# Supporting Information

## Copper-Catalyzed Asymmetric Reduction of β,β-Disubstituted Alkenylboramides

Yeji Park and Jaesook Yun*

Department of Chemistry and Institute of Basic Science
Sungkyunkwan University, Suwon 16419, Korea
Fax: (+82)-31-290-7075; e-mail: jaesook@skku.edu

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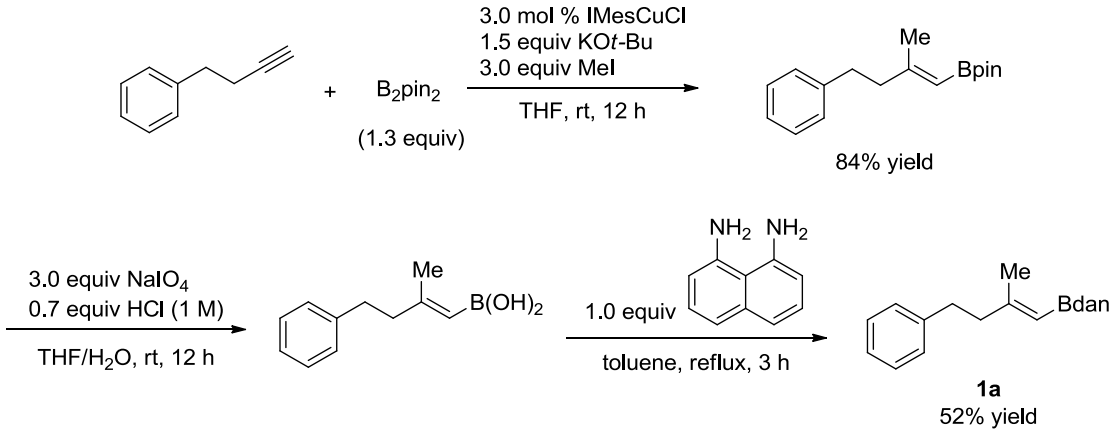
## General Methods

$Cu(OAc)_2$, *t*-BuOH, methyldiethoxysilane (DEMS), and other commercial reagents were purchased from Aldrich and used as received. Chiral ligands were purchased from TCI and Strem. **1a**–**1s** were prepared by following literature procedures.[1,2] Toluene was purified using PureSolv solvent purification system (Innovative Technology, Inc). All reactions were carried out with standard Schlenk technique. Flash chromatography was performed on silica gel (70-230 mesh) from Merch. All $^1H$ NMR spectra were obtained on Bruker at 500 systems and reported in parts per million (ppm) downfield from tetramethylsilane. $^{13}C$ NMR spectra were reported in ppm referenced to deuteriochloroform (77.16 ppm). $^{11}B$ NMR spectra were obtained on Bruker at 400 systems at Kyonggi University, Suwon, Korea. High performance liquid chromatography (HPLC) was performed using Younglin Acme 9100 series. Gas chromatography (GC) was performed using Younglin Acme 6100 series. Infrared spectra (IR) were obtained on Nicolet 205 FT-IR and were recorded in $cm^{-1}$. High resolution mass spectra (HRMS) were obtained at Korea Basic Science Institutes (Daegu, Korea and Cheongju, Korea) and reported in form of m/z.

## Procedure A: Preparation of (*E*)-β,β-Disubstituted Alkenylboramides (1a–1f, 1h –1n)[1]

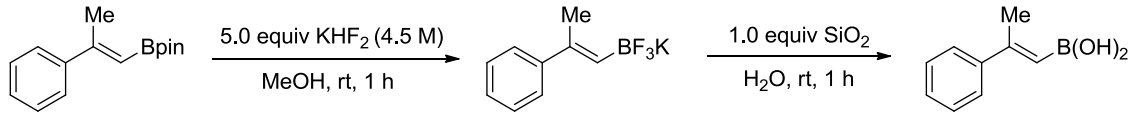



To an oven dried round bottomed flask, IMesCuCl (0.015 mmol, 61 mg), KO*t*-Bu (7.5 mmol, 842 mg), $B_2pin_2$ (6.5 mmol, 1.65 g) and anhydrous THF (20 mL) were charged under an atmosphere of nitrogen and cooled to 0 ℃. The mixture was allowed to stir at 0 ℃ for 10 min. Then, alkyne (5.0 mmol) in THF (5 mL) and iodomethane (15 mmol, 0.95 mL) were added to the solution. The reaction mixture was stirred at room temperature for 12 h. The resulting mixture was quenched by adding saturated aq. $NH_4Cl$ solution and extracted three times with diethyl ether. The

combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude was purified by silica gel column chromatography to give alkenyl pinacol boronate.

To a solution of the alkenyl pinacol boronate (4.2 mmol) in THF (12 mL) and $H_2O$ (3 mL) was added $NaIO_4$ (12.6 mmol, 2.7 g), and the reaction mixture was stirred at room temperature for 30 min. Then, aq. HCl (1.0 M, 3.0 mL) was added to the reaction mixture and allowed to stir at room temperature for 12 h. Upon completion of the reaction, the resulting mixture was extracted with ethyl acetate and washed with brine. The combined organic layers were dried over $MgSO_4$, filtered, concentrated in vacuo, and used for next reaction without further purification. The crude product and 1,8-diaminonaphthalene (4.2 mmol, 664 mg) were dissolved in toluene (17 mL) equipped with Dean-Stark apparatus and the reaction mixture was heated to reflux for 3 h. After cooled to room temperature, the reaction mixture was concentrated in vacuo and purified by silica gel chromatography.

## Procedure B: Preparation of (*E*)-β,β-Disubstituted Alkenylboramides (1g, 1o–1s)[1,2]

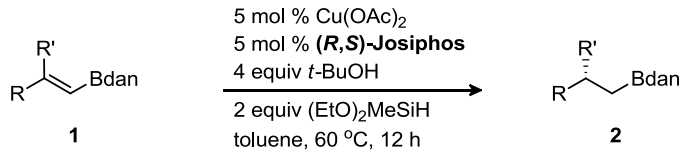



62% yield

Aryl-substituted alkenyl boronic acids were synthesized via the corresponding trifluoroborate salts from alkenyl pinacol boronate that was prepared by procedure A using LiO*t*-Bu base, due to isolation problem; To a solution of the alkenyl pinacol boronate (3.9 mmol) in MeOH (8 mL) was added aq. $KHF_2$ (4.5 M, 4.3 mL) slowly. After the reaction mixture was stirred at room temperature for 1 h, the solution was concentrated in vacuo and dried. The excess $KHF_2$ was filtered off by washing with acetone. Then, filtrate was concentrated and a mixture of diethyl ether and hexanes were added to form a precipitate, which was filtered to give alkenyltrifluoroborate.

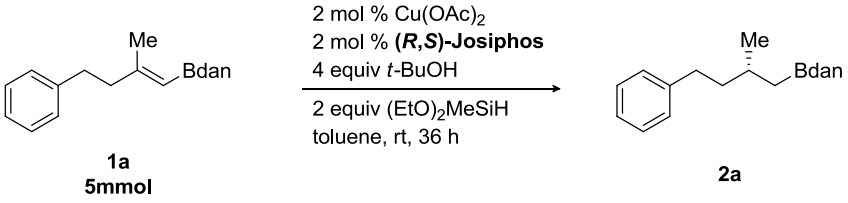
To a flask the alkenyltrifluoroborate (2.4 mmol) and $SiO_2$ (2.4 mmol, 144 mg) was added $H_2O$ (8 mL). The reaction mixture was stirred at room temperature for 1 h. Then, the mixture was extracted with ethyl acetate and washed with $H_2O$. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo.

## General Procedure for the Copper-Catalyzed Asymmetric Reduction of β,β-Disubstituted Alkenylboramides (Scheme 2)




A mixture of $Cu(OAc)_2$ (0.015 mmol, 2.7 mg) and (*R,S*)-Josiphos (0.015 mmol, 9.6 mg) in toluene (0.5 mL) was stirred for 10 min in a Schlenk tube under an atmosphere of nitrogen. DEMS (0.6 mmol, 96 μL) was added to the reaction mixture and stirred for another 10 min at room temperature. Substrate **1** dissolved in toluene (1.0 mL) and *t*-BuOH (1.2 mmol, 114 μL) were added. The reaction mixture was stirred at 60 ℃ for 12 h and monitored by NMR. Upon completion of the reaction, the reaction mixture was diluted with diethyl ether (5 mL). The mixture was quenched by the adding saturated $NH_4F$/MeOH (5 mL) and stirred for 20 min. The solution was extracted three times with diethyl ether, washed with brine, and dried over $MgSO_4$. After evaporating the solvent under vacuo, the residue was purified by silica gel chromatography.

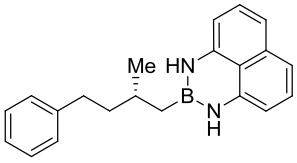
## Procedure for Gram-Scale Asymmetric Reduction of 1a (Scheme 3a)




A mixture of $Cu(OAc)_2$ (0.1 mmol, 18.2 mg) and (*R,S*)-Josiphos (0.1 mmol, 64.1 mg) in toluene (8.0 mL) was stirred for 10 min in a Schlenk tube under an atmosphere of nitrogen. DEMS (10 mmol, 1.6 mL) was added to the reaction mixture and stirred for another 10 min at room temperature. Substrate **1a** (5.0 mmol, 1.56 g) dissolved in toluene (2.0 mL) and *t*-BuOH (20 mmol, 1.9 mL) were added. The reaction mixture was stirred at rt for 36 h and monitored by NMR. Upon completion of the reaction, the reaction mixture was diluted with diethyl ether (10 mL). The mixture was quenched by the adding saturated $NH_4F$/MeOH (20 mL) slowly and stirred for 20 min. The solution was extracted three times with diethyl ether, washed with brine, and dried over $MgSO_4$. After evaporating the solvent under vacuo, the residue was purified by silica gel chromatography. ($NEt_3$:hexanes = 1:40). **2a** was obtained in 89% yield (1.40 g).

## Charaterization of 2 (Scheme 2)

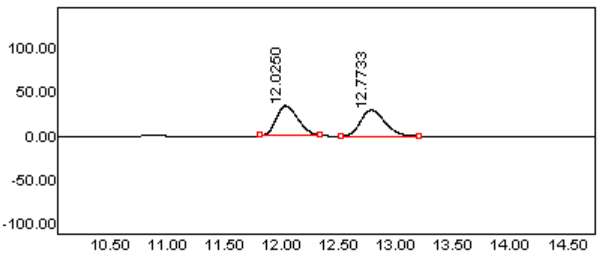
### (*R*)-2-(2-methyl-4-phenylbutyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2a)




**2a**

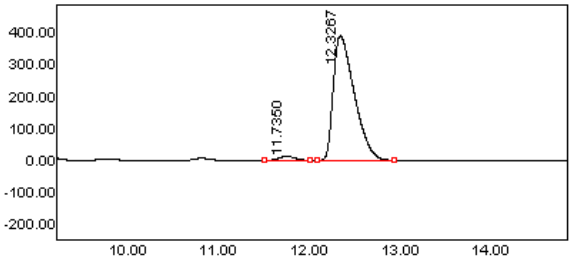
By following the general procedure, **2a** was obtained in 95% yield (colorless oil, 89.8 mg) by column chromatography ($NEt_3$:hexanes = 1:40). $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.30–7.27 (m, 2H), 7.21–7.18 (m, 3H), 7.10–7.06 (m, 2H), 6.99 (d, *J* = 8.2 Hz, 2H), 6.23 (d, *J* = 7.3 Hz, 2H) 5.50 (brs, 2H), 2.75–2.66 (m, 1H), 2.64–2.56 (m, 1H), 1.70–1.60 (m, 2H), 1.57–1.49 (m, 1H), 1.02 (d, *J* = 6.2 Hz, 3H), 0.95 (dd, *J* = 15.0, 6.0 Hz, 1H), 0.71 (dd, *J* = 15.0, 7.8 Hz, 1H); $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 142.8, 141.1, 136.3, 128.5, 128.4, 127.6, 125.7, 119.6, 117.4, 105.4, 41.3, 33.7, 29.4, 22.4.; $^{11}B$ NMR (128 MHz, $CDCl_3$) δ 32.2; IR (neat) 3409, 3054, 2951, 1600, 1506, 1411 $cm^{-1}$; HRMS (EI) calcd for $[C_{21}H_{23}BN_2^+]$: 314.1954, found: 314.1952; 95% ee was measured by chiral HPLC on OZ-H column (*i*-PrOH:hexanes = 1:99, 0.5 mL/min); $t_R$= 12.03 min (minor), $t_R$ = 12.77 min (major).

**[rac-2a]**



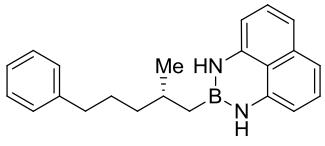

| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 12.0250 | 447.2379 | 50.78 |
| 12.7733 | 433.5020 | 49.22 |
| | 880.7399 | |

**[chi-2a]**




| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 11.7350 | 161.6908 | 2.52 |
| 12.3267 | 6263.3828 | 97.48 |
| | 6425.0737 | |

### (*R*)-2-(2-methyl-5-phenylpentyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2b)

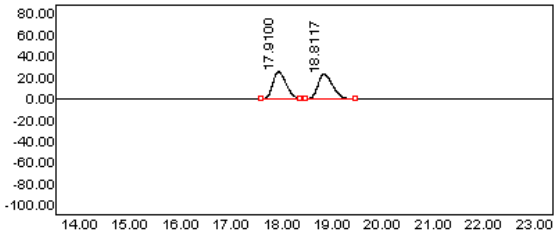



**2b**

By following the general procedure, **2b** was obtained in 98% yield (colorless oil, 96.4 mg) by column chromatography ($NEt_3$:hexanes = 1:40). $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.29–7.26 (m, 2H), 7.20–7.17 (m, 3H), 7.10 (t, *J* = 7.8 Hz, 2H), 7.00 (d, *J* = 8.2 Hz, 2H), 6.29 (d, *J* = 7.3 Hz, 2H), 5.58 (brs, 2H), 2.66–2.56 (m, 2H), 1.74–1.59 (m, 3H), 1.44–1.36 (m, 1H), 1.31–1.24 (m, 1H), 0.96 (d, *J* = 6.5 Hz, 3H), 0.94 (dd, *J* = 15.0, 5.9 Hz, 1H), 0.69 (dd, *J* = 15.0, 8.6 Hz, 1H); $^{13}C$ NMR (125 MHz, $CDCl_3$) δ. 142.8, 141.2, 136.3, 128.4, 128.3, 127.6, 125.7, 119.5, 117.4, 105.4, 39.4, 36.2,

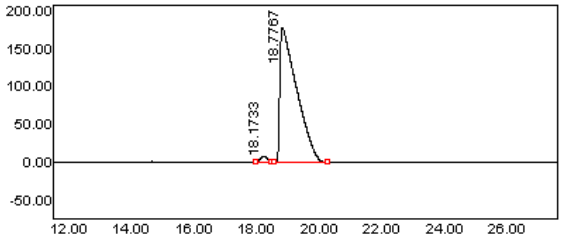
30.2, 29.3, 22.5; IR (neat) 3408, 3054, 2932, 1600, 1505 $cm^{-1}$; HRMS (ESI) calcd for [$C_{22}H_{25}BN_2$+$H^+$]: 329.2189, found: 329.2188; 97% ee was measured by chiral HPLC on OJ-H column with the corresponding alcohol obtained after oxidation[3] (*i*-PrOH:hexanes = 3:97, 0.5 mL/min); $t_R$= 17.91 min (minor), $t_R$ = 18.81 min (major).

**[rac-2b]**



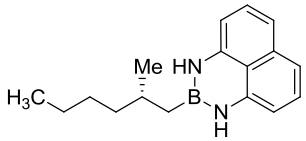

| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 17.9100 | 462.6696 | 49.56 |
| 18.8117 | 470.9311 | 50.44 |
| | 933.6007 | |

**[chi-2b]**




| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 18.1733 | 116.3188 | 1.72 |
| 18.7767 | 6632.0635 | 98.28 |
| | 6748.3823 | |

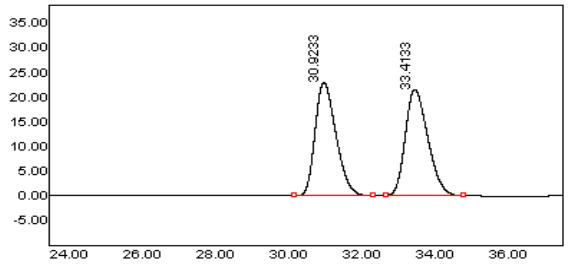
**(*R*)-2-(2-methylhexyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2c)**



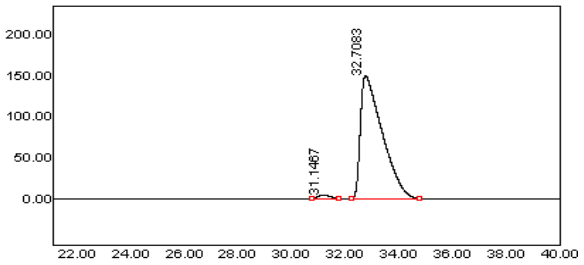

**2c**

By following the general procedure, **2c** was obtained in 81% yield (colorless oil, 65.1 mg) by column chromatography ($NEt_3$:hexanes = 1:40). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.09 (t, *J* = 7.8 Hz, 2H), 7.00 (d, *J* = 8.2 Hz, 2H), 6.30 (d, *J* = 7.3 Hz, 2H), 5.60 (brs, 2H), 1.68–1.59 (m, 1H), 1.31–1.19 (m, 6H), 0.96 (d, *J* = 6.5 Hz, 3H), 0.93–0.89 (m, 4H), 0.69 (dd, *J* = 15.0, 8.5 Hz, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 141.2, 136.3, 127.6, 119.6, 117.3, 105.4, 39.5, 30.3, 29.7, 23.0, 22.5, 14.2; IR (neat) 3435, 3054, 2956, 1601, 1506, 1412 $cm^{-1}$; HRMS (EI) calcd for [$C_{17}H_{23}BN_2^+$]: 266.1954, found: 266.1956; 97% ee was measured by chiral HPLC on OD-H column (*i*-PrOH:hexanes = 1:99, 0.5 mL/min); $t_R$= 30.92 min (minor), $t_R$ = 33.41 min (major).

**[rac-2c]**



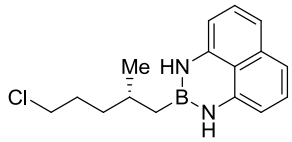

**[chi-2c]**



| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 30.9233 | 912.4486 | 49.83 |
| 33.4133 | 918.7720 | 50.17 |
| | 1831.2206 | |

| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 31.1467 | 137.4159 | 1.60 |
| 32.7083 | 8434.3711 | 98.40 |
| | 8571.7871 | |

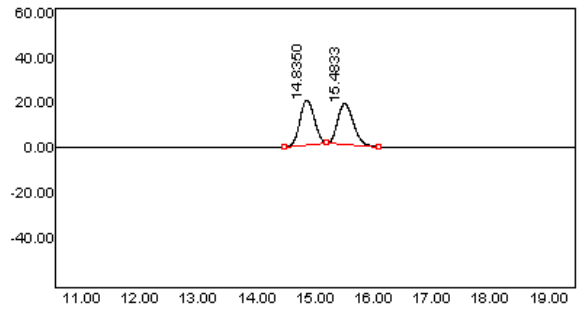
**(*R*)-2-(5-chloro-2-methylpentyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2d)**




**2d**

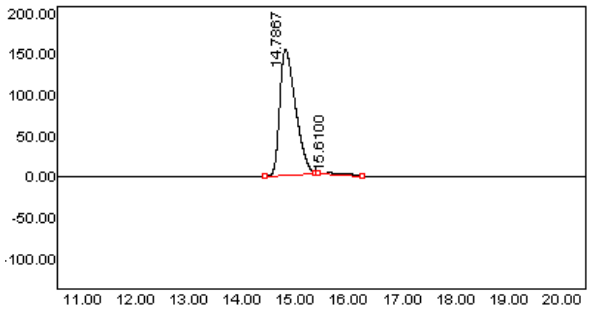
By following the general procedure, **2d** was obtained in 97% yield (pale yellow oil, 83.3 mg) by column chromatography ($NEt_3$:hexanes = 1:40). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.12–7.09 (m, 2H) 7.01 (d, *J* = 8.3 Hz, 2H), 6.31 (d, *J* = 7.3 Hz, 2H), 5.62 (brs, 2H), 3.56 (t, *J* = 6.7 Hz, 2H), 1.88–1.77(m, 2H), 1.74–1.65 (m, 1H), 1.54–1.47 (m, 1H), 1.39–1.32 (m, 1H), 0.99 (d, *J* = 6.6 Hz, 3H), 0.95 (dd, *J* = 15.0, 6.1 Hz, 1H), 0.73 (dd, *J* = 15.0, 8.5 Hz, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 141.1, 136.3, 127.6, 119.6, 117.5, 105.5, 45.4, 36.7, 30.5, 29.7, 24.1 (C–B), 22.4; IR (neat) 3412, 3053, 2954, 1599, 1507, 1412 $cm^{-1}$; HRMS (EI) calcd for [$C_{16}H_{20}BClN_2^+$]: 286.1408, found: 286.1405; 95% ee was measured by chiral HPLC on IA column (*i*-PrOH:hexanes = 1:99, 1.0 mL/min); $t_R$= 14.84 min (major), $t_R$ = 15.48 min (minor).

**[rac-2d]**



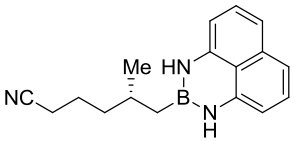

| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 14.8350 | 342.1762 | 50.34 |
| 15.4833 | 337.5298 | 49.66 |
| | 679.7061 | |

**[chi-2d]**




| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 14.7867 | 3173.2722 | 97.60 |
| 15.6100 | 78.1778 | 2.40 |
| | 3251.4500 | |

**(*R*)-5-methyl-6-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)hexanenitrile (2e)**

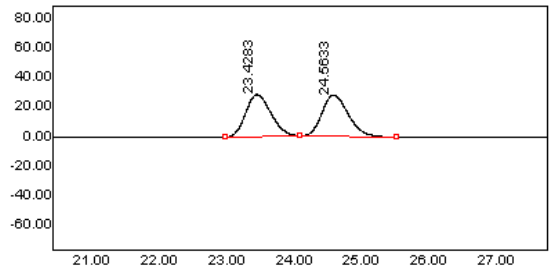



**2e**

By following the general procedure, **2e** was obtained in 72% yield (white solid, 60.0mg) by column chromatography ($NEt_3$:$Et_2O$:hexanes = 1:4:40). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.12–7.08 (m, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.31 (d, *J* = 7.3 Hz, 2H), 5.62 (s, 2H), 2.35 (td, *J* = 7.1, 3.0 Hz,

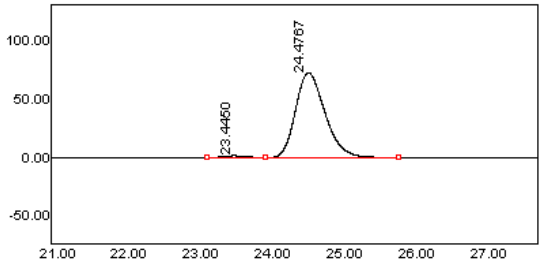
2H), 1.78–1.64 (m, 3H), 1.53–1.46 (m, 1H), 1.43–1.35 (m, 1H), 0.99 (d, *J* = 6.6 Hz, 3H), 0.96 (dd, *J* = 14.9, 6.0 Hz, 1H), 0.72 (dd, *J* = 14.9, 8.8 Hz, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 141.0, 136.3, 127.6, 119.9, 119.6, 117.5, 105.5, 38.7, 29.8, 23,3, 22.2, 17.4; IR (neat) 3398, 3054, 2955, 2245, 1599, 1509, 1412 cm$^{-1}$; HRMS (FAB) calcd for [$C_{17}H_{20}BN_3^+$]: 277.1750, found: 277.1746; 96% ee was measured by chiral HPLC on IA column (*i*-PrOH:hexanes = 10:90, 0.5 mL/min); $t_R$= 23.43 min (minor), $t_R$ = 24.56 min (major).

**[rac-2e]**



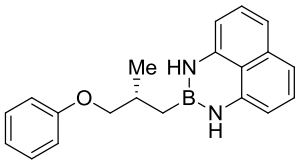

| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 23.4283 | 743.5322 | 49.44 |
| 24.5633 | 760.3132 | 50.56 |
| | 1503.8455 | |

**[chi-2e]**




| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 23.4450 | 42.5782 | 2.01 |
| 24.4767 | 2078.3989 | 97.99 |
| | 2120.9771 | |

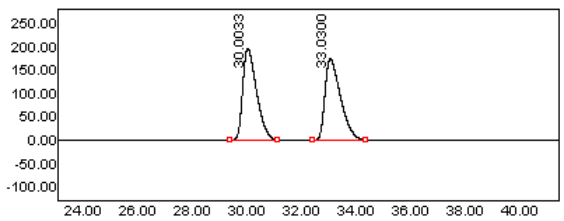
**(*R*)-2-(2-methyl-3-phenoxypropyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2f)**



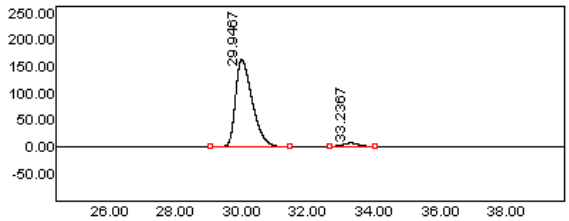

**2f**

By following the general procedure, **2f** was obtained in 80% yield (white solid, 76.0 mg) by column chromatography ($NEt_3$:hexanes = 1:40). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.29–7.28 (m, 2H), 7.11–7.07 (m, 2H), 7.00 (d, *J* = 8.1 Hz, 2H), 6.94 (t, *J* = 7.4 Hz, 1H), 6.90 (d, *J* = 7.9 Hz, 2H), 6.27 (d, *J* = 7.3 Hz, 2H), 5.70 (brs, 2H), 3.84 (dd, *J* = 8.9, 6.0 Hz, 1H), 3.77 (dd, *J* = 8.9, 6.9 Hz, 1H), 2.24–2.15 (m, 1H), 1.14–1.10 (m, 4H), 0.86 (dd, *J* = 15.0, 8.0 Hz, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 159.0, 141.1, 136.3, 129.5, 127.6, 120.7, 119.6, 117.4, 114.6, 105.5, 74.7, 30.5, 20.8 (C–B), 19.7; IR (neat) 3406, 3053, 2956, 1599, 1506, 1243 cm$^{-1}$; HRMS (FAB) calcd for [$C_{20}H_{21}BN_2O^+$]: 316.1747, found: 316.1748; 92% ee was measured by chiral HPLC on IA column (*i*-PrOH:hexanes = 1:99, 0.5 mL/min); $t_R$= 30.00 min (major), $t_R$ = 33.03 min (minor).

**[rac-2f]**



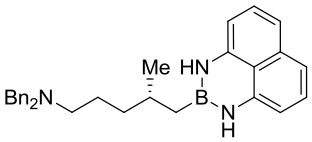

**[chi-2f]**



| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 30.0033 | 6897.0752 | 50.04 |
| 33.0300 | 6887.3687 | 49.96 |
| | 13784.4434 | |

| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 29.9467 | 5709.8350 | 96.10 |
| 33.2367 | 231.8996 | 3.90 |
| | 5941.7344 | |

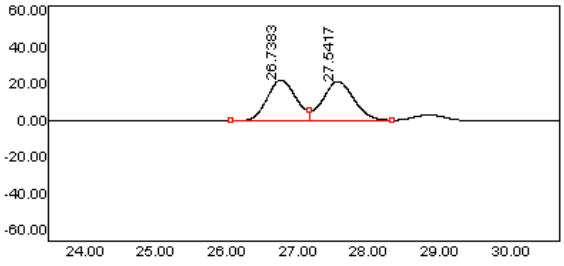
**(*R*)-*N*,*N*-dibenzyl-4-methyl-5-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)pentan-1-amine (2g)**




**2g**

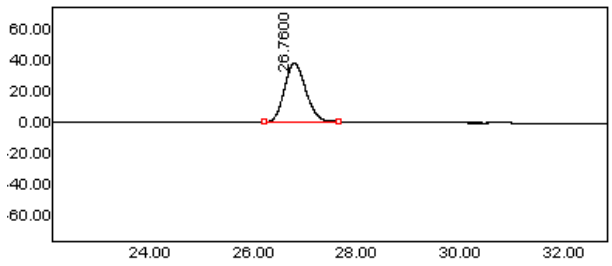
By following the general procedure, **2g** was obtained in 75% yield (colorless oil, 100.6 mg) by column chromatography ($NEt_3$:$Et_2O$:hexanes = 1:4:40). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.39–7.37 (m, 4H), 7.32–7.29 (m, 4H), 7.25–7.22 (m, 2H), 7.10 (t, *J* = 7.8 Hz, 2H), 7.01 (d, *J* = 8.2 Hz, 2H), 6.28 (d, *J* = 7.3 Hz, 2H) 5.54 (brs, 2H), 3.56 (s, 4H), 2.41 (t, *J* = 6.9 Hz, 2H), 1.61–1.48 (m, 3H), 1.36–1.29 (m, 1H), 1.23–1.16 (m, 1H), 0.92–0.88 (m, 3H), 0.63 (dd, *J* = 14.8, 8.8 Hz, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 141.2, 140.1, 136.4, 128.8, 128.2, 127.6, 126.8, 119.6, 117.4, 105.4, 58.4, 53.4, 37.1, 29.8, 24.7, 24.2 (C–B), 22.5; IR (neat) 3411, 3027, 2946, 1600, 1411 $cm^{-1}$; HRMS (ESI) calcd for [$C_{30}H_{34}BN_3$+$H^+$]: 448.2924, found: 448.2926; >99% ee was measured by chiral HPLC on IA column (*i*-PrOH:hexanes = 3:97, 0.3 mL/min); $t_R$= 26.74 min (major), $t_R$ = 27.54 min (minor).

