Palladium-Catalyzed Enantioselective Csp^3–Csp^3 Cross-Coupling for the Synthesis of (Poly)fluorinated Chiral Building Blocks

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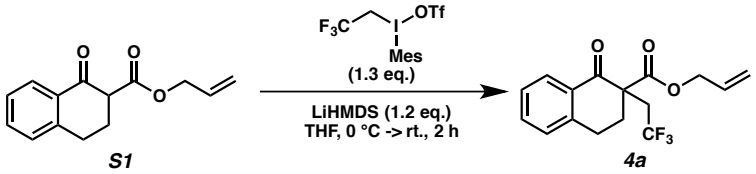
Table of Contents

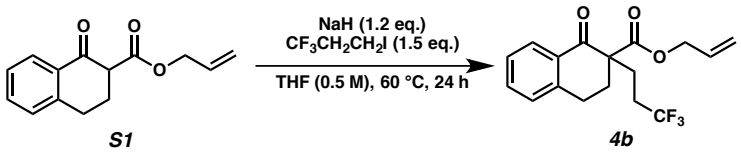
Materials and Methods

Unless stated otherwise, reactions were performed in flame-dried or oven-dried glassware under an argon or nitrogen atmosphere using dry, deoxygenated solvents (distilled or passed over a column of activated alumina).[1] Commercially obtained reagents were used as received with the exception of dipalladium tris(dibenzylideneacetone) ($Pd_2(dba)_3$), tetrakis(triphenylphosphine)palladium(0), which were stored in a nitrogen-filled glovebox. Dipalladium tris(para-methoxydibenzylideneacetone) ($Pd_2(pmdba)_3$),[2] (*S*)-*t*-BuPHOX,[3] (*S*)-$(CF_3)_3$-*t*BuPHOX,[4] were prepared by known methods. Reactions requiring external heat were modulated to the specified temperatures using an IKAmag temperature controller. Reaction progress was monitored by thin-layer chromatography (TLC), which was performed using E. Merck silica gel 60 F254 precoated glass plates (0.25 mm) and visualized by UV fluorescence quenching, potassium permanganate, or *p*-anisaldehyde staining. Silicycle SiliaFlash® P60 Academic Silica gel (particle size 40-63 nm) was used for column chromatography. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Inova 500 (500 MHz and 126 MHz, respectively), and a Bruker AV III HD spectrometer equipped with a Prodigy liquid nitrogen temperature cryoprobe (400 MHz and 101 MHz, respectively) and are reported in terms of chemical shift relative to $CHCl_3$ (δ 7.26 and δ 77.16, respectively). ^{19}F NMR spectra were recorded on a Varian Inova 300 spectrometer (282 MHz) and are reported in terms of absolute chemical shift according to IUPAC standard recommendations from $CFCl_3$. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br s = broad singlet, app t = apparently triplet. Infrared (IR) spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer using thin films deposited on NaCl plates and are reported in frequency of absorption (cm^{-1}). Optical rotations were measured with a Jasco P-2000 polarimeter operating on the sodium D-line (589 nm), using a 100 mm path-length cell and are reported as: $[\alpha]^D_T$ (concentration in g/100 mL, solvent). Analytical SFC was performed with a Mettler SFC supercritical CO_2 analytical chromatography system utilizing Chiralpak (AD-H, AS-H, IC) or Chiralcel (OD-H, OJ-H) columns (4.6 mm x 25 cm) obtained from Daicel Chemical Industries, Ltd. High resolution mass spectra were obtained from the Caltech Mass Spectral Facility using a JEOL JMS-600H. High Resolution Mass Spectrometer in fast atom bombardment (FAB+) ionization mode or a Agilent 6200 Series TOF with an Agilent G1978A Multimode source in electrospray ionization (ESI+), atmospheric pressure chemical ionization (APCI+), or mixed (ESI/APCI) ionization mode. Julabo Presto LH45 was used to control reaction temperatures inside the nitrogen-filled glovebox.



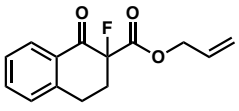
Allyl 1-oxo-2-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (4a): To a solution of **S1**[5] (780 mg, 3.39 mmol, 1.0 equiv) in THF (10 mL) was added LiHMDS (2M solution in THF, 4.0 mmol, 1.2 equiv) at 0 °C, the resulting solution was allowed to stir at room temperature for 15 min. Then the mixture was cooled again to 0 °C, followed an addition of a THF solution (7 mL) of mesityl(2,2,2-trifluoroethyl)-λ^3-iodanyl trifluoromethanesulfonate[6] (2.1 g, 4.4 mmol, 1.3 equiv). After 2 hours stirring at room temperature, the mixture was quenched with aqueous solution of NH_4Cl, extracted with Et_2O, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude oil was purified by column chromatography (SiO_2, 5% EtOAc in hexane) to afford ketoester **4a** (570 mg, 54% yield) as a white solid; R_f = 0.43 (10:1 Hexane:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.50 (app td, *J* = 7.5, 1.5 Hz, 1H), 7.33 (app t, *J* = 7.7 Hz, 1H), 7.24 (d, *J* = 7.7 Hz, 1H), 5.82 – 5.74 (m, 1H),

5.20 – 5.13 (m, 2H), 4.66 – 4.54 (m, 2H), 3.26 – 3.16 (m, 1H), 3.10 – 3.00 (m, 1H), 2.98 – 2.91 (m, 2H), 2.74 (dt, J = 14.0, 4.3 Hz, 1H), 2.35 – 2.30 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.29, 169.54, 143.06, 134.14, 131.25, 131.05, 128.94, 128.54, 127.08, 126.02 (q, $J_{C\text{-}F}$ = 278.5 Hz, 1C), 118.94, 66.58, 54.70 (q, $J_{C\text{-}F}$ = 1.8 Hz, 1C), 37.35 (q, $J_{C\text{-}F}$ = 29.3 Hz, 1C), 29.74 (q, $J_{C\text{-}F}$ = 1.7 Hz, 1C), 25.83. ^{19}F NMR (282 MHz, $CDCl_3$) δ -59.46 (t, J = 11.1 Hz, 3F). IR (thin film, NaCl) 1737, 1693, 1601, 1260, 1134 cm $^{-1}$. HRMS (APCI/ESI) m/z calc'd for $C_{16}H_{16}F_3O_3$ $[M+H]^+$: 313.1046, found: 313.1044.

