Supporting information

Gold-catalyzed Fluorination of Alkynyl Esters and Ketones: Access to Fluorinated 1,3-Dicarbonyl Compounds

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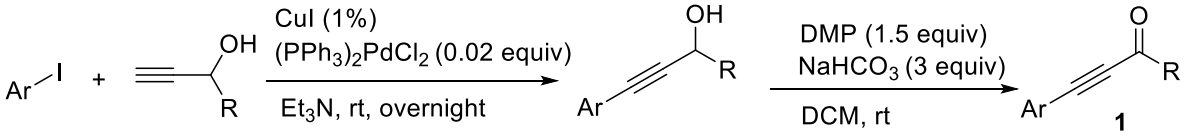
1. General

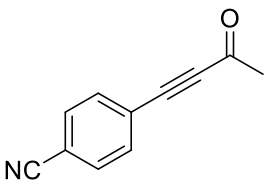
Commercial reagents and solvents were obtained from the commercial providers and used without further purification. The products were purified using a commercial flash chromatography system or a regular glass column. TLC was developed on silica gel 60 F254 glass plates. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker NMR apparatus. The chemical shifts are reported in δ (ppm) values (^{1}H and ^{13}C NMR relative to $CHCl_3$, δ 7.26 ppm for ^{1}H NMR and δ 77.0 ppm for ^{13}C NMR). Or alternatively, ^{1}H NMR chemical shifts were referenced to tetramethylsilane signal (0 ppm). Multiplicities are recorded by s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), h (hextet), m (multiplet) and br (broad). Coupling constants (*J*), are reported in Hertz (Hz). GC analyses were performed using a Shimadzu GC-2010ultragas chromatography–mass spectrometry instrument equipped with a Shimadzu AOC-20s autosampler.

2. General procedure for the synthesis of alkynyl ketones 1

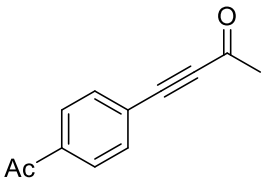


A mixture of aryl iodide (5 mmol), 3-butyn-2-ol or 1-octyne-3-ol (5.5 mmol) and $(PPh_3)_2PdCl_2$ (2 mol %) and Et_3N (10 mL) was stirred for ten minutes at the room temperature, then CuI (1 mmol%) was added slowly. Finally, the reaction was stirred overnight at room temperature under a nitrogen atmosphere. Then the reaction was concentrated under reduced pressure and the residue was purified by flash chromatography to give the desired product propargyl alcohol derivatives.

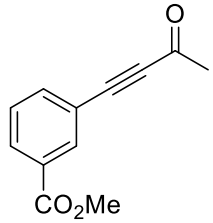
Under stirring, a solution of propargyl alcohol derivatives (1 equiv) in DCM (20 mL) was added DMP (1.5 equiv) and $NaHCO_3$ (3 equiv). The reaction vessel was wrapped in aluminum foil to avoid light exposure. Finally, the reaction was monitored by TLC. Then the reaction was quenched by addition of saturated Na_2SO_3 solution and extracted with DCM. The solvent was removed under reduced pressure and the residue was purified by flash chromatography to obtain the alkynone derivatives **1**.



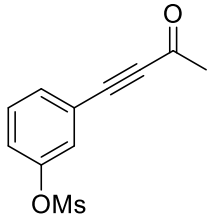
4-(3-Oxobut-1-yn-1-yl)benzonitrile **(1b)**. White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (q, *J* = 8.2 Hz, 4H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.90, 133.20, 132.22, 124.68, 117.82, 113.96, 90.54, 86.81, 32.68. HRMS (ESI^+) calcd. for $C_{11}H_8NO_2[M+H]^+$: 170.0606, found:170.0600.



4-(4-Acetylphenyl)but-3-yn-2-one **(1e)**. White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 8.2 Hz, 2H), 2.59 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.97, 184.19, 138.02, 132.99, 128.28, 124.46, 89.97, 88.29, 32.72, 32.68, 26.64. HRMS (ESI^+) calcd. for $C_{12}H_{11}O_2[M+H]^+$:187.0759, found:187.0753.

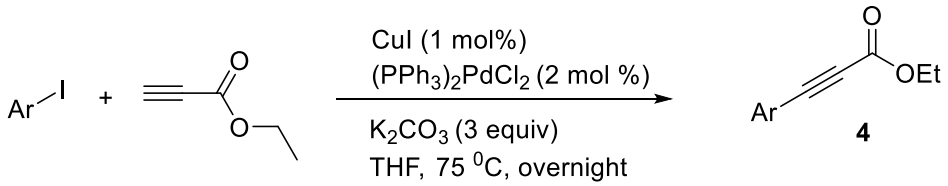


Methyl 3-(3-oxobut-1-yn-1-yl)benzoate **(1f)**. White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 8.12 – 8.00 (m, 1H), 7.79 – 7.64 (m, 1H), 7.46 (t, *J* = 7.9 Hz, 1H), 3.92 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.24, 165.75, 136.83, 134.02, 131.50, 130.79, 128.81, 120.39, 88.59, 88.52, 52.40, 32.69. HRMS (ESI^+) calcd. for $C_{12}H_{11}O_3[M+H]^+$: 203.0708, found:203.0720.

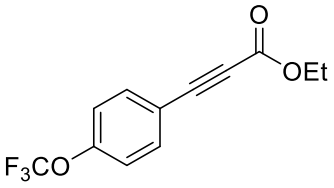


3-(3-Oxobut-1-yn-1-yl)phenyl methanesulfonate **(1g).** White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.34 (m, 4H), 3.17 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.13, 148.84, 131.79, 130.36, 126.15, 124.58, 121.97, 88.85, 87.58, 37.74, 32.68. HRMS (ESI^+) calcd. for $C_{11}H_{11}SO_4[M+H]^+$: 239.0378, found:239.0371.

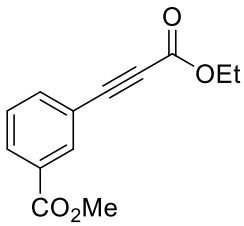
3. General procedure for the synthesis of alkynyl esters 4



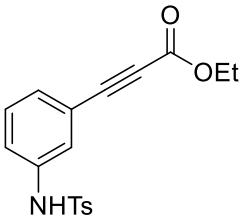
To a mixture of aryl iodide (5 mmol), ethyl propiolate (6 mmol) and $(PPh_3)_2PdCl_2$ (2 mol %) in THF (20 mL), K_2CO_3 (15 mmol) was added. The reaction was stirred for 10 min at the room temperature, then CuI (1 mmol%) was added slowly. Finally, the reaction was stirred overnight at 75 ^oC under a nitrogen atmosphere. Then the solution was filtered, the filtrate was concentrated under deduced pressure and the residue was purified by flash silica gel chromatography to give the pure product **4**.



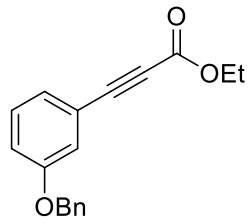
Ethyl 3-(4-(trifluoromethoxy)phenyl)propiolate **(4e)**. Pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.58 (m, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 4.30 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.75. ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.77, 150.58, 135.67 – 133.74 (m), 120.24 (q, *J* = 258.8 Hz, 1H). 120.83 (d, *J* = 18.5 Hz), 118.24, 84.25, 81.30, 62.23, 14.01. HRMS (ESI^+) calcd. for $C_{12}H_9F_3O_3[M+H]^+$: 259.0582, found:259.0576.



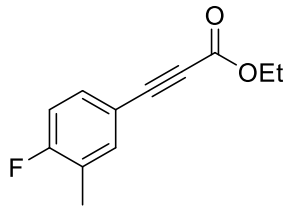
Methyl 3-(3-oxobut-1-yn-1-yl)benzoate **(4f)**. White solid. ^1H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 8.10 (d, *J* = 7.8 Hz, 1H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 1H), 4.30 (d, *J* = 7.1 Hz, 2H), 3.92 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.77, 153.73, 136.78, 134.02, 131.44, 130.76, 128.75, 120.15, 84.54, 81.24, 62.20, 52.38, 14.04. HRMS (ESI^+) calcd. for $C_{13}H_{12}O_4$ $[M+H]^+$: 233.0814, found:233.0807.



Ethyl 3-(3-((4-methylphenyl)sulfonamido)phenyl)propiolate **(4g)**. Pale red solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 8.4, 2.0 Hz, 2H), 7.25 (ddt, *J* = 17.2, 8.9, 2.5 Hz, 6H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.37 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.90, 144.24, 137.17, 135.66, 129.80, 129.43, 127.23, 124.73, 123.20, 120.64, 85.01, 80.95, 76.71, 62.26, 14.03. HRMS (ESI^+) calcd. for $C_{18}H_{18}NSO_4[M+H]^+$: 344.0957, found:344.0949.



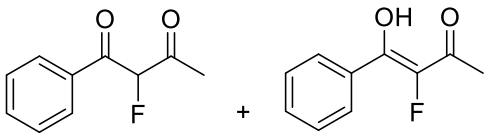
Ethyl 3-(3-(benzyloxy)phenyl)propiola **(4h)**. White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.24 (m, 6H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.06 (d, *J* = 7.6 Hz, 1H), 5.05 (s, 2H), 4.29 (d, *J* = 7.0 Hz, 2H), 1.35 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.51, 153.99, 136.32, 129.69, 128.62, 128.12, 127.41, 125.76, 120.60, 118.39, 118.28, 85.88, 80.43, 70.13, 62.08, 14.06. HRMS (ESI^+) calcd. for $C_{18}H_{17}O_3[M+H]^+$: 281.1178, found:281.1171.



4-(4-Fluoro-3-methylphenyl)but-3-yn-2-one **(4i)**. Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.32 (m, 2H), 6.99 (t, *J* = 8.9 Hz, 1H), 4.28 (d, *J* = 7.1 Hz, 2H), 2.26 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.97. ^{13}C NMR (100 MHz, $CDCl_3$) 162.57 (d, *J* = 252.1 Hz), 154.01.136.39 (d, *J* = 14.7 Hz), 132.57 (d, *J* = 12.7 Hz), 125.81 (d, *J* = 18.3 Hz), 115.62 (d, *J* = 23.5 Hz), 115.30 (d, *J* = 3.9 Hz), 62.05, 14.25, 14.07. HRMS (ESI^+) calcd. for $C_{12}H_{12}FO_2$ $[M+H]^+$: 207.0821, found:207.0815.

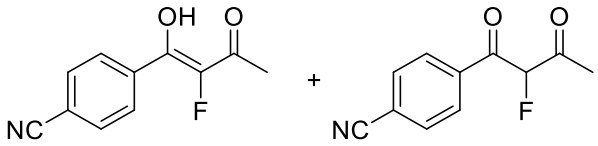
4. General procedure for fluorination of 1 or 4

A polypropylene vial was charged with alkynone **1** or alkynoate **4** (0.2 mmol, 1 equiv), 2,6-dibromopyridine N-oxide **2d** (0.28 mmol, 70 mg), and HF-pyridine (HF content 70 wt/wt%, 0.8 mmol, 27 mg, 4 equiv) and $PhCF_3$ (0.4 mL). The reaction was commenced by the addition of $JohnPhosAuNTf_2$ (5 mol%, 7.75 mg) and the reaction mixture was heated to 40 °C, the progress of the reaction was monitored by TLC. The reaction typically took 4 h or overnight to complete. Upon completion, the mixture was quenched with saturated sodium bicarbonate. The mixture was extracted with DCM and washed with 1N HCl. The organic layers were collected, dried over anhydrous $MgSO_4$ and filtered. The solvent was removed under reduced pressure and the residue was subjected to flash column chromatography purification (eluent: hexanes / ethyl acetate) to give 2-fluoro-1,3-dicarbonyl compounds **3** or **5**.



3a (major) 3a' (minor)

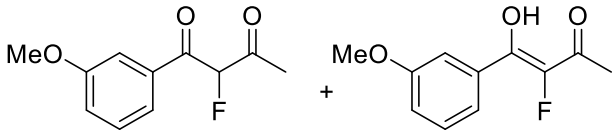
Colorless oil, 79% yield (28.4 mg), **3a**/**3a'** = 3.5/1[1]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.74 (d, *J* = 3.5 Hz, 1H-minor), 8.04 (d, *J* = 7.8 Hz, 2H-major), 7.98 (d, *J* = 7.4 Hz, 1H-minor), 7.67 (t, *J* = 7.4 Hz, 1H-major), 7.53 (t, *J* = 7.7 Hz, 2H-major), 7.49 (d, *J* = 6.8 Hz, 1H-minor), 5.97 (d, *J* = 50.1 Hz, 1H-major), 2.38 (s, 3H-minor), 2.37 (d, *J* = 4.1 Hz, 3H-major). ^{19}F NMR (377 MHz, $CDCl_3$) δ -170.10 (p, *J* = 4.3 Hz,1F-minor), -189.58 (dq, *J* = 50.4, 4.8 Hz,1F-major).



3b (major) 3b' (minor)

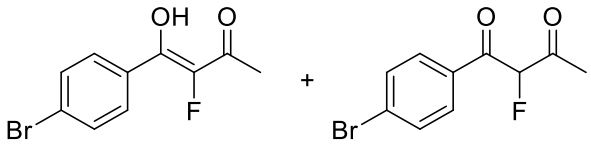
White solid, 80% yield (32.8 mg), **3b**/**3b'** = 6.5/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.36 (s, 1H-major), 8.09 (d, *J* = 8.0 Hz, 2H-minor), 8.02 (d, *J* = 8.7 Hz, 2H-major), 7.79 (d, *J* = 8.6 Hz, 2H-minor), 7.74 (d, J = 8.4 Hz, 2H-major), 5.92 (d, *J* = 49.8 Hz, 1H-minor), 2.38 (d, *J* = 4.2 Hz, 3H-major), 2.35 (d, *J* = 4.1 Hz, 3H-minor). ^{19}F NMR (376 MHz, $CDCl_3$) δ -167.71 (d, *J* = 4.3 Hz，1F-major), -189.96 (dq, *J* = 49.9, 4.2 Hz，1F-minor). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.46 (d, *J* = 29.5 Hz, major), 159.88 (d, *J* = 19.8 Hz, major),

143.80 (d, *J* = 236.9 Hz, major), 135.46 (d, *J* = 5.2 Hz, minor), 132.49(major), 132.13(major), 130.05 (d, *J* = 3.4 Hz, minor), 129.08(major), 128.99(major), 118.05(major), 114.88(minor), 96.57 (d, *J* = 200.0 Hz), 26.10 (minor), 23.30 (major). HRMS (ESI$^+$) calcd. for $C_{11}H_9FNO_2$ [M+H]$^+$: 206.0617, found:206.0612.



3c (major) 3c' (minor)

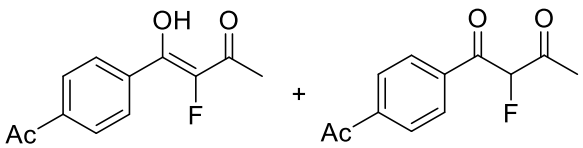
Pale yellow solid, 78% yield (32.7mg), **3b**/**3b'** = 2/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.71 (s, 1H-minor), 7.59 (d, *J* = 7.3 Hz, 1H-major), 7.54 (d, *J* = 7.8 Hz, 1H-minor), 7.51 (s, 1H-major), 7.46 (s, 1H-minor), 7.44 – 7.35 (m, 1H-major), 7.40 – 7.31 (m, 1H-monor), 7.17 (d, *J* = 8.3 Hz, 1H-major), 7.05 (d, *J* = 8.9 Hz, 1H-monor), 5.90 (d, *J* = 50.1 Hz, 1H-major), 3.85 (s, 3H-major), 3.84 (s, 3H-minor), 2.33 (d, *J* = 4.1 Hz, 3H-major), 2.32 (d, *J* = 2.1 Hz, 3H-minor). ^{19}F NMR (376 MHz, $CDCl_3$) δ -169.51(s, 1F-minor), -189.31 (dq, *J* = 50.0, 4.3 Hz, 1F-major). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.45 (d, *J* = 24.2 Hz, major), 190.22 (minor), 190.01 (d, *J* = 18.2 Hz, major), 165.23 (d, *J* = 19.5 Hz), 159.83(minor), 159.50(minor), 143.71 (d, *J* = 232.7 Hz, minor), 134.65(major), 132.92 (d, *J* = 5.1 Hz, minor), 129.80(major), 129.47(minor), 122.46 (d, *J* = 3.5 Hz, major), 121.42(major), 121.36(minor), 121.25(minor), 118.21(major), 113.33(major), 96.49 (d, *J* = 198.1 Hz, major), 55.47(major), 55.36, 25.92(major), 22.39(minor). HRMS (ESI$^+$) calcd. for $C_{11}H_{12}FO_3$ [M+H]$^+$: 211.0770, found:211.0766.



3d (major) 3d' (minor)

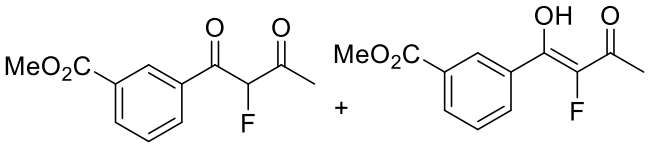
Pale yellow solid, 84% yield (43.2 mg), **3d**/**3d'** = 7/1. ^{1}H NMR (400 MHz, $CDCl_3$) 13.60 (s, 1H-major), 7.87 (d, *J* = 8.3 Hz, 2H-minor), 7.81 (d, *J* = 8.8 Hz, 2H-major), 7.64 (d, *J* = 8.3 Hz, 2H-minor), 7.59 (d, *J* = 8.5 Hz, 2H-major), 5.88 (d, *J* = 50.2 Hz, 1H-minor), 2.44 (d, *J* = 1.2 Hz, 3H-minor), 2.34 (d, *J* = 4.1 Hz, 3H-major). ^{19}F NMR (376 MHz, $CDCl_3$) δ -169.32 (s, 1F-major), -189.53 (dd, *J* = 49.7, 4.3 Hz, 1F-minor). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.19 (d, *J* = 23.8 Hz, minor), 190.55 (d, *J* = 29.0 Hz, major), 163.79 (d, *J* = 19.5 Hz, major), 143.65 (d, *J* = 233.1 Hz, major), 134.26(minor), 132.18(minor), 131.79 (major), 131.06 (d, *J* = 3.3 Hz, minor), 130.53 (d, *J* = 5.2 Hz, minor), 130.20(major), 130.11(major), 126.75(major), 96.56

(d, *J* = 194.9 Hz, minor), 25.94(minor), 22.49(major). HRMS (ESI$^+$) calcd. for $C_{10}H_9BrFO_2[M+H]^+$: 258.9770, found:258.9764.



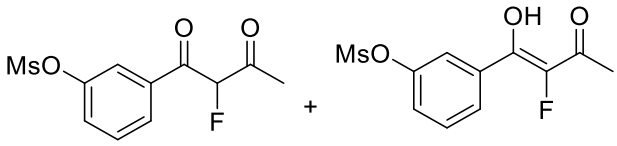
3e (major) 3e' (minor)

White solid, 92% yield (40.8 mg), **3e/3e'** = 16/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.46 (s, 1H-major), 8.00 (s, 4H-major), 5.94 (d, *J* = 49.9 Hz, 1H-minor), 2.62 (s, 3H), 2.36 (d, *J* = 4.2 Hz, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -168.37 (s, 1F-major), -189.87 (dq, *J* = 50.6, 4.2 Hz, 1F-minor). ^{13}C NMR (100 MHz, $CDCl_3$) for 3e major δ 197.34, 192.69 (d, *J* = 29.2 Hz), 161.60 (d, *J* = 19.9 Hz), 143.81 (d, *J* = 235.4 Hz), 138.94, 135.47 (d, *J* = 5.3 Hz), 128.79 (d, *J* = 8.9 Hz), 128.19, 26.75, 23.10. HRMS (ESI$^+$) calcd. for $C_{12}H_{12}FO_3$ $[M+H]^+$: 223.0770, found:233.0765.



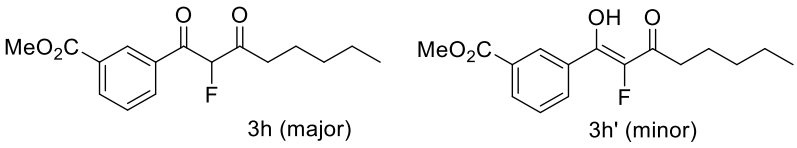
3f (major) 3f' (minor)

Pale yellow oil, 88% yield (41.8mg), **3f/3f'** = 10/9. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.57 (s, 1H-minor), 8.63 (s, 1H-minor), 8.58 (s, 1H-major), 8.28 (d, *J* = 7.5 Hz, 1H-minor), 8.17 (t, *J* = 7.7 Hz, 2H-minor), 8.10 (d, *J* = 7.3 Hz, 1H-major), 7.56 (dt, *J* = 16.0, 7.8 Hz, 2H-major), 5.97 (d, *J* = 49.9 Hz, 1H-major), 3.94 (d, *J* = 1.3 Hz 3H-minor), 3.93 (d, *J* = 1.4 Hz 3H-major), 2.36 (s, 3H-minor), 2.35 (s, 3H-major). ^{19}F NMR (376 MHz, $CDCl_3$) δ -169.50(s, 1F-minor), -190.05 (dd, *J* = 50.0, 4.4 Hz s, 1F-major). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.30 (d, *J* = 24.2 Hz, major), 190.96 (d, *J* = 29.1 Hz), 189.62 (d, *J* = 19.3 Hz, major), 166.25(major), 165.76(minor), 163.54 (d, *J* = 19.9 Hz, minor), 143.68 (d, *J* = 233.6 Hz, minor), 135.16(major), 133.74(minor), 133.60 (d, *J* = 3.3 Hz, major), 132.76(minor), 132.64(major), 130.98(minor), 130.72 (d, *J* = 3.1 Hz, minor), 130.59(major), 129.81 (d, *J* = 9.0 Hz, minor), 129.04(minor), 128.66(major), 96.28 (d, *J* = 199.0 Hz), 52.50, 52.35(major), 26.06(minor), 22.59(major). HRMS (EI$^+$) calcd. for $C_{12}H_{10}FO_4$ $[M-H^+]^-$: 237.0567, found: 237.0558.



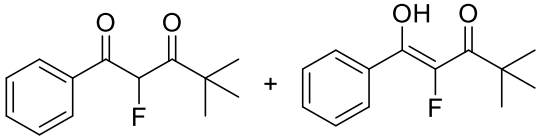
3g (major) 3g' (minor)

Pale yellow solid, 81% yield (44.3 mg), **3g**/**3g'** = 10/3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.49 (s, 1H-minor), 7.98 (d, *J* = 4.4 Hz, 1H-major), 7.92 (s, 1H-minor), 7.90 (s, 1H-major), 7.83 (s, 1H-minor), 7.61 – 7.52 (m, 2H-major), 7.51 (d, *J* = 7.9 Hz, 1H-minor), 7.44 (d, *J* = 8.2 Hz, 1H-minor), 5.91 (d, *J* = 49.9 Hz, 4H), 3.20 (s, 3H-major), 3.17 (s, 3H-minor), 2.36 (d, *J* = 4.0 Hz, 3H-minor), 2.34 (d, *J* = 4.2 Hz, 3H-major). ^{19}F NMR (376 MHz, $CDCl_3$) δ -168.83(s,1F-minor), -189.83 (dd, *J* = 49.8, 4.1 Hz,1F-major). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.12 (d, *J* = 23.7 Hz, major), 191.62 (d, *J* = 29.3 Hz), 188.80 (d, *J* = 19.5 Hz, major), 162.06 (d, *J* = 19.6 Hz), 149.24(major), 149.11(minor), 143.67 (d, *J* = 235.1 Hz, minor), 135.09(major), 133.64 (d, *J* = 4.7 Hz, minor), 130.57(major), 130.17(minor), 128.56 (d, *J* = 3.7 Hz, major), 128.36(major), 127.52 (d, *J* = 9.3 Hz, minor), 126.80 (minor), 125.41(major), 122.97 (d, *J* = 3.2 Hz, major), 122.11 (d, *J* = 9.1 Hz, minor), 121.36(minor), 96.56 (d, *J* = 199.4 Hz, major), 37.77(major), 37.61(minor), 26.04 (major), 22.77(minor). HRMS (ESI$^+$) calcd. for $C_{11}H_{12}FSO_5$[M+H]$^+$: 275.0389, found: 275.0384.



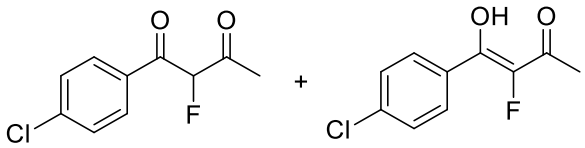
3h (major) 3h' (minor)

Colorless oil, 78% yield (34.6 mg), **3h**/**3h'** = 1.3/1. Major product **3h**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.64 (s, 1H), 8.11-8.22 (m, 2H), 7.51-7.58 (m, 2H), 6.02 (d, *J* = 49.1 Hz, 1H), 3.94 (s, 3H), 2.99 (t, *J* = 6.8 Hz, 2H), 1.18 – 1.75 (m, 6H), 0.91 - 0.94 (m, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -171.07 (s) (s,1F-minor), -192.05 (d, *J* = 49.1 Hz, 1F-major). HRMS (ESI$^+$) calcd. for $C_{16}H_{20}FO_4$[M+H]$^+$: 295.1346, found: 259.1340.



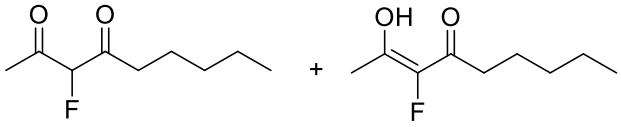
3i (major) 3i' (minor)

Colorless oil, 78% yield (34.6 mg), **3i**/**3i**' = 5/1. Major product: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.4 Hz, 2H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 2H), 6.14 (dd, *J* = 49.1 Hz, 1H), 1.24 (s, 9H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -167.60, (s,1F-minor), -187.14 (d, *J* = 49.0 Hz, 1F-major). It is spectroscopic data is consistent with literature report.[2]



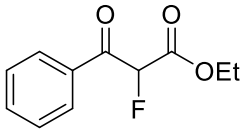
3j (major) 3j'(minor)

Pale yellow solid, 81% yield (34.6 mg), **3j**/**3j'** = 2/1. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 13.65 (s, 1H-minor), 7.97 (d, *J* = 8.3 Hz, 2H-major), 7.91 (d, *J* = 8.4 Hz, 2H-minor), 7.49 (d, *J* = 8.4 Hz, 2H-major), 7.45 (d, *J* = 8.5 Hz, 2H-minor), 5.91 (d, *J* = 50.1 Hz, 1H-major), 2.35 (s, 3H-major), 2.35 (s, 3H-minor). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -169.43(s,1F-minor), -189.53 (d, *J* = 50.2 Hz,1F-major). It is spectroscopic data is consistent with literature report.[3]



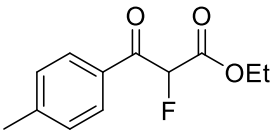
3k (major) 3k' (minor)

Colorless oil, 63% yield (21.9 mg), **3k**/**3k'** = 5/2. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 12.88 (s, 0.4H-minor), 5.23 (d, *J* = 50.7 Hz, 1H-major), 2.72 – 2.39 (m, 2H-major,0.8H-minor), 2.29 (d, *J* = 4.0 Hz, 3H-major), 2.16 (d, *J* = 3.8 Hz, 1.2H-minor), 1.68 – 1.55 (m, 2H-major,0.8H-minor), 1.38 – 1.25 (m, 4H-major,1.6 H-minor), 0.96 – 0.75 (m, 3H-major,1.2H-minor). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -174.63(s,1F-minor), -193.08 (d, *J* = 50.6 Hz, 1F-major). It is spectroscopic data is consistent with literature report.[2]

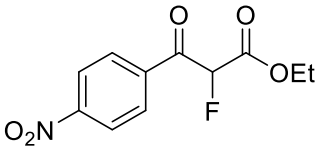


Ethyl 2-fluoro-3-oxo-3-phenylpropanoate[1] **(5a).** Colorless oil, 81% yield (34 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 – 7.86 (m, 2H), 7.69 – 7.54 (m, 1H), 7.54 – 7.43

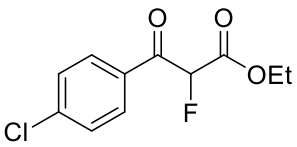
(m, 2H), 5.85 (dd, *J* = 48.8, 1.7 Hz, 1H), 4.29 (qt, *J* = 9.2, 2.6 Hz, 2H), 1.37 – 1.15 (m, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -190.36 (d, *J* = 48.8 Hz).



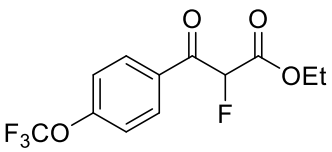
ethyl 2-fluoro-3-oxo-3-(p-tolyl)propanoate[4] **(5b).** Colorless oil, 80% yield (36.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.73 (m, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 5.83 (d, *J* = 48.9 Hz, 1H), 4.29 (dt, *J* = 7.1, 3.4 Hz, 2H), 2.42 (s, 3H), 1.25 (t, *J* = 7.0 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -190.26 (d, *J* = 48.6 Hz).



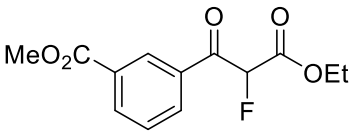
Ethyl 2-fluoro-3-(4-nitrophenyl)-3-oxopropanoate **(5c).** Pale yellow oil, 77% yield (39.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 – 8.27 (m, 2H), 8.29 – 8.10 (m, 2H), 5.84 (dd, *J* = 48.7, 0.8 Hz, 1H), 4.46 – 4.11 (m, 2H), 1.28 (td, *J* = 7.1, 0.7 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -190.19 (d, *J* = 48.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.52 (d, *J* = 21.7 Hz), 164.17 (d, *J* = 24.1 Hz), 150.92, 137.62, 130.66, 123.92, 90.49 (d, *J* = 196.5 Hz), 63.17, 13.93. HRMS (ESI$^+$) calcd. for $C_{11}H_{11}FNO_5$ [M+H]$^+$: 256.0621, found:256.0615.



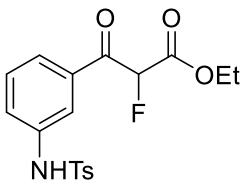
Ethyl 3-(4-chlorophenyl)-2-fluoro-3-oxopropanoate[4] **(5d)**. Pale yellow oil, 87% yield (42.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 – 7.77 (m, 2H), 7.62 – 7.26 (m, 2H), 5.80 (d, *J* = 48.9 Hz, 1H), 4.29 (dd, *J* = 7.0, 2.9 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -190.01 (d, *J* = 48.8 Hz).



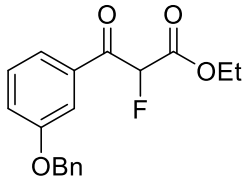
Ethyl 2-fluoro-3-oxo-3-(4-(trifluoromethoxy)phenyl)propanoate **(5e)**. Pale yellow oil, 80% yield (47 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.8 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 5.80 (d, *J* = 48.8 Hz, 1H), 4.30 (dd, *J* = 7.0, 3.1 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.65, -189.93 (d, *J* = 49.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.13 (d, *J* = 20.8 Hz), 164.61 (d, *J* = 24.1 Hz), 153.54, 131.72 (d, *J* = 4.0 Hz), 131.37, 120.34, 120.18 (q, *J* = 259.5 Hz). 90.30 (d, *J* = 198.3 Hz), 62.84, 13.89. HRMS (ESI$^+$) calcd. for $C_{12}H_{11}F_4O_4$ [M+H]$^+$: 294.0593, found:259.05888.



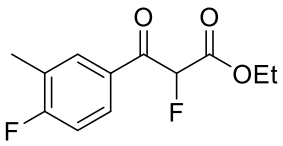
Methyl 3-(3-ethoxy-2-fluoro-3-oxopropanoyl)benzoate **(5f)**. Colorless oil, 85% yield (45 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 8.28 (d, *J* = 6.6 Hz, 1H), 8.21 (d, *J* = 7.7 Hz, 1H), 7.59 (t, *J* = 7.8 Hz, 1H), 5.90 (d, *J* = 48.6 Hz, 1H), 4.29 (q, *J* = 4.9, 4.3 Hz, 2H), 3.94 (s, 3H), 1.55 – 0.89 (m, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -190.89 (d, *J* = 48.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.90 (d, *J* = 20.6 Hz), 165.78, 164.51 (d, *J* = 23.9 Hz), 135.11, 133.62, 133.44 (d, *J* = 3.7 Hz), 131.00, 130.54 (d, *J* = 3.2 Hz), 129.07, 89.88 (d, *J* = 198.0 Hz), 62.81, 52.49, 13.89. HRMS (ESI$^+$) calcd. for $C_{13}H_{14}FO_5$ [M+H]$^+$: 269.0825, found:269.0819



Ethyl 2-fluoro-3-(3-((4-methylphenyl)sulfonamido)phenyl)-3-oxopropanoate **(5g)**. Pale yellow solid, 91% yield (68.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 14.1, 8.0 Hz, 4H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.37 (t, *J* = 7.9 Hz, 1H), 7.30 – 7.16 (m, 2H), 5.78 (d, *J* = 48.7 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 2.36 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -190.31 (d, *J* = 48.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.91 (d, *J* = 20.5 Hz), 164.67 (d, *J* = 24.0 Hz), 144.26, 135.76, 134.28, 129.80, 127.27, 126.54, 125.84 (d, *J* = 3.8 Hz), 121.18 (d, *J* = 3.3 Hz), 89.91 (d, *J* = 196.1 Hz), 62.83, 21.51, 13.89. HRMS (ESI$^+$) calcd. for $C_{18}H_{19}NSFO_5$ [M+H]$^+$: 380.0968, found: 380.0962.

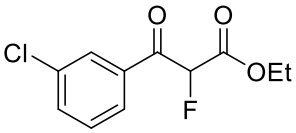


Ethyl 3-(3-(benzyloxy)phenyl)-2-fluoro-3-oxopropanoate **(5h).** Pale yellow oil, 88% yield (55.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 7.52 (m, 2H), 7.55 – 7.29 (m, 6H), 5.83 (d, *J* = 48.8 Hz, 1H), 5.11 (s, 2H), 4.29 (q, *J* = 7.1 Hz, 2H), 1.25 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -190.09 (d, *J* = 48.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.21 (d, *J* = 20.1 Hz), 164.85 (d, *J* = 24.2 Hz), 159.01, 136.23, 134.58, 129.87, 128.64, 128.18, 127.55, 122.41 (d, *J* = 4.0 Hz), 122.05, 114.39 (d, *J* = 2.9 Hz), 89.99 (d, *J* = 197.6 Hz), 70.23, 62.68, 13.94. HRMS (ESI$^+$) calcd. for $C_{18}H_{18}FO_4$ [M+H]$^+$: 317.1189, found:317.1182.

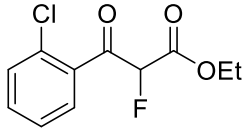


Ethyl 3-(4-fluoro-3-methylphenyl)propiolate **(5i).** Colorless oil, 87% yield (42.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (t, *J* = 7.2 Hz, 2H), 7.10 (t, *J* = 8.8 Hz, 1H), 5.80 (d, *J* = 48.9 Hz, 1H), 4.35 – 4.21 (m, 2H), 2.32 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.01, -189.69 (d, *J* = 48.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.16 (d, *J* = 20.4 Hz), 164.85 (d, *J* = 24.1 Hz), 165.16 (d, *J* = 256.4 Hz), 133.39 (d, *J* = 3.5 Hz), 129.76

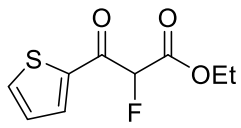
(d, *J* = 5.8 Hz), 129.45, 125.99 (d, *J* = 18.0 Hz), 115.60 (d, *J* = 23.3 Hz), 62.70, 14.50, 13.92. HRMS (ESI$^+$) calcd. for $C_{12}H_{13}F_2O_3$ [M+H]$^+$: 242.0833, found:243.0826.



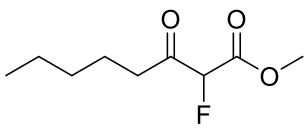
Ethyl 3-(3-chlorophenyl)-2-fluoro-3-oxopropanoate **(5j).** Colorless oil, 83% yield (40.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.92 (d, *J* = 7.5 Hz, 1H), 7.60 (d, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.9 Hz, 1H), 5.81 (d, *J* = 48.7 Hz, 1H), 4.30 (dd, *J* = 7.1, 2.9 Hz, 2H), 1.27 (t, *J* = 7.0 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -190.36 (d, *J* = 49.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.45 (d, *J* = 20.8 Hz), 164.48 (d, *J* = 23.9 Hz), 135.21, 134.77, 134.42, 130.11, 129.40 (d, *J* = 3.5 Hz), 127.62 (d, *J* = 4.2 Hz), 90.07 (d, *J* = 199.7 Hz), 62.87, 13.92. HRMS (ESI$^+$) calcd. for $C_{11}H_{11}ClFO_3$ [M+H]$^+$: 245.0381, found:245.0375.



Ethyl 3-(2-chlorophenyl)-2-fluoro-3-oxopropanoate **(5k).** Colorless oil, 35% yield (17 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.4 Hz, 1H), 7.54 – 7.41 (m, 2H), 7.40 – 7.30 (m, 1H), 5.94 (d, *J* = 48.2 Hz, 1H), 4.49 – 3.90 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -192.38 (d, *J* = 48.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.48 (d, *J* = 23.0 Hz), 163.96 (d, *J* = 24.2 Hz), 134.96, 133.04, 131.95, 130.60, 130.05 (d, *J* = 2.8 Hz), 126.92, 90.43 (d, *J* = 199.2 Hz), 62.70, 13.88. HRMS (ESI$^+$) calcd. for $C_{11}H_{11}ClFO_3$ [M+H]$^+$: 245.0381, found:245.0374.

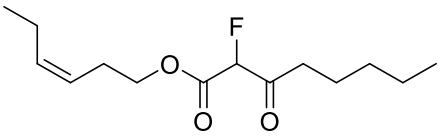


Ethyl 2-fluoro-3-oxo-3-(thiophen-2-yl)propanoate[4] **(5l).** Colorless oil, 84% yield (36.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.78 (d, *J* = 4.9 Hz, 1H), 7.18 (d, *J* = 4.8 Hz, 1H), 5.68 (d, *J* = 48.9 Hz, 1H), 4.57 – 3.77 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -189.23 (d, *J* = 48.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.32 (d, *J* = 21.8 Hz), 164.55 (d, *J* = 24.4 Hz), 139.53, 136.21, 135.33 (d, *J* = 6.9 Hz), 128.66, 90.52 (d, *J* = 198.8 Hz), 62.77, 13.94.

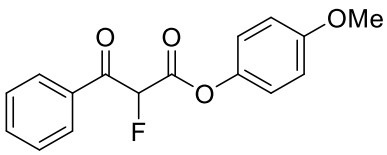


Methyl 2-fluoro-3-oxooctanoate **(5m)**. Colorless oil, 86% yield (37.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.20 (d, *J* = 49.4 Hz, 1H), 3.84 (s, 3H), 2.65 (qd, *J* = 7.2, 3.0 Hz, 2H), 1.58-1.62 (m, 2H), 1.26-1.28 (m, 4H), 0.88 (t, *J* = 6.7 Hz,

3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -194.92 (d, *J* = 49.6 Hz).^{13}C NMR (100 MHz, $CDCl_3$) δ 201.30 (d, *J* = 23.0 Hz), 164.62 (d, *J* = 24.2 Hz), 91.26 (d, *J* = 198.5 Hz), 53.13, 38.39, 31.04, 22.30 (d, *J* = 3.8 Hz), 13.79.

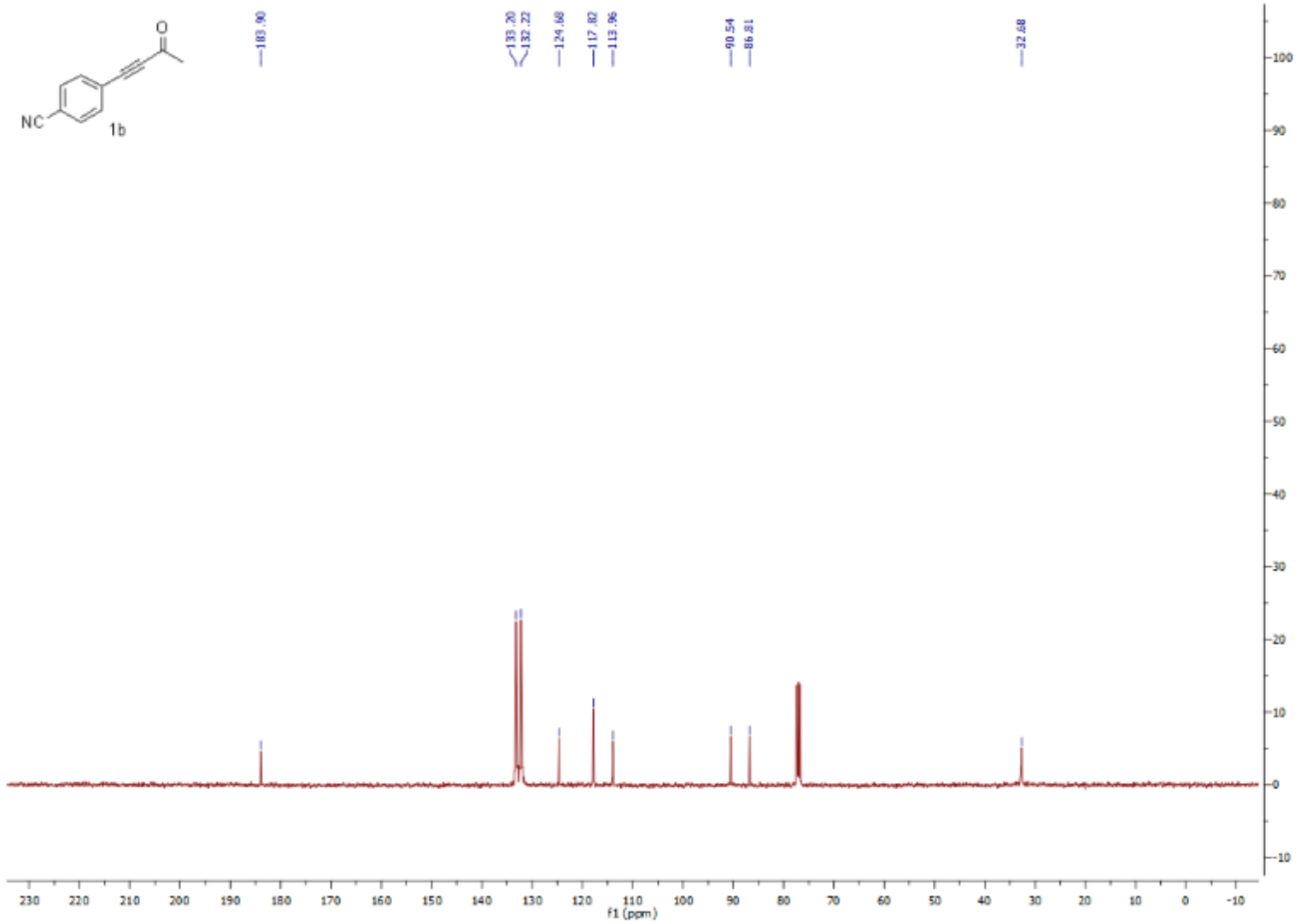


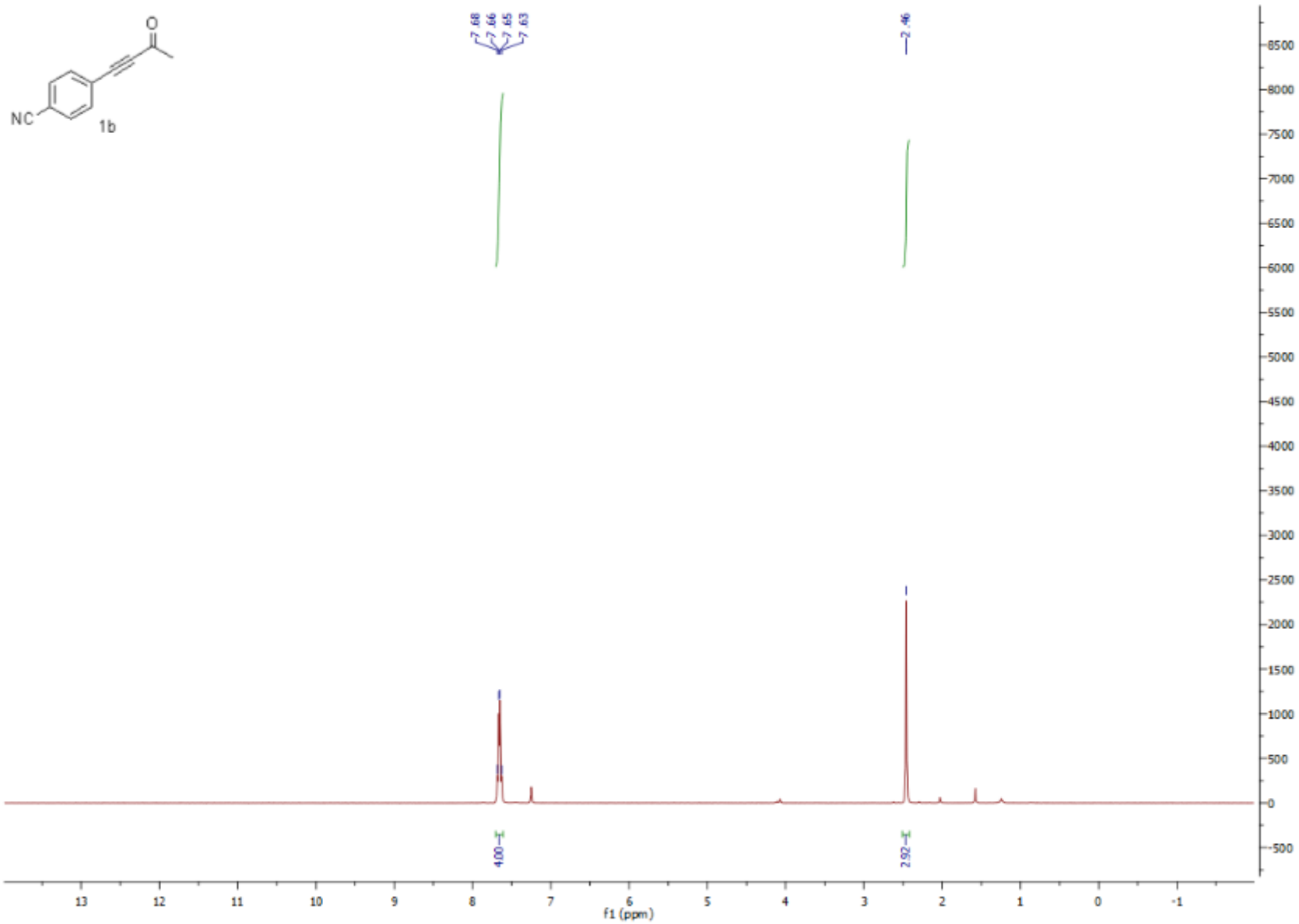
(Z)-hex-3-en-1-yl 2-fluoro-3-oxononanoate (**5n**). Colorless oil, 68% yield (37 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.71 – 5.43 (m, 1H), 5.29 (ddq, *J* = 8.9, 3.3, 1.6 Hz, 1H), 5.20 (d, *J* = 49.5 Hz, 1H), 4.24 (t, *J* = 7.0 Hz, 2H), 2.80 – 2.57 (m, 2H), 2.55 – 2.30 (m, 2H), 2.06 (td, *J* = 7.5, 1.7 Hz, 2H), 1.61 (q, *J* = 7.3 Hz, 2H), 1.29 (q, *J* = 2.9, 2.4 Hz, 4H), 0.98 (t, *J* = 7.5 Hz, 3H), 0.89 (t, *J* = 6.9 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -194.70 (d, *J* = 49.7 Hz).^{13}C NMR (100 MHz, $CDCl_3$) δ 201.24 (d, *J* = 22.6 Hz), 164.20 (d, *J* = 24.0 Hz), 122.63 (d, *J* = 12.9 Hz), 91.23 (d, *J* = 197.1 Hz), 65.88, 38.43, 31.43, 28.59, 26.47, 22.52 (d, *J* = 21.4 Hz), 20.58, 13.99. HRMS (ESI$^+$) calcd. for $C_{15}H_{26}FO_3$: 273.1866, found:273.1860.



