

Supporting Information for:

Regio- and stereoselective copper-catalyzed β -borylation of allenates by a preactivated diboron

*Steven B. Thorpe, Xi Guo and Webster L. Santos**

Department of Chemistry, Virginia Tech, Blacksburg, VA 24061

General methods	S2
Instrumentation	S2
Optimization of the catalyzed β-boration of ethyl 2,3-butadienoate	S2
Representative procedure for the β-boration of substrates 1a-1l	S3
Characterization of compounds 3a-3l	S3
Preparation of allenates	S7
Procedure for Suzuki-Miyaura cross-coupling	S9
References	S9
^1H, ^{13}C and ^{11}B NMR spectra for compounds 3a-3l	S10
Examples of 1D NOESY experiments	S47
^1H and ^{13}C NMR spectra for compound 9	S49

Abbreviations: ACN: acetonitrile; DCM: dichloromethane, THF: tetrahydrofuran; TFE: 2,2,2-trifluoroethanol.

General methods:

All reactions were carried out in oven-dried glassware under a nitrogen atmosphere using standard Schlenk techniques, unless otherwise noted. THF, DCM, ACN and DMF were prepared using an Innovative Technology Pure Solv-MD solvent purification system. CuCl, bis(pinacolato)diboron, ethyl 2,3-butadienoate, and other commercial catalysts and substrates were purchased and used as received. PDIPA diboron was synthesized as previously reported.¹ TLC analyses were performed using EMD silica gel 60 F₂₅₄ plates and spots were visualized with permanganate stain.

Instrumentation:

¹H NMR spectra were recorded on either a JEOL EclipsePlus-500 (500 MHz) or a Varian Inova-400 (400 MHz) spectrometer. Chemical shifts are reported in ppm with the solvent resonance as the internal standard (CDCl₃: 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz), and assignment. ¹³C NMR spectra were recorded on a JEOL EclipsePlus-500 (125 MHz) spectrometer. Chemical shifts are reported in ppm with the solvent resonance as the internal standard (CDCl₃: 77.16 ppm). The carbon directly attached to boron was not observed due to quadrupolar relaxation. ¹¹B NMR spectra were recorded on a JEOL EclipsePlus-500 (160 MHz) spectrometer. Chemical shifts are reported in ppm with boron trifluoride diethyl etherate as an external standard (BF₃O(C₂H₅)₂: 0 ppm). High resolution mass spectra (HRMS) were performed on an Agilent LC-ESI-TOF. Gas chromatography (GC) analyses were performed on a Hewlett Packard 6890 Series GC system coupled to a HP 5973 Mass Selective Detector. The column was an Agilent DB-5MS with a length of 60 m, I.D. of 260 μm, and film thickness of 0.26 μm. The general method consisted of a splitless injection, holding the oven temperature at 60°C for 5 minutes, ramping the temperature at a rate of 25°C/min to 300°C, and holding for an additional 10 minutes. The total run time was 24.60 minutes.

Optimization of the catalyzed β-boration of ethyl-2,3-butadienoate:

Method 1 (Entry 1). 1,3-Dimethylimidazolium-2-carboxylate (2.5 mg, 0.018 mmol) and copper(I) chloride (1.8 mg, 0.018 mmol) were added to a 10 mL, 2-neck, round-bottomed flask. ACN (2 ml) was added and the reaction was stirred for 15 min. Bis(pinacolato)diboron (100 mg, 0.394 mmol) in ACN (2 ml) was added, followed by ethyl 2,3-butadienoate (0.042 ml, 0.358 mmol) and the black reaction mixture was stirred at room temperature for 2 hours.²

Method 2 (Entry 2). 1,3-dicyclohexylimidazolium tetrafluoroborate (5.7 mg, 0.018 mmol), sodium tert-butoxide (3.4 mg, 0.036 mmol) and copper(I) chloride (1.8 mg, 0.018 mmol) were added to a 10 mL, 2-neck, round-bottomed flask. THF (3 ml) was added and the reaction was stirred for 2.5 hours. Bis(pinacolato)diboron (100 mg, 0.392 mmol) in THF (1 ml) was added

via syringe. After 10 minutes, ethyl 2,3-butadienoate (0.041 ml, 0.357 mmol) was added and the reaction was stirred at room temperature for 2 hours.³

Method 3 (Entries 3-8). Copper(I) chloride (3.5 mg, 0.036 mmol) was added to a 10 mL, 2-neck, round-bottomed flask fitted with a reflux condenser (for entries 5-6, NaO^tBu and DPEphos were also added at this time). DCM (0.5 ml) was added and the reaction was stirred for 2 min. PDIPA diboron (115 mg, 0.428 mmol) in DCM (4 ml) was injected via syringe. After 10 minutes, ethyl 2,3-butadienoate (0.041 ml, 0.357 mmol) was added and the reaction was stirred at reflux for 2 hours (for entries 3 and 7, TFE was added directly after the allenolate).

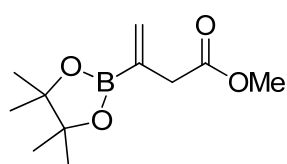
Method 4 (Entries 9-18). Copper(I) chloride (3.5 mg, 0.036 mmol) and PDIPA diboron (115 mg, 0.428 mmol) were added to a 10 mL, 2-neck, round-bottomed flask fitted with a reflux condenser. THF (4.5 ml) was added (for entry 9, DMF was used instead). After 10 minutes, ethyl 2,3-butadienoate (0.041 ml, 0.357 mmol) was added and the reaction was stirred at the indicated temperature for 2 hours. For entries 12-18, copper(I) chloride was substituted for the indicated catalyst.

Representative procedure for the β -boration of substrates 1a-1l:

Copper(I) chloride (3.53 mg, 0.036 mmol) and PDIPA diboron (115 mg, 0.428 mmol) were added to a 10 mL, 2-neck, round-bottomed flask and purged with vacuum / nitrogen. THF (2.5 ml) was added and the suspension was stirred for 5 min, producing a black mixture. Ethyl 2,3-butadienoate (40 mg, 0.357 mmol) dissolved in THF (0.5 ml) was added, washing once more with THF (0.5 ml), and the reaction was stirred at room temperature and followed by TLC until the starting material was gone (typically 2-3 hours). The contents were then filtered through celite, washing with diethyl ether, and concentrated by rotary evaporation. Compounds **3a**, **b**, **g**, **h**, **i**, and **j** were purified by vacuum distillation and compounds **3c**, **d**, **e**, **f**, and **k** were purified by flash chromatography on silica gel.

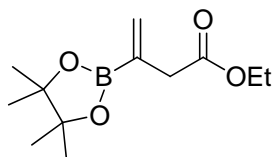
Characterization of compounds 3a-3l:

Methyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-enoate (**3a**):



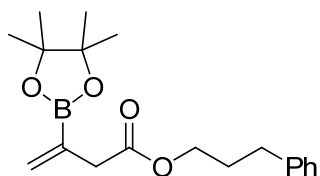
Colorless oil; ¹H NMR (500 MHz, CDCl₃) δ 5.89 (d, J = 2.9 Hz, 1H), 5.69 (s, 1H), 3.66 (s, 3H), 3.19 (s, 2H), 1.26 (d, J = 4.7 Hz, 12H); ¹³C NMR (126 MHz) δ 172.75, 132.02, 83.89, 51.81, 40.62, 24.81; ¹¹B NMR (160 MHz) δ 29.58; HRMS (ESI⁺): Calcd for C₁₁H₂₀BO₄ [M+H]⁺: 227.1449, Found 227.1444; Calcd for C₁₁H₂₃BNO₄ [M+NH₄]⁺: 244.1715, Found: 244.1718; TLC: 1:9 / EtOAc:Hexanes, R_f 0.28.

Ethyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-enoate (3b):



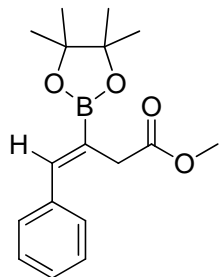
Colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 5.89 (d, $J = 2.9$ Hz, 1H), 5.69 (s, 1H), 4.12 (q, $J = 7.1$ Hz, 2H), 3.17 (s, 2H), 1.26 (s, 12H), 1.25 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (126 MHz) δ 172.35, 131.94, 83.85, 60.60, 40.84, 24.78, 14.38; ^{11}B NMR (160 MHz) δ 29.57; HRMS (ESI+): Calcd for $\text{C}_{12}\text{H}_{22}\text{BO}_4$ $[\text{M}+\text{H}]^+$: 241.1606, Found: 241.1600; Calcd for $\text{C}_{12}\text{H}_{21}\text{BNaO}_4$ $[\text{M}+\text{Na}]^+$: 263.1425, Found: 263.1435; TLC: 1:9 / EtOAc:Hexanes, R_f 0.35.

3-Phenylpropyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-enoate (3c):



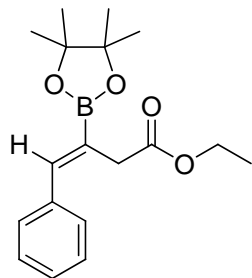
Light yellow oil; ^1H NMR (500 MHz, CDCl_3) δ 7.30 – 7.26 (m, 2H), 7.21 – 7.17 (m, 3H), 5.92 (d, $J = 2.9$ Hz, 1H), 5.71 (s, 1H), 4.10 (t, $J = 6.6$ Hz, 2H), 3.19 (s, 2H), 2.68 (t, $J = 7.6$ Hz, 2H), 1.99 – 1.92 (m, 2H), 1.26 (s, 12H); ^{13}C NMR (126 MHz) δ 172.40, 141.44, 132.10, 128.57, 128.56, 126.11, 83.88, 63.94, 40.68, 32.27, 30.41, 24.86; ^{11}B NMR (160 MHz) δ 29.69; HRMS (ESI+): Calcd for $\text{C}_{19}\text{H}_{28}\text{BO}_4$ $[\text{M}+\text{H}]^+$: 331.2075, Found: 331.2083; Calcd for $\text{C}_{19}\text{H}_{27}\text{BNaO}_4$ $[\text{M}+\text{Na}]^+$: 353.1895, Found: 353.1917; TLC: 1:9 / EtOAc:Hexanes, R_f 0.34.

(Z)-Methyl 4-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-enoate (3d):



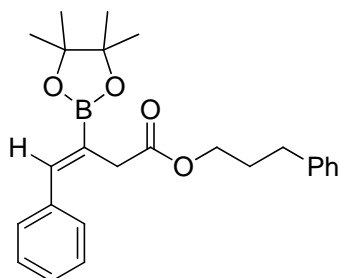
Light yellow oil; ^1H NMR (500 MHz, CDCl_3) δ 7.41 – 7.26 (m, 6H), 3.68 (s, 3H), 3.41 (d, $J = 1.3$ Hz, 2H), 1.30 (s, 12H); ^{13}C NMR (126 MHz) δ 173.01, 144.35, 137.03, 129.03, 128.41, 127.77, 83.92, 51.91, 35.10, 24.86; ^{11}B NMR (160 MHz) δ 30.19; HRMS (ESI+): Calcd for $\text{C}_{17}\text{H}_{24}\text{BO}_4$ $[\text{M}+\text{H}]^+$: 303.1762, Found: 303.1779; Calcd for $\text{C}_{17}\text{H}_{23}\text{BNaO}_4$ $[\text{M}+\text{Na}]^+$: 325.1582, Found: 325.1596; TLC: 1:9 / EtOAc:Hexanes, R_f 0.31.

(Z)-Ethyl 4-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-enoate (3e):



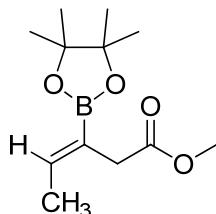
Light yellow oil; ^1H NMR (500 MHz, CDCl_3) δ 7.41 – 7.27 (m, 6H), 4.14 (q, $J = 7.1$ Hz, 2H), 3.39 (d, $J = 1.3$ Hz, 2H), 1.31 (s, 12H), 1.25 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (126 MHz) δ 174.18, 144.28, 137.11, 129.06, 128.38, 127.72, 83.88, 60.68, 35.33, 24.89, 14.39; ^{11}B NMR (160 MHz) δ 30.20; HRMS (ESI+): Calcd for $\text{C}_{18}\text{H}_{26}\text{BO}_4$ $[\text{M}+\text{H}]^+$: 317.1924, Found: 317.1883; Calcd for $\text{C}_{18}\text{H}_{25}\text{BNaO}_4$ $[\text{M}+\text{Na}]^+$: 339.1738, Found: 339.1713; TLC: 1:9 / EtOAc:Hexanes, R_f 0.33.

(Z)-3-Phenylpropyl 4-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-enoate (3f):



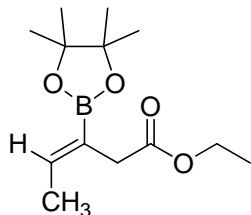
Light yellow oil; ^1H NMR (500 MHz, CDCl_3) δ 7.43 – 7.14 (m, 11H), 4.11 (t, $J = 6.5$ Hz, 2H), 3.41 (s, 2H), 2.68 (t, $J = 7.7$ Hz, 2H), 2.00 – 1.90 (m, 2H), 1.30 (s, 12H); ^{13}C NMR (126 MHz) δ 172.64, 144.47, 141.42, 137.13, 129.06, 128.58, 128.55, 128.42, 127.78, 126.10, 83.91, 63.98, 35.27, 32.25, 30.43, 24.91; ^{11}B NMR (160 MHz) δ 30.19; HRMS (ESI+): Calcd for $\text{C}_{25}\text{H}_{32}\text{BO}_4$ $[\text{M}+\text{H}]^+$: 407.2388, Found: 407.2416; Calcd for $\text{C}_{25}\text{H}_{31}\text{BKO}_4$ $[\text{M}+\text{K}]^+$: 445.1947, Found: 445.1961; TLC: 1:9 / EtOAc:Hexanes, R_f 0.31.

(Z)-Methyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-3-enoate (3g):



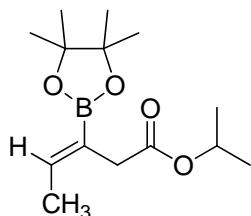
Colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 6.56 (q, $J = 6.8$, 1H), 3.65 (s, 3H), 3.20 (s, 2H), 1.73 (d, $J = 6.8$ Hz, 3H), 1.25 (s, 12H); ^{13}C NMR (126 MHz) δ 172.90, 143.21, 83.55, 51.77, 33.53, 24.83, 14.70; ^{11}B NMR (160 MHz) δ 30.12; HRMS (ESI+): Calcd for $\text{C}_{12}\text{H}_{22}\text{BO}_4$ $[\text{M}+\text{H}]^+$: 241.1606, Found: 241.1618; Calcd for $\text{C}_{12}\text{H}_{21}\text{BNaO}_4$ $[\text{M}+\text{Na}]^+$: 263.1425, Found: 263.1440; TLC: 1:9 / EtOAc:Hexanes, R_f 0.33.

(Z)-Ethyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-3-enoate (3h):



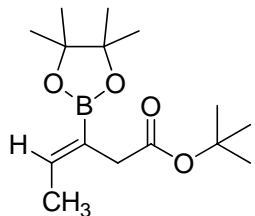
Colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 6.56 (q, $J = 6.8$ Hz, 1H), 4.10 (q, $J = 7.1$ Hz, 2H), 3.18 (s, 2H), 1.73 (t, $J = 5.0$ Hz, 3H), 1.25 – 1.22 (m, 15H); ^{13}C NMR (126 MHz) δ 172.47, 143.17, 83.51, 60.49, 33.79, 24.85, 14.72, 14.37; ^{11}B NMR (160 MHz) δ 29.98; HRMS (ESI+): Calcd for $\text{C}_{13}\text{H}_{24}\text{BO}_4$ $[\text{M}+\text{H}]^+$: 255.1762, Found: 255.1753; Calcd for $\text{C}_{13}\text{H}_{23}\text{BNaO}_4$ $[\text{M}+\text{Na}]^+$: 277.1582, Found: 277.1589; TLC: 1:9 / EtOAc:Hexanes, R_f 0.34.

(Z)-Isopropyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-3-enoate (3i):



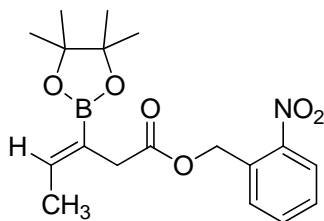
Colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 6.58 – 6.51 (m, 1H), 4.96 (m, 1H), 3.13 (s, 2H), 1.73 (d, $J = 6.8$ Hz, 3H), 1.24 (s, 12H), 1.20 (d, $J = 6.3$ Hz, 6H); ^{13}C NMR (126 MHz) δ 172.02, 143.14, 83.49, 67.66, 34.09, 24.87, 21.96, 14.72; ^{11}B NMR (160 MHz) δ 30.01; HRMS (ESI+): Calcd for $\text{C}_{14}\text{H}_{26}\text{BO}_4$ $[\text{M}+\text{H}]^+$: 269.1919, Found: 269.1893; TLC: 1:9 / EtOAc:Hexanes, R_f 0.37.

(Z)-Tert-butyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-3-enoate (3j):



Colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 6.56 – 6.51 (m, 1H), 3.09 (s, 2H), 1.73 (d, $J = 6.8$ Hz, 3H), 1.42 (s, 9H), 1.24 (s, 12H); ^{13}C NMR (126 MHz) δ 171.73, 142.73, 83.36, 80.01, 34.93, 28.14, 24.81, 14.64; ^{11}B NMR (160 MHz) δ 30.05; HRMS (ESI+): Calcd for $\text{C}_{15}\text{H}_{28}\text{BO}_4$ $[\text{M}+\text{H}]^+$: 283.2075, Found: 283.2081; Calcd for $\text{C}_{15}\text{H}_{27}\text{BNaO}_4$ $[\text{M}+\text{Na}]^+$: 305.1895, Found: 305.1894; TLC: 1:9 / EtOAc:Hexanes, R_f 0.44.

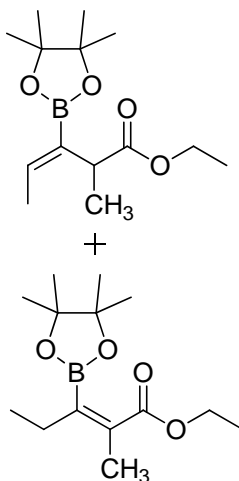
(Z)-2-Nitrobenzyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-3-enoate (3k):



Yellow oil; ^1H NMR (500 MHz, CDCl_3) δ 8.12 (d, $J = 8.4$ Hz, 1H), 7.63 (d, $J = 3.9$ Hz, 2H), 7.50 – 7.54 (m, 1H), 6.62 (q, $J = 7.0$ Hz, 1H), 5.53 (s, 2H), 3.32 (s, 2H), 1.77 (d, $J = 6.8$ Hz, 3H), 1.22 (s, 12H); ^{13}C NMR (126 MHz) δ 171.73, 147.7*, 144.01, 133.82, 128.74, 128.56, 125.14, 83.63, 62.91, 33.59, 24.86, 14.83; ^{11}B NMR (160 MHz) δ 29.88; HRMS (ESI+): Calcd for $\text{C}_{18}\text{H}_{25}\text{BNO}_6$ $[\text{M}+\text{H}]^+$: 362.1769, Found: 362.1746; Calcd for $\text{C}_{18}\text{H}_{24}\text{BNNaO}_6$ $[\text{M}+\text{Na}]^+$: 384.1589, Found: 384.1565; TLC: 1:4 / EtOAc:Hexanes, R_f 0.38.

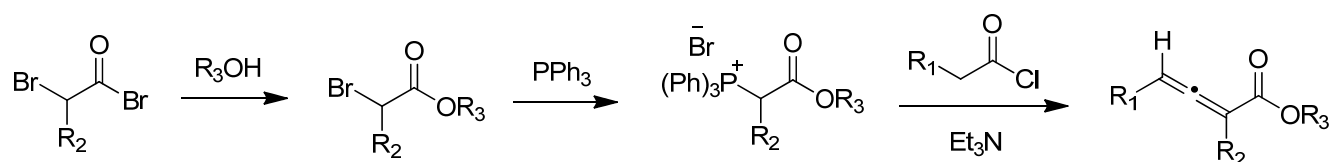
***Note:** The carbon directly attached to the nitro group was not observed in the normal ^{13}C spectrum. HMBC spectroscopy identified a peak at approximately 147.7 ppm, which shows multiple bond correlation to other signals from the aromatic ring. SEE S43.

(Z)-Ethyl 2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-3-enoate (3l):



Colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 6.45 (q, $J = 6.8$ Hz, 1H), 4.22 (q, $J = 7.1$ Hz, 0.5H), 4.17 – 4.04 (m, 2H), 3.47 (q, $J = 7.1$ Hz, 1H), 2.29 – 2.21 (m, 0.5H), 1.80 (s, 0.75H), 1.74 (d, $J = 6.8$ Hz, 3H), 1.34 (s, 3H), 1.30 – 1.19 (m, 22H), 1.05 (t, $J = 7.7$ Hz, 0.75H); ^{13}C NMR (126 MHz) δ 175.52, 171.14, 140.58, 131.66, 83.26, 83.20, 68.12, 61.55, 60.47, 38.89, 25.75, 25.13, 24.83, 16.62, 14.38, 14.25, 12.44, 11.77; ^{11}B NMR (160 MHz) δ 30.05; HRMS (ESI+): Calcd for $\text{C}_{14}\text{H}_{26}\text{BO}_4$ $[\text{M}+\text{H}]^+$: 269.1919, Found: 269.1924; Calcd for $\text{C}_{14}\text{H}_{25}\text{BNaO}_4$ $[\text{M}+\text{Na}]^+$: 291.1738, Found: 291.1737; TLC: 1:9 / EtOAc:Hexanes, R_f 0.34.

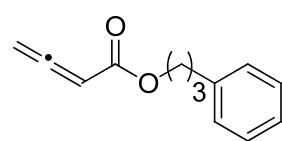
Preparation of allenates:



Allenates were prepared following a published procedure by Kwon, as described above.⁴ References for previously reported allenates are provided in the table below. Spectral data for unreported allenates follows.

