Difluorinative Ring Expansions of Benzo-Fused Carbocycles and Heterocycles are Achieved with *p*-(Difluoroiodo)toluene

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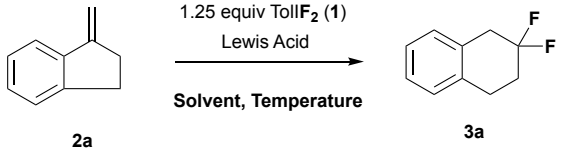
General Experimental and Characterization Details:

Reactions were carried out in oven-dried glassware under a nitrogen atmosphere. Solvents were dried and purified using a JC Meyer solvent purification system and were used without further purification. Transfer of anhydrous solvents and reagents was accomplished with oven-dried syringes. Thin layer chromatography was performed on glass plates pre-coated with 0.25 mm Kieselgel 60 F254 (Silicycle). Flash chromatography columns were packed with 230-400 mesh silica gel (Silicycle). Infrared spectra were recorded on a Perkin Elmer FT-IR Spectrum Two with ATR Two. Proton NMR spectra (^{1}H NMR) were recorded at 300 or 500 MHz, and are reported (ppm) relative to the residual chloroform peak (7.26 ppm), and coupling constants (*J*) are reported in hertz (Hz). Carbon NMR spectra (^{13}C NMR) were recorded at 126 or 75 MHz and are reported (ppm) relative to the center line of the triplet from $CDCl_3$ (77.16 ppm). Fluorine NMR spectra (^{19}F NMR) were recorded at 282 or 470 MHz, and are reported (ppm) relative to the peak of trifluoroacetic acid (-76.53 ppm). High resolution mass spectroscopy was performed on a Thermo Fisher Scientific Q-Exactive hybrid mass spectrometer equipped with an Agilent HPLC pump interfaced with the Q-Exactive's APCI and ESI source or a Kratos MS50G Double focusing sector (EB) with a direct insertion probe and EI source.

Reaction Optimization for Synthesis of 3a (Tables SI-1 – SI-2):

To an over dried flask with a magnetic stir bar was charged alkene **2a** (26 mg, 0.20 mmol, 1.0 equiv) and anhydrous solvent (1 mL), and the resulting solution was placed under a nitrogen atmosphere. To this, a solution of (difluoroiodo)toluene (63 mg, 0.25 mmol, 1.25 equiv) in solvent (1 mL) was added. The reaction flask was stirred under room temperature while Lewis Acid was added. The reaction was monitored by TLC analysis, and upon consumption of the alkene **3a** (20 mins) the reaction mixture was concentrated under vacuum by rotary evaporation. The resulting crude product **3a** mixture was used to test ^{19}F NMR yield using 4-Fluorotoluene as an internal standard.

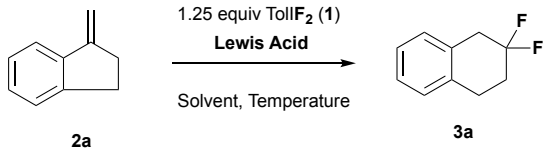
Table SI-1. Screening of Temperature and Solvent



Entry	Lewis Acid (mol %)	Solvent	Temperature	Yield[a]
1	without	DCE	RT	45%
2	**$BF_3{\cdot}Et_2O$ (20)**	**DCE**	**RT**	**74%**
3	$BF_3{\cdot}Et_2O$ (20)	DCE	Reflux	64%
4	$BF_3{\cdot}Et_2O$ (20)	DCE	0 ^oC	35%
5	$BF_3{\cdot}Et_2O$ (20)	DCE	RT[b]	69%
6	$BF_3{\cdot}Et_2O$ (20)	DCE	RT[c]	65%
7	$BF_3{\cdot}Et_2O$ (20)	DCM	RT	34%
8	$BF_3{\cdot}Et_2O$ (20)	PhCl	RT	25%
9	$BF_3{\cdot}Et_2O$ (20)	Toluene	RT	20%
10	$BF_3{\cdot}Et_2O$ (20)	CH_3CN	RT	n.r.
11	$BF_3{\cdot}Et_2O$ (20)	MeOH	RT	n.r.
12	$BF_3{\cdot}Et_2O$ (20)	$CHCl_3$	RT	15%
13	$BF_3{\cdot}Et_2O$ (20)	THF	RT	trace

[a] ^{19}F NMR yield using 4-fluorotoluene as an internal standard.
[b] Open the air; [c] Reaction performed in Teflon vessel.

Table SI-2. Screening of Lewis Acid

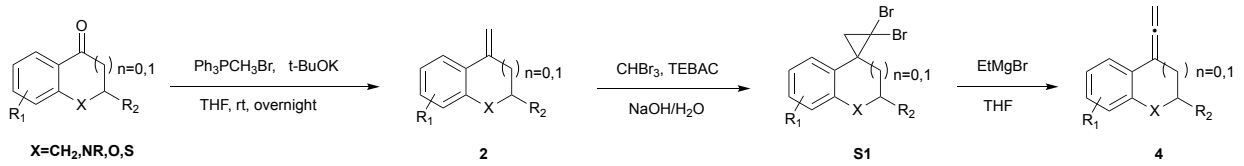


2a 3a

Entry	Lewis Acid (mol %)	Solvent	Temperature	Yield[a]
1	$BF_3{\cdot}Et_2O$ (20)	DCE	RT	74%
2	TiF_3 (20)	DCE	RT	31%
3	TiF_4 (20)	DCE	RT	31%
4	AlF_3 (20)	DCE	RT	27%
5	lnF_3 (20)	DCE	RT	34%
6	SbF_3 (20)	DCE	RT	32%
7	BiF_3 (20)	DCE	RT	26%
8	FeF_3 (20)	DCE	RT	29%
9	FeF_2 (20)	DCE	RT	30%
10	SnF_3 (20)	DCE	RT	32%
11	$BF_3{\cdot}Et_2O$ (1)	DCE	RT	70%
12	**$BF_3{\cdot}Et_2O$ (5)**	**DCE**	**RT**	**78% (63%)[b]**
13	$BF_3{\cdot}Et_2O$ (10)	DCE	RT	73%
14	$BF_3{\cdot}Et_2O$ (20)	DCE	RT	74%
15	$BF_3{\cdot}Et_2O$ (30)	DCE	RT	57%

[a] ^{19}F NMR yield using 4-fluorotoluene as an internal standard.
[b] Isolated yield.

General procedure for Alkene and Allene synthesis (GP-A1 – A3):[1]

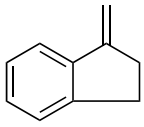


Step A1: In an oven dried flask, was added methyl triphenylphosphonium bromide (1.2 mmol, 1.2 equiv) followed by THF (2.5 mL/mmol). Then t-BuOK (1.2 mmol, 1.2 equiv) was added and the resulting yellow suspension was stirred at room temperature for 60 min. To this suspension, a solution of ketone (1.0 mmol, 1.0 equiv) was added in one portion and the resulting mixture was further stirred at room temperature overnight. Water and DCM were added to the reaction mixture, and the aqueous phase was extracted with DCM (3 × 50 mL). The combined organic phases were washed with saturated NaCl solution, dried over Na_2SO_4 and the solvent removed under reduced pressure. The reaction mixture was purified by column chromatography over silica gel to afford alkene **2a-2u, 2x**. **2v** and **2w** were made according the literature.[2]

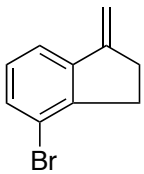
Step A2: To a solution of alkene (1.0 mmol, 1.0 equiv), bromoform (1.5 mmol, 1.5 equiv) and $BnNEt_3Cl$ (1.0 mol%) was added dropwise a solution of 50% NaOH, and the mixture was stirred at room temperature for 60 min, then heated to 60 °C and further stirred until conversion was complete as observed by TLC analysis. Water and DCM were added and the aqueous phase was extracted with DCM (3 x 50 mL). The combined organic phases were washed with saturated NaCl solution, dried over Na_2SO_4 and the solvent removed under reduced pressure. The reaction mixture was purified by column chromatography to afford **S1**.

Step A3: EtMgBr (1.5 mmol, 3.0 M in ether, 1.5 equiv) was added dropwise to a pre-cooled (ice-bath) solution of **S1** (1.0 mmol, 1.0 equiv) in dry THF (1.0 mL/mmol) under nitrogen atmosphere. After EtMgBr was added the mixture was then slowly warmed to room temperature, and stirred at room temperature for an additional 2 hours. Then the reaction was quenched by HCl (0.5 N, 10 ml) solution, water was added, and the mixture extracted with ether (3 x 50 mL). The combined organic layers were washed with brine, dried with anhydrous Na_2SO_4 and filtered. After removing the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel to afford allenes **4a**-**4i**.

Characterization data for the synthesis of alkenes 2:

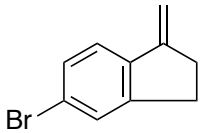


1-methylene-2,3-dihydro-1*H*-indene (2a):[3] The corresponding ketone (1.32 g, 10.0 mmol, 1.0 equiv) was treated with GP-A1 and purified by silica gel column chromatography eluting with hexane to obtain **2a** (800 mg, 6.2 mmol, 62%) as a colorless liquid. R_f=0.7 (Hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 – 7.49 (m, 1H), 7.27 – 7.19 (m, 3H), 5.46 (br. s, 1H), 5.04 (br. s, 1H), 3.01 – 2.96 (m, 2H), 2.84 – 2.78 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.5, 146.6, 141.0, 128.1, 126.3, 125.2, 120.5, 102.3, 31.1, 30.0.

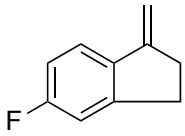


4-bromo-1-methylene-2,3-dihydro-1*H*-indene (2b): The corresponding ketone (422 mg, 2.0 mmol, 1.0 equiv) was treated with GP-A1 and purified by silica gel column chromatography eluting with hexane to obtain **2b** (380 mg, 1.8 mmol, 91%) as a colorless liquid. R_f=0.65 (Hexane). IR (ATR): 2921, 1640, 1562, 1457, 1283, 1131, 1094, 871, 797, 776, 731, 536 cm^{-1}**.** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (d, J = 7.6 Hz, 1H), 7.37 (d, J = 7.8 Hz, 1H), 7.07 (t, J = 7.7 Hz, 1H), 5.48 (br. s, 1H), 5.08 (s, 1H), 3.01 – 2.96 (m, 2H), 2.84 – 2.80 (m, 2H). ^{13}C NMR

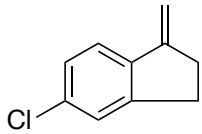
(75 MHz, $CDCl_3$) δ 150.3, 146.7, 143.0, 130.9, 128.2, 120.8, 119.3, 104.2, 31.5, 30.2. HRMS-ESI calcd for $C_{10}H_{10}Br$ $[M+H]^+$ 208.9960, found 208.9960.



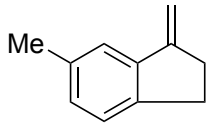
5-bromo-1-methylene-2,3-dihydro-1*H*-indene (2c):[4] The corresponding ketone (422 mg, 2.0 mmol, 1.0 equiv) was treated with GP-A1 and purified by silica gel column chromatography eluting with hexane to obtain **2c** (200 mg, 0.96 mmol, 48%) as a colorless liquid. R_f=0.65 (Hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (s, 1H), 7.35 – 7.29 (m, 2H), 5.44 (br. s, 1H), 5.06 (br. s, 1H), 2.98 – 2.93 (m, 2H), 2.82 – 2.77 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.4, 148.8, 140.1, 129.6, 128.5, 122.1, 122.0, 103.4, 31.2, 29.9.



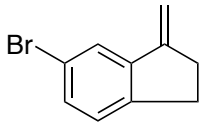
5-fluoro-1-methylene-2,3-dihydro-1H-indene (2d):[5] The corresponding ketone (300 mg, 2.0 mmol, 1.0 equiv) was treated with GP-A1 and purified by silica gel column chromatography eluting with hexanes to obtain **2d** (210 mg, 1.4 mmol, 71%) as a colorless liquid. R_f=0.65 (Hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (t, J = 7.0 Hz, 1H), 6.95 – 6.87 (m, 2H), 5.37 (br. s, 1H), 5.01 (br. s, 1H), 2.99 – 2.94 (m, 2H), 2.85 – 2.80 (m, 2H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -114.4. ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.2 (d, J = 246.5 Hz), 149.3, 148.9 (d, J = 8.4 Hz), 137.2, 121.8 (d, J = 9.2 Hz), 113.9 (d, J = 23.1 Hz), 112.0 (d, J = 21.8 Hz), 102.0, 31.6, 30.1.



5-chloro-1-methylene-2,3-dihydro-1*H*-indene (2e):[4] The corresponding ketone (332 mg, 2.0 mmol, 1.0 equiv) was treated with GP-A1 and purified by silica gel column chromatography eluting with hexane to obtain **2e** (270 mg, 1.6 mmol, 82%) as a colorless liquid. R_f=0.65 (Hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (d, J = 8.3 Hz, 1H), 7.22 (s, 1H), 7.15 (d, J = 8.3 Hz, 1H), 5.41 (br. s, 1H), 5.03 (br. s, 1H), 2.96 – 2.92 (m, 2H), 2.83 – 2.77 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.2, 148.3, 139.6, 133.7, 126.7, 125.3, 121.5, 103.0, 31.2, 29.8.

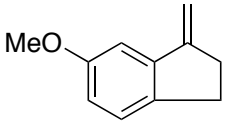


6-methyl-1-methylene-2,3-dihydro-1*H*-indene (2f): The corresponding ketone (292 mg, 2.0 mmol, 1.0 equiv) was treated with GP-A1 and purified by silica gel column chromatography eluting with hexane to obtain **2f** (260 mg, 1.8 mmol, 90%) as a colorless liquid. R_f=0.60 (Hexane). IR (ATR): 2916, 1739, 1611, 1471, 1438, 1377, 1216, 1001, 945, 804, 606, 527 cm^{-1}**.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (s, 1H), 7.21 (d, J = 7.7 Hz, 1H), 7.10 (d, J = 7.6 Hz, 1H), 5.49 (br. s, J = 2.9 Hz, 1H), 5.07 (br. s, 1H), 3.01 – 2.98 (m, 2H), 2.87 – 2.84 (m, 2H), 2.42 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.7, 143.9, 141.2, 136.0, 129.4, 125.1, 121.1, 102.1, 31.6, 29.7, 21.3. HRMS-ESI calcd for $C_{11}H_{13}$ $[M+H]^+$ 145.1011, found 145.1013.

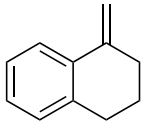


6-bromo-1-methylene-2,3-dihydro-1*H*-indene (2g): The corresponding ketone (422 mg, 2.0 mmol, 1.0 equiv) was treated with GP-A1 and purified by silica gel column chromatography eluting with hexane to obtain **2g** (400 mg, 1.9 mmol, 96%) as a colorless liquid. R_f=0.65 (Hexane). IR (ATR): 2926, 1639, 1466, 1428, 1092, 873, 816,

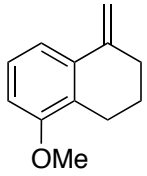
710, 556 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.30 (d, *J* = 7.9 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 1H), 5.43 (br. s, 1H), 5.06 (br. s, 1H), 2.93 – 2.88 (m, 2H), 2.82 – 2.77 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.3, 145.5, 143.4, 131.0, 126.8, 123.8, 120.5, 103.9, 31.4, 29.7. HRMS-ESI calcd for $C_{10}H_{10}Br$ $[M+H]^+$ 208.9960, found 208.9960.



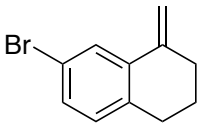
6-methoxy-1-methylene-2,3-dihydro-1*H*-indene (2h):[6] The corresponding ketone (324 mg, 2.0 mmol, 1.0 equiv) was treated with GP-A1 and purified by silica gel column chromatography eluting with hexane and dichloromethane to obtain **2h** (192 mg, 1.2 mmol, 60%) as a colorless liquid. R_f=0.30 (Hexane: dichloromethane=85: 15). ^1H NMR (300 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.3 Hz, 1H), 6.99 (s, 1H), 6.80 (dd, *J* = 8.3, 2.5 Hz, 1H), 5.40 (br. s, 1H), 5.02 (br. s, 1H), 3.82 (s, 3H), 2.93 – 2.88 (m, 2H), 2.83 – 2.78 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.9, 150.8, 142.3, 139.1, 126.0, 115.7, 104.6, 102.4, 55.5, 31.9, 29.3.



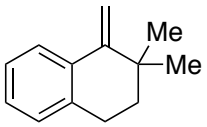
1-methylene-1,2,3,4-tetrahydronaphthalene (2i):[7] The corresponding ketone (1.46 g, 10 mmol, 1.0 equiv) was treated with GP-A1 and purified by silica gel column chromatography eluting with hexane to obtain **2i** (1.0 g, 6.9 mmol, 69%) as a colorless liquid. R_f=0.7 (Hexane). ^1H NMR (500 MHz, $CDCl_3$) δ 7.81 – 7.79 (m, 1H), 7.32 – 7.28 (m, 2H), 7.24 – 7.23 (m, 1H), 5.63 (br. s, 1H), 5.10 (br. s, 1H), 2.98 (t, *J* = 6.3 Hz, 2H), 2.74 – 2.68 (m, 2H), 2.05 – 2.00 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.6, 137.4, 134.8, 129.3, 127.7, 126.0, 124.3, 108.0, 33.4, 30.6, 24.0.



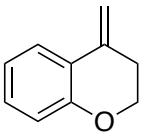
5-methoxy-1-methylene-1,2,3,4-tetrahydronaphthalene (2j): The corresponding ketone (810 mg, 5.0 mmol, 1.0 equiv) was treated with GP-A1 and purified by silica gel column chromatography eluting with hexane and dichloromethane to obtain **2j** (790 mg, 4.9 mmol, 99%) as a colorless liquid. R_f=0.30 (Hexane: dichloromethane=85: 15). IR (ATR): 2941, 1737, 1579, 1486, 1428, 1287, 1230, 1032, 869, 708, 654 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.26 (d, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 8.0 Hz, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 5.45 (s, 1H), 4.95 (s, 1H), 3.82 (s, 3H), 2.73 (t, *J* = 6.5 Hz, 2H), 2.50 – 2.46 (m, 2H), 1.91 – 1.83 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.0, 136.0, 126.3, 126.0, 116.6, 116.6, 108.6, 108.3, 55.4, 33.0, 23.7, 23.4. HRMS-ESI calcd for $C_{12}H_{15}O$ $[M+H]^+$175.1117, found 175.1119.



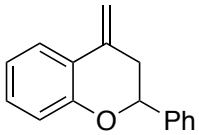
7-bromo-1-methylene-1,2,3,4-tetrahydronaphthalene (2k):[8] The corresponding ketone (450 mg, 2.0 mmol, 1.0 equiv) was treated with GP-A1 and purified by silica gel column chromatography eluting with hexane to obtain **2k** (415 mg, 1.86 mmol, 93%) as a colorless liquid. R_f=0.65 (Hexane). ^1H NMR (300 MHz, $CDCl_3$) δ 7.74 (br. s, 1H), 7.26 (d, *J* = 6.8 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 5.44 (s, 1H), 4.98 (s, 1H), 2.77 (t, *J* = 6.3 Hz, 2H), 2.53 – 2.49 (m, 2H), 1.89 – 1.81 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.1, 136.7, 136.0, 130.7, 130.2, 127.0, 119.6, 109.1, 32.7, 29.9, 23.4.



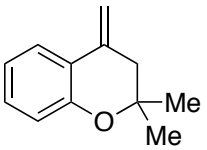
2,2-dimethyl-1-methylene-1,2,3,4-tetrahydronaphthalene (2l): The corresponding ketone (2.7 g, 15 mmol, 1.0 equiv) was treated with GP-A1 and purified by silica gel column chromatography eluting with hexane to obtain **2l** (1.7 g, 9.8 mmol, 65%) as colorless liquid. R_f=0.55 (Hexane: dichloromethane=85:15). IR (ATR): 2959, 1623, 1449, 1429, 1284, 1232, 943, 881, 777, 761, 708, 675 cm^{-1}**.** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 1H), 7.20 – 7.08 (m, 3H), 5.44 (br. s, 1H), 5.07 (br. s, 1H), 2.86 (t, *J* = 6.5 Hz, 2H), 1.68 (t, *J* = 6.6 Hz, 2H), 1.15 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.5, 136.2, 135.2, 128.8, 127.2, 125.9, 125.3, 106.2, 37.2, 34.8, 27.7, 26.5. HRMS-ESI calcd for $C_{13}H_{17}$ $[M+H]^+$ 173.1324, found 173.1325.



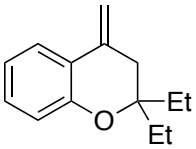
4-methylenechromane (2m):[9] The corresponding ketone (750 mg, 5.1 mmol, 1.0 equiv) was treated with GP-A1 and purified by silica gel column chromatography eluting with hexane to obtain **2m** (48 mg, 0.33 mmol, 6.5%) as a colorless liquid. R_f=0.61 (Hexane: dichloromethane=80: 20). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 7.9, 1.21 Hz, 1H), 7.18 (t, *J* = 7.0 Hz, 1H), 6.93 – 6.85 (m, 2H), 5.53 (br. s, 1H), 4.90 (br. s 1H), 4.26 (t, *J* = 5.7, 2H), 2.70 (t, *J* = 5.6 Hz, 2H).



4-methylene-2-phenylchromane (2n): The corresponding ketone (448 mg, 2 mmol, 1 equiv) was treated with GP-A1 and purified by silica gel column chromatography eluting with hexane and dichloromethane to obtain **2n** (133 mg, 0.60 mmol, 30%) as a colorless liquid. R_f=0.35 (Hexane: dichloromethane=85: 15). IR (ATR): 2970, 1738, 1451, 1365, 1228, 1217, 754, 697, 527 cm^{-1}**.** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.8 Hz, 1H), 7.46 – 7.30 (m Hz, 5H), 7.19 (t, *J* = 7.5 Hz, 1H), 6.95 – 6.90 (m, 2H), 5.56 (br. s, 1H), 5.09 (dd, *J* = 10.8, 3.3 Hz, 1H), 4.92 (br. s, 1H), 2.91 – 2.75 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.7, 140.7, 137.1, 129.5, 128.5, 128.0, 126.0, 124.3, 121.3, 120.7, 117.5, 107.5, 78.3, 39.1. HRMS-ESI calcd for $C_{16}H_{15}O$ $[M+H]^+$ 223.1117, found 223.1118.

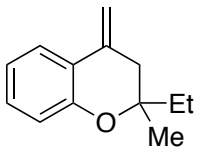


2,2-dimethyl-4-methylenechromane (2o): The corresponding ketone (352 mg, 2.0 mmol, 1.0 equiv) was treated with GP-A1 and purified by silica gel column chromatography eluting with hexane and dichloromethane to obtain **2o** (278 mg, 1.6 mmol, 80%) as a colorless liquid. R_f=0.30 (Hexane: dichloromethane=85: 15). IR (ATR): 2970, 1634, 1572, 1480, 1455, 1257, 1230, 1171, 937, 879, 826, 747, 532 cm^{-1}**.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.7 Hz, 1H), 7.20 (t, *J* = 7.7 Hz, 1H), 6.90 (t, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 8.2 Hz, 1H), 5.57 (s, 1H), 4.92 (s, 1H), 2.52 (s, 2H), 1.36 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.3, 136.8, 129.6, 124.2, 120.9, 119.9, 117.7, 108.0, 75.5, 42.8, 26.6. HRMS-ESI calcd for $C_{12}H_{15}O$ $[M+H]^+$ 175.1117, found 175.1119.

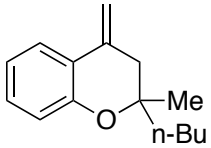


2,2-diethyl-4-methylenechromane (2p): The corresponding ketone (408 mg, 2.0 mmol, 1.0 equiv) was treated with GP-A1 and purified by silica gel column chromatography eluting with hexane and dichloromethane to

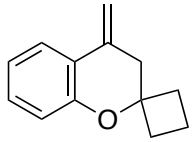
obtain **2p** (210 mg, 1.0 mmol, 52%) as colorless liquid. R_f=0.30 (Hexane: dichloromethane=85: 15). IR (ATR): 2970, 1737, 1607, 1481, 1457, 1231, 1217, 1037, 887, 752, 527 cm^{-1}**.** ^1H NMR (300 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.15 (td, *J* = 7.8, 1.6 Hz, 1H), 6.86 – 6.80 (m, 2H), 5.52 (br. s, 1H), 4.87 (br. s, 1H), 2.48 (s, 2H), 1.74 – 1.51 (m, 4H), 0.89 (t, *J* = 7.5 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.3, 136.6, 129.5, 123.9, 121.2, 119.6, 117.6, 107.9, 79.6, 38.1, 28.0, 7.4. HRMS-ESI calcd for $C_{14}H_{19}O$ $[M+H]^+$ 203.1430, found 203.1432.



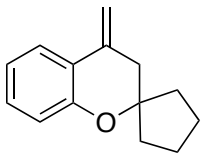
2-ethyl-2-methyl-4-methylenechromane (2q): The corresponding ketone (380 mg, 2.0 mmol, 1.0 equiv) was treated with GP-A1 and purified by silica gel column chromatography eluting with hexane and dichloromethane to obtain **2q** (290 mg, 1.5 mmol, 77%) as a colorless liquid. R_f=0.30 (Hexane: dichloromethane=85: 15). IR (ATR): 2970, 1738, 1481, 1456, 1229, 1217, 1129, 750 cm^{-1}**.** ^1H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.8 Hz, 1H), 7.19 (t, *J* = 7.8 Hz, 1H), 6.89 (t, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 8.2 Hz, 1H), 5.57 (s, 1H), 4.91 (s, 1H), 2.56 (d, *J* = 14.3 Hz, 1H), 2.46 (d, *J* = 14.3 Hz, 1H), 1.76 – 1.68 (m, 1H), 1.66 – 1.57 (m,= 1H), 1.29 (s, 3H), 0.98 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.3, 136.7, 129.6, 124.1, 121.1, 119.8, 117.7, 108.1, 77.7, 40.6, 31.9, 23.5, 7.9. HRMS-ESI calcd for $C_{13}H_{17}O$ $[M+H]^+$ 189.1273, found 189.1275.



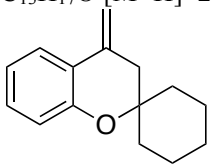
2-butyl-2-methyl-4-methylenechromane (2r): The corresponding ketone (436 mg, 2.0 mmol, 1.0 equiv) was treated with GP-A1 and purified by silica gel column chromatography eluting with hexane and dichloromethane to obtain **2r** (320 mg, 1.5 mmol, 74%) as a colorless liquid. R_f=0.25 (Hexane: dichloromethane=85: 15). IR (ATR): 2955, 1738, 1608, 1480, 1456, 1377, 1227, 1129, 1042, 880, 750 cm^{-1}**.** ^1H NMR (300 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.8 Hz, 1H), 7.18 (t, *J* = 7.8 Hz, 1H), 6.89 – 6.81 (m, 2H), 5.55 (br. s, 1H), 4.89 (br. s, 1H), 2.55 (d, *J* = 14.3 Hz, 1H), 2.44 (d, *J* = 14.3 Hz, 1H), 1.68 – 1.53 (m, 2H), 1.44 – 1.28 (m, 7H), 0.91 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.3, 136.8, 129.6, 124.2, 121.1, 119.8, 117.8, 108.1, 77.6, 41.0, 39.1, 25.8, 24.0, 23.2, 14.1. HRMS-ESI calcd for $C_{15}H_{21}O$ $[M+H]^+$ 217.1586, found 217.1587.



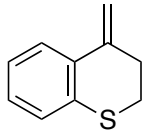
4-methylenespiro[chromane-2,1'-cyclobutane] (2s): The corresponding ketone (404 mg, 2.0 mmol, 1.0 equiv) was treated with GP-A1 by and purified by silica gel column chromatography eluting with hexane and dichloromethane to obtain **2s** (250 mg, 1.3 mmol, 63%) as a colorless liquid. R_f=0.30 (Hexane: dichloromethane=85: 15). IR (ATR): 2937, 1738, 1606, 1480, 1455, 1304, 1226, 1131, 1068, 960, 884, 750 cm^{-1}**.** ^1H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.7 Hz, 1H), 7.16 (t, *J* = 7.8 Hz, 1H), 6.89 – 6.83 (m, 2H), 5.56 (br. s, 1H), 4.94 (s, 1H), 2.64 (s, 2H), 2.31 – 2.20 (m, 2H), 2.09 – 2.00 (m, 2H), 1.89 – 1.76 (m, 1H), 1.76 – 1.58 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.0, 136.3, 129.5, 124.1, 121.6, 120.2, 117.6, 108.6, 78.0, 39.2, 33.5, 12.1. HRMS-ESI calcd for $C_{13}H_{15}O$ $[M+H]^+$ 187.1117, found 187.1119.



4-methylenespiro[chromane-2,1'-cyclopentane] (2t): The corresponding ketone (404 mg, 2.0 mmol, 1.0 equiv) was treated with GP-A1 and purified by silica gel column chromatography eluting with hexane and dichloromethane to obtain **2t** (150 mg, 0.76 mmol, 38%) as a colorless liquid. R_f=0.30 (Hexane: dichloromethane=85: 15). IR (ATR): 2969, 1738, 1607, 1455, 1365, 1229, 1216, 755, 527 cm^{-1}**.** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.7 Hz, 1H), 7.14 (t, *J* = 7.7 Hz, 1H), 6.84 (t, *J* = 7.5 Hz, 1H), 6.78 (d, *J* = 8.1 Hz, 1H), 5.50 (s, 1H), 4.87 (s, 1H), 2.55 (s, 2H), 1.91 – 1.82 (m, 4H), 1.71 – 1.52 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.5, 137.2, 129.3, 124.1, 121.5, 119.9, 117.8, 107.5, 86.8, 40.8, 37.5, 24.1. HRMS-ESI calcd for $C_{13}H_{17}O$ $[M+H]^+$ 201.1273, found 201.1275.

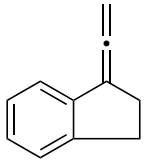


4-methylenespiro[chromane-2,1'-cyclohexane] (2u): The corresponding ketone (432 mg, 2.0 mmol , 1.0 equiv) was treated with GP-A1 and purified by silica gel column chromatography eluting with hexane and dichloromethane to obtain **2u** (90 mg, 0.42 mmol, 21%) as a colorless liquid. R_f=0.30 (Hexane: dichloromethane=85: 15). IR (ATR): 2932, 1738, 1608, 1480, 1455, 1231, 1127, 971, 910, 815, 750 cm^{-1}**.** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.8 Hz, 1H), 7.16 (t, *J* = 8.0 Hz, 1H), 6.86 – 6.83 (m, 2H), 5.52 (s, 1H), 4.87 (s, 1H), 2.48 (s, 2H), 1.87 – 1.25 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.1, 136.4, 129.5, 124.1, 121.4, 119.9, 117.8, 108.0, 76.2, 41.5, 34.9, 25.8, 21.7. HRMS-ESI calcd for $C_{15}H_{19}O$ $[M+H]^+$ 215.1430, found 215.1431.

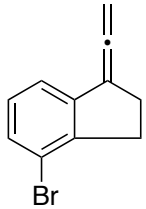


4-methylenethiochromane (2x):[10] The corresponding ketone (1.74 g, 10 mmol, 1.0 equiv) was treated with GP-A1 and purified by silica gel column chromatography eluting with hexane to obtain **2x** (1.2 g, 7.5 mmol, 75%) as a colorless liquid. R_f=0.45 (Hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.8 Hz, 1H), 7.11 – 7.09 (m, 2H), 7.04 – 6.99 (m, 1H), 5.48 (br. s, 1H), 4.98 (br. s, 1H), 3.09 – 3.05 (m, 2H), 2.85 – 2.82 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.4, 133.3, 132.7, 128.0, 126.6, 126.2, 124.1, 111.5, 32.8, 27.7.

<u>Characterization data for the synthesis of allenes 4:</u>

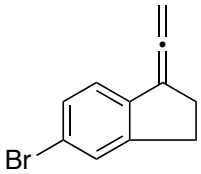


1-vinylidene-2,3-dihydro-1*H*-indene (4a):[11] Compound **2a** (1.30 g, 10 mmol, 1.0 equiv) was treated with GP-A2-3 and purified by silica gel column chromatography eluting with hexane to obtain **4a** (650 mg, 4.3 mmol, 43%) as a colorless liquid. R_f=0.7 (Hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 – 7.30 (m, 1H), 7.24 – 7.17 (m, 3H), 5.14 (t, *J* = 4.7 Hz, 2H), 3.07 – 3.02 (m, 2H), 2.96 – 2.88 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.3, 143.9, 139.0, 127.2, 126.7, 124.8, 122.4, 106.8, 79.6, 30.6, 28.6.

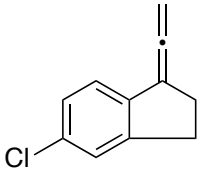


4-bromo-1-vinylidene-2,3-dihydro-1*H*-indene (4b): The corresponding ketone (1.5 g, 7.5 mmol, 1.0 equiv) was treated with GP-A1-3 and purified by silica gel column chromatography eluting with hexane to obtain **4b**

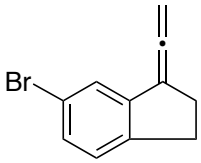
(0.9 g, 4.1 mmol, 54%) as a colorless liquid. R_f=0.65 (Hexane). IR (ATR): 2921, 1721, 1563, 1447, 1378, 1228, 1217, 1114, 887, 773, 714 cm^{-1}**.** ^1H NMR (300 MHz, $CDCl_3$) δ 7.30 (d, *J* = 7.8 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.04 (t, *J* = 7.7 Hz, 1H), 5.15 (t, *J* = 4.7 Hz, 2H), 3.03 – 2.98 (m, 2H), 2.94 – 2.86 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.7, 143.9, 141.0, 129.9, 128.5, 121.1, 120.3, 107.1, 80.0, 32.1, 27.6. HRMS-ESI calcd for $C_{11}H_{10}Br$ $[M+H]^+$ 220.9960, found 220.9969.



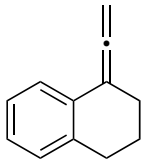
5-bromo-1-vinylidene-2,3-dihydro-1*H*-indene (4c): Compound **2c** (209 mg, 1 mmol, 1 equiv) was treated with GP-A2-3 and purified by silica gel column chromatography eluting with hexane to obtain **4c** (133 mg, 0.60 mmol, 60%) as a colorless liquid. R_f=0.65 (Hexane). IR (ATR): 2925, 1713, 1593, 1468, 1412, 1316, 1196, 1055, 1031, 856, 580 cm^{-1}**.** ^1H NMR (300 MHz, $CDCl_3$) δ 7.33 (s, 1H), 7.28 (d, *J* = 8.2 Hz, 1H), 7.11 (d, *J* = 8.1 Hz, 1H), 5.10 (t, *J* = 4.6 Hz, 2H), 3.01 - 2.96 (m, 2H), 2.92 – 2.86 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.3, 145.9, 138.2, 129.8, 128.0, 123.6, 120.9, 106.0, 80.0, 30.4, 28.6. HRMS-ESI calcd for $C_{11}H_{10}Br$ $[M+H]^+$ 220.9960, found 220.9969.



5-chloro-1-vinylidene-2,3-dihydro-1*H*-indene (4d): The corresponding ketone (1.1 g, 6.7 mmol, 1.0 equiv) was treated with GP-A1-3 and purified by silica gel column chromatography eluting with hexane to obtained **4d** (1.5 g, 4.5 mmol, 67%) as a colorless liquid. R_f=0.65 (Hexane). IR (ATR): 2936, 1947, 1717, 1470, 1435, 1412, 1316, 1199, 1070, 870, 822, 602 cm^{-1}**.** ^1H NMR (300 MHz, $CDCl_3$) δ 7.19 – 7.13 (m, 3H), 5.14 – 5.11 (m, 2H), 3.01 – 2.97 (m, 2H), 2.94 – 2.88 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.4, 145.7, 137.8, 132.9, 127.1, 125.1, 123.4, 106.0, 80.1, 30.5, 28.8. HRMS-ESI calcd for $C_{11}H_{10}Cl$ $[M+H]^+$ 177.0465, found 177.0465.

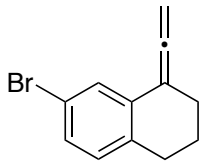


6-bromo-1-vinylidene-2,3-dihydro-1*H*-indene (4e): The corresponding ketone (2.11 g, 10 mmol, 1.0 equiv) was treated with GP-A1-3 and purified by silica gel column chromatography eluting with hexane to obtain **4e** (0.80 g, 3.6 mmol, 36%) as a colorless liquid. R_f=0.65 (Hexane). IR (ATR): 2936, 1686,1588, 1476, 1261, 1220, 1081, 884, 807 cm^{-1}**.** ^1H NMR (300 MHz, $CDCl_3$) δ 7.37 (br. s, 1H), 7.25 – 7.23 (m, 1H), 7.06 – 7.03 (m, 1H), 5.14 (br. s, 2H), 2.97 – 2.87 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.3, 142.6, 141.5, 130.1, 126.2, 125.3, 120.5, 106.0, 80.1, 30.1, 28.7. HRMS-ESI calcd for $C_{11}H_{10}Br$ $[M+H]^+$ 220.9960, found 220.9969.

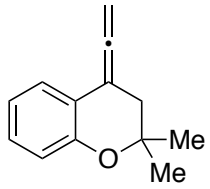


1-vinylidene-1,2,3,4-tetrahydronaphthalene (4f):[7] Compound **2i** (1.4 g, 10 mmol, 1.0 equiv) was treated with GP-A2-3 then purified by silica gel column chromatography eluting with hexane to obtain **4f** (900 mg, 8.5 mmol, 85%) as a colorless liquid. R_f=0.70 (Hexane). ^1H NMR (300 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.4 Hz, 1H), 7.21 –

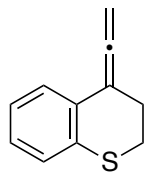
7.15 (m, 2H), 5.14 (br. s, 2H), 2.87 (t, J = 6.3 Hz, 2H), 2.67 – 2.65 (m, 2H), 2.01 – 1.93 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.5, 136.3, 131.1, 129.1, 126.8, 126.5, 126.0, 101.0, 77.9, 30.1, 28.7, 22.8.



7-bromo-1-vinylidene-1,2,3,4-tetrahydronaphthalene (4g): The corresponding ketone (1.12 g, 5.0 mmol, 1.0 equiv) was treated with GP-A1-3 and purified by silica gel column chromatography eluting with hexane to obtain **4g** (0.89 g, 3.8 mmol, 76%) as a colorless liquid. R_f=0.65 (Hexane). IR (ATR): 2925, 1712, 1468, 1439, 1256, 1240, 1191, 1112, 830, 663, 556 cm^{-1}**.** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.19 – 7.17 (m, 1H), 6.95 – 6.92 (m, 1H), 5.16 – 5.01 (m, 2H), 2.71 (t, J = 6.2 Hz, 2H), 2.57 – 2.50 (m, 2H), 1.90 – 1.82 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.3, 135.0, 133.4, 130.6, 129.3, 129.2, 119.6, 100.1, 78.5, 29.5, 28.1, 22.4. HRMS-ESI calcd for $C_{12}H_{12}Br$ $[M+H]^+$235.0116, found 235.0110.

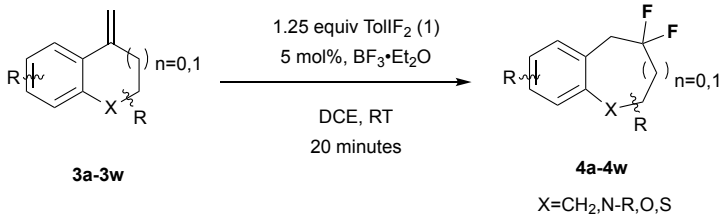


2,2-dimethyl-4-vinylidenechromane (4h): Compound **3o** (900 mg, 5.2 mmol, 1.0 equiv) was treated with GP-A2 and purified by silica gel column chromatography with hexanes and dichloromethane to obtain **S1h** (1.5 g, 4.1 mmol, 79%). Compound **S1h** (2.5 mmol, 915 mg, 1.0 equiv) was then treated with GP-A3 then purified by silica gel column chromatography eluting with hexane and dichloromethane to obtain **4h** (300 mg, 1.5 mmol, 58%) as a colorless liquid. R_f=0.60 (Hexane: dichloromethane=85: 15). IR (ATR): 2977, 1688, 1607, 1485, 1463, 1371, 1308, 1253, 1142, 929 cm^{-1}**.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, J = 7.8 Hz, 1H), 7.10 (t, J = 6.9 Hz, 1H), 6.86 (t, J = 7.6 Hz, 1H), 6.80 – 6.79 (m, 1H), 5.14 (br. s, 2H), 2.53 (br. s, 2H), 1.37 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.5, 153.1, 129.1, 127.3, 120.9, 118.4, 118.1, 96.3, 79.6, 75.3, 39.2, 27.2. HRMS-ESI calcd for $C_{13}H_{15}O$ $[M+H]^+$ 187.1117, found 187.1119.



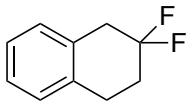
4-vinylidenethiochromane (4i): Compound **2x** (600 mg, 3.7 mmol, 1.0 equiv) was treated with GP-A2-3 and purified by silica gel column chromatography eluting with hexane and dichloromethane to obtain **4i** (460 mg, 3.6 mmol, 96%) as a colorless liquid. R_f=0.45 (Hexane: dichloromethane=85: 15). IR (ATR): 2919, 1940, 1743, 1471, 1432, 1286, 1253, 1217, 1127, 982, 754, 727 cm^{-1}**.** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 - 7.44 (m, 1H), 7.12 – 7.09 (m, 1H), 7.06 – 6.97(m, 2H), 5.09 – 5.08 (m, 2H), 3.07 – 3.03 (m, 2H), 2.91 – 2.86 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.4, 132.1, 128.4, 128.2, 127.2, 126.9, 124.4, 99.5, 78.1, 29.4, 26.7. HRMS-ESI calcd for $C_{11}H_{11}S$ $[M+H]^+$ 175.0576, found 175.0577.

General procedure for fluorinative ring-expansion with alkenes (GP-B):

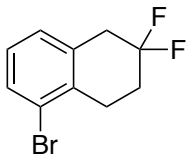


To an over dried flask with a magnetic stir bar was charged alkene **2a-2x** (0.20 mmol, 1.0 equiv) and anhydrous DCE (1 mL), and the resulting solution was placed under a nitrogen atmosphere. To this, a solution of (difluoroiodo)toluene (63 mg, 0.25 mmol, 1.25 equiv) in DCE (1 mL) was added. The reaction flask was stirred under room temperature while $BF_3{\cdot}Et_2O$ (1.3 μL, 5 mol%) was added. The reaction was monitored by TLC analysis, and upon consumption of the alkene (20 mins), then the reaction mixture was concentrated by under vacuum by rotary evaporation. The resulting crude product mixture was purified by silica gel chromatography to provide the *gem*-difluorides.

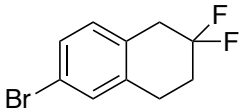
Characterization data for *gem*-difluorides 3:



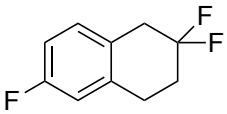
2,2-difluoro-1,2,3,4-tetrahydronaphthalene (3a):[12] Compound **2a** (26.0 mg, 0.20 mmol, 1.0 equiv) was treated with GP-B and purified by silica gel column chromatography eluting with hexane to obtain **3a** (21 mg, 0.13 mmol, 63%) as a colorless liquid. R_f=0.60 (Hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 – 7.18 (m, 3H), 7.13 – 7.12 (m, 1H), 3.29 (t, *J* = 15.1 Hz, 2H), 3.05 (t, *J* = 6.9 Hz, 2H), 2.29 – 2.21 (m, 2H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -95.8. ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.1, 131.8 (t, *J* = 5.6 Hz), 129.1, 128.5, 126.7, 126.4, 123.1 (t, *J* = 239.4 Hz), 38.0 (t, *J* = 26.9 Hz), 31.1 (t, *J* = 24.2 Hz), 27.0 (t, *J* = 5.5 Hz).



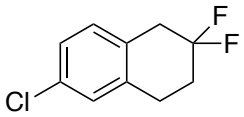
5-bromo-2,2-difluoro-1,2,3,4-tetrahydronaphthalene (3b): Compound **2b** (41.8 mg, 0.20 mmol, 1.0 equiv) was treated with GP-B and purified by silica gel column chromatography eluting with hexane to obtain **3b** (37 mg, 0.15 mmol, 75%) as a colorless liquid. R_f=0.55 (Hexane). IR (ATR): 2946, 1738, 1443, 1374, 1227, 1099, 961, 902, 770, 650 cm^{-1}**.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (t, *J* = 4.6 Hz, 1H), 7.08 – 7.07 (m, 2H), 3.30 (t, *J* = 14.6 Hz, 2H), 3.07 (t, *J* = 7.0 Hz, 2H), 2.31 – 2.23 (m, 2H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -97.7. ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.0 (t, *J* = 5.5 Hz), 133.8, 131.0, 128.4, 127.7, 125.1, 123.5 (t, *J* = 240.1 Hz), 38.1 (t, *J* = 27.1 Hz), 30.8 (t, *J* = 24.4 Hz), 28.2 (t, *J* = 5.5 Hz). HRMS-APCI calcd for $C_{10}H_9BrF_2$ $[M]^+$ 245.9850, found 245.9852.



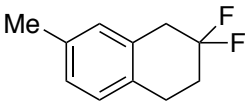
6-bromo-2,2-difluoro-1,2,3,4-tetrahydronaphthalene (3c): Compound **2c** (41.8 mg, 0.20 mmol, 1.0 equiv) was treated with GP-B and purified by silica gel column chromatography eluting with hexane to obtain **3c** (38 mg, 0.15 mmol, 77%) as a colorless liquid. R_f=0.55 (Hexane). IR (ATR): 2943, 738, 1593, 1484, 1451, 1405, 1377, 1335, 1287, 1217, 1201, 1098, 1062, 943, 910, 814, 640, 564 cm^{-1}**.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 2H), 6.99 (d, *J* = 8.0 Hz, 1H), 3.22 (t, *J* = 14.9 Hz, 2H), 3.02 (t, *J* = 6.9 Hz, 2H), 2.27 – 2.19 (m, 2H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -96.1. ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.3, 131.4, 130.7 (t, *J* = 5.6 Hz), 129.5, 122.7 (t, *J* = 240.1 Hz), 120.4, 37.6 (t, *J* = 27.3 Hz), 30.7 (t, *J* = 24.3 Hz), 26.8 (t, *J* = 5.6 Hz). HRMS-APCI calcd for $C_{10}H_9BrF_2$ $[M]^+$ 245.9850, found 245.9852.



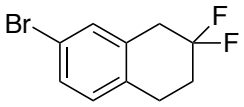
2,2,6-trifluoro-1,2,3,4-tetrahydronaphthalene (3d): Compound **2d** (29.6 mg, 0.20 mmol, 1.0 equiv) was treated with GP-B and purified by silica gel column chromatography eluting with hexane to obtain **3d** (28 mg, 0.15 mmol, 75%) as a colorless liquid. R_f=0.55 (Hexane). IR (ATR): 2946, 1738, 1593, 1503, 1431, 1373, 1267, 1233, 1087, 1068, 970, 872, 807, 522 cm^{-1}**.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 – 7.06 (m, 1H), 6.93 – 6.87 (m, 2H), 3.24 (t, *J* = 14.9 Hz, 2H), 3.03 (t, *J* = 6.9 Hz, 2H), 2.28 – 2.20 (m, 2H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -96.3, -116.7. ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.5 (d, *J* = 244.8 Hz), 136.11 (d, *J* = 7.5 Hz), 130.5 (d, *J* = 8.2 Hz), 127.3, 122.9 (t, *J* = 240.0 Hz), 114.9 (d, *J* = 21.1 Hz), 113.7 (d, *J* = 21.7 Hz), 37.4 (t, *J* = 27.2 Hz), 30.7 (t, *J* = 24.4 Hz), 27.1 (t, *J* = 5.5 Hz). HRMS-APCI calcd for $C_{10}H_9F_3$ $[M]^+$186.0650, found 186.0647.



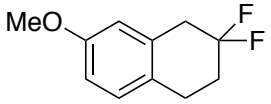
6-chloro-2,2-difluoro-1,2,3,4-tetrahydronaphthalene (3e): Compound **2e** (32.8 mg, 0.20 mmol, 1.0 equiv) was treated with GP-B and purified by silica gel column chromatography eluting with hexane to obtain **3e** (29 mg, 0.14 mmol, 72%) as a colorless liquid. R_f=0.55 (Hexane). IR (ATR): 2945, 1738, 1488, 1373, 1225, 1129, 1099, 1071, 967, 880, 808 cm^{-1}**.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19- 7.17 (m, 2H), 7.05 (d, *J* = 8.8 Hz, 1H), 3.24 (t, *J* = 14.9 Hz, 2H), 3.02 (t, *J* = 6.9 Hz, 2H), 2.23 (tt, *J* = 13.7, 6.9 Hz, 2H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -96.2. ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.9, 132.3, 130.4, 130.2 (t, *J* = 5.6 Hz), 128.4, 126.6, 122.8 (t, *J* = 240.2 Hz), 37.6 (t, *J* = 27.3 Hz), 30.7 (t, *J* = 24.4 Hz), 26.8 (t, *J* = 5.6 Hz). HRMS-APCI calcd for $C_{10}H_9ClF_2$ $[M]^+$ 202.0355, found 202.0351.



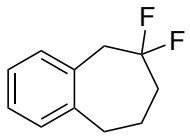
2,2-difluoro-7-methyl-1,2,3,4-tetrahydronaphthalene (3f): Compound **2f** (28.8 mg, 0.20 mmol, 1.0 equiv) was treated with GP-B and purified by silica gel column chromatography eluting with hexane and dichloromethane to obtain **3f** (15.7 mg, 0.086 mmol, 43%) as a colorless liquid. R_f=0.60 (Hexane: dichloromethane=85: 15). IR (ATR): 2926, 1507, 1439, 1370, 1275, 1155, 1097, 1070, 968, 857, 770, 509 cm^{-1}**.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.07 (d, *J* = 7.8 Hz, 1H), 7.02 (d, *J* = 7.9 Hz, 1H), 6.94 (s, 1H), 3.24 (t, *J* = 15.1 Hz, 2H), 3.00 (t, *J* = 6.9 Hz, 2H), 2.33 (s, 3H), 2.27 – 2.18 (m, 2H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -95.9. ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.0, 131.6 (t, *J* = 5.4 Hz), 131.0, 129.6, 128.4, 127.5, 123.3 (t, *J* = 240.0 Hz), 38.0 (t, *J* = 26.8 Hz), 31.2 (t, *J* = 24.1 Hz), 26.6 (t, *J* = 5.5 Hz), 20.9. HRMS-APCI calcd for $C_{11}H_{12}F_2$ $[M]^+$ 182.0901, found 182.0899.



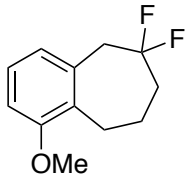
7-bromo-2,2-difluoro-1,2,3,4-tetrahydronaphthalene (3g): Compound **2g** (41.8 mg, 0.20 mmol, 1.0 equiv) was treated with GP-B and purified by silica gel column chromatography eluting with hexane to obtain **3g** (28 mg, 0.11 mmol, 57%) as a colorless liquid. R_f=0.55 (Hexane). IR (ATR): 2943, 1594, 1372, 1268, 1098, 1071, 967, 854, 811, 663 cm^{-1}**.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.3 Hz, 1H), 7.29 – 7.27 (m, 1H), 7.05 (d, *J* = 8.1 Hz, 1H), 3.25 (t, *J* = 14.8 Hz, 2H), 2.98 (t, *J* = 6.9 Hz, 2H), 2.27 – 2.10 (m, 2H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -96.2. ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.1 (t, *J* = 5.6 Hz), 133.1, 131.8, 130.2, 129.8, 122.6 (t, *J* = 240.2 Hz), 120.0, 37.7 (t, *J* = 27.3 Hz), 30.9 (t, *J* = 24.2 Hz), 26.5 (t, *J* = 5.6 Hz). HRMS-APCI calcd for $C_{10}H_9BrF_2$ $[M]^+$ 245.9850, found 245.9852.



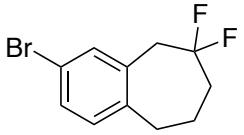
2,2-difluoro-7-methoxy-1,2,3,4-tetrahydronaphthalene (3h): Compound **2h** (32.0 mg, 0.20 mmol, 1.0 equiv) was treated with GP-B and purified by silica gel column chromatography eluting with hexane and dichloromethane to obtain **3h** (19.4 mg, 0.098 mmol, 49%) as a colorless liquid. R_f=0.25 (Hexane: dichloromethane=85: 15). IR (ATR): 2940, 1614, 1506, 1371, 1340, 1318, 1279, 1216, 1117, 1069, 1039, 966, 841, 771, 729 cm^{-1}**.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.4 Hz, 1H), 6.78 (dd, *J* = 8.4, 2.7 Hz, 1H), 6.64 (d, *J* = 2.7 Hz, 1H), 3.81 (s, 3H), 3.26 (t, *J* = 15.0 Hz, 2H), 2.97 (t, *J* = 6.9 Hz, 2H), 2.27 – 2.18 (m, 2H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -96.1. ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.1, 132.9 (t, *J* = 5.5 Hz), 129.5, 126.1, 123.2 (t, *J* = 239.7 Hz), 113.6, 113.1, 55.3, 38.3 (t, *J* = 27.1 Hz), 31.3 (t, *J* = 24.1 Hz), 26.1 (t, *J* = 5.7 Hz). HRMS-ESI calcd for $C_{11}H_{13}OF_2$ $[M+H]^+$ 199.0929, found 199.0929.



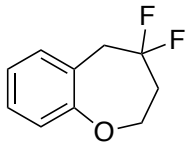
6,6-difluoro-6,7,8,9-tetrahydro-5*H*-benzo[7]annulene (3i):[12] Compound **2i** (28.8 mg, 0.20 mmol, 1.0 equiv) was treated with GP-B and purified by silica gel column chromatography eluting with hexane to obtain **3i** (27.2 mg, 0.15 mmol, 75%) as a colorless liquid. R_f=0.60 (Hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 – 7.18 (m, 3H), 7.16 – 7.14 (m, 1H), 3.36 (t, *J* = 15.0 Hz, 2H), 2.87 – 2.85 (t, 2H), 2.30 – 2.22 (m, 2H), 1.84 – 1.79 (m, 2H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -90.3 (br. s). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.0, 132.4 (t, *J* = 7.3 Hz), 131.2, 129.1, 127.6, 126.7, 121.6 (t, *J* = 240.9 Hz), 44.0 (t, *J* = 28.3 Hz), 39.4 (t, *J* = 25.8 Hz), 34.8, 22.7 (t, *J* = 5.9 Hz).



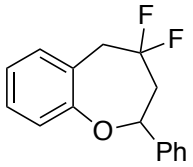
6,6-difluoro-1-methoxy-6,7,8,9-tetrahydro-5*H*-benzo[7]annulene (3j): Compound **2j** (34.8 mg, 0.20 mmol, 1.0 equiv) was treated with GP-B and purified by silica gel column chromatography eluting with hexane and dichloromethane to obtain **3j** (21 mg, 0.098 mmol, 49%) as a colorless liquid. R_f=0.25 (Hexane: dichloromethane=85: 15). IR (ATR): 2940, 1738, 1614, 1505, 1452, 1371, 1339, 1318, 1273, 1159, 1068, 1038, 966, 771, 529 cm^{-1}**.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 (t, *J* = 7.9 Hz, 1H), 6.87 – 6.83 (m, 2H), 3.85 (s, 3H), 3.35 (t, *J* = 13.7 Hz, 2H), 2.96 – 2.94 (m, 2H), 2.28 – 2.20 (m, 2H), 1.78 – 1.73 (m, 2H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -90.1. ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.3, 134.3 (t, *J* = 7.1 Hz), 130.4, 126.9, 123.6, 121.7 (t, *J* = 241.1 Hz), 110.0, 55.8, 43.9 (t, *J* = 28.3 Hz), 39.3 (t, *J* = 25.7 Hz), 23.7, 22.1 (t, *J* = 5.9 Hz). HRMS-ESI calcd for $C_{12}H_{15}OF_2$ $[M+H]^+$ 213.1085, found 213.1086.



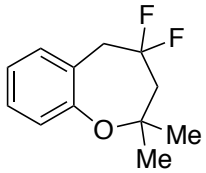
2-bromo-8,8-difluoro-6,7,8,9-tetrahydro-5*H*-benzo[7]annulene (3k): Compound **2k** (44.6 mg, 0.20 mmol, 1.0 equiv) was treated with GP-B and purified by silica gel column chromatography eluting with hexane to obtain **3k** (43 mg, 0.18 mmol, 89%) as a colorless liquid. R_f=0.55 (Hexane). IR (ATR): 2944, 1738, 1594, 1485, 1372, 1343, 1277, 1134, 1096, 1070, 967, 877, 805, 511 cm^{-1}**.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.33 (m, 2H), 7.01 (d, *J* = 8.0 Hz, 1H), 3.30 (t, *J* = 15 Hz, 2H), 2.81 – 2.79 (m, 2H), 2.28 – 2.20 (m, 2H), 1.81 – 1.77 (m, 2H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -90.3. ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.0, 134.6 (t, *J* = 7.3 Hz), 133.9, 130.7, 130.5, 121.2 (t, *J* = 241.9 Hz), 120.0, 43.6 (t, *J* = 28.7 Hz), 39.3 (t, *J* = 25.8 Hz), 34.2, 22.5 (t, *J* = 6.0 Hz). HRMS-ESI calcd for $C_{11}H_{11}BrF_2$ $[M]^+$ 260.0006, found 260.0007.



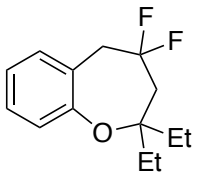
4,4-difluoro-2,3,4,5-tetrahydrobenzo[*b*]oxepine (3m): Compound **2m** (29.2 mg, 0.20 mmol, 1.0 equiv) was treated with GP-B and purified by silica gel column chromatography eluting with hexane and dichloromethane to obtain **3m** (15.4 mg, 0.084 mmol, 42%) as a colorless liquid. R_f=0.25 (Hexane:dichloromethane=80: 20). IR (ATR) 3080, 3042, 2965, 2933, 1606, 1584, 1491, 1278, 1226, 1082, 997, 912, 786, 764, 522 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.26 – 7.17 (m, 2H), 7.09 – 7.00 (m, 2H), 4.08 (t, *J* = 10.7 Hz, 2H), 3.32 (t, *J* = 13.7 Hz, 2H), 2.4 – 2.37 (m, 2H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -94.4. ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.9, 132.1, 129.1, 125.5 (t, *J* = 7.7 Hz), 124.5, 121.5, 121.1 (t, *J* = 241.0 Hz), 67.6 (t, *J* = 6.2 Hz), 42.2 (t, *J* = 28.1 Hz), 40.3 (t, *J* = 25.6). GC-HRMS-EI calcd for $C_{10}H_{10}F_2O$ $[M]^{+\bullet}$ 184.0700, found 184.0699.



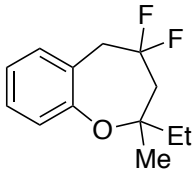
4,4-difluoro-2-phenyl-2,3,4,5-tetrahydrobenzo[*b*]oxepine (3n): Compound **2n** (22 mg, 0.1 mmol, 1.0 equiv) was treated with GP-B and purified by silica gel column chromatography eluting with hexane and dichloromethane to obtain **3n** (17.3 mg, 0.067 mmol, 67%) as a colorless liquid. R_f=0.25 (Hexane: dichloromethane=85: 15). IR (ATR): 1490, 1379, 1236, 1207, 1121, 1069, 1045, 762, 698, 554 cm^{-1}**.** ^1H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.4 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.1 Hz, 1H), 7.29 – 7.25 (m, 2H), 7.14 (t, *J* = 7.4 Hz, 1H), 7.08 (d, *J* = 7.8 Hz, 1H), 4.88 (d, *J* = 11.8 Hz, 1H), 3.66 (dd, *J* = 34.4, 14.5 Hz, 1H), 3.28 – 3.20 (m, 1H), 2.80 – 2.68 (m, 1H), 2.63 – 2.56 (m, 1H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -87.0 (d, *J* = 245.0 Hz), -98.9 (d, *J* = 245.9 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.0, 140.8, 131.8, 129.1, 128.7, 128.1, 125.9 (d, *J* = 14.0 Hz), 125.8, 124.7, 121.8, 120.9 (dd, *J* = 242.2, 240.5 Hz), 79.7 (d, *J*=12.6 Hz), 46.9 (dd, *J* = 25.4 Hz, *J* = 25.4 Hz), 41.7 (dd, *J* = 28.8, 27.3 Hz). HRMS-ESI calcd for $C_{16}H_{15}OF_2$ $[M+H]^+$ 261.1085, found 261.1085.



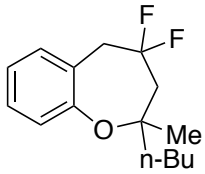
4,4-difluoro-2,2-dimethyl-2,3,4,5-tetrahydrobenzo[*b*]oxepine (3o): Compound **2o** (34.8 mg, 0.20 mmol, 1.0 equiv) was treated with GP-B and purified by silica gel column chromatography eluting with hexane and dichloromethane to obtain **3o** (26 mg, 0.12 mmol, 61%) as a colorless liquid. R_f=0.25 (Hexane: dichloromethane=85: 15). IR (ATR): 2979, 1738, 1584, 1488, 1390, 1370, 1345, 1236, 1214, 1184, 1041, 925, 782, 735, 532 cm^{-1}**.** ^1H NMR (500 MHz, $CDCl_3$) δ 7.26 (t, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 7.4 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 6.98 (d, *J* = 7.9 Hz, 1H), 3.32 (t, *J* = 14.7 Hz, 2H), 2.25 (t, *J* = 14.7 Hz, 2H), 1.37 (s, 6H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -86.6. ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.9, 130.9, 128.7, 127.6 (t, *J* = 7.2 Hz), 124.3, 123.61, 121.6 (t, *J* = 242.0 Hz), 76.6 (t, *J* = 5.4 Hz), 47.9 (t, *J* = 24.1 Hz), 41.0 (t, *J* = 27.8 Hz), 28.4. HRMS-ESI calcd for $C_{12}H_{15}OF_2$ $[M+H]^+$ 213.1085, found 213.1087.



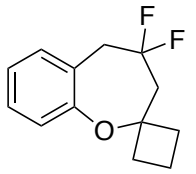
2,2-diethyl-4,4-difluoro-2,3,4,5-tetrahydrobenzo[*b*]oxepine (3p): Compound **2p** (40.4 mg, 0.20 mmol, 1.0 equiv) was treated with GP-B and purified by silica gel column chromatography eluting with hexane and dichloromethane to obtain **3p** (29 mg, 0.12 mmol, 60%) as a colorless liquid. R_f=0.25 (Hexane: dichloromethane=85: 15). IR (ATR): 2971, 1583, 1488, 1456, 1372, 1276, 1239, 1166, 1130, 1103, 1037, 815, 732, 530 cm^{-1}**.** ^1H NMR (500 MHz, $CDCl_3$) δ 7.25 (t, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 7.3 Hz, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.97 (d, *J* = 7.9 Hz, 1H), 3.31 (t, *J* = 14.9 Hz, 2H), 2.19 (t, *J* = 14.9 Hz, 2H), 1.72 – 1.65 (m, 2H), 1.63 – 1.56 (m, 2H), 0.98 (t, *J* = 7.5 Hz, 6H). ^{19}F NMR (470 MHz, CDCl3) δ -86.3. ^{13}C NMR (126 MHz, CDCl3) δ 154.4, 130.6, 128.6, 128.0 (t, *J* = 7.1 Hz), 124.0, 123.6, 122.1 (t, *J* = 242.1 Hz), 81.5 (d, *J* = 5.2 Hz), 43.3 (t, *J* = 24.2 Hz), 41.0 (t, *J* = 27.8 Hz), 28.9, 7.9. HRMS-ESI calcd for $C_{14}H_{19}OF_2$ $[M+H]^+$ 241.1398, found 241.1398.



2-ethyl-4,4-difluoro-2-methyl-2,3,4,5-tetrahydrobenzo[*b*]oxepine (3q): Compound **2q** (37.6 mg, 0.20 mmol, 1.0 equiv) was treated with GP-B and purified by silica gel column chromatography eluting with hexane to obtain **3q** (26 mg, 0.12 mmol, 58%) as a colorless liquid. Compound R_f=0.3 (Hexane). IR (ATR): 2973, 1489, 1457, 1369, 1240, 1183, 1080, 1039, 911, 783, 734, 532 cm^{-1}**.** ^1H NMR (500 MHz, $CDCl_3$) δ 7.25 (t, *J* = 7.8 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 7.9 Hz, 1H), 3.41 – 3.23 (m, 2H), 2.32 – 2.13 (m, 2H), 1.78 – 1.64 (m, 2H), 1.25 (s, 3H), 1.05 (t, *J* = 7.5 Hz, 3H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -84.1 (d, *J* = 246.2 Hz), -88.1 (d, *J* = 244.9 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.8, 130.8, 128.6, 127.9, 124.1, 123.6, 121.9 (dd, *J* = 241.1, 241.1 Hz,),79.1 – 78.8 (m), 46.0 (dd, *J* = 24.1, 24.1 Hz), 41.0 (dd, *J* = 27.9, 27.9 Hz), 34.6, 23.6 (d, *J* = 3.3 Hz), 8.3. HRMS-ESI calcd for $C_{13}H_{16}OF_2$ $[M+H]^+$ 227.1242, found 227.1239.

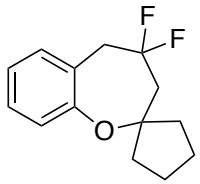


2-butyl-4,4-difluoro-2-methyl-2,3,4,5-tetrahydrobenzo[*b*]oxepine (3r): Compound **2r** (43.2 mg, 0.20 mmol, 1.0 equiv) was treated with GP-B and purified by silica gel column chromatography eluting with hexane and dichloromethane to obtain **3r** (30 mg, 0.12 mmol, 59%) as a colorless liquid. R_f=0.20 (Hexane: dichloromethane=85: 15). IR (ATR): 2958, 1738, 1584, 1488, 1368, 1286, 1236, 1206, 1179, 1162, 1105, 1043, 1020, 780, 733, 533 cm^{-1}**.** ^1H NMR (500 MHz, $CDCl_3$) δ 7.25 (t, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 7.3 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 6.96 (d, *J* = 7.9 Hz, 1H), 3.42 – 3.22 (m, 2H), 2.32 – 2.13 (m, 2H), 1.71 – 1.61 (m, 2H), 1.54 – 1.35 (m, 4H), 1.25 (s, 3H), 0.97 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -83.9 (d, *J* = 244.7 Hz), -88.1 (d, *J* = 245.1 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.7, 130.7, 128.6, 127.8 (dd, *J* = 8.5, 5.7 Hz), 124.1, 123.6, 121.9 (dd, *J* = 241.9, 241.9 Hz), 78.7 (dd, *J* = 7.5, 2.6 Hz), 46.4 (dd, *J* = 23.9, 23.9 Hz), 41.7, 41.0 (dd, *J* = 27.9, 27.9 Hz), 26.1, 24.2, 23.1, 14.1. HRMS-ESI calcd for $C_{15}H_{21}OF_2$ $[M+H]^+$ 255.1555, found 255.1552.

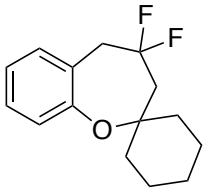


4,4-difluoro-4,5-dihydro-3*H*-spiro[benzo[*b*]oxepine-2,1'-cyclobutane] (3s): Compound **2s** (37.3 mg, 0.20 mmol, 1.0 equiv) was treated with GP-B and purified by silica gel column chromatography eluting with hexane and dichloromethane to obtain **3s** (30 mg, 0.13 mmol, 67%). R_f=0.25 (Hexane: dichloromethane=85: 15). IR (ATR): 2943, 1738, 1585, 1488, 1456, 1372, 13606, 1257, 1234, 1125, 1038, 1014, 772, 532 cm^{-1}**.** ^1H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 1H), 7.18 (d, *J* = 7.3 Hz, 1H), 7.10 – 7.06 (m, 2H), 3.29 (t, *J* = 14.1 Hz, 2H), 2.52 (t, *J* = 13.9 Hz, 2H), 2.29 – 2.26 (m, 2H), 2.07 – 2.02 (m, 2H), 1.98 – 1.92 (m, 1H), 1.73 – 1.67 (m,

1H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -89.4. ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.9, 131.5, 128.6, 126.5 (t, *J* = 7.6 Hz), 124.3, 123.7, 121.4 (t, *J* = 242.0 Hz), 79.7 (t, *J* = 5.1 Hz), 45.9 (t, *J* = 24.1 Hz), 41.5 (t, *J* = 27.8 Hz), 32.9, 13.1. HRMS-ESI calcd for $C_{13}H_{15}OF_2$ $[M+H]^+$ 225.1085 found 225.1084.

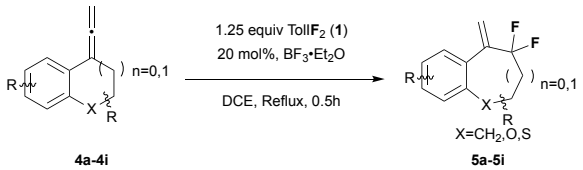


4,4-difluoro-4,5-dihydro-3*H*-spiro[benzo[*b*]oxepine-2,1'-cyclopentane] (3t): Compound **2t** (40 mg, 0.20 mmol, 1.0 equiv) was treated with GP-B and purified by silica gel column chromatography eluting with hexane and dichloromethane to obtain **3t** (21 mg, 0.088 mmol, 44%) as a colorless liquid. R_f=0.25 (Hexane: dichloromethane=85: 15). IR (ATR): 2963, 1584, 1488, 1375, 1238, 1189, 1072, 1045, 1019, 922, 813, 733 cm^{-1}**.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (t, *J* = 7.7 Hz, 1H), 7.19 (d, *J* = 7.4 Hz, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.94 (d, *J* = 7.9 Hz, 1H), 3.31 (t, *J* = 14.3 Hz, 2H), 2.45 (t, *J* = 14.5 Hz, 2H), 1.96 – 1.89 (m, 4H), 1.74 – 1.72 (m, 2H), 1.57 – 1.53 (m, 2H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -89.3. ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.0, 131.3, 128.5, 127.1 (t, *J* = 7.5 Hz), 124.0, 123.1, 121.6 (t, *J* = 241.5 Hz), 87.7 (t, *J* = 5.5 Hz), 47.1 (t, *J* = 24.7 Hz), 41.7 (t, *J* = 28.0 Hz), 37.8, 23.1. HRMS-ESI calcd for $C_{14}H_{16}OF$ $[M-F]^+$ 219.1179, found 219.1183.



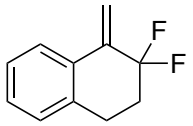
4,4-difluoro-4,5-dihydro-3*H*-spiro[benzo[*b*]oxepine-2,1'-cyclohexane] (3u): Compound **2u** (42.8 mg, 0.20 mmol, 1.0 equiv) was treated with GP-B and purified by silica gel column chromatography eluting with hexane and dichloromethane to obtain **3u** (30 mg, 0.12 mmol, 60%) as a colorless liquid. R_f=0.25 (Hexane: dichloromethane=85: 15). IR (ATR): 2934, 1738, 1487, 1374, 1274, 1233, 1205, 1171, 1068, 1033, 969, 780, 539 cm^{-1}**.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (t, *J* = 7.7 Hz, 1H), 7.19 (d, *J* = 7.4 Hz, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 7.9 Hz, 1H), 3.31 (t, *J* = 14.9 Hz, 2H), 2.18 (t, *J* = 15.0 Hz, 2H), 1.88 – 1.78 (m, 4H), 1.70 – 1.31 (m, 6H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -85.6. ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.3, 130.6, 128.5, 128.0 (t, *J* = 7.0 Hz), 124.0, 123.5, 122.0 (t, *J* = 242.0 Hz), 77.6 (t, *J* = 5.2 Hz), 46.6 (t, *J* = 24.9 Hz), 41.0 (t, *J* = 27.9 Hz), 36.2, 25.4, 21.9. HRMS-ESI calcd for $C_{15}H_{19}OF_2$ $[M+H]^+$ 253.1398, found 253.1399.

General procedure for fluorinative ring-expansion with allene (GP-C):

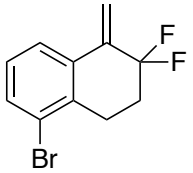


To an over dried flask with a magnetic stir bar was charged allenes **4a-4i** (0.20 mmol, 1.0 equiv) and anhydrous DCE (1 mL), and the resulting solution was placed under a nitrogen atmosphere. To this, a solution of (difluoroiodo)toluene (63 mg, 0.25 mmol, 1.25 equiv) in DCE (1 mL) was added. The reaction flask was immersed in a preheated 85 °C oil bath, and stirred while $BF_3{\cdot}Et_2O$ (5 μL, 20 mol%) was added. The reaction was monitored by TLC analysis, and upon consumption of the allene (30 min), the reaction mixture was cooled to room temperature and concentrated by under vacuum by rotary evaporation. The resulting crude product mixture was purified by silica gel chromatography to provide difluorides **5**.

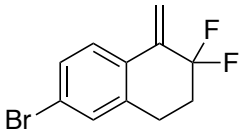
Characterization data for the synthesis of allenes 5:



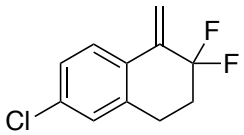
2,2-difluoro-1-methylene-1,2,3,4-tetrahydronaphthalene (5a):[13] Compound **4a** (30.4 mg, 0.20 mmol, 1.0 equiv) was treated with GP-C and purified by silica gel column chromatography eluting with hexane to obtain **5a** (28 mg, 0.15 mmol, 74%) as a colorless liquid. R_f=0.60 (Hexane). IR (ATR): 2926, 2921, 1685, 1623, 1383, 1217, 890, 775, 759 cm^{-1}**.** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 – 7.62 (m, 1H), 7.24 – 7.21 (m, 2H), 7.16 – 7.14 (m, 1H), 5.85 (br. s, 1H), 5.76 (br. s, 1H), 3.02 (t, *J* = 6.7 Hz, 2H), 2.36 – 2.23 (m, 2H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -98.5. ^{13}C NMR (75 MHz, CDCl3) δ 138.7 (t, *J* = 22.3 Hz), 134.4, 131.4, 128.7, 128.4, 126.6, 124.3, 117.6 (t, *J* = 240.3 Hz), 110.84 (t, *J* = 7.6 Hz), 31.84 (t, *J* = 24.9 Hz), 26.4 (t, *J* = 5.9 Hz).



5-bromo-2,2-difluoro-1-methylene-1,2,3,4-tetrahydronaphthalene (5b): Compound **4b** (44.2 mg 0.20 mmol, 1.0 equiv) was treated with GP-C and purified by silica gel column chromatography eluting with hexane to obtain **5b** (35.6 mg, 0.14 mmol, 69%) as a colorless liquid. Compound R_f=0.55 (Hexane). IR (ATR): 1715, 1590, 1479, 1444, 1364, 1337, 1194, 1153, 1074, 945, 929, 820, 701 cm^{-1}**.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.14 (t, *J* = 7.9 Hz, 1H), 5.88 (br. s, 1H), 5.82 (br. s, 1H), 3.10 (t, *J* = 6.8 Hz, 2H), 2.41 – 2.33 (m, 2H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -100.7. ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.5 (t, *J* = 22.5 Hz), 134.0, 133.9, 132.6, 127.9, 125.3, 124.0, 118.8 (t, *J* = 240.5 Hz), 112.0 (t, *J* = 7.6 Hz), 31.5 (t, *J* = 25.2 Hz), 27.5 (t, *J* = 5.8 Hz). HRMS-APCI calcd for $C_{11}H_9BrF_2$ $[M]^+$ 257.9850, found 257.9851.

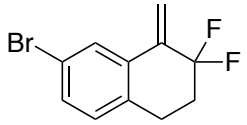


6-bromo-2,2-difluoro-1-methylene-1,2,3,4-tetrahydronaphthalene (5c): Compound **4c** (44 mg , 0.20 mmol, 1.0 equiv) was treated with GP-C and purified by silica gel column chromatography eluting with hexane to obtain **5c** (40 mg, 0.16 mmol, 78%) as a colorless liquid. R_f=0.55 (Hexane). IR (ATR): 2935, 1715, 1590, 1480, 1364, 1236, 1194, 1153, 1075, 954, 929, 820 cm^{-1}**.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.5 Hz, 1H), 7.38 (d, *J* = 8.6 Hz, 1H), 7.35 (s, 1H), 5.88 (br. s, 1H), 5.83 (br. s, 1H), 3.04 (t, *J* = 6.7 Hz, 2H), 2.36 – 2.28 (m, 2H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -98.7. ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.2 (t, *J* = 22.6 Hz), 136.4, 131.6, 130.6 (t, *J* = 2.5 Hz) 129.9, 126.1, 122.5, 120.8 (t, *J* = 240.7 Hz), 111.6 (t, *J* = 7.5 Hz), 31.6 (t, *J* = 25.2 Hz), 26.2 (t, *J* = 5.9 Hz). HRMS-APCI calcd for $C_{11}H_9BrF_2$ $[M]^+$ 257.9850, found 257.9851.

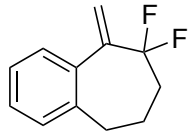


6-chloro-2,2-difluoro-1-methylene-1,2,3,4-tetrahydronaphthalene (5d): Compound **4d** (35.2 mg, 0.20 mmol, 1.0 equiv) was treated with GP-C and purified by silica gel column chromatography eluting with hexane to obtain **5d** (24 mg, 0.11 mmol, 56%) as a colorless liquid. R_f=0.55 (Hexane). IR (ATR): 2969, 1738, 1482, 1364, 1340, 1238, 1196, 1152, 1087, 1074, 946, 822, 529 cm^{-1}**.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.5 Hz, 1H), 7.23 (d, *J* = 8.7 Hz, 1H), 7.19 (s, 1H), 5.87 (s, 1H), 5.82 (s, 1H), 3.04 (t, *J* = 6.7 Hz, 2H), 2.37 – 2.29 (m, 2H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -98.7. ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.2 (t, *J* = 22.5 Hz), 136.1, 134.3, 130.1 (t, *J* =

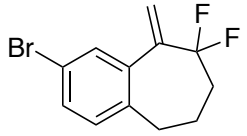
3.0 Hz), 128.6, 127.1, 125.9, 118.9 (t, J = 240.6 Hz), 111.5 (t, J = 7.5 Hz), 31.7 (t, J = 25.1 Hz), 26.3 (t, J = 6.0 Hz). HRMS-APCI calcd for $C_{11}H_9ClF_2$ $[M]^+$ 214.0355, found 214.0355.



