

Supporting Information

Automated library synthesis of cyclopropyl boronic esters with diazomethane in a tube in tube flow reactor

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1. Experimental section - General remarks

CH₂N₂ is a highly toxic, carcinogenic and **very explosive gas**. The reactions should not be undertaken without stringent hazard assessment and proper safety precautions put in place!

Proton nuclear magnetic resonance spectra (¹H NMR, 500 or 400 MHz) and proton decoupled carbon nuclear magnetic resonance spectra (¹³C NMR, 125 or 100 MHz) were obtained in deuteriochloroform (CDCl₃) or deuterodimethylsulfoxide (DMSO-*d*₆) with residual solvent as the internal standard unless otherwise noted on a Varian 400-MR NMR spectrometer or Varian 500 NMR spectrometer, respectively. Chemical shifts are followed by multiplicity, coupling constants (*J*, Hz) and integration. DCI mass spectral data was collected using a Thermo Scientific DSQ II instrument. Flash chromatography was performed using a Teledyne ISCO Combiflash[®] Rf automated purification system and standard silica columns. All starting materials including Diazald[®] (Sigma-Aldrich) as well as solvents were commercially available reagents and were used without purification unless noted.

2. Methylation of benzoic acid as validation reaction

Table S1: Methylation of benzoic acid **1**.



Entry	residence time (min) ^a	eq. Diazald ^{®b}	conversion (%) ^c
1	10	5	50
2	20	10	95

a) General reaction conditions: KOH (0.6 M, MeOH/H₂O 1:1), Diazald[®] (0.3 M, MeOH); **1** (0.15 mmol, 0.15 M, THF). Combined diazomethane stream flow rate 0.5 ml/min.

b) Based on relative concentrations and flow rates of inner and outer stream.

c) Based on ¹H-NMR analysis of the crude reaction mixture.

3. Initial optimization of the cyclopropanation reaction with first generation reactor

Table S2: Cyclopropanation of styryl-boronic ester **3a**.^a



Entry	residence time (min)	conversion (%) ^b
1	5	28
2	10	41
3	20	66

a) General reaction conditions: KOH (0.6 M, MeOH/H₂O 1:1), Diazald[®] (0.3 M, MeOH); **3a** (0.15 mmol, 0.15 M, THF), 5% Pd(OAc)₂. Combined diazomethane stream flow rate 0.5 ml/min.

b) Based on ¹H-NMR analysis of the crude reaction mixtures.

4. Procedure for the cyclopropanation with second generation reactor

General reaction procedure employed in test reactions and library synthesis: All stock and sample solutions were sonicated in an ultrasound bath prior to use. The syringe pumps for the makeup of the diazomethane solution were always started at least 2 minutes prior to the respective experiment or kept running at the respective flow rate during a set of experiments to ensure full saturation of diazomethane of the inner tube. A solution of **3** of the respective concentration with the appropriate amount of Pd(OAc)₂ in THF was aspirated into the DRIFT reactor through the inlet probe while the preincubation of the THF stream in the tube-in-tube reactor for the respective time was already ongoing by control of the system software. The two streams were mixed at the T-mixer at room temperature at their respective flow rates by the syringe pumps controlled by the software. Upon exiting of the reaction mixture the outlet probe collected the latter into the collection vessels into which was added ~0.2ml of AcOH prior to the start of the experiment. Upon complete processing of the sample the reaction mixture was flushed into the collection vial with 2ml of THF and the reactor and inlet and outlet probes were then washed with DMF, MeOH and THF (4ml, 4ml and 10ml, respectively). The reactor tubing and outlet probe was thereupon purged with a stream of nitrogen for several seconds. The collected crude reaction mixture was evaporated, adsorbed onto Celite and purified by automated flash chromatography on 12g of silica (heptanes/ethyl acetate as eluent) to provide the pure products.

General reaction procedure employed for large scale reactions: All stock and sample solutions were sonicated in an ultrasound bath prior to use. The syringe pumps for the makeup of the diazomethane solution were always started at least 2 minutes prior to the respective experiment. A fraction of a solution of **3a** or **6**, respectively, of the respective concentration with the appropriate amount of Pd(OAc)₂ in THF was aspirated into the DRIFT reactor through the bulk mode inlet tubing while the preincubation of the THF stream in the tube-in-tube reactor for the respective time was already ongoing. The two streams were mixed at the T-mixer at room temperature at their respective flow rates. Thereupon the THF-diazomethane stream was not stopped until the end of the sample being processed by individual injections of a fraction of substrate solution via the T-mixer and repeated aspiration of sample, respectively. The output of the reactor was collected via the outlet probe into a suitably large flask containing at least 40ml of AcOH. Upon complete processing of the sample the reaction mixture was flushed into the collection flask with 2ml of THF and the reactor outlet probe was then washed and purged as described above. The collected crude reaction mixture was evaporated, adsorbed onto Celite® and purified by automated flash chromatography (heptanes/ethyl acetate as eluent) to provide the pure products.

5. Library of cyclopropyl-derivatives

Following the general procedure 0.3 mmol of the respective styrene and 0.67 mg Pd(OAc)₂ were dissolved in 1.5 ml THF and processed in the reactor.

trans-4,4,5,5-tetramethyl-2-(2-phenylcyclopropyl)-1,3,2-dioxaborolane (**4a**)¹

53 mg clear oil (72%). ¹H NMR (400 MHz, CDCl₃) δ 7.33 – 7.23 (m, 2H), 7.22 – 7.05 (m, 3H), 2.23 – 2.02 (m, 1H), 1.29 (s, 6H), 1.27 (s, 6H), 1.23 – 1.19 (m, 1H), 1.09 – 0.96 (m, 1H), 0.41 – 0.26 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 143.3, 128.2, 125.6, 125.5, 83.1, 24.76, 24.71, 21.9, 15.0, 5.6.

trans-4,4,5,5-tetramethyl-2-(2-(*p*-tolyl)cyclopropyl)-1,3,2-dioxaborolane (**4b**)²

54 mg pale brown oil (69%). ¹H NMR (400 MHz, CDCl₃) δ 7.04 (d, *J* = 7.8 Hz, 2H), 6.97 (d, *J* = 8.2 Hz, 2H), 2.29 (s, 3H), 2.13 – 2.01 (m, 1H), 1.24 (s, 6H), 1.23 (s, 6H), 1.12 (ddd, *J* = 8.2, 6.8, 3.6 Hz, 1H), 0.96 (ddd, *J* = 9.8, 5.3, 3.6 Hz, 1H), 0.26 (ddd, *J* = 9.7, 6.7, 5.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 140.2, 135.0, 128.9, 125.6, 83.1, 24.77, 24.70, 21.6, 20.9, 14.8, 5.6.

trans-2-(2-(4-methoxyphenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4c**)²

55 mg pale yellow wax (67%). ¹H NMR (400 MHz, CDCl₃) δ 7.01 (d, *J* = 8.7 Hz, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 3.75 (s, 3H), 2.18 – 1.94 (m, 1H), 1.24 (s, 6H), 1.23 (s, 6H), 1.10 (ddd, *J* = 8.1, 6.7, 3.6 Hz, 1H), 0.93 (ddd, *J* = 9.7, 5.3, 3.6 Hz, 1H), 0.21 (ddd, *J* = 9.7, 6.7, 5.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 157.7, 135.3, 126.8, 113.7, 83.1, 55.3, 24.76, 24.72, 21.2, 14.5, 5.1.

trans-2-(2-(3-methoxyphenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4d**)

47 mg pale white wax (57%). ¹H NMR (400 MHz, CDCl₃) δ 7.15 (t, *J* = 7.9 Hz, 1H), 6.79 – 6.47 (m, 3H), 3.77 (s, 3H), 2.14 – 1.97 (m, 1H), 1.25 (s, 6H), 1.23 (s, 6H), 1.14 (ddd, *J* = 8.2, 6.8, 3.7 Hz, 1H), 1.00 (ddd, *J* = 9.8, 5.2, 3.7 Hz, 1H), 0.30 (ddd, *J* = 9.8, 6.8, 5.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 145.1, 129.2, 118.1, 111.5, 110.9, 83.1, 55.1, 55.1, 24.7, 24.7, 21.9, 15.0, 6.3. MS (DCI) *m/z* (%): 305 (100, [M+H]⁺), 322 (10, [M+NH₄]⁺). *trans*-4,4,5,5-tetramethyl-2-(2-(thiophen-3-yl)cyclopropyl)-1,3,2-dioxaborolane (**4e**)

46 mg clear oil (61%). ¹H NMR (500 MHz, CDCl₃) δ 7.19 (dd, *J* = 5.0, 3.0 Hz, 1H), 6.89 (dd, *J* = 3.0, 1.3 Hz, 1H), 6.80 (dd, *J* = 5.0, 1.3 Hz, 1H), 2.15 (dt, *J* = 8.1, 5.4 Hz, 1H), 1.24 (s, 6H), 1.23 (s, 6H), 1.10 (ddd, *J* = 8.1, 6.7, 3.6 Hz, 1H), 0.94 (ddd, *J* = 9.7, 5.2, 3.6 Hz, 1H), 0.25 (ddd, *J* = 9.7, 6.7, 5.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 144.6, 125.8, 125.3, 118.2, 83.1, 24.7, 24.7, 17.7, 14.4, 4.8. MS (DCI) *m/z* (%): 268 (100, [M+NH₄]⁺), 251 (15, [M+H]⁺).

trans-2-(2-(4-ethylphenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4f**)

59 mg clear oil (72%). ¹H NMR (400 MHz, CDCl₃) δ 7.07 (d, *J* = 8.2 Hz, 2H), 7.00 (d, *J* = 8.1 Hz, 2H), 2.59 (q, *J* = 7.6 Hz, 2H), 2.08 (dt, *J* = 8.1, 5.4 Hz, 1H), 1.24 (s, 6H), 1.23 (s, 6H), 1.20 (t, *J* = 7.6 Hz, 2H), 0.97 (ddd, *J* = 9.7, 5.3, 3.6 Hz, 1H), 0.27 (ddd, *J* = 9.7, 6.8, 5.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 141.5, 140.5, 127.7, 125.6, 83.1, 28.4, 24.79, 24.71, 21.6, 15.7, 14.8, 5.6. MS (DCI) *m/z* (%): 290 (100, [M+NH₄]⁺).

trans-4,4,5,5-tetramethyl-2-(2-(3-(trifluoromethyl)phenyl)cyclopropyl)-1,3,2-dioxaborolane (**4g**)

67 mg clear oil (71%). ¹H NMR (500 MHz, CDCl₃) δ 7.43 – 7.30 (m, 3H), 7.22 (d, *J* = 7.6 Hz, 1H), 2.15 (dt, *J* = 8.2, 5.4 Hz, 1H), 1.26 (s, 6H), 1.25 (s, 6H), 1.23 – 1.18 (m, 1H), 1.03 (ddd, *J* = 9.4, 5.3, 3.9 Hz, 1H), 0.33 (ddd, *J* = 9.8, 6.9, 5.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 144.4, 128.8, 128.8, 128.6 (2C), 122.6 (d, *J* = 3 Hz), 122.3 (d, *J* = 3 Hz), 83.3, 24.7, 21.6, 15.1, 5.9. MS (DCI) *m/z* (%): 329 (100, [M+NH₄]⁺).

trans-2-(2-(3,5-bis(trifluoromethyl)phenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4h**)³

49 mg clear oil (43%). ¹H NMR (400 MHz, CDCl₃) δ 7.63 (s, 1H), 7.49 (d, *J* = 1.6 Hz, 2H), 2.21 (dt, *J* = 8.1, 5.3 Hz, 1H), 1.32 – 1.27 (m, 1H), 1.26 (s, 6H), 1.25 (s, 6H), 1.08 (ddd, *J* = 9.6, 5.2, 4.0 Hz, 1H), 0.38 (ddd, *J* = 9.9, 7.0, 5.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 149.6, 132.0, 126.1, 119.1, 108.9, 83.4, 24.72, 24.70, 21.9, 15.9, 7.7.

trans-2-(2-(3,5-difluorophenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4i**)

39 mg clear oil (46%). ¹H NMR (400 MHz, CDCl₃) δ 6.81 – 6.37 (m, 3H), 2.12 – 2.02 (m, 1H), 1.30 – 1.15 (overlapping signals, 13H), 0.98 (ddd, *J* = 9.3, 5.2, 3.9 Hz, 1H), 0.28 (ddd, *J* = 10.0, 7.0, 5.4 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 163.0 (dd, *J* = 246, 13 Hz), 147.9 (dd, *J* = 9 Hz), 108.4 (d, *J* = 25 Hz), 100.8 (dd, *J* = 25, 25 Hz), 83.4, 24.73, 24.70, 15.2, 7.5. MS (DCI) *m/z* (%): 298 (100, [M+NH₄]⁺).

trans-2-(2-(2,4-difluorophenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4j**)

51 mg clear oil (60%). ¹H NMR (500 MHz, CDCl₃) δ 6.95 – 6.80 (m, 1H), 6.80 – 6.69 (m, 2H), 2.22 (dt, *J* = 8.2, 5.6 Hz, 1H), 1.25 (bs, 12H), 1.15 (ddd, *J* = 8.2, 6.8, 3.8 Hz, 1H), 0.98 (ddd, *J* = 9.4, 5.5, 3.8 Hz, 1H), 0.23 (ddd, *J* = 9.8, 6.7, 5.8 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 161.4 (dd, *J* = 249, 12 Hz), 160.9 (dd, *J* = 244, 13 Hz), 126.8 (dd, *J* = 9, 5 Hz), 125.9 (dd, *J* = 14, 3 Hz), 110.7 (dd, *J* = 21, 3 Hz), 103.8 – 102.7 (m), 83.2, 24.7, 24.6, 14.8, 12.9, 3.6. MS (DCI) *m/z* (%): 298 (100, [M+NH₄]⁺).

trans-2-(2-(4-chlorophenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4k**)⁴

41 mg clear oil (49%). ¹H NMR (400 MHz, CDCl₃) δ 7.18 (d, *J* = 8.5 Hz, 2H), 6.99 (d, *J* = 8.5 Hz, 2H), 2.07 (dt, *J* = 8.1, 5.4 Hz, 1H), 1.24 (s, 6H), 1.23 (s, 6H), 1.16 (ddd, *J* = 8.1, 6.8, 3.7 Hz, 1H), 0.95 (ddd, *J* = 9.8, 5.2, 3.7 Hz, 1H), 0.25 (ddd, *J* = 9.8, 6.8, 5.5 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 141.9, 131.0, 128.2, 127.0, 83.2, 24.75, 24.72, 21.3, 15.0, 5.9.

trans-2-(2-(3-chlorophenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4l**)

54 mg clear oil (64%). ¹H NMR (400 MHz, CDCl₃) δ 7.21 – 7.01 (m, 3H), 6.99 – 6.87 (m, 1H), 2.10 – 2.02 (m, 1H), 1.25 (s, 6H), 1.24 (s, 6H), 1.21 – 1.10 (m, 1H), 1.00 (ddd, *J* = 9.4, 5.2, 3.8 Hz, 1H), 0.46 – 0.15 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 145.6, 134.1, 129.4, 126.0, 125.6, 123.8, 83.2, 24.74, 24.72, 21.5, 14.9, 6.5. MS (DCI) *m/z* (%): 296 (100, [M+NH₄]⁺).

2-(1-(4-fluorophenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4m**)

39 mg white solid (49%). ¹H NMR (400 MHz, CDCl₃) δ 7.32 – 7.06 (m, 2H), 6.97 – 6.78 (m, 2H), 1.20 (s, 12H), 1.10 (q, *J* = 3.5 Hz, 2H), 0.85 (q, *J* = 3.5 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 160.8 (d, *J* = 242 Hz), 140.4 (d, *J* = 3 Hz), 130.3 (d, *J* = 7 Hz), 114.6 (d, *J* = 21 Hz), 83.4, 24.6, 13.4, 10.3. MS (DCI) *m/z* (%): 280 (100, [M+NH₄]⁺).

4,4,5,5-tetramethyl-2-(1,1a,6,6a-tetrahydrocyclopropa[a]inden-6a-yl)-1,3,2-dioxaborolane (**4n**)

35 mg beige solid (45%). ¹H NMR (400 MHz, CDCl₃) δ 7.27 (dd, *J* = 6.8, 1.9 Hz, 1H), 7.18 – 6.98 (m, 3H), 3.29 (d, *J* = 17.1 Hz, 1H), 2.90 (dd, *J* = 17.1, 1.7 Hz, 1H), 2.54 (ddd, *J* = 7.7, 3.8, 1.8 Hz, 1H), 1.41 (dd, *J* = 7.7, 3.6 Hz, 1H), 1.24 (s, 6H), 1.23 (s, 6H), 0.33 (t, *J* = 3.7 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 146.3, 142.8, 125.7, 125.6, 125.5, 123.1, 83.2, 36.6, 32.1, 24.8, 24.7, 23.0, 11.8. MS (DCI) *m/z* (%): 274 (100, [M+NH₄]⁺), 257 (10, [M+H]⁺).

6. Optimization for the cyclopropanation of 6

Table S2: Reaction optimization for the cyclopropanation of 6.

Tube-in-tube reactor volume [approx. μl; outer/inner]	THF stream flow rate [μl/min]	Residence time THF stream [min]	Diazald stream rate ^b [μl/min]	flow	Residence loop volume [μl]	Substrate flow rate [μl/min]	Residence time substrate [min]	Initial substrate concentration [M]	Effective substrate concentration ^c [M]	Conversion [%, NMR] ^d
4500/700	700	6.4	1000		1000	140	1.19	0.15	0.025	55
4500/700	700	6.4	1000		1000	120	1.22	0.15	0.021	71
4500/700	700	6.4	700		1000	120	1.22	0.15	0.021	86 ^e
4500/700	700	6.4	700		1000	80	1.28	0.15	0.015	87 ^f

a) General conditions: 0.3 M Diazald[®] solution (THF) ; 0.6 M KOH (MeOH/H₂O; 1:1). 1% Pd(OAc)₂. Reactions performed on 0.15 mmol scale.

b) After mixing with KOH solution.

c) In residence loop.

d) Based on ¹H-NMR analysis of the crude reaction mixture. *Vide infra* for example.

e) This experiment demonstrates that more diazomethane is available at a lower (optimized) inner flow rate.

f) This experiment marks a limit in conversion despite even higher excess of diazomethane. An increase in residence seems to be unlikely to increase conversion for this reaction.

7. Large scale reactions

Following the general procedure 3.0 mmol of (*E*)-4-phenylbut-3-en-2-one (**5**, 439 mg) and 6.7 mg Pd(OAc)₂ were dissolved in 20 ml THF and reacted under the optimized condition (Table S1).

trans-1-(2-phenylcyclopropyl)ethanone (**6**)⁵

384 mg pale yellow oil (80%). ¹H NMR (500 MHz, CDCl₃) δ 7.30 – 7.26 (m, 2H), 7.23 – 7.17 (m, 1H), 7.11 – 7.06 (m, 2H), 2.52 (ddd, *J* = 9.1, 6.6, 4.0 Hz, 1H), 2.30 (s, 3H), 2.21 (ddd, *J* = 8.1, 5.3, 4.0 Hz, 1H), 1.67 (ddd, *J* = 9.3, 5.3, 4.2 Hz, 1H), 1.37 (ddd, *J* = 8.1, 6.6, 4.2 Hz, 1H).

Following the general procedure 2.4 mmol of (*E*)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (**3a**, 552 mg) and 5.3 mg Pd(OAc)₂ were dissolved in 16 ml THF and reacted under the optimized condition.

trans-4,4,5,5-tetramethyl-2-(2-phenylcyclopropyl)-1,3,2-dioxaborolane (**4a**)¹

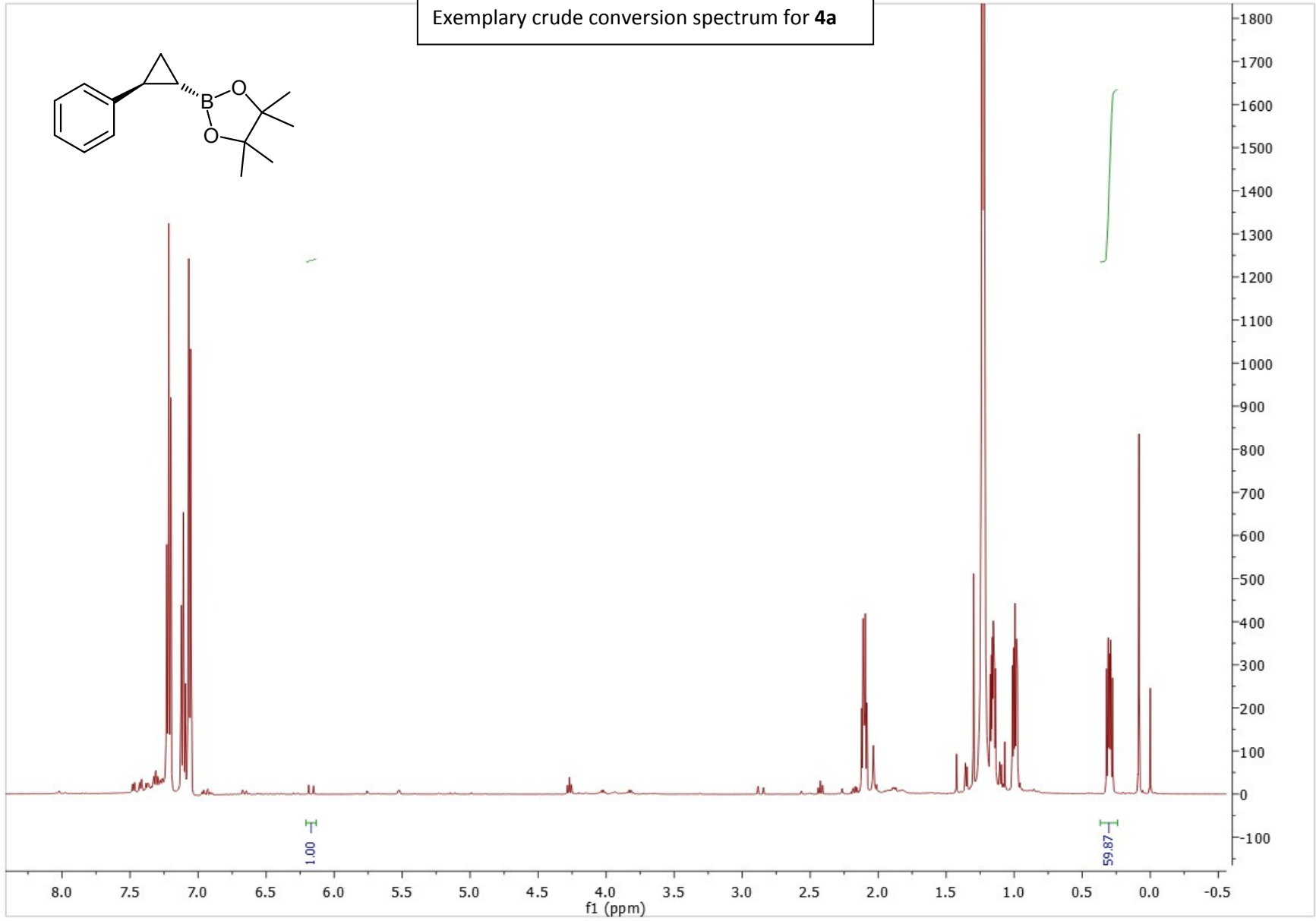
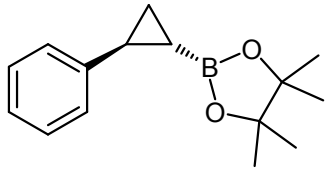
381 mg clear oil (65%). Analytics match the previously obtained sample.

