Supporting Information

Syntheses of Asymmetrical Magnesium(I) Complexes and Their Catalytic Application in Epoxide Hydroboration

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Contents

Experimental section

General Methods: All air-sensitive compounds were carried out using standard Schlenk-line or glovebox techniques under high-purity argon. Diethyl ether, toluene, THF and hexane were dried and distilled from molten sodium. ^{1}H, $^{13}C\{^{1}H\}$ and ^{11}B NMR spectra were recorded at 25 °C with a Bruker Avance III 600 MHz spectrometer and were referenced to the resonances of the solvent used. Melting points were determined with an INESA-WRR apparatus and are uncorrected. Other reagents were used as received.

Synthesis of 1a

2-Acetylcyclopentanone (5.00 g, 39.6 mmol), 2,6-dimethylaniline (9.61 g, 79.3 mmol) and p-toluenesulfonic acid monohydrate (15.05 g, 79.1 mmol) were combined in a round bottomed flask in 150 mL of toluene. A Dean-Stark apparatus was attached and the solution was refluxed for 4-5 days under argon. The solvent was removed under reduced pressure to give a yellow oil. The obtained oil was treated with CH_2Cl_2 (50 mL) and neutralized with excess saturated $NaHCO_3$ solution. After complete dissolution, the aqueous phase was extracted with diethyl ether (2 x 20 mL). The combined organic phases were dried over $MgSO_4$, filtered and dried under vacuum to afford a yellow oil. Yellow crystals of **1a** (Yield 11.2 g, 86%) were obtained after recrystallization from methanol. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 11.26 (s, 1 H, N*H*), 7.06−6.91 (m, 6 H, Ar-*H*), 2.66 (t, $^{3}J_{HH}$ = 6.8 Hz, 2 H, C*H*$_2$), 2.18 (s, 6 H, Ar-C*H*$_3$), 2.16 (s, 8 H, Ar-C*H*$_3$ + C*H*$_2$ overlap), 1.82 (quintet, $^{3}J_{HH}$ = 7.3 Hz, 2 H, C*H*$_2$), 1.71 (s, 2 H, C*H*$_3$). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz): δ 167.1, 156.5 (N*C*CH$_3$ and N*C*CH$_2$), 145.9, 143.5, 133.1, 131.4, 127.9, 127.8, 124.5, 123.9 (Ar-*C*), 101.9 (=*C*CH$_2$), 33.3, 30.4, 22.0, 18.7, 18.6, 17.7 (*C*H$_2$ and *C*H$_3$). HRMS (ESI): m/z Calcd. for $C_{23}H_{28}N_2$ [M^{+}+H]: 333.2330; Found: 333.2346.

Synthesis of 1b

The ligand **1b** was synthesized following the similar procedure to that employed for the preparation of **1a**, but by using 2,4,6-trimethylaniline (10.82 g, 80.0 mmol).

The pale-yellow product was solidified from methanol (Yield 12.1 g, 84%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 11.21 (s, 1 H, N*H*), 6.88 (s, 2 H, Ar-*H*), 6.85 (s, 2 H, Ar-*H*), 2.66 (t, $^3J_{HH}$ = 7.2 Hz, 2 H, CH_2), 2.27 (d, $^3J_{HH}$ = 7.4 Hz, 6 H, Ar-CH_3), 2.18 (t, $^3J_{HH}$ = 7.6 Hz, 2 H, CH_2), 2.15 (s, 6 H, Ar-CH_3), 2.13 (s, 6 H, Ar-CH_3), 1.82 (quintet, $^3J_{HH}$ = 7.2 Hz, 2 H, CH_2), 1.71 (s, 2 H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 151 MHz): δ 167.2, 156.7 (N*C*CH_3 and N*C*CH_2), 143.3, 140.9, 133.7, 133.1, 132.7, 131.1, 128.6, 128.5 (Ar-*C*), 101.8 (=*C*CH_2), 33.3, 30.5, 22.0, 21.0, 18.6, 18.5, 17.6 (*C*H_2 and *C*H_3). HRMS (ESI): m/z Calcd. for $C_{25}H_{32}N_2$ [M^++H]: 361.2643; Found: 361.2658.

Synthesis of 2a

MeMgI (2.10 mL, 3 M in Et_2O, 6.30 mmol) was added dropwise to a solution of ligand **1a** (2.00 g, 6.02 mmol) in diethyl ether (30 mL) at –60 °C. The mixture was warmed to room temperature and stirred for overnight to yield a white precipitate. The precipitate of **2a** was collected by filtration. The supernatant solution was concentrated to ca. 10 mL and cooled to –30 °C to afford a second crop (Yield 2.43 g, 73%). M.p. 194-201 °C. ^{1}H NMR (C_6D_6, 600 MHz): δ 7.01−6.94 (m, 6 H, Ar-*H*), 3.12 (br, 4 H, OCH_2CH_3), 2.67 (br, 6 H, Ar-CH_3), 2.51 (br, 2 H, CH_2), 2.09 (br, 6 H, Ar-CH_3), 2.03 (br, 2 H, CH_2), 1.59 (s, 3 H, CH_3), 1.52 (m, 2 H, CH_2), 0.48 (br, 6 H, OCH_2CH_3). ^{13}C{^{1}H} NMR (C_6D_6, 151 MHz): δ 174.5, 167.1 (N*C*CH_3 and N*C*CH_2), 148.9, 147.7, 134.1, 133.4, 131.7, 129.5, 124.7, 124.6 (Ar-*C*), 101.3 (=*C*CH_2), 65.9 (O*C*H_2CH_3), 36.3, 33.2, 22.0, 21.2, 20.0, 19.0, 13.2 (OCH_2*C*H_3). Anal. Calc. for $C_{27}H_{37}IMgN_2O$: C, 58.24; H, 6.70; N, 5.03. Found: C, 58.69; H, 7.12; N, 4.78.

Synthesis of 2b

The complex **2b** was synthesized following the similar procedure to that employed for the preparation of **2a**, a pale yellow precipitate was obtained (Yield: 75%). M.p. 212-220 °C. ^{1}H NMR (C_6D_6, 600 MHz): δ 6.83 (br, 4 H, Ar-*H*), 3.18 (br, 4 H, OCH_2CH_3), 2.65, 2.55 (br, 8 H, Ar-CH_3 + CH_2 overlap), 2.21, 2.09 (br, 14 H, Ar-CH_3 + CH_2 overlap), 1.63 (s, 3 H, CH_3), 1.55 (m, 2 H, CH_2), 0.54 (br, 6 H,

OCH_2CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 151 MHz): δ 174.7, 167.3 (N*C*CH_3 and N*C*CH_2), 146.4, 145.1, 133.6, 133.3, 131.6, 131.3, 130.2, 129.0 (Ar-*C*), 101.2 (=*C*CH_2), 65.9 (O*C*H_2CH_3), 36.3, 33.3, 22.0, 21.0, 19.9, 18.9, 13.2 (OCH_2*C*H_3). Anal. Calc. for $C_{29}H_{41}IMgN_2O$: C, 59.55; H, 7.07; N, 4.79. Found: C, 59.92; H, 7.43; N, 4.35.

Synthesis of 3a

A solution of **2a** (1.50 g, 2.69 mmol) in toluene (30 mL) was stirred vigorously for 5 days over a sodium mirror (0.56 g, 24.3 mmol) at room temperature. The yellow-green suspension was filtered and the solvent was removed in vacuo. The residue was extracted with n-hexane (30 mL), filtered and concentrated to ca. 10 mL to give yellow crystals of **3a**. A second crop of **3a** was isolated after further concentration and cooled to –30°C. (Yield 0.40 g, 42%). M.p. 218-220 °C. ^1H NMR (C_6D_6, 600 MHz): δ 7.03–6.87 (m, 6H, Ar-*H*), 2.53-2.58 (m, 2H, $CH_2CH_2CH_2$), 2.13 (s, 3H, Ar-CH_3), 2.02 (t, $^3J_{HH}$ = 7.8 Hz, 2H, CH_2), 1.97 (s, 3H, Ar-CH_3), 1.74 (s, 3H, Ar-CH_3), 1.62 (s, 3H, Ar-CH_3), 1.58 (t, $^3J_{HH}$ = 6.6 Hz, 2H, CH_2), 1.46 (s, 3H, $NCCH_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 151 MHz): δ 173.9 (N*C*CH_3), 167.0 (N*C*CH_3), 150.3, 148.6, 133.4, 133.2, 133.1, 132.8, 124.2, 123.9 (Ar-*C*), 102.3 (=*C*CH_2), 36.6, 33.2, 19.7, 19.0, 18.8, 18.3 (*C*H_2 and *C*H_3). Anal. Calc. for $C_{46}H_{54}Mg_2N_4$: C, 77.65; H, 7.65; N, 7.87. Found: C, 78.04; H, 8.02; N, 7.39.

Synthesis of 3b

The complex **3b** was synthesized by using a similar procedure to that employed for the preparation of **3a**. After work-up complex **3b** was obtained as yellow crystals (Yield: 45%). M.p. 220-223 °C. ^1H NMR (C_6D_6, 600 MHz): δ 6.90 (s, 2 H, Ar-*H*), 6.87 (s, 2 H, Ar-*H*), 2.56 (t, $^3J_{HH}$ = 7.2 Hz, 2 H, CH_2), 2.31 (d, $^3J_{HH}$ = 4.2 Hz, 6 H, Ar-CH_3), 2.07 (t, $^3J_{HH}$ = 7.8 Hz, 2 H, CH_2), 1.98 (s, 6 H, Ar-CH_3), 1.90 (s, 6 H, Ar-CH_3), 1.60 (s, 3 H, CH_3), 1.56 (quintet, $^3J_{HH}$ = 6.6 Hz, 2 H, CH_2). $^{13}C\{^1H\}$ NMR (C_6D_6, 151 MHz): δ 172.2, 164.5 (N*C*CH_3 and N*C*CH_2), 146.6, 145.5, 132.6, 132.5, 131.8, 131.3, 129.2, 129.1 (Ar-*C*), 101.2 (=*C*CH_2), 35.9, 33.0, 22.3, 21.2, 19.9, 19.4, 19.3 (*C*H_2 and *C*H_3). Anal. Calc. for $C_{50}H_{62}Mg_2N_4$: C, 78.23; H, 8.14; N, 7.30. Found:

C, 78.69; H, 8.42; N, 6.93.

Synthesis of ligand 4b: 4b was synthesized by the similar procedure as **4a** and **4c**.[s1]

2-Acetylcyclohexanone (5.55 g, 39.59 mmol), 2,4,6-trimethylaniline (10.70 g, 79.14 mmol) and *p*-toluenesulfonic acid monohydrate (15.06 g, 79.17 mmol) were combined in a round bottomed flask in 150 mL of toluene. A Dean-Stark apparatus was attached and the solution was refluxed (160 °C) for 4 days under argon. The solvent was removed under reduced pressure to give a yellow oil. The obtained oil was treated with CH_2Cl_2 (50 mL) and neutralized with excess saturated $NaHCO_3$ solution. After complete dissolution, the aqueous phase was extracted with diethyl ether (2 x 20 mL). The combined organic phases were dried over $MgSO_4$, filtered and dried under vacuum to afford a yellow oil. Yellow crystals of **4b** were obtained after recrystallization from methanol or purified by flash chromatography (Yield 8.6 g, 58%). M.p. 173-175 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 12.99 (s, 1H, N*H*), 6.87 (s, 4H, Ar-*H*), 2.46 (t, $^3J_{HH}$ = 6.6 Hz, 2H, CH_2), 2.28 (s, 6H, Ar-CH_3), 2.18 (s, 6H, Ar-CH_3), 2.08 (s, 6H, Ar-CH_3), 1.99 (t, $^3J_{HH}$ = 6.6 Hz, 2H, CH_2), 1.78 (s, 3H, CH_3), 1.72 (m, 2H, CH_2), 1.61 (m, 2H, CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 151 MHz): δ 173.7, 172.1 (N*C*CH_3, N*C*CH_2), 155.1, 145.2, 137.7, 135.4, 131.7, 128.6, 128.5, 125.9 (Ar-*C*), 97.7 (=*C*CH_2), 31.5, 27.9, 27.1, 24.1, 22.5, 21.8, 20.9, 18.6, 18.0 (*C*H_2, *C*H_3). HRMS (ESI): m/z Calcd. for $C_{26}H_{37}N_2$ [M^++H]: 375.2800; Found: 375.2805.

Synthesis of 5a

MeMgI (2.10 mL, 3 M in Et_2O, 6.30 mmol) was added dropwise to the mixture diethyl ether and toluene (ca. 1: 1) solution of ligand **4a** (2.01 g, 5.80 mmol) at –35°C. The mixture was warmed to room temperature and stirred for overnight to yield a yellow solution. This mixture solution was filtered and concentrated to ca. 8 mL to afforded yellow precipitate of **5a**. The supernatant solution was concentrated again to afford a second crop (Yield 2.15 g, 65%). M.p. 279-281 °C. ^{1}H NMR (C_6D_6, 600 MHz): δ 7.14-7.01 (m, 6H, Ar-*H*), 2.22 (br, 2H, CH_2), 2.18 (br, 6H, Ar-CH_3), 2.14 (br, 6H, Ar-CH_3), 1.97 (br, 2H, CH_2), 1.62 (s, 3H, NCCH_3), 1.39 (br, 2H, CH_2), 1.26 (br, 2H, C*H*$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 151 MHz): δ 169.8, 168.9 (N*C*CH$_3$ and N*C*CH$_2$), 146.8, 132.2, 129.2, 128.3, 124.7, 124.4 (Ar-*C*), 99.7 (=*C*CH$_2$), 31.9, 29.7, 23.8, 22.8, 19.9, 19.7 (*C*H$_2$ and *C*H$_3$). Anal. Calc. for $C_{48}H_{58}I_2Mg_2N_4$: C, 58.03; H, 5.88; N, 5.64. Found: C, 58.35; H, 6.13; N, 5.31.

Synthesis of 5b

This complex was synthesized by using a similar procedure to that employed for the preparation of **5a**, but by using ligand **4b** (3.08 g, 8.22 mmol). After work-up complex **5b** was obtained as a pale-yellow solid (Yield 3.38 g, 69%). M.p. 286-288 °C. ^{1}H NMR (C$_6$D$_6$, 600 MHz): δ 7.07-6.89 (br, 4H, Ar-*H*), 2.65 (br, 2H, C*H*$_2$), 2.39-2.05 (br, 18H, Ar-C*H*$_3$), 1.71 (br, 3H, NCC*H*$_3$), 1.42 (br, 2H, C*H*$_2$), 1.30 (br, 2H, C*H*$_2$), 0.90 (br, 2H, C*H*$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 151 MHz): δ 163.1, 136.1, 129.7, 129.3, 129.0, 125.7 (Ar-*C*), 90.0 (=*C*CH$_2$), 29.8, 23.8, 22.9, 21.4, 21.1, 19.7 (*C*H$_2$ and *C*H$_3$). (N.B. this complex has a very poor solubility in C$_6$D$_6$, and only gave a partial ^{13}C spectrum of **2b** after carrying out NMR data collection over 20 hours). Anal. Calc. for $C_{52}H_{66}I_2Mg_2N_4$: C, 59.51; H, 6.34; N, 5.34. Found: C, 59.92; H, 6.62; N, 5.01.

Synthesis of 5c

This complex was synthesized by using a similar procedure to that employed for the preparation of **5a**, but by using ligand **4c** (2.01 g, 4.38 mmol) and in only toluene (30 mL). After work-up complex **5c** was obtained as a pale-yellow solid (Yield 2.15 g, 81%). M.p. 194-196 °C. ^{1}H NMR (C$_6$D$_6$, 600 MHz): δ 7.14 (br, 6H, Ar-*H*), 3.31 (br, 4H, C*H*(CH$_3$)$_2$), 2.27 (br, 2H, C*H*$_2$), 2.16 (br, 2H, C*H*$_2$), 1.76 (s, 3H, NCC*H*$_3$), 1.50 (br, 4H, C*H*$_2$), 1.19 (br, 24H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 151 MHz): δ 170.6, 170.3 (N*C*CH$_3$ and N*C*CH$_2$), 145.4, 145.3, 143.1, 141.2, 125.7, 125.3, 124.4, 124.2 (Ar-*C*), 100.8 (=*C*CH$_2$), 32.0, 29.1, 28.4, 28.1, 25.1, 24.9, 23.2, 22.6, 22.2 (*C*H$_2$ and *C*H$_3$). Anal. Calc. for $C_{64}H_{90}I_2Mg_2N_4$: C, 63.12; H, 7.45; N, 4.60. Found: C, 63.54; H, 7.72; N, 4.27.

Synthesis of 6a

A solution of **5a** (1.00 g, 1.75 mmol) in toluene (30 mL) was stirred vigorously for 4 days over a sodium mirror (0.56 g, 24.3 mmol) at room temperature. The yellow-green suspension was filtered and the solvent was removed in *vacuo*. The residue was extracted with n-hexane (30 mL), filtered and concentrated to ca. 4 mL to give yellow crystals of **6a**. A second crop of **6a** was isolated after further concentration (Yield 0.29 g, 45%). M.p. 206-208 °C. ^{1}H NMR (C_6D_6, 600 MHz): δ 7.08–6.96 (m, 6H, Ar-*H*), 2.32 (t, $^3J_{HH}$ = 6.6 Hz, 2H, C*H*$_2$), 1.97 (t, $^3J_{HH}$ = 6.6 Hz, 2H, C*H*$_2$), 1.94 (s, 6H, Ar-C*H*$_3$), 1.88 (s, 6H, Ar-C*H*$_3$), 1.63 (s, 3H, NCC*H*$_3$), 1.48 (m, 2H, C*H*$_2$), 1.30 (m, 2H, C*H*$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 151 MHz): δ 166.8, 165.5 (N*C*CH$_3$ and N*C*CH$_2$), 148.54, 148.48, 132.01, 131.97, 128.5, 127.9, 123.9, 123.8 (Ar-*C*), 98.5 (=*C*CH$_2$), 32.2, 29.6, 24.4, 23.1, 19.69, 19.67, 19.63 (*C*H$_2$ and *C*H$_3$). Anal. Calc. for $C_{48}H_{58}Mg_2N_4$: C, 77.95; H, 7.90; N, 7.58. Found: C, 78.31; H, 8.21; N, 7.20.