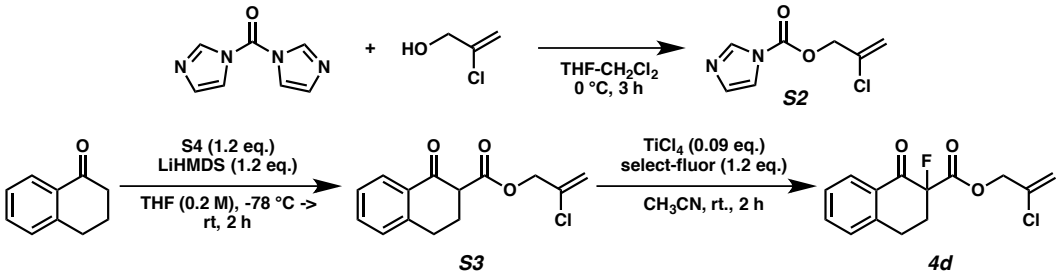


S1 *4b*

Allyl 1-oxo-2-(3,3,3-trifluoropropyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (4b): To a suspension of NaH (60% in oil, 72 mg, 1.8 mmol, 1.2 equiv) in THF (2 mL) was added a THF solution of **S1** (345 mg, 1.5 mmol, 1.0 equiv), the mixture was allowed to stir at room temperature for 15 minutes followed the addition of 1,1,1-trifluoro-3-iodopropane. The resulting mixture was allowed to heat at 60 °C for 24 hours. After cooling to room temperature, quenched with aqueous solution of NH_4Cl, extracted with Et_2O, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude oil was purified by column chromatography (SiO_2, 10% Et_2O in hexane) to afford ester **4b** (148 mg, 30% yield) as a colorless oil; R_f = 0.43 (10:1 Hexane:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (dd, J = 7.9, 1.4 Hz, 1H), 7.49 (app td, J = 7.5, 1.5 Hz, 1H), 7.33 (dd, J = 7.9 Hz, 1H), 7.23 (d, J = 7.6 Hz, 1H), 5.79 (ddt, J = 17.6, 10.1, 5.6 Hz, 1H), 5.26 – 5.09 (m, 2H), 4.70 – 4.51 (m, 2H), 3.14 – 3.05 (m, 1H), 2.96 (dt, J = 17.4, 5.0 Hz, 1H), 2.59 (dt, J = 13.6, 4.9 Hz, 1H), 2.47 – 2.30 (m, 1H), 2.28 – 2.06 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.82, 171.10, 142.74, 133.93, 131.89, 131.25, 128.89, 128.17, 127.13, 127.09 (q, $J_{C\text{-}F}$ = 277.4 Hz, 1C), 118.87, 66.08, 56.26, 31.62, 29.80 (q, $J_{C\text{-}F}$ = 29.1 Hz, 1C), 26.67 (q, $J_{C\text{-}F}$ = 3.2 Hz, 1C), 25.90. ^{19}F NMR (282 MHz, $CDCl_3$) δ -66.78 (t, J = 11.1 Hz, 3F). IR (thin film, NaCl) 1735, 1670, 1602, 1258, 1228 cm^{-1}. HRMS (APCI/ESI) m/z calc'd for $C_{17}H_{18}F_3O_3$ $[M+H]^+$: 327.1203, found: 327.1204.


4c

Allyl 2-fluoro-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (4c): The title compound **4c** was synthesized according to the known method as describe. All spectroscopic data were in agreement with the literature.[7] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, J = 7.9 Hz, 1H), 7.55 (app td, J = 7.5, 1.4 Hz, 1H), 7.36 (m, 1H), 7.28 (d, J = 7.8 Hz, 1H), 5.91 – 5.82 (m, 1H), 5.30 – 5.22 (m, 2H), 4.76 – 4.68 (m, 2H), 3.19 (dt, J = 17.2, 5.2 Hz, 1H), 3.08 (ddd, J = 17.1, 7.8, 5.0 Hz, 1H), 2.79 – 2.70 (m, 1H), 2.60 – 2.52 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.51 (d, $J_{C\text{-}F}$ = 19.0 Hz, 1C), 167.05 (d, $J_{C\text{-}F}$ = 25.9 Hz, 1C), 143.17, 134.66, 130.81, 130.47, 128.84, 128.37 (d, $J_{C\text{-}F}$ = 0.94 Hz, 1C), 127.29, 119.12, 93.25 (d, $J_{C\text{-}F}$ = 194.2 Hz, 1C), 66.56, 31.87 (d, $J_{C\text{-}F}$ = 22.6 Hz, 1C), 24.83 (d, $J_{C\text{-}F}$ = 7.24 Hz, 1C). ^{19}F NMR (282 MHz, $CDCl_3$) δ -164.16 (ddd, J = 22.8, 11.0, 1.2 Hz, 1F).

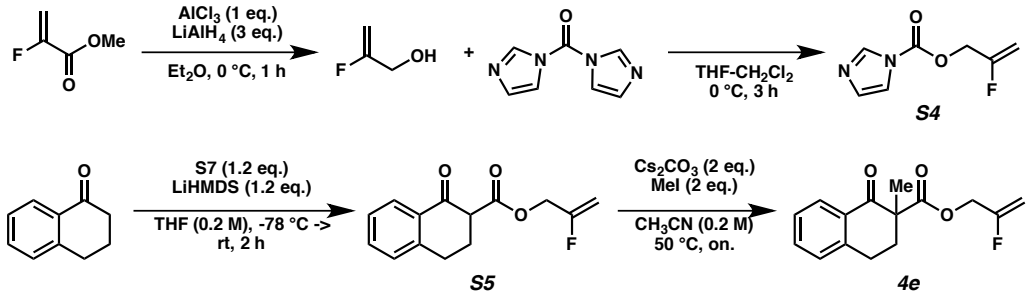


To the mixture of 1,1-carbonyldiimidazole (**CDI)** (4.86 g, 30 mmol) and THF (15 mL) was added a solution of 2-chloro allyl alcohol (20 mmol) in 15 mL of CH_2Cl_2 at 0 °C slowly, the resulting mixture was allowed to stir for 3 h at the same temperature. Most solvent was removed in vacuo and the crude product was purified by column chromatography (SiO_2, 35% EtOAc in hexane) to afford **2-chloroallyloxycarbonyl imidazole (S2)** (3.2 g, 86% yield) as a white solid; R_f = 0.15 (3:1 Hexane:EtOAC); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (m, 1H), 7.46 (m, 1H), 7.10 (dd, *J* = 1.6, 0.8 Hz, 1H), 5.61 (dt, *J* = 2.1, 1.0 Hz, 1H), 5.55 (d, *J* = 2.0 Hz, 1H), 4.97 (dd, *J* = 1.1, 0.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.11, 137.27, 134.40, 131.05, 117.35, 117.24, 69.30. IR (thin film, NaCl) 3137, 3122, 1755, 1650, 892, 758 cm^{-1}. HRMS (APCI/ESI) m/z calc'd for $C_7H_8ClN_2O_2$ $[M+H]^+$: 187.0269, found: 187.0265.

To a solution of Tetralone (585 mg, 4 mmol, 1.0 equiv) in THF (8 mL) was added LiHMDS (2M solution in THF, 4.4 mmol, 1.1 equiv) at -78 °C, the resulting solution was allowed to stir at the same temperature for 15 min. Then a THF solution (7 mL) of **2-chloroallyloxycarbonyl imidazole (S2)** (896 mg, 4.8 mmol, 1.2 equiv) was added. After 2 hours stirring at room temperature, the mixture was quenched with aqueous solution of NH_4Cl, extracted with Et_2O, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude oil was purified by column chromatography (SiO_2, 5% EtOAc in hexane) to afford **S3** (718 mg, 67% yield) as a light yellow oil; R_f = 0.41 (10:1 Hexane:EtOAc); Mixture of enol ketone form (3/2). ^{1}H NMR (500 MHz, $CDCl_3$): for enol form: δ 12.22 (s, 0.6H), 7.81 (dd, *J* = 7.6, 1.4 Hz, 0.6H), 7.36 – 7.25 (m, 1.2H), 7.20 – 7.18 (m, 0.6H), 5.70 – 5.37 (m, 1.2H), 4.77 – 4.72 (m, 1.2H), 2.85 (dd, *J* = 8.8, 6.7 Hz, 1.2H), 2.64 (dd, *J* = 8.8, 6.6 Hz, 1.2H); for ketone form δ 8.05 (dd, *J* = 7.9, 1.4 Hz, 0.4H), 7.51 (app td, *J* = 7.5, 1.5 Hz, 0.4H), 7.36 – 7.25 (m, 0.4H), 5.67 – 5.37 (m, 0.8H), 4.80 (s, 0.8H), 3.70 (dd, *J* = 10.8, 4.7 Hz, 0.4H), 3.29 – 2.93 (m, 0.8H), 2.55 (dddd, *J* = 13.4, 10.9, 9.6, 5.0 Hz, 0.4H), 2.48 – 2.36 (m, 0.4H). ^{13}C NMR (101 MHz, $CDCl_3$): for enol form: δ 169.44, 166.16, 139.61, 135.95, 130.94, 129.81, 128.95, 127.59, 126.73, 114.82, 96.44, 65.84, 27.78, 26.47; for ketone form: ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.86, 171.65, 143.67, 135.29, 134.13, 131.71, 127.84, 127.07, 124.57, 115.07, 66.40, 54.60, 27.75, 20.50. IR (thin film, NaCl) 1750, 1686, 1651, 1617, 1597, 1569, 1266, 1212, 1132, 1085 cm^{-1}. HRMS (APCI/ESI) m/z calc'd for $C_{14}H_{14}ClO_2$ $[M+H]^+$: 265.0626, found: 265.0627.