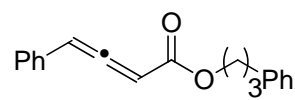
Substrate	R1	R2	R3	Reference
1a	H	H	Me	<i>J. Chem. Soc.(C)</i> 1969, 2443
1b	H	H	Et	Available from Sigma-Aldrich
1c	H	H	(CH ₂) ₃ C ₆ H ₅	Unknown in the literature
1d	Ph	H	Me	<i>Helv. Chim. Acta</i> 1980, 63 , 438
1e	Ph	H	Et	<i>J. Am. Chem. Soc.</i> 2007, 129 , 1494
1f	Ph	H	(CH ₂) ₃ C ₆ H ₅	Unknown in the literature
1g	Me	H	Me	<i>Helv. Chim. Acta</i> 1980, 63 , 438
1h	Me	H	Et	<i>Org. Synth.</i> 1990, Coll. Vol. 7 , 232
1i	Me	H	ⁱ Pr	Unknown in the literature
1j	Me	H	^t Bu	Unknown in the literature
1k	Me	H	<i>o</i> -nitrobenzyl	Unknown in the literature
1l	Me	Me	Et	<i>Helv. Chim. Acta</i> 1980, 63 , 438

3-Phenylpropyl buta-2,3-dienoate (1c):



Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ 7.29 (t, *J* = 7.5 Hz, 2H), 7.19 (m, *J* = 7.6 Hz, 3H), 5.65 (t, *J* = 6.5 Hz, 1H), 5.23 (d, *J* = 6.5 Hz, 2H), 4.17 (t, *J* = 6.5 Hz, 2H), 2.70 (t, *J* = 7.7 Hz, 2H), 2.03 – 1.96 (m, 2H); ¹³C NMR (126 MHz) δ 215.99, 165.89, 141.30, 128.58, 128.55, 126.15, 88.12, 79.40, 64.39, 32.20, 30.33; HRMS (APCI⁺): Calcd for C₁₃H₁₅O₂ [M+H]⁺: 203.1072, Found 203.1080; TLC: 1:9 / EtOAc:Hexanes, R_f 0.39.

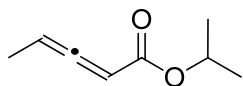
3-Phenylpropyl 4-phenylbuta-2,3-dienoate (1f):



Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ 7.48 – 7.13 (m, 10H), 6.64 (d, *J* = 6.4 Hz, 1H), 6.03 (d, *J* = 6.4 Hz, 1H), 4.20 (t, *J* = 6.4 Hz, 2H), 2.74 (t, *J* = 7.6 Hz, 2H), 2.06 - 1.94 (m, 2H); HRMS (APCI⁺): Calcd

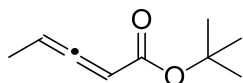
for C₁₉H₁₉O₂ [M+H]⁺: 279.1380, Found 279.1386; TLC: 1:9 / EtOAc:Hexanes, R_f 0.37.

Isopropyl penta-2,3-dienoate (1i):



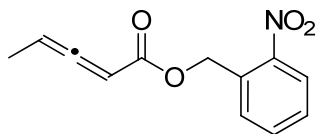
Colorless oil; ¹H NMR (500 MHz, CDCl₃) δ 5.61 – 5.51 (m, 1H), 5.11 – 4.99 (m, 1H), 3.19 (q, *J* = 2.6 Hz, 1H), 1.84 – 1.77 (m, 3H), 1.27 – 1.24 (m, 6H); HRMS (APCI⁺): Calcd for C₁₈H₁₃O₂ [M+H]⁺: 141.0910, Found 141.0909; TLC: 1:9 / EtOAc:Hexanes, R_f 0.45.

tert-butyl penta-2,3-dienoate (1j):



Colorless oil; ¹H NMR (500 MHz, CDCl₃) δ 5.61 – 5.44 (m, 1H), 3.14 (q, *J* = 2.5 Hz, 1H), 1.87 – 1.72 (m, 3H), 1.47 (d, *J* = 6.5 Hz, 9H); GC/MS (EI⁺): Calcd for C₉H₁₄O₂: 154, Found 154; TLC: 1:9 / EtOAc:Hexanes, R_f 0.50.

2-Nitrobenzyl penta-2,3-dienoate (1k):



White solid; ¹H NMR (500 MHz, CDCl₃) δ 8.12 (t, *J* = 7.6 Hz, 1H), 7.69 – 7.58 (m, 2H), 7.53 – 7.46 (m, 1H), 5.59 (d, *J* = 5.6 Hz, 2H), 3.34 (q, *J* = 2.5 Hz, 1H), 1.95 – 1.77 (m, 3H); HRMS (APCI⁺): Calcd for C₁₂H₁₂NO₄ [M+H]⁺: 234.0761, Found 234.0764; TLC: 1:4 / EtOAc:Hexanes, R_f 0.35.

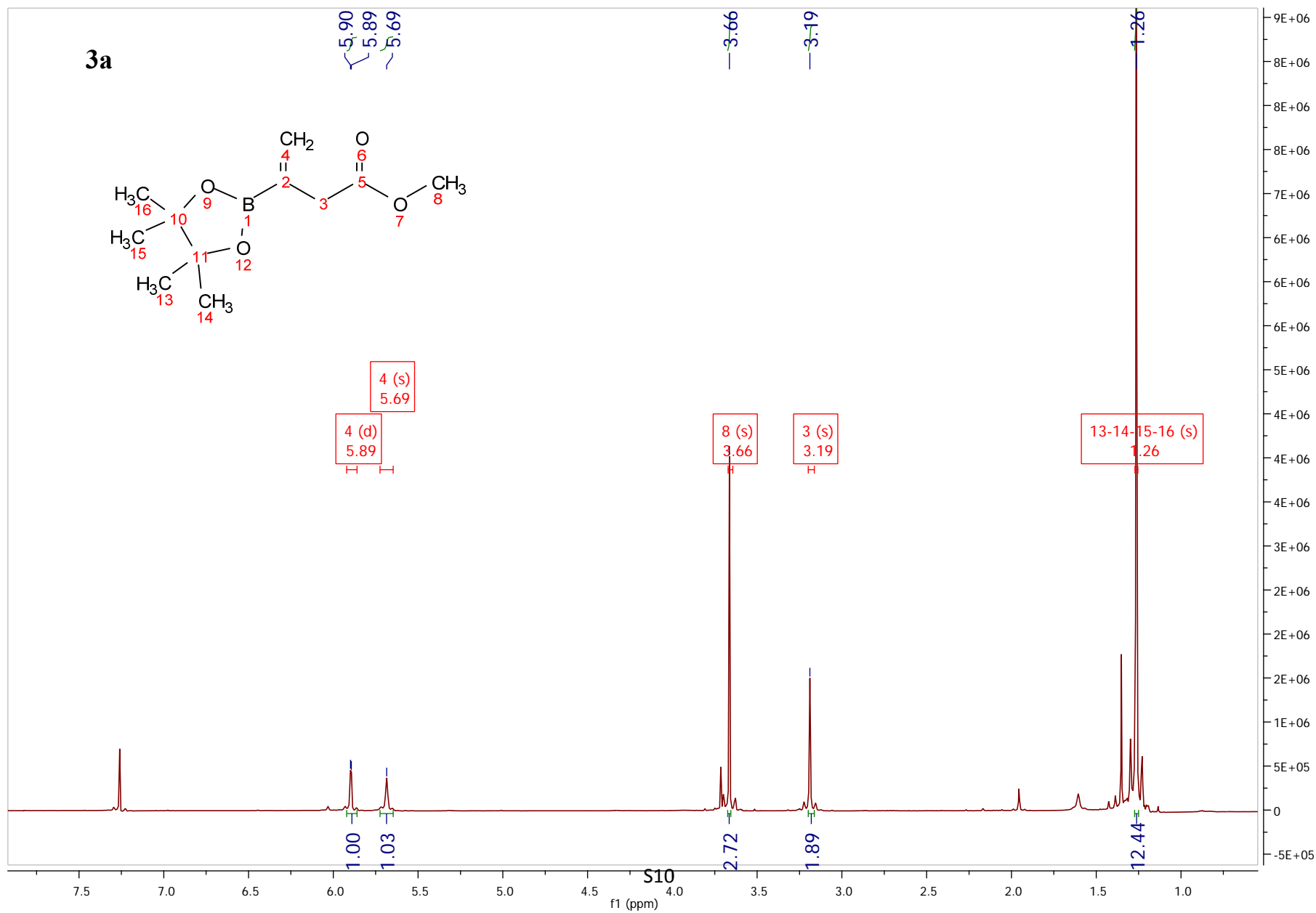
Procedure for Suzuki-Miyaura cross-coupling:

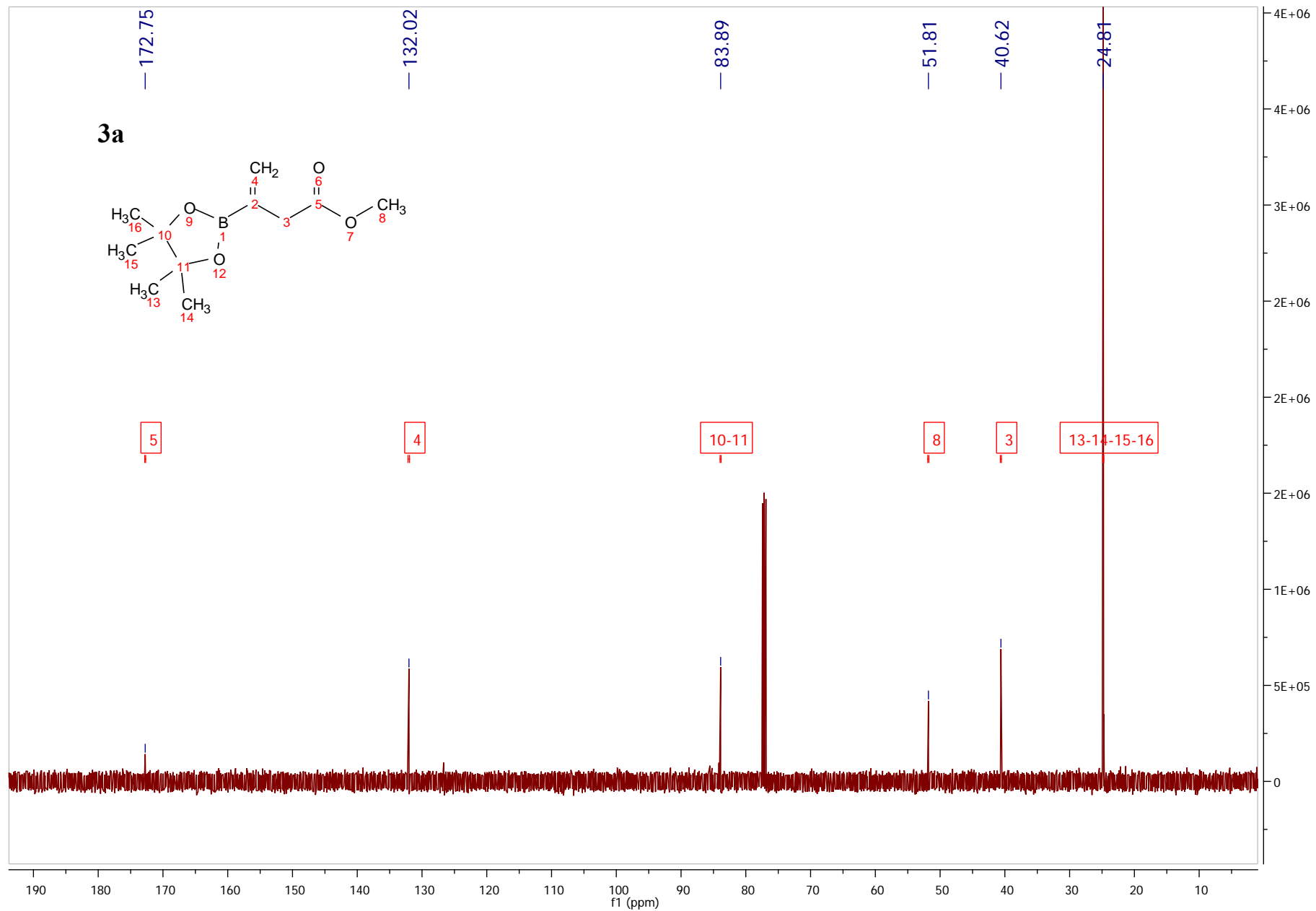
$\text{PdCl}_2(\text{PPh}_3)_2$ (4 mg, 0.05 equiv) and K_2CO_3 (28 mg, 2 equiv) were added to a 10 mL, 2-neck, round-bottomed flask fitted with a reflux condenser and purged several times with vacuum and nitrogen. DMF (2 ml) was added. Iodobenzene (22 μl , 2 equiv) followed by **3g** (24 mg, 1 equiv) dissolved in DMF (1 ml) was added, washing with additional DMF, and the reaction was heated to 90 °C and stirred for 18 hours. The crude mixture was diluted with diethyl ether (10 ml) and DMF was removed by washing with saturated LiBr (3 X 5 ml). The organic layer was dried over Na_2SO_4 , filtered, concentrated by rotary evaporation, and purified by flash chromatography on silica gel to afford **9** as a light yellow oil (19 mg, 100%). Spectral data is consistent with the literature⁵ and is provided below. TLC analysis was performed using 1:9 / EtOAc:Hexanes and the product $R_f = 0.42$.

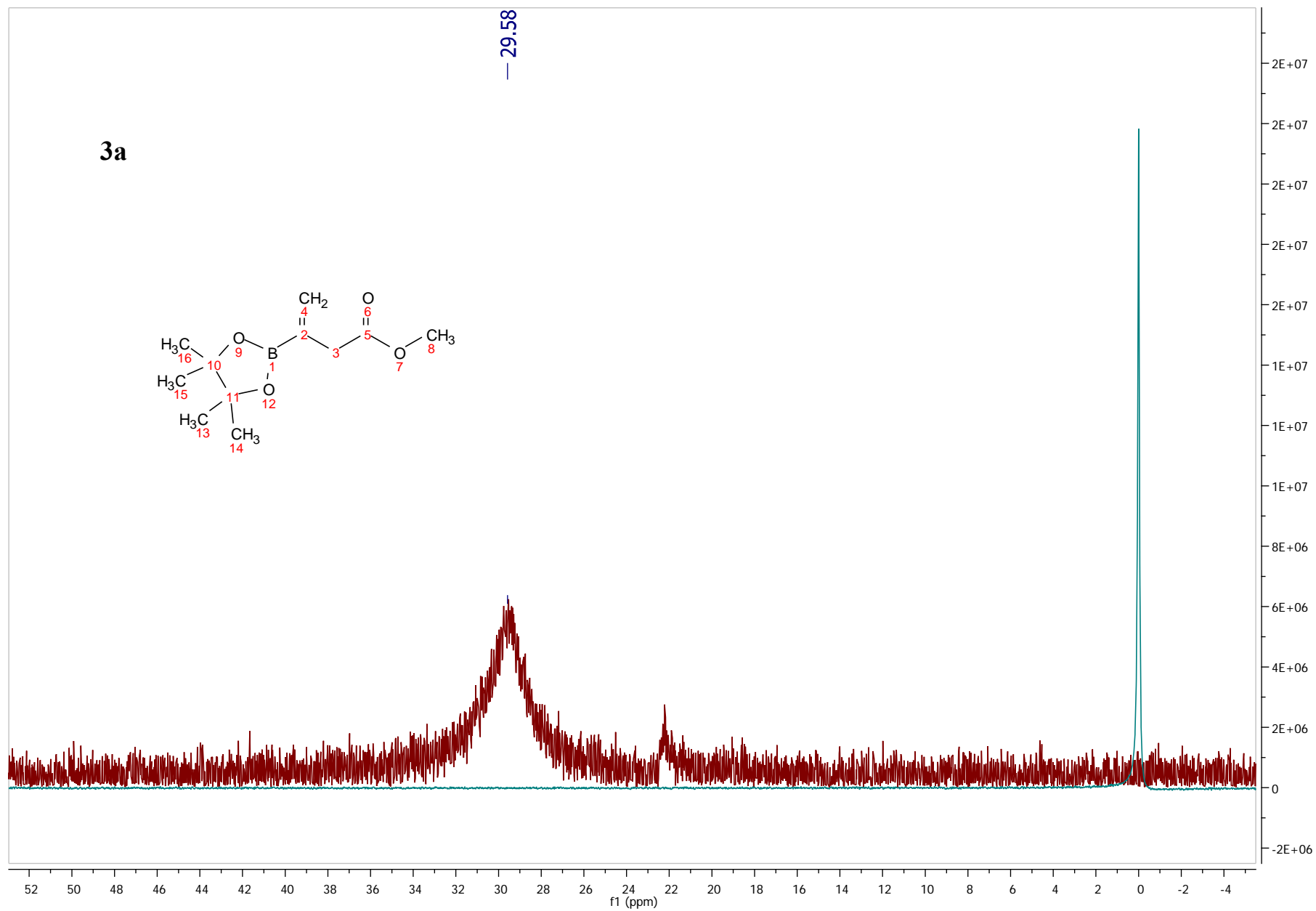
References:

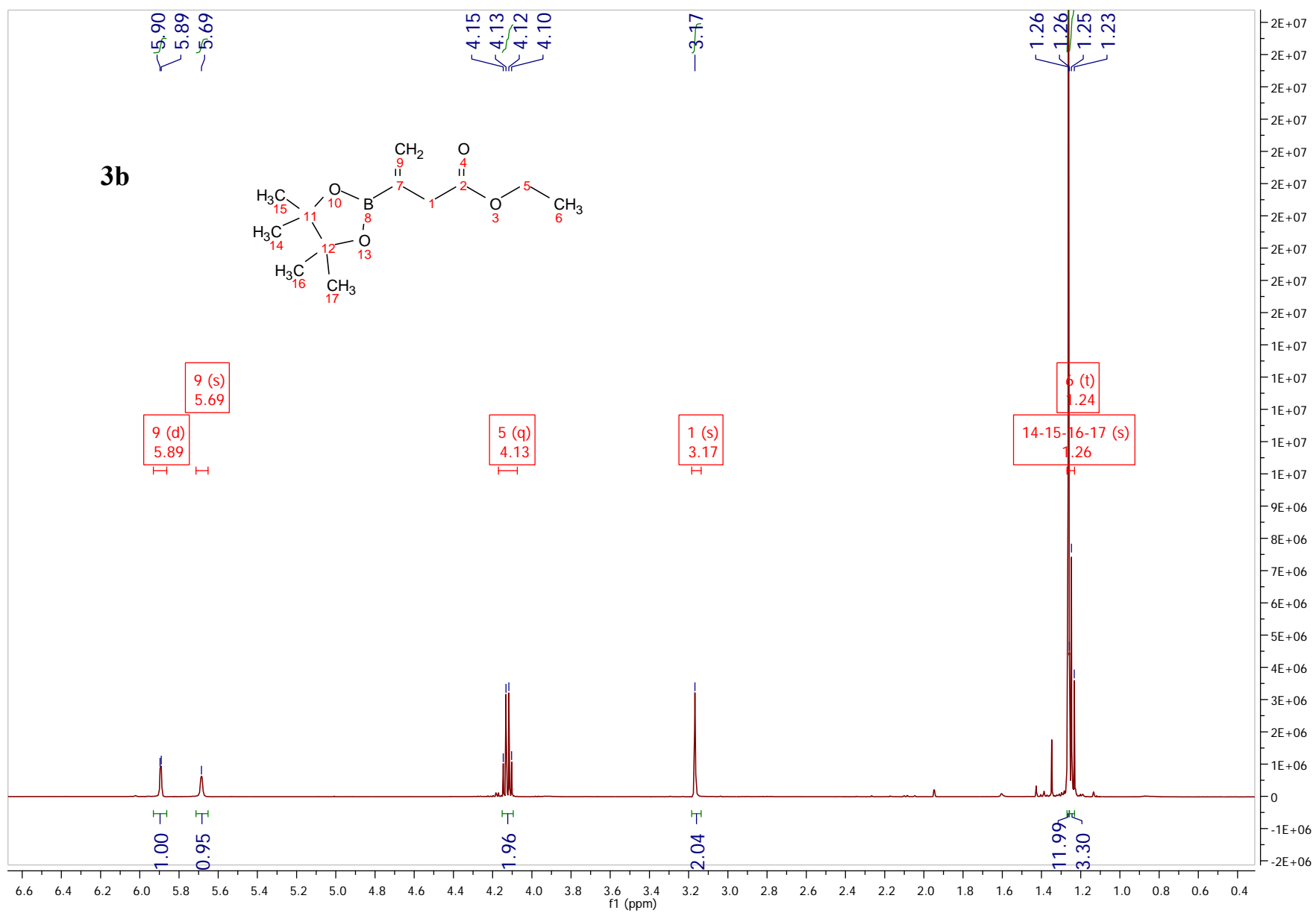
1. M. Gao, S. B. Thorpe and W. L. Santos, *Org. Lett.*, 2009, **11**, 3478.
2. A. M. Voutchkova, M. Feliz, E. Clot, O. Eisenstein and R. H. Crabtree, *J. Am. Chem. Soc.*, 2007, **129**, 12834.
3. D. S. Laitar, E. Y. Tsui and J. P. Sadighi, *J. Am. Chem. Soc.*, 2006, **128**, 11036.
4. X.-F. Zhu, C. E. Henry, J. Wang, T. Dudding and O. Kwon, *Org. Lett.*, 2005, **7**, 1387.
5. A. Oku, M. Abe and M. Iwamoto, *J. Org. Chem.*, 1994, **59**, 7445.