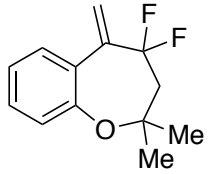
7-bromo-2,2-difluoro-1-methylene-1,2,3,4-tetrahydronaphthalene (5e): Compound **4e** was observed in 56% ^{19}F NMR yield, comparing the signals with 4-Fluorotoluene. ^{19}F NMR (470 MHz, $CDCl_3$) δ -98.8.



6,6-difluoro-5-methylene-6,7,8,9-tetrahydro-5*H*-benzo[7]annulene (5f): Compound **4f** (31.2 mg, 0.20 mmol, 1 equiv) was treated with GP-C and purified by silica gel column chromatography eluting with hexane to obtain **5f** (17 mg, 0.088 mmol, 44%) as a colorless liquid. R_f=0.60 (Hexane). IR (ATR) 2924, 1457, 1363, 1194, 1171, 1068, 955, 939, 918, 772, 731 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.19 (m, 3H), 7.11 – 7.10 (m, 1H), 5.76 (s, 1H), 5.34 (br. s, 1H), 2.78 – 2.75 (m, 2H), 2.26 (tt, J = 13.6, 6.2 Hz, 2H), 1.90 – 1.85 (m, 2H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -93.9. ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.3 (t, J = 26.5 Hz), 140.0, 137.9, 130.4, 129.4, 128.9, 127.4, 121.2 (t, J = 242.1 Hz), 118.0 (t, J = 7.8 Hz), 40.2 (t, J = 27.3 Hz), 35.3, 23.5 (t, J = 6.2 Hz). HRMS-APCI calcd for $C_{12}H_{12}F_2$ $[M]^+$194.0901, found 194.0902.



2-bromo-8,8-difluoro-9-methylene-6,7,8,9-tetrahydro-5*H*-benzo[7]annulene (5g): Compound **4g** (46.8 mg, 0.20 mmol, 1.0 equiv) was treated with GP-C and purified by silica gel column chromatography eluting with hexane to obtained **5g** (22 mg, 0.082 mmol, 41%) as a colorless liquid. Compound. R_f=0.55 (Hexane). IR (ATR): 2926, 1445, 1169, 1119, 1085, 1061, 990, 931, 815, 699 cm^{-1}**.** ^1H NMR (500 MHz, $CDCl_3$) δ 7.41 (br. s, 1H), 7.39 – 7.37 (m, 1H), 7.00 (d, J = 8.0 Hz, 1H), 5.82 (br. s, 1H), 5.39 (s, 1H), 2.77 – 2.70 (m, 2H), 2.34 – 2.24 (m, 2H), 1.91 – 1.86 (m, 2H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -93.9. ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.1 (t, J = 26.2 Hz), 139.8, 139.1, 133.0, 131.8 (2C), 131.1, 120.8 (t, J = 242.9 Hz), 118.9 (t, J = 7.7 Hz), 40.1 (t, J = 27.2 Hz), 34.8, 24.2 (t, J = 6.3 Hz). HRMS-APCI calcd for $C_{12}H_{11}BrF_2$ $[M]^+$ 272.0006, found 272.0006.



4,4-difluoro-2,2-dimethyl-5-methylene-2,3,4,5-tetrahydrobenzo[*b*]oxepine (5h): Compound **4h** (37.2 mg, 0.20 mmol, 1.0 equiv)was treated with GP-C and purified by silica gel column chromatography eluting with hexanes and dichloromethane to obtain **5h** (13 mg, 0.058 mmol, 29%) as a colorless liquid. R_f=0.20 (Hexane: dichloromethane=85: 15). IR (ATR): 2927, 1483, 1450, 1371, 1258, 1189, 1157, 1049, 1033, 924, 765 cm^{-1}**.** ^1H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.25 (m, 2H), 7.10 (t, J = 7.5 Hz, 1H), 6.93 (d, J = 8.0 Hz, 1H), 5.83 (br. s, 1H), 5.45 (s, 1H), 2.35 (t, J = 14.7 Hz, 2H), 1.38 (s, 6H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -88.2. ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.36, 144.7 (t, J = 24.7 Hz), 131.7, 130.5, 130.4, 125.0, 124.3, 119.9 (t, J = 242.1 Hz), 119.0 (t, J = 7.4 Hz), 77.8, 48.6 (t, J = 24.8 Hz), 29.1. HRMS-ESI calcd for $C_{13}H_{15}F_2O$ $[M+H]^+$ 225.1085, found 225.1086.

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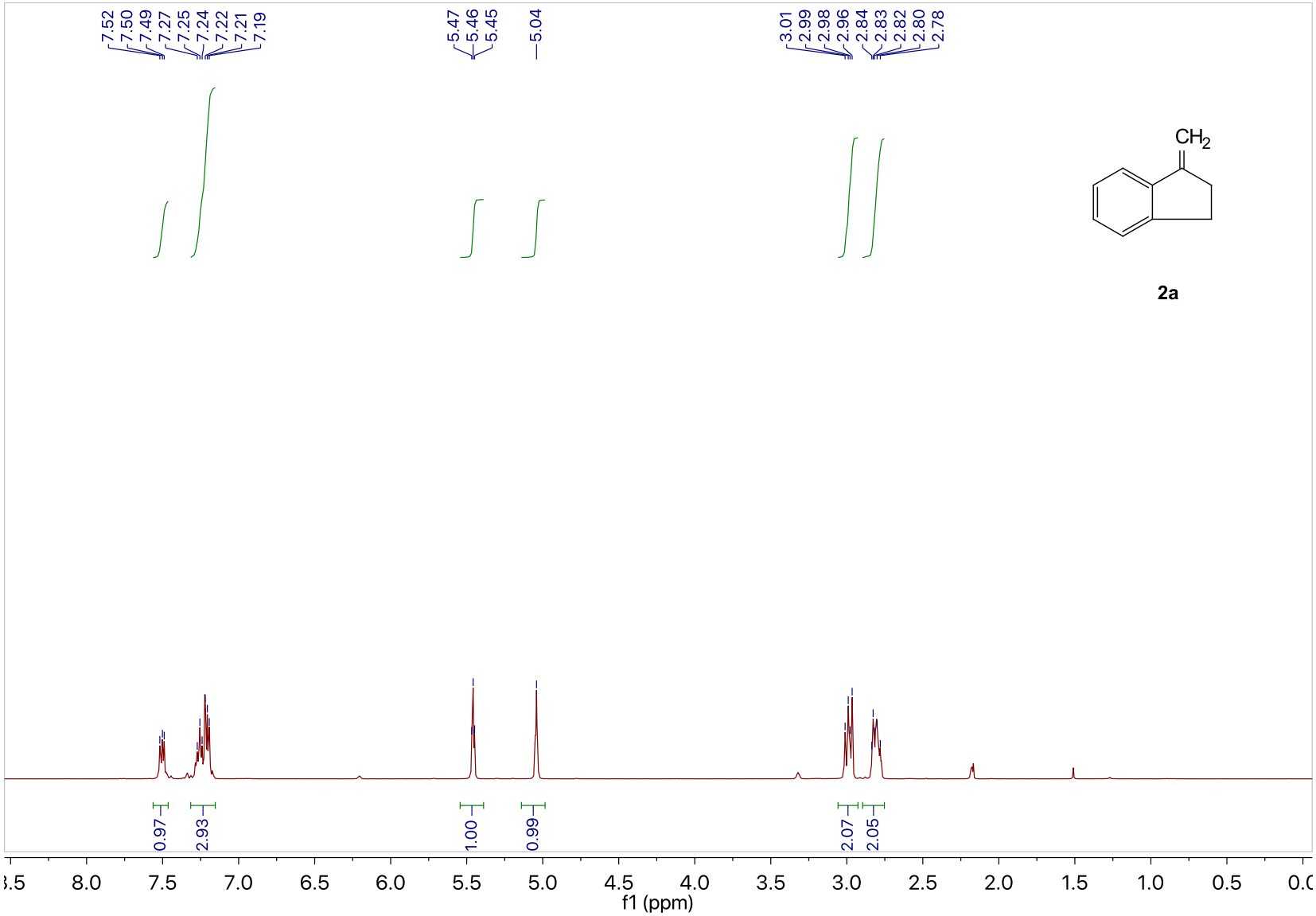
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2.99
2.98
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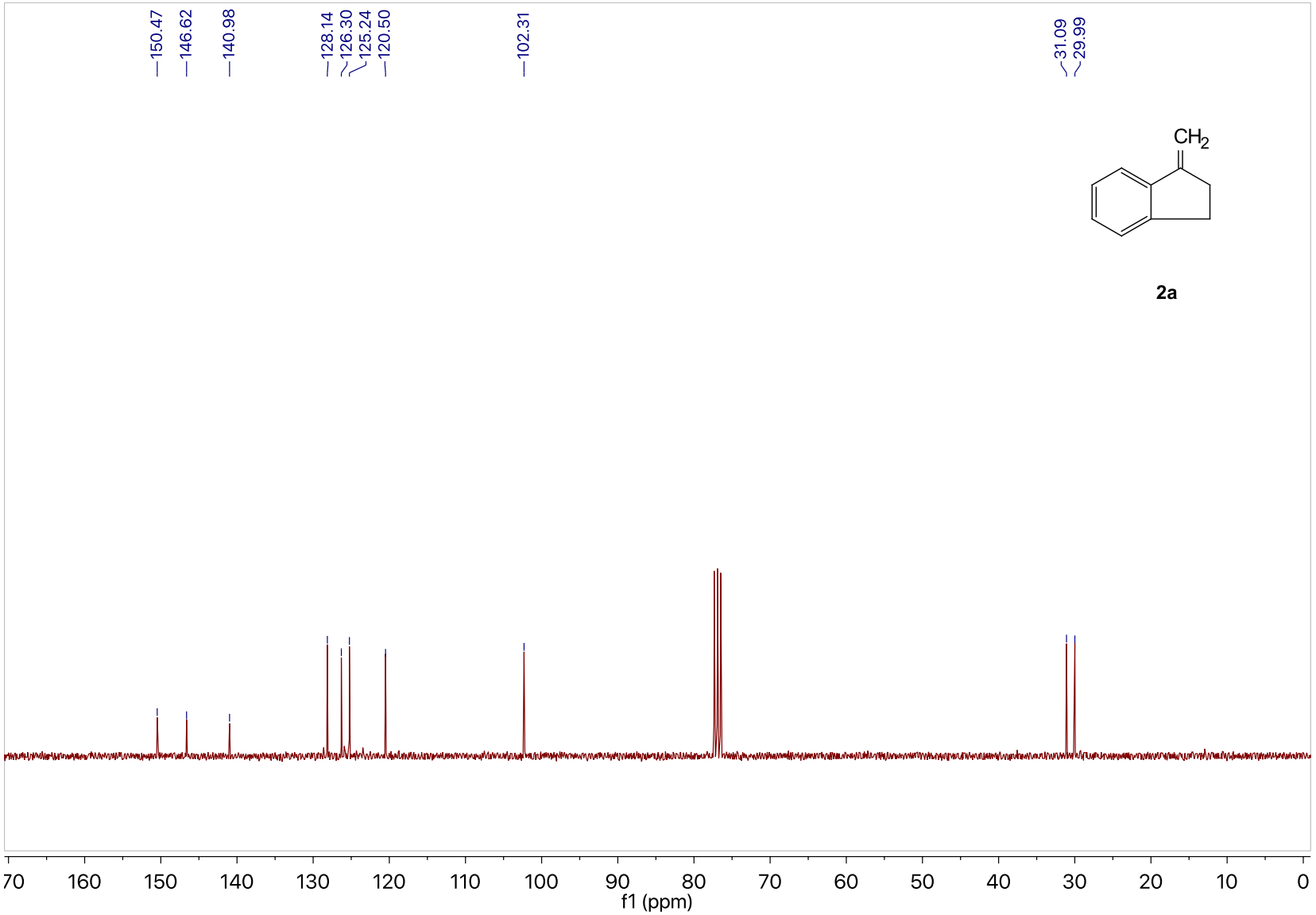
f1 (ppm)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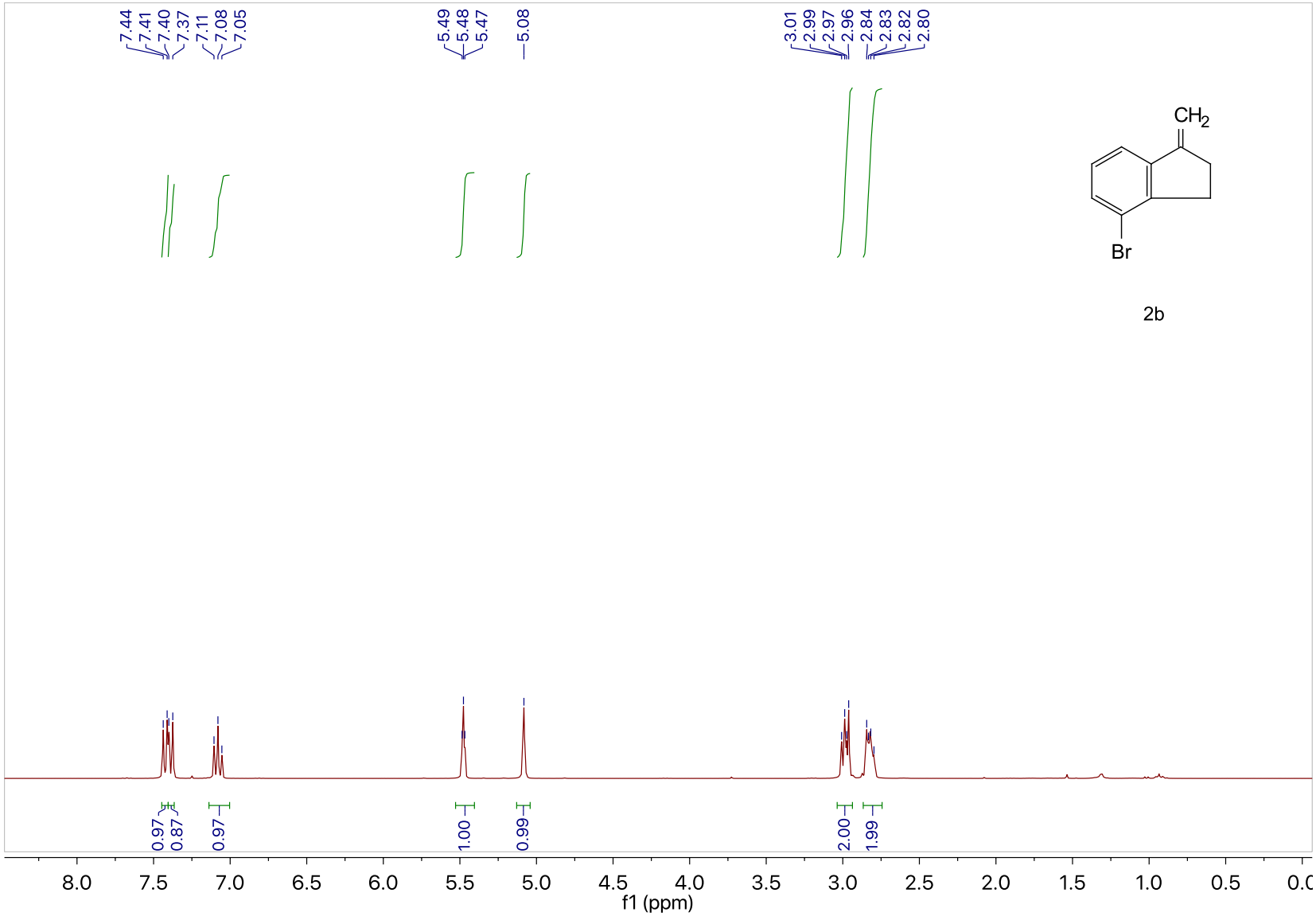
f1 (ppm)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2.82
2.80
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Br
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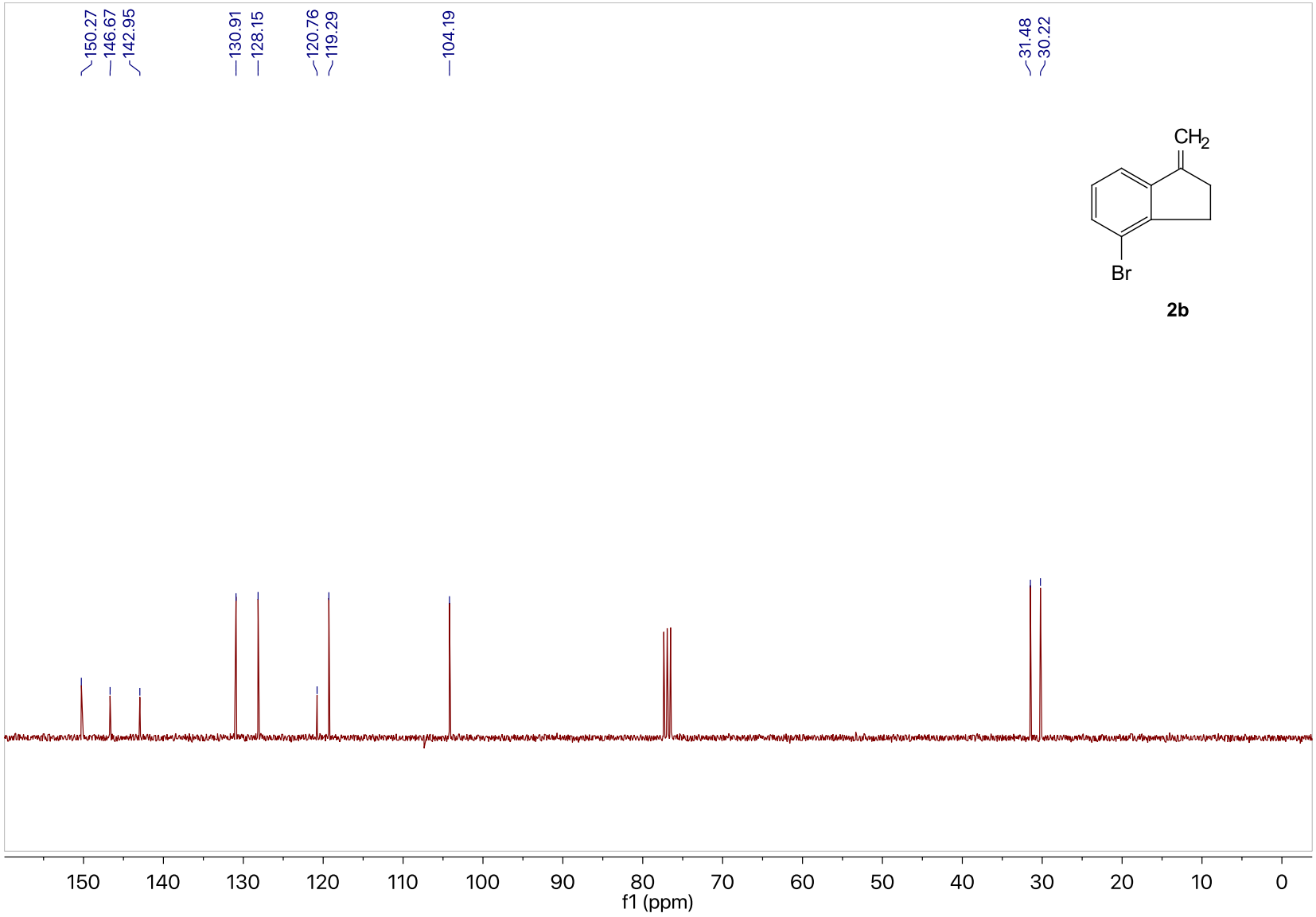
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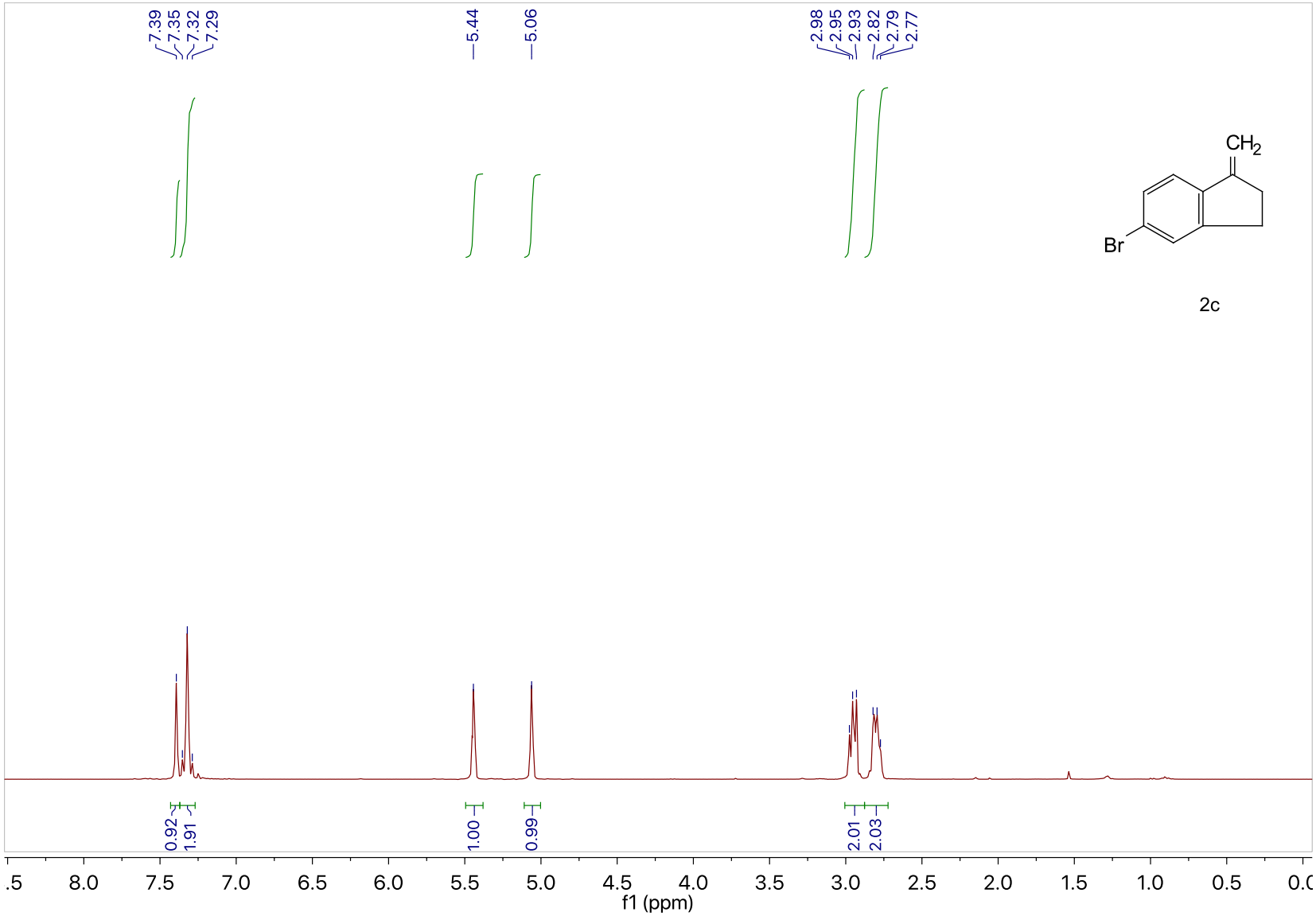
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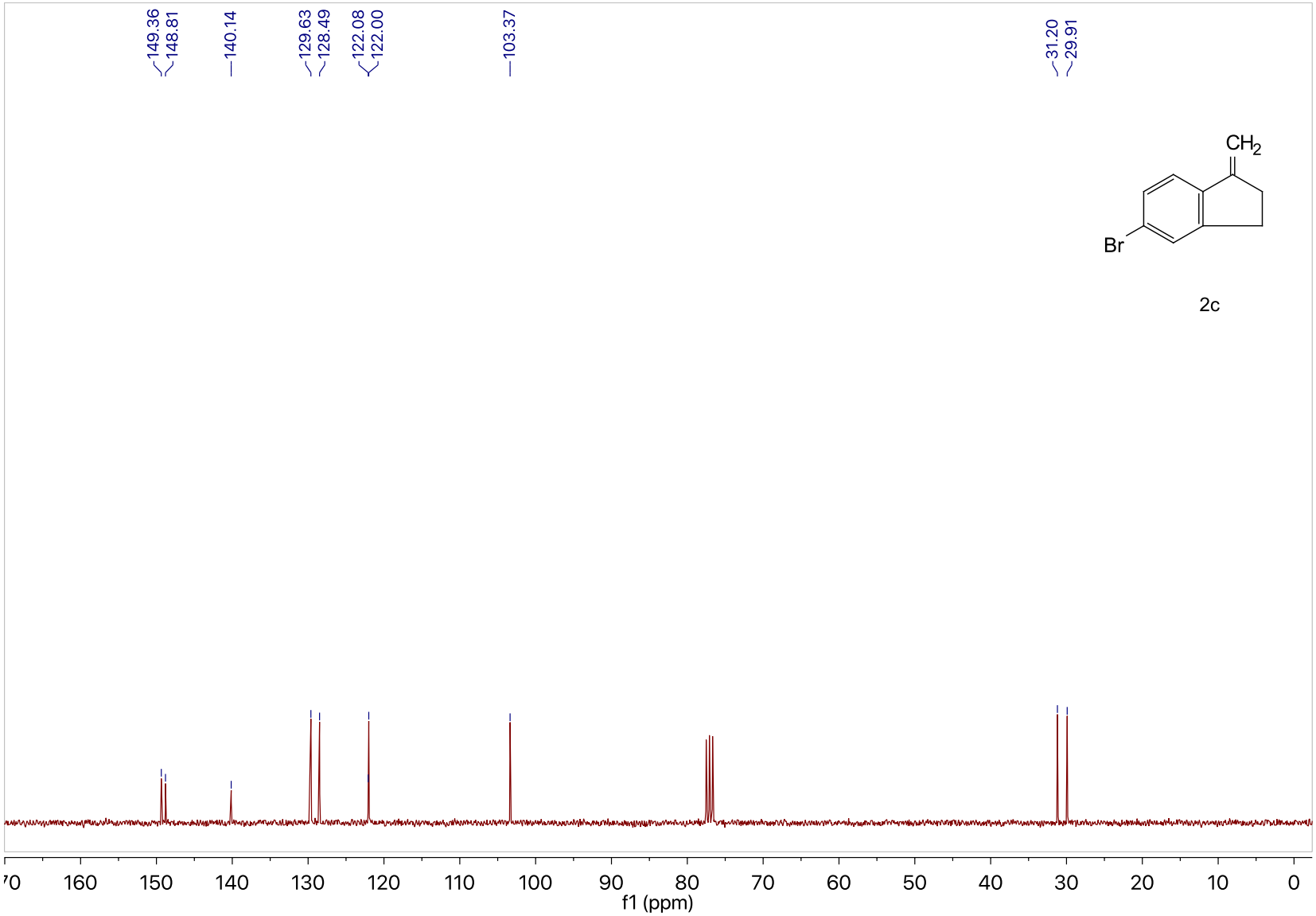
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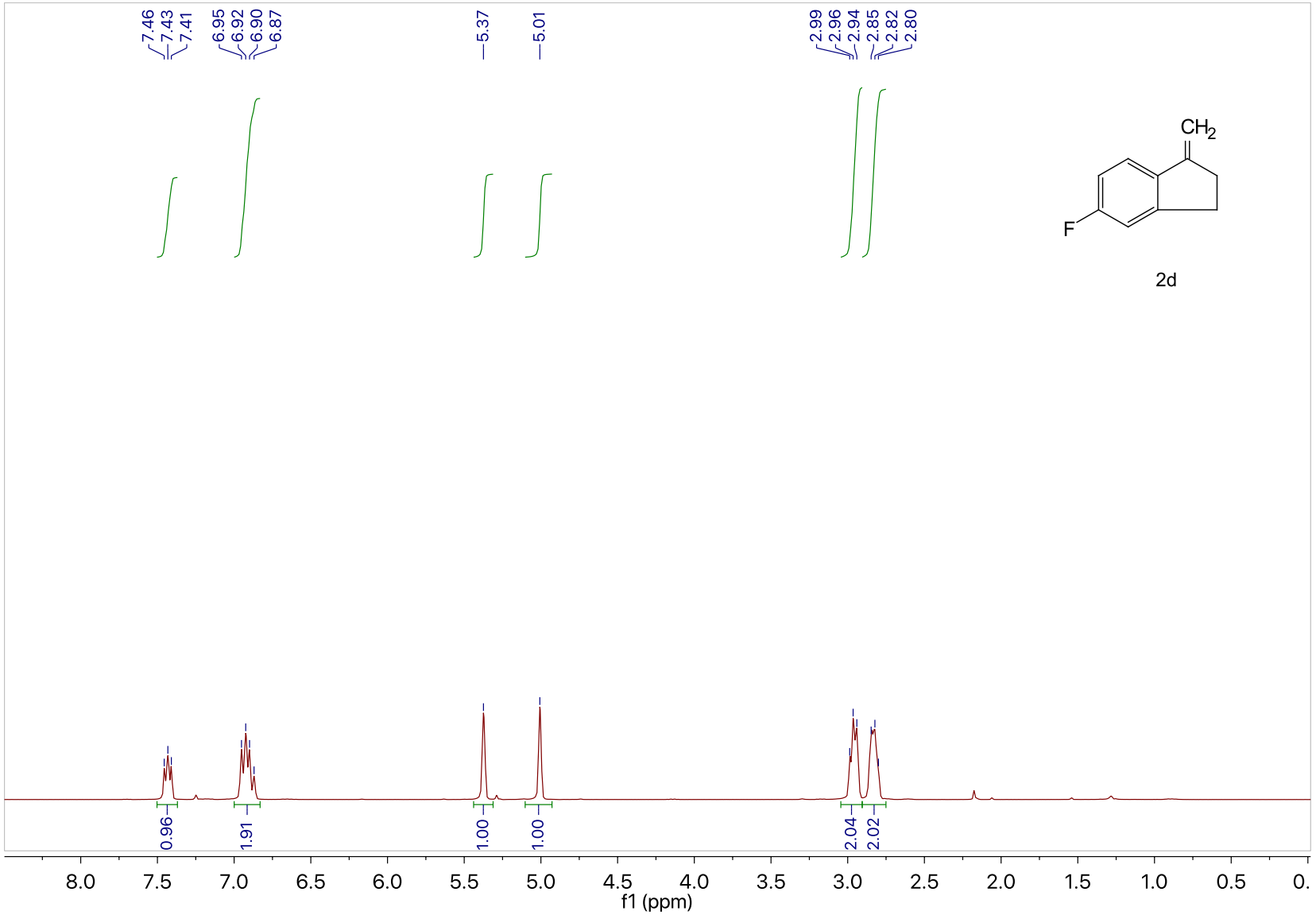
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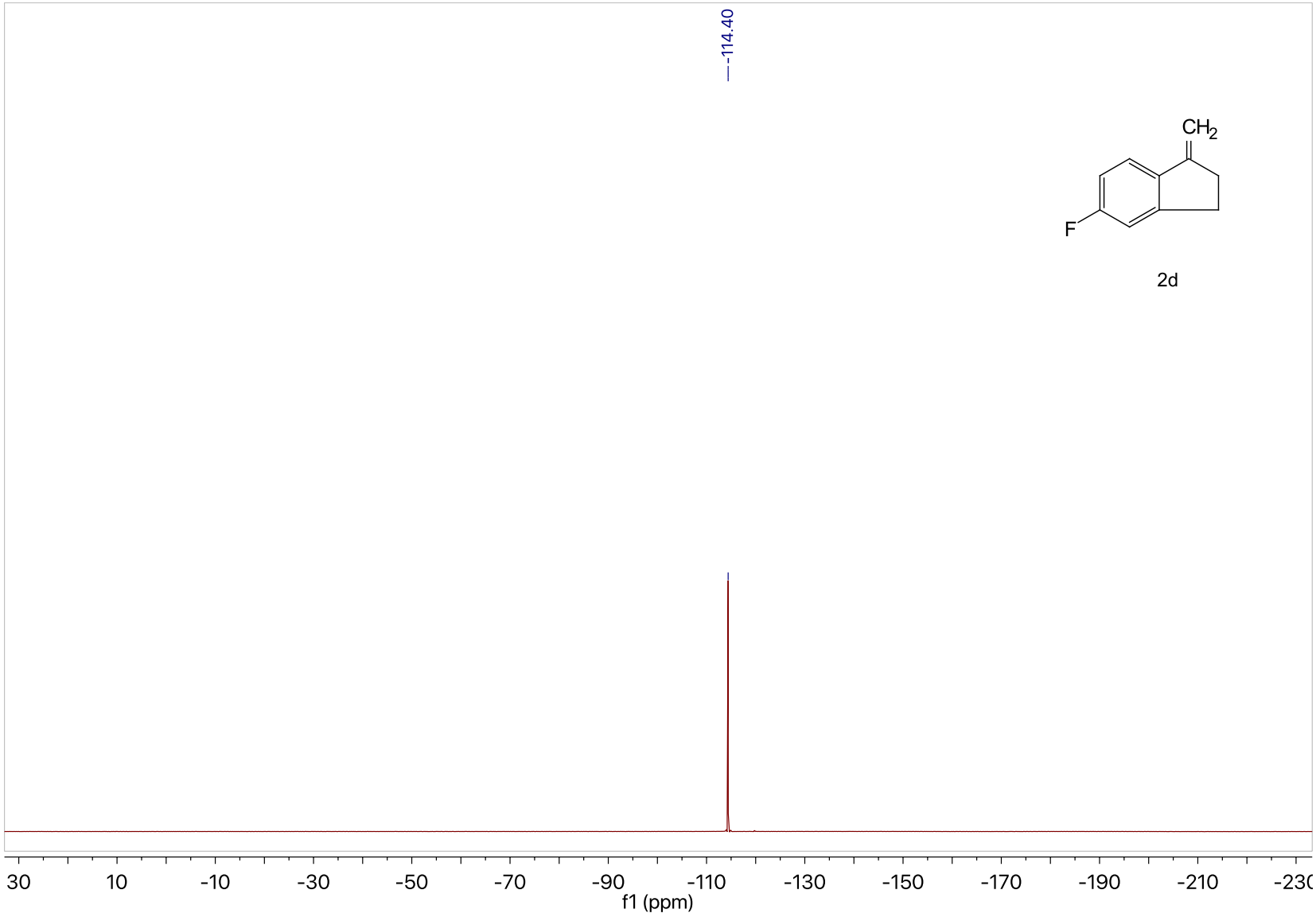
f1 (ppm)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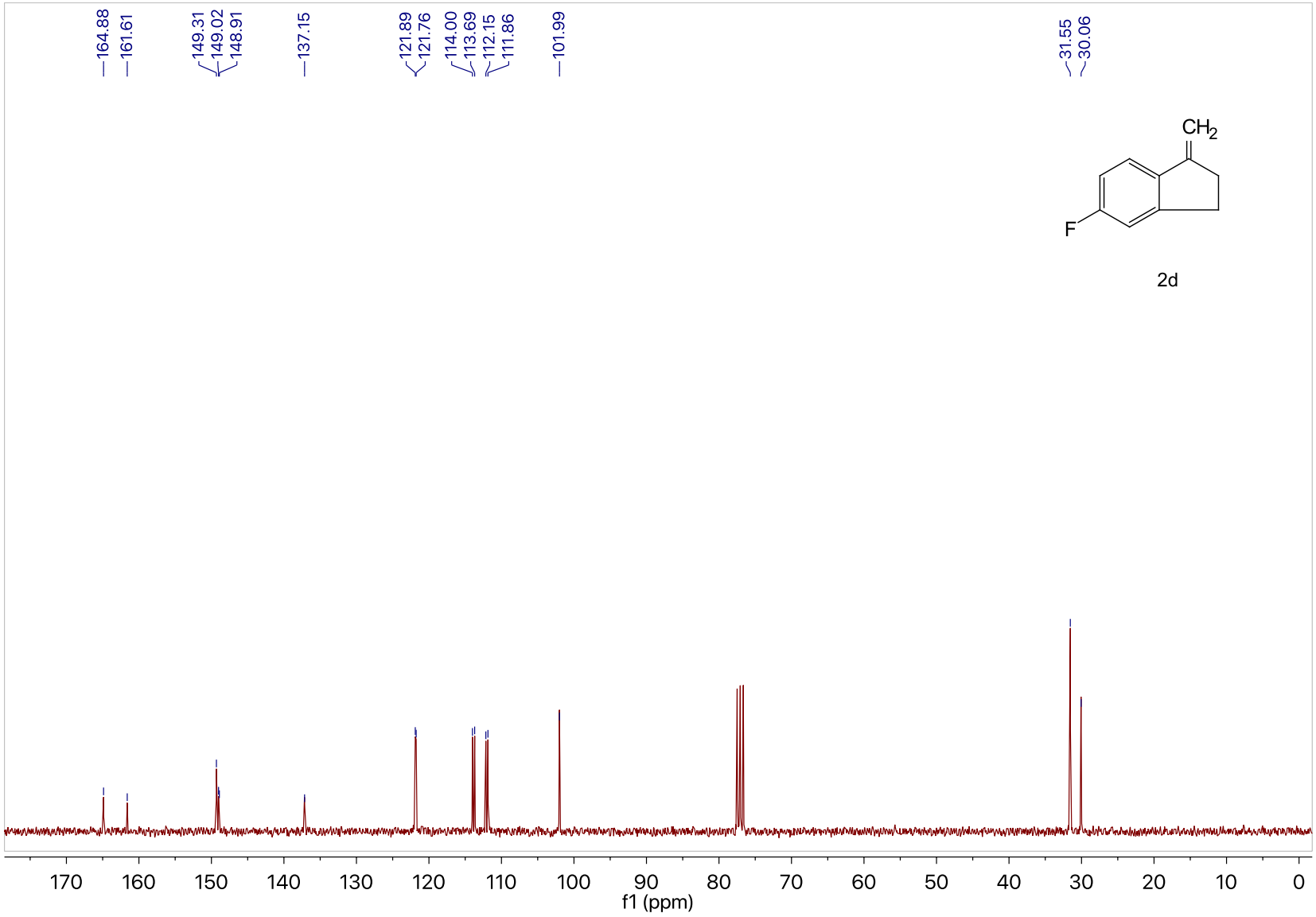
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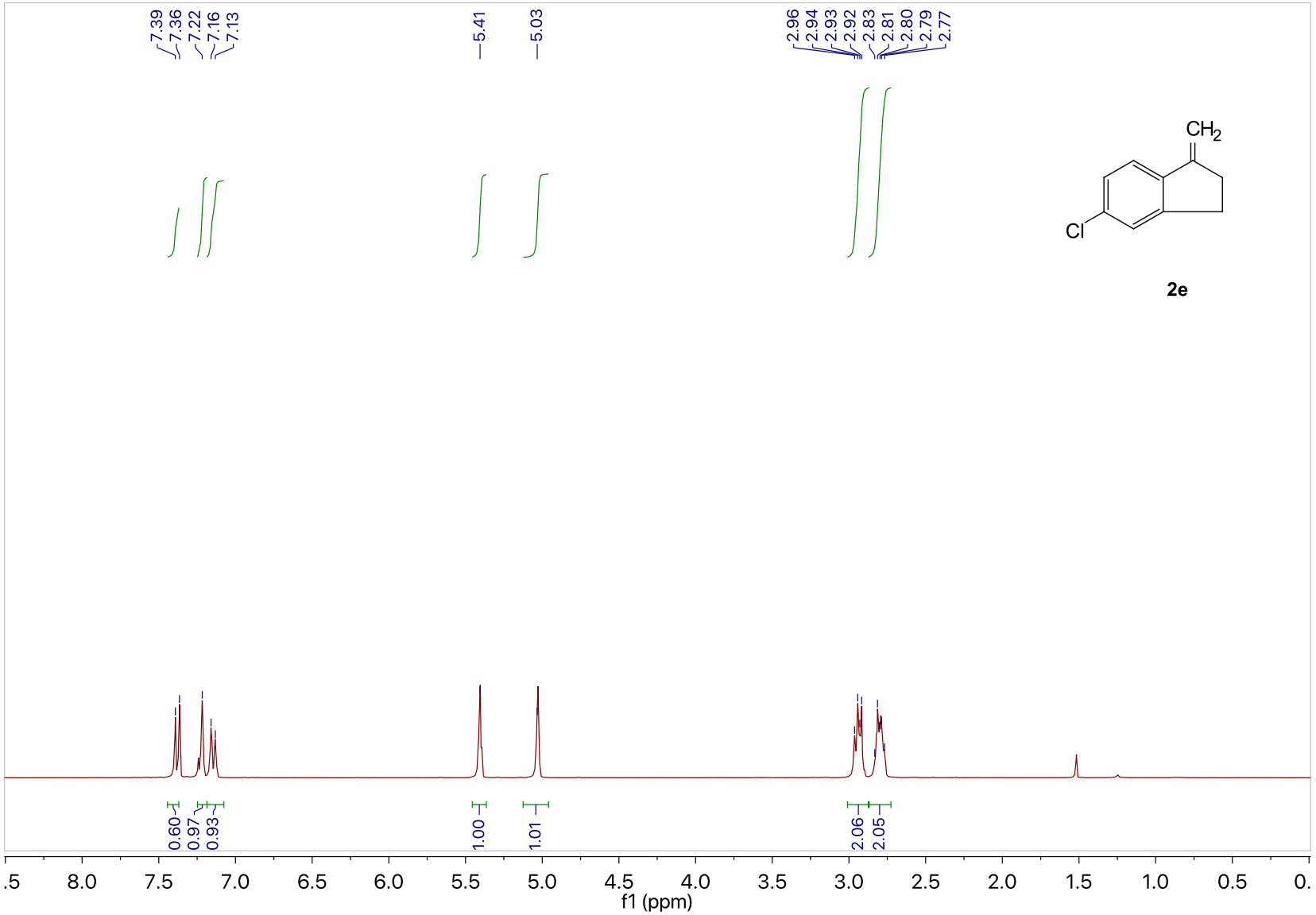
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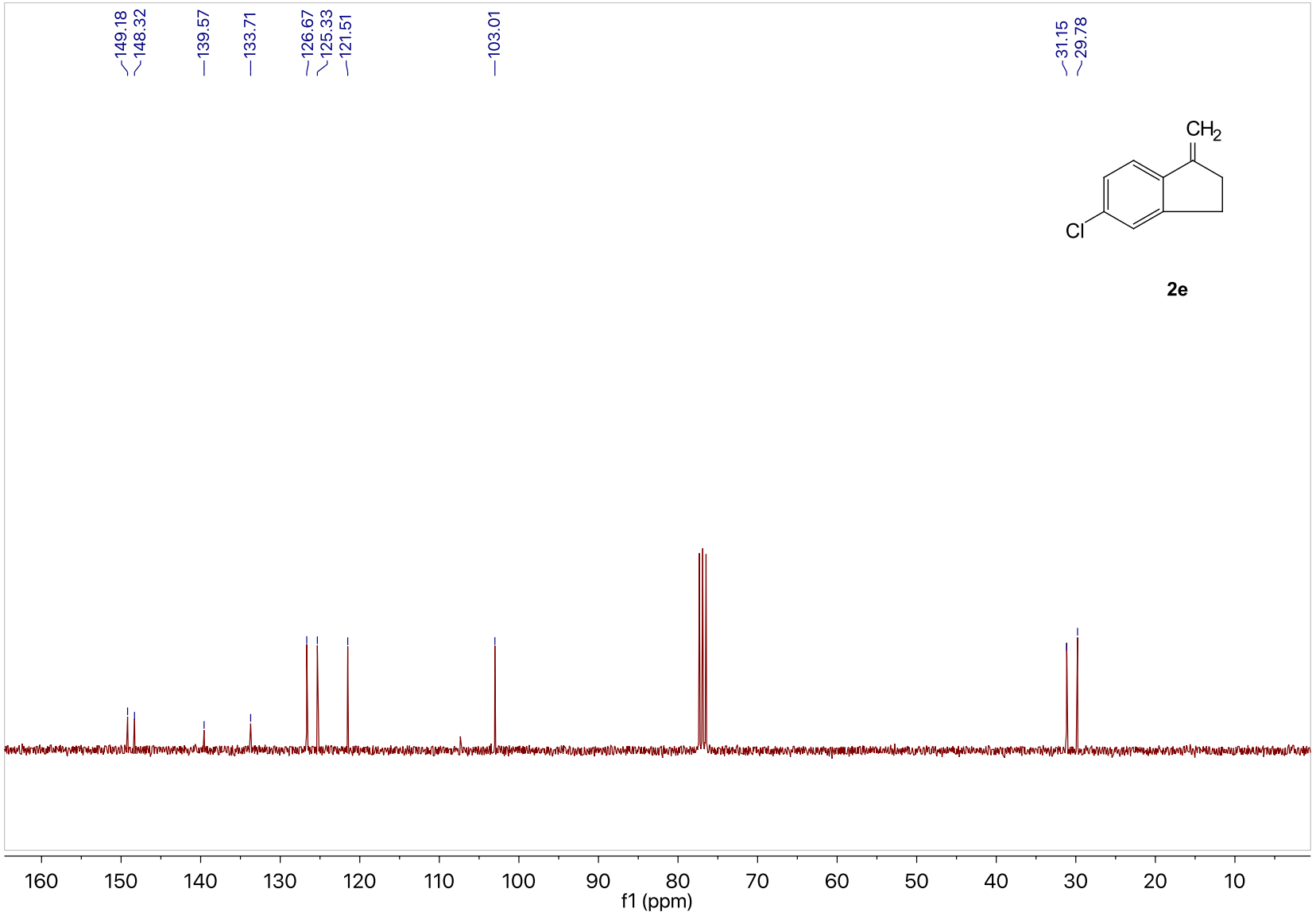
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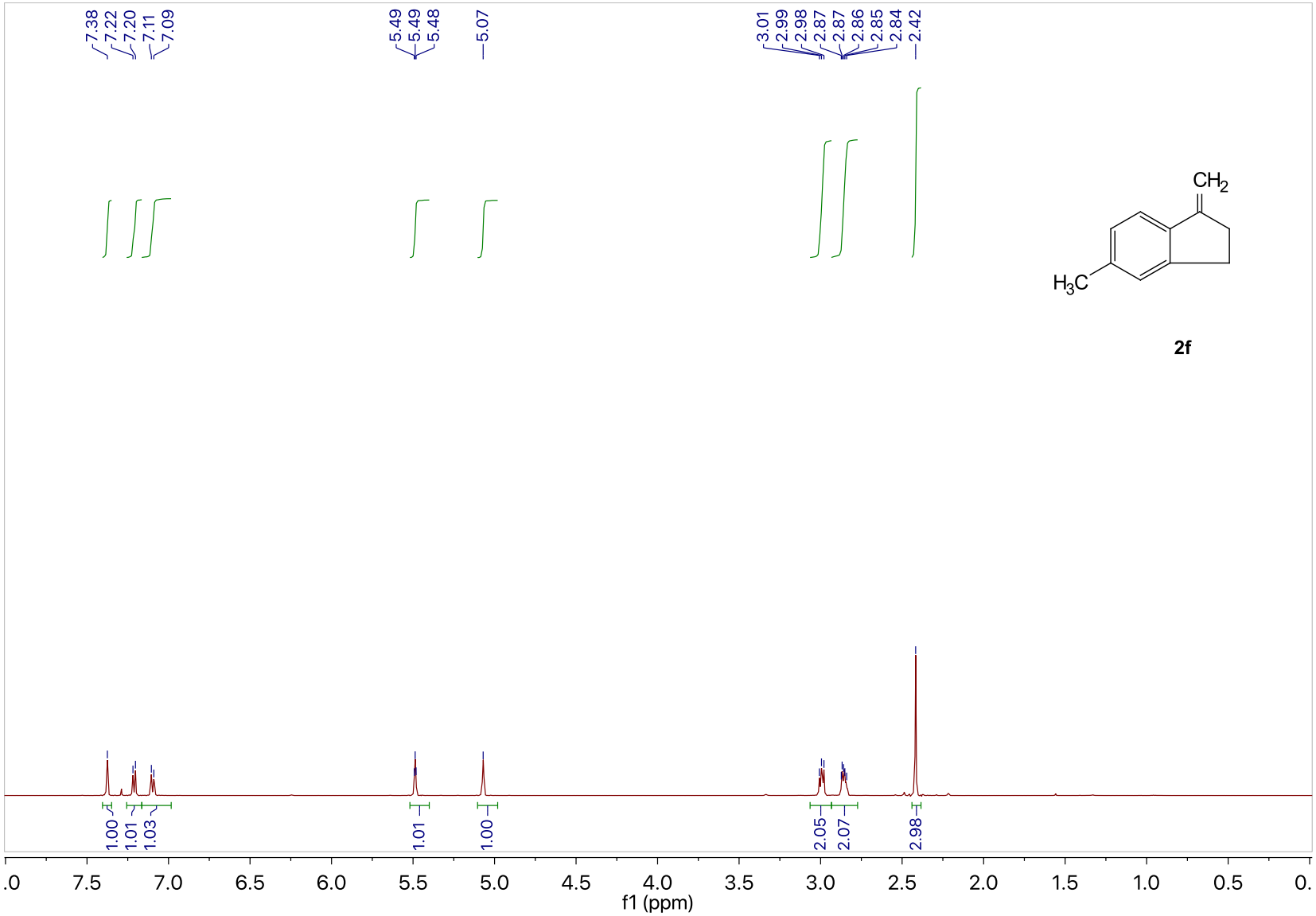
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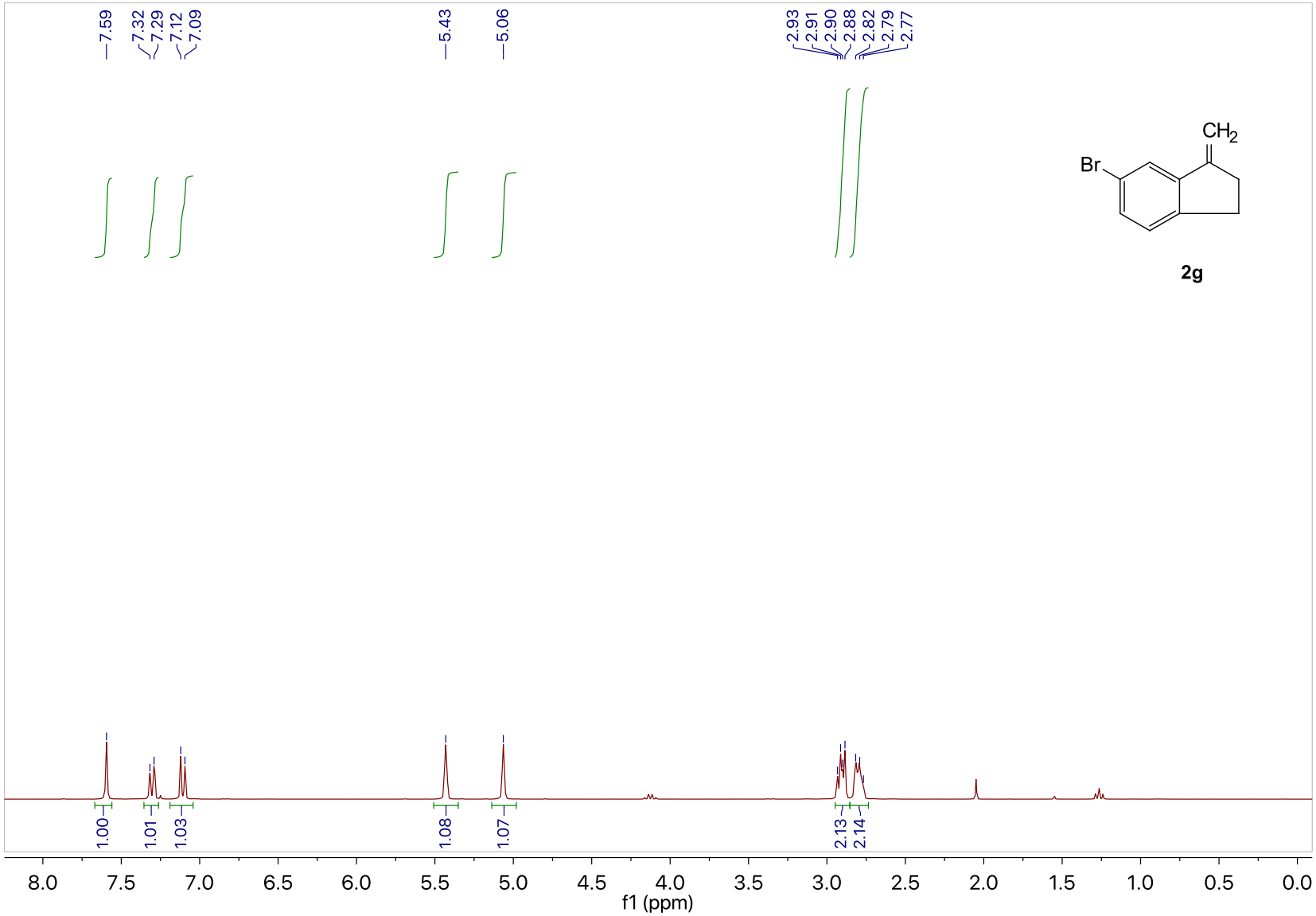
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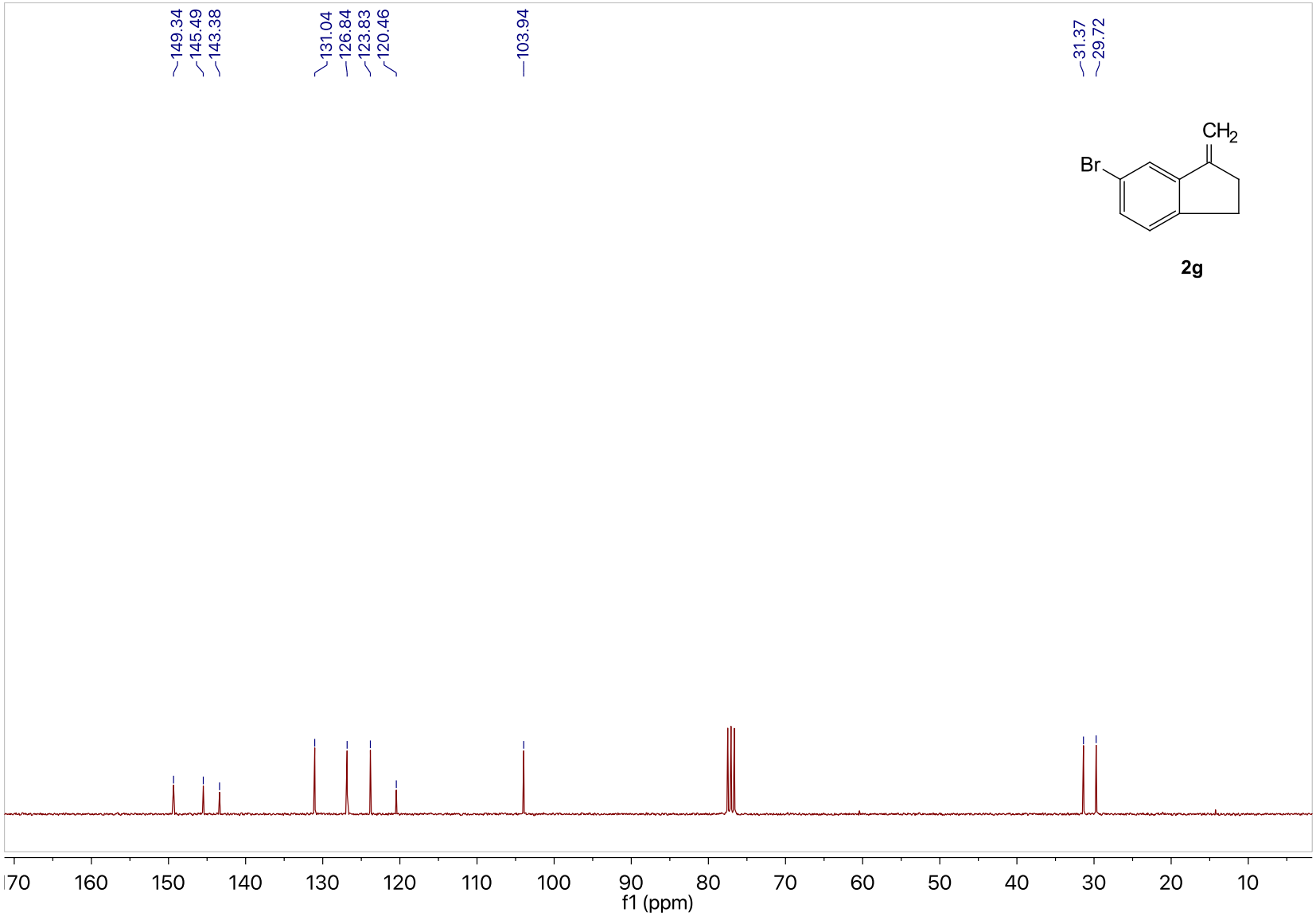
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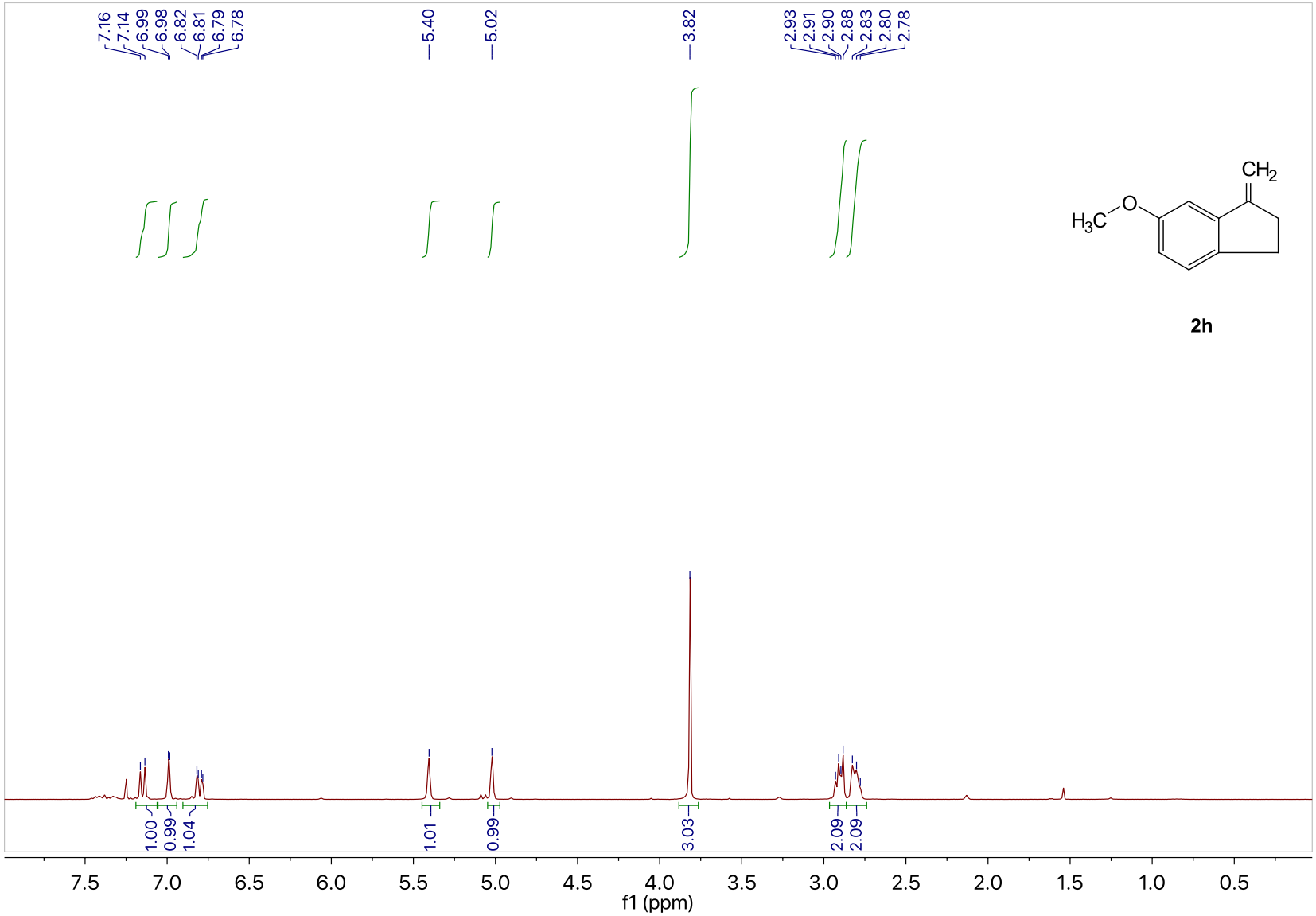
10
f1 (ppm)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7.14
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6.98
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6.81
6.79
6.78
5.40
5.02
3.82
2.93
2.91
2.90
2.88
2.83
2.80
2.78
CH2
H3C
O
2h
1.00
0.99
1.04
1.01
0.99
3.03
2.09
2.09
7.5
7.0
6.5
6.0
5.5
5.0
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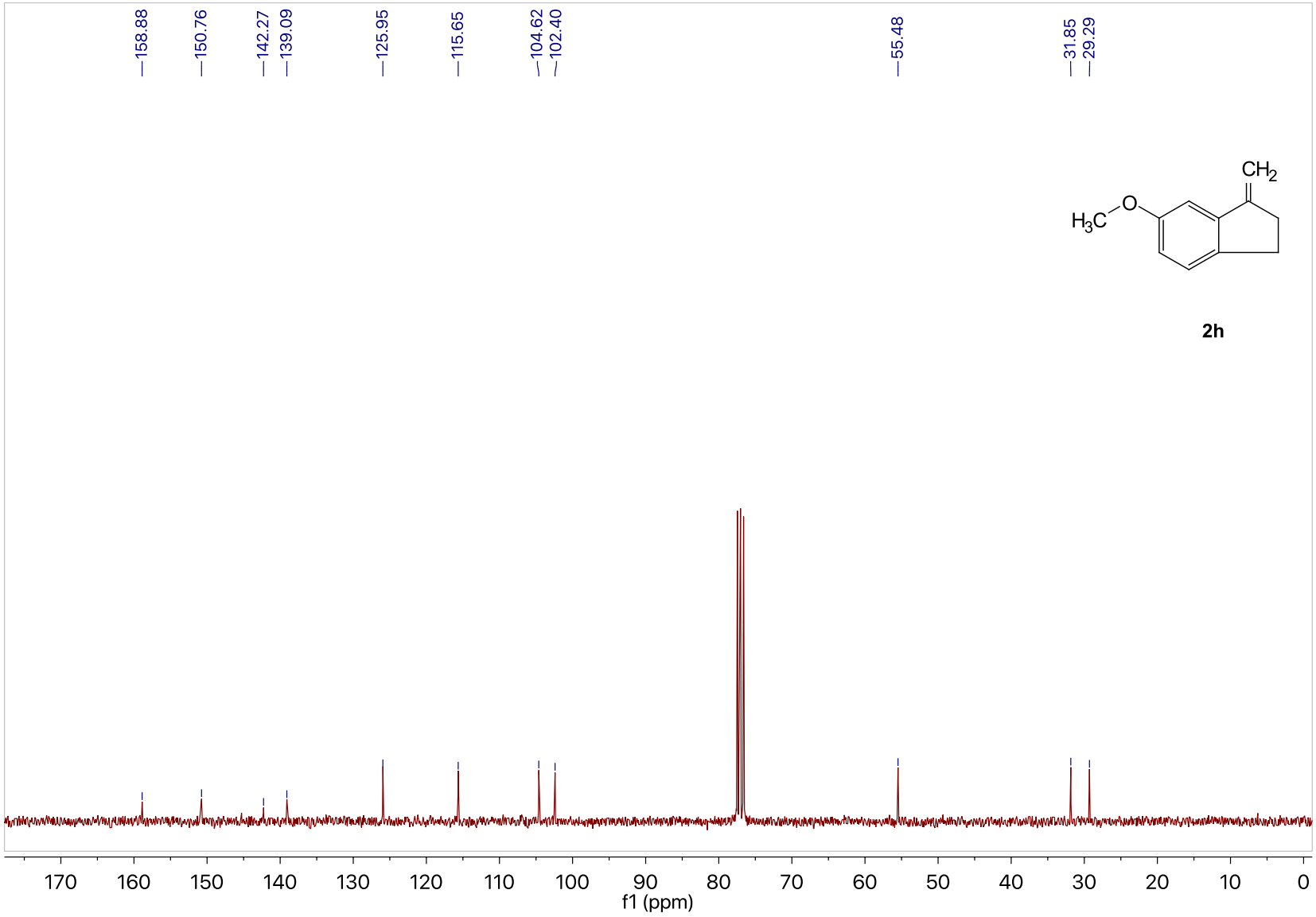
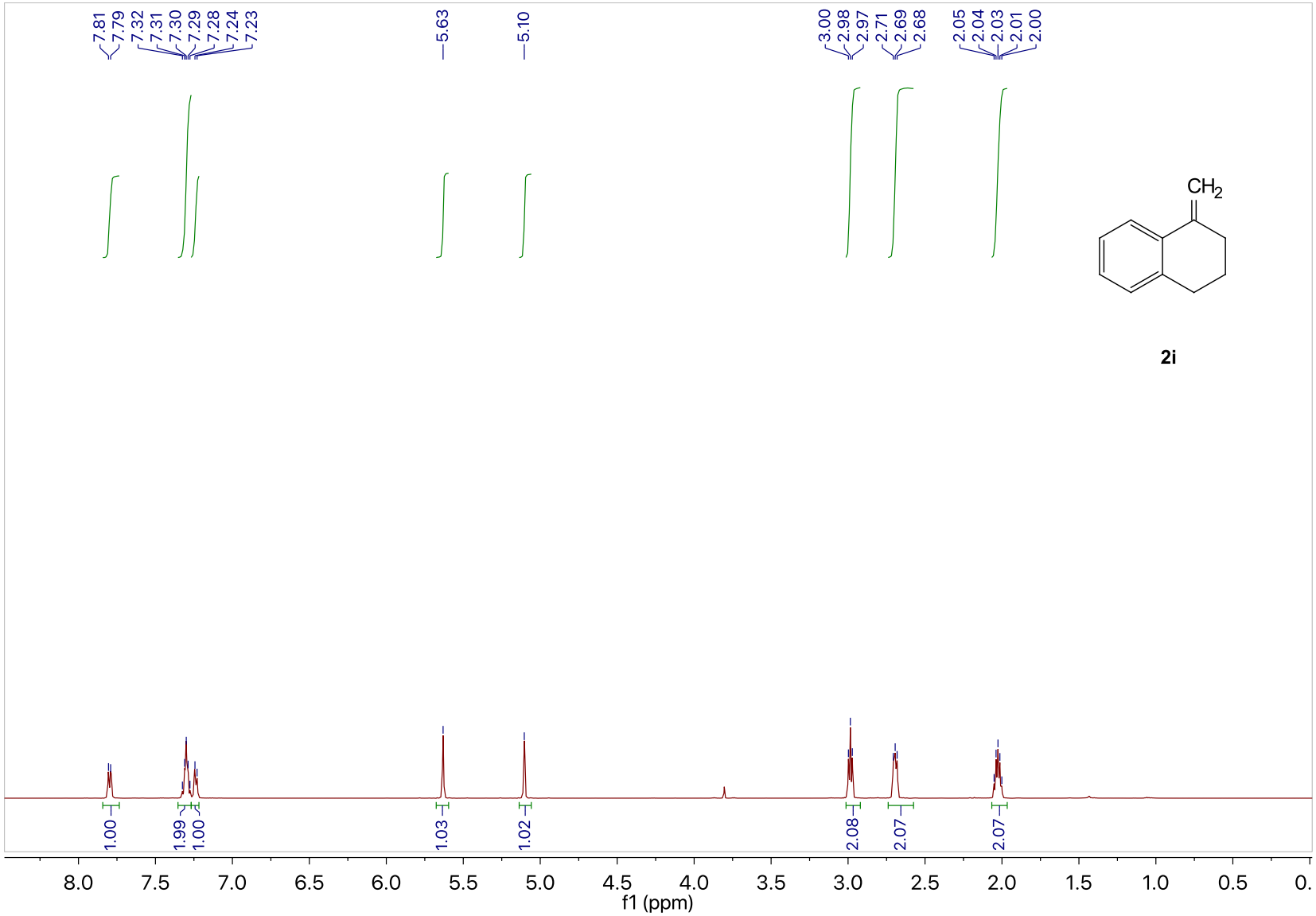
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