Neat $TiCl_4$ (10 μL, 0.09 mmol, 0.09 equiv) was added to a solution of **S3** (265 mg, 1.0 mmol, 1.0 equiv) in CH_3CN (5 mL), resulting in an immediate color change from pale yellow to dark orange-brown. After 5 min, Selectfluor (425 mg, 1.2 mmol, 1.2 equiv) was added in one portion. The mixture was stirred vigorously at room temperature for 2 h, during which time the dark orange-brown color faded to yellow. The reaction was quenched by addition of H_2O, extracted with Et_2O, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude oil was purified by column chromatography (SiO_2, 10% EtOAc in hexane) to afford ester **4d** (217 mg, 77% yield) as a colorless oil;[7] R_f = 0.12 (10:1 Hexane:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.56 (app td, *J* = 7.5, 1.4 Hz, 1H), 7.38 (app t, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 7.7 Hz, 1H), 5.49 – 5.34 (m, 2H), 4.79 (dd, *J* = 13.7, 41.56 Hz, 2H), 3.22 (ddd, *J* = 17.2, 7.7, 5.7 Hz, 1H), 3.11 (ddd, *J* = 17.2, 7.4, 5.0 Hz, 1H), 2.86 – 2.69 (m, 1H), 2.67 – 2.53 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.16 (d, $J_{C\text{-}F}$ = 18.5 Hz), 166.56 (d, $J_{C\text{-}F}$ = 26.8 Hz, 1C), 143.18, 134.78, 134.35, 130.30, 128.88, 128.37 (d, $J_{C\text{-}F}$ = 1.2 Hz, 1C), 127.32, 115.82, 93.22 (d, $J_{C\text{-}F}$ = 194.0 Hz, 1C), 66.96, 31.79 (d, $J_{C\text{-}F}$ = 22.2 Hz, 1C), 24.67 (d, $J_{C\text{-}F}$ = 7.1 Hz, 1C). ^{19}F NMR (282 MHz, $CDCl_3$) δ -164.46 (dd, *J* = 23.7, 11.3 Hz, 1F). IR (thin film, NaCl) 1764, 1701,

1600,1272, 1184, 1084 cm^{-1}. HRMS (APCI/ESI) m/z calc'd for $C_{14}H_{13}ClFO_3$ $[M+H]^+$: 283.0532, found: 283.0530.



The procedure for preparation of 2-fluoroprop-2-en-1-ol was adapted from the work of Herzon and coworkers.[8]

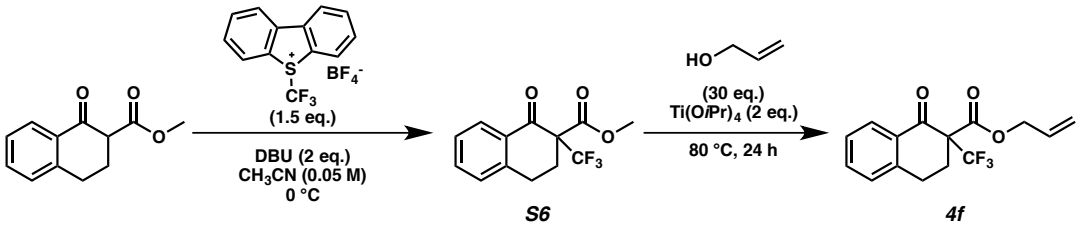
Solid aluminum chloride (1.0 g, 8.78 mmol, 1.0 equiv) was added portion-wise over 10 min to a solution of lithium aluminum hydride (1.17 g, 26.3 mmol, 3.0 equiv) in Et_2O (20 mL) at 0 °C. The resulting mixture was stirred for 30 min at 0 °C. Methyl 2-fluoroacrylate (820 µL, 8.78 mmol, 1.0 equiv) was then added dropwise via syringe to the mixture. The reaction mixture was stirred for 1 h at 0 °C at atmosphere of nitrogen. Distilled water (1.0 mL) and 15% aqueous sodium hydroxide solution (1.0 mL) were then added in sequence dropwise via syringe over 20 min (10 min addition of each reagent). A second portion of distilled water (3.0 mL) was then added dropwise via syringe over 5 min. The resulting mixture was stirred for 10 min at 0 °C. The heterogeneous mixture was filtered through a Buchner funnel, and the filter cake was rinsed with Et_2O (100 mL). The filtrates were combined and and dried over anhydrous $MgSO_4$. The dried solution was filtered and the filtrate was concentrated (150 torr, 0 °C). The product is very volatile, therefore Et_2O was not completely removed. The solution of 2- fluoroallyl alcohol in Et_2O was used directly and immediately in the following step.

To the mixture of 1,1-carbonyldiimidazole (CDI)(1.3 g, 8 mmol) and CH_2Cl_2 (5 mL) was added a solution of 2- fluoroallyl alcohol from last step in Et_2O at 0 °C slowly, the resulting mixture was allowed to stir for 3 h at the same temperature. Most solvent was removed in vacuo and the crude product was purified by column chromatography (SiO_2, 50% EtOAc in hexane) to afford **2-flouroallyloxycarbonyl imidazole (S4)** (1.3 g, 86% yield over two steps) as a white solid; R_f = 0.43 (1:1 Hexane:EtOAC); ^1H NMR (500 MHz, $CDCl_3$) δ 8.16 (m, 1H), 7.44 (dd, *J* = 2.8, 1.4 Hz, 1H), 7.09 (m, 1H), 4.96 (ddd, *J* = 15.1, 3.5, 1.2 Hz, 1H), 4.92 (d, *J* = 15.5 Hz, 2H), 4.79 (dd, *J* = 46.2, 3.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.55 (d, $J_{C\text{-}F}$ = 258.7 Hz, 1C), 148.26, 137.29, 131.05, 117.26, 96.83 (d, $J_{C\text{-}F}$ = 16.9 Hz, 1C), 64.73 (d, $J_{C\text{-}F}$ = 32.7 Hz, 1C). ^{19}F NMR (282 MHz, $CDCl_3$) δ -105.69 – -106.02 (m, 1F). IR (thin film, NaCl) 1766, 1682, 1408, 1384, 1316, 1295, 1242, 1168, 997 cm^{-1}. HRMS (APCI/ESI) m/z calc'd for $C_7H_7FN_2O_2$ $[M+H]^+$: 171.0564, found: 171.0564.