**[rac-2g]**



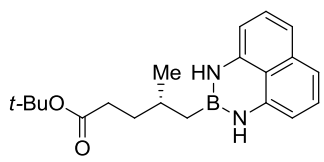

| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 26.7383 | 622.2554 | 49.44 |
| 27.5417 | 636.4290 | 50.56 |
| | 1258.6843 | |

**[chi-2g]**




| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 26.7600 | 1081.9417 | 100.00 |
| | 1081.9417 | |

**(*R*)-*tert*-butyl 4-methyl-5-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)pentanoate (2h)**

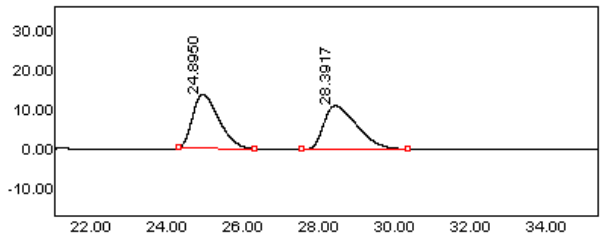



**2h**

By following the general procedure, **2h** was obtained in 98% yield (colorless oil, 99.1mg) by column chromatography ($NEt_3$:hexanes = 1:40). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.11–7.08 (m, 2H), 7.00 (dd, *J* = 8.2, 0.5 Hz, 2H), 6.32 (dd, *J* = 7.3, 0.8 Hz, 2H), 5.90 (brs, 2H), 2.31–2.28 (m, 2H), 1.78–1.66 (m, 2H), 1.48 (s, 9H), 1.42–1.35 (m, 1H), 0.97 (d, *J* = 6.5 Hz, 3H), 0.91 (dd, *J*

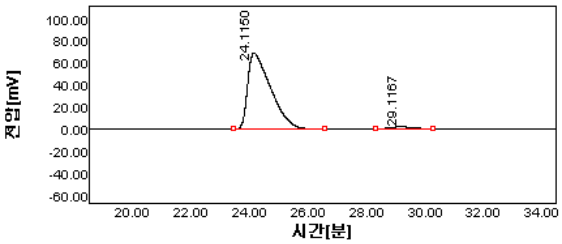
= 15.4, 7.2 Hz, 1H), 0.77 (dd, *J* = 15.4, 6.9 Hz, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 173.8, 141.4, 136.3, 127.6, 119.6, 117.2, 105.4, 80.3, 34.1, 33.2, 29.3, 28.2, 24.1 (C–B), 22.4; IR (neat) 3431, 3054, 2978, 1715, 1601, 1150 cm$^{-1}$; HRMS (ESI) calcd for [$C_{20}H_{27}BN_2O_2$+H$^+$]: 339.2244, found: 339.2244; 95% ee was measured by chiral HPLC on OD-H column (*i*-PrOH:hexanes = 1:99, 1.0 mL/min); $t_R$= 24.90 min (major), $t_R$ = 28.39 min (minor).

**[rac-2h]**



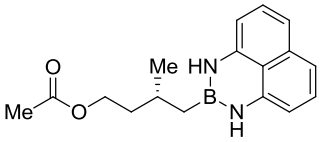

| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 24.8950 | 657.2397 | 49.18 |
| 28.3917 | 679.1615 | 50.82 |
| | 1336.4012 | |

**[chi-2h]**




| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 24.1150 | 3741.5073 | 97.43 |
| 29.1167 | 98.5888 | 2.57 |
| | 3840.0962 | |

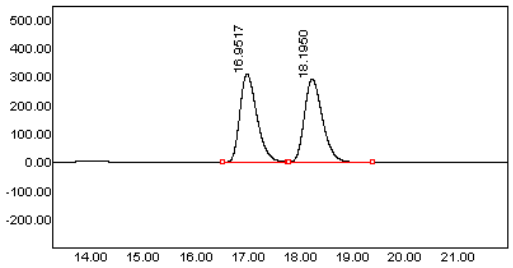
**(*R*)-3-methyl-4-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)butyl acetate (2i)**



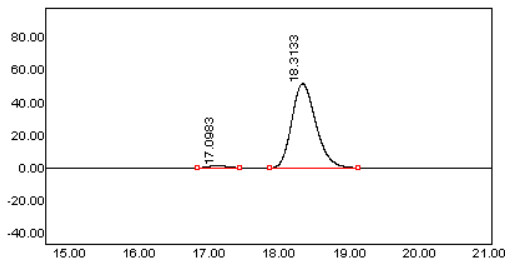
**2i**

By following the general procedure, **2i** was obtained in 93% yield (yellow solid, 82.6 mg) by column chromatography ($NEt_3$:$Et_2O$:hexanes = 1:4:40). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.12–7.08 (m, 2H), 7.01 (d, *J* = 7.8 Hz, 2H), 6.31 (dd, *J* = 7.3, 0.8 Hz, 2H), 5.67 (brs, 2H), 4.20–4.11 (m, 2H), 2.07 (s, 3H), 1.85–1.75 (m, 1H), 1.73–1.66 (m, 1H), 1.60–1.53 (m, 1H), 1.01 (d, *J* = 6.6 Hz, 3H), 0.98 (dd, *J* = 14.9, 6.1 Hz, 1H), 0.76 (dd, *J* = 14.9, 8.3 Hz, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 171.3, 141.1, 136.3, 127.6, 119.6, 117.5, 105.5, 63.0, 38.0, 27.3, 24.0 (C–B), 22.5, 21.1; IR (neat) 3398, 3053, 2956, 1724, 1600, 1251 cm$^{-1}$; HRMS (ESI) calcd for [$C_{17}H_{21}BN_2O_2$+H$^+$]: 297.1774, found: 297.1776; 96% ee was measured by chiral HPLC on AD-H column (*i*-PrOH:hexanes = 10:90, 0.5 mL/min); $t_R$= 16.95 min (minor), $t_R$ = 18.20 min (major).

**[rac-2i]**



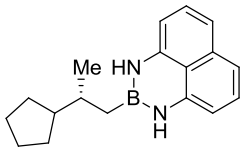

**[chi-2i]**



| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 16.9517 | 6980.8672 | 50.00 |
| 18.1950 | 6981.7334 | 50.00 |
| | 13962.6006 | |

| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 17.0983 | 27.2640 | 2.15 |
| 18.3133 | 1243.2694 | 97.85 |
| | 1270.5333 | |

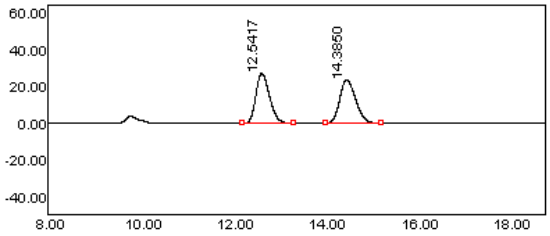
**(*R*)-2-(2-cyclopentylpropyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2j)**




**2j**

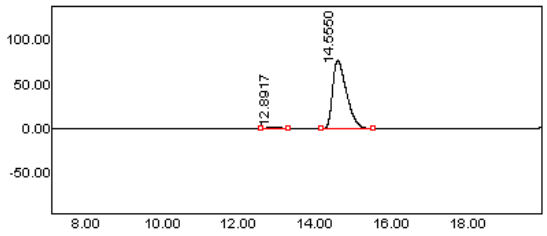
By following the general procedure, **2j** was obtained in 97% yield (yellow solid, 81.0 mg) by column chromatography ($NEt_3$:hexanes = 1:40). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.09 (t, *J* = 7.8 Hz, 2H), 7.00 (d, *J* = 8.3 Hz, 2H), 6.29 (d, *J* = 7.3 Hz, 2H), 5.60 (s, 2H), 1.81–1.72 (m, 2H), 1.64–1.57 (m, 3H), 1.56–1.47 (m, 3H), 1.20–1.10 (m, 2H), 1.07 (dd, *J* = 14.9, 4.5 Hz, 1H), 0.96 (d, *J* = 6.6 Hz, 3H), 0.63 (dd, *J* = 14.9, 9.7 Hz, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 141.3, 136.3, 127.6, 119.5, 117.3, 105.4, 48.7, 35.7, 31.1, 30.4, 25.7, 25.6, 21.1; IR (neat) 3435, 3049, 2949, 1600, 1505, 1411 $cm^{-1}$; HRMS (FAB) calcd for [$C_{18}H_{23}BN_2^+$]: 278.1954, found: 278.1951; 96% ee was measured by chiral HPLC on OD-H column (*i*-PrOH:hexanes = 5:95, 1.0 mL/min); $t_R$= 12.54 min (minor), $t_R$ = 14.39 min (major).

**[rac-2j]**



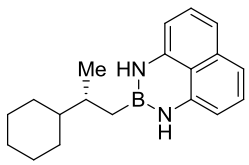

| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 12.5417 | 562.4398 | 50.11 |
| 14.3850 | 559.9915 | 49.89 |
| | 1122.4313 | |

**[chi-2j]**




| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 12.8917 | 42.2858 | 2.14 |
| 14.5550 | 1937.8265 | 97.86 |
| | 1980.1123 | |

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

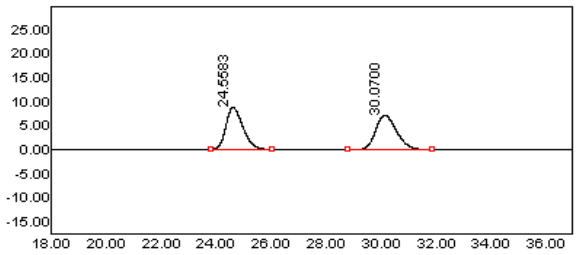



**2k**

By following the general procedure, **2k** was obtained in 94% yield (pale yellow oil, 82.3 mg) by column chromatography ($NEt_3$:hexanes = 1:40). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.10 (dd, *J* = 8.2, 7.4 Hz, 2H), 7.00 (dd, *J* = 8.3, 0.7 Hz, 2H), 6.30 (dd, *J* = 7.3, 0.8 Hz, 2H), 5.60 (brs, 2H), 1.77–1.74 (m, 2H), 1.70–1.66 (m, 3H), 1.56–1.48 (m, 1H), 1.27–1.11 (m, 4H), 1.07–0.98 (m, 3H), 0.92 (d, *J* = 6.8 Hz, 3H), 0.64 (dd, *J* = 14.9, 9.9 Hz 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 141.3, 136.3, 127.6, 119.5, 117.3, 105.4, 44.9, 35.4, 30.5, 29.2, 26.9, 26.8, 26.8, 19.2; $^{11}$B NMR (128 MHz, $CDCl_3$) δ 32.5; IR (neat) 3434, 3053,

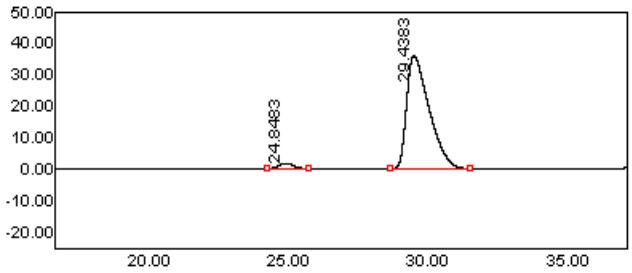
2924, 1601, 1505, 1411 $cm^{-1}$; HRMS (EI) calcd for [$C_{19}H_{25}BN_2^+$]: 292.2111, found: 292.2113 ; 94% ee was measured by chiral HPLC on OD-H column (*i*-PrOH:hexanes = 1:99, 1.0 mL/min); $t_R$= 24.56 min (minor), $t_R$ = 30.07 min (major).

**[rac-2k]**



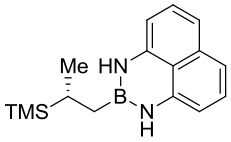

| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 24.5583 | 369.2576 | 49.59 |
| 30.0700 | 375.3123 | 50.41 |
| | 744.5699 | |

**[chi-2k]**




| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 24.8483 | 66.0549 | 3.17 |
| 29.4383 | 2020.4320 | 96.83 |
| | 2086.4868 | |

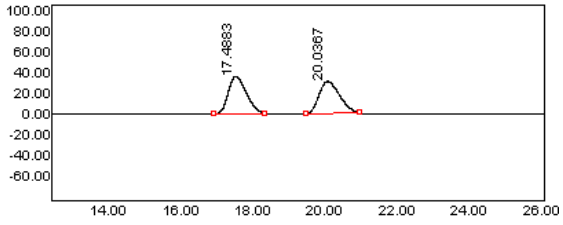
**(*R*)-2-(2-(trimethylsilyl)propyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2l)**




**2l**

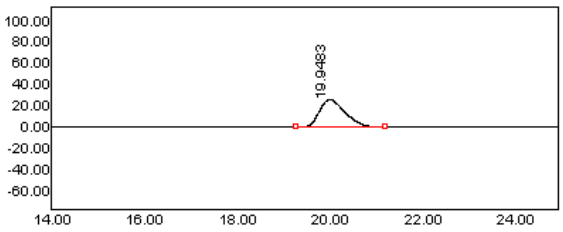
By following the general procedure, **2l** was obtained in 91% yield (white solid, 76.5 mg) by column chromatography ($NEt_3$:$Et_2O$:hexanes = 1:2:40). $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.11–7.08 (m, 2H), 7.00 (d, *J* = 8.2 Hz, 2H), 6.30 (d, *J* = 7.3 Hz, 2H), 5.62 (brs, 2H), 1.04–0.99 (m, 4H), 0.80–0.73 (m, 1H), 0.60 (dd, *J* = 15.1, 11.1 Hz, 1H), -0.01 (s, 9H); $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 141.2, 136.3, 127.6, 119.6, 117.3, 105.4, 17.0, 15.9, 3.5; $^{11}B$ NMR (128 MHz, $CDCl_3$) δ 32.7; IR (neat) 3434, 3053, 2952, 1601, 1504, 1411 $cm^{-1}$; HRMS (EI) calcd for [$C_{16}H_{23}BN_2Si^+$]: 282.1724, found: 282.1725; >99% ee was measured by chiral HPLC on OD-H column (*i*-PrOH:hexanes = 1:99, 1.0 mL/min); $t_R$= 17.49 min (minor), $t_R$ = 20.04 min (major).

**[rac-2l]**



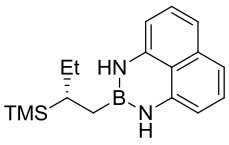

| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 17.4883 | 1247.4319 | 50.25 |
| 20.0367 | 1234.9851 | 49.75 |
| | 2482.4170 | |

**[chi-2l]**




| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 19.9483 | 996.8141 | 100.00 |
| | 996.8141 | |

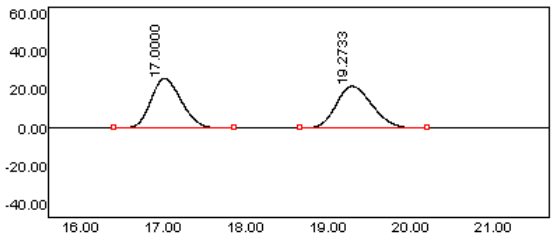
**(*S*)-2-(2-(trimethylsilyl)butyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2m)**




**2m**

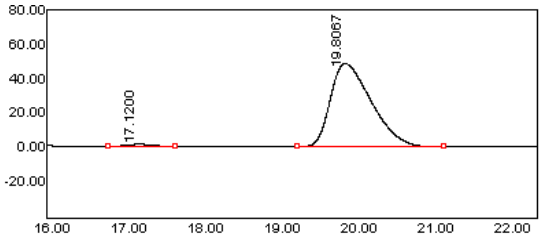
By following the general procedure, **2m** was obtained in 97% yield (pale yellow oil, 86.2 mg) by column chromatography ($NEt_3$:$Et_2O$:hexanes = 1:2:40). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.10 (t, *J* = 7.8 Hz, 2H), 7.00 (d, *J* = 8.2 Hz, 2H), 6.30 (d, *J* = 7.3 Hz, 2H), 5.60 (brs, 2H), 1.62–1.54 (m, 1H), 1.38–1.31 (m, 1H), 0.96 (t, *J* = 7.4 Hz, 3H), 0.90 (dd, *J* = 15.5, 6.3 Hz, 1H), 0.81 (dd, *J* = 15.5, 8.7 Hz, 1H), 0.66–0.61 (m, 1H) 0.01 (s, 9H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 141.2, 136.3, 127.5, 119.5, 117.3, 105.4, 25.5, 23.7, 14.0, -2.4; IR (neat) 3433, 3053, 2957, 1601, 1505, 1411 $cm^{-1}$; HRMS (FAB) calcd for [$C_{17}H_{25}BN_2Si^+$]: 296.1880, found: 296.1877; 96% ee was measured by chiral HPLC on OD-H column (*i*-PrOH:hexanes = 1:99, 1.0 mL/min); $t_R$= 17.00 min (minor), $t_R$ = 19.27 min (major).

**[rac-2m]**



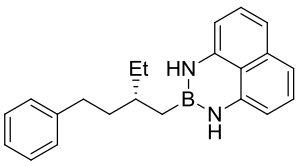

| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 17.0000 | 669.9557 | 50.10 |
| 19.2733 | 667.4044 | 49.90 |
| | 1337.3601 | |

**[chi-2m]**




| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 17.1200 | 35.0374 | 1.91 |
| 19.8067 | 1802.5686 | 98.09 |
| | 1837.6060 | |

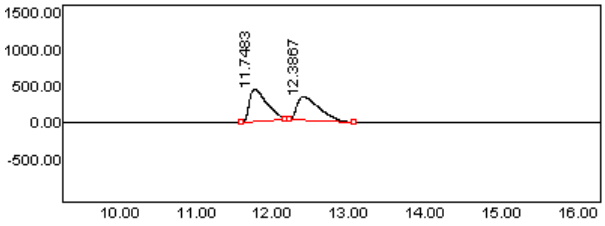
**(*S*)-2-(2-ethyl-4-phenylbutyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2n)**




**2n**

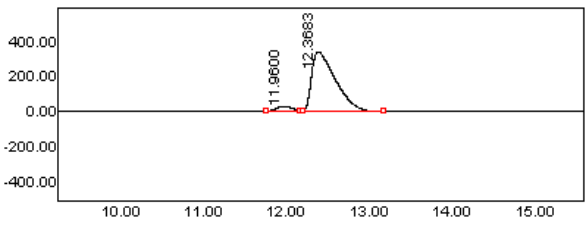
By following the general procedure, **2n** was obtained in 98% yield (colorless oil, 96.6 mg) by column chromatography ($NEt_3$:hexanes = 1:40). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.5 Hz, 2H), 7.20 (t, *J* = 7.9 Hz, 3H), 7.10 (t, *J* = 7.8 Hz, 2H), 7.00 (d, *J* = 8.2 Hz, 2H), 6.25 (d, *J* = 7.3 Hz, 2H), 5.51 (brs, 2H), 2.66 (t, *J* = 7.8 Hz, 2H), 1.73–1.66 (m, 1H), 1.63–1.56 (m, 1H), 1.53–1.45 (m, 2H), 1.41–1.34 (m, 1H), 0.92 (t, *J* = 7.2 Hz, 3H), 0.89–0.87 (m, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 142.8, 141.2, 136.3, 128.5, 128.4, 127.6, 125.7, 119.5, 117.4, 105.5, 37.8, 35.6, 33.3, 28.7, 20.5 (C–B), 11.1; IR (neat) 3432, 3054, 2962, 1601, 1506, 1412 $cm^{-1}$; HRMS (FAB) calcd for [$C_{22}H_{25}BN_2^+$]: 328.2111, found: 328.2109; 90% ee was measured by chiral HPLC on OZ-H column (*i*-PrOH:hexanes = 1:99, 0.5 mL/min); $t_R$= 11.75 min (minor), $t_R$ = 12.39 min (major).

**[rac-2n]**



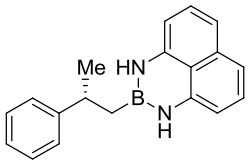

| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 11.7483 | 7027.0947 | 50.88 |
| 12.3867 | 6782.7642 | 49.12 |
| | 13809.8594 | |

**[chi-2n]**




| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 11.9600 | 346.0340 | 4.96 |
| 12.3683 | 6636.0103 | 95.04 |
| | 6982.0444 | |

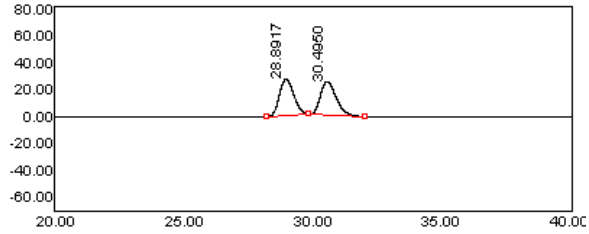
**(*R*)-2-(2-phenylpropyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2o)**




**2o**

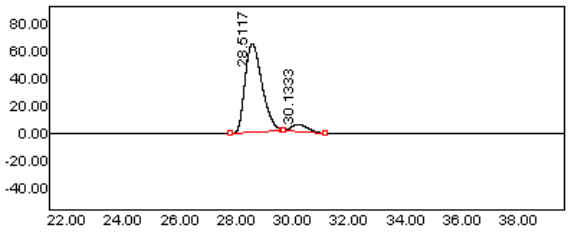
By following the general procedure, **2o** was obtained in 98% yield (colorless oil, 84.0 mg) by column chromatography ($NEt_3$:$Et_2O$:hexanes = 1:4:40). $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.5 Hz, 2H), 7.29 (d, *J* = 7.2 Hz, 2H), 7.23 (t, *J* = 7.1 Hz, 1H), 7.06 (t, *J* = 7.8 Hz, 2H), 6.98 (d, *J* = 8.3 Hz, 2H), 6.17 (d, *J* = 7.3 Hz, 2H), 5.40 (brs, 2H), 2.99 (sext, *J* = 6.9 Hz, 1H), 1.35 (d, *J* = 6.9 Hz, 3H), 1.31 (dd, *J* = 15.2, 8.4 Hz, 1H), 1.20 (dd, *J* = 15.2, 6.8 Hz, 1H); $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 148.6, 141.1, 136.3, 128.6, 127.5, 126.7, 126.2, 119.5, 117.3, 105.4, 36.7, 25.4; IR (neat) 3416, 3054, 2956, 1598, 1506, 1411 $cm^{-1}$; HRMS (ESI) calcd for [$C_{19}H_{19}BN_2$+$H^+$]: 287.1720, found: 287.1719; 87% ee was measured by chiral HPLC on AS-H column with the corresponding alcohol obtained after oxidation[3] (*i*-PrOH:hexanes = 1:99, 0.5 mL/min); $t_R$= 28.89 min (major), $t_R$ = 30.50 min (minor).

**[rac-2o]**



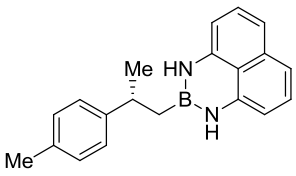

| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 28.8917 | 1065.8917 | 49.86 |
| 30.4950 | 1072.0725 | 50.14 |
| | 2137.9644 | |

**[chi-2o]**




| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 28.5117 | 2701.4102 | 93.49 |
| 30.1333 | 187.9556 | 6.51 |
| | 2889.3657 | |

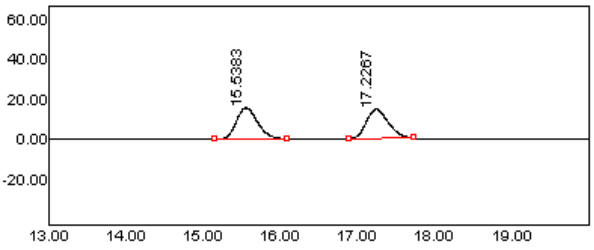
**(*R*)-2-(2-(*p*-tolyl)propyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2p)**




**2p**

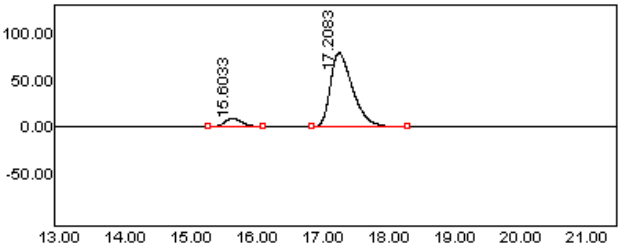
By following the general procedure, **2p** was obtained in 98% yield (colorless oil, 87.8 mg) by column chromatography ($NEt_3$:$Et_2O$:hexanes = 1:4:40). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.08–7.05 (m, 2H), 6.98 (dd, *J* = 8.3, 0.7 Hz, 2H), 6.17 (dd, *J* = 7.3, 0.8 Hz, 2H), 5.42 (brs, 2H), 2.96 (sext, *J* = 6.9 Hz, 1H), 2.35 (s, 3H), 1.32 (d, *J* = 6.9 Hz, 3H), 1.29 (dd, *J* = 15.2, 8.5 Hz, 1H), 1.18 (dd, *J* = 15.2, 6.7 Hz, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 145.6, 141.1, 136.3, 135.6, 129.3, 127.5, 126.5, 119.5, 117.3, 105.4, 36.2, 25.5, 25.3 (C–B), 21.0; IR (neat) 3418, 3051, 2957, 1600, 1506, 1412 cm$^{-1}$; HRMS (ESI) calcd for [$C_{20}H_{21}BN_2$+H$^+$]: 301.1876, found: 301.1874; 83% ee was measured by chiral HPLC on AD-H column with the corresponding alcohol obtained after oxidation[3] (*i*-PrOH:hexanes = 1:99, 1.0 mL/min); $t_R$= 15.54 min (minor), $t_R$ = 17.23 min (major).

**[rac-2p]**



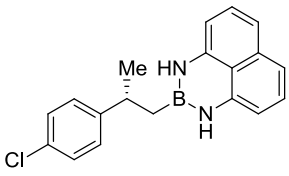

| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 15.5383 | 301.9670 | 50.92 |
| 17.2267 | 291.0564 | 49.08 |
| | 593.0234 | |

**[chi-2p]**




| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 15.6033 | 170.9006 | 8.36 |
| 17.2083 | 1872.7242 | 91.64 |
| | 2043.6249 | |

**(*R*)-2-(2-(4-chlorophenyl)propyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2q)**

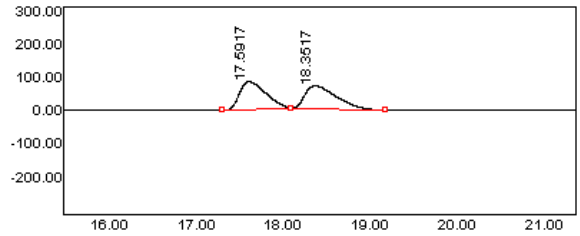



**2q**

By following the general procedure, **2q** was obtained in 89% yield (colorless oil, 86.0 mg) by column chromatography ($NEt_3$:$Et_2O$:hexanes = 1:4:40). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.09–7.06 (m, 2H), 6.99 (d, *J* = 8.3 Hz, 2H), 6.21 (d, *J* = 7.3 Hz, 2H), 5.43 (brs, 2H), 2.97 (sext, *J* = 6.9 Hz, 1H), 1.31 (d, *J* = 6.9 Hz, 3H), 1.26 (dd, *J* = 15.1, 8.1 Hz, 1H), 1.17 (dd, *J* = 15.1, 7.2 Hz, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 147.1, 140.9, 136.3, 131.7, 128.7, 128.0, 127.5, 119.5, 117.5, 105.5, 36.1, 25.2; IR (neat) 3431, 3053, 2962, 1601, 1507, 1412, 1264 cm$^{-1}$; HRMS (ESI) calcd for [$C_{19}H_{18}BClN_2$+H$^+$]: 321.1330, found: 321.1327; 91% ee was measured by chiral HPLC on OZ-H column (*i*-PrOH:hexanes = 1:99, 0.5 mL/min); $t_R$=

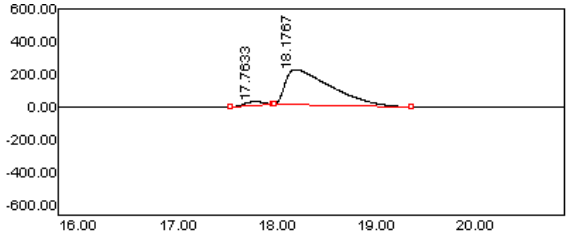
17.59 min (minor), $t_R$ = 18.35 min (major).

**[rac-2q]**



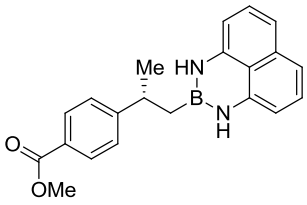

| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 17.5917 | 1753.9846 | 50.54 |
| 18.3517 | 1716.4236 | 49.46 |
| | 3470.4082 | |

**[chi-2q]**




| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 17.7633 | 324.1522 | 4.55 |
| 18.1767 | 6801.0806 | 95.45 |
| | 7125.2329 | |

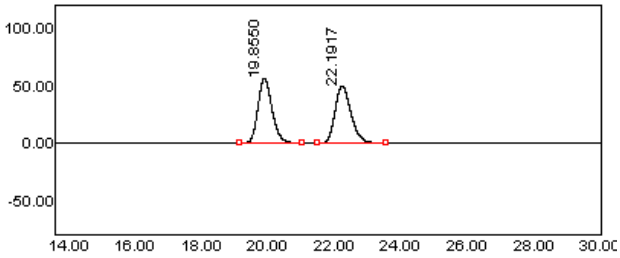
**(*R*)-methyl 4-(1-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)propan-2-yl)benzoate (2r)**




**2r**

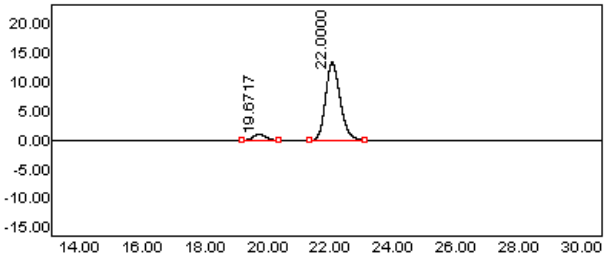
By following the general procedure, **2r** was obtained in 88% yield (pale yellow solid, 91.1 mg) by column chromatography ($NEt_3$:$Et_2O$:hexanes = 1:4:40). $^1$H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.08–7.05 (m, 2H), 6.98 (d, *J* = 8.1 Hz, 2H), 6.20 (d, *J* = 7.3 Hz, 2H), 5.44 (brs, 2H), 3.91 (s, 3H), 3.04 (sext, *J* = 6.9 Hz, 1H), 1.35 (d, *J* = 6.9 Hz, 3H), 1.31 (dd, *J* = 15.2, 8.0 Hz, 1H), 1.21 (dd, *J* = 15.2, 7.3 Hz, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 167.1, 154.2, 140.9, 136.2, 130.0, 128.1, 127.5, 126.6, 119.5, 117.5, 105.5, 52.0, 36.8, 25.1 (C–B), 24.9; $^{11}$B NMR (128 MHz, $CDCl_3$) δ 32.2; IR (neat) 3431, 3054, 2957, 1716, 1601, 1282 $cm^{-1}$; HRMS (ESI) calcd for [$C_{21}H_{21}BN_2O_2$+$H^+$]: 345.1774, found: 345.1772; 87% ee was measured by chiral HPLC on AD-H column (*i*-PrOH:hexanes = 7:93, 1.0 mL/min); $t_R$= 19.86 min (minor), $t_R$ = 22.19 min (major).