158.88
150.76
142.27
139.09
125.95
115.65
104.62
102.40
55.48
31.85
29.29
CH2
H3C
O
2h
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.79
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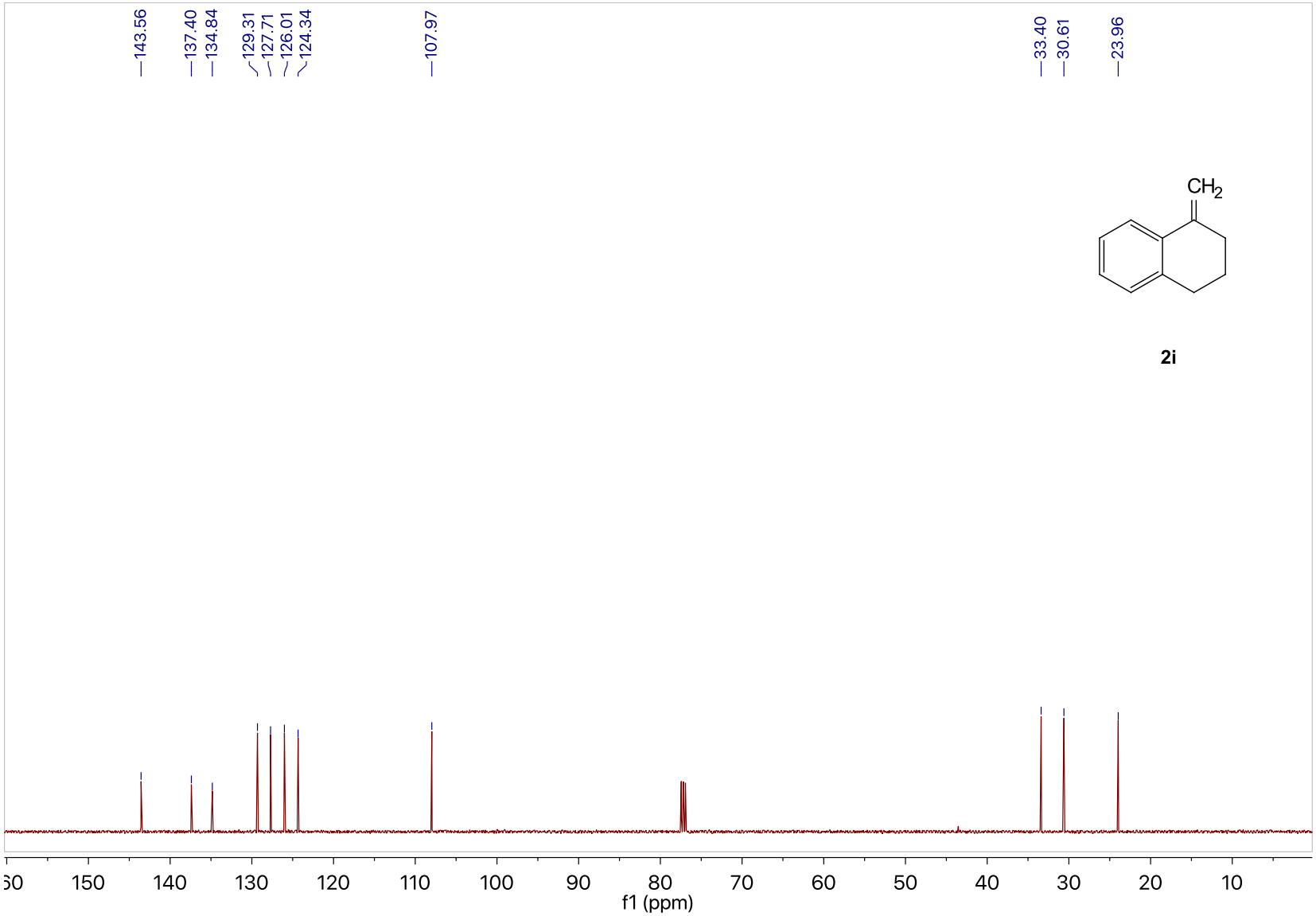
7.28
7.24
7.23
5.63
5.10
3.00
2.98
2.97
2.71
2.69
2.68
2.05
2.04
2.03
2.01
2.00
CH2
2i
1.00
1.99
1.00
1.03
1.02
2.08
2.07
2.07
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)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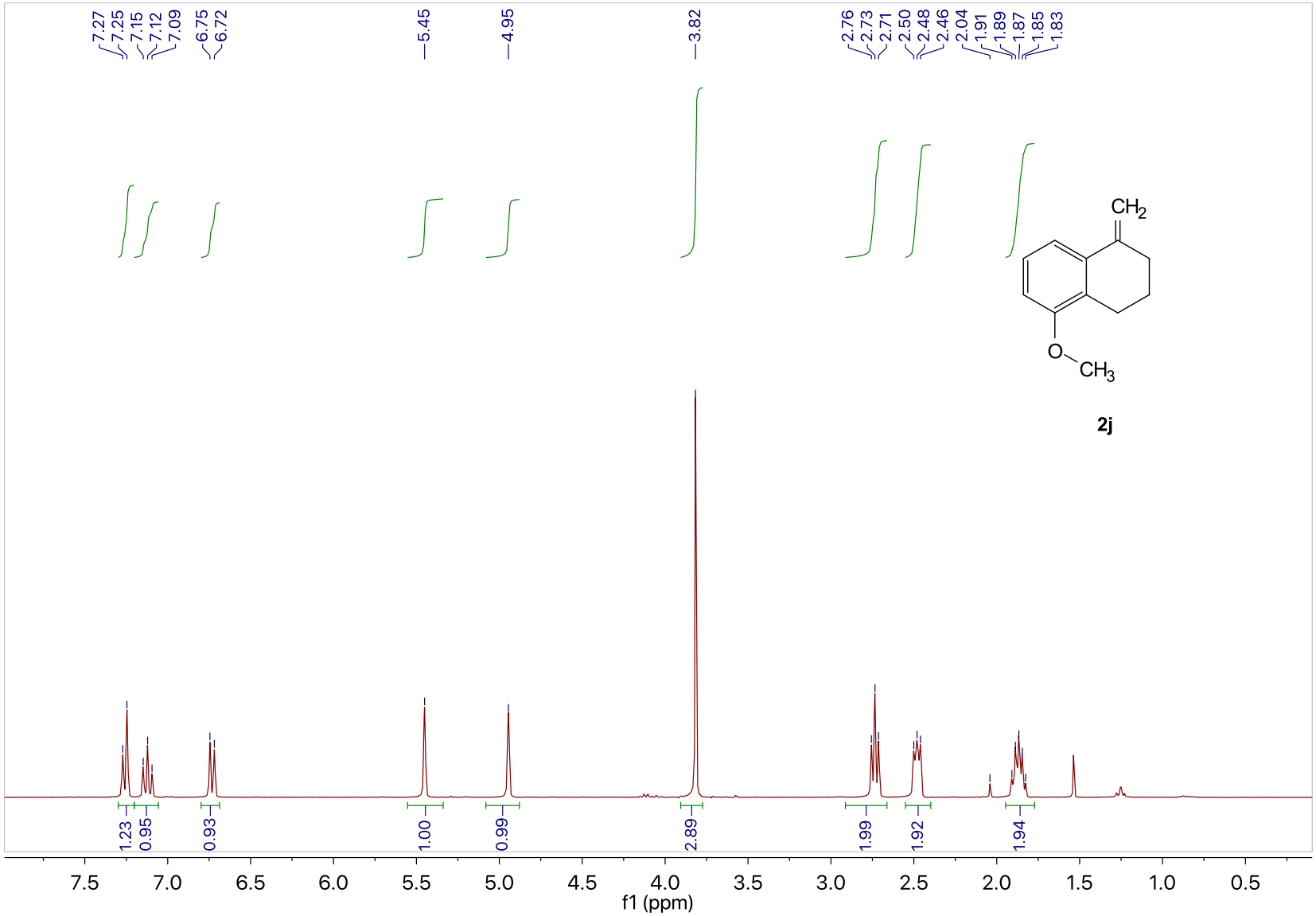
137.40
134.84
129.31
127.71
126.01
124.34
107.97
33.40
30.61
23.96
CH2
2i
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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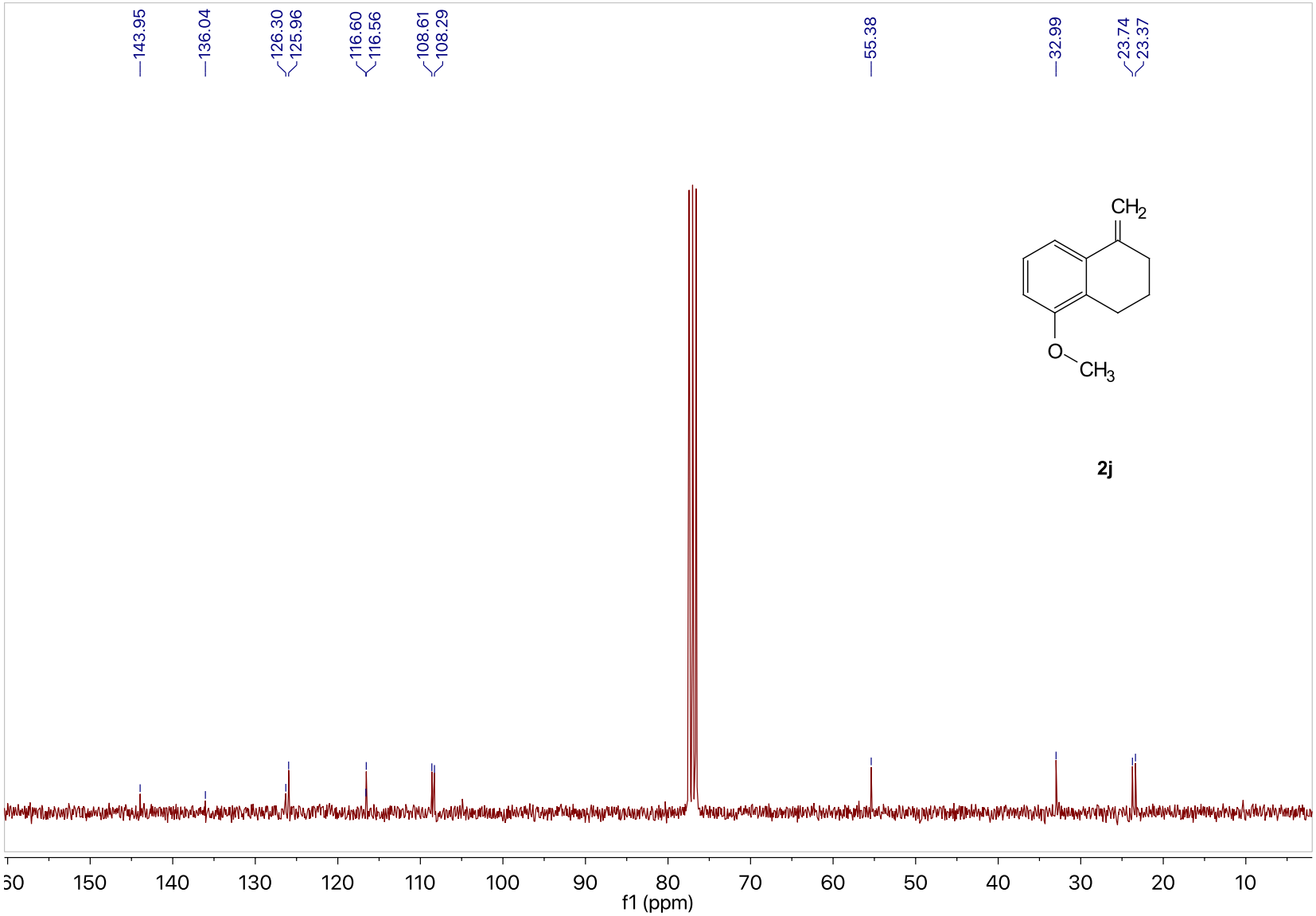
7.12
7.09
6.75
6.72
5.45
4.95
3.82
2.76
2.73
2.71
2.50
2.48
2.46
2.04
1.91
1.89
1.87
1.85
1.83
CH2
O
CH3
2j
1.23
0.95
0.93
1.00
0.99
2.89
1.99
1.92
1.94
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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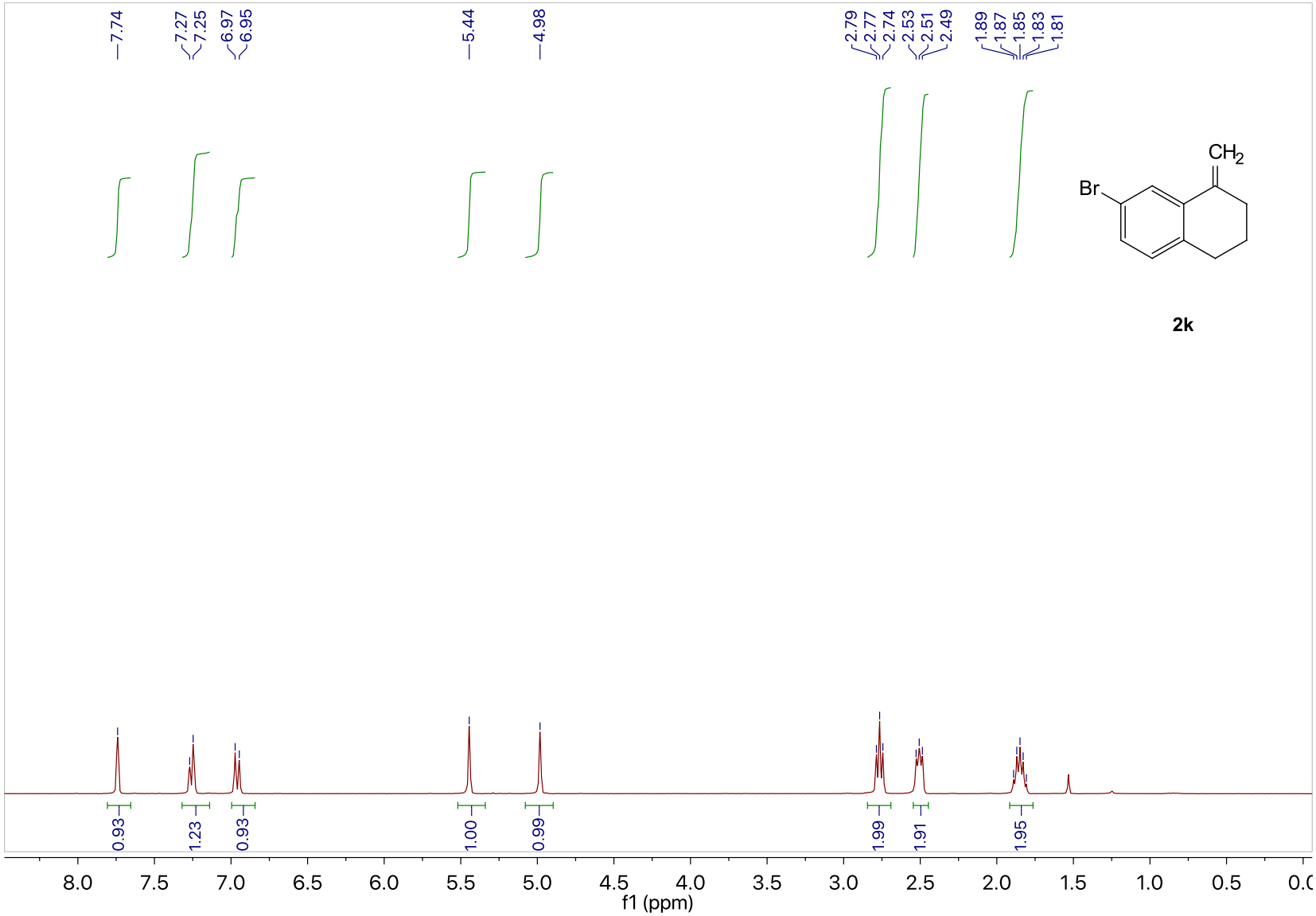
136.04
126.30
125.96
116.60
116.56
108.61
108.29
55.38
32.99
23.74
23.37
CH2
O
CH3
2j
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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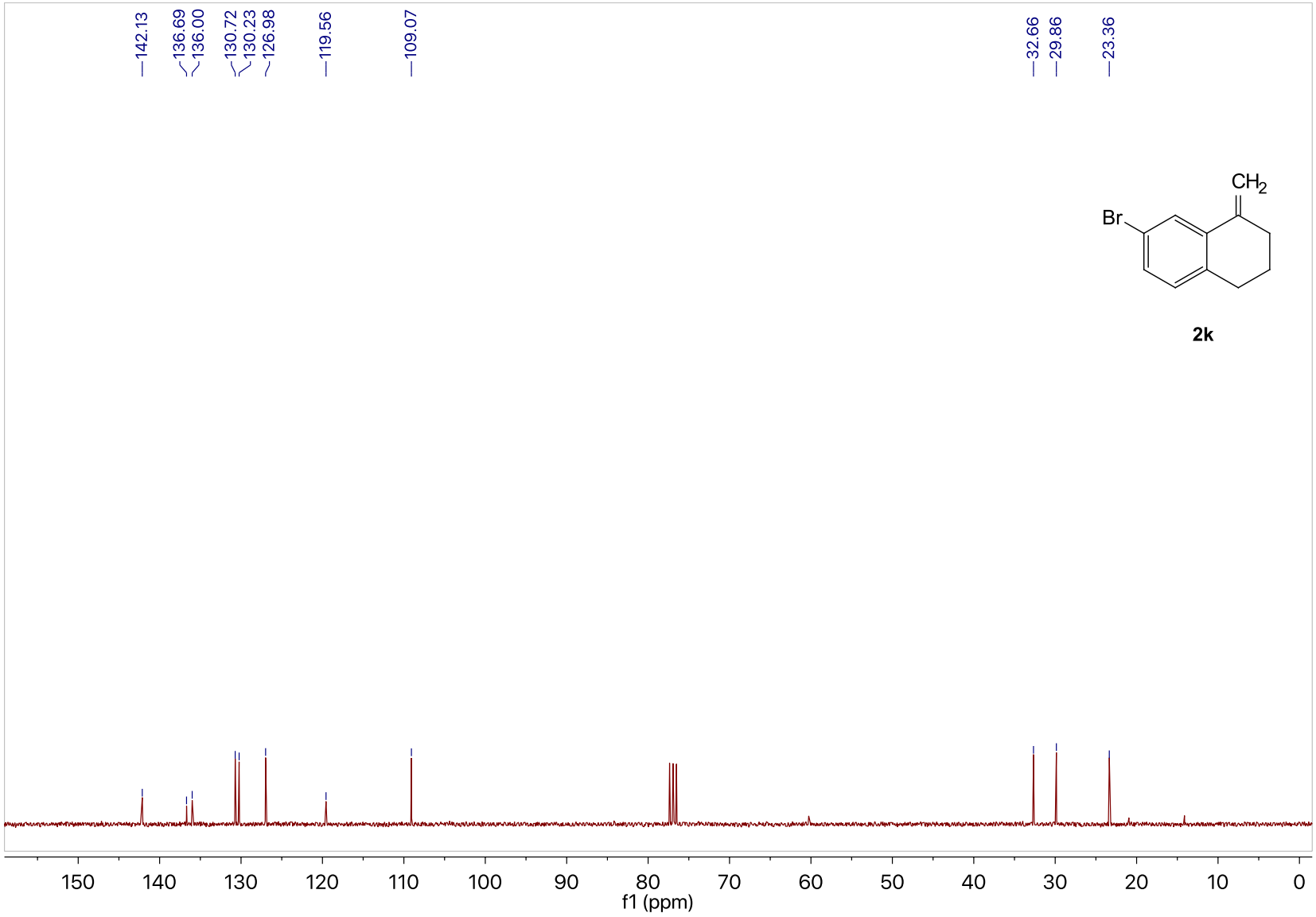
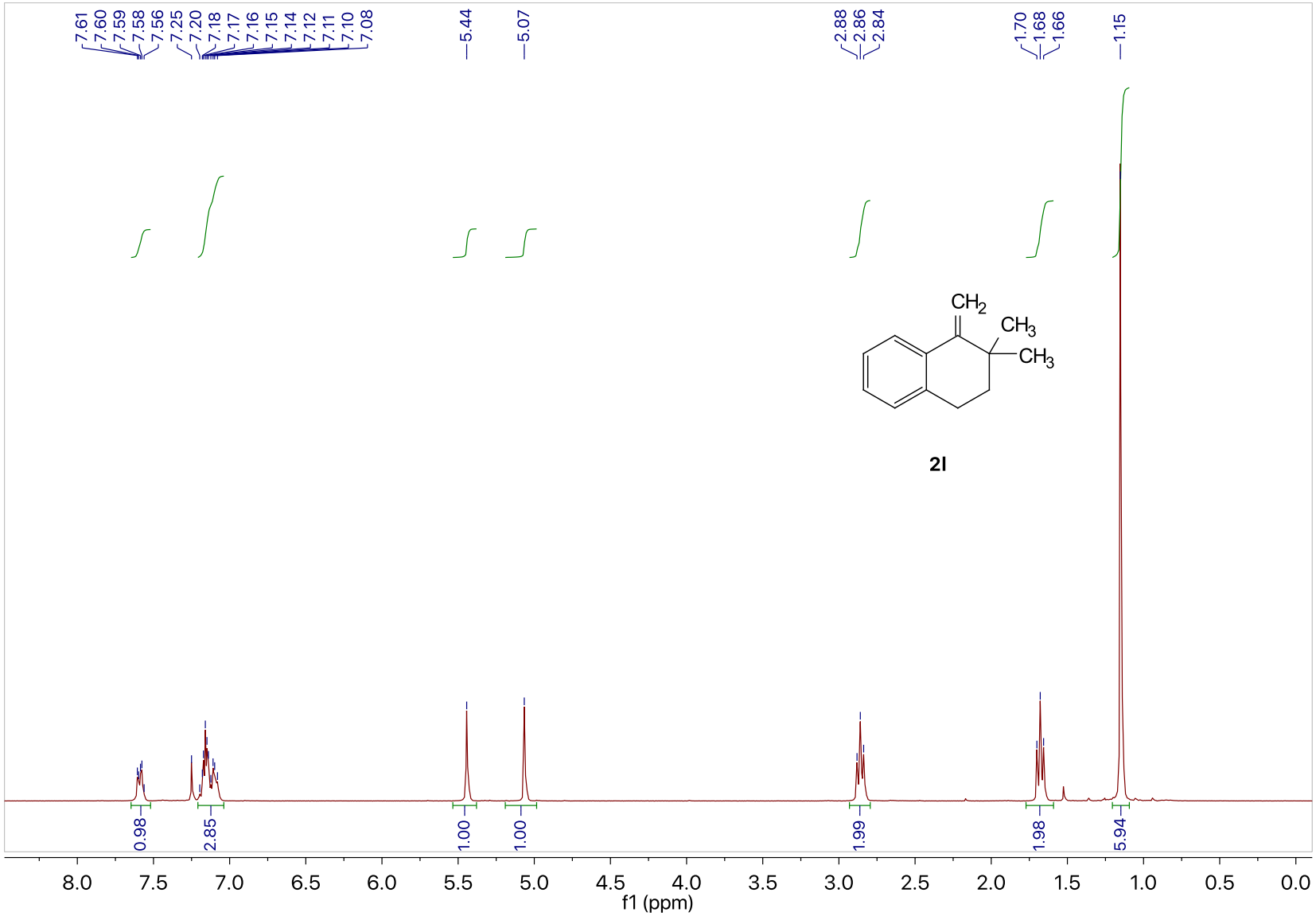
7.27
7.25
6.97
6.95
5.44
4.98
2.79
2.77
2.74
2.53
2.51
2.49
1.89
1.87
1.85
1.83
1.81
CH2
Br
2k
0.93
1.23
0.93
1.00
0.99
1.99
1.91
1.95
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


142.13
136.69
136.00
130.72
130.23
126.98
119.56
109.07
32.66
29.86
23.36
CH2
Br
2k
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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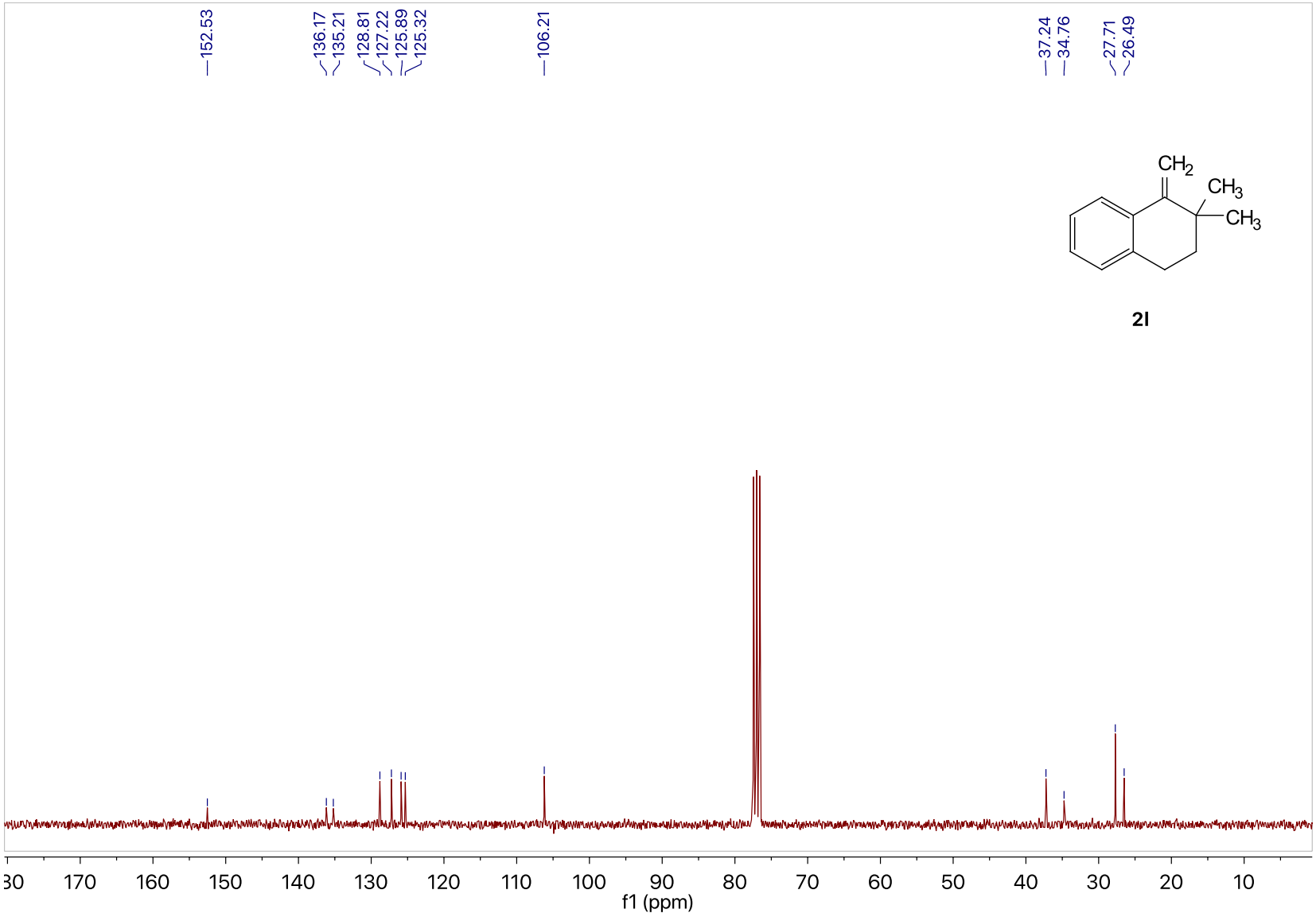
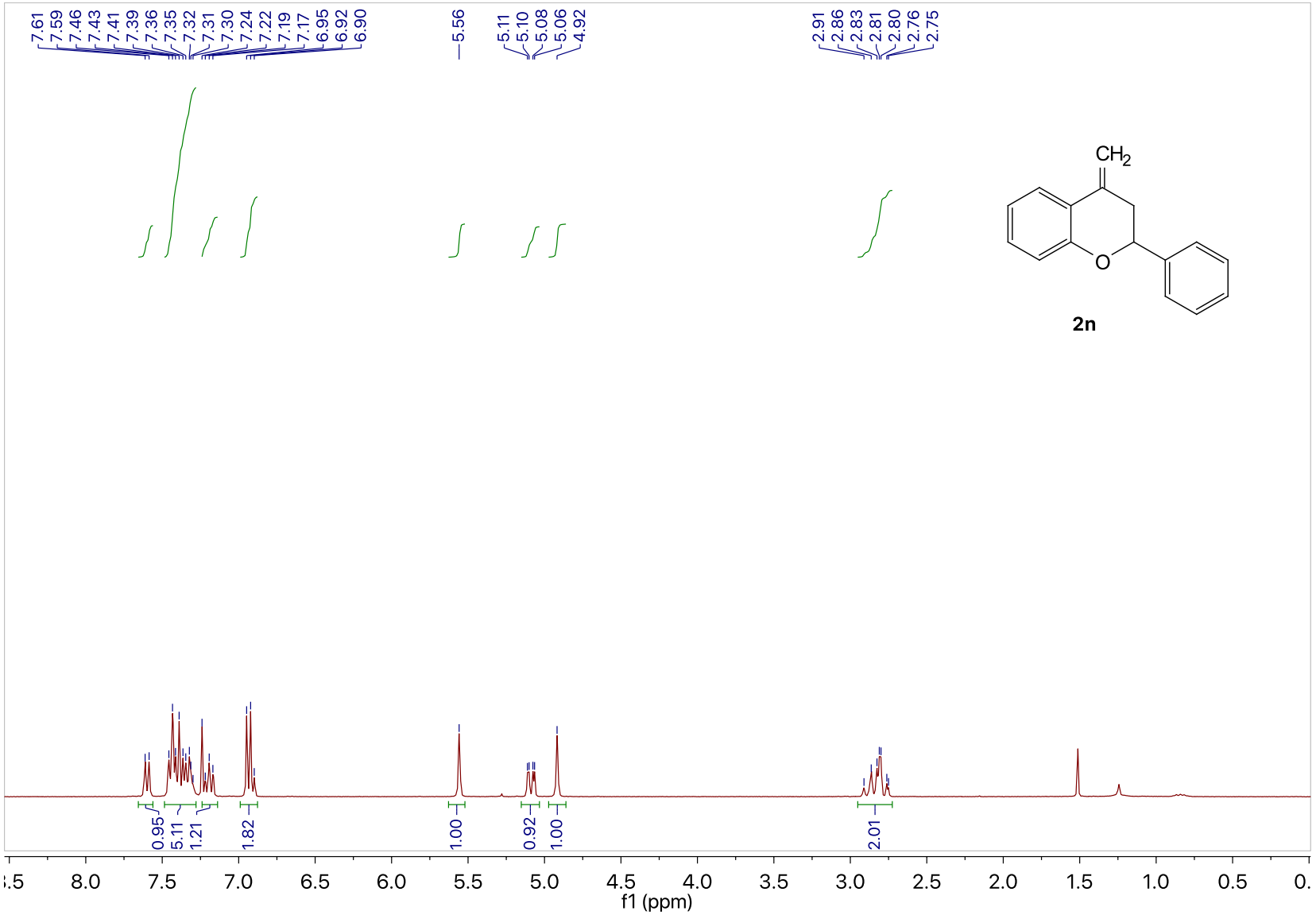
7.58
7.56
7.25
7.20
7.18
7.17
7.16
7.15
7.14
7.12
7.11
7.10
7.08
5.44
5.07
2.88
2.86
2.84
1.70
1.68
1.66
1.15
CH2
CH3
CH3
0.98
2.85
1.00
1.00
1.99
1.98
5.94
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

2l


152.53
136.17
135.21
128.81
127.22
125.89
125.32
106.21
37.24
34.76
27.71
26.49
CH2
CH3
CH3
2l
30
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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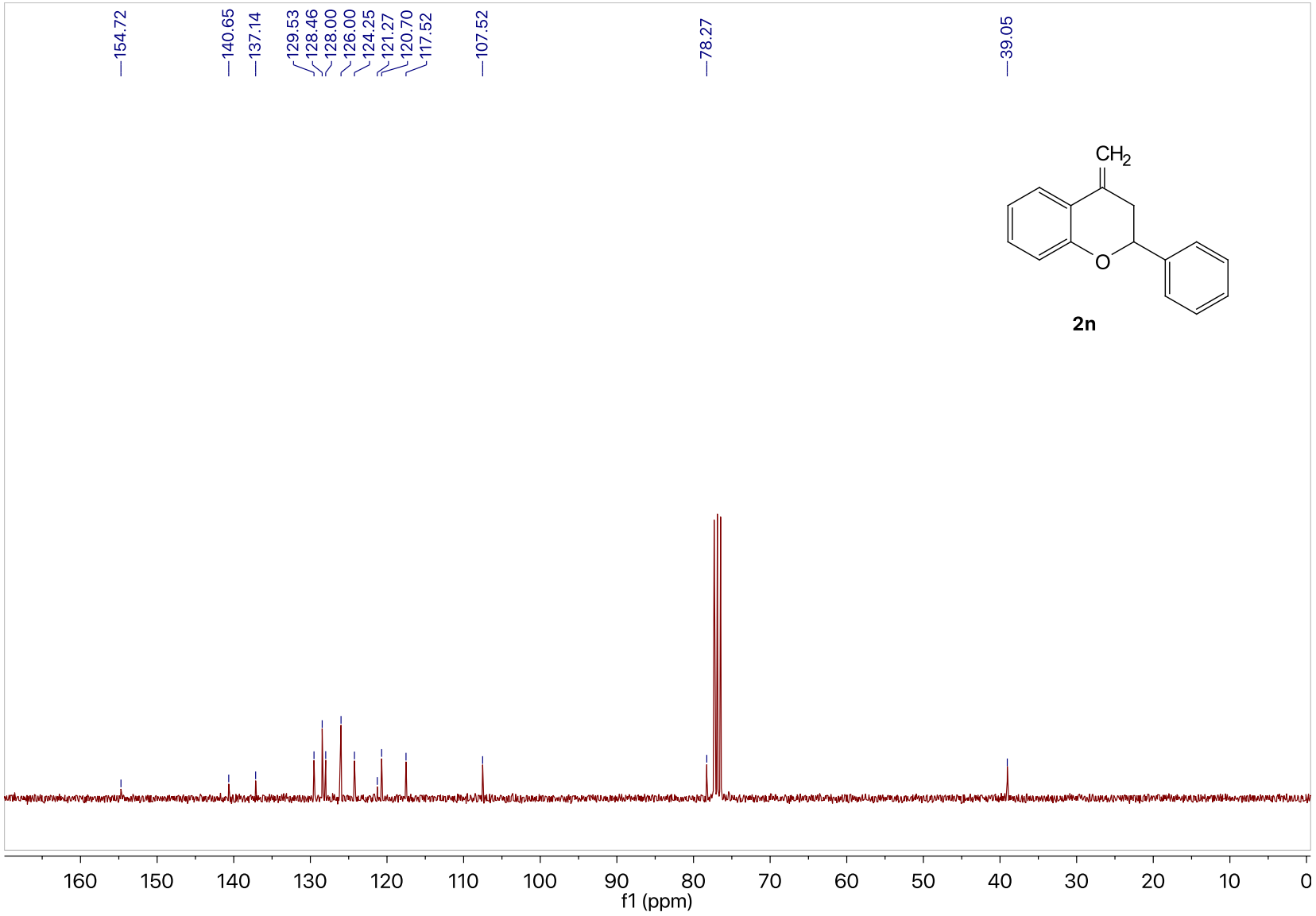
7.43
7.41
7.39
7.36
7.35
7.32
7.31
7.30
7.24
7.22
7.19
7.17
6.95
6.92
6.90
5.56
5.11
5.10
5.08
5.06
4.92
2.91
2.86
2.83
2.81
2.80
2.76
2.75
CH2
O
2n
0.95
5.11
1.21
1.82
1.00
0.92
1.00
2.01
f1 (ppm)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137.14
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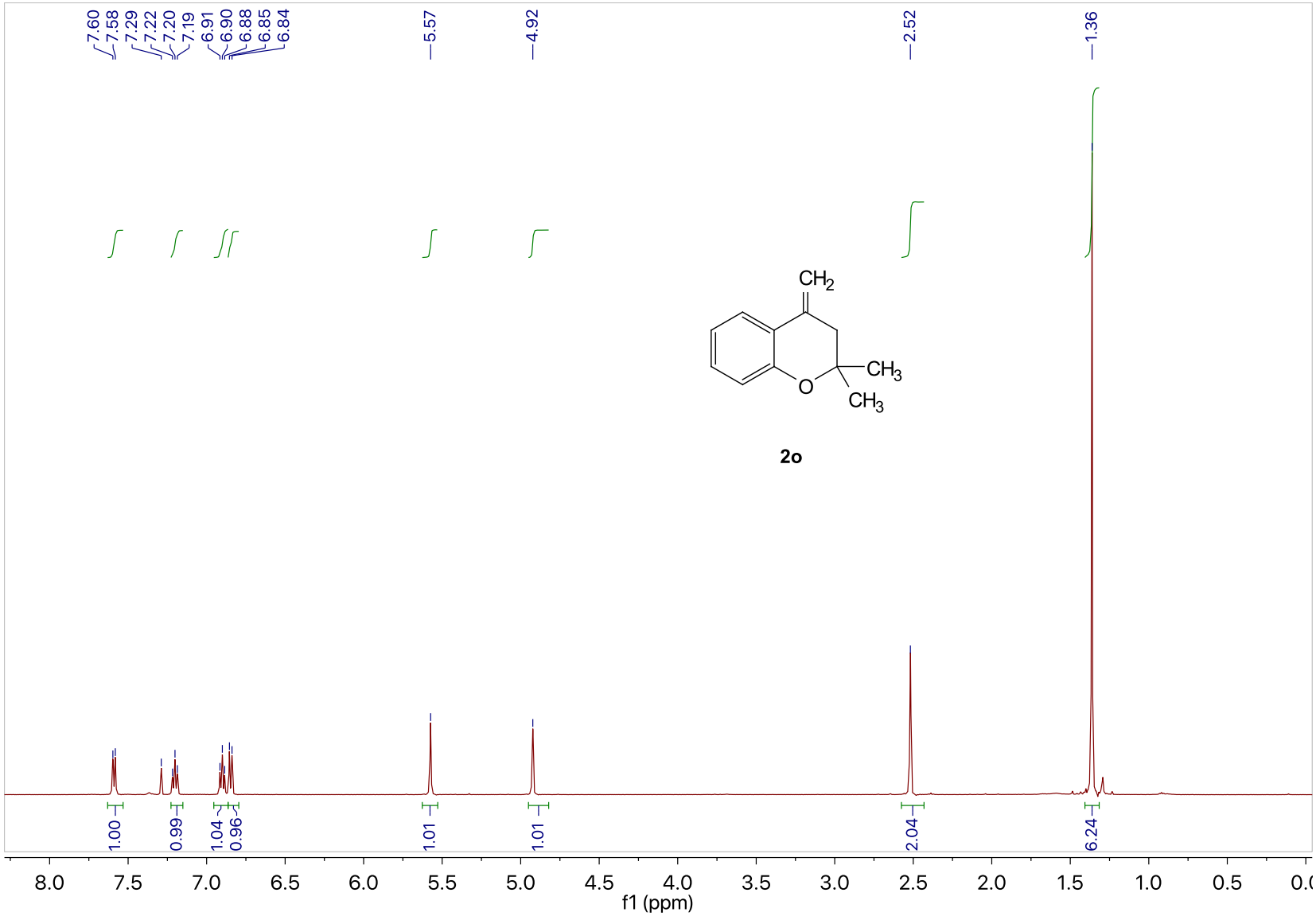
128.00
126.00
124.25
121.27
120.70
117.52
107.52
78.27
39.05
CH2
O
2n
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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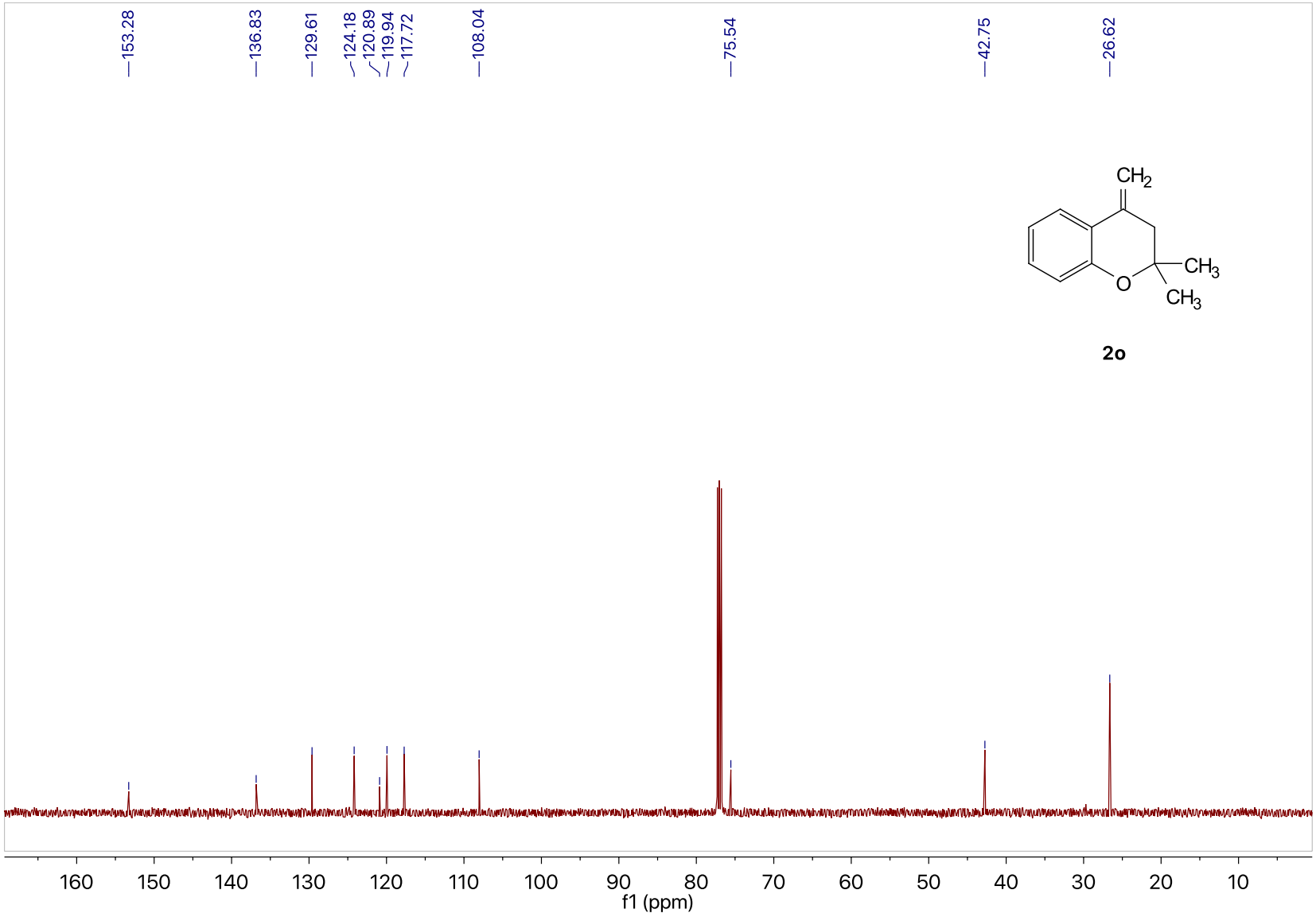
7.19
6.91
6.90
6.88
6.85
6.84
5.57
4.92
2.52
1.36
CH2
CH3
O
CH3
2o
1.00
0.99
1.04
0.96
1.01
1.01
2.04
6.24
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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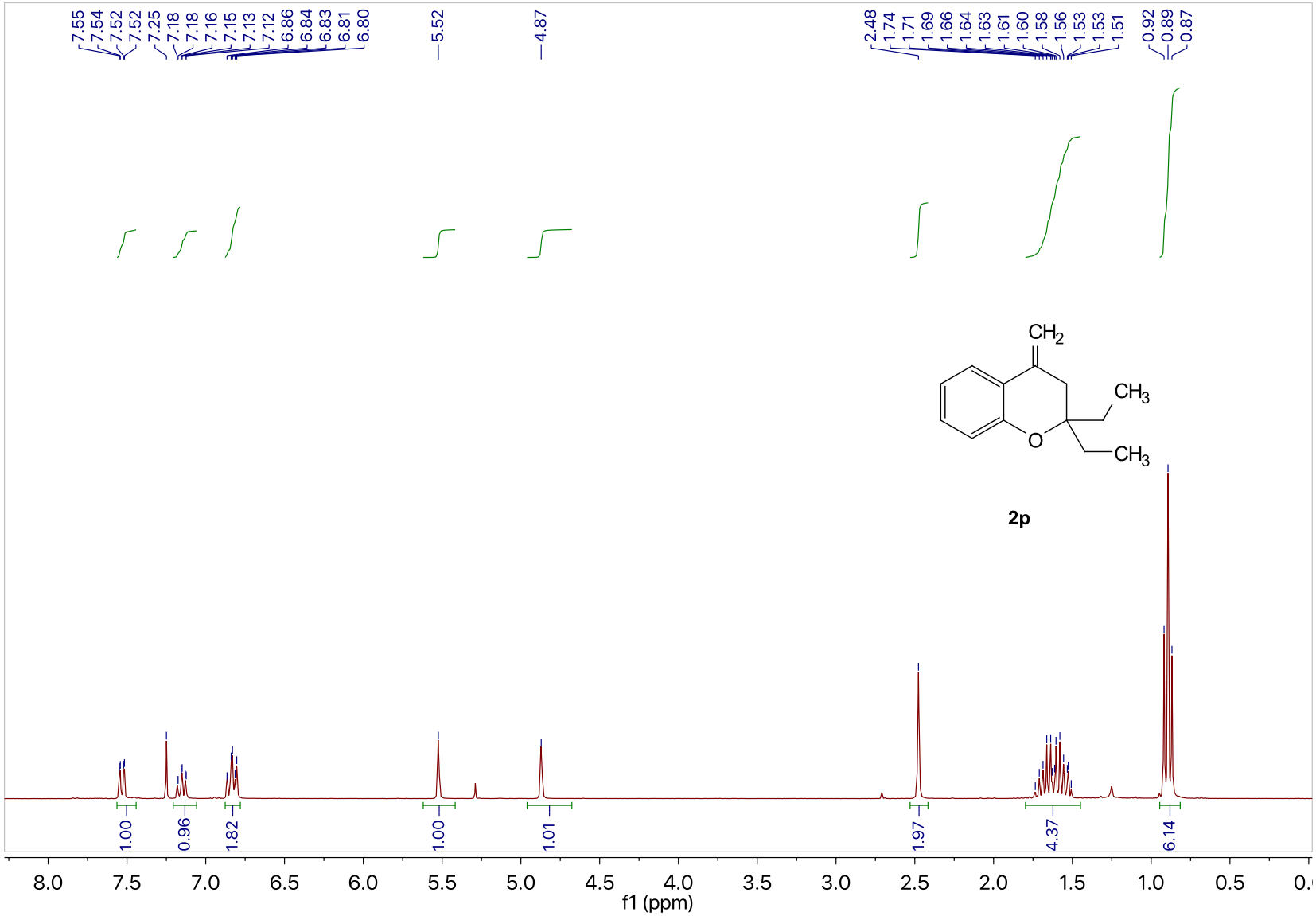
136.83
129.61
124.18
120.89
119.94
117.72
108.04
75.54
42.75
26.62
CH2
CH3
CH3
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

2o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7.52
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7.18
7.18
7.16
7.15
7.13
7.12
6.86
6.84
6.83
6.81
6.80
5.52
4.87
2.48
1.74
1.71
1.69
1.66
1.64
1.63
1.61
1.60
1.58
1.56
1.53
1.53
1.51
0.92
0.89
0.87
CH2
CH3
CH3
O
2p
1.00
0.96
1.82
1.00
1.01
1.97
4.37
6.14
8.0
7.5
7.0
6.5
6.0
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5.0
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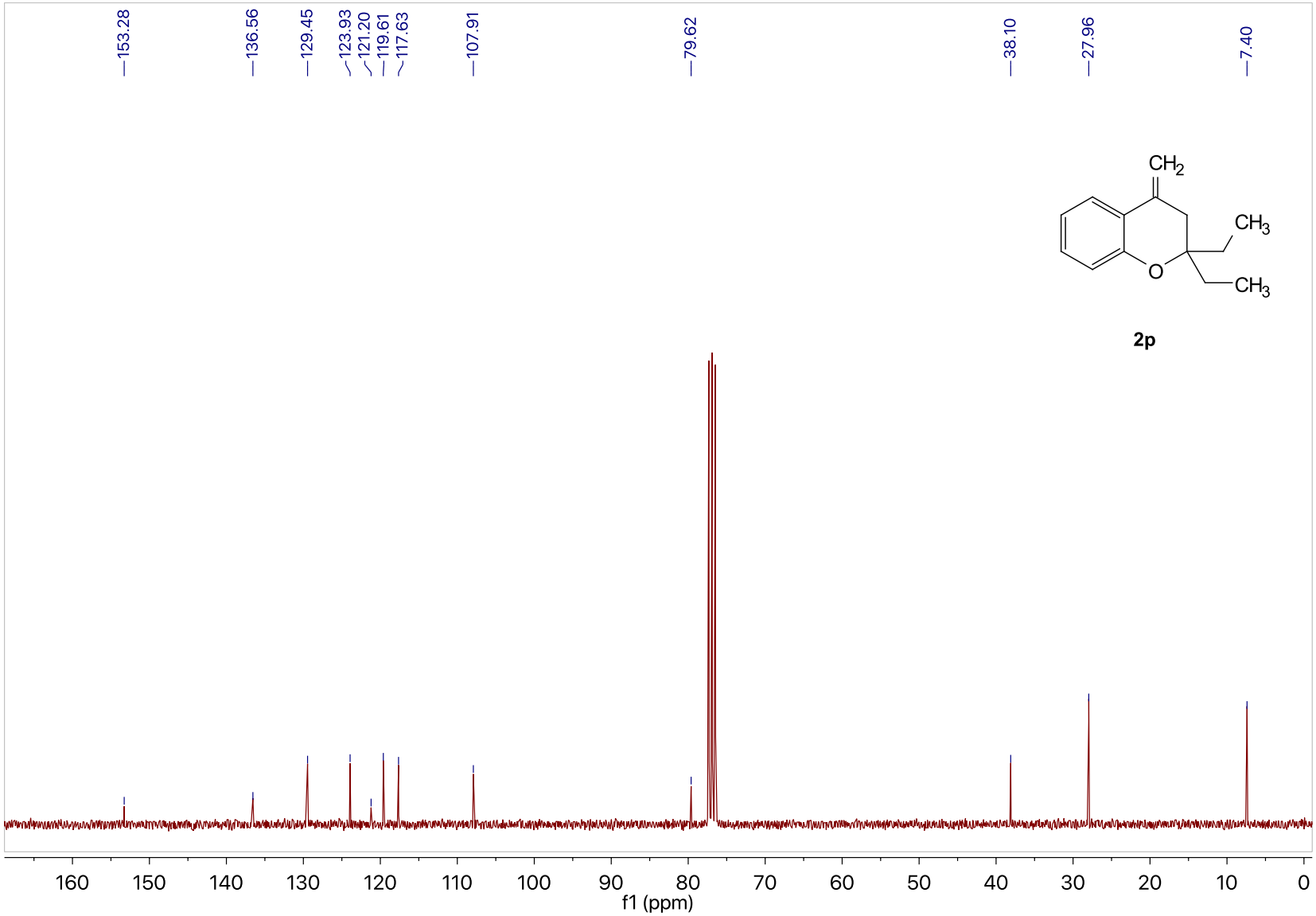
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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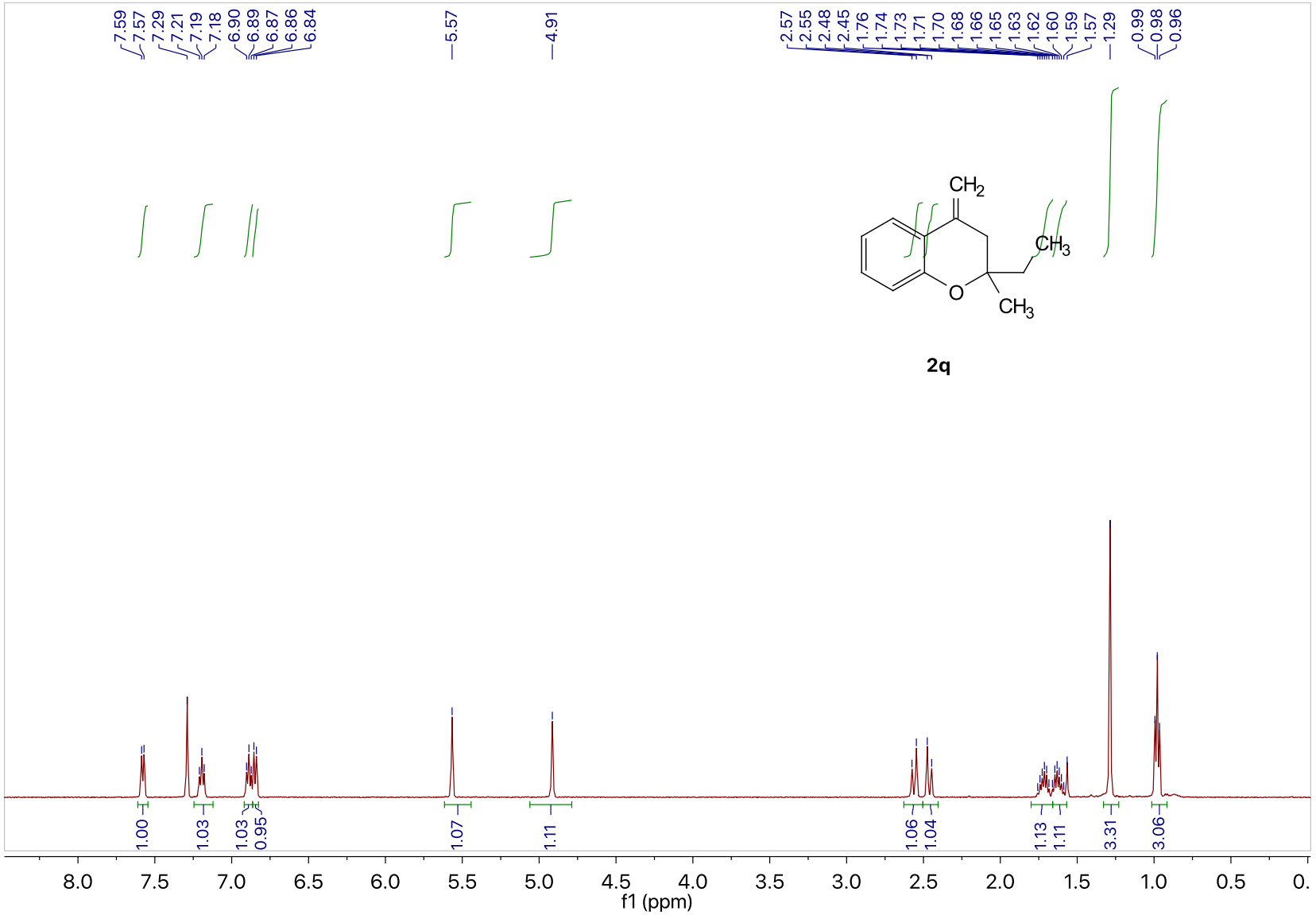
119.61
117.63
107.91
79.62
38.10
27.96
7.40
CH2
CH3
O
CH3
2p
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.18
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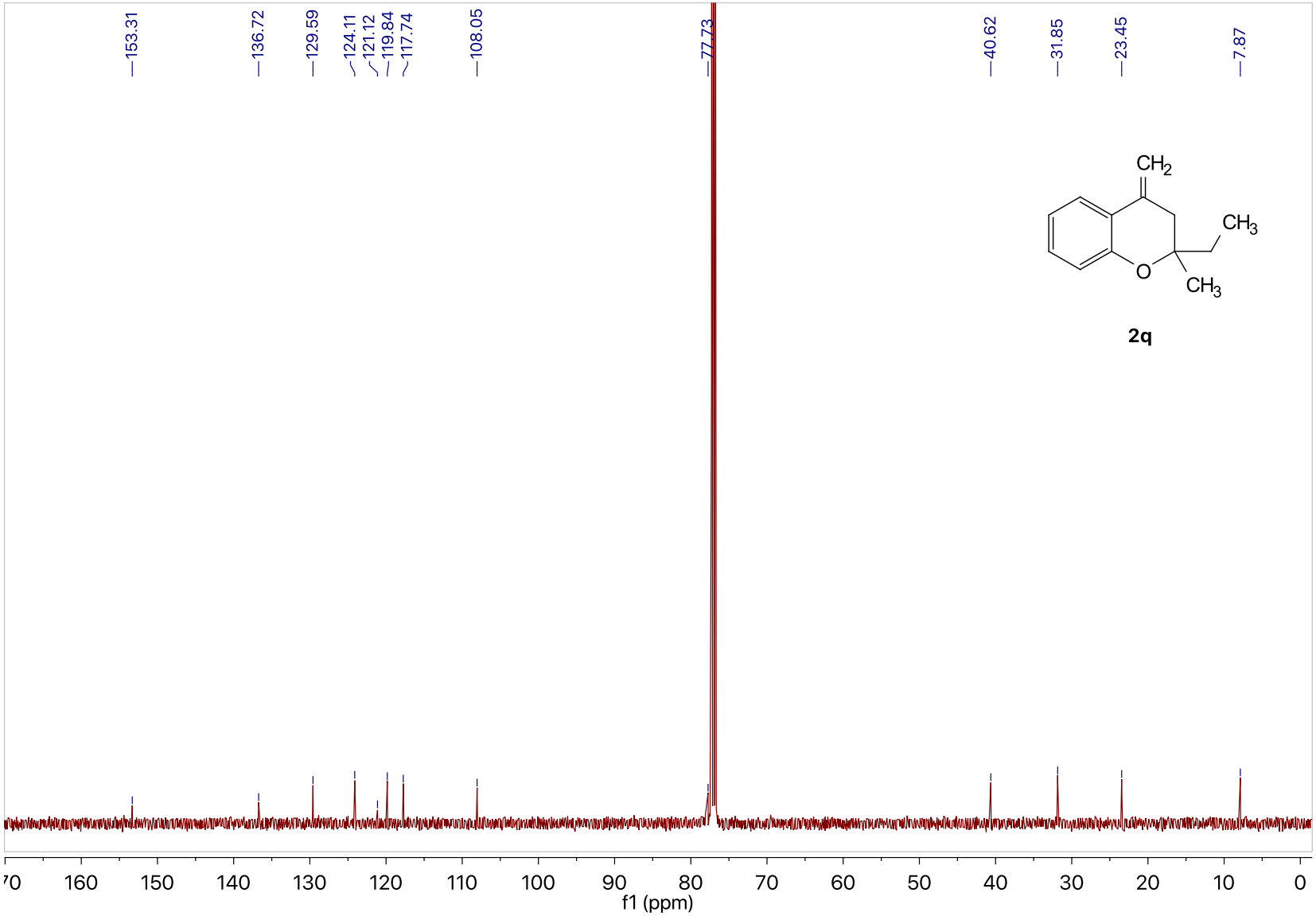
6.89
6.87
6.86
6.84
5.57
4.91
2.57
2.55
2.48
2.45
1.76
1.74
1.73
1.71
1.70
1.68
1.66
1.65
1.63
1.62
1.60
1.59
1.57
1.29
0.99
0.98
0.96
CH2
CH3
O
CH3
2q
1.00
1.03
1.03
0.95
1.07
1.11
1.06
1.04
1.13
1.11
3.31
3.06
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)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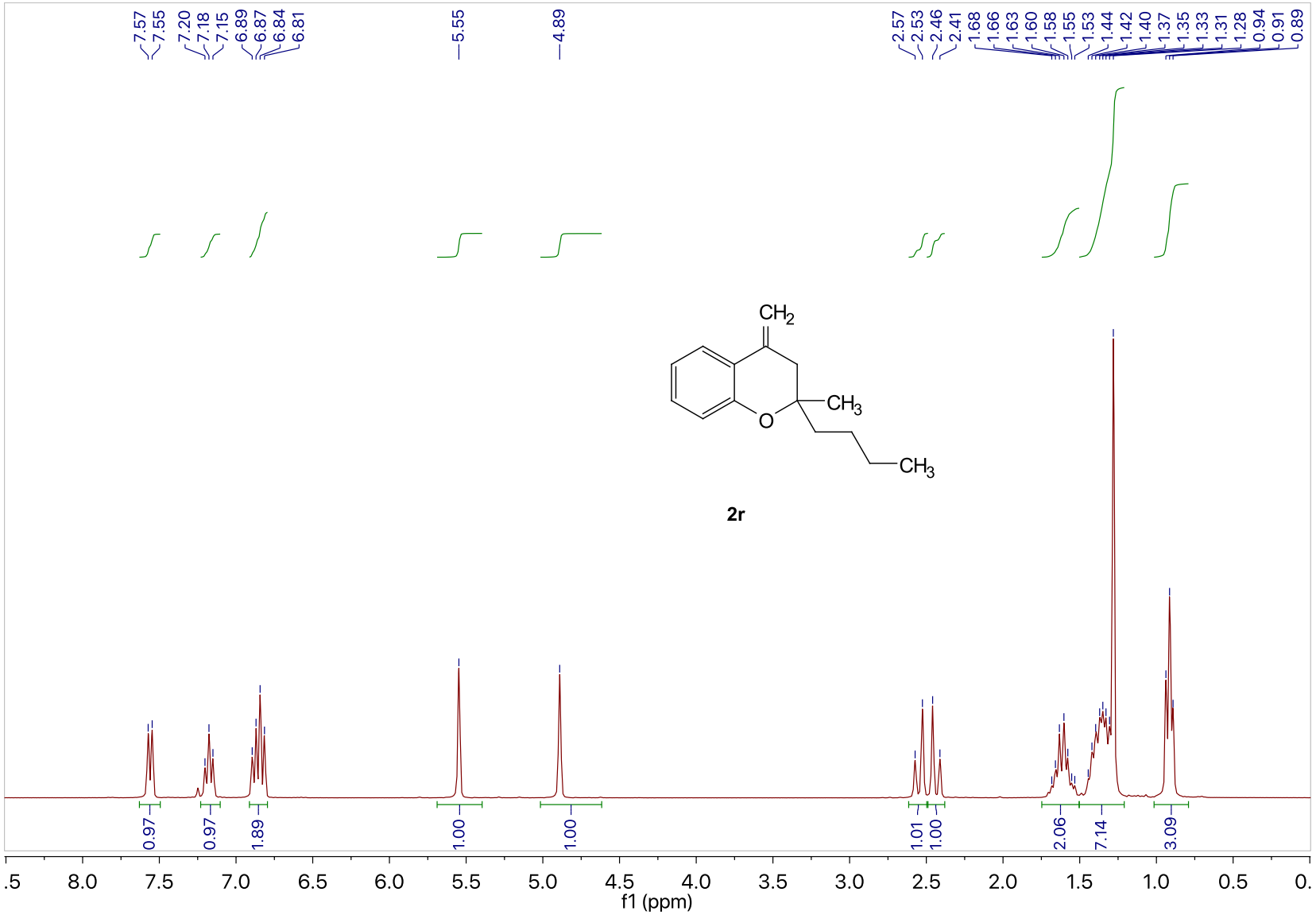
124.11
121.12
119.84
117.74
108.05
77.73
40.62
31.85
23.45
7.87
CH2
CH3
O
CH3
2q
f1 (ppm)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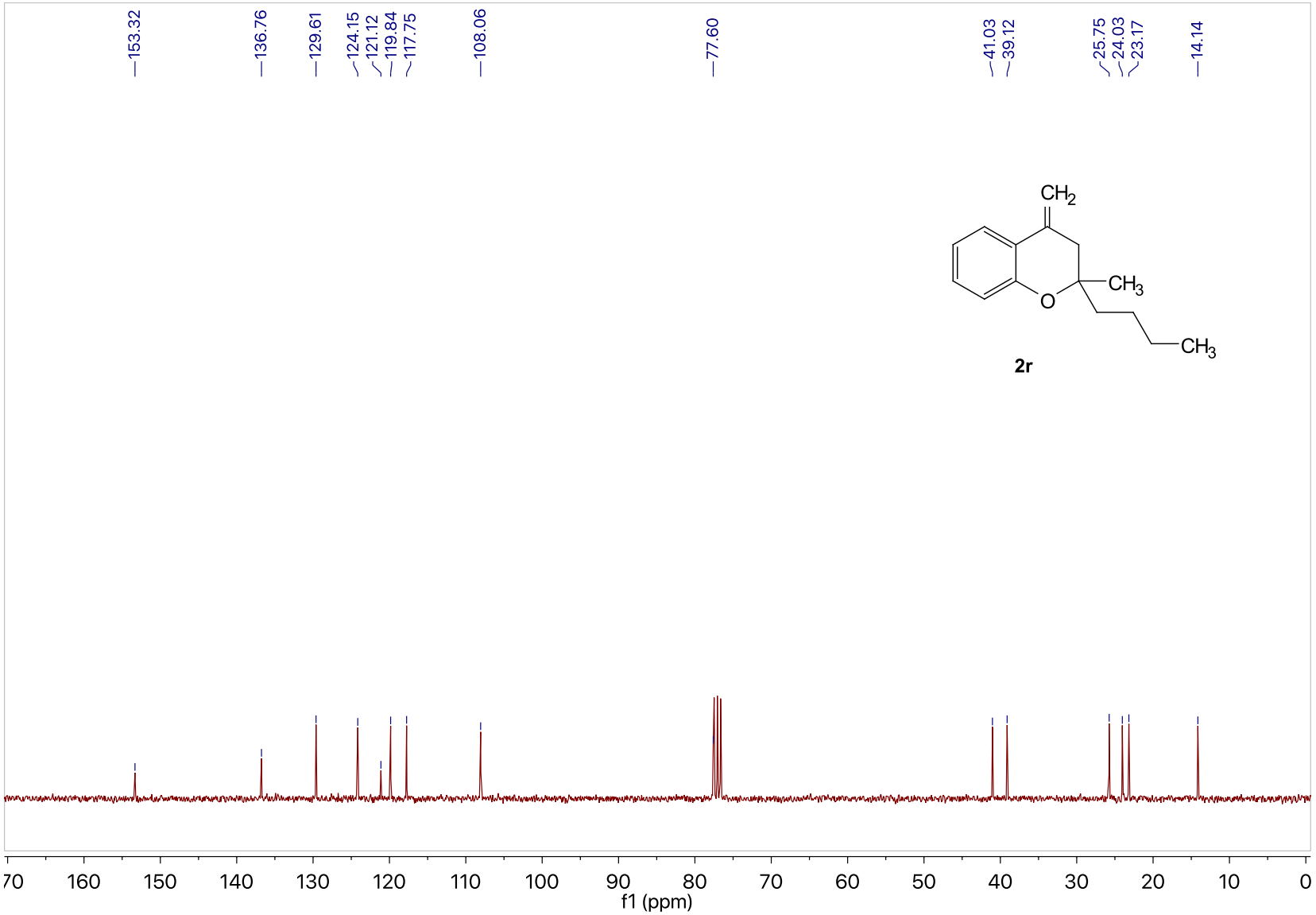
6.89
6.87
6.84
6.81
5.55
4.89
2.57
2.53
2.46
2.41
1.68
1.66
1.63
1.60
1.58
1.55
1.53
1.44
1.42
1.40
1.37
1.35
1.33
1.31
1.28
0.94
0.91
0.89
CH2
CH3
O
CH3
2r
0.97
0.97
1.89
1.00
1.00
1.01
1.00
2.06
7.14
3.09
f1 (ppm)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119.84
117.75
108.06
77.60
41.03
39.12
25.75
24.03
23.17
14.14
CH2
CH3
O
CH3
2r
70
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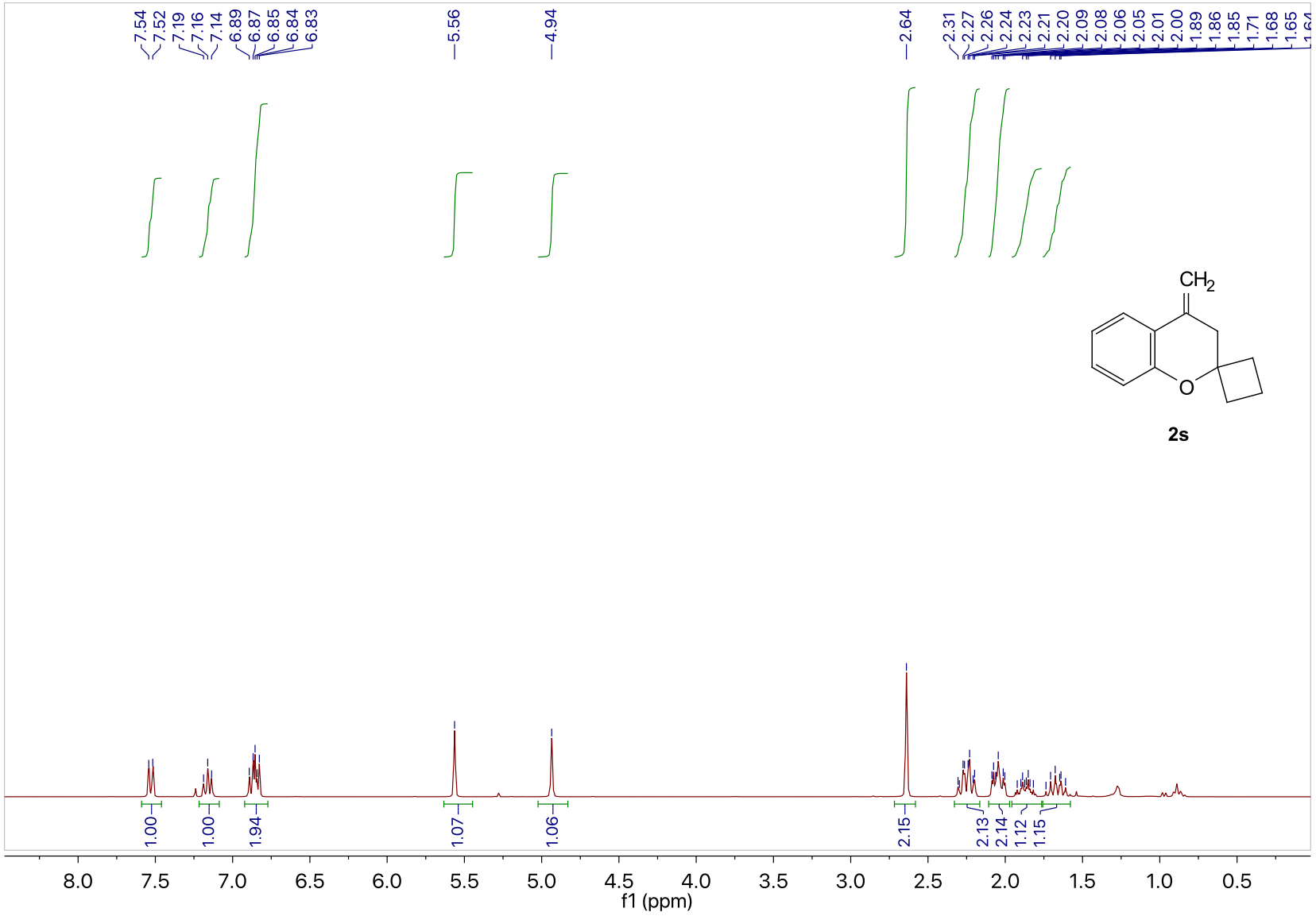
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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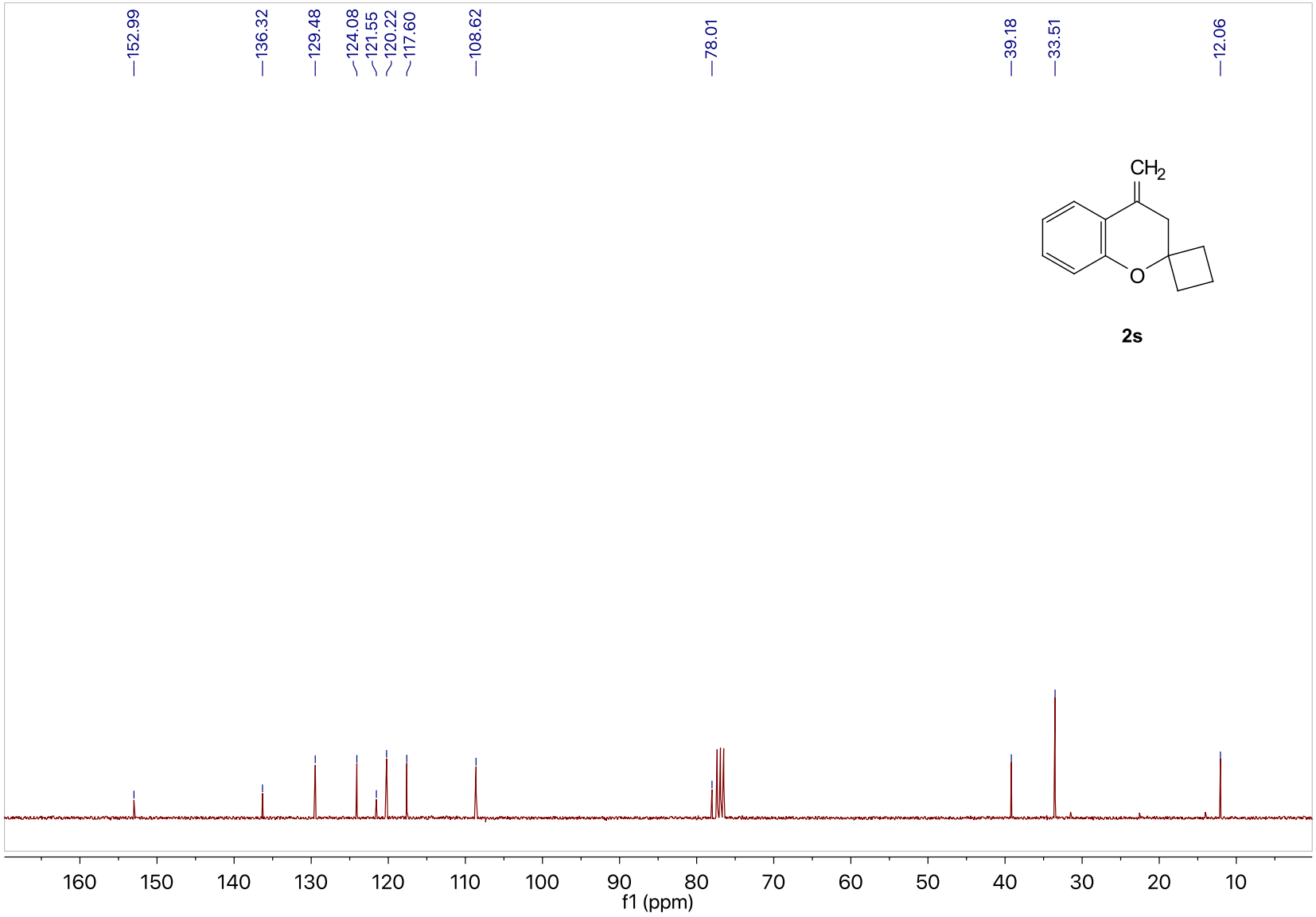
6.85
6.84
6.83
5.56
4.94
2.64
2.31
2.27
2.26
2.24
2.23
2.21
2.20
2.09
2.08
2.06
2.05
2.01
2.00
1.89
1.86
1.85
1.71
1.68
1.65
CH2
O
2s
1.00
1.00
1.94
1.07
1.06
2.15
2.13
2.14
1.12
1.15
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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120.22
117.60
108.62
78.01
39.18
33.51
12.06
CH2
O
2s
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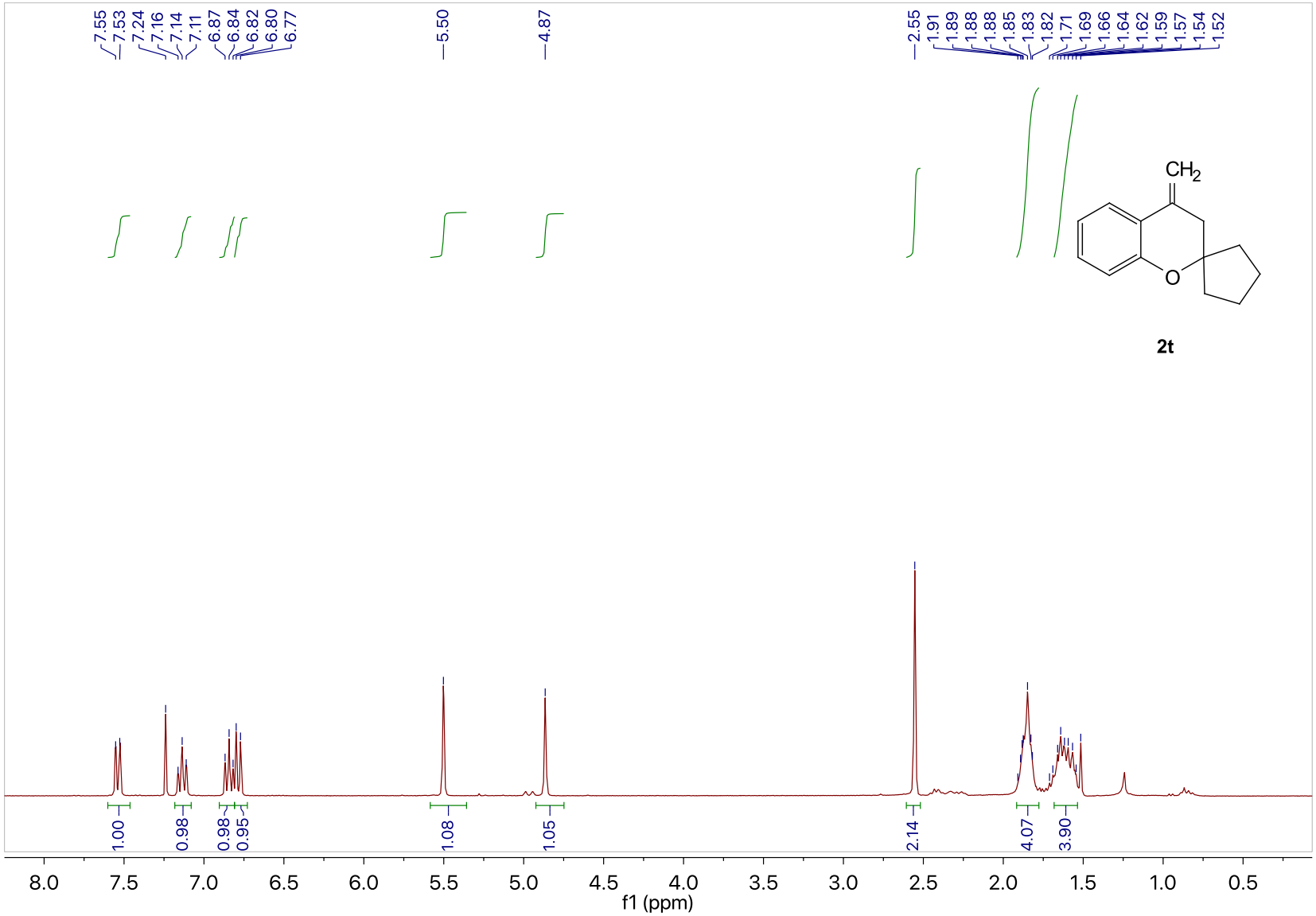
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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7.11
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6.84
6.82
6.80
6.77
5.50
4.87
2.55
1.91
1.89
1.88
1.88
1.85
1.83
1.82
1.71
1.69
1.66
1.64
1.62
1.59
1.57
1.54
1.52
CH2
O
2t
1.00
0.98
0.98
0.95
1.08
1.05
2.14
4.07
3.90
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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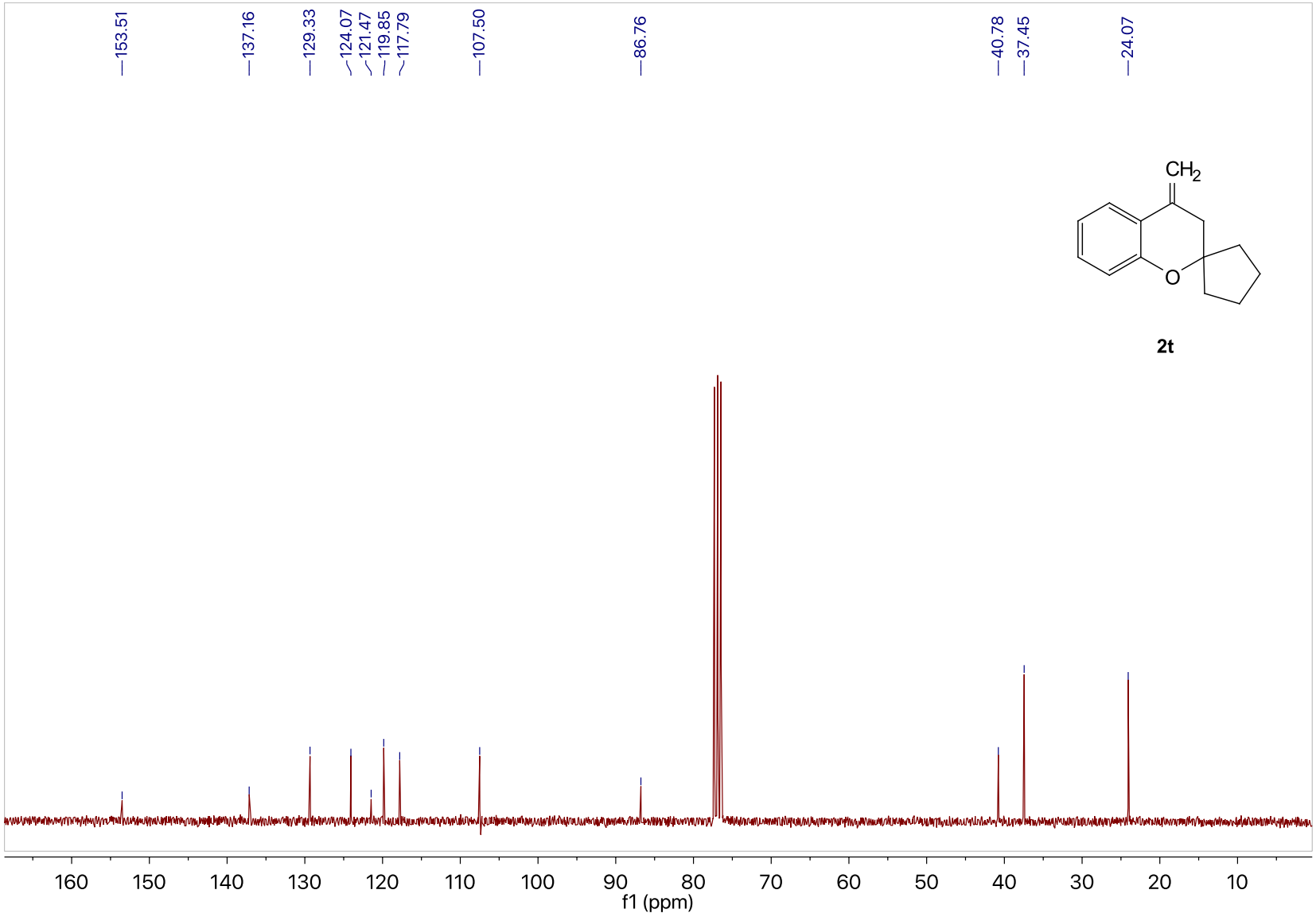
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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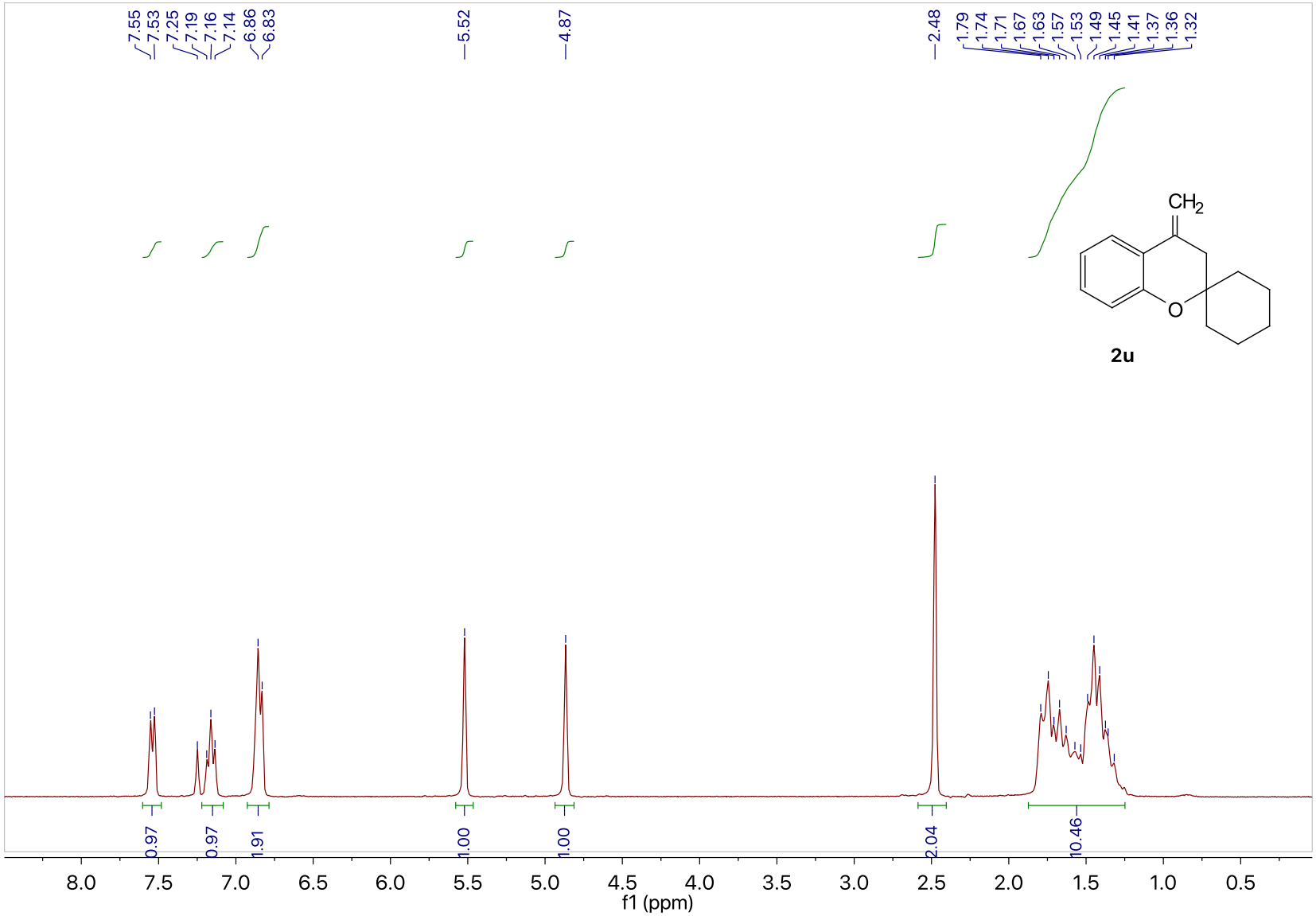
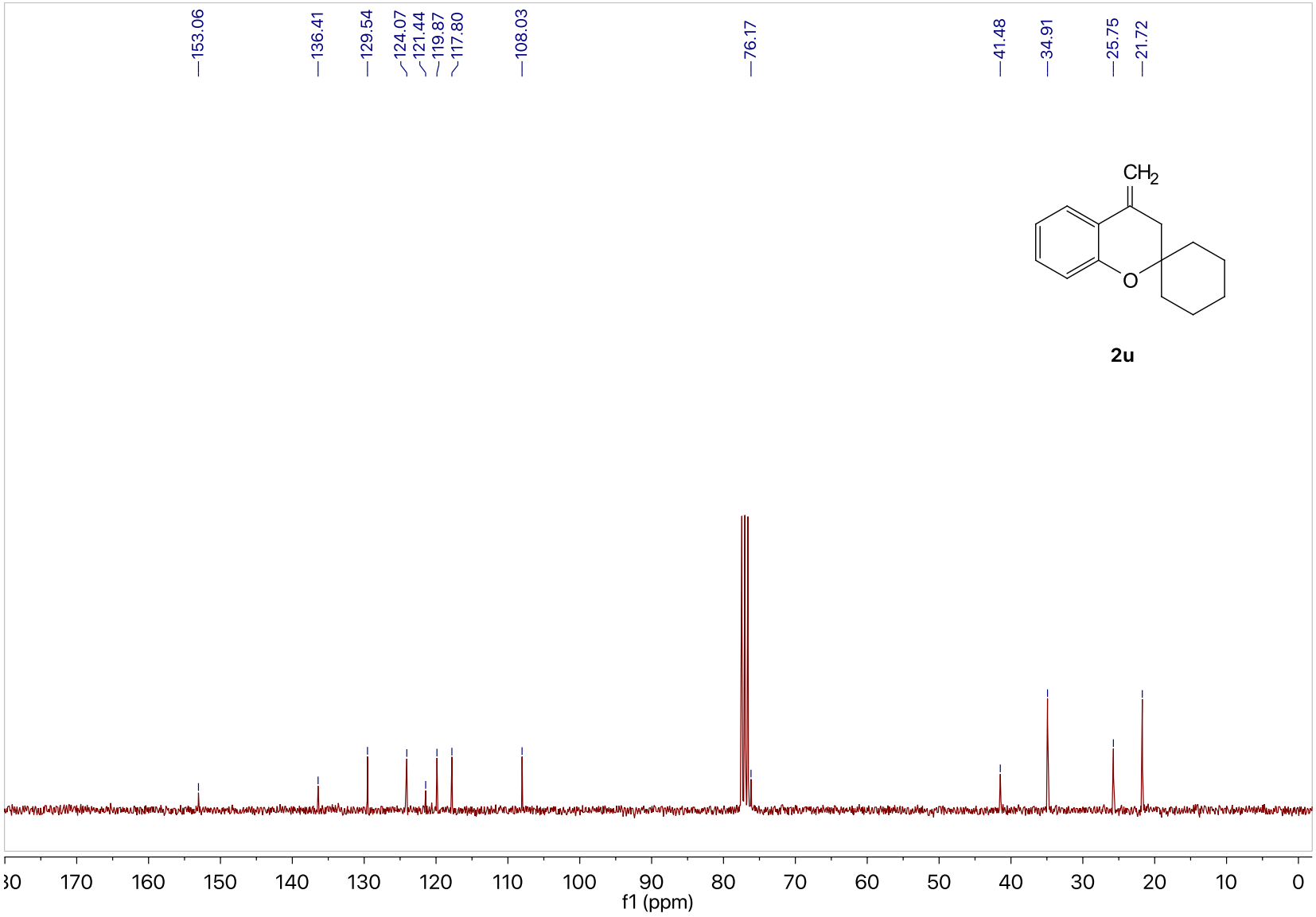
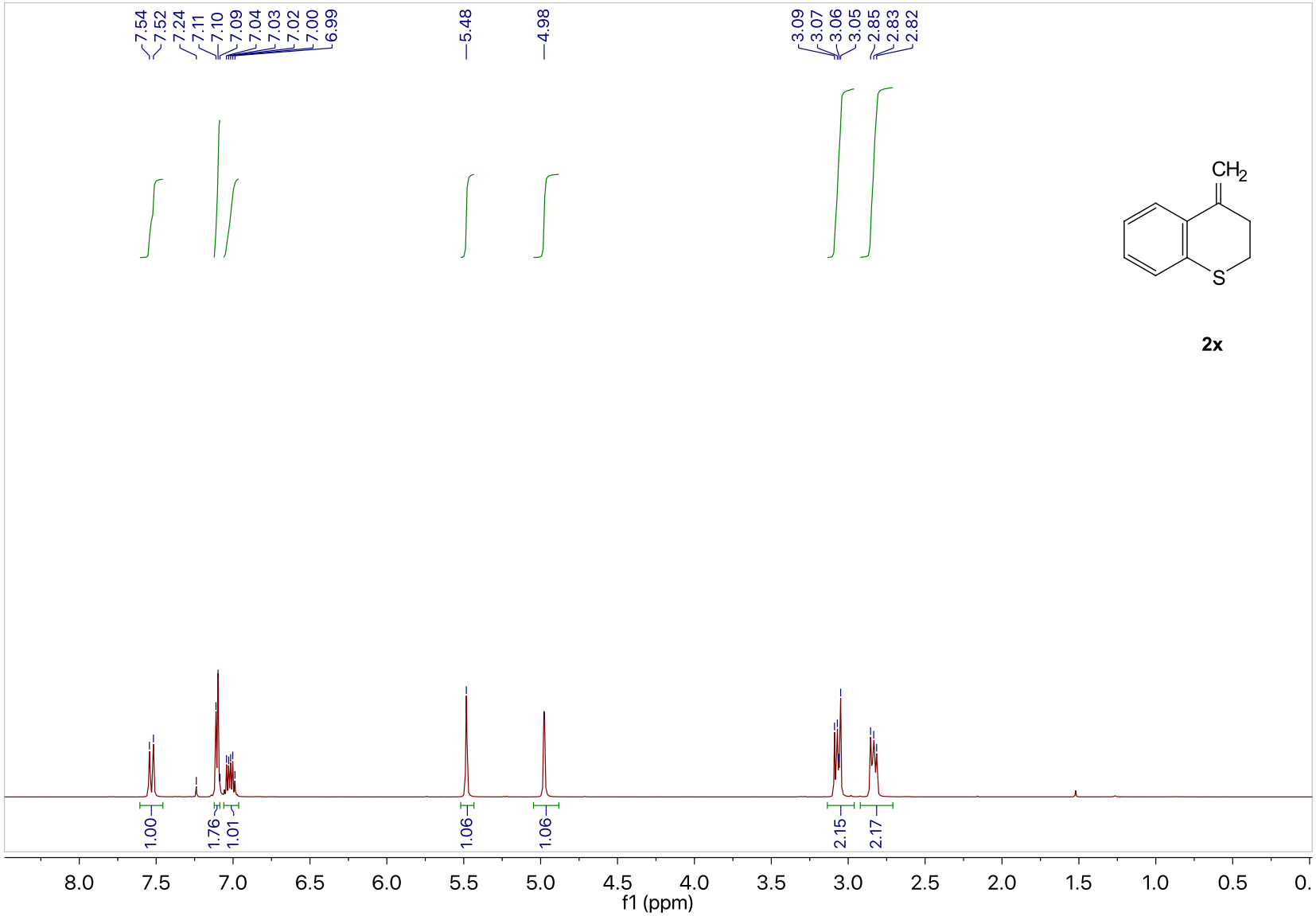
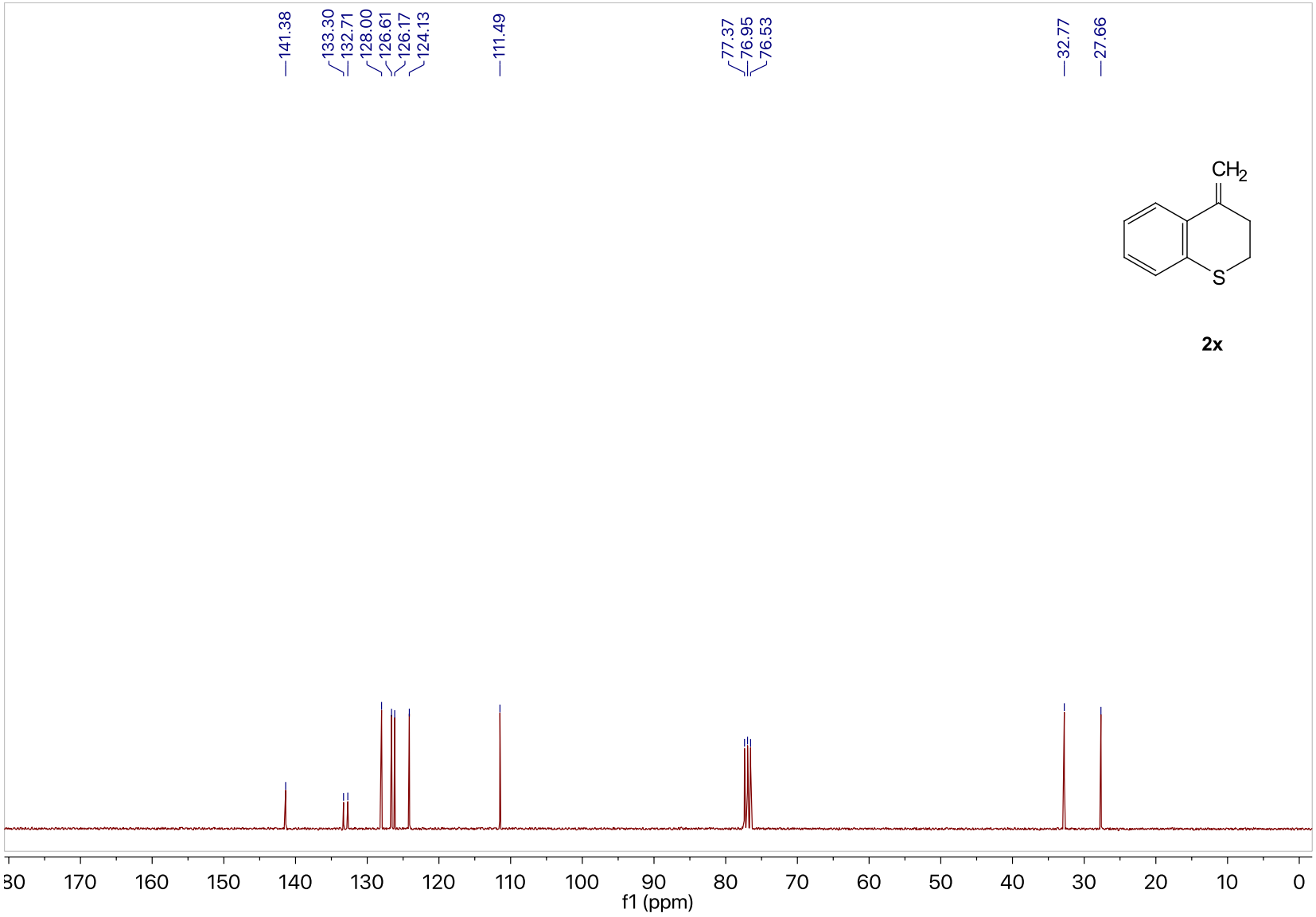
119.85
117.79
107.50
86.76
40.78
37.45
24.07
CH2
O
2t
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