To a solution of Tetralone (585 mg, 4 mmol, 1.0 equiv) in THF (8 mL) was added LiHMDS (2M solution in THF, 4.8 mmol, 1.2 equiv) at -78 °C, the resulting solution was allowed to stir at the same temperature for 15 min. Then a THF solution (7 mL) of **2-fluoroallyloxycarbonyl imidazole (S4)** (817 mg, 4.8 mmol, 1.2 equiv) was added. After 2 hours stirring at room temperature, the mixture was quenched with aqueous solution of NH_4Cl, extracted with Et_2O, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude oil was purified by column chromatography (SiO_2, 10% Et_2O in hexane) to afford **S5** (417 mg, 42% yield) as a light yellow oil; R_f = 0.43 (10:1 Hexane:EtOAc); Mixture of enol ketone form (3/2). ^1H NMR (500 MHz, $CDCl_3$): for enol form: δ 12.22 (s, 0.6H), 7.86 – 7.76 (m, 0.6H), 7.42 – 7.27 (m, 1.2H), 7.22 – 7.15 (m, 0.6H), 4.86 (dd, *J* = 16.0, 3.2 Hz, 0.6H), 4.79 – 4.69 (m, 1.8H), 2.90 – 2.78 (m, 1.2H), 2.69 – 2.57 (m, 1.2H); for ketone form: δ 8.09 – 8.00 (m, 0.4H), 7.51 (dd, *J* = 7.5, 1.5 Hz, 0.4H), 7.38 – 7.28 (m, 0.8H), 4.83 (dd, *J* = 16.3, 3.3 Hz, 0.4H), 4.74 – 4.64 (m, 1.2H), 3.69 (dd, *J* =

11.0, 4.7 Hz, 0.4H), 3.13 – 2.99 (m, 0.8H), 2.57 – 2.49 (m, 0.4H), 2.44 – 2.36 (m, 0.4H). ^{13}C NMR (101 MHz, $CDCl_3$): for enol form δ 169.69, 166.15, 160.39 (d, $J_{C\text{-}F}$ = 257.9 Hz, 0.6C), 139.69, 130.97, 129.87, 128.97, 127.63, 124.62, 96.51, 94.56 (d, $J_{C\text{-}F}$ = 17.1 Hz, 0.6C), 61.31 (d, $J_{C\text{-}F}$ = 34.4 Hz, 0.6C), 27.84, 26.48; for ketone form: δ 192.88, 171.88, 159.94 (d, $J_{C\text{-}F}$ = 257.9 Hz, 0.4C), 143.70, 134.17, 131.75, 127.93, 127.13, 126.77, 94.63 (d, $J_{C\text{-}F}$ = 16.8 Hz, 0.4C), 61.89 (d, J = 34.8 Hz, 0.4C), 54.66, 27.84, 20.55. ^{19}F NMR (282 MHz, $CDCl_3$) δ -105.33 – -105.98 (m, 1F). IR (thin film, NaCl) 1749, 1686, 1651, 1617, 1598, 1569, 1263, 1210, 1198, 1132, 1085 cm^{-1}. HRMS (APCI/ESI) m/z calc'd for $C_{14}H_{14}FO_3$ $[M+H]^+$: 249.0921, found: 249.0923.

The mixture of **S5** (451 mg, 1.81 mmol, 1.0 equiv), cesium carbonate (1.29 g, 3.92 mmol, 2.0 equiv) and MeI (244 mL, 3.92 mmol, 2.0 equiv) in CH_3CN was heated at 50 °C for 12 hours. After cooling, the solution was filtered and concentrated in vacuo. The crude product was purified by column chromatography (SiO_2, 10% Et_2O in hexane) to furnish β-ketoester **4e** (370 mg, 78% yield) as a colorless oil; R_f = 0.28 (10:1 Hexane:EtOAC); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (dd, J = 7.8, 1.4 Hz, 1H), 7.48 (app td, J = 7.5, 1.5 Hz, 1H), 7.32 (app t, J = 7.8 Hz, 1H), 7.23 (d, J = 7.8 Hz, 1H), 4.72 (dd, J = 16.1, 3.3 Hz, 1H), 4.69 – 4.54 (m, 2H), 4.48 (dd, J = 3.3, 47.7 Hz, 1H), 3.06 (ddd, J = 17.4, 9.3, 4.9 Hz, 1H), 2.97 (dt, J = 17.3, 5.5 Hz, 1H), 2.70 (ddd, J = 13.6, 6.2, 4.8 Hz, 1H), 2.15 (ddd, J = 13.9, 9.2, 4.9 Hz, 1H), 1.54 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.79, 172.35, 159.79 (d, $J_{C\text{-}F}$ = 258.7 Hz, 1C), 143.16, 133.76, 131.59, 128.90, 128.22, 127.02, 94.15 (d, $J_{C\text{-}F}$ = 16.5 Hz, 1C), 61.72 (d, $J_{C\text{-}F}$ = 35.2 Hz, 1C), 54.07, 33.81, 25.95, 20.47. ^{19}F NMR (282 MHz, $CDCl_3$) δ -106.01 – -106.32 (m, 1F). IR (thin film, NaCl) 1738, 1682, 1601, 1227, 1164 cm^{-1}. HRMS (APCI/ESI) m/z calc'd for $C_{15}H_{16}FO_3$ $[M+H]^+$: 263.1078, found: 263.1078.

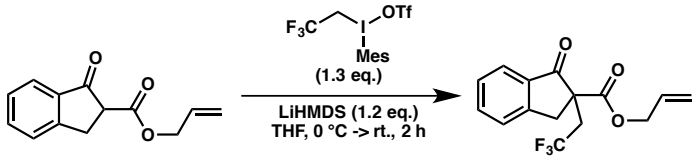


The procedure for preparation of **4f** was adapted from the work of Shibata and coworkers.[9]

To a stirred solution of **methyl 1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate**[10] (224 mg, 1.1 mmol, 1.0 equiv) in CH_3CN (11 mL) was added DBU (328 mL, 2.2 mmol, 2.0 equiv) at room temperature. After stirring at room temperature for 15 min, the mixture was cooled down to 0 °C and a solution of the trifluoromethylating reagent (561 mg, 1.65 mmol, 1.5 equiv.) in acetonitrile (11 mL) was added dropwise at the same temperature. Reaction mixture was stirred 10 min, and then warmed up to room temperature, the solvent was evaporated, and the crude product was purified by column chromatography (SiO_2, 10% EtOAc in pentane) to furnish **α-trifluoromethyl-β-ketoester S6** (281mg, 94% yield) as a colorless oil; R_f = 0.18 (10:1 Hexane:EtOAc).