**[rac-2r]**



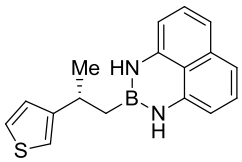

| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 19.8550 | 1664.4202 | 49.99 |
| 22.1917 | 1664.8469 | 50.01 |
| | 3329.2671 | |

**[chi-2r]**




| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 19.6717 | 29.0859 | 6.31 |
| 22.0000 | 431.9191 | 93.69 |
| | 461.0050 | |

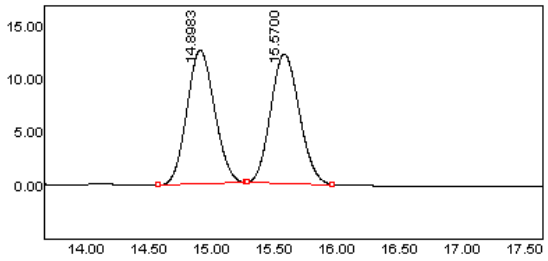
**(*R*)-2-(2-(thiophen-3-yl)propyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2s)**




**2s**

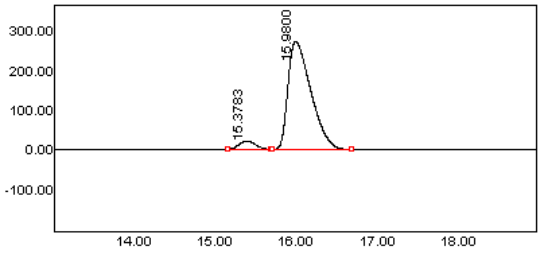
By following the general procedure, **2s** was obtained in 97% yield (yellow oil, 85.3 mg) by column chromatography ($NEt_3$:$Et_2O$:hexanes = 1:4:40). $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 4.8, 3.0 Hz, 1H), 7.09–7.06 (m, 3H), 7.02–6.98 (m, 3H), 6.19 (d, *J* = 7.3 Hz, 2H), 5.43 (brs, 2H), 3.13 (sext, *J* = 6.8 Hz, 1H), 1.35 (d, *J* = 6.8 Hz, 3H), 1.29 (dd, *J* = 15.1, 8.0 Hz, 1H), 1.20 (dd, *J* = 15.1, 6.6 Hz, 1H); $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 149.7, 141.0, 136.3, 127.5, 126.8, 125.8, 119.6, 118.8, 117.4, 105.5, 31.9, 25.1 (C–B), 24.7; IR (neat) 3430, 3053, 2961, 1600, 1507, 1413, 1264 $cm^{-1}$; HRMS (FAB) calcd for [$C_{17}H_{17}BN_2S^+$]: 292.1205, found: 292.1207; 89% ee was measured by chiral HPLC on OZ-H column (*i*-PrOH:hexanes = 1:99, 0.5 mL/min); $t_R$= 14.90 min (minor), $t_R$ = 15.57 min (major).

**[rac-2s]**




| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 14.8983 | 195.0424 | 50.15 |
| 15.5700 | 193.8764 | 49.85 |
| | 388.9188 | |

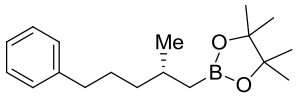
**[chi-2s]**




| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 15.3783 | 319.0046 | 5.60 |
| 15.9800 | 5376.0610 | 94.40 |
| | 5695.0654 | |

## Derivatizations of β-Chiral Dialkyl Boron (Scheme 3b)

**(*R*)-4,4,5,5-tetramethyl-2-(2-methyl-5-phenylpentyl)-1,3,2-dioxaborolane (3b)**

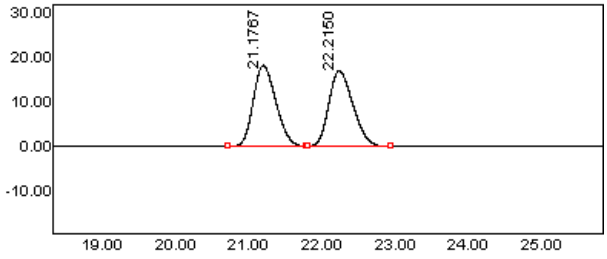



**3b**

To a solution of **2b** (0.17 mmol, 56 mg) in THF (1 mL) was added aq. $H_2SO_4$ (2.0 M, 0.51 mmol, 0.26 mL) and pinacol (0.85 mmol, 100.5 mg) sequentially. Then, the reaction mixture was stirred for 24 h at rt. Upon completion of the reaction, the reaction mixture was extracted three times with diethyl ether and washed with $H_2O$. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude was purified by silica gel chromatography (EtOAc:hexanes = 1:20). **3b** was obtained in 84% yield (colorless oil, 41.0 mg). $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.28–7.25 (m, 2H), 7.18–7.15 (m, 3H), 2.59 (t, *J* = 7.8 Hz, 2H), 1.77–1.69 (m, 1H), 1.68–1.55 (m, 2H), 1.36–1.29 (m, 1H), 1.27

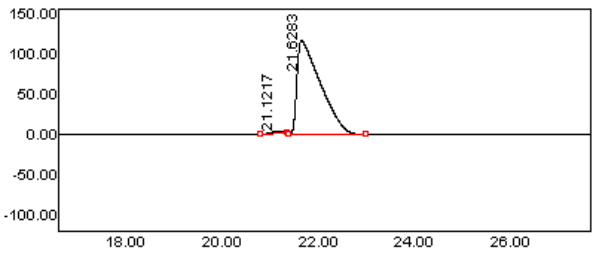
–1.19 (m, 1H), 1.23 (s, 12H), 0.92 (d, *J* = 6.6 Hz, 3H), 0.89 (dd, *J* = 15.3, 5.9 Hz, 1H), 0.66 (dd, *J* = 15.3, 8.3 Hz, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 143.0, 128.4, 128.2, 125.5, 82.8, 39.2, 36.2, 29.5, 29.2, 24.9, 24.8, 22.4, 19.8 (C–B); IR (neat) 2978, 1454, 1370, 1316, 1145 cm$^{-1}$; HRMS (ESI) calcd for [$C_{18}H_{29}BO_2$+$Na^+$]: 311.2158, found: 311.2156; 97% ee was measured by chiral HPLC on OJ-H column with the corresponding alcohol obtained after oxidation[3] (*i*-PrOH:hexanes = 3:97, 0.5 mL/min); $t_R$= 21.18 min (minor), $t_R$ = 21.22 min (major).

**[rac-3b]**



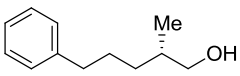

| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 21.1767 | 390.9311 | 50.14 |
| 22.2150 | 388.6917 | 49.86 |
| | 779.6228 | |

**[chi-3b]**




| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 21.1217 | 61.8685 | 1.55 |
| 21.6283 | 3925.6167 | 98.45 |
| | 3987.4854 | |

**Enantioselective synthesis of (*S*)-Rosaphen (4b)**

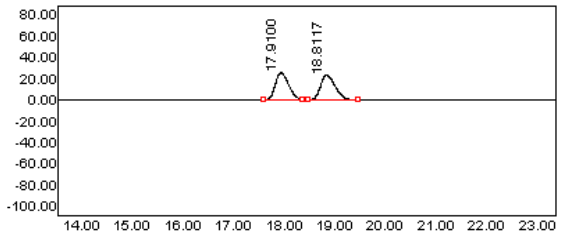



**4b**

To a solution of **2b** (1 equiv, 0.3 mmol) in THF (0.1 M) was added aq. HCl (5.0 M, 3.0 mmol). The mixture was stirred at rt for 24 h and monitored by TLC. The resulting mixture was extracted three times with ethyl acetate and washed with $H_2O$. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. After the crude was dissolved in MeOH (0.63 M) and THF (0.63 M), hydrogen peroxide 35% (100 eqiuv, 30 mmol) was added at 0 ℃ and stirred at room temperature for 12 h. Upon completion of the reaction, saturated aq. $Na_2S_2O_3$ solution was added to the reaction mixture. The resulting mixture was extracted with ethyl acetate and washed with brine. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. It was purified by silica gel chromatography (EtOAc:hexanes = 1:5). **4b** was obtained in 61% yield (pale yellow oil, 32.8 mg). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.30–7.26 (m, 2H), 7.19–7.17 (m, 3H), 3.49–3.44 (m, 1H), 3.44–3.41 (m, 1H), 2.66–2.56 (m, 2H), 1.75–1.59 (m, 3H), 1.47 (ddt, *J* = 13.4, 10.8, 5.4 Hz, 1H), 1.25 (brs, 1H), 1.17 (dddd, *J* = 13.3, 10.6, 8.1, 5.2 Hz, 1H), 0.92 (d, *J* = 6.7 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 142.6, 128.4, 128.3, 125.7, 68.3, 36.2, 35.7, 32.8, 28.9, 16.5; $[\alpha]_D$= –12.8 (c = 1.0, EtOH) (lit.[4] $[\alpha]_D$= +10.9 (c

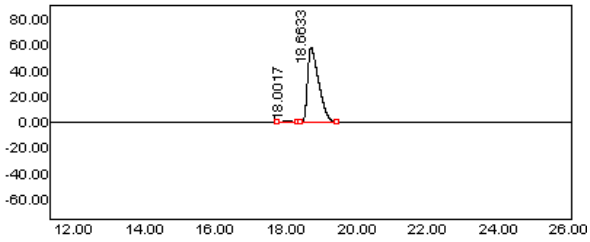
= 1.0, EtOH)). 97% ee was measured by chiral HPLC on OJ-H column (*i*-PrOH:hexanes = 3:97, 0.5 mL/min); $t_R$= 17.91 min (minor), $t_R$ = 18.81 min (major).

**[rac-4b]**



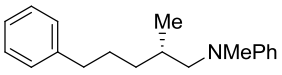

| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 17.9100 | 462.6696 | 49.56 |
| 18.8117 | 470.9311 | 50.44 |
| | 933.6007 | |

**[chi-4b]**




| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 18.0017 | 22.4628 | 1.72 |
| 18.6633 | 1285.6807 | 98.28 |
| | 1308.1434 | |

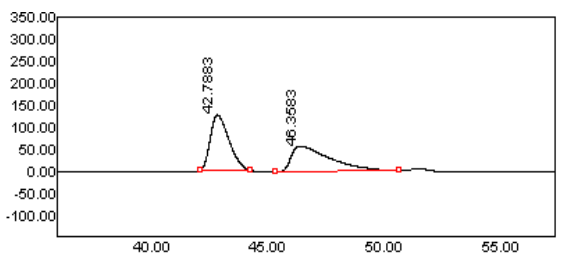
**(*S*)-*N*-methyl-*N*-(2-methyl-5-phenylpentyl)aniline (5b)**



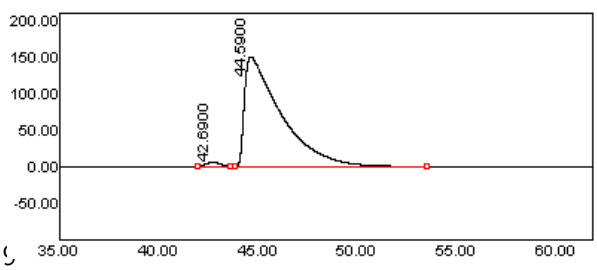

**5b**

A solution of $Cu(OAc)_2$ (10 mol %, 0.03 mmol) in toluene (0.5 mL) was stirred for 10 min in a Schlenk tube under an atmosphere of nitrogen. **2b** (1 equiv, 0.3 mmol) dissolved in toluene (0.7 mL), $(t\text{-BuO})_2$ (3.0 equiv, 0.9 mmol) and *N*-methylaniline (1 equiv, 0.3 mmol) were added. The reaction mixture was stirred at 85 ℃ and monitored by GC. The resulting mixture was filtered by pad of Celite and concentrated. It was purified by silica gel chromatography (EtOAc:hexanes = 1:20). **5b** was obtained in 48% yield (yellow oil, 38.7 mg). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.30–7.27 (m, 2H), 7.24–7.21 (m, 2H), 7.20–7.17 (m, 3H), 6.68–6.67 (m, 3H), 3.21 (dd, *J* = 14.5, 6.6 Hz, 1H), 3.04 (dd, *J* = 14.5, 7.8 Hz, 1H), 2.94 (s, 3H), 2.66–2.54 (m, 2H), 2.00–1.91 (m, 1H), 1.78–1.69 (m, 1H), 1.65–1.58 (m, 1H), 1.50–1.43 (m, 1H), 1.21–1.13 (m, 1H), 0.91 (d, *J* = 6.6 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 149.7, 142.6, 129.1, 128.4, 128.3, 125.7, 115.6, 111.8, 59.8, 39.5, 36.3, 34.3, 32.1, 29.0, 17.7; IR (neat) 2933, 1599, 1506, 1343 $cm^{-1}$; HRMS (ESI) calcd for $[C_{19}H_{25}N+H^+]$: 268.2065, found: 268.2064; 97% ee was measured by chiral HPLC on OJ-H column (*i*-PrOH:hexanes = 1:99, 0.5 mL/min); $t_R$= 42.79 min (minor), $t_R$ = 46.36 min (major).

**[rac-5b]**



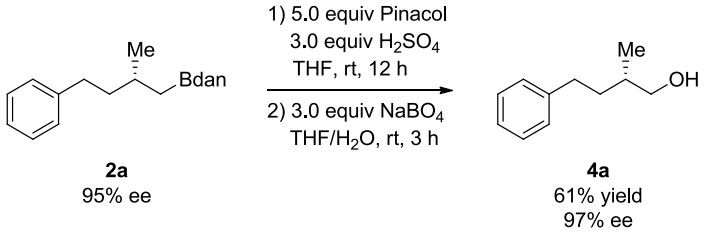

**[chi-5b]**



| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 42.7883 | 6953.0635 | 50.82 |
| 46.3583 | 6729.5283 | 49.18 |
| | 13682.5918 | |

| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 42.6900 | 341.0244 | 1.72 |
| 44.5900 | 19507.9043 | 98.28 |
| | 19848.9297 | |

## Determination of Absolute Configuration of 2a and 2p

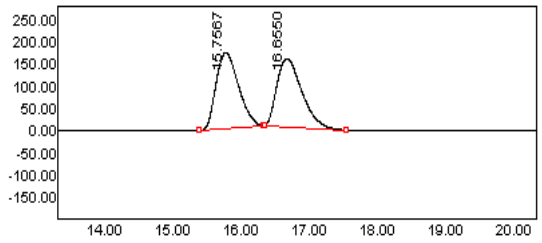



**2a**
95% ee

**4a**
61% yield
97% ee

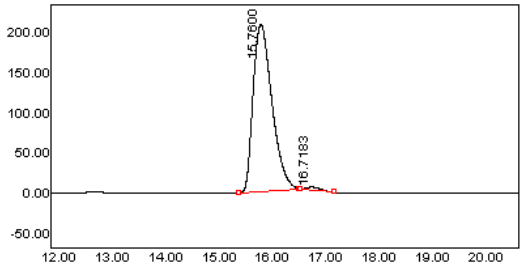
**(*S*)-2-methyl-4-phenylbutan-1-ol (4a)** $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.30–7.26 (m, 2H), 7.20–7.16 (m, 3H), 3.56–3.53 (m, 1H), 3.49–3.46 (m, 1H), 2.71 (ddd, *J* = 13.8, 10.1, 5.6 Hz, 1H), 2.60 (ddd, *J* = 13.8, 10.1, 6.4 Hz, 1H), 1.80–1.73 (m, 1H), 1.71–1.64 (m, 1H), 1.49–1.41 (m, 1H), 1.26 (brs, 1H), 0.99 (d, *J* = 6.7 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 142.6, 128.3, 125.7, 68.2, 35.4, 35.0, 33.3, 16.5; $[\alpha]_D$ = –18.7 (c = 1.03, $CHCl_3$) (lit.[5] $[\alpha]_D$ = –12.3 (c = 1.01, $CHCl_3$)). 97% ee was measured by chiral HPLC on AS-H column (*i*-PrOH:hexanes = 2:98, 0.5 mL/min); $t_R$ = 15.76 min (major), $t_R$ = 16.66 min (minor).

**[rac-4a]**

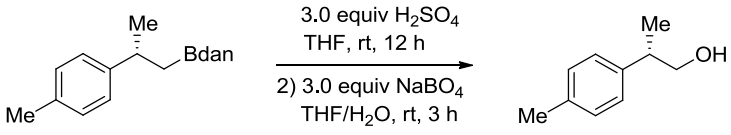



| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 15.7567 | 3949.8521 | 50.47 |
| 16.6550 | 3876.1938 | 49.53 |
| | 7826.0459 | |

**[chi-4a]**




| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 15.7600 | 5111.7822 | 98.71 |
| 16.7183 | 66.7460 | 1.29 |
| | 5178.5283 | |

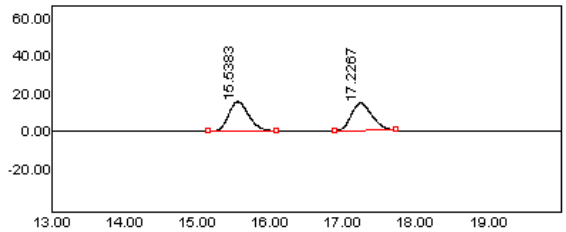



**2p**

**4p**
60% yield
83% ee

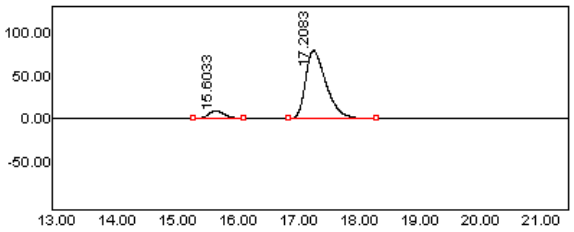
**(*S*)-2-(*p*-tolyl)propan-1-ol (4p)** $^1$H NMR (500 MHz, $CDCl_3$) δ 7.21–7.10 (m, 4H), 3.68 (t, *J* = 6.2 Hz, 2H), 2.92 (sext, *J* = 7.0 Hz, 1H), 2.34 (s, 3H), 1.37 (t, *J* = 5.6 Hz, 1H), 1.26 (d, *J* = 7.0 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 140.6, 136.2, 129.4, 127.4, 68.8, 42.0, 21.0, 17.7; $[\alpha]_D$= −13.1 (c = 2.4, $CHCl_3$) (lit.[6] $[\alpha]_D$= +14.1 (c = 2.75, $CHCl_3$)). 83% ee was measured by chiral HPLC on AD-H column (*i*-PrOH:hexanes = 1:99, 1.0 mL/min); $t_R$ = 15.54 min (minor), $t_R$ = 17.23 min (major).

**[rac-4p]**



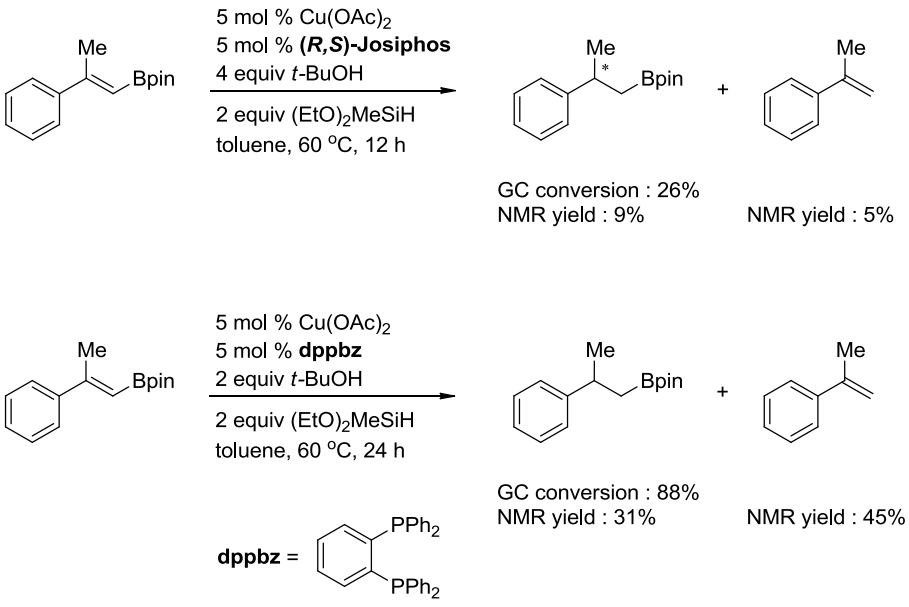

| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 15.5383 | 301.9670 | 50.92 |
| 17.2267 | 291.0564 | 49.08 |
| | 593.0234 | |

**[chi-4p]**




| RT [min] | Area [mV·s] | Area% |
|---|---|---|
| 15.6033 | 170.9006 | 8.36 |
| 17.2083 | 1872.7242 | 91.64 |
| | 2043.6249 | |

## Scheme S1. Reduction of β,β-Disubstituted Alkenyl Pinacol Boronates

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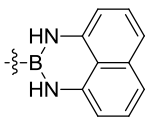
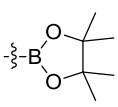
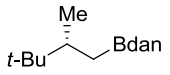
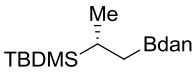
Bdan = 


Bpin = 

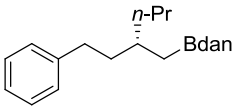
## Scheme S2. Inefficient Substrates under the Standard Reaction Conditions



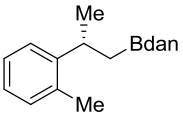

NMR conversion : 51%
ee : 45%




NMR conversion : 30%
ee : 93%




NMR conversion : 59%
ee : 95%




NMR conversion : 33%

## References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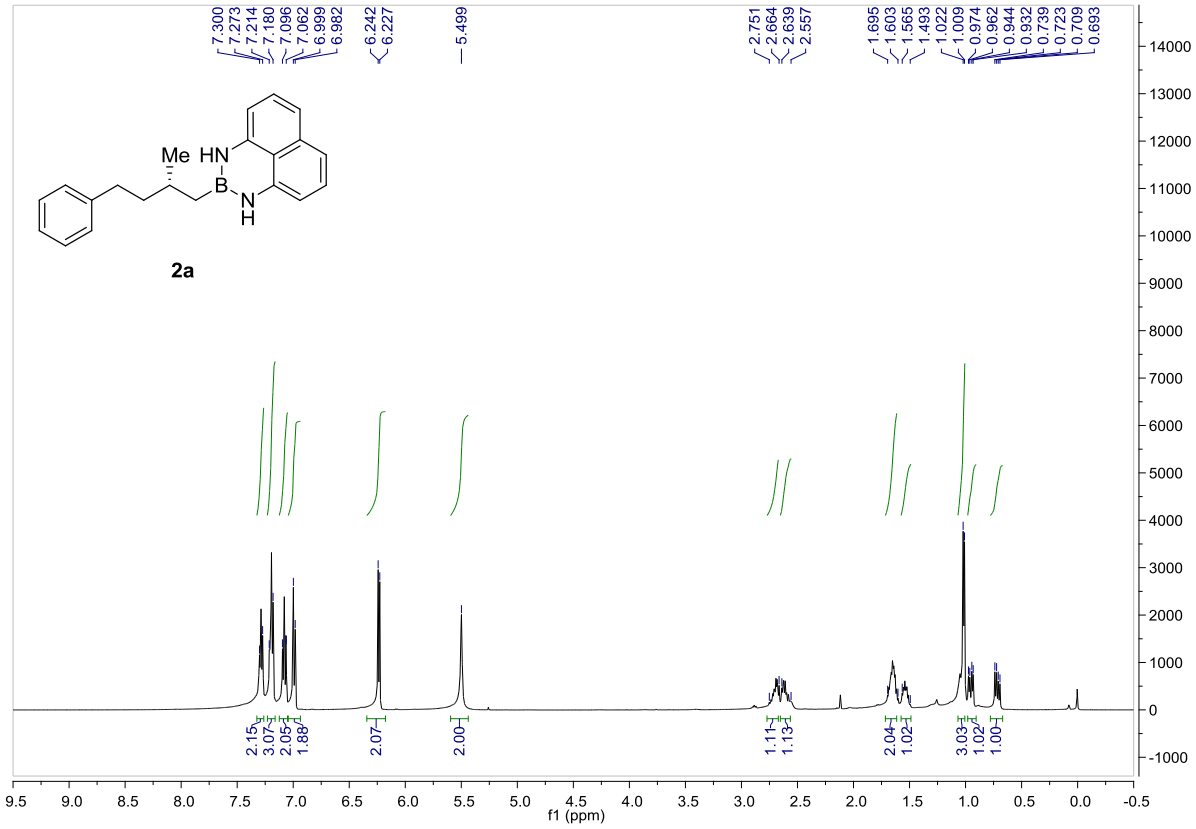
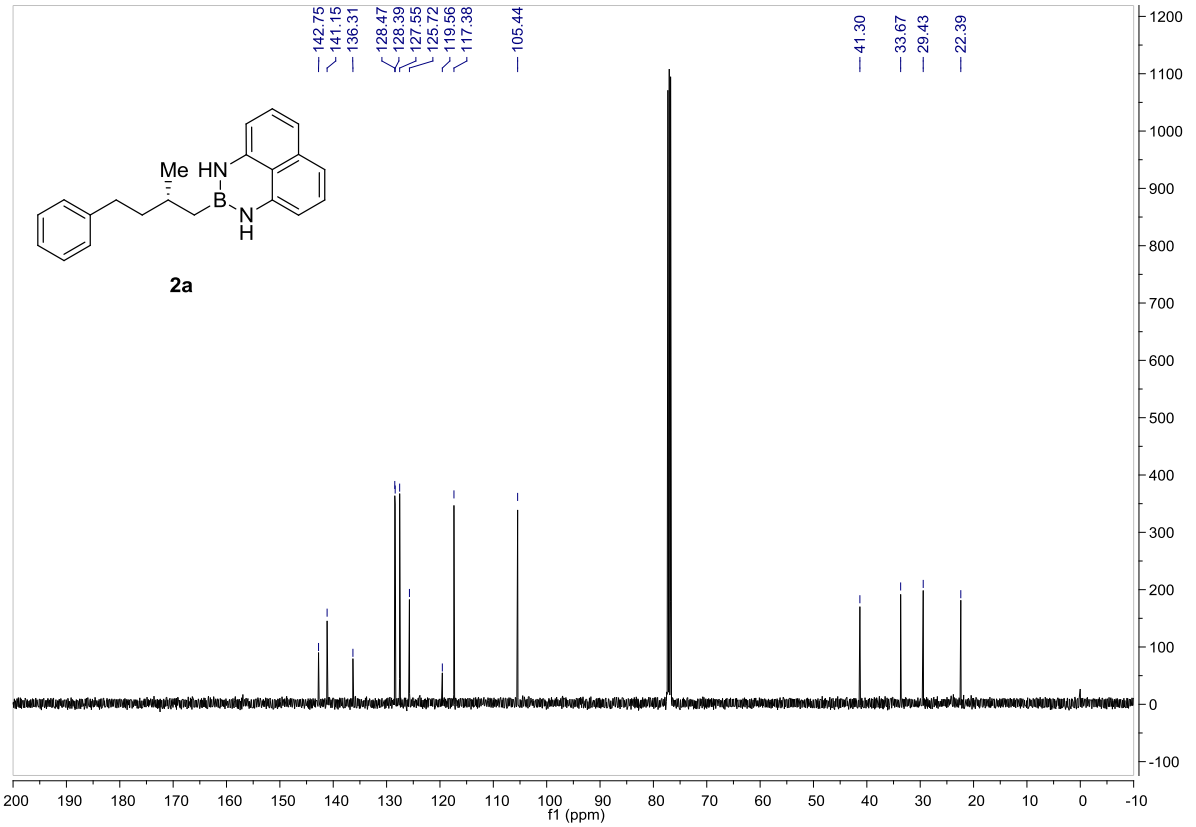
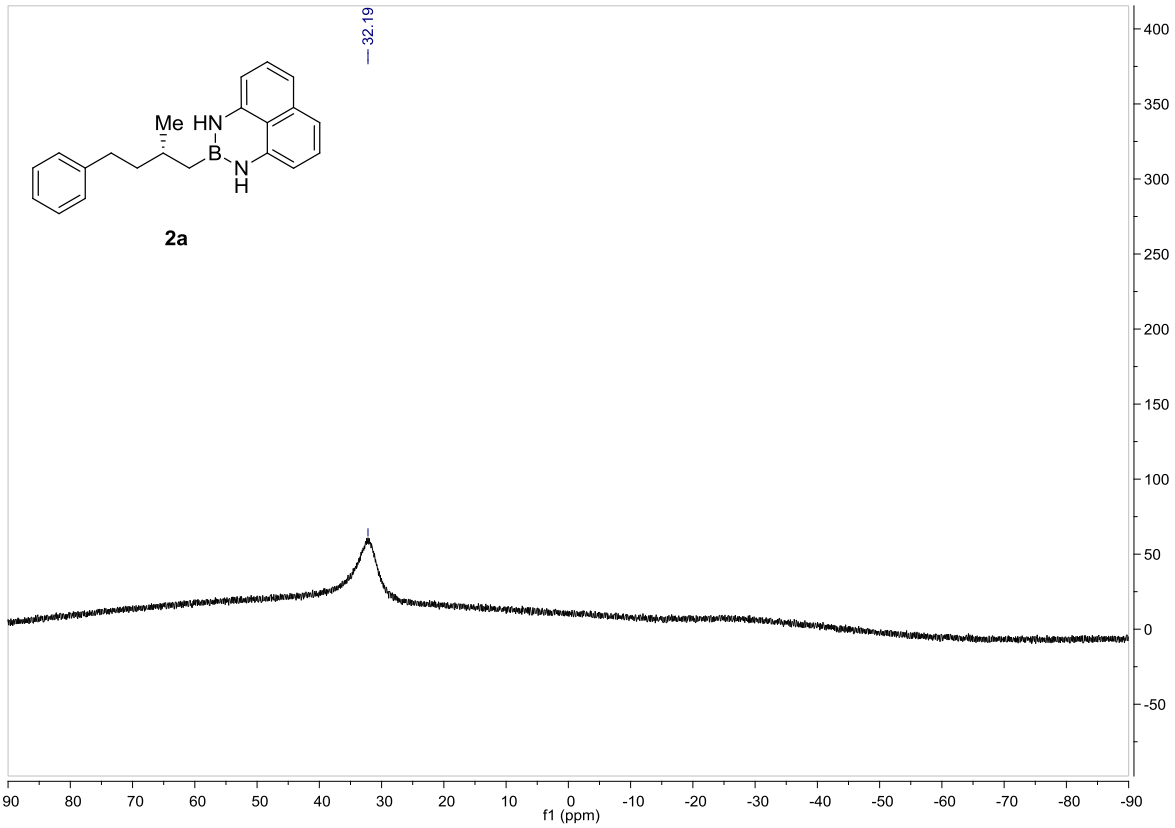
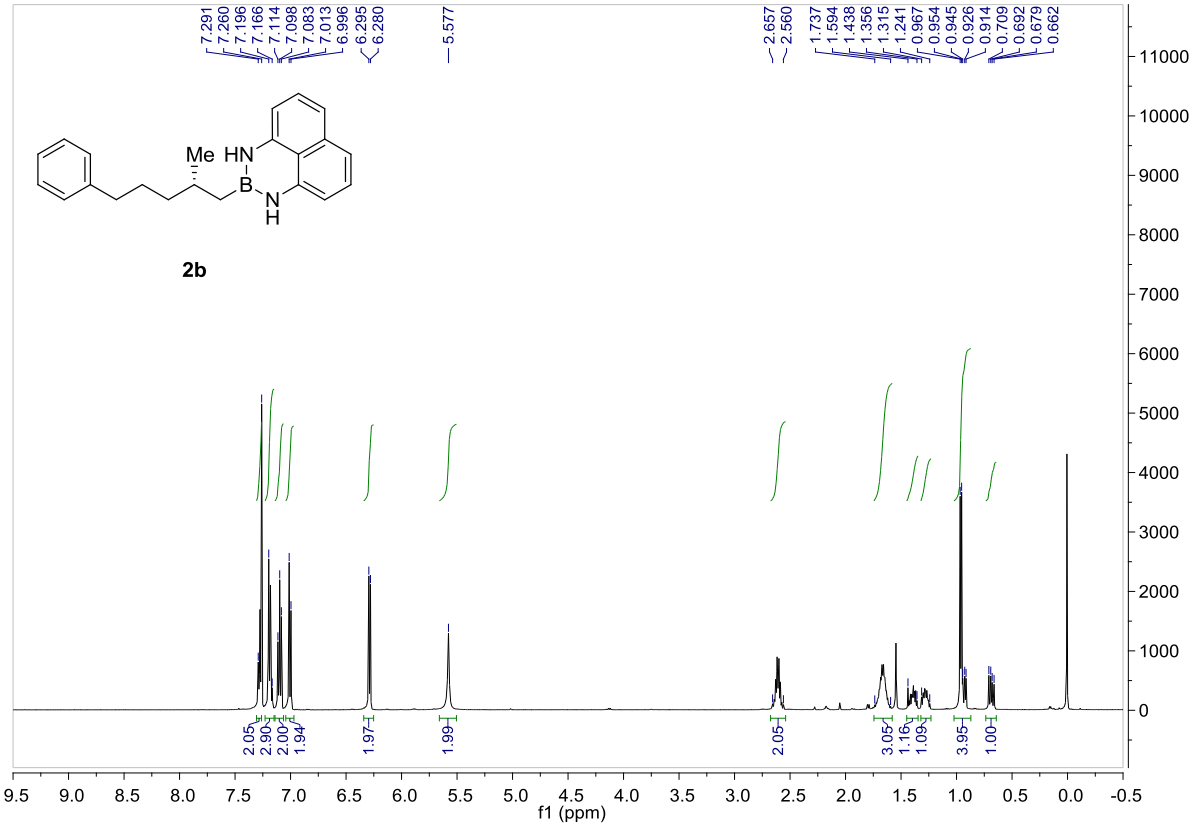
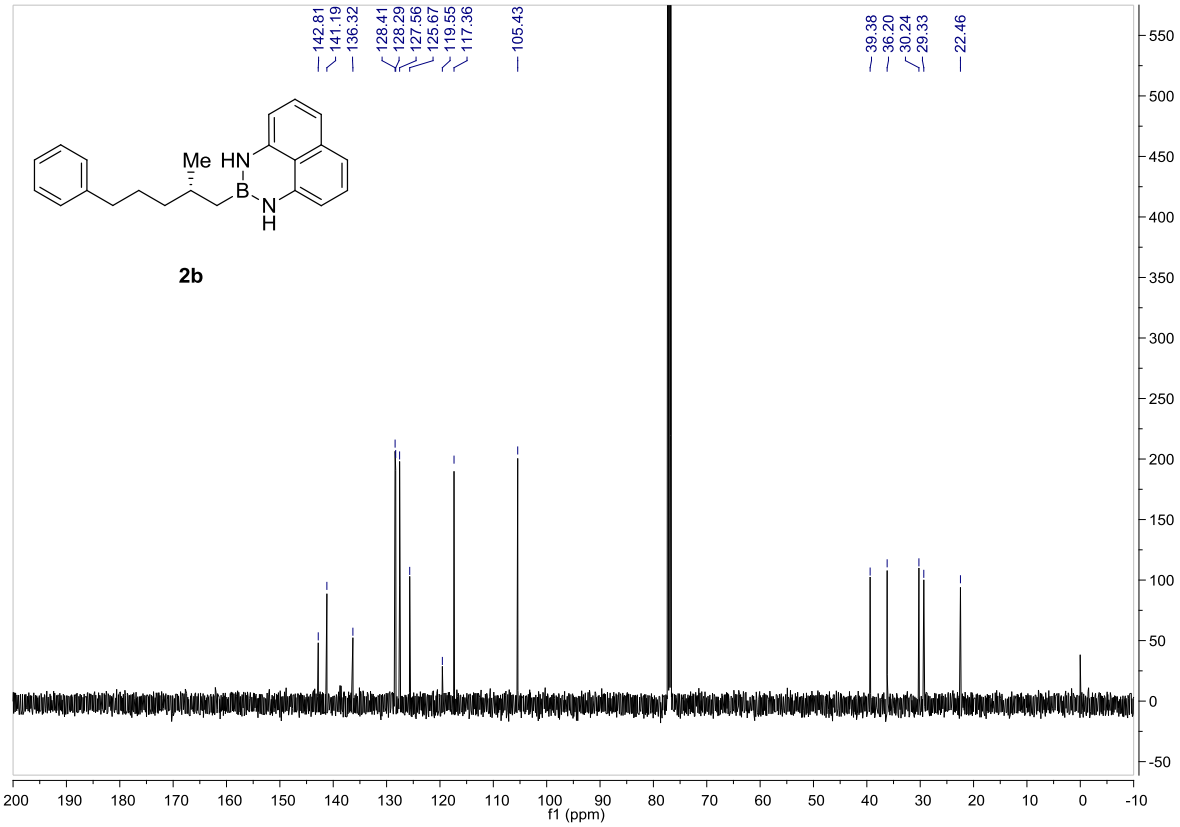
## NMR Spectra