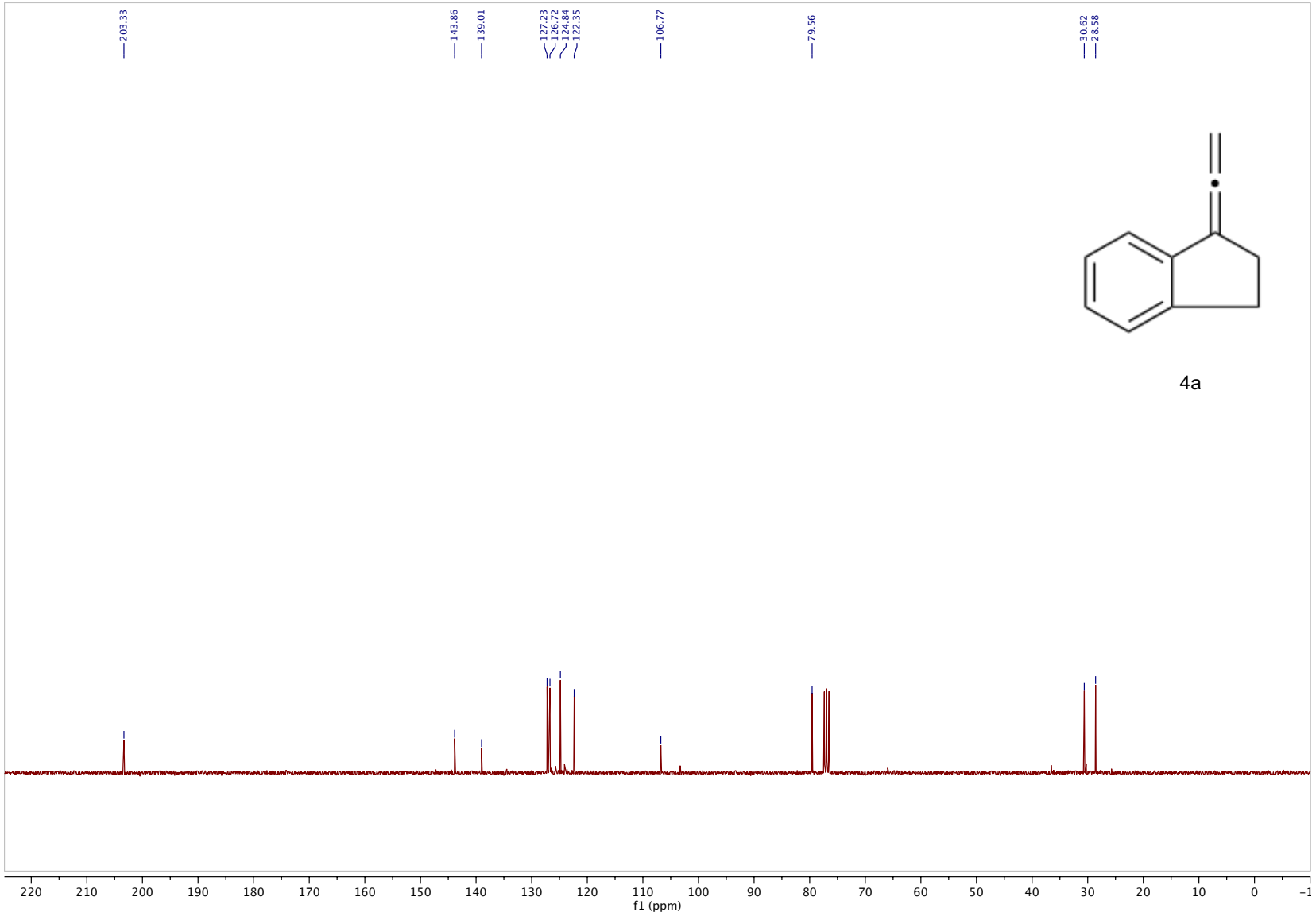

7.55
7.53
7.25
7.19
7.16
7.14
6.86
6.83
5.52
4.87
2.48
1.79
1.74
1.71
1.67
1.63
1.57
1.53
1.49
1.45
1.41
1.37
1.36
1.32
CH2
O
2u
0.97
0.97
1.91
1.00
1.00
2.04
10.46
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

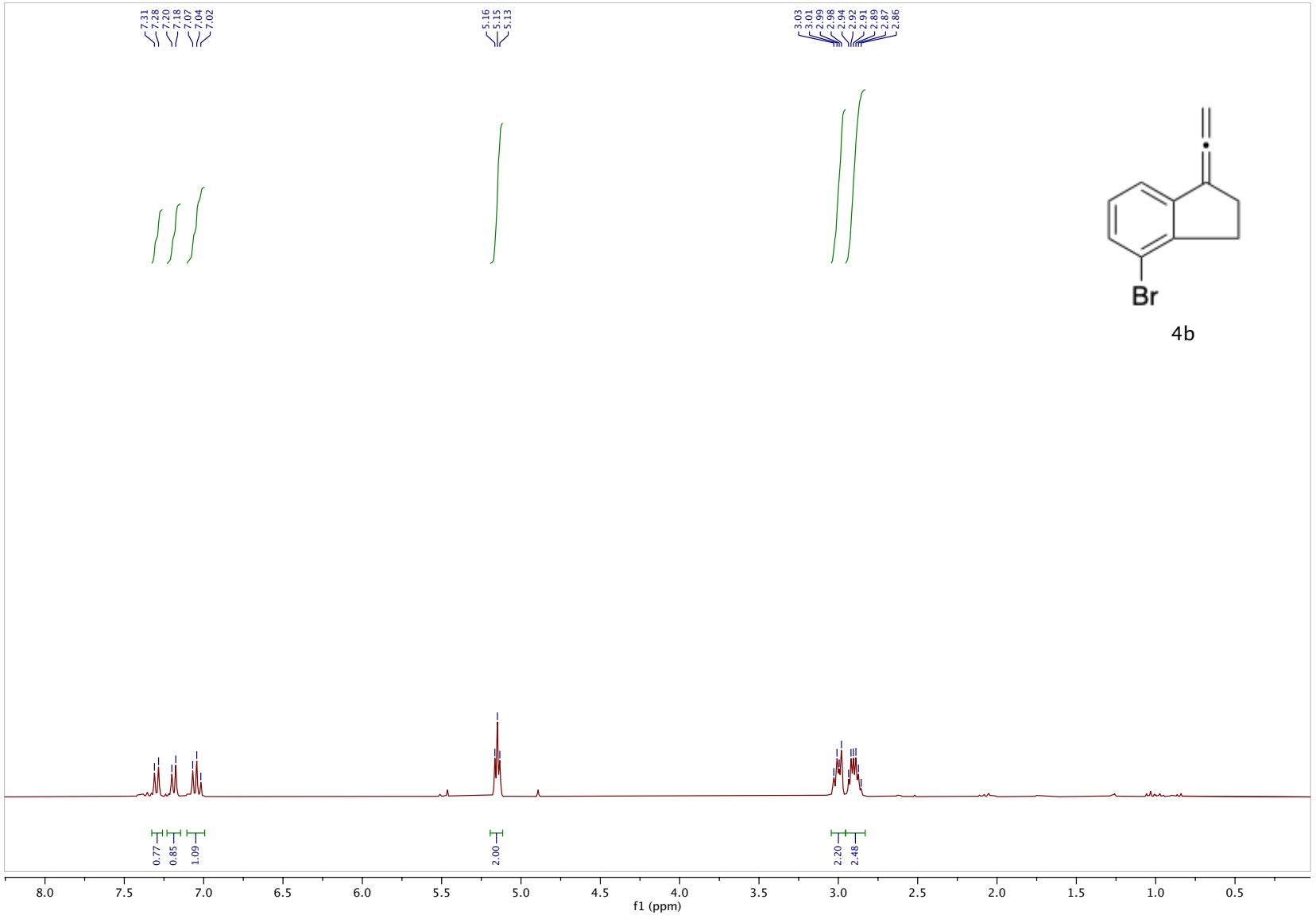

153.06
136.41
129.54
124.07
121.44
119.87
117.80
108.03
76.17
41.48
34.91
25.75
21.72
CH2
O
2u
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

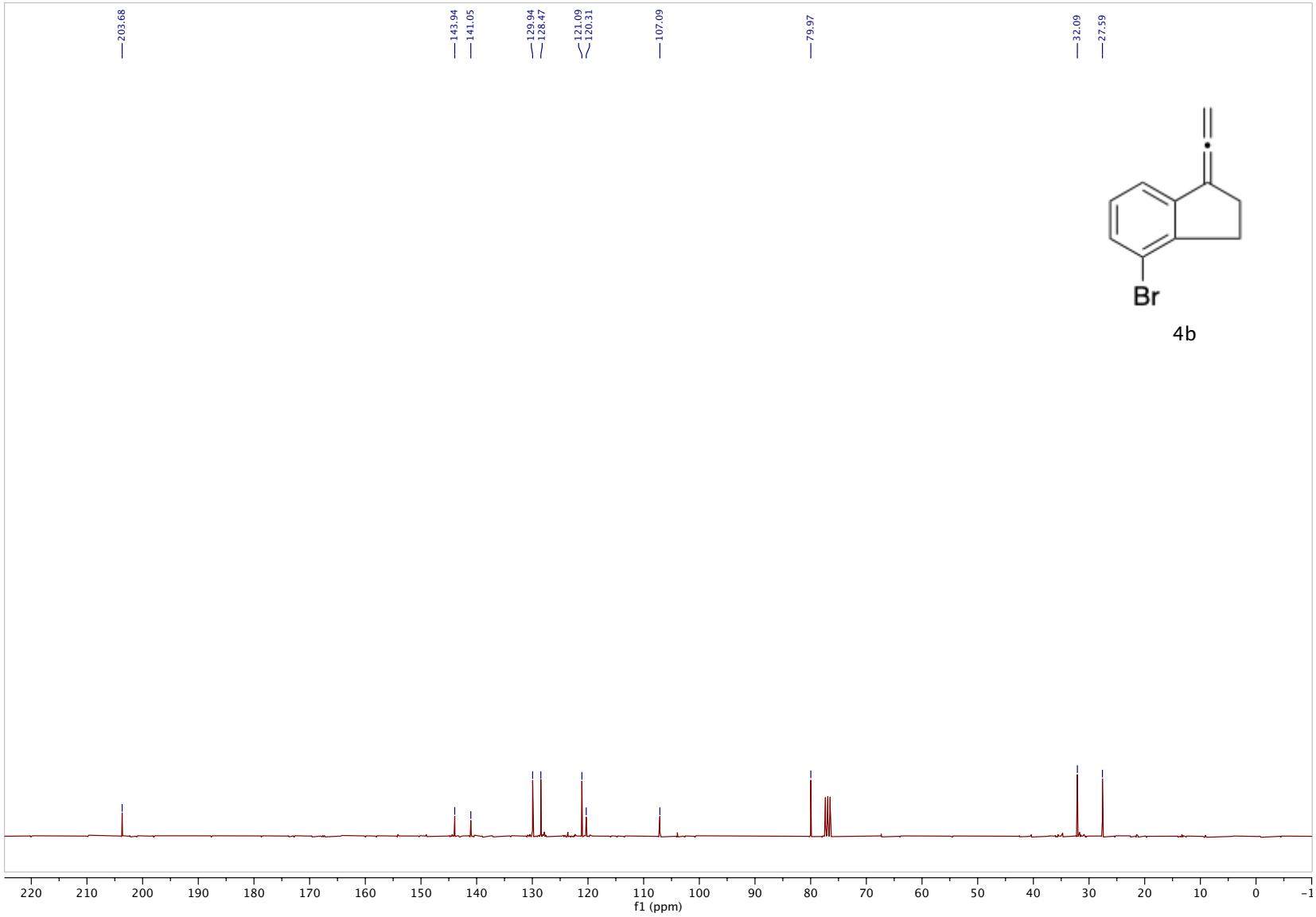

7.54
7.52
7.24
7.11
7.10
7.09
7.04
7.03
7.02
7.00
6.99
5.48
4.98
3.09
3.07
3.06
3.05
2.85
2.83
2.82
CH2
S
2x
1.00
1.76
1.01
1.06
1.06
2.15
2.17
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

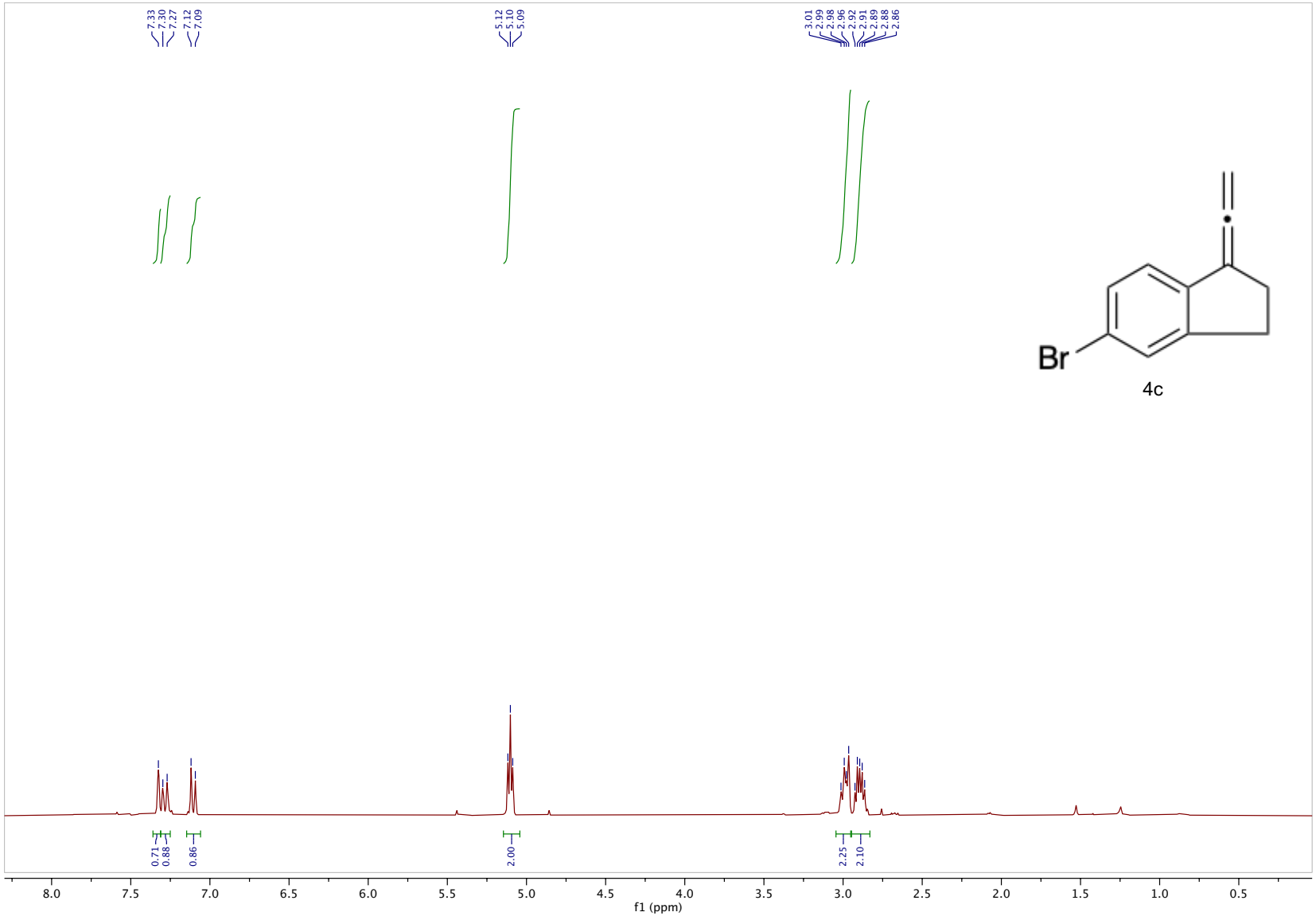

141.38
133.30
132.71
128.00
126.61
126.17
124.13
111.49
77.37
76.95
76.53
32.77
27.66
CH2
S
2x
f1 (ppm)

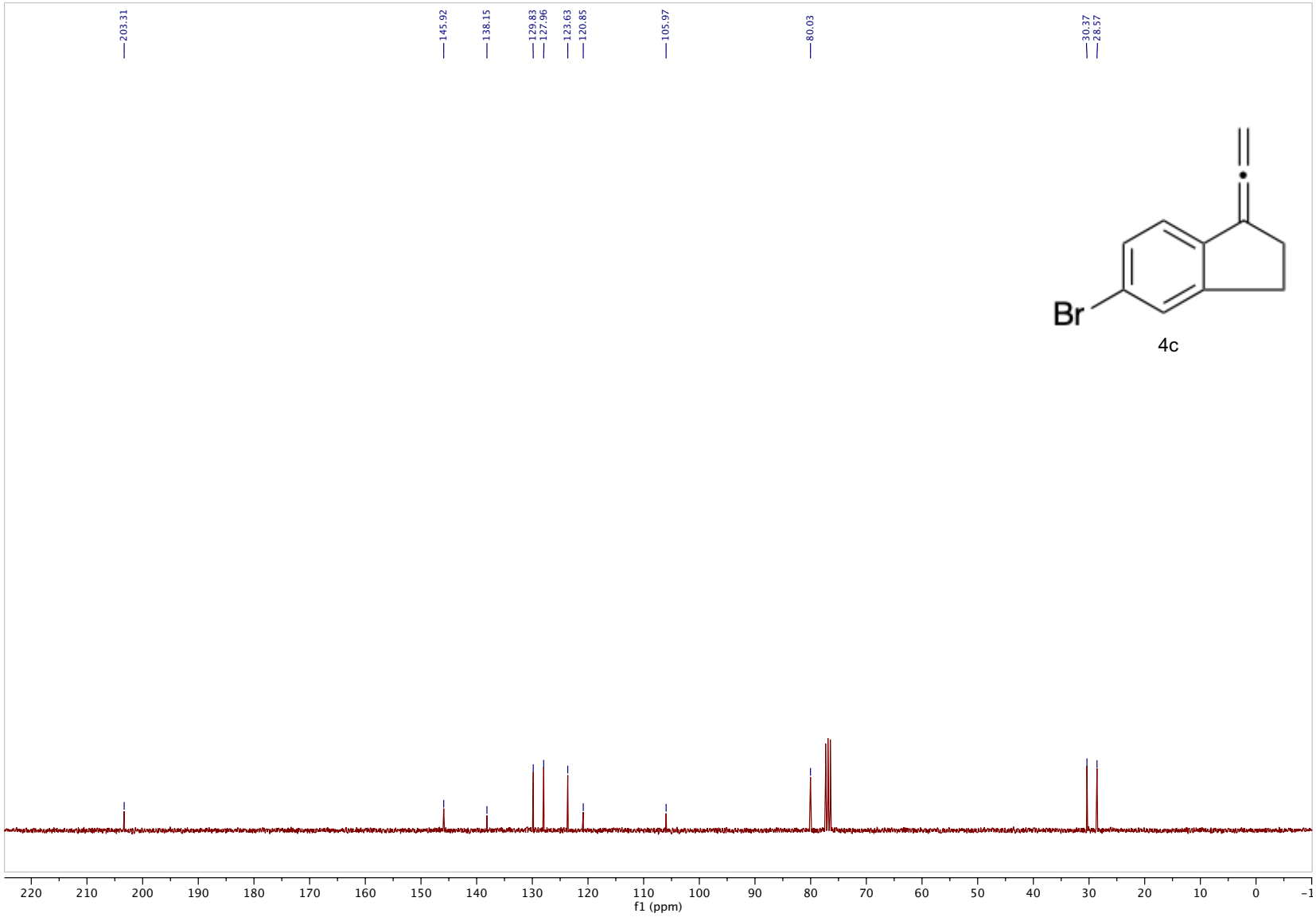

7.32
7.30
7.24
7.21
7.19
7.17
5.16
5.14
5.13
3.07
3.05
3.02
2.96
2.94
2.93
2.91
2.90
2.88
4a
0.93
2.93
2.00
2.19
2.14
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


203.33
143.86
139.01
127.23
126.72
124.84
122.35
106.77
79.56
30.62
28.58
4a
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


7.31
7.28
7.20
7.18
7.07
7.04
7.02
5.16
5.15
5.13
3.03
3.01
2.99
2.98
2.94
2.92
2.91
2.89
2.87
2.86
Br
4b
0.77
0.85
1.09
2.00
2.20
2.48
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

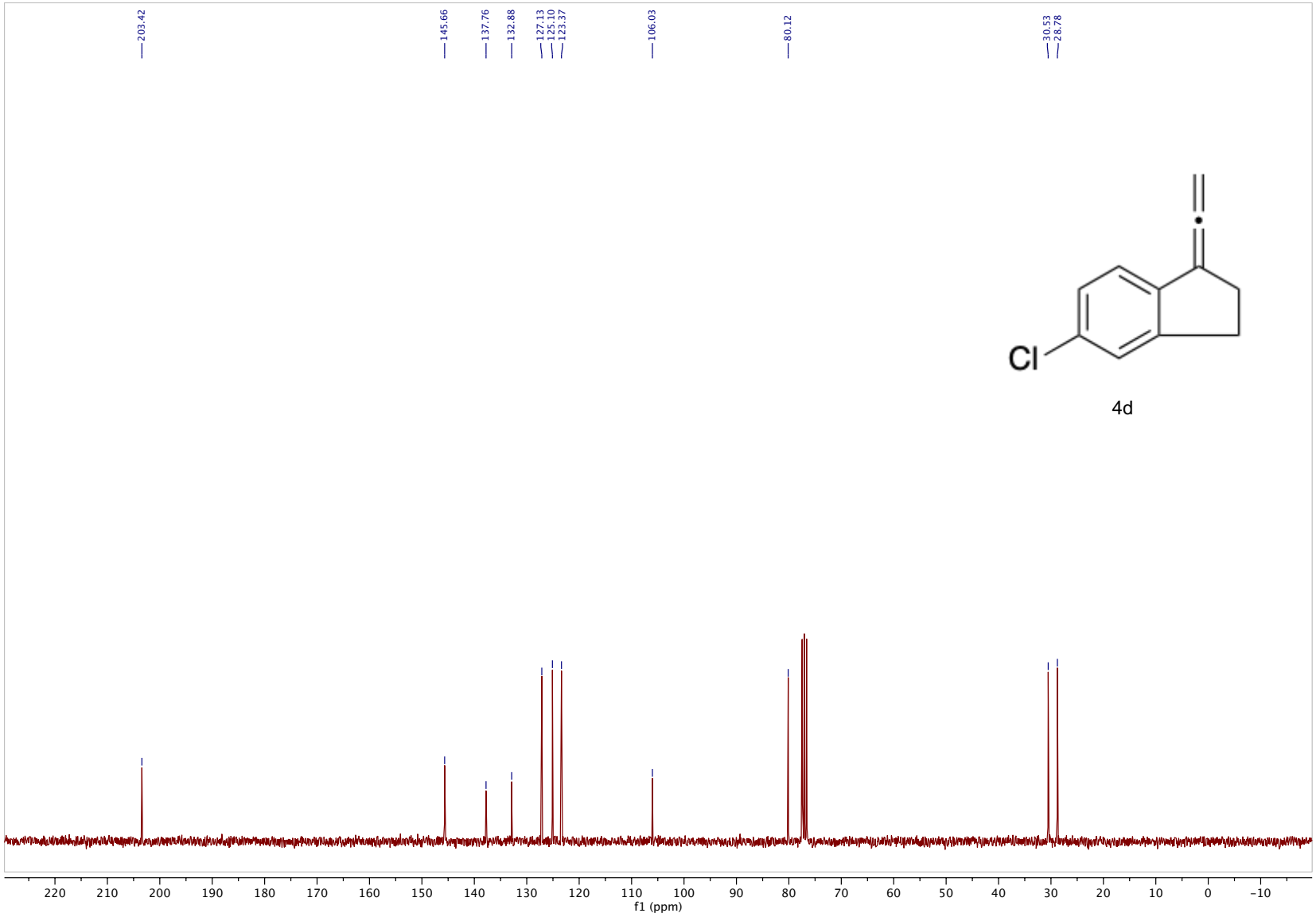

203.68
143.94
141.05
129.94
128.47
121.09
120.31
107.09
79.97
32.09
27.59
Br
4b
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

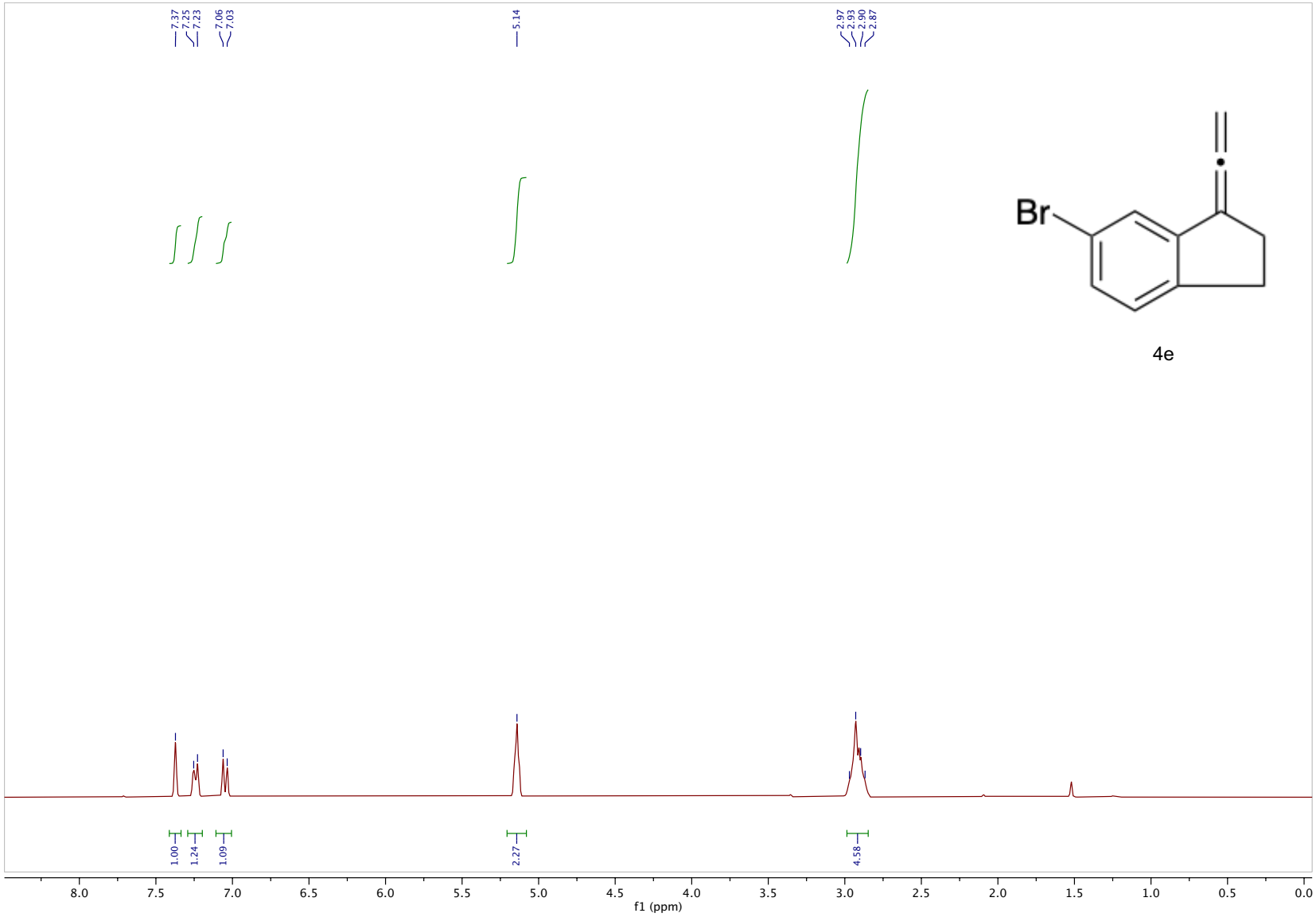

7.33
7.30
7.27
7.12
7.09
5.12
5.10
5.09
3.01
2.99
2.98
2.96
2.92
2.91
2.89
2.88
2.86
Br
4c
0.71
0.88
0.86
2.00
2.25
2.10
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

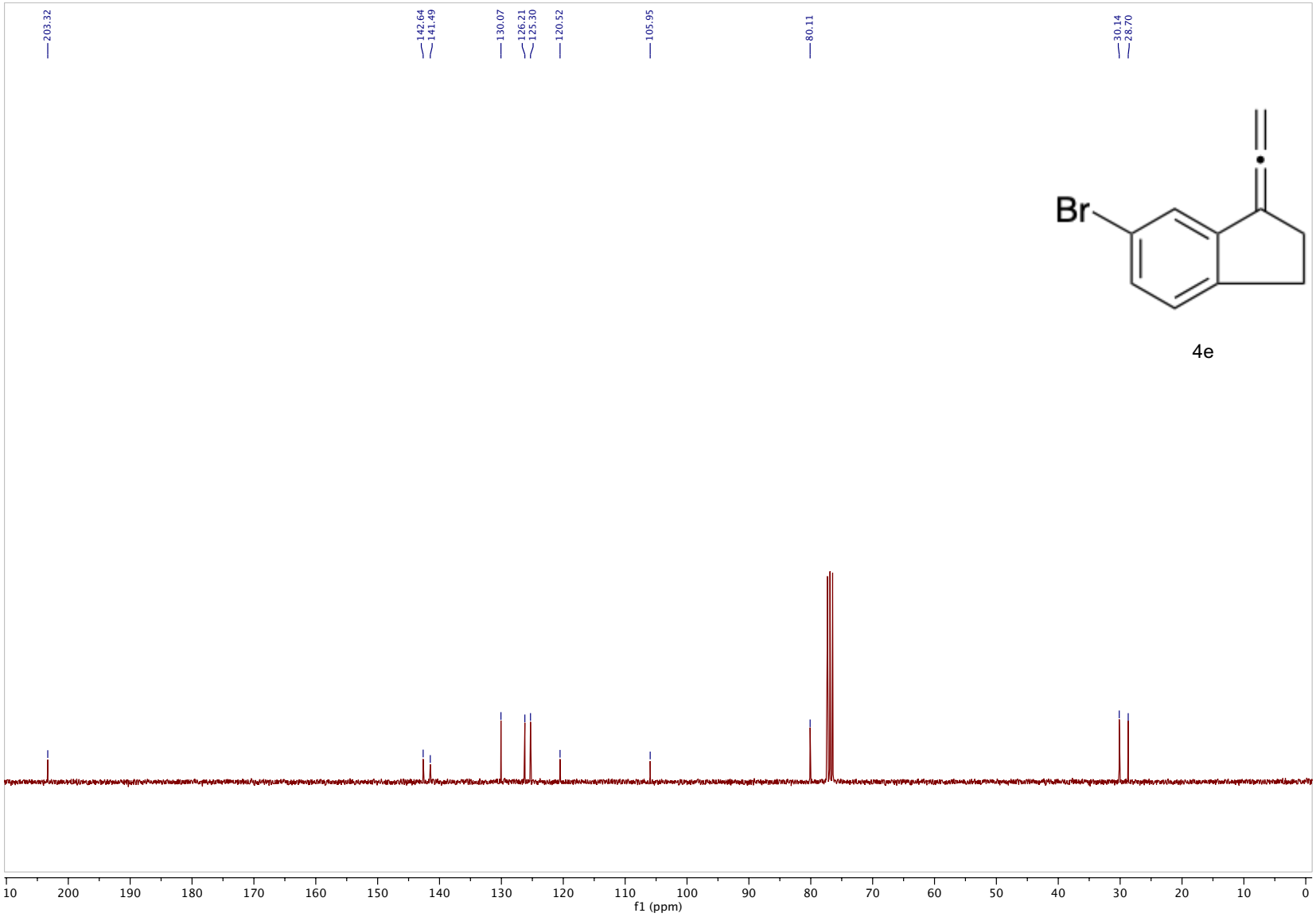

203.31
145.92
138.15
129.83
127.96
123.63
120.85
105.97
80.03
30.37
28.57
Br
4c
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

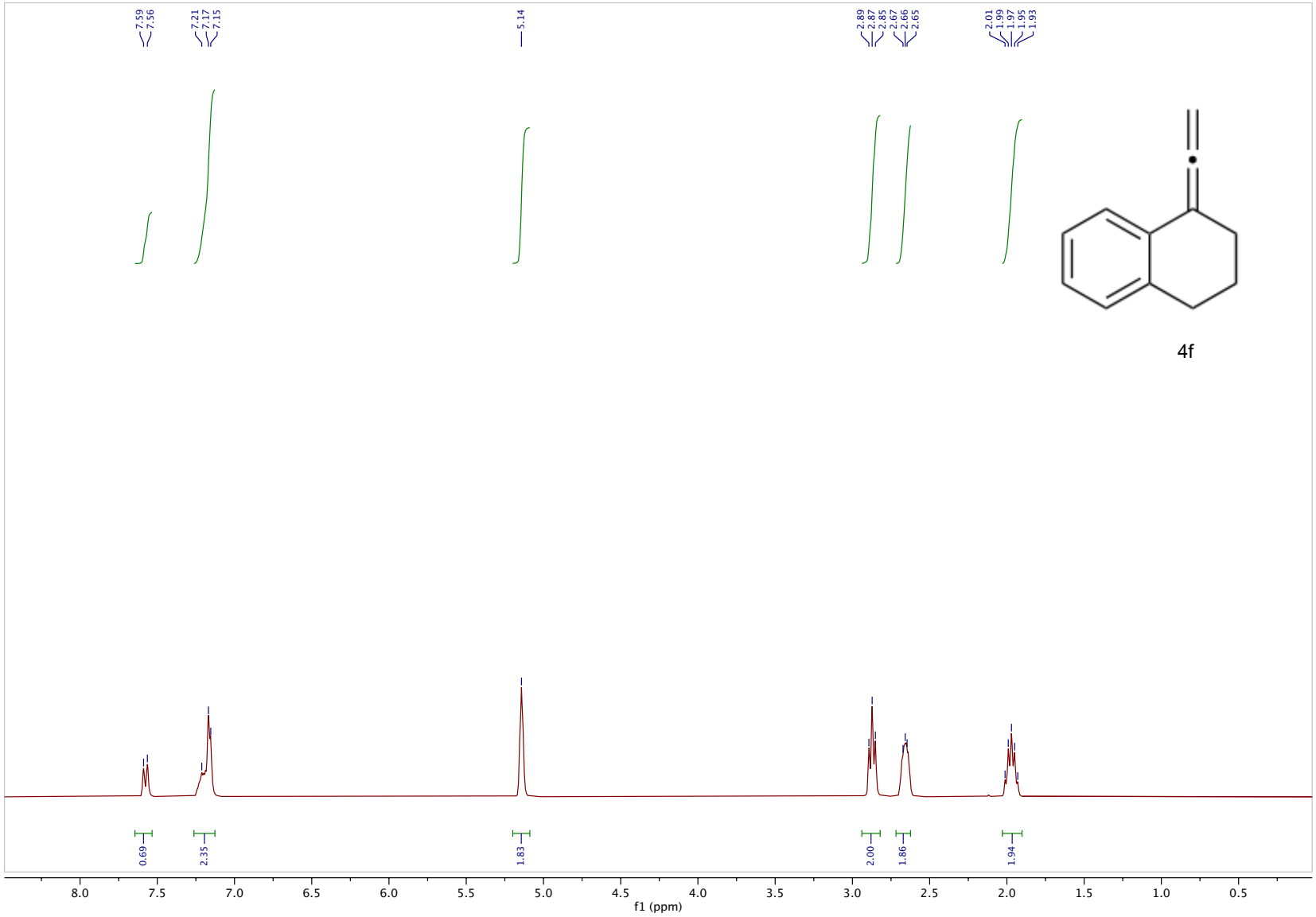

7.19
7.18
7.16
7.15
7.13
5.14
5.13
5.11
3.01
2.99
2.98
2.97
2.94
2.93
2.91
2.90
2.88
Cl
2.50
2.00
2.18
2.10
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

4d

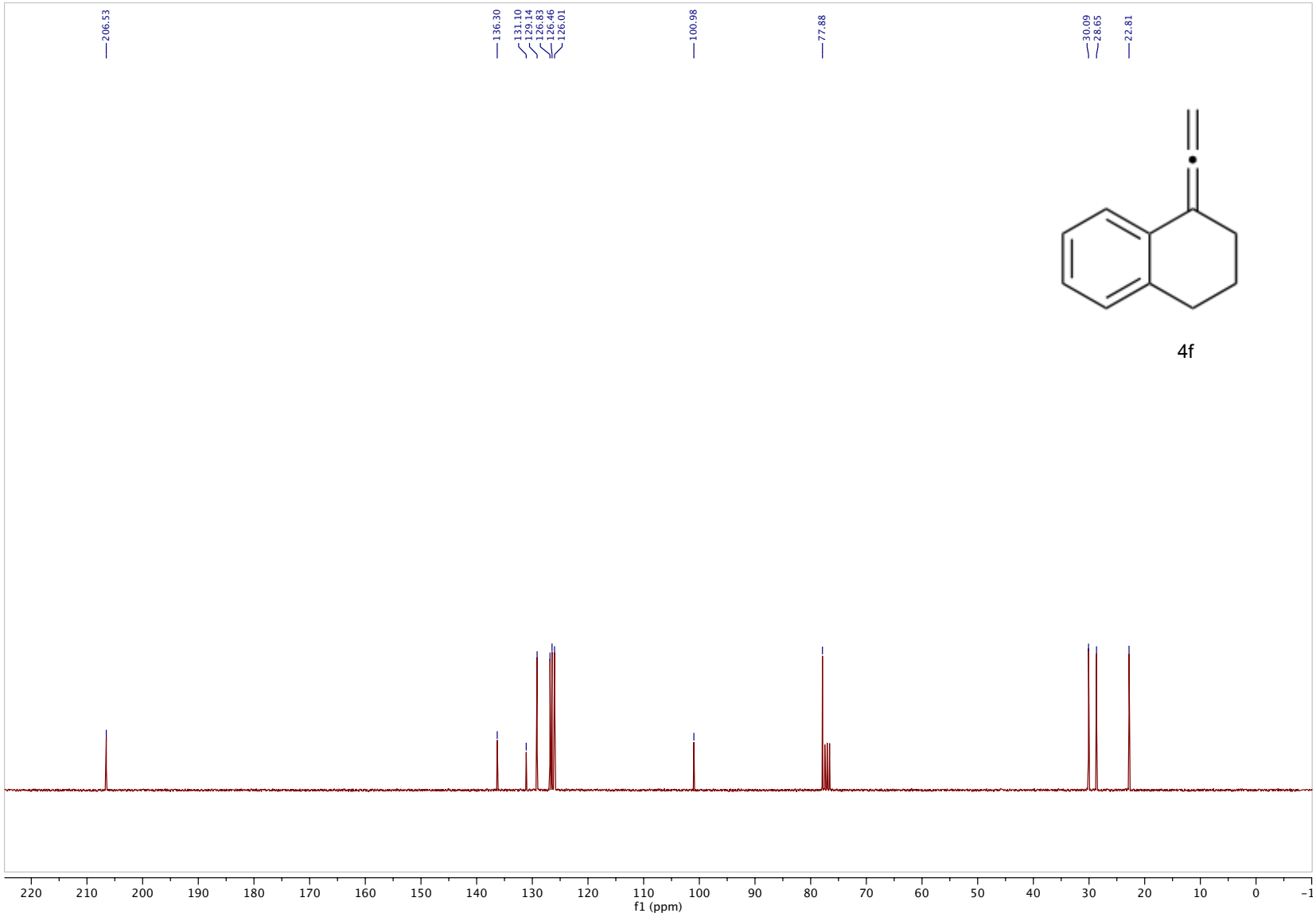

203.42
145.66
137.76
132.88
127.13
125.10
123.37
106.03
80.12
30.53
28.78
Cl
4d
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

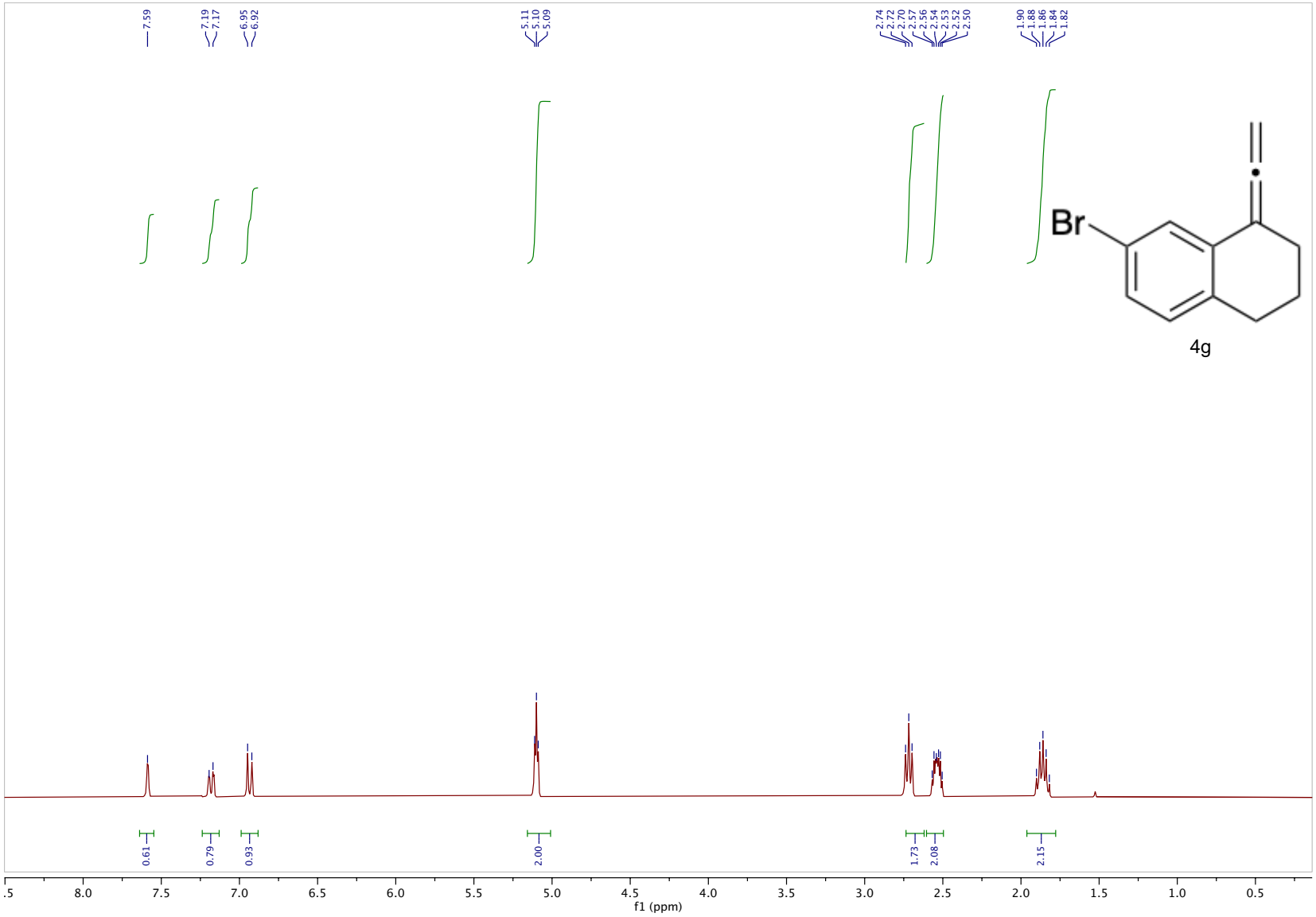

7.37
7.25
7.23
7.06
7.03
5.14
2.97
2.93
2.90
2.87
Br
4e
1.00
1.24
1.09
2.27
4.58
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

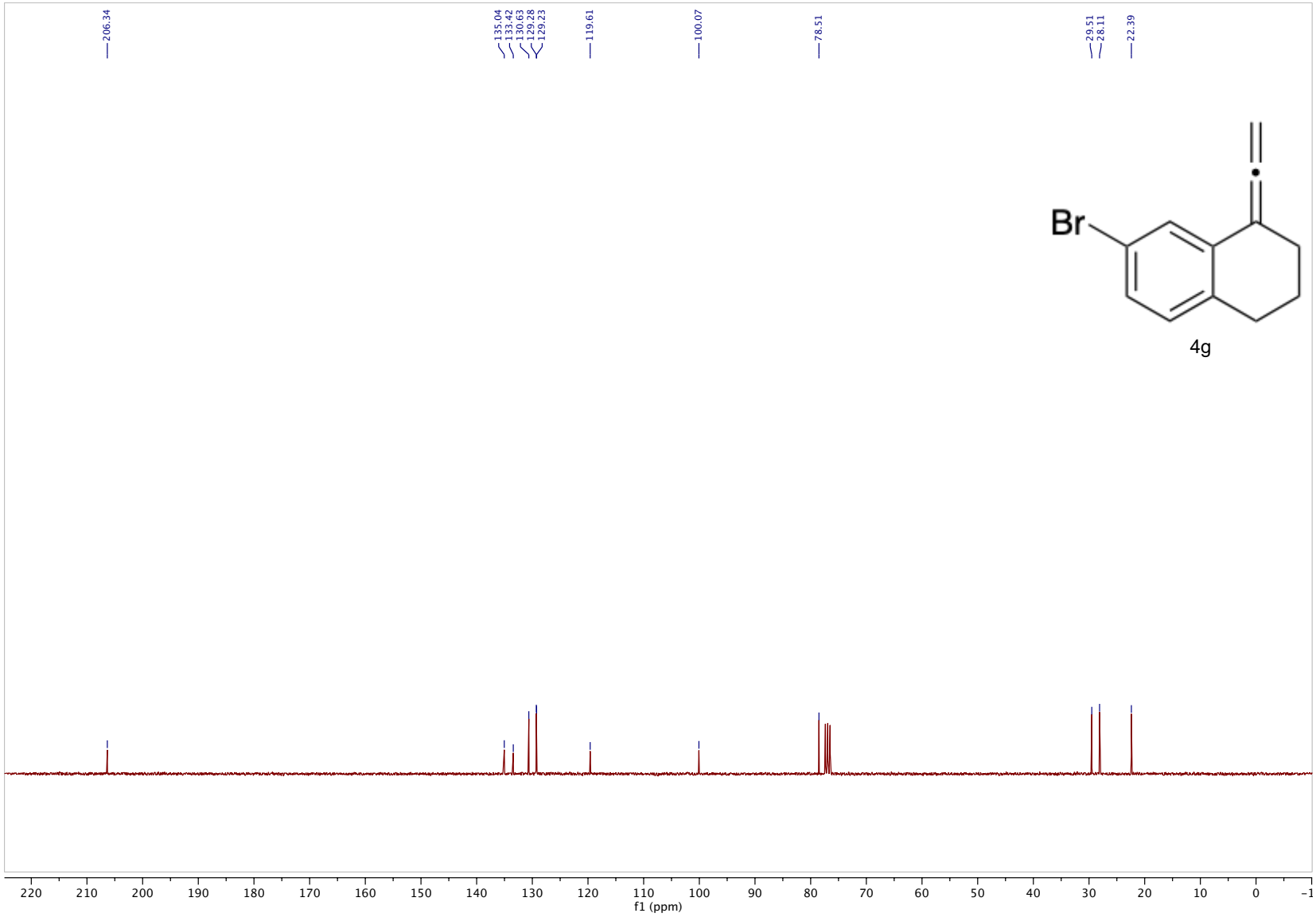

203.32
142.64
141.49
130.07
126.21
125.30
120.52
105.95
80.11
30.14
28.70
Br
4e
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

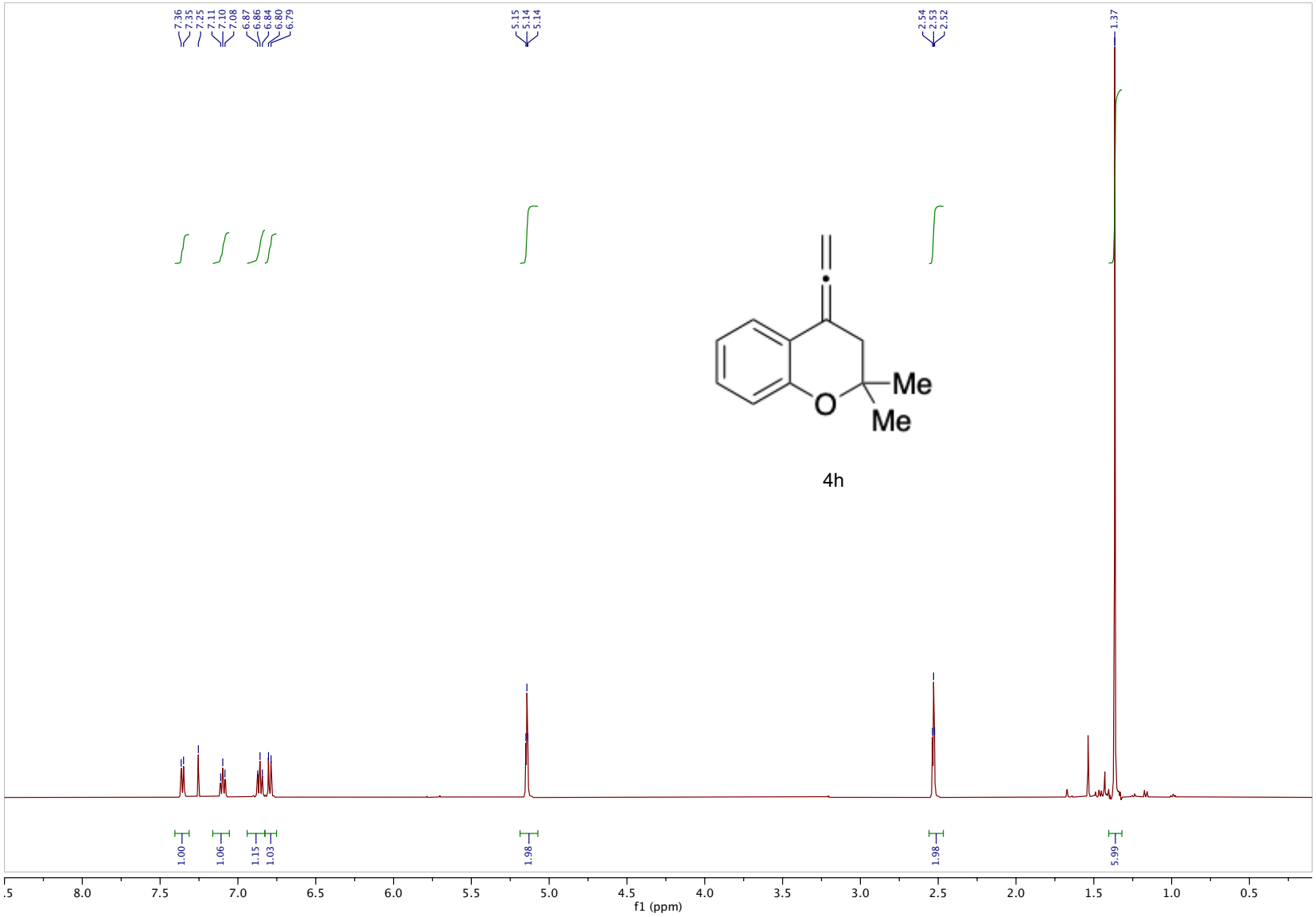

7.59
7.56
7.21
7.17
7.15
5.14
2.89
2.87
2.85
2.67
2.66
2.65
2.01
1.99
1.97
1.95
1.93
0.69
2.35
1.83
2.00
1.86
1.94
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

4f

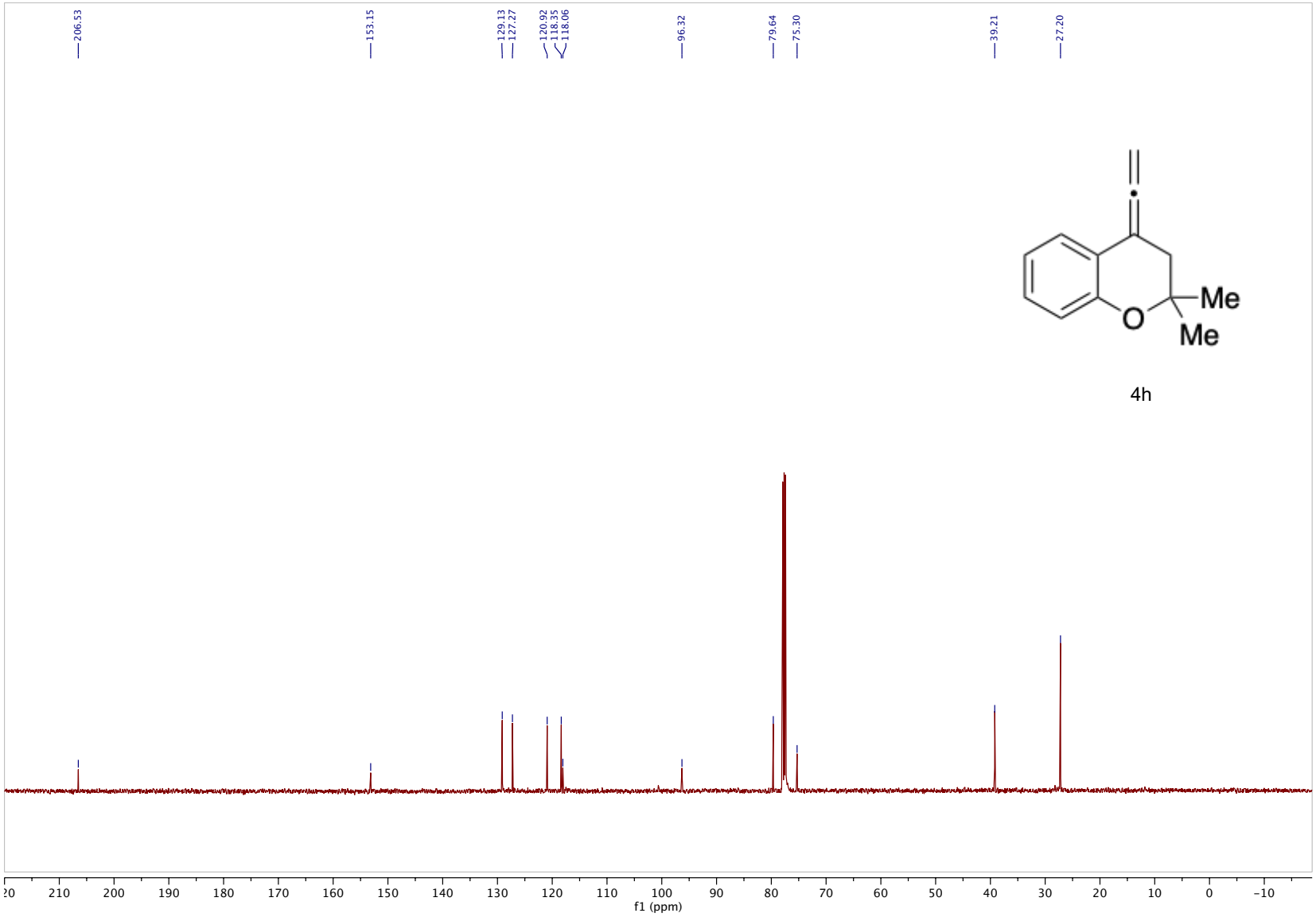

206.53
136.30
131.10
129.14
126.83
126.46
126.01
100.98
77.88
30.09
28.65
22.81
4f
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

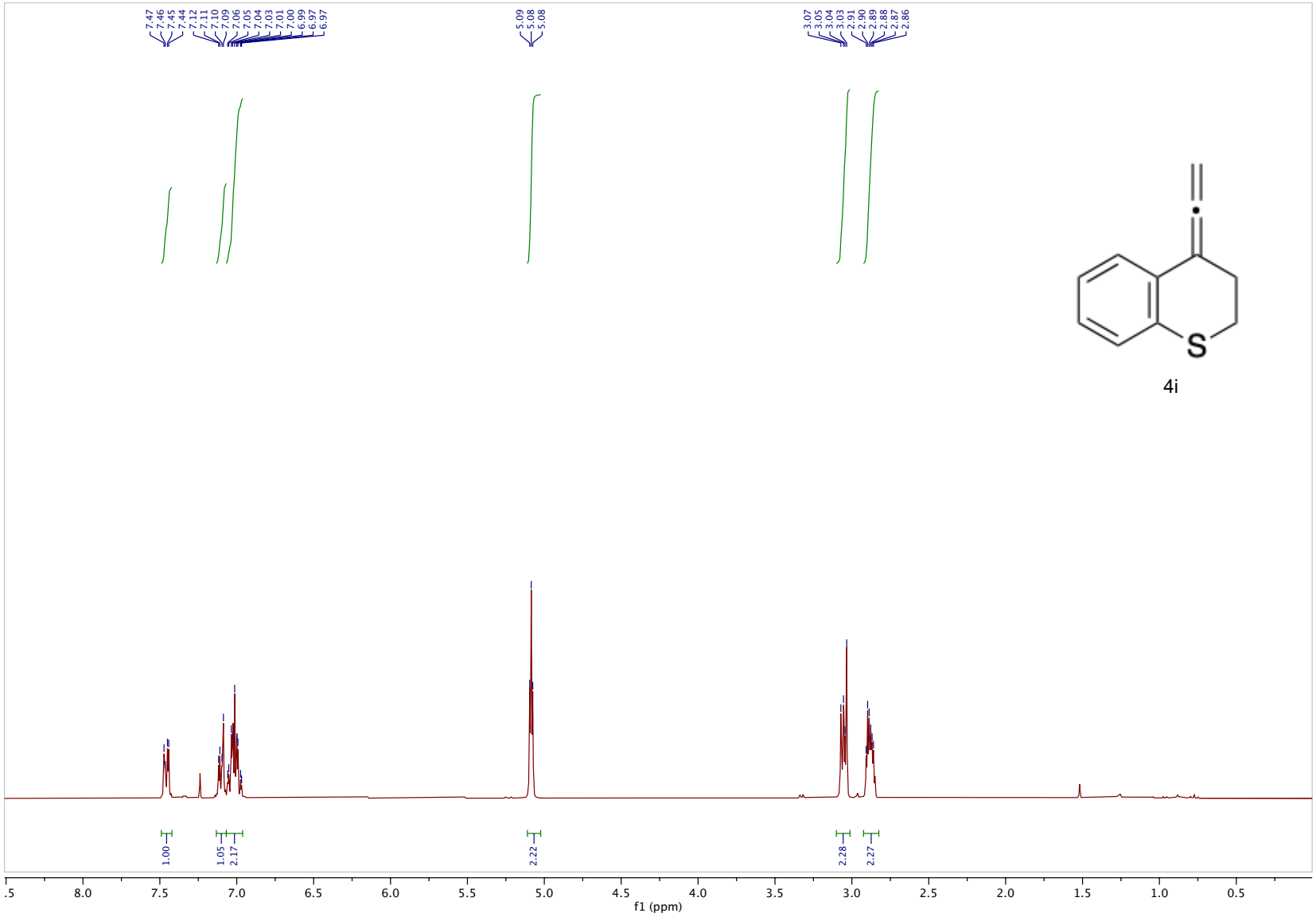

7.59
7.19
7.17
6.95
6.92
5.11
5.10
5.09
2.74
2.72
2.70
2.57
2.56
2.54
2.53
2.52
2.50
1.90
1.88
1.86
1.84
1.82
Br
4g
0.61
0.79
0.93
2.00
1.73
2.08
2.15
f1 (ppm)


206.34
135.04
133.42
130.63
129.28
129.23
119.61
100.07
78.51
29.51
28.11
22.39
Br
4g
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

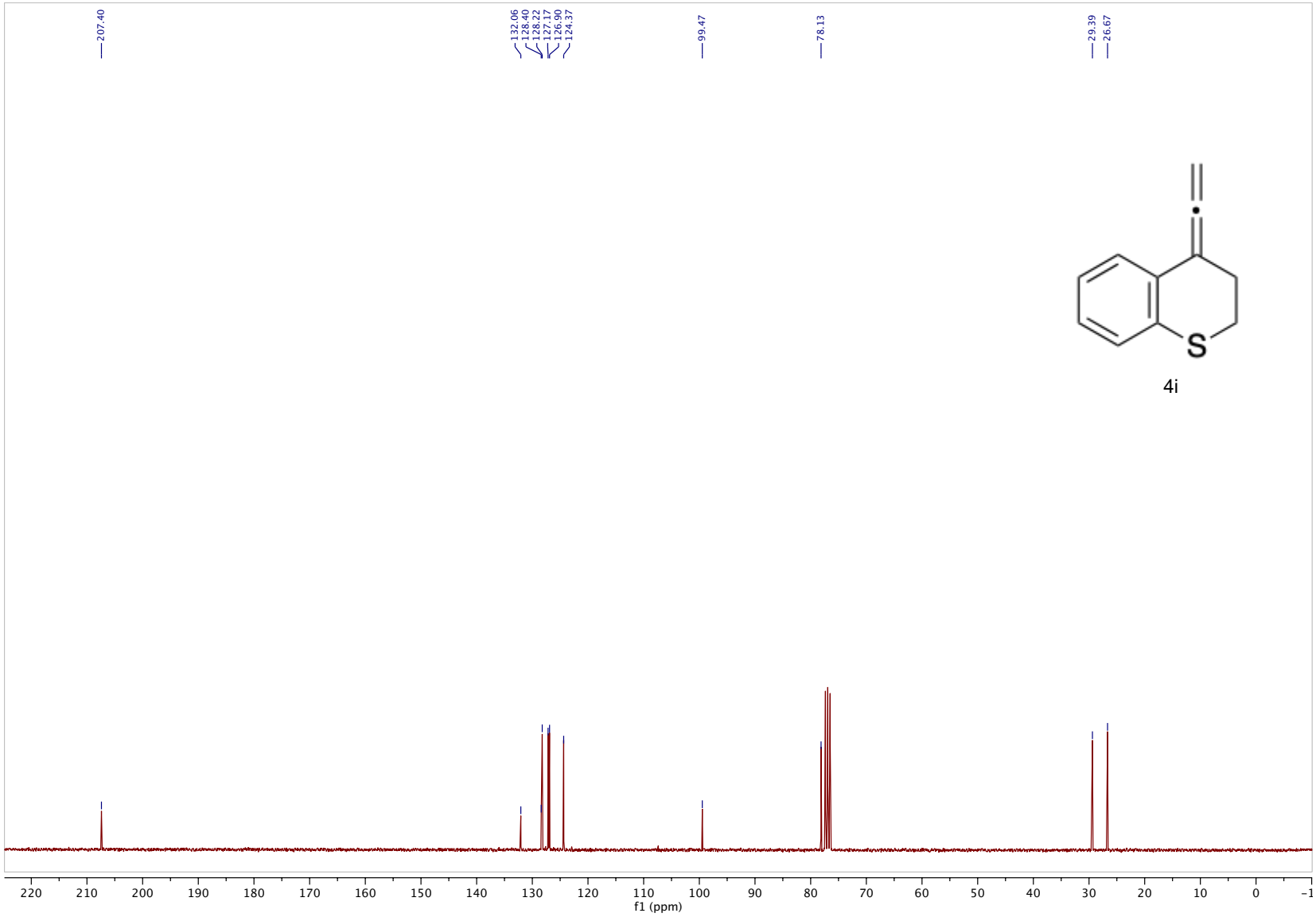

7.36
7.35
7.25
7.11
7.10
7.08
6.87
6.86
6.84
6.80
6.79
5.15
5.14
5.14
2.54
2.53
2.52
1.37
Me
Me
O
1.00
1.06
1.15
1.03
1.98
1.98
5.99
f1 (ppm)

4h

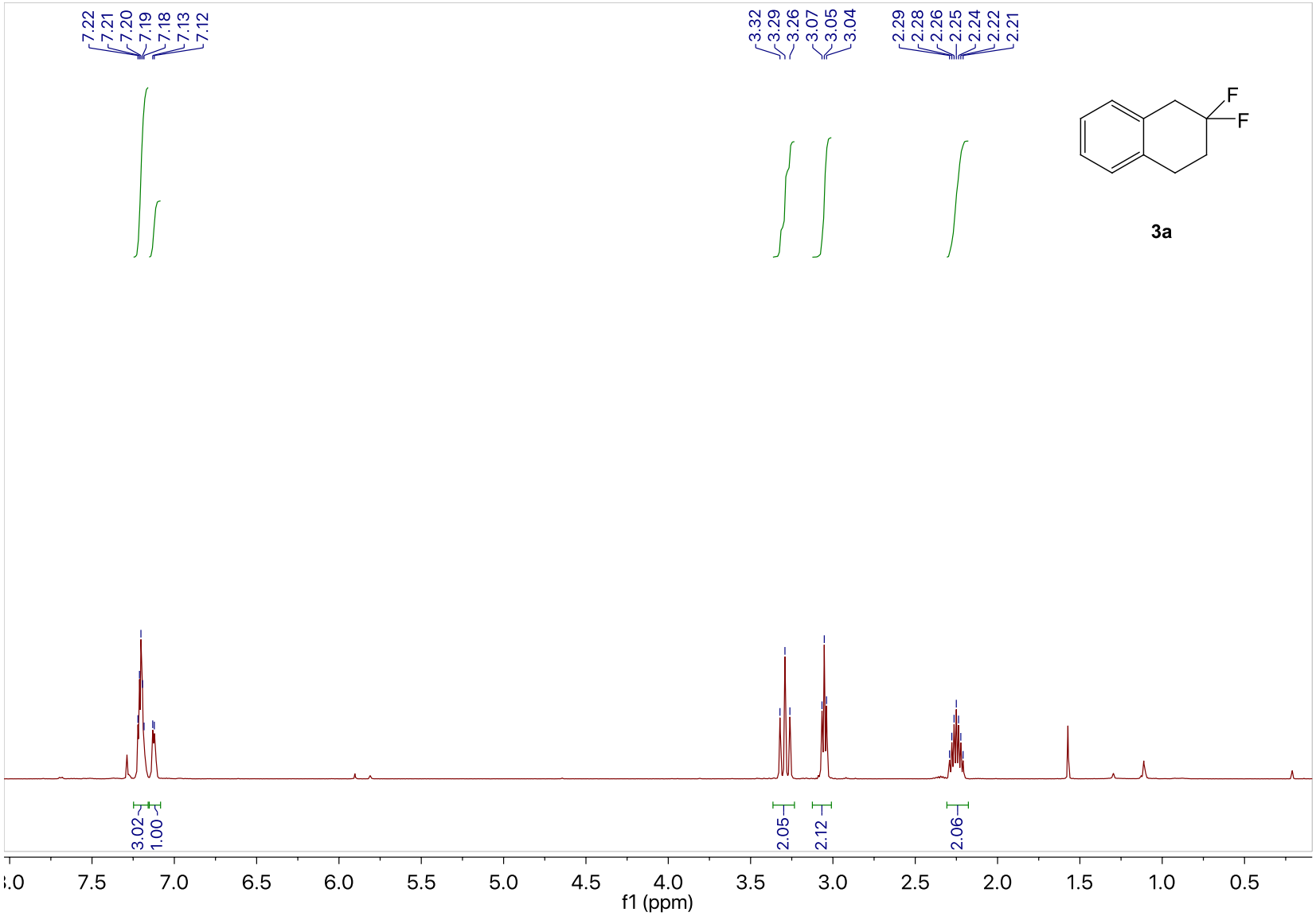

206.53
153.15
129.13
127.27
120.92
118.35
118.06
96.32
79.64
75.30
39.21
27.20
O
Me
Me
4h
f1 (ppm)

