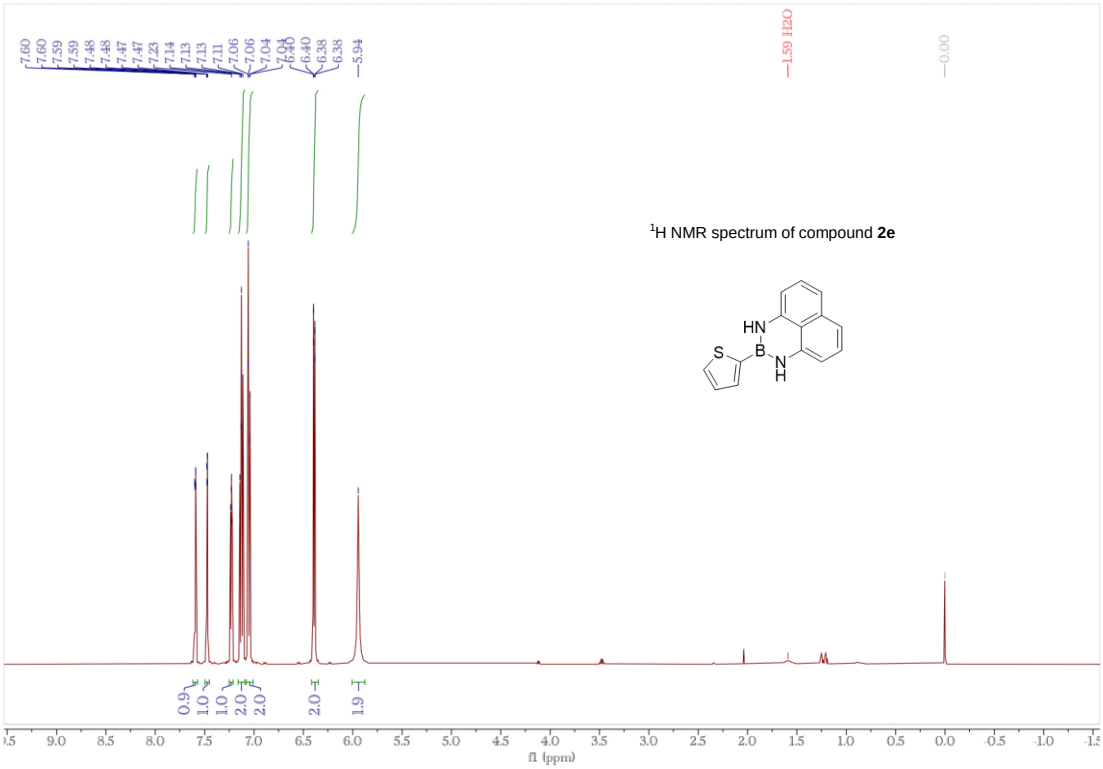
^{1}H NMR spectrum of compound **2d**



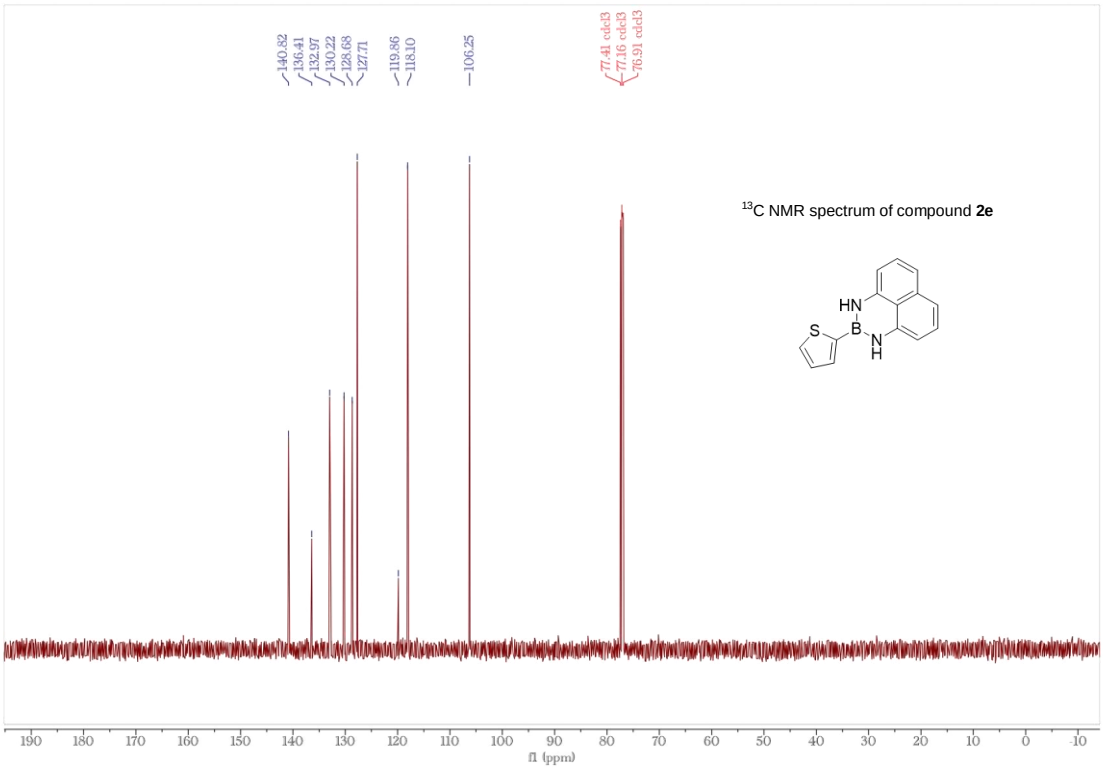
^{13}C NMR spectrum of compound **2d**



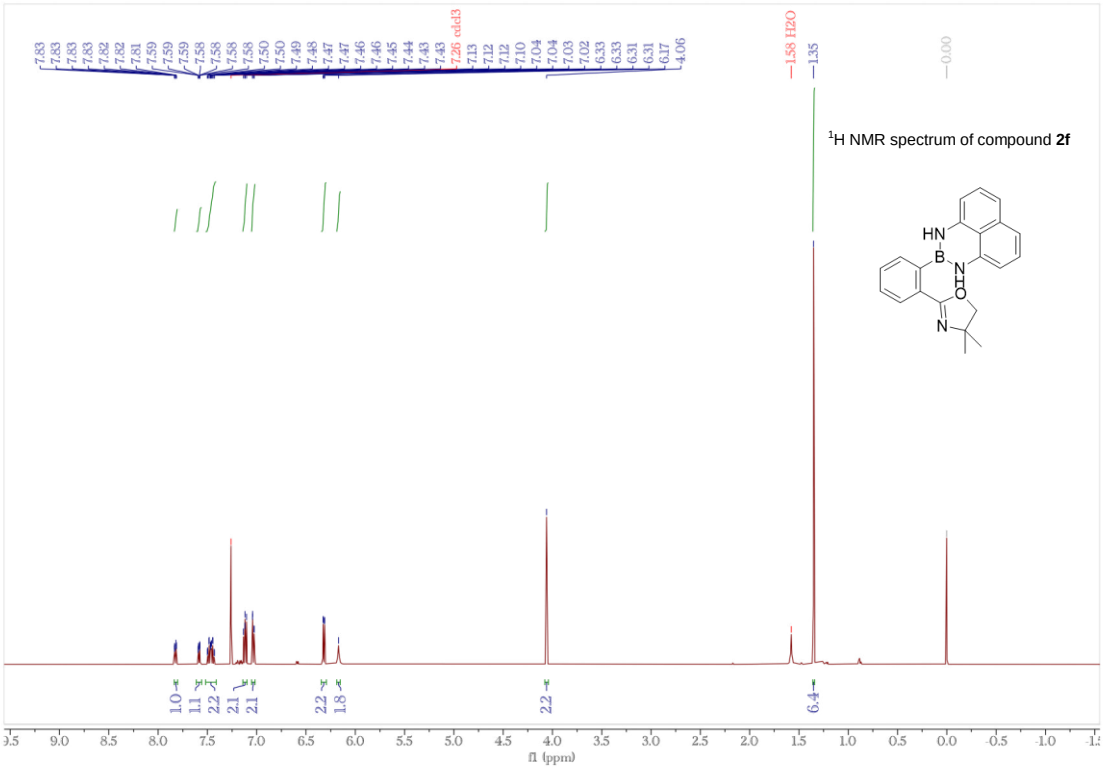
^{11}B NMR spectrum of compound **2d**



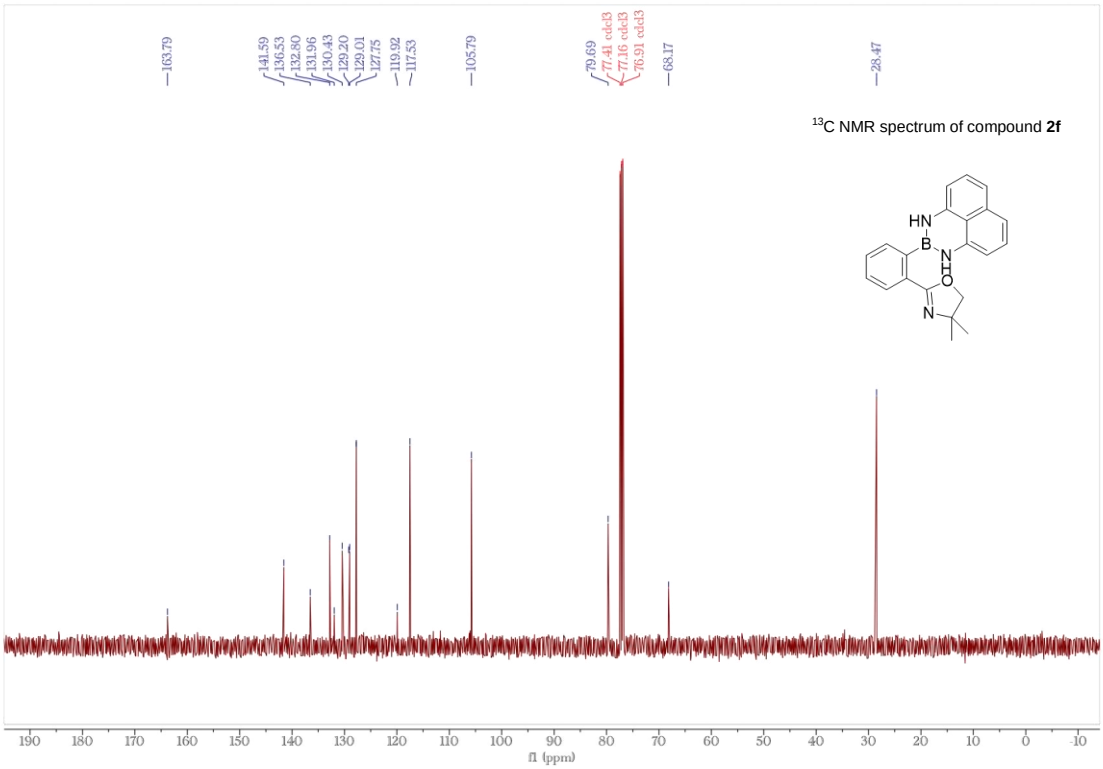
^{1}H NMR spectrum of compound **2e**



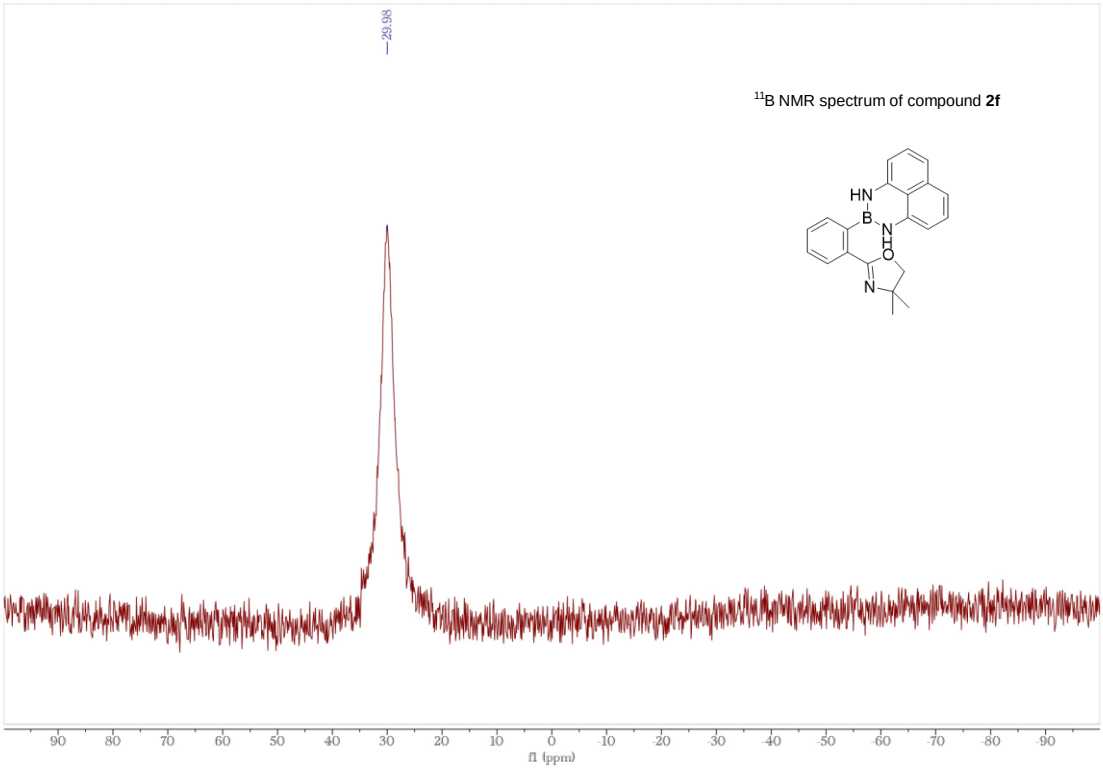
^{13}C NMR spectrum of compound **2e**

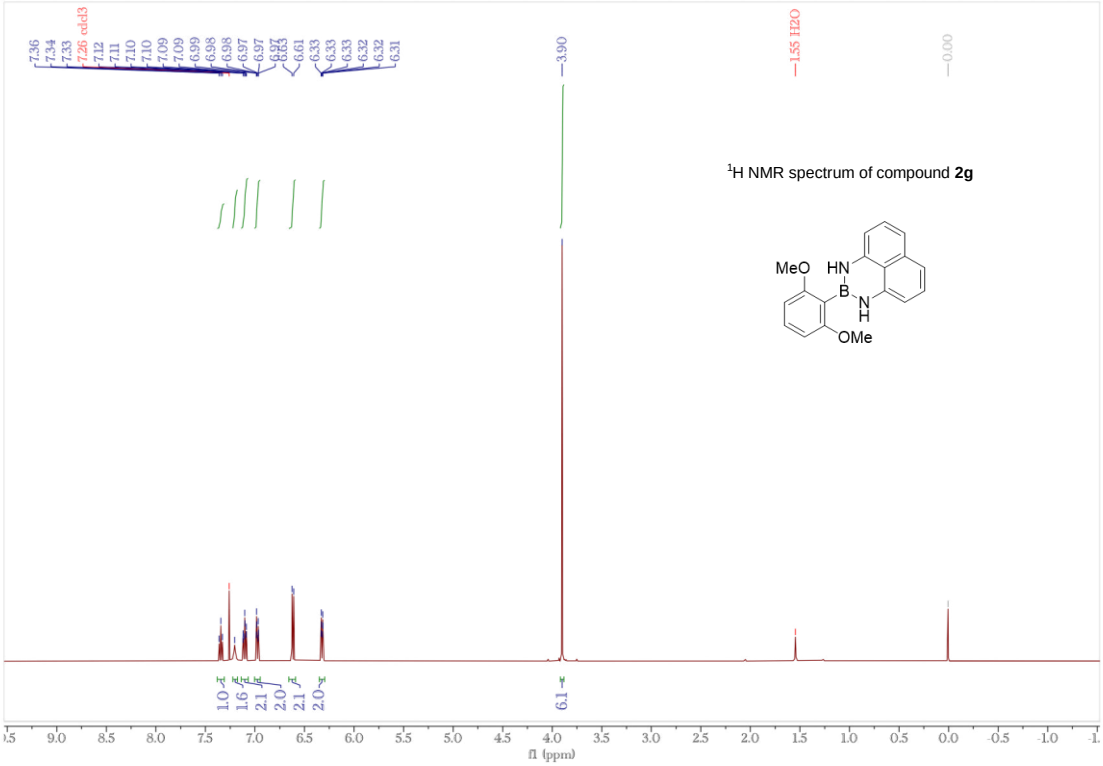


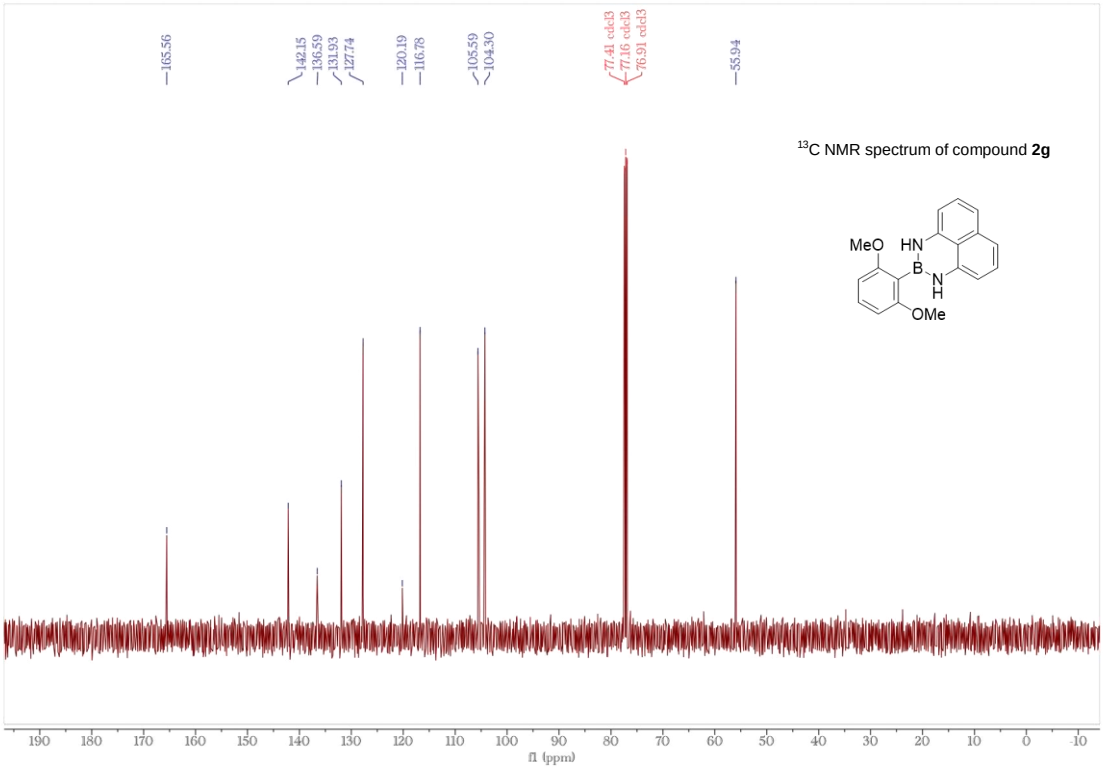
^{1}H NMR spectrum of compound **2f**



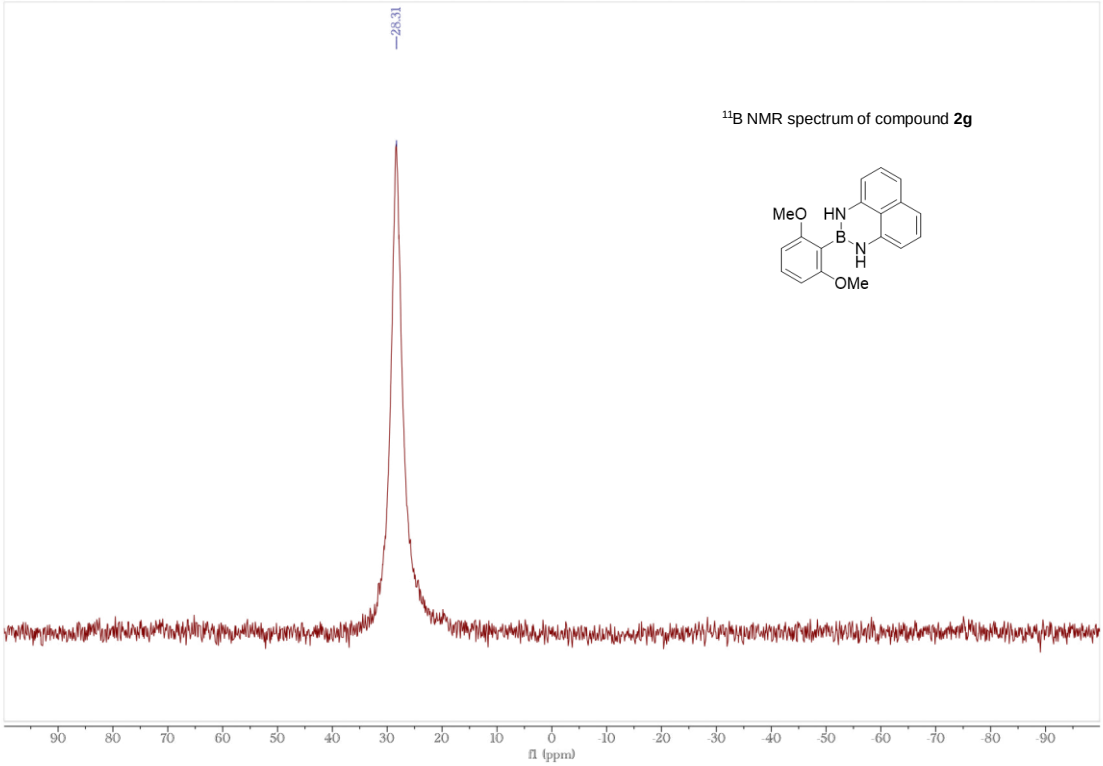
^{13}C NMR spectrum of compound **2f**


29.98
11B NMR spectrum of compound 2f
HN
B
N
H
O
N
f1 (ppm)

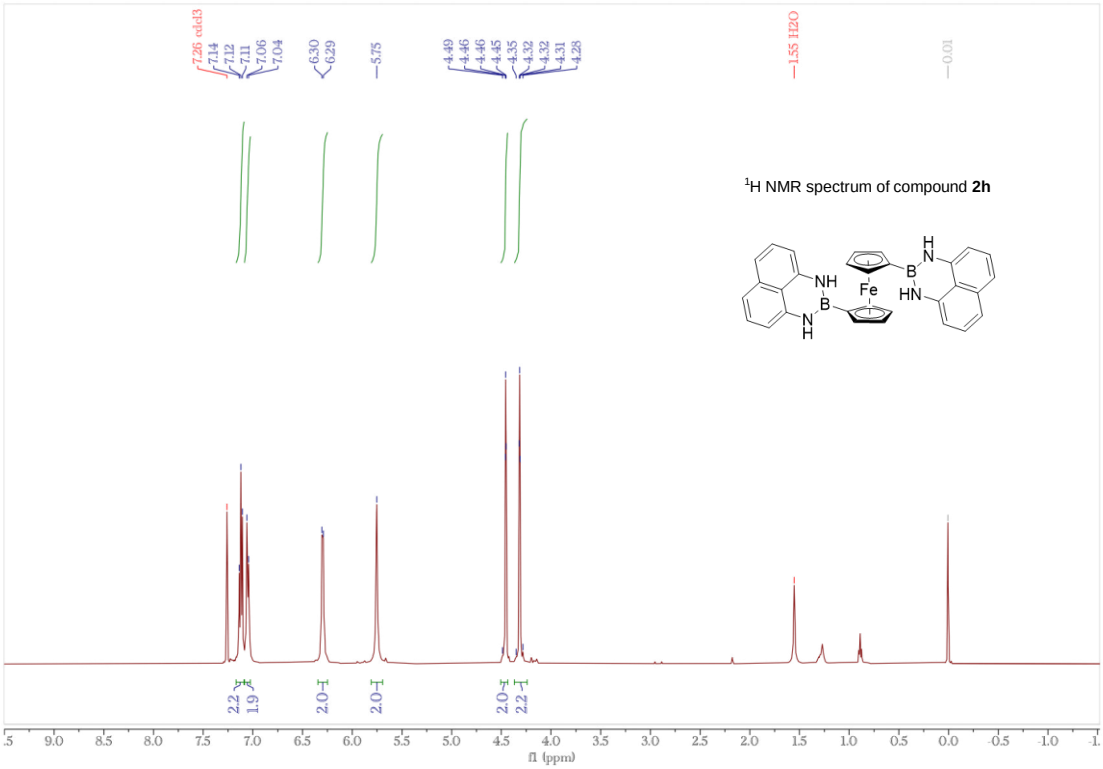

7.36
7.34
7.33
7.26 cdcl3
7.12
7.11
7.10
7.10
7.09
7.09
6.99
6.98
6.98
6.97
6.97
6.63
6.61
6.33
6.33
6.33
6.32
6.32
6.31
3.90
1.55 H2O
0.00
1H NMR spectrum of compound 2g
MeO
HN
B
N
H
OMe
1.0
1.6
2.1
2.0
2.1
2.0
6.1
f1 (ppm)