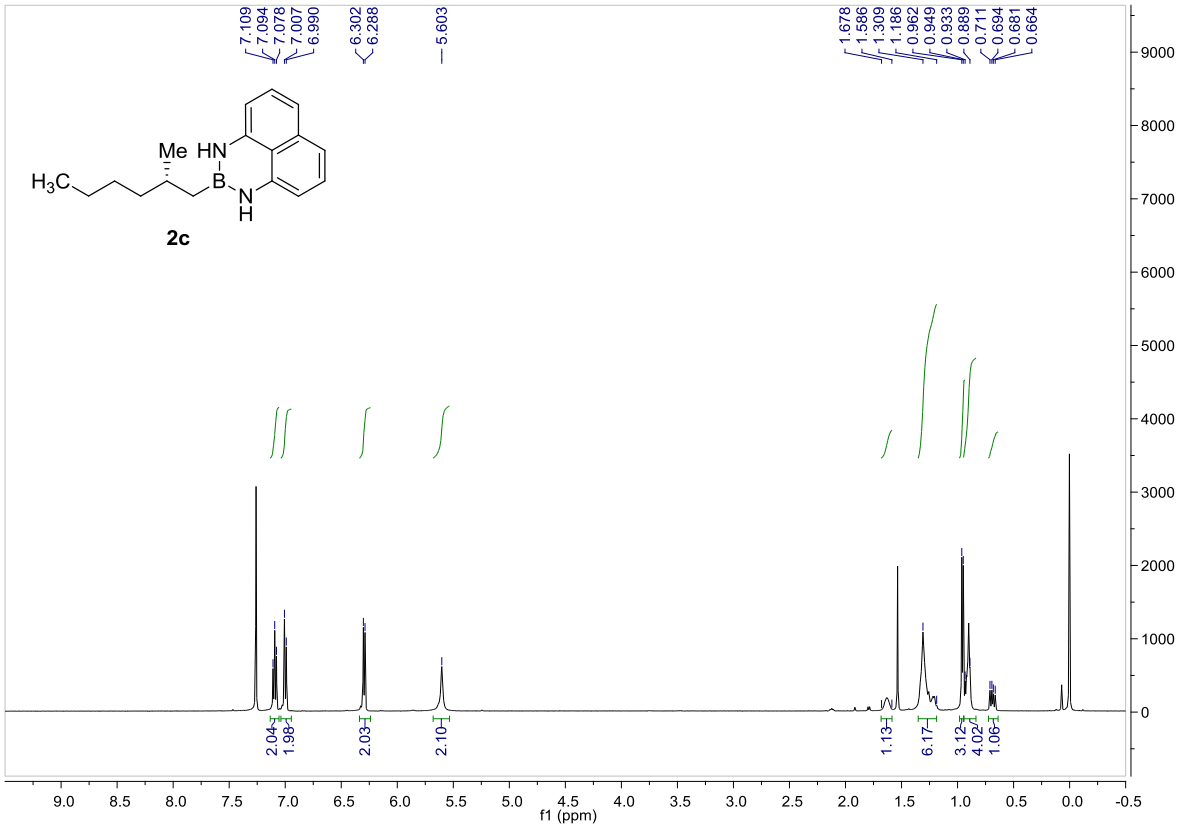

7.300
7.273
7.214
7.180
7.096
7.062
6.999
6.982
6.242
6.227
5.499
2.751
2.664
2.639
2.557
1.695
1.603
1.565
1.493
1.022
1.009
0.974
0.962
0.944
0.932
0.739
0.723
0.709
0.693
Me HN
B
N
H
2a
2.15
3.07
2.05
1.88
2.07
2.00
1.11
1.13
2.04
1.02
3.03
1.02
1.00
f1 (ppm)

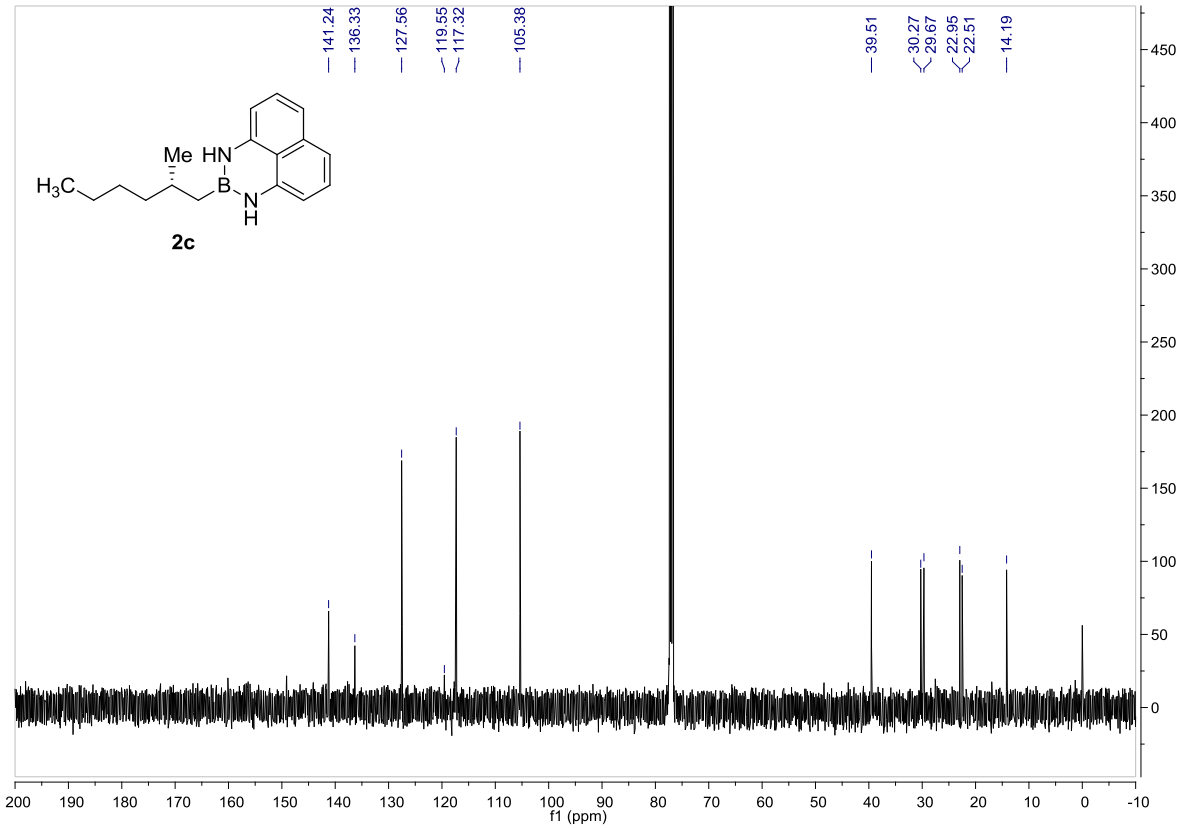

142.75
141.15
136.31
128.47
128.39
127.55
125.72
119.56
117.38
105.44
41.30
33.67
29.43
22.39
Me HN
B
N
H
2a
f1 (ppm)


32.19
Me
HN
B
N
H
2a
400
350
300
250
200
150
100
50
0
-50
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)


7.291
7.260
7.196
7.166
7.114
7.098
7.083
7.013
6.996
6.295
6.280
5.577
2.657
2.560
1.737
1.594
1.438
1.356
1.315
1.241
0.967
0.954
0.945
0.926
0.914
0.709
0.692
0.679
0.662
Me HN
B
N
H
2b
2.05
2.90
2.00
1.94
1.97
1.99
2.05
3.05
1.16
1.09
3.95
1.00
f1 (ppm)


142.81
141.19
136.32
128.41
128.29
127.56
125.67
119.55
117.36
105.43
39.38
36.20
30.24
29.33
22.46
Me HN
B
N
H
2b
f1 (ppm)


7.109
7.094
7.078
7.007
6.990
6.302
6.288
5.603
1.678
1.586
1.309
1.186
0.962
0.949
0.933
0.889
0.711
0.694
0.681
0.664
Me HN
H3C
B
N
H
2c
2.04
1.98
2.03
2.10
1.13
6.17
3.12
4.02
1.06
f1 (ppm)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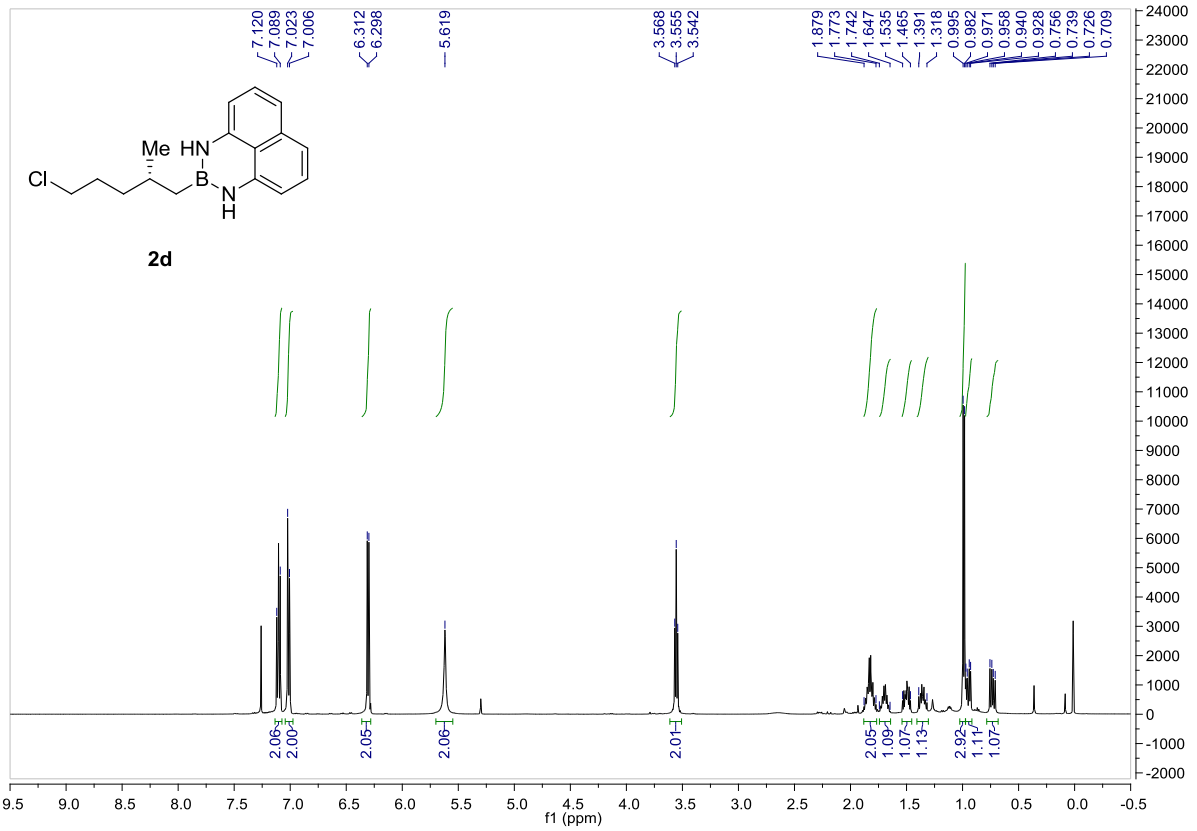
136.33
127.56
119.55
117.32
105.38
39.51
30.27
29.67
22.95
22.51
14.19
Me HN
H3C
B
N
H
2c
f1 (ppm)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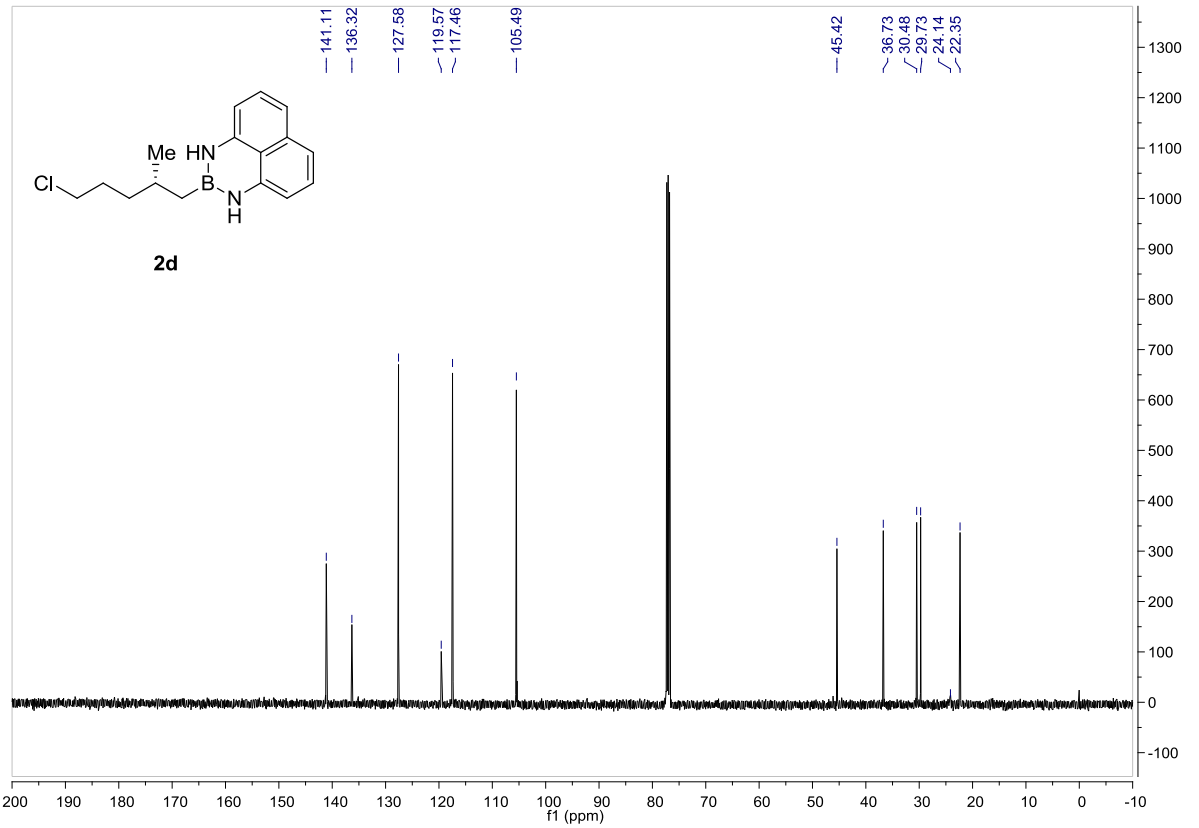
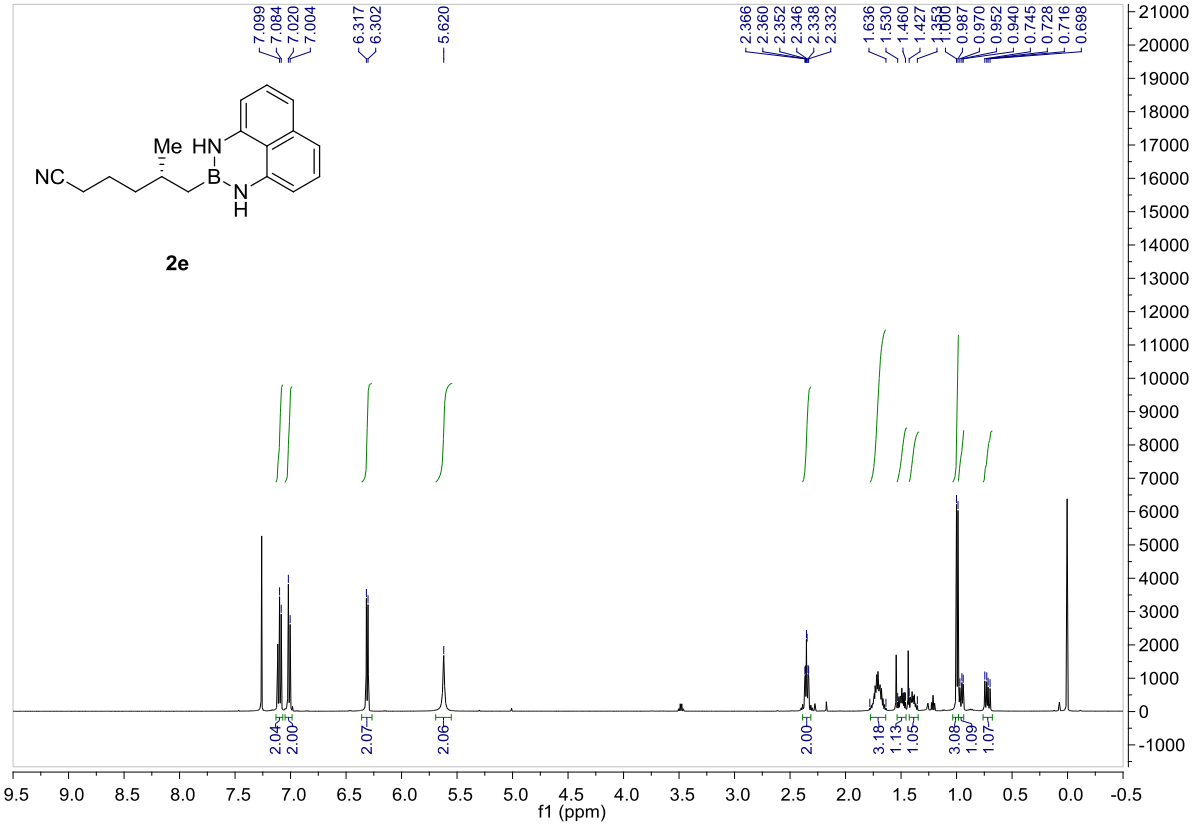
7.023
7.006
6.312
6.298
5.619
3.568
3.555
3.542
1.879
1.773
1.742
1.647
1.535
1.465
1.391
1.318
0.995
0.982
0.971
0.958
0.940
0.928
0.756
0.739
0.726
0.709
Me HN
Cl
B
N
H
2d
2.06
2.00
2.05
2.06
2.01
2.05
1.09
1.07
1.13
2.92
1.11
1.07
f1 (ppm)