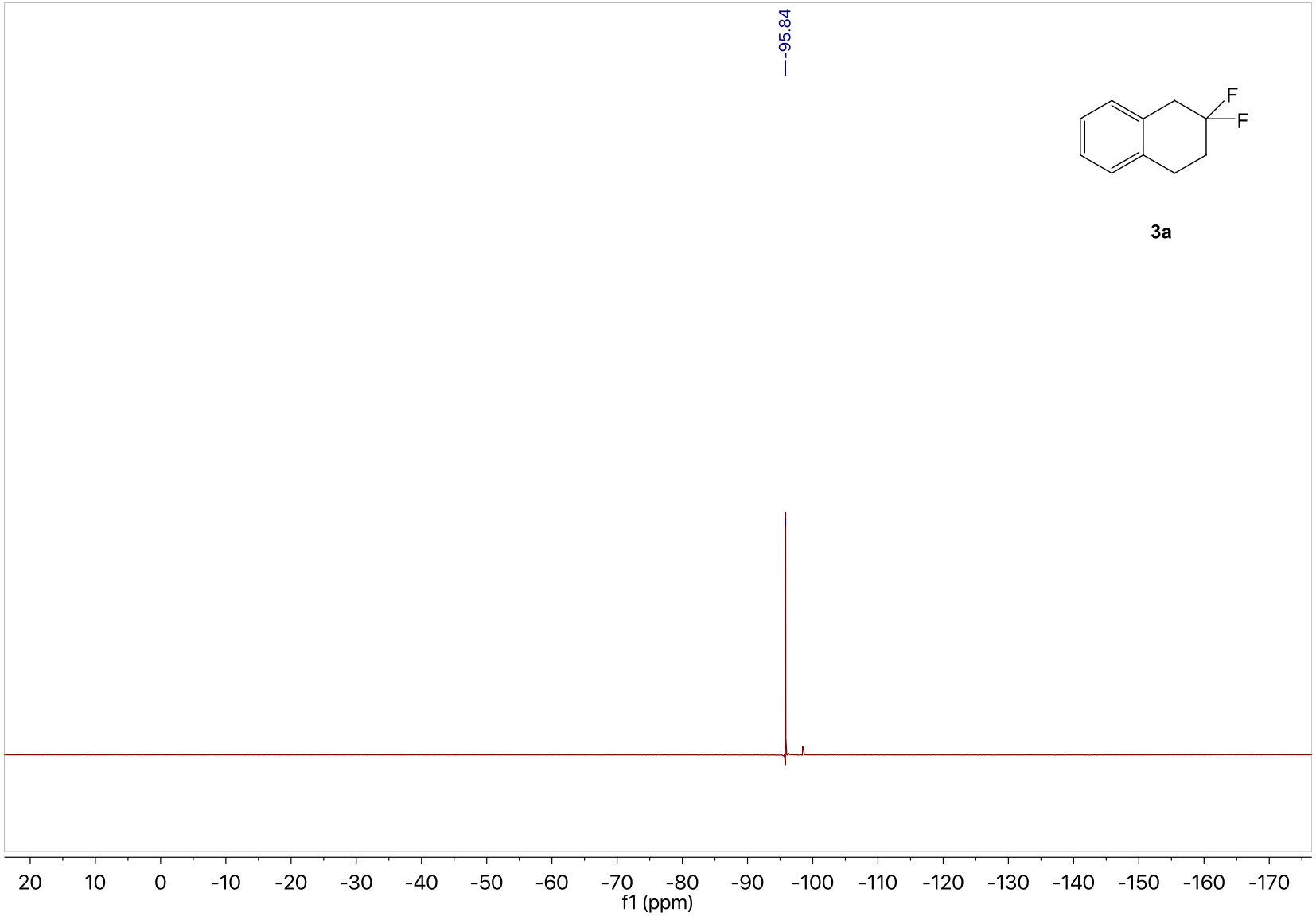

7.47
7.46
7.45
7.44
7.12
7.11
7.10
7.09
7.06
7.05
7.04
7.03
7.01
7.00
6.99
6.97
6.97
5.09
5.08
5.08
3.07
3.05
3.04
3.03
2.91
2.90
2.89
2.88
2.87
2.86
S
1.00
1.05
2.17
2.22
2.28
2.27
f1 (ppm)

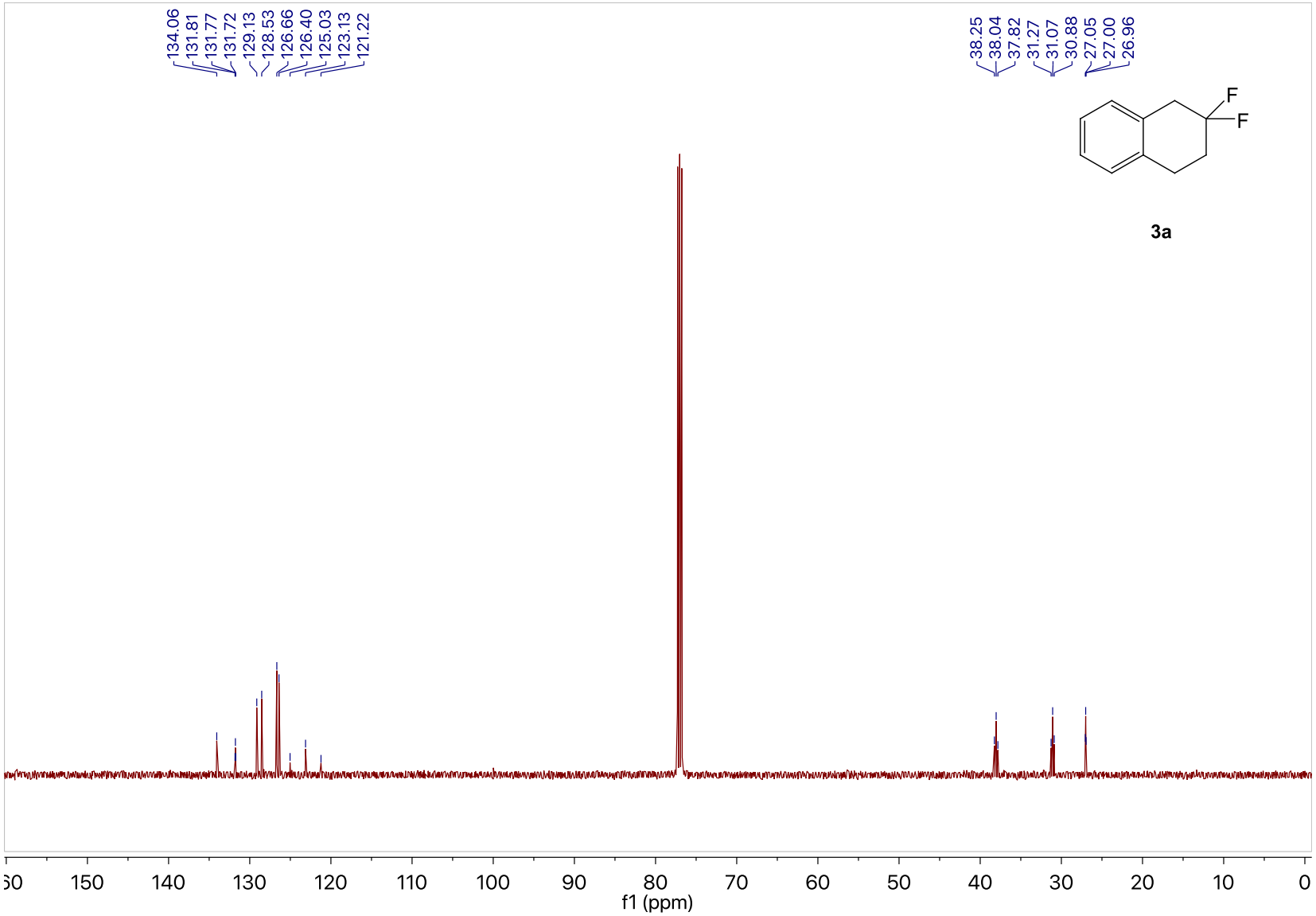
4i

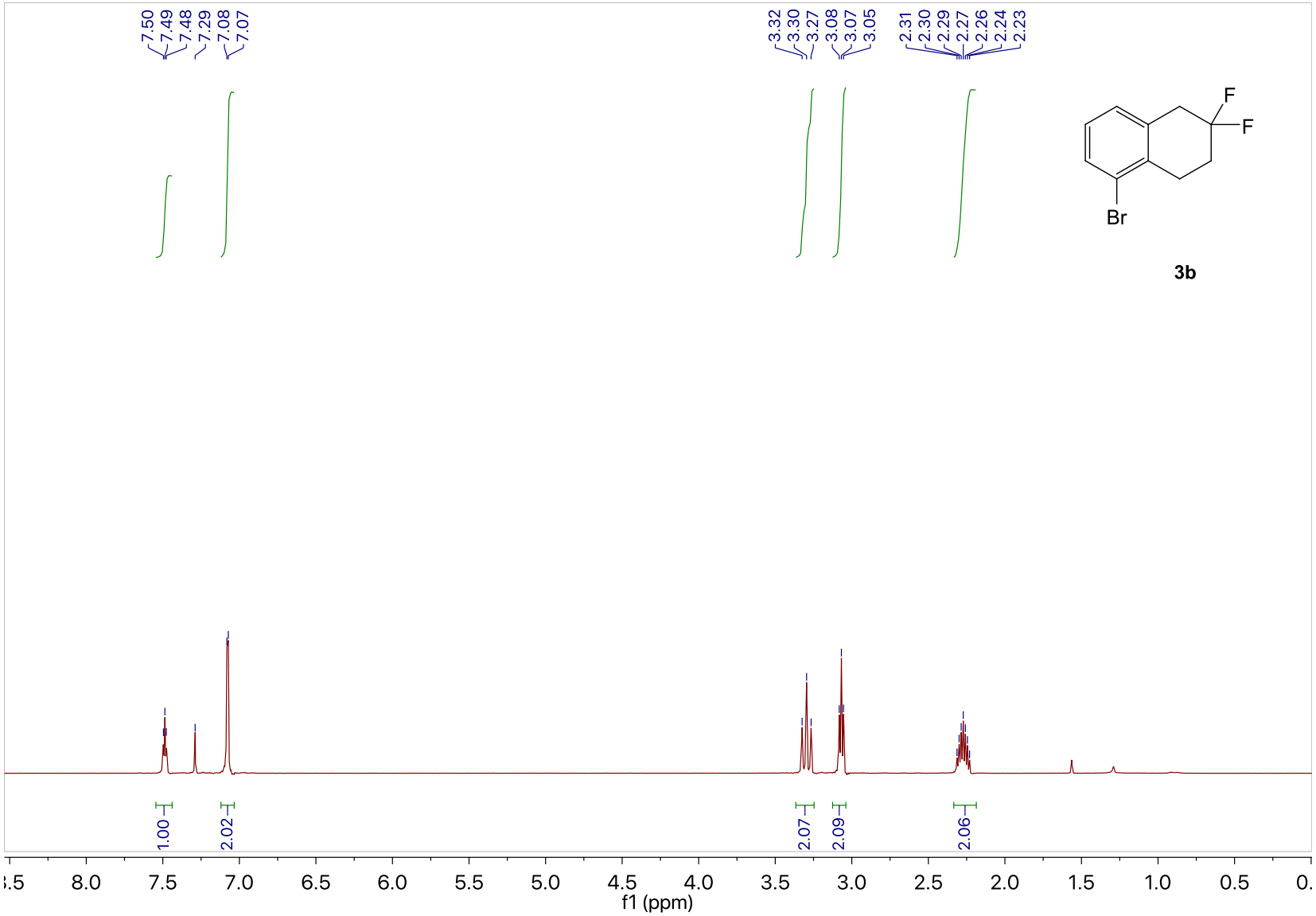

207.40
132.06
128.40
128.22
127.17
126.90
124.37
99.47
78.13
29.39
26.67
S
4i
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1
f1 (ppm)

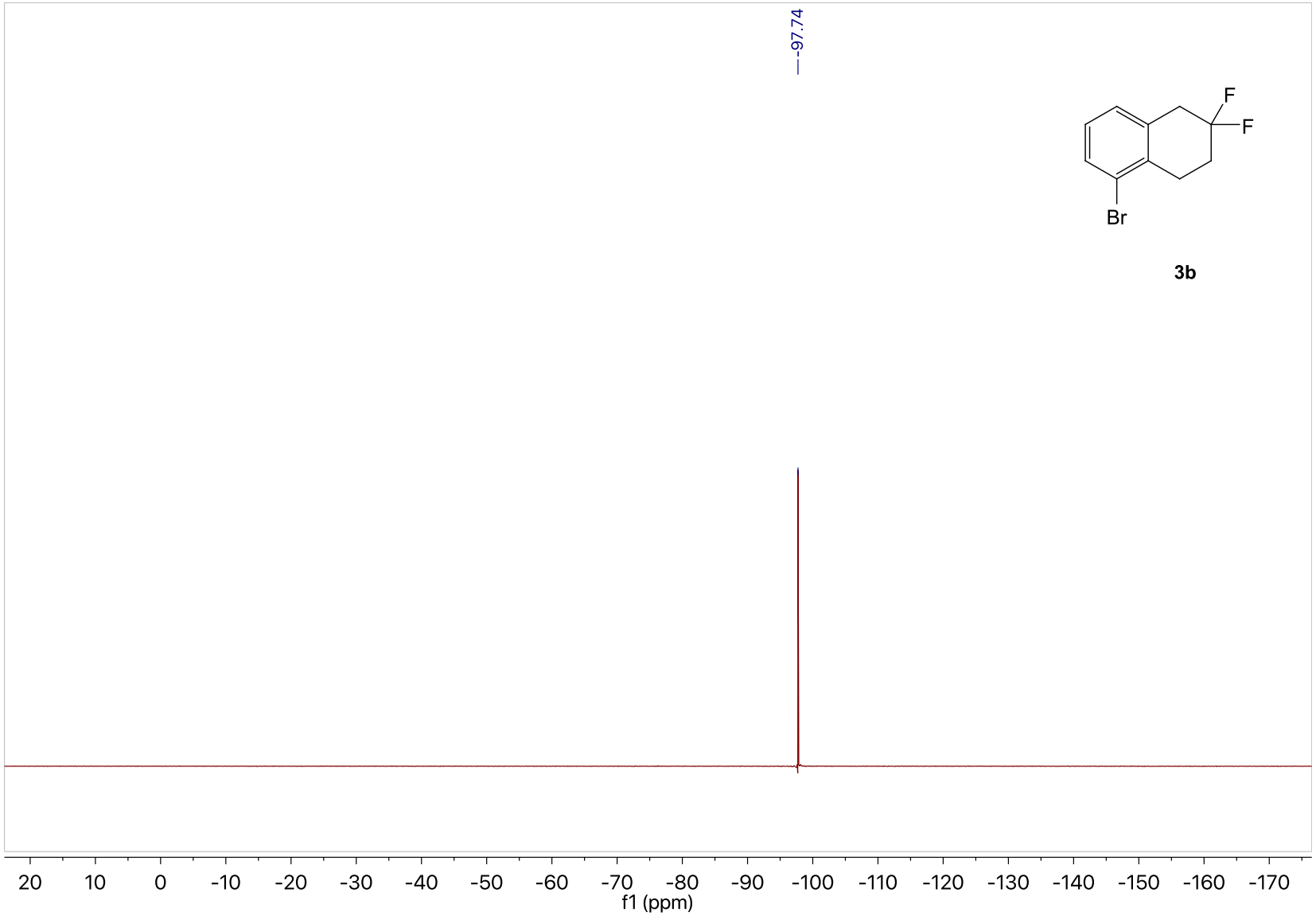
[1]H NMR, [19]F and [13]C NMR Spectra of Products:

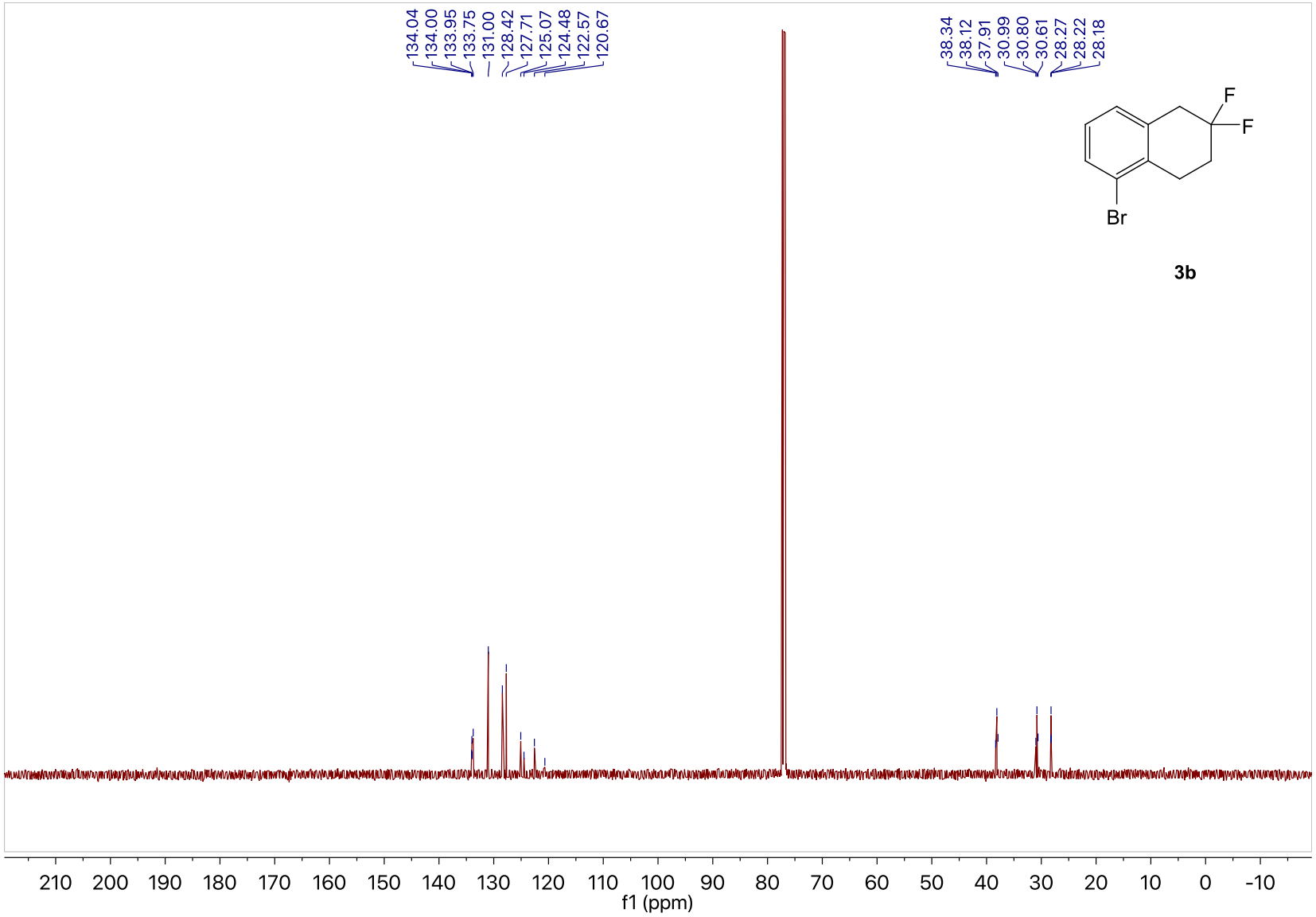


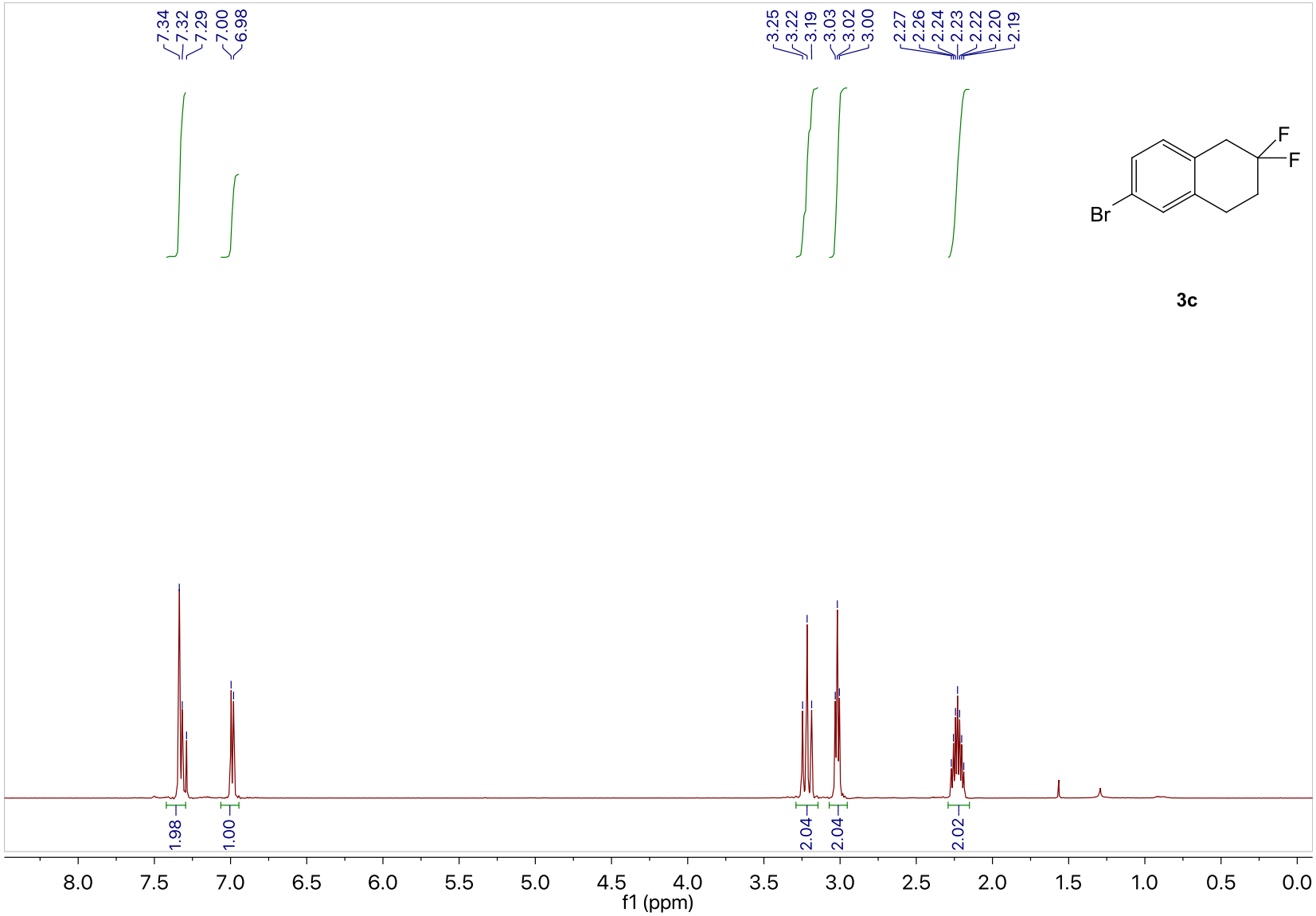

-95.84
F
F
3a
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

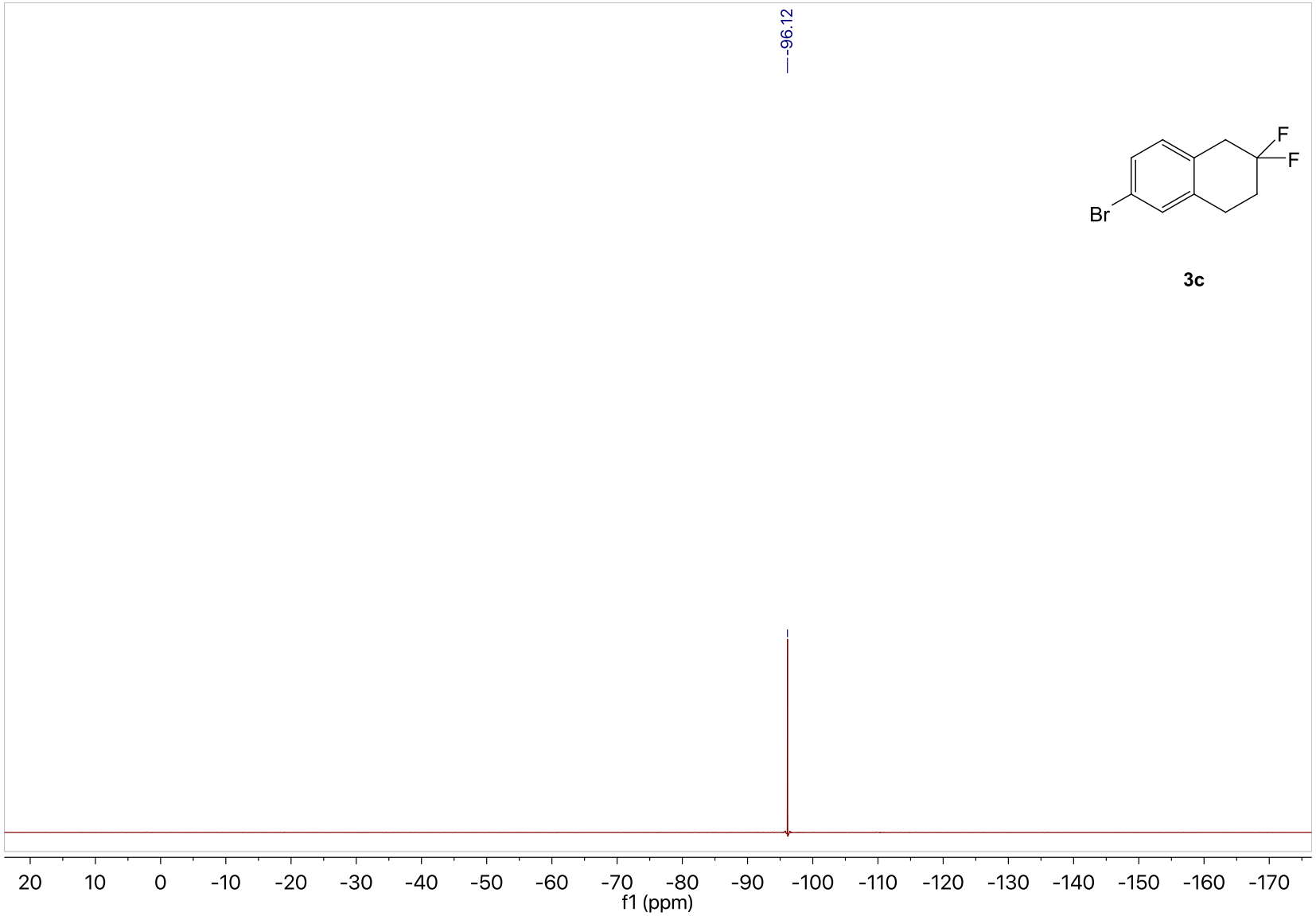

134.06
131.81
131.77
131.72
129.13
128.53
126.66
126.40
125.03
123.13
121.22
38.25
38.04
37.82
31.27
31.07
30.88
27.05
27.00
26.96
F
F
3a
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

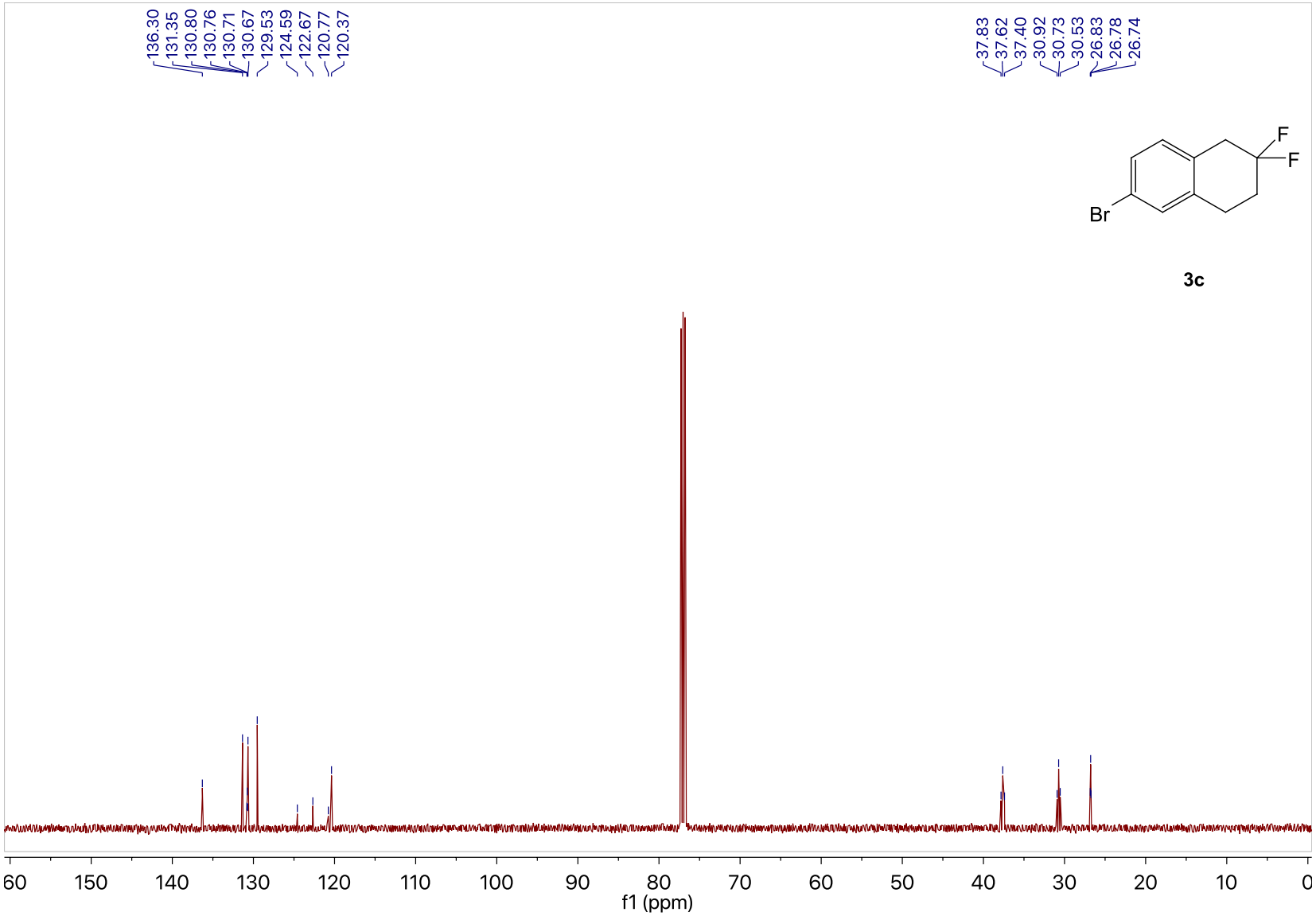

7.50
7.49
7.48
7.29
7.08
7.07
3.32
3.30
3.27
3.08
3.07
3.05
2.31
2.30
2.29
2.27
2.26
2.24
2.23
F
F
Br
3b
1.00
2.02
2.07
2.09
2.06
f1 (ppm)

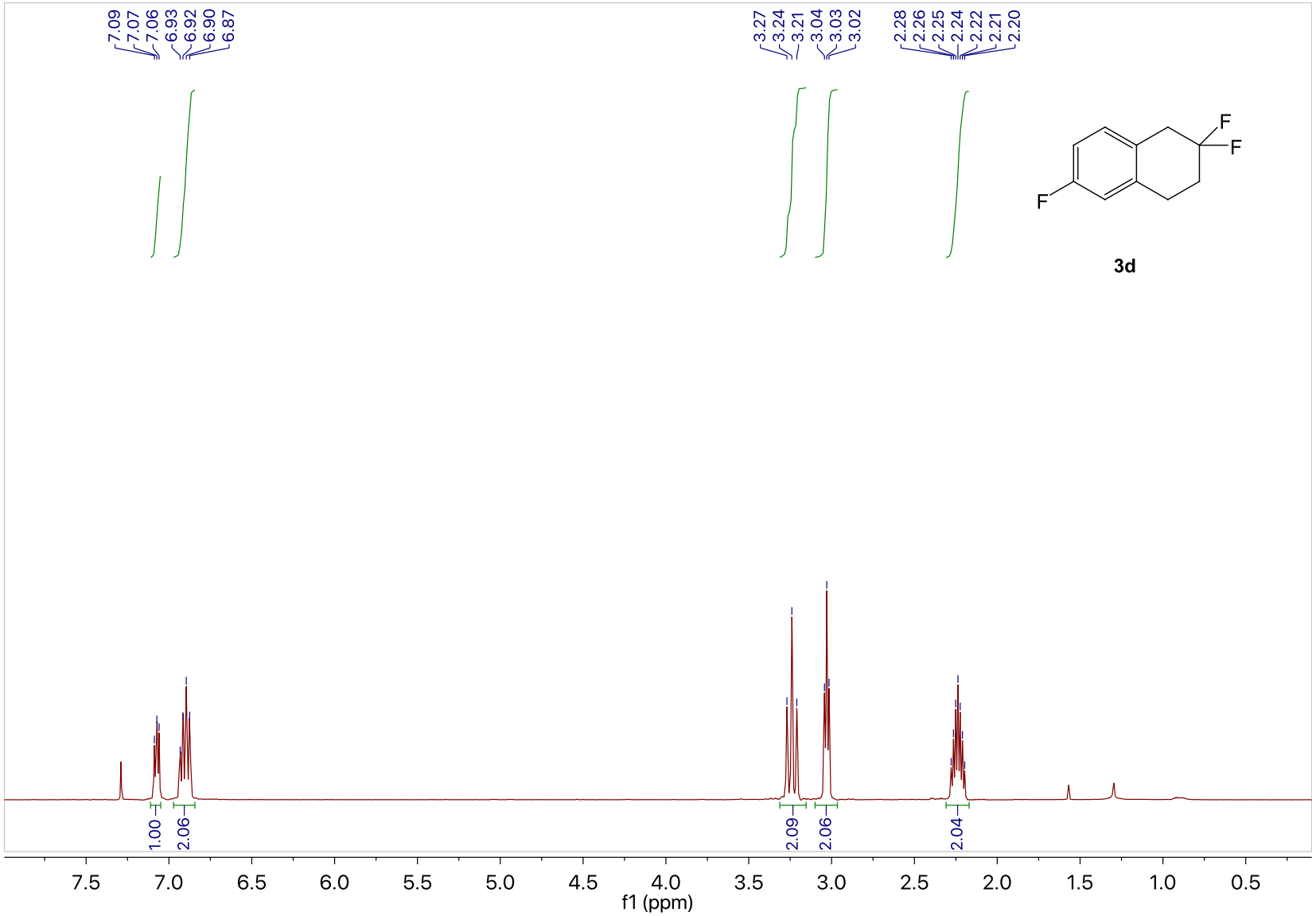

-97.74
F
F
Br
3b
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

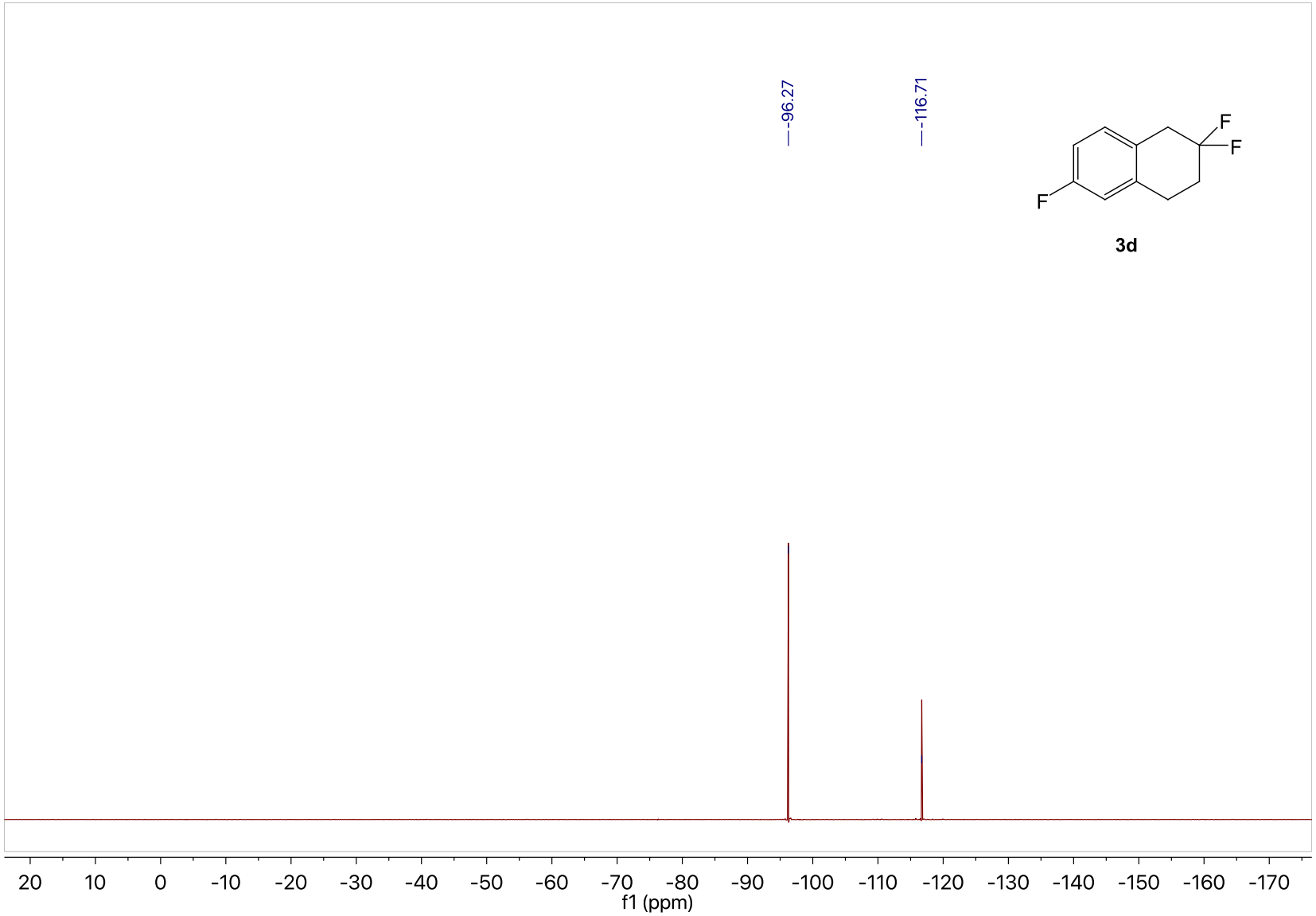

134.04
134.00
133.95
133.75
131.00
128.42
127.71
125.07
124.48
122.57
120.67
38.34
38.12
37.91
30.99
30.80
30.61
28.27
28.22
28.18
F
F
Br
3b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

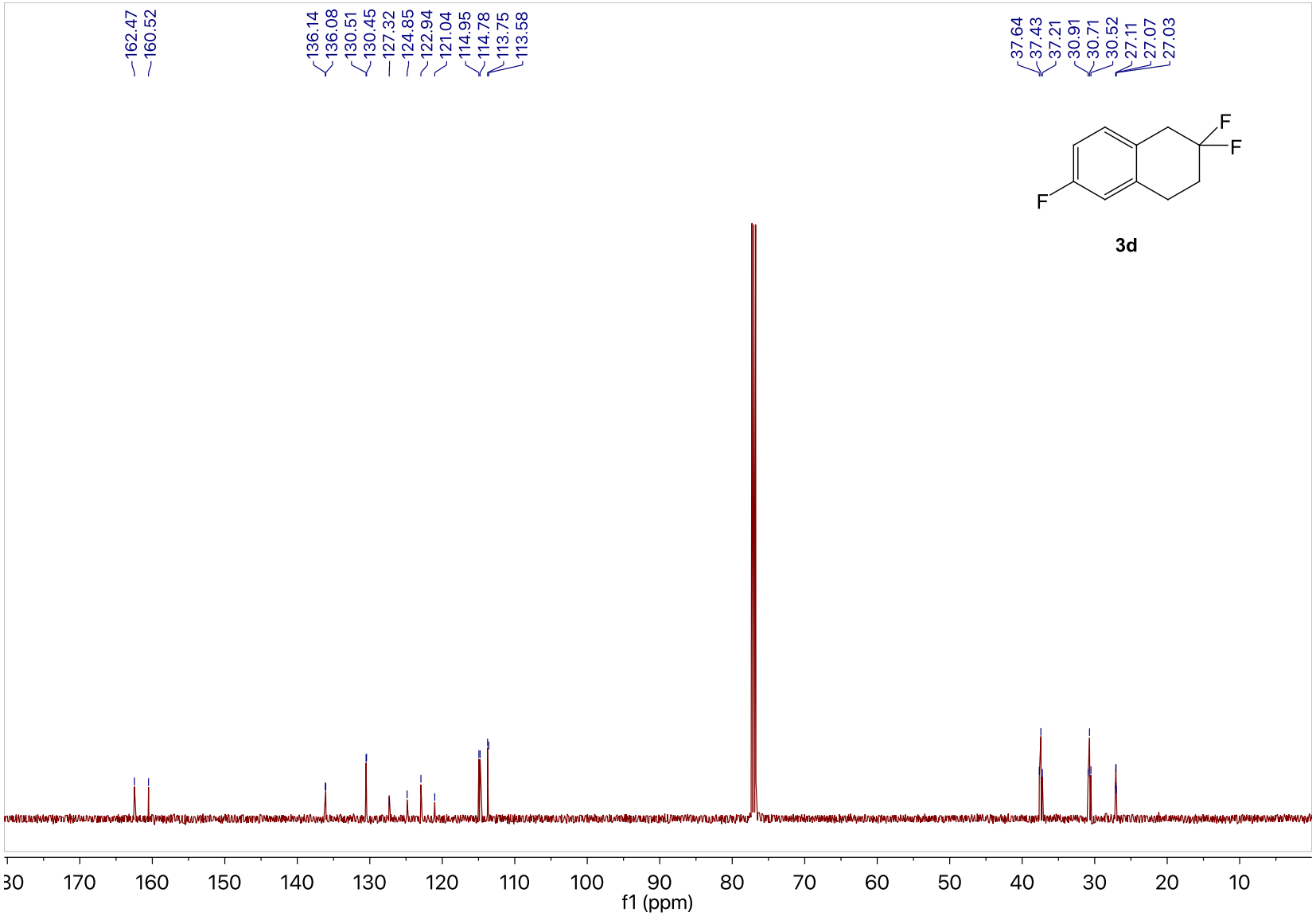

7.34
7.32
7.29
7.00
6.98
3.25
3.22
3.19
3.03
3.02
3.00
2.27
2.26
2.24
2.23
2.22
2.20
2.19
F
F
Br
3c
1.98
1.00
2.04
2.04
2.02
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


-96.12
F
F
Br
3c
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)


136.30
131.35
130.80
130.76
130.71
130.67
129.53
124.59
122.67
120.77
120.37
37.83
37.62
37.40
30.92
30.73
30.53
26.83
26.78
26.74
F
F
Br
3c
60
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.09
7.07
7.06
6.93
6.92
6.90
6.87
3.27
3.24
3.21
3.04
3.03
3.02
2.28
2.26
2.25
2.24
2.22
2.21
2.20
F
F
F
3d
1.00
2.06
2.09
2.06
2.04
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


-96.27
-116.71
F
F
F
3d
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)


162.47
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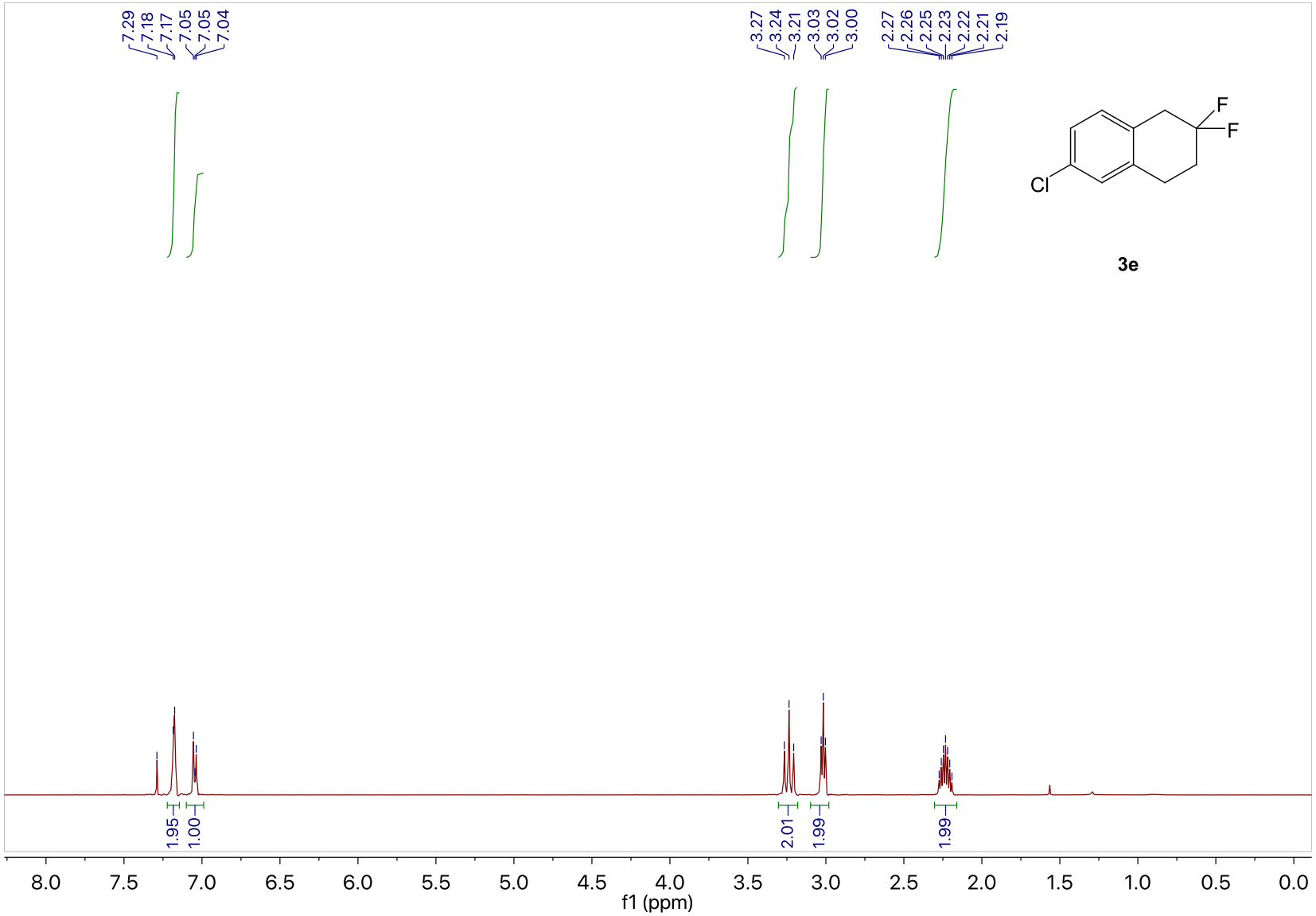
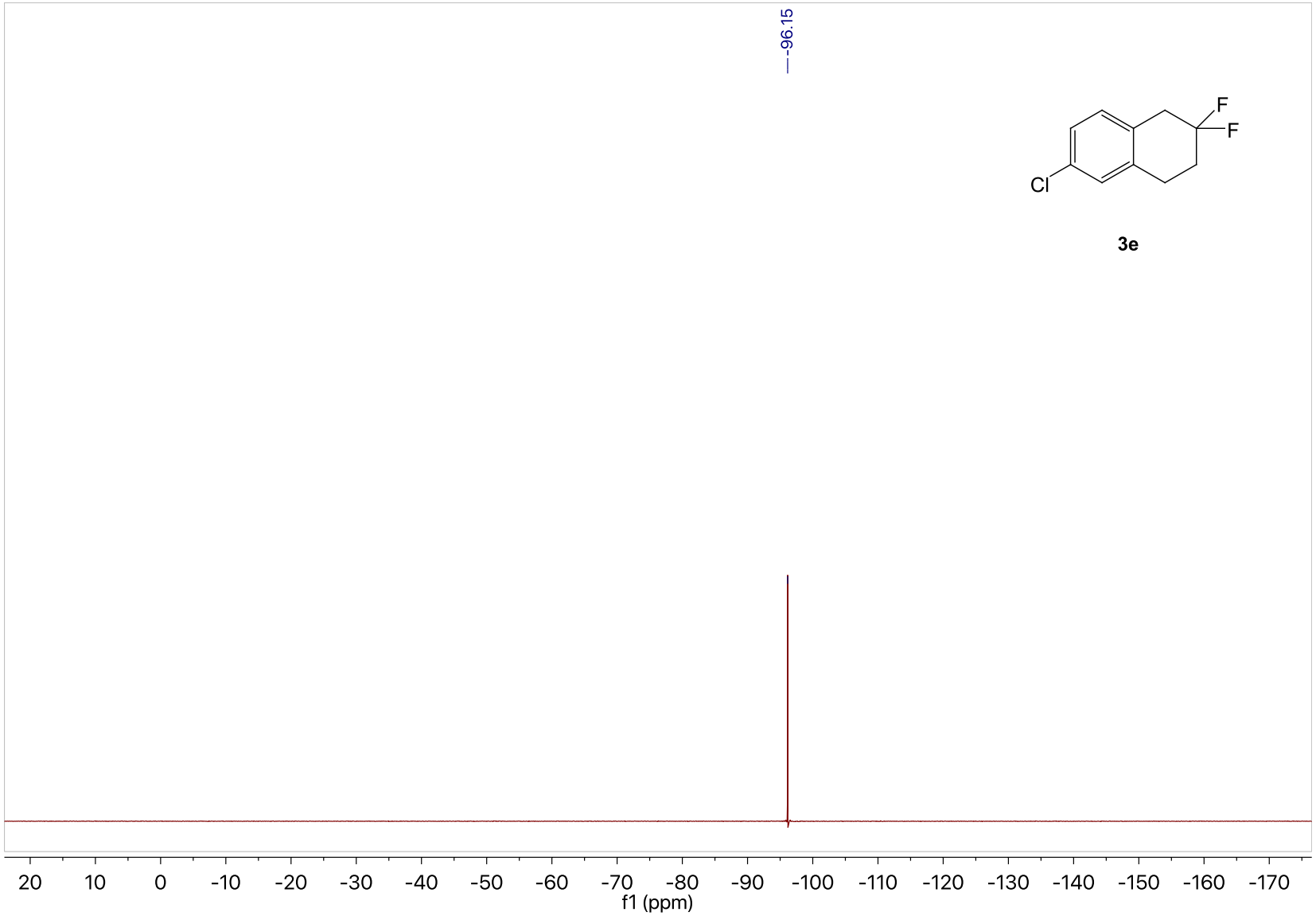
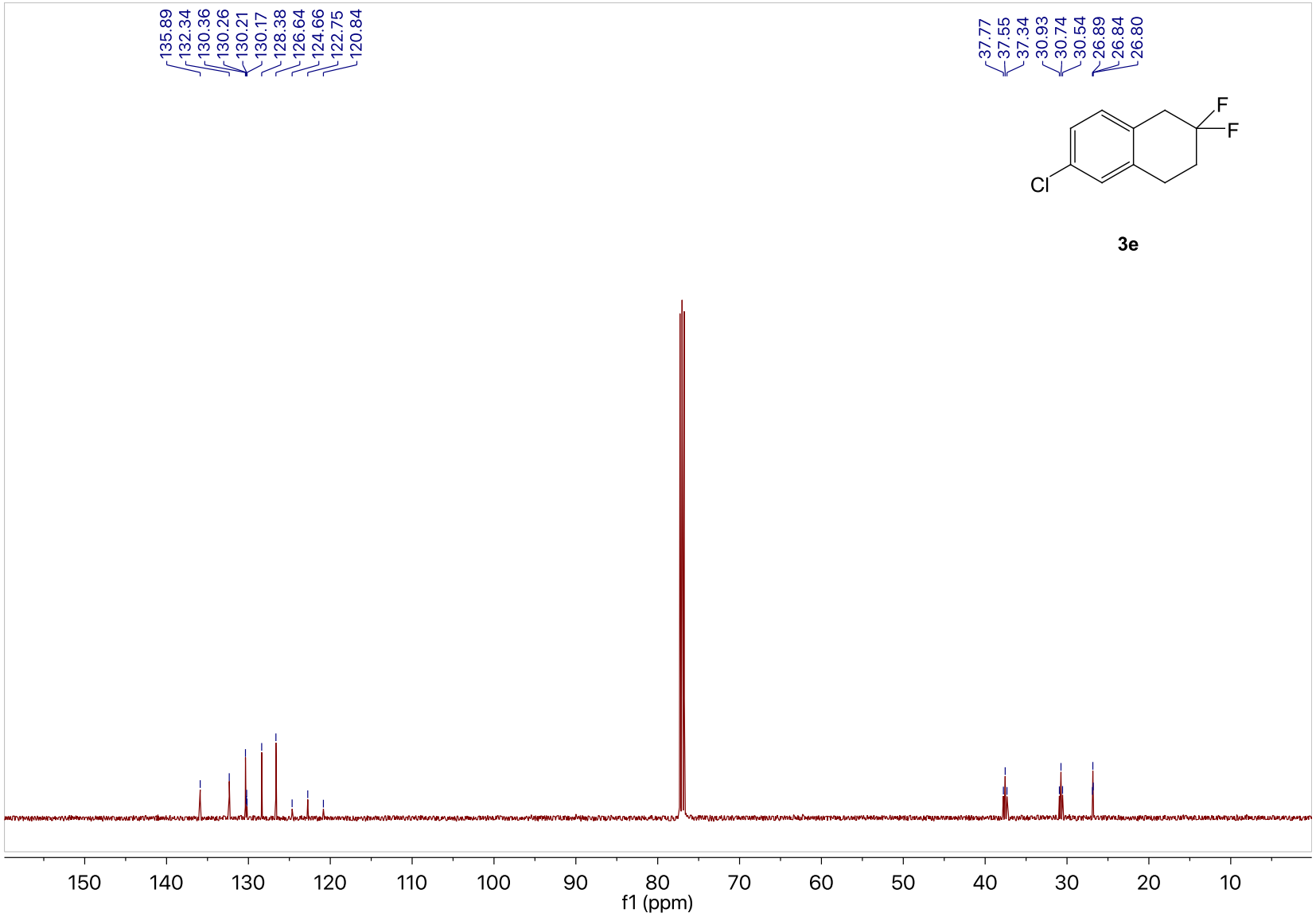
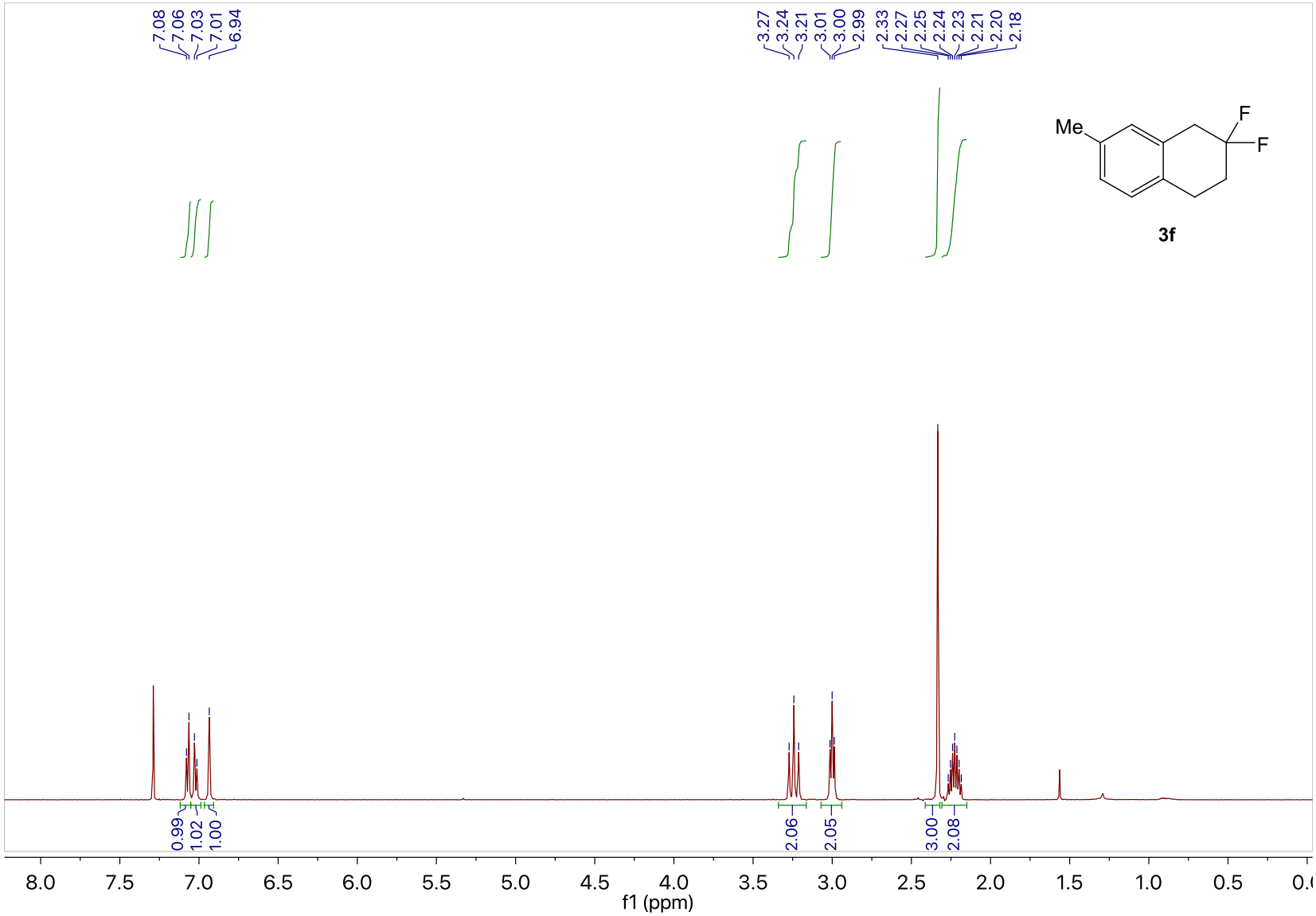
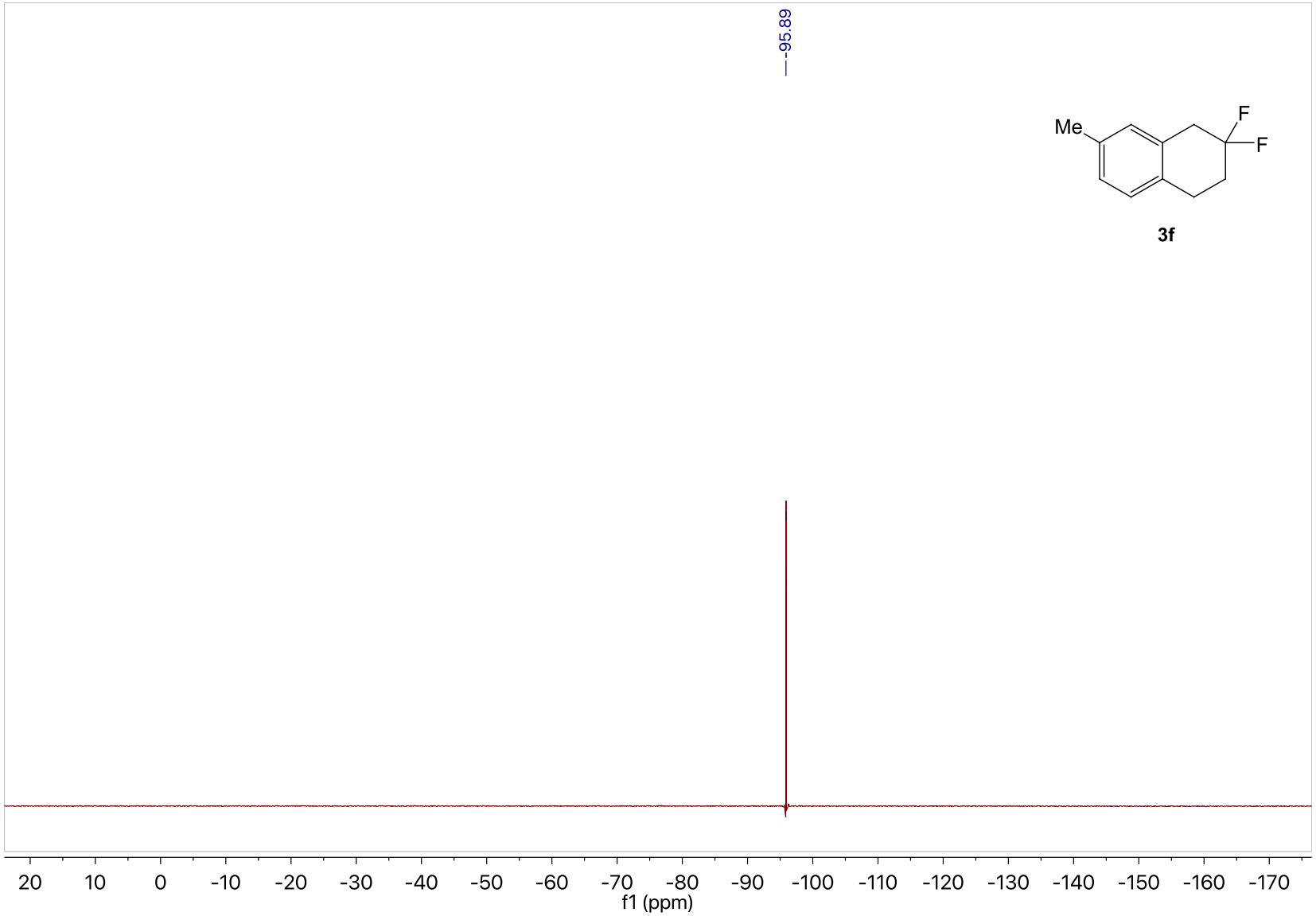
136.08
130.51
130.45
127.32
124.85
122.94
121.04
114.95
114.78
113.75
113.58
37.64
37.43
37.21
30.91
30.71
30.52
27.11
27.07
27.03
F
F
F
3d
f1 (ppm)

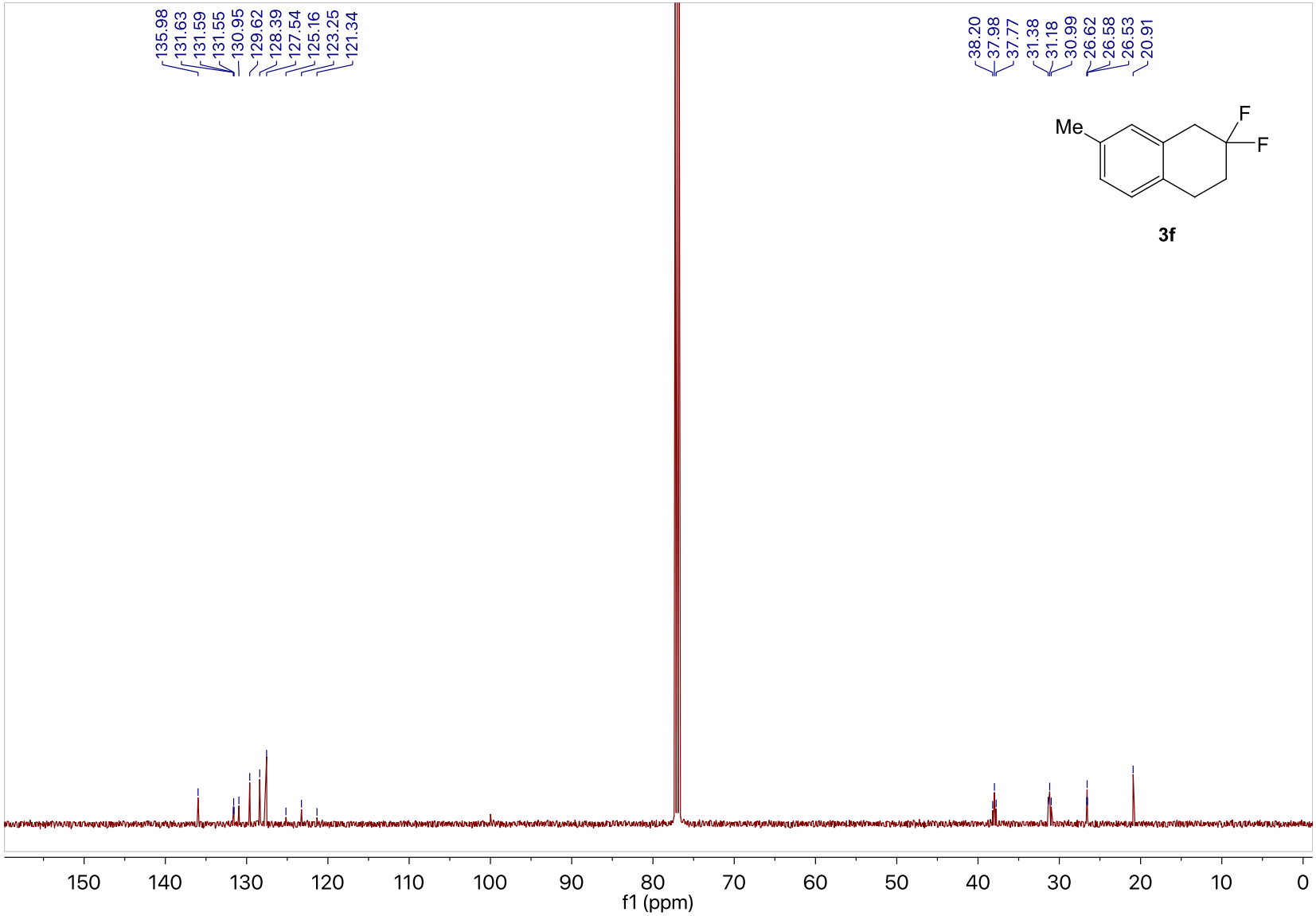

7.29
7.18
7.17
7.05
7.05
7.04
3.27
3.24
3.21
3.03
3.02
3.00
2.27
2.26
2.25
2.23
2.22
2.21
2.19
F
F
Cl
3e
1.95
1.00
2.01
1.99
1.99
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

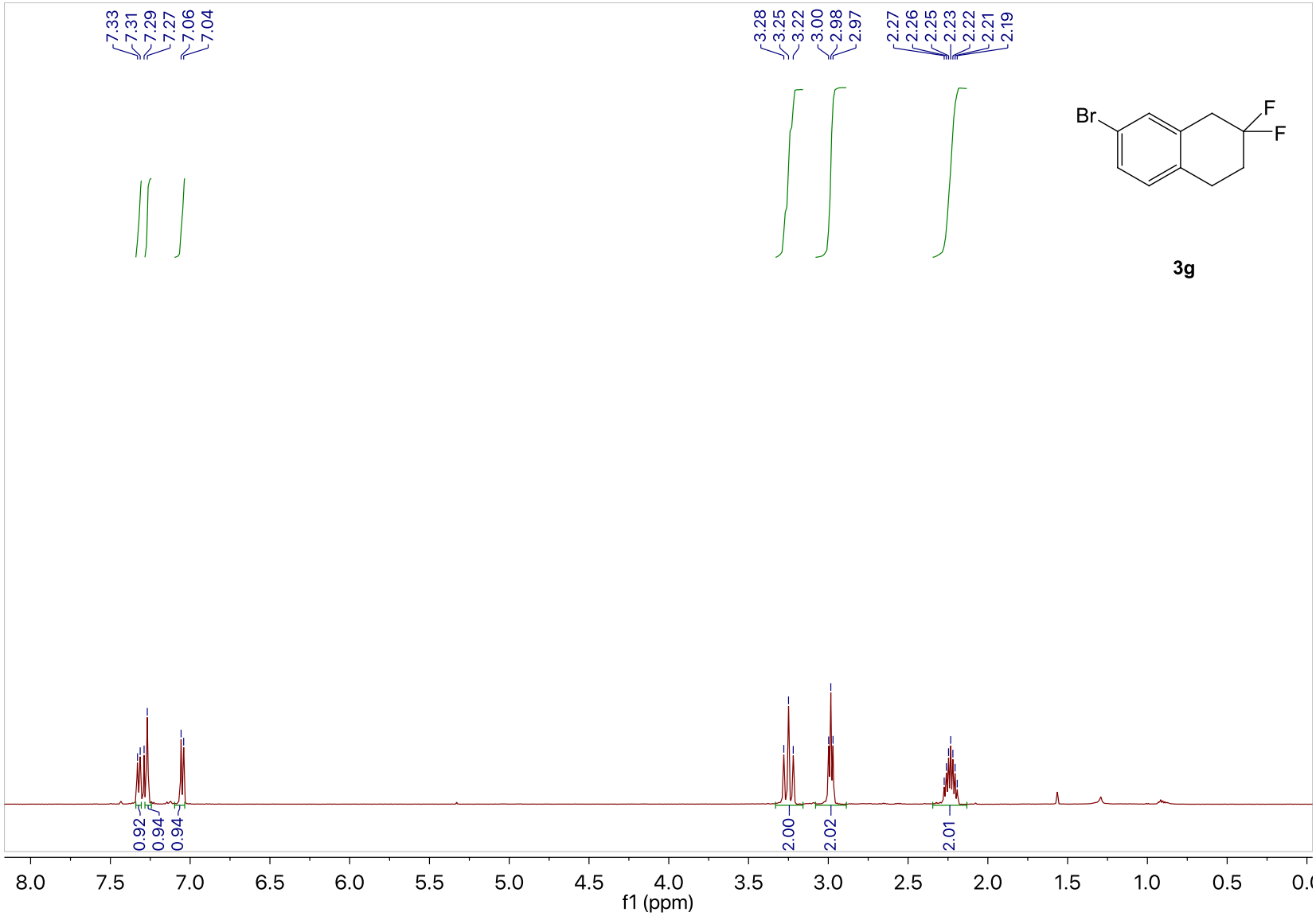

-96.15
F
F
Cl
3e
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

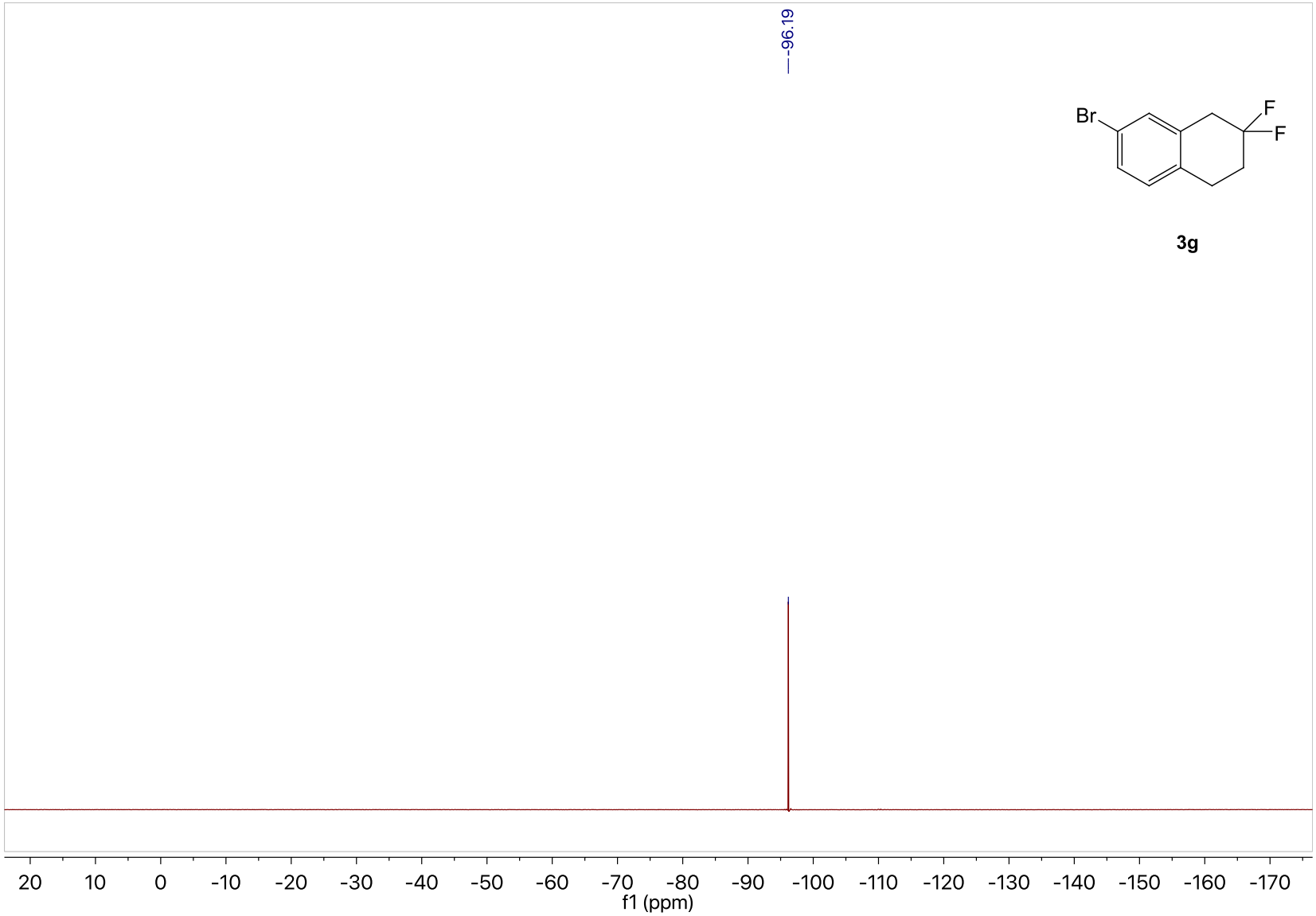

135.89
132.34
130.36
130.26
130.21
130.17
128.38
126.64
124.66
122.75
120.84
37.77
37.55
37.34
30.93
30.74
30.54
26.89
26.84
26.80
F
F
Cl
3e
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

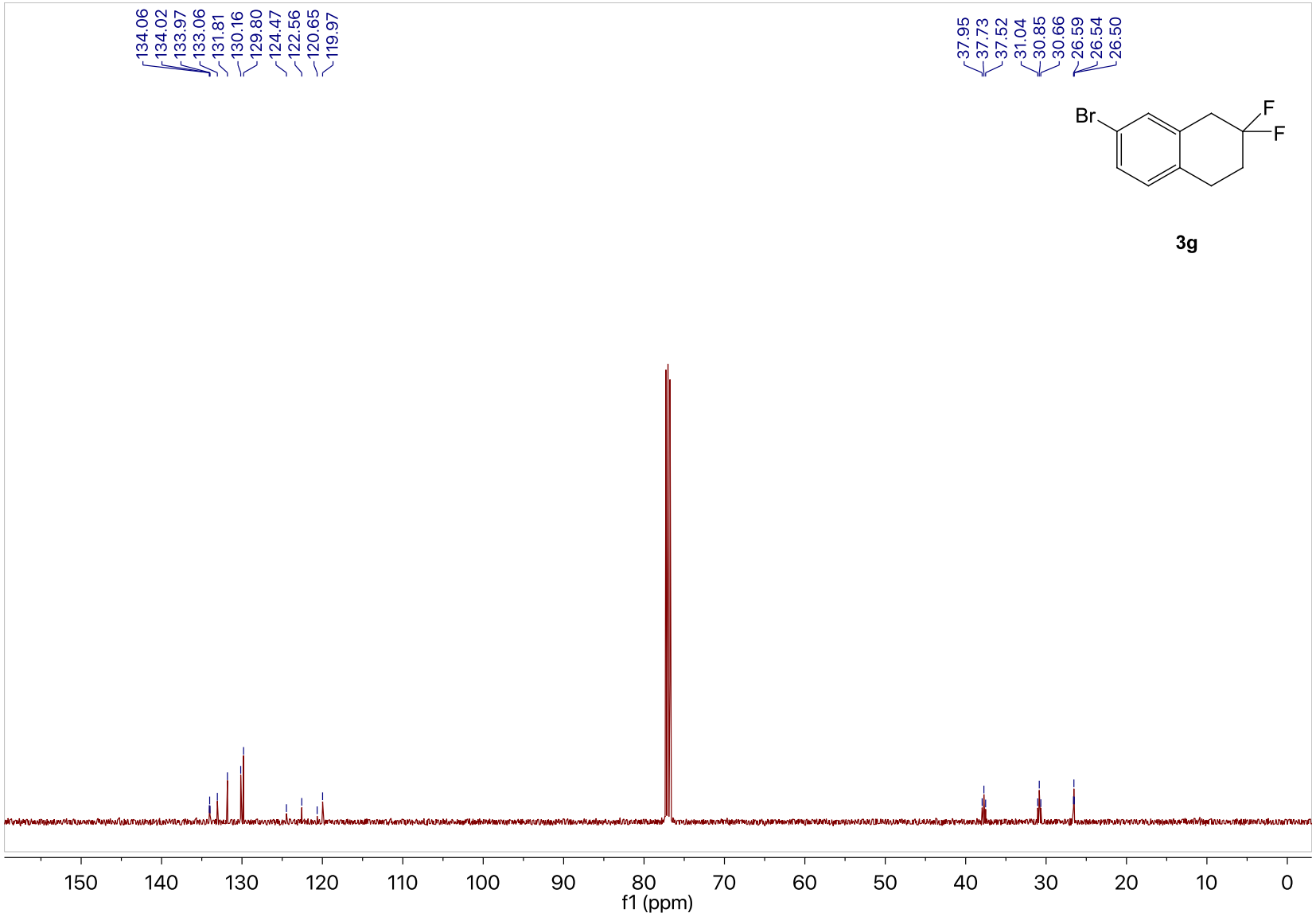

7.08
7.06
7.03
7.01
6.94
3.27
3.24
3.21
3.01
3.00
2.99
2.33
2.27
2.25
2.24
2.23
2.21
2.20
2.18
Me
F
F
3f
0.99
1.02
1.00
2.06
2.05
3.00
2.08
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

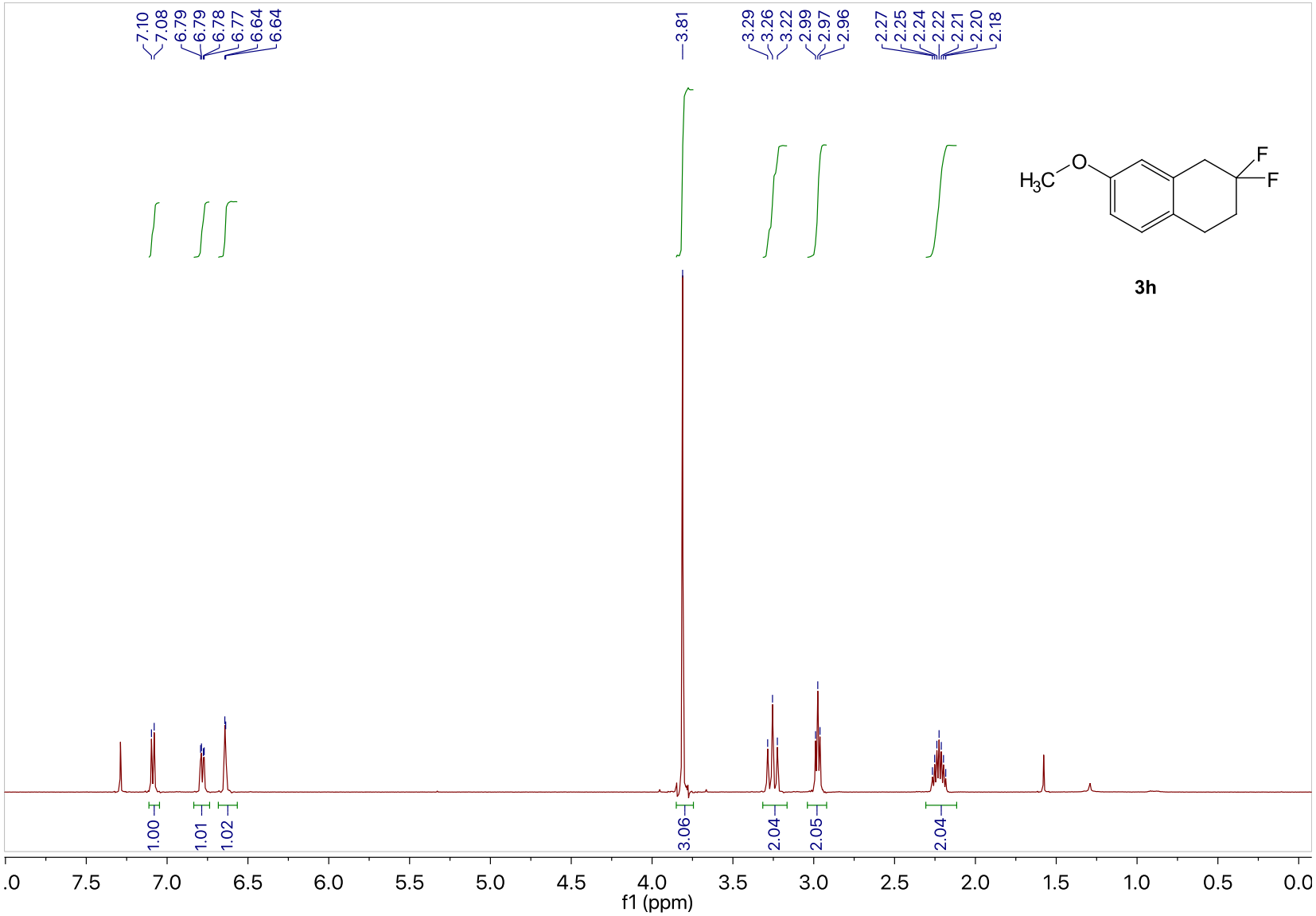

-95.89
Me
F
F
3f
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)