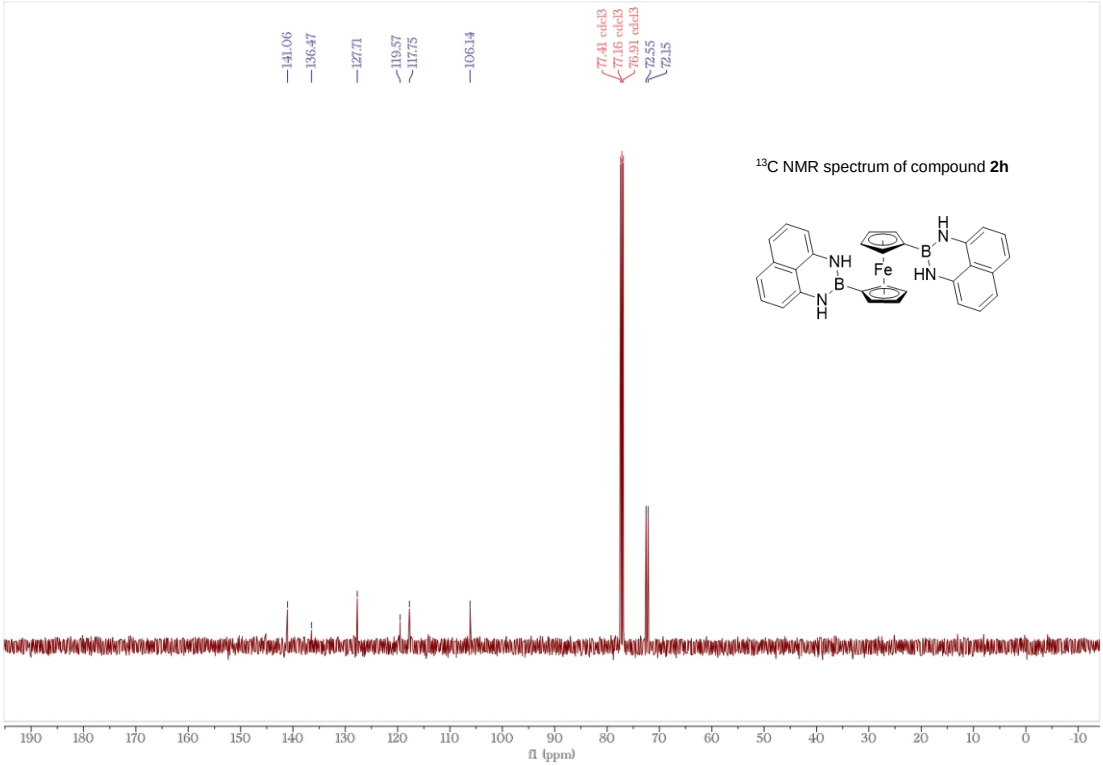
^{13}C NMR spectrum of compound **2g**



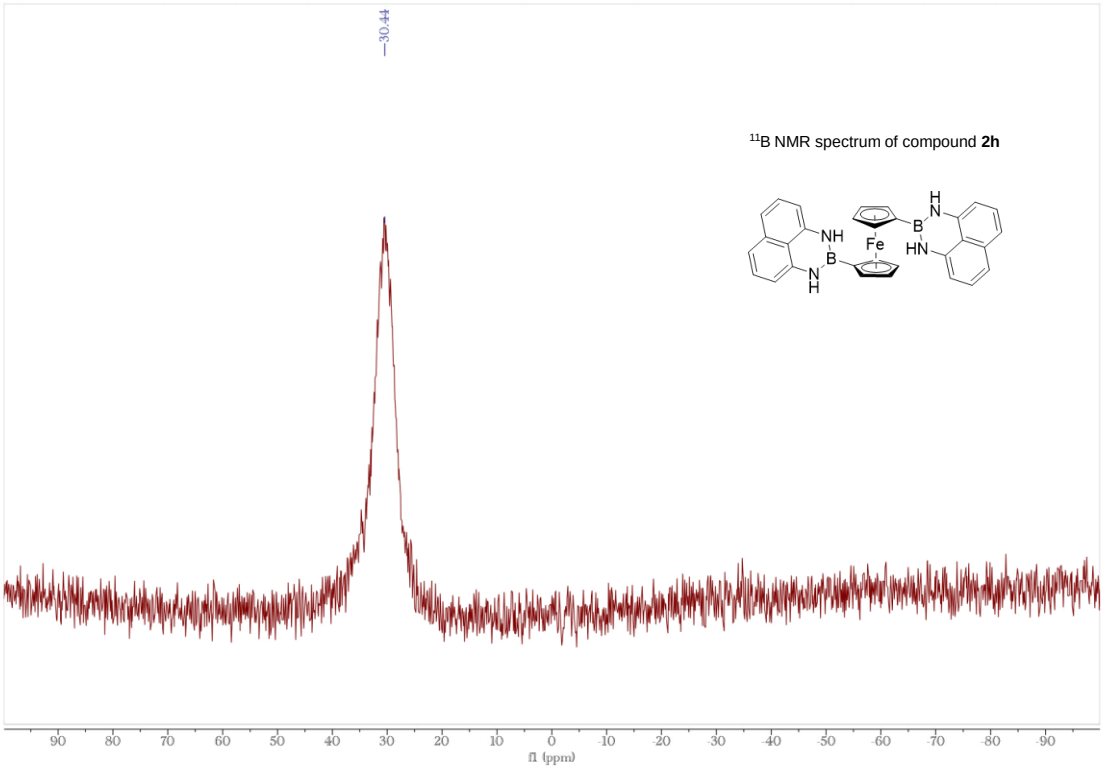
^{11}B NMR spectrum of compound **2g**

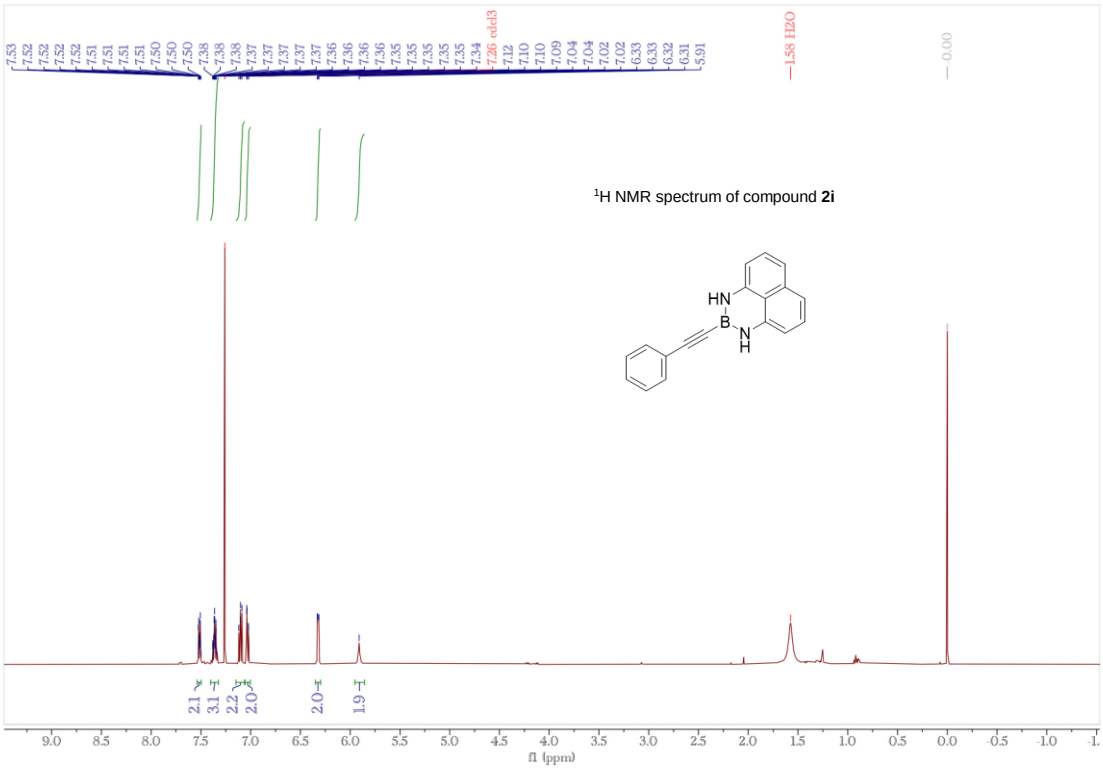


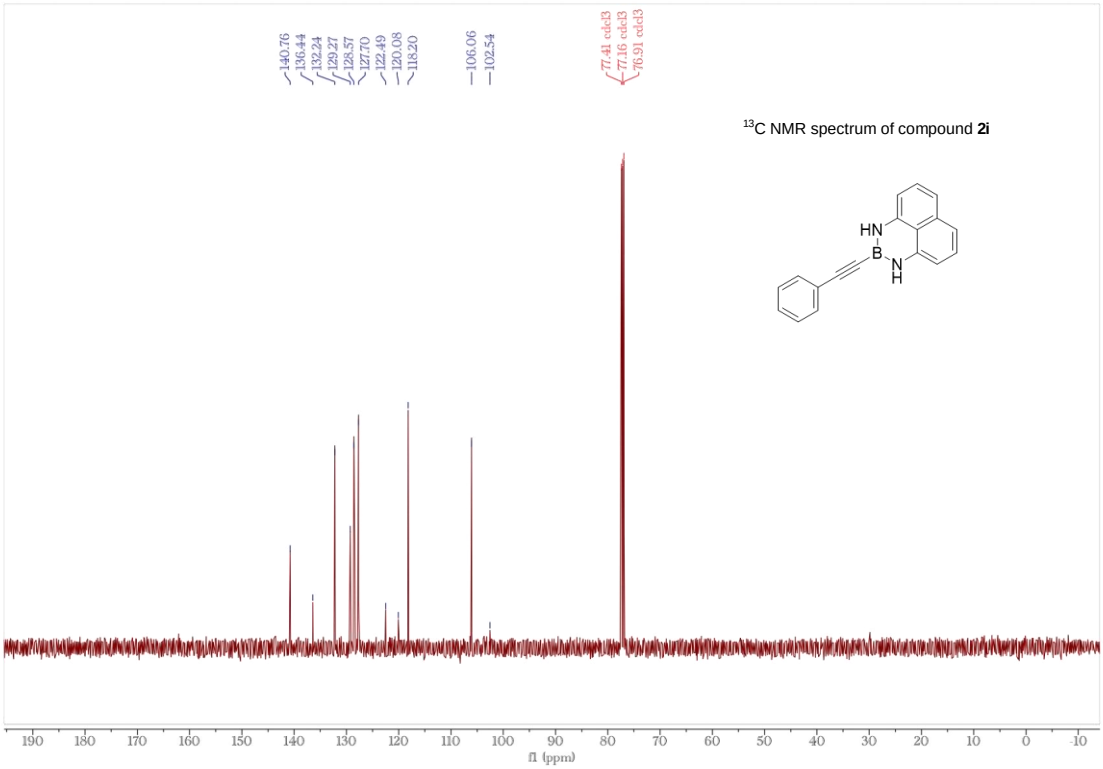
^{1}H NMR spectrum of compound **2h**



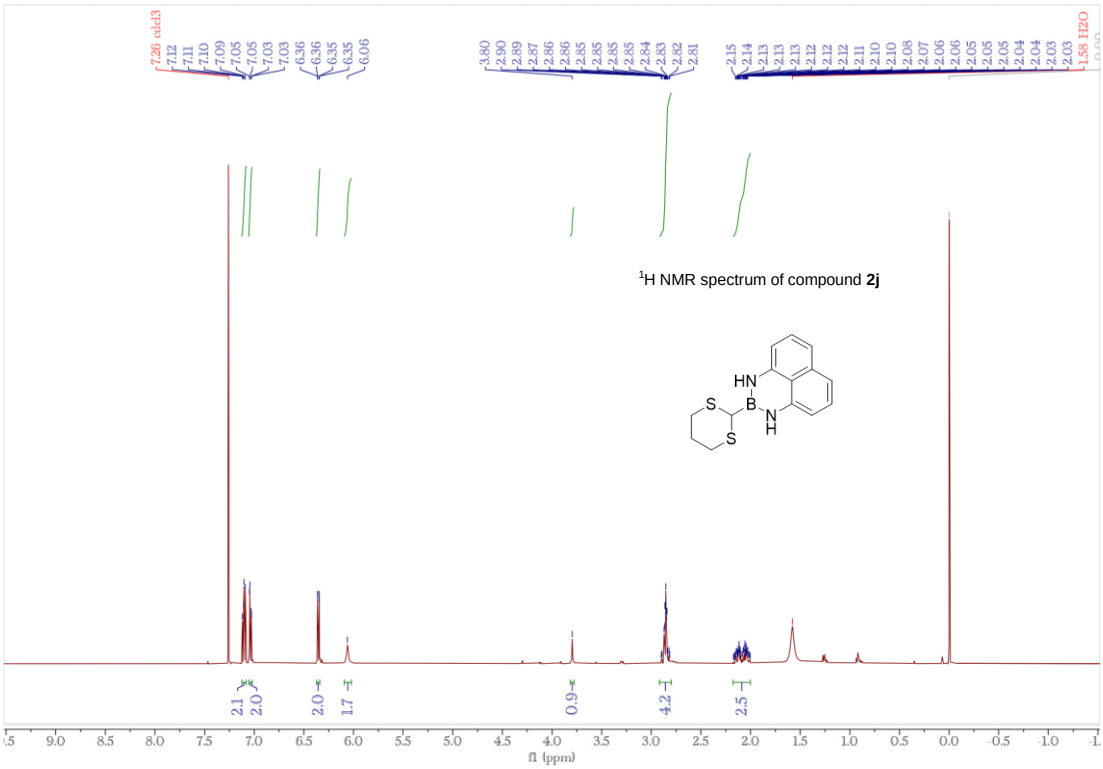
^{13}C NMR spectrum of compound **2h**


30.44
11B NMR spectrum of compound 2h
NH
B
N
H
Fe
B
HN
H
N
f1 (ppm)