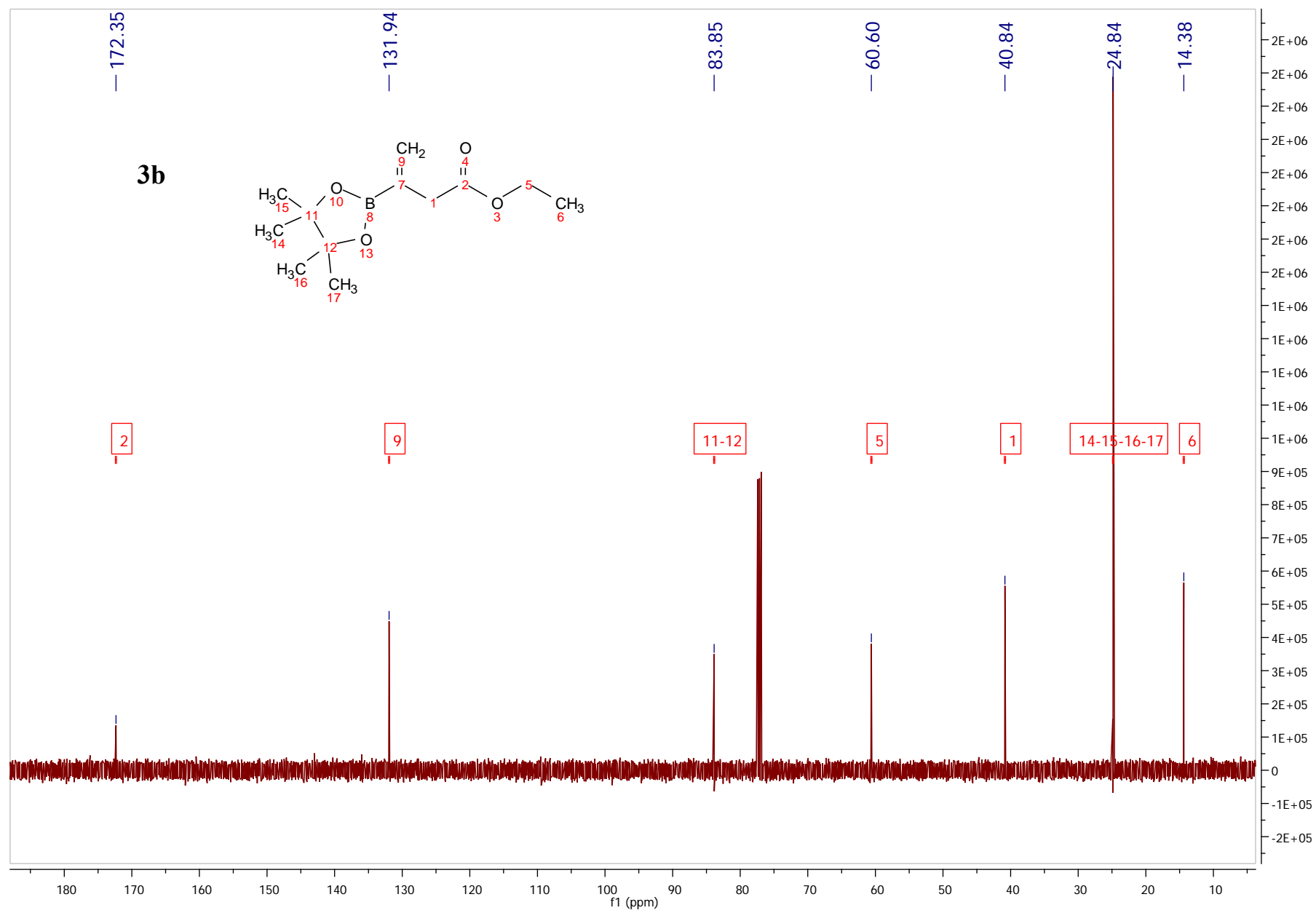
^1H , ^{13}C , and ^{11}B NMR spectra of compounds 3a-3l:

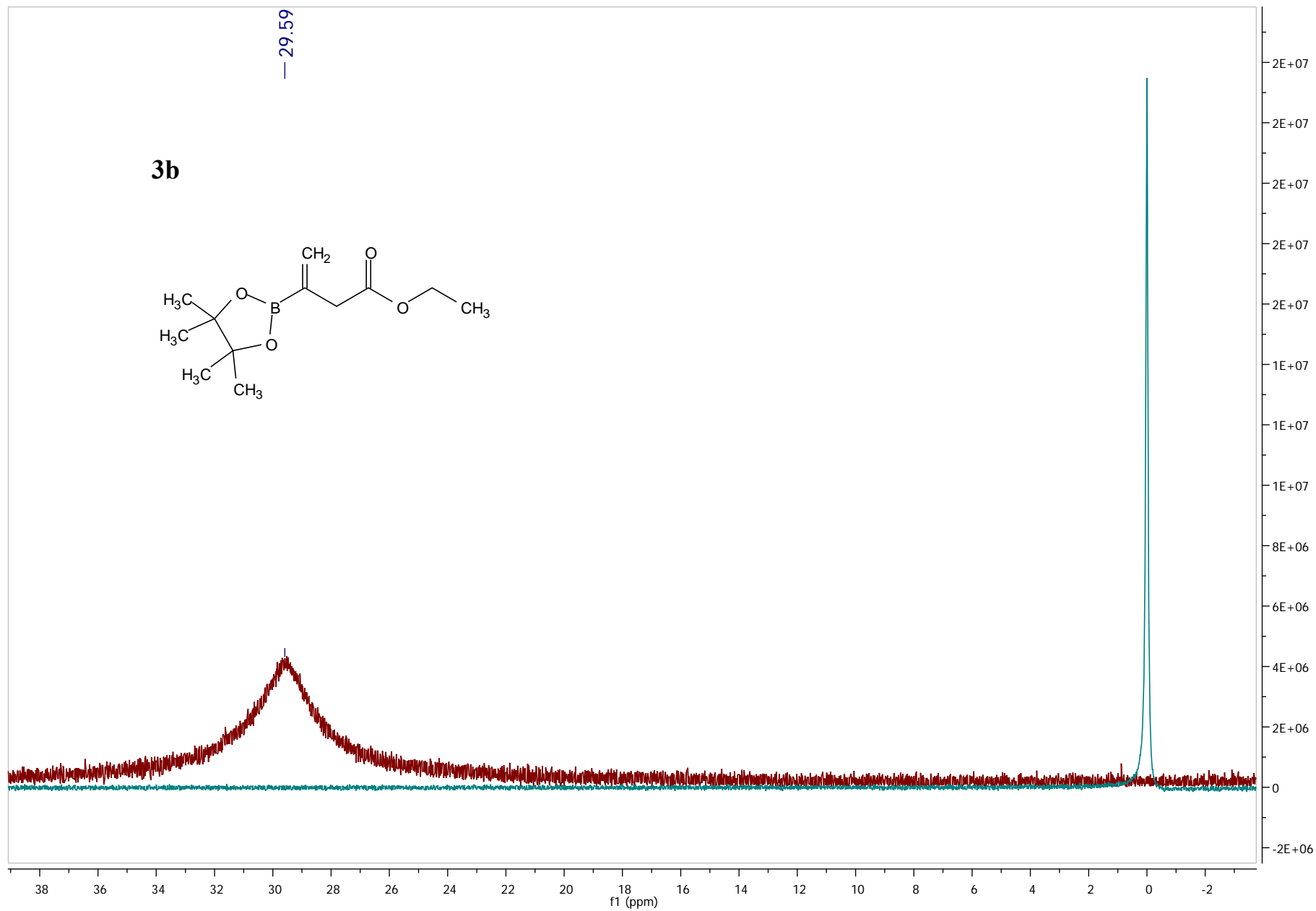


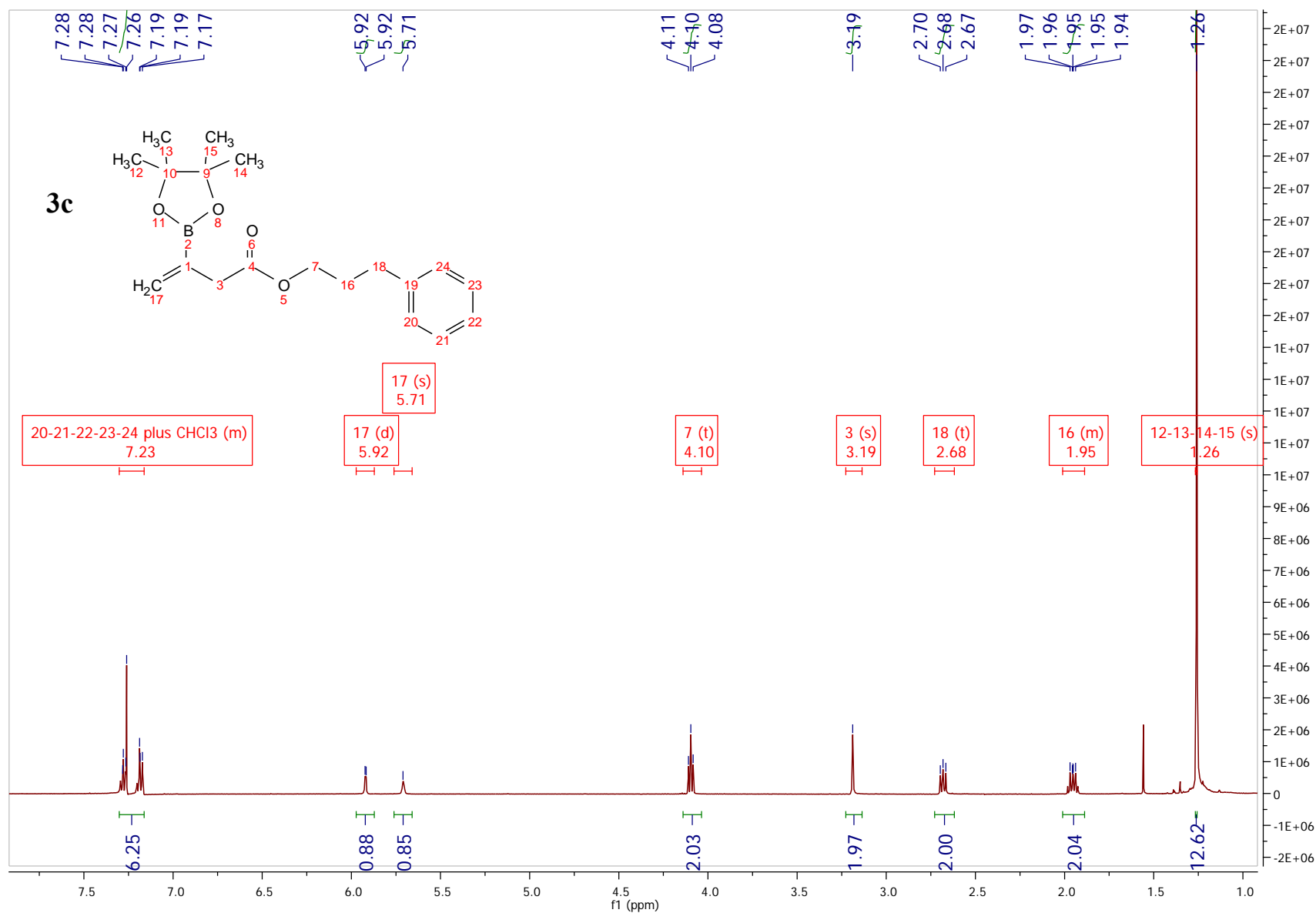


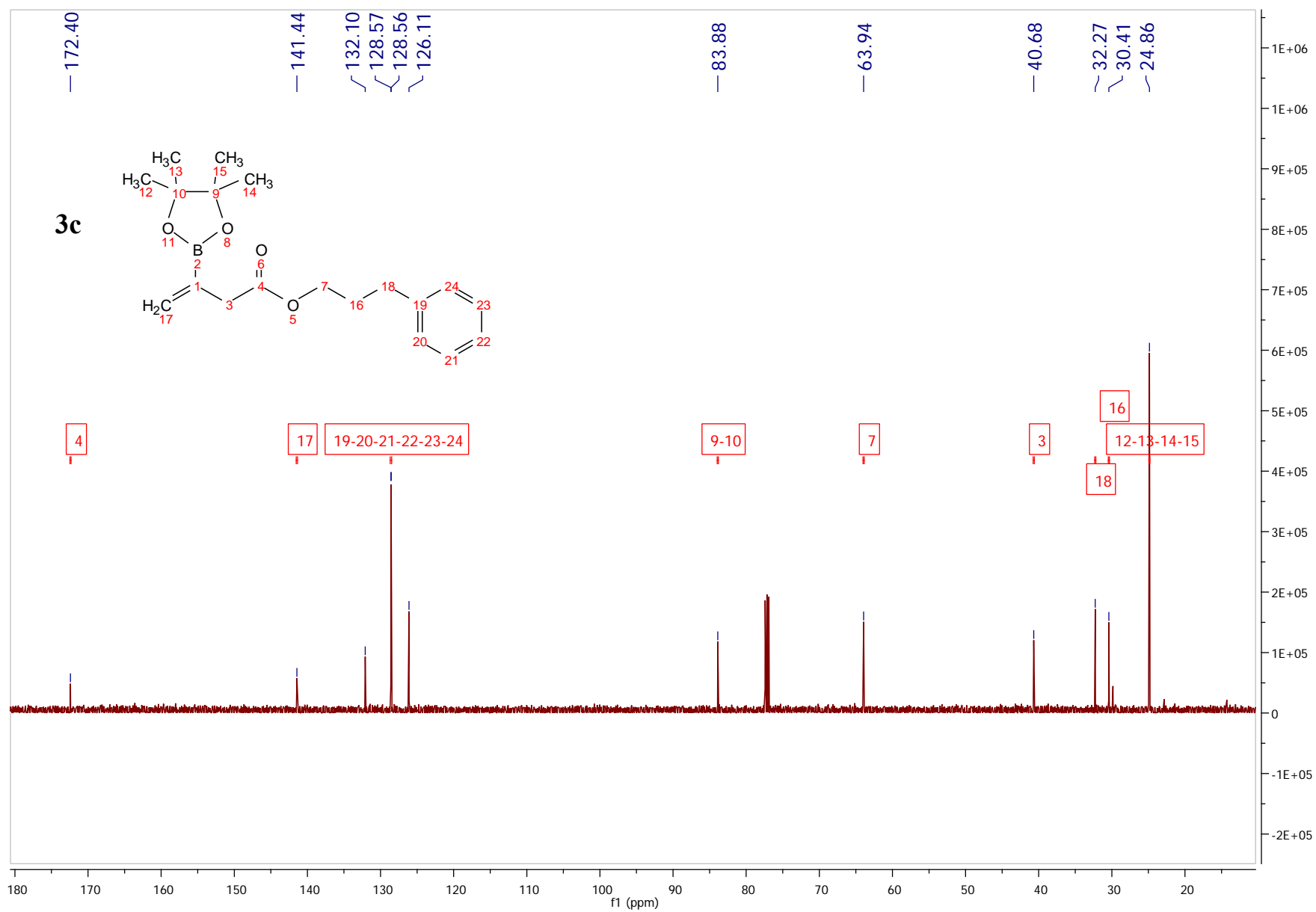


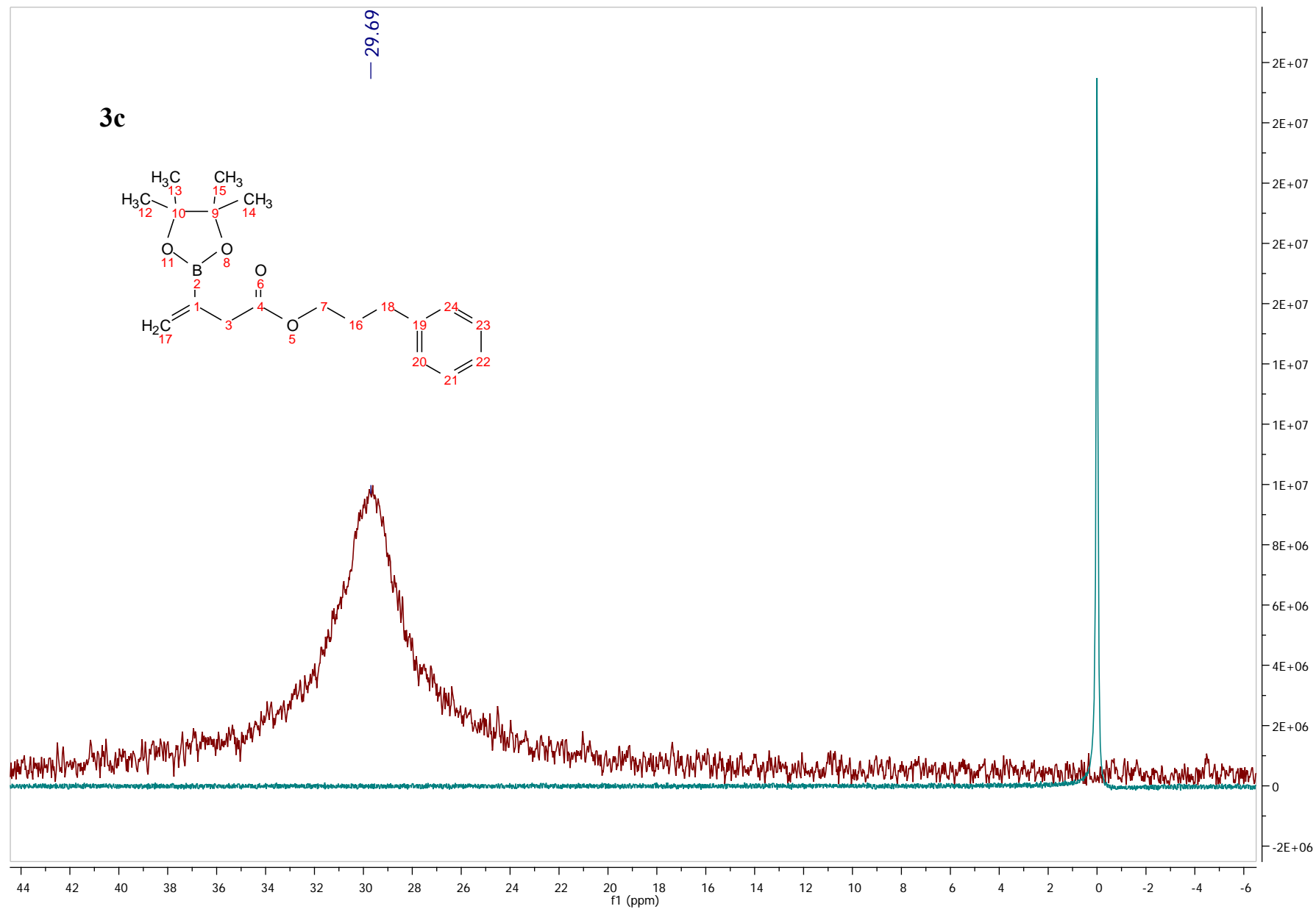


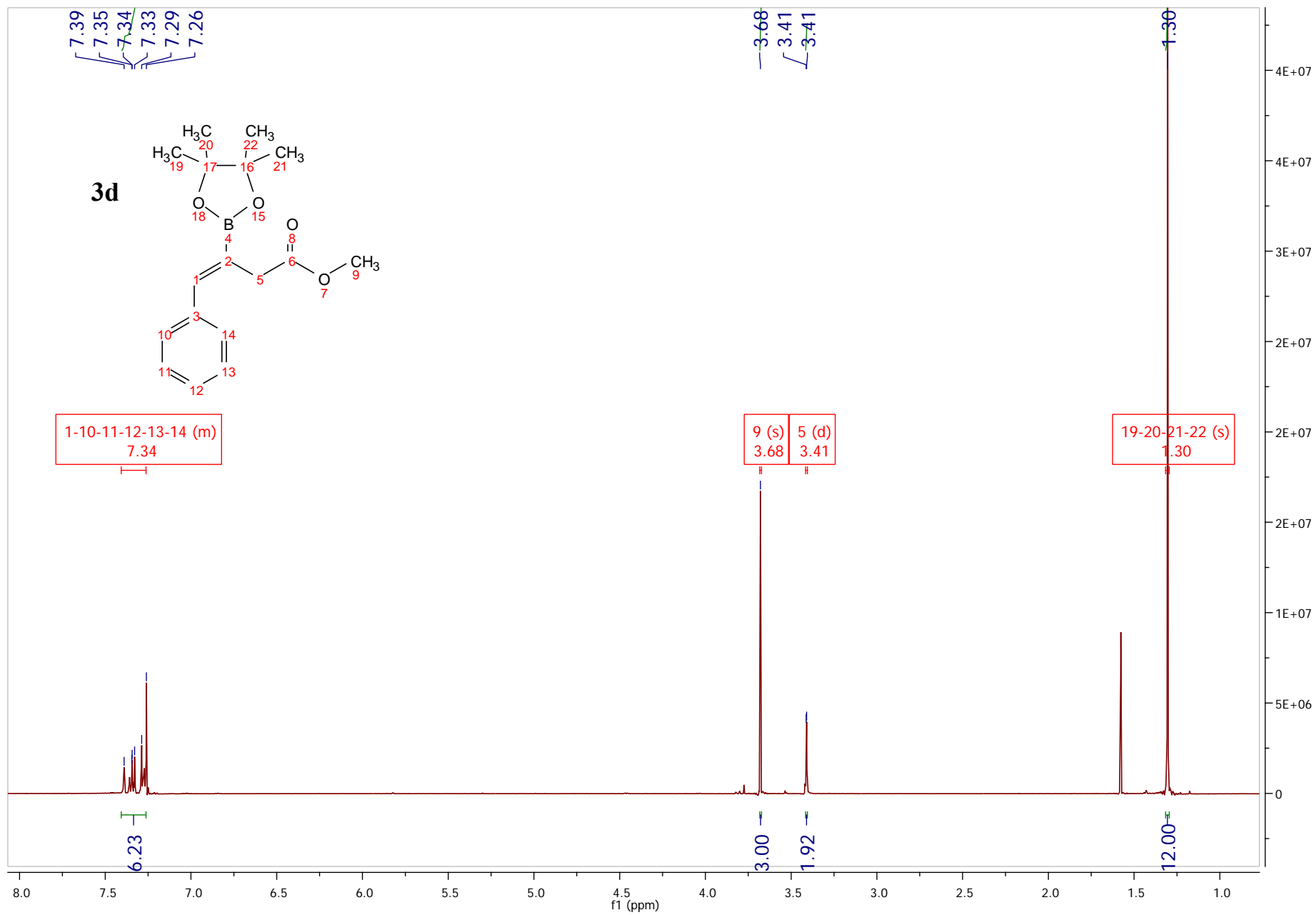


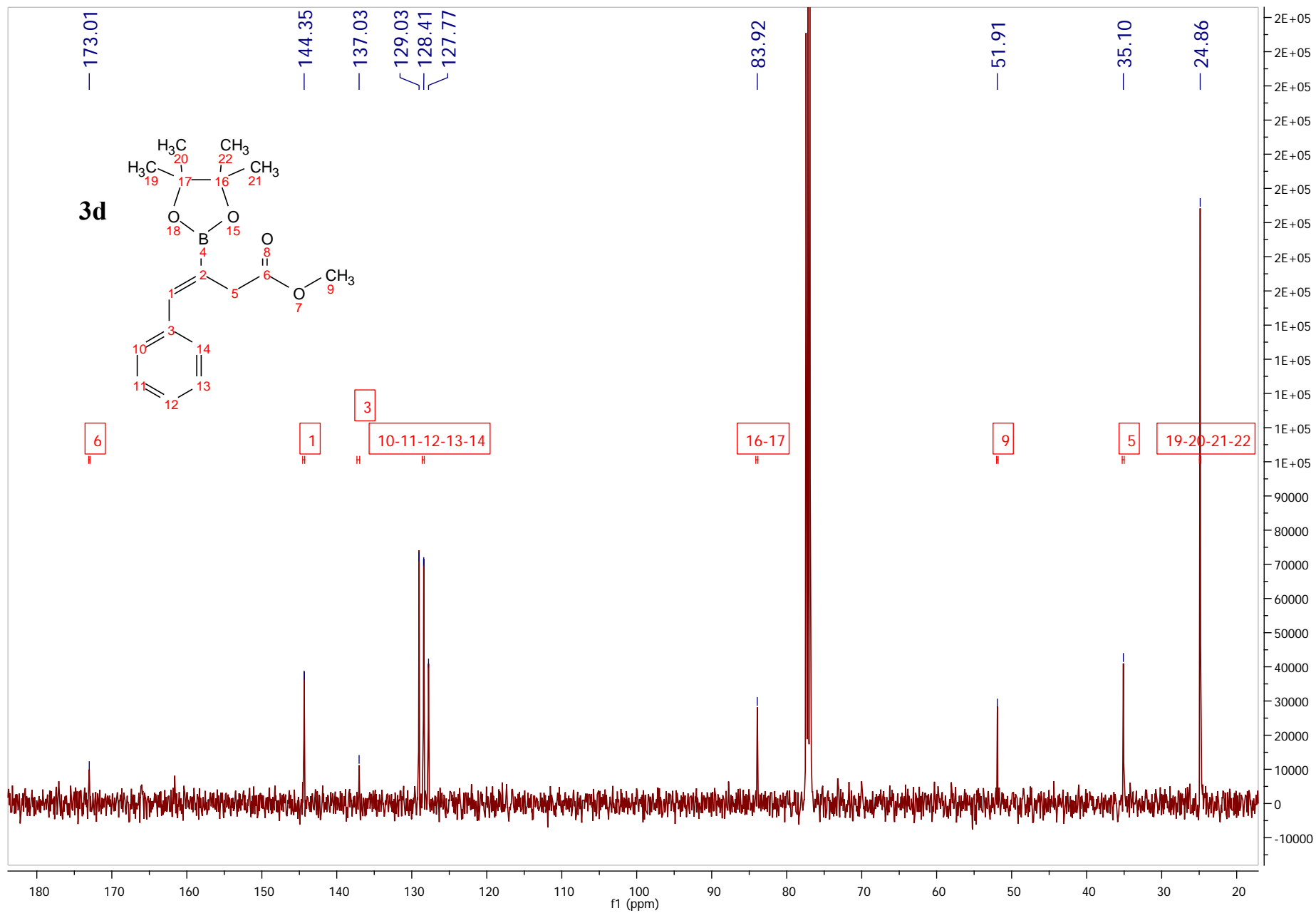


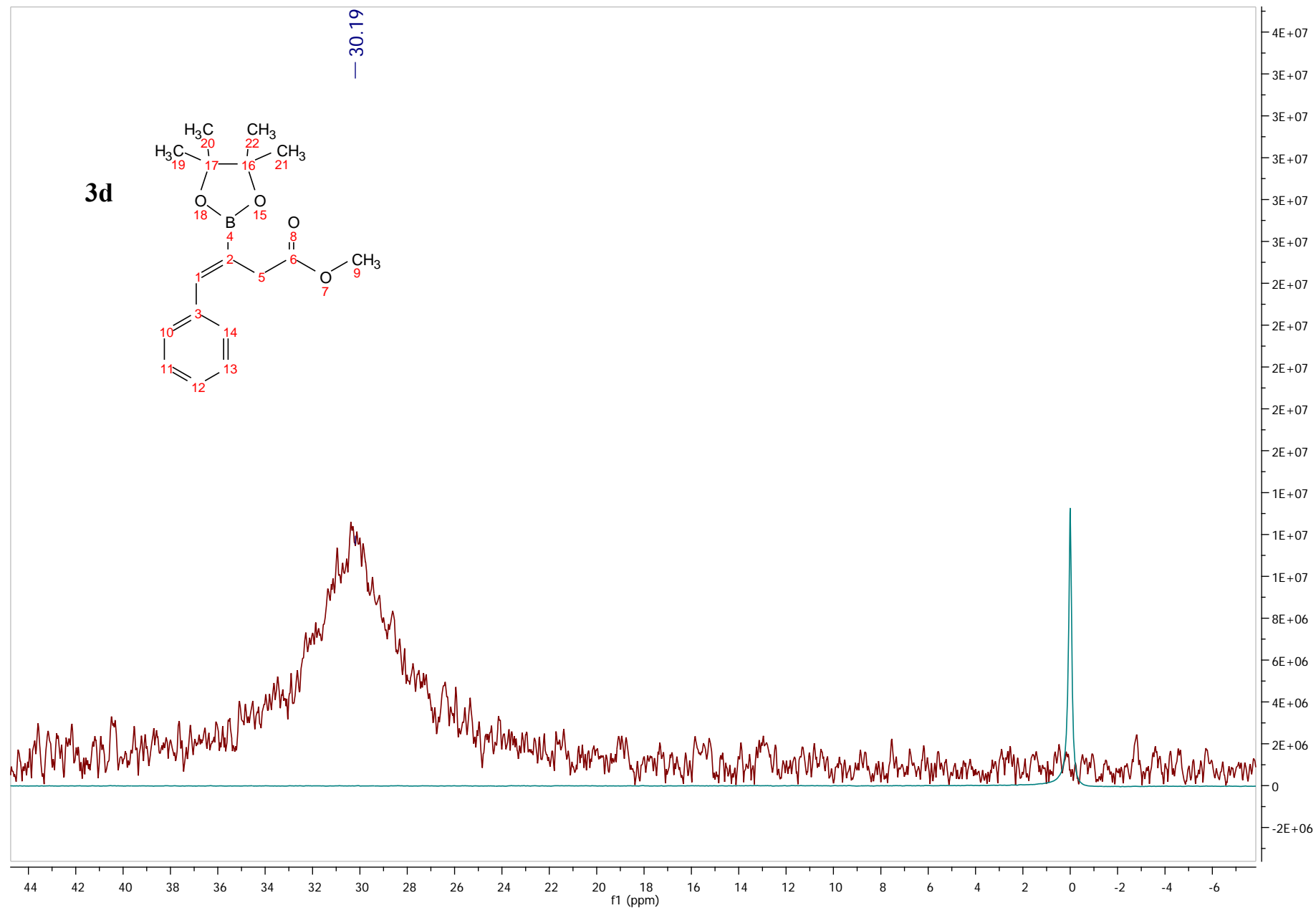


