# *Supplementary Information for*

## Transition metal-free B(dan)-installing reaction (dan: naphthalene-1,8-diaminato): H–B(dan) as a B(dan) electrophile

Jialun Li,[a] Michinari Seki,[a] Shintaro Kamio[a] and Hiroto Yoshida[b]*

[a] *Applied Chemistry Program, Graduate School of Advanced Science and Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan.*
[b] *Basic Chemistry Program, Graduate School of Advanced Science and Engineering, Hiroshima University, Higashi-Hiroshima 739-8526, Japan.*

e-mail: yhiroto@hiroshima-u.ac.jp

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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, 186 MHz; $^{19}$F, 470 MHz) or a Varian 400MR ($^{1}$H, 400 MHz) spectrometer using residual chloroform ($^{1}$H, δ = 7.26), $CDCl_3$ ($^{13}$C, δ = 77.16), a residual proton in DMSO-$d_6$ ($^{1}$H, δ = 2.50), DMSO-$d_6$ ($^{13}$C, δ = 39.52) or tetramethylsilane ($^{1}$H and $^{13}$C, δ = 0) as an internal standard, and boron trifluoride diethyl etherate ($^{11}$B, δ = 0.00) or benzotrifluoride ($^{19}$F, δ = -63.72) as an external standard. $^{1}$H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, m = multiplet), coupling constants (Hz), integration. GC analysis was performed on a Shimadzu GC-2014 (GC conditions: Column: TC-1 (GLScience), 30 m x 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 or JEOL JMS–T100GCV spectrometer. Melting points were measured with Yanaco Micro Melting Point apparatus and uncorrected. Column chromatography was carried out using Merck Kieselgel 60 or Florisil. Unless otherwise noted, commercially available reagents were used without purification. All solvents were dried over activated molecular sieve 4Å.

## 2. GC calibration curves

**$C_{13}H_{28}$** : Tridecane

**H–B(dan)**: Naphthalene-1,8-diaminoborane

**Table S1** Data for the GC Calibration Curve (**H–B(dan)**)

| Entry | GC Area | | x | Amount of Substance (mmol) | | y |
|---|---|---|---|---|---|---|
| | **H–B(dan)** | **$C_{13}H_{28}$** | | **H–B(dan)** | **$C_{13}H_{28}$** | |
| 1 | 726432 | 1099505 | 0.660690037 | 0.10 | 0.10 | 1.0 |
| 2 | 672789 | 2115179 | 0.318076626 | 0.10 | 0.20 | 0.5 |
| 3 | 1638713 | 1268933 | 1.291410185 | 0.20 | 0.10 | 2.0 |

**x** = (GC area of **H–B(dan)**)/(GC area of **$C_{13}H_{28}$**)

**y** = (amount of substance of **H–B(dan)**)/(amount of substance of **$C_{13}H_{28}$**)

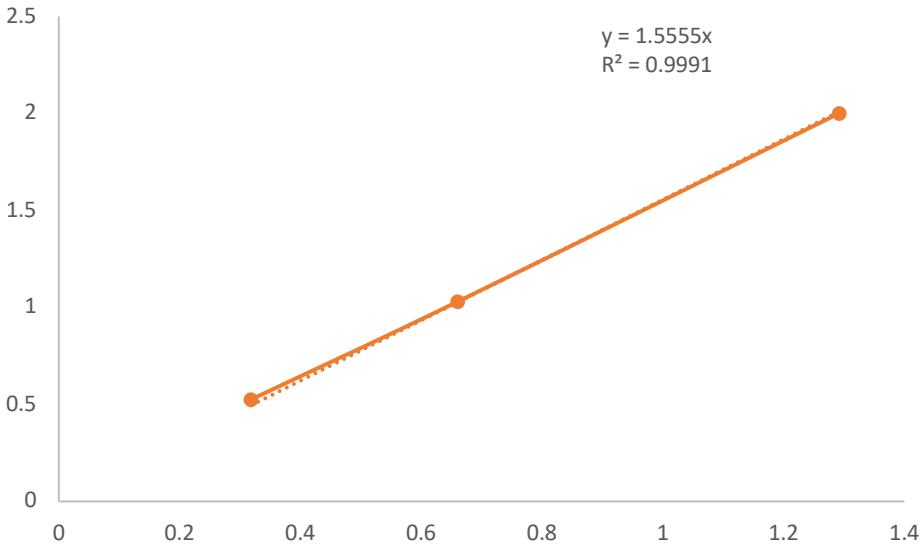



**Fig. S1 GC Calibration Curve for Decision of the Yield (H–B(dan))**

**Table S2** Data for the GC Calibration Curve (**3a**)

| Entry | GC Area | | x | Amount of Substance (mmol) | | y |
|---|---|---|---|---|---|---|
| | **3a** | **$C_{13}H_{28}$** | | **3a** | **$C_{13}H_{28}$** | |
| 1 | 3468580 | 3203419 | 1.082774373 | 0.10 | 0.10 | 1.0 |
| 2 | 4421180 | 6375830 | 0.69342815 | 0.10 | 0.20 | 0.5 |
| 3 | 7290385 | 3367502 | 2.164923733 | 0.20 | 0.10 | 2.0 |

**x** = (GC area of **3a**)/(GC area of **$C_{13}H_{28}$**)

**y** = (amount of substance of **3a**)/(amount of substance of **$C_{13}H_{28}$**)

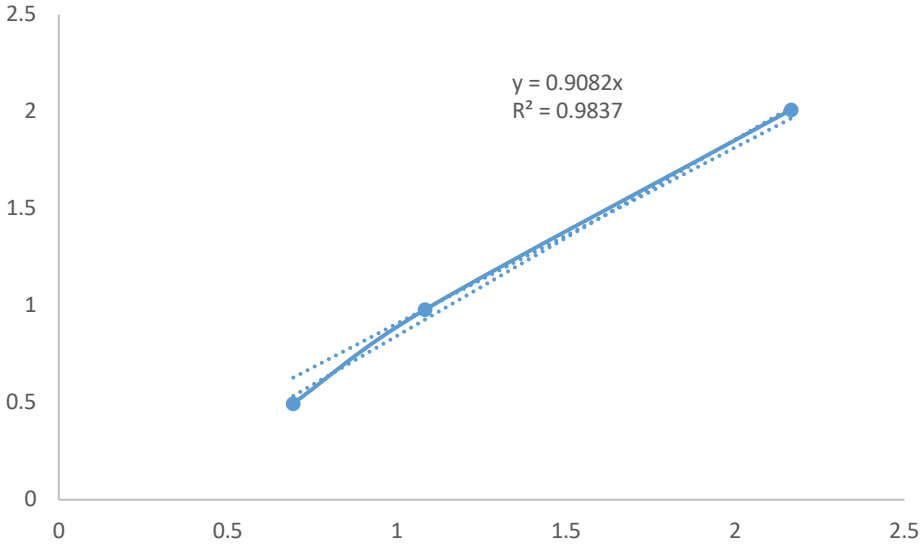
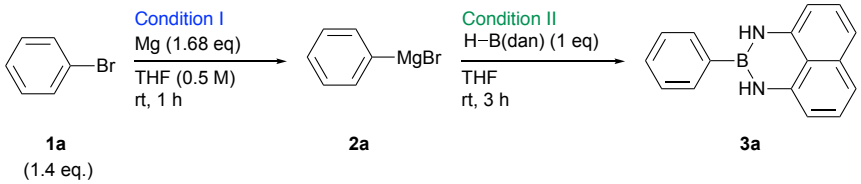



**Fig. S2 GC Calibration Curve for Decision of the Yield (3a)**

## 3. Optimization of reaction conditions

**Table S3 Optimization of Reaction Conditions**[a]




**1a** (1.4 eq.) **2a** **3a**

| Entry | Changes from Condition I | Changes from Condition II | Yield (%)[b] |
|---|---|---|---|
| 1 | - | - | 93(87[c]) |
| 2 | DME | DME | 0 |
| 3 | 1,4-dioxane | 1,4-dioxane | 0 |
| 4 | Ether | Ether | 0 |
| 5 | Ph–Br (1.2 eq), Mg (1.44 eq) | - | 57 |
| 6 | Ph–Br (1.3 eq), Mg (1.56 eq) | - | 78 |
| 7 | Ph–Br (1.5 eq), Mg (1.8 eq) | - | 89 |
| 8 | Ph–Br (2 eq), Mg (2.4 eq) | - | 89 |
| 9[d] | - | - | 83 |

[a] Standard conditions: **1a** (1.4 mmol), Mg (1.68 mmol), THF (2 mL), H–B(dan) (1.0 mmol). [b] GC yield. [c] Isolated yield. [d] **1a** (1.0 mmol), Mg (1.2 mmol), THF (2 mL), H–B(dan) (2.0 mmol).

## 4. Experimental procedures and compounds characterization data

### 4-1. Procedure A: Reaction of aryl Grignard reagents with H–B(dan) using Mg.[1]

A 25 mL of Schlenk tube was charged with magnesium turnings (1.68 mmol, 1.68 eq). After the tube was heated under vacuum for 5 minutes with the aid of a heating gun, the tube was cooled to room temperature and back-filled with argon. Iodine (0.01 mmol, 1 mol %) and THF (2 mL) were then added. After stirring for 10 minutes at room temperature, an aryl bromide (1.4 mmol, 1.4 eq) was added. After stirring for 1 h at room temperature, H–B(dan) (1 mmol, 1 eq) was added to the mixture and the resulting mixture was stirred for additional 3 h. The reaction mixture was quenched with sat. $NH_4Cl$ aq (5 mL). The layers were allowed to separate and the aqueous layer was extracted with diethyl ether (3 x 10 mL). The combined organics were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The crude material was purified on $SiO_2$ (10% to 25% EtOAc/Hexane) to afford the target compound.

### 4-2. Procedure B: Reaction of heteroaryl Grignard reagents with H–B(dan) using Turbo Grignard reagent.[2]

To a flame dried 25 mL of Schlenk tube were added *i*-PrMgCl•LiCl (0.75 mmol, 1.5 eq), a heteroaryl bromide (0.7 mmol, 1.4 eq) and *p*-xylene (1 mL). After stirring for 3 h at room temperature, H–B(dan) (0.5 mmol, 1 eq) was added and the resulting mixture was stirred for additional 3 h. The reaction mixture was quenched with sat. $NH_4Cl$ aq. (5 mL). The layers were allowed to separate and the aqueous layer was extracted with diethyl ether (3 x 10 mL). The combined organics were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation.

The crude material was purified on $SiO_2$ (10% to 25% EtOAc/Hexane) to afford the target compound.

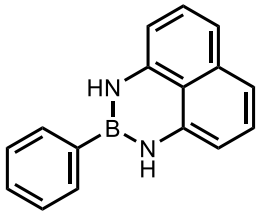
**4-3. Procedure C: Reaction of alkyl Grignard reagents with H–B(dan) using Mg.**

A 25 mL of Schlenk tube was charged with magnesium turnings (2.4 mmol, 2.4 eq). After the tube was heated under vacuum for 5 minutes with the aid of a heating gun, the tube was cooled to room temperature and back-filled with argon. Iodine (0.01 mmol, 1 mol %) and THF (2 mL) were then added. After stirring for 10 minutes at room temperature, an alkyl halide (2 mmol, 2 eq) was added and then stirred for 2 h at reflux temperature. After returning to room temperature, H–B(dan) (1 mmol, 1 eq) was added and the resulting mixture was stirred for additional 24 h. The reaction mixture was quenched with sat. $NH_4Cl$ aq. (5 mL). The layers were allowed to separate and the aqueous layer was extracted with diethyl ether (3 x 10 mL). The combined organics were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The crude material was purified on $SiO_2$ (10% to 25% EtOAc/Hexane) to afford the target compound.

**4-4. Procedure D: Reaction of commercially available Grignard reagents with H–B(dan).**

To a flame dried 25 mL of Schlenk tube were added a Grignard reagent (2 mmol, 2 eq), H–B(dan) (1 mmol, 1 eq) and THF (2 mL). After stirring for 24 h at room temperature, the reaction mixture was quenched with sat. $NH_4Cl$ aq. (5 mL). The layers were allowed to separate and the aqueous layer was extracted with diethyl ether (3 x 10 mL). The combined organics were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The crude material was purified on $SiO_2$ (10% to 25% EtOAc/Hexane) to afford the target compound.

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

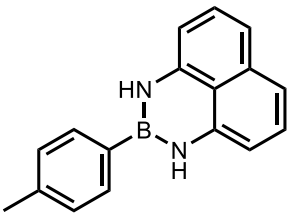



Isolated in 87% yield as a brown solid (Procedure A).

**$^1$H NMR** (500 MHz, $CDCl_3$) $\delta$ 7.68-7.64 (m, 2H), 7.54-7.43 (m, 3H), 7.17 (t, J = 7.8 Hz, 2H), 7.09 (d, J = 8.2 Hz, 2H), 6.43 (d, J = 7.3 Hz, 2H), 6.03 (brs, 2H).

**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 141.18, 136.47, 131.55, 130.41, 128.39, 127.75, 119.97, 117.95, 106.16.

**2-(*p*-tolyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3b)**[4]

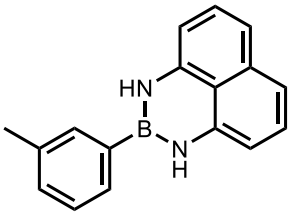



Isolated in 93% yield as a brown solid (Procedure A).

**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.56 (d, J = 7.9 Hz, 2H), 7.28 (d, J = 7.5 Hz, 2H), 7.16 (dd, J = 8.3, 7.3 Hz, 2H), 7.07 (dd, J = 8.3, 1.0 Hz, 2H), 6.42 (dd, J = 7.2, 1.0 Hz, 2H), 6.03 (brs, 2H), 2.42 (s, 3H).

**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 141.28, 140.51, 136.47, 131.57, 129.17, 127.74, 119.91, 117.84, 106.08, 21.71.

**2-(*m*-tolyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3c)**[4]

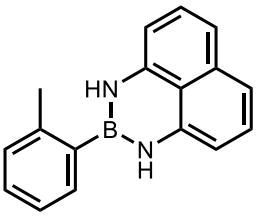



Isolated in 92% yield as a gray solid (Procedure A).

**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.52-7.46 (m, 2H), 7.41 (t, J = 7.3 Hz, 1H), 7.36 (d, J = 7.7 Hz, 1H), 7.23 (dd, J = 8.3, 7.2 Hz, 2H), 7.15 (d, J = 8.2 Hz, 2H), 6.46 (d, J = 7.3 Hz, 2H), 6.05 (brs, 2H), 2.49 (s, 3H).

**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 141.19, 137.67, 136.41, 132.22, 131.09, 128.56, 128.22, 127.69, 119.91, 117.80, 106.08, 21.60.

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

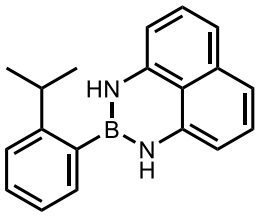



Isolated in 94% yield as a gray solid (Procedure A).

**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.44 (d, J = 8.1 Hz, 1H), 7.31 (t, J = 7.3 Hz, 1H), 7.21 (d, J = 4.2 Hz, 2H), 7.12 (t, J = 7.8 Hz, 2H), 7.05 (d, J = 8.3 Hz, 2H), 6.33 (d, J = 7.3 Hz, 2H), 5.80 (brs, 2H), 2.48 (s, 3H).

**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 141.21, 140.76, 136.47, 132.36, 129.81, 129.44, 127.75, 125.41, 119.89, 117.95, 106.03, 22.53.

**2-(2-isopropylphenyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3e)**[5]

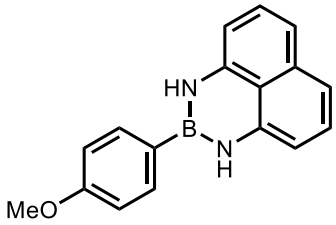



Isolated in 91% yield as a gray solid (Procedure A).

**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.43-7.34 (m, 3H), 7.22 (td, J = 7.2, 1.4 Hz, 1H), 7.17-7.10 (m, 2H), 7.06 (d, J = 8.3 Hz, 2H), 6.35 (d, J = 7.2 Hz, 2H), 5.80 (brs, 2H), 3.24-3.13 (m, 1H), 1.28 (dd, J = 6.9, 2.3 Hz, 6H).

**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 151.95, 141.09, 136.39, 132.20, 129.48, 127.66, 125.46, 124.83, 119.83, 117.88, 106.00, 33.78, 24.83.

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

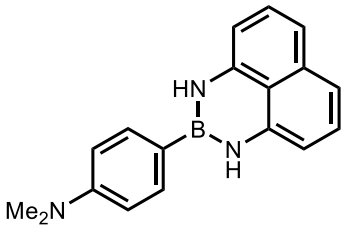



Isolated in 81% yield as a gray solid (Procedure A).

**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.59 (d, J = 8.6 Hz, 2H), 7.14 (dd, J = 8.3, 7.3 Hz, 2H), 7.05 (d, J = 7.4 Hz, 2H), 6.98 (d, J = 8.5 Hz, 2H), 6.42 (dd, J = 7.3, 1.0 Hz, 2H), 5.99 (brs, 2H), 3.86 (s, 3H).

**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 161.54, 141.32, 136.48, 133.13, 127.75, 119.80, 117.81, 113.99, 106.05, 55.31.

***N,N*-dimethyl-4-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)aniline (3g)**




Isolated in 90% yield as a white solid (Procedure A).

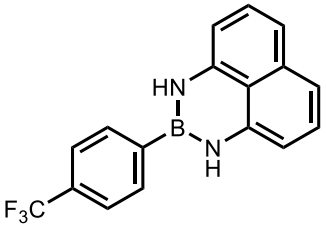
mp: 164–165 °C.

**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.55 (d, J = 8.6 Hz, 2H), 7.17 (t, J = 7.8 Hz, 2H), 7.07 (d, J = 8.3 Hz, 2H), 6.79 (d, J = 8.6 Hz, 2H), 6.43 (d, J = 6.2 Hz, 2H), 6.01 (brs, 2H), 3.02 (s, 6H).

**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 152.00, 141.61, 136.47, 132.78, 127.71, 119.64, 117.44, 111.90, 105.84, 40.25.

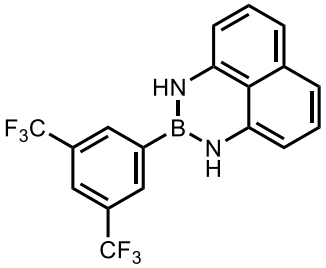
**$^{11}$B NMR** (186 MHz, $CDCl_3$) δ 28.86.
HRMS (APCI) Calcd for $C_{18}H_{18}BN_3$: $[M+H]^+$, 288.16665. Found: m/z 288.16702

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



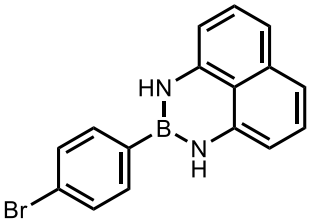

Isolated in 90% yield as a gray solid (Procedure A).
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.71-7.63 (m, 4H), 7.19 (t, J = 7.7 Hz, 2H), 7.12 (d, J = 8.1 Hz, 2H), 6.42 (d, J = 7.2 Hz, 2H), 5.96 (brs, 2H).
**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 140.68, 136.36, 131.92 (q, J = 32.4 Hz), 131.73, 127.70, 124.86 (q, J = 3.8 Hz), 124.21 (q, J = 272.3 Hz), 119.99, 118.26, 106.36.