141.11
136.32
127.58
119.57
117.46
105.49
45.42
36.73
30.48
29.73
24.14
22.35
Me HN
Cl
B
N
H
2d
f1 (ppm)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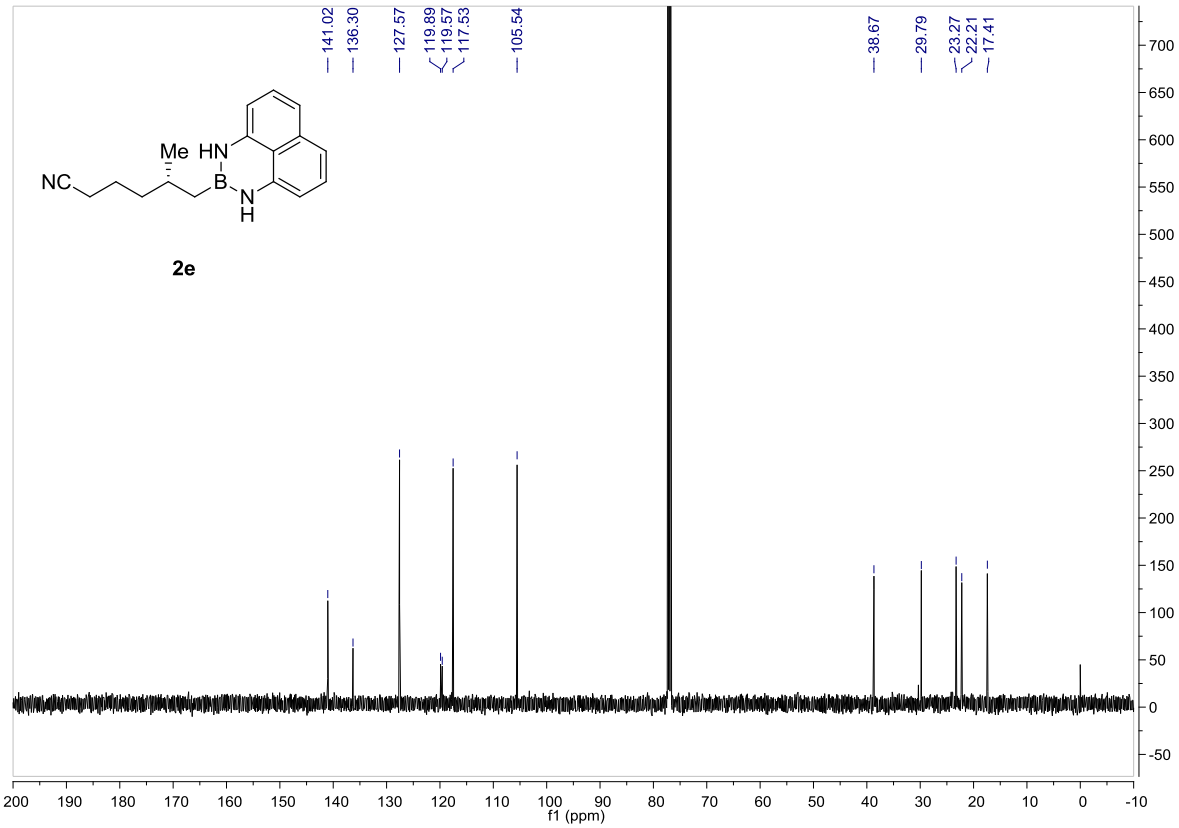
7.020
7.004
6.317
6.302
5.620
2.366
2.360
2.352
2.346
2.338
2.332
1.636
1.530
1.460
1.427
0.987
0.970
0.952
0.940
0.745
0.728
0.716
0.698
Me HN
NC
B
N
H
2e
2.04
2.00
2.07
2.06
2.00
3.18
1.13
1.05
3.08
1.09
1.07
f1 (ppm)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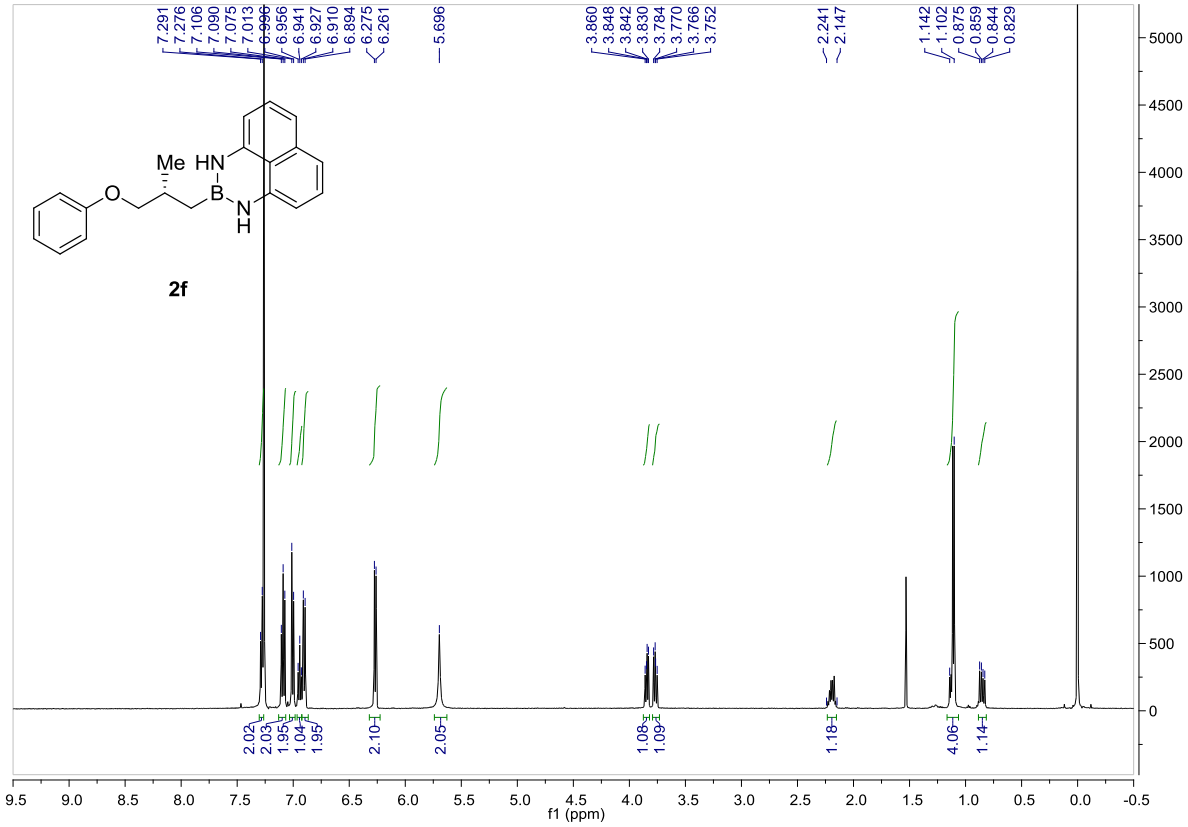
136.30
127.57
119.89
119.57
117.53
105.54
38.67
29.79
23.27
22.21
17.41
Me HN
NC
B
N
H
2e
f1 (ppm)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7.106
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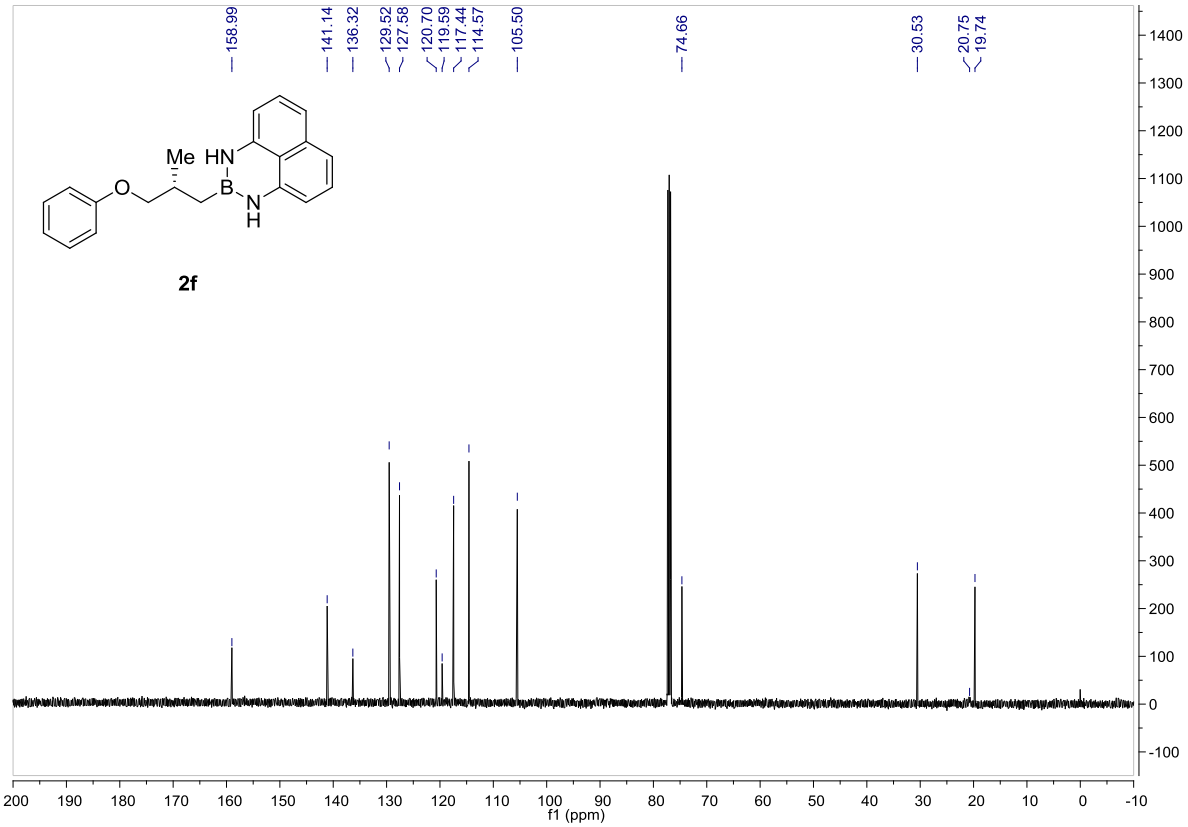
7.075
7.013
6.956
6.941
6.927
6.910
6.894
6.275
6.261
5.696
3.860
3.848
3.842
3.830
3.784
3.770
3.766
3.752
2.241
2.147
1.142
1.102
0.875
0.859
0.844
0.829
Me HN
B
N
H
O
2f
2.02
2.03
1.95
1.04
1.95
2.10
2.05
1.08
1.09
1.18
4.06
1.14
f1 (ppm)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141.14
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129.52
127.58
120.70
119.59
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114.57
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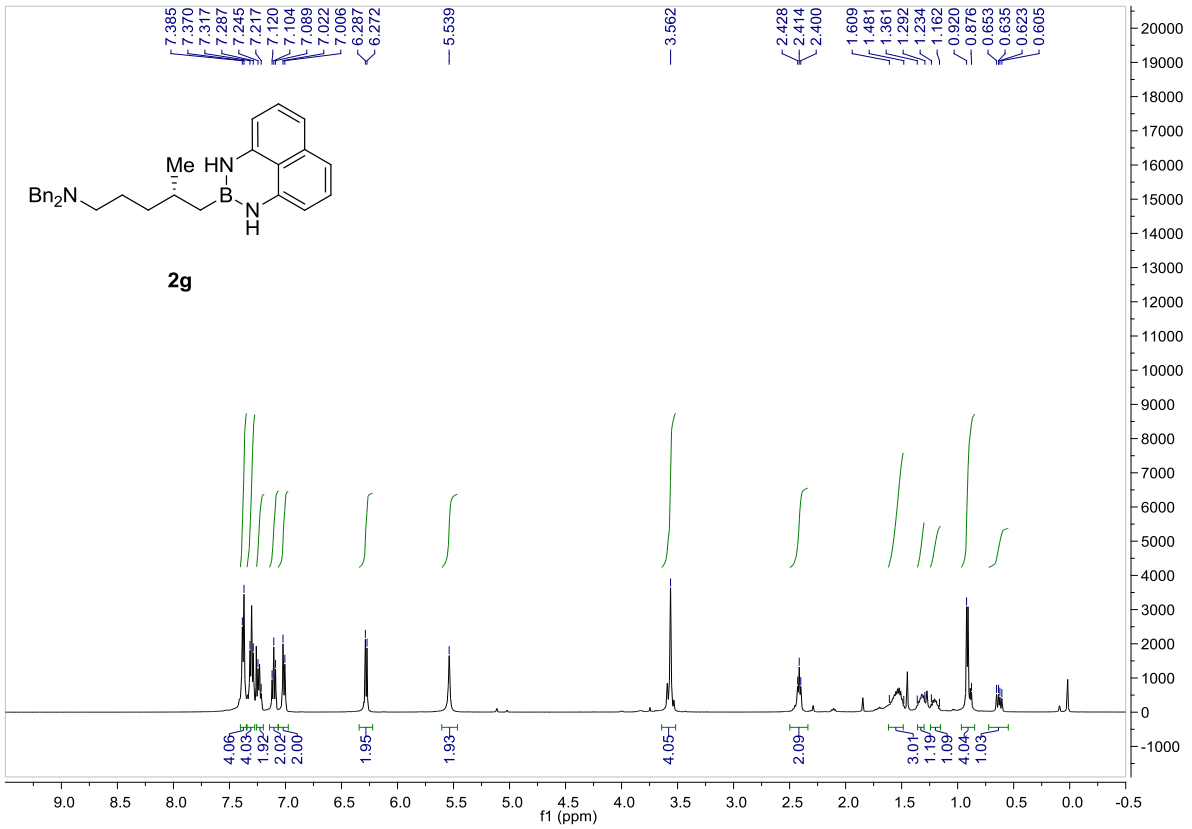
74.66
30.53
20.75
19.74
Me HN
B
N
H
O
2f
f1 (ppm)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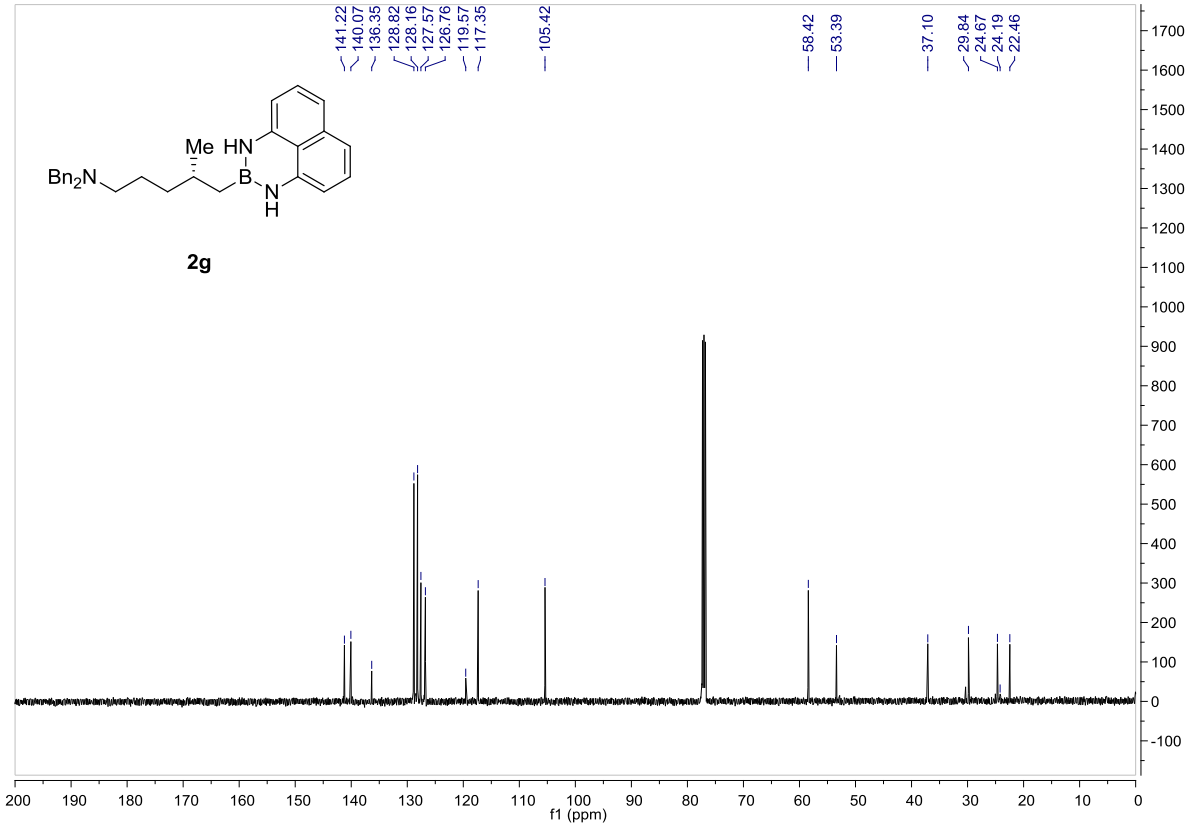
7.317
7.287
7.245
7.217
7.120
7.104
7.089
7.022
7.006
6.287
6.272
5.539
3.562
2.428
2.414
2.400
1.609
1.481
1.361
1.292
1.234
1.162
0.920
0.876
0.653
0.635
0.623
0.605
Me HN
Bn2N
B
N
H
2g
4.06
4.03
1.92
2.02
2.00
1.95
1.93
4.05
2.09
3.01
1.19
1.09
4.04
1.03
f1 (ppm)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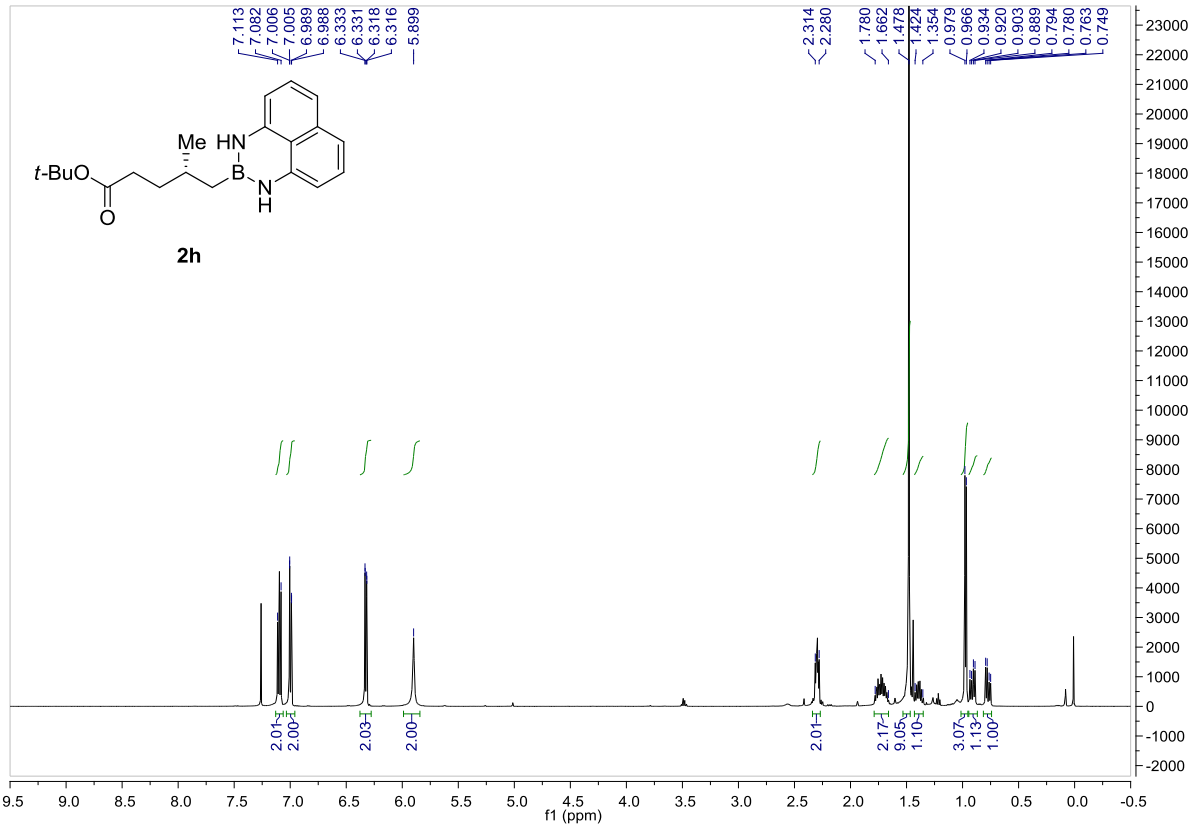
140.07
136.35
128.82
128.16
127.57
126.76
119.57
117.35
105.42
58.42
53.39
37.10
29.84
24.67
24.19
22.46
Me HN
Bn2N
B
N
H
2g
f1 (ppm)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7.006
7.005
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6.988
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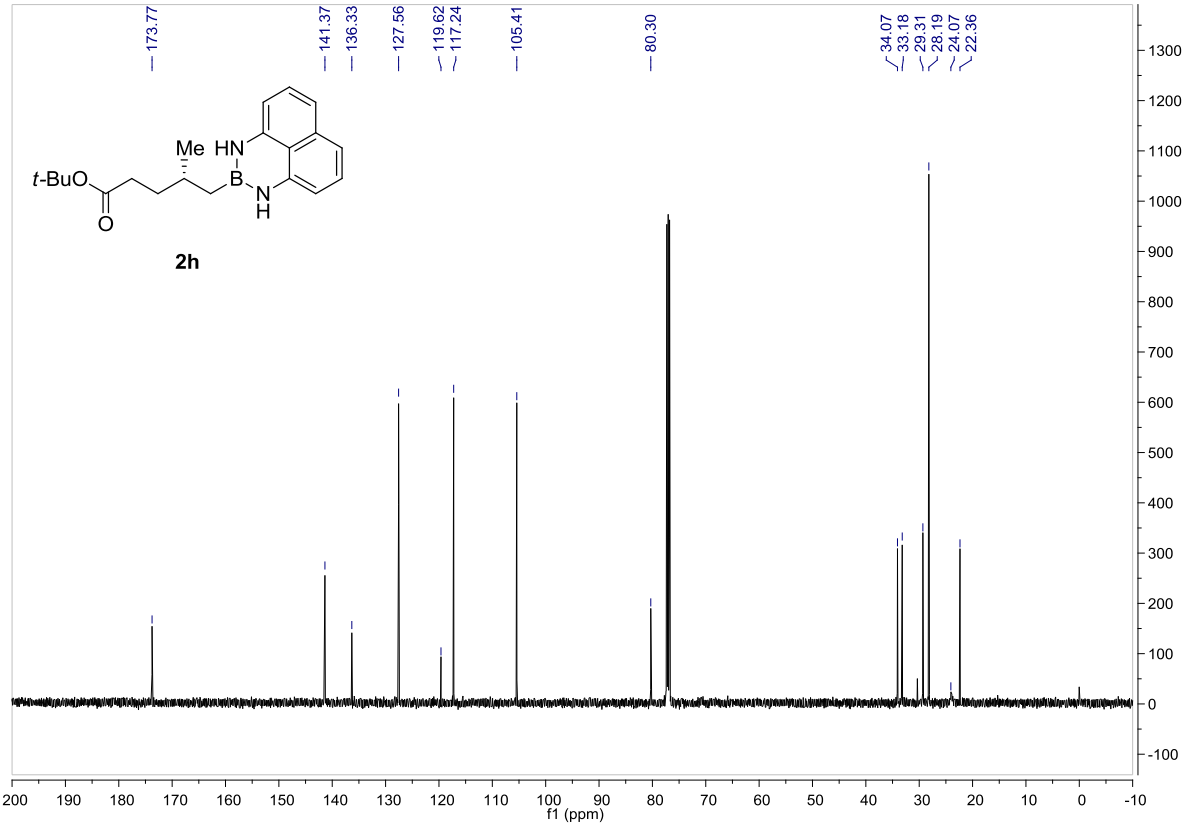
6.331
6.318
6.316
5.899
2.314
2.280
1.780
1.662
1.478
1.424
1.354
0.979
0.966
0.934
0.920
0.903
0.889
0.794
0.780
0.763
0.749
Me HN
t-BuO
B
N
H
O
2h
2.01
2.00
2.03
2.00
2.01
2.17
9.05
1.10
3.07
1.13
1.00
f1 (ppm)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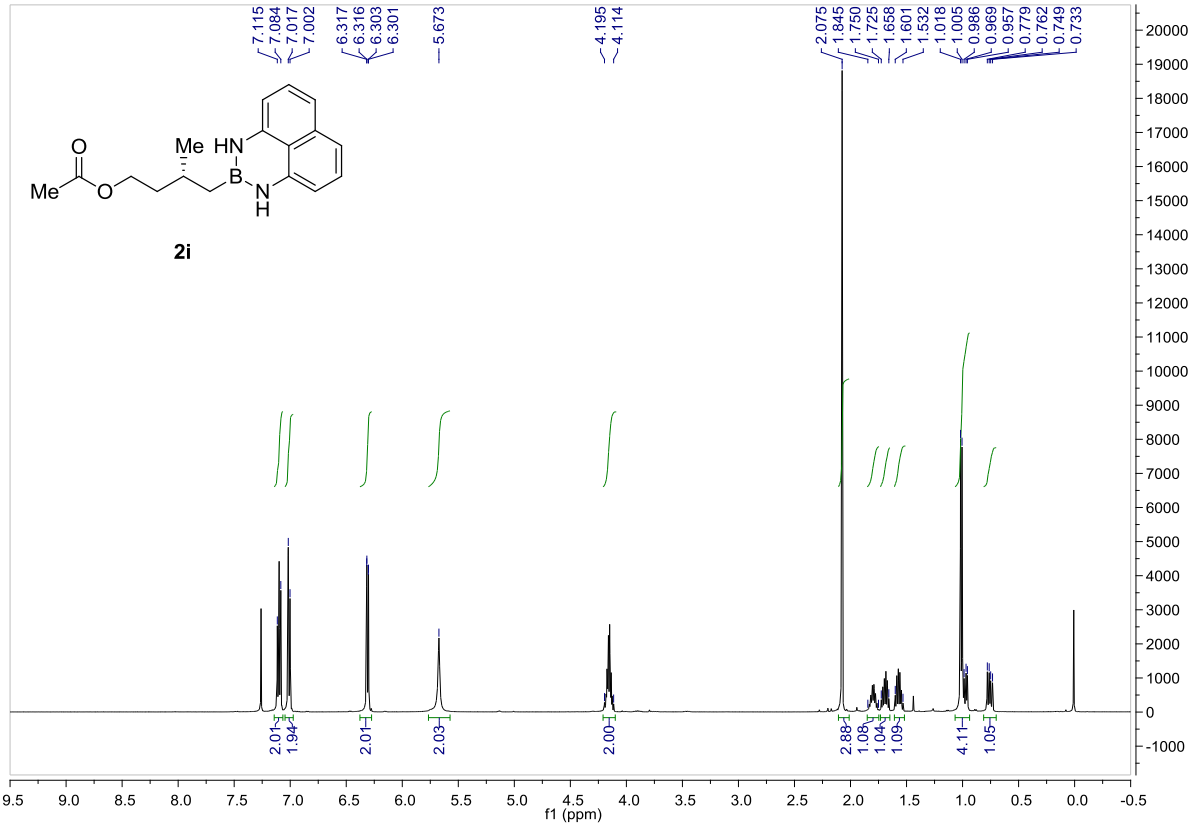
141.37
136.33
127.56
119.62
117.24
105.41
80.30
34.07
33.18
29.31
28.19
24.07
22.36
Me HN
t-BuO
B
N
H
O
2h
f1 (ppm)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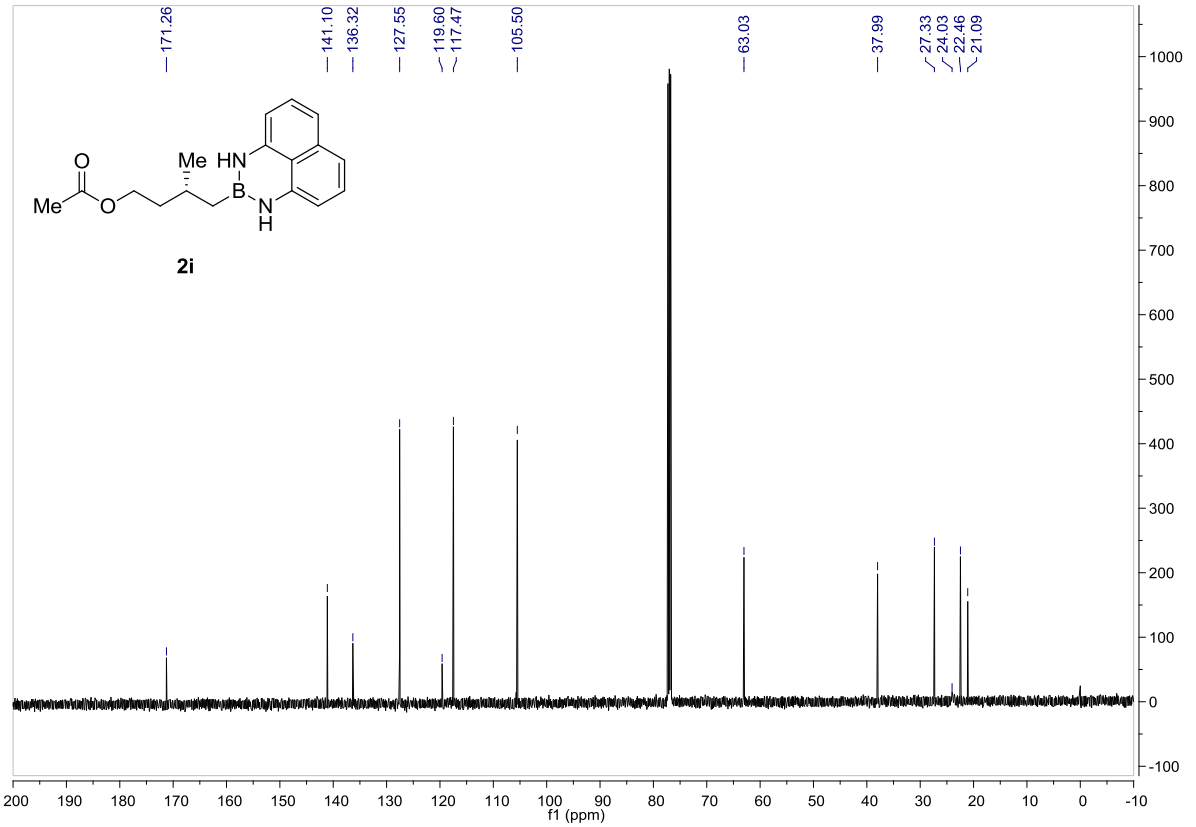
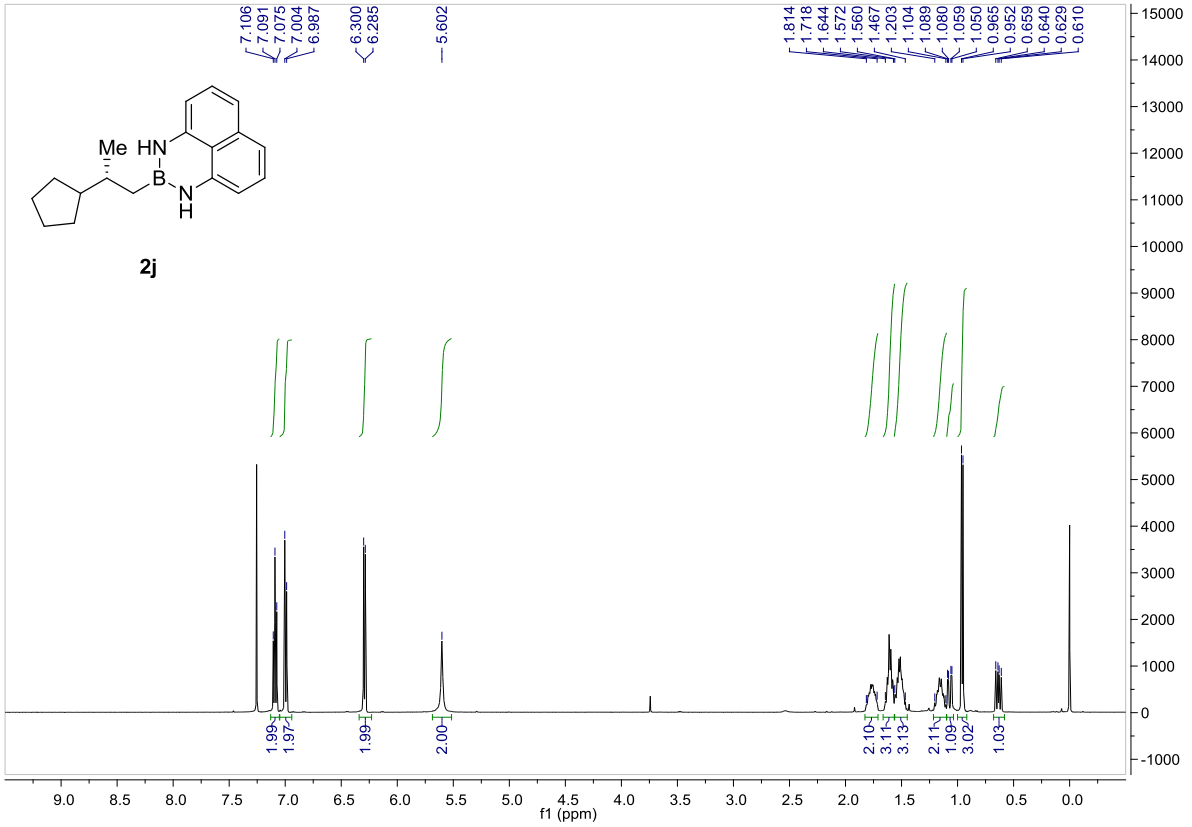
7.084
7.017
7.002
6.317
6.316
6.303
6.301
5.673
4.195
4.114
2.075
1.845
1.750
1.725
1.658
1.601
1.532
1.018
1.005
0.986
0.969
0.957
0.779
0.762
0.749
0.733
Me HN
O
Me
O
B
N
H
2i
2.01
1.94
2.01
2.03
2.00
2.88
1.08
1.04
1.09
4.11
1.05
f1 (ppm)


