Supporting Information

Synthesis of Amines with Pendant Boronic Esters by Borrowing Hydrogen Catalysis

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Genaral Experimental Methods

All reactions requiring an anhydrous, inert atmosphere were carried out under an argon or nitrogen atmosphere using Dean-Stark, Schlenk line techniques or use of Radley's or Young's tap carousel tubes. All reaction reagents were purchased from commercial suppliers Aldrich-sigma, Fisher, Lancaster, Frontier and TCI. All solvents were distilled or obtained and stored in the presence of 3 Å molecular sieves prior to use.

TLC was carried out on plastic, aluminium or glass backed plates covered with neutral silica was used to monitor reactions where appropriate. These plates were visualised by 254nm UV light, followed by further visualisation using vanillin, $KMnO_4$ or ninhydin as required. Organic layers were usually dried with $MgSO_4$ and concentrated *in vacuo*. If necessary, high vacuum was used for further drying. For further purification, flash column chromatography was carried out using 60 Å silica gel purchased from Fisher Scientific.

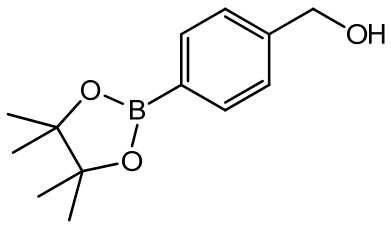
^{1}H NMR and ^{13}C NMR spectra were run in $CDCl_3$ or MeOD using a Bruker Avance 250 (250 MHz) or a Bruker Avance 300 (300 MHz). Chemical shifts are reported as parts per million (ppm) with reference to tetramethylsilane (TMS) unless otherwise stated. In ^{1}H NMR coupling constants (***J***) are recorded in Hz and signal multiplicities are reported as singlet (s), doublet (d), triplet (t). quartet (q), doublet to doublet (dd), doublet of triplets (dt), triplet of triplets (tt), pentet (p), unresolved multiplet (m), broad (br.) or apparent (app.).

For mass spectrometry data, a micrOTOF electrospray time-of-flight (ESI-TOF) mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) was used; this was coupled to an Agilent 1200 LC system (Agilent Technologies, Waldbronn, Germany). 10 µL of sample was injected into a 30:70 flow of water:acetonitrile at 0.3 mL/min

to the mass spectrometer. For each acquisition 10 µL of a calibrant of 5mM sodium formate was injected after the sample. The observed mass and isotope pattern matched the corresponding theoretical values as calculated from the expected elemental formula.

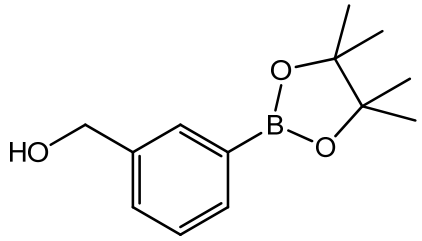
Synthesis and Characterization of Substrates

(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanol[1]



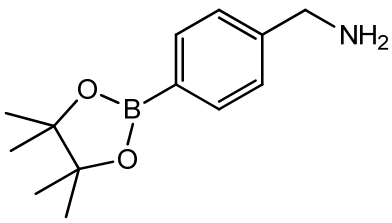
(4-(Hydroxymethyl)phenyl)boronic acid (3.81 g, 25 mmol) and pinacol (3.54 g, 30 mmol) were mixed in toluene (300 mL) in a round-bottomed flask. A Dean stark head was fitted and the reaction was heated under reflux condition for 2 hours. The mixture was allowed to cool to room temperature, and then washed with water (3 x 150 mL). The organic layer was condensed under reduced pressure and DCM (100mL) was added. This was washed with water (3 x 150 mL), dried over $MgSO_4$ and filtered. The solvents were again removed under reduced pressure to yield compound **9** as a white solid (4.84 g, 82.7%); m.p.: 62-64 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.84 (2H, d, *J* = 8.0 Hz, Ar**H**), 7.40 (2H, d, *J* = 7.7 Hz, Ar**H**), 4.75 (2H, s, Ph**C**$\mathbf{H}_2$OH), 1.37 (12H, s, (C$\mathbf{H}_3$)$_2$CC(C$\mathbf{H}_3$)$_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ 144.1, 135.1, 126.1, 83.8, 65.2, 24.8; ESI-MA: Calculated for $C_{13}H_{19}BO_3$ $[M+H]^+$:234.1336. Found: 234.1324.

(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanol



(3-(Hydroxymethyl)phenyl)boronic acid (3.04 g, 20 mmol) and pinacol (2.83 g, 24 mmol) were mixed in toluene (150 mL). A Dean-Stark head was fitted and the reaction was heated under reflux condition for 2 hours. The mixture was allowed to cool to room temperature, and then washed with water (3 x 100 mL). The organic layer was condensed under reduced pressure and DCM (100 mL) was added. This was washed with water (3 x 100 mL), Dried over $MgSO_4$ and filtered. The solvents were again removed under reduced pressure to yield compound **9** as a white solid (2.76 g, 88.7%); m.p.: 62-64°C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.82 (1H, s, Ar**H**), 7.77 (1H, d, *J* = 7.2 Hz, Ar**H**), 7.52 (1H, d, *J* = 6.1 Hz, Ar**H**), 7.41 (1H, t, *J* = 7.4 Hz, Ar**H**), 4.73 (2H, s, PhC**H**$_2$OH), 1.38 (12H, s, (C**H**$_3$)$_2$CC(C**H**$_3$)$_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ 140.1, 134.1, 133.3, 130.1, 128.1, 83.9, 65.3, 24.8; ESI-MA: Calculated for $C_{13}H_{19}BO_3$ $[M+H]^+$:234.1321. Found: 234.1324.

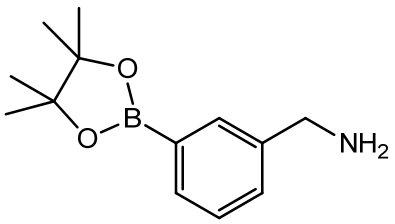
(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanamine



(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanamine (0.9 g, 6 mmol) and pinacol (0.83 g, 7 mmol) were mixed in toluene (60 mL). A Dean stark head was

fitted and the reaction was heated under reflux condition for 2 hours. The mixture was allowed to cool to room temperature, and then filtered to get a white crystal (1.14 g, 81.4%); m.p.: 65-68 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.86-7.83 (2H, d, *J* = 7.7 Hz, Ar**H**), 7.46 (2H, d, *J* = 7.8 Hz, Ar**H**), 4.00 (2H, s, PhC**H**$_2$OH), 1.33 (12H, s, (C**H**$_3$)$_2$CC(C**H**$_3$)$_2$); ^{13}C NMR (75.5 MHz, CD_3OD, 25 °C): δ 137.8, 136.8, 129.5, 85.7, 44.6, 25.6; ESI-MA: Calculated for $C_{13}H_{20}BNO_2$ $[M+H]^+$:233.1587. Found: 233.1591.

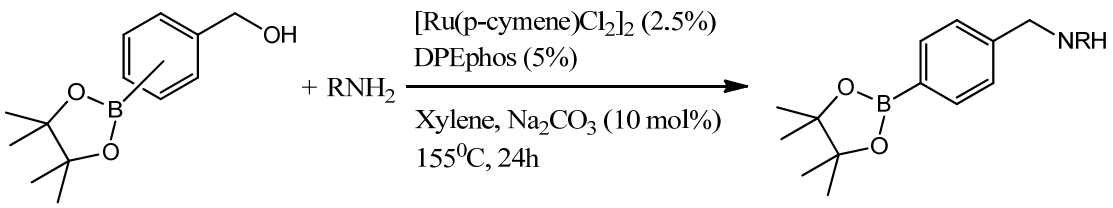
(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanamine

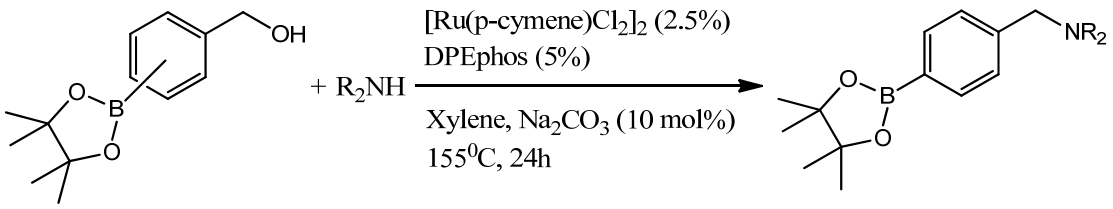


(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanamine (0.91 g, 6 mmol) and pinacol (0.83 g, 7 mmol) were mixed in toluene (60 mL). A Dean stark head was fitted and the reaction was heated under reflux condition for 2 hours. The mixture was allowed to cool to room temperature, and then filtered to get a white crystal (1.33 g, 95.6%); m.p.: 64-67 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.80 (1H, d, *J* = 8.1 Hz, Ar**H**), 7.78 (1H, s, Ar**H**), 7.69 (1H, d, *J* = 7.8 Hz, Ar**H**), 7.40 (1H, t, *J* = 7.5 Hz, Ar**H**), 4.10 (2H, s, PhC**H**$_2$OH), 1.34 (12H, s, (C**H**$_3$)$_2$CC(C**H**$_3$)$_2$); ^{13}C NMR (75.5 MHz, CD_3OD, 25 °C): δ 136.8, 134.2, 133.3, 130.1, 85.7, 44.7, 25.6; ESI-MA: Calculated for $C_{13}H_{20}BNO_2$ $[M+H]^+$:233.1587. Found: 233.1589.

Synthesis and Characterization of Products

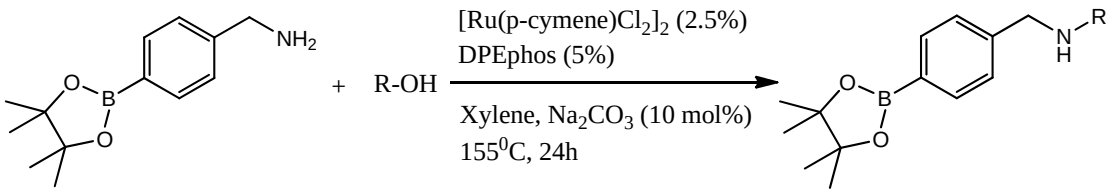
General Procedure I for the Ruthenium-catalysed N-Alkylation of amine with boronic ester alcohol by borrowing hydrogen[2]

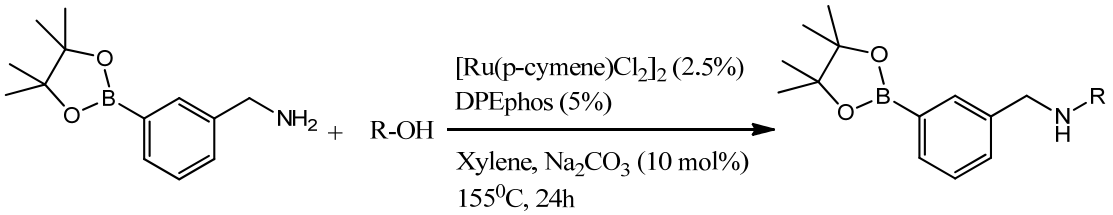




To an oven-dried, nitrogen-purged Radley's carousel tube containing [Ru(*p*-cymene)Cl_2]$_2$ (15.3 mg, 0.025 mmol), DPEphos (53.8 mg, 0.05 mmol), Na_2CO_3 (10.6 mg, 0.1 mmol), xylene (2 mL), amine (1 mmol) and boronic ester alcohol (1 mmol). The reaction mixture was allowed to stir under a nitrogen atmosphere at room temperature and then increased the temperature to 155 ^{0}C to reflux for 24 hours. The resulting crude compounds were evaporated *in vacuo* and conversion was determined by analysis of the peak integral ratios characteristic of boronic ester alcohol and amine products in the proton NMR spectrum if the crude reaction mixture. All products were purified by recrystallised using DCM:Hexane (1:20).

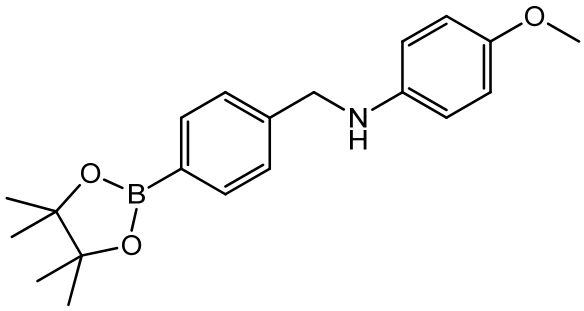
General Procedure II for the Ruthenium-catalysed N-Alkylation of boronic ester amine with alcohol by borrowing hydrogen[2]





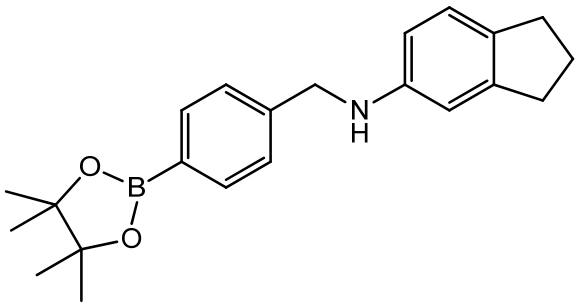
To an oven-dried, nitrogen-purged Radley's carousel tube containing [Ru(*p*-cymene)Cl_2]$_2$ (15.3 mg,0.025 mmol), DPEphos (53.8 mg, 0.05 mmol), Na_2CO_3 (10.6 mg, 0.1 mmol), xylene (2 mL), boronic ester amine (1 mmol) and alcohol (1 mmol). The reaction mixture was allowed to stir under a nitrogen atmosphere at room temperature and then increased the temperature to 155 ^{0}C to reflux for 24 hours. The resulting crude compounds were evaporated *in vacuo* and conversion was determined by analysis of the peak integral ratios characteristic of boronic ester alcohol and amine products in the proton NMR spectrum if the crude reaction mixture. All products were purified by recrystallised using DCM:Hexane (1:20).

N-(4-Methoxybenzyl)-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanamine (Table 2, entry 1)



Following **general procedure I**, used boronic ester alcohol (0.2345 g, 1 mmol) and p-Anisidine (0.1243 g, 1 mmol) to give the title compound as a purple oil (0.25 g, 72%), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.71 (2H, d, *J* = 8.1 Hz, Ar**H**), 7.30 (2H, d, *J* = 8.1 Hz, Ar**H**), 6.69 (2H, d, *J* = 9.0 Hz, Ar**H**), 6.52 (2H, d, *J* = 9.0 Hz, Ar**H**), 4.23 (2H, s, PhC**H**$_2$NH), 3.66 (3H, s, OC**H**$_3$), 1.27 (12H, s, (C**H**$_3$)$_2$CC(C**H**$_3$)$_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ 152.2, 142.9, 142.2, 135.1, 127.7, 126.8, 114.9, 114.4, 83.7, 55.8, 49.3, 24.8; ESI-MA: Calculated for $C_{20}H_{26}BNO_3$ $[M+H]^+$: 340.2082. Found: 340.2083.

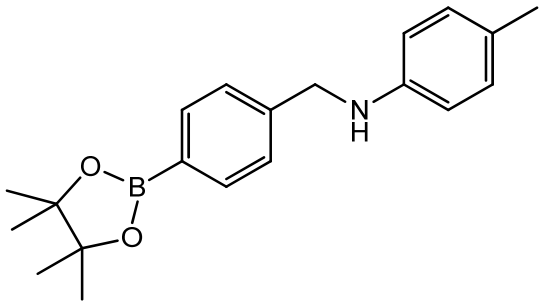
N-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)-2,3-dihydro-1H-inden-5-amine (Table 2, entry 2)



Following **general procedure I**, used boronic ester alcohol (0.2362 g, 1 mmol) and 5-Aminoindan (0.1332 g, 1 mmol) to give the title compound as a black oil (0.25 g, 72%), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.82 (1H, s, Ar**H**), 7.73 (2H, d, *J* = 8.0 Hz, Ar**H**), 7.29 (2H, d, *J* = 8.1 Hz, Ar**H**), 6.93 (1H, d, *J* = 8.2 Hz, Ar**H**), 6.42 (1H, d, *J* = 7.9 Hz,

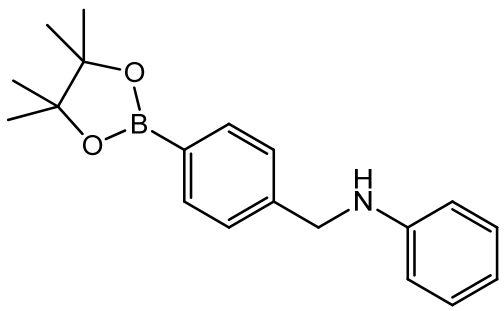
Ar**H**), 4.64 (2H, s, PhC**H**$_2$NH), 2.73 (4H, dd, *J* = 7.0 Hz, Ph(C**H**$_2$)$_2$CH$_2$), 1.98 (2H, dp, *J* = 7.3 Hz, Ph(CH$_2$)$_2$C**H**$_2$), 1.27 (12H, s, (C**H**$_3$)$_2$CC(C**H**$_3$)$_2$); ^{13}C NMR (75.5 MHz, CDCl$_3$, 25 °C): δ 135.6, 127.8, 126.1, 124.7, 113.3, 111.5, 83.8, 65.2, 33.0, 31.9, 25.7, 24.8; ESI-MA: Calculated for $C_{22}H_{28}BNO_2$ $[M+H]^+$: 349.2213. Found: 349.2215.

4-Methyl-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)aniline (Table 2, entry 3)



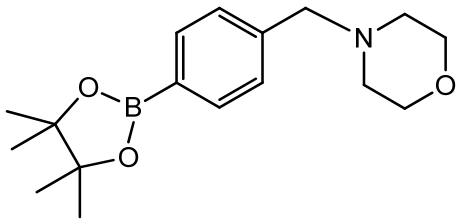
Following **general procedure I**, used boronic ester alcohol (0.2348 g, 1 mmol) and p-Toluidine (0.1073 g, 1 mmol) to give the title compound as a brown oil (0.23 g, 70%), ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ 7.79 (2H, d, *J* = 8.1 Hz, Ar**H**), 7.38 (1H, d, *J* = 8.2 Hz, Ar**H**), 6.97 (2H, d, *J* = 8.0 Hz, Ar**H**), 6.55 (2H, d, *J* = 8.4 Hz, Ar**H**), 4.32 (2H, s, PhC**H**$_2$NH), 2.23 (3H, s, PhC**H**$_3$), 1.35 (12H, s, (C**H**$_3$)$_2$CC(C**H**$_3$)$_2$); ^{13}C NMR (75.5 MHz, CDCl$_3$, 25 °C): δ 149.3, 145.8, 142.9, 138.6, 136.0, 135.1, 129.7, 127.8, 126.7, 120.8, 113.1, 83.7, 48.7, 24.9, 20.4; ESI-MA: Calculated for $C_{20}H_{26}BNO_2$ $[M+H]^+$: 323.2102. Found: 323.2097.

N-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)aniline (Table 2, entry 4)



Following **general procedure I**, used boronic ester alcohol (0.2366 g, 1 mmol) and aniline (0.129 mL, 1 mmol) to give the title compound as a dark brown oil (0.16 g, 52%), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.81 (2H, d, *J* = 8.1 Hz, Ar**H**), 7.39 (2H, d, *J* = 8.1 Hz, Ar**H**), 7.17 (3H, t, *J* = 8.0 Hz, Ar**H**), 6.63 (2H, d, *J* = 7.6 Hz, Ar**H**), 4.35 (2H, s, PhC**H**$_2$NH), 1.35 (12H, s, (C**H**$_3$)$_2$CC(C**H**$_3$)$_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ 148.1, 142.7, 135.1, 129.2, 126.7, 126.1, 120.2, 118.6, 117.6, 115.2, 112.9, 83.8, 48.4, 24.9; ESI-MA: Calculated for $C_{19}H_{24}BNO_2$ $[M+H]^+$: 309.2004. Found: 309.2000.

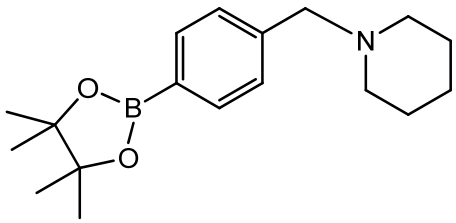
4-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)morpholine (Table 2, entry 6)



Following **general procedure I**, used boronic ester alcohol (0.2347 g, 1 mmol) and Morpholine (0.09 mL, 1 mmol) to give the title compound as a yellow solid (0.25 g, 84 %), m.p.: 87-89 °C, ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.70 (2H, d, *J* = 8.0 Hz, Ar**H**), 7.28 (2H, d, *J* = 8.0 Hz, Ar**H**), 3.65-3.62 (4H, t, N(CH$_2$C**H**$_2$)$_2$O), 3.45 (2H, s, PhC**H**$_2$N), 2.38-2.35 (4H, t, N(C**H**$_2$CH$_2$)$_2$O), 1.27 (12H, s, (C**H**$_3$)$_2$CC(C**H**$_3$)$_2$); ^{13}C NMR (75.5 MHz,

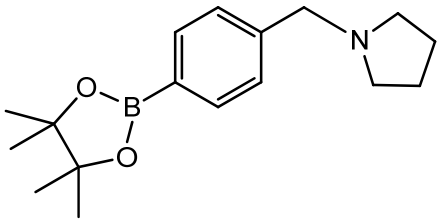
$CDCl_3$, 25 °C): δ 134.8, 128.6, 83.7, 66.9, 63.4, 53.6, 24.8; ESI-MA: Calculated for $C_{17}H_{26}BNO_3$ $[M+H]^+$: 304.2126. Found: 304.2083.

1-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)piperidine (Table 2, entry 7)



Following **general procedure I**, used boronic ester alcohol (0.2366 g, 1 mmol) and piperidine (0.098 mL, 1 mmol) to give the title compound as a dark red solid (0.24 g, 80%), m.p.: 97-99 °C, ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.69 (2H, d, *J* = 8.0 Hz, Ar**H**), 7.26 (2H, d, *J* = 8.1 Hz, Ar**H**), 3.42 (2H, s, PhC**H**$_2$N), 2.34-2.23 (4H, m, N(C**H**$_2$CH$_2$)$_2$CH$_2$), 1.48 (4H, dd, *J* = 10.5, 5.5 Hz, N(CH$_2$C**H**$_2$)$_2$CH$_2$), 1.36-1.27 (2H, m, N(CH$_2$CH$_2$)$_2$C**H**$_2$), 1.26 (12H, s, (C**H**$_3$)$_2$CC(C**H**$_3$)$_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ 134.6, 128.6, 83.6, 63.9, 54.5, 25.9, 24.8, 24.3; ESI-MA: Calculated for $C_{18}H_{28}BNO_2$ $[M+H]^+$: 301.2349. Found: 301.2376.

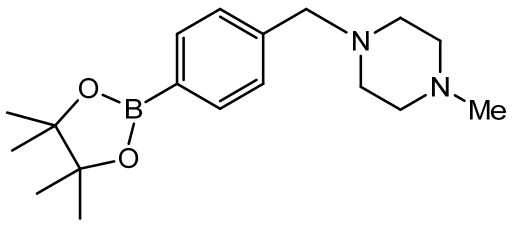
1-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)pyrrolidine (Table 2, entry 8)



Following **general procedure I**, used boronic ester alcohol (0.2345 g, 1 mmol) and

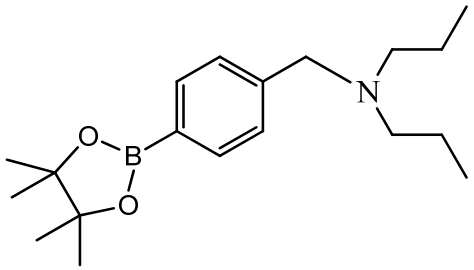
Pyrrolidine (0.083 mL, 1 mmol) to give the title compound as a dark brown oil (0.22 g, 75%), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.69 (2H, d, *J* = 8.0 Hz, Ar**H**), 7.27 (2H, d, *J* = 8.0 Hz, Ar**H**), 3.56 (2H, s, PhC**H**$_2$N), 2.45-2.40 (4H, m, N(C**H**$_2$CH$_2$)$_2$), 1.73-1.68 (4H, m, N(CH$_2$C**H**$_2$)$_2$), 1.26 (12H, s, (C**H**$_3$)$_2$CC(C**H**$_3$)$_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ 134.7 128.2, 83.7, 60.7, 54.1, 24.8, 23.4; ESI-MA: Calculated for $C_{17}H_{26}BNO_2$ $[M+H]^+$:287.2181. Found: 287.2185.

1-Methyl-4-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)piperazine (Table 2, entry 9)



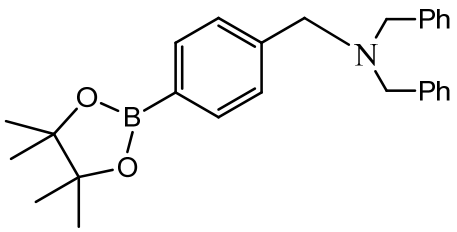
Following **general procedure I**, used boronic ester alcohol (0.2365 g, 1 mmol) and 1-Methylpiperazine (0.11 mL, 1 mmol) to give the title compound as a dark brown oil (0.26 g, 83%), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.69 (2H, d, *J* = 8.0 Hz, Ar**H**), 7.26 (2H, d, *J* = 8.1 Hz, Ar**H**), 3.44 (2H, s, PhC**H**$_2$N), 2.38 (8H, bro, N(C**H**$_2$C**H**$_2$)$_2$N), 2.21 (3H, s, NC**H**$_3$), 1.26 (12H, s, (C**H**$_3$)$_2$CC(C**H**$_3$)$_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ 134.7,128.9, 83.7, 63.1, 55.1, 53.1, 46.1, 21.8; ESI-MA: Calculated for $C_{18}H_{29}BN_2O_2$ $[M+H]^+$:316.2435. Found: 316.2470.

N-Propyl-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)propan-1-amine (Table 2, entry 10)



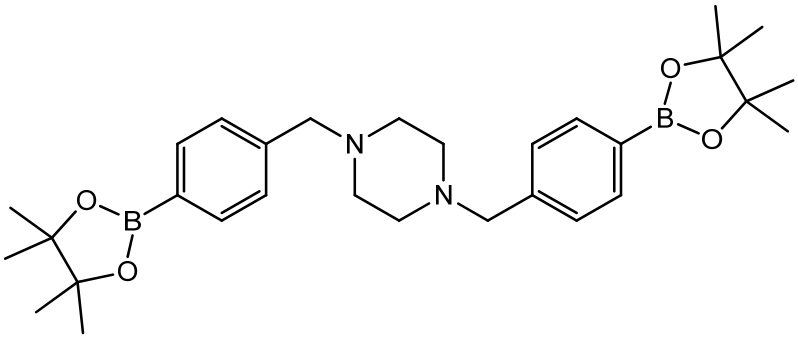
Following **general procedure I**, used boronic ester alcohol (0.2354 g, 1 mmol) and dipropylamine (0.13 mL, 1 mmol) to give the title compound as a black oil (0.28 g, 87%), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.67 (2H, d, *J* = 8.0 Hz, Ar**H**), 7.27 (2H, d, *J* = 8.0 Hz, Ar**H**), 3.49 (2H, s, PhC**H**$_2$N), 2.32-2.25 (4H, m, N(C**H**$_2$CH$_2$CH$_3$)$_2$), 1.47-1.32 (4H, m, N(CH$_2$C**H**$_2$CH$_3$)$_2$), 1.27 (12H, s, (C**H**$_3$)$_2$CC(C**H**$_3$)$_2$), 0.77 (6H, t, *J* = 7.3 Hz, N(CH$_2$CH$_2$C**H**$_3$)$_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ 134.6, 128.9, 83.6, 58.8, 55.9, 31.6, 24.8, 22.6, 20.2, 11.8; ESI-MA: Calculated for $C_{19}H_{32}BNO_2$ $[M+H]^+$:317.2618. Found: 317.2699.

N,N-Dibenzyl-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanamine (Table 2, entry 11)



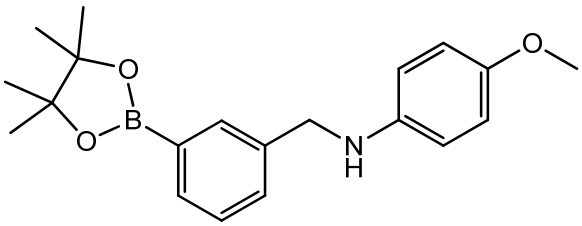
Following **general procedure I**, used boronic ester alcohol (0.2344 g, 1 mmol) and dibenzylamine (0.228 mL, 1 mmol) to give the title compound as a brown oil (0.29 g, 59%), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.82-7.26 (14H, m, Ar**H**), 3.59-3.57 (6H, m, (PhC**H**$_2$)$_3$N), 1.36 (12H, s, (C**H**$_3$)$_2$CC(C**H**$_3$)$_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ 143.1, 142.9, 140.3, 139.5, 134.9, 129.7, 128.8, 127.5, 126.9, 83.7, 57.9, 24.9; ESI-MA: Calculated for $C_{27}H_{32}BNO_2$ $[M+H]^+$:413.2633. Found: 413.2652.

1,4-Bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)piperazine (Table 2, entry 12)



Following **general procedure I**, used boronic ester alcohol (0.4698 g, 2 mmol) and piperazine (0.0861 g, 1 mmol) to give the title compound as a orange soild (0.34 g, 65%), m.p.: 122-125 °C, ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.68 (2H, d, *J* = 7.9 Hz, Ar**H**), 7.24 (2H, d, *J* = 7.9 Hz, Ar**H**), 3.44 (4H, s, $(PhC\mathbf{H}_2N)_2$), 2.38 (8H, bro, $N(C\mathbf{H}_2C\mathbf{H}_2)_2N$), 1.26 (12H, s, $(C\mathbf{H}_3)_2CC(C\mathbf{H}_3)_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ 141.5, 134.7, 128.9, 83.7, 63.1, 53.1, 24.8; ESI-MA: Calculated for $C_{30}H_{44}B_2N_2O_4$ $[M+H]^+$:518.3586. Found: 518.3565.

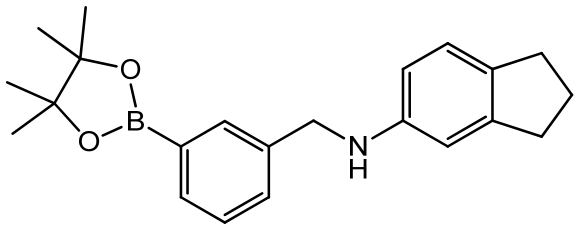
N-(4-Methoxybenzyl)-1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanamine (Table 3, entry 1)



Following **general procedure I**, used boronic ester alcohol (0.2339 g, 1 mmol) and p-anisidine (0.1231 g, 1 mmol) to give the title compound as a purple oil (0.22 g, 66%), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.81 (1H, s, Ar**H**), 7.72 (1H, d, *J* = 7.3 Hz, Ar**H**), 7.49

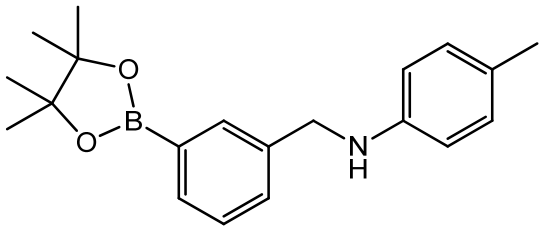
(1H, d, *J* = 7.3 Hz, ArH), 7.35 (1H, t, *J* = 7.5 Hz, ArH), 6.77 (2H, d, *J* = 9.0 Hz, ArH), 6.61 (2H, d, *J* = 9.0 Hz, ArH), 4.27 (2H, s, PhC**H**$_2$N), 3.74 (3H, s, OCH_3), 1.35 (12H, s, (C**H**$_3$)$_2$CC(C**H**$_3$)$_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ 145.1, 134.1, 133.7, 130.6, 128.1, 122.1, 114.9, 114.2, 83.8, 55.8, 49.3, 24.9; ESI-MA: Calculated for $C_{20}H_{26}BNO_3$ $[M+H]^+$:340.2081. Found: 340.2089.

N-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)-2,3-dihydro-1H-inden-5-amine (Table 3, entry 2)



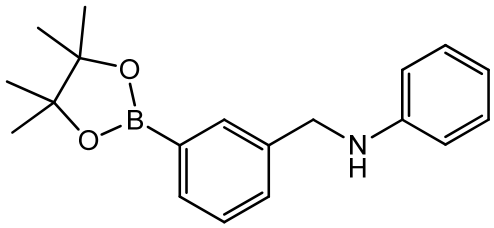
Following **general procedure I**, used boronic ester alcohol (0.2351 g, 1 mmol) and 5-aminoindan (0.1331 g, 1 mmol) to give the title compound as a dark brown oil (0.25 g, 71%), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.82 (1H, s, Ar**H**), 7.72 (1H, d, *J* = 7.3 Hz, Ar**H**), 7.51 (1H, s, ArH), 7.35 (1H, t, *J* = 7.5 Hz, ArH), 7.02 (1H, d, *J* = 8.0 Hz, ArH), 6.55 (1H, s, ArH), 6.46 (1H, d, *J* = 8.0 Hz, ArH), 4.31 (2H, s, PhC**H**$_2$N), 2.84-2.77 (4H, m, Ph(C**H**$_2$)$_2$CH$_2$), 2.05-2.00 (2H, m, Ph(CH$_2$)$_2$C**H**$_2$), 1.35 (12H, s, (C**H**$_3$)$_2$CC(C**H**$_3$)$_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ 147.1, 145.4, 138.9, 137.4, 135.7, 133.9, 130.5, 128.2, 124.7, 119.1, 111.3, 109.1, 83.8, 48.9, 32.9, 25.7, 24.9; ESI-MA: Calculated for $C_{22}H_{28}BNO_2$ $[M+H]^+$:349.2268. Found: 349.2271.

4-Methyl-N-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)aniline (Table 3, entry 3)



Following **general procedure I**, used boronic ester alcohol (0.2341 g, 1 mmol) and p-toluidine (0.1071 g, 1 mmol) to give the title compound as a purple oil (0.20 g, 62%), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.82 (1H, s, Ar**H**), 7.72 (1H, d, *J* = 7.3 Hz, Ar**H**), 7.49 (1H, dd, *J* = 7.5 Hz, ArH), 7.34 (1H, t, *J* = 7.5 Hz, ArH), 6.98 (2H, d, *J* = 8.1 Hz, ArH), 6.57 (2H, d, *J* = 8.4 Hz, ArH), 4.30 (2H, s, PhC**H**$_2$N), 2.23 (3H, s, $PhCH_3$), 1.35 (12H, s, (C**H**$_3$)$_2$CC(C**H**$_3$)$_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ 145.9, 138.8, 133.9, 130.5, 129.7, 128.2, 126.7, 120.8, 113.1, 83.8, 48.7, 24.9, 21.1; ESI-MA: Calculated for $C_{20}H_{26}BNO_2$ $[M+H]^+$:323.2103. Found: 323.2108.

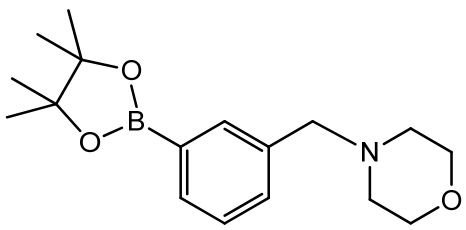
N-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)aniline (Table 3, entry 4)



Following **general procedure I**, used boronic ester alcohol (0.2374 g, 1 mmol) and aniline (0.129 mL, 1 mmol) to give the title compound as a pale purple oil (0.14 g, 43%), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.75 (1H, s, Ar**H**), 7.65 (1H, d, *J* = 7.3 Hz, Ar**H**), 7.41 (1H, d, *J* = 7.6 Hz, ArH), 7.27 (1H, t, *J* = 7.5 Hz, ArH), 7.11-7.06 (2H, m, ArH), 6.63 (1H, tt, *J* = 7.3 Hz, ArH), 6.56 (2H, d, *J* = 7.6 Hz, ArH), 4.24 (2H, s, PhC**H**$_2$N), 1.27 (12H, s, (C**H**$_3$)$_2$CC(C**H**$_3$)$_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ 148.2, 138.6, 133.9,

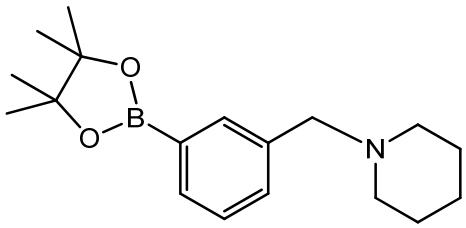
130.5, 129.2, 128.1, 120.2, 117.5, 112.8, 83.9, 48.3, 24.9; ESI-MA: Calculated for $C_{19}H_{24}BNO_2$ $[M+H]^+$:332.1830. Found: 332.1797.

4-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)morpholine (Table 3, entry 6)



Following **general procedure I**, used boronic ester alcohol (0.2346 g, 1 mmol) and morpholine (0.09 mL, 1 mmol) to give the title compound as a dark brown oil (0.24 g, 80%), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.65 (1H, s, Ar**H**), 7.64-7.62 (1H, m, Ar**H**), 7.49 (1H, d, *J* = 7.6 Hz, ArH), 7.27 (1H, d, *J* = 7.7 Hz, ArH), 3.64-3.61 (4H, m, $N(CH_2C\mathbf{H}_2)_2O$), 3.42 (2H, s, $PhC\mathbf{H}_2N$), 2.38-2.35 (4H, m, $N(C\mathbf{H}_2CH_2)_2O$), 1.27 (12H, s, $(C\mathbf{H}_3)_2CC(C\mathbf{H}_3)_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ 136.9, 135.6, 133.7, 132.3, 127.7, 83.8, 67.1, 63.4, 53.6, 24.9; ESI-MA: Calculated for $C_{17}H_{26}BNO_3$ $[M+H]^+$:303.2201. Found: 303.2204.

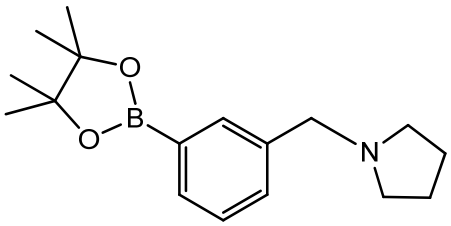
1-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)piperidine (Table 3, entry 7)



Following **general procedure I**, used boronic ester alcohol (0.2347 g, 1 mmol) and

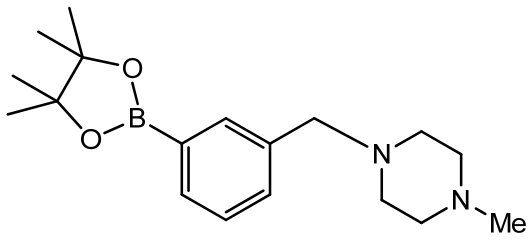
piperidine (0.098 mL, 1 mmol) to give the title compound as a black oil (0.24 g, 79%), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.70 (1H, s, Ar**H**), 7.70-7.68 (1H, m, Ar**H**), 7.47-7.44 (1H, m, ArH), 7.32 (1H, t, *J* = 7.6 Hz, ArH), 3.47 (2H, s, PhC**H**$_2$N), 2.38-2.35 (4H, m, N(C**H**$_2$CH$_2$)$_2$CH$_2$), 1.57 (4H, dt, *J* = 10.7, 5.5 Hz, N(CH$_2$C**H**$_2$)$_2$CH$_2$), 1.42 (2H, dd, *J* = 10.9, 5.7 Hz, N(CH$_2$CH$_2$)$_2$C**H**$_2$), 1.34 (12H, s, (C**H**$_3$)$_2$CC(C**H**$_3$)$_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ 137.8, 135.7, 133.4, 132.3, 127.5, 83.7, 63.8, 54.4, 25.9, 24.9, 24.4; ESI-MA: Calculated for $C_{18}H_{28}BNO_2$ $[M+H]^+$:302.2395. Found: 302.2399.

1-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)pyrrolidine (Table 3, entry 8)



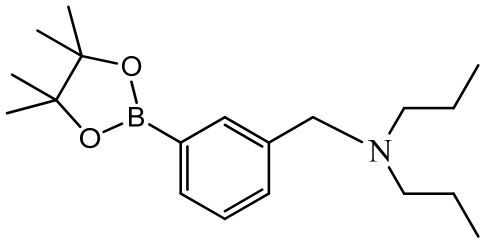
Following **general procedure I**, used boronic ester alcohol (0.2354 g, 1 mmol) and pyrrolidine (0.083 mL, 1 mmol) to give the title compound as a dark brown oil (0.22 g, 78%), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.74 (1H, s, Ar**H**), 7.70 (1H, d, *J* = 7.3 Hz, Ar**H**), 7.47-7.45 (1H, m, ArH), 7.31 (1H, d, *J* = 7.5 Hz, ArH), 3.62 (2H, s, PhC**H**$_2$N), 2.52-2.48 (4H, m, N(C**H**$_2$CH$_2$)$_2$), 1.79-1.75 (4H, m, N(CH$_2$C**H**$_2$)$_2$), 1.34 (12H, s, (C**H**$_3$)$_2$CC(C**H**$_3$)$_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ 138.6, 135.3, 133.4, 132.1, 127.6, 83.7, 60.6, 54.1, 21.9, 24.4; ESI-MA: Calculated for $C_{17}H_{26}BNO_2$ $[M+H]^+$:287.2057. Found: 287.2095.

1-Methyl-4-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)piperazine (Table 3, entry 9)



Following **general procedure I**, used boronic ester alcohol (0.2348 g, 1 mmol) and 1-methylpiperazine (0.11 mL, 1 mmol) to give the title compound as a brown oil (0.25 g, 80%), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.74 (1H, s, Ar**H**), 7.70-7.68 (1H, m, Ar**H**), 7.46-7.44 (1H, m, ArH), 7.32 (1H, t, *J* = 7.7 Hz, ArH), 3.50 (2H, s, PhC**H**$_2$N), 2.45 (8H, bro, N(C**H**$_2$C**H**$_2$)$_2$N), 2.27 (3H, s, NC**H**$_3$), 1.34 (12H, s, (C**H**$_3$)$_2$CC(C**H**$_3$)$_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ 137.4, 135.6, 133.5, 132.2, 127.6, 83.7, 63.1, 55.1, 53.1, 46.1, 24.6; ESI-MA: Calculated for $C_{18}H_{29}BN_2O_2$ $[M+H]^+$:316.2488. Found: 316.2492.

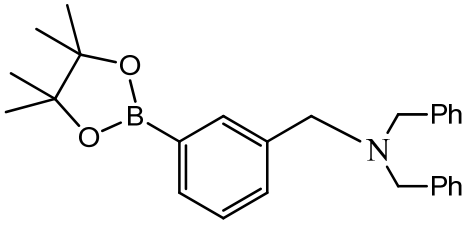
N-Propyl-N-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)propan-1-amine (Table 3, entry 10)



Following **general procedure I**, used boronic ester alcohol (0.2346 g, 1 mmol) and dipropylamine (0.13 mL, 1 mmol) to give the title compound as a yellow oil (0.22 g, 69%), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.61 (1H, s, Ar**H**), 7.60 (1H, d, *J* = 8.2 Hz, Ar**H**), 7.43 (1H, d, *J* = 7.7 Hz, ArH), 7.24 (1H, s, ArH), 3.47 (2H, s, PhC**H**$_2$N), 2.31-2.26 (4H, tt, N(C**H**$_2$CH$_2$CH$_3$)$_2$), 1.39 (4H, m, N(CH$_2$C**H**$_2$CH$_3$)$_2$), 1.27 (12H, s, (C**H**$_3$)$_2$CC(C**H**$_3$)$_2$),

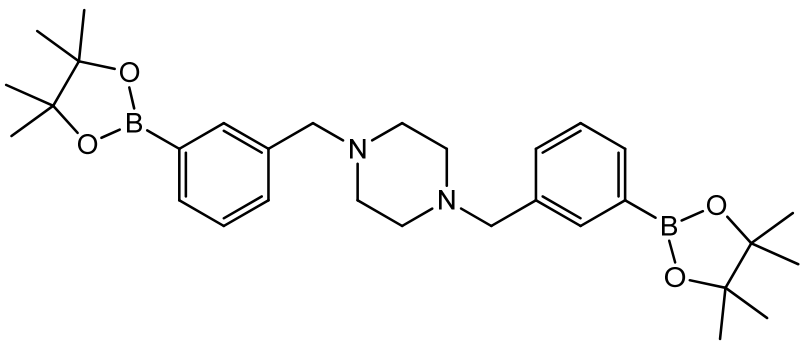
0.78 (6H, t, *J* = 7.3 Hz, $N(CH_2CH_2C\mathbf{H}_3)_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ 139.6, 135.1, 134.5, 133.7, 131.9, 128.3, 127.7, 83.7, 58.6, 55.8, 24.8, 20.1, 11.8; ESI-MA: Calculated for $C_{18}H_{29}BN_2O_2$ $[M+H]^+$:317.2679. Found: 317.2683.

N,N-Dibenzyl-1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanamine (Table 3, entry 11)



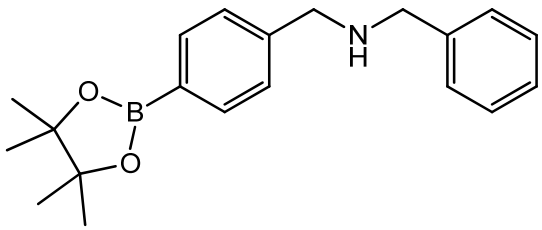
Following **general procedure I**, used boronic ester alcohol (0.2345 g, 1 mmol) and dibenzylamine (0.228 mL, 1 mmol) to give the title compound as a yellow solid (0.27 g, 65%), m.p.: 154-156 °C, ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.66 (1H, s, Ar**H**), 7.60 (1H, d, *J* = 7.3 Hz, Ar**H**), 7.54-7.51 (1H, m, ArH), 7.43-7.38 (1H, m, ArH),7.34-7.20 (10H, m, 2Ar**H**), 3.49-3.46 (6H, s, $(PhC\mathbf{H}_2)_3N$), 1.27 (12H, s, $(C\mathbf{H}_3)_2CC(C\mathbf{H}_3)_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ 139.6, 135.2, 131.7, 128.7, 126.8, 83.7, 57.9, 24.9; ESI-MA: Calculated for $C_{27}H_{32}BNO_2$ $[M+H]^+$:413.2660. Found: 413.2675.

1,4-Bis(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)piperazine (Table 3, entry 12)



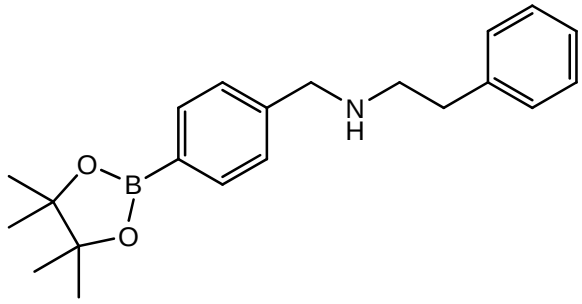
Following **general procedure I**, used boronic ester alcohol (0.4709 g, 2 mmol) and piperazine (0.0861 g, 1 mmol) to give the title compound as a brown solid (0.34 g, 65%), m.p.: 175-177 °C, ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ 7.64-7.60 (4H, m, Ar**H**), 7.38-7.35 (2H, m, ArH), 7.24 (2H, t, *J* = 7.6 Hz, ArH), 3.43 (2H, s, PhC**H**$_2$N), 2.40 (8H, bro, N(C**H**$_2$C**H**$_2$)$_2$N), 1.27 (12H, s, (C**H**$_3$)$_2$CC(C**H**$_3$)$_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ 137.3, 135.6, 133.5, 132.3, 128.9, 127.6, 83.7, 63.1, 53.1, 21.9; ESI-MA: Calculated for $C_{30}H_{44}B_2N_2O_4$ $[M+H]^+$:518.3556. Found: 518.3565.

N-Benzyl-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanamine (Table 4, entry 1)



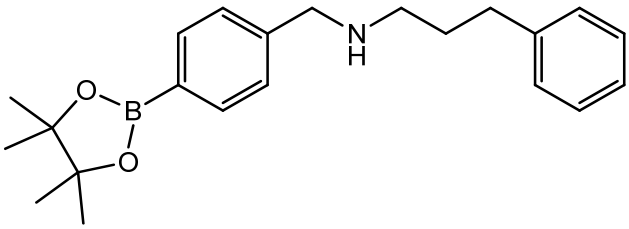
Following **general procedure II**, used boronic ester amine (0.2350 g, 1 mmol) and benzylalcohol (0.103 mL, 1 mmol) to give the title compound as a pale red solid (0.19 g, 60%), m.p.: 132-135 °C, ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.80 (2H, d, *J* = 8.1 Hz, ArH), 7.48 (4H, d, *J* = 8.0 Hz, Ar**H**), 7.36 (3H, t, *J* = 7.1 Hz, Ar**H**), 3.84 (4H, s, (PhC**H**$_2$)$_2$NH), 1.29 (12H, s, (C**H**$_3$)$_2$CC(C**H**$_3$)$_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ 135.4, 130.4, 129.9, 129.3, 128.5, 83.9, 48.6, 24.8; ESI-MA: Calculated for $C_{20}H_{26}BNO_2$ $[M+H]^+$:323.2185. Found: 323.2134.

2-Phenyl-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)ethanamine (Table 4, entry 2)



Following **general procedure II**, used boronic ester amine (0.2350 g, 1 mmol) and 2-phenylethanol (0.12 mL, 1 mmol) to give the title compound as a dark brown oil (0.19 g, 61%), m.p.: 155-157 °C, ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ7.85 (2H, d, *J* = 8.1 Hz, ArH), 7.76 (2H, d, Ar**H**), 7.69 (2H, d, *J* = 8.1 Hz, Ar**H**), 7.29 (3H, m, Ar**H**), 3.84 (2H, s, PhC**H**$_2$NH), 3.03 (2H, t, *J* = 7.5 Hz, NHC**H**$_2$CH$_2$Ph), 2.88 (2H, d, *J* = 7.4 Hz, NHCH$_2$C**H**$_2$Ph), 1.34 (12H, s, (C**H**$_3$)$_2$CC(C**H**$_3$)$_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ 139.7, 134.9, 129.1, 128.7, 128.3, 127.5, 127.2, 126.3, 126.1, 83.7, 63.3, 50.2, 36.1, 24.8; ESI-MA: Calculated for $C_{21}H_{28}BNO_2$ $[M+H]^+$:337.2283. Found: 337.2293.

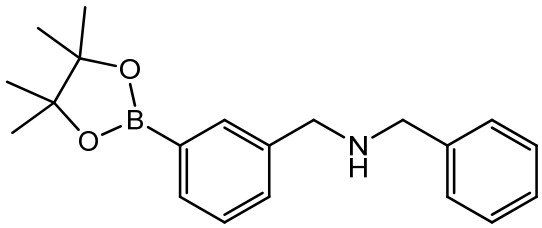
3-Phenyl-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)propan-1-amine (Table 4, entry 3)



Following **general procedure II**, used boronic ester amine (0.2350 g, 1 mmol) and 3-phenyl-1-propanol (0.135 mL, 1 mmol) to give the title compound as a green solid (0.23 g, 64%), m.p.: 188-190 °C, ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ7.73 (2H, d, *J* = 7.9 Hz, ArH), 7.45 (2H, d, *J* = 8.0 Hz, Ar**H**), 7.13-7.11 (2H, m, Ar**H**), 7.08-7.06 (1H, m, Ar**H**),

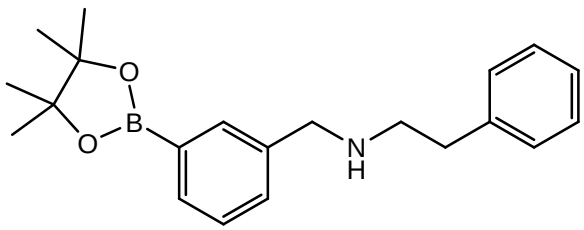
7.03-7.00 (2H, m, Ar**H**), 3.88 (2H, s, PhC**H**$_2$NH), 2.66-2.61 (2H, m, NHC**H**$_2$CH$_2$CH$_2$Ph), 2.52 (2H, t, *J* = 7.4 Hz, NHCH$_2$CH$_2$C**H**$_2$Ph), 2.11-2.03 (2H, dd, *J* = 13.7, 6.0 Hz, NHCH$_2$C**H**$_2$CH$_2$Ph), 1.22 (12H, s, (C**H**$_3$)$_2$CC(C**H**$_3$)$_2$); ^{13}C NMR (75.5 MHz, CDCl$_3$, 25°C): δ 139.8, 135.4, 129.6, 128.5, 128.3, 126.2, 83.9, 51.7, 45.2, 32.6, 27.1, 24.8; ESI-MA: Calculated for $C_{22}H_{30}BNO_2$ $[M+H]^+$:351.2447. Found: 351.2451.

N-Benzyl-1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanamine (Table 5, entry 1)



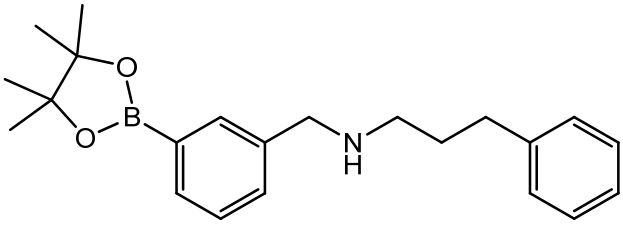
Following **general procedure II**, used boronic ester amine (0.2361 g, 1 mmol) and benzylalcohol (0.103 mL, 1 mmol) to give the title compound as a brown liquid (0.20 g, 61%), ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ 7.74 (1H, d, *J* = 7.7 Hz, ArH), 7.65 (2H, t, *J* = 7.8 Hz, Ar**H**), 7.59 (1H, s, Ar**H**), 7.42 (2H, dd, *J* = 6.4, 2.8 Hz, Ar**H**), 7.29-7.23 (3H m, Ar**H**), 3.89 (4H, d, *J* = 7.6 Hz, (PhC**H**$_2$)$_2$NH), 1.21 (12H, s, (C**H**$_3$)$_2$CC(C**H**$_3$)$_2$); ^{13}C NMR (75.5 MHz, CDCl$_3$, 25°C): δ 141.1, 140.7, 139.9, 137.7, 136.4, 135.7, 134.9, 133.7, 133.3, 131.8, 131.6, 88.7, 69.3, 54.7, 29.5; ESI-MA: Calculated for $C_{20}H_{26}BNO_2$ $[M+H]^+$:323.2152. Found: 323.2199.

2-Phenyl-N-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)ethanamine (Table 5, entry 2)



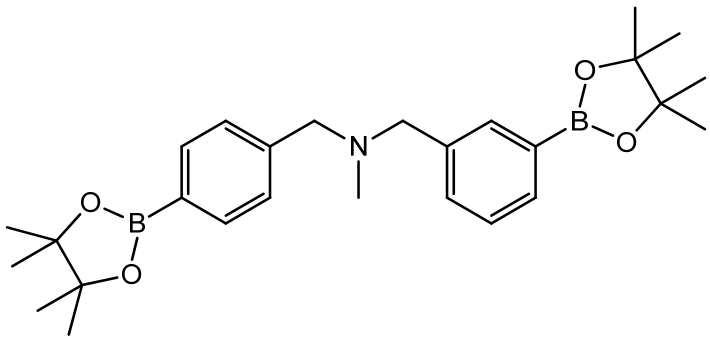
Following **general procedure II**, used boronic ester amine (0.2350 g, 1 mmol) and 2-phenylethanol (0.12 mL, 1 mmol) to give the title compound as a yellow solid (0.18 g, 53%), M.P.: 90-92 °C, ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 8.07 (1H, s, Ar**H**), 7.86-7.84 (1H, m, Ar**H**), 7.70 (2H, d, *J* = 7.3 Hz, Ar**H**), 7.42 (3H, t, *J* = 7.5 Hz, Ar**H**), 7.28 (2H, d, *J* = 1.2 Hz, Ar**H**), 3.83 (2H, s, PhC**H**$_2$NH), 3.02 (2H, t, *J* = 7.6 Hz, NHC**H**$_2$CH$_2$Ph), 2.89 (2H, s, NHCH$_2$C**H**$_2$Ph), 1.35 (12H, s, (C**H**$_3$)$_2$CC(C**H**$_3$)$_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25°C): δ 139.9, 136.9, 135.5, 134.6, 131.2, 130.2, 129.1, 128.7, 126.3, 126.1, 83.8, 63.3, 53.6, 37.5, 24.6; ESI-MA: Calculated for $C_{21}H_{28}BNO_2$ $[M+H]^+$:337.2239. Found: 337.2246.

3-Phenyl-N-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)propan-1-amine (Table 5, entry 3)



Following **general procedure II**, used boronic ester amine (0.2347 g, 1 mmol) and 3-phenyl-1-propanol (0.135 mL, 1 mmol) to give the title compound as a brown oil (0.21 g, 60%), ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ 7.75-7.28 (9H, m, ArH), 3.79 (2H, s, PhC**H**$_2$NH), 2.67-2.63 (4H, m, NHC**H**$_2$CH$_2$C**H**$_2$Ph), 1.90-1.80 (2H, m, NHCH$_2$C**H**$_2$CH$_2$Ph), 1.35 (12H, s, (C**H**$_3$)$_2$CC(C**H**$_3$)$_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25°C): δ 134.6, 133.5, 131.3, 128.4, 128.3, 127.9, 126.1, 125.7, 83.8, 53.8, 48.5, 33.2, 24.9; ESI-MA: Calculated for $C_{22}H_{30}BNO_2$ $[M+H]^+$:351.2447. Found: 351.2454.

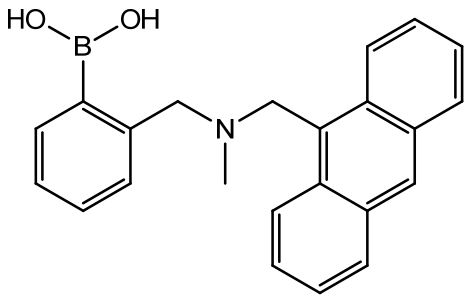
General Procedure for the Preparation of N-Methyl-N-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanamine [2]



(4-formylphenyl)boronic acid (1.49 g, 10 mmol) and pinacol (1.41 g, 12 mmol) were mixed in toluene (100 mL). A Dean-Stark head was fitted and the reaction was heated under reflux condition for 2 hours. The mixture was allowed to cool to room temperature, and then washed with water (4 x 100 mL). The organic layer was condensed under reduced pressure and DCM was added. This was washed with water (3 x 100 mL) and dried over sodium sulphate and filtered. The solvents were again removed under reduced pressure to obtain the boronic ester aldehydes. These boronic ester aldehydes (2.23 g, 9.6 mmol) was dissolved in MeOH (100 mL) and $MeNH_2$ (40% in H_2O, 0.69 mL) was added. The reaction mixture was stirred in 0°C for 2 hours under N_2 atmosphere. After that, NaBH4 (0.76 g) was added slowly and the mixture stirred in 0°C for 30 mins. The all reaction mixture was stirred at room temperature for 48 hours. The solvents were removed under reduced pressure and DCM was added. This was washed with water (5 x 100 mL) and dried over sodium sulphate and filtered. The solvent were again removed under reduced pressure to obtain the product amine (N-methyl-1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanamine). To an oven-dried, nitrogen-purged Radley's carousel tube

containing the product amine from last step (0.2488 g, 1 mmol) and meta-boronic ester alcohol (0.2346 g, 1 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (15.3 mg, 0.02 5mmol), DPEphos (53.8 mg, 0.05 mmol), Na_2CO_3 (10.6 mg, 0.1 mmol) and xylene (2 mL). The reaction mixture was allowed to stir under a nitrogen atmosphere at room temperature and then increased the temperature to 155^{0}C to reflux for 24 hours. The resulting crude compounds were evaporated *in vacuo* and conversion was determined by analysis of the peak integral ratios characteristic of boronic ester alcohol and amine products in the proton NMR spectrum if the crude reaction mixture. The title compound was purify by recrystallised with DCM:Hexane (1:20) and give a yellow solid (0.38 g, 82%), m.p.: 298-300°C, ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.73-7.28 (8H, m, ArH), 3.45-3.44 (4H, s, (PhC**H**$_2$)$_2$NCH$_3$), 2.08 (3H, s, (PhCH$_2$)$_2$NC**H**$_3$), 1.27 (24H, s, 2 x (C**H**$_3$)$_2$CC(C**H**$_3$)$_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25°C): δ 142.6, 138.4, 135.3, 134.7, 133.5, 132.0, 130.0, 128.3, 127.7, 125.3, 83.8, 83.7, 65.3, 61.8, 42.2, 24.8, 22.1; ESI-MA: Calculated for $C_{27}H_{39}B_2NO_4$ [M+H]$^+$:486.2954. Found: 486.2962.

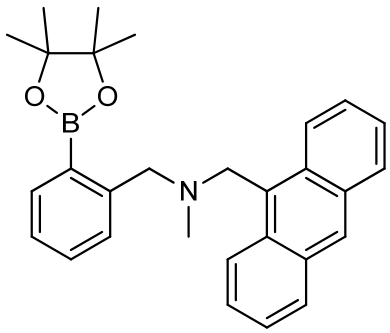
General Procedure for the Preparation of (2-(((Anthracen-9-ylmethyl)(methyl)amino)methyl)phenyl)boronic acid[2]



To an oven-dried, nitrogen-purged Radley's carousel tube containing K_2CO_3 (27.6 mg, 0.2 mmol), methanol (4 mL), boronic acid aldehyde (4 mmol) and

9-(Methylaminomethyl)anthracene (2 mmol). The reaction mixture was allowed to stir under a nitrogen atmosphere at room temperature for overnight. After that, $NaBH_4$ (151.3mg, 4mmol) was dissolved in 6ml methanol and added into the carousel tube. The mixture was stirring for 1 hour and the resulting crude compounds were evaporated in *vacuo* and conversion was determined by analysis of the peak integral ratios characteristic of products in the proton NMR spectrum. The product was purified by recrystallised using DCM:methanol(100:1). Finally, we get the title compound as a yellow solid (0.411 g, 58%), m.p.:145-148°C, ^{1}H NMR (300 MHz, CD_3OD, 25 °C): δ 8.47 (1H, s, Ar**H**), 7.98 (4H, dd, *J* = 20.7, 8.6 Hz, Ar**H**), 7.62 (2H, d, *J* = 6.6 Hz, Ar**H**), 7.41-7.16 (7H, m, Ar**H**), 4.89 (2H, s, PhC**H**$_2$NCH$_3$CH$_2$Ar), 4,31 (2H, s, PhCH$_2$NCH$_3$C**H**$_2$Ar), 2.31 (3H, s, PhCH$_2$NC**H**$_3$CH$_2$Ar); ^{13}C NMR (75.5 MHz, CD_3OD, 25°C): δ 135.9, 133.1, 133.0, 132.3, 131.6, 130.8, 129.4, 128.6, 128.3, 126.7, 125.1, 64.7, 40.4; ESI-MA: Calculated for $C_{27}H_{39}B_2NO_4$ $[M+H]^+$:355.1744. Found: 355.1641.

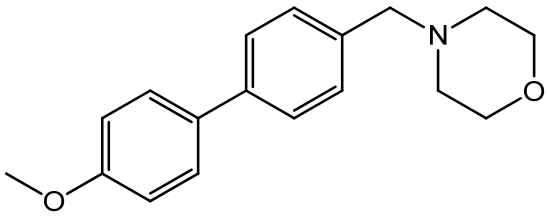
General Procedure for the Preparation of 1-(Anthracen-9-yl)-N-methyl-N-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) benzyl)methanamine[2]



To an oven-dried, nitrogen-purged Radley's carousel tube containing $[Ru(p\text{-cymene})Cl_2]_2$ (15.3 mg, 0.025 mmol), DPEphos (53.8 mg, 0.05 mmol), Na_2CO_3 (10.6 mg, 0.1 mmol), xylene (2 mL), 9-(Methylaminomethyl)anthracene (1 mmol) and boronic ester alcohol (1 mmol). The reaction mixture was allowed to stir under a

nitrogen atmosphere at room temperature and then increased the temperature to 155 ^{0}C to reflux for 24 hours. The resulting crude compounds were evaporated in *vacuo* and conversion was determined by analysis of the peak integral ratios characteristic of boronic ester alcohol and amine products in the proton NMR spectrum if the crude reaction mixture. The product was purified by recrystallised using DCM:methanol (100:1) to give the title compound as a orange yellow solid (0.25 g, 84 %), m.p.: 113-115 °C, ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): 8.37-8.30 (2H, m, Ar**H**), 7.95 (1H, d, *J* = 2.4 Hz, Ar**H**), 7.85 (1H, d, *J* = 7.0 Hz, Ar**H**), 7.47-7.40 (9H, m, Ar**H**), 4.38 (2H, s, PhC**H**$_2$NCH$_3$CH$_2$Ar), 4.00 (2H, s, PhCH$_2$NCH$_3$C**H**$_2$Ar), 2.22 (3H, s, PhCH$_2$NC**H**$_3$CH$_2$Ar), 1.28 (12H, s, (C**H**$_3$)$_2$CC(C**H**$_3$)$_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25°C): δ 145.1, 135.3, 131.4, 131.3, 130.6, 130.3, 129.7, 129.1, 128.8, 128.3, 127.2, 126.4, 125.9, 125.4, 124.9, 124.7, 124.4, 83.4, 62.2, 52.1, 42.5, 24.9; ESI-MA: Calculated for $C_{27}H_{39}B_2NO_4$ $[M+H]^+$:437.2526. Found: 437.1329.

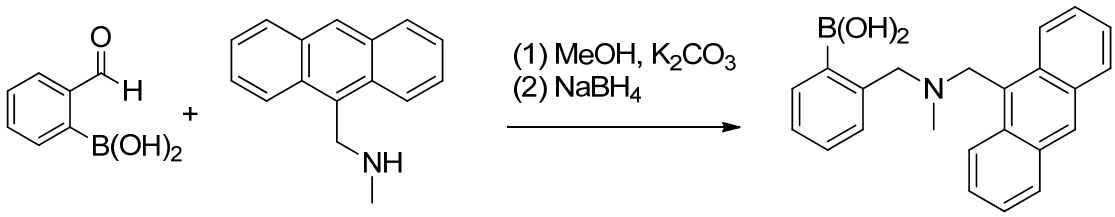
General Procedure for the Preparation of 4-((4'-Methoxy-[1,1'-biphenyl]-4-yl)methyl)morpholine[3]



To an oven-dried, nitrogen-purged Radley's carousel tube containing $Pd(PPh_3)_4$ (115.5 mg, 0.1 mmol), 4-Iodoanisole (0.234g, 1mmol), 4-(4-Morpholinomethyl)phenylboronic acid pinacol ester (0.3032g, 1mmol), xylene (1.5 mL) and 2M sodium carbonate (0.5ml), The reaction mixture was heated at 155 ^{0}C for 12h, cooled down to room temperature. The solvent was removed under reduced pressure. The product was purified by recrystallised using DCM:methanol(100:0.5). Finally, we get the title compound as a yellow solid (0.1882

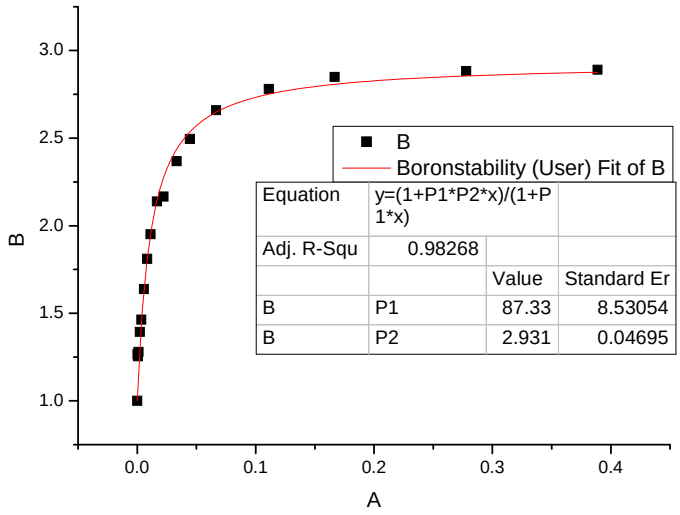
g, 67%), m.p.: 62-65°C, ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): 7.61-7.36 (8H, m, Ar**H**), 3.85 (3H, s, ArOC**H**$_3$), 3.74 (4H, t, *J* = 7.8 Hz, N(CH_2C**H**$_2$)$_2$O), 3.54 (2H, s, ArC**H**$_2$N) 2.49 (4H, t, *J* = 8.1 Hz, N(C**H**$_2$$CH_2$)$_2$O); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25°C): δ 159.1, 133.4, 129.7, 128.7, 128.0, 127.2, 127.0, 126.6, 114.2, 66.9, 63.1, 55.3, 53.6; ESI-MA: Calculated for $C_{27}H_{39}B_2NO_4$ $[M+H]^+$:283.1572. Found: 283.1736.

Fluorescence

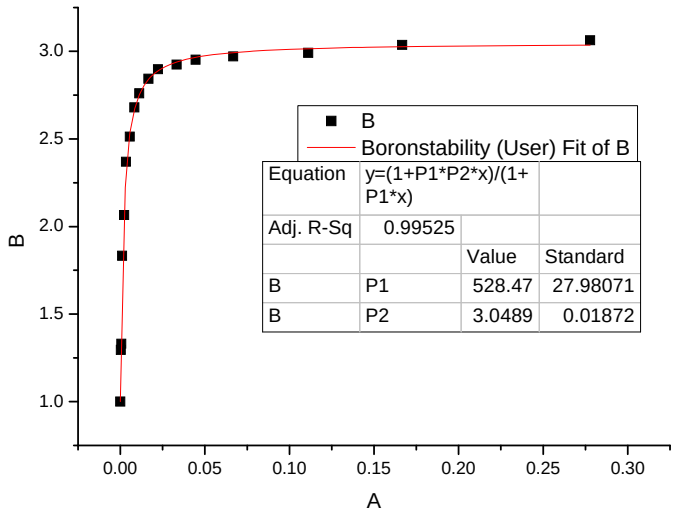


added sugar (g)	mol/L
0	0
0.005	0.000278
0.01	0.000556
0.02	0.001111
0.04	0.002222
0.06	0.003333
0.1	0.005556
0.15	0.008333
0.2	0.011111
0.3	0.016667
0.4	0.022222
0.6	0.033333
0.8	0.044444
1.2	0.066667
2	0.111111
3	0.166667
5	0.277778
7	0.388889

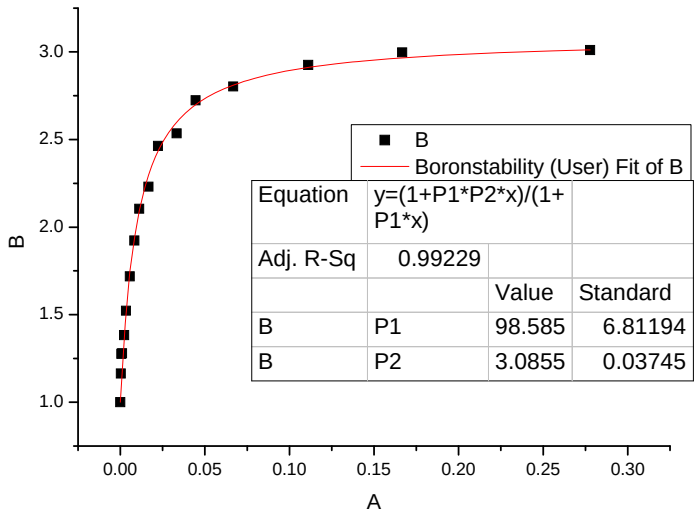
1. D-glucose

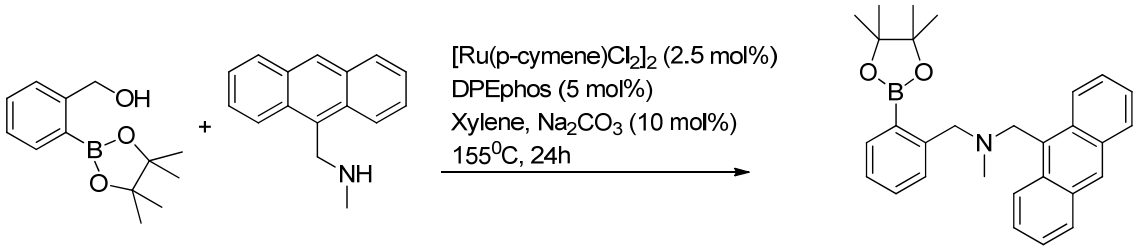


2. D-fluctose



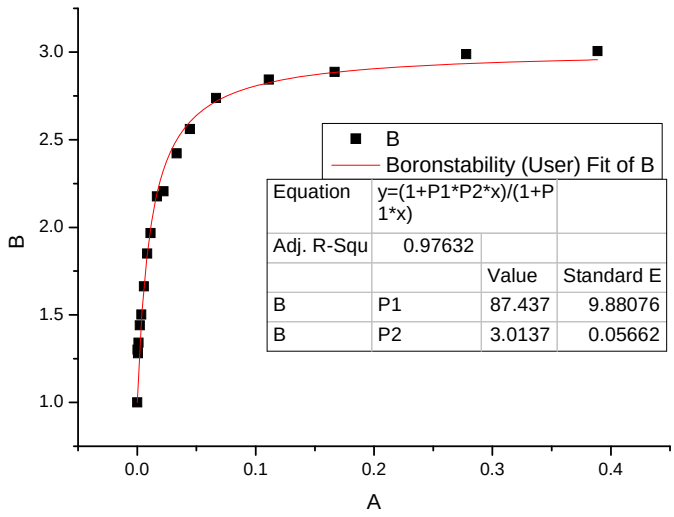
3. D-galactose


B
Boronstability (User) Fit of B
Equation
y=(1+P1*P2*x)/(1+P1*x)
Adj. R-Sq
0.99229
Value
Standard
B
P1
98.585
6.81194
B
P2
3.0855
0.03745
B
A
3.0
2.5
2.0
1.5
1.0
0.00
0.05
0.10
0.15
0.20
0.25
0.30

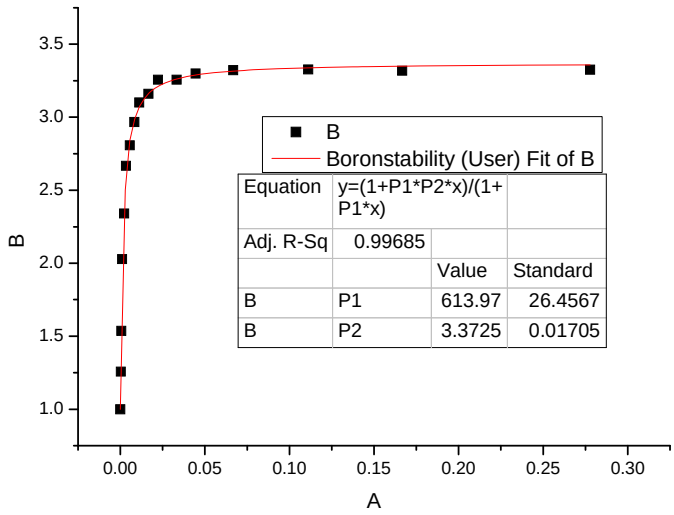


added sugar (g)	mol/L
0	0
0.005	0.000278
0.01	0.000556
0.02	0.001111
0.04	0.002222
0.06	0.003333
0.1	0.005556
0.15	0.008333
0.2	0.011111
0.3	0.016667
0.4	0.022222
0.6	0.033333
0.8	0.044444
1.2	0.066667
2	0.111111
3	0.166667
5	0.277778
7	0.388889

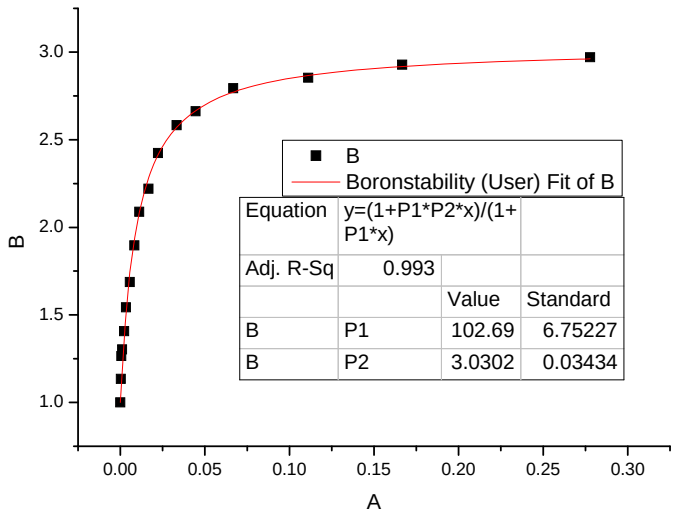
1. D-glucose



2. D-fluctose



3. D-galactose



References

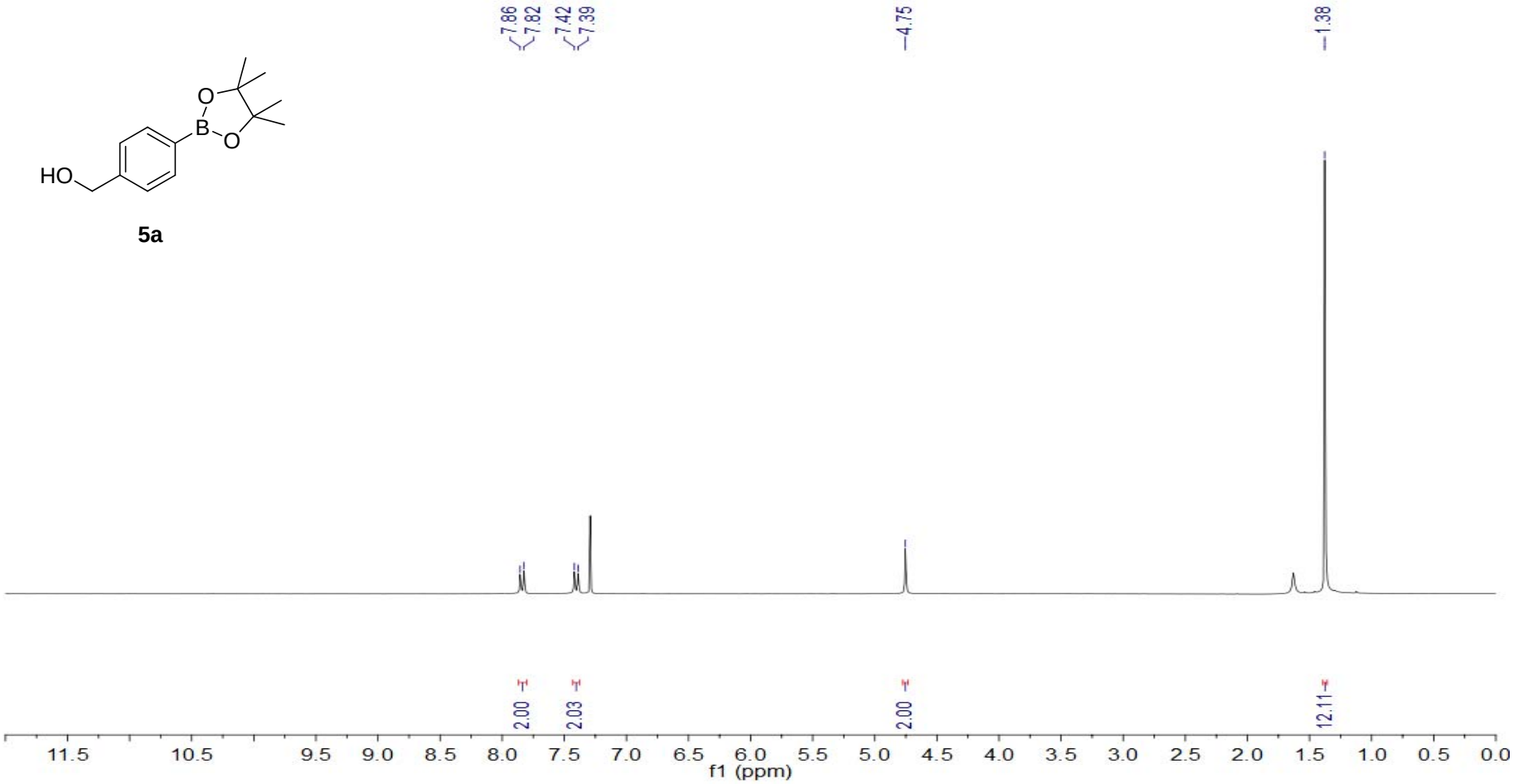
[1] Gillis, E. P.; Burke, M. D., *J.Am. Chem. Soc.* **2008**, *130*, 14084-+.

[2] Hamid, M. H. S. A.; Allen, C. L.; Gareth, G. W.; Maxwell, A. C.; Maytum, H. C.; Watson, A. J. A.; Williams, J. M. J., *J.Am. Chem. Soc.* **2009**, *131*, 1766-1774.

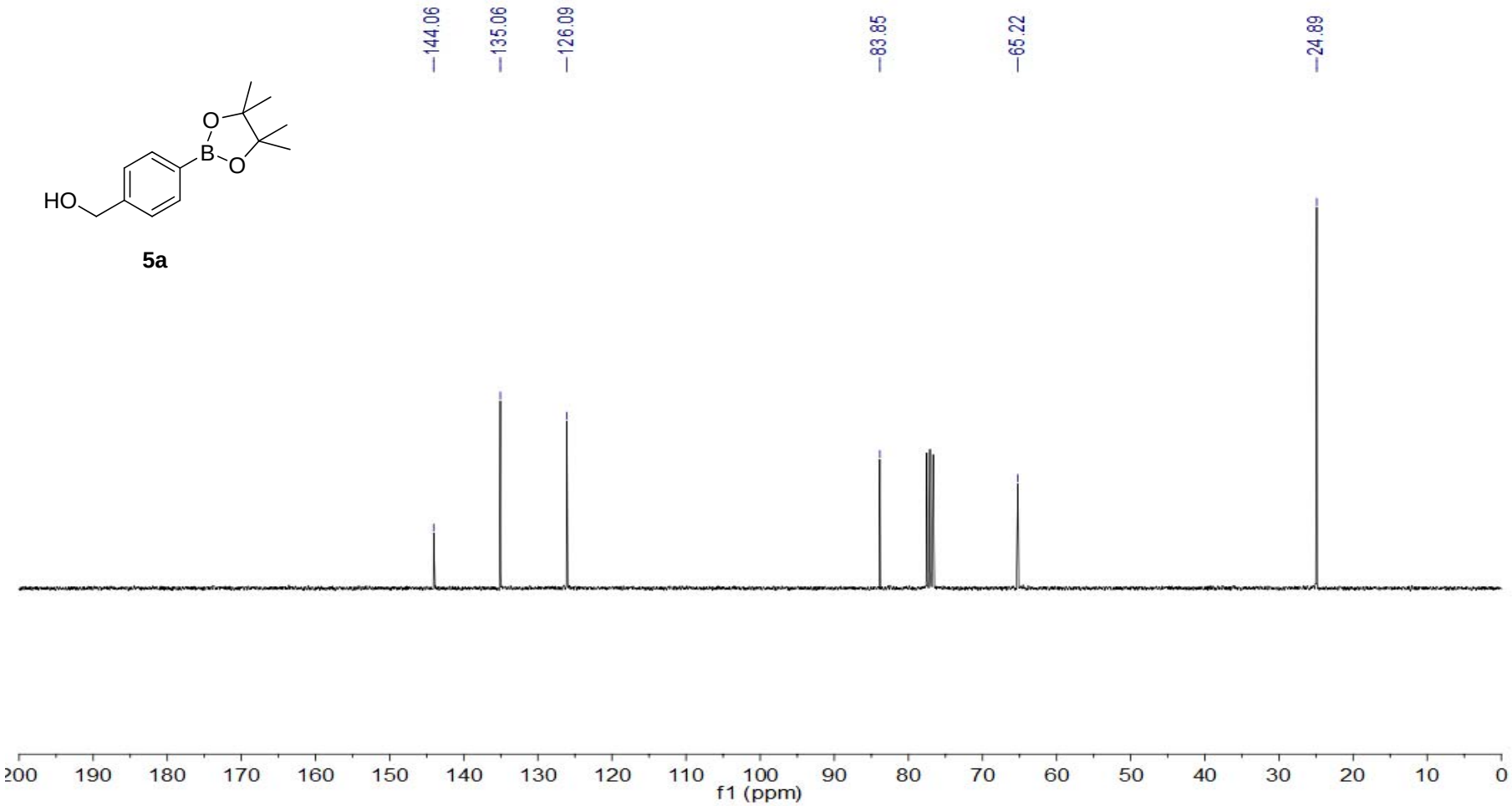
[3] Liu, C.; Ni, Q.; Bao, F.; Qiu, J., *Green Chemistry* **2011**, *13*, 1260-1266.

^{1}H NMR Spectra (300 MHz, $CDCl_3$, 25 °C)

5a

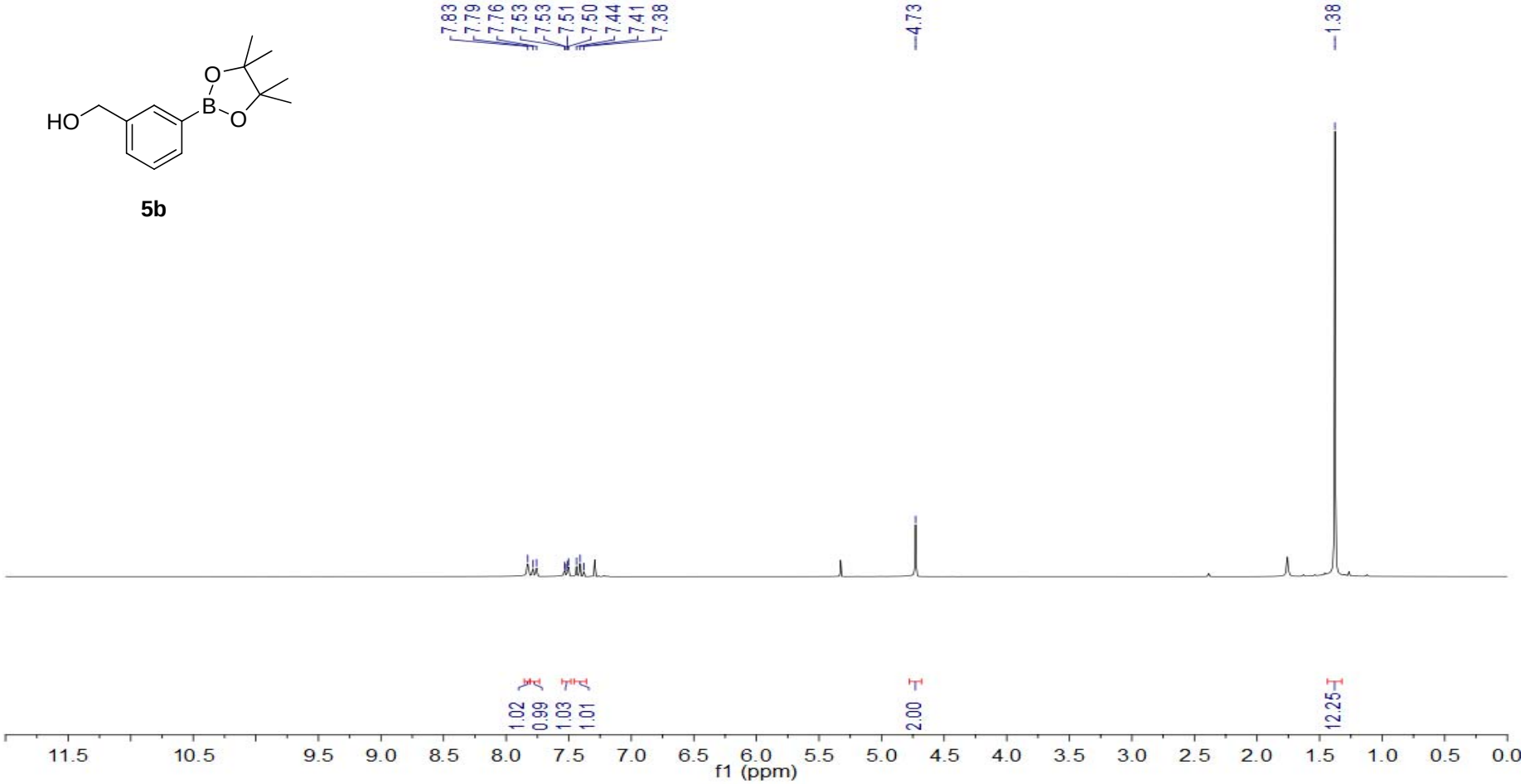


^{13}C NMR Spectra (75.5 MHz, $CDCl_3$, 25 °C)

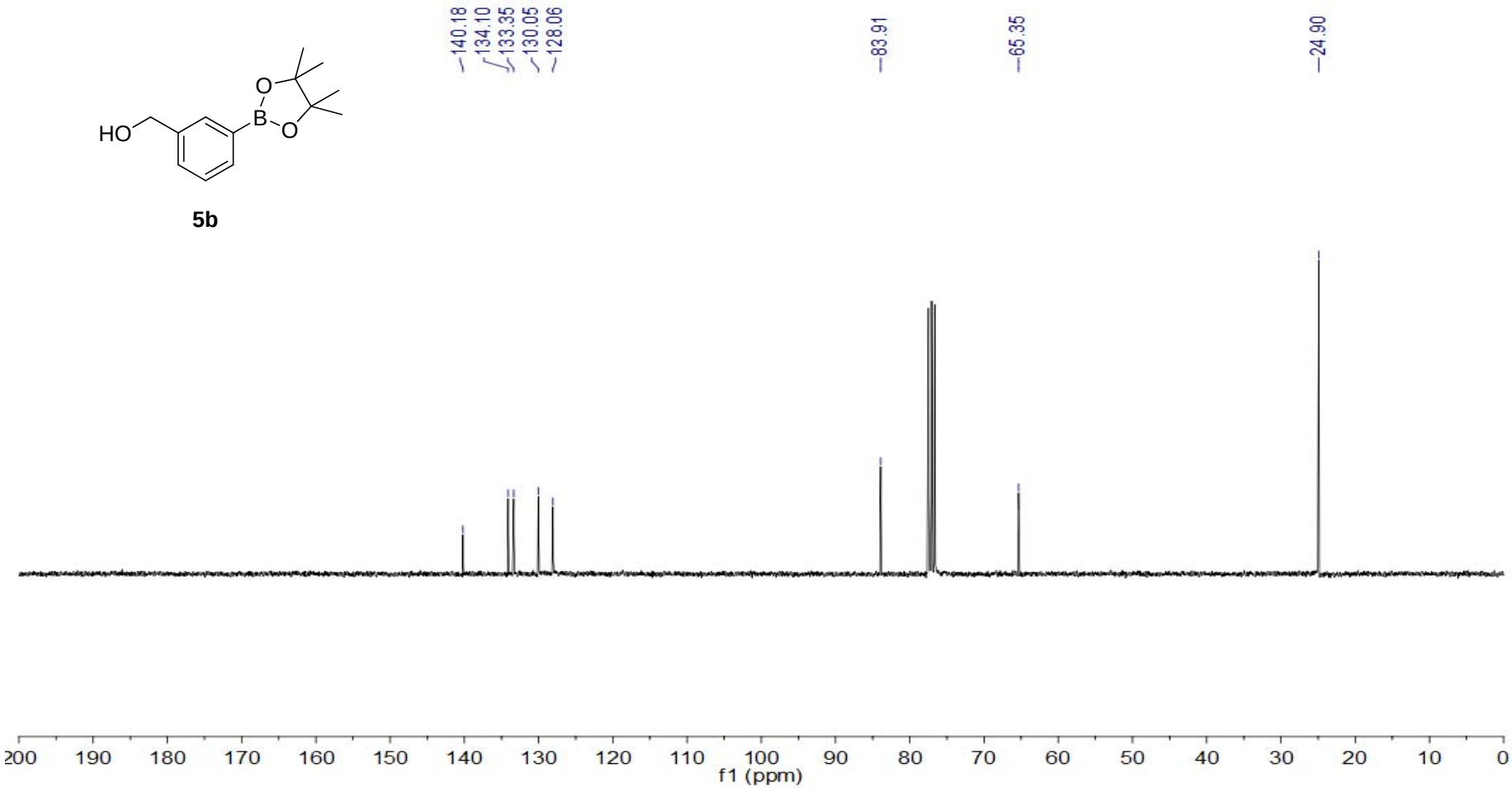


^{1}H NMR Spectra (300 MHz, $CDCl_3$, 25 °C)

5b



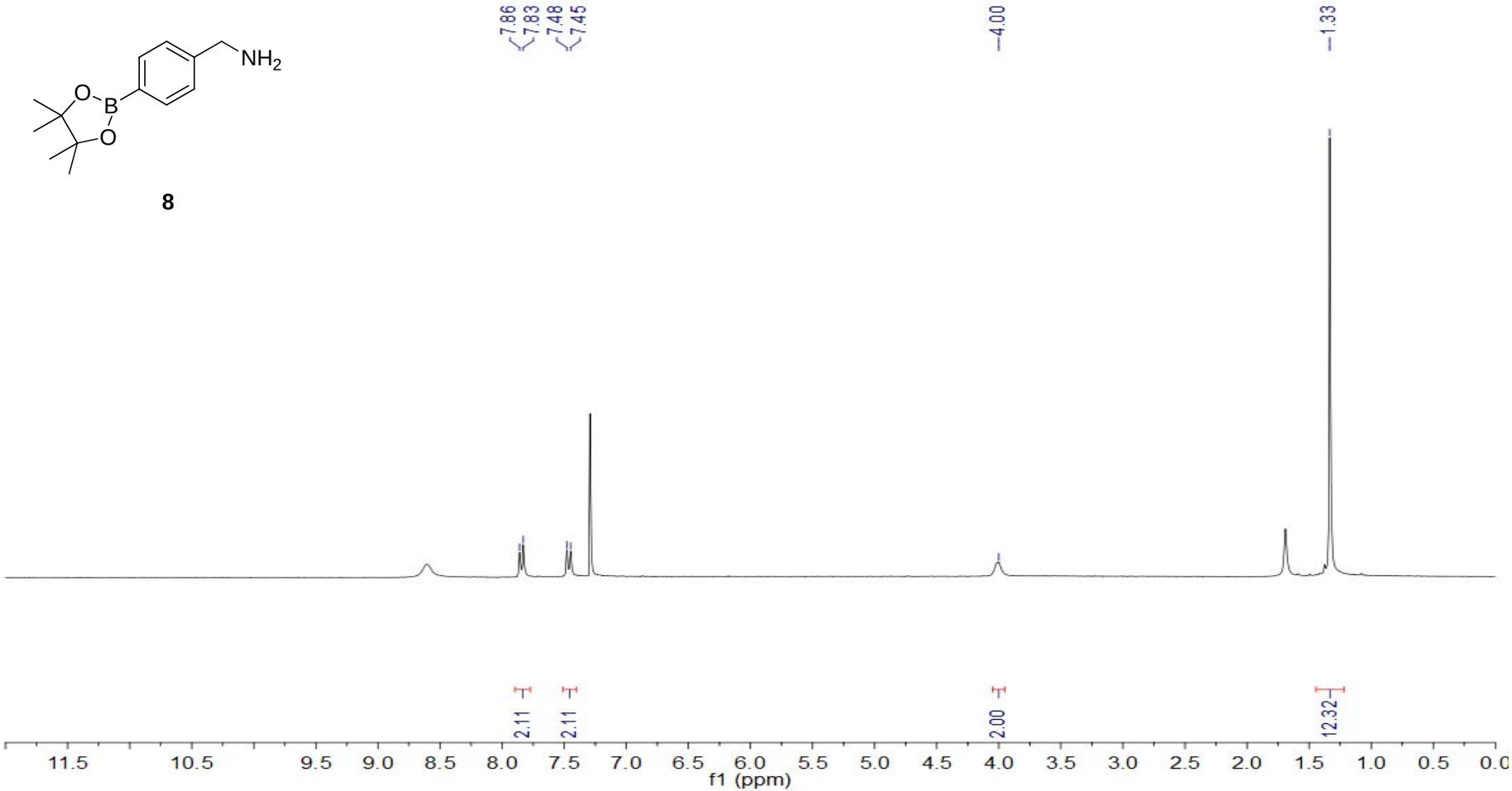
^{13}C NMR Spectra (75.5 MHz, $CDCl_3$, 25 °C)



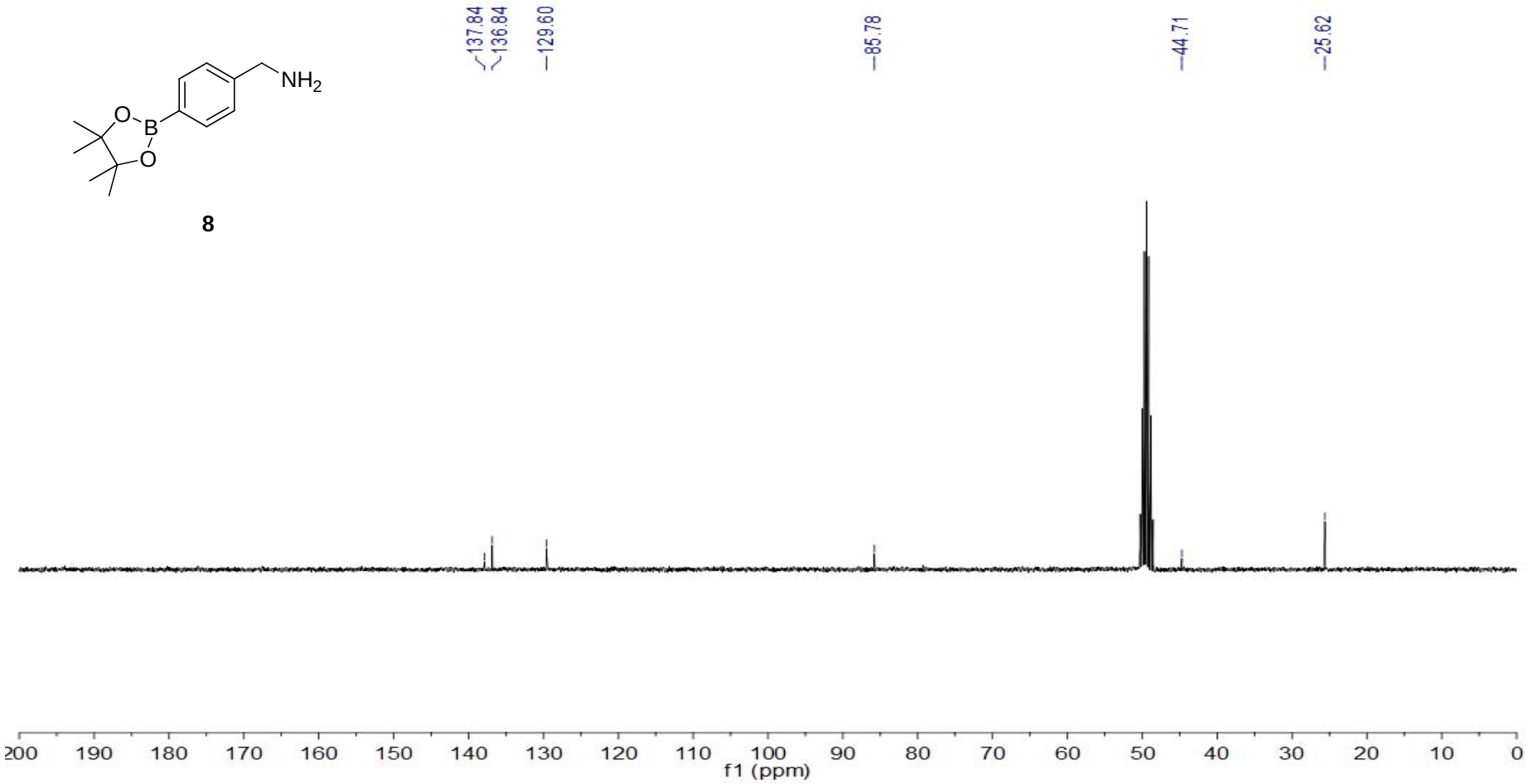
5b

^{1}H NMR Spectra (300 MHz, $CDCl_3$, 25 °C)

8

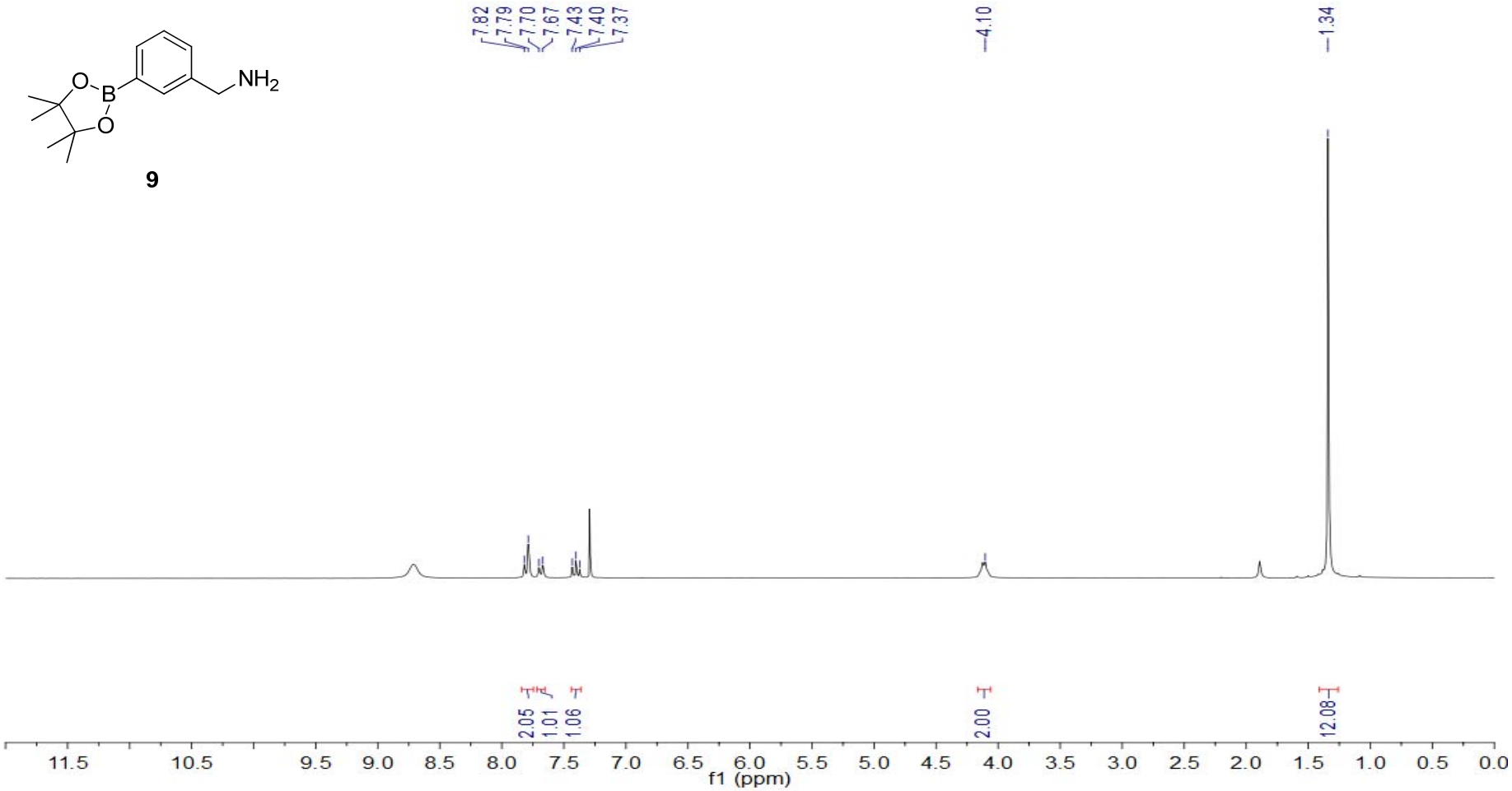


^{13}C NMR Spectra (75.5 MHz, CD_3OD, 25 °C)



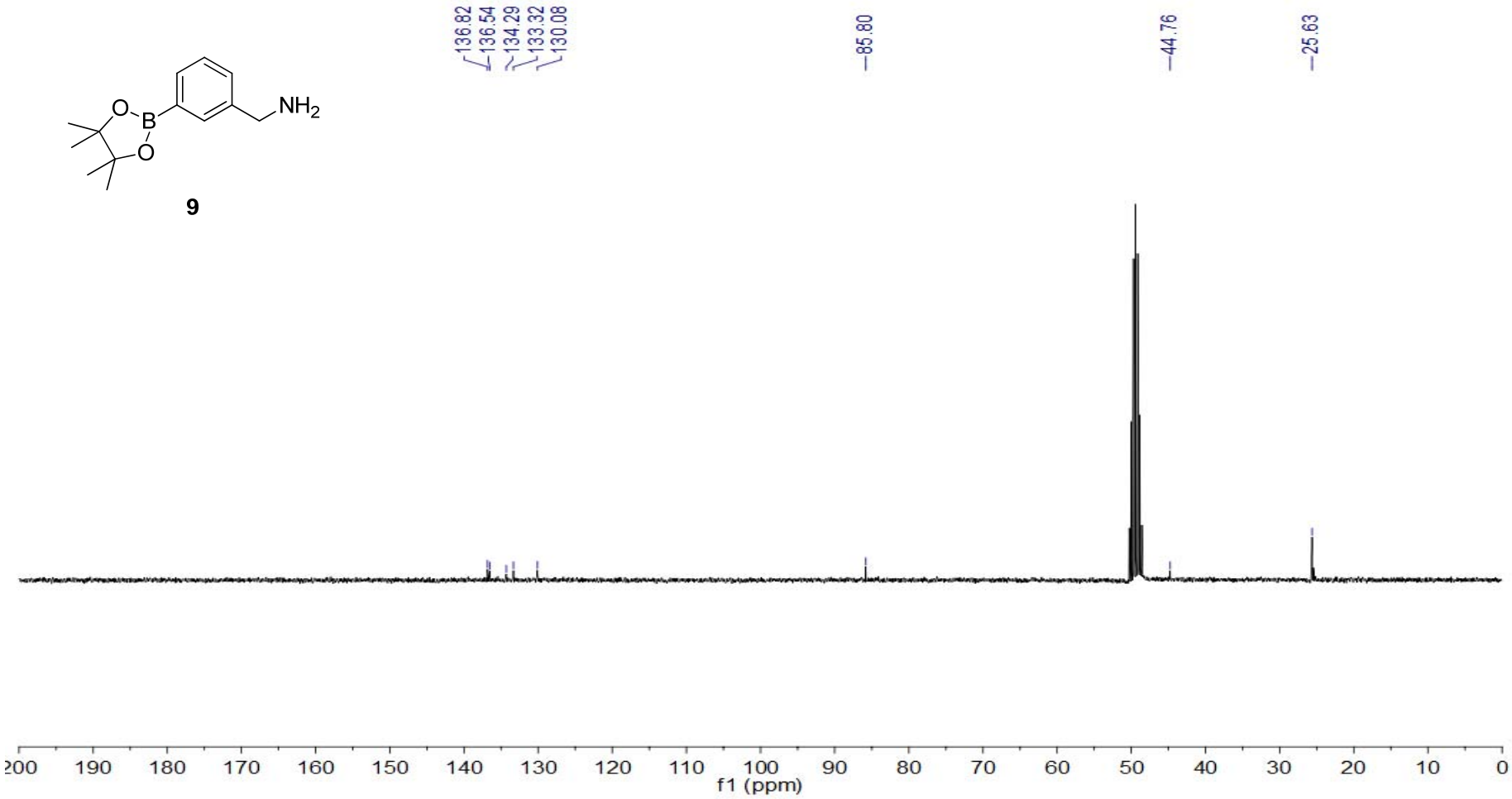
^{1}H NMR Spectra (300 MHz, $CDCl_3$, 25 °C)

9

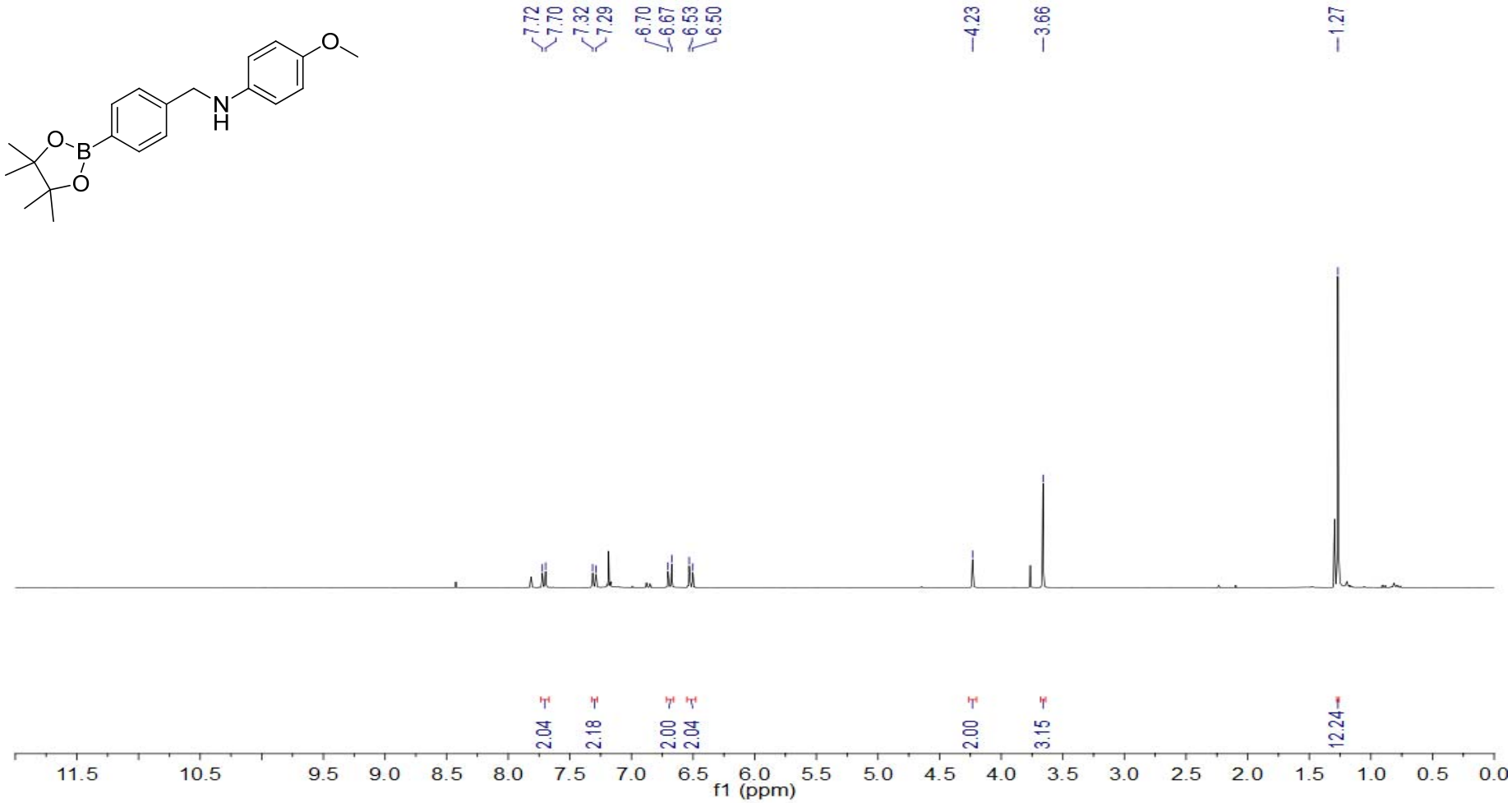


^{13}C NMR Spectra (300 MHz, CD_3OD, 25 °C)

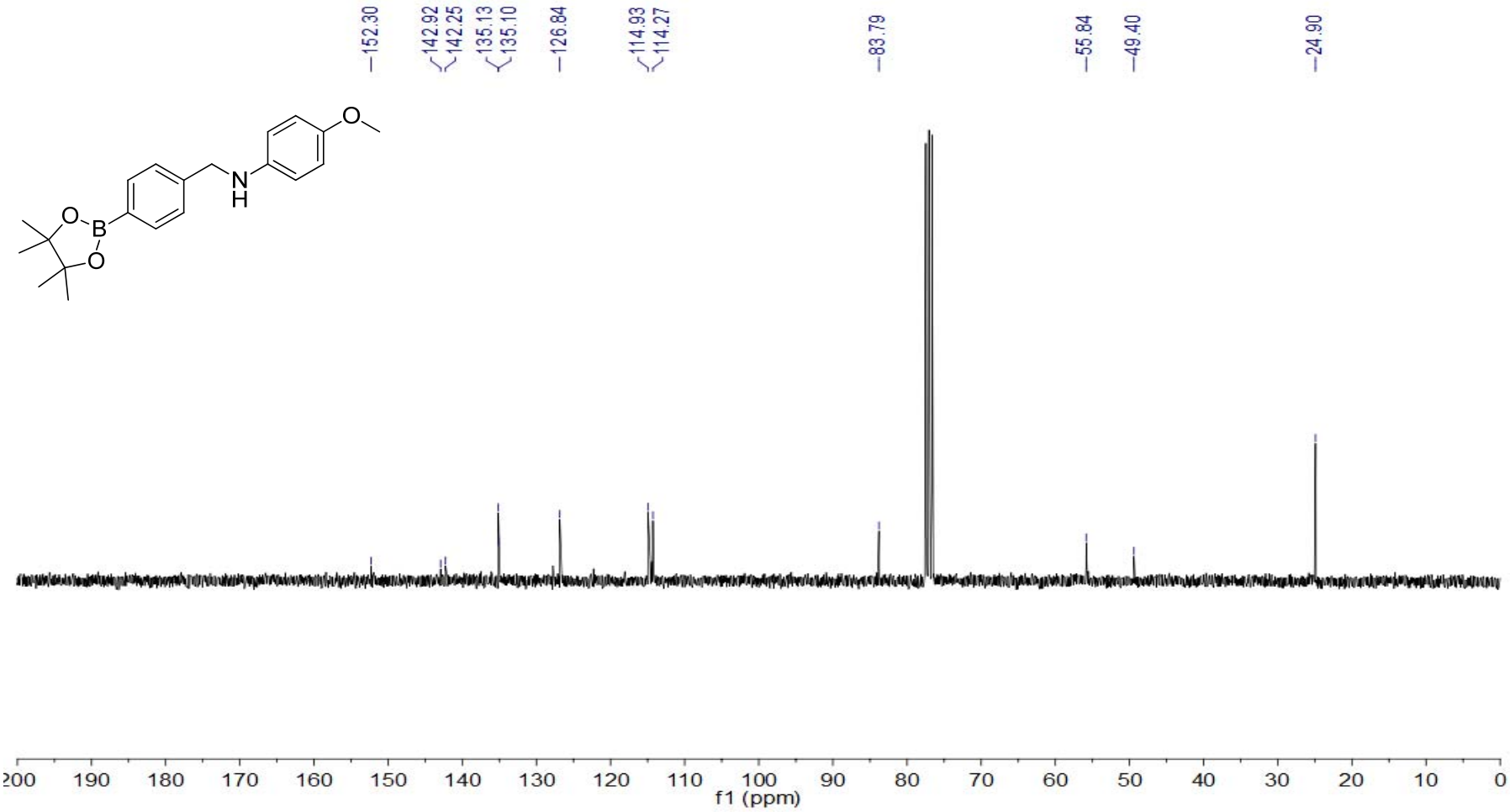
9



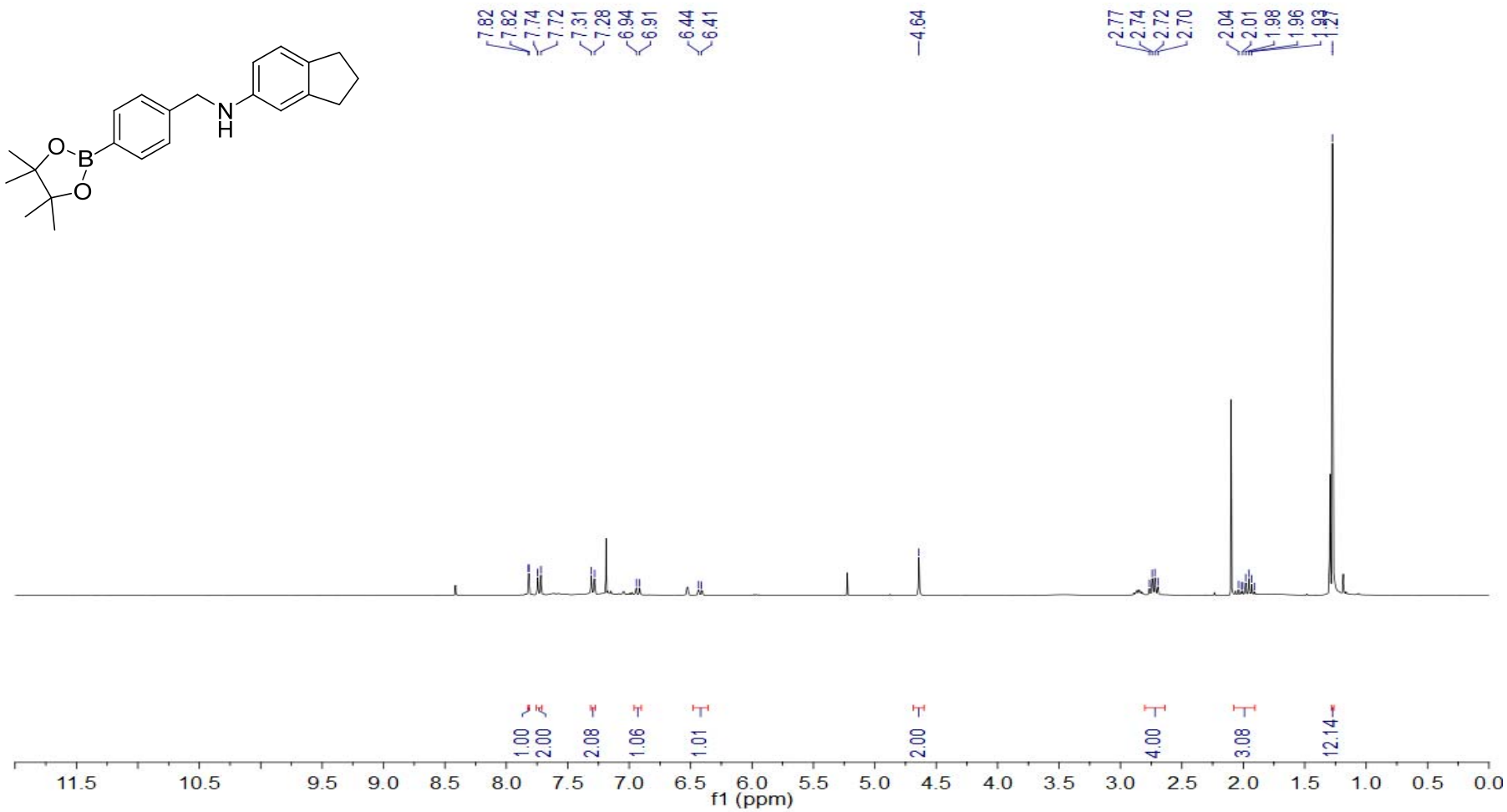
^{1}H NMR Spectra (300 MHz, $CDCl_3$, 25 °C) (Table 2, entry 1)



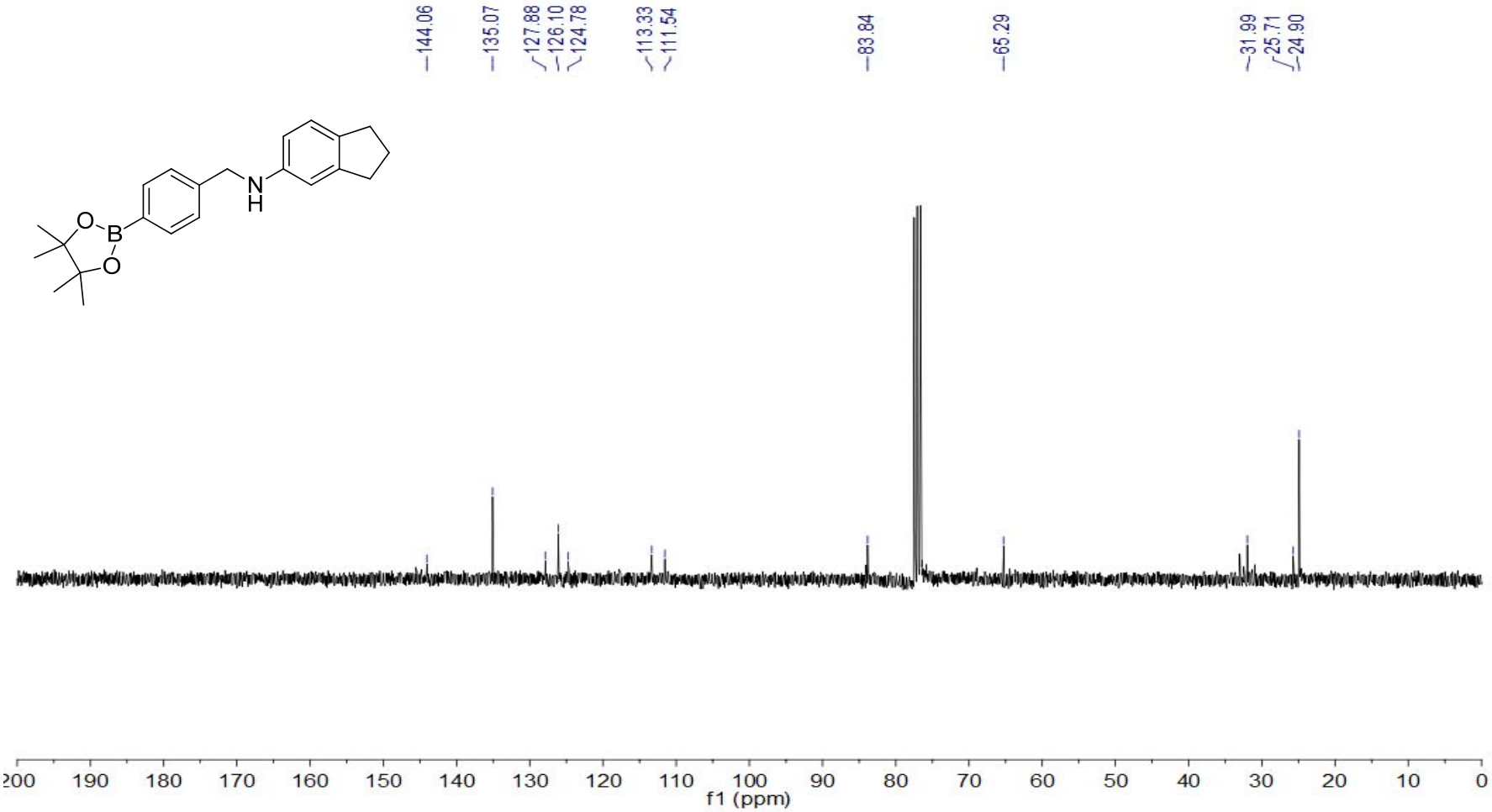
^{13}C NMR Spectra (75.5 MHz, $CDCl_3$, 25 °C) (Table 2, entry 1)



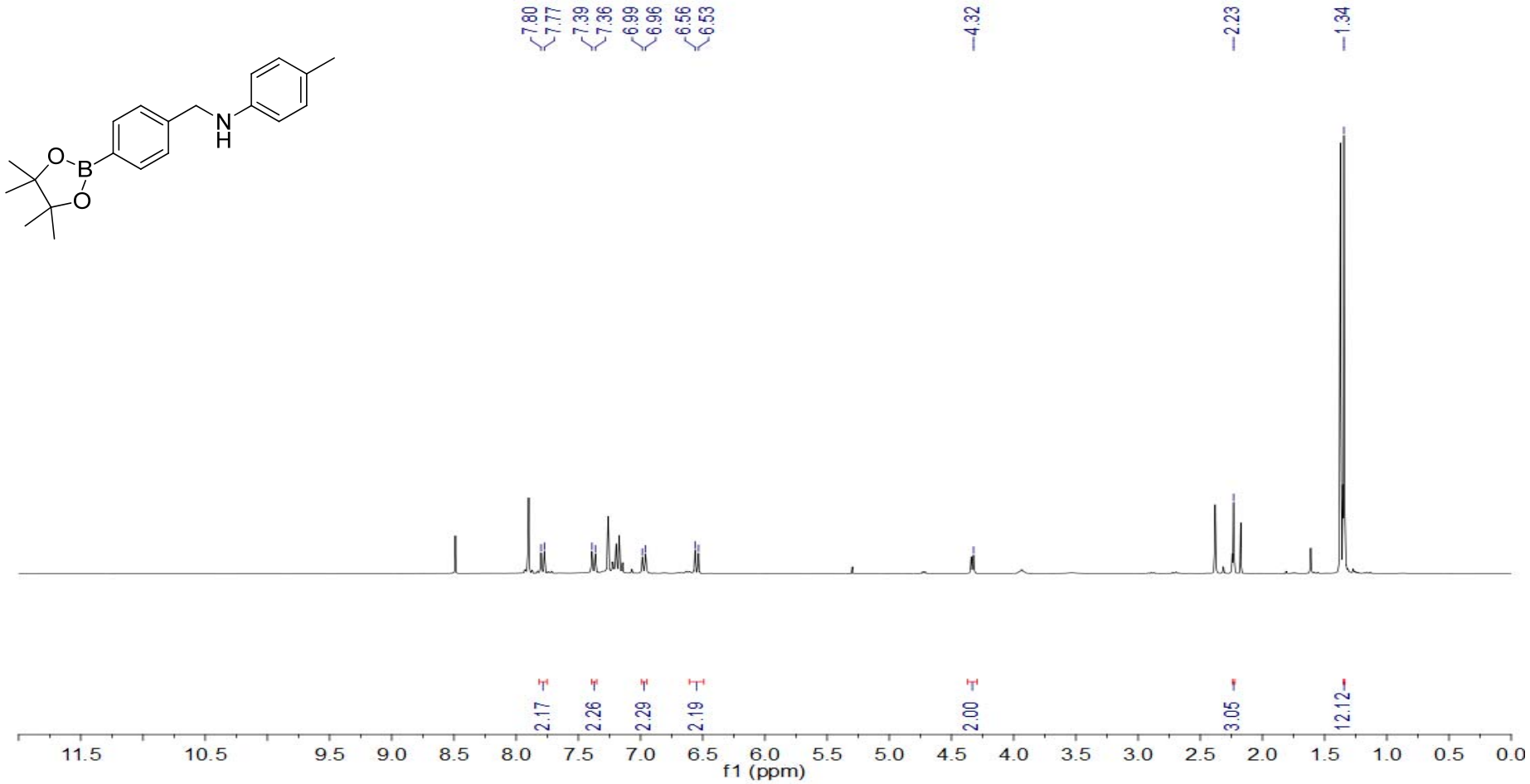
^{1}H NMR Spectra (300 MHz, $CDCl_3$, 25 °C) (Table 2, entry 2)



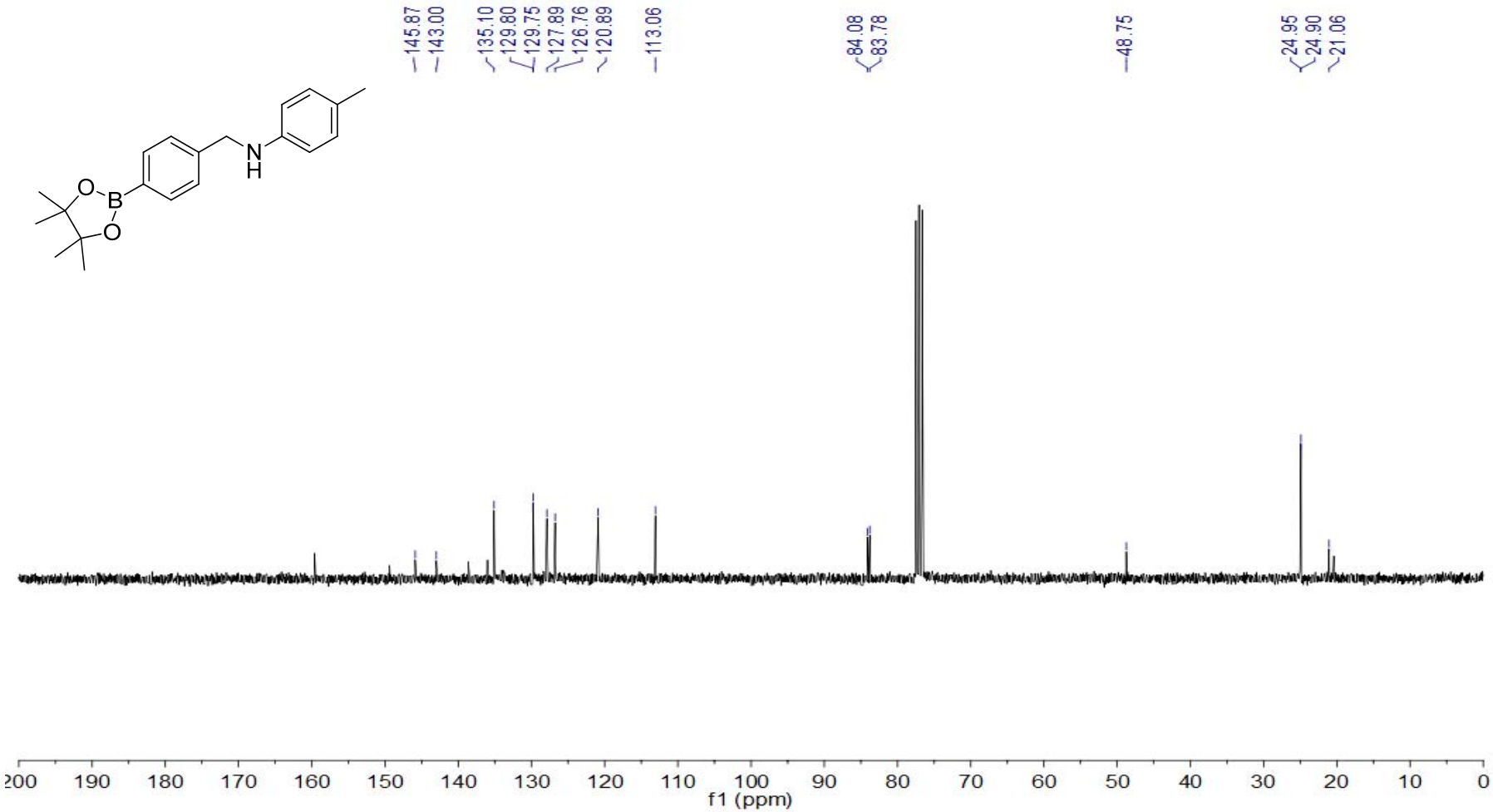
^{13}C NMR Spectra (75.5 MHz, $CDCl_3$, 25 °C) (Table 2, entry 2)



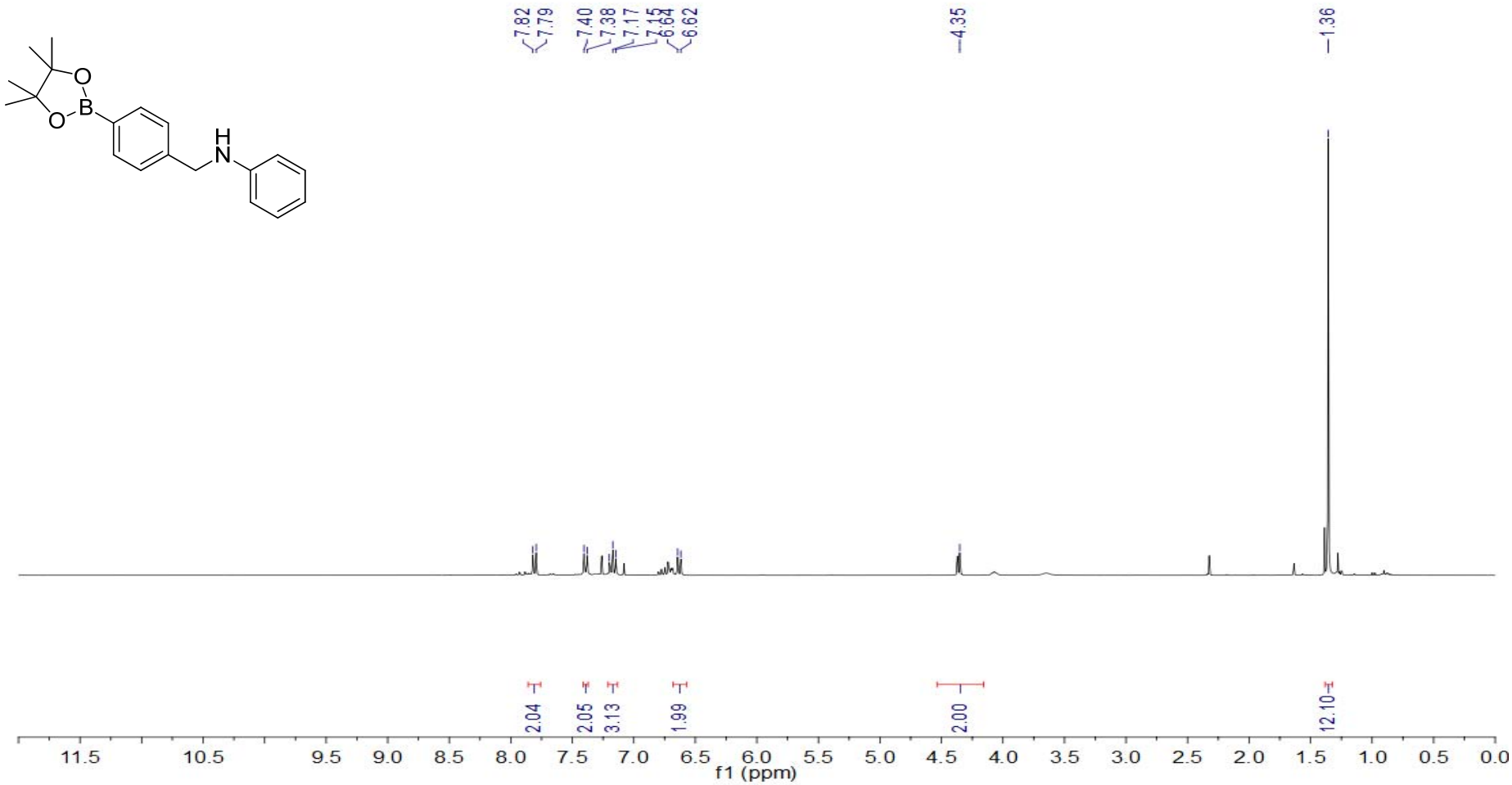
^{1}H NMR Spectra (300 MHz, $CDCl_3$, 25 °C) (Table 2, entry 3)



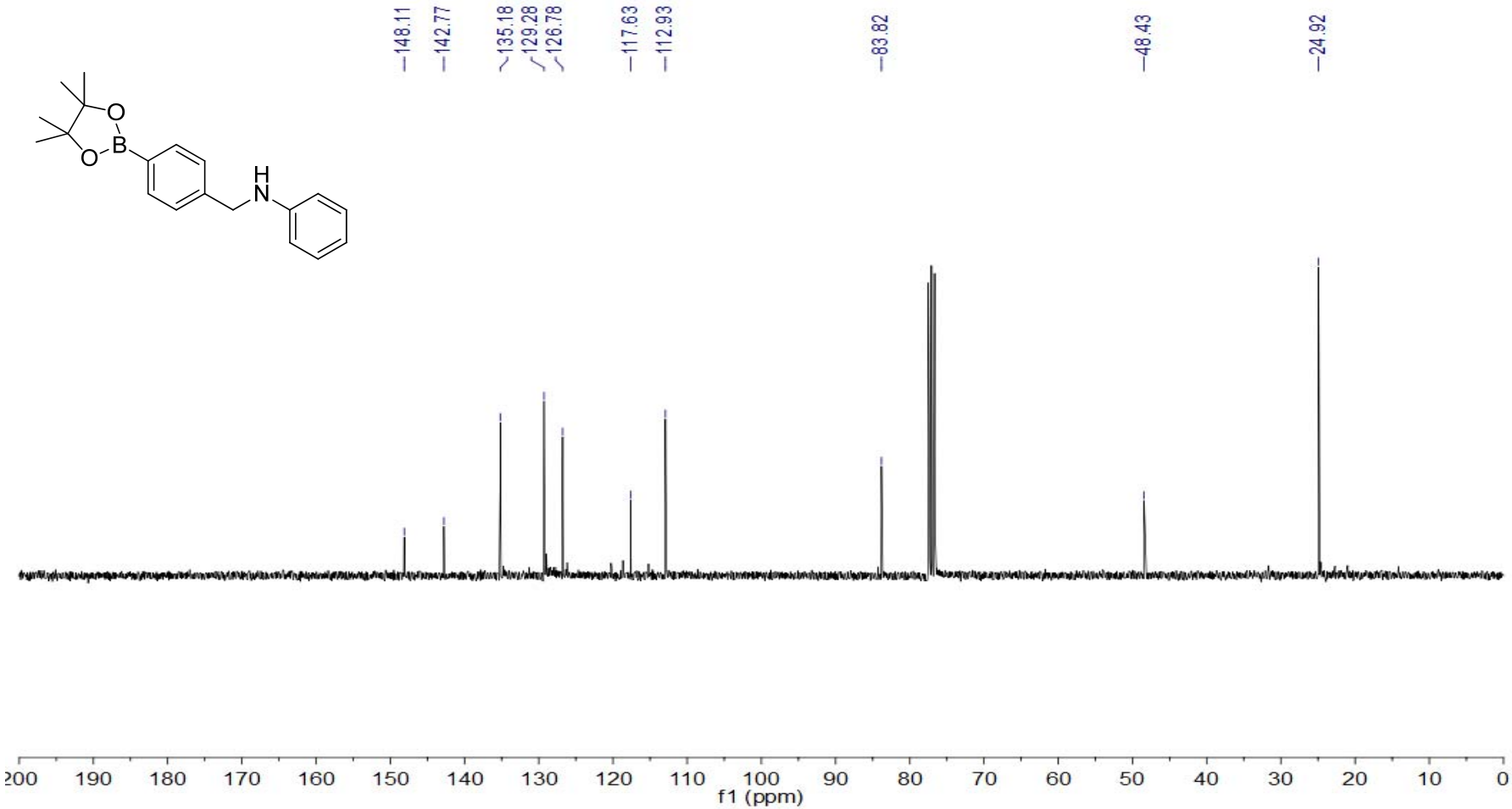
^{13}C NMR Spectra (75.5 MHz, $CDCl_3$, 25 °C) (Table 2, entry 3)



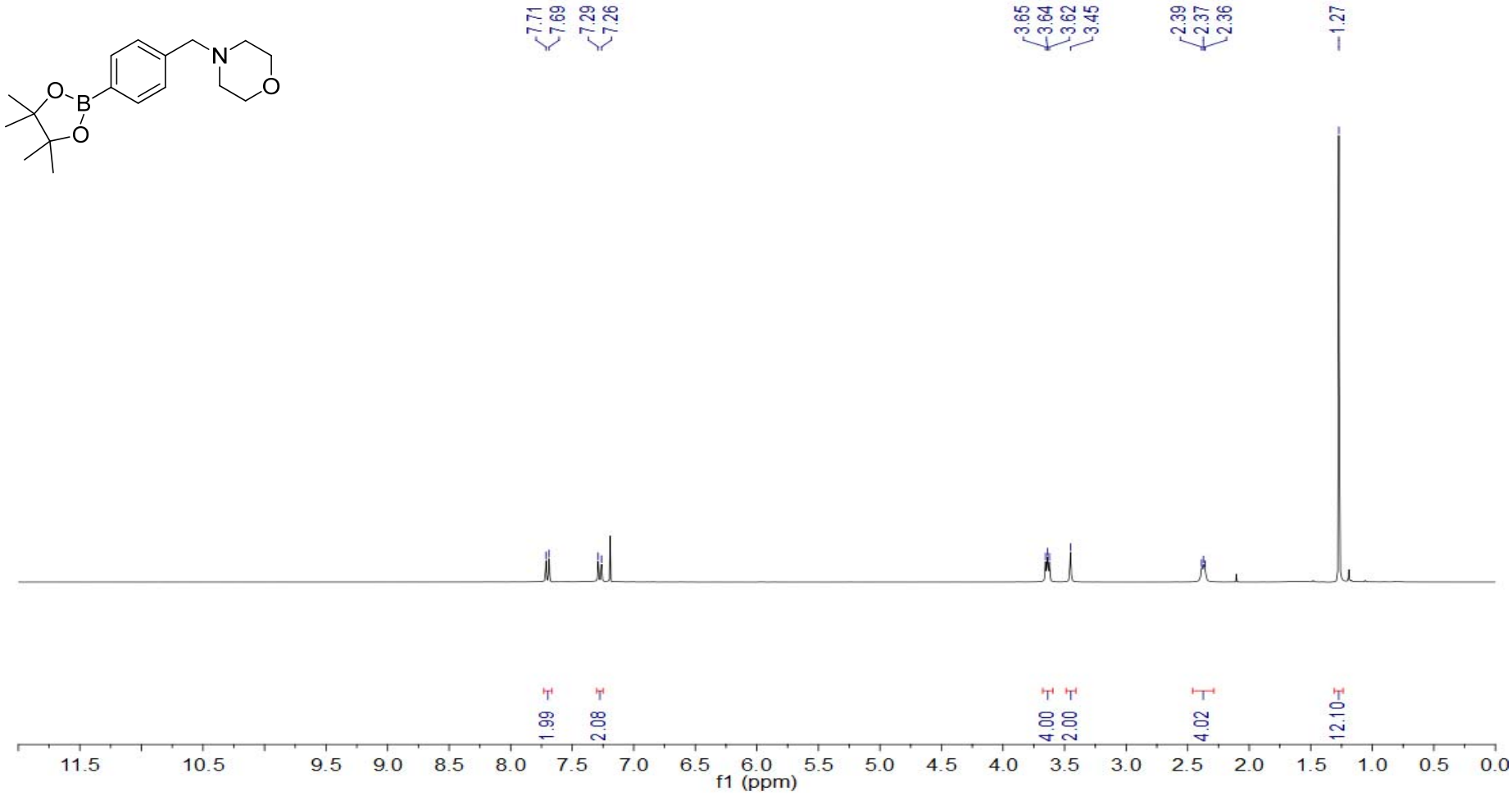
^{1}H NMR Spectra (300 MHz, $CDCl_3$, 25 °C) (Table 2, entry 4)



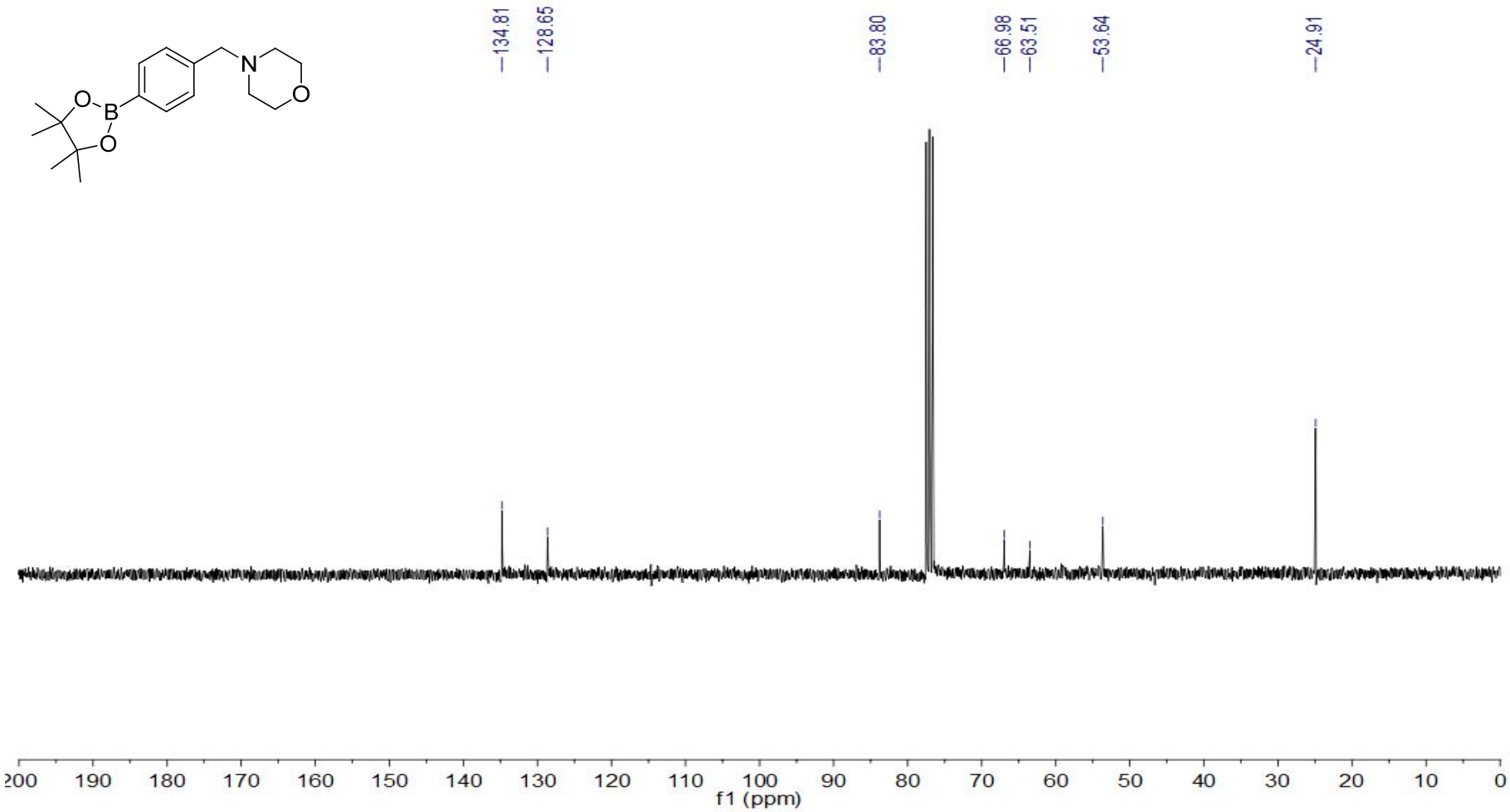
^{13}C NMR Spectra (75.5 MHz, $CDCl_3$, 25 °C) (Table 2, entry 4)



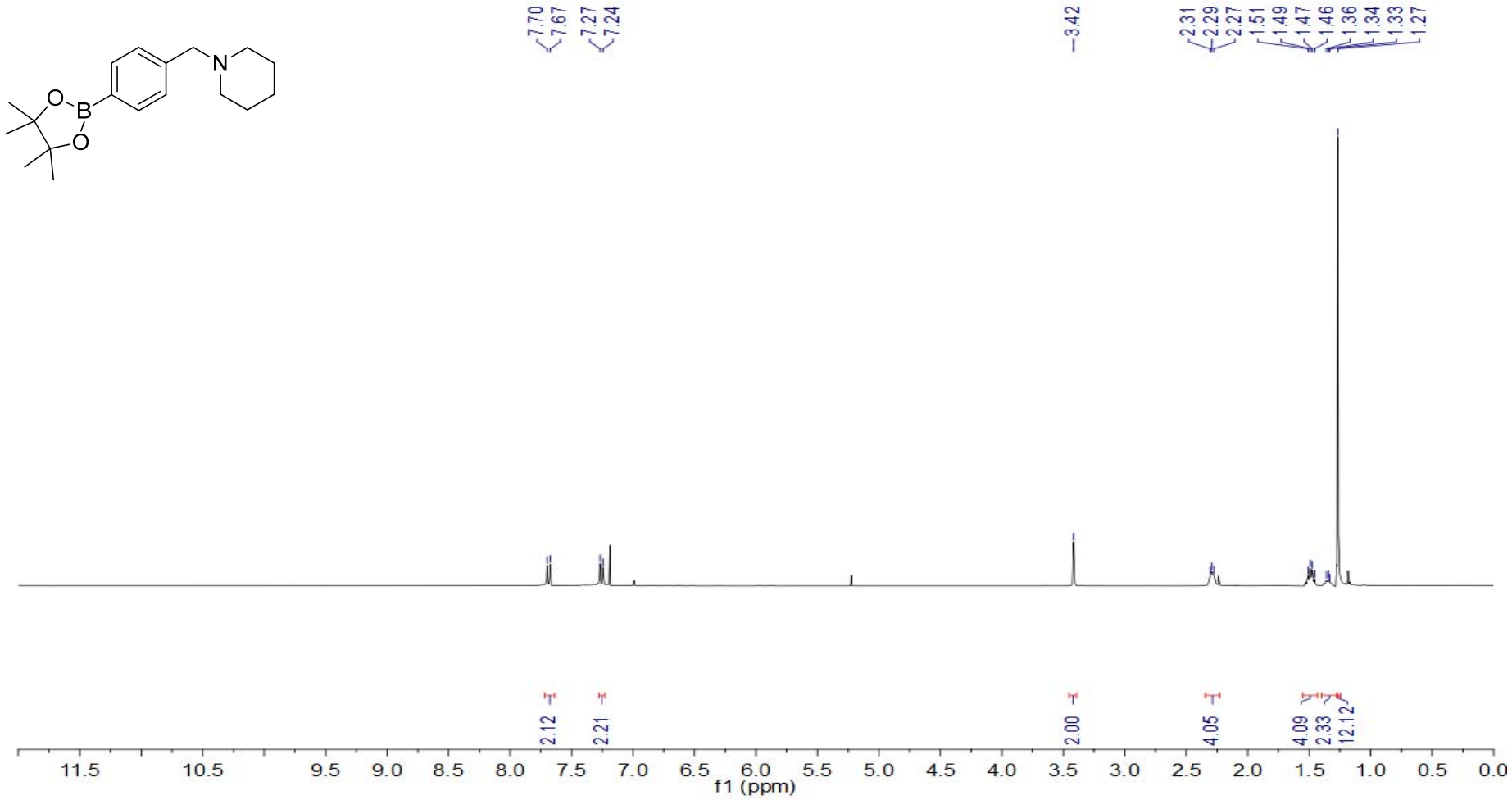
^{1}H NMR Spectra (300 MHz, $CDCl_3$, 25 °C) (Table 2, entry 6)



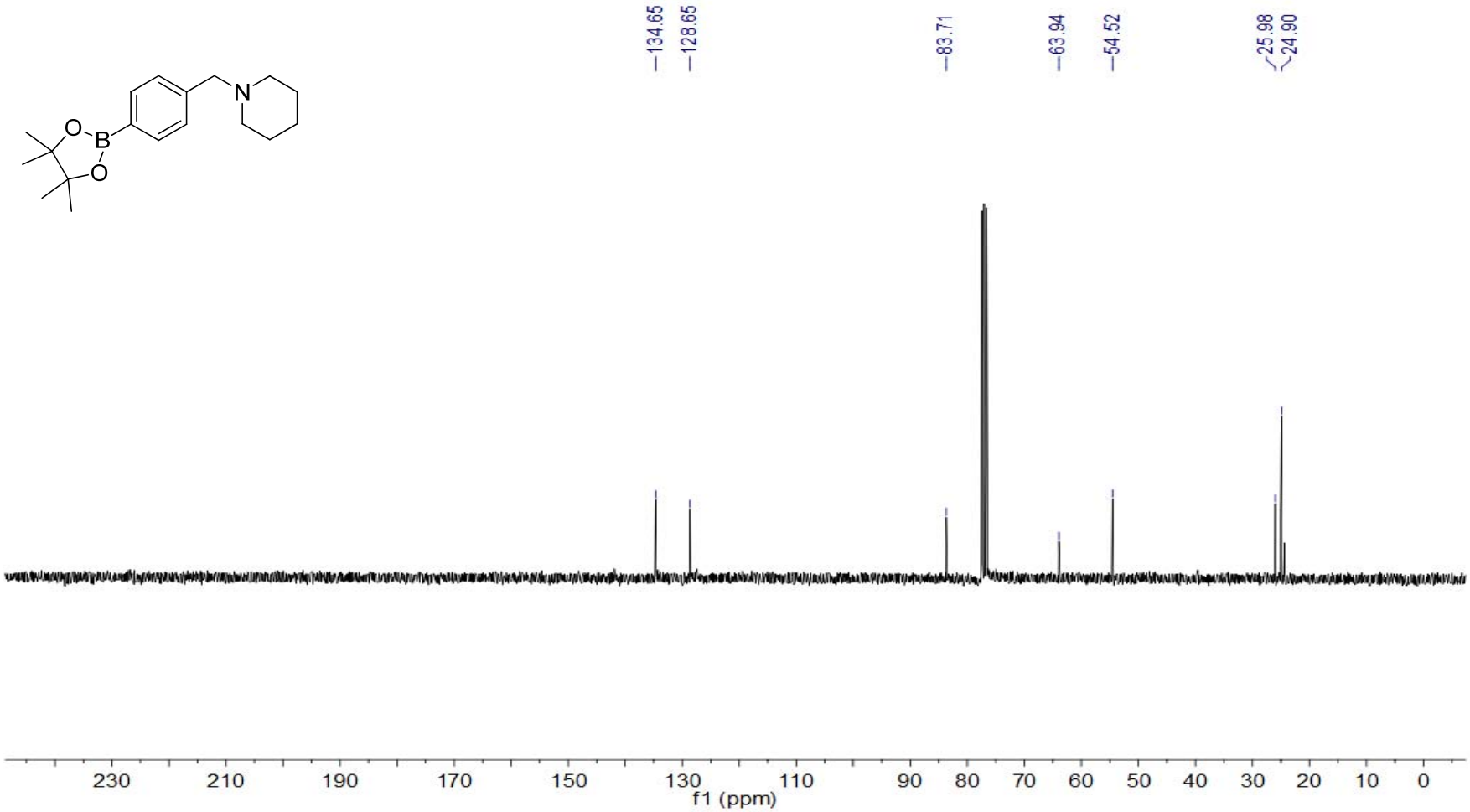
^{13}C NMR Spectra (75.5 MHz, $CDCl_3$, 25 °C) (Table 2, entry 6)



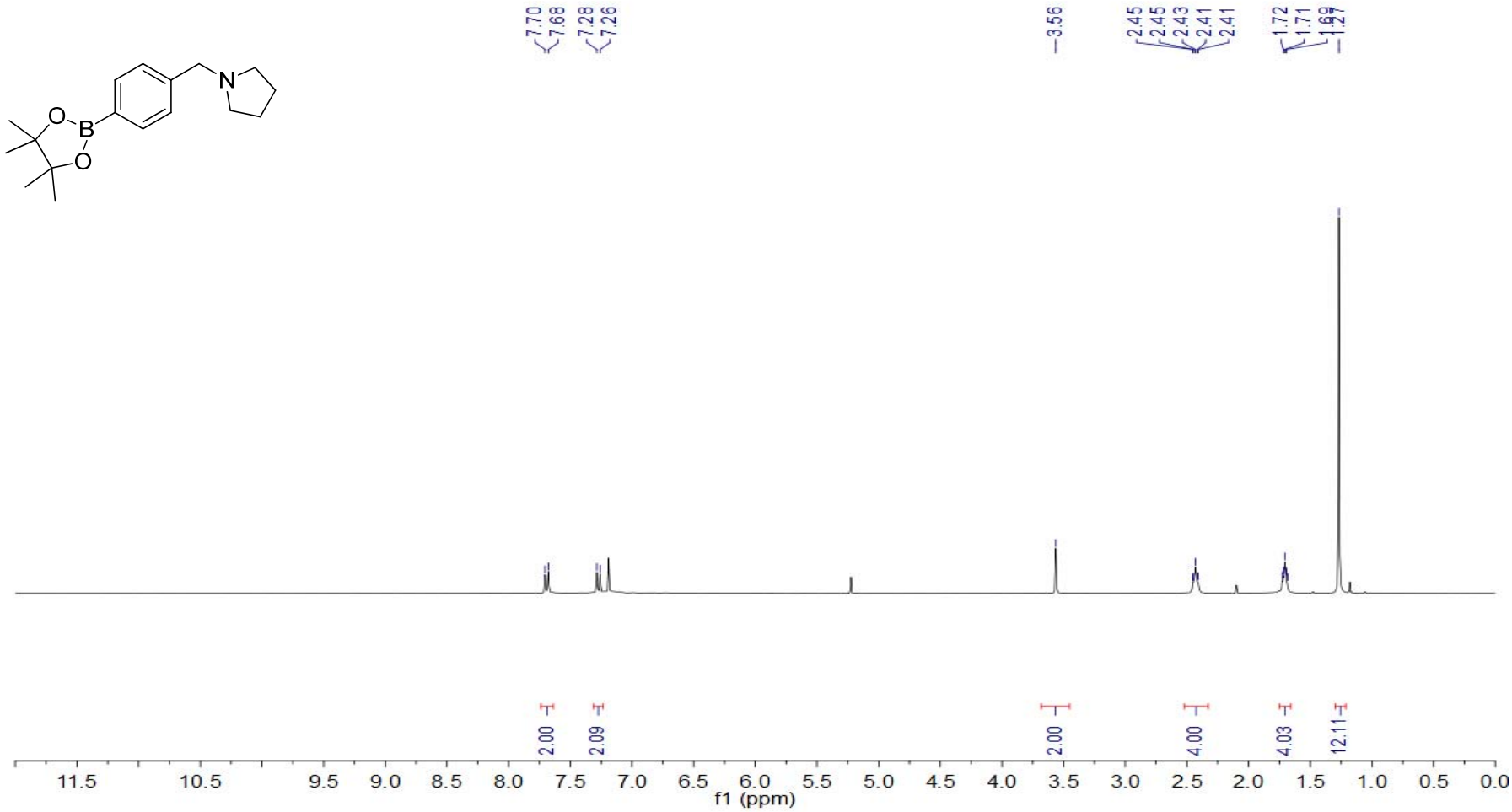
^{1}H NMR Spectra (300 MHz, $CDCl_3$, 25 °C) (Table 2, entry 7)



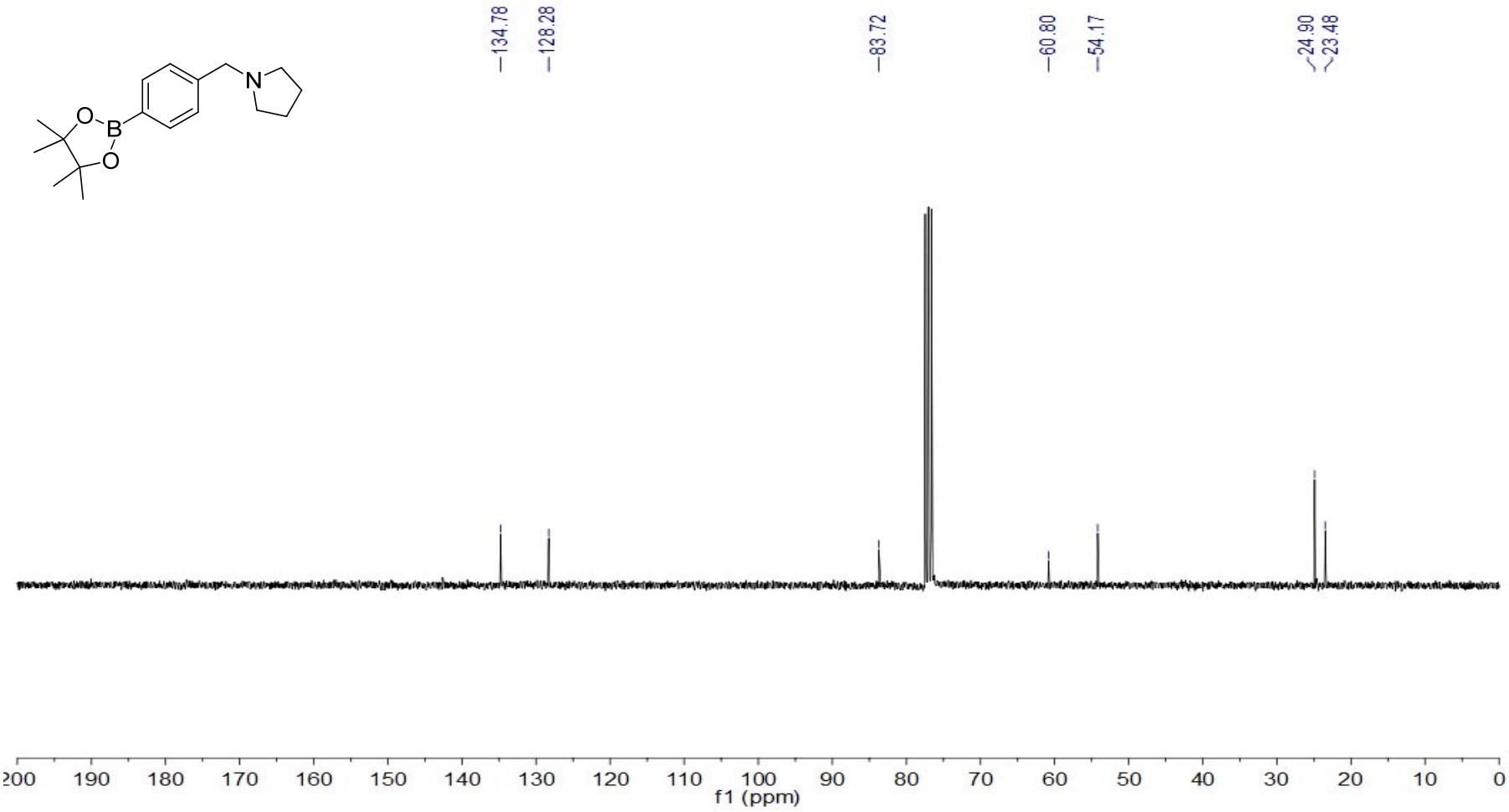
^{13}CNMR Spectra (75.5 MHz, $CDCl_3$, 25 °C) (Table 2, entry 7)



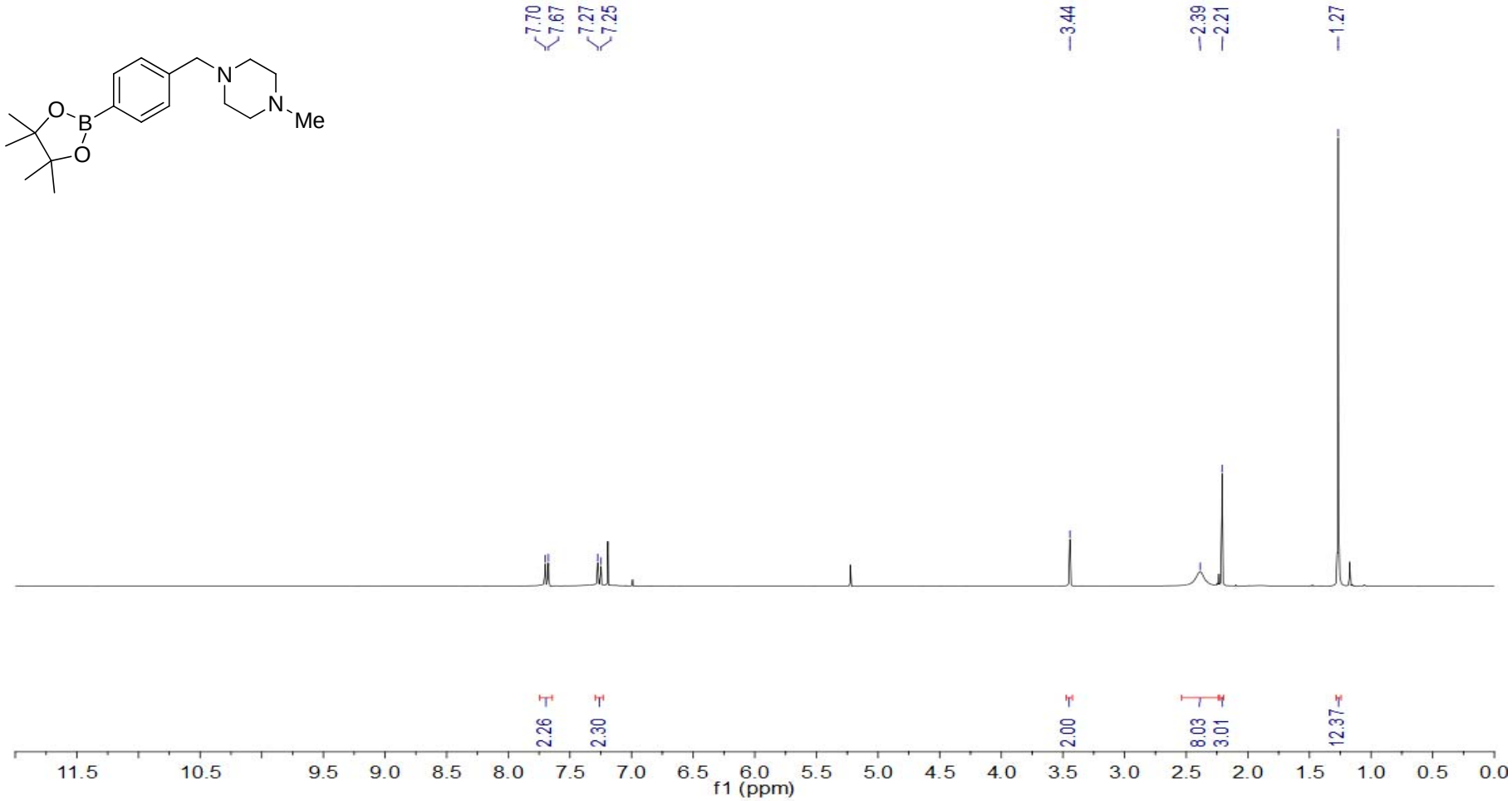
^{1}H NMR Spectra (300 MHz, $CDCl_3$, 25 °C) (Table 2, entry 8)



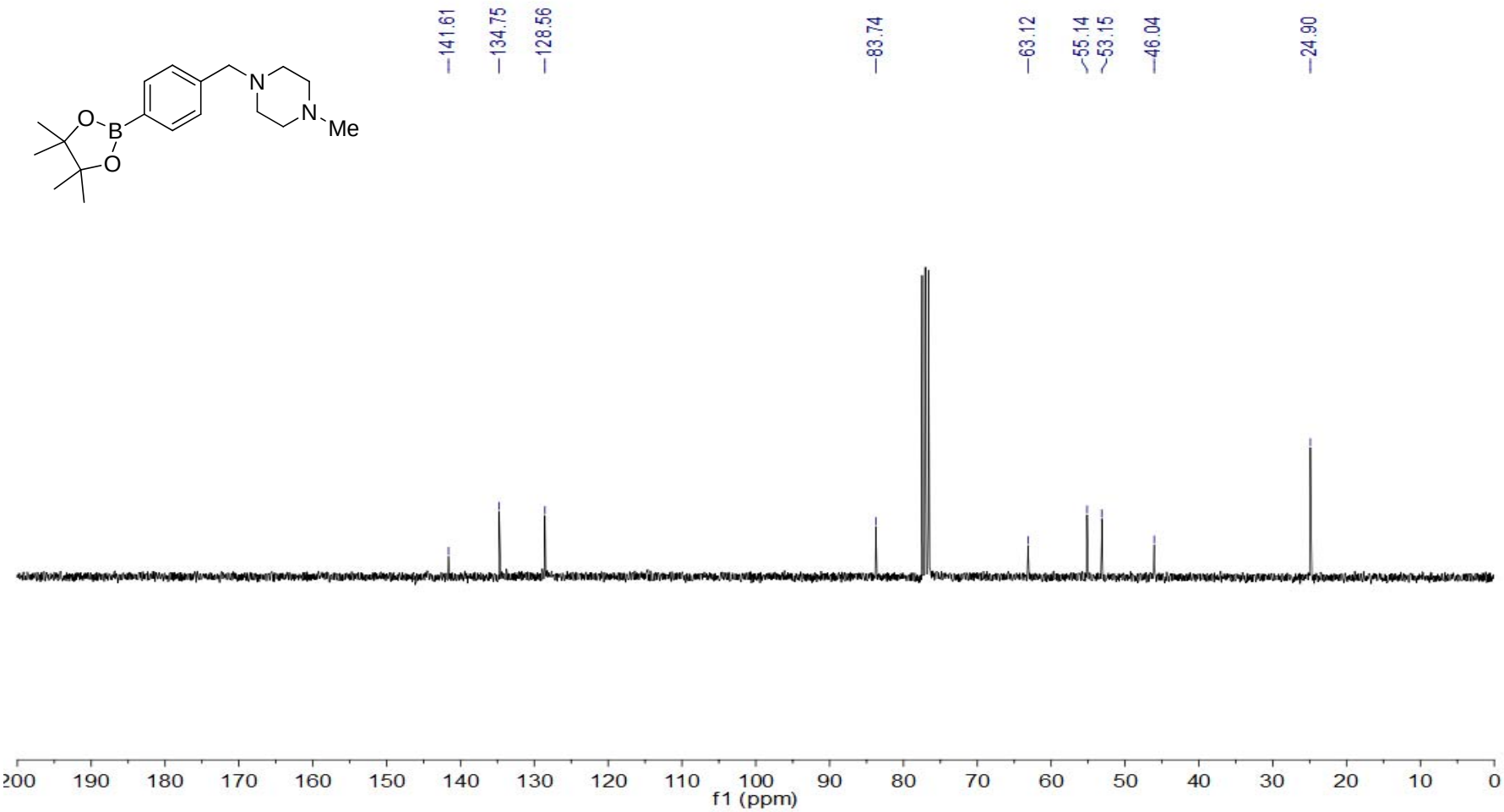
^{13}C NMR Spectra (75.5 MHz, $CDCl_3$, 25 °C) (Table 2, entry 8)



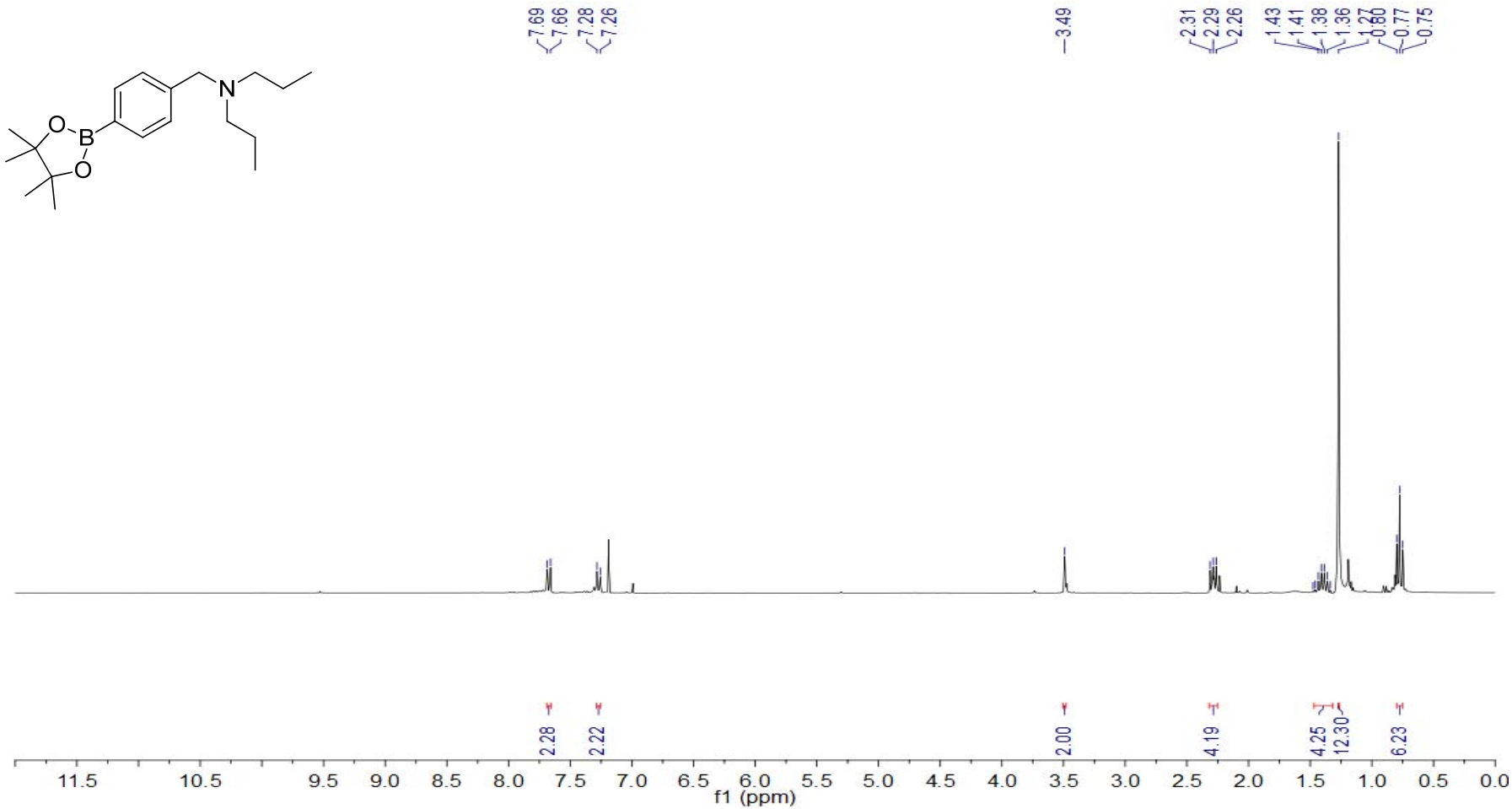
^{1}H NMR Spectra (300 MHz, $CDCl_3$, 25 °C) (Table 2, entry 9)



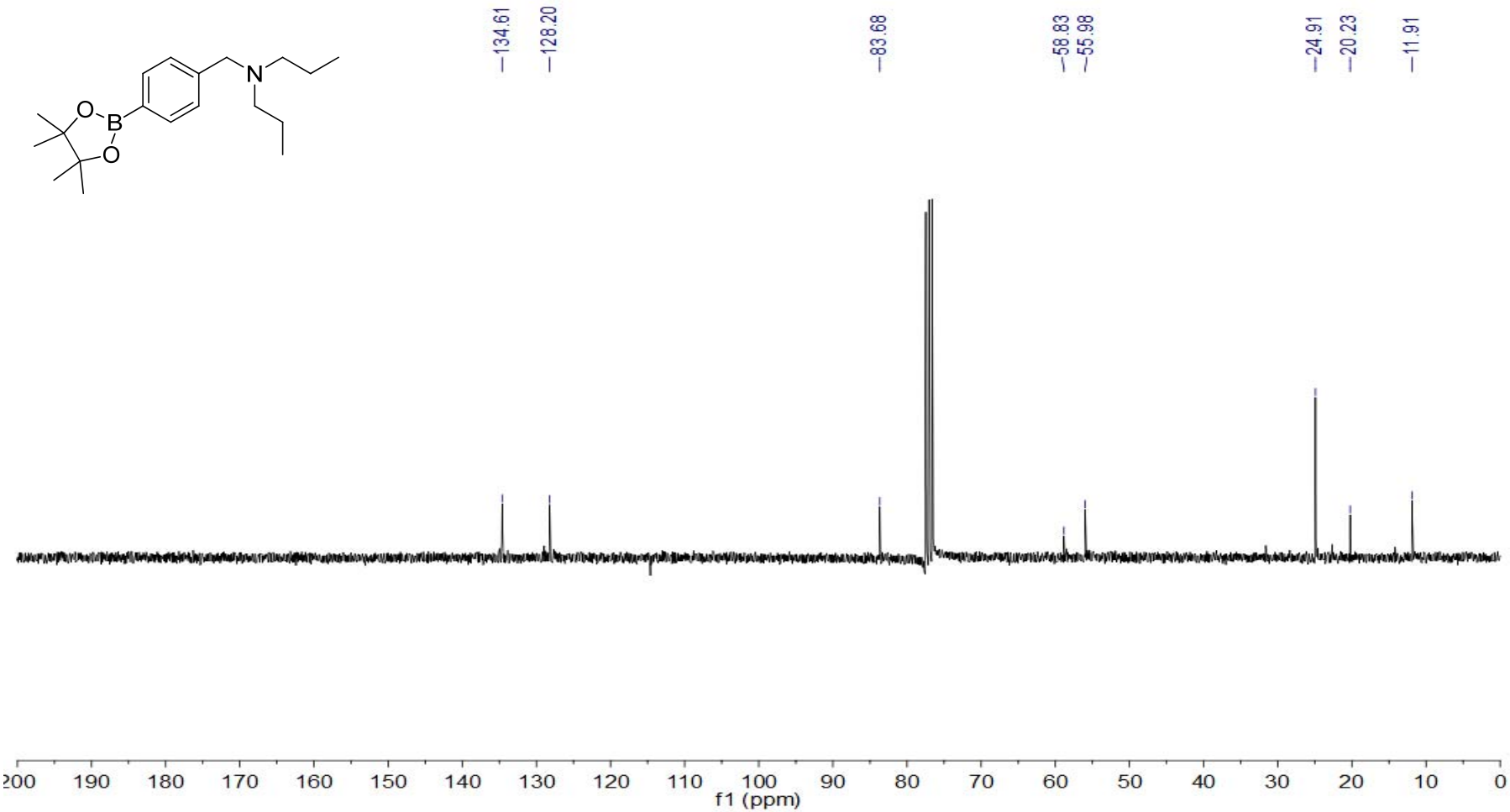
^{13}C NMR Spectra (75.5 MHz, $CDCl_3$, 25 °C) (Table 2, entry 9)



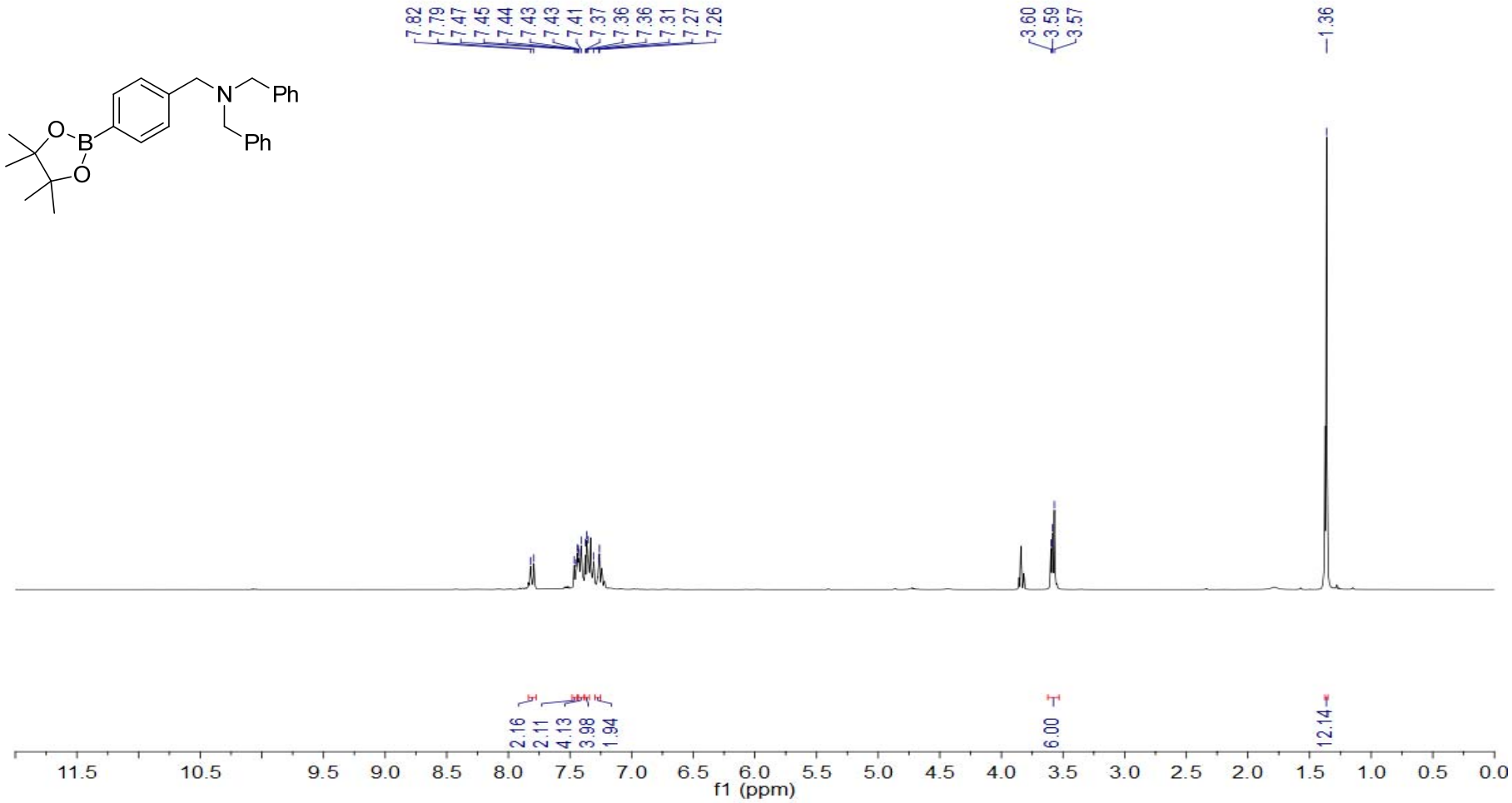
^{1}H NMR Spectra (300 MHz, $CDCl_3$, 25 °C) (Table 2, entry 10)



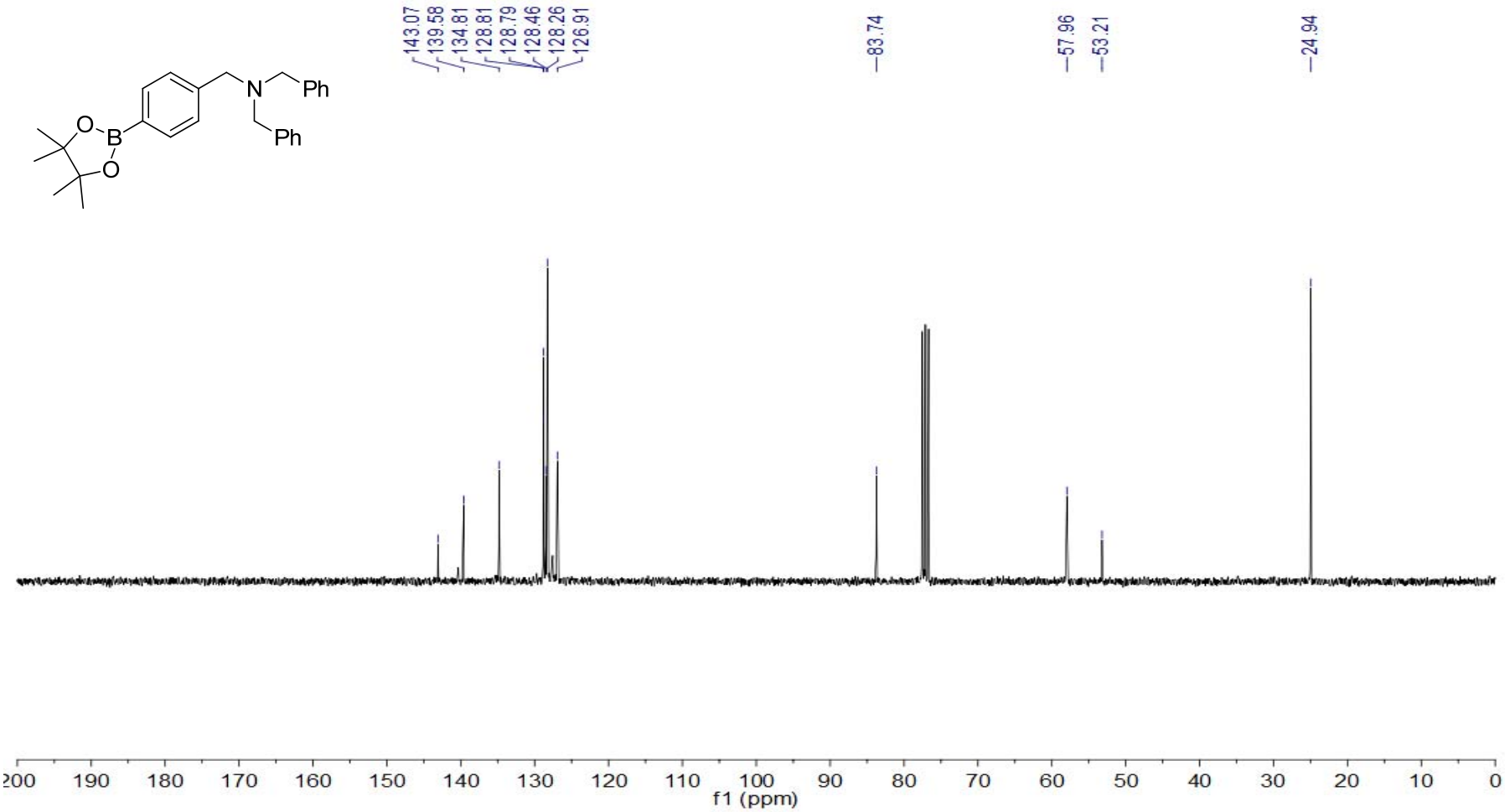
^{13}C NMR Spectra (75.5 MHz, $CDCl_3$, 25 °C) (Table 2, entry 10)



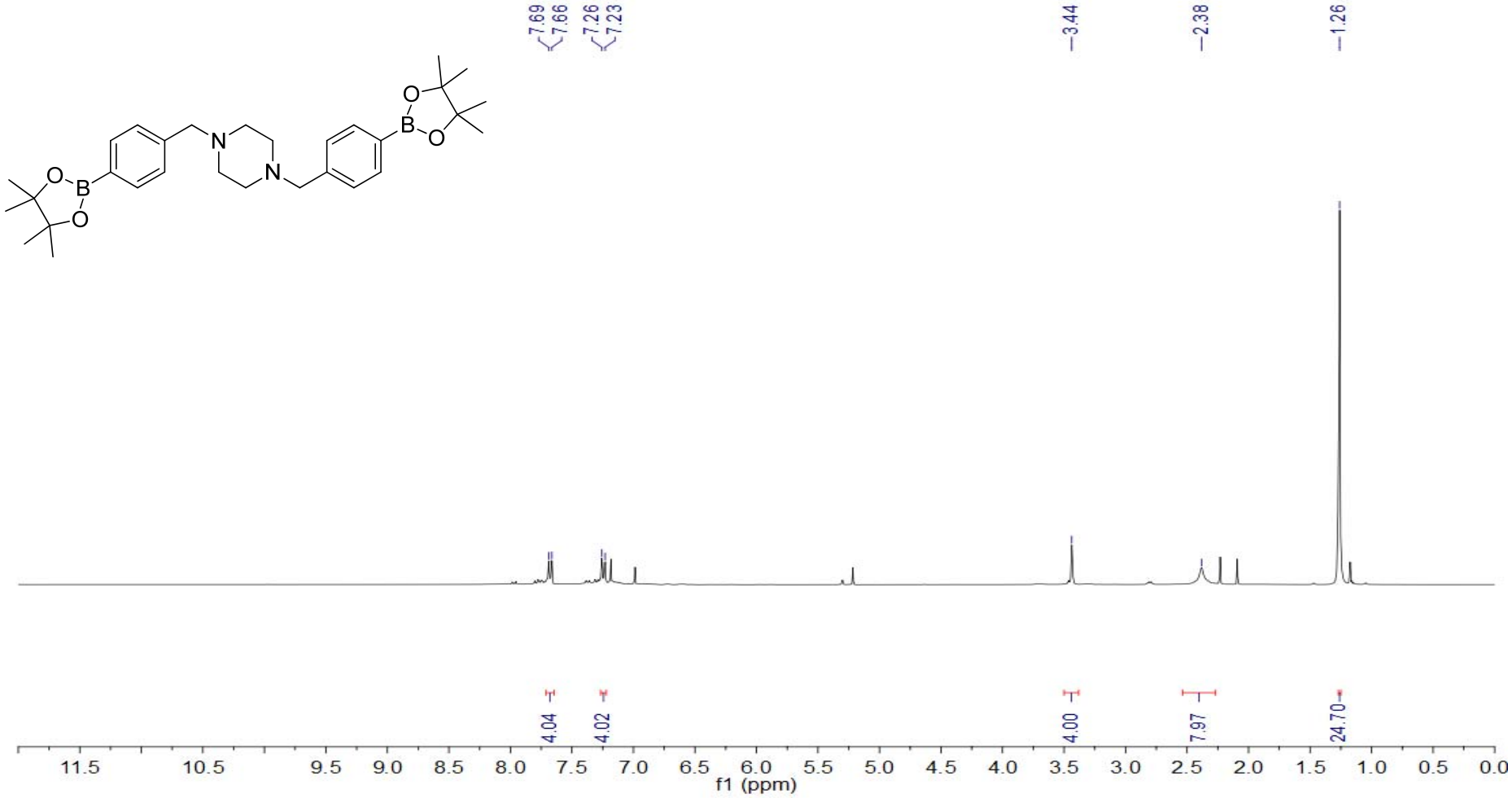
^{1}H NMR Spectra (300 MHz, $CDCl_3$, 25 °C) (Table 2, entry 11)



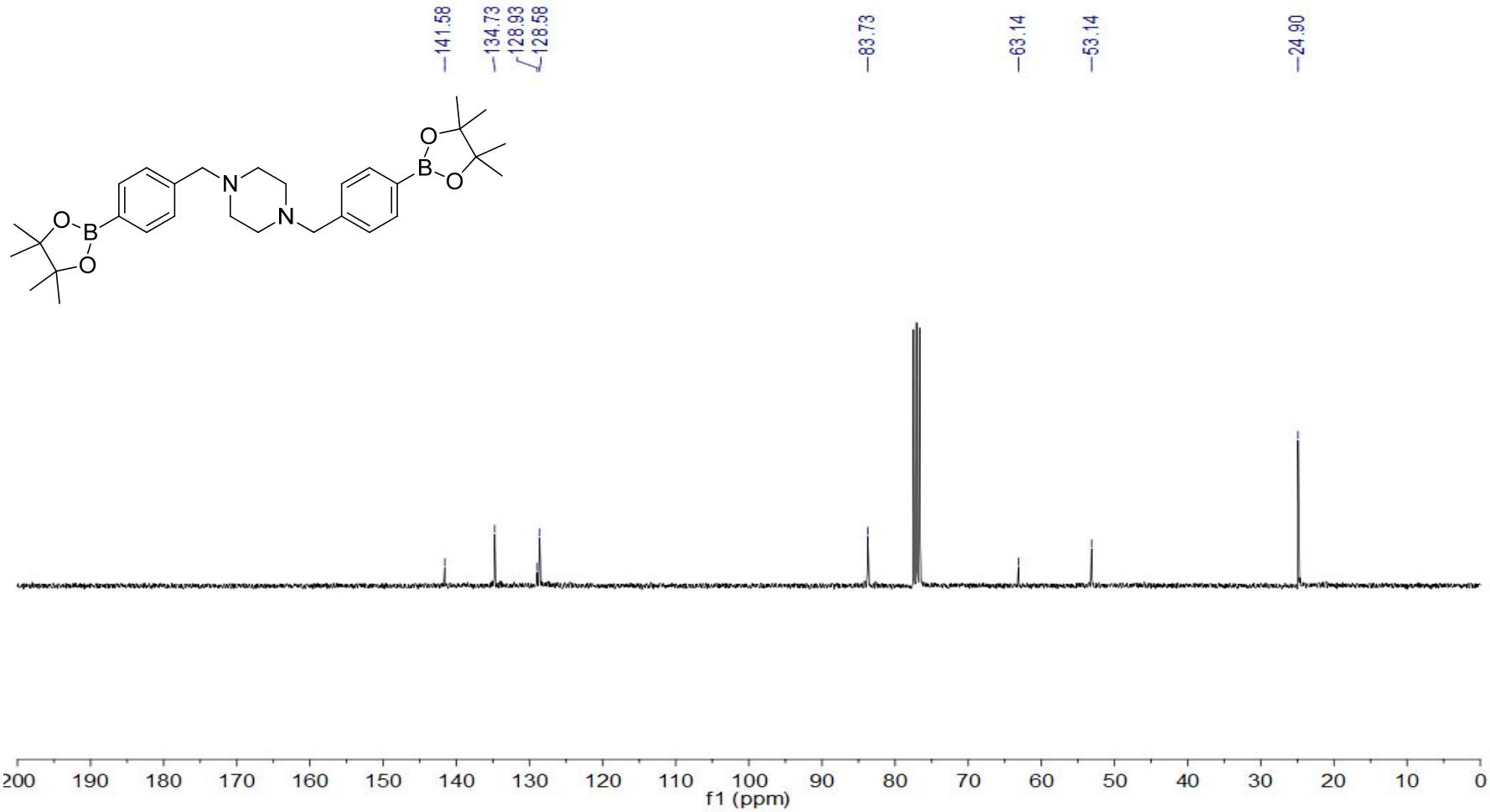
^{13}C NMR Spectra (75.5 MHz, $CDCl_3$, 25 °C) (Table 2, entry 11)



^{1}H NMR Spectra (300 MHz, $CDCl_3$, 25 °C) (Table 2, entry 12)



^{13}C NMR Spectra (75.5 MHz, $CDCl_3$, 25 °C) (Table 2, entry 12)



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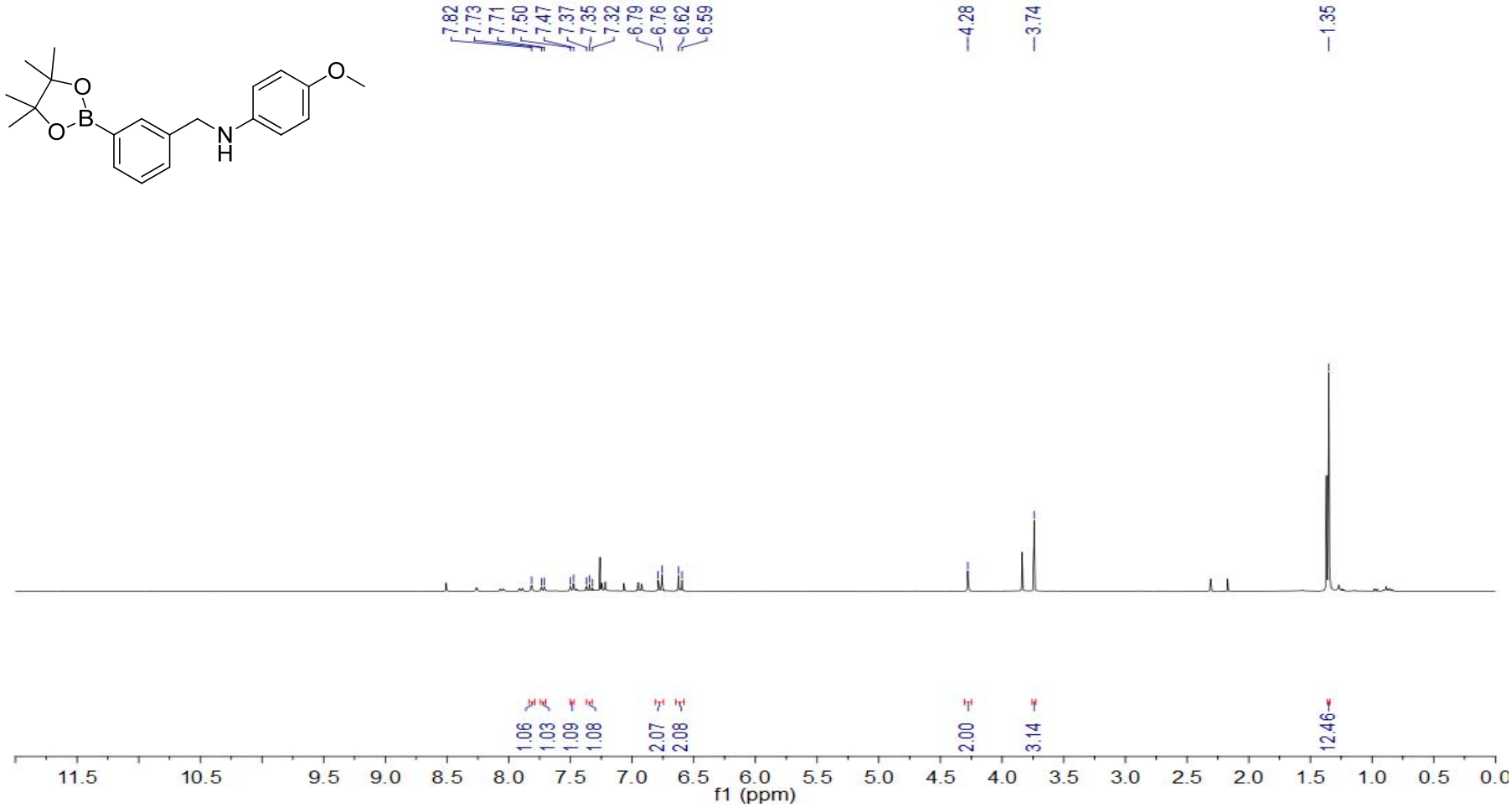
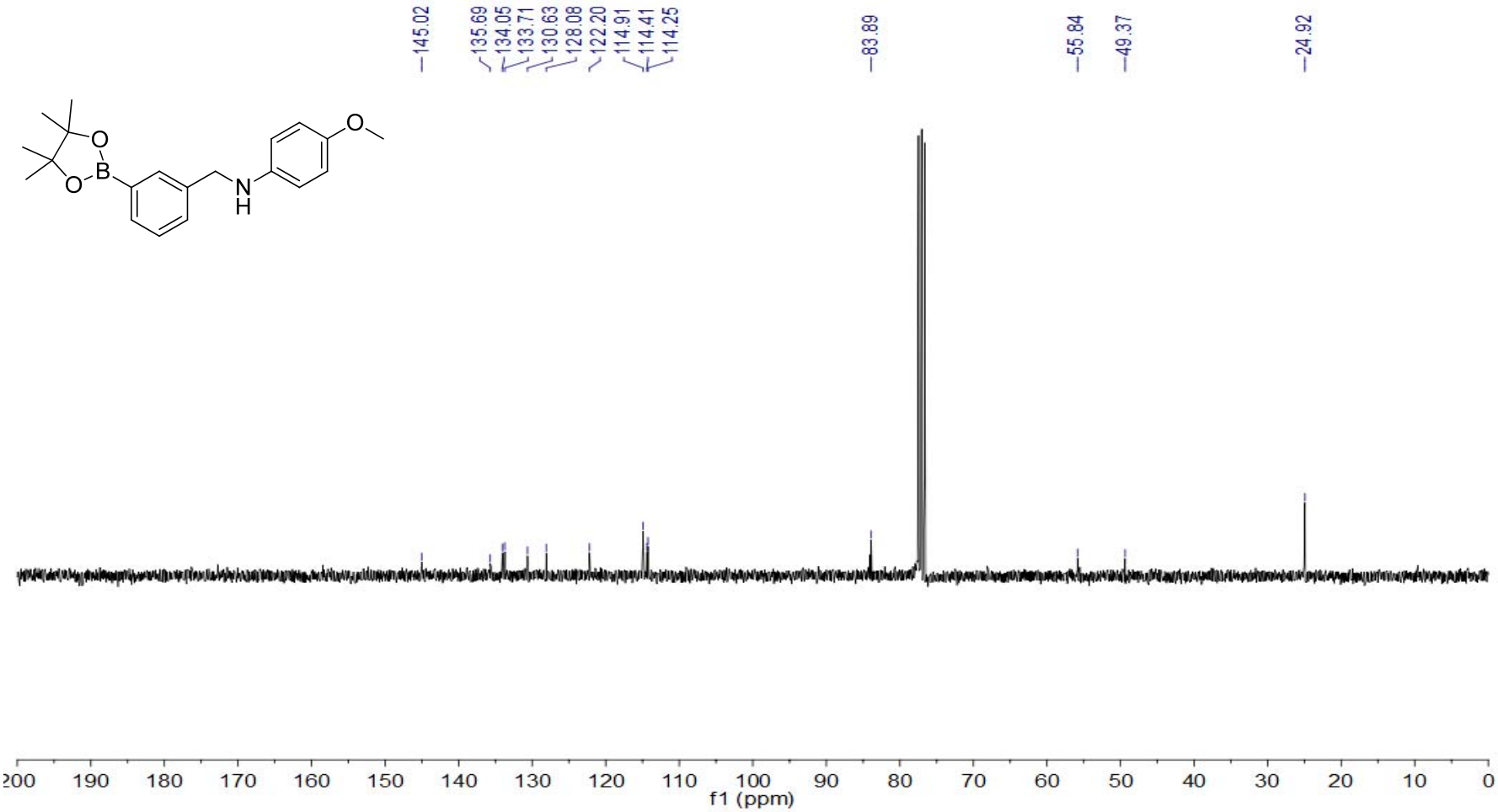
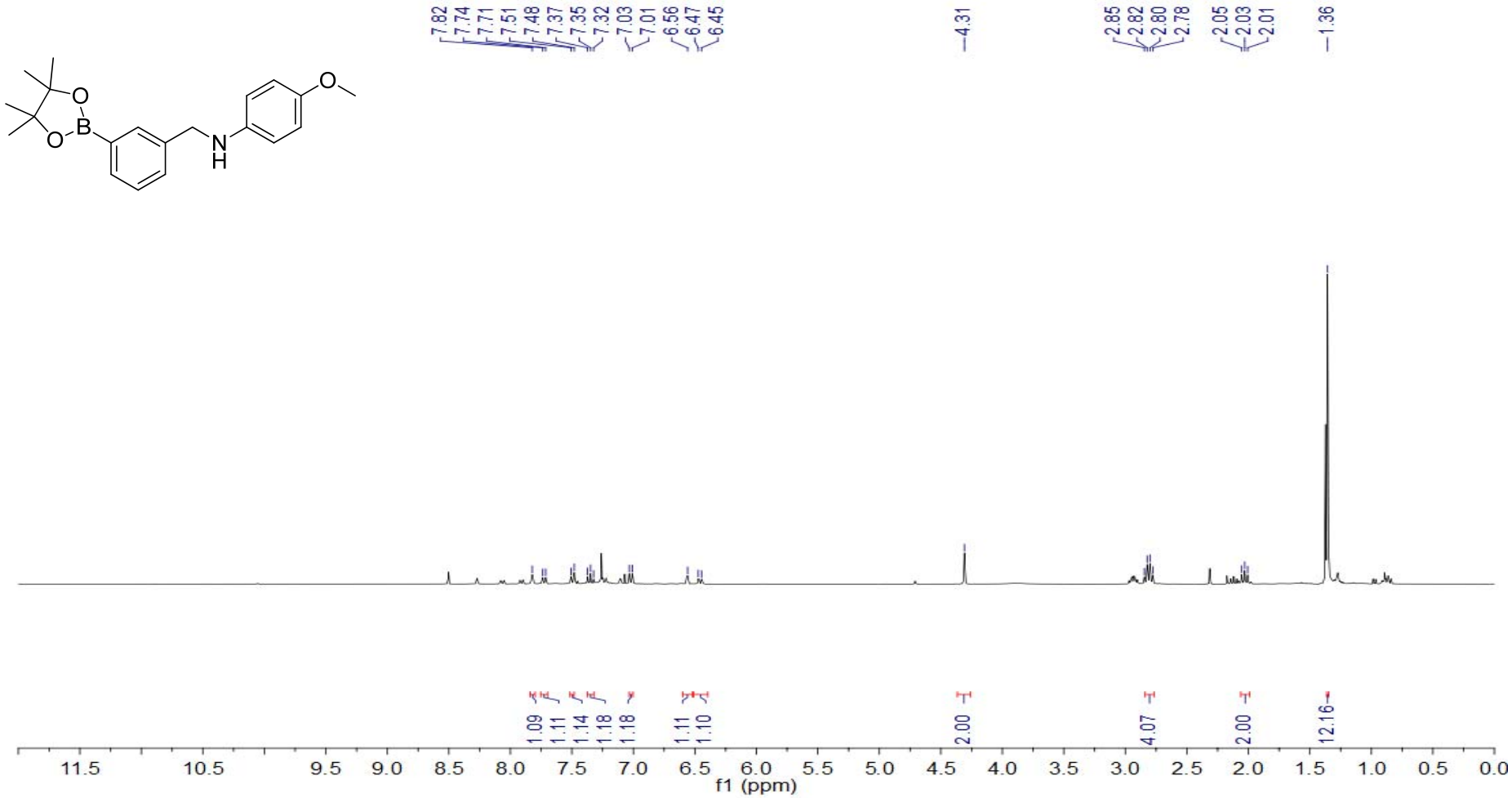


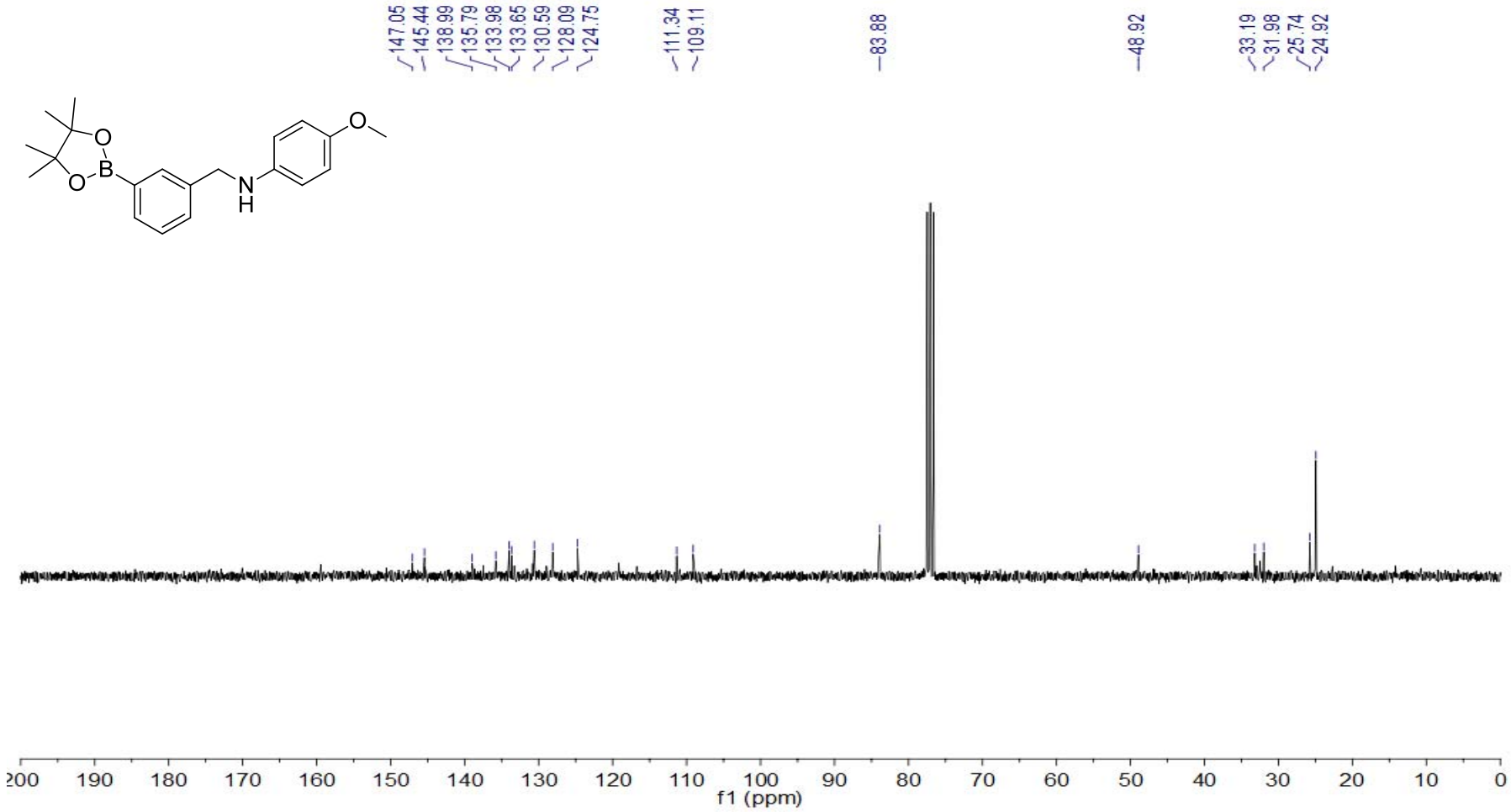
^{13}C NMR Spectra (75.5 MHz, $CDCl_3$, 25 °C) (Table 3, entry 1)



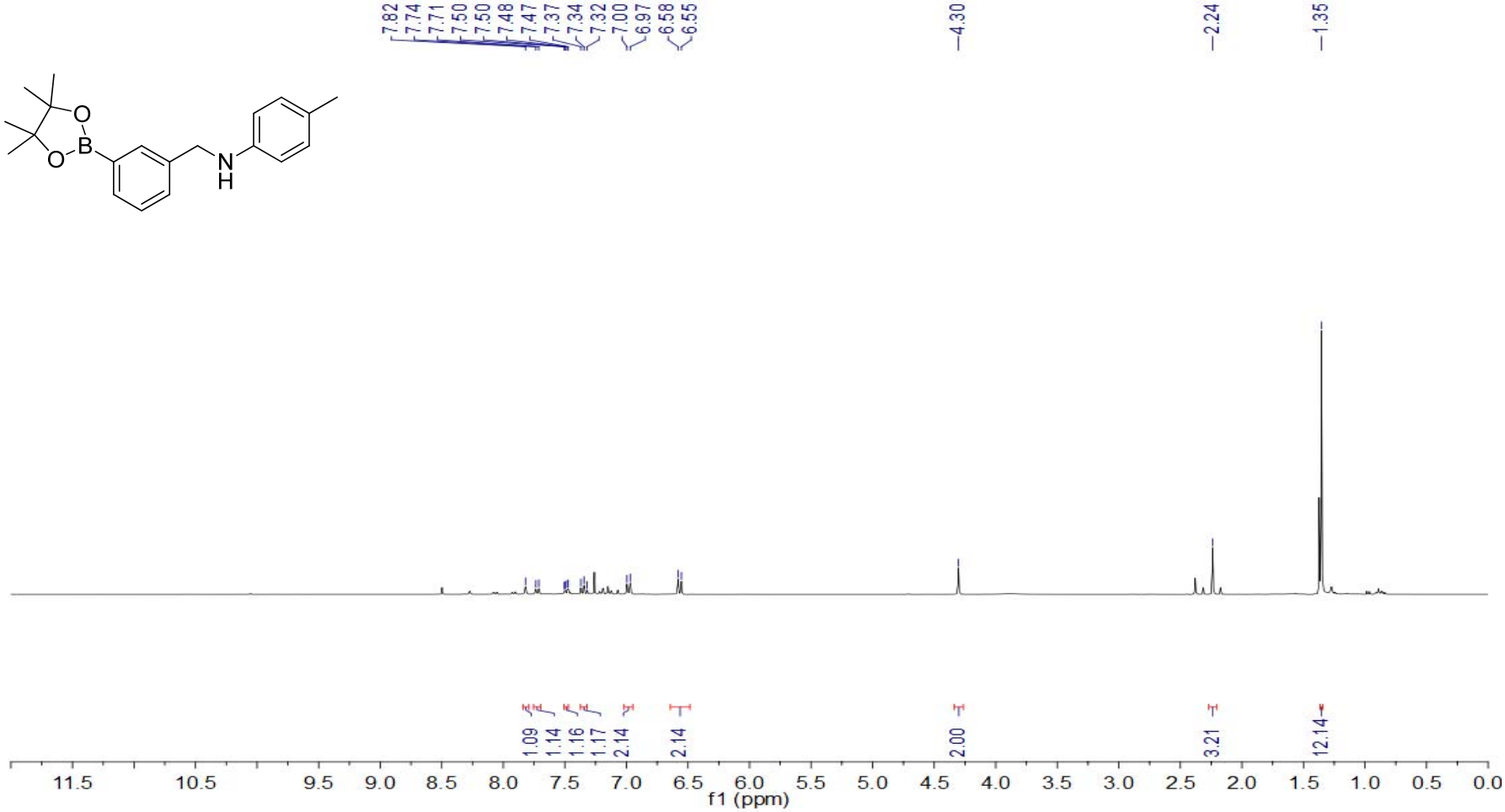
^{1}H NMR Spectra (300 MHz, $CDCl_3$, 25 °C) (Table 3, entry 2)



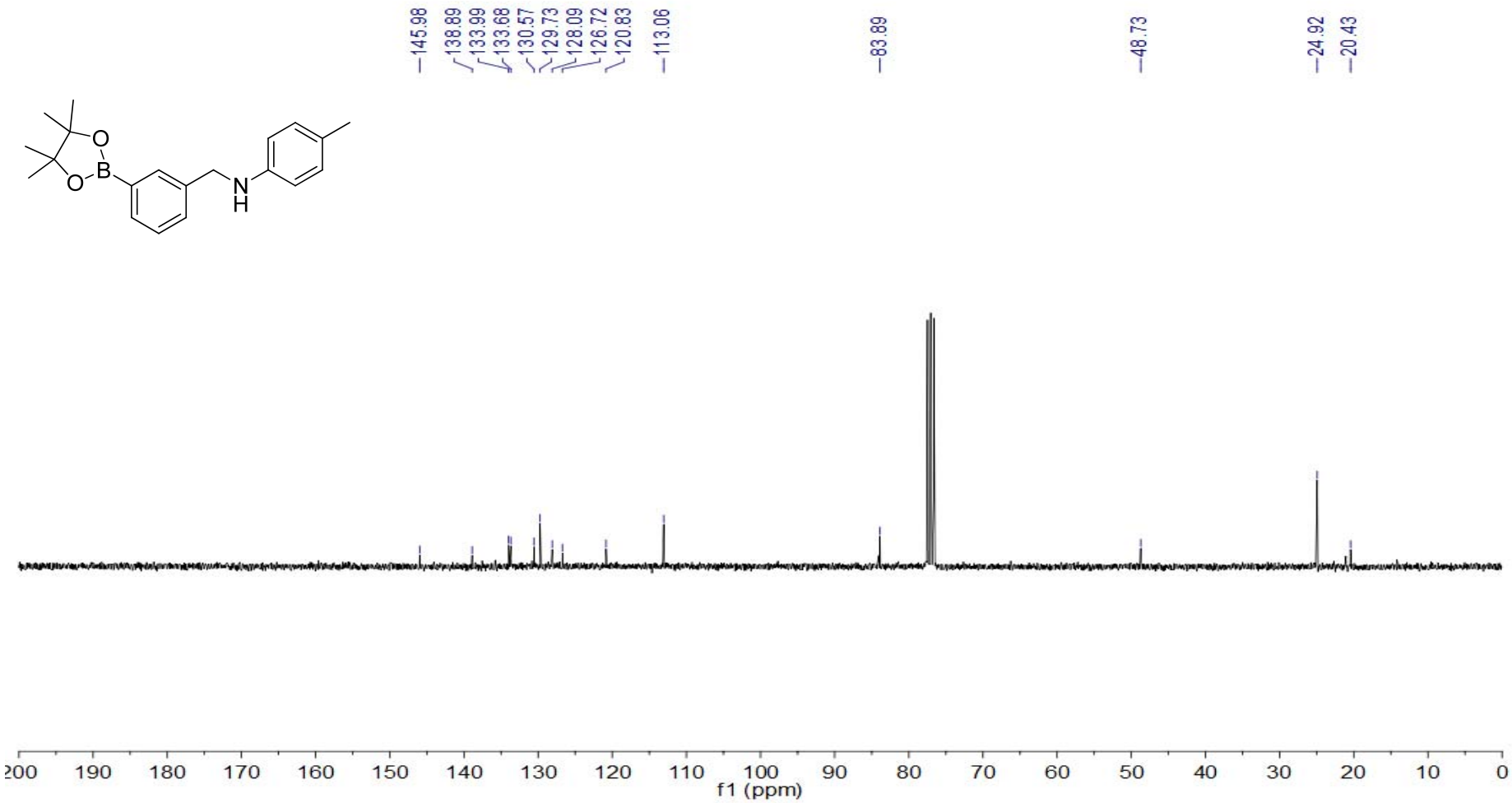
^{13}C NMR Spectra (75.5 MHz, $CDCl_3$, 25 °C) (Table 3, entry 2)



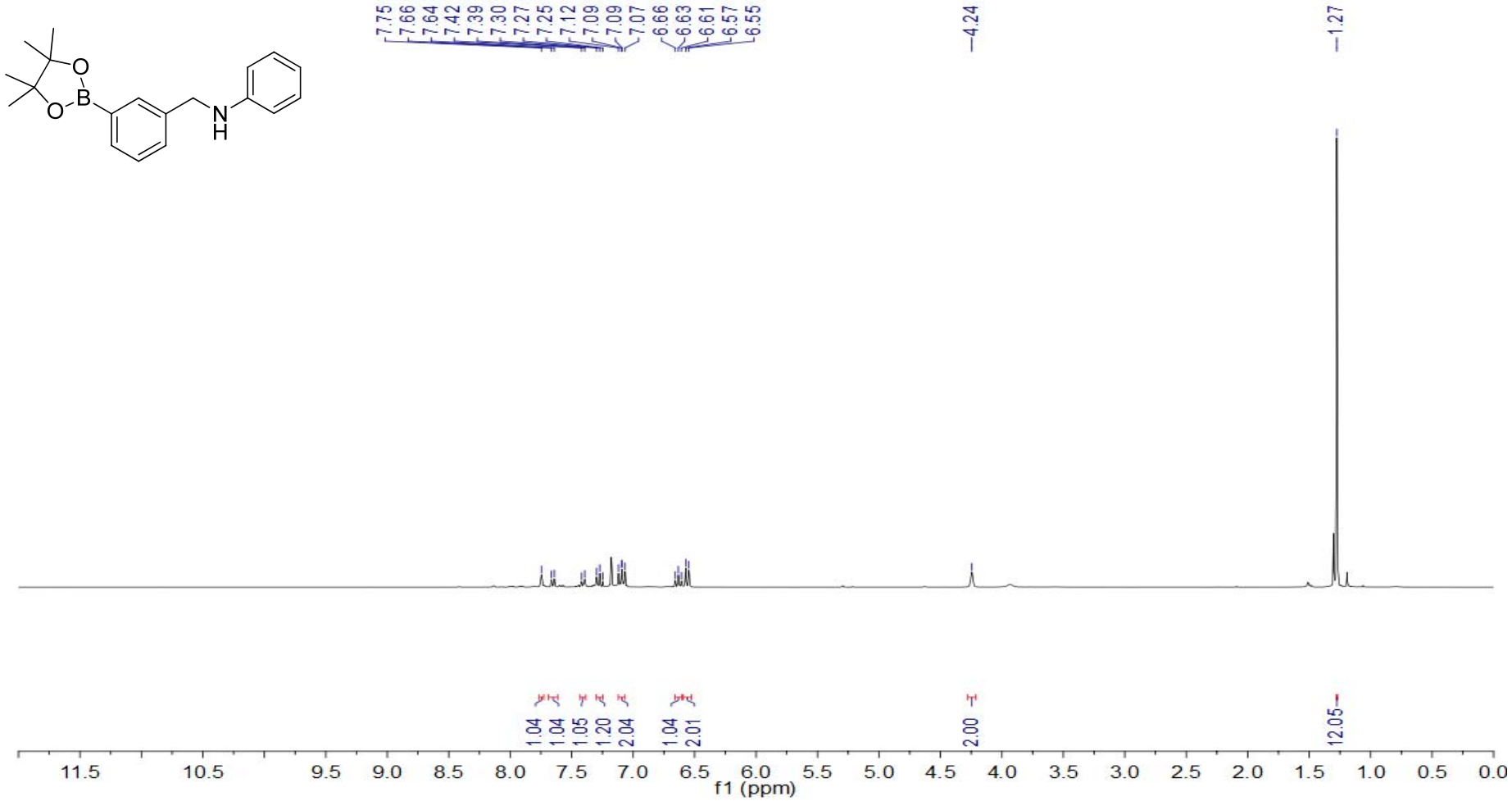
^{1}H NMR Spectra (300 MHz, $CDCl_3$, 25 °C) (Table 3, entry 3)



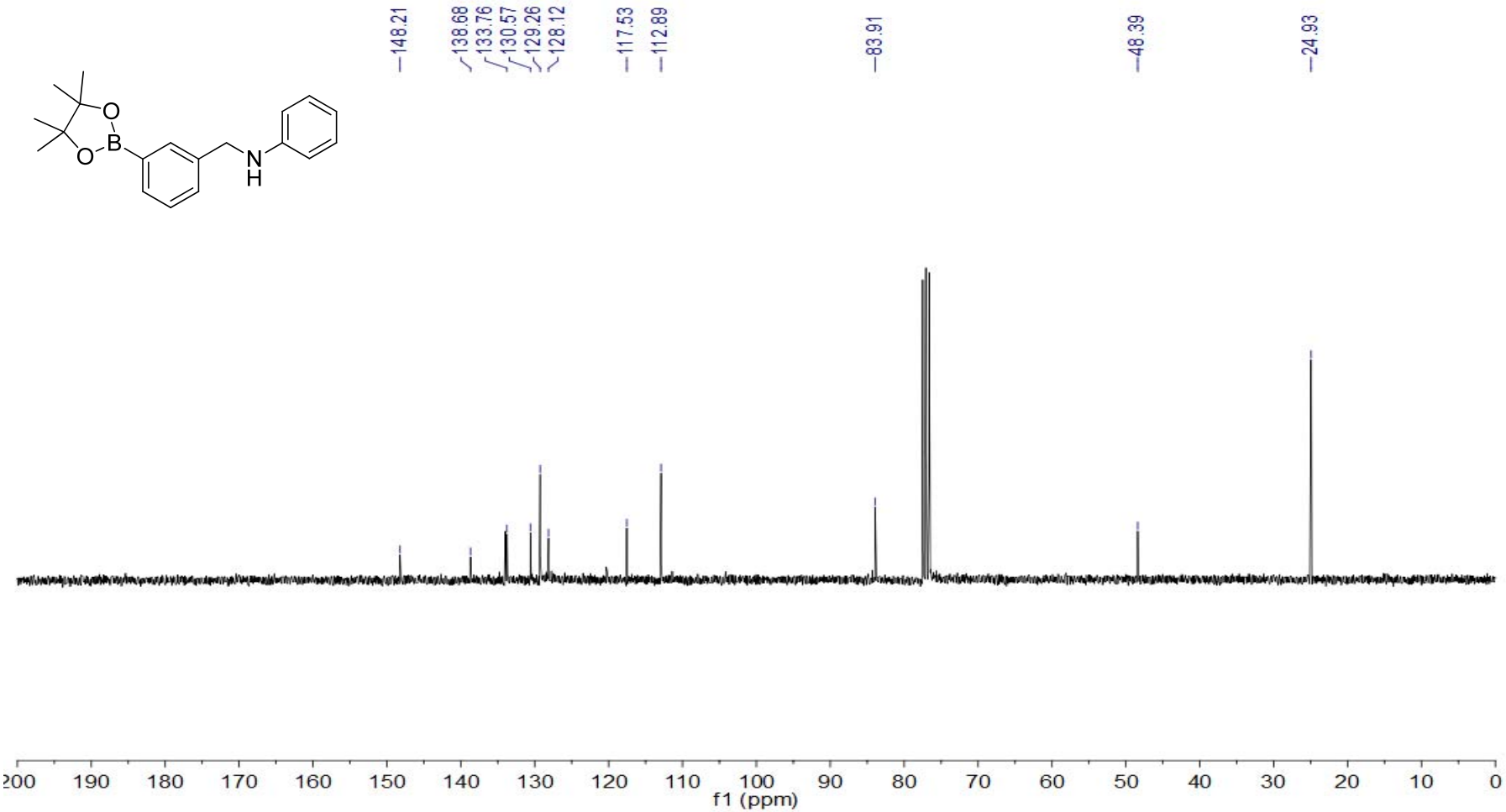
^{13}C NMR Spectra (75.5 MHz, $CDCl_3$, 25 °C) (Table 3, entry 3)



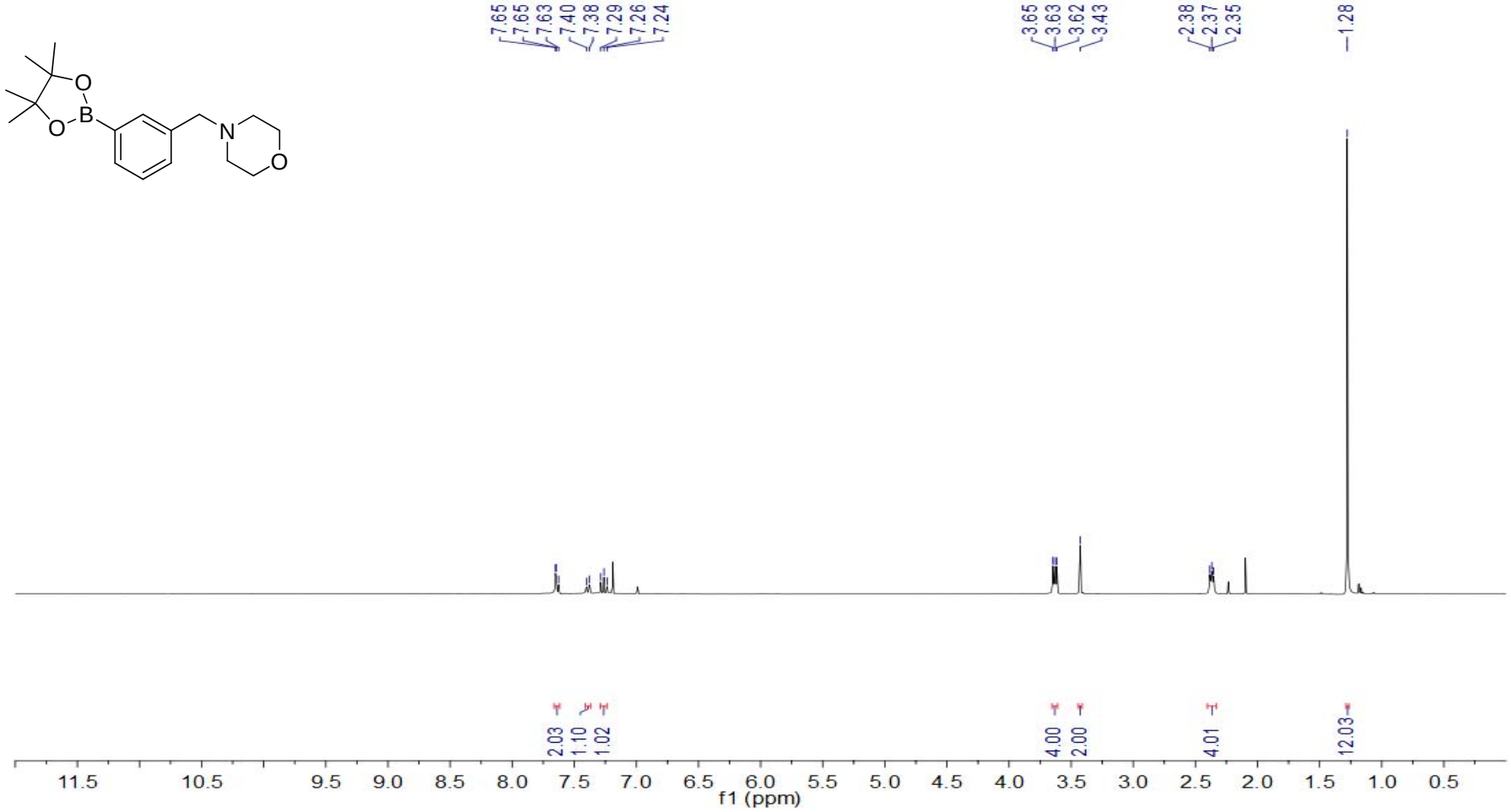
^{1}H NMR Spectra (300 MHz, $CDCl_3$, 25 °C) (Table 3, entry 4)



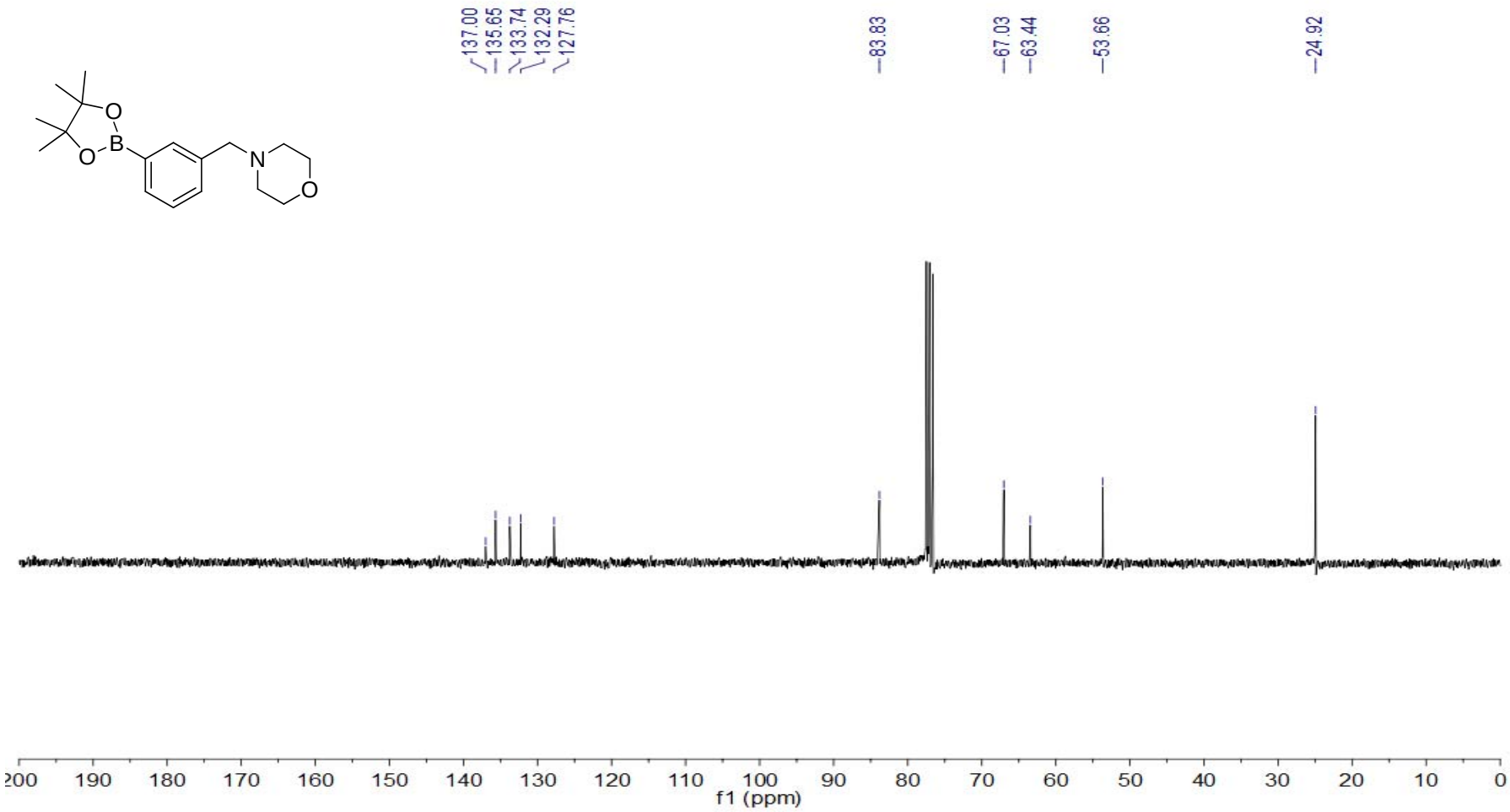
^{13}C NMR Spectra (75.5 MHz, $CDCl_3$, 25 °C) (Table 3, entry 4)



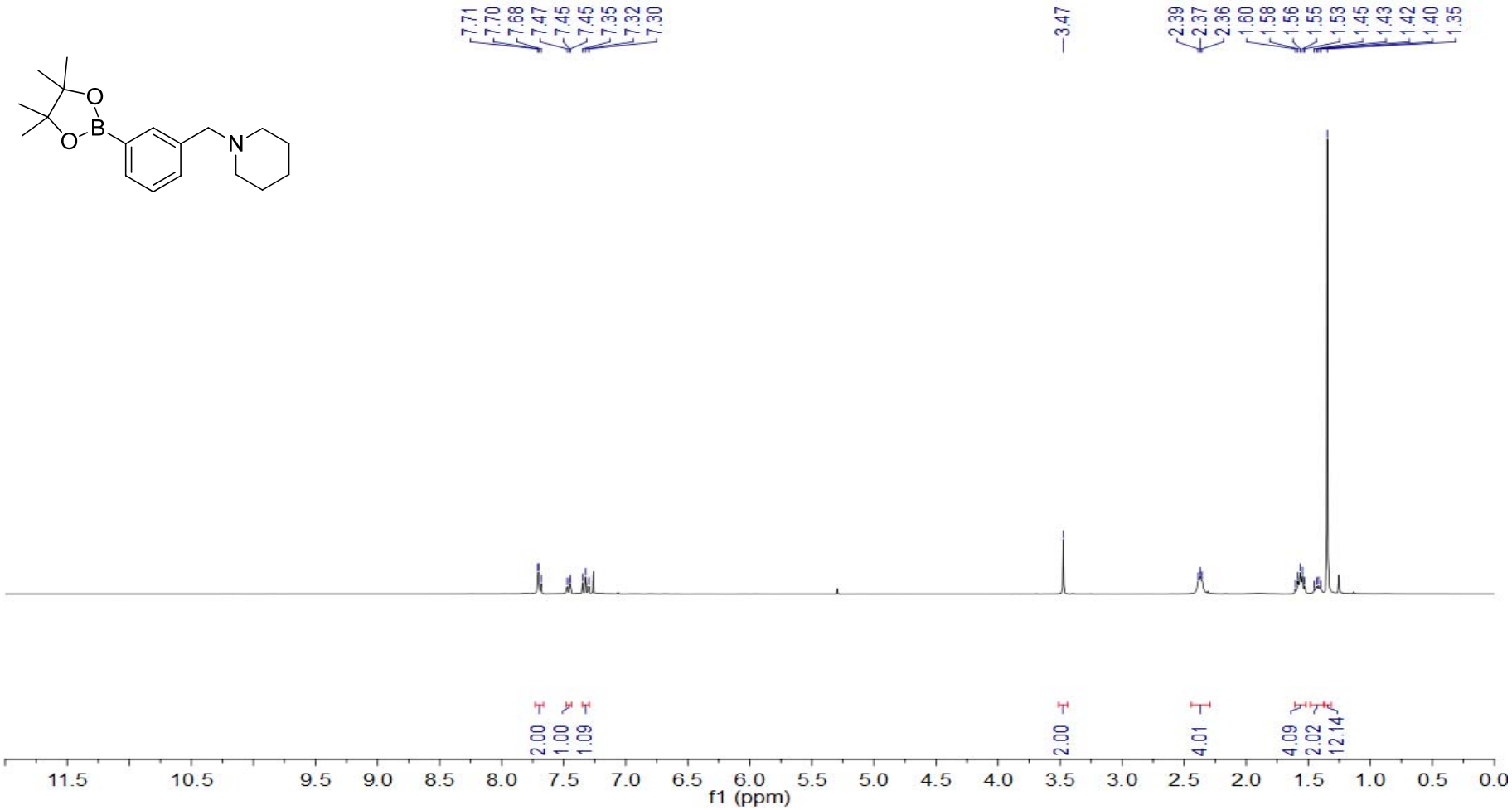
^{1}H NMR Spectra (300 MHz, $CDCl_3$, 25 °C) (Table 3, entry 6)



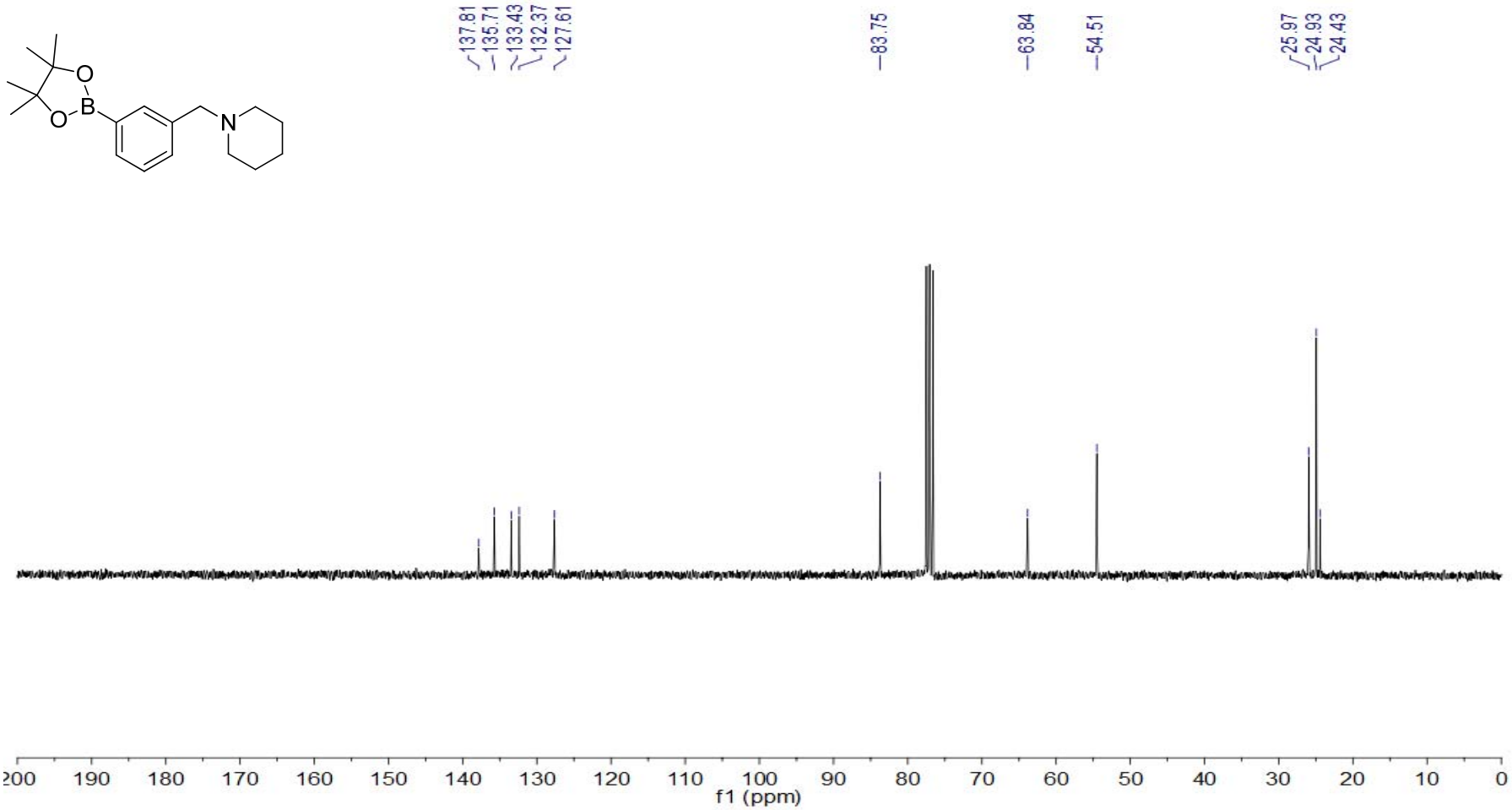
^{13}C NMR Spectra (75.5 MHz, $CDCl_3$, 25 °C) (Table 3, entry 6)



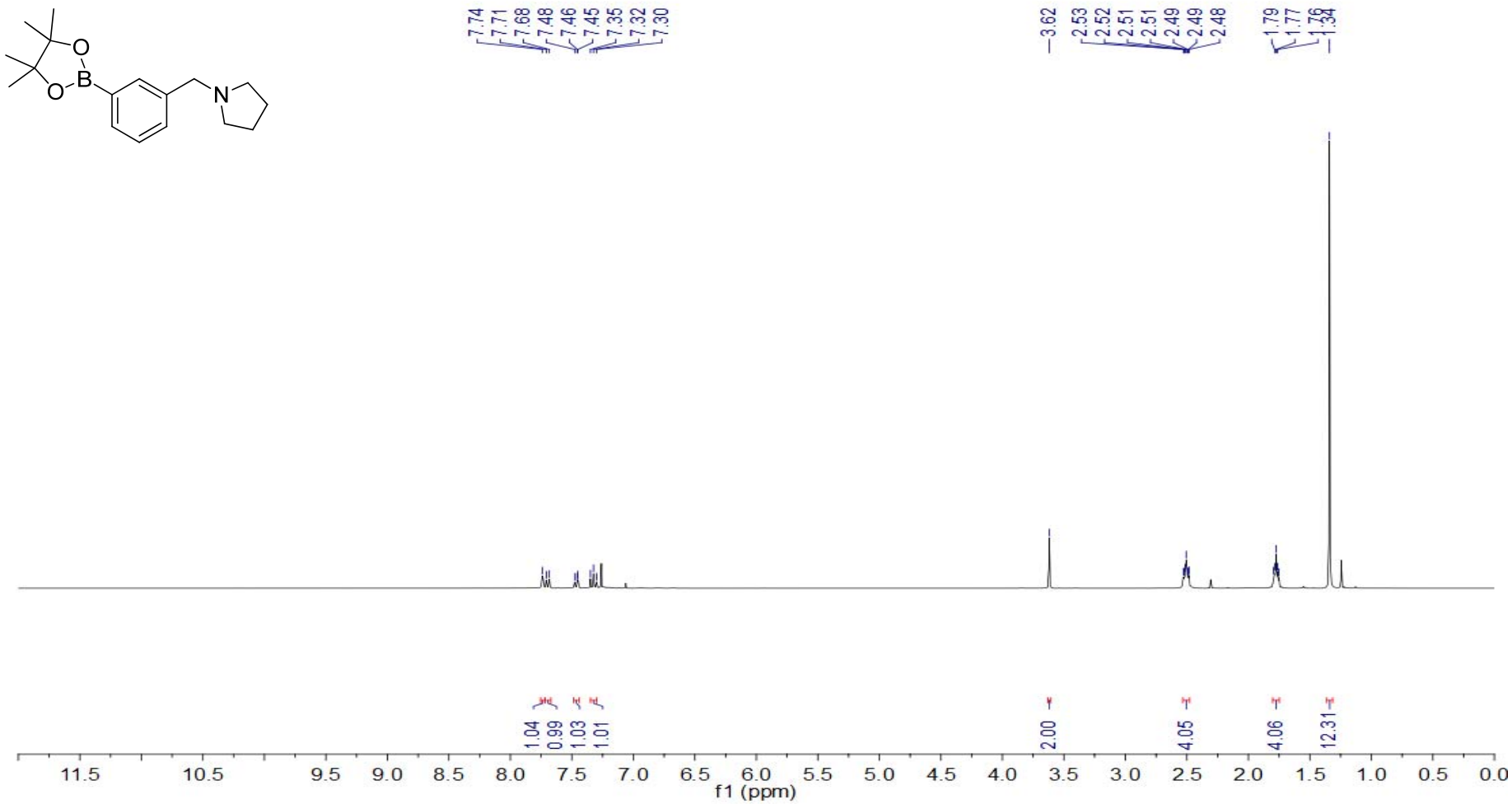
^{1}H NMR Spectra (300 MHz, $CDCl_3$, 25 °C) (Table 3, entry 7)



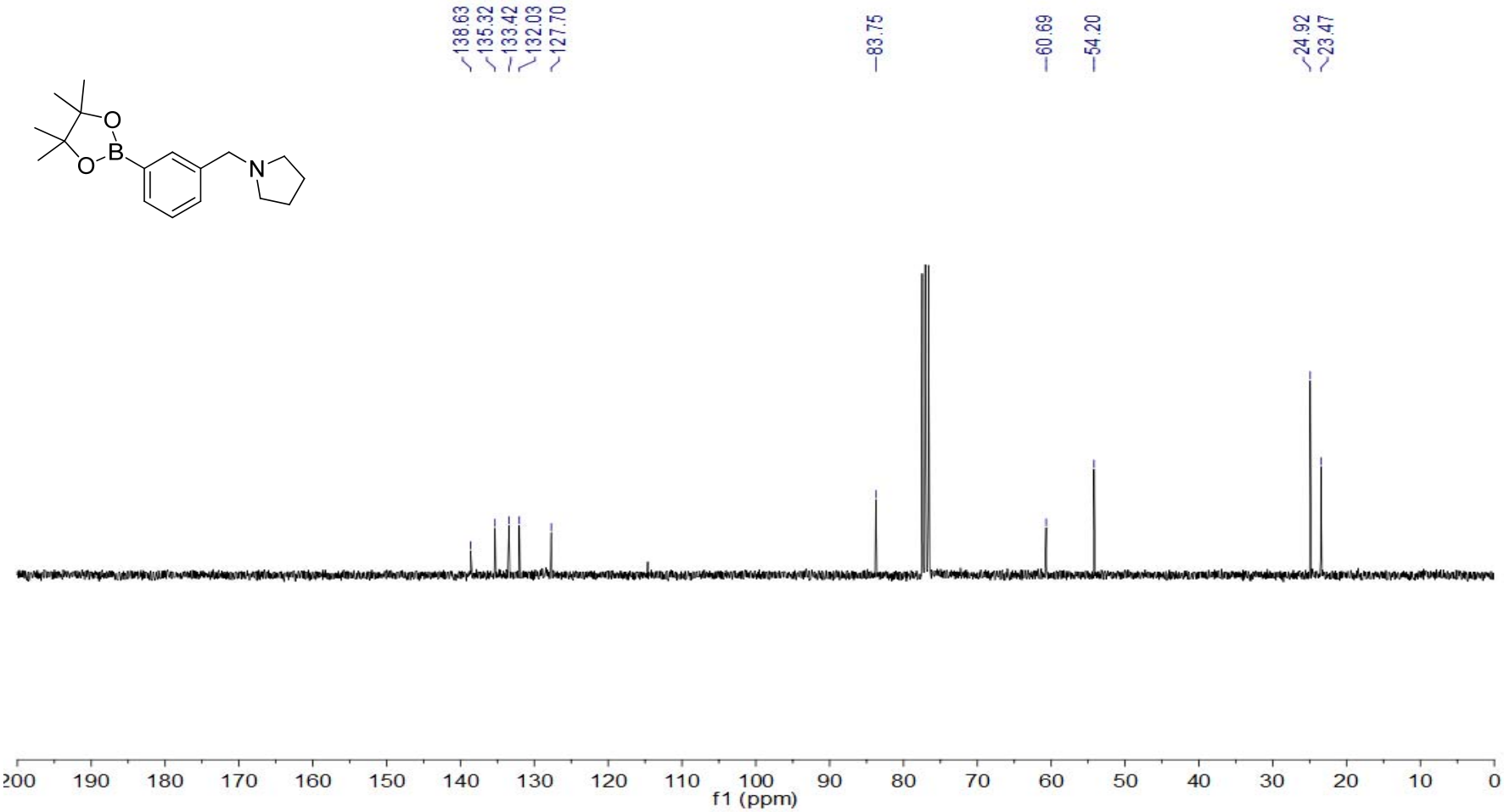
^{13}C NMR Spectra (75.5 MHz, $CDCl_3$, 25 °C) (Table 3, entry 7)



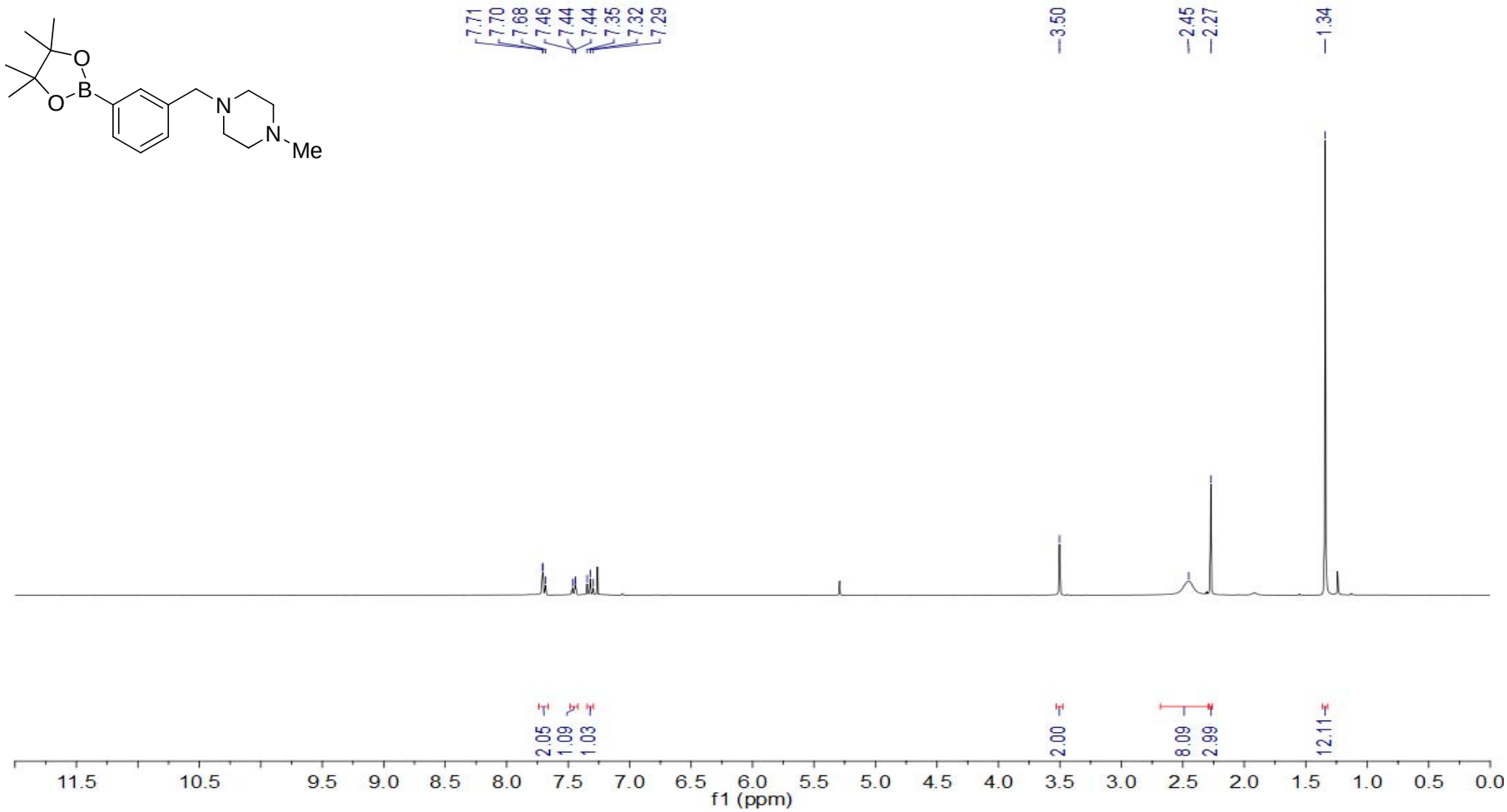
^{1}H NMR Spectra (300 MHz, $CDCl_3$, 25 °C) (Table 3, entry 8)



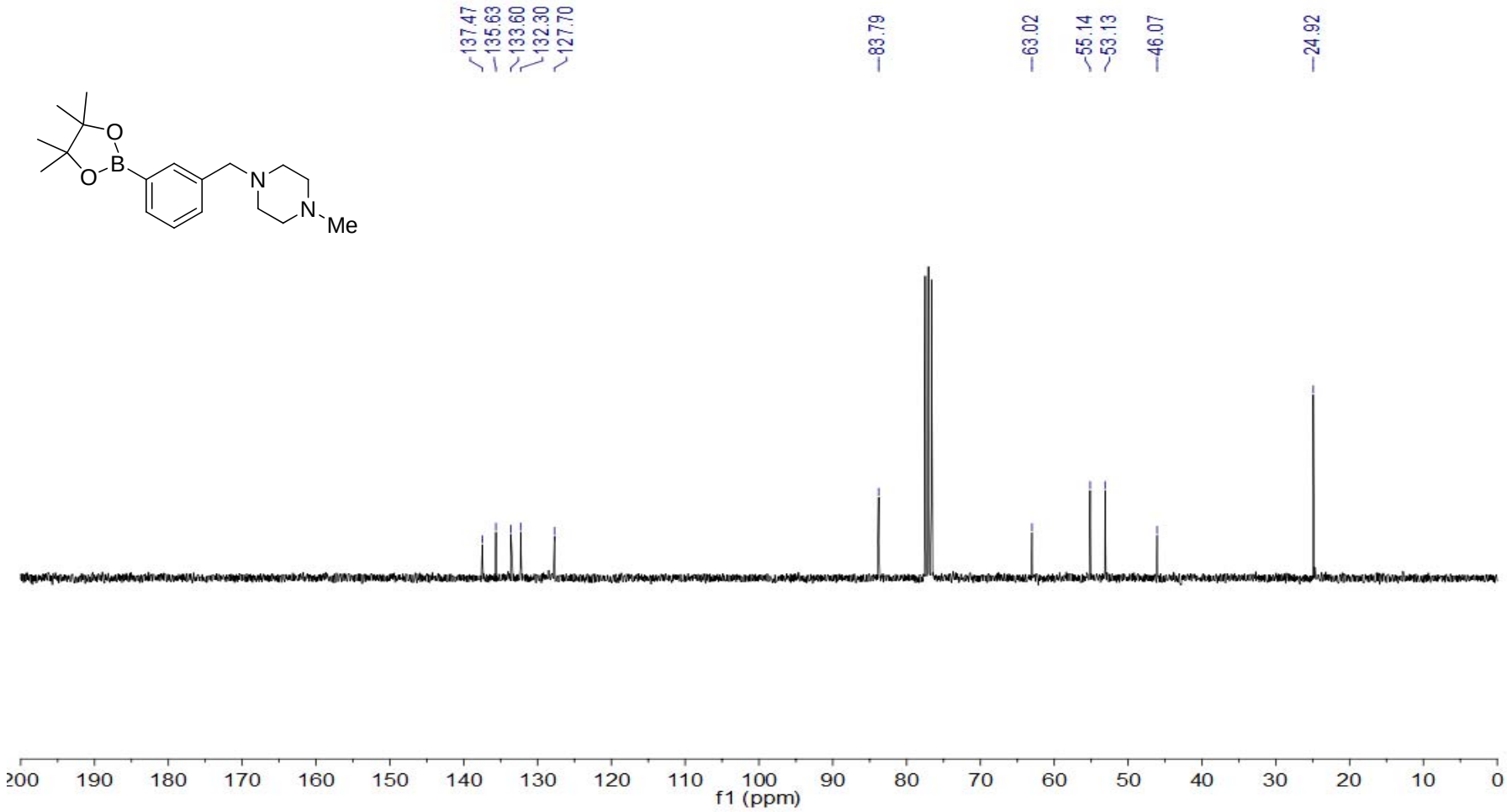
^{13}C NMR Spectra (75.5 MHz, $CDCl_3$, 25 °C) (Table 3, entry 8)



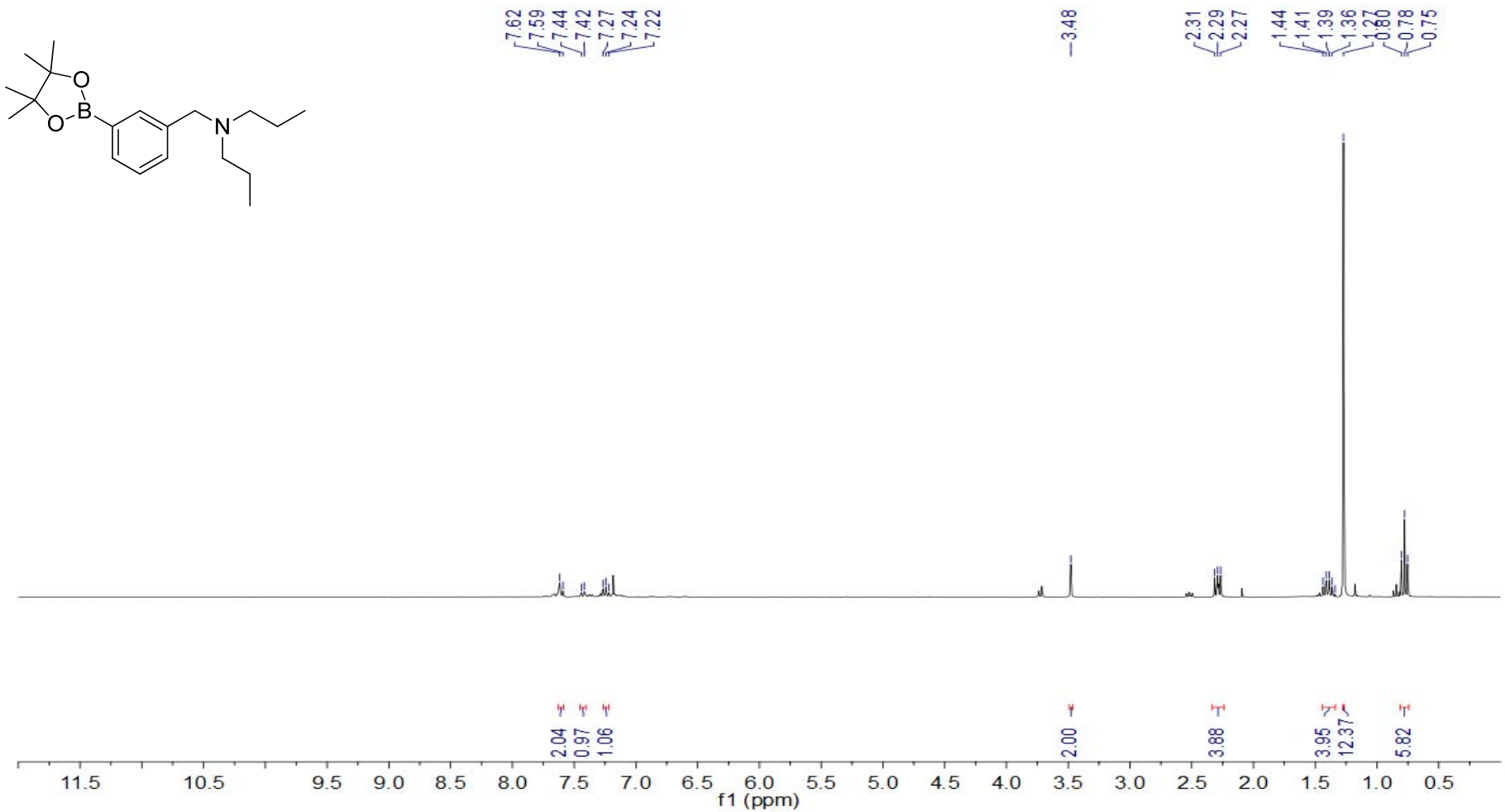
^{1}H NMR Spectra (300 MHz, $CDCl_3$, 25 °C) (Table 3, entry 9)



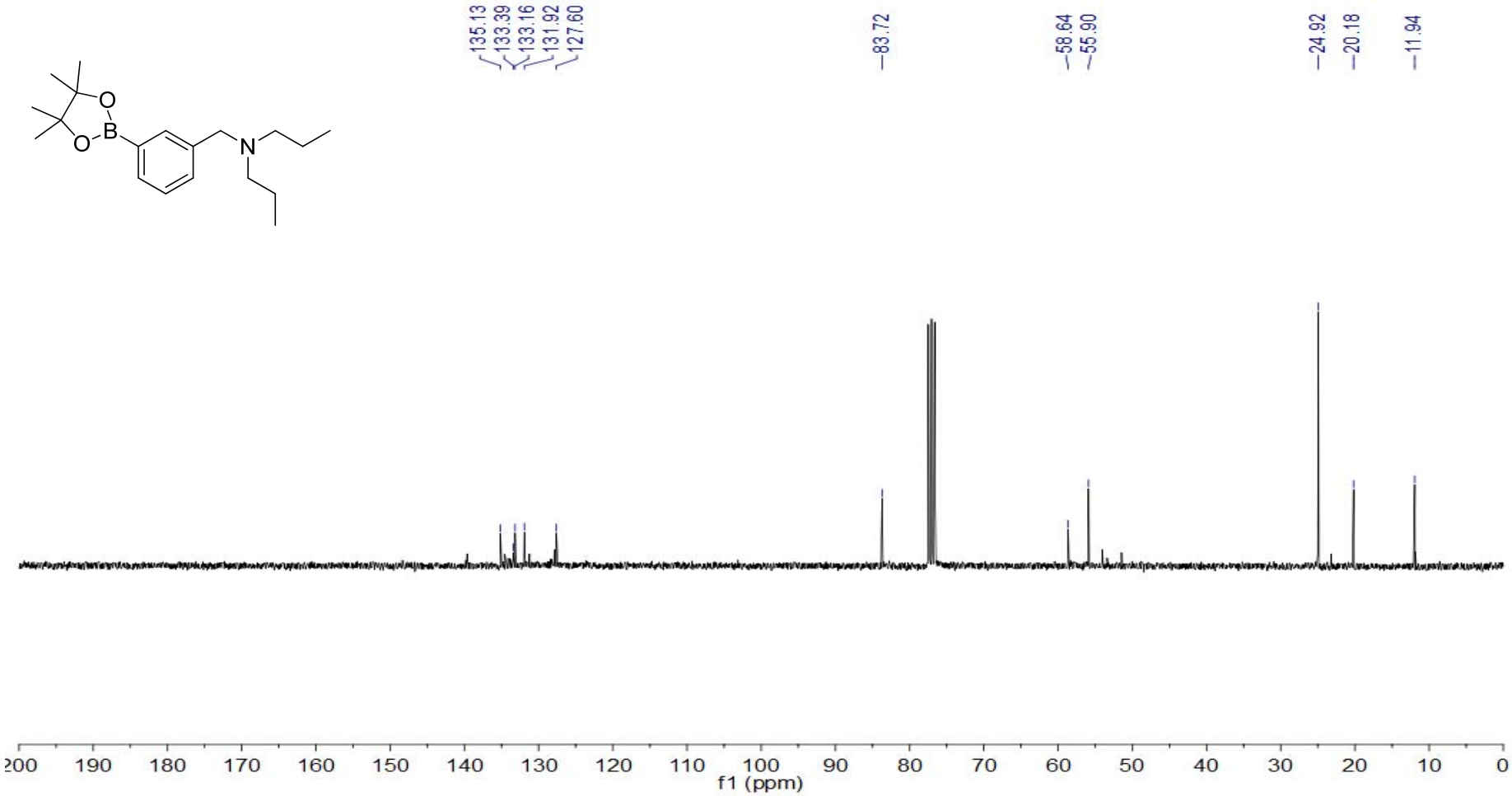
^{13}C NMR Spectra (75.5 MHz, $CDCl_3$, 25 °C) (Table 3, entry 9)



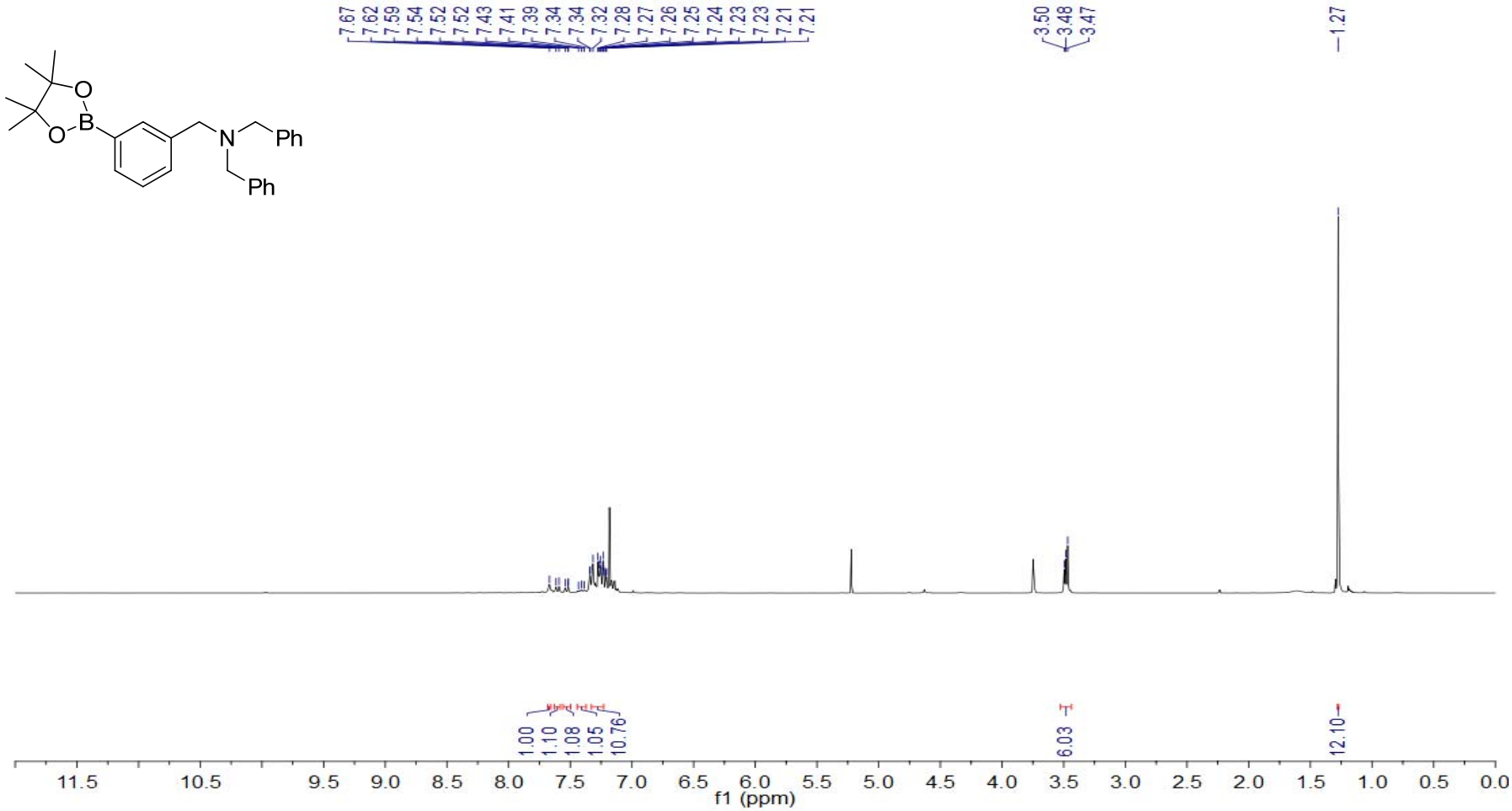
^{1}H NMR Spectra (300 MHz, $CDCl_3$, 25 °C) (Table 3, entry 10)



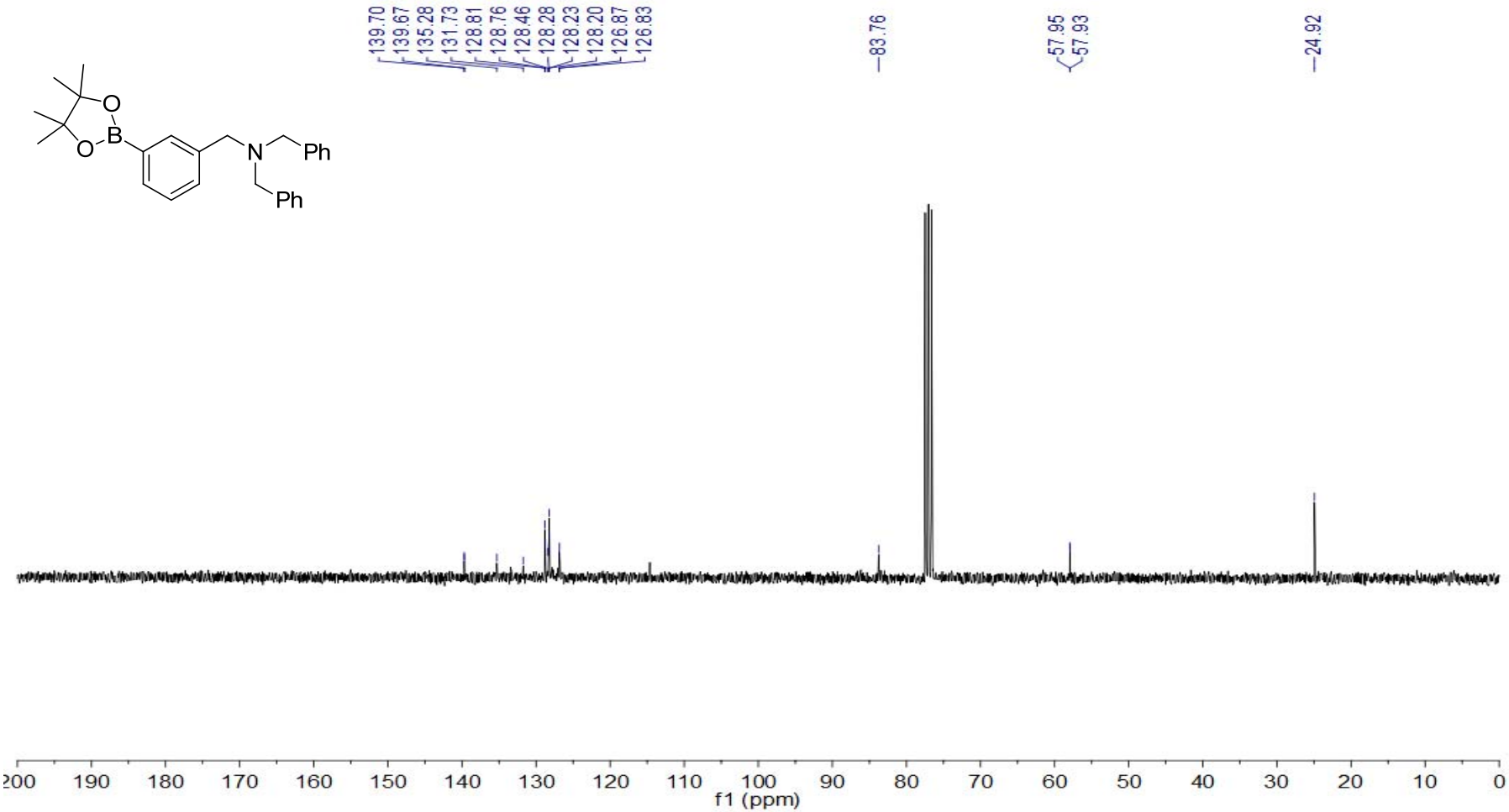
^{13}C NMR Spectra (75.5 MHz, $CDCl_3$, 25 °C) (Table 3, entry 10)



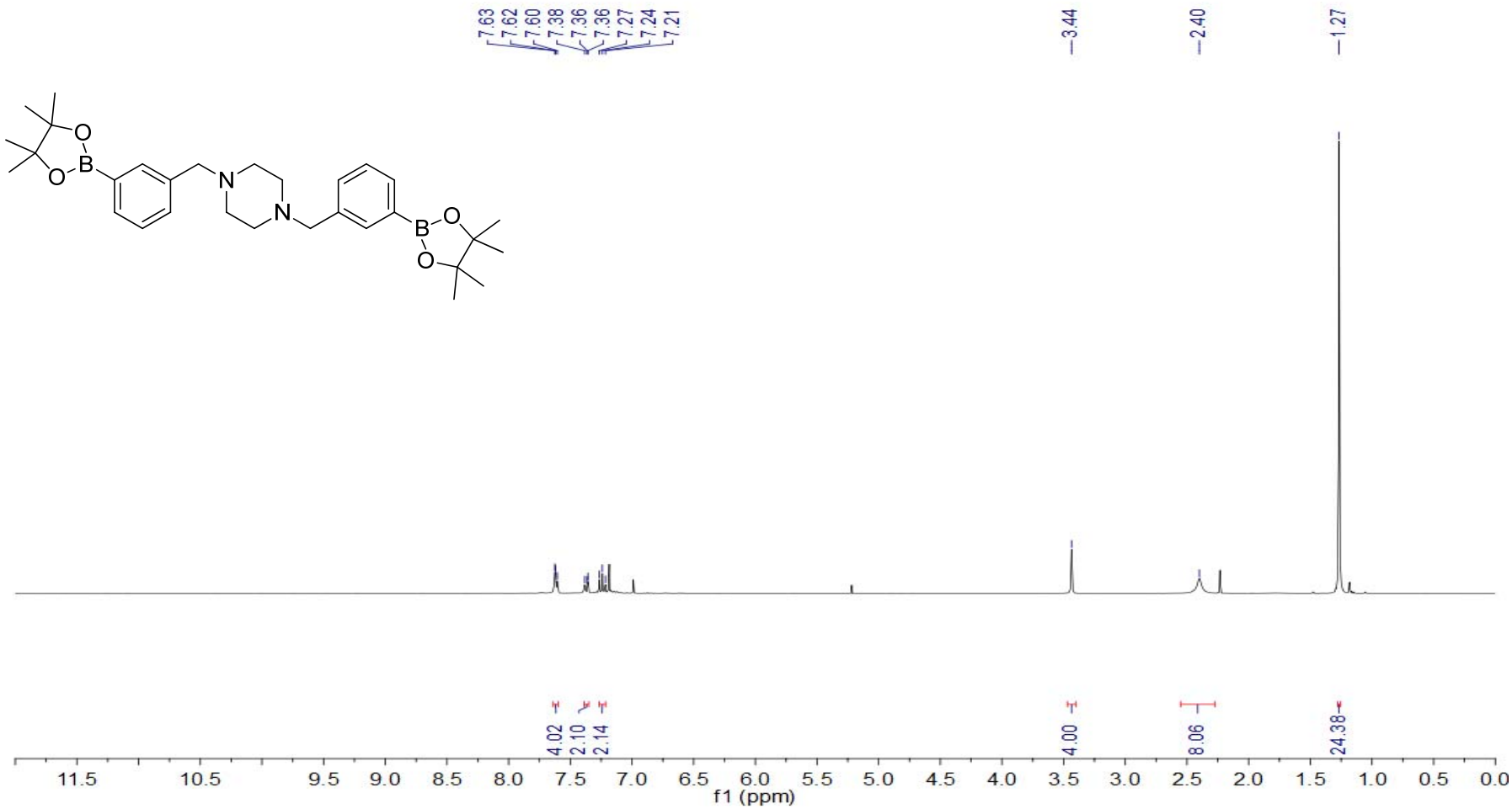
^{1}H NMR Spectra (300 MHz, $CDCl_3$, 25 °C) (Table 3, entry 11)



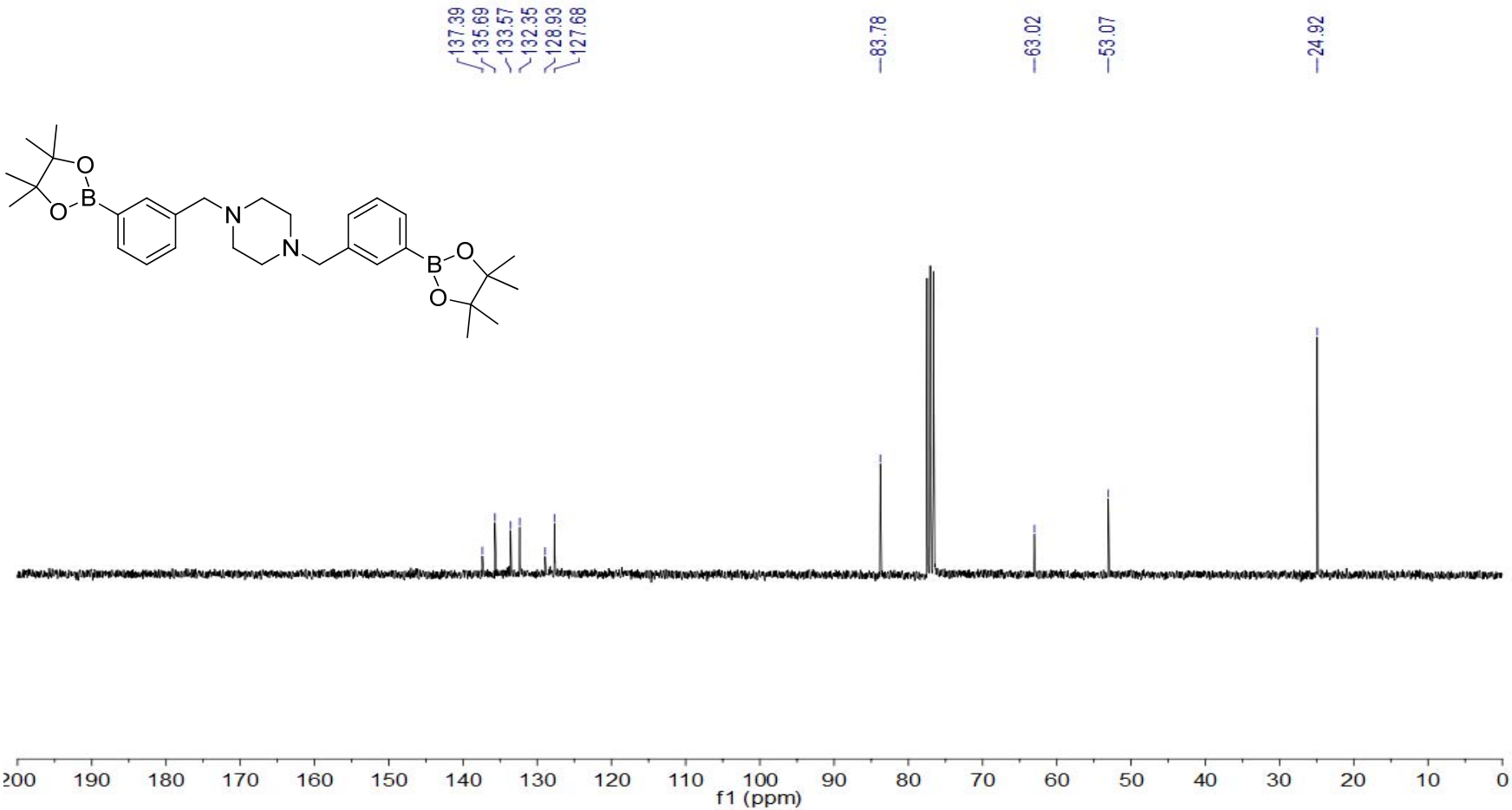
^{13}C NMR Spectra (75.5 MHz, $CDCl_3$, 25 °C) (Table 3, entry 11)



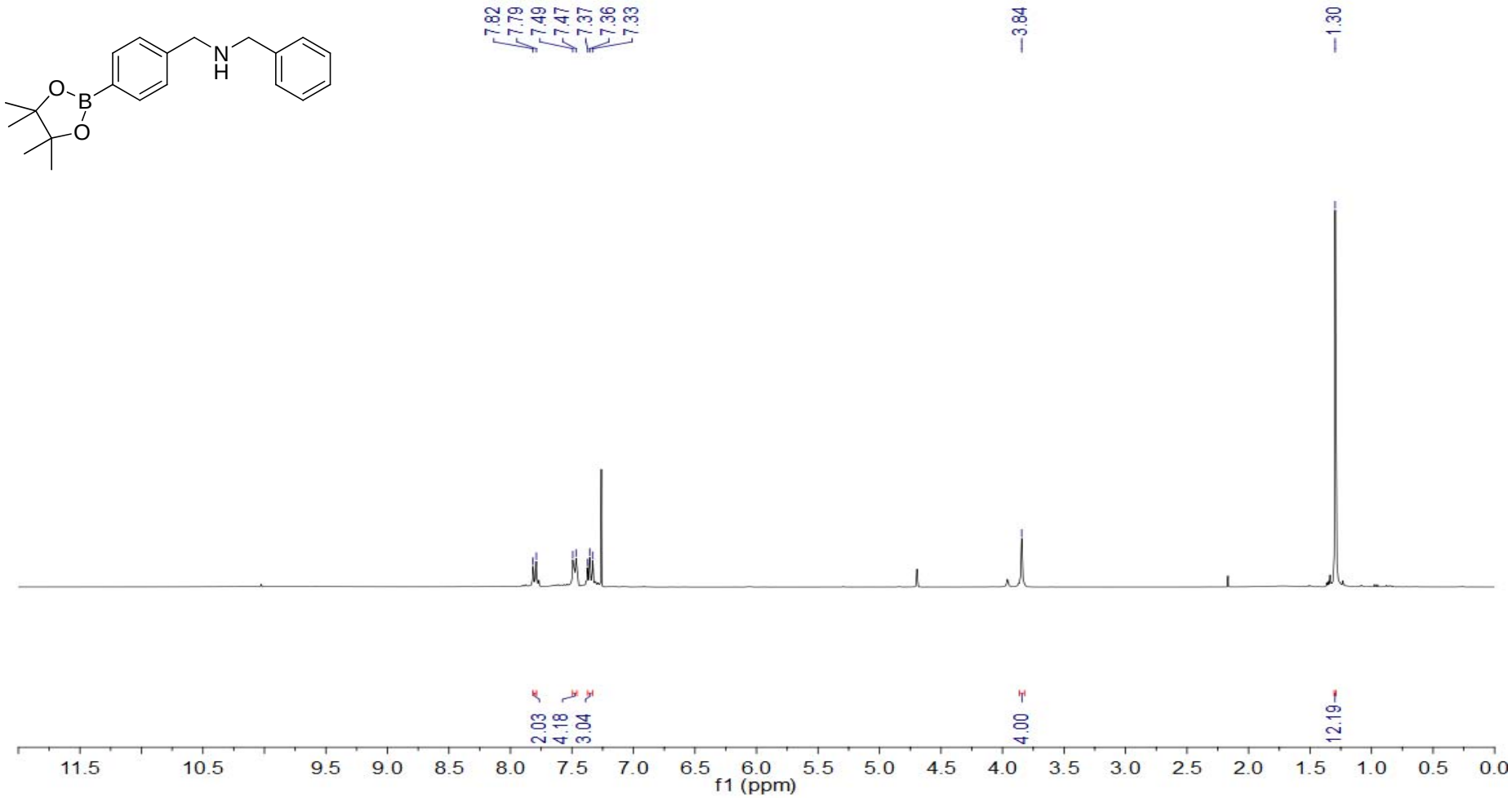
^{1}H NMR Spectra (300 MHz, $CDCl_3$, 25 °C) (Table 3, entry 12)



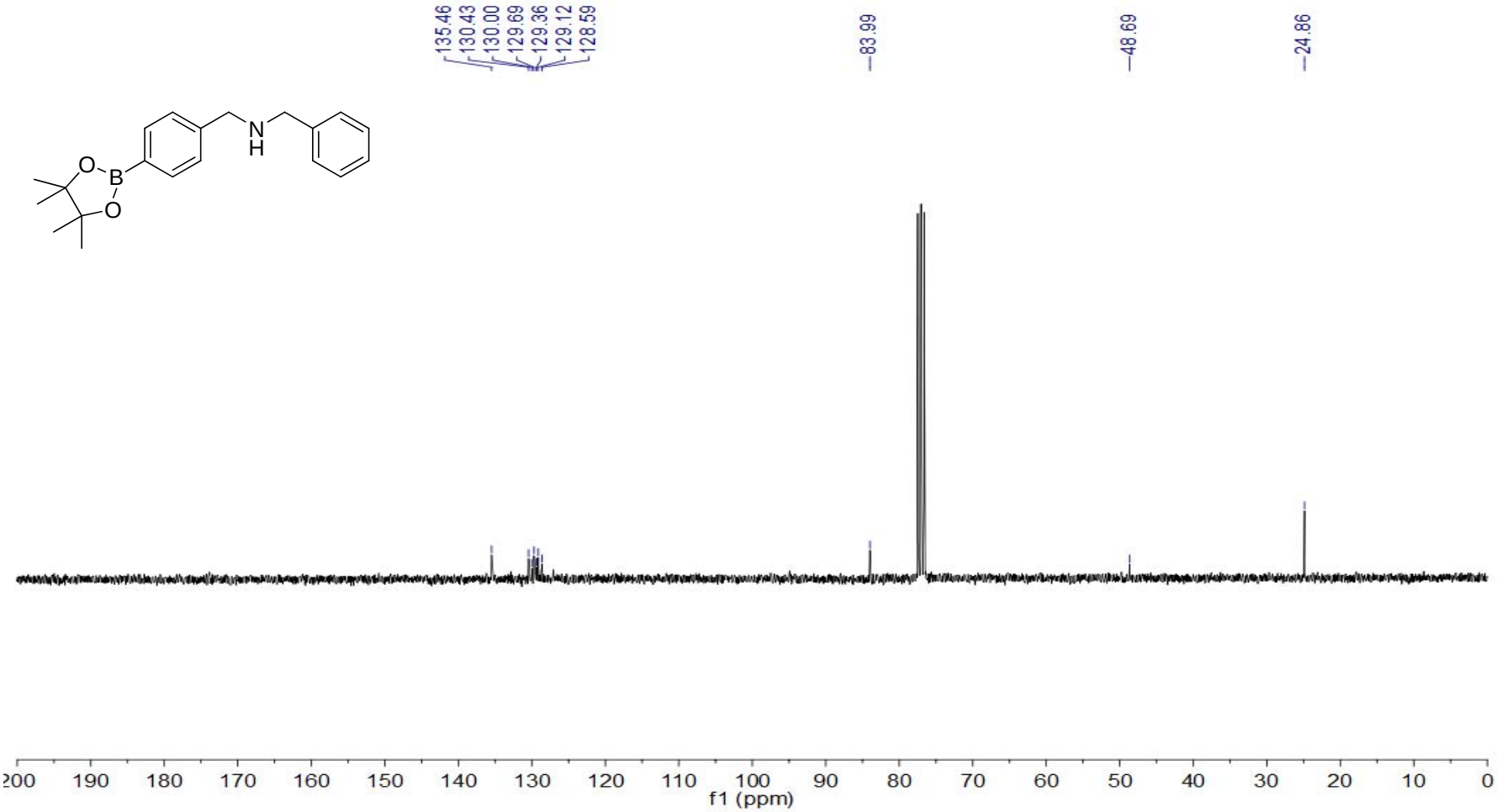
^{13}C NMR Spectra (75.5 MHz, $CDCl_3$, 25 °C) (Table 3, entry 12)



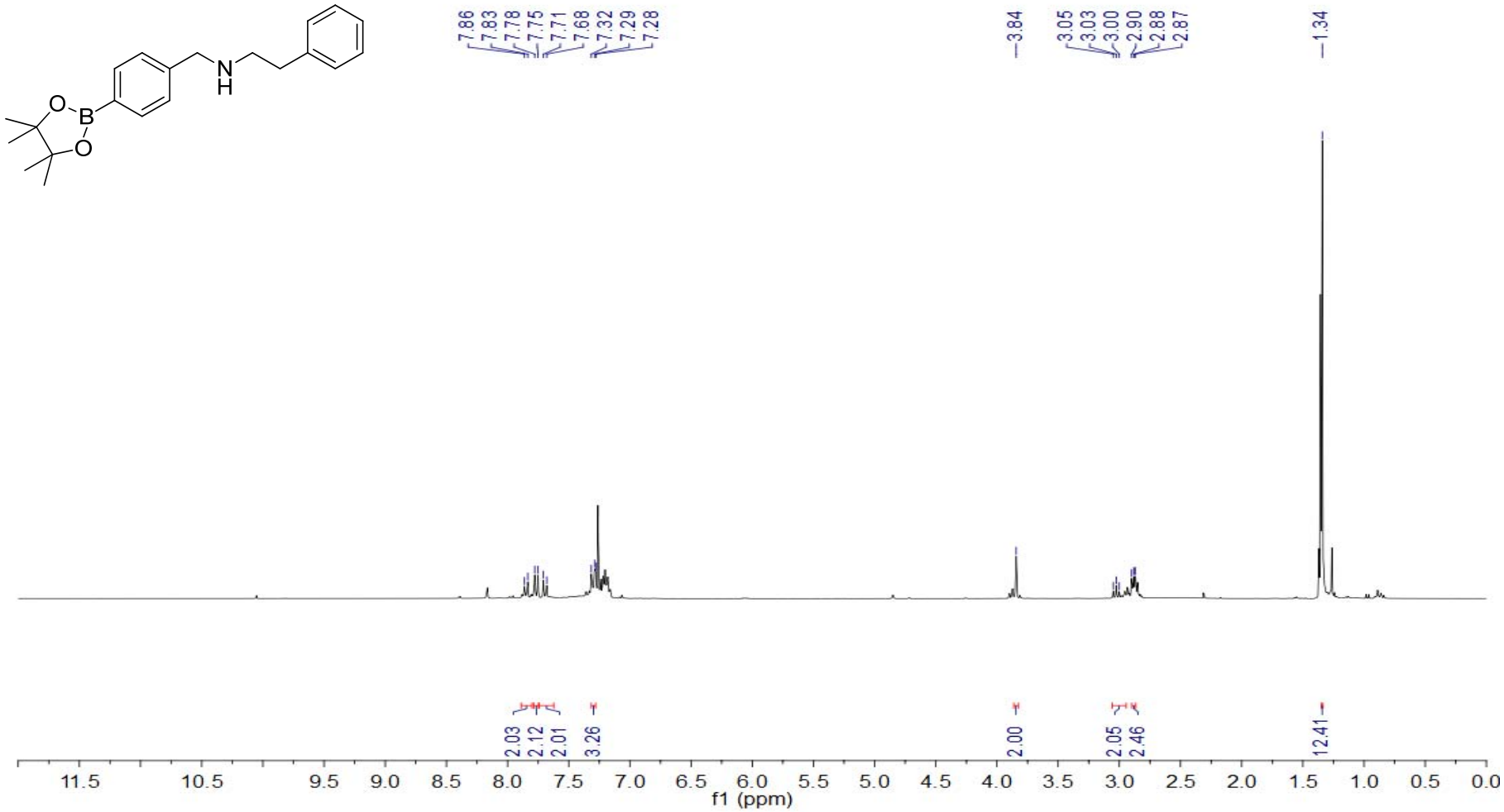
^{1}H NMR Spectra (300 MHz, $CDCl_3$, 25 °C) (Table 4, entry 1)



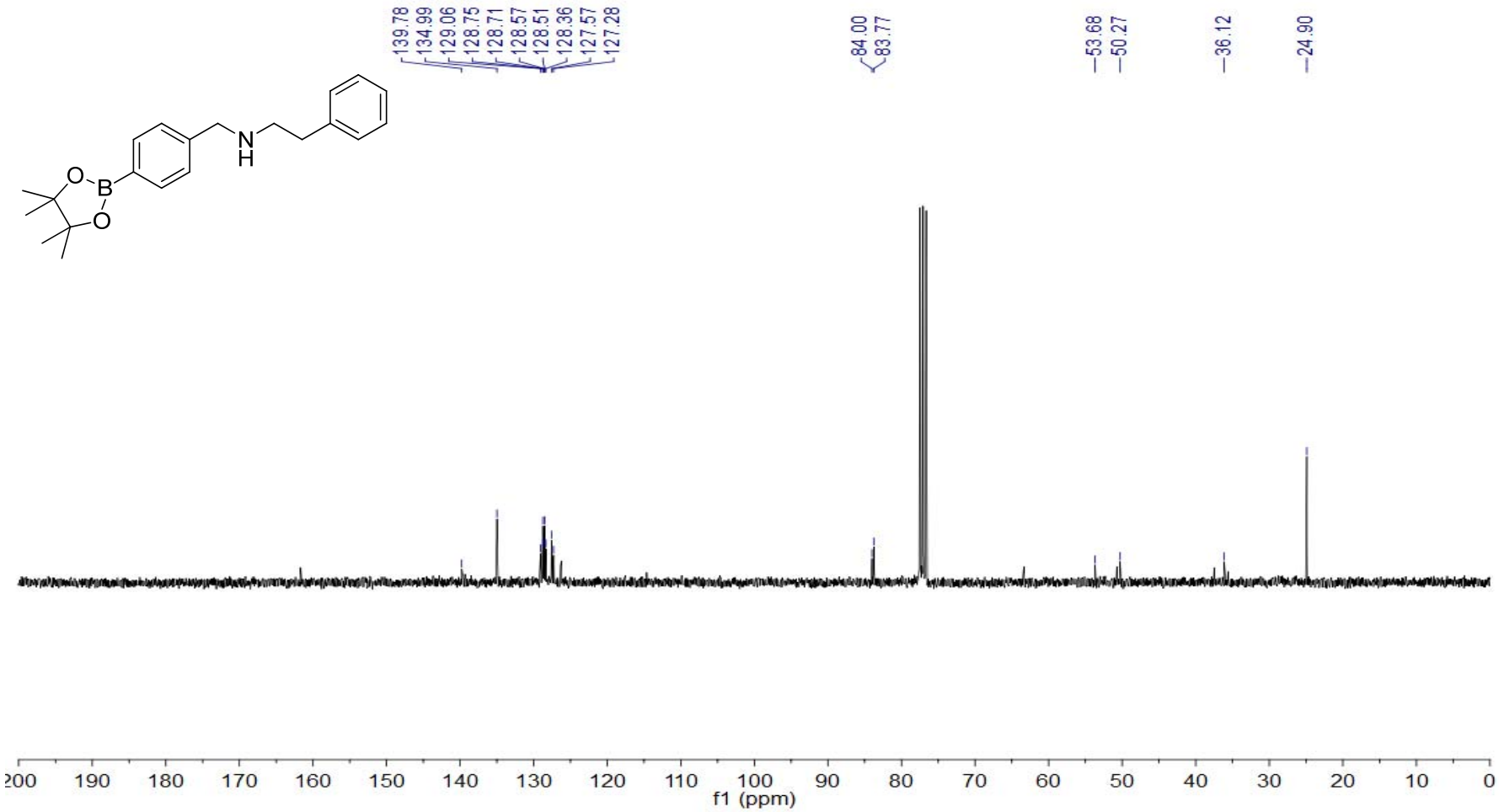
^{13}C NMR Spectra (75.5 MHz, $CDCl_3$, 25 °C) (Table 4, entry 1)



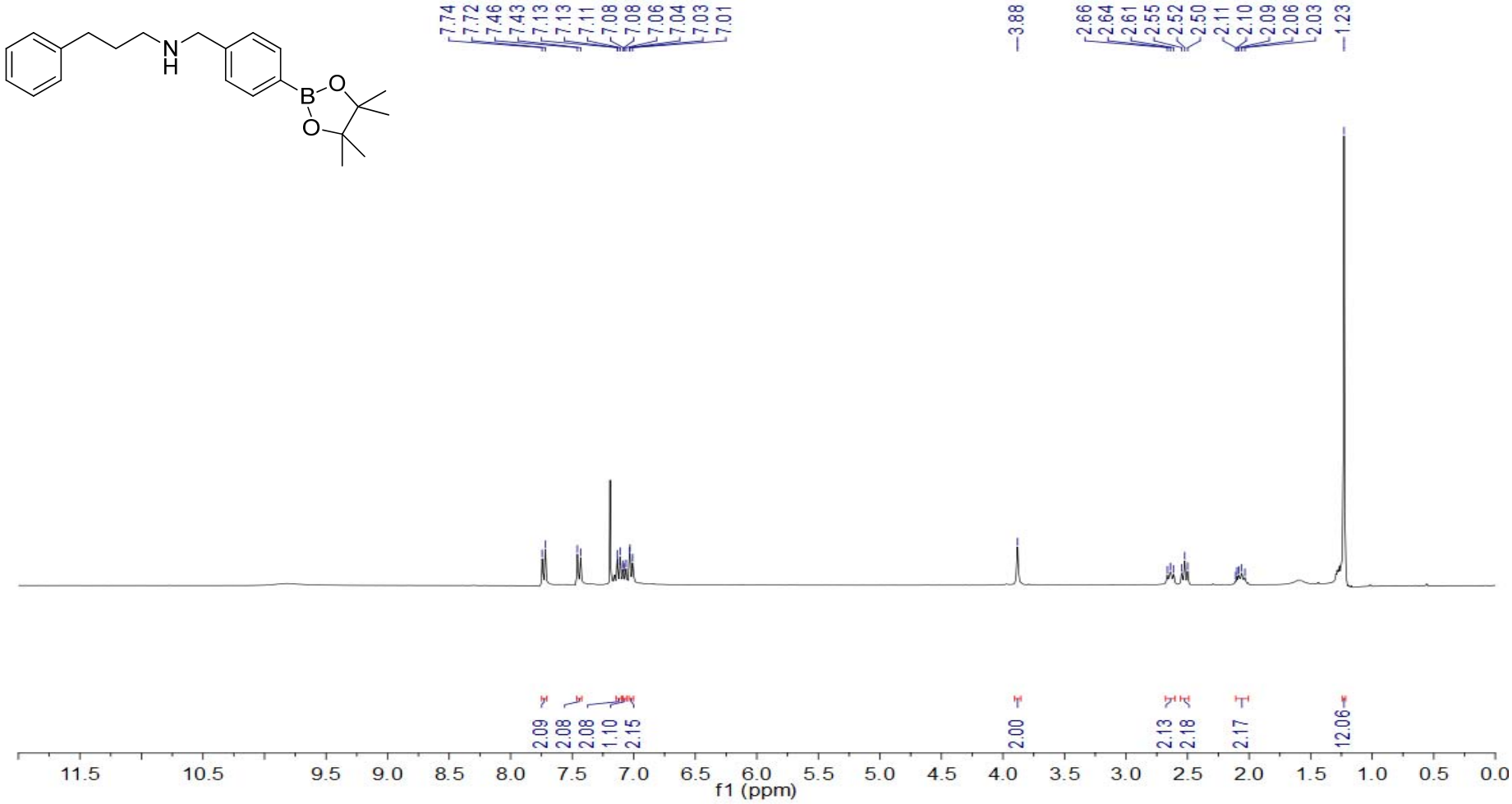
^{1}H NMR Spectra (300 MHz, $CDCl_3$, 25 °C) (Table 4, entry 2)



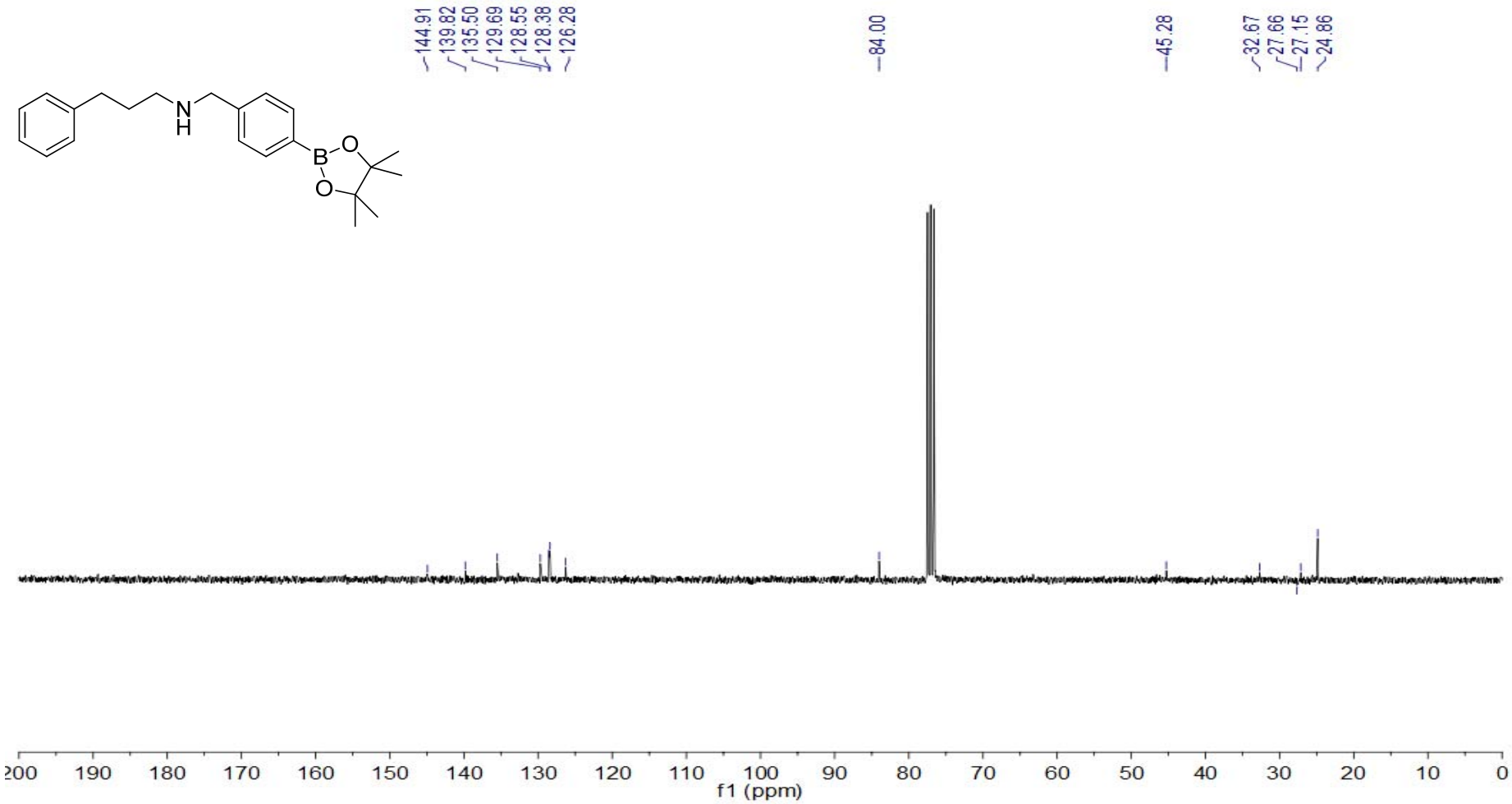
^{13}C NMR Spectra (75.5 MHz, $CDCl_3$, 25 °C) (Table 4, entry 2)



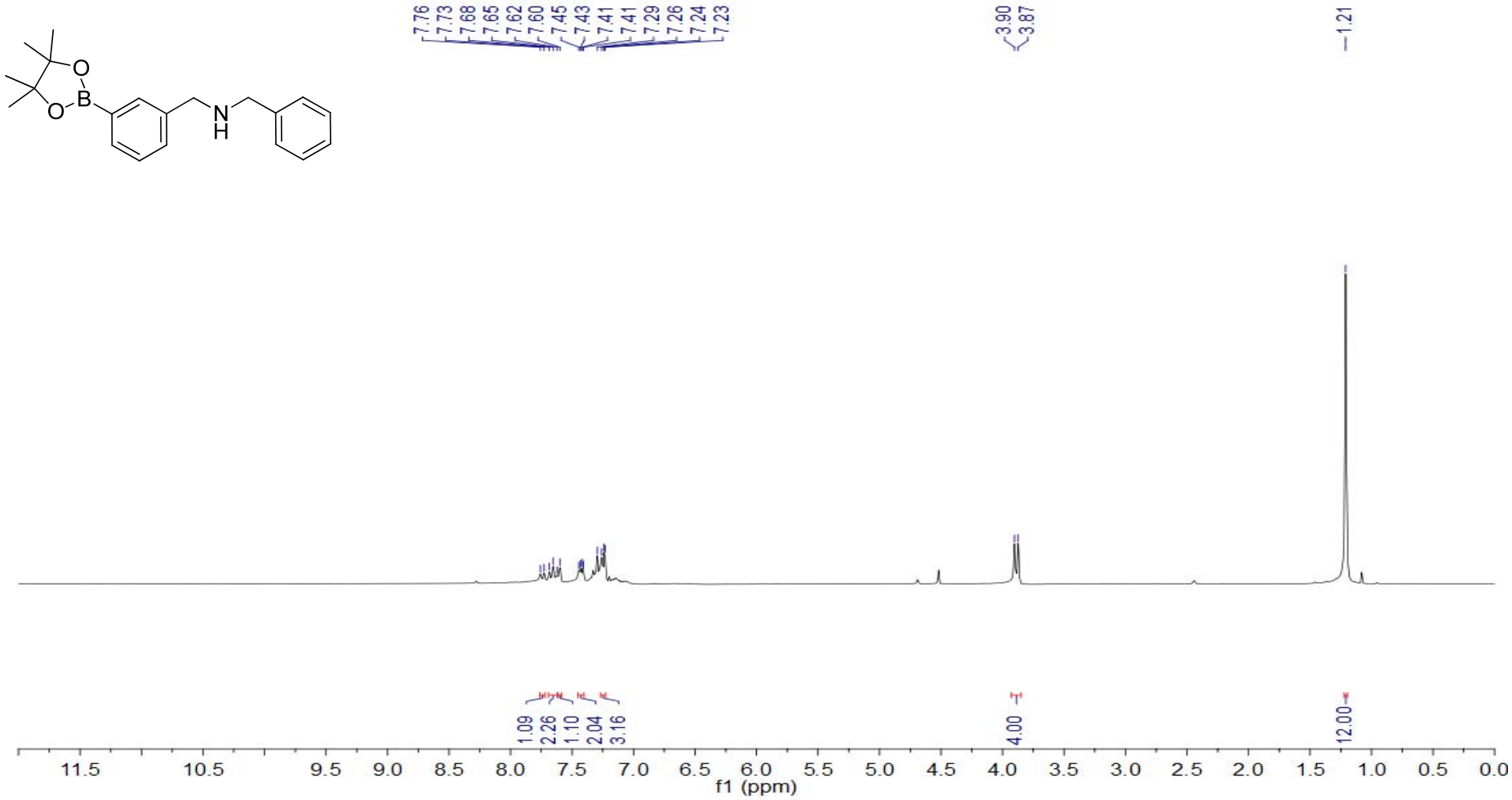
^{1}H NMR Spectra (300 MHz, $CDCl_3$, 25 °C) (Table 4, entry 3)



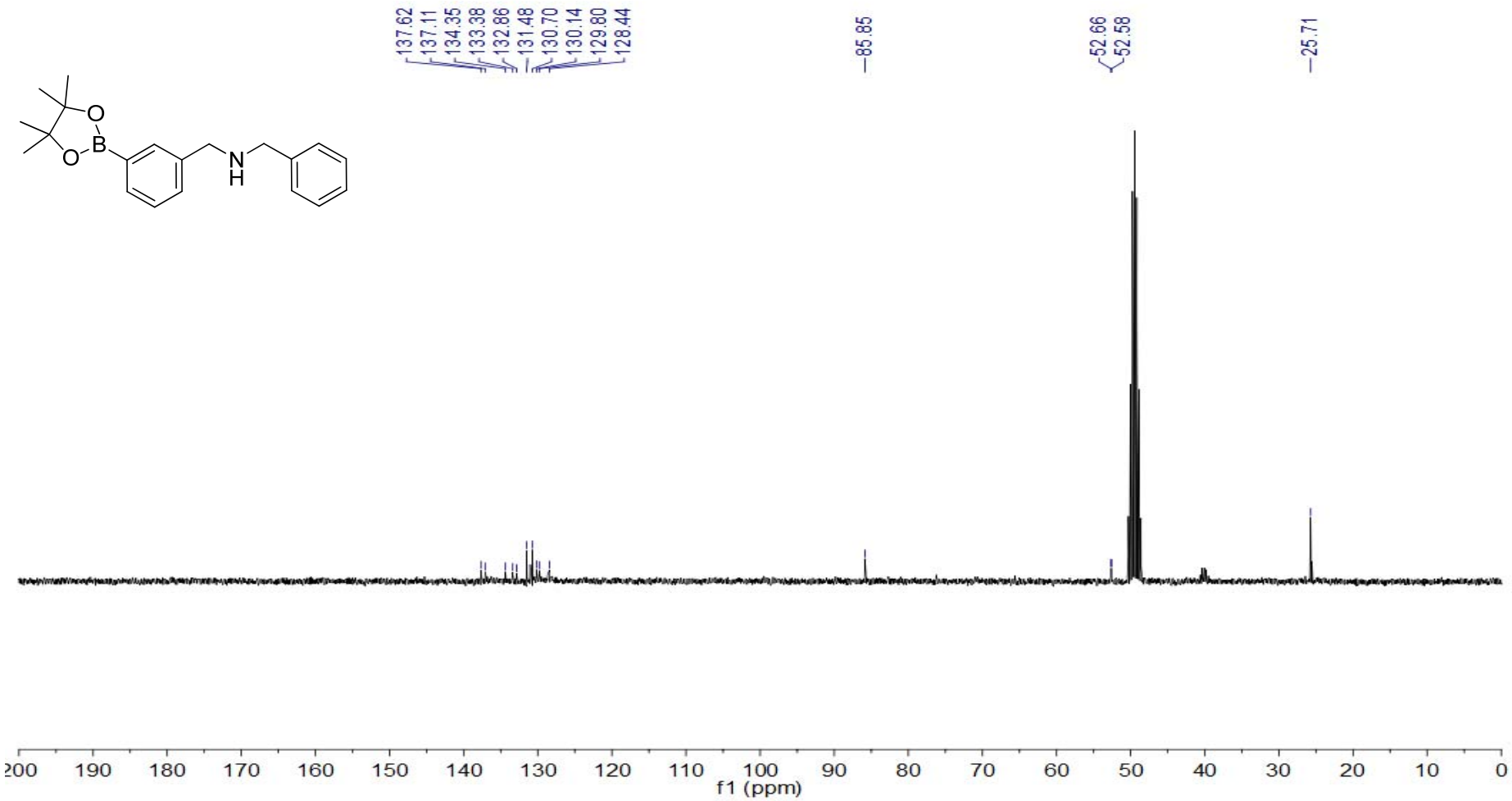
^{13}C NMR Spectra (75.5 MHz, $CDCl_3$, 25 °C) (Table 4, entry 3)



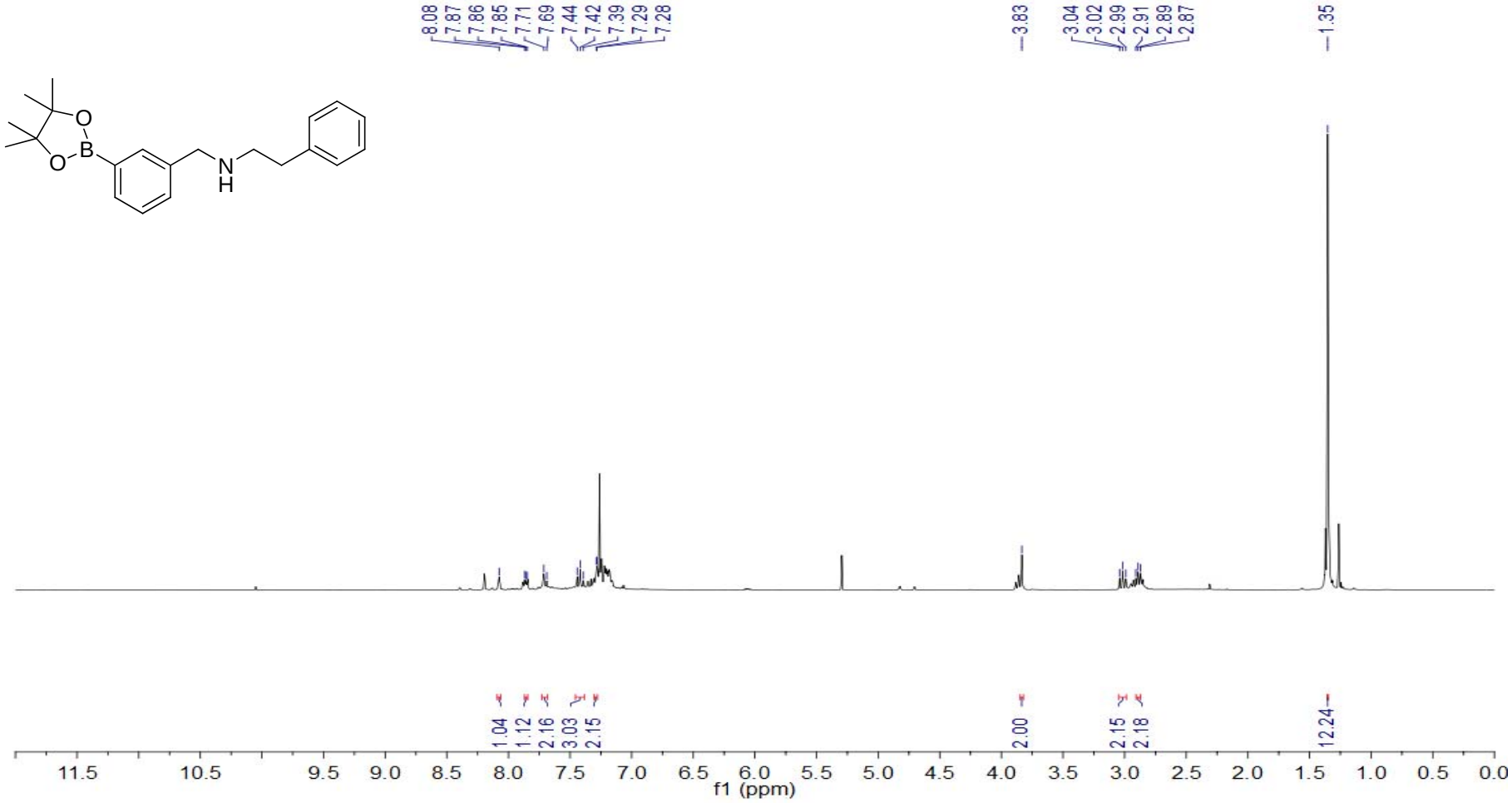
^{1}H NMR Spectra (300 MHz, $CDCl_3$, 25 °C) (Table 5, entry 1)



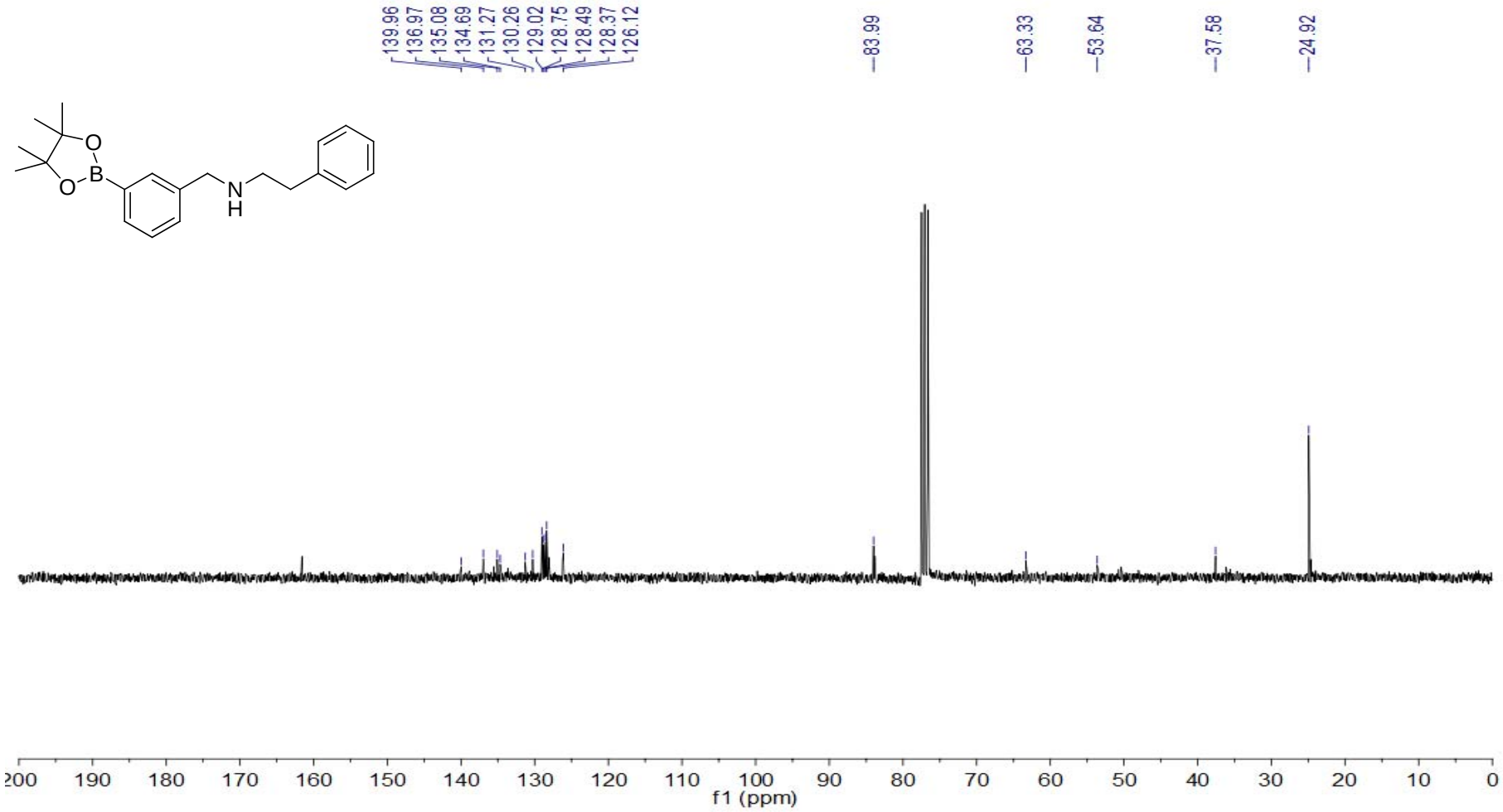
^{13}C NMR Spectra (75.5 MHz, $CDCl_3$, 25 °C) (Table 5, entry 1)



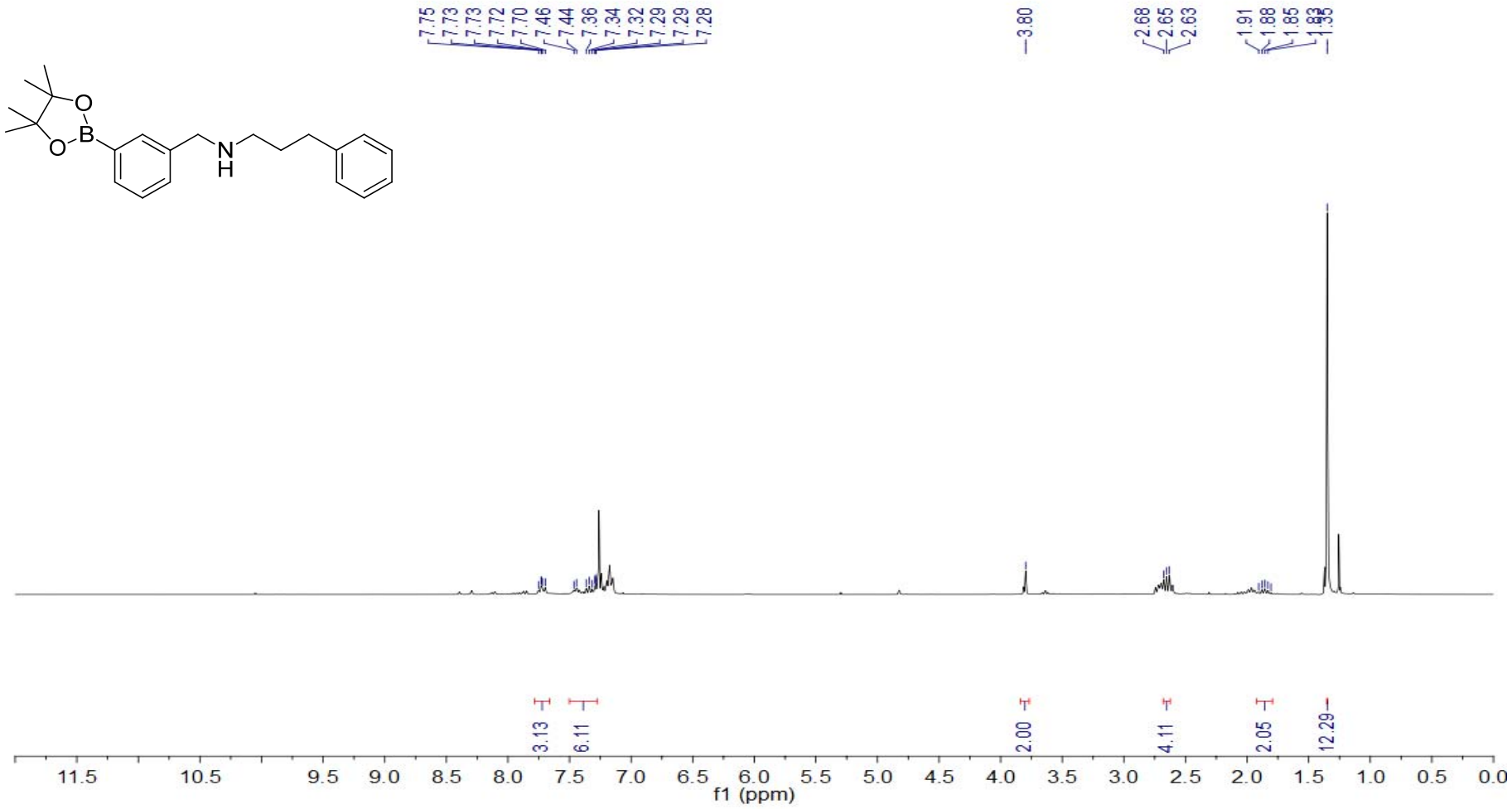
^{1}H NMR Spectra (300 MHz, $CDCl_3$, 25 °C) (Table 5, entry 2)



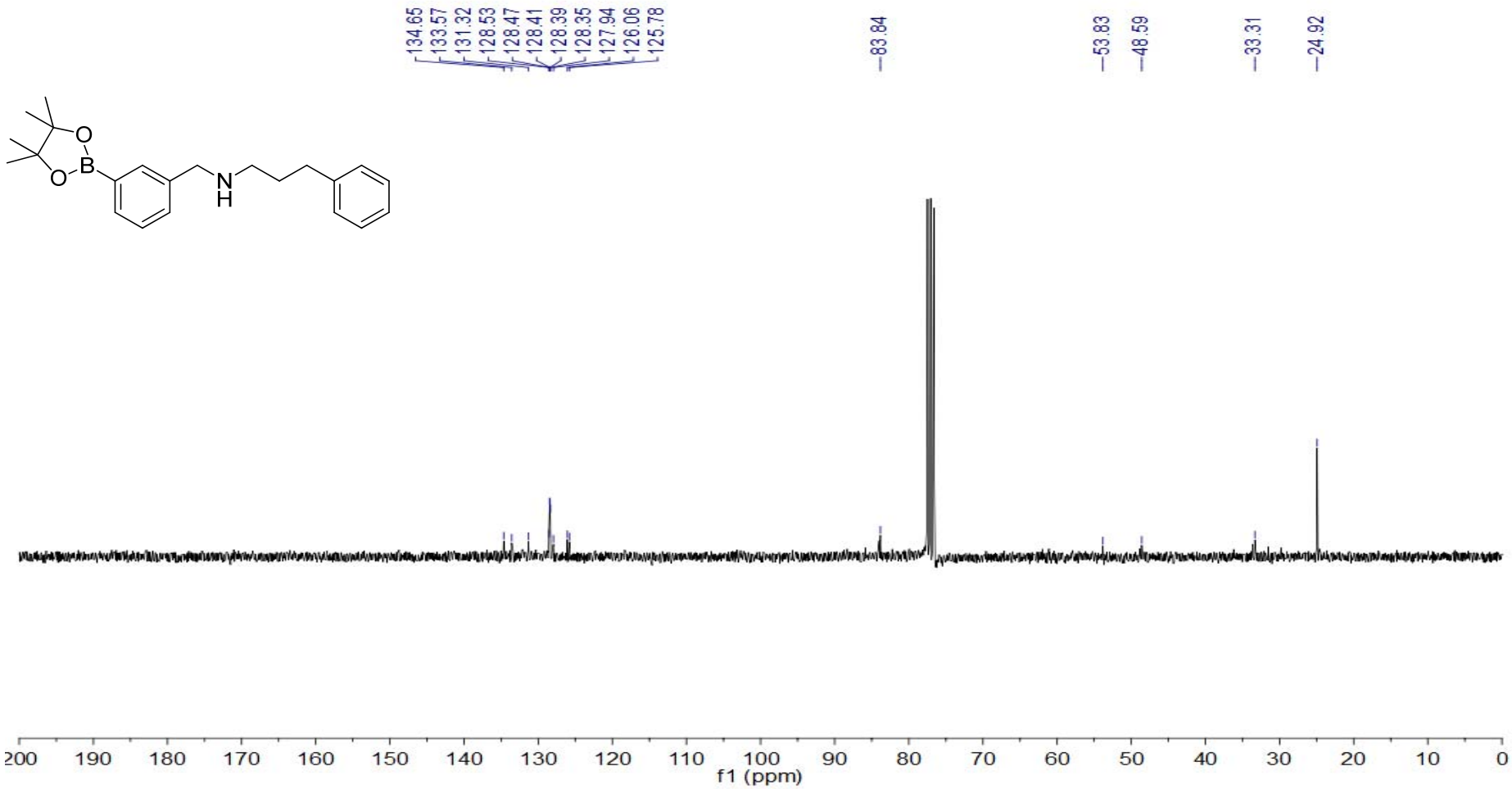
^{13}C NMR Spectra (75.5 MHz, $CDCl_3$, 25 °C) (Table 5, entry 2)



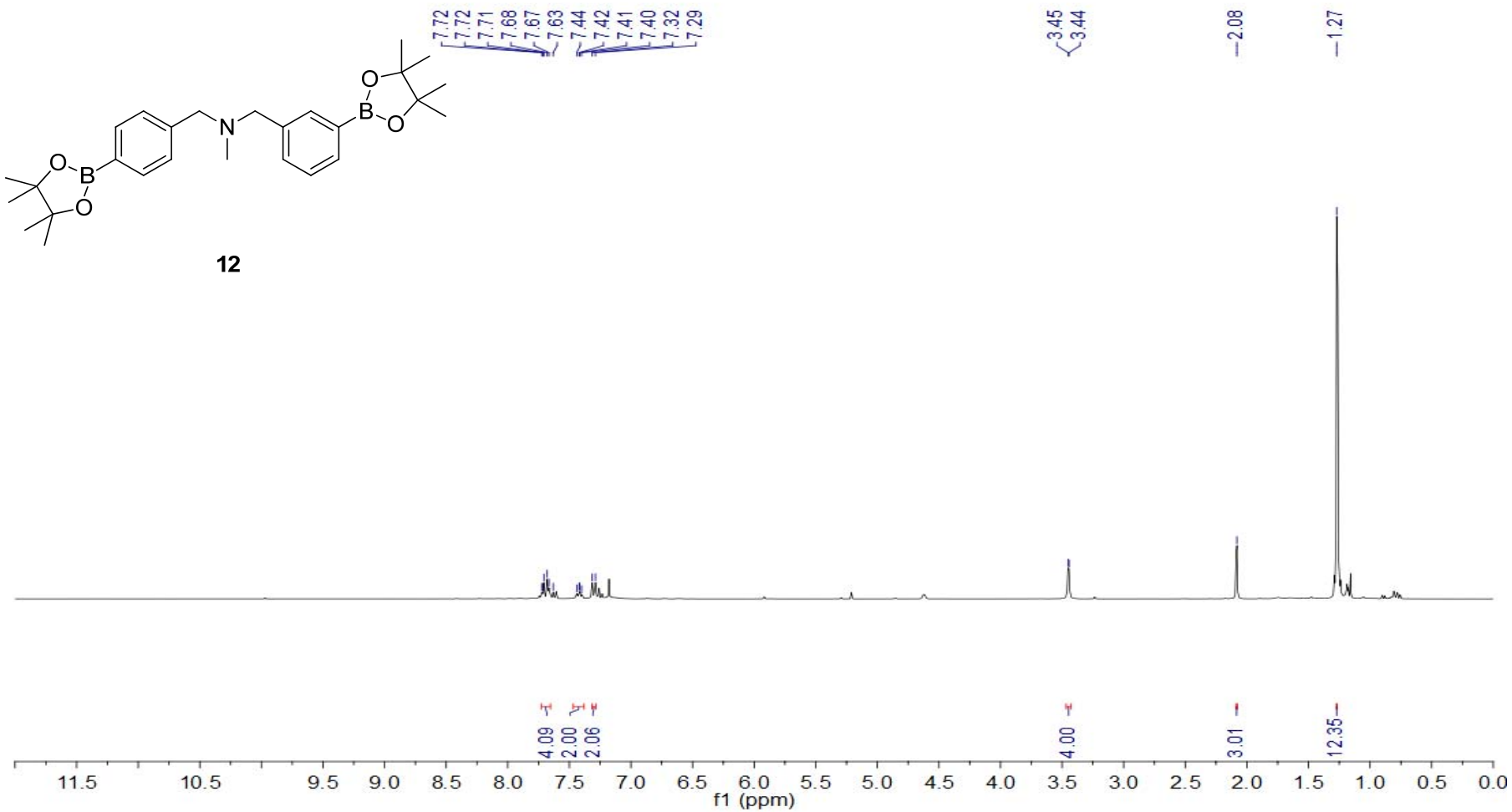
^{1}H NMR Spectra (300 MHz, $CDCl_3$, 25 °C) (Table 5, entry 3)



^{13}C NMR Spectra (75.5 MHz, $CDCl_3$, 25 °C) (Table 5, entry 3)



^{1}H NMR Spectra (300 MHz, $CDCl_3$, 25 °C)



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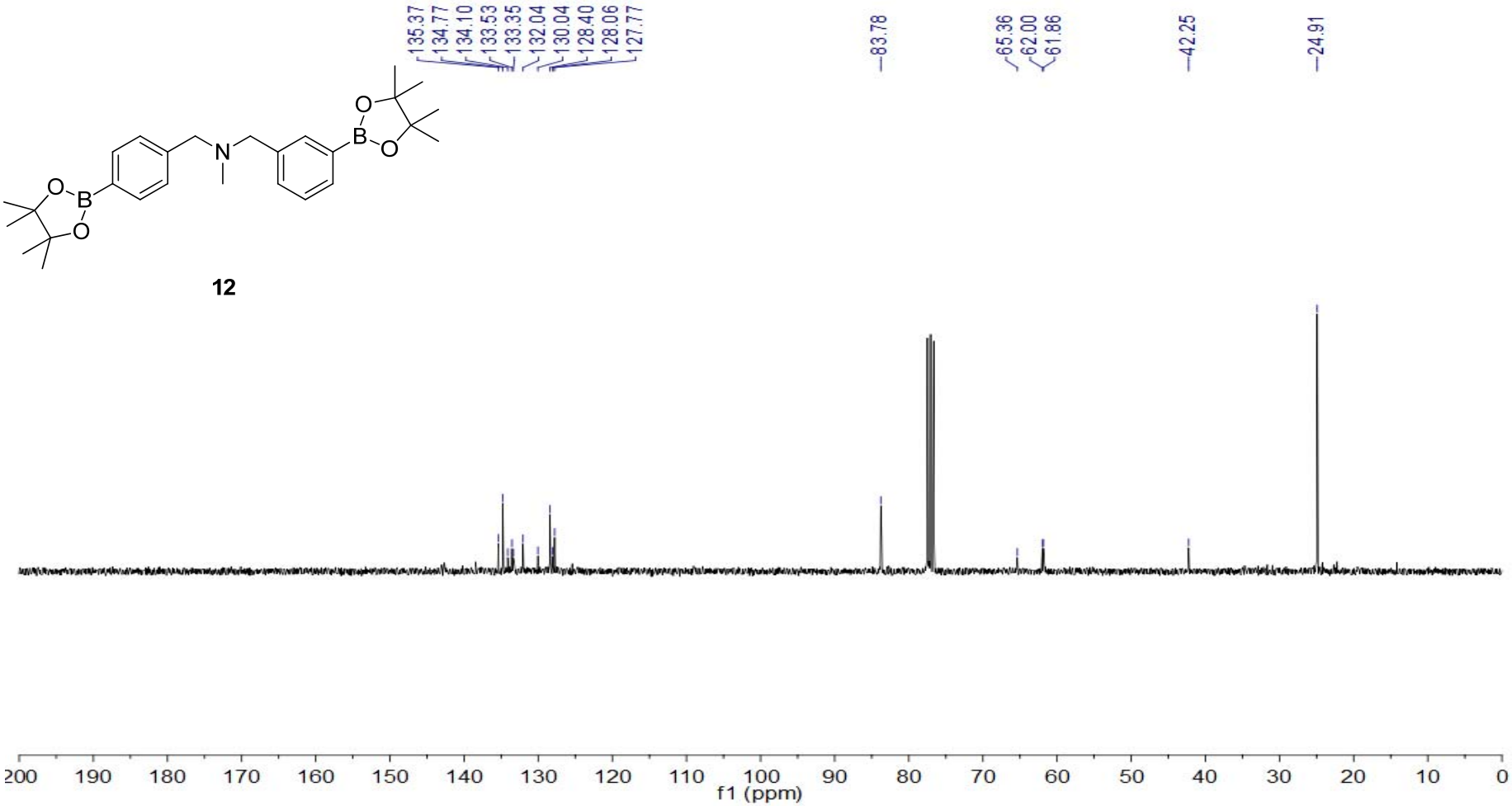
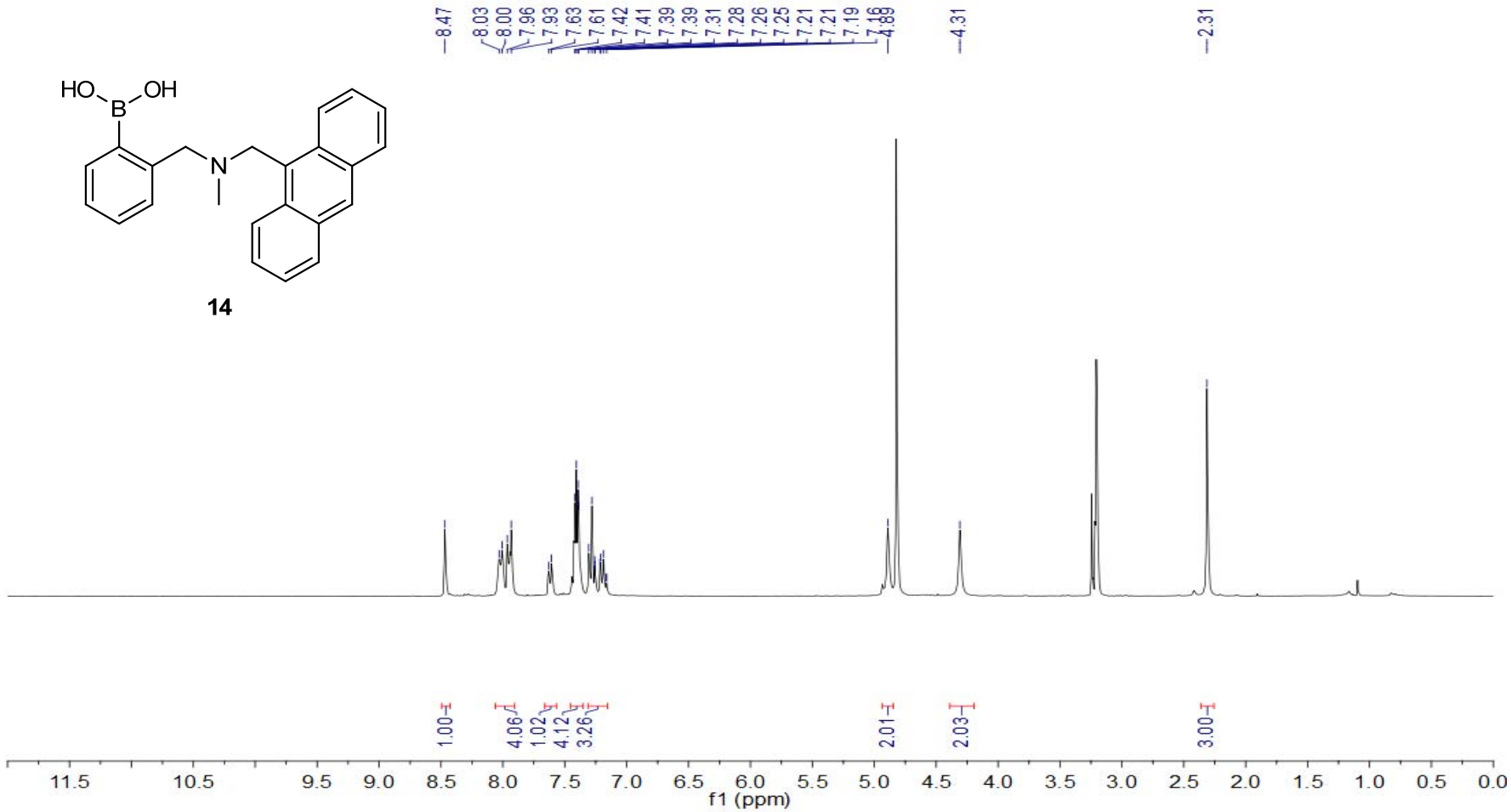
^{13}C NMR Spectra (75.5 MHz, $CDCl_3$, 25 °C)

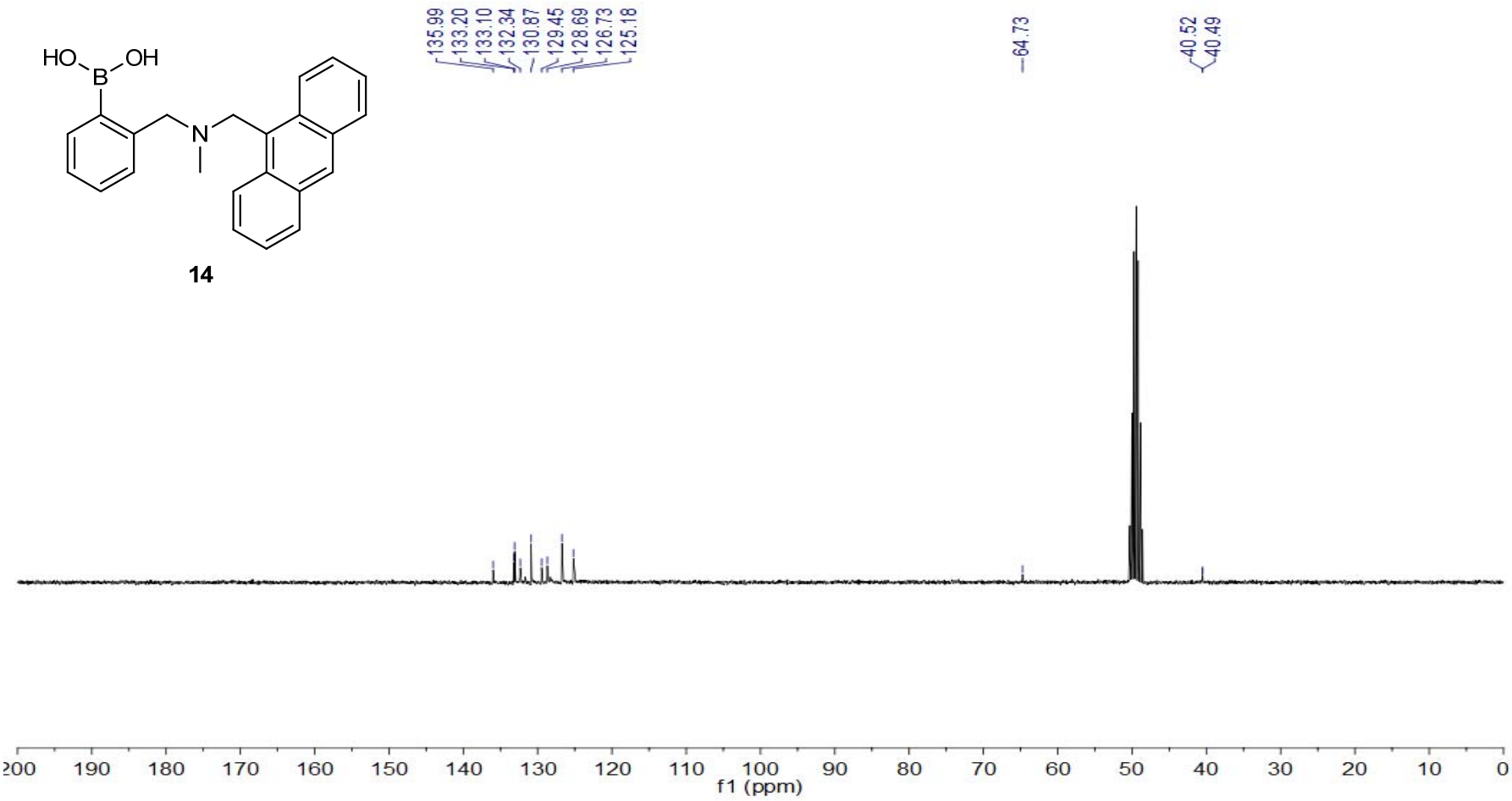


12

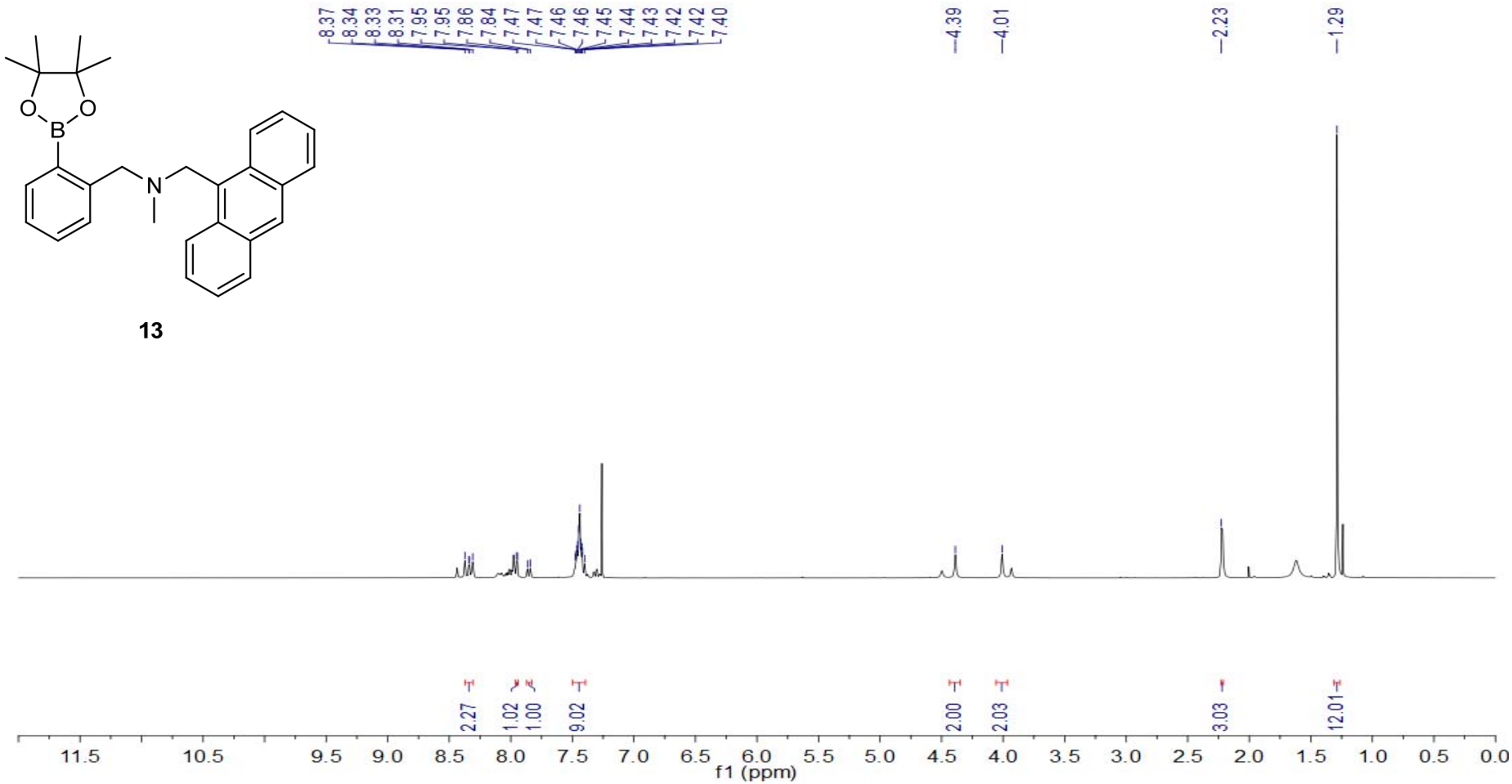
^{1}H NMR Spectra (300 MHz, CD_3OD, 25 °C)



^{13}C NMR Spectra (300 MHz, CD_3OD, 25 °C)

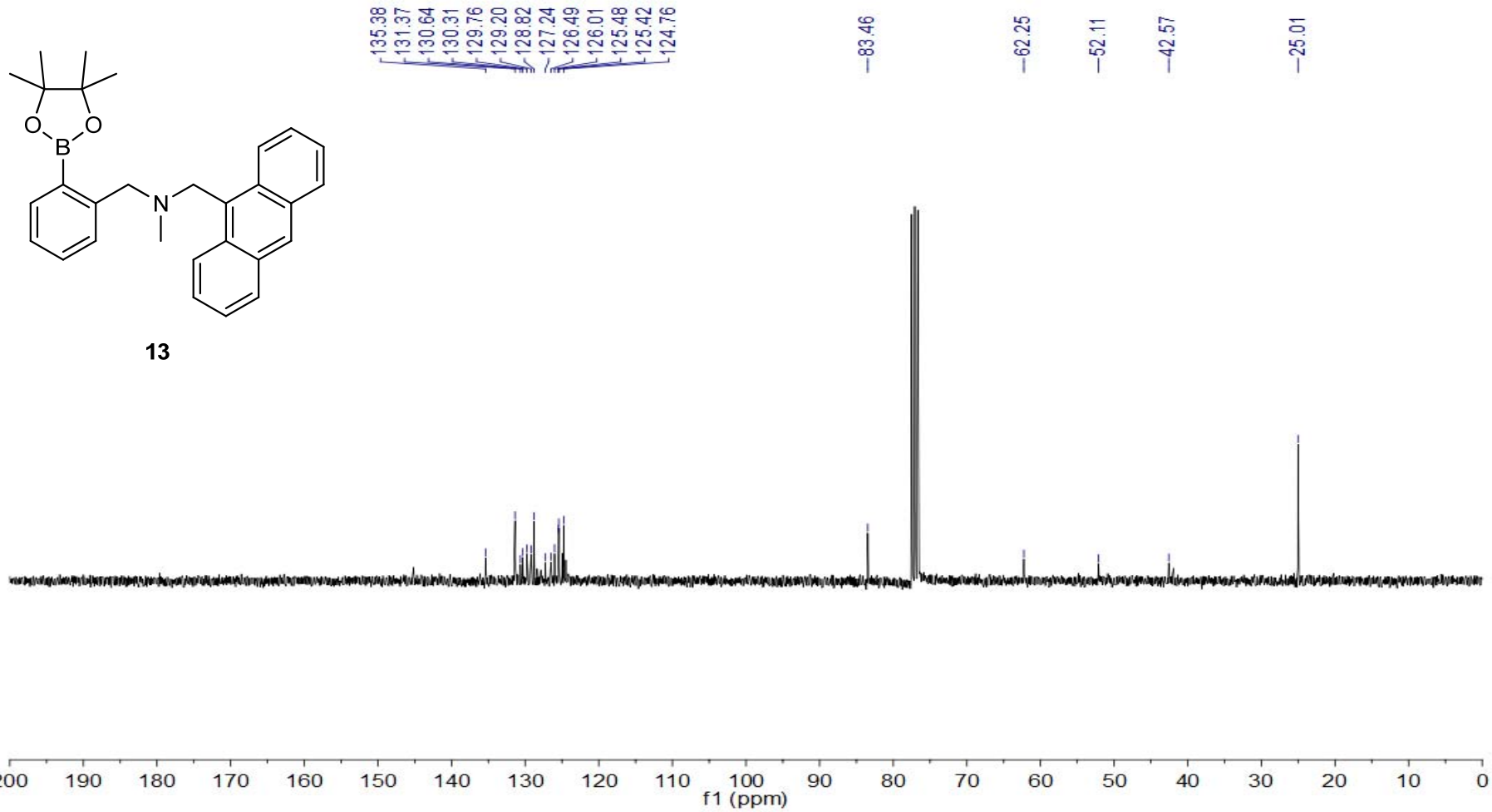


^{1}H NMR Spectra (300 MHz, $CDCl_3$, 25 °C)



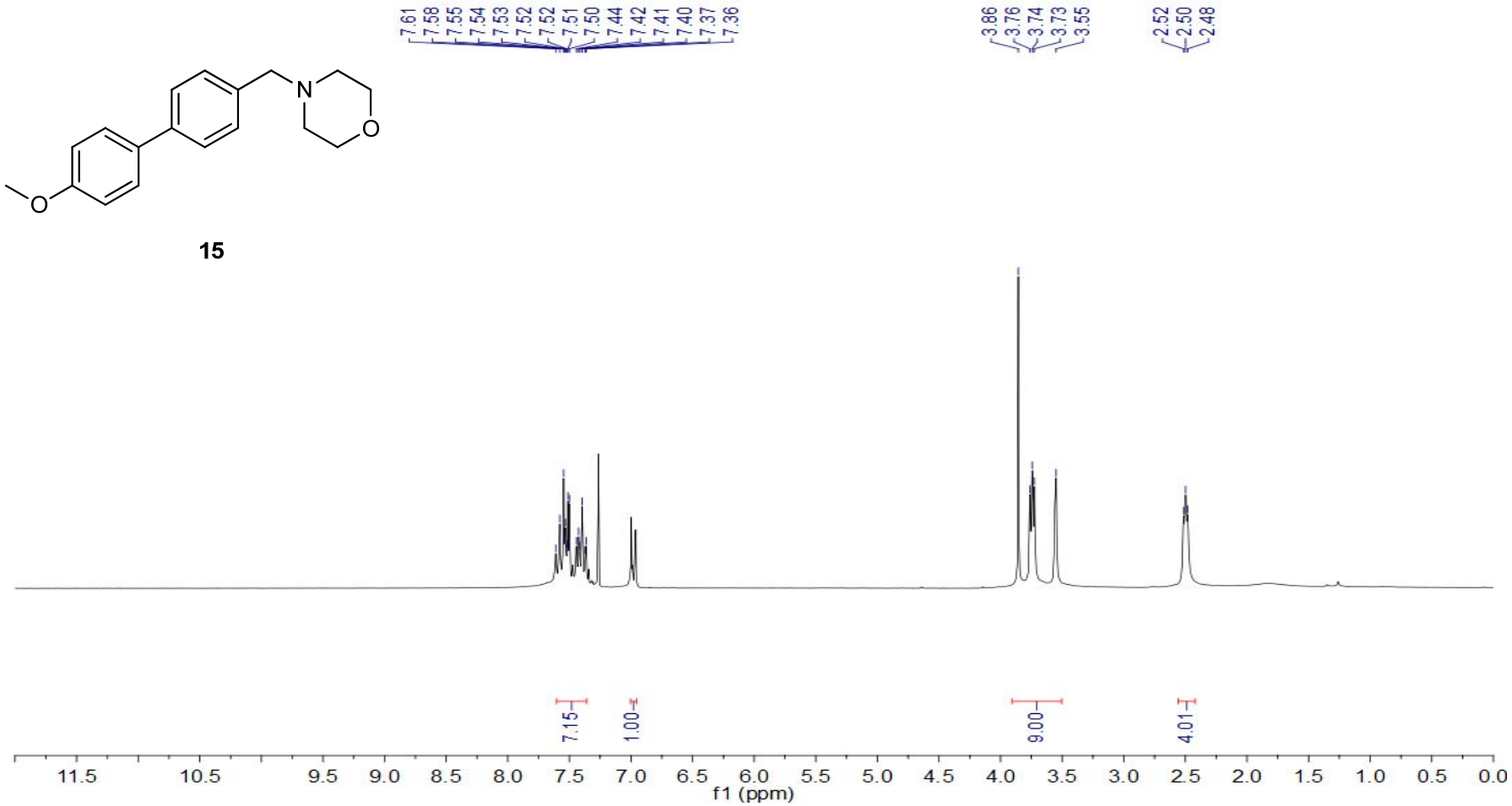
13

^{13}C NMR Spectra (300 MHz, $CDCl_3$, 25 °C)

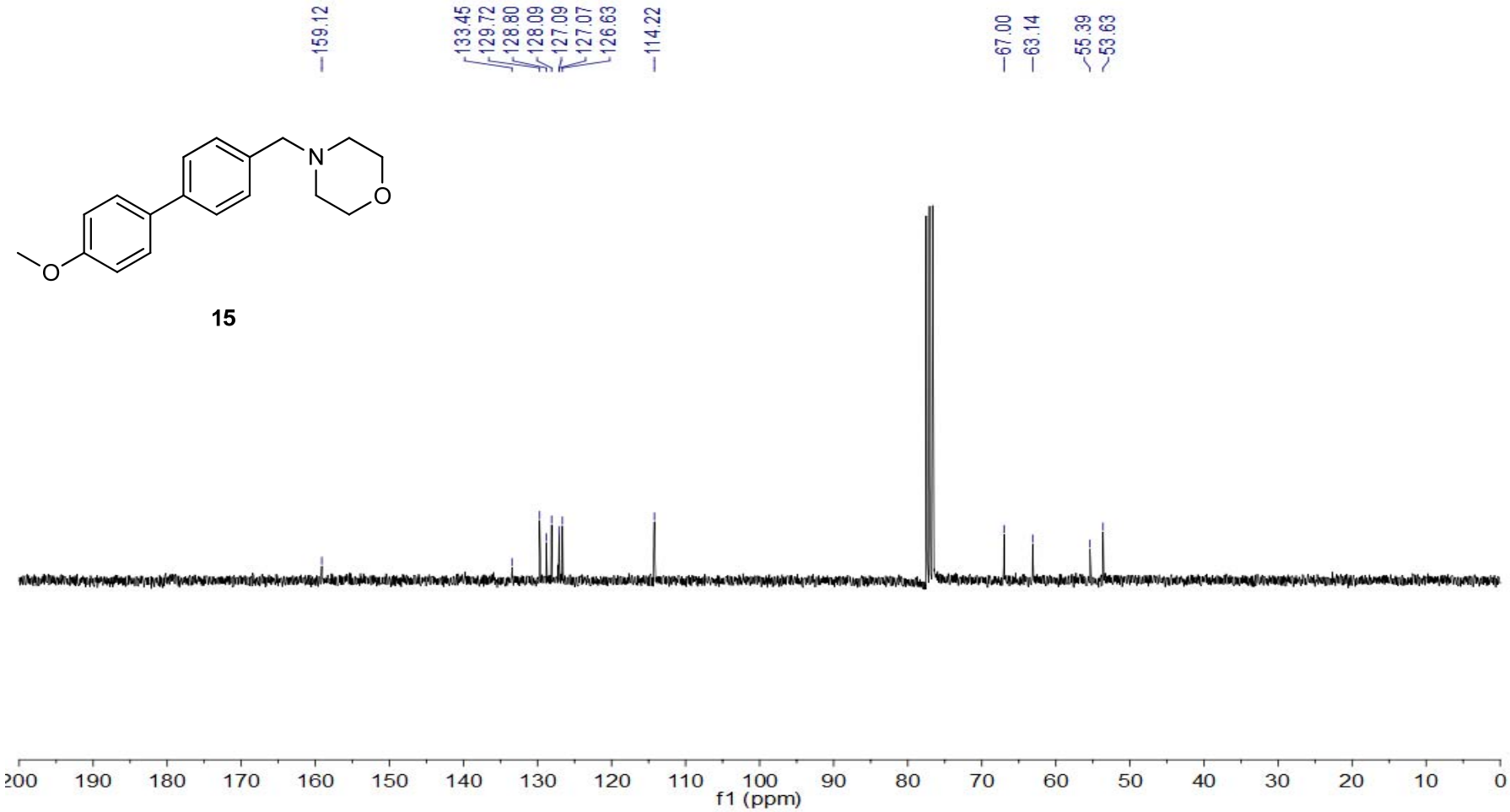


13

^{1}H NMR Spectra (300 MHz, $CDCl_3$, 25 °C)



^{13}C NMR Spectra (300 MHz, $CDCl_3$, 25 °C)



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