**2-(3,5-bis(trifluoromethyl)phenyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3i)**[5]




Isolated in 71% yield as a yellow solid (Procedure A).
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.06 (s, 2H), 8.04-7.96 (m, 1H), 7.17 (dd, J = 8.3, 7.2 Hz, 2H), 7.11 (dd, J = 8.4, 1.1 Hz, 2H), 6.48 (dd, J = 7.2, 1.1 Hz, 2H), 6.02 (brs, 2H).
**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 140.30, 136.39, 131.57, 131.54 (q, J = 32.9 Hz), 127.81, 123.96, 123.60 (q, J = 273.1 Hz), 120.13, 118.80, 106.75.

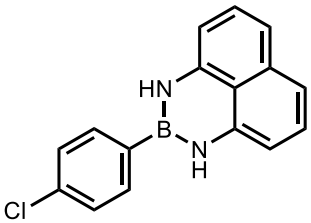
**2-(4-bromophenyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3j)**[6]




Isolated in 40% yield as a dark green solid (Procedure A).
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, J = 7.9 Hz, 2H), 7.50 (d, J = 8.0 Hz, 2H), 7.15 (t, J = 7.8 Hz, 2H), 7.07 (d, J = 8.2 Hz, 2H), 6.42 (d, J = 7.2 Hz, 2H), 5.97 (brs, 2H).

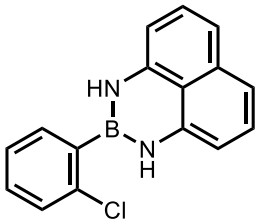
**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 140.90, 136.44, 133.15, 131.58, 127.76, 125.04, 119.97, 118.19, 106.30.

**2-(4-chlorophenyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3k)**[7]



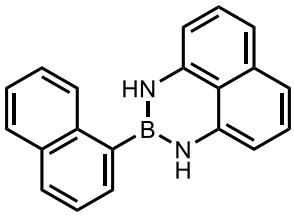

Isolated in 88% yield as a gray solid (Procedure A).
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.55 (d, J = 7.8 Hz, 2H), 7.41 (d, J = 7.8 Hz, 2H), 7.15 (t, J = 7.8 Hz, 2H), 7.08 (d, J = 8.2 Hz, 2H), 6.41 (d, J = 7.3 Hz, 2H), 5.97 (brs, 2H).
**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 140.92, 136.53, 136.43, 132.92, 128.62, 127.75, 119.94, 118.15, 106.27.

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




Isolated in 57% yield as a purple solid (Procedure A).
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.53 (dd, J = 7.1, 2.1 Hz, 1H), 7.42-7.29 (m, 3H), 7.14 (dd, J = 8.3, 7.2 Hz, 2H), 7.06 (dd, J = 8.4, 1.0 Hz, 2H), 6.39 (dd, J = 7.3, 1.0 Hz, 2H), 6.08 (brs, 2H).
**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 140.99, 137.99, 136.46, 134.01, 131.13, 129.68, 127.75, 126.63, 120.00, 118.07, 106.20.

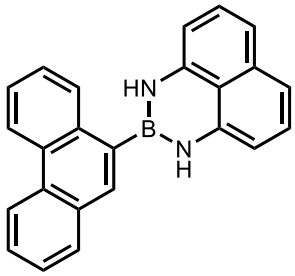
**2-(naphthalen-1-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3m)**[4]




Isolated in 84% yield as a gray solid (Procedure A).
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 8.26-8.20 (m, 1H), 7.97-7.91 (m, 2H), 7.71 (d, J = 5.5 Hz, 1H), 7.59-7.51 (m, 3H), 7.20 (dd, J = 8.3, 7.1 Hz, 2H), 7.15 (d, J = 7.2 Hz, 2H), 6.36 (d, J = 7.2 Hz, 2H), 5.99 (brs, 2H).
**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 141.20, 136.52, 135.52, 133.37, 130.78, 129.63, 128.89, 128.02,

127.78, 126.34, 125.95, 125.51, 120.05, 118.09, 106.16.

**2-(phenanthren-9-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3n)**[5]

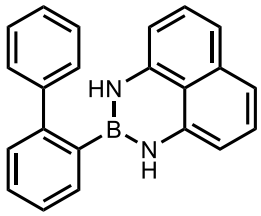



Isolated in 83% yield as a gray solid (Procedure A).

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.77 (d, J = 8.3 Hz, 1H), 8.71 (d, J = 7.4 Hz, 1H), 8.25 (dd, J = 8.1, 1.3 Hz, 1H), 7.98 (s, 1H), 7.91 (dd, J = 7.8, 1.4 Hz, 1H), 7.66 (s, 4H), 7.17 (dd, J = 8.3, 7.2 Hz, 2H), 7.11 (dd, J = 8.4, 1.0 Hz, 2H), 6.42 (dd, J = 7.2, 1.1 Hz, 2H), 6.08 (brs, 2H).

**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 141.18, 136.53, 133.76, 132.49, 131.35, 130.91, 130.16, 128.86, 128.83, 127.80, 127.33, 126.89, 126.69, 126.65, 123.32, 122.68, 120.10, 118.14, 106.21.

**2-([1,1'-biphenyl]-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3o)**[4]

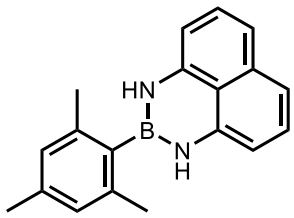



Isolated in 52% yield as a brown solid (Procedure A).

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.69 (d, J = 8.8 Hz, 1H), 7.55-7.36 (m, 8H), 7.08 (t, J = 7.2 Hz, 2H), 7.02 (d, J = 8.3 Hz, 2H), 6.13 (d, J = 7.0 Hz, 2H), 5.50 (brs, 2H).

**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 146.52, 142.78, 141.17, 136.32, 132.89, 129.81, 129.53, 129.20, 128.88, 128.49, 127.67, 127.57, 127.29, 127.03, 119.58, 117.63, 105.87.

**2-mesityl-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3p)**[5]



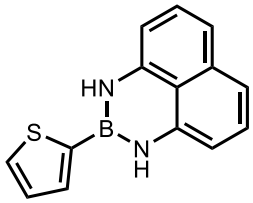

Isolated in 90% yield as a red solid (Procedure A).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.17 (ddd, J = 8.5, 7.2, 1.3 Hz, 2H), 7.10 (d, J = 8.3 Hz, 2H), 6.92 (s, 2H), 6.35 (d, J = 7.2 Hz, 2H), 5.78 (brs, 2H), 2.42 (s, 6H), 2.35 (s, 3H).

**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 141.28, 140.75, 138.62, 136.46, 127.72, 127.34, 119.89, 117.91,

105.99, 22.40, 21.32.

**2-(thiophen-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3q)**[4]



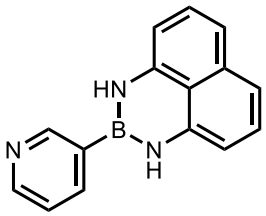

Isolated in 84% yield as a gray solid.

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.58 (dd, J = 4.7, 0.9 Hz, 1H), 7.45 (dd, J = 3.4, 0.9 Hz, 1H), 7.21 (dd, J = 4.7, 3.4 Hz, 1H), 7.12 (dd, J = 8.3, 7.2 Hz, 2H), 7.04 (d, J = 7.2 Hz, 2H), 6.37 (d, J = 7.2 Hz, 2H), 5.92 (brs, 2H).

**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 140.81, 136.39, 132.97, 130.22, 128.68, 127.70, 119.85, 118.08, 106.24.

This compound was synthesized by a similar method to Procedure A: A 25 mL of Schlenk tube was charged with magnesium turnings (1.68 mmol, 1.68 eq). After the tube was heated under vacuum for 5 minutes with the aid of a heating gun, the tube was cooled to room temperature and back-filled with argon. Iodine (0.01 mmol, 1 mol %) and THF (2 mL) were then added. After stirring for 10 minutes at room temperature, 2-bromothiophene (1.4 mmol, 1.4 eq) was added and then stirred for 2 h at reflux temperature. After cooling to room temperature, H–B(dan) (168.0 mg, 1 mmol, 1 eq) was added and the resulting mixture was stirred for additional 3 h. The reaction mixture was quenched with sat. $NH_4Cl$ aq. (5 mL). The layers were allowed to separate and the aqueous layer was extracted with diethyl ether (3 x 10 mL). The combined organics were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The crude material was purified on $SiO_2$ (10% to 25% EtOAc/Hexane) to afford **3q**.

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




Isolated in 52% yield as a black solid.

mp: 204–205 °C.

**$^{1}$H NMR** (500 MHz, DMSO-*d6*) δ 9.07 (s, 1H), 8.64 (dd, J = 4.9, 1.8 Hz, 1H), 8.42 (brs, 2H), 8.27 (dt, J = 7.6, 1.9 Hz, 1H), 7.45 (dd, J = 7.6, 4.8 Hz, 1H), 7.10 (t, J = 7.8 Hz, 2H), 6.93 (d, J = 8.2 Hz, 2H), 6.59 (d, J = 7.5 Hz, 2H).

**$^{13}$C NMR** (125 MHz, DMSO-*d6*) δ 153.38, 150.82, 142.08, 140.22, 135.99, 127.74, 123.27,

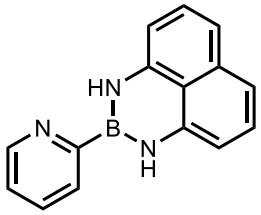
119.84, 116.61, 105.85.

**$^{11}$B NMR** (186 MHz, DMSO-*d6*) δ 29.82.

HRMS (APCI) Calcd for $C_{15}H_{12}BN_3$: $[M+H]^+$, 246.1970. Found: m/z 246.12006

This compound was synthesized by a similar method to Procedure B: To a flame dried 25 mL of Schlenk tube were added *i*-PrMgCl•LiCl (0.7 mmol, 1.4 eq), 3-bromopyridine (0.5 mmol, 1 eq) and *p*-xylene (1 mL). After stirring for 3 h at room temperature, H–B(dan) (0.5 mmol, 1 eq) was added and the resulting mixture was stirred for additional 3 h. The reaction mixture was quenched with sat. $NH_4Cl$ aq. (5 mL). The layers were allowed to separate and the aqueous layer was extracted with diethyl ether (3 x 10 mL). The combined organics were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The crude material was purified on $SiO_2$ (10% to 25% EtOAc/Hexane) to afford **3r**.

**2-(pyridin-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3s)**[9]

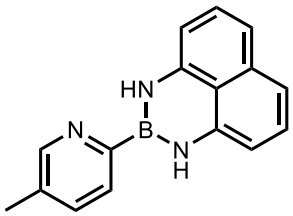



Isolated in 71% yield as a brown solid (Procedure B).

**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 8.82-8.77 (m, 1H), 7.69 (td, J = 7.6, 1.7 Hz, 1H), 7.61 (dt, J = 7.6, 1.2 Hz, 1H), 7.32 (ddd, J = 7.6, 4.8, 1.3 Hz, 1H), 7.15 (dd, J = 8.3, 7.3 Hz, 2H), 7.06 (dd, J = 8.4, 1.0 Hz, 2H), 6.57 (brs, 2H), 6.45 (dd, J = 7.3, 1.0 Hz, 2H).

**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 150.19, 141.10, 136.52, 134.98, 127.74, 126.82, 124.55, 120.47, 117.98, 106.31.

**2-(5-methylpyridin-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3t)**[9]




Isolated in 74% yield as a yellow solid.

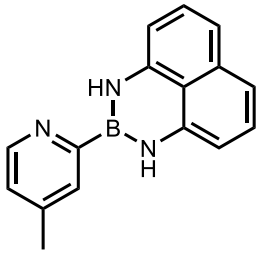
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 8.63 (s, 1H), 7.58-7.50 (m, 2H), 7.14 (dd, J = 8.3, 7.2 Hz, 2H), 7.05 (dd, J = 8.3, 1.0 Hz, 2H), 6.53 (brs, 2H), 6.45 (dd, J = 7.3, 1.0 Hz, 2H), 2.39 (s, 3H).

**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 150.97, 141.21, 136.56, 135.51, 134.43, 127.76, 126.48, 120.43, 117.92, 106.27, 18.88.

This compound was synthesized by a similar method to Procedure B: To a flame dried 25 mL

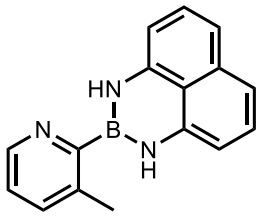
of Schlenk tube were added *i*-PrMgCl•LiCl (0.7 mmol, 1.4 eq), 3-bromopyridine (0.5 mmol, 1 eq) and *p*-xylene (1 mL). After stirring for 3 h at room temperature, H–B(dan) (0.5 mmol, 1 eq) was added and the resulting mixture was stirred for additional 3 h. The reaction mixture was quenched with sat. $NH_4Cl$ aq. (5 mL). The layers were allowed to separate and the aqueous layer was extracted with diethyl ether (3 x 10 mL). The combined organics were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The crude material was purified on $SiO_2$ (10% to 25% EtOAc/Hexane) to afford **3t**.

**2-(4-methylpyridin-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3u)**



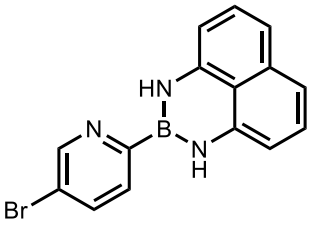

Isolated in 69% yield as a gray solid (Procedure B).
mp: 187‑188 °C.
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.64 (d, J = 5.9 Hz, 1H), 7.44 (s, 1H), 7.17-7.10 (m, 3H), 7.05 (dd, J = 8.3, 1.0 Hz, 2H), 6.57 (brs, 2H), 6.44 (dd, J = 7.3, 1.0 Hz, 2H), 2.37 (s, 3H).
**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 149.94, 145.91, 141.16, 136.51, 128.02, 127.72, 125.44, 120.45, 117.88, 106.25, 21.17.
**$^{11}$B NMR** (186 MHz, $CDCl_3$) δ 27.53.
HRMS (APCI) Calcd for $C_{16}H_{14}BN_3$: $[M+H]^+$, 260.13535. Found: m/z 260.13568

**2-(3-methylpyridin-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3v)**[9]




Isolated in 34% yield as a gray solid (Procedure B).
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.61 (dd, J = 4.7, 0.9 Hz, 1H), 7.48 (ddd, J = 7.8, 1.6, 0.8 Hz, 1H), 7.22 (dd, J = 7.8, 4.7 Hz, 1H), 7.13 (dd, J = 8.3, 7.3 Hz, 2H), 7.05 (dd, J = 8.3, 1.0 Hz, 2H), 6.44 (brs, 2H), 6.41 (dd, J = 7.3, 1.0 Hz, 2H), 2.59 (s, 3H).
**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 147.42, 141.24, 137.62, 137.16, 136.50, 127.75, 123.82, 120.25, 117.90, 106.29, 20.77.

**2-(5-bromopyridin-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3w)**



Isolated in 53% yield as a yellow solid (Procedure B).

mp: 158–159 °C

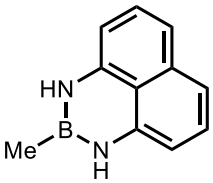
**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.85 (dd, J = 2.3, 0.8 Hz, 1H), 7.86 (dd, J = 8.1, 2.3 Hz, 1H), 7.53 (dd, J = 8.1, 0.8 Hz, 1H), 7.14 (dd, J = 8.3, 7.2 Hz, 2H), 7.06 (dd, J = 8.3, 1.0 Hz, 2H), 6.48 (brs, 2H), 6.45 (dd, J = 7.3, 1.1 Hz, 2H).

**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 151.40, 140.84, 137.58, 136.51, 127.75, 127.68, 122.47, 120.46, 118.20, 106.43.

**$^{11}$B NMR** (186 MHz, $CDCl_3$) δ 27.29.

HRMS (APCI) Calcd for $C_{15}H_{11}BBrN_3$: $[M+H]^+$, 324.03022. Found: m/z 324.03085

**2-methyl-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (4a)**[10]

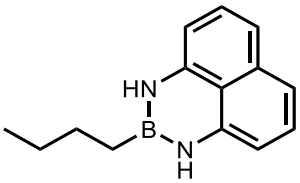


Isolated in 49% yield as a gray solid (Procedure D).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.13 (dd, J = 8.3, 7.3 Hz, 2H), 7.05 (dd, J = 8.3, 1.1 Hz, 2H), 6.30 (dd, J = 7.2, 1.1 Hz, 2H), 5.62 (brs, 2H), 0.37 (s, 3H).

**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 141.35, 136.41, 127.70, 119.52, 117.43, 105.49.

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



Isolated in 96% yield as a black liquid.

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.11 (t, J = 7.8 Hz, 2H), 7.02 (d, J = 8.3 Hz, 2H), 6.31 (d, J = 7.2 Hz, 2H), 5.61 (brs, 2H), 1.48-1.34 (m, 4H), 1.00-0.91 (m, 3H), 0.91-0.83 (m, 2H).

**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 141.35, 136.43, 127.67, 119.65, 117.41, 105.50, 27.13, 25.61, 14.11.

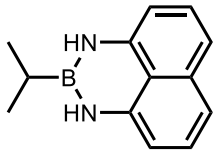
**$^{11}$B NMR** (186 MHz, $CDCl_3$) δ 31.95.

HRMS (APCI) Calcd for $C_{14}H_{17}BN_2$: $M^+$, 224.14793. Found: m/z 224.14804

This compound was synthesized by a similar method to Procedure C: A 25-mL of Schlenk tube

was charged with magnesium turnings (2.4 mmol, 2.4 eq.). After the tube was heated under vacuum for 5 minutes with the aid of a heating gun, the tube was cooled to room temperature and back-filled with argon. Iodine (0.01 mmol, 1 mol %) and THF (2 mL) were then added. After stirring for 10 minutes at room temperature, 1-bromobutane (2 mmol, 2 eq.) was added and the mixture was stirred for 1 h. To the mixture was added H–B(dan) (1 mmol, 1 eq.), and the resulting mixture was stirred for additional 24 h. The reaction mixture was quenched with sat. $NH_4Cl$ aq. (5 mL). The layers were allowed to separate and the aqueous layer was extracted with diethyl ether (3 x 10 mL). The combined organics were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The crude material was purified on $SiO_2$ (10% to 25% EtOAc/Hexane) to afford **4b**.

**2-isopropyl-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (4c)**[5]



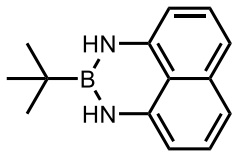

Isolated in 83% yield as a gray solid.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.14 (t, 2H), 7.04 (dd, J = 8.3, 1.1 Hz, 2H), 6.34 (dd, J = 7.3, 1.1 Hz, 2H), 5.61 (brs, 2H), 1.23-1.12 (m, 1H), 1.10 (d, 6H).