4-Methoxyphenyl 2-fluoro-3-oxo-3-phenylpropanoate **(5o)**. Colorless oil, 90% yield (51.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.7 Hz, 1H), 7.66 (t, *J* = 6.8 Hz, 1H), 7.53 (t, *J* = 7.9 Hz, 2H), 6.99 (d, *J* = 8.9 Hz, 2H), 6.85 (d, *J* = 9.0 Hz, 2H), 6.09 (d, *J* = 48.6 Hz, 1H), 3.77 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -189.89 (d, *J* = 48.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.15 (d, *J* = 20.1 Hz), 163.93 (d, *J* = 24.7 Hz), 157.77, 143.23, 134.71, 133.34, 128.95, 121.77, 114.55, 89.74 (d, *J* = 196.2 Hz), 55.55. HRMS (ESI$^+$) calcd. for $C_{16}H_{14}FO_4[M+H]^+$: 289.0876, found:289.0870.

5. Copies of NMR Spectra for compounds 3 and 5.

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NC
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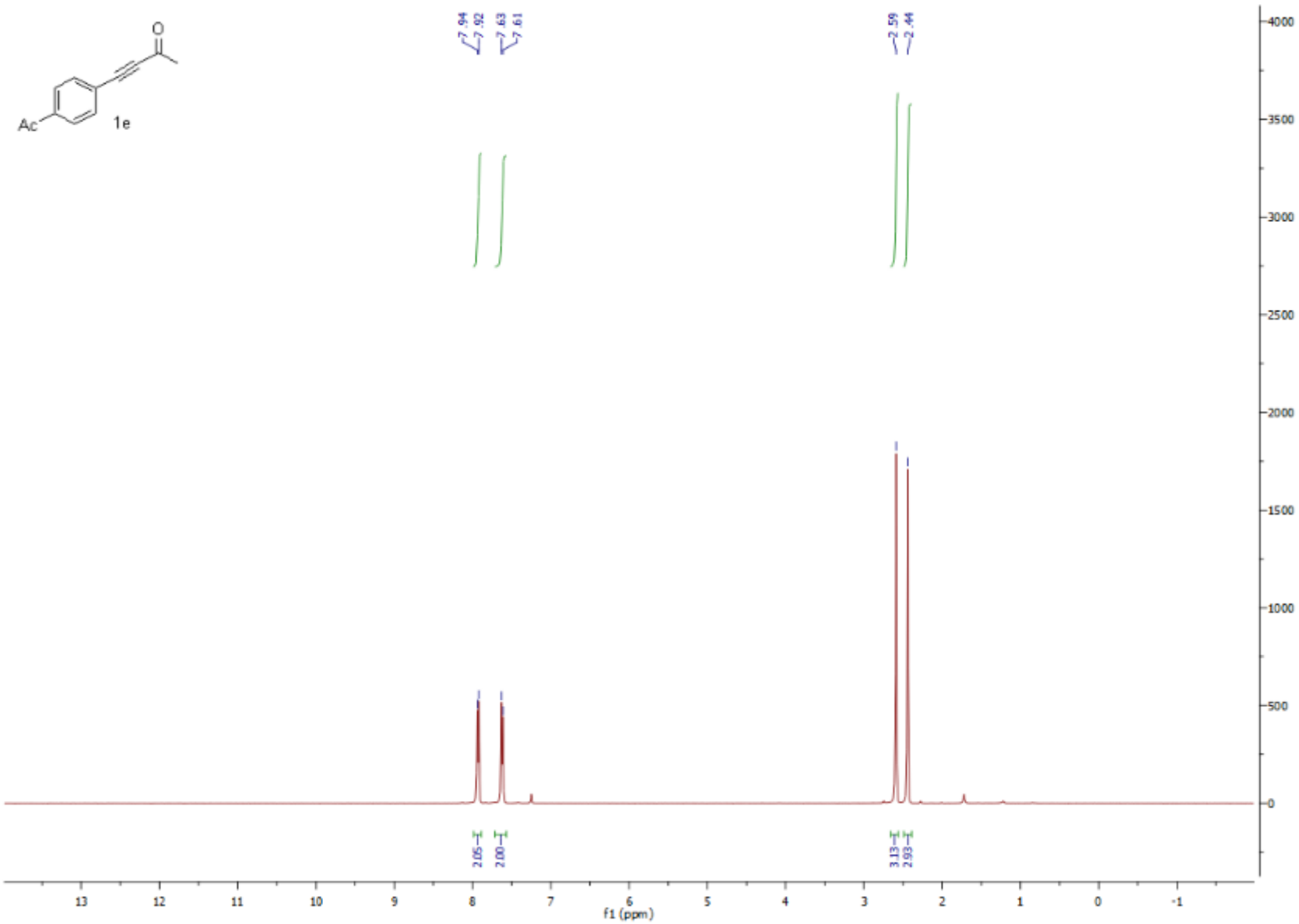
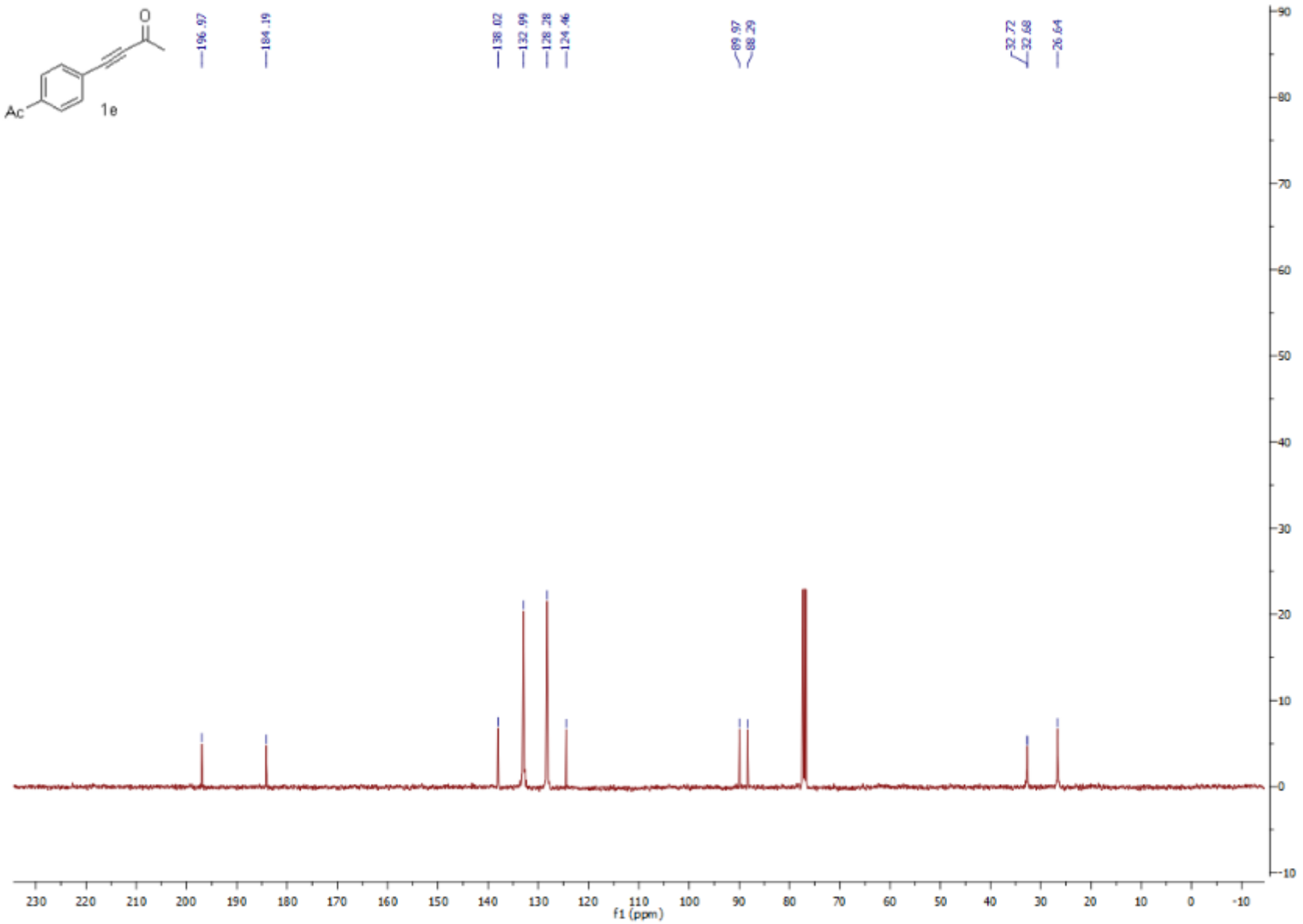
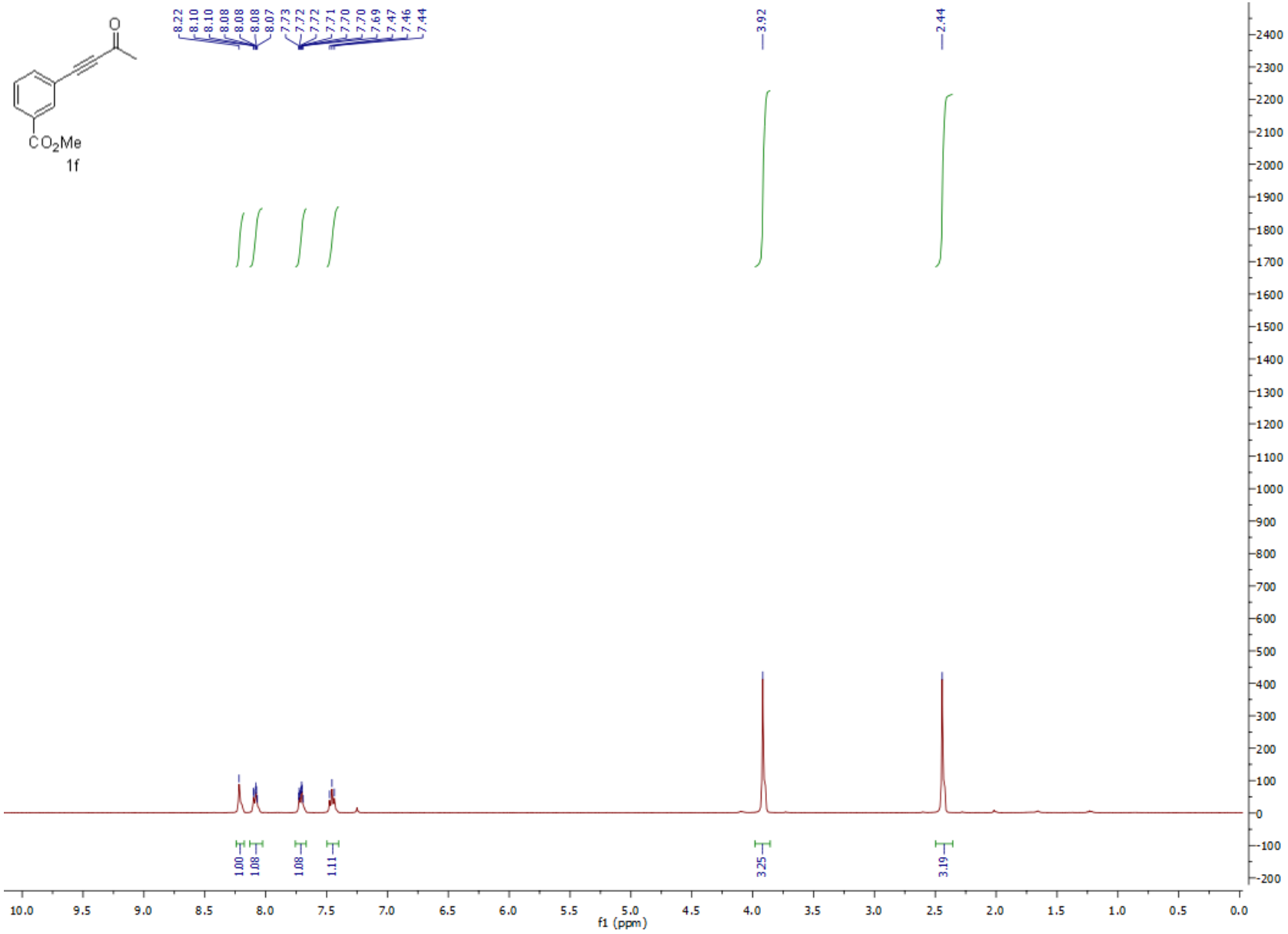
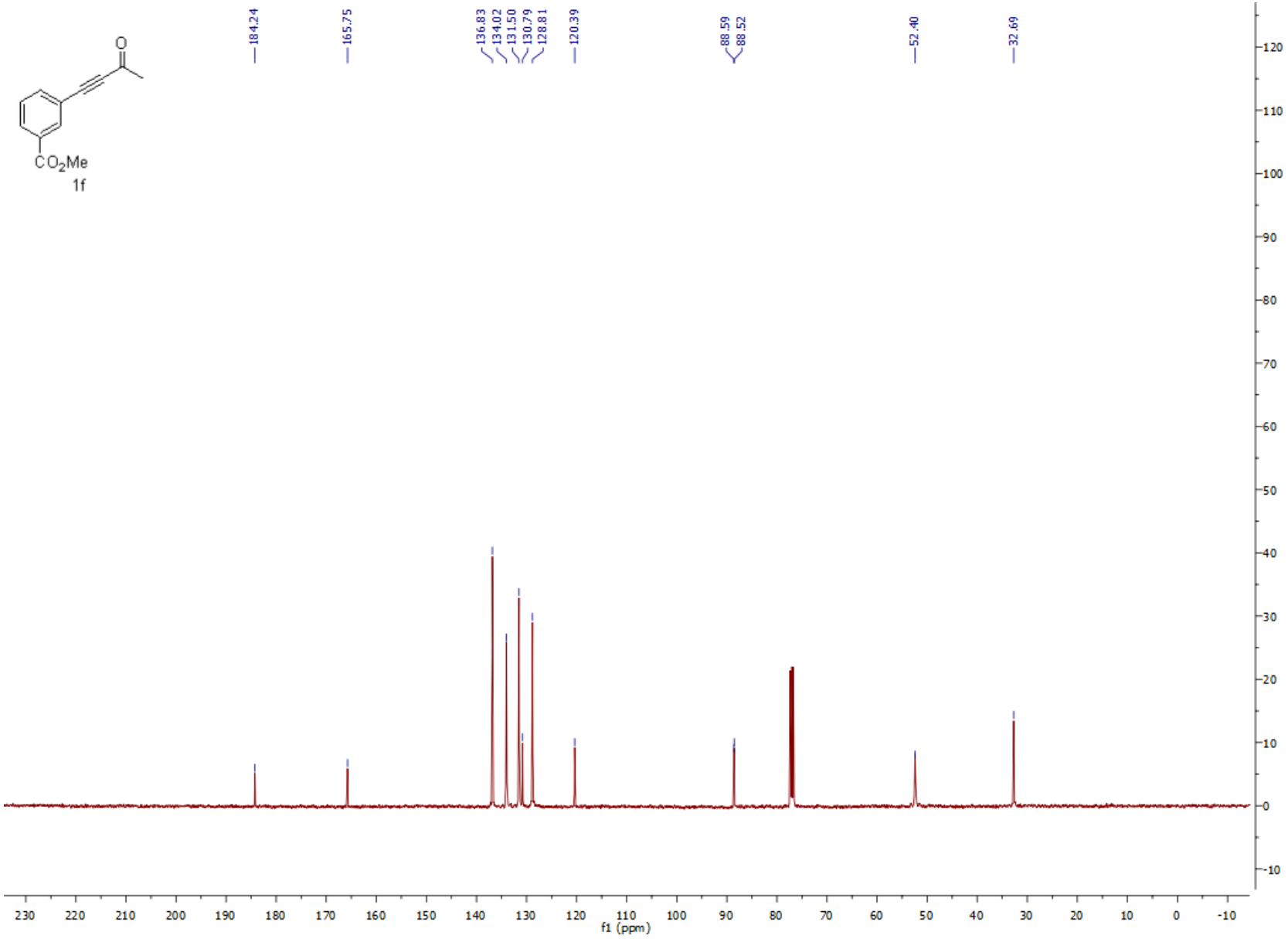
7.66
7.65
7.63
2.46
4.00
2.92
f1 (ppm)


O
Ac
1e
7.94
7.92
7.63
7.61
2.59
2.44
2.05
2.00
3.13
2.93
f1 (ppm)


O
Ac
1e
196.97
184.19
138.02
132.99
128.28
124.46
89.97
88.29
32.72
32.68
26.64
f1 (ppm)


8.22
8.10
8.10
8.08
8.08
8.08
8.07
7.73
7.72
7.72
7.71
7.70
7.70
7.69
7.47
7.46
7.44
3.92
2.44
O
CO2Me
1f
1.00
1.08
1.08
1.11
3.25
3.19
f1 (ppm)


O
CO2Me
1f
184.24
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130.79
128.81
120.39
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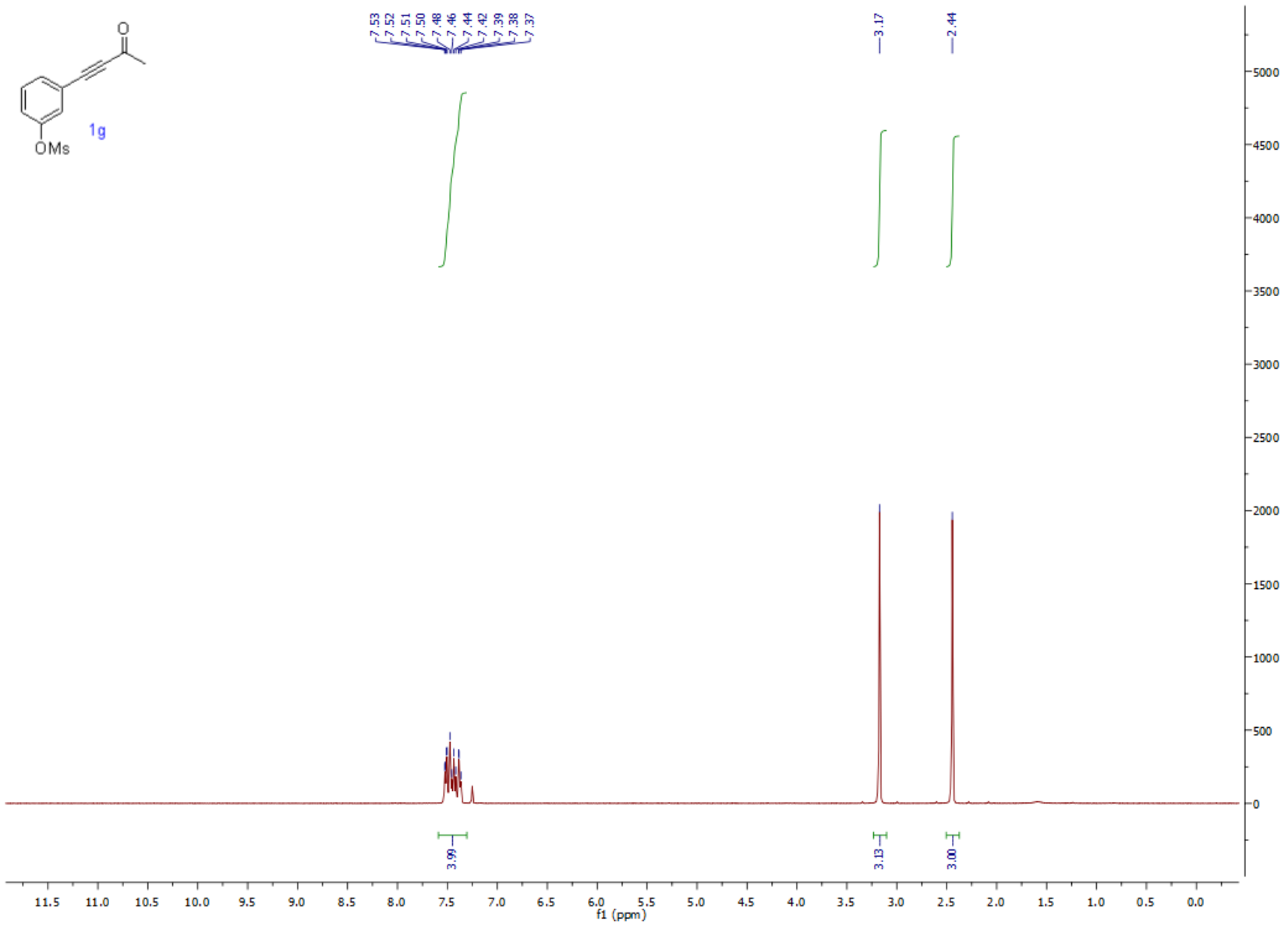
88.52
52.40
32.69
f1 (ppm)