Synthesis of 6b

This complex was synthesized by using a similar procedure to that employed for the preparation of **6a**, but by using complex **5b** (1.00 g, 1.67 mmol). After work-up complex **6b** was obtained as yellow crystals (Yield 0.28 g, 42%). M.p. 210-212 °C. ^{1}H NMR (C_6D_6, 600 MHz): δ 6.91 (s, 2H, Ar-*H*), 6.88 (s, 2H, Ar-*H*), 2.37 (t, $^3J_{HH}$ = 6.6 Hz, 2H, C*H*$_2$), 2.32 (s, 3H, Ar-C*H*$_3$), 2.30 (s, 3H, Ar-C*H*$_3$), 2.03 (t, $^3J_{HH}$ = 6.6 Hz, 2H, C*H*$_2$), 1.93 (s, 6H, Ar-C*H*$_3$), 1.87 (s, 6H, Ar-C*H*$_3$), 1.68 (s, 3H, NCC*H*$_3$), 1.51 (m, 2H, C*H*$_2$), 1.35 (m, 2H, C*H*$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 151 MHz): δ 167.0, 165.7 (N*C*CH$_3$ and N*C*CH$_2$), 145.9, 145.8, 132.5, 132.3, 131.7, 131.6, 129.24, 129.20 (Ar-*C*), 98.5 (=*C*CH$_2$), 32.1, 29.7, 24.5, 23.2, 21.14, 21.11, 19.6, 19.53, 19.49 (*C*H$_2$ and *C*H$_3$). Anal. Calc. for $C_{52}H_{66}Mg_2N_4$: C, 78.49; H, 8.36; N, 7.04. Found: C, 78.83; H, 8.71; N, 6.71.

Synthesis of 6c

This complex was synthesized by using a similar procedure to that employed for the preparation of **6a**, but by using complex **5c** (0.91 g, 0.75 mmol) and directly concentrated to 5 mL in toluene solution and filtered. After work-up complex **6c** was obtained as a yellow powder (Yield 0.20 g, 28%). M.p. 218-220 °C. ^{1}H NMR (C_6D_6, 600 MHz): δ 7.10–7.08 (m, 6 H, Ar-*H*), 3.17 (sept, $^3J_{HH}$ = 6.6 Hz, 2H, C*H*(CH_3)$_2$), 3.10 (sept, $^3J_{HH}$ = 6.6 Hz, 2H, C*H*(CH_3)$_2$), 2.17 (t, $^3J_{HH}$ = 6.6 Hz, 2H, C*H*$_2$), 2.00 (t, $^3J_{HH}$ = 6.6 Hz, 2H, C*H*$_2$), 1.63 (s, 3H, C*H*$_3$), 1.35 (m, 2H, C*H*$_2$), 1.25 (m, 2H, C*H*$_2$), 1.23 (d, $^3J_{HH}$ = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 1.16 (d, $^3J_{HH}$ = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 1.01 (d, $^3J_{HH}$ = 7.2 Hz, 6H, CH(C*H*$_3$)$_2$), 0.98 (d, $^3J_{HH}$ = 7.2 Hz, 6H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 151 MHz): δ 168.1, 167.9 (N*C*CH_3 and N*C*CH_2), 146.2, 145.9, 142.6, 142.4, 125.2, 125.1, 124.1, 124.0 (Ar-*C*), 100.5 (=*C*CH_2), 32.2, 29.3, 28.6, 28.3, 25.6, 25.0, 24.5, 24.4, 23.6, 22.4, 21.7 (*C*H_2 and *C*H_3). Anal. Calc. for $C_{64}H_{90}Mg_2N_4$: C, 79.74; H, 9.41; N, 5.81. Found: C, 80.10; H, 9.72; N, 5.47.

X-ray crystal structure determination

Crystallographic data for complexes **1b**, **2a**, **2b**, **3a**, **3b**, **4b**, **5c**, **6a** and **6b** are given in Table S1. Diffraction data was collected on a Bruker D8 VENTURE PHOTON 100 diffractometer using a graphite-monochromated MoKα radiation (0.71073Å) in the ω-2θ scan mode. In all cases, an empirical absorption correction by SADABS was applied to the intensity data. The structure was solved by direct methods and refined on F2 by full-matrix least-squares methods using the SHELXTL crystallographic software package. All non-hydrogen atoms were refined anisotropically with hydrogen atoms included in calculated positions (riding model). CCDC 2014496, 2014497, 2014500, 2014501, 2014505, 1845328-1845331 contain the supplementary crystallographic data for complexes **1b**, **2a**, **2b**, **3a**, **3b**, **4b**, **5c**, **6a** and **6b.** The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

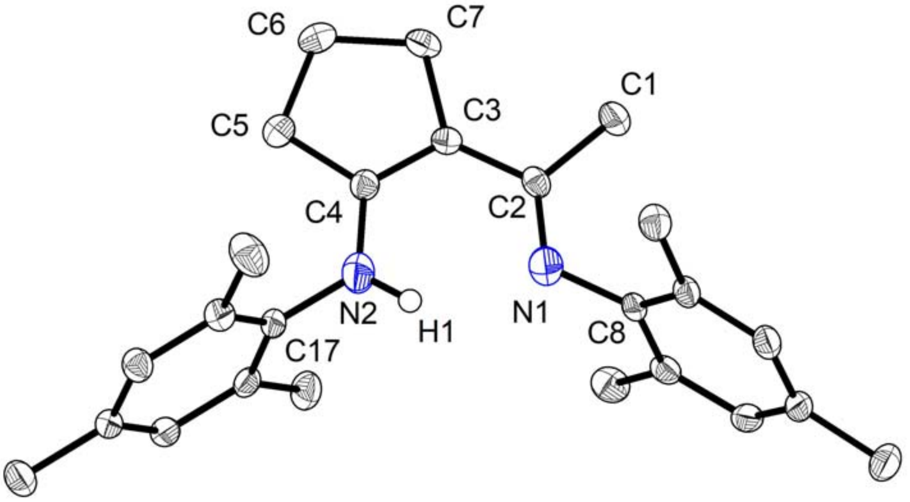


Figure S1 Molecular structure of **1b**. Selected bond lengths(Å) and angles (°): N(1)−C(2) 1.295(3), N(1)−C(8) 1.410(2), N(2)−C(4) 1.350(3), N(2)−C(17) 1.430(3), N(2)−H(1) 0.88, C(1)−C(2) 1.509(3), C(2)−C(3) 1.431(3), C(3)−C(4) 1.365(3), C(4)−C(5) 1.489(3), C(2)−N(1)−C(8) 121.62(16), N(1)−C(2)−C(3) 121.76(17), C(2)−C(3)−C(4) 124.53(17), N(2)−C(4)−C(3) 123.88(18), C(4)−N(2)−C(17), 124.58(17), C(4)−N(2)−H(1), 117.7.

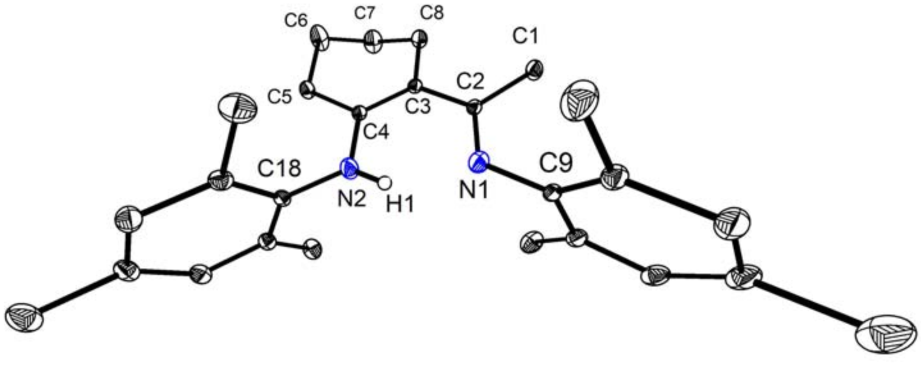


Figure S2 Molecular structure of **4b**. Selected bond lengths(Å) and angles (°): N(1)−C(2) 1.3097(19), N(1)−C(9) 1.4244(18), N(2)−C(4) 1.3709(19), N(2)−C(18) 1.4329(18), N(2)−H(1) 0.90(3), C(1)−C(2) 1.518(2), C(2)−C(3) 1.4640(19), C(3)−C(4) 1.3862(19), C(4)−C(5) 1.517(2), C(2)−N(1)−C(9) 121.50(12), N(1)−C(2)−C(3) 121.14(12), C(2)−C(3)−C(4) 121.79(12), N(2)−C(4)−C(3) 121.79(12), C(4)−N(2)−C(18), 124.48(12), C(4)−N(2)−H(1), 113.2(16).

Table S1 Summary of crystallographic data for **1b**, **2a**, **2b**, **3a**, **3b**, **4b**, **5c**, **6a** and **6b.**

	1b	**2a**	**2b**
Formula	$C_{25}H_{32}N_2$	$C_{27}H_{37}IMgN_2O$	$C_{29}H_{41}IMgN_2O$
Mr	360.53	556.80	584.85
Temp (K)	130(2)	120(2)	130(2)
Crystal system	monoclinic	monoclinic	tetragonal
Space group	$P2_1/c$	$P2_1/c$	$P\text{-}42_1/c$
a (Å)	12.740(4)	17.9401(8)	19.5752(16)
b (Å)	21.018(6)	15.0689(11)	19.5752(16)
c (Å)	16.448(5)	19.9466(13)	15.2135(14)
α (°)	90	90	90
β (°)	106.050(8)	90.100(3)	90
γ (°)	90	90	90
V (A^3)	4233(2)	5392.3(6)	5829.6(11)
Z	8	8	8
ρ_{calc} (g cm^{-3})	1.131	1.372	1.333
μ/mm^{-1}	0.066	1.231	1.143
F(000)	1568	2288	2416
GOF on F^2	1.048	1.021	1.109
R_1 (obs data)	0.0571	0.0567	0.0285
wR_2 (obs data)	0.1535	0.1427	0.0671
CCDC	2014496	2014497	2014500

Table S1 Summary of crystallographic data for **1b**, **2a**, **2b**, **3a**, **3b**, **4b**, **5c**, **6a** and **6b.**

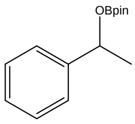
	3a	**3b**	**4b**
Formula	$C_{53}H_{62}Mg_2N_4$	$C_{50}H_{62}Mg_2N_4$	$C_{26}H_{34}N_2$
Mr	803.68	767.66	374.55
Temp (K)	130(2)	130(2)	130(2)
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	Pbcn	P2/n	$P2_1/n$
a (Å)	12.9060(11)	13.6352(11)	12.523(5)
b (Å)	16.3663(14)	8.1397(7)	7.898(3)
c (Å)	22.729(2)	20.7709(16)	22.984(9)
α (°)	90	90	90
β (°)	90	97.278(3)	92.957(10)
γ (°)	90	90	90
V (A^3)	4800.9(7)	2286.7(3)	2270.1(16)
Z	4	4	4
ρ_{calc} (g cm^{-3})	1.112	1.115	1.096
μ/mm^{-1}	0.088	0.089	0.063
F(000)	1728	828	816
GOF on F^2	1.007	1.043	1.036
R_1 (obs data)	0.0656	0.0481	0.0708
wR_2 (obs data)	0.1306	0.1264	0.1990
CCDC	2014501	2014505	1845328

Table S1 Summary of crystallographic data for **1b**, **2a**, **2b**, **3a**, **3b**, **4b**, **5c**, **6a** and **6b.**

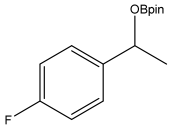
	5c	**6a**	**6b**
Formula	$C_{75}H_{100}I_2Mg_2N_4O$	$C_{48}H_{58}Mg_2N_4$	$C_{52}H_{66}Mg_2N_4$
Mr	1376.01	739.60	795.70
Temp (K)	130(2)	140(2)	130(2)
Crystal system	triclinic	monoclinic	monoclinic
Space group	P-1	C2/c	$P2_1/n$
a (Å)	14.173(4)	21.247(2)	12.804(2)
b (Å)	15.372(4)	11.2261(13)	20.974(4)
c (Å)	19.224(5)	20.029(2)	18.209(3)
α (°)	104.191(5)	90	90
β (°)	104.112(5)	111.166(2)	97.196(5)
γ (°)	103.012(5)	90	90
V (A^3)	3752.7(17)	4455.2(9)	4851.4(15)
Z	2	8	8
ρ_{calc} (g cm^{-3})	1.218	1.103	1.089
μ/mm^{-1}	0.897	0.089	0.086
F(000)	1432	1592	1720
GOF on F^2	1.085	1.043	1.104
R_1 (obs data)	0.0755	0.0677	0.0909
wR_2 (obs data)	0.1790	0.1800	0.2341
CCDC	1845331	1845329	1845330

General Procedure for Catalytic Hydroboration of Epoxides and Their Hydrolysis to Alcohols. In a glove box, catalyst **6a** (5 mol%) was added to a solution of epoxides (0.25 mmol) and HBpin (1.5 equiv) in a J. Young NMR tube equipped with a Teflon screw cap, which was charged with C_6D_6 (0.4 mL). The progress of the reaction was monitored by ^{1}H and ^{11}B NMR. The ratio of products (**a**:**b**) was based on the appearance of a new C*H*OBpin and C*H₂*OBpin resonance. The selected corresponding crude products were purified by flash column chromatography on silica gel with acetate/hexane as eluents to give the corresponding alcohols.

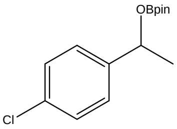
Spectroscopic Data for Epoxides Hydroboration major Products.



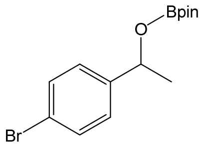
^{1}H NMR (600 MHz, C_6D_6): δ 1.00 (s, 6 H, BOC*Me*$_2$), 1.03 (s, 6 H, BOC*Me*$_2$), 1.44 (d, $^3J_{HH}$ = 6.6 Hz, 3 H, OCHC*H*$_3$), 5.38 (q, $^3J_{HH}$ = 6.6 Hz, 1 H, OC*H*), 7.04-7.36 (m, 5 H, Ar−*H*). ^{13}C{^{1}H} NMR (151 MHz, C_6D_6): δ 24.6 (BOC*Me*$_2$), 24.7 (BOC*Me*$_2$), 25.8 (*C*H$_3$CHO), 72.9 (O*C*H), 82.5 (BO*C*Me$_2$), 125.7, 127.4, 128.5, 145.4 (Ar−*C*). ^{11}B{^{1}H} NMR (193 MHz, C_6D_6): δ 22.6.



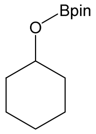
^{1}H NMR (600 MHz, C_6D_6): δ 1.01 (s, 6 H, BOC*Me*$_2$), 1.03 (s, 6 H, BOC*Me*$_2$), 1.36 (d, $^3J_{HH}$ = 6.6 Hz, 3 H, OCHC*H*$_3$), 5.26 (q, $^3J_{HH}$ = 6.6 Hz, 1 H, OC*H*), 6.78 (m, 2 H, Ar−*H*), 7.13 (m, 2 H, Ar−*H*). ^{13}C NMR (151 MHz, C_6D_6): δ 24.6 (BOC*Me*$_2$), 24.7 (BOC*Me*$_2$), 25.6 (OCH*C*H3), 72.3 (O*C*H), 82.6 (BO*C*Me$_2$), 115.2, 115.3, 127.4, 127.4, 141.1, 141.1, 161.6, 163.2 (Ar−*C*). ^{11}B{^{1}H} NMR (193 MHz, C_6D_6): δ 22.5.



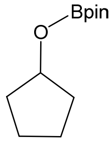
^{1}H NMR (600 MHz, C_6D_6): δ 1.01 (s, 6 H, BOC*Me*$_2$), 1.03 (s, 6 H, BOC*Me*$_2$), 1.33 (d, $^3J_{HH}$ = 6.6 Hz, 3 H, OCHC*H*$_3$), 5.22 (q, $^3J_{HH}$ = 6.6 Hz, 1 H, OC*H*), 7.04-7.09 (m, 4 H, Ar−*H*). ^{13}C NMR (151 MHz, C_6D_6): δ 24.6 (BOC*Me*$_2$), 24.7 (BOC*Me*$_2$), 25.5 (OCH*C*H3), 72.2 (O*C*H), 82.5 (BO*C*Me$_2$), 127.2, 128.7, 132.4, 137.5 (Ar−*C*). ^{11}B{^{1}H} NMR (193 MHz, C_6D_6): δ 22.4.



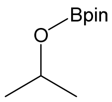
^{1}H NMR (600 MHz, C_6D_6): δ 1.00 (d, $^3J_{HH}$ = 1.2 Hz, 12 H, BOC*Me*$_2$), 1.32 (d, $^3J_{HH}$ = 6.6 Hz, 3 H, OCHC*H*$_3$), 5.20 (q, $^3J_{HH}$ = 6.6 Hz, 1 H, OC*H*), 7.16-7.24 (m, 4 H, Ar−*H*). ^{13}C NMR (151 MHz, C_6D_6): δ 24.2 (BOC*Me*$_2$), 24.6 (BOC*Me*$_2$), 25.1 (OCH*C*H3), 71.8 (O*C*H), 82.7 (BO*C*Me$_2$), 127.7, 130.9, 131.2, 143.9 (Ar−*C*). ^{11}B{^{1}H} NMR (193 MHz, C_6D_6): δ 22.3.



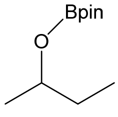
^{1}H NMR (600 MHz, C_6D_6): δ 1.08 (s, 12 H, BOC*Me*$_2$), 1.12−1.15 (m, 2 H, C_6*H*$_{11}$), 1.29-1.32 (m, 2 H, C_6*H*$_{11}$), 1.42-1.48 (m, 2 H, C_6*H*$_{11}$), 1.60-1.63 (m, 2 H, C_6*H*$_{11}$), 1.84-1.87 (m, 2 H, C_6*H*$_{11}$), 4.16 (sept, $^3J_{HH}$ = 4.2 Hz, 1 H, OC*H*). ^{13}C{^{1}H} NMR (151 MHz, C_6D_6): δ 24.1 (*C*$_6$H$_{11}$), 24.8 (BOC*Me*$_2$), 25.9, 34.8, 72.7 (*C*$_6$H$_{11}$), 82.2 (BO*C*Me$_2$). ^{11}B{^{1}H} NMR (193 MHz, C_6D_6): δ 22.3.