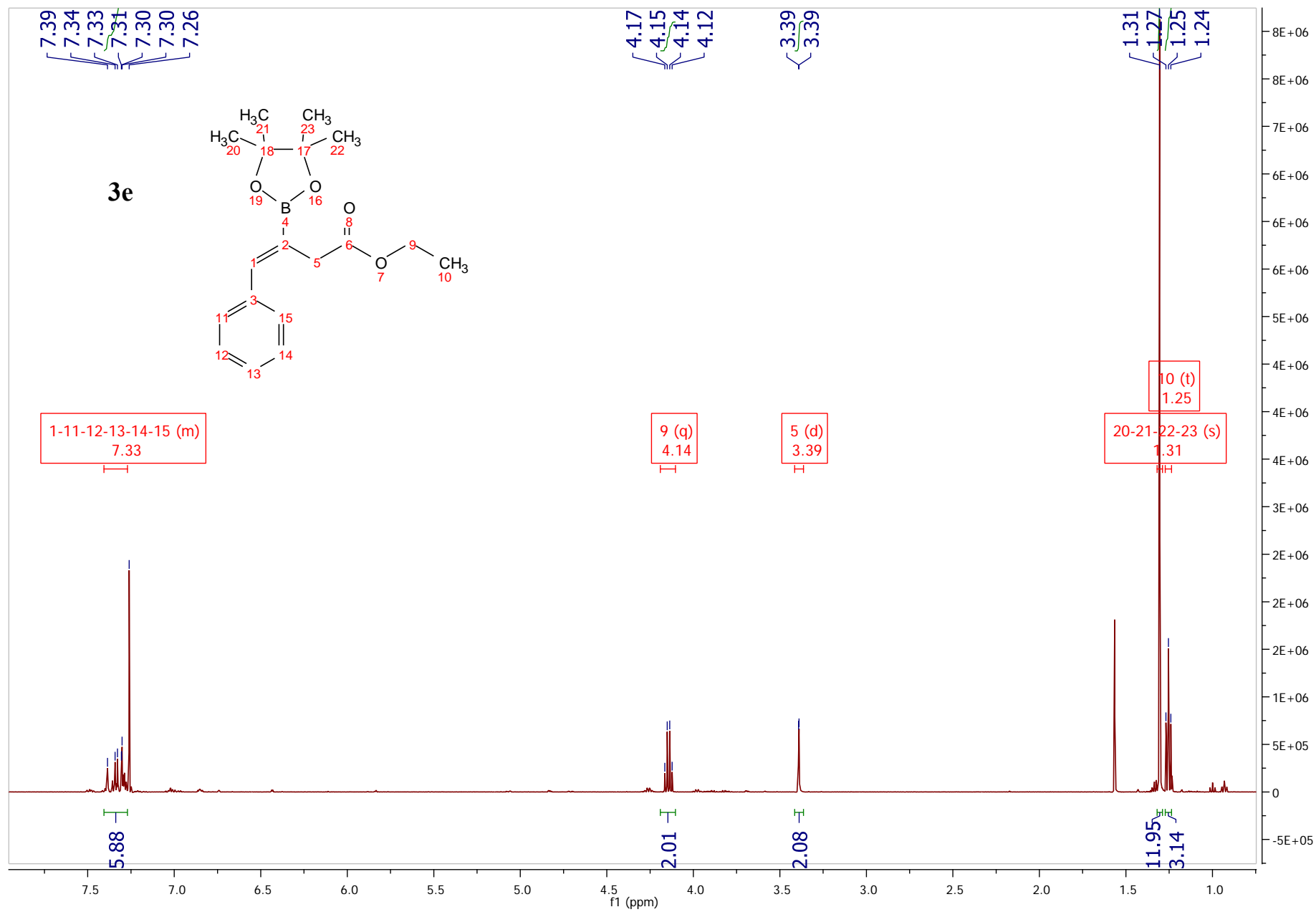


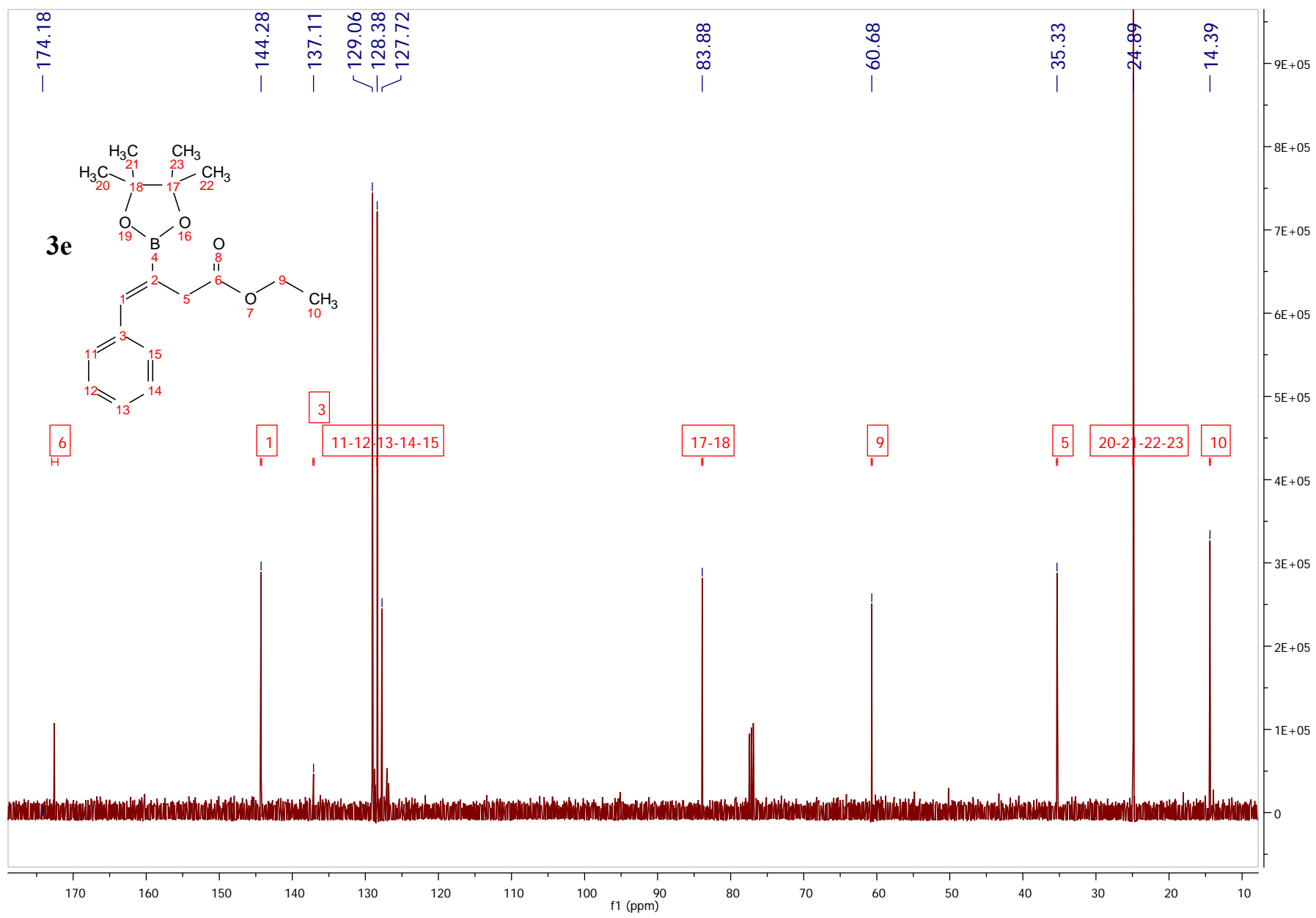


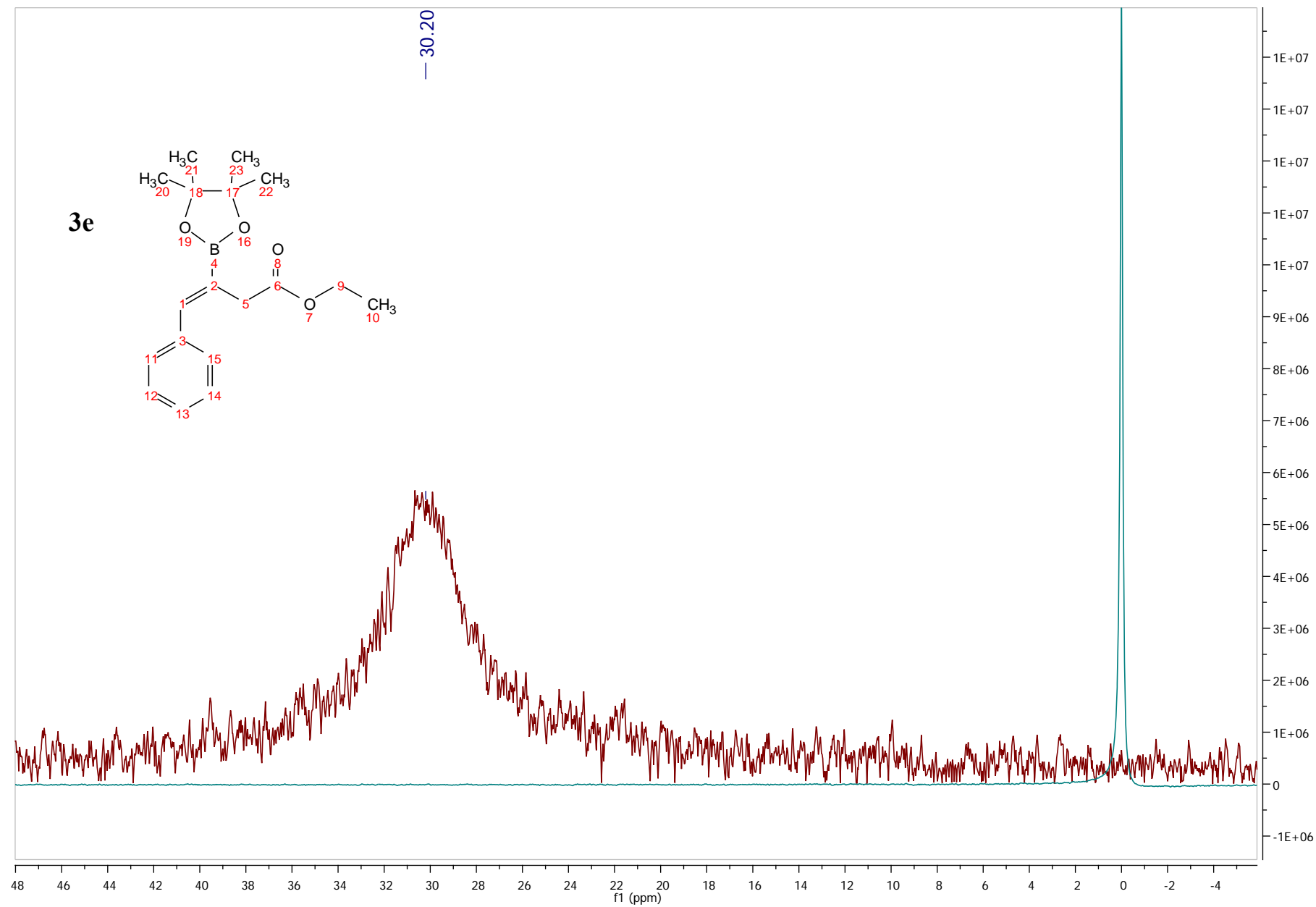


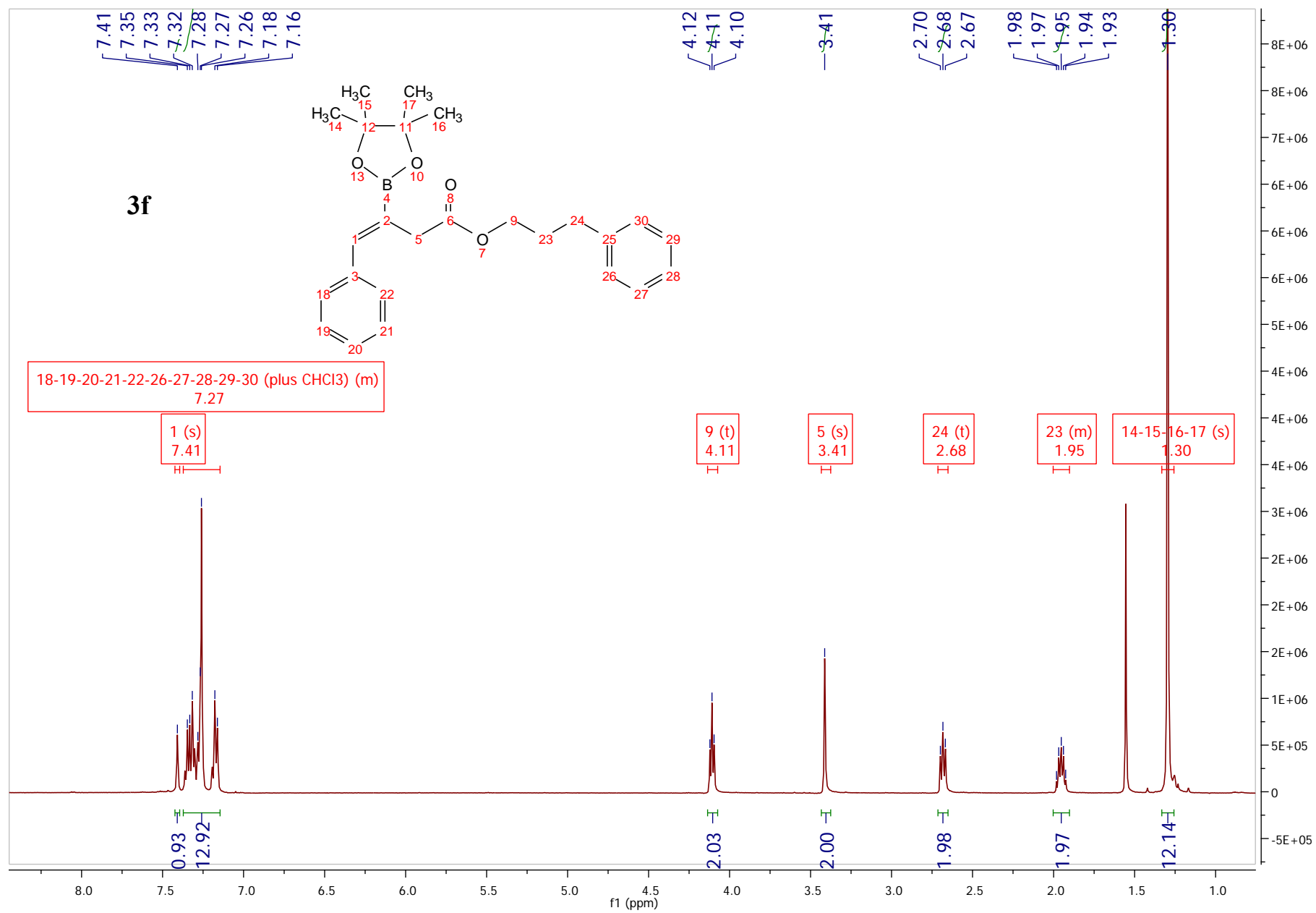


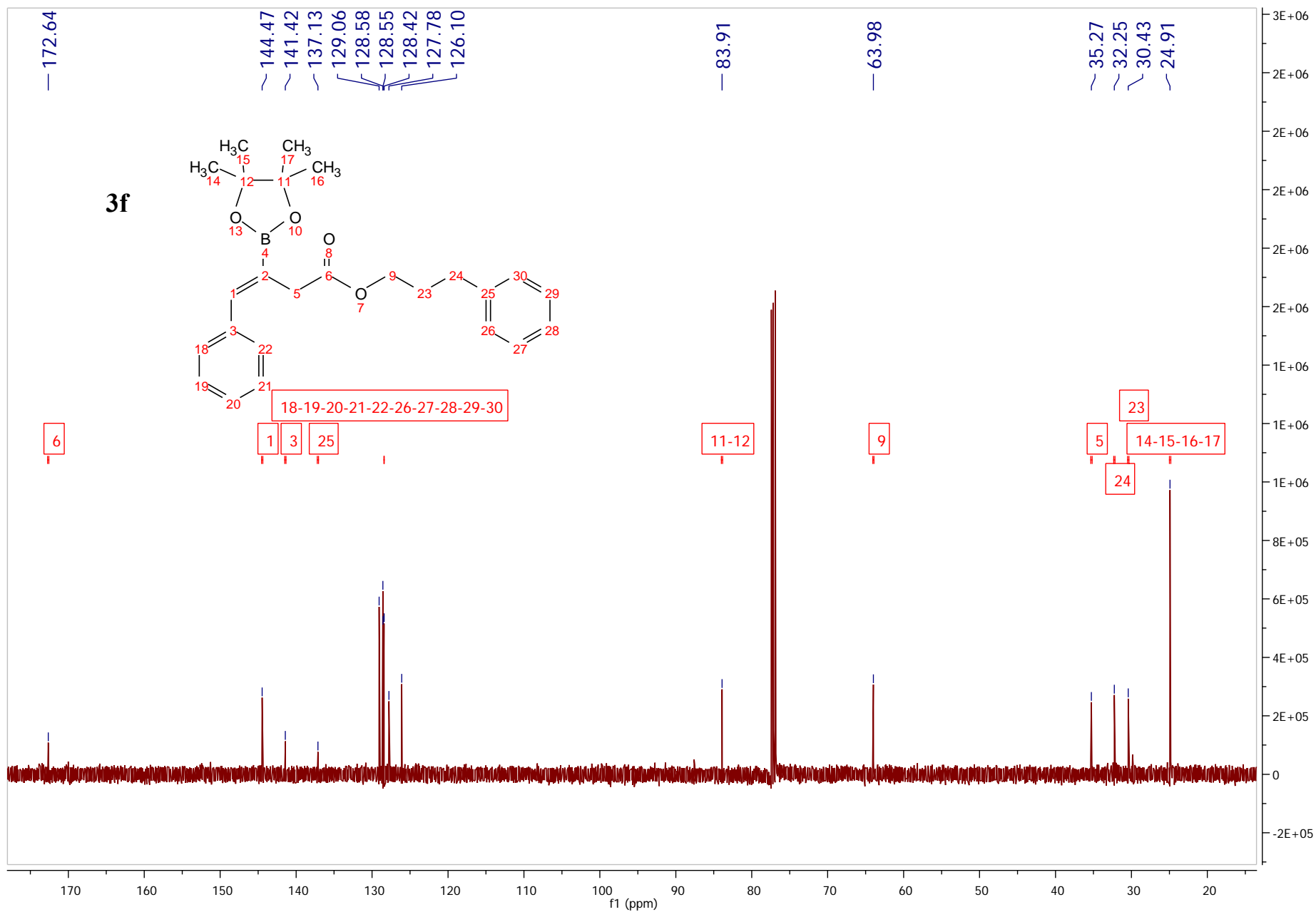


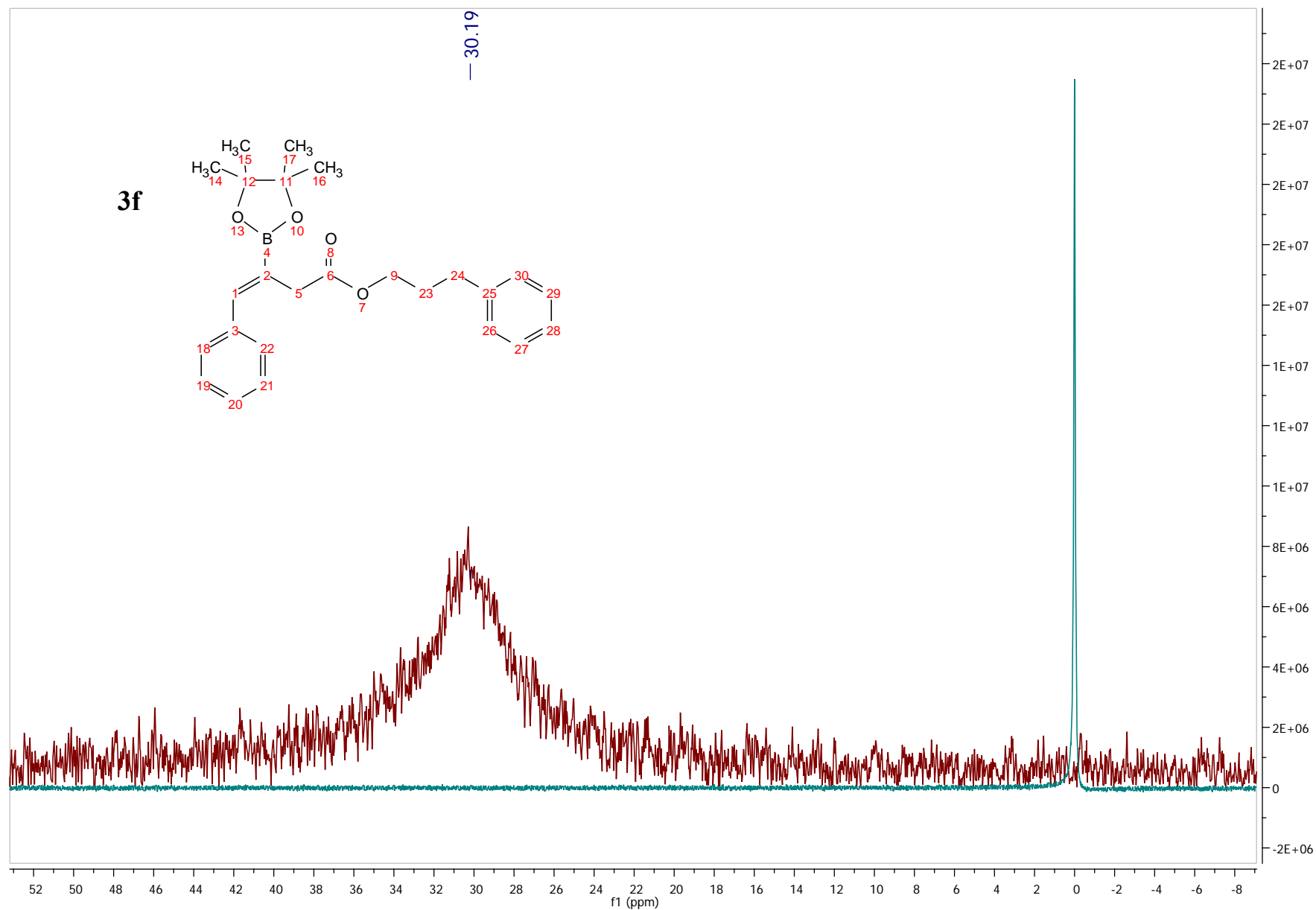


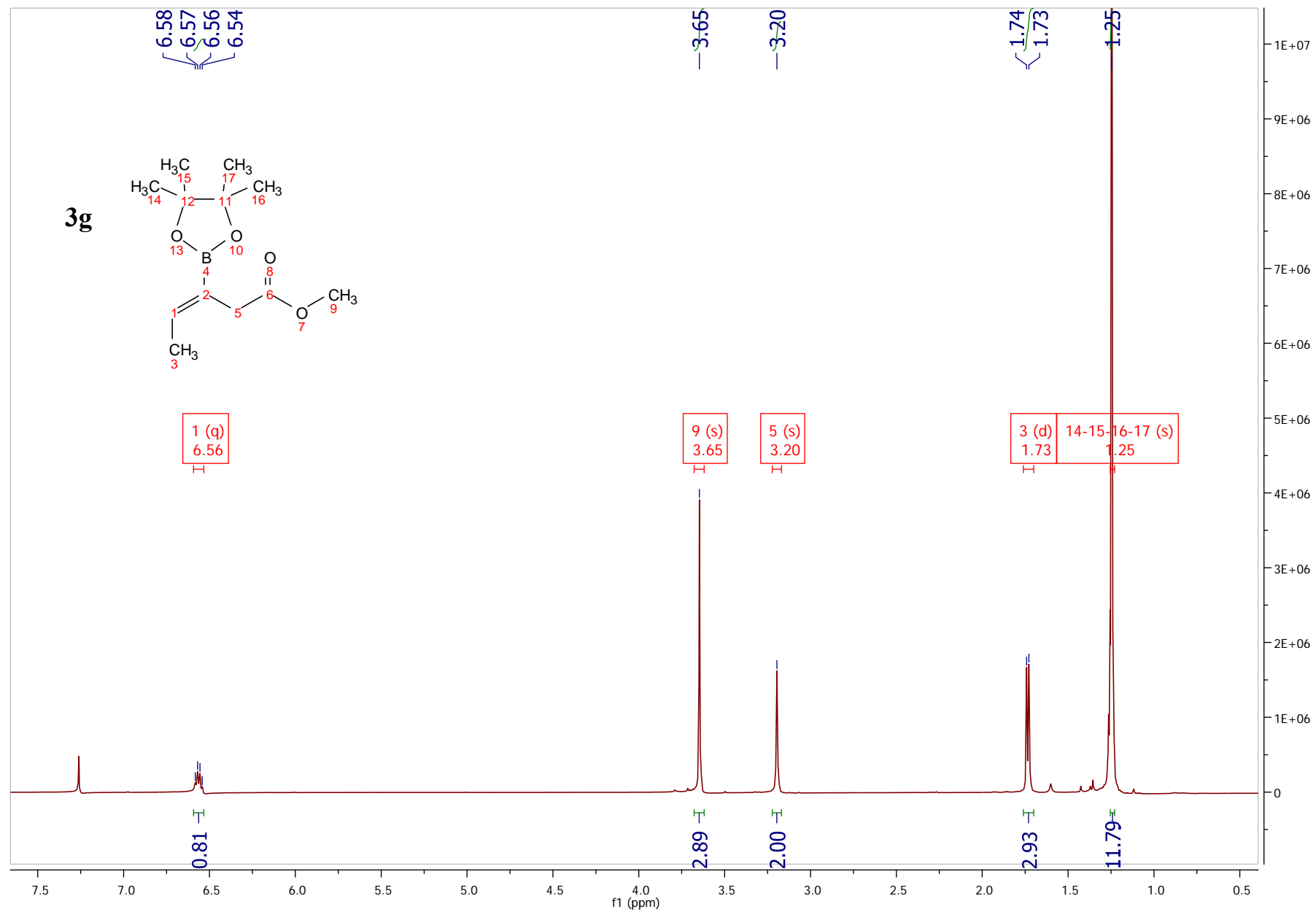


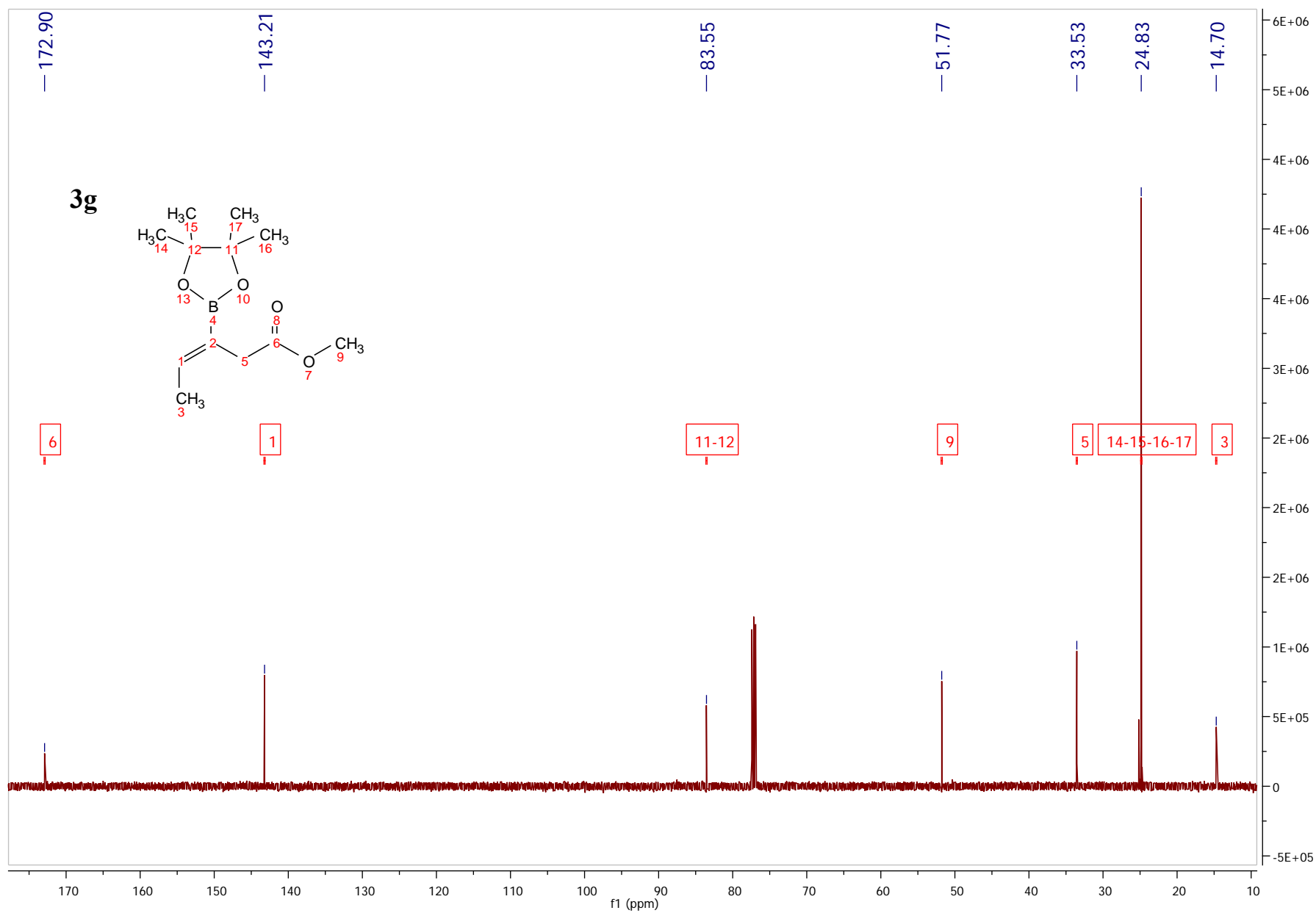