O
OMs
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7.52
7.51
7.50
7.48
7.46
7.44
7.42
7.39
7.38
7.37
3.17
2.44
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
3.99
3.13
3.00
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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2.0
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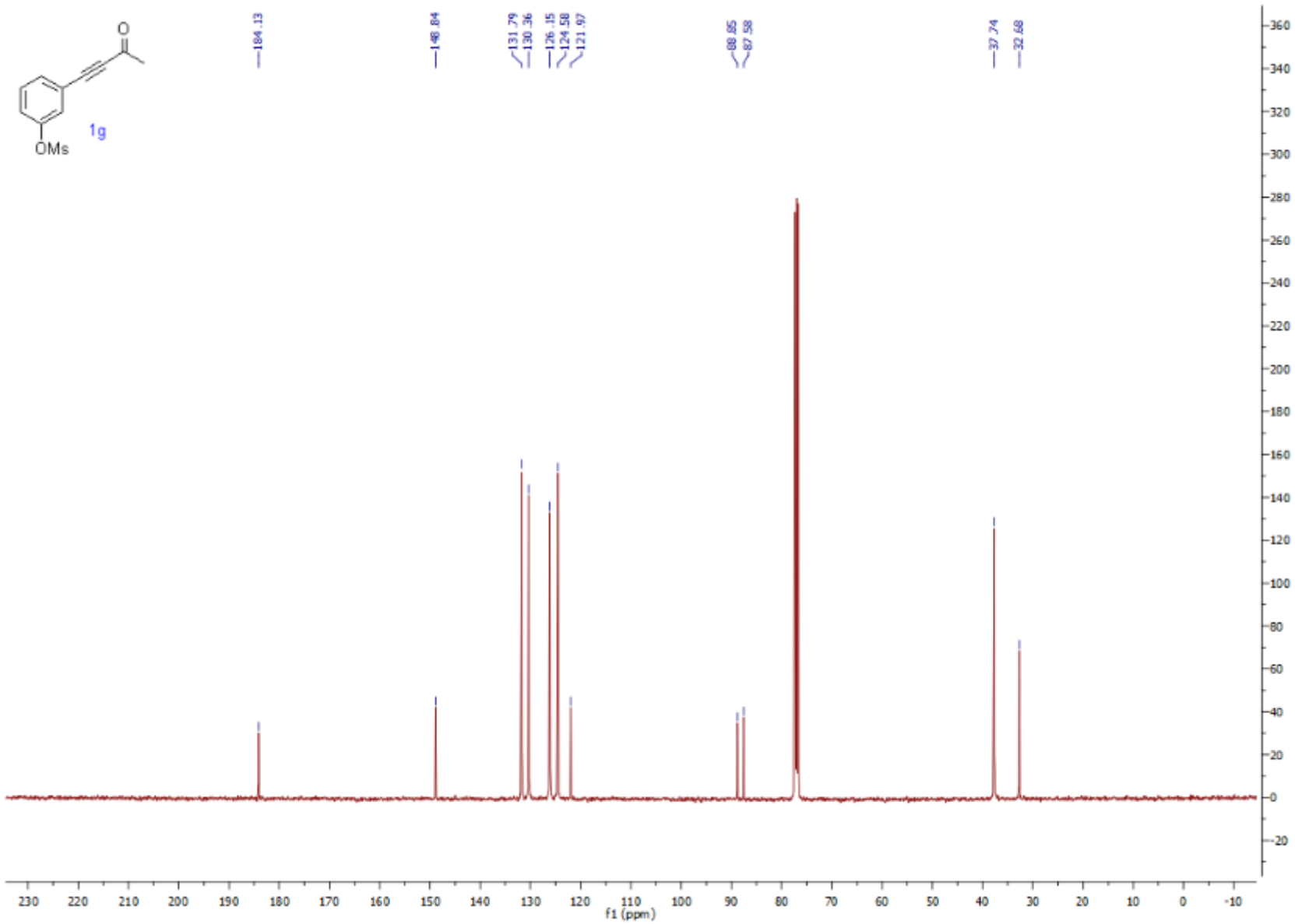
0.0
f1 (ppm)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OMs
1g
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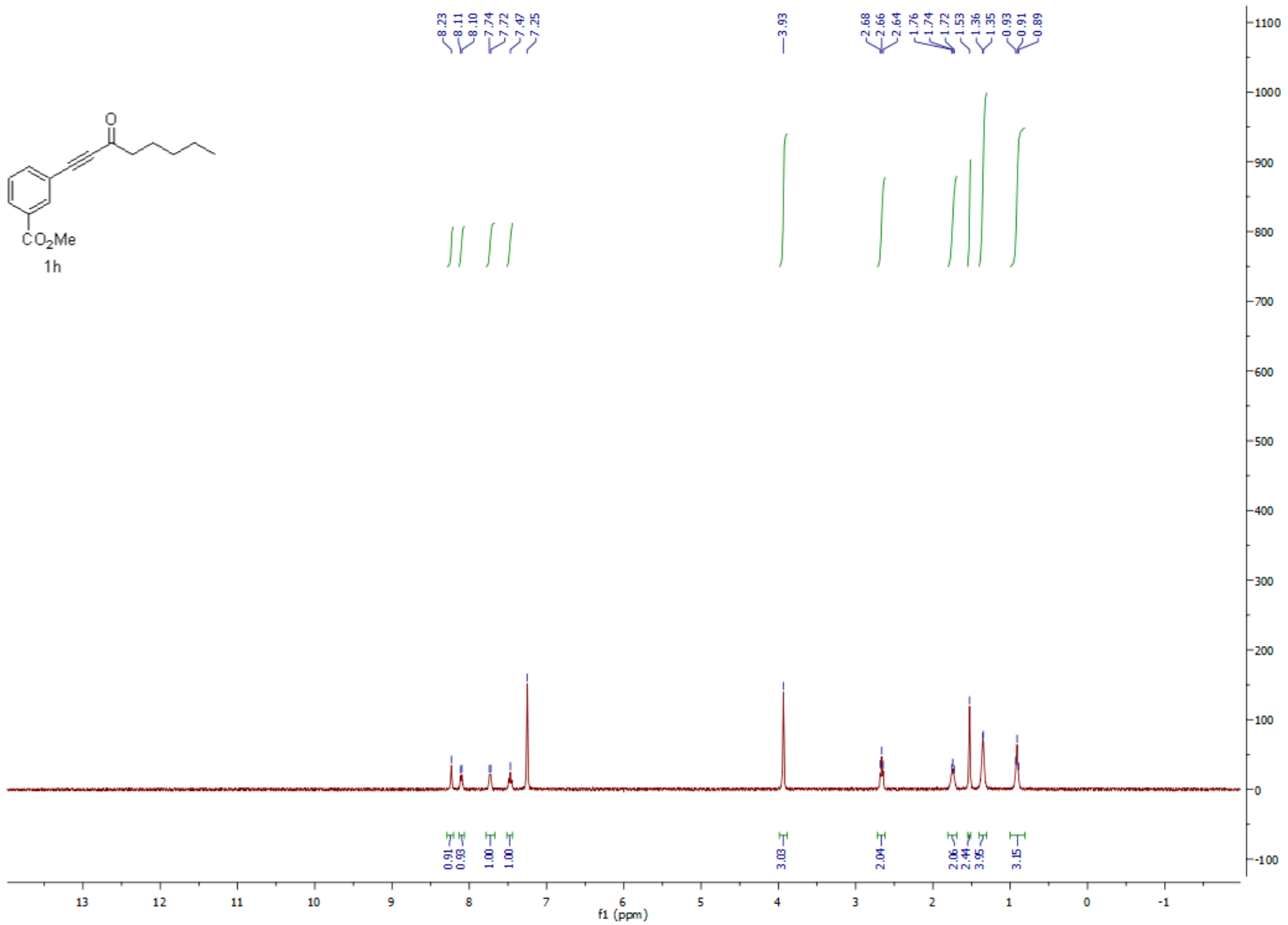
88.85
87.58
37.74
32.68
f1 (ppm)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8.10
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7.72
7.47
7.25
3.93
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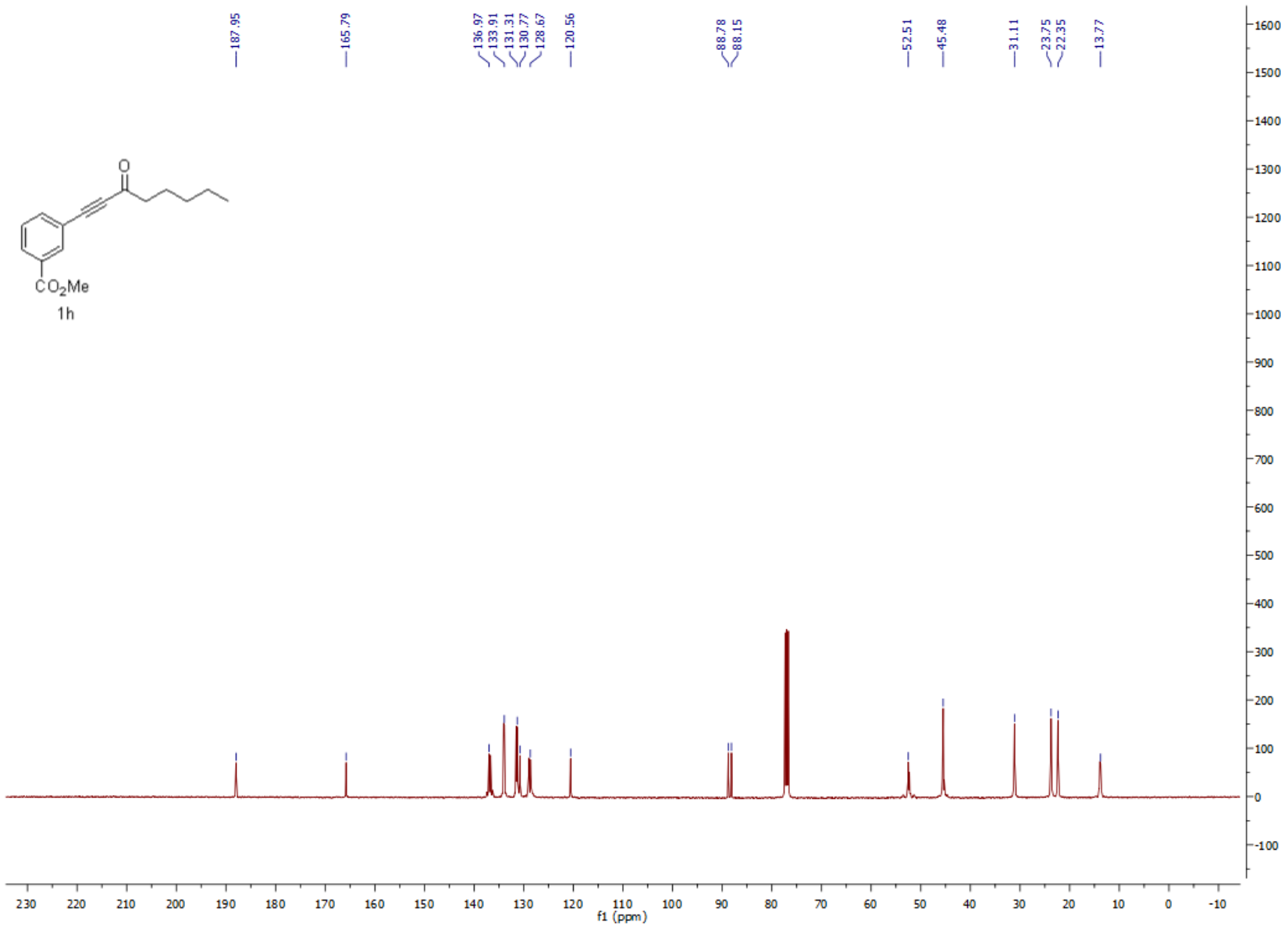
2.66
2.64
1.76
1.74
1.72
1.53
1.36
1.35
0.93
0.91
0.89
O
CO2Me
1h
0.91
0.93
1.00
1.00
3.03
2.04
2.06
2.44
3.95
3.15
f1 (ppm)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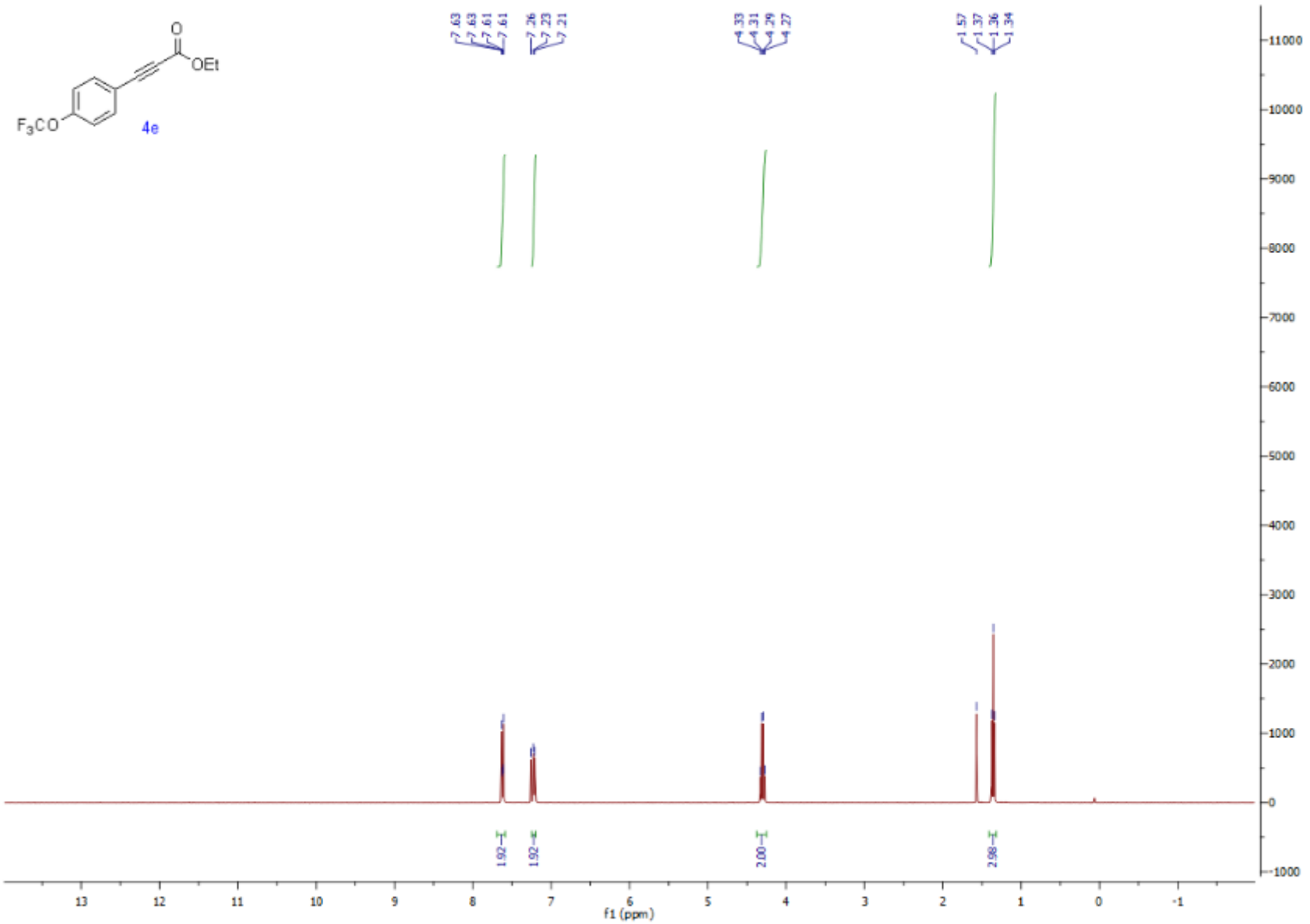
133.91
131.31
130.77
128.67
120.56
88.78
88.15
52.51
45.48
31.11
23.75
22.35
13.77
O
CO2Me
1h
f1 (ppm)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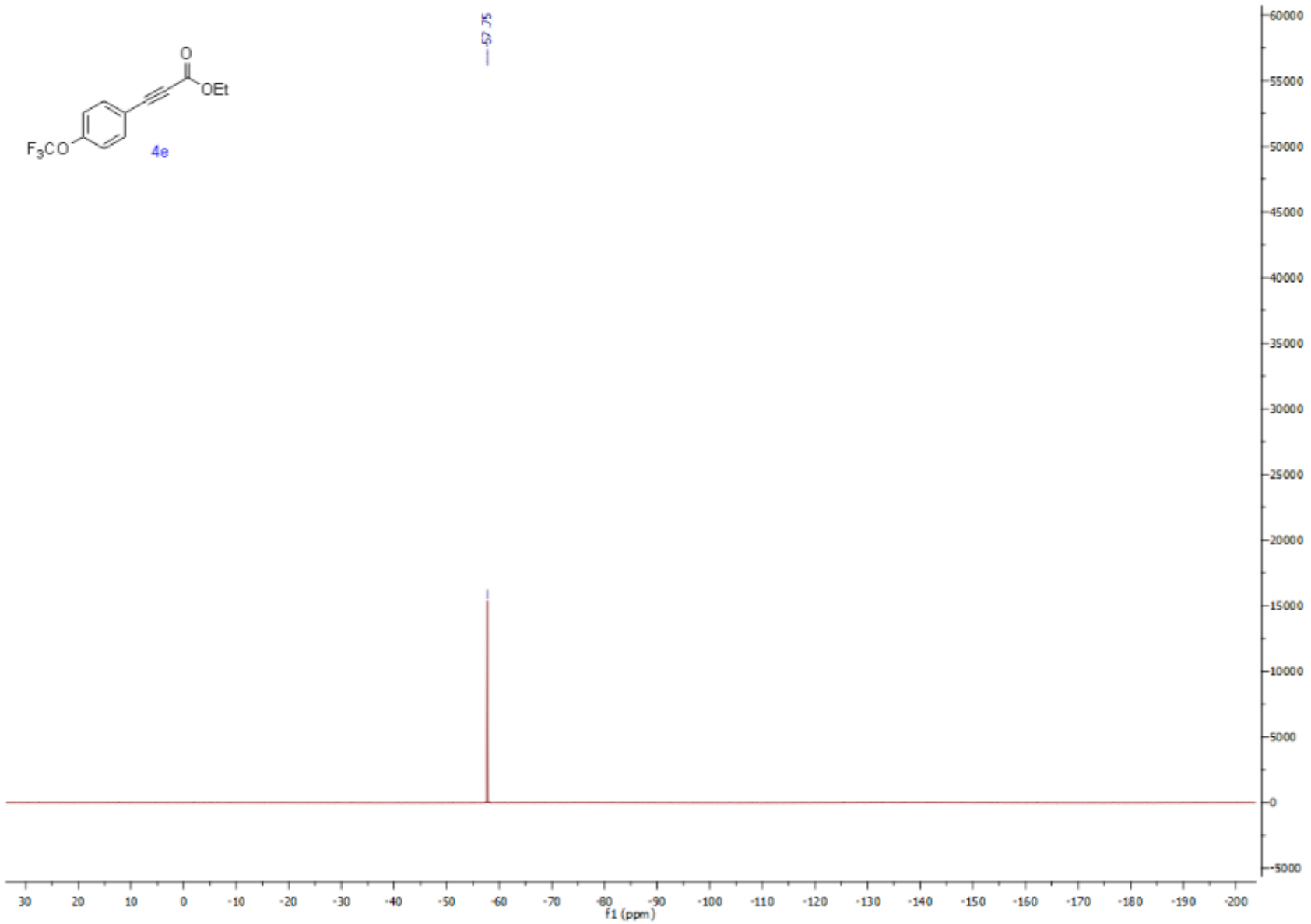
OEt
F3CO
4e
7.63
7.63
7.61
7.61
7.26
7.23
7.21
4.33
4.31
4.29
4.27
1.57
1.37
1.36
1.34
1.92
1.92
2.00
2.98
f1 (ppm)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F3CO
4e
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45000
40000
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30000
25000
20000
15000
10000
5000
0
-5000
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
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-90
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-120
-130
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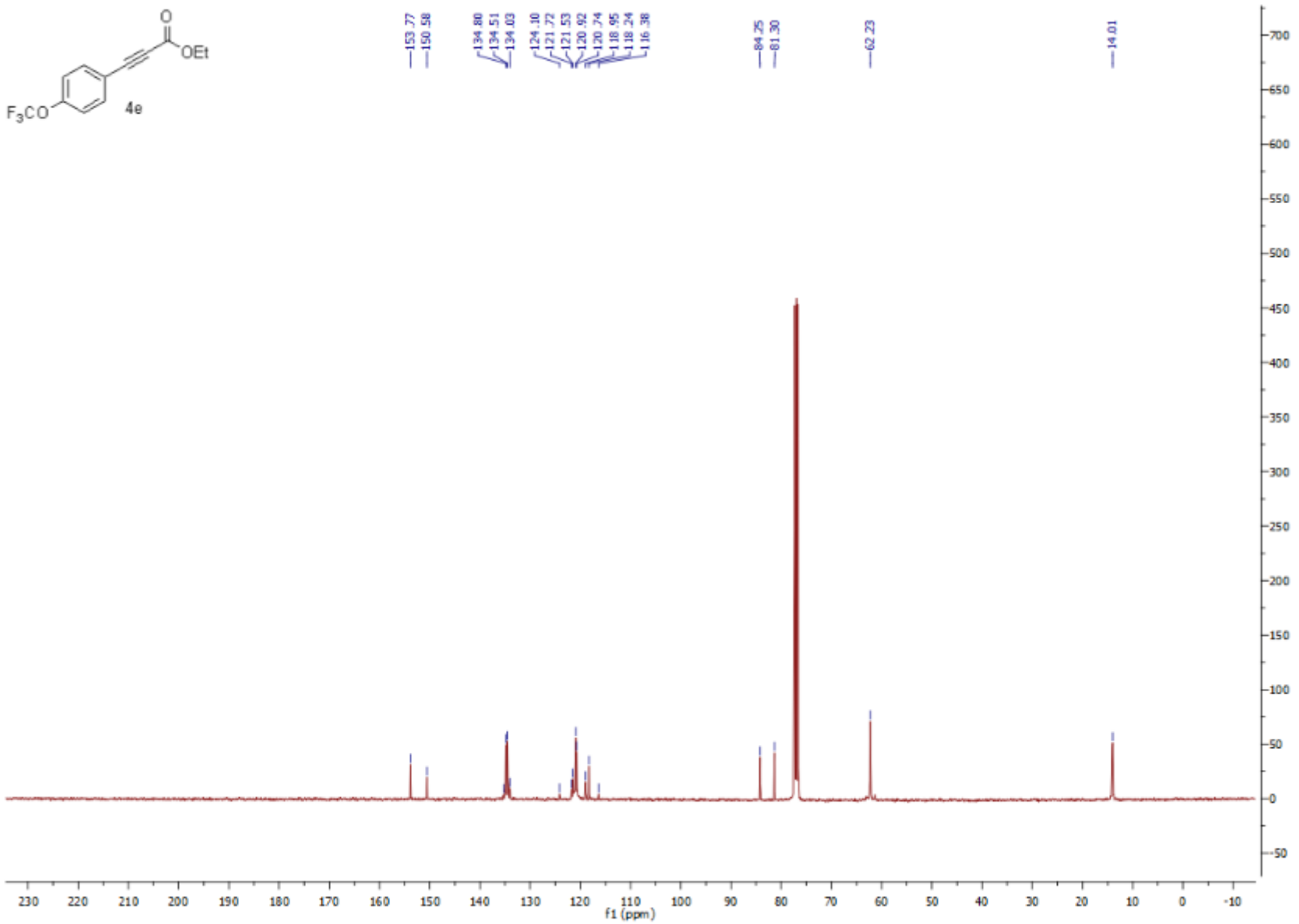
-150
-160
-170
-180
-190
-200
f1 (ppm)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134.51
134.03
124.10
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121.53
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120.74
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118.24
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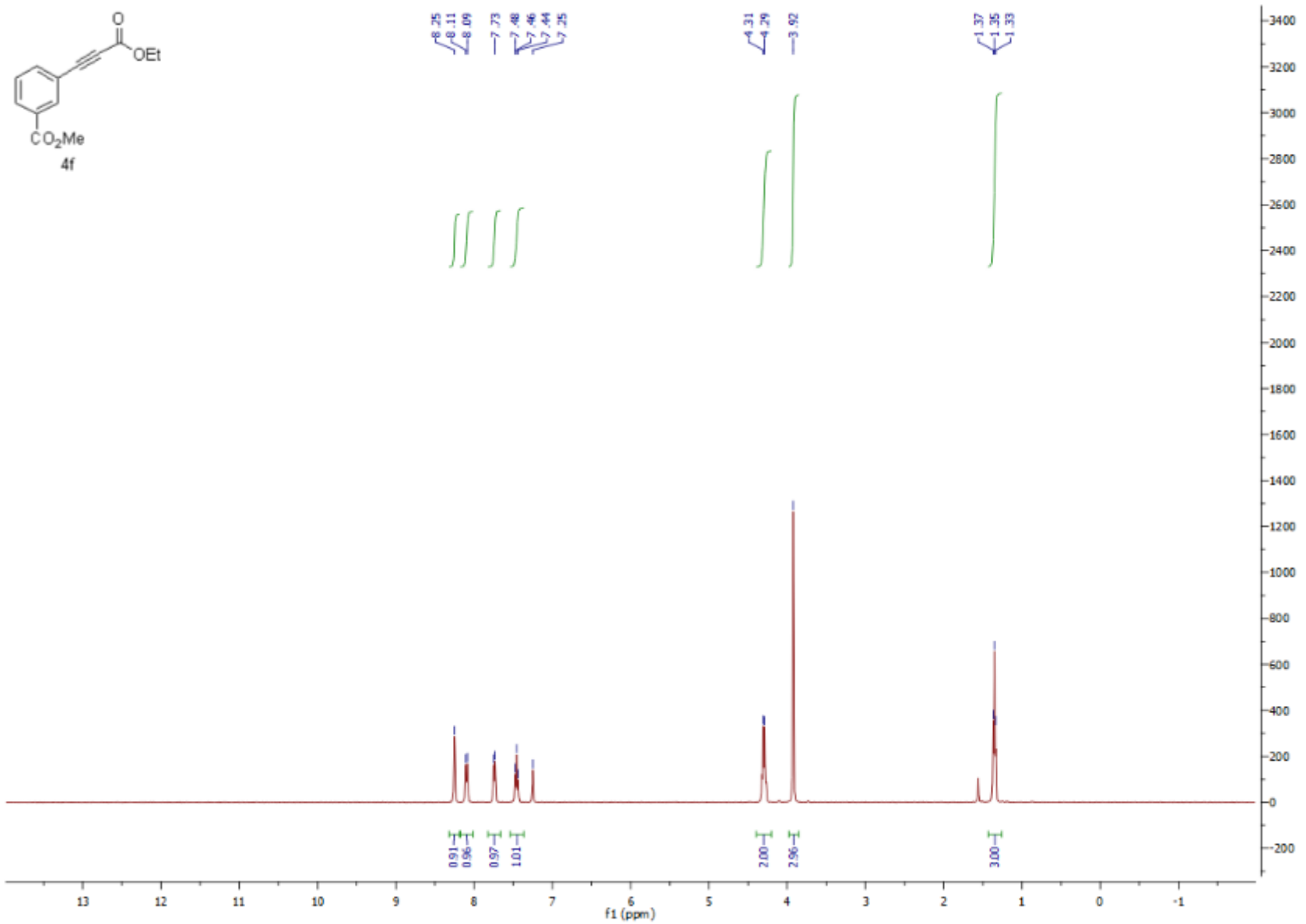
84.25
81.30
62.23
14.01
f1 (ppm)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CO2Me
4f
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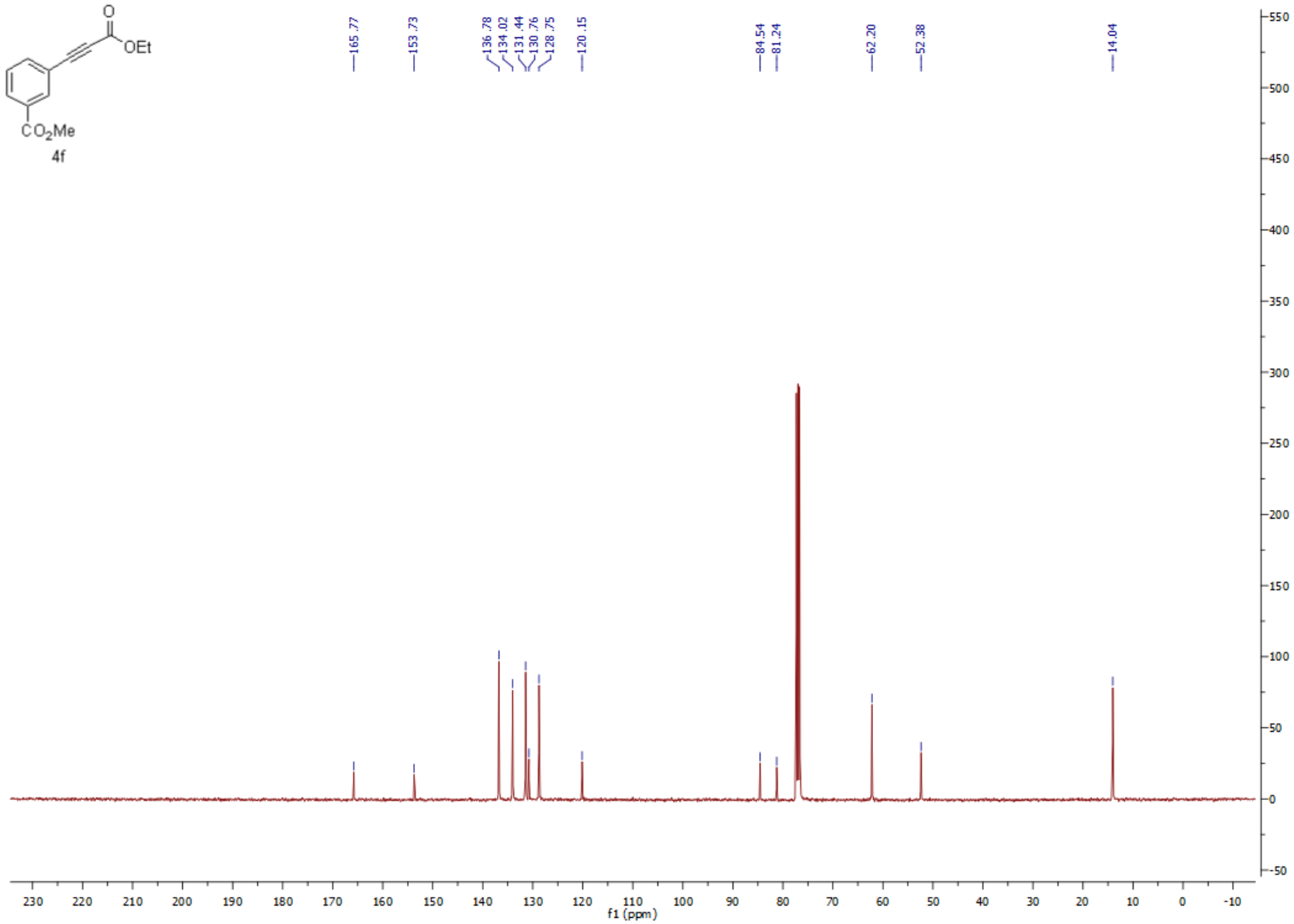
8.11
8.09
7.73
7.48
7.46
7.44
7.25
4.31
4.29
3.92
1.37
1.35
1.33
0.91
0.96
0.97
1.01
2.00
2.96
3.00
f1 (ppm)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62.20
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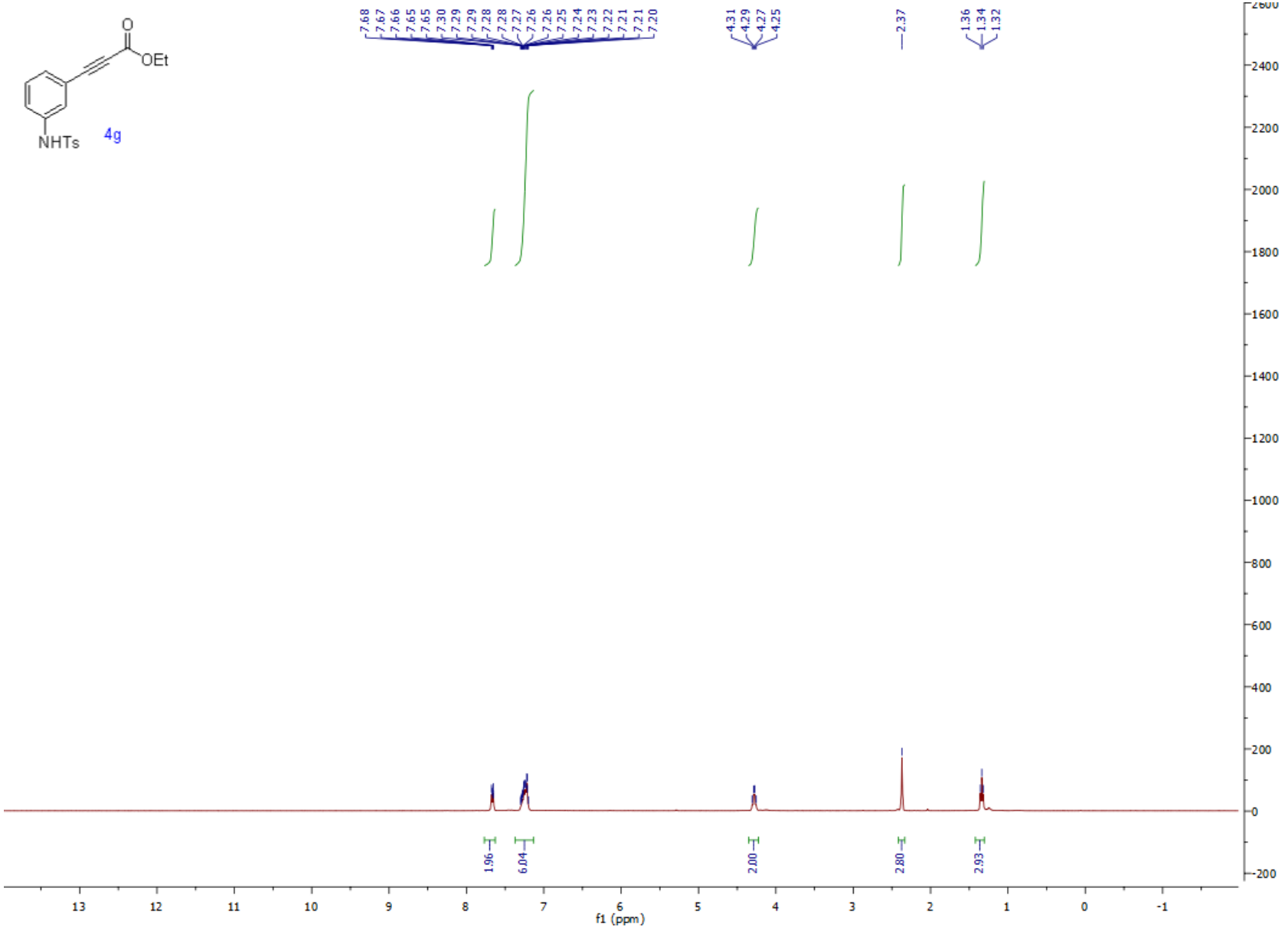
f1 (ppm)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7.28
7.28
7.27
7.26
7.26
7.25
7.24
7.23
7.22
7.21
7.21
7.20
4.31
4.29
4.27
4.25
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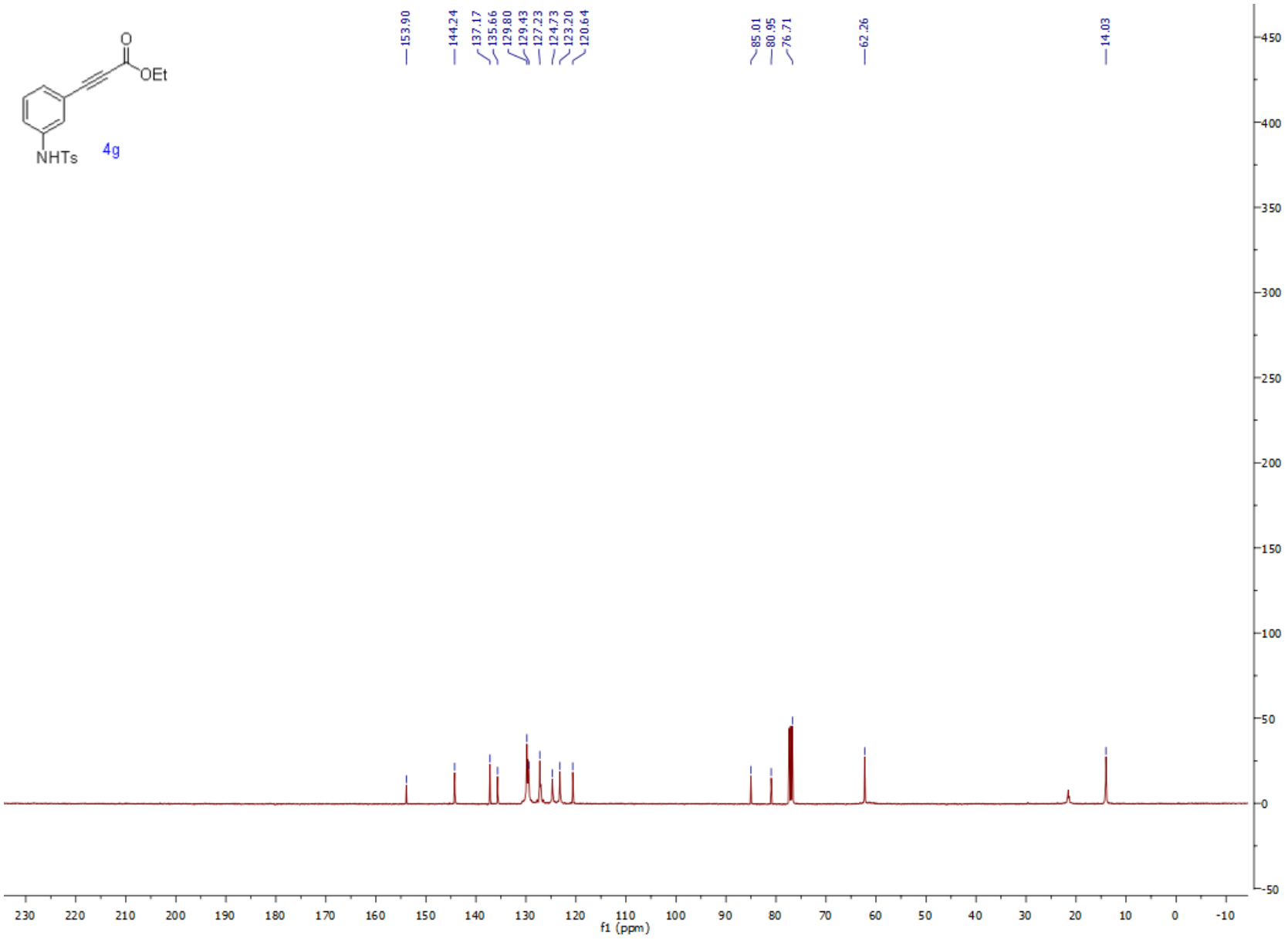
1.34
1.32
1.96
6.04
2.00
2.80
2.93
f1 (ppm)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NHTs
4g
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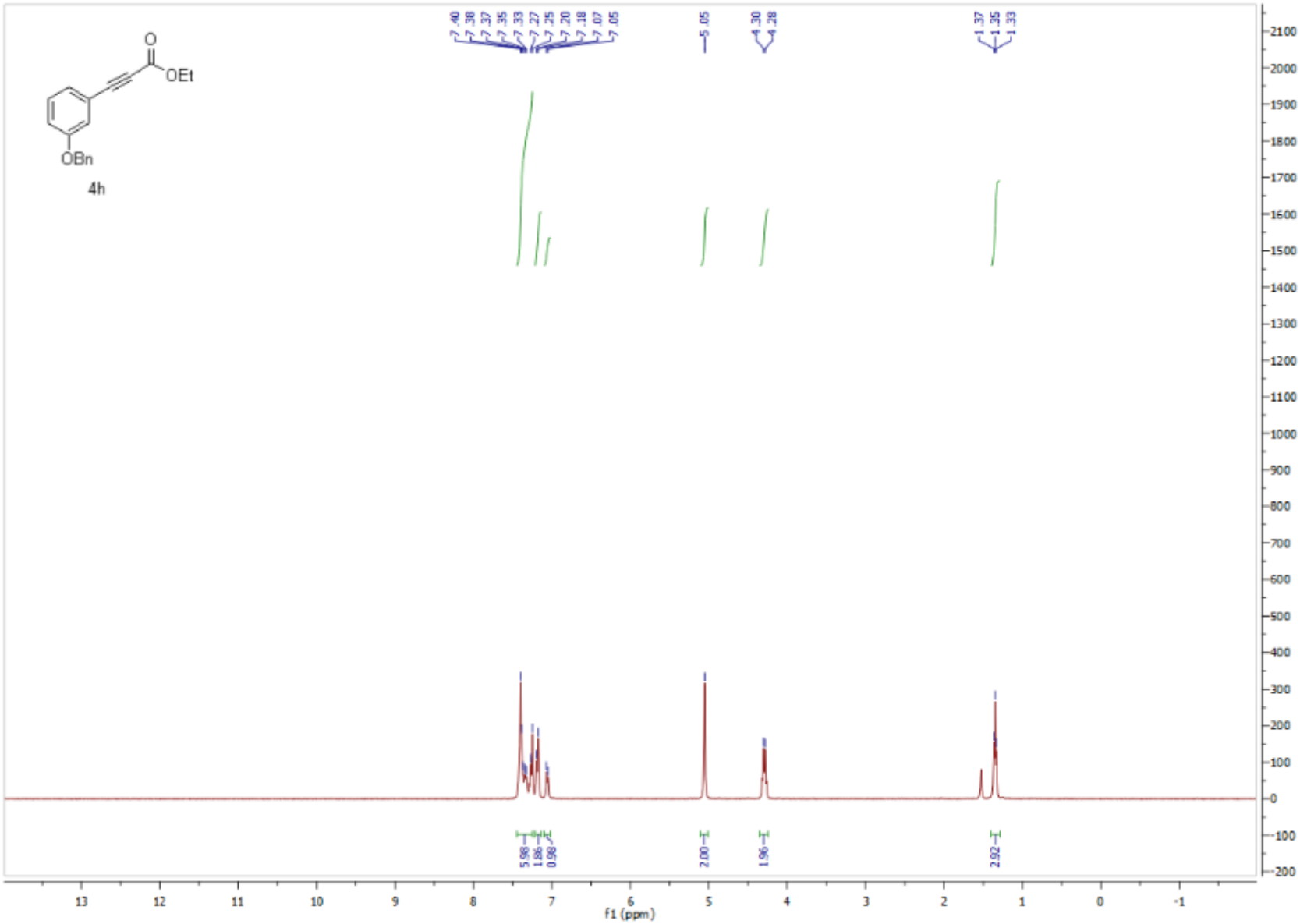
14.03
f1 (ppm)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4h
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7.07
7.05
5.05
4.30
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1.35
1.33
5.98
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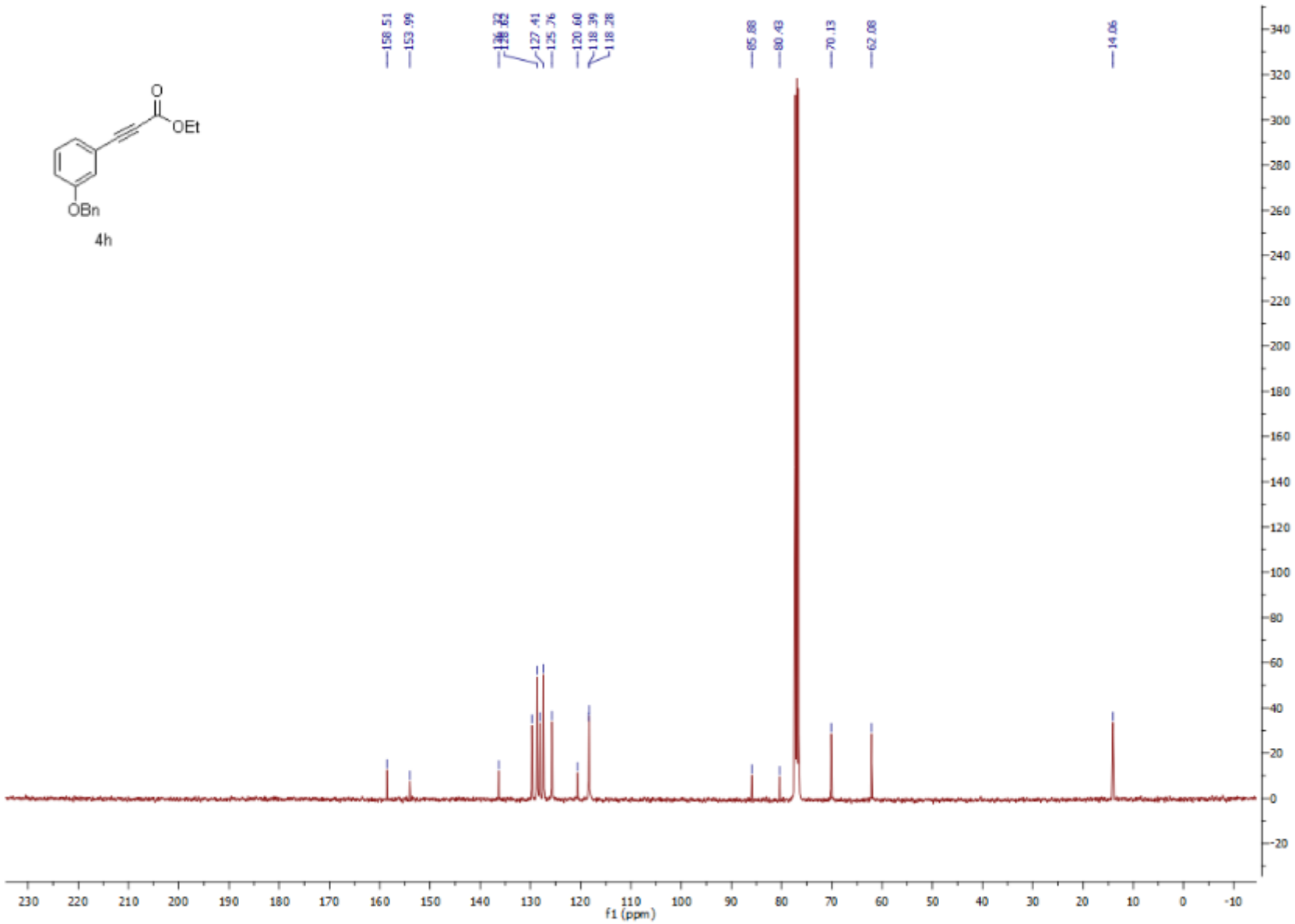
0.98
2.00
1.96
2.92
f1 (ppm)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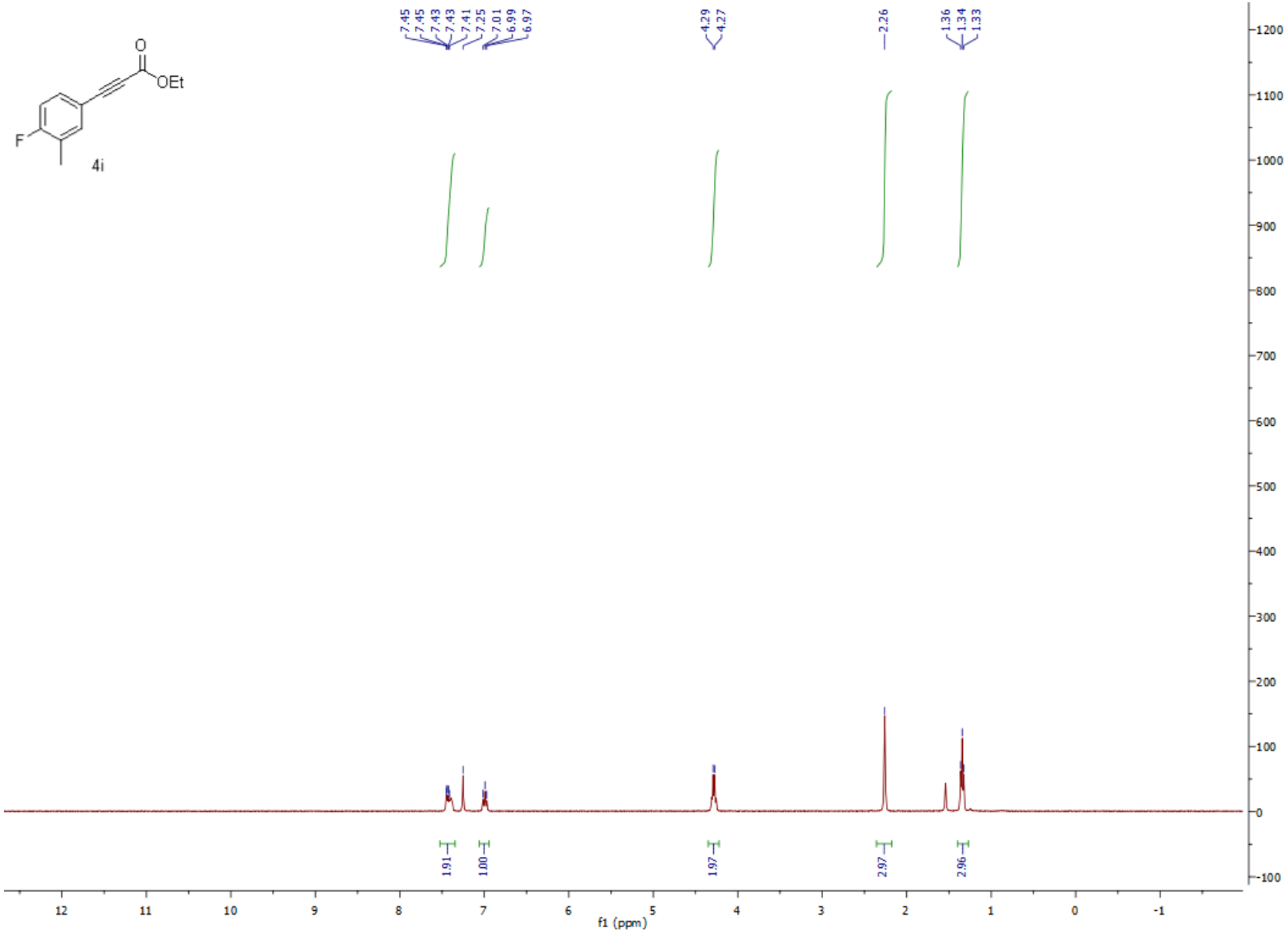
80.43
70.13
62.08
14.06
O
OEt
OBn
4h
f1 (ppm)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OEt
F
4i
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7.45
7.43
7.43
7.41
7.25
7.01
6.99
6.97
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4.27
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1.34
1.33
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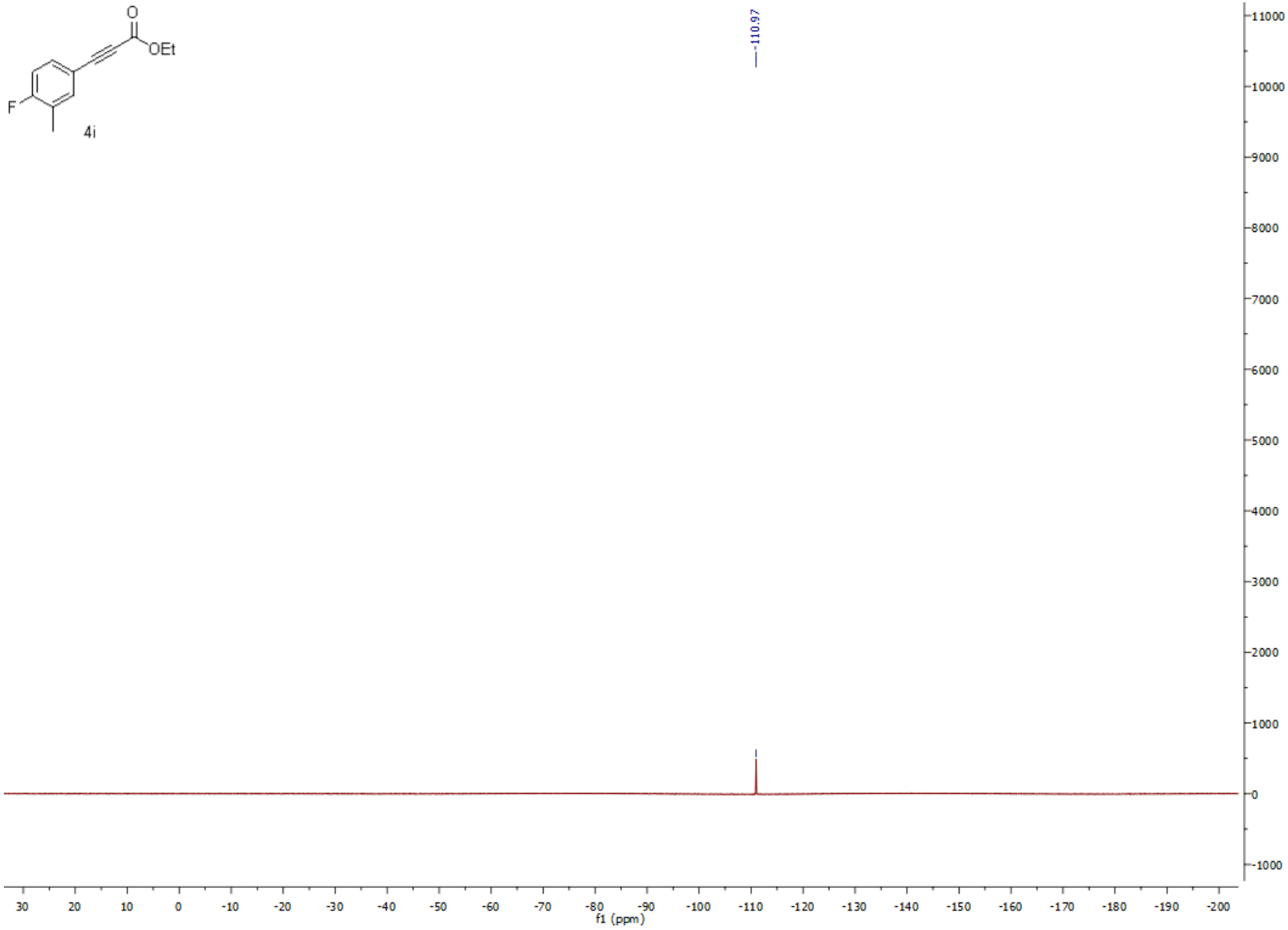
1.00
1.97
2.97
2.96
f1 (ppm)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OEt
F
4i
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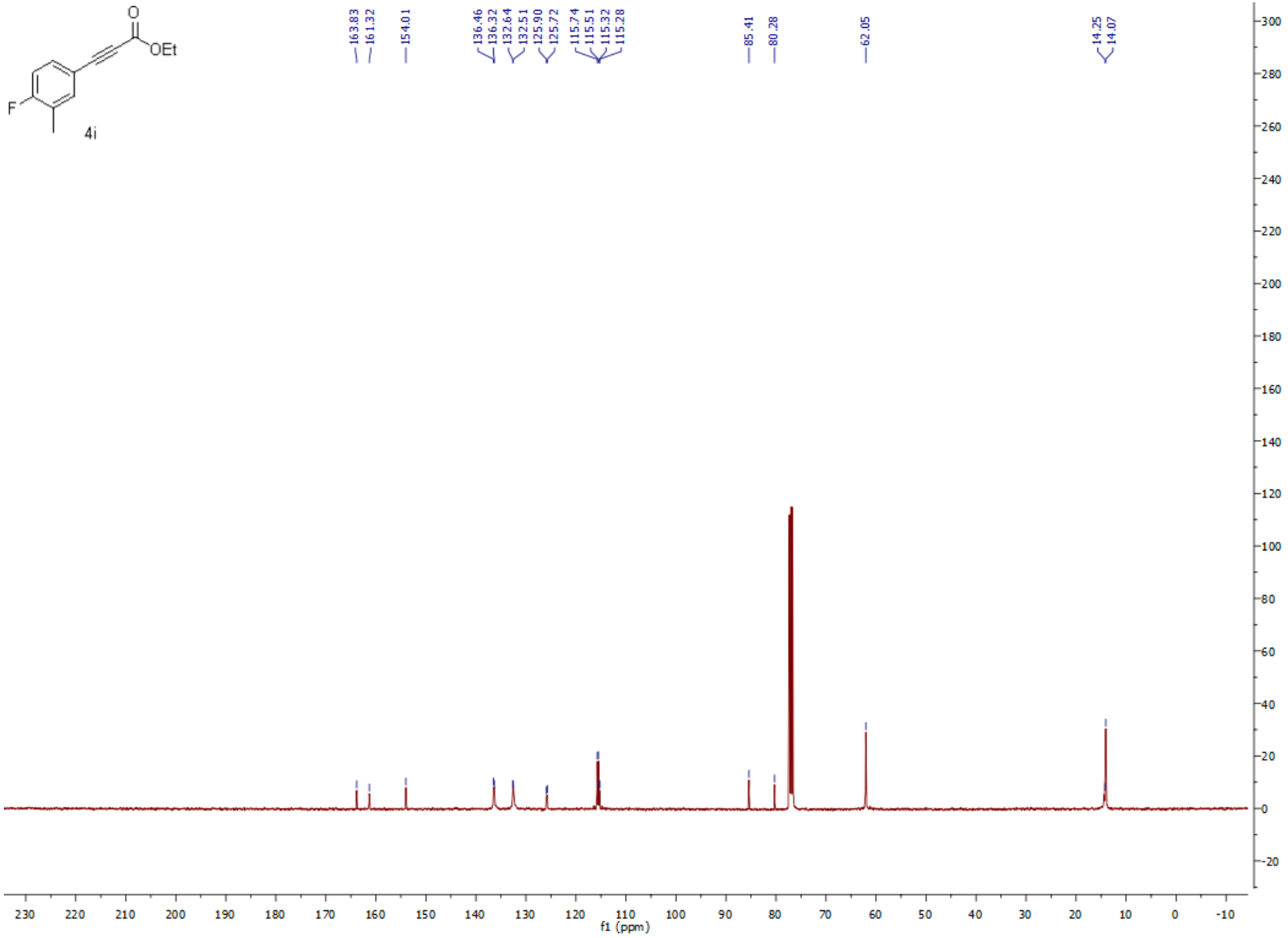
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)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F
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132.51
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80.28
62.05
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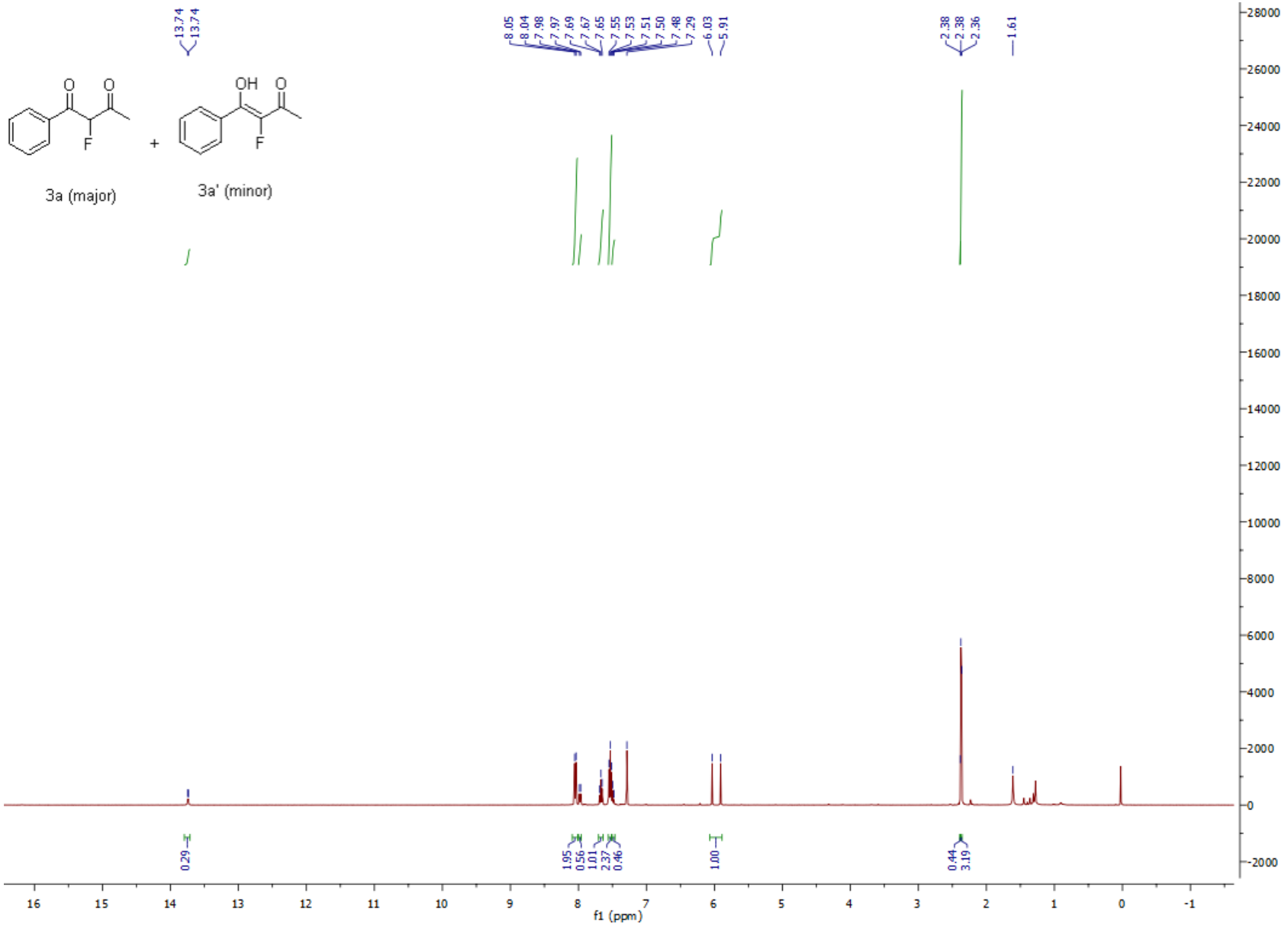
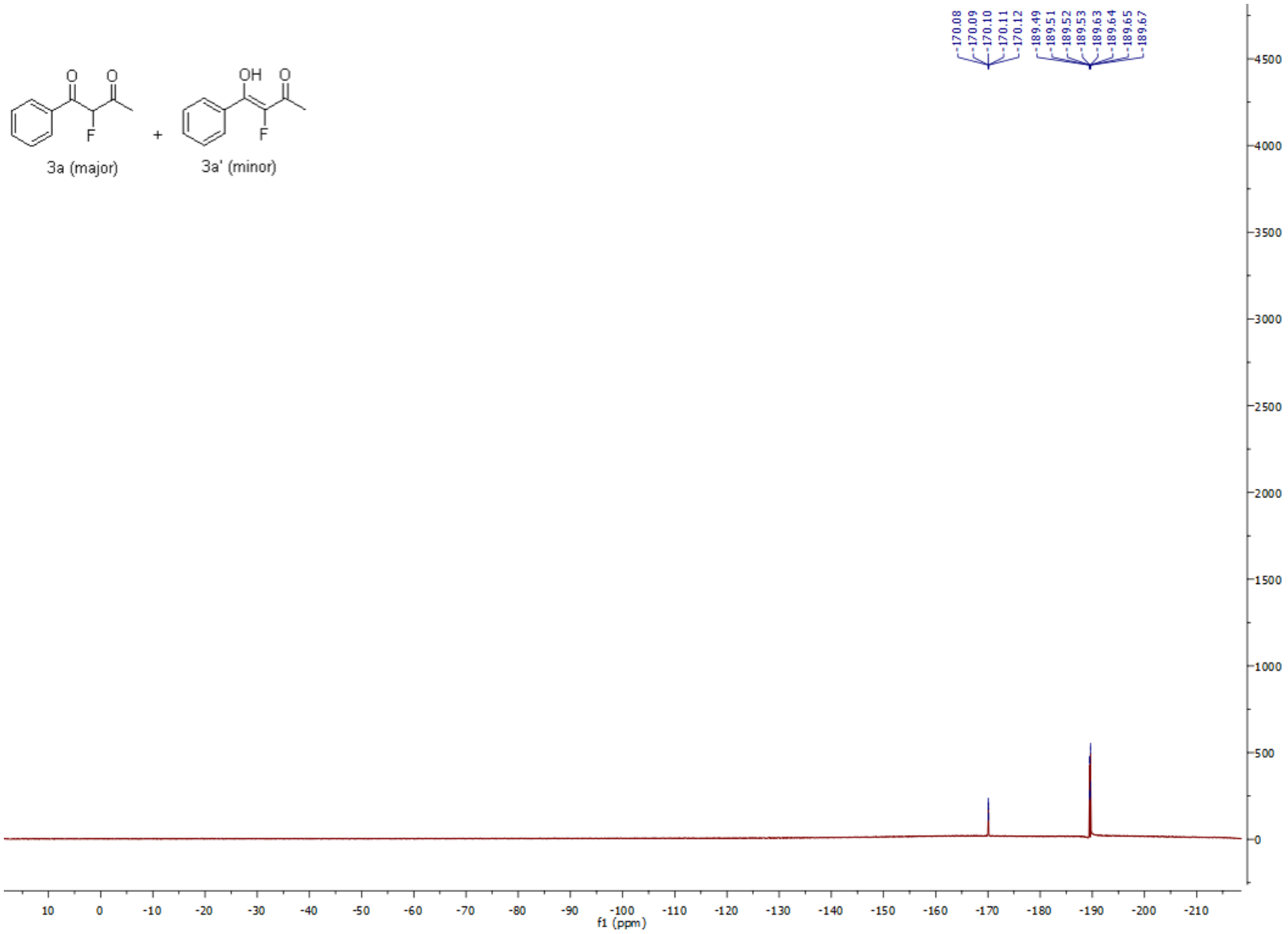
14.07
f1 (ppm)


3a (major)
3a' (minor)
f1 (ppm)