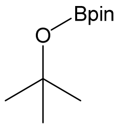
^{1}H NMR (600 MHz, $CDCl_3$): δ 1.25 (s, 12 H, BOC*Me*$_2$), 1.53−1.55 (m, 2 H, C_5*H*$_9$), 1.63-1.65 (m, 2 H, C_5*H*$_9$), 1.72-1.77 (m, 4 H, C_5*H*$_9$), 4.60 (m, 1 H, OC*H*). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 23.3 (*C*$_5$H$_9$), 24.7 (BOC*Me*$_2$), 34.9, 76.8 (*C*$_5$H$_9$), 82.6 (BO*C*Me$_2$). ^{11}B{^{1}H} NMR (193 MHz, $CDCl_3$): δ 21.8.



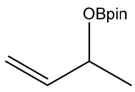
^{1}H NMR (600 MHz, C_6D_6): δ 1.01 (s, 12 H, BOC*Me*$_2$), 1.15 (d, $^3J_{HH}$ = 6 Hz, 6 H, CH(*Me*)$_2$), 4.44 (sept, $^3J_{HH}$ = 6 Hz, 1 H, C*H*(Me)$_2$). ^{13}C{^{1}H} NMR (151 MHz, C_6D_6): δ 24.6 (CH(*Me*)$_2$), 24.7 (BOC*Me*$_2$), 67.3 (*C*H(Me)$_2$), 82.2 (BO*C*Me$_2$). ^{11}B{^{1}H} NMR (193 MHz, C_6D_6): δ 22.3.



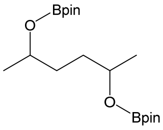
^{1}H NMR (600 MHz, C_6D_6): δ 0.87 (t, $^3J_{HH}$ = 7.2 Hz, 3 H, CH$_2$*Me*$_2$), 1.07 (s, 12 H, BOC*Me*$_2$), 1.16 (d, $^3J_{HH}$ = 6 Hz, 3 H, OCH*Me*), 1.39 (m, 1 H, OCHC*H*$_2$Me), 1.53 (m, 1 H, OCHC*H*$_2$Me), 4.23 (m, 1 H, OC*H*). ^{13}C{^{1}H} NMR (151 MHz, C_6D_6): δ 10.0, 22.3, 24.7 (BOC*Me*$_2$), 31.5, 72.2 (O*C*H), 82.2 (BO*C*Me$_2$). ^{11}B{^{1}H} NMR (193 MHz, C_6D_6): δ 22.3.



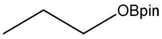
^{1}H NMR (600 MHz, C_6D_6): δ 1.03 (s, 12 H, BOC*Me*$_2$), 1.34 (s, 9 H, C(*Me*)$_3$). ^{13}C{^{1}H} NMR (151 MHz, C_6D_6): δ 24.6 (BOC*Me*$_2$), 39.8 (C(*Me*)$_3$), 73.1 (O*C*), 81.8 (BO*C*Me$_2$). ^{11}B{^{1}H} NMR (193 MHz, C_6D_6): δ 22.5.



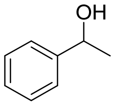
^{1}H NMR (600 MHz, C_6D_6): δ 1.05 (s, 12 H, BOC*Me*$_2$), 1.22 (m, 3 H, OCH*Me*), 4.79 (m, 1 H, OC*H*), 4.94 (m, 1 H, CH=C*H*$_2$), 5.25 (m, 1 H, CH=C*H*$_2$), 5.83 (m, 1 H, C*H*=CH$_2$). ^{13}C{^{1}H} NMR (151 MHz, C_6D_6): δ 24.7 (BOC*Me*$_2$), 25.0, 71.5 (O*C*H), 82.4 (BO*C*Me$_2$), 113.3 (CH=*C*H$_2$), 141.4 (*C*H=CH$_2$). ^{11}B{^{1}H} NMR (193 MHz, C_6D_6): δ 22.4.



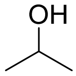
^{1}H NMR (600 MHz, C_6D_6): δ 1.06 (t, 24 H, BOC*Me*$_2$), 1.14 (dd, $^{3}J_{HH}$ = 6.2 Hz, $^{3}J_{HH}$ = 11.6 Hz, 6 H, OCH*Me*), 1.56 (m, 4 H, OCHC*H*$_2$), 4.25, 4.32 (m, 2 H, OC*H*). $^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6): δ 22.8, 22.9 (BOC*Me*$_2$), 24.7, 24.8 (OCH*C*H$_2$), 34.4, 34.9 (OCH*Me*), 70.7, 71.1 (O*C*H), 82.2, 82.2 (BO*C*Me$_2$). $^{11}B\{^{1}H\}$ NMR (193 MHz, C_6D_6): δ 22.4.



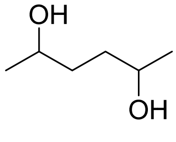
^{1}H NMR (600 MHz, C_6D_6): δ 0.80 (t, $^{3}J_{HH}$ = 7.2 Hz, 3 H, CH$_2$*Me*), 1.06 (s, 12 H, BOC*Me*$_2$), 1.50 (m, 2 H, OCH$_2$C*H*$_2$Me), 3.82 (t, $^{3}J_{HH}$ = 6.6 Hz, 2 H, OC*H*$_2$CH$_2$Me). $^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6): δ 9.91 (OCH$_2$CH$_2$*Me*), 24.5 (BOC*Me*$_2$), 25.0 (OCH$_2$*C*H$_2$Me), 66.2 (O*C*H$_2$), 82.4 (BO*C*Me$_2$). $^{11}B\{^{1}H\}$ NMR (193 MHz, C_6D_6): δ 22.5.



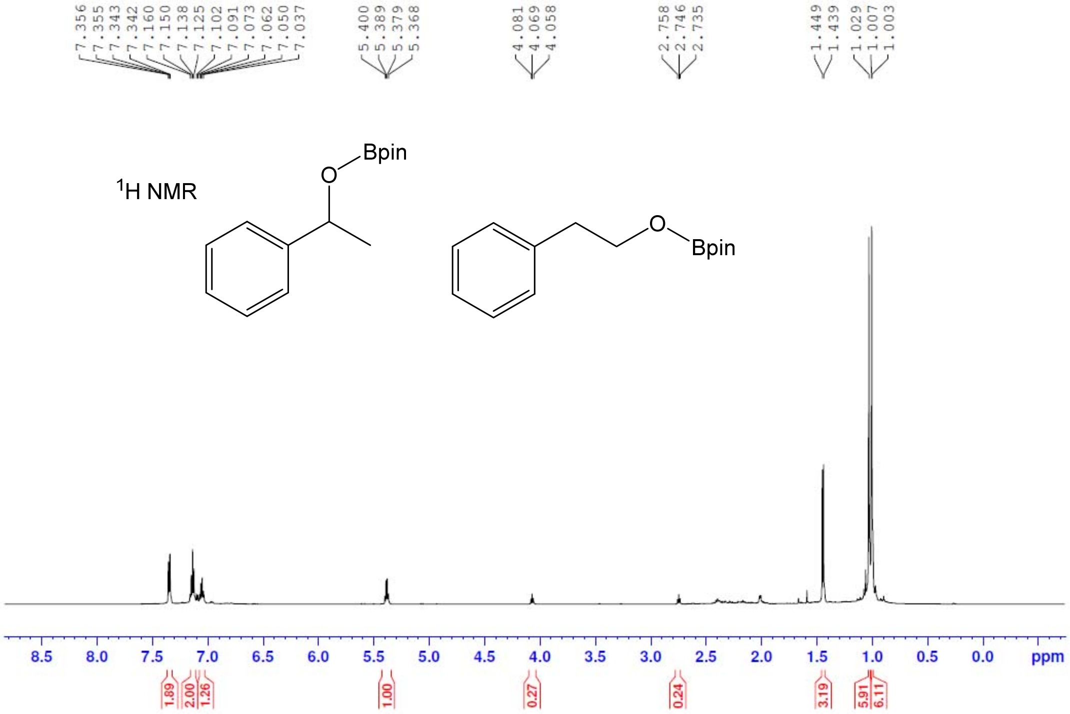
^{1}H NMR (600 MHz, $CDCl_3$): *δ* 1.50 (d, *J* = 6.6 Hz, 3H, C*H*$_3$), 2.61 (s, 1H, O*H*), 4.87 (q, *J* = 6.6 Hz, 1H, C*H*OH), 7.28–7.40 (m, 5H, Ar-*H*).



^{1}H NMR (600 MHz, $CDCl_3$): δ 1.04 (d, *J* = 7.2 Hz, 6H, C*H*$_3$), 3.43 (s, 1H, O*H*), 3.84 (m, *J* = 6.0 Hz, 1H, C*H*OH).