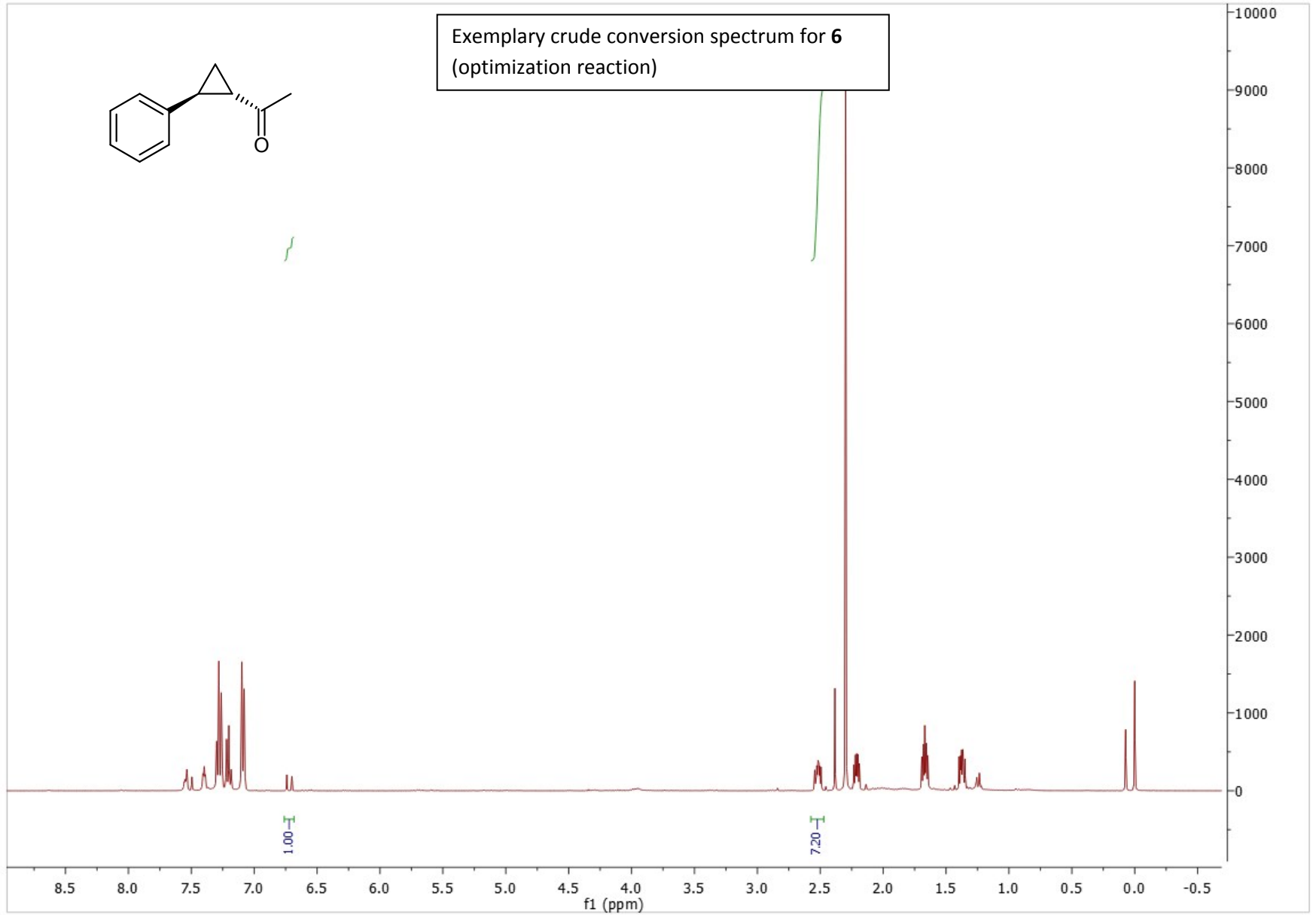
8. References

1. Brondani, P. B.; Dudek, H.; Reis, J. S.; Fraaije, M. W.; Andrade, L. H. *Tetrahedron: Asymmetry* **2012**, *23*, 703–708.
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3. Hartwig, J. F.; Liskey, C.W. US20120226041.
4. Zhong, C.; Kunii, S.; Kosaka, Y.; Sawamura, M.; Ito, H. *J. Am. Chem. Soc.* **2010**, *132*, 11440–11442.
5. Concellón J. M.; Rodríguez-Solla H.; Méjica C.; Blanco E. G. *Org. Lett.* **2007**, *9*, 2981–2984.

9. Crude reaction spectrums for 4a and 6

Exemplary crude conversion spectrum for **4a**





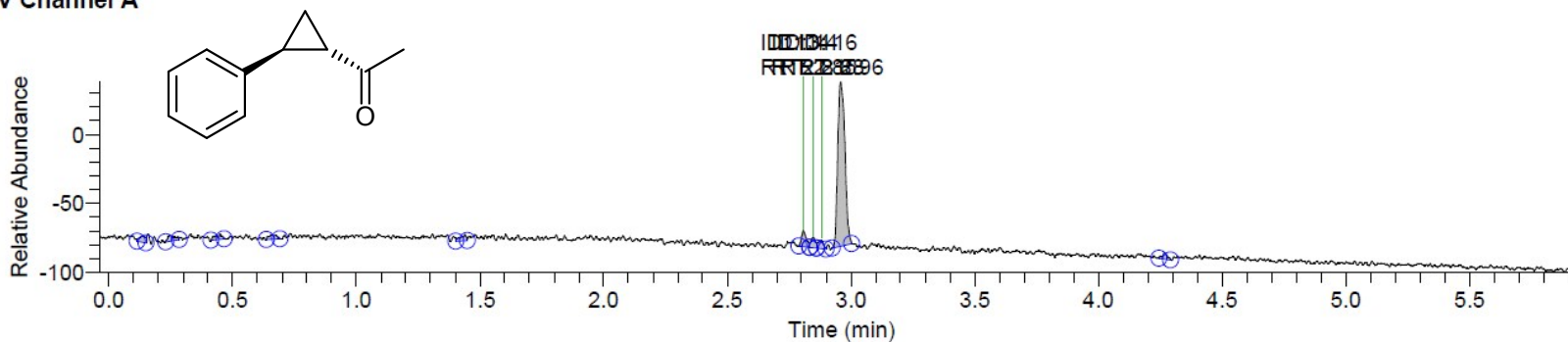
Exemplary crude HPLC chromatogram for **6** (bulk reaction)

User: Hannes Koolman
Sample: ██████████-1856-CR-TFALONG (MS Number = ar46006)
Raw File: C:\XCalibur\Data\031616MSQ2610_09404058.raw

Mass: 160
Vial: 10

UV Channel A = 220nm
UV Channel B = 254nm
A/D Card Ch1 = ELSD

UV Channel A

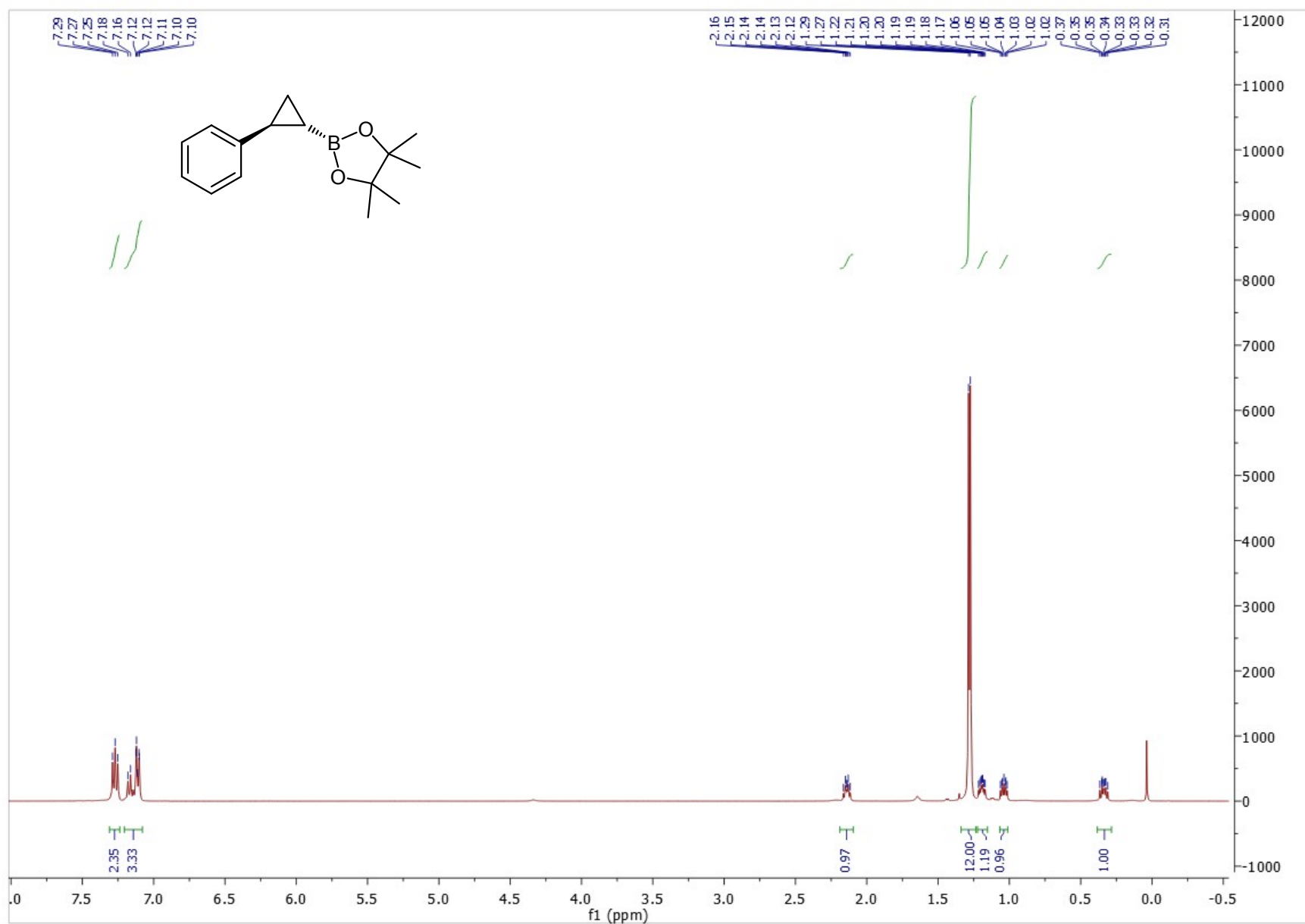


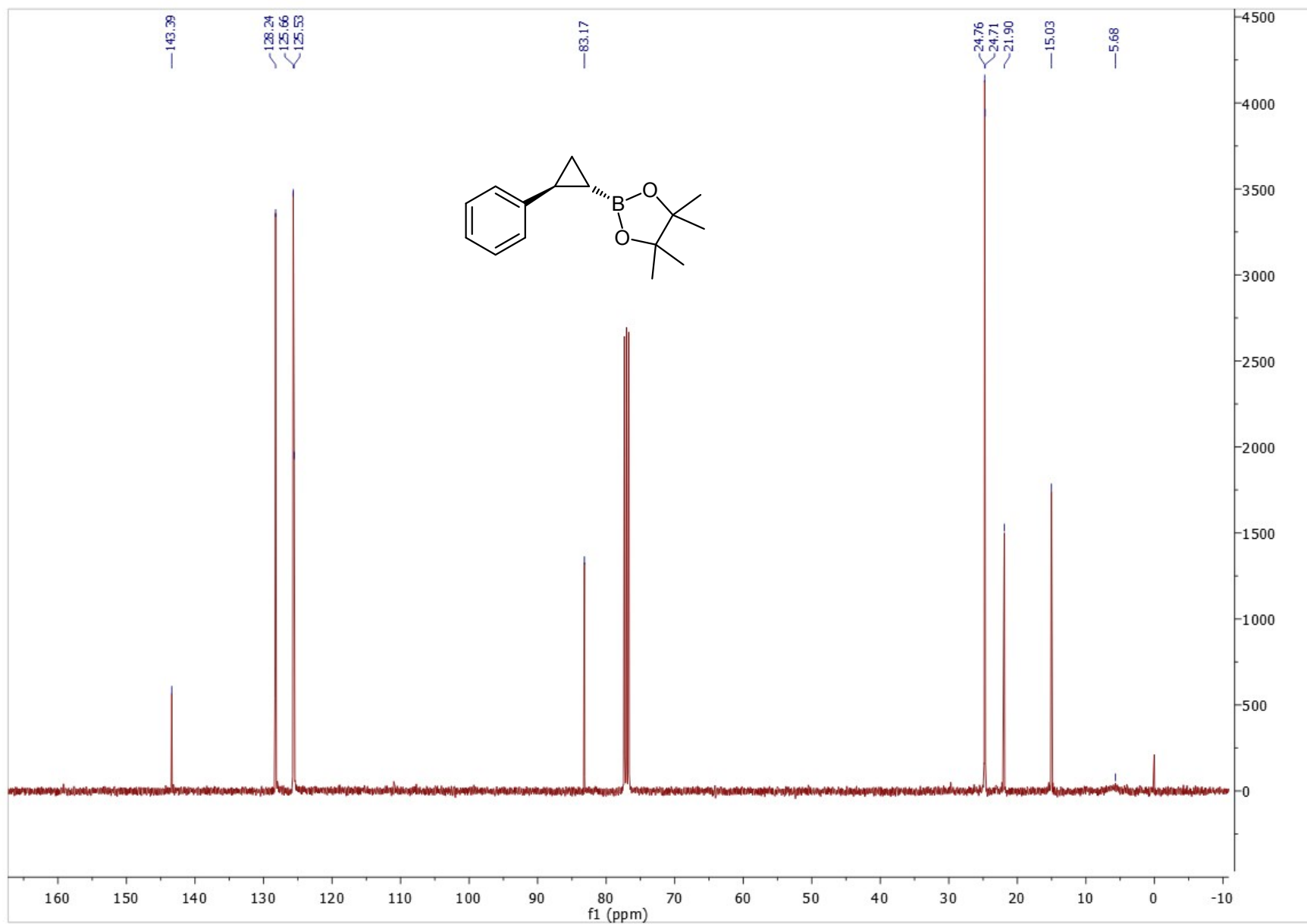
NL:
6.44E5
Channel A

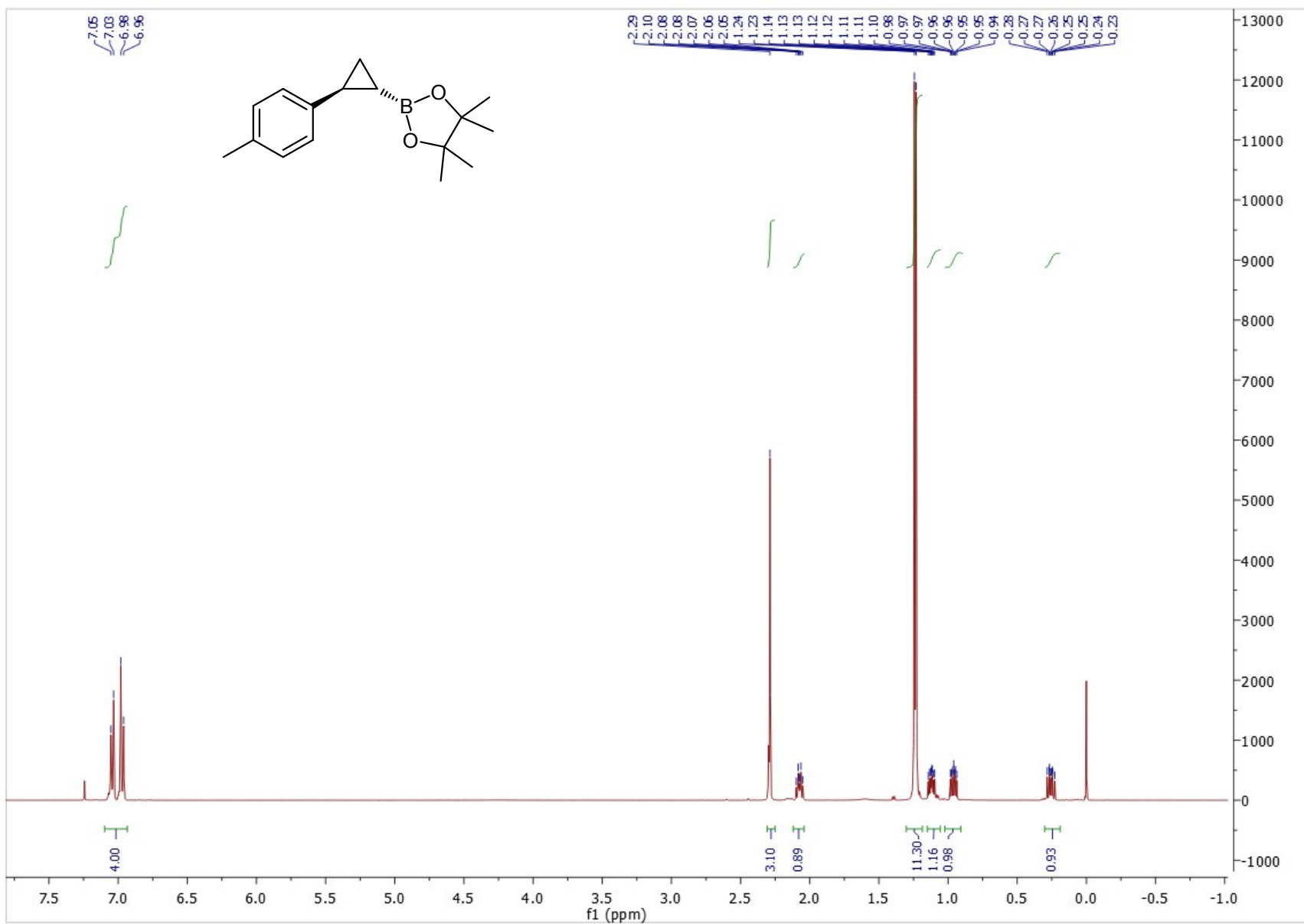
Peak Information For UV Channel A

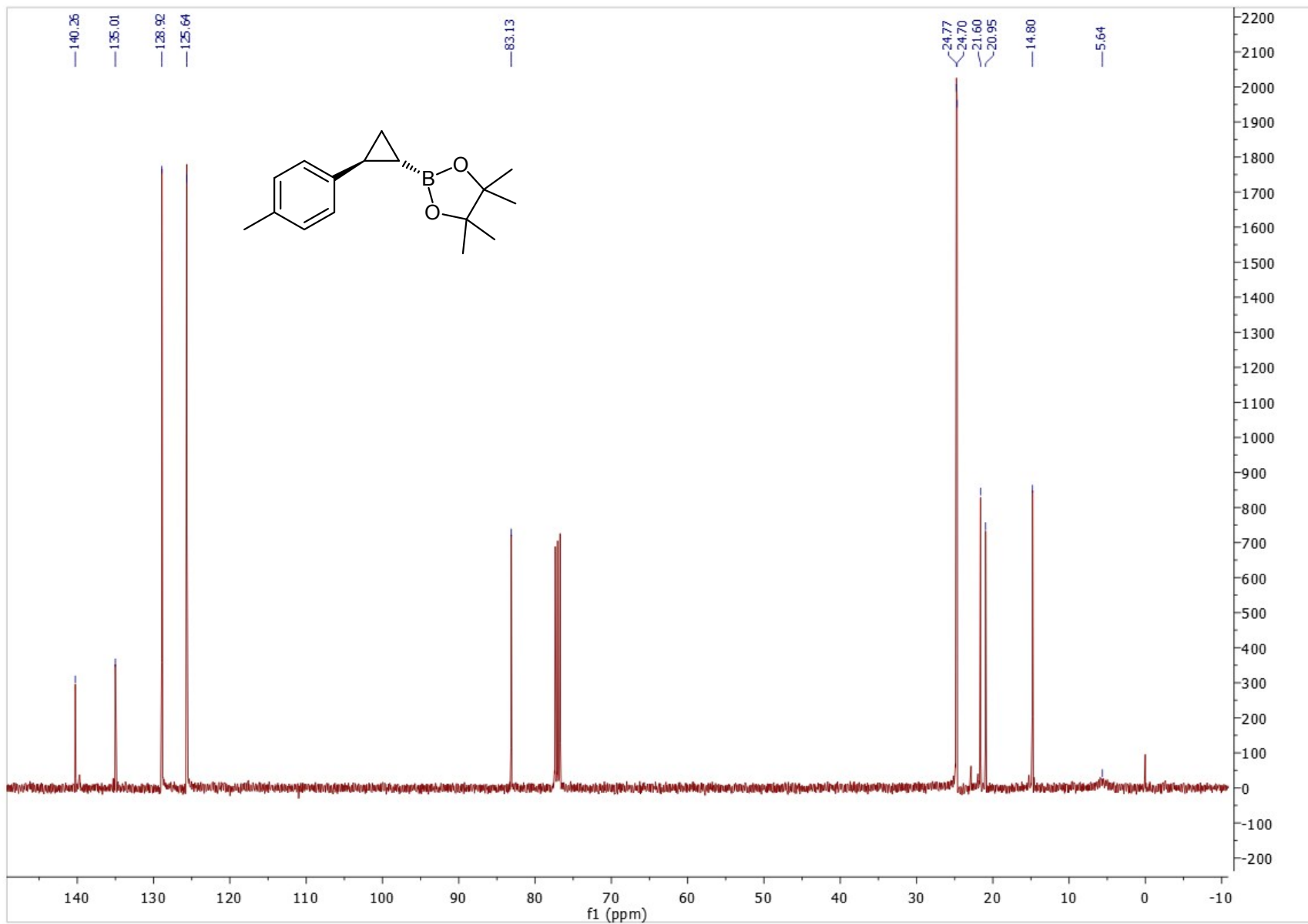
Peak ID	RT	Height	Area	%Height	%Area
2	0.13	25299.298	40924.597	2.6	2.2
4	0.25	26395.927	50415.278	2.7	2.8
6	0.45	23080.956	43573.041	2.4	2.4
7	0.66	20286.770	41986.045	2.1	2.3
8	1.44	26357.695	43531.495	2.7	2.4
13	2.81	67124.183	89993.881	6.9	4.9
14	2.85	41983.545	51917.635	4.3	2.8
14	2.88	35839.011	51019.555	3.7	2.8
16	2.96	684928.879	1376079.965	70.0	75.3
21	4.27	27014.785	38256.316	2.8	2.1