171.26
141.10
136.32
127.55
119.60
117.47
105.50
63.03
37.99
27.33
24.03
22.46
21.09
Me HN
O
Me
O
B
N
H
2i
f1 (ppm)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7.091
7.075
7.004
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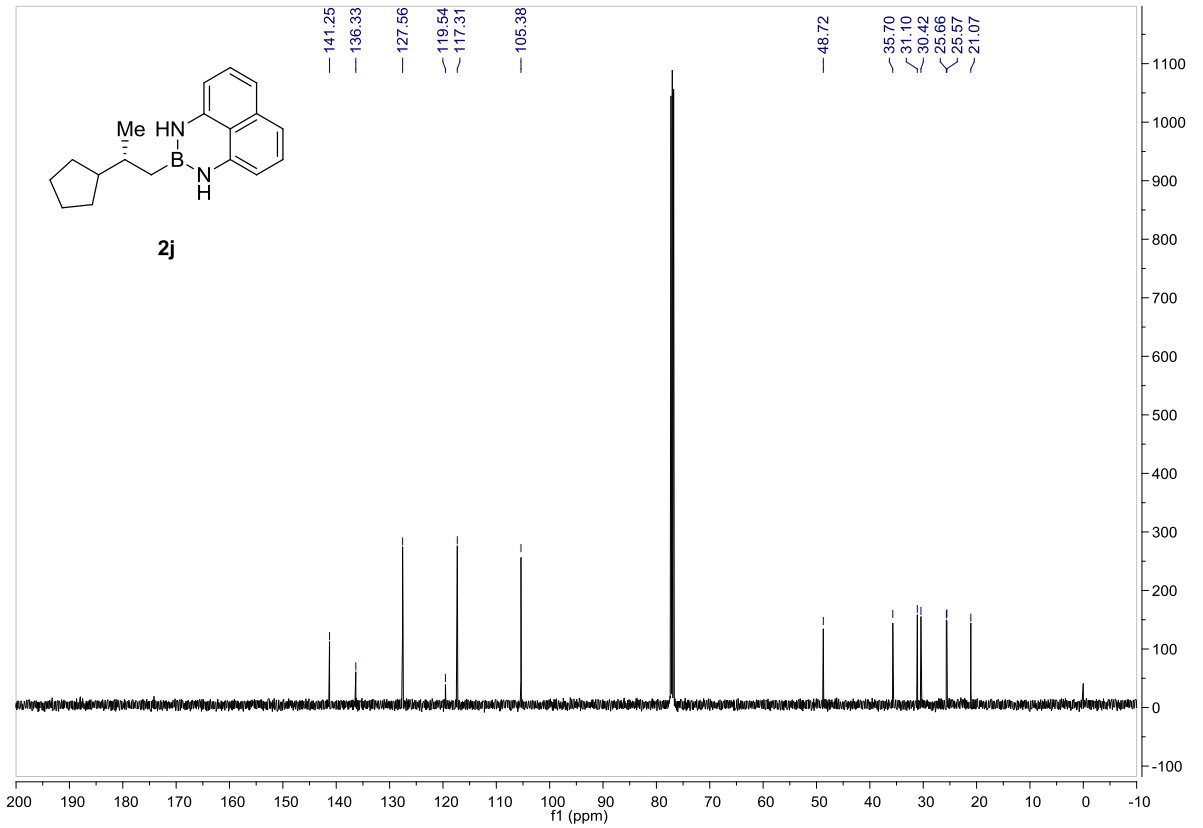
6.300
6.285
5.602
1.814
1.718
1.644
1.572
1.560
1.467
1.203
1.104
1.089
1.080
1.059
1.050
0.965
0.952
0.659
0.640
0.629
0.610
Me HN
B
N
H
2j
1.99
1.97
1.99
2.00
2.10
3.11
3.13
2.11
1.09
3.02
1.03
f1 (ppm)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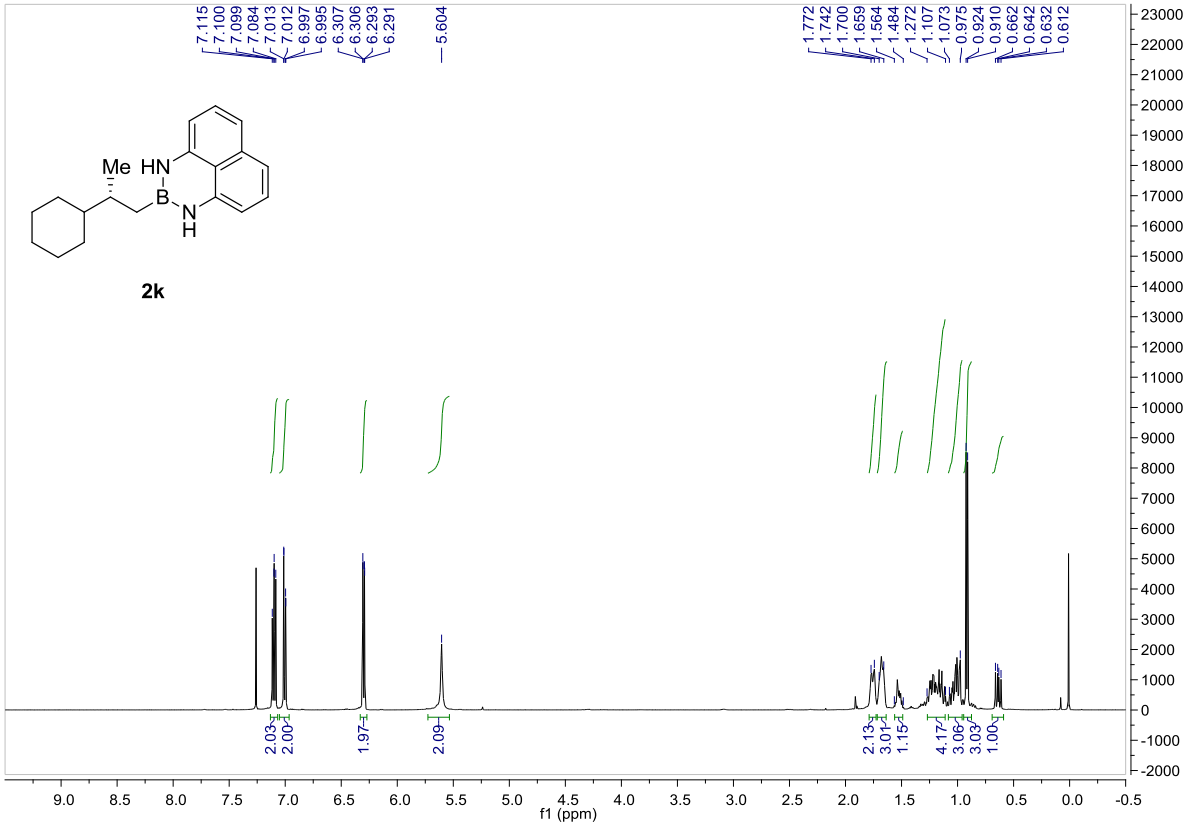
136.33
127.56
119.54
117.31
105.38
48.72
35.70
31.10
30.42
25.66
25.57
21.07
Me HN
B
N
H
2j
f1 (ppm)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7.100
7.099
7.084
7.013
7.012
6.997
6.995
6.307
6.306
6.293
6.291
5.604
1.772
1.742
1.700
1.659
1.564
1.484
1.272
1.107
1.073
0.975
0.924
0.910
0.662
0.642
0.632
0.612
Me HN
B
N
H
2k
2.03
2.00
1.97
2.09
2.13
3.01
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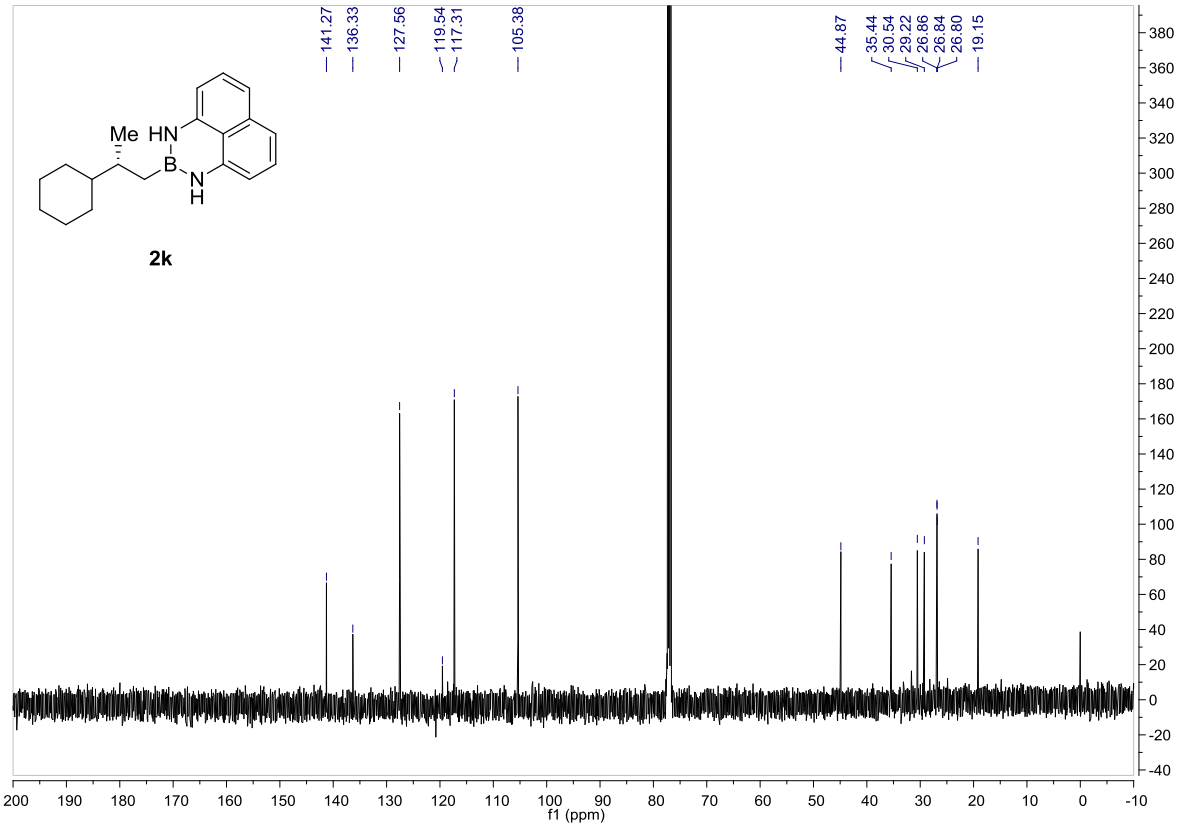
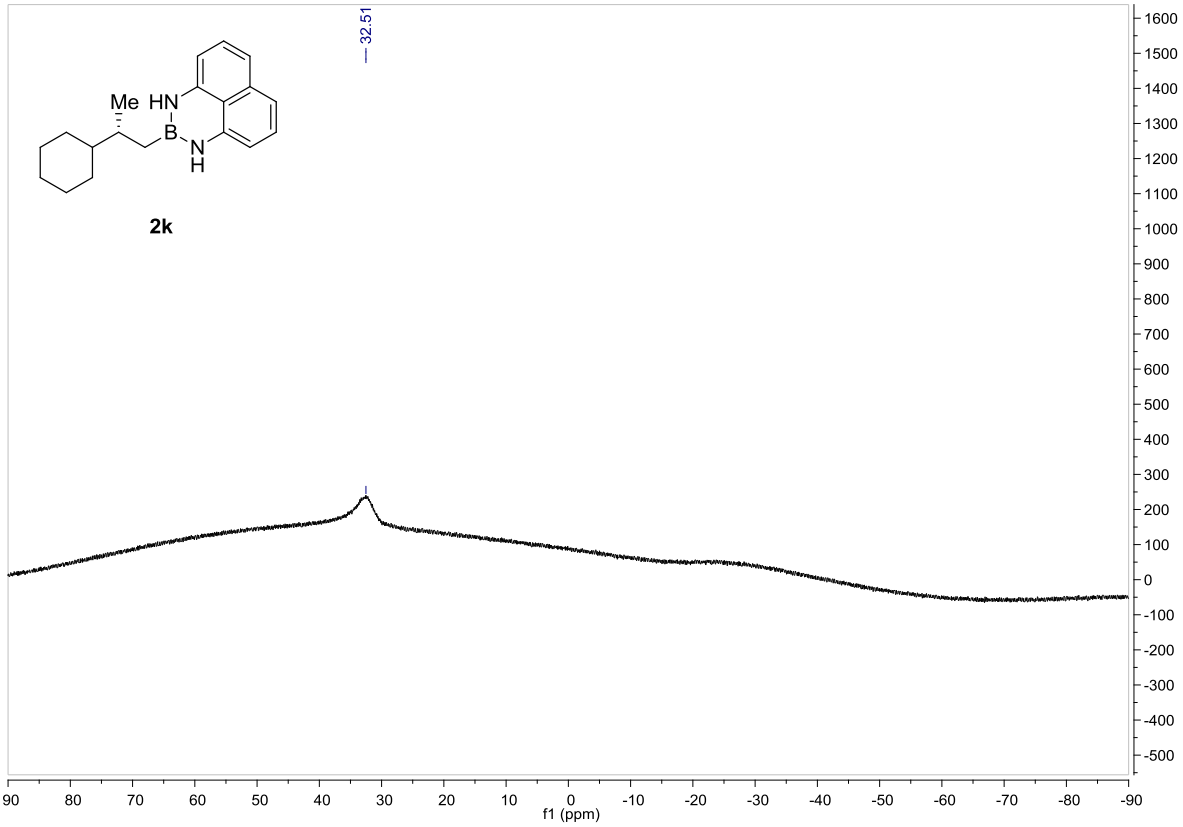
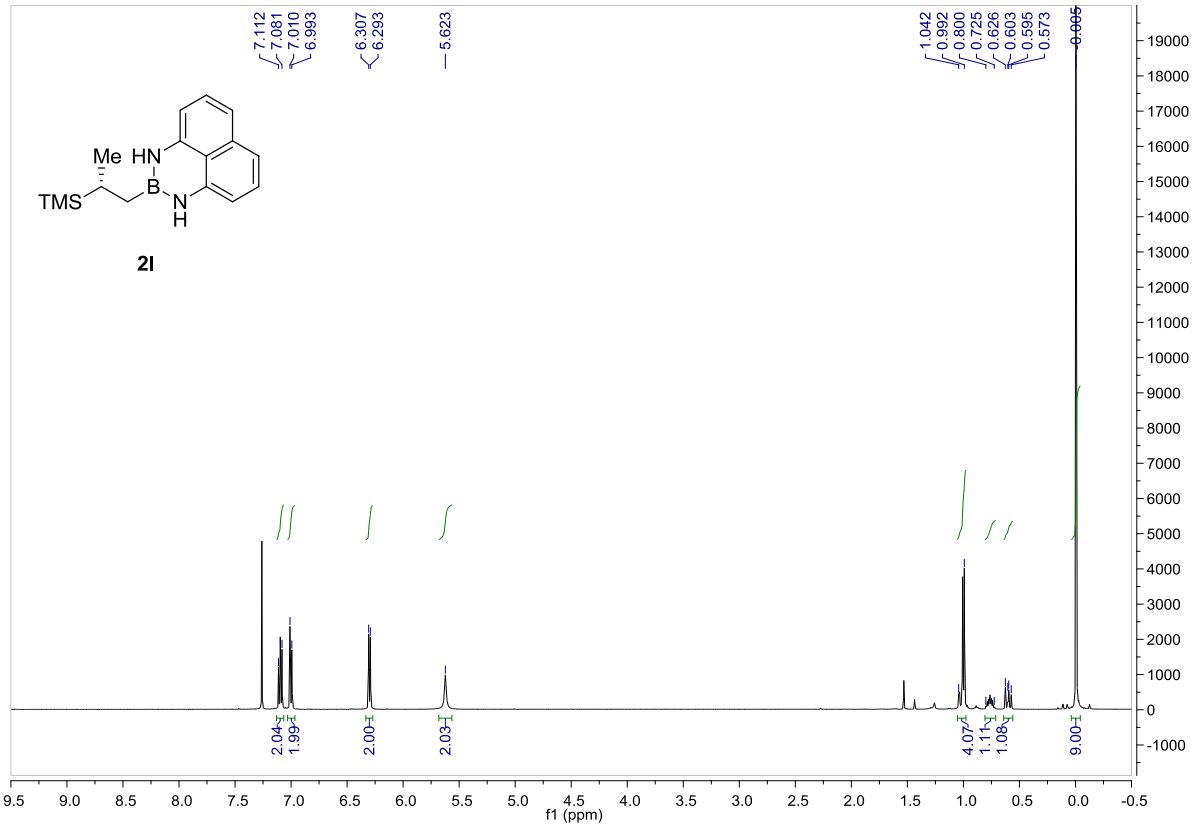
4.17
3.06
3.03
1.00
f1 (ppm)


141.27
136.33
127.56
119.54
117.31
105.38
44.87
35.44
30.54
29.22
26.86
26.84
26.80
19.15
Me HN
B
N
H
2k
f1 (ppm)


32.51
Me HN
B
N
H
2k
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
-300
-400
-500
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)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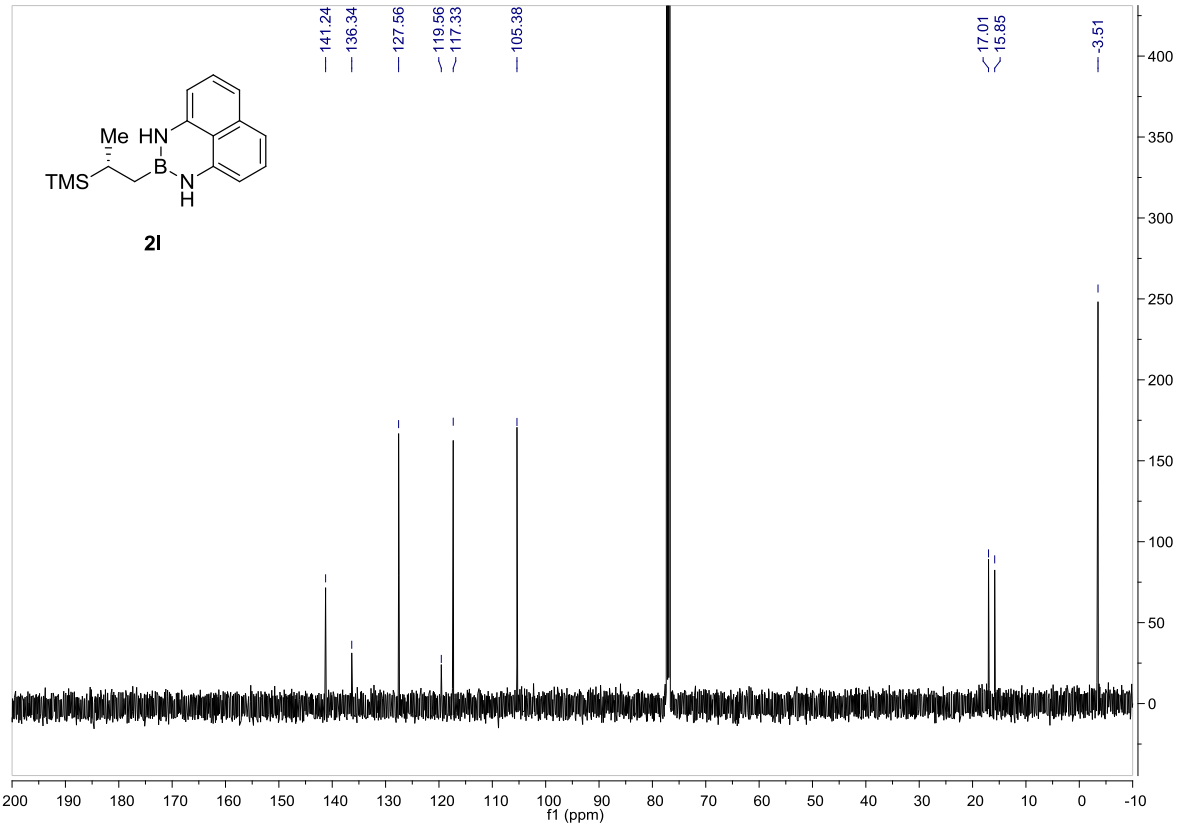
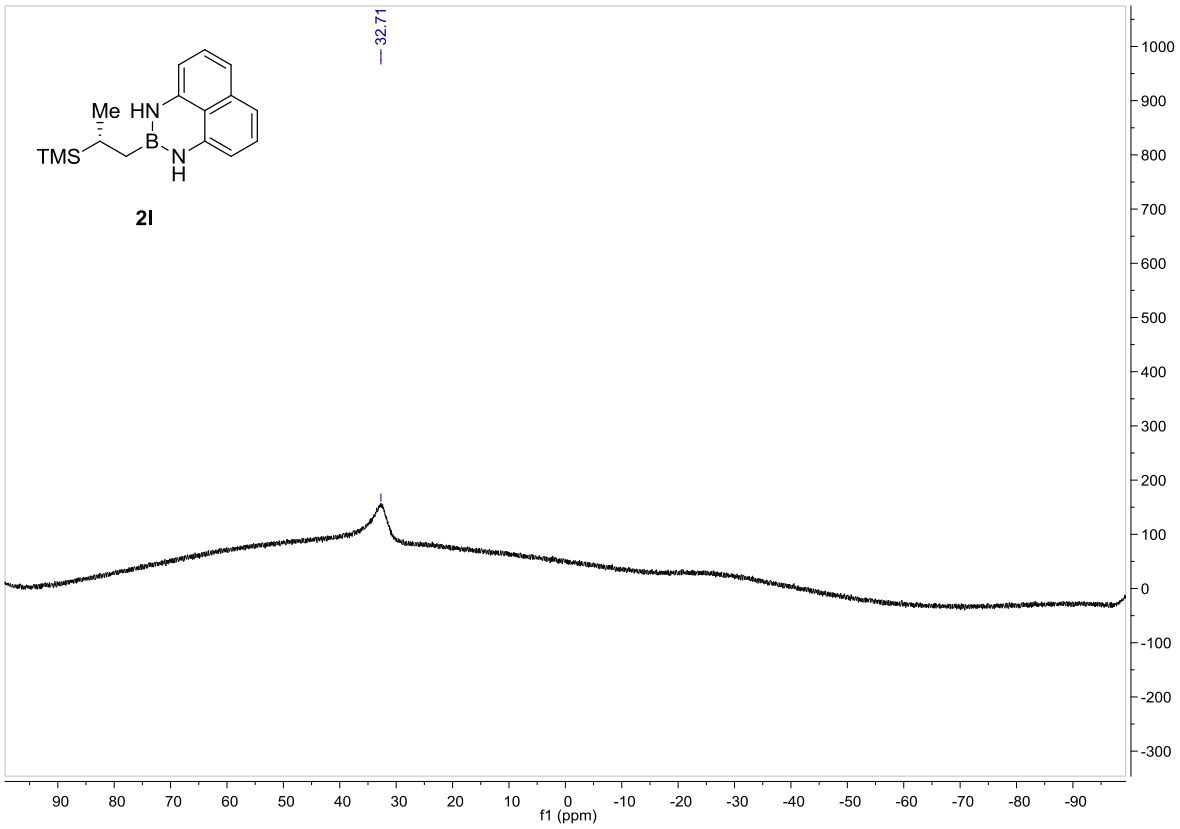
7.010
6.993
6.307
6.293
5.623
1.042
0.992
0.800
0.725
0.626
0.603
0.595
0.573
0.005
Me HN
TMS
B
N
H
2l
2.04
1.99
2.00
2.03
4.07
1.11
1.08
9.00
f1 (ppm)


141.24
136.34
127.56
119.56
117.33
105.38
17.01
15.85
-3.51
Me HN
TMS
B
N
H
2l
f1 (ppm)