^{1}H NMR (600 MHz, $CDCl_3$): δ 1.19 (d, *J* = 6.0 Hz, 6H, C*H*$_3$), 1.50-1.60 (m, 4H, C*H*$_2$), 2.40-2.48 (m, 2H, O*H*), 3.80-3.86 (m, 2H, C*H*OH).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1.003
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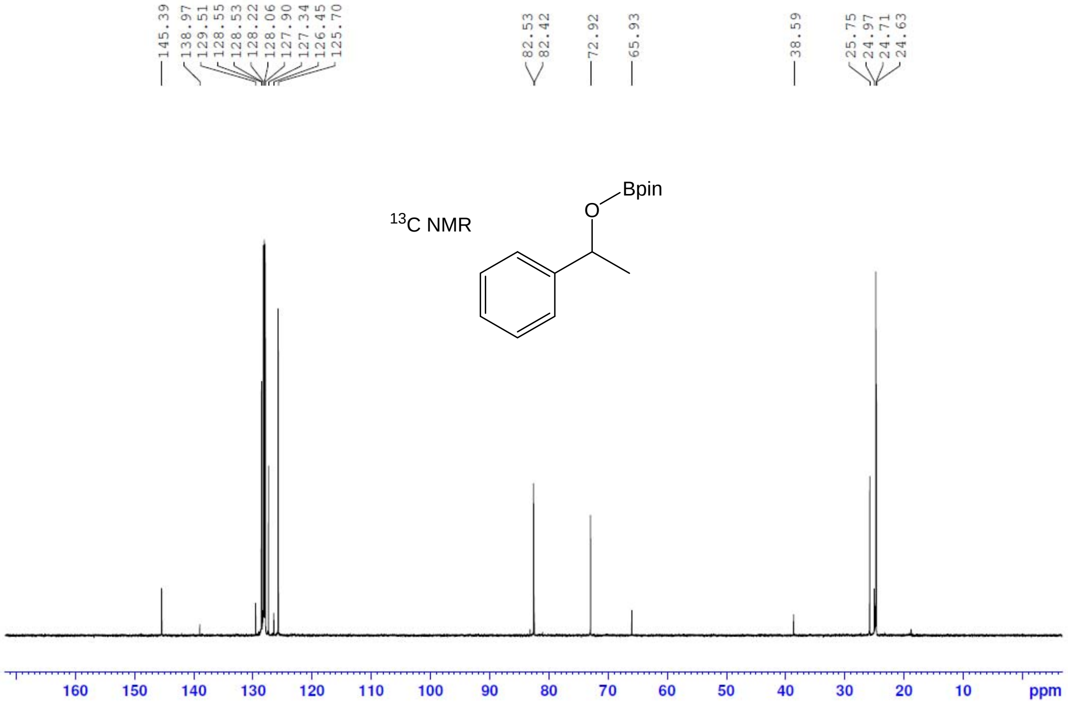
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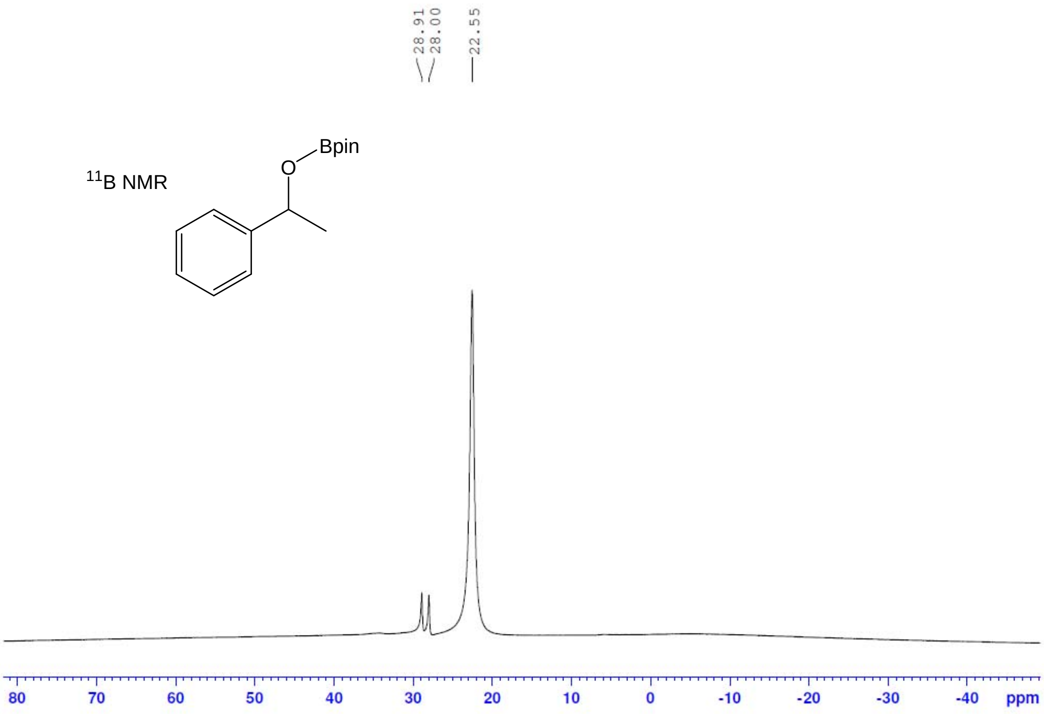
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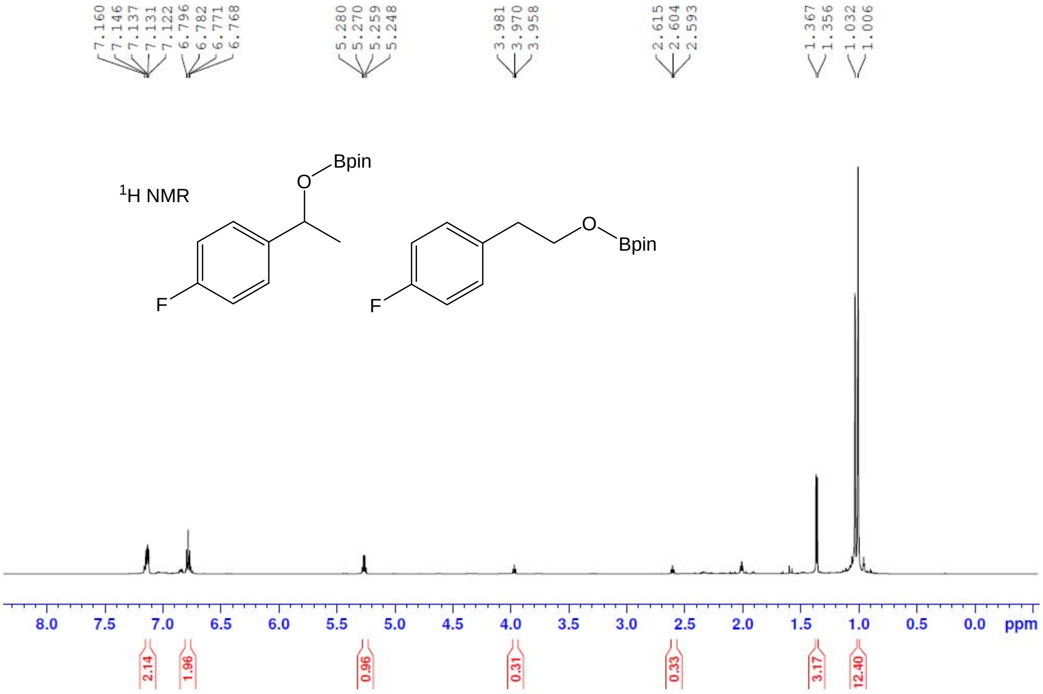
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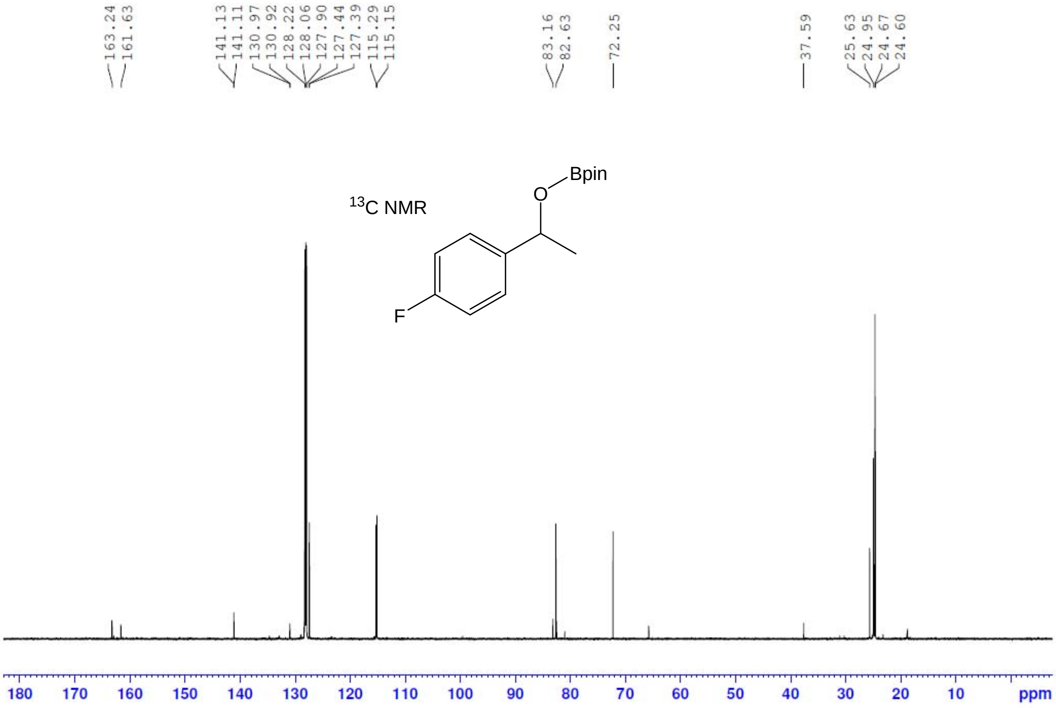
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24.67
24.60
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Bpin
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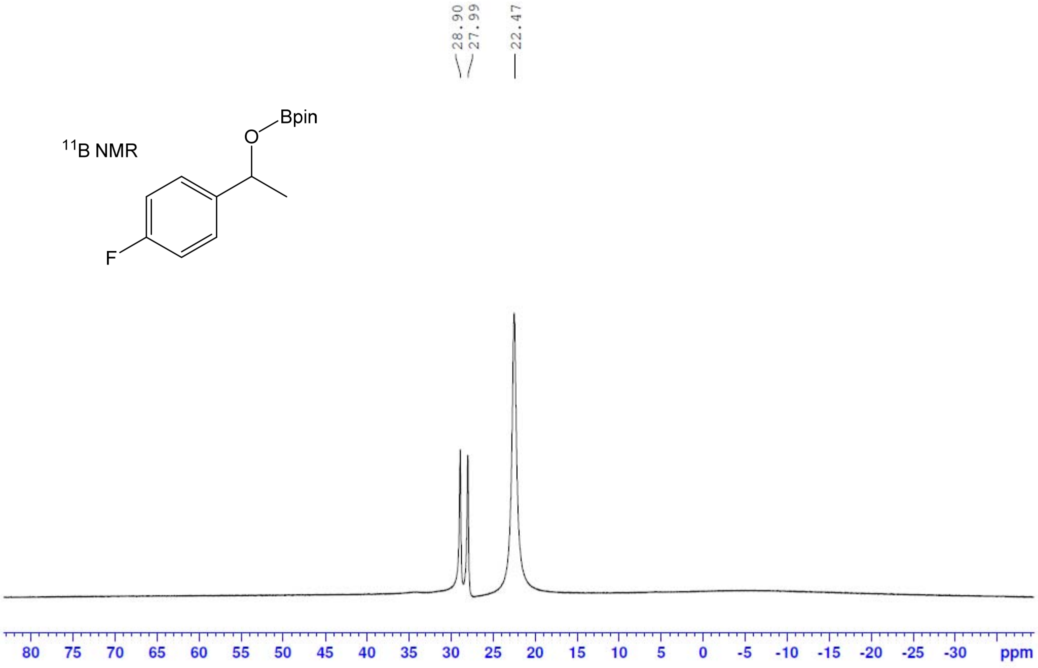
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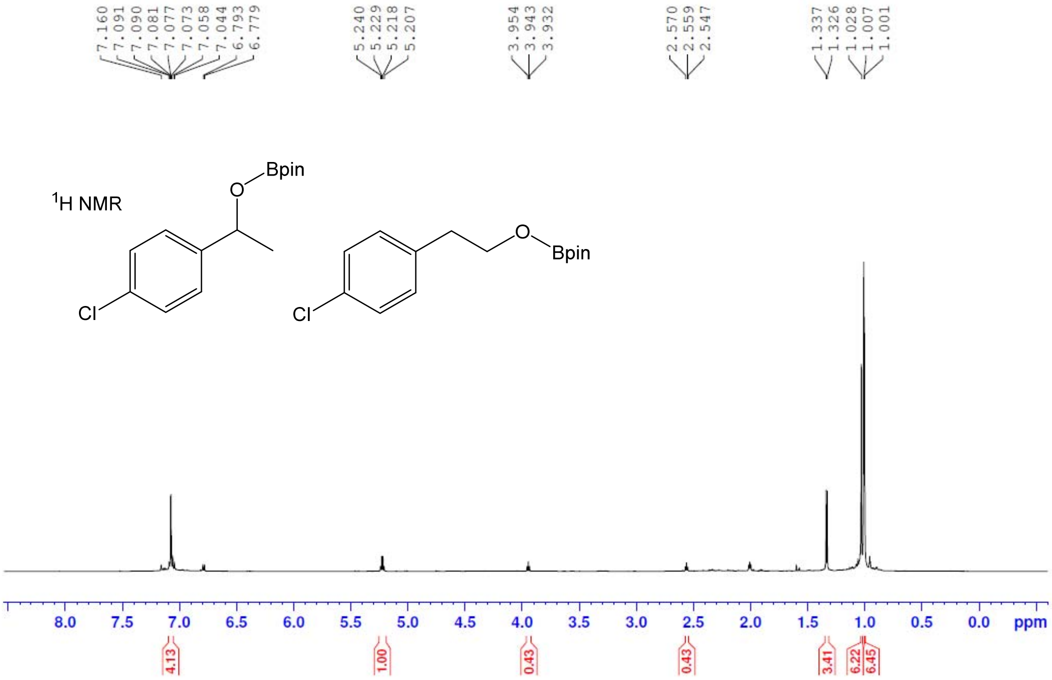
ppm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Bpin
Cl
O
Bpin
Cl
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7.0
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6.0
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2.0
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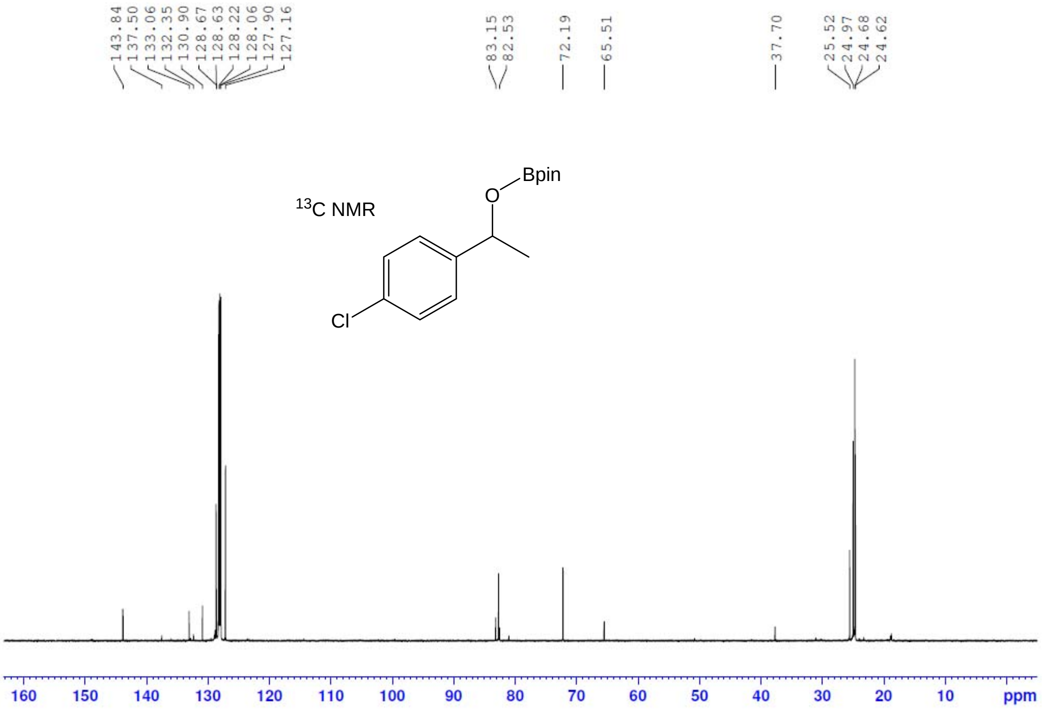
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65.51
37.70
25.52
24.97
24.68
24.62
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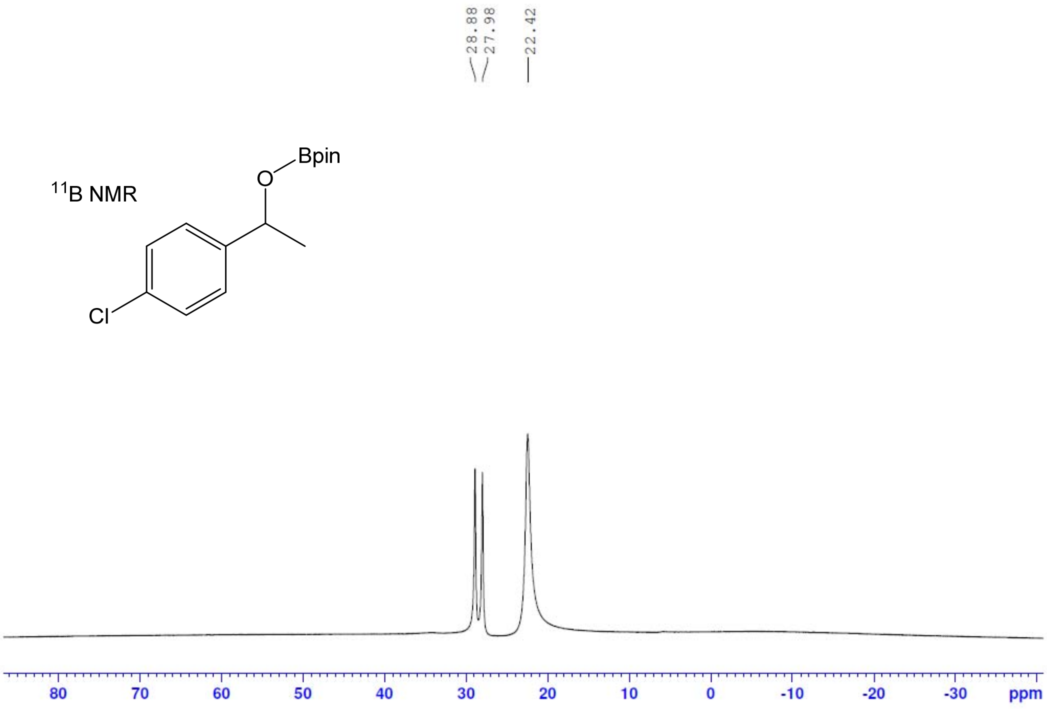
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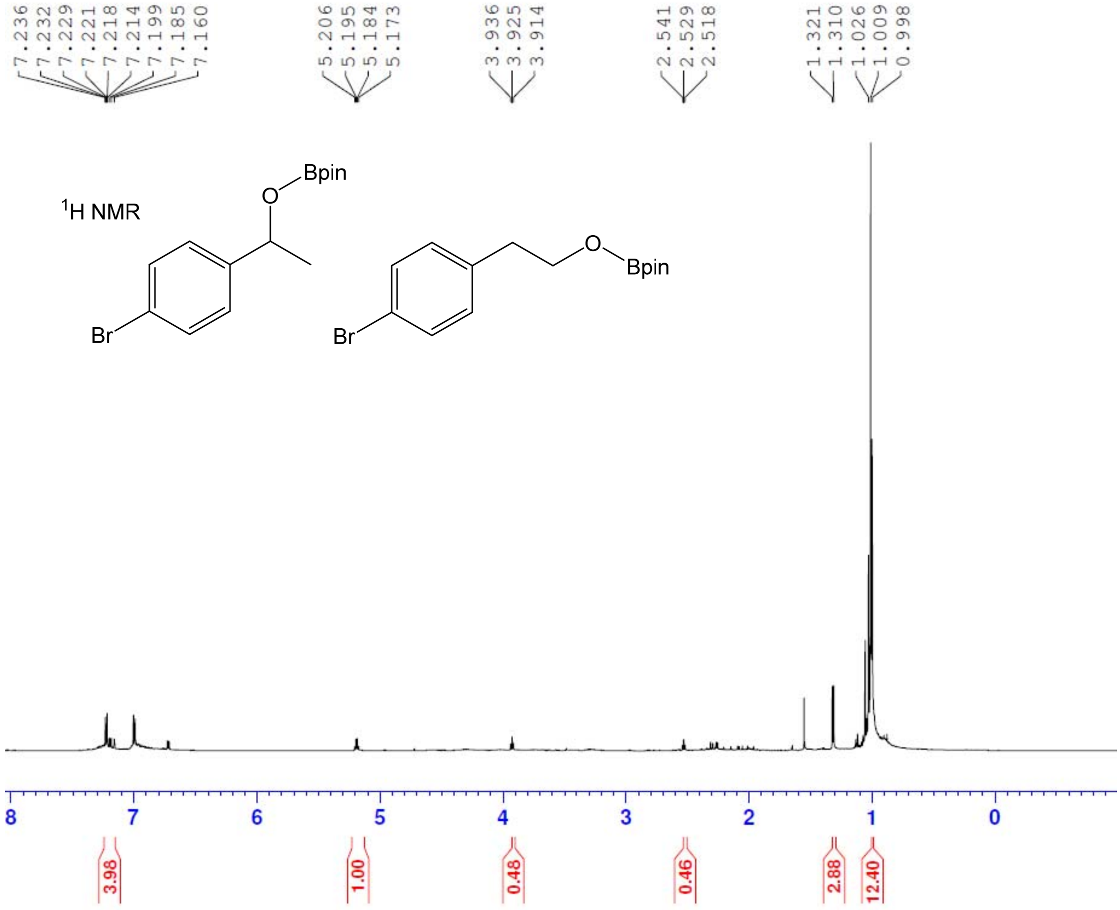
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3.936
3.925
3.914
2.541
2.529
2.518
1.321
1.310
1.026
1.009
0.998
^{1}H NMR
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O
Br
O
Bpin
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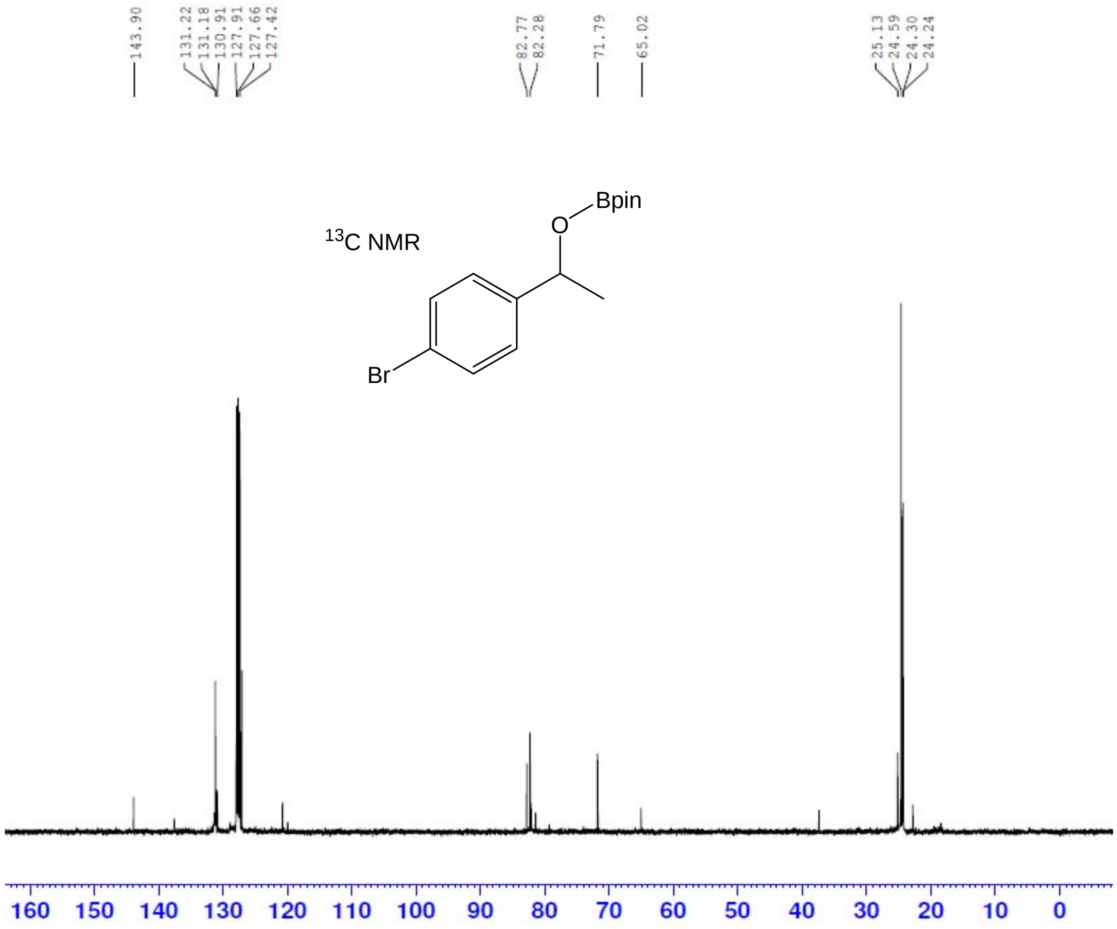
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24.30
24.24
^{13}C NMR
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Br
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150
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130
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10
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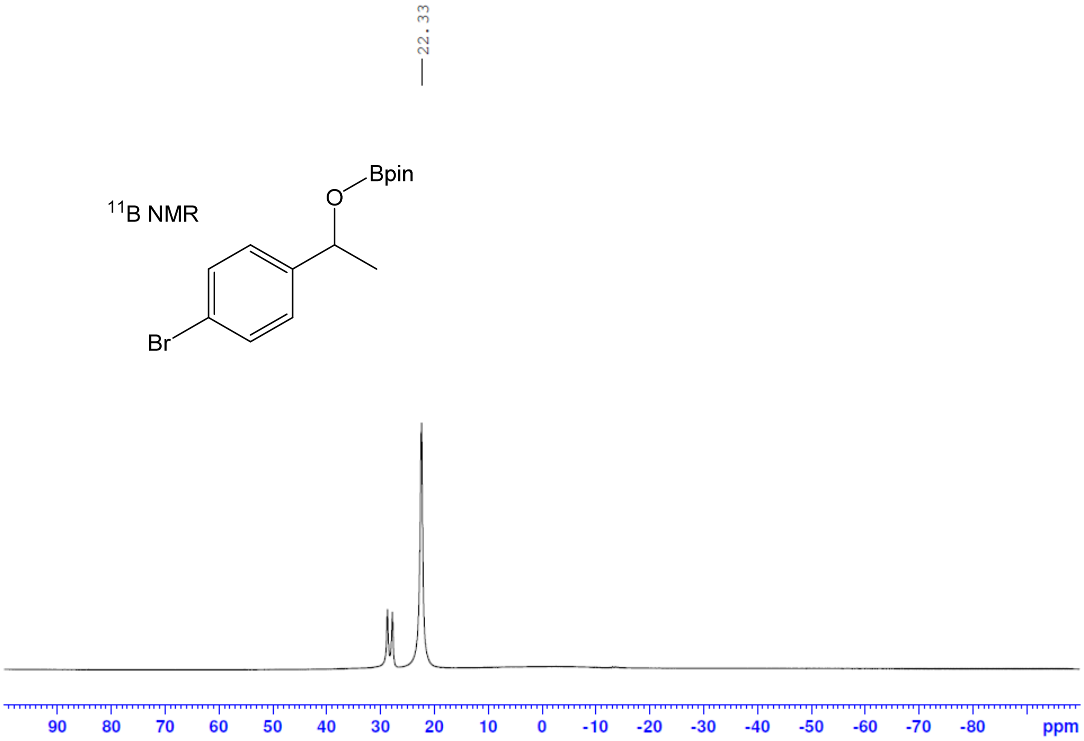
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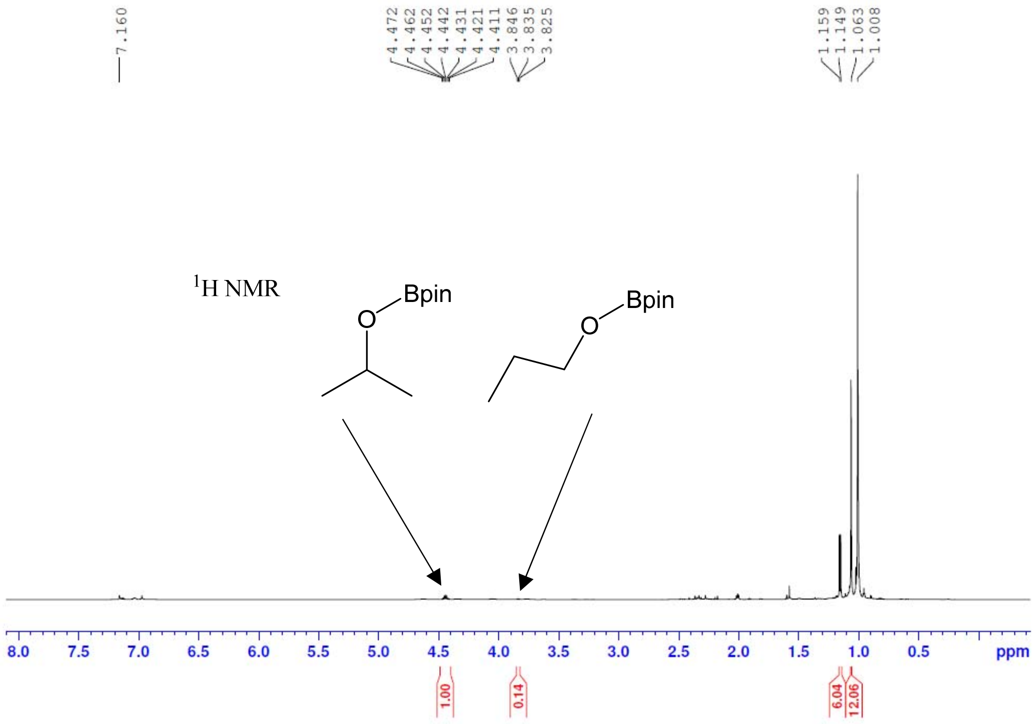
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1.149
1.063
1.008
^{1}H NMR
O
Bpin
O
Bpin
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7.5
7.0
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6.0
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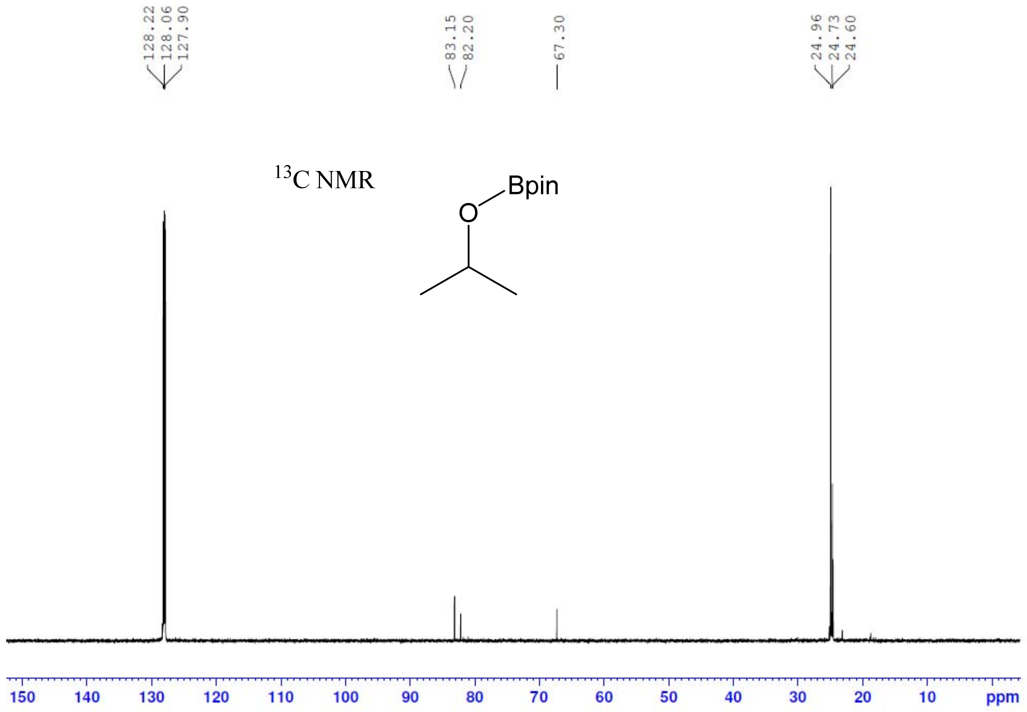
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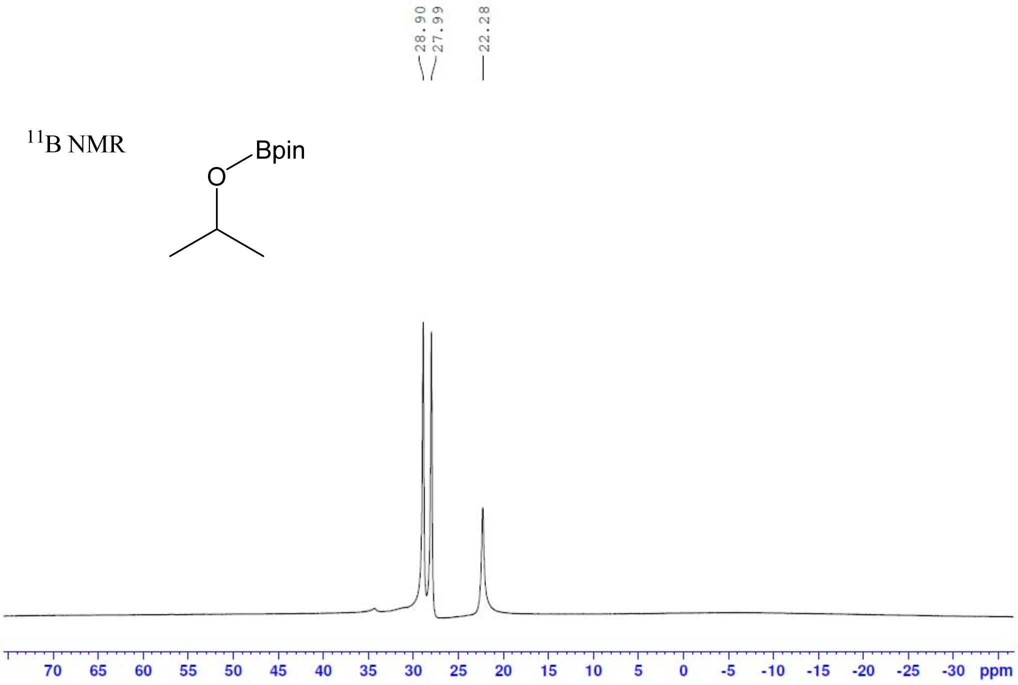
ppm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O
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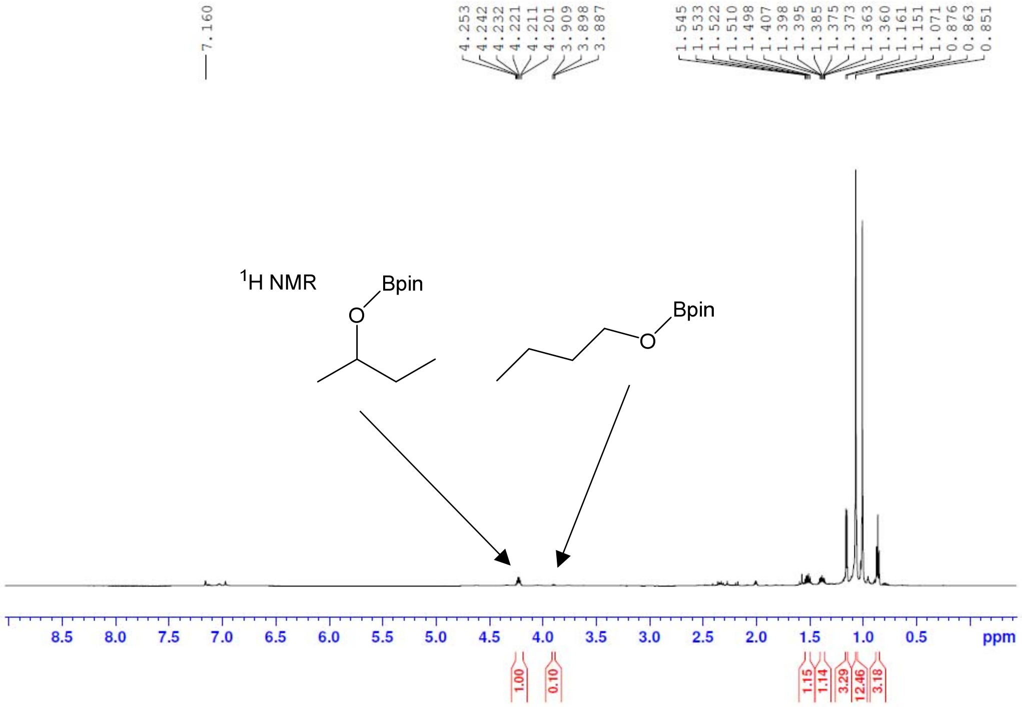
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4.211
4.201
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1.522
1.510
1.498
1.407
1.398
1.395
1.385
1.375
1.373
1.363
1.360
1.161
1.151
1.071
0.876
0.863
0.851
1H NMR
Bpin
O
Bpin
O
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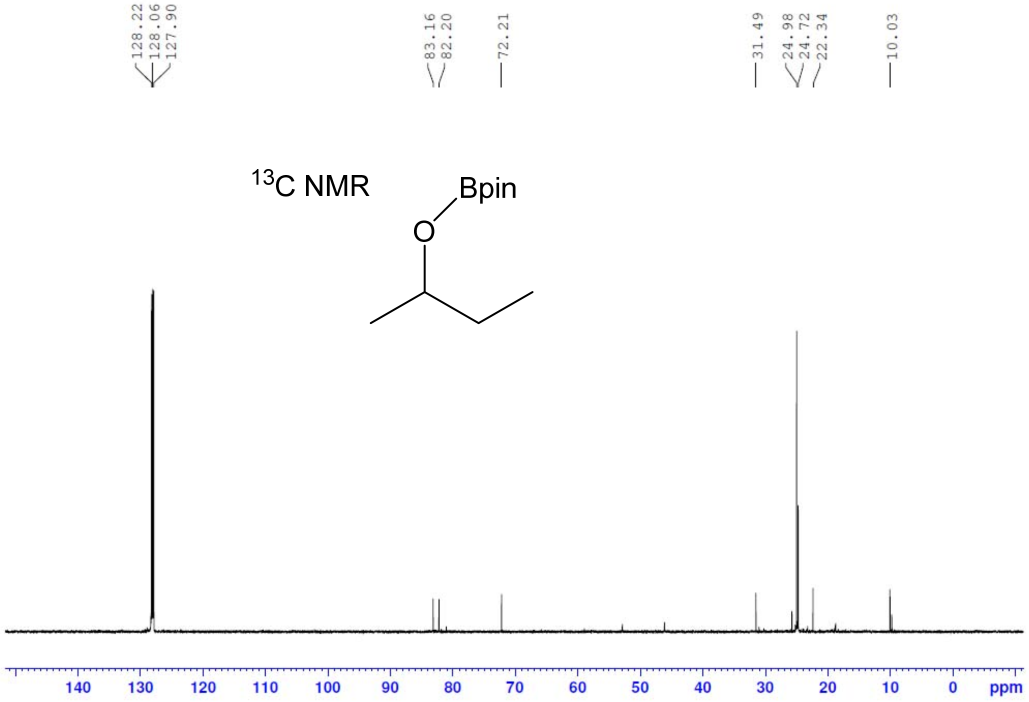
3.29
12.46
3.18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10.03
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80
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60
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0
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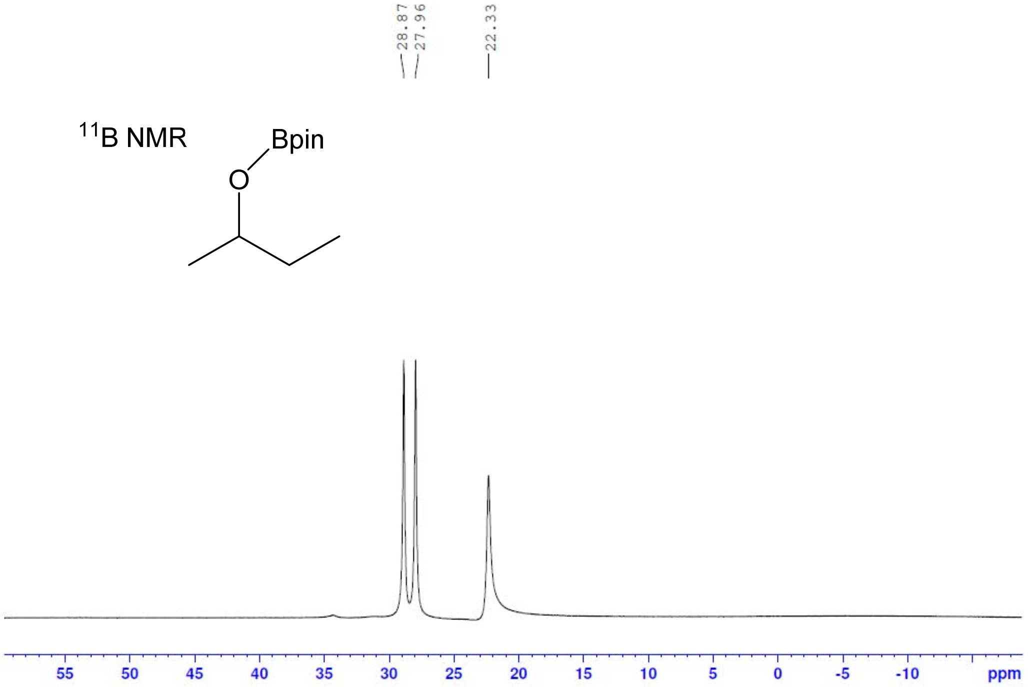
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40
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30
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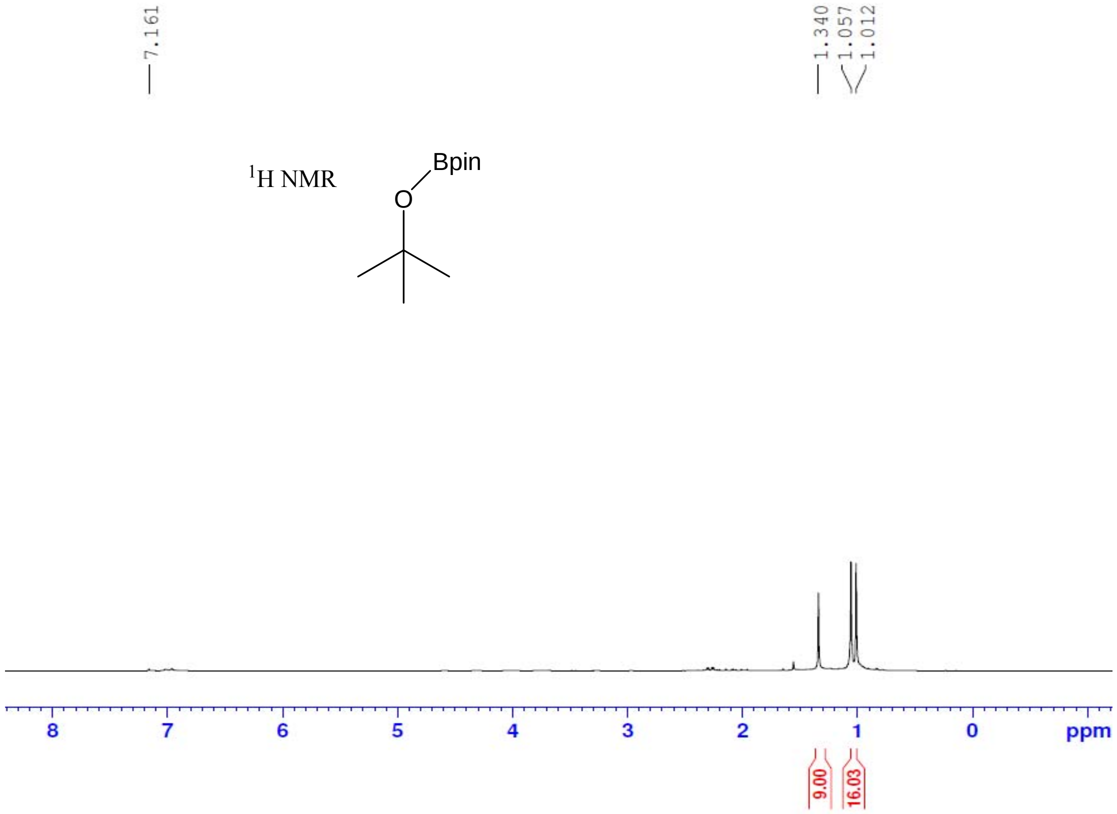
-5
-10
ppm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6
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2
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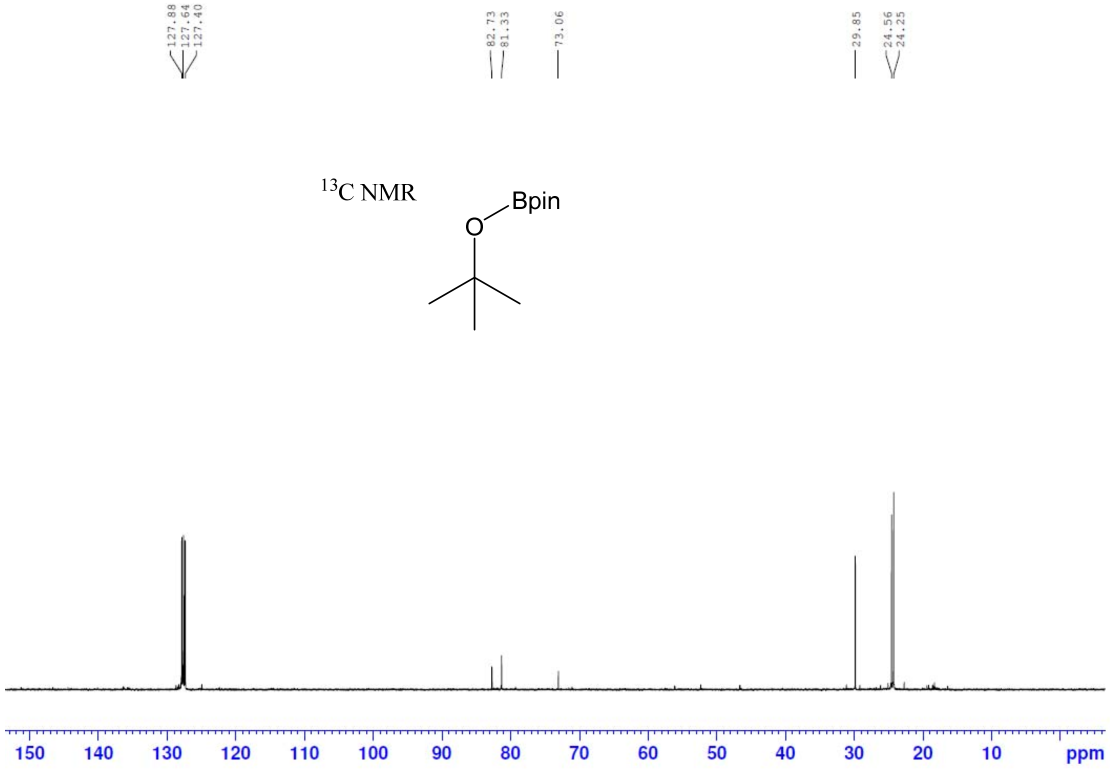
ppm
9.00
16.03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127.64
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24.56
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140
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100
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80
70
60
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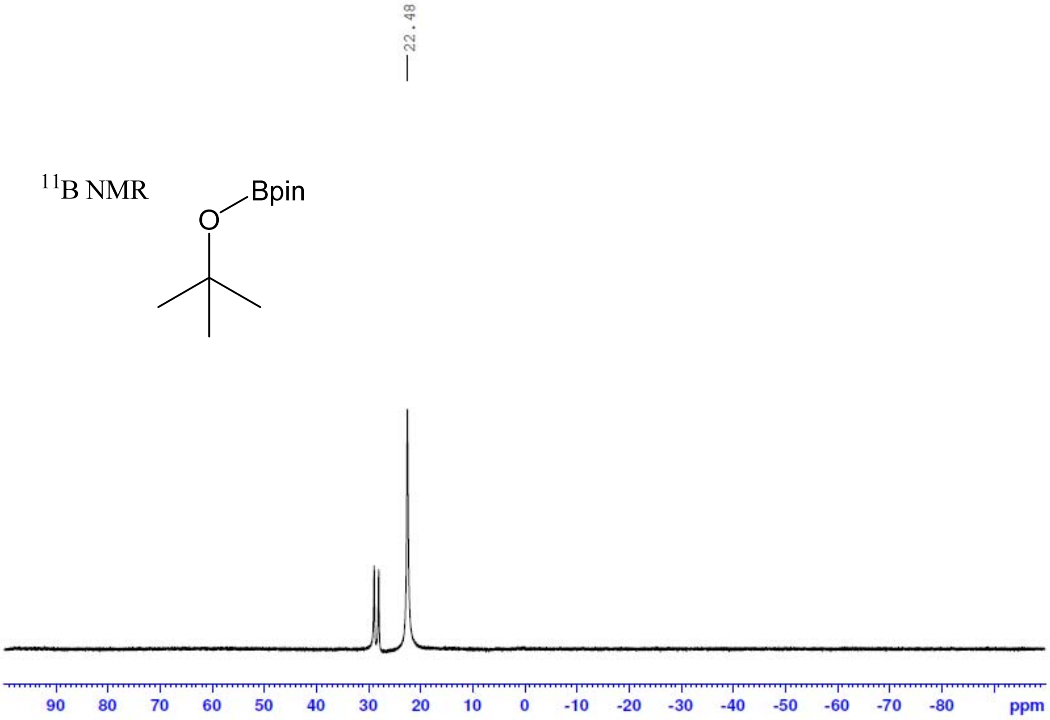
40
30
20
10
ppm