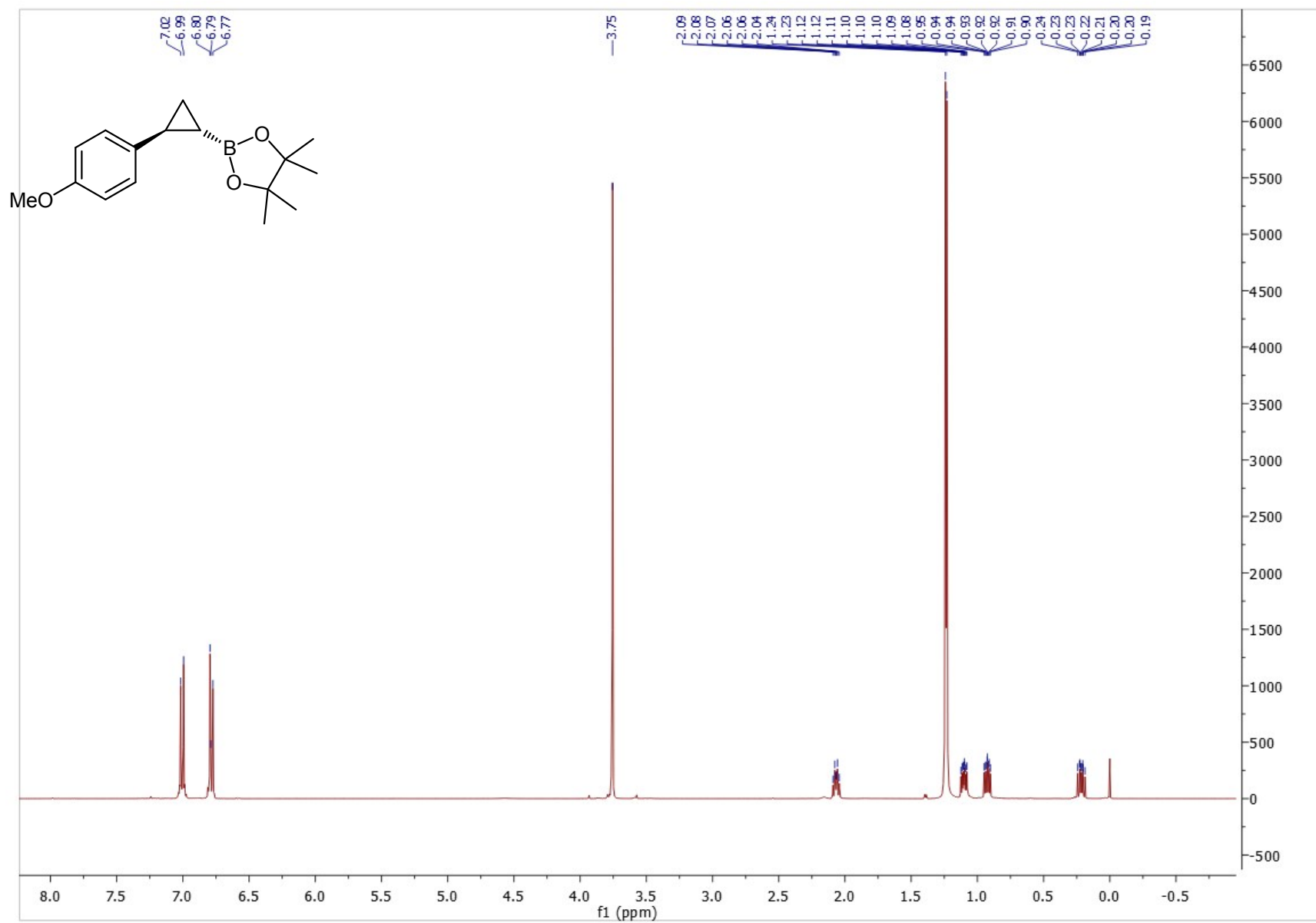
10. ^1H NMR / ^{13}C NMR / MS

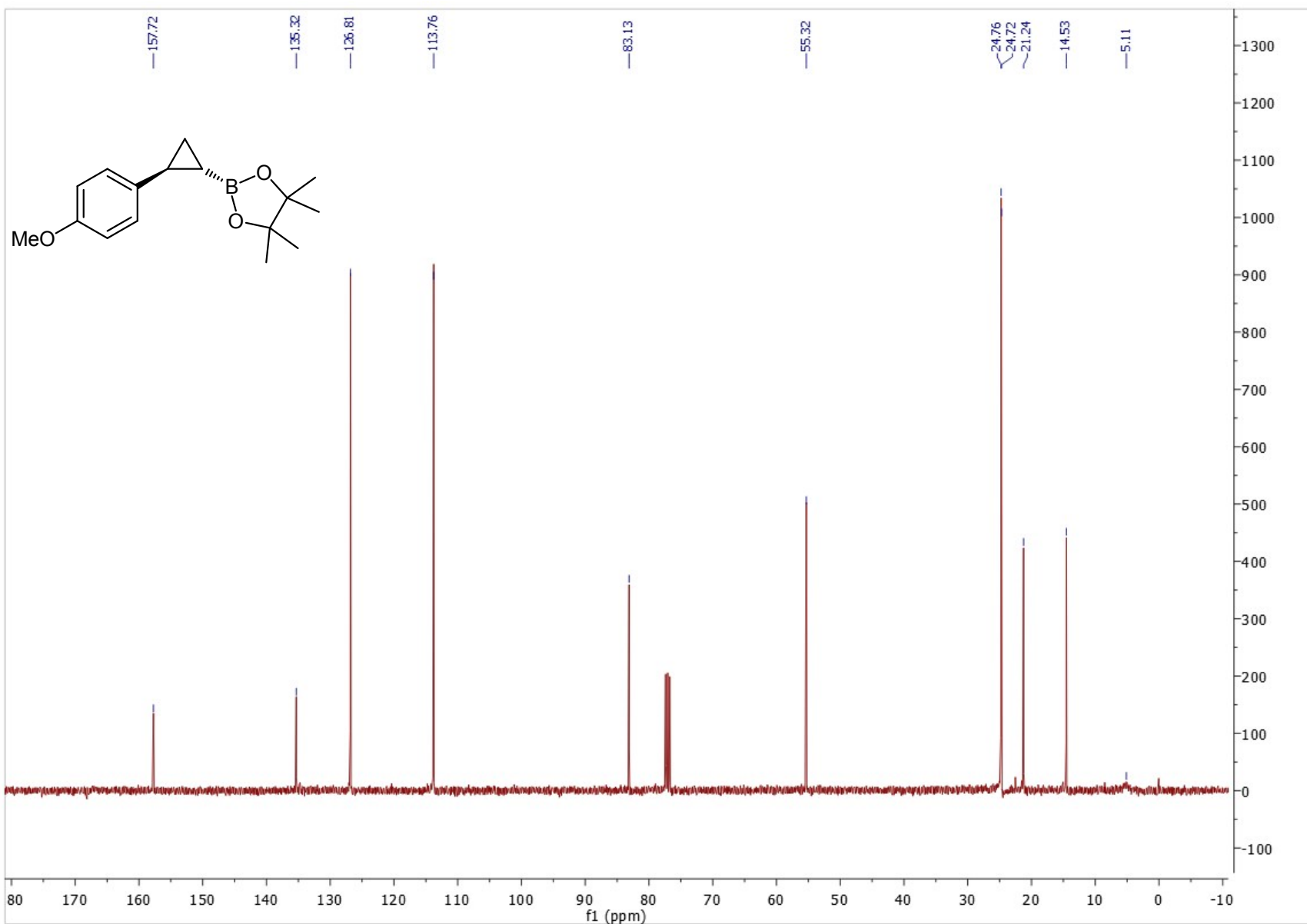


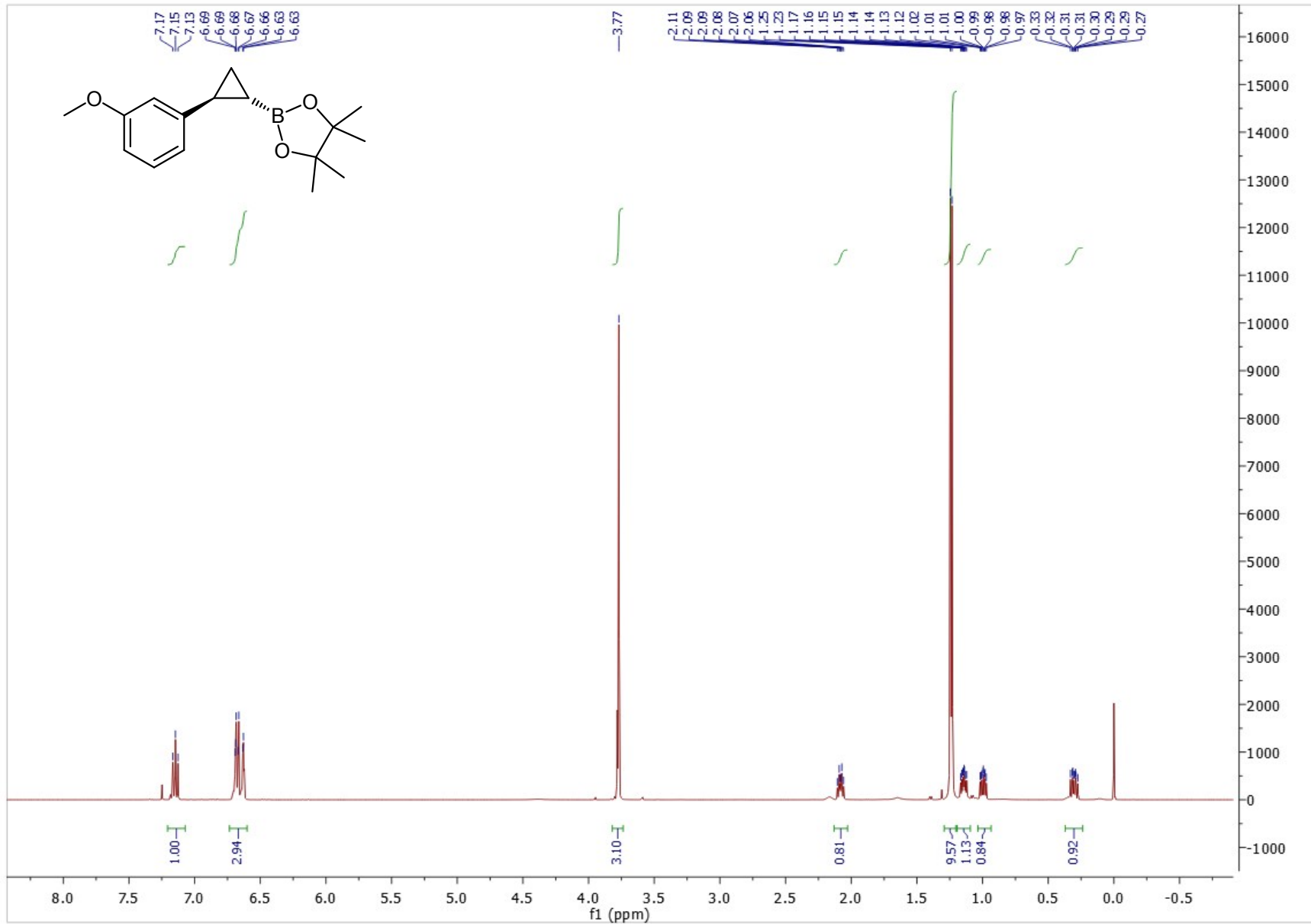


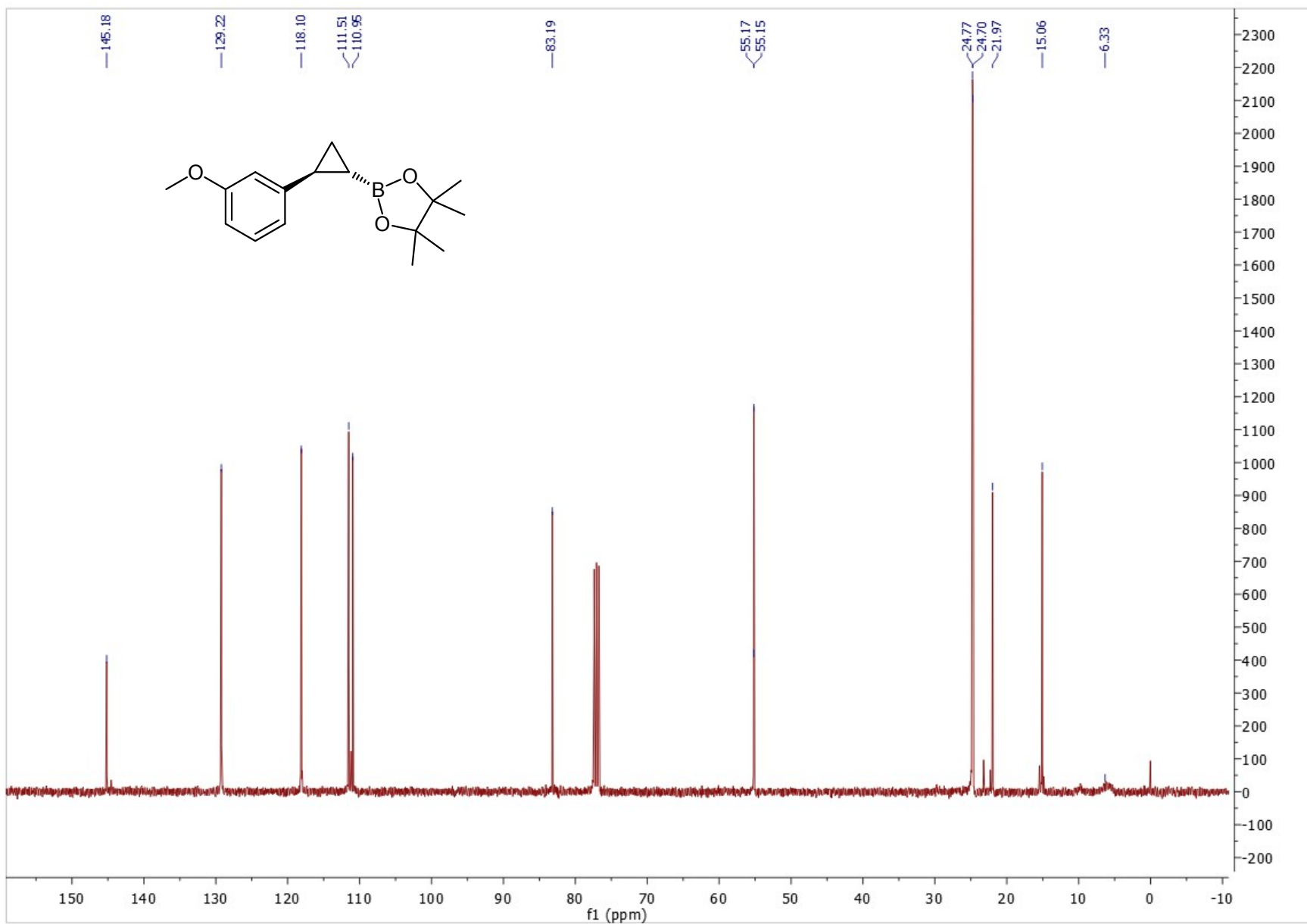


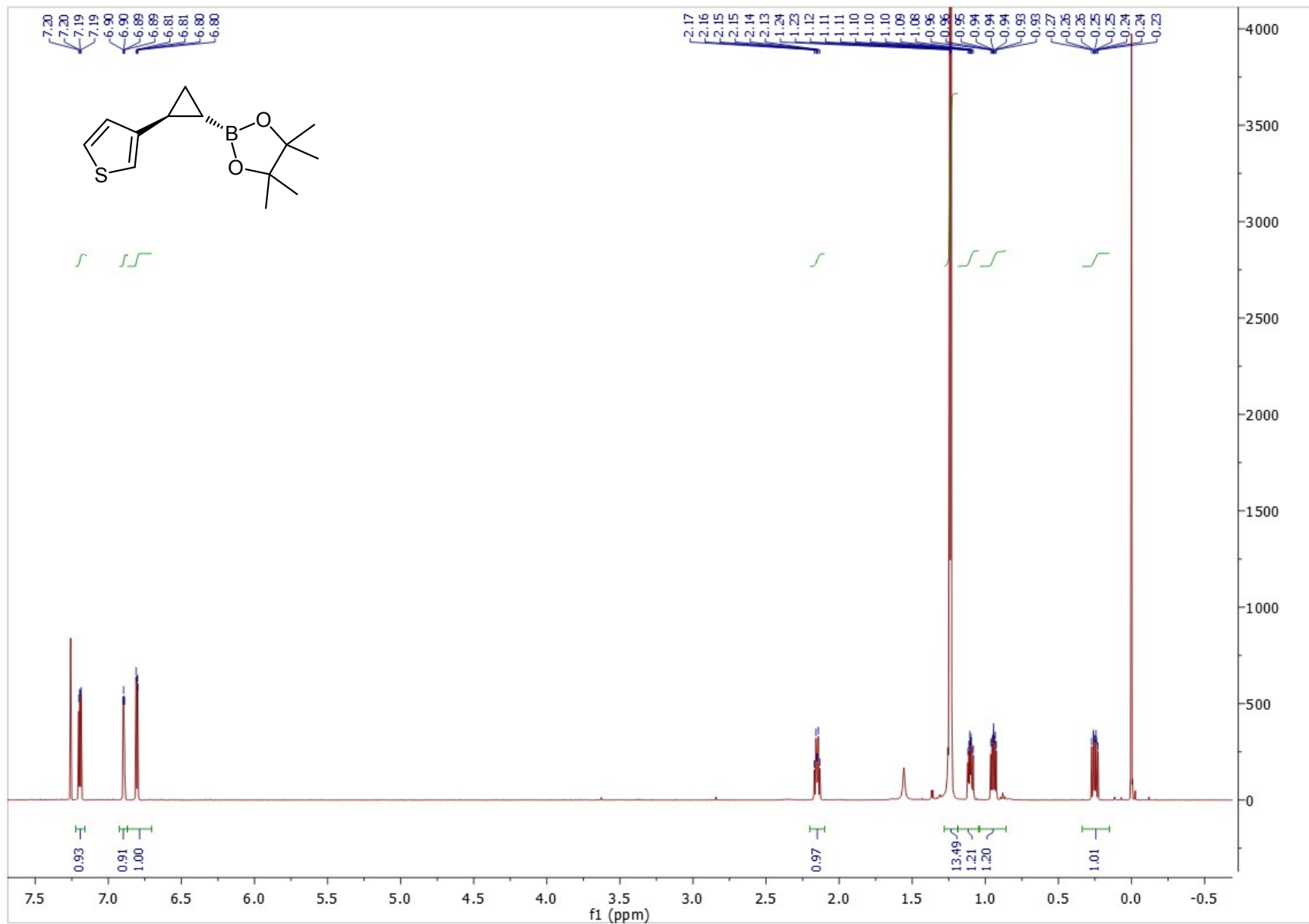


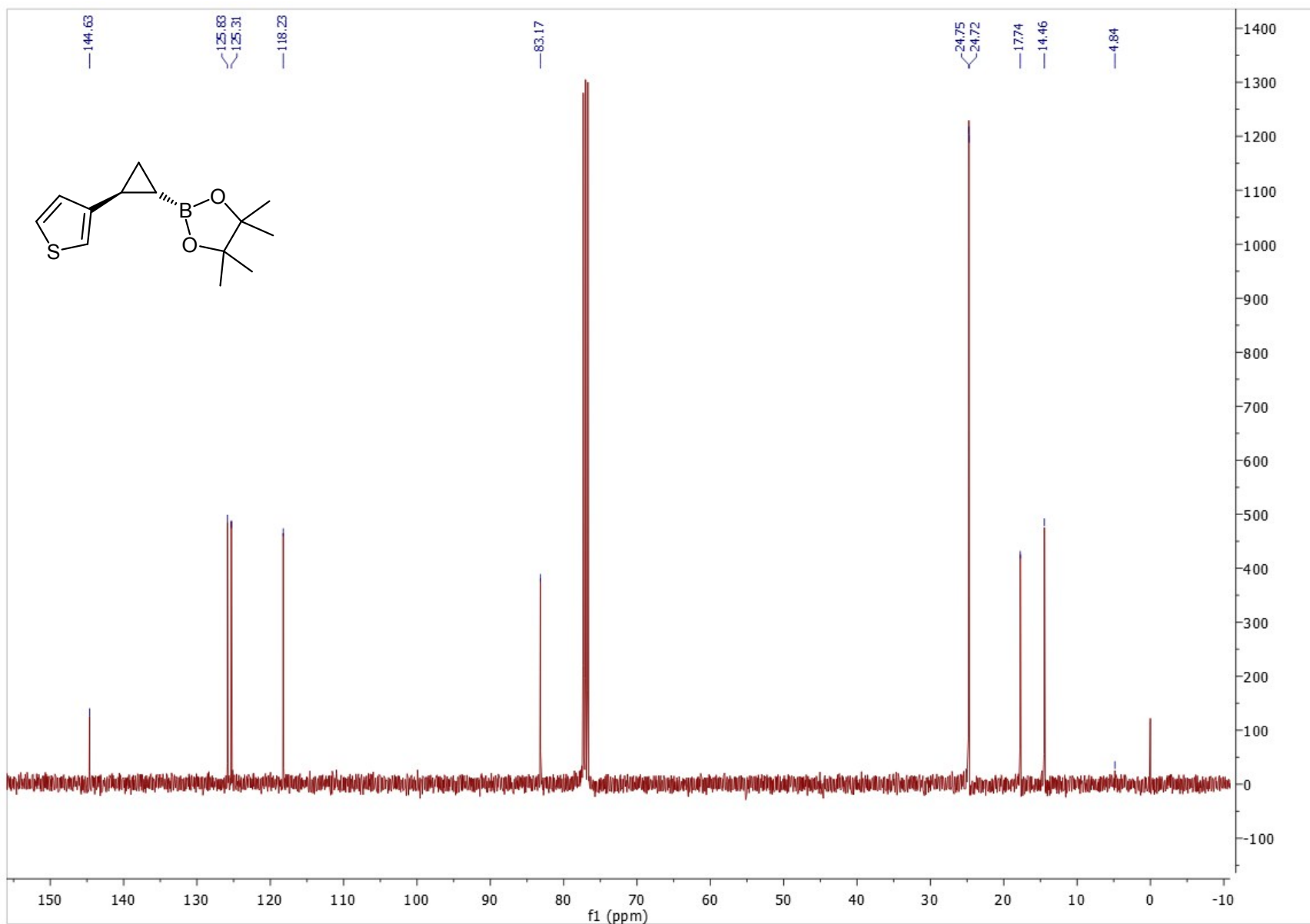


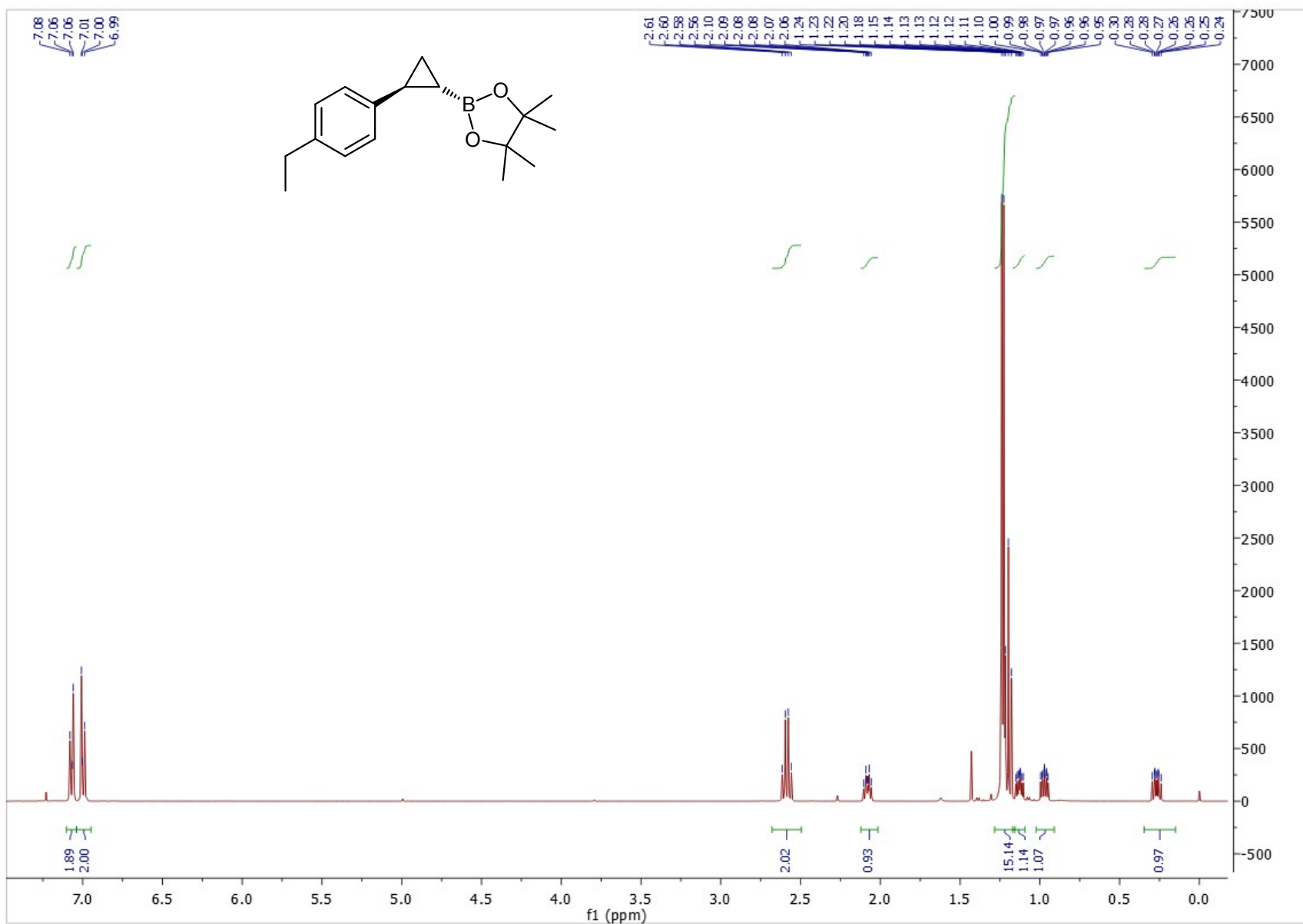


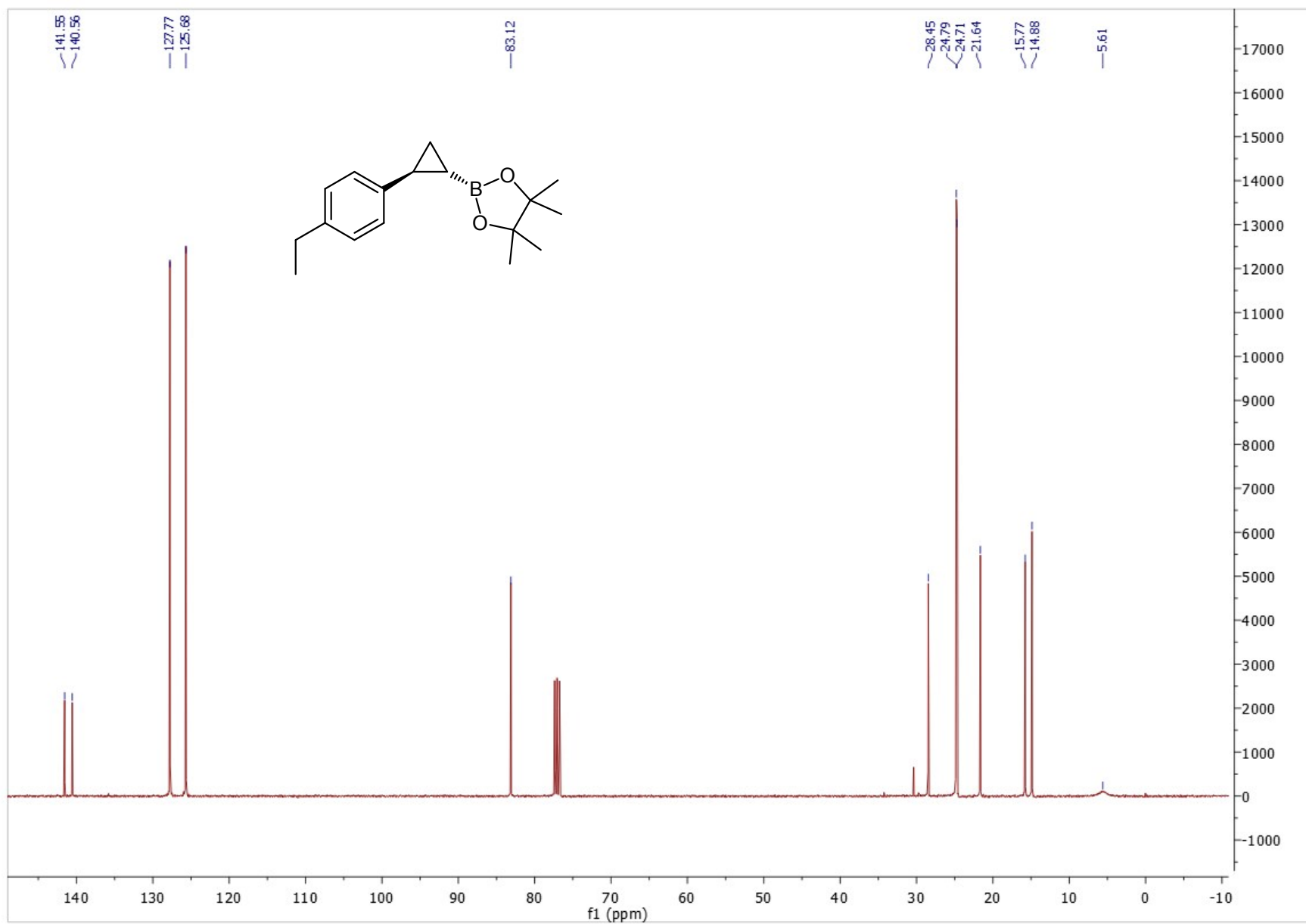


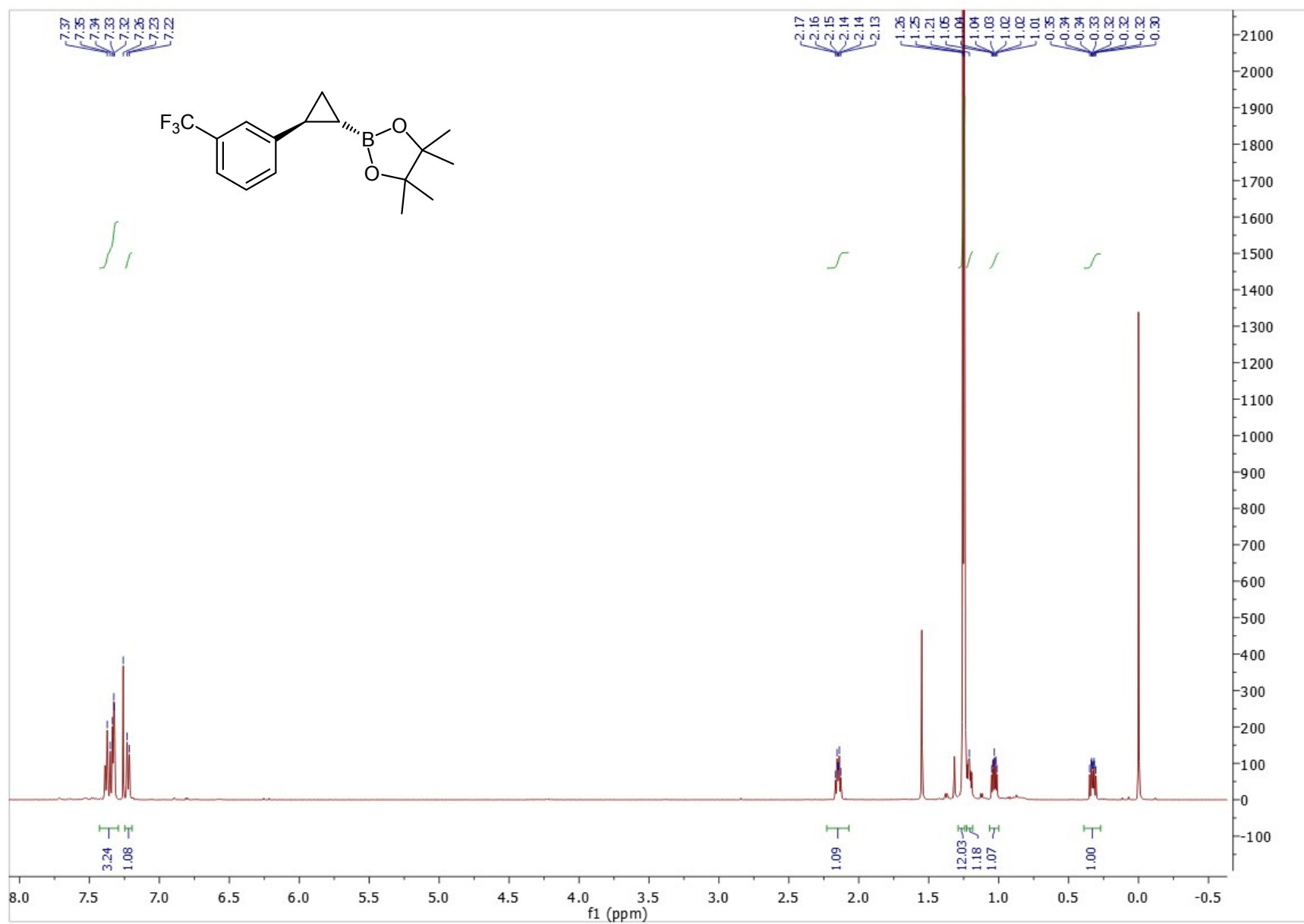


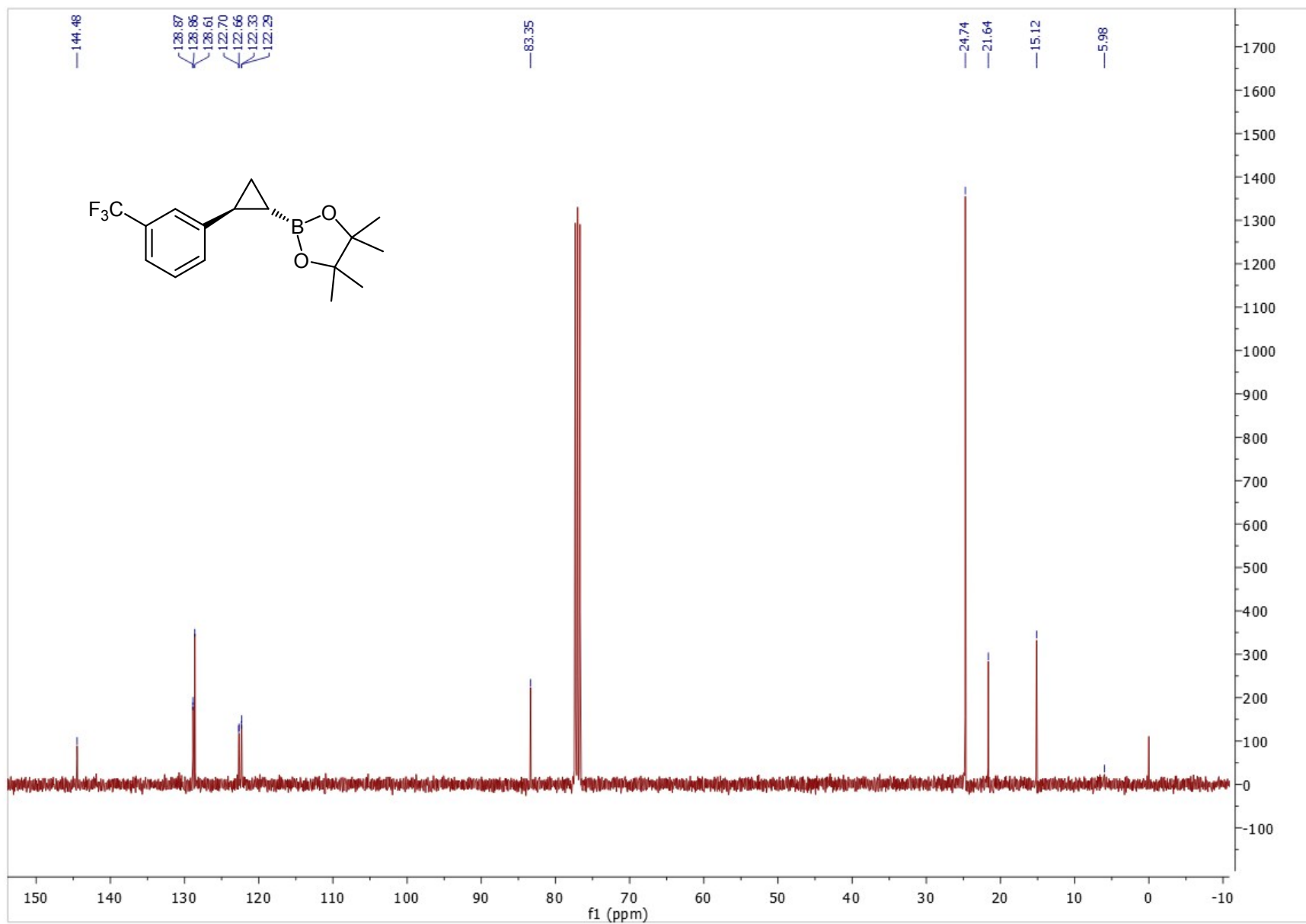