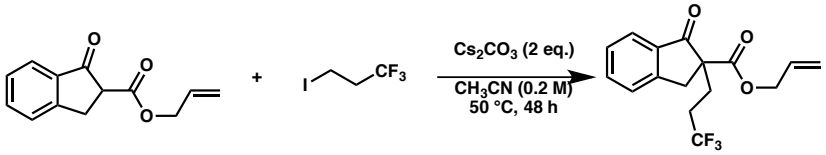
To a stirred solution of **S6** (281mg, 1.03 mmol, 1.0 equiv) in allyl alcohol (30.0 equiv.) was added Ti(O*i*Pr)$_4$ (2.0 equiv) at 80 °C under nitrogen atmosphere. After reaction mixture was stirred at the same temperature for 24 h, it was cooled down to room temperature and quenched with aqueous solution of NH_4Cl. Aqueous layer was extracted with CH_2Cl_2 (20 mL x 4), and the combined organic layers was washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude oil was purified by column chromatography (SiO_2, 10% EtOAc in hexane) to afford **4f** (242 mg, 74% yield) as a light yellow oil; R_f = 0.50 (5:1 Hexane:EtOAc); All spectroscopic data were in agreement with the literature[9] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (dd, J = 7.8, 1.4 Hz, 1H), 7.53 (app td, J = 7.5, 1.4 Hz, 1H), 7.38 –7.32 (m, 1H), 7.24 (d, J = 7.8 Hz, 1H), 5.92 – 5.67 (m, 1H), 5.32 – 5.07 (m, 2H), 4.84 – 4.56 (m, 2H), 3.22 – 2.97 (m, 2H), 2.85 (dt, J = 13.6, 4.2 Hz, 1H), 2.50 (ddd, J = 13.6, 10.3, 6.7 Hz, 1H). ^{13}C NMR (101

MHz, $CDCl_3$) δ 187.09, 165.11 (q, $J_{C\text{-}F}$ = 1.9 Hz, 1C), 142.14, 134.44, 131.62 (q, $J_{C\text{-}F}$ = 1.5 Hz, 1C), 130.53, 128.82, 128.54, 127.44, 123.95 (q, $J_{C\text{-}F}$ = 284.0 Hz, 1C), 119.28, 67.09, 62.15 (q, $J_{C\text{-}F}$ = 24.1 Hz, 1C), 27.83 (q, $J_{C\text{-}F}$ = 2.3 Hz, 1C), 25.19. ^{19}F NMR (282 MHz, $CDCl_3$) δ -68.73 (s, 3F).



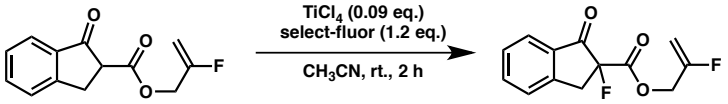
S7 *4g*

Allyl 1-oxo-2-(2,2,2-trifluoroethyl)-2,3-dihydro-1*H*-indene-2-carboxylate (4g) was synthesized using the same method with **4a** from **allyl 1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate** (**S7**)[11]. The crude oil was purified by column chromatography (SiO_2, 50% CH_2Cl_2 in hexane) to afford **4g** (110 mg, 37% yield) as a light yellow oil; R_f = 0.38 (1:1 Hexane:CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.66 (app td, *J* = 7.5, 1.2 Hz, 1H), 7.53 (app dt, *J* = 7.7, 1.0 Hz, 1H), 7.42 (app td, *J* = 7.9, 0.9 Hz, 1H), 5.81 (ddt, *J* = 17.2, 10.5, 5.6 Hz, 1H), 5.39 – 5.15 (m, 2H), 4.64 – 4.53 (m, 2H), 3.88 (d, *J* = 17.3 Hz, 1H), 3.52 – 3.15 (m, 2H), 2.66 (dq, *J* = 15.5, 10.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.24, 168.43, 153.15, 136.10, 133.83, 131.18, 128.20, 126.50, 126.10 (q, $J_{C\text{-}F}$ = 277.7 Hz, 1C), 125.32, 118.86, 66.91, 57.37 (q, $J_{C\text{-}F}$ = 1.9 Hz, 1C), 37.62 (q, $J_{C\text{-}F}$ = 29.1 Hz, 1C), 35.34 (q, $J_{C\text{-}F}$ = 1.7 Hz 1C). ^{19}F NMR (282 MHz, $CDCl_3$) -60.61 (t, *J* = 10.5 Hz, 3F). IR (thin film, NaCl) 1745, 1719, 1608, 1257, 1169 cm^{-1}. HRMS (APCI/ESI) m/z calc'd for $C_{15}H_{14}F_3O_3$ $[M+H]^+$: 299.0890, found: 299.0898.



S8 *4h*

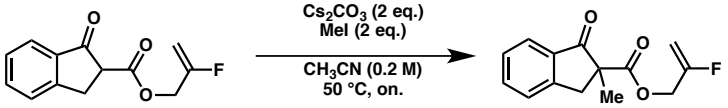
Allyl 1-oxo-2-(3,3,3-trifluoropropyl)-2,3-dihydro-1*H*-indene-2-carboxylate (4h): The mixture of **allyl 1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate** (**S8**) (216 mg, 1.0 mmol, 1.0 equiv), Cesium carbonate (652 mg, 2.0 mmol, 2.0 equiv) and 1,1,1-trifluoro-3-iodopropane (447 mL, 2.0 mmol, 2.0 equiv) in CH_3CN (5 mL) was heated at 50 °C for 48 hours. After cooling, the solution was filtered and concentrated in vacuo. The crude product was purified by column chromatography (SiO_2, 50% CH_2Cl_2 in hexane) to furnish β-ketoester **4h** (98 mg, 31% yield) as a colorless oil; R_f = 0.37 (1:1 Hexane:CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (ddd, *J* = 7.7, 1.3, 0.8 Hz, 1H), 7.66 (app td, *J* = 7.5, 1.2 Hz, 1H), 7.50 (app dt, *J* = 7.7, 0.9 Hz, 1H), 7.44 (ddd, *J* = 7.9, 7.2, 0.9 Hz, 1H), 5.83 (ddt, *J* = 17.1, 10.4, 5.6 Hz, 1H), 5.34 – 5.14 (m, 2H), 4.69 – 4.54 (m, 2H), 3.73 (d, *J* = 17.2 Hz, 1H), 3.06 (d, *J* = 17.2 Hz, 1H), 2.39 – 2.24 (m, 2H), 2.22 – 2.06 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.52, 170.28, 152.45, 135.93, 134.96, 131.37, 128.34, 126.89 (q, $J_{C\text{-}F}$ = 275.9 Hz, 1C), 126.58, 125.20, 118.83, 66.36, 58.81, 37.62, 29.70 (q, $J_{C\text{-}F}$ = 29.2 Hz, 1C), 27.16 (q, $J_{C\text{-}F}$ = 3.3 Hz, 1C). ^{19}F NMR (282 MHz, $CDCl_3$) δ -66.70 (t, *J* = 10.1 Hz, 3F). IR (thin film, NaCl) 1741, 1711, 1255, 1141 cm^{-1}. HRMS (APCI/ESI) m/z calc'd for $C_{16}H_{16}F_3O_3$ $[M+H]^+$: 313.1046, found: 313.1040.