**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 141.36, 136.44, 127.69, 119.69, 117.48, 105.66, 18.92.

This compound was synthesized by a similar method to Procedure C: A 25 mL of Schlenk tube was charged with magnesium turnings (2.4 mmol, 2.4 eq.). After the tube was heated under vacuum for 5 minutes with the aid of a heating gun, the tube was cooled to room temperature and back-filled with argon. Then THF (2 mL) was added (Iodine was not necessary in this case). After stirring for 10 minutes at room temperature, 2-isopropyl bromide (2 mmol, 2 eq.) was added and the mixture was stirred for 1 h. H–B(dan) (1 mmol, 1 eq.) was added and the resulting mixture was stirred for additional 24 h. The reaction mixture was quenched with sat. $NH_4Cl$ aq. (5 mL). The layers were allowed to separate and the aqueous layer was extracted with diethyl ether (3 x 10 mL). The combined organics were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The crude material was purified on $SiO_2$ (10% to 25% EtOAc/Hexane) to afford **4c**.

**2-(*tert*-butyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine(4d)**




Isolated in 55% yield as a brown solid (Procedure D).

mp: 107–108 °C.

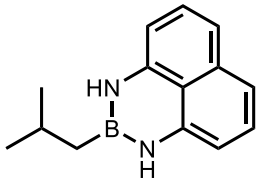
**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.16 (dd, J = 8.3, 7.3 Hz, 2H), 7.06 (dd, J = 8.3, 1.0 Hz, 2H), 6.37 (dd, J = 7.3, 1.1 Hz, 2H), 5.64 (brs, 2H), 1.07 (s, 9H).

**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 141.37, 136.43, 127.71, 119.59, 117.52, 105.74, 27.83.

**$^{11}$B NMR** (186 MHz, $CDCl_3$) δ 33.17.

HRMS (APCI) Calcd for $C_{14}H_{17}BN_2$: $[M+H]^+$, 225.15576. Found: m/z 225.15550

**2-neopentyl-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (4e)**[7]

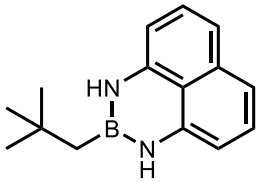



Isolated in 86% yield as a purple solid (Procedure C).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.16 (dd, J = 8.3, 7.3 Hz, 2H), 7.07 (dd, J = 8.3, 1.1 Hz, 2H), 6.33 (dd, J = 7.3, 1.1 Hz, 2H), 5.63 (brs, 2H), 1.94-1.82 (m, 1H), 1.04 (d, J = 6.6 Hz, 6H), 0.84 (d, J = 7.3 Hz, 2H).

**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 141.33, 136.41, 127.65, 119.65, 117.41, 105.50, 25.65, 25.51.

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




Isolated in 72% yield as a purple solid (Procedure C).

mp: 91–92 °C.

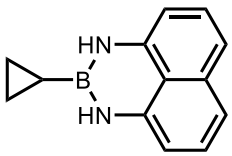
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.13 (dd, J = 8.2, 7.3 Hz, 2H), 7.04 (d, J = 8.3 Hz, 2H), 6.32 (d, J = 7.3 Hz, 2H), 5.61 (s, 2H), 1.07 (brs, 9H), 0.89 (s, 2H).

**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 141.35, 136.43, 127.70, 119.67, 117.45, 105.53, 32.47, 30.56.

**$^{11}$B NMR** (186 MHz, $CDCl_3$) δ 31.13.

HRMS (APCI) Calcd for $C_{15}H_{19}BN_2$: $M^+$, 238.16358. Found: m/z 238.16386

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

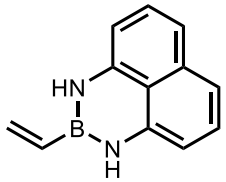



Isolated in 66% yield as a purple solid (Procedure C).

mp: 64–65 °C.

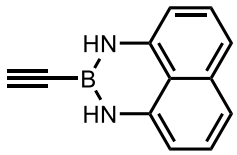
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.10 (dd, J = 8.3, 7.2 Hz, 2H), 7.00 (dd, J = 8.4, 1.1 Hz, 2H), 6.29 (td, J = 7.1, 1.1 Hz, 2H), 5.44 (brs, 2H), 0.79-0.67 (m, 2H), 0.44 (td, J = 5.9, 3.9 Hz, 2H), -0.08 (tt, J = 9.4, 6.3 Hz, 1H).
**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 141.25, 136.41, 127.65, 119.52, 117.42, 105.52, 4.07.
**$^{11}$B NMR** (186 MHz, $CDCl_3$) δ 31.47.
HRMS (APCI) Calcd for $C_{13}H_{13}BN_2$: $M^+$, 208.11663. Found: m/z 208.11682

**2-vinyl-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (4h)**[11]



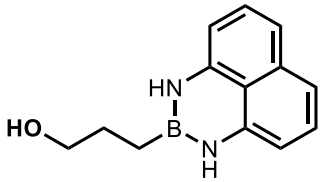

Isolated in 73% yield as a purple liquid (Procedure D).
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.11 (ddd, J = 8.4, 7.2, 2.3 Hz, 2H), 7.03 (dd, J = 7.7, 3.4 Hz, 2H), 6.34 (d, J = 7.3 Hz, 2H), 6.09-5.99 (m, 1H), 5.92 (d, J = 17.4 Hz, 2H), 5.75 (brs, 2H).
**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 141.10, 136.39, 130.85, 127.63, 119.96, 117.65, 105.84.

**2-ethynyl-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (4i)**[12]




Isolated in 46% yield as a purple solid.
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.11 (dd, J = 8.3, 7.3 Hz, 2H), 7.05 (dd, J = 8.3, 1.1 Hz, 2H), 6.30 (dd, J = 7.3, 1.1 Hz, 2H), 5.85 (brs, 2H), 2.61 (s, 1H).
**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 140.38, 136.37, 127.66, 120.14, 118.19, 106.01, 90.78.
This compound was synthesized by a similar method to Procedure D: After a 25 mL of Schlenk tube were heated under vacuum for 5 minutes with the aid of a heating gun, the tube was cooled to room temperature and back-filled with argon. Ethynyl magnesium chloride (0.5 M in THF, 2 mmol, 2 eq.) and H–B(dan) (1 mmol, 1 eq.) were added and then stirred for 24 h at 0 °C. The reaction mixture was quenched with sat. $NH_4Cl$ aq. (5 mL). The layers were allowed to separate and the aqueous layer was extracted with diethyl ether (3 x 10 mL). The combined organics were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The crude material was purified on $SiO_2$ (10% to 25% EtOAc/Hexane) to afford the target compound.

**3-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)propan-1-ol (4j)**



Isolated in 85% yield as a gray solid.

mp: 98–99 °C.

**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.09 (dd, J = 8.3, 7.3 Hz, 2H), 7.00 (dd, J = 8.3, 1.0 Hz, 2H), 6.30 (dd, J = 7.3, 1.0 Hz, 2H), 5.70 (brs, 2H), 3.69 (td, J = 6.4, 4.0 Hz, 2H), 1.77-1.67 (m, 2H), 1.36 (t, J = 5.0 Hz, 1H), 0.96-0.89 (m, 2H).

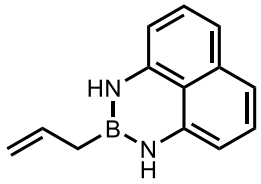
**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 141.24, 136.41, 127.68, 119.67, 117.51, 105.60, 64.92, 27.88.

**$^{11}$B NMR** (186 MHz, $CDCl_3$) δ 31.68.

HRMS (APCI) Calcd for $C_{13}H_{15}BN_2O$: [M+H]+, 227.13502. Found: m/z 227.13438

This compound was synthesized by a similar method to Procedure C: After a 25 mL of Schlenk tube was heated under vacuum for 5 minutes with the aid of a heating gun, the tube was cooled to room temperature and back-filled with argon. 3-Chloro-1-propanol (2 mmol, 2 eq.) and THF (2 mL) were then added. After cooling to -20 °C, *tert*-butyl magnesium chloride (2 mmol, 2 eq.) was added dropwise and then stirred for 1 h. After raising to room temperature, the mixture was heated to reflux for 15 minutes and cooled to room temperature. To the mixture were added magnesium turnings (2.4 mmol, 2.4 eq.) and 1,2-dibromoethane (1-2 drop), and the mixture was heated to reflux for 9 h. H–B(dan) (168.0 mg, 1 mmol, 1 eq.) was added after the mixture was cooled to room temperature. After stirring for additional 8 h at room temperature, the mixture was quenched with sat. $NH_4Cl$ aq. (5 mL). The layers were allowed to separate and the aqueous layer was extracted with diethyl ether (3 x 10 mL). The combined organics were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The crude material was purified on $SiO_2$ (10% to 25% EtOAc/Hexane) to afford **4j**.

**2-allyl-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (4k)**[5]



Isolated in 95% yield as a gray liquid.

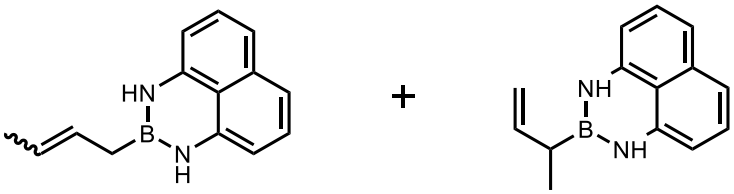
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.10 (dd, J = 8.3, 7.2 Hz, 2H), 7.02 (dd, J = 8.4, 1.0 Hz, 2H), 6.31 (dd, J = 7.3, 1.0 Hz, 2H), 5.97-5.85 (m, 1H), 5.62 (brs, 2H), 5.11-5.03 (m, 2H), 1.82 (d, J = 7.8 Hz, 2H).

**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 141.10, 136.42, 135.26, 127.67, 119.71, 117.70, 115.73, 105.73.

This compound was synthesized by a similar method to Procedure C: A 25 mL of Schlenk tube was charged with magnesium turnings (1.2 mmol, 1.2 eq.). After the tube was heated under

vacuum for 5 minutes with the aid of a heating gun, the tube was cooled to room temperature and back-filled with argon. Iodine (0.01 mmol, 1 mol %) and THF (2 mL) were then added. After stirring for 10 minutes at room temperature, 3-bromoprop-1-ene (2 mmol, 2 eq.) and H–B(dan) (1 mmol, 1 eq.) were added and the resulting mixture was stirred for 24 h. The reaction mixture was quenched with sat. $NH_4Cl$ aq. (5 mL). The layers were allowed to separate and the aqueous layer was extracted with diethyl ether (3 x 10 mL). The combined organics were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The crude material was purified on $SiO_2$ (10% to 25% EtOAc/Hexane) to afford **4k**.

**2-(but-2-en-1-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine(4l) and 2-(but-3-en-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (4'l)**[5]




Isolated in 67% yield (42:58) as a black liquid.

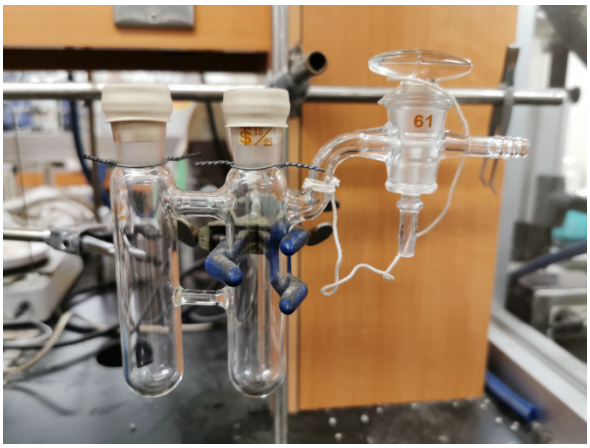
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.13 (t, J = 8.5 Hz, 4H, **4l + 4'l**), 7.04 (d, J = 7.2 Hz, 4H, **4l + 4'l**), 6.33 (d, J = 7.0 Hz, 4H, **4l + 4'l**), 6.03-5.89 (m, 1H, **4'l**), 5.61 (s, 4H, **4l + 4'l**), 5.56-5.44 (m, 2H, **4l**), 5.12-5.03 (m, 2H, **4'l**), 1.97 (quint, J = 7.6 Hz, 1H, **4'l**), 1.77-1.64 (m, 5H, **4l**), 1.20 (d, J = 7.3 Hz, 3H, **4'l**).

**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 142.09, 141.21, 141.15, 136.42, 128.14, 127.06, 126.25, 126.16, 124.50, 119.70, 118.00, 117.69, 117.58, 112.76, 106.42, 106.01, 105.81, 105.66, 18.27, 14.89, 12.77.

These compounds were synthesized by a similar procedure to that for **4k**.

## 5. Mechanic studies

### 5-1 $H_2$ Trapping Experiment.[13]




Two-chamber Schlenk tube (chamber I: left; chamber II: right)

**The procedure for Fig. 6A.** As shown in the above photo, a two-chamber Schlenk tube was used for this experiment. At first, magnesium turnings (81.7 mg, 3.36 mmol, 1.68 eq.) was placed in the chamber I. After the tube was heated under vacuum for 5 minutes with the aid of a heating gun, the tube was cooled to room temperature and back-filled with argon. Iodine (2.6 mg, 0.02 mmol, 1 mol %) and THF (4 mL) were then added. After stirring for 10 minutes at room temperature, phenyl bromide (439.8 mg, 2.8 mmol, 1.4 eq.) was added and the mixture was stirred for 1 h at room temperature. Next, chamber Ⅱ was charged with 5% Pd/C (10.6 mg, 5.00 μmol, 1 mol % of Pd), *trans*-stilbene (90.1 mg, 0.50 mmol, 0.5 eq.) and THF (0.50 mL). To the chamber I, H–B(dan) (336.0 mg, 2 mmol, 1 eq.) was added. After stirring at room temperature for 16 h, the resulting each solution was treated separately for subsequent work-up. Regarding the solution in the chamber I, the mixture was quenched with sat. $NH_4Cl$ aq. (10 mL). The layers were allowed to separate and the aqueous layer was extracted with diethyl ether (3 x 10 mL). The combined organics were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The crude material was purified on $SiO_2$ (EtOAc/Hexane = 1/5) to afford **3a** in 87% yield. On the other hand, the solution in the chamber Ⅱ was filtered through a pad of Celite (***CAUTION***: the Celite pad may not be dried up after the filtration due to possible ignition of the activated Pd/C), and then evaporation of the solvent followed by column chromatography on silica gel (EtOAc/Hexane = 1/20) gave 1,2-diphenylethane in 88% yield. Accordingly, only $^1$H NMR data of 1,2-diphenylethane are provided here. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.35-7.28 (m, 4H), 7.26-7.19 (m, 6H), 2.96 (s, 4H).

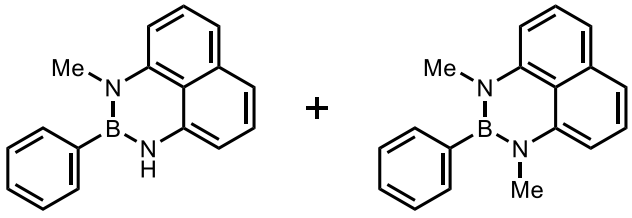
### 5-2 Quenching with Me–OTs

**The procedure for Fig. 6B, Exp. 1.** A 25 mL of Schlenk tube was charged with magnesium

turnings (1.68 mmol, 1.68 eq.). After the tube was heated under vacuum for 5 minutes with the aid of a heating gun, the tube was cooled to room temperature and back-filled with argon. Iodine (0.01 mmol, 1 mol %) and THF (2 mL) were then added. After stirring for 10 minutes at room temperature, phenyl bromide (1.4 mmol, 1.4 eq.) was added. After stirring for 1 h at room temperature, H–B(dan) (1 mmol, 1 eq.) was added and the mixture was stirred for 3 h. To the resulting mixture was added MeOTs (372.5 mg, 2 mmol, 2 eq.) and stirring was continued at room temperature for additional 24 h. The reaction mixture was quenched with sat. $NH_4Cl$ aq. (5 mL). The layers were allowed to separate and the aqueous layer was extracted with diethyl ether (3 x 10 mL). The combined organics were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The crude material was purified on $SiO_2$ (EtOAc/Hexane = 1/20) to afford **3a** in 55% yield, **3'a** in 29% yield, and **3"a** in 12% yield (**3'a** and **3"a** were obtained as an inseparable mixture).

**The procedure for Fig. 6B, Exp. 2.** A 25 mL of Schlenk tube was heated under vacuum for 5 minutes with the aid of a heating gun, and the tube was cooled to room temperature and back-filled with argon. Isolated **3a** (5 mmol, 1 eq.), MeOTs (0.5 mmol, 1 eq.) and THF (1 mL) were then added. After stirring for 24 h at room temperature, the reaction mixture was quenched with sat. $NH_4Cl$ aq. (5 mL). The layers were allowed to separate and the aqueous layer was extracted with diethyl ether (3 x 10 mL). The combined organics were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The crude material was found to only contain **3a** (100% recovery) by $^1H$ NMR.

**1-methyl-2-phenyl-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3'a) and 1,3-dimethyl-2-phenyl-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3"a)**



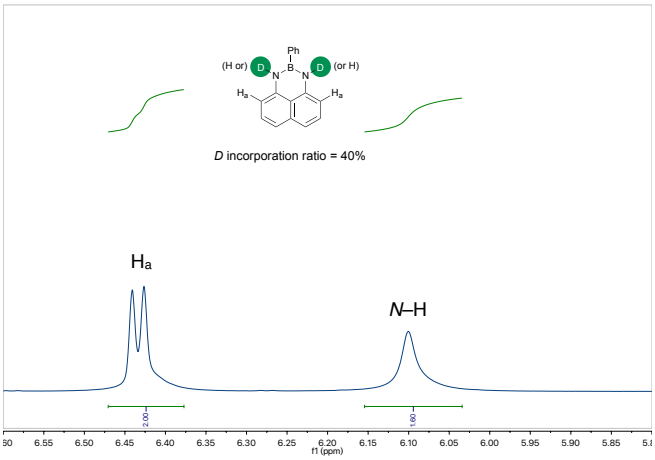

**$^1H$ NMR** (500 MHz, $CDCl_3$) δ 7.63-7.56 (m, **3'a**), 7.49-7.43 (m, **3'a** + **3"a**), 7.38-7.10 (m, **3'a** + **3"a**), 6.52 (dd, J = 14.6, 7.7 Hz, **3'a**), 6.40 (dd, J = 7.1, 1.3 Hz, **3"a**), 5.92 (brs, **3'a**), 3.09 (s, **3"a)**, 2.92 (s, **3'a**).

**$^{13}C$ NMR** (125 MHz, $CDCl_3$) δ 143.99, 143.21, 140.49, 136.26, 135.98, 132.45, 131.86, 129.09, 128.40, 128.24, 128.21, 127.81, 127.41, 127.38, 118.36, 118.29, 117.79, 105.94, 103.76, 103.69, 35.74, 34.84.