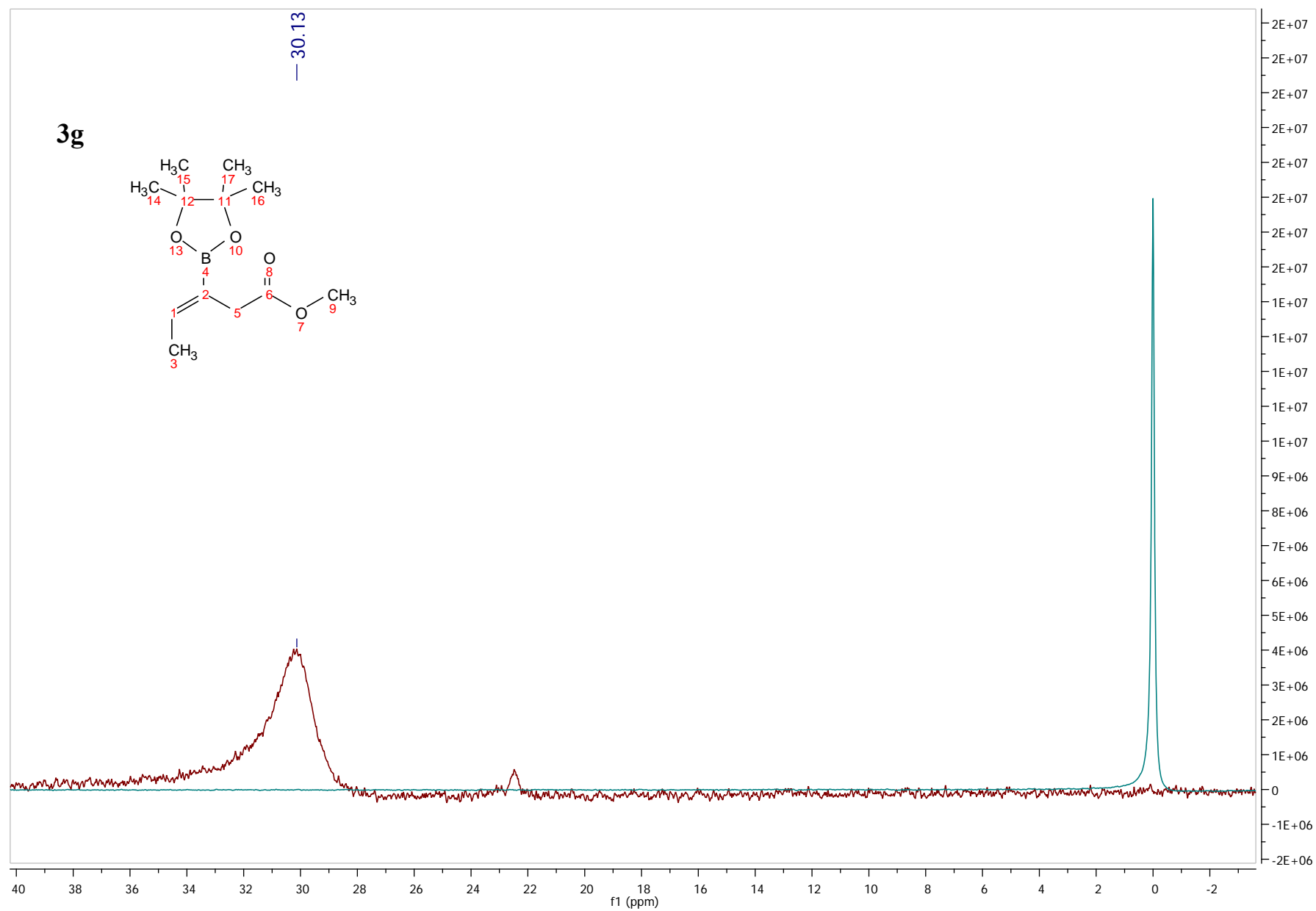


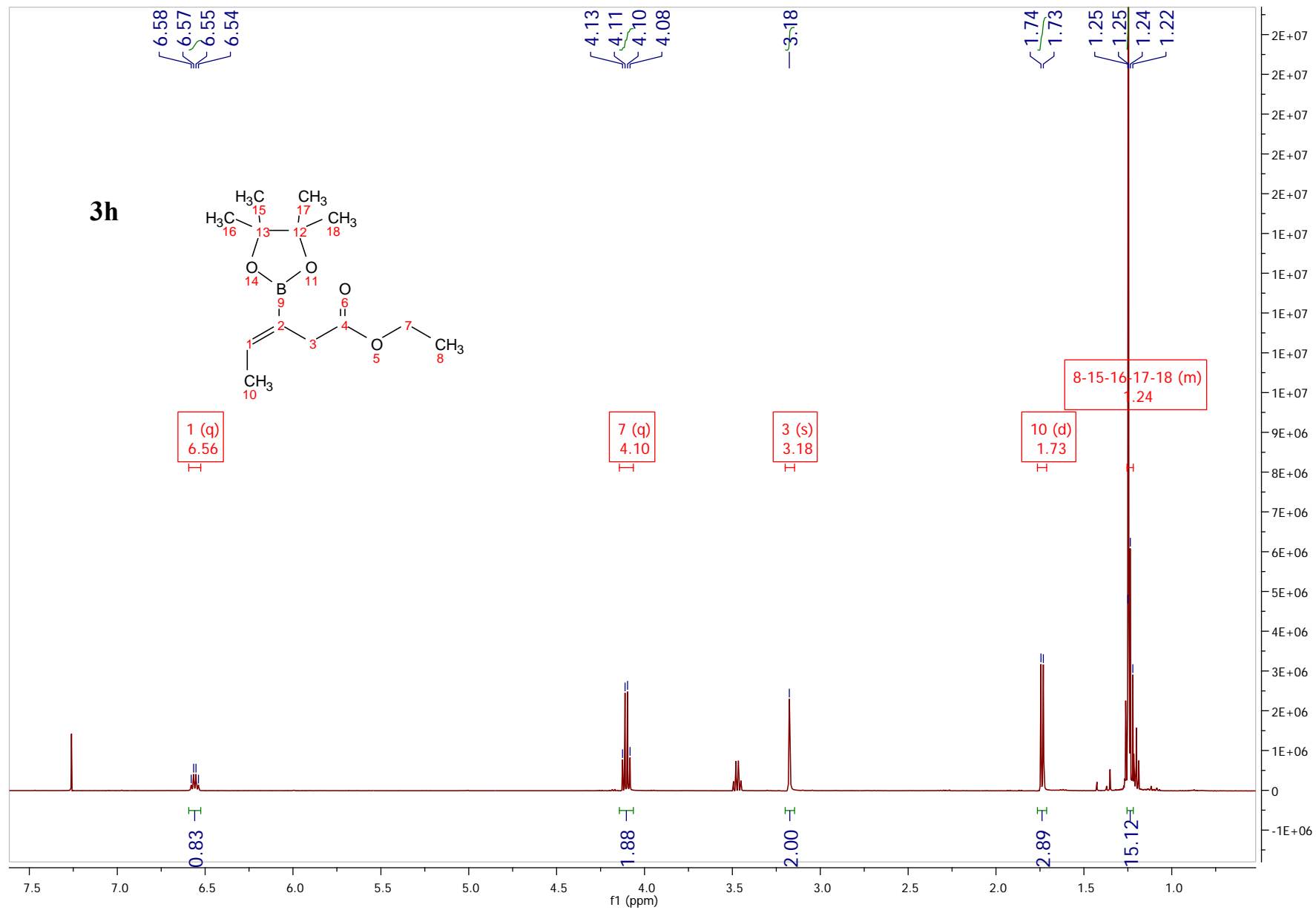


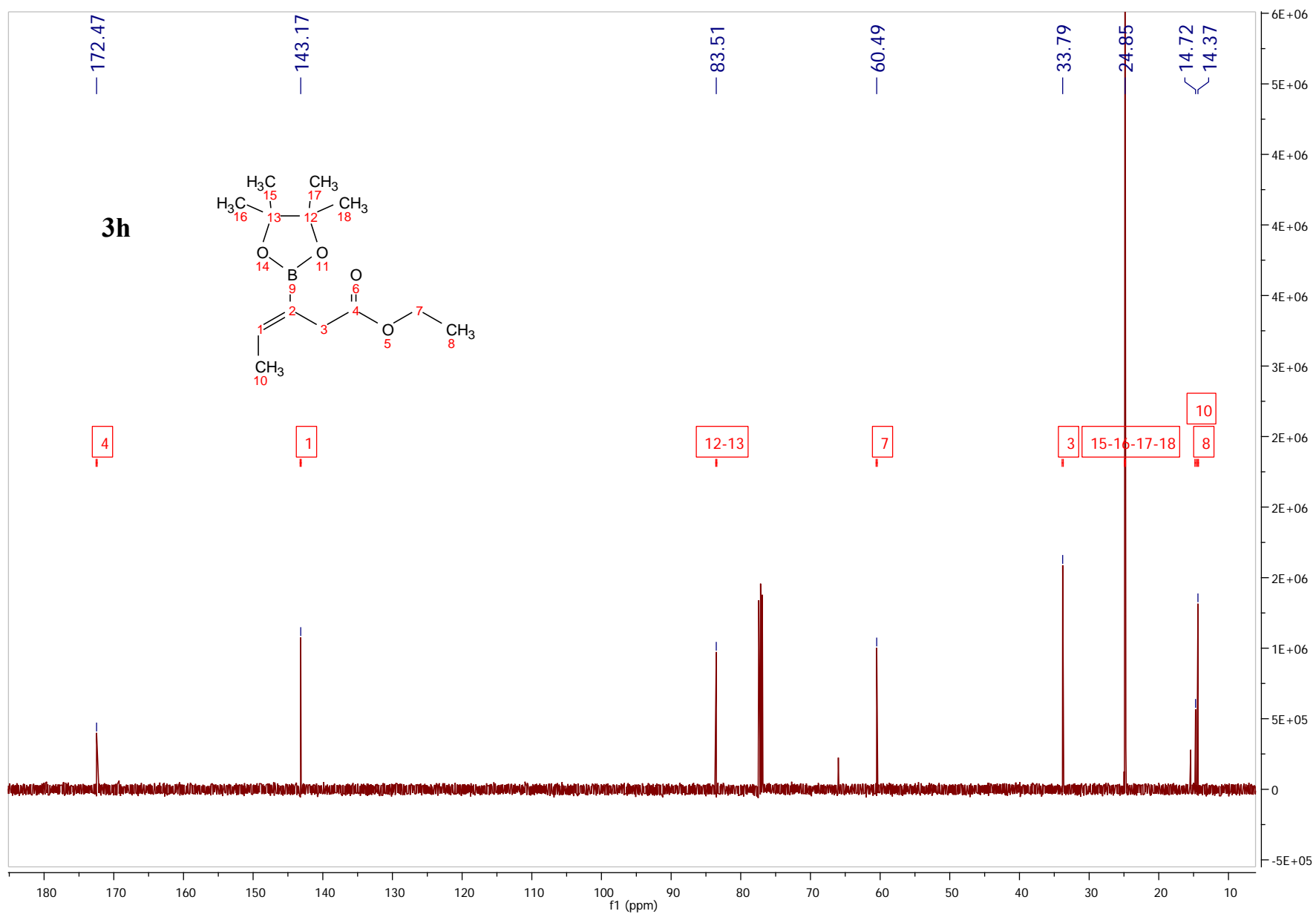


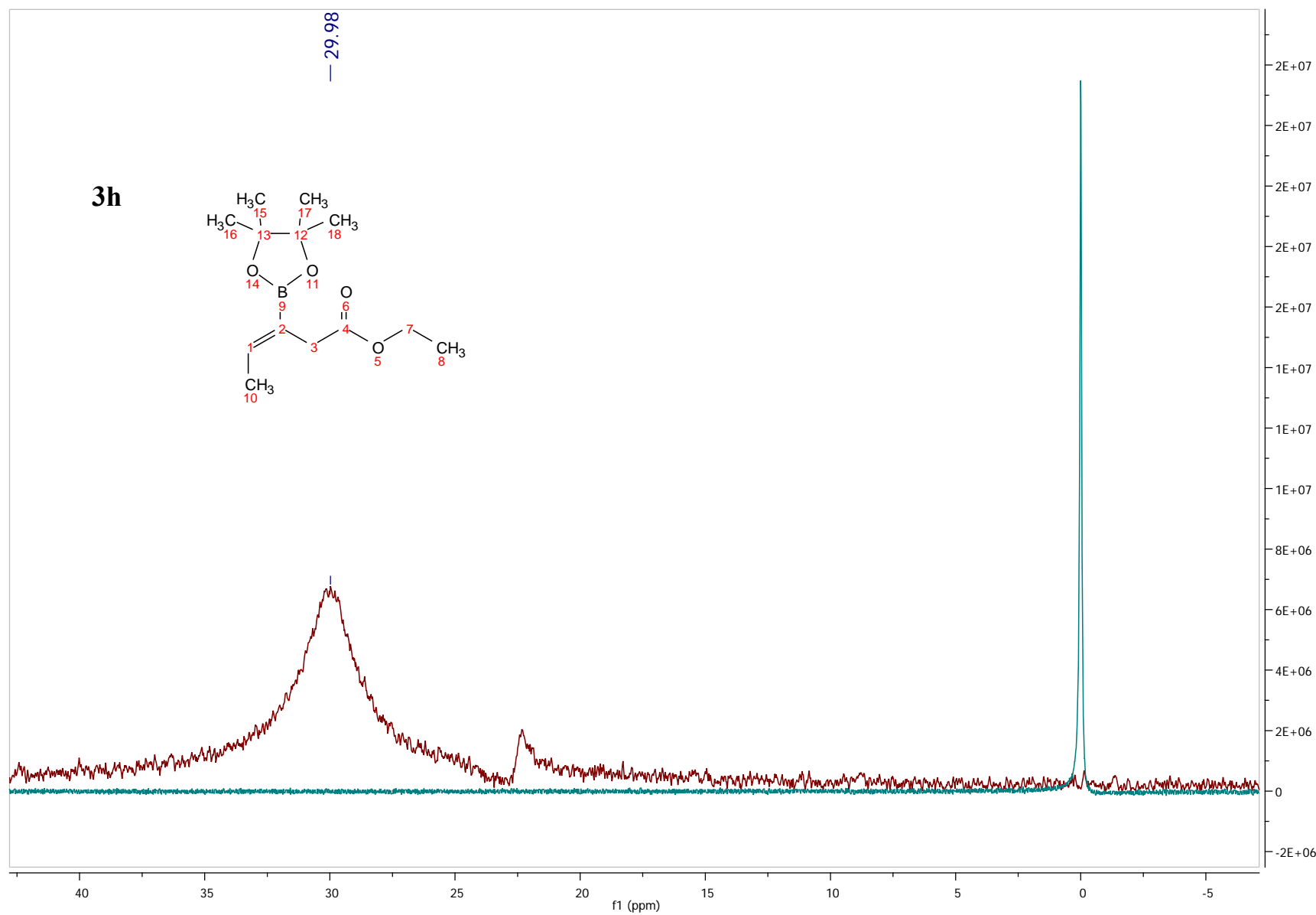


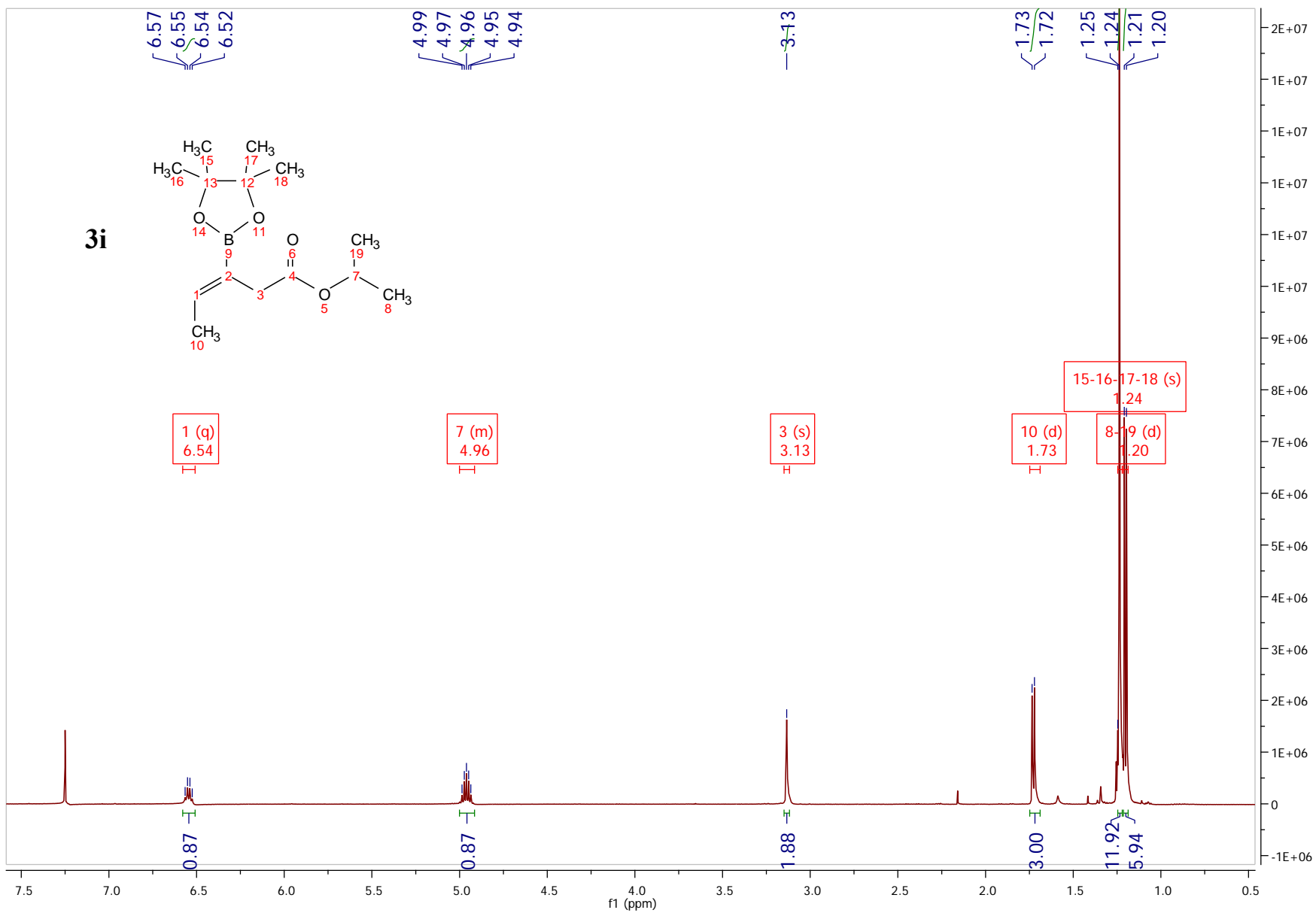


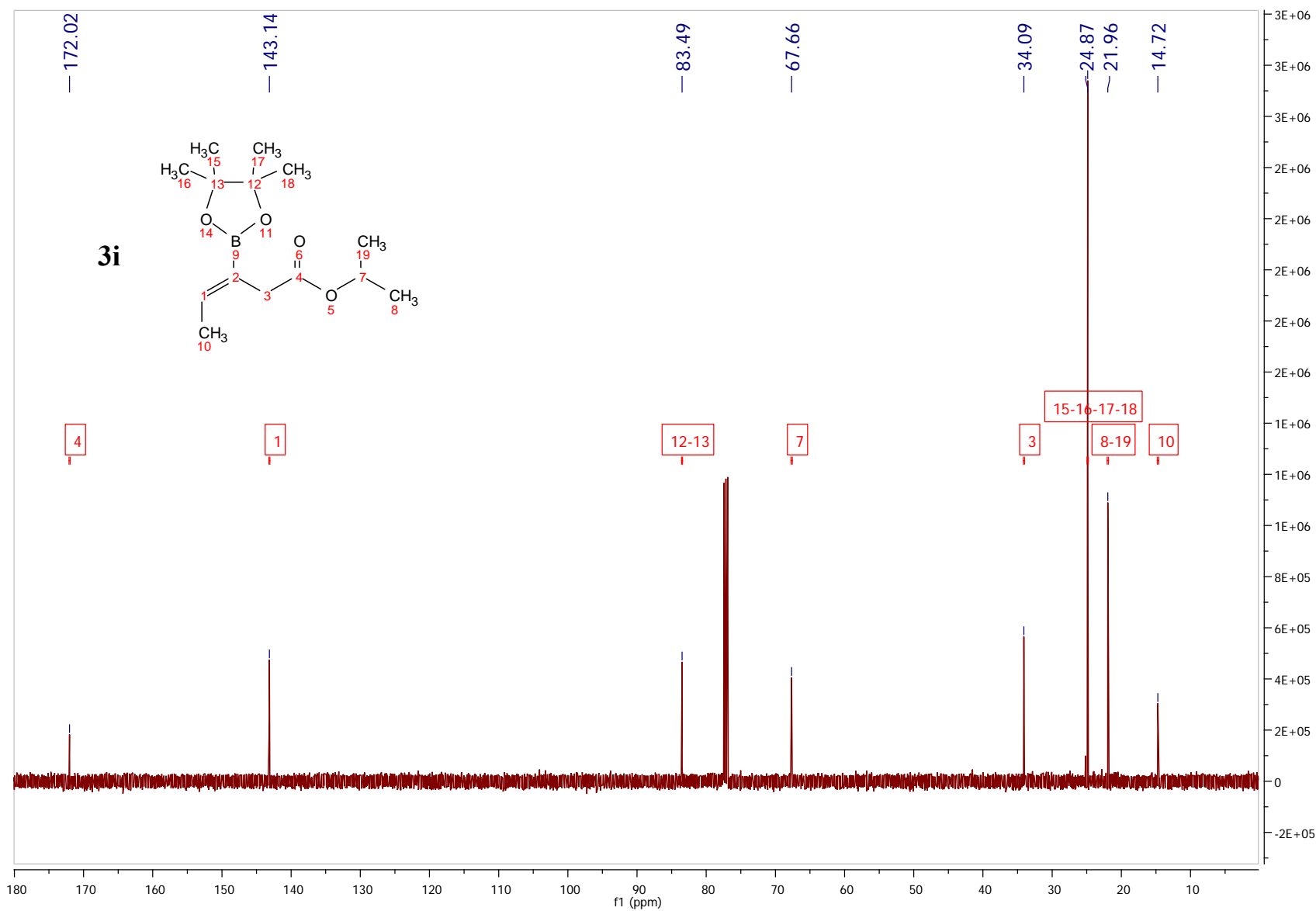


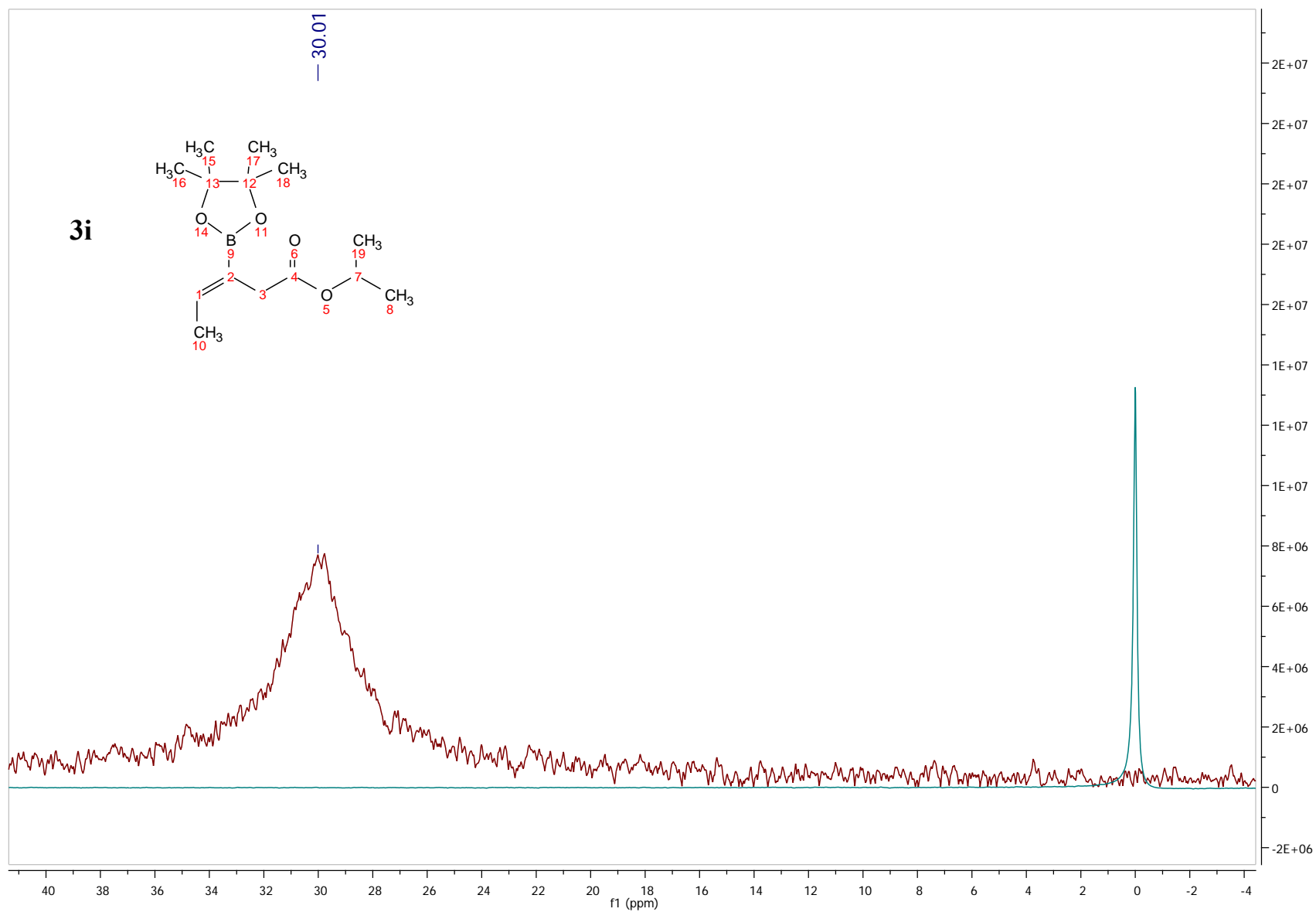