32.71
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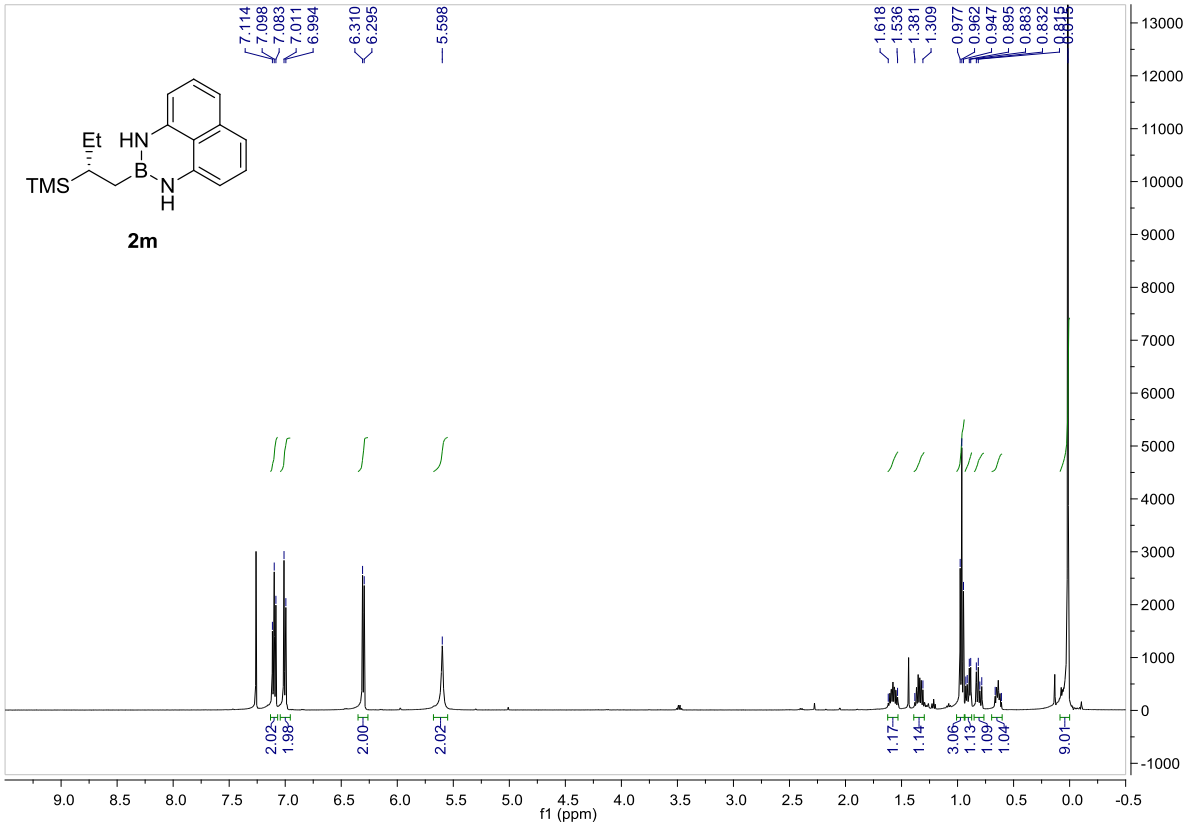
HN
TMS
B
N
H
2l
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
-300
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)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6.295
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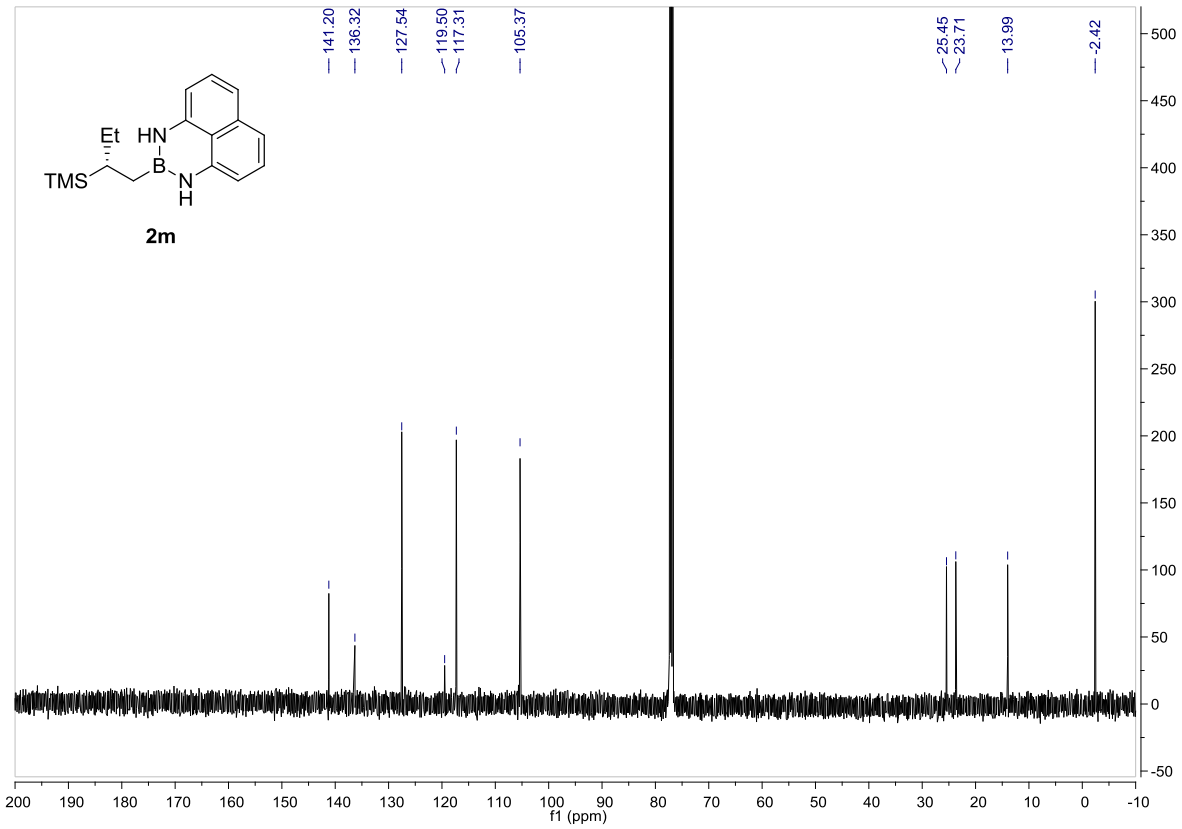
1.536
1.381
1.309
0.977
0.962
0.947
0.895
0.883
0.832
0.815
Et
HN
TMS
B
N
H
2m
2.02
1.98
2.00
2.02
1.17
1.14
3.06
1.13
1.09
1.04
9.01
f1 (ppm)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136.32
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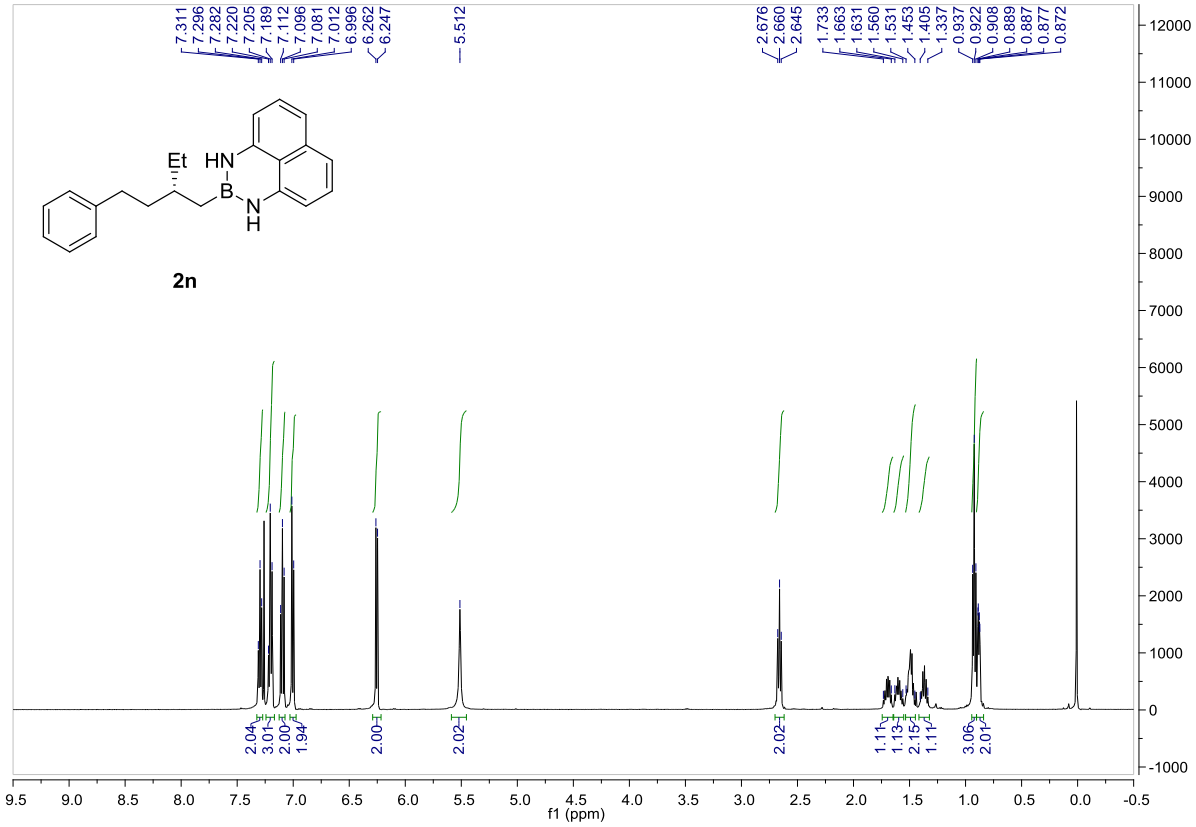
105.37
25.45
23.71
13.99
-2.42
Et
HN
TMS
B
N
H
2m
f1 (ppm)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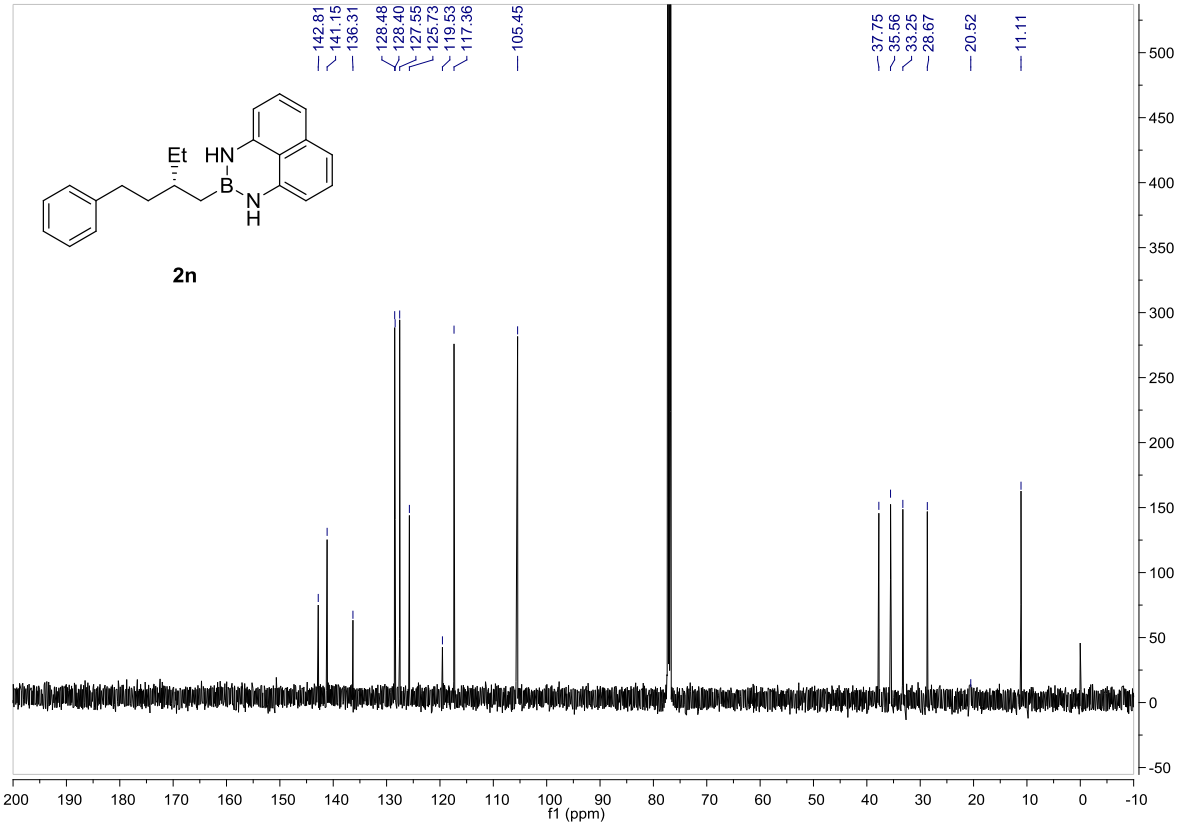
7.096
7.081
7.012
6.996
6.262
6.247
5.512
2.676
2.660
2.645
1.733
1.663
1.631
1.560
1.531
1.453
1.405
1.337
0.937
0.922
0.908
0.889
0.887
0.877
0.872
Et
HN
B
N
H
2n
2.04
3.01
2.00
1.94
2.00
2.02
2.02
1.11
1.13
2.15
1.11
3.06
2.01
f1 (ppm)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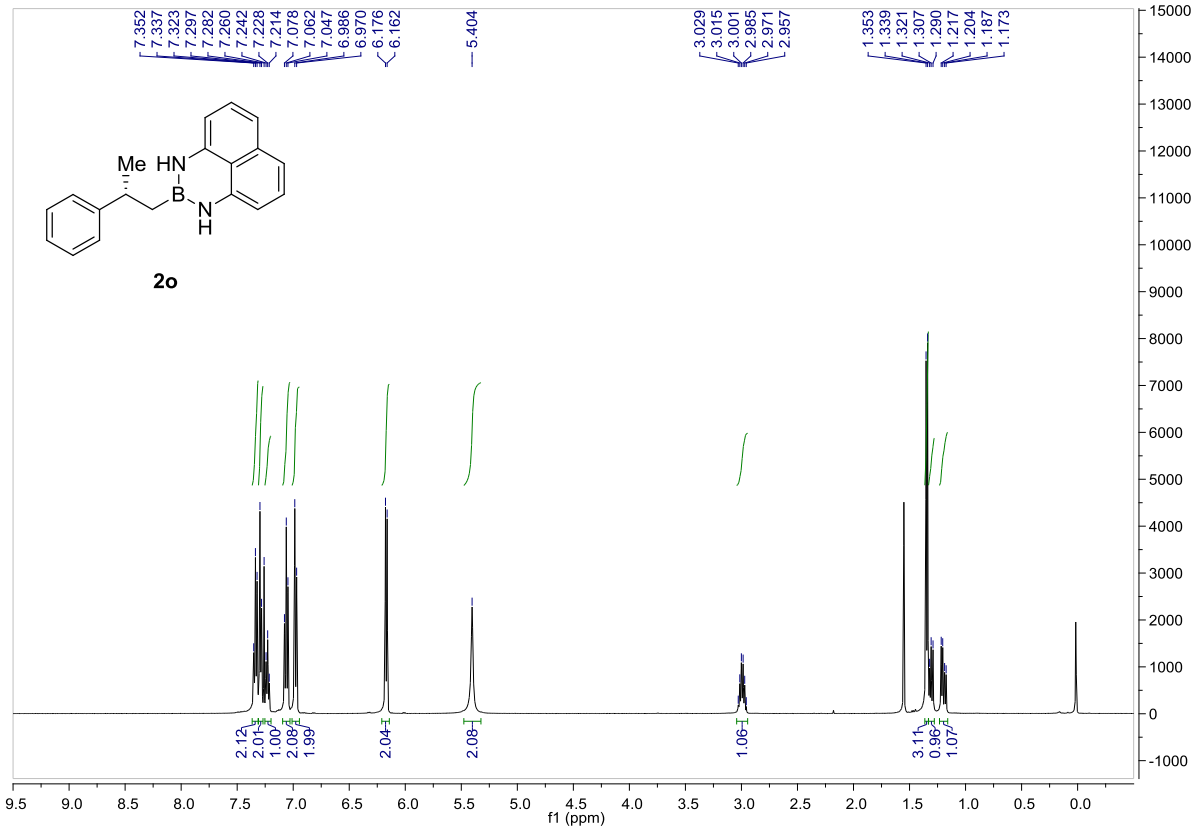
128.48
128.40
127.55
125.73
119.53
117.36
105.45
37.75
35.56
33.25
28.67
20.52
11.11
Et
HN
B
N
H
2n
f1 (ppm)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7.242
7.228
7.214
7.078
7.062
7.047
6.986
6.970
6.176
6.162
5.404
3.029
3.015
3.001
2.985
2.971
2.957
1.353
1.339
1.321
1.307
1.290
1.217
1.204
1.187
1.173
Me HN
B
N
H
2o
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2.08
1.99
2.04
2.08
1.06
3.11
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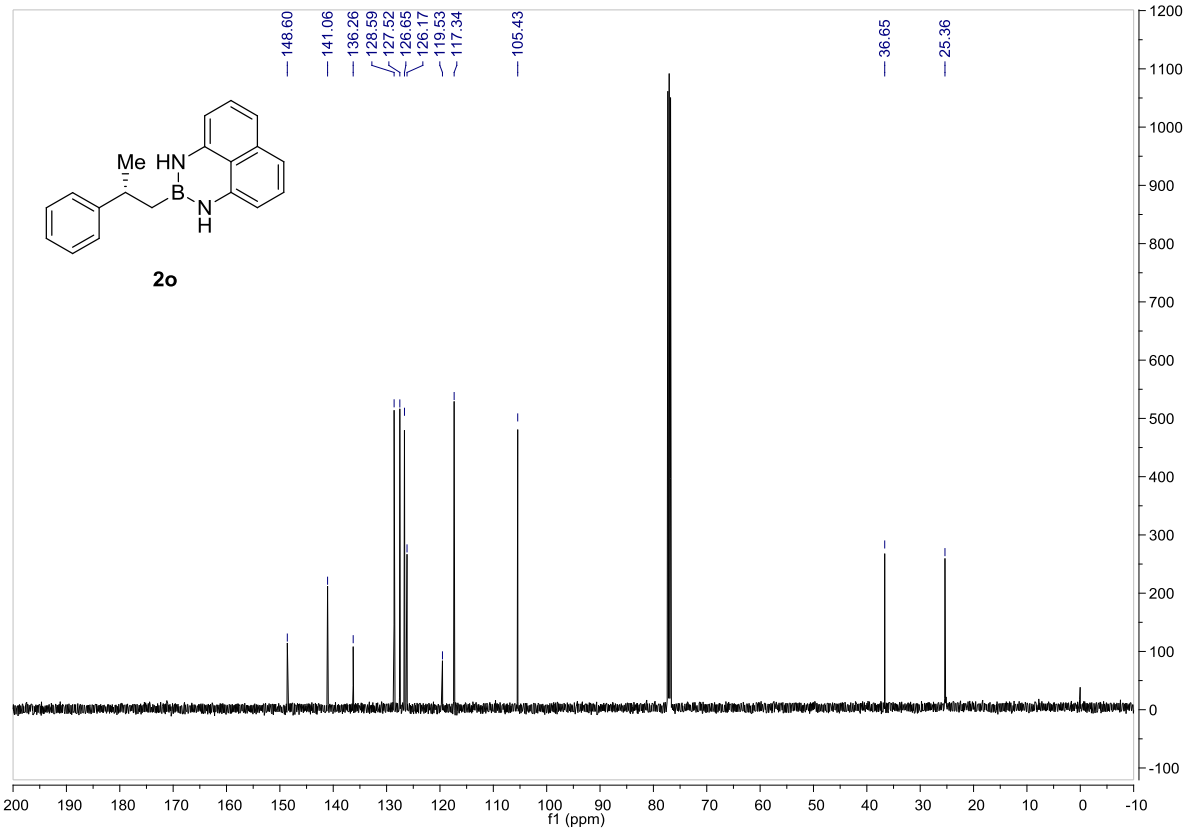
1.07
f1 (ppm)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127.52
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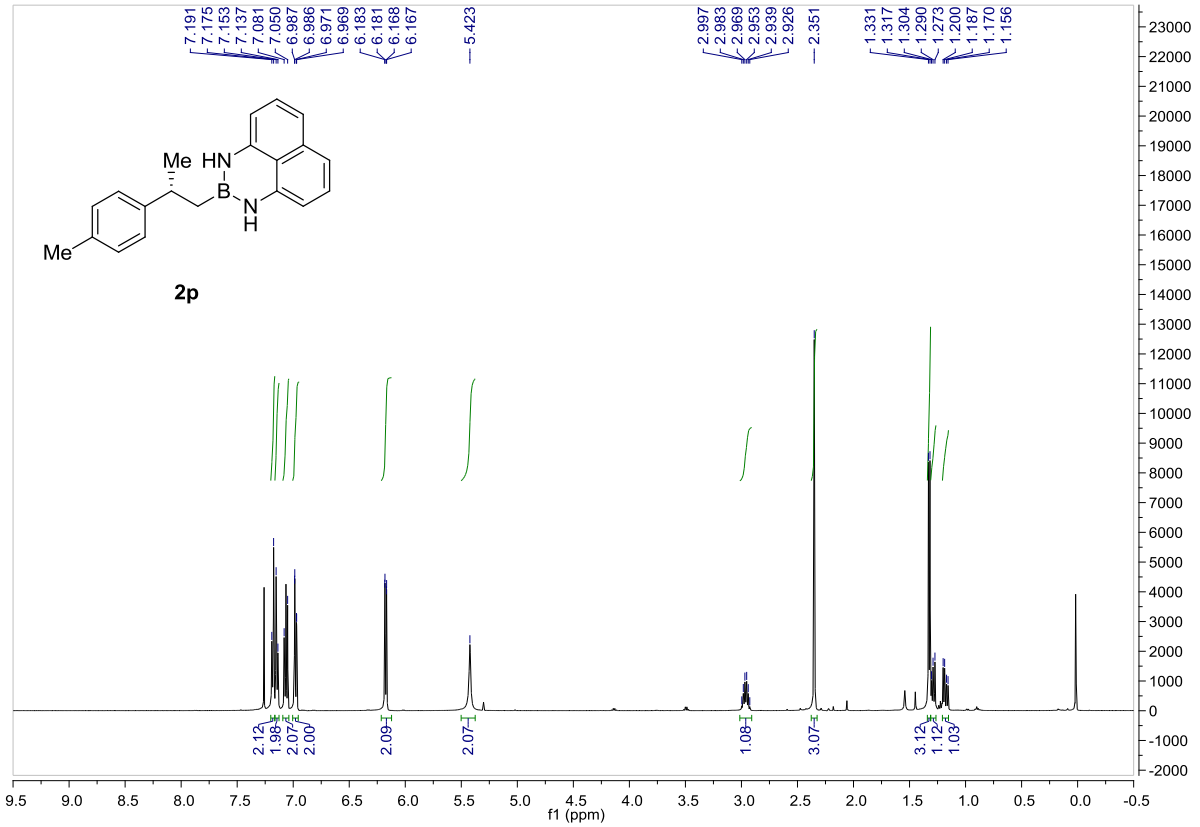
36.65
25.36
Me HN
B
N
H
2o
f1 (ppm)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7.050
6.987
6.986
6.971
6.969
6.183
6.181
6.168
6.167
5.423
2.997
2.983
2.969
2.953
2.939
2.926
2.351
1.331
1.317
1.304
1.290
1.273
1.200
1.187
1.170
1.156
Me
HN
B
N
H
Me
2p
2.12
1.98
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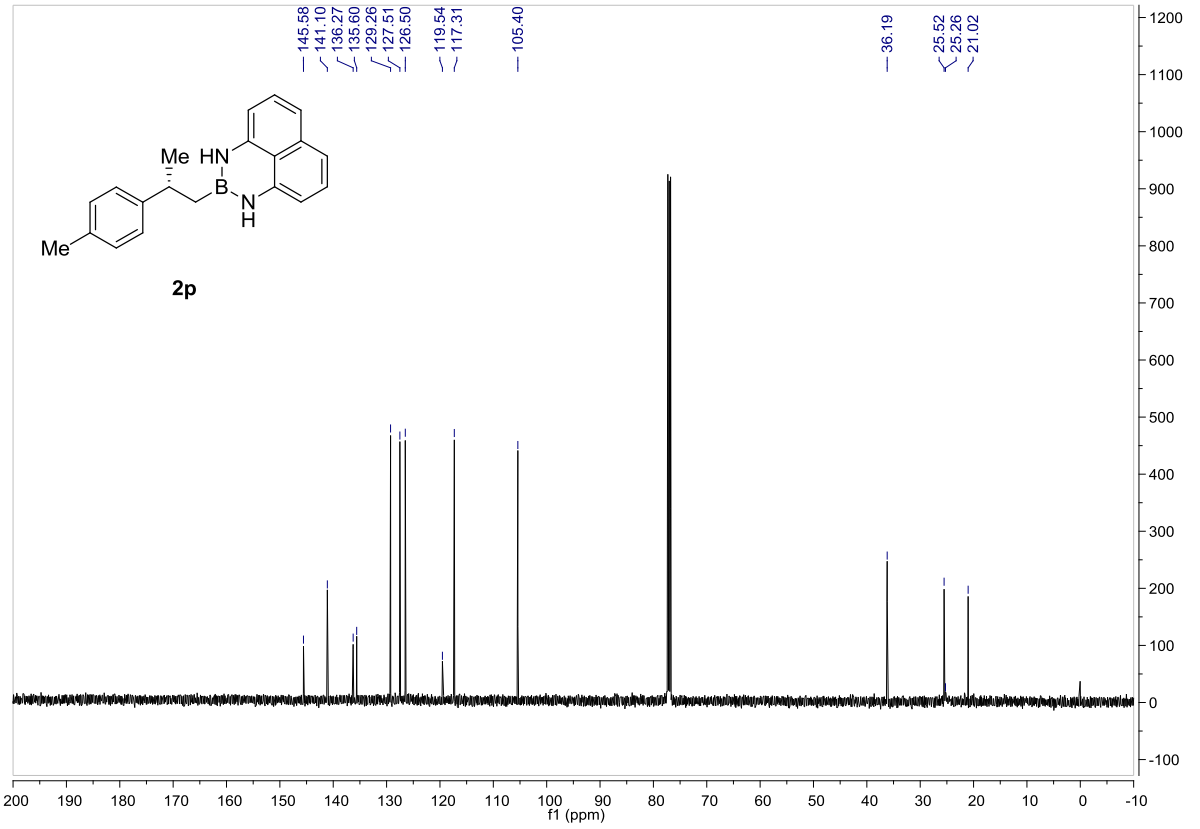
2.00
2.09
2.07
1.08
3.07
3.12
1.12
1.03
f1 (ppm)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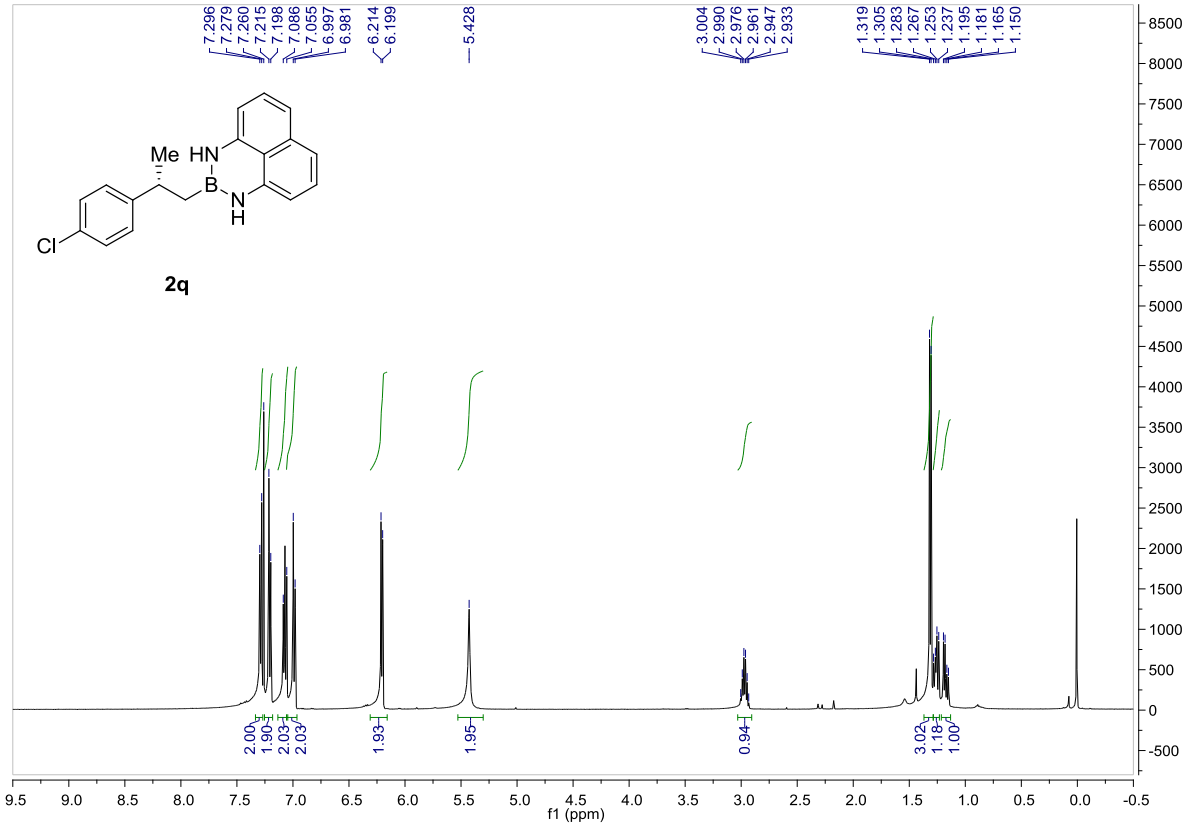
135.60
129.26
127.51
126.50
119.54
117.31
105.40
36.19
25.52
25.26
21.02
Me
HN
B
N
H
Me
2p
f1 (ppm)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7.215
7.198
7.086
7.055
6.997
6.981
6.214
6.199
5.428
3.004
2.990
2.976
2.961
2.947
2.933
1.319
1.305
1.283
1.267
1.253
1.237
1.195
1.181
1.165
1.150
Me HN
B
N
H
Cl
2q
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2.03
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1.95
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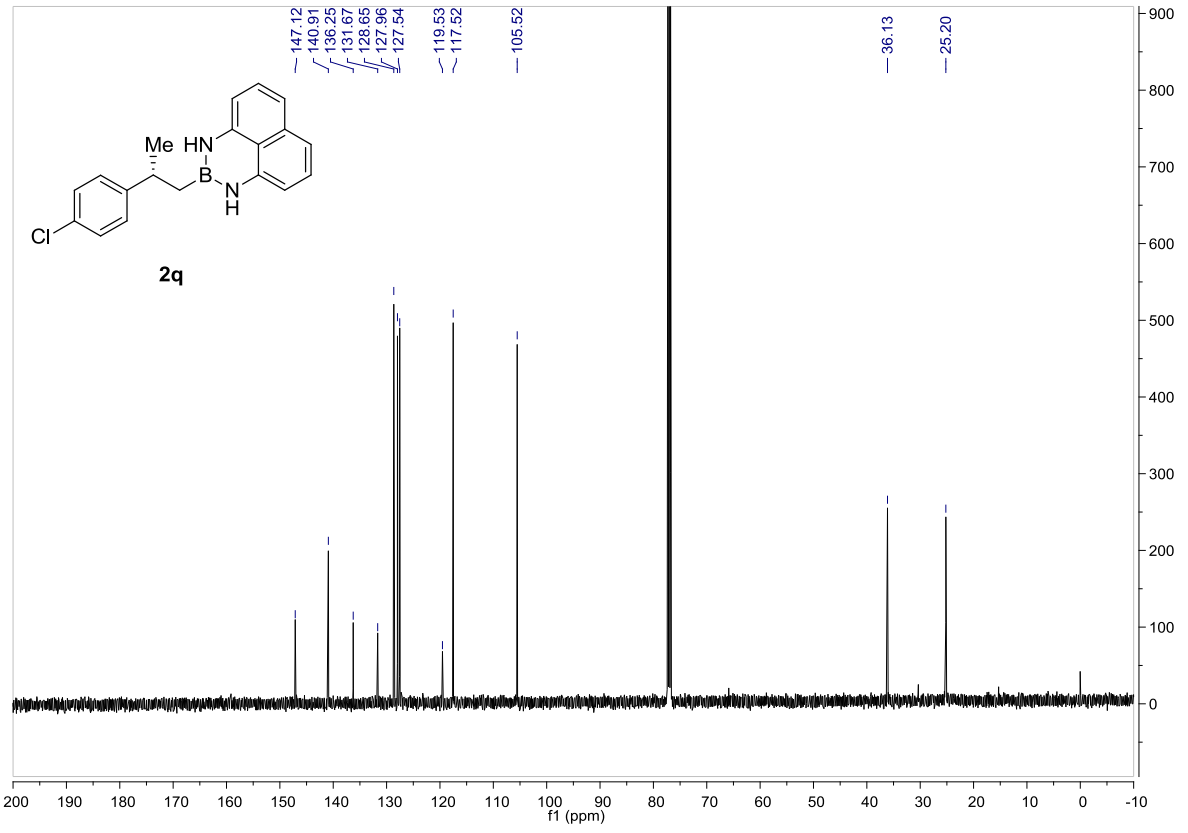
3.02
1.18
1.00
f1 (ppm)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131.67
128.65
127.96
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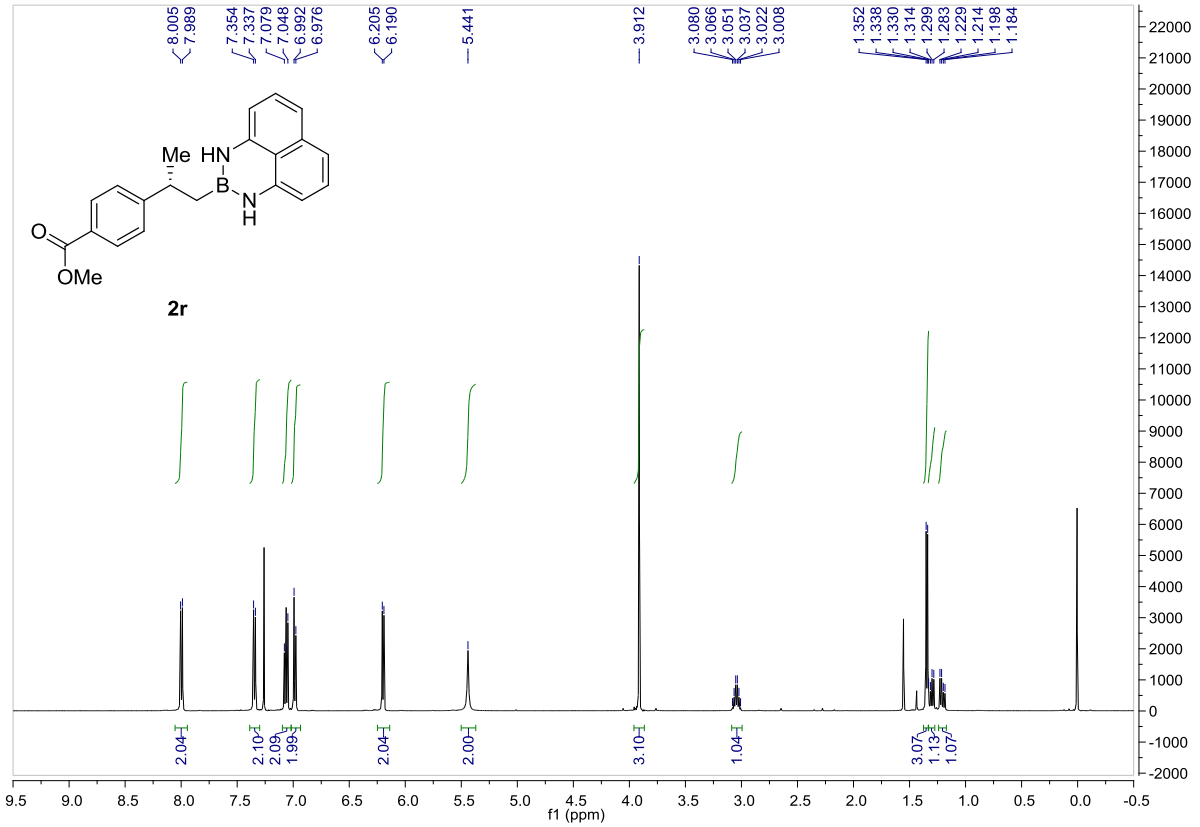
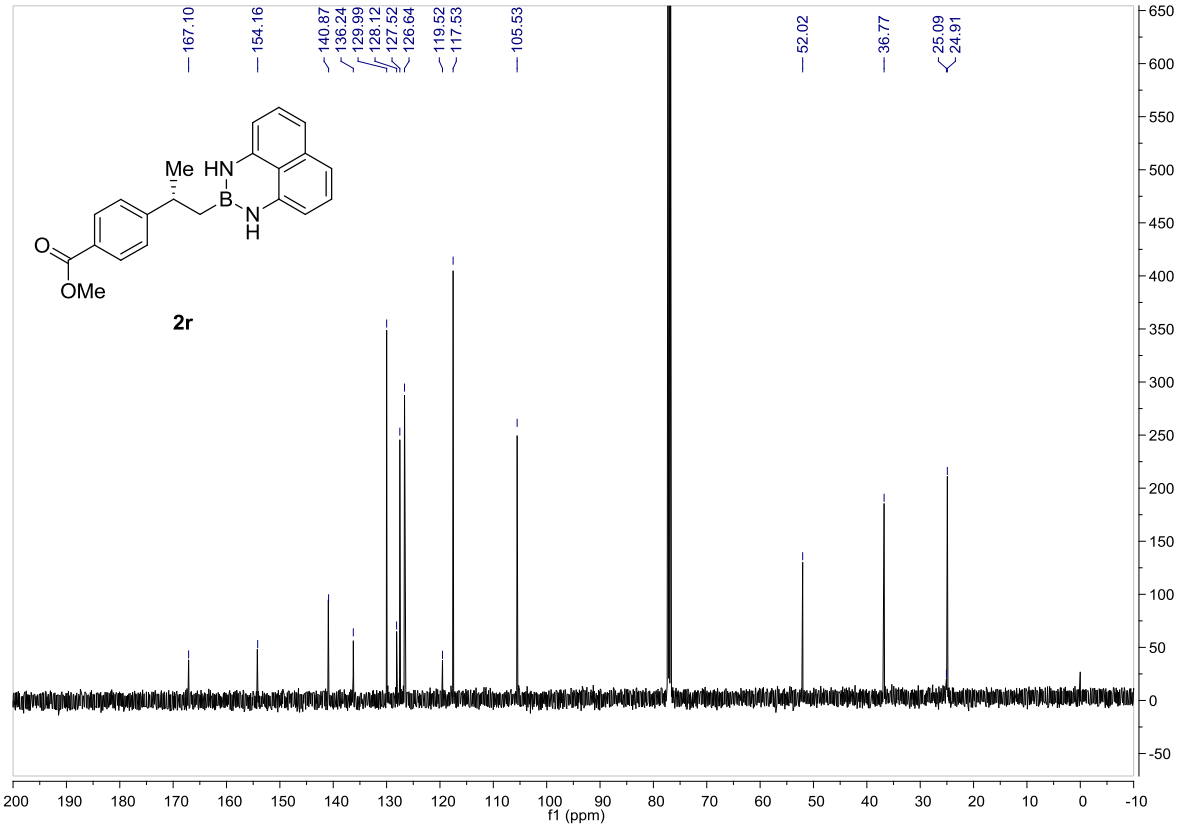
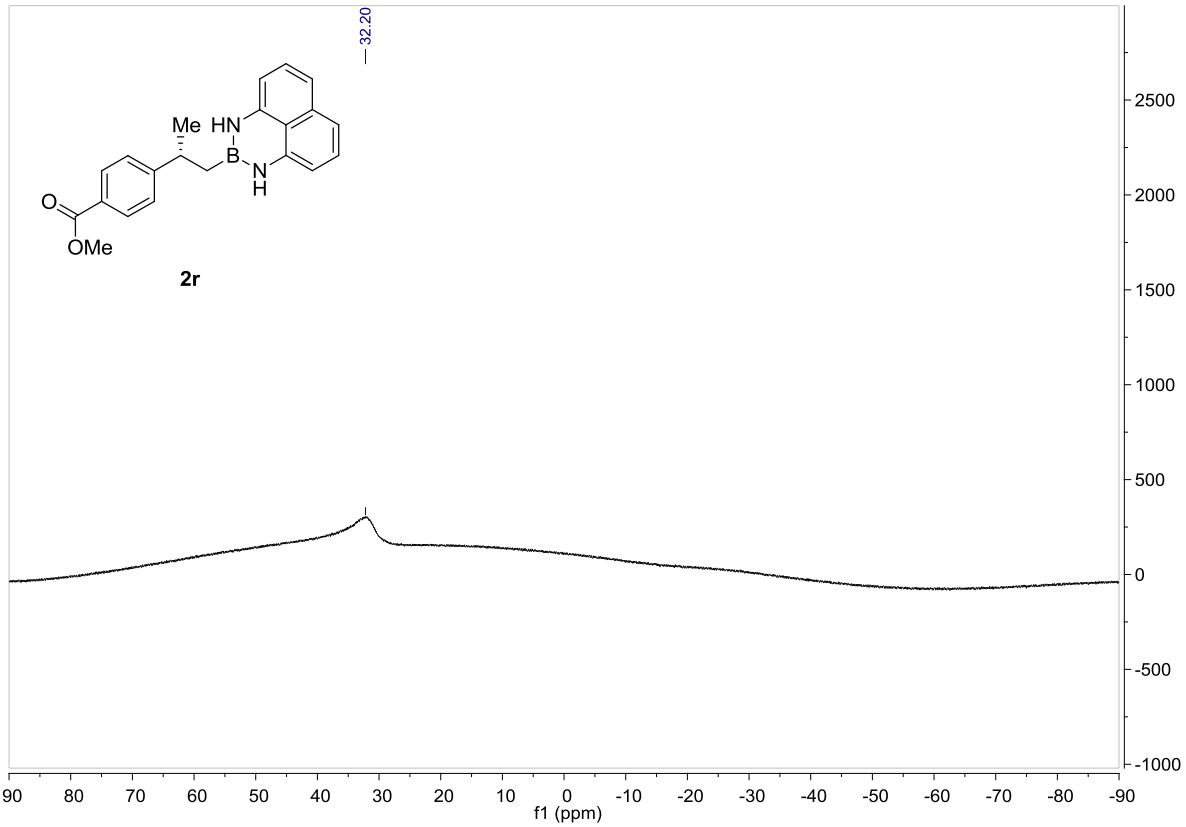
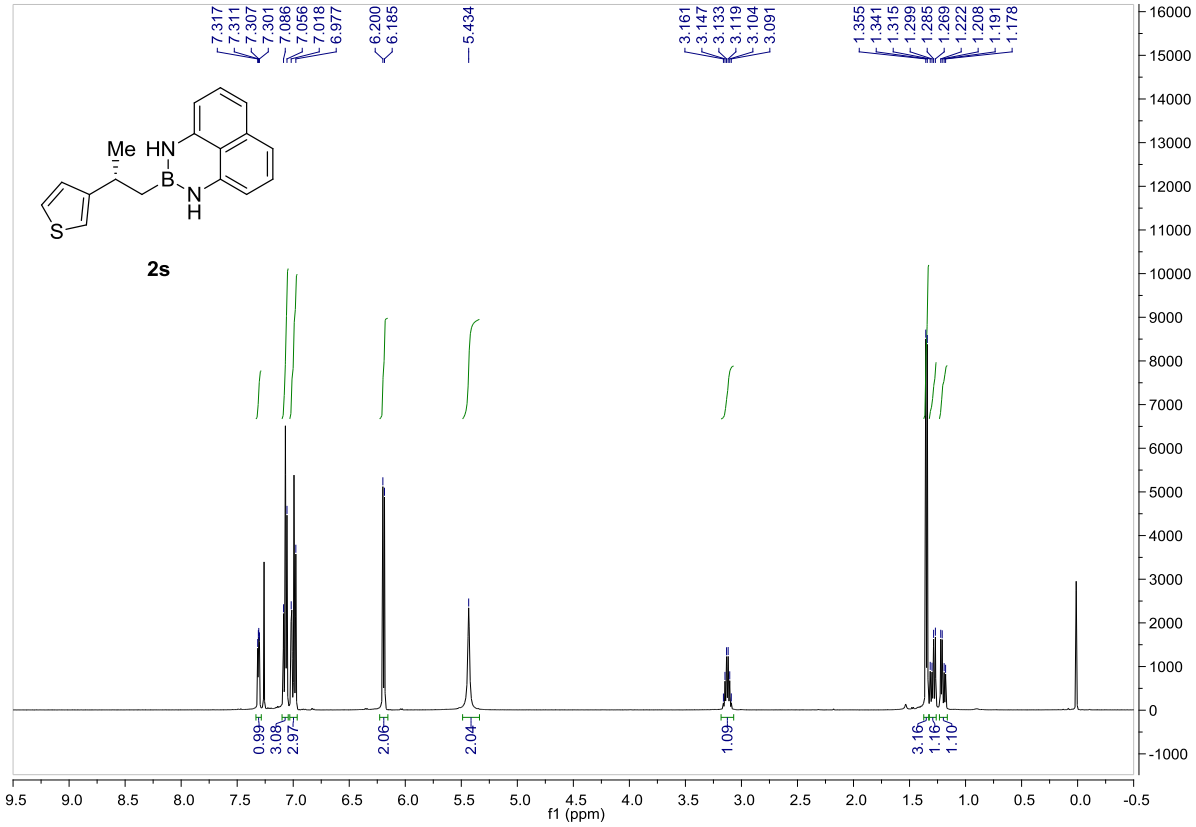
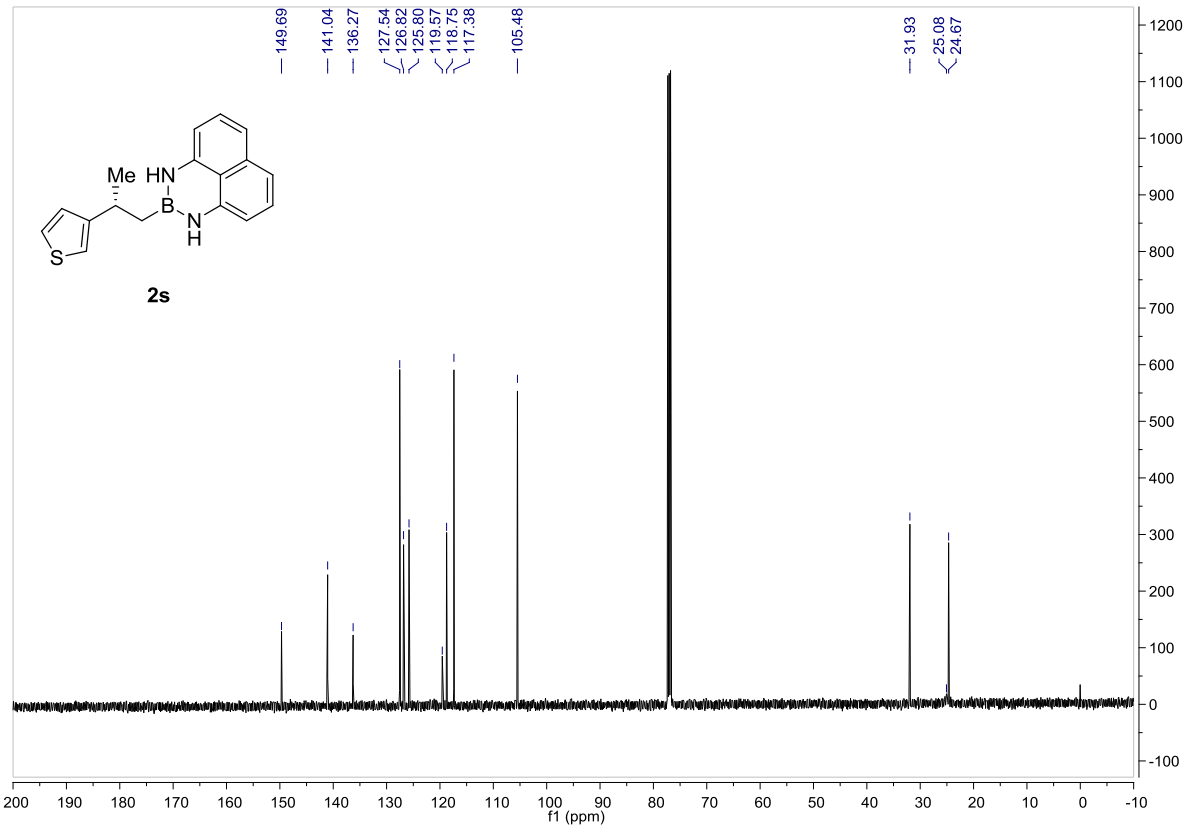
119.53
117.52
105.52
36.13
25.20
Me HN
B
N
H
Cl
2q
f1 (ppm)