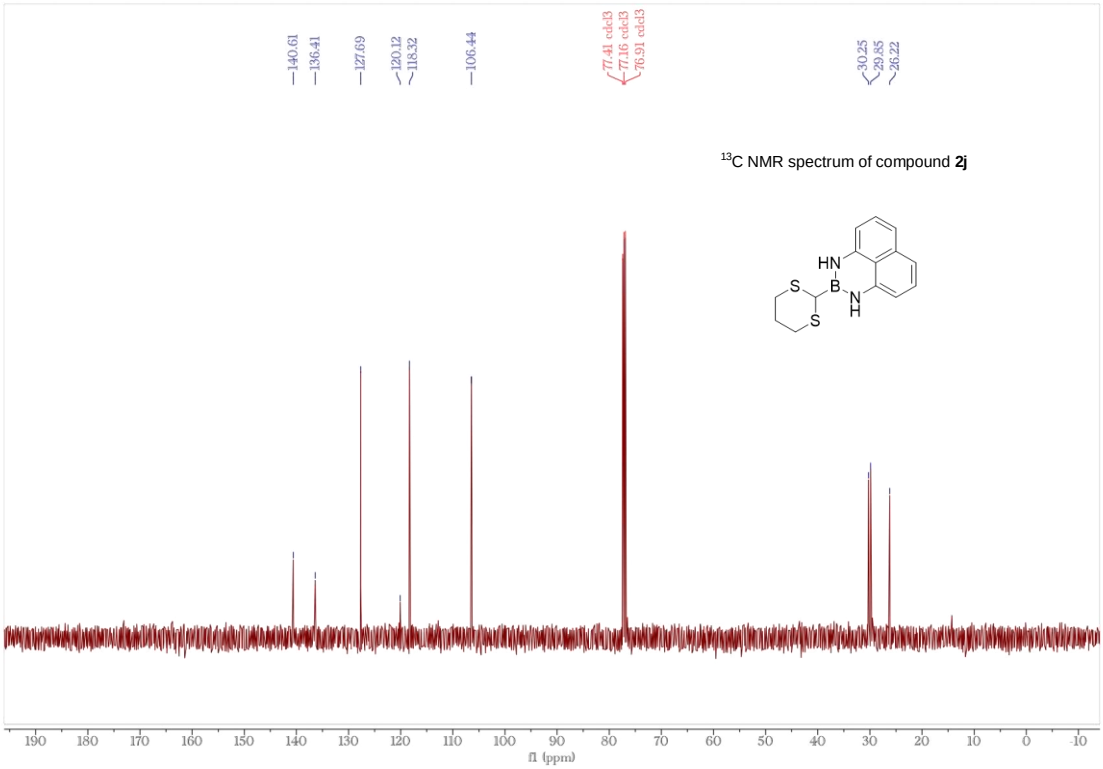

1.58 H2O
0.00
1H NMR spectrum of compound 2i
HN
B
N
H
2.1
3.1
2.2
2.0
2.0
1.9
f1 (ppm)



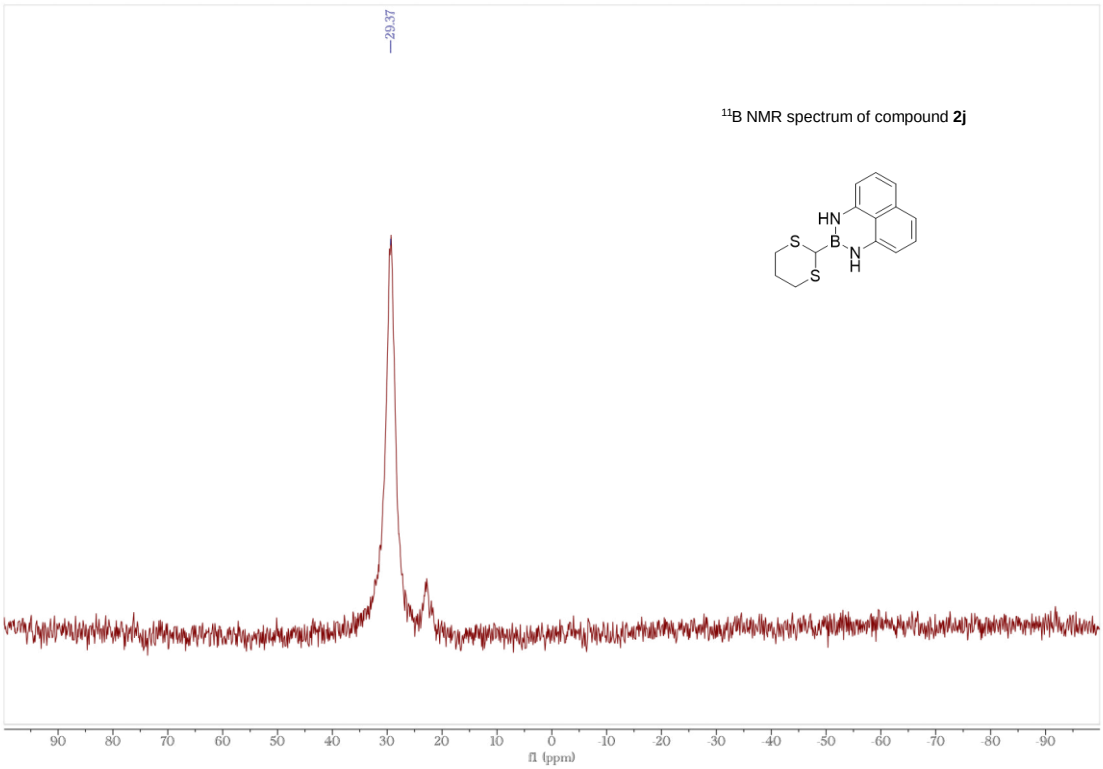
^{13}C NMR spectrum of compound **2i**



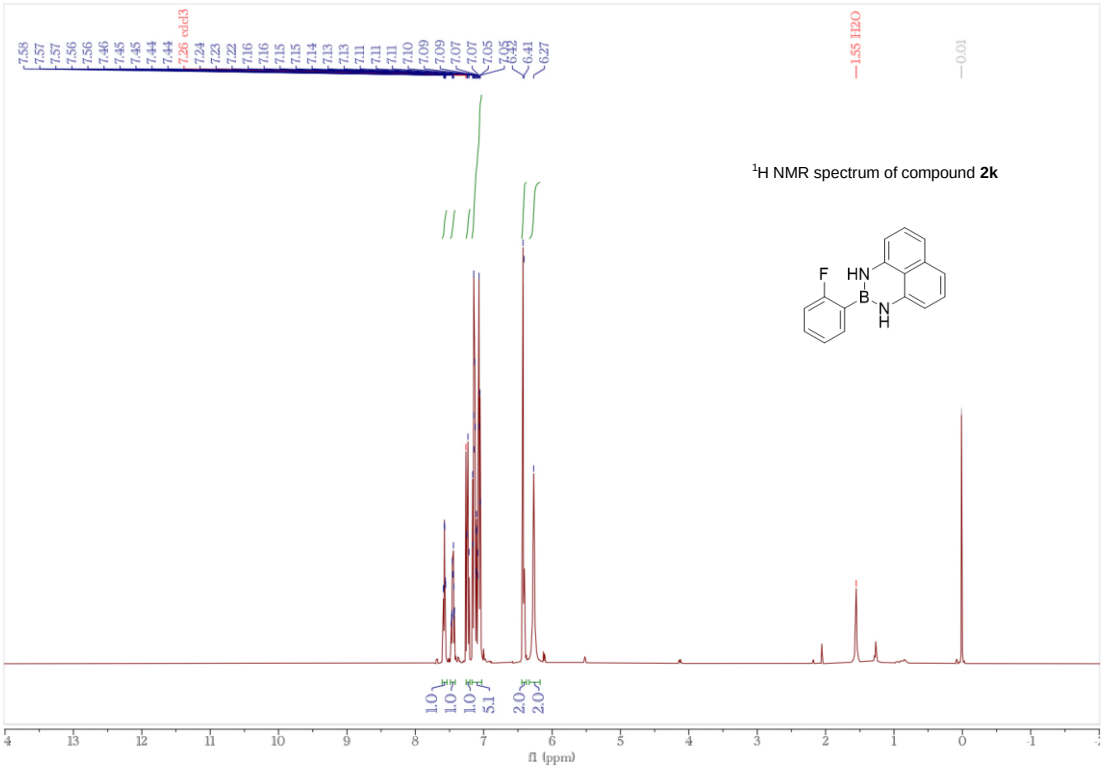
^{1}H NMR spectrum of compound **2j**



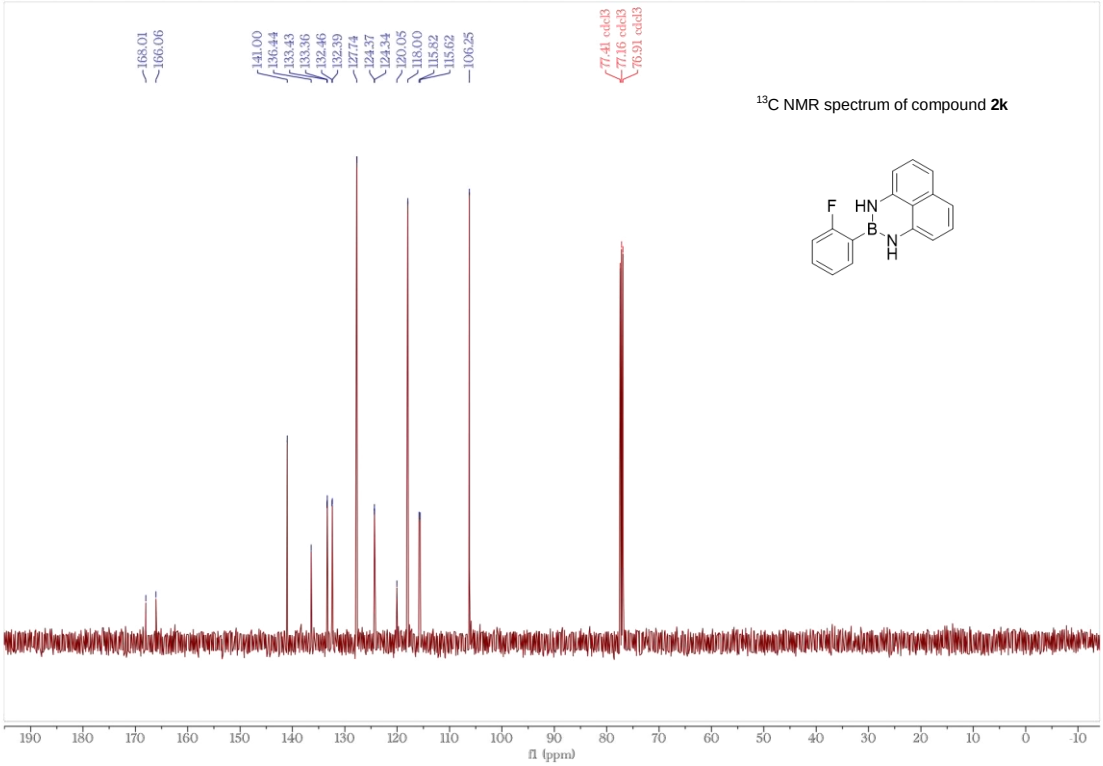
^{13}C NMR spectrum of compound **2j**



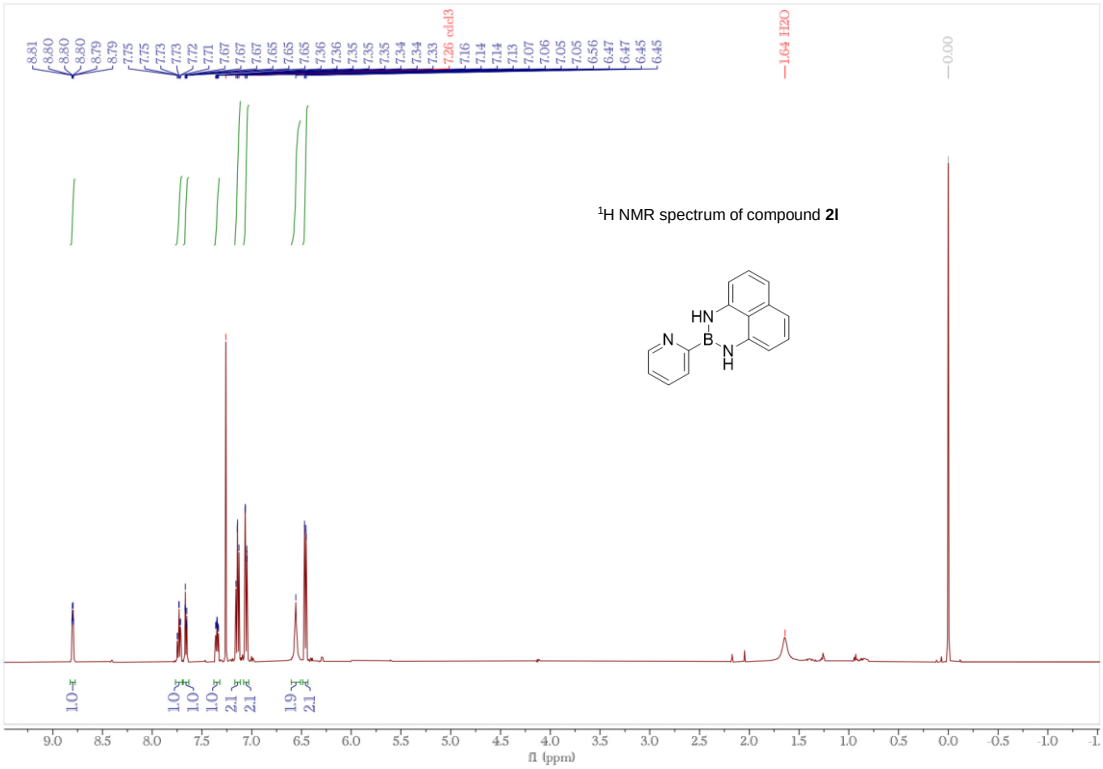
^{11}B NMR spectrum of compound **2j**



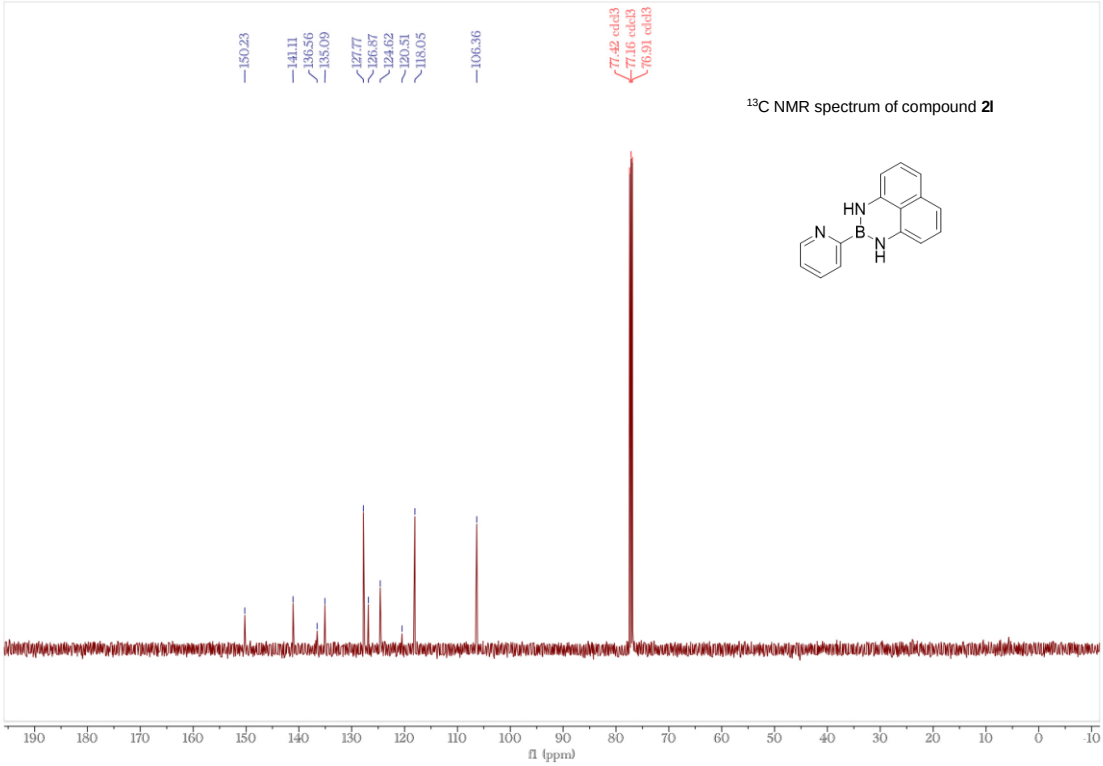
^{1}H NMR spectrum of compound **2k**



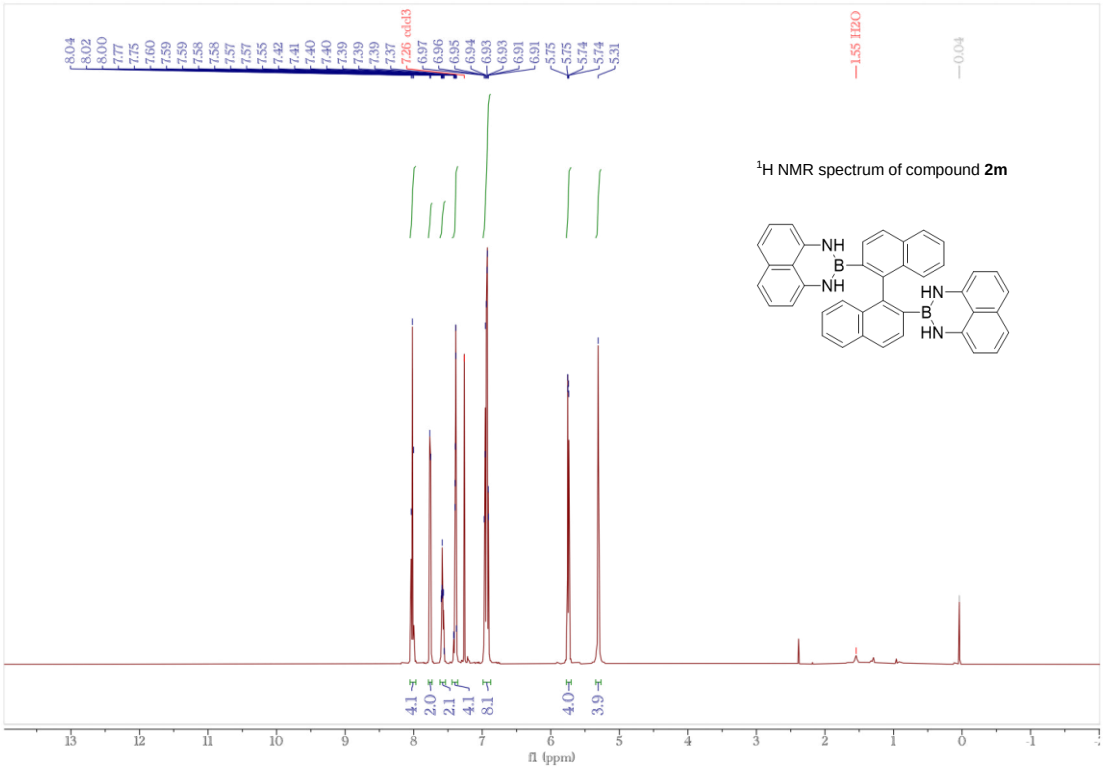