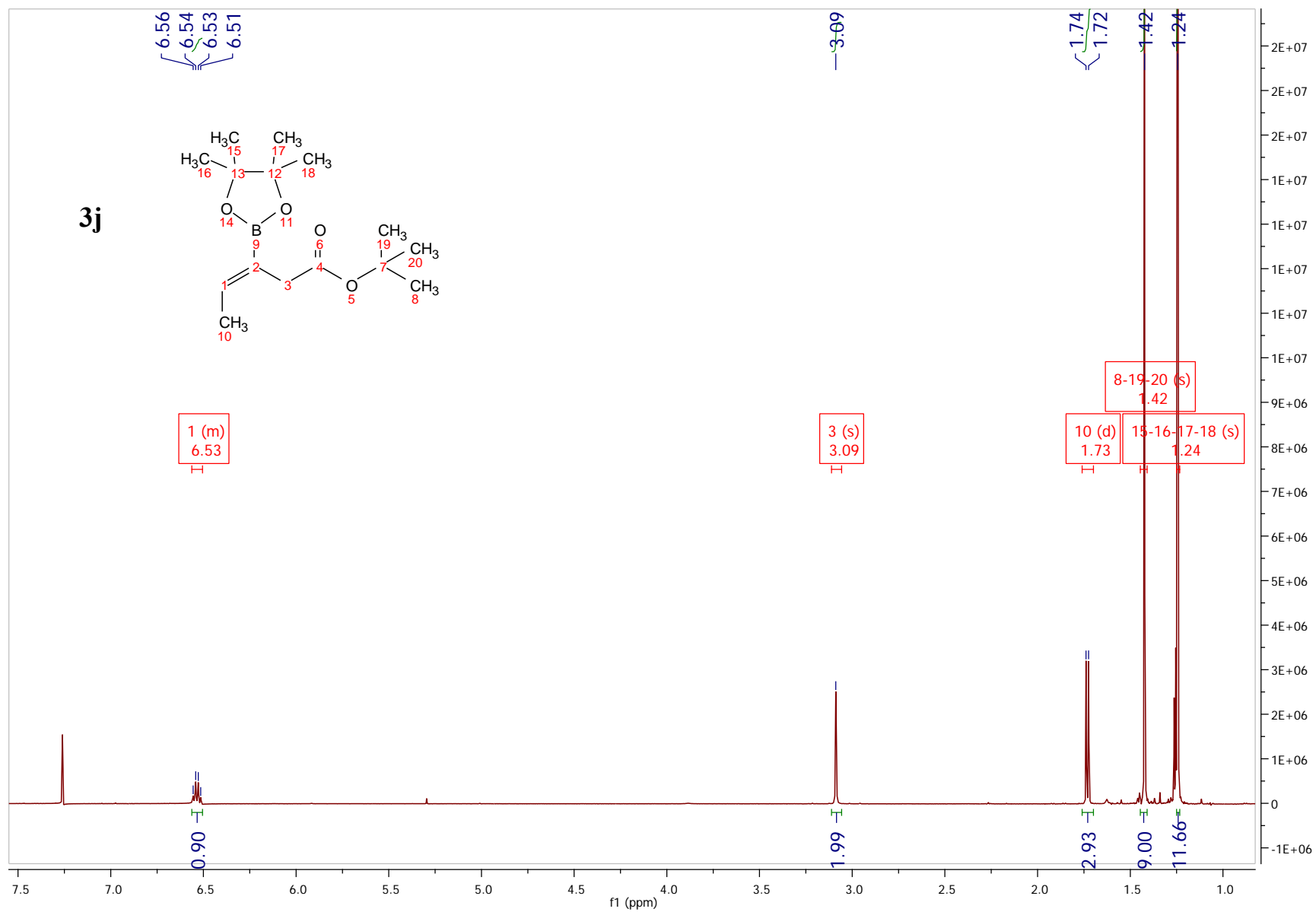


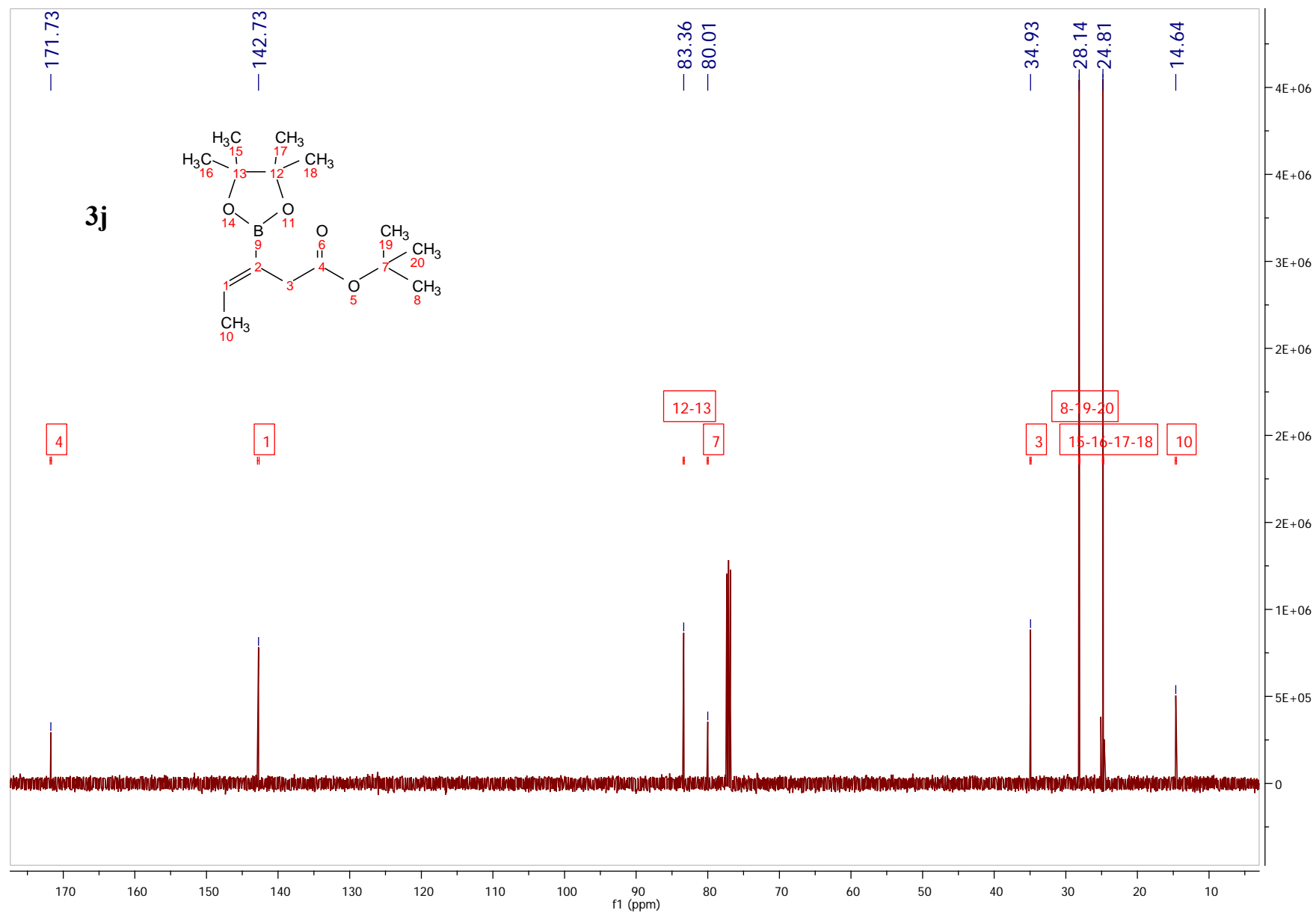


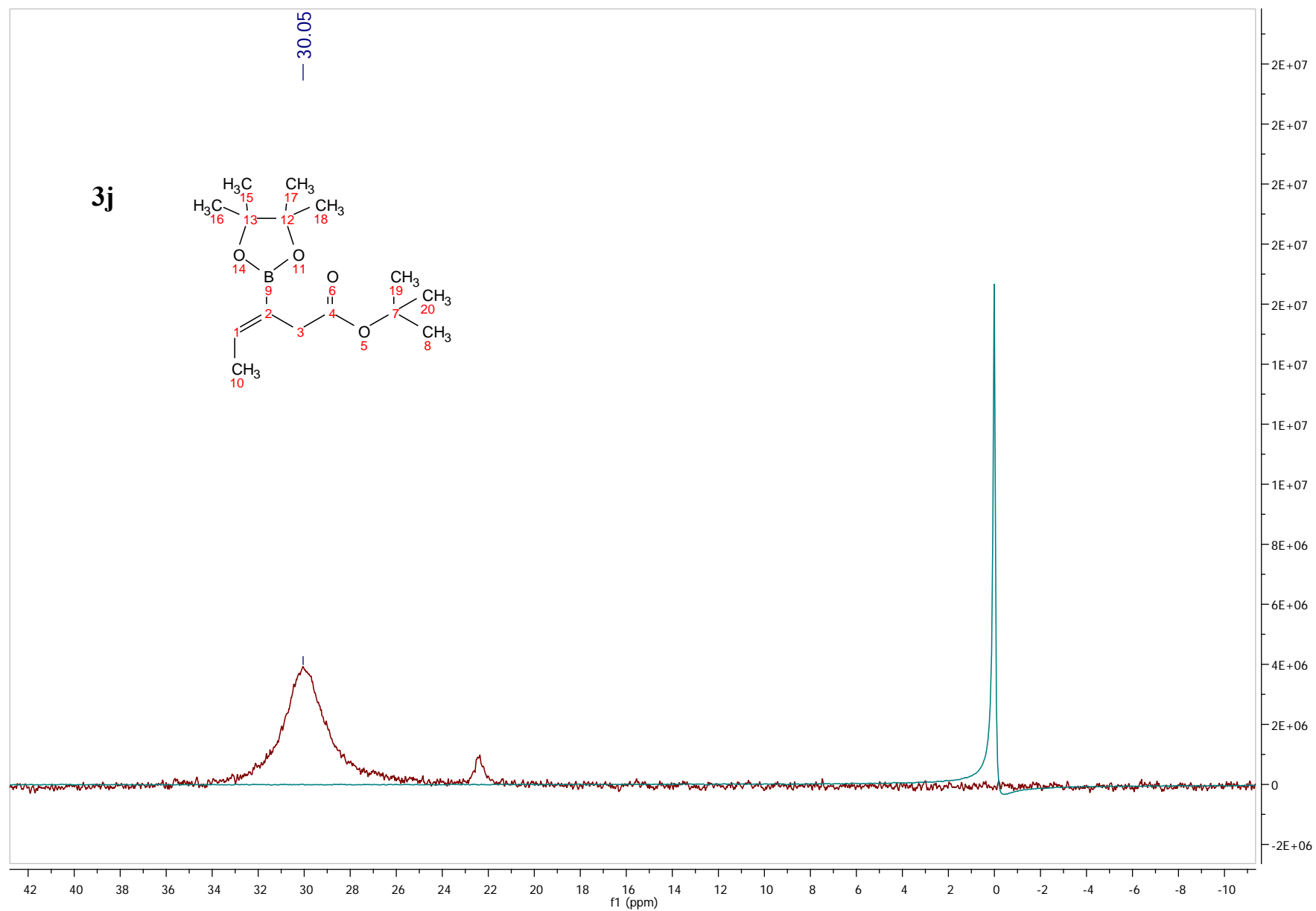


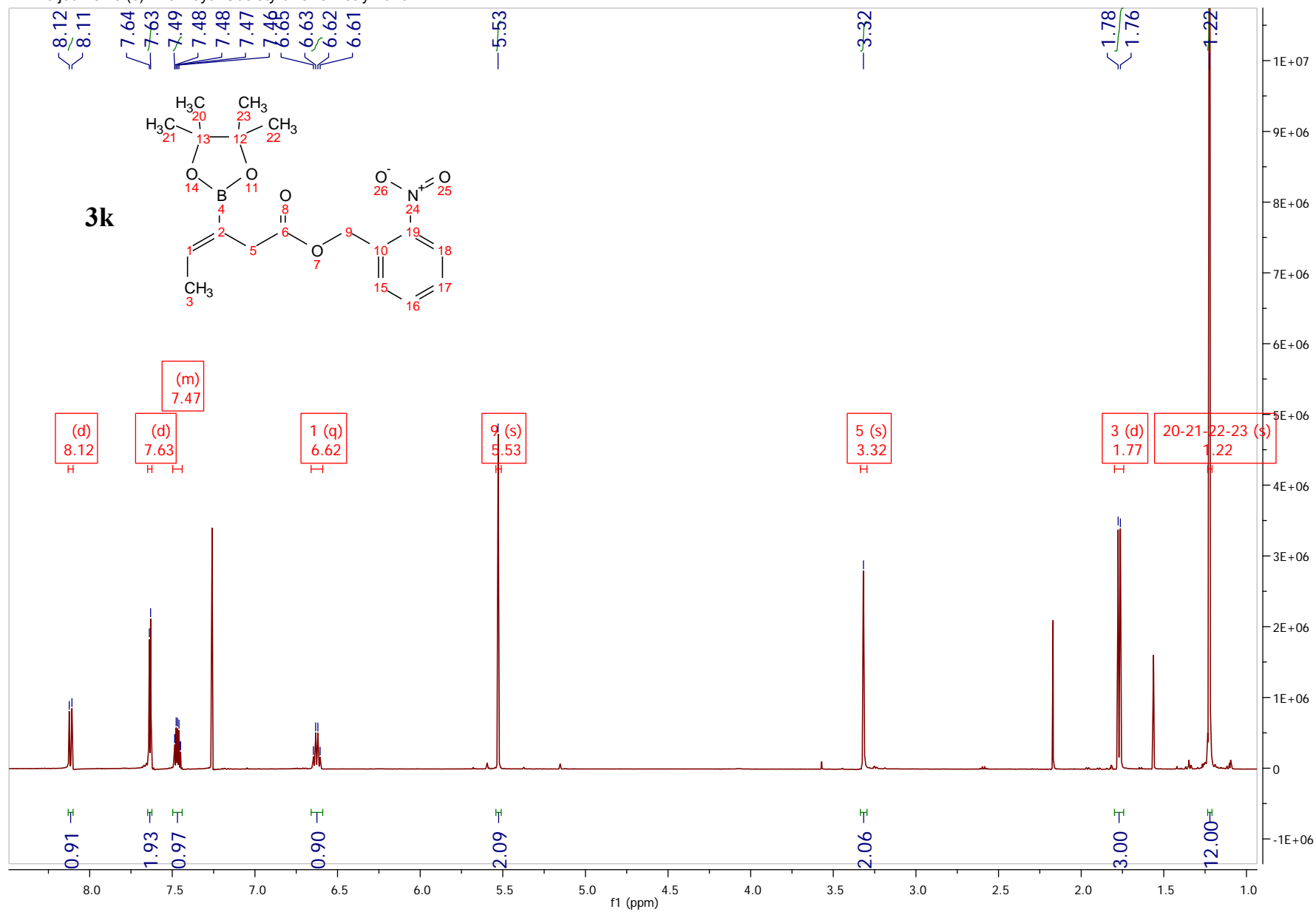


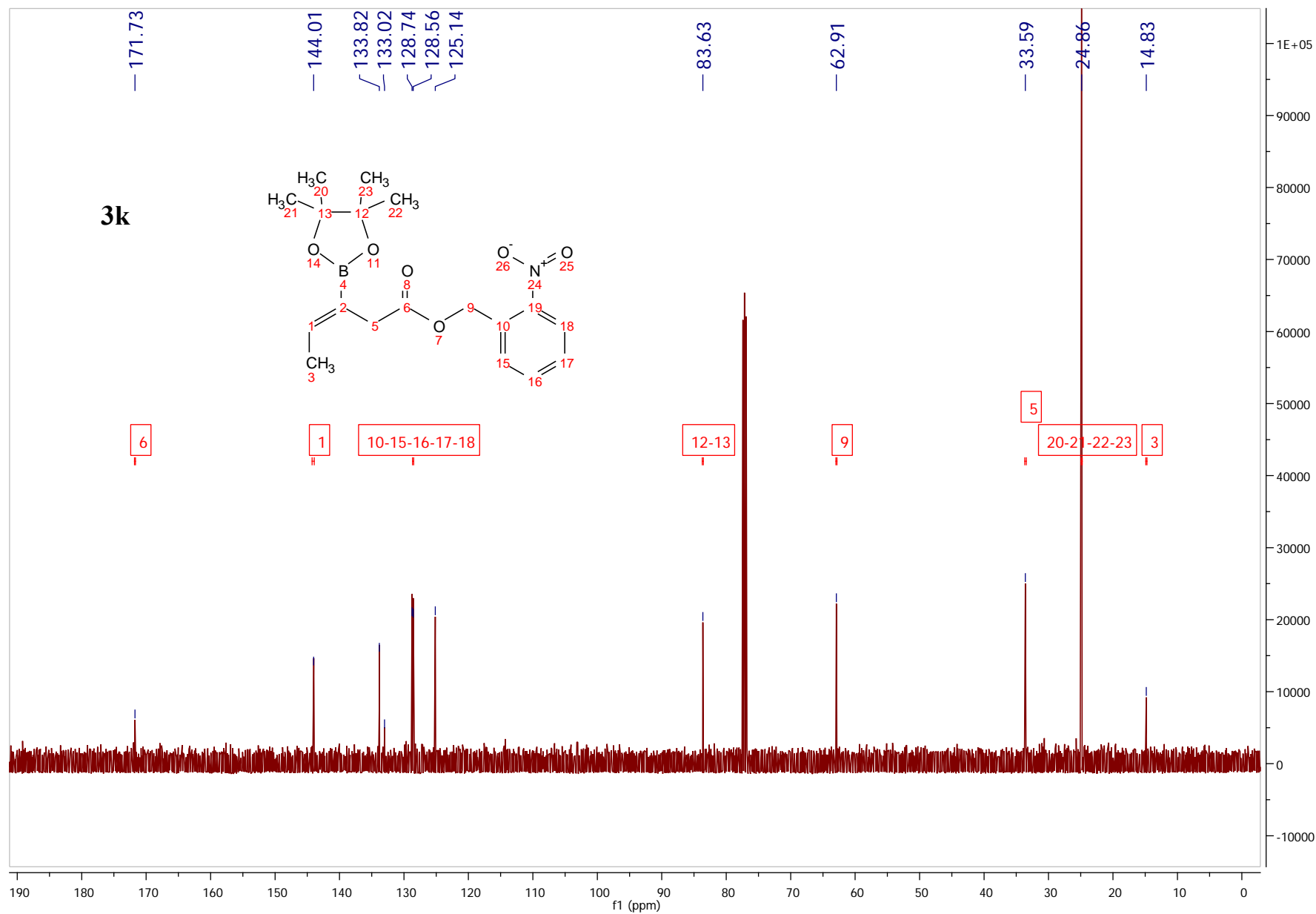


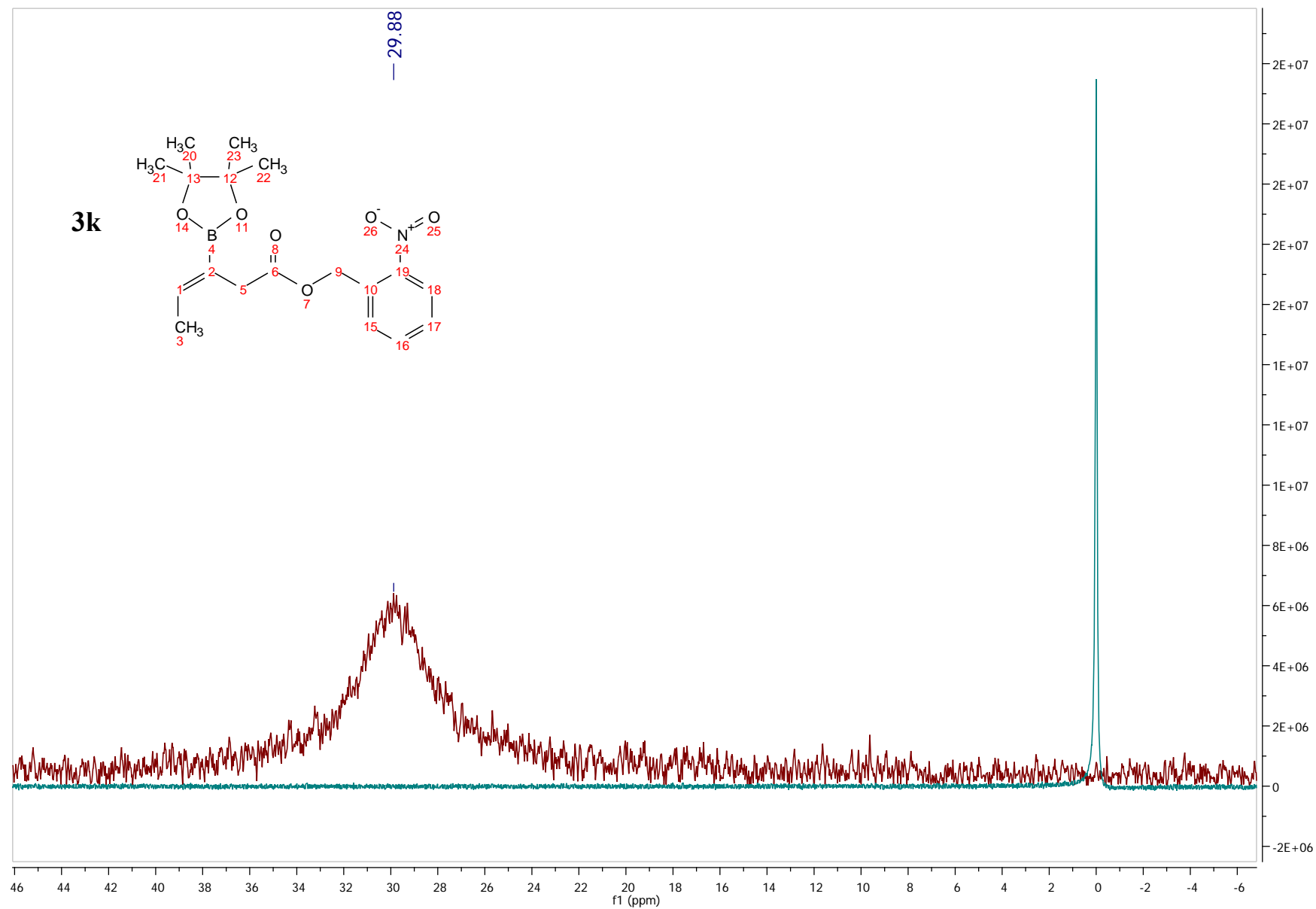


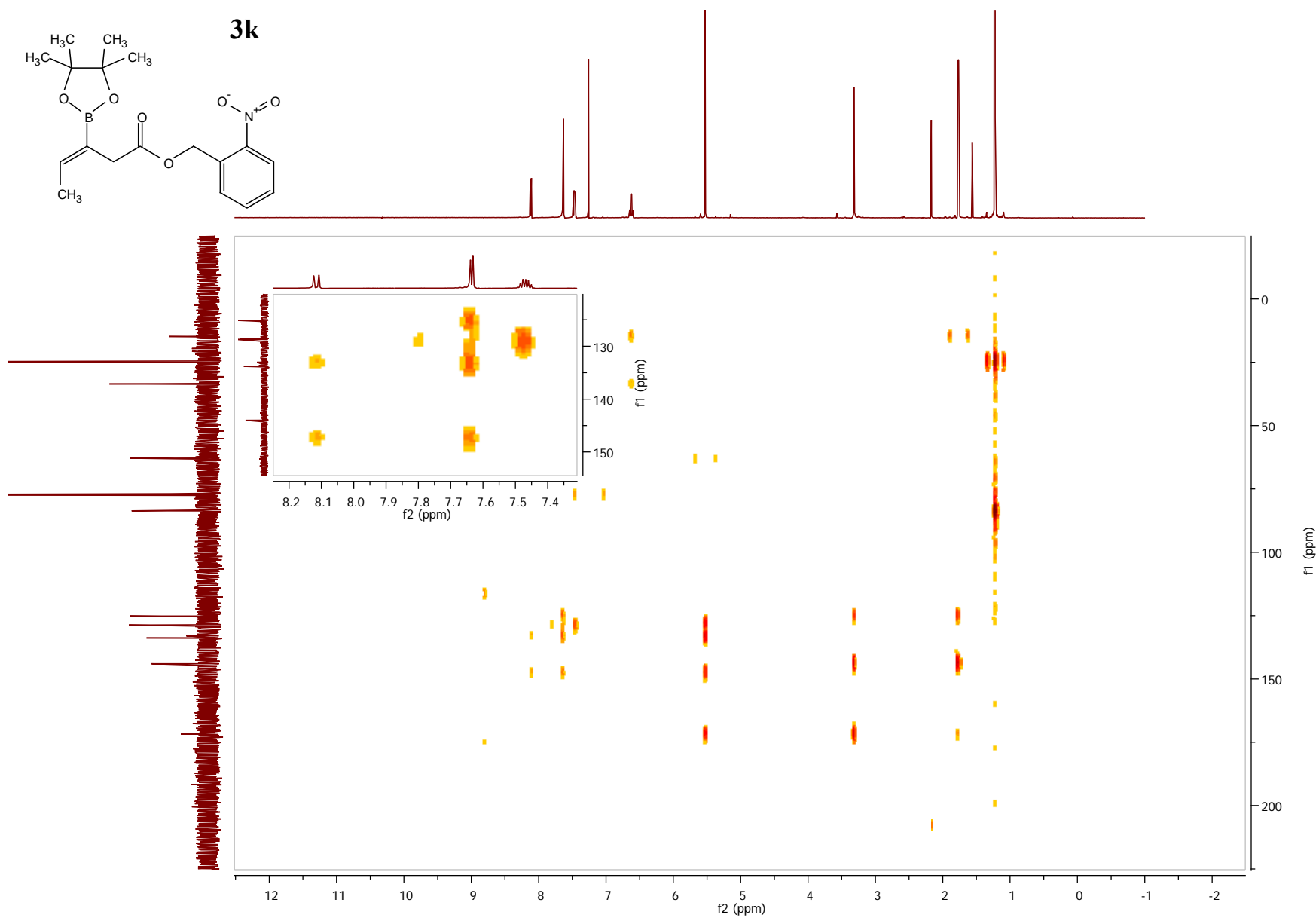
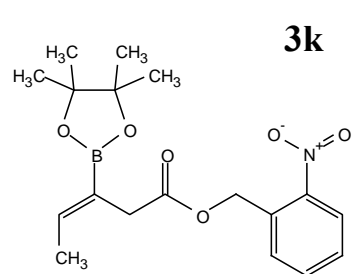