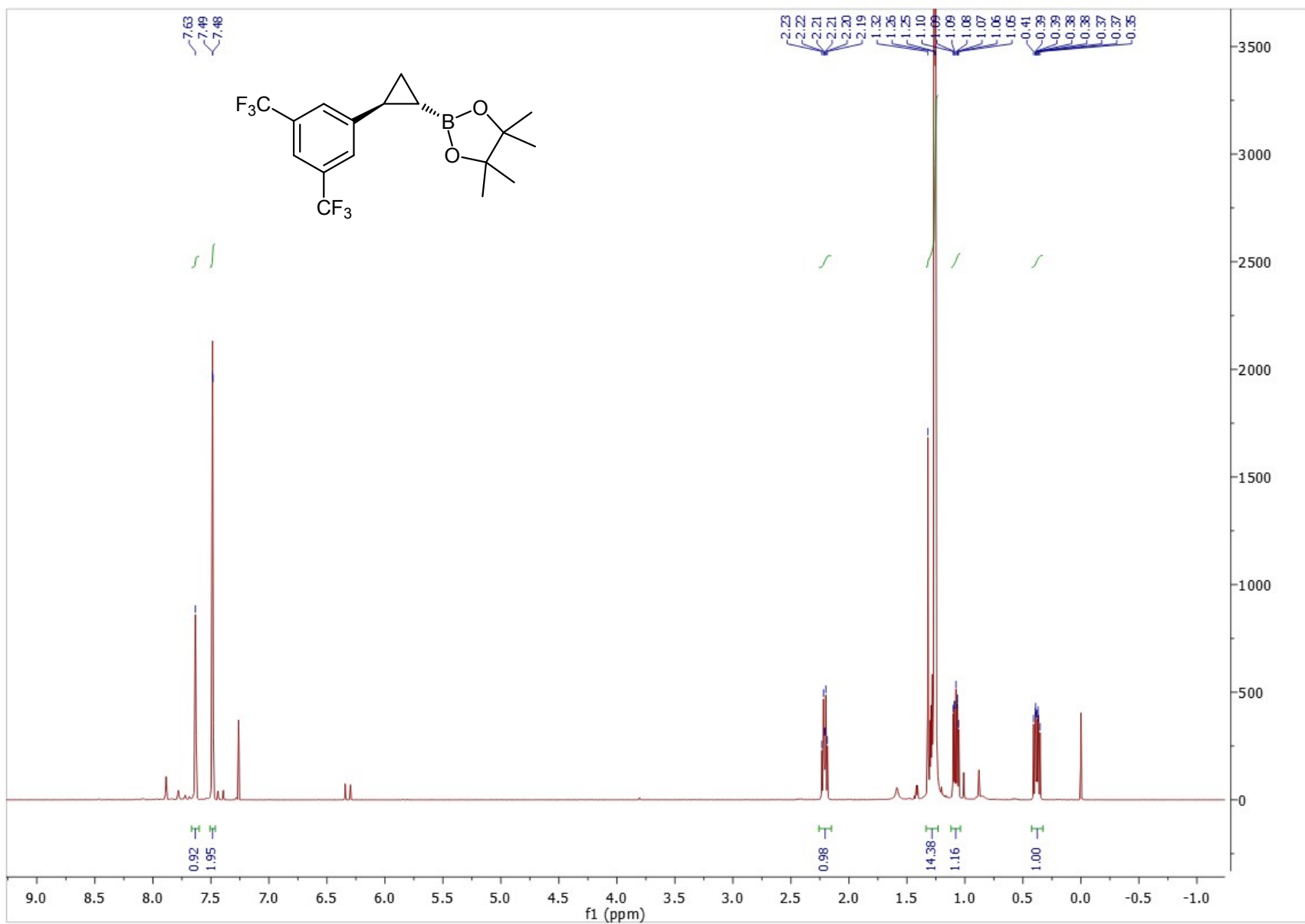


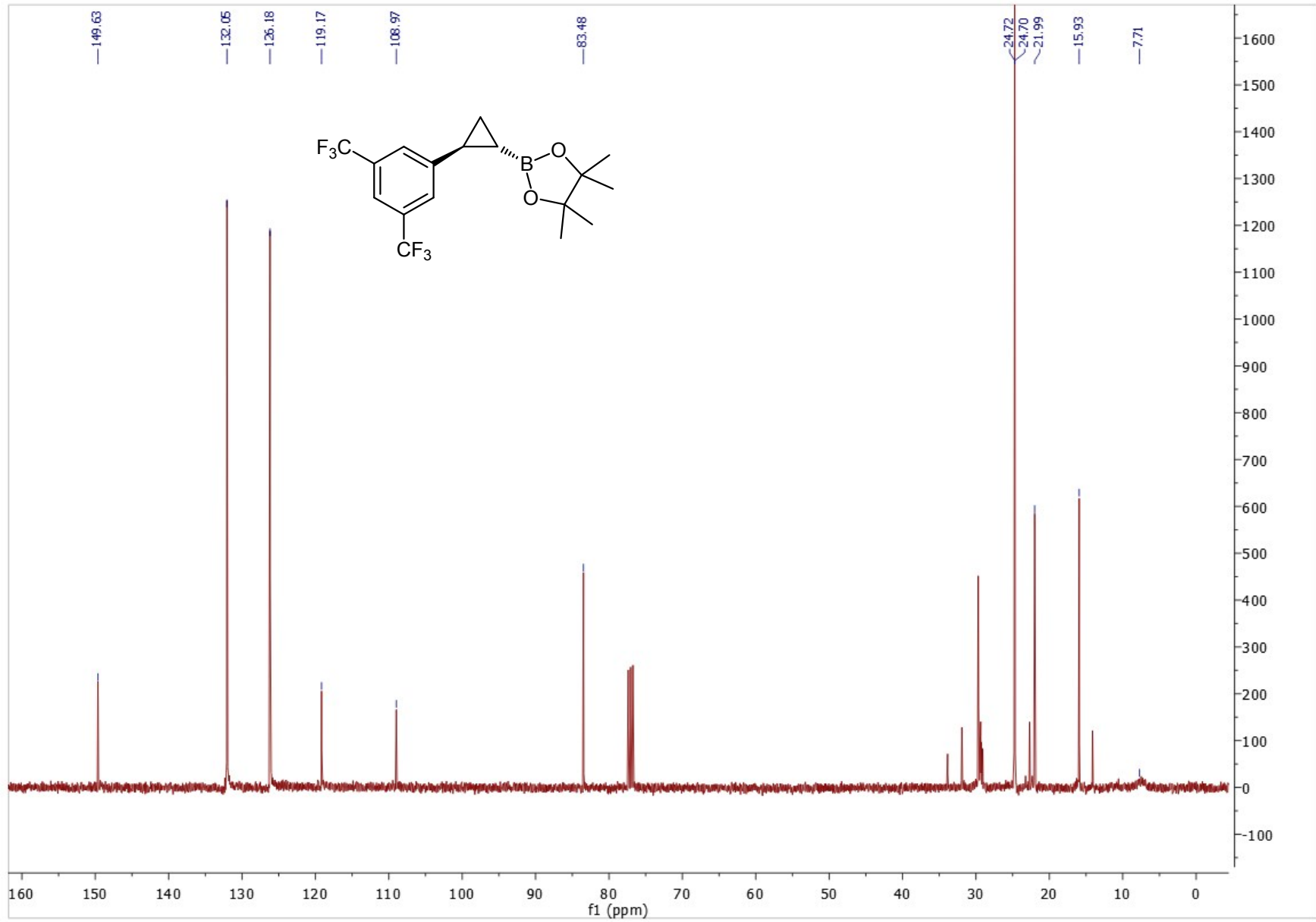


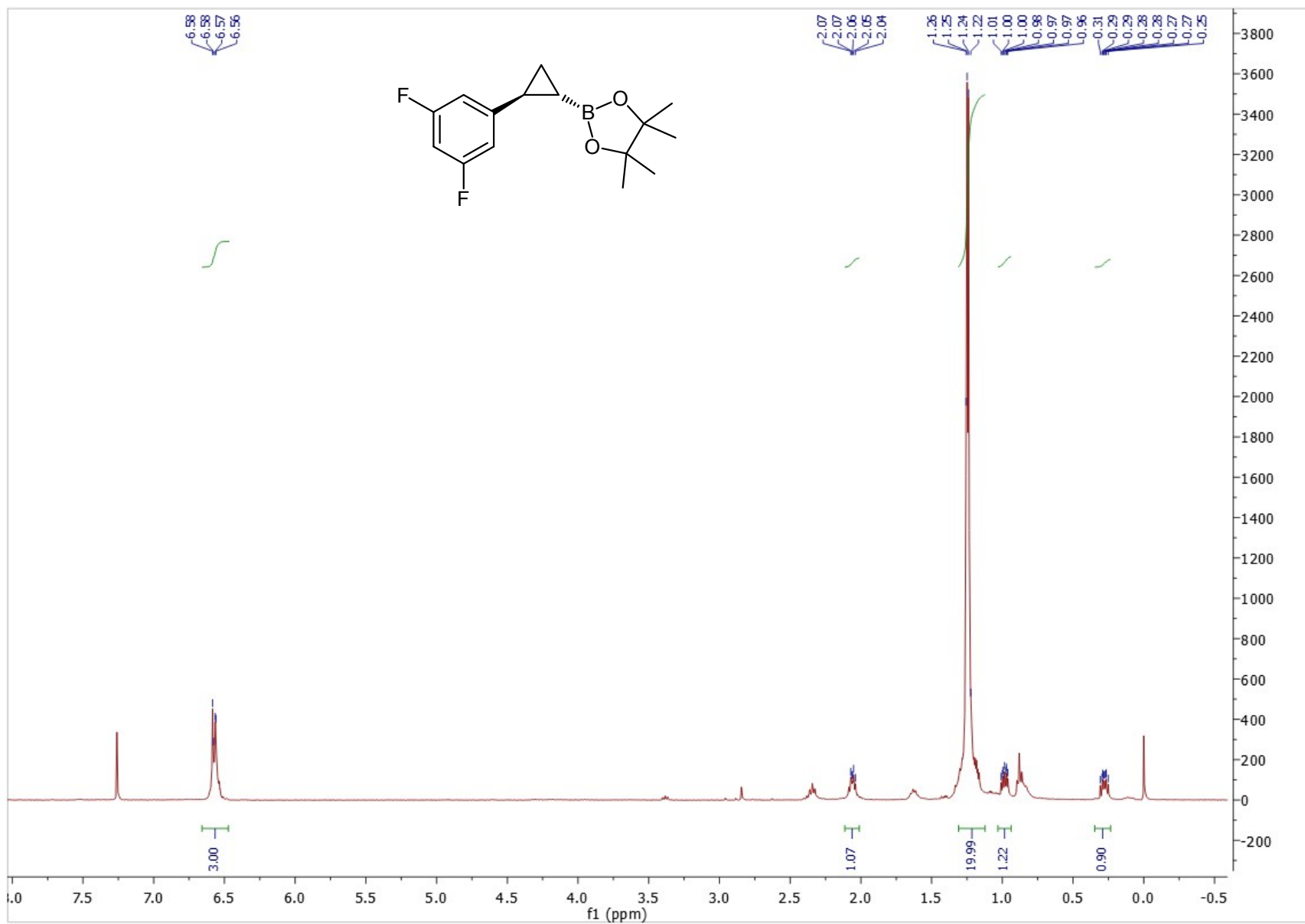


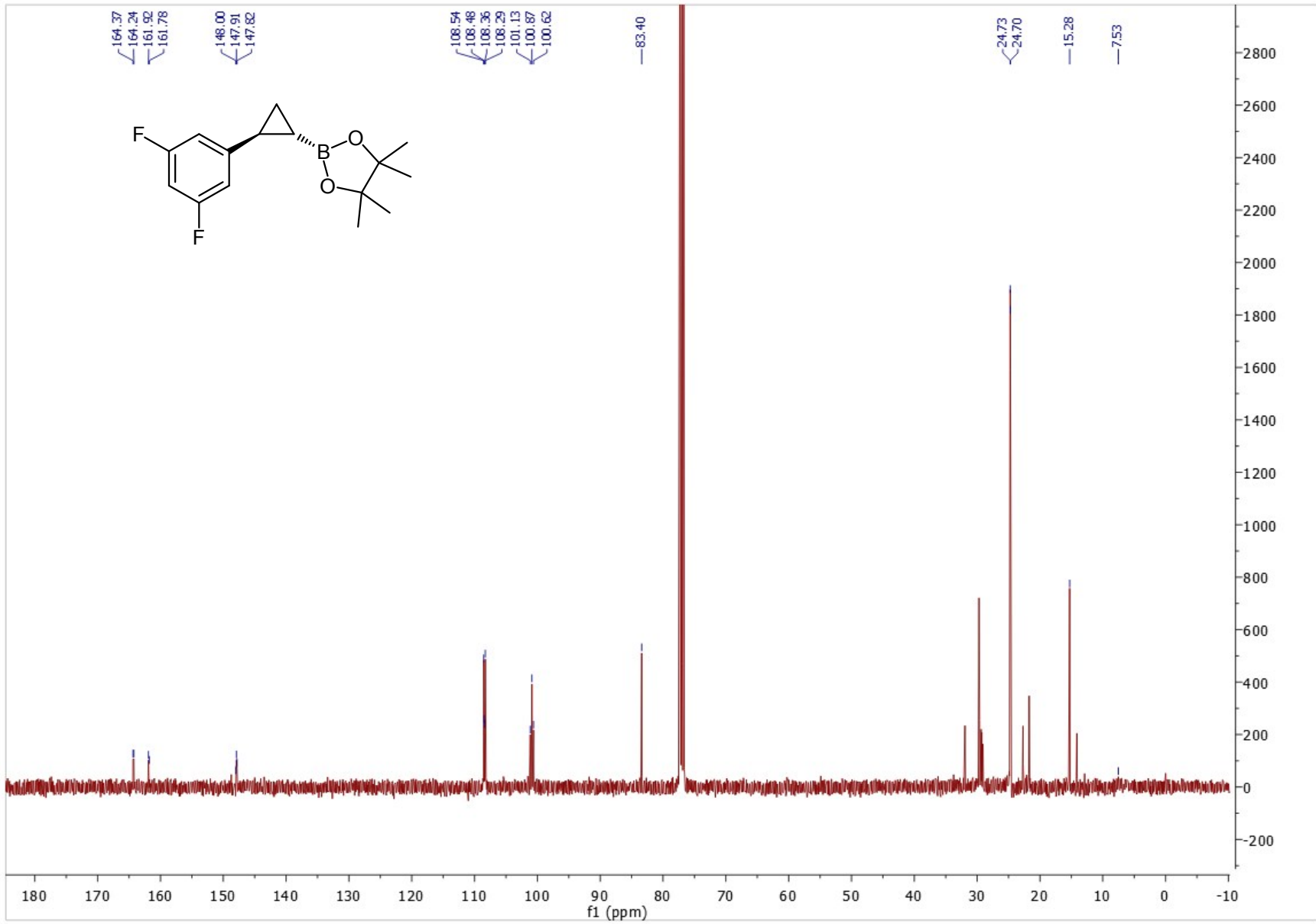


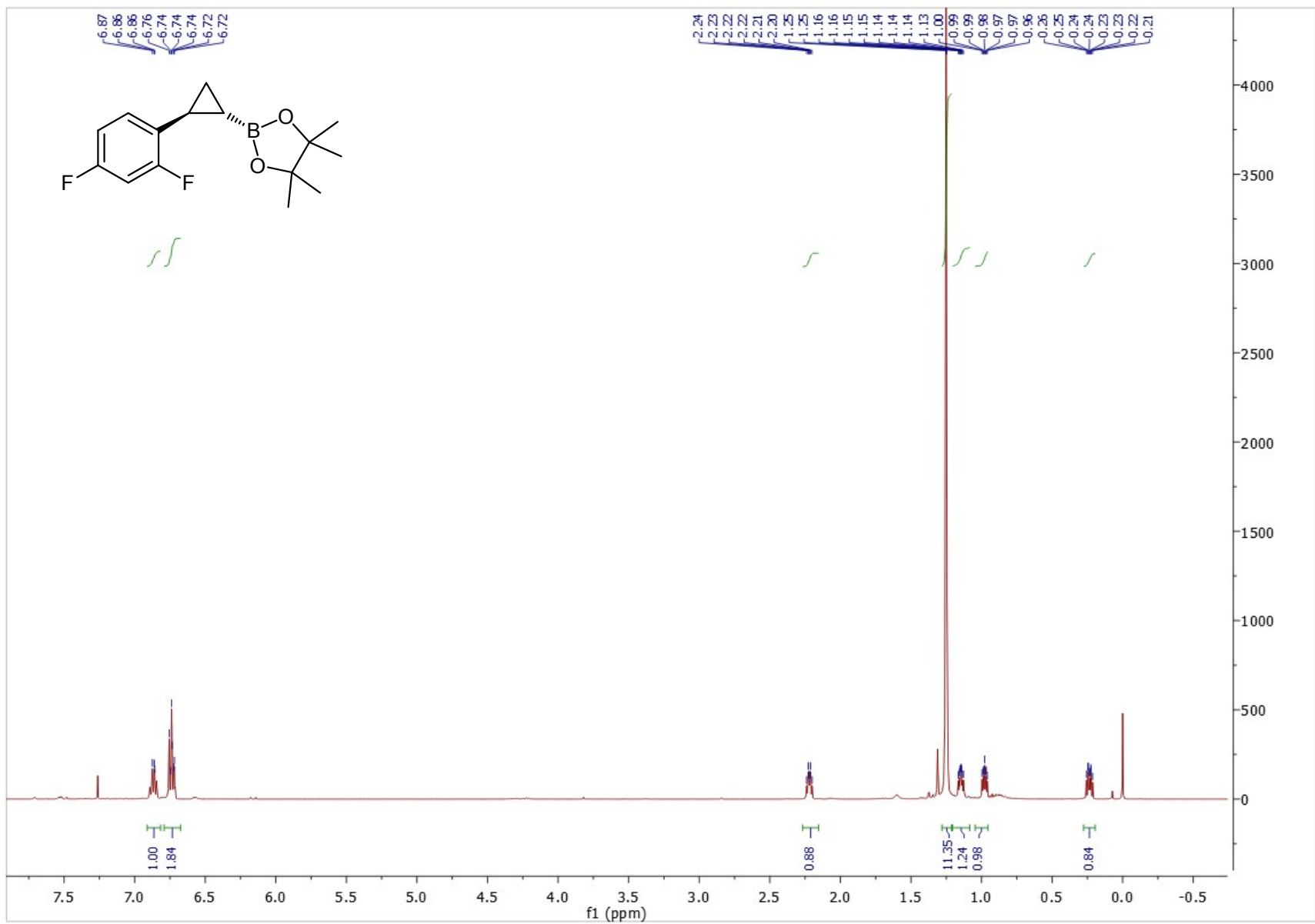


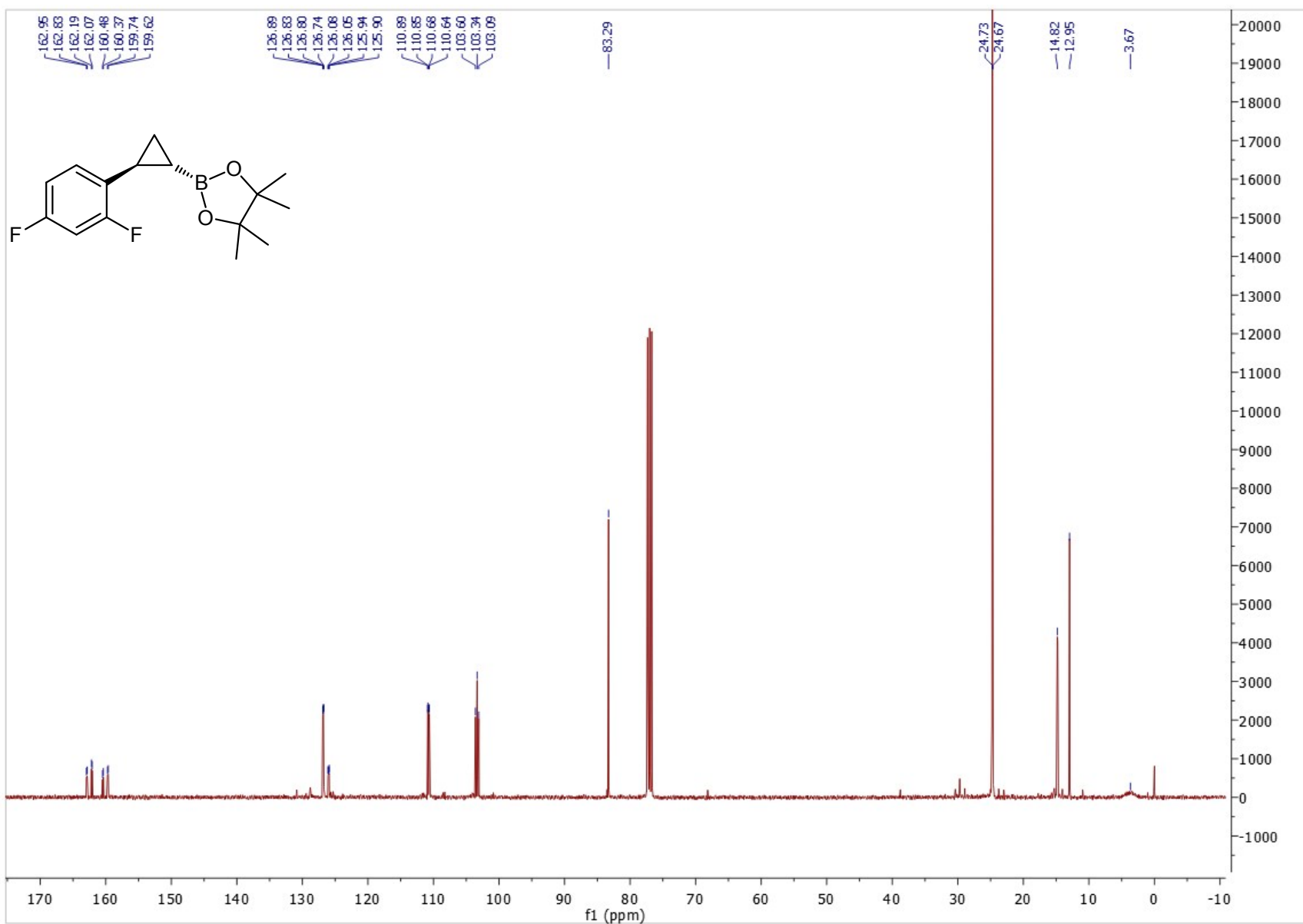


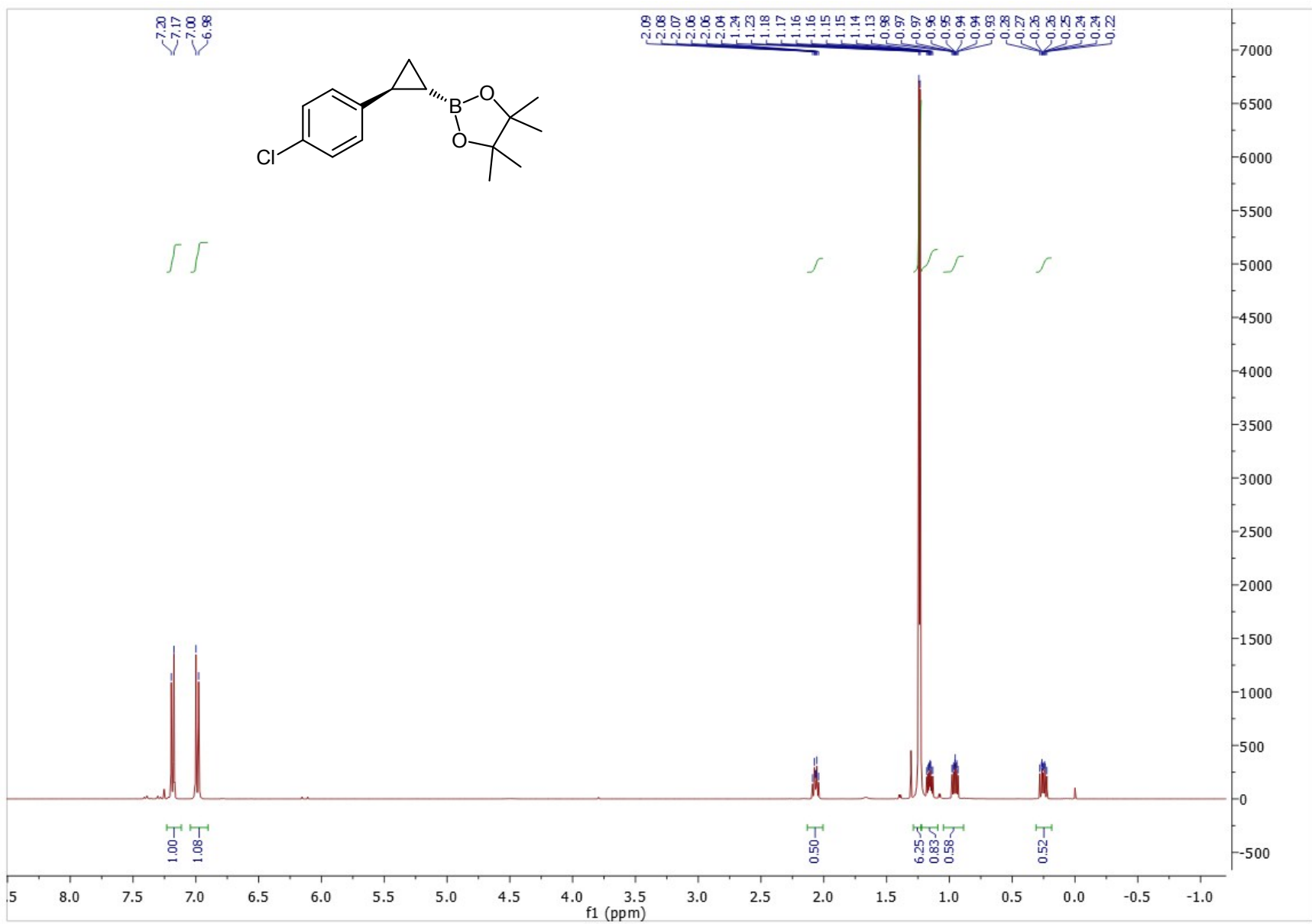


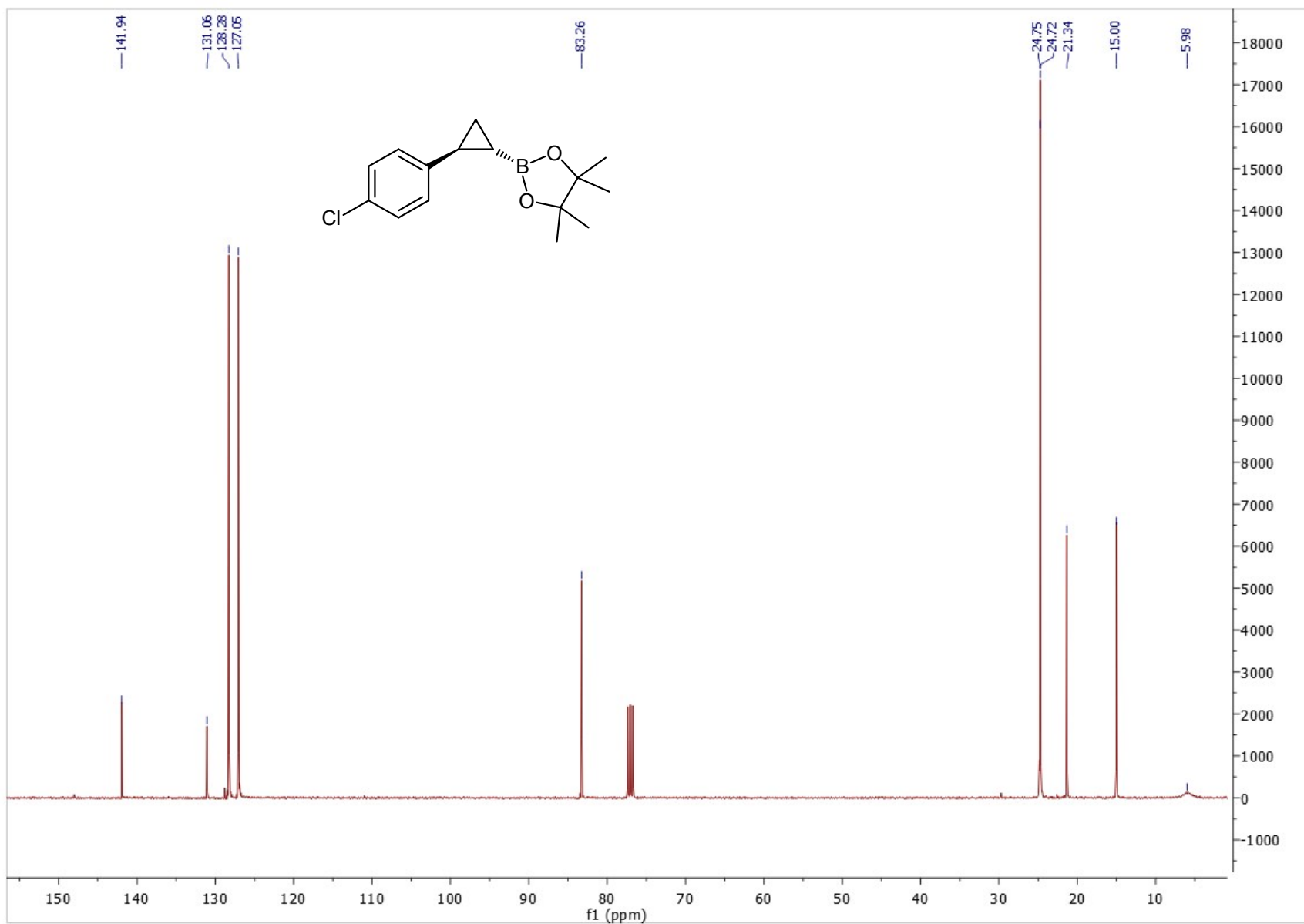


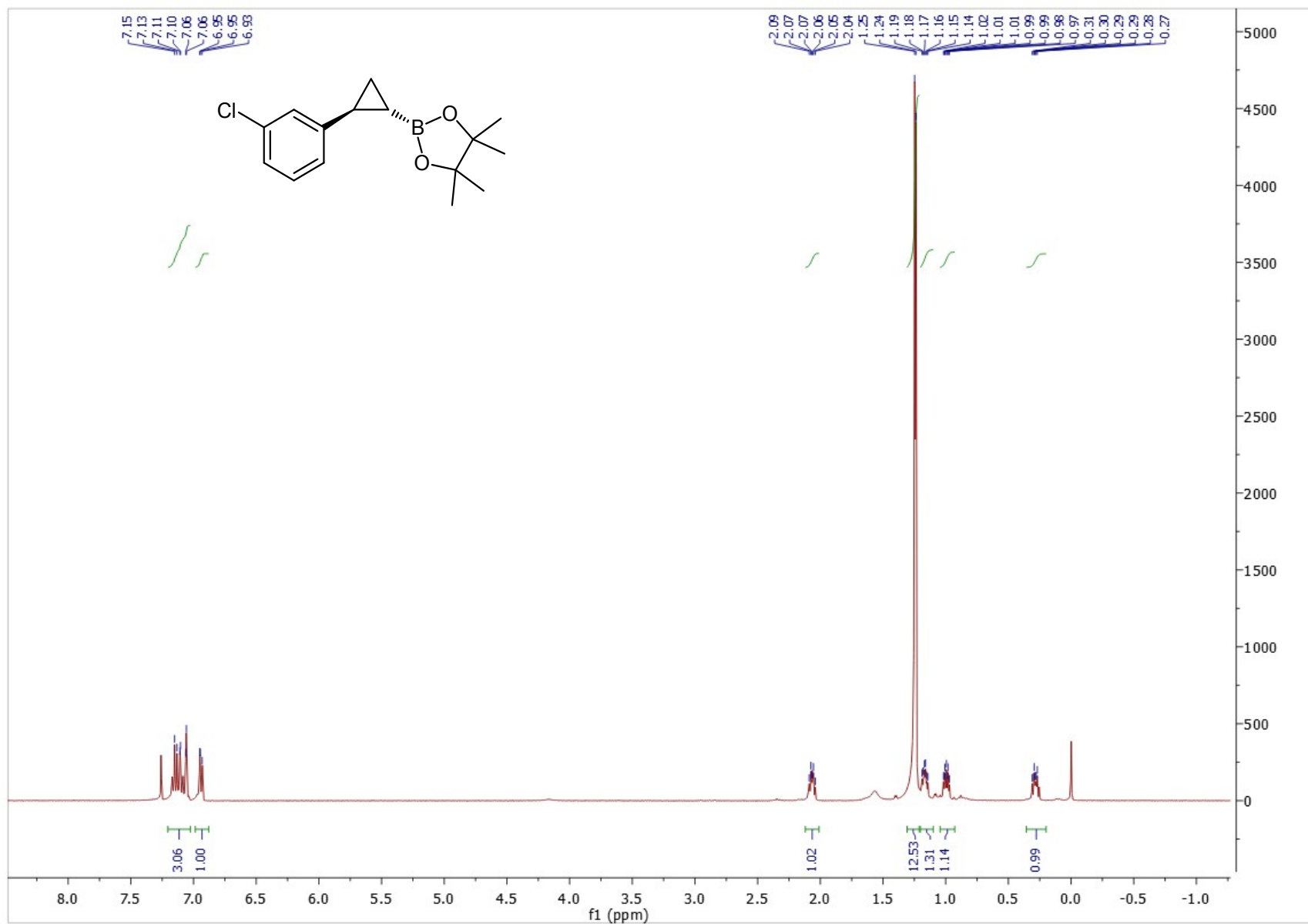


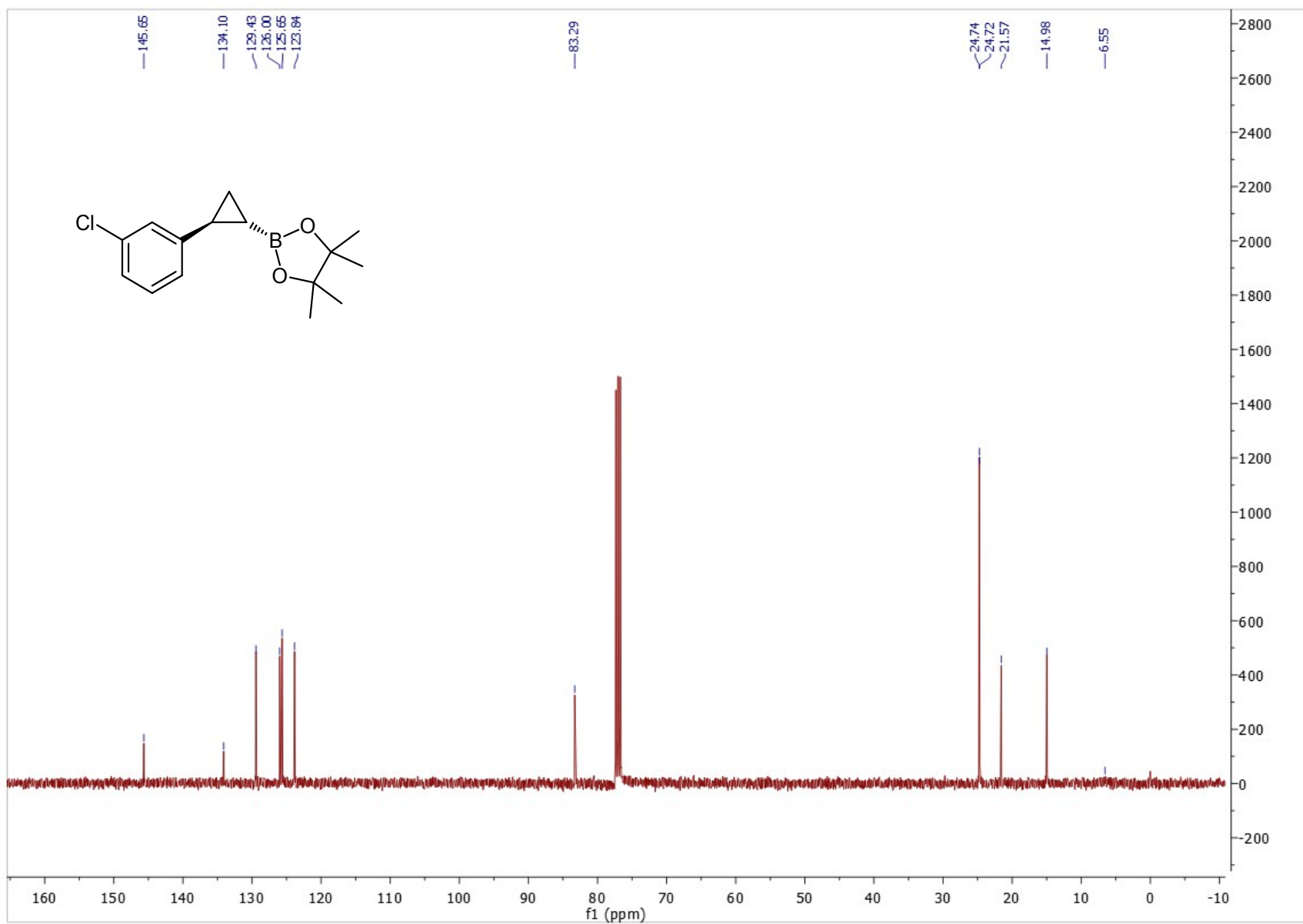


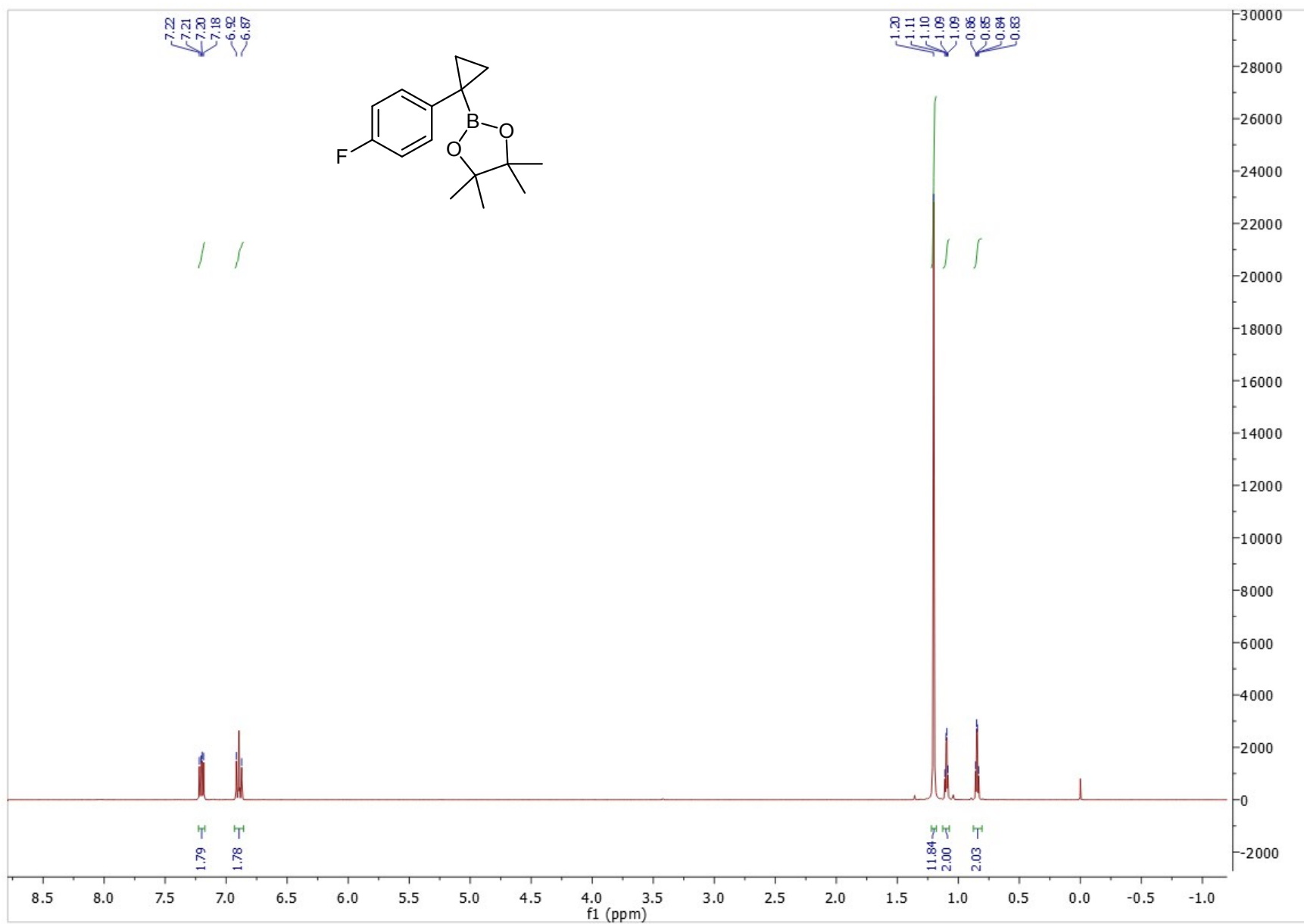