S9 *4i*

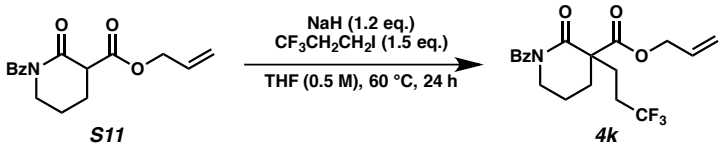
2-Fluoroallyl 1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (S9) was synthesized using the same method with **S5** from **1-Indanone and S4**. The crude oil was purified by column chromatography (SiO_2, 20% Et_2O in hexane) to afford **S9** (515 mg, 73% yield) as a colorless oil; R_f = 0.28 (10:1 Hexane: EtOAc); Mixture of enol ketone form (1/4). ^{1}H NMR (300 MHz, $CDCl_3$): ketone form δ 7.82 – 7.74 (m, 0.8H), 7.69 – 7.59 (m, 0.8H), 7.56 – 7.47 (m, 0.8H), 7.47 – 7.36 (m, 0.8H), 4.95 – 4.57 (m, 3.2H), 3.79 (dd, *J* = 8.3, 4.2 Hz, 0.8H), 3.70 – 3.51 (m, 0.8H), 3.49 – 3.30 (m, 0.8H). ^{13}C NMR (101 MHz, $CDCl_3$): ketone form δ 199.00, 168.60, 159.81 (d, $J_{C\text{-}F}$ = 257.5 Hz, 0.8C), 153.54, 135.70, 135.23, 128.06, 126.70, 124.92, 94.69 (d, $J_{C\text{-}F}$ = 16.6 Hz, 0.8C), 62.20 (d, $J_{C\text{-}F}$ = 35.1 Hz, 0.8C), 53.16, 30.38. ^{19}F NMR (282 MHz, $CDCl_3$) δ -105.40 – -105.71 (m, 0.2F), -105.72 – -106.08 (m, 0.8F). IR (thin film, NaCl) 1745, 1713, 1685, 1204, 1150, 761 cm^{-1}; HRMS (APCI/ESI) m/z calc'd for $C_{13}H_{10}FO_3$ $[M\text{-}H]^-$: 233.0619, found: 233.0618.

2-Fluoroallyl 2-fluoro-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (4i) was synthesized using the same method with **4d** from **S9**. The crude oil was purified by column chromatography (SiO_2, 10% EtOAc in hexane) to afford **4i** (176 mg, 70% yield) as a pale solid; R_f = 0.28 (10:1 Hexane:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 7.7, 0.7 Hz, 1H), 7.72 (app td, *J* = 7.5, 1.2 Hz, 1H), 7.55 – 7.43 (m, 2H), 4.85 – 4.64 (m, 3H), 4.60 (dd, *J* = 47.0, 3.5 Hz, 1H), 3.82 (dd, *J* = 17.7, 11.7 Hz, 1H), 3.48 (dd, *J* = 23.3, 17.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.81 (d, $J_{C\text{-}F}$ = 18.2 Hz, 1C), 166.79 (d, $J_{C\text{-}F}$ = 28.5 Hz, 1C), 158.91 (d, $J_{C\text{-}F}$ = 257.6 Hz, 1C), 150.85 (d, $J_{C\text{-}F}$ = 3.4 Hz, 1C), 137.02, 133.20, 128.88, 126.76 (d, $J_{C\text{-}F}$ = 1.3 Hz, 1C), 125.87 (d, $J_{C\text{-}F}$ = 1.1 Hz, 1C), 95.41 (d, *J* = 16.6 Hz, 1C), 94.57 (d, $J_{C\text{-}F}$ = 202.0 Hz, 1C), 62.67 (d, $J_{C\text{-}F}$ = 34.7 Hz, 1C), 38.33 (d, $J_{C\text{-}F}$ = 23.8 Hz, 1C). ^{19}F NMR (282 MHz, $CDCl_3$) δ -106.19 – -106.51 (m, 1F), -164.54 (dd, *J* = 23.3, 11.9 H, 1F). IR (thin film, NaCl) 1771, 1724, 1600, 1282, 1184, 1071 cm^{-1}. HRMS (APCI/ESI) m/z calc'd for $C_{13}H_{11}F_2O_2$ $[M+H]^+$: 253.0671, found: 253.0672.



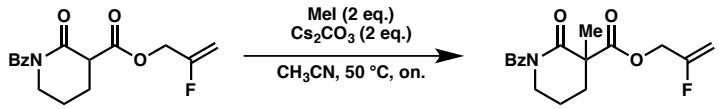
S10 *4j*

2-Fluoroallyl 2-methyl-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (4j) was synthesized using the same method with **4e** from **S10**. The crude oil was purified by column chromatography (SiO_2, 100% CH_2Cl_2) to afford **4j** (170 mg, 69% yield) as a colorless oil; R_f = 0.34 (10:1 Hexane:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 7.7, 0.5 Hz, 1H), 7.64 (app td, *J* = 7.5, 1.2 Hz, 1H), 7.49 (app dt, *J* = 7.7, 1.0 Hz, 1H), 7.45 – 7.40 (m, 1H), 4.75 (dd, *J* = 16.1, 3.3 Hz, 1H), 4.70 – 4.47 (m, 3H), 3.74 (dd, *J* = 17.1, 0.9 Hz, 1H), 3.04 (dq, *J* = 17.0, 0.7 Hz, 1H), 1.55 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.01, 171.38, 159.77 (d, $J_{C\text{-}F}$ = 257.4 Hz, 1C), 152.58, 135.62, 134.61, 128.07, 126.63, 125.18, 94.21 (d, $J_{C\text{-}F}$ = 16.6 Hz, 1C), 61.90 (d, $J_{C\text{-}F}$ = 35.4 Hz, 1C), 56.08, 40.04, 21.13. ^{19}F NMR (282 MHz, $CDCl_3$) δ -106.09 – -106.41 (m, 1F). IR (thin film, NaCl) 1748, 1712, 1606, 1280, 1156, 1091 cm^{-1}; HRMS (APCI/ESI) m/z calc'd for $C_{14}H_{14}FO_3$ $[M+H]^+$: 249.0921, found: 249.0919.



S11 *4k*

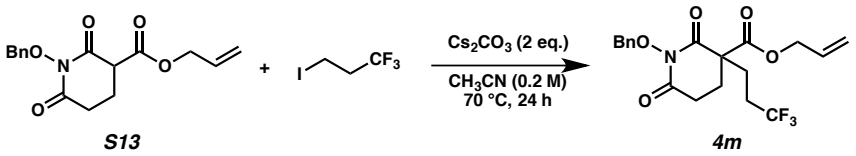
Allyl 1-benzoyl-2-oxo-3-(3,3,3-trifluoropropyl)piperidine-3-carboxylate (4k) was synthesized using the same method with **4b** from **allyl 1-benzoyl-2-oxopiperidine-3-carboxylate (S11)** [12]. The crude oil was purified by column chromatography (SiO_2, 100% CH_2Cl_2) to afford **4k** (142 mg, 37% yield) as a colorless oil; R_f = 0.54 (3:1 Hexane:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 – 7.70 (m, 2H), 7.52 – 7.48 (m, 1H), 7.41 – 7.38 (m, 2H), 5.99 (ddt, *J* = 17.2, 10.4, 6.1 Hz, 1H), 5.43 (dq, *J* = 17.1, 1.4 Hz, 1H), 5.37 (dq, *J* = 10.4, 1.1 Hz, 1H), 4.76 (dq, *J* = 6.1, 1.1 Hz, 2H), 3.87 – 3.25 (m, 2H), 2.52 – 2.40 (m, 1H), 2.42 – 2.28 (m, 1H), 2.18 – 1.99 (m, 5H), 1.87 (ddd, *J* = 13.7, 9.6, 5.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.99, 171.51, 171.21, 135.65, 132.12, 131.09, 128.31 (2C), 128.22 (2C), 126.89 (q, $J_{C\text{-}F}$ = 276.4 Hz, 1C), 120.47, 67.02, 55.42, 46.71, 31.71, 29.97 (q, $J_{C\text{-}F}$ = 29.0 Hz), 28.41 (q, $J_{C\text{-}F}$ = 3.3 Hz, 1C), 20.24. ^{19}F NMR (282 MHz, $CDCl_3$) δ -66.79 (t, *J* = 10.1 Hz, 3F). IR (thin film, NaCl) 1735, 1685, 1451, 1393, 1276, 1256, 1147 cm^{-1}. HRMS (APCI/ESI) m/z calc'd for $C_{19}H_{21}F_3NO_4$ $[M+H]^+$: 384.1417, found: 384.1414.