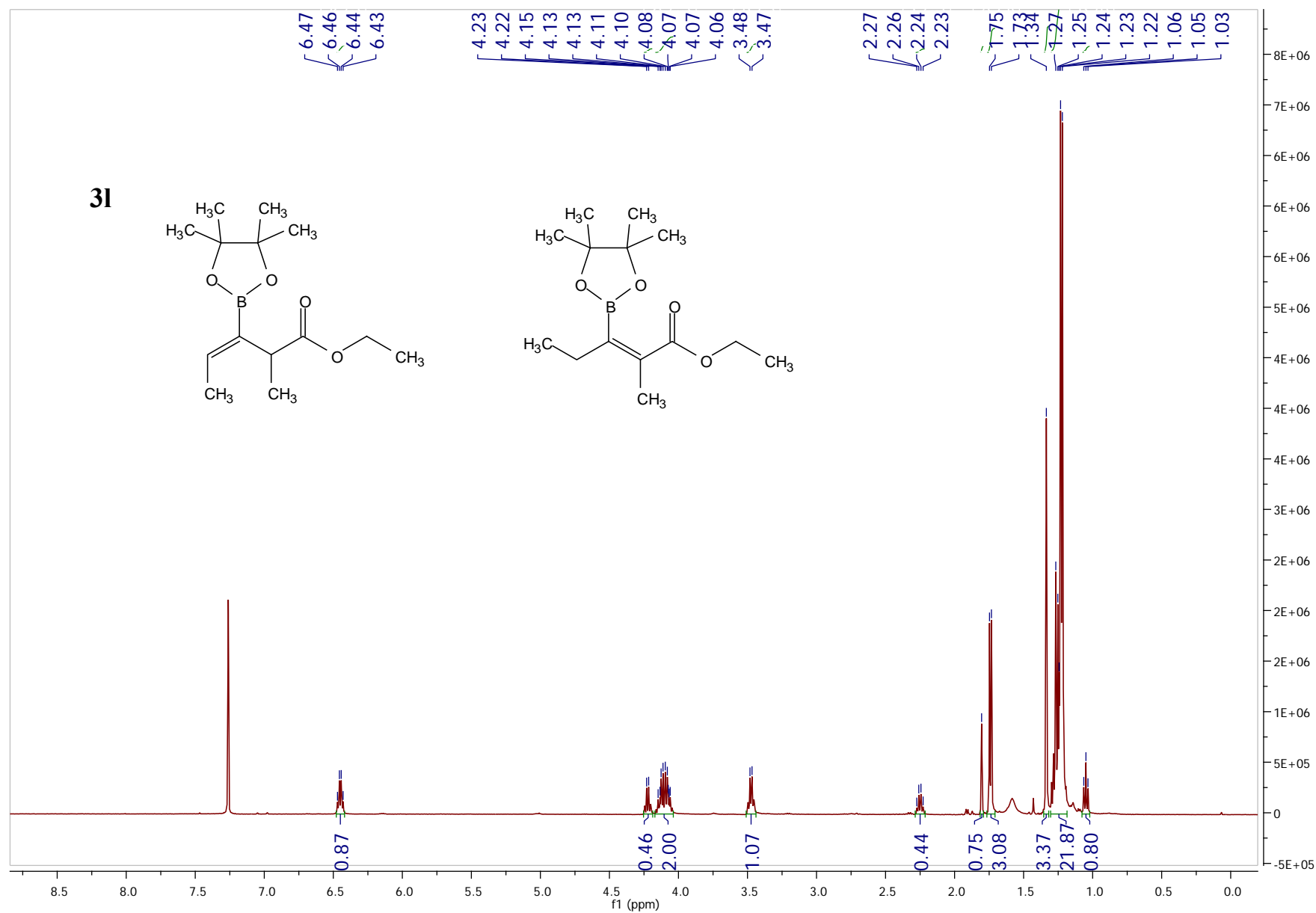


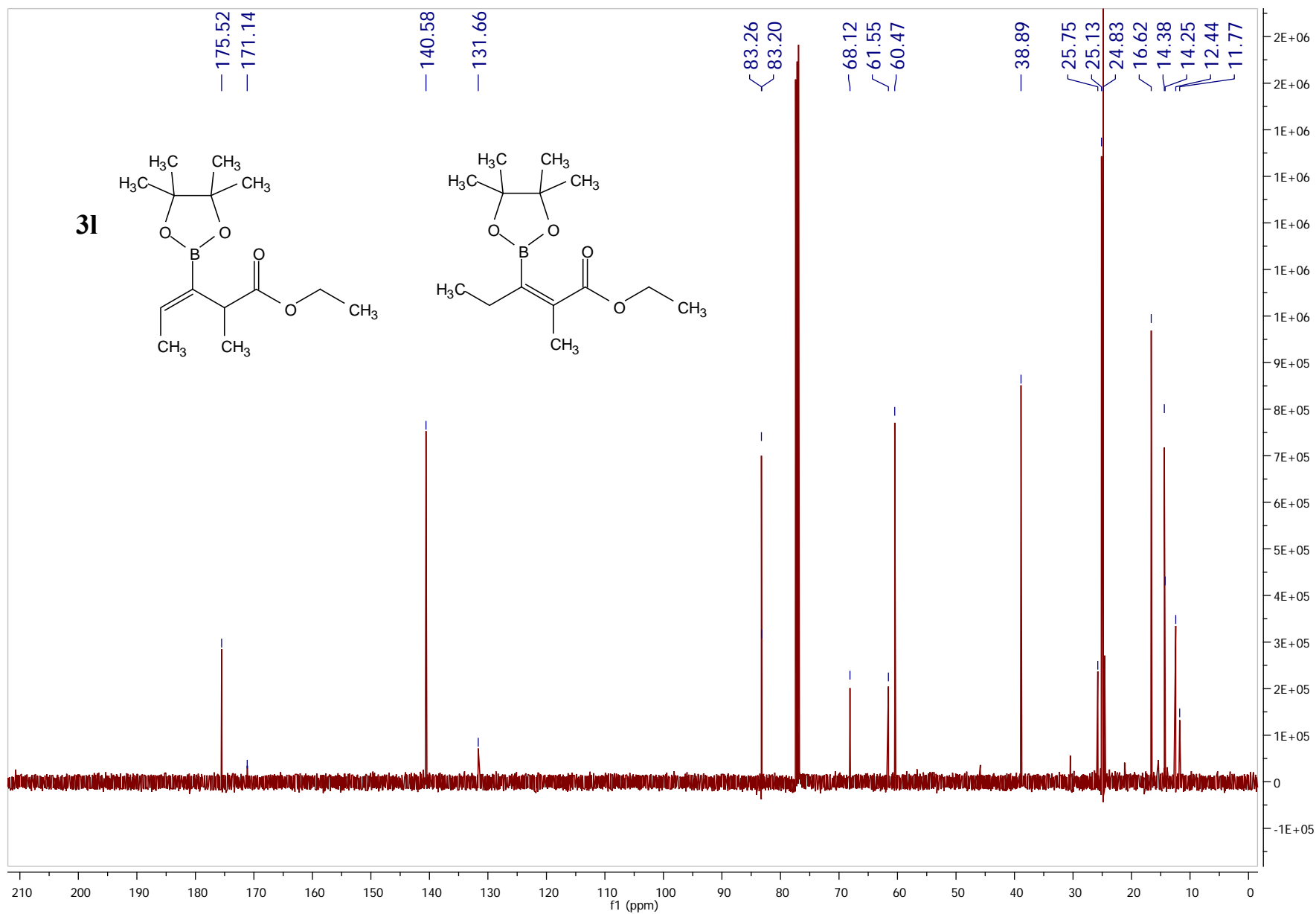


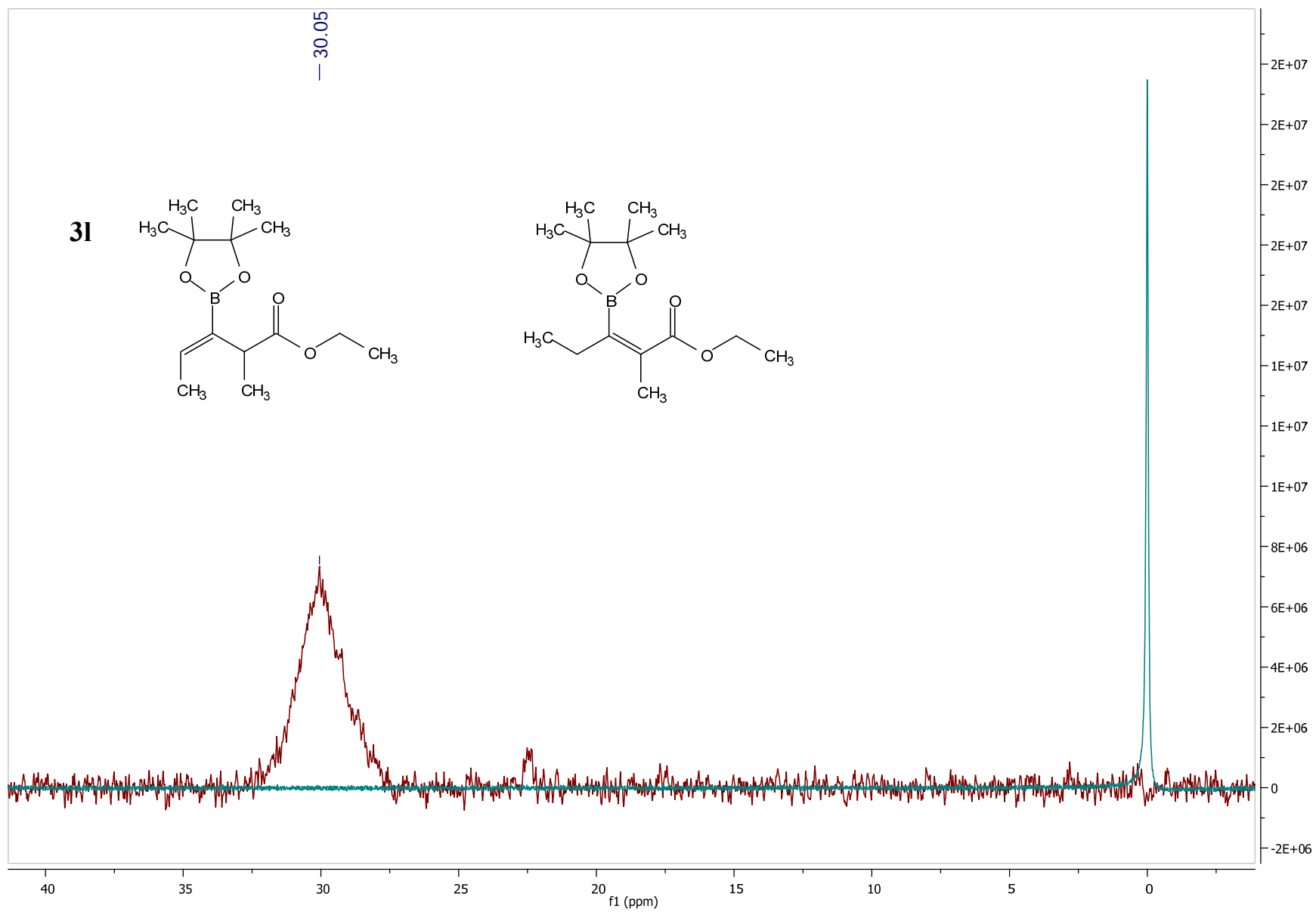




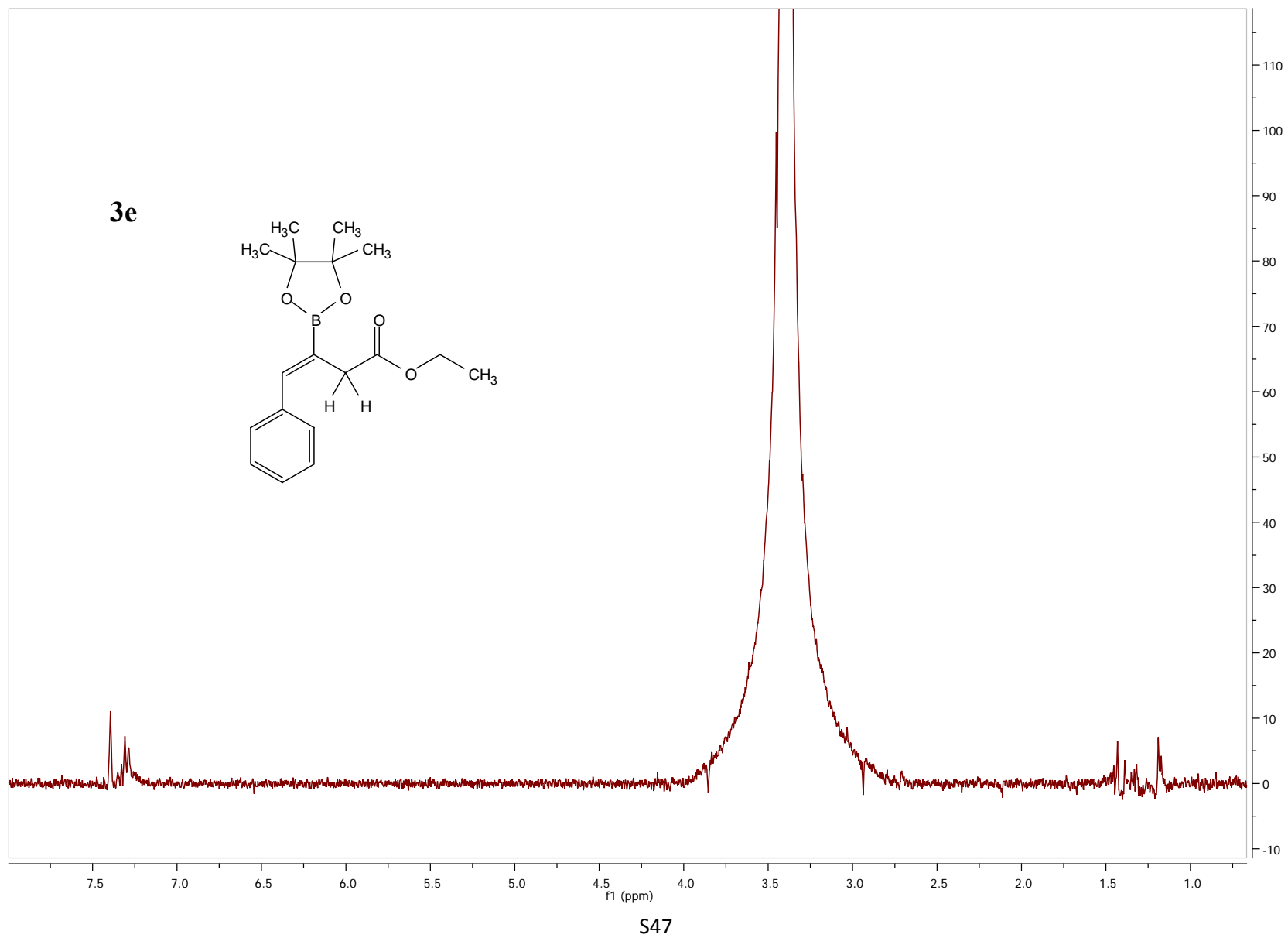


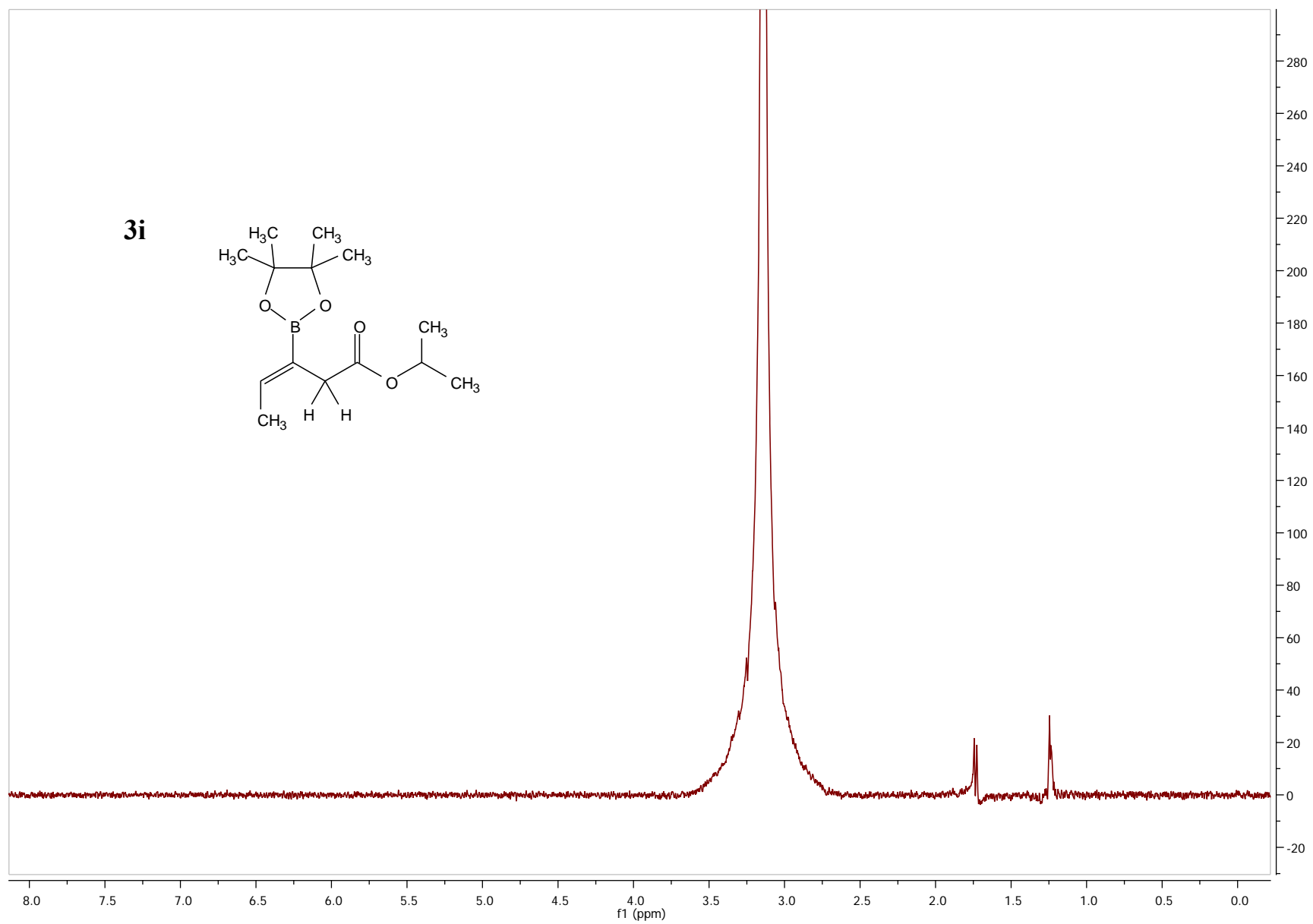






Examples of 1D NOESY experiments:





^1H and ^{13}C NMR spectra of compound 9:



