

Ni-catalyzed Arylboration of Unactivated Alkenes: Scope and Mechanistic Studies

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General Considerations: Infrared (IR) spectra were recorded on a Bruker Tensor II FT-IR Spectrometer, ν_{max} in cm^{-1} . Bands are characterized as broad (br), strong (s), medium (m), and weak (w). ¹H NMR spectra were recorded at room temperature unless otherwise noted on a Varian I400 (400 MHz), Varian VXR400 (400 MHz), Varian I500 (500 MHz), or a Varian I600 (600 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the residual solvent resonance as the internal standard (CHCl_3 : δ 7.26 ppm or C_7H_9 : δ 2.08 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz), and integration. ¹³C NMR spectra were recorded on a Varian I400 (100 MHz), Varian VXR400 (100 MHz), Varian I500 (125 MHz), or a Varian I600 (150 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl_3 : δ 77.16 ppm or C_7D_9 : δ 20.43). ¹⁹F NMR spectra were recorded on Varian VXR400 (375 MHz) spectrometer. High-resolution mass spectrometry (HRMS) was performed on either a Waters/Micromass LCT Classic (ESI-TOF) or a Thermo Electron Corporation MAT 95XP-Trap (GC/MS). Melting points were obtained on a Thomas Hoover capillary melting point apparatus without correction. The diastereomeric and regioisomeric ratios were determined using NMR analysis of unpurified reaction mixtures. GC analyses were performed by means of Agilent 6850 Gas Chromatograph equipped with Agilent 19091Z-413E, 30 m x 320 μm x 0.25 μm column. Helium was used as the GC carrier gas and maintained at a constant flow rate of 25.0 mL/min. The capillary column was held for 1.0 minutes at the initial temperature (60 °C) and subsequently ramped at a rate of 25 °C /min to a final temperature of 300 °C. Total run time was 9.60 min. Unless otherwise noted, all reactions have been carried out with distilled and degassed solvents under an atmosphere of dry N_2 in oven- (135 °C) and flame-dried glassware with standard vacuum-line techniques. Tetrahydrofuran and N,N-Dimethylformamide were purified under a positive pressure of dry argon by passage through two columns of activated alumina. Toluene was purified under a positive pressure of dry argon by passage through columns of activated alumina and Q5 (Grubbs apparatus). All work-up and purification procedures were carried out with reagent grade solvents (purchased from Sigma-Aldrich) in air. Standard column chromatography techniques using ZEOprep 60/40-63 μm silica gel or a CombiFlash Rf 150 with pre-packed silica cartridges were used for purification.

■ Reagents and Catalysts:

(((3-Methylbut-3-en-1-yl)oxy)methyl)benzene was synthesized in accordance with literature procedure.¹

(2-Bromoethylidene)cyclohexane was synthesized in accordance with literature procedure.²

(3-Methoxypropyl)triphenylphosphonium bromide was synthesized in accordance with literature procedure.³

(3-Methylbut-3-en-1-yl)benzene was synthesized in accordance with literature procedure.⁴

1,3,5-Trimethylbenzene was purchased from Sigma-Aldrich and purified via column chromatography (100% pentane) and stored over activated 4Å molecular sieves.

(E)-1-Bromo-2-methylbut-2-ene was synthesized in accordance with literature procedure.⁵

(E)-3-Methylpent-2-ene was purchased from TCI and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

(Z)-3-Methylpent-2-ene was purchased from TCI and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

2-(4-Bromophenyl)-1,3-dioxolane was synthesized in accordance with literature procedure.⁶

3-Methylbut-3-en-1-yl benzoate was synthesized in accordance with literature procedure.⁷

4-(4-Bromobenzyl)morpholine was synthesized in accordance with literature procedure.⁸

4-(5-Bromopyridin-2-yl)morpholine was purchased from Synthonix and used as received.

1-Benzyl-3-methyl-1,2,5,6-tetrahydropyridine was synthesized in accordance with literature procedure.⁹

1-Boc-piperidine-4-carboxaldehyde was purchased from Combi Blocks and used as received.

1-Bromo-2-((3-methylbut-3-en-1-yl)oxy)benzene was synthesized in accordance with literature procedure.¹⁰

1-Bromo-2-(but-3-en-1-yl)benzene was prepared in accordance with literature procedure.¹¹

1-Bromo-2-methylprop-1-ene was purchased from Sigma-Aldrich and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

1-Bromo-3-chlorobenzene was purchased from Oakwood and used as received.

1-Bromo-4-chlorobenzene was purchased from Sigma-Aldrich and used as received.

1-Bromo-4-fluorobenzene was purchased from Oakwood and used as received.

1-Bromo-4-(trifluoromethoxy)benzene was purchased from Combi-Blocks and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

1-Methylcyclopent-1-ene was purchased from TCI and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

2-Bromotoluene was purchased from Sigma-Aldrich and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

3-(2-bromophenyl)propanal was synthesized in accordance with literature procedure.¹²

3-Bromobenzyl alcohol was purchased from Combi-Blocks and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

3-Bromofuran was purchased from Combi-Blocks and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

4-Bromoanisole was purchased from Combi-Blocks and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

5-Bromo-2-methoxypyridine was purchased from Combi-Blocks and used as received.

8-Ethylidene-1,4-dioxaspiro[4.5]decane was synthesized in accordance with literature procedure.¹³

8-Methylene-1,4-dioxaspiro[4.5]decane was synthesized in accordance with literature procedure.¹⁴

Allylbenzene was purchased from Alfa Aesar and purified via neat filtration through a 2cm pad of dry silica in a 5.75-inch pipet prior to use.

Allylcyclohexane was purchased from Sigma-Aldrich and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

Benzyl 3-methylenepyrrolidine-1-carboxylate was synthesized in accordance with literature procedure.¹⁵

Bis(pinacolato)diboron was purchased from Oakwood and purified via recrystallization from pentane prior to use.

Bromobenzene was purchased from Sigma-Aldrich and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

But-3-en-1-ylbenzene was prepared in accordance with literature procedure.¹⁶

But-3-en-2-ylbenzene was prepared in accordance with literature procedure.¹⁷

Cyclohexyltriphenylphosphonium bromide was synthesized in accordance with literature procedure.¹⁸

Dess-Martin periodinane was purchased from Chem Impex and used as received.

Dibromomethane was purchased from Oakwood and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

Dodecane was purchased from Sigma-Aldrich and used as received.

Di-tert-butyl dicarbonate was purchased from Oakwood and used as received.

Ethyl 3-bromobenzoate was purchased from Oakwood and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

Lithium tert-butoxide was purchased from Strem and used as received.

Methyl cis-1-Boc-4-hydroxy-D-prolinate was purchased from Combi-Blocks and used as received.

Methyl trans-1-Boc-4-hydroxy-L-prolinate was purchased from Oakwood and used as received.

Methyltriphenylphosphonium bromide was purchased from TCI and used as received.

n-butyl lithium (2.5 M in hexane) was purchased from Sigma-Aldrich in a Sure-Seal™ bottle and titrated prior to use.

N,N-Dimethylacetamide (DMA) was purchased from Sigma-Aldrich in a Sure-Seal™ bottle and used as received.

Nickel(II) chloride ethylene glycol dimethyl ether complex (Ni(DME)Cl₂) was purchased from Strem and used as received.

Pd₂(dba)₃ was purchased from Strem and used as received.

Potassium tert-butoxide was purchased from Oakwood and used as received.

Prop-1-en-2-ylcyclohexane was synthesized in accordance with literature procedure.¹⁹

RuPhos was purchased from Sigma-Aldrich and used as received.

Sodium hydride (60% dispersion in mineral oil) was purchased from Sigma Aldrich and used as received.

Sodium iodide was purchased from EMD and used as received.

Sodium tert-butoxide was purchased from Strem and used as received.

tert-Butyl 2,5-dihydro-1H-pyrrole-1-carboxylate was purchased from Combi-Blocks and used as received.

tert-Butyl 2-bromobenzylcarbamate was purchased from Combi Blocks and used as received.

tert-Butyl 3-bromo-9H-carbazole-9-carboxylate was synthesized in accordance with literature procedure.²⁰

tert-Butyl 3-ethylideneazetidine-1-carboxylate was synthesized in accordance with literature procedure.²¹

***tert*-Butyl 3-methyl-2,5-dihydro-1*H*-pyrrole-1-carboxylate** was synthesized in accordance with literature procedure.²²

***tert*-Butyl 3-methylenepiperidine-1-carboxylate** was synthesized in accordance with literature procedure.²³

***tert*-Butyl 4-(cyclobutylidenemethyl)piperidine-1-carboxylate** was synthesized in accordance with the literature procedure.²⁴

***tert*-Butyl 4-ethylidenepiperidine-1-carboxylate** was synthesized in accordance with literature procedure.²⁵

***tert*-Butyl (4-bromophenyl)(methyl)carbamate** was synthesized in accordance with literature procedure.²⁶

***tert*-Butyl 4-methylenepiperidine-1-carboxylate** was synthesized in accordance with literature procedure.²⁷

***tert*-Butyl 4-vinylpiperidine-1-carboxylate** was synthesized in accordance with literature procedure.²⁸

***tert*-Butyl allyl(methyl)carbamate** was synthesized in accordance with literature procedure.²⁹

***tert*-Butylethylene** was purchased from Sigma Aldrich and purified via neat filtration through a 2cm pad of dry silica in a 5.75-inch pipet prior to use.

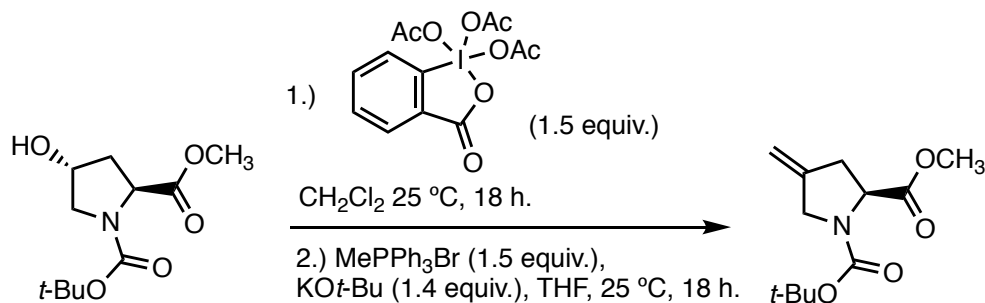
***tert*-Butyl methyl(2-methylallyl)carbamate** was prepared in accordance with literature procedure.³⁰

***tert*-Butyl methyl carbamate** was purchased from Combi-Blocks and used as received.

Vinylcyclohexane was purchased from Alfa Aesar and purified via neat filtration through a 2cm pad of dry silica in a 5.75-inch pipet prior to use.

Vinylcyclopropane Was prepared in accordance with literature procedure.³¹

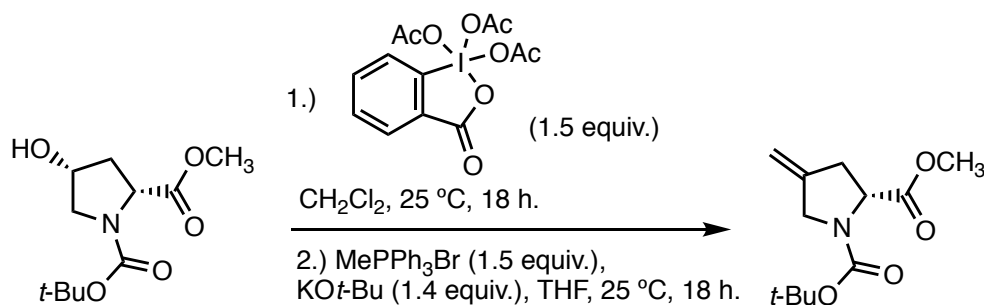
■ Substrate Synthesis



1-(*tert*-Butyl) 2-methyl (*S*)-4-methylenepyrrolidine-1,2-dicarboxylate ((*S*)-72): To a flame-dried round-bottom flask was added methyl *trans*-1-Boc-4-hydroxy-L-prolinate (3.68 g, 15 mmol, 1 equiv.), and Dess-Martin periodinane (9.54 g, 22.5 mmol, 1.5 equiv.). The flask was inerted with three evacuation/backfill (N_2) cycles before adding CH_2Cl_2 (75 mL) via syringe. The mixture was allowed to stir for 18 h. at 25 °C before quenching with saturated NaHCO_3 (25 mL). The aqueous layer was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic extracts were washed with saturated $\text{Na}_2\text{S}_2\text{O}_3$ (3 x 20 mL), and saturated NaHCO_3 (3 x 20 mL). The organic layer was dried over MgSO_4 , filtered and concentrated under reduced pressure. The crude material (2.46 g) was used in the next step without further purification. To a flame-dried round bottom flask was added methyltriphenylphosphonium bromide (5.41 g, 15.2 mmol, 1.5 equiv.) and potassium *tert*-butoxide (1.58 g, 14.1 mmol, 1.4 equiv.). The flask was inerted with three evacuation/backfill (N_2) cycles before adding THF (25 mL) via syringe. The yellow solution was allowed to stir for 0.5 h. before

dropwise addition of the ketone, obtained from the previous step, in a solution of THF (1 M). The reaction was allowed to stir for 18 h. at 25 °C. Pentane (25 mL) was added, and the suspension was filtered over a glass frit via suction filtration. The filtrate was concentrated under reduced pressure. Purification via silica gel chromatography (5:1 hexanes:EtOAc) yields (**S**)-**72** as a colorless oil (1.39 g, 38% over 2 steps). Analytical data was in accordance with literature values.³² The enantiomeric purity was established via HPLC analysis using a chiral column. A racemic sample was obtained by preparing a 1:1 mixture of (**S**)-**72** and (**R**)-**72**.

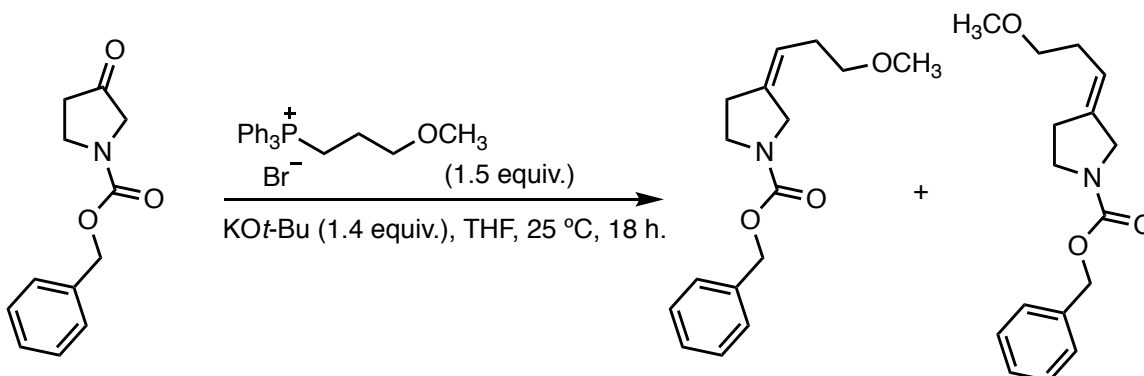
¹H NMR (600 MHz, CDCl₃, mixture of rotamers): δ 5.06 – 4.95 (m, 2H), 4.51 (*minor rotamer* dd, *J* = 9.5, 2.9 Hz, 1H), 4.40 (dd, *J* = 9.5, 3.4 Hz, 1H), 4.15 – 3.98 (m, 2H), 3.73 (s, 3H), 3.06 – 2.86 (m, 1H), 2.73 – 2.51 (m, 1H), 1.48 (*minor rotamer* s, 9H), 1.43 (s, 9H); **¹³C NMR (125 MHz, CDCl₃, mixture of rotamers):** δ 173.2, 172.9, 154.4, 153.8, 143.5, 142.4, 108.0, 107.8, 80.2, 59.1, 58.6, 52.2, 52.1, 50.8, 50.6, 36.8, 36.1, 28.4, 28.3; **HPLC:** ChiralPak IA, 22 °C, 0.6 mL/min, 95:5 hexane:isopropanol, 215 nm. *t_R* = 9.560 min, *t_S* = 11.032 min, 96:4 e.r.



1-(*tert*-Butyl) 2-methyl (*R*)-4-methylenepyrrolidine-1,2-dicarboxylate ((R**)-**72**):** To a flame-dried round-bottom flask was added methyl *cis*-1-Boc-4-hydroxy-D-prolinate (3.68 g, 15 mmol, 1.0 equiv.), and Dess-Martin periodinane (9.54 g, 22.5 mmol, 1.5 equiv.). The flask was inerted with three evacuation/backfill (N₂) cycles before adding CH₂Cl₂ (75 mL) via syringe. The mixture was allowed to stir for 18 h. at 25 °C before quenching with saturated NaHCO₃ (25 mL). The aqueous layer was extracted with CH₂Cl₂ (3 x 20 mL). The combined organic extracts were washed with saturated Na₂S₂O₃ (3 x 20 mL), and saturated NaHCO₃ (3 x 20 mL). The organic layer was dried over MgSO₄, filtered and concentrated under reduced pressure. The crude material (2.28 g) was used in the next step without further purification. To a flame-dried round bottom flask was added methyltriphenylphosphonium bromide (5.04 g, 14.1 mmol, 1.5 equiv.) and potassium *tert*-butoxide (1.47 g, 13.1 mmol, 1.4 equiv.). The flask was inerted with three evacuation/backfill (N₂) cycles before adding THF (25 mL) via syringe. The yellow solution was allowed to stir for 0.5 h. before dropwise addition of the ketone, obtained from the previous step, in a solution of THF (1 M). The reaction was allowed to stir for 18 h. at 25 °C. Pentane (25 mL) was added, and the suspension was filtered over a glass frit via suction filtration. The filtrate was concentrated under reduced pressure. Purification via silica gel chromatography (5:1 hexanes:EtOAc) yields (**R**)-**72** as a colorless oil (1.32 g, 36% over 2 steps). Analytical data was in accordance with literature values.²⁵ The enantiomeric purity was established via HPLC analysis using a chiral column. A racemic sample was obtained by preparing a 1:1 mixture of (**S**)-**72** and (**R**)-**72**.

¹H NMR (600 MHz, CDCl₃, mixture of rotamers): δ 5.06 – 4.95 (m, 2H), 4.51 (*minor rotamer* dd, *J* = 9.5, 2.9 Hz, 1H), 4.40 (dd, *J* = 9.5, 3.4 Hz, 1H), 4.15 – 3.98 (m, 2H), 3.73 (s, 3H), 3.06 – 2.86 (m, 1H), 2.73 – 2.51 (m, 1H), 1.48 (*minor rotamer* s, 9H), 1.43 (s, 9H); **¹³C NMR (125 MHz, CDCl₃, mixture of rotamers):** δ 173.2, 172.9, 154.4, 153.8, 143.5, 142.4, 108.0, 107.8, 80.2, 59.1,

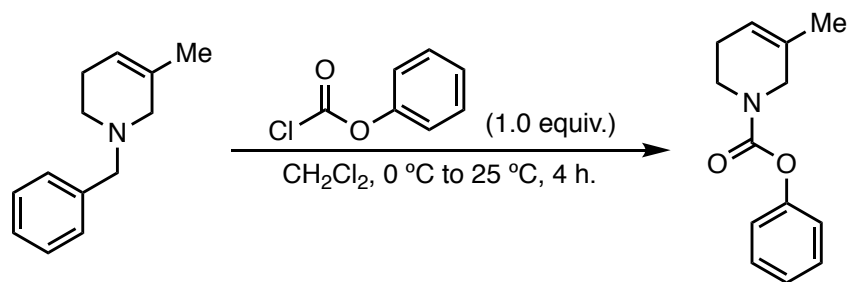
58.6, 52.2, 52.1, 50.8, 50.6, 36.8, 36.1, 28.4, 28.3; **HPLC**: ChiralPak IA, 22 °C, 0.6 mL/min, 95:5 hexane:isopropanol, 215 nm. t_R = 9.549 min, t_S = 11.071 min, 99:1 e.r.



Benzyl (*E*)/(*Z*)-3-(3-methoxypropylidene)pyrrolidine-1-carboxylate (58/60**):** To a flame-dried round bottom flask was added (3-methoxypropyl)triphenylphosphonium bromide (12.5 g, 30 mmol, 1.5 equiv.), and potassium *tert*-butoxide (3.14 g, 28 mmol, 1.4 equiv.). The flask was then inerted with three evacuation/backfill (N_2) cycles before the addition of THF (50 mL) via syringe. The orange solution was allowed to stir for 0.5 h. at 25 °C. Benzyl 3-oxopyrrolidine-1-carboxylate (4.4 g, 20 mmol, 1.0 equiv.) was then added dropwise via syringe. The reaction was allowed to stir for 18 h. at 25 °C. Pentane (50 mL) was then added, and the suspension filtered over a glass frit via suction filtration. The filtrate was then concentrated under reduced pressure. Purification via careful silica gel chromatography (Gradient: 5% to 30% EtOAc in hexane) yields isomerically pure alkenes: yield of (*Z*)-isomer (**59**) (387.8 mg, 7%), yield of (*E*)-isomer (**57**) (780.3 mg, 14%). Low yields are due to difficult separation of the alkene isomers.

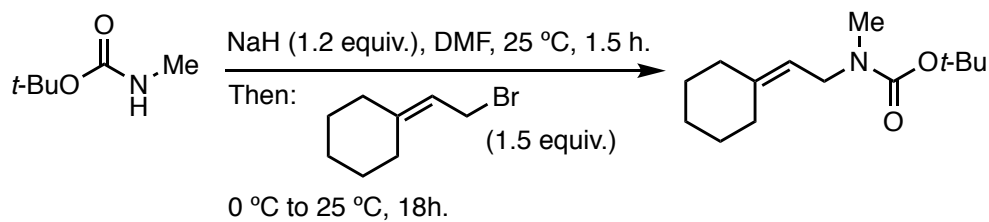
Characterization for (*Z*)-isomer (**60**) (less polar compound): **IR (neat)**: 3032 (w), 2977 (m), 1701 (s), 1416 (m), 1356 (m), 1107 (m), 909 (m), 696 (s) cm^{-1} ; **1H NMR (600 MHz, $CDCl_3$, mixture of rotamers)**: δ 7.50 – 7.27 (m, 5H), 5.51 – 5.30 (m, 1H), 5.15 (s, 2H), 4.11 – 3.90 (m, 2H), 3.52 (dt, J = 14.9, 7.4 Hz, 2H), 3.40 (q, J = 6.7 Hz, 2H), 3.34 (s, 3H), 2.68 – 2.43 (m, 2H), 2.37 – 2.13 (m, 2H); **^{13}C NMR (126 MHz, $CDCl_3$, mixture of rotamers)**: δ 154.9, 138.1, 137.2, 137.0, 128.5, 128.1, 128.0, 127.9, 119.0, 118.9, 72.0, 66.8, 58.7, 48.0, 47.5, 45.7, 45.4, 32.1, 31.4, 30.0, 29.9; **HRMS (EI+)**: Calculated for $C_{16}H_{21}BNO_3$ $[M]^+$: 275.1516, Found: 275.1521. The geometry of the double bond was determined via NOESY (see end of supporting information for NOESY spectrum).

Characterization for (*E*)-isomer (**58**) (more polar compound): **IR (neat)**: 3032 (w), 2924 (m), 1700 (s), 1416 (m), 1356 (m), 1100 (m), 911 (m), 696 (s) cm^{-1} ; **1H NMR (600 MHz, $CDCl_3$, mixture of rotamers)**: δ 7.41 – 7.33 (m, 4H), 7.33 – 7.28 (m, 1H), 5.51 – 5.28 (m, 1H), 5.14 (s, 2H), 4.10 – 3.93 (m, 2H), 3.57 (dt, J = 15.0, 7.5 Hz, 2H), 3.40 (t, J = 6.7 Hz, 2H), 3.34 (s, 3H), 2.60 – 2.49 (m, 2H), 2.35 – 2.26 (m, 2H); **^{13}C NMR (126 MHz, $CDCl_3$, mixture of rotamers)**: δ 154.8, 138.0, 137.2, 137.0, 128.5, 128.0, 127.9, 118.5, 72.0, 66.7, 58.7, 50.9, 50.4, 45.9, 45.6, 29.8, 27.8, 27.2; **HRMS (EI+)**: Calculated for $C_{16}H_{21}BNO_3$ $[M]^+$: 275.1516, Found: 275.1520. The geometry of the double bond was determined via NOESY (see end of supporting information for NOESY spectrum).



Phenyl 5-methyl-3,6-dihydropyridine-1(2H)-carboxylate (68): A flame-dried round bottom flask was charged with 1-benzyl-3-methyl-1,2,5,6-tetrahydropyridine (4.5 g, 24 mmol, 1.0 equiv.), and inerted with three evacuation/backfill (N_2) cycles. CH_2Cl_2 (24 mL) was then added via syringe and cooled to 0 °C. Phenyl chloroformate (3.1 mL, 24 mmol, 1.0 equiv.) was then added dropwise via syringe. The reaction was then warmed to 25 °C and allowed to stir for 4 h. The reaction was quenched by the addition of H_2O (20 mL), and the aqueous layer was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic extracts were dried over $MgSO_4$, gravity filtered, and concentrated under reduced pressure. Purified via silica gel chromatography (Gradient: 5% to 20% EtOAc in hexanes) yields **68** as a colorless oil (1.5 g, 29%).

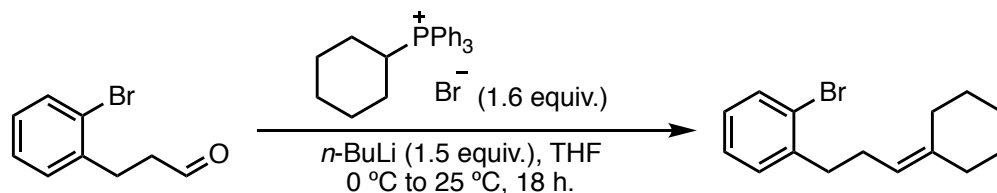
IR (neat): 3009 (w), 2967 (w), 2843 (m), 1715 (s), 1419 (s), 1190 (m), 1083 (m), 691 (m) cm^{-1} ; **1H NMR (600 MHz, $CDCl_3$):** δ 7.41 – 7.32 (m, 2H), 7.22 – 7.17 (m, 1H), 7.13 (d, J = 8.0 Hz, 2H), 5.65 – 5.54 (m, 1H), 4.01 (s, 1H), 3.91 (s, 1H), 3.69 (t, J = 5.7 Hz, 1H), 3.60 (t, J = 5.7 Hz, 1H), 2.26 – 2.15 (m, 2H), 1.79 – 1.68 (m, 3H); **^{13}C NMR (126 MHz, $CDCl_3$, mixture of rotamers):** δ 153.9, 153.7, 151.4, 131.4, 130.7, 129.3, 129.2, 125.2, 121.8, 120.0, 119.5, 47.4, 47.3, 41.2, 40.4, 25.1, 24.5, 20.5; **HRMS (EI+):** Calculated for $C_{13}H_{15}BNO_2$ $[M]^+$: 217.1097, Found: 217.1097.



tert-Butyl (2-cyclohexylideneethyl)(methyl)carbamate: A flame-dried round bottom flask was charged with *tert*-butyl methyl carbamate (1.38 mL, 10.5 mmol, 1.0 equiv.). The flask was inerted with three evacuation/backfill (N_2) cycles before DMF (20 mL) was added via syringe. Sodium hydride (60% dispersion in mineral oil) (500 mg, 12.6 mmol, 1.2 equiv.) was then added portionwise. The solution was cooled to 0 °C before addition of (2-bromoethylidene)cyclohexane (2.97 g, 15.7 mmol, 1.5 equiv.) and sodium iodide (310 mg, 2.1 mmol, 0.2 equiv.). The solution was warmed to 25 °C and stirred for 18 h. The reaction was quenched by the addition of sat. NH_4Cl (20 mL), and the aqueous layer was extracted with Et_2O (3 x 20 mL). The combined organic extracts were washed with brine (3 x 50 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification via silica gel chromatography (10:1 hexanes: EtOAc) yields the title compound as a colorless oil (1.42 g, 56%).

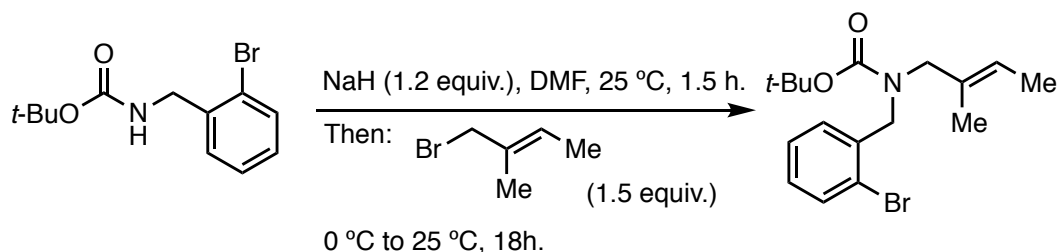
IR (neat): 2926 (m), 2854 (w), 1692 (s), 1364 (m), 1143 (s) cm^{-1} ; **1H NMR (600 MHz, $CDCl_3$):** δ 5.17 – 4.98 (t, J = 7.3 Hz, 1H), 3.81 (br s, 2H), 2.78 (s, 3H), 2.18 (t, J = 5.9 Hz, 2H), 2.10 (t, J = 5.6 Hz, 2H), 1.57 – 1.49 (m, 6H), 1.46 (s, 9H); **^{13}C NMR (126 MHz, $CDCl_3$, mixture of**

rotamers): δ 155.7, 122.6, 116.8, 79.1, 45.4, 44.7, 37.1, 33.1, 28.7, 28.6, 28.5, 27.9, 26.8; **HRMS (EI+)**: Calculated for $C_{14}H_{25}NO_2$ $[M]^+$: 239.1885, Found: 239.1884.



1-Bromo-2-(3-cyclohexylidenepropyl)benzene: A flame-dried round bottom flask was charged with cyclohexyltriphenylphosphonium bromide (8.1 g, 19 mmol, 1.6 equiv.) then inerted with three evacuation/backfill (N_2) cycles. THF (20 mL) was added via syringe and the solution cooled to 0 °C in an ice bath. *n*-butyl lithium (2.2 M in hexanes) (8.1 mL, 17.9 mmol, 1.5 equiv.) was added dropwise and reaction was stirred for 30 minutes at 25 °C. A solution of 3-(2-bromophenyl)propanal (2.53 g, 11.9 mmol, 1.0 equiv.) in THF (10 mL) was then added dropwise and the reaction stirred for 18 h. at 25 °C. Reaction was then diluted with pentane (50 mL) and filtered over a pad of celite. The filtrate was then concentrated under reduced pressure. Purification via silica gel column chromatography (100% hexanes) yields the title compound as a colorless oil (3.1 g, 94%).

IR (neat): 2923 (m), 2850 (m), 1470 (m), 1437 (m), 1023 (m), 746 (s); **1H NMR (600 MHz, $CDCl_3$)**: δ 7.54 – 7.48 (d, J = 7.9, 1H), 7.24 – 7.15 (m, 2H), 7.04 (ddd, J = 7.7, 6.5, 2.5 Hz, 1H), 5.14 (t, J = 7.5 Hz, 1H), 2.75 (t, J = 7.4 Hz, 2H), 2.31 (q, J = 7.6 Hz, 2H), 2.06 (t, J = 6.0 Hz, 4H), 1.50 (t, J = 3.0 Hz, 4H), 1.41 – 1.30 (m, 2H); **^{13}C NMR (126 MHz, $CDCl_3$)**: δ 141.6, 141.0, 132.8, 130.8, 127.5, 127.3, 124.6, 119.9, 37.3, 36.9, 28.9, 28.8, 27.8, 27.6, 27.0; **HRMS (EI+)**: Calculated for $C_{15}H_{19}Br$ $[M]^+$: 278.0670, Found: 278.0663.



1-Bromo-2-(3-cyclohexylidenepropyl)benzene (50): A flame-dried round bottom flask was charged with *tert*-butyl 2-bromobenzylcarbamate (1.38 mL, 10.5 mmol, 1.0 equiv.). The flask was inerted with three evacuation/backfill (N_2) cycles before DMF (10 mL) was added via syringe. Sodium hydride (60% dispersion in mineral oil) (168 mg, 4.2 mmol, 1.2 equiv.) was then added portionwise. The solution was cooled to 0 °C before the addition of (*E*)-1-bromo-2-methylbut-2-ene (0.78 g, 5.25 mmol, 1.5 equiv.) and sodium iodide (104 mg, 0.7 mmol, 0.2 equiv.). The solution was warmed to 25 °C and stirred for 18 h. The reaction was quenched by the addition of sat. NH_4Cl (20 mL), and the aqueous layer was extracted with Et_2O (3 x 20 mL). The combined organic extracts were washed with brine (3 x 50 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification via silica gel chromatography (10:1 hexanes: $EtOAc$) yields **50** as a colorless oil (780 mg, 63%, 20:1 *E:Z*) (45:55 mixture of rotamers).

IR (neat): 2975 (m), 2917 (m), 1693 (s), 1242 (s), 1163 (s), 746 (s) cm^{-1} ; **1H NMR (400 MHz, $CDCl_3$, mixture of rotamers)**: δ 7.50 (d, J = 7.9 Hz, 1H), 7.27 (d, J = 7.5 Hz, 1H), 7.15 (s, 1H),

7.08 (t, $J = 7.8$ Hz, 1H), 5.24 (q, $J = 6.6$ Hz, 1H), 4.45 (s *minor rotomer*, 2H), 4.36 (s, 2H), 3.79 (s, 2H), 3.70 (s *minor rotomer*, 2H), 1.64 – 1.55 (m, 6H), 1.48 (s *minor rotomer*, 9H), 1.38 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3 , *mixture of rotomers*): δ 156.1, 137.6, 137.2, 132.8, 131.4, 128.4, 127.5, 123.3, 122.9, 121.9, 79.9, 54.1, 53.7, 49.2, 48.7, 28.5, 13.8, 13.4, 13.1; HRMS (ESI⁺): Calculated for $\text{C}_{17}\text{H}_{24}\text{NBrNa}$ $[\text{M}+\text{Na}]^+$: 376.0883, Found: 376.0886.

■ Optimization Studies

Table S1: Optimization of Additive

| entry | solvent | yield 1 (%) ^[a] | yield 3 (%) ^[a] |
|-------|-----------------------|-----------------------------------|-----------------------------------|
| 1 | None | 21 | 17 |
| 2 | DMA (0.5 equiv) | 19 | 16 |
| 3 | DMA (1 equiv) | 25 | 17 |
| 4 | DMA (5 equiv) | 51 | 11 |
| 5 | DMA (10 equiv) | 69 | 6 |
| 6 | DMA (20 equiv) | 80 | 5 |
| 7 | DMA (50 equiv) | 76 | 5 |
| 8 | S1 (10 equiv) | 47 | 4 |
| 9 | S2 (10 equiv) | 58 | 9 |
| 10 | S3 (10 equiv) | 54 | 5 |
| 11 | S4 (10 equiv) | 34 | 8 |
| 12 | S5 (10 equiv) | 62 | 7 |
| 13 | S6 (10 equiv) | 31 | <2 |
| 14 | S7 (10 equiv) | 10 | <2 |
| 15 | S8 (10 equiv) | 17 | 14 |
| 16 | S9 (10 equiv) | <5 | <2 |
| 17 | S10 (10 equiv) | 23 | <2 |

[a] Yield was determined via ^1H NMR analysis with an internal standard (mesitylene)

Representative procedure (**Table S1, entry 6**): In an N_2 -filled glovebox, to an oven-dried 16 x 100 mm screw-capped vial was added bis(pinacolato)diboron, (254 mg, 1.00 mmol, 2.00 equiv.), and NaOt-Bu (72.1 mg, 0.75 mmol, 1.50 equiv.). In a separate oven-dried 2-dram vial, $\text{Ni}(\text{DME})\text{Cl}_2$ (8.2 mg, 0.0375 mmol) was added. Both vials were sealed with septa, and removed from the glovebox. THF (4.5 mL) was added to the the reaction vial, followed by alkene (0.5 mmol, 1.0 equiv.) and arylbromide (0.75 mmol, 1.5 equiv.). The reaction vial was then cooled to 0 °C. DMA (1.25 mL) was then added to the vial containing $\text{Ni}(\text{DME})\text{Cl}_2$ (0.025 M in $\text{Ni}(\text{DME})\text{Cl}_2$) to prepare the catalyst solution. 1.00 mL of the catalyst solution was then added to the reaction vial (5 mol% catalyst loading). The septum was then quickly replaced by a Teflon-lined screw cap and the reaction was stirred at 4 °C for 18 h in a temperature-controlled refrigerator. The reaction was quenched upon the addition of 1 M HCl (5.0 mL), and the mixture was extracted with EtOAc (3 x 3.0 mL), dried over MgSO_4 , gravity filtered, and concentrated. Mesitylene was added as an internal standard, and the reaction mixture analyzed via ^1H NMR. Note: It was found that 20 equiv. (0.92

mL) of DMA was optimal for terminal alkenes; however, for ease of reaction set up, we elected to use 1.00 mL of DMA additive.

Table S2: Optimization for the Arylboration of 1,1-Disubstituted Alkenes

$\text{R}-\text{C}(\text{Me})=\text{CH}_2$ (1 equiv.) + $\text{Ph}-\text{Br}$ (X equiv.) $\xrightarrow[\text{Solvent, 4 } ^\circ\text{C, 18 h.}]{\text{Ni(DME)Cl}_2 \text{ (5 mol\%)}, \text{Base (1.5 equiv)}, \text{B}_2\text{pin}_2 \text{ (2 equiv)}}$

R = Cy (**S11**)
 R = $(\text{CH}_2)_2\text{Ph}$ (**30**)

R = Cy (**17**)
 R = $(\text{CH}_2)_2\text{Ph}$ (**31**)

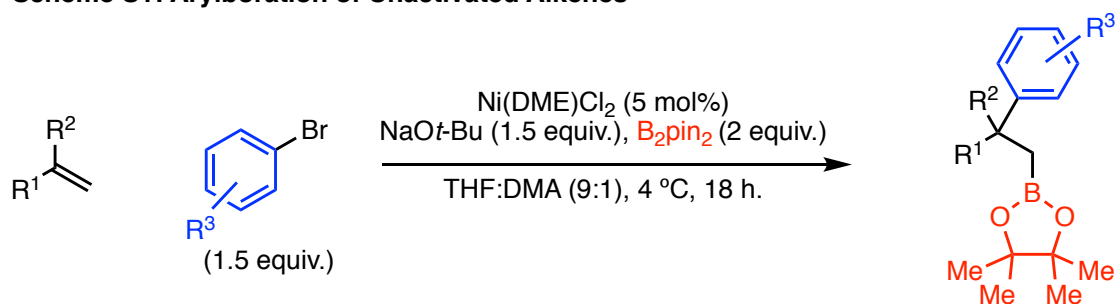
R = Cy (**S12**)
 R = $(\text{CH}_2)_2\text{Ph}$ (**S13**)

| entry | alkene | base | PhBr (equiv.) | solvent | yield 17/31 (%) ^[a] | yield S12/S13 (%) ^[a] |
|-------|------------|---------------------------------|---------------|----------------|---------------------------------------|---|
| 1 | S11 | LiO <i>t</i> -Bu ^[b] | 1.5 | THF | 35 | 37 |
| 2 | S11 | NaO <i>t</i> -Bu ^[b] | 1.5 | THF | 17 | 34 |
| 3 | S11 | LiO <i>t</i> -Bu ^[b] | 3.0 | THF | 48 | 20 |
| 4 | S11 | LiO <i>t</i> -Bu ^[b] | 1.5 | THF:DMA (9:1) | 17 | 5 |
| 5 | S11 | NaO <i>t</i> -Bu | 1.5 | THF:DMPU (9:1) | 52 | 17 |
| 6 | S11 | NaO <i>t</i> -Bu | 1.5 | THF:DMF (9:1) | 37 | 9 |
| 7 | S11 | NaO <i>t</i> -Bu | 1.5 | THF:NMP (9:1) | 56 | 18 |
| 8 | S11 | NaO <i>t</i> -Bu | 1.5 | THF:DMA (9:1) | 67 | 19 |
| 9 | S11 | NaO <i>t</i> -Bu | 3.0 | THF:DMA (9:1) | 71 | 7 |
| 10 | S11 | NaO <i>t</i> -Bu | 3.0 | THF:DMA (6:1) | 70 | 7 |
| 11 | S12 | LiO <i>t</i> -Bu | 1.5 | THF | 53 | <2 |
| 12 | S12 | NaO <i>t</i> -Bu | 1.5 | THF:DMA (9:1) | 90 | <2 |

[a] Yield was determined via GC analysis with a calibrated internal standard (dodecane) [b] reaction performed at 30 °C

Representative procedure (**Table S2, entry 12**): In an N₂-filled glovebox, to an oven-dried 16 x 100 mm screw-capped vial was added bis(pinacolato)diboron, (254 mg, 1.00 mmol, 2.00 equiv.), and NaO*t*-Bu (72.1 mg, 0.75 mmol, 1.50 equiv.). In a separate oven-dried 2-dram vial, Ni(DME)Cl₂ (8.2 mg, 0.0375 mmol) was added. Both vials were sealed with septa, and removed from the glovebox. THF (4.5 mL) was added to the the reaction vial, followed by alkene (0.5 mmol, 1.0 equiv.) and arylbromide (0.75 mmol, 1.5 equiv.). The reaction vial was then cooled to 0 °C. DMA (0.75 mL) was then added to the vial containing Ni(DME)Cl₂ (0.05 M in Ni(DME)Cl₂) to prepare the catalyst solution. 0.50 mL of the catalyst solution was then added to the reaction vial (5 mol% catalyst loading). The septum was then quickly replaced by a Teflon-lined screw cap and the reaction was stirred at 4 °C for 18 h in a temperature-controlled refrigerator. The reaction was quenched upon the addition of 1 M HCl (5.0 mL), and the mixture was extracted with EtOAc (3 x 3.0 mL), dried over MgSO₄, gravity filtered, and concentrated. Dodecane was added as an internal standard, and the reaction mixture analyzed via GC.

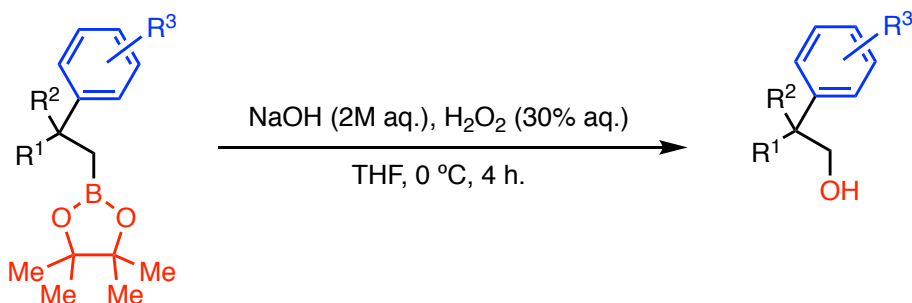
Scheme S1: Arylboration of Unactivated Alkenes



■ General Procedure A: Ni-Catalyzed Arylboration of Alkenes

In an N_2 -filled glovebox, to an oven-dried 16 x 100 mm screw-capped vial was added bis(pinacolato)diboron, (254 mg, 1.00 mmol, 2.00 equiv.), and $NaOt-Bu$ (72.1 mg, 0.75 mmol, 1.50 equiv.). In a separate oven-dried 2-dram vial, $Ni(DME)Cl_2$ (8.2 mg, 0.0375 mmol) was added. Note: if the aryl bromide is a solid, it was added to the vial in the glovebox (0.75 mmol, 1.50 equiv.). Both vials were sealed with septa, and removed from the glovebox. THF (4.5 mL) was added to the reaction vial, followed by alkene (0.5 mmol, 1.0 equiv.) and arylbromide (0.75 mmol, 1.5 equiv.) and cooled to 0 °C. DMA (0.75 mL) was then added to the vial containing $Ni(DME)Cl_2$ (0.05 M in $Ni(DME)Cl_2$) to prepare the catalyst solution. 0.50 mL of the catalyst solution was then added to the reaction vial (5 mol% catalyst loading). The septum was then quickly replaced by a Teflon-lined screw cap and the reaction was stirred at 4 °C for 18 h in a temperature-controlled refrigerator. The reaction was quenched upon the addition of 1 M HCl (5.0 mL), and the mixture was extracted with EtOAc (3 x 3.0 mL), dried over $MgSO_4$, gravity filtered, and concentrated. 1,3,5-Trimethylbenzene was added as an internal standard and a small aliquot was analyzed via 1H NMR. The NMR sample was then combined with the rest of the crude mixture and dissolved in hexanes (15 mL). The solution was then washed with 1 M KOH (3 x 5.0 mL), dried over $MgSO_4$, gravity filtered, and concentrated before purification via silica gel column chromatography. (Note: For terminal alkenes, we observed <5% of the 1,1-arylboration product unless otherwise noted).

Scheme S2: Oxidation of Alkyl Boronic Esters



■ General Procedure B: Oxidation of Alkyl Boronic Esters

Alkyl boronic ester was dissolved in THF (3 mL) and cooled to 0 °C before $NaOH$ (2M aq., 3 mL) and hydrogen peroxide (30 % aq., 3 mL) were added. The reaction was allowed to stir at 0 °C for 4 h. before being carefully quenched with saturated $Na_2S_2O_3$ (3 mL). The aqueous layer was

extracted with EtOAc (3 x 5 mL) and the combined organic extracts were dried over MgSO₄, gravity filtered, and the solvent removed under reduced pressure. The crude material was then purified via silica gel chromatography.

In cases where separation from pinacol is problematic: The crude mixture was dissolved in acetone/H₂O (1:1, 5 mL) before NaIO₄ (545.4 mg, 2.5 mmol, 5.0 equiv.) and NH₄OAc (196.6 mg, 2.6 mmol, 5.2 equiv.) were added. The mixture was stirred for 2 h. before being quenched with H₂O (5 mL). The aqueous layer was extracted with EtOAc (3 x 5 mL). The combined organic extracts were dried over MgSO₄ and gravity filtered. The solvent was then removed under reduced pressure, and the crude material was then purified via silica gel chromatography.

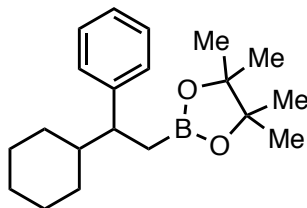
■ Gram-scale Glovebox-free Arylboration of Alkenes:

A 500-mL, three-necked, round bottom flask was equipped with a nitrogen inlet, rubber septum and a glass stopper before evacuating and flame drying. The flask was allowed to cool under vacuum before being charged with bis(pinacolato)diboron, (9.91 g, 39.0 mmol, 2.00 equiv.), and NaOt-Bu (1.87 g, 19.5 mmol, 1.50 equiv.). The flask was then inerted with 3 evacuation/backfill (N₂) cycles. A separate flame-dried 25-mL round bottom flask was charged with Ni(DME)Cl₂ (153.8 mg, 0.7 mmol) and inerted with 3 evacuation/backfill (N₂) cycles before adding DMA (14 mL) to prepare the catalyst solution (0.5 M in Ni(DME)Cl₂). THF (117 mL) was then added to the three-necked flask and the suspension was cooled to 4 °C before adding PhBr (4.2 mL, 39.0 mmol, 3.00 equiv), and 1-methyl cyclopentene (1.4 mL, 13 mmol, 1.00 equiv). 13 mL of the catalyst solution was then added to the three-necked flask (5 mol% catalyst loading). The reaction was allowed to stir at 4 °C for 6 h. before being quenched upon the addition of 1 M HCl (100 mL). The aqueous layer was then extracted with Et₂O (3 x 50 mL). The combined organic extracts were dried over MgSO₄, gravity filtered, and the solvent was removed under reduced pressure. The residue was then dissolved in hexanes (75 mL) and washed with 1M KOH (3 x 100 mL). The organic layer was dried over MgSO₄, gravity filtered, and the solvent was removed under reduced pressure. Purification via silica gel column chromatography (gradient: hexanes to 15:1 hexanes: Et₂O) yields **43** as a pale yellow oil (3.03 g, 81% yield, >20:1 d.r.).

IR (neat): 3057 (w), 2974 (m), 2956 (m), 2871 (m), 1495 (m), 1369 (s), 1142 (s), 973 (m), 697 (m); **¹H NMR (600 MHz, CDCl₃):** δ 7.36 – 7.30 (m, 2H), 7.26 – 7.20 (m, 2H), 7.16 – 7.07 (m, 1H), 2.23 (dt, *J* = 11.7, 8.7 Hz, 1H), 2.06 – 1.93 (m, 1H), 1.92 – 1.71 (m, 4H), 1.60 (dd, *J* = 8.9, 5.4 Hz, 1H), 1.35 (s, 3H), 0.95 (s, 6H), 0.90 (s, 6H); **¹³C NMR (125 MHz, CDCl₃):** δ 150.8, 127.8, 126.9, 125.4, 82.5, 49.8, 39.1, 31.3, 26.7, 24.7, 24.6, 23.8 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation); **HRMS (ESI+):** Calculated for C₁₈H₂₇BO₄ [M]⁺: 286.2102, Found: 286.2107.

■ Characterization Data:

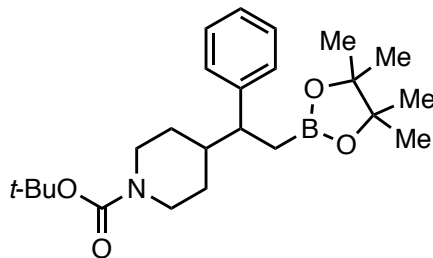
In ^{13}C NMR spectra, signals of carbons directly bonded to boron were not detected because of quadrupolar relaxation.



2-(2-cyclohexyl-2-phenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2): The title compound was prepared according to a modified version of general procedure A using a 4:1 THF:DMA mixture and 3.0 equiv of PhBr. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (Gradient: hexanes to 20:1 hexanes: EtOAc) yields **2** as a colorless oil.

Average over 2 runs: 74% NMR yield, 67% isolated yield, 30:1 r.r.,

IR (neat): 3085 (w), 2977 (m), 2850 (m), 1449 (m), 1361 (s), 1143 (s), 967 (m), 750 (m) cm^{-1} ; **^1H NMR (600 MHz, CDCl_3):** δ 7.24 – 7.19 (m, 2H), 7.18 – 7.09 (m, 3H), 2.60 (ddd, J = 10.7, 7.8, 5.8 Hz, 1H), 1.93 – 1.83 (m, 1H), 1.78 – 1.69 (m, 1H), 1.66 – 1.54 (m, 2H), 1.48 – 1.41 (m, 1H), 1.41 – 1.32 (m, 1H), 1.29 (dd, J = 15.1, 5.7 Hz, 1H), 1.24 – 1.16 (m, 1H), 1.14 – 1.04 (m, 3H), 1.02 (s, 6H), 1.00 (s, 6H), 0.92 (qd, J = 12.6, 3.8 Hz, 1H), 0.78 (qd, J = 12.3, 3.7 Hz, 1H); **^{13}C NMR (125 MHz, CDCl_3):** δ 146.4, 128.5, 127.8, 125.7, 82.9, 47.6, 45.2, 31.1, 31.0, 26.7, 26.8, 24.7, 24.8, 24.6 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation); **HRMS (ESI+):** Calculated for $\text{C}_{20}\text{H}_{31}\text{BO}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 337.2309, Found: 337.2312.

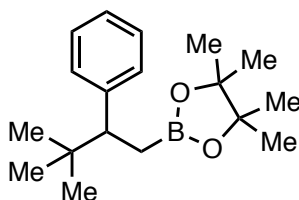


tert-butyl 4-(1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)piperidine-1-carboxylate (6): The title compound was prepared according to a modified version of general procedure A using a 4:1 THF:DMA mixture and 3.0 equiv of PhBr. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (Gradient: hexanes to 20:1 hexanes: EtOAc) yields **6** as a colorless oil.

Average over 2 runs: 75% NMR yield, 73% isolated yield, 14:1 r.r.,

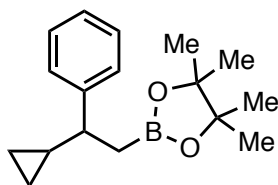
IR (neat): 3085 (w), 2977 (m), 2850 (m), 1449 (m), 1361 (s), 1143 (s), 967 (m), 750 (m) cm^{-1} ; **^1H NMR (600 MHz, CDCl_3):** δ 7.26 – 7.17 (m, 2H), 7.17 – 7.06 (m, 3H), 4.47 – 3.58 (m, 2H), 2.72

– 2.56 (m, 2H), 2.56 – 2.41 (m, 1H), 1.82 (d, $J = 13.0$ Hz, 1H), 1.59 – 1.46 (m, 2H), 1.42 (s, 9H), 1.37 – 1.23 (m, 2H), 1.22 – 1.04 (m, 2H), 1.00 (s, 6H), 0.98 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3 mixture of rotamers): δ 154.0, 144.4, 128.0, 127.4, 127.2, 127.1, 125.1, 82.2, 82.1, 78.3, 59.5, 46.0, 42.8, 29.2, 27.6, 23.7, 23.6, 13.3 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation); HRMS (ESI+): Calculated for $\text{C}_{24}\text{H}_{38}\text{BNO}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 438.2786, Found: 438.2790.



2-(3,3-dimethyl-2-phenylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7): The title compound was prepared according to a modified version of general procedure A using a 4:1 THF:DMA mixture and 3.0 equiv of PhBr. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (Gradient: hexanes to 20:1 hexanes: EtOAc) yields **7** as a colorless oil.

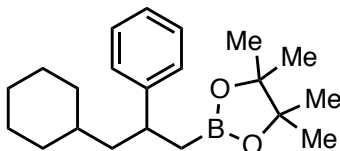
Average over 2 runs: 80% NMR yield, 78% isolated yield, >100:1 r.r. (Note: ~10% of the 1,1 arylboration reaction was observed in the crude reaction mixture, and 7% in the isolated product). IR (neat): 3085 (w), 2977 (m), 2850 (m), 1449 (m), 1361 (s), 1143 (s), 967 (m), 750 (m) cm^{-1} ; ^1H NMR (600 MHz, CDCl_3): δ 7.25 – 7.18 (m, 2H), 7.18 – 7.14 (m, 2H), 7.15 – 7.09 (m, 1H), 2.71 (dd, $J = 12.0, 5.3$ Hz, 1H), 1.31 – 1.24 (m, 1H), 1.22 (dd, $J = 15.0, 5.3$ Hz, 1H), 0.97 (s, 6H), 0.89 (s, 6H), 0.86 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3): δ 144.5, 129.8, 127.3, 125.8, 82.8, 51.8, 34.2, 27.9, 24.7, 24.4 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation. Extra signals in the attached spectrum are due to the presence of the 1,1-arylboration product). All spectroscopic data was consistent with literature values.³³



2-(2-cyclopropyl-2-phenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8): The title compound was prepared according to a modified version of general procedure A using a 4:1 THF:DMA mixture and 3.0 equiv of PhBr. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (Gradient: hexanes to 20:1 hexanes: EtOAc) yields **8** as a colorless oil.

Average over 2 runs: 67% NMR yield, 59% isolated yield, 14:1 r.r., <5% ring opening product. (Note: ~5% of the regioisomeric 1,2-arylboration product and ~3% of the ring opening product were detected in the purified product)

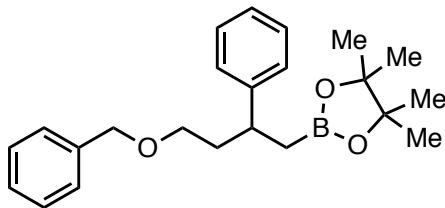
IR (neat): 3076 (w), 2993 (m), 2977 (m), 1361 (s), 1319 (s), 1143 (s), 967 (m), 845 (m), 697 (s); **¹H NMR (600 MHz, CDCl₃):** δ 7.33 – 7.19 (m, 4H), 7.18 – 7.10 (m, 1H), 2.12 (td, *J* = 8.9, 7.3 Hz, 1H), 1.34 (dd, *J* = 15.2, 7.3 Hz, 1H), 1.29 – 1.20 (m, 1H), 1.12 (s, 6H), 1.11 (s, 6H), 1.05 – 0.95 (m, 1H), 0.59 – 0.48 (m, 1H), 0.40 – 0.32 (m, 1H), 0.29 (dq, *J* = 9.7, 5.0 Hz, 1H), 0.13 (dq, *J* = 9.7, 5.0 Hz, 1H); **¹³C NMR (100 MHz, CDCl₃):** δ 147.4, 128.1, 127.4, 125.9, 83.0, 46.4, 24.9, 24.7, 19.9, 5.5, 4.5 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation. Extra signals in the attached spectrum are due to the presence of the regioisomeric 1,2-arylboration product).; **HRMS (EI):** Calculated for C₁₇H₂₅BO₂ [M]⁺: 272.1948, Found: 272.1945.



2-(3-cyclohexyl-2-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9): The title compound was prepared according to a modified version of general procedure A using a 4:1 THF:DMA mixture. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (Gradient: hexanes to 20:1 hexanes: EtOAc) yields **9** as a colorless oil.

Average over 2 runs: 94% NMR yield, 81% isolated yield, 4:1 r.r. (Note: Isolated as a mixture of regioisomers, characterization data for the major regioisomer is given. The major regioisomer was identified by the integration and multiplicity of the benzylic proton(s)).

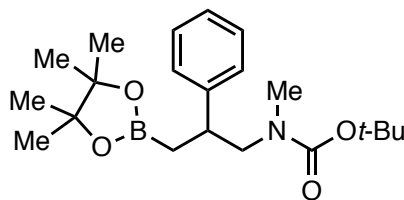
IR (neat): 2997 (m), 2920 (m), 1448 (m), 1369 (s), 1318 (s), 967 (m), 846 (m), 698 (s); **¹H NMR (600 MHz, CDCl₃):** δ 7.26 – 7.21 (m, 2H), 7.21 – 7.17 (m, 2H), 7.16 – 7.10 (m, 1H), 2.95 (tt, *J* = 9.2, 6.3 Hz, 1H), 1.86 – 1.79 (m, 1H), 1.73 – 1.46 (m, 6H), 1.46 – 1.34 (m, 1H), 1.30 – 1.22 (m, 4H), 1.22 – 1.15 (m, 1H), 1.09 (app. s, 12H), 0.88 – 0.79 (m, 2H) (integrals on attached spectrum may not be accurate due to the presence of the regioisomeric 1,2-arylboration product); **¹³C NMR (125 MHz, CDCl₃):** δ 147.9, 142.5, 129.0, 128.2, 128.1, 127.5, 125.7, 83.1, 83.0, 47.7, 39.2, 38.5, 37.9, 37.3, 35.1, 34.1, 34.0, 33.3, 33.1, 26.8, 26.6, 26.5, 26.3, 24.9, 24.8 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation. Extra signals are due to the presence of the regioisomeric 1,2-arylboration product); **HRMS (ESI⁺):** Calculated for C₂₁H₃₃BO₂Na [M+Na]⁺: 351.2466, Found: 351.2467



2-(4-(benzyloxy)-2-phenylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10): The title compound was prepared according to a modified version of general procedure A using a 4:1 THF:DMA mixture. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (Gradient: hexanes to 6:1 hexanes: Et₂O) yields **10** as a colorless oil.

Average over 2 runs: 76% NMR yield, 47% isolated yield, 3:1 r.r. (low isolated yield is due to difficult separation)

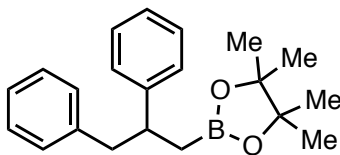
IR (neat): 3061 (m), 2976 (m), 2928 (m), 1494 (m), 1368 (s), 1319 (s), 734 (m), 697 (s); **¹H NMR (600 MHz, CDCl₃):** δ 7.36 – 7.28 (m, 4H), 7.28 – 7.22 (m, 3H), 7.22 – 7.18 (m, 2H), 7.18 – 7.11 (m, 1H), 4.43 (d, *J* = 11.9 Hz, 1H), 4.39 (d, *J* = 11.9 Hz, 1H), 3.38 – 3.27 (m, 2H), 3.08 – 2.96 (m, 1H), 2.06 – 1.96 (m, 1H), 1.93 – 1.82 (m, 1H), 1.22 (dd, *J* = 15.4, 6.9 Hz, 1H), 1.15 (dd, *J* = 15.4, 9.3 Hz, 1H), 1.09 (s, 6H), 1.08 (s, 6H); **¹³C NMR (100 MHz, CDCl₃):** δ 146.8, 138.9, 128.4, 128.3, 127.7, 127.6, 127.5, 126.0, 83.1, 72.9, 68.8, 39.1, 38.3, 24.8 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation); **HRMS (ESI⁺):** Calculated for C₂₃H₃₁BO₃Na [M+Na]⁺: 389.2258, Found: 389.2261.



tert-butyl methyl(2-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)carbamate (11): The title compound was prepared according to a modified version of general procedure A using a 4:1 THF:DMA mixture. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (Gradient: hexanes to 20:1 hexanes: EtOAc) yields **11** as a colorless oil.

Average over 2 runs: 86% NMR yield, 74% isolated yield, 3:1 r.r. (Note: Isolated as a mixture of regioisomers. The major regioisomer was identified by the integration and multiplicity of the benzylic proton(s)).

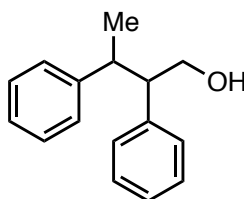
IR (neat): 2976 (m), 2929 (m), 1693 (s), 1454 (m), 1390 (s), 1364 (s), 1271 (s), 1142 (s), 847 (m), 699 (s); **(500 MHz, Toluene-*d*₈, 353K):** δ 7.16 (d, *J* = 7.6 Hz, 2H), 7.12 – 7.04 (m, 2H), 7.02 – 6.94 (m, 1H), 3.32 – 3.18 (m, 2H), 2.58 (s, 3H), 1.35 (s, 9H), 1.28 – 1.17 (m, 1H), 1.18 – 1.12 (m, 2H), 0.93 (s, 6H), 0.92 (s, 6H); **¹³C NMR (125 MHz, Toluene-*d*₈, 353K):** δ 155.3, 155.1, 145.2, 142.0, 128.8, 128.7, 127.9, 127.8, 126.0, 125.5, 82.8, 82.6, 78.2, 78.1, 57.0, 40.5, 35.1, 34.6, 34.1, 28.3, 28.2, 24.5, 24.4, 24.3, 22.2, 13.6 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation. Extra signals are due to a mixture of rotamers and regioisomers); **HRMS (EI⁺):** Calculated for C₂₁H₃₅BNO₄ [M+H]⁺: 376.2654, Found 376.2658.



2-(2,3-diphenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (12): The title compound was prepared according to a modified version of general procedure A using a 4:1 THF:DMA mixture. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (Gradient: hexanes to 20:1 hexanes: EtOAc) yields **12** as a colorless oil.

Average over 2 runs: 86% NMR yield, 78% isolated yield, 3.5:1 r.r. (Note: Isolated as a mixture of regioisomers, characterization data for the major regioisomer is given. The major regioisomer was identified by comparison to known spectra³⁴).

¹H NMR (600 MHz, CDCl₃): δ 7.28 – 7.18 (m, 4H), 7.18 – 7.10 (m, 4H), 7.04 (d, J = 7.3 Hz, 2H), 3.19 – 3.09 (m, 1H), 2.89 (dd, J = 13.3, 6.8 Hz, 1H), 2.86 (dd, J = 13.3, 7.5 Hz, 1H), 1.23 (dd, J = 15.4, 6.7 Hz, 1H), 1.17 (dd, J = 15.4, 9.5 Hz, 1H), 1.07 (s, 6H), 1.05 (s, 6H); **¹³C NMR (125 MHz, CDCl₃):** δ 146.6, 140.9, 129.5, 128.1, 128.0, 127.7, 126.0, 125.8, 83.0, 46.3, 43.7, 24.8, 24.7 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation). All spectroscopic data is in accordance with literature values.³²



4,4,5,5-Tetramethyl-2-(2-methyl-2,4-diphenylbutyl)-1,3,2-dioxaborolane (13): The title compound was prepared according to a modified version of general procedure A using a 4:1 THF:DMA mixture followed by oxidation according to general procedure B. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (Gradient: hexanes to 6:1 hexanes: EtOAc) yields **13** as a colorless oil.

Average over 2 runs: 85% NMR yield, 55% isolated yield, >20:1 r.r., 1.5:1 d.r. (the low isolated yield is due to the difficult separation of diastereomers)

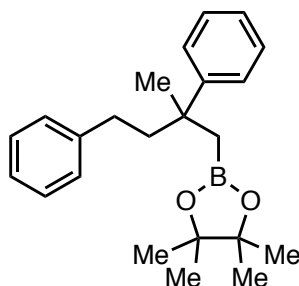
Major diastereomer:

¹H NMR (600 MHz, CDCl₃): δ 7.23 – 7.16 (m, 2H), 7.16 – 7.11 (m, 3H), 7.11 – 7.03 (m, 1H), 7.02 – 6.93 (m, 4H), 4.05 – 3.97 (m, 1H), 3.97 – 3.88 (m, 1H), 3.21 – 3.12 (m, 1H), 3.05 (td, J = 8.4, 5.1 Hz, 1H), 1.37 (d, J = 7.0 Hz, 3H), 1.23 (s, 1H); **¹³C NMR (125 MHz, CDCl₃):** δ 144.8, 140.6, 129.1, 128.1, 128.0, 127.9, 126.7, 126.2, 64.8, 55.0, 42.0, 19.9.

Minor diastereomer:

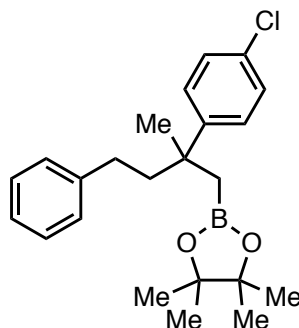
¹H NMR (600 MHz, CDCl₃): δ 7.42 – 7.36 (m, 2H), 7.34 (t, J = 7.6 Hz, 2H), 7.32 – 7.26 (m, 5H), 7.26 – 7.21 (m, 1H), 3.60 (ddd, J = 10.9, 8.1, 4.6 Hz, 1H), 3.53 (ddd, J = 10.9, 8.0, 4.3 Hz, 1H), 3.03 – 2.98 (m, 1H), 2.98 – 2.91 (m, 1H), 1.06 (d, J = 6.7 Hz, 3H), 1.02 (s, 1H); **¹³C NMR (125 MHz, CDCl₃):** δ 145.7, 141.6, 128.9, 128.8, 128.7, 127.4, 127.1, 126.6, 66.1, 55.8, 42.7, 21.1.

All spectroscopic data for both diastereomers are consistent with literature values.³⁵



4,4,5,5-Tetramethyl-2-(2-methyl-2,4-diphenylbutyl)-1,3,2-dioxaborolane (31): The title compound was prepared according to general procedure A. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (Gradient: hexanes to 15:1 hexanes: Et₂O) yields **31** as a colorless oil. Average over 2 runs: 95% NMR yield, 82% isolated yield, >20:1 r.r.

IR (neat): 3086 (w), 3059 (w), 2976 (m), 1601 (m), 1444 (m), 1355 (m), 1143 (s), 967 (m), 696 (s) cm⁻¹; **¹H NMR (600 MHz, CDCl₃):** δ 7.40 (d, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.7 Hz, 2H), 7.23 (t, *J* = 7.6 Hz, 2H), 7.20 – 7.13 (m, 1H), 7.16 – 7.10 (m, 1H), 7.09 (d, *J* = 7.2 Hz, 2H), 2.39 (td, *J* = 12.9, 5.1 Hz, 1H), 2.32 (td, *J* = 12.9, 4.7 Hz, 1H), 2.05 (td, *J* = 13.0, 4.7 Hz, 1H), 1.98 (td, *J* = 13.0, 5.1 Hz, 1H), 1.51 (s, 3H), 1.39 (d, *J* = 14.9 Hz, 1H), 1.27 (d, *J* = 14.9 Hz, 1H), 1.12 (s, 6H), 1.10 (s, 6H); **¹³C NMR (100 MHz, CDCl₃):** δ 149.4, 143.5, 128.4, 128.3, 128.1, 126.2, 125.6, 125.5, 82.9, 47.9, 39.7, 31.4, 27.3, 24.9, 24.8 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation); **HRMS (EI⁺):** Calculated for C₂₃H₃₁BO₂ [M]⁺: 350.2412, Found: 350.2408.



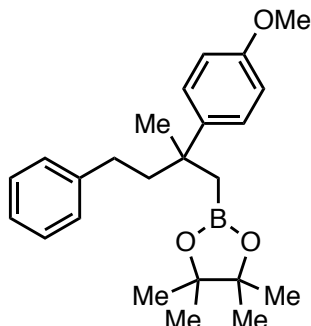
2-(2-(4-Chlorophenyl)-2-methyl-4-phenylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (32):

The title compound was prepared according to general procedure A. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (Gradient: hexanes to 15:1 hexanes: Et₂O) yields **32** as a colorless oil.

Average over 2 runs: 78% NMR yield, 74% isolated yield, >20:1 r.r.

IR (neat): 3085 (w), 2976 (m), 2929 (m), 1494 (m), 1378 (s), 1142 (s), 967 (m), 740 (m) cm⁻¹; **¹H NMR (600 MHz, CDCl₃):** δ 7.37 – 7.31 (m, 2H), 7.28 (d, *J* = 8.8 Hz, 2H), 7.24 (t, *J* = 7.6 Hz, 2H), 7.19 – 7.11 (m, 1H), 7.11 – 7.05 (m, 2H), 2.38 (td, *J* = 12.8, 5.2 Hz, 1H), 2.30 (td, *J* = 12.8, 4.8 Hz, 1H), 2.02 (ddd, *J* = 13.6, 12.8, 4.8 Hz, 1H), 1.95 (ddd, *J* = 13.6, 12.8, 5.2 Hz, 1H), 1.50 (s,

3H), 1.37 (d, $J = 14.9$ Hz, 1H), 1.25 (d, $J = 14.9$ Hz, 1H), 1.13 (s, 6H), 1.12 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 148.0, 143.1, 128.4, 128.1, 127.8, 125.7, 83.0, 47.9, 39.5, 31.4, 27.2, 24.9, 24.8 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation); HRMS (EI⁺): Calculated for $\text{C}_{23}\text{H}_{30}\text{BClO}_2$ $[\text{M}]^+$: 384.2022, Found: 384.2022.

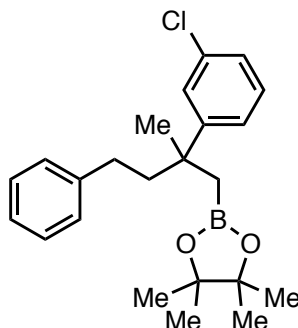


2-(2-(4-Methoxyphenyl)-2-methyl-4-phenylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

(33): The title compound was prepared according to a modified version of general procedure A, using 3.0 equiv. of arylbromide. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (Gradient: hexanes to 15:1 hexanes: Et_2O) yields **33** as a colorless oil.

Average over 2 runs: 79% NMR yield, 73% isolated yield, >20:1 r.r.

IR (neat): 3025 (w), 2976 (m), 2930 (m), 1151 (s), 1354 (s), 1142 (s), 967 (m), 731 (s) cm^{-1} ; ^1H NMR (600 MHz, CDCl_3): δ 7.36 – 7.29 (m, 2H), 7.23 (t, $J = 7.6$ Hz, 2H), 7.18 – 7.12 (m, 1H), 7.12 – 7.08 (m, 2H), 6.91 – 6.79 (m, 2H), 3.82 (s, 3H), 2.38 (td, $J = 13.0, 5.2$ Hz, 1H), 2.33 (td, $J = 13.0, 4.9$ Hz, 1H), 2.03 (ddd, $J = 13.0, 12.3, 4.9$ Hz, 1H), 1.95 (ddd, $J = 13.0, 12.3, 5.2$ Hz, 1H), 1.49 (s, 3H), 1.37 (d, $J = 14.8$ Hz, 1H), 1.26 (d, $J = 14.8$ Hz, 1H), 1.14 (s, 6H), 1.12 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3): δ 149.9, 143.3, 140.5, 128.4, 128.3, 125.6, 125.1, 124.3, 82.9, 65.9, 47.7, 40.0, 31.4, 27.4, 24.9, 24.8 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation); HRMS (ESI⁺): Calculated for $\text{C}_{24}\text{H}_{33}\text{BO}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 403.2415, Found: 403.2413.

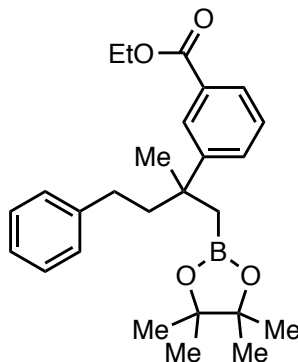


2-(2-(3-Chlorophenyl)-2-methyl-4-phenylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

(34): The title compound was prepared according to general procedure A. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (Gradient: hexanes to 15:1 hexanes: Et_2O) yields **34** as a colorless oil.

Average over two runs: 75% NMR yield, 72% isolated yield, >20:1 r.r.

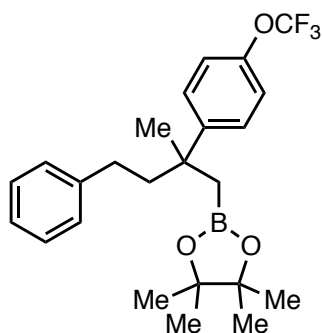
IR (neat): 3062 (m), 2976 (m), 2929 (m), 1594 (m), 1355 (s), 1142 (s), 967 (m), 697 (s) cm^{-1} ; **^1H NMR (600 MHz, CDCl_3):** δ 7.37 (t, $J = 2.0$ Hz, 1H), 7.31 – 7.25 (m, 1H), 7.24 (t, $J = 7.7$ Hz, 3H), 7.19 – 7.11 (m, 2H), 7.11 – 7.05 (m, 2H), 2.39 (td, $J = 12.9, 5.1$ Hz, 1H), 2.31 (td, $J = 12.9, 4.7$ Hz, 1H), 2.03 (ddd, $J = 13.6, 12.9, 4.7$ Hz, 1H), 1.96 (ddd, $J = 13.6, 12.9, 5.1$ Hz, 1H), 1.50 (s, 3H), 1.36 (d, $J = 15.0$ Hz, 1H), 1.24 (d, $J = 15.0$ Hz, 1H), 1.13 (s, 6H), 1.11 (s, 6H); **^{13}C NMR (100 MHz, CDCl_3):** δ 159.6, 151.8, 143.1, 134.0, 129.3, 128.4, 126.7, 125.7, 125.6, 124.6, 83.0, 47.7, 39.8, 31.4, 27.1, 24.9, 24.8 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation); **HRMS (EI+):** Calcd for $\text{C}_{23}\text{H}_{30}\text{BClO}_2$ $[\text{M}]^+$: 384.2022, Found: 384.2015.



Ethyl 3-(2-methyl-4-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-yl)benzoate (35): The title compound was prepared according to general procedure A. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (6:1 hexanes: Et_2O) yields **35** as a colorless oil.

Average over two runs: 62% NMR yield, 52% isolated yield, >20:1 r.r.

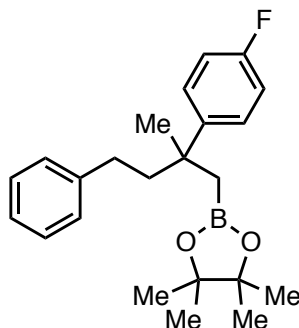
IR (neat): 3027 (m), 2978 (m), 2931 (m), 1711 (s), 1357 (m), 1270 (m), 1109 (w), 906 (s), 727 (s) cm^{-1} ; **^1H NMR (600 MHz, CDCl_3):** δ 8.09 (t, $J = 1.8$ Hz, 1H), 7.87 (dd, $J = 7.7, 1.8$ Hz, 1H), 7.61 (ddd, $J = 7.7, 1.8, 1.1$ Hz, 1H), 7.38 (t, $J = 7.7$ Hz, 1H), 7.25 – 7.20 (m, 2H), 7.18 – 7.11 (m, 1H), 7.11 – 7.05 (m, 2H), 4.44 – 4.35 (m, 2H), 2.38 (td, $J = 12.9, 5.1$ Hz, 1H), 2.31 (td, $J = 12.9, 4.7$ Hz, 1H), 2.08 (ddd, $J = 13.6, 12.9, 4.7$ Hz, 1H), 2.00 (td, $J = 13.6, 12.9, 5.1$ Hz, 1H), 1.54 (s, 3H), 1.47 – 1.38 (m, 4H), 1.30 (d, $J = 15.0$ Hz, 1H), 1.12 (s, 6H), 1.10 (s, 6H); **^{13}C NMR (125 MHz, CDCl_3):** δ 167.2, 149.9, 143.1, 130.9, 130.2, 128.4, 128.3, 128.1, 127.4, 126.9, 125.6, 83.0, 60.9, 47.6, 39.8, 31.4, 27.3, 24.9, 24.8, 14.5 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation); **HRMS (ESI+):** Calculated for $\text{C}_{26}\text{H}_{35}\text{BO}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: 445.2521, Found: 445.2527.



4,4,5,5-Tetramethyl-2-(2-methyl-4-phenyl-2-(4-(trifluoromethoxy)phenyl)butyl)-1,3,2-dioxaborolane (36): The title compound was prepared according to general procedure A. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (10:1 hexanes: Et₂O) yields **36** as a white solid.

Average over 2 runs: 71% NMR yield, 58% isolated yield, >20:1 r.r.

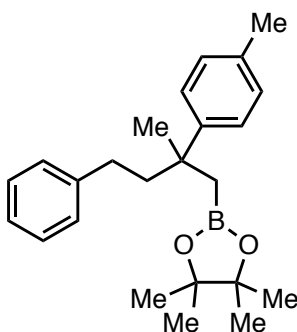
m.p.: 30-32 °C; **IR (neat):** 3027 (w), 2978 (m), 2931 (m), 1509 (m), 1357 (m), 1256 (s), 1212 (s), 1143 (s), 907 (s) cm⁻¹; **¹H NMR (600 MHz, CDCl₃):** δ 7.45 – 7.38 (m, 2H), 7.26 – 7.20 (m, 2H), 7.19 – 7.11 (m, 3H), 7.11 – 7.04 (m, 2H), 2.42 (td, *J* = 12.8, 5.0 Hz, 1H), 2.29 (td, *J* = 12.8, 4.6 Hz, 1H), 2.03 (td, *J* = 12.8, 4.6 Hz, 1H), 1.96 (td, *J* = 12.8, 5.0 Hz, 1H), 1.52 (s, 3H), 1.38 (d, *J* = 15.1 Hz, 1H), 1.25 (d, *J* = 15.1 Hz, 1H), 1.09 (s, 6H), 1.07 (s, 6H); **¹³C NMR (125 MHz, CDCl₃):** δ 148.2, 147.2, 147.1, 143.0, 128.2, 127.7, 125.7, 120.7 (q, *J* = 256 Hz), 120.5, 83.0, 48.1, 39.5, 31.4, 26.9, 24.8, 24.7 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation); **¹⁹F NMR (376 MHz, CDCl₃):** δ -58.0; **HRMS (APCI+):** Calculated for C₂₄H₃₁BO₄F₃ [M+H]⁺: 435.2313, Found: 435.2311.



2-(2-(4-Fluorophenyl)-2-methyl-4-phenylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (37): The title compound was prepared according to general procedure A. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (Gradient: hexanes to 15:1 hexanes: Et₂O) yields **37** as a white solid.

Average over two runs: 96% NMR yield, 82% isolated yield, >20:1 r.r.

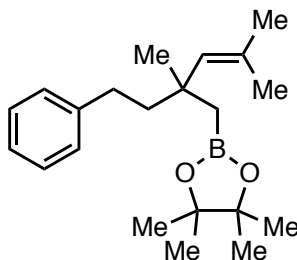
m.p.: 46-48 °C; **IR (neat):** 3062 (w), 2976 (m), 2929 (m). 1509 (s), 1378 (s), 1142 (s), 967 (m), 698 (s) cm^{-1} ; **^1H NMR (600 MHz, CDCl_3):** δ 7.40 – 7.31 (m, 2H), 7.23 (t, $J = 7.6$ Hz, 2H), 7.17 – 7.11 (m, 1H), 7.11 – 7.06 (m, 2H), 7.03 – 6.93 (m, 2H), 2.39 (td, $J = 12.8, 5.1$ Hz, 1H), 2.29 (td, $J = 12.8, 4.7$ Hz, 1H), 2.01 (td, $J = 13.5, 12.8, 4.7$ Hz, 1H), 1.95 (ddd, $J = 13.5, 12.8, 5.1$ Hz, 1H), 1.50 (s, 3H), 1.37 (d, $J = 14.9$ Hz, 1H), 1.24 (d, $J = 14.9$ Hz, 1H), 1.12 (s, 6H), 1.10 (s, 6H) **^{13}C NMR (100 MHz, CDCl_3):** δ 161.0 (d, $J = 243.4$ Hz), 145.0 (d, $J = 3.1$ Hz), 143.2, 128.4, 128.3, 127.8 (d, $J = 7.7$ Hz), 125.6, 114.6 (d, $J = 20.7$ Hz), 83.0, 48.2, 39.3, 31.4, 27.2, 24.9, 24.8 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation); **^{19}F NMR (376 MHz, CDCl_3):** δ -118.82 (ddd, $J = 14.0, 8.8, 5.3$ Hz); **HRMS (EI+):** Calcd for $\text{C}_{23}\text{H}_{30}\text{BFO}_2$ $[\text{M}]^+$: 368.2317, Found 368.2309.



4,4,5,5-tetramethyl-2-(2-methyl-4-phenyl-2-(*p*-tolyl)butyl)-1,3,2-dioxaborolane (S14): The title compound was prepared according to general procedure A. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (Gradient: hexanes to 15:1 hexanes: Et_2O) yields **S14** as a colorless oil.

Average over two runs: 85% NMR yield, 79% isolated yield, >20:1 r.r.

IR (neat): 3060 (w), 2976 (m), 2926 (m). 1603 (m), 1355 (s), 1143 (s), 967 (m), 698 (s) cm^{-1} ; **^1H NMR (600 MHz, CDCl_3):** δ 7.32 – 7.27 (m, 2H), 7.22 (t, $J = 7.6$ Hz, 2H), 7.17 – 7.04 (m, 5H), 2.41 – 2.28 (m, 5H), 2.04 (ddd, $J = 13.4, 11.5, 5.6$ Hz, 1H), 1.97 (ddd, $J = 13.4, 11.4, 6.1$ Hz, 1H), 1.48 (s, 3H), 1.36 (d, $J = 14.8$ Hz, 1H), 1.27 (d, $J = 14.8$ Hz, 1H), 1.14 (s, 6H), 1.13 (s, 6H); **^{13}C NMR (100 MHz, CDCl_3):** δ 146.5, 143.6, 134.8, 128.7, 128.4, 128.3, 126.1, 125.5, 82.9, 47.6, 39.4, 31.5, 27.7, 24.9, 24.8, 21.0 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation); **HRMS (ESI+):** Calcd for $\text{C}_{24}\text{H}_{33}\text{BO}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 387.2466, Found 387.2467.

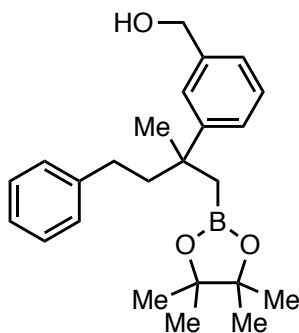


2-(2,4-Dimethyl-2-phenethylpent-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (38): The title compound was prepared according to general procedure A. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification

by silica gel column chromatography (Gradient: hexanes to 15:1 hexanes:Et₂O) yields **38** as a colorless oil.

Average for 2 runs: 82% NMR, 69% isolated, >20:1 r.r.

IR (neat): 3025 (m), 2975 (m), 2865 (m), 1453 (m), 1325 (s), 1143 (s), 968 (m), 848 (m), 697 (s) cm⁻¹; **¹H NMR (600 MHz, CDCl₃):** δ 7.29 – 7.22 (m, 1H), 7.21 – 7.13 (m, 4H), 5.24 – 5.12 (m, 1H), 2.61 – 2.53 (m, 2H), 1.84 – 1.72 (m, 5H), 1.71 (d, *J* = 1.4 Hz, 3H), 1.27 (s, 3H), 1.24 (s, 12H), 1.16 (d, *J* = 14.7 Hz, 1H), 1.00 (d, *J* = 14.7 Hz, 1H); **¹³C NMR (100 MHz, CDCl₃):** δ 144.0, 134.0, 130.7, 128.5, 128.3, 125.5, 82.8, 46.7, 37.3, 31.7, 28.6, 28.3, 25.0, 24.9, 19.2 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation); **HRMS (EI+):** Calculated for C₂₁H₃₃BO₂ [M]⁺: 328.2568, Found: 328.2571.

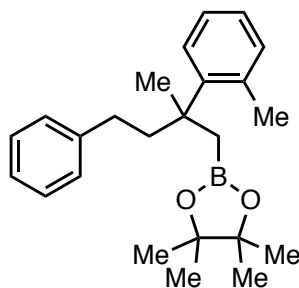


(3-(2-Methyl-4-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-yl)phenyl)methanol (39):

The title compound was prepared according to general procedure A. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (Gradient: 6:1 to 3:1 hexanes:EtOAc) yields **39** as a colorless oil.

Average for 2 runs: 81% NMR, 65% isolated, >20:1 r.r.

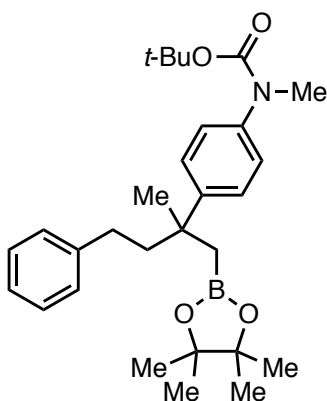
IR (neat): 3420 (br), 3024 (w), 2976 (m), 2865 (m), 1354 (s), 1142 (s), 967 (s), 729 (s) cm⁻¹; **¹H NMR (600 MHz, CDCl₃):** δ 7.40 (d, *J* = 1.8 Hz, 1H), 7.38 – 7.33 (m, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.26 – 7.21 (m, 2H), 7.21 – 7.17 (m, 1H), 7.14 (td, *J* = 7.3, 1.3 Hz, 1H), 7.12 – 7.07 (m, 2H), 4.70 (d, *J* = 5.9 Hz, 2H), 2.40 (td, *J* = 13.2, 5.2 Hz, 1H), 2.34 (td, *J* = 13.2, 4.9 Hz, 1H), 2.06 (td, *J* = 13.2, 12.3, 4.9 Hz, 1H), 2.00 (ddd, *J* = 13.2, 12.3, 5.2 Hz, 1H), 1.62 (br s, 1H), 1.52 (s, 3H), 1.40 (d, *J* = 14.9 Hz, 1H), 1.29 (d, *J* = 14.9 Hz, 1H), 1.13 (s, 6H), 1.11 (s, 6H); **¹³C NMR (125 MHz, CDCl₃):** δ 149.9, 143.3, 140.5, 128.4, 128.3, 128.2, 125.6, 125.5, 125.1, 124.3, 82.9, 65.9, 47.7, 39.7, 31.4, 27.4, 24.9, 24.8 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation); **HRMS (ESI+):** Calculated for C₂₄H₃₃BO₃Na[M+Na]⁺: 403.2415, Found: 403.2414.



4,4,5,5-Tetramethyl-2-(2-methyl-4-phenyl-2-(*o*-tolyl)butyl)-1,3,2-dioxaborolane (40): The title compound was prepared according to a modified version of general procedure A, using 3.0 equiv. of arylbromide. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (Gradient: Hexanes to 15:1 hexanes: Et₂O) yields **40** as a colorless oil. GC-MS analysis of the crude reaction mixture revealed that ~10% of the 1,1-arylboration product was formed.

Average over 2 runs: 76% NMR yield, 61% isolated yield, >20:1 r.r. (Note: 6% 1,1-arylboration product was present in the purified mixture).

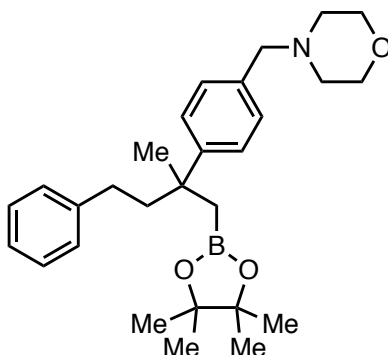
IR (neat): 3061 (m), 2977 (m), 2930 (m), 1495 (m), 1323 (s), 1143 (s), 967 (s), 727 (s) cm⁻¹; **¹H NMR (600 MHz, CDCl₃):** δ 7.37 (dd, J = 7.6, 1.6 Hz, 1H), 7.24 (t, J = 7.6 Hz, 2H), 7.18 – 7.03 (m, 6H), 2.58 (s, 3H), 2.42 (td, J = 12.9, 4.7 Hz, 1H), 2.31 (td, J = 12.9, 4.3 Hz, 1H), 2.20 (td, J = 12.9, 4.3 Hz, 1H), 1.99 (td, J = 12.9, 4.7 Hz, 1H), 1.64 (s, 3H), 1.31 – 1.18 (m, 2H), 1.05 (s, 6H), 1.04 (s, 6H); **¹³C NMR (125 MHz, CDCl₃):** δ 145.8, 143.5, 136.6, 132.6, 132.8, 128.4, 128.3, 128.0, 126.0, 125.6, 125.5, 82.8, 45.4, 41.2, 31.9, 24.8, 24.7, 23.7 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation); **HRMS (ESI⁺):** Calculated for C₂₄H₃₃BO₂Na[M+Na]⁺: 387.2466, Found: 387.2465.



Tert-butyl methyl(4-(2-methyl-4-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-yl)phenyl)carbamate (41): The title compound was prepared according to general procedure A. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (10:1 hexanes: EtOAc) yields **41** as a colorless oil.

Average for 2 runs: 90% NMR, 84% isolated, >20:1 r.r.

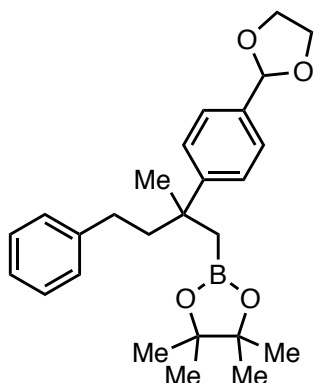
IR (neat): 3026 (m), 2976 (m), 2930 (m), 1694 (s), 1512 (m), 1322 (s), 1144 (s), 908 (m), 729 (s) cm^{-1} ; **^1H NMR (600 MHz, CDCl_3):** δ 7.37 – 7.31 (m, 2H), 7.22 (t, J = 7.6 Hz, 2H), 7.19 – 7.10 (m, 3H), 7.10 – 7.06 (m, 2H), 3.25 (s, 3H), 2.37 (td, J = 12.9, 5.4 Hz, 1H), 2.32 (td, J = 12.9, 4.4 Hz, 1H), 2.02 (td, J = 12.9, 4.4 Hz, 1H), 1.96 (td, J = 12.9, 5.4 Hz, 1H), 1.49 (s, 3H), 1.45 (s, 9H), 1.37 (d, J = 14.9 Hz, 1H), 1.26 (d, J = 14.9 Hz, 1H), 1.13 (s, 6H), 1.12 (s, 6H); **^{13}C NMR (125 MHz, CDCl_3):** δ 155.1, 146.6, 143.4, 141.3, 128.4, 128.3, 126.4, 125.6, 125.0, 82.9, 80.1, 47.8, 39.4, 37.5, 31.4, 28.5, 27.4, 24.9, 24.8 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation); **HRMS (ESI+):** Calculated for $\text{C}_{29}\text{H}_{42}\text{BO}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: 502.3099, Found: 502.3104.



4-(4-(2-Methyl-4-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-yl)benzyl)morpholine (42): The title compound was prepared according to general procedure A. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (3:1 hexanes: EtOAc) yields **42** as a pale yellow oil.

Average over 2 runs: 76% NMR, 62% isolated, >20:1 r.r.

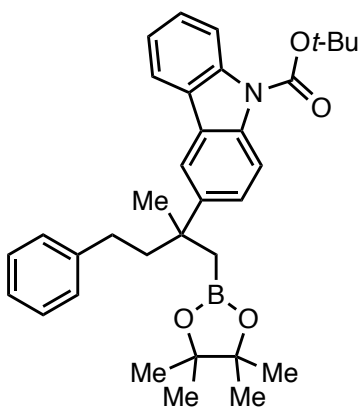
IR (neat): 3026 (w), 2976 (m), 2859 (m), 1454 (m), 1350 (m), 906 (s), 726 (s) cm^{-1} ; **^1H NMR (600 MHz, CDCl_3):** δ 7.34 (d, J = 8.2 Hz, 2H), 7.26 – 7.20 (m, 4H), 7.16 – 7.11 (m, 1H), 7.11 – 7.07 (m, 2H), 3.71 (t, J = 4.6 Hz, 4H), 3.48 (s, 2H), 2.51 – 2.42 (m, 4H), 2.38 (td, J = 12.9, 5.1 Hz, 1H), 2.31 (td, J = 12.9, 4.7 Hz, 1H), 2.04 (ddd, J = 13.0, 12.9, 4.7 Hz, 1H), 1.96 (ddd, J = 13.0, 12.9, 5.1 Hz, 1H), 1.50 (s, 3H), 1.37 (d, J = 14.8 Hz, 1H), 1.26 (d, J = 14.7 Hz, 1H), 1.11 (s, 6H), 1.09 (s, 6H); **^{13}C NMR (125 MHz, CDCl_3):** δ 148.4, 143.4, 134.6, 129.0, 128.4, 128.3, 126.1, 125.6, 82.9, 67.1, 63.3, 53.7, 47.8, 39.5, 31.4, 27.3, 24.9, 24.8 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation); **HRMS (ESI+):** Calculated for $\text{C}_{28}\text{H}_{41}\text{BNO}_3$ $[\text{M}+\text{H}]^+$: 450.3174, Found: 450.3181.



2-(2-(4-(1,3-Dioxolan-2-yl)phenyl)-2-methyl-4-phenylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (43): The title compound was prepared according to general procedure A. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (Gradient: 6:1 to 3:1 hexanes: EtOAc) yields **43** as a white solid.

Average for 2 runs: 82% NMR, 76% isolated, >20:1 r.r.

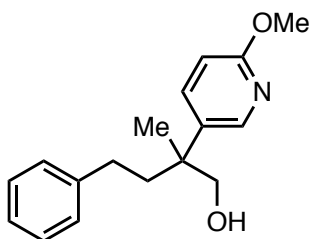
m.p. 62-63 °C; **IR (neat):** 3026 (w), 2977 (m), 2930 (m), 2885 (m), 1355 (m), 1324 (m), 1220 (m), 1143 (m), 906 (s), 727 (s) cm^{-1} ; **^1H NMR (600 MHz, CDCl_3):** δ 7.42 (s, 4H), 7.22 (t, J = 7.6 Hz, 2H), 7.16 – 7.10 (m, 1H), 7.10 – 7.06 (m, 2H), 5.81 (s, 1H), 4.20 – 4.10 (m, 2H), 4.09 – 3.99 (m, 2H), 2.39 – 2.25 (m, 2H), 2.05 (ddd, J = 13.6, 12.0, 5.2 Hz, 1H), 1.98 (ddd, J = 13.6, 12.0, 5.6 Hz, 1H), 1.50 (s, 3H), 1.38 (d, J = 14.8 Hz, 1H), 1.28 (d, J = 14.8 Hz, 1H), 1.13 (s, 6H), 1.12 (s, 6H); **^{13}C NMR (125 MHz, CDCl_3):** δ 150.7, 143.4, 135.0, 128.4, 128.3, 126.3, 126.2, 125.6, 104.0, 83.0, 65.4, 47.6, 39.7, 31.4, 27.6, 24.9, 24.8 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation); **HRMS (ESI+):** Calculated for $\text{C}_{26}\text{H}_{36}\text{BO}_4$ $[\text{M}+\text{H}]$: 423.2701, Found: 423.2700.



Tert-butyl 3-(2-methyl-4-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-yl)-9H-carbazole-9-carboxylate (44): The title compound was prepared according to general procedure A. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (Gradient: hexanes to 10:1 hexanes: Et_2O) yields **44** as a colorless oil.

Average over 2 runs: 70% NMR, 47% isolated, >20:1 r.r.

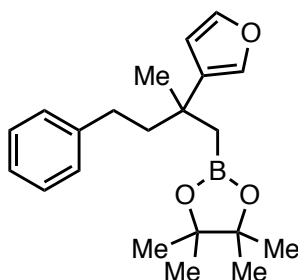
IR (neat): 3024 (w), 2975 (m), 2929 (m), 1724 (s), 1487 (m), 1355 (s), 1142 (s), 845 (m) cm^{-1} ; **^1H NMR (600 MHz, CDCl_3):** δ 8.31 (d, J = 8.4 Hz, 1H), 8.20 (d, J = 8.7 Hz, 1H), 8.06 – 7.95 (m, 2H), 7.54 (dd, J = 8.8, 2.0 Hz, 1H), 7.45 (ddd, J = 8.4, 7.2, 1.3 Hz, 1H), 7.35 (td, J = 7.5, 1.0 Hz, 1H), 7.22 (t, J = 7.6 Hz, 2H), 7.17 – 7.10 (m, 1H), 7.10 – 7.06 (m, 2H), 2.46 – 2.28 (m, 2H), 2.15 (td, J = 12.7, 12.1, 4.9 Hz, 1H), 2.07 (ddd, J = 13.5, 12.1, 5.4 Hz, 1H), 1.77 (s, 9H), 1.63 (s, 3H), 1.52 (d, J = 14.9 Hz, 1H), 1.38 (d, J = 14.9 Hz, 1H), 1.11 (s, 6H), 1.09 (s, 6H); **^{13}C NMR (125 MHz, CDCl_3):** δ 151.3, 144.4, 143.4, 139.0, 136.6, 128.5, 128.3, 126.9, 126.4, 125.7, 125.6, 125.5, 123.0, 119.5, 117.1, 116.4, 115.9, 83.8, 82.3, 48.2, 39.8, 31.5, 28.6, 27.9, 24.9, 24.8 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation); **HRMS (ESI+):** Calculated for $\text{C}_{34}\text{H}_{42}\text{BNO}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: 562.3099, Found: 562.3112.



2-(6-Methoxypyridin-3-yl)-2-methyl-4-phenylbutan-1-ol (45): The title compound was prepared according to a modified version of general procedure A, performing the reaction at 30 °C and 7.5 mol% catalyst loading, followed by oxidation via general procedure B. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (Gradient: 10% to 20% acetone in hexane) yields **45** as a yellow oil.

Average over 2 runs: 52% NMR, 43% isolated, >20:1 r.r.

IR (neat): 3391 (br), 2944 (w), 1709 (m), 1603 (s), 1493 (s), 1397 (m), 1288 (s), 829 (m) cm^{-1} ; **^1H NMR (600 MHz, CDCl_3):** δ 8.18 (d, J = 2.6 Hz, 1H), 7.61 (dd, J = 8.7, 2.6 Hz, 1H), 7.27 – 7.22 (m, 2H), 7.18 – 7.13 (m, 1H), 7.12 – 7.08 (m, 2H), 6.75 (d, J = 8.7 Hz, 1H), 3.93 (s, 3H), 3.70 (d, J = 10.9 Hz, 1H), 3.58 (d, J = 10.9 Hz, 1H), 2.51 (td, J = 13.1, 5.1 Hz, 1H), 2.30 (td, J = 13.1, 4.4 Hz, 1H), 2.05 (td, J = 13.1, 4.4 Hz, 1H), 2.51 (td, J = 13.2, 5.1 Hz, 1H), 1.60 (br s, 1H), 1.43 (s, 3H); **^{13}C NMR (150 MHz, CDCl_3):** δ 162.9, 145.4, 142.5, 137.5, 132.5, 128.5, 128.3, 125.9, 110.8, 72.3, 53.5, 42.0, 40.5, 30.5, 21.4; **HRMS (EI+):** Calculated for $\text{C}_{17}\text{H}_{21}\text{NO}_2$ $[\text{M}]^+$: 271.1564, Found: 271.1564.

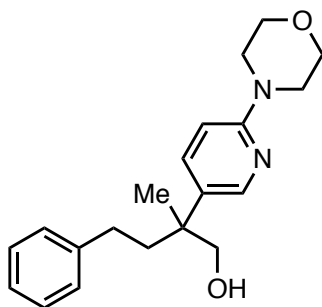


2-(2-(Furan-3-yl)-2-methyl-4-phenylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (46): The title compound was prepared according to general procedure A. NMR yield of the unpurified

reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (30:1 hexanes: Et₂O) yields **46** as a colorless oil

Average over 2 runs: 59% NMR, 42% isolated, >20:1 r.r.

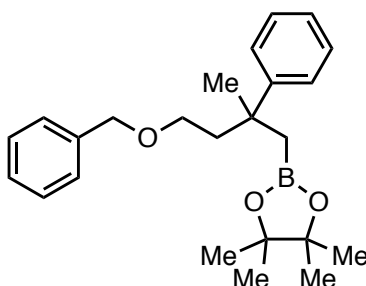
IR (neat): 3026 (w), 2977 (w), 1714 (w), 1353 (s), 1320 (s), 1142 (s), 1054 (m), 1026 (m), 968 (m), 848 (s), 730 (s) cm⁻¹; **¹H NMR (600 MHz, CDCl₃):** δ 7.41 – 7.36 (m, 1H), 7.30 – 7.24 (m, 3H), 7.20 – 7.12 (m, 3H), 6.42 – 6.37 (m, 1H), 2.55 – 2.41 (m, 2H), 1.99 – 1.78 (m, 2H), 1.41 (s, 3H), 1.27 – 1.24 (m, 2H), 1.22 (s, 6H), 1.21 (s, 6H); **¹³C NMR (150 MHz, CDCl₃):** δ 143.5, 142.8, 138.3, 134.8, 128.5, 128.4, 125.6, 109.4, 83.0, 46.6, 34.8, 31.5, 27.7, 25.0, 24.9 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation); **HRMS (EI+):** Calculated for C₂₁H₂₉BO₃ [M]⁺: 340.2208, Found 340.2210.



2-Methyl-2-(6-morpholinopyridin-3-yl)-4-phenylbutan-1-ol (47): The title compound was prepared according to a modified version of general procedure A, performing the reaction at 30 °C, followed by oxidation via general procedure B. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (Gradient: 10% to 20% acetone in hexane) yields **47** as a white solid.

Average over 2 runs: 59% NMR, 32% isolated, >20:1 r.r. Low recovery was attributed to difficult separation from the phenol derived from the oxidation of the arylBpin byproduct.

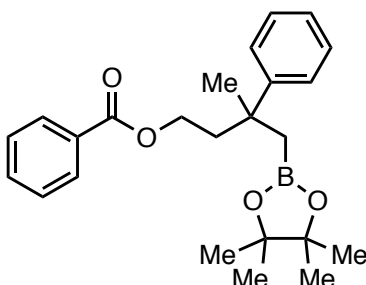
m.p. 83-90 °C **IR (neat):** 3474 (br), 2959 (m), 2920 (m), 1605 (s), 1554 (m), 1320 (s), 1117 (s), 817 (m) cm⁻¹; **¹H NMR (600 MHz, CDCl₃):** δ 8.23 (d, *J* = 2.6 Hz, 1H), 7.54 (dd, *J* = 8.9, 2.6 Hz, 1H), 7.28 – 7.19 (m, 2H), 7.19 – 7.12 (m, 1H), 7.12 – 7.03 (m, 2H), 6.65 (d, *J* = 8.8 Hz, 1H), 3.88 – 3.75 (m, 4H), 3.67 (d, *J* = 10.8 Hz, 1H), 3.55 (d, *J* = 10.8 Hz, 1H), 3.51 – 3.41 (m, 4H), 2.51 (td, *J* = 13.1, 5.1 Hz, 1H), 2.32 (td, *J* = 13.1, 4.4 Hz, 1H), 2.04 (td, *J* = 13.1, 4.4 Hz, 1H), 1.82 (td, *J* = 13.1, 5.1 Hz, 1H), 1.66 (br, 1H), 1.41 (s, 3H); **¹³C NMR (150 MHz, CDCl₃):** δ 158.2, 146.6, 142.7, 136.5, 129.3, 128.5, 128.3, 125.9, 106.9, 72.4, 66.9, 45.8, 41.8, 40.5, 30.4, 21.3; **HRMS (EI+):** Calculated for C₂₀H₂₇N₂O₂ [M+H]⁺: 327.2067, Found: 327.2071.



2-(4-(Benzyloxy)-2-methyl-2-phenylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (14): The title compound was prepared according to general procedure A. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (10:1 hexanes: Et₂O) yields **14** as a white solid.

Average for 2 runs: 98% NMR, 82% isolated, >20:1 r.r.

m.p.: 38-40 °C; **IR (neat):** 2974 (m), 2930 (m), 1445 (m), 1353 (s), 1303 (s), 1215 (m), 1140 (s), 966 (m), 845 (m), 696 (s) cm⁻¹; **¹H NMR (600 MHz, CDCl₃):** δ 7.39 – 7.33 (m, 2H), 7.33 – 7.28 (m, 2H), 7.28 – 7.22 (m, 5H), 7.18 – 7.12 (m, 1H), 4.38 (s, 2H), 3.35 (td, *J* = 9.4, 5.7 Hz, 1H), 3.28 (td, *J* = 9.4, 5.4 Hz, 1H), 2.18 (ddd, *J* = 13.5, 9.4, 5.4 Hz, 1H), 2.08 (ddd, *J* = 13.5, 9.4, 5.7 Hz, 1H), 1.48 (s, 3H), 1.36 (d, *J* = 15.0 Hz, 1H), 1.22 (d, *J* = 15.0 Hz, 1H), 1.10 (s, 6H), 1.08 (s, 6H); **¹³C NMR (125 MHz, CDCl₃):** δ 149.2, 138.8, 128.4, 128.0, 127.6, 127.4, 126.1, 125.5, 82.8, 72.9, 67.9, 44.4, 38.3, 27.5, 24.9, 24.7 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation); **HRMS (EI⁺):** Calculated for C₂₄H₃₃BO₃ [M]⁺: 380.2517, Found: 380.2514.

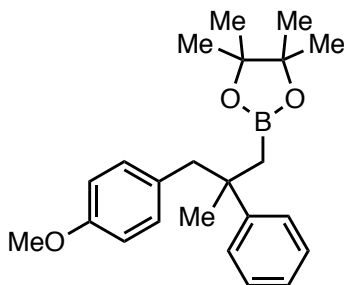


3-Methyl-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl benzoate (15): The title compound was prepared according to general procedure A. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (10:1 hexanes: Et₂O) yields **15** as a colorless oil.

Average for 2 runs: 81% NMR, 69% isolated, >20:1 r.r.

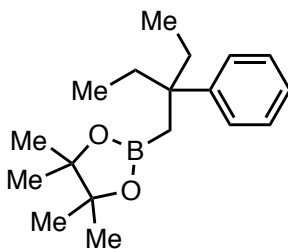
IR (neat): 3059 (m), 2975 (m), 2928 (m), 1716 (s), 1356 (s), 1270 (s), 1140 (m), 967 (m), 706 (s), 698 (s); **¹H NMR (600 MHz, CDCl₃):** δ 7.92 – 7.85 (m, 2H), 7.57 – 7.46 (m, 1H), 7.43 – 7.34 (m, 4H), 7.31 – 7.26 (m, 2H), 7.14 (t, *J* = 7.2 Hz, 1H), 4.22 (ddd, *J* = 11.2, 8.2, 6.1 Hz, 1H), 4.12 (ddd, *J* = 11.2, 8.2, 6.1 Hz, 1H), 2.31 (ddd, *J* = 14.2, 8.2, 6.1 Hz, 1H), 2.19 (ddd, *J* = 14.2, 8.2, 6.1 Hz, 1H), 1.55 (s, 3H), 1.42 (d, *J* = 15.0 Hz, 1H), 1.28 (d, *J* = 15.0 Hz, 1H), 1.09 (s, 6H), 1.07 (s, 6H); **¹³C NMR (125 MHz, CDCl₃):** δ 166.7, 148.7, 132.8, 130.6, 129.6, 128.3, 128.2, 126.1, 125.7, 83.0, 62.8, 43.4, 38.4, 27.2, 24.9, 24.7 (signal of carbon directly bonded to boron was not detected).

because of quadrupolar relaxation); **HRMS (ESI+)**: Calculated for $C_{24}H_{31}BO_4Na$ $[M+Na]^+$: 417.2208, Found: 417.2212.



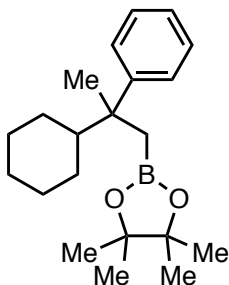
2-(3-(4-methoxyphenyl)-2-methyl-2-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (21): The title compound was prepared according to general procedure A. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (10:1 hexanes: Et_2O) yields **21** as a colorless oil. Average for 2 runs: 90% NMR, 83% isolated, >20:1 r.r.

IR (neat): 3057 (m), 2976 (m), 2929 (m), 1610 (s), 1354 (s), 1244 (s), 1143 (m), 969 (m), 756 (m), 697 (s); **1H NMR (600 MHz, $CDCl_3$)**: δ 7.32 – 7.22 (m, 4H), 7.18 – 7.11 (m, 1H), 6.75 – 6.69 (m, 2H), 6.69 – 6.63 (m, 2H), 3.75 (s, 3H), 2.92 (d, J = 13.2 Hz, 1H), 2.86 (d, J = 13.2 Hz, 1H), 1.44 (d, J = 15.4 Hz, 1H), 1.42 (s, 3H), 1.14 – 1.06 (m, 7H), 1.04 (s, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 157.9, 149.1, 131.6, 131.3, 127.7, 126.7, 125.5, 112.9, 82.8, 55.2, 51.5, 40.6, 26.5, 24.9, 24.6; (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation); **HRMS (ESI+)**: Calculated for $C_{23}H_{31}BO_3Na$ $[M+Na]^+$: 389.2263, Found: 389.2258.



4,4,5,5-Tetramethyl-2-(3-methyl-3-phenylpentan-2-yl)-1,3,2-dioxaborolane (16): The title compound was prepared according to general procedure A. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (Gradient: hexanes to 15:1 hexanes: Et_2O) yields **16** as a colorless oil. Average for 2 runs: 81% NMR, 71% isolated, >20:1 r.r.

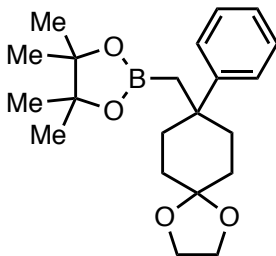
IR (neat): 3088 (w), 2972 (m), 2933 (m), 2877 (m), 1353 (m), 1142 (s), 872 (m), 697 (m) cm^{-1} ; **1H NMR (400 MHz, $CDCl_3$)**: δ 7.36 – 7.29 (m, 2H), 7.29 – 7.23 (m, 2H), 7.17 – 7.09 (m, 1H), 1.89 – 1.70 (m, 4H), 1.25 (s, 2H), 1.15 (s, 12H), 0.66 (t, J = 7.4 Hz, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 148.6, 127.8, 126.9, 125.1, 82.7, 43.1, 33.2, 24.9, 8.8 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation); **HRMS (ESI+)**: Calculated for $C_{18}H_{30}BO_2$ $[M+H]^+$: 289.2333, Found: 289.2333.



2-(2-Cyclohexyl-2-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (17): The title compound was prepared according to a modified version of general procedure A, using 3.0 equiv of PhBr. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (Gradient: hexanes to 15:1 hexanes: Et₂O) yields **17** as a white solid.

Average for 2 runs: 69% NMR, 57% isolated, >20:1 r.r.

m.p. 54-58 °C; **IR (neat):** 3087 (m), 3057 (m), 2976 (s), 2851 (m), 1445 (m), 1353 (m), 1320 (m), 1142 (m), 968 (m), 732 (s) cm⁻¹; **¹H NMR (600 MHz, CDCl₃):** δ 7.33 – 7.27 (m, 2H), 7.25 – 7.20 (m, 2H), 7.14 – 7.07 (m, 1H), 1.83 – 1.69 (m, 2H), 1.67 – 1.56 (m, 2H), 1.43 (tt, *J* = 11.9, 2.9 Hz, 1H), 1.38 (s, 3H), 1.33 (d, *J* = 14.8 Hz, 1H), 1.29 – 1.23 (m, 1H), 1.23 – 1.11 (m, 2H), 1.11 – 1.01 (m, 2H), 0.99 (s, 6H), 0.96 – 0.91 (m, 7H), 0.91 – 0.79 (m, 1H); **¹³C NMR (125 MHz, CDCl₃):** δ 149.8, 127.5, 126.9, 125.1, 82.6, 51.5, 42.3, 28.1, 27.8, 27.4, 27.3, 26.9, 24.8, 24.5, 21.5 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation); **HRMS (ESI⁺):** Calculated for C₂₁H₃₃BO₂Na [M+Na]⁺: 351.2466, Found: 351.2468.

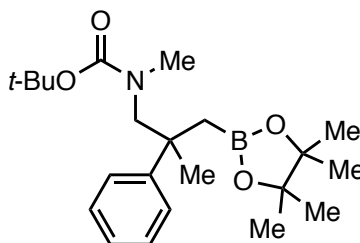


4,4,5,5-Tetramethyl-2-((8-phenyl-1,4-dioxaspiro[4.5]decan-8-yl)methyl)-1,3,2-

dioxaborolane (18): The title compound was prepared according to general procedure A. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (8:1 hexanes: EtOAc) yields **18** as a white solid.

Average for 2 runs: 98% NMR, 88% isolated, >20:1 r.r.

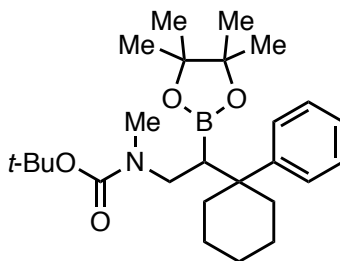
m.p. 110-112 °C; **IR (neat):** 3043 (m), 2977 (m), 2873 (m), 1453 (m), 1139 (s), 1085 (m), 928 (m), 770 (m); **¹H NMR (600 MHz, CDCl₃):** δ 7.42 – 7.36 (m, 2H), 7.29 – 7.23 (m, 2H), 7.16 – 7.09 (m, 1H), 3.95 (ddd, *J* = 6.4, 5.7, 1.2 Hz, 2H), 3.90 (ddd, *J* = 7.1, 5.7, 1.2 Hz, 2H), 2.42 – 2.23 (m, 2H), 1.91 (ddd, *J* = 14.1, 10.6, 3.7 Hz, 2H), 1.75 – 1.63 (m, 2H), 1.63 – 1.52 (m, 2H), 1.16 (s, 2H), 1.04 (s, 12H); **¹³C NMR (125 MHz, CDCl₃):** δ 128.2, 126.5, 125.5, 109.2, 82.9, 64.3, 64.2, 39.0, 35.4, 31.8, 24.9 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation); **HRMS (ESI⁺):** Calculated for C₂₁H₃₂BO₄ [M+H]⁺: 359.2388, Found: 359.2390.



***Tert*-butyl methyl(2-methyl-2-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)carbamate (19):** The title compound was prepared according to general procedure A. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (20:1 hexanes: EtOAc) yields **19** as a white solid.

Average over 2 runs: 78% NMR, 74% isolated, >20:1 r.r.

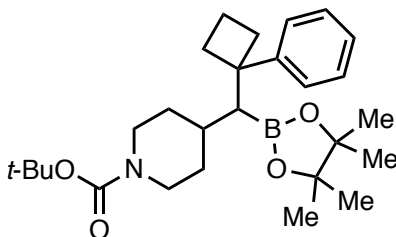
m.p. 56-64 °C; **IR (neat):** 2923 (m), 2851 (w), 1692 (s), 1137 (s) cm^{-1} ; **^1H NMR (500 MHz, C_7D_8 , 353 K):** δ 7.38-7.24 (m, 2H), 7.17-7.03 (m, 3H), 3.58 (d, $J = 14.1$ Hz, 1H), 3.25 (d, $J = 14.1$ Hz, 1H), 2.38 (s, 3H), 1.57 (s, 3H), 1.50 (d, $J = 15.3$ Hz, 1H), 1.39 (s, 9H), 1.16 (d, $J = 15.3$ Hz, 1H), 0.92 (s, 6H), 0.88 (s, 6H); **^{13}C NMR (125 MHz, C_7D_8 , 353 K, mixture of rotamers):** δ 156.4, 148.9, 128.4, 128.2, 127.2, 127.1, 126.0, 82.9, 78.8, 63.2, 42.3, 37.1, 37.0, 28.7, 25.4, 25.2, 25.0, 24.8 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation); **HRMS (APCI+):** Calculated for $\text{C}_{22}\text{H}_{37}\text{BNO}_4$ $[\text{M}+\text{H}]^+$: 390.2814, Found: 390.2814.



***Tert*-butyl methyl(2-(1-phenylcyclohexyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)carbamate (20):** The title compound was prepared according to general procedure A. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (20:1 Hexanes: EtOAc) yields **20** as a colorless oil.

Average over 2 runs: 71% NMR, 55% isolated, >20:1 r.r.

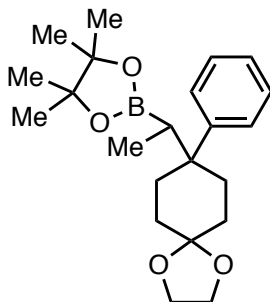
IR (neat): 2975 (w), 2929 (m), 2858 (m), 1692 (s), 1137 (m) cm^{-1} ; **^1H NMR (500 MHz, C_7D_8 , 353K):** δ 7.31 – 7.25 (m, 2H), 7.17 – 7.12 (m, 2H), 7.02 – 6.97 (m, 1H), 3.56 – 3.23 (m, 1H), 2.91 (dd, $J = 13.3, 5.0$ Hz, 1H), 2.55 (s, 3H), 2.41 – 2.33 (m, 1H), 2.22 (dd, $J = 13.9, 3.6$ Hz, 1H), 1.95 (ddd, $J = 13.9, 12.3, 3.6$ Hz, 1H), 1.81 – 1.71 (m, 1H), 1.71 – 1.61 (m, 1H), 1.58 – 1.41 (m, 2H), 1.39 (s, 9H), 1.29 – 1.19 (m, 2H), 1.09 (s, 6H), 1.07 (s, 6H); **^{13}C NMR (125 MHz, C_7D_8 , 353K):** δ 155.7, 146.3, 137.6, 128.4, 125.7, 83.3, 78.5, 47.4, 43.6, 37.3, 34.7, 33.7, 28.8, 27.5, 25.6, 25.2, 23.2 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation); **HRMS (APCI+):** Calculated for $\text{C}_{26}\text{H}_{43}\text{BNO}_4$ $[\text{M}+\text{H}]^+$: 444.3282, Found: 443.3282



Tert-butyl 4-((1-phenylcyclobutyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)piperidine-1-carboxylate (22): The title compound was prepared according to general procedure A. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (20:1 Hexanes: EtOAc) yields **22** as a white solid.

Average over 2 runs: 84% NMR, 71% isolated, >20:1 r.r.

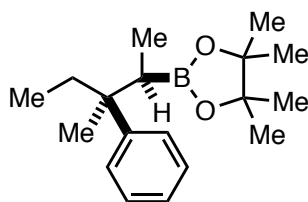
m.p. 128-132 °C; **IR (neat):** 2928 (m), 2851 (m), 1684 (m), 1138 (m), 755 (s) cm^{-1} ; **^1H NMR (600 MHz, CDCl_3):** δ 7.25 – 7.17 (m, 4H), 7.17 – 7.12 (m, 1H), 4.12 (br s, 1H), 3.91 (br s, 1H), 2.62 (br s, 1H), 2.50 (br s, 1H), 2.36 (d, J = 10.4 Hz, 1H), 2.17 (s, 1H), 1.97 (q, J = 11.1 Hz, 1H), 1.92 – 1.79 (s, 3H), 1.66 (s, 3H), 1.43 (s, 9H), 1.31 (s, 6H), 1.29 (s, 6H), 1.21 – 1.01 (m, 2H), 0.89 (m, 1H); **^{13}C NMR (100 MHz, CDCl_3):** δ 155.0, 143.7, 129.1, 128.0, 125.9, 83.1, 79.2, 63.1, 40.9, 35.5, 31.7, 29.9, 28.6, 27.2, 24.9, 18.5 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation); **HRMS (APCI+):** Calculated for $\text{C}_{27}\text{H}_{43}\text{BNO}_4$ $[\text{M}+\text{H}]^+$: 456.3285, Found: 456.3272.



4,4,5,5-Tetramethyl-2-((8-phenyl-1,4-dioxaspiro[4.5]decan-8-yl)methyl)-1,3,2-dioxaborolane (23): The title compound was prepared according to general procedure A. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (8:1 hexanes: EtOAc) yields **23** as a white solid.

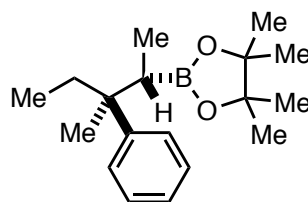
Average for 2 runs: 97% NMR, 78% isolated, >20:1 r.r.

m.p. 117-119 °C; **IR (neat):** 3083 (m), 2984 (m), 2872 (m), 1461 (m), 1138 (s), 1087 (m), 921 (m), 767 (m) cm^{-1} ; **^1H NMR (600 MHz, CDCl_3):** δ 7.37 – 7.32 (m, 2H), 7.31 – 7.23 (m, 2H), 7.19 – 7.11 (m, 1H), 3.95 – 3.90 (m, 2H), 3.90 – 3.84 (m, 2H), 2.45 – 2.26 (m, 2H), 1.98 (td, J = 13.8, 3.8 Hz, 1H), 1.91 (td, J = 13.8, 3.6 Hz, 1H), 1.70 – 1.60 (m, 1H), 1.60 – 1.50 (m, 2H), 1.44 (td, J = 13.4, 3.6 Hz, 1H), 1.27 – 1.21 (m, 1H), 1.20 (s, 6H), 1.19 (s, 6H), 0.74 (d, J = 7.5 Hz, 3H); **^{13}C NMR (100 MHz, CDCl_3):** δ 144.4, 128.0, 127.6, 125.5, 109.5, 82.9, 64.2, 64.1, 42.7, 32.8, 31.7, 31.6, 30.2, 24.9, 24.8, 10.9 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation); **HRMS (APCI+):** Calculated for $\text{C}_{22}\text{H}_{34}\text{BO}_4$ $[\text{M}+\text{H}]^+$: 373.2545, Found: 373.2546.



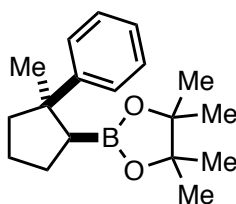
4,4,5,5-Tetramethyl-2-(3-methyl-3-phenylpentan-2-yl)-1,3,2-dioxaborolane (24): The title compound was prepared according to general procedure A. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (Gradient: hexanes to 15:1 hexanes: Et₂O) yields **24** as a colorless oil. Average for 2 runs: 51% NMR, 41% isolated, >20:1 r.r., >20:1 d.r. The major diastereomer was determined by analogy to product **71**.

IR (neat): 3087 (w), 2973 (m), 2931 (m), 2871 (m), 1372 (m), 1139 (s), 853 (m), 698 (m) cm⁻¹; **¹H NMR (600 MHz, CDCl₃):** δ 7.28 – 7.21 (m, 4H), 7.16 – 7.08 (m, 1H), 1.86 (dq, *J* = 14.7, 7.4 Hz, 1H), 1.63 (dq, *J* = 14.7, 7.3 Hz, 1H), 1.52 (q, *J* = 7.3 Hz, 1H), 1.31 (s, 3H), 1.25 (s, 12H), 0.64 (d, *J* = 7.3 Hz, 3H), 0.55 (t, *J* = 7.3 Hz, 3H); **¹³C NMR (125 MHz, CDCl₃):** δ 147.8, 127.8, 127.0, 125.1, 82.9, 43.4, 36.2, 25.0, 24.9, 19.5, 11.4, 9.1 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation); **HRMS (EI⁺):** Calculated for C₁₈H₂₉BO₂ [M]⁺: 288.2255, Found: 288.2254.



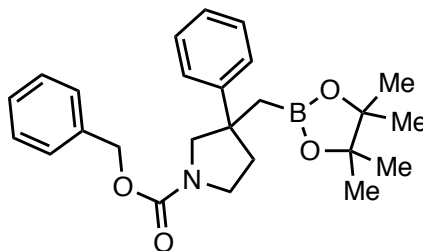
4,4,5,5-Tetramethyl-2-(3-methyl-3-phenylpentan-2-yl)-1,3,2-dioxaborolane (25): The title compound was prepared according to general procedure A. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (Gradient: hexanes to 15:1 hexanes:Et₂O) yields **25** as a colorless oil. Average for 2 runs: 52% NMR, 39% isolated, >20:1 r.r., >20:1 d.r. The major diastereomer was determined by analogy to product **71**.

IR (neat): 3088 (w), 2970 (m), 2930 (m), 2871 (m), 1376 (m), 1144 (s), 851 (m), 697 (m); **¹H NMR (600 MHz, CDCl₃):** δ 7.35 – 7.29 (m, 2H), 7.29 – 7.21 (m, 2H), 7.17 – 7.06 (m, 1H), 1.84 – 1.69 (m, 2H), 1.49 (q, *J* = 7.5 Hz, 1H), 1.36 (s, 3H), 1.02 (s, 6H), 1.00 (s, 6H), 0.94 (d, *J* = 7.5 Hz, 3H), 0.61 (t, *J* = 7.4 Hz, 3H); **¹³C NMR (100 MHz, CDCl₃):** δ 148.6, 127.7, 127.1, 125.3, 82.5, 42.0, 32.9, 24.6, 20.9, 22.2, 8.9 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation); **HRMS (ESI⁺):** Calculated for C₁₈H₂₉BO₂Na [M+Na]⁺: 311.2153, Found: 311.2135.



4,4,5,5-Tetramethyl-2-(2-methyl-2-phenylcyclopentyl)-1,3,2-dioxaborolane (26): The title compound was prepared according to general procedure A. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (Gradient: hexanes to 15:1 hexanes: Et₂O) yields **26** as a colorless oil. Average for 2 runs: 86% NMR, 66% isolated, >20:1 r.r. The major diastereomer was determined by analogy to product **71**.

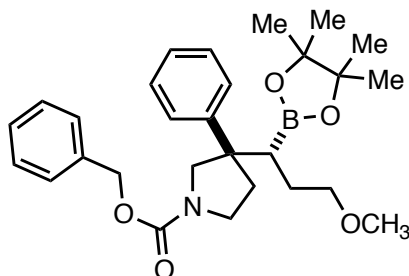
IR (neat): 3057 (w), 2974 (m), 2956 (m), 2871 (m), 1495 (m), 1369 (s), 1142 (s), 973 (m), 697 (m); **¹H NMR (600 MHz, CDCl₃):** δ 7.36 – 7.30 (m, 2H), 7.26 – 7.20 (m, 2H), 7.16 – 7.07 (m, 1H), 2.23 (dt, *J* = 11.7, 8.7 Hz, 1H), 2.06 – 1.93 (m, 1H), 1.92 – 1.71 (m, 4H), 1.60 (dd, *J* = 8.9, 5.4 Hz, 1H), 1.35 (s, 3H), 0.95 (s, 6H), 0.90 (s, 6H); **¹³C NMR (125 MHz, CDCl₃):** δ 150.8, 127.8, 126.9, 125.4, 82.5, 49.8, 39.1, 31.3, 26.7, 24.7, 24.6, 23.8 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation); **HRMS (ESI⁺):** Calculated for C₁₈H₂₇BO₄ [M]⁺: 286.2102, Found: 286.2107.



Benzyl 3-phenyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)pyrrolidine-1-carboxylate (53): The title compound was prepared according to general procedure A. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (Gradient: hexanes to 15:1 hexanes: Et₂O) yields **53** as a colorless oil.

Average for 2 runs: 95% NMR, 88% isolated, >20:1 r.r. (57:43 mixture of rotamers)

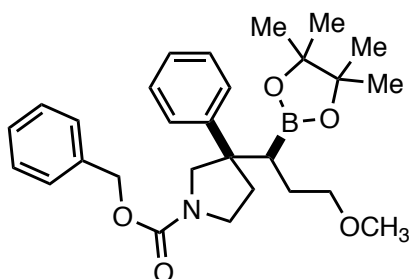
IR (neat): 3061 (w), 2977 (m), 2883 (m), 2871 (m), 1696 (m), 1358 (s), 1212 (m), 908 (m), 696 (m) cm⁻¹; **¹H NMR (600 MHz, CDCl₃, mixture of rotamers):** δ 7.42 – 7.38 (m, 1H), 7.38 – 7.34 (m, 3H), 7.34 – 7.29 (m, 1H), 7.29 – 7.26 (m, 4H), 7.20 – 7.15 (m, 1H), 5.27 – 5.09 (m, 2H), 3.84 (d, *J* = 10.9 Hz, 1H), 3.80 (*minor rotamer* d, *J* = 10.6 Hz, 1H), 3.75 (*minor rotamer* d, *J* = 10.6 Hz, 1H), 3.70 (d, *J* = 10.6 Hz, 1H), 3.67 – 3.46 (m, 2H), 3.42 (*minor rotamer* ddd, *J* = 10.7, 8.0, 5.1 Hz, 1H), 2.41 – 2.24 (m, 1H), 2.24 – 2.13 (m, 1H), 1.38 (d, *J* = 15.3 Hz, 1H), 1.34 (*minor rotamer* d, *J* = 15.2 Hz, 1H), 1.29 – 1.23 (m, 1H), 1.07 – 1.00 (m, 12H); **¹³C NMR (125 MHz, CDCl₃, mixture of rotamers):** δ 155.2, 155.1, 146.4, 146.2, 137.3, 137.2, 128.5, 128.3, 127.9, 127.8, 127.7, 126.4, 126.3, 126.2, 83.1, 66.7, 57.7, 57.6, 47.4, 46.6, 45.1, 44.7, 38.5, 37.3, 24.8, 24.7 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation); **HRMS (ESI⁺):** Calculated for C₂₅H₃₃BNO₄ [M+H]⁺: 422.2497, Found: 422.2499.



Benzyl 3-(3-methoxy-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-3-phenylpyrrolidine-1-carboxylate (61): The title compound was prepared according to general procedure A. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (Gradient: hexanes to 3:1 hexanes: EtOAc) yields **61** as a colorless oil. The major diastereomer was determined by analogy to product **71**.

Average for 2 runs: 99% NMR, 93% isolated, >20:1 r.r. (51:49 mixture of rotamers)

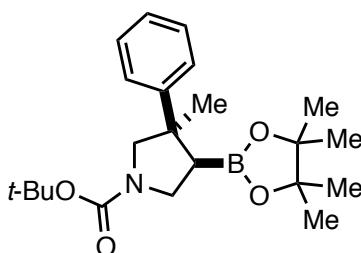
IR (neat): 3032 (w), 2978 (m), 2930 (m), 2874 (m), 1693 (s), 1418 (m), 1141 (m), 907 (m), 697 (m) cm^{-1} ; **^1H NMR (600 MHz, CDCl_3 , mixture of rotamers):** δ 7.40 – 7.33 (m, 2H), 7.33 – 7.24 (m, 7H), 7.21 – 7.15 (m, 1H), 5.20 – 5.02 (m, 2H), 4.00 (d, J = 11.4 Hz, 1H), 3.88 (*minor rotamer* d, J = 11.1 Hz, 1H), 3.76 – 3.61 (m, 1H), 3.67 (dd, J = 12.7, 11.2 Hz, 1H), 3.62 – 3.46 (m, 1H), 3.36 – 3.14 (m, 5H), 2.51 – 2.30 (m, 1H), 2.30 – 2.13 (m, 1H), 1.61 – 1.46 (m, 3H), 1.18 (s, 6H), 1.15 (s, 6H), 1.14 (*minor rotamer* s, 6H), 1.12 (*minor rotamer* s, 3H); **^{13}C NMR (125 MHz, CDCl_3 , mixture of rotamers):** δ 156.0, 155.9, 146.0, 145.8, 138.2, 138.1, 129.5, 129.4, 129.2, 129.1, 128.9, 128.8, 128.7, 128.0, 127.9, 127.4, 84.3, 84.2, 73.8, 67.7, 67.6, 59.4, 56.5, 55.9, 52.4, 51.5, 46.0, 45.5, 36.5, 35.0, 28.9, 28.8, 26.1, 26.0, 25.9 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation); **HRMS (EI+):** Calculated for $\text{C}_{28}\text{H}_{38}\text{BNO}_5$ $[\text{M}]^+$: 479.2843, Found: 479.2835



Benzyl 3-(3-methoxy-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-3-phenylpyrrolidine-1-carboxylate (59): The title compound was prepared according to general procedure A. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (Gradient: hexanes to 3:1 hexanes:EtOAc) yields **55** as a colorless oil. The major diastereomer was determined by analogy to product **71**.

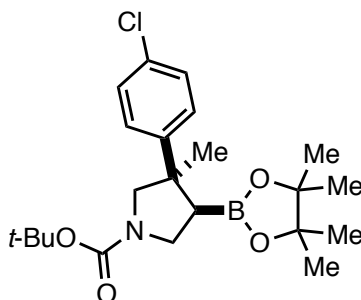
Average for 2 runs: 98% NMR, 92% isolated, >20:1 r.r. (53:47 mixture of rotamers)

IR (neat): 3032 (w), 2978 (m), 2930 (m), 2874 (m), 1692 (s), 1419 (m), 1141 (m), 907 (m), 697 (m) cm^{-1} ; **^1H NMR (600 MHz, CDCl_3 , mixture of rotamers):** δ 7.44 – 7.35 (m, 2H), 7.35 – 7.23 (m, 7H), 7.22 – 7.14 (m, 1H), 5.19 (d, J = 12.5 Hz, 1H), 5.16 (d, J = 12.5 Hz, 1H), 5.12 (minor rotamer s, 2H), 4.13 – 4.08 (minor rotamer d, J = 11.6, 1H), 3.95 (d, J = 11.4 Hz, 1H), 3.79 (d, J = 11.4 Hz, 1H), 3.73 (minor rotamer d, J = 11.6 Hz, 1H), 3.52 – 3.45 (m, 1H), 3.45 – 3.40 (minor rotamer m, 1H), 3.27 – 3.16 (m, 5H), 3.15 – 3.09 (m, 1H), 3.09 – 3.02 (minor rotamer m, 1H), 2.28 – 2.16 (m, 2H), 1.66 – 1.49 (m, 2H), 1.47 – 1.39 (m, 1H), 1.22 (s, 6H), 1.21 (s, 6H); **^{13}C NMR (125 MHz, CDCl_3 , mixture of rotamers):** δ 155.0, 154.9, 144.9, 144.8, 137.4, 137.2, 128.6, 128.5, 128.4, 128.3, 127.9, 127.8, 127.7, 126.8, 126.7, 126.4, 126.3, 83.4, 72.9, 66.8, 66.6, 58.5, 58.4, 53.5, 53.4, 51.4, 50.7, 44.8, 44.4, 37.5, 36.5, 28.1, 28.0, 25.1, 25.0 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation); **HRMS (ESI+):** Calculated for $\text{C}_{28}\text{H}_{39}\text{BNO}_5$ $[\text{M}+\text{H}]^+$: 480.2916, Found: 480.2917



Tert-butyl 3-methyl-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrrolidine-1-carboxylate (71): The title compound was prepared according to a modified version of general procedure A, using 3.0 equiv of PhBr and performing the reaction at 30 °C. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (Gradient: 10:1 to 6:1 hexanes: EtOAc) yields **70** as a white solid. Crystals suitable for X-ray analysis were prepared by slow diffusion of pentane into a concentrated solution of **71** in CH_2Cl_2 .

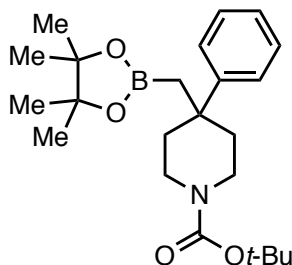
Average for 2 runs: 92% NMR, 89% isolated, >20:1 r.r., >20:1 d.r. (54:44 mixture of rotamers) **m.p.** 85-87 °C; **IR (neat):** 3085 (w), 2975 (m), 2924 (m), 2883 (m), 1682 (m), 1402 (s), 1138 (s), 874 (m), 702 (m) cm^{-1} ; **^1H NMR (600 MHz, CDCl_3 , mixture of rotamers):** δ 7.30 – 7.22 (m, 4H), 7.21 – 7.13 (m, 1H), 3.83 (minor rotamer d, J = 10.2 Hz, 1H), 3.75 – 3.55 (m, 1H), 3.91 (d, J = 10.5 Hz, 1H), 3.83 (minor rotamer d, J = 10.2 Hz, 1H), 3.75 – 3.55 (m, 1H), 3.51 (dd, J = 11.1, 5.8 Hz, 1H), 3.47 (d, J = 10.5 Hz, 1H), 3.44 (minor rotamer d, J = 10.2 Hz, 1H), 3.39 (dd, J = 11.1, 7.4 Hz, 1H), 1.89 – 1.73 (m, 1H), 1.54 – 1.45 (m, 12H), 1.03 (s, 6H), 0.99 (minor rotamer s, 6H), 0.93 (s, 6H), 0.88 (minor rotamer s, 6H); **^{13}C NMR (125 MHz, CDCl_3 , mixture of rotamers):** δ 154.9, 154.8, 147.0, 146.6, 128.2, 126.4, 126.3, 126.2, 126.2, 83.2, 83.1, 58.3, 58.1, 47.7, 47.3, 46.9, 46.8, 29.1, 28.7, 28.4, 24.8, 24.7, 24.6, 24.5 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation); **HRMS (ESI+):** Calculated for $\text{C}_{22}\text{H}_{34}\text{BO}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: 410.2473, Found: 410.2476.



Tert-butyl 3-(4-chlorophenyl)-3-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrrolidine-1-carboxylate (76): The title compound was prepared according to a modified version of general procedure A, using 3.0 equiv of ArBr and performing the reaction at 30 °C. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (Gradient: 10:1 to 6:1 hexanes: EtOAc) yields **76** as a white solid. The major diastereomer was determined by analogy to product **71**.

Average for 2 runs: 73% NMR, 63% isolated, >20:1 r.r., >20:1 d.r. (55:45 mixture of rotamers)

m.p. 78-80 °C; **IR (neat):** 2977 (w), 2931 (m), 2882 (m), 1682 (m), 1403 (s), 1135 (s), 908 (m), 728 (m) cm^{-1} ; **^1H NMR (600 MHz, CDCl_3 , mixture of rotamers):** δ 7.26 – 7.17 (m, 4H), 3.86 (d, J = 10.6 Hz, 1H), 3.77 (minor rotamer d, J = 10.3 Hz, 1H), 3.64 (minor rotamer dd, J = 11.2, 8.4 Hz, 1H), 3.60 (dd, J = 11.1, 8.3 Hz, 1H), 3.49 (minor rotamer dd, J = 11.2, 6.2 Hz, 1H), 3.46 – 3.39 (m, 1H), 3.36 (dd, J = 11.1, 7.8 Hz, 1H), 1.85 – 1.74 (m, 1H), 1.57 – 1.41 (m, 12H), 1.05 (s, 6H), 1.01 (minor rotamer s, 6H), 0.97 (s, 6H), 0.92 (minor rotamer s, 6H); **^{13}C NMR (125 MHz, CDCl_3 , mixture of rotamers):** δ 154.8, 154.7, 145.5, 145.2, 132.1, 132.0, 128.2, 127.9, 127.8, 83.4, 83.3, 79.3, 58.4, 58.3, 47.3, 47.2, 46.9, 46.5, 28.7, 28.1, 24.8, 24.7, 24.6, 24.5 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation); **HRMS (ESI+):** Calculated for $\text{C}_{22}\text{H}_{33}\text{BCINO}_4$ $[\text{M}]^+$: 421.2191, Found: 421.2192.

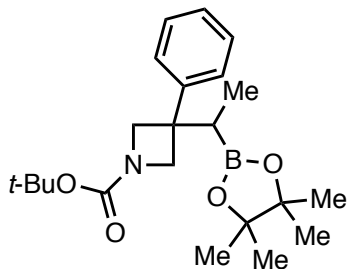


Tert-butyl 3-(4-chlorophenyl)-3-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrrolidine-1-carboxylate (65): The title compound was prepared according to general procedure A. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (Gradient: 10:1 hexanes:EtOAc to 6:1 hexanes:EtOAc) yields **65** as a colorless oil.

Average for 2 runs: 97% NMR, 86% isolated, >20:1 r.r.

IR (neat): 2976 (w), 2930 (m), 2868 (m), 1688 (m), 1362 (m), 1143 (s), 912 (m), 730 (m); **^1H NMR (600 MHz, CDCl_3):** δ 7.37 – 7.31 (m, 2H), 7.31 – 7.27 (m, 2H), 7.18 – 7.12 (m, 1H), 3.63 – 3.46 (m, 2H), 3.28 (ddd, J = 13.4, 8.5, 3.4 Hz, 2H), 2.23 – 2.10 (m, 2H), 1.85 (ddd, J = 13.4, 8.5, 3.4 Hz, 2H), 1.45 (s, 9H), 1.19 (s, 2H), 1.03 (s, 12H); **^{13}C NMR (125 MHz, CDCl_3 , 328K, mixture**

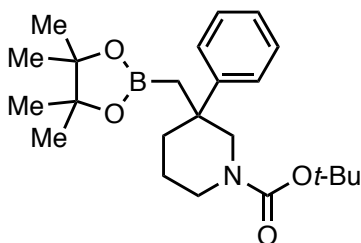
of rotamers): δ 155.1, 147.3, 128.3, 126.4, 125.8, 82.8, 79.1, 40.8, 38.1, 37.2, 28.6, 24.8 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation); **HRMS (CI⁺)**: Calculated for C₂₃H₃₇BNO₄ [M+H]⁺: 402.2810, Found: 402.2823.



Tert-butyl 3-phenyl-3-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)azetidine-1-carboxylate (57): The title compound was prepared according to a modified version of general procedure A, using 3.0 equiv of PhBr. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by column chromatography (Gradient: 10:1 hexanes:EtOAc to 6:1 hexanes:EtOAc) yields **57** as a colorless oil

Average for 2 runs: 85% NMR, 73% isolated, >20:1 r.r.

IR (neat): 3060 (w), 3026 (m), 2877 (m), 1688 (s), 1391 (m), 1141 (m), 908 (m), 701 (m); **¹H NMR (600 MHz, CDCl₃)**: δ 7.29 (t, J = 7.7 Hz, 2H), 7.22 – 7.17 (m, 1H), 7.17 – 7.13 (m, 2H), 4.26 (d, J = 8.4 Hz, 1H), 4.19 (d, J = 8.4 Hz, 1H), 4.17 – 4.11 (m, 2H), 1.62 (q, J = 7.4 Hz, 1H), 1.43 (s, 9H), 1.21 (s, 6H), 1.19 (s, 6H), 0.88 (d, J = 7.4 Hz, 3H); **¹³C NMR (125 MHz, CDCl₃, 328K, mixture of rotamers)**: δ 155.5, 145.0, 127.0, 126.9, 126.0, 125.2, 82.4, 78.1, 59.1, 58.1, 42.9, 27.7, 27.6, 24.0, 23.9, 10.1 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation); **HRMS (ESI⁺)**: Calculated for C₂₂H₃₄BNO₄Na [M+Na]⁺: 410.2473, Found: 410.2473.

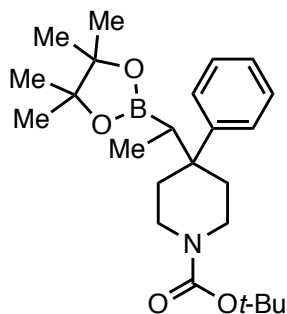


Tert-butyl 3-phenyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)piperidine-1-carboxylate (63): The title compound was prepared according to general procedure A. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by column chromatography (Gradient: 10:1 to 6:1 hexanes: EtOAc) yields **63** as a white solid

Average for 2 runs: 98% NMR, 87% isolated, >20:1 r.r.

m.p. 90-92 °C; **IR (neat)**: 3004 (w), 3975 (m), 2863 (m), 1692 (s), 1355 (m), 1144 (m), 872 (m), 702 (m); **¹H NMR (400 MHz, CDCl₃)**: δ 7.40 (d, J = 7.8 Hz, 2H), 7.30 – 7.23 (m, 2H), 7.21 – 7.05 (m, 1H), 4.35 – 4.06 (m, 1H), 3.67 – 3.43 (m, 1H), 3.42 – 2.98 (m, 2H), 2.28 – 2.08 (m, 1H),

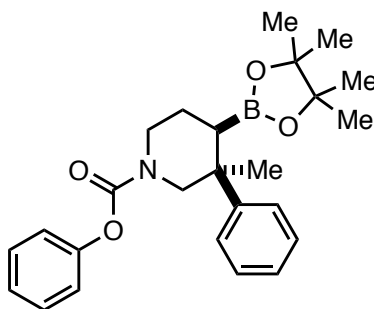
1.81 (ddd, $J = 13.6, 10.0, 3.6$ Hz, 1H), 1.58 – 1.30 (m, 11H), 1.20 (d, $J = 15.2$ Hz, 1H), 1.13 – 0.85 (m, 13H); ^{13}C NMR (125 MHz, CDCl_3 , mixture of rotamers): δ 154.9, 146.0, 128.1, 126.8, 125.8, 82.9, 79.4, 54.2, 43.7, 40.1, 37.4, 28.6, 24.9, 24.8, 22.0 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation); HRMS (ESI⁺): Calculated for $\text{C}_{23}\text{H}_{36}\text{BNO}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: 424.2630, Found: 424.2634.



Tert-butyl 4-phenyl-4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)piperidine-1-carboxylate (67): The title compound was prepared according to general procedure A. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (Gradient: 10:1 to 6:1 hexanes: EtOAc) yields **67** as a white solid.

Average for 2 runs: 92% NMR, 80% isolated, >20:1 r.r.

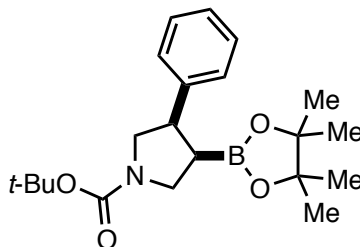
m.p. 97-99 °C; **IR** (neat): 3083 (w), 2976 (m), 2865 (m), 1684 (s), 1352 (m), 1140 (m), 858 (m), 766 (m); ^1H NMR (600 MHz, CDCl_3): δ 7.34 – 7.27 (m, 4H), 7.20 – 7.15 (m, 1H), 4.08 – 3.65 (m, 2H), 3.00 – 2.51 (m, 2H), 2.42 – 2.18 (m, 2H), 1.94 – 1.84 (m, 1H), 1.77 (ddd, $J = 13.8, 12.2, 4.1$ Hz, 1H), 1.43 (s, 9H), 1.28 – 1.24 (m, 1H), 1.19 (s, 6H), 1.18 (s, 6H), 0.73 (d, $J = 7.5$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3 , 328K): δ 155.3, 144.2, 128.3, 127.9, 125.8, 83.1, 79.1, 42.2, 41.1, 35.0, 32.8, 28.7, 25.0, 10.4 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation); HRMS (ESI⁺): Calculated for $\text{C}_{24}\text{H}_{39}\text{BNO}_4$ $[\text{M}+\text{H}]^+$: 416.2967, Found: 416.2964.



Phenyl 3-methyl-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidine-1-carboxylate (69): The title compound was prepared according to general procedure A. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (Gradient: 10:1 to 6:1 hexanes: EtOAc) yields **69** as a colorless oil. The major diastereomer was determined by analogy to product **71**.

Average for 2 runs: 95% NMR, 84% isolated, >20:1 r.r., >20:1 d.r. (60:40 mixture of rotamers)

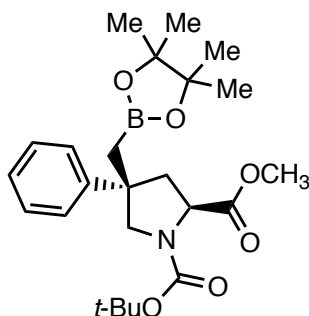
IR (neat): 3059 (w), 2976 (m), 1709 (s), 1431 (m), 1140 (m), 907 (m), 852 (m) cm^{-1} ; **^1H NMR (600 MHz, CDCl_3 , mixture of rotamers):** δ 7.39 – 7.32 (m, 4H), 7.29 (t, J = 7.6 Hz, 2H), 7.18 (t, J = 7.2 Hz, 2H), 7.14 – 7.10 (m, 1H), 7.07 – 7.02 (m, 1H), 4.20 – 4.01 (m, 2H), 3.98 – 3.85 (m, 1H), 3.40 (minor rotamer td, J = 12.9, 12.3, 3.3 Hz, 1H), 3.33 (td, J = 11.8, 10.6, 3.2 Hz, 1H), 2.19 – 2.05 (m, 1H), 1.85 – 1.61 (m, 2H), 1.43 (s, 3H), 1.39 (minor rotamer s, 3H), 1.01 (s, 12H), 0.98 (minor rotamer s, 6H), 0.97 (minor rotamer s, 6H); **^{13}C NMR (125 MHz, CDCl_3 , mixture of rotamers):** δ 154.4, 151.7, 148.2, 147.9, 129.3, 128.3, 126.1, 126.0, 125.9, 125.7, 125.2, 125.1, 121.9, 121.8, 83.0, 52.3, 51.3, 43.4, 43.1, 38.8, 38.7, 27.5, 24.6, 24.5, 23.8, 23.3 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation); **HRMS (ESI+):** Calculated for $\text{C}_{25}\text{H}_{33}\text{BNO}_4$ $[\text{M}+\text{H}]^+$: 422.2497, Found: 422.2501.



Tert-butyl 3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrrolidine-1-carboxylate (55): The title compound was prepared according to a modified version of general procedure A, using 3 equiv of bromobenzene and performing the reaction at 30 °C. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (Gradient: 10:1 to 6:1 hexanes: EtOAc) yields **55** as a white solid.

Average for 2 runs: 80% NMR, 66% isolated, >20:1 d.r. (66:44 mixture of rotamers)

^1H NMR (600 MHz, CDCl_3 , mixture of rotamers): δ 7.26 – 7.21 (m, 2H), 7.21 – 7.14 (m, 3H), 3.75 – 3.58 (m, 3H), 3.58 – 3.51 (m, 2H), 2.13 – 2.00 (m, 1H), 1.51 (s, 9H), 1.48 (minor rotamer s, 9H), 1.01 (minor rotamer s, 6H), 0.98 (minor rotamer s, 6H), 0.92 (s, 6H), 0.91 (s, 6H); **^{13}C NMR (125 MHz, CDCl_3 , mixture of rotamers):** δ 154.7, 143.6, 128.4, 127.7, 126.6, 83.5, 83.4, 79.3, 79.2, 53.3, 53.0, 47.1, 45.8, 44.9, 28.8, 28.7, 24.9, 24.8, 24.6 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation). Analytical data was in accordance with literature values.³⁶

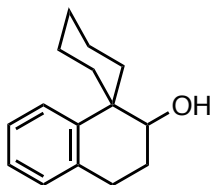


1-(Tert-butyl) 2-methyl (2S,4S)-4-phenyl-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)pyrrolidine-1,2-dicarboxylate (73): The title compound was prepared according to a modified version of general procedure A, using 3.0 equiv. of PhBr. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification

by silica gel column chromatography (4:1 hexanes:EtOAc) yields **73** as a white solid. Crystals suitable for X-ray crystallography were obtained via slow diffusion of pentane into a saturated solution of **73** in diethyl ether.

Average for 2 runs: 94% NMR, 72% isolated, >20:1 r.r., 18:1 d.r. (75:25 mixture of rotamers)

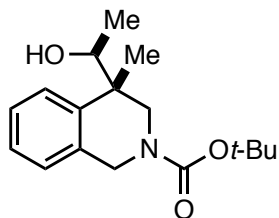
m.p. 87-91 °C; **IR (neat)**: 3060 (w), 2977 (m), 2931 (m), 1751 (s), 1393 (m), 1142 (m), 846 (m), 728 (m) cm^{-1} ; **^1H NMR (600 MHz, CDCl_3 , mixture of rotamers)**: δ 7.35 – 7.26 (m, 4H), 7.21 – 7.14 (m, 1H), 4.38 (dd, J = 11.4, 1.7 Hz, 1H), 4.18 – 4.10 (*minor rotamer* m, 2H), 3.96 (dd, J = 9.3, 7.4 Hz, 1H), 3.74 (*minor rotamer* s, 3H), 3.71 (s, 3H), 3.53 (*minor rotamer* d, J = 11.3 Hz, 1H), 3.50 (d, J = 11.4 Hz, 1H), 2.80 – 2.74 (*minor rotamer* m, 1H), 2.69 (ddd, J = 12.7, 7.4, 1.8 Hz, 1H), 2.27 – 2.17 (m, 1H), 1.51 (d, J = 15.3 Hz, 1H), 1.46 (*minor rotamer* s, 9H), 1.38 (s, 9H), 1.25 (d, J = 15.3 Hz, 1H), 1.05 (*minor rotamer* s, 6H), 1.03 (*minor rotamer* s, 6H), 1.01 (s, 6H), 0.99 (s, 6H); **^{13}C NMR (125 MHz, CDCl_3 , mixture of rotamers)**: δ 173.7, 173.5, 154.4, 153.7, 145.3, 145.0, 128.4, 126.6, 126.5, 126.1, 126.0, 83.2, 80.0, 58.7, 58.6, 58.3, 57.0, 52.1, 51.9, 47.3, 46.6, 45.3, 43.2, 28.5, 28.3, 24.7, 24.6 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation); **HRMS (APCI+)**: Calculated for $\text{C}_{24}\text{H}_{37}\text{BNO}_6$ $[\text{M}+\text{H}]^+$: 446.2708, Found: 446.2712. **HPLC**: Lux 3u Cellulose-1, 22 °C, 1.2 mL/min, 98:2 hexane: isopropanol, 215 nm. t_{major} = 6.567 min, t_{minor} = 8.280 min, 95:5 e.r. (A racemic sample was prepared by performing the arylboration with a 1:1 mixture of (*S*)-**71** and (*R*)-**71**). **Optical rotation**: $[\alpha]_{\text{D}}^{20}$: +74.9 (c = 1.00, CHCl_3).



3',4'-Dihydro-2'*H*-spiro[cyclohexane-1,1'-naphthalen]-2'-ol (49**)**: The title compound was prepared according to a modified version of general procedure A, omitting the arylbromide since the reaction is intramolecular, followed by oxidation according to general procedure B. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (10:1 hexanes: EtOAc) yields **48** as a white solid.

Average for 2 runs: 49% isolated, >20:1 r.r.

m.p. 84-89 °C; **IR (neat)**: 3361 (br), 2928 (m), 2852 (m), 959 (m), 754 (s) cm^{-1} ; **^1H NMR (500 MHz, CDCl_3)**: δ 7.44 (d, J = 7.9 Hz, 1H), 7.21 (ddd, J = 8.3, 6.5, 2.3 Hz, 1H), 7.17 – 7.07 (m, 2H), 4.51 (s, 1H), 3.11 (ddd, J = 17.5, 11.9, 7.1 Hz, 1H), 2.76 (ddd, J = 17.3, 6.9, 2.0 Hz, 1H), 2.17 – 1.99 (m, 3H), 1.95 (td, J = 12.9, 4.1 Hz, 1H), 1.83 (m, 1H), 1.80 – 1.67 (m, 3H), 1.55 (m, 3H), 1.46 – 1.33 (m, 2H); **^{13}C NMR (125 MHz, CDCl_3)**: δ 143.6, 135.5, 129.1, 127.0, 126.4, 125.7, 66.8, 41.6, 39.8, 32.1, 26.2, 24.9, 23.9, 22.4, 21.9; **HRMS (EI+)**: Calculated for $\text{C}_{15}\text{H}_{18}$ $[\text{M}-\text{H}_2\text{O}]^+$: 198.1409, Found: 198.1404.



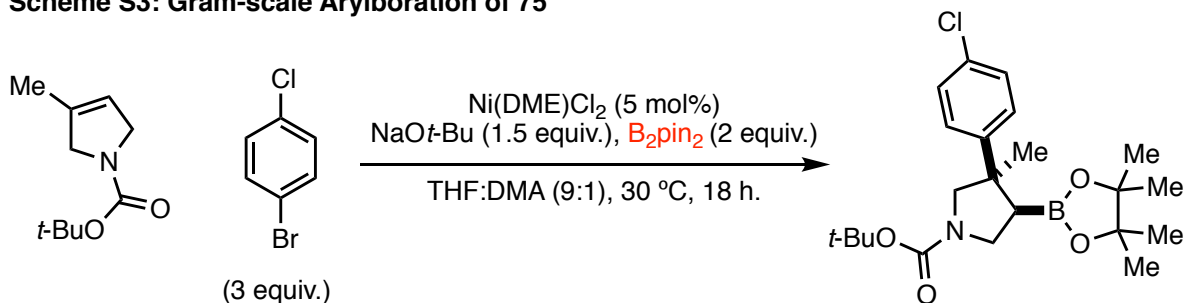
***Tert*-Butyl 4-(-1-hydroxyethyl)-4-methyl-3,4-dihydroisoquinoline-2(1*H*)-carboxylate (51):**

The title compound was prepared according to a modified version of general procedure A, omitting the arylbromide since the reaction is intramolecular, followed by oxidation via general procedure B. Purification by silica gel column chromatography (3:1 hexanes: EtOAc) yields **50** as a colorless oil.

Average over 2 runs: 43% isolated yield. >20:1 r.r., 20:1 d.r.

IR (neat): 3440 (br), 2974 (m), 2931 (w), 1672 (s), 1424 (s), 1157 (s), 727 (s); **¹H NMR (600 MHz, CDCl₃, 323K):** δ 7.36 – 7.29 (m, 1H), 7.23 – 7.15 (m, 2H), 7.15 – 7.04 (m, 1H), 4.81 (d, *J* = 17.1 Hz, 1H), 4.39 (d, *J* = 17.1 Hz, 1H), 4.13 (br s, 1H), 3.86 (q, *J* = 6.5 Hz, 1H), 2.93 (br s, 1H), 1.50 (s, 9H), 1.27 (s, 3H), 1.14 (d, *J* = 6.5 Hz, 3H); **¹³C NMR (125 MHz, CDCl₃, 323K, mixture of rotamers):** δ 154.9, 140.9, 133.2, 127.2, 126.7, 126.5, 80.2, 72.6, 48.7, 46.6, 42.4, 28.7, 28.6, 28.5, 20.0, 18.1; **HRMS (ESI+):** Calculated for C₁₇H₂₅O₃NNa [M+Na]⁺: 314.1727, Found: 314.1728.

Scheme S3: Gram-scale Arylboration of 75



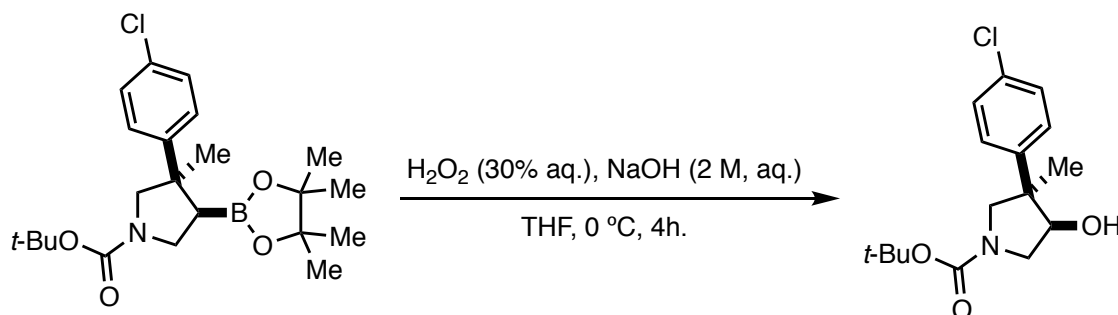
***Tert*-butyl 3-(4-chlorophenyl)-3-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrrolidine-1-carboxylate (76):**

In an N₂-filled glovebox, an oven-dried round bottom flask was charged with NaOt-Bu (793 mg, 8.25 mmol, 1.5 equiv.), bis(pinacolato)diboron (2.79 g, 11 mmol, 2.0 equiv.), and 1-bromo-4-chlorobenzene (3.16 g, 16.5 mmol, 3.0 equiv.). A separate oven-dried 16 x 100 mm vial was then charged with Ni(DME)Cl₂ (63.2 mg, 0.29 mmol). Both the flask and vial were sealed with septa before removing from the glovebox. The reaction flask was then charged with THF (49.5 mL) and *tert*-butyl 3-methyl-2,5-dihydro-1*H*-pyrrole-1-carboxylate (**75**) (1.10 mL, 5.50 mmol, 1.0 equiv) and allowed to stir at 30 °C. DMA (5.75 mL) was then added to the vial containing Ni(DME)Cl₂ (0.05 M in Ni(DME)Cl₂) to prepare the catalyst solution. 5.5 mL of the catalyst solution was then added to the reaction flask (5 mol% catalyst loading). The reaction was allowed to stir for 18 h at 30 °C. The reaction was then quenched upon the addition of 1 M HCl (50 mL), and the mixture was extracted with EtOAc (3 x 30 mL), dried over MgSO₄, gravity filtered, and concentrated. The crude material was dissolved in hexanes (50 mL) and washed with 1 M KOH (3 x 50 mL). The organic layer was dried over MgSO₄, gravity filtered, and concentrated under reduced pressure. Purification via silica gel column chromatography (Gradient: 10:1

hexanes:EtOAc to 6:1 hexanes: EtOAc) yield **76** as a white solid (1.5 g, 64% yield). Analytical data matched that which was obtained above.

■ Further Functionalization:

Scheme S4: Oxidation of Alkyl Boronic Ester **76**

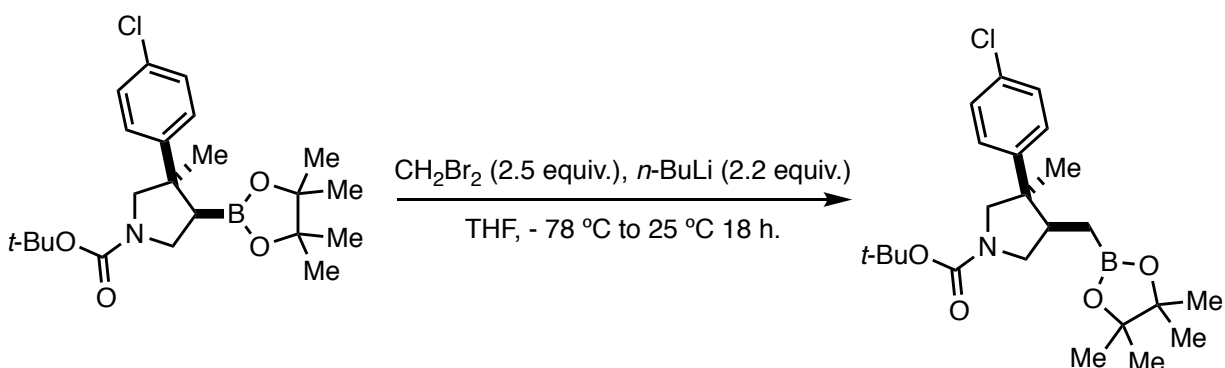


Tert-butyl 3-(4-chlorophenyl)-4-hydroxy-3-methylpyrrolidine-1-carboxylate (77**):** The title compound was prepared according to general procedure B. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (2:1 hexanes: EtOAc) yields **77** as white solid.

99% NMR, 95% isolated, >20:1 d.r. (49:51 mixture of rotamers)

m.p. 125-128 °C; **IR (neat):** 3410 (br), 2975 (m), 1672 (s), 1412 (m), 1366 (m), 1159 (m), 725 (m) cm^{-1} ; **^1H NMR (600 MHz, CDCl_3 , mixture of rotamers):** δ 7.39 – 7.33 (m, 2H), 7.20 – 7.15 (m, 2H), 4.31 – 4.24 (m, 1H), 3.83 (t, J = 9.9 Hz, 1H), 3.78 – 3.64 (m, 2H), 3.58 (minor rotamer d, J = 10.0 Hz, 1H), 3.49 (d, J = 12.2 Hz, 1H), 3.45 (d, J = 12.2 Hz, 1H), 1.51 (minor rotamer s, 9H), 1.49 (s, 9H), 1.28 (s, 3H); **^{13}C NMR (125 MHz, CDCl_3 , mixture of rotamers):** δ 155.1, 155.0, 141.2, 140.9, 132.9, 129.4, 129.2, 128.3, 128.2, 79.9, 79.8, 76.3, 53.4, 52.8, 50.9, 50.2, 28.7, 28.6, 26.9, 26.8; **HRMS (EI+):** Calculated for $\text{C}_{16}\text{H}_{22}\text{ClNO}_3$ $[\text{M}]^+$: 311.1283, Found: 311.1284.

Scheme S5: Matteson Homologation of Alkyl Boronic Ester **76**



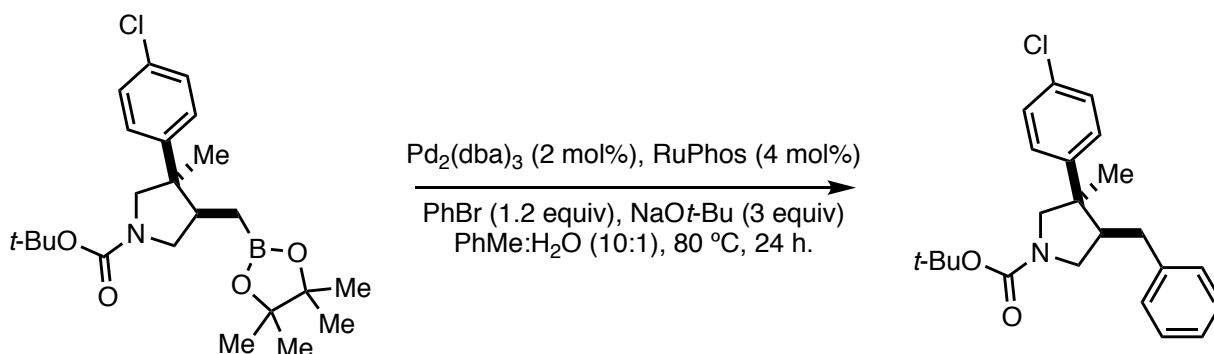
Tert-butyl 3-(4-chlorophenyl)-3-methyl-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)pyrrolidine-1-carboxylate (78**):** The title compound was prepared via a modified version of a literature procedure:³⁷ To an oven-dried 13 x 100 mm screw-cap vial was added boronic ester **76** (126.5 mg, 0.3 mmol, 1 equiv.). The vial was then inerted with three evacuation/backfill (N_2) cycles and sealed with a septum. THF (3 mL), and CH_2Br_2 (52 μL , 0.75

mmol, 2.5 equiv.) were then added via syringe. The solution was cooled to -78 °C before the addition of 2.2 M *n*-BuLi in hexane (0.3 mL, 0.66 mmol, 2.2 equiv.) dropwise over 10 min. The reaction was stirred for 5 min. at -78 °C before warming to 25 °C. The reaction was allowed to stir for 18 h. at 25 °C before being quenched upon the addition of H₂O (3 mL). The aqueous layer was then extracted with EtOAc (3 x 2 mL), and the combined organic layers were dried over MgSO₄, filtered, and concentrated under reduced pressure. 1,3,5-trimethylbenzene was added as an internal standard, and a small aliquot was analyzed via ¹H NMR. Purification via silica gel chromatography (10:1 hexanes: acetone) yield **78** as a white solid.

80% NMR, 60% isolated yield (55:45 mixture of rotamers). (Note: due to difficult separation 9% of the starting boronic ester was present in the purified material).

m.p. 130-137 °C; **IR (neat)**: 3391 (w), 2944 (m), 1709 (s), 1493 (m), 1379 (m), 1288 (m), 728 (m) cm⁻¹; **¹H NMR (600 MHz, CDCl₃, mixture of rotamers)**: δ 7.26 – 7.23 (m, 2H), 7.10 – 7.04 (m, 2H), 3.87 (*minor rotamer* d, *J* = 11.1 Hz, 1H), 3.78 (d, *J* = 11.1 Hz, 1H), 3.75 (dd, *J* = 11.1, 7.2 Hz, 1H), 3.63 (*minor rotamer* dd, *J* = 11.1, 7.1 Hz, 1H), 3.40 (*minor rotamer* d, *J* = 11.1 Hz, 1H), 3.36 (d, *J* = 11.1 Hz, 1H), 2.95 – 2.72 (m, 1H), 2.42 – 2.20 (m, 1H), 1.50 (s, 9H), 1.48 (*minor rotamer* s, 9H), 1.38 (s, 3H), 1.21 (*minor rotamer* s, 6H), 1.20 (*minor rotamer* s, 6H), 1.19 (s, 6H), 1.18 (s, 6H), 0.74 – 0.63 (m, 1H), 0.20 – 0.01 (m, 1H); **¹³C NMR (150 MHz, CDCl₃, mixture of rotamers)**: δ 154.4, 142.5, 132.2, 128.5, 128.4, 128.3, 83.4, 79.5, 79.4, 58.1, 57.2, 51.6, 51.1, 48.2, 47.5, 44.6, 44.0, 28.7, 25.9, 25.6, 25.0, 24.8, 24.7 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation); **HRMS (EI⁺)**: Calculated for C₂₃H₃₆BClNO₄ [M]⁺: 436.2425, Found: 436.2420.

Scheme S6: Suzuki Coupling of Alkyl Boronic Ester **76**



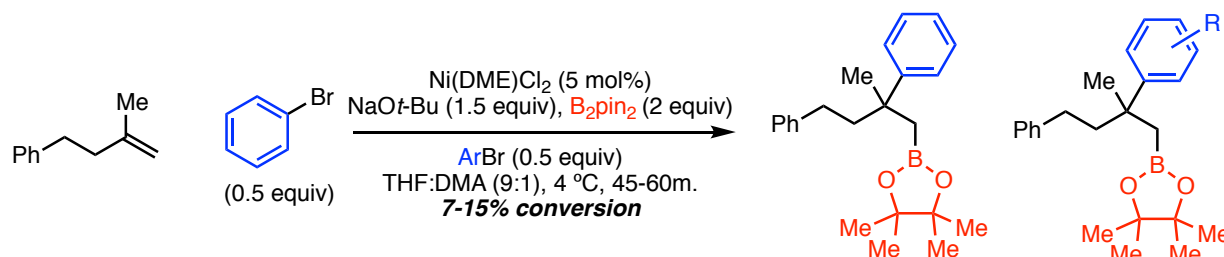
Tert-butyl 4-benzyl-3-(4-chlorophenyl)-3-methylpyrrolidine-1-carboxylate (79): In an N₂ filled glovebox, an oven-dried 2 dram vial was charged with boronic ester **77** (48.0 mg, 0.1 mmol, 1 equiv), Pd₂(dba)₃ (1.8 mg, 2.0 μmol, 2 mol%), RuPhos (1.9 mg, 4 μmol, 4 mol%), and NaO*t*-Bu (28.8 mg, 0.3 mmol, 3.0 equiv.). The vial was sealed with a septum and removed from the glovebox. 10:1 toluene/H₂O (0.17 mL) and bromobenzene (13 μL, 0.12 mmol, 1.2 equiv.) were then added via syringe. The septum was quickly replaced with a Teflon-lined screw cap and the reaction mixture was then heated to 80 °C for 24 h. The crude material was then subjected to oxidation via general procedure B to allow for facile separation from the boronic ester **78**. 1,3,5-trimethylbenzene was added as an internal standard and a small aliquot was analyzed via ¹H NMR. Purification via silica gel column chromatography (2% acetone in hexanes) yields **79** as a colorless oil.

78% NMR, 64% isolated yield, >20:1 d.r. (45:55 mixture of rotamers)

IR (neat): 3062 (w), 3027 (m), 2972 (m), 1688 (s), 1454 (m), 1253 (m), 881 (m) cm^{-1} ; **^1H NMR (600 MHz, CDCl_3 , mixture of rotamers):** δ 7.34 (d, J = 8.4 Hz, 2H), 7.31 – 7.24 (m, 1H), 7.24 – 7.12 (m, 4H), 7.09 – 6.96 (m, 2H), 3.92 (minor rotamer d, J = 11.0 Hz, 1H), 3.83 (d, J = 11.0 Hz, 1H), 3.54 – 3.46 (m, 1H), 3.46 – 3.37 (m, 1H), 3.18 – 2.96 (m, 1H), 2.68 – 2.51 (m, 1H), 2.51 – 2.31 (m, 1H), 1.95 – 1.71 (m, 1H), 1.51 (minor rotamer s, 9H), 1.49 – 1.45 (m, 12H); **^{13}C NMR (125 MHz, CDCl_3 , mixture of rotamers):** δ 154.4, 142.5, 132.2, 128.5, 128.4, 128.3, 83.4, 79.5, 79.4, 58.1, 57.2, 51.6, 51.1, 48.2, 47.5, 44.6, 44.0, 28.7, 25.9, 25.6, 25.0, 24.8, 24.7; **HRMS (ESI+):** Calculated for $\text{C}_{23}\text{H}_{28}\text{ClNO}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 408.1701, Found: 408.1703.

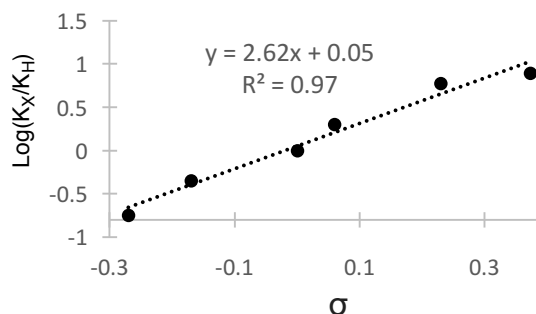
■ Mechanism Studies:

Table S3: Hammett Analysis of Ni-Catalyzed Arylboration



| entry | Arylbromide | σ | $\text{Log}(K_X/K_H)^{[a]}$ |
|-------|-------------|----------|-----------------------------|
| 1 | 4-OMe | -0.27 | -0.75 |
| 2 | 4-Me | -0.17 | -0.35 |
| 3 | H | 0 | 0 |
| 4 | 4-F | 0.06 | 0.30 |
| 5 | 4-Cl | 0.23 | 0.78 |
| 6 | 3-Cl | 0.37 | 0.90 |

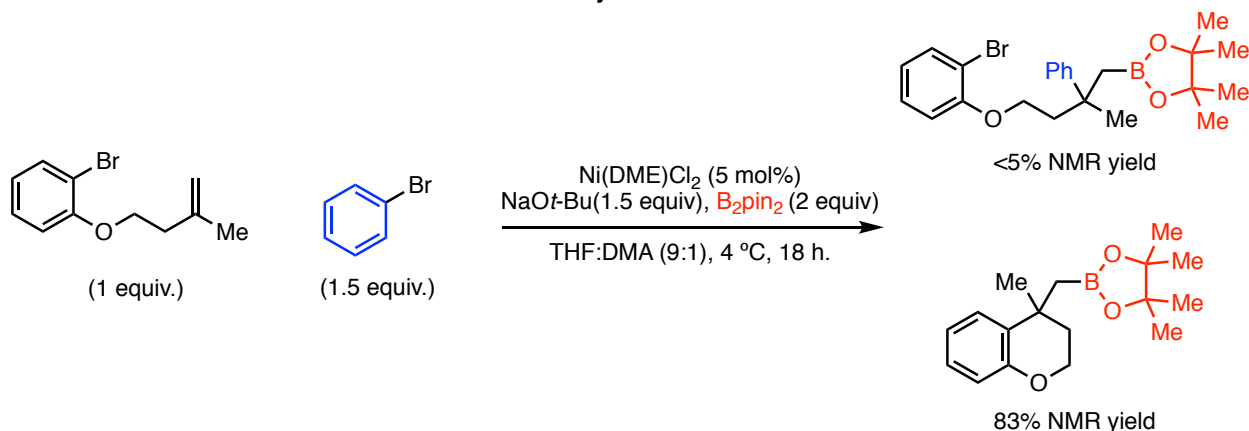
[a] Product ratios were determined via GC analysis relative to a calibrated internal standard (dodecane), average of two independent experiments.



■ General procedure for Hammett plot experiments:

In an N_2 -filled glovebox, to an oven-dried 16 x 100 mm screw-capped vial was added bis(pinacolato)diboron, (254 mg, 1.00 mmol, 2.00 equiv.), and NaOt-Bu (72.1 mg, 0.75 mmol, 1.50 equiv.). In a separate oven-dried 2-dram vial, $\text{Ni}(\text{DME})\text{Cl}_2$ (8.2 mg, 0.0375 mmol) was added. Note: if the aryl bromide is a solid, it was added to the vial in the glovebox (0.375 mmol, 0.50 equiv.). Both vials were sealed with septa, and removed from the glovebox. THF (4.5 mL) was added to the the reaction vial, followed by alkene (0.5 mmol, 1.0 equiv.), bromobenzene (40 μL , 0.375 mmol, 0.50 equiv.), and substituted arylbromide (0.375 mmol, 0.5 equiv.) before cooling to 0 $^\circ\text{C}$. DMA (0.75 mL) was then added to the vial containing $\text{Ni}(\text{DME})\text{Cl}_2$ (0.05 M in $\text{Ni}(\text{DME})\text{Cl}_2$) to prepare the catalyst solution. 0.50 mL of the catalyst solution was then added to the reaction vial (5 mol% catalyst loading). Dodecane (114 μL , 0.50 mmol, 1 equiv.) was then added as a GC standard. The reaction was allowed to proceed for 45-60m. before a small aliquot was taken and analyzed via GC (reactions were typically ~7-15% conversion) to determine the ratio of arylboration products. $\text{Log}(K_X/K_H)$ values in table S2 are the result of the average of two experiments.

Scheme S7: Intramolecular Versus Intermolecular Arylboration



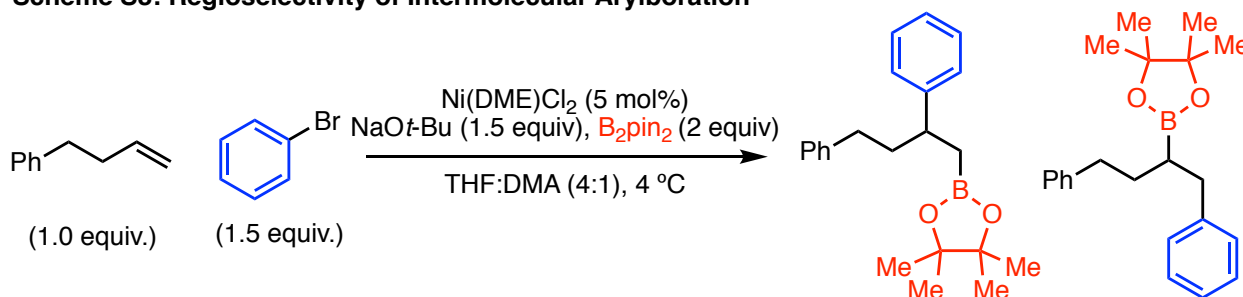
4,4,5,5-tetramethyl-2-((4-methylchroman-4-yl)methyl)-1,3,2-dioxaborolane:

In an N_2 -filled glovebox, to an oven-dried 16 x 100 mm screw-capped vial was added bis(pinacolato)diboron, (254 mg, 1.00 mmol, 2.00 equiv.), and NaOt-Bu (72.1 mg, 0.75 mmol, 1.50 equiv.). In a separate oven-dried 2-dram vial, Ni(DME)Cl_2 (8.2 mg, 0.0375 mmol) was added. Note: if the aryl bromide is a solid, it was added to the vial in the glovebox (0.75 mmol, 1.50 equiv.). Both vials were sealed with septa, and removed from the glovebox. THF (4.5 mL) was added to the reaction vial, followed by alkene (0.5 mmol, 1.0 equiv.) and arylbromide (0.75 mmol, 1.5 equiv.) and cooled to 0 °C. DMA (0.75 mL) was then added to the vial containing Ni(DME)Cl_2 (0.05 M in Ni(DME)Cl_2) to prepare the catalyst solution. 0.50 mL of the catalyst solution was then added to the reaction vial (5 mol% catalyst loading). The septum was then quickly replaced by a Teflon-lined screw cap and the reaction was stirred at 4 °C for 18 h in a temperature-controlled refrigerator. The reaction was quenched upon the addition of 1 M HCl (5.0 mL), and the mixture was extracted with EtOAc (3 x 3.0 mL), dried over MgSO_4 , gravity filtered, and concentrated. 1,3,5-Trimethylbenzene was added as an internal standard and a small aliquot was analyzed via ^1H NMR. The results above were the average of 2 independent experiments.

IR (neat): 2978 (m), 2927 (m), 2883 (m), 1487 (m), 1354 (m), 1141 (s), 906 (m) cm^{-1} ; **^1H NMR (600 MHz, CDCl_3):** δ 7.28 (dd, J = 7.8, 1.7 Hz, 1H), 7.03 (ddd, J = 8.1, 7.2, 1.7 Hz, 1H), 6.85 (ddd, J = 7.8, 7.2, 1.3 Hz, 1H), 6.74 (dd, J = 8.1, 1.3 Hz, 1H), 4.24 (ddd, J = 11.0, 6.2, 3.5 Hz, 1H), 4.16 (ddd, J = 11.0, 9.1, 2.8 Hz, 1H), 2.25 (ddd, J = 13.8, 9.1, 3.5 Hz, 1H), 1.81 (ddd, J = 13.8, 6.2, 2.8 Hz, 1H), 1.41 (s, 3H), 1.30 (s, 2H), 1.17 (s, 6H), 1.12 (s, 6H); **^{13}C NMR (125 MHz, CDCl_3):** δ 153.7, 132.7, 127.4, 127.0, 120.4, 116.8, 83.1, 63.2, 36.6, 32.3, 31.8, 24.9, 24.8 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation); **HRMS (EI+):** Calculated for $\text{C}_{17}\text{H}_{26}\text{BO}_3$ $[\text{M}+\text{H}]^+$: 288.1970, Found: 289.1971.

■ Regioselectivity of Intra- and Intermolecular Arylboration:

Scheme S8: Regioselectivity of Intermolecular Arylboration

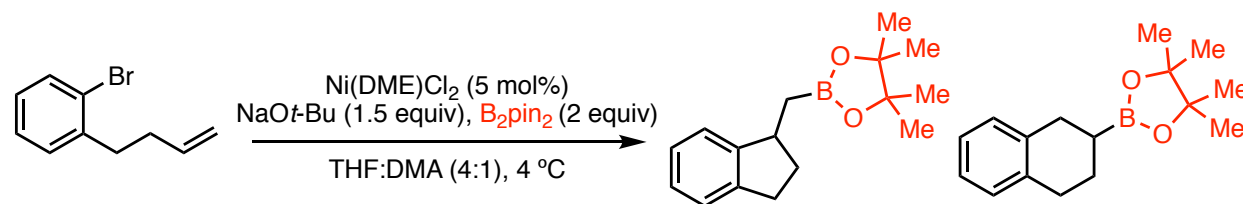


2-(2,4-diphenylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (88): The title compound was prepared according to a modified version of general procedure A, using a 4:1 THF:DMA solvent mixture. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an ^1H NMR standard. Purification via silica gel column chromatography (Gradient: Hexanes to 15:1 Hexanes: Et_2O) yields a mixture of **88** and **89** as a colorless oil.

Average over two runs: 88% NMR yield, 71% isolated yield, 2.5:1 r.r. (Note: Isolated as a mixture of regioisomers, characterization data for the major regioisomer is given. The major³⁸ and minor³⁹ regioisomers were identified by comparison to spectroscopic data available in the literature.)

^1H NMR (500 MHz, CDCl_3): δ 7.35 – 7.23 (m, 5H), 7.23 – 7.11 (m, 5H), 2.97 – 2.86 (m, 1H), 2.57 – 2.42 (m, 2H), 2.07 – 1.88 (m, 2H), 1.27 (dd, J = 15.3, 7.1 Hz, 1H), 1.21 – 1.16 (m, 1H), 1.13 (s, 12H) (integrals on attached spectrum may not be accurate due to the presence of the regioisomeric 1,2-arylboration product); ^{13}C NMR (125 MHz, CDCl_3): δ 147.1, 142.8, 128.5, 128.3, 128.2, 127.7, 126.0, 125.7, 83.1, 41.4, 41.2, 34.1, 24.8, 24.7 (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation. Additional signals on attached spectrum is due to the presence of the minor regioisomer.)

Scheme S9: Regioselectivity of Intramolecular Arylboration



2-((2,3-dihydro-1H-inden-1-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (85): The title compound was prepared according to a modified version of general procedure A, using a 4:1 THF:DMA solvent mixture. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an ^1H NMR standard. Purification via silica gel column chromatography (Gradient: Hexanes to 15:1 Hexanes: Et_2O) yields a mixture of **85** and **86** as a colorless oil.

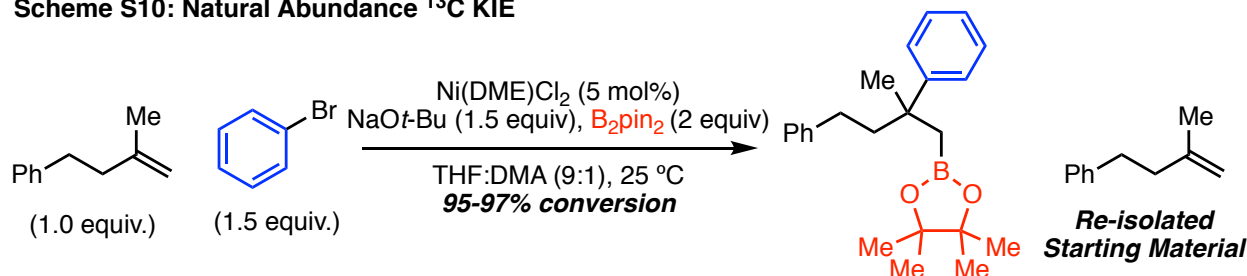
Average over two runs: 81% NMR yield, 75% isolated yield, 2.6:1 r.r. (Note: Isolated as a mixture of regioisomers, characterization data for the major regioisomer is given. The major⁴⁰ and minor⁴¹ regioisomers were identified by comparison to spectroscopic data available in the literature.)

^1H NMR (500 MHz, CDCl_3): δ 7.25 – 7.18 (m, 2H), 7.18 – 7.10 (m, 2H), 3.38 – 3.25 (m, 1H), 2.91 (ddd, J = 15.7, 8.6, 3.8 Hz, 1H), 2.86 – 2.78 (m, 1H), 2.42 – 2.31 (m, 1H), 1.70 – 1.59 (m,

1H), 1.37 (dd, $J = 15.6, 5.4$ Hz, 1H), 1.28 (s, 6H), 1.27 (s, 6H), 0.99 (dd, $J = 15.6, 9.5$ Hz, 1H); (integrals on attached spectrum may not be accurate due to the presence of the regioisomeric 1,2-arylboration product); ^{13}C NMR (125 MHz, CDCl_3): δ 149.3, 143.9, 126.2, 126.1, 124.3, 123.4, 83.2, 40.9, 35.0, 31.5, 25.1, 24.9; (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation. Additional signals on attached spectrum is due to the presence of the minor regioisomer.)

■ Natural Abundance Kinetic Isotope Effect Experiment:

Scheme S10: Natural Abundance ^{13}C KIE



(3-methylbut-3-en-1-yl)benzene (**30**):

In an N_2 filled glovebox, a 1-L three-necked round-bottom flask was charged with bis(pinacolato)diboron (15.2 g, 60 mmol, 2.0 equiv.), and NaOt-Bu (4.3 g, 45 mmol, 1.5 equiv.). The flask was fitted with a vacuum adapter (with stopcock), rubber septum, and a glass stopper. A separate 100-mL round-bottomed flask was charged with $\text{Ni}(\text{DME})\text{Cl}_2$ (340 mg, 1.55 mmol) and the flask sealed with a septum, both flasks were then removed from the glovebox. The 1-L reaction flask was charged with THF (270 mL) via syringe and the suspension stirred for 1 h. DMA (31 mL) was then added via syringe to the flask containing $\text{Ni}(\text{DME})\text{Cl}_2$ (0.05 M in $\text{Ni}(\text{DME})\text{Cl}_2$) to prepare the catalyst solution. Alkene **29** (4.9 mL, 30 mmol, 1.0 equiv.), and bromobenzene (4.8 mL, 45 mmol, 1.5 equiv.) were then added to the reaction flask via syringe. Finally, the catalyst solution (30 mL, 1.5 mmol, 5 mol%) was added to the reaction flask. The reaction was allowed to stir at 22 °C for 1.75 h. before being quenched upon the addition of 1M HCl (300 mL) (reaction was monitored via GC to determine percent conversion). The aqueous layer was extracted with EtOAc (3 x 300 mL), and the combined organic extracts washed with 1M KOH (3 x 300 mL), and brine (300 mL). The organic layer was dried over MgSO_4 , gravity filtered, and concentrated under reduced pressure. Unreacted starting material was isolated via silica gel column chromatography (pentane) to yield a colorless oil. All spectroscopic data was in accordance with literature values.⁴

Sample A: 60 mmol scale, 97% conversion

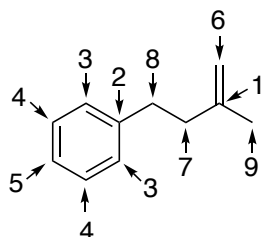
Sample B: 90 mmol scale, 95% conversion

■ Sample Preparation:

Sample A and Standard A: A new 5mm NMR tube was charged with 100 μL of recovered **29**, 120 μL of 0.1M $\text{Cr}(\text{acac})_3$ in CDCl_3 , and 380 μL CDCl_3 (final volume: 600 μL). The NMR tube was then flame sealed.

Sample B and Standard B: A new 5mm NMR tube was charged with 190 μL of recovered **29**, 120 μL of 0.1M $\text{Cr}(\text{acac})_3$ in CDCl_3 , and 290 μL CDCl_3 (final volume: 600 μL). The NMR tube was then flame sealed.

■ KIE at Natural Abundance Determination



Numbering Scheme for **29**

The quantitative ^{13}C spectra were recorded at 125.7 MHz on a Varian Inova 500 NMR spectrometer with a 5mm $^1\text{H}/^{13}\text{C}$ dual probe. Sample temperature was set at 298K. Inverse-gated decoupling was applied to eliminate NOE. Waltz decoupling sequence was employed. ^{13}C pulse width was set to 90° . 64K data points were collected for each FID. Spectral window was set to 31,422 Hz. Acquisition time was 1.04 second. Relaxation delay was set to 25 seconds, which is longer than $10 \times T_{1\text{max}}$ (the longest T_1 in the molecule). For each sample (and standard), nine spectra were collected. 192 scans were recorded for each spectrum leading to a signal/noise ratio of 260 for Sample A, 360 for Standard A, 480 for Sample B, and 660 for Standard B. Each spectrum took 83 minutes. To obtain optimal lineshape, the Z shims were optimized using gradient shimming and the XY shims were optimized using the VnmrJ Autoslim feature. The ^1H and ^{13}C 90° pulse widths were calibrated for each sample (and standard). T_1 values were measured by inversion recovery method.

In order to achieve high signal/noise ratio data with a large number of scans in a reasonable amount of time, $\text{Cr}(\text{acac})_3$ was added into the samples (including standards) as a relaxation agent to reduce the relaxation time of carbons (especially the quaternary carbons) so to decrease the relaxation delay for each scan.⁴² The optimal concentration of $\text{Cr}(\text{acac})_3$ was determined to be 20 mM, which reduces T_1 of the quaternary carbons by one order of magnitude while minimizing the amount of line broadening.

NMR data was processed using VnmrJ. Each FID was right shifted by two data points. The first five data points were then reconstructed using backward linear prediction. The resulting FID was zero-filled to 512K points and apodized with a line broadening of 1 Hz. After Fourier transformation, one spectrum for each set of FIDs was manually phased. All spectra showed a flat baseline with no DC offset. No baseline correction was applied. Regions of integration for each peak were set to a width of 20 Hz with 10 Hz on each side of the peak, except for peak 4 which was set to 17 Hz with 7 Hz on right side to avoid overlap with an impurity peak. Peak 3 and 4 partially overlapped each other and impurity peaks; therefore, they were excluded from the analysis. The integration data were then imported to Excel where KIEs and their uncertainties were calculated. The average integrations for all carbons are shown in Table S4.

Table S4

| Standard A Raw Integrations | | | | | | | | | |
|------------------------------------|--|-----------------------------|--|-------------------------------|--|-----------------------------|--|----------|----------|
| 1 | 99.7352 | 100.0990 | 99.4628 | 100.5730 | 99.2143 | 99.5632 | 100.0750 | 99.9068 | 100.3430 |
| 2 | 100.0000 | 99.8460 | 100.2100 | 99.8083 | 100.2110 | 100.3010 | 100.1650 | 100.0700 | 100.7170 |
| 5 | 94.8721 | 94.3986 | 95.2958 | 94.7365 | 93.9919 | 94.6321 | 94.9077 | 94.7656 | 94.8636 |
| 6 | 91.4035 | 91.2892 | 91.0012 | 91.8034 | 91.1363 | 91.5208 | 90.8621 | 91.2580 | 91.4798 |
| 7 | 97.3138 | 96.3875 | 96.1336 | 96.5407 | 96.5151 | 96.6571 | 95.8161 | 97.1800 | 96.1242 |
| 8 | 97.0833 | 96.7914 | 97.6402 | 97.1143 | 97.5677 | 97.1618 | 97.1957 | 97.1905 | 97.4464 |
| 9 | 96.2703 | 95.9588 | 94.8058 | 95.5682 | 95.8864 | 95.9101 | 95.5172 | 95.7535 | 95.9094 |
| Sample A Raw Integrations | | | | | | | | | |
| 1 | 101.5060 | 100.9370 | 101.3150 | 101.8620 | 101.4180 | 99.3668 | 101.4030 | 100.1040 | 100.8810 |
| 2 | 100.0000 | 97.4001 | 98.9652 | 97.0129 | 97.9377 | 98.1895 | 98.8351 | 97.6771 | 98.6687 |
| 5 | 94.1255 | 93.8089 | 94.9396 | 94.4997 | 94.1189 | 94.0202 | 93.8912 | 94.6693 | 94.1194 |
| 6 | 92.1804 | 91.8851 | 92.6929 | 91.8184 | 91.1851 | 91.0095 | 91.8907 | 92.2448 | 92.1578 |
| 7 | 94.9649 | 95.4952 | 93.6636 | 94.0071 | 95.0173 | 95.8433 | 94.7315 | 94.1200 | 93.7739 |
| 8 | 96.5770 | 97.5559 | 96.4504 | 96.1490 | 96.7117 | 96.8086 | 96.5422 | 96.0677 | 96.6961 |
| 9 | 94.3466 | 94.8940 | 94.3420 | 94.9611 | 94.0804 | 94.1881 | 94.2292 | 95.4072 | 94.8411 |
| Standard B Raw Integrations | | | | | | | | | |
| 1 | 99.7979 | 99.7418 | 99.5927 | 99.8477 | 99.4761 | 99.7967 | 100.5590 | 99.7008 | 99.7078 |
| 2 | 100.0000 | 99.8268 | 99.9823 | 99.4367 | 99.9037 | 100.1710 | 100.1680 | 99.7593 | 100.3670 |
| 5 | 95.1185 | 95.5972 | 95.3518 | 95.0451 | 94.8969 | 95.5356 | 95.0605 | 95.0056 | 94.8873 |
| 6 | 92.8624 | 92.4835 | 92.5874 | 92.8545 | 92.8926 | 92.5953 | 92.9752 | 92.4999 | 92.3117 |
| 7 | 97.3212 | 96.9515 | 97.3657 | 96.7642 | 96.6201 | 97.2183 | 96.8853 | 96.7679 | 96.7029 |
| 8 | 96.8183 | 96.5321 | 96.5347 | 96.4267 | 96.5290 | 96.9432 | 96.1136 | 96.5510 | 96.1999 |
| 9 | 95.2695 | 94.9804 | 94.9132 | 94.9324 | 94.8978 | 94.9548 | 95.2901 | 94.6213 | 94.7331 |
| Sample B Raw Integrations | | | | | | | | | |
| 1 | 102.9560 | 102.2720 | 102.6250 | 102.6160 | 102.9380 | 102.2650 | 102.4200 | 102.4340 | 101.8480 |
| 2 | 100.0000 | 100.2940 | 100.3120 | 100.7790 | 100.6140 | 100.0910 | 100.3780 | 100.4120 | 100.6950 |
| 5 | 96.6344 | 96.5479 | 96.2780 | 96.5653 | 96.0996 | 96.5411 | 96.6738 | 96.1975 | 96.7599 |
| 6 | 95.1498 | 94.4314 | 94.6186 | 94.8200 | 94.4340 | 94.5639 | 95.2065 | 94.9927 | 94.8205 |
| 7 | 97.2675 | 97.3112 | 97.1592 | 97.3892 | 97.0495 | 97.3217 | 97.1937 | 97.6358 | 97.3342 |
| 8 | 97.9050 | 97.9586 | 98.2405 | 97.9235 | 97.4574 | 98.2762 | 97.8916 | 98.1718 | 97.6894 |
| 9 | 95.6723 | 96.1498 | 95.6158 | 94.8865 | 95.9135 | 95.1058 | 96.1283 | 95.9550 | 94.9471 |
| Average Standard A | Standard Deviation Standard A | Average Sample A | Standard Deviation Sample A | Average Standard B | Standard Deviation Standard B | Average Sample B | Standard Deviation Sample B | | |
| 1 | 99.8858 | 0.4358 | 100.9770 | 0.7841 | 99.8023 | 0.3058 | 102.4860 | 0.3482 | |
| 2 | 100.1476 | 0.2715 | 98.2985 | 0.9187 | 99.9572 | 0.2717 | 100.3972 | 0.2626 | |

| | | | | | | | | |
|---|---------|--------|---------|--------|---------|--------|---------|--------|
| 5 | 94.7182 | 0.3630 | 94.2436 | 0.3774 | 95.1665 | 0.2648 | 96.4775 | 0.2293 |
| 6 | 91.3060 | 0.2860 | 91.8961 | 0.5248 | 92.6736 | 0.2286 | 94.7819 | 0.2918 |
| 7 | 96.5187 | 0.4878 | 94.6241 | 0.7752 | 96.9552 | 0.2793 | 97.2958 | 0.1648 |
| 8 | 97.2435 | 0.2651 | 96.6176 | 0.4314 | 96.5165 | 0.2612 | 97.9460 | 0.2638 |
| 9 | 95.7311 | 0.4122 | 94.5877 | 0.4518 | 94.9547 | 0.2174 | 95.5971 | 0.4988 |

| | R/R0 Sample A | KIE Sample A (97% conversion) | Δ KIE Sample A | R/R0 Sample B | KIE Sample B (95% conversion) | Δ KIE Sample B |
|---|------------------|--|--------------------------|------------------|--|--------------------------|
| 1 | 1.0299 | 1.0085 | 0.0003 | 1.0224 | 1.0074 | 0.0007 |
| 2 | 1.0000 | 1.0000 | 0.0005 | 1.0000 | 1.0000 | 0.0001 |
| 5 | 1.0137 | 1.0039 | 0.0001 | 1.0093 | 1.0031 | 0.0004 |
| 6 | 1.0254 | 1.0072 | 0.0002 | 1.0183 | 1.0061 | 0.0006 |
| 7 | 0.9988 | 0.9997 | 0.0005 | 0.9991 | 0.9997 | 0.0001 |
| 8 | 1.0123 | 1.0035 | 0.0002 | 1.0104 | 1.0035 | 0.0004 |
| 9 | 1.0066 | 1.0019 | 0.0003 | 1.0024 | 1.0008 | 0.0002 |

The average integrations of peak 2 are set to 100.00. The isotope effects were calculated via equation 1. The uncertainties were calculated by equations 2-5.⁴³ In these equations, $\frac{R}{R_0}$ is the ratio of a peak's average integrations for a sample analysis divided by that in the analysis of the standard, F is fractional conversion, ΔF is the uncertainty in the conversion (estimated to be 1%), I_S is the average integration for the sample for the carbon peak of interest, I_0 is the average integration for standard for the carbon peak of interest, and ΔI_S and ΔI_0 are the 95% confidence ranges in the measurement.

$$KIE = \frac{\ln(1-F)}{\ln\left[(1-F)\left(\frac{R}{R_0}\right)\right]} \quad (1)$$

$$\Delta \frac{R}{R_0} = \frac{R}{R_0} \sqrt{\left(\frac{\Delta I_S}{I_S}\right)^2 + \left(\frac{\Delta I_0}{I_0}\right)^2} \quad (2)$$

$$\Delta KIE_F = \frac{-\ln\left(\frac{R}{R_0}\right)}{(1-F)\ln^2\left[(1-F)\frac{R}{R_0}\right]} \Delta F \quad (3)$$

$$\Delta KIE_R = \frac{-\ln(1-F)}{\left(\frac{R}{R_0}\right)\ln^2\left[(1-F)\frac{R}{R_0}\right]} \Delta \frac{R}{R_0} \quad (4)$$

$$\Delta KIE = KIE * \sqrt{\left(\left(\frac{\Delta KIE_R}{KIE}\right)^2 + \left(\frac{\Delta KIE_F}{KIE}\right)^2\right)} \quad (5)$$

■ Computational Methods:

All calculations were performed using Gaussian 09.⁴⁴ Images of the 3D structures of molecules were generated using CYLview.⁴⁵ Geometry optimizations and vibrational frequency calculations were performed using the UB3LYP⁴⁶ functional in gas phase with the LANL2DZ effective core potential basis set for nickel and the 6-31G(d) basis set for other atoms. The nature of all stationary points was confirmed by the number of imaginary frequencies. All minima have zero imaginary frequency, and all transition states have only one imaginary frequency. Single-point energy calculations were carried out using the UM06⁴⁷ functional and the SDD basis set for Ni and 6-311+G(d,p) for other atoms. The SMD⁴⁸ solvation model was used in the single-point energy calculations to incorporate solvent effects with tetrahydrofuran as the solvent. Thermal corrections to the Gibbs free energies and enthalpies were calculated using the harmonic oscillator approximation at 298.15 K.

■ Relative Stability of Different Ni(I)–Bpin Precatalysts:

In the reaction conditions of Ni-catalyzed arylboration of alkene several possible ligands e.g. THF, DMA and alkene could potentially bind to form the Ni(I)–Bpin precatalyst. The relative stability of these complexes was considered computationally (Figure S11). The calculations indicate that the formation of the Ni(I)–Bpin complex **INT-1** is the most favorable thermodynamically. Thus, Ni(I)–Bpin complex **INT-1** was used as the precatalyst in the calculations of the Ni-catalyzed arylboration of alkene (Figure S11).

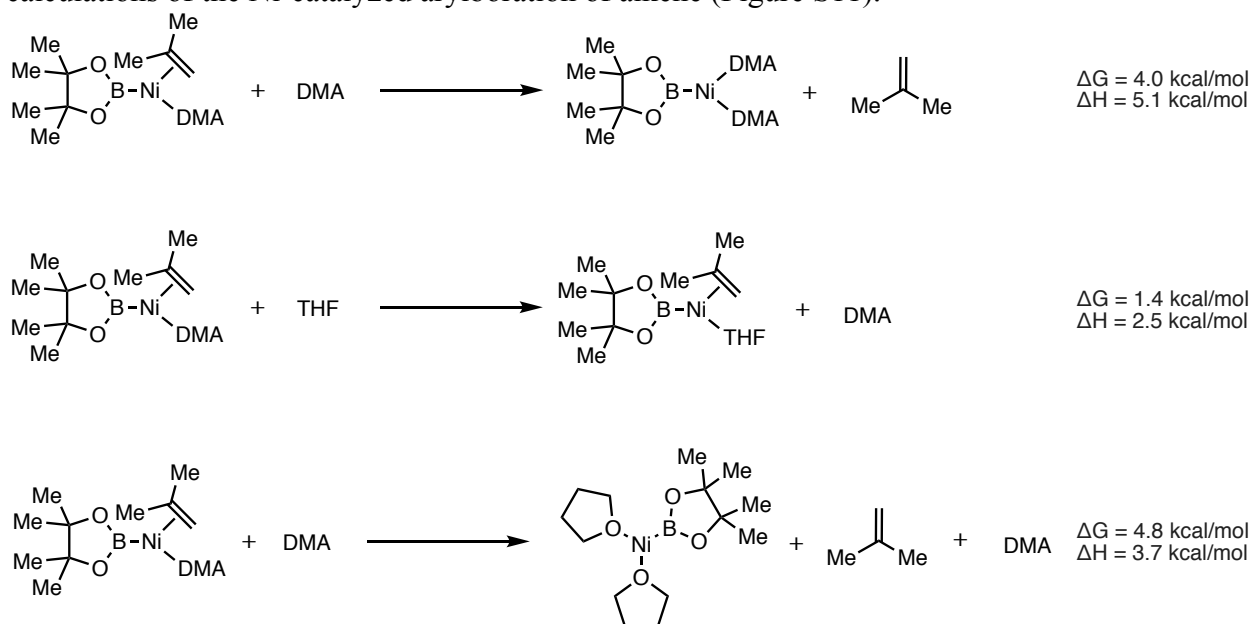
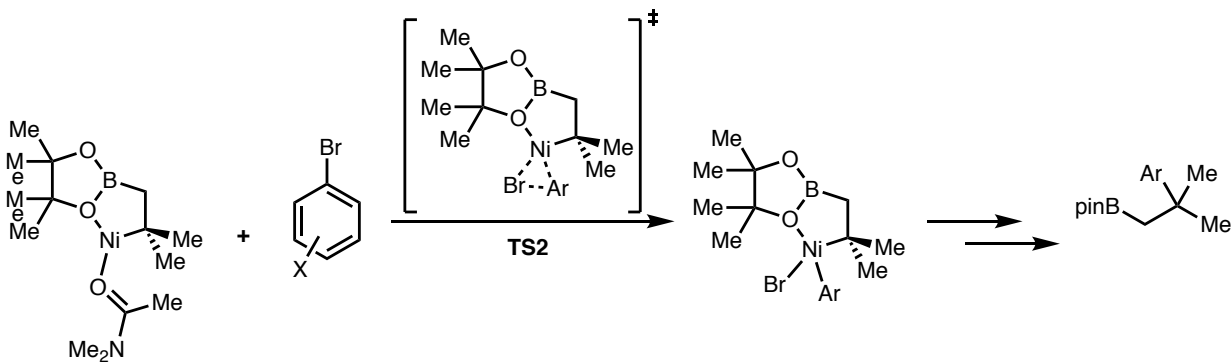


Figure S11. Relative stability of Ni(I)-Bpin complexes.

■ DFT-Computed Relative Rates of Reactions with Different Arylbromides:

The DFT-computed relative rates of the reactions with different arylbromides ($k_{\text{ArBr}}/k_{\text{PhBr}}$) were calculated using the Eyring equation ($T = 277.15\text{K}$) and the computed activation energies of the oxidative addition transition states ($\Delta G_{\text{ArBr}}^{\ddagger}(\text{TS2})$) with respect to the alkyl-[Ni] intermediate **INT-2**. As shown in Figure 2, overall, a good correlation between the DFT-computed $k_{\text{ArBr}}/k_{\text{PhBr}}$ and the experimentally observed relative rates was observed. The calculated $k_{\text{ArBr}}/k_{\text{PhBr}}$ for *para*-fluorobromobenzene ($X = 4\text{-F}$) has a slightly larger deviation from the experimental data. The computations overestimated the barrier of $\Delta G_{\text{ArBr}}^{\ddagger}(\text{TS2})$ for this substrate by a few tenths of a kcal/mol as compared to the experimental trend.



INT-2

| ArBr | | $\Delta G_{\text{ArBr}}^{\ddagger}(\text{TS2})$ (kcal/mol) | DFT- calculated $\log(k_{\text{ArBr}}/k_{\text{PhBr}})$ |
|-------|-------------|---|---|
| entry | substituent | | |
| 1 | 4-OMe | 6.72 | -0.520 |
| 2 | 4-Me | 6.58 | -0.410 |
| 3 | H | 6.06 | 0.000 |
| 4 | 4-F | 6.33 | -0.211 |
| 5 | 4-Cl | 5.39 | 0.535 |
| 6 | 3-Cl | 5.39 | 0.533 |

■ Cartesian Coordinates

95

B3LYP electronic energy: -157.22421795 a.u.
B3LYP enthalpy: -157.109452 a.u.
B3LYP free energy: -157.142992 a.u.
M06 SCF energy in solution: -157.13454382 a.u.
M06 enthalpy in solution: -157.019778 a.u.
M06 free energy in solution: -157.053318 a.u.

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| C | 0.000000 | 0.122890 | 0.000000 |
| C | 0.000000 | 1.459828 | 0.000000 |
| H | -0.924755 | 2.031861 | 0.000000 |
| H | 0.924755 | 2.031861 | 0.000000 |
| C | 1.278385 | -0.679086 | 0.000000 |
| H | 2.163435 | -0.035361 | -0.000002 |
| H | 1.332605 | -1.335067 | 0.880116 |
| H | 1.332603 | -1.335071 | -0.880113 |
| C | -1.278385 | -0.679086 | 0.000000 |
| H | -1.332604 | -1.335069 | -0.880115 |
| H | -1.332603 | -1.335070 | 0.880114 |
| H | -2.163436 | -0.035362 | 0.000000 |

96

B3LYP electronic energy: -800.17146064 a.u.
B3LYP enthalpy: -799.763924 a.u.
B3LYP free energy: -799.831606 a.u.
M06 SCF energy in solution: -799.83005938 a.u.
M06 enthalpy in solution: -799.422523 a.u.
M06 free energy in solution: -799.490205 a.u.

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| C | 1.849278 | -1.576668 | -0.132246 |
| C | 0.576973 | -1.748177 | -1.027478 |
| H | 0.814649 | -1.469008 | -2.061204 |
| C | -2.312792 | 0.690805 | -0.610043 |
| C | -2.510378 | -0.250219 | 0.643579 |
| O | -1.258600 | -0.992118 | 0.676220 |
| O | -1.350953 | -0.053809 | -1.408423 |
| B | -0.688748 | -0.921489 | -0.574432 |
| C | -1.652277 | 2.034113 | -0.269403 |
| H | -0.740079 | 1.894973 | 0.318537 |
| H | -1.374643 | 2.537215 | -1.200832 |
| H | -2.332482 | 2.688899 | 0.286152 |
| C | -3.565557 | 0.921445 | -1.454530 |
| H | -4.340272 | 1.434894 | -0.873244 |
| H | -3.315670 | 1.551039 | -2.314686 |
| H | -3.978408 | -0.016343 | -1.833658 |
| C | -2.677420 | 0.471779 | 1.979761 |

| | | | |
|---|-----------|-----------|-----------|
| H | -3.585747 | 1.085439 | 1.982259 |
| H | -2.764627 | -0.264056 | 2.785971 |
| H | -1.821651 | 1.113828 | 2.199869 |
| C | -3.627303 | -1.286664 | 0.461039 |
| H | -3.570262 | -2.017490 | 1.273888 |
| H | -4.619074 | -0.822662 | 0.483559 |
| H | -3.517784 | -1.825705 | -0.485338 |
| C | 2.148147 | -0.076133 | 0.053377 |
| C | 2.377137 | 0.737161 | -1.071615 |
| C | 2.197665 | 0.540052 | 1.312702 |
| C | 2.648202 | 2.098663 | -0.945792 |
| H | 2.340127 | 0.302509 | -2.066615 |
| C | 2.468894 | 1.905701 | 1.445130 |
| H | 2.021216 | -0.042966 | 2.209632 |
| C | 2.697076 | 2.692607 | 0.317486 |
| H | 2.820800 | 2.696646 | -1.837179 |
| H | 2.502673 | 2.350222 | 2.436875 |
| H | 2.909744 | 3.753559 | 0.419248 |
| H | 0.327217 | -2.819817 | -1.054063 |
| C | 1.624112 | -2.300223 | 1.209891 |
| H | 1.435993 | -3.363798 | 1.022771 |
| H | 2.508246 | -2.232148 | 1.854687 |
| H | 0.761415 | -1.902195 | 1.750713 |
| C | 3.052701 | -2.250488 | -0.834577 |
| H | 3.959678 | -2.167062 | -0.223902 |
| H | 2.849498 | -3.316081 | -0.998153 |
| H | 3.262859 | -1.797568 | -1.809193 |

INT-1

| | |
|------------------------------|---------------------|
| B3LYP electronic energy: | -1025.63044126 a.u. |
| B3LYP enthalpy: | -1025.178282 a.u. |
| B3LYP free energy: | -1025.267950 a.u. |
| M06 SCF energy in solution: | -1026.95830775 a.u. |
| M06 enthalpy in solution: | -1026.506148 a.u. |
| M06 free energy in solution: | -1026.595816 a.u. |

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| Ni | -1.405936 | -0.615659 | -0.374902 |
| C | 2.867455 | -0.044187 | 0.024198 |
| C | 2.766877 | -1.610392 | 0.045801 |
| B | 0.632578 | -0.701810 | -0.174846 |
| O | 1.409180 | -1.837898 | -0.403886 |
| O | 1.482483 | 0.356721 | 0.209022 |
| C | 3.723623 | -2.341046 | -0.898105 |
| H | 4.770393 | -2.146640 | -0.633107 |
| H | 3.552760 | -3.420488 | -0.827706 |
| H | 3.566227 | -2.046479 | -1.938340 |
| C | 2.874984 | -2.210165 | 1.457400 |
| H | 2.583758 | -3.264433 | 1.413626 |
| H | 3.894831 | -2.151038 | 1.855248 |
| H | 2.197130 | -1.704181 | 2.151883 |
| C | 3.320805 | 0.515114 | -1.334017 |

| | | | |
|---|-----------|-----------|-----------|
| H | 3.187525 | 1.602650 | -1.337859 |
| H | 4.377437 | 0.303419 | -1.533720 |
| H | 2.721068 | 0.099029 | -2.149194 |
| C | 3.712228 | 0.569287 | 1.141971 |
| H | 4.756564 | 0.240741 | 1.074095 |
| H | 3.701514 | 1.662266 | 1.060521 |
| H | 3.329409 | 0.302402 | 2.130016 |
| C | -3.403238 | -0.952528 | -1.238583 |
| C | -3.456126 | -1.583311 | -0.026550 |
| H | -3.753593 | 0.068579 | -1.358923 |
| H | -3.164721 | -1.502845 | -2.146599 |
| O | -2.006999 | 1.426263 | 0.107288 |
| C | -1.124051 | 2.185989 | 0.559360 |
| C | -0.752120 | 2.129035 | 2.026356 |
| H | 0.227100 | 1.646930 | 2.120711 |
| H | -0.712553 | 3.115058 | 2.500012 |
| H | -1.497102 | 1.517213 | 2.535739 |
| N | -0.484156 | 3.068171 | -0.246207 |
| C | 0.710971 | 3.799995 | 0.153084 |
| H | 0.722129 | 3.980445 | 1.227122 |
| H | 1.613699 | 3.237890 | -0.116572 |
| H | 0.726788 | 4.768791 | -0.357031 |
| C | -0.731758 | 3.017835 | -1.684464 |
| H | -0.687546 | 4.032513 | -2.093959 |
| H | 0.021646 | 2.394256 | -2.182290 |
| H | -1.715759 | 2.587880 | -1.860583 |
| C | -4.023301 | -0.913839 | 1.203385 |
| H | -4.121188 | 0.165134 | 1.067010 |
| H | -5.012800 | -1.334674 | 1.435904 |
| H | -3.386169 | -1.095094 | 2.078323 |
| C | -3.166325 | -3.062152 | 0.107725 |
| H | -2.482993 | -3.260131 | 0.942445 |
| H | -4.097417 | -3.609710 | 0.315943 |
| H | -2.723196 | -3.477680 | -0.802562 |

INT-2

B3LYP electronic energy: -1025.64792091 a.u.
 B3LYP enthalpy: -1025.195520 a.u.
 B3LYP free energy: -1025.281611 a.u.
 M06 SCF energy in solution: -1026.98009402 a.u.
 M06 enthalpy in solution: -1026.527693 a.u.
 M06 free energy in solution: -1026.613784 a.u.

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| Ni | -0.588934 | 1.188751 | -0.195577 |
| C | 0.758141 | 2.660561 | -0.155386 |
| C | 2.040361 | 2.060933 | -0.804580 |
| H | 1.923144 | 2.063878 | -1.902393 |
| C | 1.584076 | -1.614134 | -0.003895 |
| C | 3.134301 | -1.454814 | 0.250259 |
| O | 3.422505 | -0.156713 | -0.338683 |
| O | 1.158304 | -0.223325 | -0.063245 |

| | | | |
|---|-----------|-----------|-----------|
| B | 2.258174 | 0.569310 | -0.394821 |
| C | 0.800974 | -2.313784 | 1.105187 |
| H | 0.929260 | -1.814349 | 2.068091 |
| H | -0.265065 | -2.297639 | 0.857047 |
| H | 1.116291 | -3.358864 | 1.206941 |
| C | 1.246036 | -2.238509 | -1.364349 |
| H | 1.486550 | -3.306913 | -1.389816 |
| H | 0.174151 | -2.117760 | -1.549579 |
| H | 1.786144 | -1.741141 | -2.176003 |
| C | 3.499503 | -1.353896 | 1.737640 |
| H | 3.379427 | -2.313708 | 2.251864 |
| H | 4.545958 | -1.045404 | 1.823375 |
| H | 2.885724 | -0.604970 | 2.247825 |
| C | 4.012414 | -2.501045 | -0.435012 |
| H | 5.065432 | -2.289206 | -0.223537 |
| H | 3.787430 | -3.507269 | -0.062208 |
| H | 3.879888 | -2.492083 | -1.519265 |
| H | 2.940654 | 2.675839 | -0.607765 |
| O | -2.052019 | -0.202289 | -0.250527 |
| C | -3.210071 | -0.190830 | 0.213208 |
| N | -4.088493 | -1.174092 | -0.119791 |
| C | -3.664170 | 0.916381 | 1.145515 |
| H | -4.503766 | 1.480134 | 0.723507 |
| H | -3.972220 | 0.523257 | 2.120697 |
| H | -2.819298 | 1.593146 | 1.290763 |
| C | -5.447586 | -1.279413 | 0.390258 |
| H | -5.573300 | -2.215739 | 0.949766 |
| H | -5.688714 | -0.448386 | 1.049893 |
| H | -6.163568 | -1.281036 | -0.441447 |
| C | -3.683670 | -2.240163 | -1.030074 |
| H | -2.693258 | -2.015445 | -1.420180 |
| H | -3.661657 | -3.204313 | -0.505829 |
| H | -4.398278 | -2.311695 | -1.858740 |
| C | 0.366361 | 3.947936 | -0.895103 |
| H | -0.525638 | 4.413853 | -0.452745 |
| H | 1.175110 | 4.706010 | -0.860488 |
| H | 0.143882 | 3.760472 | -1.953887 |
| C | 1.082680 | 3.021781 | 1.306031 |
| H | 1.911578 | 3.756739 | 1.370814 |
| H | 0.218452 | 3.466503 | 1.817251 |
| H | 1.387994 | 2.145736 | 1.896291 |

INT-3

B3LYP electronic energy: -3540.85347217 a.u.
 B3LYP enthalpy: -3540.444362 a.u.
 B3LYP free energy: -3540.526867 a.u.
 M06 SCF energy in solution: -3544.79351457 a.u.
 M06 enthalpy in solution: -3544.384404 a.u.
 M06 free energy in solution: -3544.466909 a.u.

Cartesian coordinates

| ATOM | X | Y | Z |
|------|----------|----------|----------|
| Ni | 0.809006 | 0.710892 | 0.161650 |

| | | | |
|----|-----------|-----------|-----------|
| C | 0.132033 | 2.314221 | -0.818153 |
| C | -1.100092 | 1.844626 | -1.637165 |
| H | -1.697851 | 2.691067 | -2.024904 |
| C | -3.714202 | -0.218343 | 0.234337 |
| C | -2.378809 | -1.010699 | 0.505257 |
| O | -1.371738 | -0.030879 | 0.090512 |
| O | -3.335246 | 0.677485 | -0.845454 |
| B | -1.976495 | 0.850205 | -0.814238 |
| C | -4.144967 | 0.668483 | 1.411452 |
| H | -3.315409 | 1.286943 | 1.768565 |
| H | -4.941892 | 1.338105 | 1.074085 |
| H | -4.525595 | 0.075661 | 2.250020 |
| C | -4.888405 | -1.075299 | -0.235734 |
| H | -5.166141 | -1.811958 | 0.527009 |
| H | -5.756732 | -0.434574 | -0.419100 |
| H | -4.658033 | -1.602493 | -1.164098 |
| C | -2.148689 | -1.388664 | 1.966359 |
| H | -2.969798 | -2.014679 | 2.333851 |
| H | -1.224925 | -1.967211 | 2.067095 |
| H | -2.071580 | -0.506060 | 2.605567 |
| C | -2.202601 | -2.235727 | -0.400540 |
| H | -1.170175 | -2.591207 | -0.329856 |
| H | -2.872640 | -3.050774 | -0.106841 |
| H | -2.398113 | -1.986364 | -1.448004 |
| C | 2.301847 | -0.756550 | 0.140900 |
| C | 1.728337 | -0.941449 | 1.423479 |
| C | 3.418382 | 0.105133 | -0.013745 |
| C | 2.259429 | -0.235354 | 2.524017 |
| H | 0.955797 | -1.686390 | 1.568959 |
| C | 3.914940 | 0.788006 | 1.089993 |
| H | 3.871159 | 0.220534 | -0.991912 |
| C | 3.343110 | 0.619704 | 2.364960 |
| H | 1.817651 | -0.386427 | 3.505091 |
| H | 4.759108 | 1.459013 | 0.958827 |
| H | 3.748586 | 1.154545 | 3.217993 |
| Br | 1.887030 | -1.999499 | -1.278521 |
| H | -0.750902 | 1.297096 | -2.529381 |
| C | -0.323099 | 3.372819 | 0.204207 |
| H | 0.515587 | 3.743744 | 0.808791 |
| H | -0.774035 | 4.252946 | -0.296035 |
| H | -1.078134 | 2.987226 | 0.904858 |
| C | 1.170761 | 2.950811 | -1.751152 |
| H | 0.761438 | 3.830720 | -2.284990 |
| H | 2.054336 | 3.299191 | -1.197240 |
| H | 1.520570 | 2.244673 | -2.516432 |

INT-4

B3LYP electronic energy: -3540.90248539 a.u.
 B3LYP enthalpy: -3540.491807 a.u.
 B3LYP free energy: -3540.572650 a.u.
 M06 SCF energy in solution: -3544.83794279 a.u.
 M06 enthalpy in solution: -3544.427264 a.u.
 M06 free energy in solution: -3544.508107 a.u.

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| Ni | -0.781376 | 0.618424 | 0.336570 |
| C | -0.678350 | -0.323329 | 2.131085 |
| C | 0.392609 | -1.416452 | 2.021380 |
| H | 0.835527 | -1.606660 | 3.013613 |
| C | 3.472232 | -0.820000 | -0.189137 |
| C | 2.360505 | 0.081809 | -0.878368 |
| O | 1.283052 | 0.016925 | 0.128567 |
| O | 2.711855 | -1.647895 | 0.751544 |
| B | 1.512613 | -1.053630 | 0.979398 |
| C | 4.472869 | -0.026516 | 0.659190 |
| H | 3.964864 | 0.626172 | 1.375886 |
| H | 5.092560 | -0.729560 | 1.224056 |
| H | 5.129161 | 0.589111 | 0.036168 |
| C | 4.215661 | -1.753131 | -1.142546 |
| H | 4.774688 | -1.179129 | -1.889664 |
| H | 4.929819 | -2.358835 | -0.576071 |
| H | 3.534655 | -2.430840 | -1.661760 |
| C | 2.733553 | 1.548006 | -1.078625 |
| H | 3.542939 | 1.637667 | -1.812149 |
| H | 1.862071 | 2.096789 | -1.447270 |
| H | 3.053724 | 2.020613 | -0.147679 |
| C | 1.790940 | -0.500227 | -2.174002 |
| H | 0.920935 | 0.088456 | -2.479561 |
| H | 2.532539 | -0.458200 | -2.977972 |
| H | 1.472581 | -1.539353 | -2.051227 |
| C | -1.911242 | -0.813474 | -0.265669 |
| C | -3.273793 | -0.509882 | -0.377949 |
| C | -1.436561 | -2.029426 | -0.762401 |
| C | -4.145755 | -1.410720 | -0.997242 |
| H | -3.661642 | 0.435355 | -0.006621 |
| C | -2.310848 | -2.929081 | -1.384934 |
| H | -0.385573 | -2.294071 | -0.683394 |
| C | -3.666851 | -2.622651 | -1.500586 |
| H | -5.199787 | -1.159551 | -1.088939 |
| H | -1.927431 | -3.868926 | -1.775623 |
| H | -4.346660 | -3.322204 | -1.979780 |
| Br | -1.027437 | 2.741381 | -0.681665 |
| H | -0.073737 | -2.365555 | 1.726131 |
| C | -0.161554 | 0.951366 | 2.811990 |
| H | -0.930194 | 1.729310 | 2.871520 |
| H | 0.132258 | 0.702720 | 3.845897 |
| H | 0.721851 | 1.382157 | 2.326356 |
| C | -1.976574 | -0.793785 | 2.764284 |
| H | -2.755931 | -0.025240 | 2.712904 |
| H | -2.360533 | -1.700497 | 2.291950 |
| H | -1.803206 | -1.013064 | 3.830827 |

INT-5

B3LYP electronic energy: -3540.96195650 a.u.

B3LYP enthalpy: -3540.548779 a.u.

B3LYP free energy: -3540.626108 a.u.
 M06 SCF energy in solution: -3544.90157188 a.u.
 M06 enthalpy in solution: -3544.488394 a.u.
 M06 free energy in solution: -3544.565723 a.u.

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| Ni | 0.724181 | -0.691669 | 0.299719 |
| C | 1.227488 | 2.453477 | -0.425223 |
| C | 0.028738 | 2.064449 | -1.342828 |
| H | -0.386738 | 2.979240 | -1.789818 |
| C | -2.416129 | 0.143830 | 0.913169 |
| C | -3.226869 | 0.305127 | -0.424577 |
| O | -2.443313 | 1.307985 | -1.148413 |
| O | -1.041860 | 0.484411 | 0.459688 |
| B | -1.166259 | 1.278575 | -0.681575 |
| C | -2.433222 | -1.252832 | 1.520154 |
| H | -1.998488 | -1.998831 | 0.852920 |
| H | -1.861852 | -1.262586 | 2.454610 |
| H | -3.465501 | -1.536366 | 1.757226 |
| C | -2.768323 | 1.194370 | 1.972819 |
| H | -3.753644 | 0.997436 | 2.407161 |
| H | -2.028527 | 1.153616 | 2.778536 |
| H | -2.770664 | 2.207549 | 1.558188 |
| C | -3.238864 | -0.962837 | -1.286053 |
| H | -3.895109 | -1.725663 | -0.854076 |
| H | -3.619136 | -0.707766 | -2.280296 |
| H | -2.239418 | -1.395468 | -1.394513 |
| C | -4.643845 | 0.848730 | -0.252918 |
| H | -5.117979 | 0.943106 | -1.234727 |
| H | -5.250653 | 0.164099 | 0.350334 |
| H | -4.650554 | 1.833378 | 0.220737 |
| Br | 0.302699 | -2.829885 | -0.559484 |
| H | 0.396801 | 1.474539 | -2.195452 |
| C | 2.036419 | 1.201120 | -0.003929 |
| C | 2.075056 | 0.722972 | 1.333409 |
| C | 2.909939 | 0.574624 | -0.932424 |
| C | 2.978323 | -0.296537 | 1.717584 |
| H | 1.488528 | 1.210475 | 2.103728 |
| C | 3.801804 | -0.418996 | -0.544413 |
| H | 2.896603 | 0.887432 | -1.971193 |
| C | 3.846371 | -0.857059 | 0.787558 |
| H | 2.991504 | -0.626805 | 2.752096 |
| H | 4.454341 | -0.870411 | -1.285822 |
| H | 4.534932 | -1.642228 | 1.083627 |
| C | 2.159323 | 3.412429 | -1.208807 |
| H | 3.051326 | 3.665070 | -0.624011 |
| H | 2.488308 | 2.988567 | -2.162385 |
| H | 1.626456 | 4.343587 | -1.433445 |
| C | 0.704421 | 3.239686 | 0.796198 |
| H | 1.526928 | 3.575870 | 1.438142 |
| H | 0.169339 | 4.131907 | 0.450962 |
| H | 0.010539 | 2.655621 | 1.406656 |

INT-6

B3LYP electronic energy: -3828.80804766 a.u.
B3LYP enthalpy: -3828.252383 a.u.
B3LYP free energy: -3828.355790 a.u.
M06 SCF energy in solution: -3832.63835075 a.u.
M06 enthalpy in solution: -3832.082686 a.u.
M06 free energy in solution: -3832.186093 a.u.

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| Ni | 1.140632 | -0.045309 | 0.107106 |
| C | -2.962783 | -1.322045 | 1.540072 |
| C | -1.771143 | -0.362188 | 1.877427 |
| H | -1.881972 | -0.037411 | 2.923787 |
| C | -2.170023 | 2.769389 | -0.283101 |
| C | -0.606301 | 2.590052 | -0.284700 |
| O | -0.478200 | 1.213183 | 0.246998 |
| O | -2.593193 | 1.872001 | 0.786400 |
| B | -1.639186 | 0.912645 | 0.965654 |
| C | -2.847391 | 2.275854 | -1.567911 |
| H | -2.540037 | 1.257614 | -1.823003 |
| H | -3.930928 | 2.267866 | -1.415173 |
| H | -2.624982 | 2.933951 | -2.414253 |
| C | -2.651603 | 4.178265 | 0.058511 |
| H | -2.308524 | 4.899196 | -0.692267 |
| H | -3.745960 | 4.195712 | 0.068186 |
| H | -2.300419 | 4.502745 | 1.040567 |
| C | 0.055545 | 2.647994 | -1.657167 |
| H | -0.096276 | 3.636298 | -2.106930 |
| H | 1.130454 | 2.480572 | -1.550151 |
| H | -0.348089 | 1.891794 | -2.334348 |
| C | 0.124642 | 3.500672 | 0.706829 |
| H | 1.162330 | 3.168085 | 0.789603 |
| H | 0.114748 | 4.540571 | 0.363751 |
| H | -0.335444 | 3.460287 | 1.699635 |
| Br | 2.124214 | -2.184079 | 0.068013 |
| C | -2.944156 | -1.654738 | 0.035239 |
| C | -4.044719 | -1.433072 | -0.806079 |
| C | -1.784558 | -2.203800 | -0.543505 |
| C | -3.991345 | -1.743773 | -2.168804 |
| H | -4.960061 | -1.010973 | -0.405791 |
| C | -1.725403 | -2.509947 | -1.903056 |
| H | -0.902687 | -2.398108 | 0.060492 |
| C | -2.831606 | -2.281921 | -2.725246 |
| H | -4.863334 | -1.562381 | -2.792753 |
| H | -0.807996 | -2.926229 | -2.310342 |
| H | -2.789925 | -2.523322 | -3.784294 |
| H | -0.827358 | -0.921570 | 1.841672 |
| C | -4.282555 | -0.660838 | 1.981794 |
| H | -5.139002 | -1.322220 | 1.807085 |
| H | -4.245711 | -0.451751 | 3.057297 |
| H | -4.461792 | 0.286844 | 1.465703 |
| C | -2.787879 | -2.628649 | 2.350147 |
| H | -2.772506 | -2.412497 | 3.425745 |

| | | | |
|---|-----------|-----------|-----------|
| H | -3.614852 | -3.321165 | 2.153675 |
| H | -1.853689 | -3.139902 | 2.096335 |
| C | 3.773511 | 0.853922 | 0.467626 |
| C | 4.101130 | 0.726087 | 1.940803 |
| H | 5.104316 | 1.088780 | 2.186659 |
| H | 3.363048 | 1.303918 | 2.498050 |
| H | 4.022657 | -0.324532 | 2.242572 |
| C | 4.269366 | 0.400931 | -1.857252 |
| H | 5.173754 | 0.463504 | -2.469368 |
| H | 3.720003 | -0.517649 | -2.096257 |
| H | 3.629465 | 1.259137 | -2.055009 |
| C | 5.767676 | -0.483041 | -0.104680 |
| H | 6.132799 | -0.284521 | 0.902099 |
| H | 5.449571 | -1.531442 | -0.168455 |
| H | 6.588311 | -0.312246 | -0.807942 |
| N | 4.654749 | 0.399636 | -0.445312 |
| O | 2.689536 | 1.384422 | 0.113005 |

INT-7

B3LYP electronic energy: -1490.41514137 a.u.
 B3LYP enthalpy: -1489.729488 a.u.
 B3LYP free energy: -1489.845487 a.u.
 M06 SCF energy in solution: -1491.54284419 a.u.
 M06 enthalpy in solution: -1490.857191 a.u.
 M06 free energy in solution: -1490.973190 a.u.

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| Ni | -1.217747 | 0.493842 | -0.364151 |
| O | -2.749812 | -0.786528 | 0.095137 |
| C | 2.360593 | -0.314206 | 2.431255 |
| C | 1.008088 | -0.822059 | 1.838098 |
| H | 0.587317 | -1.565194 | 2.534071 |
| C | 1.823083 | -2.494898 | -1.500667 |
| C | 0.338256 | -2.023633 | -1.732743 |
| O | 0.142717 | -1.117545 | -0.589786 |
| O | 1.971834 | -2.370051 | -0.054848 |
| B | 1.067720 | -1.449097 | 0.397156 |
| C | 2.866674 | -1.563196 | -2.130668 |
| H | 2.691644 | -0.518559 | -1.857033 |
| H | 3.857487 | -1.841557 | -1.759720 |
| H | 2.870559 | -1.645791 | -3.222635 |
| C | 2.103888 | -3.945414 | -1.888175 |
| H | 1.943730 | -4.098984 | -2.961489 |
| H | 3.147708 | -4.187297 | -1.664454 |
| H | 1.470182 | -4.643992 | -1.336793 |
| C | 0.094928 | -1.247627 | -3.023234 |
| H | 0.297443 | -1.883527 | -3.893164 |
| H | -0.950799 | -0.927292 | -3.069782 |
| H | 0.722015 | -0.356386 | -3.085849 |
| C | -0.699004 | -3.140908 | -1.576990 |
| H | -1.692711 | -2.687371 | -1.528514 |
| H | -0.667953 | -3.834115 | -2.424153 |

| | | | |
|---|-----------|-----------|-----------|
| H | -0.537234 | -3.709351 | -0.655451 |
| C | 3.092666 | 0.573939 | 1.405490 |
| C | 4.459798 | 0.424975 | 1.125566 |
| C | 2.398608 | 1.598230 | 0.732650 |
| C | 5.112601 | 1.259068 | 0.213949 |
| H | 5.033951 | -0.353359 | 1.616201 |
| C | 3.049950 | 2.432007 | -0.178375 |
| H | 1.336478 | 1.761488 | 0.898570 |
| C | 4.411117 | 2.268445 | -0.443839 |
| H | 6.172914 | 1.114268 | 0.020536 |
| H | 2.483531 | 3.213206 | -0.678224 |
| H | 4.916580 | 2.919472 | -1.152569 |
| O | -1.184711 | 2.329057 | -0.121680 |
| C | -1.391760 | 3.365519 | -1.042259 |
| C | -2.891824 | 3.487379 | -1.391704 |
| H | -3.090094 | 4.306531 | -2.095969 |
| H | -3.246633 | 2.551989 | -1.843043 |
| H | -3.477356 | 3.671919 | -0.482655 |
| C | -0.916092 | 4.679740 | -0.384212 |
| H | 0.146641 | 4.604740 | -0.125532 |
| H | -1.052857 | 5.549656 | -1.040347 |
| H | -1.473243 | 4.853876 | 0.543661 |
| C | -0.592306 | 3.127245 | -2.341558 |
| H | -0.700750 | 3.951801 | -3.059485 |
| H | 0.472563 | 3.010738 | -2.108017 |
| H | -0.935597 | 2.202172 | -2.821868 |
| H | 0.277109 | -0.003419 | 1.813580 |
| C | 3.202002 | -1.532009 | 2.862040 |
| H | 4.123978 | -1.228695 | 3.370753 |
| H | 2.628241 | -2.141258 | 3.570520 |
| H | 3.465342 | -2.165199 | 2.009469 |
| C | 2.057967 | 0.535543 | 3.689562 |
| H | 1.513617 | -0.059665 | 4.434186 |
| H | 2.985362 | 0.893608 | 4.152034 |
| H | 1.447056 | 1.410024 | 3.441144 |
| C | -3.715546 | -0.477481 | 0.826407 |
| C | -3.831789 | 0.906521 | 1.433708 |
| H | -4.786172 | 1.377555 | 1.173884 |
| H | -3.765482 | 0.858357 | 2.527398 |
| H | -3.015585 | 1.530403 | 1.054222 |
| C | -4.615616 | -2.732250 | 0.512251 |
| H | -5.464896 | -2.897156 | -0.163455 |
| H | -3.685785 | -2.830921 | -0.043001 |
| H | -4.651853 | -3.489359 | 1.305352 |
| C | -5.857671 | -1.145571 | 1.916632 |
| H | -5.808397 | -0.166405 | 2.387742 |
| H | -6.771958 | -1.197540 | 1.310032 |
| H | -5.929743 | -1.905204 | 2.705264 |
| N | -4.682847 | -1.397417 | 1.095051 |

INT-9

B3LYP electronic energy: -1512.77838719 a.u.

B3LYP enthalpy: -1512.114013 a.u.

B3LYP free energy: -1512.228939 a.u.
M06 SCF energy in solution: -1513.95361132 a.u.
M06 enthalpy in solution: -1513.289237 a.u.
M06 free energy in solution: -1513.404163 a.u.

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| Ni | 0.683378 | -0.469011 | -0.659208 |
| O | 2.423255 | -0.621784 | 0.433504 |
| C | 0.396112 | 3.951874 | -0.330135 |
| C | 1.428691 | 2.763128 | -0.305904 |
| O | 0.528435 | 1.607375 | -0.161585 |
| O | -0.733165 | 3.412108 | 0.423162 |
| B | -0.676976 | 2.048505 | 0.376075 |
| C | -0.134487 | 4.274371 | -1.733138 |
| H | -0.484311 | 3.372402 | -2.244634 |
| H | -0.982244 | 4.959992 | -1.641036 |
| H | 0.631140 | 4.752443 | -2.353166 |
| C | 0.865228 | 5.228950 | 0.363958 |
| H | 1.743249 | 5.648210 | -0.140894 |
| H | 0.066036 | 5.976039 | 0.329663 |
| H | 1.116339 | 5.051765 | 1.412028 |
| C | 2.252131 | 2.578586 | -1.576773 |
| H | 2.891965 | 3.452002 | -1.749929 |
| H | 2.893289 | 1.698192 | -1.470662 |
| H | 1.618012 | 2.428680 | -2.452993 |
| C | 2.338570 | 2.760603 | 0.927849 |
| H | 2.857052 | 1.799844 | 0.975918 |
| H | 3.082051 | 3.563251 | 0.874004 |
| H | 1.760340 | 2.883910 | 1.849186 |
| O | -0.418470 | -1.704556 | -1.486575 |
| C | -0.260171 | -2.237591 | -2.775525 |
| C | -1.267541 | -3.397945 | -2.938065 |
| H | -1.193585 | -3.876632 | -3.923505 |
| H | -1.085205 | -4.158753 | -2.169771 |
| H | -2.291869 | -3.029706 | -2.811578 |
| C | -0.547282 | -1.157676 | -3.841215 |
| H | 0.171452 | -0.335422 | -3.733637 |
| H | -0.477364 | -1.548652 | -4.865558 |
| H | -1.553523 | -0.747809 | -3.695229 |
| C | 1.169780 | -2.785103 | -2.978485 |
| H | 1.304497 | -3.245126 | -3.967190 |
| H | 1.899231 | -1.972048 | -2.871784 |
| H | 1.390321 | -3.540260 | -2.213728 |
| C | -3.798510 | -0.305064 | 0.631765 |
| C | -2.877875 | -0.913464 | 1.767726 |
| B | -1.882326 | 0.932720 | 0.823844 |
| O | -1.633227 | -0.162050 | 1.615544 |
| O | -3.168650 | 0.986039 | 0.363170 |
| C | -3.377190 | -0.635103 | 3.190956 |
| H | -4.288254 | -1.199863 | 3.416490 |
| H | -2.603135 | -0.934145 | 3.905215 |
| H | -3.582386 | 0.429322 | 3.343127 |
| C | -2.548376 | -2.396279 | 1.591124 |
| H | -1.921626 | -2.734942 | 2.424104 |

| | | | |
|---|-----------|-----------|-----------|
| H | -3.461760 | -3.002590 | 1.593689 |
| H | -2.004978 | -2.565879 | 0.658113 |
| C | -3.751342 | -1.088048 | -0.686222 |
| H | -4.261664 | -2.053579 | -0.592728 |
| H | -4.269264 | -0.504632 | -1.455224 |
| H | -2.721252 | -1.262218 | -1.016648 |
| C | -5.247722 | -0.044651 | 1.043048 |
| H | -5.784355 | 0.413747 | 0.206276 |
| H | -5.755548 | -0.982544 | 1.296528 |
| H | -5.317127 | 0.632073 | 1.898369 |
| C | 2.634549 | -1.472420 | 1.323070 |
| C | 1.486505 | -2.075118 | 2.107241 |
| H | 0.575744 | -1.529610 | 1.854443 |
| H | 1.342930 | -3.128470 | 1.838831 |
| H | 1.651815 | -2.015011 | 3.188141 |
| C | 5.026989 | -1.310017 | 0.851377 |
| H | 4.641170 | -0.653083 | 0.074824 |
| H | 5.683591 | -0.741289 | 1.522727 |
| H | 5.612879 | -2.115472 | 0.392585 |
| C | 4.266699 | -2.847833 | 2.614234 |
| H | 4.894970 | -3.630006 | 2.170640 |
| H | 4.836840 | -2.371627 | 3.423610 |
| H | 3.384350 | -3.321406 | 3.039656 |
| N | 3.905450 | -1.874168 | 1.594413 |

INT-11

B3LYP electronic energy: -1025.64785641 a.u.
 B3LYP enthalpy: -1025.195186 a.u.
 B3LYP free energy: -1025.281553 a.u.
 M06 SCF energy in solution: -1026.98128770 a.u.
 M06 enthalpy in solution: -1026.528617 a.u.
 M06 free energy in solution: -1026.614984 a.u.

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| Ni | -0.842297 | 1.001714 | 0.066897 |
| C | 0.374259 | 2.525444 | 0.352806 |
| C | 1.773739 | 2.200488 | -0.251985 |
| H | 0.025608 | 3.494876 | -0.039646 |
| C | 1.537145 | -1.593056 | -0.018263 |
| C | 3.061817 | -1.370567 | 0.327946 |
| O | 3.272118 | 0.022157 | -0.033117 |
| O | 1.012570 | -0.241410 | 0.115562 |
| B | 2.059204 | 0.667254 | -0.038771 |
| C | 0.769479 | -2.505534 | 0.936089 |
| H | 0.829108 | -2.153724 | 1.968472 |
| H | -0.285708 | -2.519544 | 0.646189 |
| H | 1.155812 | -3.530636 | 0.891739 |
| C | 1.289039 | -2.020606 | -1.471065 |
| H | 1.606586 | -3.054116 | -1.646966 |
| H | 0.217529 | -1.942141 | -1.679308 |
| H | 1.818243 | -1.369930 | -2.174283 |
| C | 3.368770 | -1.487540 | 1.827354 |

| | | | |
|---|-----------|-----------|-----------|
| H | 3.298436 | -2.523494 | 2.176187 |
| H | 4.387368 | -1.130360 | 2.007686 |
| H | 2.685685 | -0.872129 | 2.421337 |
| C | 4.037927 | -2.229296 | -0.475301 |
| H | 5.064804 | -1.980544 | -0.188671 |
| H | 3.878474 | -3.295382 | -0.275214 |
| H | 3.937927 | -2.056519 | -1.549276 |
| O | -2.137627 | -0.496140 | -0.289346 |
| C | -3.345480 | -0.796290 | -0.317092 |
| N | -4.311181 | -0.067687 | 0.301868 |
| C | -3.752078 | -2.047044 | -1.079704 |
| H | -4.316401 | -2.749299 | -0.457073 |
| H | -4.364040 | -1.802284 | -1.955584 |
| H | -2.837635 | -2.530944 | -1.422965 |
| C | -5.737268 | -0.354257 | 0.207931 |
| H | -6.267287 | 0.521675 | -0.187074 |
| H | -5.934739 | -1.197751 | -0.450236 |
| H | -6.147364 | -0.580362 | 1.200765 |
| C | -3.989947 | 1.113208 | 1.100233 |
| H | -2.912613 | 1.172588 | 1.275393 |
| H | -4.314910 | 2.026911 | 0.587019 |
| H | -4.508827 | 1.047480 | 2.064136 |
| H | 0.480717 | 2.665469 | 1.442694 |
| C | 1.737738 | 2.434035 | -1.785934 |
| H | 1.515075 | 3.490448 | -1.992647 |
| H | 2.695444 | 2.194225 | -2.267524 |
| H | 0.948175 | 1.837727 | -2.259747 |
| C | 2.893191 | 3.081727 | 0.348455 |
| H | 3.881394 | 2.844925 | -0.069596 |
| H | 2.687140 | 4.142943 | 0.151163 |
| H | 2.956116 | 2.958311 | 1.437060 |

TS1

B3LYP electronic energy: -1025.60945352 a.u.
 B3LYP enthalpy: -1025.159082 a.u.
 B3LYP free energy: -1025.244000 a.u.
 M06 SCF energy in solution: -1026.94945831 a.u.
 M06 enthalpy in solution: -1026.499087 a.u.
 M06 free energy in solution: -1026.584005 a.u.
 Imaginary frequency: -193.3364 cm⁻¹

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| Ni | 0.656495 | 1.071547 | -0.246318 |
| C | -3.050459 | -0.828926 | -0.745583 |
| C | -2.517945 | -1.348936 | 0.643904 |
| B | -1.179479 | 0.375715 | -0.124919 |
| O | -1.591142 | -0.305407 | 1.032416 |
| O | -1.945747 | -0.020366 | -1.219091 |
| C | -3.578148 | -1.485298 | 1.737983 |
| H | -4.335912 | -2.229160 | 1.463598 |
| H | -3.104303 | -1.813634 | 2.669318 |
| H | -4.078253 | -0.534076 | 1.934284 |

| | | | |
|---|-----------|-----------|-----------|
| C | -1.717599 | -2.656273 | 0.532143 |
| H | -1.225923 | -2.854198 | 1.490625 |
| H | -2.361472 | -3.510821 | 0.296303 |
| H | -0.944692 | -2.579186 | -0.239107 |
| C | -4.266063 | 0.102489 | -0.620566 |
| H | -4.450416 | 0.573627 | -1.591329 |
| H | -5.170273 | -0.440873 | -0.324124 |
| H | -4.085256 | 0.898036 | 0.109315 |
| C | -3.336965 | -1.914890 | -1.783210 |
| H | -4.130469 | -2.590368 | -1.441119 |
| H | -3.669410 | -1.449129 | -2.716804 |
| H | -2.445212 | -2.506320 | -2.004395 |
| C | -0.924546 | 2.256649 | 0.023817 |
| C | 0.359012 | 2.958555 | 0.280061 |
| H | -1.442636 | 2.566730 | -0.887389 |
| H | -1.611901 | 2.246716 | 0.877720 |
| O | 2.109513 | -0.118707 | -0.566770 |
| C | 2.656923 | -0.979158 | 0.163102 |
| N | 3.818730 | -1.552952 | -0.240065 |
| C | 4.566091 | -2.531163 | 0.537372 |
| H | 4.216662 | -2.568552 | 1.567741 |
| H | 4.482208 | -3.533851 | 0.096538 |
| H | 5.626008 | -2.251271 | 0.547958 |
| C | 4.395156 | -1.214433 | -1.538700 |
| H | 3.730073 | -0.525509 | -2.054875 |
| H | 5.377232 | -0.744304 | -1.405189 |
| H | 4.521936 | -2.124165 | -2.138279 |
| C | 2.038453 | -1.378358 | 1.484163 |
| H | 2.039719 | -2.461514 | 1.639187 |
| H | 2.577766 | -0.912481 | 2.318520 |
| H | 1.008861 | -1.013998 | 1.497178 |
| C | 0.681790 | 3.316862 | 1.717830 |
| H | 1.757175 | 3.494686 | 1.857654 |
| H | 0.164841 | 4.242083 | 2.039021 |
| H | 0.384264 | 2.523402 | 2.414259 |
| C | 0.798081 | 4.000380 | -0.730932 |
| H | 0.295394 | 4.973565 | -0.566489 |
| H | 1.878461 | 4.191764 | -0.669127 |
| H | 0.576276 | 3.692398 | -1.759797 |

TS2

B3LYP electronic energy: -3540.84983702 a.u.
 B3LYP enthalpy: -3540.441873 a.u.
 B3LYP free energy: -3540.521983 a.u.
 M06 SCF energy in solution: -3544.78815305 a.u.
 M06 enthalpy in solution: -3544.380189 a.u.
 M06 free energy in solution: -3544.460299 a.u.
 Imaginary frequency: -40.4446 cm⁻¹

Cartesian coordinates

| ATOM | X | Y | Z |
|------|----------|----------|-----------|
| Ni | 0.736483 | 0.275099 | -0.572651 |
| C | 0.341366 | 2.229988 | -0.674749 |

| | | | |
|----|-----------|-----------|-----------|
| C | -1.130613 | 2.332923 | -1.162021 |
| H | -1.548094 | 3.348709 | -1.026717 |
| C | -3.743016 | 0.105787 | 0.529382 |
| C | -2.563491 | -0.895435 | 0.216892 |
| O | -1.475914 | 0.030857 | -0.096867 |
| O | -3.384209 | 1.276856 | -0.255784 |
| B | -2.036170 | 1.246860 | -0.496587 |
| C | -3.786162 | 0.557015 | 1.996081 |
| H | -2.805504 | 0.906107 | 2.334798 |
| H | -4.489040 | 1.390658 | 2.087737 |
| H | -4.118490 | -0.248726 | 2.659252 |
| C | -5.125901 | -0.367764 | 0.084775 |
| H | -5.415050 | -1.283520 | 0.613335 |
| H | -5.866924 | 0.404277 | 0.314963 |
| H | -5.161970 | -0.557749 | -0.990216 |
| C | -2.134978 | -1.781821 | 1.383461 |
| H | -2.959004 | -2.433463 | 1.695777 |
| H | -1.298682 | -2.417554 | 1.075369 |
| H | -1.814944 | -1.190063 | 2.244342 |
| C | -2.796164 | -1.744440 | -1.039127 |
| H | -1.862864 | -2.250818 | -1.303632 |
| H | -3.566061 | -2.505172 | -0.872519 |
| H | -3.098604 | -1.124677 | -1.889095 |
| C | 2.324535 | -0.728441 | 0.261076 |
| C | 2.183548 | -0.706616 | 1.661184 |
| C | 3.367876 | -0.039213 | -0.385915 |
| C | 3.038356 | 0.107098 | 2.401120 |
| H | 1.414337 | -1.300083 | 2.141996 |
| C | 4.208337 | 0.769013 | 0.384939 |
| H | 3.512685 | -0.138773 | -1.455655 |
| C | 4.048016 | 0.844438 | 1.769801 |
| H | 2.919833 | 0.158575 | 3.479978 |
| H | 5.000562 | 1.327399 | -0.105798 |
| H | 4.714716 | 1.465673 | 2.360277 |
| Br | 1.440184 | -2.224104 | -0.761568 |
| H | -1.168005 | 2.148381 | -2.249950 |
| C | 0.445240 | 2.841366 | 0.730643 |
| H | 1.466213 | 2.774438 | 1.127415 |
| H | 0.163900 | 3.912959 | 0.731835 |
| H | -0.215539 | 2.339684 | 1.452504 |
| C | 1.269817 | 2.994478 | -1.625036 |
| H | 1.012804 | 4.070497 | -1.675169 |
| H | 2.318185 | 2.932928 | -1.301560 |
| H | 1.218814 | 2.604926 | -2.651075 |

TS3

B3LYP electronic energy: -3540.89384006 a.u.
 B3LYP enthalpy: -3540.483647 a.u.
 B3LYP free energy: -3540.561067 a.u.
 M06 SCF energy in solution: -3544.83476811 a.u.
 M06 enthalpy in solution: -3544.424575 a.u.
 M06 free energy in solution: -3544.501995 a.u.
 Imaginary frequency: -203.9359 cm⁻¹

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| Ni | 0.736356 | 0.647878 | 0.343689 |
| C | 0.992225 | -0.998316 | 1.773613 |
| C | -0.198326 | -1.941482 | 1.534618 |
| H | 0.139730 | -2.863305 | 1.044588 |
| C | -2.429497 | 0.239305 | -0.665487 |
| C | -3.425659 | -0.924132 | -0.253408 |
| O | -2.546067 | -1.932111 | 0.344208 |
| O | -1.293206 | -0.028202 | 0.242281 |
| B | -1.385477 | -1.326937 | 0.708106 |
| C | -2.928165 | 1.656087 | -0.398606 |
| H | -3.224753 | 1.795866 | 0.643196 |
| H | -2.126916 | 2.367554 | -0.617867 |
| H | -3.788102 | 1.881030 | -1.040014 |
| C | -1.883917 | 0.129597 | -2.091443 |
| H | -2.666871 | 0.343491 | -2.825909 |
| H | -1.081751 | 0.862213 | -2.221025 |
| H | -1.477493 | -0.865177 | -2.298689 |
| C | -4.422282 | -0.525629 | 0.841701 |
| H | -5.160010 | 0.192994 | 0.471215 |
| H | -4.952182 | -1.420940 | 1.181075 |
| H | -3.916045 | -0.084994 | 1.706306 |
| C | -4.162132 | -1.576554 | -1.421321 |
| H | -4.785134 | -2.394791 | -1.046878 |
| H | -4.816124 | -0.853335 | -1.920895 |
| H | -3.470212 | -1.988435 | -2.159181 |
| C | 1.908019 | -0.779107 | -0.193137 |
| C | 1.510264 | -1.761619 | -1.109946 |
| C | 3.248272 | -0.352656 | -0.190653 |
| C | 2.425795 | -2.280866 | -2.031113 |
| H | 0.485952 | -2.121619 | -1.132665 |
| C | 4.154650 | -0.865595 | -1.118985 |
| H | 3.584367 | 0.397111 | 0.521711 |
| C | 3.748248 | -1.836046 | -2.039219 |
| H | 2.098663 | -3.032797 | -2.745181 |
| H | 5.181095 | -0.507707 | -1.119740 |
| H | 4.458115 | -2.243483 | -2.753678 |
| Br | 0.727859 | 2.933814 | -0.203312 |
| H | -0.577757 | -2.271908 | 2.516428 |
| C | 2.209282 | -1.766498 | 2.292099 |
| H | 2.504802 | -2.582856 | 1.628981 |
| H | 3.075390 | -1.114597 | 2.440636 |
| H | 1.951402 | -2.199339 | 3.271086 |
| C | 0.653492 | 0.101467 | 2.806764 |
| H | -0.254285 | 0.671150 | 2.580939 |
| H | 0.487208 | -0.390511 | 3.779954 |
| H | 1.477847 | 0.809752 | 2.942937 |

TS4

B3LYP electronic energy: -1512.76933787 a.u.

B3LYP enthalpy: -1512.106511 a.u.

B3LYP free energy: -1512.216034 a.u.
 M06 SCF energy in solution: -1513.95446621 a.u.
 M06 enthalpy in solution: -1513.291639 a.u.
 M06 free energy in solution: -1513.401162 a.u.
 Imaginary frequency: -100.4866 cm⁻¹

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| Ni | 0.794954 | -0.810135 | 0.607908 |
| O | -0.969626 | -1.670985 | 1.046877 |
| C | -1.547278 | -1.796656 | 2.374790 |
| C | -1.732607 | -0.435168 | 3.057660 |
| H | -2.115133 | -0.583141 | 4.075407 |
| H | -0.786147 | 0.109144 | 3.114161 |
| H | -2.441045 | 0.183814 | 2.502963 |
| C | -2.892634 | -2.522882 | 2.239637 |
| H | -2.758898 | -3.487995 | 1.738607 |
| H | -3.331712 | -2.705116 | 3.228111 |
| H | -3.591203 | -1.916314 | 1.657981 |
| C | -0.553432 | -2.660656 | 3.161863 |
| H | -0.929902 | -2.867923 | 4.170168 |
| H | -0.386410 | -3.614620 | 2.649352 |
| H | 0.410153 | -2.144874 | 3.256322 |
| C | -3.206607 | -0.076292 | -1.224905 |
| C | -2.435634 | -1.235702 | -1.975112 |
| O | -2.572185 | -0.046347 | 0.072013 |
| O | -1.148880 | -1.217015 | -1.338012 |
| B | -1.314299 | -0.702376 | -0.015801 |
| C | -4.702828 | -0.328301 | -1.015219 |
| H | -5.138019 | 0.501649 | -0.447866 |
| H | -5.228973 | -0.393451 | -1.975462 |
| H | -4.886116 | -1.249591 | -0.457261 |
| C | -3.012944 | 1.294452 | -1.886864 |
| H | -3.536278 | 1.359548 | -2.847735 |
| H | -3.420768 | 2.065764 | -1.224919 |
| H | -1.953278 | 1.505633 | -2.045593 |
| C | -3.060450 | -2.625973 | -1.758041 |
| H | -4.018819 | -2.734299 | -2.279843 |
| H | -2.370614 | -3.382359 | -2.147114 |
| H | -3.215788 | -2.833022 | -0.696173 |
| C | -2.234920 | -1.006137 | -3.476026 |
| H | -1.671984 | -1.845116 | -3.900162 |
| H | -3.195075 | -0.944737 | -4.002952 |
| H | -1.669645 | -0.091208 | -3.667631 |
| C | 0.520418 | 3.163397 | 1.148869 |
| C | 0.522518 | 3.246633 | -0.425595 |
| B | 0.055479 | 1.068260 | 0.273293 |
| O | -0.098055 | 1.878631 | 1.396197 |
| O | 0.460728 | 1.844712 | -0.815771 |
| C | -0.297588 | 4.242154 | 1.861328 |
| H | -1.343784 | 4.228605 | 1.548015 |
| H | -0.269636 | 4.064166 | 2.941427 |
| H | 0.112801 | 5.241606 | 1.672403 |
| C | 1.929780 | 3.099472 | 1.761612 |
| H | 2.463230 | 4.052034 | 1.665251 |

| | | | |
|---|-----------|-----------|-----------|
| H | 1.840356 | 2.861406 | 2.826356 |
| H | 2.527892 | 2.311222 | 1.293584 |
| C | 1.783437 | 3.854612 | -1.044283 |
| H | 1.702732 | 3.830808 | -2.136450 |
| H | 1.909119 | 4.900171 | -0.738528 |
| H | 2.681974 | 3.301151 | -0.760337 |
| C | -0.714049 | 3.949048 | -0.998871 |
| H | -0.737736 | 3.807314 | -2.084208 |
| H | -1.634920 | 3.532765 | -0.584696 |
| H | -0.693221 | 5.025617 | -0.794726 |
| O | 2.723838 | -1.066882 | 0.353462 |
| C | 3.400418 | -1.081998 | -0.702737 |
| C | 2.896885 | -0.398097 | -1.954862 |
| H | 3.677040 | 0.187613 | -2.450331 |
| H | 2.518941 | -1.140839 | -2.667821 |
| H | 2.069845 | 0.261231 | -1.683567 |
| C | 5.444328 | -1.854867 | -1.895975 |
| H | 4.924469 | -1.535461 | -2.796894 |
| H | 6.365436 | -1.267175 | -1.788148 |
| H | 5.723185 | -2.908179 | -2.018193 |
| C | 5.114662 | -2.344452 | 0.495015 |
| H | 4.471669 | -2.086332 | 1.333646 |
| H | 5.138753 | -3.434851 | 0.376453 |
| H | 6.134371 | -1.991037 | 0.687488 |
| N | 4.599018 | -1.713099 | -0.717399 |

TS5

B3LYP electronic energy: -1025.60082674 a.u.
 B3LYP enthalpy: -1025.150227 a.u.
 B3LYP free energy: -1025.233455 a.u.
 M06 SCF energy in solution: -1026.94696894 a.u.
 M06 enthalpy in solution: -1026.496369 a.u.
 M06 free energy in solution: -1026.579597 a.u.
 Imaginary frequency: -253.7282 cm⁻¹

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| Ni | 0.542478 | 1.457304 | -0.166884 |
| C | -2.418985 | -1.425275 | -0.749395 |
| C | -1.700533 | -1.801953 | 0.602775 |
| B | -1.069691 | 0.325656 | -0.056365 |
| O | -1.185006 | -0.522358 | 1.052308 |
| O | -1.706871 | -0.230086 | -1.158930 |
| C | -2.612905 | -2.365514 | 1.693143 |
| H | -3.063814 | -3.314518 | 1.378937 |
| H | -2.027566 | -2.553411 | 2.599547 |
| H | -3.412772 | -1.667673 | 1.950423 |
| C | -0.494881 | -2.734626 | 0.404836 |
| H | 0.049105 | -2.819205 | 1.351668 |
| H | -0.803508 | -3.740386 | 0.099043 |
| H | 0.191154 | -2.336574 | -0.349595 |
| C | -3.895267 | -1.039134 | -0.572722 |
| H | -4.262308 | -0.608273 | -1.509601 |

| | | | |
|---|-----------|-----------|-----------|
| H | -4.516073 | -1.908535 | -0.328255 |
| H | -4.022626 | -0.289792 | 0.214040 |
| C | -2.294728 | -2.464388 | -1.865324 |
| H | -2.769889 | -3.410444 | -1.579002 |
| H | -2.795292 | -2.093832 | -2.765887 |
| H | -1.250542 | -2.659654 | -2.120236 |
| C | -1.311118 | 2.327831 | 0.203454 |
| C | -0.123878 | 3.206785 | 0.333131 |
| H | 0.131849 | 3.549730 | 1.337849 |
| H | 0.004504 | 3.977293 | -0.429805 |
| C | 2.863691 | -0.225329 | 0.211656 |
| O | 2.092665 | 0.384004 | -0.567624 |
| N | 4.072377 | -0.641651 | -0.239011 |
| C | 2.462408 | -0.481665 | 1.647231 |
| H | 2.763158 | -1.469630 | 2.006441 |
| H | 2.908713 | 0.276134 | 2.303808 |
| H | 1.376107 | -0.390541 | 1.713030 |
| C | 4.444913 | -0.438031 | -1.637248 |
| H | 5.285627 | 0.262921 | -1.707843 |
| H | 4.747968 | -1.393966 | -2.080978 |
| H | 3.591905 | -0.034709 | -2.178668 |
| C | 5.081204 | -1.294596 | 0.584411 |
| H | 6.053729 | -0.822418 | 0.403748 |
| H | 4.852052 | -1.197102 | 1.644038 |
| H | 5.166791 | -2.360527 | 0.333700 |
| C | -2.191906 | 2.682040 | -1.001883 |
| H | -1.598314 | 2.744316 | -1.919748 |
| H | -2.993404 | 1.958172 | -1.174422 |
| H | -2.648942 | 3.667314 | -0.828159 |
| C | -2.126143 | 2.220638 | 1.503305 |
| H | -2.563005 | 3.206768 | 1.717887 |
| H | -2.947163 | 1.496744 | 1.446449 |
| H | -1.492563 | 1.937393 | 2.348993 |

OtBu

B3LYP electronic energy: -233.03449815 a.u.
 B3LYP enthalpy: -232.906760 a.u.
 B3LYP free energy: -232.942987 a.u.
 M06 SCF energy in solution: -233.04883096 a.u.
 M06 enthalpy in solution: -232.921093 a.u.
 M06 free energy in solution: -232.957320 a.u.

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| C | -0.000084 | -0.000119 | 0.161428 |
| C | 1.388263 | -0.461979 | -0.437078 |
| H | 1.612460 | -1.470546 | -0.061061 |
| H | 1.454596 | -0.480326 | -1.541354 |
| H | 2.171851 | 0.208139 | -0.055279 |
| C | -1.094351 | -0.970438 | -0.438124 |
| H | -0.903810 | -1.985407 | -0.060930 |
| H | -2.078791 | -0.662451 | -0.057608 |
| H | -1.146683 | -1.014084 | -1.542452 |

| | | | |
|---|-----------|-----------|-----------|
| C | -0.293428 | 1.433400 | -0.436540 |
| H | -1.266842 | 1.776479 | -0.057596 |
| H | 0.466584 | 2.131432 | -0.057218 |
| H | -0.307083 | 1.500663 | -1.540796 |
| O | -0.000586 | -0.001135 | 1.484523 |

bromide

B3LYP electronic energy: -2571.46436594 a.u.
 B3LYP enthalpy: -2571.462005 a.u.
 B3LYP free energy: -2571.480541 a.u.
 M06 SCF energy in solution: -2574.17376114 a.u.
 M06 enthalpy in solution: -2574.171400 a.u.
 M06 free energy in solution: -2574.189936 a.u.

Cartesian coordinates

| ATOM | X | Y | Z |
|------|----------|----------|----------|
| Br | 0.000000 | 0.000000 | 0.000000 |

DMA

B3LYP electronic energy: -287.82491311 a.u.
 B3LYP enthalpy: -287.685266 a.u.
 B3LYP free energy: -287.725907 a.u.
 M06 SCF energy in solution: -287.72448965 a.u.
 M06 enthalpy in solution: -287.584843 a.u.
 M06 free energy in solution: -287.625484 a.u.

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| C | 0.729004 | -0.293398 | 0.000000 |
| O | 1.067339 | -1.472774 | 0.000000 |
| N | -0.596526 | 0.083738 | 0.000000 |
| C | 1.779160 | 0.813325 | 0.000000 |
| H | 1.703211 | 1.454074 | -0.886022 |
| H | 1.703211 | 1.454074 | 0.886023 |
| H | 2.755376 | 0.327529 | 0.000000 |
| C | -1.623870 | -0.946362 | 0.000000 |
| H | -2.261643 | -0.855981 | 0.889959 |
| H | -2.261642 | -0.855982 | -0.889959 |
| H | -1.132673 | -1.918350 | 0.000001 |
| C | -1.084035 | 1.450387 | 0.000000 |
| H | -1.704182 | 1.641176 | 0.887594 |
| H | -0.262060 | 2.164604 | 0.000001 |
| H | -1.704179 | 1.641177 | -0.887597 |

THF

B3LYP electronic energy: -232.44540031 a.u.
 B3LYP enthalpy: -232.321888 a.u.
 B3LYP free energy: -232.356978 a.u.
 M06 SCF energy in solution: -232.35427480 a.u.

M06 enthalpy in solution: -232.230762 a.u.
M06 free energy in solution: -232.265852 a.u.

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| C | -1.132151 | -0.471618 | 0.157142 |
| O | -0.000001 | -1.203935 | -0.294534 |
| C | 1.132149 | -0.471620 | 0.157144 |
| C | 0.777214 | 1.017453 | -0.050074 |
| C | -0.777212 | 1.017455 | -0.050071 |
| H | -1.999129 | -0.807869 | -0.418280 |
| H | -1.321030 | -0.680060 | 1.224248 |
| H | 1.321024 | -0.680059 | 1.224251 |
| H | 1.999129 | -0.807875 | -0.418274 |
| H | 1.199764 | 1.649505 | 0.737261 |
| H | 1.164226 | 1.379148 | -1.007523 |
| H | -1.199757 | 1.649504 | 0.737269 |
| H | -1.164227 | 1.379156 | -1.007517 |

bpin2bpin2

B3LYP electronic energy: -822.53218816 a.u.
B3LYP enthalpy: -822.145915 a.u.
B3LYP free energy: -822.213406 a.u.
M06 SCF energy in solution: -822.24211139 a.u.
M06 enthalpy in solution: -821.855838 a.u.
M06 free energy in solution: -821.923329 a.u.

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| C | -3.003651 | -0.654540 | 0.438656 |
| C | -3.004029 | 0.654464 | -0.438600 |
| O | -1.615048 | -0.735705 | 0.875237 |
| O | -1.615493 | 0.736363 | -0.875310 |
| B | -0.852169 | 0.000521 | -0.000096 |
| C | 3.003666 | -0.654629 | -0.438567 |
| C | 3.004028 | 0.654535 | 0.438549 |
| B | 0.852171 | 0.000524 | 0.000060 |
| O | 1.615487 | 0.736471 | 0.875195 |
| O | 1.615075 | -0.735854 | -0.875128 |
| C | 3.283259 | -1.931707 | 0.366342 |
| H | 3.069985 | -2.801419 | -0.262976 |
| H | 4.328805 | -1.986889 | 0.688326 |
| H | 2.642367 | -1.991850 | 1.251540 |
| C | 3.894673 | -0.611830 | -1.679242 |
| H | 4.949575 | -0.504171 | -1.400717 |
| H | 3.786124 | -1.546306 | -2.239134 |
| H | 3.623145 | 0.211519 | -2.343613 |
| C | 3.284157 | 1.931396 | -0.366499 |
| H | 3.071283 | 2.801283 | 0.262710 |
| H | 4.329717 | 1.986072 | -0.688525 |
| H | 2.643256 | 1.991680 | -1.251682 |
| C | 3.895110 | 0.611415 | 1.679165 |
| H | 4.949922 | 0.503058 | 1.400564 |

| | | | |
|---|-----------|-----------|-----------|
| H | 3.787190 | 1.546054 | 2.238902 |
| H | 3.623140 | -0.211643 | 2.343711 |
| C | -3.283185 | -1.931713 | -0.366116 |
| H | -3.070029 | -2.801325 | 0.263380 |
| H | -4.328690 | -1.986897 | -0.688241 |
| H | -2.642178 | -1.992013 | -1.251219 |
| C | -3.894724 | -0.611617 | 1.679294 |
| H | -4.949602 | -0.503953 | 1.400676 |
| H | -3.786236 | -1.546032 | 2.239294 |
| H | -3.623240 | 0.211801 | 2.343596 |
| C | -3.895170 | 0.611087 | -1.679167 |
| H | -4.949964 | 0.502839 | -1.400454 |
| H | -3.787238 | 1.545562 | -2.239168 |
| H | -3.623295 | -0.212180 | -2.343498 |
| C | -3.284141 | 1.931474 | 0.366229 |
| H | -3.071275 | 2.801232 | -0.263165 |
| H | -4.329690 | 1.986227 | 0.688275 |
| H | -2.643214 | 1.991927 | 1.251379 |

Bpin-OtBu

B3LYP electronic energy: -644.39580207 a.u.
 B3LYP enthalpy: -644.068260 a.u.
 B3LYP free energy: -644.127109 a.u.
 M06 SCF energy in solution: -644.16155714 a.u.
 M06 enthalpy in solution: -643.834015 a.u.
 M06 free energy in solution: -643.892864 a.u.

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| C | -1.982814 | -0.717024 | 0.054665 |
| C | -1.609398 | 0.813121 | -0.066619 |
| B | 0.275033 | -0.453146 | 0.176187 |
| O | -0.750094 | -1.299081 | 0.545089 |
| O | -0.178784 | 0.758282 | -0.319868 |
| C | -2.281717 | -1.373527 | -1.301019 |
| H | -2.321709 | -2.458862 | -1.166399 |
| H | -3.240490 | -1.040294 | -1.712596 |
| H | -1.495629 | -1.152747 | -2.030395 |
| C | -3.098882 | -1.036202 | 1.048406 |
| H | -4.039812 | -0.560519 | 0.748262 |
| H | -3.261730 | -2.118416 | 1.080277 |
| H | -2.845763 | -0.705532 | 2.058265 |
| C | -2.276534 | 1.559366 | -1.220667 |
| H | -3.365856 | 1.572637 | -1.099379 |
| H | -1.926315 | 2.596755 | -1.239483 |
| H | -2.038461 | 1.106189 | -2.185775 |
| C | -1.802535 | 1.587211 | 1.244817 |
| H | -1.335731 | 2.572805 | 1.149403 |
| H | -2.862910 | 1.730432 | 1.478348 |
| H | -1.330556 | 1.068234 | 2.085300 |
| O | 1.565764 | -0.836533 | 0.308677 |
| C | 2.732820 | -0.036287 | -0.004022 |
| C | 2.743360 | 1.229239 | 0.863964 |

| | | | |
|---|----------|-----------|-----------|
| H | 1.884158 | 1.865056 | 0.634365 |
| H | 2.707897 | 0.960561 | 1.925667 |
| H | 3.658894 | 1.805192 | 0.687595 |
| C | 3.921836 | -0.939086 | 0.342021 |
| H | 3.885167 | -1.860216 | -0.248910 |
| H | 4.869239 | -0.429333 | 0.135170 |
| H | 3.896913 | -1.212837 | 1.401958 |
| C | 2.733509 | 0.308295 | -1.499950 |
| H | 2.690365 | -0.608295 | -2.098830 |
| H | 1.875043 | 0.935047 | -1.756994 |
| H | 3.649163 | 0.847895 | -1.767542 |

phbr

B3LYP electronic energy: -2803.04746433 a.u.
 B3LYP enthalpy: -2802.949927 a.u.
 B3LYP free energy: -2802.987427 a.u.
 M06 SCF energy in solution: -2805.54169951 a.u.
 M06 enthalpy in solution: -2805.444162 a.u.
 M06 free energy in solution: -2805.481662 a.u.

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| C | -2.181312 | -1.207878 | 0.000001 |
| C | -0.784832 | -1.215984 | 0.000006 |
| C | -0.102781 | -0.000020 | -0.000019 |
| C | -0.784823 | 1.215976 | -0.000004 |
| C | -2.181277 | 1.207899 | 0.000011 |
| C | -2.881803 | 0.000006 | -0.000005 |
| H | -2.718776 | -2.152256 | 0.000004 |
| H | -0.233895 | -2.150197 | 0.000006 |
| H | -0.233832 | 2.150159 | -0.000005 |
| H | -2.718760 | 2.152267 | 0.000016 |
| H | -3.967997 | 0.000035 | -0.000010 |
| Br | 1.810692 | 0.000000 | 0.000001 |

phbr-4-OMe

B3LYP electronic energy: -2917.56814685 a.u.
 B3LYP enthalpy: -2917.435198 a.u.
 B3LYP free energy: -2917.478829 a.u.
 M06 SCF energy in solution: -2920.03577107 a.u.
 M06 enthalpy in solution: -2919.902822 a.u.
 M06 free energy in solution: -2919.946453 a.u.

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| C | -0.056201 | -1.101045 | 0.000000 |
| C | -1.450171 | -0.988906 | -0.000001 |
| C | -2.048366 | 0.276934 | 0.000000 |
| C | -1.240497 | 1.424803 | 0.000000 |
| C | 0.144332 | 1.311782 | 0.000000 |
| C | 0.731868 | 0.044086 | 0.000000 |

| | | | |
|----|-----------|-----------|-----------|
| H | 0.406727 | -2.081849 | 0.000000 |
| H | -2.048823 | -1.892414 | -0.000001 |
| H | -1.720526 | 2.398255 | 0.000000 |
| H | 0.765499 | 2.200738 | 0.000000 |
| Br | 2.638226 | -0.114417 | 0.000000 |
| O | -3.393303 | 0.500501 | 0.000000 |
| C | -4.261271 | -0.621681 | 0.000001 |
| H | -4.118965 | -1.241847 | 0.894989 |
| H | -5.274605 | -0.216284 | 0.000002 |
| H | -4.118966 | -1.241848 | -0.894987 |

phbr-4-Me

B3LYP electronic energy: -2842.36488353 a.u.
 B3LYP enthalpy: -2842.237926 a.u.
 B3LYP free energy: -2842.280721 a.u.
 M06 SCF energy in solution: -2844.83694754 a.u.
 M06 enthalpy in solution: -2844.709990 a.u.
 M06 free energy in solution: -2844.752785 a.u.

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| C | 0.346162 | 1.212006 | -0.004326 |
| C | 1.741466 | 1.200921 | -0.010302 |
| C | 2.463336 | 0.000000 | -0.010133 |
| C | 1.741466 | -1.200921 | -0.010302 |
| C | 0.346162 | -1.212006 | -0.004326 |
| C | -0.341105 | 0.000000 | -0.000408 |
| H | -0.199271 | 2.149565 | -0.006772 |
| H | 2.275993 | 2.148085 | -0.016956 |
| H | 2.275993 | -2.148085 | -0.016956 |
| H | -0.199271 | -2.149565 | -0.006772 |
| Br | -2.254452 | 0.000000 | 0.003139 |
| C | 3.974286 | 0.000000 | 0.015495 |
| H | 4.354271 | 0.000014 | 1.045960 |
| H | 4.383725 | -0.886004 | -0.481264 |
| H | 4.383725 | 0.885992 | -0.481287 |

phbr-4-F

B3LYP electronic energy: -2902.27896065 a.u.
 B3LYP enthalpy: -2902.188799 a.u.
 B3LYP free energy: -2902.228398 a.u.
 M06 SCF energy in solution: -2904.78156920 a.u.
 M06 enthalpy in solution: -2904.691408 a.u.
 M06 free energy in solution: -2904.731007 a.u.

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|----------|
| C | -0.383870 | -1.214903 | 0.000000 |
| C | -1.779238 | -1.215987 | 0.000000 |
| C | -2.453944 | 0.000000 | 0.000000 |
| C | -1.779237 | 1.215987 | 0.000000 |

| | | | |
|----|-----------|-----------|-----------|
| C | -0.383870 | 1.214903 | 0.000000 |
| C | 0.301754 | 0.000000 | 0.000000 |
| H | 0.163769 | -2.150739 | 0.000000 |
| H | -2.341810 | -2.143624 | 0.000000 |
| H | -2.341810 | 2.143623 | 0.000000 |
| H | 0.163770 | 2.150739 | 0.000000 |
| Br | 2.212671 | 0.000000 | 0.000000 |
| F | -3.801887 | 0.000001 | -0.000001 |

phbr-4-Cl

B3LYP electronic energy: -3262.63884661 a.u.
 B3LYP enthalpy: -3262.549762 a.u.
 B3LYP free energy: -3262.590678 a.u.
 M06 SCF energy in solution: -3265.13569420 a.u.
 M06 enthalpy in solution: -3265.046610 a.u.
 M06 free energy in solution: -3265.087526 a.u.

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| C | 0.025116 | -1.213681 | -0.000001 |
| C | -1.370204 | -1.214312 | -0.000001 |
| C | -2.056497 | -0.000001 | -0.000001 |
| C | -1.370203 | 1.214312 | -0.000001 |
| C | 0.025116 | 1.213680 | 0.000000 |
| C | 0.711443 | -0.000001 | -0.000002 |
| H | 0.570872 | -2.150724 | 0.000000 |
| H | -1.917626 | -2.150785 | 0.000000 |
| H | -1.917627 | 2.150784 | 0.000000 |
| H | 0.570874 | 2.150722 | 0.000000 |
| Br | 2.620427 | 0.000000 | 0.000000 |
| Cl | -3.812356 | 0.000001 | 0.000001 |

phbr-3-Cl

B3LYP electronic energy: -3262.63869691 a.u.
 B3LYP enthalpy: -3262.549649 a.u.
 B3LYP free energy: -3262.590571 a.u.
 M06 SCF energy in solution: -3265.13552328 a.u.
 M06 enthalpy in solution: -3265.046475 a.u.
 M06 free energy in solution: -3265.087397 a.u.

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|----------|
| C | 0.403791 | 1.667327 | 0.000000 |
| C | -0.894631 | 2.179398 | 0.000000 |
| C | -2.001284 | 1.329263 | 0.000000 |
| C | -1.788917 | -0.049195 | 0.000000 |
| C | -0.503627 | -0.591770 | 0.000000 |
| C | 0.580697 | 0.284465 | 0.000000 |
| H | 1.263292 | 2.327736 | 0.000000 |
| H | -1.045360 | 3.255097 | 0.000000 |
| H | -0.355045 | -1.664546 | 0.000000 |

| | | | |
|----|-----------|-----------|----------|
| Br | 2.349413 | -0.435557 | 0.000000 |
| Cl | -3.168088 | -1.136188 | 0.000000 |
| H | -3.011031 | 1.724468 | 0.000000 |

Ni-bpin-2THF

B3LYP electronic energy: -1045.47211417 a.u.
 B3LYP enthalpy: -1045.026959 a.u.
 B3LYP free energy: -1045.110806 a.u.
 M06 SCF energy in solution: -1046.80231277 a.u.
 M06 enthalpy in solution: -1046.357158 a.u.
 M06 free energy in solution: -1046.441005 a.u.

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| Ni | 0.882493 | 0.477404 | 0.061017 |
| O | 1.396153 | -1.704055 | 0.098537 |
| C | 0.795555 | -2.407710 | 1.217622 |
| C | 1.031431 | -2.357054 | -1.145066 |
| C | -0.225349 | -3.366292 | 0.605874 |
| H | 1.593312 | -2.938850 | 1.754797 |
| H | 0.347314 | -1.659235 | 1.875846 |
| C | 0.421213 | -3.702306 | -0.746971 |
| H | 0.304152 | -1.719649 | -1.659884 |
| H | 1.934752 | -2.443545 | -1.757436 |
| H | -1.168265 | -2.833921 | 0.453163 |
| H | -0.401456 | -4.245878 | 1.233181 |
| H | -0.296504 | -4.063976 | -1.489933 |
| H | 1.201839 | -4.464002 | -0.627896 |
| O | 2.940479 | 0.900721 | 0.026642 |
| C | 3.473967 | 2.102730 | -0.579368 |
| C | 3.994578 | 0.128377 | 0.643389 |
| C | 4.954702 | 2.141194 | -0.184087 |
| H | 3.338990 | 2.025044 | -1.664515 |
| H | 2.898049 | 2.958294 | -0.214982 |
| C | 5.283290 | 0.651534 | 0.011988 |
| H | 3.978649 | 0.305754 | 1.727661 |
| H | 3.779067 | -0.923796 | 0.451763 |
| H | 5.086782 | 2.685404 | 0.758242 |
| H | 5.573727 | 2.625998 | -0.944650 |
| H | 6.159238 | 0.482415 | 0.645542 |
| H | 5.460328 | 0.166083 | -0.955121 |
| C | -3.261497 | 1.470797 | 0.128249 |
| C | -3.331631 | -0.069483 | -0.170100 |
| B | -1.105610 | 0.603697 | 0.022276 |
| O | -1.974779 | -0.499608 | 0.114228 |
| O | -1.864315 | 1.768594 | -0.105393 |
| C | -4.294722 | -0.862387 | 0.715063 |
| H | -5.328278 | -0.519544 | 0.581838 |
| H | -4.257039 | -1.923945 | 0.445820 |
| H | -4.033714 | -0.775153 | 1.772453 |
| C | -3.601352 | -0.392499 | -1.648665 |
| H | -3.430353 | -1.461494 | -1.814900 |
| H | -4.632749 | -0.162110 | -1.939963 |

| | | | |
|---|-----------|----------|-----------|
| H | -2.921372 | 0.163364 | -2.301507 |
| C | -3.553396 | 1.822040 | 1.596647 |
| H | -3.280551 | 2.868308 | 1.767899 |
| H | -4.612770 | 1.696311 | 1.849557 |
| H | -2.955478 | 1.205058 | 2.274611 |
| C | -4.109172 | 2.353870 | -0.789276 |
| H | -5.177526 | 2.128324 | -0.682431 |
| H | -3.958359 | 3.405922 | -0.524640 |
| H | -3.829556 | 2.230942 | -1.838278 |

Ni-bpin-DMA-THF
 B3LYP electronic energy: -1100.85497235 a.u.
 B3LYP enthalpy: -1100.393533 a.u.
 B3LYP free energy: -1100.486409 a.u.
 M06 SCF energy in solution: -1102.17460073 a.u.
 M06 enthalpy in solution: -1101.713161 a.u.
 M06 free energy in solution: -1101.806037 a.u.

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| Ni | 0.708559 | -0.070881 | 0.034464 |
| O | 0.765152 | 2.146671 | 0.015448 |
| C | 0.321522 | 2.696210 | -1.247070 |
| C | 0.021136 | 2.750571 | 1.104297 |
| C | -0.990821 | 3.418835 | -0.945049 |
| H | 1.094909 | 3.383318 | -1.618319 |
| H | 0.211747 | 1.864547 | -1.948946 |
| C | -0.749897 | 3.920753 | 0.487286 |
| H | -0.656201 | 1.991572 | 1.507698 |
| H | 0.737266 | 3.052172 | 1.875574 |
| H | -1.813067 | 2.697606 | -0.952201 |
| H | -1.203195 | 4.221336 | -1.658827 |
| H | -1.676072 | 4.134295 | 1.029914 |
| H | -0.139345 | 4.832494 | 0.482124 |
| C | -3.539724 | -0.333165 | 0.246813 |
| C | -3.192343 | -1.805086 | -0.175100 |
| B | -1.226312 | -0.571738 | 0.029061 |
| O | -1.763927 | -1.863150 | 0.050648 |
| O | -2.286660 | 0.356677 | 0.011137 |
| C | -3.864117 | -2.899282 | 0.656811 |
| H | -4.956255 | -2.858901 | 0.559553 |
| H | -3.530374 | -3.882172 | 0.306804 |
| H | -3.604973 | -2.816475 | 1.715002 |
| C | -3.422207 | -2.079431 | -1.670723 |
| H | -2.969153 | -3.042982 | -1.925672 |
| H | -4.488111 | -2.121687 | -1.924310 |
| H | -2.945174 | -1.311456 | -2.287457 |
| C | -3.856471 | -0.187350 | 1.744288 |
| H | -3.879956 | 0.877727 | 1.998670 |
| H | -4.827734 | -0.623746 | 2.005248 |
| H | -3.083625 | -0.662551 | 2.356224 |
| C | -4.635757 | 0.342680 | -0.579062 |
| H | -5.592024 | -0.185240 | -0.477025 |

| | | | |
|---|-----------|-----------|-----------|
| H | -4.781045 | 1.370601 | -0.228405 |
| H | -4.373741 | 0.383863 | -1.639118 |
| O | 2.760681 | -0.087057 | 0.036830 |
| C | 3.569267 | -1.032695 | 0.001838 |
| N | 4.907539 | -0.788782 | 0.056710 |
| C | 3.090409 | -2.469808 | -0.101743 |
| H | 3.472070 | -2.958069 | -1.005345 |
| H | 3.405073 | -3.062139 | 0.764748 |
| H | 1.999358 | -2.464068 | -0.142005 |
| C | 5.393881 | 0.583337 | 0.156971 |
| H | 6.036451 | 0.819098 | -0.700702 |
| H | 4.540843 | 1.258912 | 0.172330 |
| H | 5.980592 | 0.708890 | 1.075697 |
| C | 5.940820 | -1.811966 | 0.020791 |
| H | 5.509312 | -2.809080 | -0.039896 |
| H | 6.594822 | -1.662814 | -0.848522 |
| H | 6.560591 | -1.756949 | 0.925318 |

Ni-bpin-2DMA

B3LYP electronic energy: -1156.23393687 a.u.
 B3LYP enthalpy: -1155.756491 a.u.
 B3LYP free energy: -1155.855014 a.u.
 M06 SCF energy in solution: -1157.54052254 a.u.
 M06 enthalpy in solution: -1157.063077 a.u.
 M06 free energy in solution: -1157.161600 a.u.

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| Ni | 0.740030 | 0.757362 | -0.097631 |
| C | -2.873297 | -1.541768 | 0.184104 |
| C | -1.805806 | -2.651330 | -0.123214 |
| B | -0.751379 | -0.565143 | -0.007104 |
| O | -0.562512 | -1.953877 | 0.121704 |
| O | -2.141263 | -0.322628 | -0.098089 |
| C | -1.865572 | -3.883814 | 0.781363 |
| H | -2.819343 | -4.414390 | 0.668715 |
| H | -1.061542 | -4.576650 | 0.509838 |
| H | -1.736489 | -3.617859 | 1.833222 |
| C | -1.793159 | -3.093209 | -1.596326 |
| H | -0.900235 | -3.701797 | -1.773554 |
| H | -2.673889 | -3.692222 | -1.856342 |
| H | -1.746293 | -2.228126 | -2.264787 |
| C | -3.285024 | -1.490747 | 1.664834 |
| H | -3.876518 | -0.585404 | 1.839731 |
| H | -3.894109 | -2.355258 | 1.953693 |
| H | -2.405573 | -1.448470 | 2.314491 |
| C | -4.124294 | -1.581150 | -0.695607 |
| H | -4.678760 | -2.517369 | -0.555322 |
| H | -4.791951 | -0.754592 | -0.427060 |
| H | -3.875252 | -1.480671 | -1.754762 |
| O | 0.245269 | 2.831857 | -0.394762 |
| C | -0.988675 | 2.887117 | -0.594354 |
| O | 2.798490 | 0.493930 | -0.001327 |

| | | | |
|---|-----------|-----------|-----------|
| C | 3.533403 | -0.509536 | 0.053458 |
| N | 4.887459 | -0.358712 | 0.093304 |
| C | 5.474235 | 0.976396 | 0.069518 |
| H | 4.673835 | 1.712382 | 0.027695 |
| H | 6.078286 | 1.139487 | 0.971119 |
| H | 6.123427 | 1.088851 | -0.808195 |
| C | 5.843927 | -1.452636 | 0.154541 |
| H | 5.341533 | -2.417629 | 0.167579 |
| H | 6.513941 | -1.421246 | -0.715002 |
| H | 6.459848 | -1.369277 | 1.059877 |
| C | 2.949513 | -1.908819 | 0.078429 |
| H | 3.293655 | -2.497216 | -0.780115 |
| H | 3.239210 | -2.443448 | 0.990446 |
| H | 1.860491 | -1.838103 | 0.043968 |
| C | -1.548782 | 2.677544 | -1.986781 |
| H | -0.709527 | 2.655925 | -2.682662 |
| H | -2.065441 | 1.712144 | -2.025151 |
| H | -2.248356 | 3.465752 | -2.285503 |
| C | -3.286940 | 2.903222 | 0.308758 |
| H | -3.808005 | 3.504123 | 1.060166 |
| H | -3.655543 | 3.199419 | -0.674137 |
| H | -3.511764 | 1.841431 | 0.466593 |
| C | -1.316219 | 3.192210 | 1.780471 |
| H | -1.257925 | 2.183408 | 2.209564 |
| H | -0.312960 | 3.615397 | 1.754132 |
| H | -1.968121 | 3.816618 | 2.399264 |
| N | -1.851790 | 3.145747 | 0.421883 |

TS2-4-OMe

B3LYP electronic energy: -3655.37059860 a.u.
 B3LYP enthalpy: -3654.926945 a.u.
 B3LYP free energy: -3655.012142 a.u.
 M06 SCF energy in solution: -3659.28249597 a.u.
 M06 enthalpy in solution: -3658.838842 a.u.
 M06 free energy in solution: -3658.924039 a.u.
 Imaginary frequency: -45.8449 cm⁻¹

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| Ni | -0.219556 | 0.173408 | -0.891931 |
| C | -0.055181 | -1.708845 | -1.537153 |
| C | 1.460786 | -1.945941 | -1.781218 |
| H | 1.706742 | -3.018992 | -1.893372 |
| C | 3.939108 | -0.759100 | 0.884687 |
| C | 2.977133 | 0.479276 | 0.703974 |
| O | 1.864518 | -0.126424 | -0.026392 |
| O | 3.598224 | -1.596087 | -0.255927 |
| B | 2.338778 | -1.265044 | -0.682136 |
| C | 3.639278 | -1.586045 | 2.142332 |
| H | 2.575567 | -1.834941 | 2.211424 |
| H | 4.200855 | -2.523762 | 2.089779 |
| H | 3.934640 | -1.057929 | 3.055188 |
| C | 5.430035 | -0.432088 | 0.814149 |

| | | | |
|----|-----------|-----------|-----------|
| H | 5.720289 | 0.248053 | 1.623394 |
| H | 6.011495 | -1.353382 | 0.920822 |
| H | 5.698672 | 0.025760 | -0.140555 |
| C | 2.442867 | 1.086234 | 1.998940 |
| H | 3.262013 | 1.495534 | 2.601453 |
| H | 1.753471 | 1.903687 | 1.764807 |
| H | 1.906513 | 0.347565 | 2.599327 |
| C | 3.554597 | 1.575577 | -0.199753 |
| H | 2.762354 | 2.289587 | -0.444521 |
| H | 4.367181 | 2.117409 | 0.295541 |
| H | 3.936630 | 1.158384 | -1.136736 |
| C | -1.821936 | 1.090212 | -0.008899 |
| C | -1.919896 | 0.616219 | 1.308901 |
| C | -2.860820 | 0.862028 | -0.935065 |
| C | -2.996897 | -0.194785 | 1.667030 |
| H | -1.154949 | 0.863042 | 2.036471 |
| C | -3.927020 | 0.052768 | -0.565015 |
| H | -2.820389 | 1.302299 | -1.924993 |
| C | -4.003081 | -0.483242 | 0.731674 |
| H | -3.043375 | -0.587869 | 2.675976 |
| H | -4.724921 | -0.169577 | -1.266286 |
| Br | -0.594050 | 2.672678 | -0.370080 |
| H | 1.751503 | -1.482419 | -2.740377 |
| C | -0.536262 | -2.659437 | -0.430772 |
| H | -1.600818 | -2.513265 | -0.207443 |
| H | -0.404889 | -3.721515 | -0.717963 |
| H | 0.014390 | -2.515894 | 0.510375 |
| C | -0.850381 | -1.987482 | -2.817913 |
| H | -0.729387 | -3.034038 | -3.159567 |
| H | -1.926716 | -1.824695 | -2.667904 |
| H | -0.532410 | -1.341213 | -3.647584 |
| O | -5.096191 | -1.253149 | 0.985952 |
| C | -5.225302 | -1.842823 | 2.270732 |
| H | -5.296625 | -1.081248 | 3.058582 |
| H | -6.151350 | -2.419417 | 2.242483 |
| H | -4.385607 | -2.514961 | 2.490351 |

TS2-4-Me

B3LYP electronic energy: -3580.16737616 a.u.
 B3LYP enthalpy: -3579.729945 a.u.
 B3LYP free energy: -3579.815003 a.u.
 M06 SCF energy in solution: -3584.08296691 a.u.
 M06 enthalpy in solution: -3583.645536 a.u.
 M06 free energy in solution: -3583.730594 a.u.
 Imaginary frequency: -55.6228 cm⁻¹

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|----------|-----------|
| Ni | 0.481748 | 0.063047 | -0.753602 |
| C | 0.244169 | 2.022505 | -1.049851 |
| C | -1.256095 | 2.219901 | -1.401277 |
| H | -1.566253 | 3.280390 | -1.341360 |
| C | -3.877371 | 0.432225 | 0.740138 |

| | | | |
|----|-----------|-----------|-----------|
| C | -2.817115 | -0.699139 | 0.444259 |
| O | -1.688902 | 0.087914 | -0.052988 |
| O | -3.493994 | 1.480803 | -0.193292 |
| B | -2.180852 | 1.301175 | -0.539229 |
| C | -3.753548 | 1.029828 | 2.148320 |
| H | -2.721134 | 1.318746 | 2.369270 |
| H | -4.374070 | 1.929272 | 2.205673 |
| H | -4.091383 | 0.327607 | 2.917873 |
| C | -5.328570 | 0.045295 | 0.459683 |
| H | -5.646584 | -0.780266 | 1.106982 |
| H | -5.979486 | 0.902333 | 0.659901 |
| H | -5.474225 | -0.250759 | -0.581596 |
| C | -2.358335 | -1.498876 | 1.660918 |
| H | -3.196857 | -2.052410 | 2.098970 |
| H | -1.595566 | -2.222607 | 1.356861 |
| H | -1.928688 | -0.853397 | 2.430805 |
| C | -3.229936 | -1.645377 | -0.690073 |
| H | -2.369386 | -2.259313 | -0.973165 |
| H | -4.042112 | -2.311990 | -0.381323 |
| H | -3.555516 | -1.089306 | -1.574911 |
| C | 2.067241 | -0.917833 | 0.084122 |
| C | 2.068316 | -0.717557 | 1.476709 |
| C | 3.122494 | -0.444340 | -0.716111 |
| C | 3.070839 | 0.068943 | 2.035345 |
| H | 1.292191 | -1.156052 | 2.093825 |
| C | 4.109585 | 0.343419 | -0.120770 |
| H | 3.164547 | -0.685543 | -1.772368 |
| C | 4.102381 | 0.617593 | 1.253261 |
| H | 3.057040 | 0.253995 | 3.107054 |
| H | 4.910571 | 0.736963 | -0.741971 |
| Br | 0.970928 | -2.464798 | -0.658675 |
| H | -1.424192 | 1.929591 | -2.453179 |
| C | 0.554735 | 2.768305 | 0.256224 |
| H | 1.602505 | 2.638584 | 0.556179 |
| H | 0.374524 | 3.856984 | 0.157516 |
| H | -0.066163 | 2.418995 | 1.093858 |
| C | 1.131160 | 2.579234 | -2.169273 |
| H | 0.972018 | 3.664693 | -2.320175 |
| H | 2.198139 | 2.442698 | -1.944498 |
| H | 0.932830 | 2.089969 | -3.132814 |
| C | 5.165759 | 1.487493 | 1.879607 |
| H | 5.428591 | 1.140695 | 2.885142 |
| H | 6.079319 | 1.501335 | 1.276355 |
| H | 4.821079 | 2.526095 | 1.974575 |

TS2-4-F

B3LYP electronic energy: -3640.08081902 a.u.
 B3LYP enthalpy: -3639.680146 a.u.
 B3LYP free energy: -3639.762527 a.u.
 M06 SCF energy in solution: -3644.02750996 a.u.
 M06 enthalpy in solution: -3643.626837 a.u.
 M06 free energy in solution: -3643.709218 a.u.
 Imaginary frequency: -50.7248 cm⁻¹

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| Ni | 0.492555 | 0.102491 | -0.682147 |
| C | 0.244010 | 2.066682 | -0.930587 |
| C | -1.245630 | 2.251416 | -1.332401 |
| H | -1.572395 | 3.305729 | -1.257117 |
| C | -3.909326 | 0.377311 | 0.679360 |
| C | -2.826228 | -0.733581 | 0.387852 |
| O | -1.693973 | 0.079015 | -0.057421 |
| O | -3.511157 | 1.454142 | -0.215210 |
| B | -2.186782 | 1.299308 | -0.526119 |
| C | -3.836353 | 0.940760 | 2.105062 |
| H | -2.815234 | 1.237311 | 2.364941 |
| H | -4.470086 | 1.830714 | 2.165459 |
| H | -4.188367 | 0.215533 | 2.846405 |
| C | -5.346099 | -0.019782 | 0.344249 |
| H | -5.673217 | -0.865347 | 0.960402 |
| H | -6.013677 | 0.823996 | 0.545635 |
| H | -5.455703 | -0.290860 | -0.708157 |
| C | -2.392699 | -1.556364 | 1.598353 |
| H | -3.236473 | -2.130073 | 1.998524 |
| H | -1.612629 | -2.263877 | 1.299973 |
| H | -1.993655 | -0.924500 | 2.395436 |
| C | -3.192891 | -1.657639 | -0.780071 |
| H | -2.316034 | -2.253681 | -1.051305 |
| H | -4.004853 | -2.341168 | -0.510568 |
| H | -3.499493 | -1.085240 | -1.661214 |
| C | 2.104018 | -0.895730 | 0.078766 |
| C | 2.133289 | -0.718588 | 1.476216 |
| C | 3.131094 | -0.390113 | -0.742990 |
| C | 3.133015 | 0.072528 | 2.034443 |
| H | 1.377343 | -1.178976 | 2.101705 |
| C | 4.126076 | 0.402664 | -0.169574 |
| H | 3.144256 | -0.609817 | -1.804275 |
| C | 4.110129 | 0.621495 | 1.204289 |
| H | 3.170442 | 0.260910 | 3.102293 |
| H | 4.916043 | 0.835492 | -0.774169 |
| Br | 1.012938 | -2.435408 | -0.659634 |
| H | -1.371191 | 1.986017 | -2.396697 |
| C | 0.493155 | 2.780804 | 0.406206 |
| H | 1.532884 | 2.668380 | 0.739311 |
| H | 0.291248 | 3.867221 | 0.331737 |
| H | -0.147773 | 2.394110 | 1.211742 |
| C | 1.161903 | 2.667261 | -2.001129 |
| H | 0.989092 | 3.753228 | -2.129663 |
| H | 2.221994 | 2.543298 | -1.740039 |
| H | 1.007918 | 2.200523 | -2.983798 |
| F | 5.080598 | 1.374897 | 1.756015 |

TS2-4-Cl

B3LYP electronic energy: -4000.43969109 a.u.

B3LYP enthalpy: -4000.040262 a.u.

B3LYP free energy: -4000.124486 a.u.
 M06 SCF energy in solution: -4004.38244837 a.u.
 M06 enthalpy in solution: -4003.983019 a.u.
 M06 free energy in solution: -4004.067243 a.u.
 Imaginary frequency: -40.0209 cm⁻¹

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| Ni | -0.310605 | -0.035289 | -0.368700 |
| C | -0.208639 | -1.975206 | -0.871398 |
| C | 1.227593 | -2.180337 | -1.431723 |
| H | 1.503623 | -3.249977 | -1.496923 |
| C | 4.176931 | -0.644603 | 0.466079 |
| C | 3.121451 | 0.528839 | 0.425425 |
| O | 1.912434 | -0.184974 | 0.016400 |
| O | 3.634810 | -1.595659 | -0.492312 |
| B | 2.292950 | -1.361240 | -0.635111 |
| C | 4.233616 | -1.368417 | 1.818589 |
| H | 3.234973 | -1.664558 | 2.155154 |
| H | 4.832639 | -2.277193 | 1.706649 |
| H | 4.693398 | -0.745920 | 2.593587 |
| C | 5.586094 | -0.259114 | 0.018442 |
| H | 6.013586 | 0.501671 | 0.681772 |
| H | 6.233616 | -1.140937 | 0.053627 |
| H | 5.596314 | 0.123163 | -1.004798 |
| C | 2.855662 | 1.215968 | 1.762379 |
| H | 3.763925 | 1.704157 | 2.133745 |
| H | 2.087206 | 1.985626 | 1.635036 |
| H | 2.507362 | 0.508649 | 2.518497 |
| C | 3.408111 | 1.571651 | -0.662518 |
| H | 2.537018 | 2.225373 | -0.768136 |
| H | 4.274905 | 2.190187 | -0.407175 |
| H | 3.593935 | 1.096626 | -1.630941 |
| C | -1.886951 | 1.291513 | -0.037434 |
| C | -1.966012 | 0.753628 | 1.264883 |
| C | -2.871615 | 1.008577 | -1.003785 |
| C | -3.026252 | -0.109604 | 1.577326 |
| H | -1.268414 | 1.062560 | 2.034673 |
| C | -3.913624 | 0.148878 | -0.677550 |
| H | -2.811543 | 1.454445 | -1.990006 |
| C | -3.984561 | -0.398839 | 0.611303 |
| H | -3.105607 | -0.534386 | 2.571990 |
| H | -4.669724 | -0.097300 | -1.414820 |
| Br | -0.630596 | 2.754758 | -0.369818 |
| H | 1.267640 | -1.811022 | -2.471648 |
| C | -0.369740 | -2.825773 | 0.398421 |
| H | -1.368793 | -2.713161 | 0.839283 |
| H | -0.228217 | -3.904634 | 0.189761 |
| H | 0.359310 | -2.556266 | 1.176772 |
| C | -1.240601 | -2.427503 | -1.910541 |
| H | -1.114706 | -3.494959 | -2.177977 |
| H | -2.267296 | -2.311131 | -1.539173 |
| H | -1.161788 | -1.852261 | -2.843245 |
| Cl | -5.319239 | -1.461992 | 1.012764 |

TS2-3-Cl

B3LYP electronic energy: -4000.43929162 a.u.
 B3LYP enthalpy: -4000.039810 a.u.
 B3LYP free energy: -4000.124186 a.u.
 M06 SCF energy in solution: -4004.38221673 a.u.
 M06 enthalpy in solution: -4003.982735 a.u.
 M06 free energy in solution: -4004.067111 a.u.
 Imaginary frequency: -47.0903 cm⁻¹

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| Ni | -0.329733 | -0.151454 | -0.070786 |
| C | -0.151612 | -2.135188 | -0.296422 |
| C | 1.190485 | -2.345247 | -1.053170 |
| H | 1.533138 | -3.396688 | -1.013625 |
| C | 4.278870 | -0.397759 | 0.098253 |
| C | 3.149600 | 0.705860 | 0.057275 |
| O | 1.945722 | -0.117238 | -0.044237 |
| O | 3.664638 | -1.509879 | -0.610747 |
| B | 2.303606 | -1.361920 | -0.567877 |
| C | 4.591236 | -0.899005 | 1.514849 |
| H | 3.678236 | -1.182236 | 2.048150 |
| H | 5.226670 | -1.786858 | 1.442055 |
| H | 5.120512 | -0.143569 | 2.105251 |
| C | 5.572744 | -0.022458 | -0.622810 |
| H | 6.043958 | 0.849664 | -0.154762 |
| H | 6.276868 | -0.858620 | -0.566000 |
| H | 5.398599 | 0.198349 | -1.678294 |
| C | 3.039873 | 1.578332 | 1.305071 |
| H | 3.952006 | 2.169386 | 1.446293 |
| H | 2.200521 | 2.272939 | 1.194496 |
| H | 2.870769 | 0.980657 | 2.203801 |
| C | 3.194092 | 1.580258 | -1.201818 |
| H | 2.275063 | 2.171720 | -1.257226 |
| H | 4.046296 | 2.267613 | -1.183607 |
| H | 3.259083 | 0.970548 | -2.108433 |
| C | -1.960919 | 1.082260 | 0.312583 |
| C | -1.834118 | 0.734278 | 1.673596 |
| C | -3.039081 | 0.630049 | -0.472829 |
| C | -2.787396 | -0.134364 | 2.225197 |
| H | -1.064169 | 1.182408 | 2.290383 |
| C | -3.960321 | -0.224390 | 0.120747 |
| C | -3.848775 | -0.612863 | 1.463153 |
| Br | -0.861747 | 2.552221 | -0.383618 |
| H | 1.037701 | -2.134425 | -2.126257 |
| C | -0.044992 | -2.785848 | 1.091635 |
| H | -0.970019 | -2.661210 | 1.669765 |
| H | 0.148513 | -3.874427 | 1.020305 |
| H | 0.771404 | -2.358282 | 1.692148 |
| C | -1.295544 | -2.795572 | -1.073312 |
| H | -1.128269 | -3.882261 | -1.207178 |
| H | -2.256646 | -2.682976 | -0.554826 |
| H | -1.412915 | -2.363504 | -2.076335 |

| | | | |
|----|-----------|-----------|-----------|
| H | -4.589732 | -1.275880 | 1.895273 |
| H | -3.141378 | 0.936291 | -1.506232 |
| H | -2.702568 | -0.421220 | 3.269136 |
| Cl | -5.302691 | -0.822819 | -0.835786 |

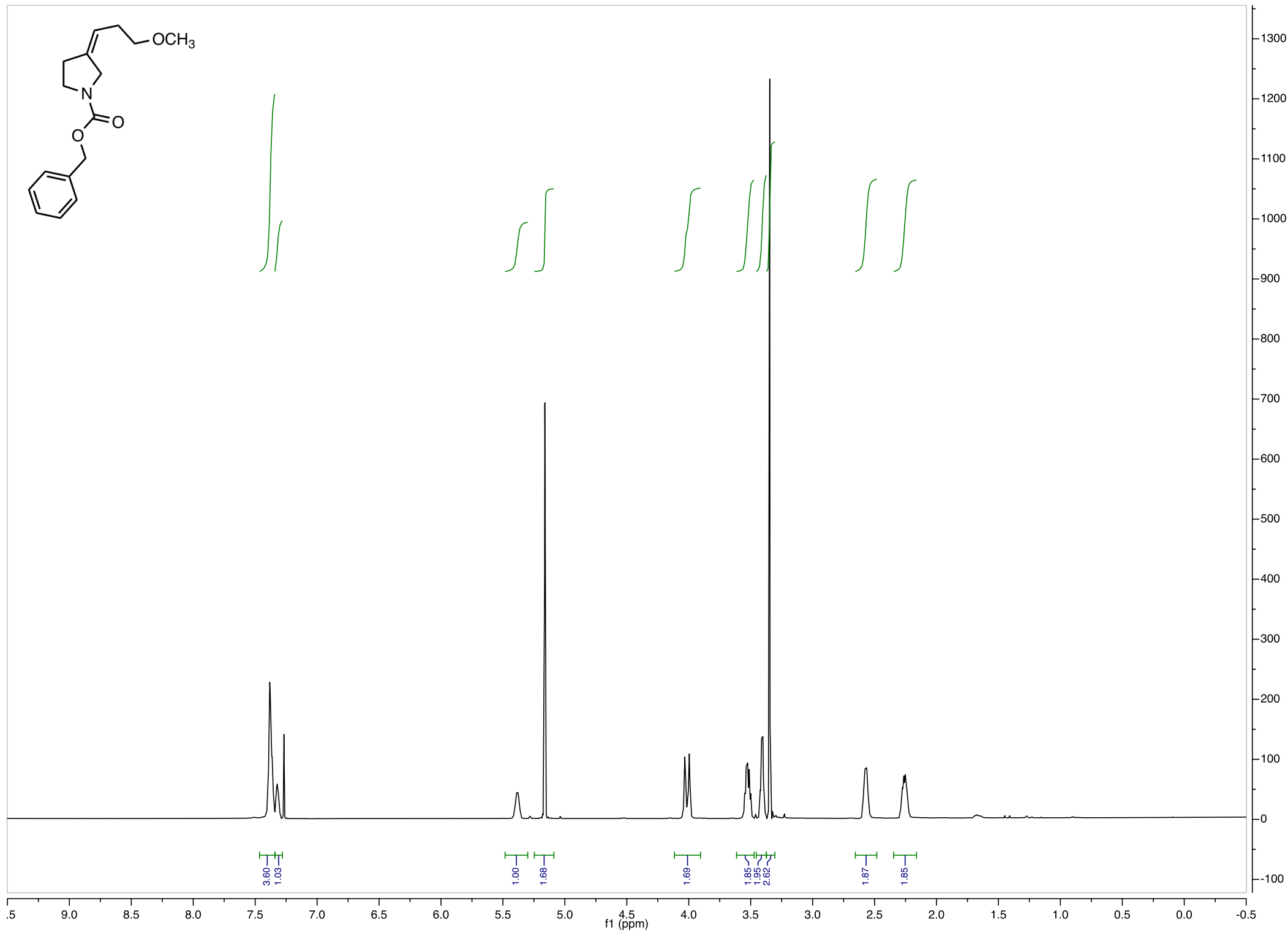
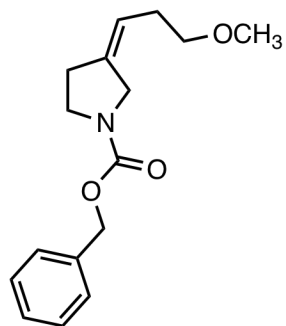
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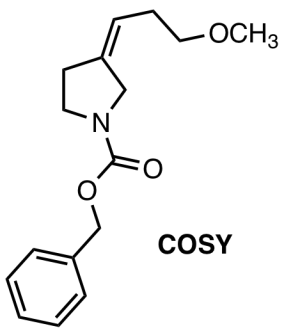
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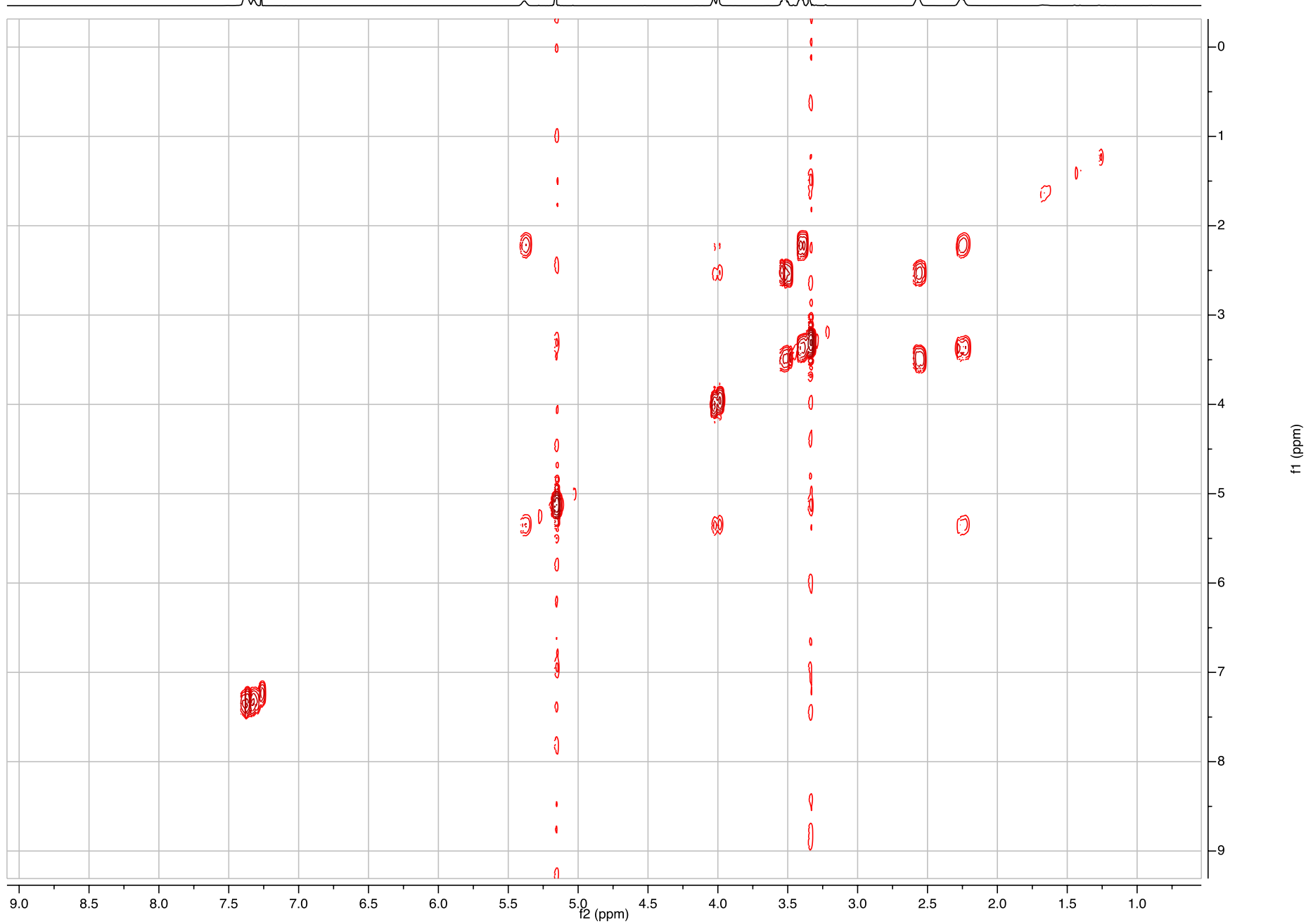
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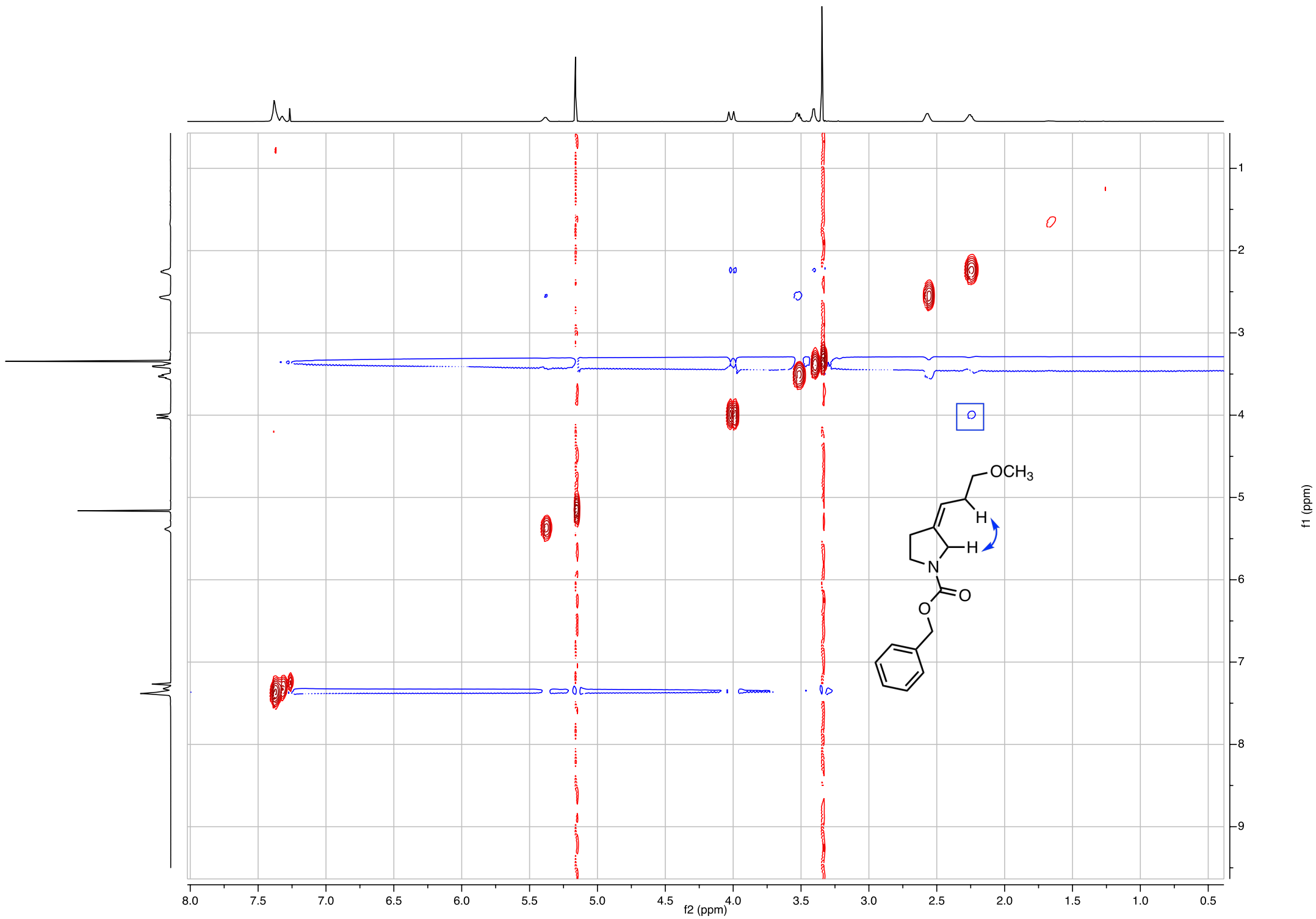
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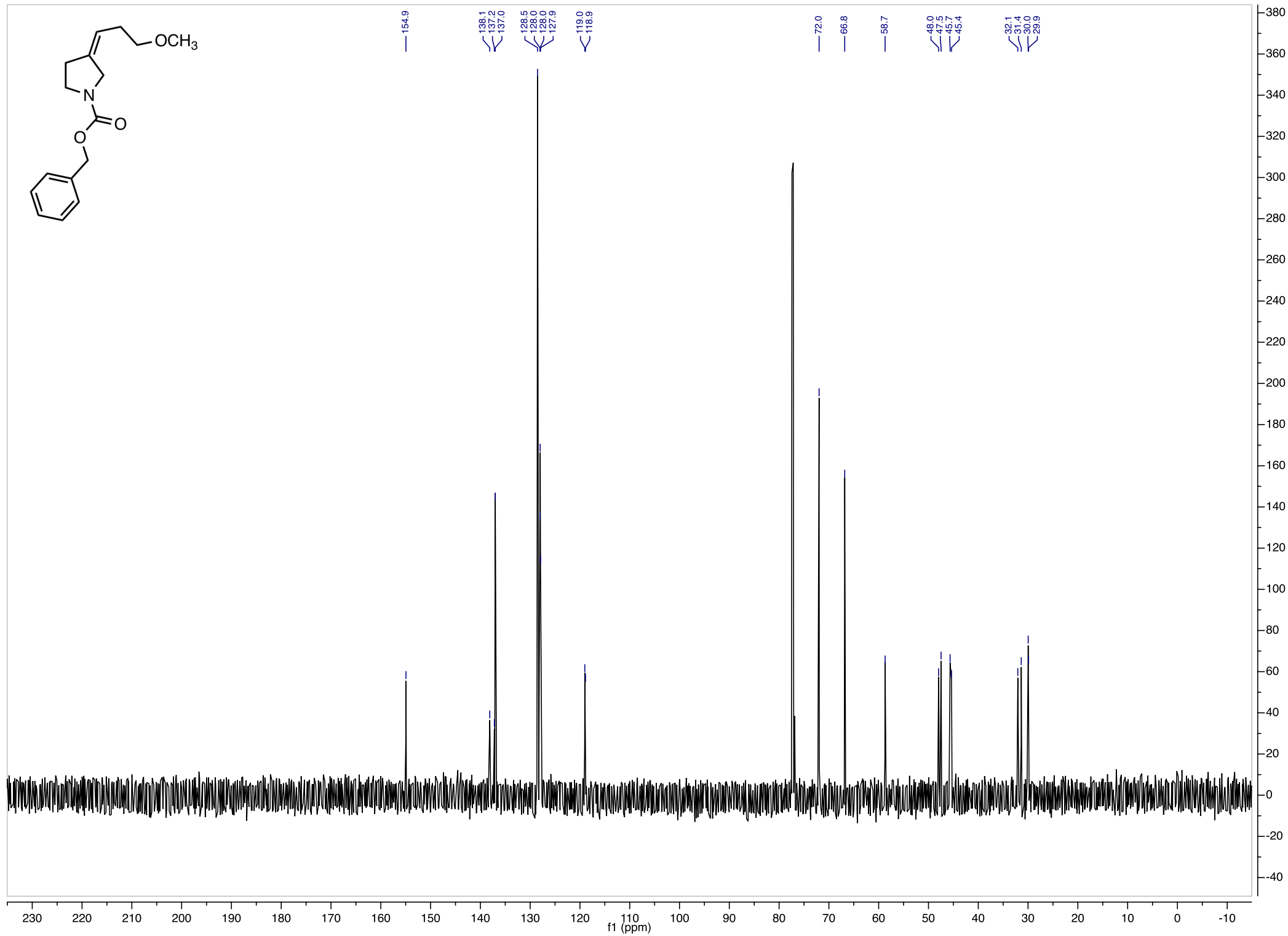
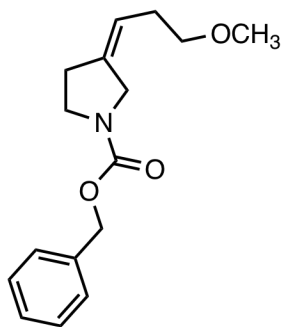


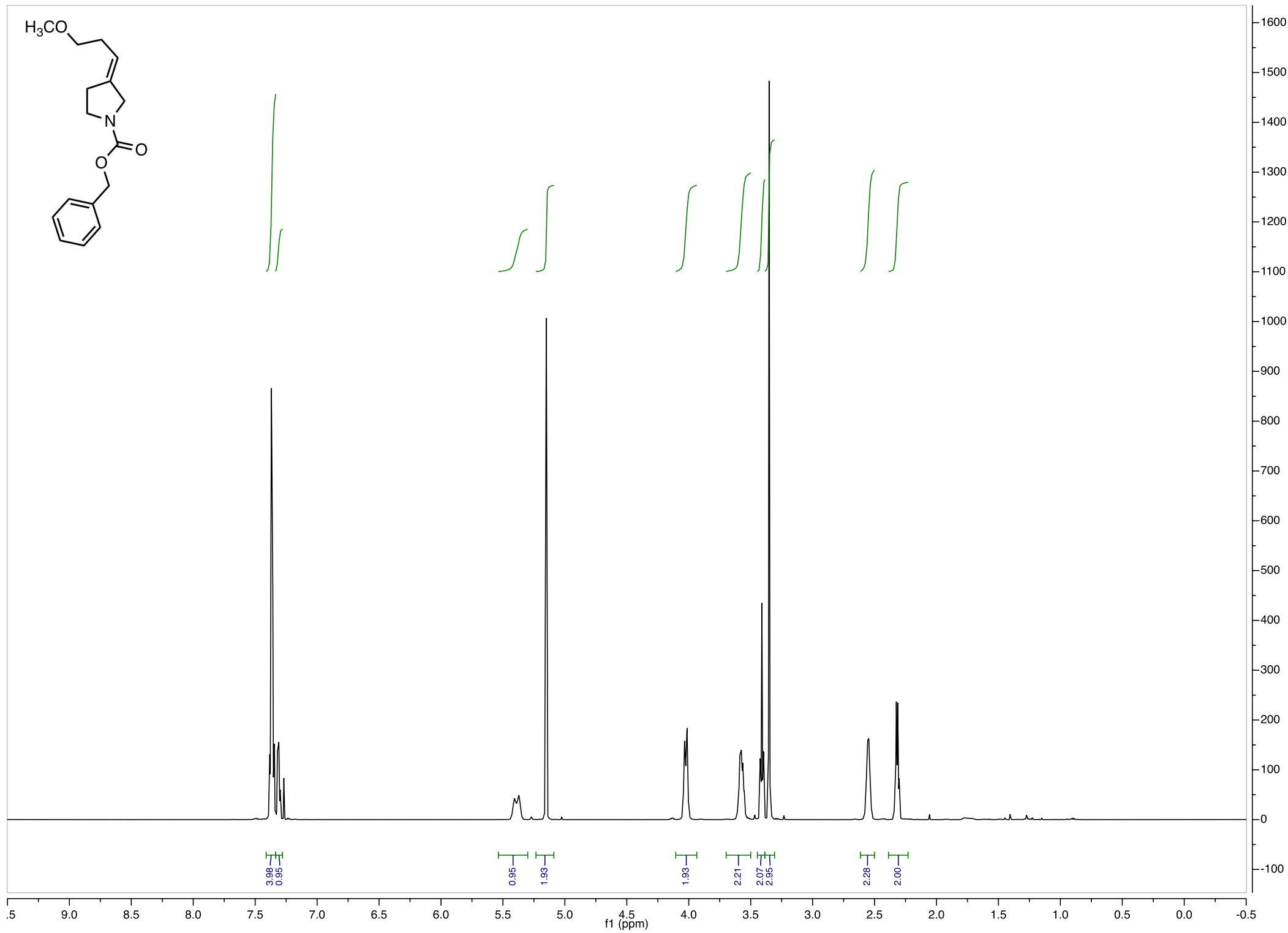
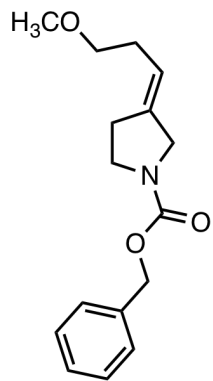


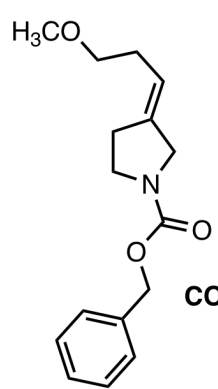
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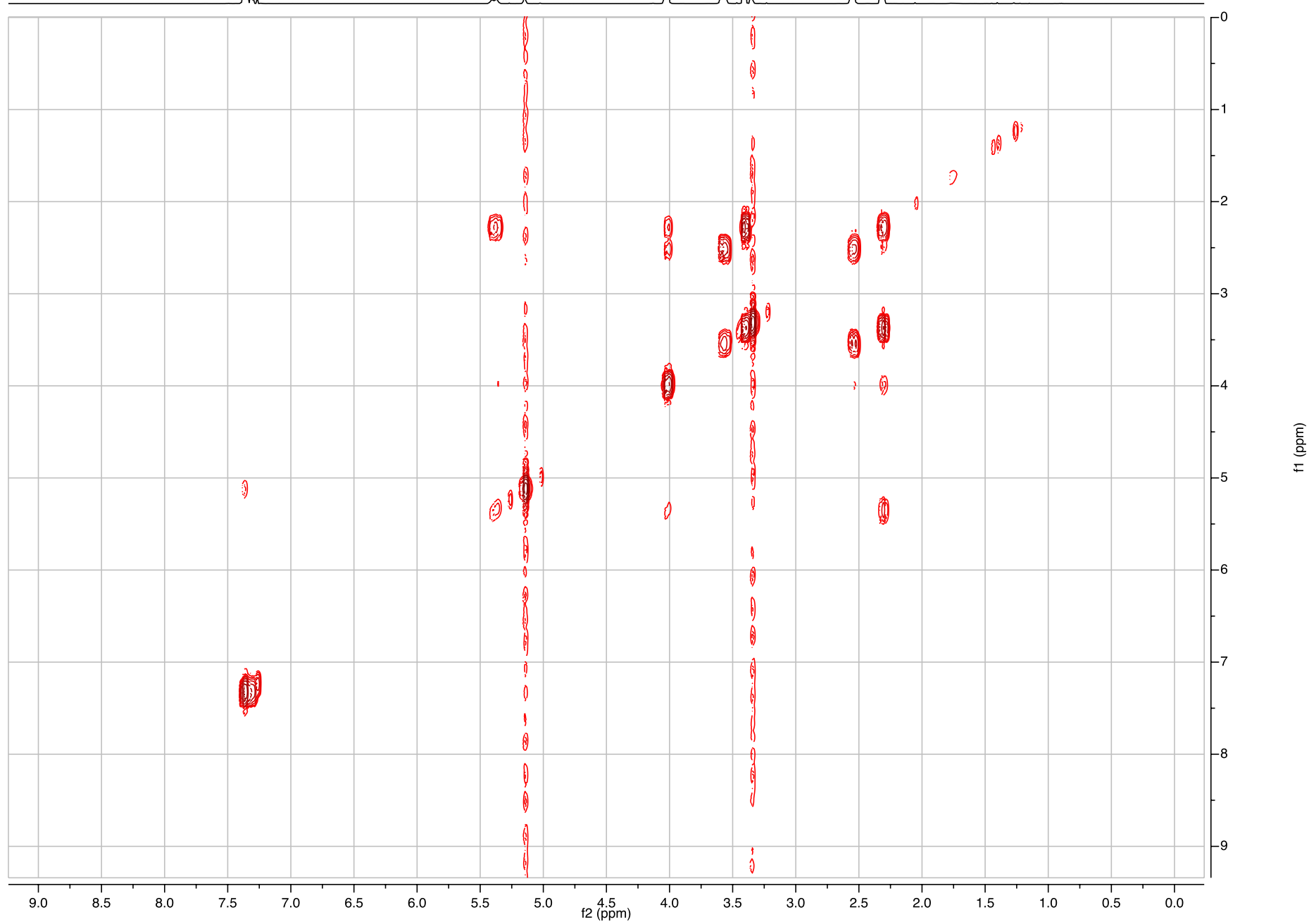


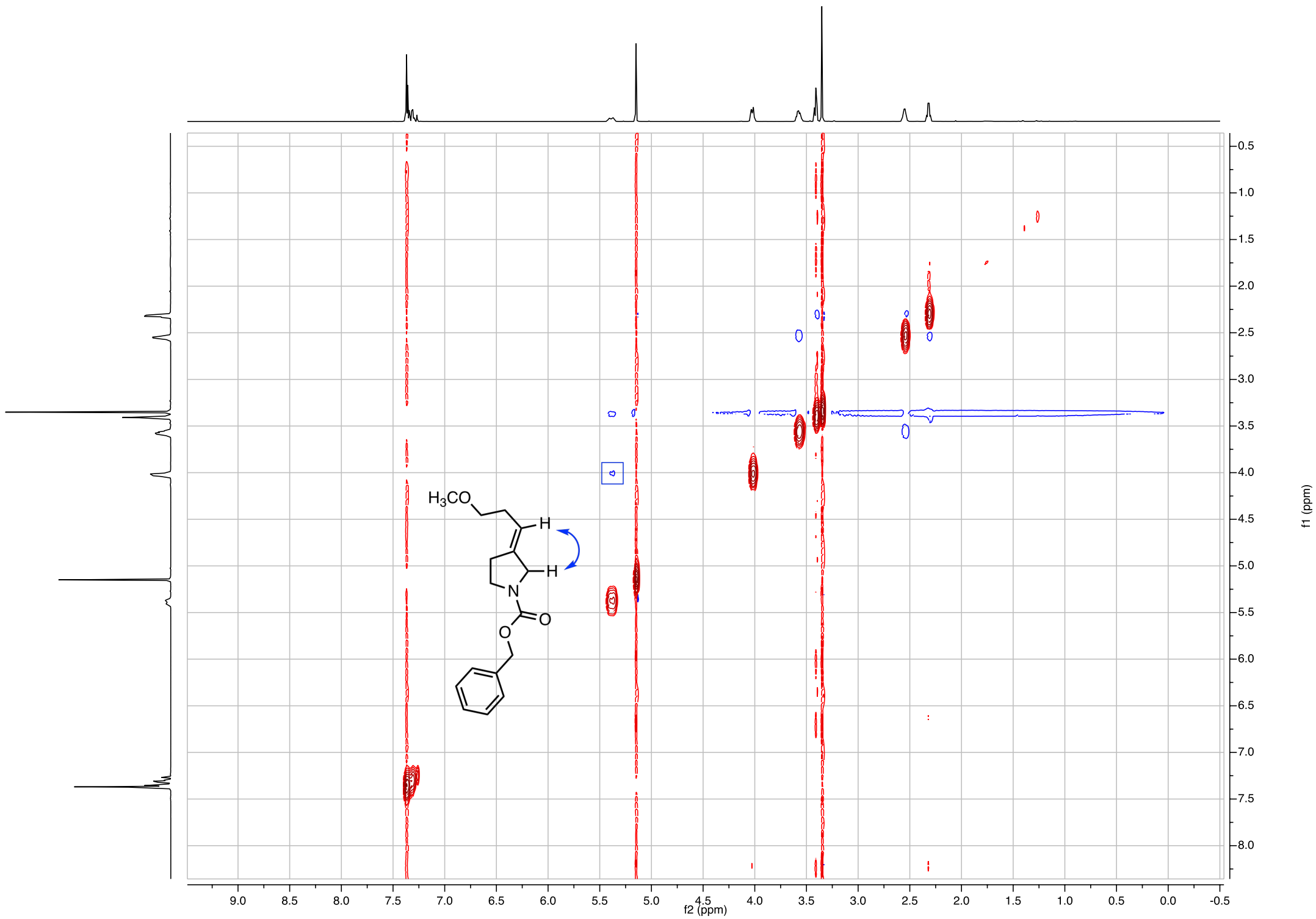


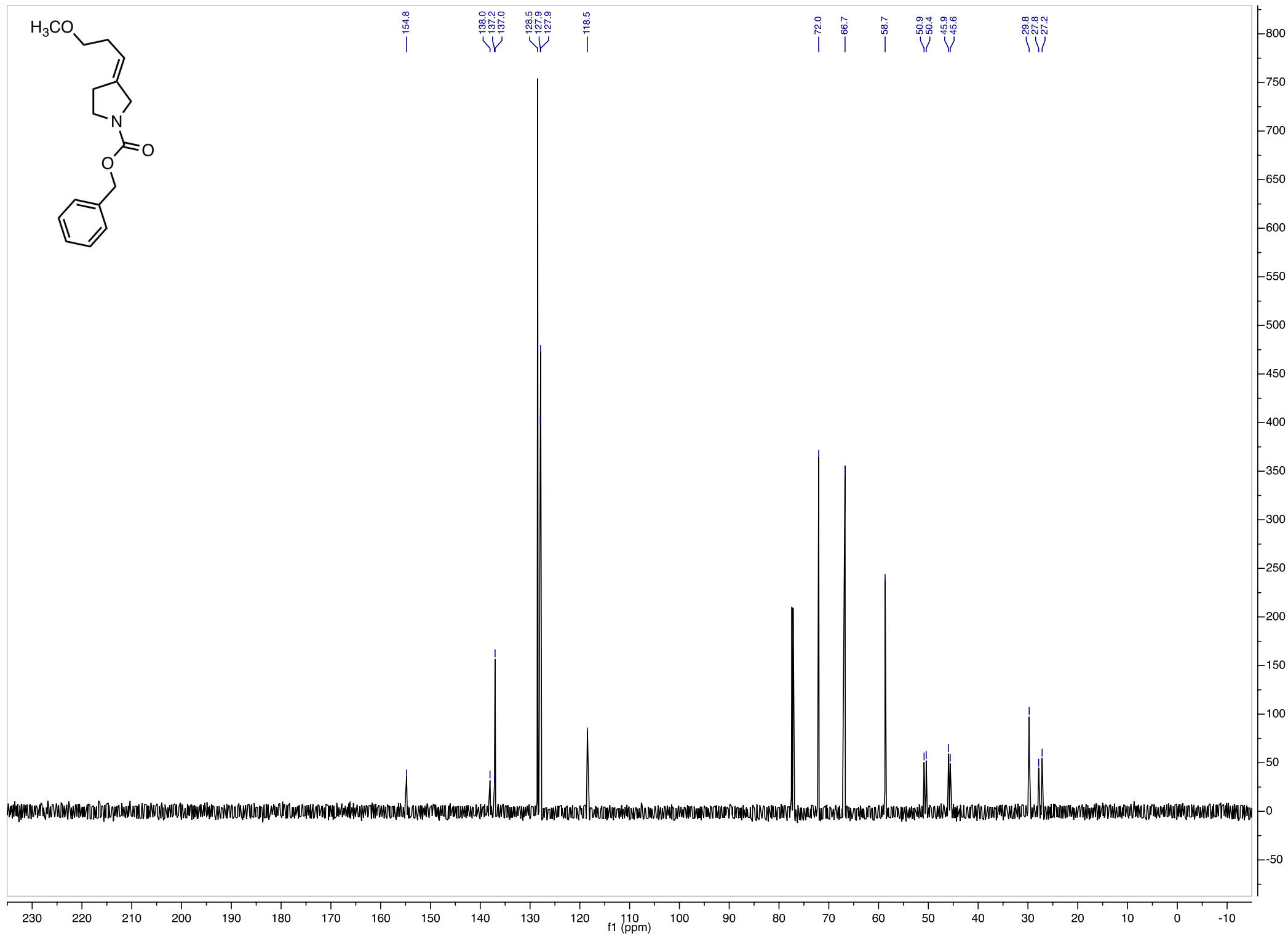
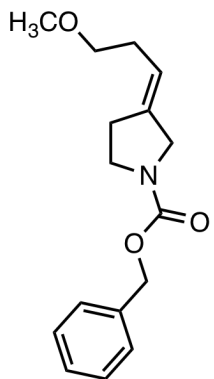


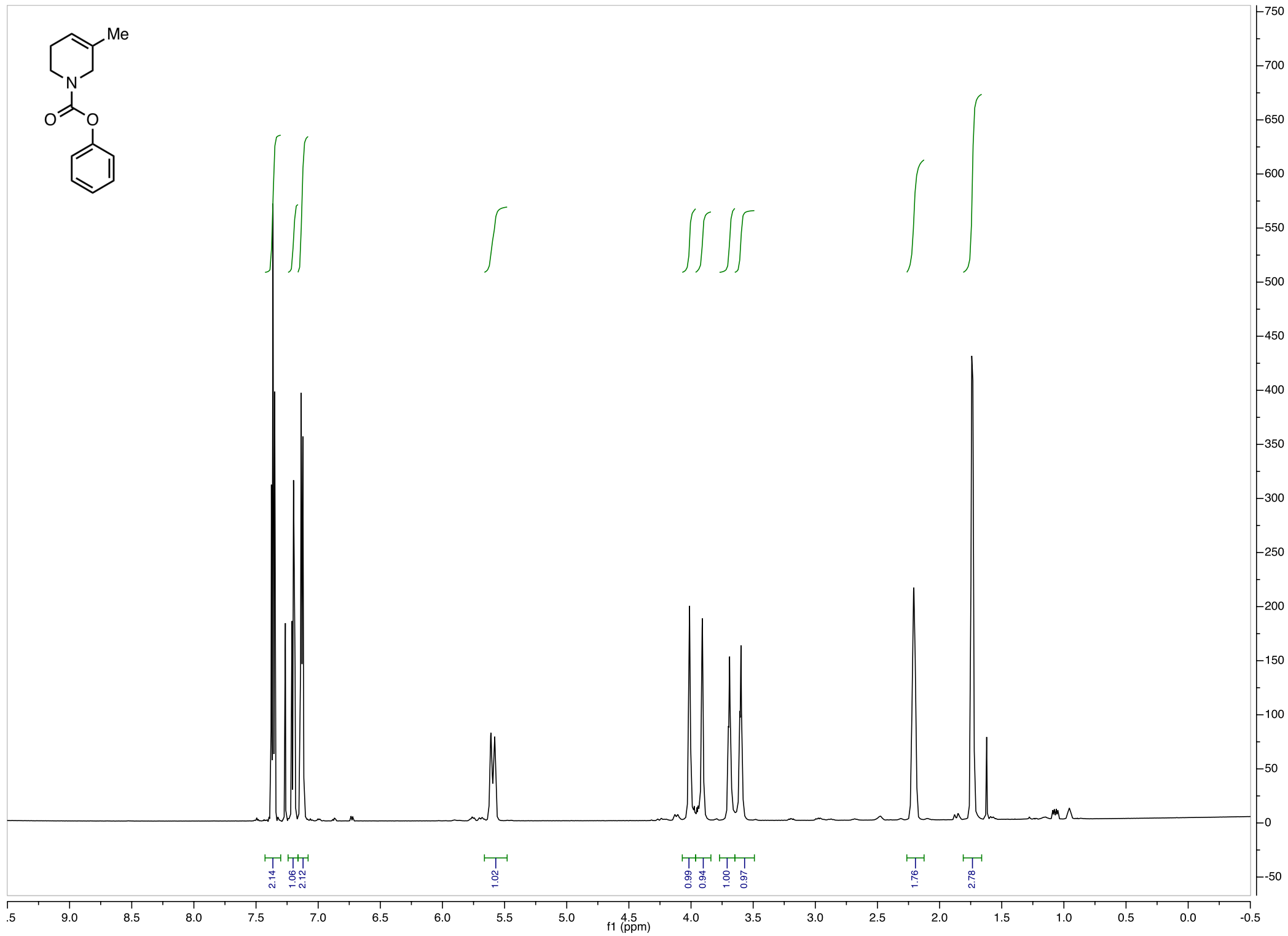
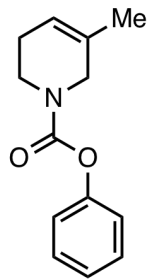


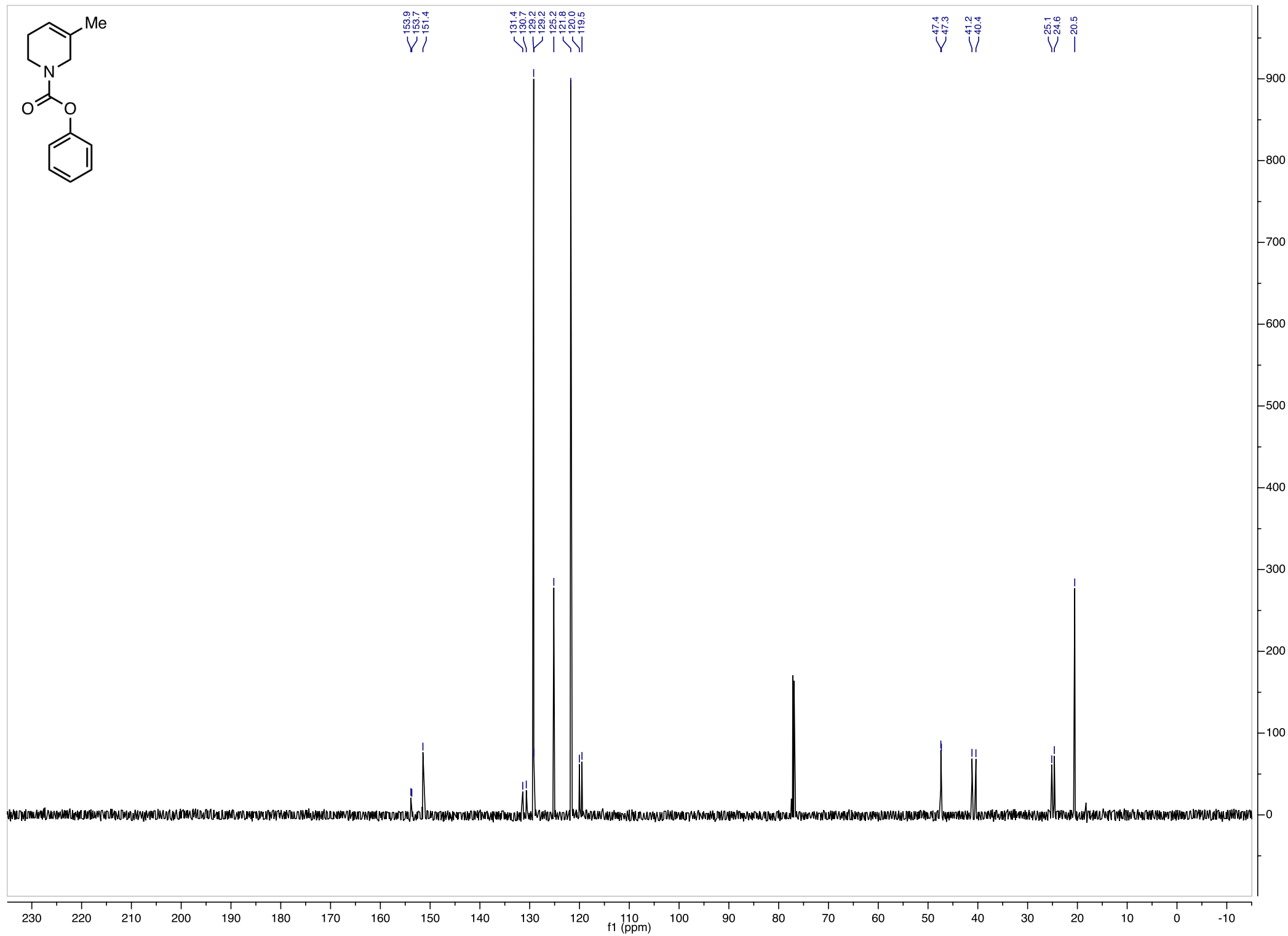
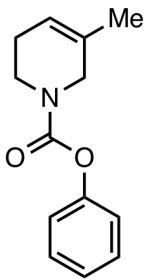
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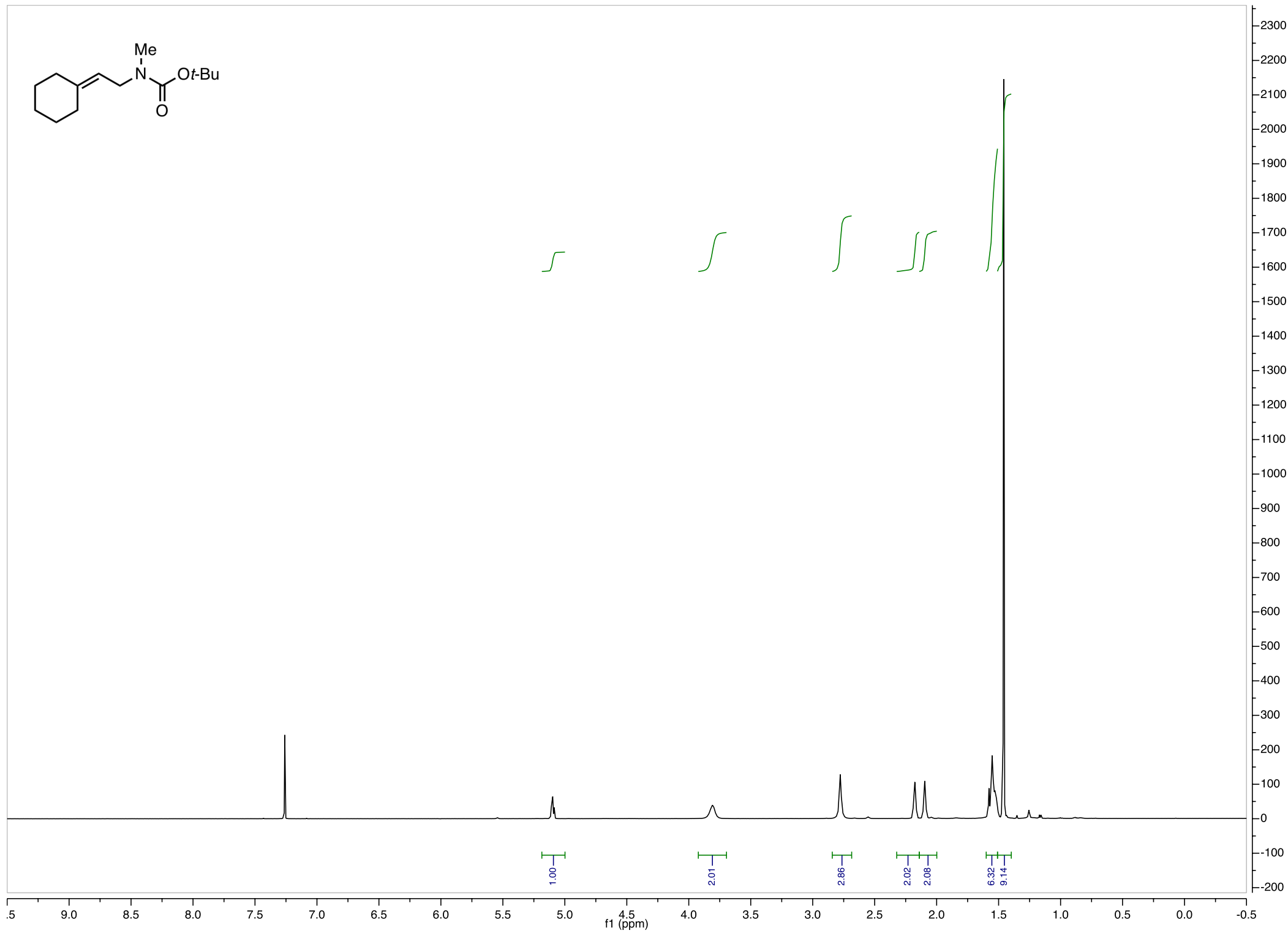
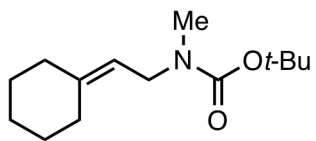


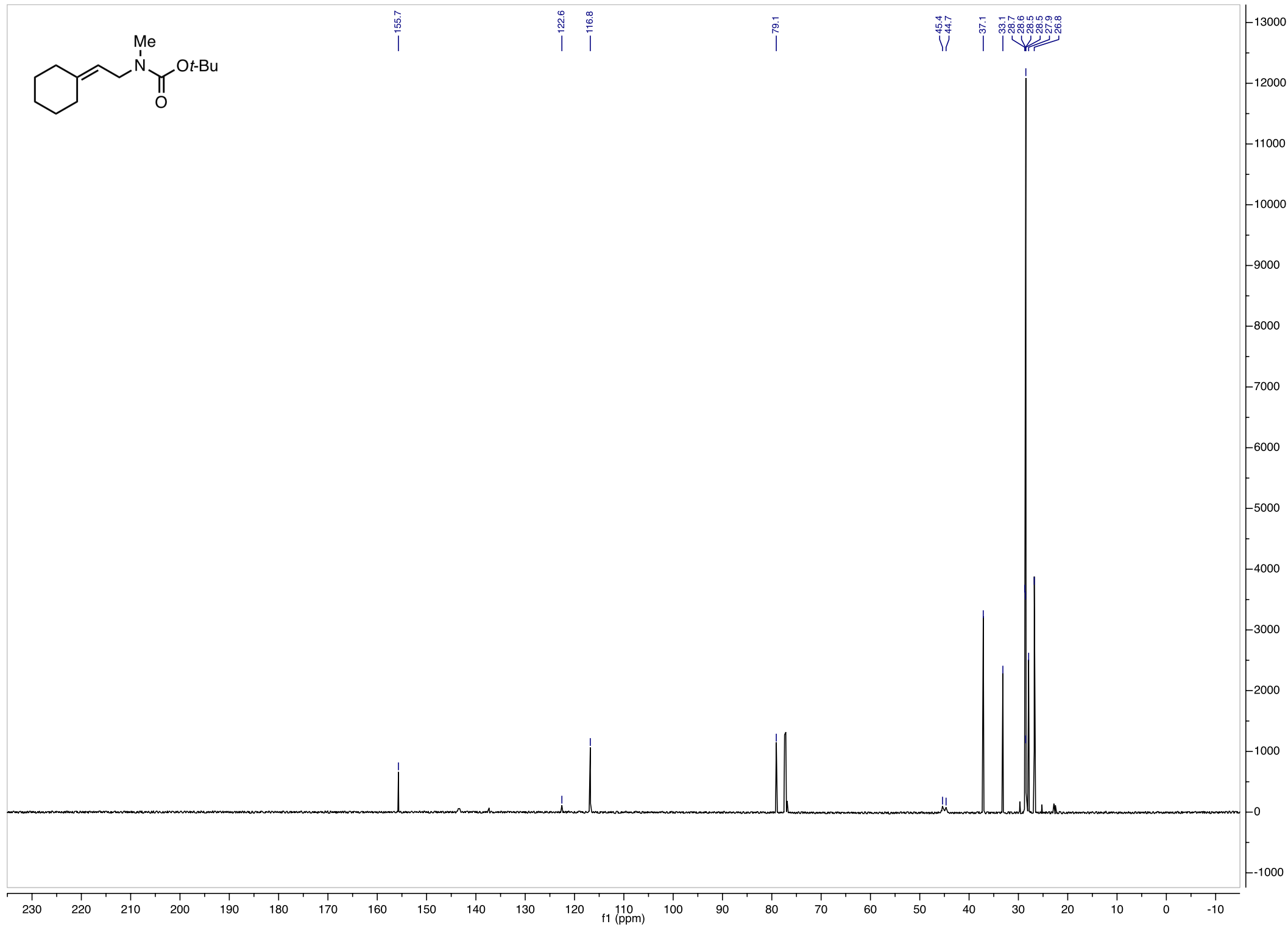
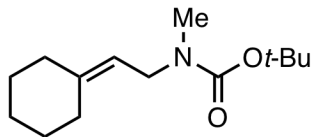


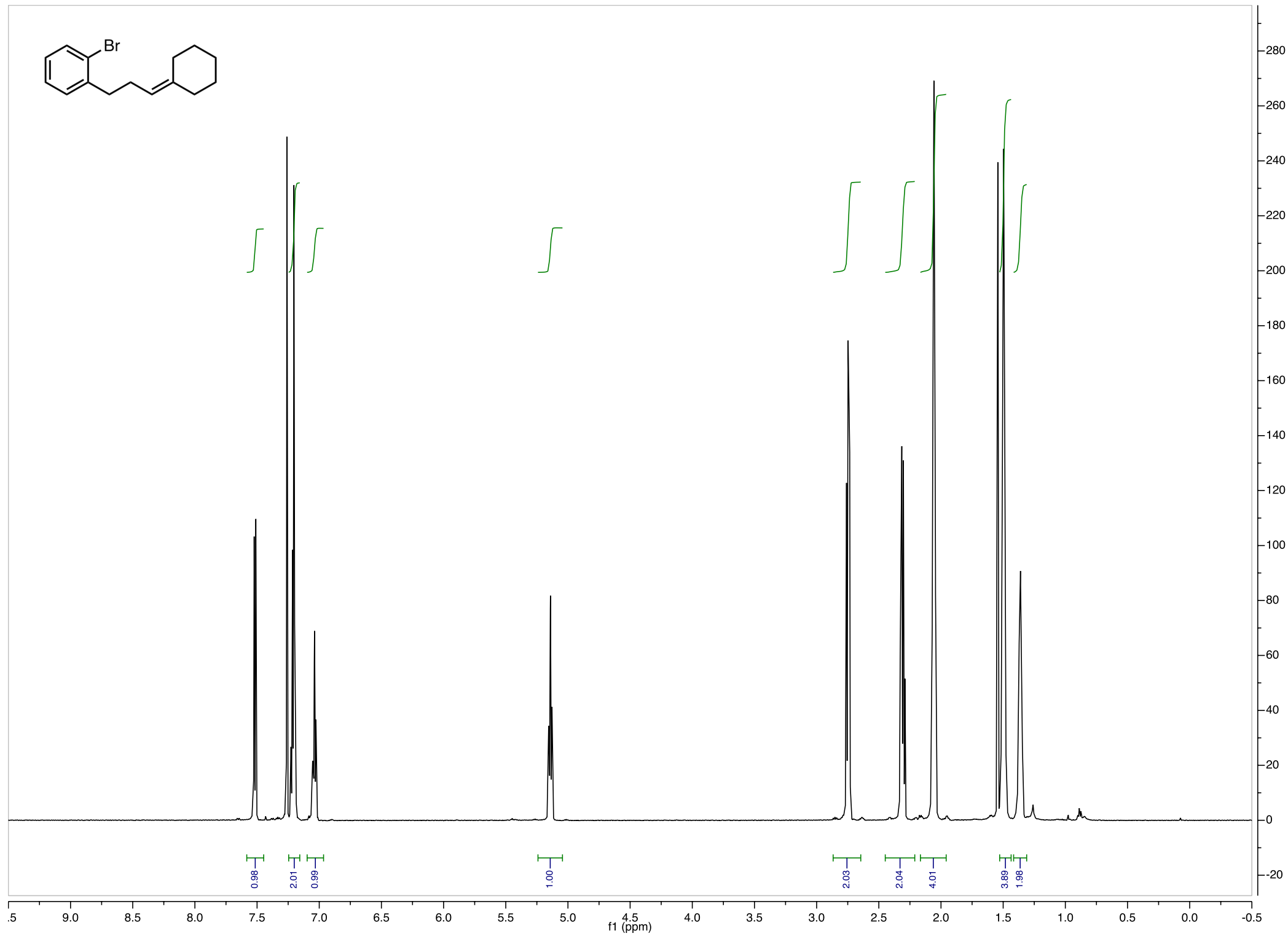
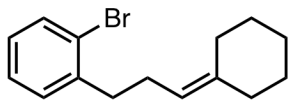


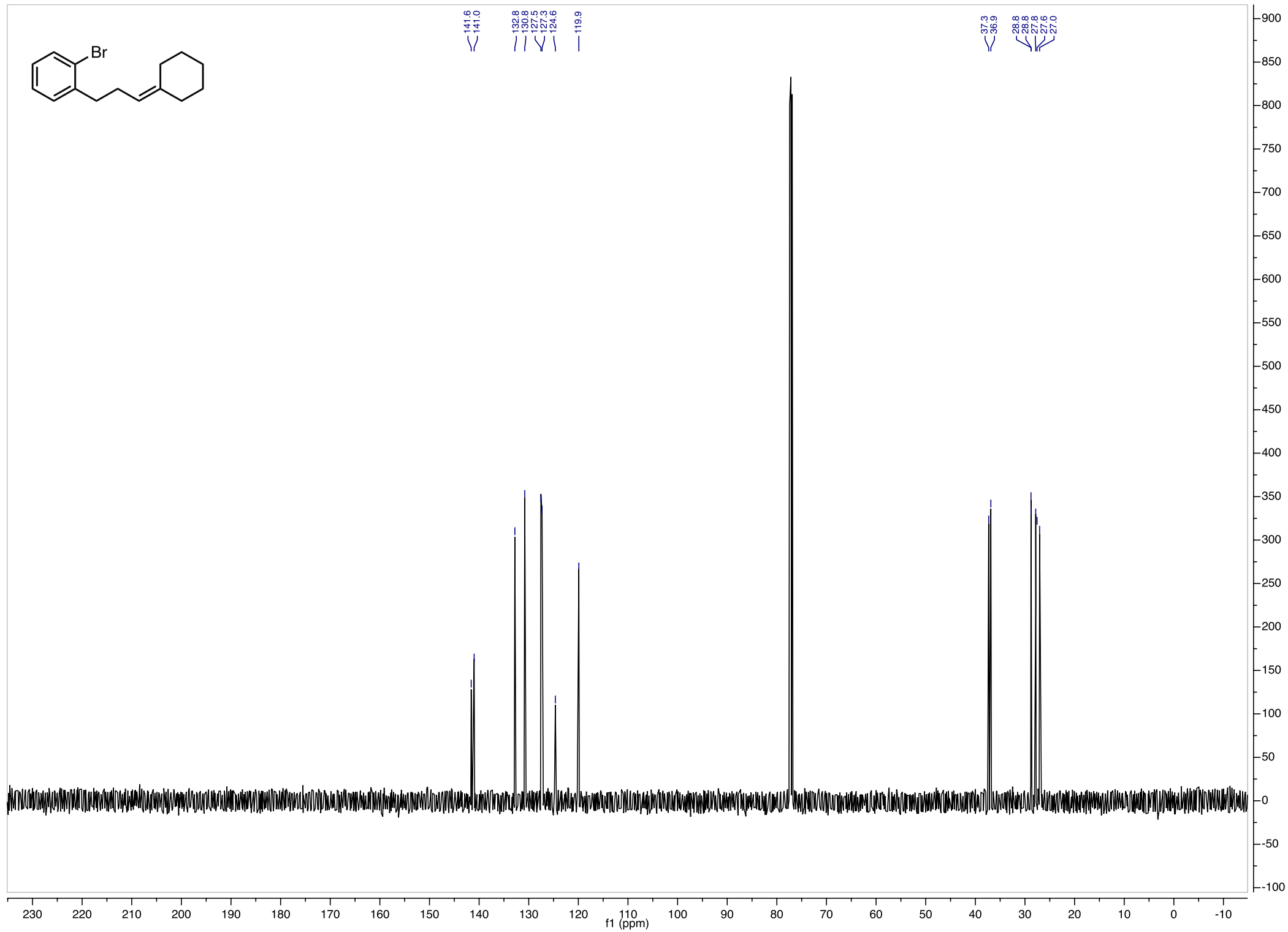
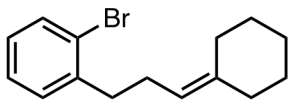


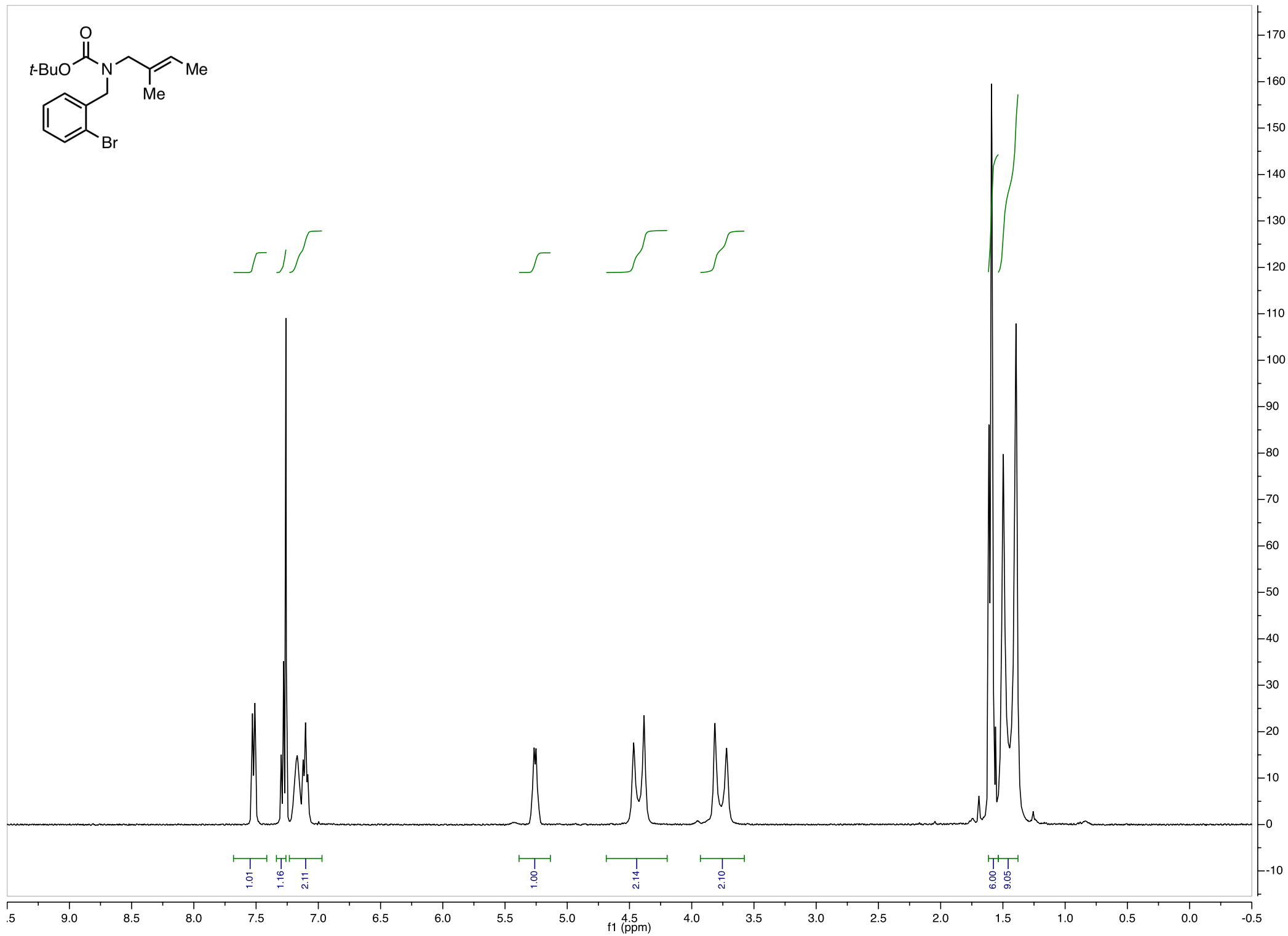
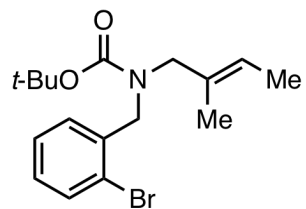


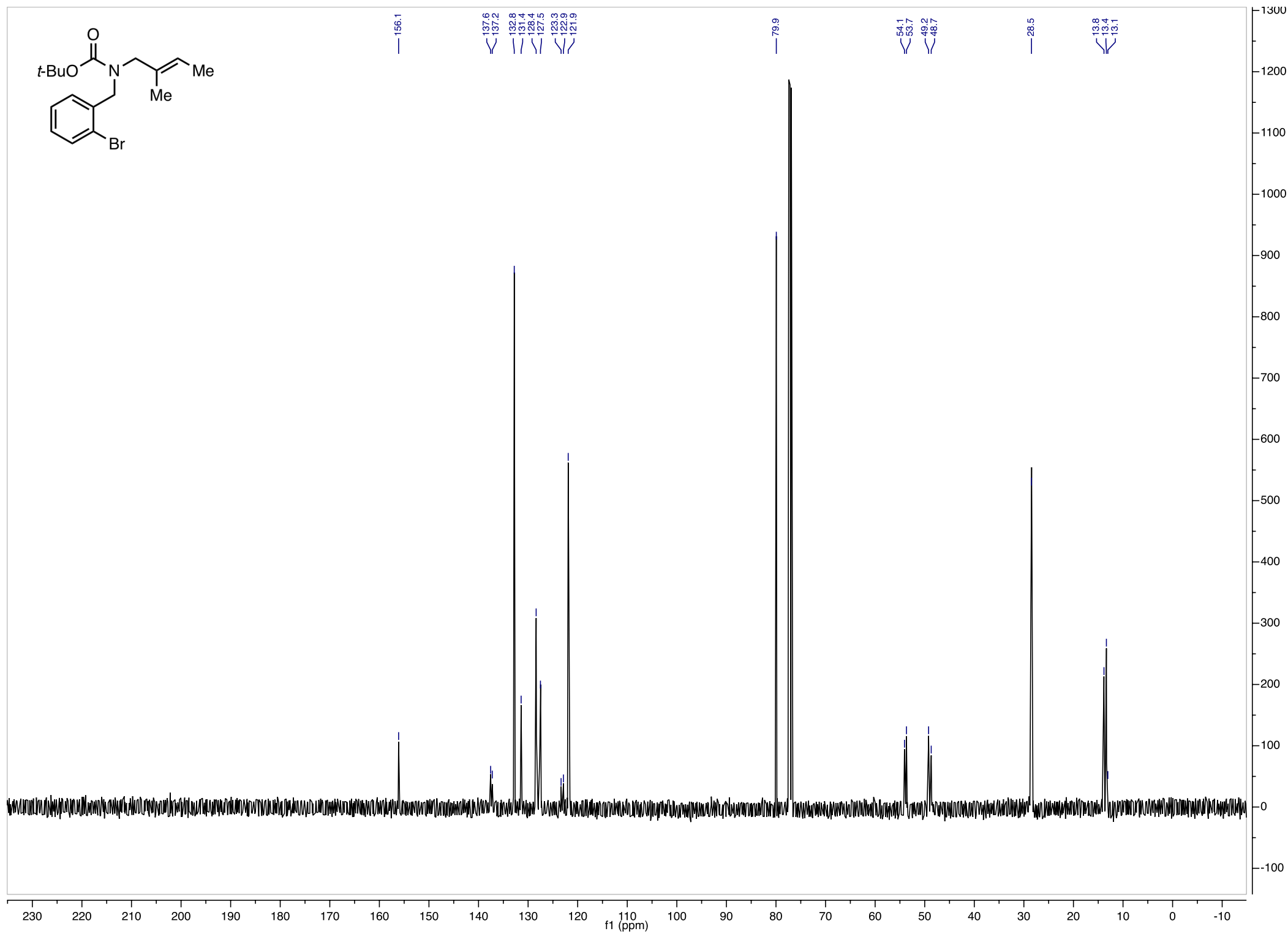
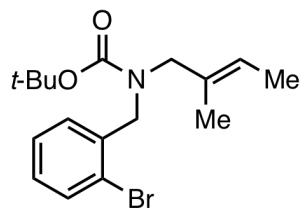


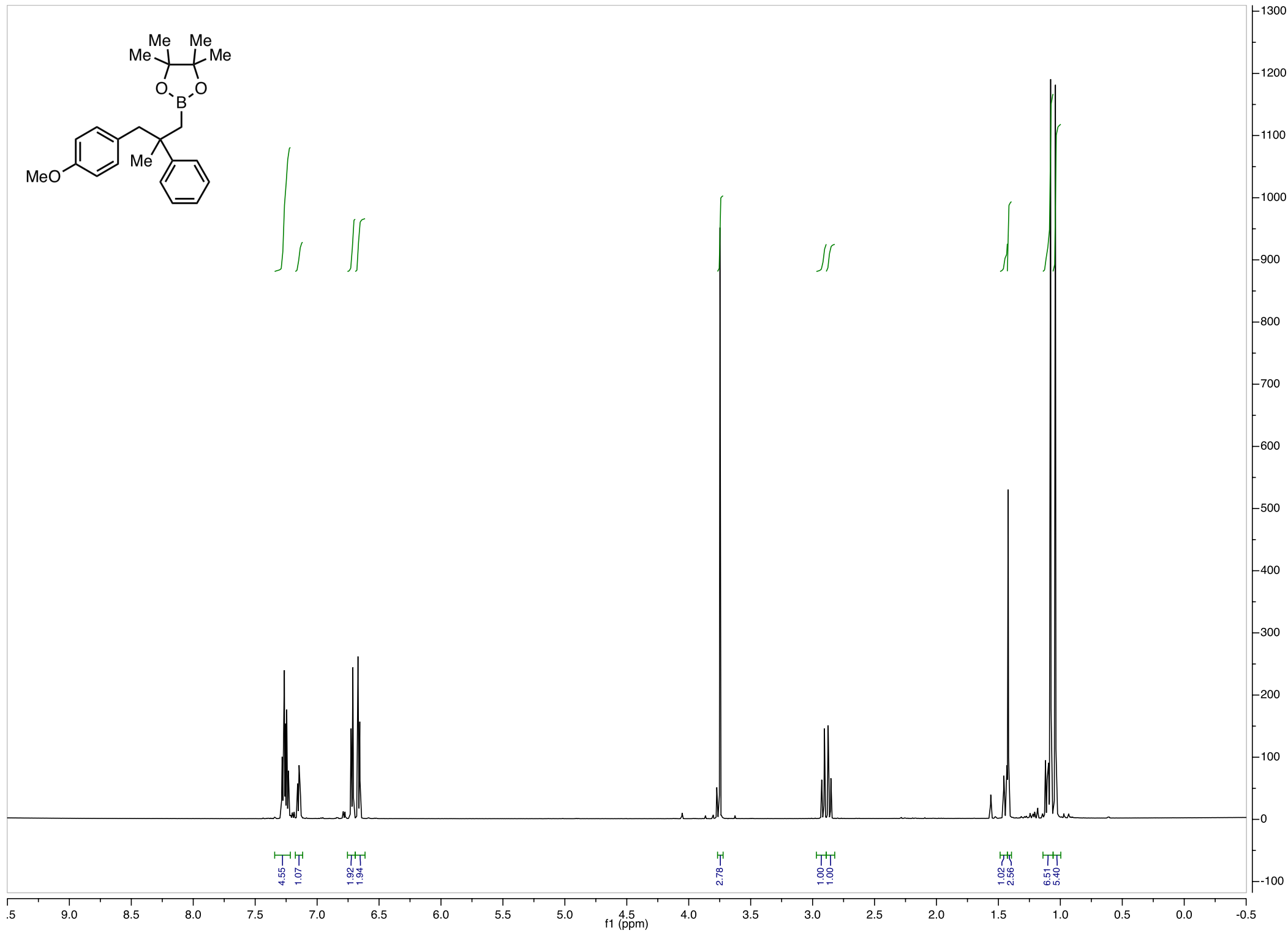
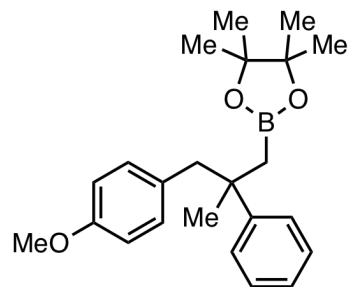


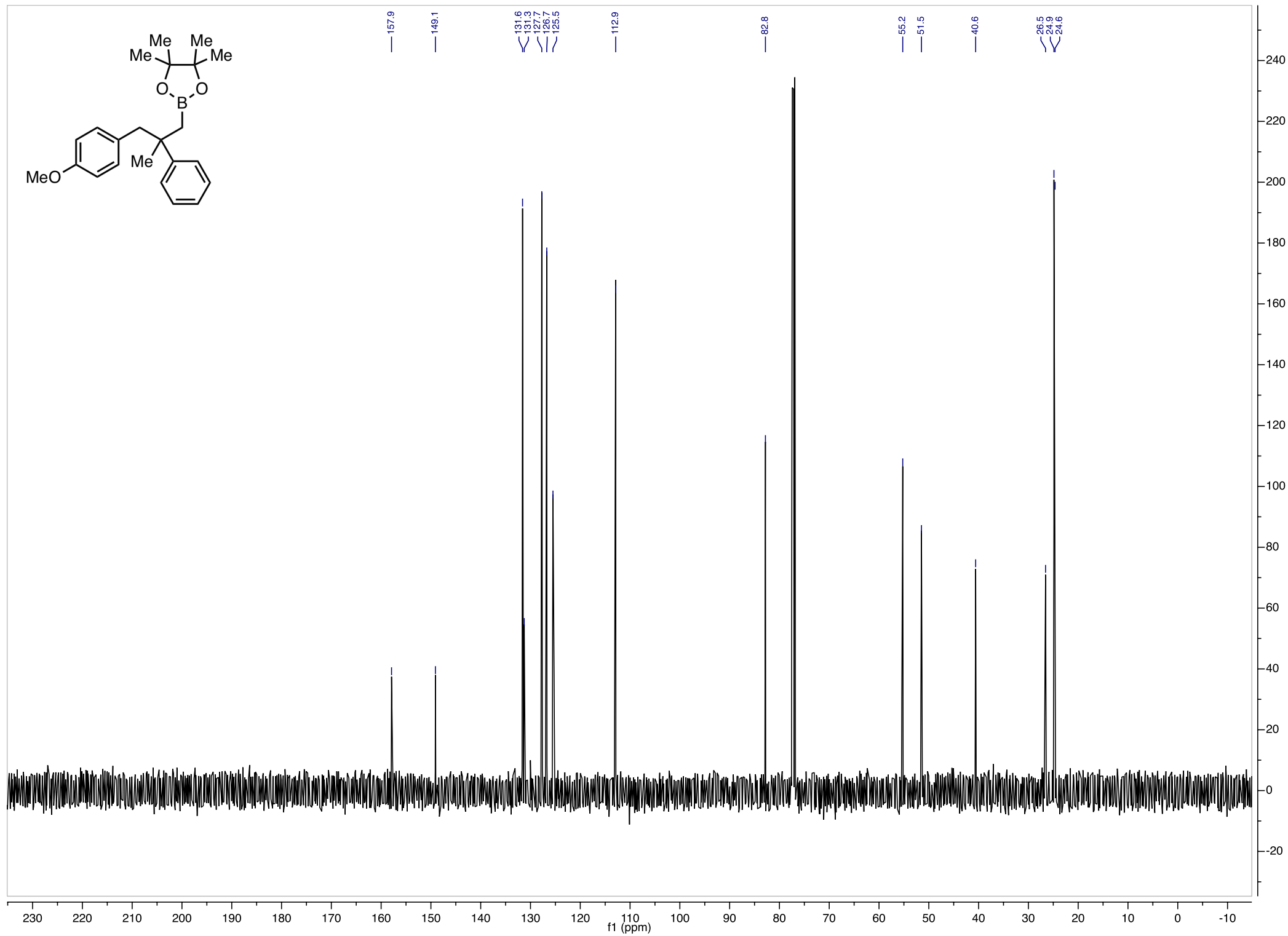
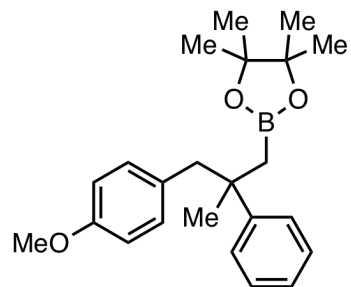


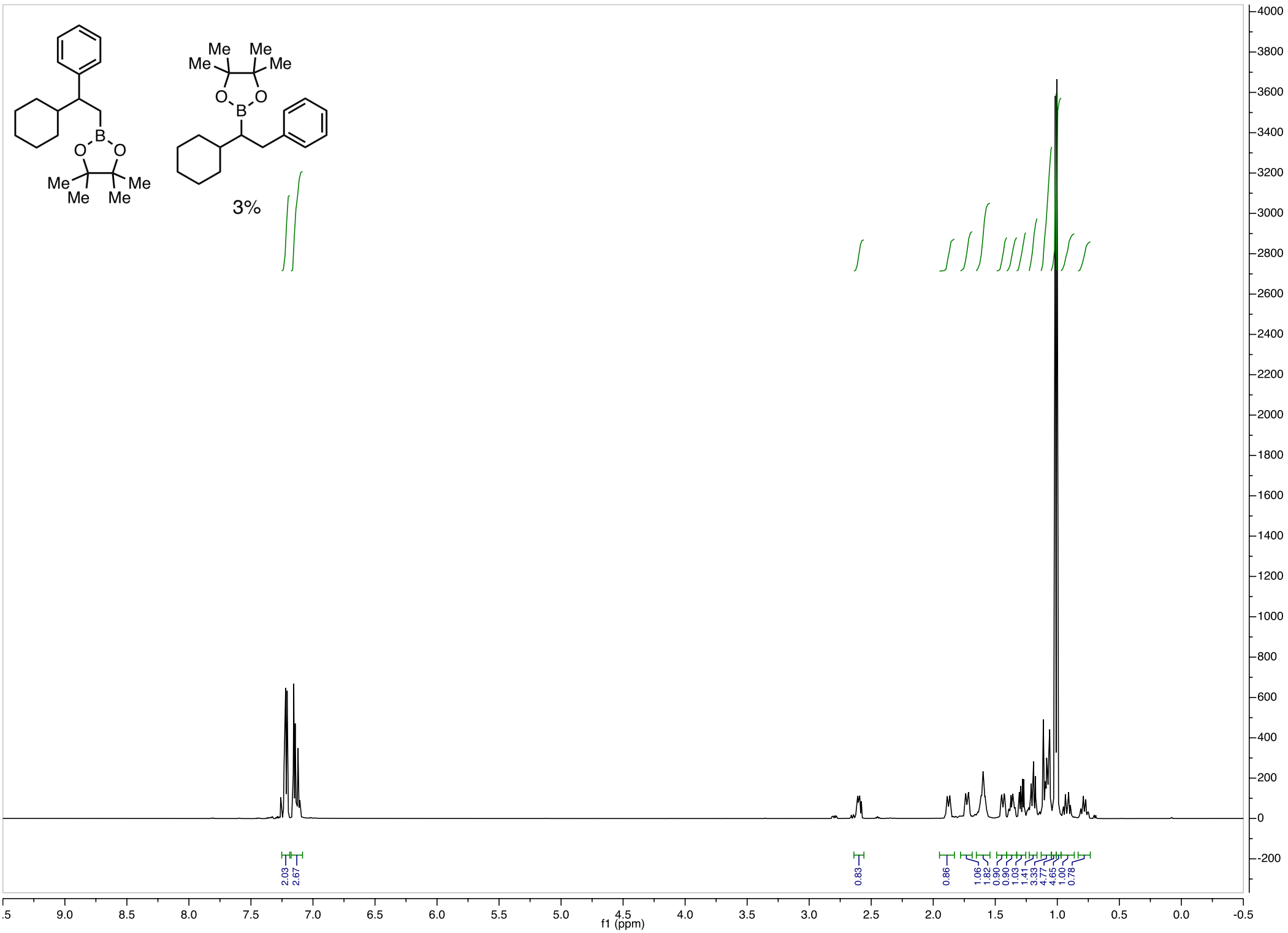


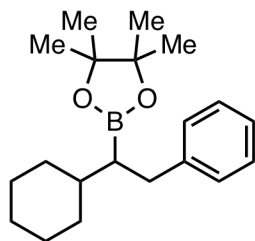
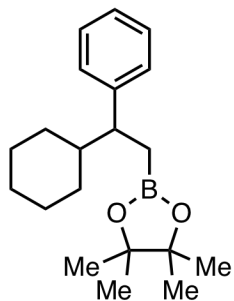




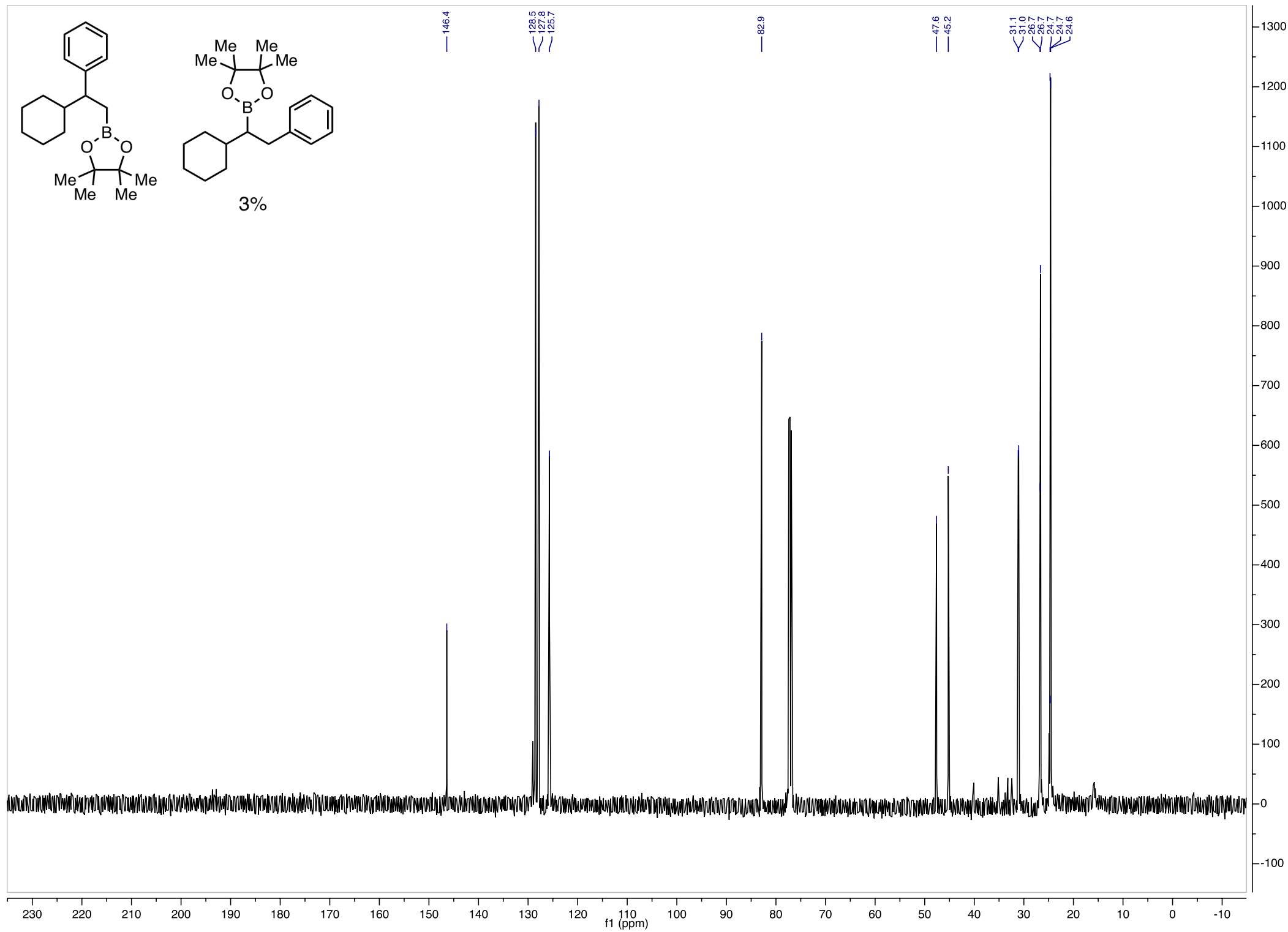


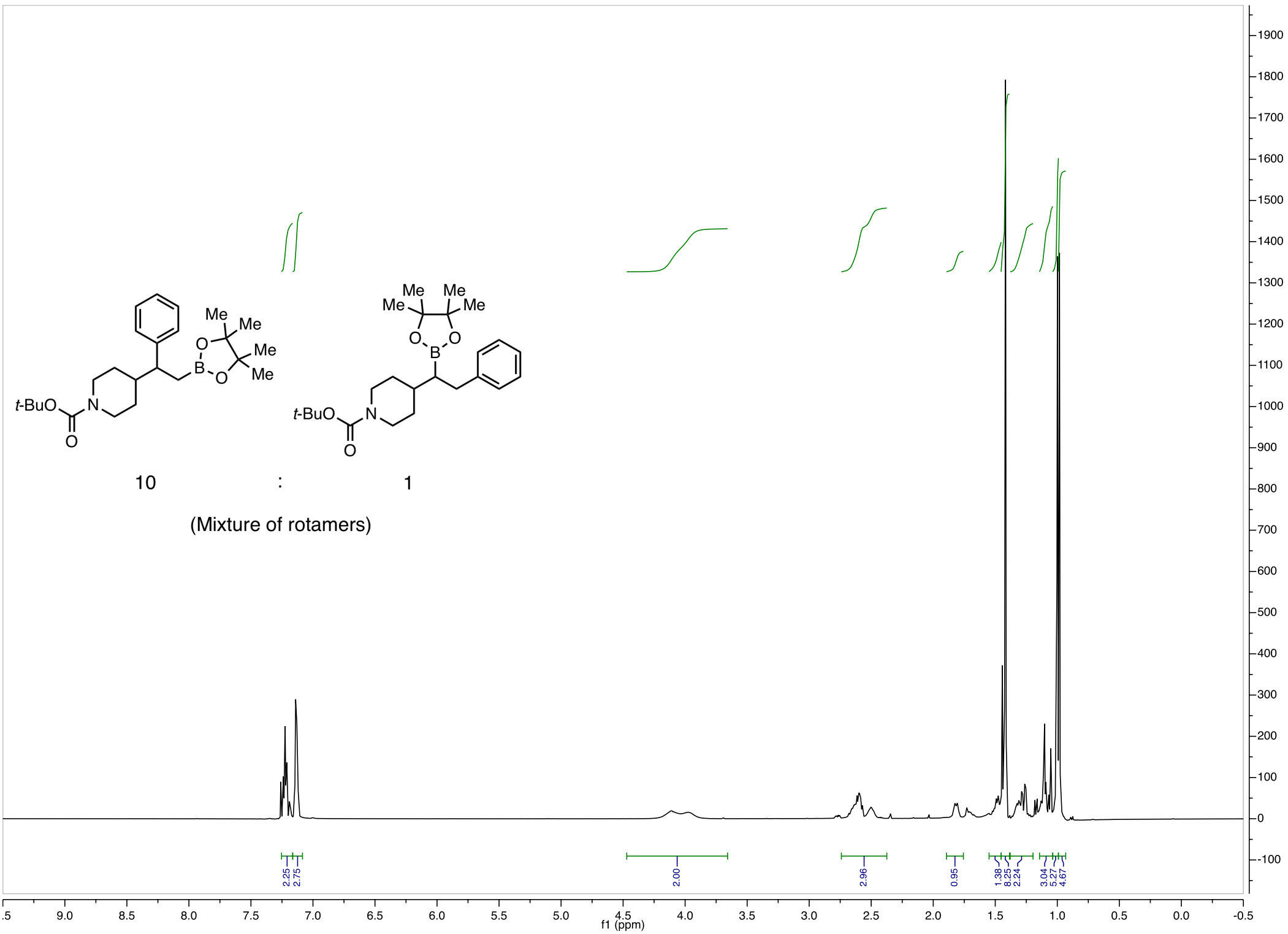


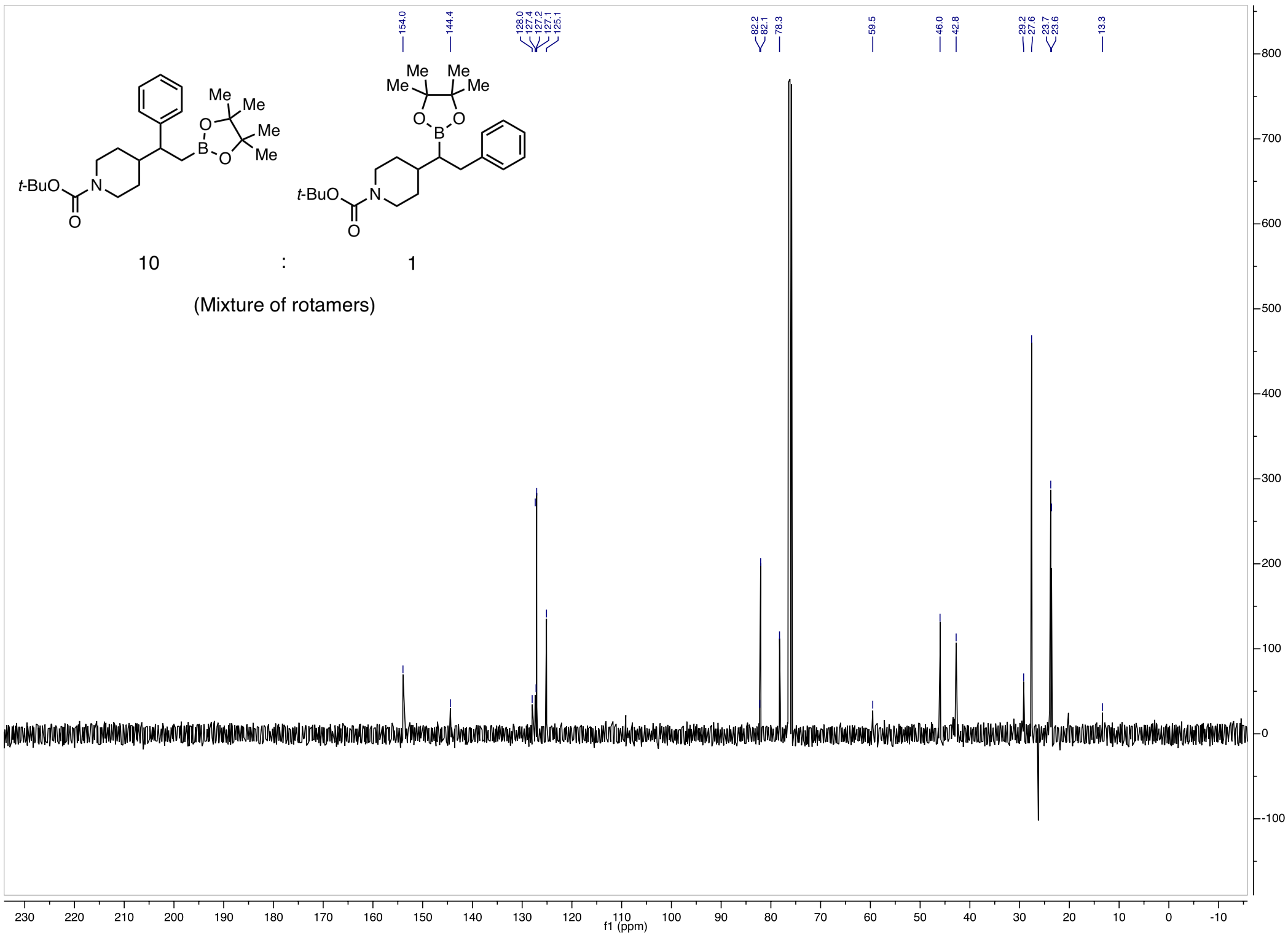


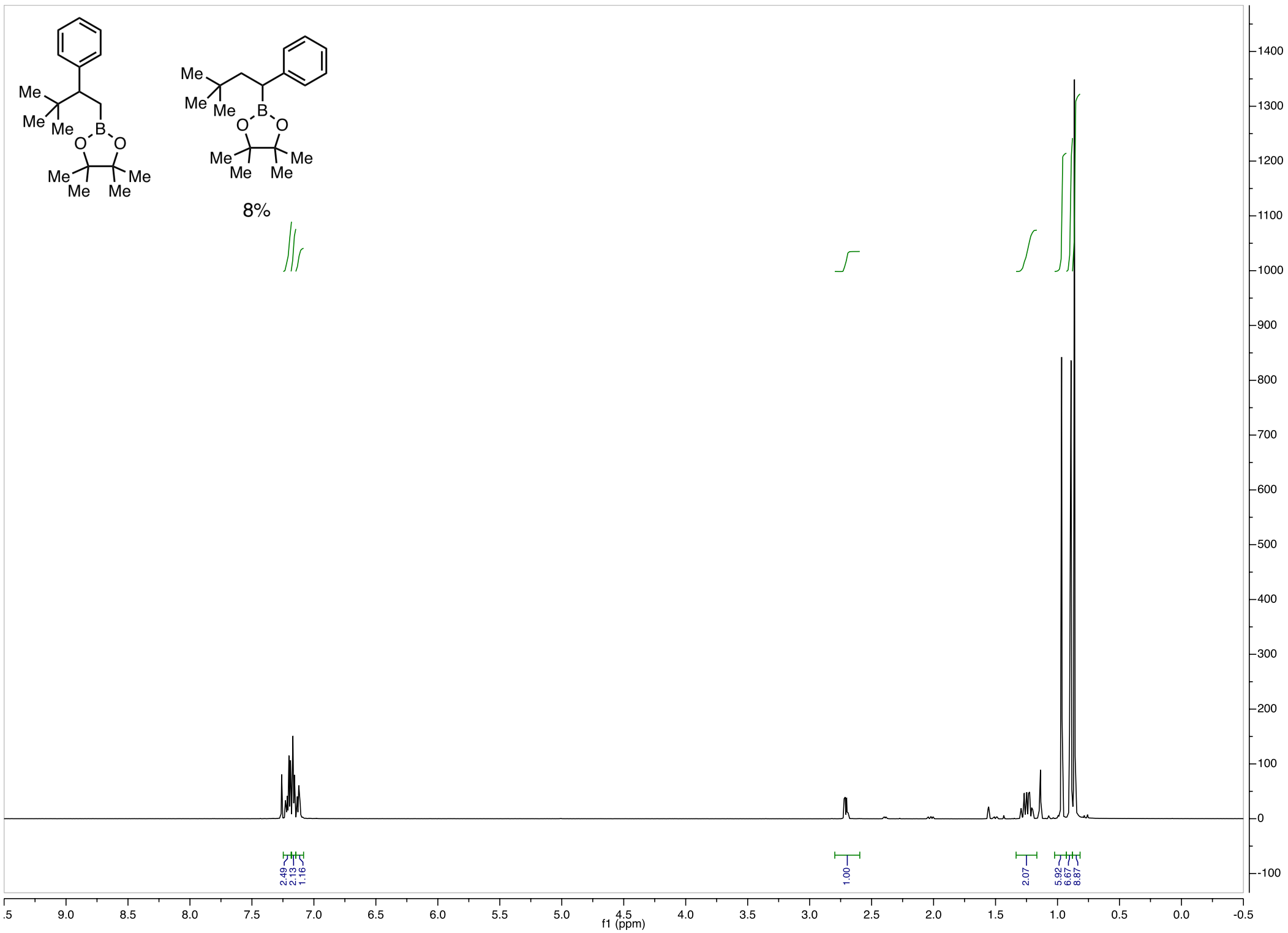


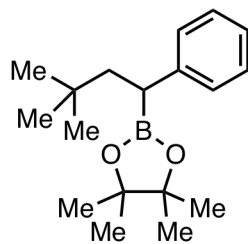
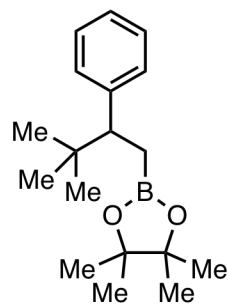
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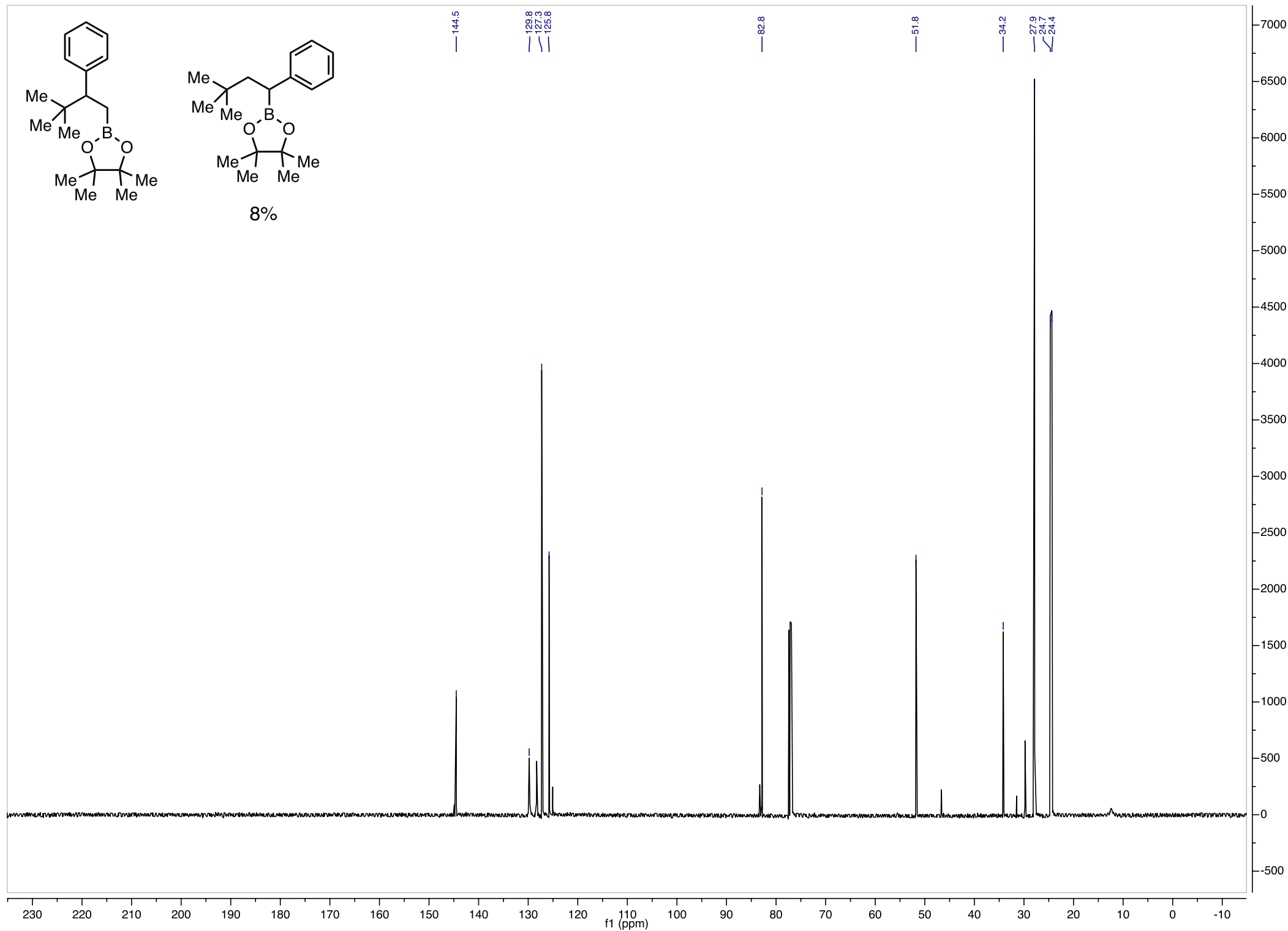


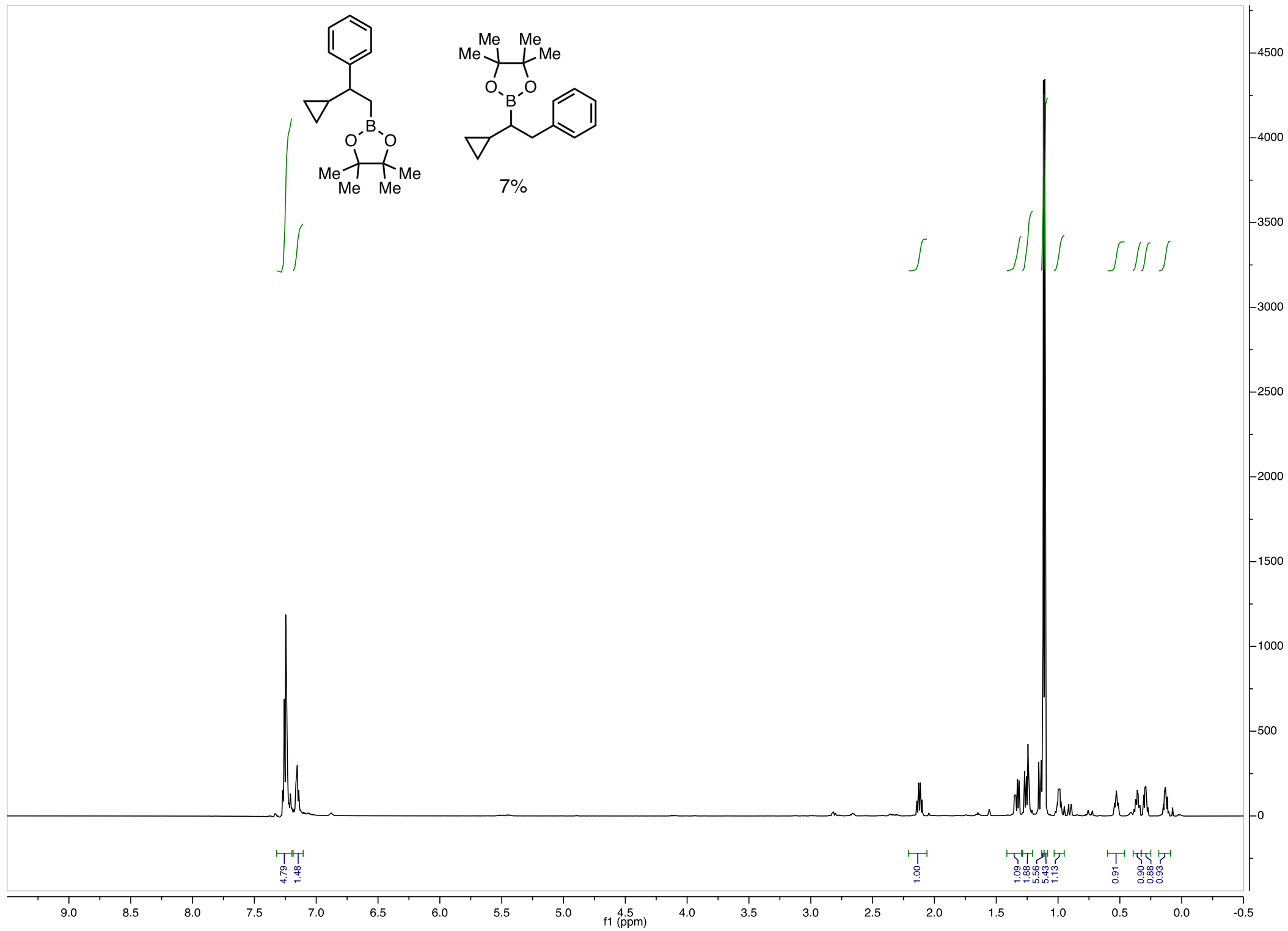


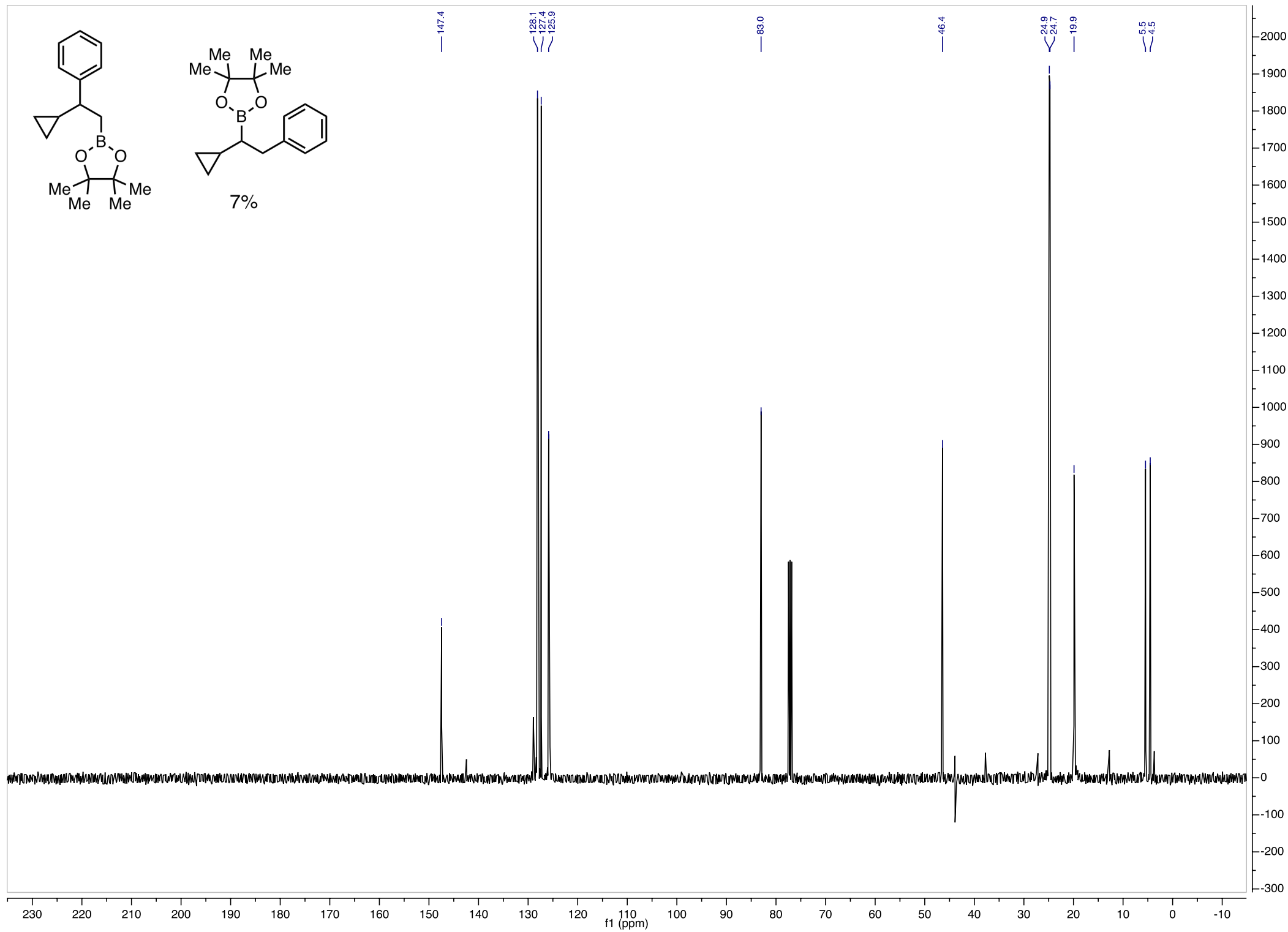
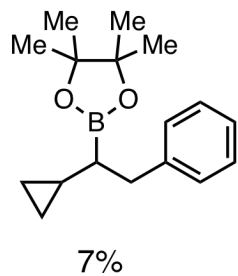


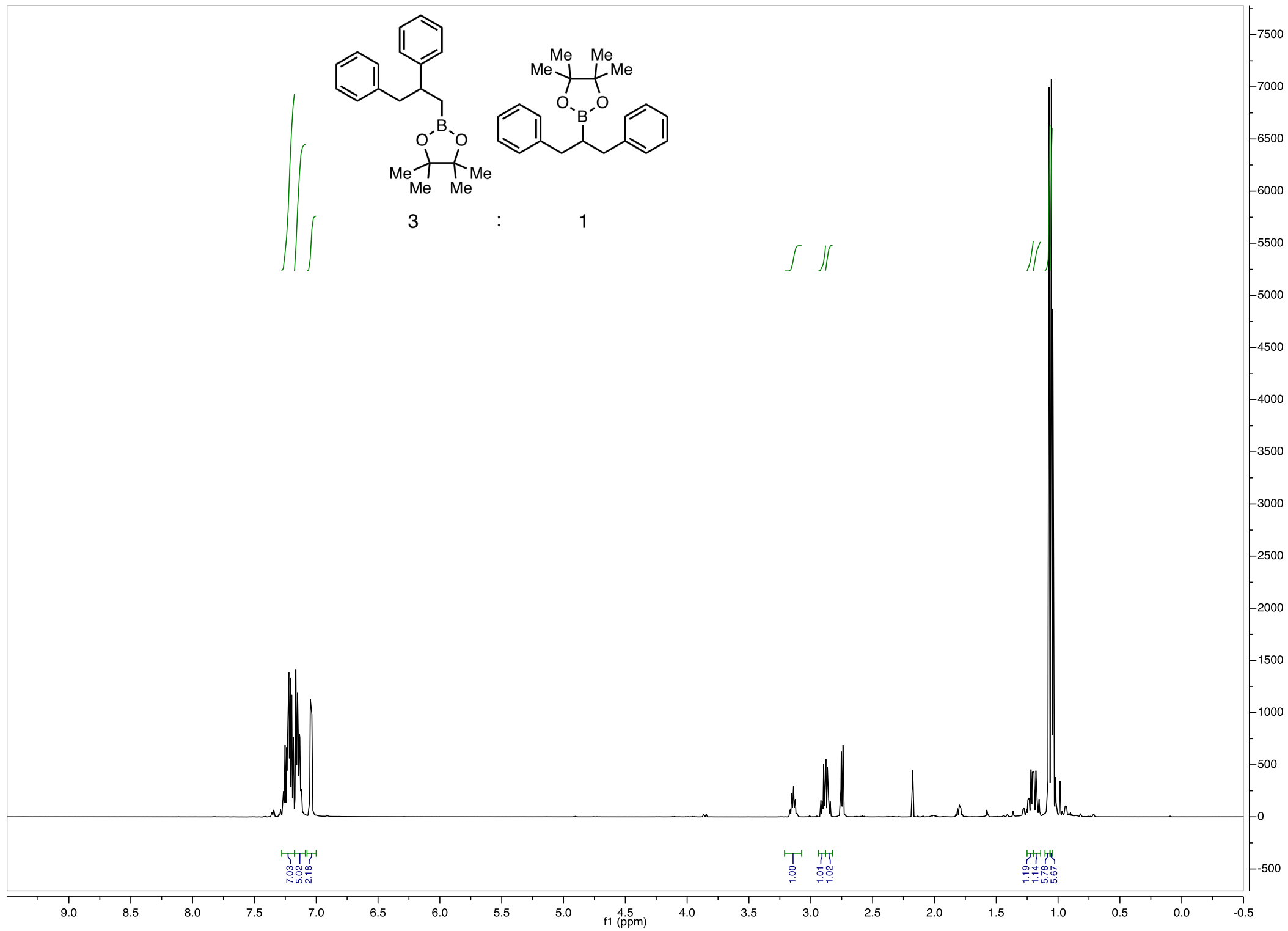


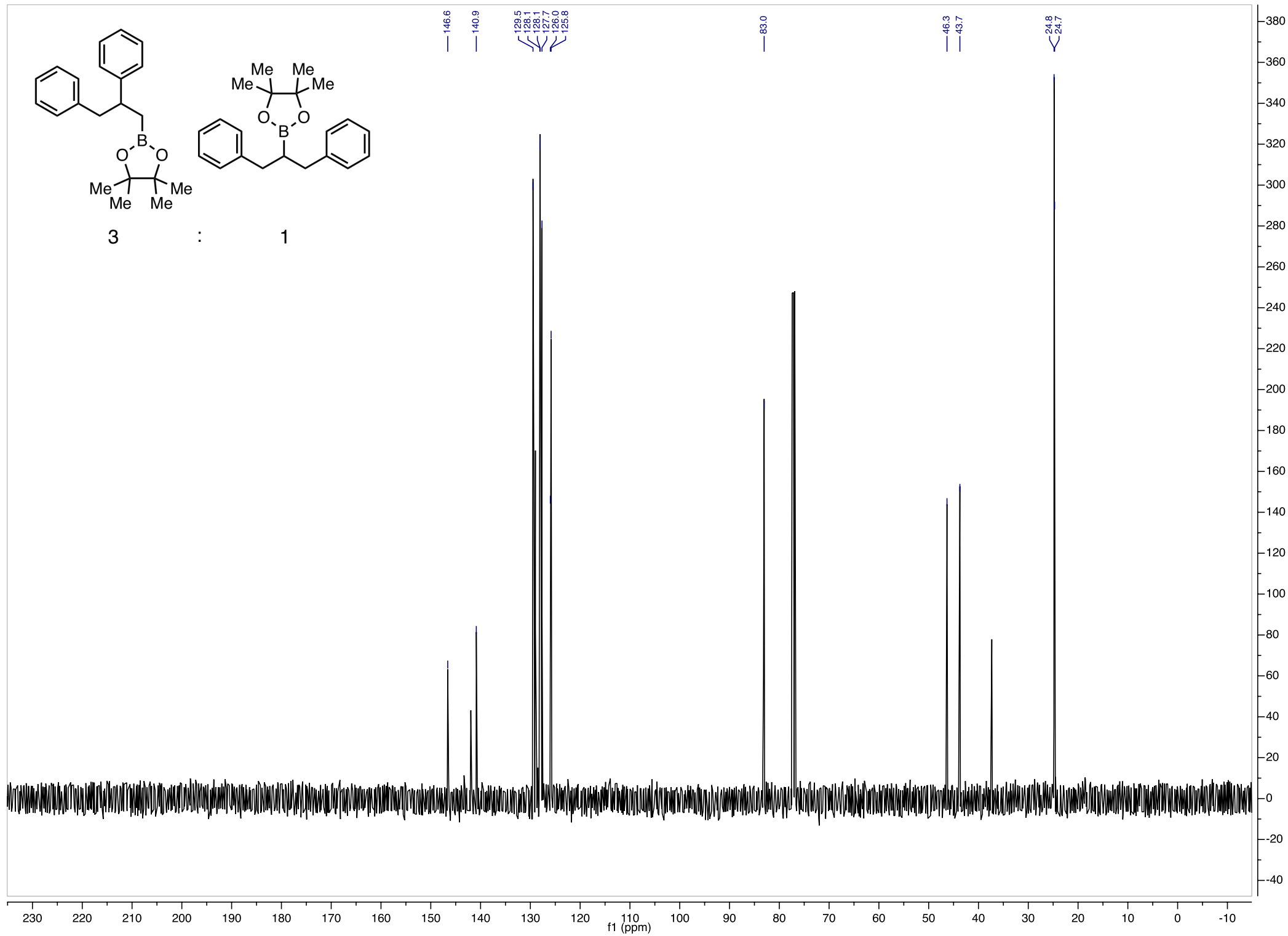
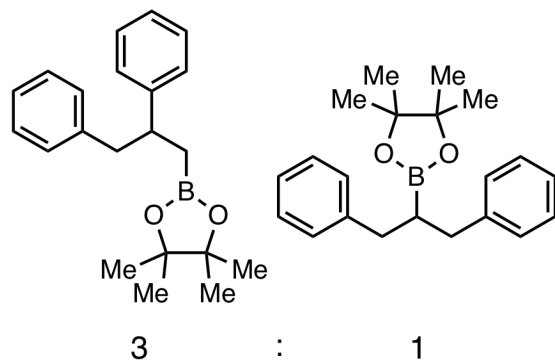
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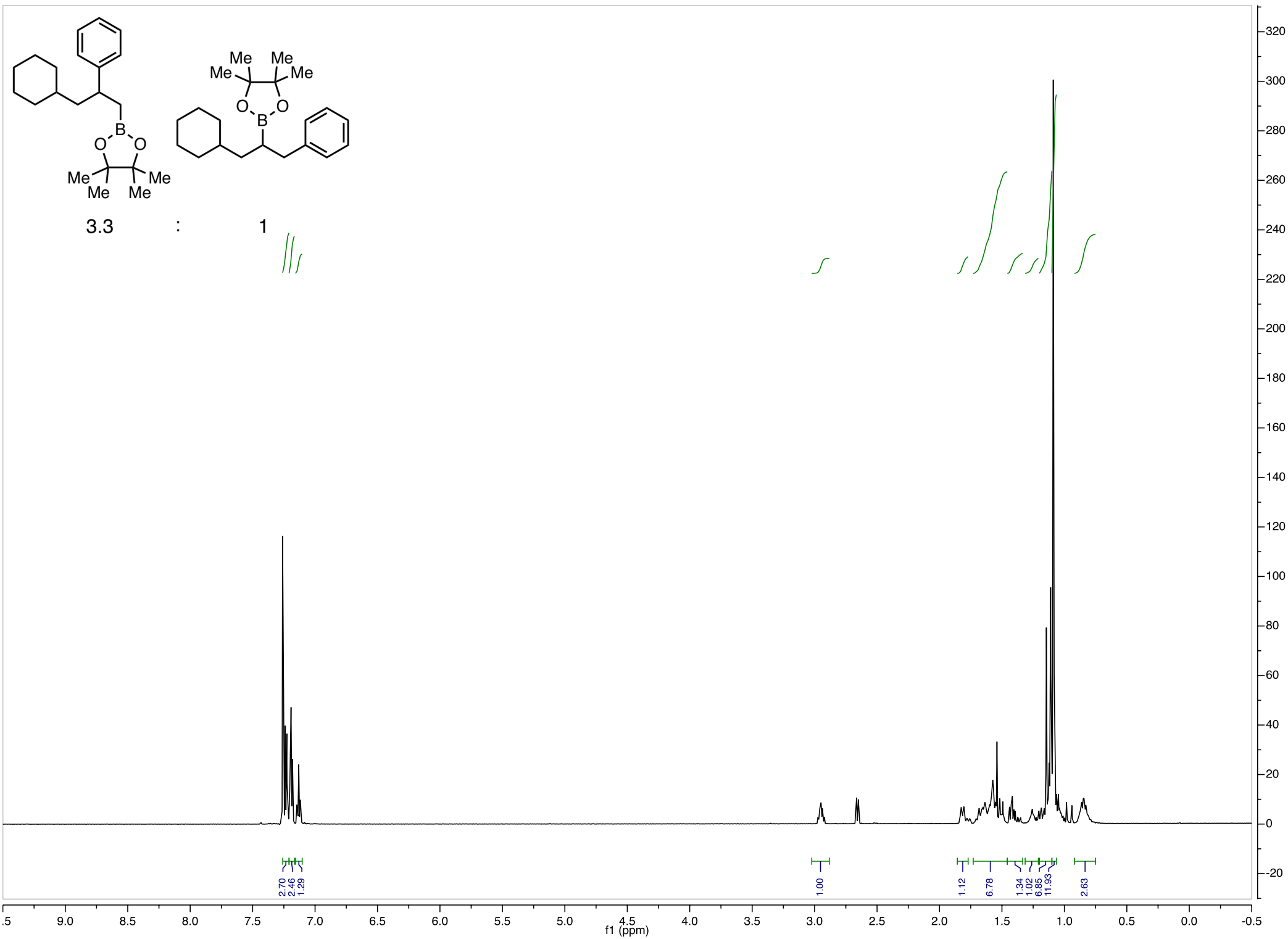


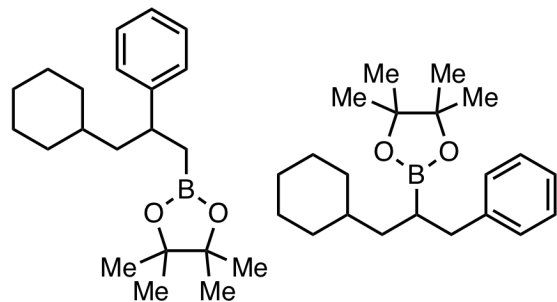




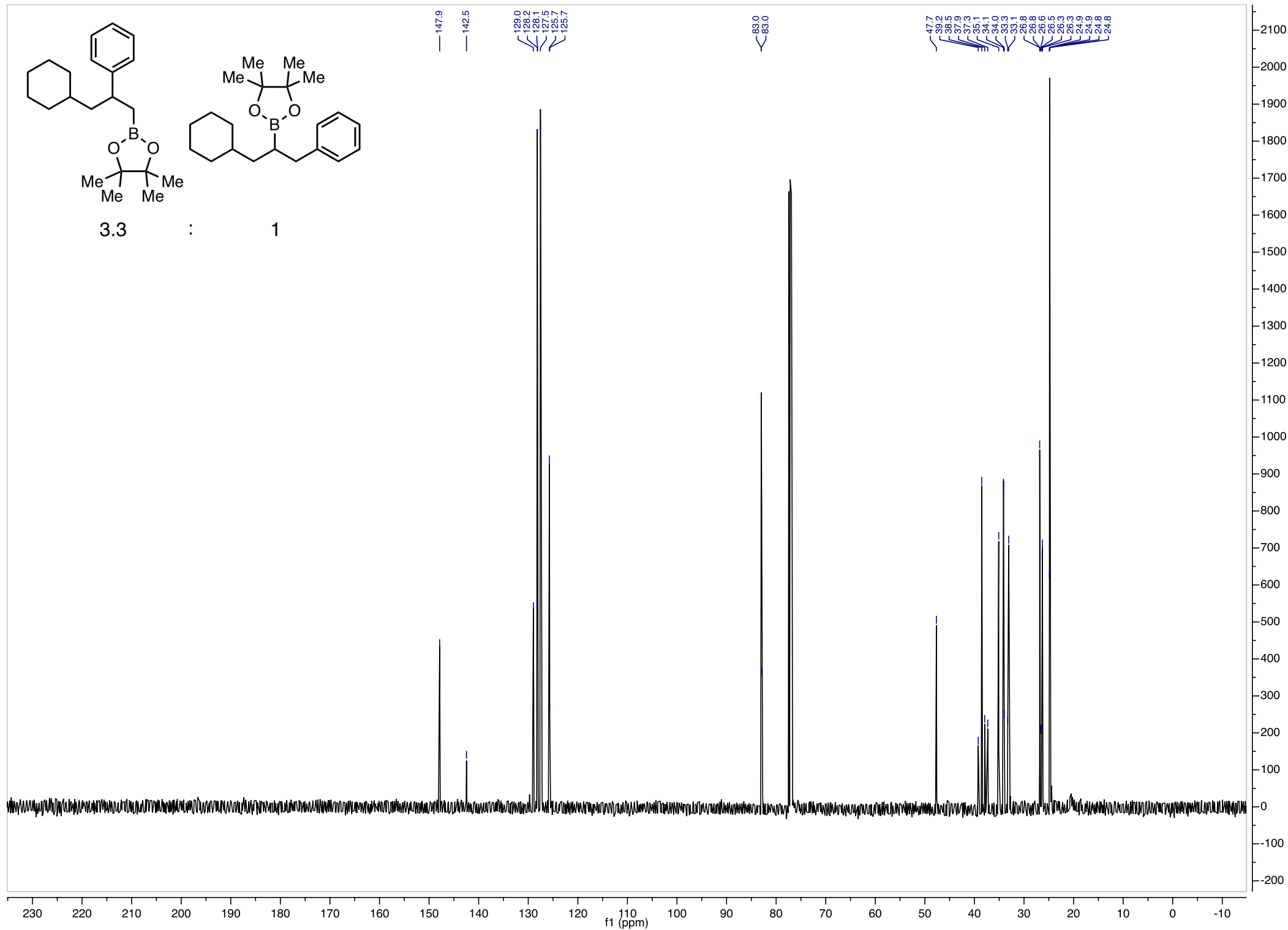


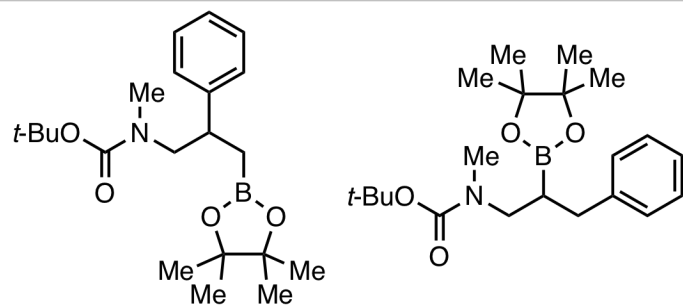






3.3 : 1



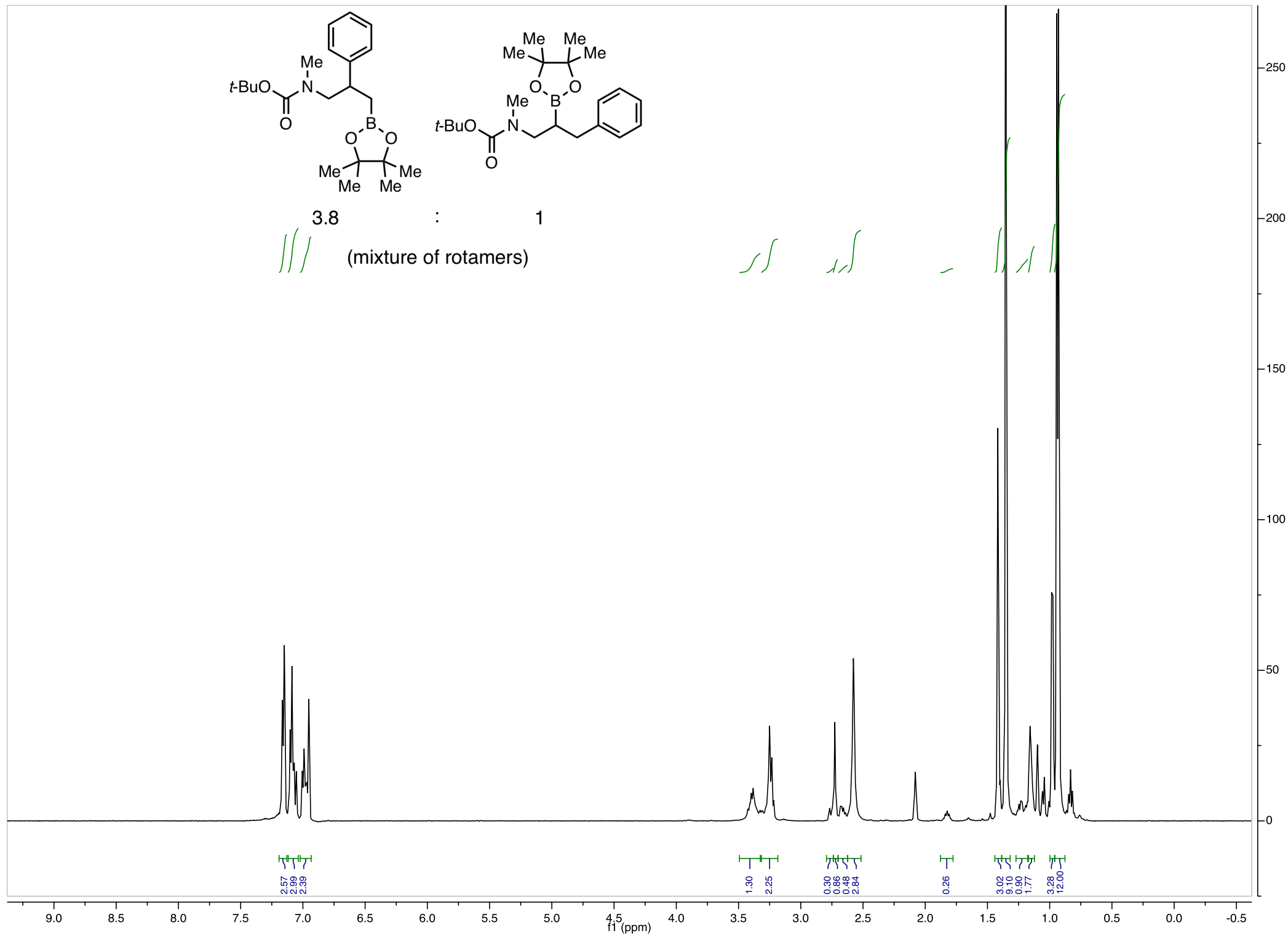


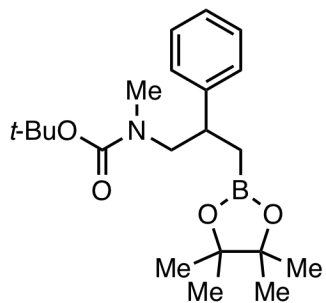
3.8

:

1

(mixture of rotamers)



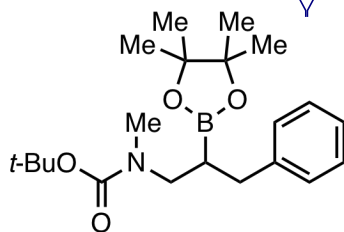


3.8

:

1

(mixture of rotamers)



155.9
155.6

145.8

142.6

128.4

128.3

128.5

128.4

126.5

126.1

83.4

83.2

78.8

78.7

57.6

41.1

35.7

35.1

34.6

28.8

28.7

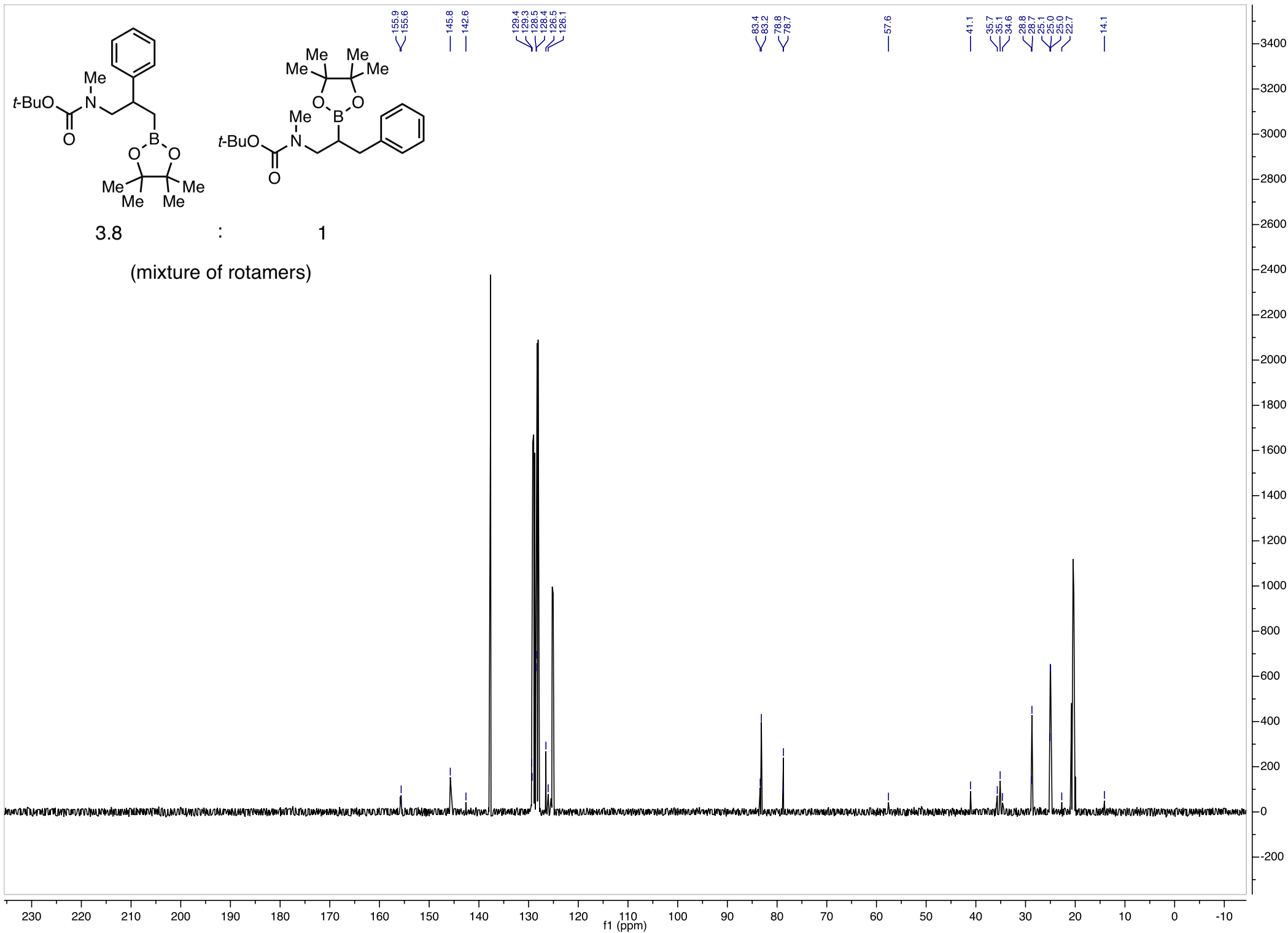
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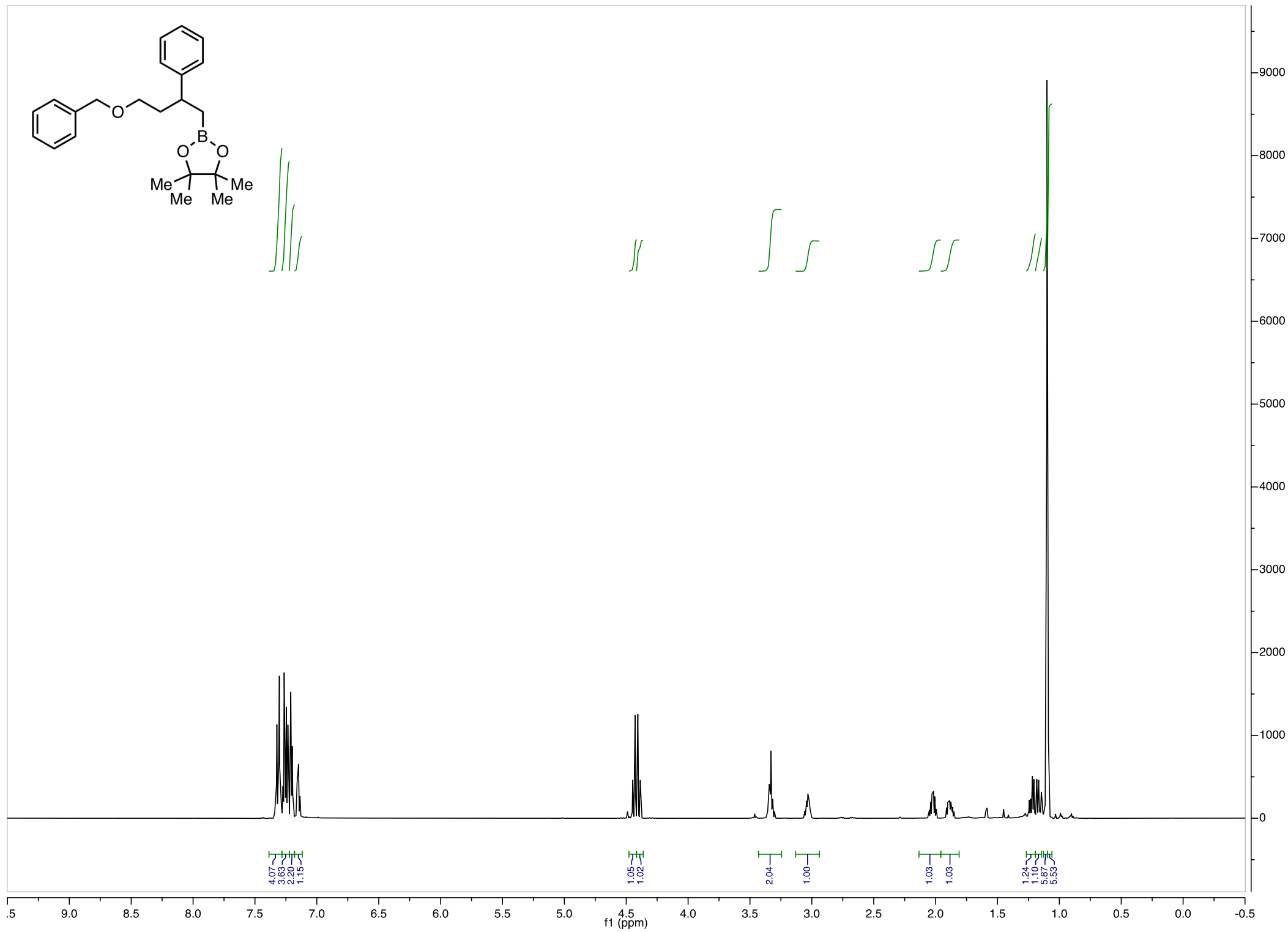
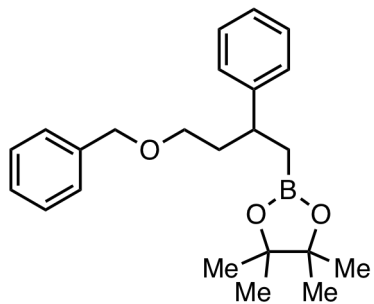
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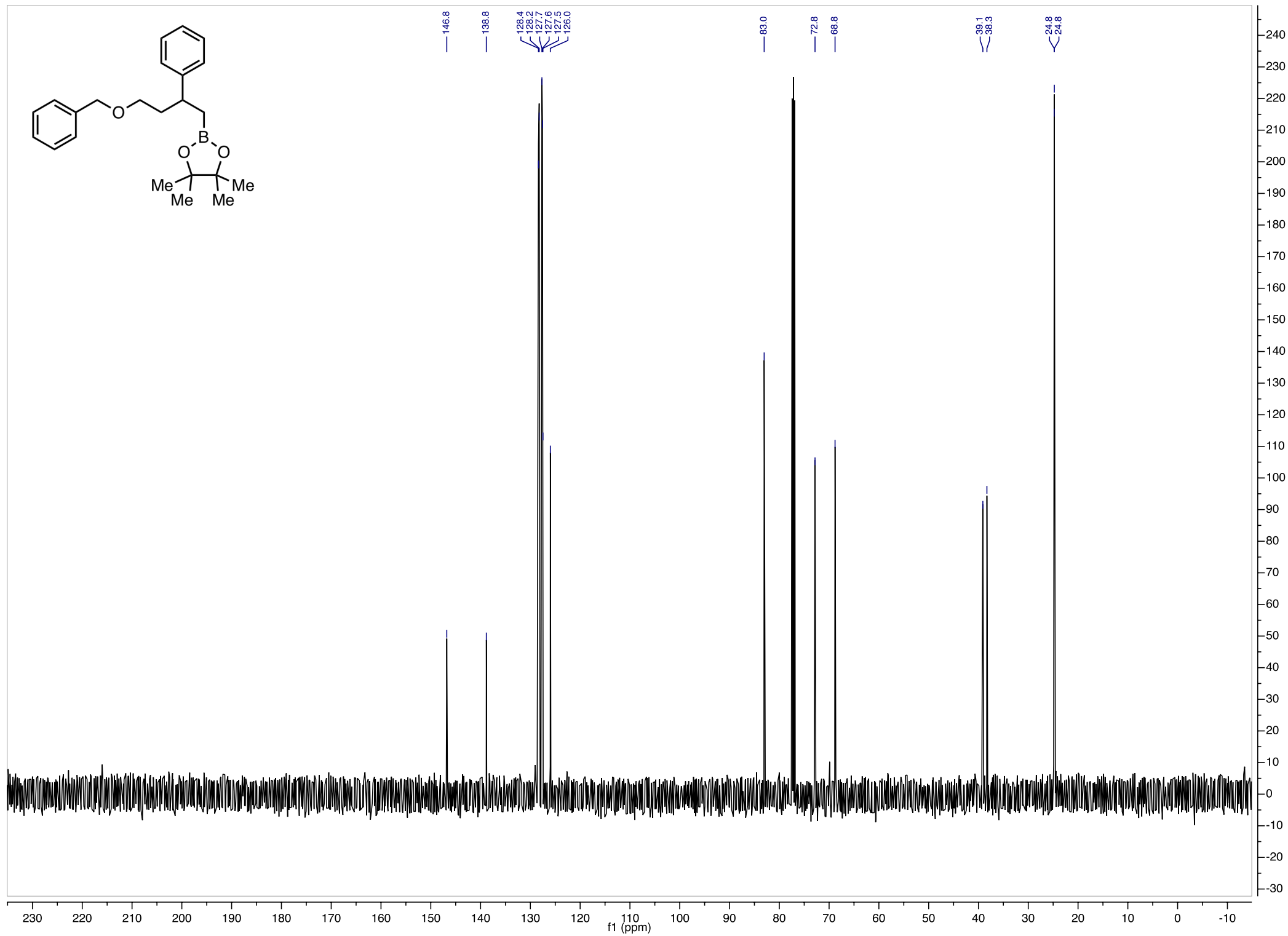
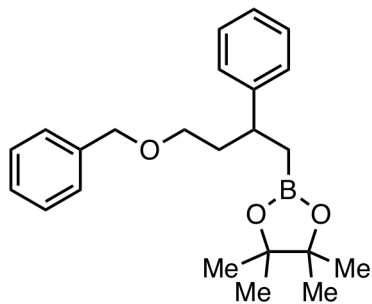
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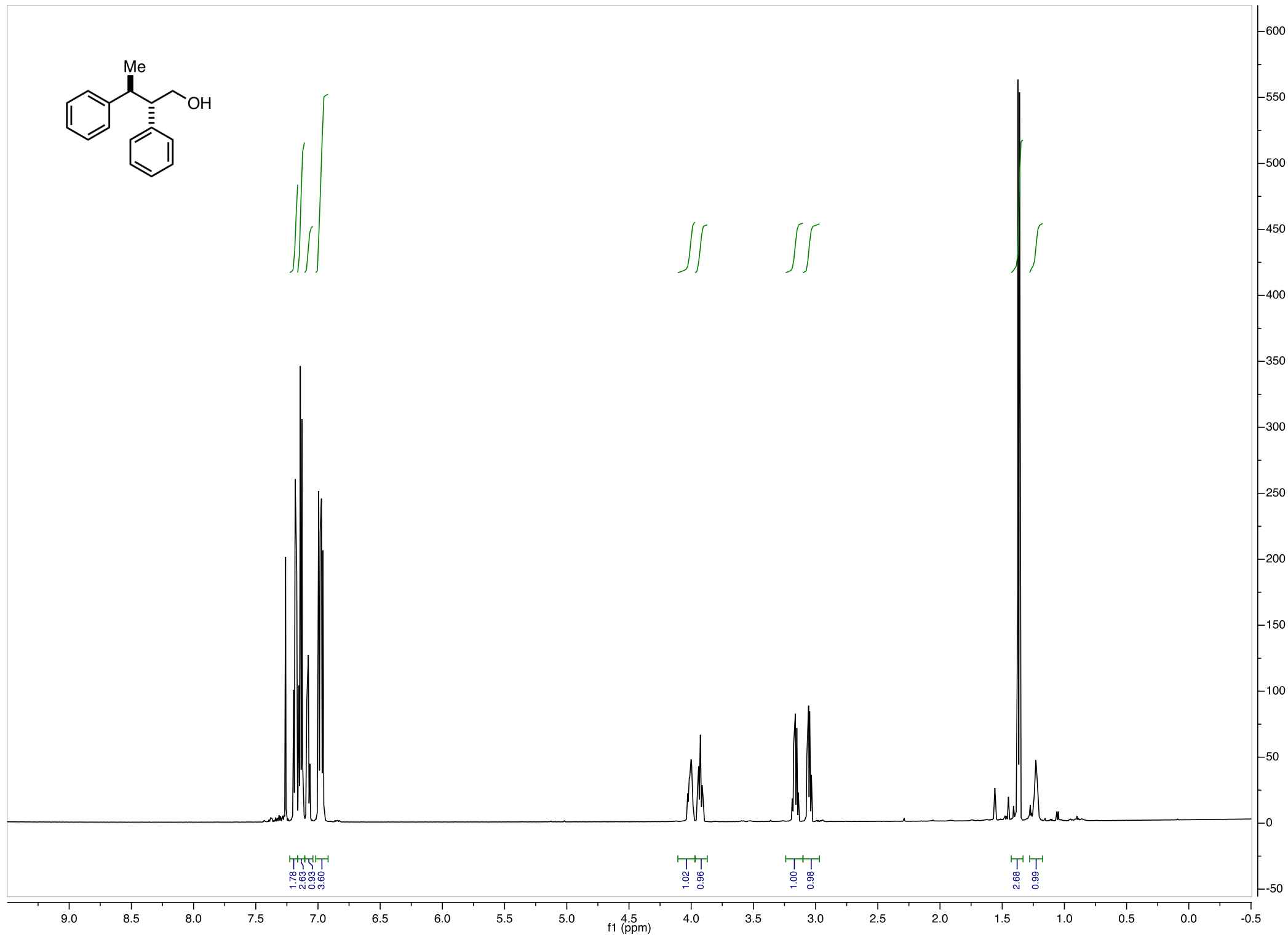
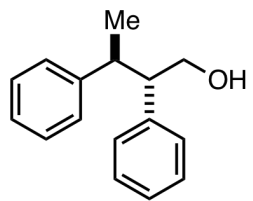
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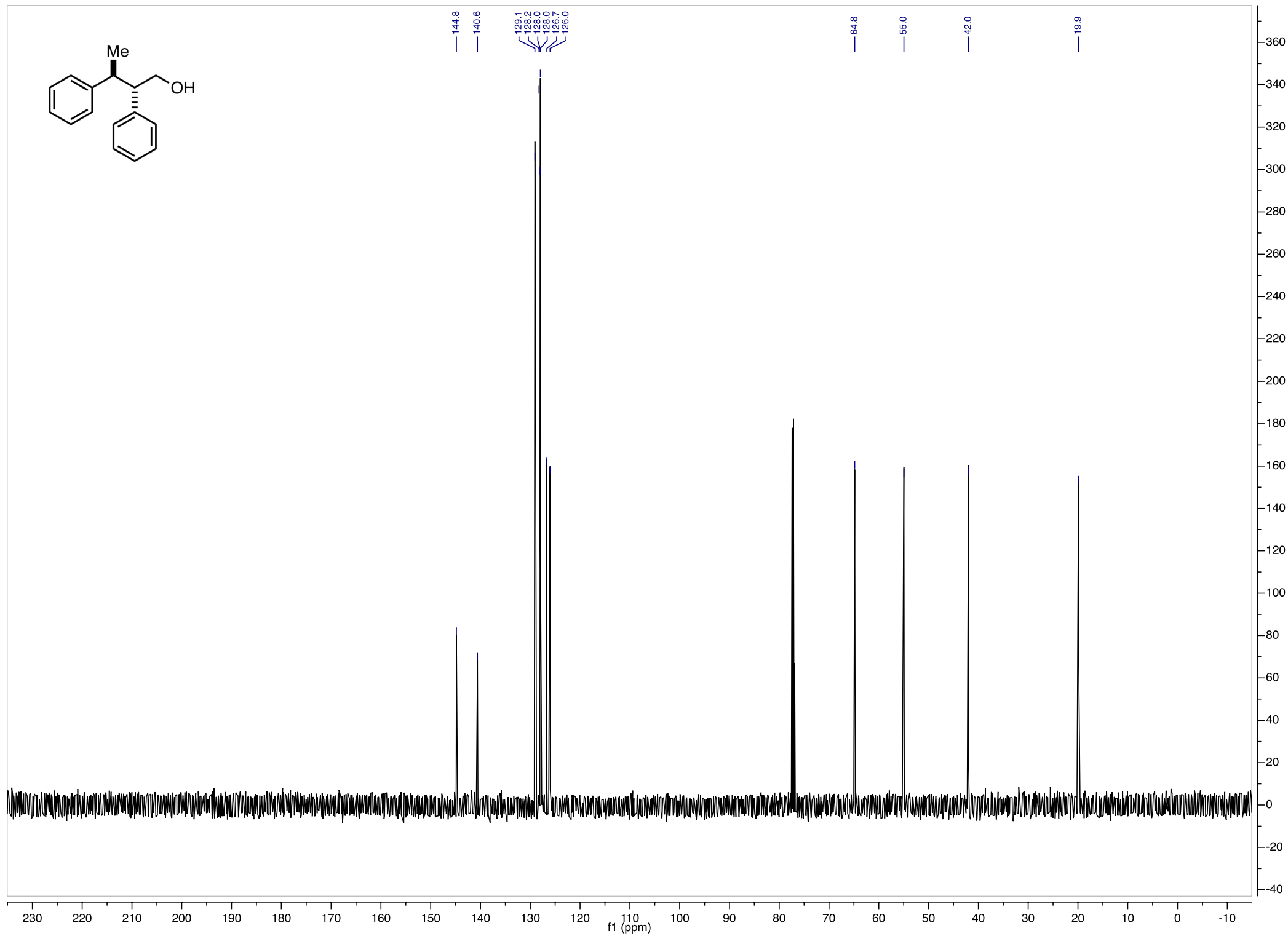
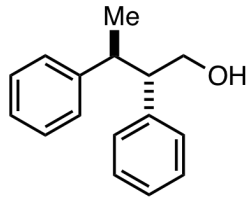
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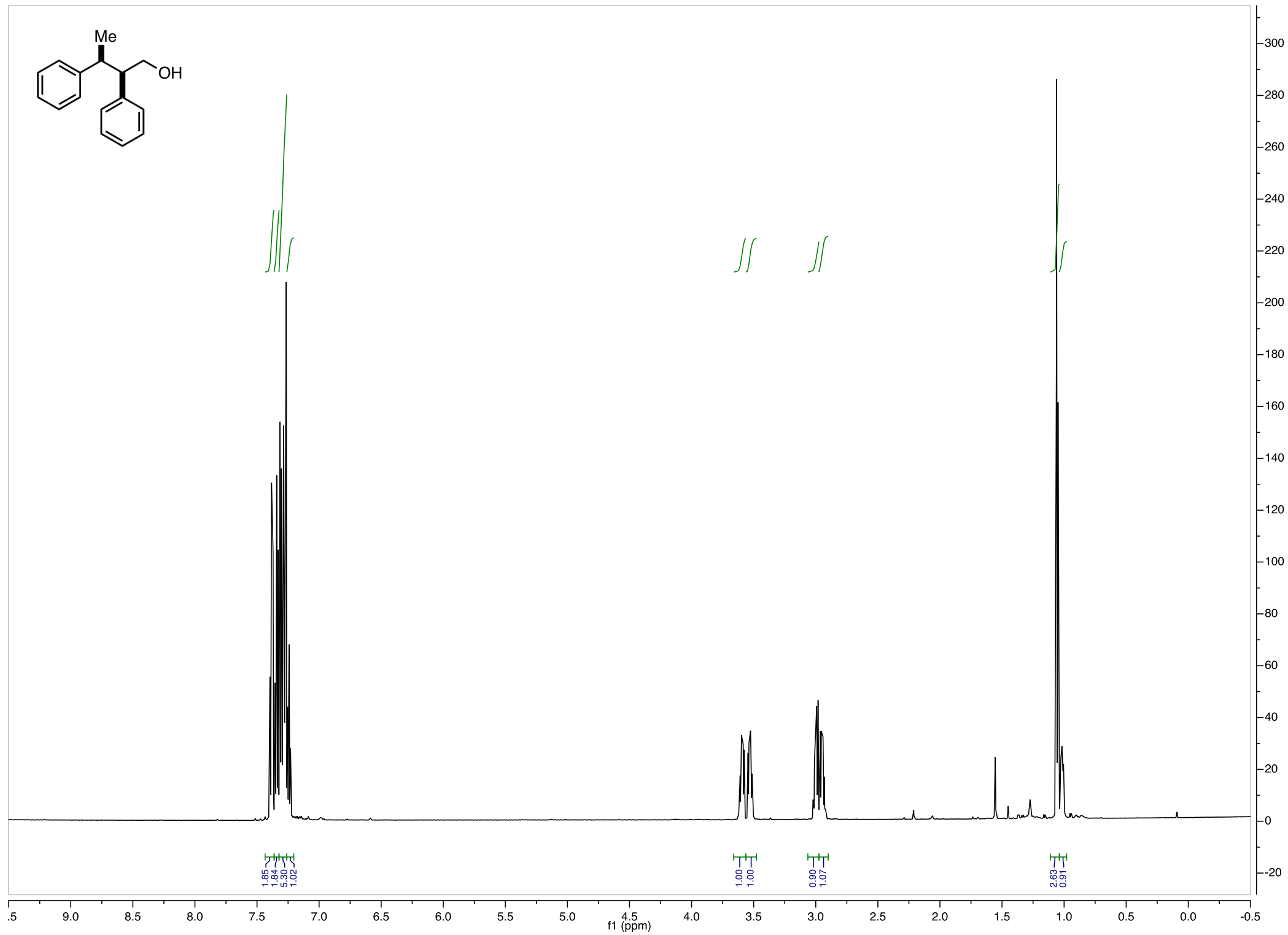
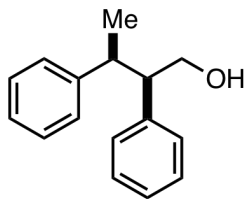


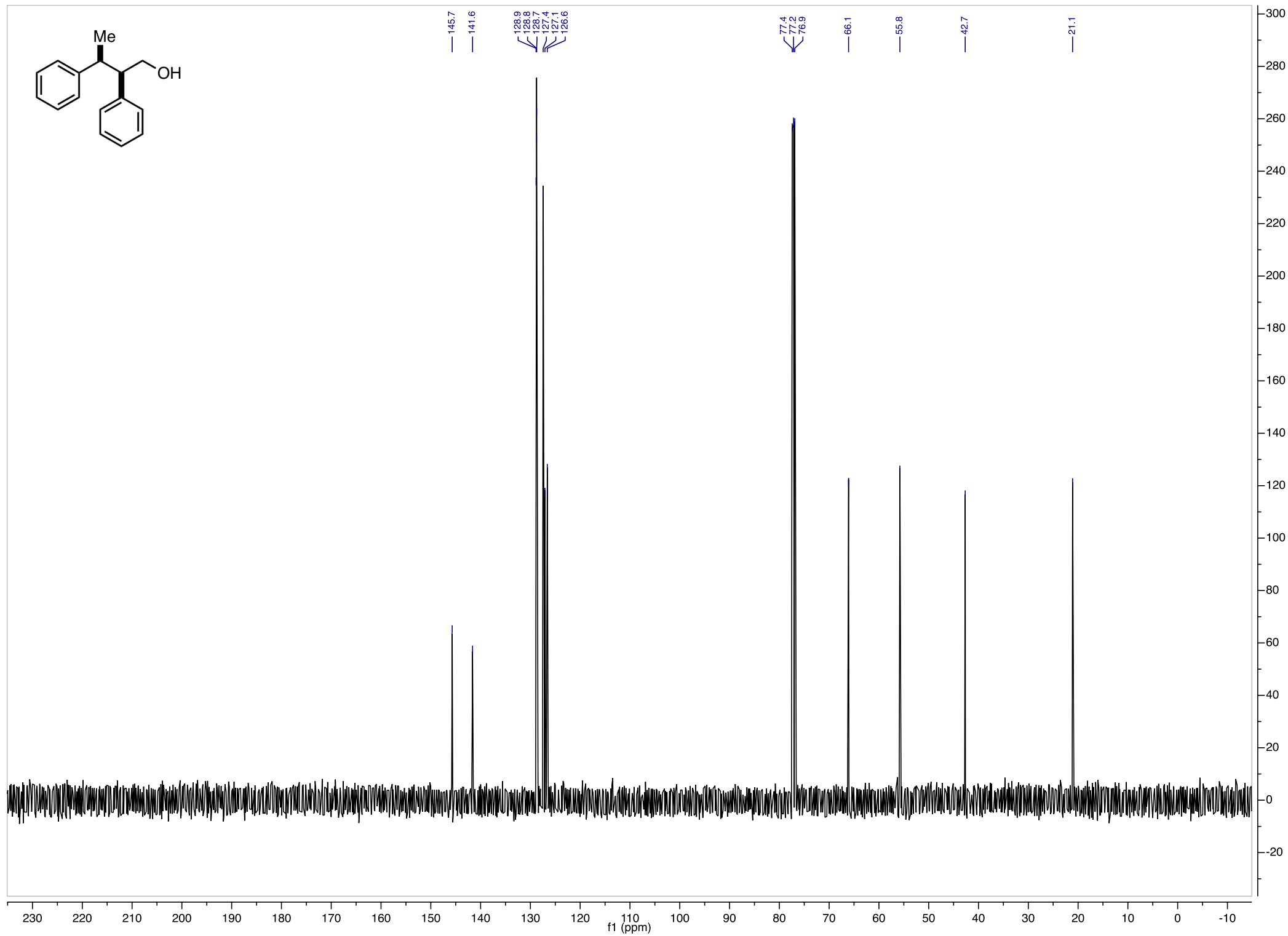
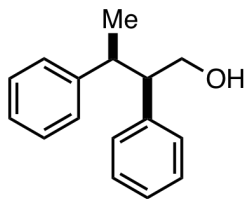


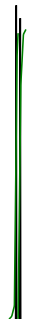
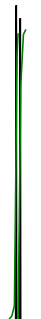
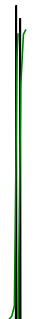
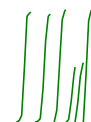
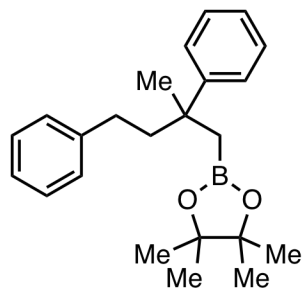












2.04
2.01
2.09
1.02
1.10
2.11

1.00
1.03

1.03
1.00

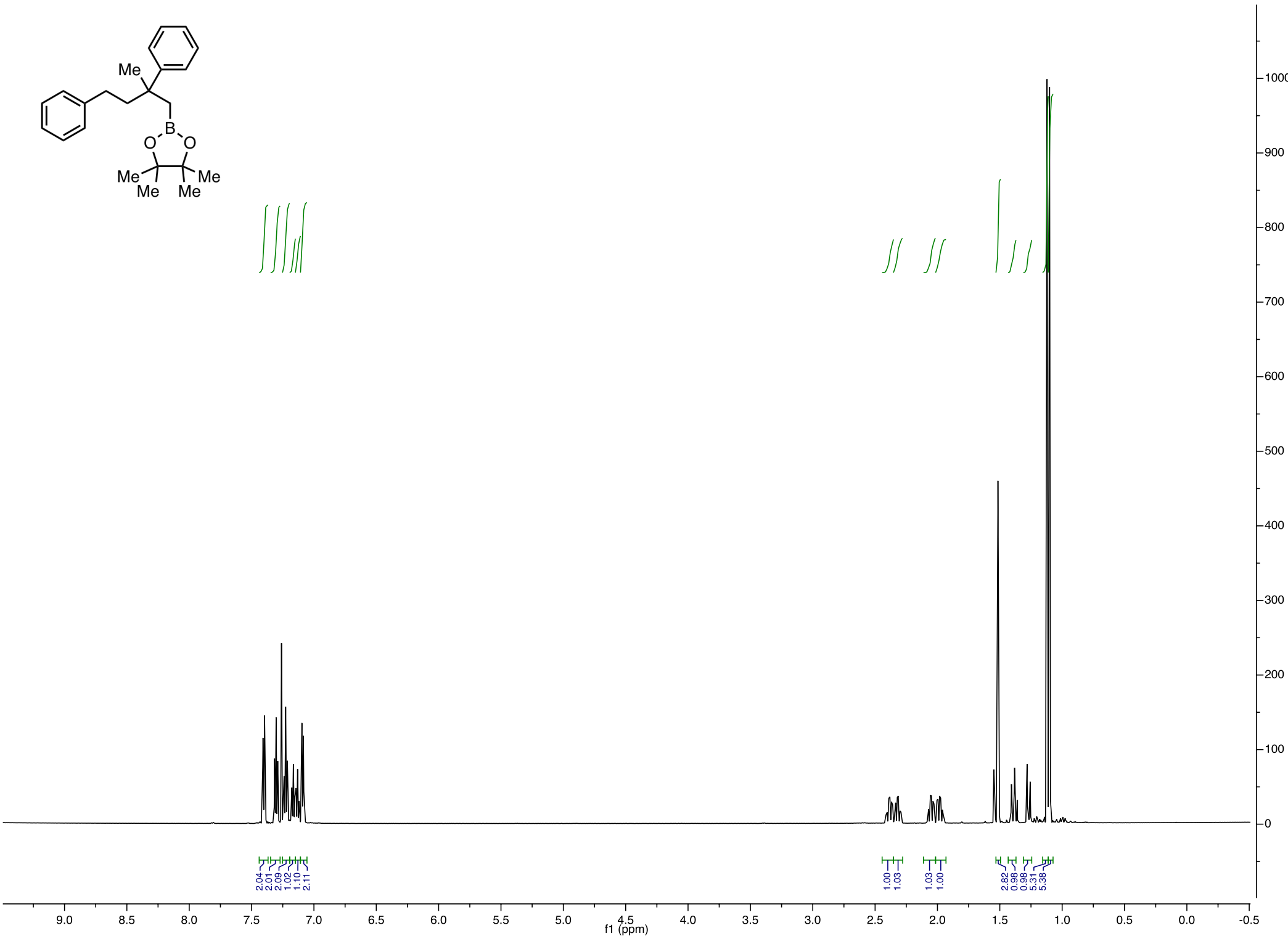
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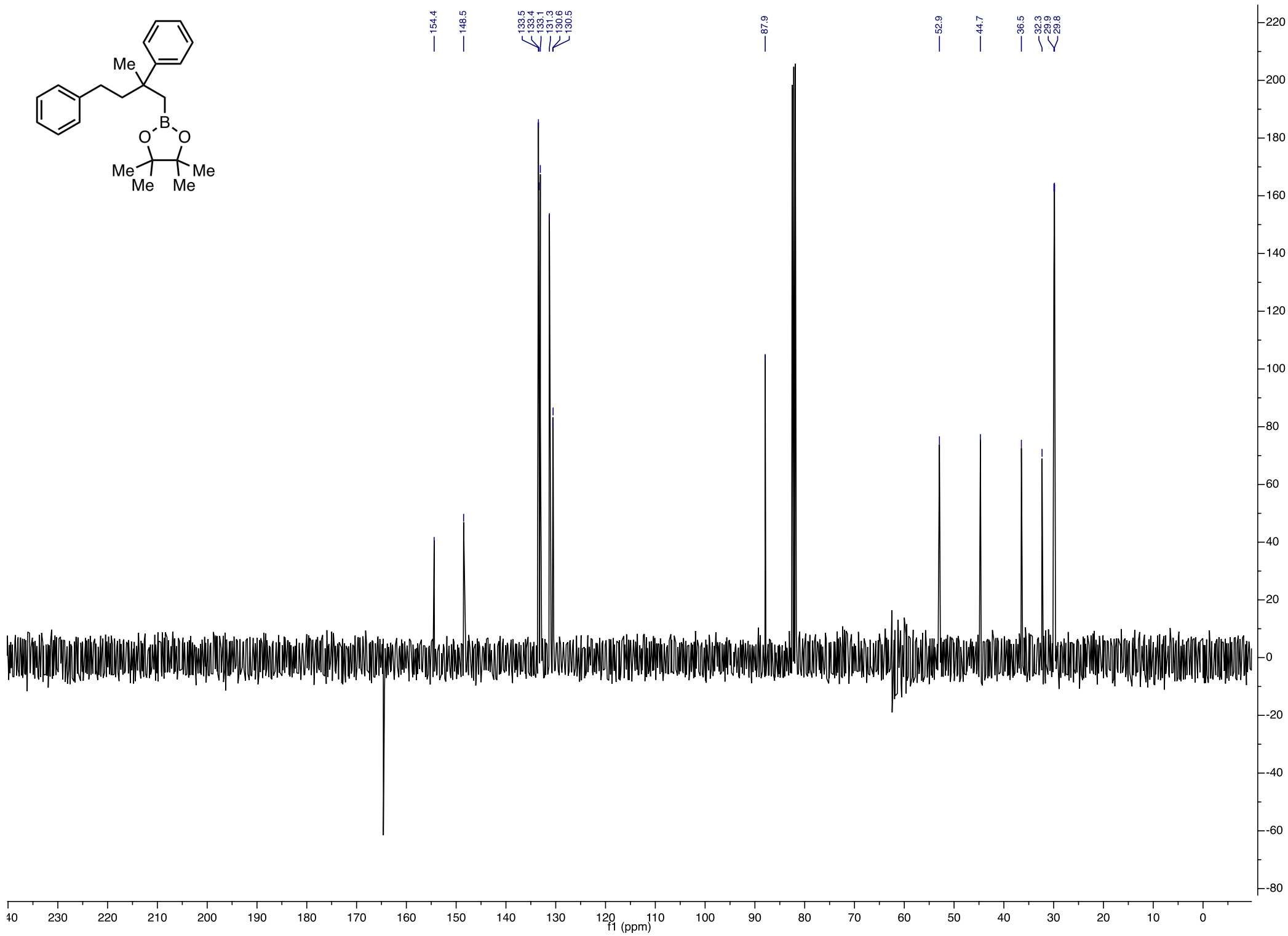
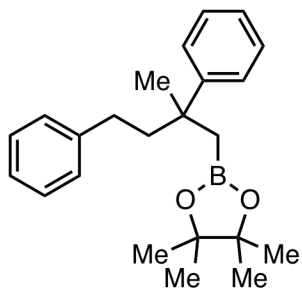
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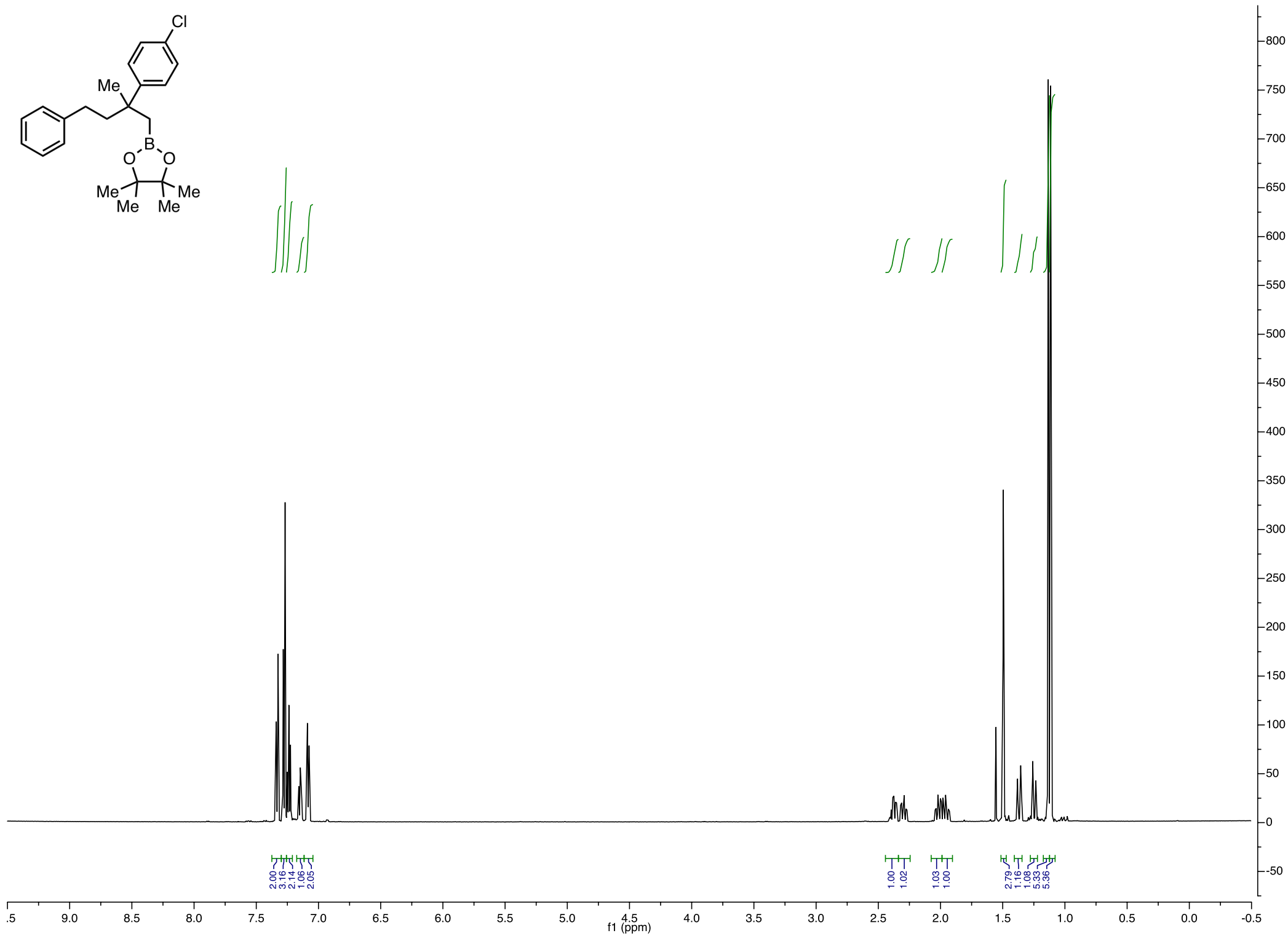
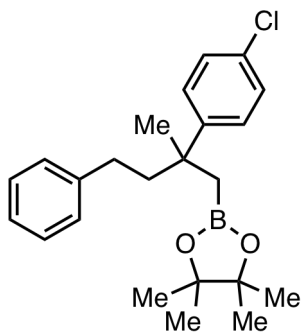
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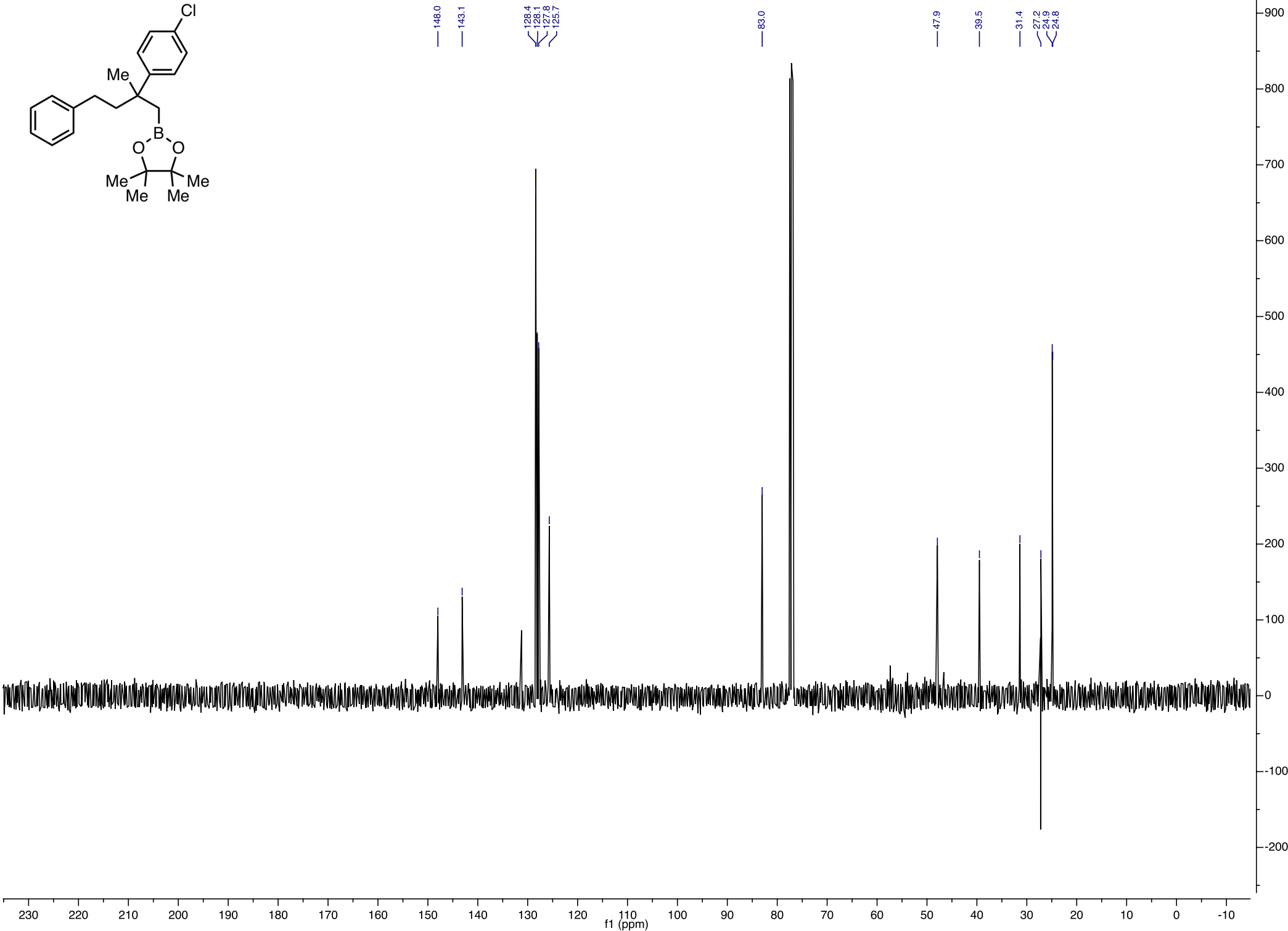
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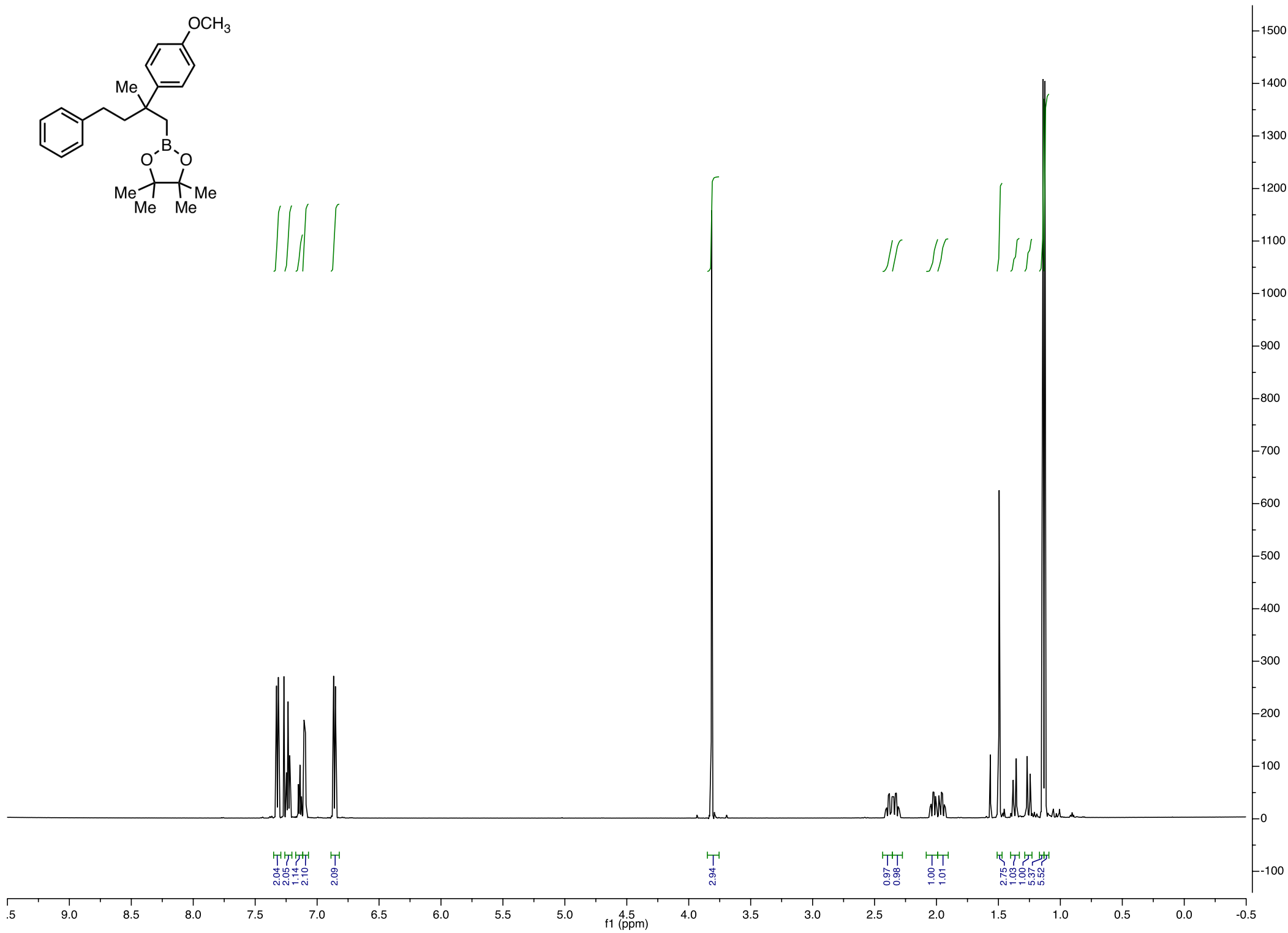
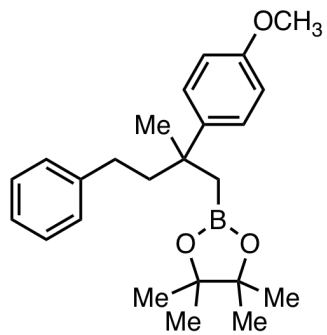
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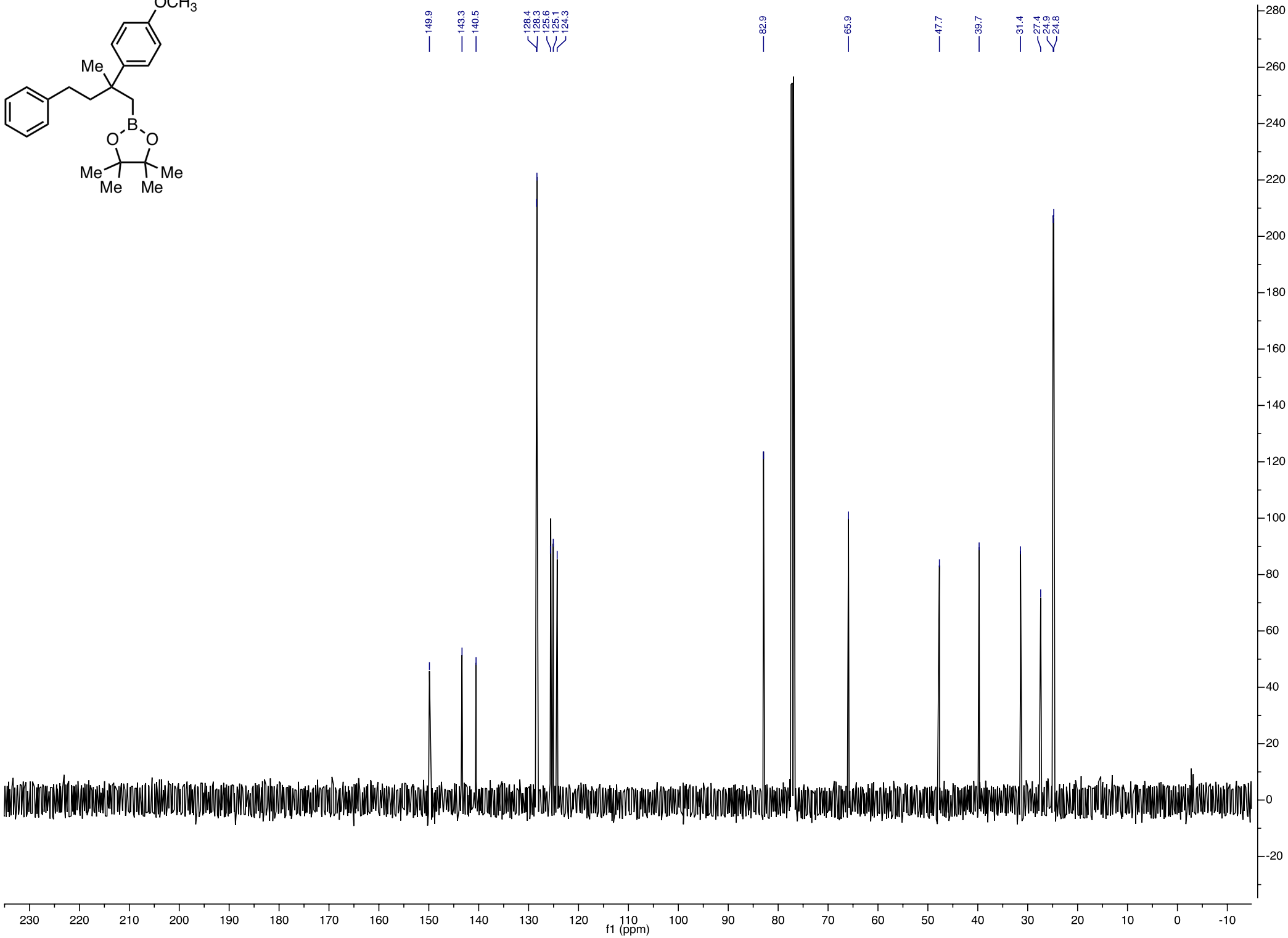
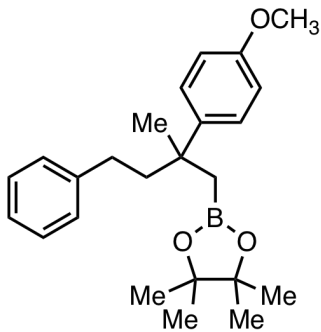


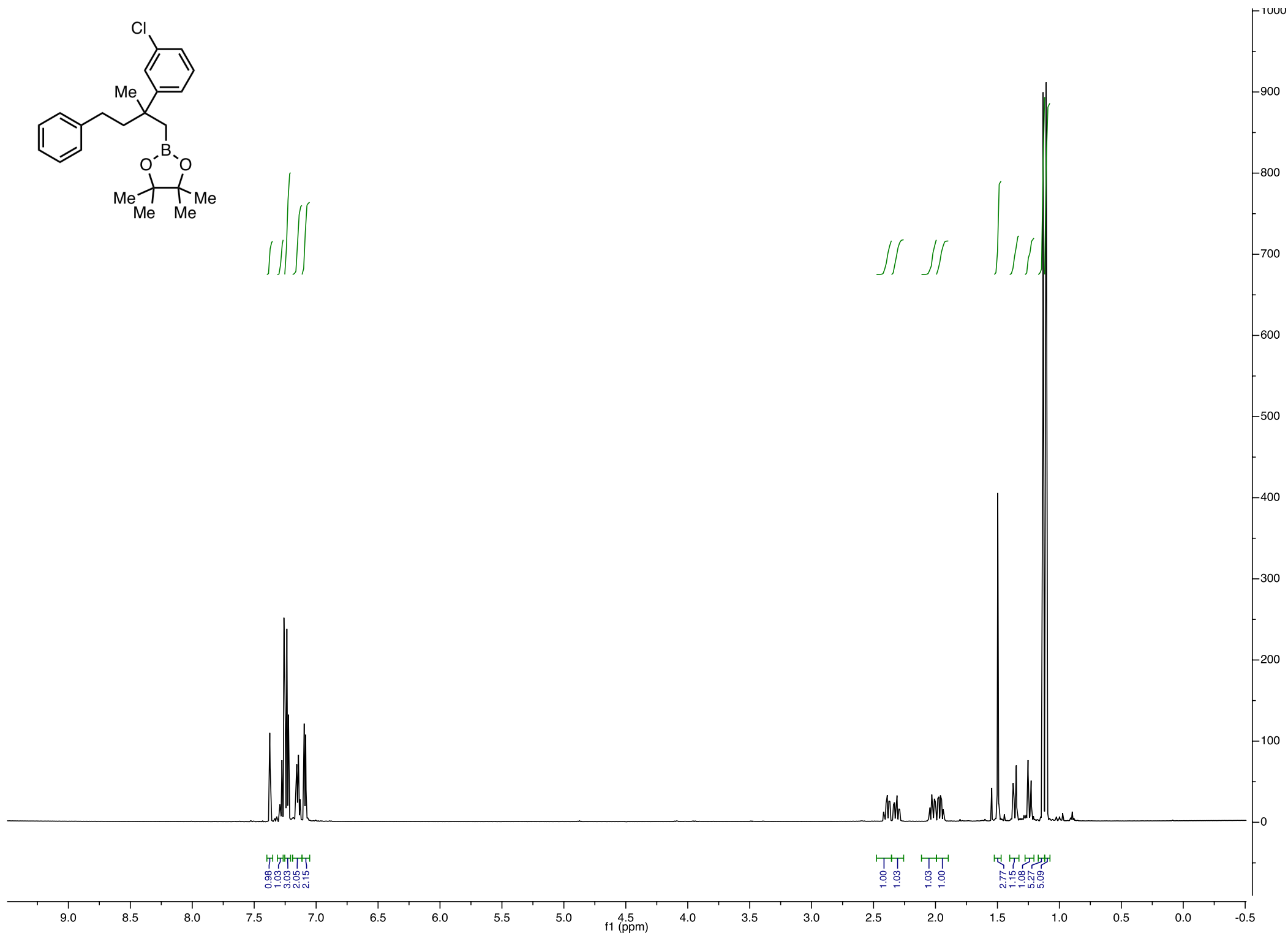
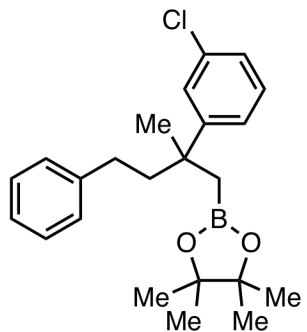


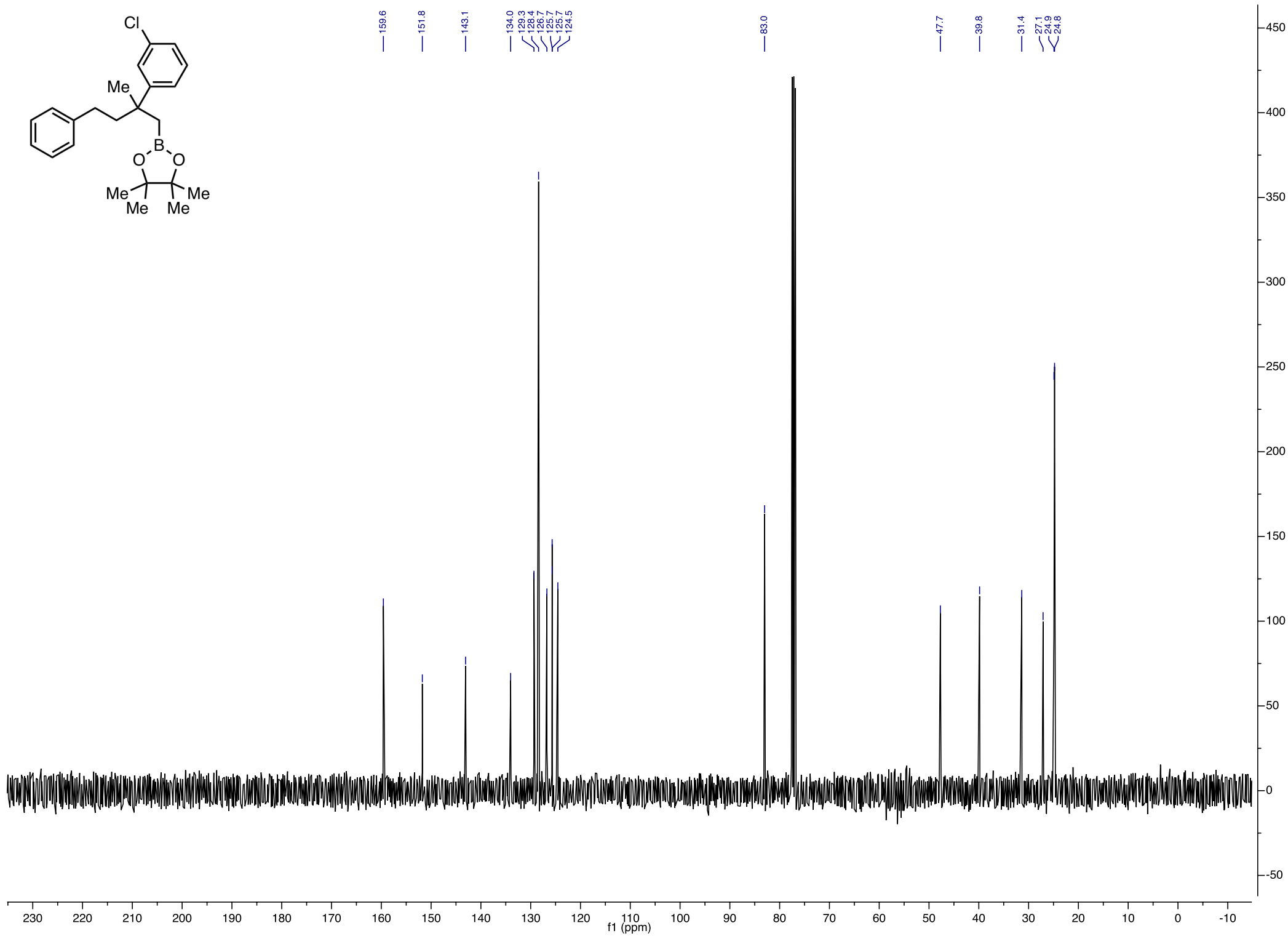
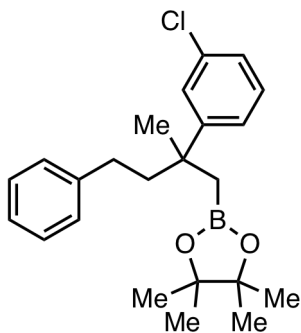


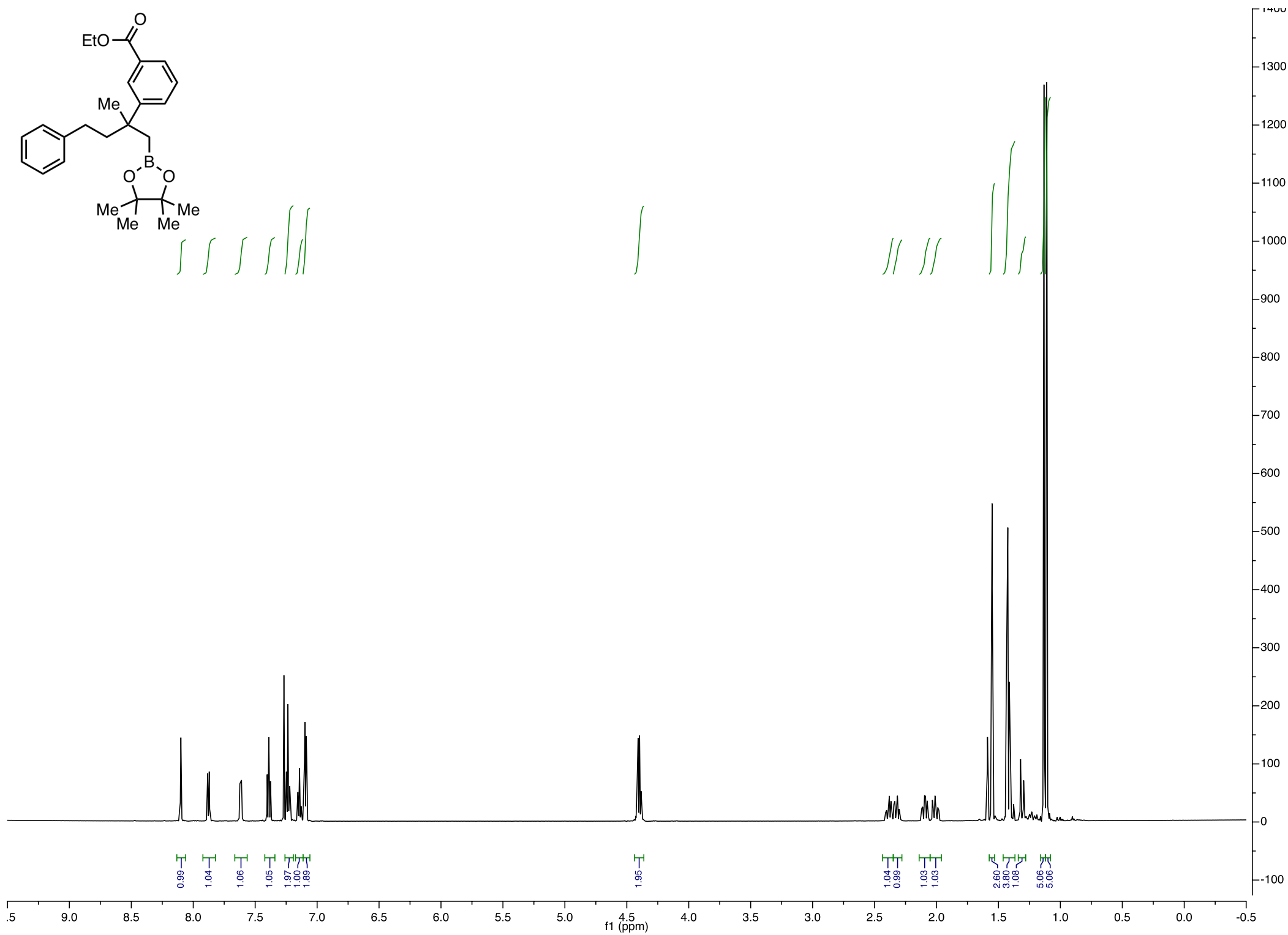
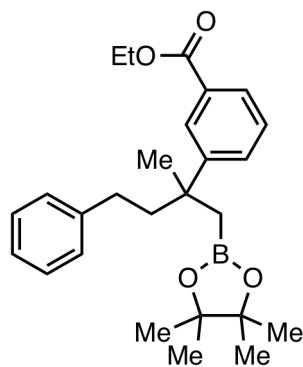


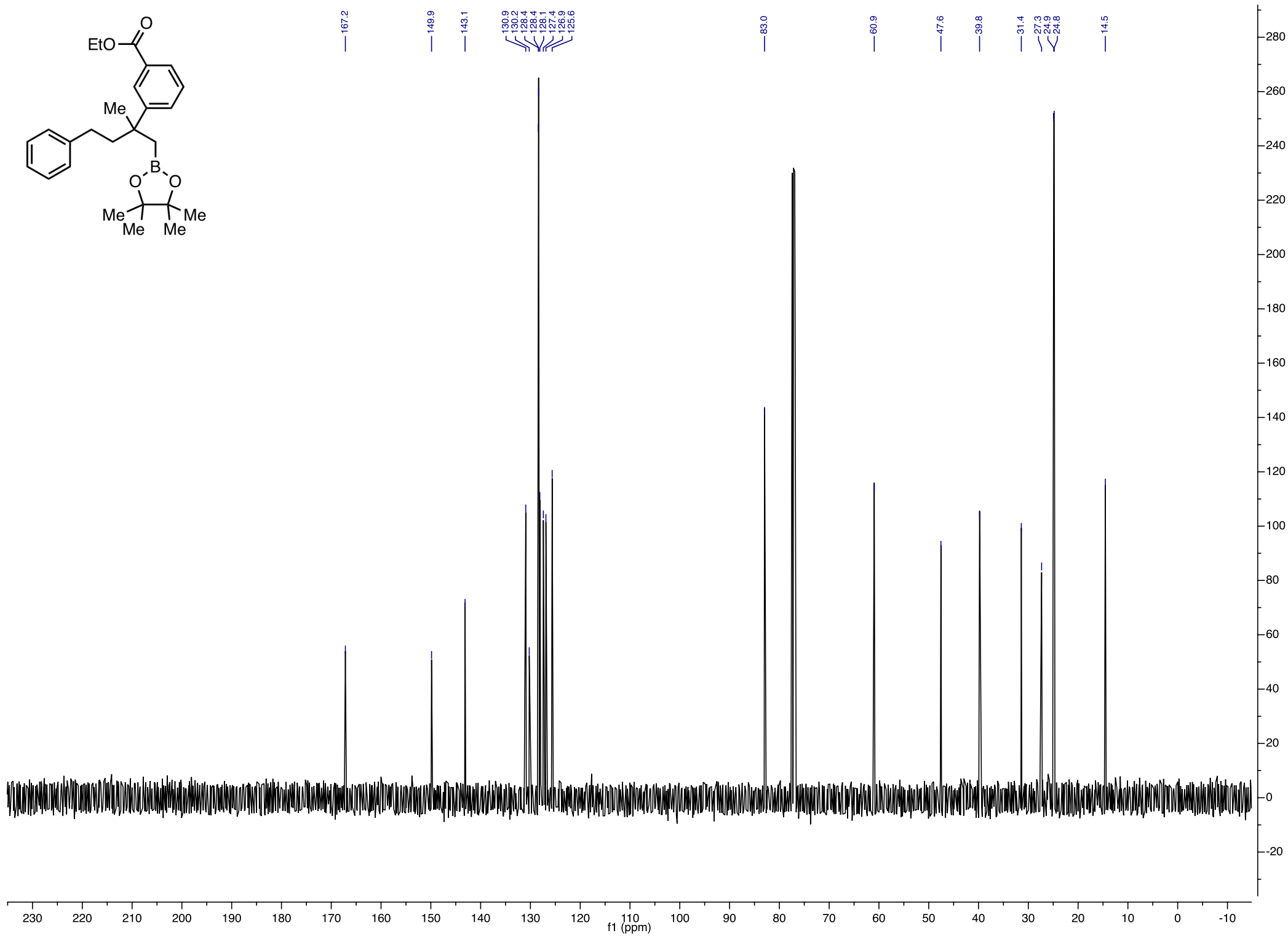
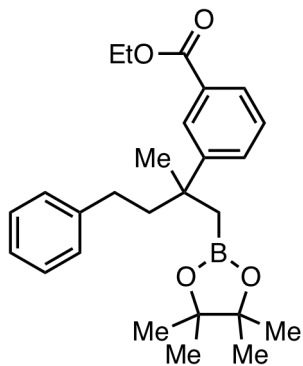


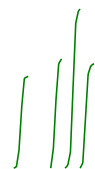
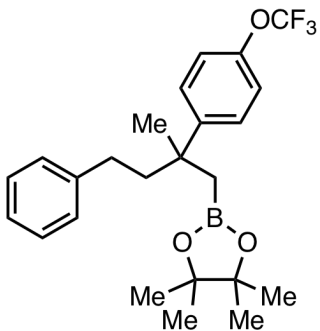












1.69

2.01

2.93

1.93

1.00

1.06

0.95

0.89

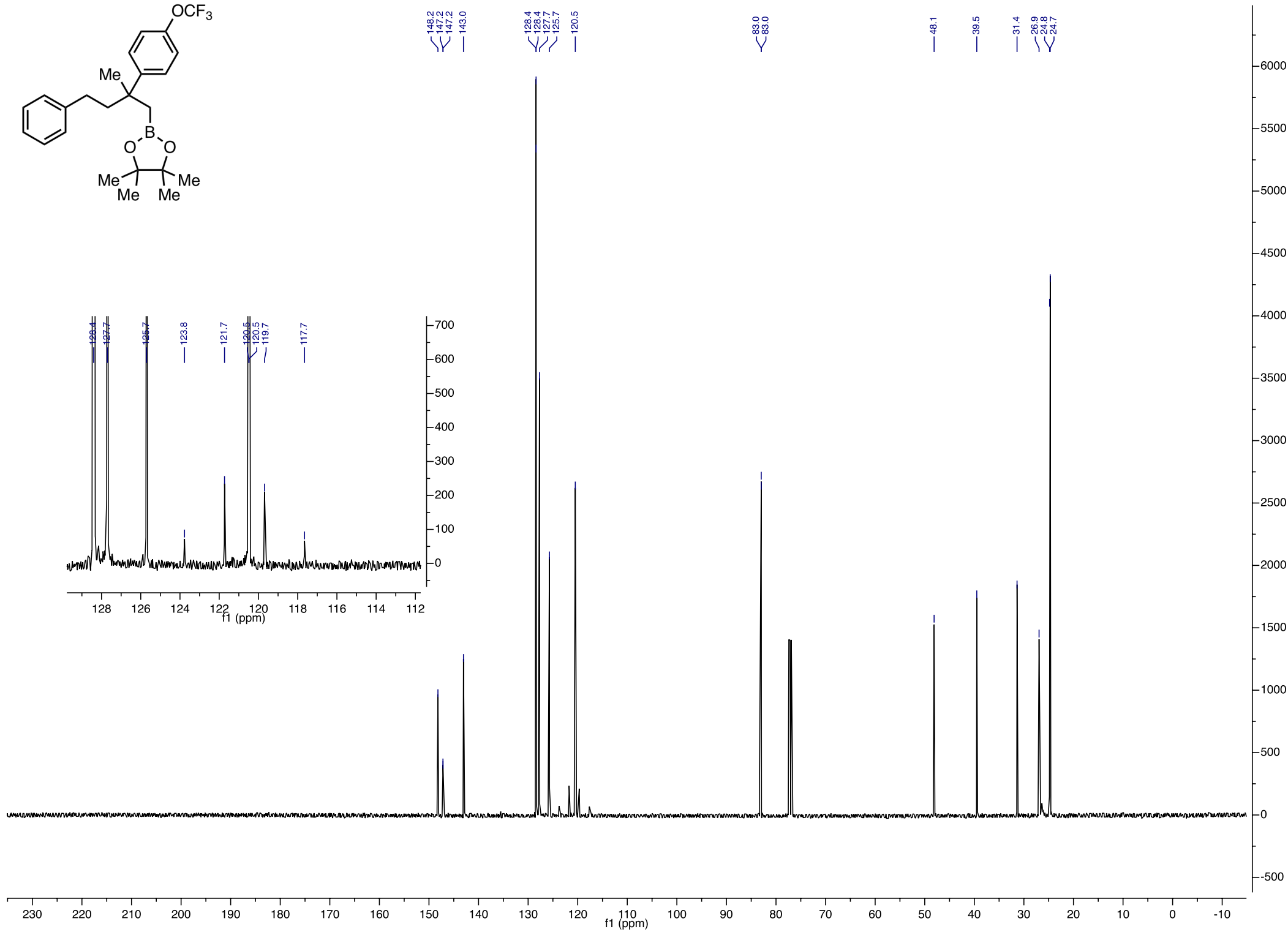
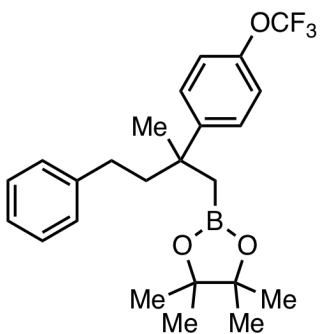
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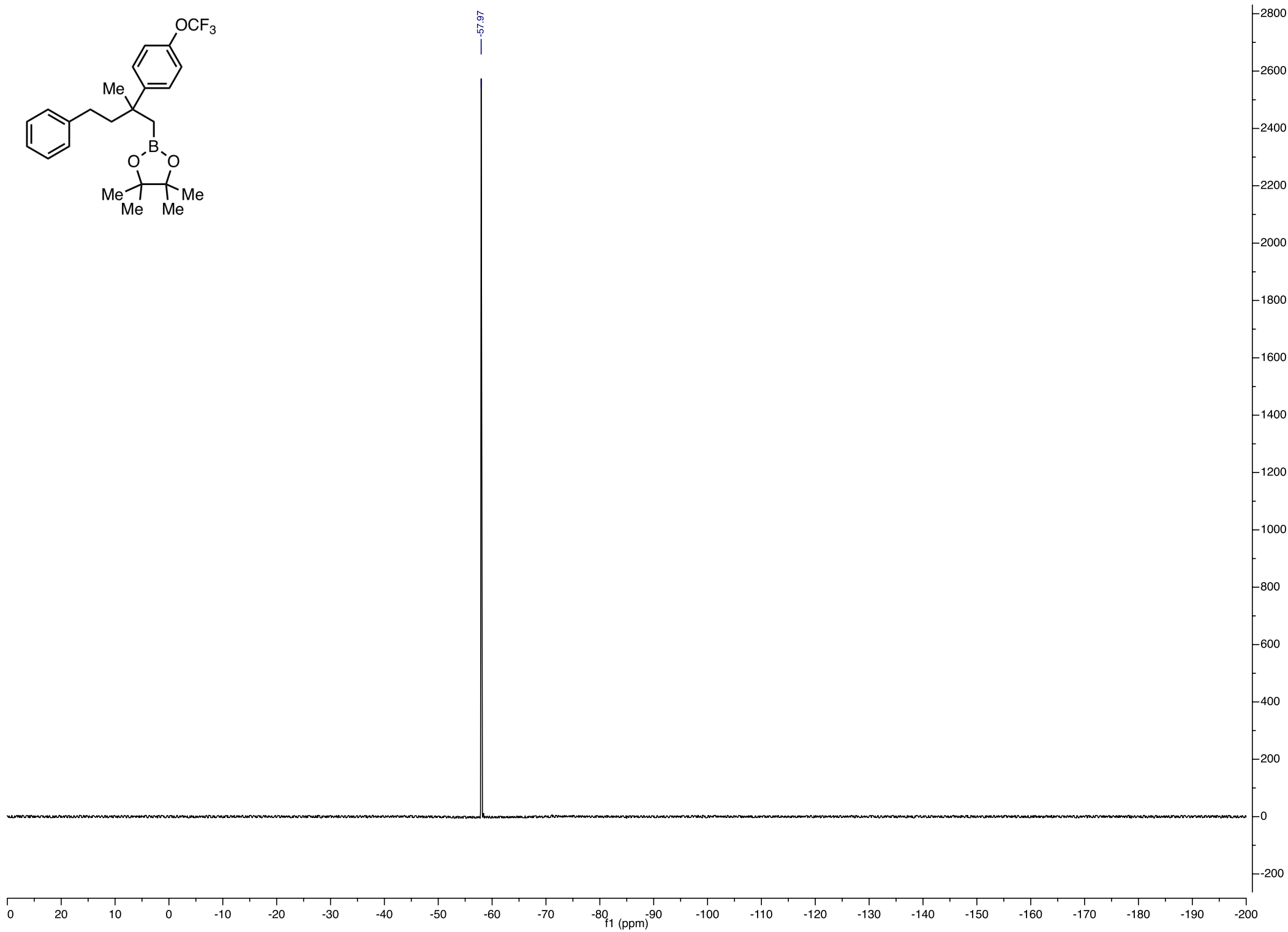
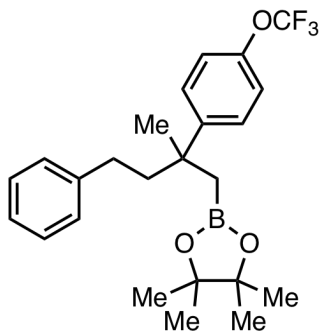
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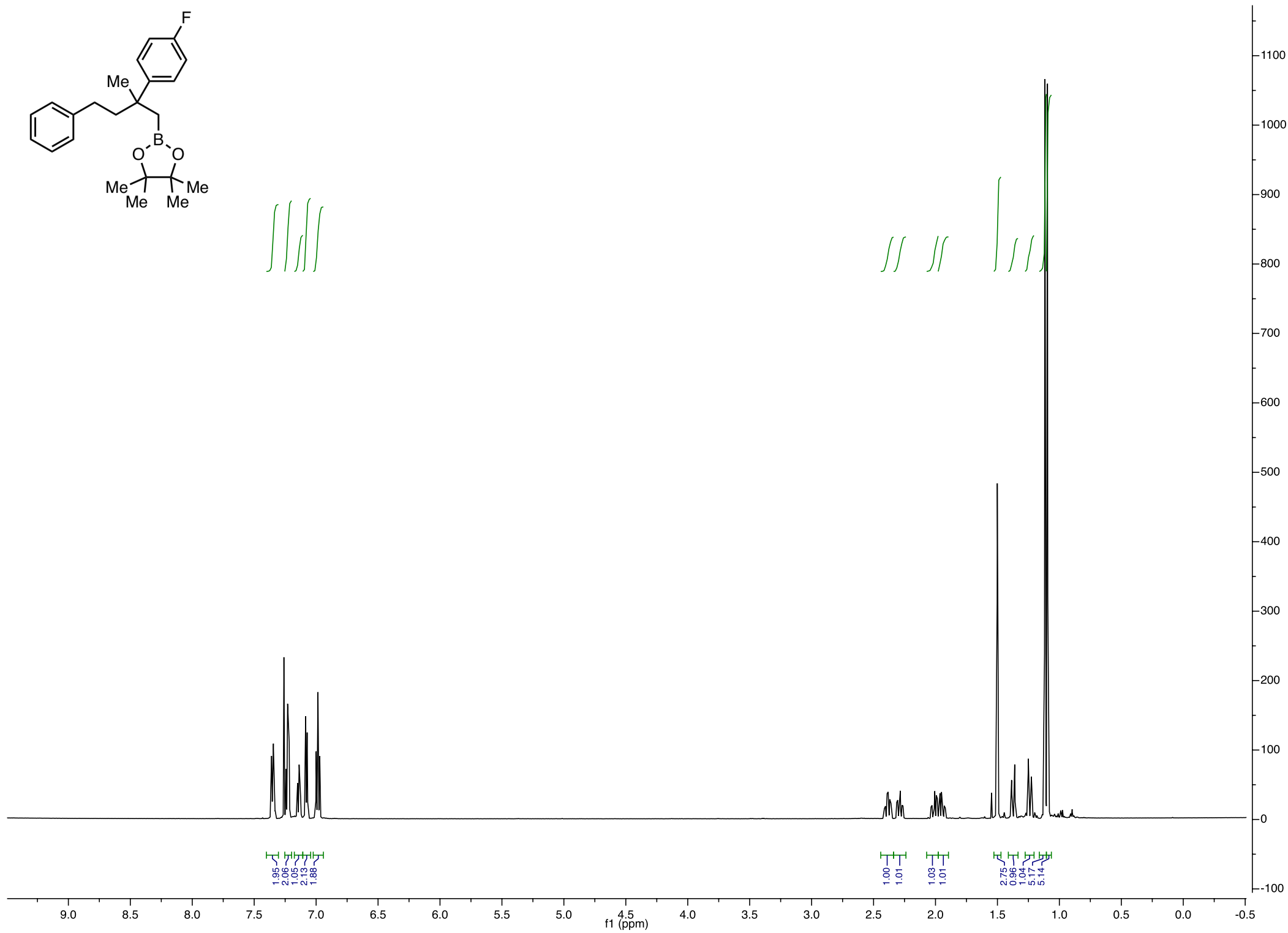
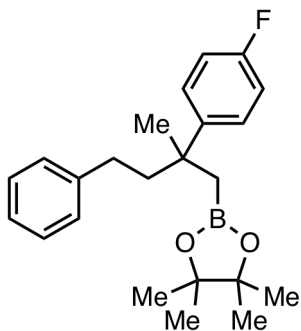
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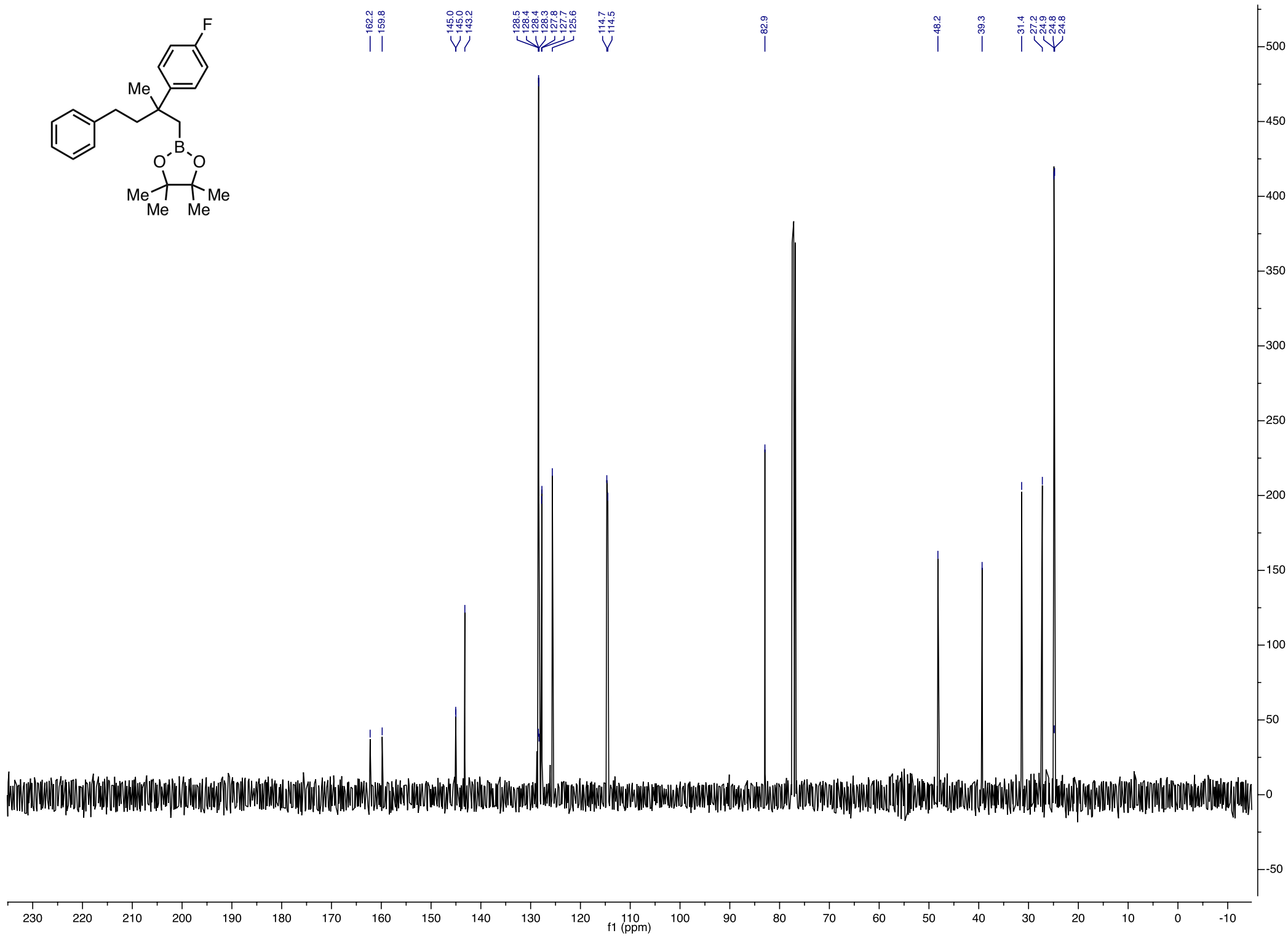
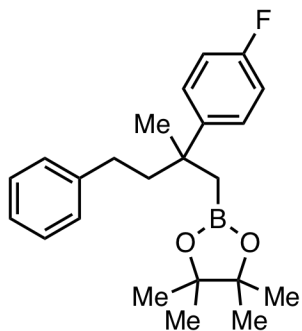
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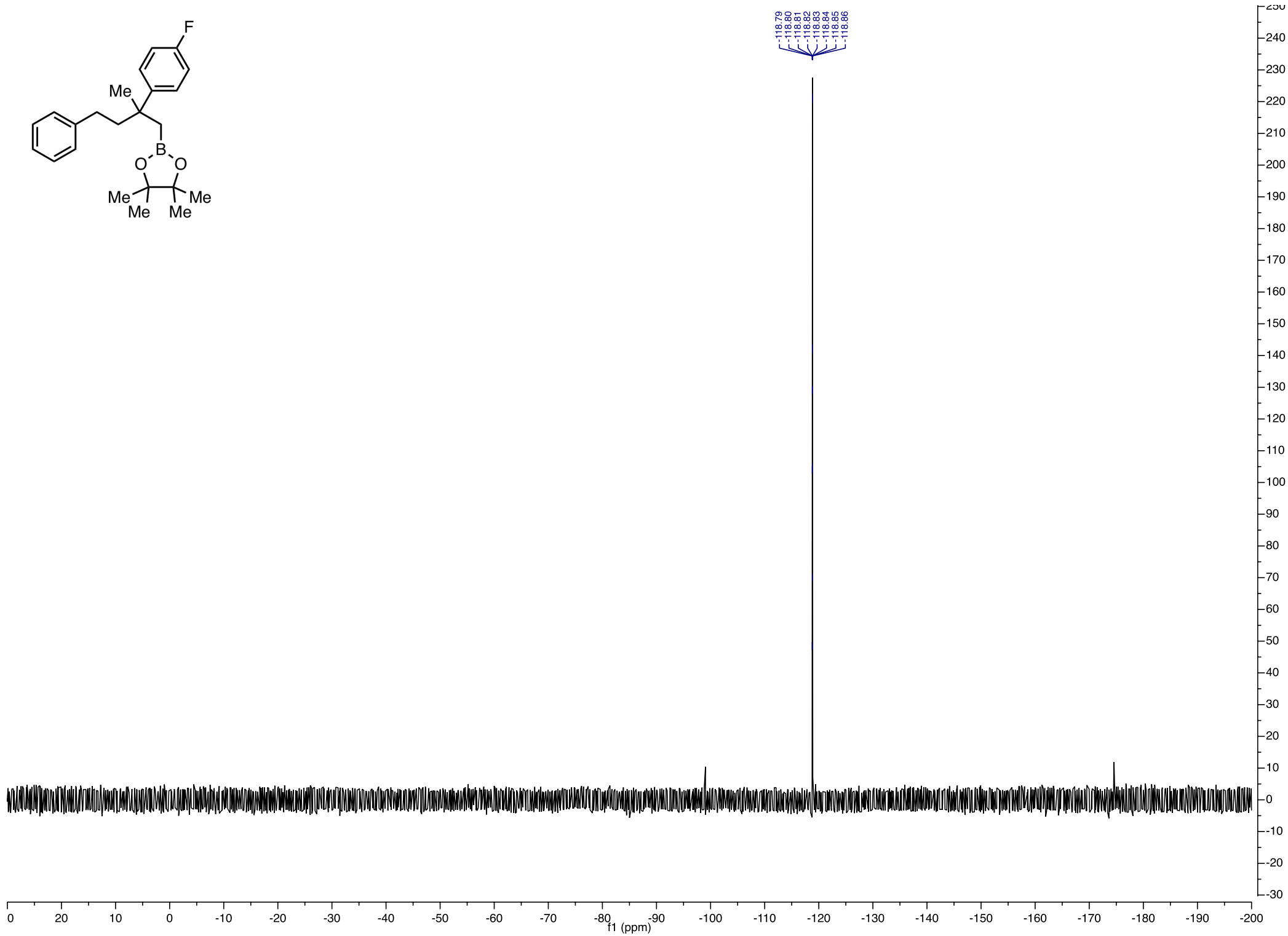
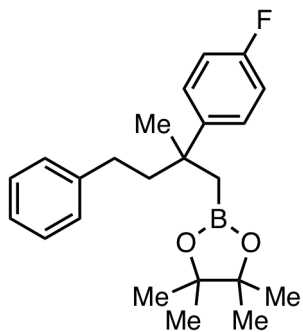
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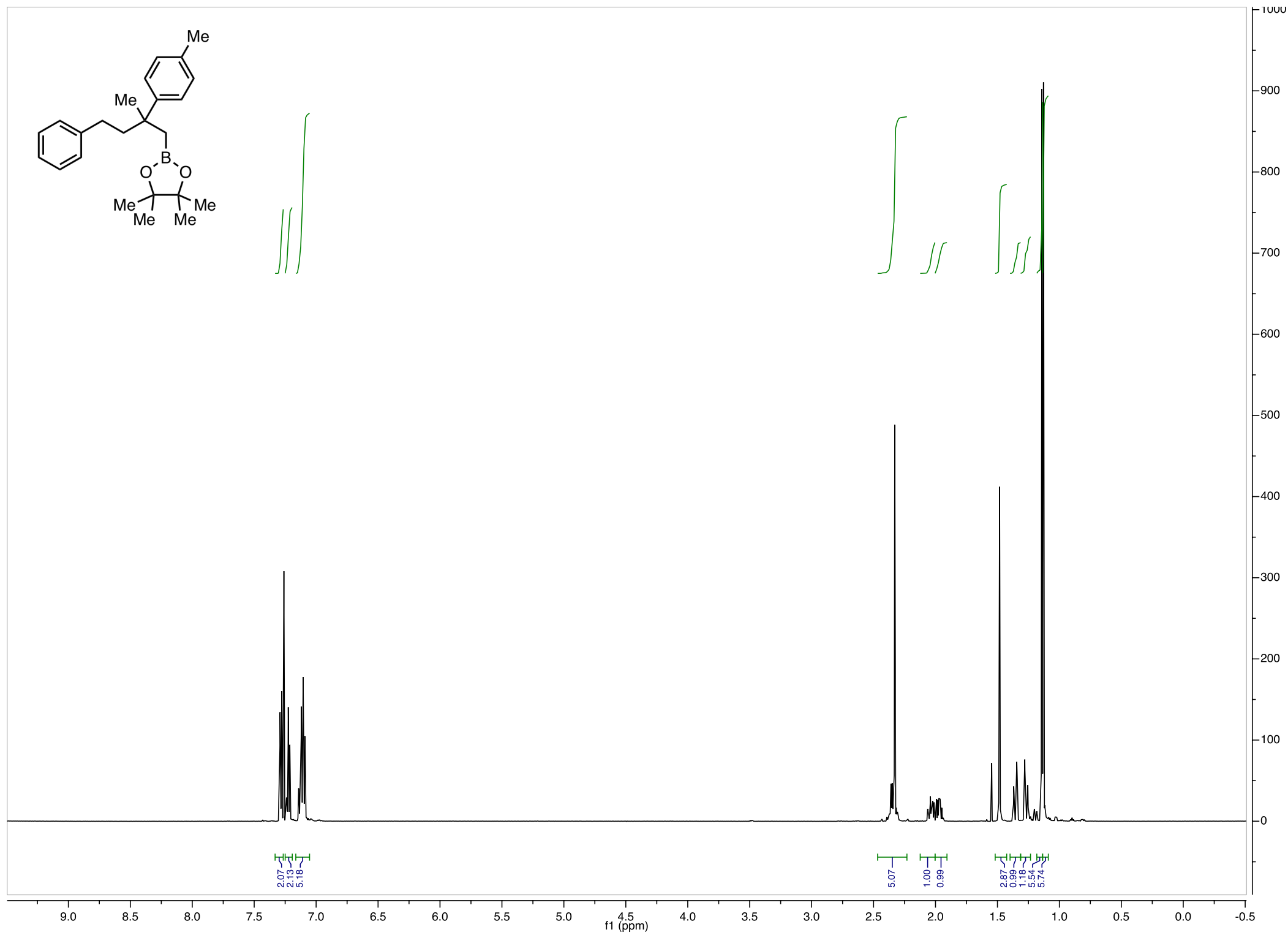
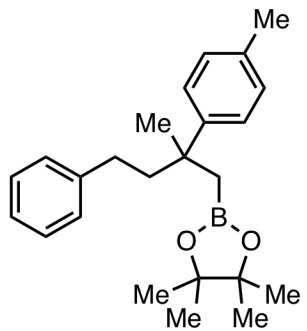


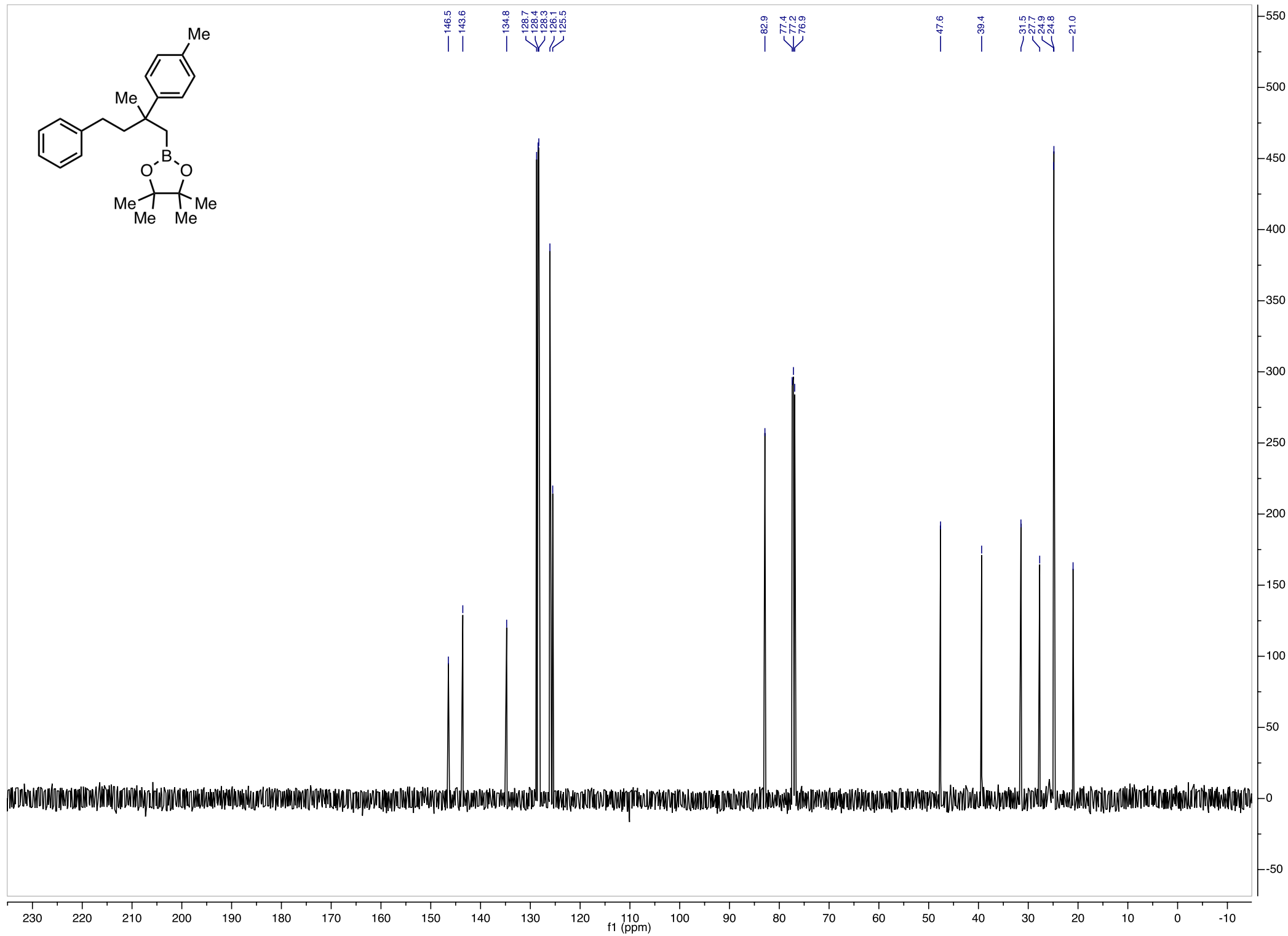
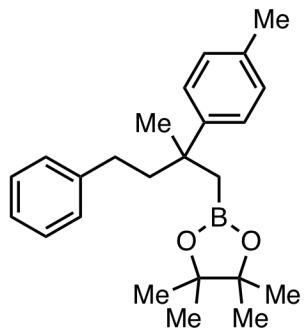


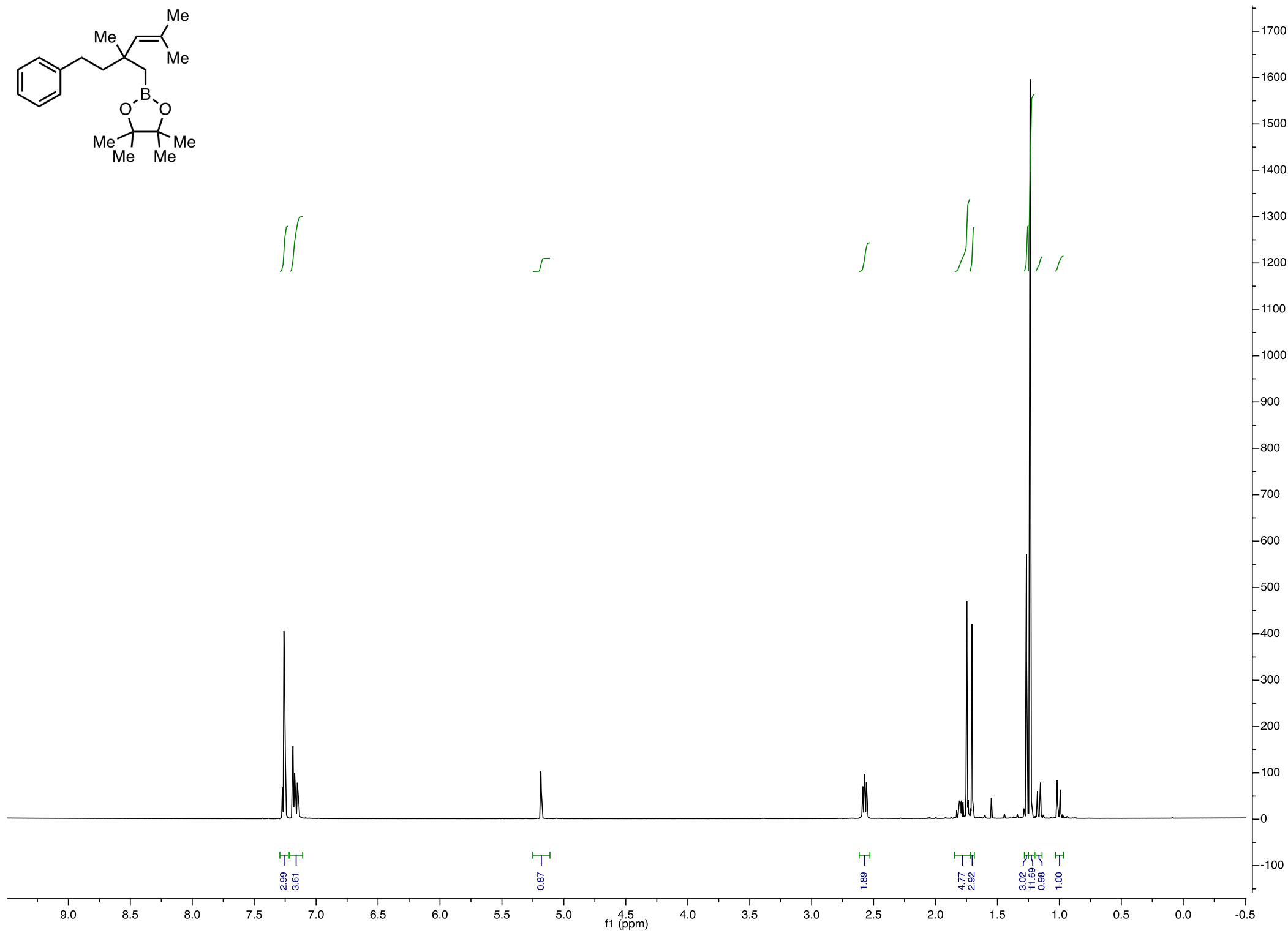
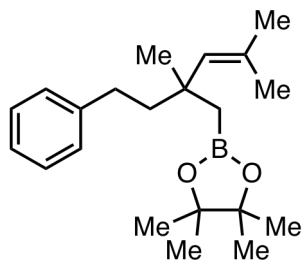


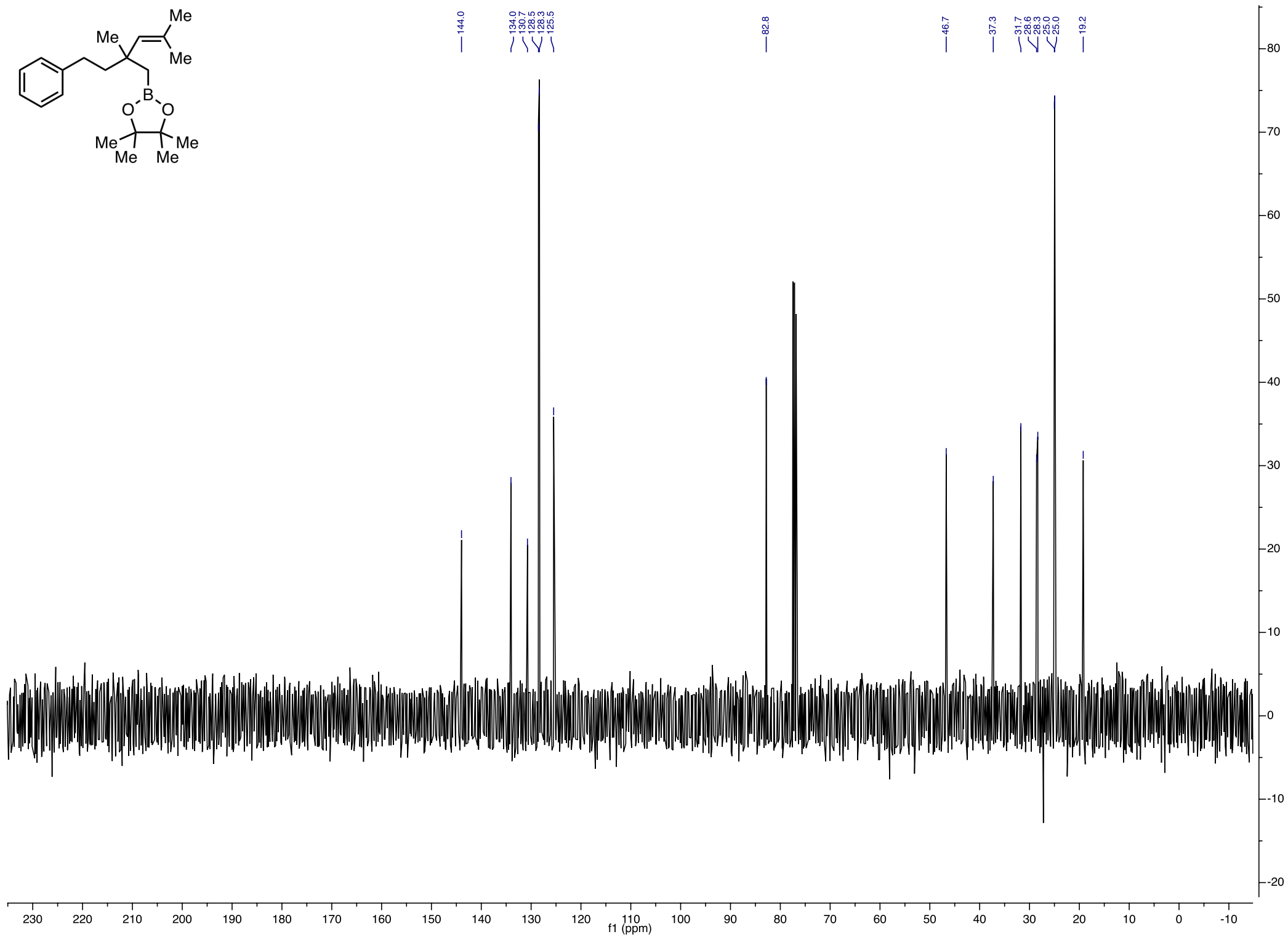
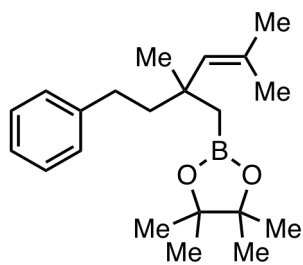


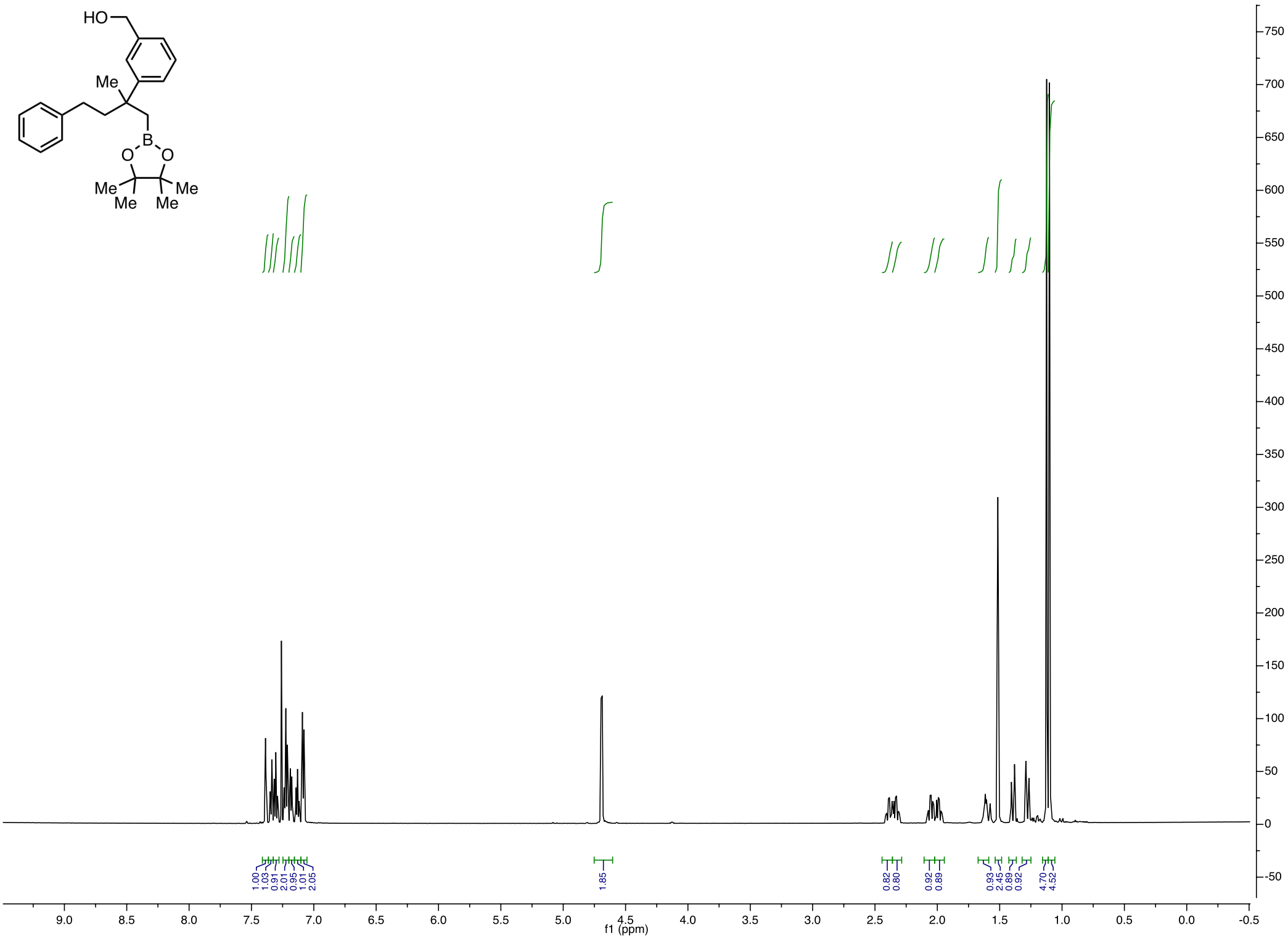
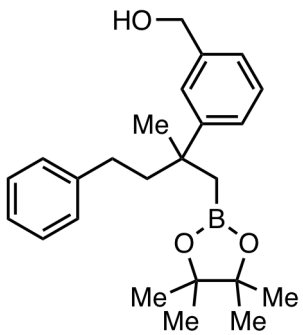


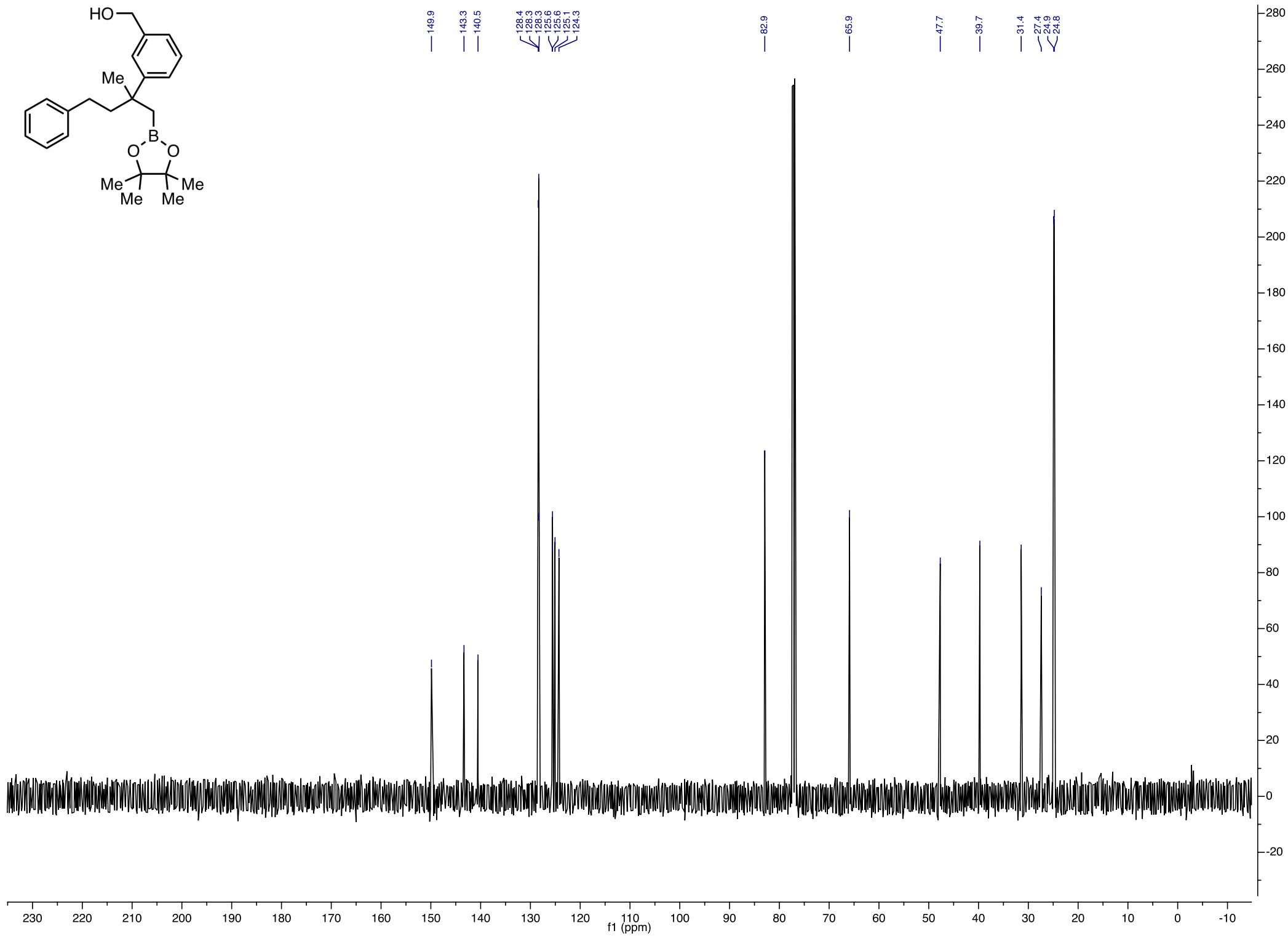
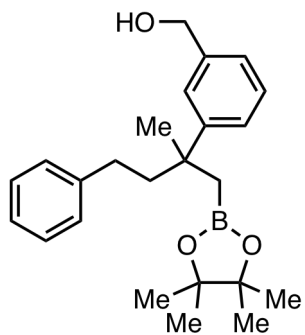


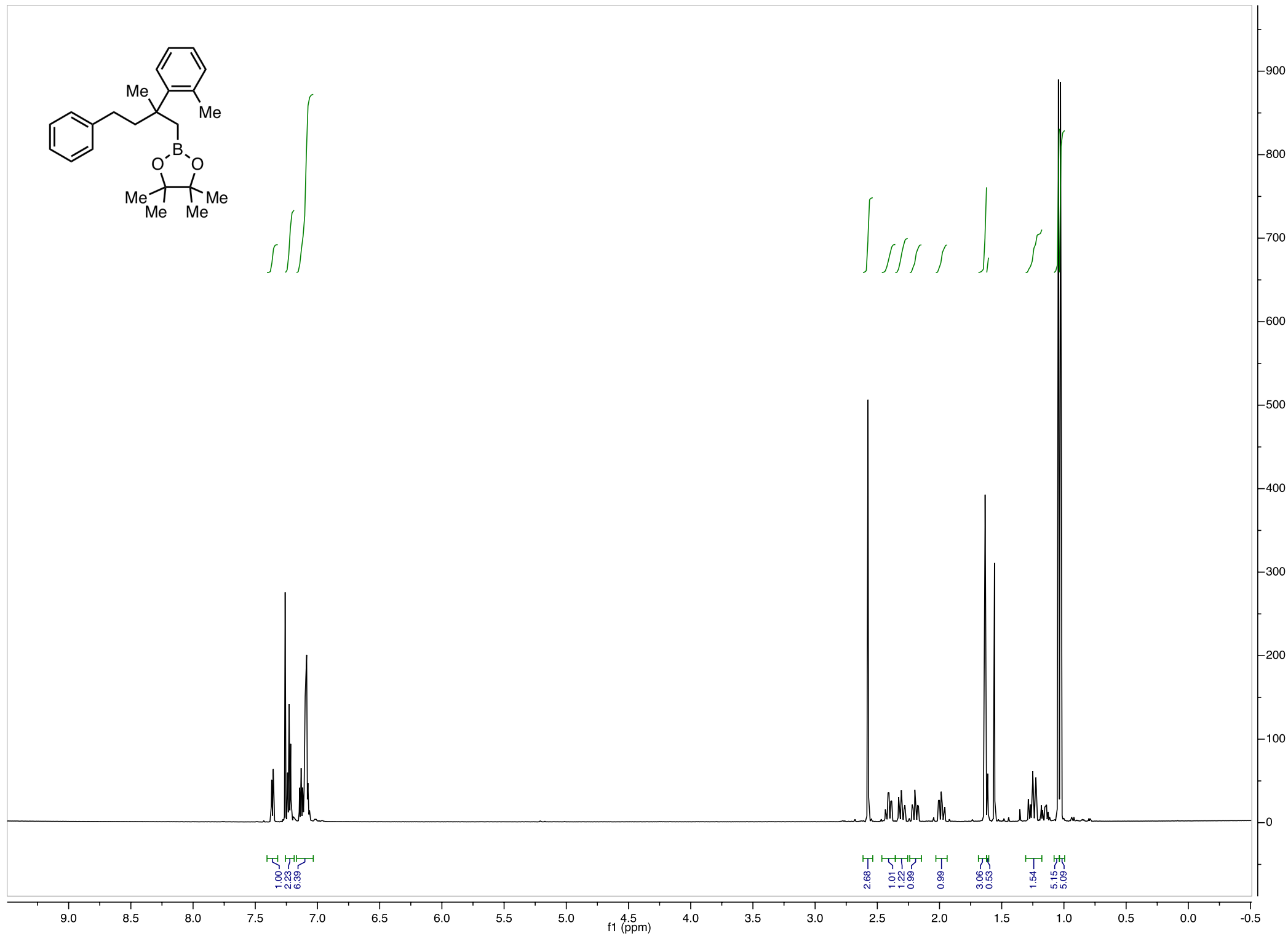
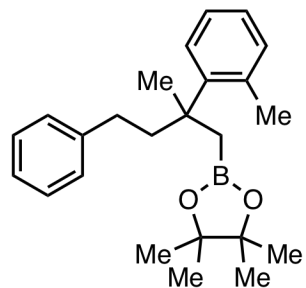