135.98
131.63
131.59
131.55
130.95
129.62
128.39
127.54
125.16
123.25
121.34
38.20
37.98
37.77
31.38
31.18
30.99
26.62
26.58
26.53
20.91
Me
F
F
3f
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.33
7.31
7.29
7.27
7.06
7.04
3.28
3.25
3.22
3.00
2.98
2.97
2.27
2.26
2.25
2.23
2.22
2.21
2.19
Br
F
F
3g
0.92
0.94
0.94
2.00
2.02
2.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

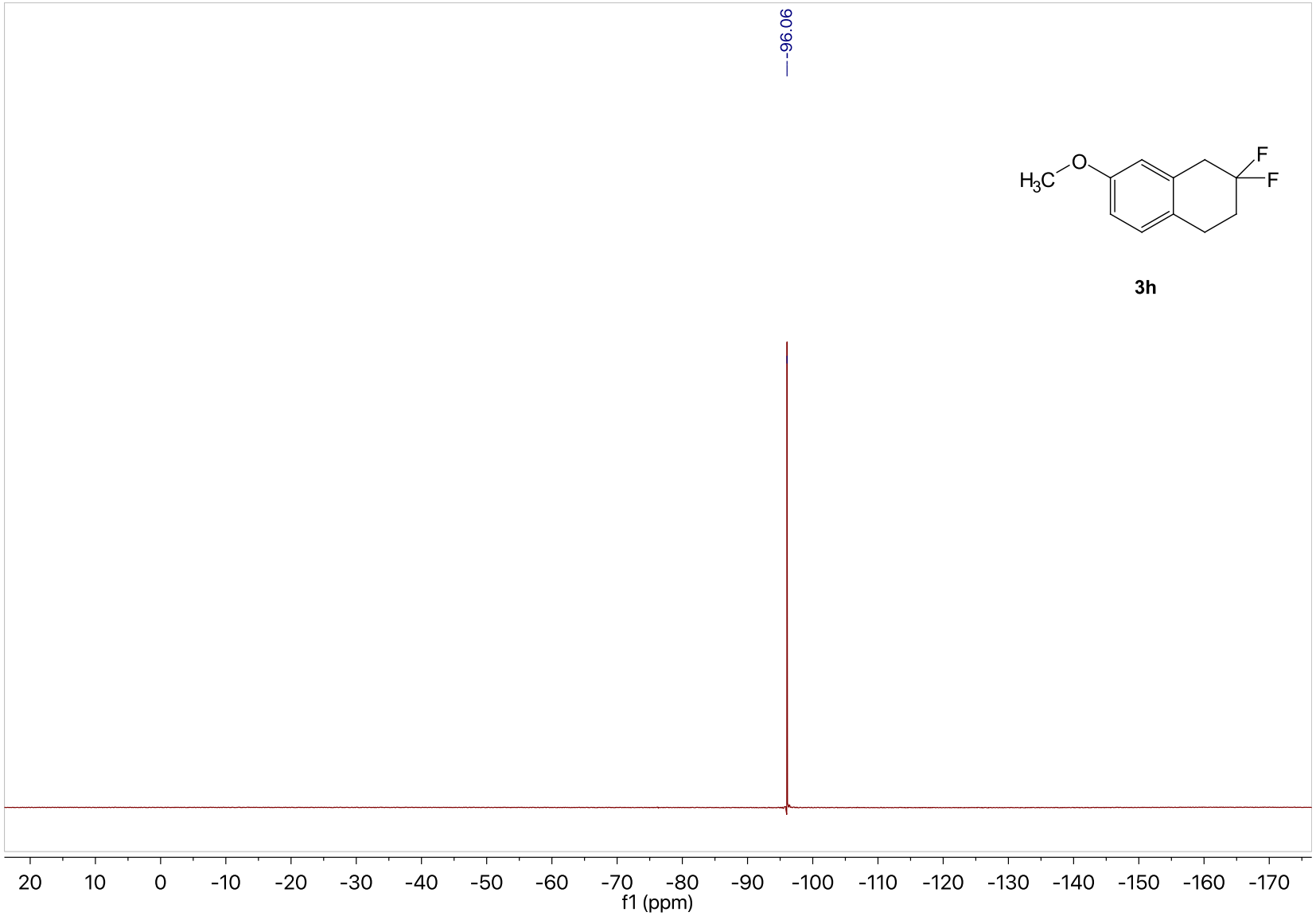

-96.19
Br
F
F
3g
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

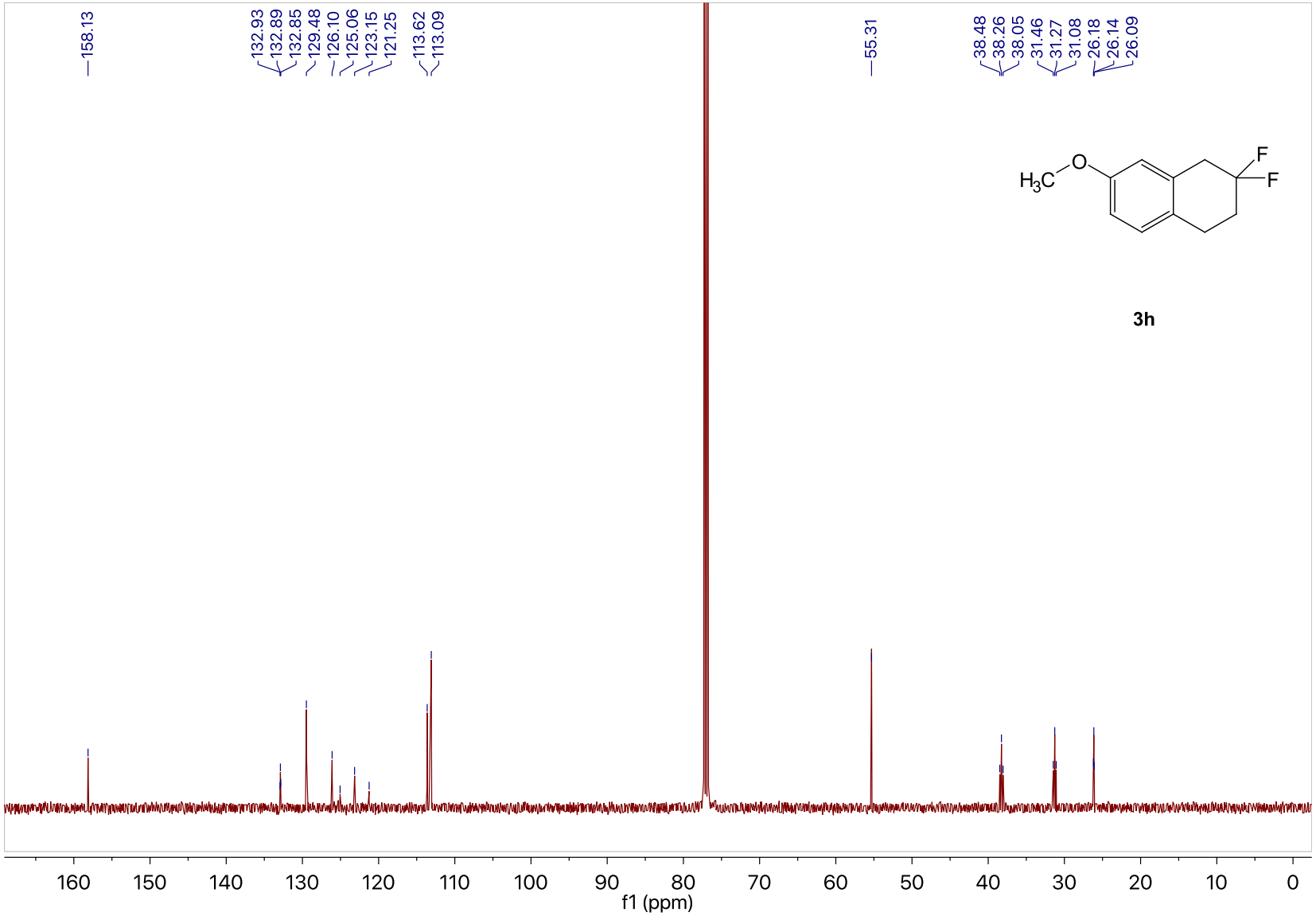

134.06
134.02
133.97
133.06
131.81
130.16
129.80
124.47
122.56
120.65
119.97
37.95
37.73
37.52
31.04
30.85
30.66
26.59
26.54
26.50
Br
F
F
3g
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.10
7.08
6.79
6.79
6.78
6.77
6.64
6.64
3.81
3.29
3.26
3.22
2.99
2.97
2.96
2.27
2.25
2.24
2.22
2.21
2.20
2.18
1.00
1.01
1.02
3.06
2.04
2.05
2.04
f1 (ppm)

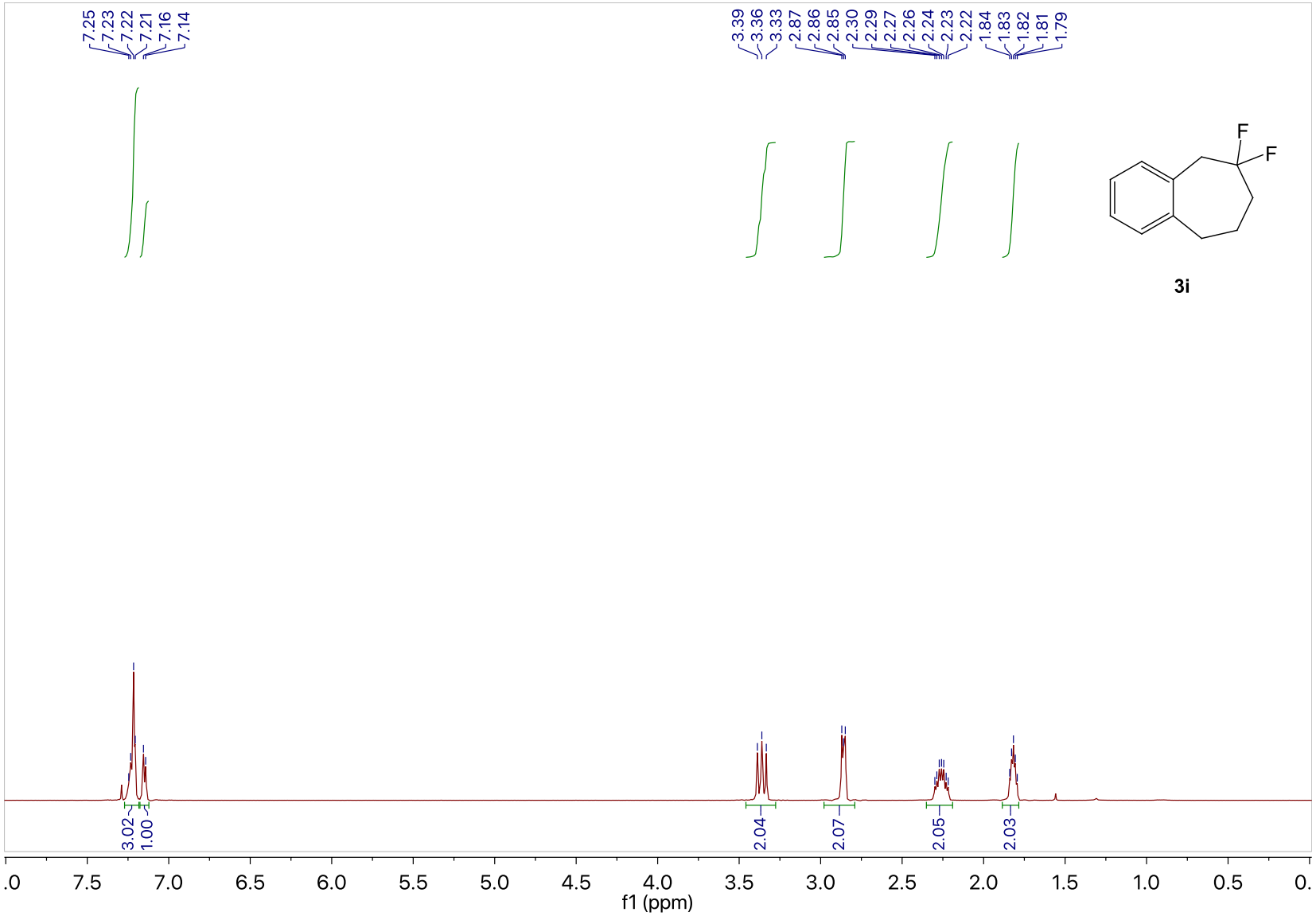
O
H3C
F
F

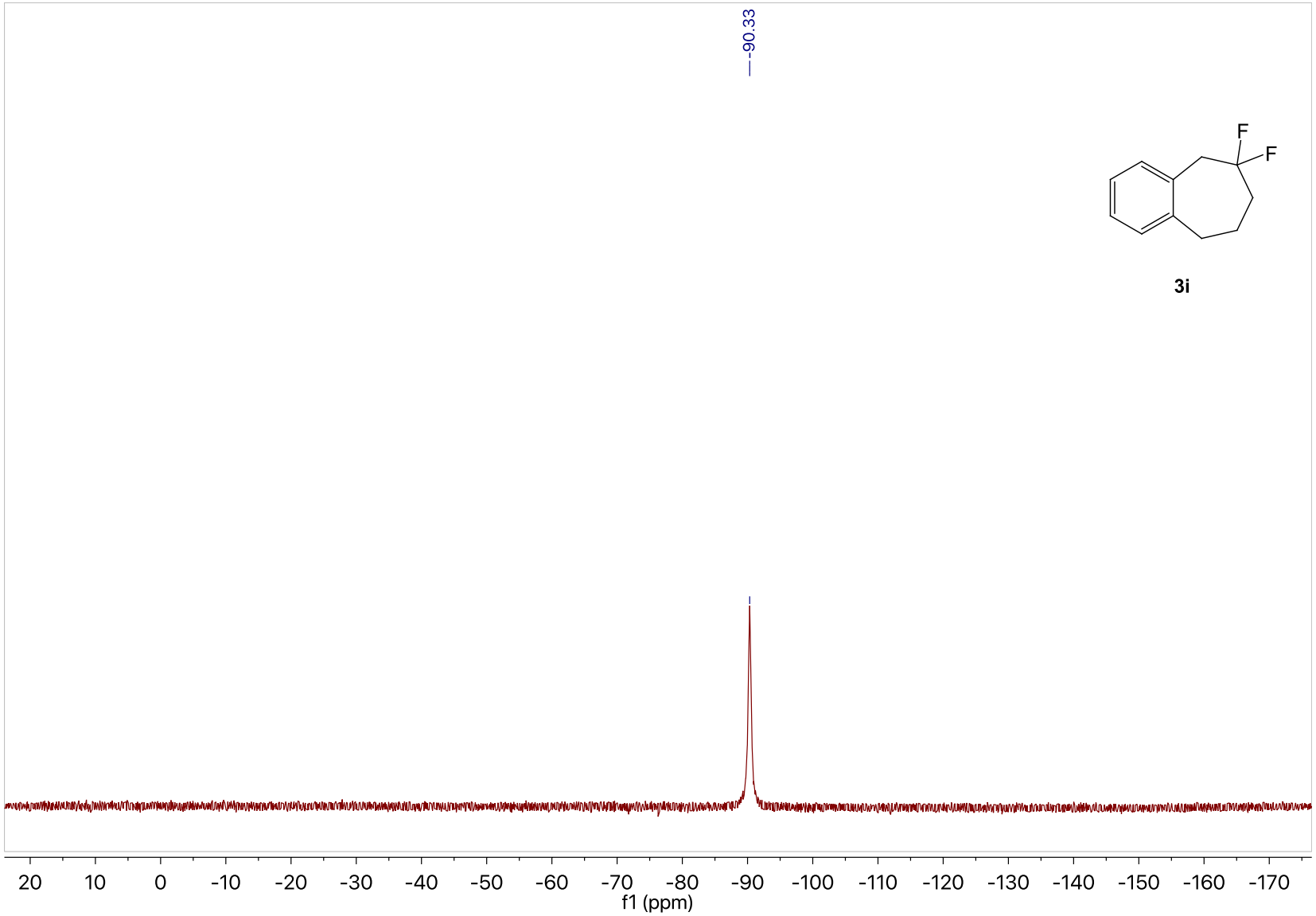
3h

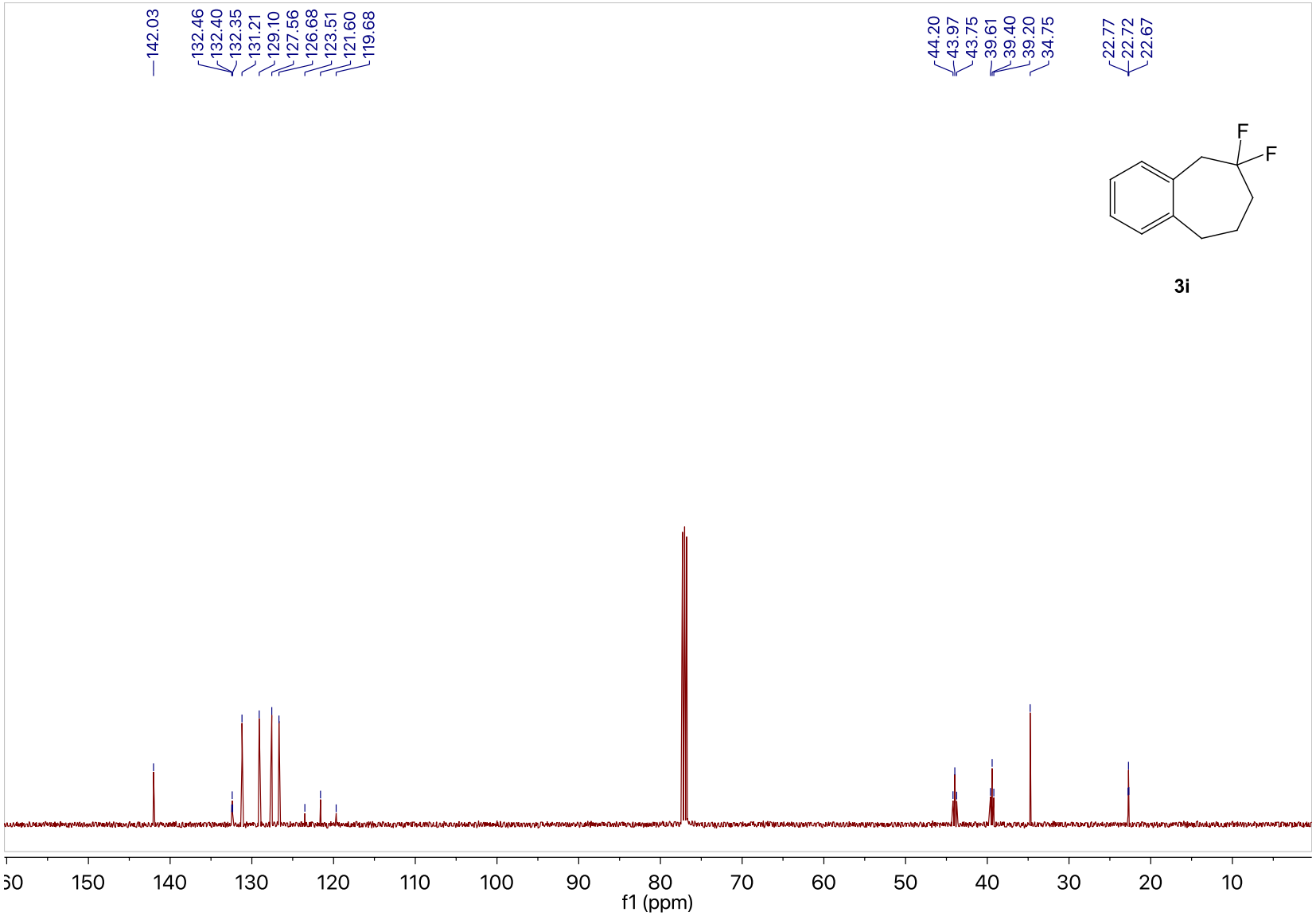

-96.96
H3C
O
F
F
3h
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

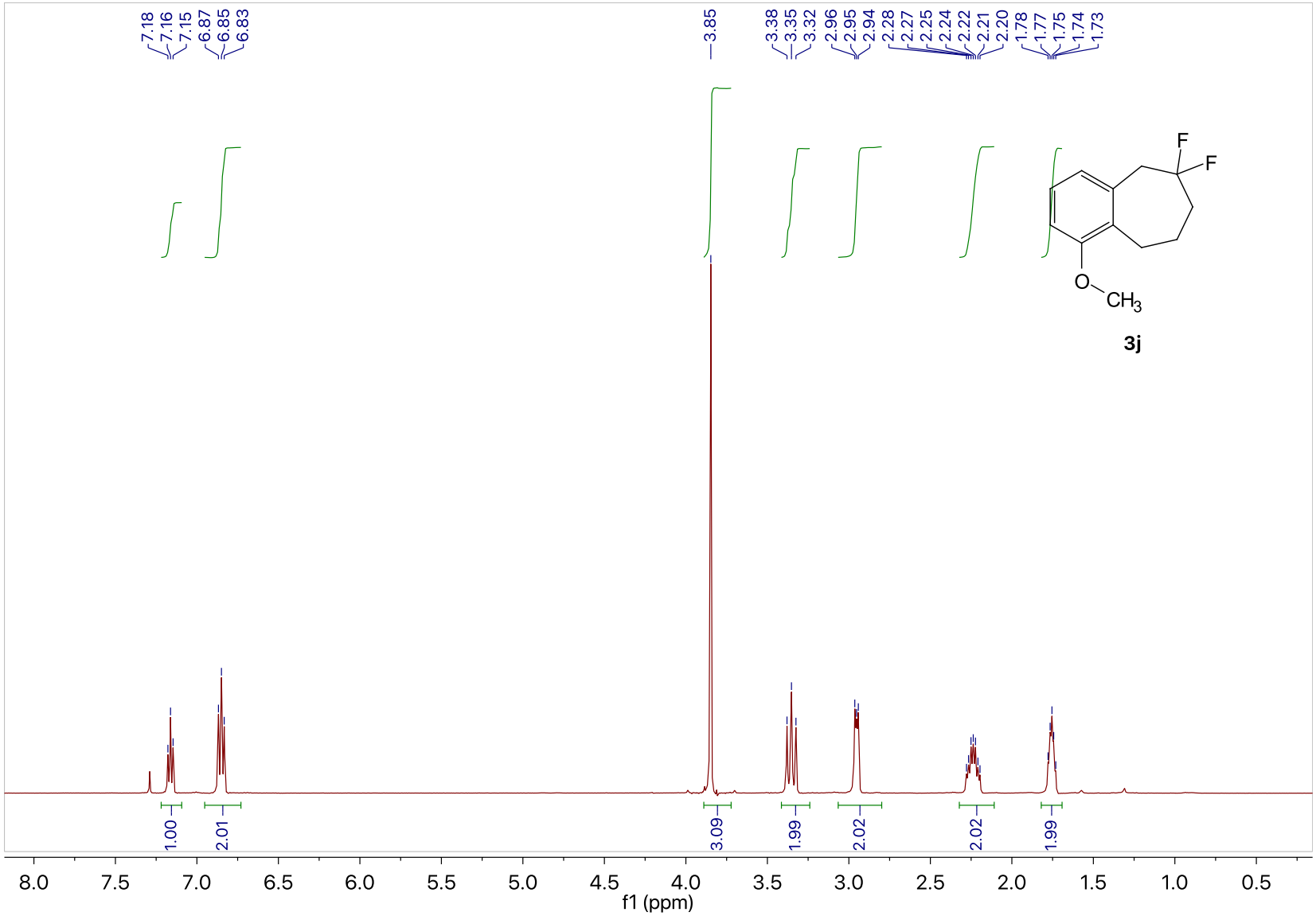

158.13
132.93
132.89
132.85
129.48
126.10
125.06
123.15
121.25
113.62
113.09
55.31
38.48
38.26
38.05
31.46
31.27
31.08
26.18
26.14
26.09
O
H3C
F
F
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

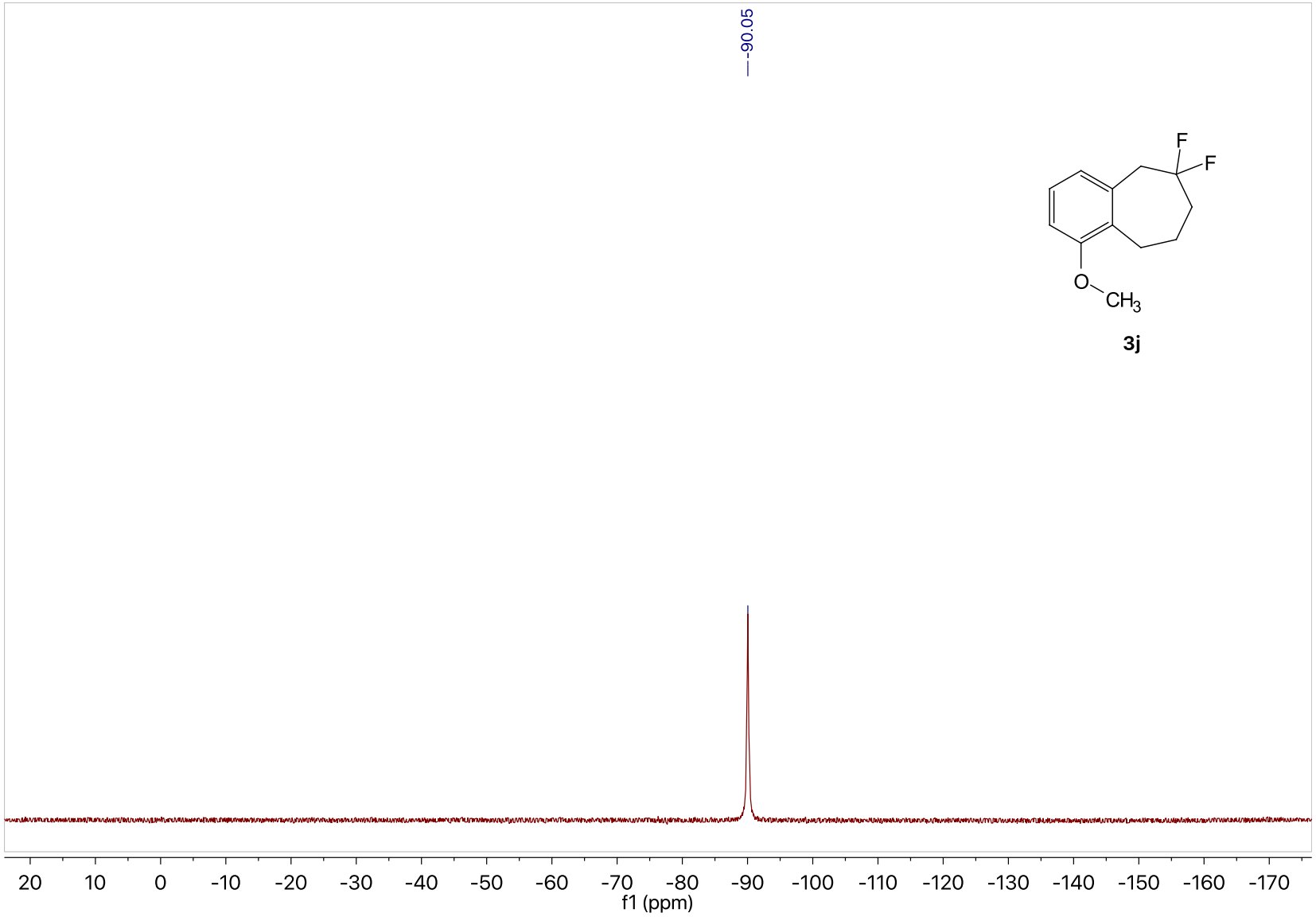
3h

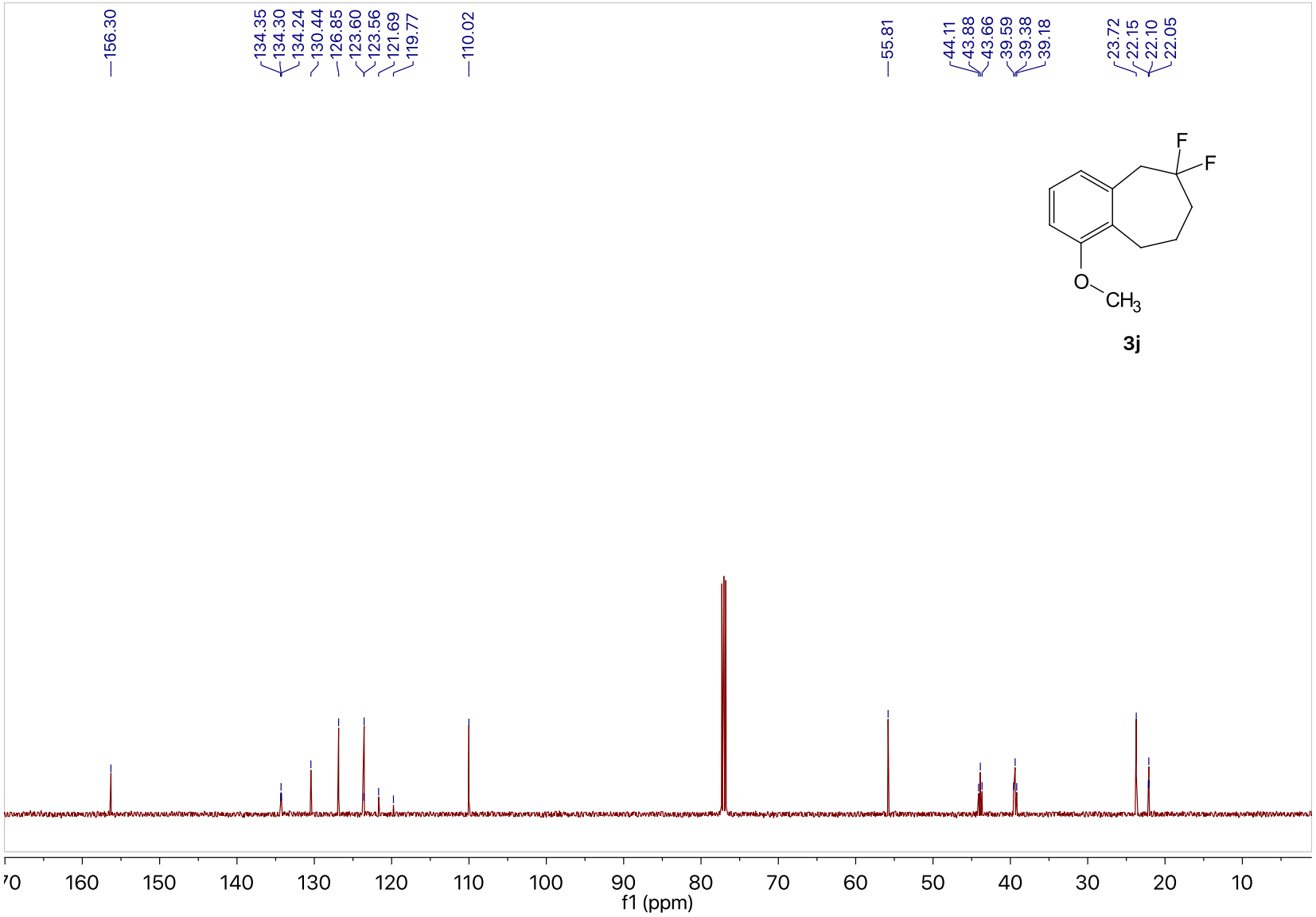

7.25
7.23
7.22
7.21
7.16
7.14
3.39
3.36
3.33
2.87
2.86
2.85
2.30
2.29
2.27
2.26
2.24
2.23
2.22
1.84
1.83
1.82
1.81
1.79
F
F
3i
3.02
1.00
2.04
2.07
2.05
2.03
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

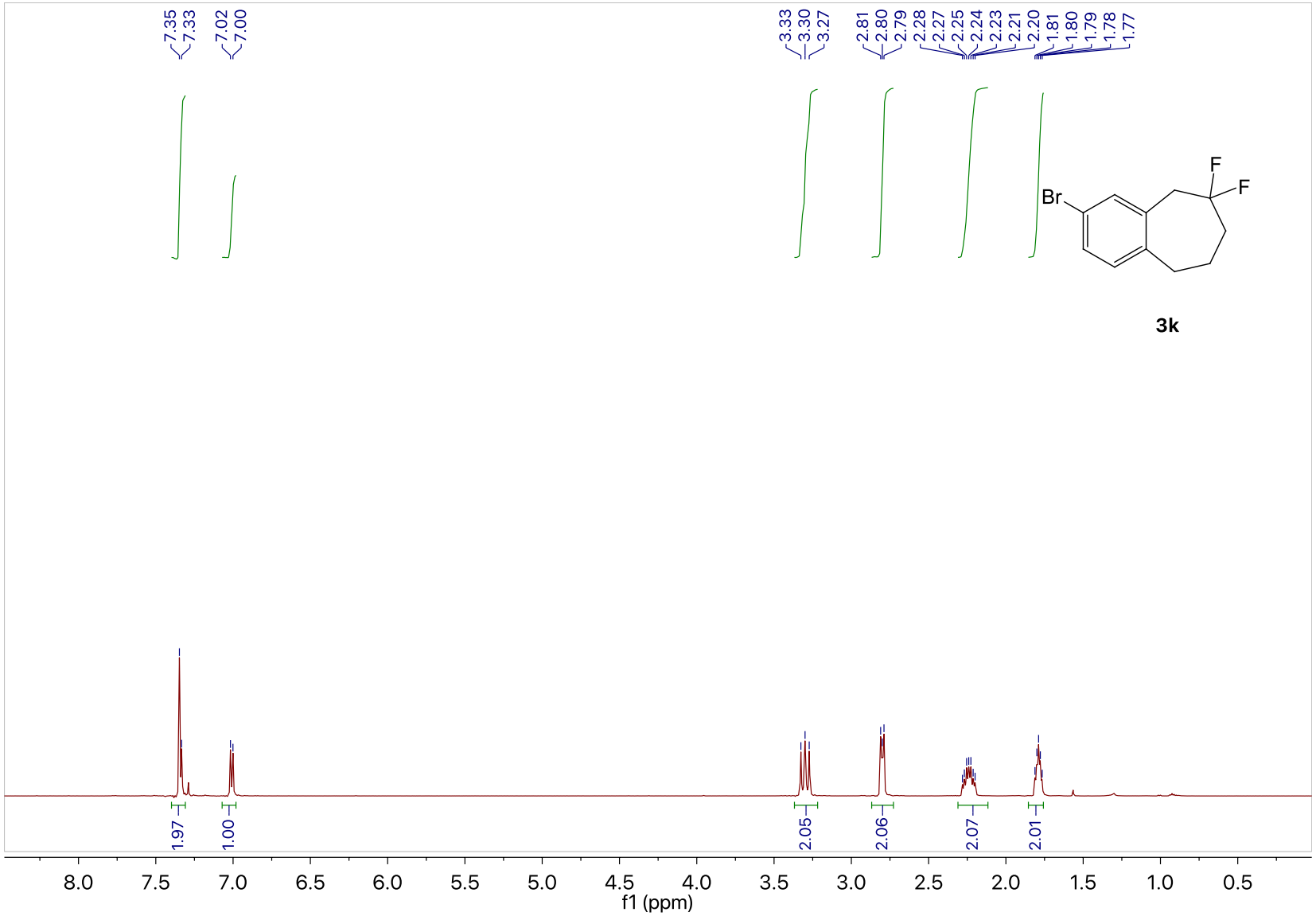

-90.33
F
F
3i
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

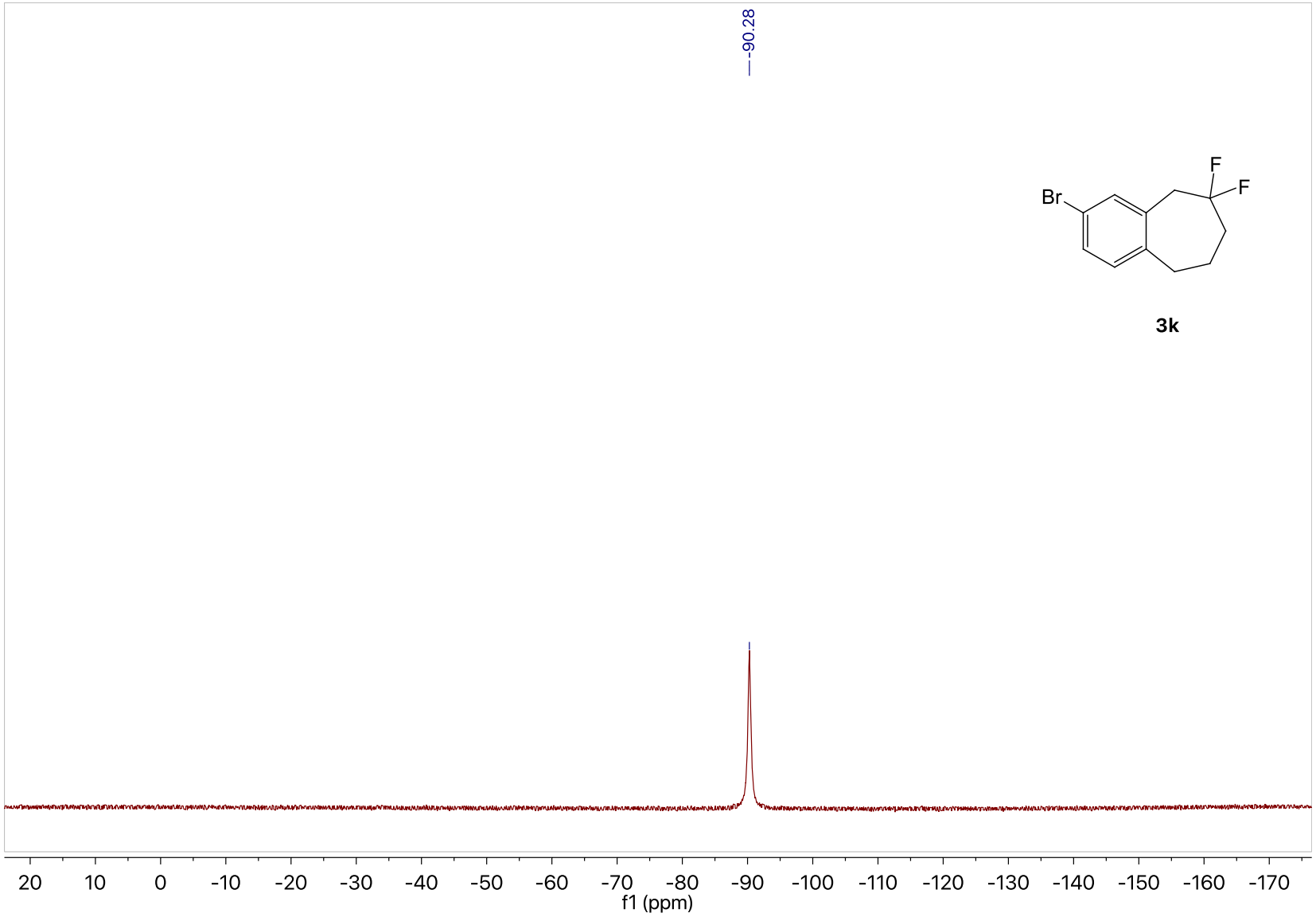

142.03
132.46
132.40
132.35
131.21
129.10
127.56
126.68
123.51
121.60
119.68
44.20
43.97
43.75
39.61
39.40
39.20
34.75
22.77
22.72
22.67
F
F
3i
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.18
7.16
7.15
6.87
6.85
6.83
3.85
3.38
3.35
3.32
2.96
2.95
2.94
2.28
2.27
2.25
2.24
2.22
2.21
2.20
1.78
1.77
1.75
1.74
1.73
F
F
O
CH3
3j
1.00
2.01
3.09
1.99
2.02
2.02
1.99
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


-90.05
F
F
O
CH3
3j
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)


156.30
134.35
134.30
134.24
130.44
126.85
123.60
123.56
121.69
119.77
110.02
55.81
44.11
43.88
43.66
39.59
39.38
39.18
23.72
22.15
22.10
22.05
F
F
O
CH3
3j
f1 (ppm)


7.35
7.33
7.02
7.00
3.33
3.30
3.27
2.81
2.80
2.79
2.28
2.27
2.25
2.24
2.23
2.21
2.20
1.81
1.80
1.79
1.78
1.77
F
F
Br
3k
1.97
1.00
2.05
2.06
2.07
2.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


-90.28
F
F
Br
3k
20
10
0
-10
-20
-30
-40
-50
-60
-70
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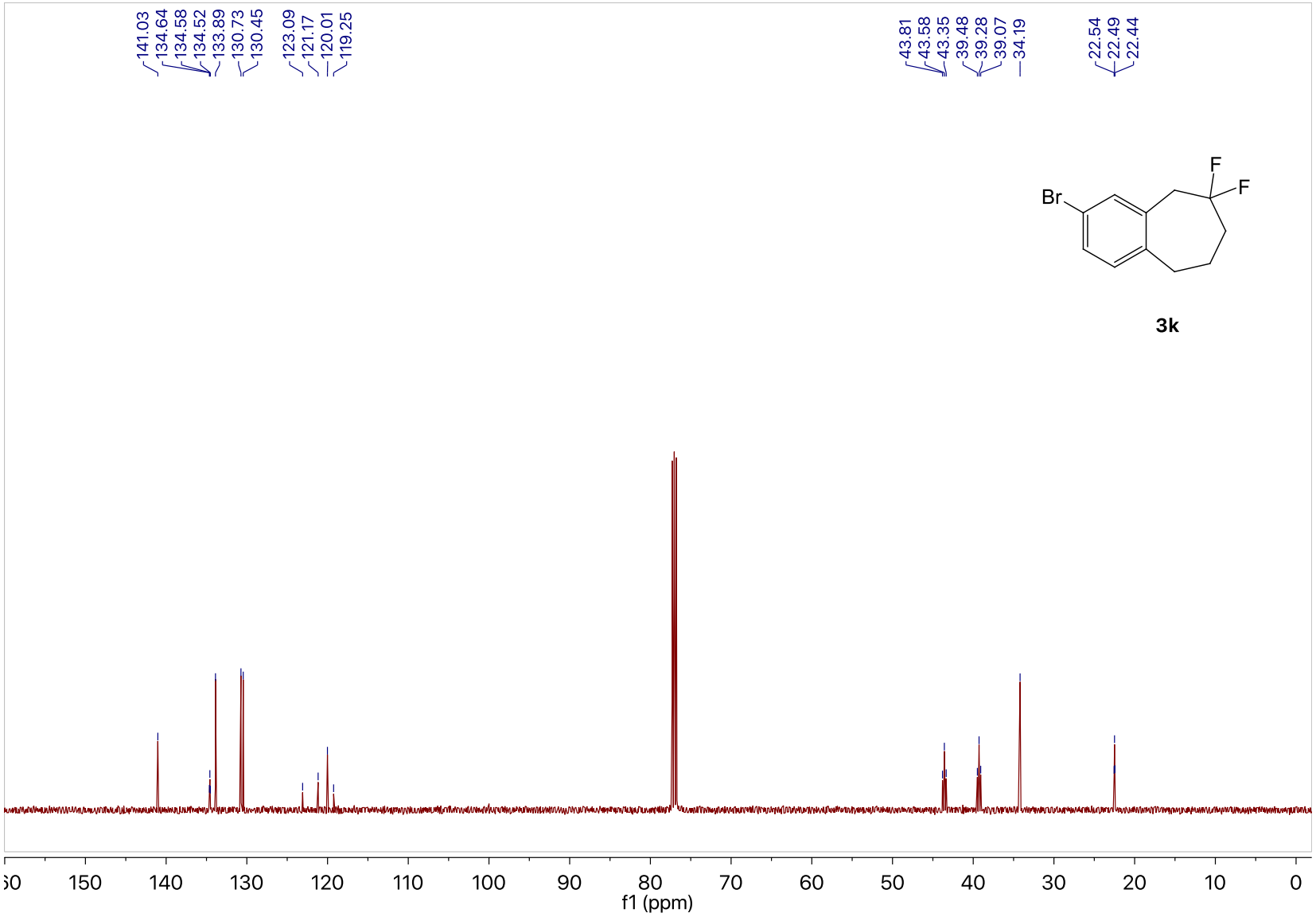
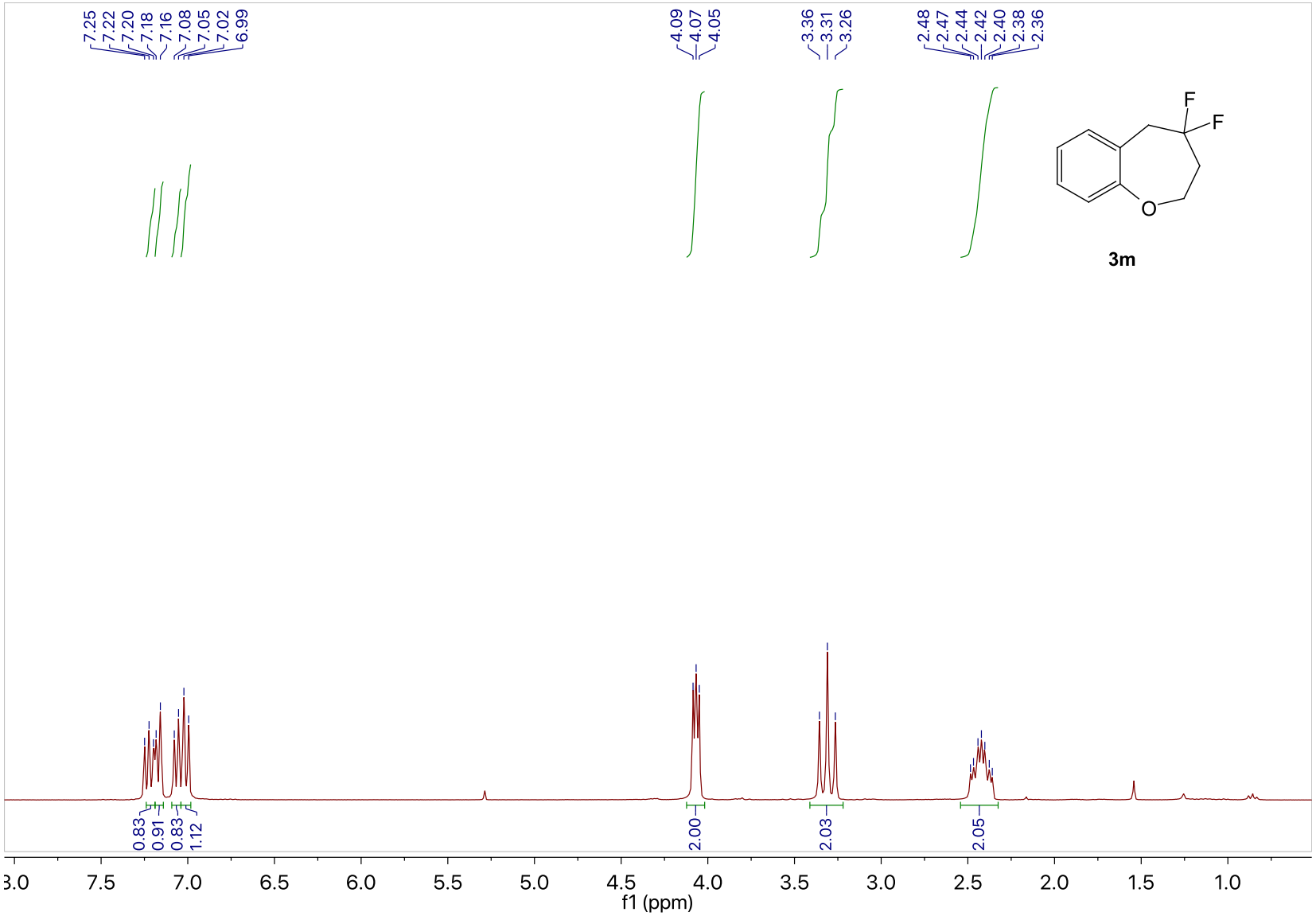
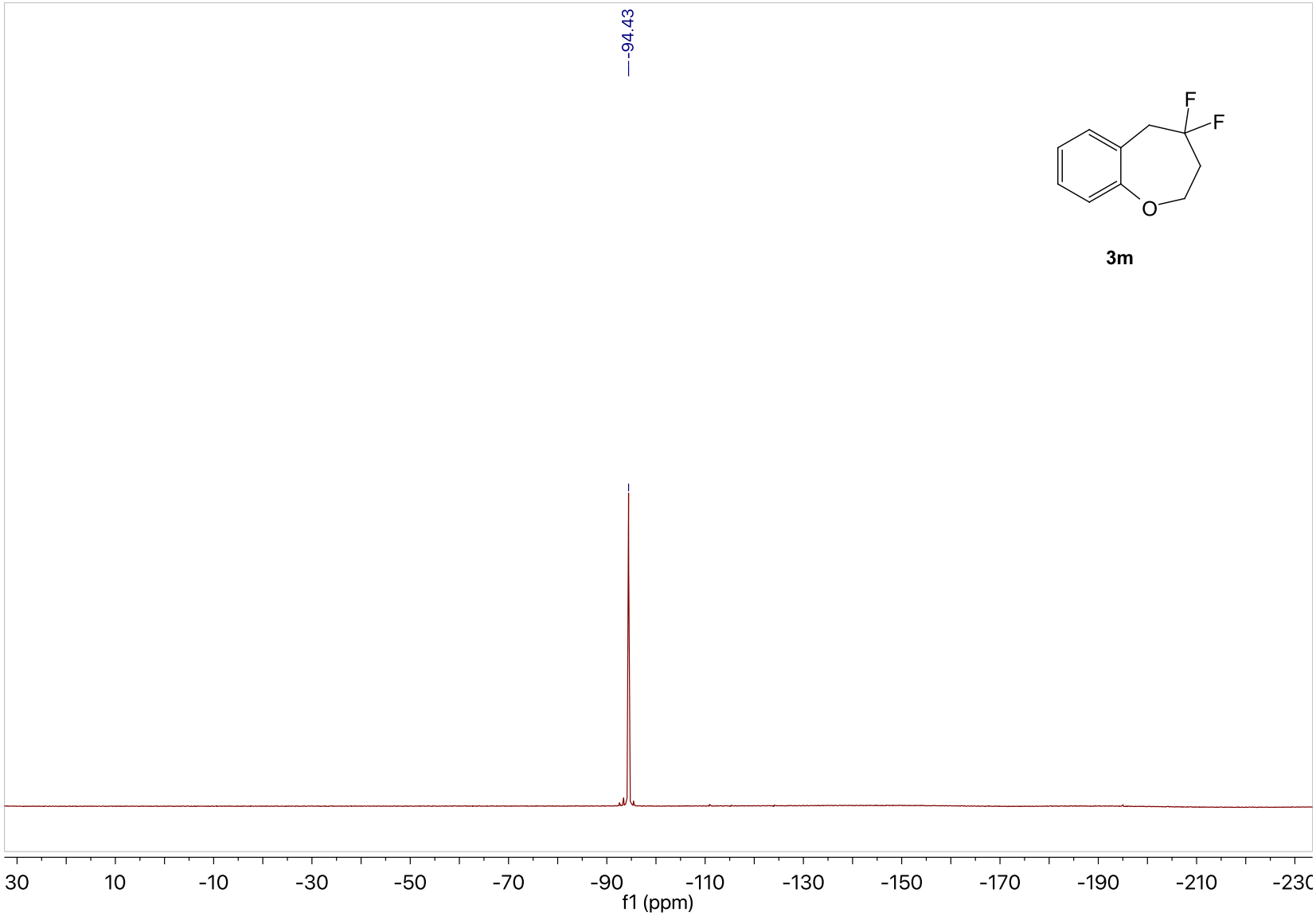
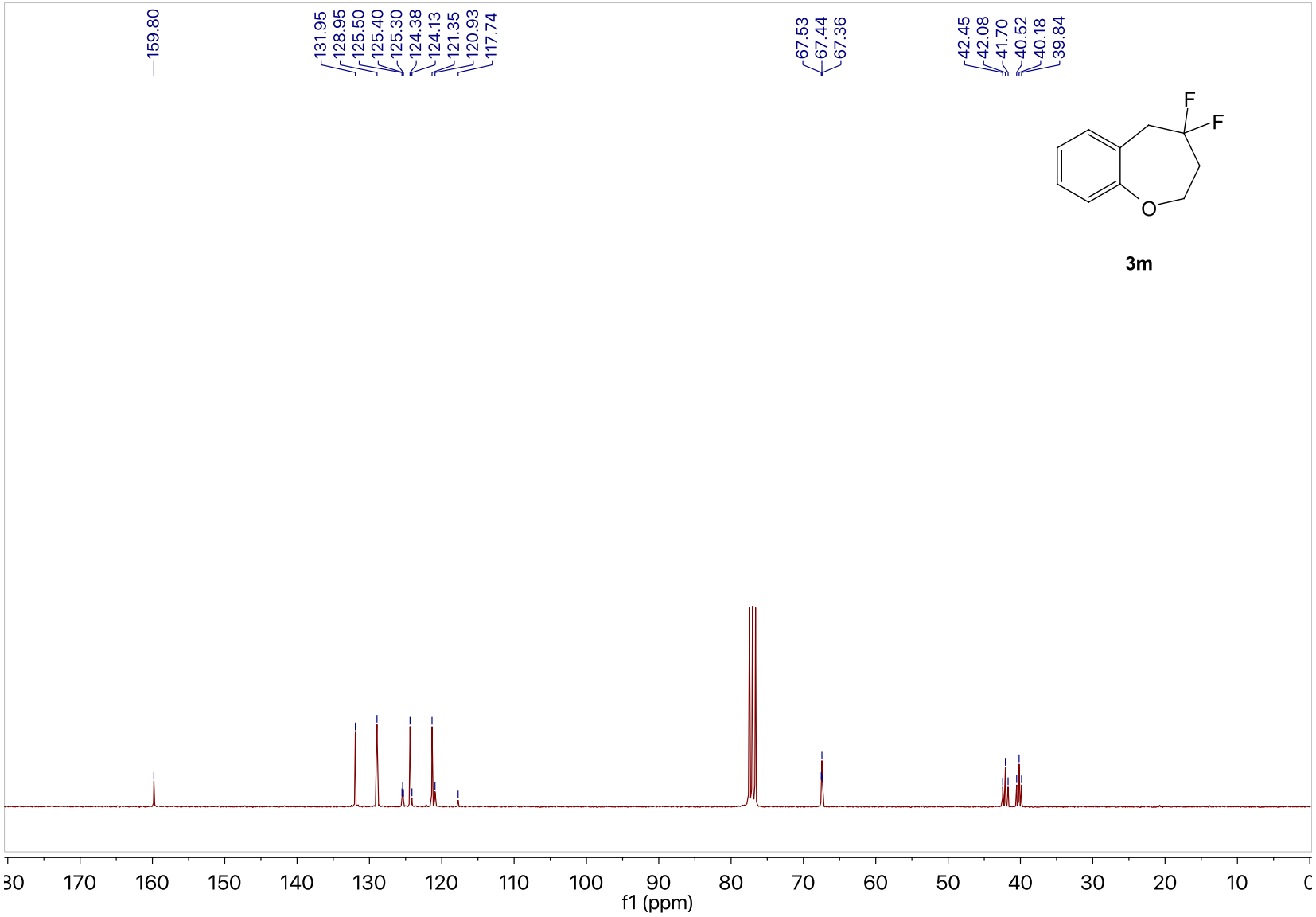
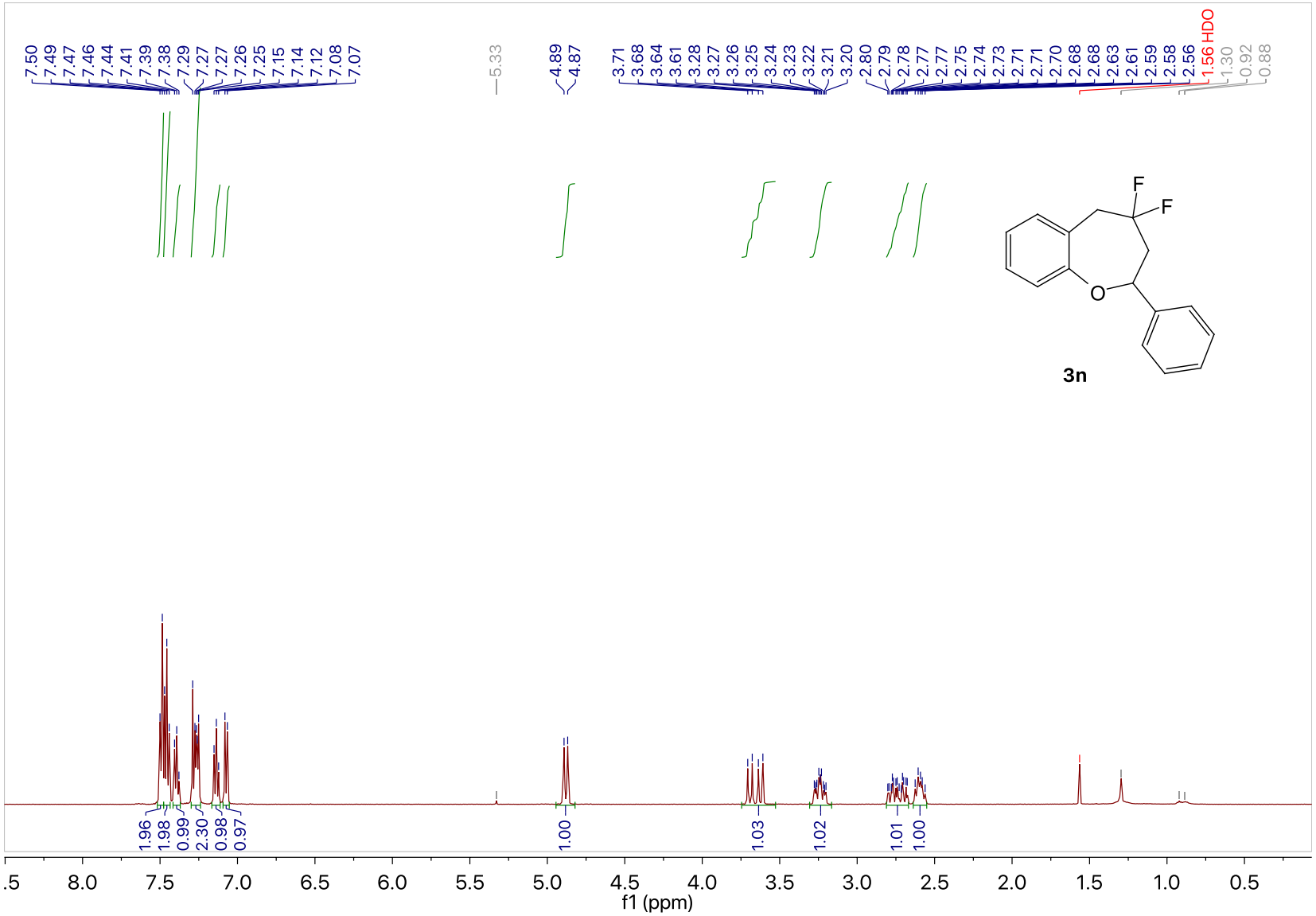
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

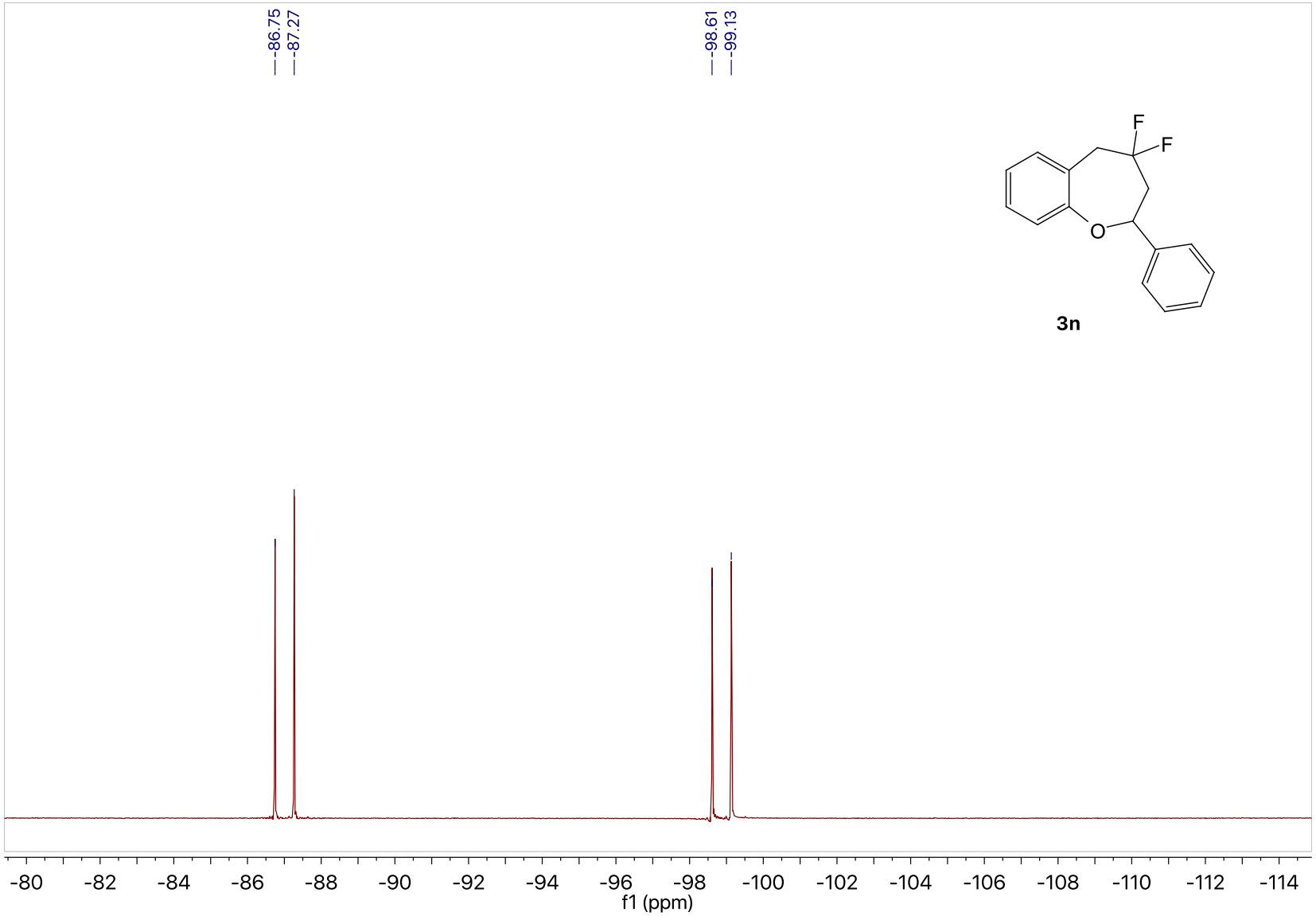

141.03
134.64
134.58
134.52
133.89
130.73
130.45
123.09
121.17
120.01
119.25
43.81
43.58
43.35
39.48
39.28
39.07
34.19
22.54
22.49
22.44
Br
F
F
3k
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

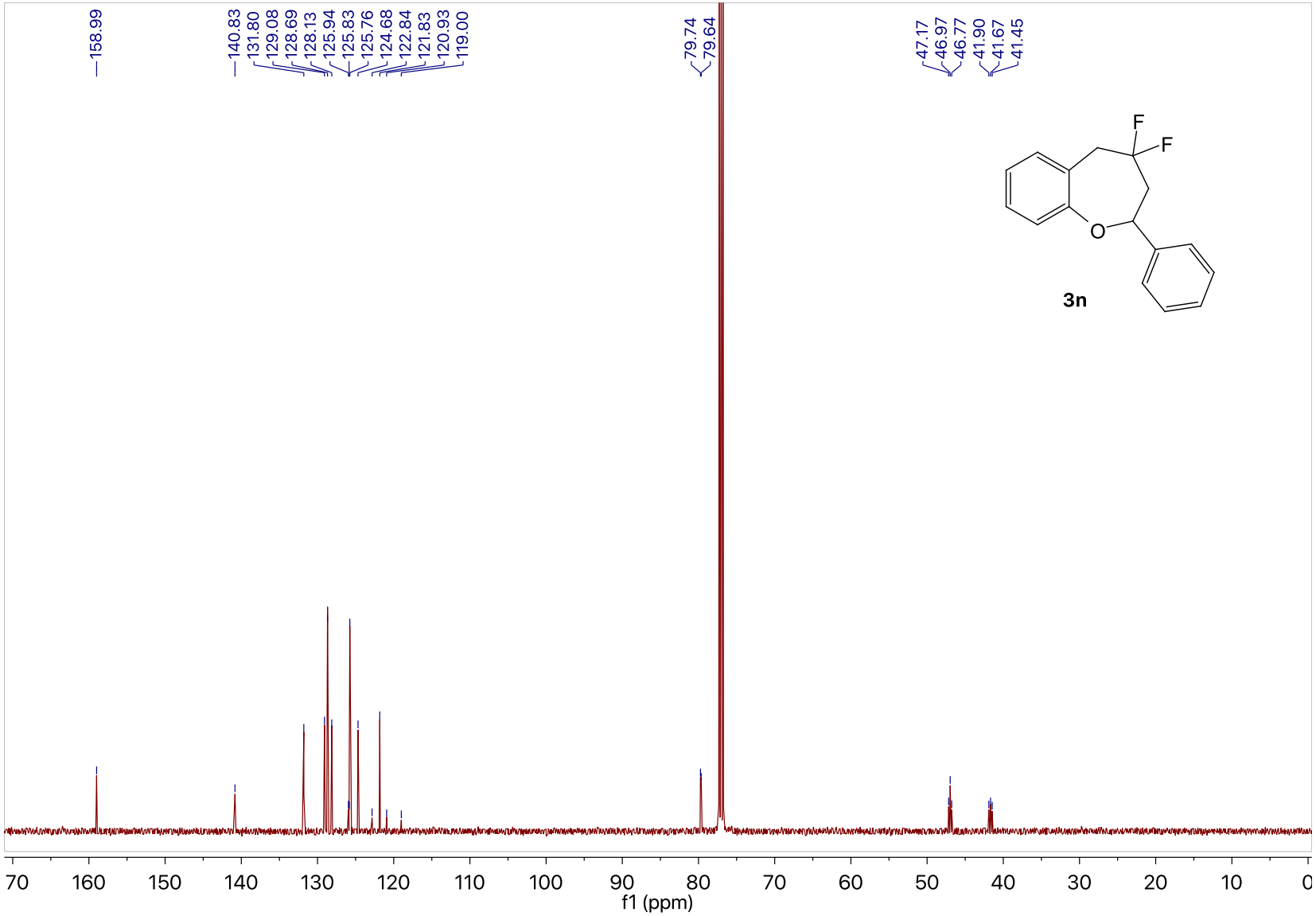

7.25
7.22
7.20
7.18
7.16
7.08
7.05
7.02
6.99
4.09
4.07
4.05
3.36
3.31
3.26
2.48
2.47
2.44
2.42
2.40
2.38
2.36
F
F
O
3m
0.83
0.91
0.83
1.12
2.00
2.03
2.05
f1 (ppm)

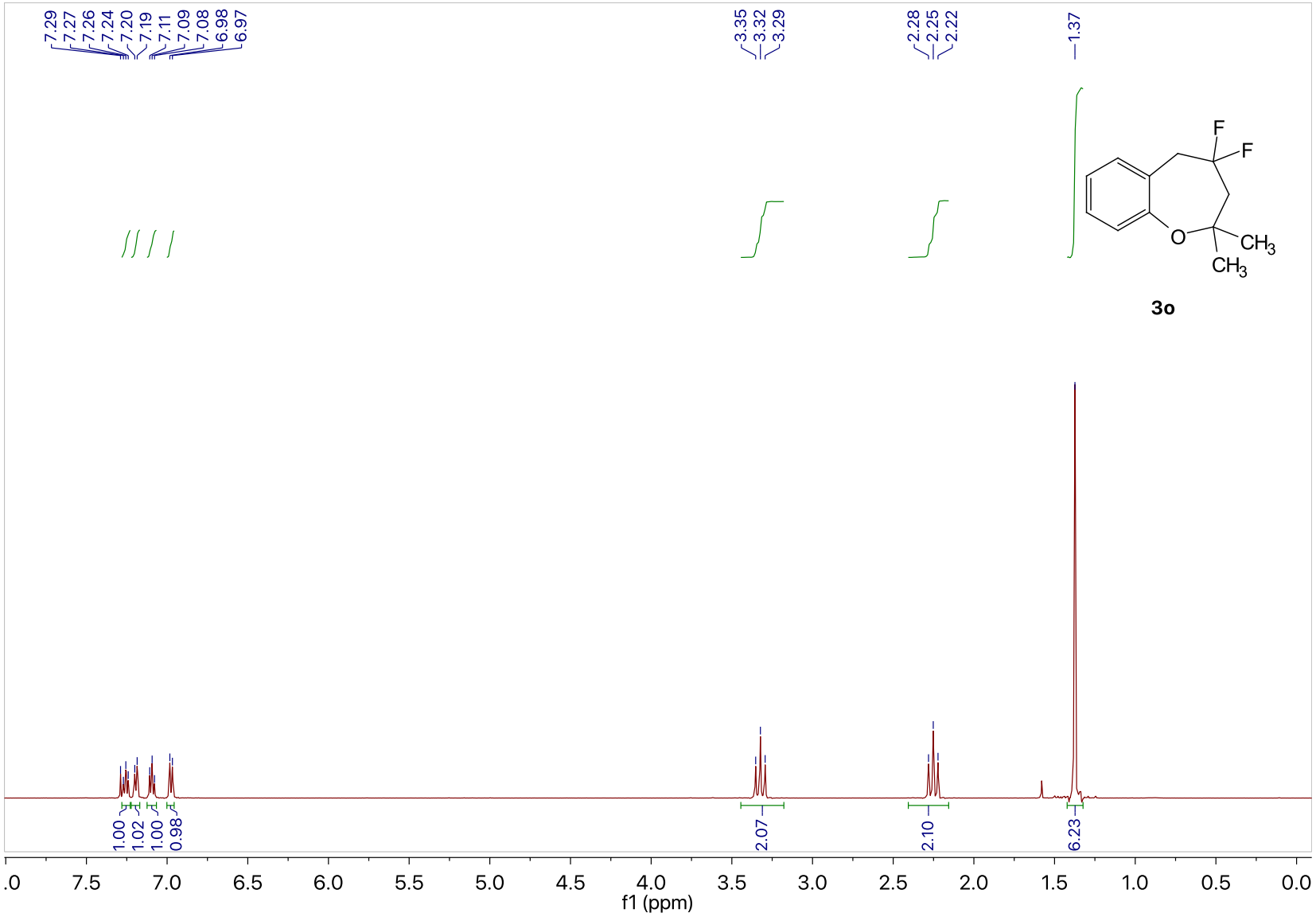

-94.43
F
F
O
3m
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

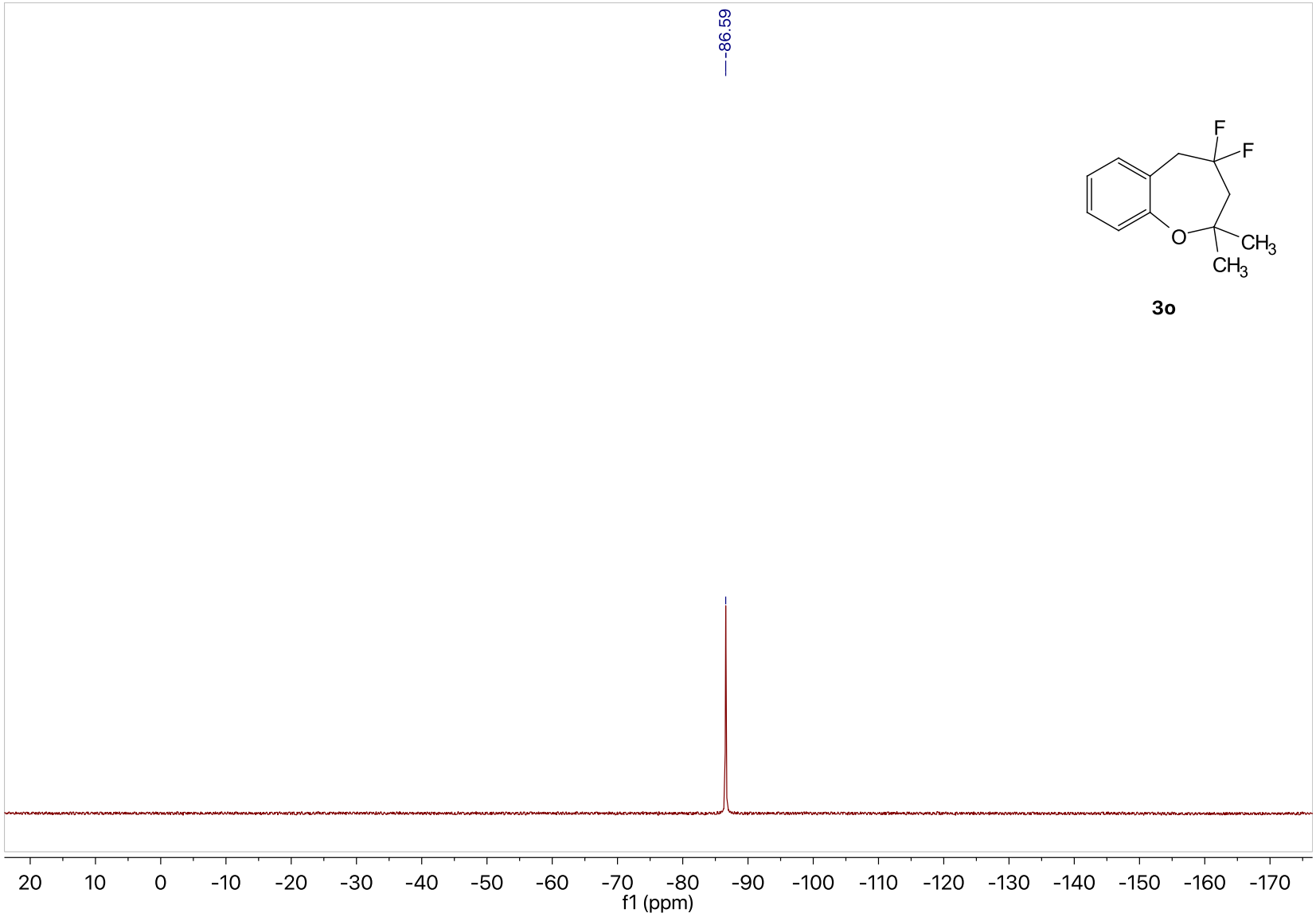

159.80
131.95
128.95
125.50
125.40
125.30
124.38
124.13
121.35
120.93
117.74
67.53
67.44
67.36
42.45
42.08
41.70
40.52
40.18
39.84
F
F
O
3m
f1 (ppm)

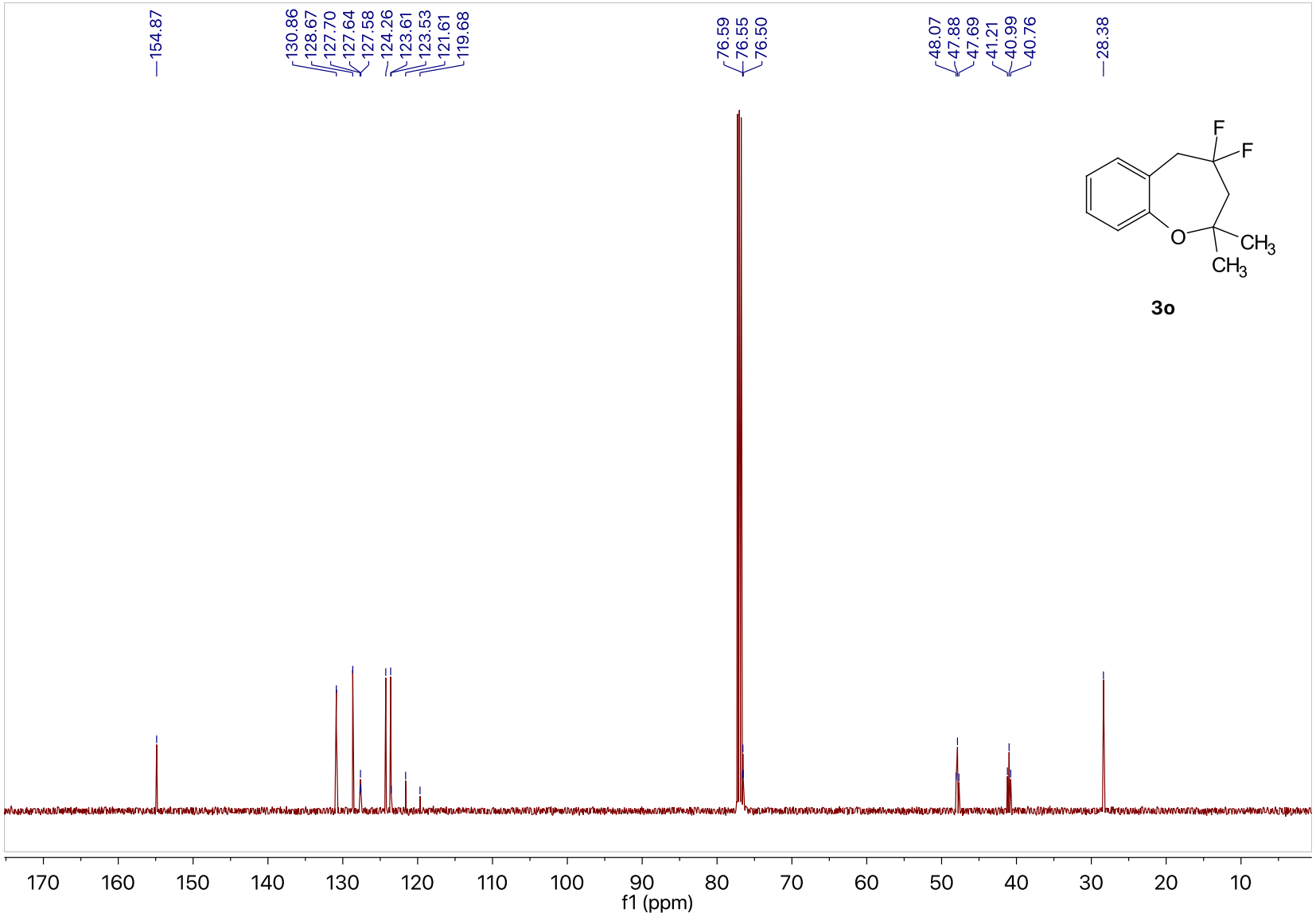

7.50
7.49
7.47
7.46
7.44
7.41
7.39
7.38
7.29
7.27
7.27
7.26
7.25
7.15
7.14
7.12
7.08
7.07
5.33
4.89
4.87
3.71
3.68
3.64
3.61
3.28
3.27
3.26
3.25
3.24
3.23
3.22
3.21
3.20
2.80
2.79
2.78
2.77
2.77
2.75
2.74
2.73
2.71
2.71
2.70
2.68
2.68
2.63
2.61
2.59
2.58
2.56
1.56 HDO
1.30
0.92
0.88
F
F
O
3n
1.96
1.98
0.99
2.30
0.98
0.97
1.00
1.03
1.02
1.01
1.00
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

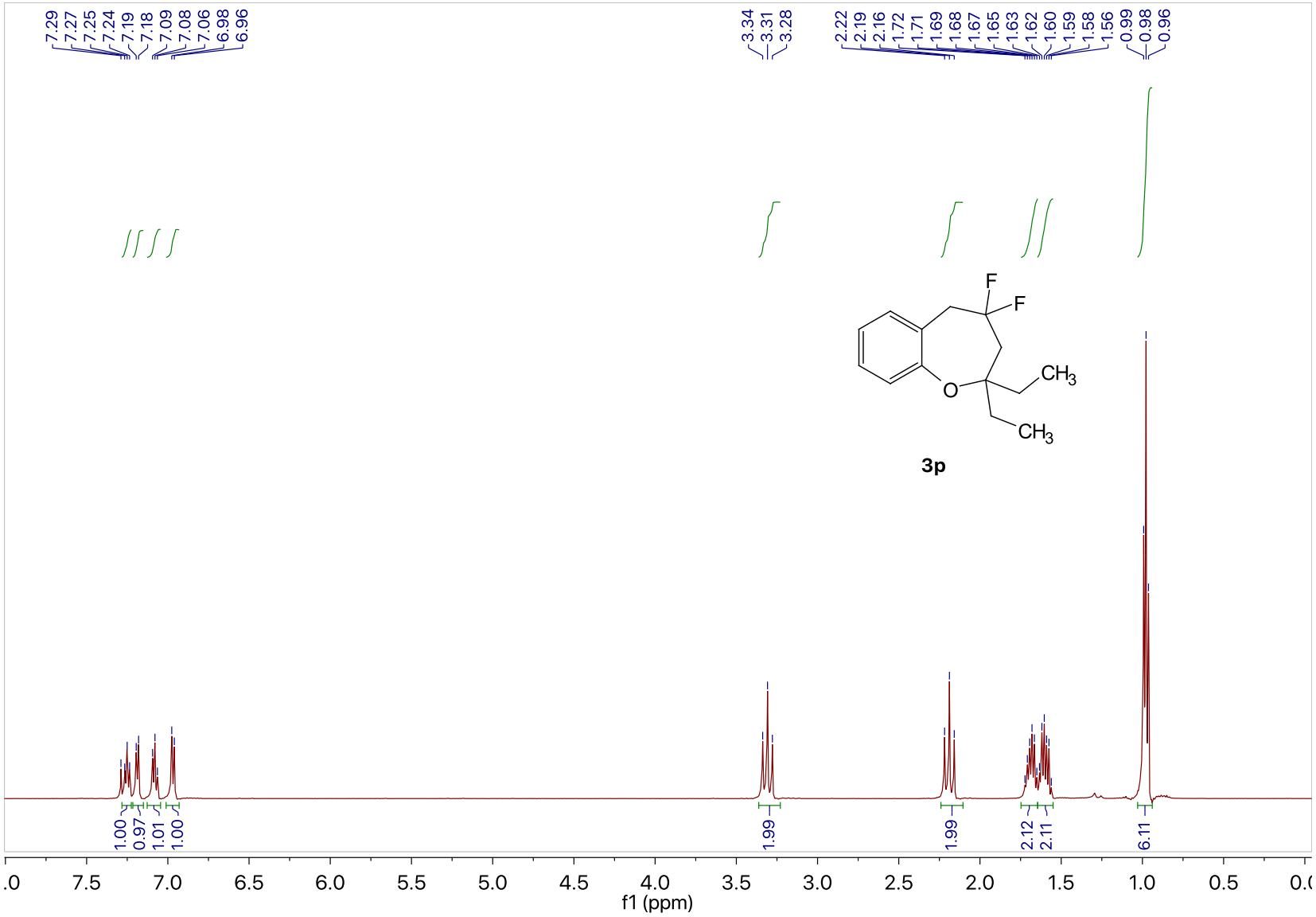

-86.75
-87.27
-98.61
-99.13
F
F
O
3n
-80
-82
-84
-86
-88
-90
-92
-94
-96
-98
-100
-102
-104
-106
-108
-110
-112
-114
f1 (ppm)

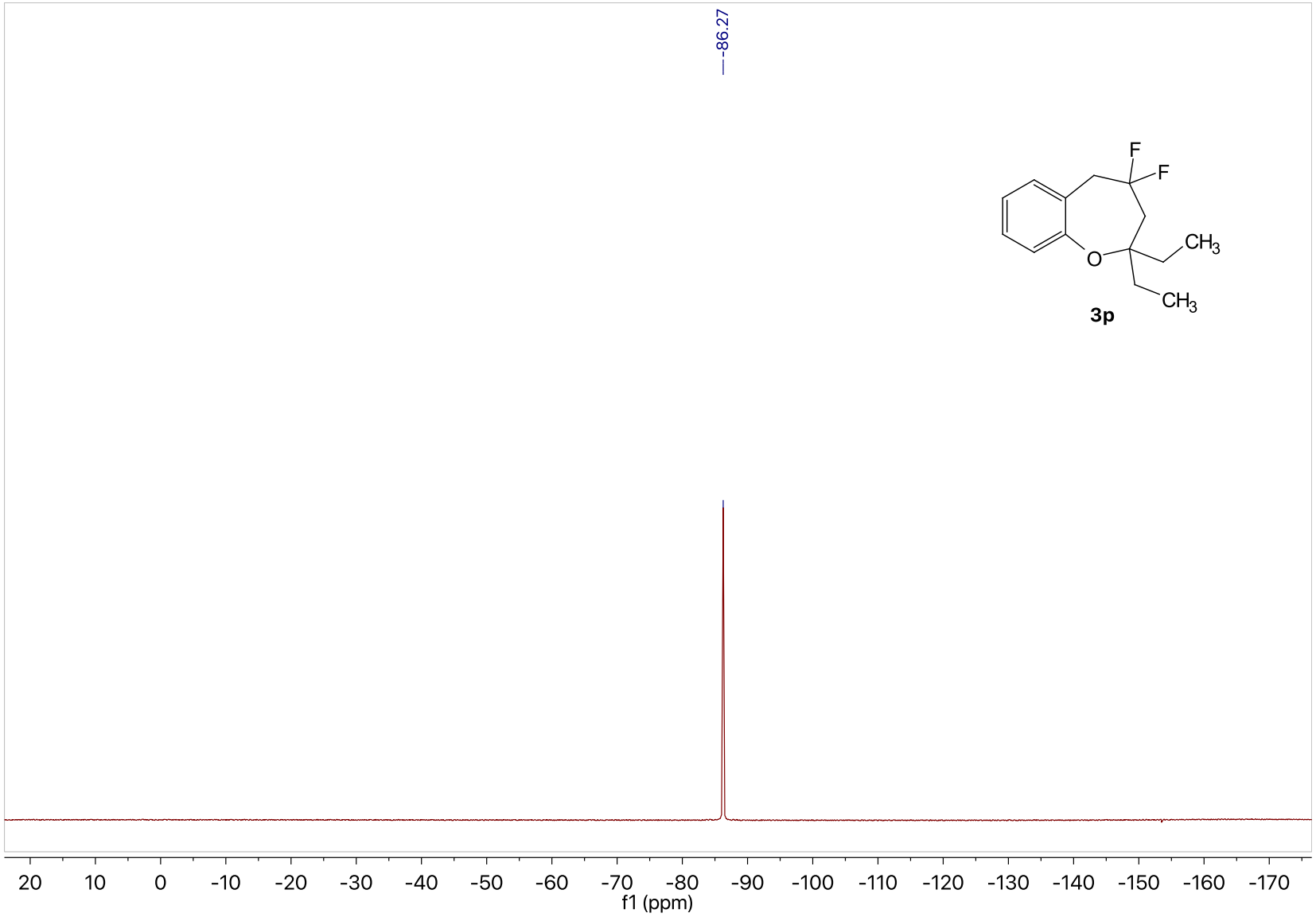

158.99
140.83
131.80
129.08
128.69
128.13
125.94
125.83
125.76
124.68
122.84
121.83
120.93
119.00
79.74
79.64
47.17
46.97
46.77
41.90
41.67
41.45
F
F
O
3n
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

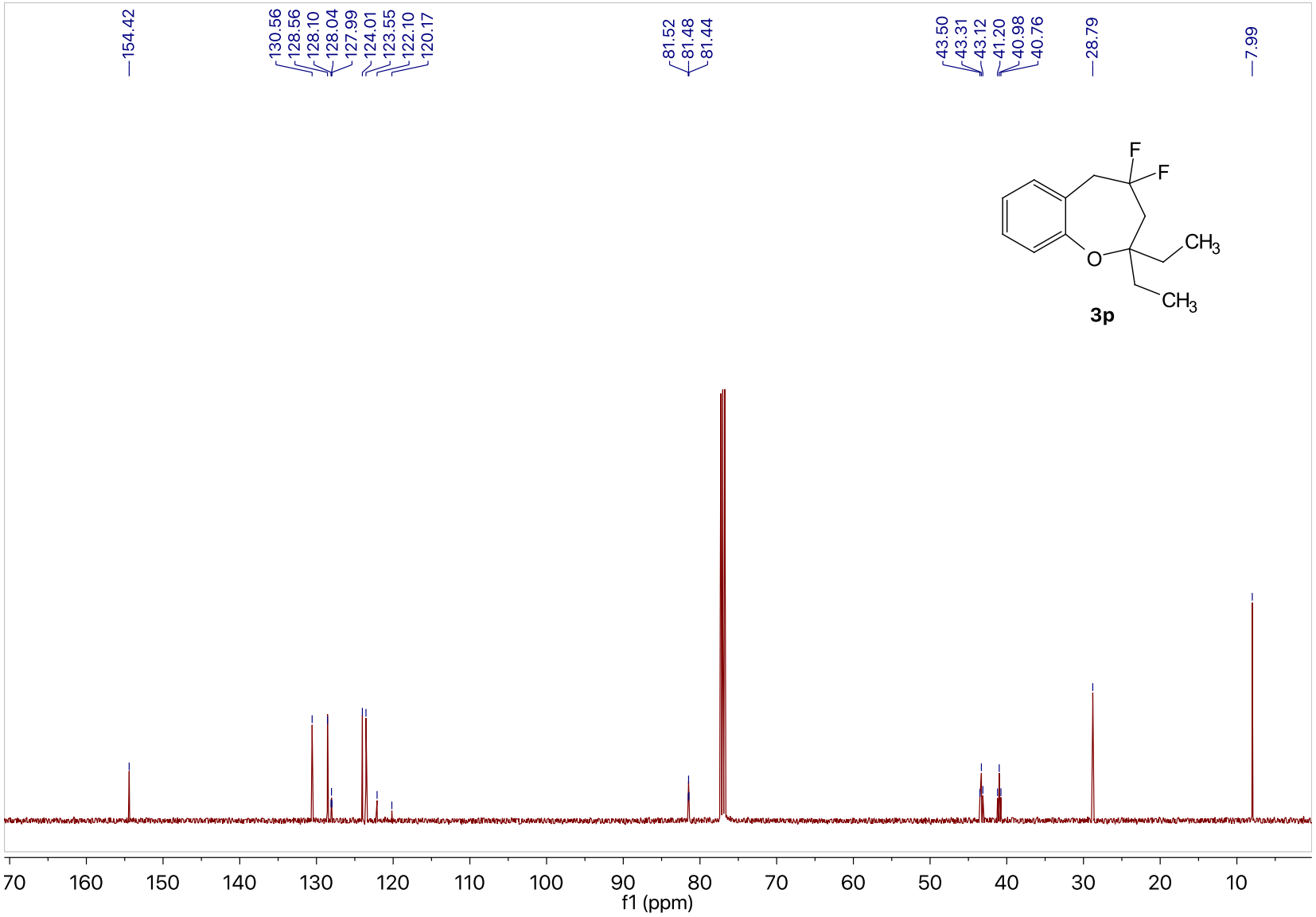

7.29
7.27
7.26
7.24
7.20
7.19
7.11
7.09
7.08
6.98
6.97
3.35
3.32
3.29
2.28
2.25
2.22
1.37
F
F
O
CH3
CH3
3o
1.00
1.02
1.00
0.98
2.07
2.10
6.23
f1 (ppm)

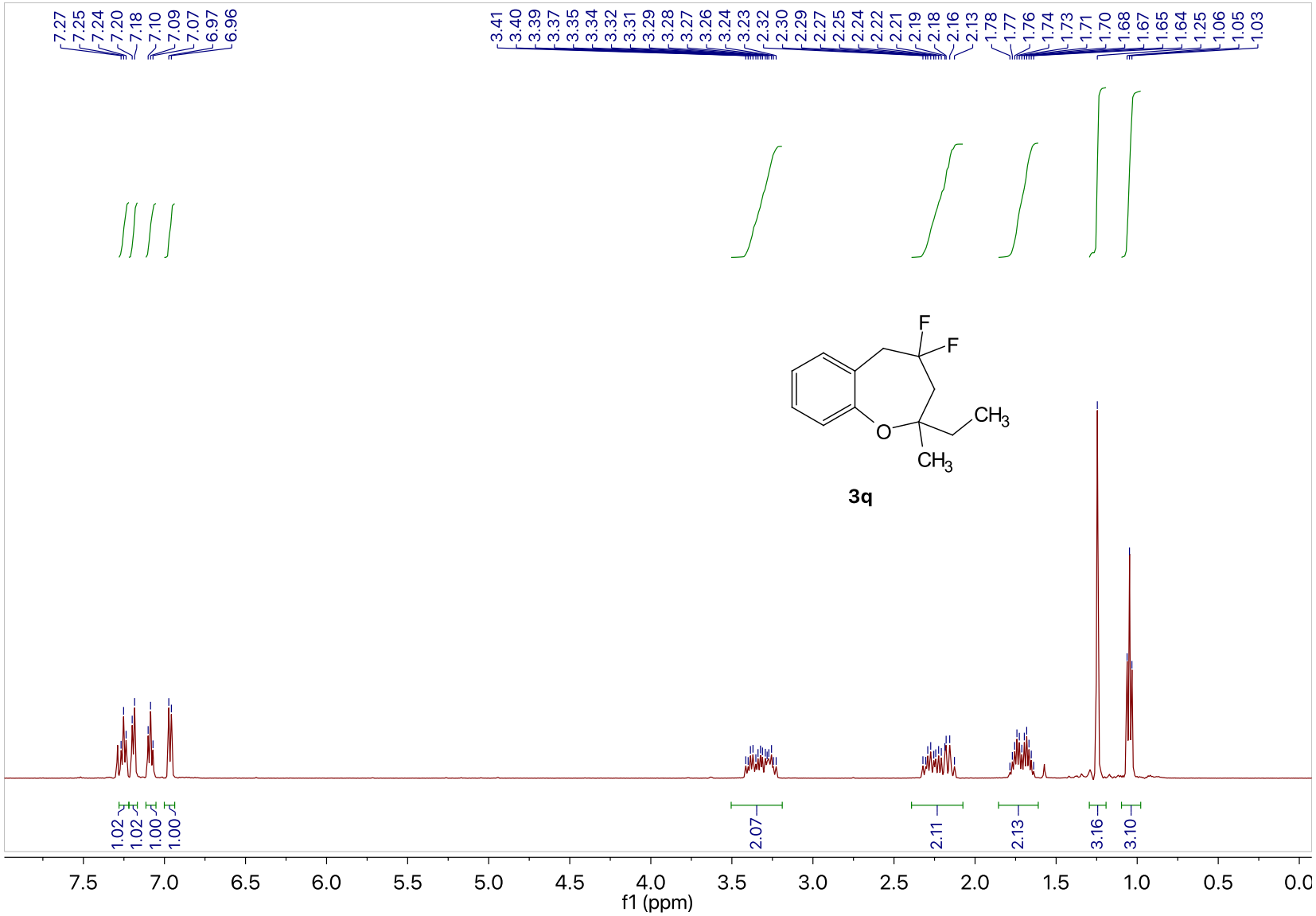

-86.59
F
F
O
CH3
CH3
3o
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

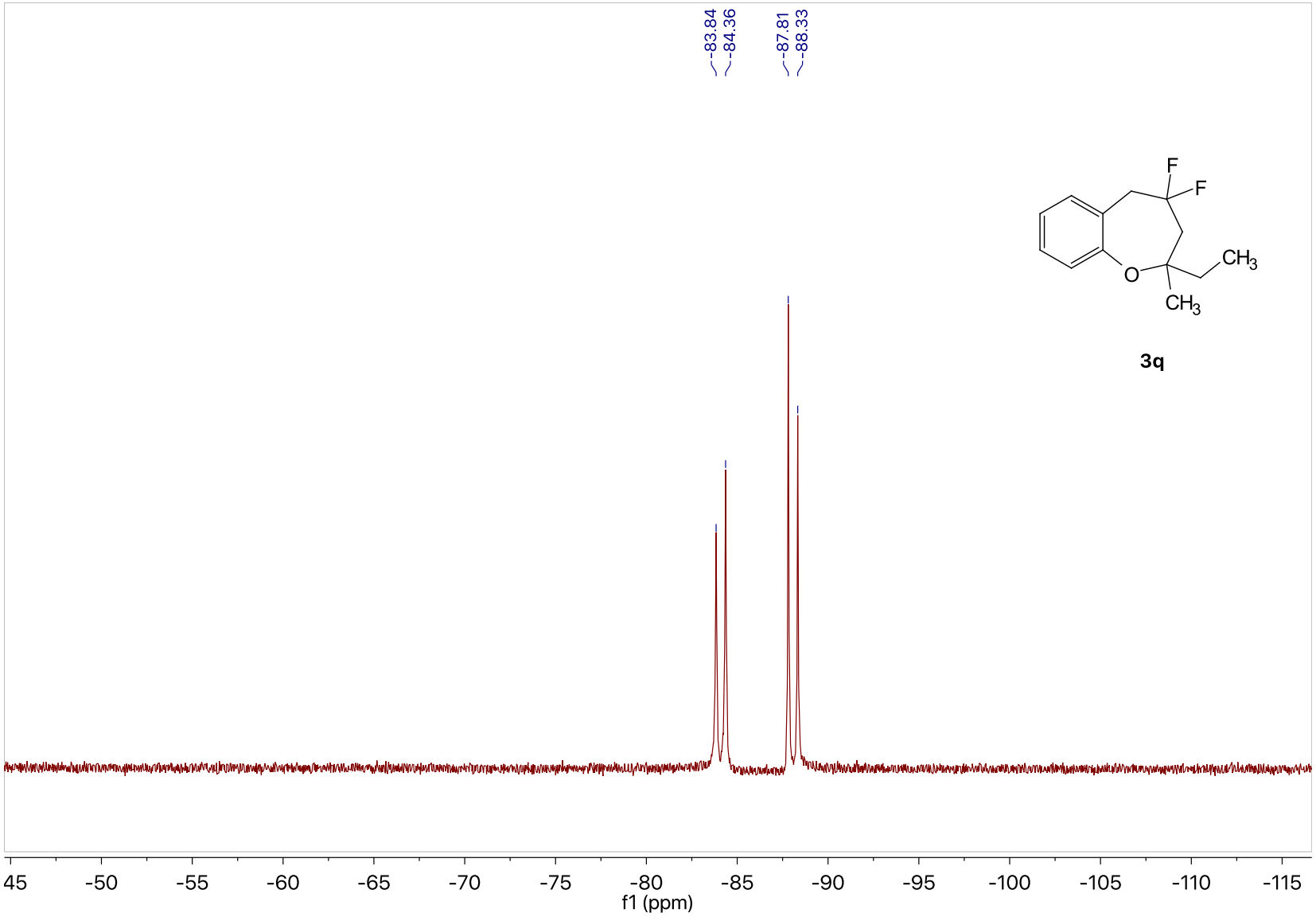

154.87
130.86
128.67
127.70
127.64
127.58
124.26
123.61
123.53
121.61
119.68
76.59
76.55
76.50
48.07
47.88
47.69
41.21
40.99
40.76
28.38
F
F
O
CH3
CH3
3o
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

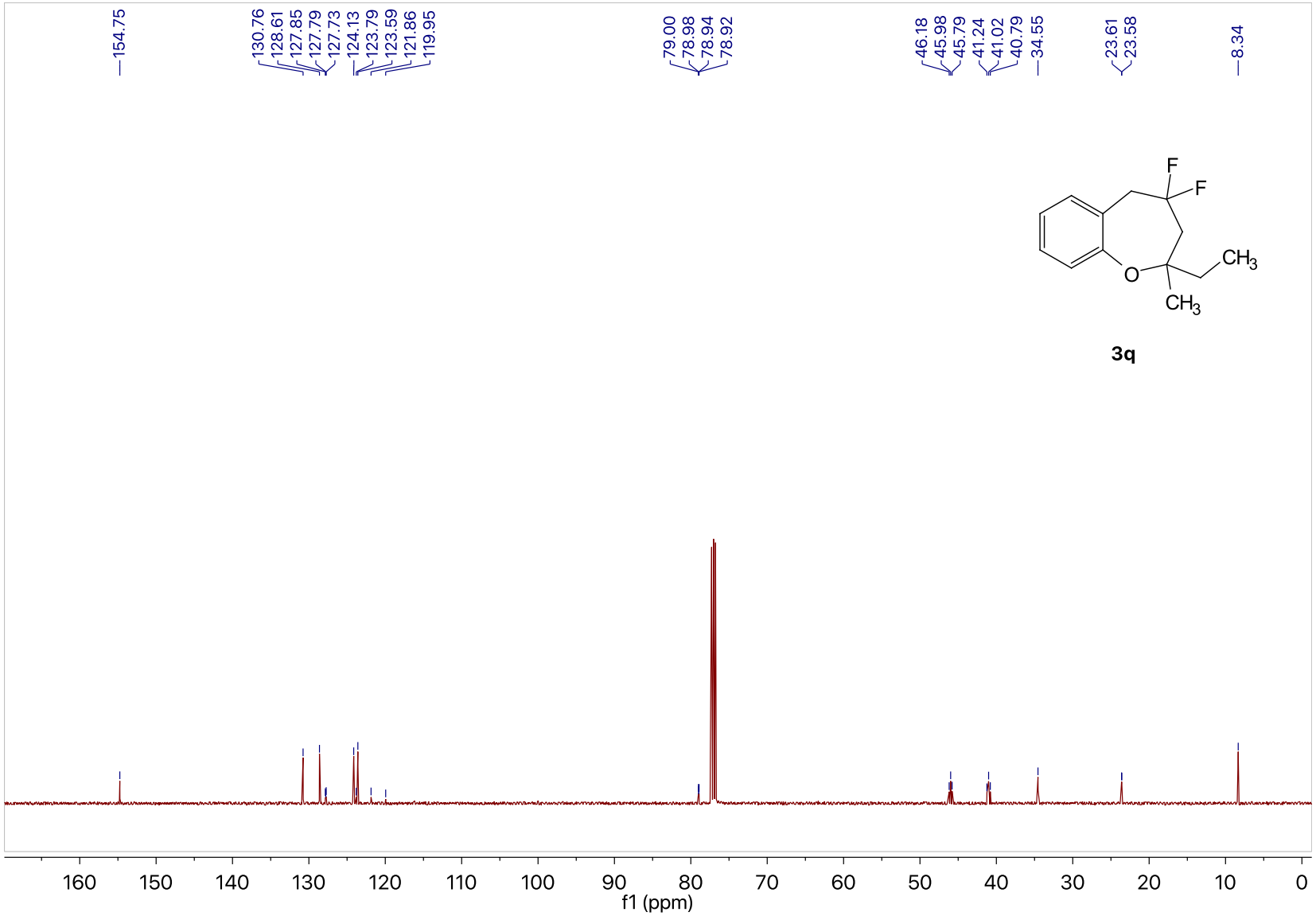

7.29
7.27
7.25
7.24
7.19
7.18
7.09
7.08
7.06
6.98
6.96
3.34
3.31
3.28
2.22
2.19
2.16
1.72
1.71
1.69
1.68
1.67
1.65
1.63
1.62
1.60
1.59
1.58
1.56
0.99
0.98
0.96
F
F
CH3
O
CH3
3p
1.00
0.97
1.01
1.00
1.99
1.99
2.12
2.11
6.11
f1 (ppm)


-86.27
F
F
CH3
O
CH3
3p
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

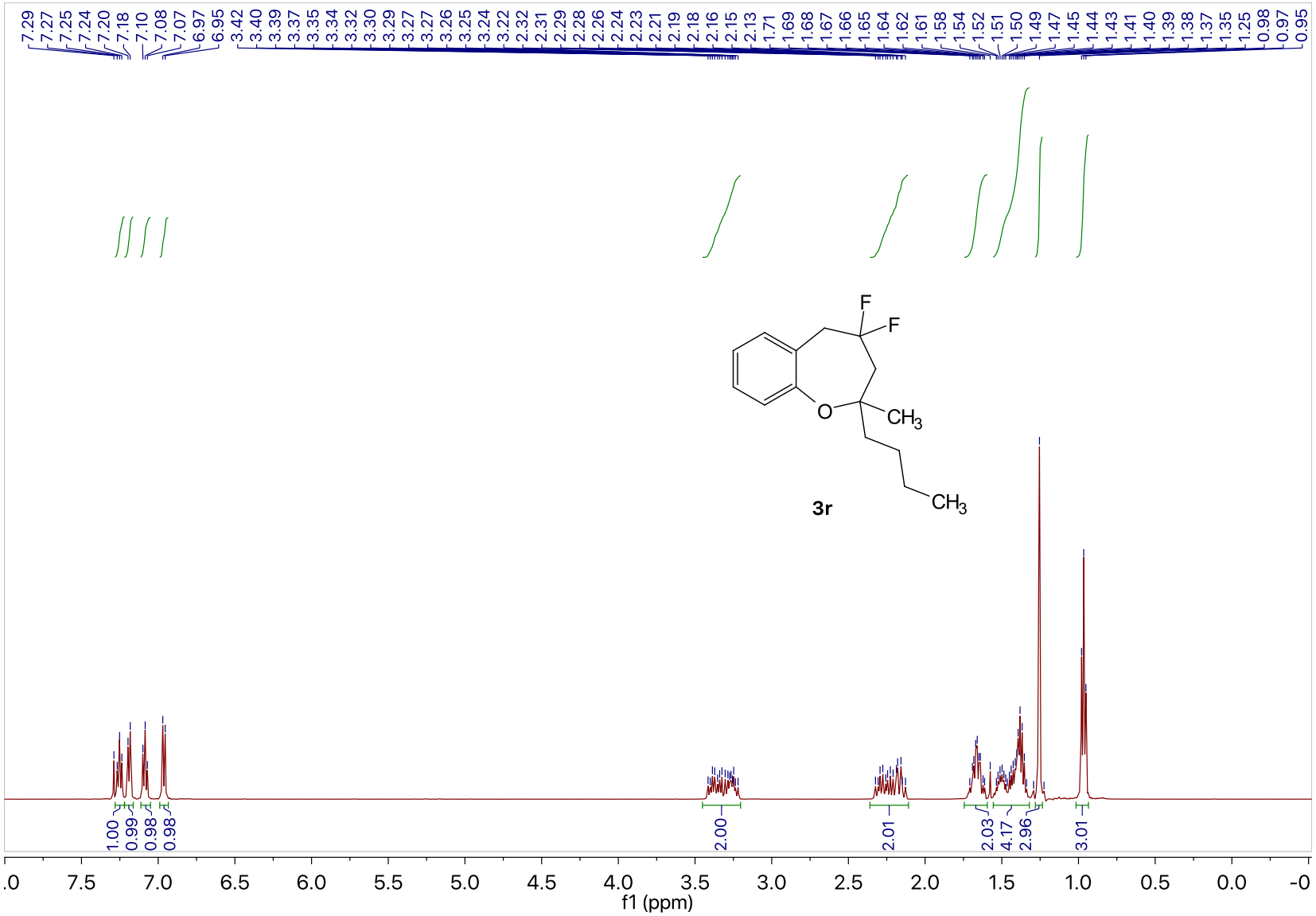

154.42
130.56
128.56
128.10
128.04
127.99
124.01
123.55
122.10
120.17
81.52
81.48
81.44
43.50
43.31
43.12
41.20
40.98
40.76
28.79
7.99
F
F
CH3
O
CH3
3p
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

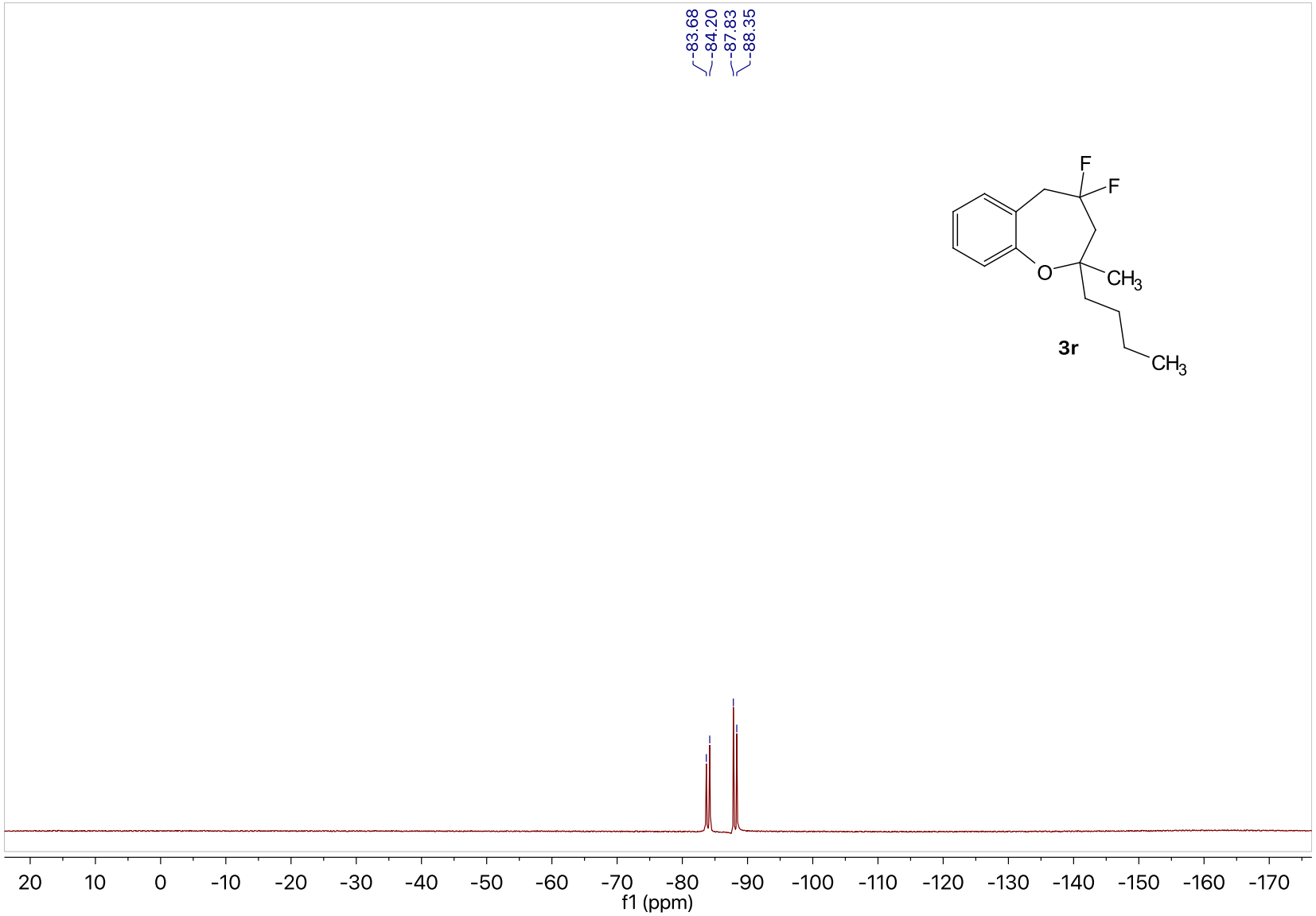

7.27
7.25
7.24
7.20
7.18
7.10
7.09
7.07
6.97
6.96
3.41
3.40
3.39
3.37
3.35
3.34
3.32
3.31
3.29
3.28
3.27
3.26
3.24
3.23
2.32
2.30
2.29
2.27
2.25
2.24
2.22
2.21
2.19
2.18
2.16
2.13
1.78
1.77
1.76
1.74
1.73
1.71
1.70
1.68
1.67
1.65
1.64
1.25
1.06
1.05
1.03
F
F
CH3
O
CH3
3q
1.02
1.02
1.00
1.00
2.07
2.11
2.13
3.16
3.10
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

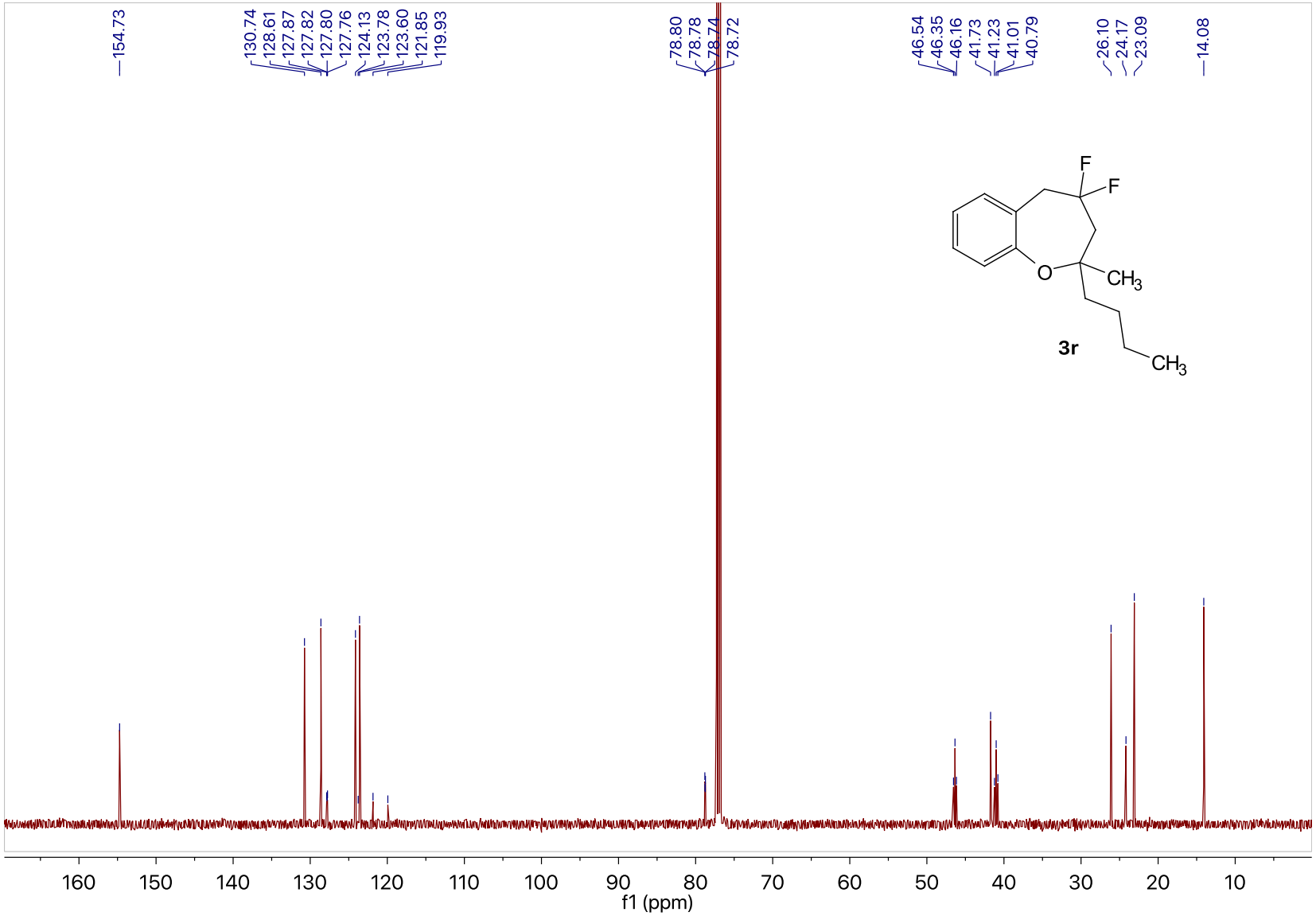

-83.84
-84.36
-87.81
-88.33
F
F
CH3
O
CH3
3q
45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
f1 (ppm)

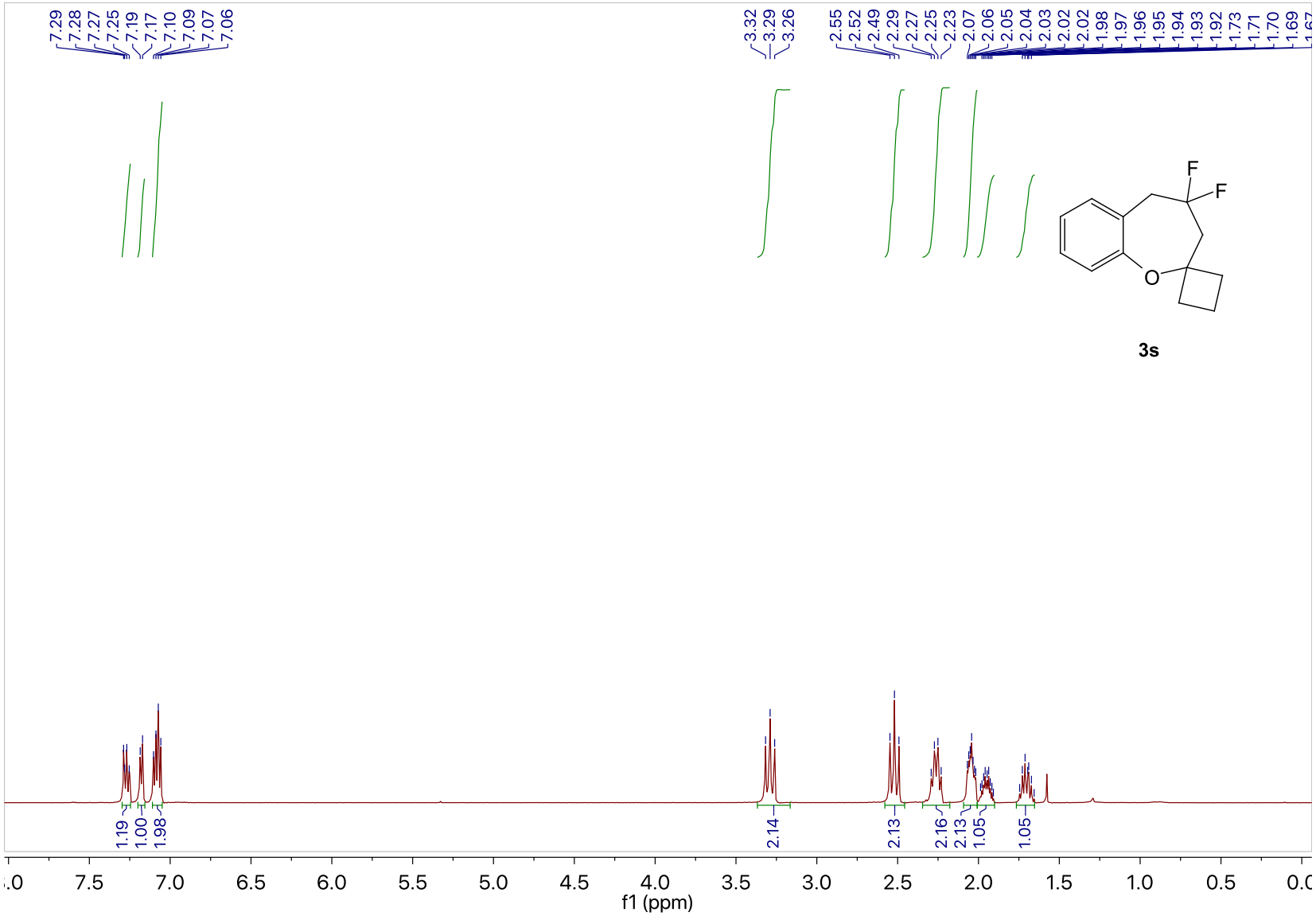

154.75
130.76
128.61
127.85
127.79
127.73
124.13
123.79
123.59
121.86
119.95
79.00
78.98
78.94
78.92
46.18
45.98
45.79
41.24
41.02
40.79
34.55
23.61
23.58
8.34
F
F
O
CH3
CH3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

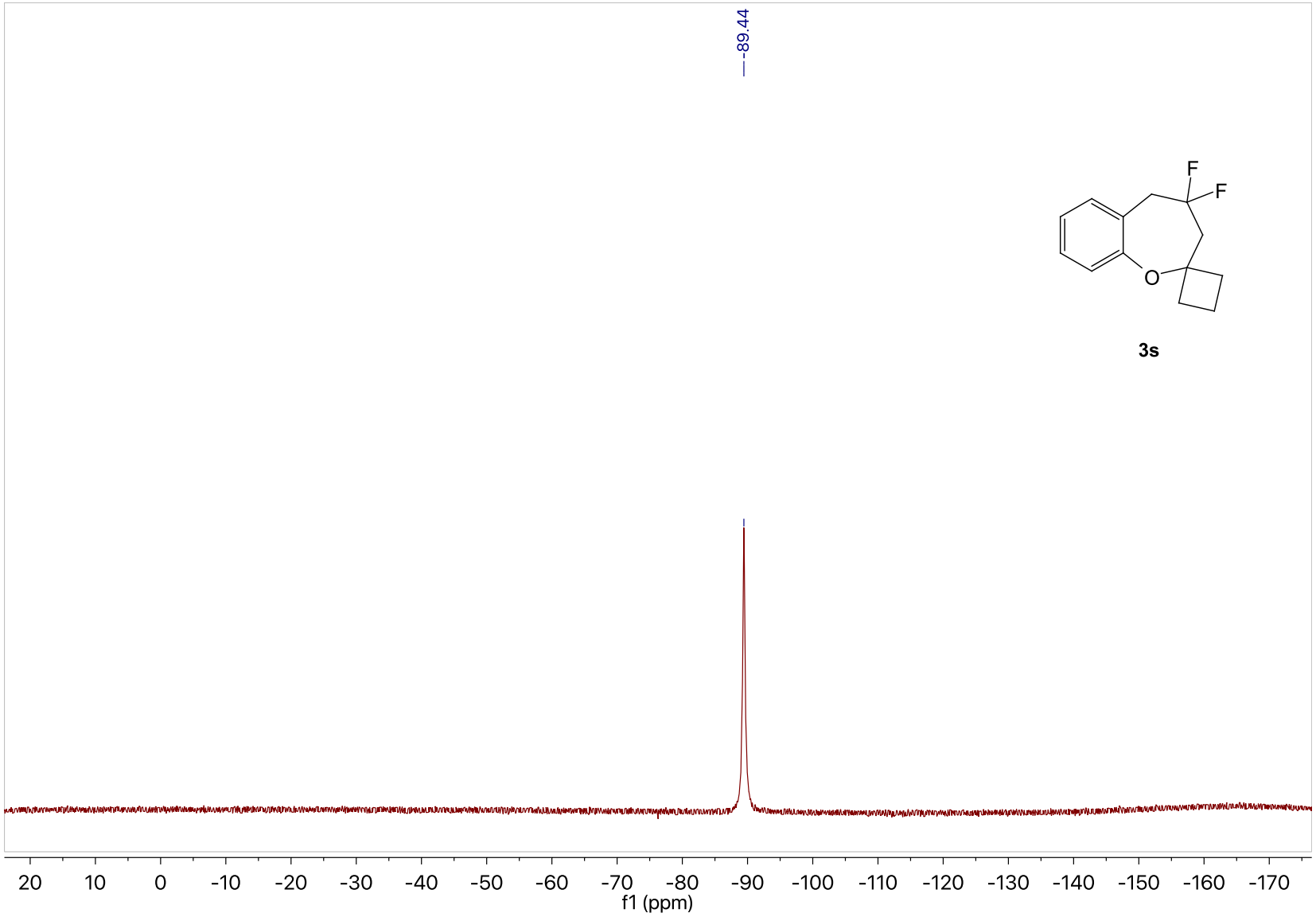
3q

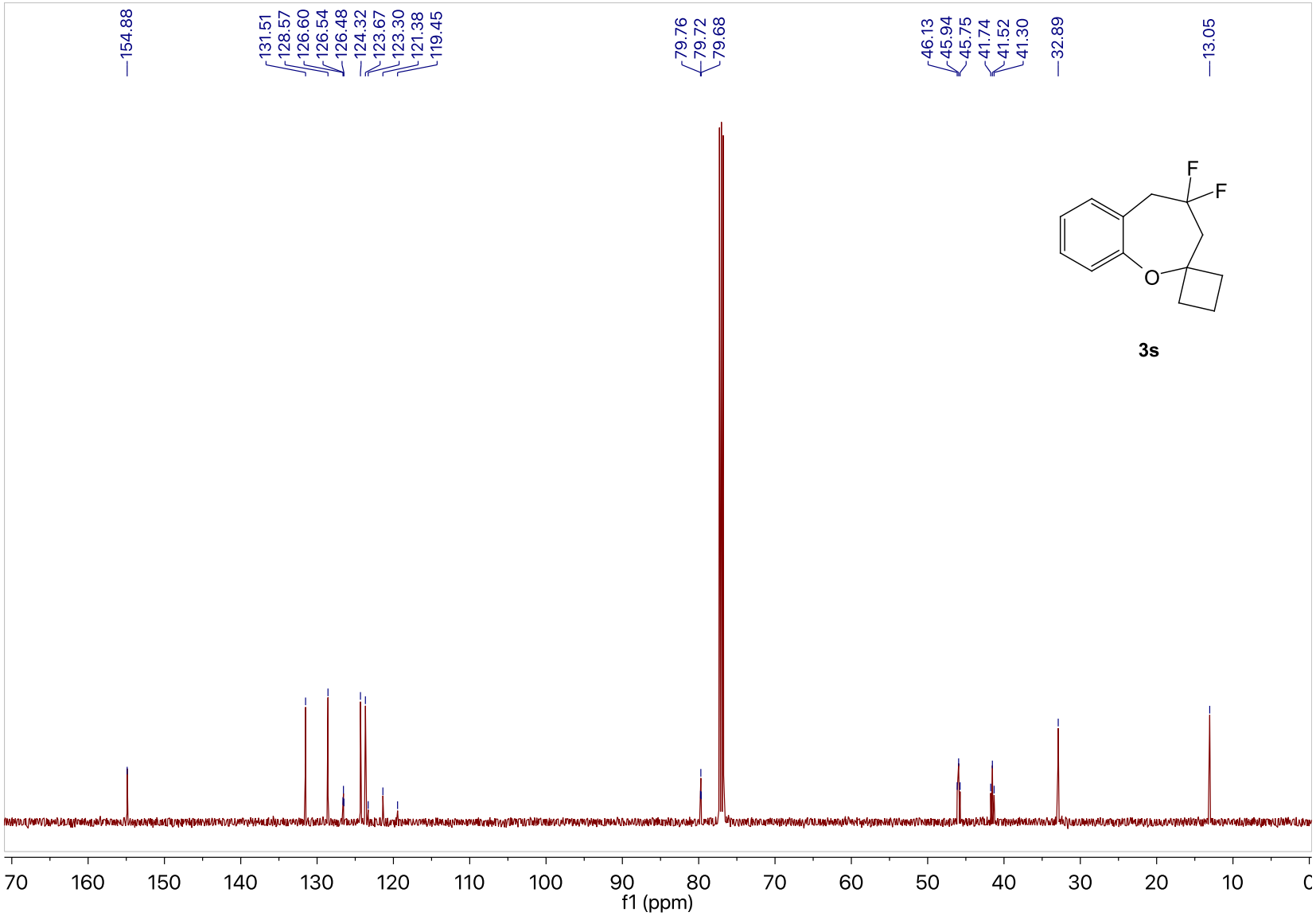

7.29
7.27
7.25
7.24
7.20
7.18
7.10
7.08
7.07
6.97
6.95
3.42
3.40
3.39
3.37
3.35
3.34
3.32
3.30
3.29
3.27
3.27
3.26
3.25
3.24
3.22
2.32
2.31
2.29
2.28
2.26
2.24
2.23
2.21
2.19
2.18
2.16
2.15
2.13
1.71
1.69
1.68
1.67
1.66
1.65
1.64
1.62
1.61
1.58
1.54
1.52
1.51
1.50
1.49
1.47
1.45
1.44
1.43
1.41
1.40
1.39
1.38
1.37
1.35
1.25
0.98
0.97
0.95
F
F
O
CH3
CH3
3r
1.00
0.99
0.98
0.98
2.00
2.01
2.03
4.17
2.96
3.01
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

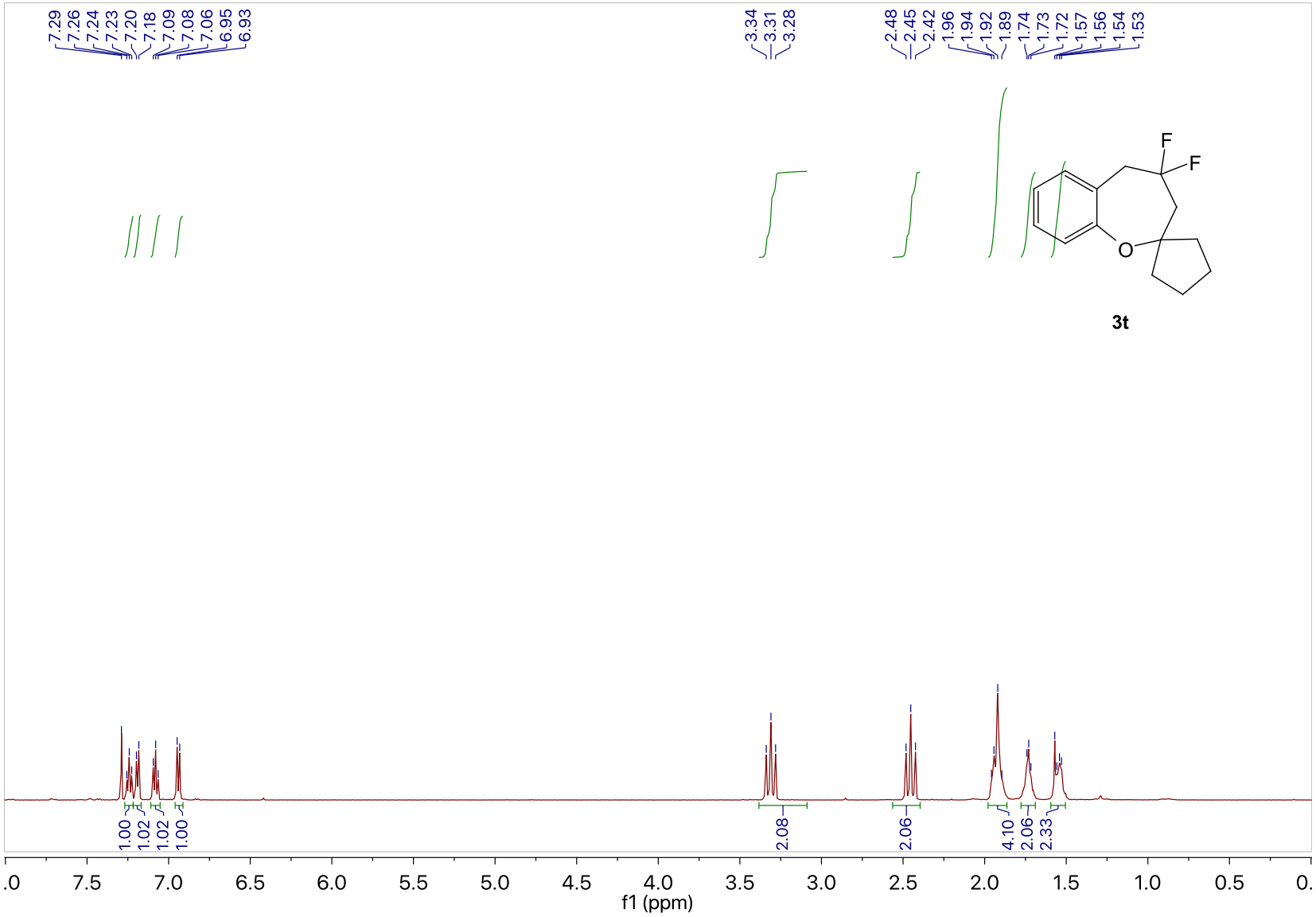

-83.68
-84.20
-87.83
-88.35
F
F
O
CH3
3r
CH3
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170
f1 (ppm)

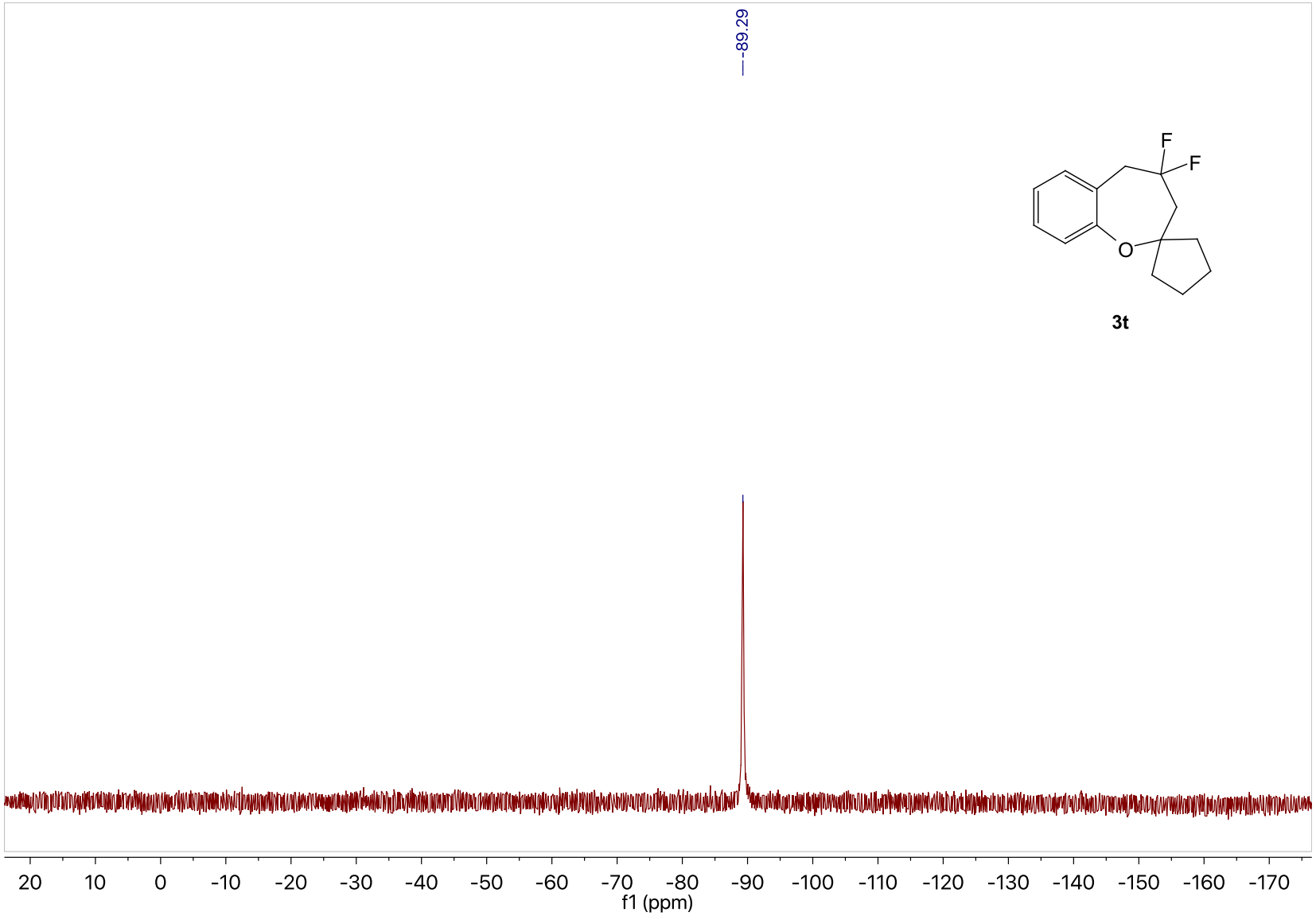

154.73
130.74
128.61
127.87
127.82
127.80
127.76
124.13
123.78
123.60
121.85
119.93
78.80
78.78
78.74
78.72
46.54
46.35
46.16
41.73
41.23
41.01
40.79
26.10
24.17
23.09
14.08
F
F
O
CH3
CH3
3r
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

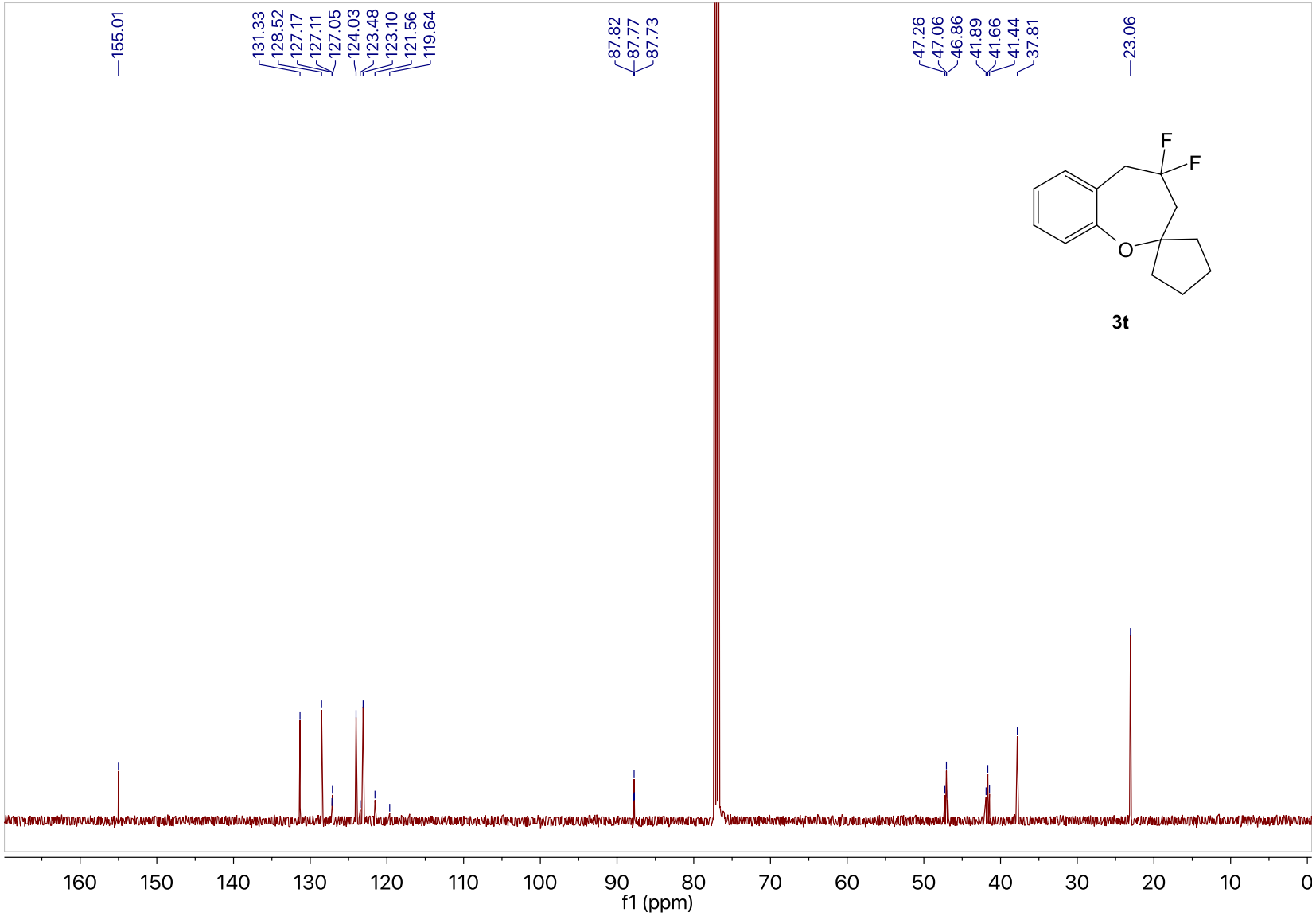

7.29
7.28
7.27
7.25
7.19
7.17
7.10
7.09
7.07
7.06
3.32
3.29
3.26
2.55
2.52
2.49
2.29
2.27
2.25
2.23
2.07
2.06
2.05
2.04
2.03
2.02
2.02
1.98
1.97
1.96
1.95
1.94
1.93
1.92
1.73
1.71
1.70
1.69
F
F
O
3s
1.19
1.00
1.98
2.14
2.13
2.16
2.13
1.05
1.05
f1 (ppm)

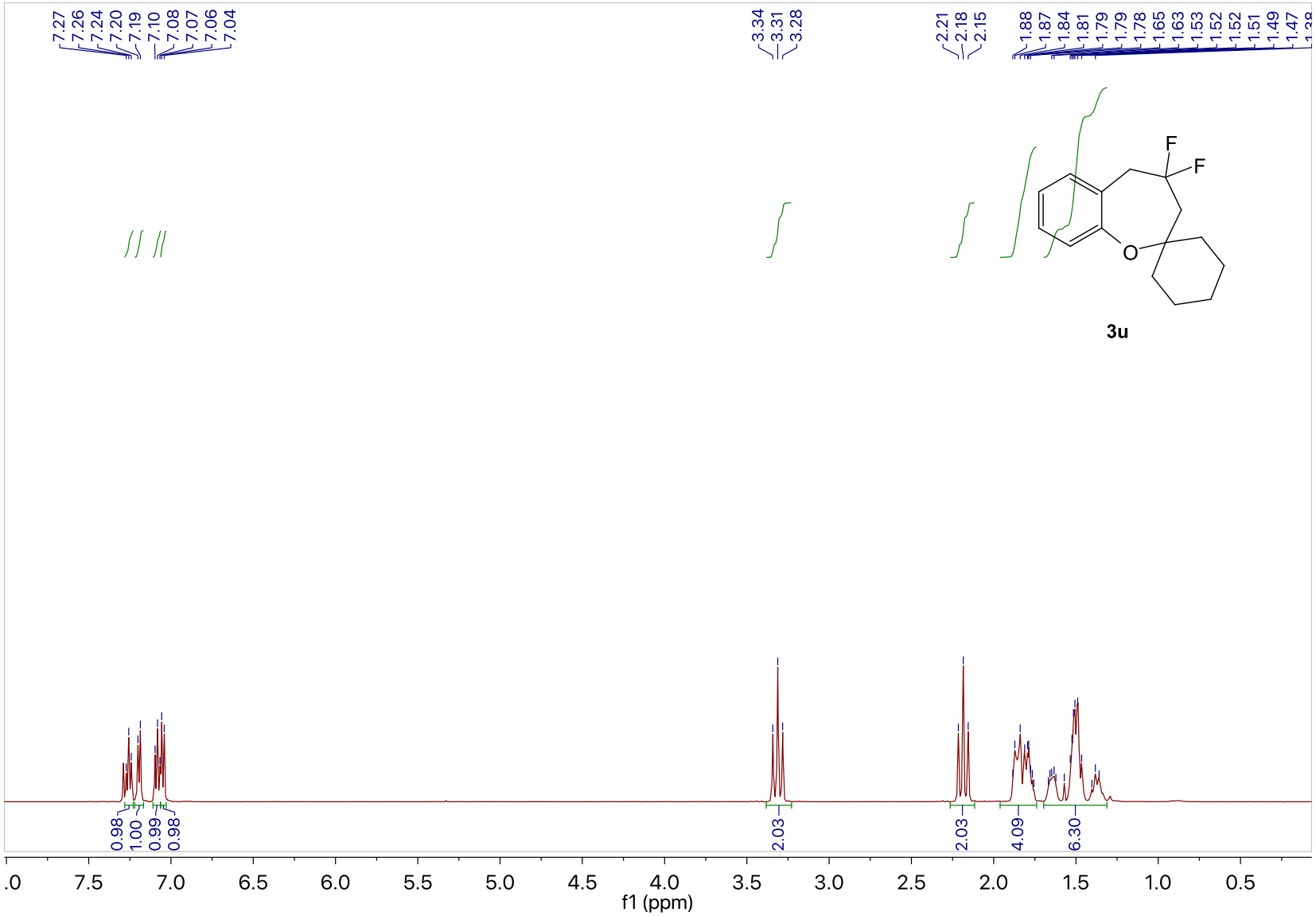

-89.44
F
F
O
3s
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

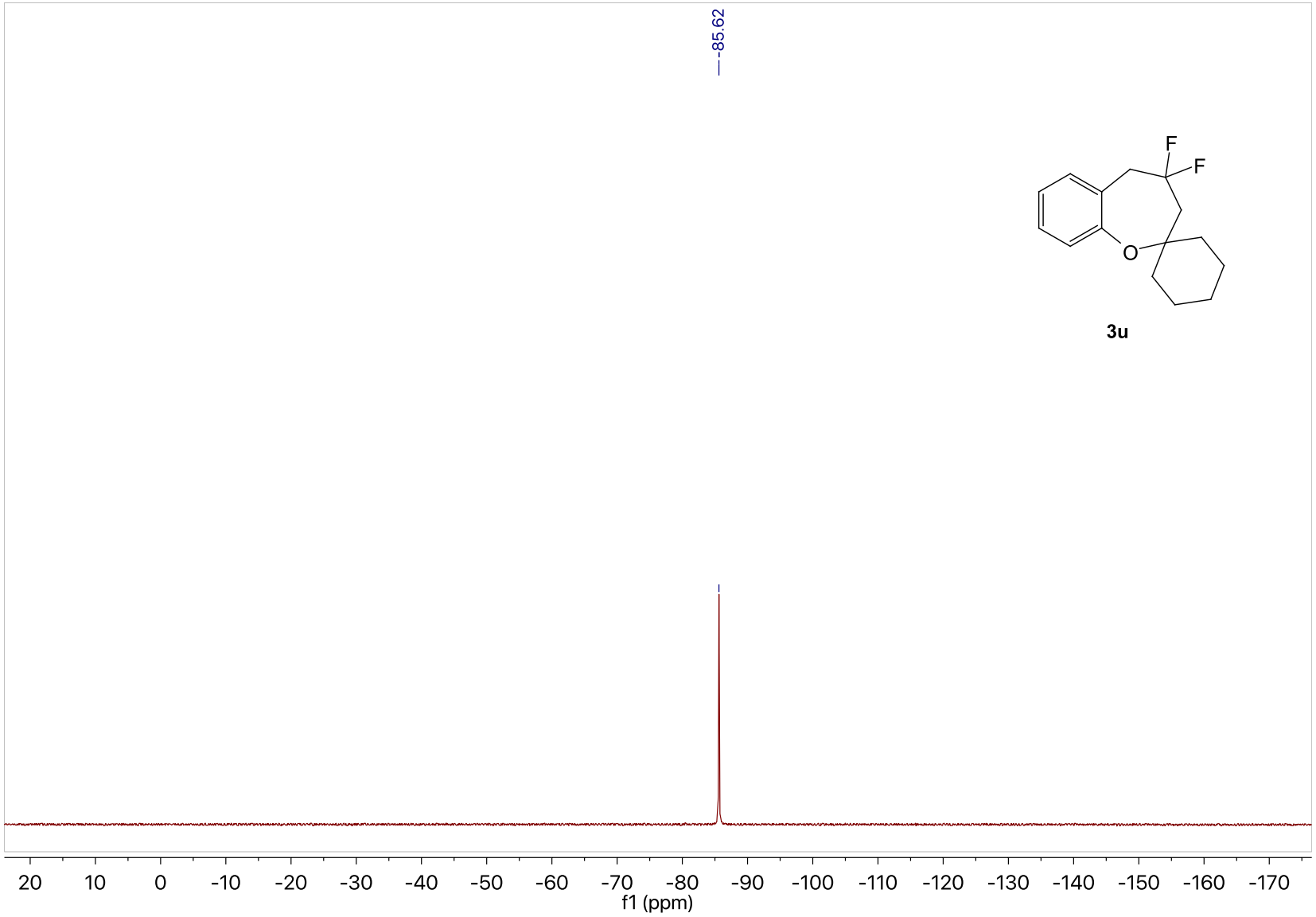

154.88
131.51
128.57
126.60
126.54
126.48
124.32
123.67
123.30
121.38
119.45
79.76
79.72
79.68
46.13
45.94
45.75
41.74
41.52
41.30
32.89
13.05
F
F
O
3s
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

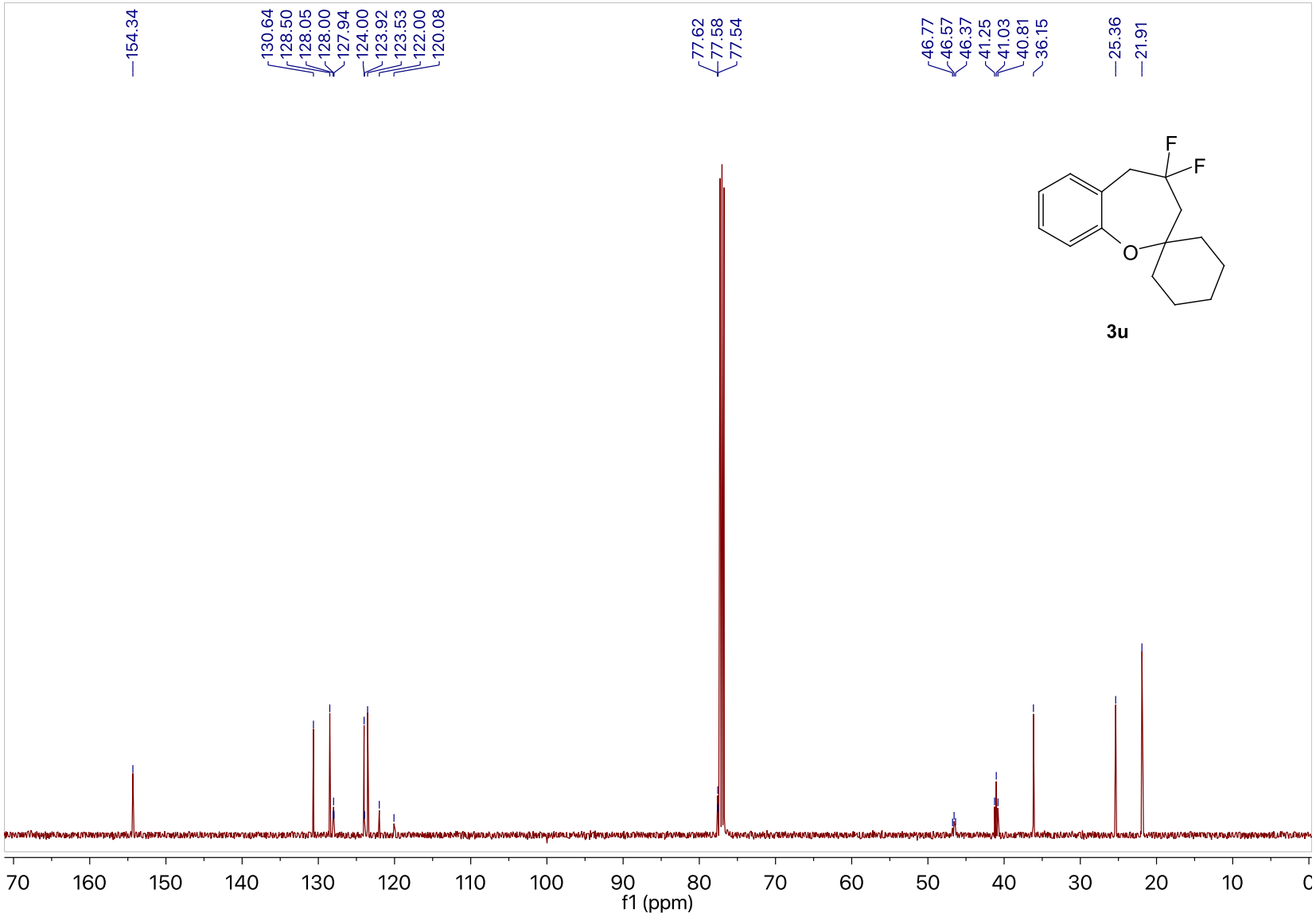

7.29
7.26
7.24
7.23
7.20
7.18
7.09
7.08
7.06
6.95
6.93
3.34
3.31
3.28
2.48
2.45
2.42
1.96
1.94
1.92
1.89
1.74
1.73
1.72
1.57
1.56
1.54
1.53
F
F
O
3t
1.00
1.02
1.02
1.00
2.08
2.06
4.10
2.06
2.33
f1 (ppm)

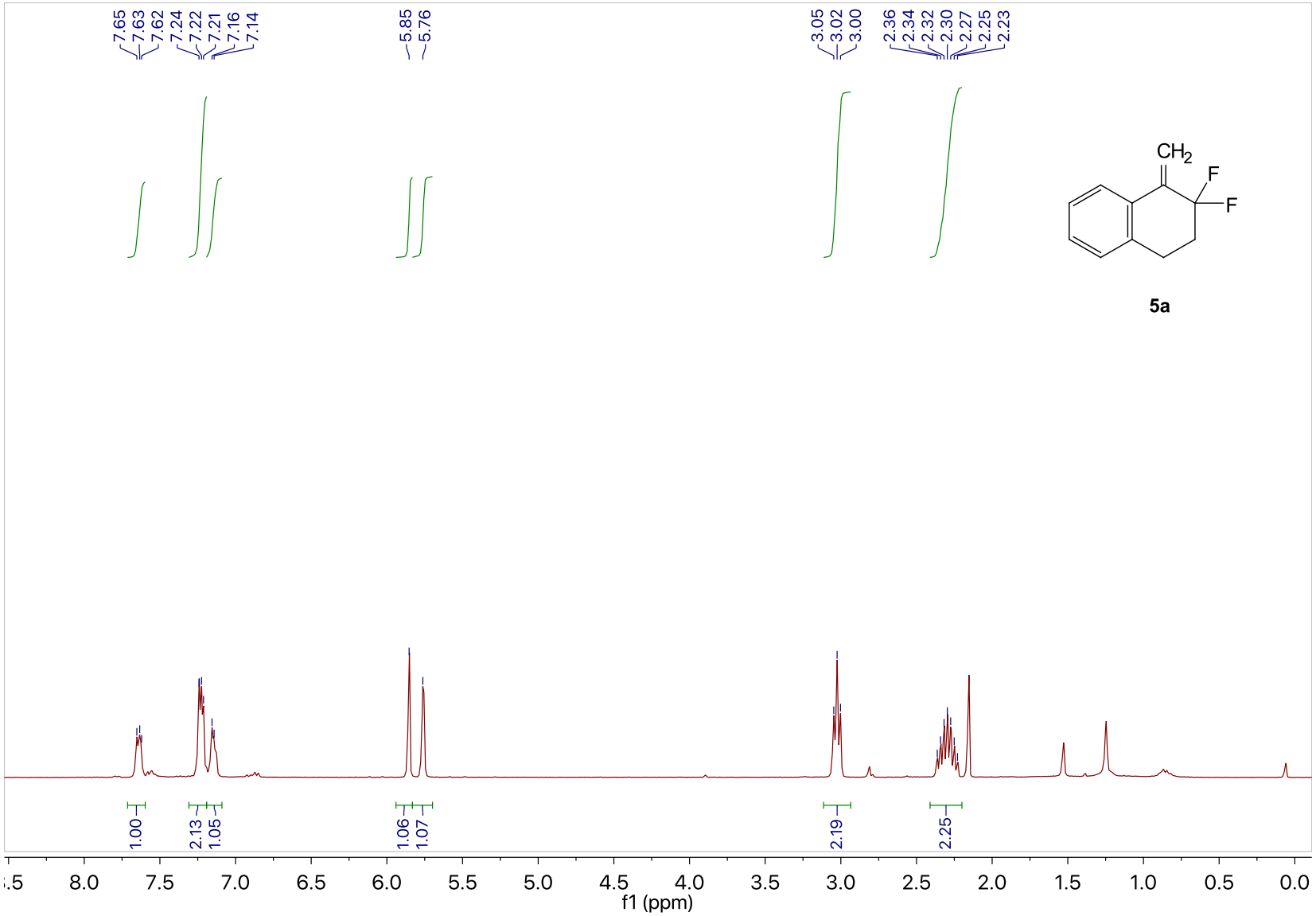

-89.29
F
F
O
3t
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

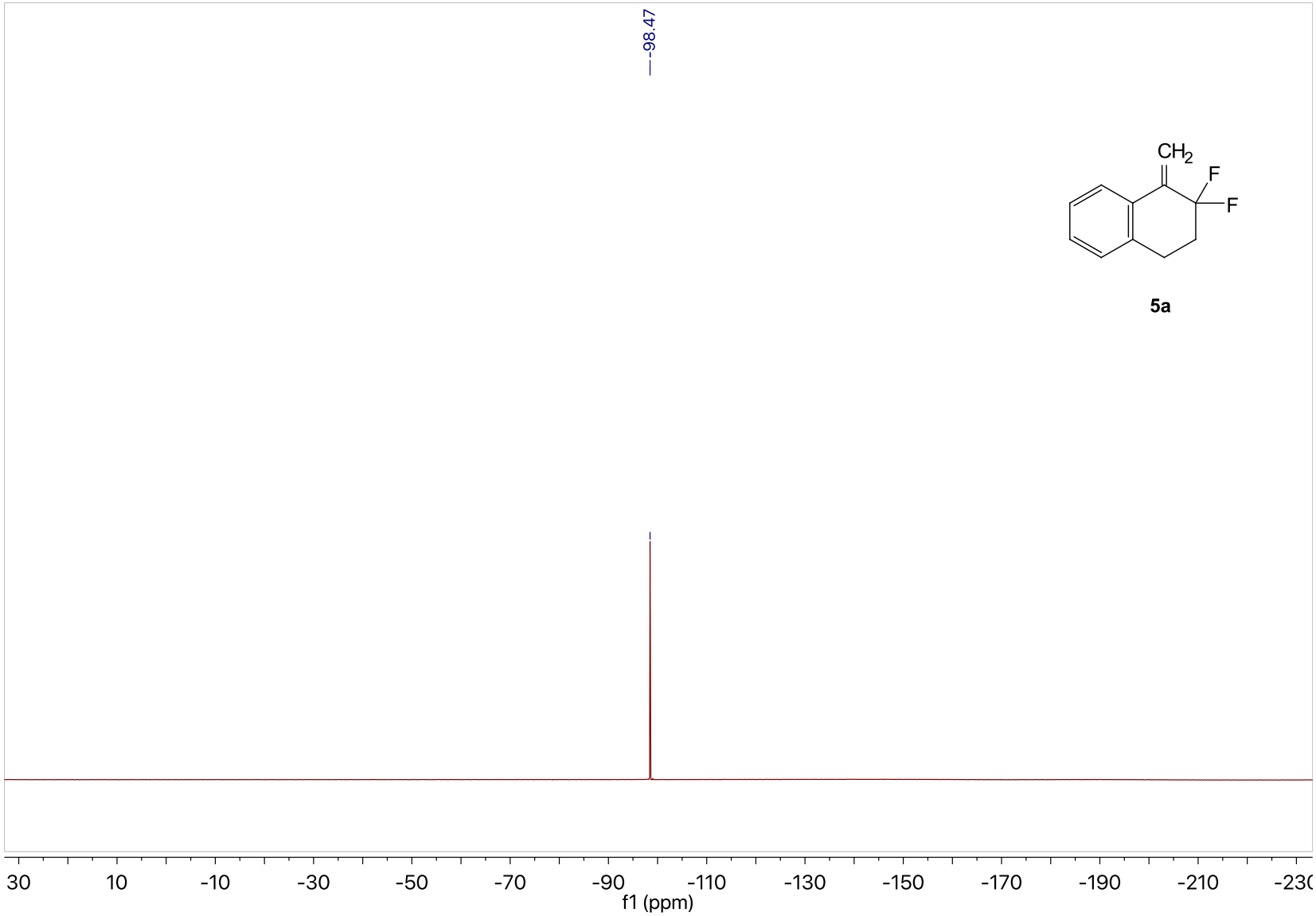

155.01
131.33
128.52
127.17
127.11
127.05
124.03
123.48
123.10
121.56
119.64
87.82
87.77
87.73
47.26
47.06
46.86
41.89
41.66
41.44
37.81
23.06
F
F
O
3t
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