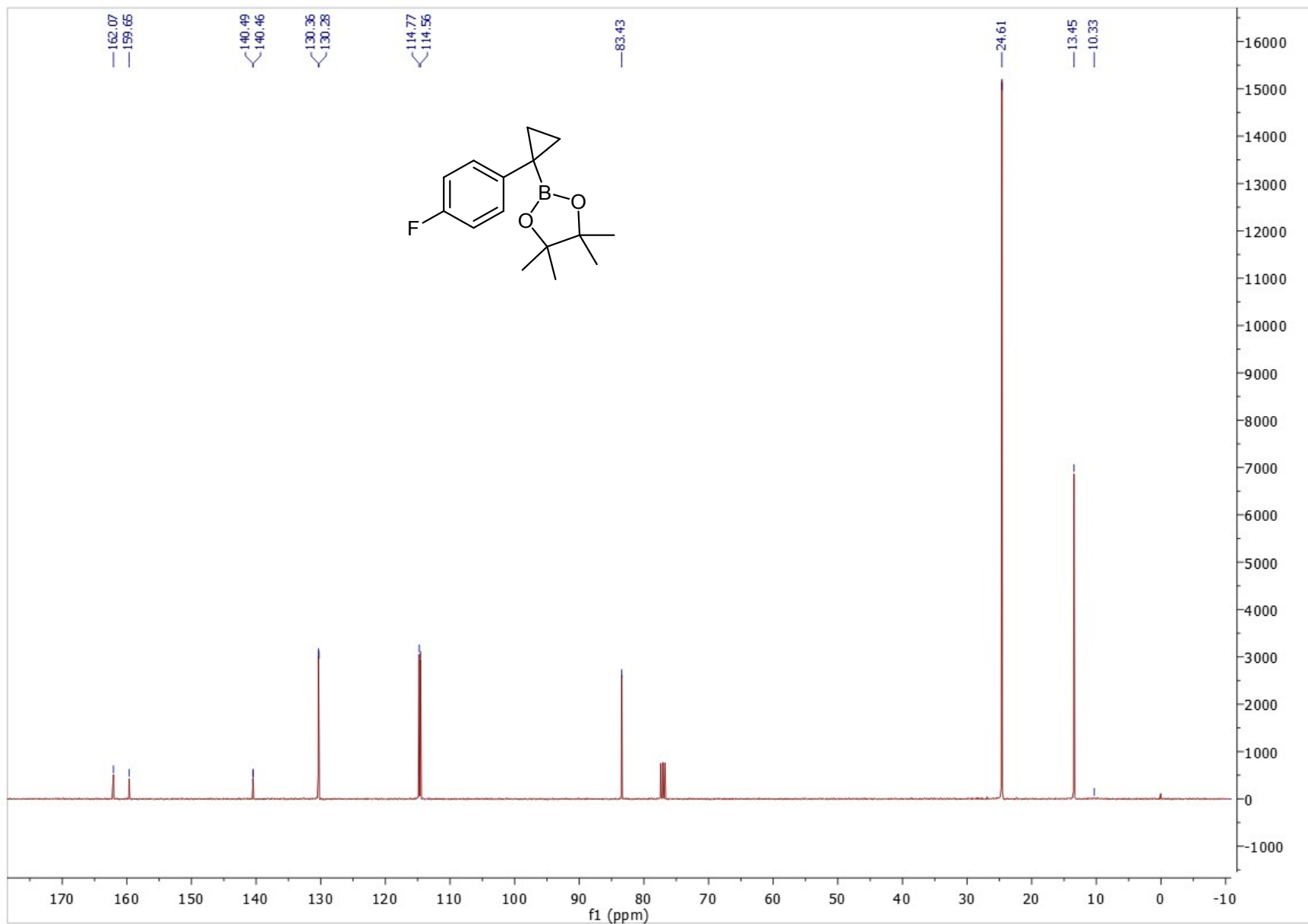


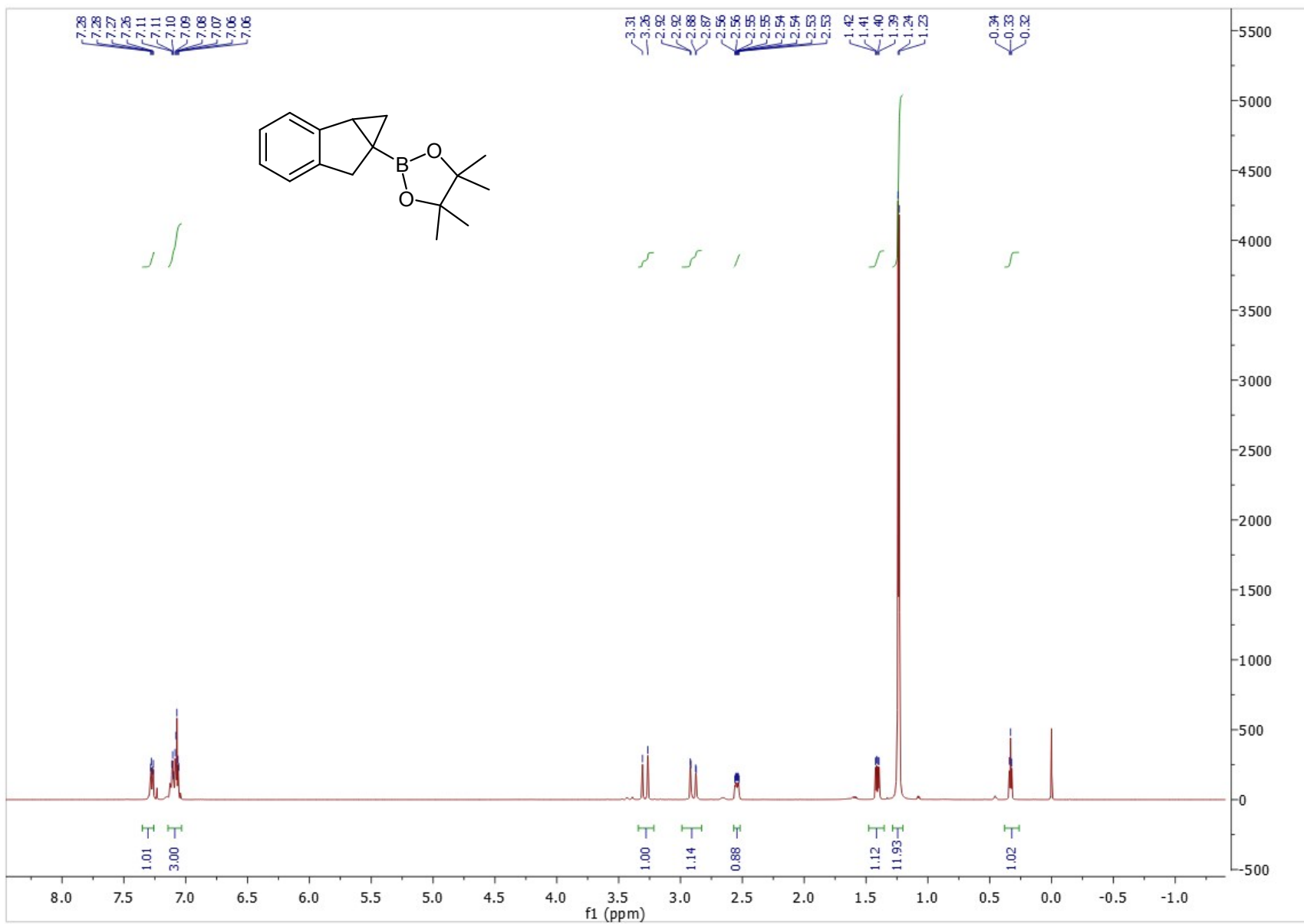


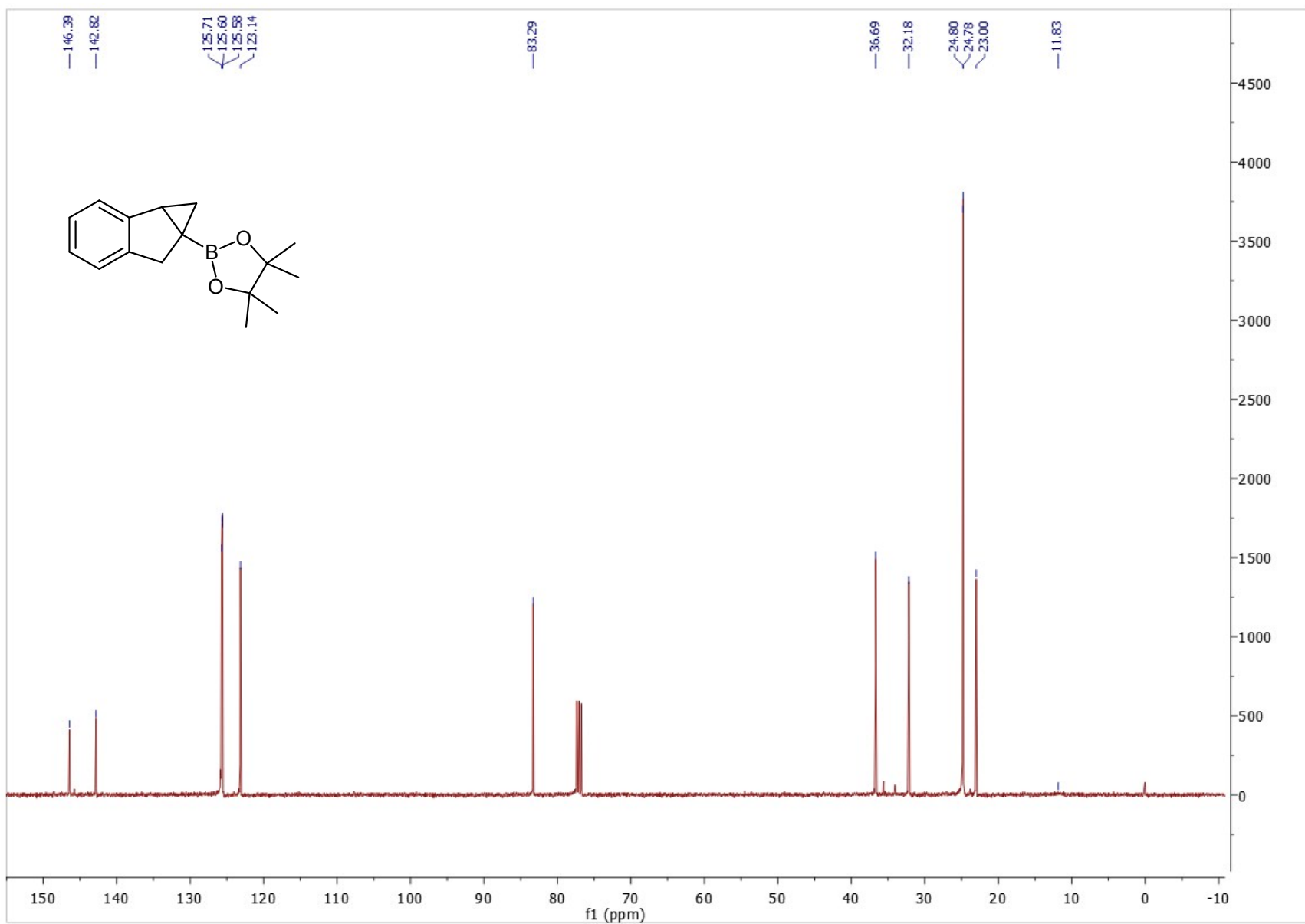


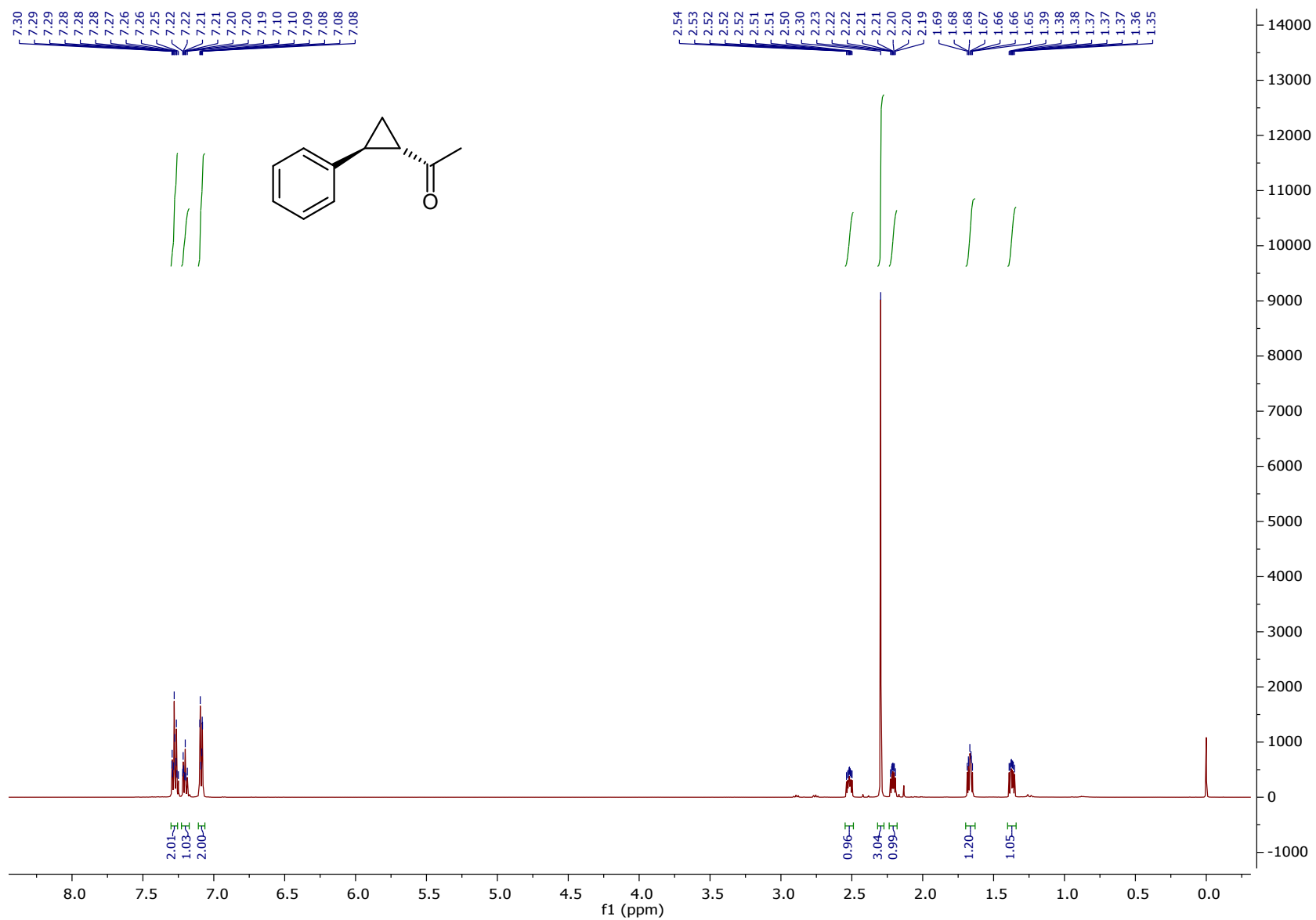










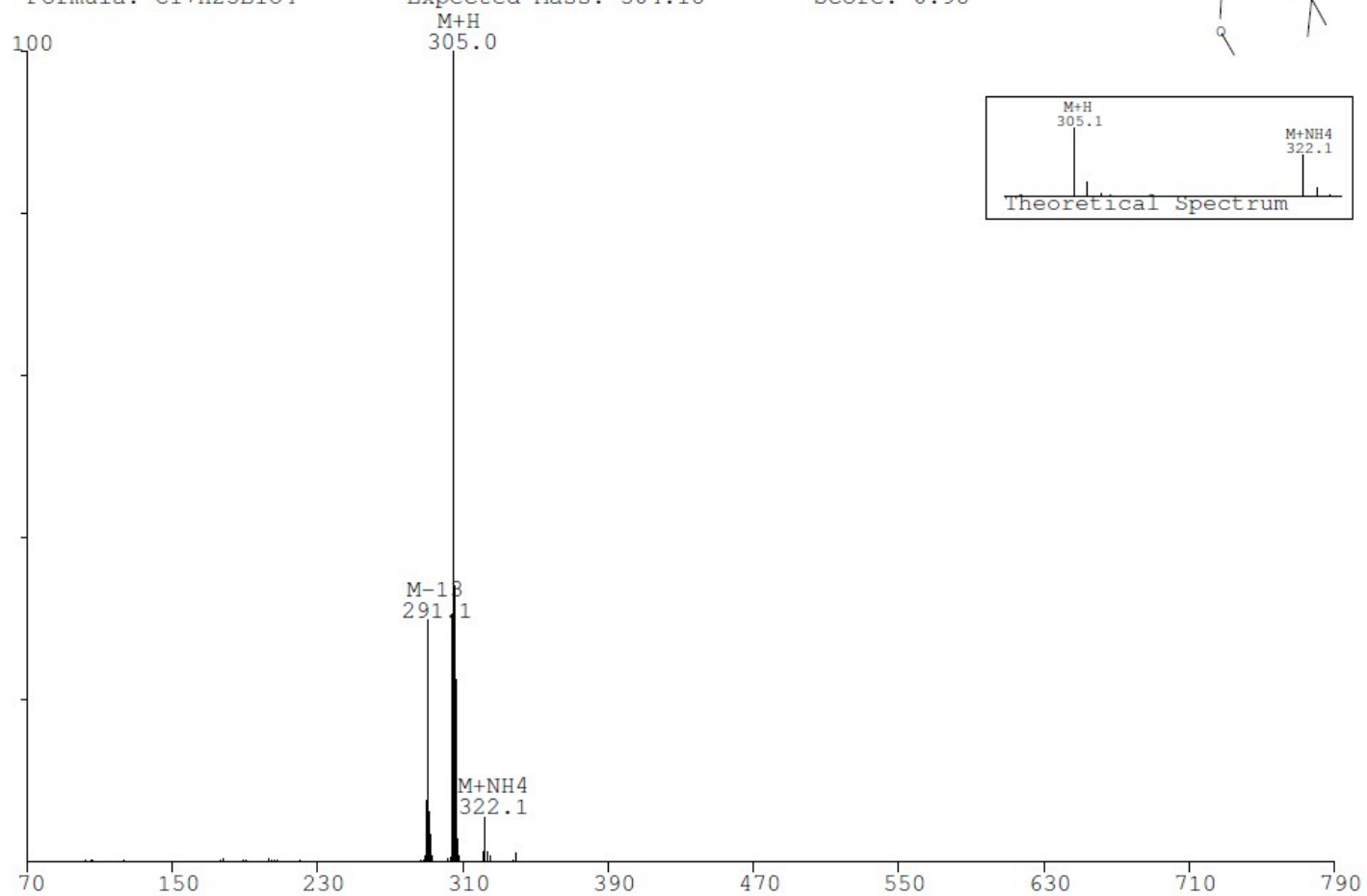
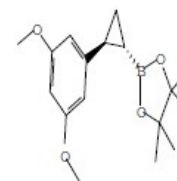


File: as11120y (18-May-2016 09:30:54)
Samp: MS-as11120
Cmnt: DSQII/LC869889 DCI/NH3
Mode: +DCI Oper: PPDR4181
Base: 305.08 Intensity: 1737851
Formula: C17H25B1O4 Expected Mass: 304.18