O
O
F
+
OH
O
F
3a (major)
3a' (minor)
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-170.09
-170.10
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-189.49
-189.51
-189.52
-189.53
-189.63
-189.64
-189.65
-189.67
4500
4000
3500
3000
2500
2000
1500
1000
500
0
10
0
-10
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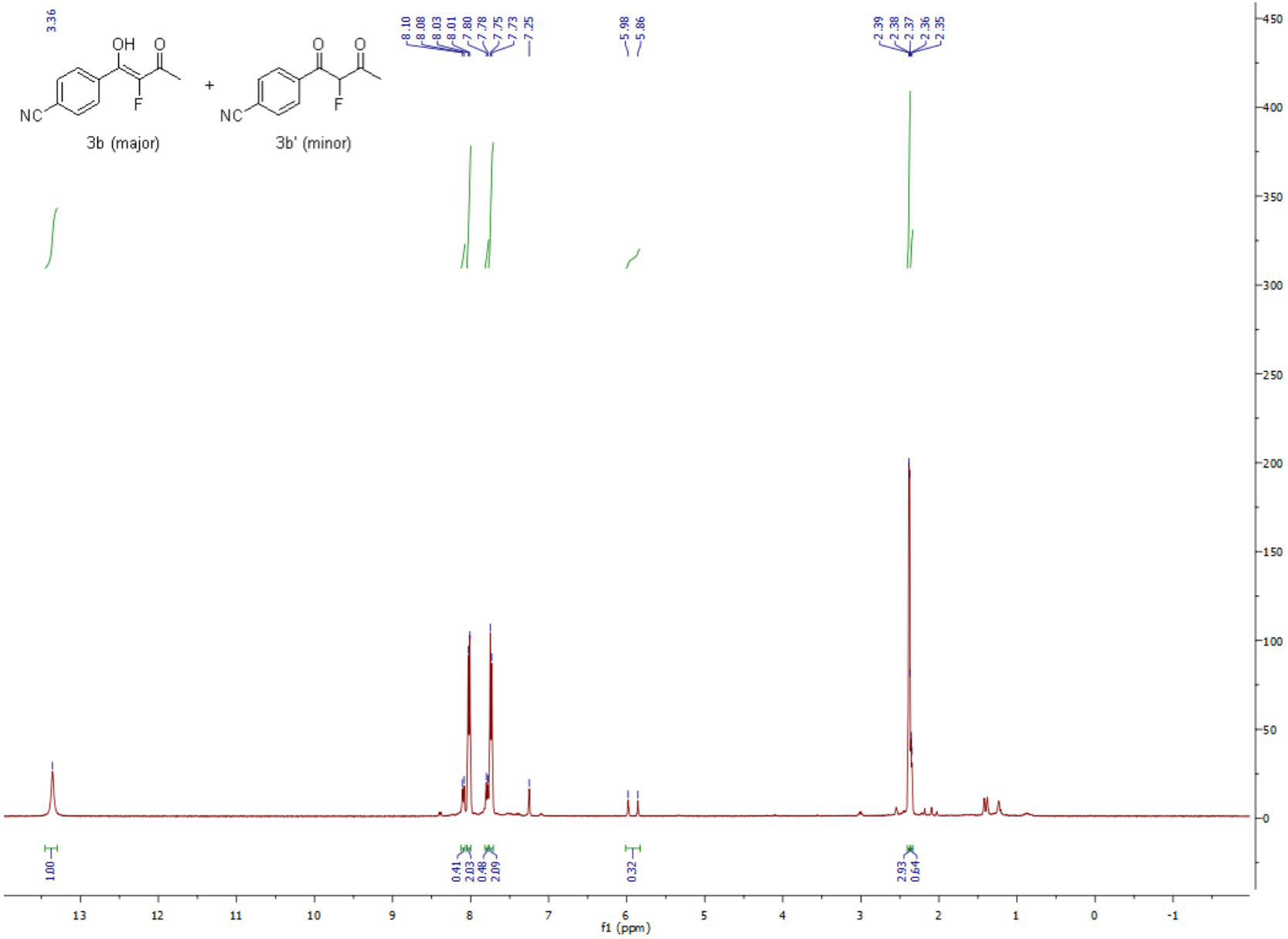
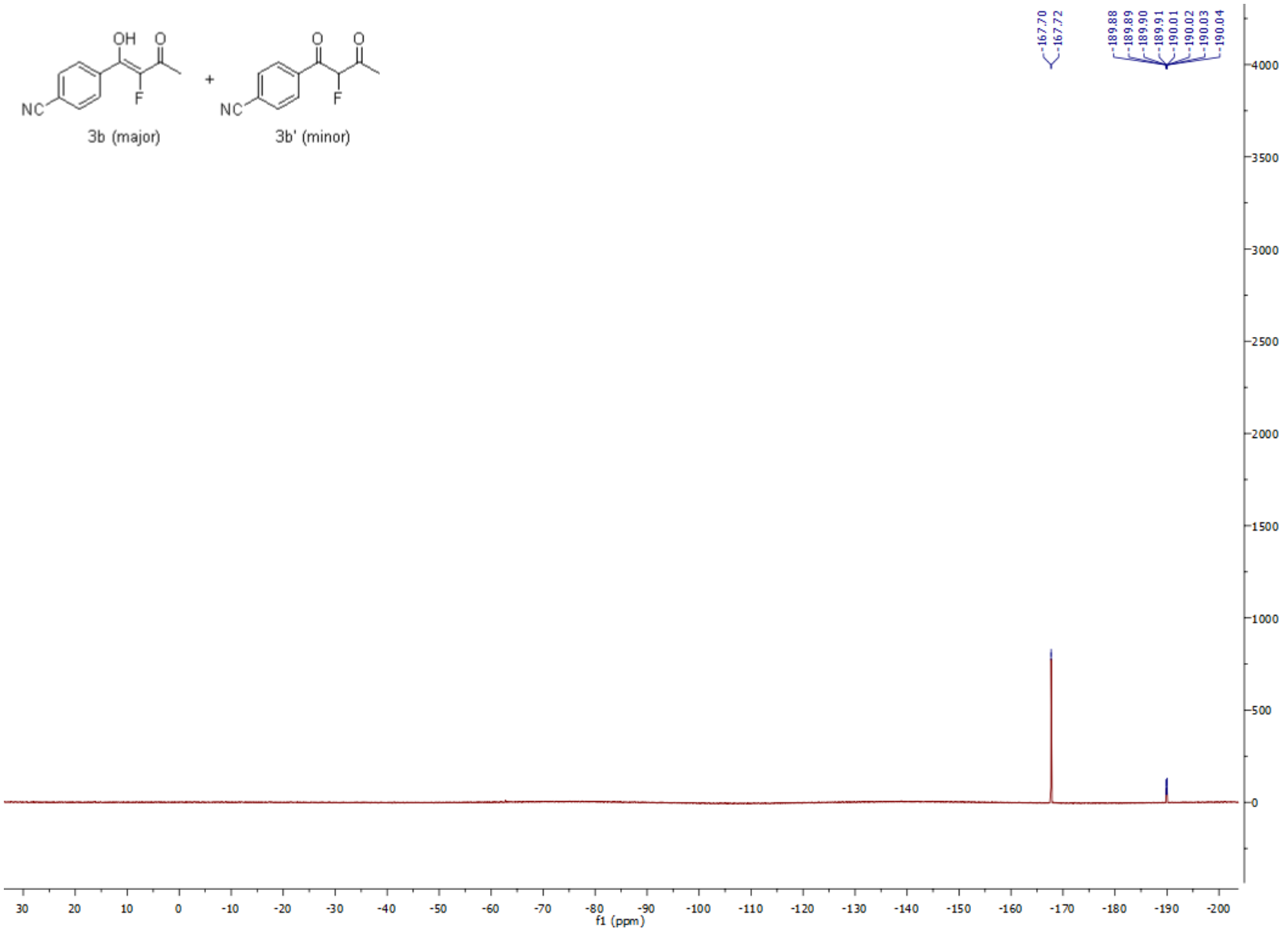
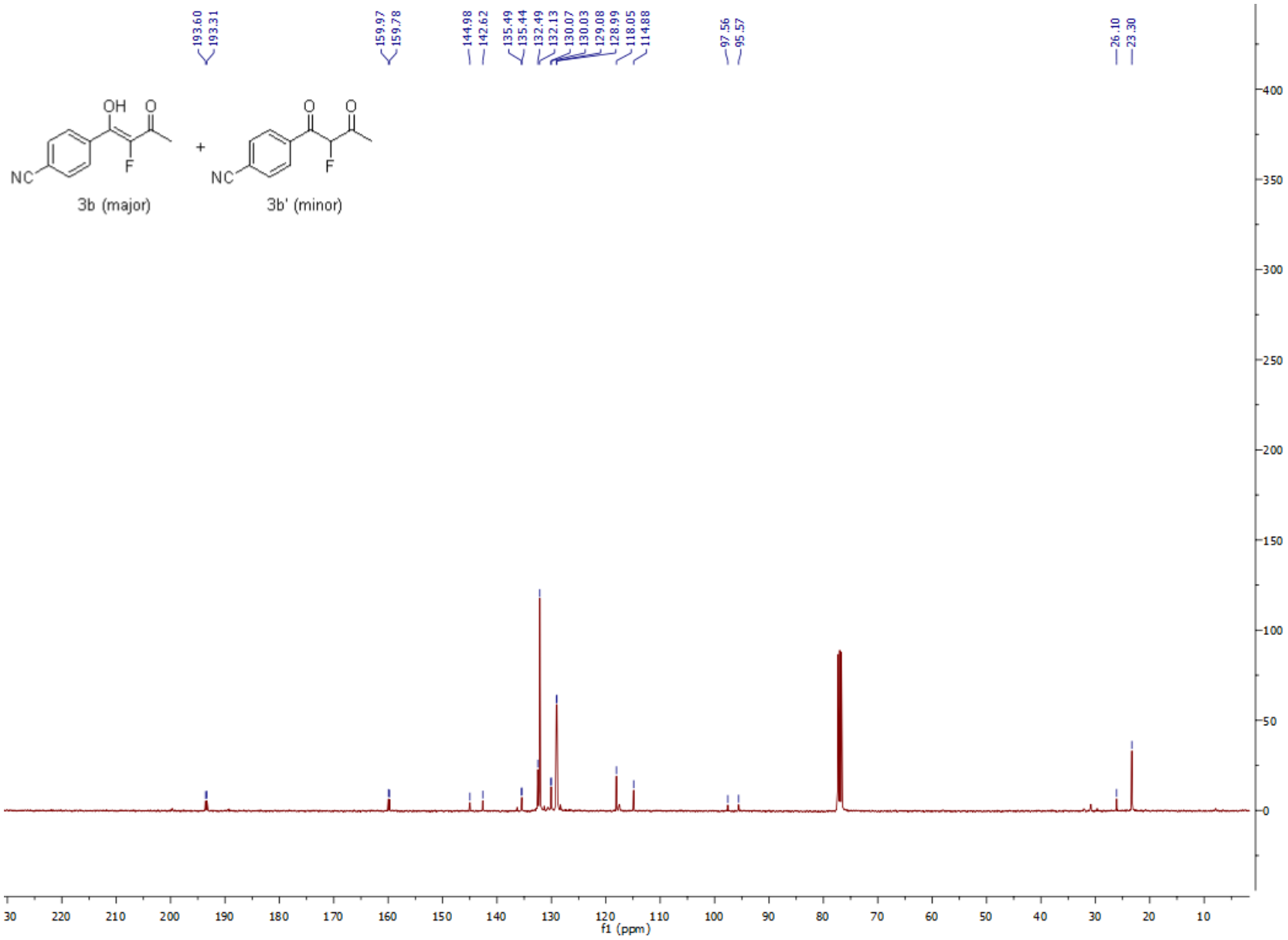
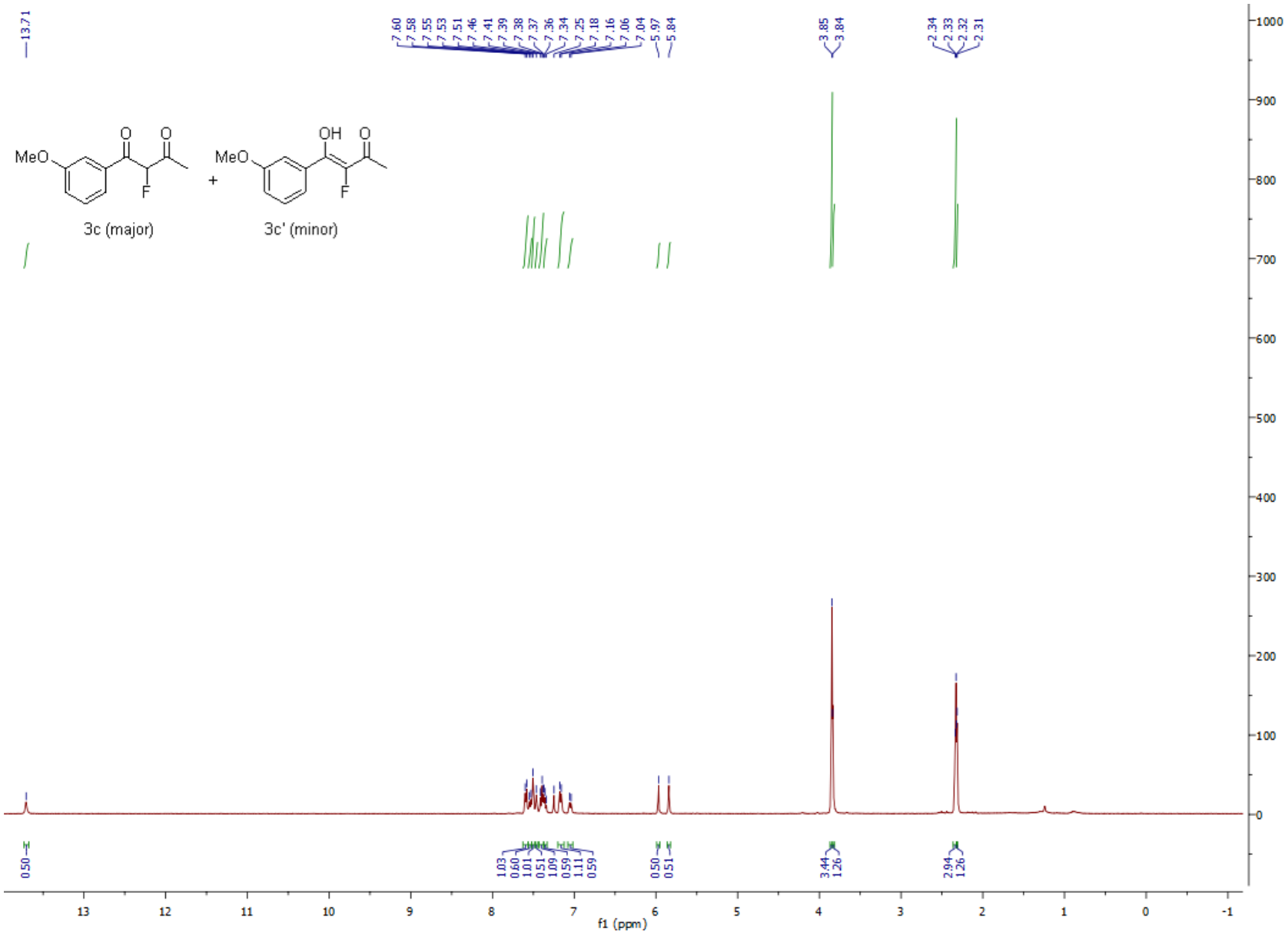
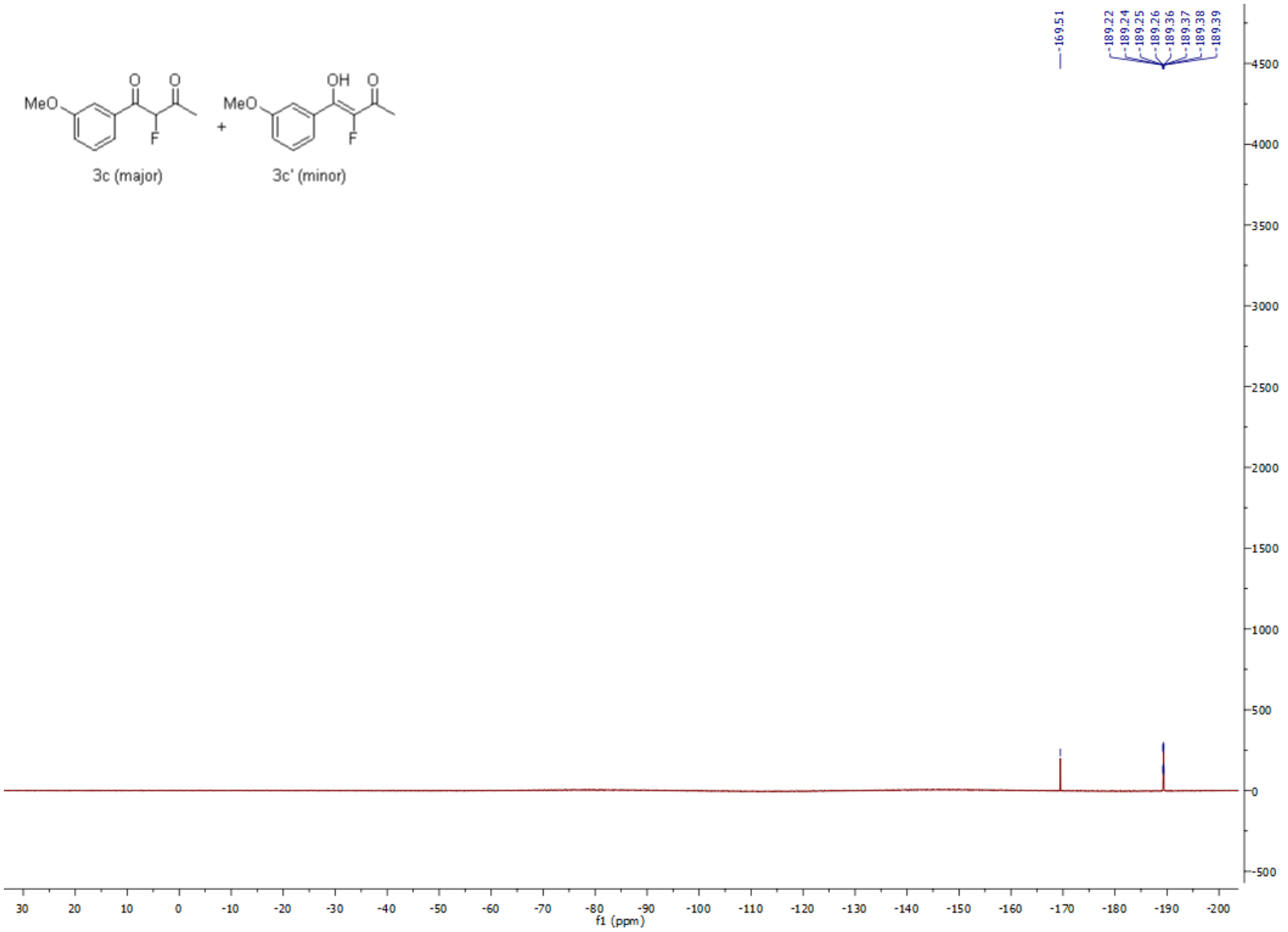
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

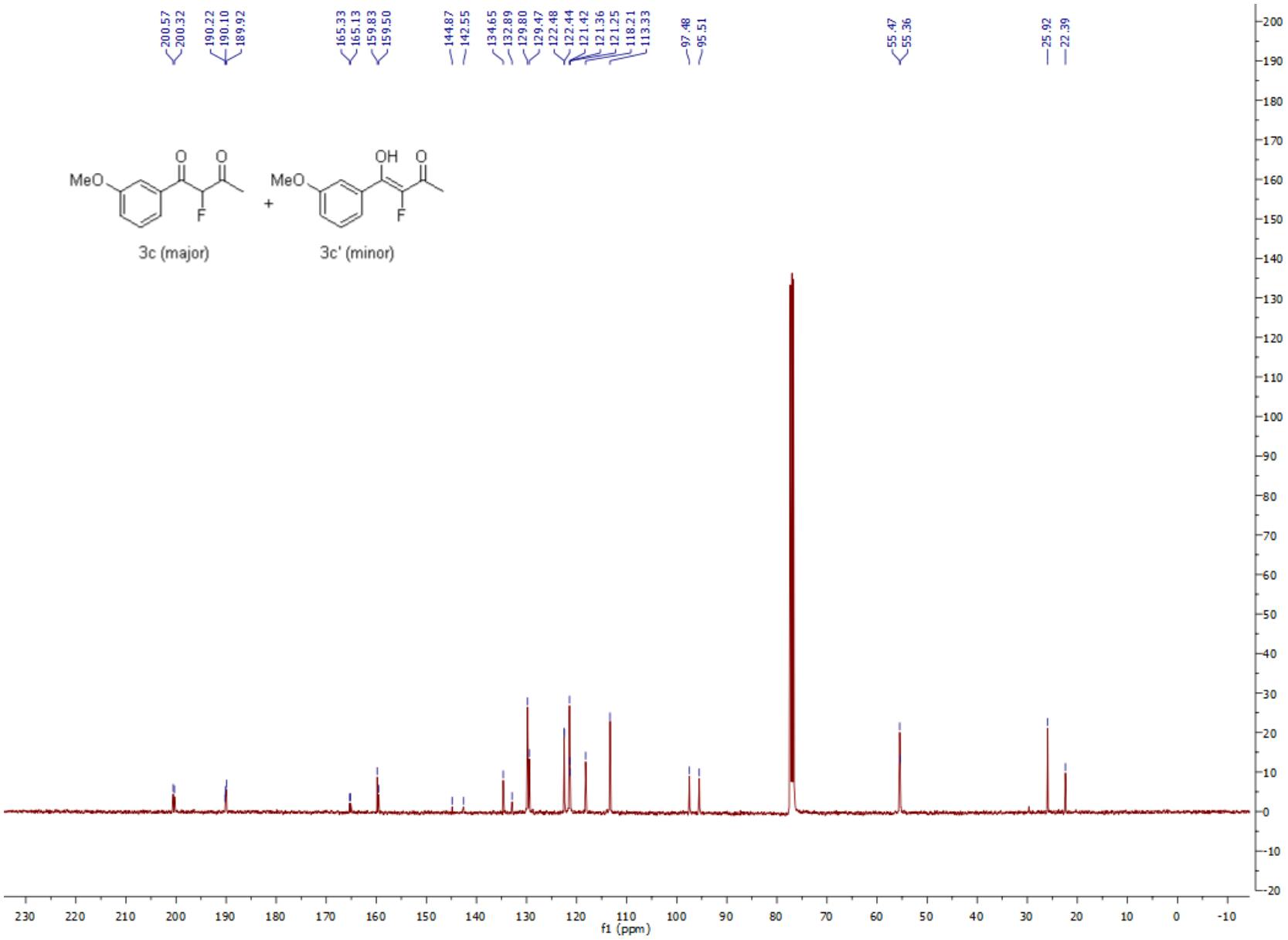

3.36
OH
O
NC
F
3b (major)
+
O
O
NC
F
3b' (minor)
8.10
8.08
8.03
8.01
7.80
7.78
7.75
7.73
7.25
5.98
5.86
2.39
2.38
2.37
2.36
2.35
450
400
350
300
250
200
150
100
50
0
1.00
0.41
2.03
0.48
2.09
0.32
2.93
0.64
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

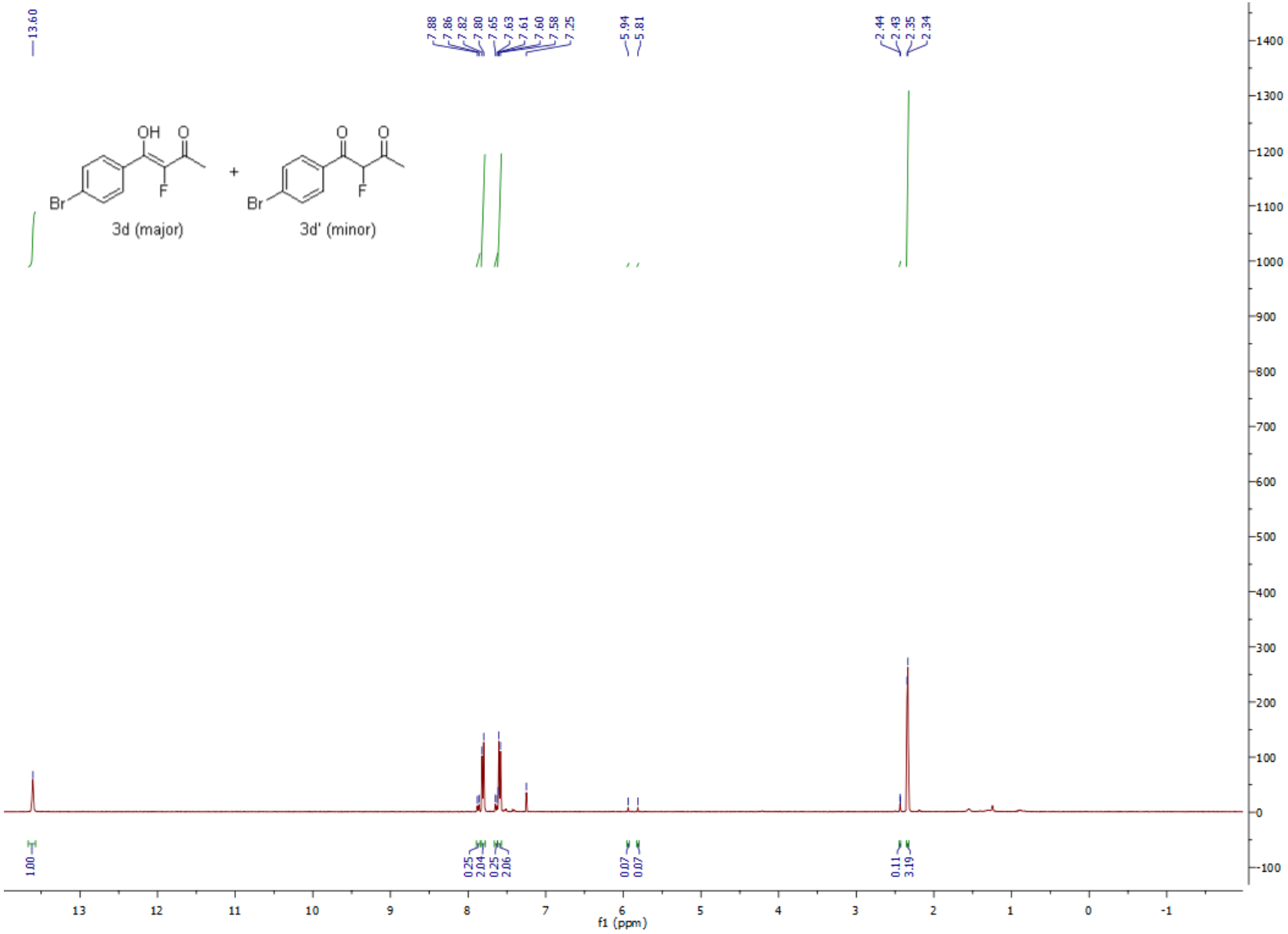

OH
O
F
NC
3b (major)
+
O
O
F
NC
3b' (minor)
-167.70
-167.72
-189.88
-189.89
-189.90
-189.91
-190.01
-190.02
-190.03
-190.04
4000
3500
3000
2500
2000
1500
1000
500
0
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

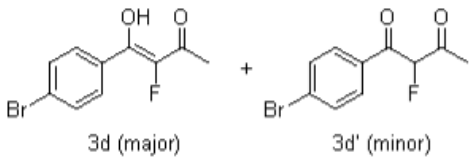

193.60
193.31
159.97
159.78
144.98
142.62
135.49
135.44
132.49
132.13
130.07
130.03
129.08
128.99
118.05
114.88
97.56
95.57
26.10
23.30
OH
O
F
NC
3b (major)
+
O
O
F
NC
3b' (minor)
400
350
300
250
200
150
100
50
0
30
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


13.71
7.60
7.58
7.55
7.53
7.51
7.46
7.41
7.39
7.38
7.37
7.36
7.34
7.25
7.18
7.16
7.06
7.04
5.97
5.84
3.85
3.84
2.34
2.33
2.32
2.31
MeO
O
O
F
3c (major)
+
MeO
OH
O
F
3c' (minor)
0.50
1.03
0.60
1.01
0.51
1.09
0.59
1.11
0.59
0.50
0.51
3.44
1.26
2.94
1.26
f1 (ppm)

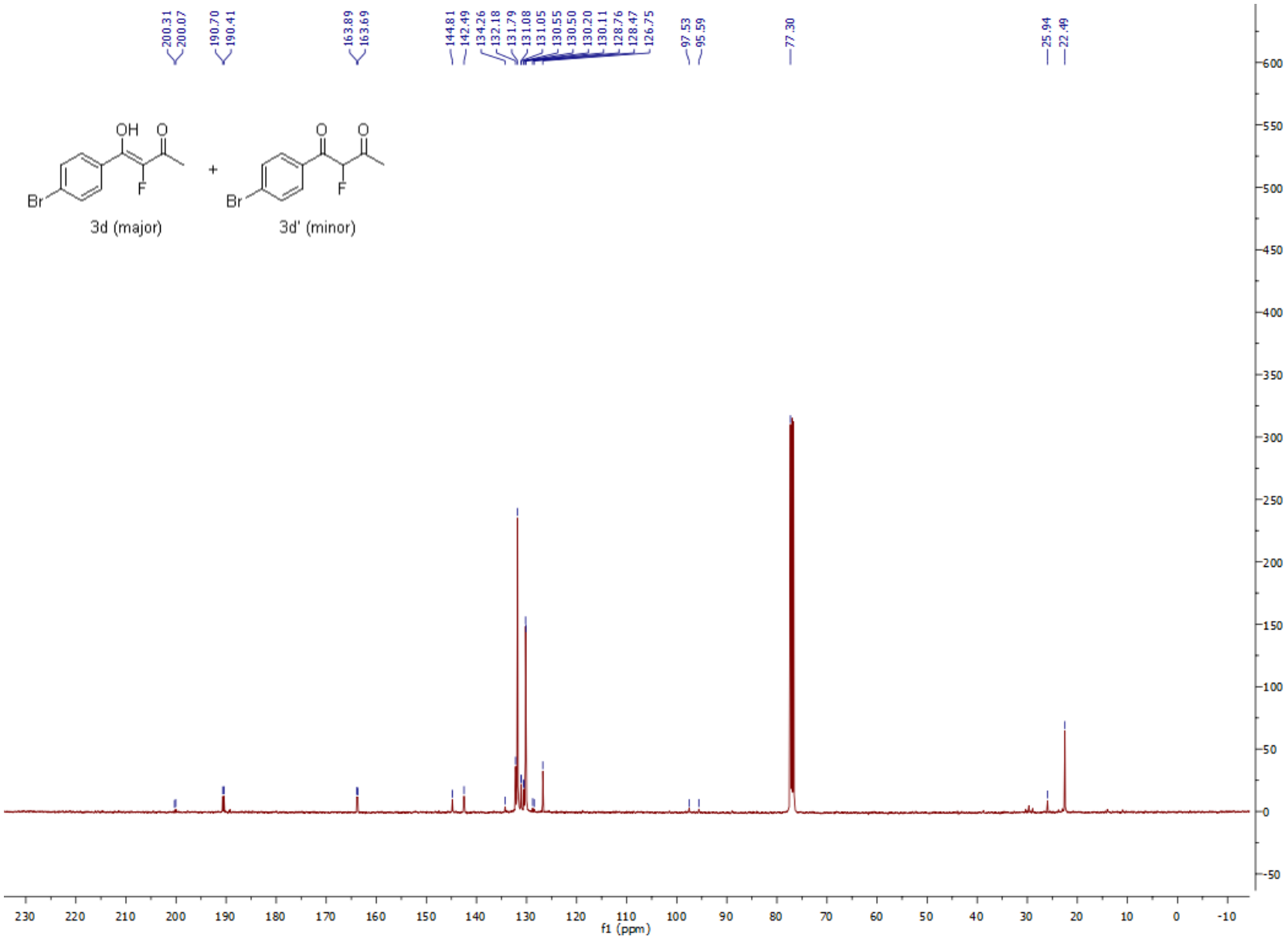

MeO
O
O
F
3c (major)
+
MeO
OH
O
F
3c' (minor)
-169.51
-189.22
-189.24
-189.25
-189.26
-189.36
-189.37
-189.38
-189.39
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


200.57
200.32
190.22
190.10
189.92
165.33
165.13
159.83
159.50
144.87
142.55
134.65
132.89
129.80
129.47
122.48
122.44
121.42
121.36
121.25
118.21
113.33
97.48
95.51
55.47
55.36
25.92
22.39
MeO
O
O
F
3c (major)
+
MeO
OH
O
F
3c' (minor)
f1 (ppm)

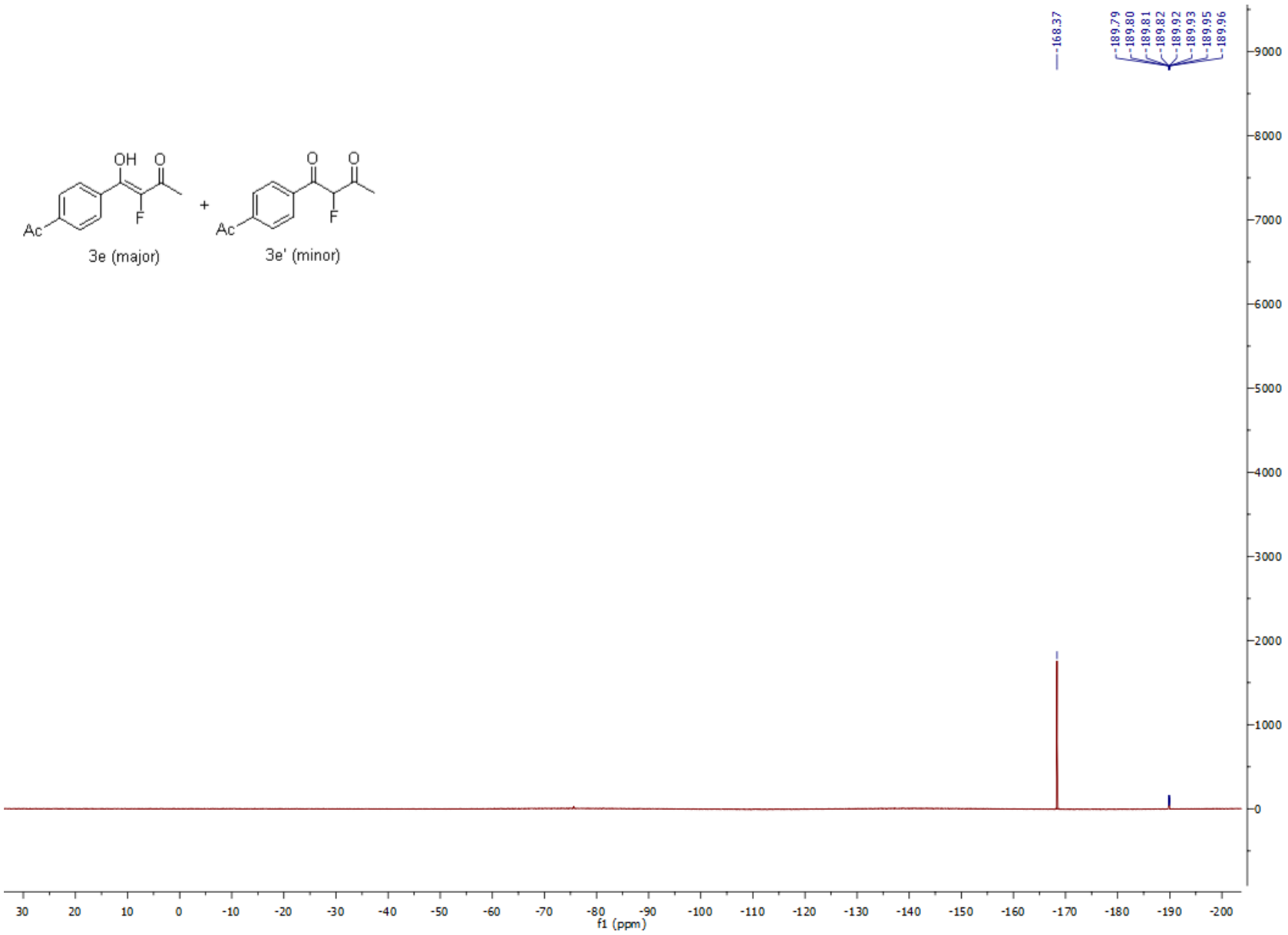

13.60
7.88
7.86
7.82
7.80
7.65
7.63
7.61
7.60
7.58
7.25
5.94
5.81
2.44
2.43
2.35
2.34
OH
O
F
Br
3d (major)
+
O
O
F
Br
3d' (minor)
1.00
0.25
2.04
0.25
2.06
0.07
0.07
0.11
3.19
f1 (ppm)

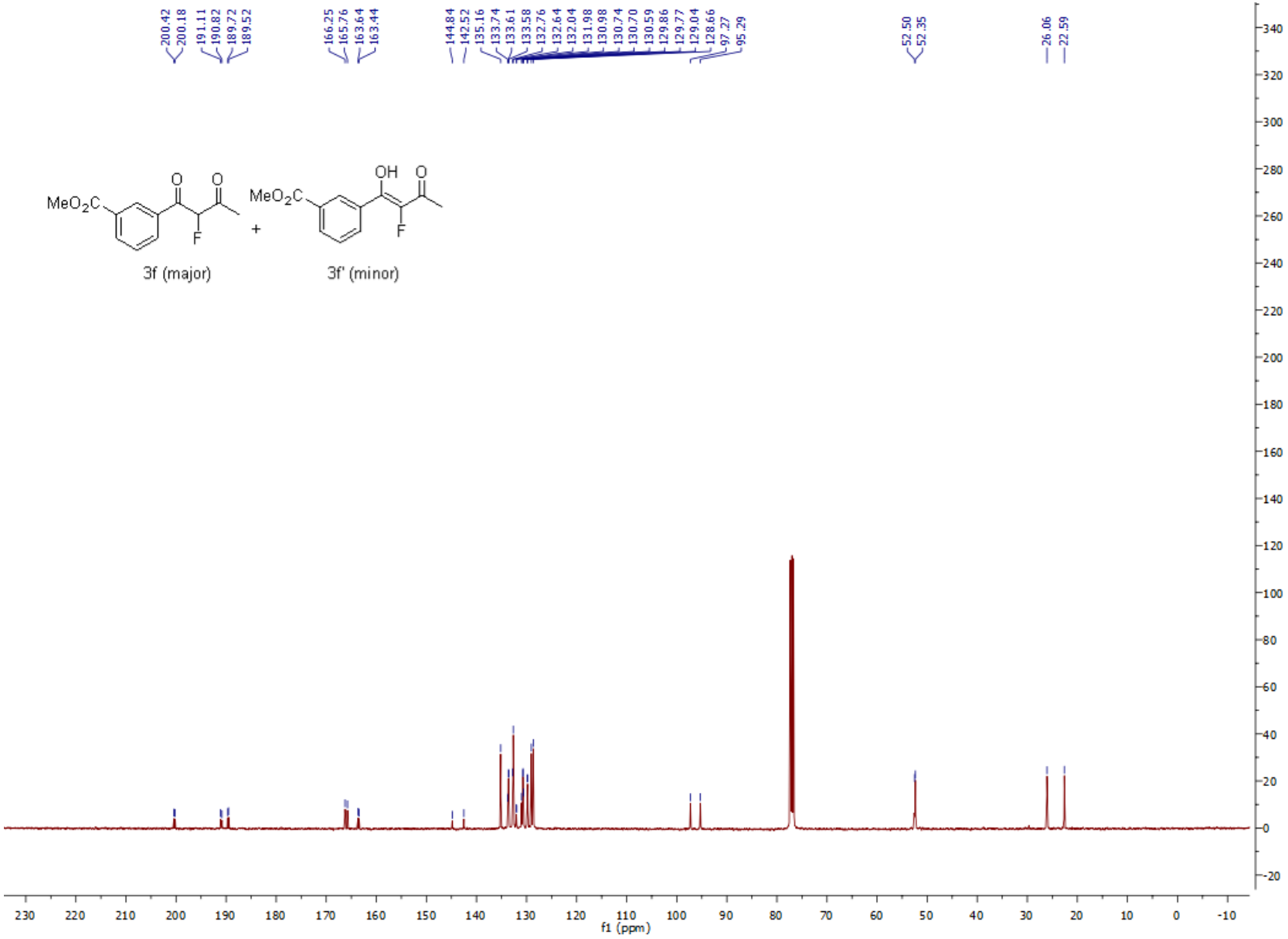

OH
O
F
Br
3d (major)
+
O
O
F
Br
3d' (minor)

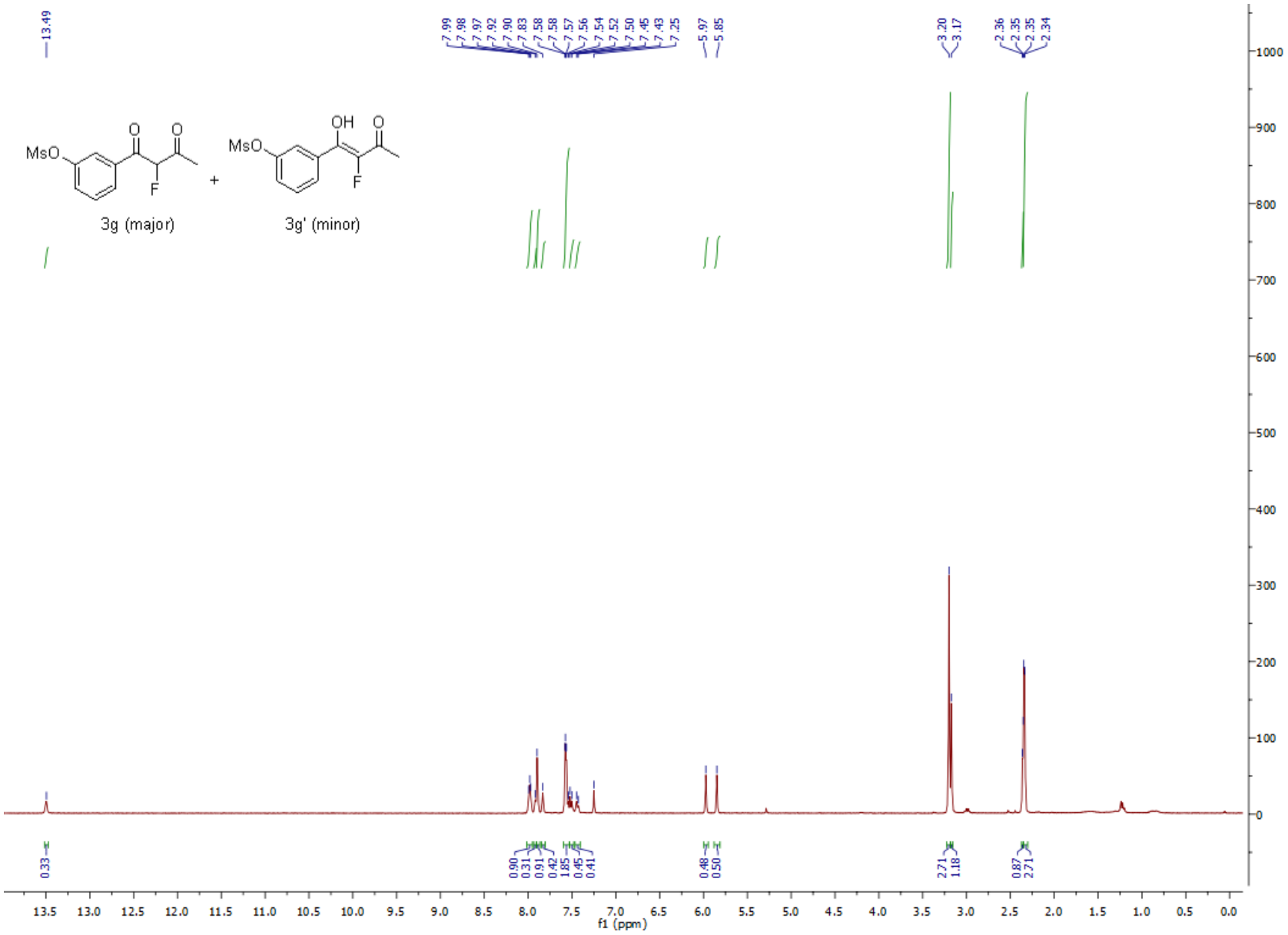
-169.32
-189.44
-189.45
-189.47
-189.57
-189.59
-189.60
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

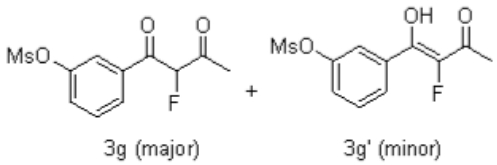

200.31
200.07
190.70
190.41
163.89
163.69
144.81
142.49
134.26
132.18
131.79
131.08
131.05
130.55
130.50
130.20
130.11
128.76
128.47
126.75
97.53
95.59
77.30
25.94
22.49
OH
O
F
Br
3d (major)
+
O
O
F
Br
3d' (minor)
f1 (ppm)


13.46
8.00
6.00
5.88
2.62
2.37
2.36
OH
O
F
Ac
3e (major)
+
O
O
F
Ac
3e' (minor)
1.00
4.10
0.03
0.03
3.31
3.08
f1 (ppm)

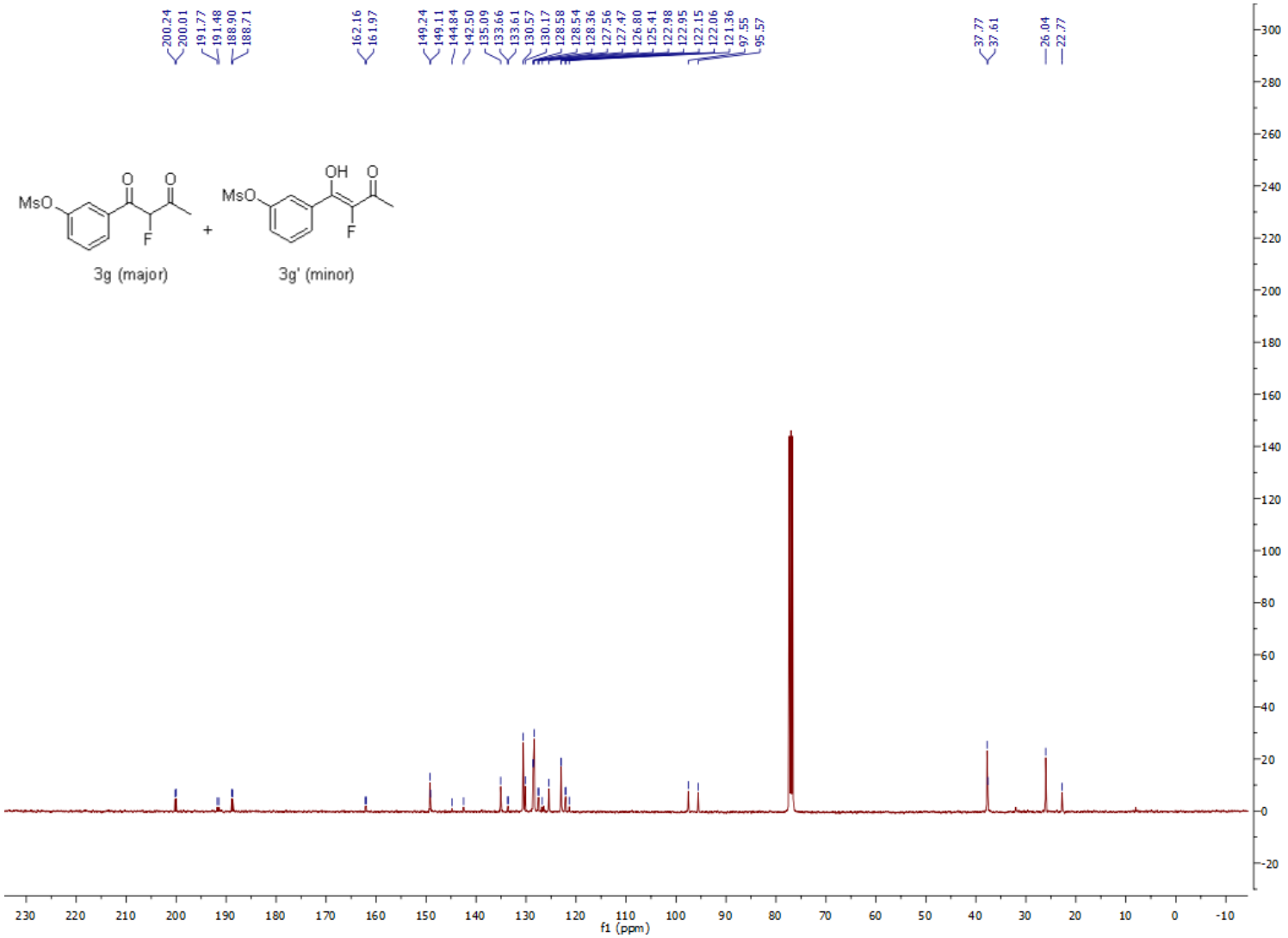

OH
O
F
Ac
3e (major)
+
O
O
F
Ac
3e' (minor)
-168.37
-189.79
-189.80
-189.81
-189.82
-189.92
-189.93
-189.95
-189.96
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

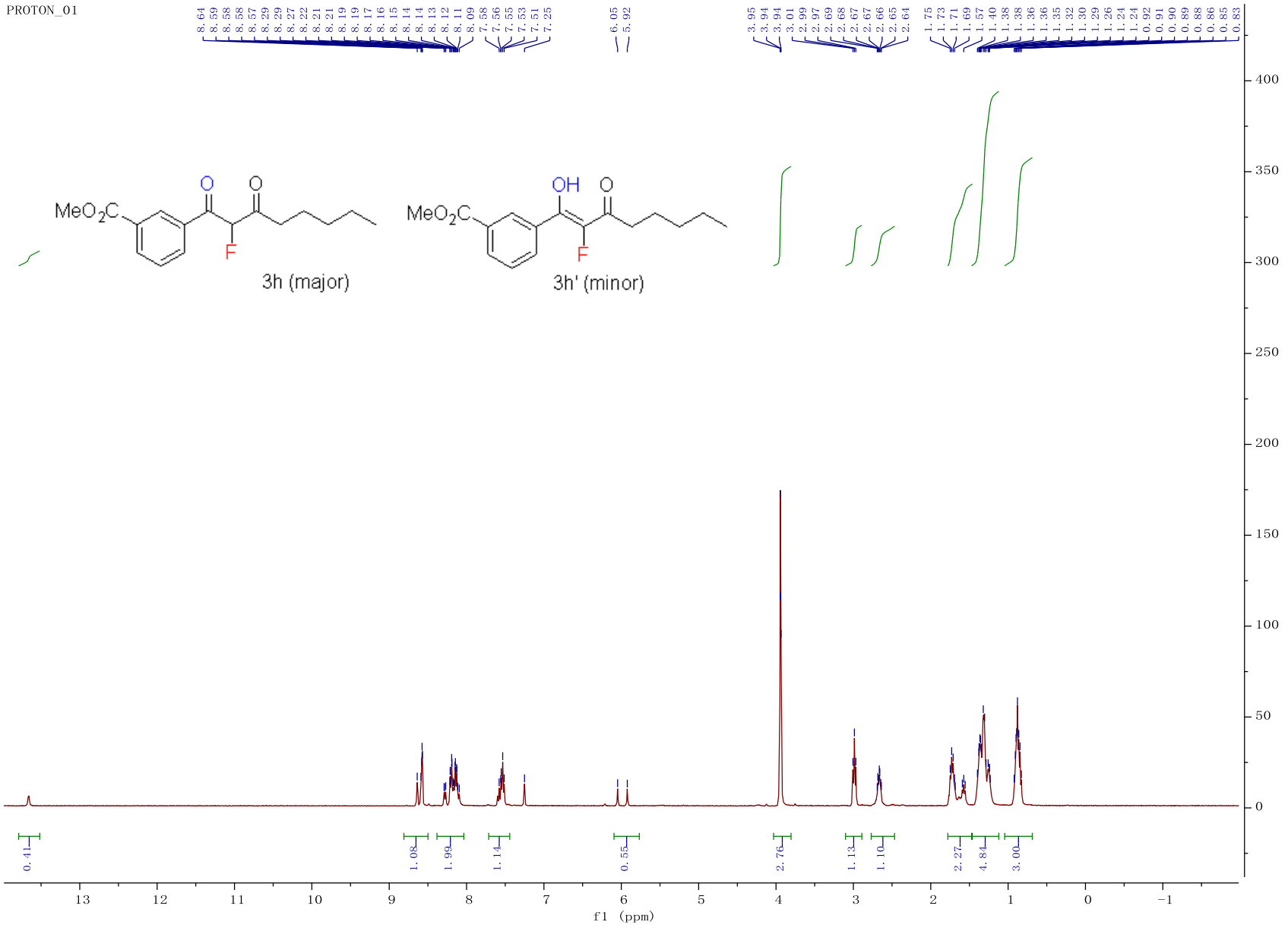

200.42
200.18
191.11
190.82
189.72
189.52
166.25
165.76
163.64
163.44
144.84
142.52
135.16
133.74
133.61
133.58
132.76
132.64
132.04
131.98
130.98
130.74
130.70
130.59
129.86
129.77
129.04
128.66
97.27
95.29
52.50
52.35
26.06
22.59
MeO2C
O
O
F
+
MeO2C
OH
O
F
3f (major)
3f' (minor)
f1 (ppm)


13.49
7.99
7.98
7.97
7.92
7.90
7.83
7.58
7.57
7.56
7.54
7.52
7.50
7.45
7.43
7.25
5.97
5.85
3.20
3.17
2.36
2.35
2.35
2.34
MsO
O
O
F
3g (major)
+
MsO
OH
O
F
3g' (minor)
1000
900
800
700
600
500
400
300
200
100
0
0.33
0.90
0.31
0.91
0.42
1.85
0.45
0.41
0.48
0.50
2.71
1.18
0.87
2.71
13.5
13.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
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
0.0
f1 (ppm)

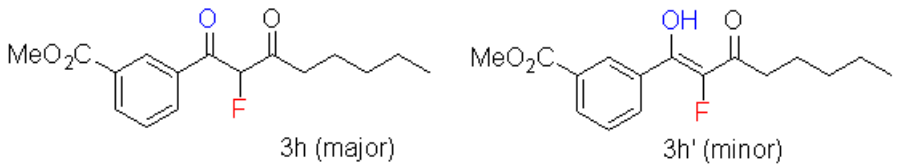


3g (major) 3g' (minor)


200.24
200.01
191.77
191.48
188.90
188.71
162.16
161.97
149.24
149.11
144.84
142.50
135.09
133.66
133.61
130.57
130.17
128.58
128.54
128.36
127.56
127.47
126.80
125.41
122.98
122.95
122.15
122.06
121.36
97.55
95.57
37.77
37.61
26.04
22.77
MsO
O
O
F
+
MsO
OH
O
F
3g (major)
3g' (minor)
f1 (ppm)

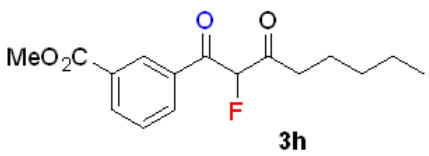

PROTON_01
8.64 8.59 8.58 8.58 8.57 8.29 8.29 8.27 8.22 8.21 8.21 8.19 8.19 8.17 8.16 8.15 8.14 8.14 8.13 8.12 8.11 8.09 7.58 7.56 7.55 7.53 7.51 7.25
6.05 5.92
3.95 3.94 3.94 3.01 2.99 2.97 2.69 2.68 2.67 2.67 2.66 2.65 2.64
1.75 1.73 1.71 1.69 1.57 1.40 1.38 1.38 1.36 1.36 1.35 1.32 1.30 1.29 1.26 1.24 1.24 0.92 0.91 0.90 0.89 0.88 0.86 0.85 0.83
MeO2C
O
O
F
3h (major)
MeO2C
OH
O
F
3h' (minor)
0.41 1.08 1.99 1.14 0.55 2.76 1.13 1.10 2.27 4.84 3.00
f1 (ppm)

FLUORINE_01

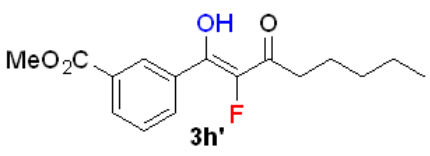

O
O
MeO2C
F
3h (major)
OH
O
MeO2C
F
3h' (minor)

-171.07
-191.98
-192.11
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

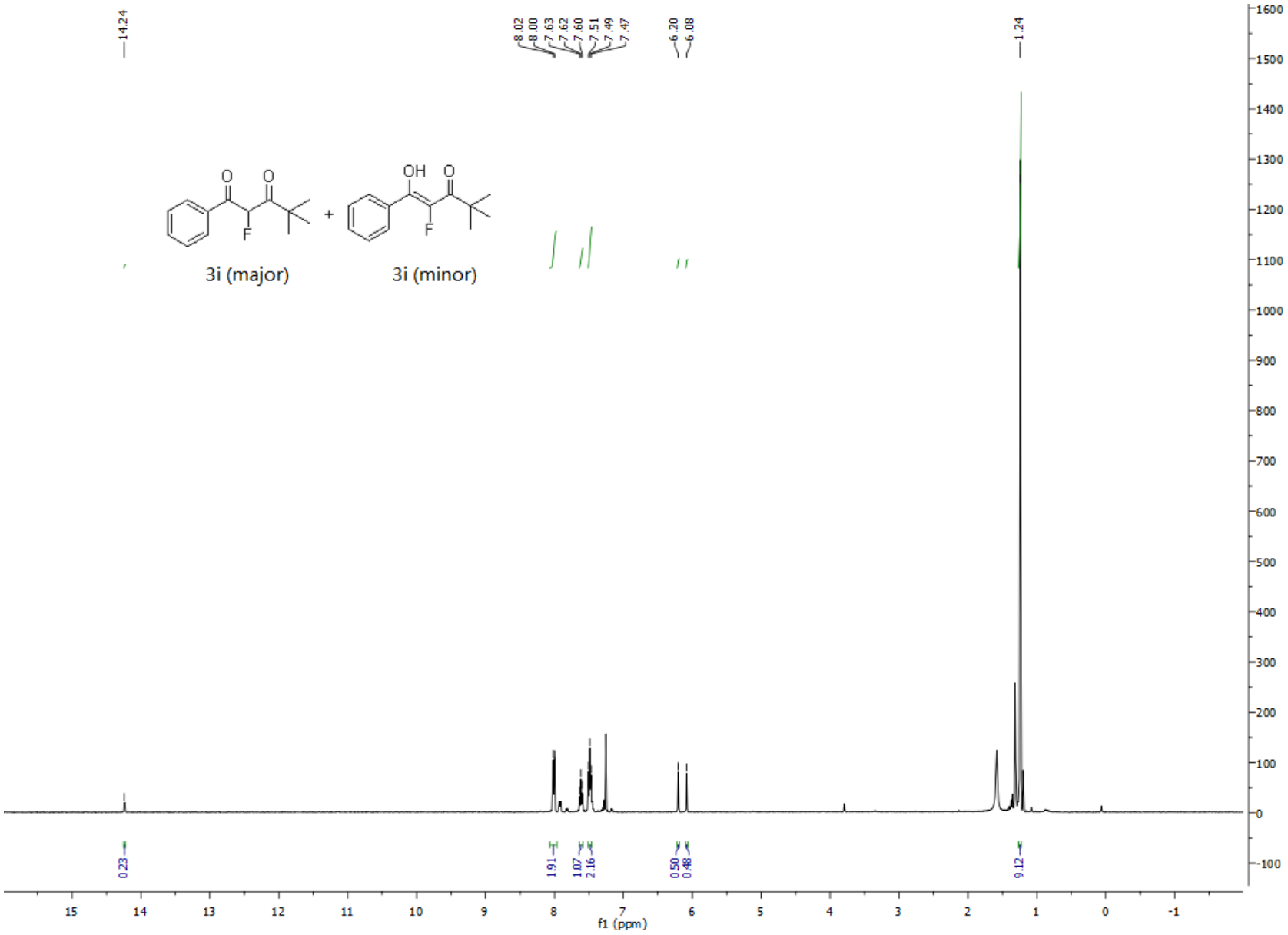
CARBON_01

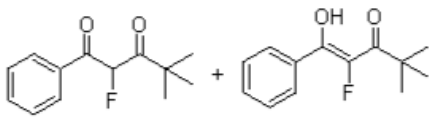


3h

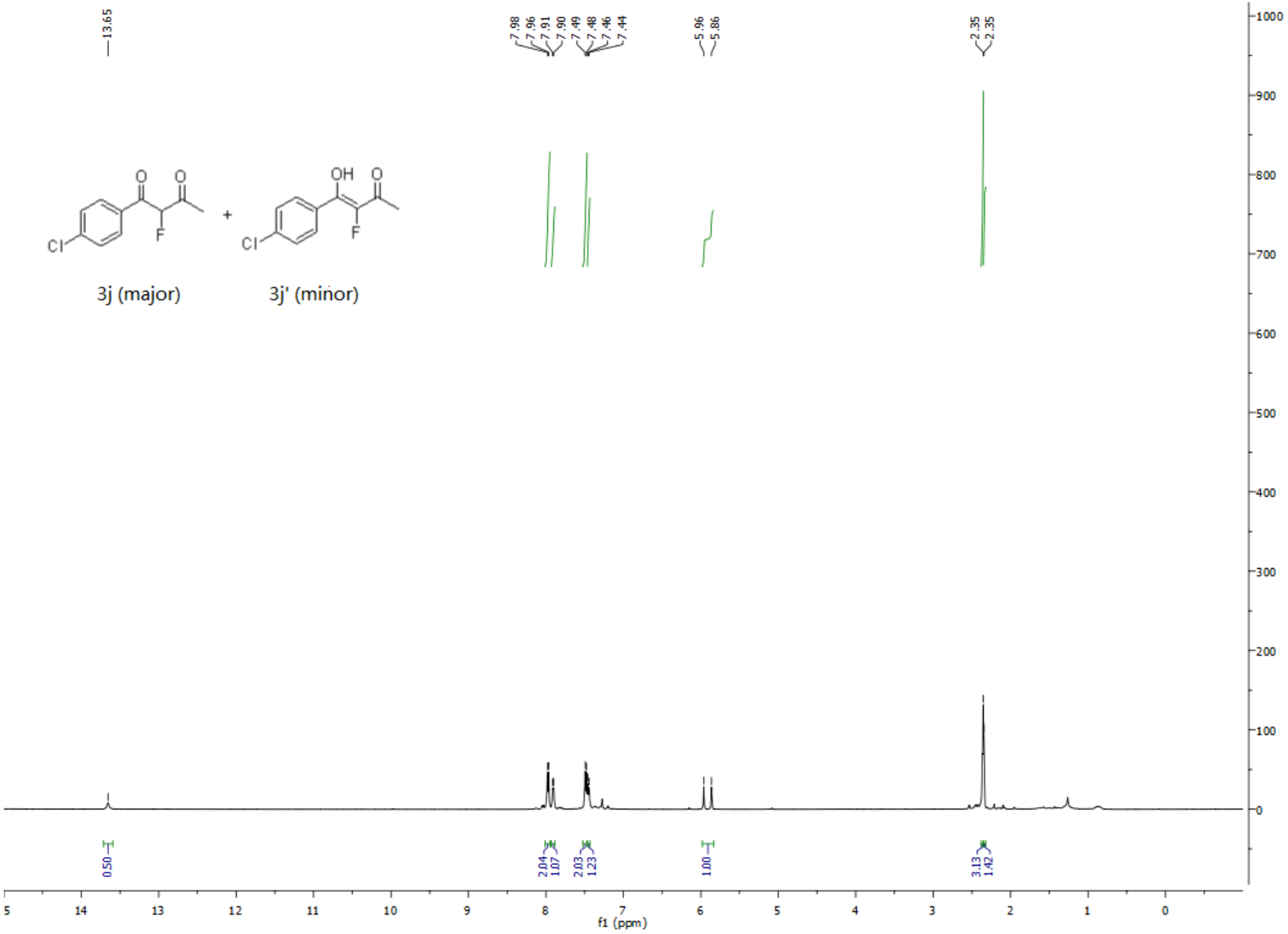


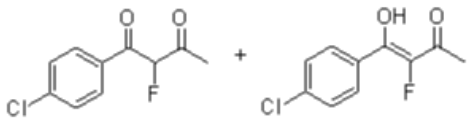
3h'


14.24
8.02
8.00
7.63
7.62
7.60
7.51
7.49
7.47
6.20
6.08
1.24
3i (major)
3i (minor)
0.23
1.91
1.07
2.16
0.50
0.48
9.12
f1 (ppm)



3i (majoy) 3i (minor)

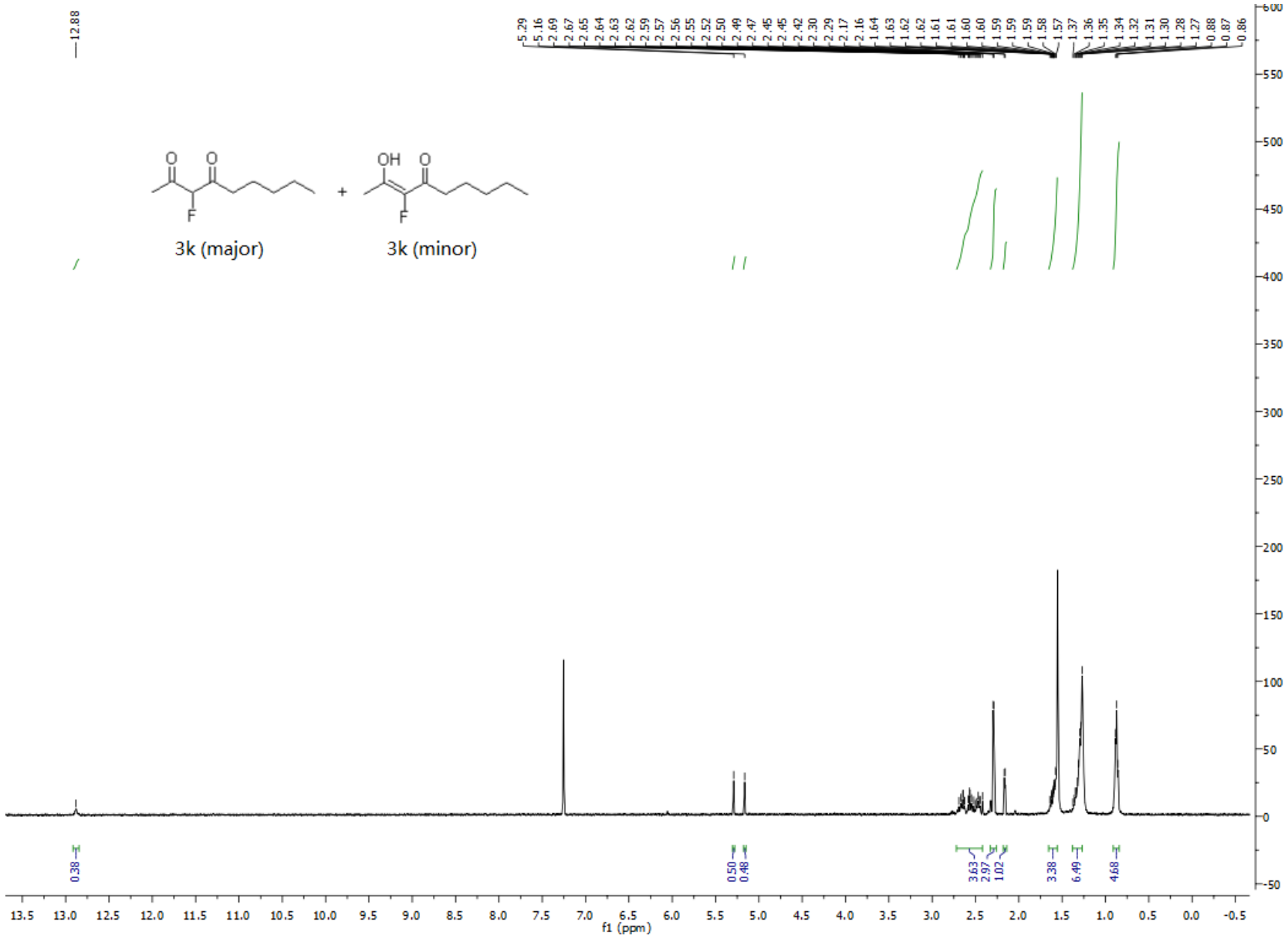

13.65
7.98
7.96
7.91
7.90
7.49
7.48
7.46
7.44
5.96
5.86
2.35
2.35
O
O
F
Cl
+
OH
O
F
Cl
3j (major)
3j' (minor)
1000
900
800
700
600
500
400
300
200
100
0
0.50
2.04
1.07
2.03
1.23
1.00
3.13
1.42
5
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

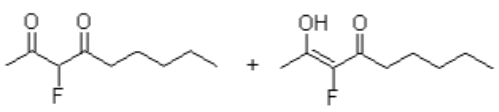


3j (major)

+

3j' (minor)

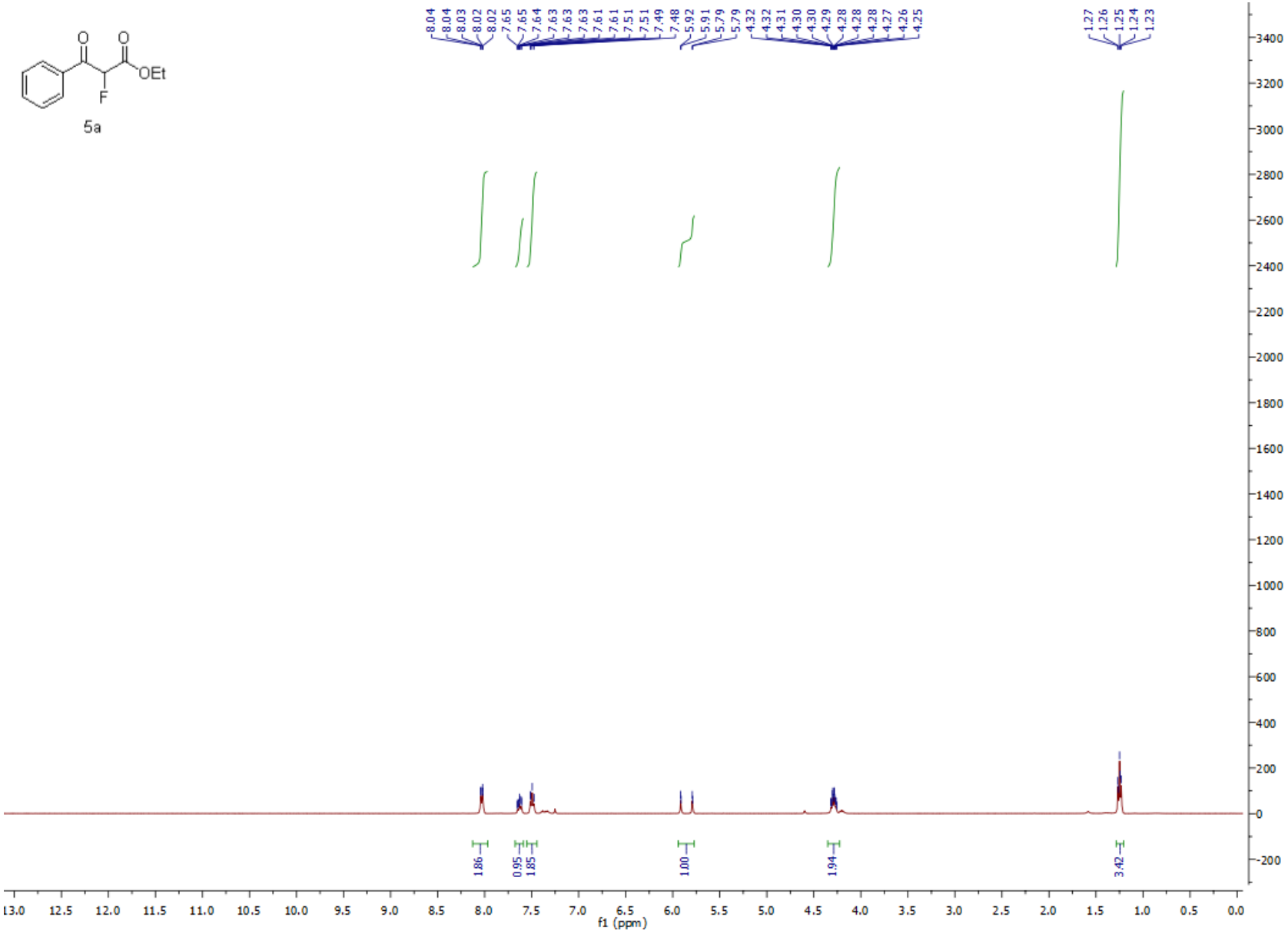

3k (major)
3k (minor)
f1 (ppm)

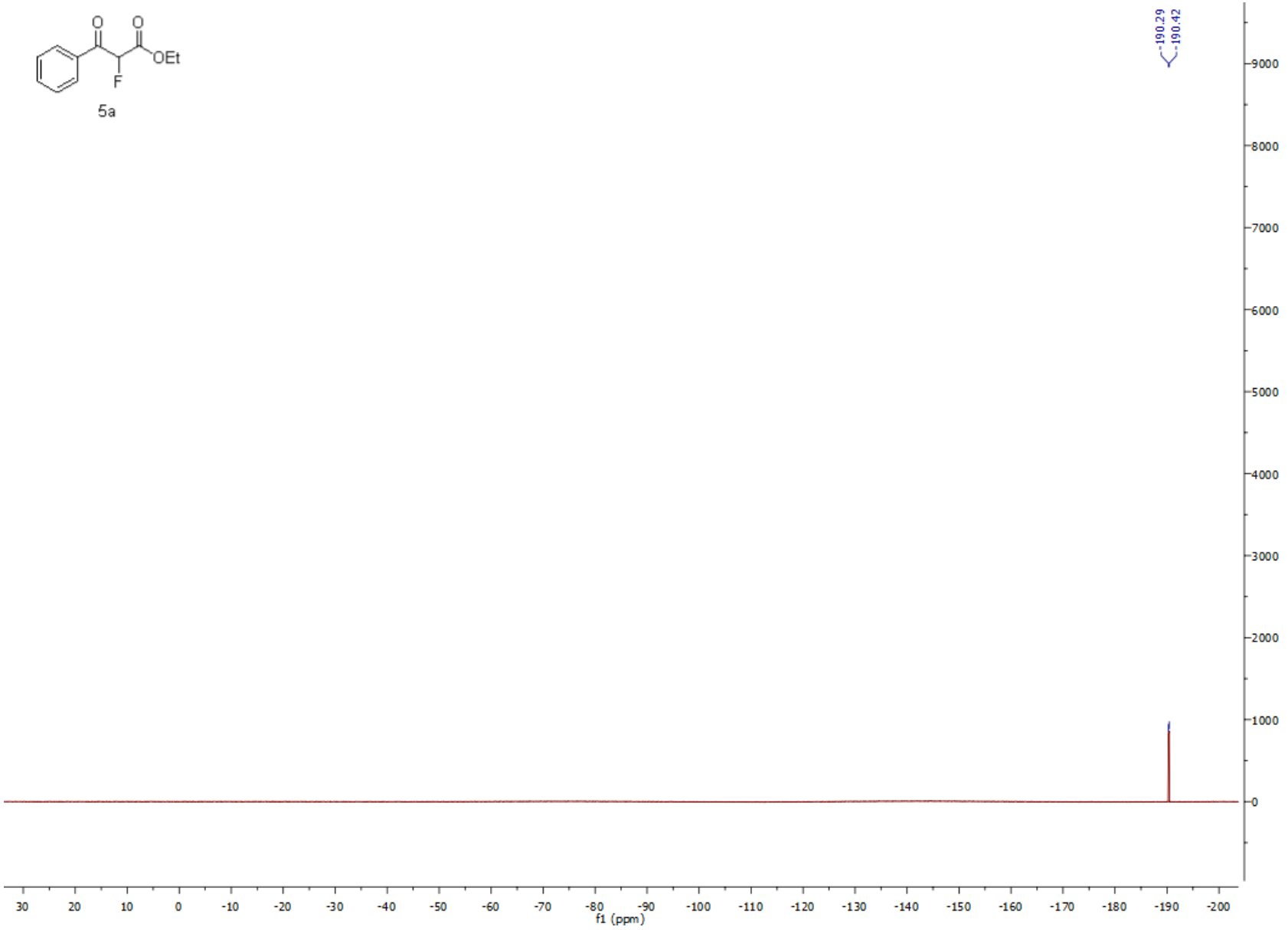


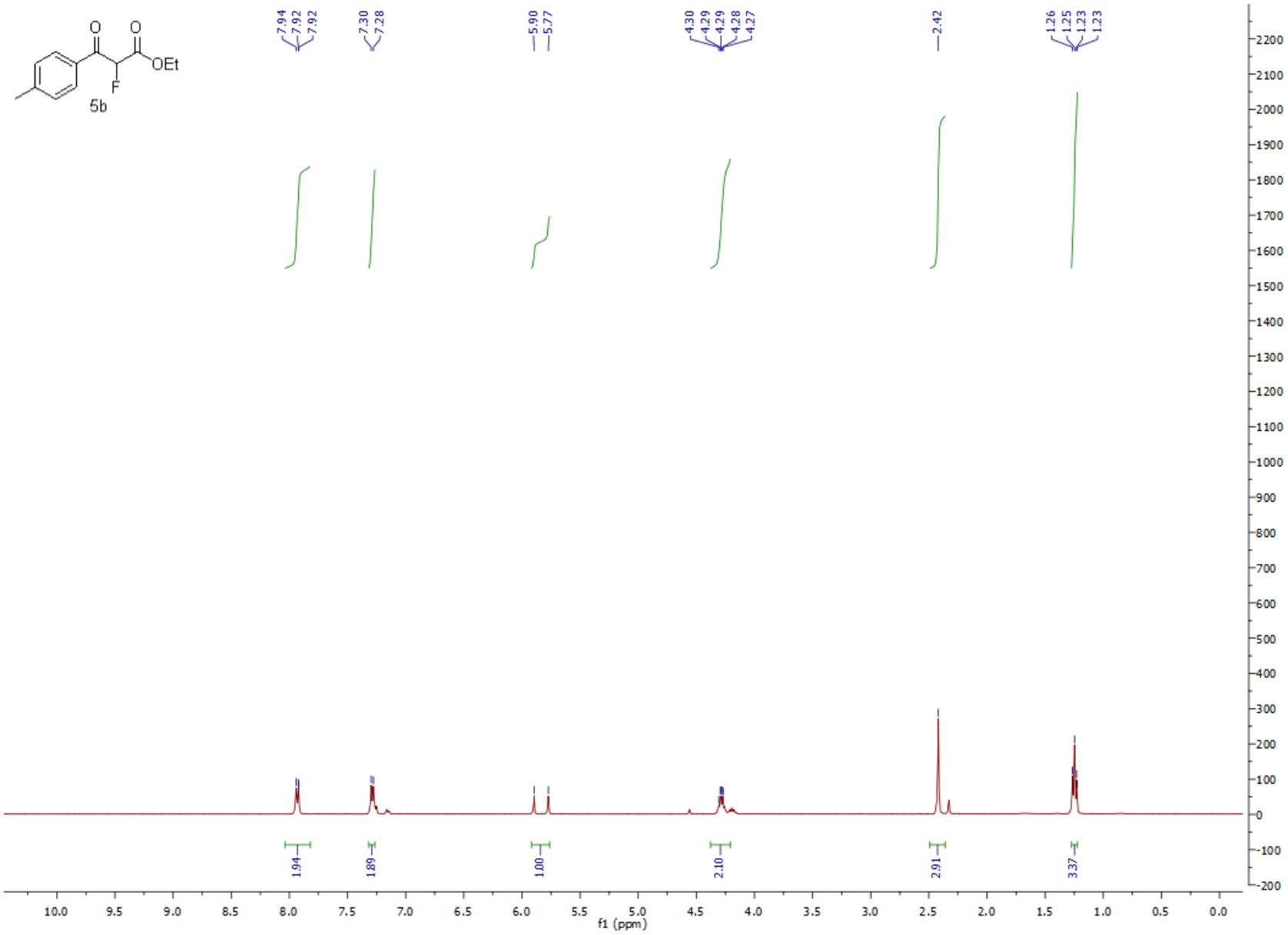
3k (major)

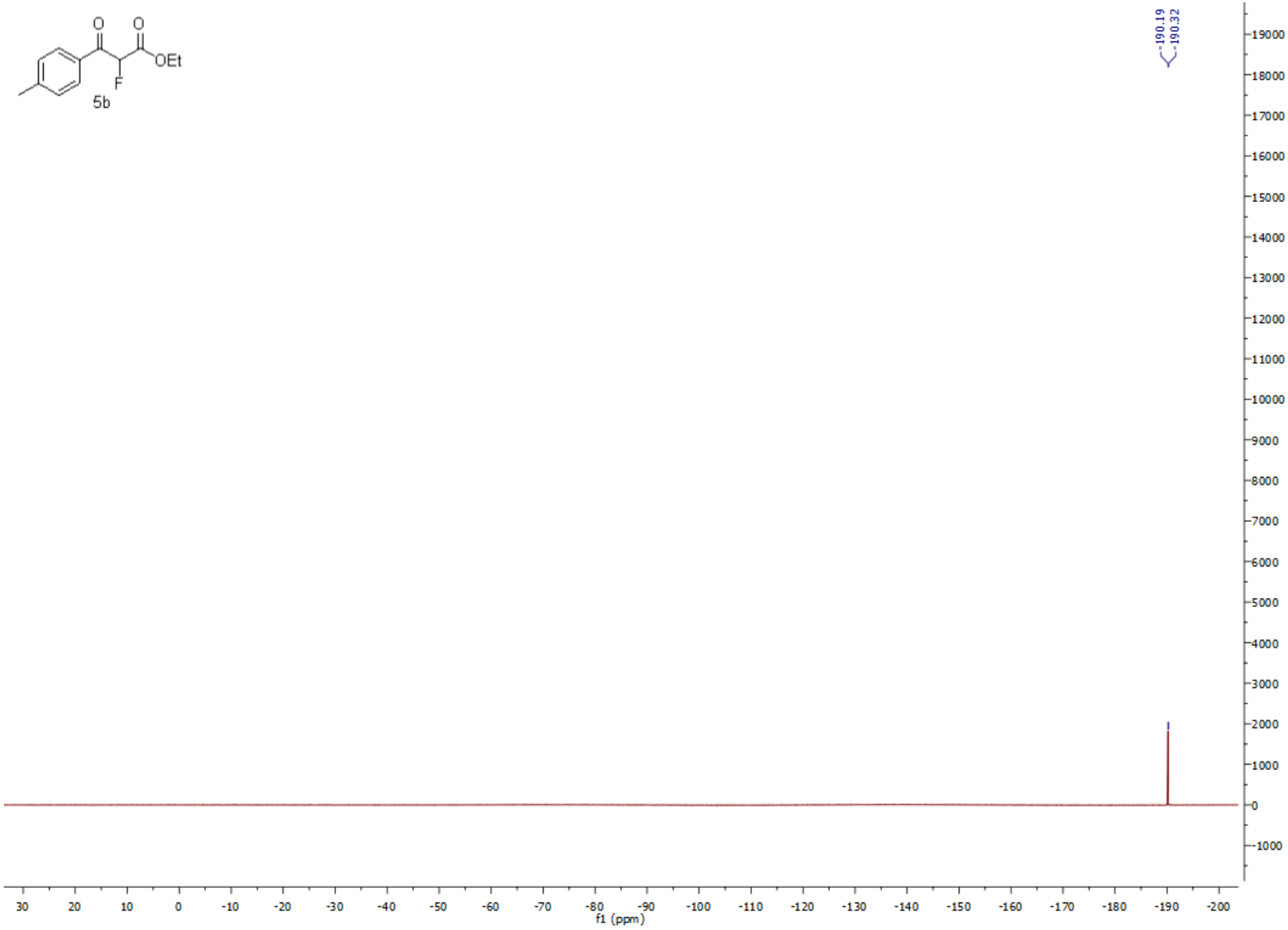
+

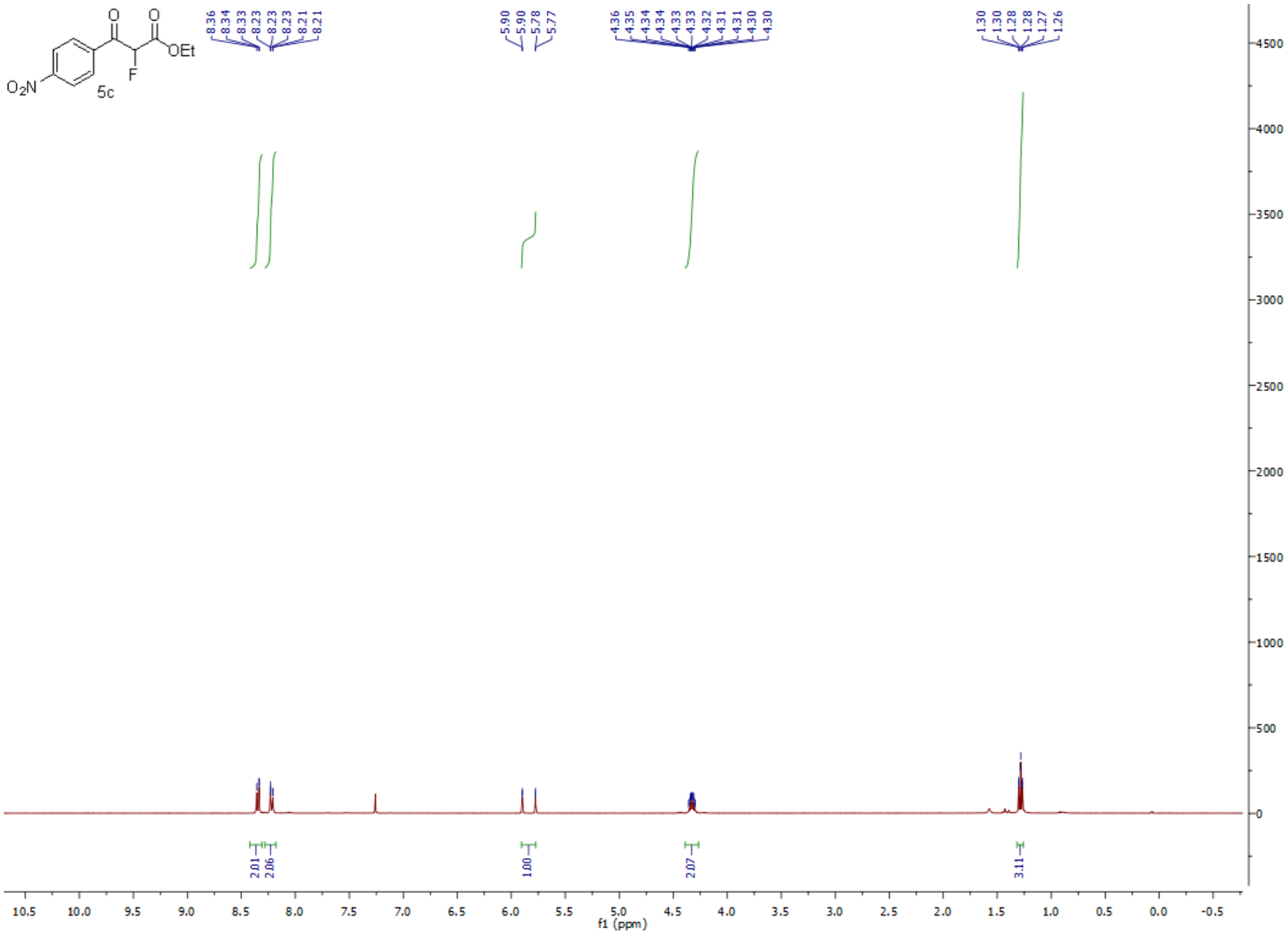
3k' (minor)


O
O
OEt
F
5a
8.04
8.04
8.03
8.02
8.02
7.65
7.65
7.64
7.63
7.63
7.63
7.61
7.61
7.51
7.51
7.49
7.48
5.92
5.91
5.79
5.79
4.32
4.32
4.31
4.30
4.30
4.29
4.28
4.28
4.28
4.27
4.26
4.25
1.27
1.26
1.25
1.24
1.23
1.86
0.95
1.85
1.00
1.94
3.42
f1 (ppm)


O
O
OEt
F
5a
-190.29
-190.42
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)


5b
7.94
7.92
7.92
7.30
7.28
5.90
5.77
4.30
4.29
4.29
4.28
4.27
2.42
1.26
1.25
1.23
1.23
1.94
1.89
1.00
2.10
2.91
3.37
f1 (ppm)


O
O
OEt
F
5b
-190.19
-190.32
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)


O
O
OEt
F
O2N
5c
8.36
8.34
8.33
8.23
8.23
8.23
8.21
8.21
5.90
5.90
5.78
5.77
4.36
4.35
4.34
4.34
4.33
4.33
4.32
4.31
4.31
4.30
4.30
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1.27
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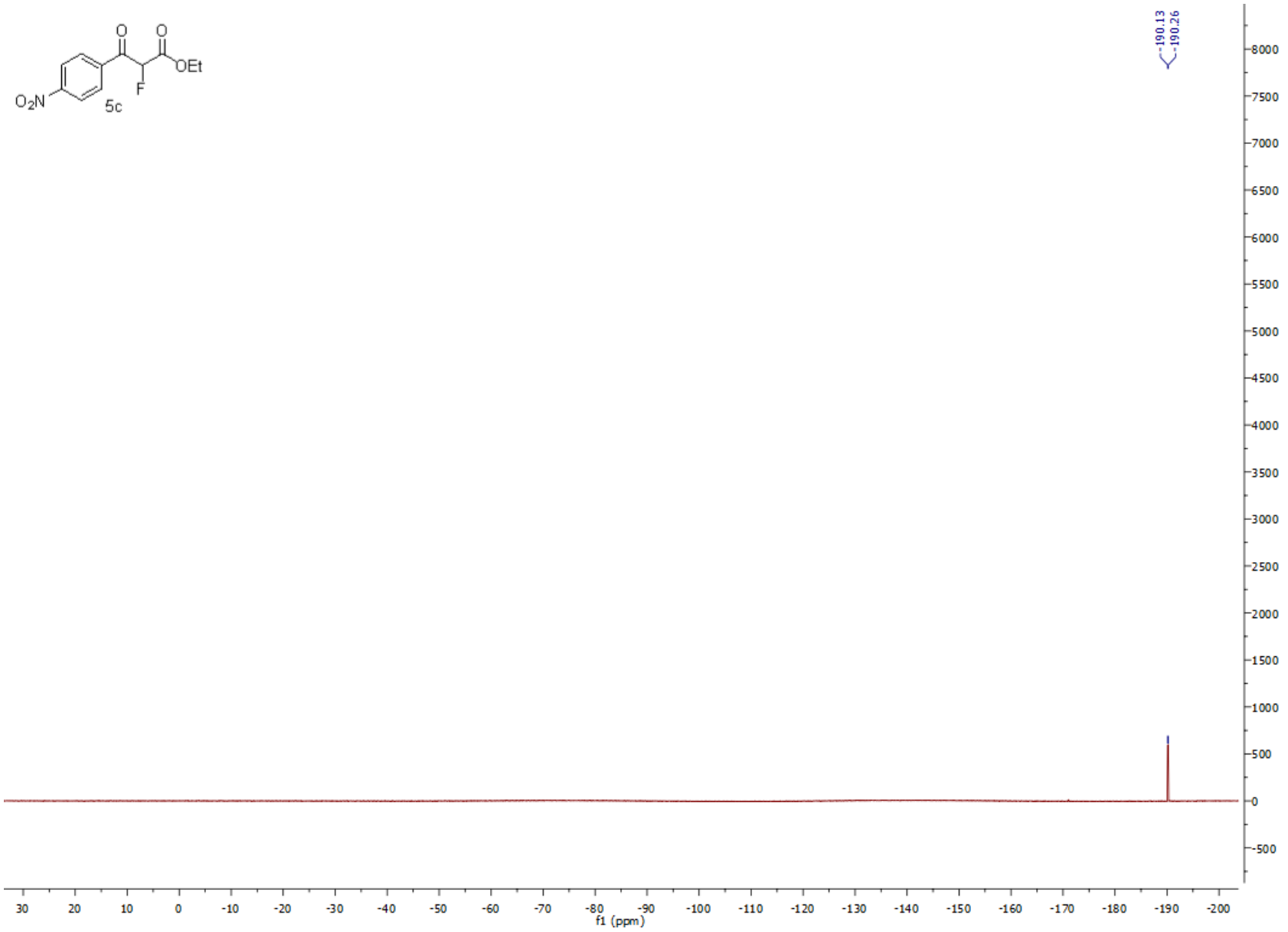
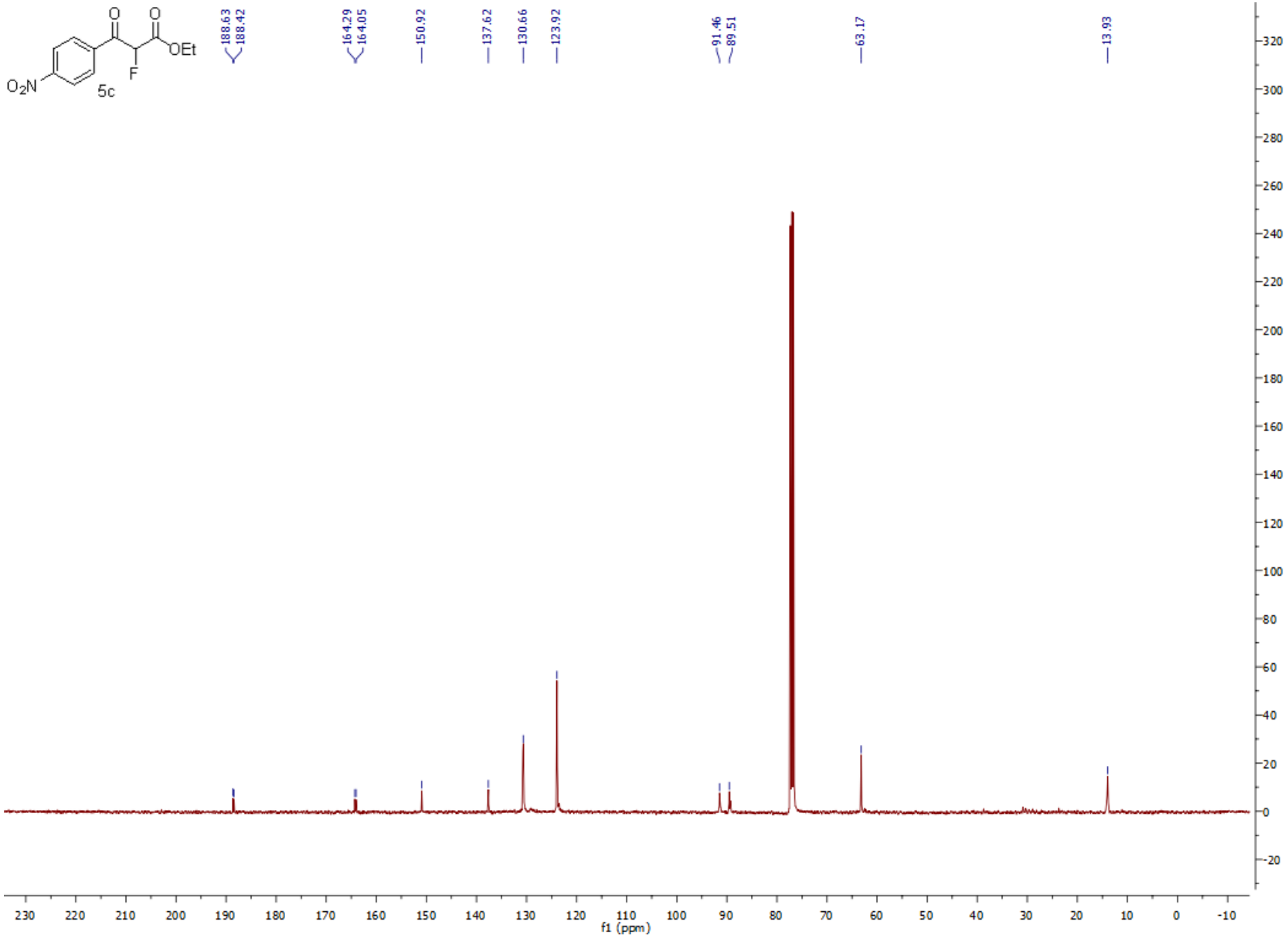
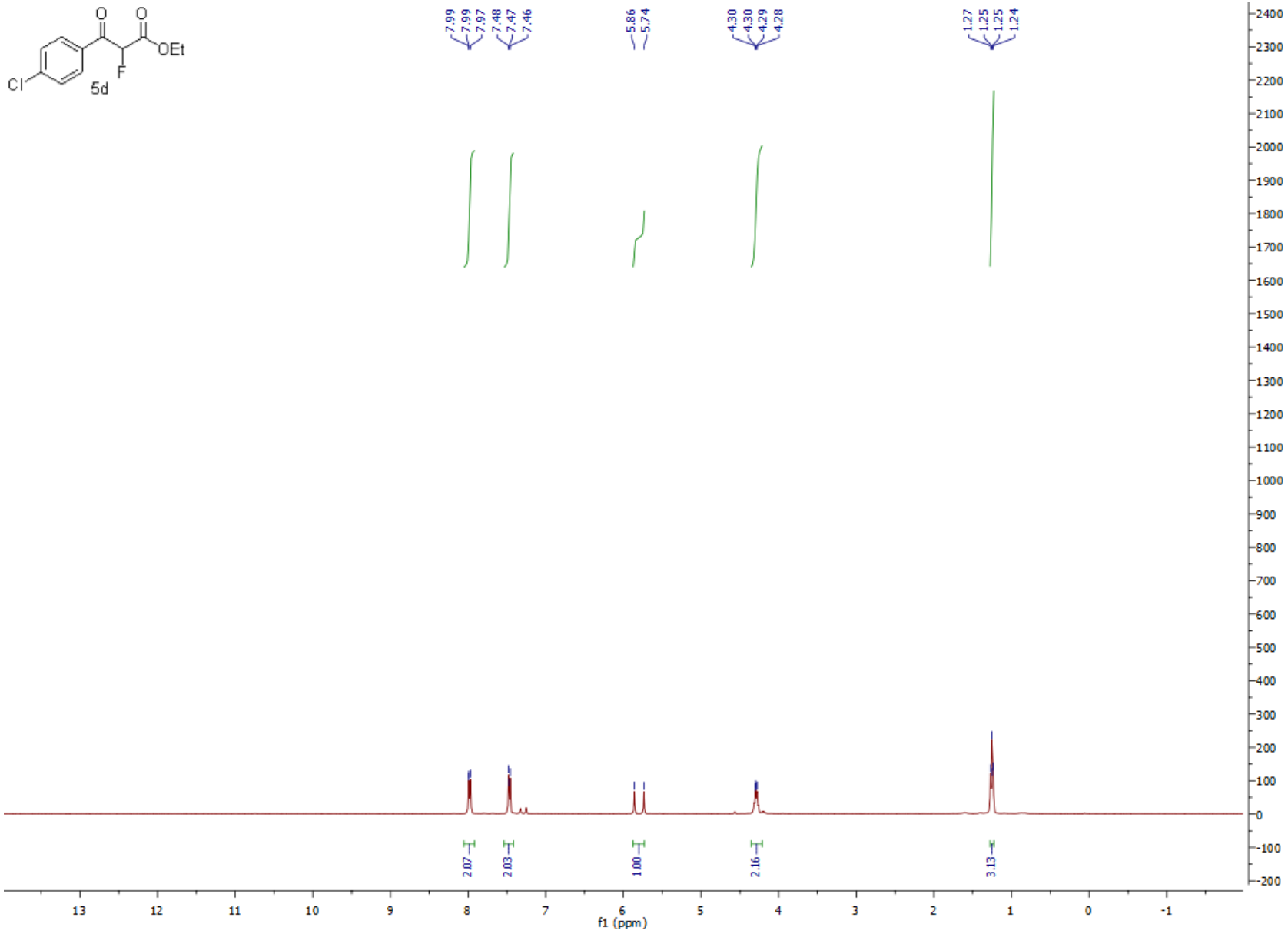
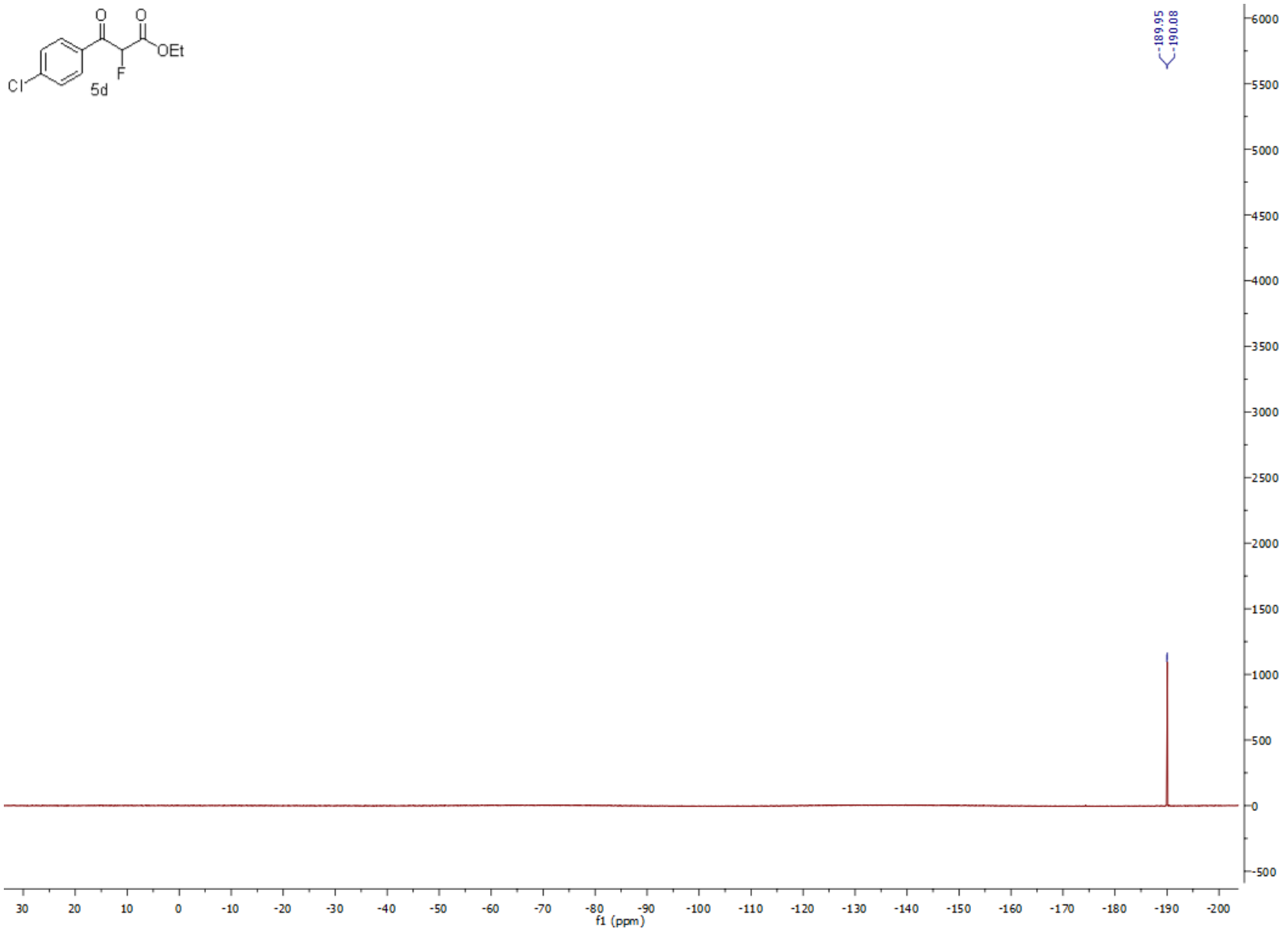
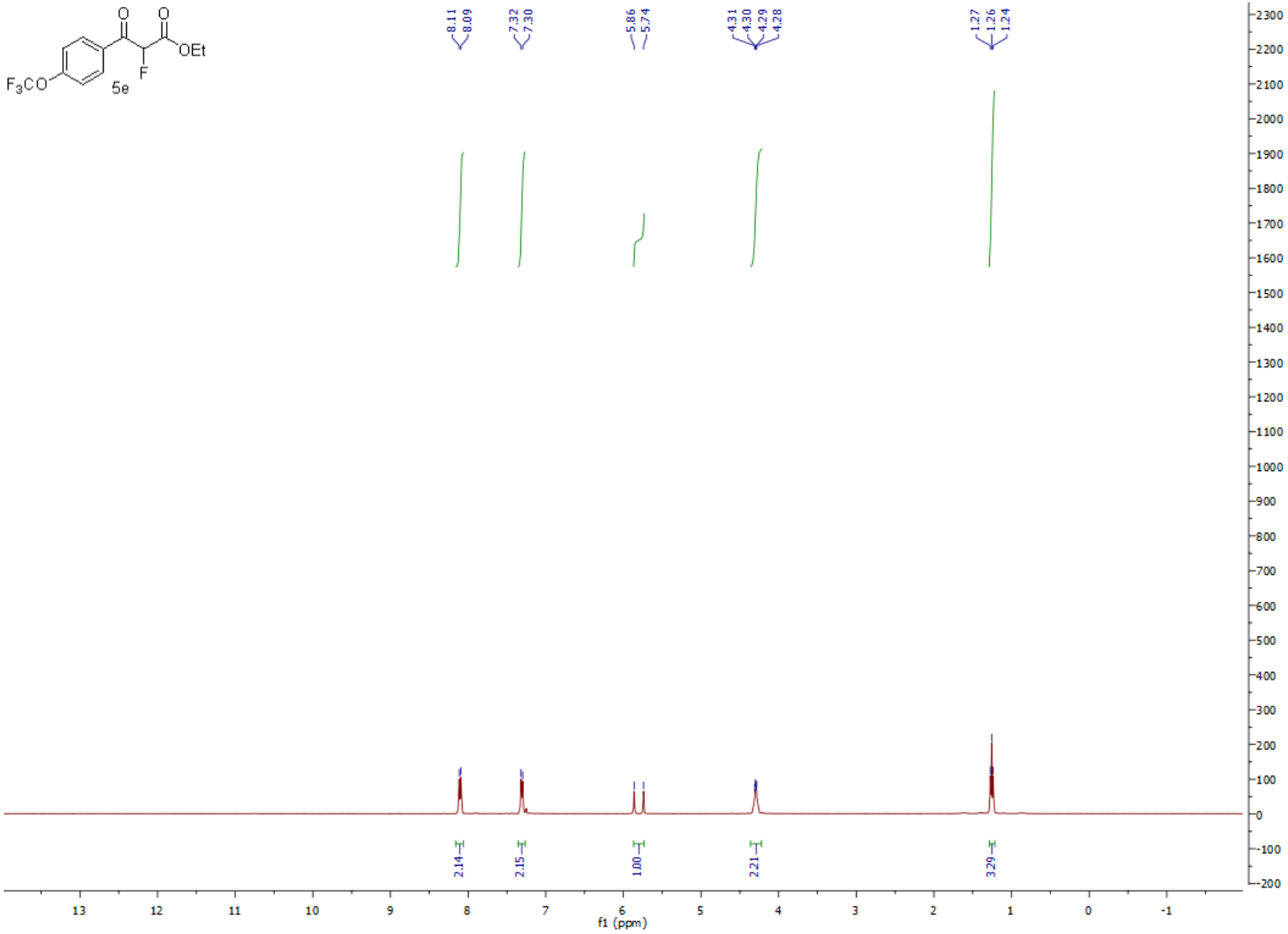
2.01
2.06
1.00
2.07
3.11
f1 (ppm)