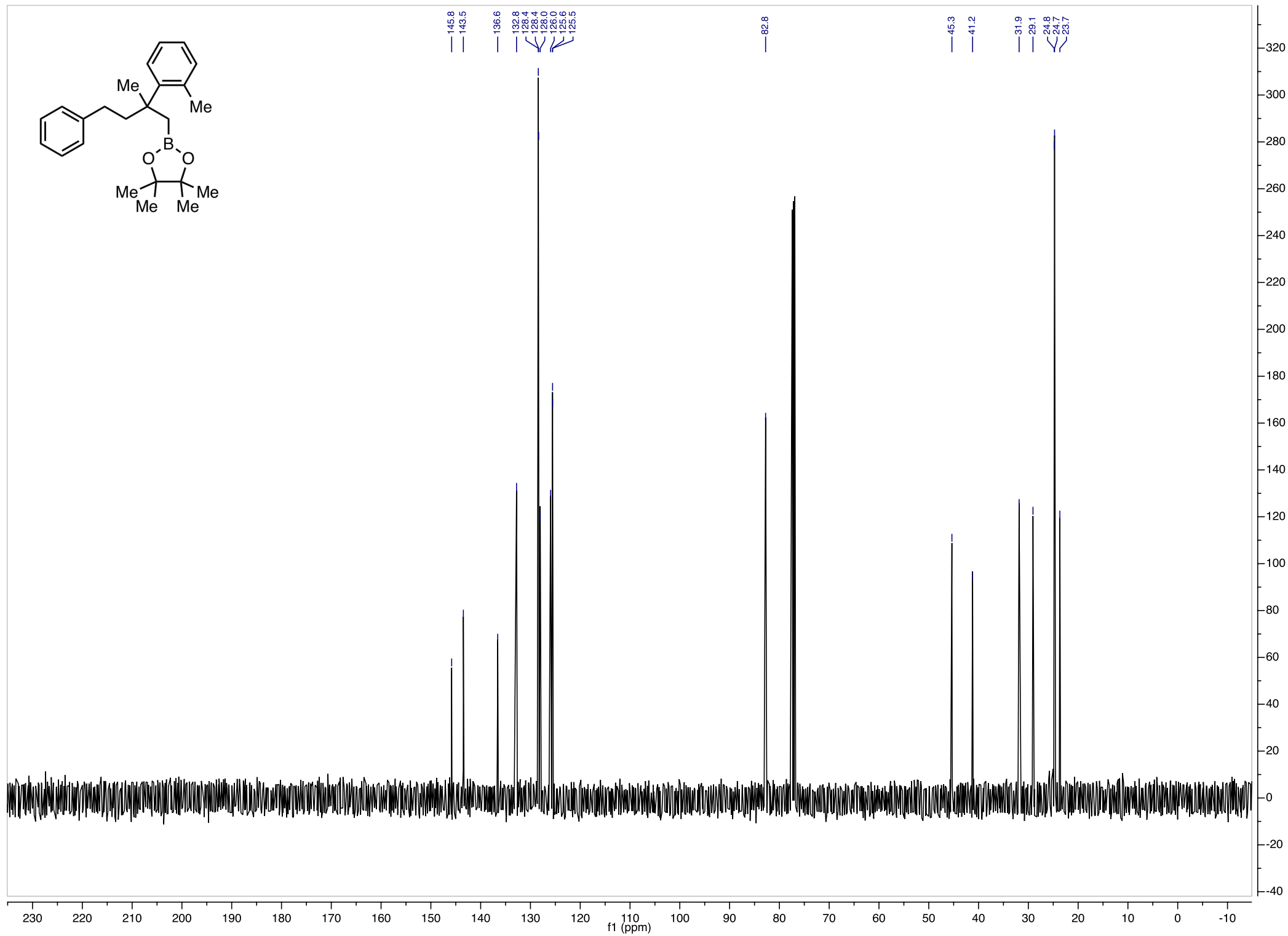
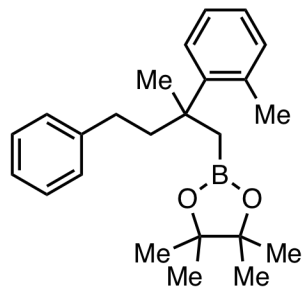


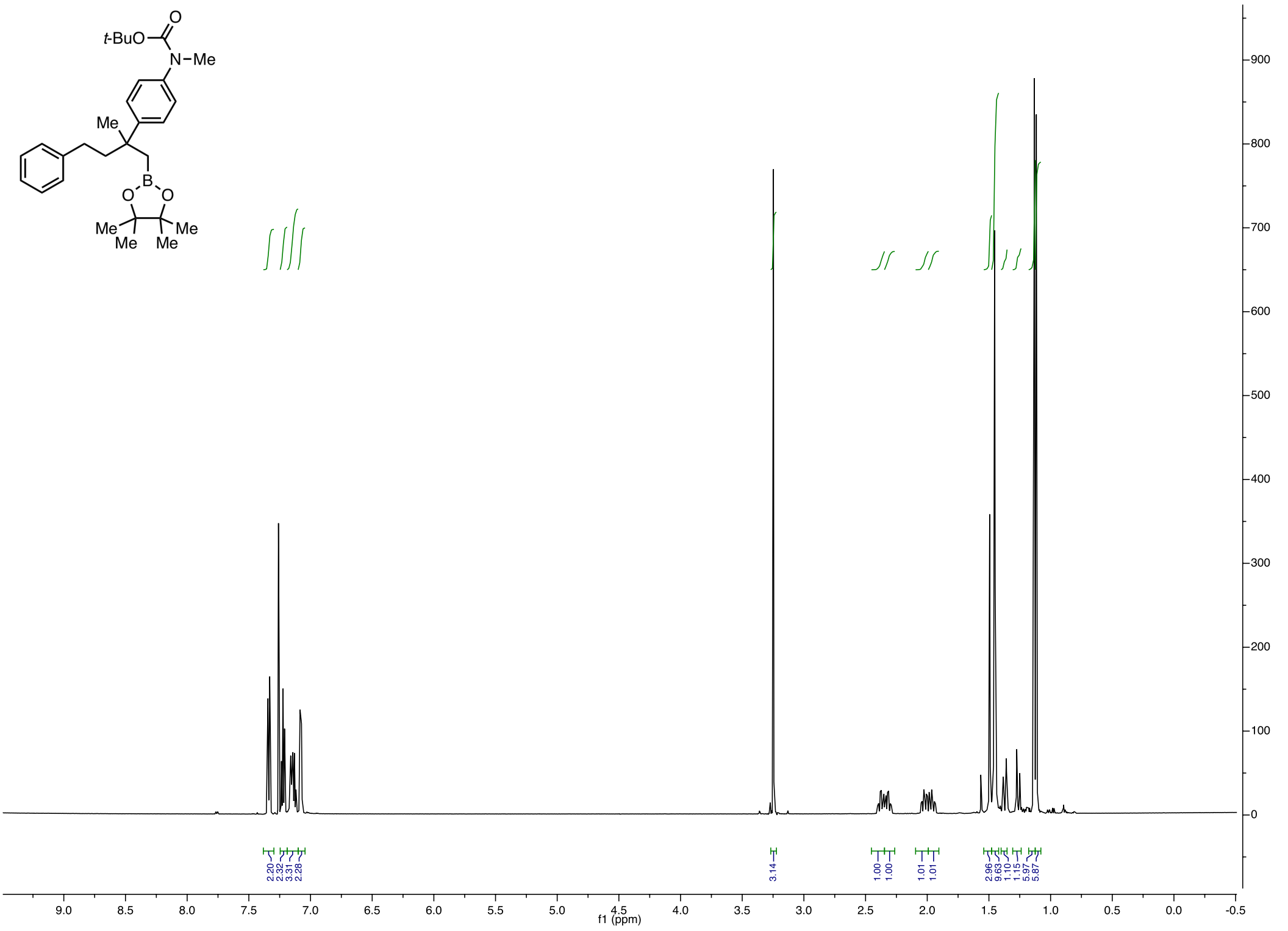
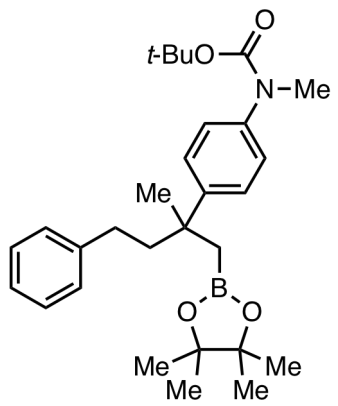


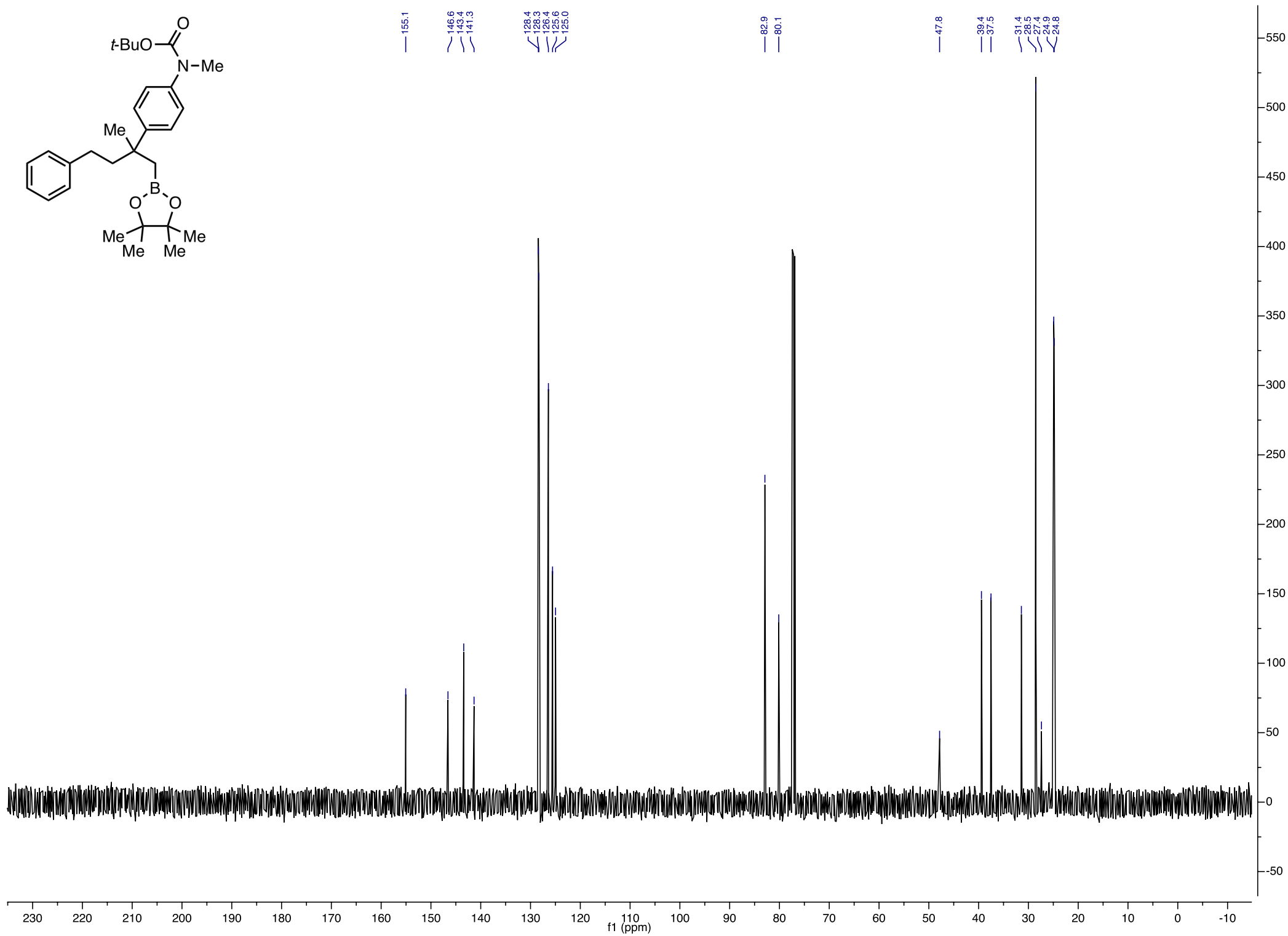
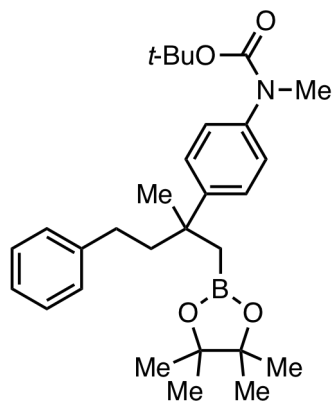


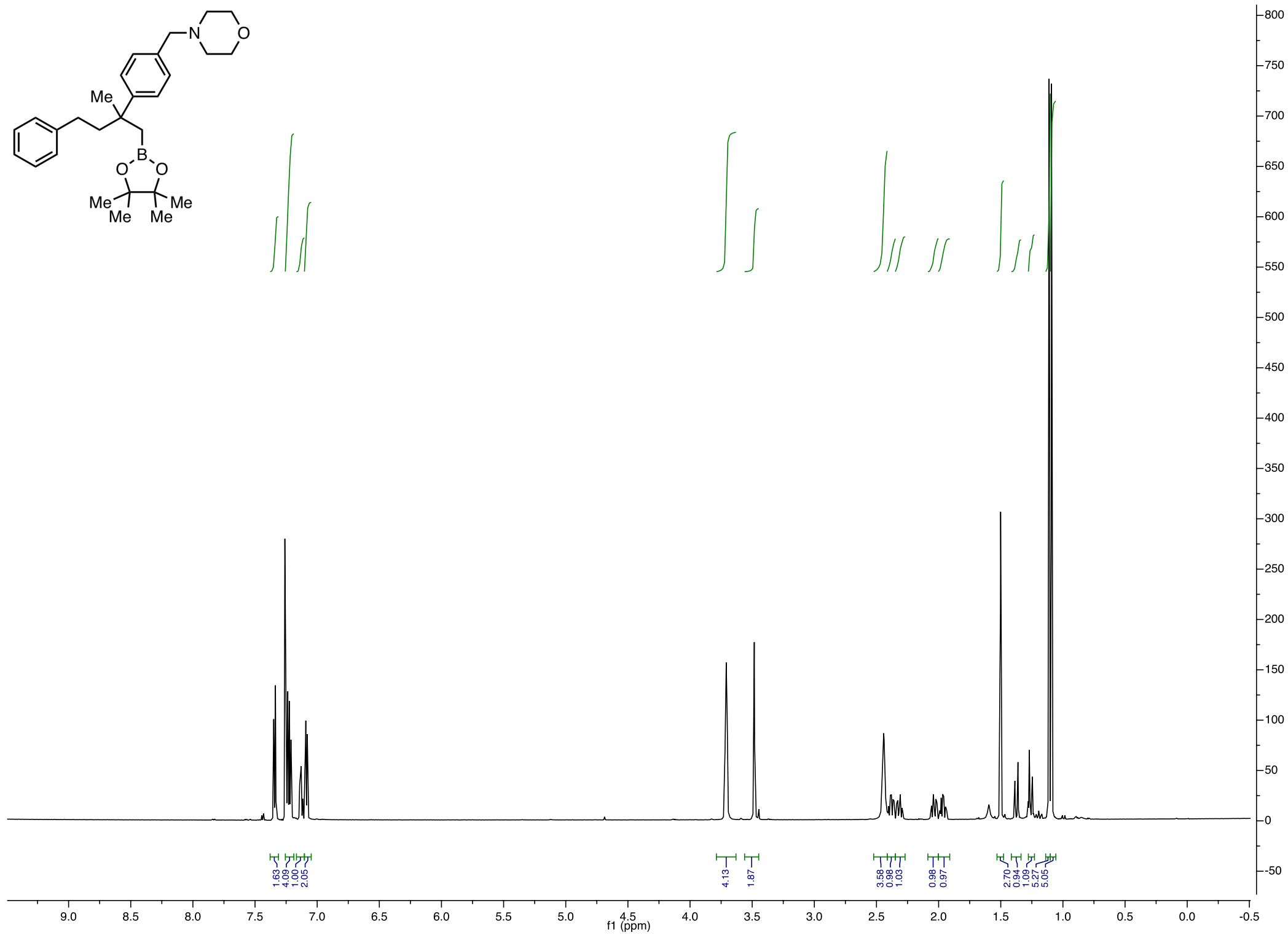
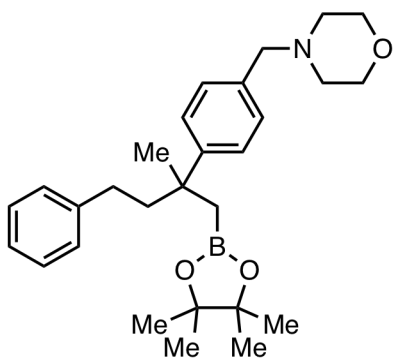


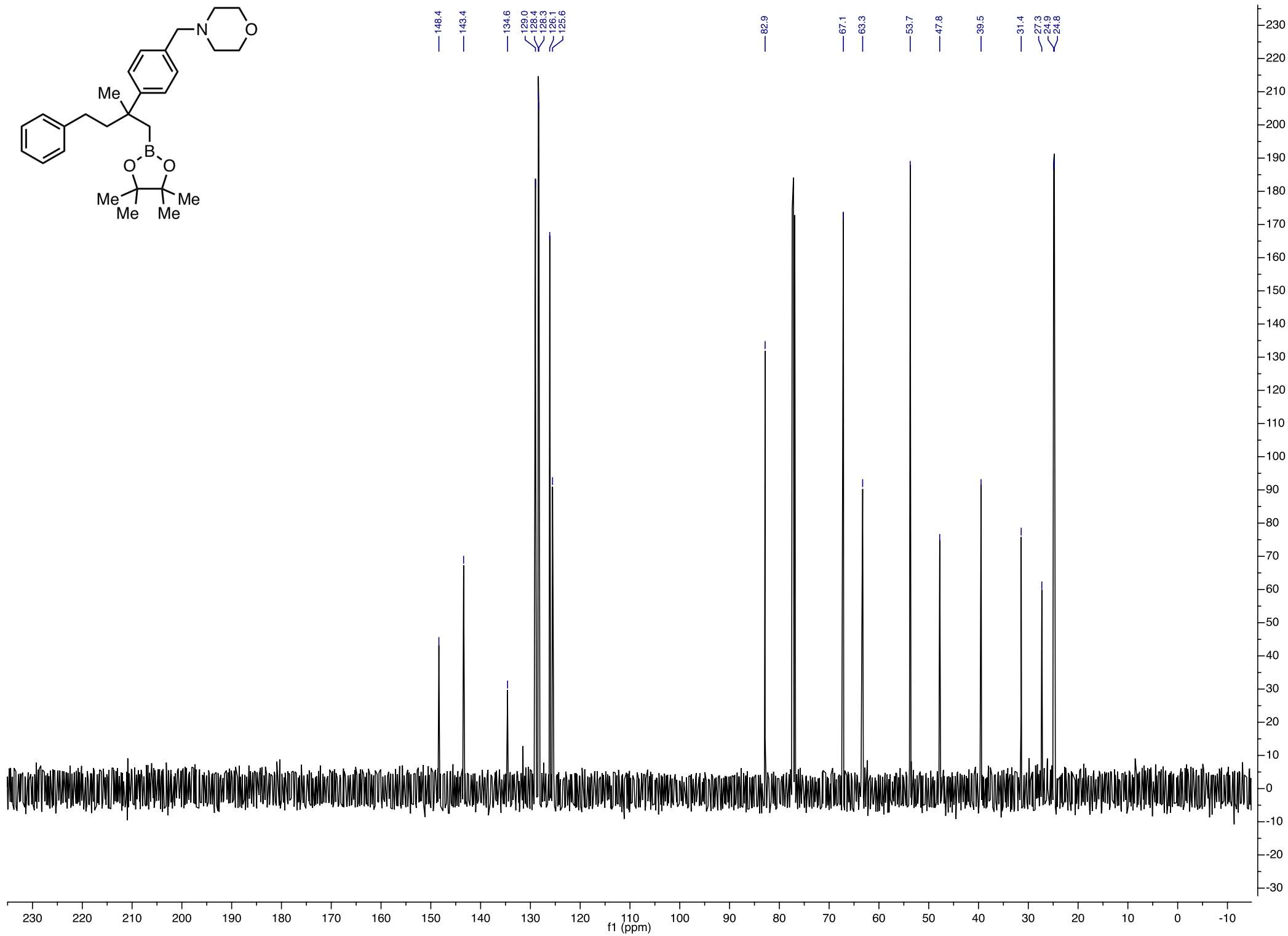
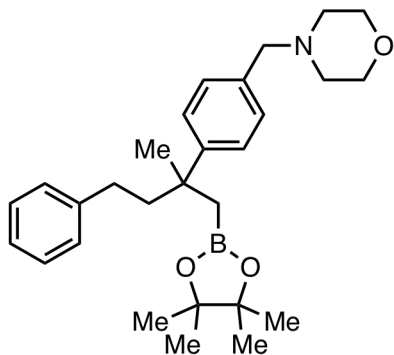


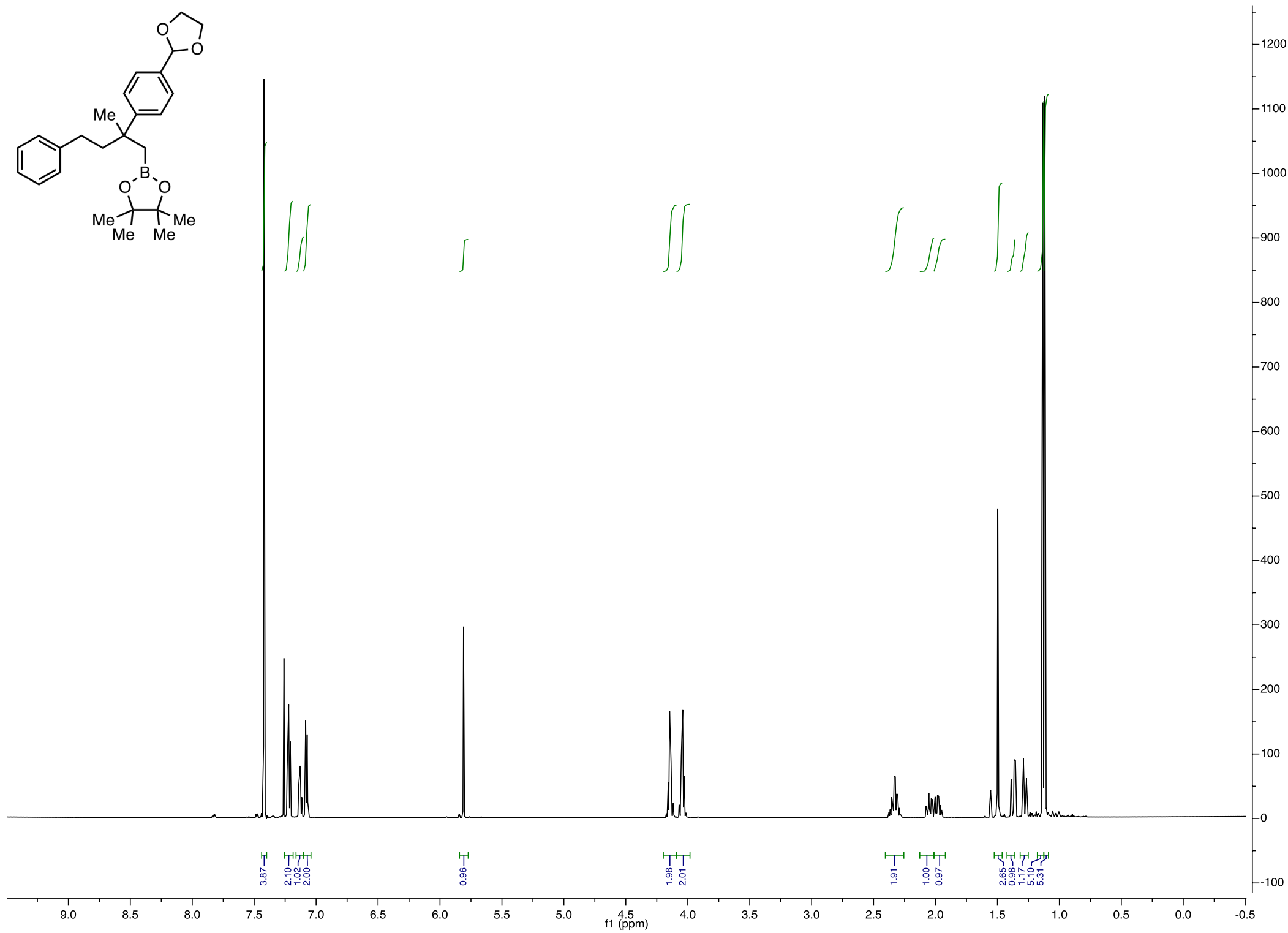
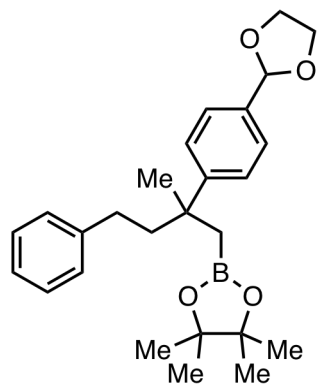


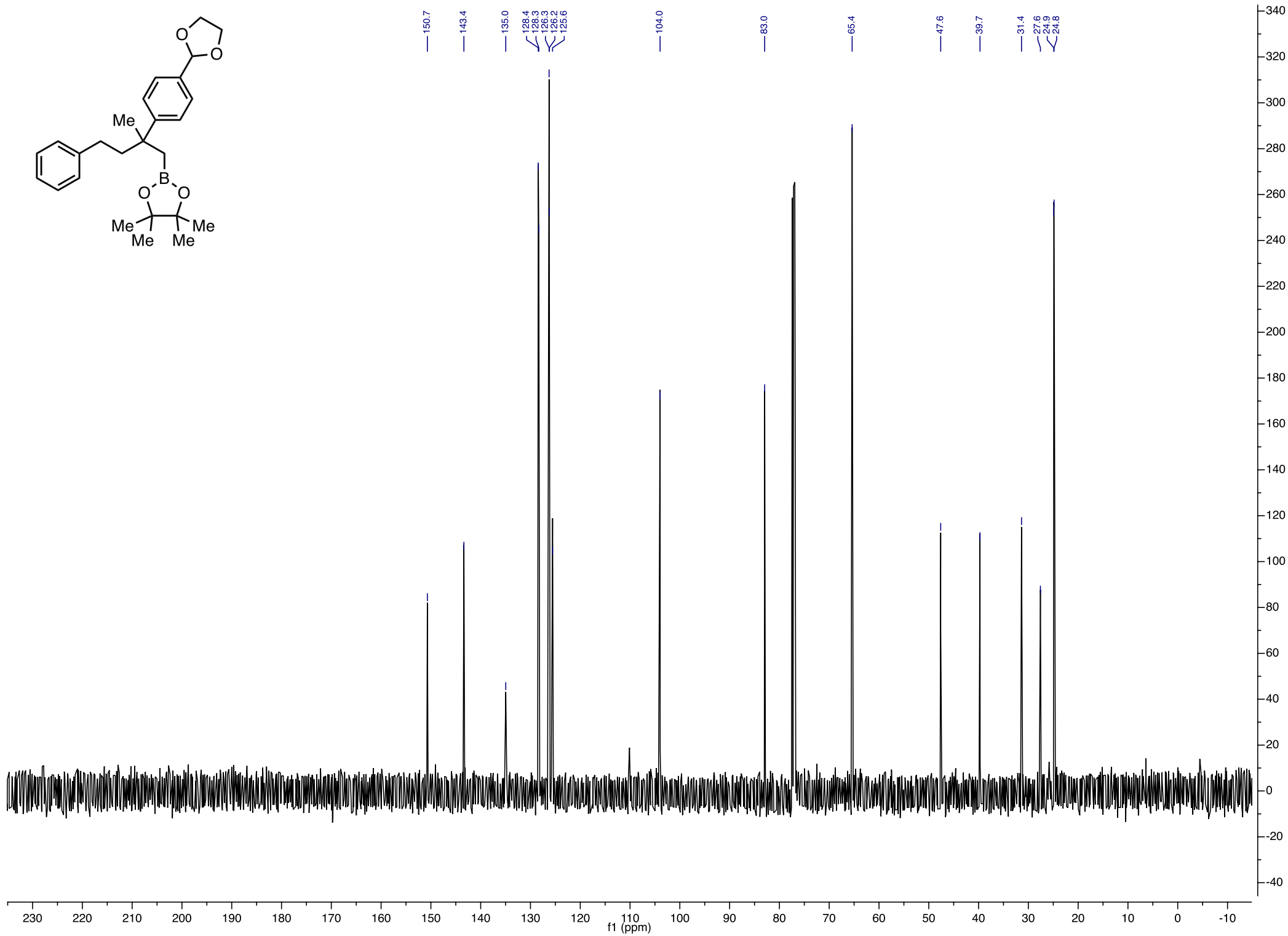
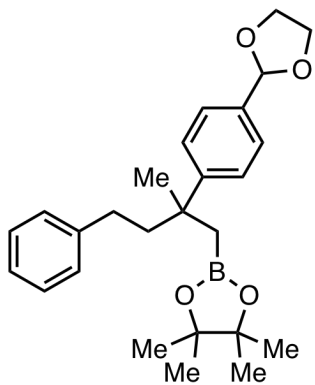


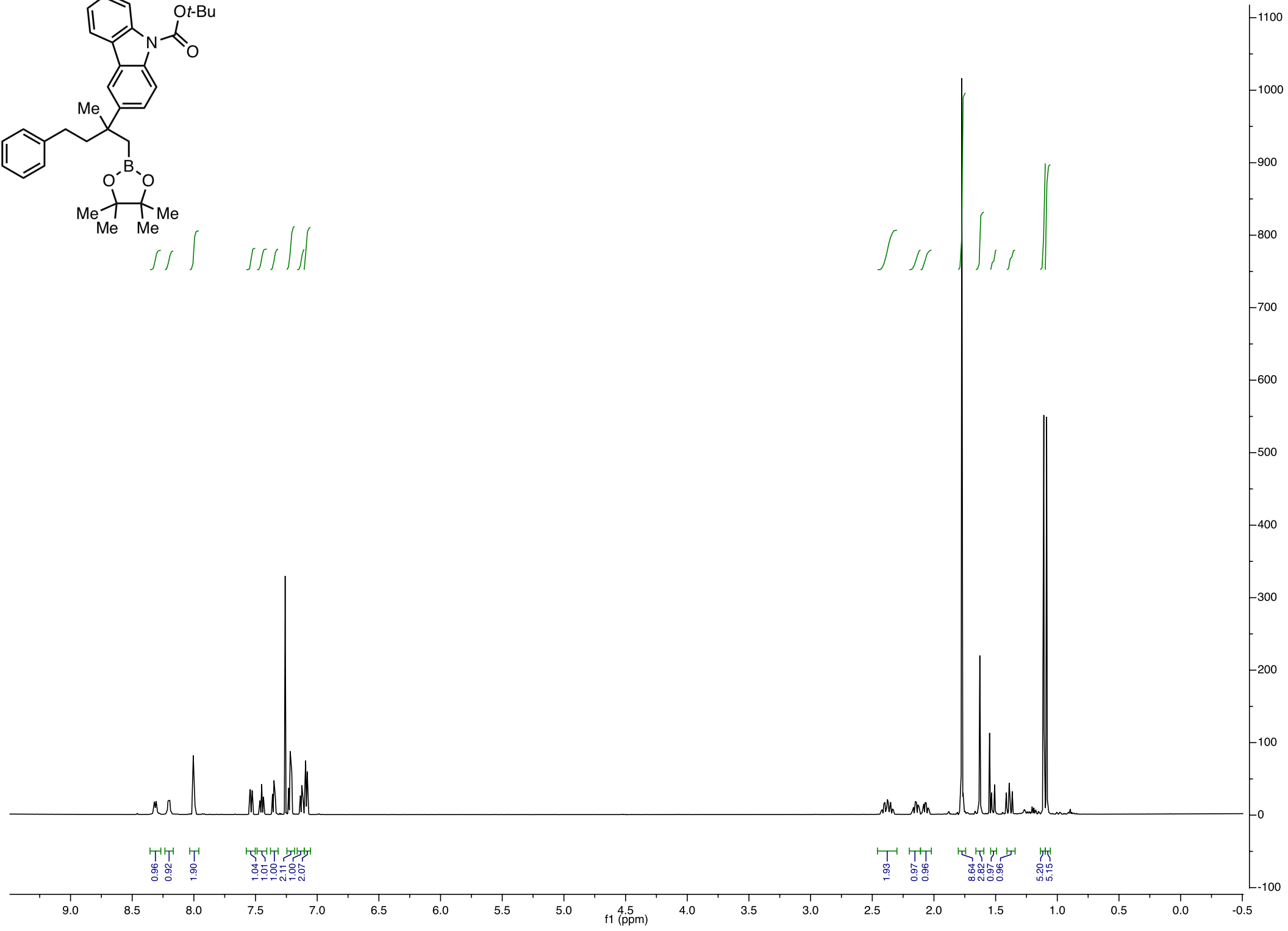
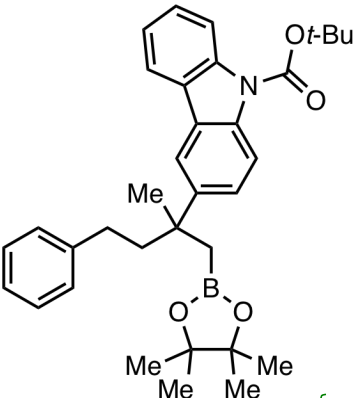


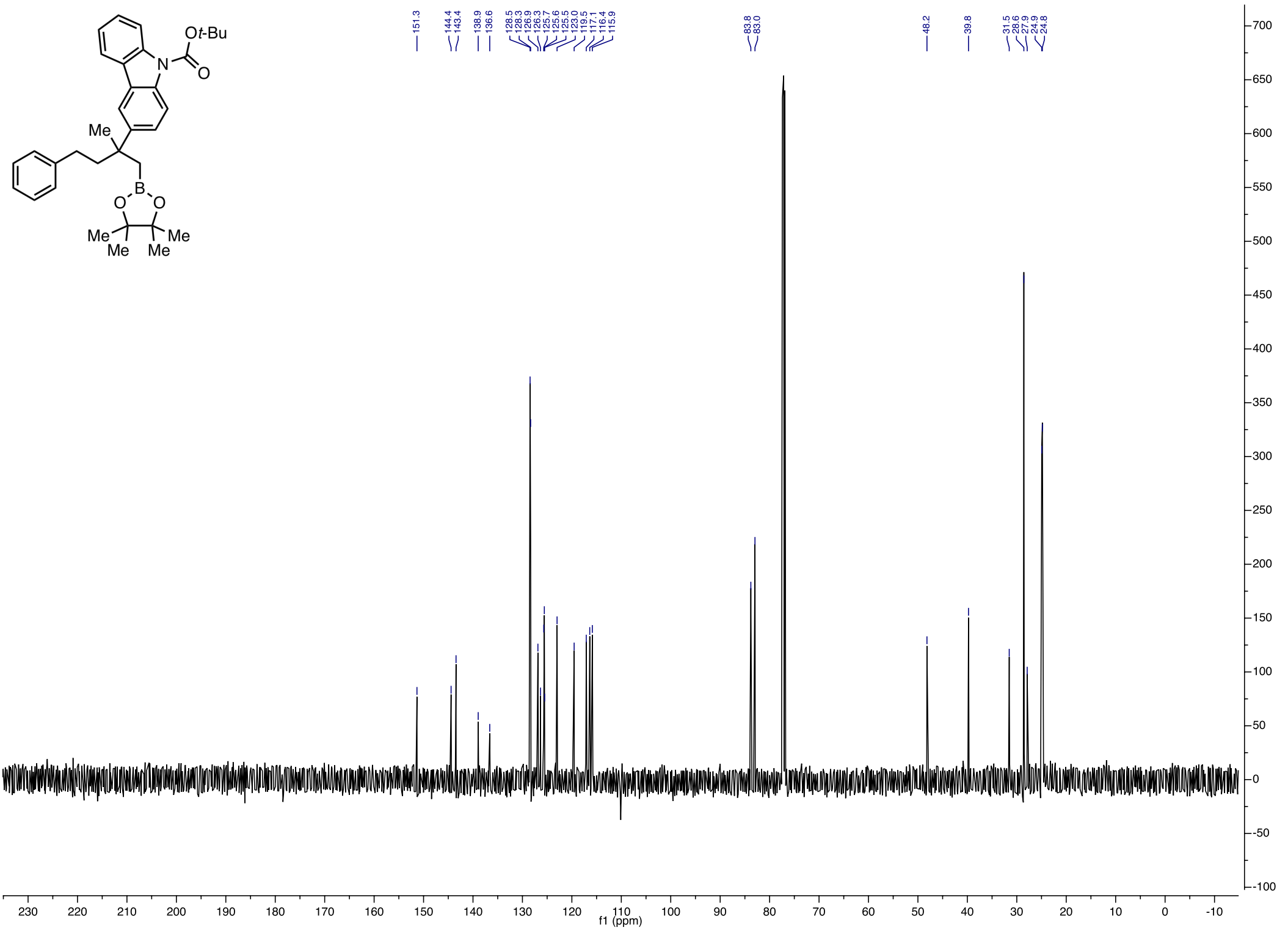


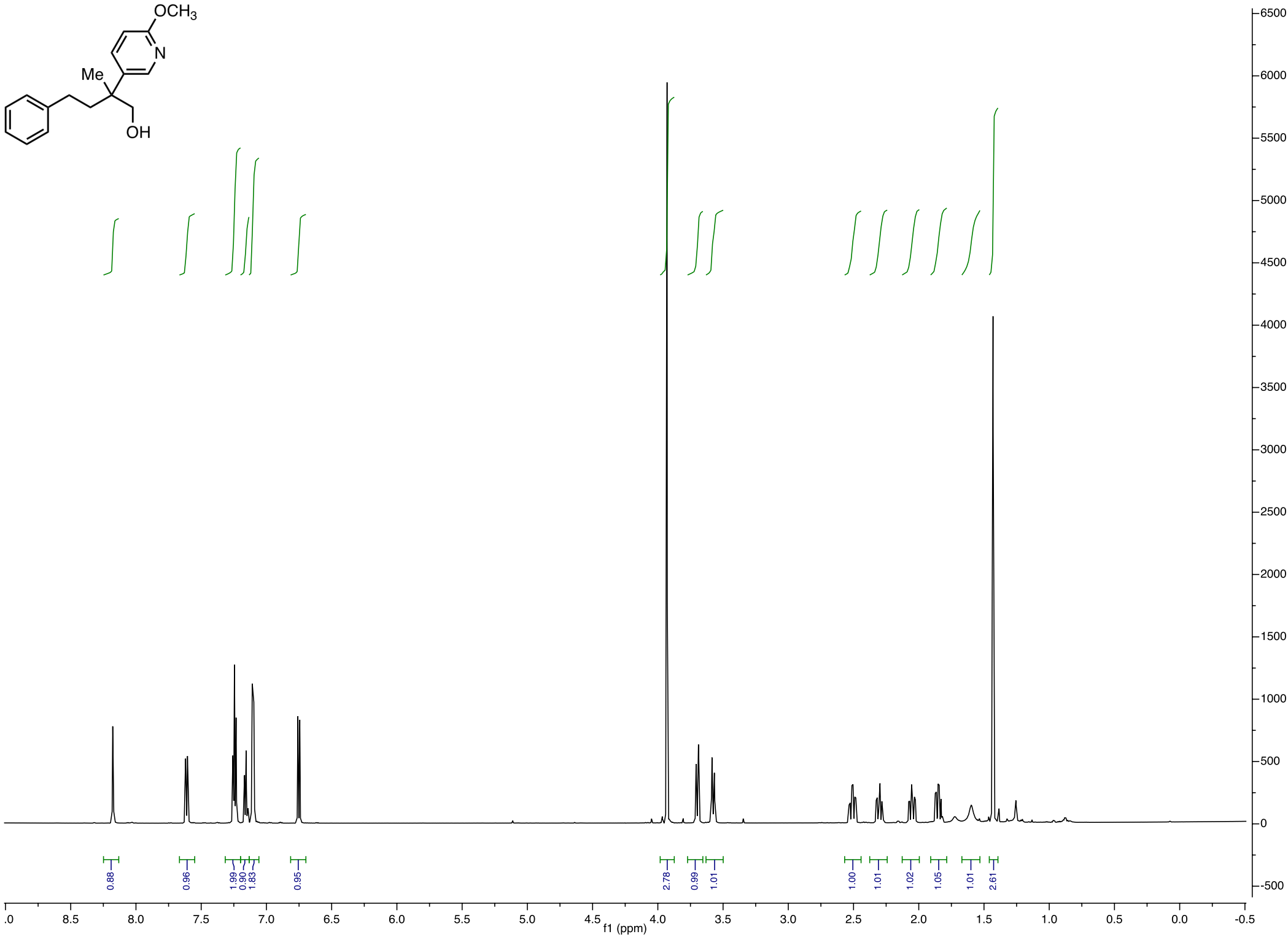
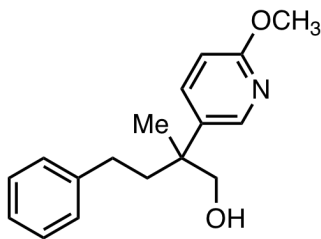


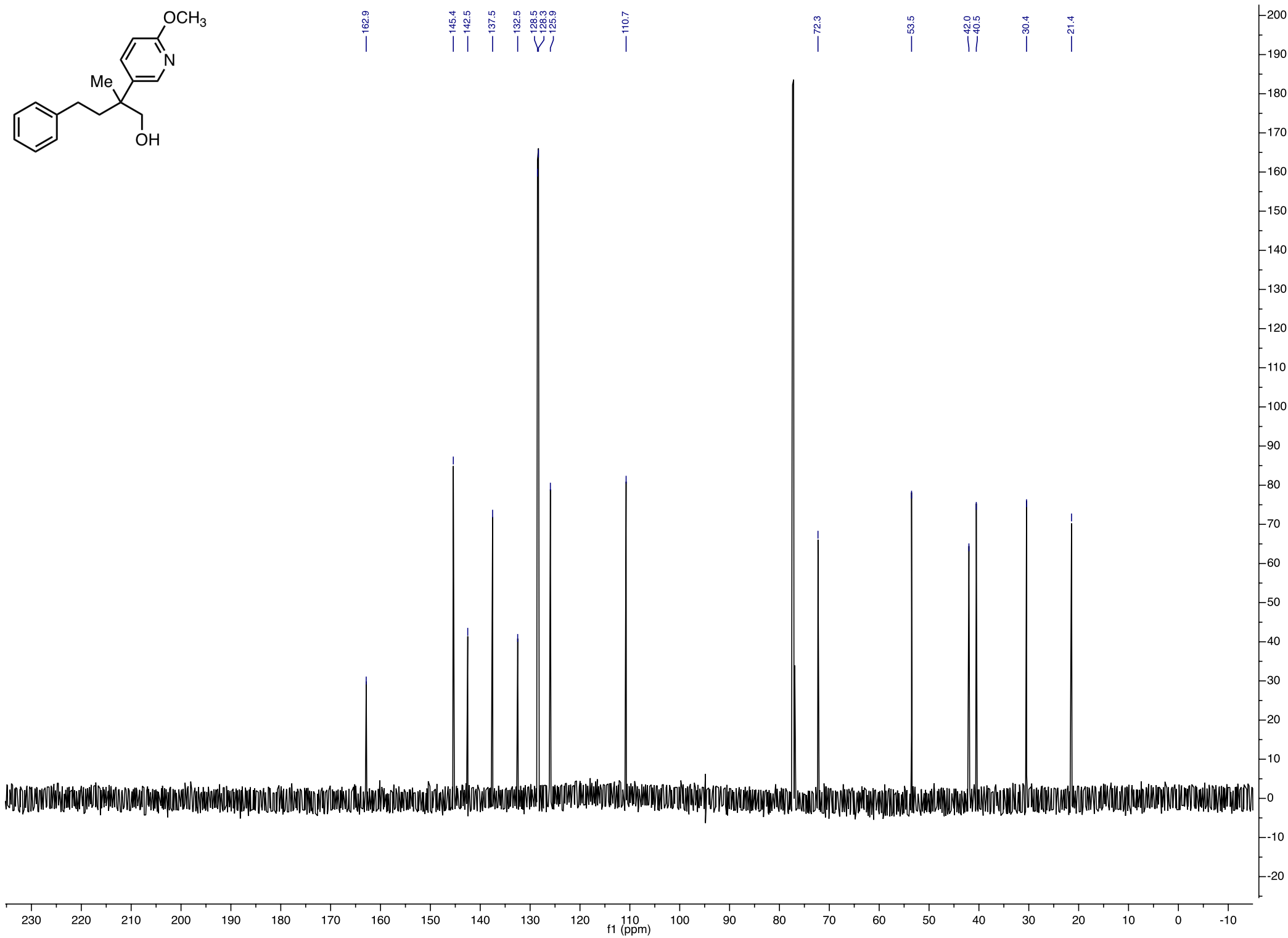
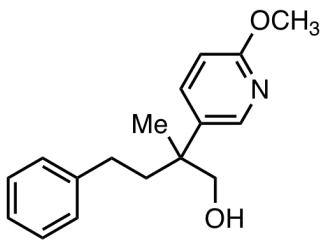


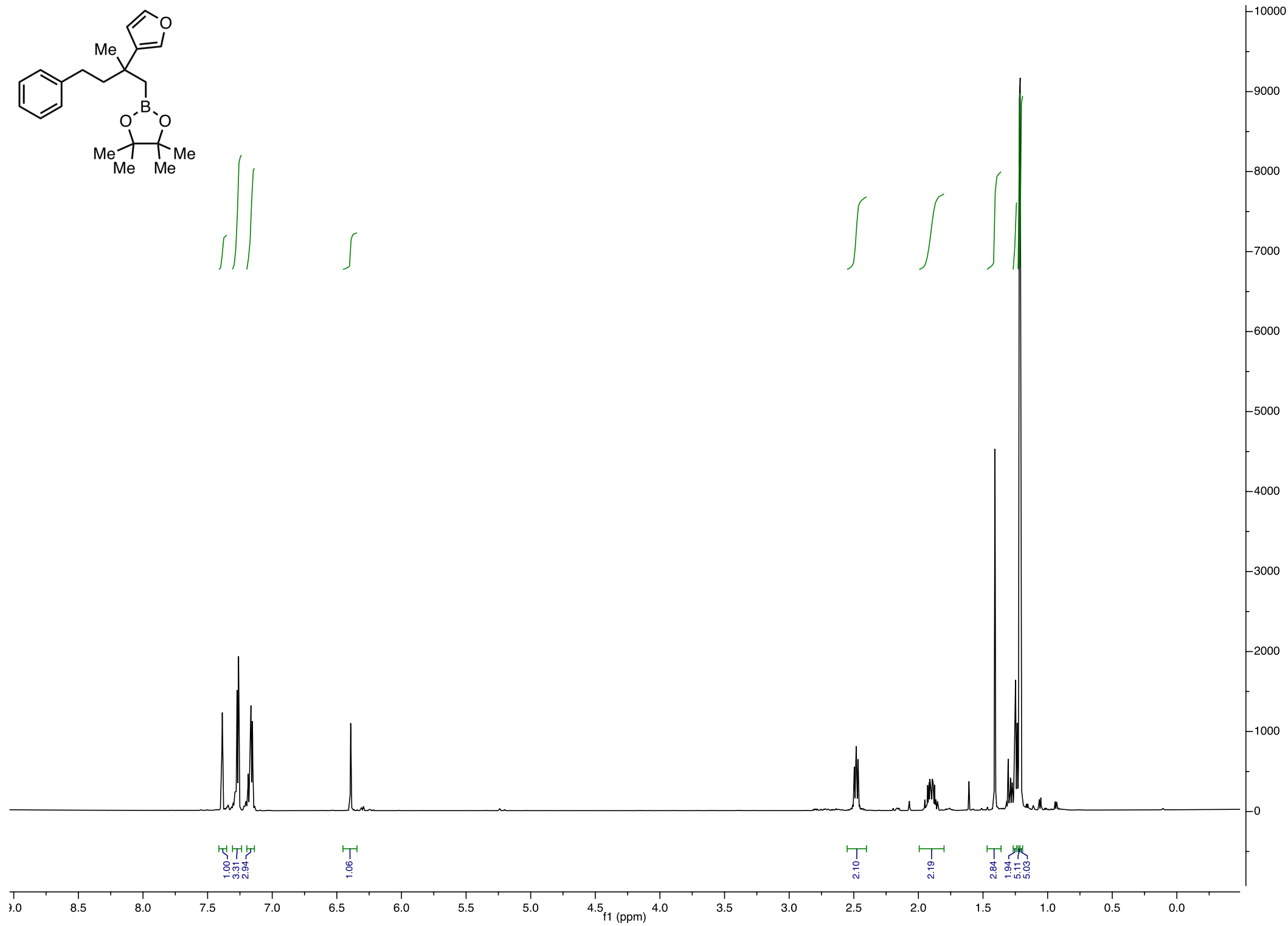
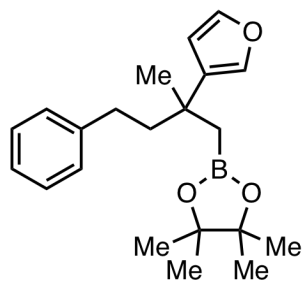


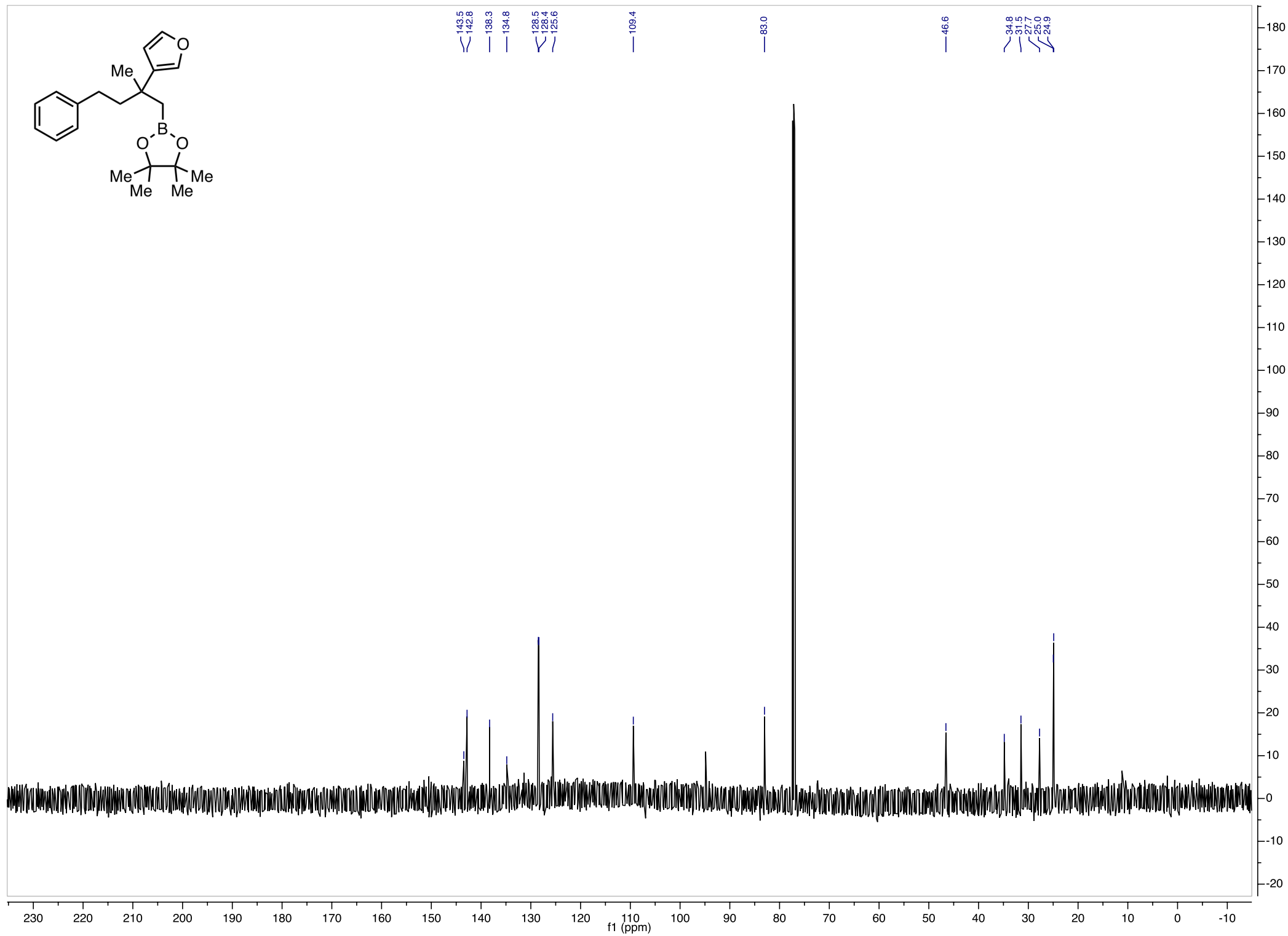
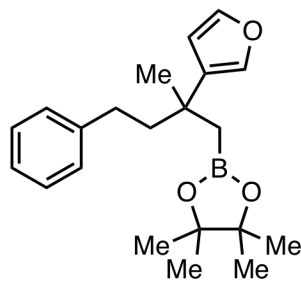


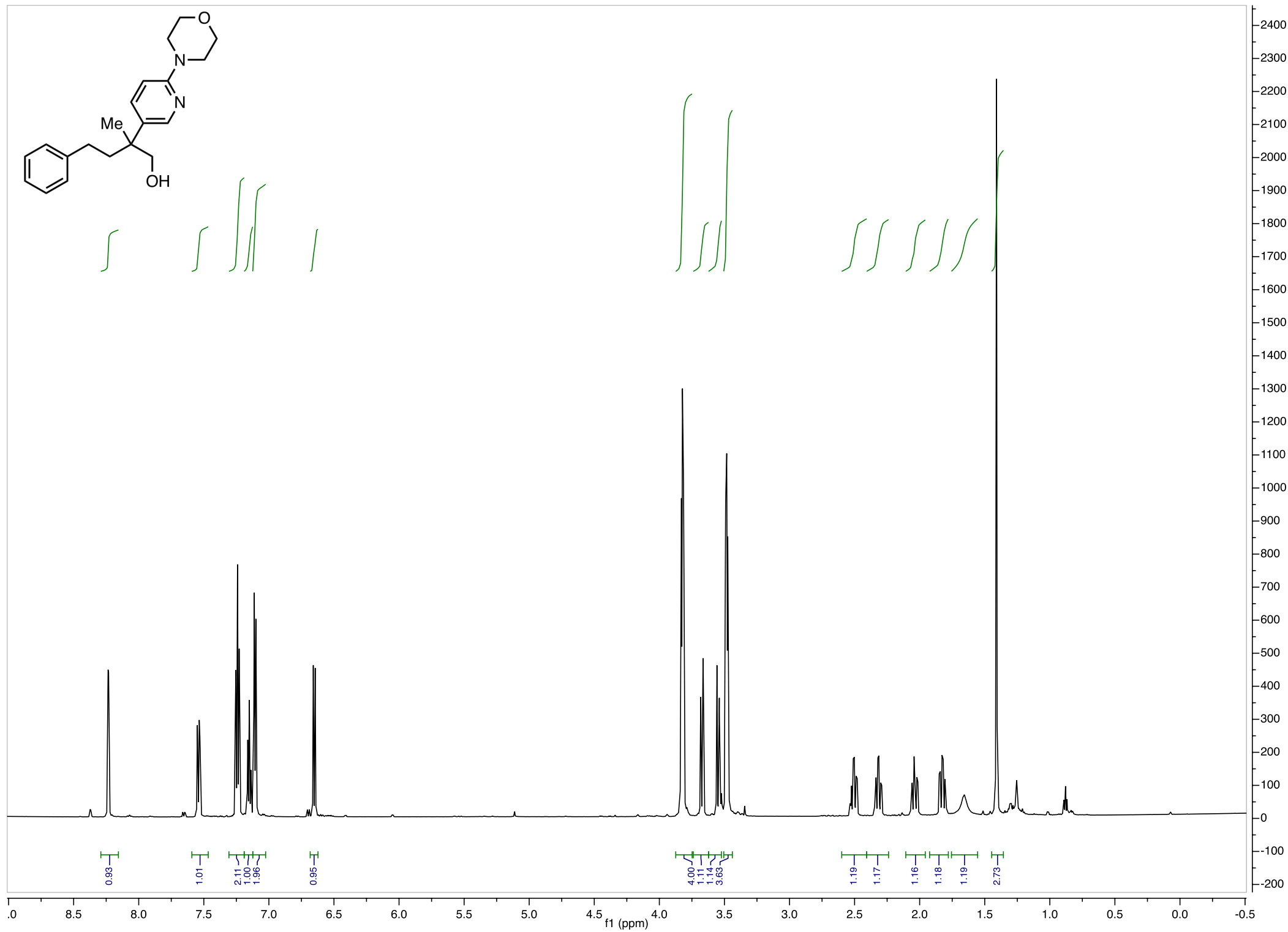
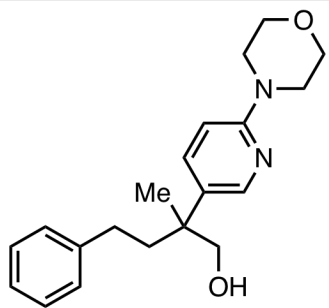


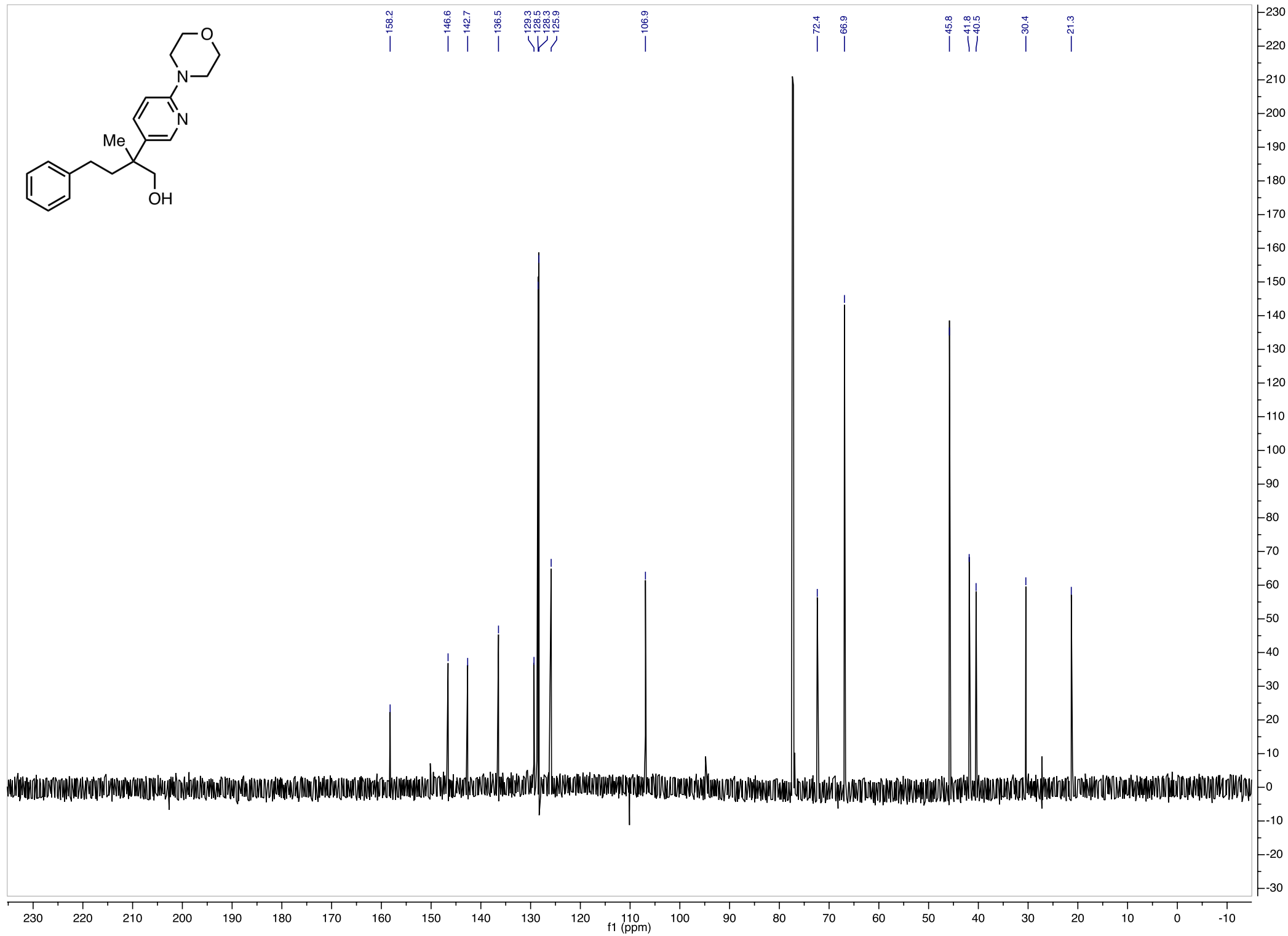
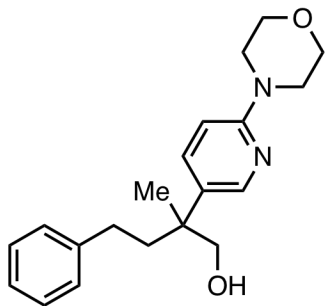


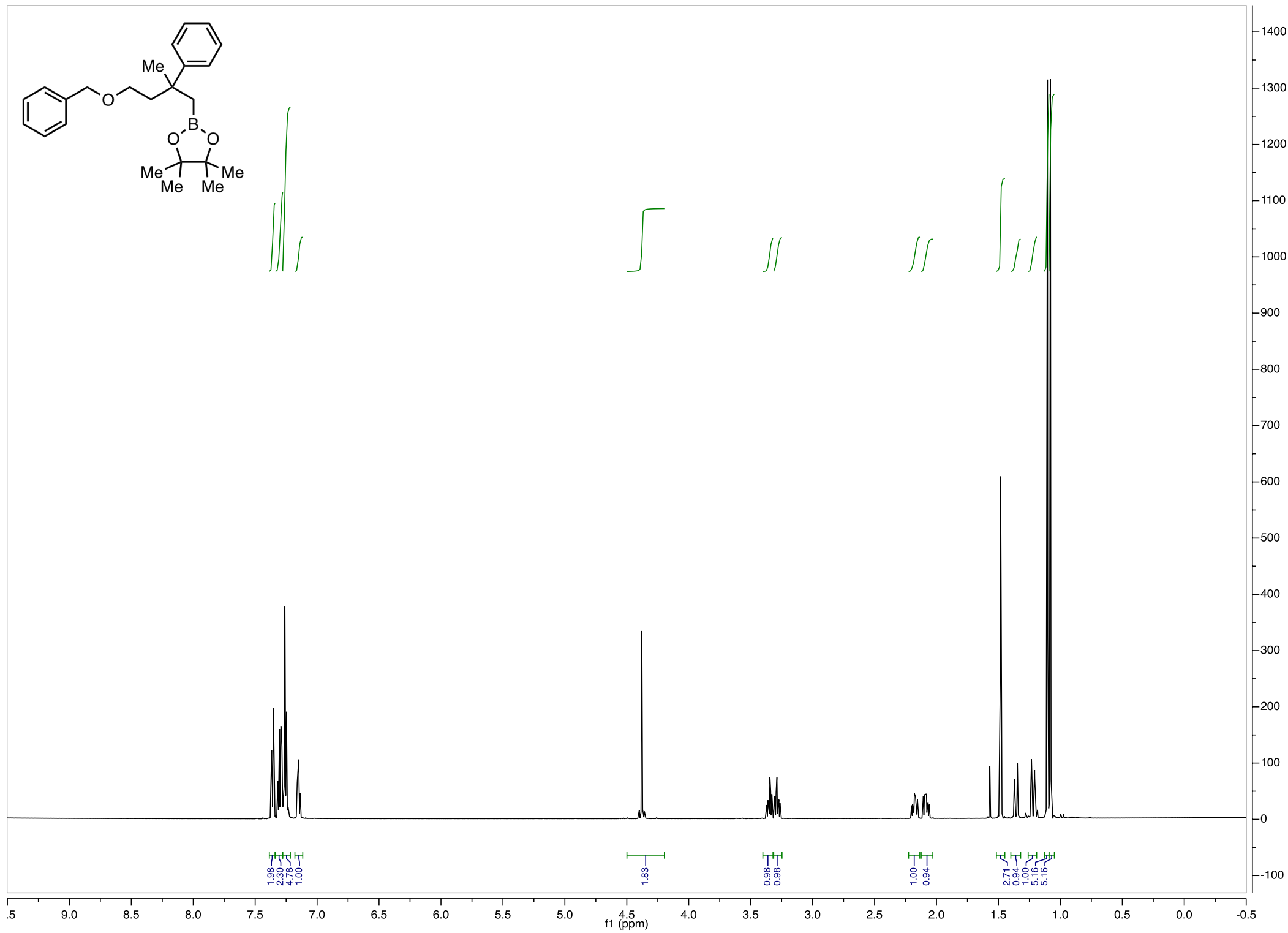
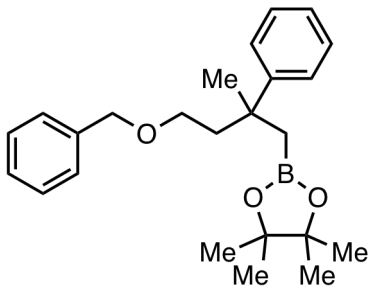


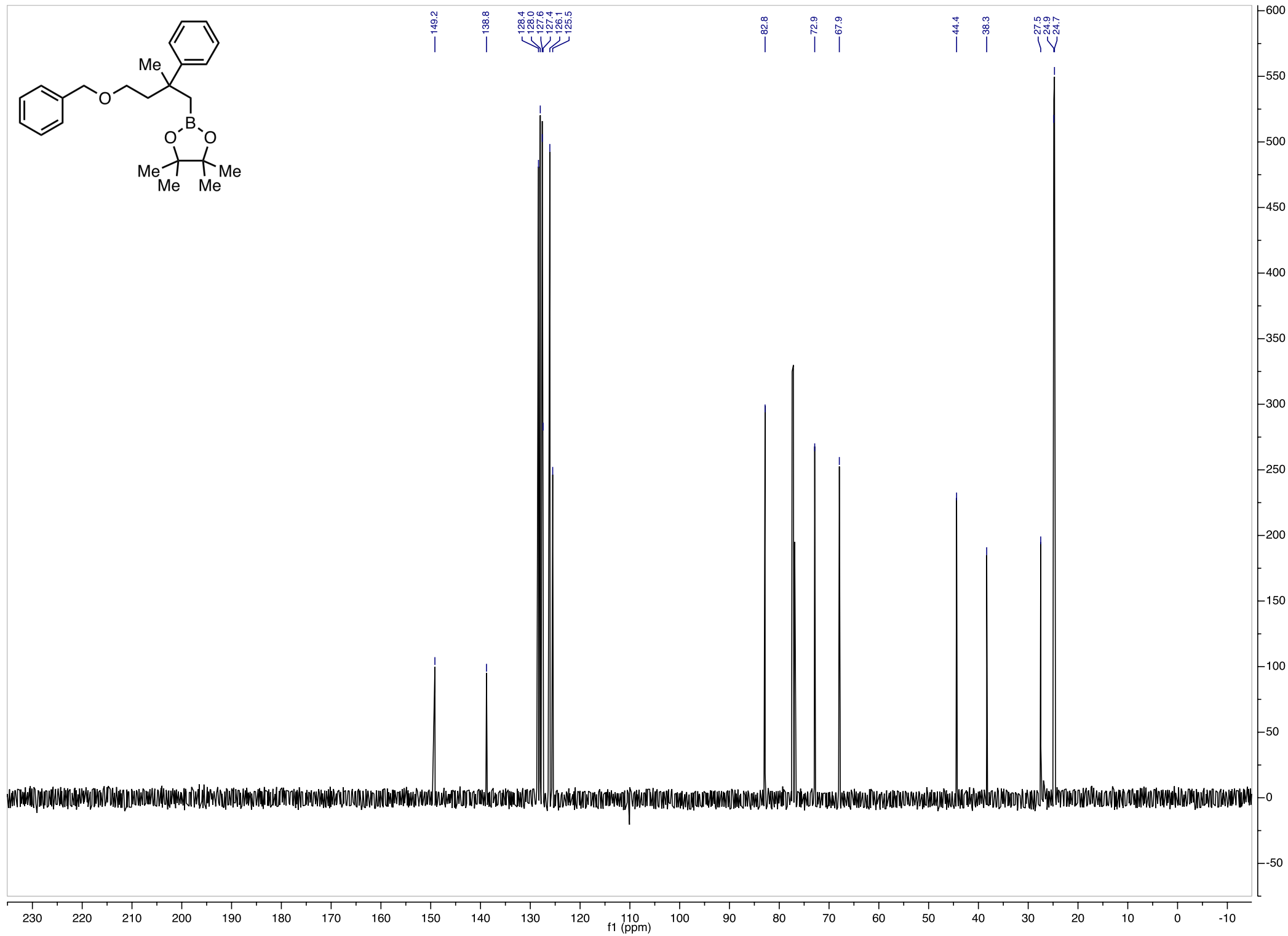
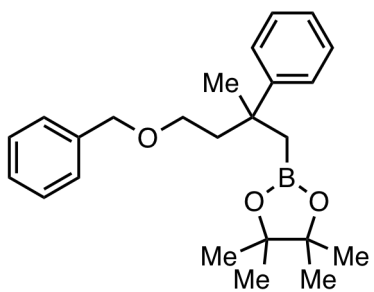


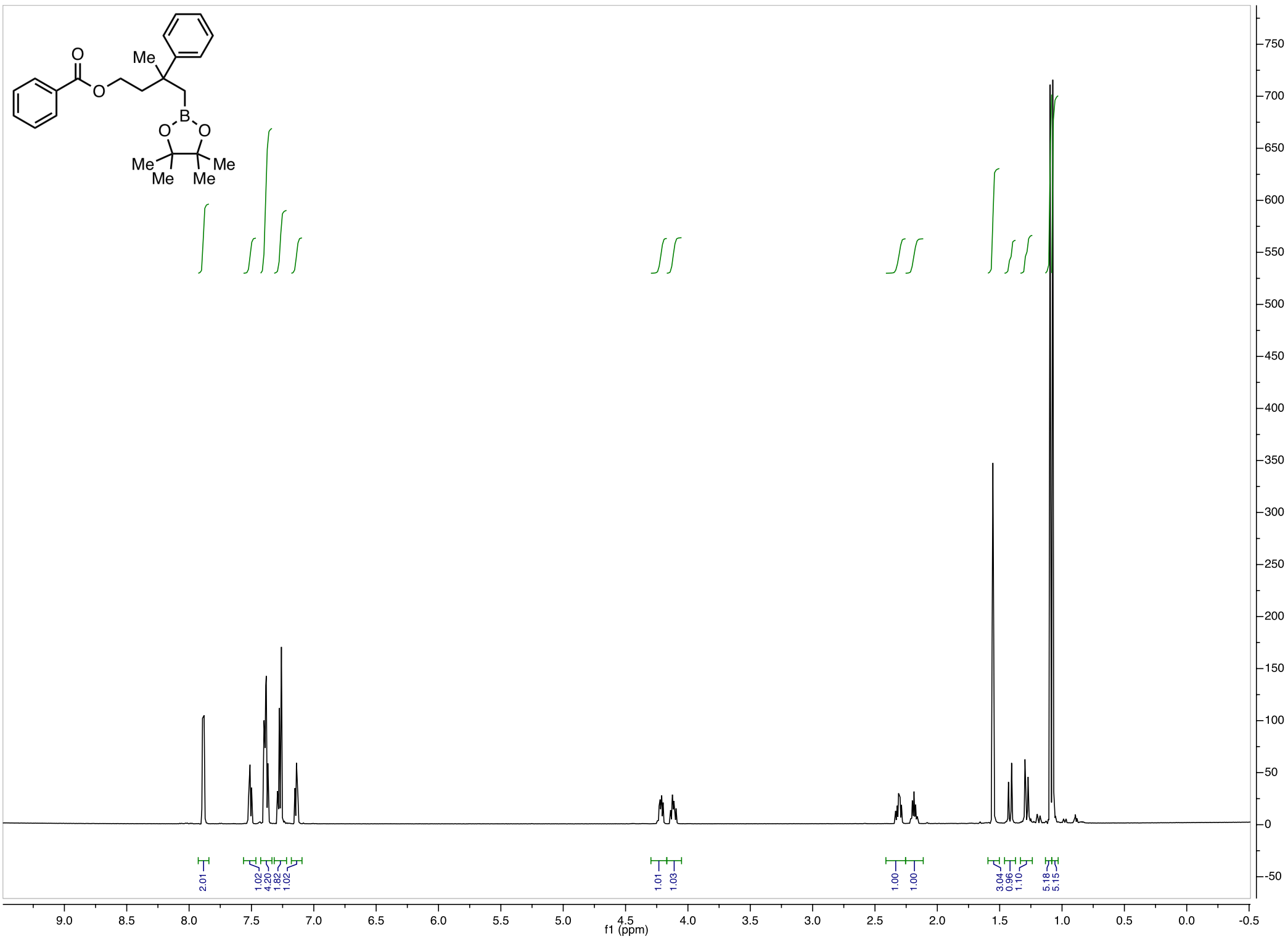


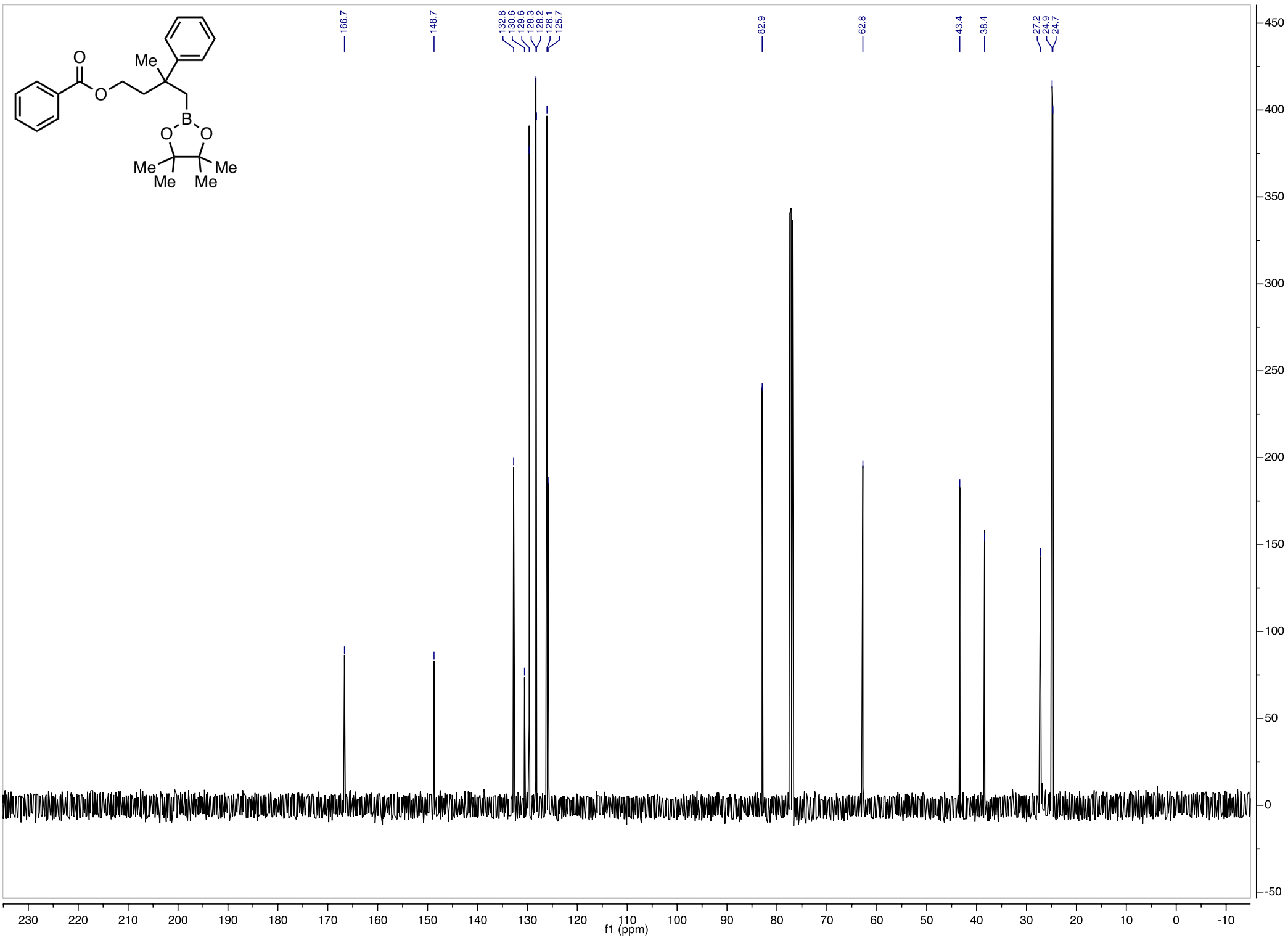


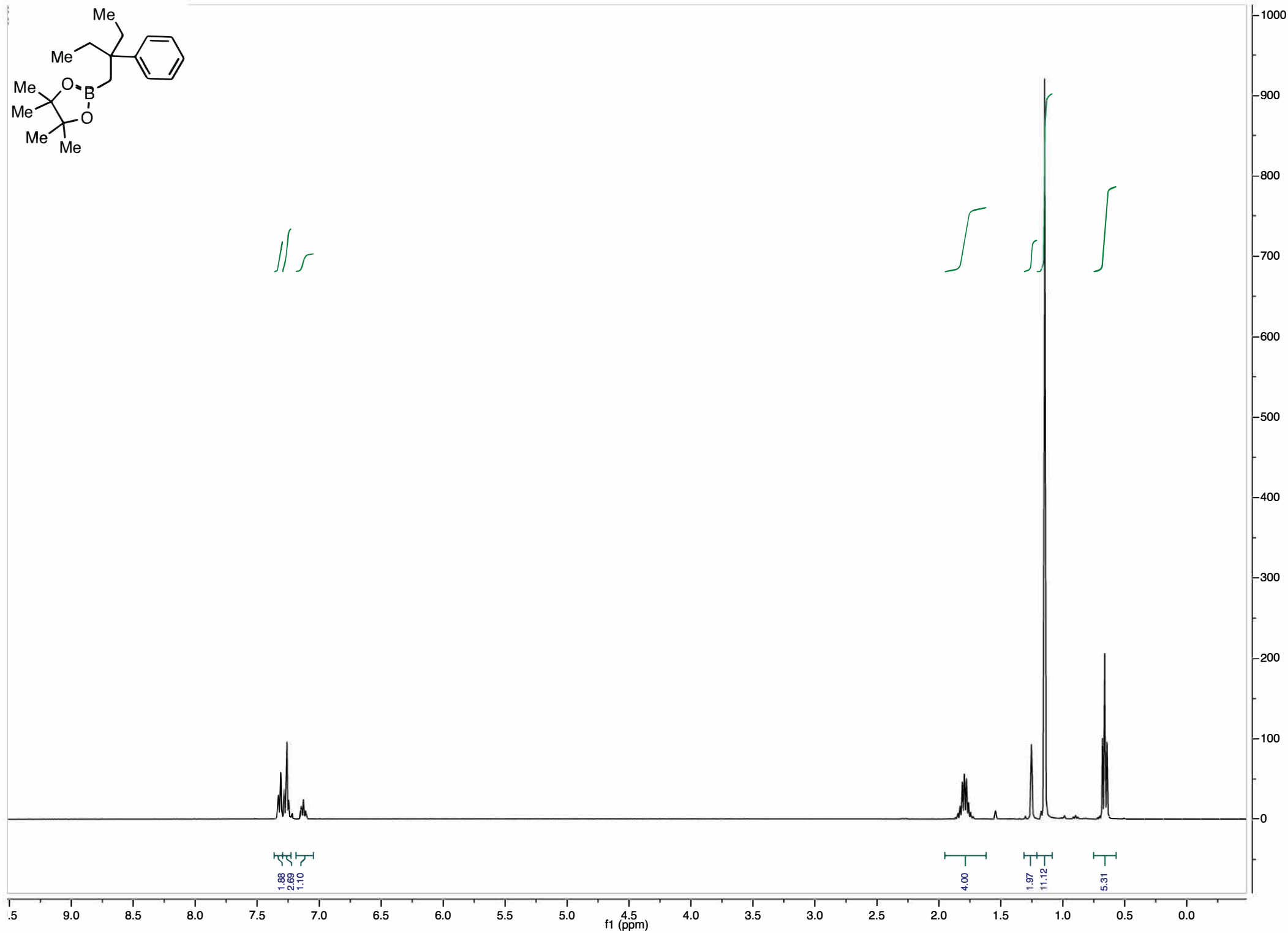
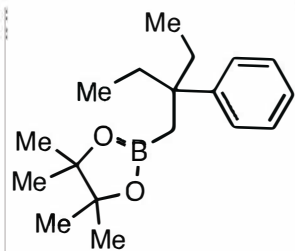


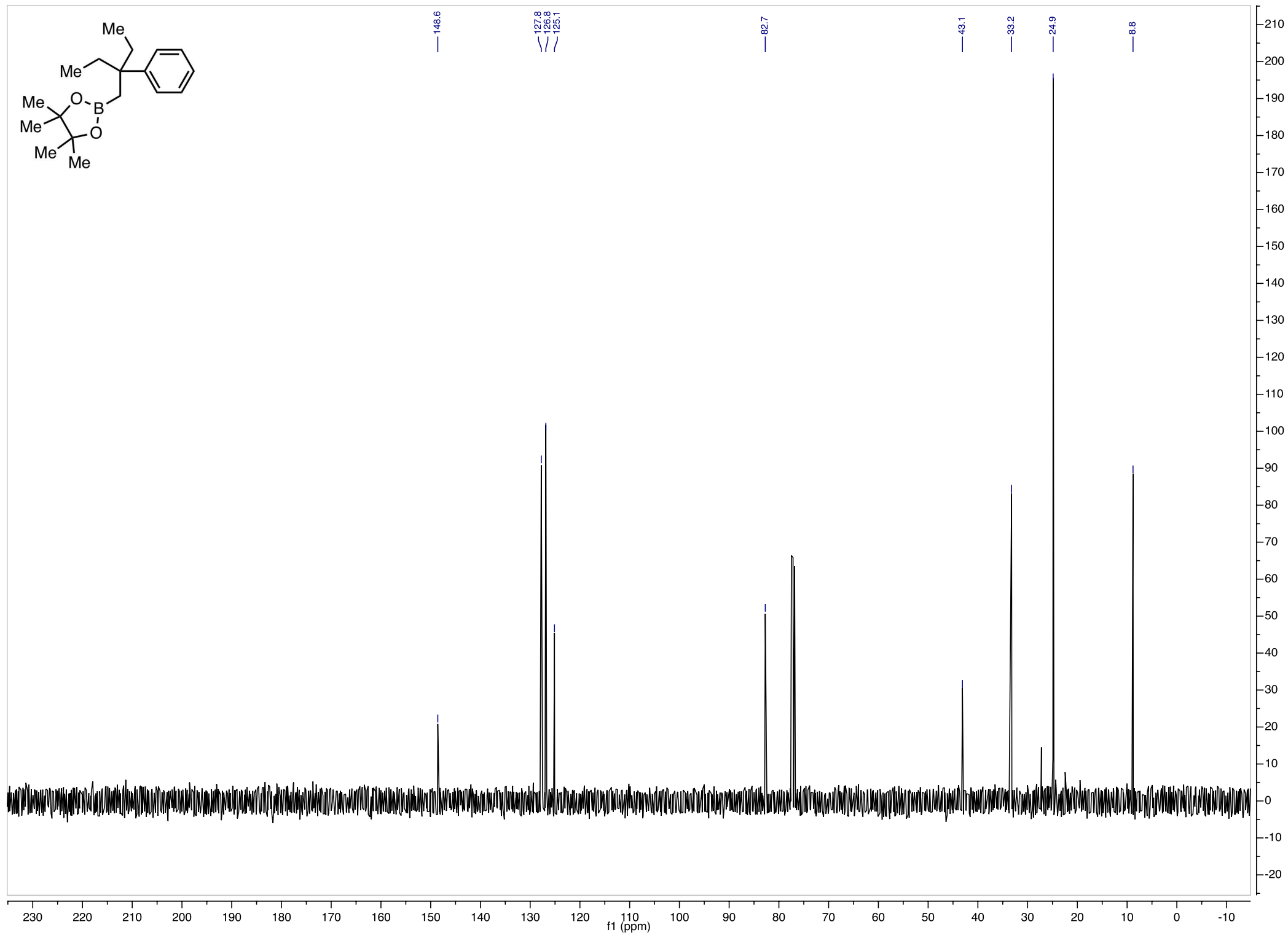
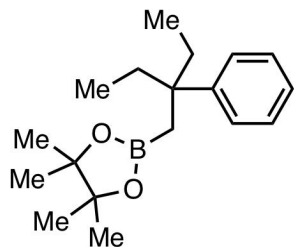


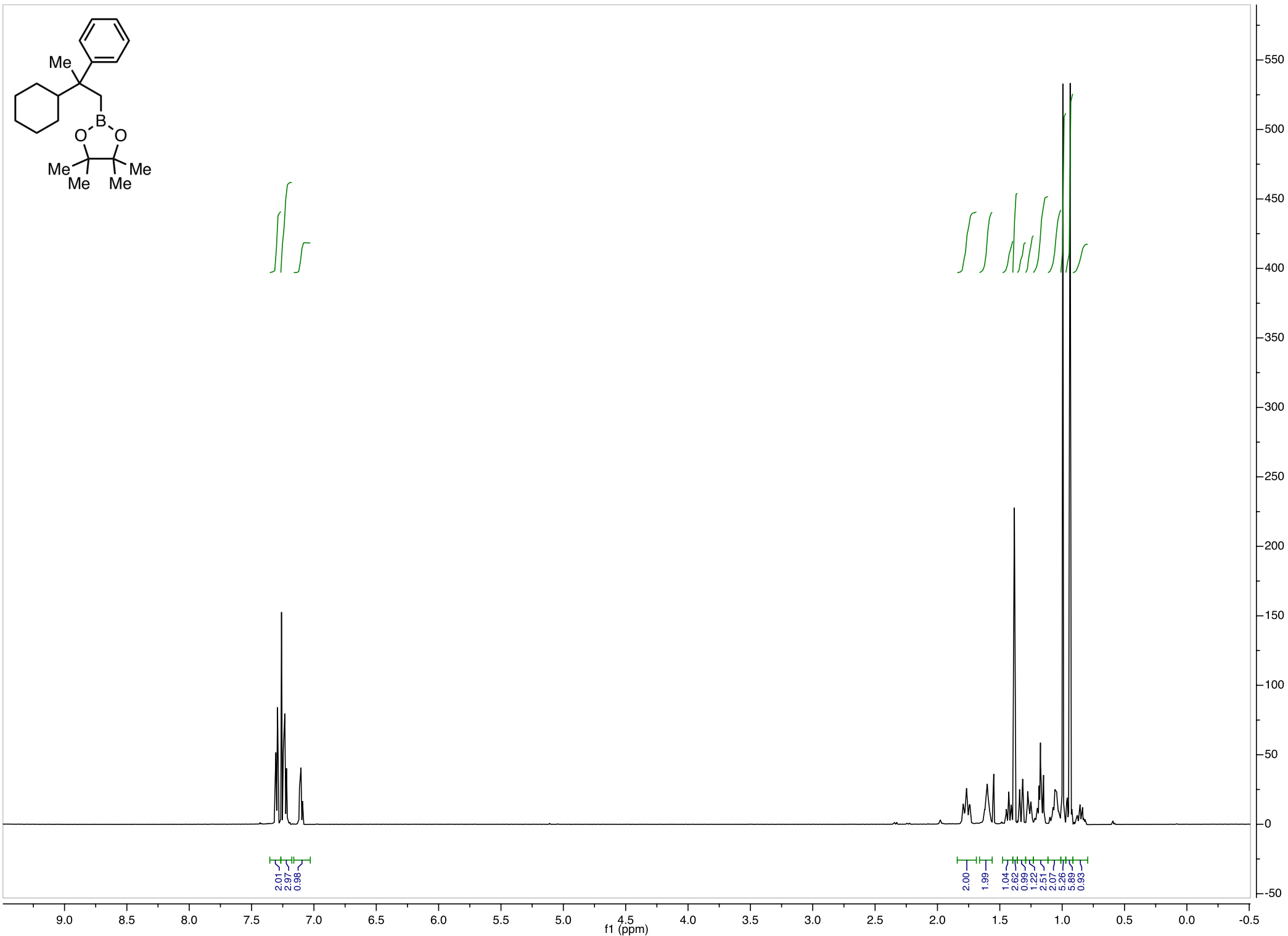


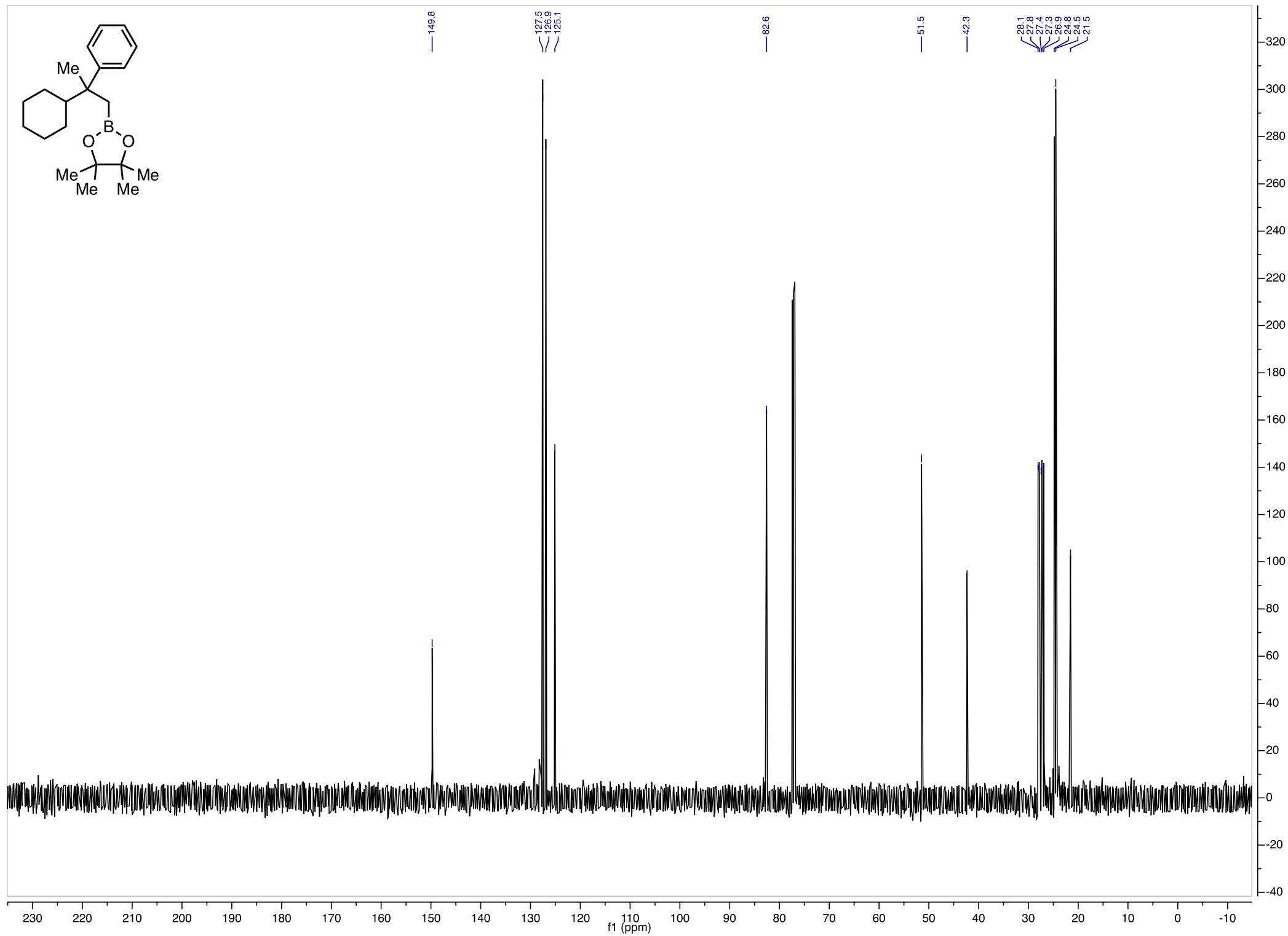
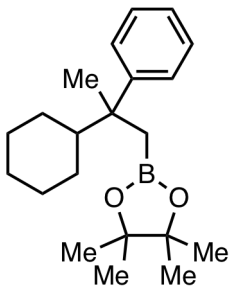


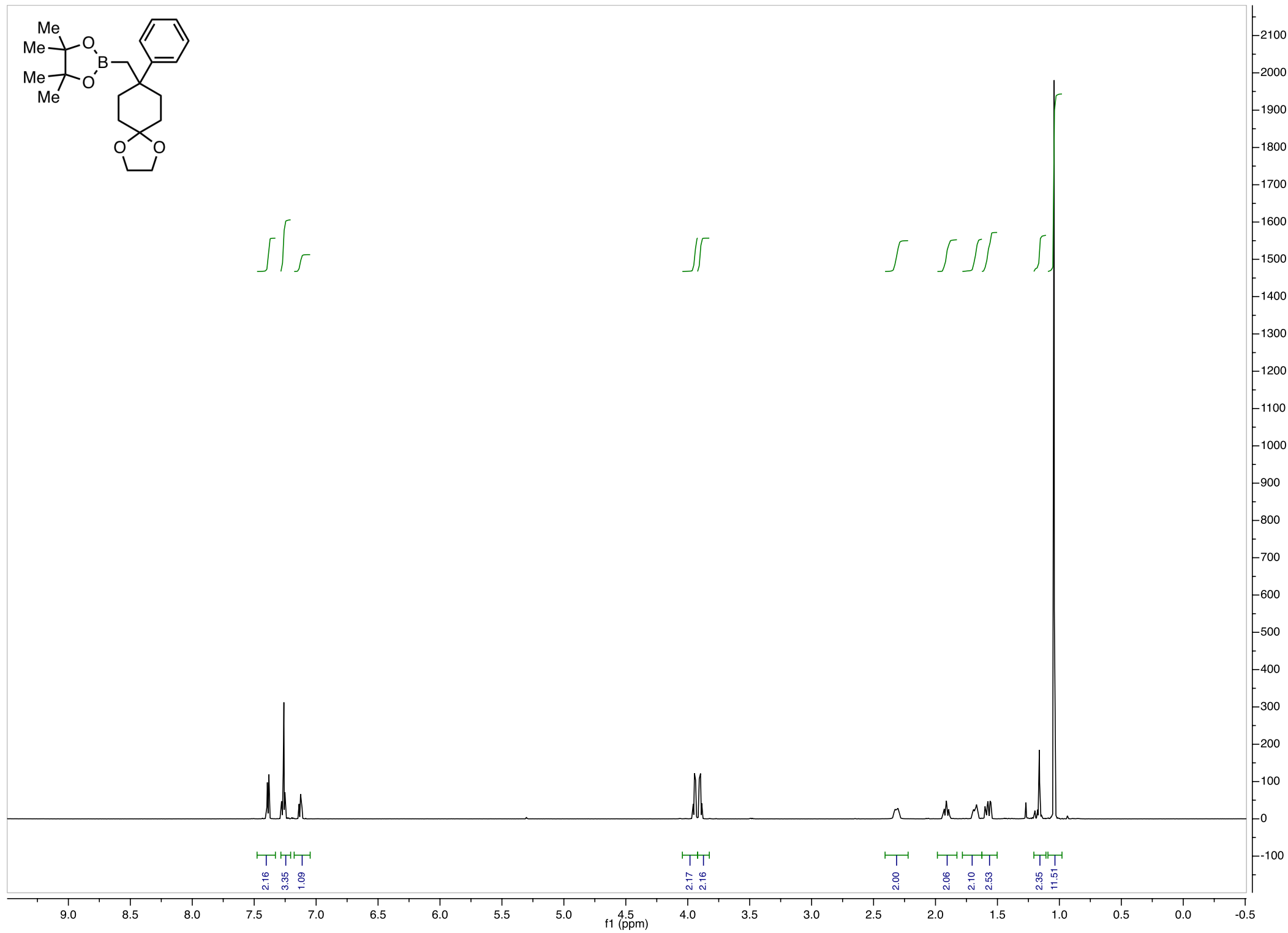
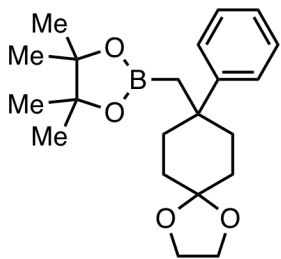


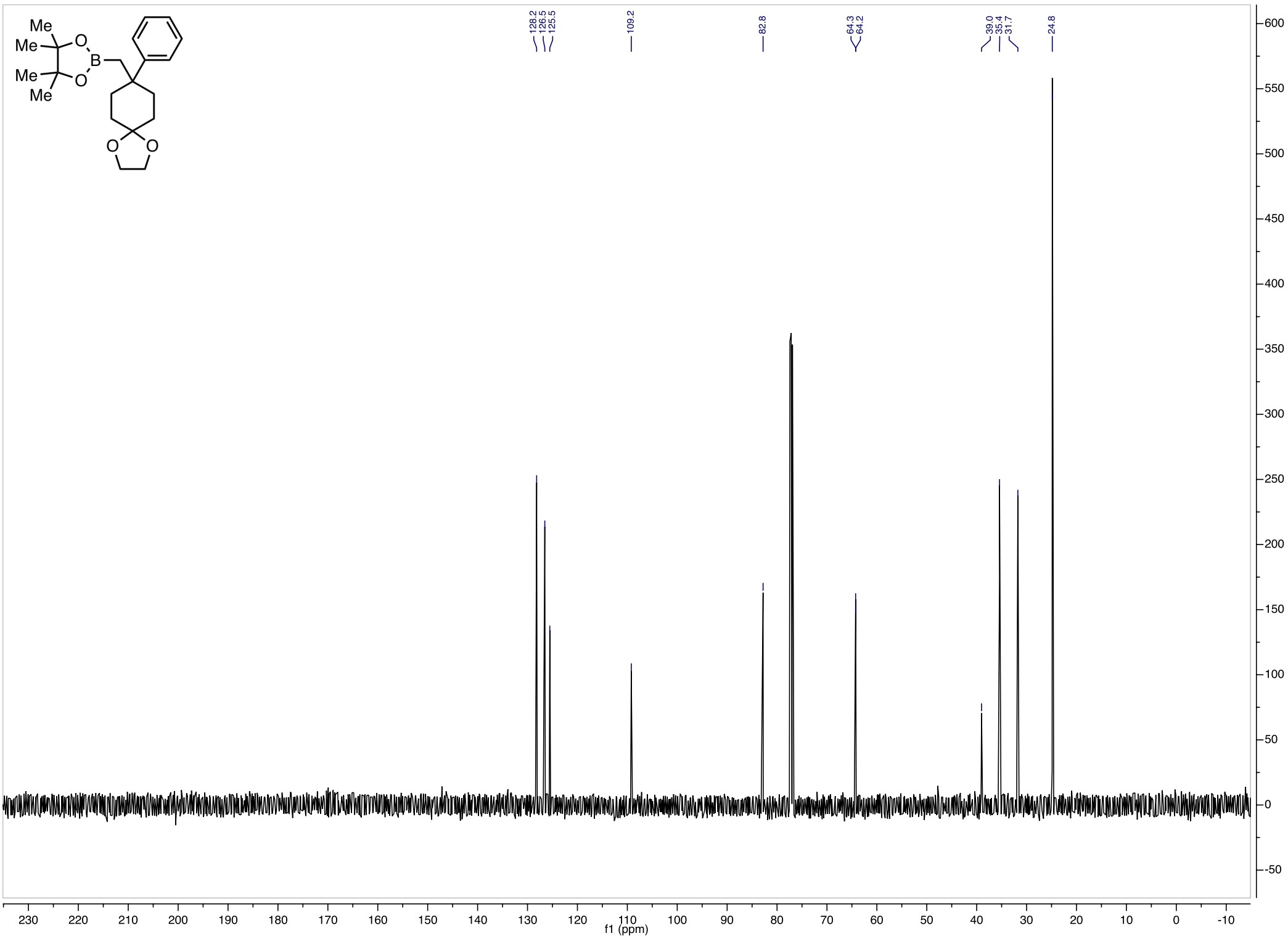
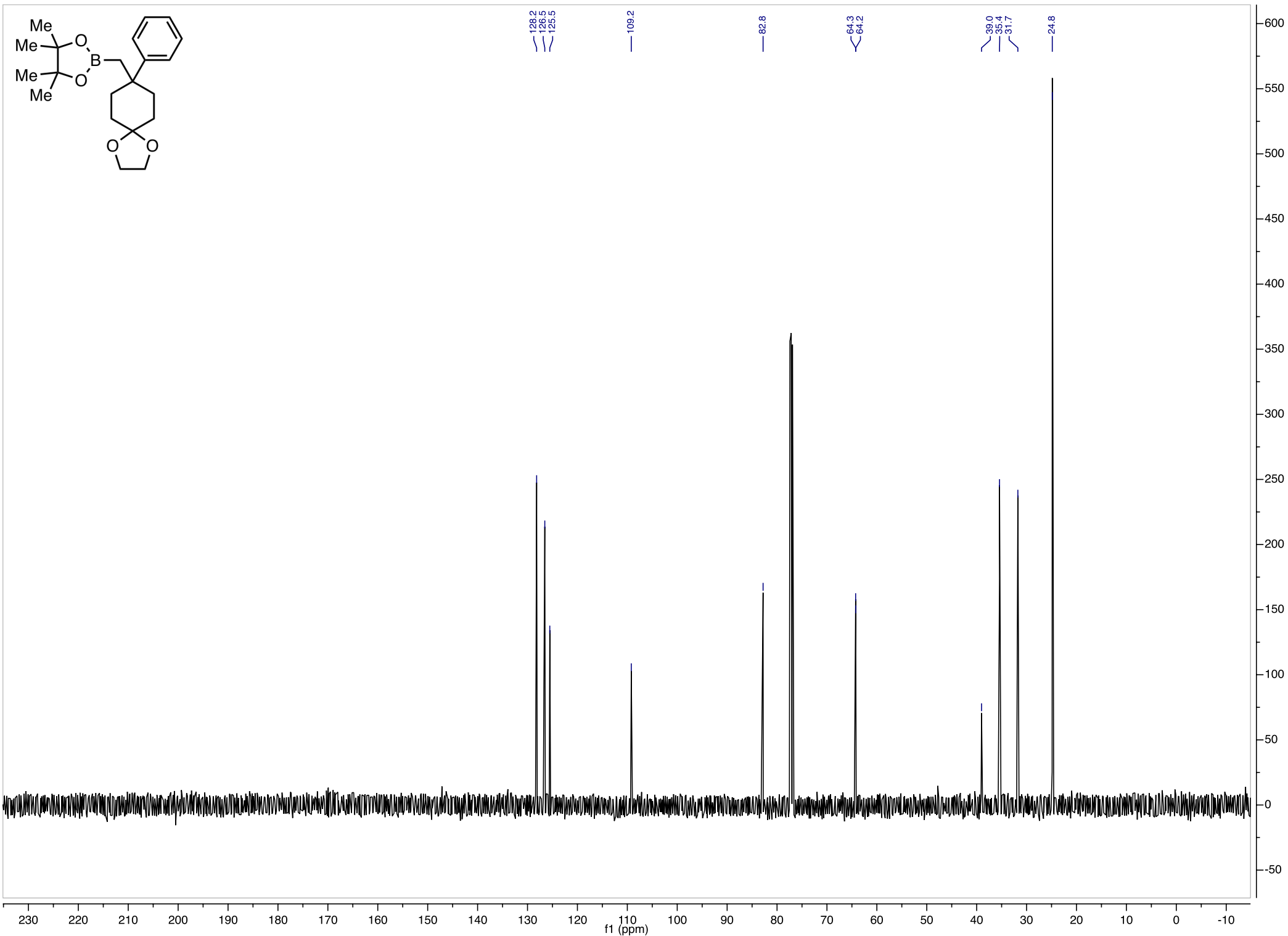


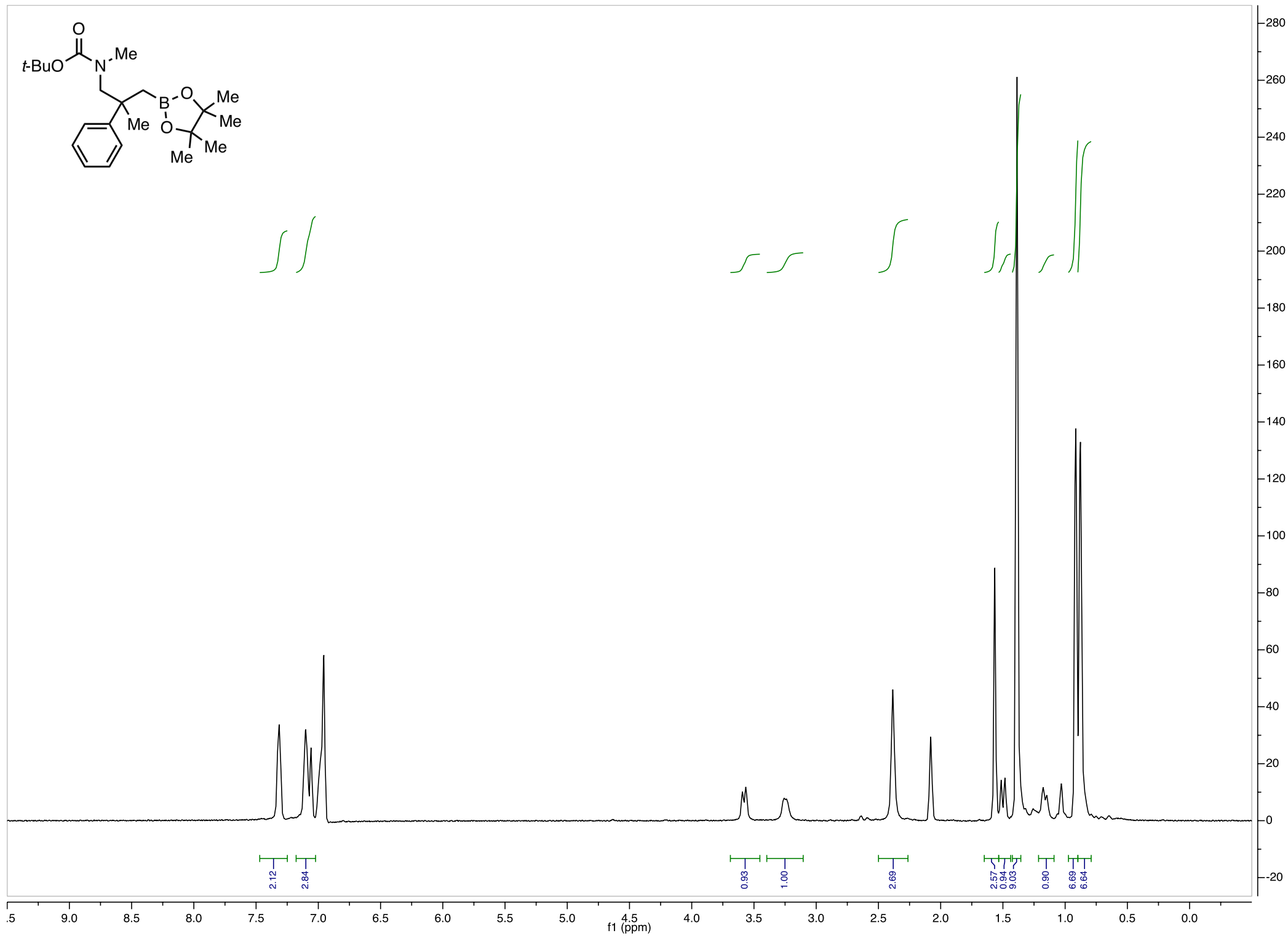
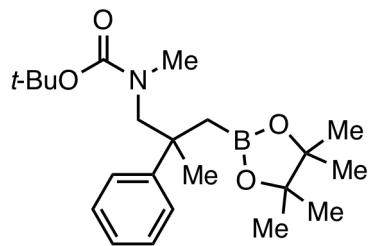


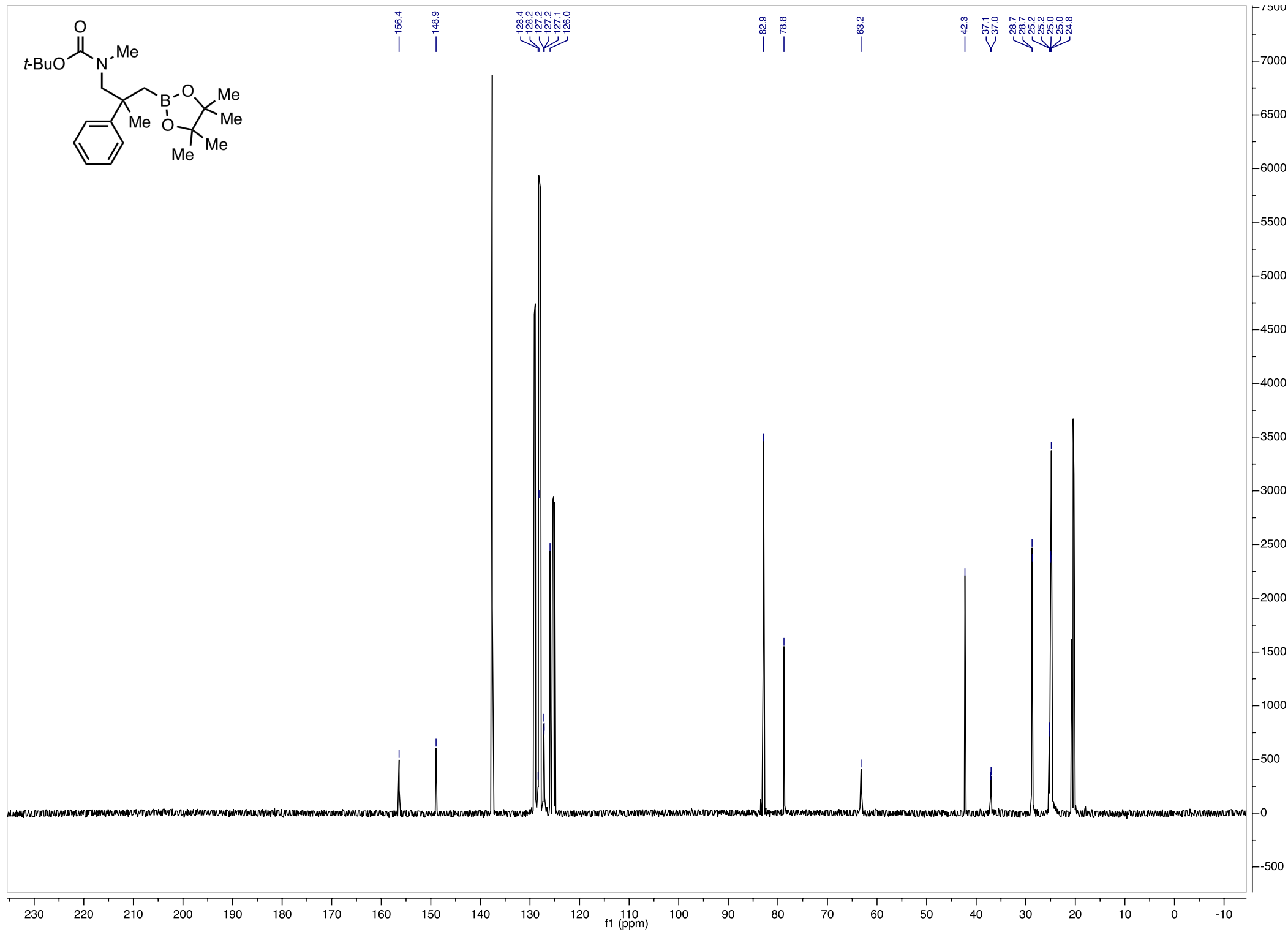
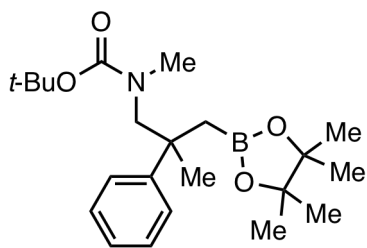


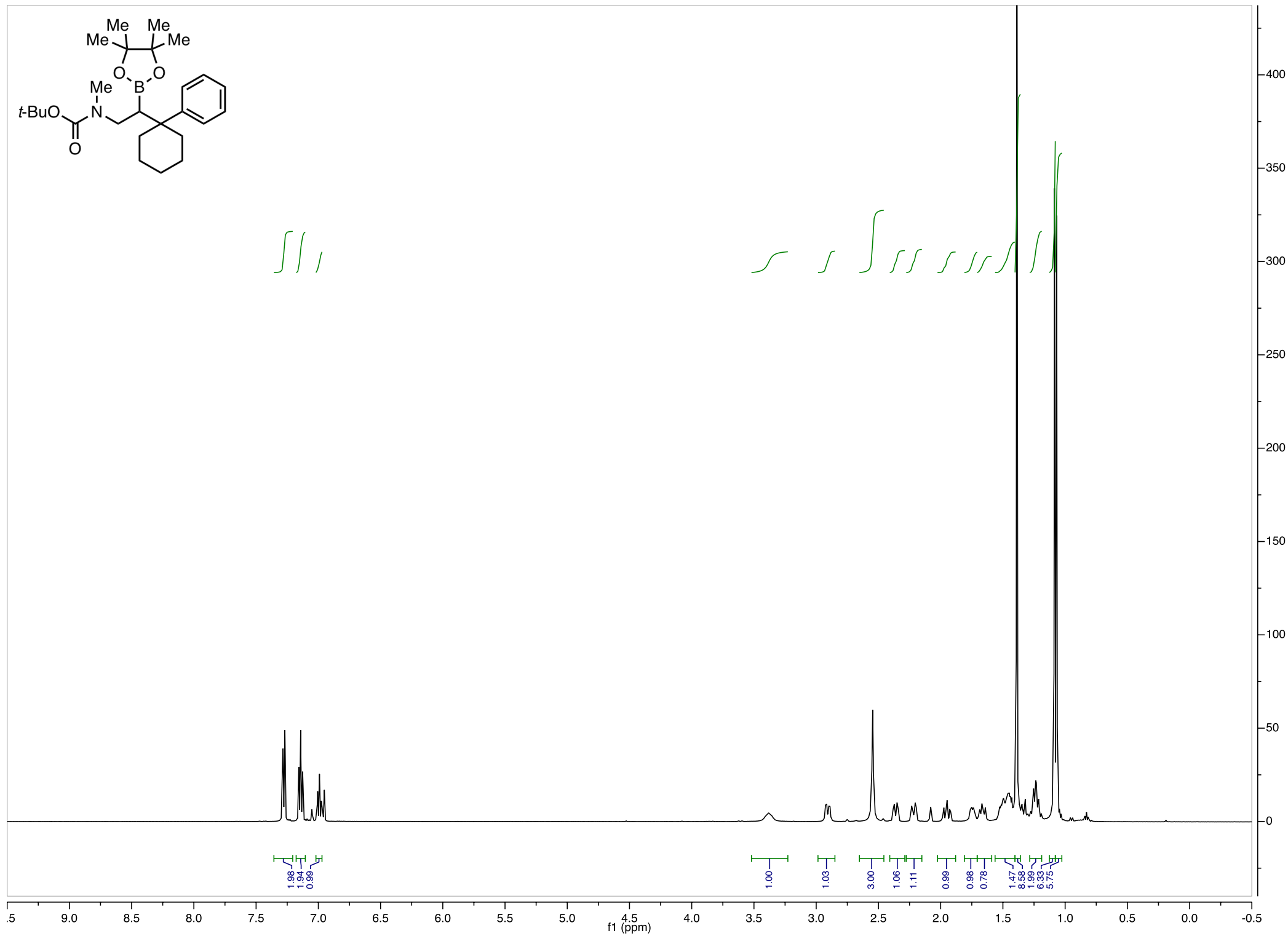
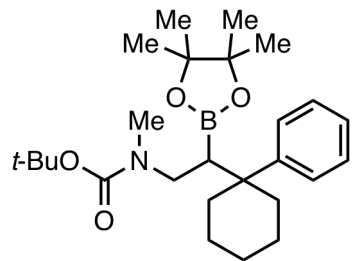


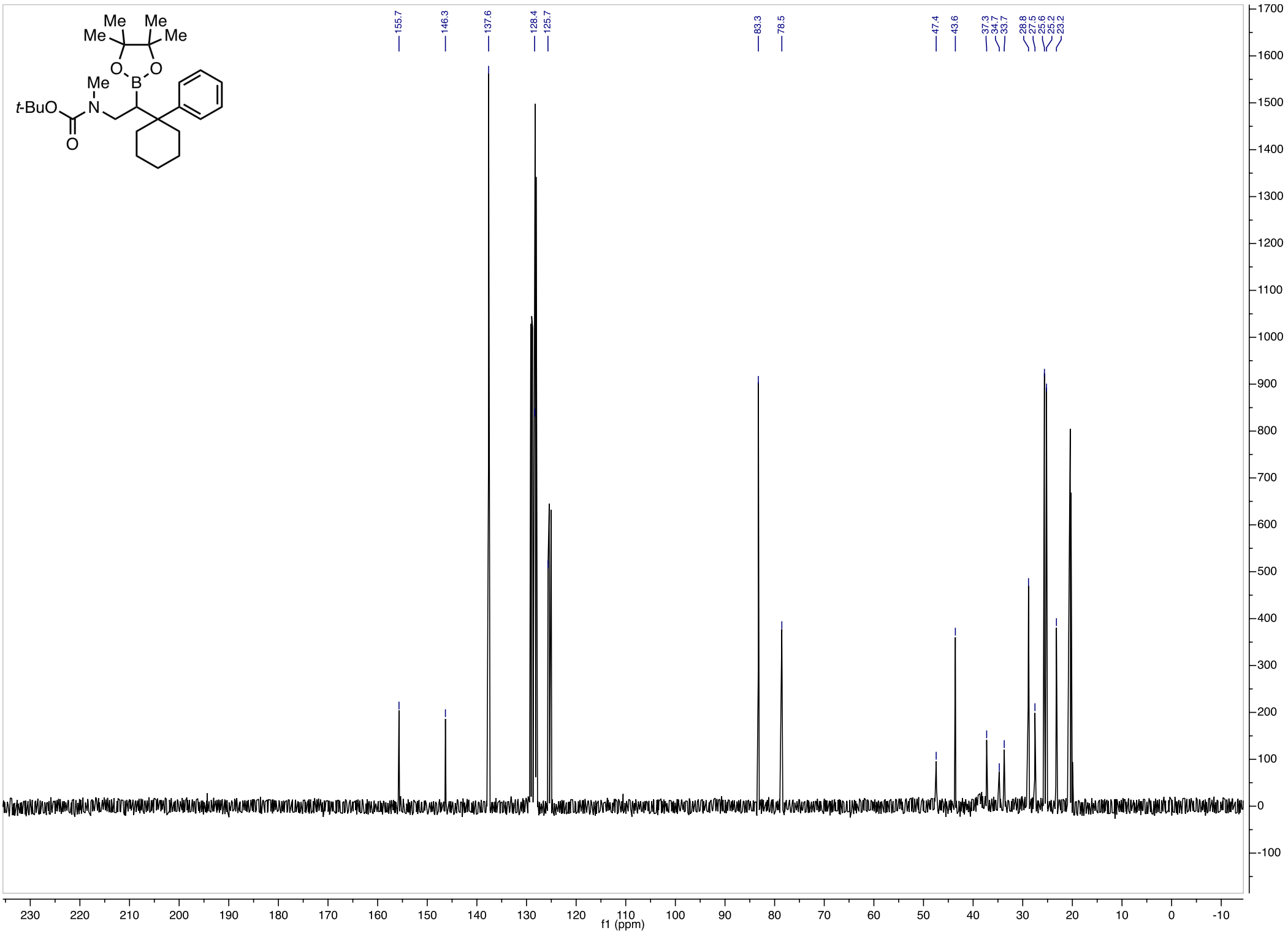
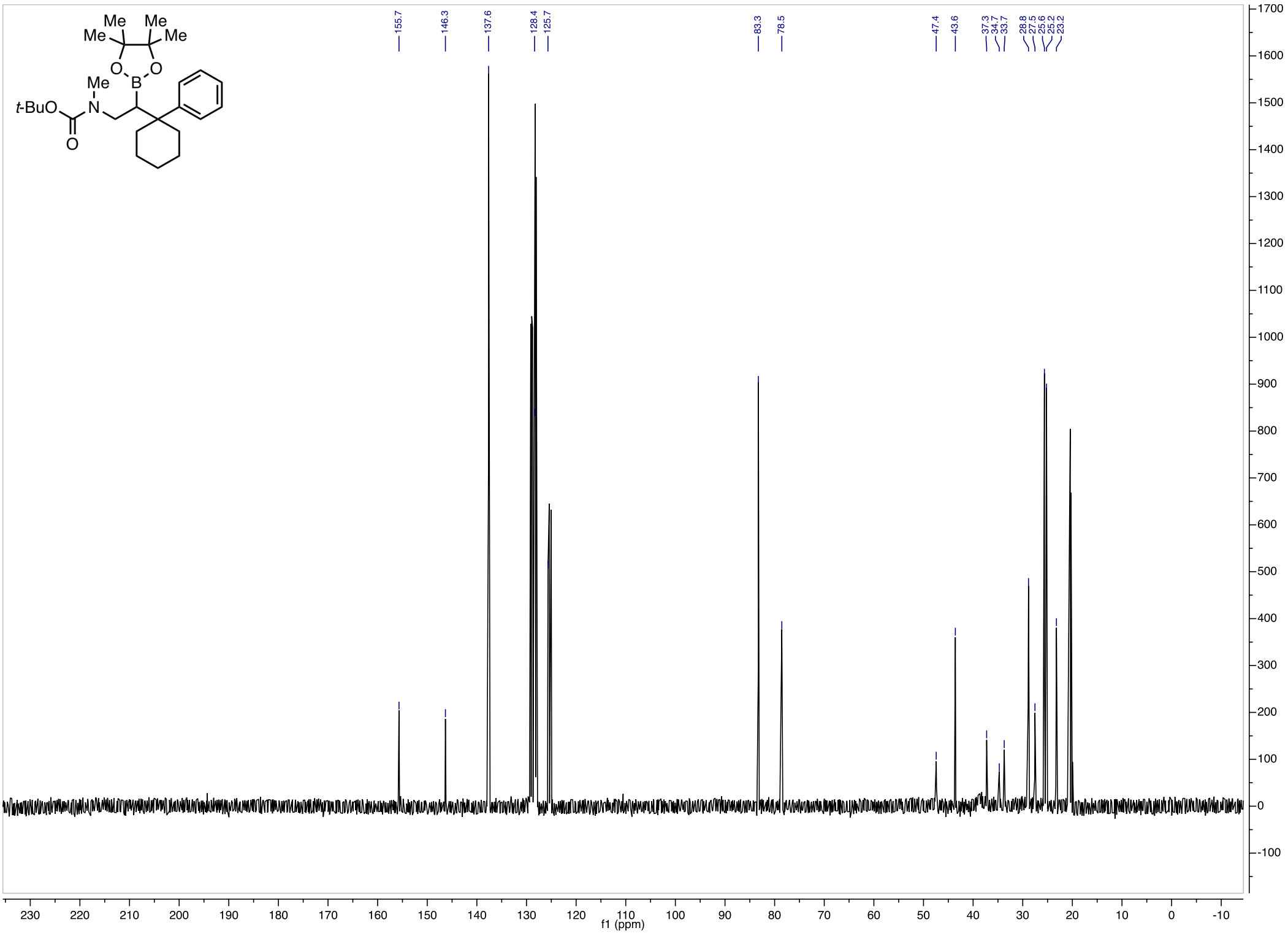


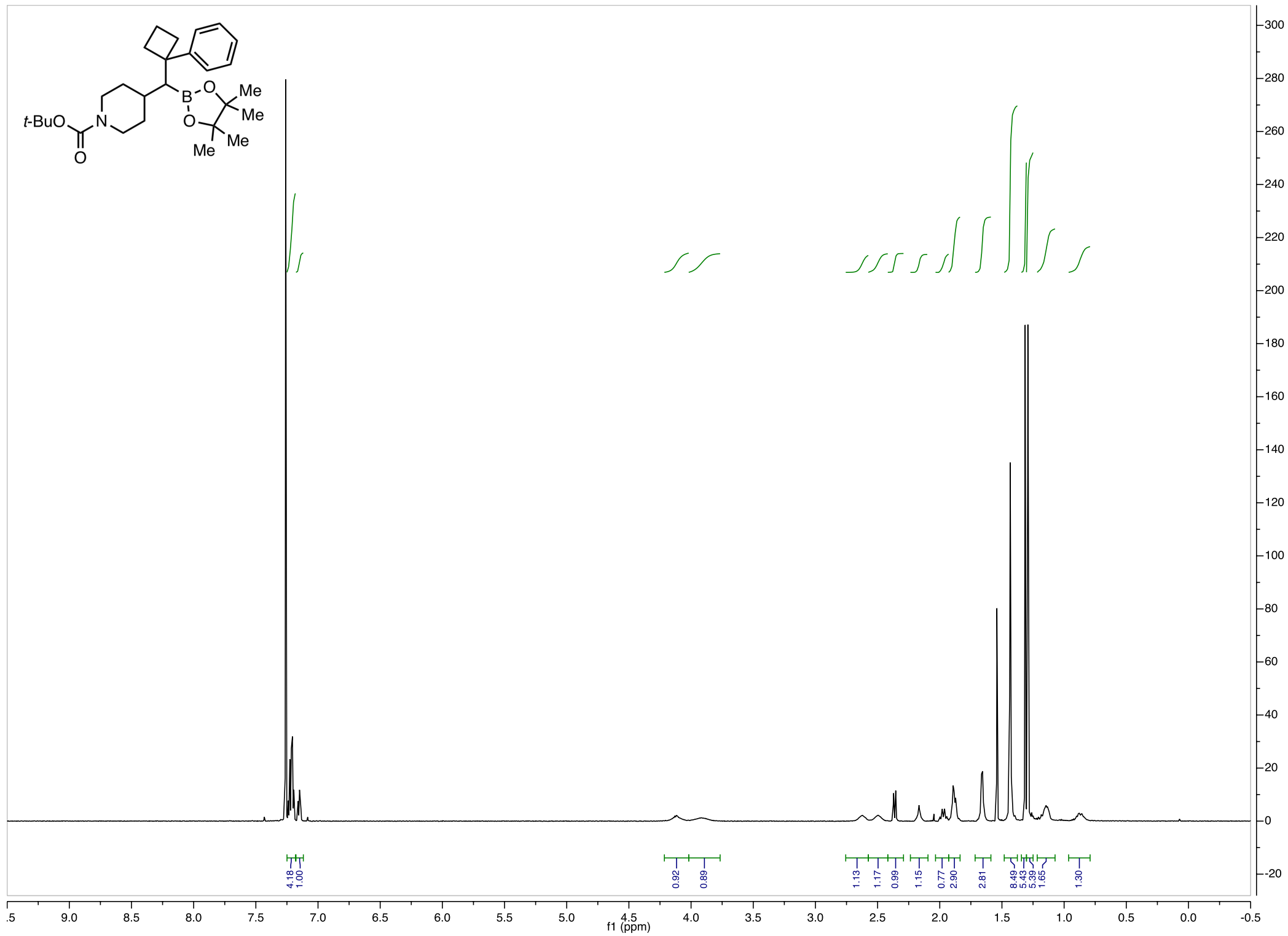


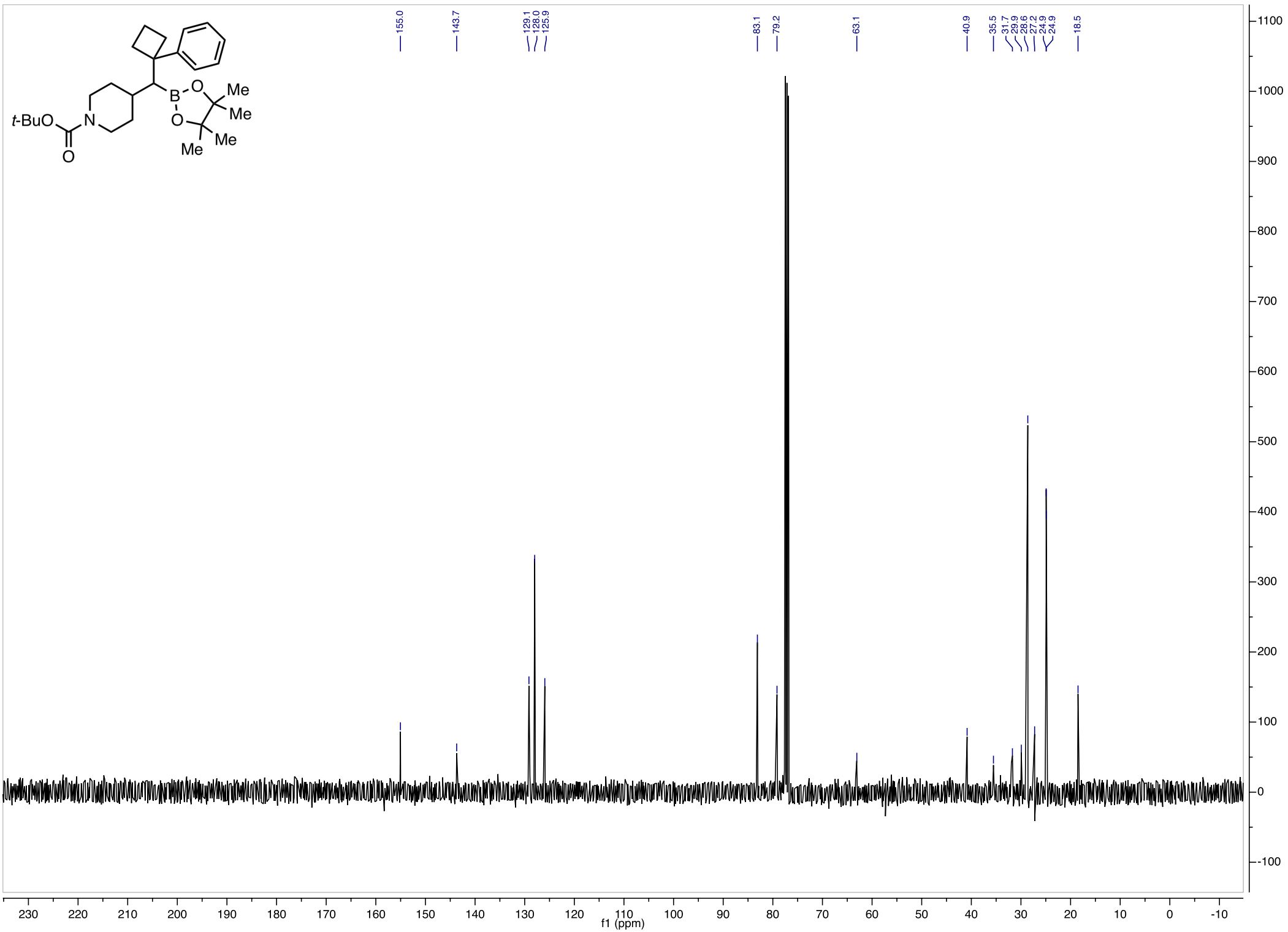


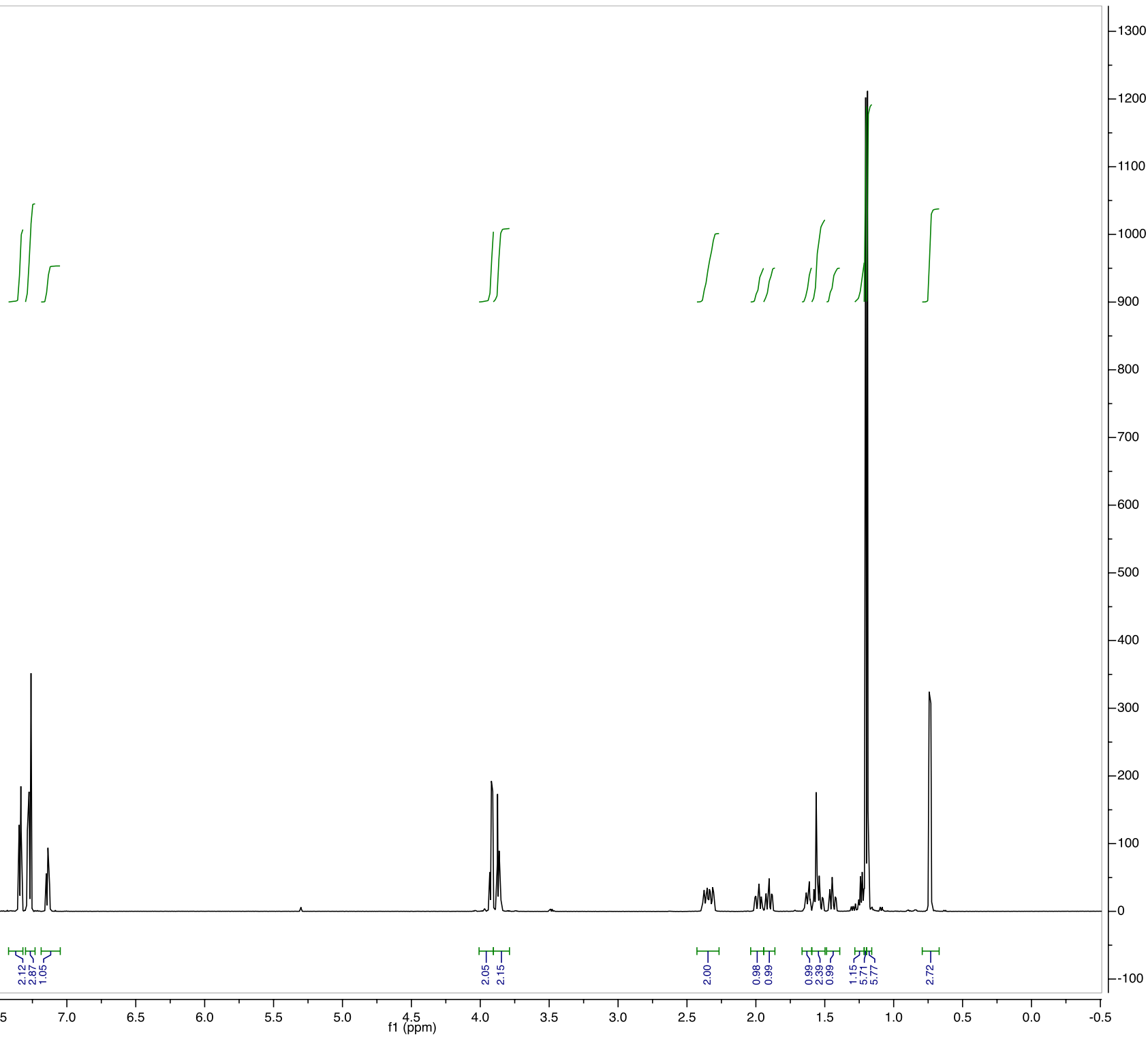
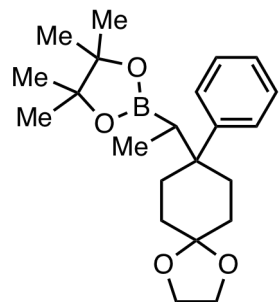


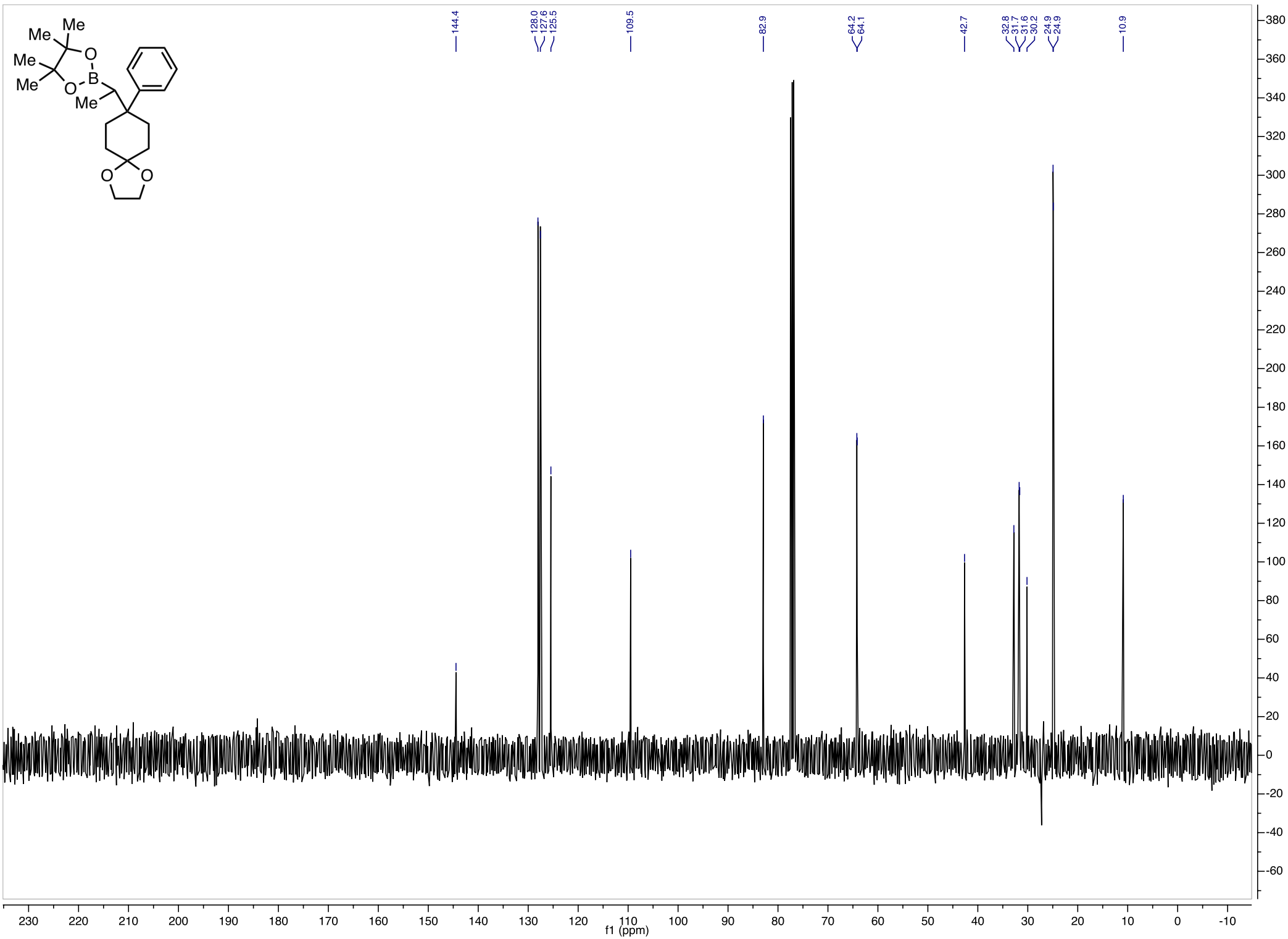


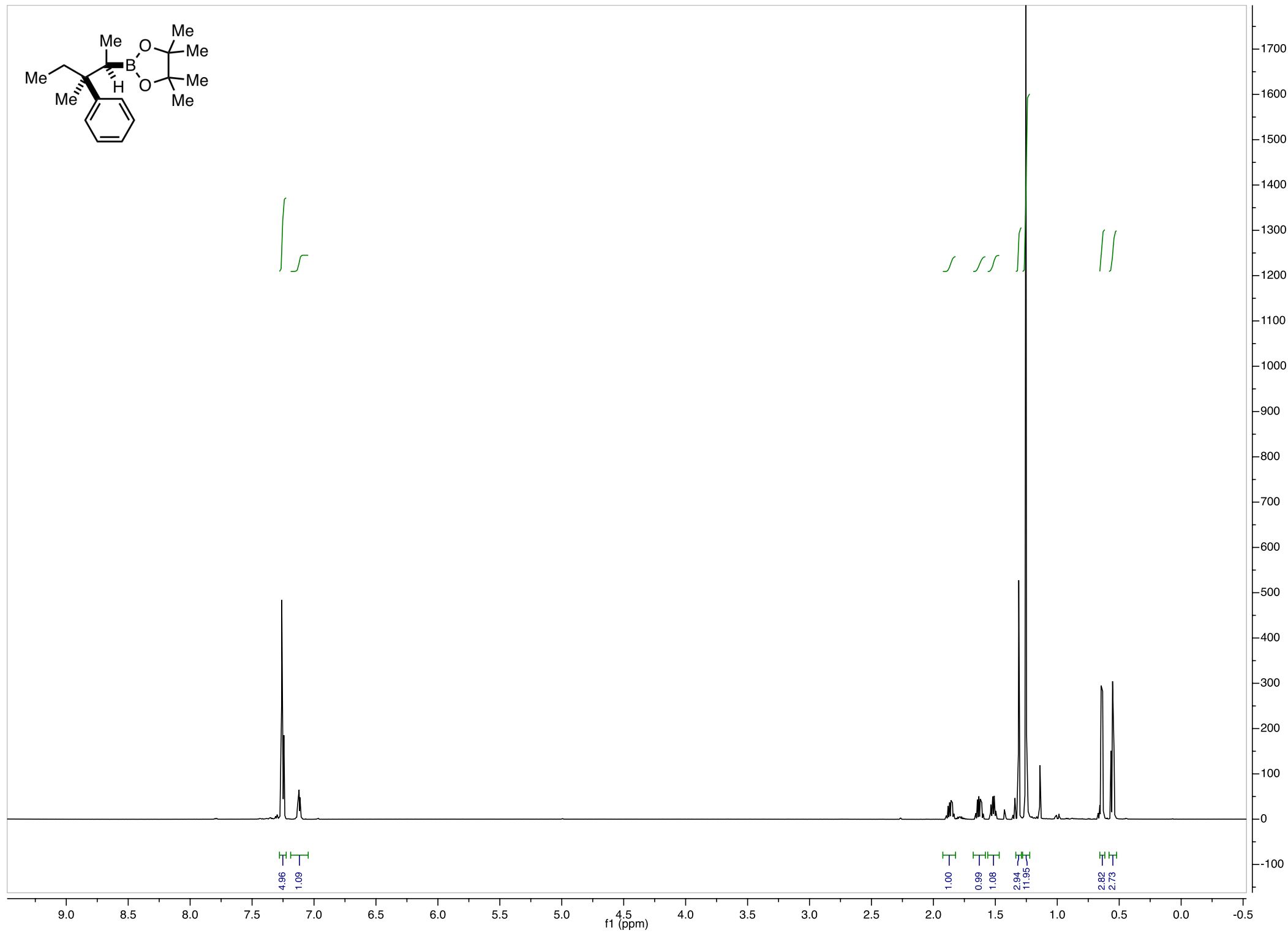
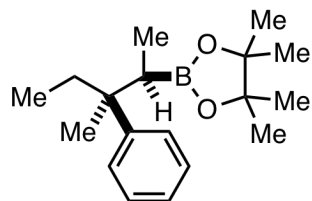


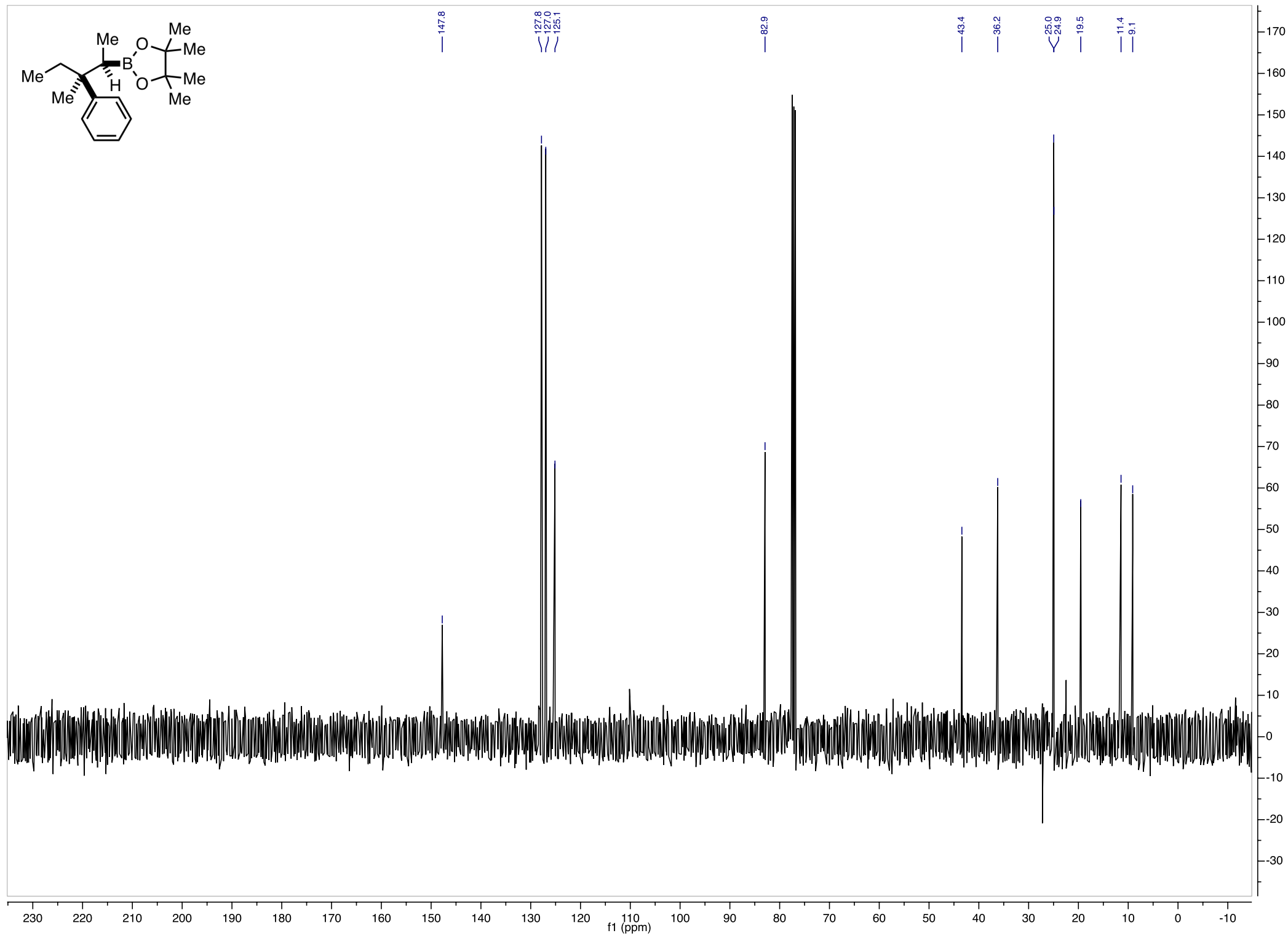
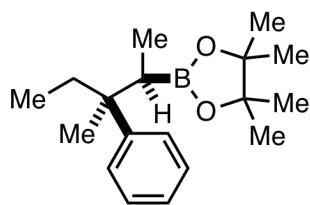


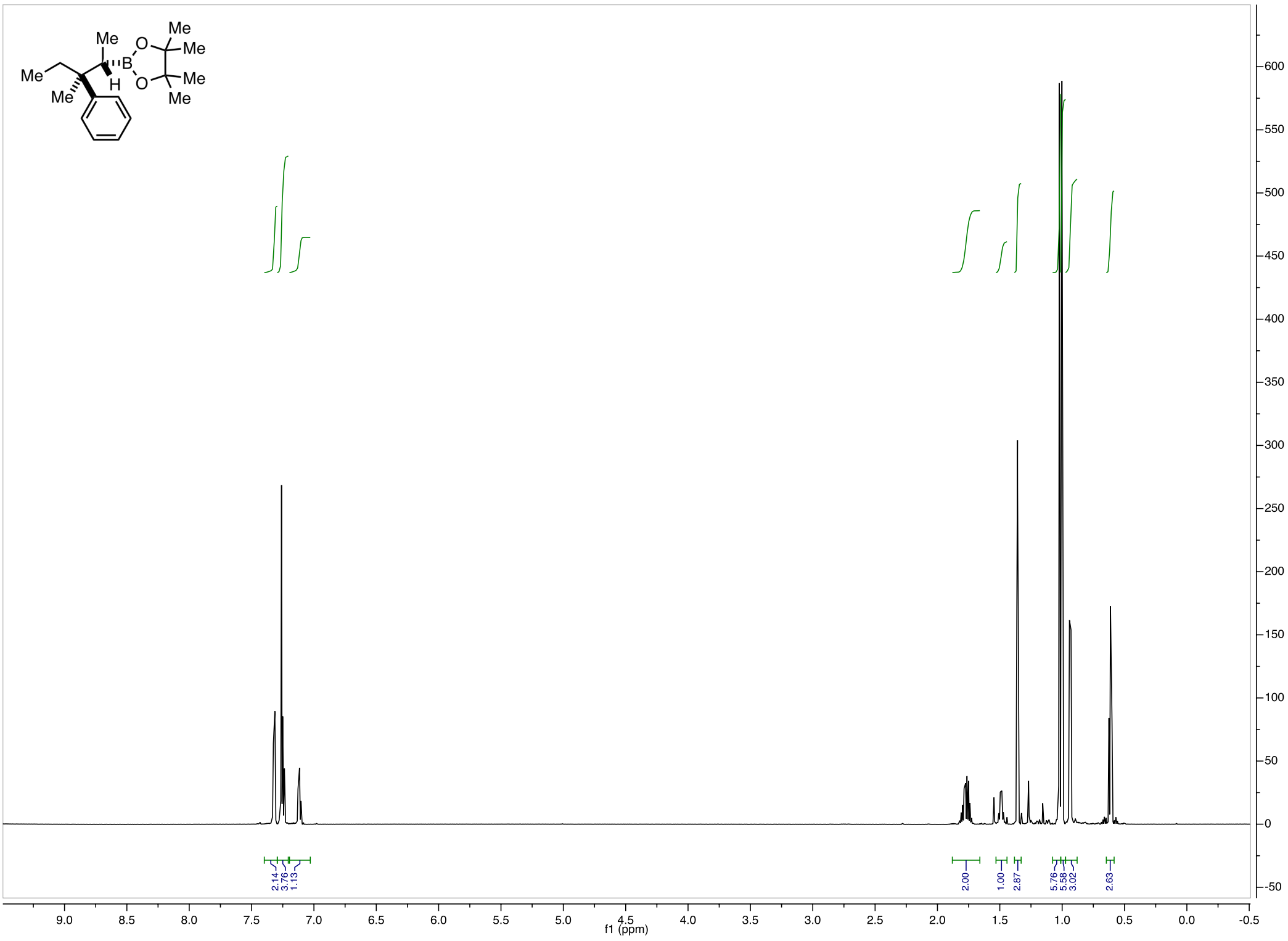
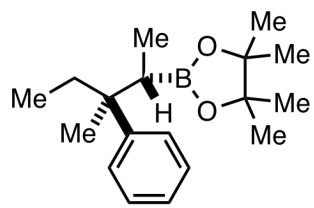


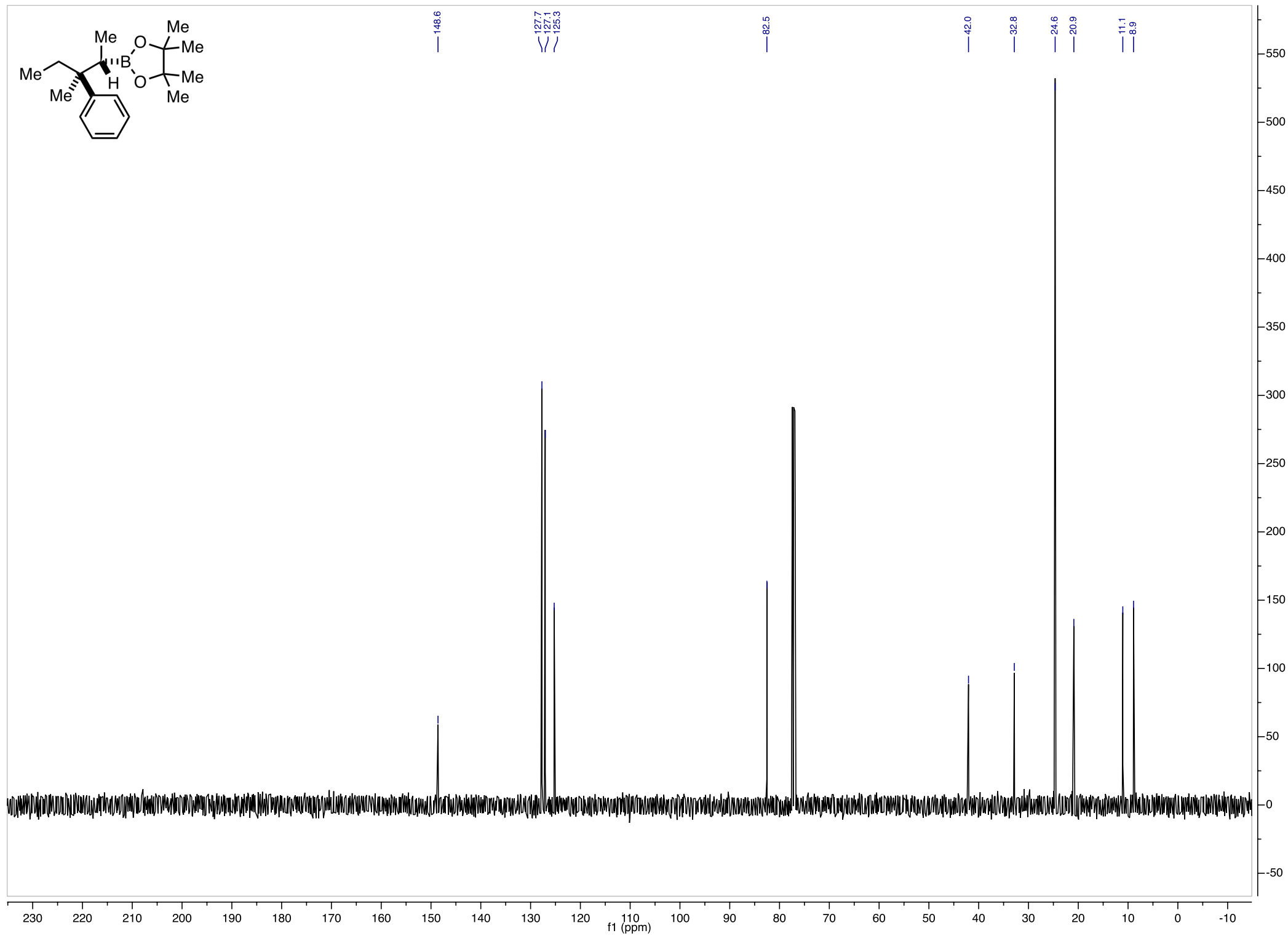
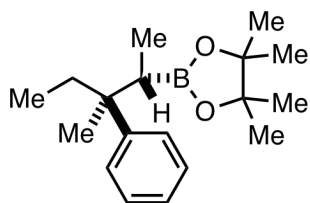


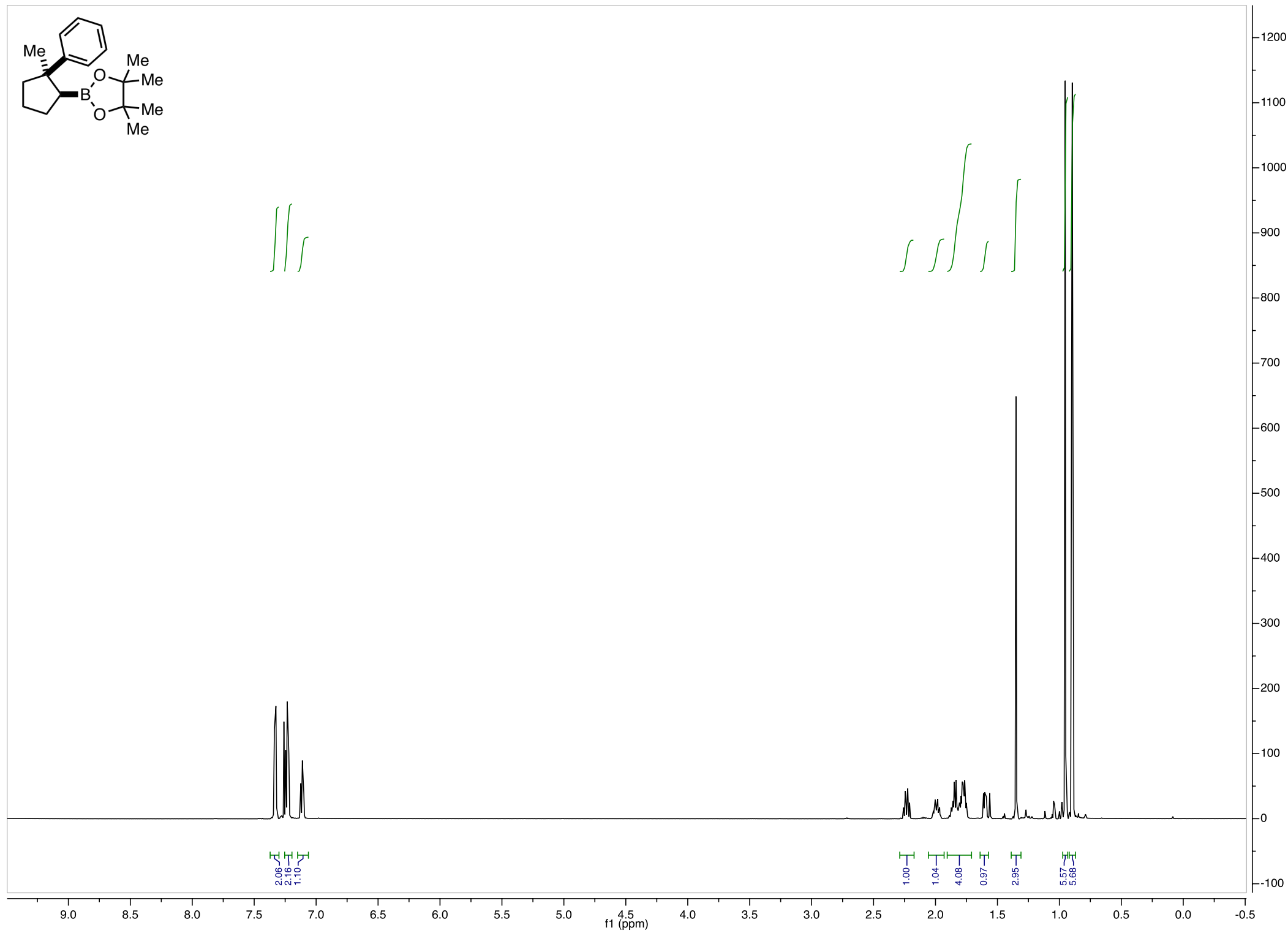
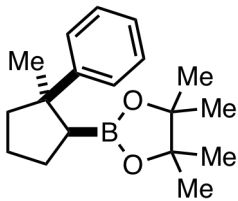


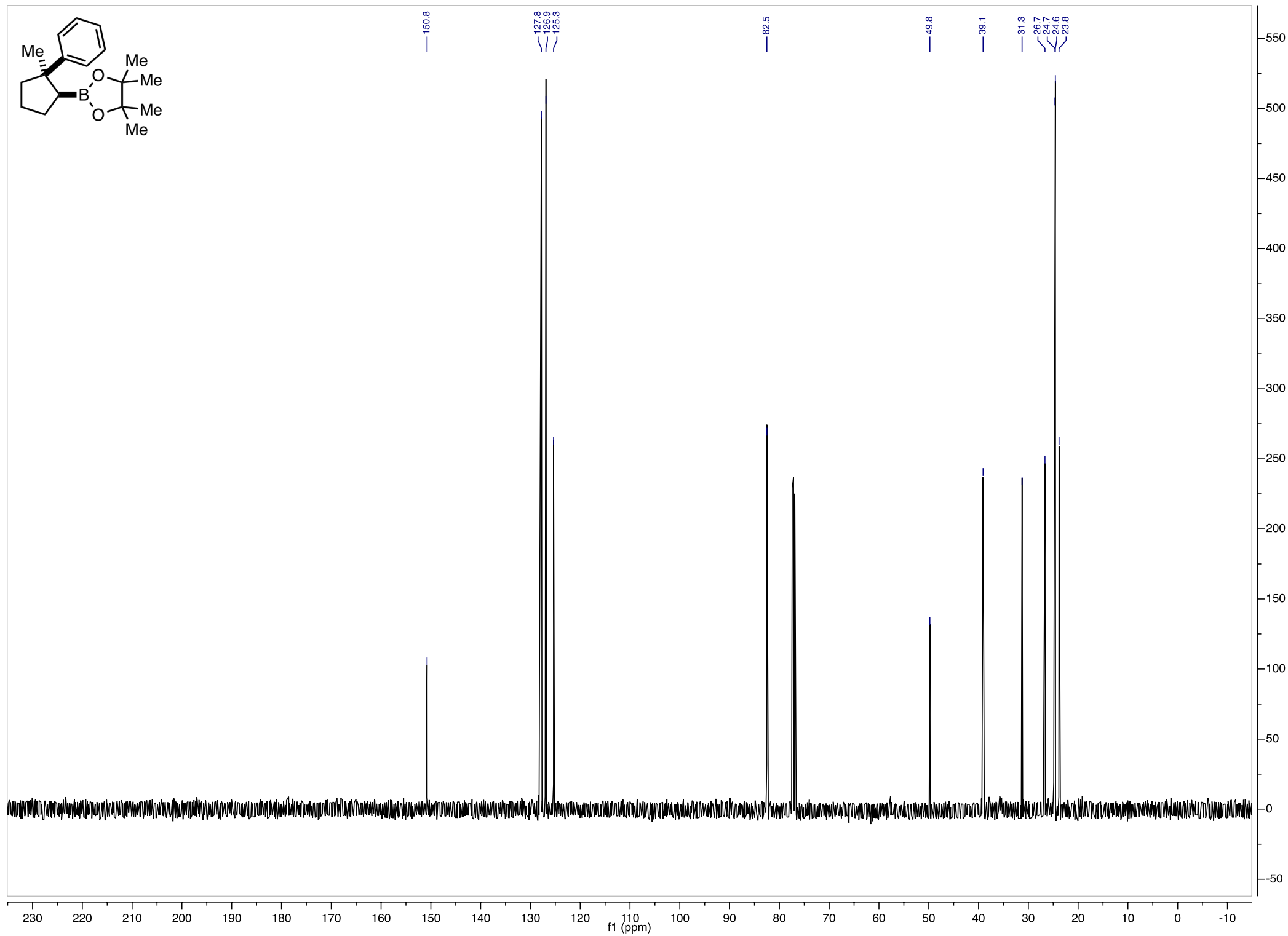
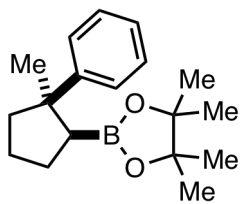


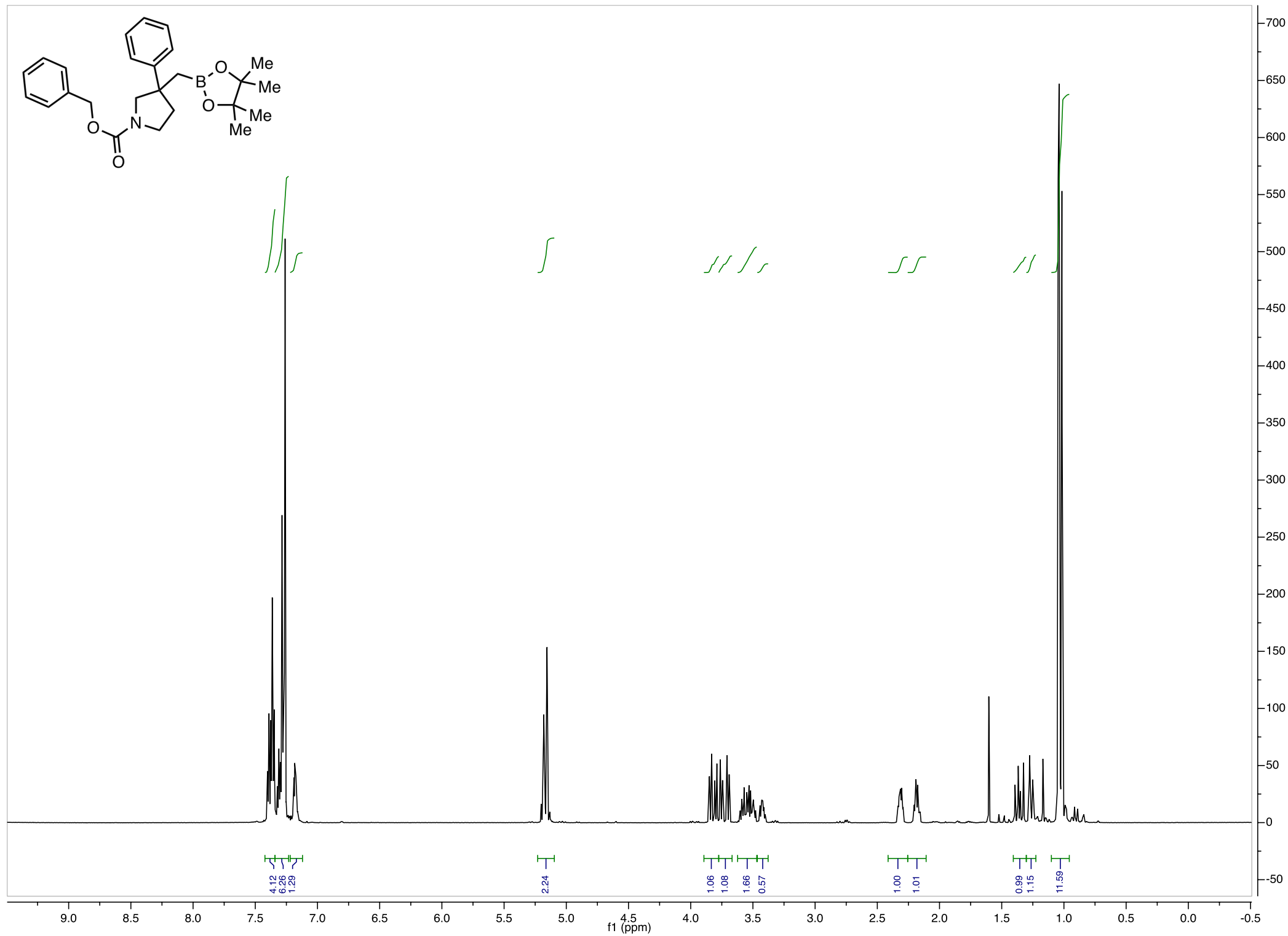
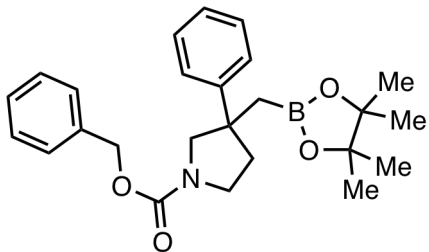


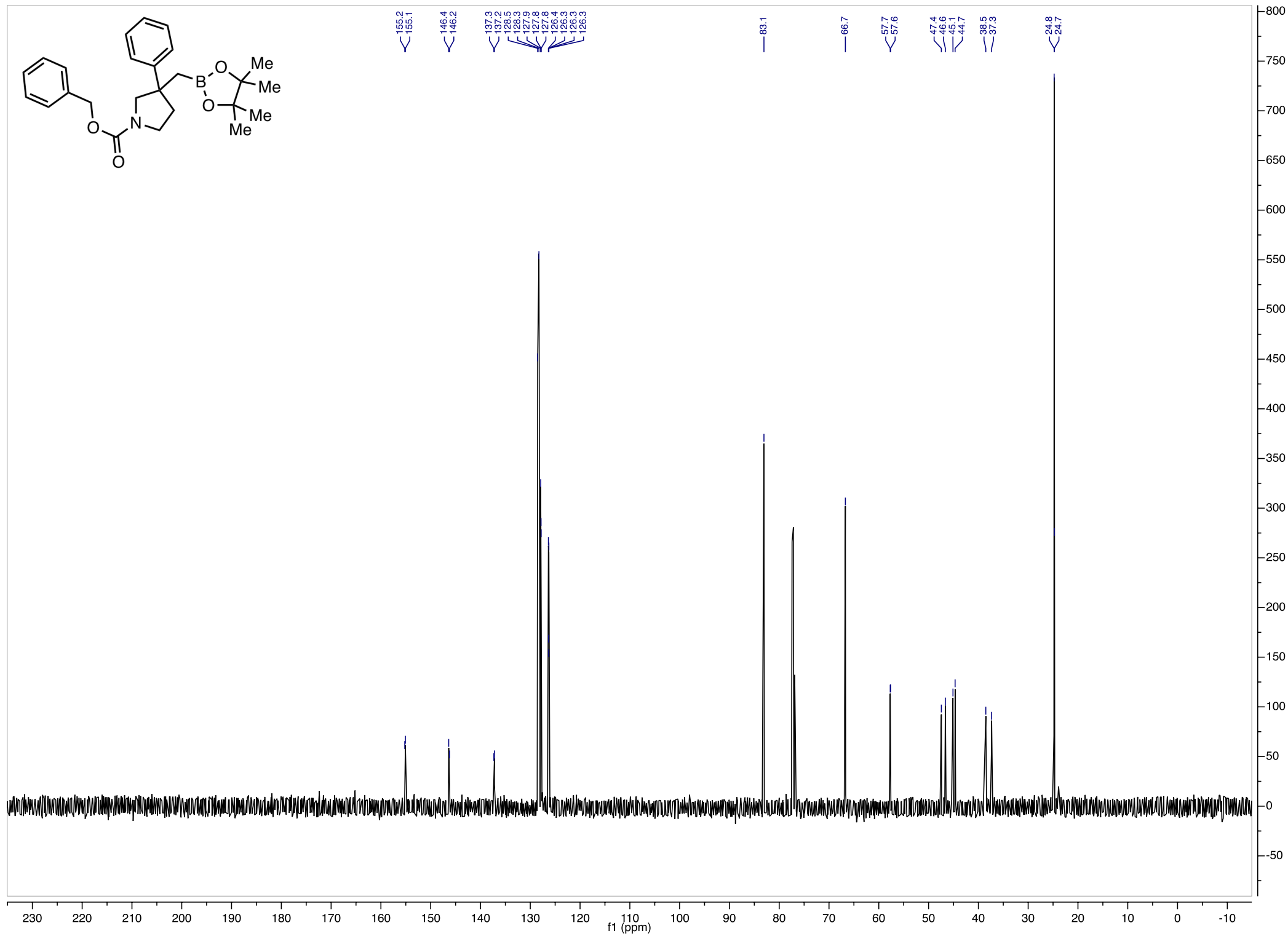
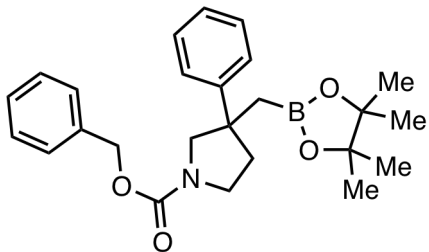


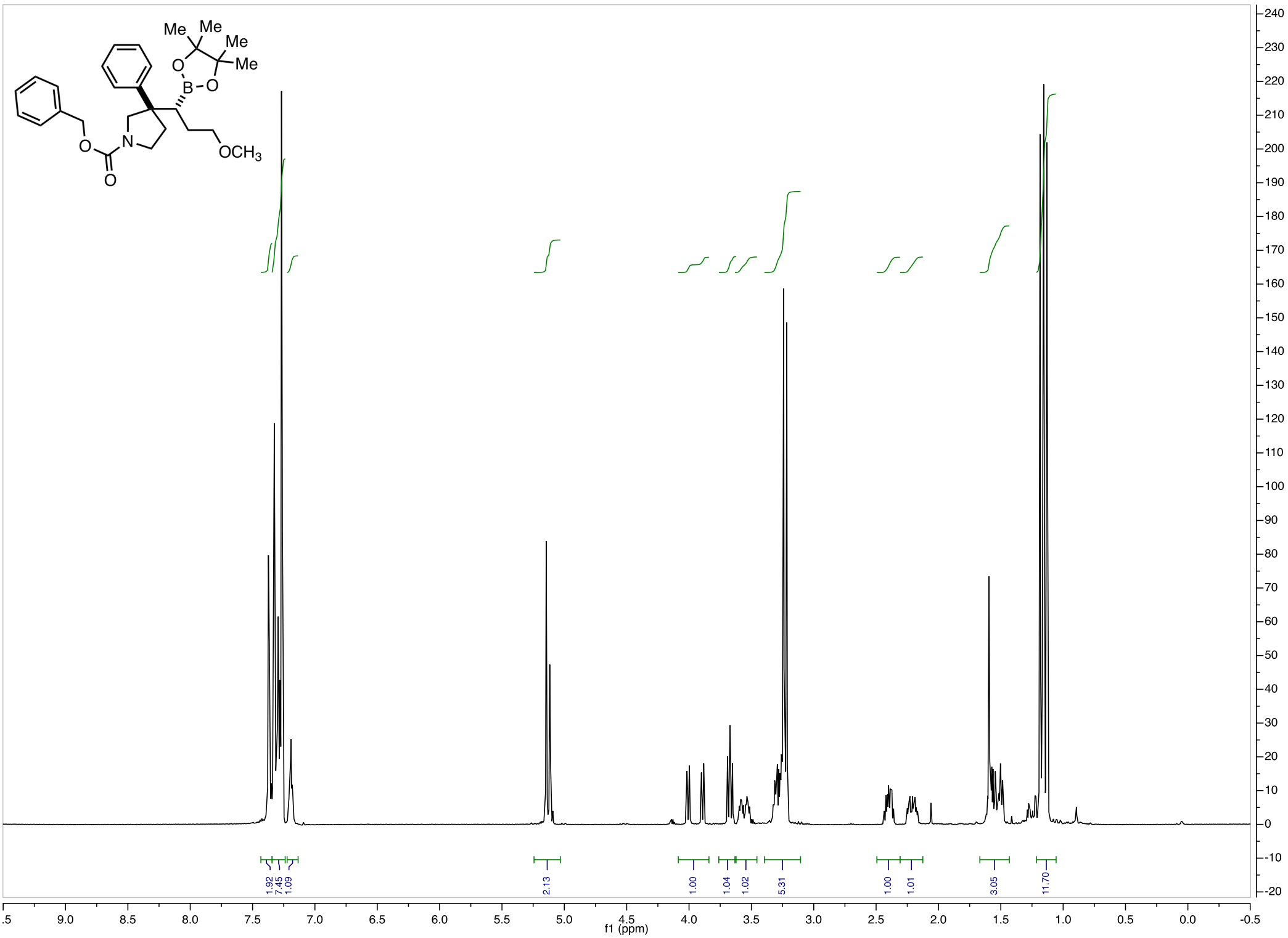


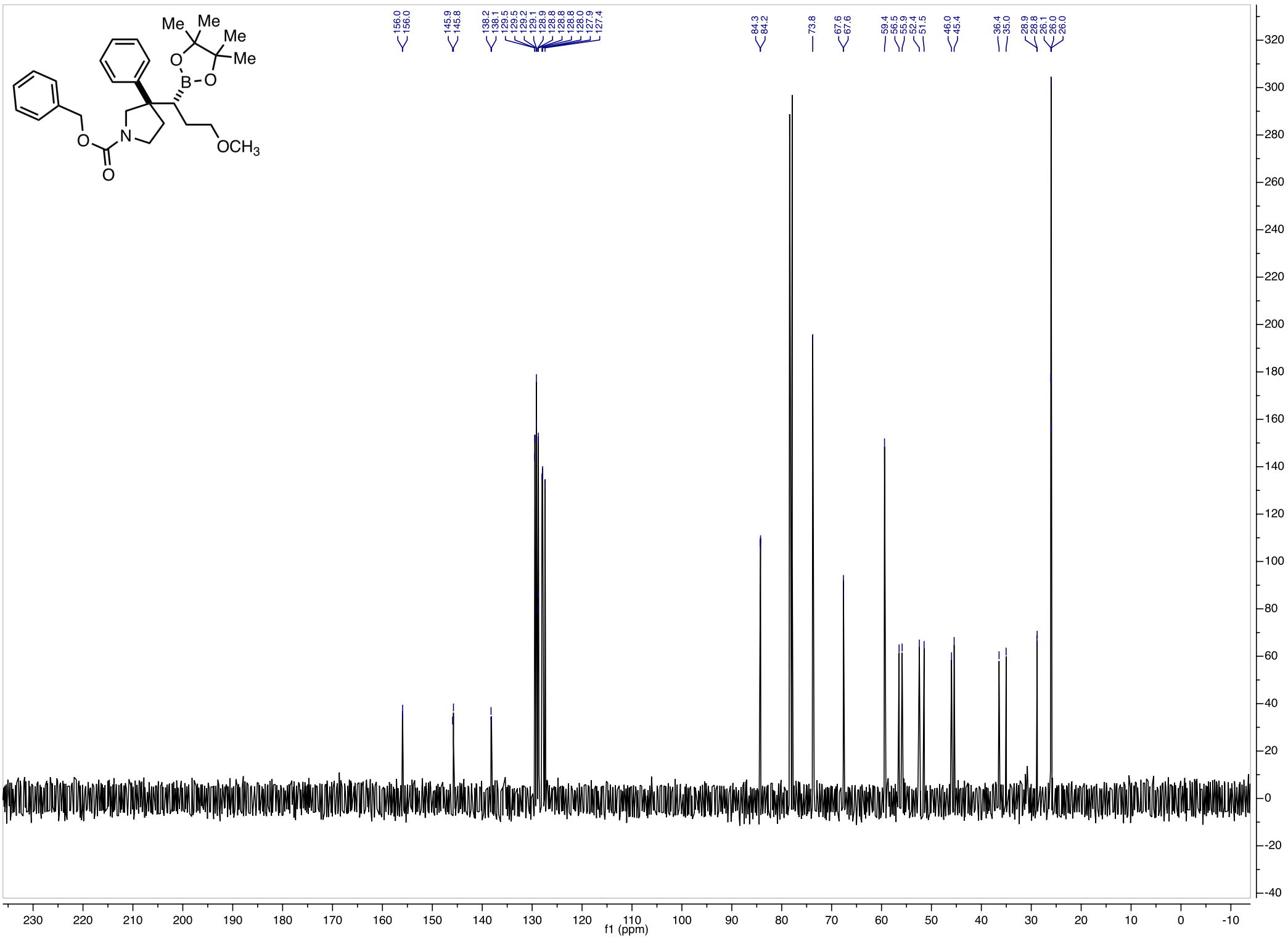


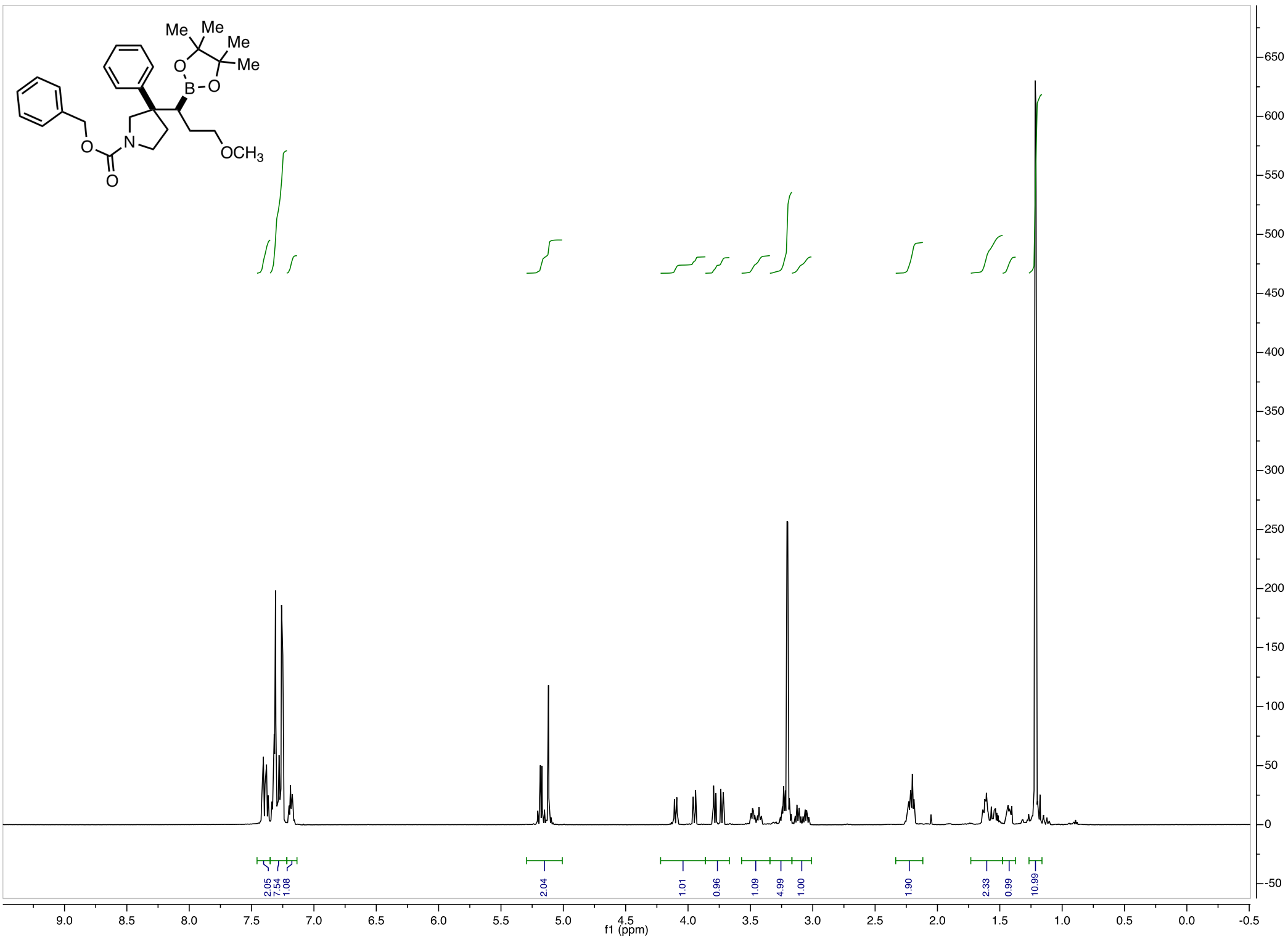


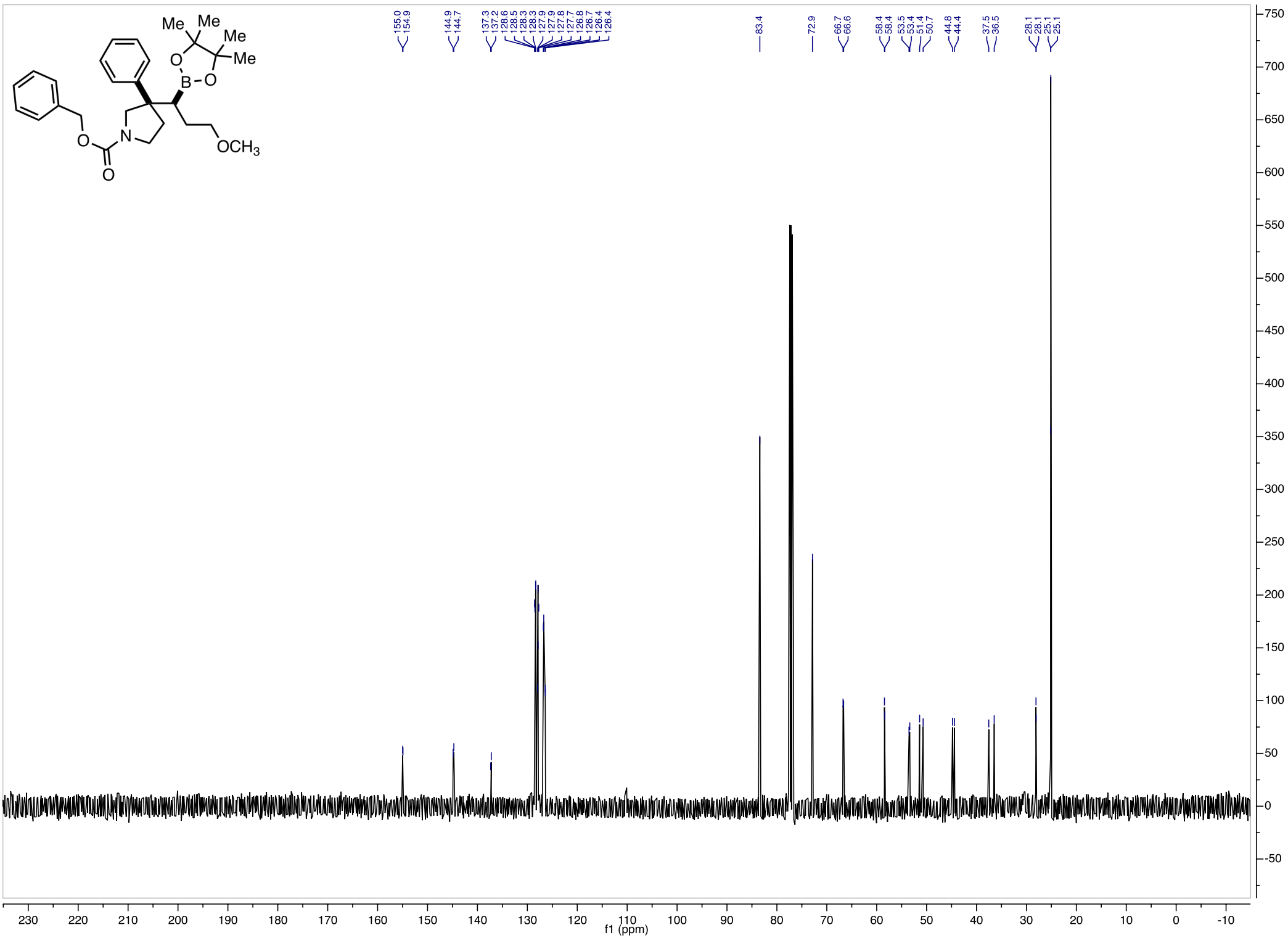


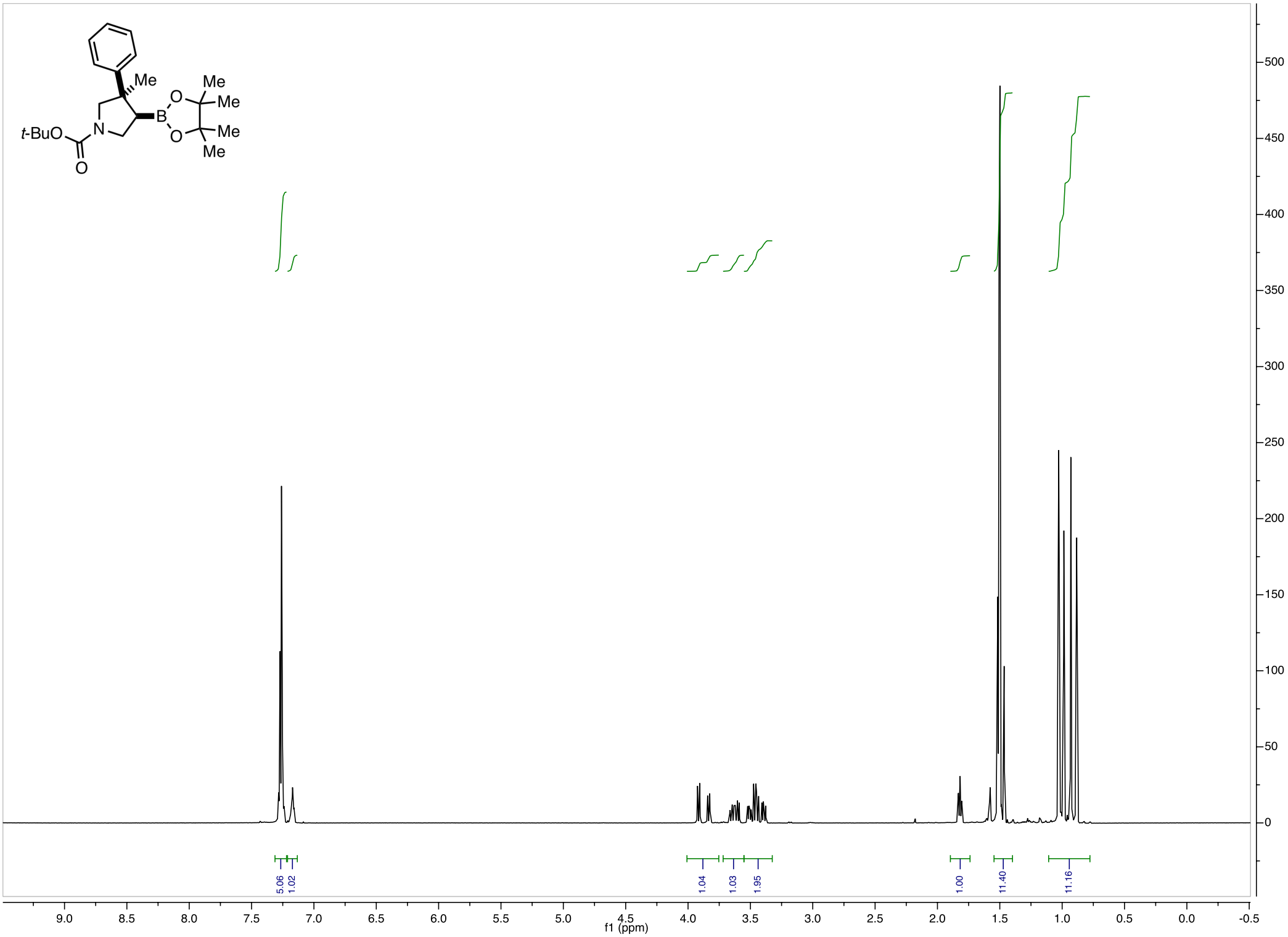


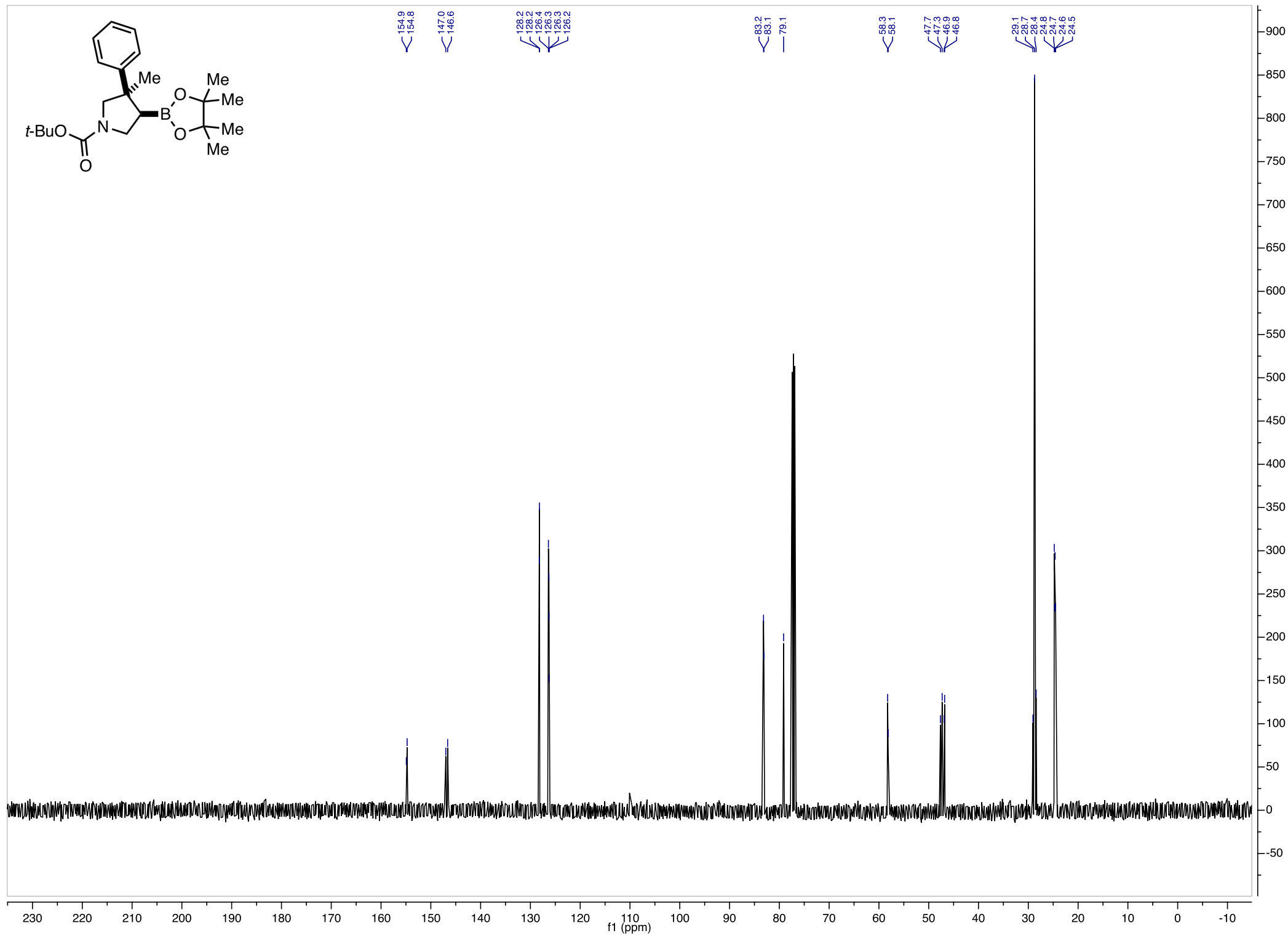
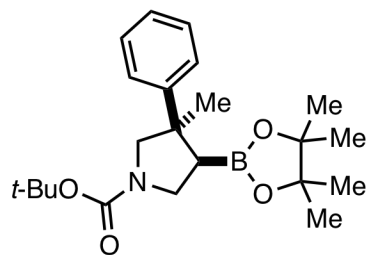


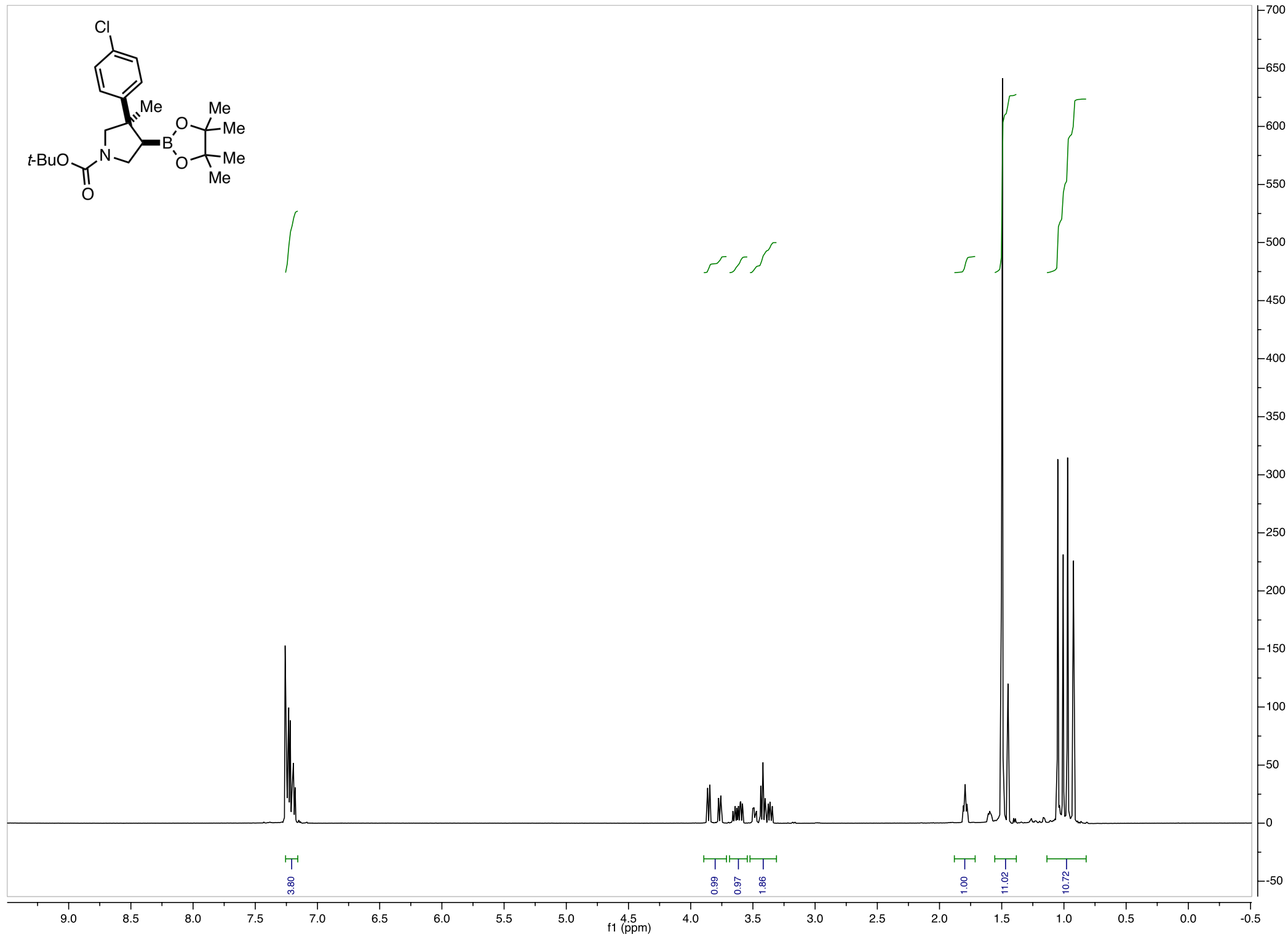
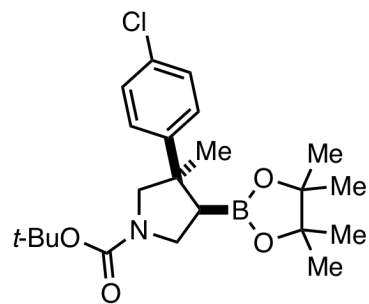


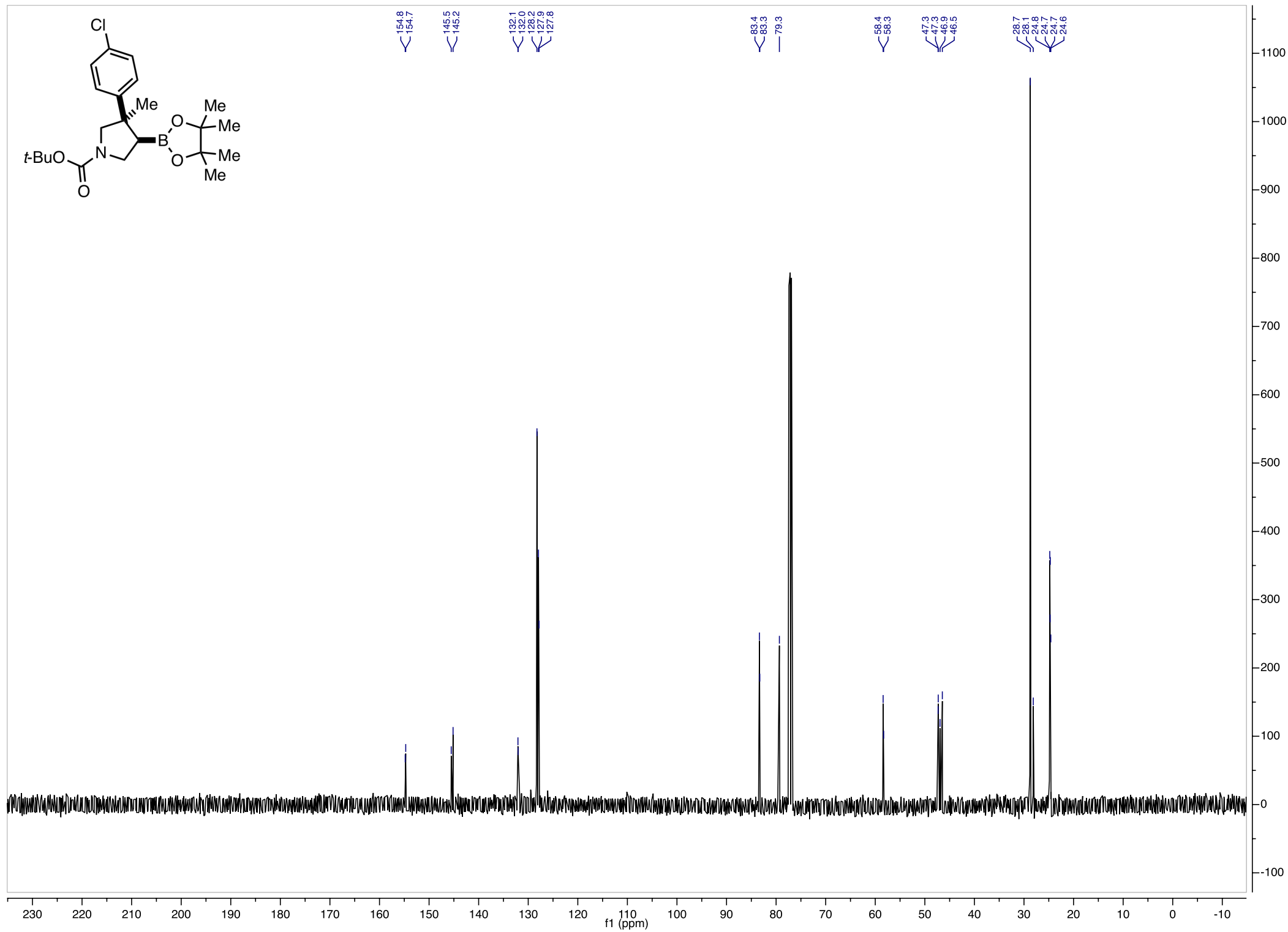
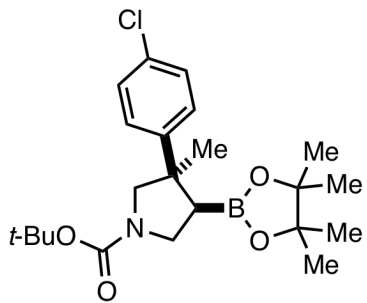


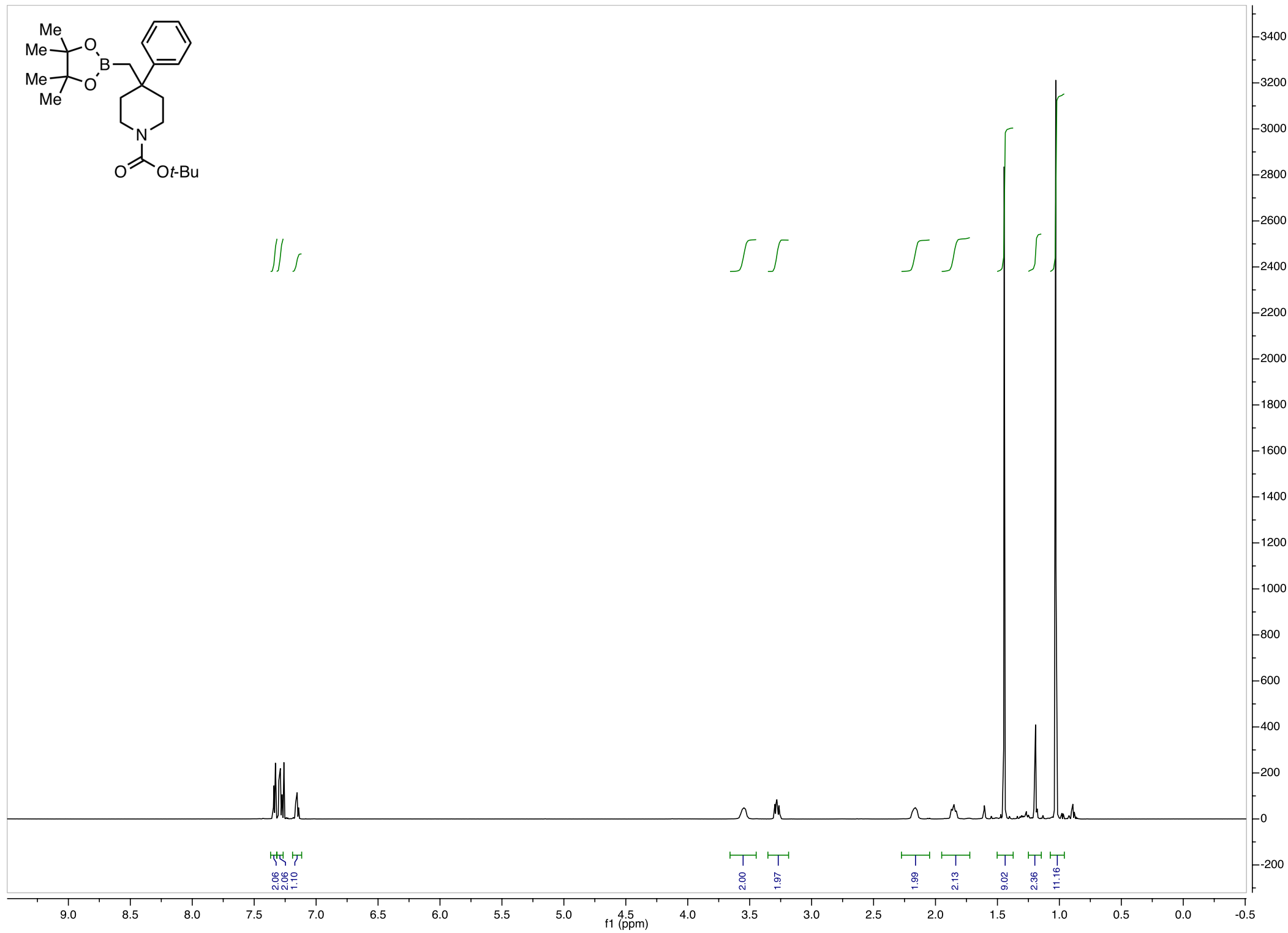
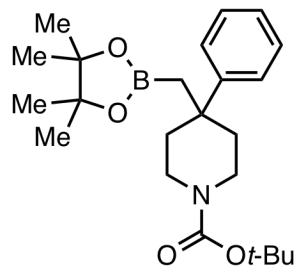


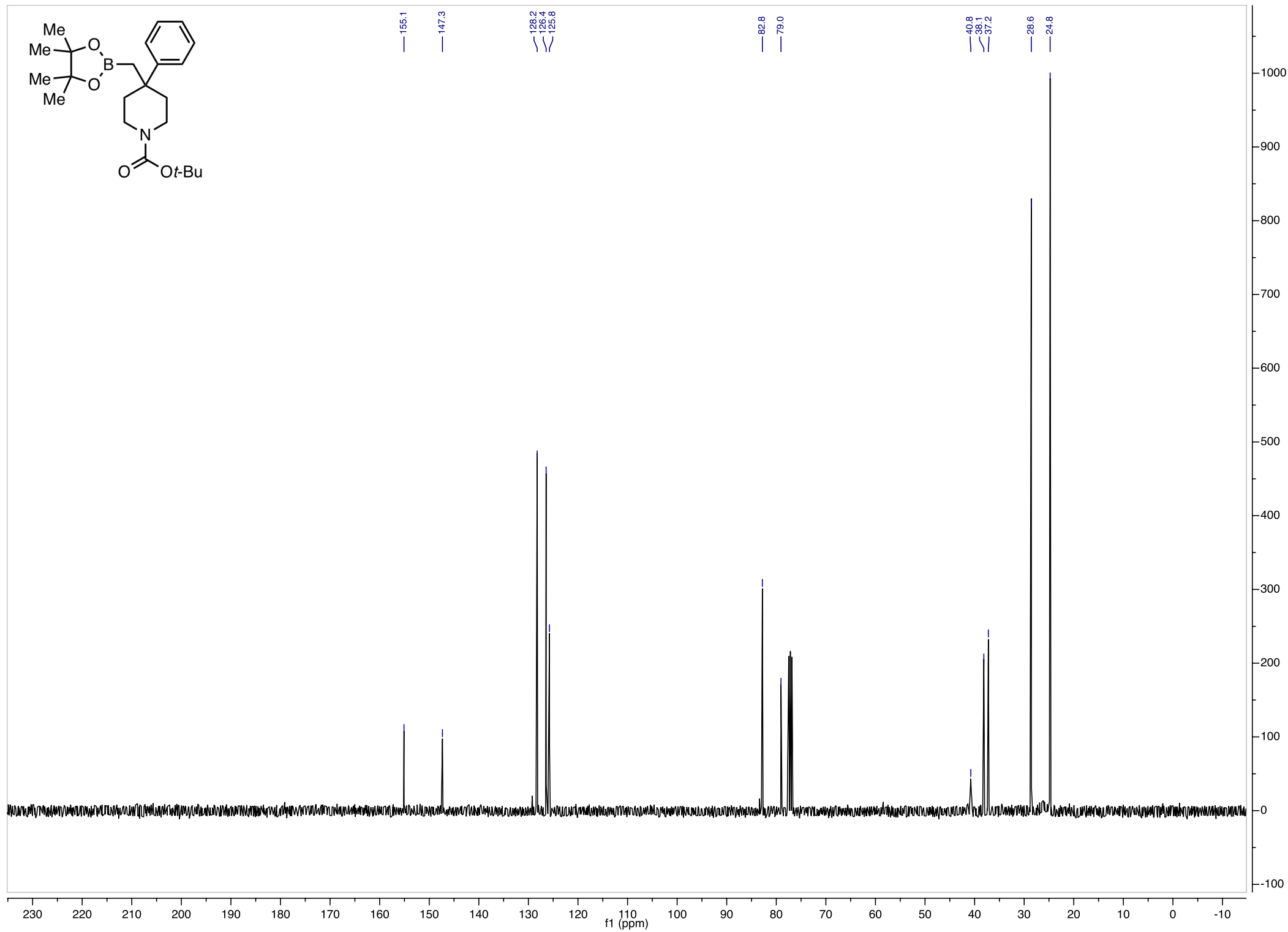
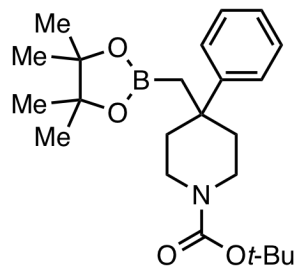


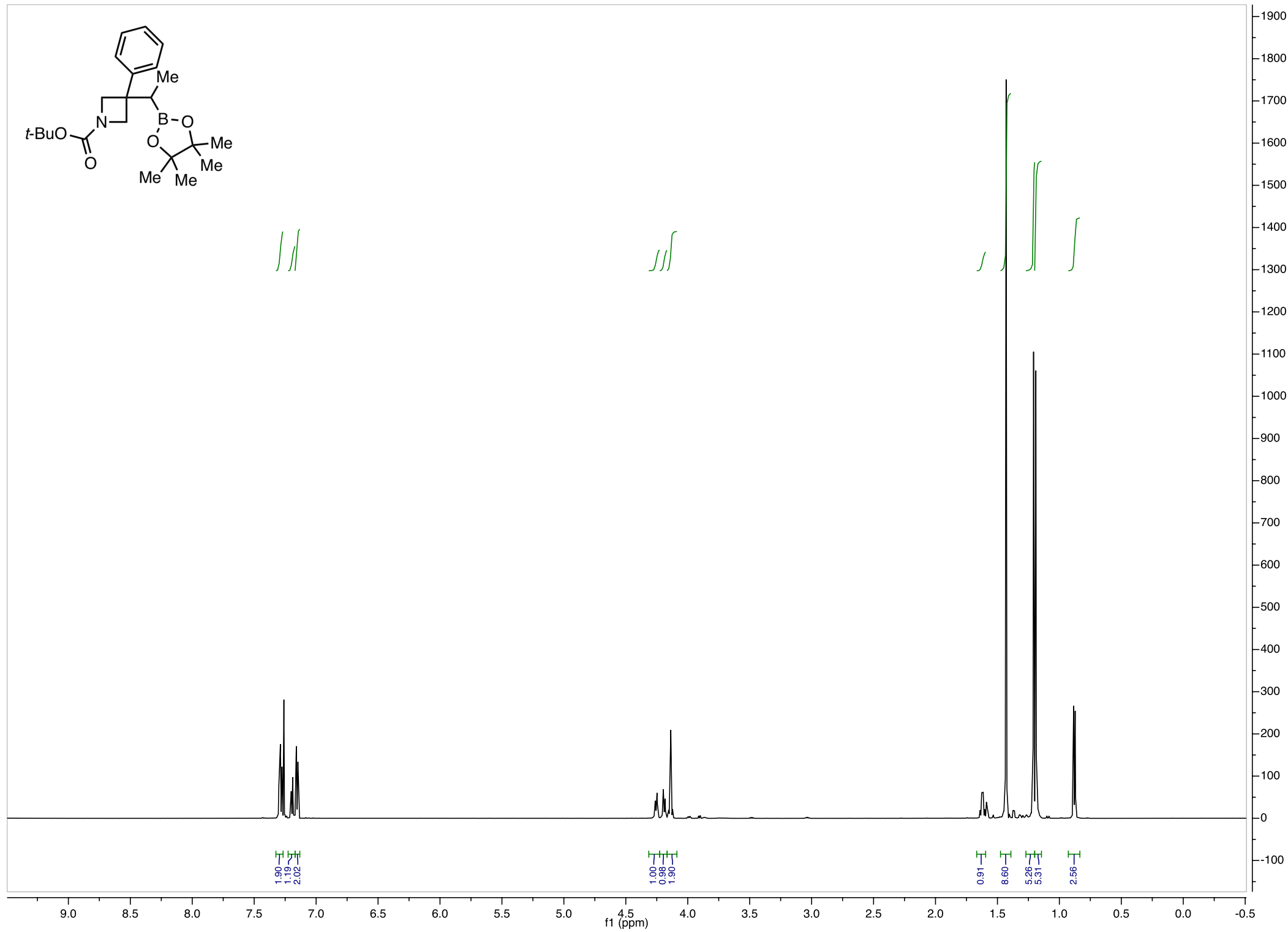
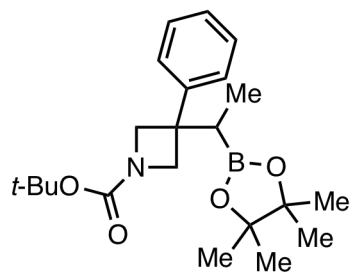


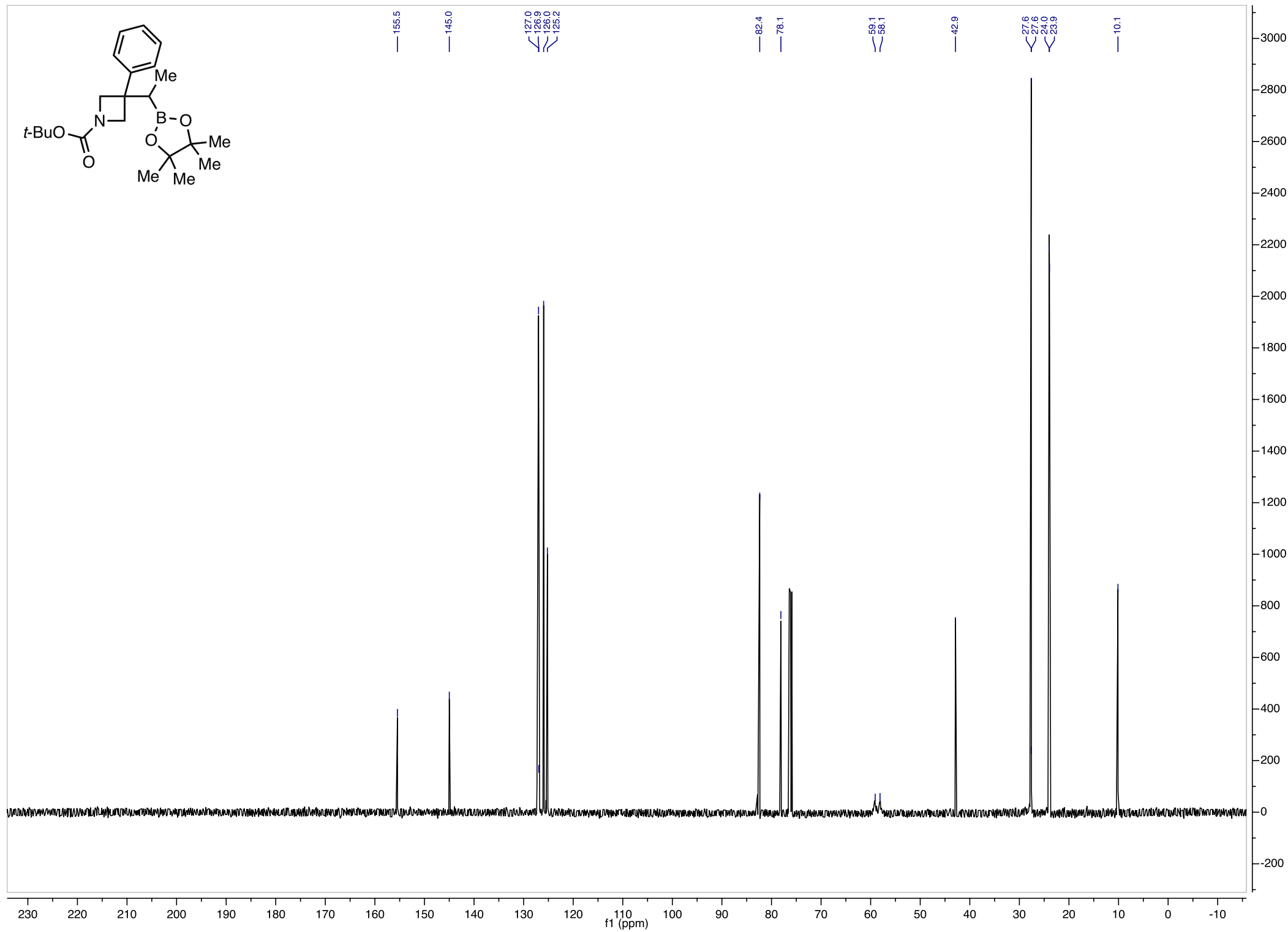
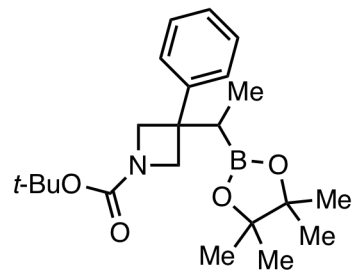


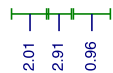
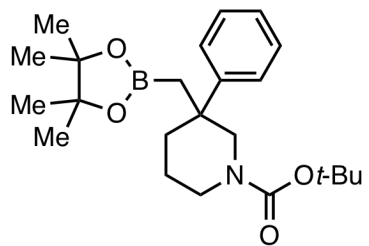












2.01

2.91

0.96

1.00

0.94

2.14

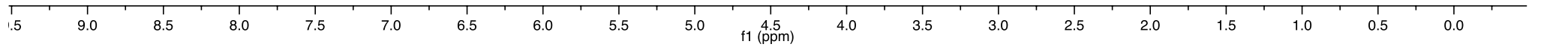
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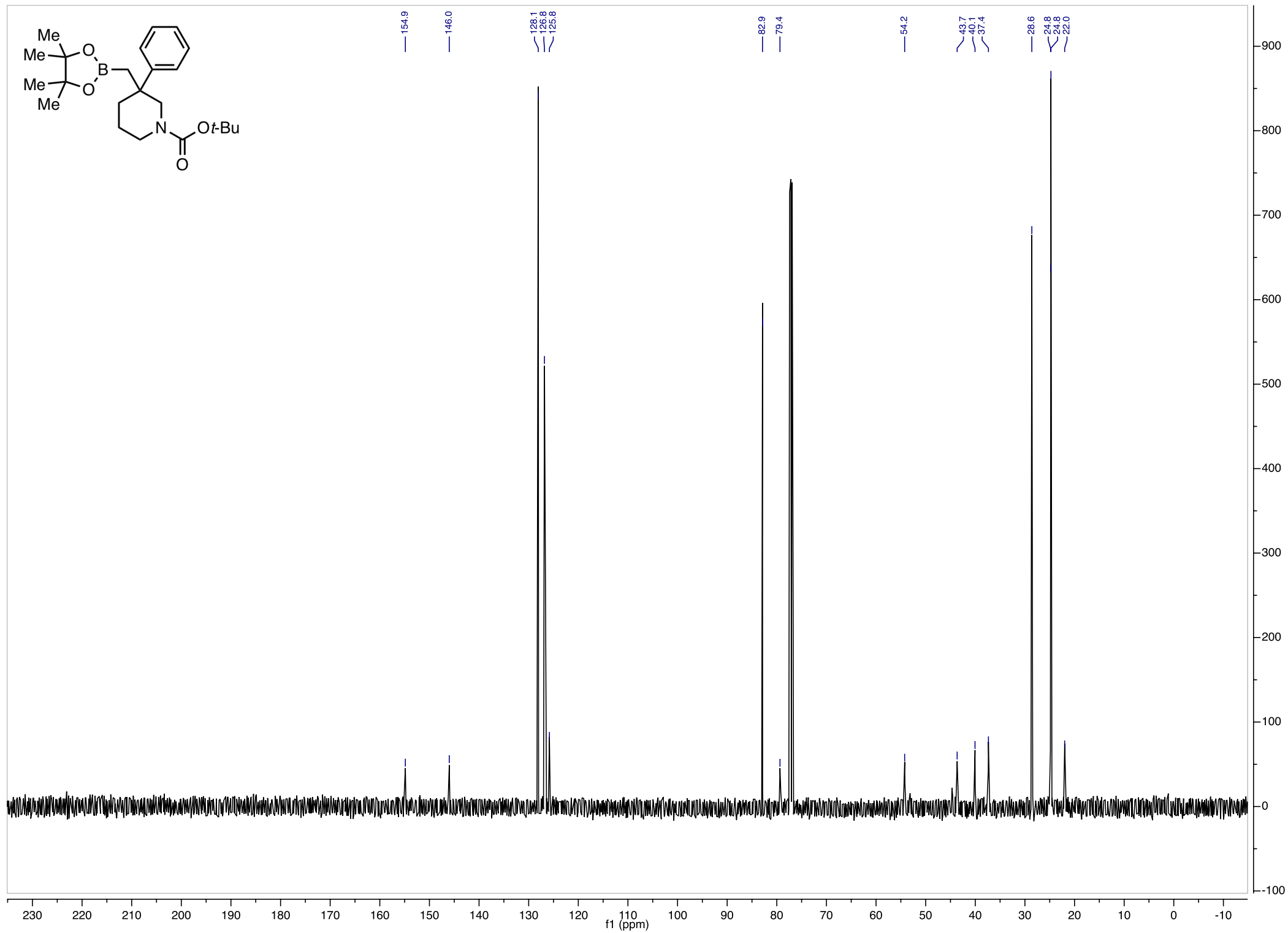
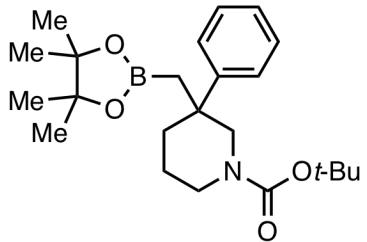
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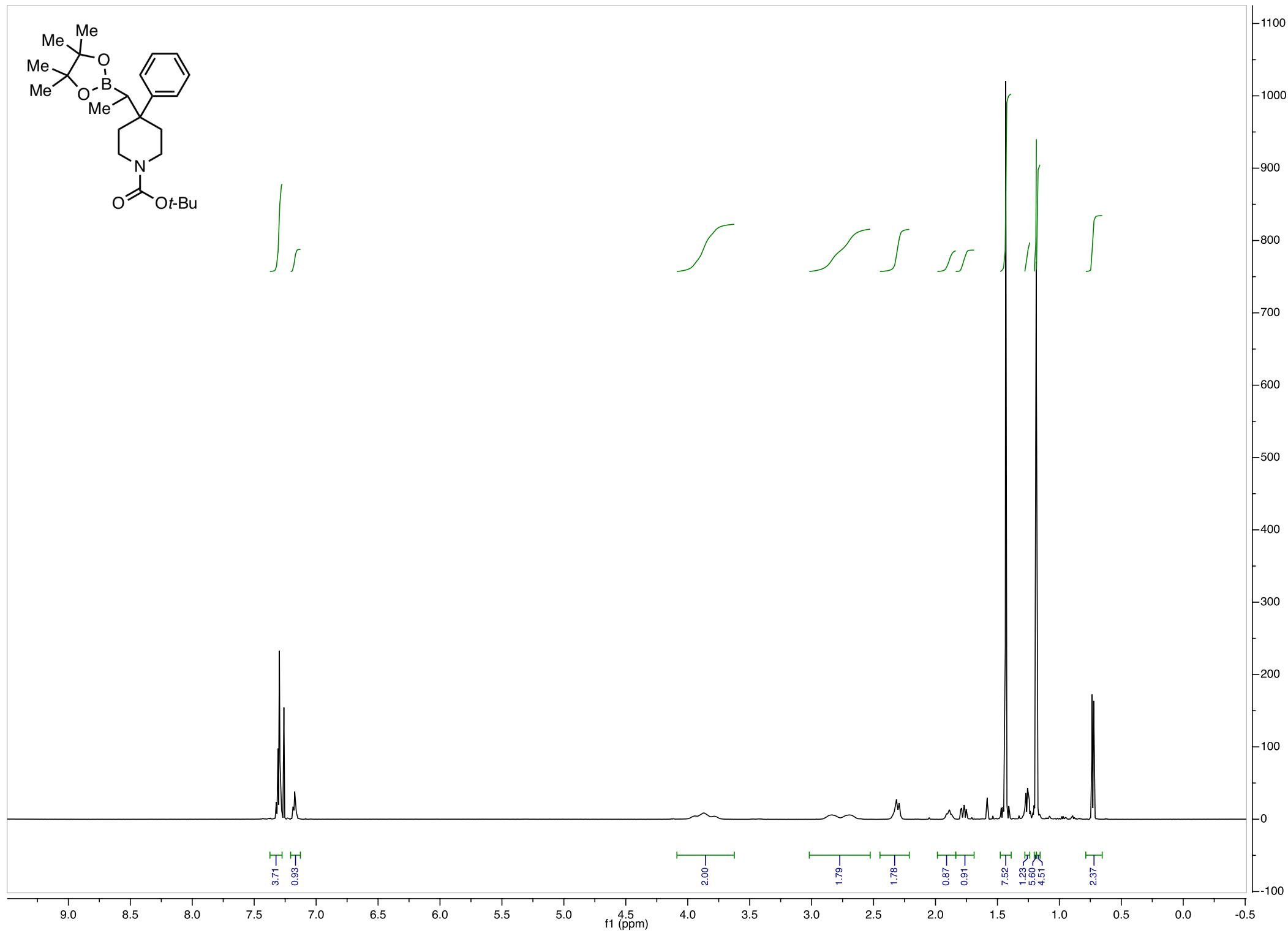
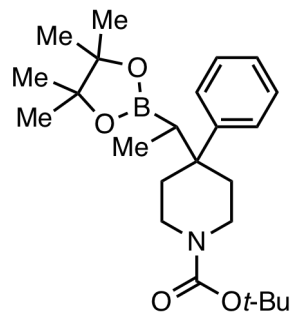
9.29

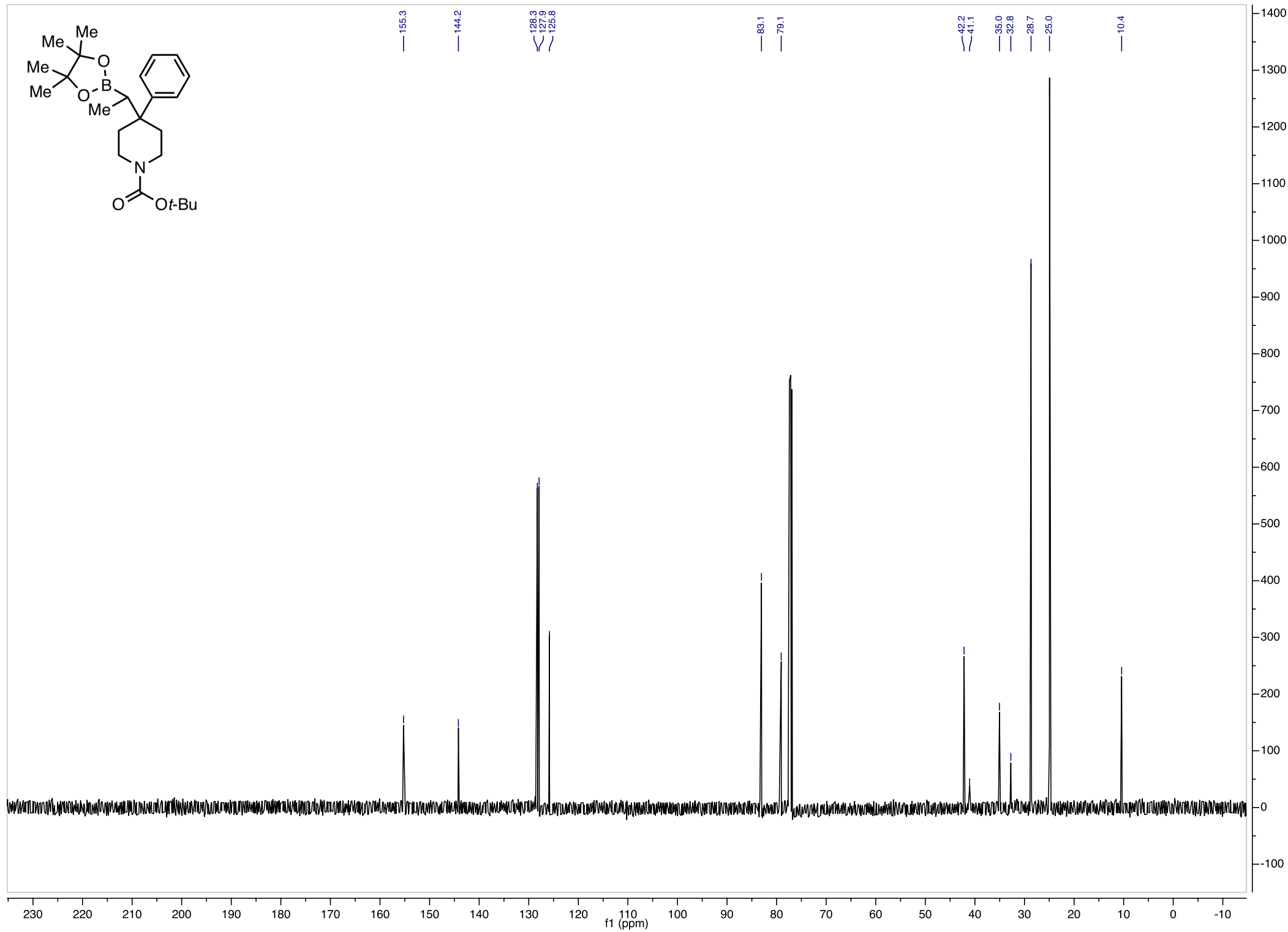
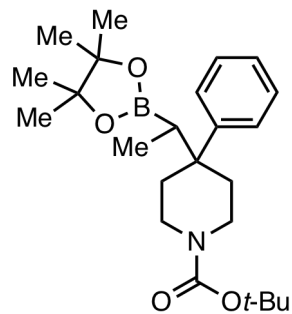
1.25

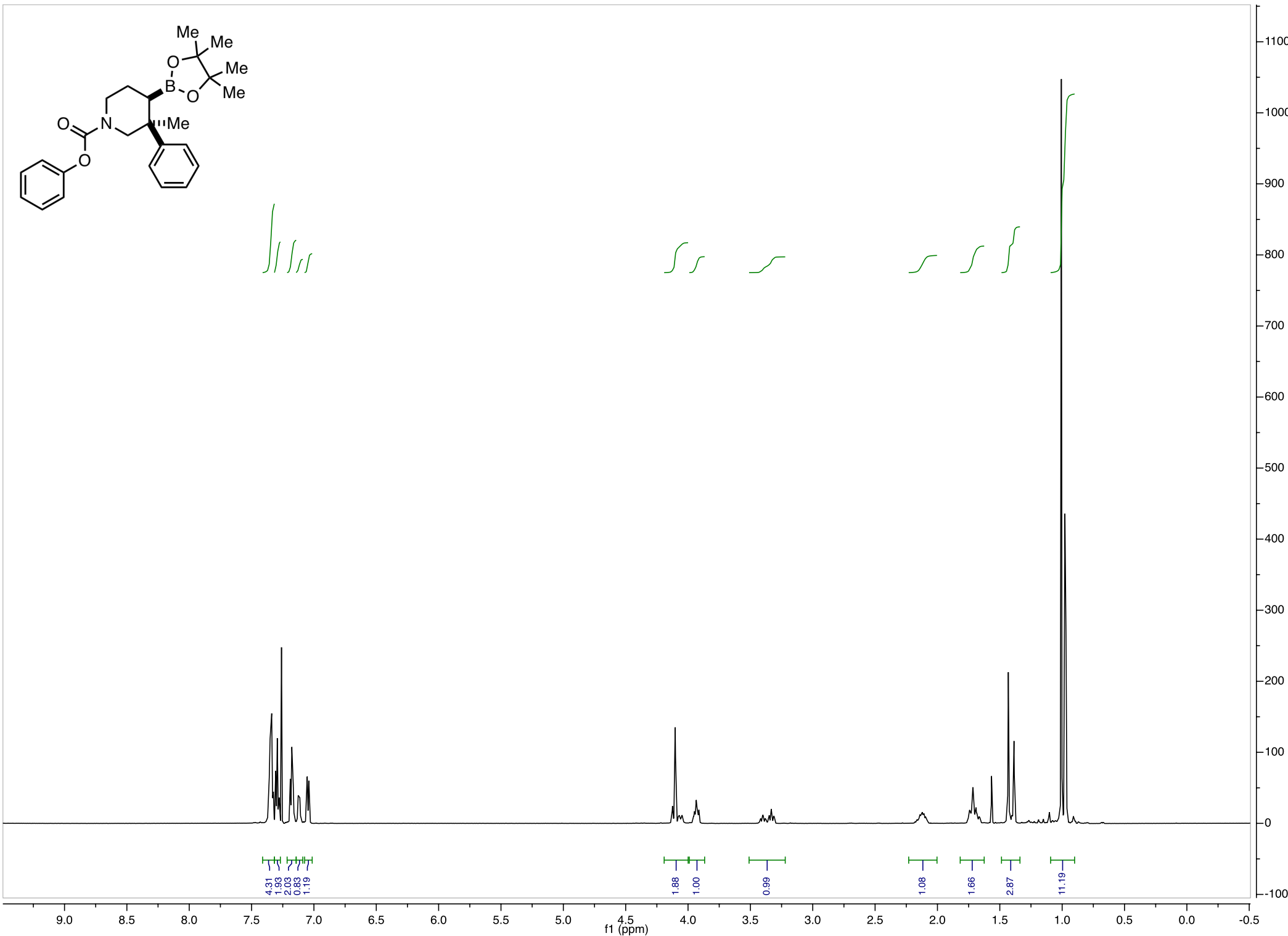
11.88

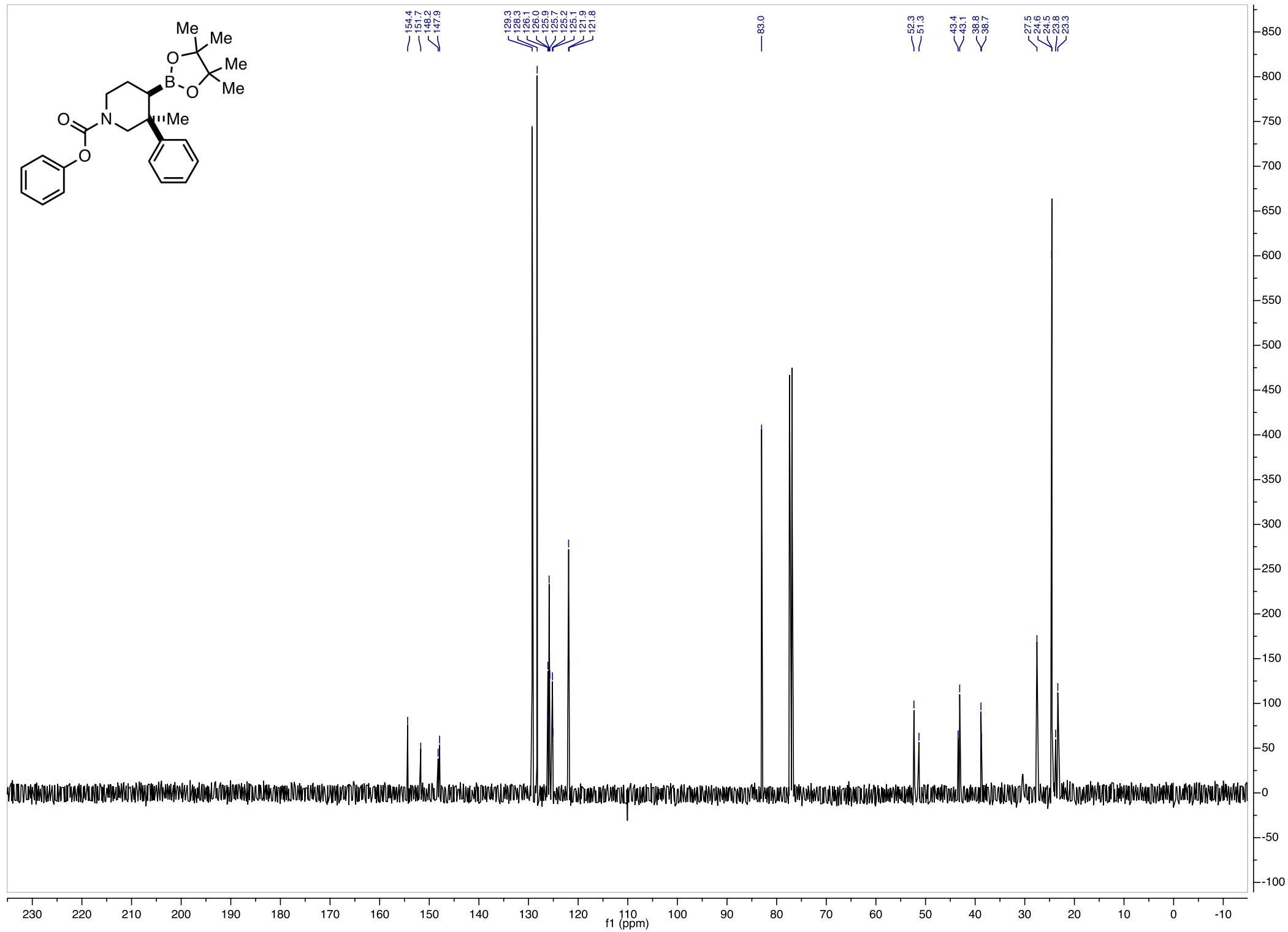
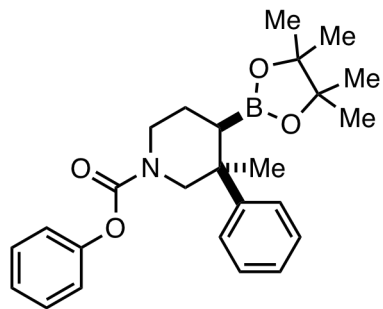


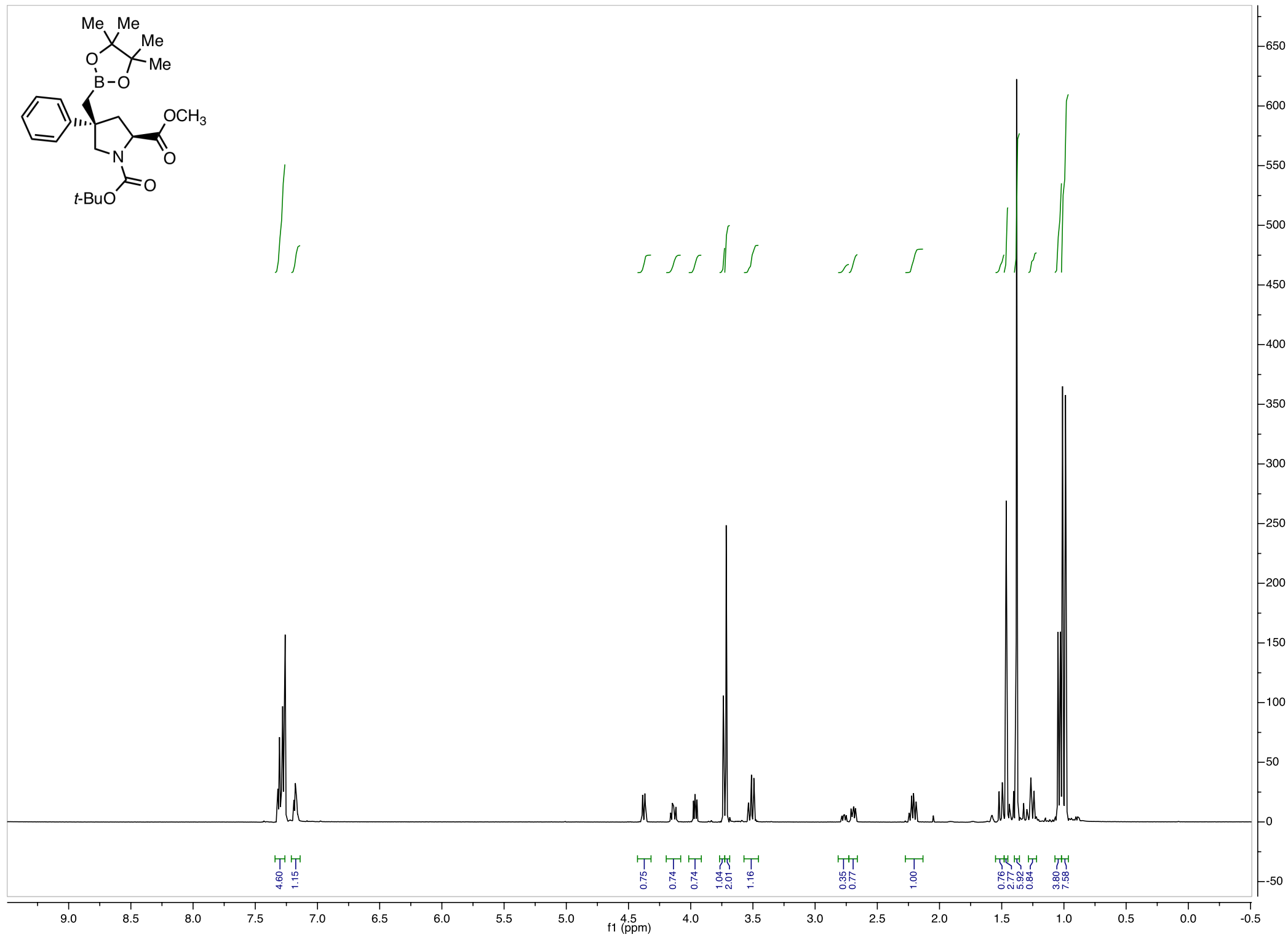
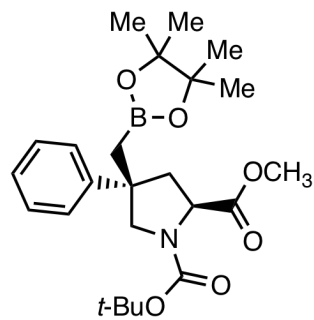


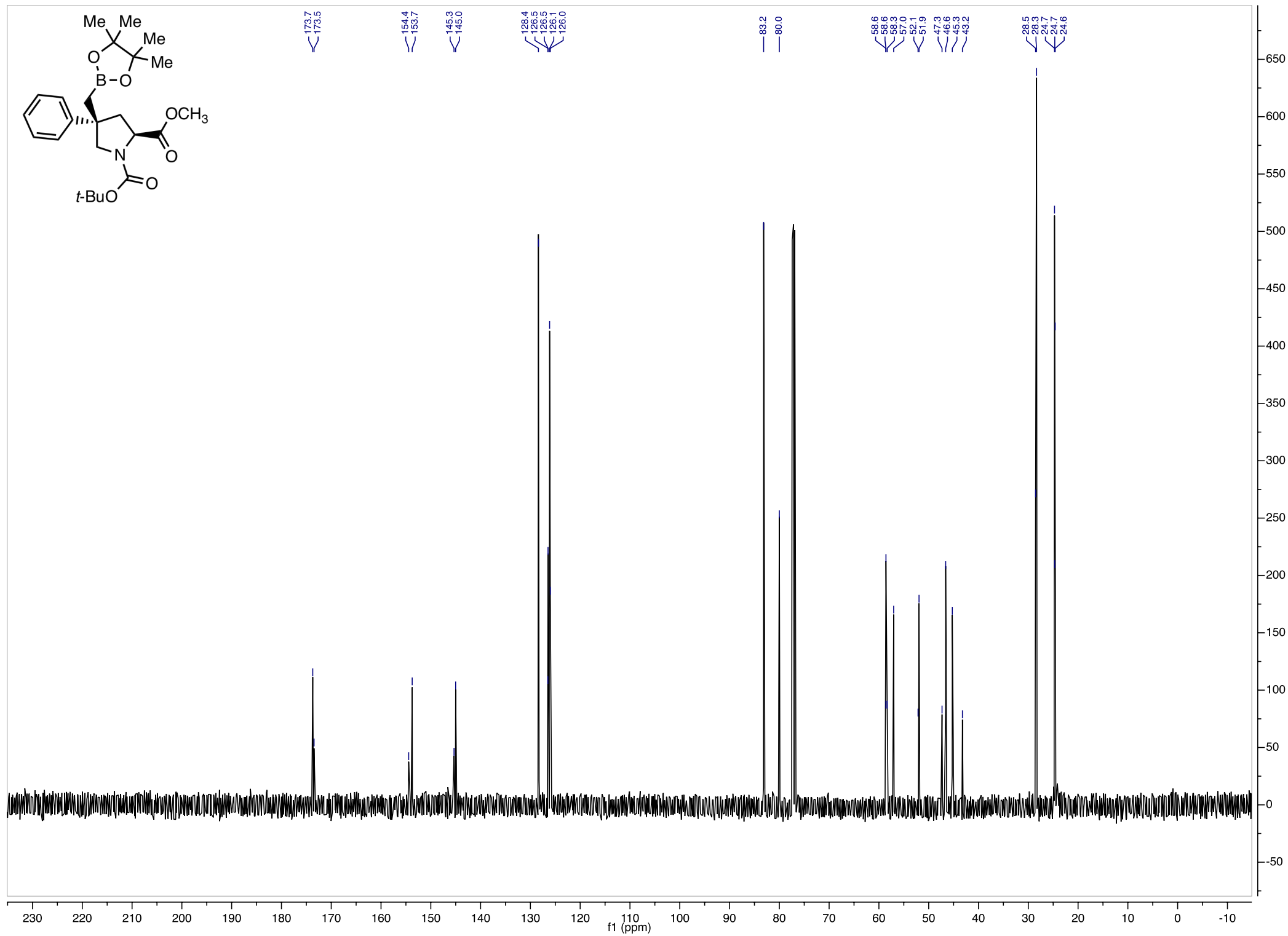
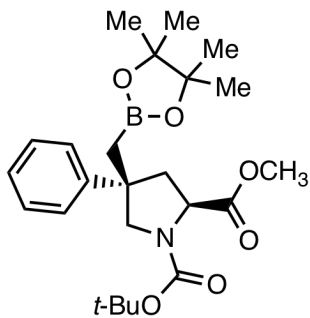


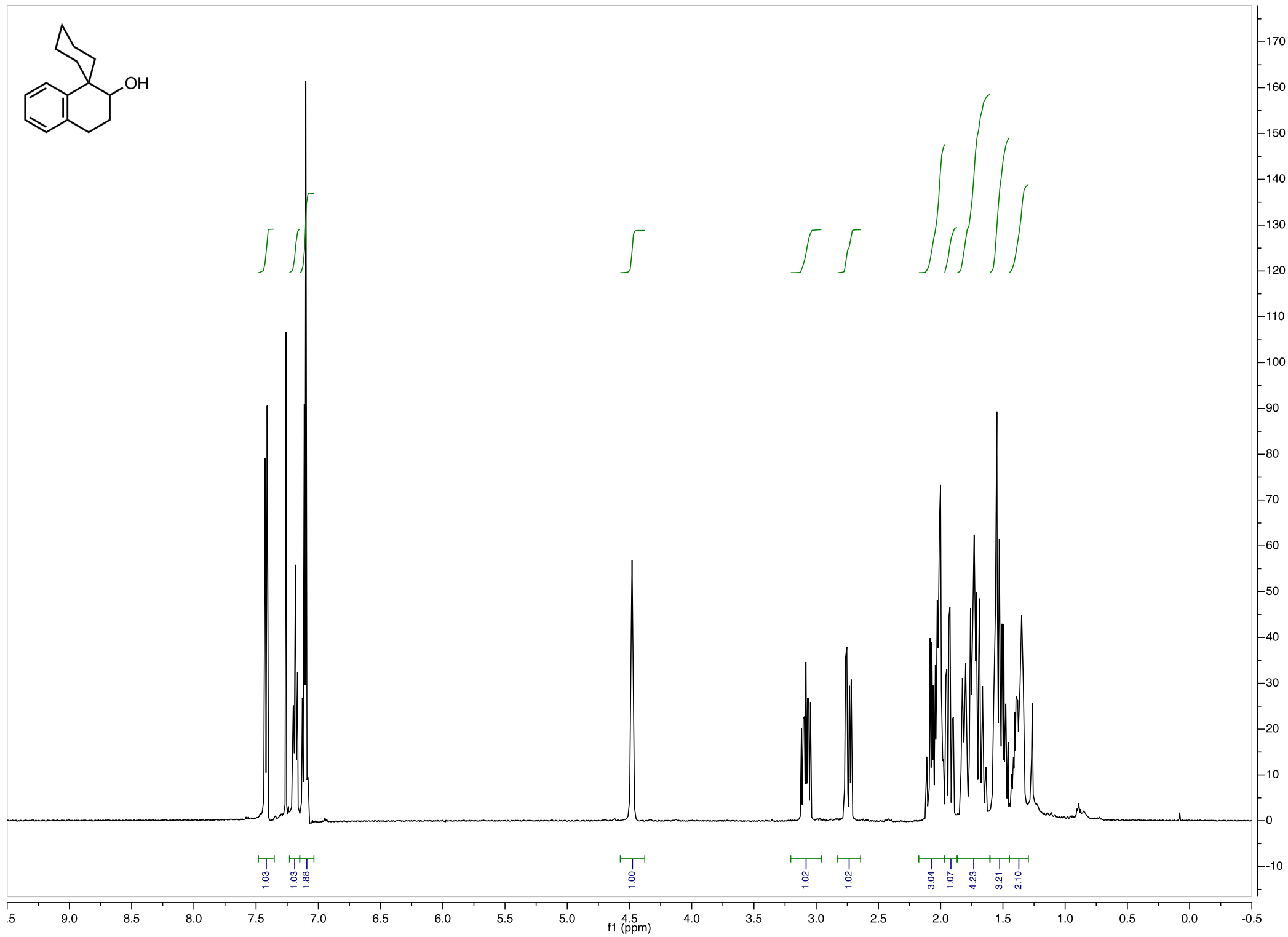
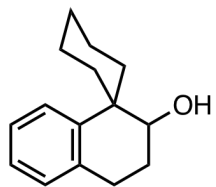


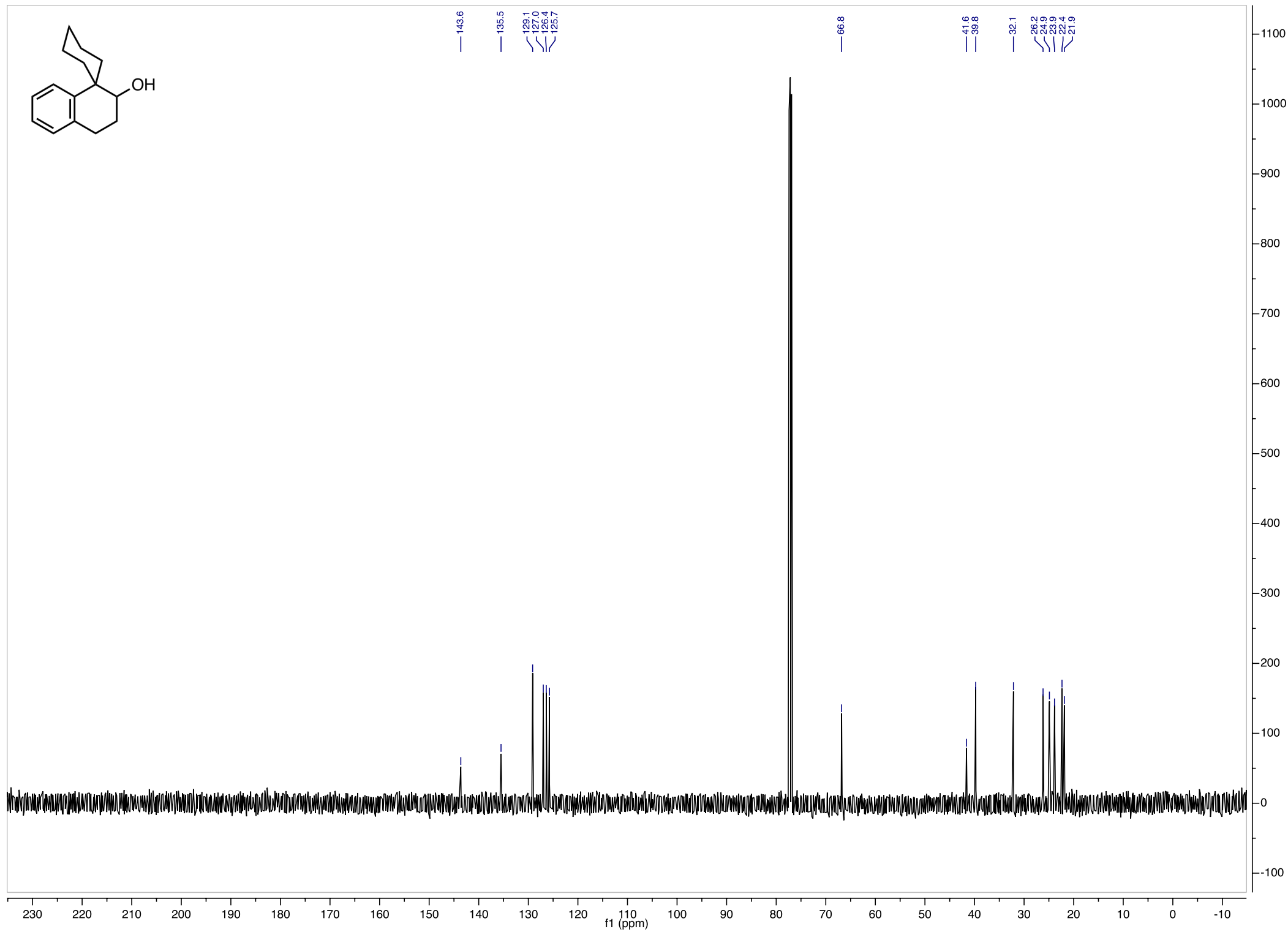
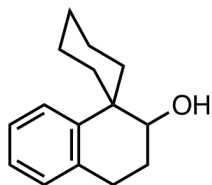


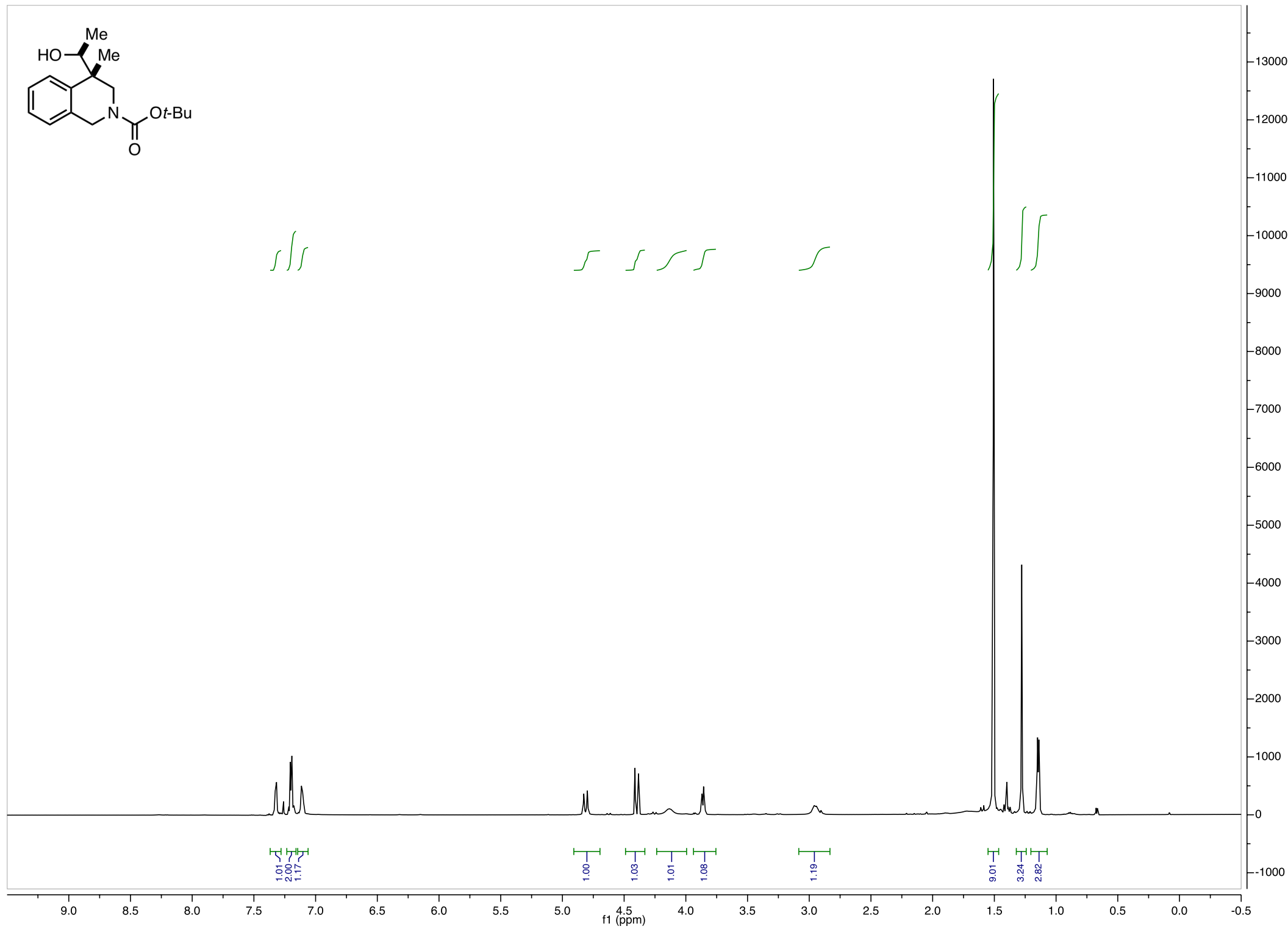
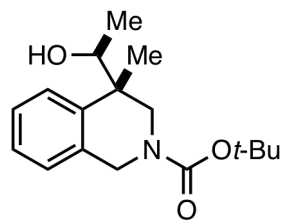


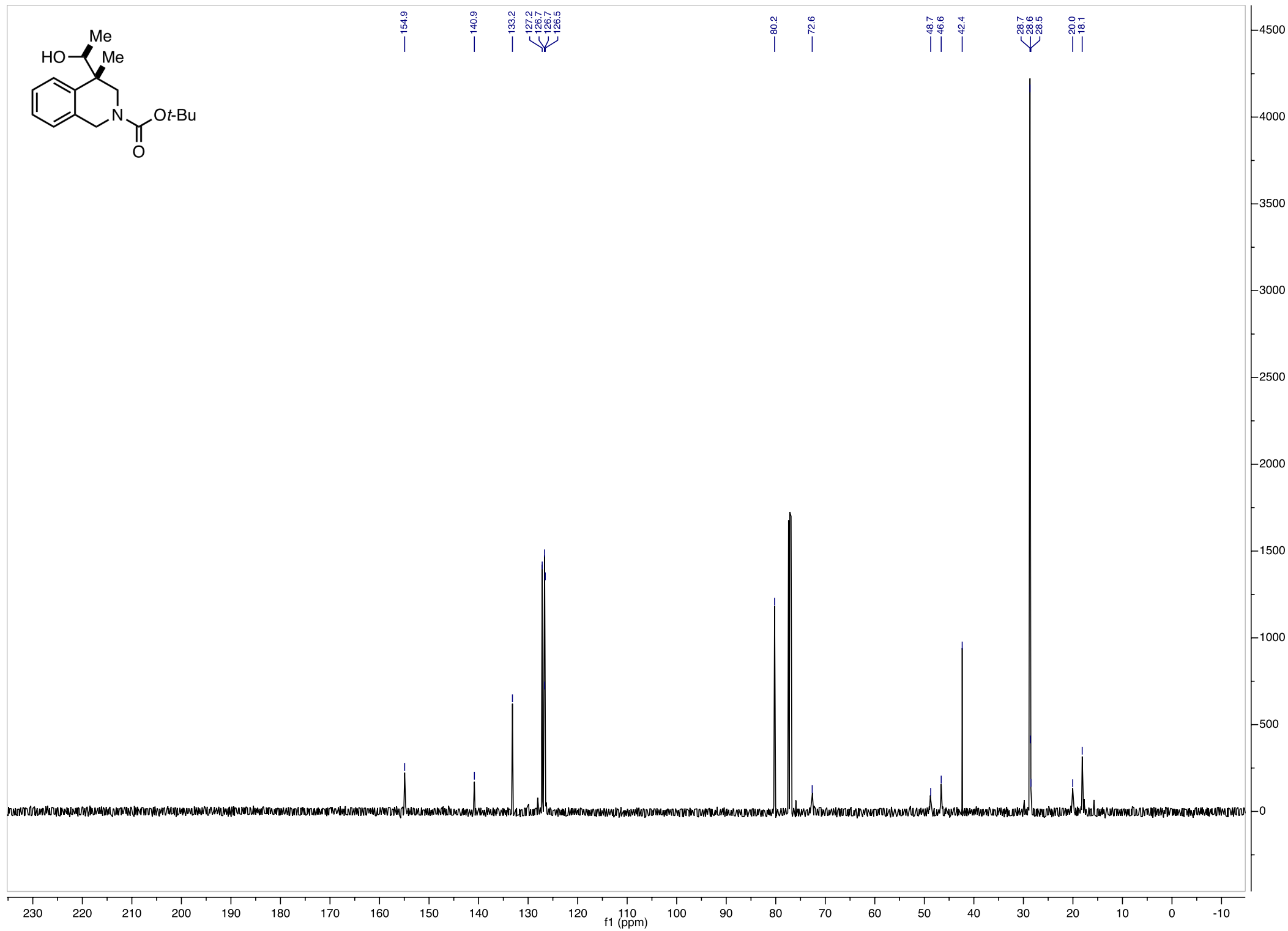
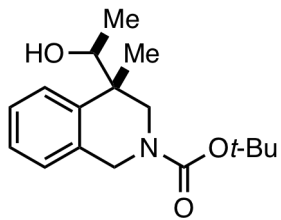


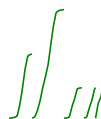
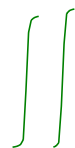
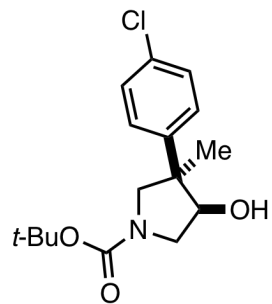












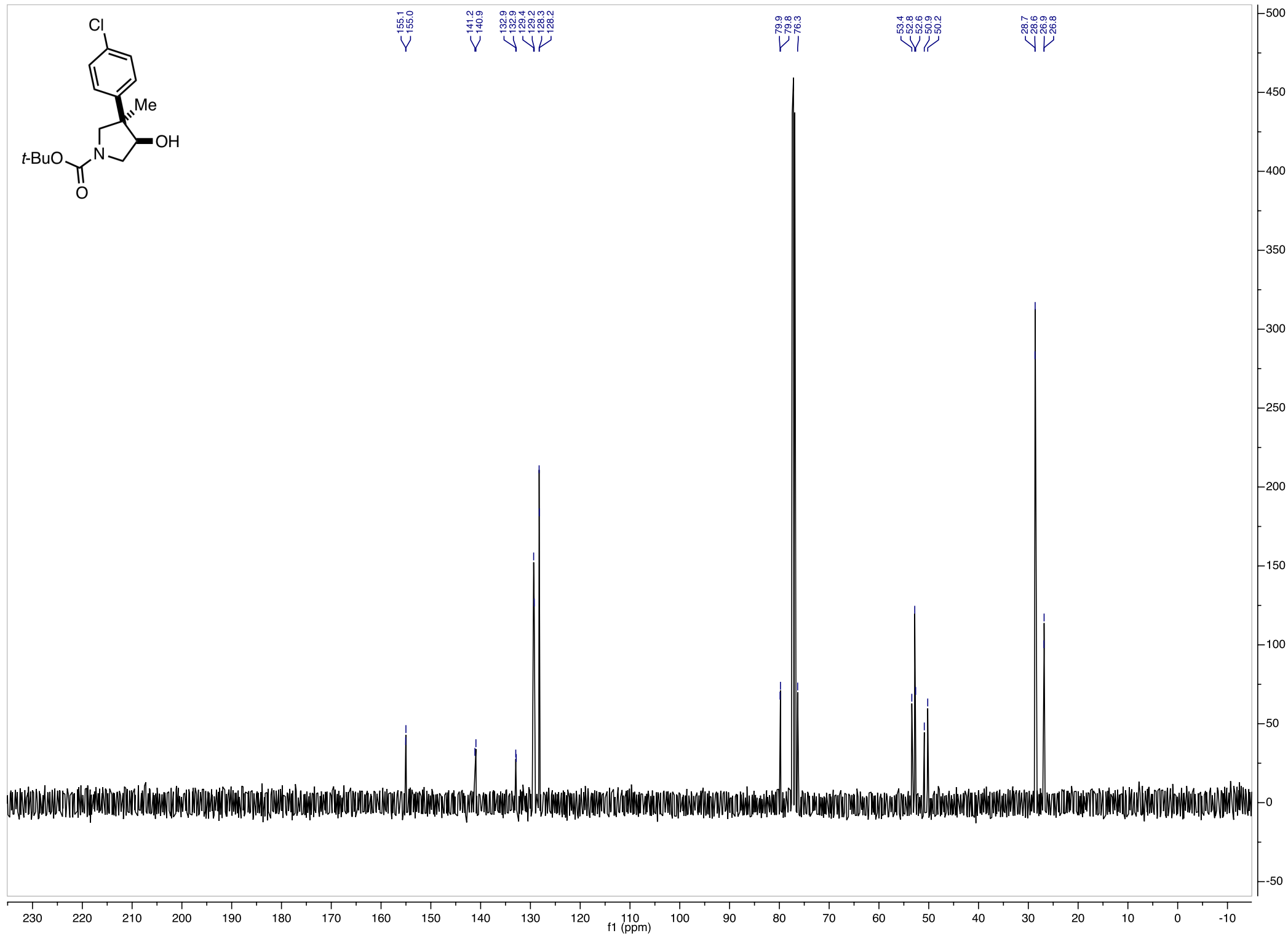
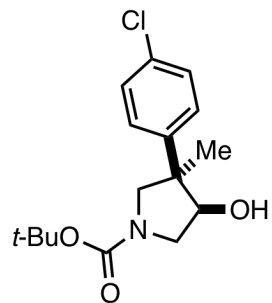
2.12
2.24

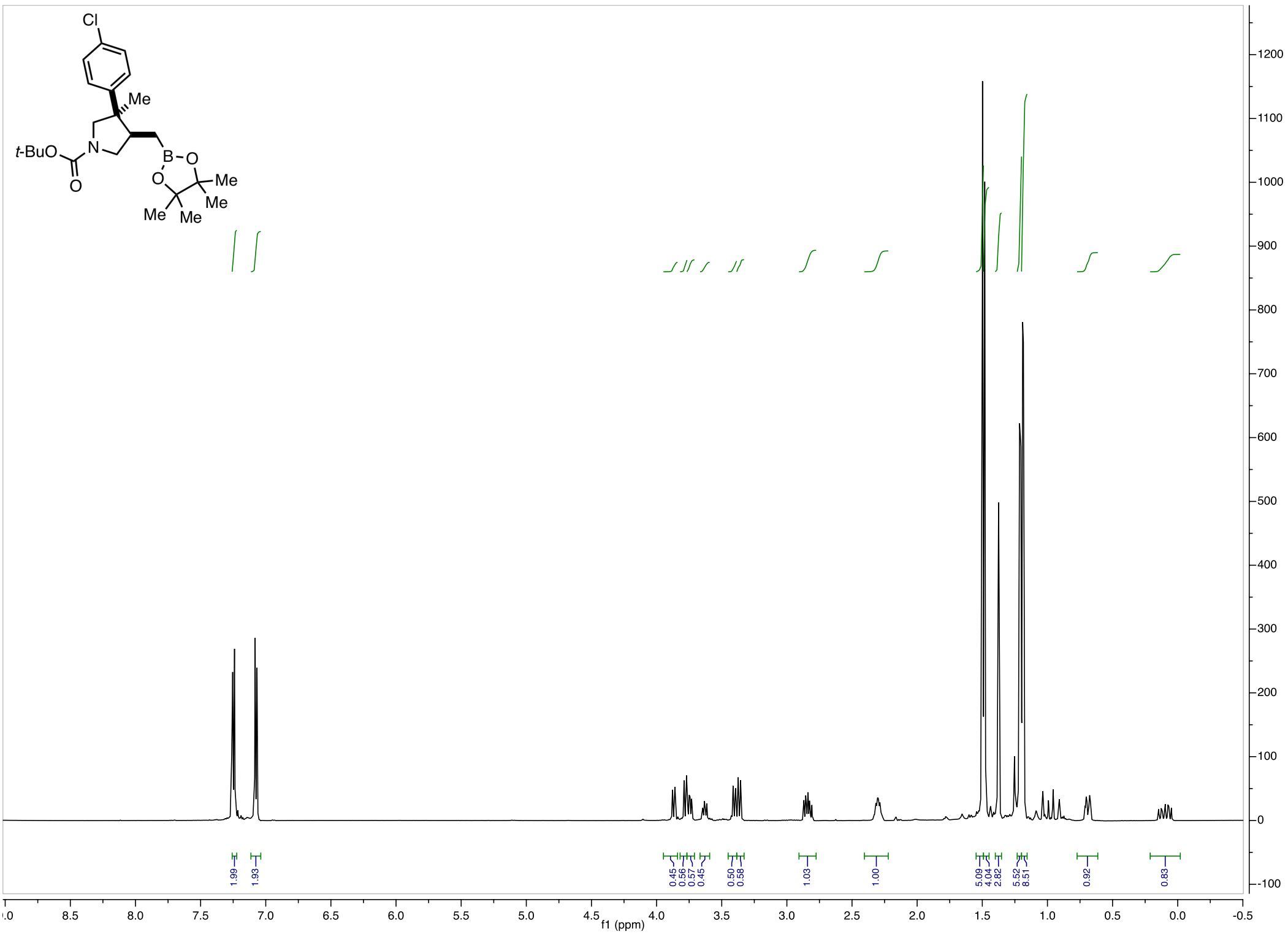
1.00

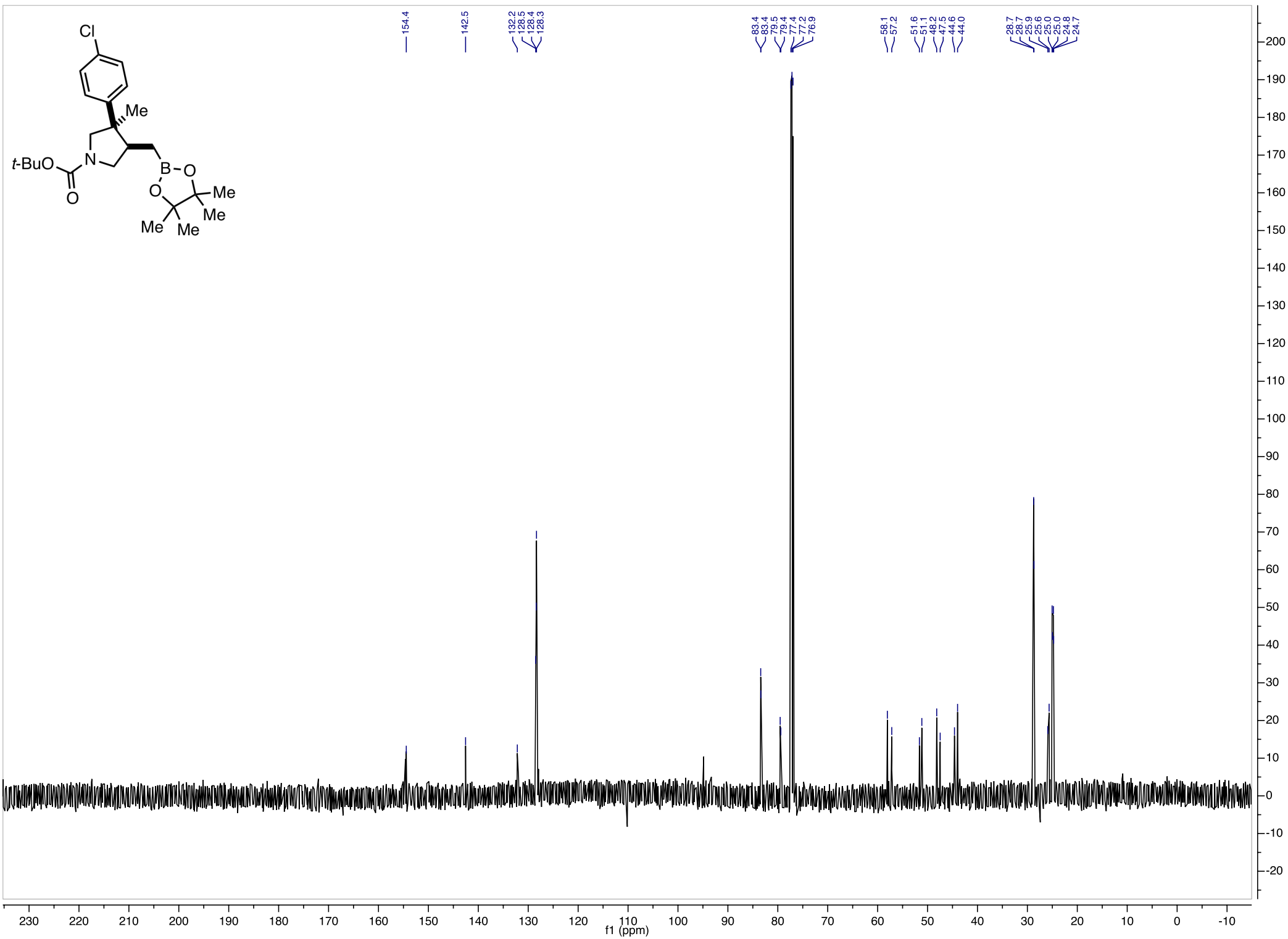
1.04
1.76
0.48
0.65
0.55

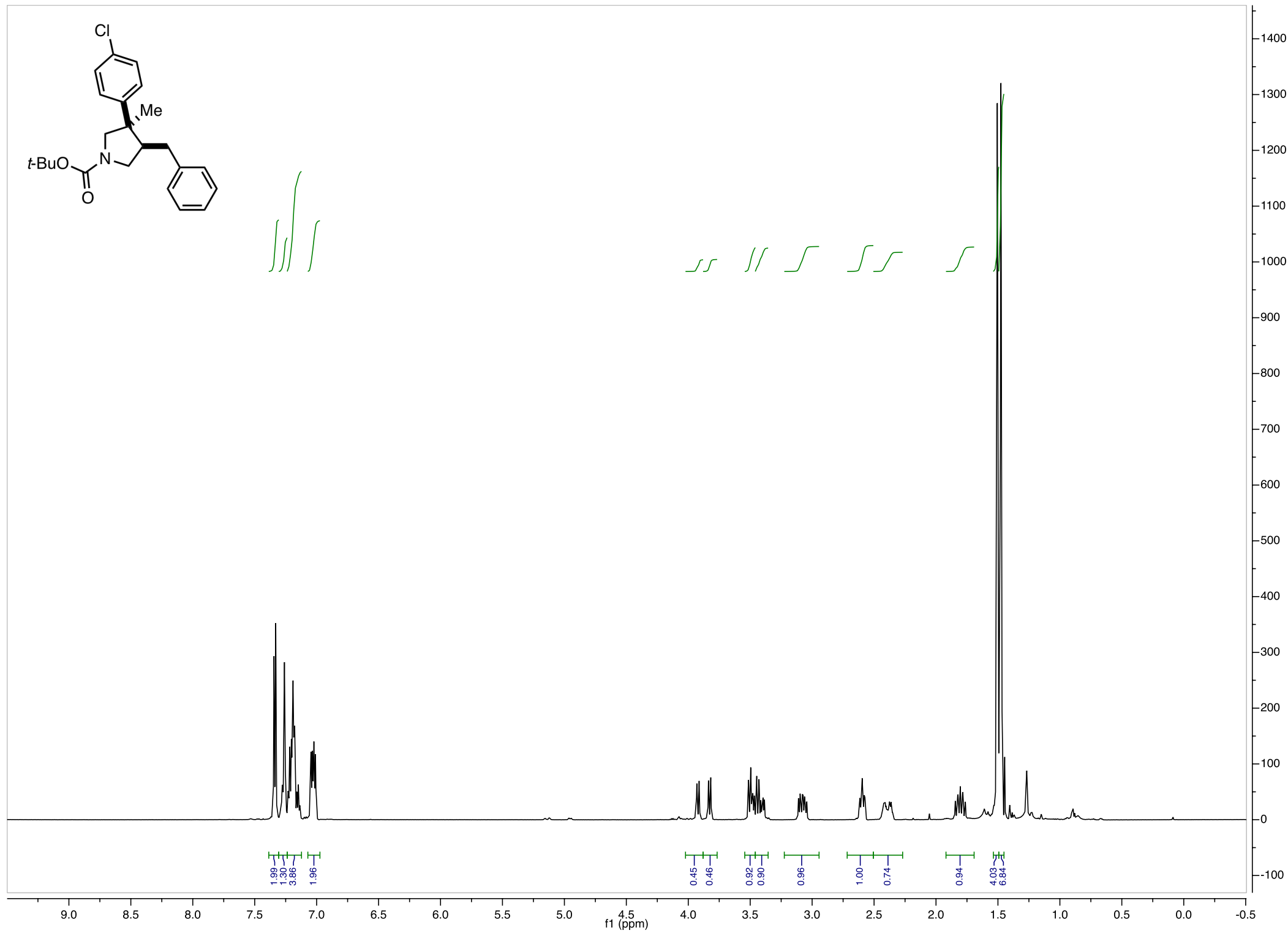
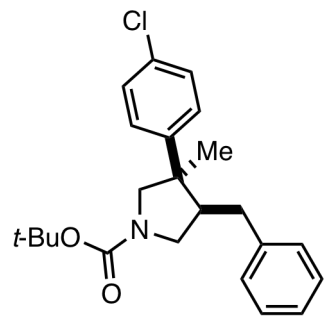
4.33
4.70
2.78

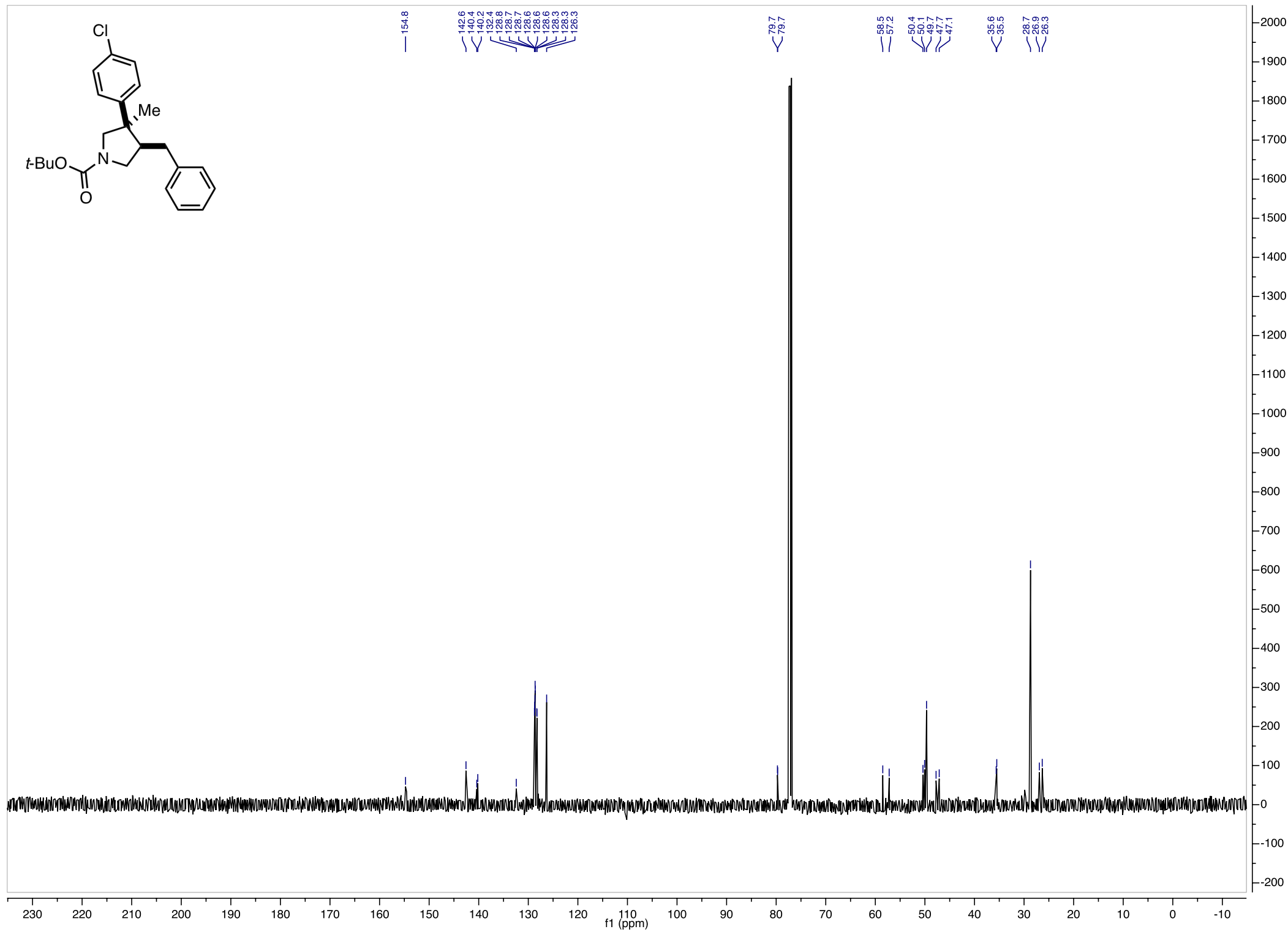
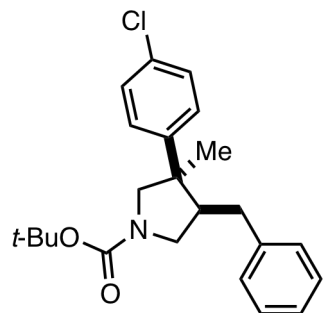
f1 (ppm)

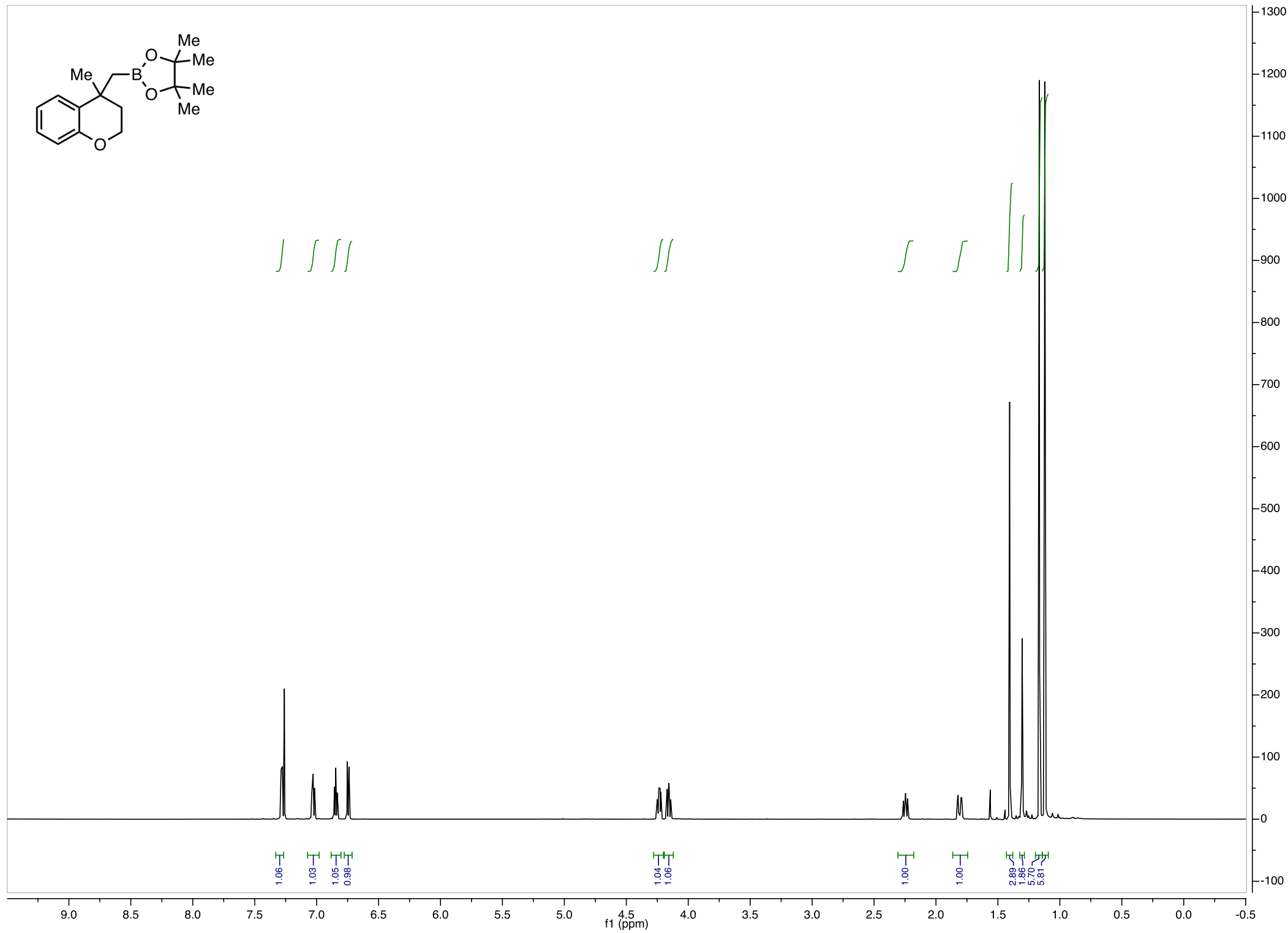
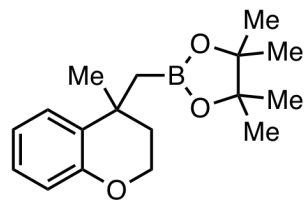


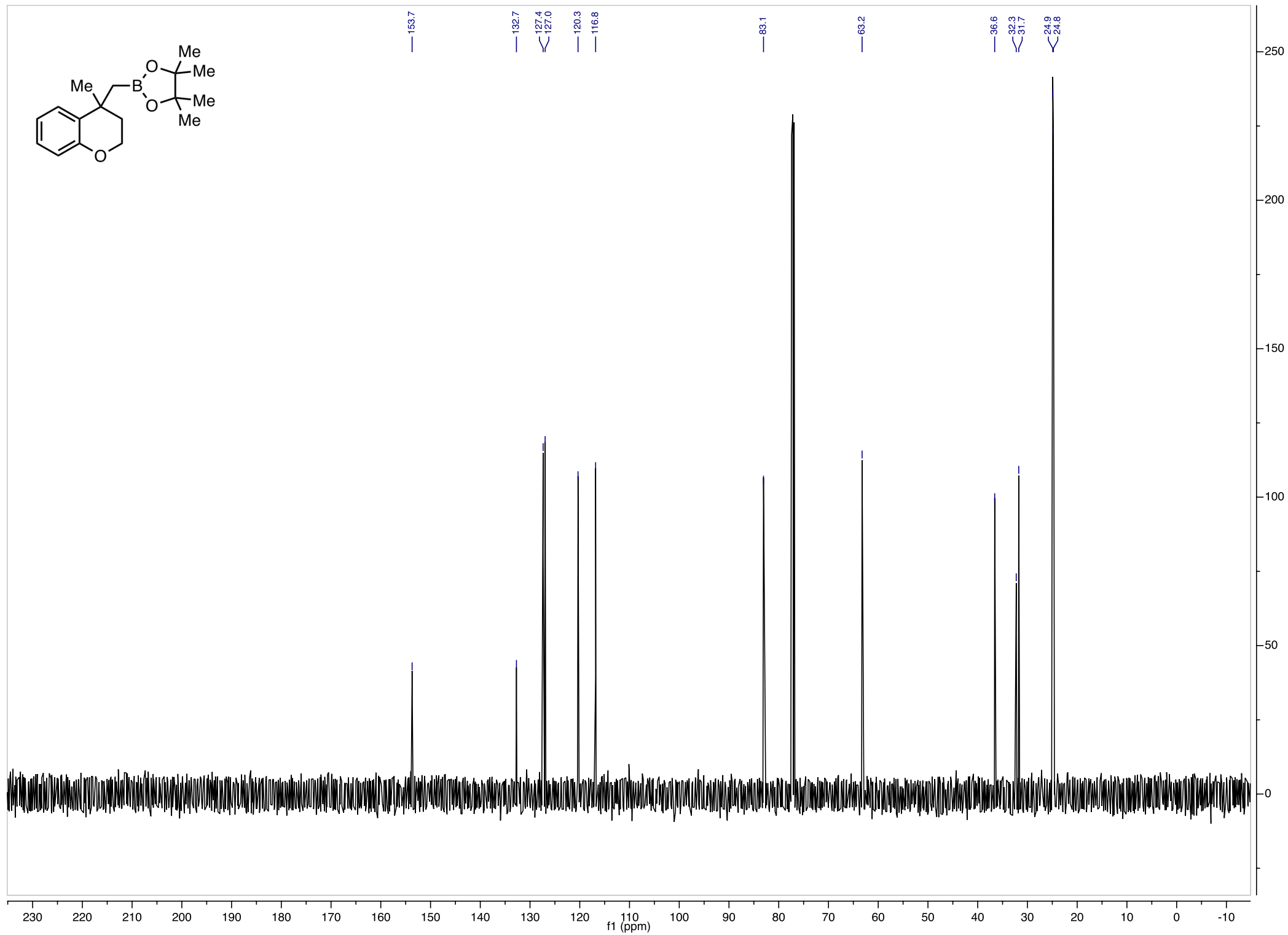
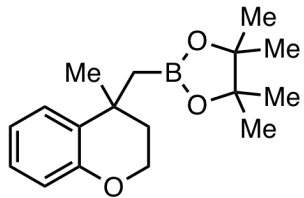


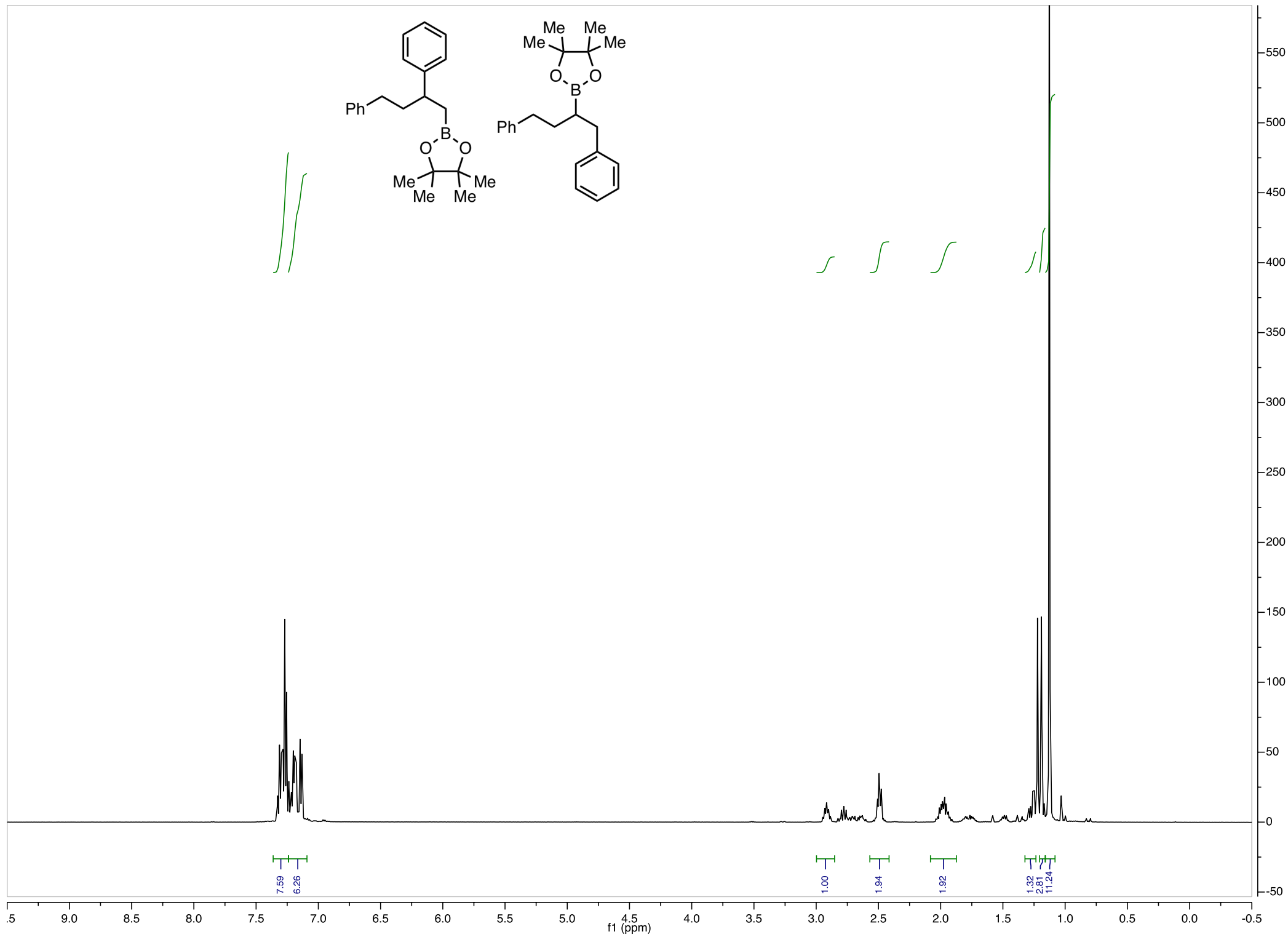


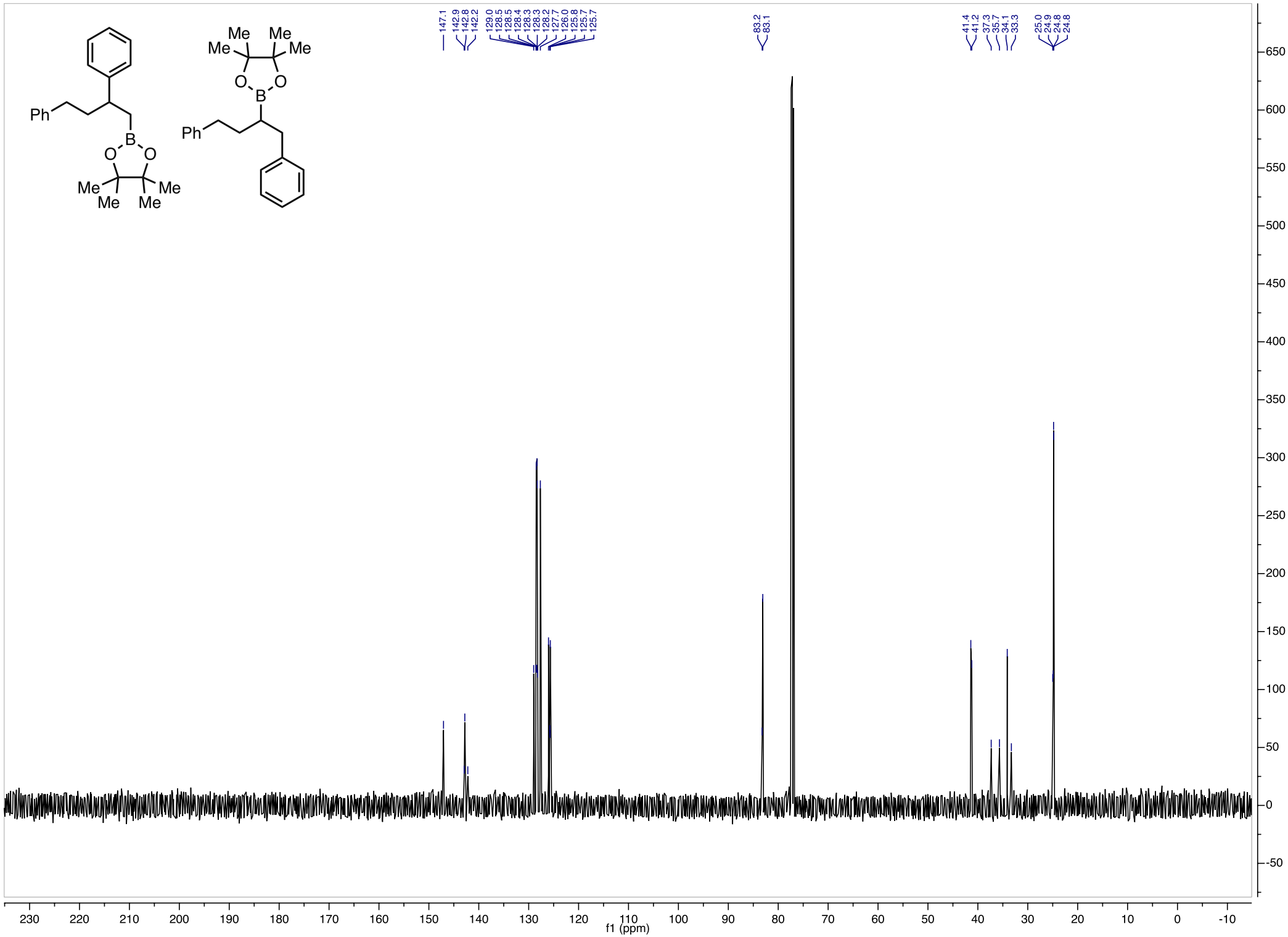


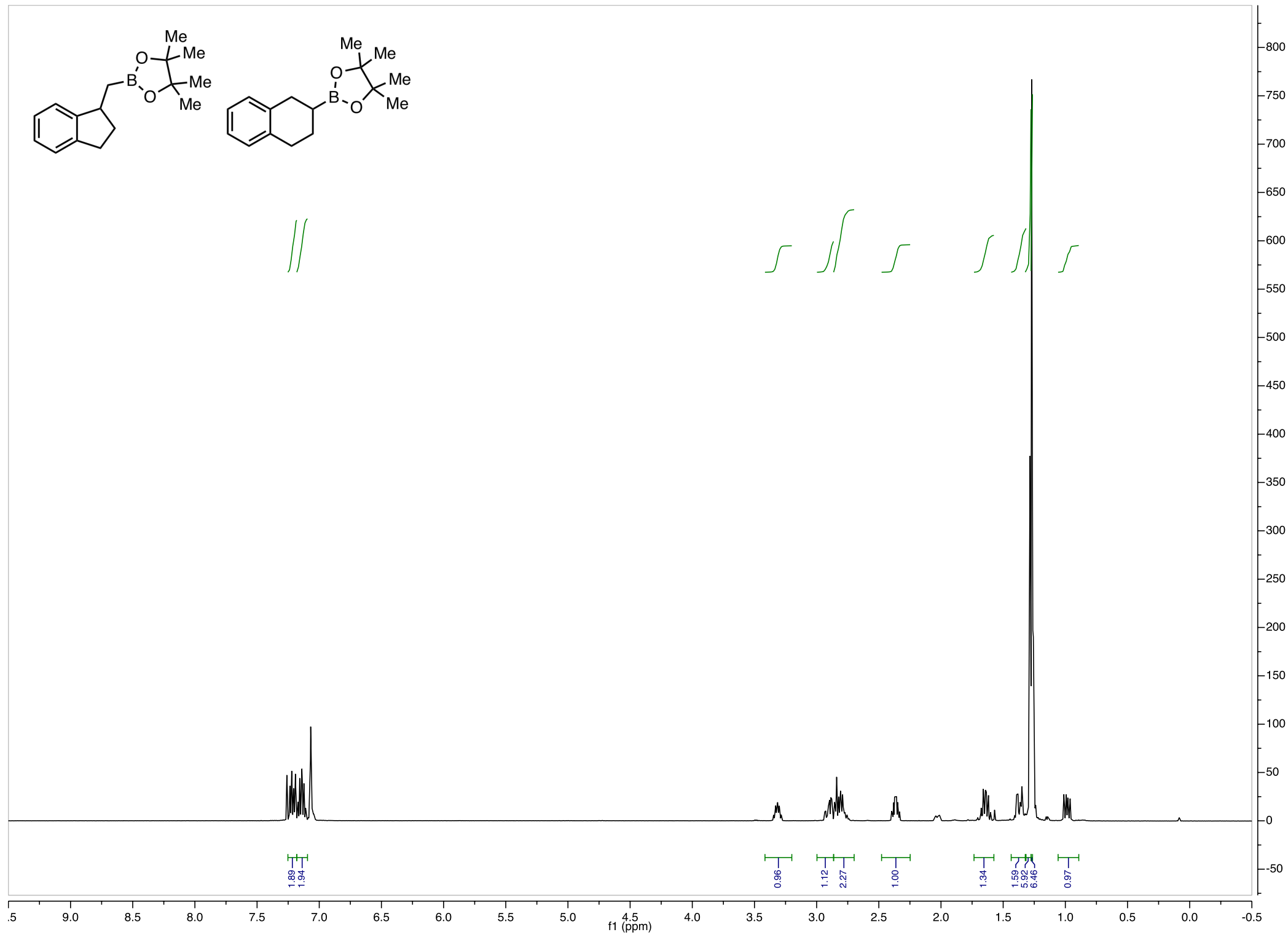
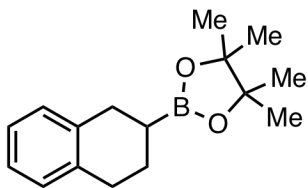
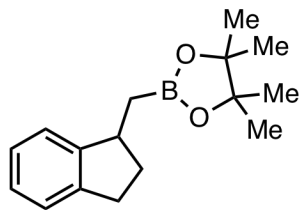


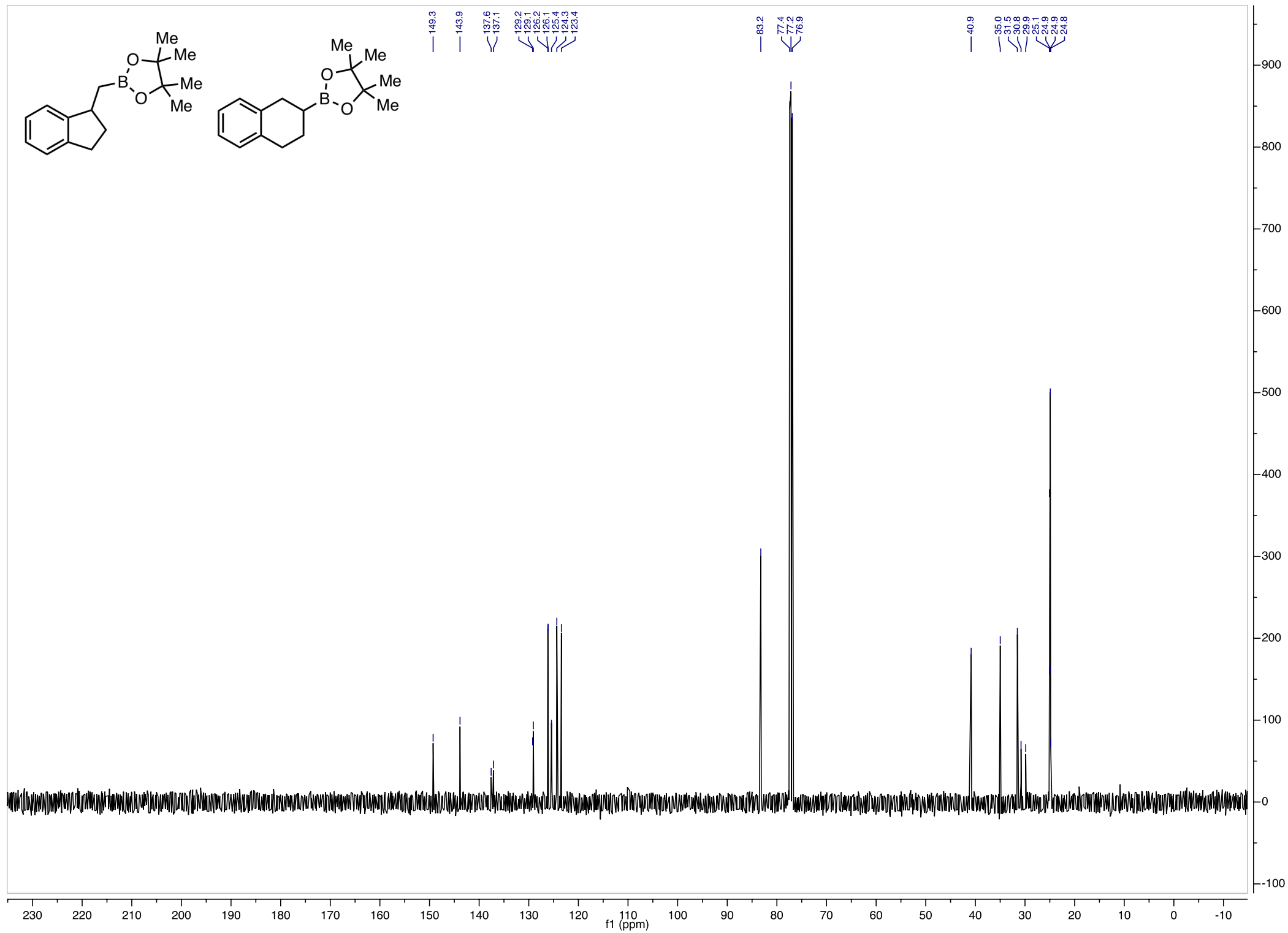
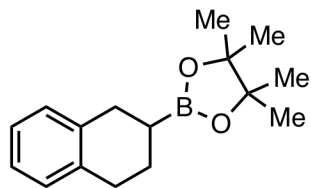








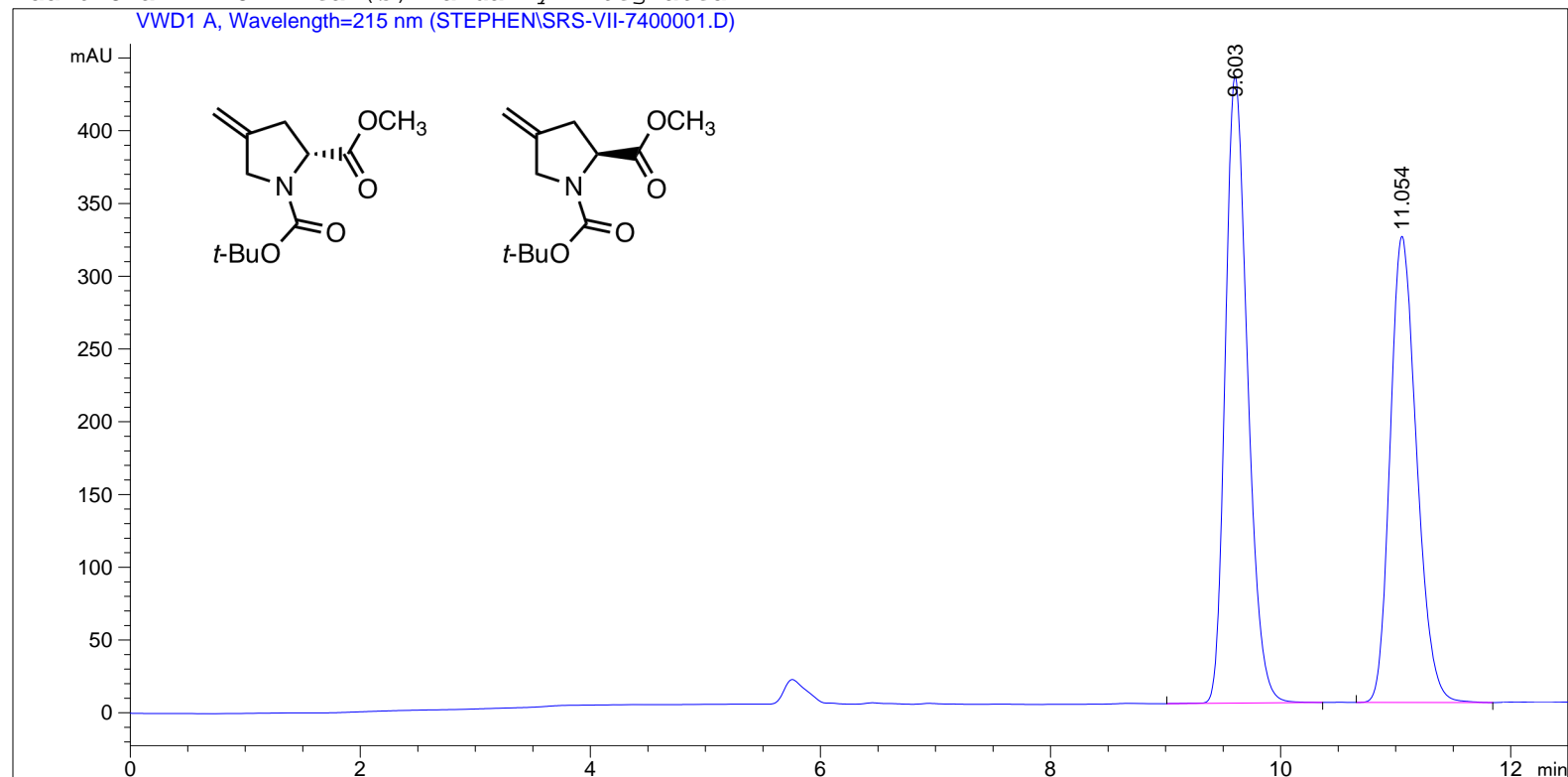




```
=====
Acq. Operator   : SYSTEM                      Seq. Line :    1
Acq. Instrument : 1220 HPLC                  Location  : Vial 61
Injection Date  : 11/15/2018 7:33:56 AM      Inj       :    1
                                           Inj Volume: 10.000 µl

Acq. Method     : C:\CHEM32\2\METHODS\SRS.M
Last changed    : 11/15/2018 7:45:53 AM by SYSTEM
                  (modified after loading)
Analysis Method : C:\CHEM32\2\METHODS\DEF_LC.M
Last changed    : 10/2/2018 2:47:22 PM by SYSTEM
Sample Info     : ChiralPak1A, 95:5 Hex:IPA, 0.6 mL/min, 215 nm
=====
```

Additional Info : Peak(s) manually integrated



Area Percent Report

```
Sorted By      :      Signal
Multiplier:    :      1.0000
Dilution:      :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: VWD1 A, Wavelength=215 nm

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1 | 9.603 | BB | 0.2082 | 5806.90430 | 430.94681 | 53.1124 |
| 2 | 11.054 | BB | 0.2477 | 5126.32813 | 320.29758 | 46.8876 |

Totals : 1.09332e4 751.24438

***End of Report ***

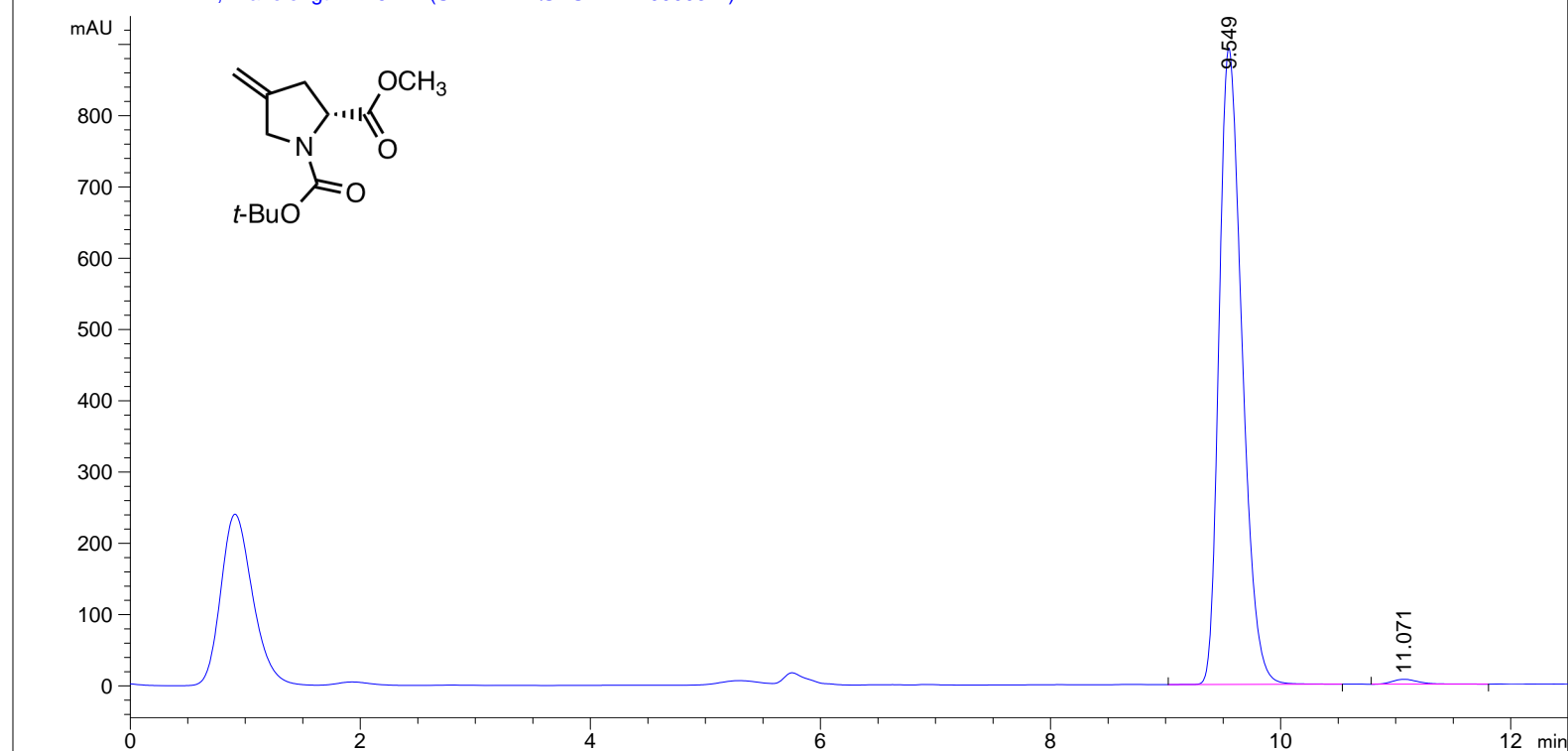
Sample Name: SRS-VII-75

```
=====
Acq. Operator   : SYSTEM                      Seq. Line :    3
Acq. Instrument : 1220 HPLC                  Location  : Vial 63
Injection Date  : 11/15/2018 8:00:47 AM      Inj       :    1
                                           Inj Volume: 10.000 µl

Acq. Method     : C:\CHEM32\2\METHODS\SRS.M
Last changed    : 11/15/2018 7:45:53 AM by SYSTEM
                  (modified after loading)
Analysis Method : C:\CHEM32\2\METHODS\DEF_LC.M
Last changed    : 10/2/2018 2:47:22 PM by SYSTEM
Sample Info     : ChiralPak1A, 95:5 Hex:IPA, 0.6 mL/min, 215 nm
=====
```

Additional Info : Peak(s) manually integrated

VWD1 A, Wavelength=215 nm (STEPHEN\SRS-VII-7400003.D)



```
=====
                          Area Percent Report
=====
```

```
Sorted By           :      Signal
Multiplier:         :      1.0000
Dilution:           :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: VWD1 A, Wavelength=215 nm

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1 | 9.549 | BB | 0.2160 | 1.23969e4 | 892.64136 | 99.1022 |
| 2 | 11.071 | BB | 0.2486 | 112.31400 | 6.90952 | 0.8978 |

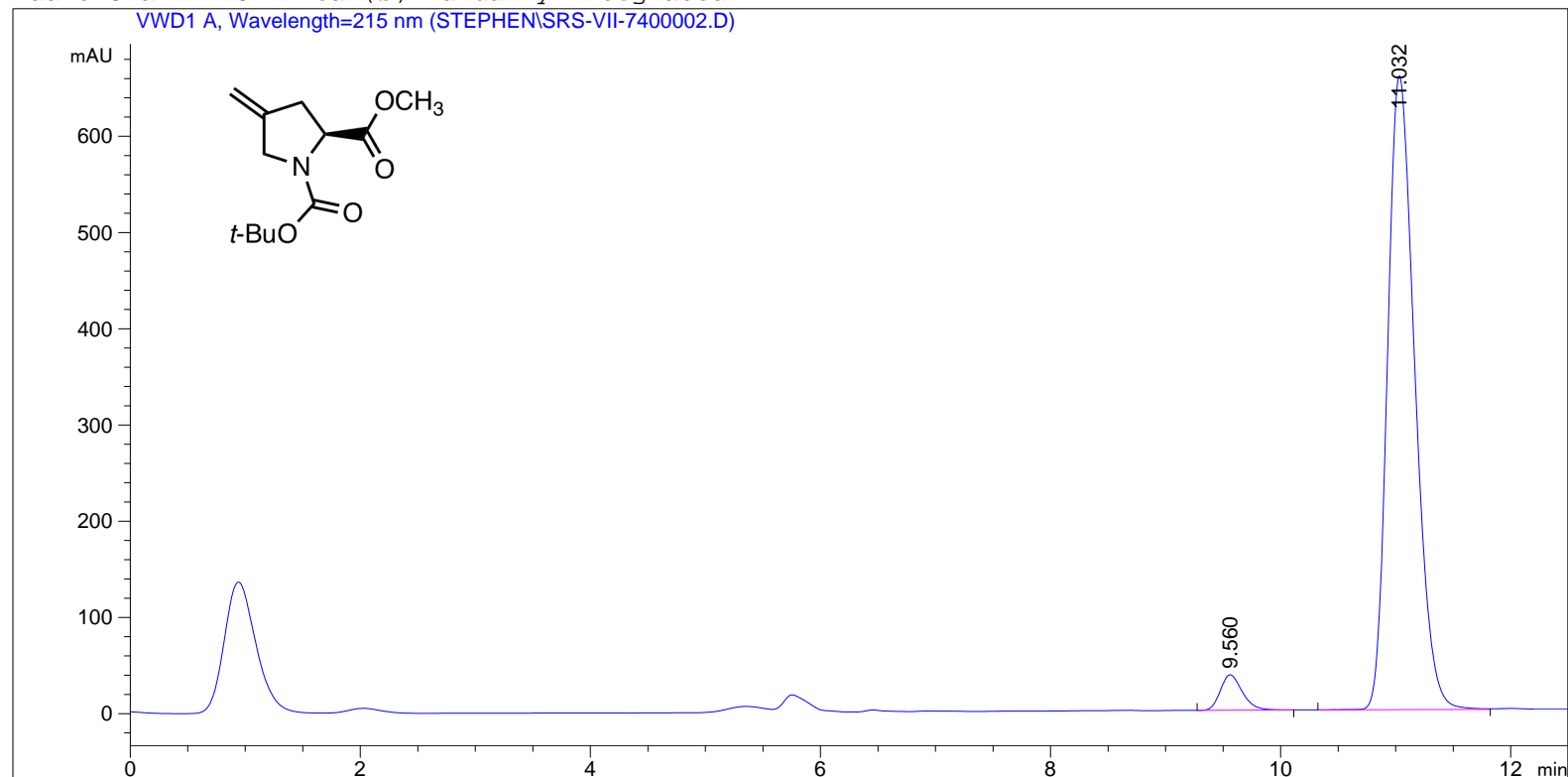
Totals : 1.25092e4 899.55088

```
=====
*** End of Report ***
=====
```

```
=====
Acq. Operator   : SYSTEM                      Seq. Line :    2
Acq. Instrument : 1220 HPLC                  Location  : Vial 62
Injection Date  : 11/15/2018 7:47:19 AM      Inj       :    1
                                           Inj Volume: 10.000 µl

Acq. Method     : C:\CHEM32\2\METHODS\SRS.M
Last changed    : 11/15/2018 7:45:53 AM by SYSTEM
                  (modified after loading)
Analysis Method : C:\CHEM32\2\METHODS\DEF_LC.M
Last changed    : 10/2/2018 2:47:22 PM by SYSTEM
Sample Info     : ChiralPak1A, 95:5 Hex:IPA, 0.6 mL/min, 215 nm
=====
```

Additional Info : Peak(s) manually integrated



```
=====
                          Area Percent Report
=====
```

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=215 nm

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1 | 9.560 | VB | 0.2034 | 487.76160 | 36.84610 | 4.3063 |
| 2 | 11.032 | BV | 0.2560 | 1.08391e4 | 658.62683 | 95.6937 |

Totals : 1.13268e4 695.47293

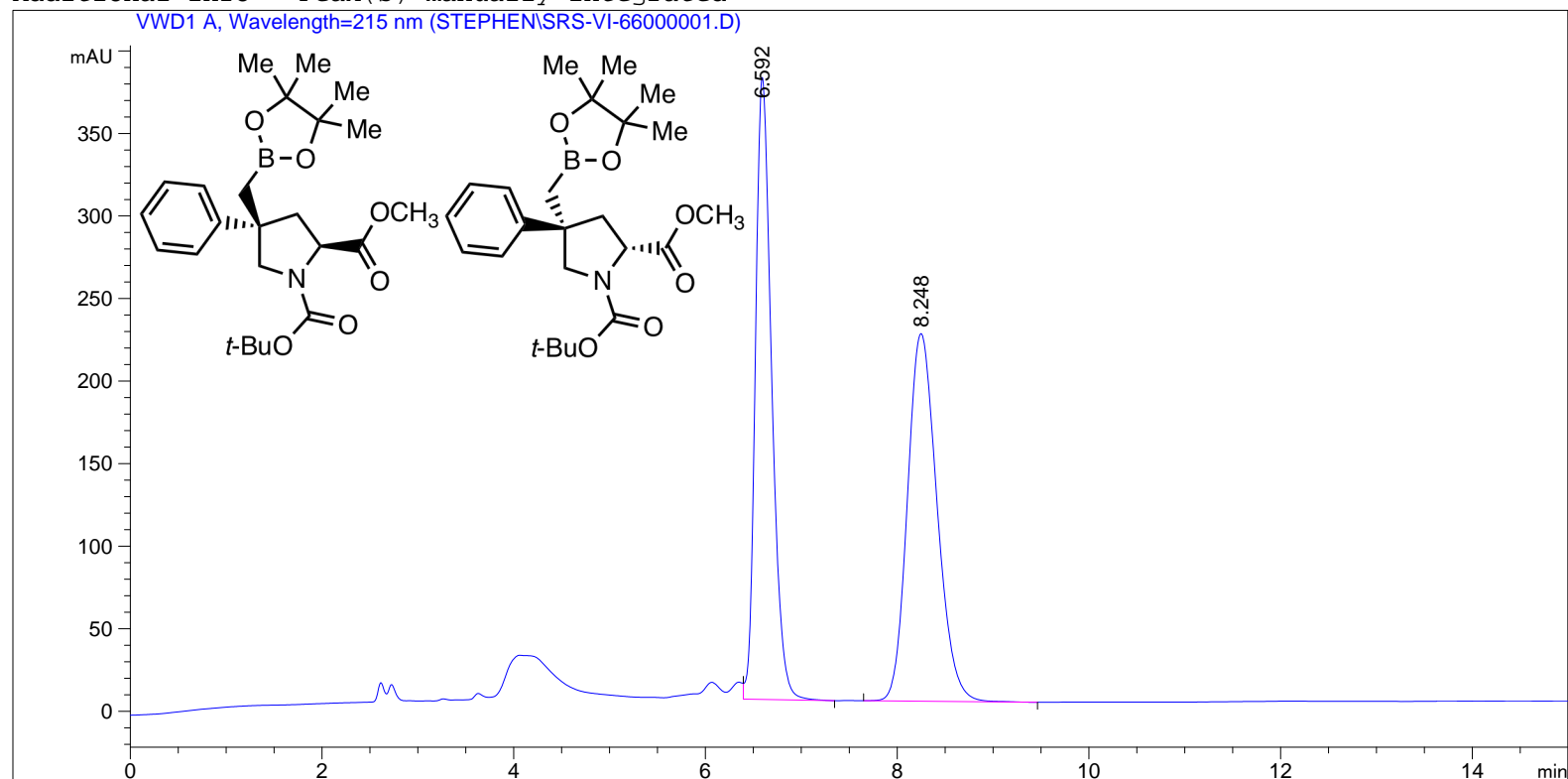
```
=====
***End of Report ***
=====
```

Sample Name: SRS-VII-84

```
=====
Acq. Operator   : SYSTEM                      Seq. Line :    1
Acq. Instrument : 1220 HPLC                  Location  : Vial 61
Injection Date  : 11/26/2018 10:59:44 AM      Inj       :    1
                                           Inj Volume: 10.000 µl

Acq. Method     : C:\CHEM32\2\METHODS\SRS.M
Last changed    : 11/26/2018 9:45:18 AM by SYSTEM
Analysis Method : C:\CHEM32\2\METHODS\DEF_LC.M
Last changed    : 10/2/2018 2:47:22 PM by SYSTEM
Sample Info     : Lux 3u Cellulose-1 98:2 Hex:IPA 1.2 mL/min 215 nm
=====
```

Additional Info : Peak(s) manually integrated



```
=====
                          Area Percent Report
=====
```

```
Sorted By           :      Signal
Multiplier:         :      1.0000
Dilution:           :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: VWD1 A, Wavelength=215 nm

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1 | 6.592 | VB | 0.1814 | 4436.06445 | 376.75540 | 48.1534 |
| 2 | 8.248 | BB | 0.3332 | 4776.30127 | 222.74611 | 51.8466 |

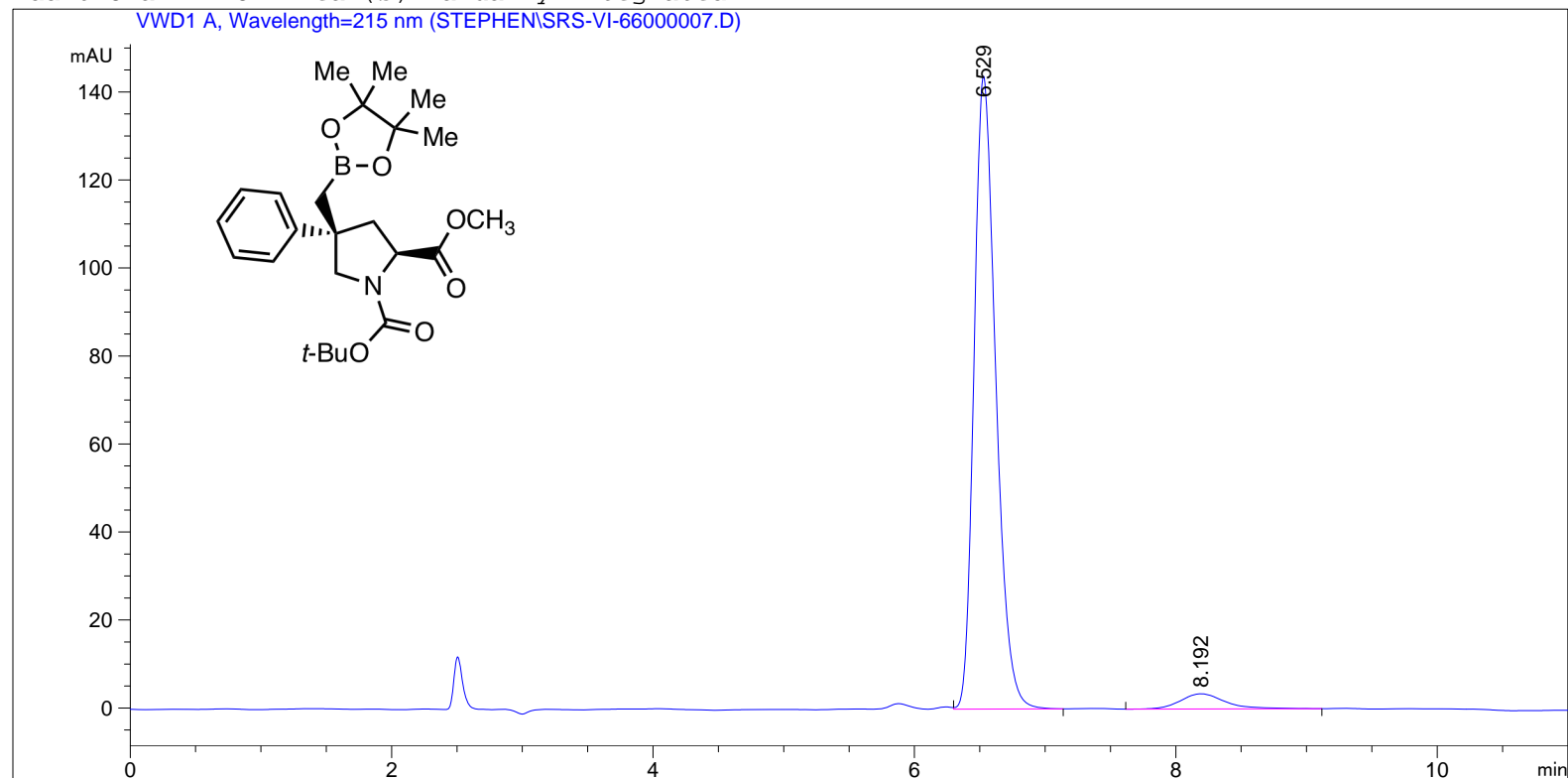
```
Totals :                      9212.36572  599.50151
```

```
=====
*** End of Report ***
```

```
=====
Acq. Operator   : SYSTEM                      Seq. Line :    4
Acq. Instrument : 1220 HPLC                  Location  : Vial 63
Injection Date  : 5/10/2019 1:47:21 PM        Inj       :    1
                                           Inj Volume: 10.000 µl

Acq. Method     : C:\CHEM32\2\METHODS\SRS.M
Last changed    : 5/10/2019 1:45:32 PM by SYSTEM
                  (modified after loading)
Analysis Method : C:\CHEM32\2\METHODS\DEF_LC.M
Last changed    : 5/6/2019 6:03:21 PM by SYSTEM
                  (modified after loading)
Sample Info     : Lux 3u Cellulose-1 98:2 Hex:IPA 1.2 mL/min 215 nm
=====
```

Additional Info : Peak(s) manually integrated



Area Percent Report

```
=====
Sorted By      :      Signal
Multiplier:    :      1.0000
Dilution:      :      1.0000
Use Multiplier & Dilution Factor with ISTDs
=====
```

Signal 1: VWD1 A, Wavelength=215 nm

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1 | 6.529 | VB | 0.1776 | 1659.65137 | 143.82709 | 95.2526 |
| 2 | 8.192 | BB | 0.3626 | 82.71717 | 3.45104 | 4.7474 |

Totals : 1742.36854 147.27813