S12 *4l*

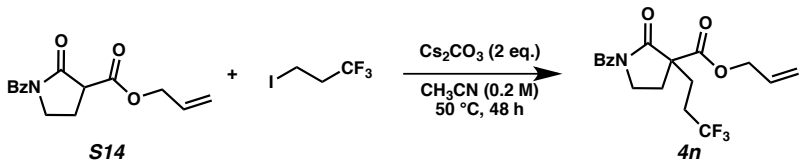
2-Fluoroallyl 1-benzoyl-2-oxopiperidine-3-carboxylate (S12) was synthesized using the same method with **S5** from **1-benzoylpiperidin-2-one and S4**. The crude oil was purified by column chromatography (SiO_2, 100% CH_2Cl_2) to afford **S12** (482 mg, 53% yield) as a colorless oil; R_f = 0.37 (3:1 Hexane: EtOAc); 93% purity, ketone form. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 – 7.64 (m, 2H), 7.52 – 7.46 (m, 1H), 7.42 – 7.36 (m, 2H), 4.87 (ddd, *J* = 15.6, 3.4, 0.6 Hz, 1H), 4.78 – 4.64 (m, 3H), 3.95 – 3.78 (m, 2H), 3.64 (t, *J* = 6.6 Hz, 1H), 2.39 – 2.32 (m, 1H), 2.26 – 2.18 (m, 1H), 2.14 – 2.06 (m, 1H), 2.03 – 1.93 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.60, 169.34, 169.05, 159.56 (d, $J_{C\text{-}F}$ = 258.1 Hz, 1C), 135.46, 132.06, 128.33 (2C), 128.29 (2C), 95.53 (d, $J_{C\text{-}F}$ = 16.9 Hz, 1C), 62.51 (d, $J_{C\text{-}F}$ = 33.1 Hz, 1C), 51.03, 46.40, 25.59, 20.75. ^{19}F NMR (282 MHz, $CDCl_3$) δ -105.57 (dq, *J* = 46.2, 15.1 Hz, 1F). IR (thin film, NaCl) 1744, 1682, 1449, 1394, 1283, 1257, 1151, 1114 cm^{-1}. HRMS (APCI/ESI) m/z calc'd for $C_{16}H_{17}FNO_4$ $[M+H]^+$: 306.1136, found: 306.1131.

2-Fluoroallyl 1-benzoyl-3-methyl-2-oxopiperidine-3-carboxylate (4l) was synthesized using the same method with **4e** from **S12**. The crude oil was purified by column chromatography (SiO_2, 100% CH_2Cl_2) to afford **4l** (186 mg, 56% yield) as light yellow oil; R_f = 0.30 (3:1 Hexane:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 – 7.66 (m, 2H), 7.52 – 7.45 (m, 1H), 7.41 – 7.35 (m, 2H), 4.90 (dd, *J* = 15.5, 3.4 Hz, 1H), 4.82 – 4.63 (m, 3H), 3.89 (dt, *J* = 12.8, 7.1 Hz, 1H), 3.83 – 3.76 (m, 1H), 2.68 – 2.43 (m, 1H), 2.12 – 1.96 (m, 2H), 1.91 – 1.80 (m, 1H), 1.52 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.06, 172.57, 172.32, 159.58 (d, $J_{C\text{-}F}$ = 258.4 Hz, 1C), 135.91, 131.84, 128.22 (2C), 128.06 (2C), 95.76 (d, $J_{C\text{-}F}$ = 17.0 Hz, 1C), 62.63 (d, $J_{C\text{-}F}$ = 32.5 Hz, 1C), 52.99, 46.91, 33.87, 22.58, 20.25. ^{19}F NMR (282 MHz, $CDCl_3$) δ-105.20 – -105.53 (m, 1F). IR (thin film, NaCl) 1718, 1684, 1458, 1390, 1276, 1189, 1127 cm^{-1}; HRMS (APCI/ESI) m/z calc'd for $C_{17}H_{19}FNO_4$ $[M+H]^+$: 320.1293, found: 320.1298.



S13 *4m*

Allyl 1-(benzyloxy)-2,6-dioxo-3-(3,3,3-trifluoropropyl)piperidine-3-carboxylate (4m) was synthesized using the same method with **4h** from **allyl 1-(benzyloxy)-2,6-dioxopiperidine-3-carboxylate (S13)**[13] except that the temperature was 70 °C and reaction time was 24 hours. The crude oil was purified by column chromatography (SiO_2, 50% EtOAc in hexane) to afford **4m** (120 mg, 30% yield) as a colorless oil; R_f = 0.28 (3:1 Hexane: EtOAc); (99.7% purity determined by ^{19}F NMR). ^1H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.49 (m, 2H), 7.40 – 7.34 (m, 3H), 5.87 (ddt, *J* = 16.5, 10.3, 6.0 Hz, 1H), 5.36 (dq, *J* = 17.2, 1.4 Hz, 1H), 5.32 (dq, *J* = 10.4, 1.1 Hz, 1H), 5.02 (s, 2H), 4.69 (d, *J* = 6.1 Hz, 2H), 2.81 (ddd, *J* = 18.1, 5.0, 3.3 Hz, 1H), 2.69 (ddd, *J* = 18.0, 12.6, 5.3 Hz, 1H), 2.49 – 2.30 (m, 1H), 2.29 – 1.98 (m, 4H), 1.90 (td, *J* = 13.2, 5.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.37, 166.85, 166.65, 133.69, 130.52, 130.24 (2C), 129.44, 128.60 (2C), 126.64 (q, $J_{C\text{-}F}$ = 276.4 Hz, 1C), 120.74, 77.98, 67.29, 54.56, 30.21, 29.58 (q, $J_{C\text{-}F}$ = 29.5 Hz, 1C), 27.82 (q, $J_{C\text{-}F}$ = 3.3 Hz, 1C), 26.30. ^{19}F NMR (282 MHz, $CDCl_3$) δ -66.78 (t, *J* = 10.1 Hz, 3F). IR (thin film, NaCl) 1738, 1710, 1454, 1258, 1189, 1160, 1000, 977 cm^{-1}. HRMS (APCI/ESI) m/z calc'd for $C_{19}H_{21}F_3NO_5$ $[M+H]^+$: 400.1366, found: 400.1379.