Scan: 17>19

Client:

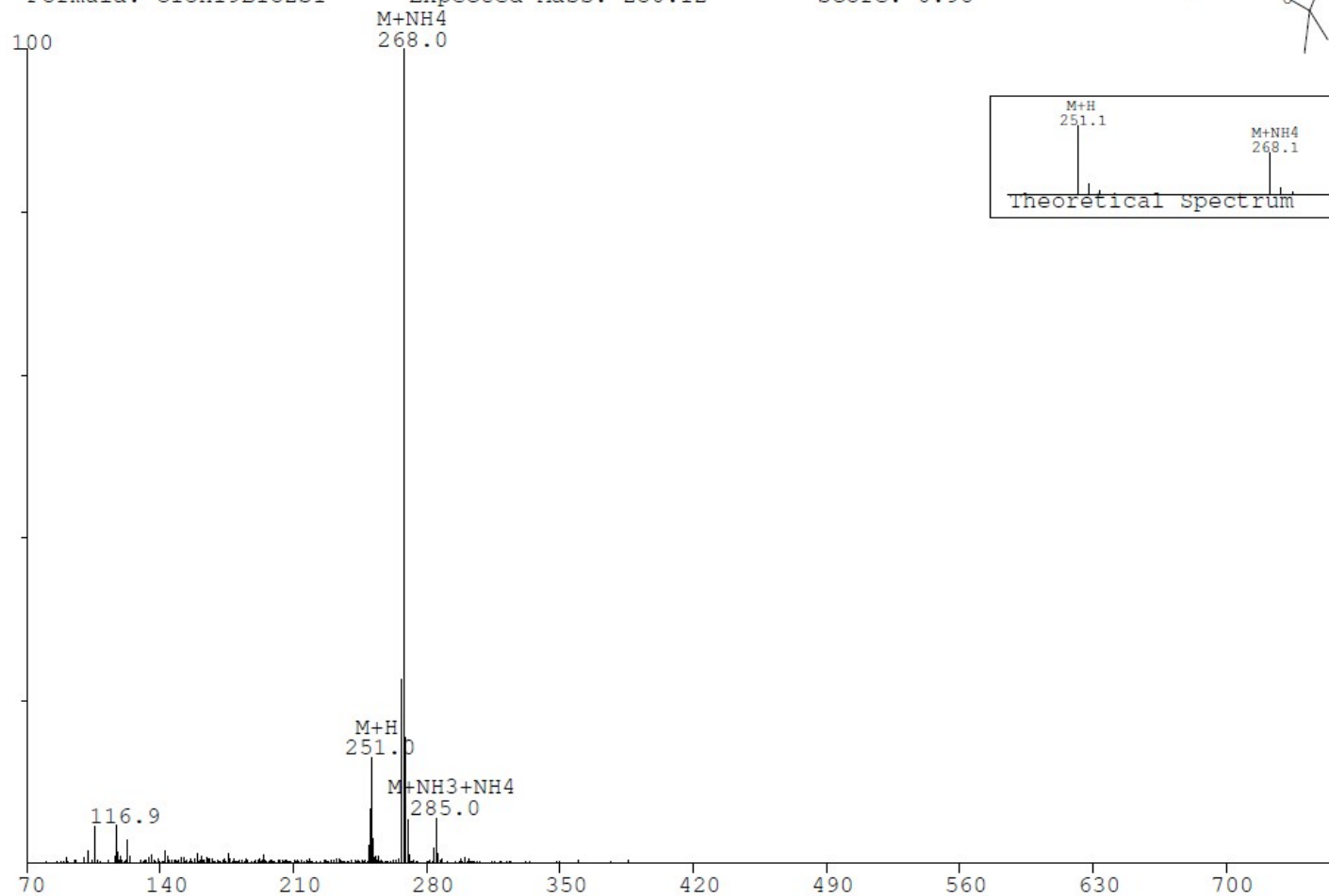
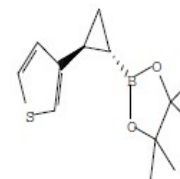
Score: 0.98



Date: Wed May 18 09:41:38 2016

Software: MSProcess 6.14

File: as11113y_160518091356 (18-May-2016 09:13:56) Scan: 33>35
Samp: ██████████ MS-as11113
Cmnt: DSQII/LC869889 DCI/NH3
Mode: +DCI Oper: PPDR4181 Client:
Base: 268.07 Intensity: 2042577
Formula: C13H19B1O2S1 Expected Mass: 250.12 Score: 0.98



Date: Wed May 18 09:20:05 2016