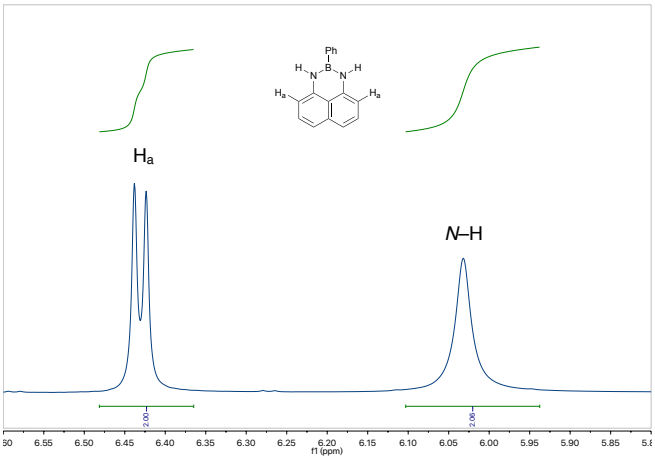
**$^{11}B$ NMR** (186 MHz, $CDCl_3$) δ 30.89.

**5-3 Quenching with $D_2O$**

**The procedure for Fig. 6C.** A 25 mL of Schlenk tube was charged with magnesium turnings (1.68 mmol, 1.68 eq.). After the tube was heated under vacuum for 5 minutes with the aid of a heating gun, the tube was cooled to room temperature and back-filled with argon. Iodine (0.01 mmol, 1 mol %) and THF (2 mL) were then added. After stirring for 10 minutes at room temperature, phenyl bromide (1.4 mmol, 1.4 eq.) was added. After stirring for 1 h at room temperature, H–B(dan) (1 mmol, 1 eq.) was added and the mixture was stirred for 3 h. To the resulting mixture was added $D_2O$ (40.1 mg, 2 mmol, 2 eq.) and stirring was continued at room temperature for additional 24 h. The reaction mixture was concentrated by rotary evaporation. The deuterium incorporation ratio (40%, see below) and the NMR yield (75%, anisole as an internal standard) were determined by $^1$H NMR spectrum of the crude material.




$^1$H NMR spectrum of **3a** + **3a-*d*$_1$** + **3a-*d*$_2$**




$^1$H NMR spectrum of **3a**

## 6. Iterative SMC of 5-bromo-2-pyridyl–B(dan)

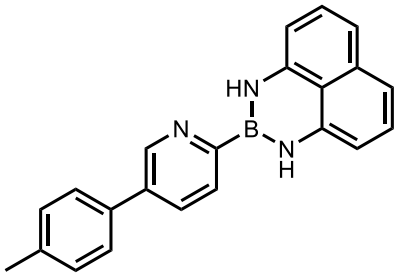
### 6-1 Selective SMC at the Ar–Br bond of 3w[6]

After a 25 mL of Schlenk tube were heated under vacuum for 5 minutes with the aid of a heating gun, the tube was cooled to room temperature and back-filled with argon. $Pd(PtBu_3)_2$ (8 μmol, 2 mol %), CsF (0.8 mmol, 2 eq.), **3w** (0.4 mmol, 1 eq.), *p*-tolyl boronic acid (0.8 mmol, 2 eq.), and THF (1 mL) was added. The resulting mixture was stirred at reflux for 6 h. After quenching the mixture with brine (20 mL), the resulting mixture was extracted with EtOAc (15 mL × 3). The combined organics were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The crude material was purified on $SiO_2$ (EtOAc/Hexane as an eluent) to afford a cross-coupling product, **6** in 45% yield.

### 6-2 Direct SMC at the Ar–B(dan) bond of 6[9,14]

After a 25-mL of Schlenk tube were heated under vacuum for 5 minutes with the aid of a heating gun, the tube was cooled to room temperature and back-filled with argon. $Pd(PPh_3)_4$ (5.8 mg, 5 μmol, 5 mol %), **6** (33.5 mg, 0.1 mmol, 1 eq.), 4-iodobenzotrifluoride (27.2 mg, 0.1 mmol, 1 eq.), and 1,4-dioxane (1 mL) was added. The mixture was stirred at 100 °C for 5 min before addition of *t*-BuOK (1 M in THF, 0.15 mL, 0.15 mmol). The resulting mixture was stirred at 100 °C for 4 h. After quenching the mixture with brine (20 mL), the resulting mixture was extracted with EtOAc (15 mL × 3). The combined organics were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The crude material was purified on $SiO_2$ (EtOAc/Hexane as an eluent) to afford a cross-coupling product, **7** in 52% yield.

**2-(5-(*p*-tolyl)pyridin-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (6)**




Isolated in 45% yield as a yellow solid.

mp: 182–183 °C.

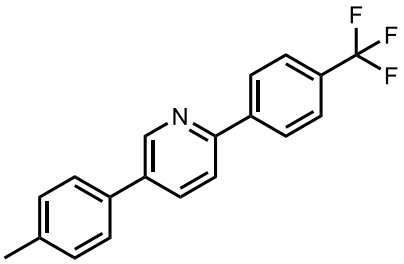
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 9.03 (dd, J = 2.3, 0.9 Hz, 1H), 7.89 (dd, J = 7.8, 2.3 Hz, 1H), 7.69 (dd, J = 7.9, 1.0 Hz, 1H), 7.56-7.51 (m, 2H), 7.32 (d, J = 8.3 Hz, 2H), 7.15 (dd, J = 8.3, 7.3 Hz, 2H), 7.06 (dd, J = 8.3, 1.0 Hz, 2H), 6.58 (brs, 2H), 6.47 (dd, J = 7.3, 1.0 Hz, 2H), 2.43 (s, 3H).

**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 148.65, 141.16, 138.51, 137.19, 136.57, 134.90, 132.95, 130.03, 127.78, 127.14, 126.77, 120.50, 118.01, 106.34, 21.34.

**$^{11}$B NMR** (186 MHz, $CDCl_3$) δ 27.70.

HRMS (APCI) Calcd for $C_{22}H_{18}BN_3$: $[M+H]^+$, 336.16665. Found: m/z 336.16724

**5-(*p*-tolyl)-2-(4-(trifluoromethyl)phenyl)pyridine (7)**




Isolated in 52% yield as a white solid.

mp: 227–228 °C.

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.95 (dd, J = 2.4, 0.9 Hz, 1H), 8.16 (d, J = 8.8 Hz, 2H), 7.98 (dd, J = 8.2, 2.4 Hz, 1H), 7.83 (dd, J = 8.3, 0.9 Hz, 1H), 7.75 (d, J = 8.2 Hz, 2H), 7.55 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 7.9 Hz, 2H), 2.43 (s, 3H).

**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 154.35, 148.35, 142.50, 138.48, 135.91, 135.16, 134.53, 130.85 (q, J = 32.4 Hz), 130.06, 127.18, 127.03, 125.87 (q, J = 3.7 Hz), 124.36 (q, J = 272.2 Hz), 120.81, 21.35.

**$^{19}$F NMR** (470 MHz, $CDCl_3$) δ -63.82.

HRMS (APCI) Calcd for $C_{19}H_{14}F_3N$: $[M+H]^+$, 314.11511. Found: m/z 314.11526

## 7. References

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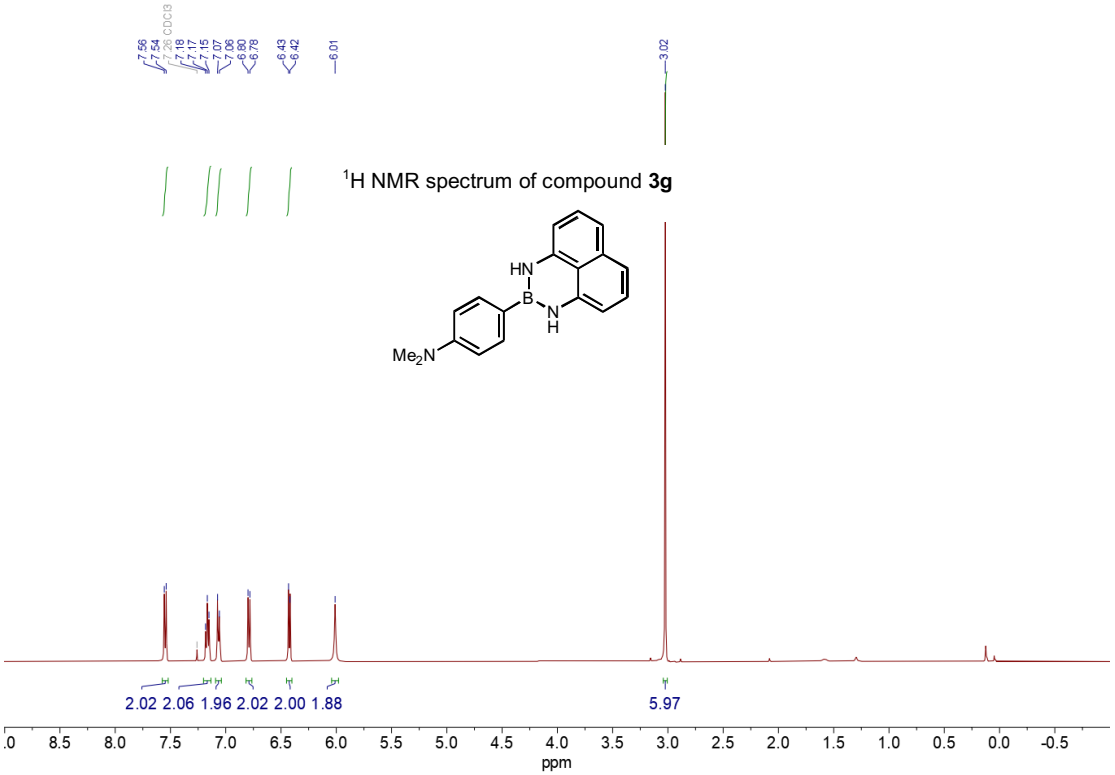
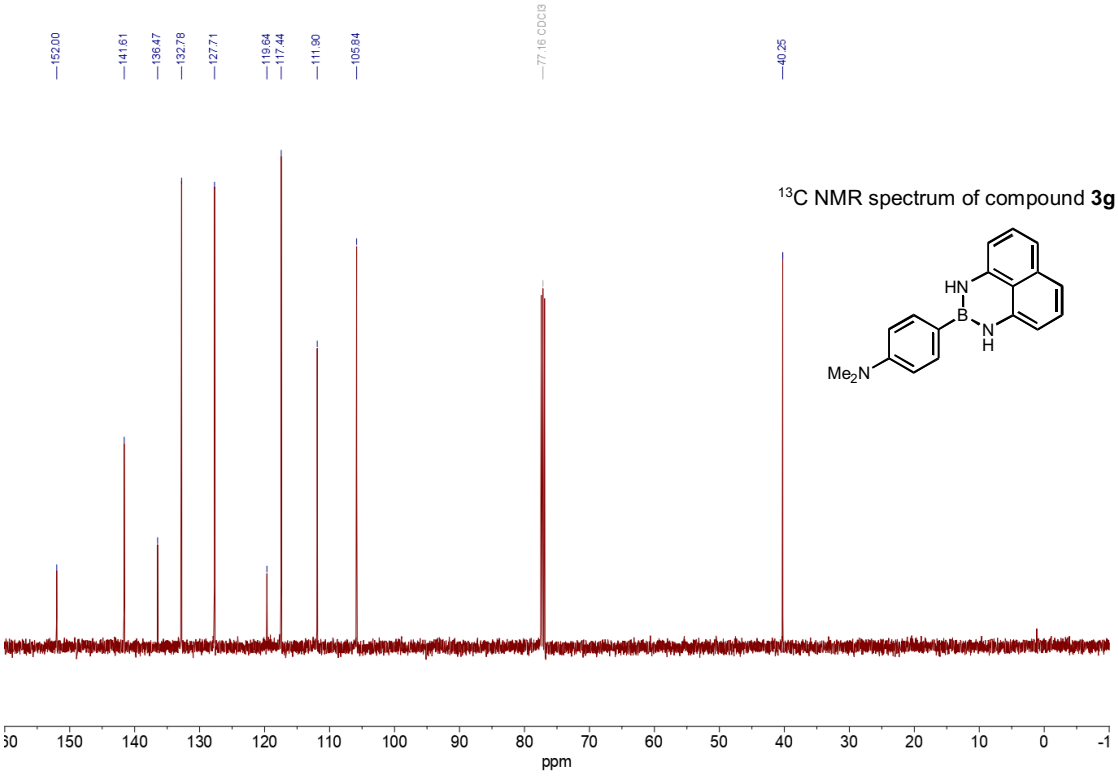
# 8. NMR spectra



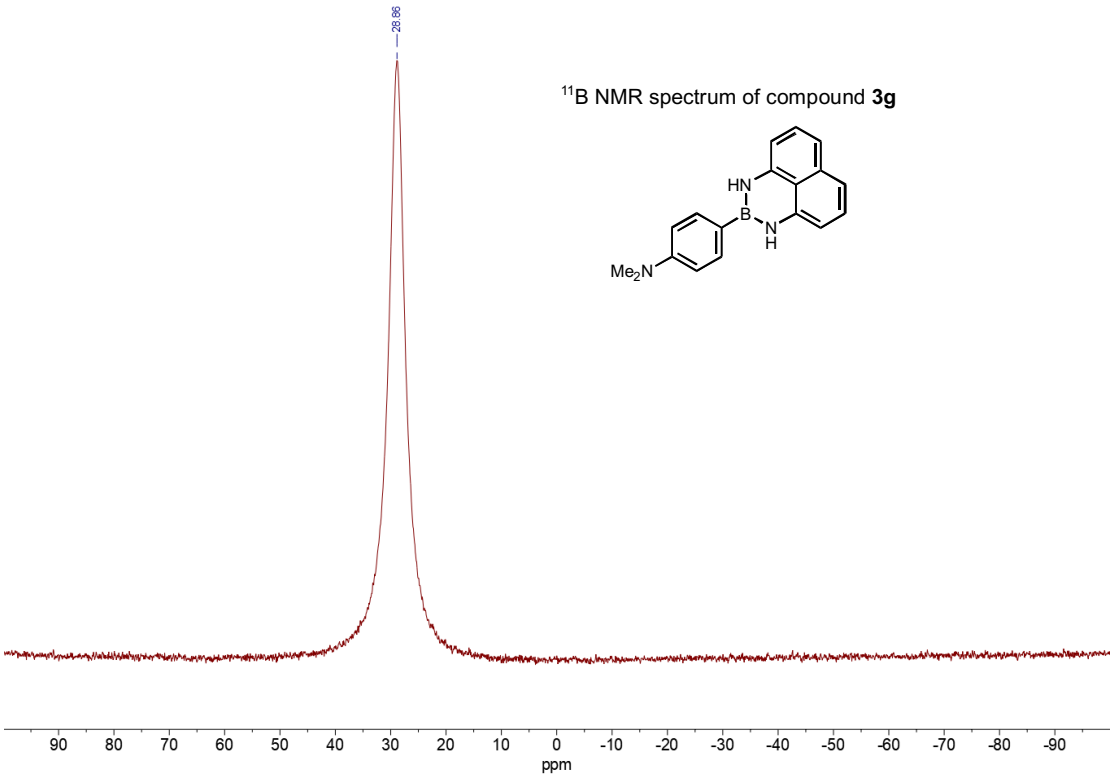

$^{1}$H NMR spectrum of compound **3g**

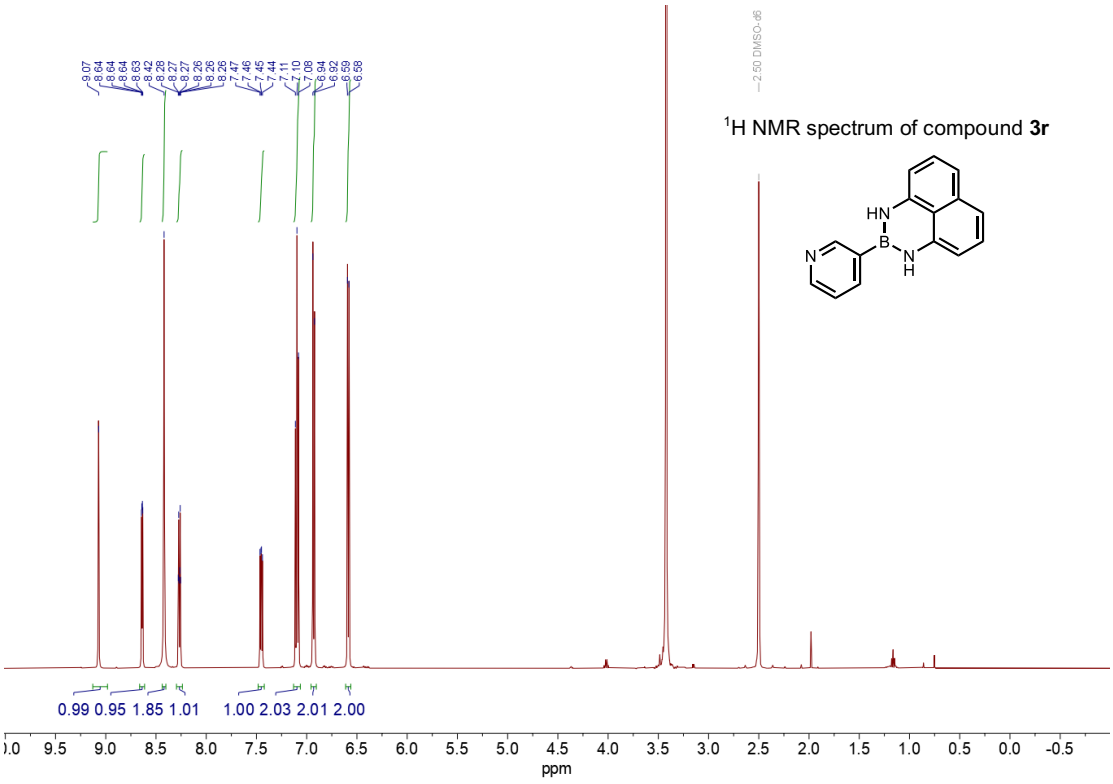



$^{13}$C NMR spectrum of compound **3g**

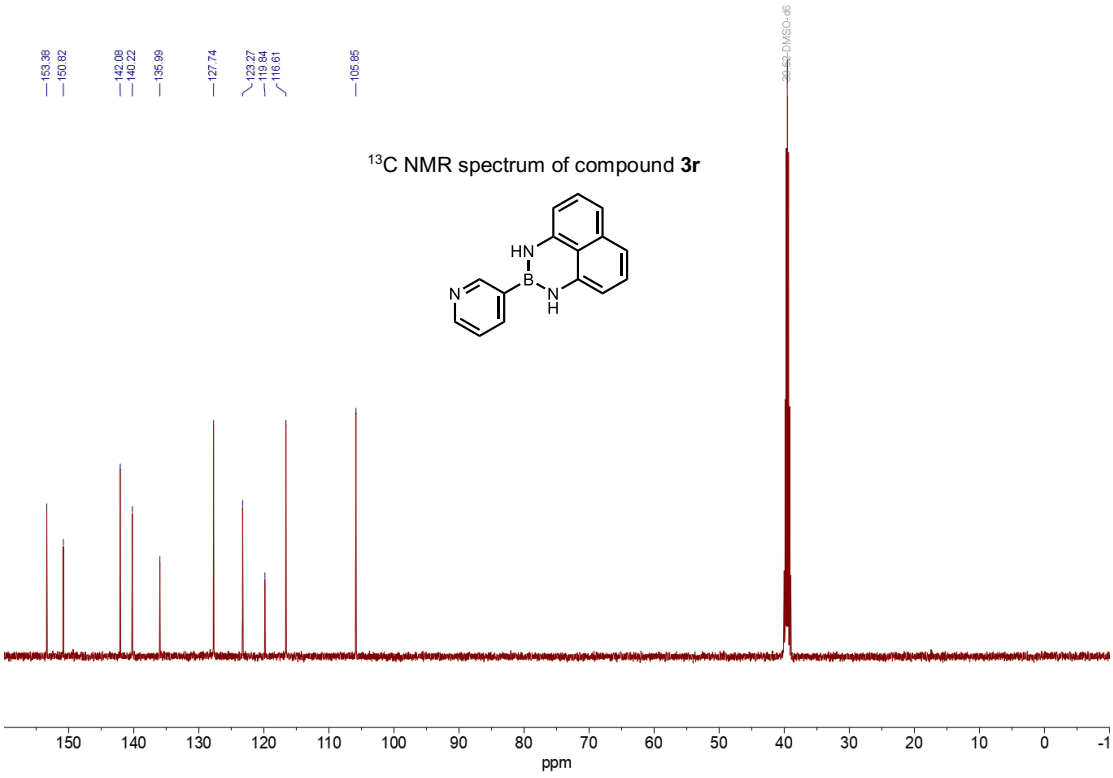
$^{11}$B NMR spectrum of compound **3g**