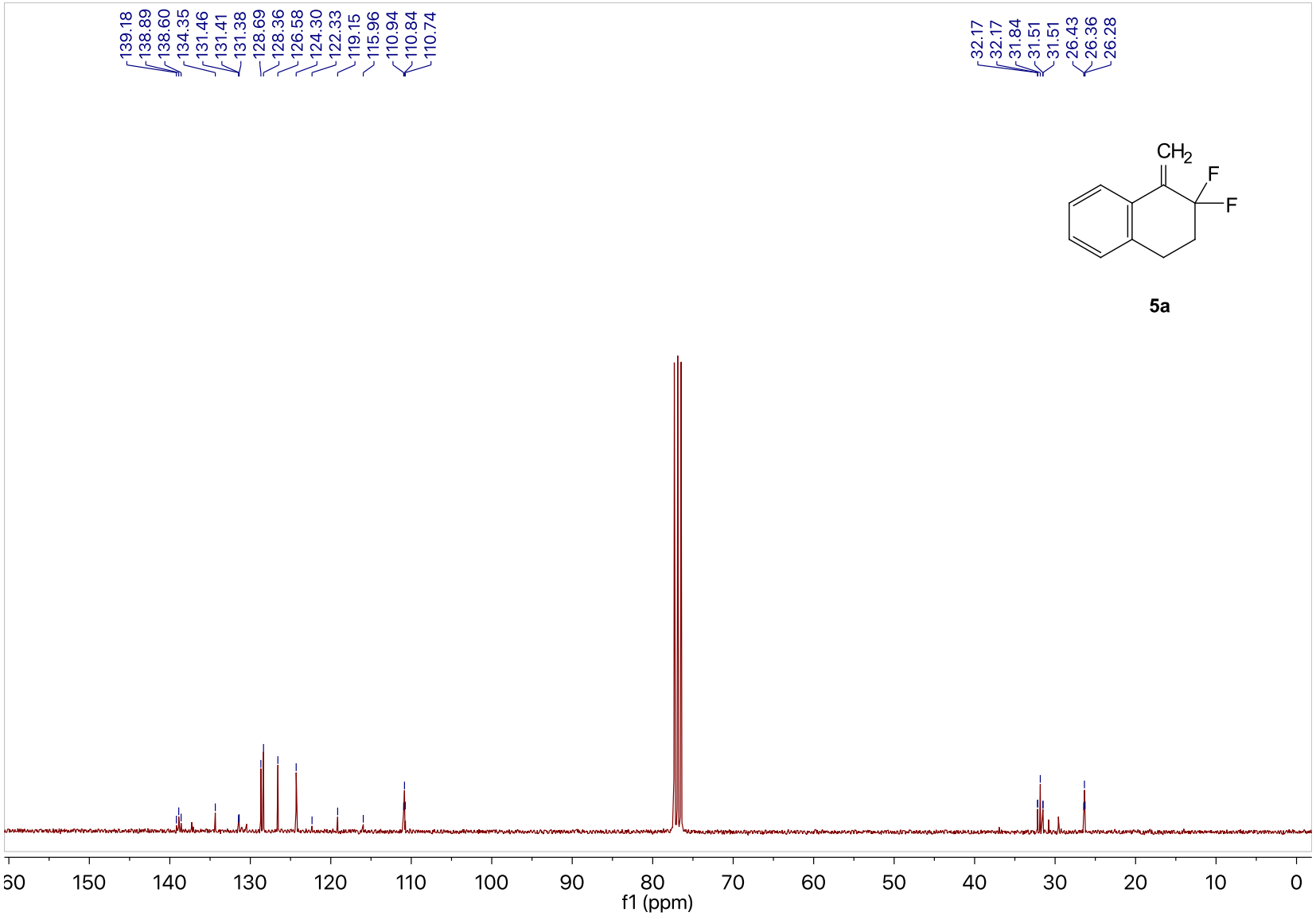

7.27
7.26
7.24
7.20
7.19
7.10
7.08
7.07
7.06
7.04
3.34
3.31
3.28
2.21
2.18
2.15
1.88
1.87
1.84
1.81
1.79
1.79
1.78
1.65
1.63
1.53
1.52
1.52
1.51
1.49
1.47
F
F
O
3u
0.98
1.00
0.99
0.98
2.03
2.03
4.09
6.30
f1 (ppm)

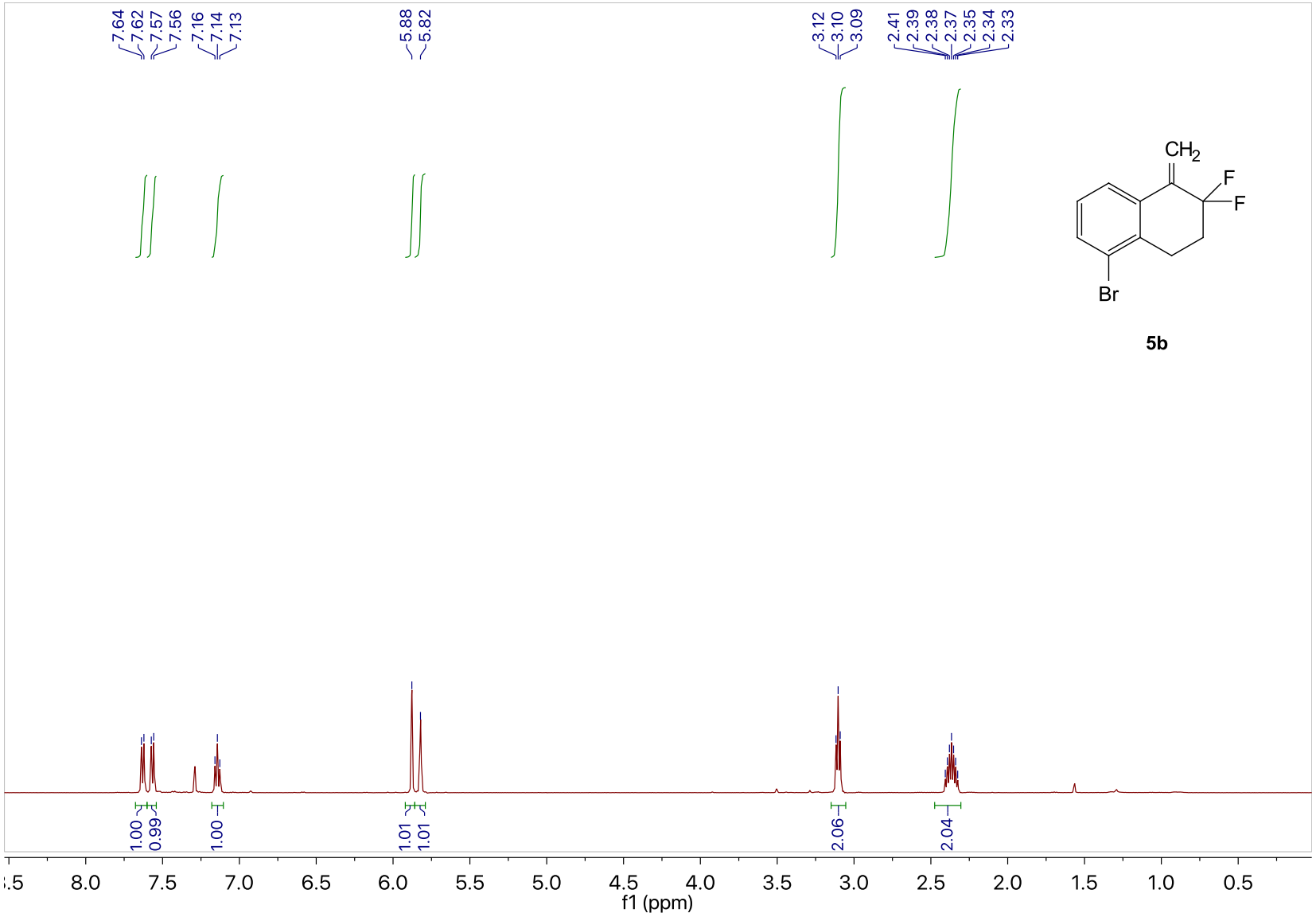

-85.62
F
F
O
3u
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

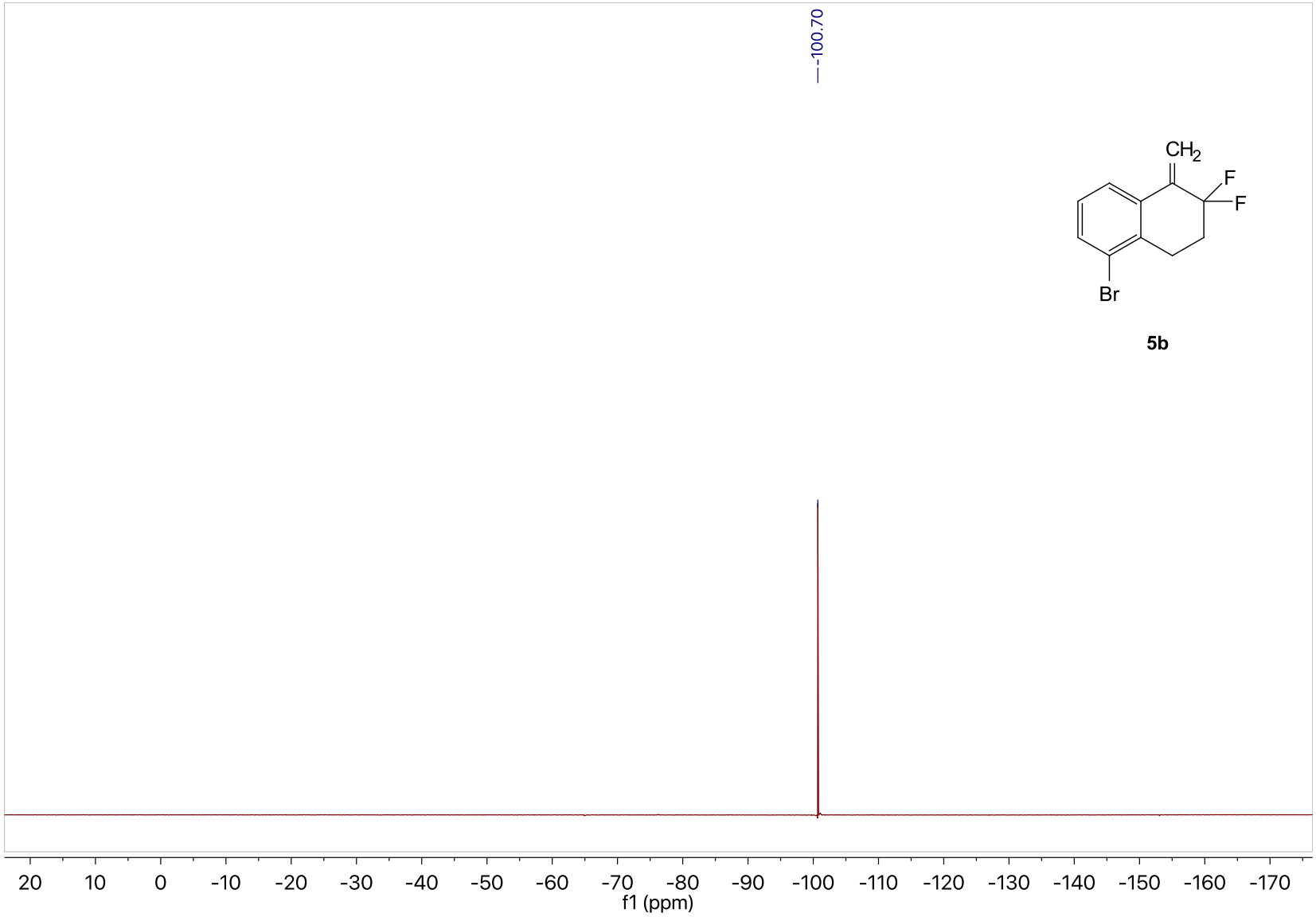

154.34
130.64
128.50
128.05
128.00
127.94
124.00
123.92
123.53
122.00
120.08
77.62
77.58
77.54
46.77
46.57
46.37
41.25
41.03
40.81
36.15
25.36
21.91
F
F
O
3u
f1 (ppm)

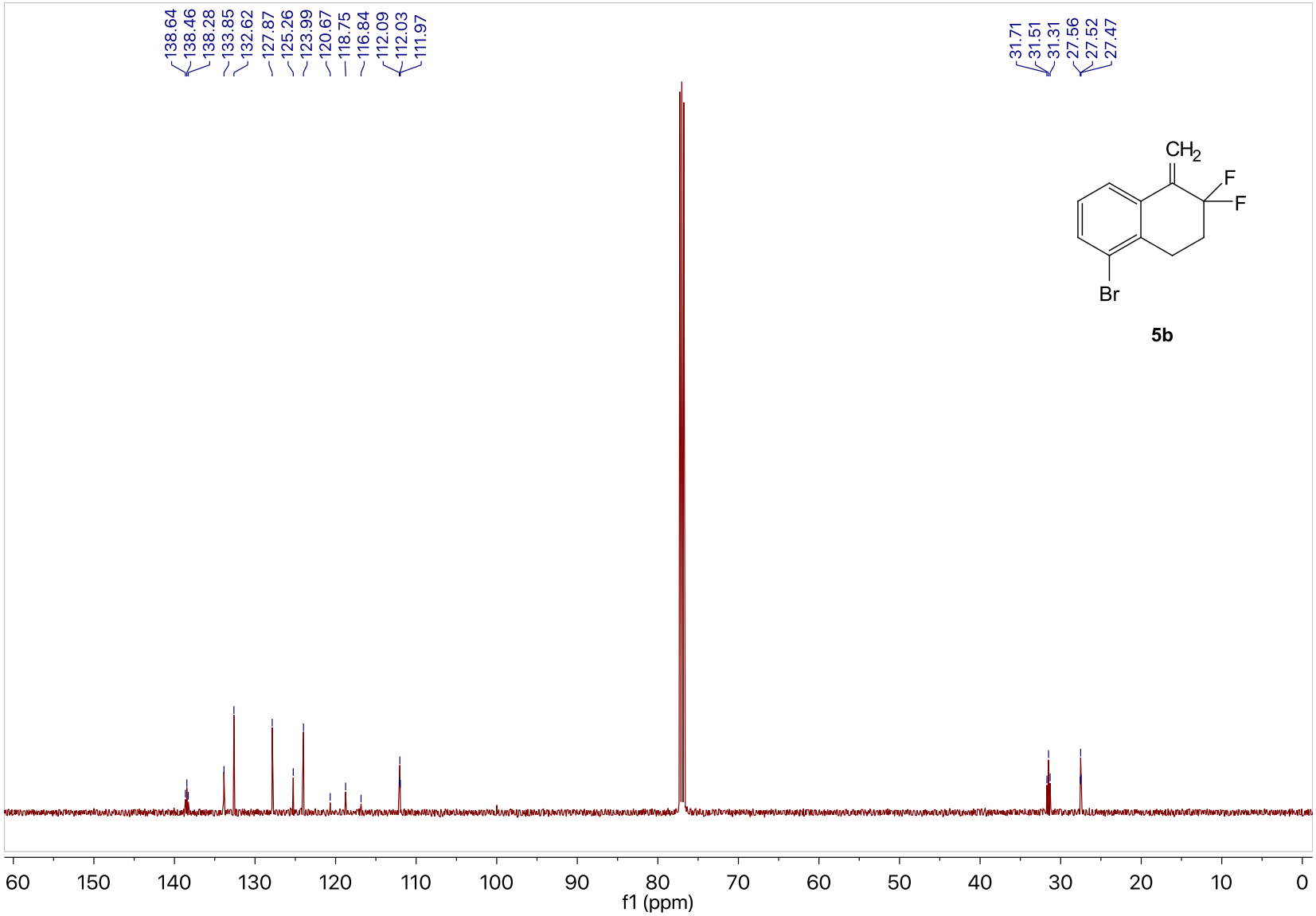

7.65
7.63
7.62
7.24
7.22
7.21
7.16
7.14
5.85
5.76
3.05
3.02
3.00
2.36
2.34
2.32
2.30
2.27
2.25
2.23
CH2
F
F
5a
1.00
2.13
1.05
1.06
1.07
2.19
2.25
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

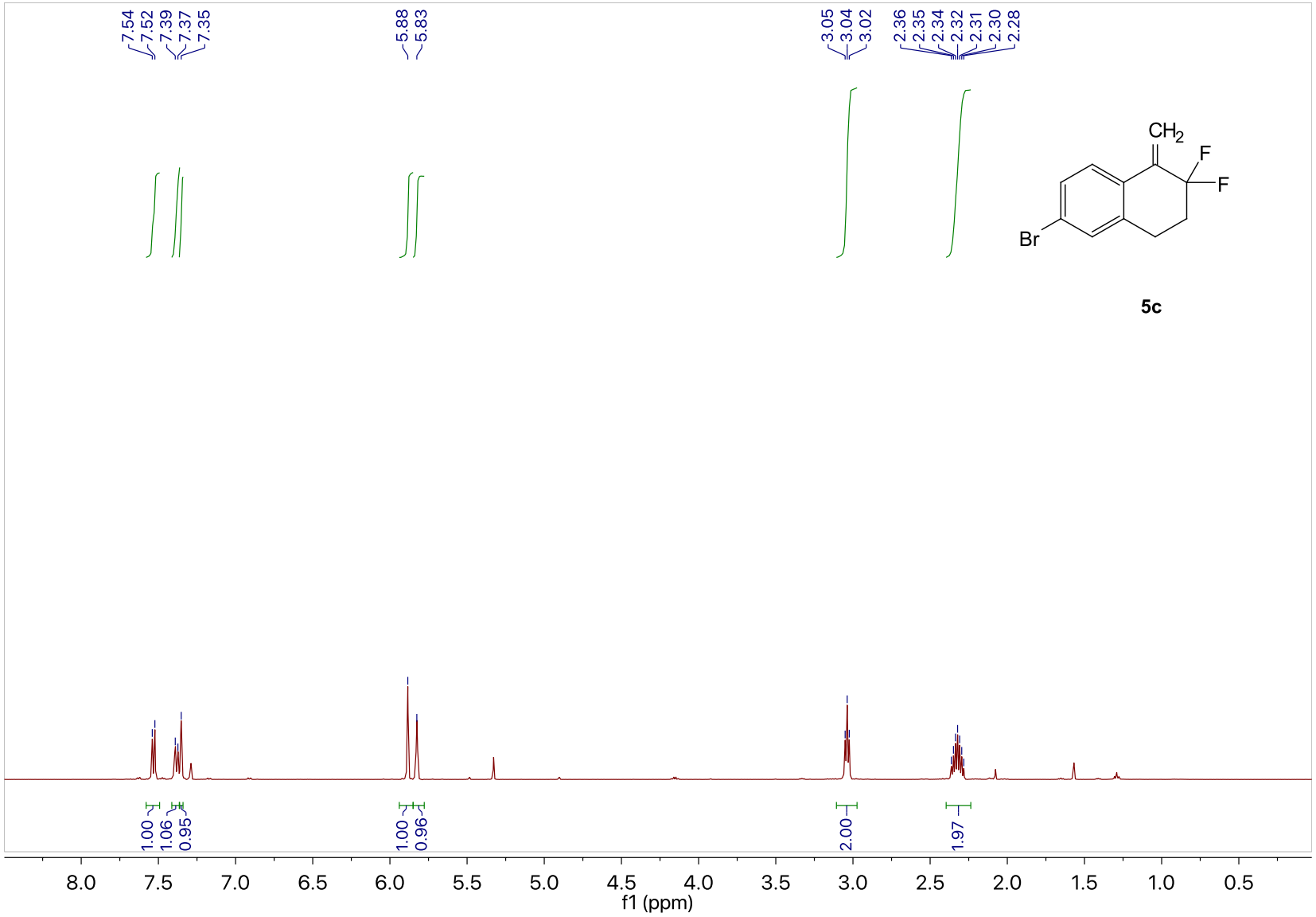

-98.47
CH2
F
F
5a
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

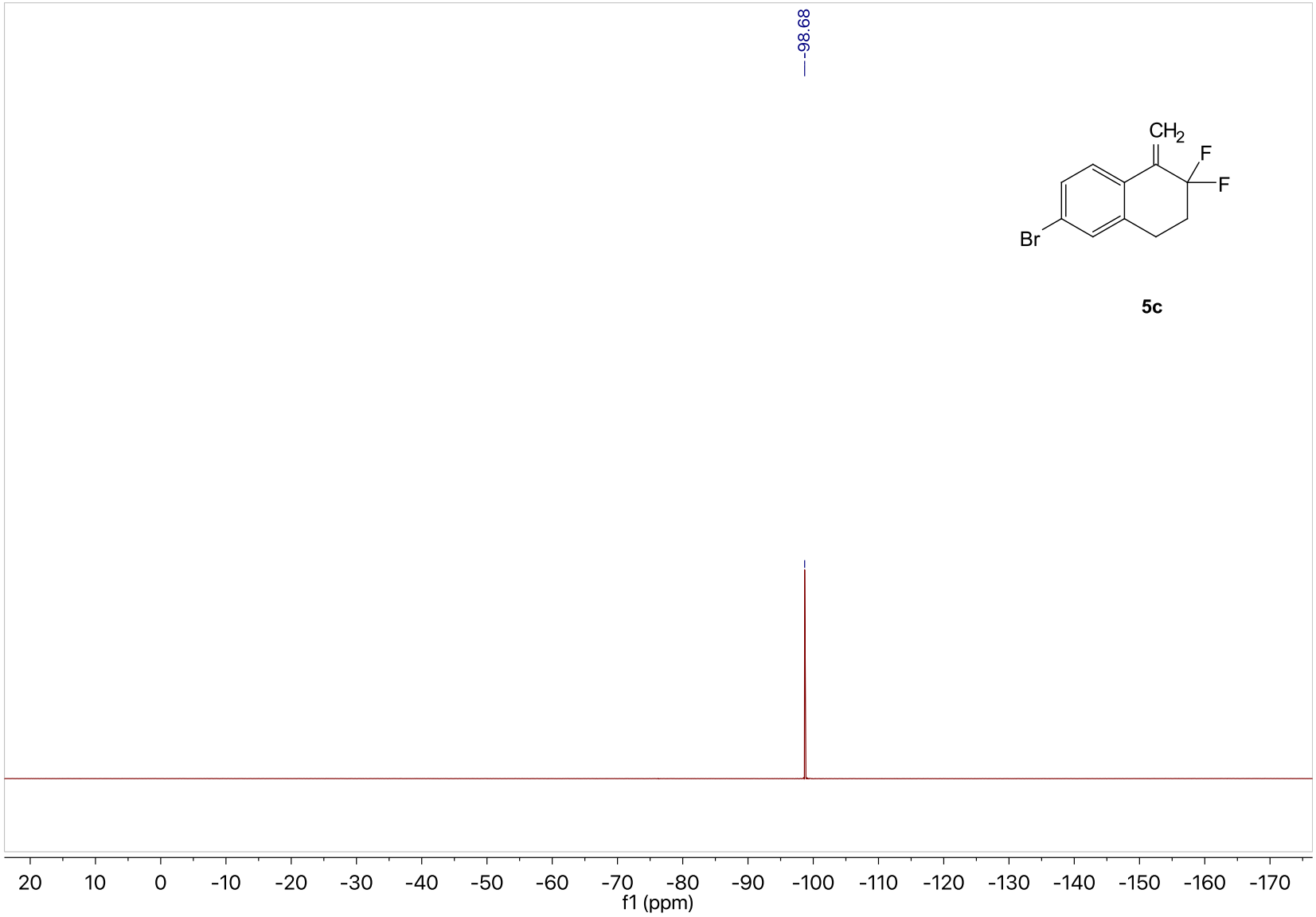

139.18
138.89
138.60
134.35
131.46
131.41
131.38
128.69
128.36
126.58
124.30
122.33
119.15
115.96
110.94
110.84
110.74
32.17
32.17
31.84
31.51
31.51
26.43
26.36
26.28
CH2
F
F
5a
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

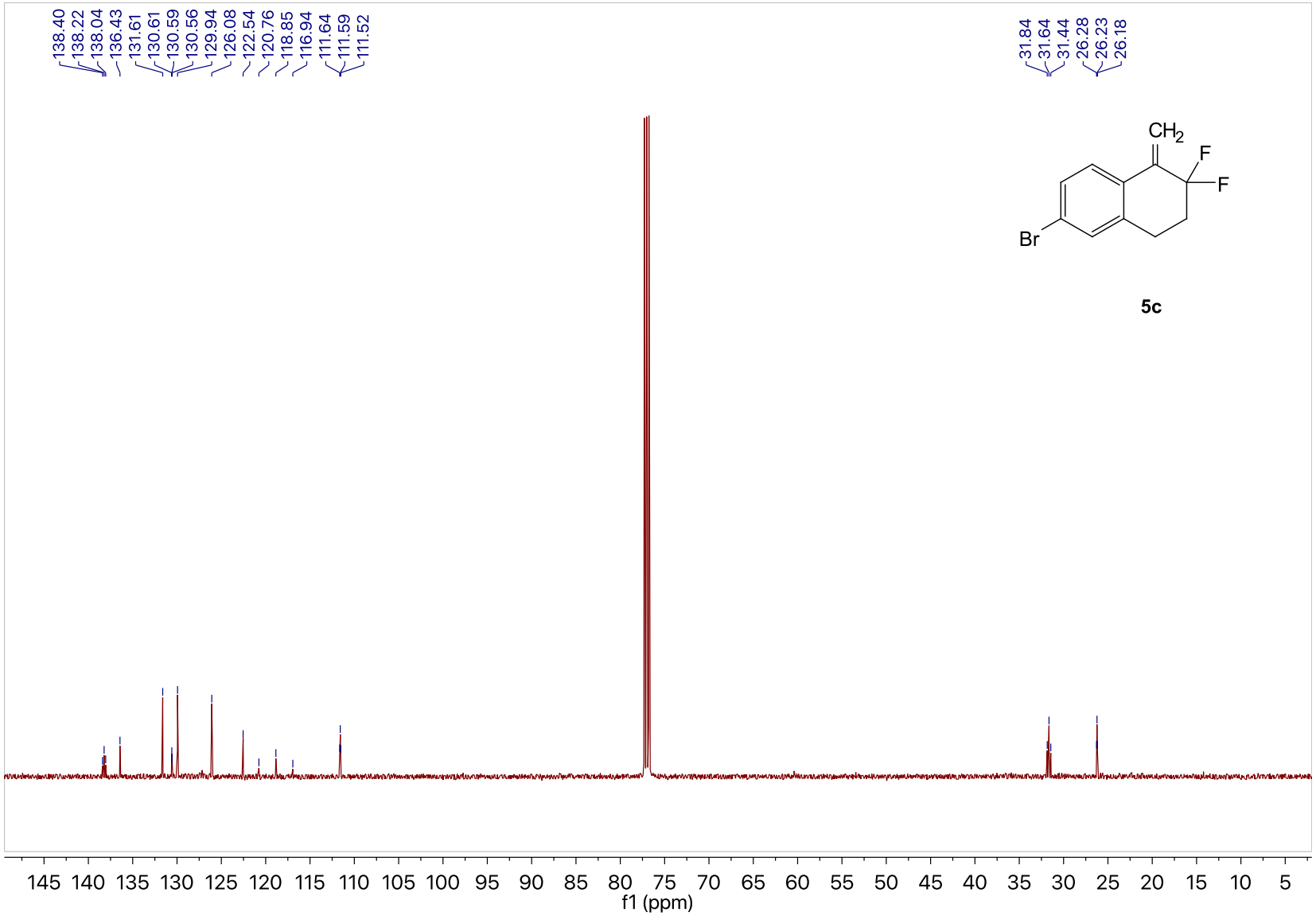

7.64
7.62
7.57
7.56
7.16
7.14
7.13
5.88
5.82
3.12
3.10
3.09
2.41
2.39
2.38
2.37
2.35
2.34
2.33
CH2
F
F
Br
5b
1.00
0.99
1.00
1.01
1.01
2.06
2.04
f1 (ppm)

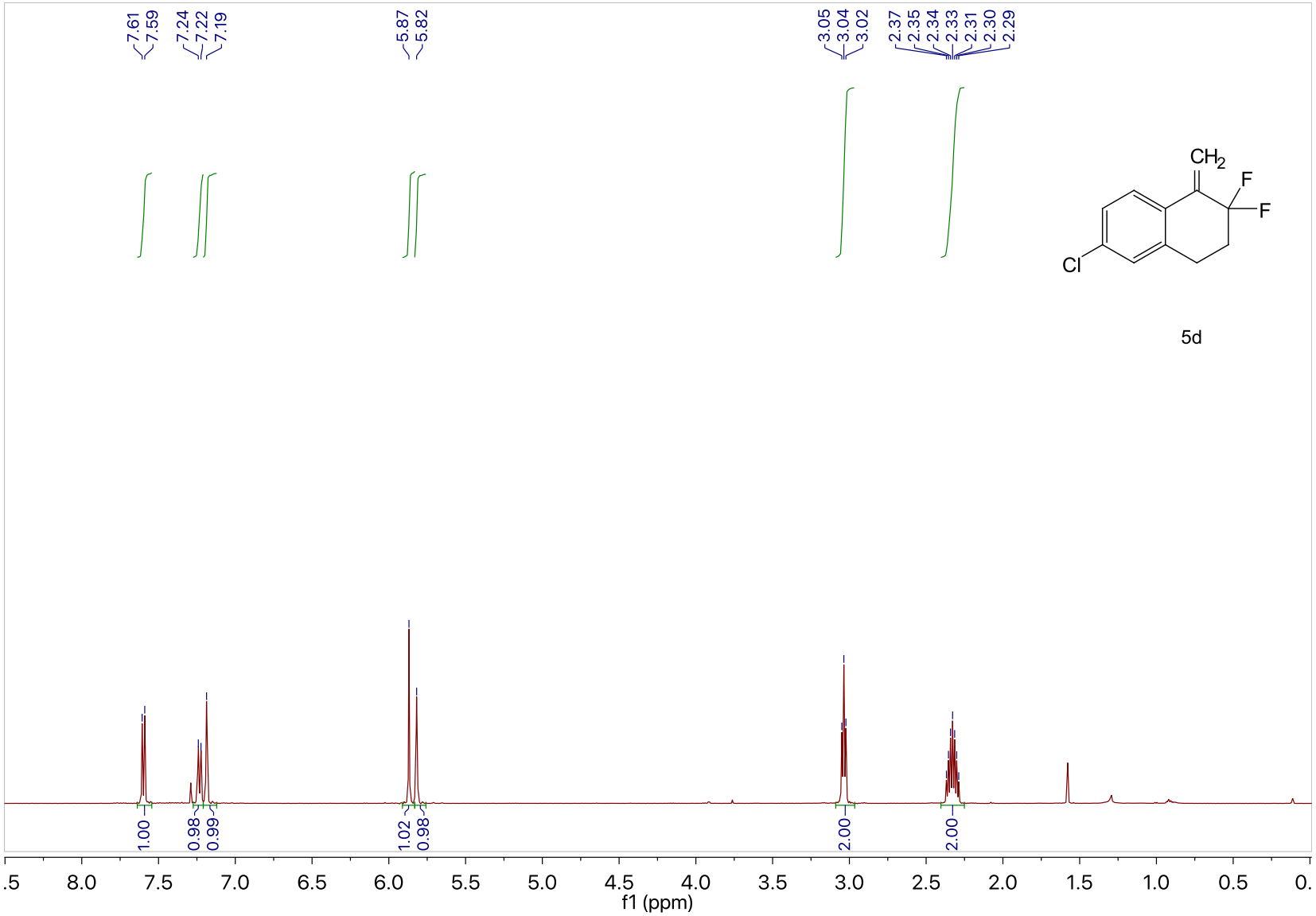

-100.70
CH2
F
F
Br
5b
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

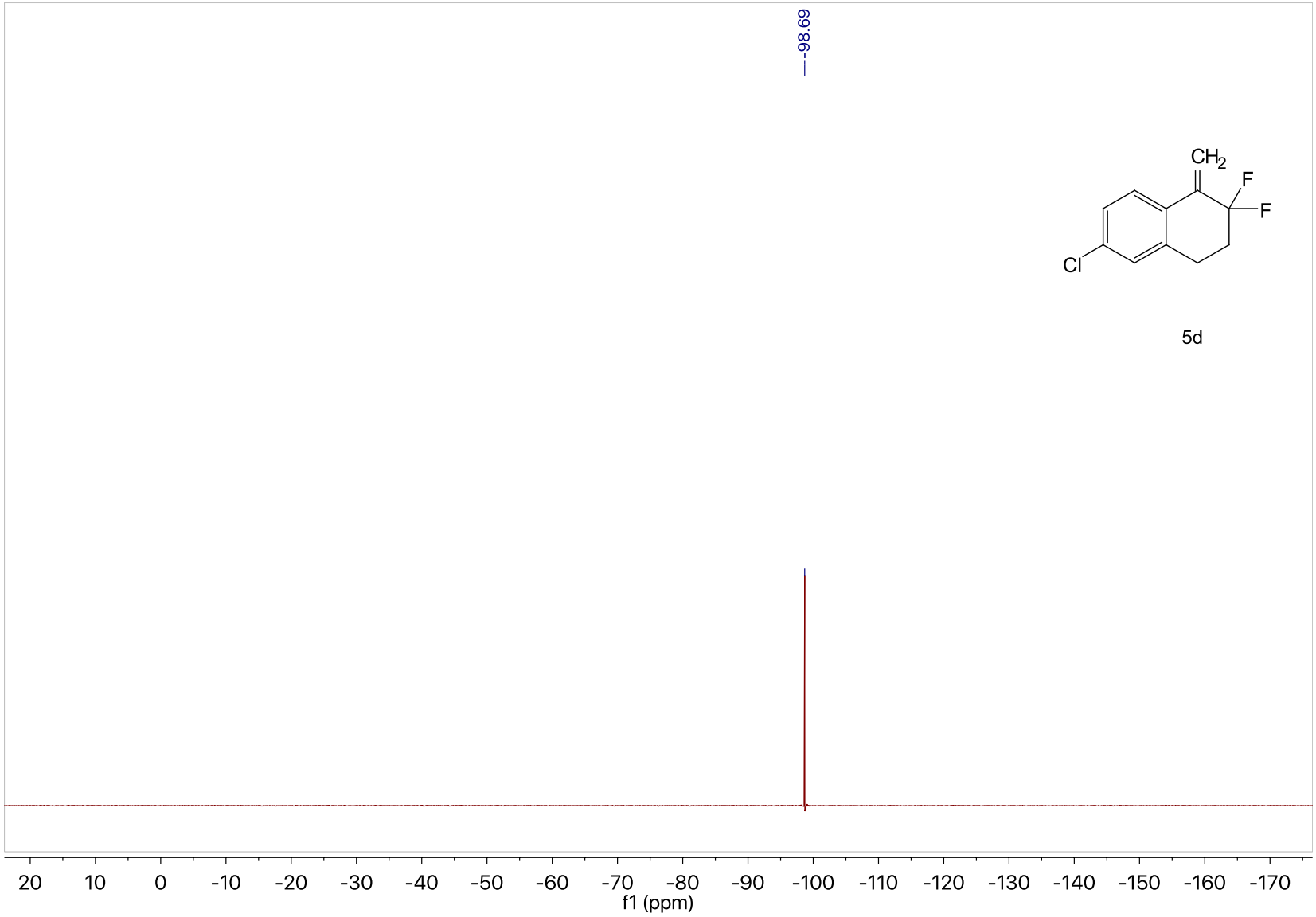

138.64
138.46
138.28
133.85
132.62
127.87
125.26
123.99
120.67
118.75
116.84
112.09
112.03
111.97
31.71
31.51
31.31
27.56
27.52
27.47
CH2
F
F
Br
5b
60
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.54
7.52
7.39
7.37
7.35
5.88
5.83
3.05
3.04
3.02
2.36
2.35
2.34
2.32
2.31
2.30
2.28
CH2
F
F
Br
5c
1.00
1.06
0.95
1.00
0.96
2.00
1.97
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


-98.68
CH2
F
F
Br
5c
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)


138.40
138.22
138.04
136.43
131.61
130.61
130.59
130.56
129.94
126.08
122.54
120.76
118.85
116.94
111.64
111.59
111.52
31.84
31.64
31.44
26.28
26.23
26.18
CH2
F
F
Br
5c
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)


7.61
7.59
7.24
7.22
7.19
5.87
5.82
3.05
3.04
3.02
2.37
2.35
2.34
2.33
2.31
2.30
2.29
CH2
F
F
Cl
5d
1.00
0.98
0.99
1.02
0.98
2.00
2.00
f1 (ppm)


-98.69
CH2
F
F
Cl
5d
20
10
0
-10
-20
-30
-40
-50
-60
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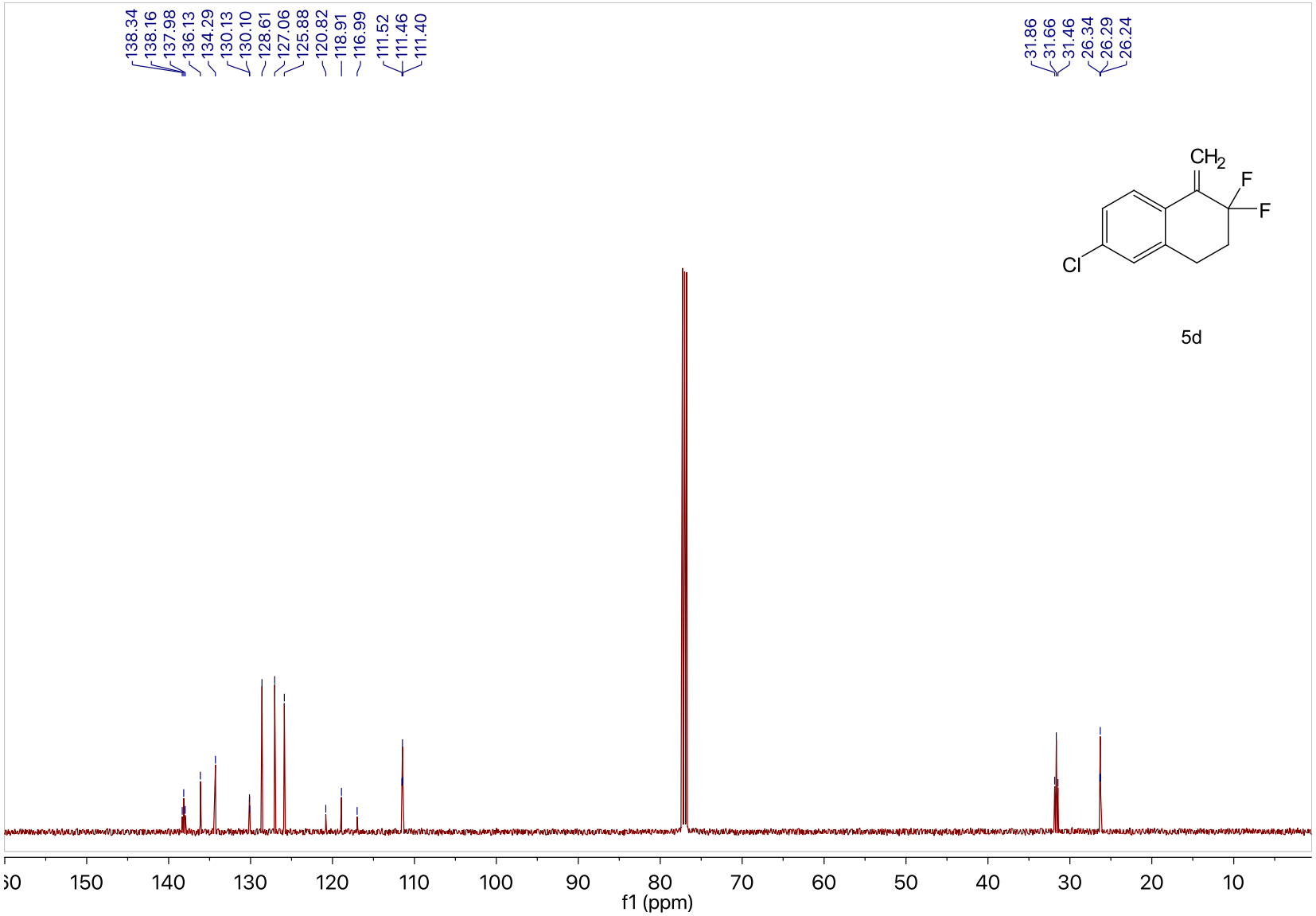
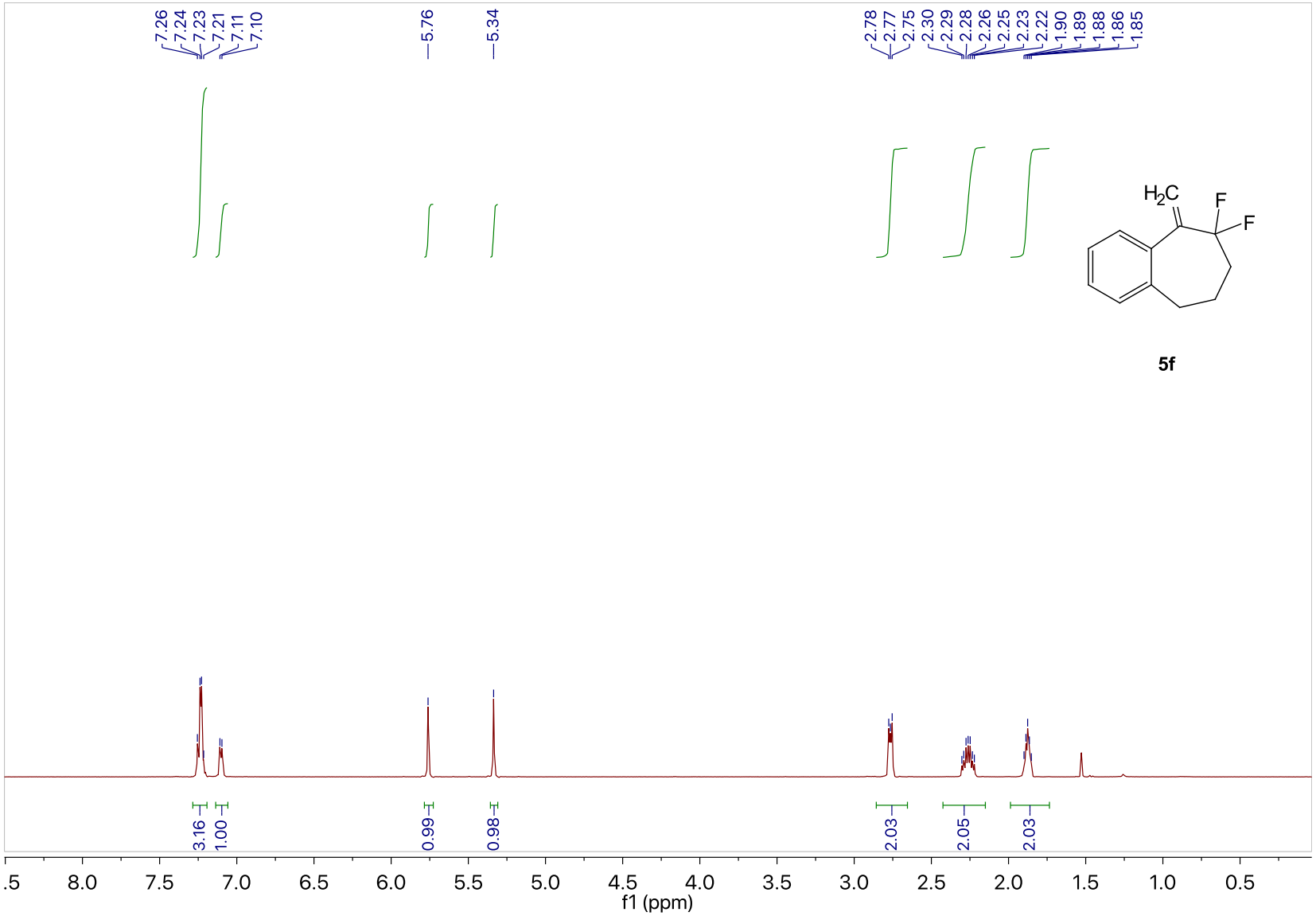
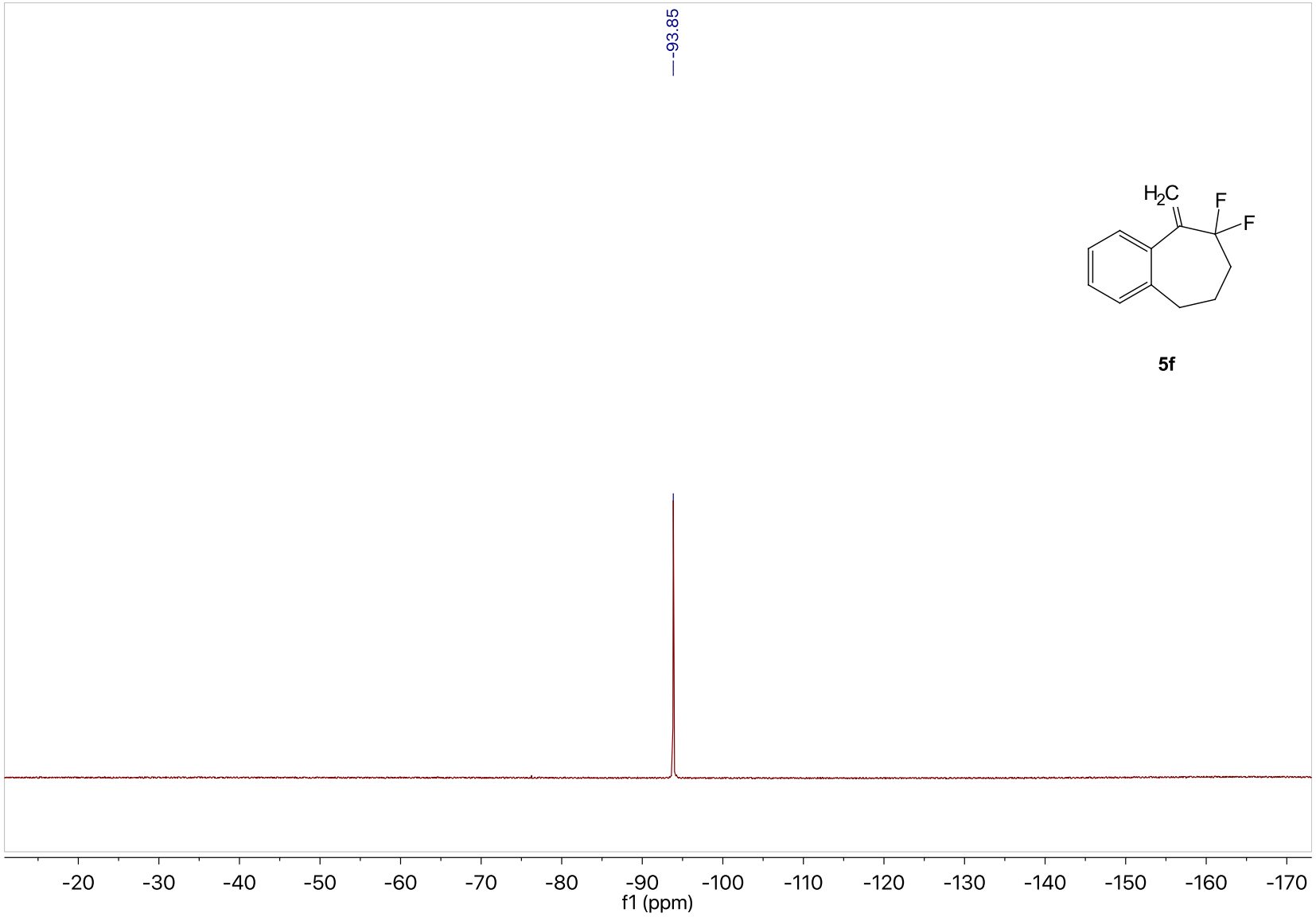
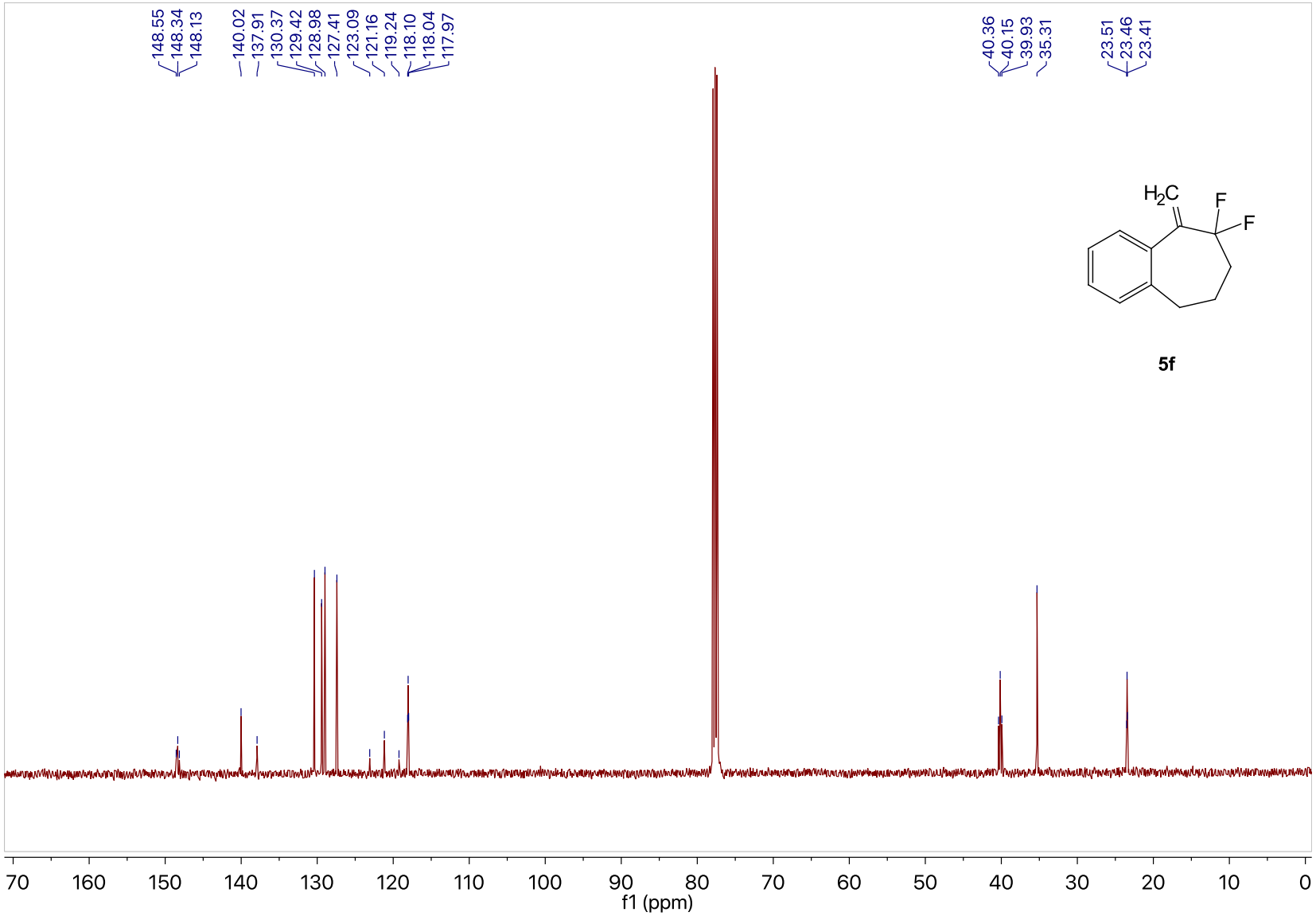
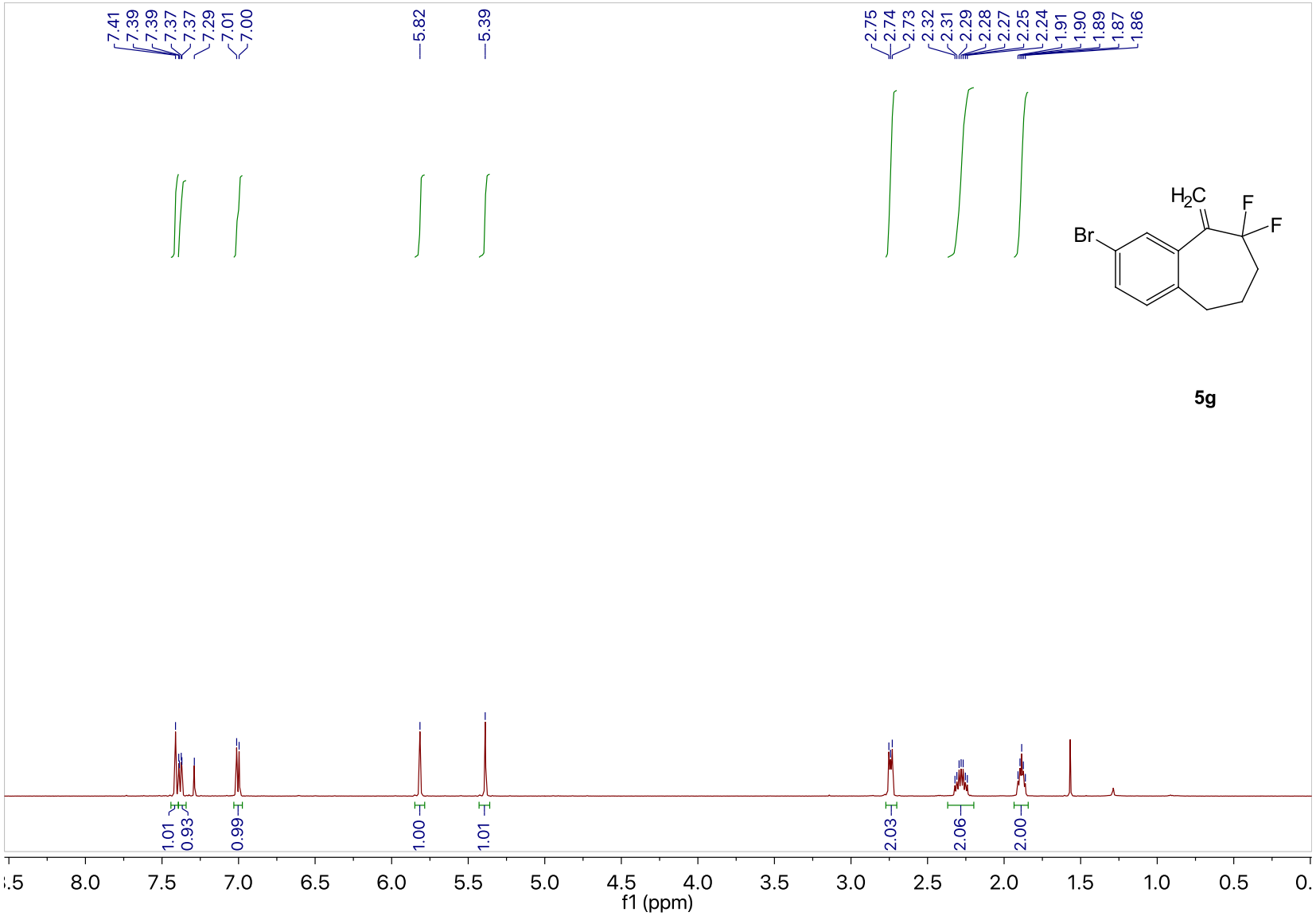
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

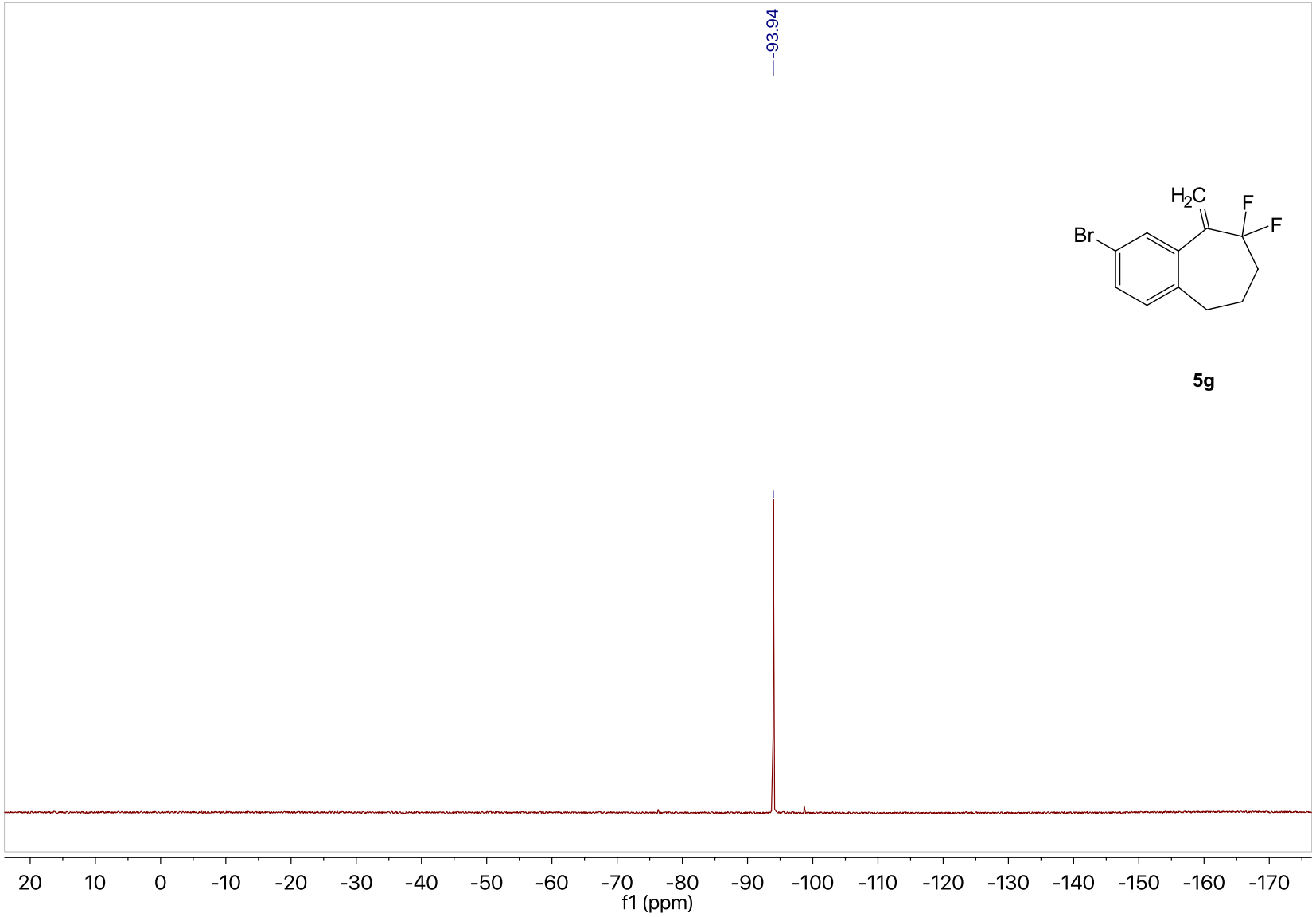

138.34
138.16
137.98
136.13
134.29
130.13
130.10
128.61
127.06
125.88
120.82
118.91
116.99
111.52
111.46
111.40
31.86
31.66
31.46
26.34
26.29
26.24
CH2
F
F
Cl
5d
f1 (ppm)


7.26
7.24
7.23
7.21
7.11
7.10
5.76
5.34
2.78
2.77
2.75
2.30
2.29
2.28
2.26
2.25
2.23
2.22
1.90
1.89
1.88
1.86
1.85
H2C
F
F
5f
3.16
1.00
0.99
0.98
2.03
2.05
2.03
f1 (ppm)


-93.85
H2C
F
F
5f
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)


148.55
148.34
148.13
140.02
137.91
130.37
129.42
128.98
127.41
123.09
121.16
119.24
118.10
118.04
117.97
40.36
40.15
39.93
35.31
23.51
23.46
23.41
H2C
F
F
5f
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.41
7.39
7.39
7.37
7.37
7.29
7.01
7.00
5.82
5.39
2.75
2.74
2.73
2.32
2.31
2.29
2.28
2.27
2.25
2.24
1.91
1.90
1.89
1.87
1.86
H2C
F
F
Br
5g
1.01
0.93
0.99
1.00
1.01
2.03
2.06
2.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


-93.94
H2C
F
F
Br
5g
20
10
0
-10
-20
-30
-40
-50
-60
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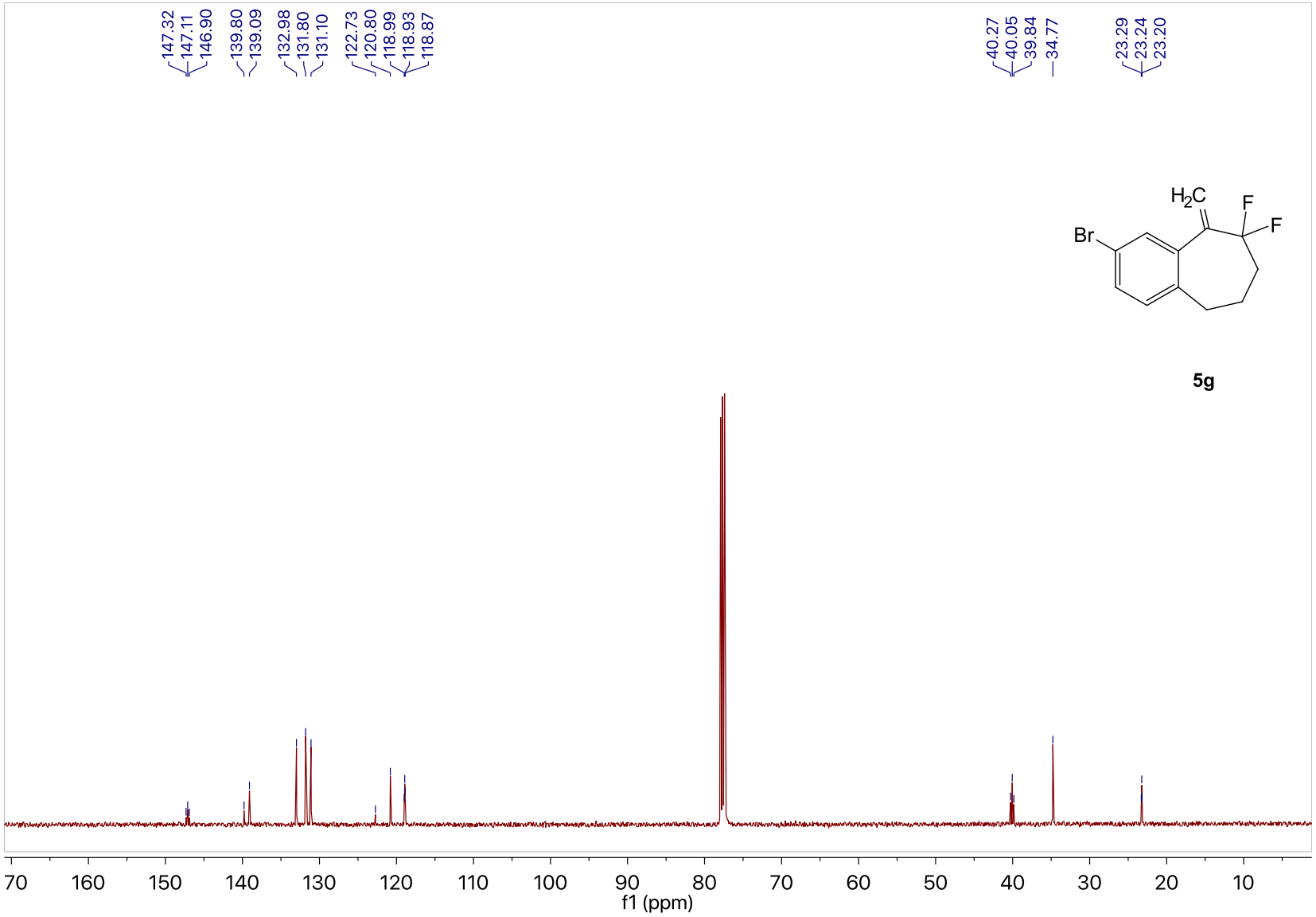
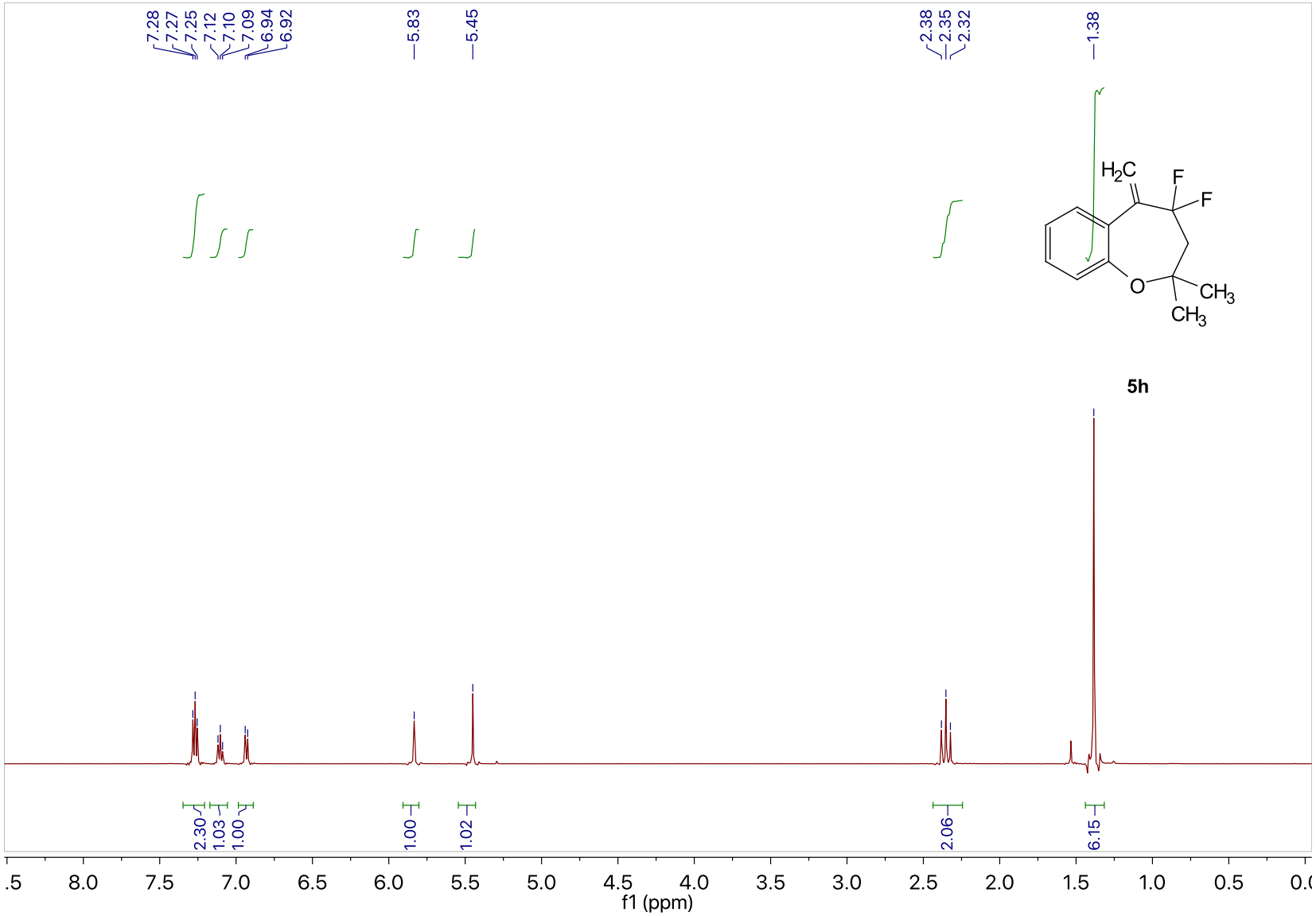
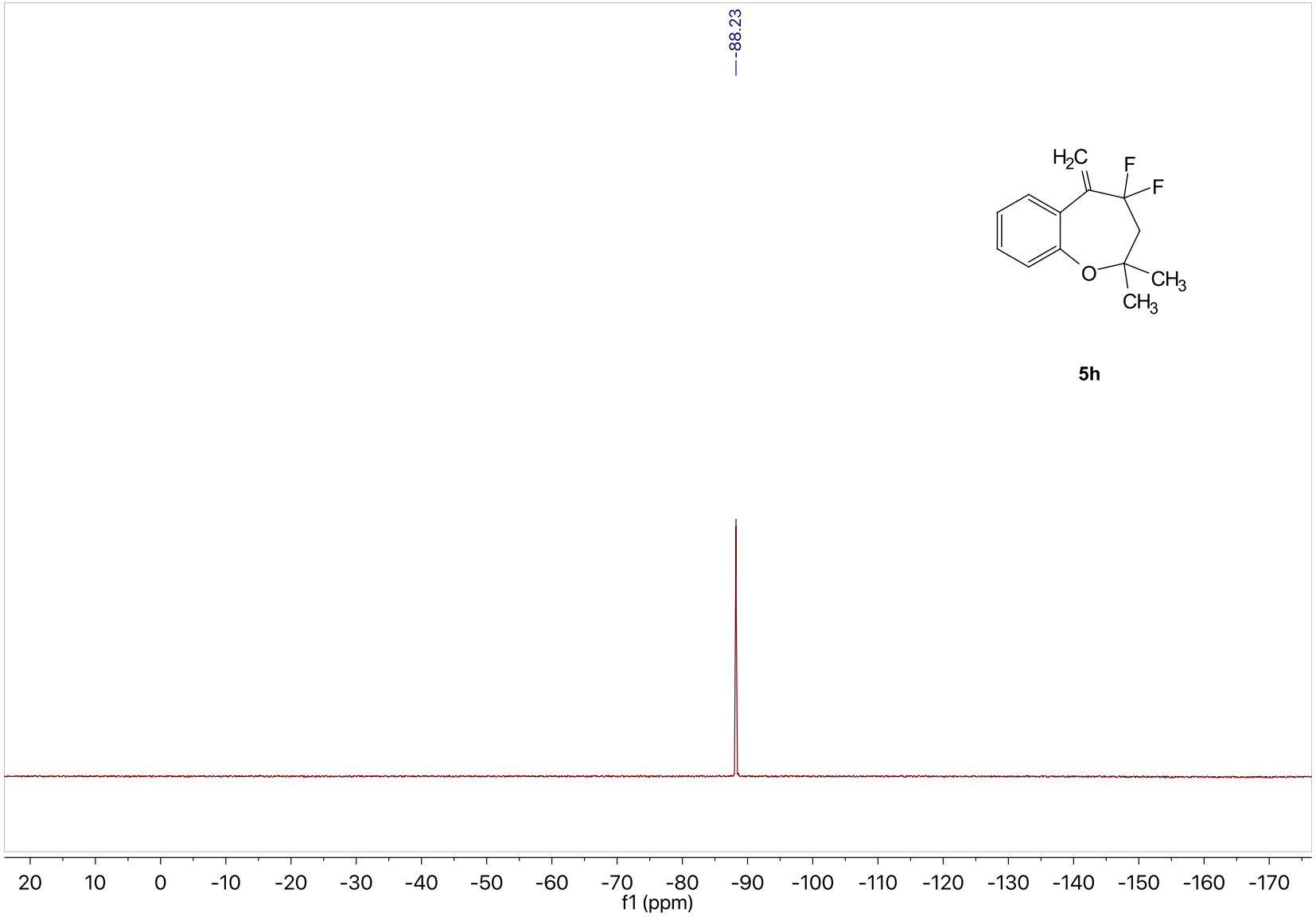
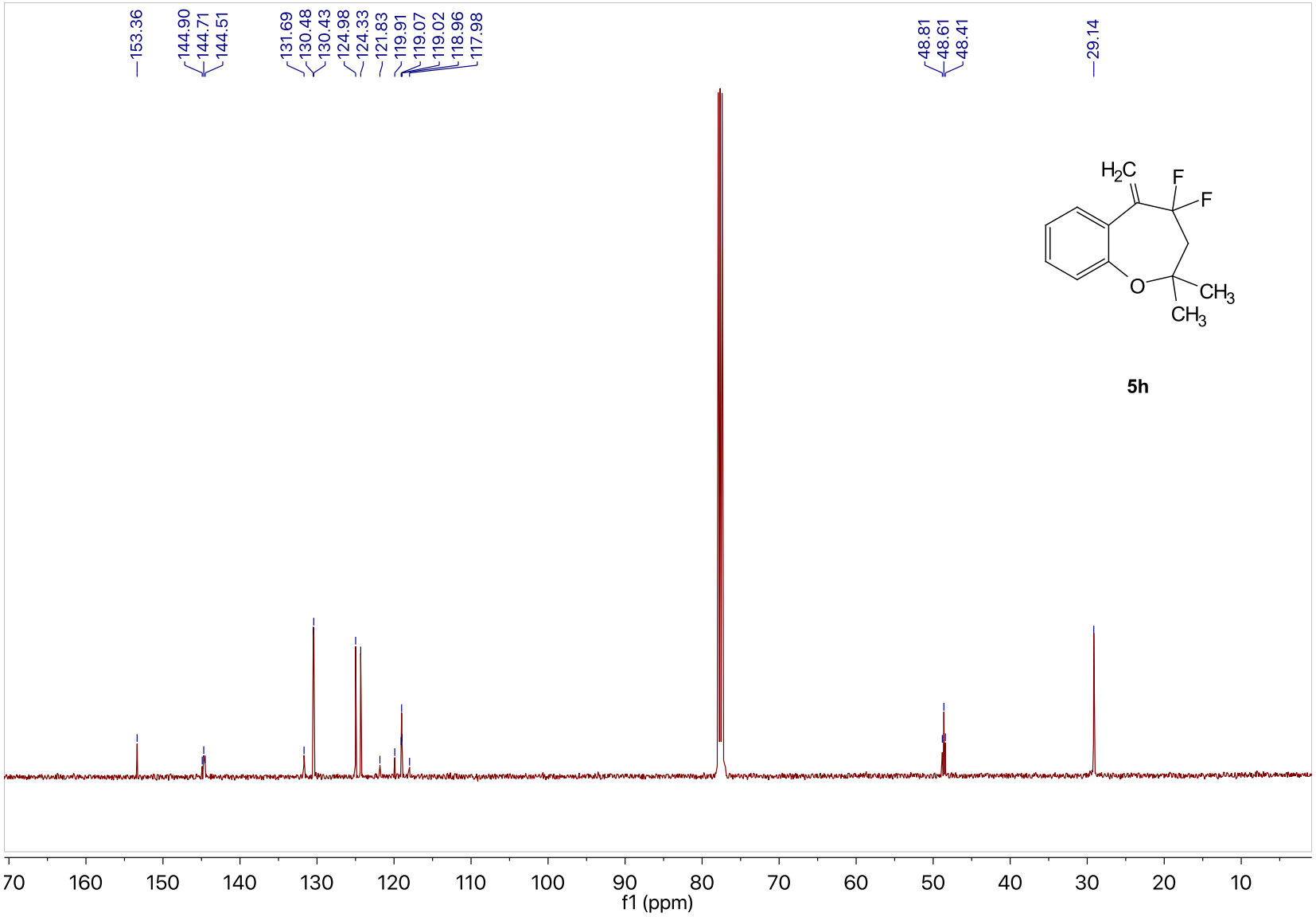
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)


147.32
147.11
146.90
139.80
139.09
132.98
131.80
131.10
122.73
120.80
118.99
118.93
118.87
40.27
40.05
39.84
34.77
23.29
23.24
23.20
H2C
F
F
Br
5g
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.28
7.27
7.25
7.12
7.10
7.09
6.94
6.92
5.83
5.45
2.38
2.35
2.32
1.38
H2C
F
F
O
CH3
CH3
5h
2.30
1.03
1.00
1.00
1.02
2.06
6.15
f1 (ppm)


-88.23
H2C
F
F
O
CH3
CH3
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

5h


153.36
144.90
144.71
144.51
131.69
130.48
130.43
124.98
124.33
121.83
119.91
119.07
119.02
118.96
117.98
48.81
48.61
48.41
29.14
H2C
F
F
O
CH3
CH3
5h
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)