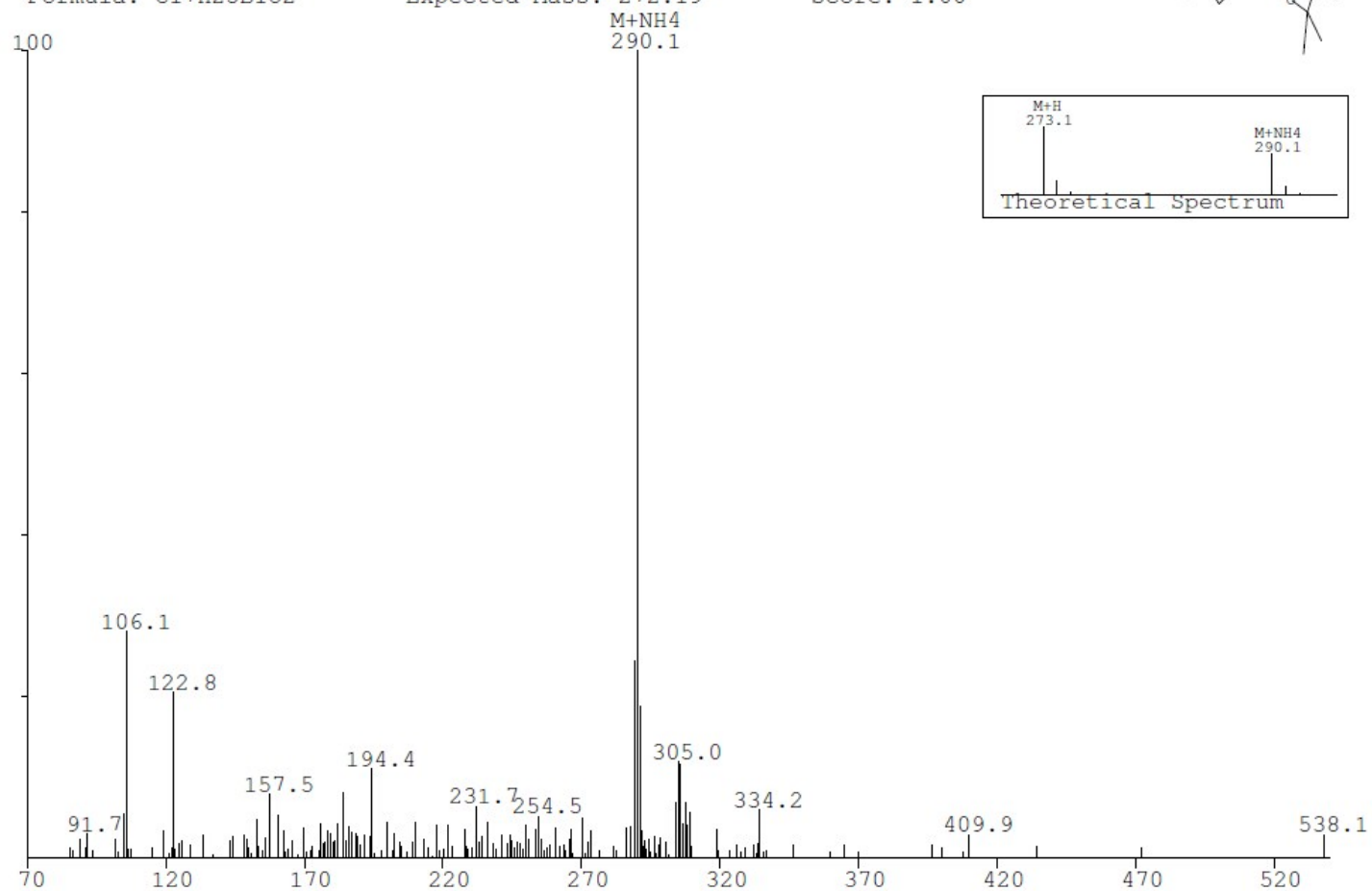
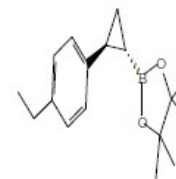
Software: MSProcess 6.14

File: as11121y (18-May-2016 09:35:14)
Samp: ██████████ MS-as11121
Cmnt: DSQII/LC869889 DCI/NH3
Mode: +DCI Oper: PPDR4181
Base: 290.18 Intensity: 44184
Formula: C17H25B1O2 Expected Mass: 272.19

Scan: 44>46

Client:

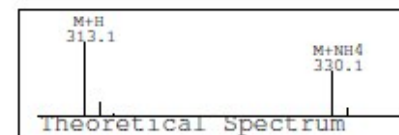
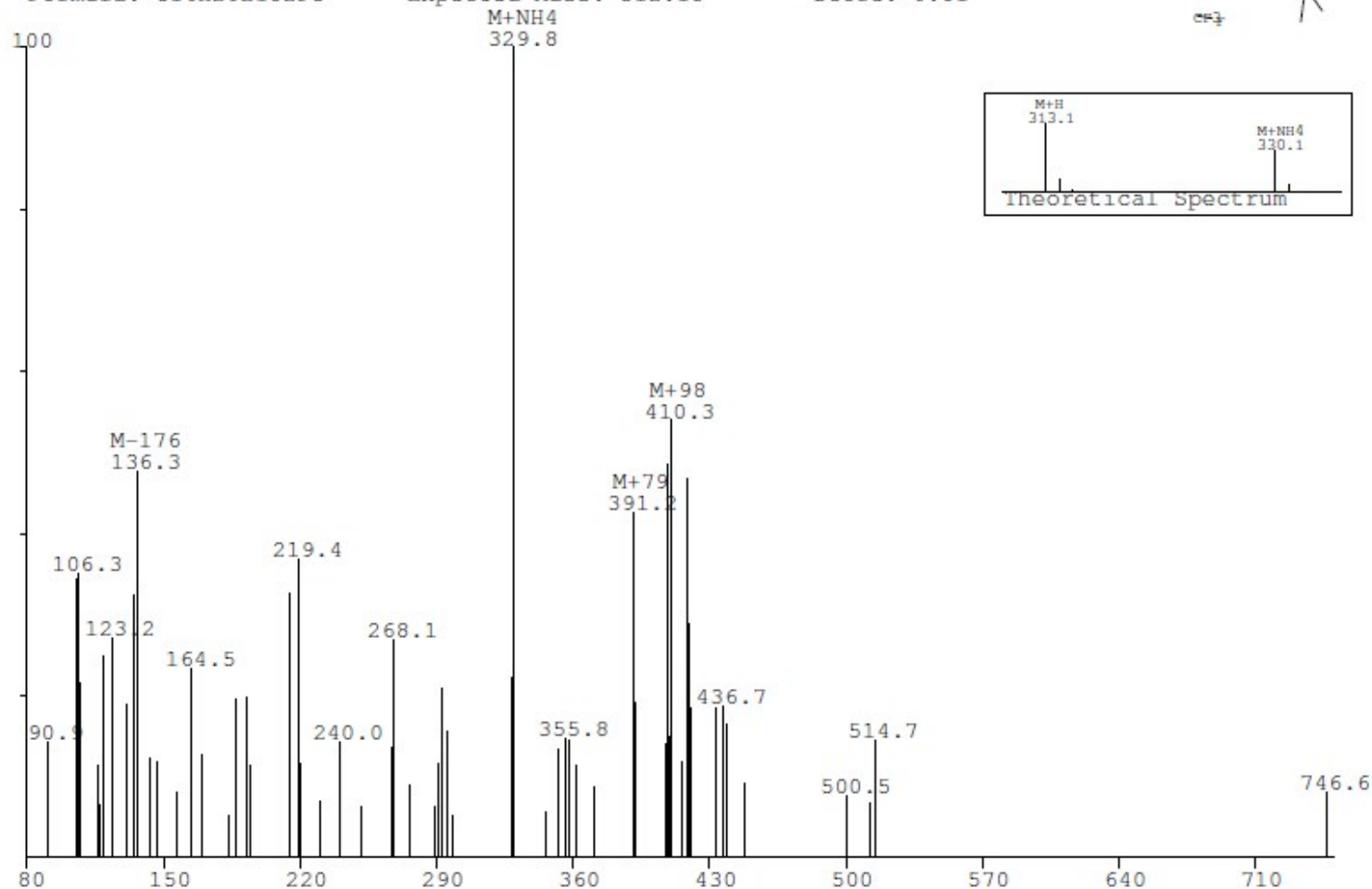
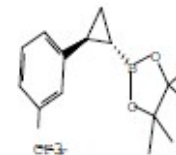
Score: 1.00