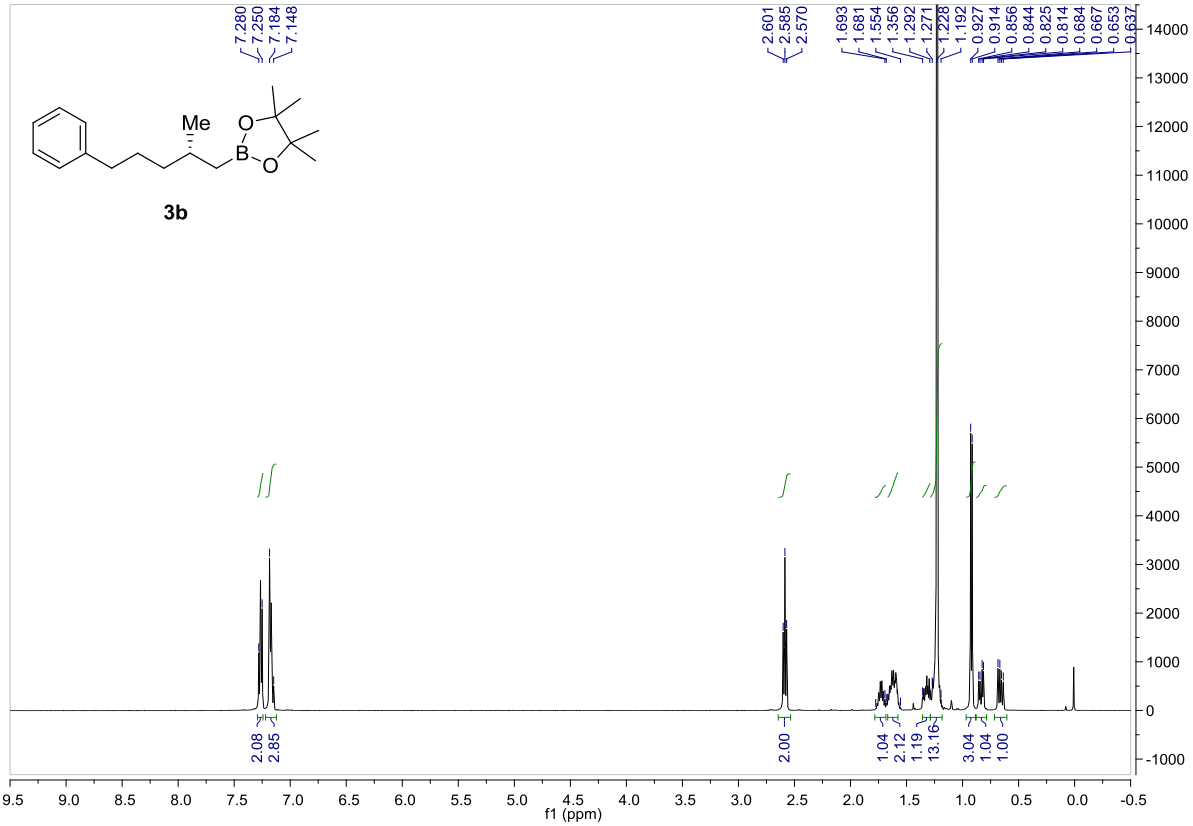

8.005
7.989
7.354
7.337
7.079
7.048
6.992
6.976
6.205
6.190
5.441
3.912
3.080
3.066
3.051
3.037
3.022
3.008
1.352
1.338
1.330
1.314
1.299
1.283
1.229
1.214
1.198
1.184
Me HN
B
N
H
O
OMe
2r
2.04
2.10
2.09
1.99
2.04
2.00
3.10
1.04
3.07
1.13
1.07
f1 (ppm)

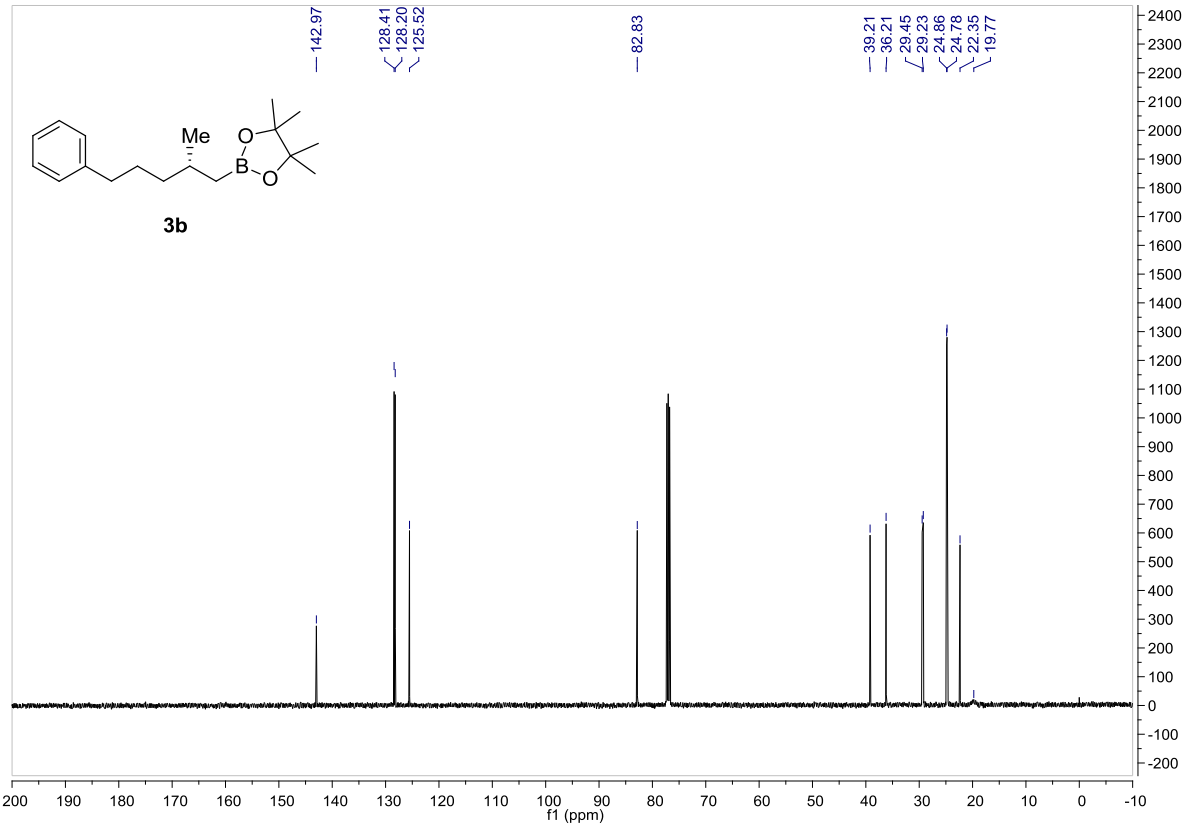

167.10
154.16
140.87
136.24
129.99
128.12
127.52
126.64
119.52
117.53
105.53
52.02
36.77
25.09
24.91
Me HN
B
N
H
O
OMe
2r
f1 (ppm)

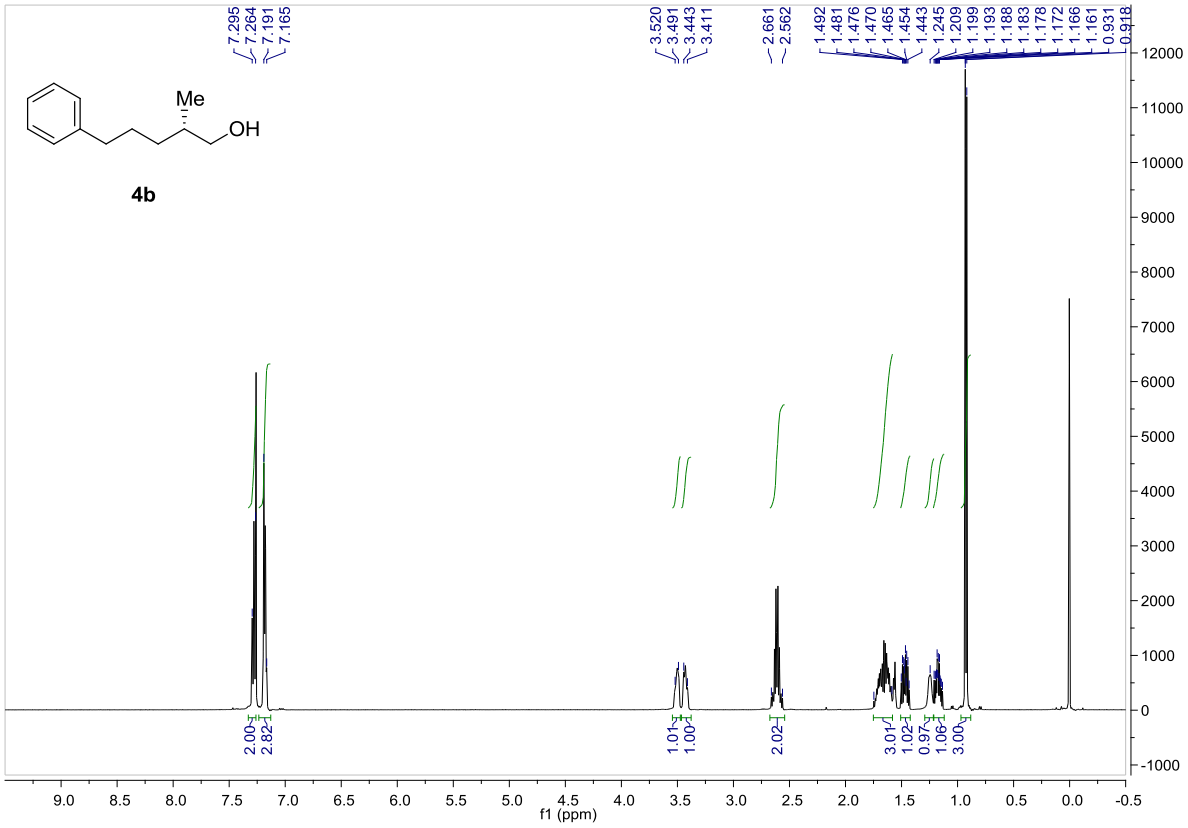

32.20
Me
HN
B
N
H
O
OMe
2r
2500
2000
1500
1000
500
0
-500
-1000
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

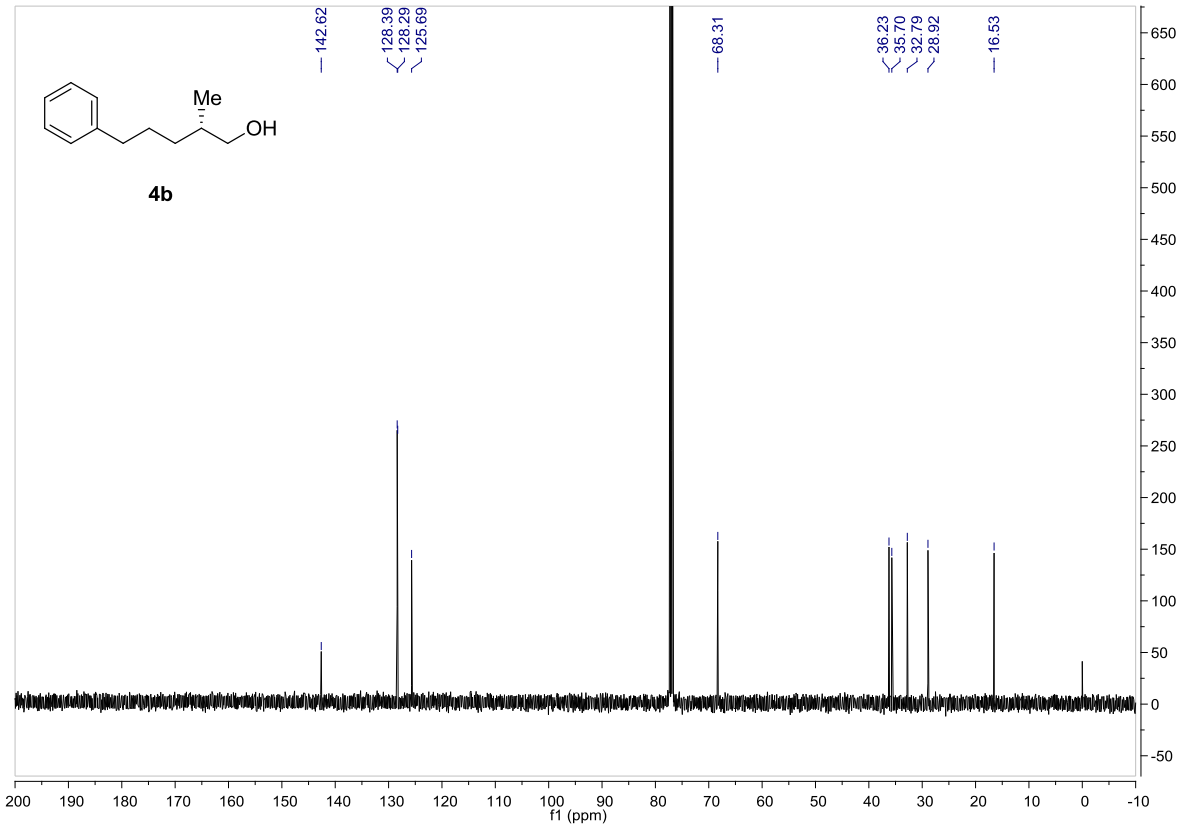

7.317
7.311
7.307
7.301
7.086
7.056
7.018
6.977
6.200
6.185
5.434
3.161
3.147
3.133
3.119
3.104
3.091
1.355
1.341
1.315
1.299
1.285
1.269
1.222
1.208
1.191
1.178
Me
HN
B
N
H
S
2s
0.99
3.08
2.97
2.06
2.04
1.09
3.16
1.16
1.10
f1 (ppm)

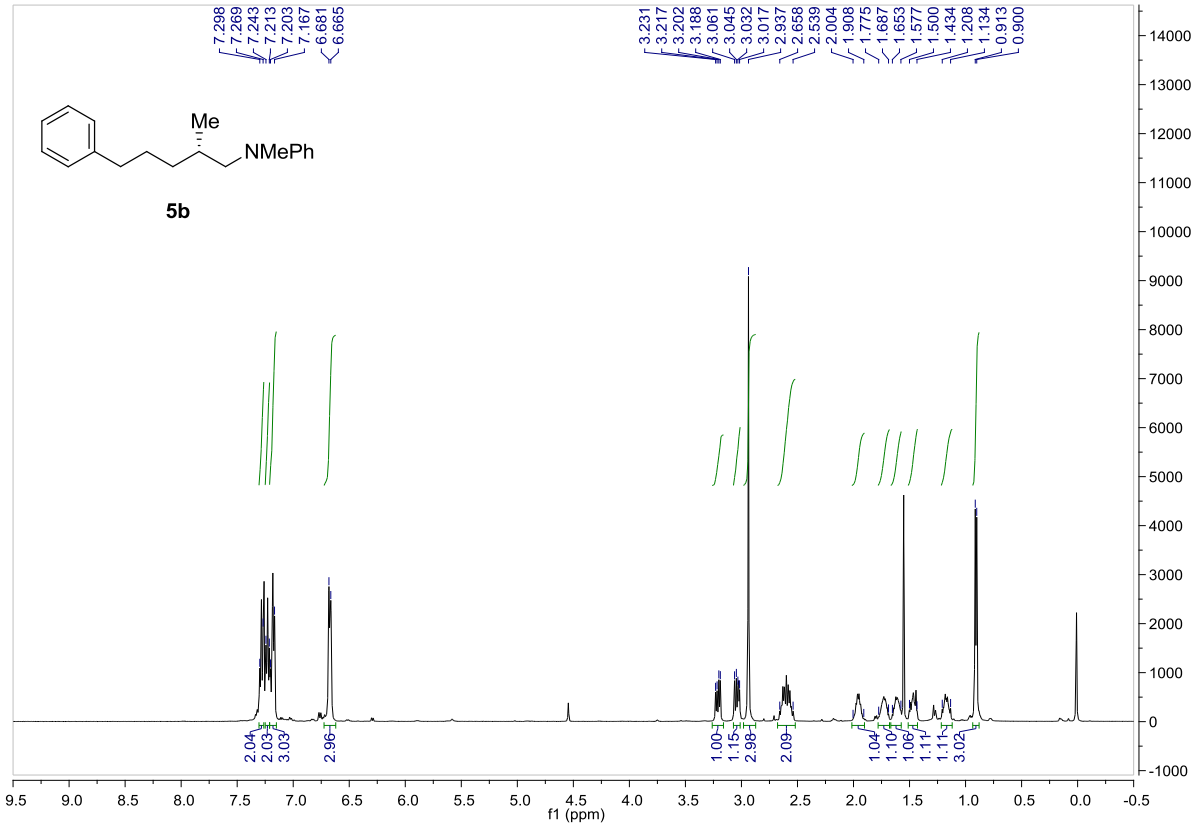

149.69
141.04
136.27
127.54
126.82
125.80
119.57
118.75
117.38
105.48
31.93
25.08
24.67
Me
HN
B
N
H
S
2s
f1 (ppm)

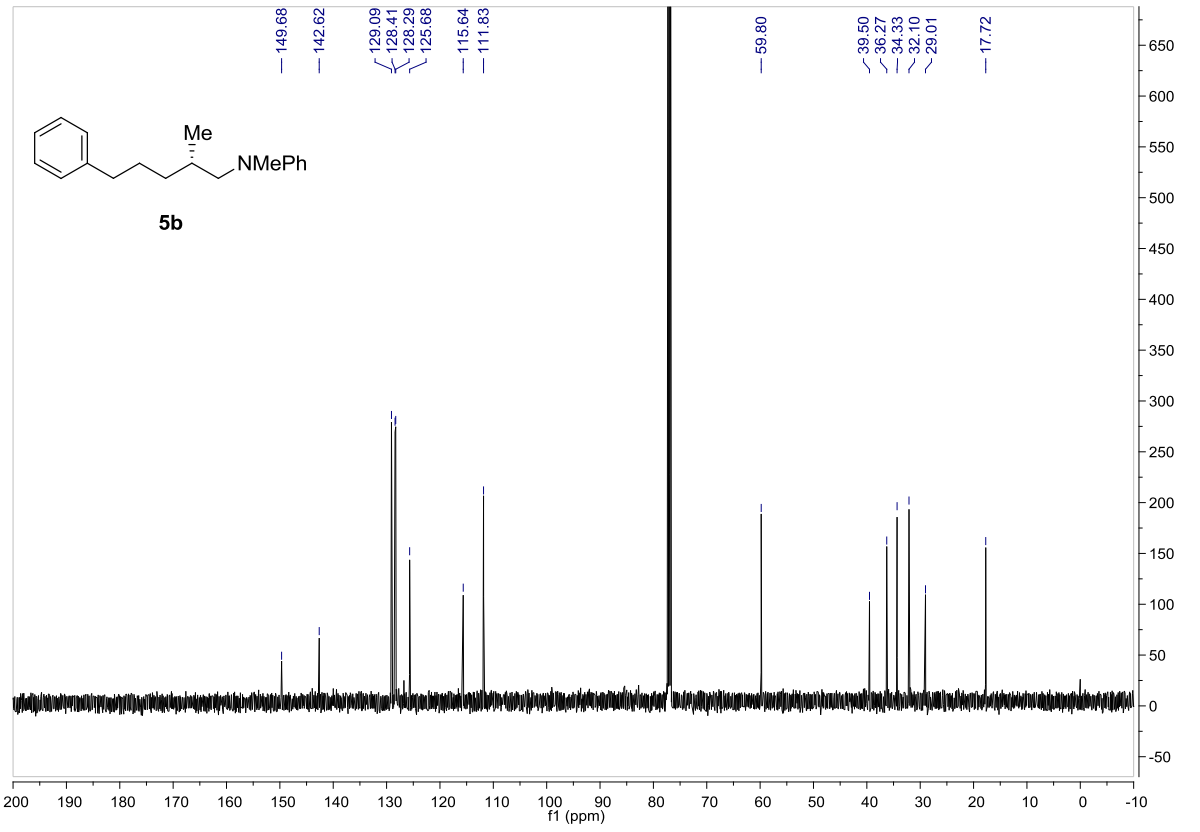

7.280
7.250
7.184
7.148
2.601
2.585
2.570
1.693
1.681
1.554
1.356
1.292
1.271
1.228
1.192
0.927
0.914
0.856
0.844
0.825
0.814
0.684
0.667
0.653
0.637
Me
O
B
O
3b
2.08
2.85
2.00
1.04
2.12
1.19
13.16
3.04
1.04
1.00
f1 (ppm)


142.97
128.41
128.20
125.52
82.83
39.21
36.21
29.45
29.23
24.86
24.78
22.35
19.77
Me
O
B
O
3b
f1 (ppm)


7.295
7.264
7.191
7.165
3.520
3.491
3.443
3.411
2.661
2.562
1.492
1.481
1.476
1.470
1.465
1.454
1.443
1.245
1.209
1.199
1.193
1.188
1.183
1.178
1.172
1.166
1.161
0.931
0.918
Me
OH
4b
2.00
2.82
1.01
1.00
2.02
3.01
1.02
0.97
1.06
3.00
f1 (ppm)


142.62
128.39
128.29
125.69
68.31
36.23
35.70
32.79
28.92
16.53
Me
OH
4b
f1 (ppm)


7.298
7.269
7.243
7.213
7.203
7.167
6.681
6.665
3.231
3.217
3.202
3.188
3.061
3.045
3.032
3.017
2.937
2.658
2.539
2.004
1.908
1.775
1.687
1.653
1.577
1.500
1.434
1.208
1.134
0.913
0.900
Me
NMePh
5b
2.04
2.03
3.03
2.96
1.00
1.15
2.98
2.09
1.04
1.10
1.06
1.11
1.11
3.02
f1 (ppm)


149.68
142.62
129.09
128.41
128.29
125.68
115.64
111.83
59.80
39.50
36.27
34.33
32.10
29.01
17.72
Me
NMePh
5b
f1 (ppm)