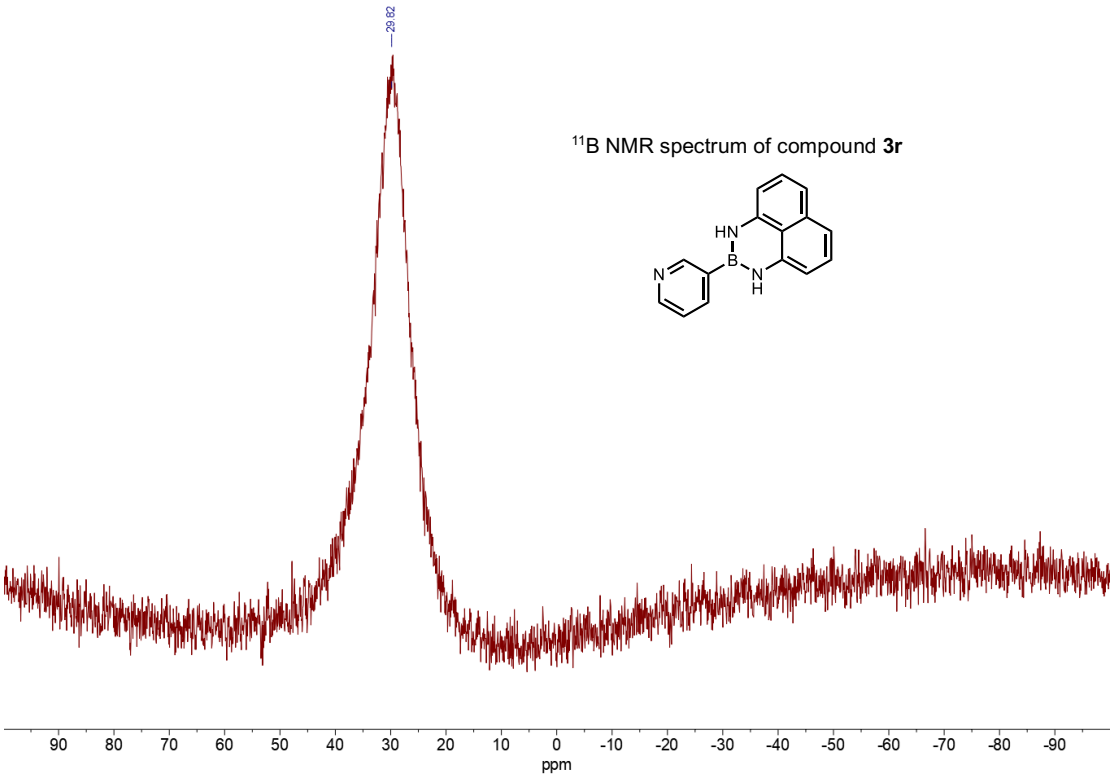



$^{1}$H NMR spectrum of compound **3r**

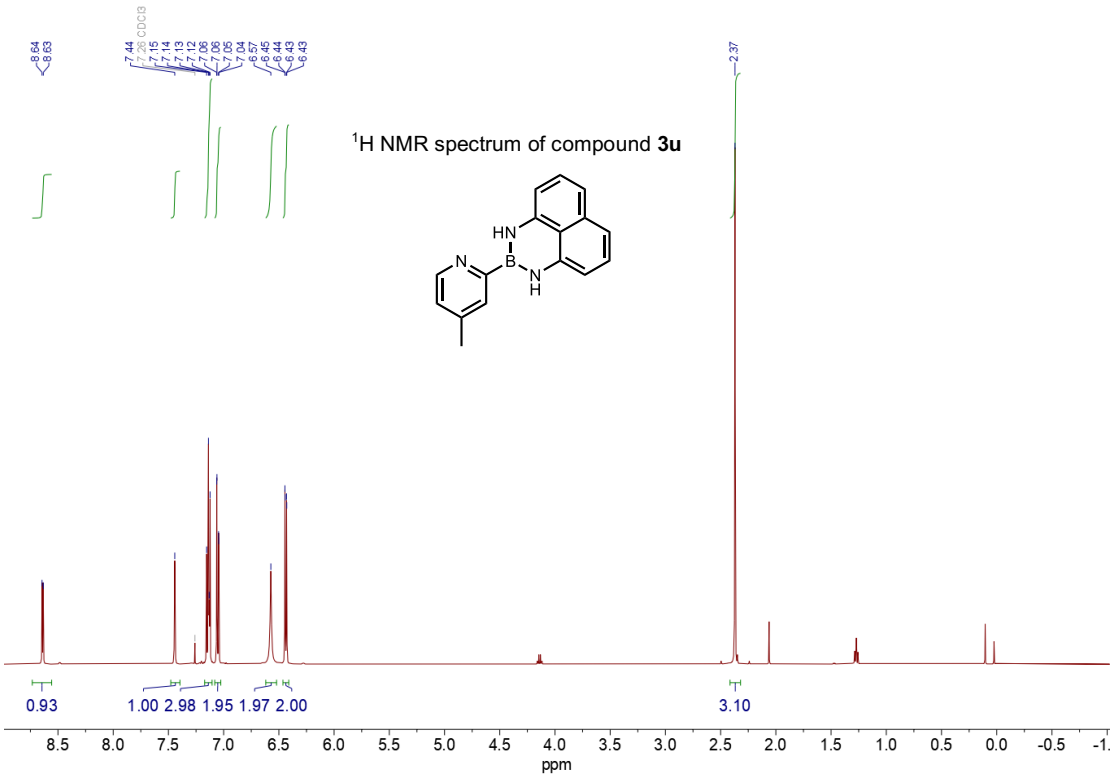



$^{13}$C NMR spectrum of compound **3r**

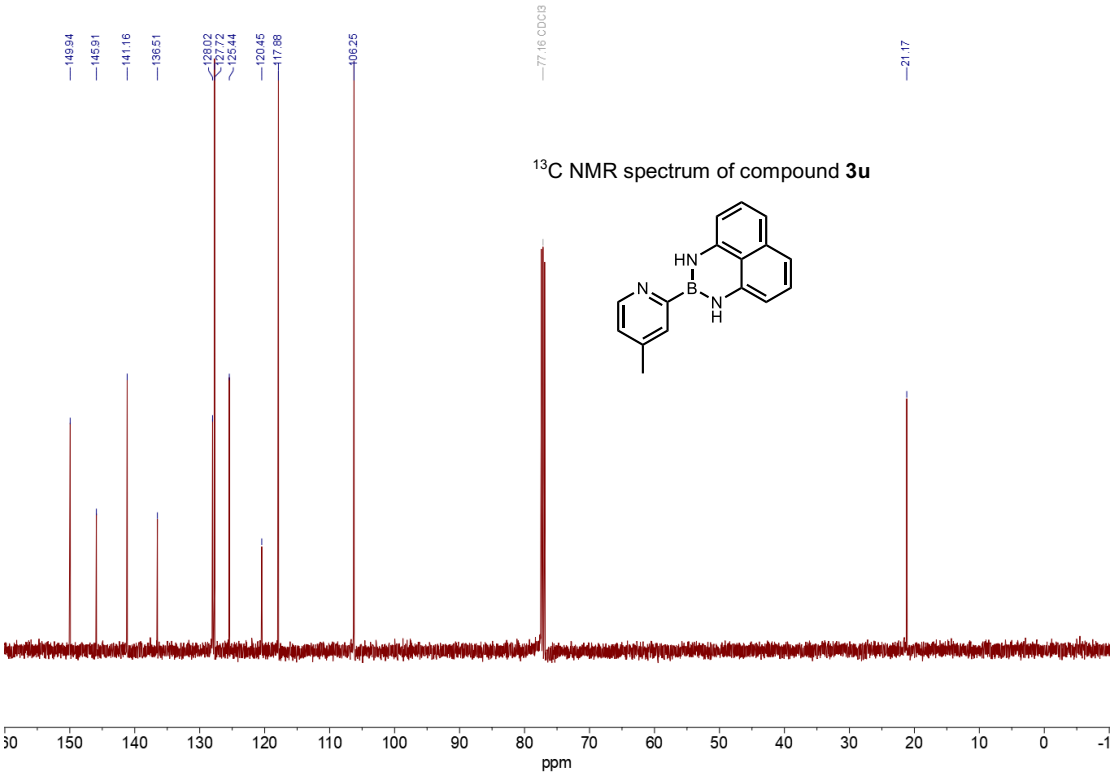



$^{11}$B NMR spectrum of compound **3r**

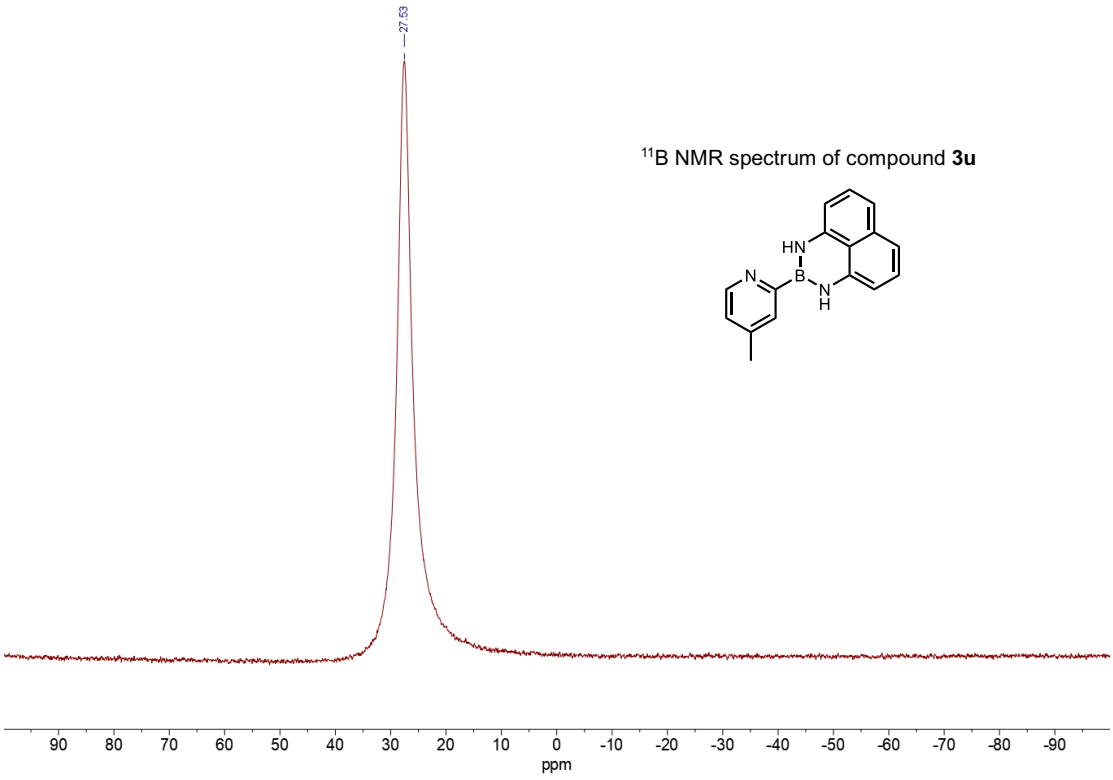



$^{1}$H NMR spectrum of compound **3u**




$^{13}$C NMR spectrum of compound **3u**

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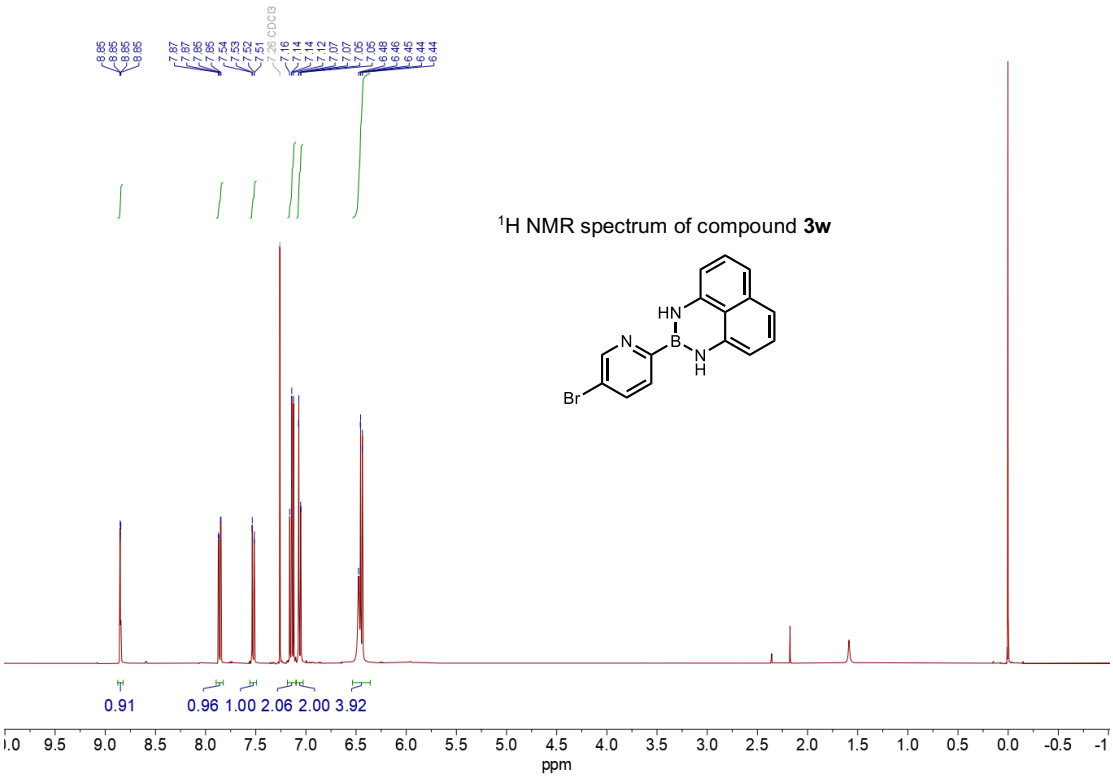


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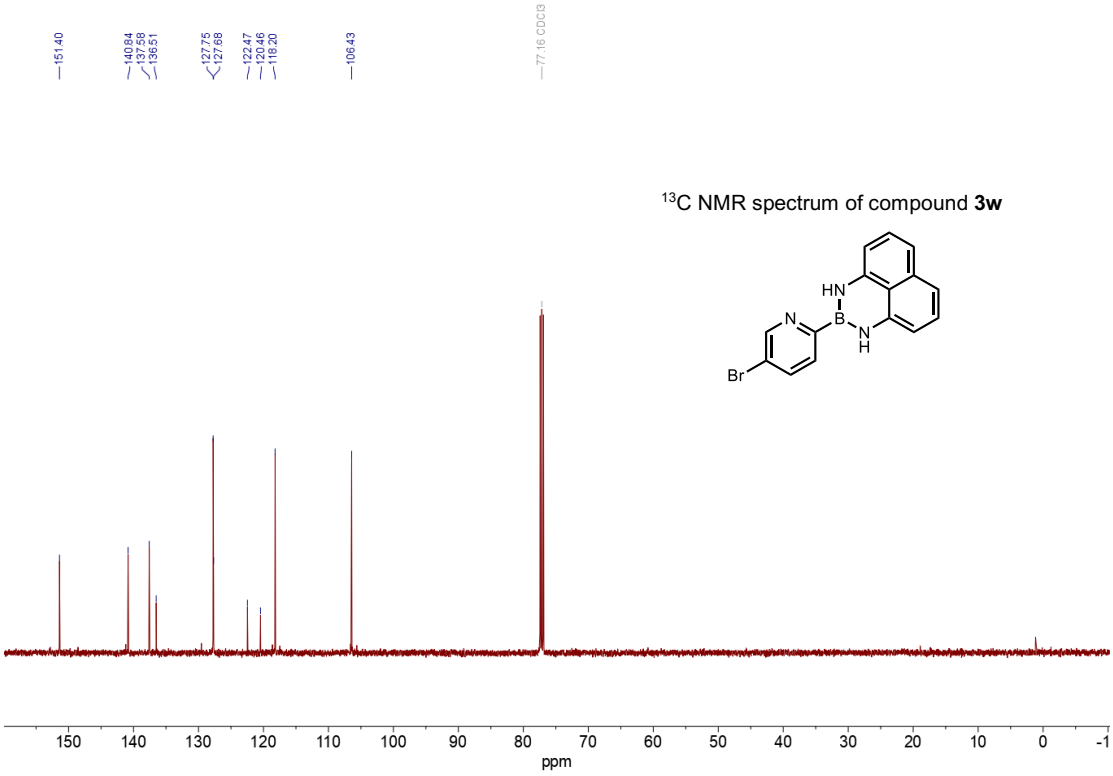
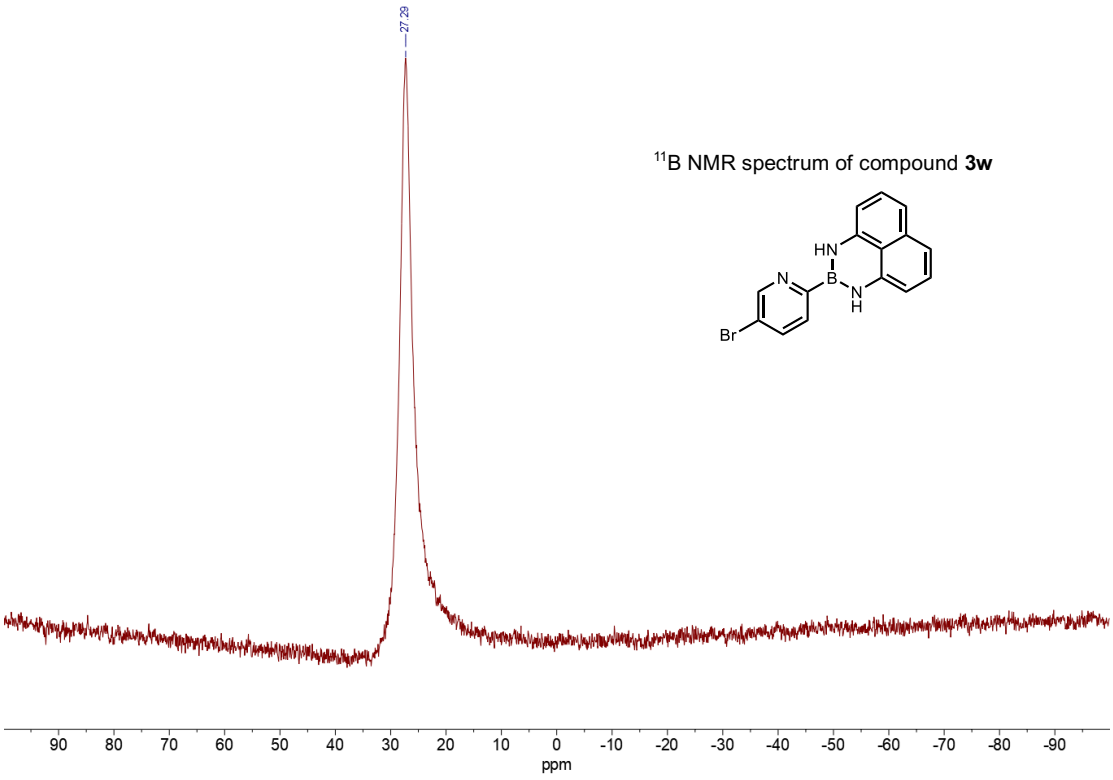



$^{13}$C NMR spectrum of compound **3w**

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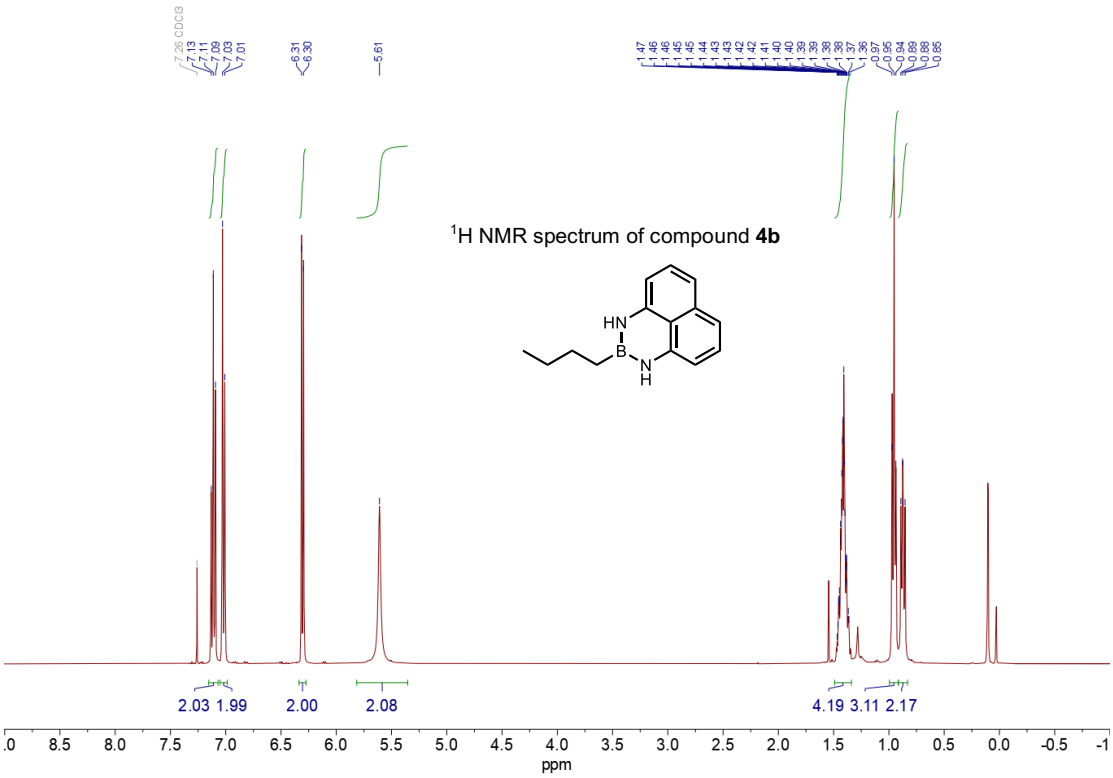
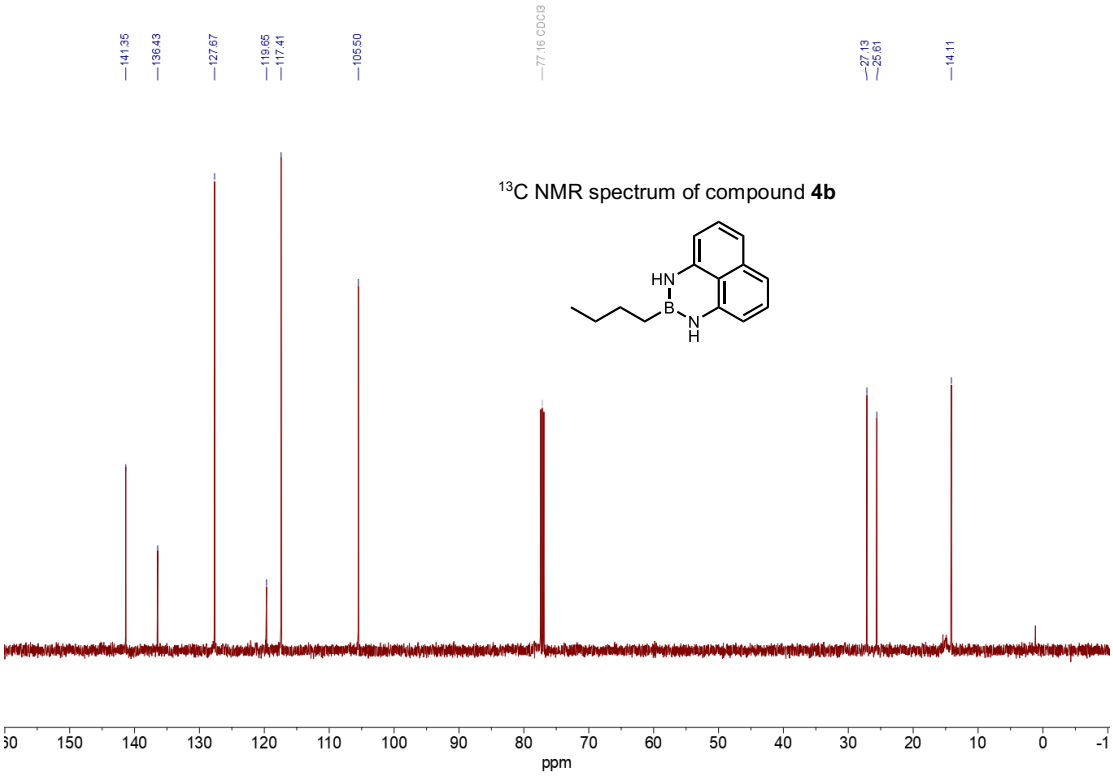
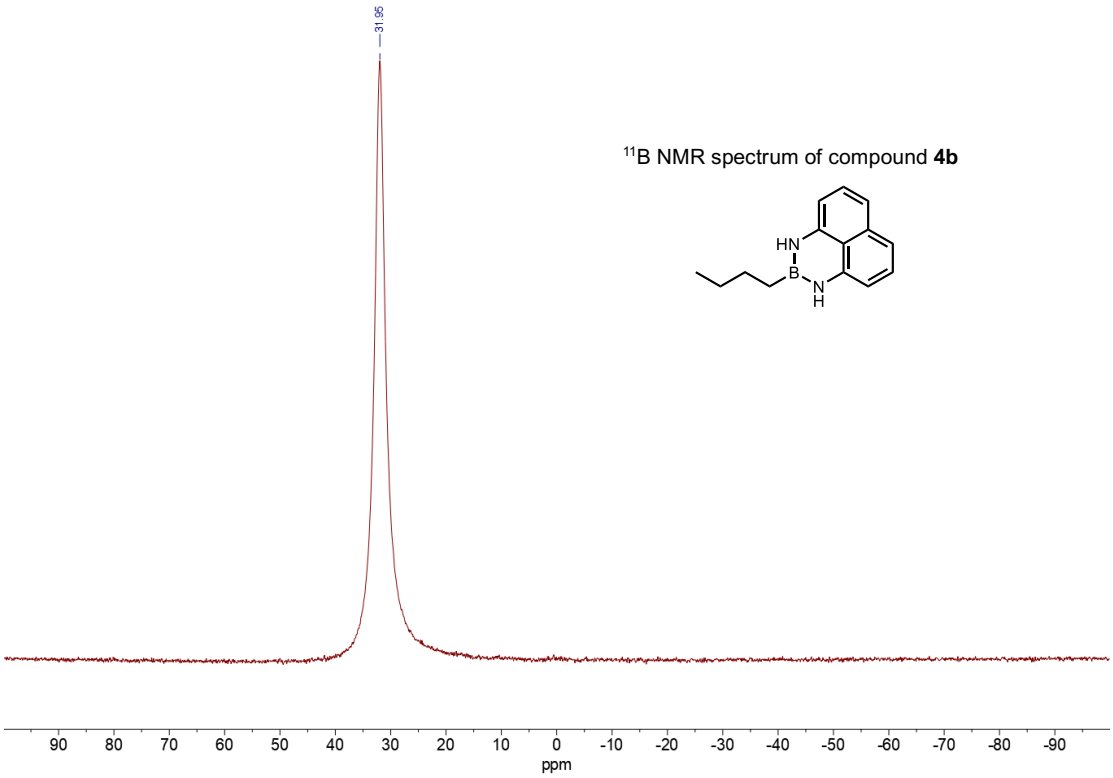



$^{1}$H NMR spectrum of compound **4b**

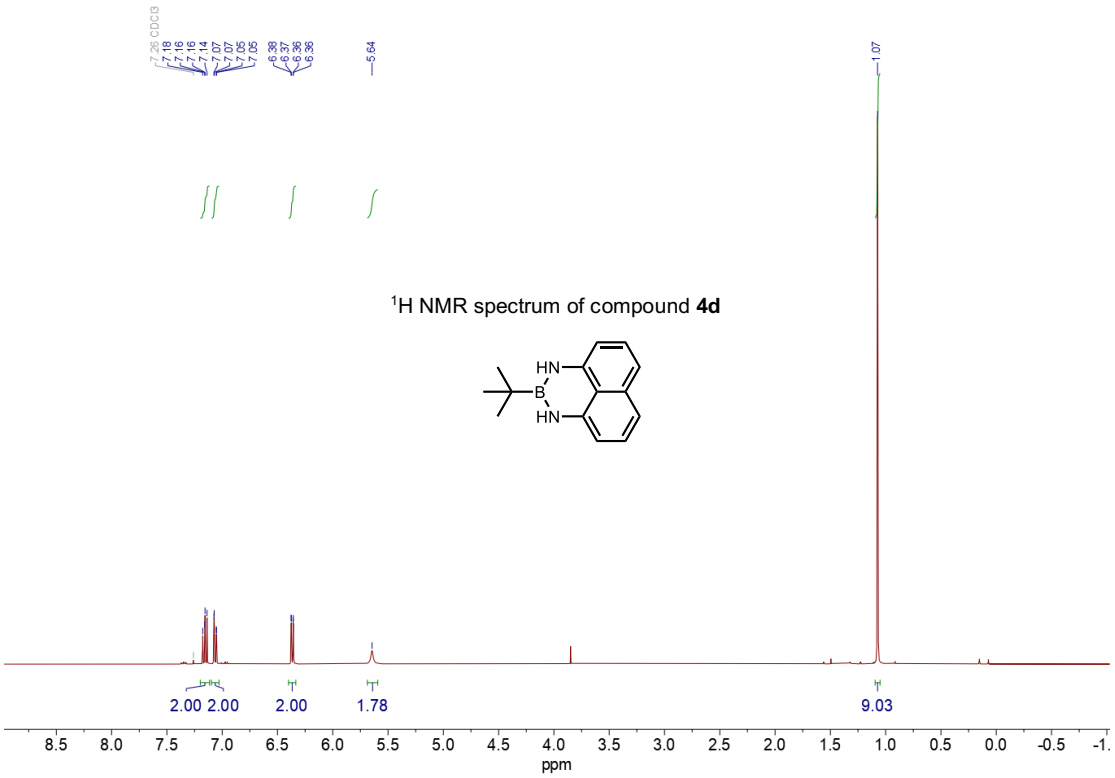



$^{13}$C NMR spectrum of compound **4b**




$^{11}$B NMR spectrum of compound **4b**

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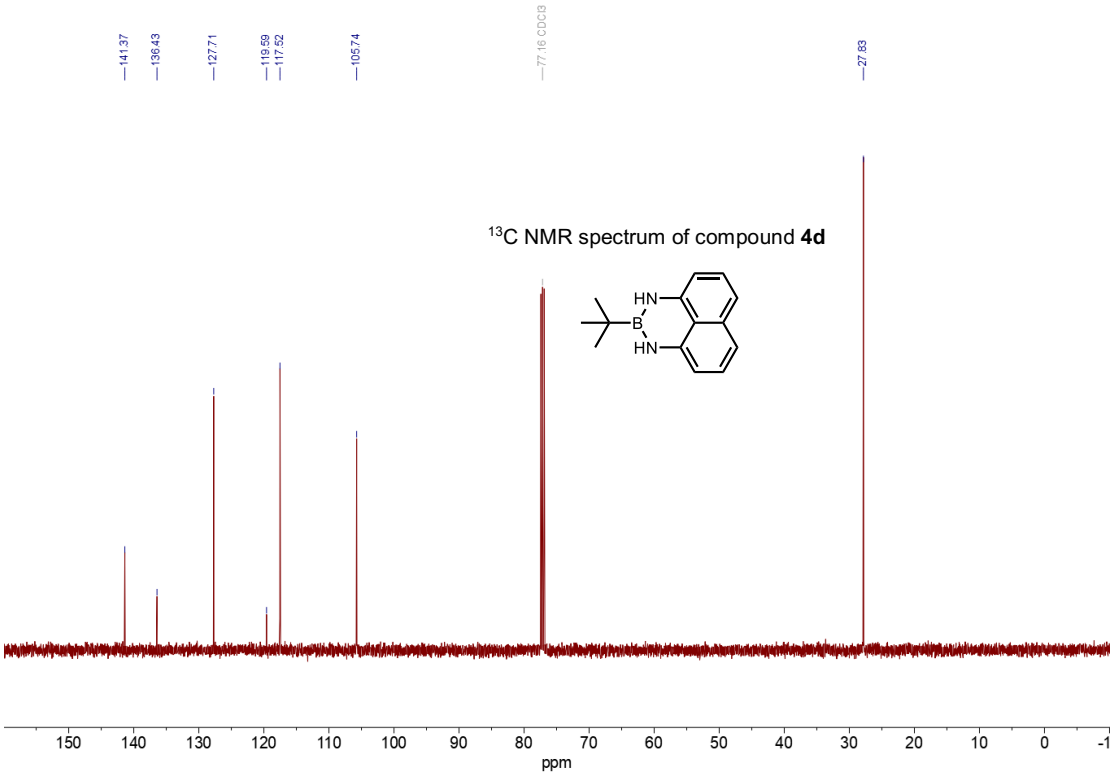
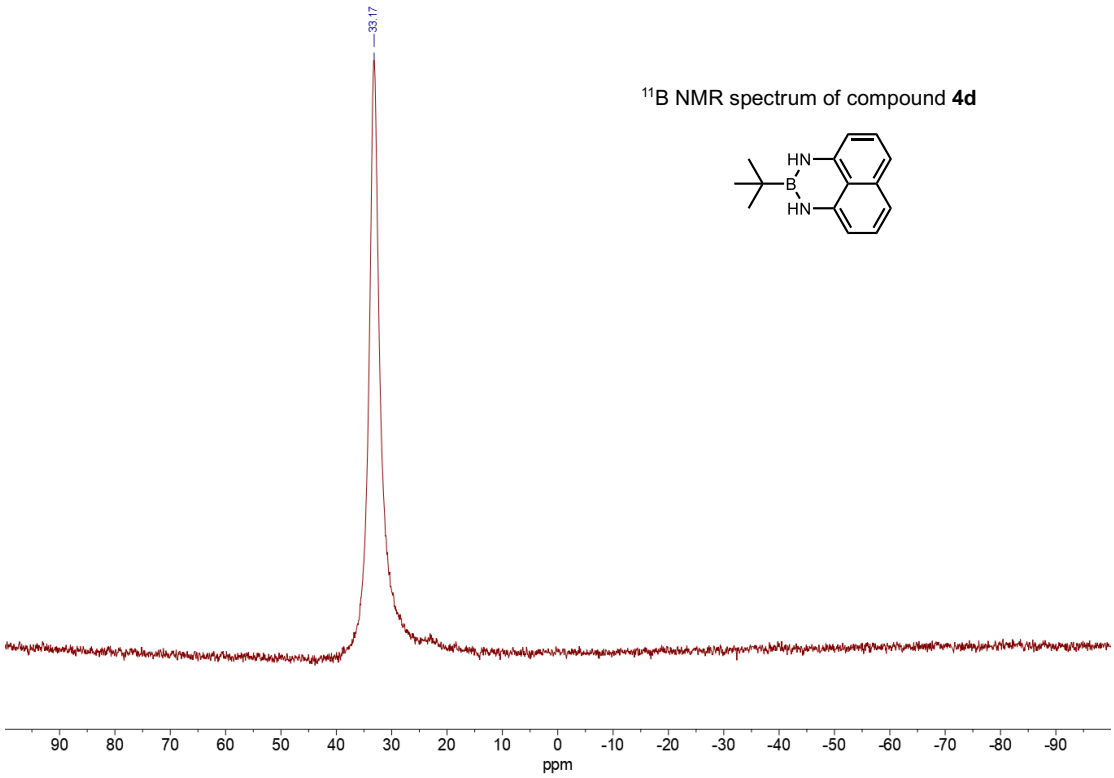