Date: Wed May 18 09:41:33 2016

Software: MSProcess 6.14

File: as11119y_160518111145 (18-May-2016 11:11:45) Scan: 27>29
Samp: ██████████ MS-as11119
Cmnt: DSQII/LC869889 DCI/NH3
Mode: +DCI Oper: PPDR4181 Client:
Base: 329.86 Intensity: 4811
Formula: C16H20B1O2F3 Expected Mass: 312.15 Score: 0.81



Date: Wed May 18 11:20:12 2016

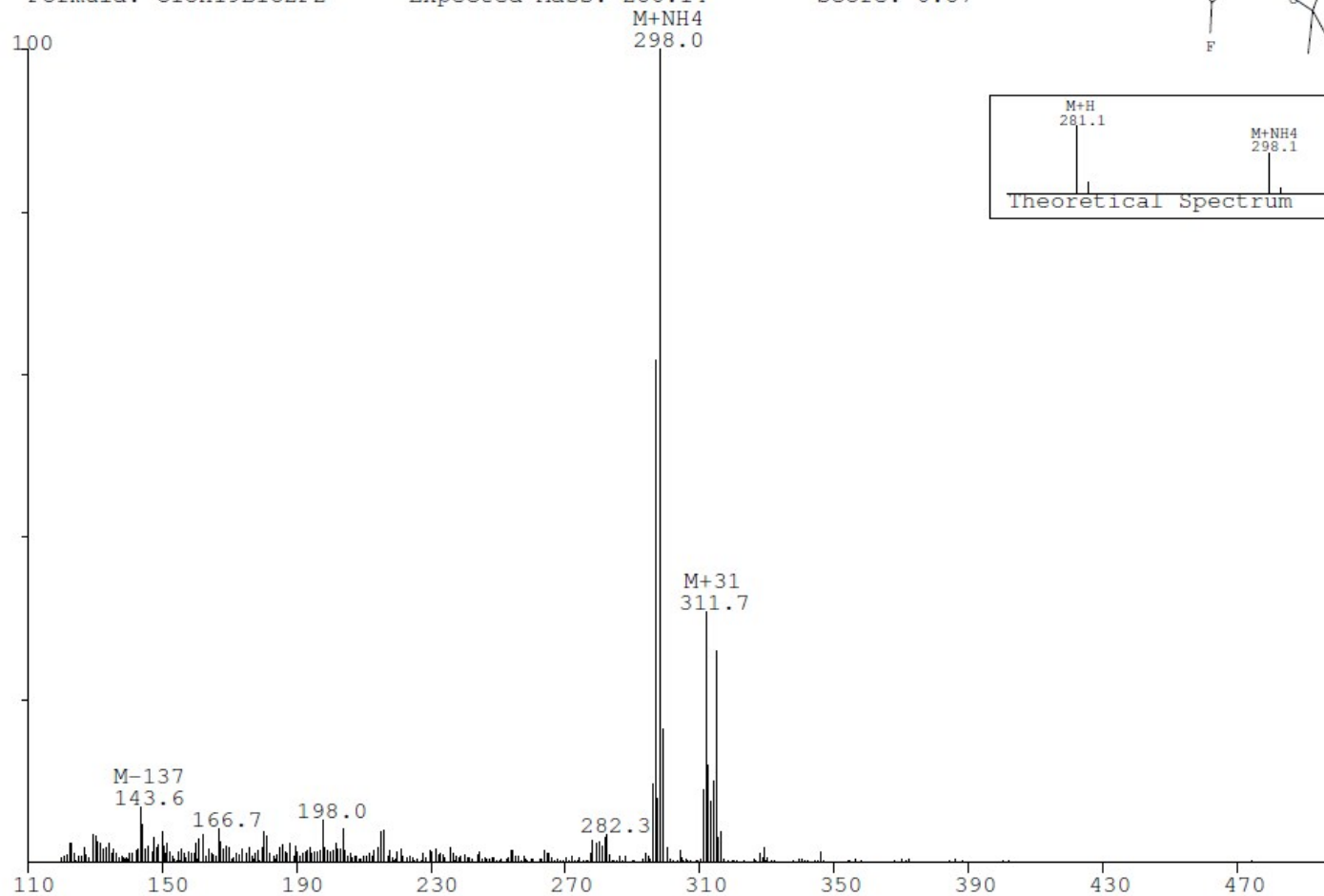
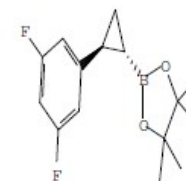
Software: MSProcess 6.14

File: as15817y (20-May-2016 14:55:51)
Samp: ██████████ MS-as15817
Cmnt: DSQII/LC869889 DCI/NH3
Mode: +DCI Oper: PPDR4181
Base: 298.08 Intensity: 15354424
Formula: C15H19B1O2F2 Expected Mass: 280.14

Scan: 25>27

Client:

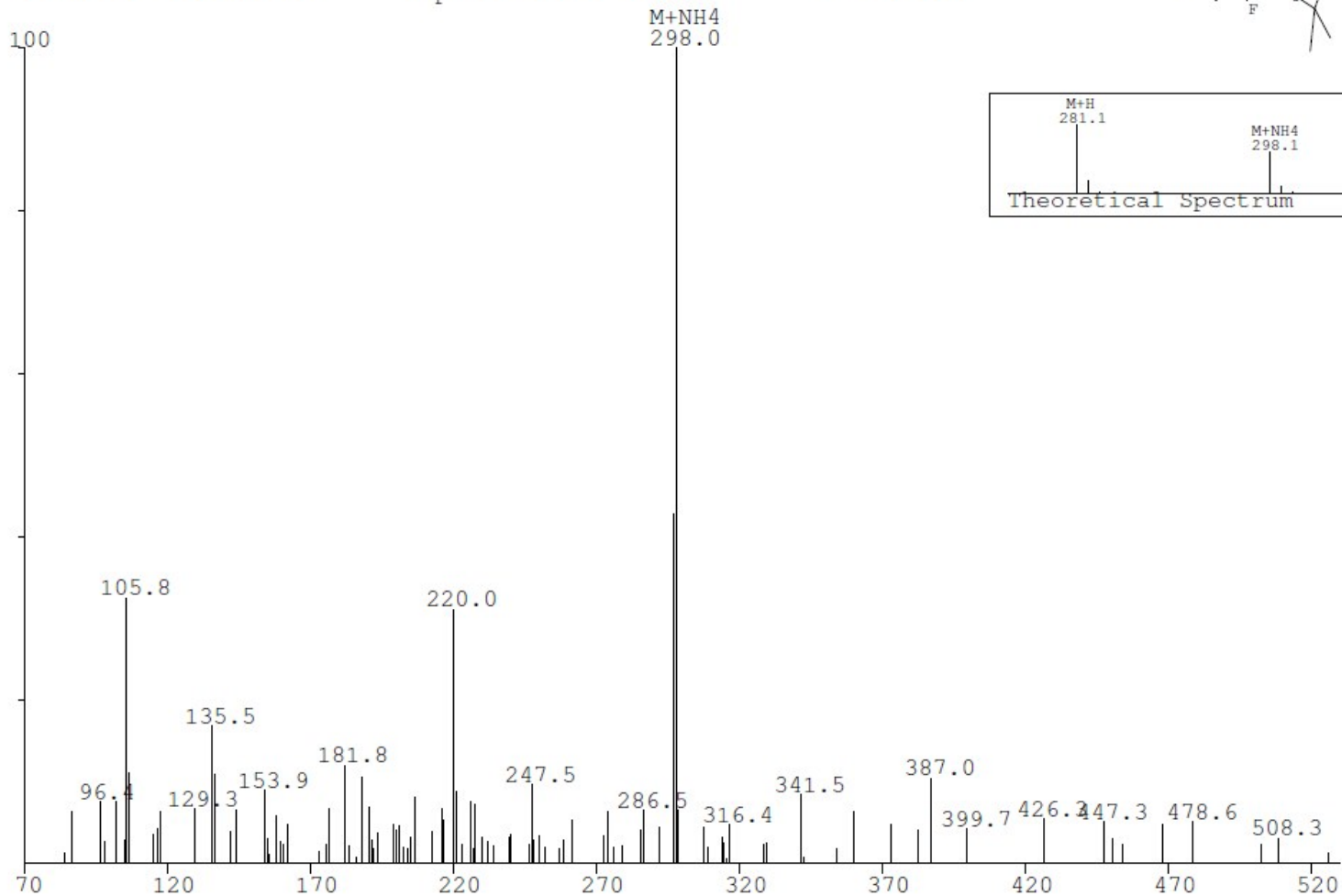
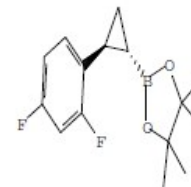
Score: 0.87



Date: Fri May 20 15:00:05 2016

Software: MSProcess 6.14

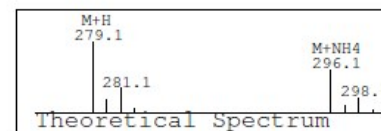
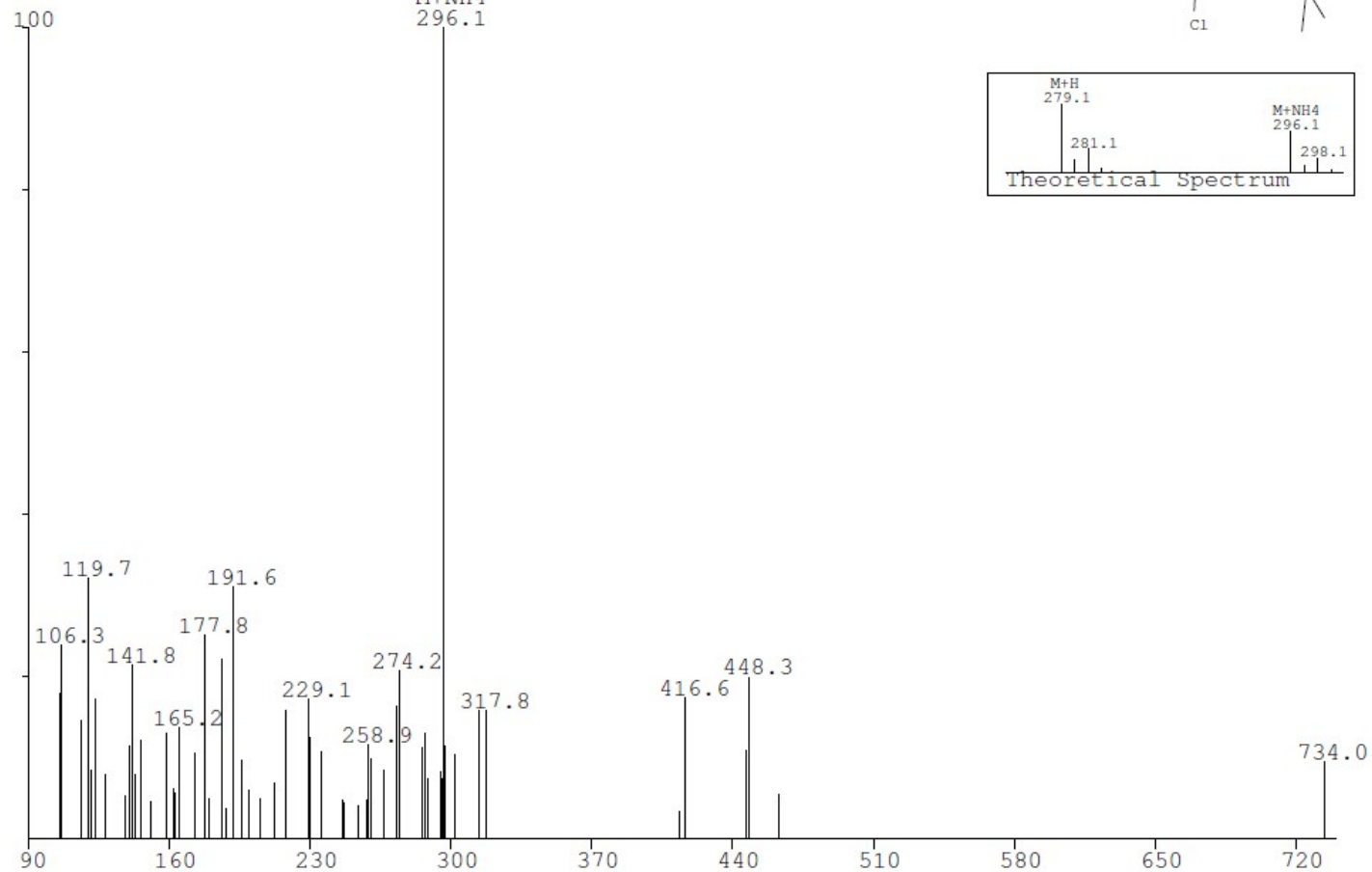
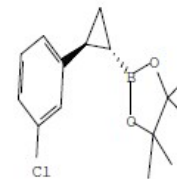
File: as11116y_160518110713 (18-May-2016 11:07:13) Scan: 40>42
Samp: ██████████ FIN MS-as11116
Cmnt: DSQII/LC869889 DCI/NH3
Mode: +DCI Oper: PPDR4181 Client:
Base: 298.04 Intensity: 18584
Formula: C15H19B1O2F2 Expected Mass: 280.14 Score: 1.00



Date: Wed May 18 11:20:05 2016

Software: MSProcess 6.14

File: as11172y_160518111606 (18-May-2016 11:16:06) Scan: 33>35
Samp: ██████████ MS-as11172
Cmnt: DSQII/LC869889 DCI/NH3
Mode: +DCI Oper: PPDR4181 Client:
Base: 296.13 Intensity: 7026
Formula: C15H20B1O2Cl1 Expected Mass: 278.12 Score: 1.00
M+NH4
296.1



Date: Wed May 18 11:30:04 2016

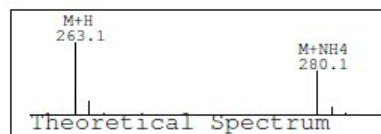
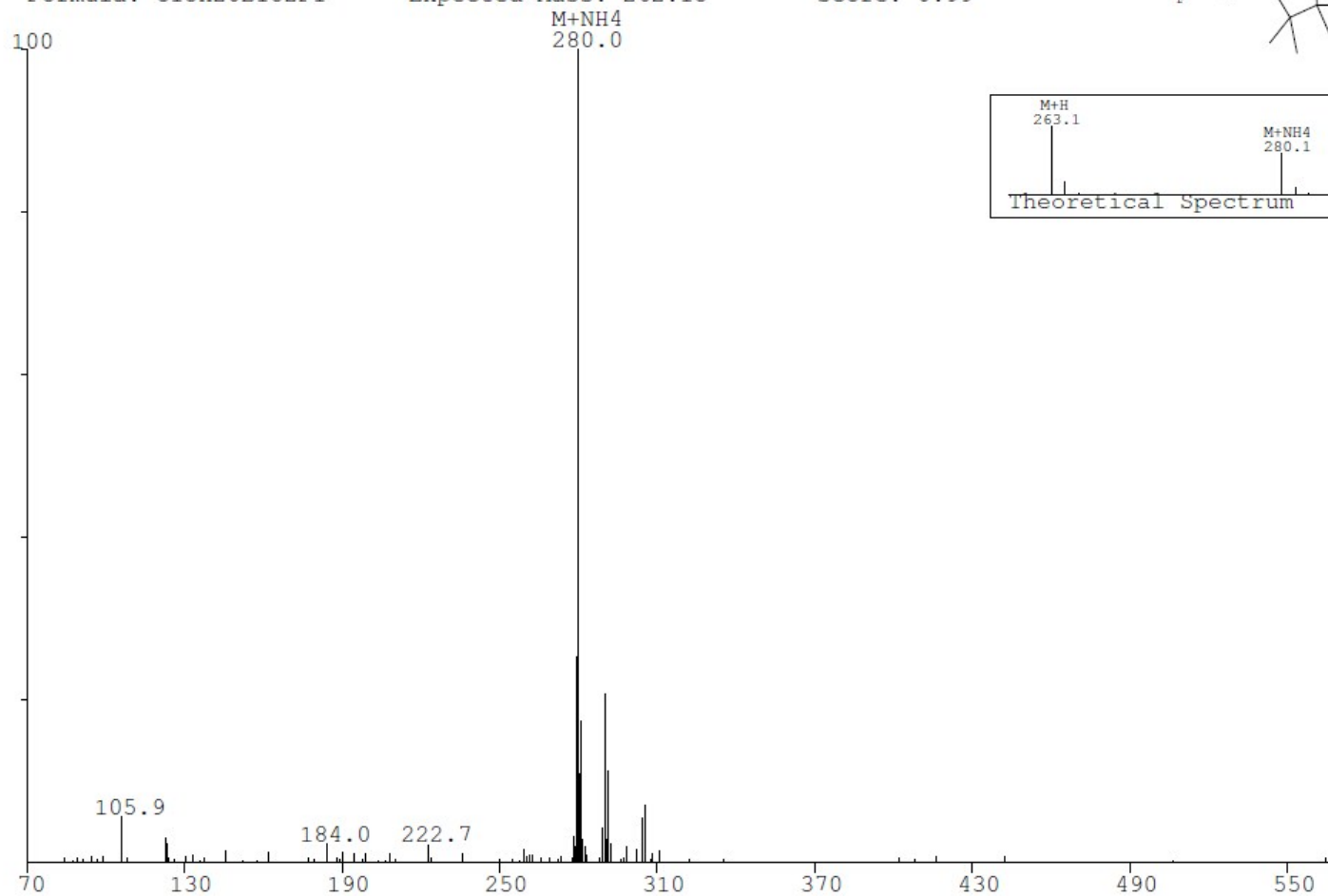
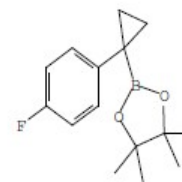
Software: MSProcess 6.14

File: as11123y (18-May-2016 09:39:41)
Samp: ██████████ N MS-as11123
Cmnt: DSQII/LC869889 DCI/NH3
Mode: +DCI Oper: PPDR4181
Base: 280.08 Intensity: 93178
Formula: C15H20B102F1 Expected Mass: 262.15

Scan: 23>25

Client:

Score: 0.99



Date: Wed May 18 09:51:31 2016

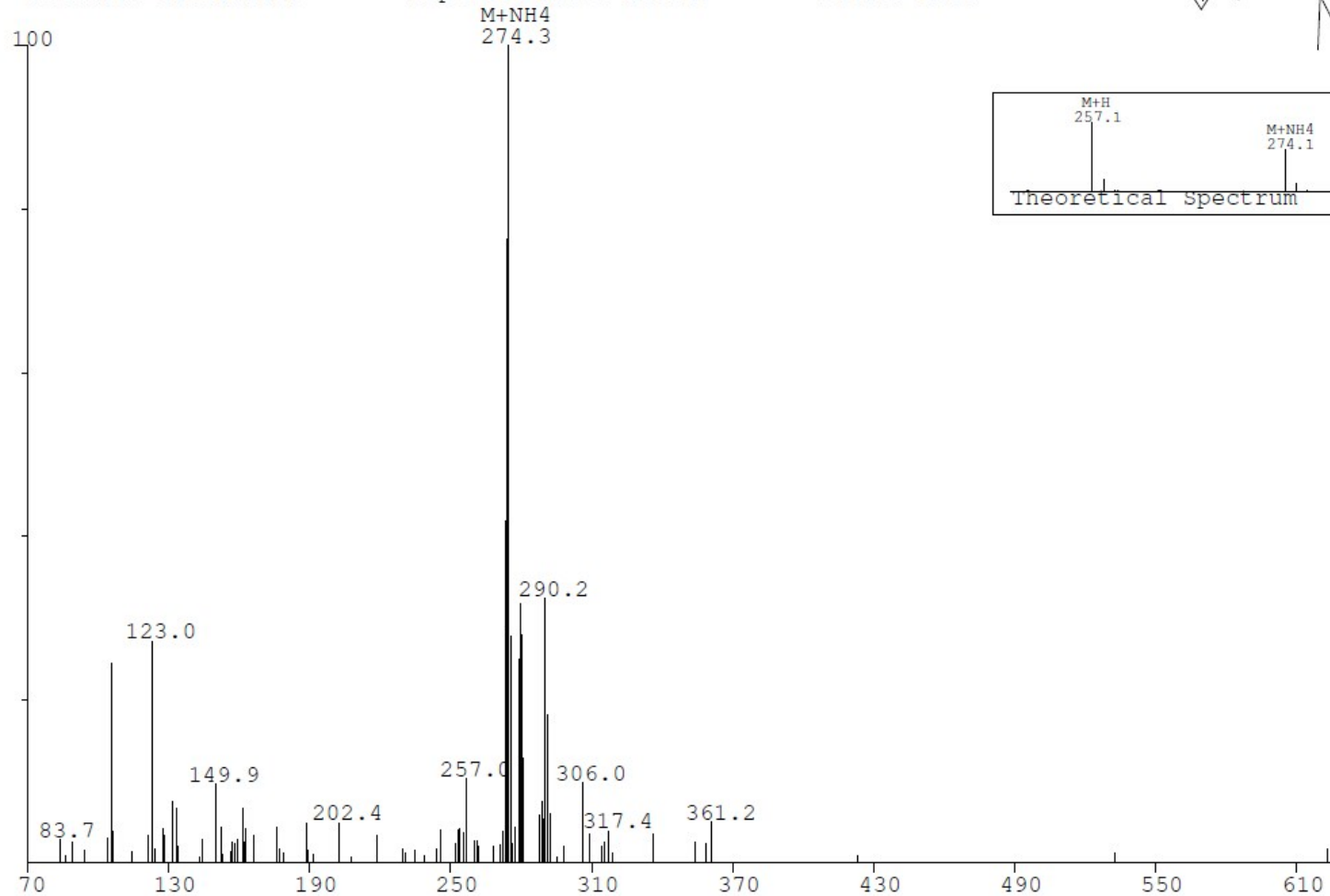
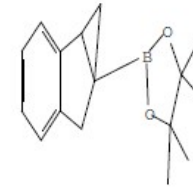
Software: MSProcess 6.14

File: as11125y (18-May-2016 09:44:13)
Samp: ██████████ MS-as11125
Cmnt: DSQII/LC869889 DCI/NH3
Mode: +DCI Oper: PPDR4181
Base: 274.30 Intensity: 22959
Formula: C16H21B1O2 Expected Mass: 256.16

Scan: 27>29

Client:

Score: 1.00



Date: Wed May 18 09:51:36 2016

Software: MSProcess 6.14