^{11}B NMR
Bpin
O
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90
80
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30
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10
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-40
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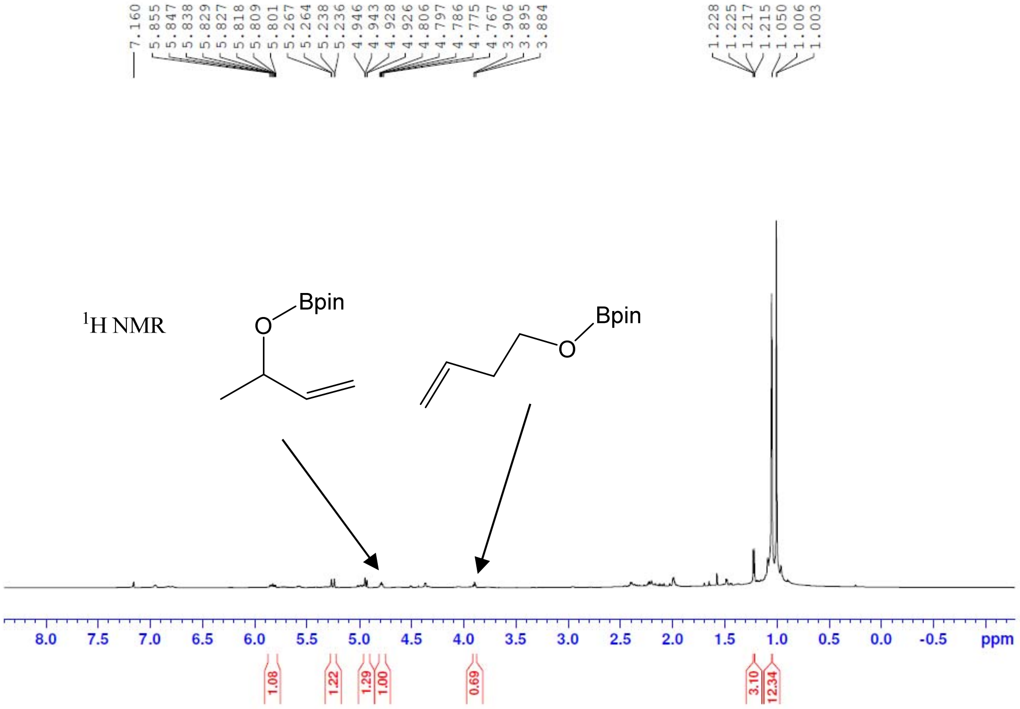
-60
-70
-80
ppm



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5.809
5.801
5.267
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5.238
5.236
4.946
4.943
4.928
4.926
4.806
4.797
4.786
4.775
4.767
3.906
3.895
3.884
1.228
1.225
1.217
1.215
1.050
1.006
1.003
^{1}H NMR
Bpin
O
Bpin
O
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
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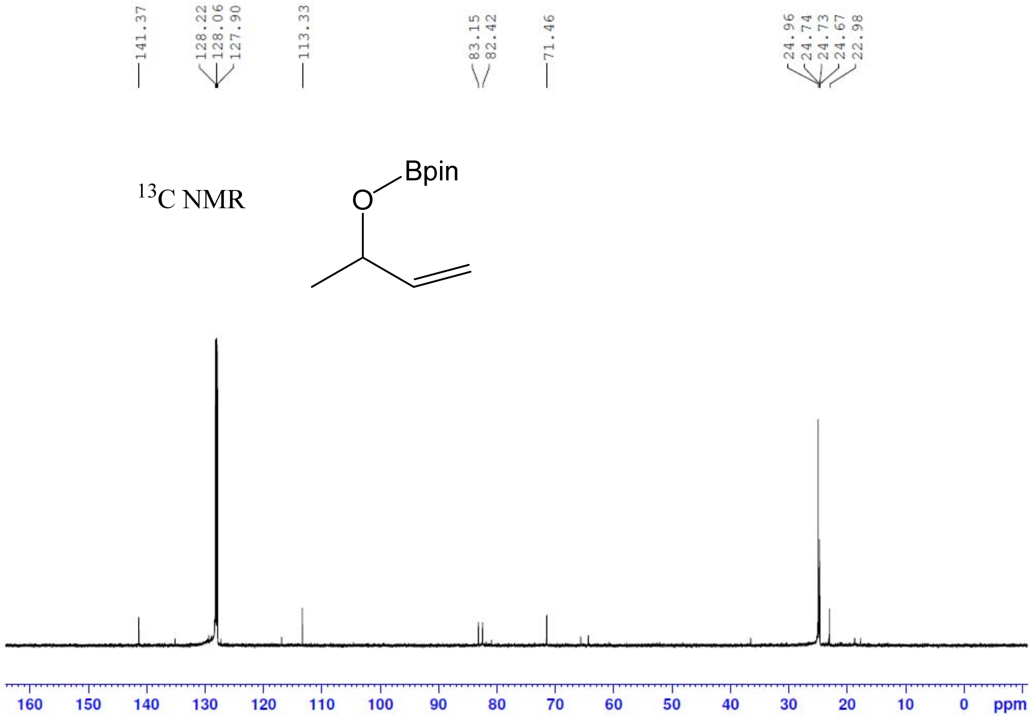
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71.46
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24.67
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Bpin
O
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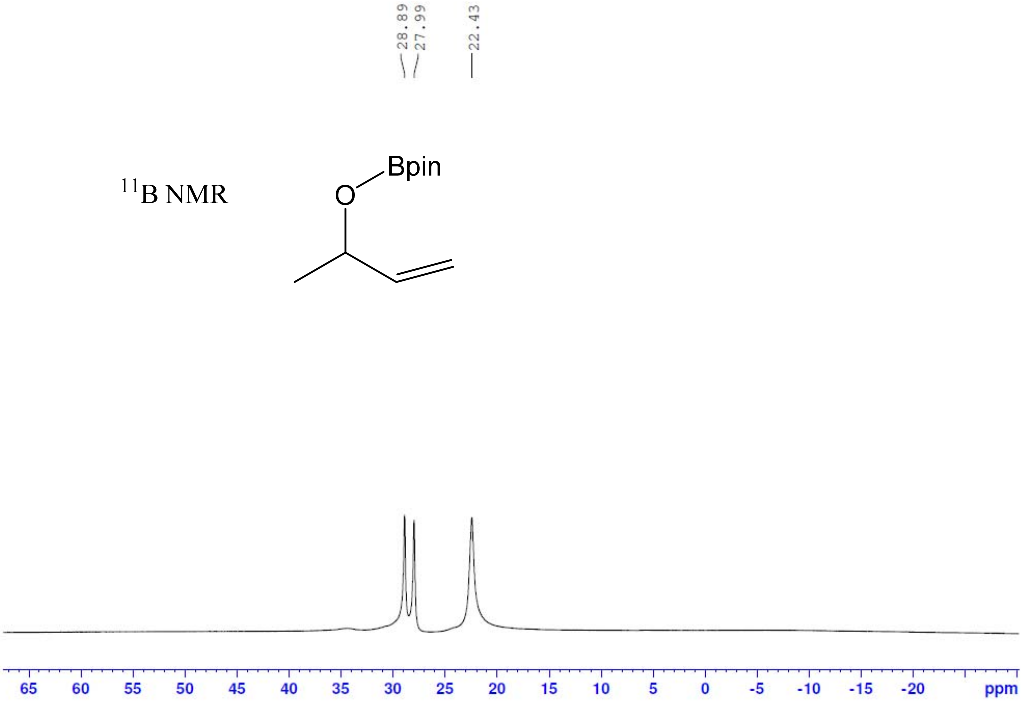
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O
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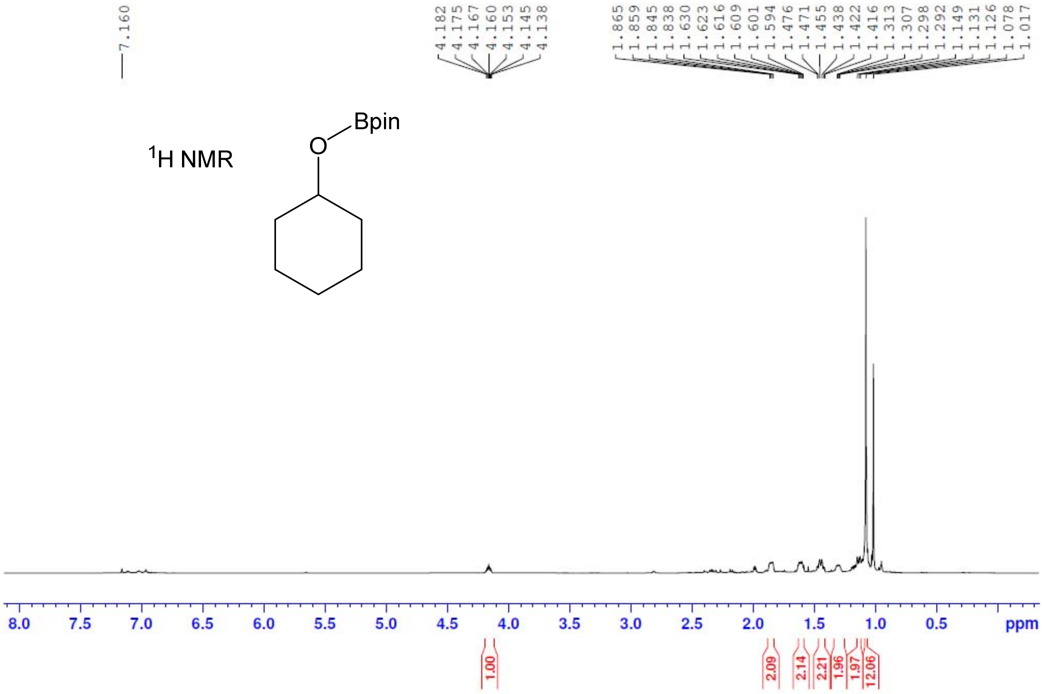
1H NMR
O
Bpin
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4.160
4.153
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1.859
1.845
1.838
1.630
1.623
1.616
1.609
1.601
1.594
1.476
1.471
1.455
1.438
1.422
1.416
1.313
1.307
1.298
1.292
1.149
1.131
1.126
1.078
1.017
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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1.0
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ppm
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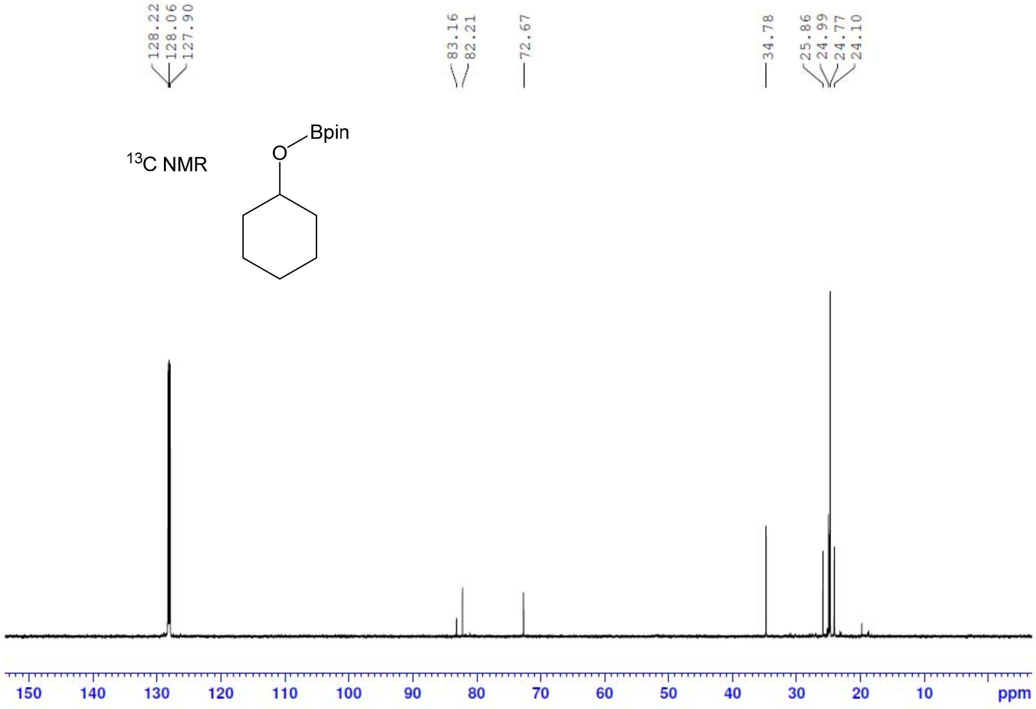
2.09
2.14
2.21
1.96
1.97
12.06


13C NMR
O
Bpin
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72.67
34.78
25.86
24.99
24.77
24.10
150
140
130
120
110
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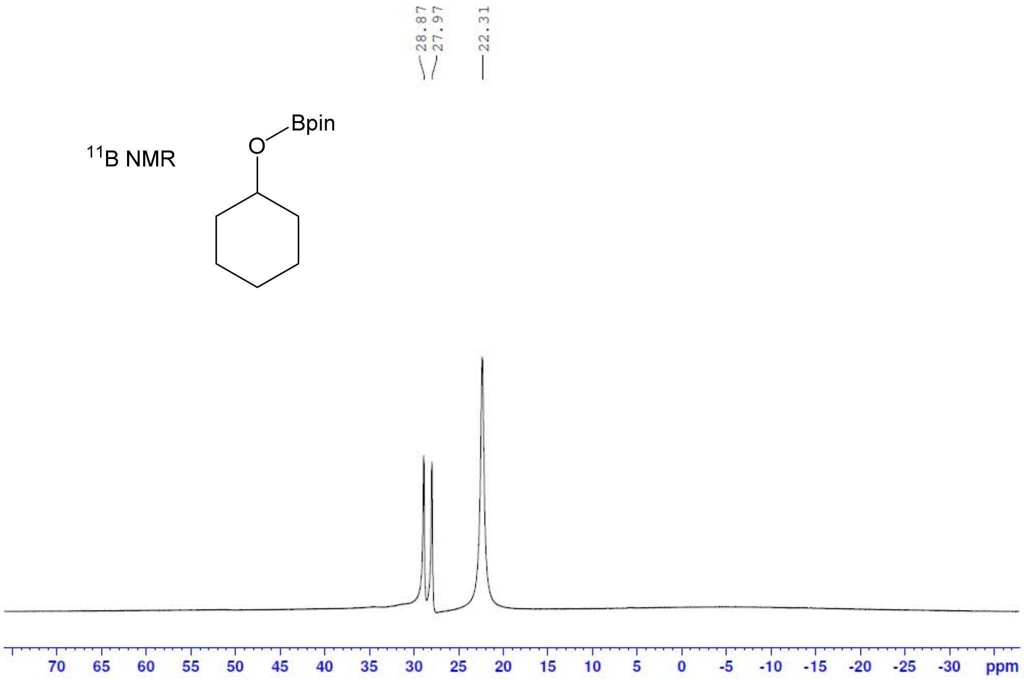
90
80
70
60
50
40
30
20
10
ppm



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27.97
22.31
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O
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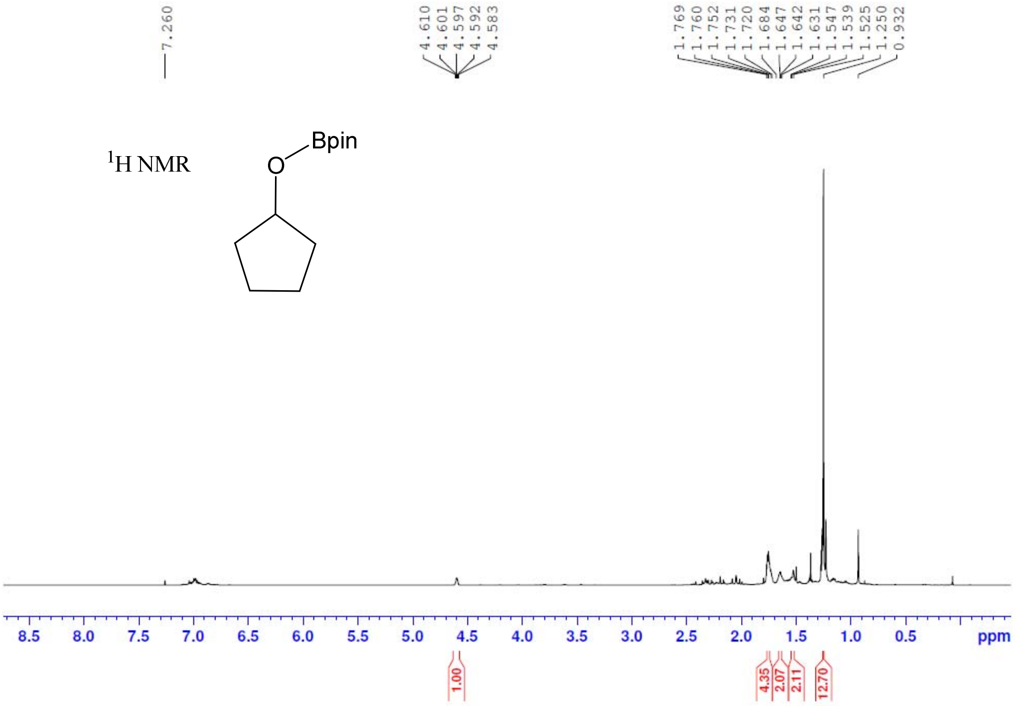

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4.610
4.601
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4.583
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1.760
1.752
1.731
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1.684
1.647
1.642
1.631
1.547
1.539
1.525
1.250
0.932
^{1}H NMR
O
Bpin
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
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4.35
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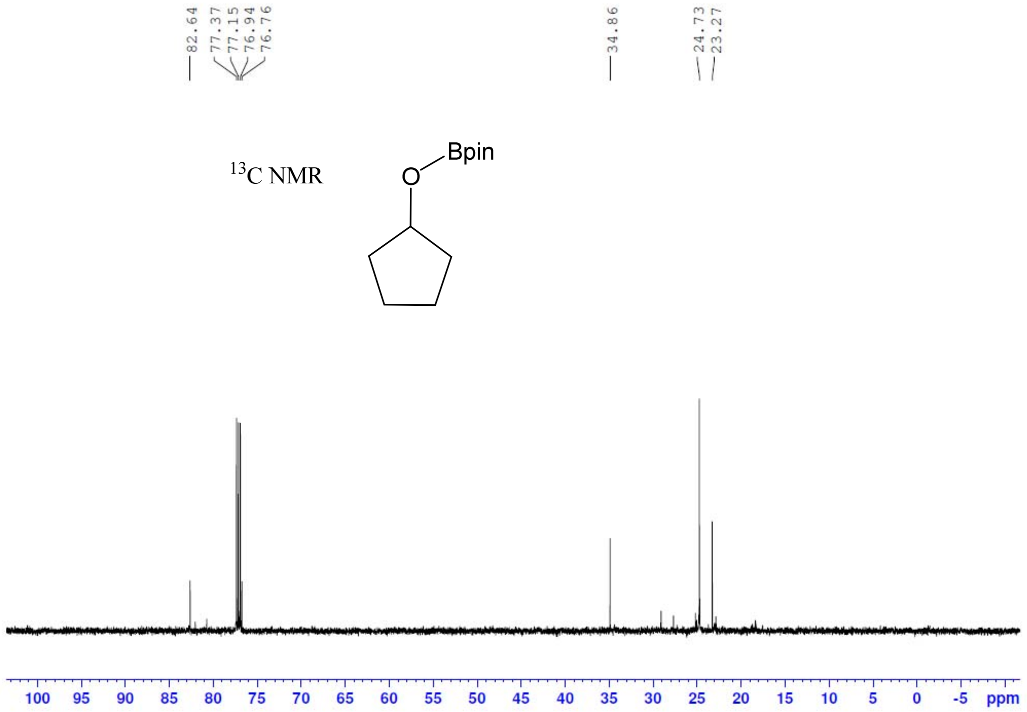
2.11
12.70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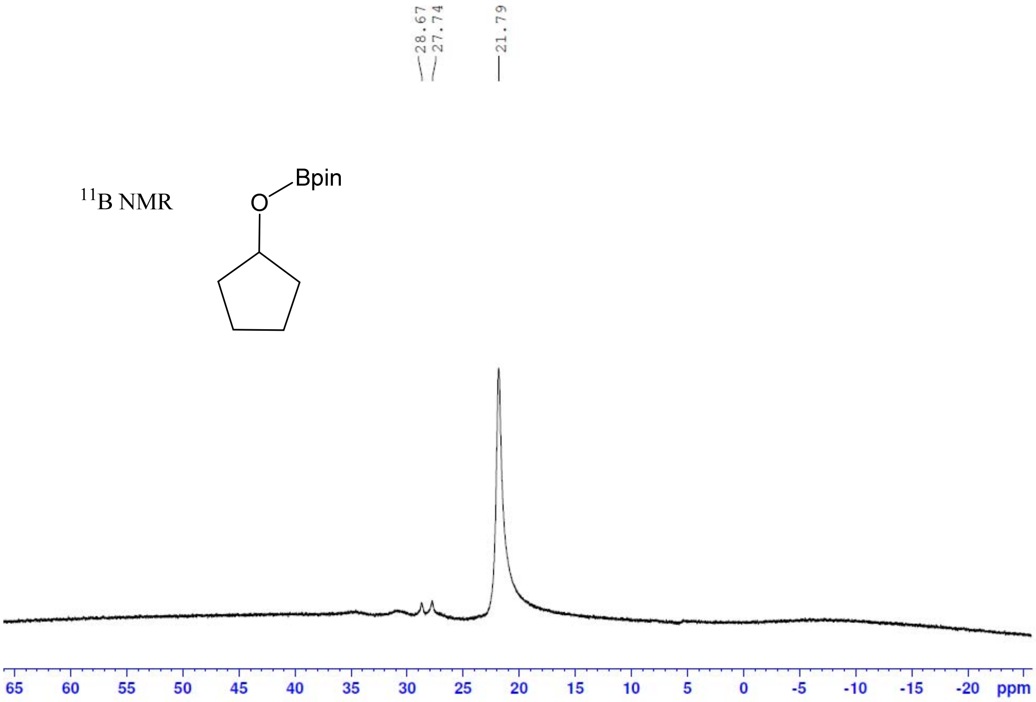
ppm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Bpin
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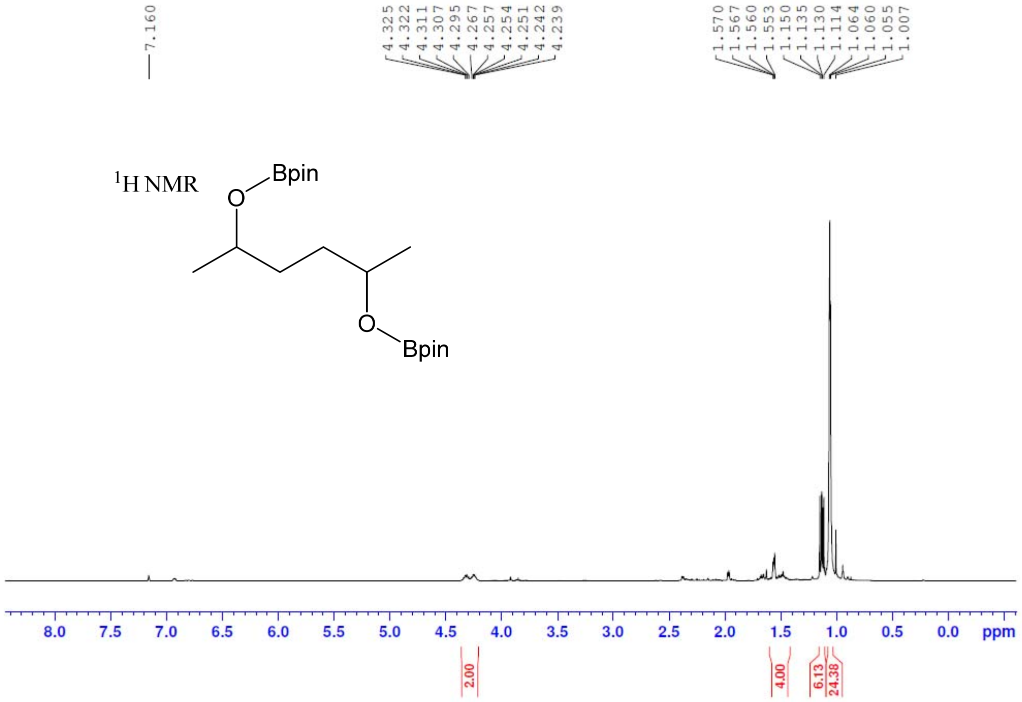
ppm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4.251
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4.239
1.570
1.567
1.560
1.553
1.150
1.135
1.130
1.114
1.064
1.060
1.055
1.007
1H NMR
O
Bpin
O
Bpin
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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ppm
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4.00
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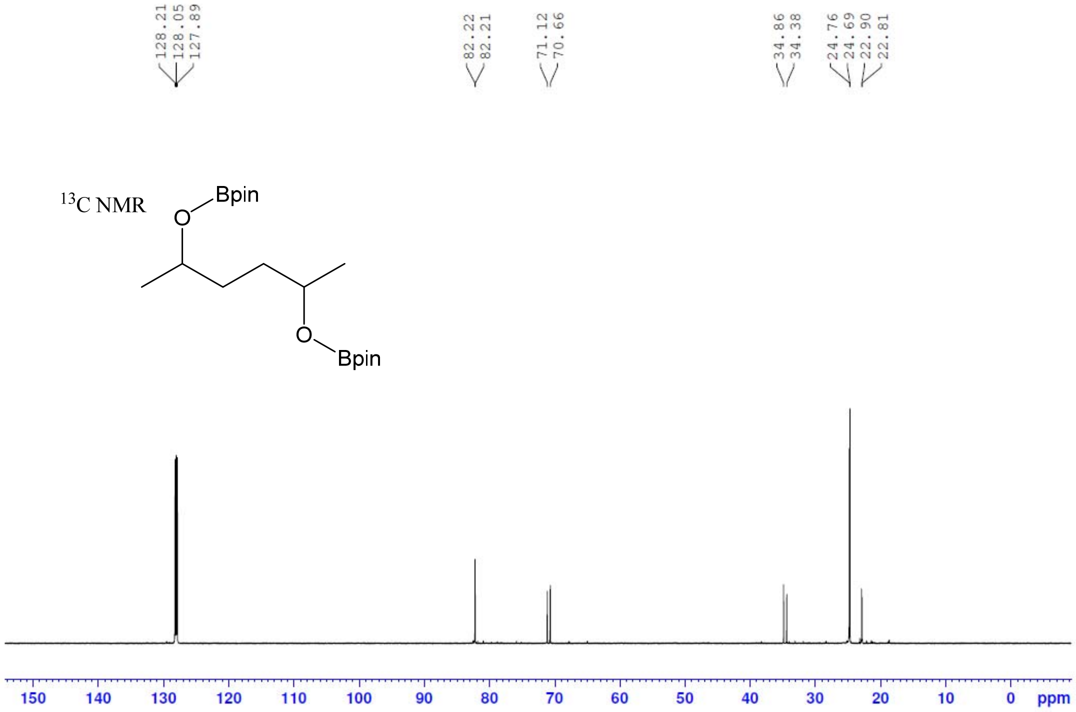
24.38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24.69
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22.81
13C NMR
O
Bpin
O
Bpin
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140
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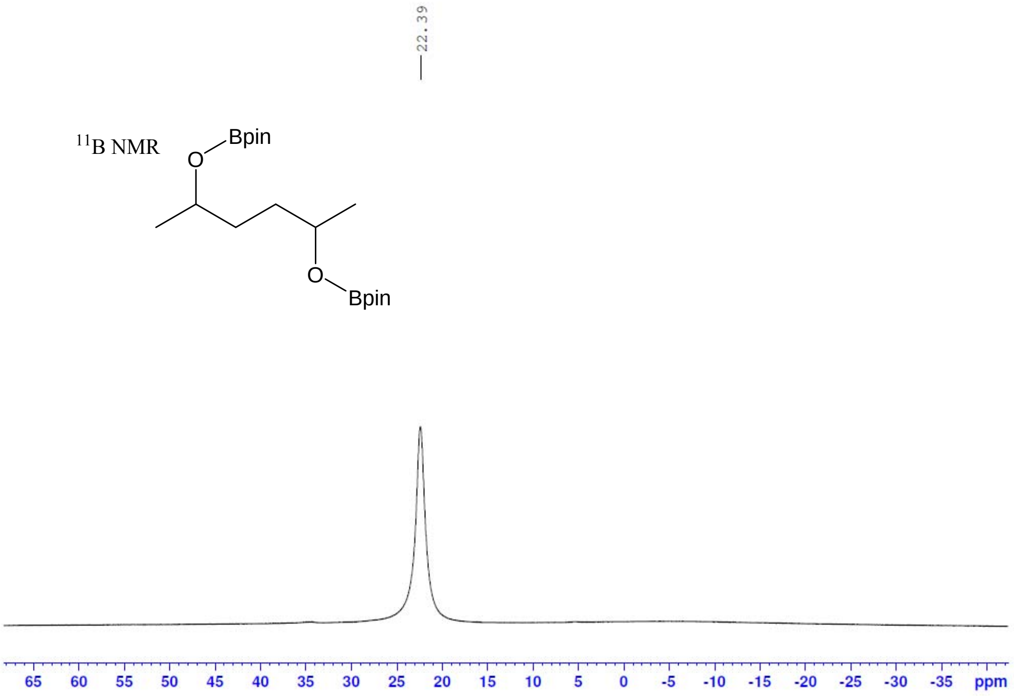
0
ppm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O
Bpin
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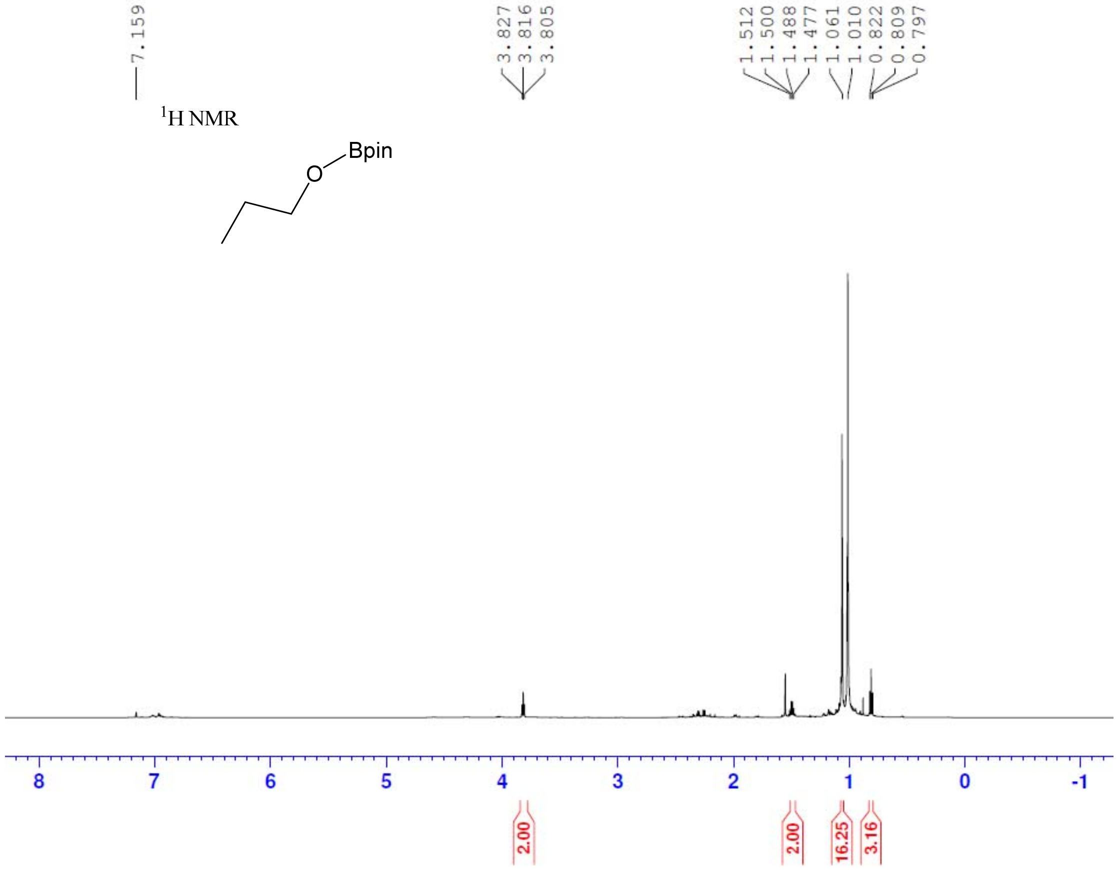
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1.488
1.477
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^{1}H NMR
O
Bpin
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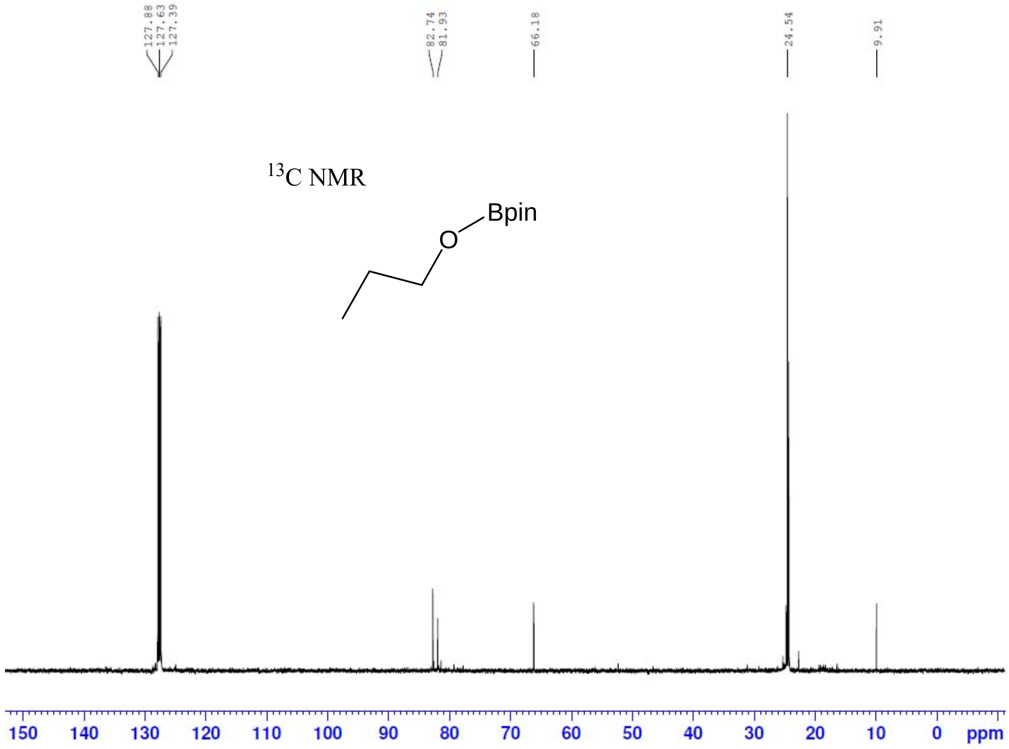
2.00
2.00
16.25
3.16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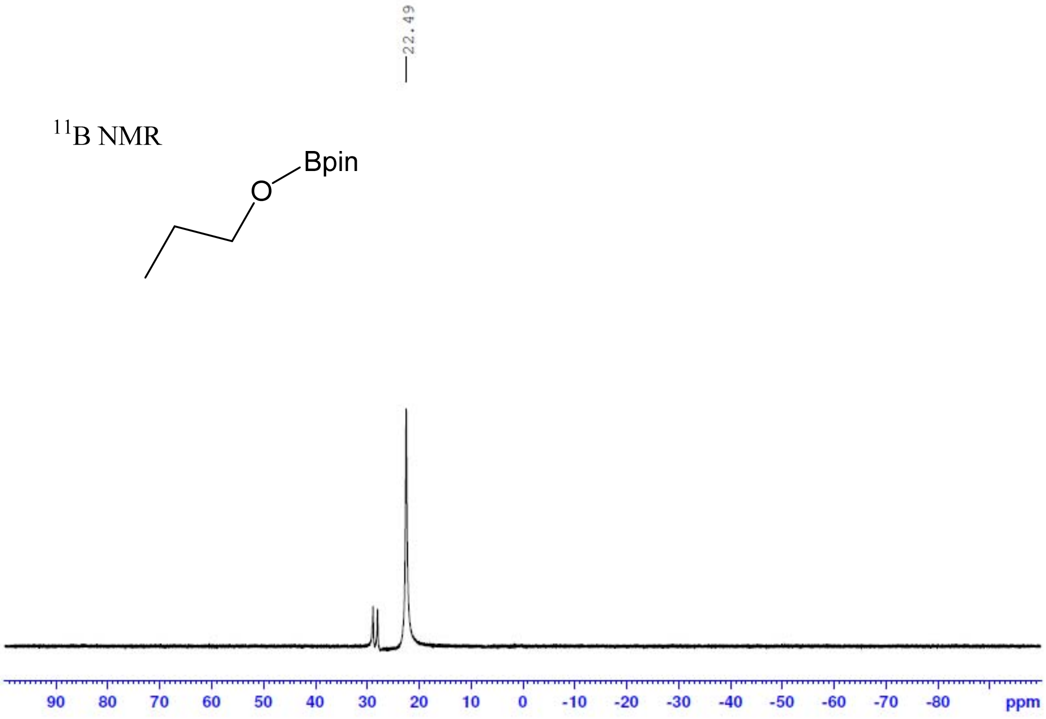
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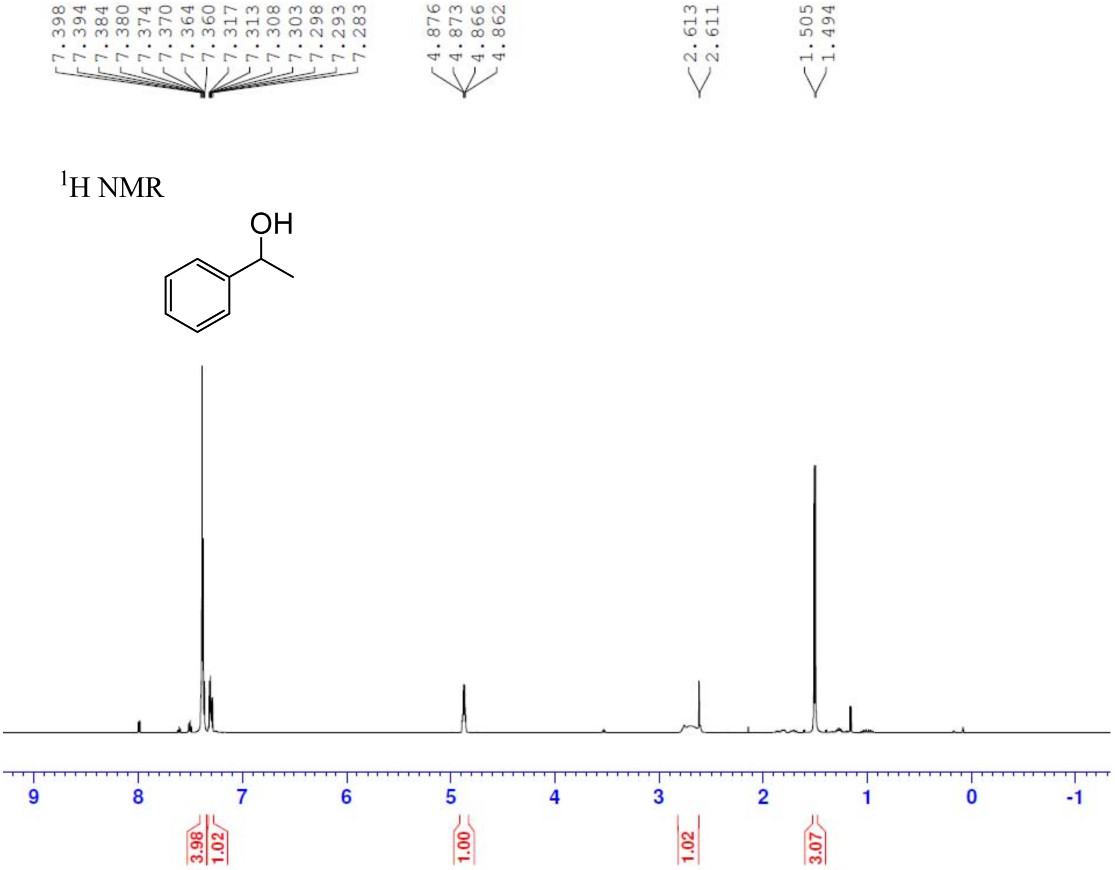
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7.298
7.293
7.283
4.876
4.873
4.866
4.862
2.613
2.611
1.505
1.494
^{1}H NMR
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6
5
4
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2
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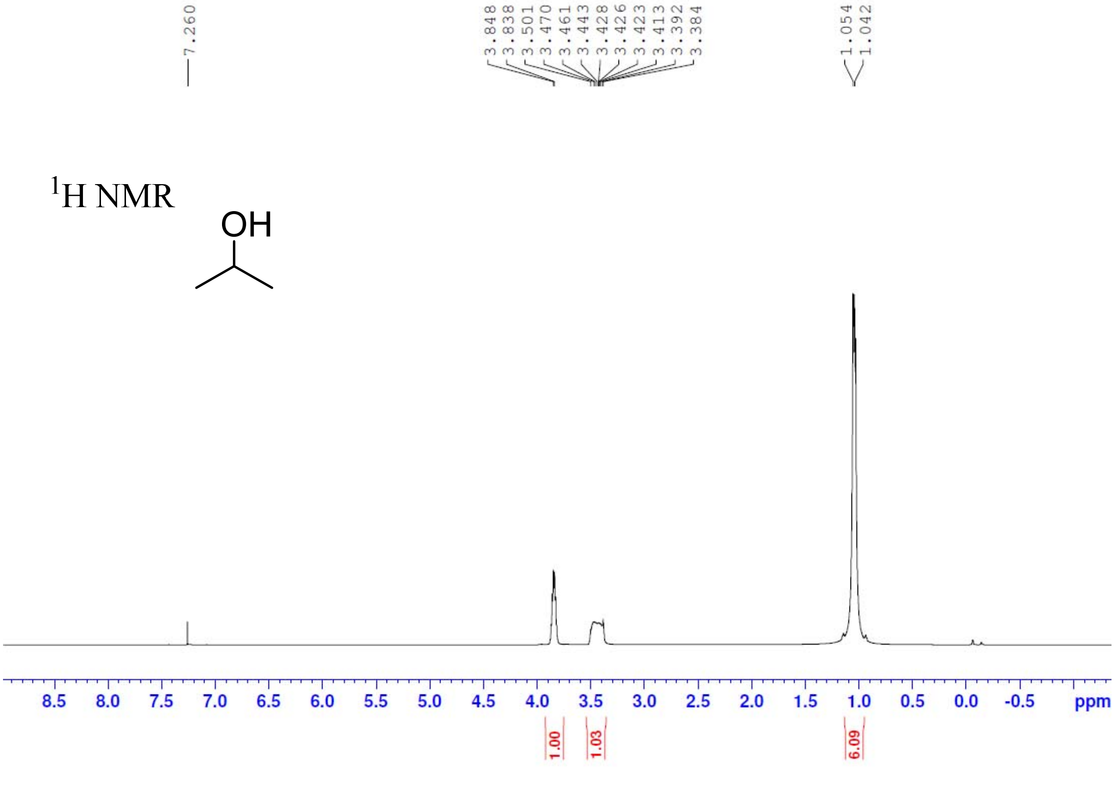
1.02
3.07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3.423
3.413
3.392
3.384
1.054
1.042
^{1}H NMR
OH
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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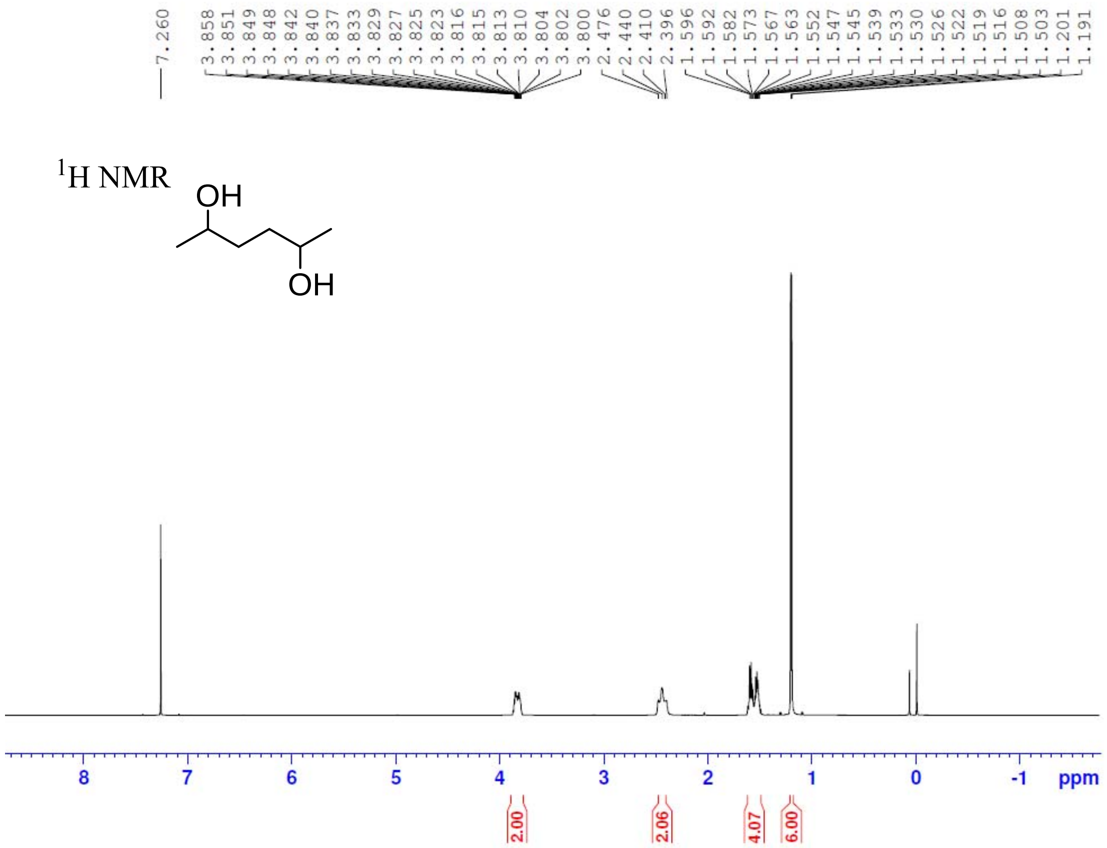
6.09



Computational Studies

The computational studies were completed using Gaussian 09.D01[2] program package. The geometries of the stationary points were optimized in gas at the B3LYP-D3[3]/def2-SVP[4] level. Single point energies of the stationary points in gas have further been calculated at B3LYP-D3/def2-TZVP[4] level.All reactant, product and intermediate have been identified as minimum (no imaginary frequency) or transition state (only one imaginary frequency) by performing analytical vibrational frequencies. thermal corrections to enthalpy and Gibbs free energy were calculated at 298.15K and 1atm. A continuum solvation model (SMD)[5] and its parameterized level M05-2X[6]/6-31G*[7] was used to calculate solvent effect in toluene. The difference between the Gibbs free energy in toluene and the Gibbs free energy in gas is the Gibbs free energy of dissolution[8].The Mayer bone order and Mulliken charge were calculated by Multiwfn program[9] at B3LYP-D3/def2-SVP.

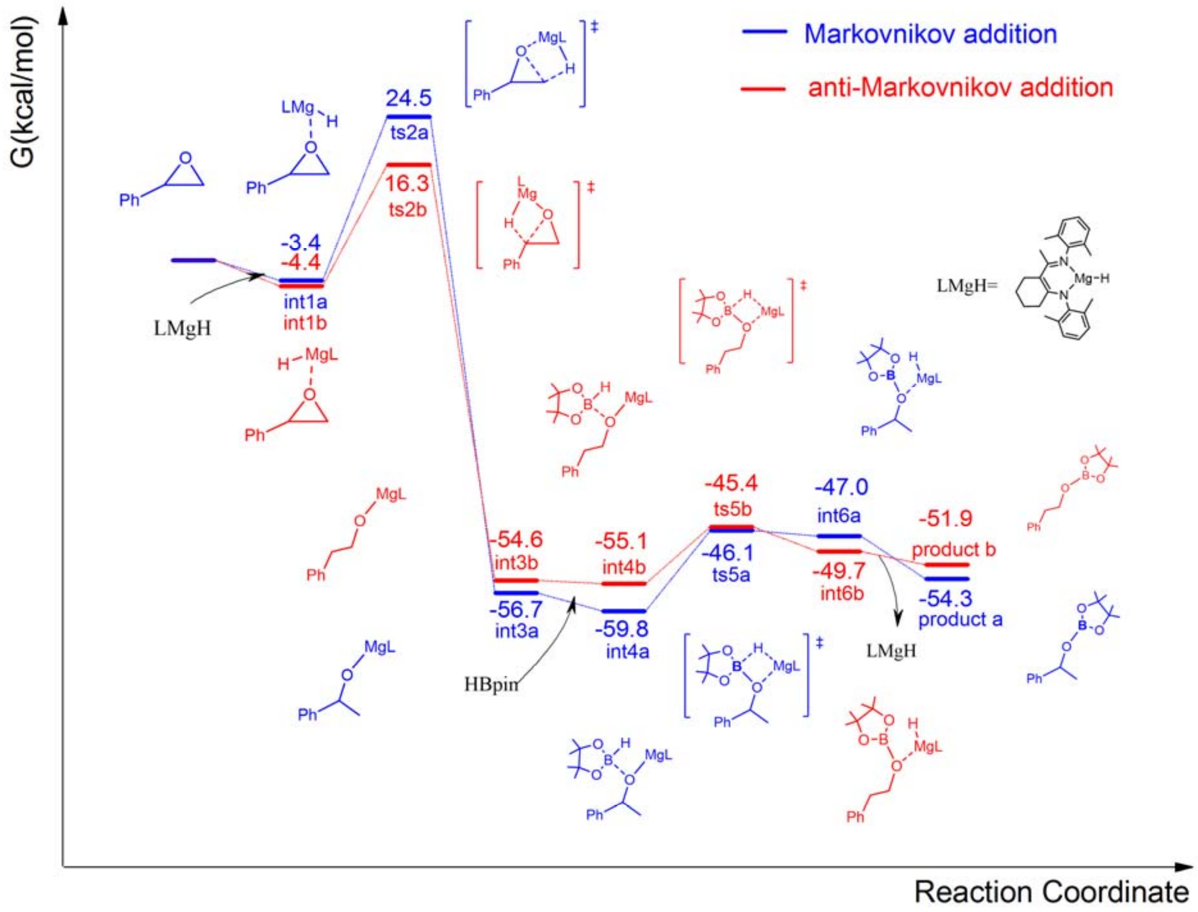


Figure S3 Calculated reaction pathway for hydroboration of styrene oxide

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