$^{13}$C NMR spectrum of compound **4d**

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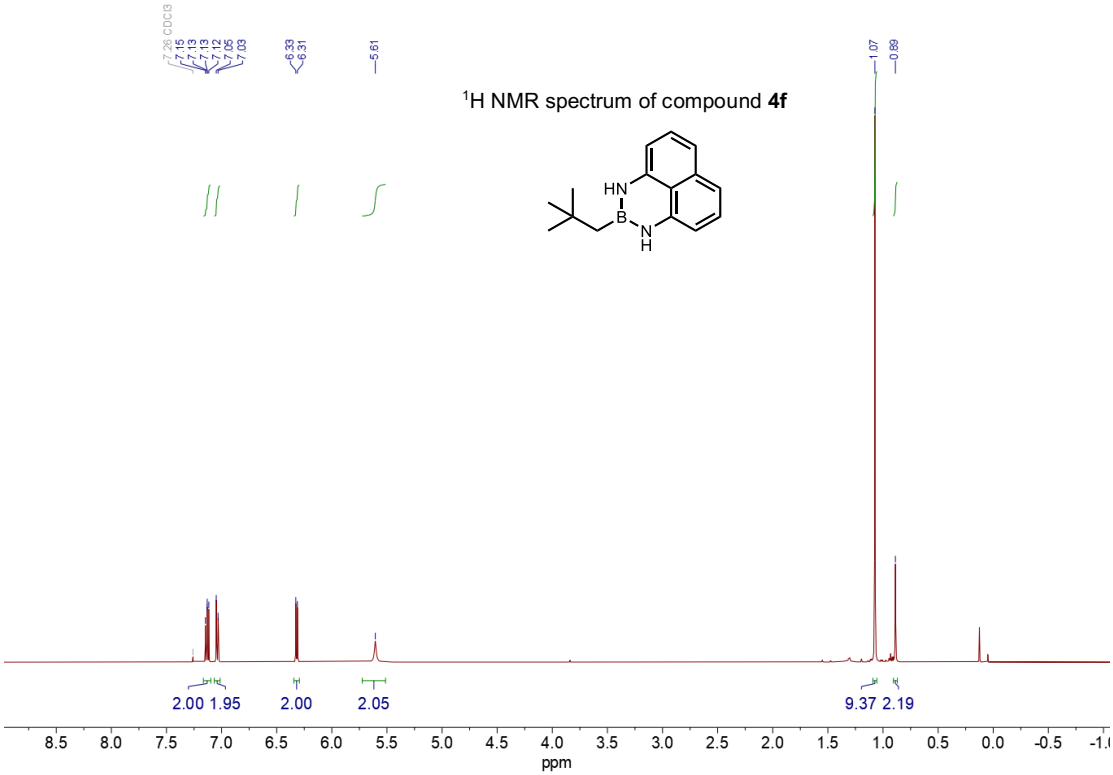


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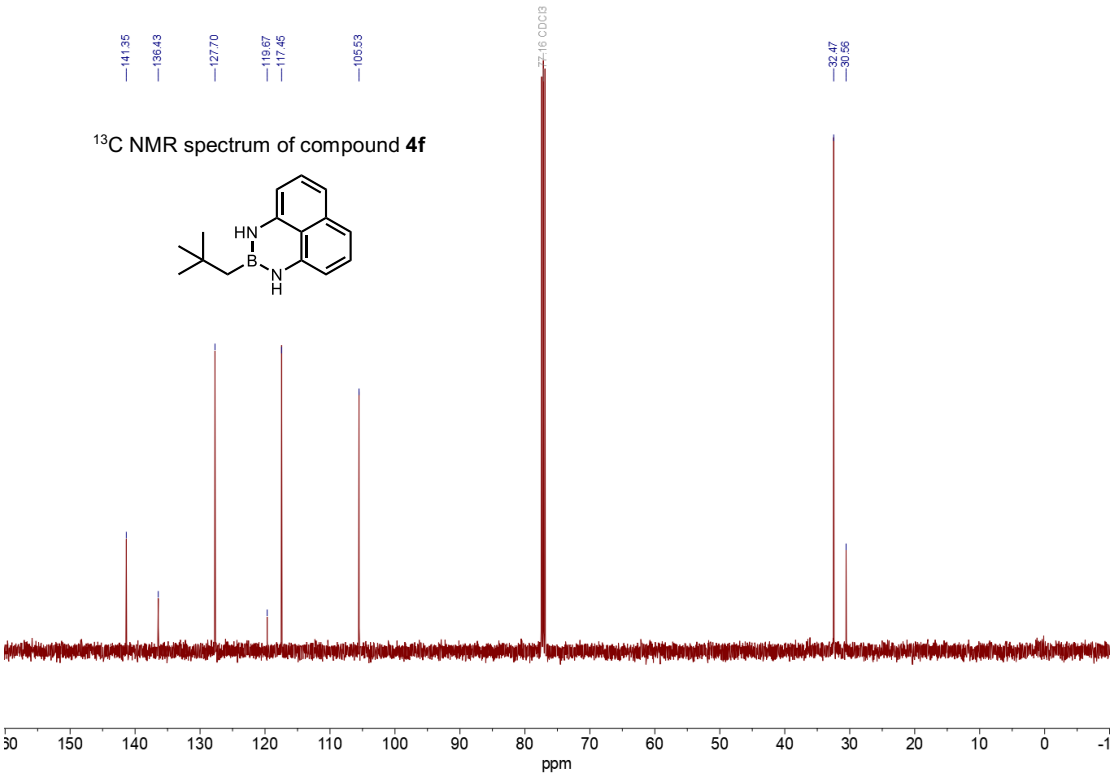


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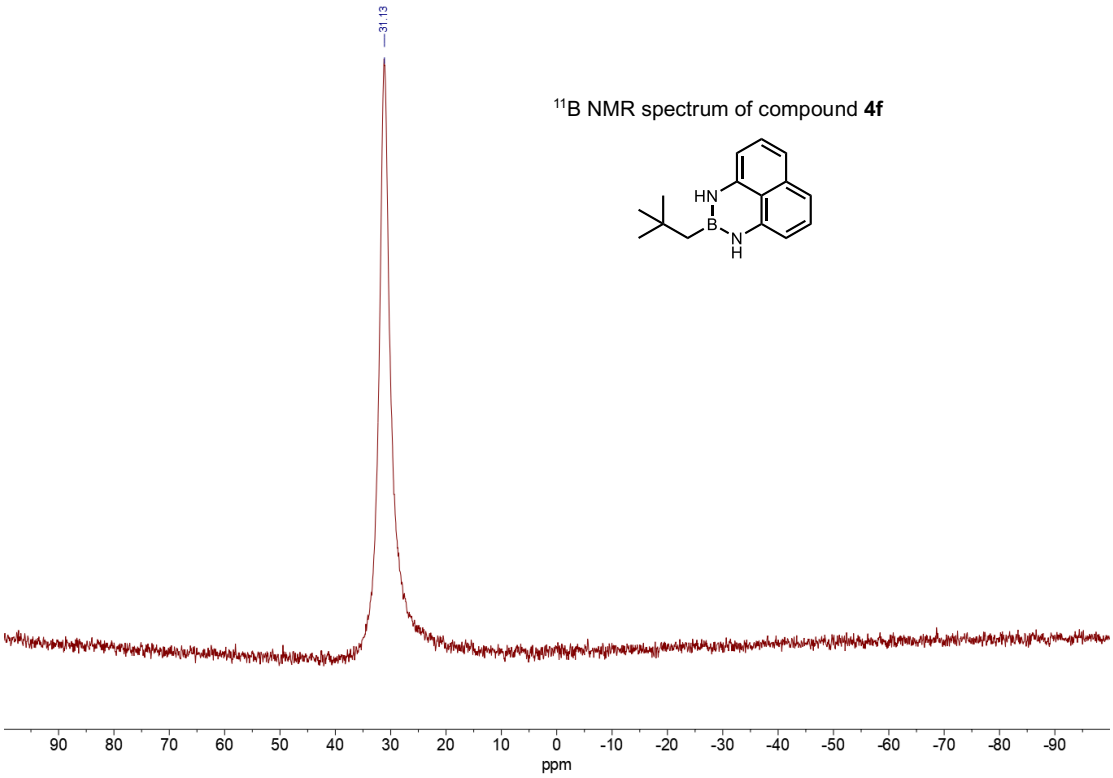


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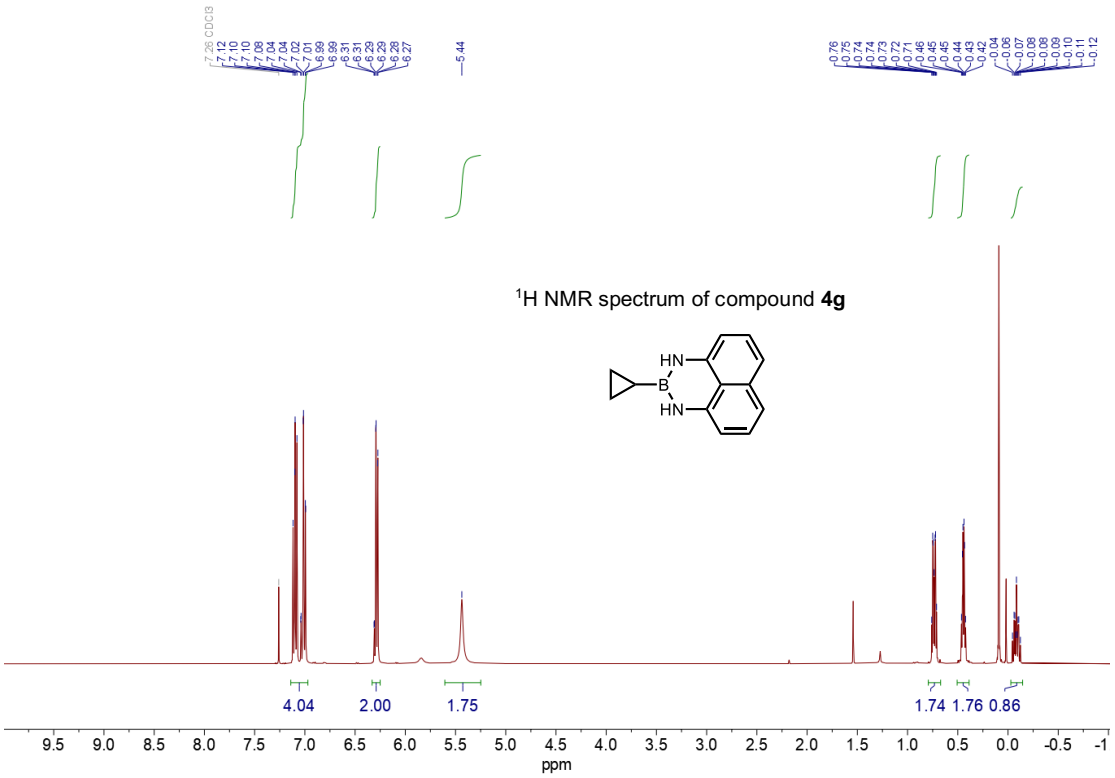


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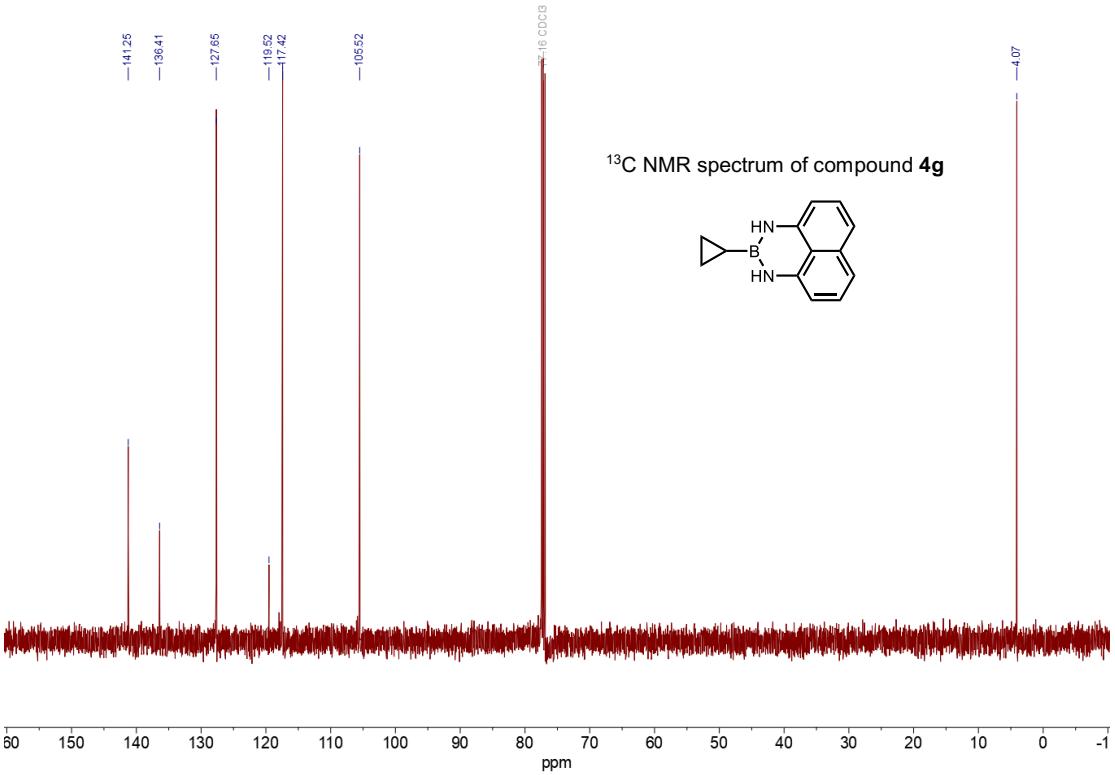


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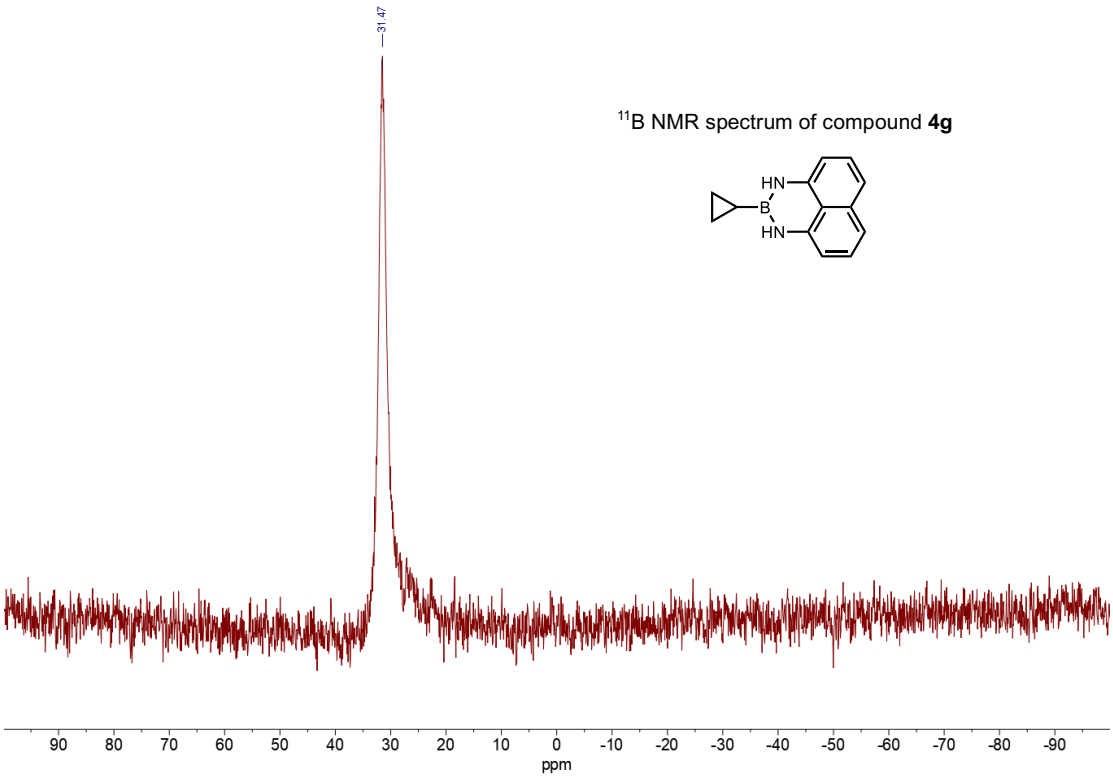


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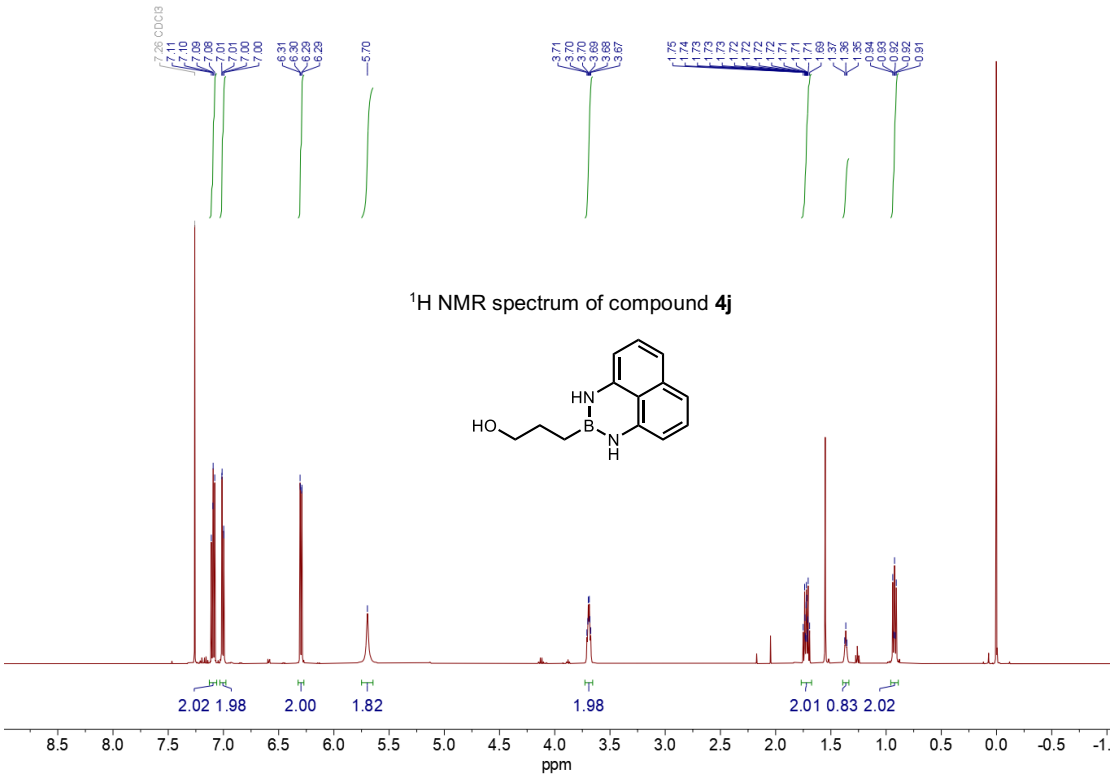


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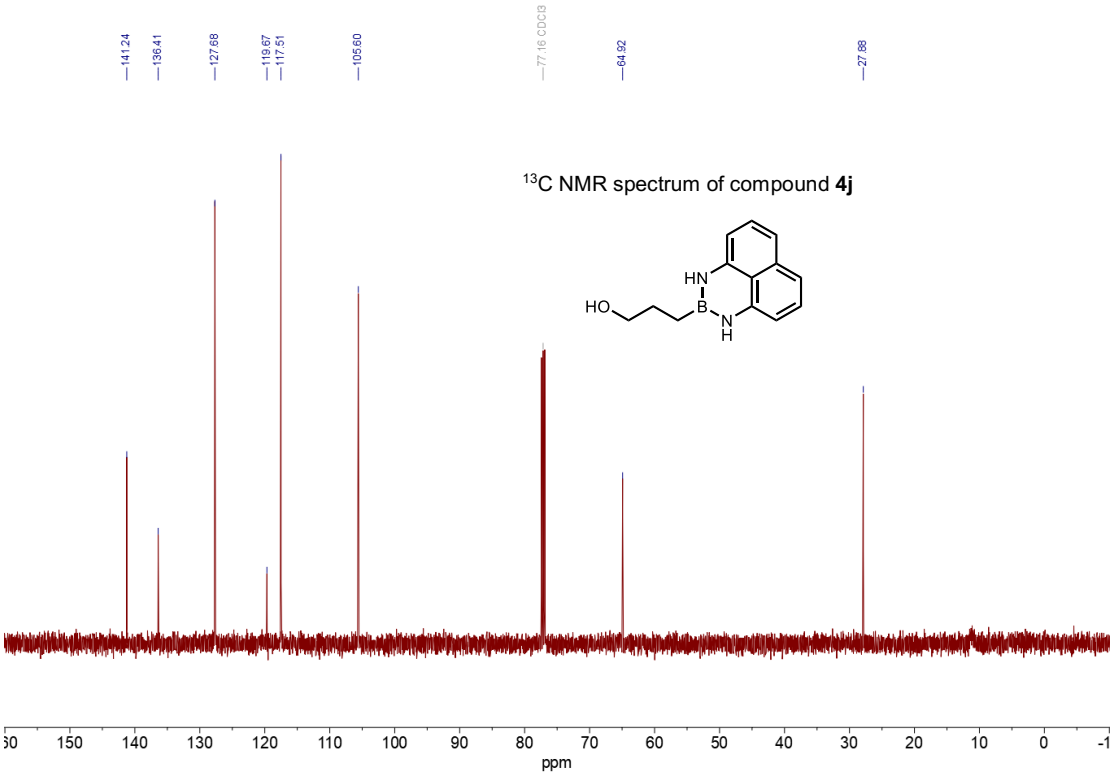


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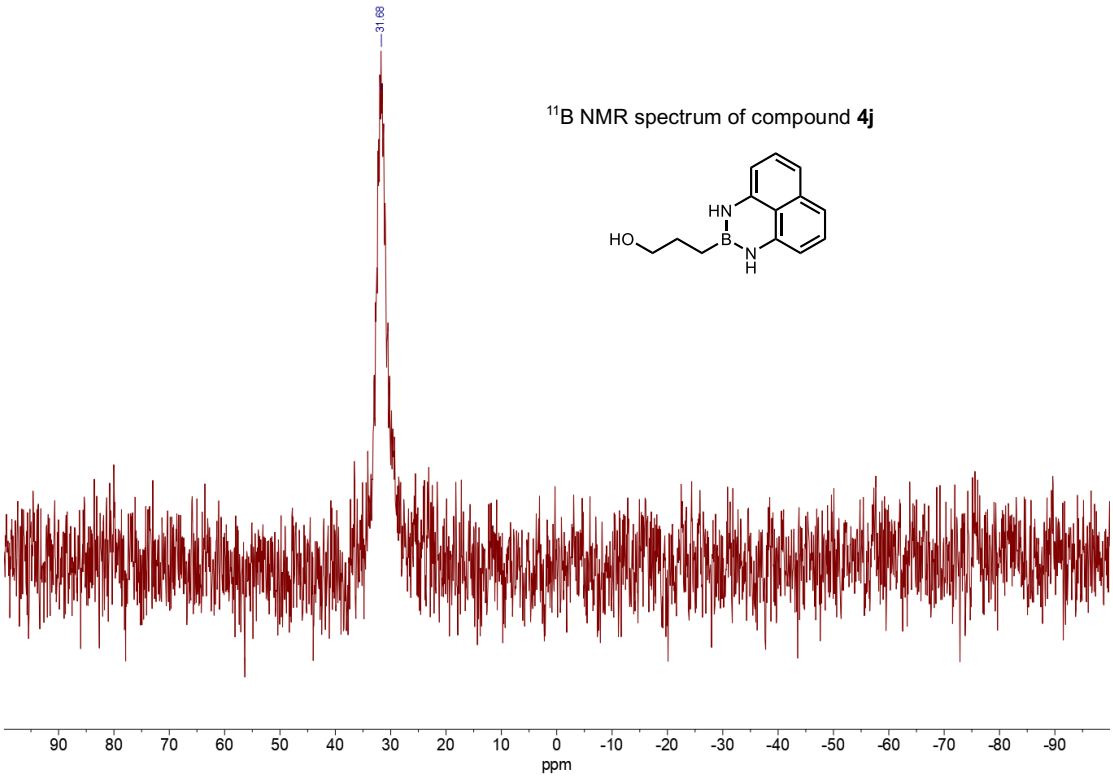


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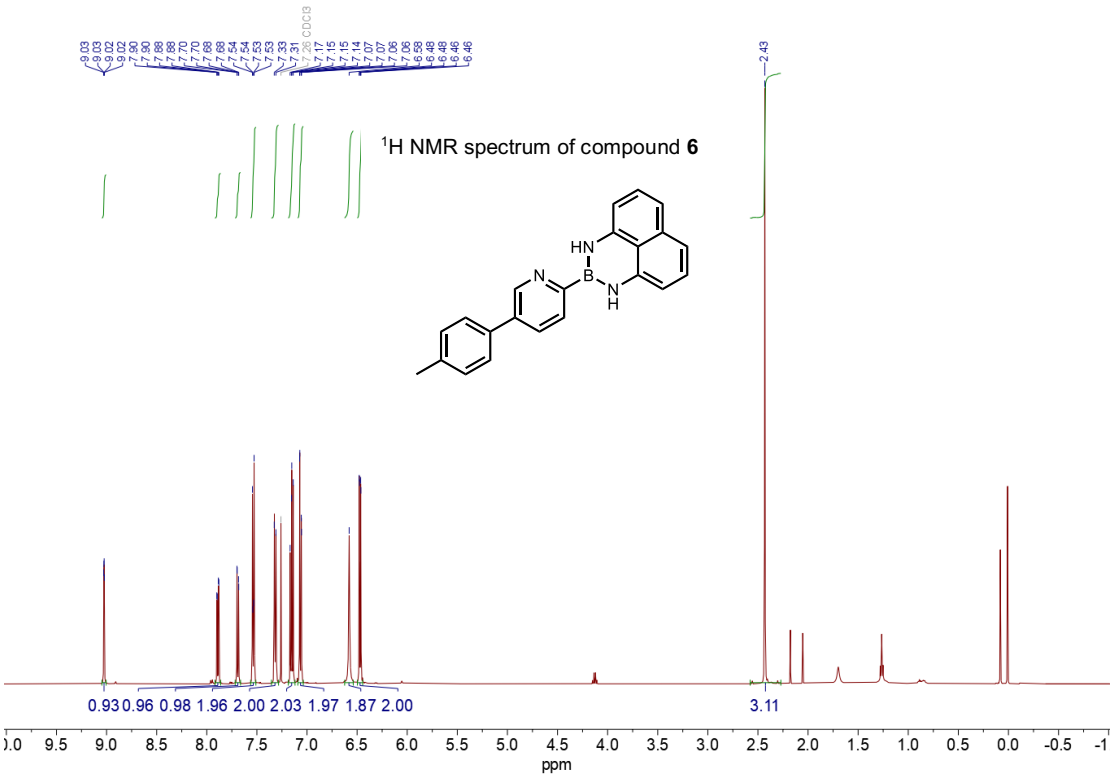


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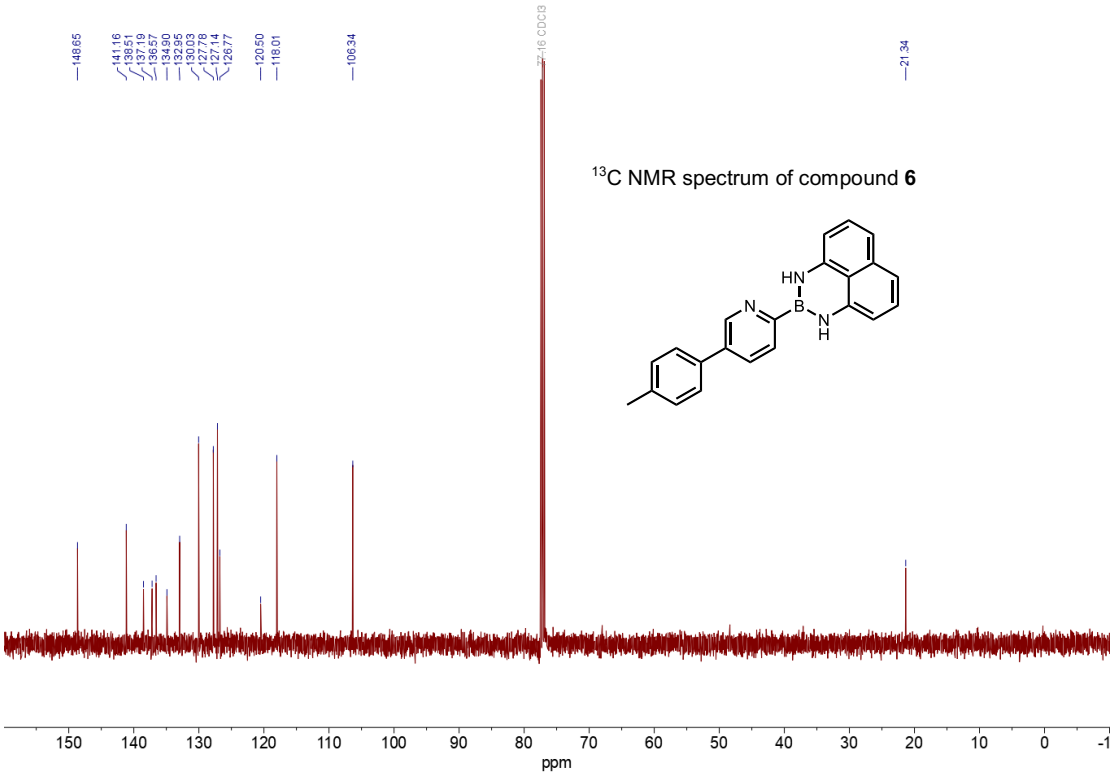


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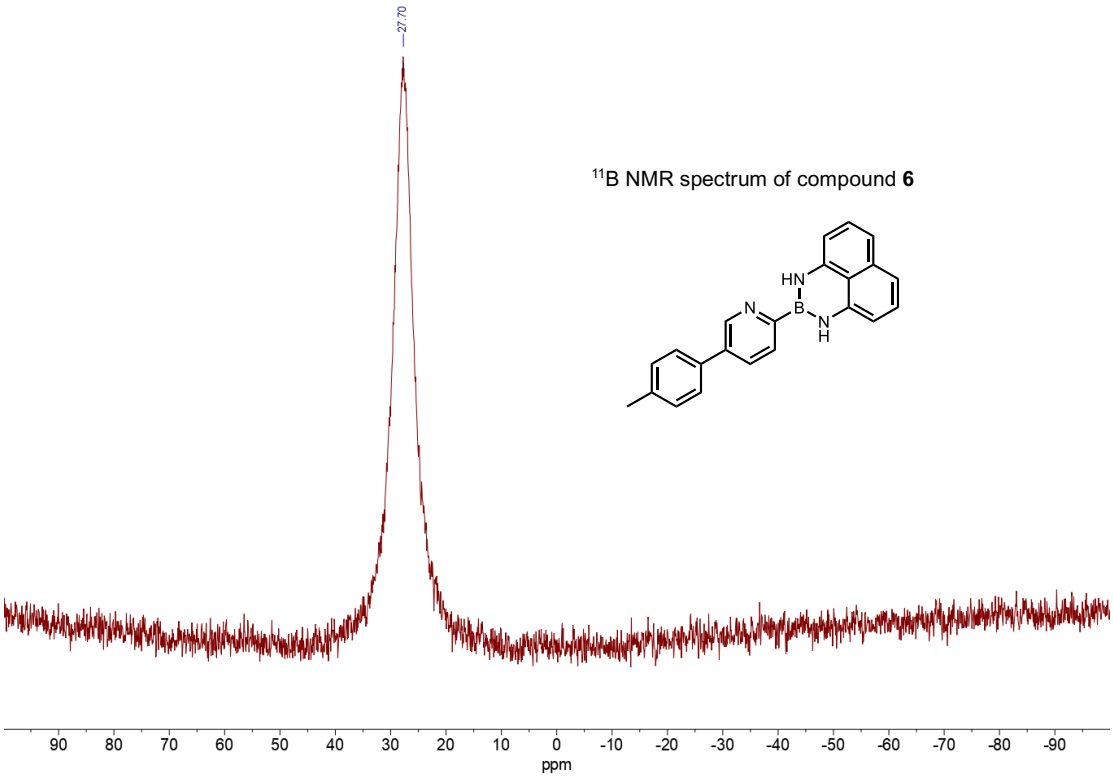


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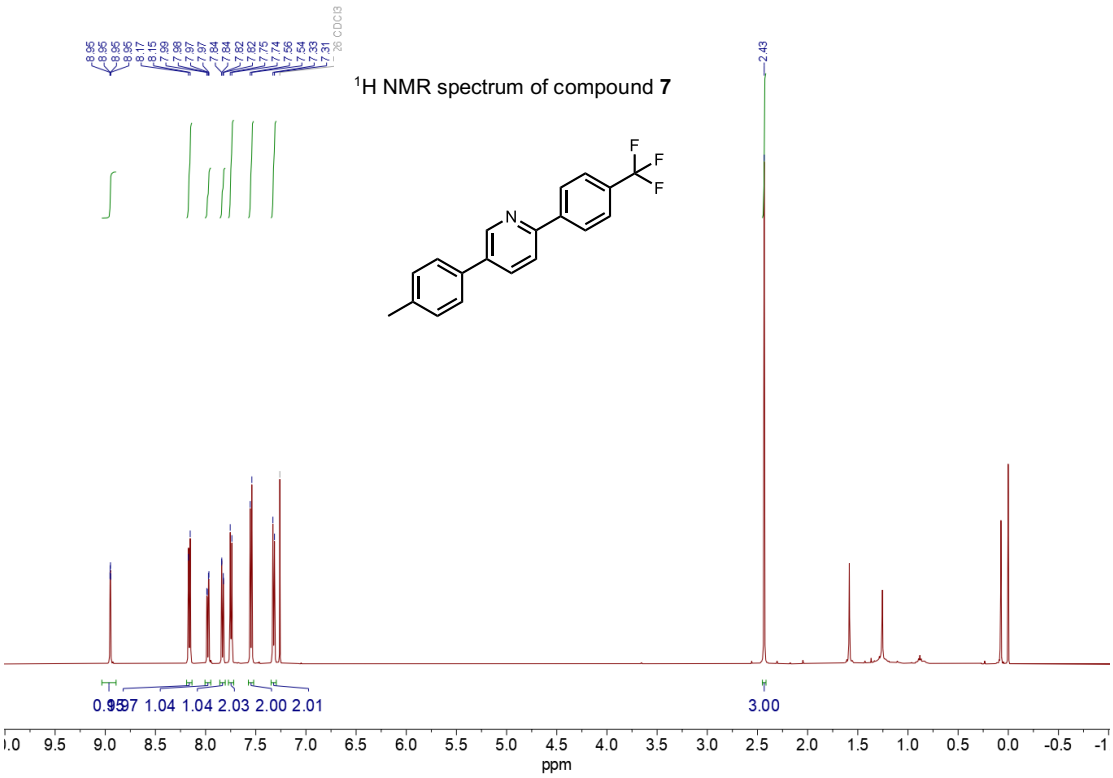


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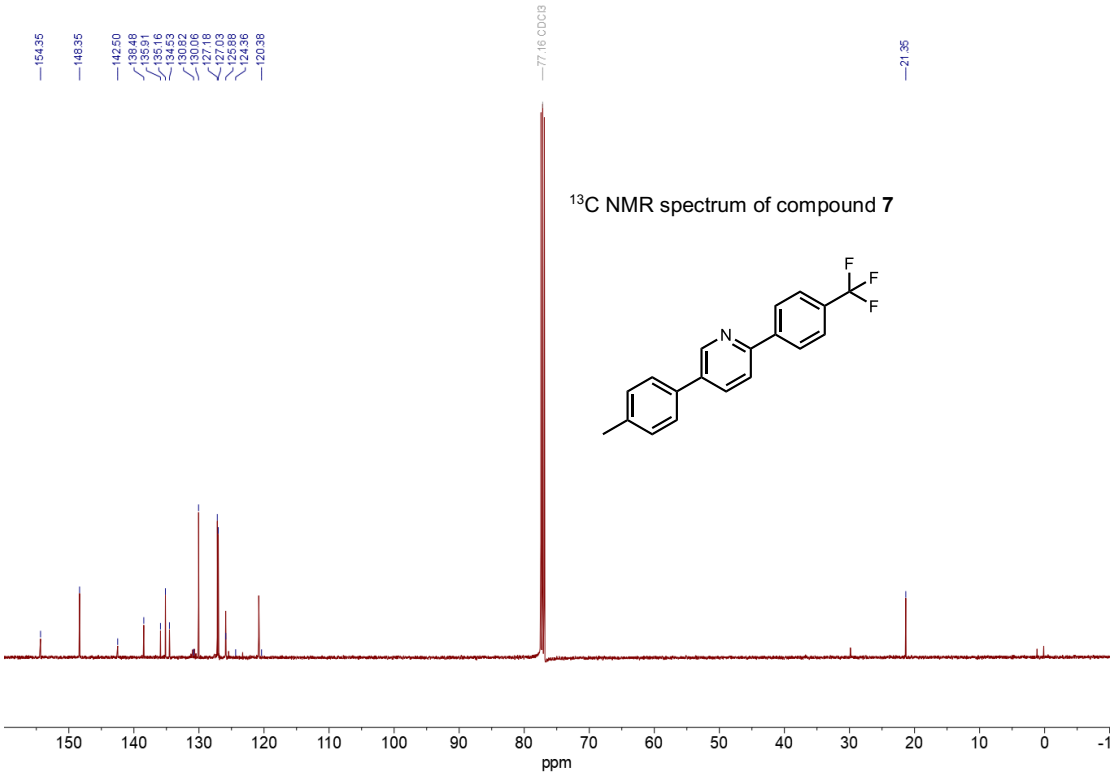


$^{13}$C NMR spectrum of compound **7**

$^{19}$F NMR spectrum of compound **7**