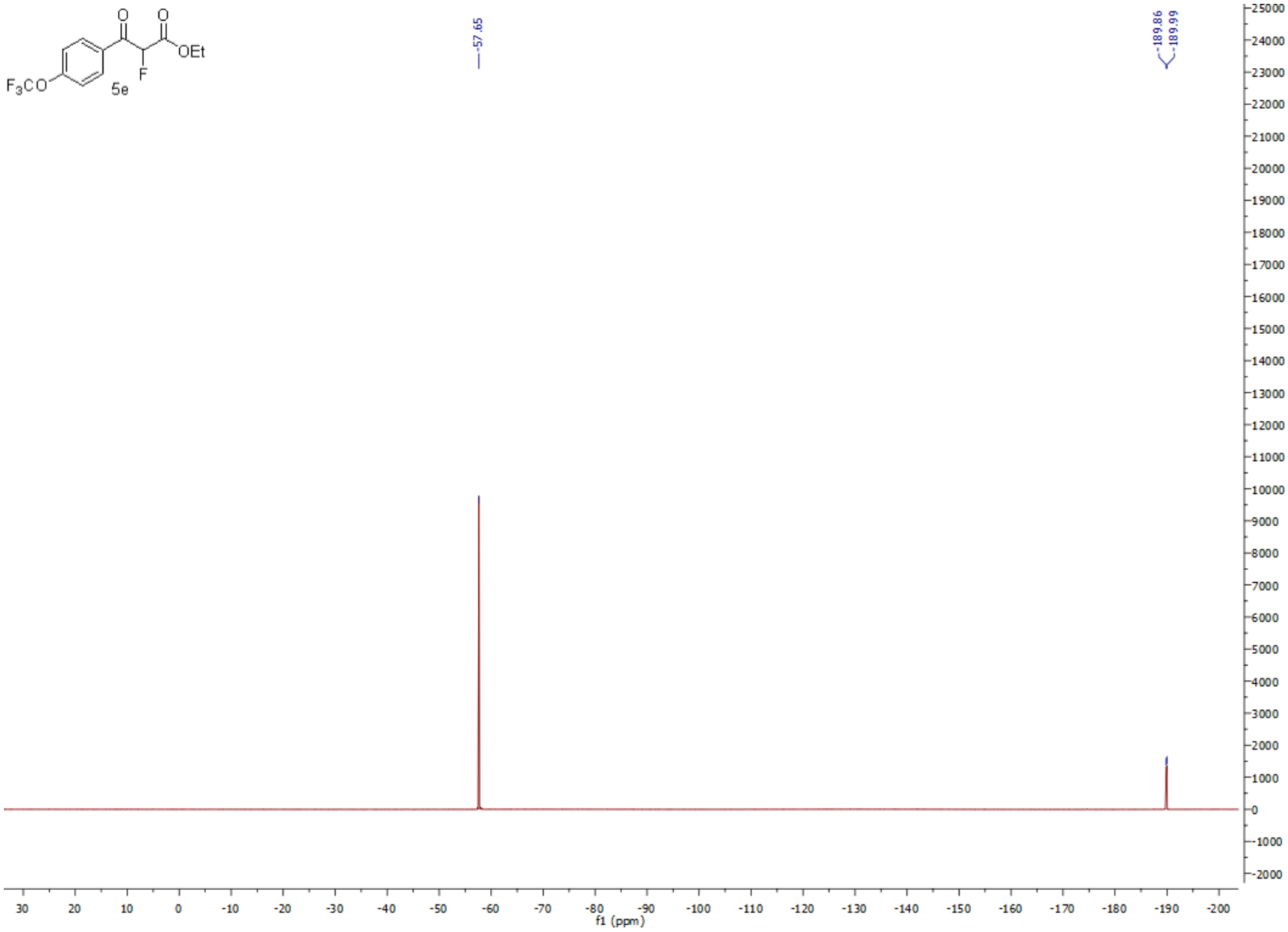

O
O
OEt
F
O2N
5c
-190.13
-190.26
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

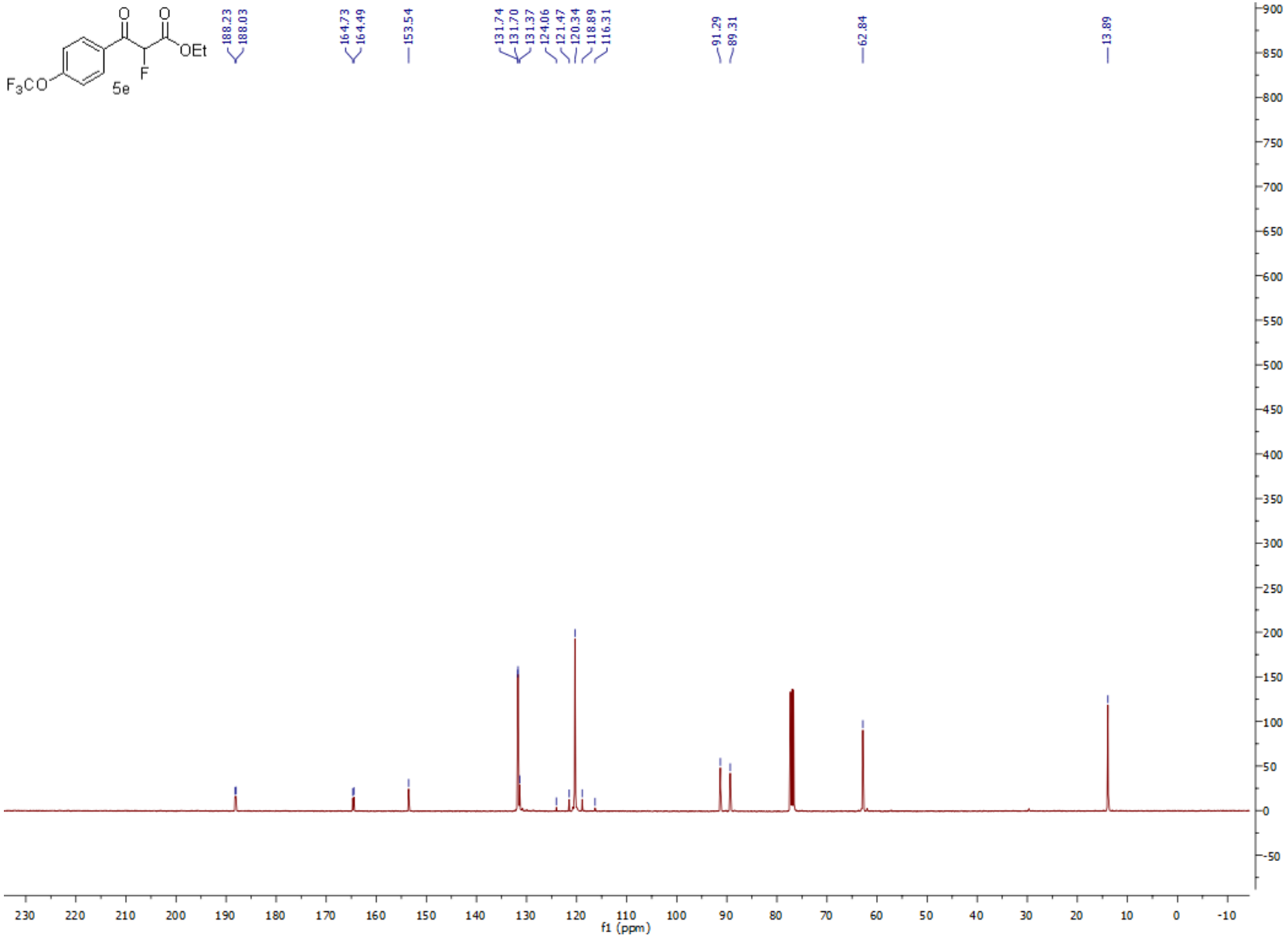

O
O
OEt
F
O2N
5c
188.63
188.42
164.29
164.05
150.92
137.62
130.66
123.92
91.46
89.51
63.17
13.93
f1 (ppm)

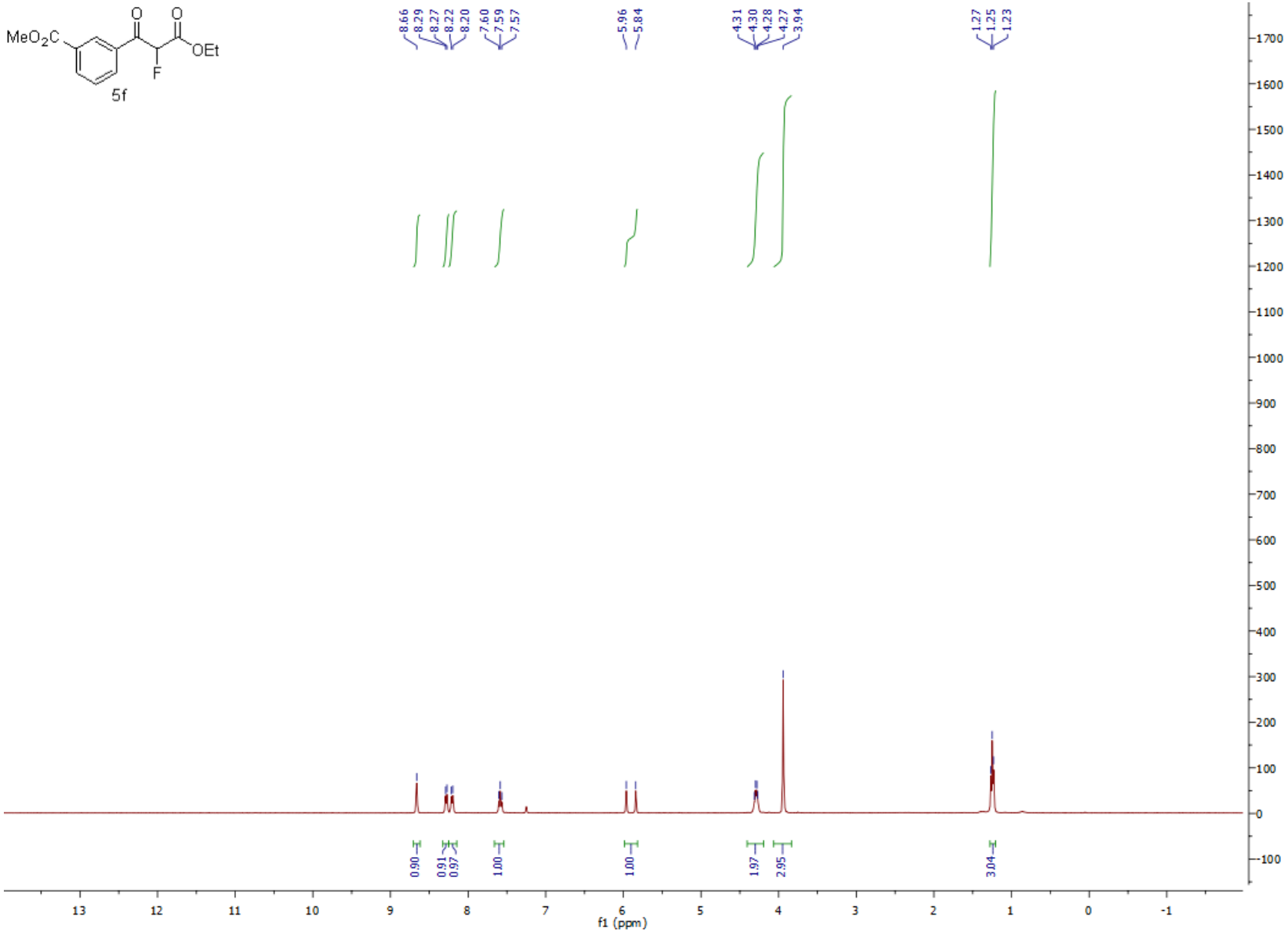

O
O
OEt
F
Cl
5d
7.99
7.99
7.97
7.48
7.47
7.46
5.86
5.74
4.30
4.30
4.29
4.28
1.27
1.25
1.25
1.24
2.07
2.03
1.00
2.16
3.13
f1 (ppm)

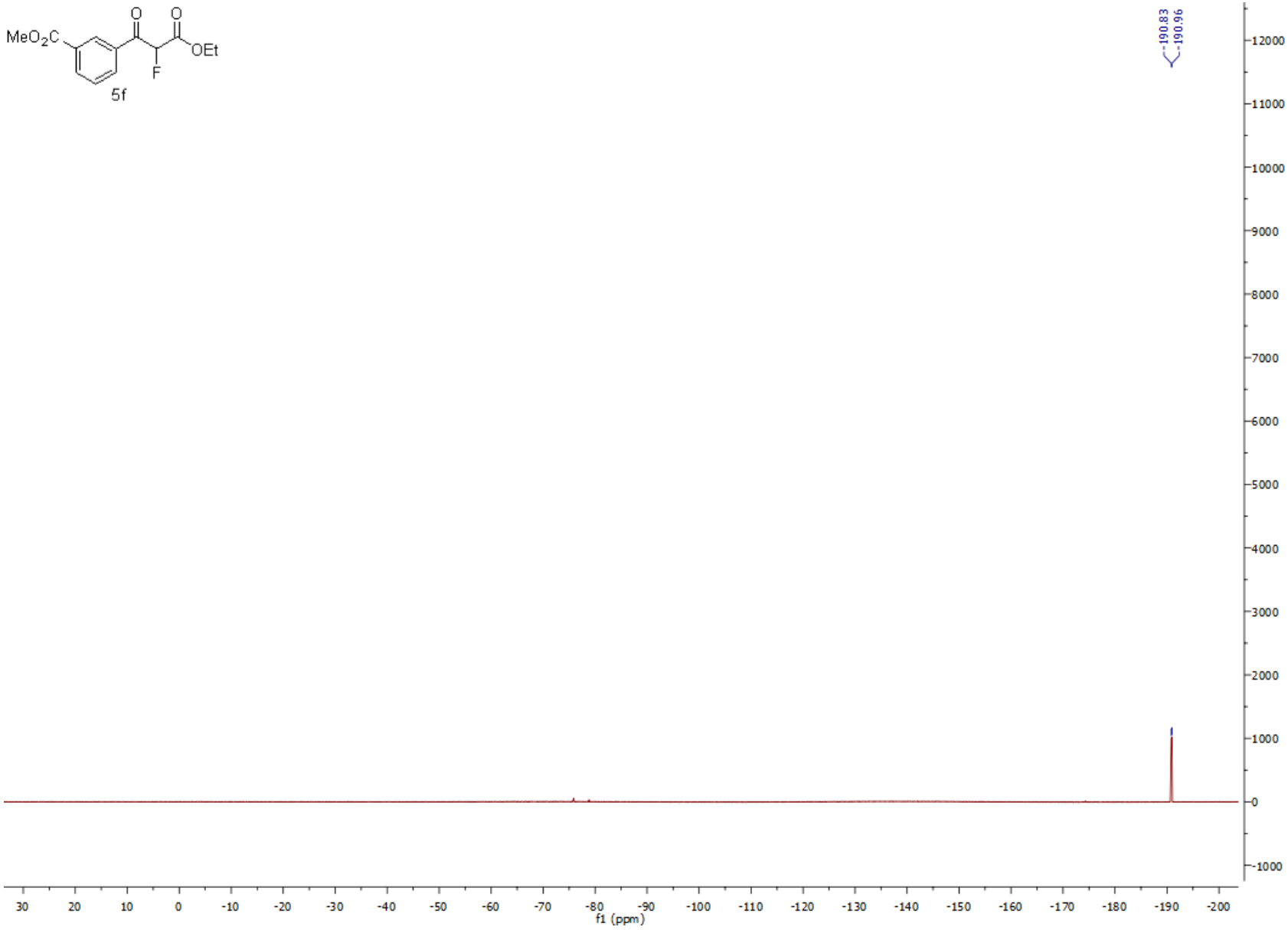

O
O
OEt
F
Cl
5d
-189.95
-190.08
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

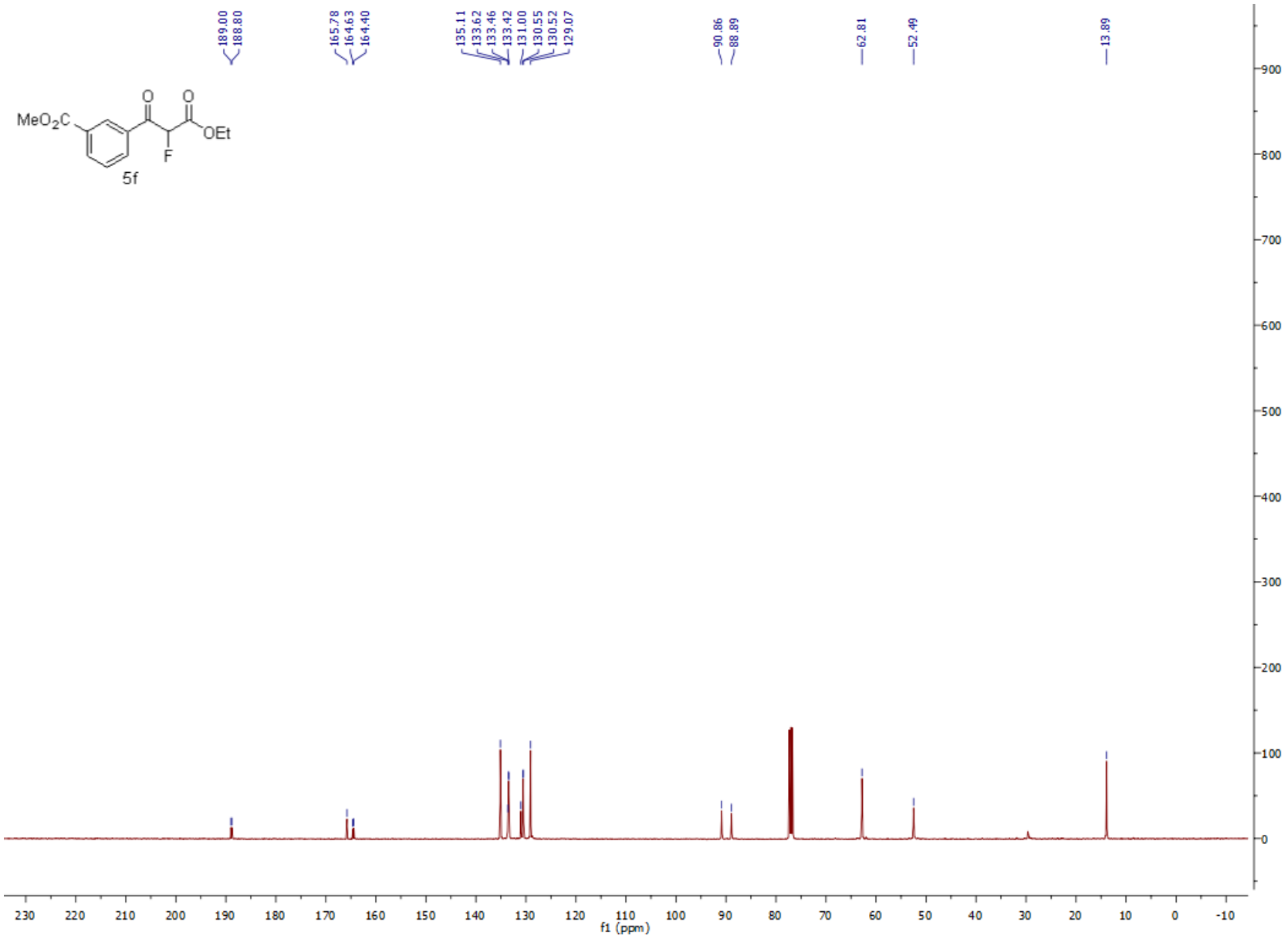

O
O
OEt
F
F3CO
5e
8.11
8.09
7.32
7.30
5.86
5.74
4.31
4.30
4.29
4.28
1.27
1.26
1.24
2.14
2.15
1.00
2.21
3.29
f1 (ppm)

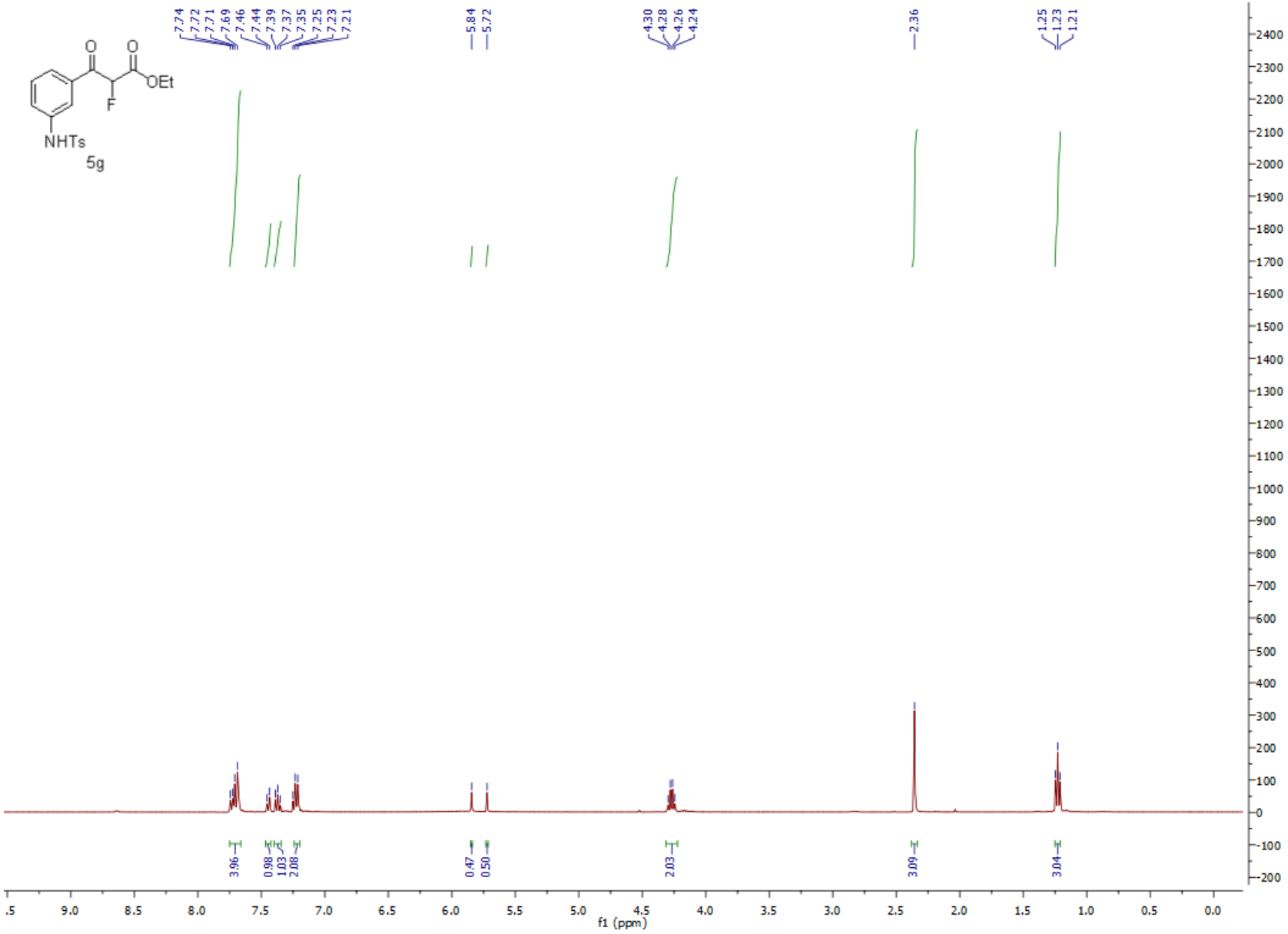

O
O
OEt
F
F3CO
5e
-57.65
-189.86
-189.99
25000
24000
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

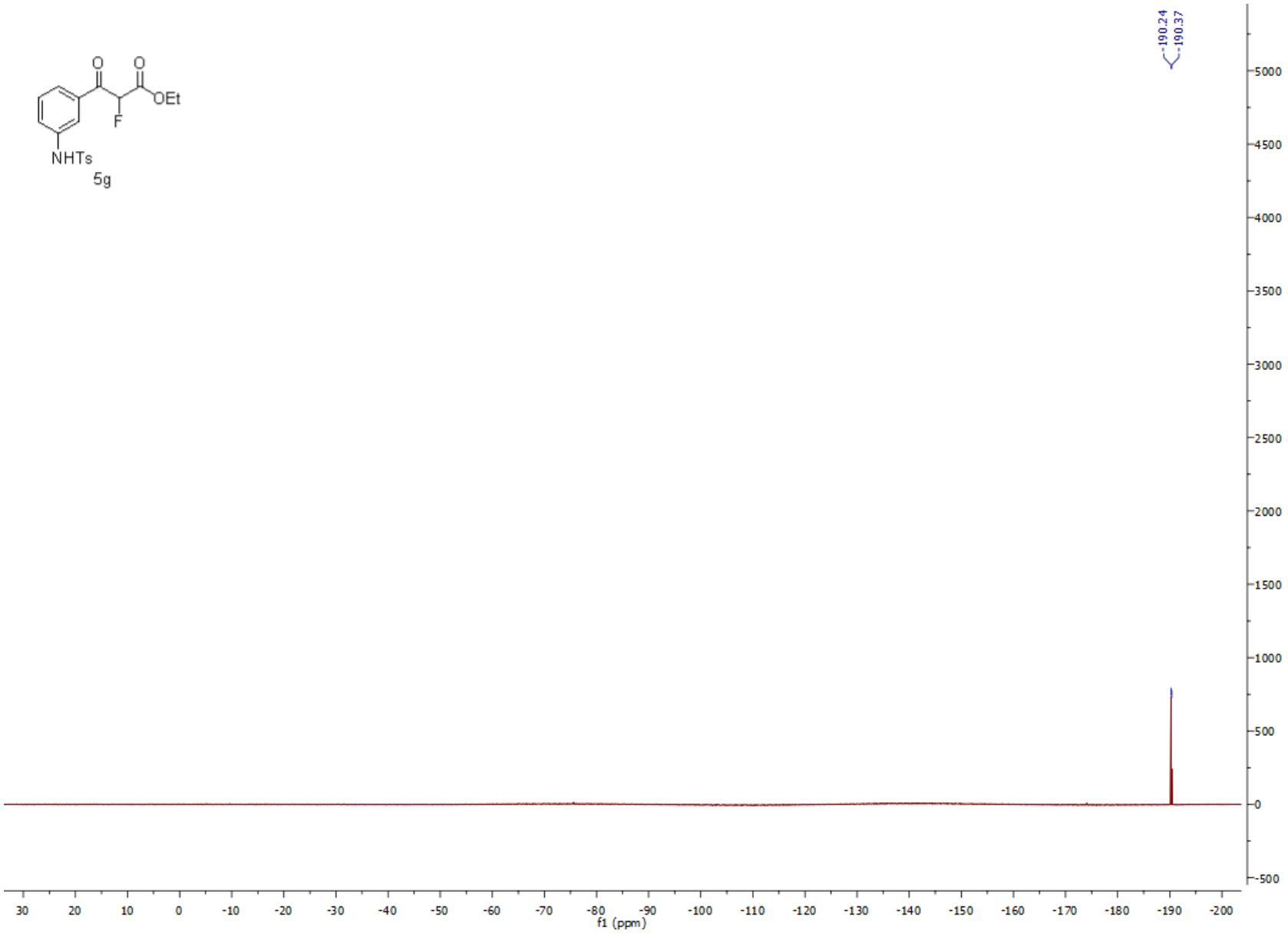

5e
188.23
188.03
164.73
164.49
153.54
131.74
131.70
131.37
124.06
121.47
120.34
118.89
116.31
91.29
89.31
62.84
13.89
f1 (ppm)

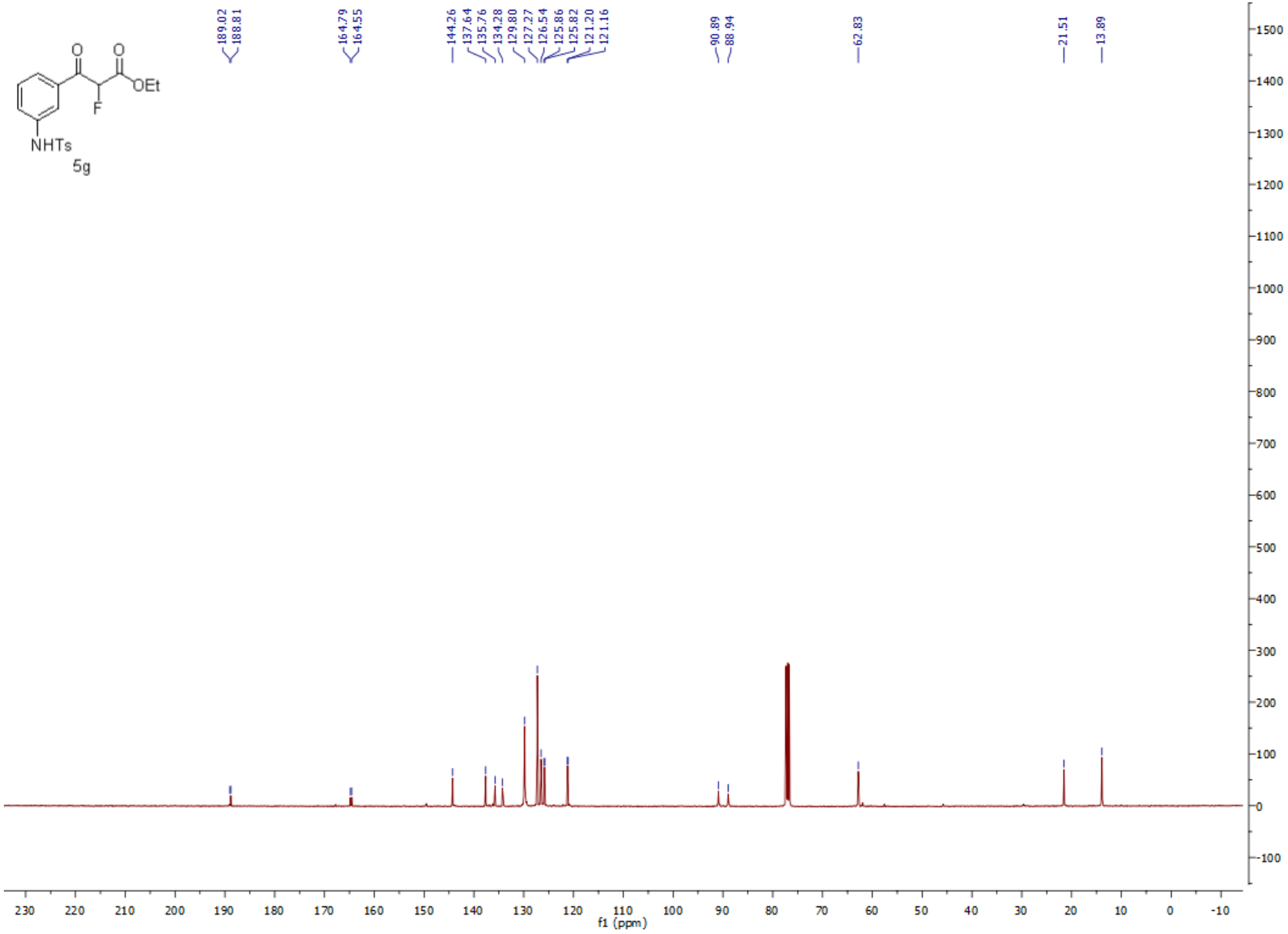

MeO2C
O
O
OEt
F
5f
8.66
8.29
8.27
8.22
8.20
7.60
7.59
7.57
5.96
5.84
4.31
4.30
4.28
4.27
3.94
1.27
1.25
1.23
0.90
0.91
0.97
1.00
1.00
1.97
2.95
3.04
f1 (ppm)

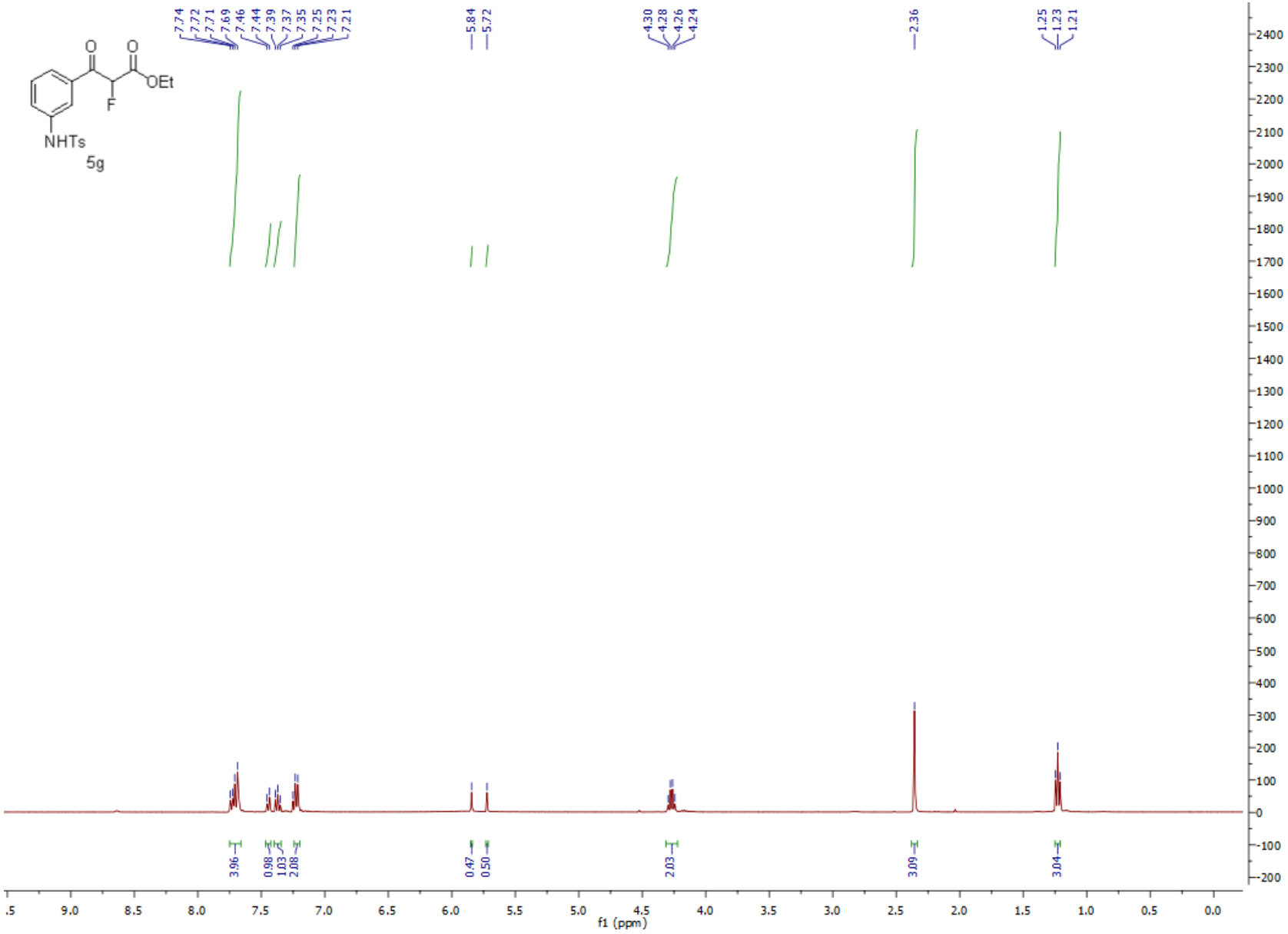

MeO2C
O
O
OEt
F
5f
-190.83
-190.96
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

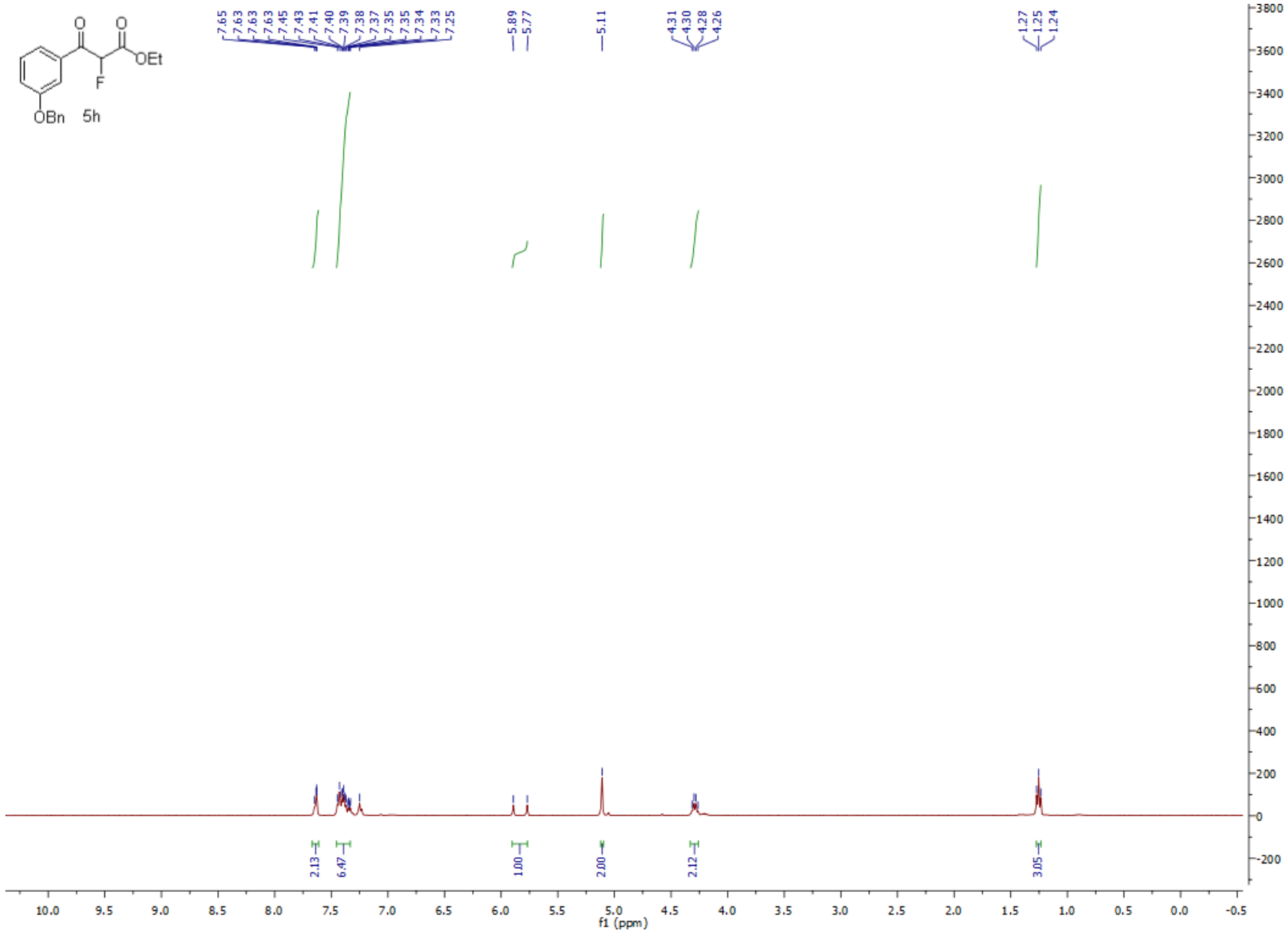

189.00
188.80
165.78
164.63
164.40
135.11
133.62
133.46
133.42
131.00
130.55
130.52
129.07
90.86
88.89
62.81
52.49
13.89
MeO2C
O
O
OEt
F
5f
f1 (ppm)

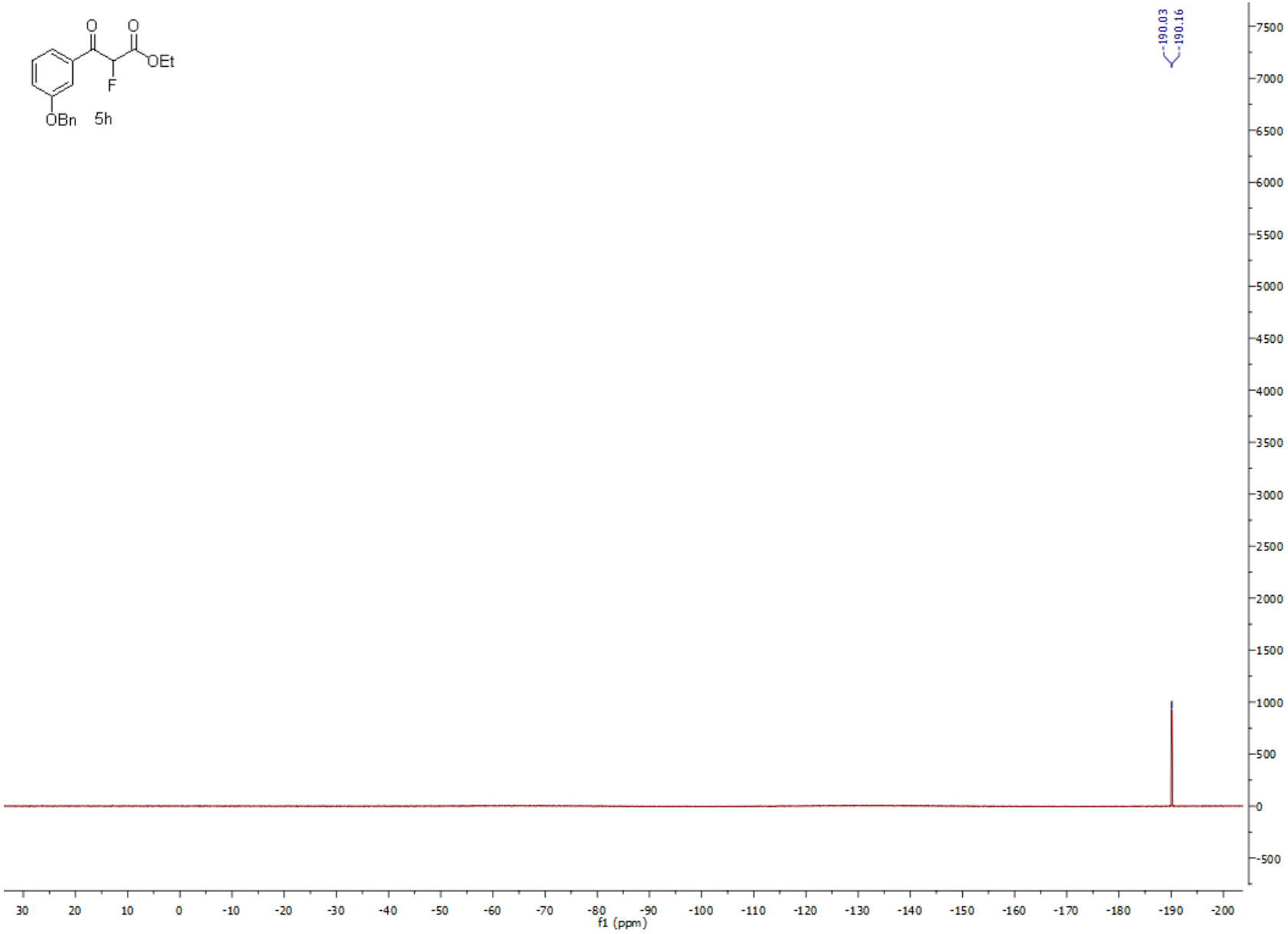

7.74
7.72
7.71
7.69
7.46
7.44
7.39
7.37
7.35
7.25
7.23
7.21
5.84
5.72
4.30
4.28
4.26
4.24
2.36
1.25
1.23
1.21
O
O
OEt
F
NHTs
5g
3.96
0.98
1.03
2.08
0.47
0.50
2.03
3.09
3.04
f1 (ppm)

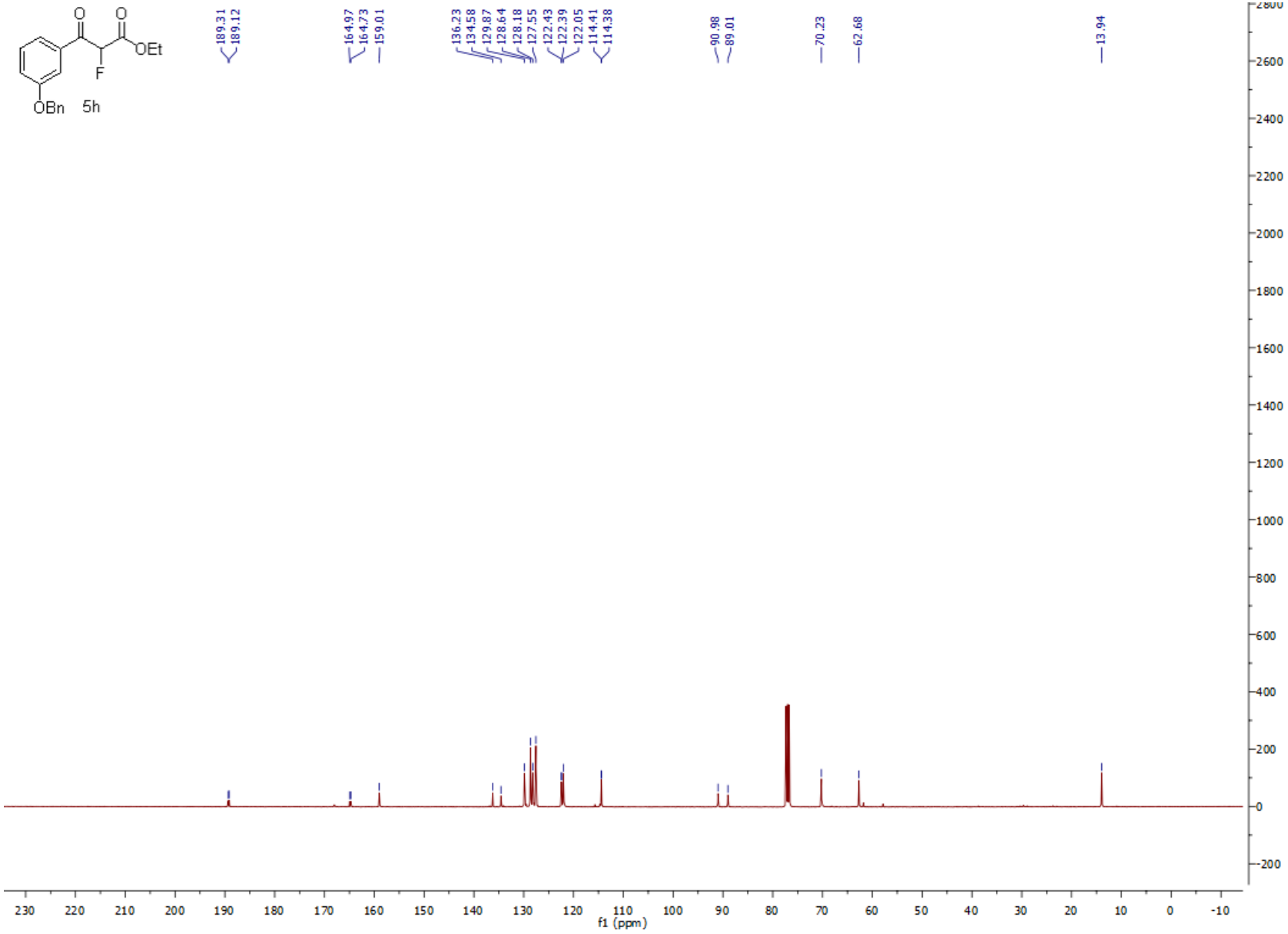

O
O
OEt
F
NHTs
5g
-190.24
-190.37
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

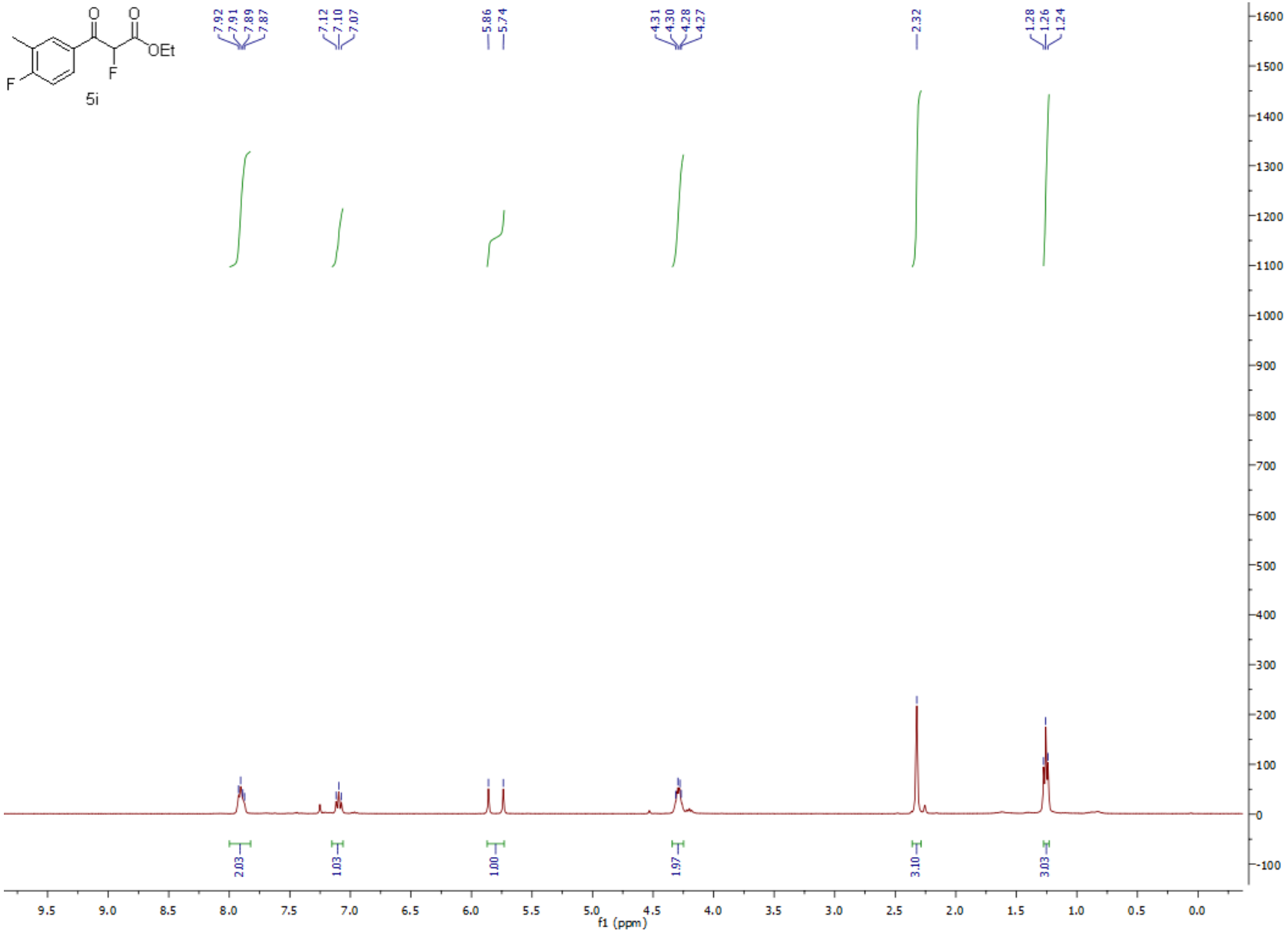

189.02
188.81
164.79
164.55
144.26
137.64
135.76
134.28
129.80
127.27
126.54
125.86
125.82
121.20
121.16
90.89
88.94
62.83
21.51
13.89
O
O
OEt
F
NHTs
5g
f1 (ppm)

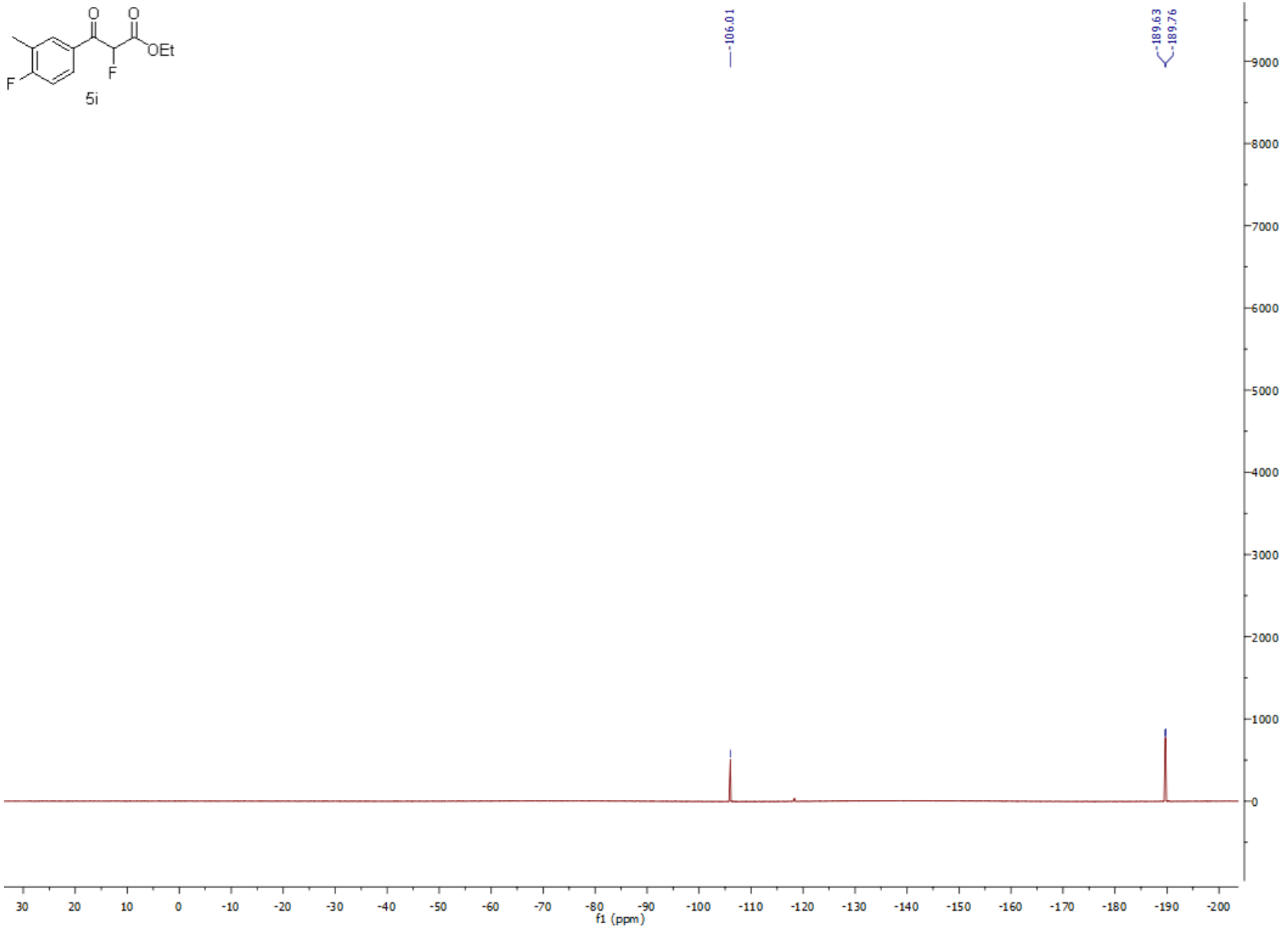

7.74
7.72
7.71
7.69
7.46
7.44
7.39
7.37
7.35
7.25
7.23
7.21
5.84
5.72
4.30
4.28
4.26
4.24
2.36
1.25
1.23
1.21
O
O
OEt
F
NHTs
5g
3.96
0.98
1.03
2.08
0.47
0.50
2.03
3.09
3.04
f1 (ppm)

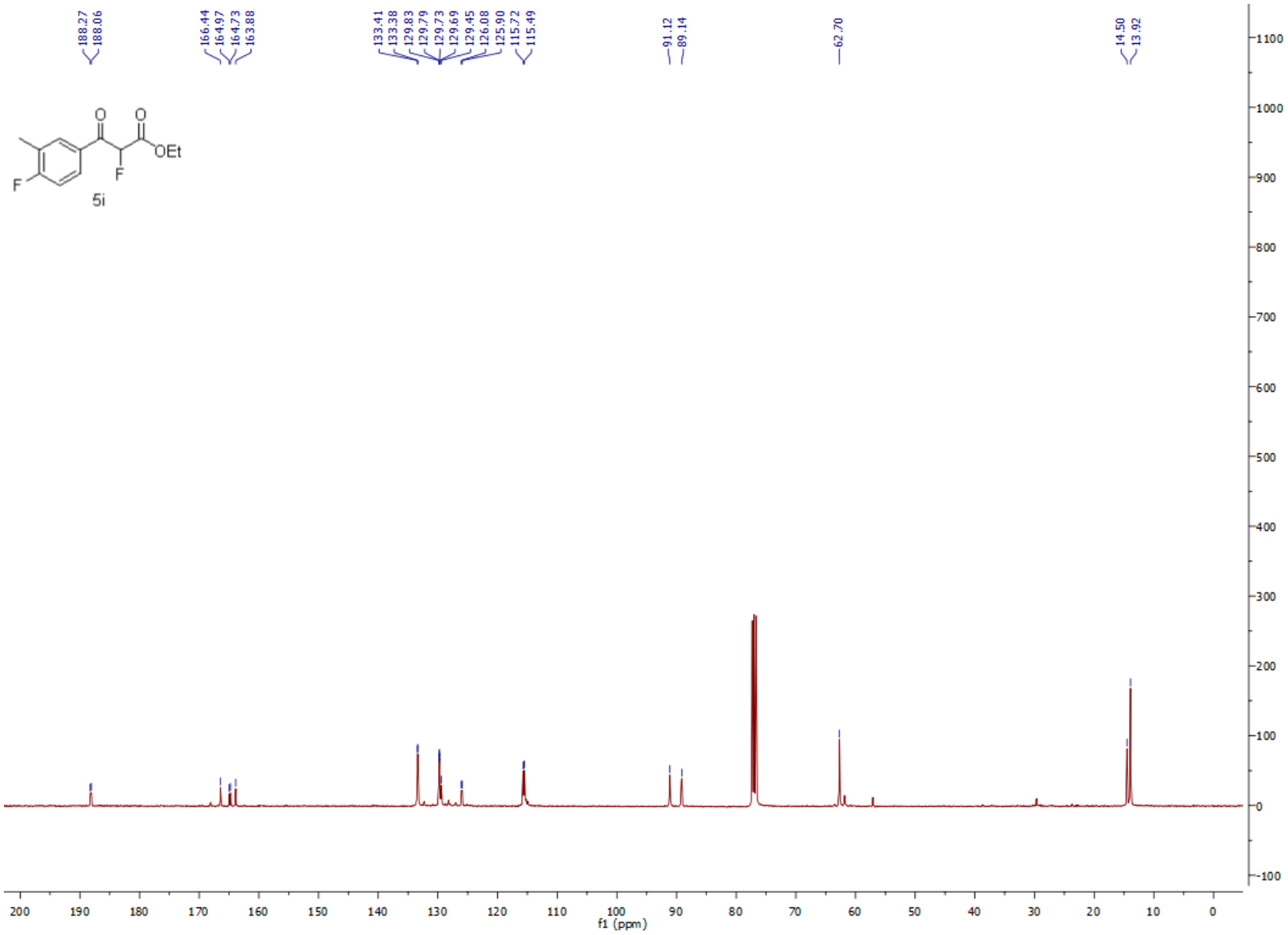

O
O
OEt
F
OBn
5h
7.65
7.63
7.63
7.63
7.45
7.43
7.41
7.40
7.39
7.38
7.37
7.35
7.35
7.34
7.33
7.25
5.89
5.77
5.11
4.31
4.30
4.28
4.26
1.27
1.25
1.24
2.13
6.47
1.00
2.00
2.12
3.05
f1 (ppm)

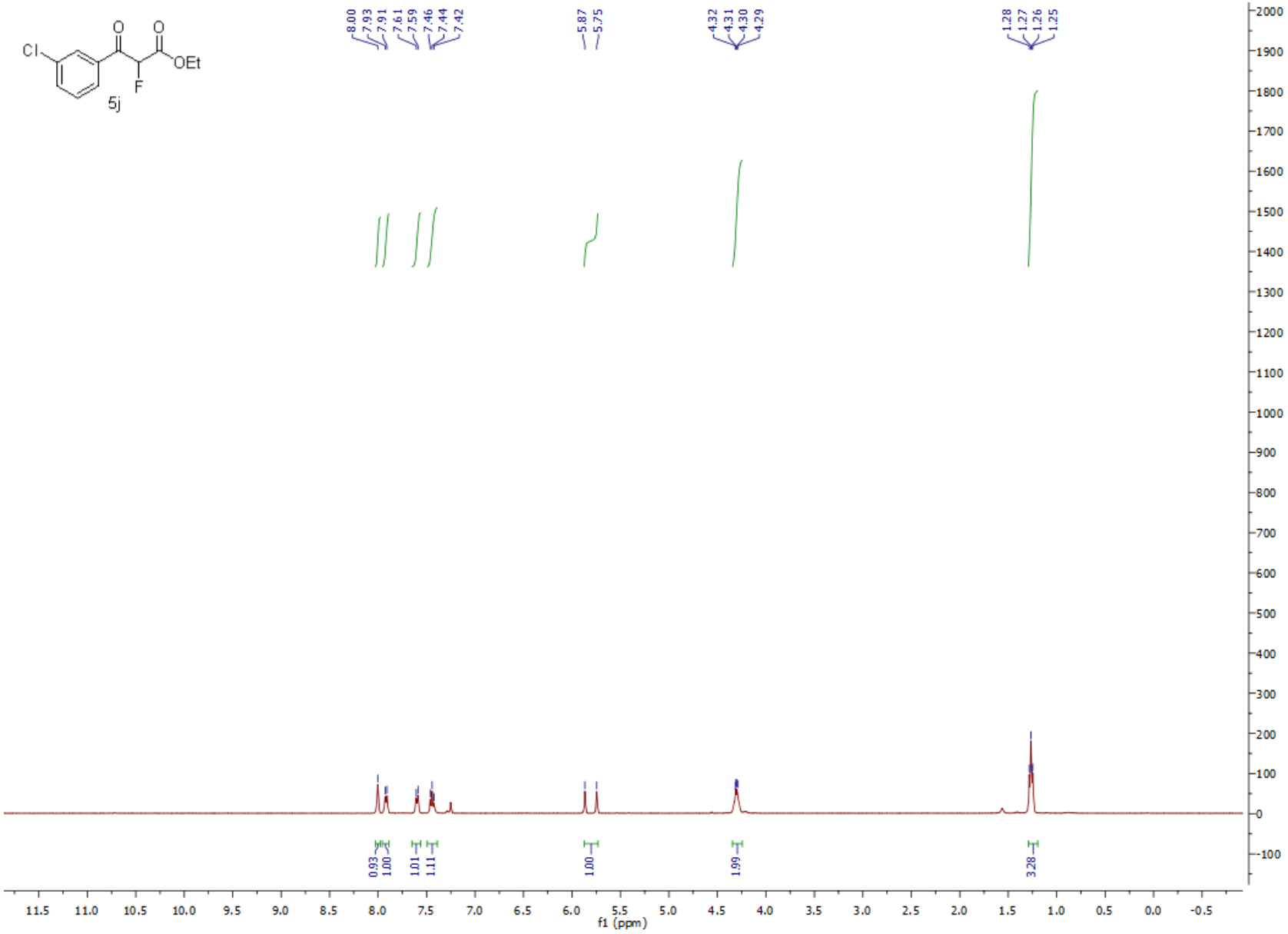

O
O
OEt
F
OBn
5h
-190.03
-190.16
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

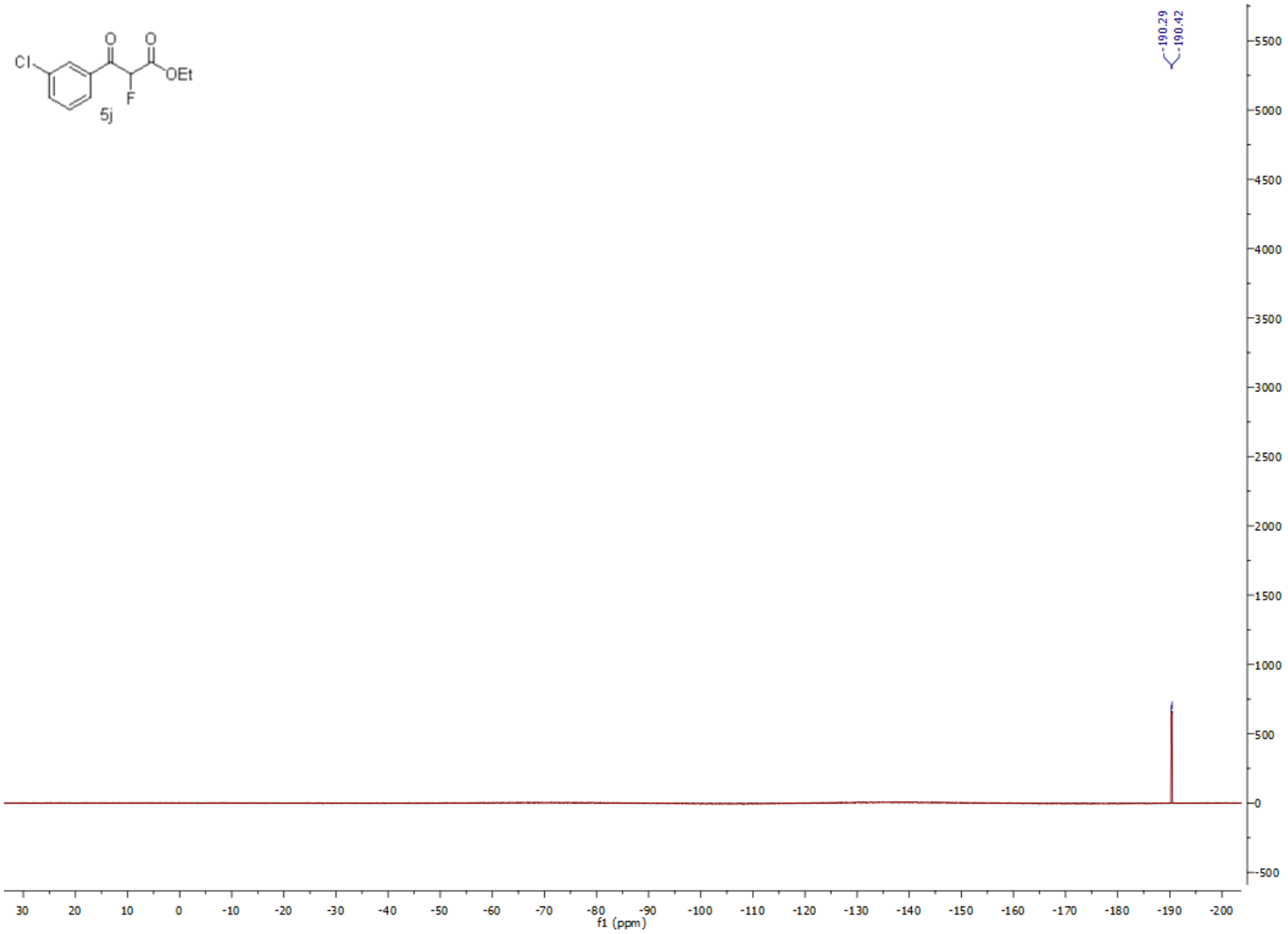

O
O
OEt
F
OBn
5h
189.31
189.12
164.97
164.73
159.01
136.23
134.58
129.87
128.64
128.18
127.55
122.43
122.39
122.05
114.41
114.38
90.98
89.01
70.23
62.68
13.94
f1 (ppm)

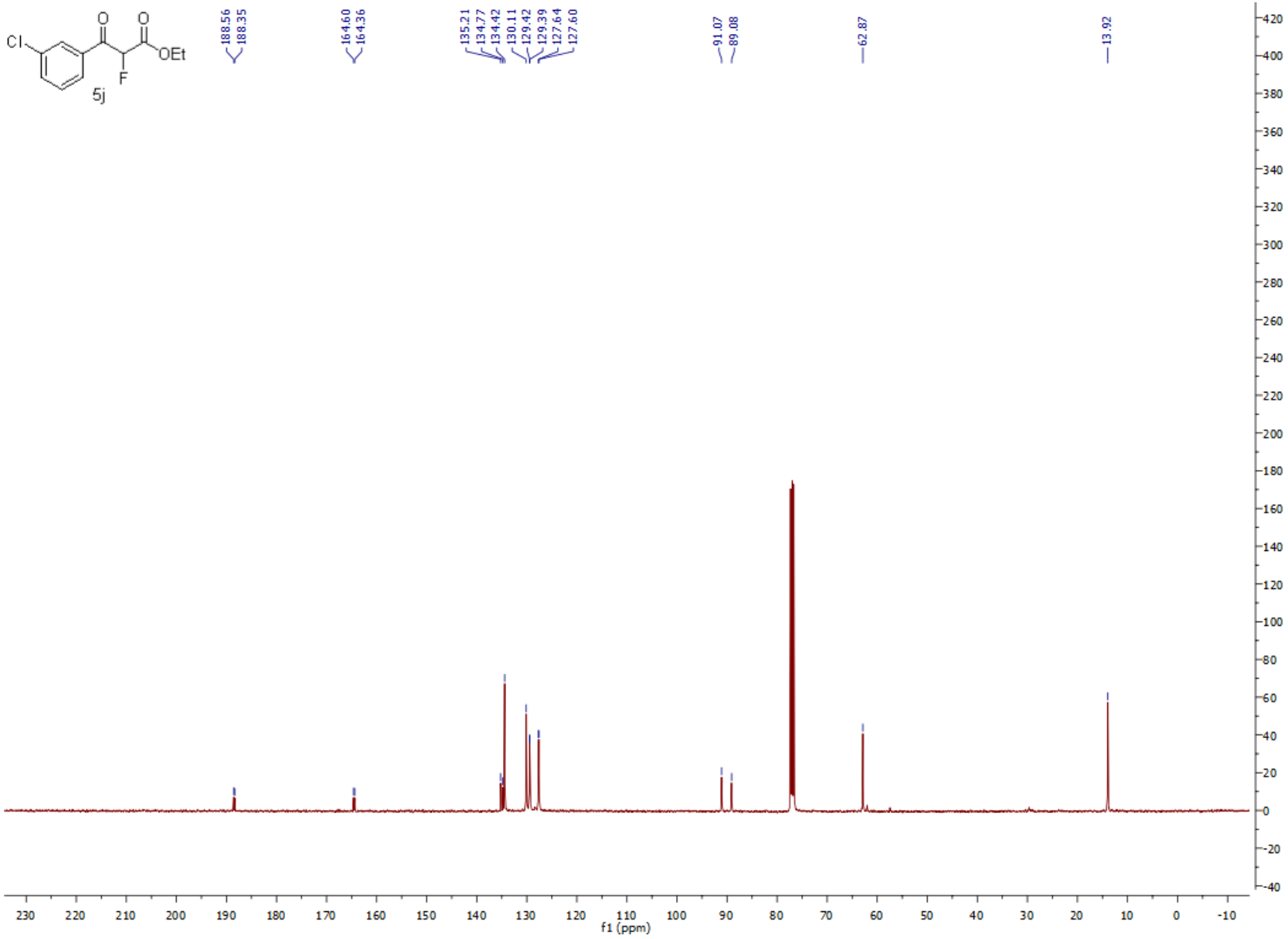

O
O
OEt
F
F
5i
7.92
7.91
7.89
7.87
7.12
7.10
7.07
5.86
5.74
4.31
4.30
4.28
4.27
2.32
1.28
1.26
1.24
2.03
1.03
1.00
1.97
3.10
3.03
f1 (ppm)

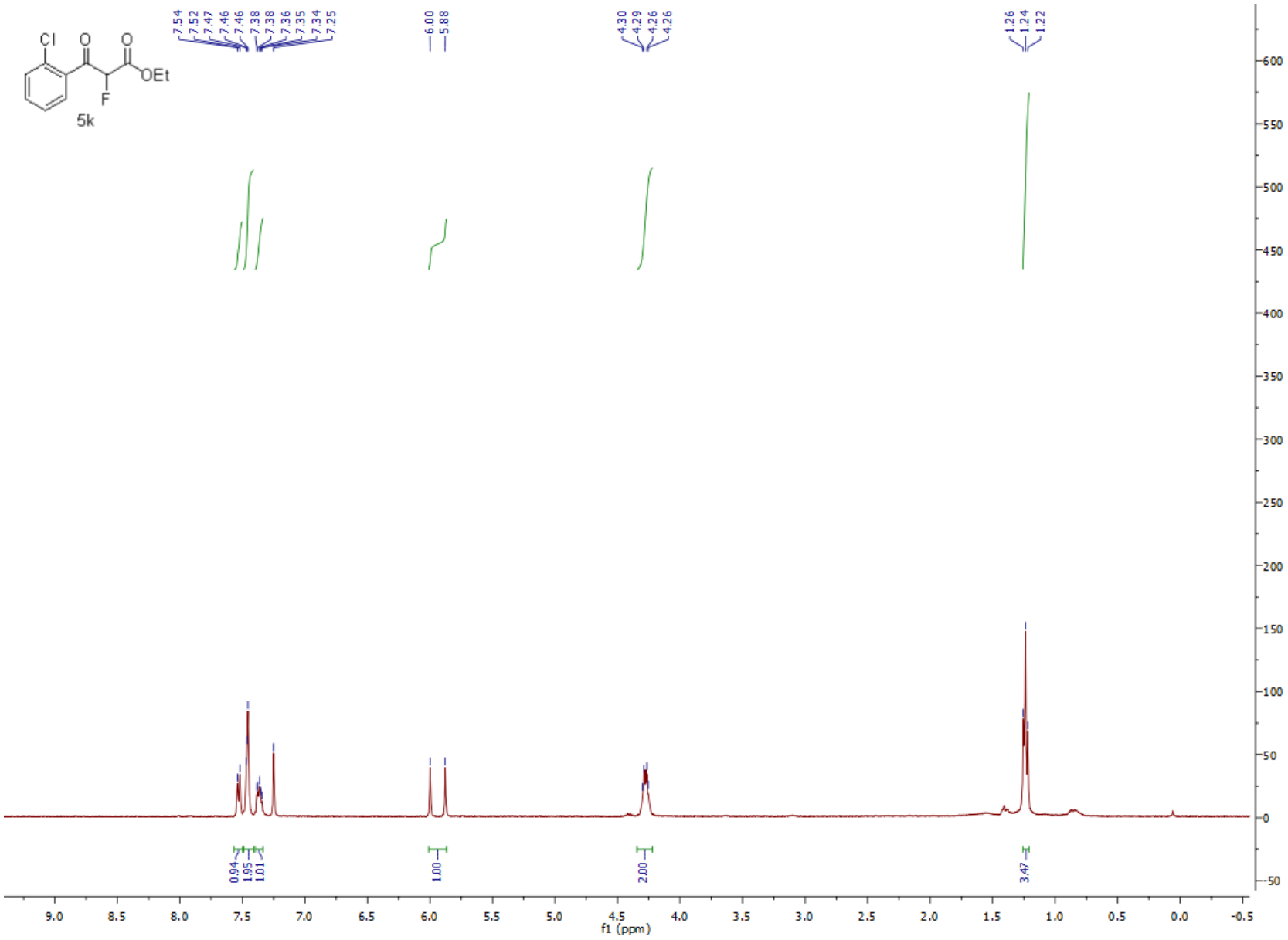

O
O
OEt
F
F
5i
-106.01
-189.63
-189.76
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

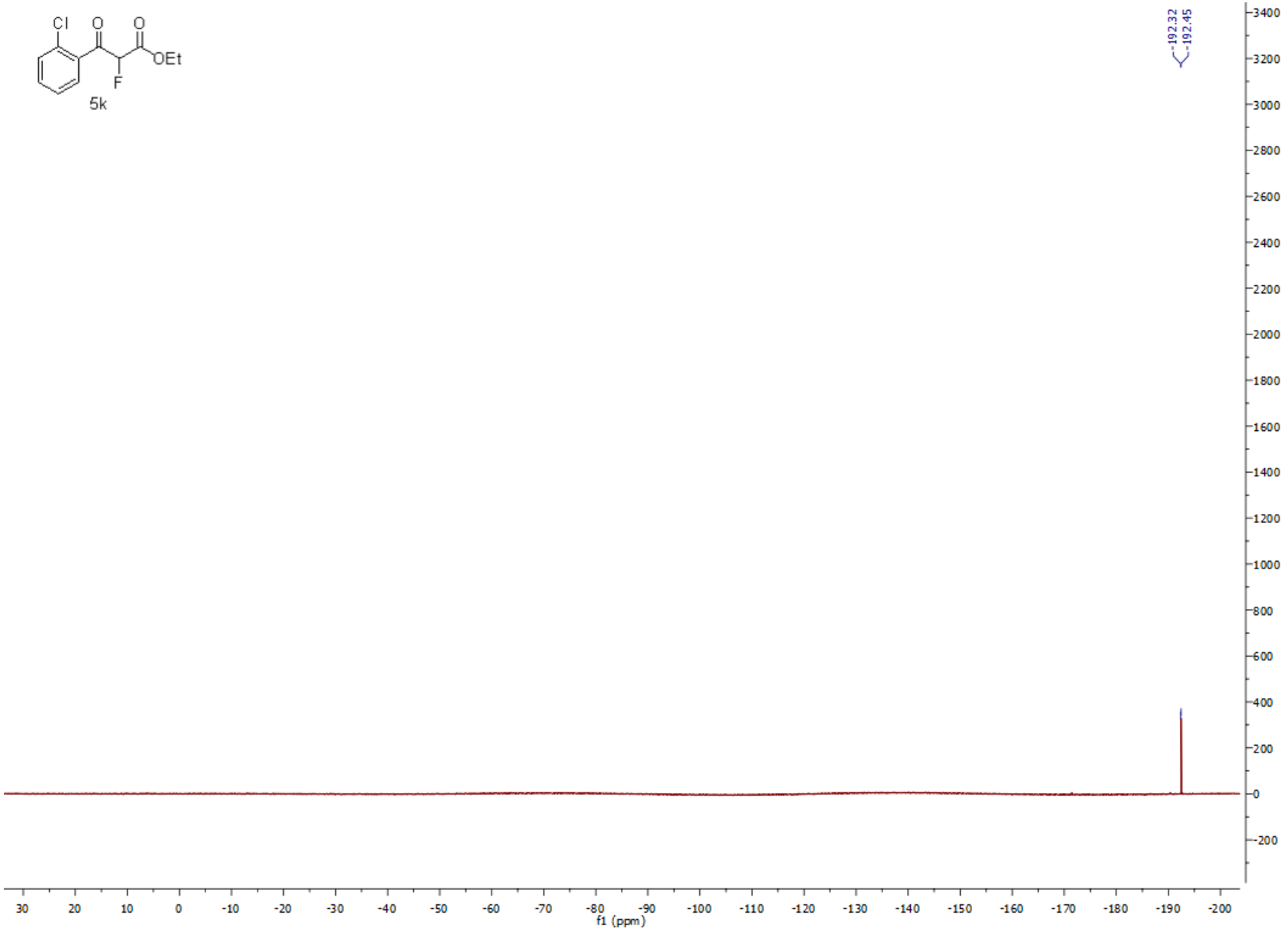

188.27
188.06
166.44
164.97
164.73
163.88
133.41
133.38
129.83
129.79
129.73
129.69
129.45
126.08
125.90
115.72
115.49
91.12
89.14
62.70
14.50
13.92
O
O
OEt
F
F
5i
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

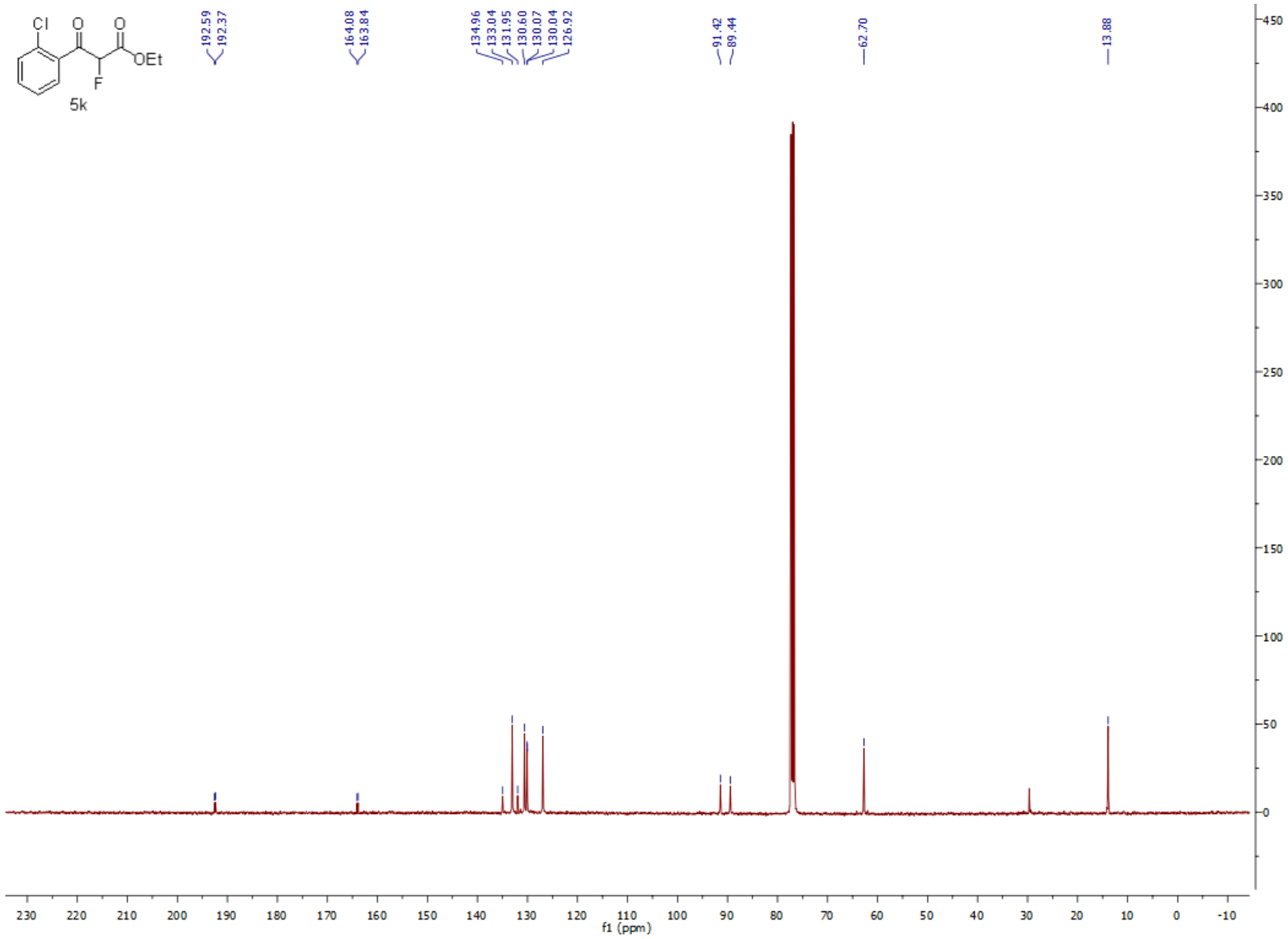

Cl
O
O
OEt
F
5j
8.00
7.93
7.91
7.61
7.59
7.46
7.44
7.42
5.87
5.75
4.32
4.31
4.30
4.29
1.28
1.27
1.26
1.25
0.93
1.00
1.01
1.11
1.00
1.99
3.28
f1 (ppm)

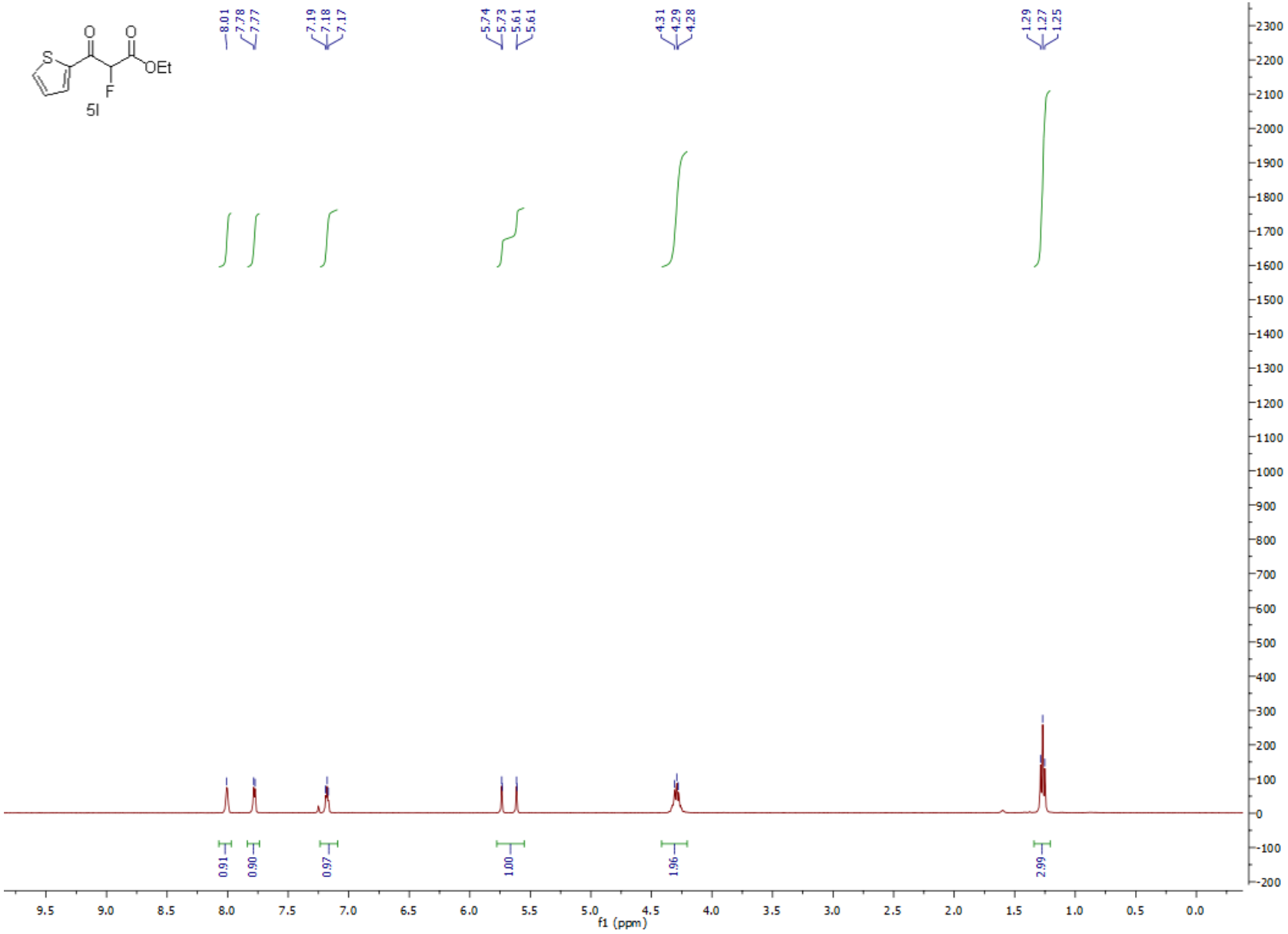

Cl
O
O
OEt
F
5j
-190.29
-190.42
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

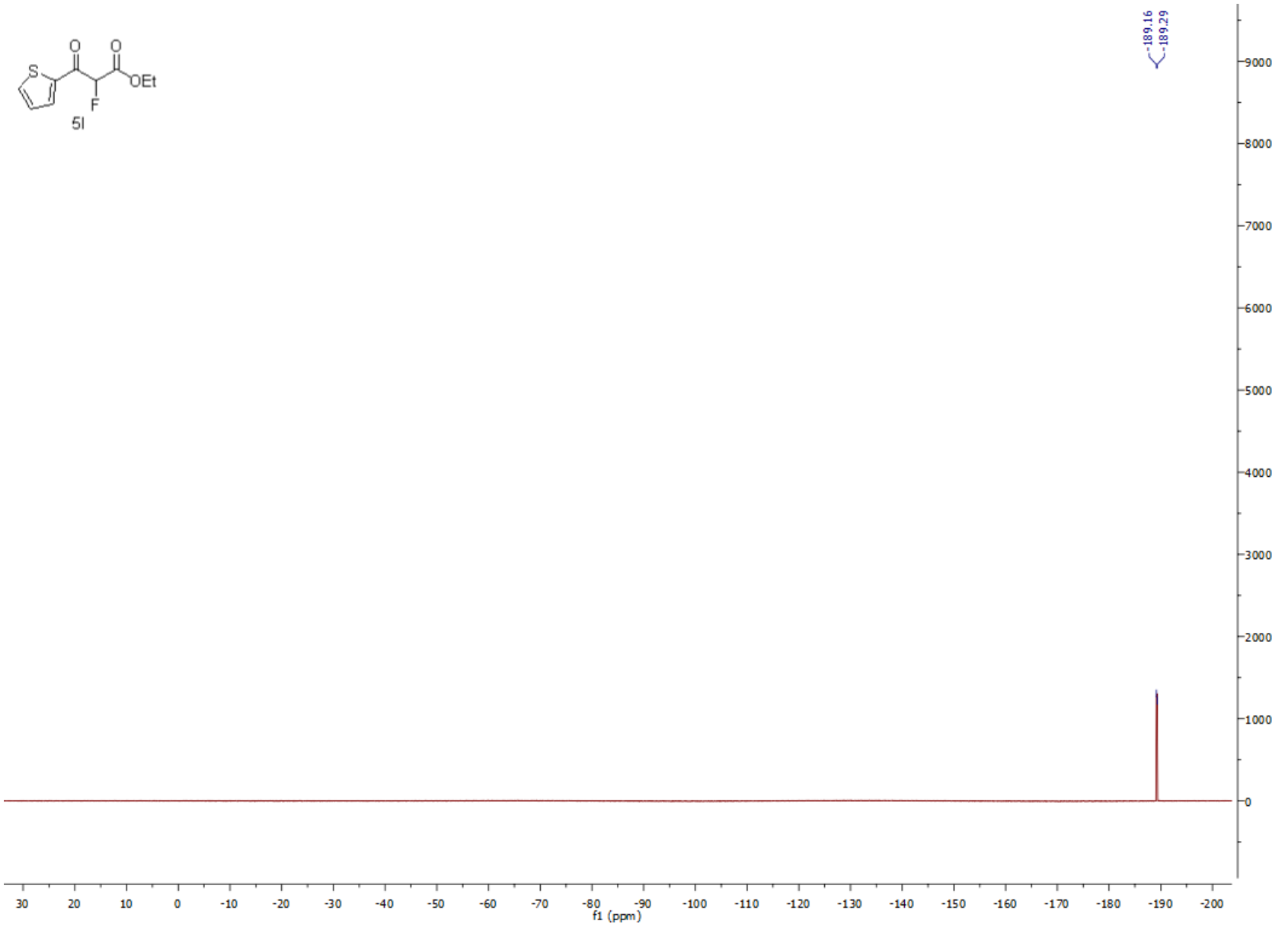

Cl
O
O
OEt
F
5j
188.56
188.35
164.60
164.36
135.21
134.77
134.42
130.11
129.42
129.39
127.64
127.60
91.07
89.08
62.87
13.92
f1 (ppm)

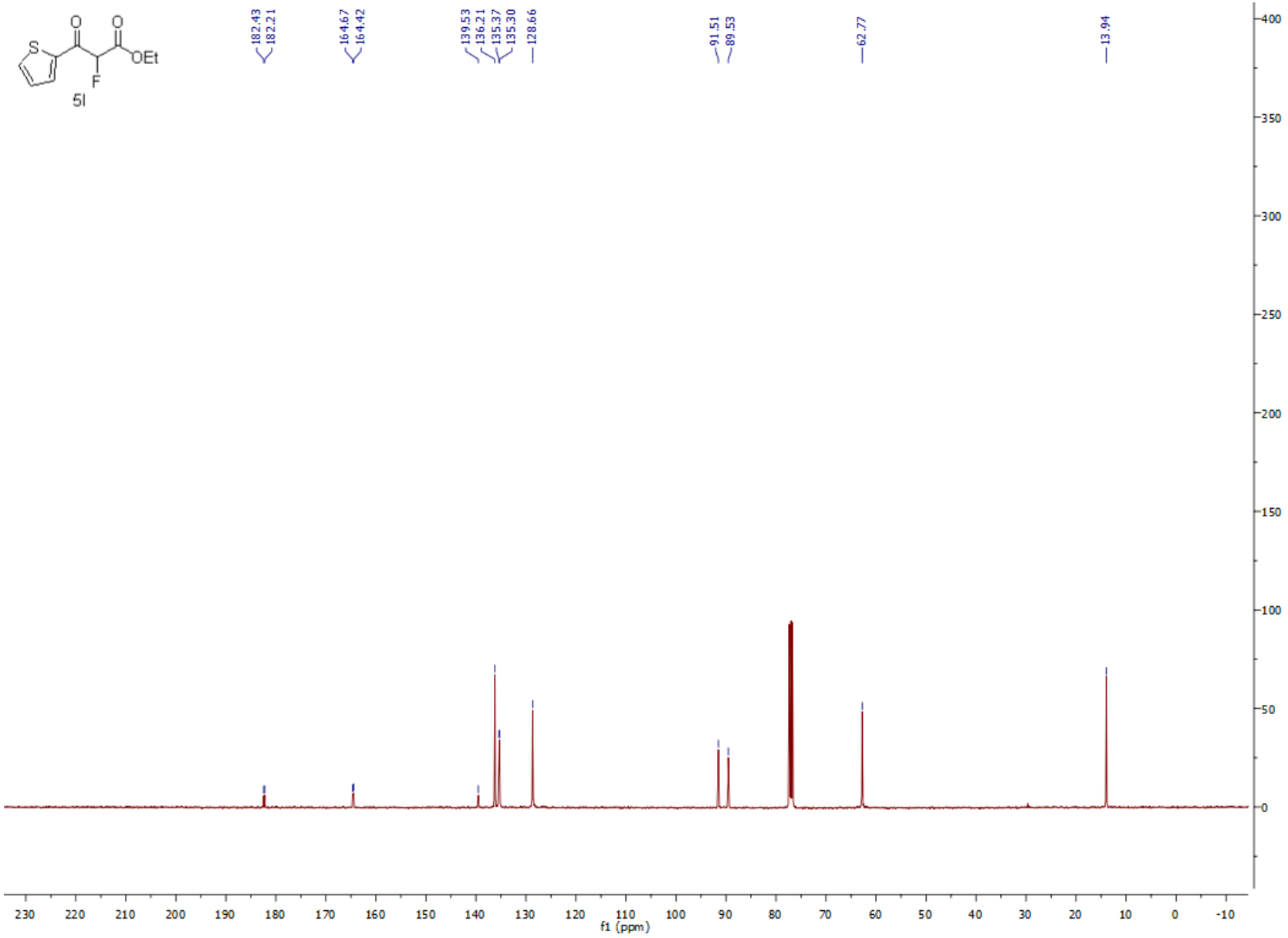

Cl
O
O
OEt
F
5k
7.54
7.52
7.47
7.46
7.46
7.38
7.38
7.36
7.35
7.34
7.25
6.00
5.88
4.30
4.29
4.26
4.26
1.26
1.24
1.22
0.94
1.95
1.01
1.00
2.00
3.47
f1 (ppm)

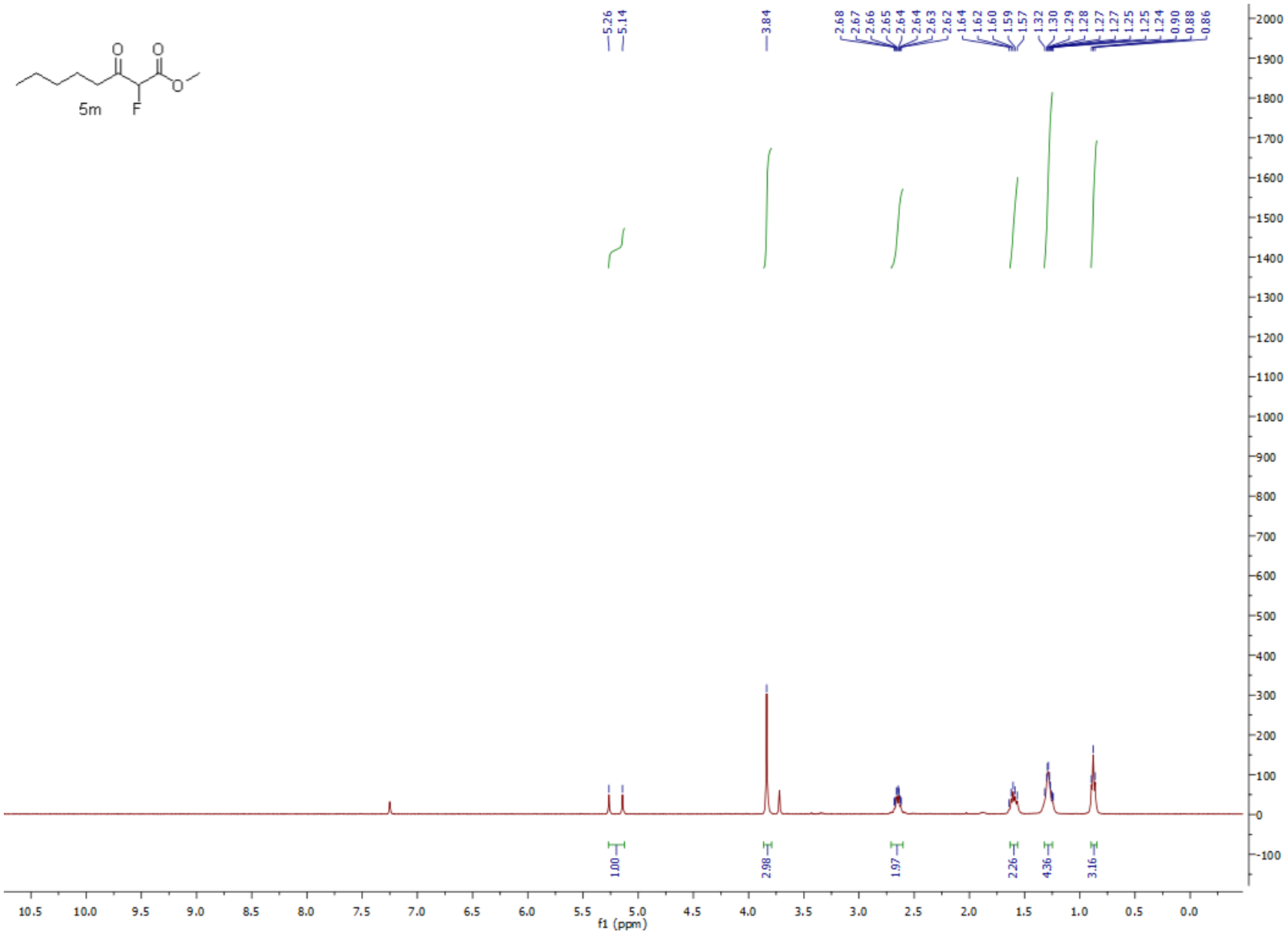

Cl
O
O
OEt
F
5k
-192.32
-192.45
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

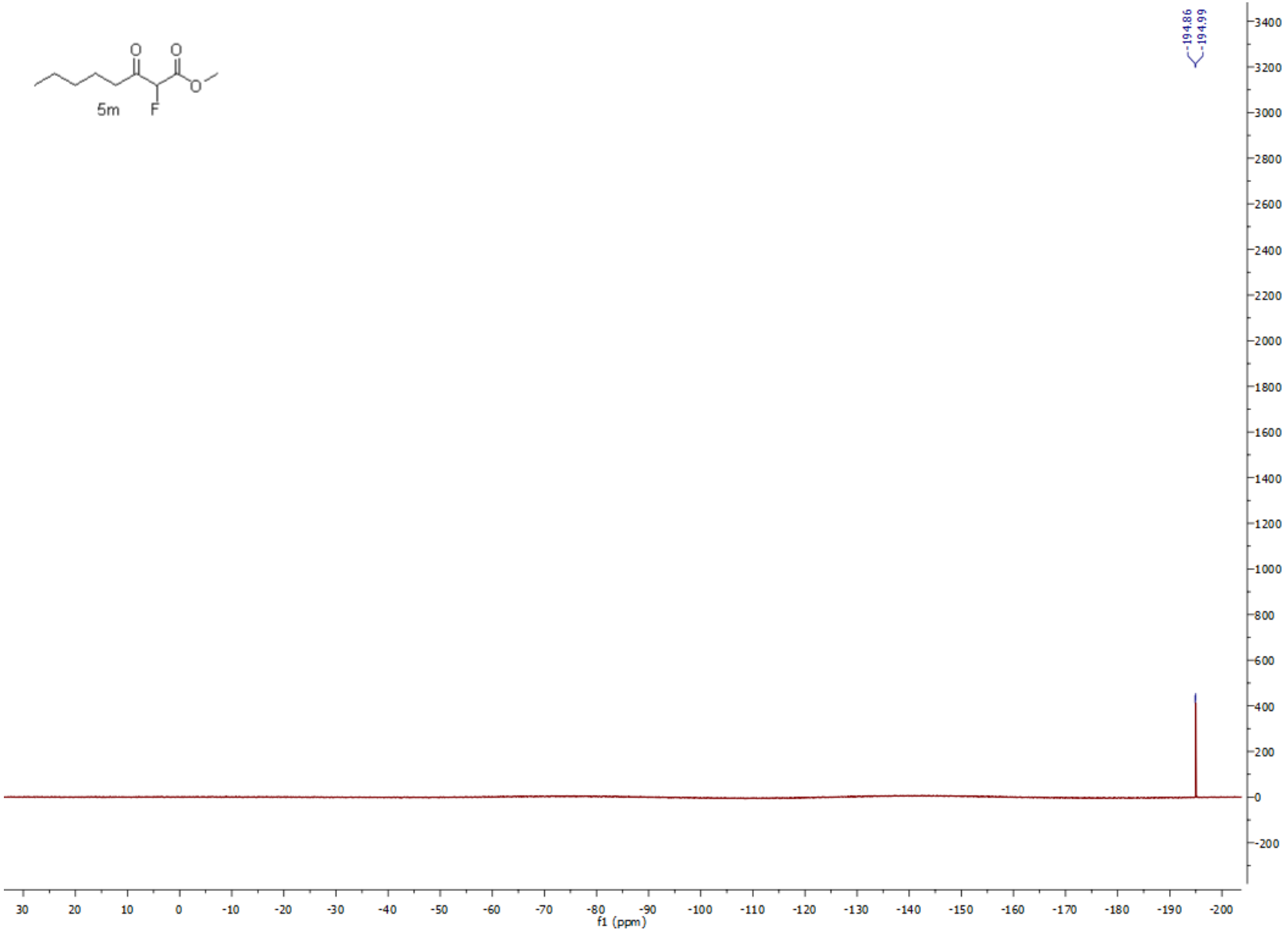

Cl
O
O
OEt
F
5k
192.59
192.37
164.08
163.84
134.96
133.04
131.95
130.60
130.07
130.04
126.92
91.42
89.44
62.70
13.88
f1 (ppm)

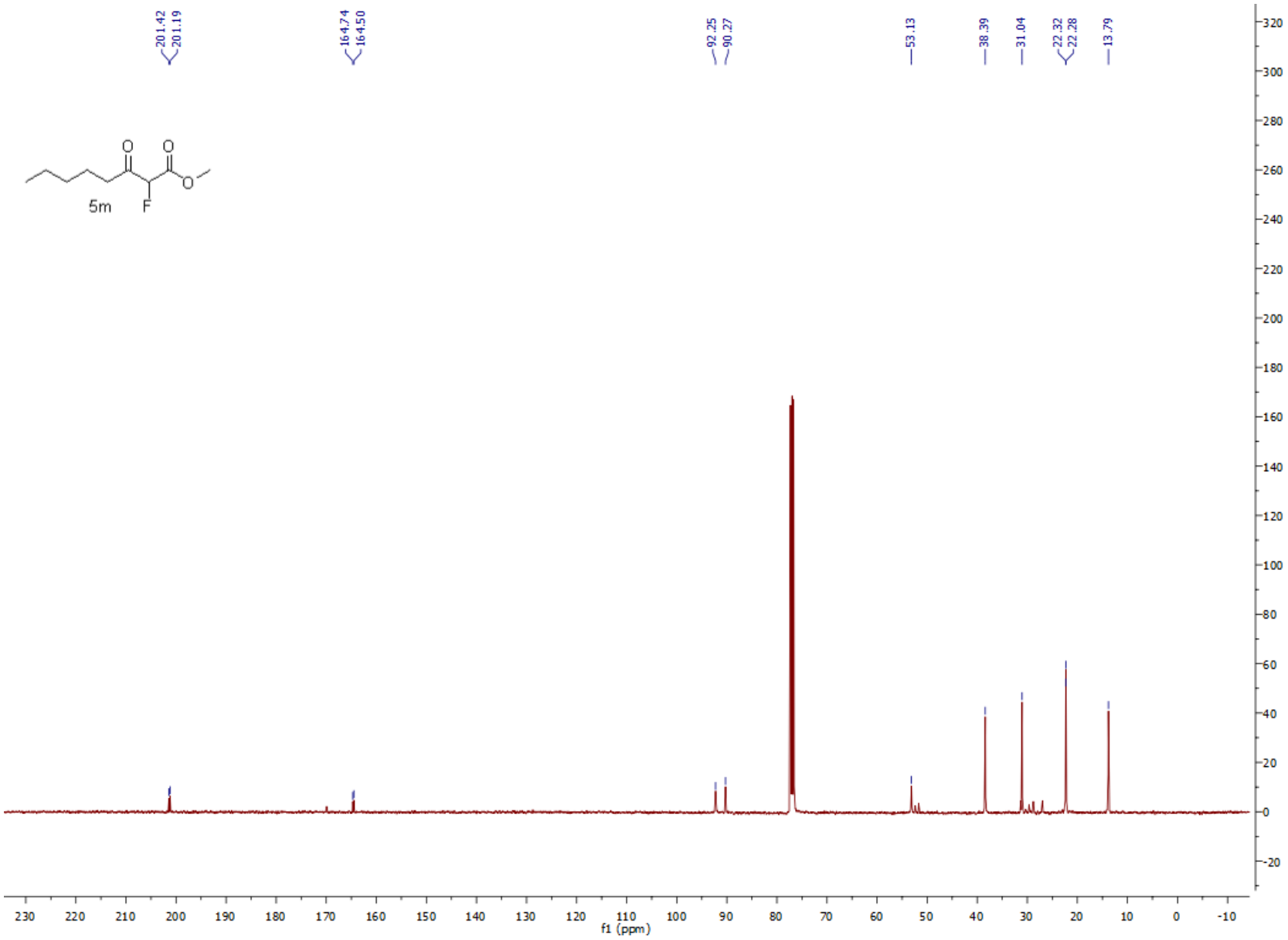

8.01
7.78
7.77
7.19
7.18
7.17
5.74
5.73
5.61
5.61
4.31
4.29
4.28
1.29
1.27
1.25
O
O
S
OEt
F
5l
0.91
0.90
0.97
1.00
1.96
2.99
f1 (ppm)

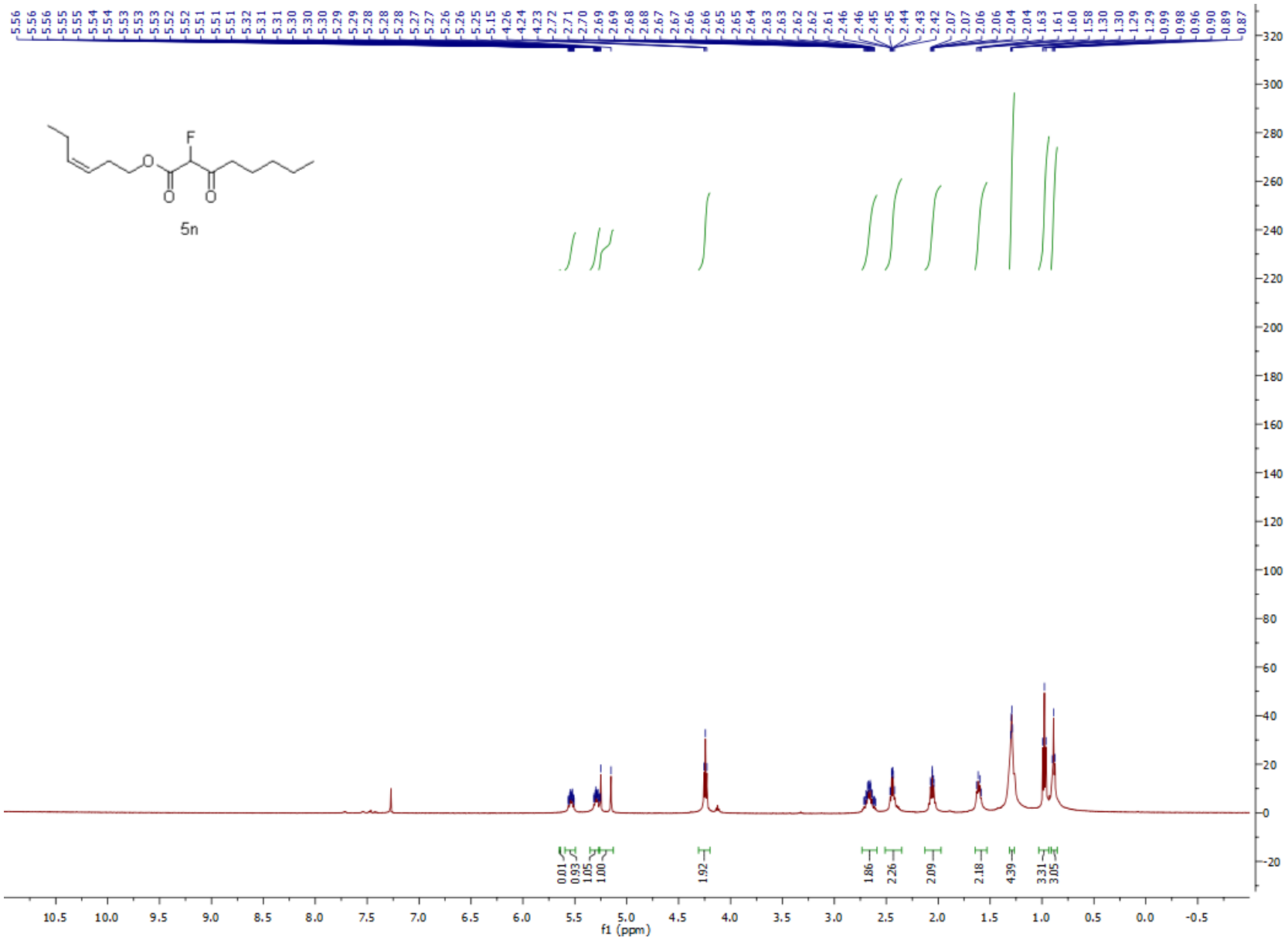

O
O
S
OEt
F
5l
-189.16
-189.29
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

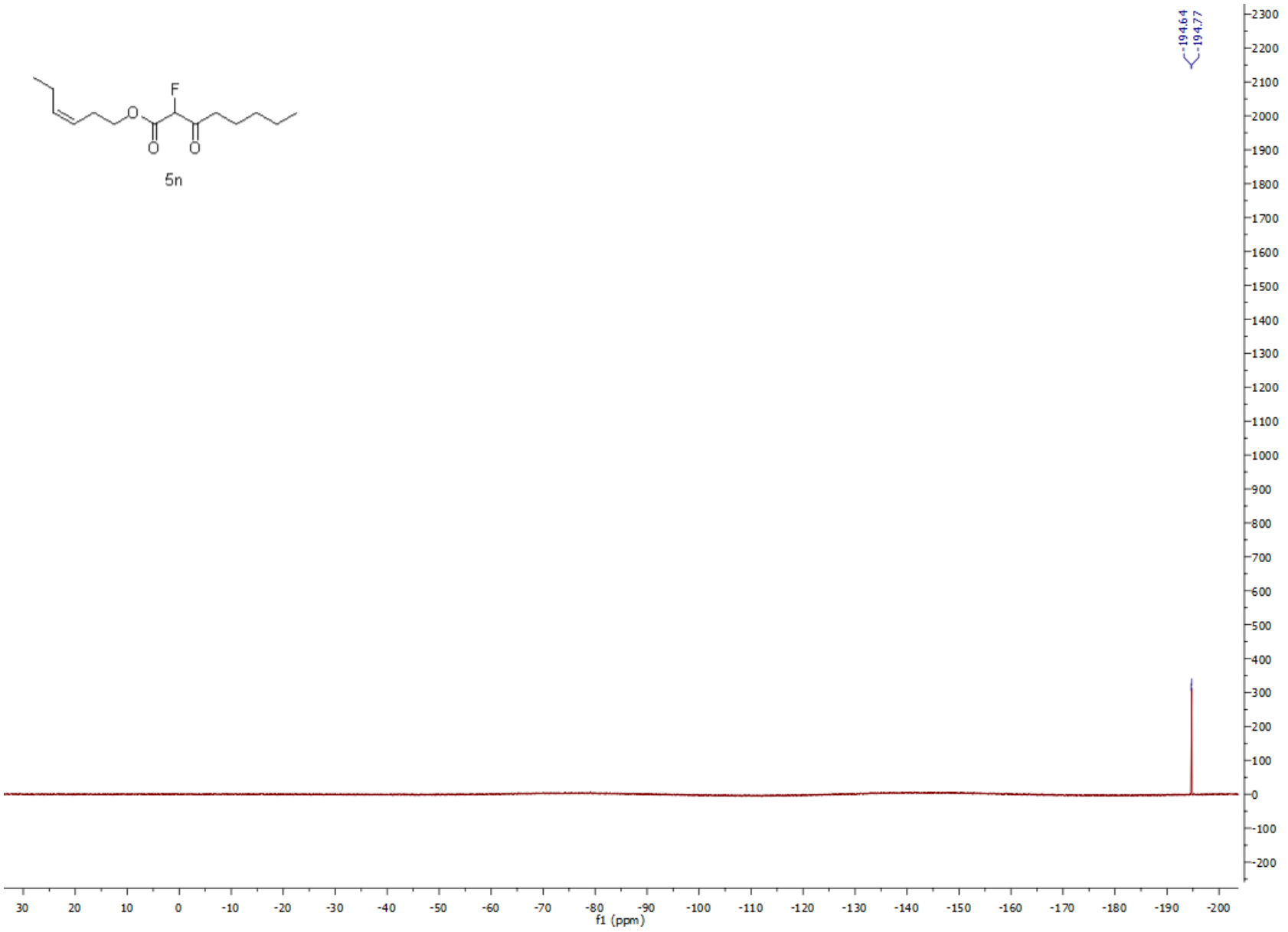

O
O
S
OEt
F
5l
182.43
182.21
164.67
164.42
139.53
136.21
135.37
135.30
128.66
91.51
89.53
62.77
13.94
400
350
300
250
200
150
100
50
0
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

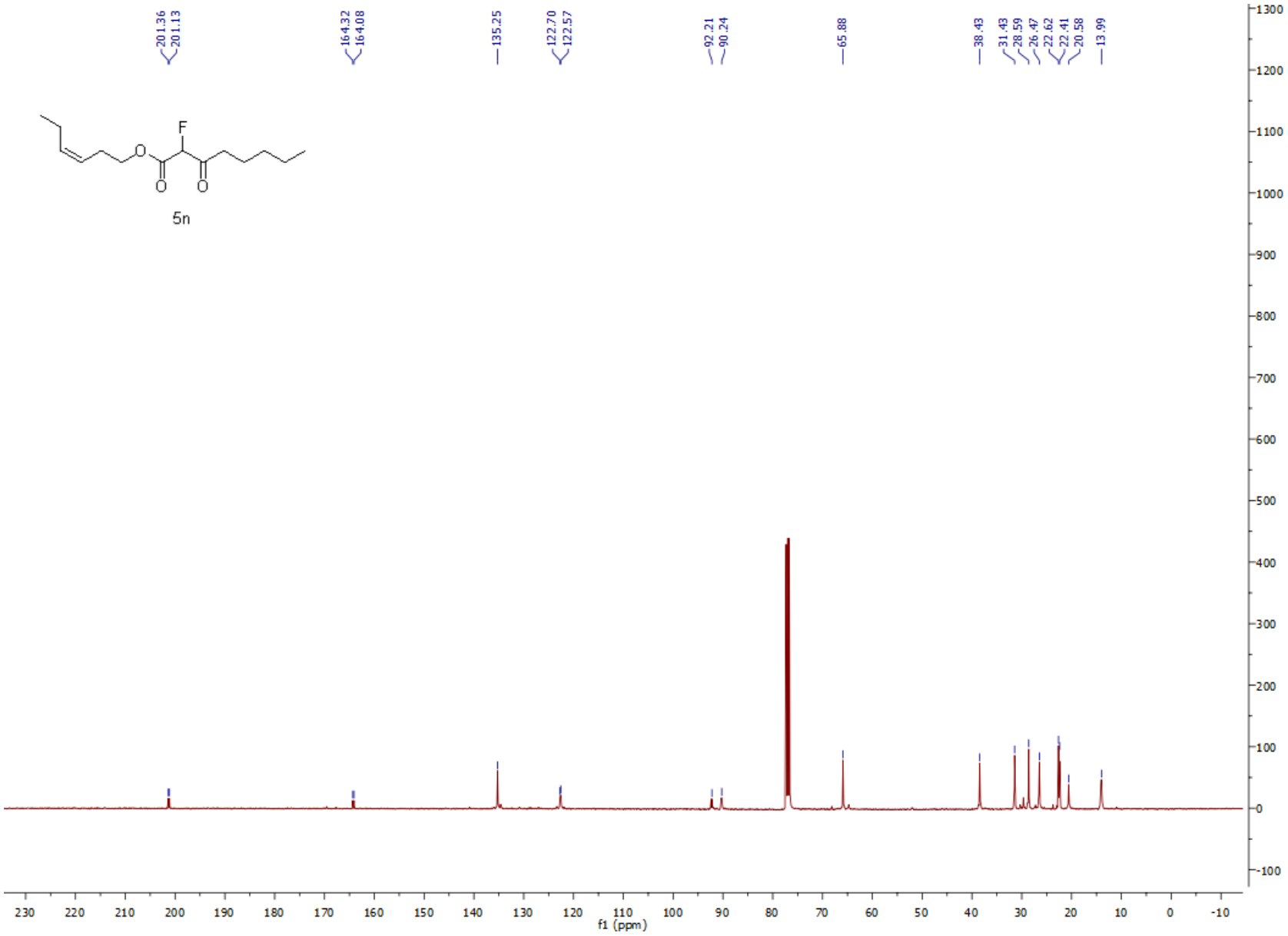

5m
F
5.26
5.14
3.84
2.68
2.67
2.66
2.65
2.64
2.64
2.63
2.62
1.64
1.62
1.60
1.59
1.57
1.32
1.30
1.29
1.28
1.27
1.27
1.25
1.25
1.24
0.90
0.88
0.86
1.00
2.98
1.97
2.26
4.36
3.16
f1 (ppm)

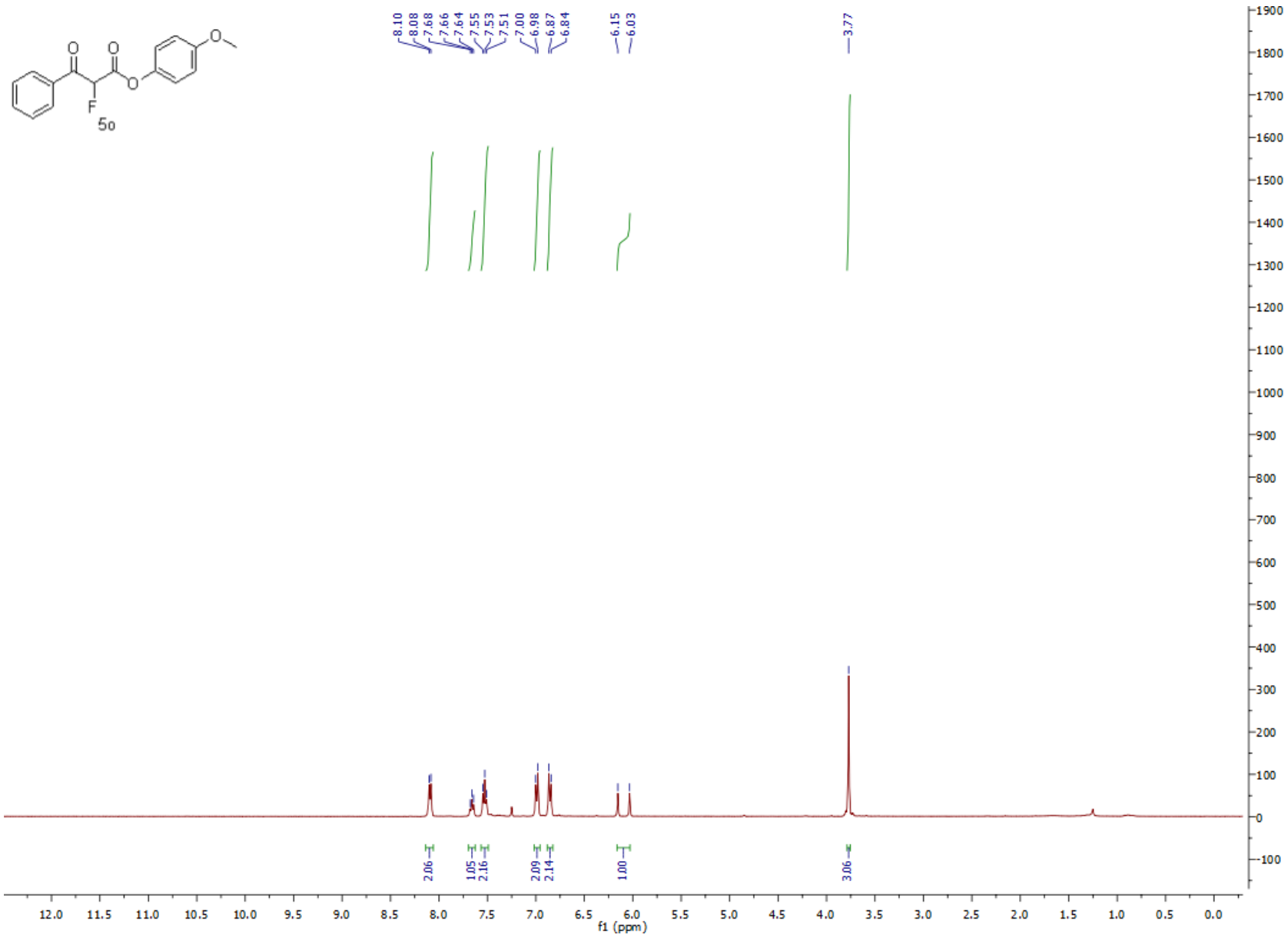

5m
F
-194.86
-194.99
f1 (ppm)


201.42
201.19
164.74
164.50
92.25
90.27
53.13
38.39
31.04
22.32
22.28
13.79
O
O
O
F
5m
f1 (ppm)


F
O
O
O
5n
f1 (ppm)


F
O
O
O
5n
-194.64
-194.77
f1 (ppm)


201.36
201.13
164.32
164.08
135.25
122.70
122.57
92.21
90.24
65.88
38.43
31.43
28.59
26.47
22.62
22.41
20.58
13.99
F
O
O
O
5n
f1 (ppm)


5o
8.10
8.08
7.68
7.66
7.64
7.55
7.53
7.51
7.00
6.98
6.87
6.84
6.15
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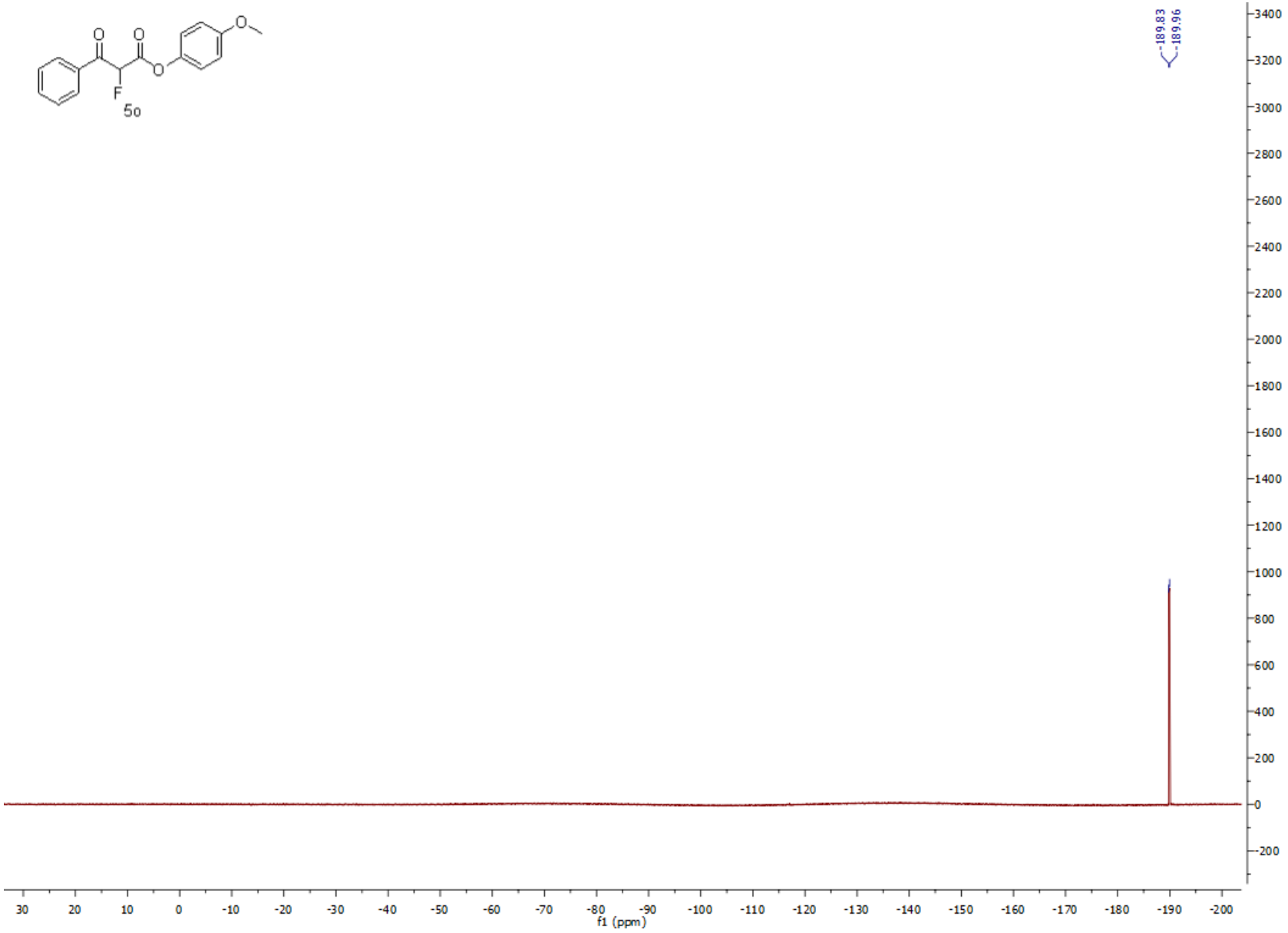
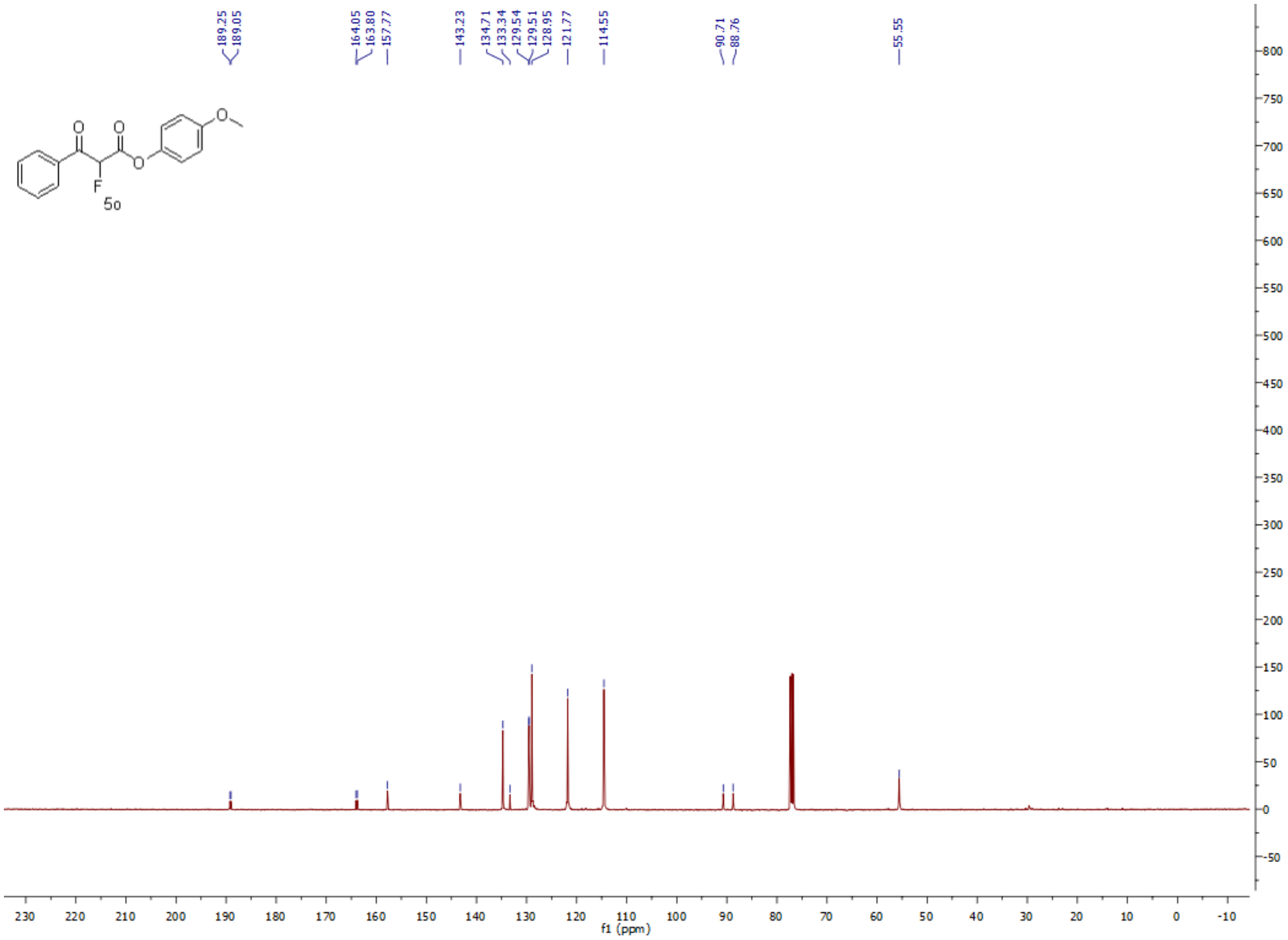
3.77
2.06
1.05
2.16
2.09
2.14
1.00
3.06
f1 (ppm)


5o
-189.83
-189.96
f1 (ppm)


189.25
189.05
164.05
163.80
157.77
143.23
134.71
133.34
129.54
129.51
128.95
121.77
114.55
90.71
88.76
55.55
O
O
O
O
F
5o
f1 (ppm)

6. References

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