^{13}C NMR spectrum of compound **2k**



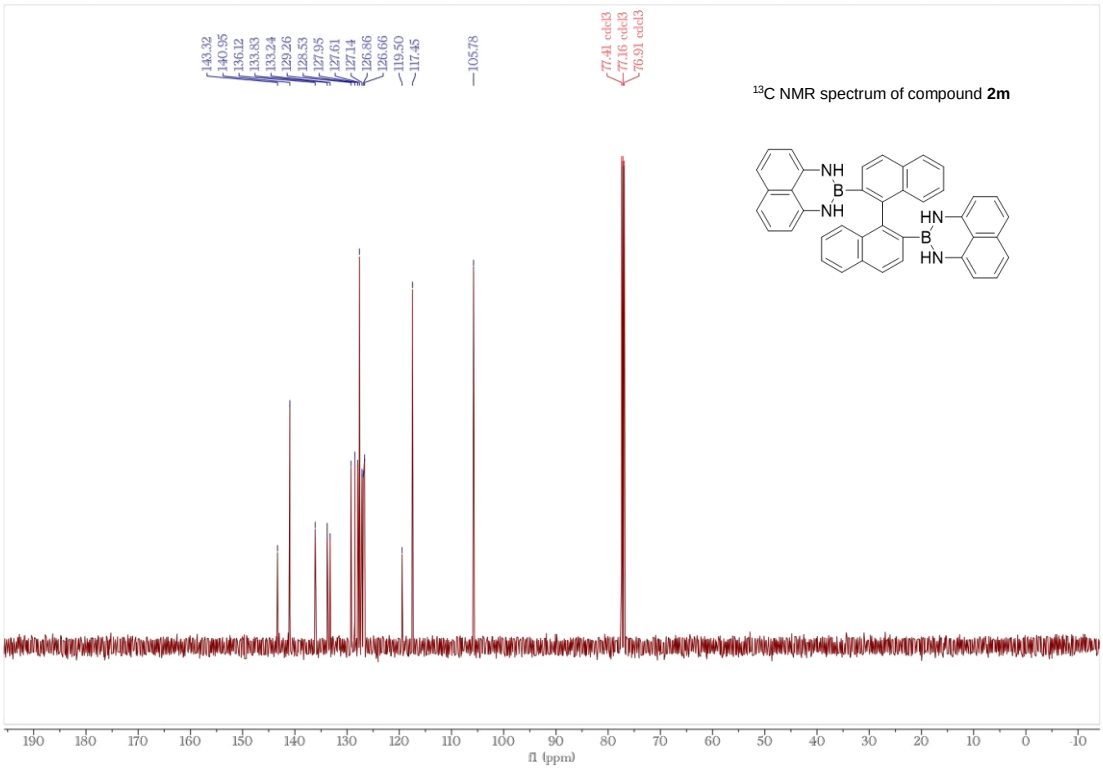
^{1}H NMR spectrum of compound **2l**



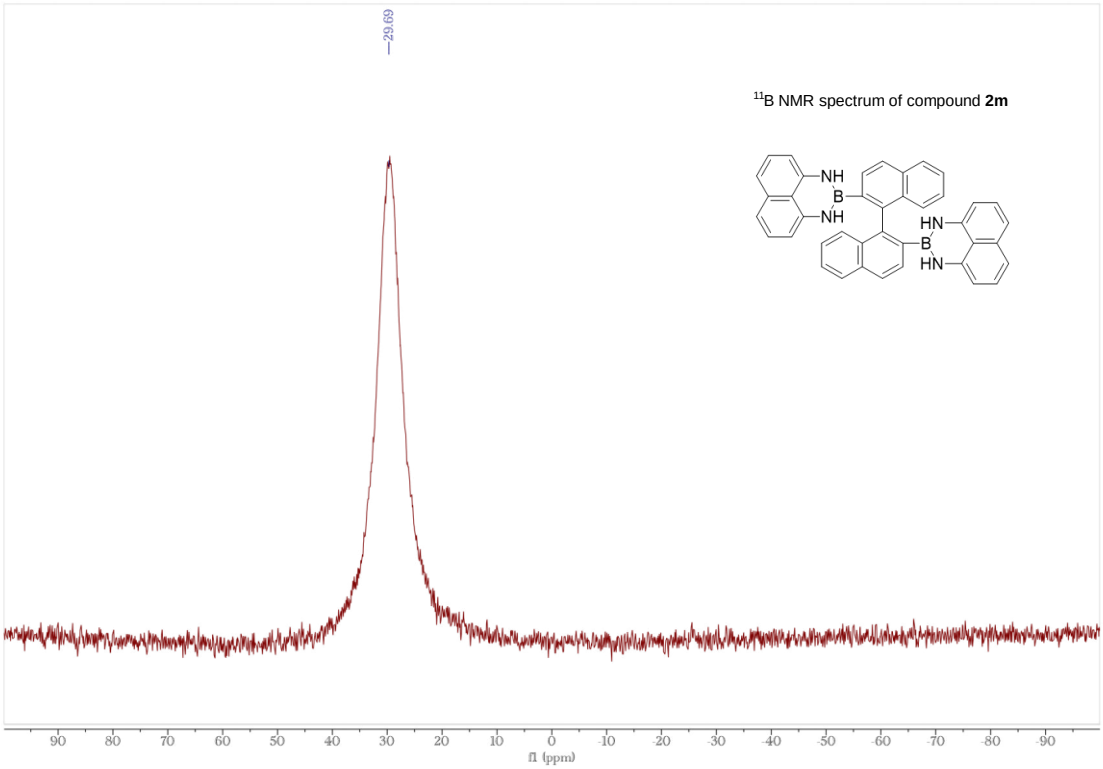
^{13}C NMR spectrum of compound **2l**



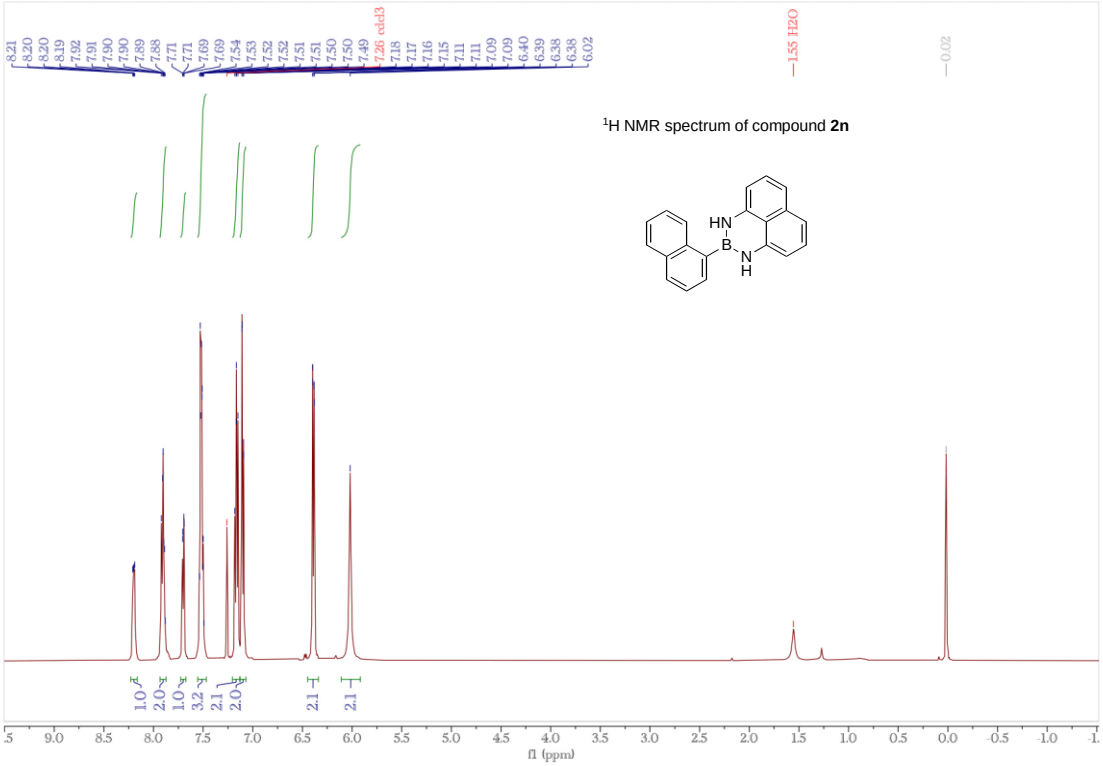
^{1}H NMR spectrum of compound **2m**



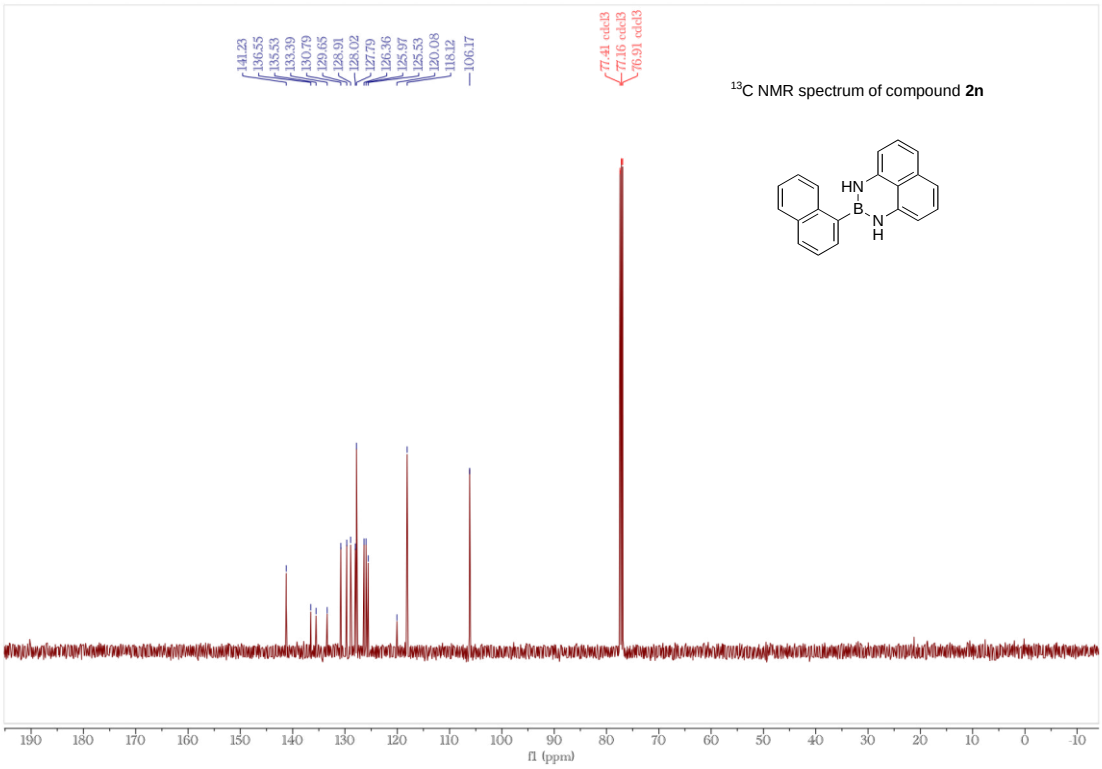
^{13}C NMR spectrum of compound **2m**



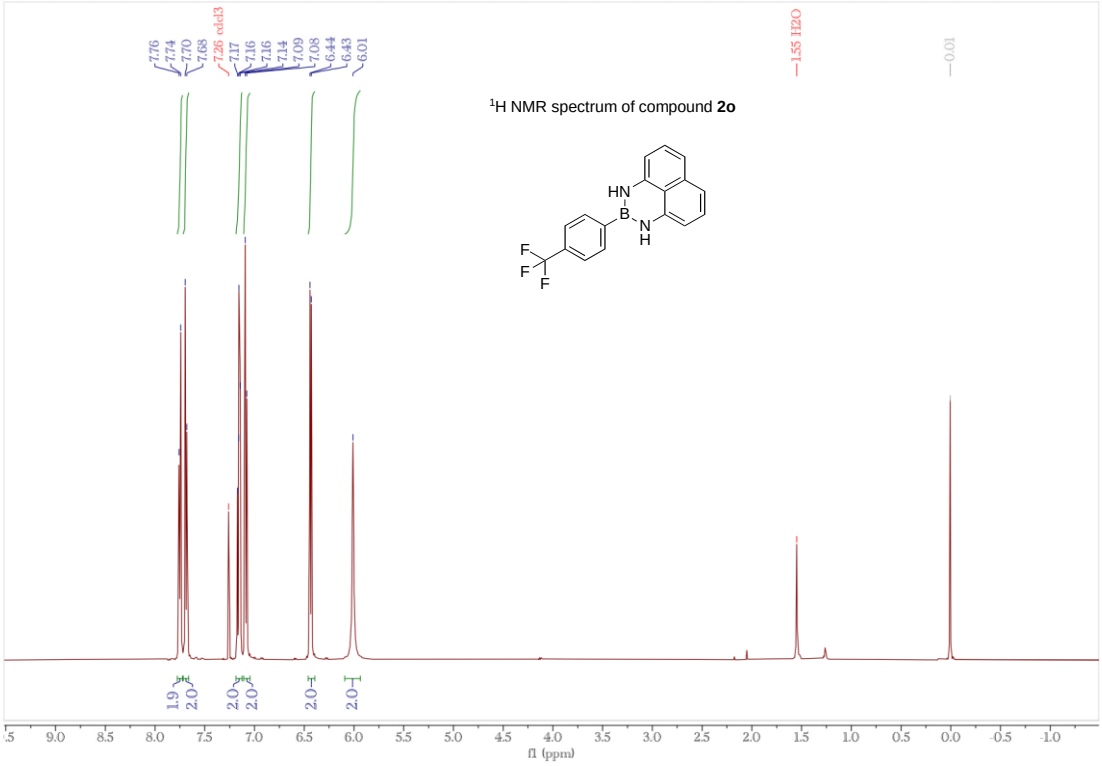
^{11}B NMR spectrum of compound **2m**



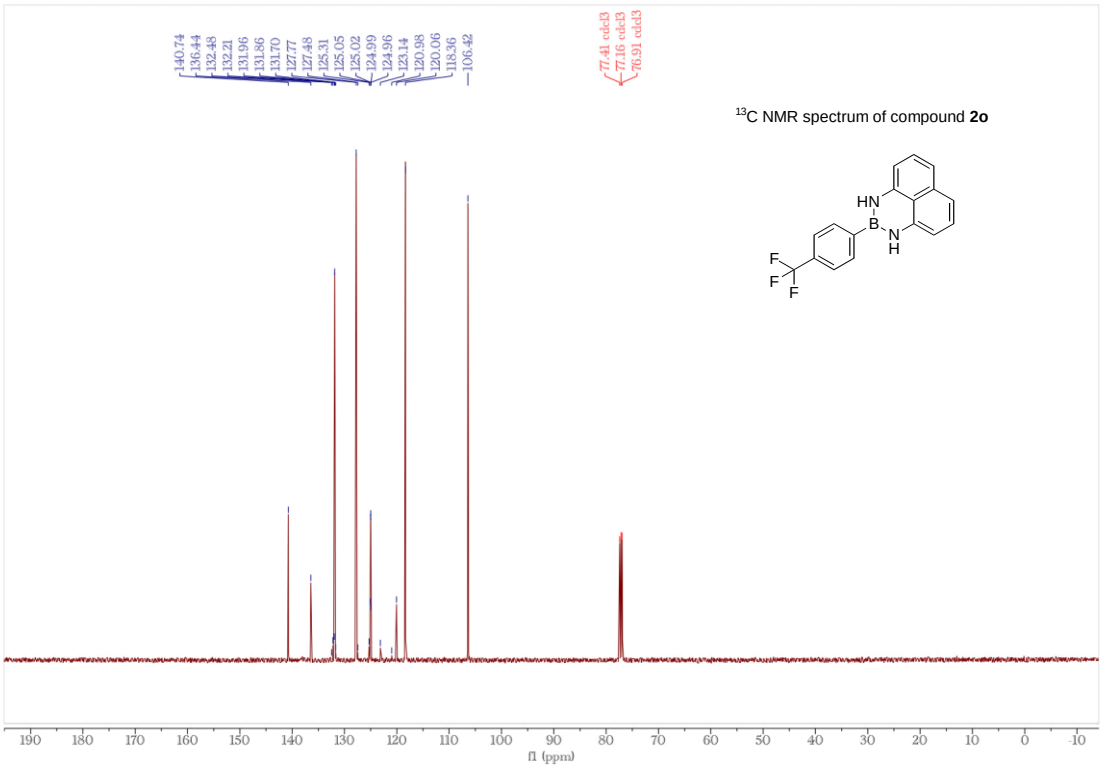
^{1}H NMR spectrum of compound **2n**



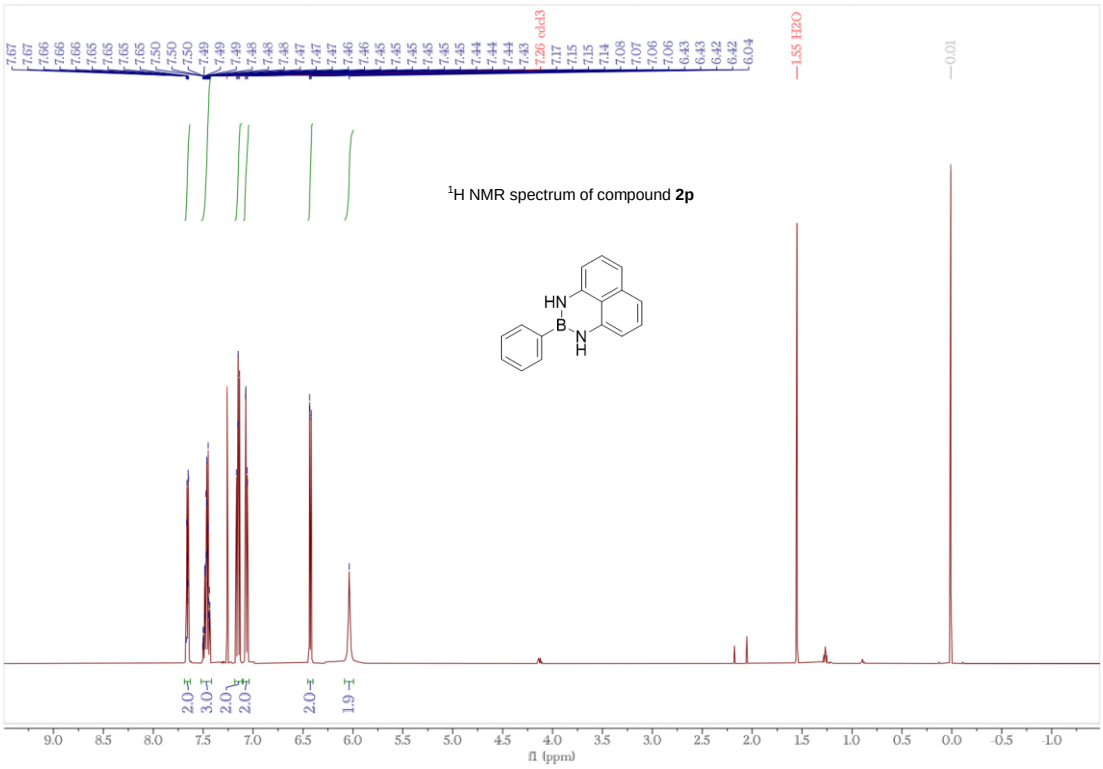
^{13}C NMR spectrum of compound **2n**



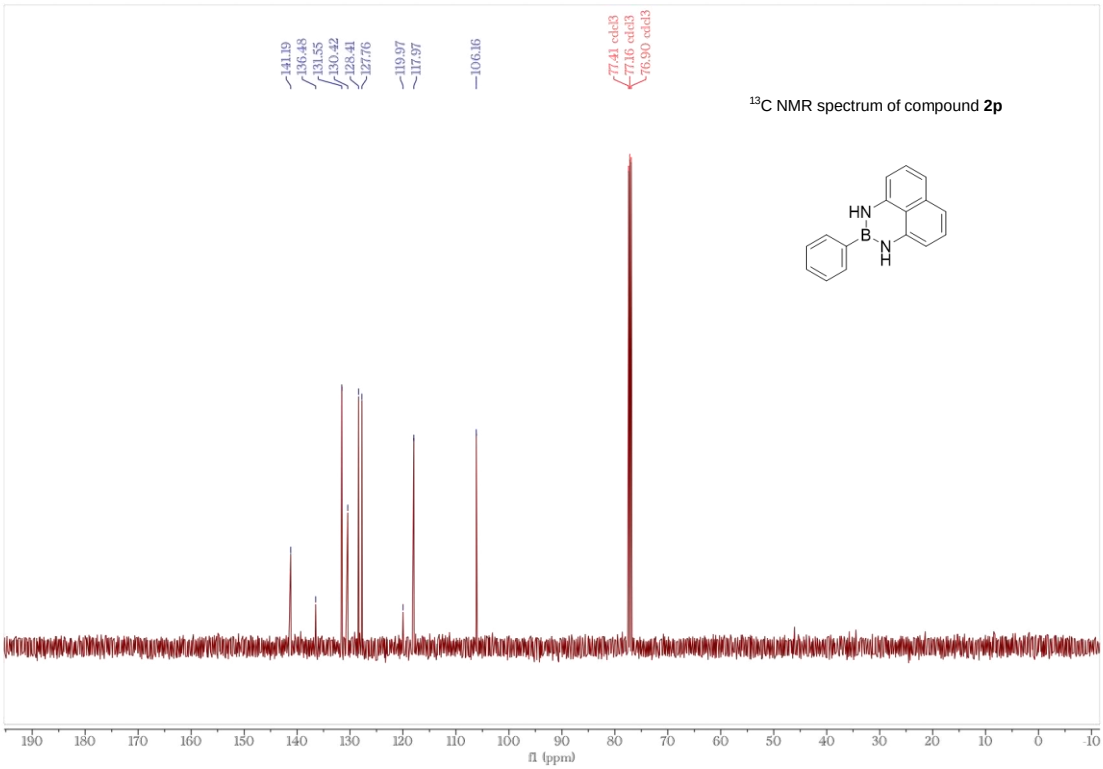
^{1}H NMR spectrum of compound **2o**



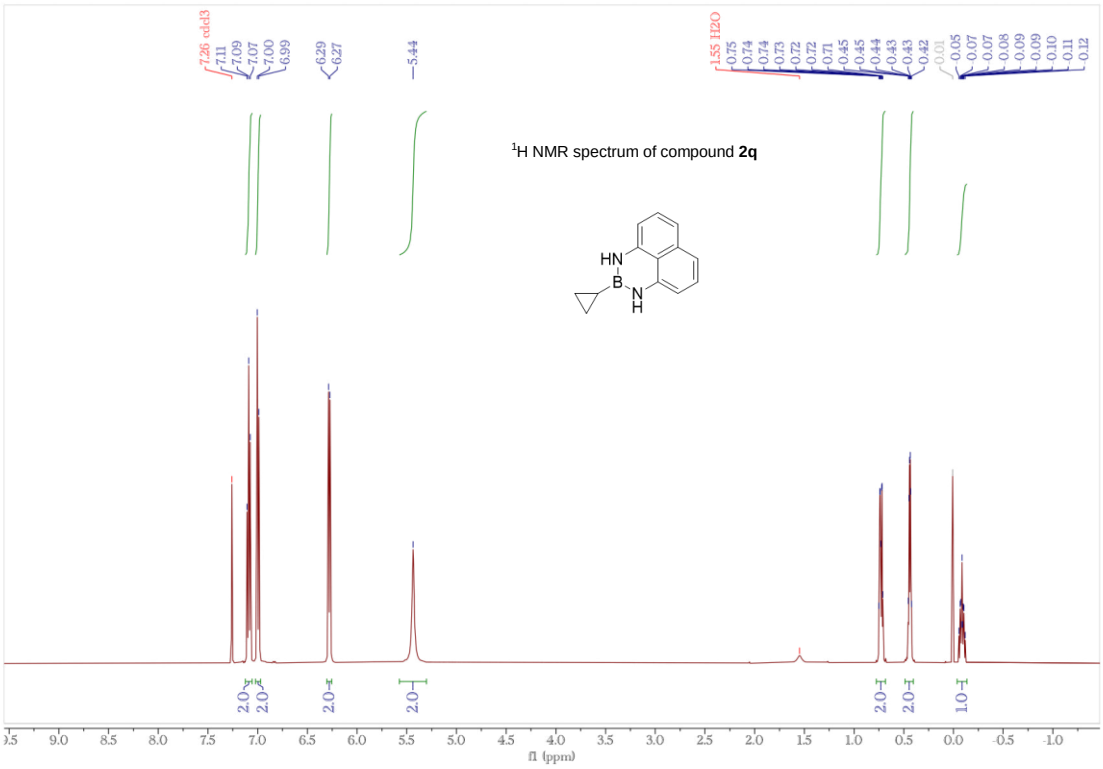
^{13}C NMR spectrum of compound **2o**



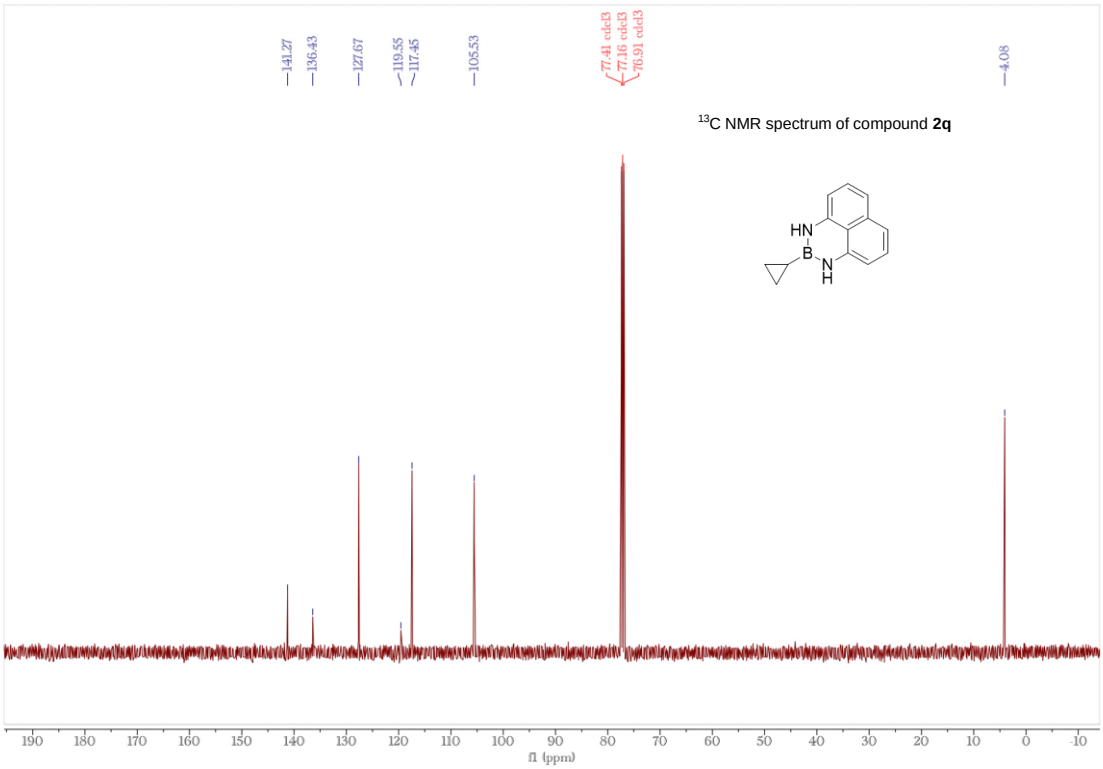
^{1}H NMR spectrum of compound **2p**



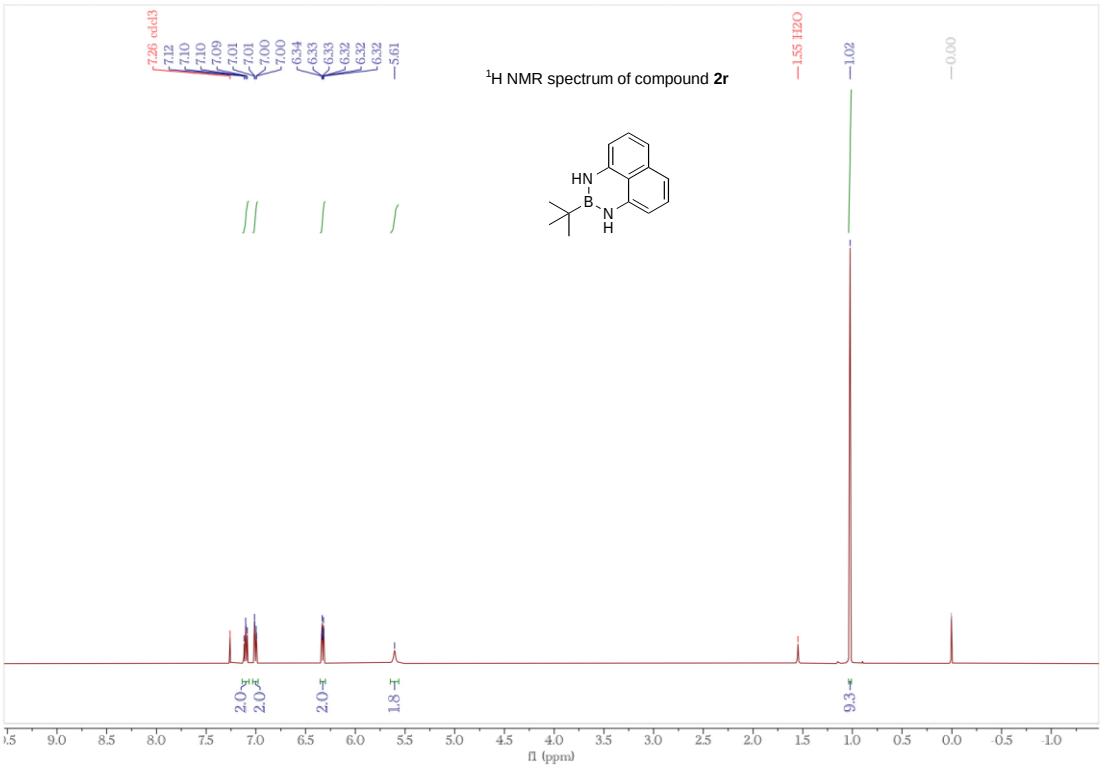
^{13}C NMR spectrum of compound **2p**



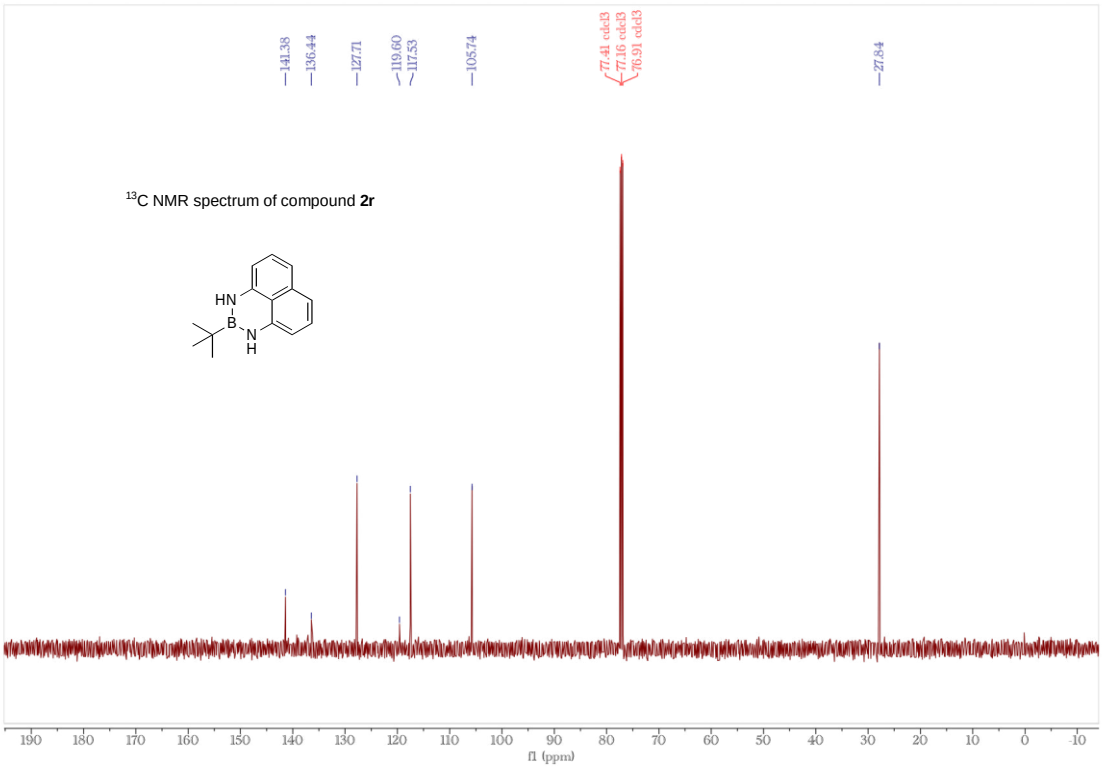
^{1}H NMR spectrum of compound **2q**



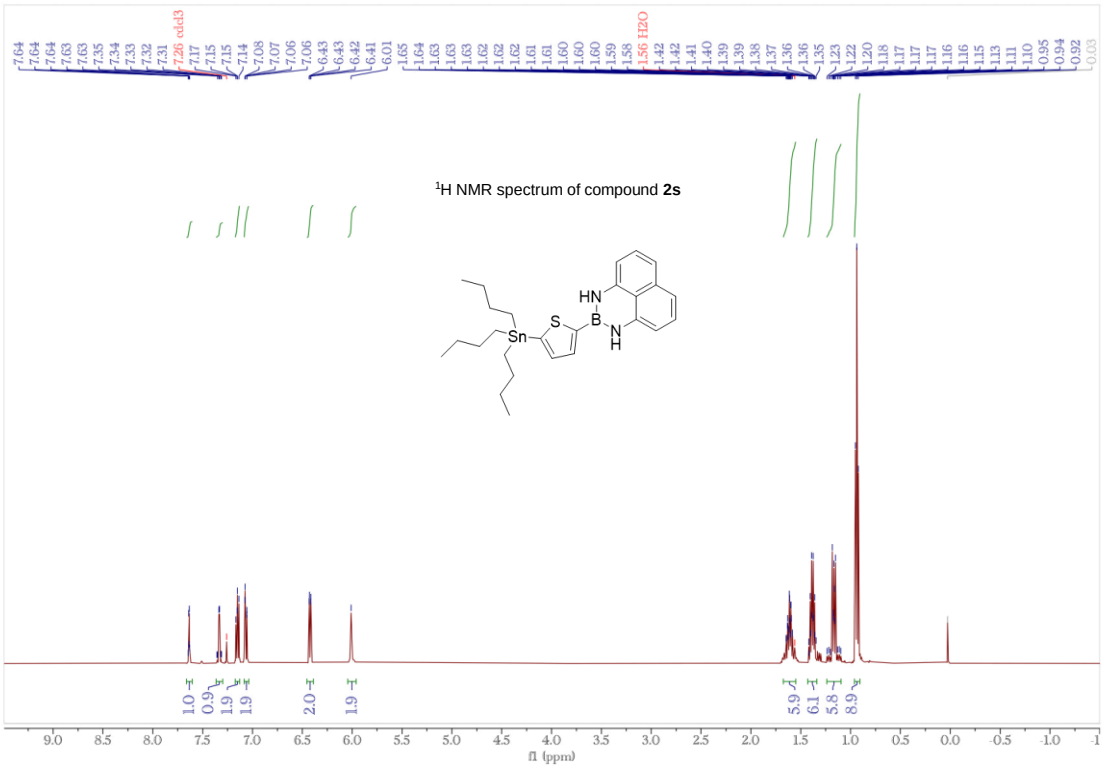
^{13}C NMR spectrum of compound **2q**



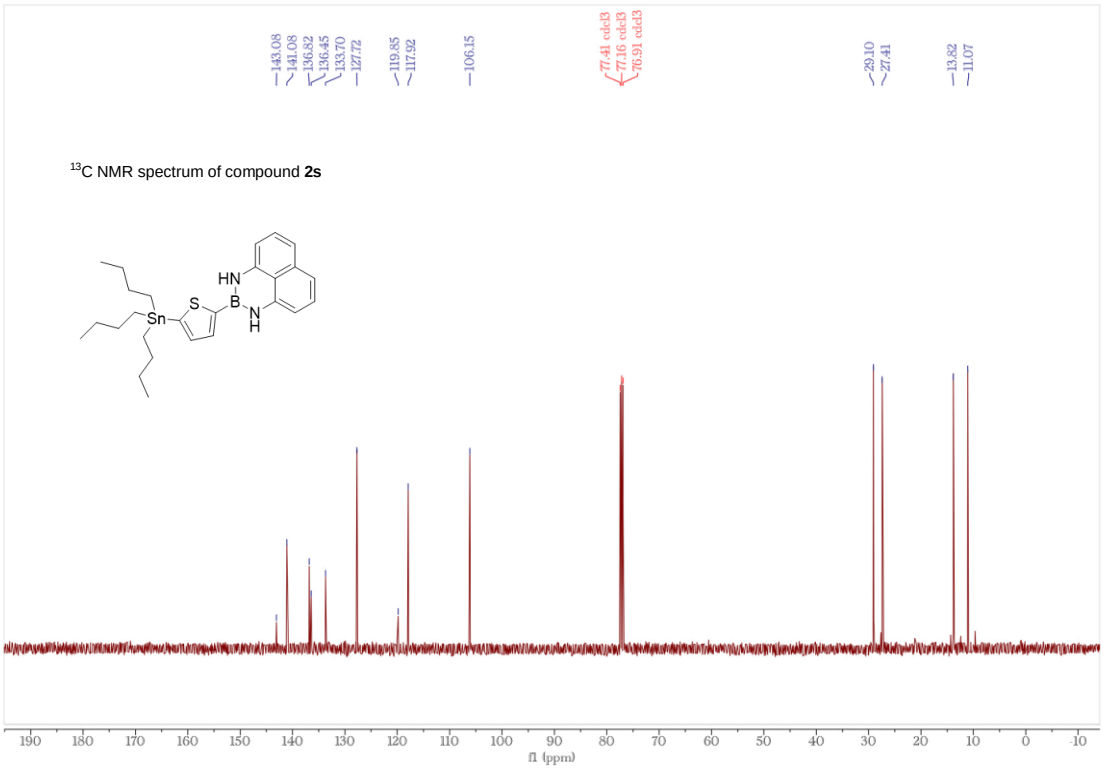
^{1}H NMR spectrum of compound **2r**



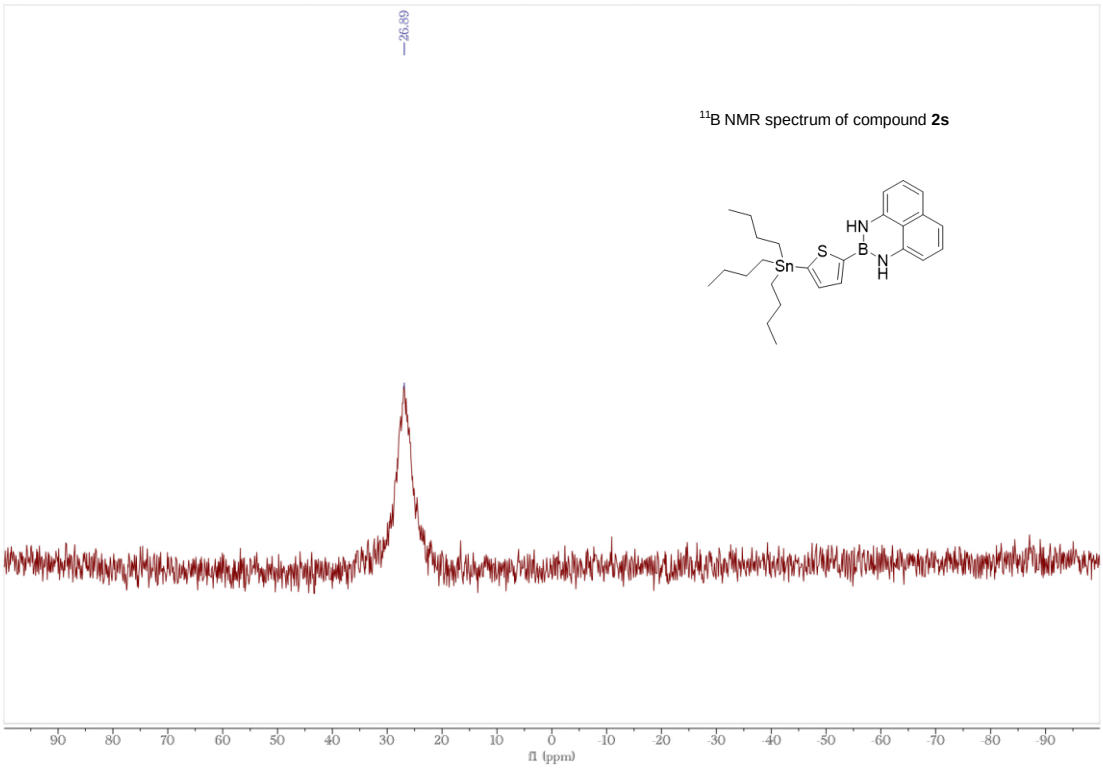
^{13}C NMR spectrum of compound **2r**



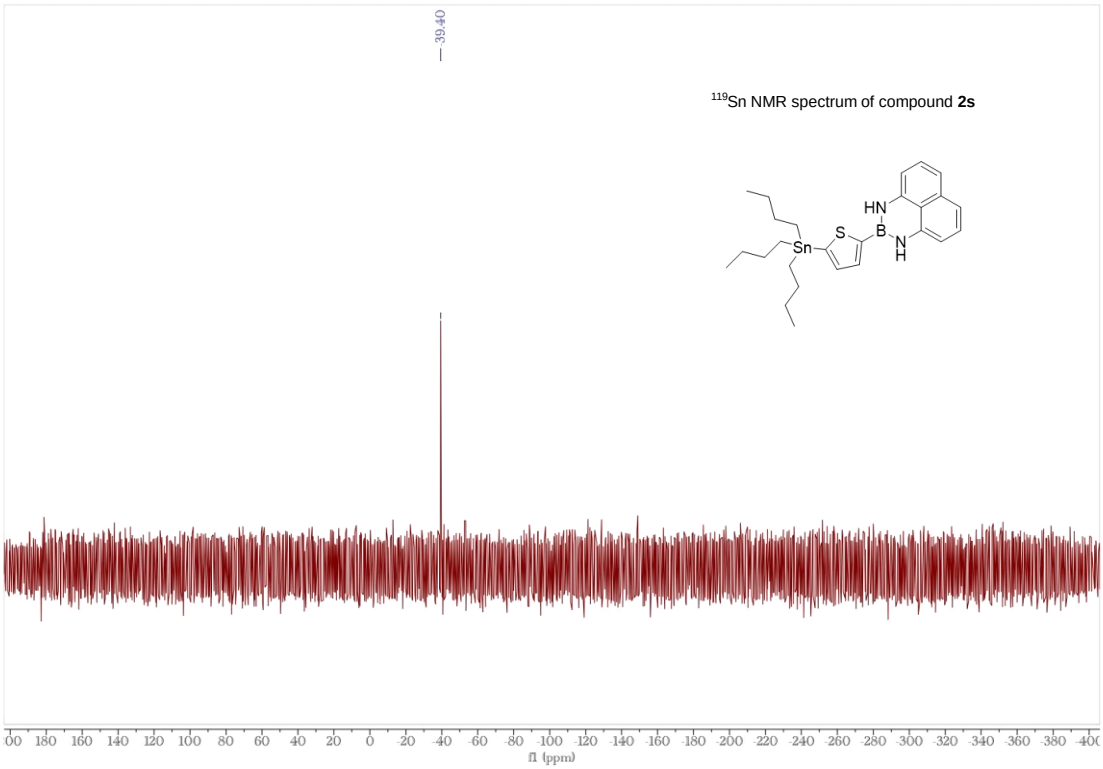
^{1}H NMR spectrum of compound **2s**

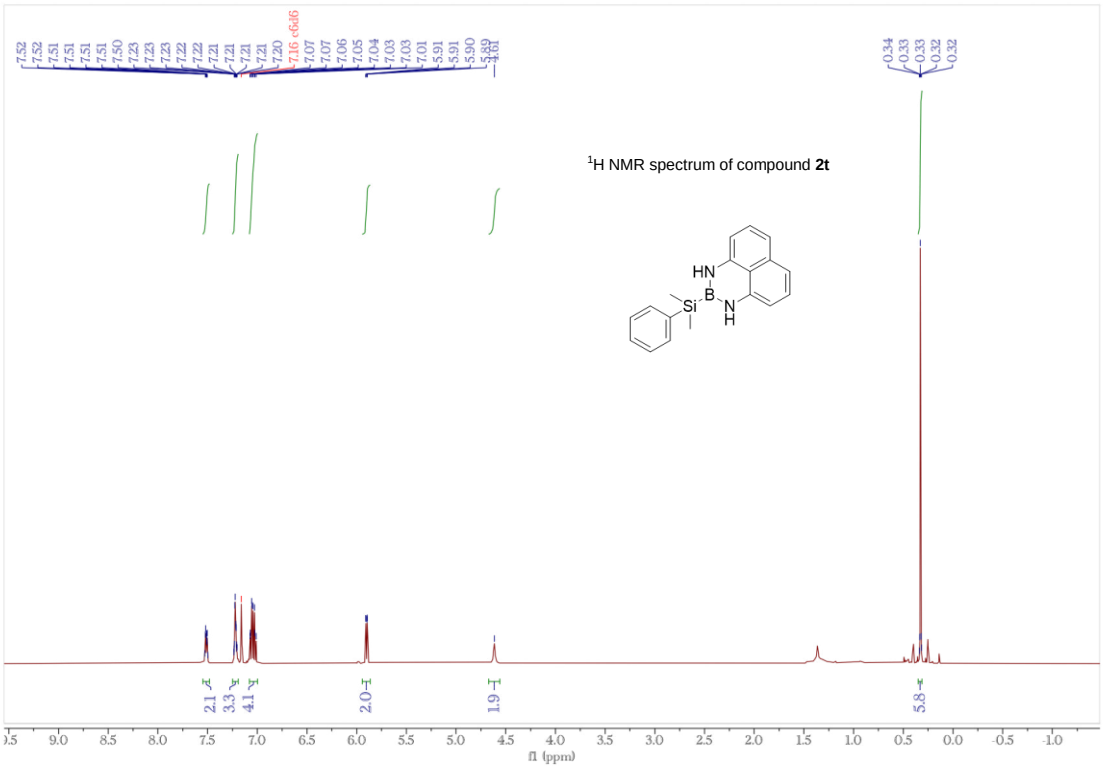


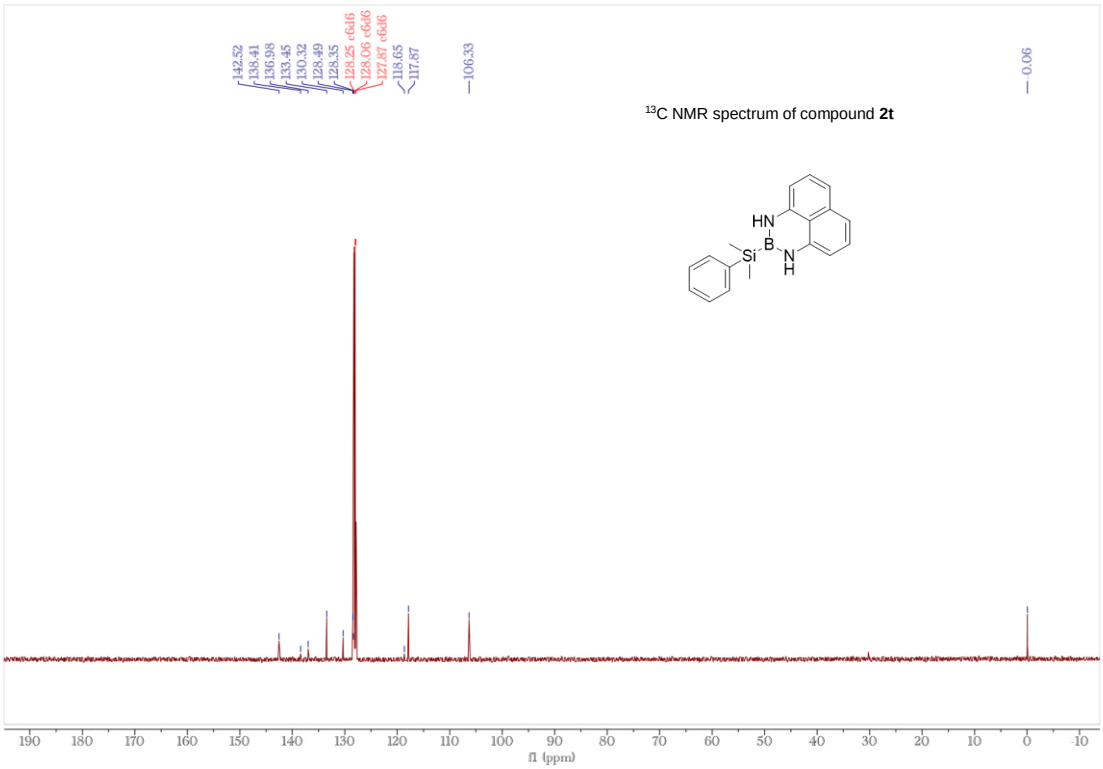
^{13}C NMR spectrum of compound **2s**



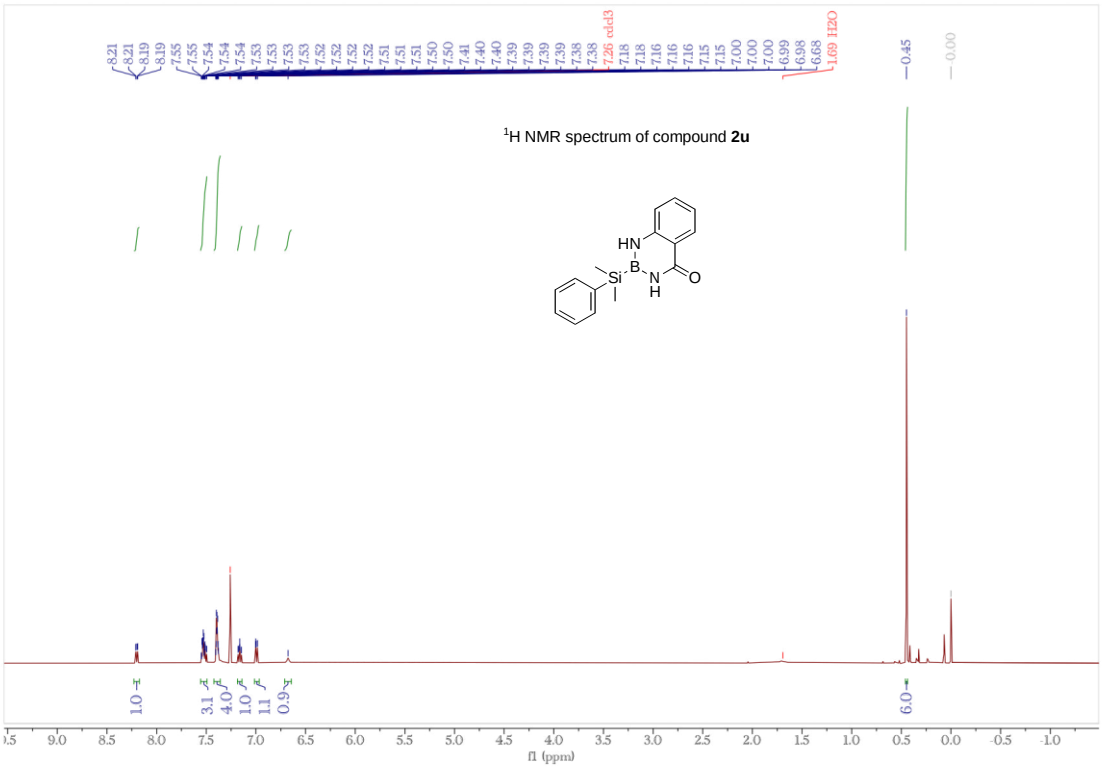
^{11}B NMR spectrum of compound **2s**


39.40
^{119}Sn NMR spectrum of compound **2s**
HN
B
N
H
S
Sn
f1 (ppm)

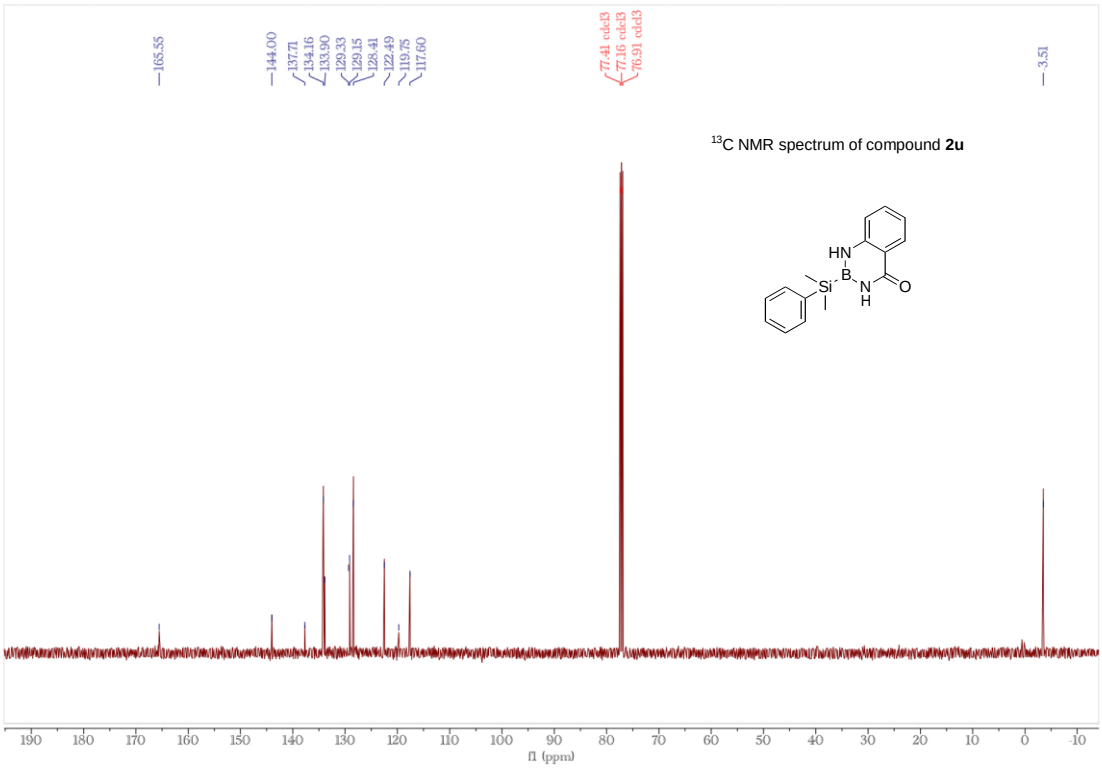

7.16 c6d6
^{1}H NMR spectrum of compound **2t**
HN
B
N
H
Si
2.1
3.3
4.1
2.0
1.9
5.8
f1 (ppm)



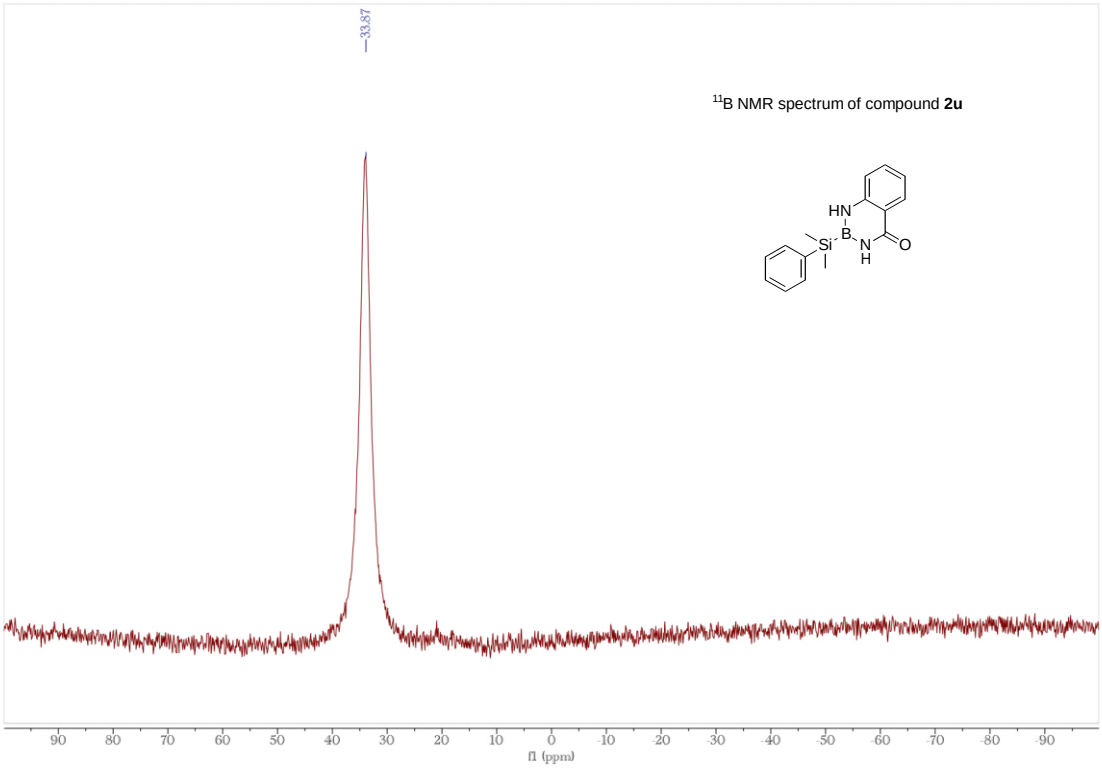
^{13}C NMR spectrum of compound **2t**



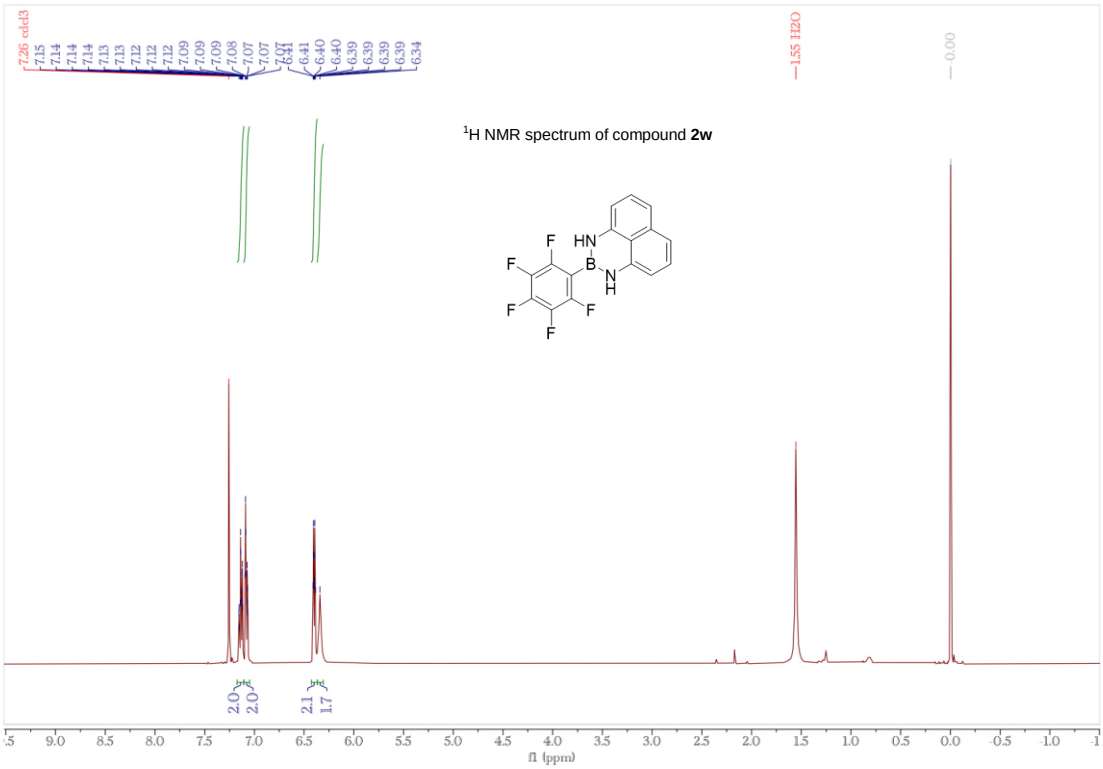
^{1}H NMR spectrum of compound **2u**



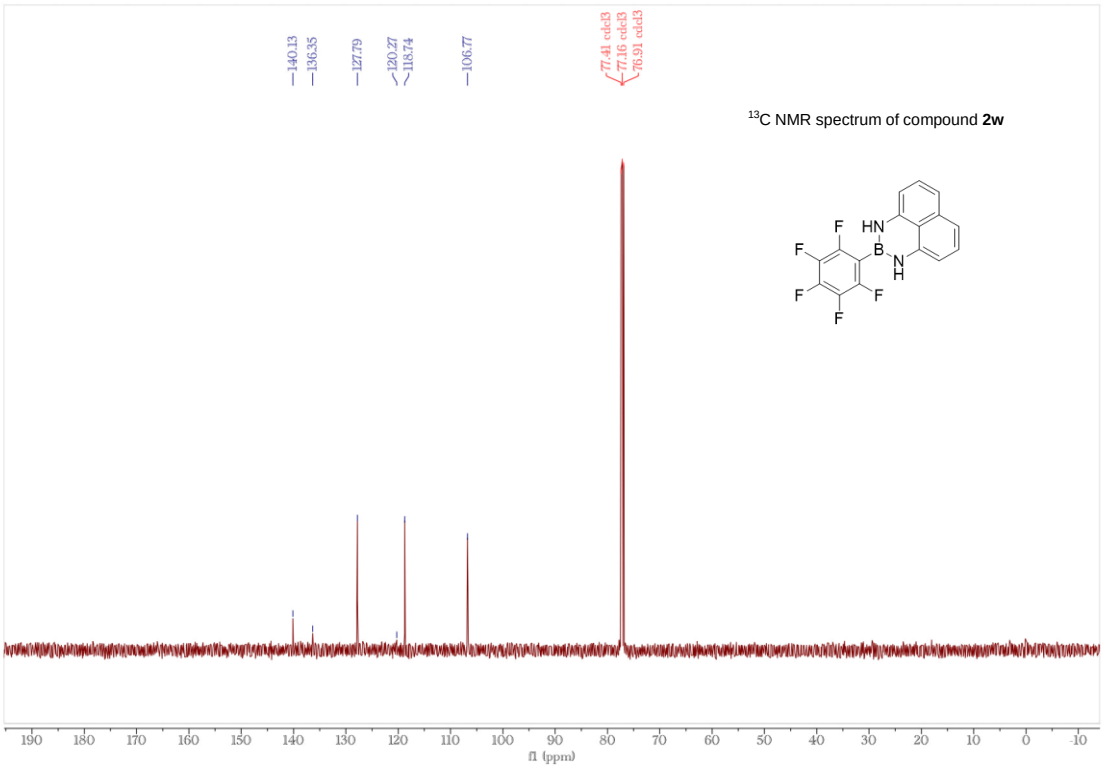
^{13}C NMR spectrum of compound **2u**



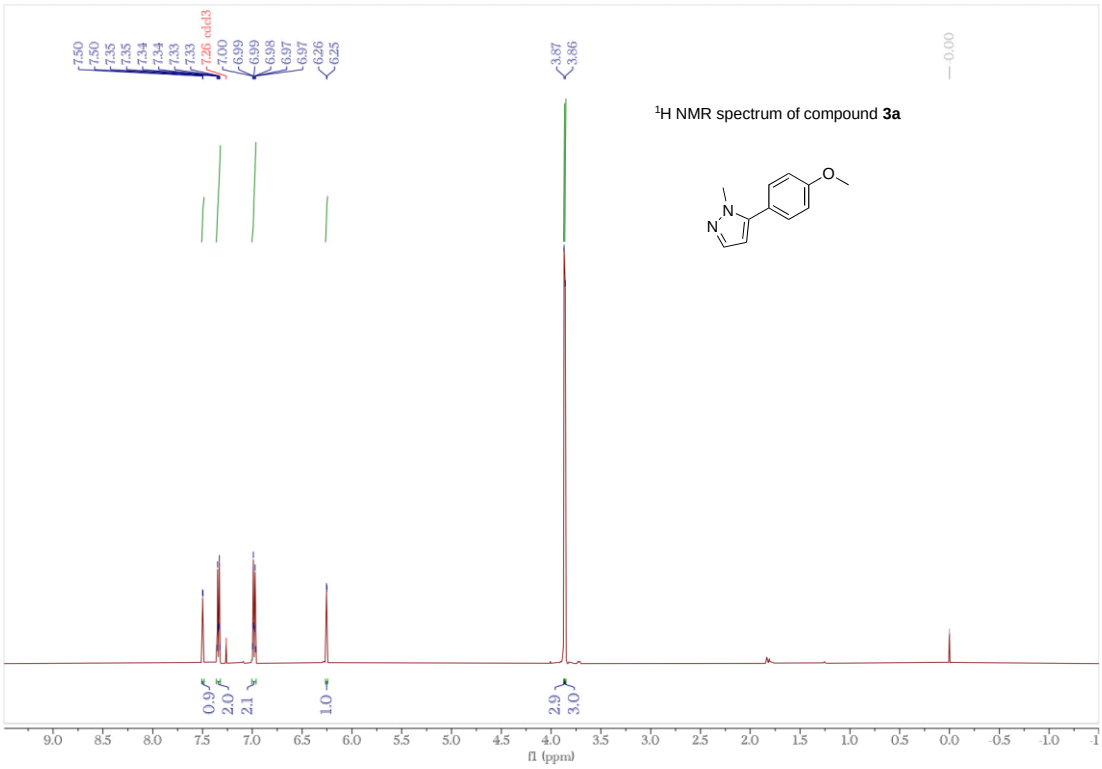
^{11}B NMR spectrum of compound **2u**



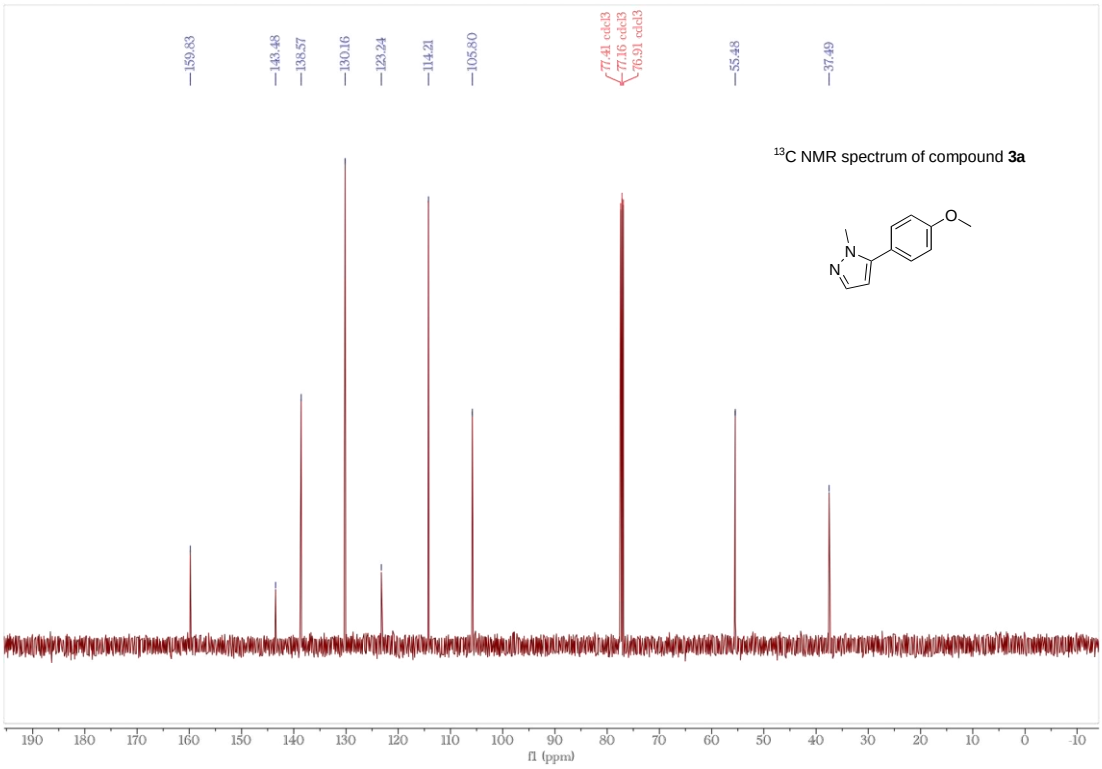
^{1}H NMR spectrum of compound **2w**



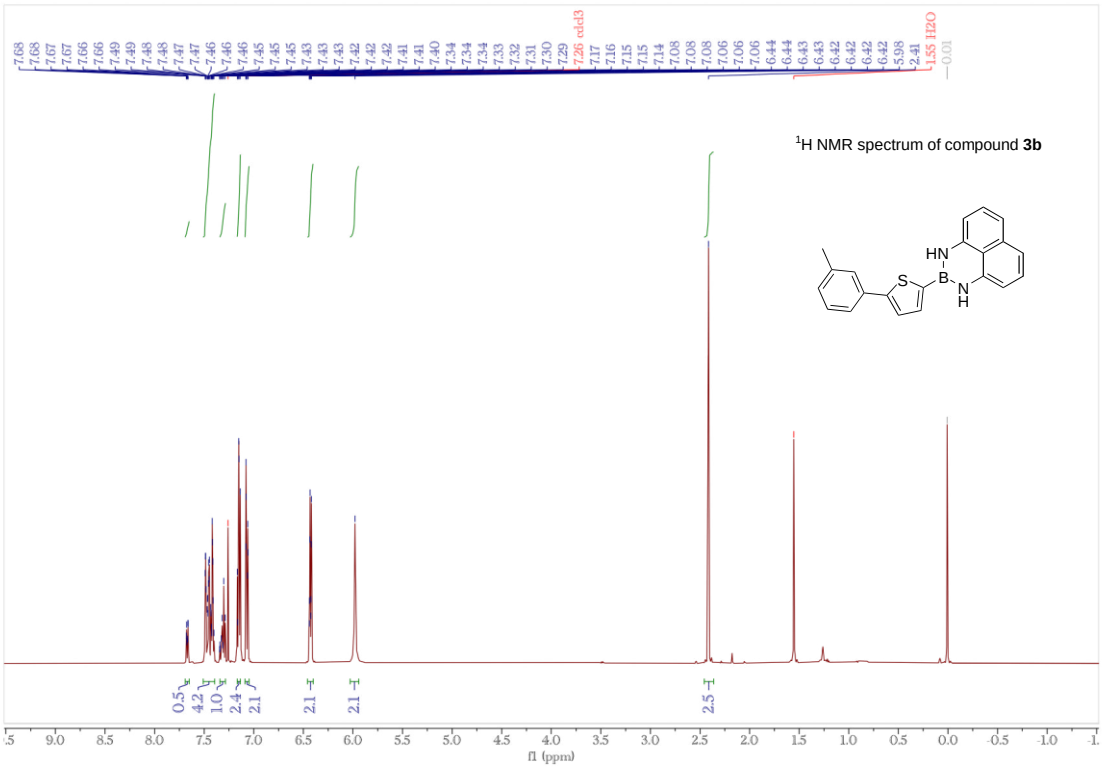
^{13}C NMR spectrum of compound **2w**



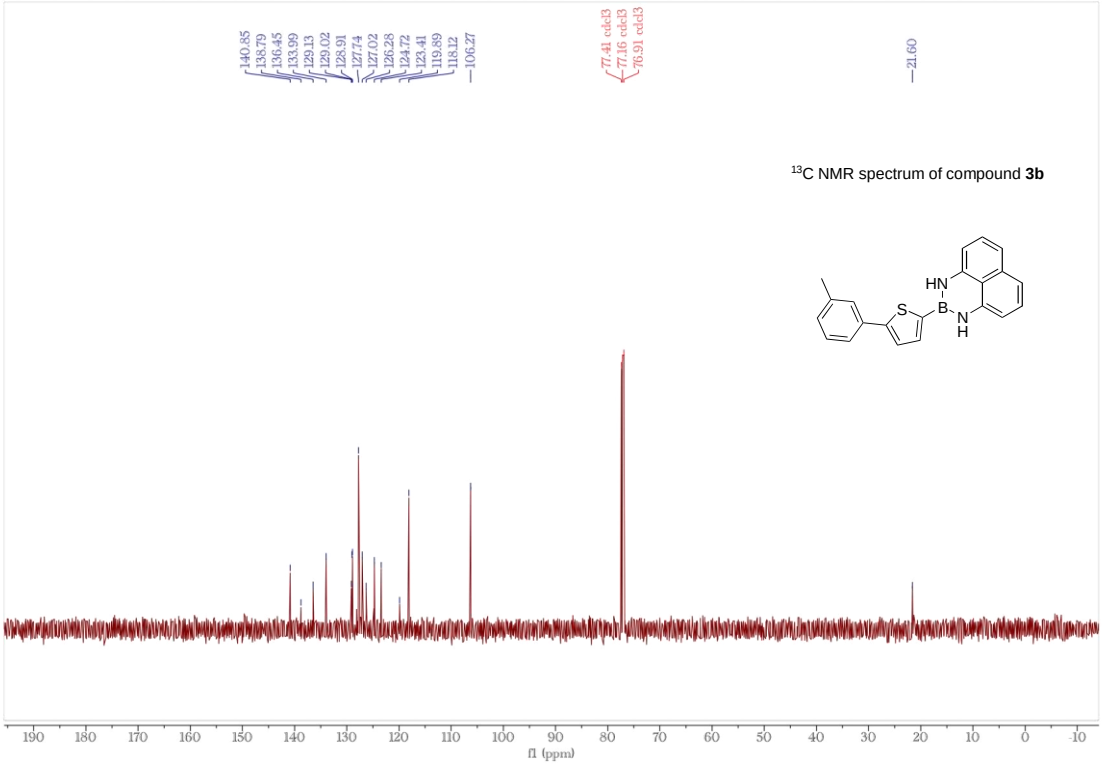
^{1}H NMR spectrum of compound **3a**



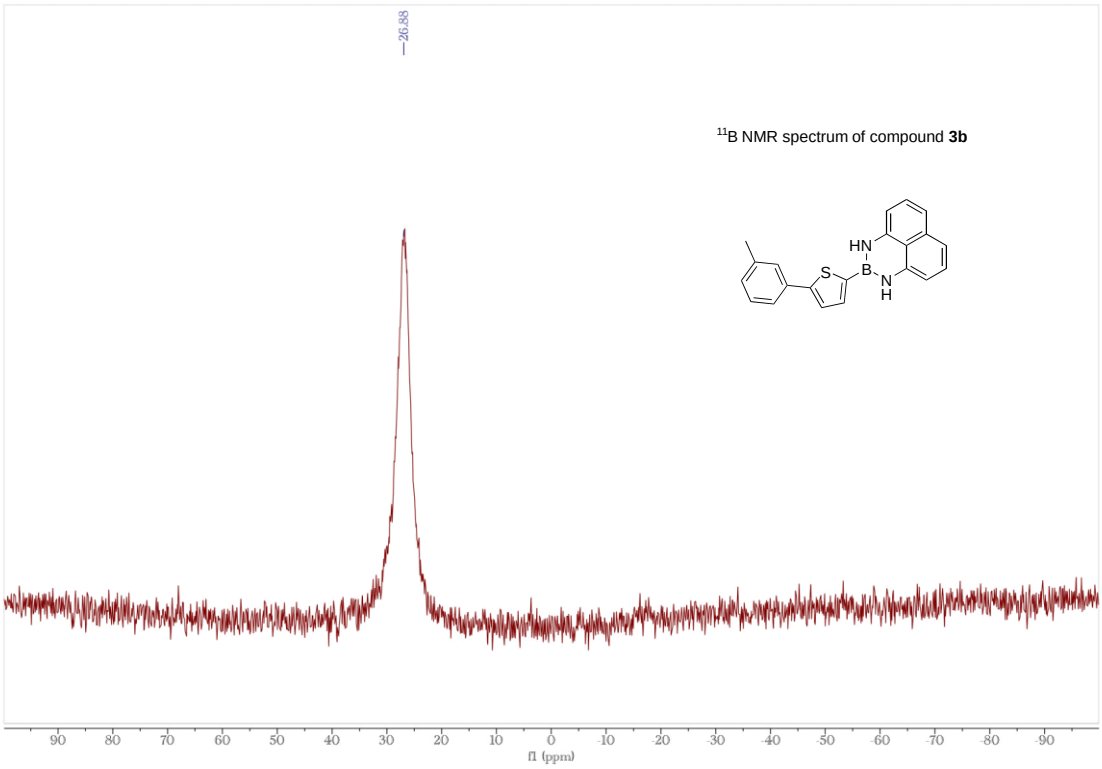
^{13}C NMR spectrum of compound **3a**



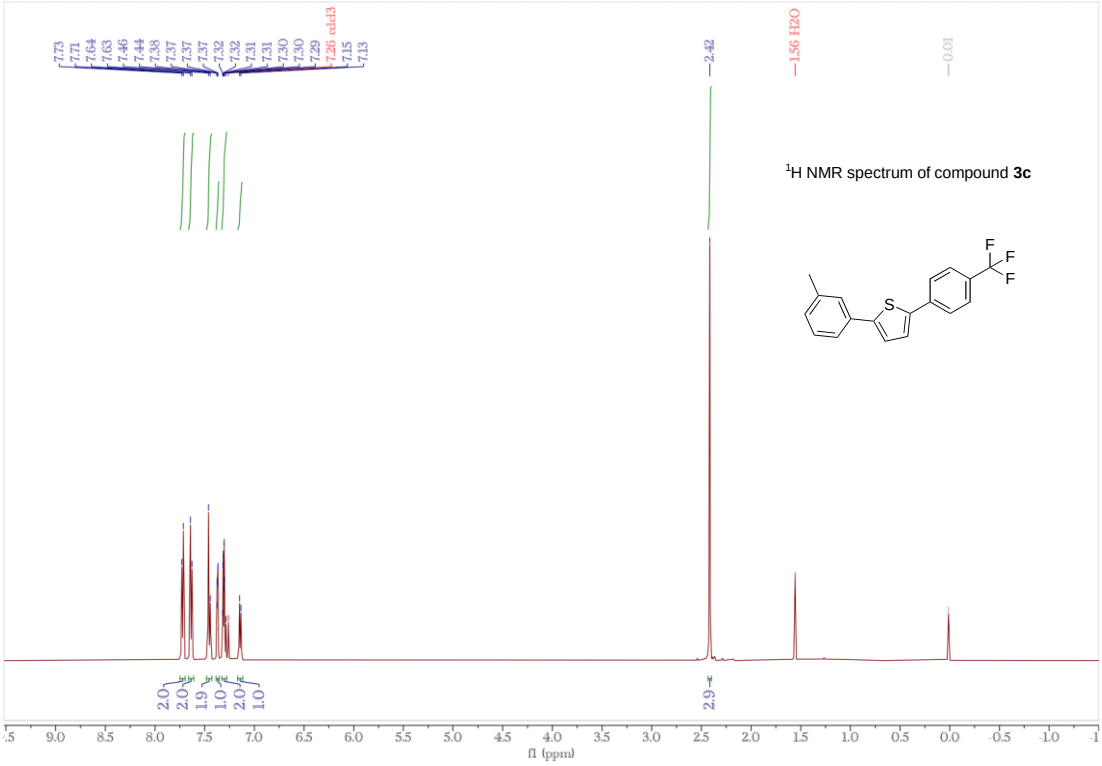
^{1}H NMR spectrum of compound **3b**



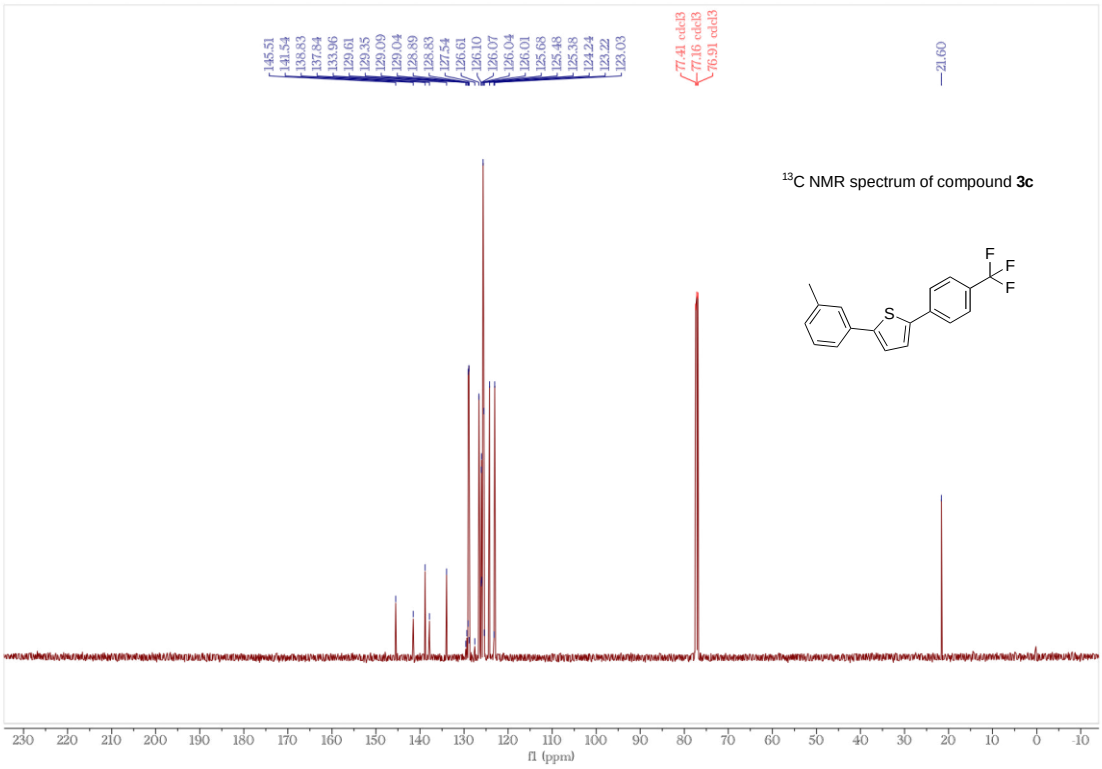
^{13}C NMR spectrum of compound **3b**



^{11}B NMR spectrum of compound **3b**



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



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