S14 *4n*

Allyl 1-benzoyl-2-oxo-3-(3,3,3-trifluoropropyl)pyrrolidine-3-carboxylate (4n) was synthesized using the same method with **4h** from **allyl 1-benzoyl-2-oxopyrrolidine-3-carboxylate (S14)**[12]. The crude oil was purified by column chromatography (SiO_2, 25% EtOAc in hexane) to afford **4n** (170 mg, 46% yield) as a colorless oil; R_f = 0.50 (3:1 Hexane: EtOAc); ^1H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.59 (m, 2H), 7.57 – 7.52 (m, 1H), 7.44 – 7.39 (m, 2H), 5.92 (ddt, *J* = 17.1, 10.3, 5.8 Hz, 1H), 5.37 (dq, *J* = 17.1, 1.4 Hz, 1H), 5.32 (dq, *J* = 10.4, 1.2 Hz, 1H), 4.71 (dt, *J* = 5.8, 1.3 Hz, 2H), 4.08 (ddd, *J* = 11.4, 8.7, 3.6 Hz, 1H), 3.96 (ddd, *J* = 11.4, 8.2, 7.7 Hz, 1H), 2.63 (ddd, *J* = 13.3, 7.7, 3.7 Hz, 1H), 2.54 – 2.36 (m, 1H), 2.28 – 1.97 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.49, 170.34, 169.63, 133.73, 132.44, 130.95, 128.94 (2C), 128.05 (2C), 126.74 (q, $J_{C\text{-}F}$ = 276.0 Hz, 1C), 119.86, 66.89, 56.37, 43.49, 29.41 (q, $J_{C\text{-}F}$ = 29.4 Hz, 1C), 28.62, 26.64 (q, $J_{C\text{-}F}$ = 3.4 Hz, 1C). ^{19}F NMR (282 MHz, $CDCl_3$) δ -66.79 (t, *J* = 9.9 Hz, 3F). IR (thin film, NaCl) 1748, 1731, 1682, 1449, 1293, 1253, 1218, 1131 cm^{-1}. HRMS (APCI/ESI) m/z calc'd for $C_{18}H_{19}F_3NO_4$ $[M+H]^+$: 370.1261, found: 370.1254.

Representative Procedure 1: Enantioselective Allylic Alkylation.

Oven-dried half-dram vials were charged with the palladium source (Pd_2dba_3 or Pd_2pmdba_3, 0.005 mmol, 0.05 equiv) and (*S*)-$(CF_3)_3$-*t*Bu-PHOX (7.4 mg, 0.0125 mmol, 0.125 equiv) and toluene (2 mL) in a nitrogen-filled glovebox. After stirring at ambient glovebox temperature (~28 °C) for 30 min, solutions of the substrates (0.1 mmol, 1.0 equiv) in 1 mL of toluene were added. The reaction vials were tightly capped and removed from the glovebox. After 24 hours at ambient temperature or heating at the desired temperatures, the solvent was removed by vacuo. The crude mixture were separated on the preparative thin layer plate, filtered, washed with Et_2O, removed solvent and analyzed for enantiomeric excess and optical rotations (see Methods for the Determination of Enantiomeric Excess).

Representative Procedure 2: Racemic Allylic Alkylation.

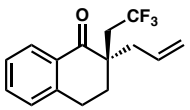
Oven-dried half-dram vials were charged with the $Pd(PPh_3)_4$ (0.1 equiv) and substrate (1.0 equiv) and toluene (0.1 M) in a nitrogen-filled glovebox. The reaction vials were tightly capped and removed from the glovebox. After 24 hours at ambient temperature or heating at the desired temperatures, the solvent was removed by vacuo. The crude mixture were separated on the preparative thin layer plate, filtered, washed with Et_2O, removed solvent to give the desired racemic products.

Representative Procedure 3: Racemic Allylic Alkylation.

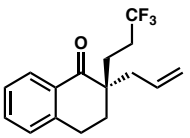
Oven-dried half-dram vials were charged with the palladium source (Pd_2dba_3 or Pd_2pmdba_3, 0.05 equiv) and Gly-PHOX (0.125 equiv) and toluene (0.1 M) in nitrogen-filled glovebox. After stirring at ambient glovebox temperature (~28 °C) for 30 min, solutions of the substrates (1.0 equiv) in toluene were added. The reaction vials were tightly capped and removed from the glovebox. After 24 hours at ambient temperature or heating at the desired temperatures, the solvent was removed by vacuo. The crude mixture were separated on the preparative thin layer plate, filtered, washed with Et_2O, removed solvent to give desired racemic products.

Representative Procedure 4: Preparatory Scale Reaction.

An oven-dried 250 mL Schlenck flask was charged with Pd_2dba_3 (94 mg, 0.103 mmol, 0.05 equiv) and (*S*)-$(CF_3)_3$-*t*-Bu-PHOX (152 mg, 0.26 mmol, 0.125 equiv) and toluene (12 mL) in a nitrogen-filled glovebox. After stirring at ambient glovebox temperature (~28 °C) for 30 min, a solution of **4c** (512 mg, 2.06 mmol, 1.0 equiv) in 50 mL of toluene was added. The reaction vessel was sealed and removed from the glovebox. After 24 hours at ambient temperature the solvent was removed in vacuo. The product was purified by column chromatography (SiO_2, 5% EtOAc in hexanes) to afford **5c** (419 mg, 99% yield, 92% ee).

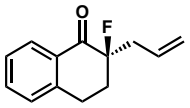


(*S*)-2-allyl-2-(2,2,2-trifluoroethyl)-3,4-dihydronaphthalen-1(2*H*)-one (5a): 26.5 mg, 99% yield; colorless oil; R_f = 0.47 (10:1 Hexane:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.50 (app td, *J* = 7.5, 1.5 Hz, 1H), 7.33 (app t, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 7.8 Hz, 1H), 5.72 (ddt, *J* = 17.4, 10.1, 7.4 Hz, 1H), 5.19 (d, *J* = 10.1 Hz, 1H), 5.12 (dd, *J* = 16.9, 1.6 Hz, 1H), 3.14 (ddd, *J* = 16.9, 11.6, 4.9 Hz, 1H), 3.00 – 2.82 (m, 2H), 2.49 (dd, *J* = 14.3, 7.4 Hz, 1H), 2.41 – 2.24 (m, 3H), 2.17 (dt, *J* = 14.0, 4.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.27, 142.73, 133.72, 132.15, 130.92, 128.88, 128.58, 127.08, 126.79 (q, $J_{C\text{-}F}$ = 277.8 Hz, 1C), 120.17, 45.95, 38.58, 37.54 (d, $J_{C\text{-}F}$ = 28.8 Hz, 1C), 29.60 (q, $J_{C\text{-}F}$ = 1.7 Hz, 1C), 24.88. ^{19}F NMR (282 MHz, $CDCl_3$) δ -58.69 (t, *J* = 11.7 Hz, 3F). IR (thin film, NaCl) 1683, 1600, 1256, 1130, 740 cm^{-1}. HRMS (FAB) m/z calc'd for $C_{15}H_{16}F_3O$ $[M+H]^+$: 269.1148, found: 269.1159.

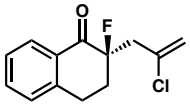


(*R*)-2-allyl-2-(3,3,3-trifluoropropyl)-3,4-dihydronaphthalen-1(2*H*)-one (5b): 27.4 mg, 97% yield; colorless oil; R_f = 0.50 (10:1 Hexane:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (ddd, *J* = 7.9, 1.4, 0.5 Hz, 1H), 7.49 (app td, *J* = 7.5, 1.5 Hz, 1H), 7.32 (app t, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 5.75 (ddt, *J* = 16.8, 10.2, 7.4 Hz, 1H), 5.23 – 5.04 (m, 2H), 3.07 (ddd, *J* = 17.5, 7.9, 5.6 Hz, 1H), 2.99 (dt, *J* = 17.5, 6.0 Hz, 1H), 2.45 (ddt, *J* = 14.2, 7.3, 1.2 Hz, 1H), 2.33 (ddt, *J* = 14.1, 7.4, 1.2 Hz, 1H), 2.24 – 2.01

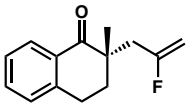
(m, 4H), 1.97 (td, J = 13.7, 4.4 Hz, 1H), 1.79 (td, J = 13.5, 4.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.39, 142.94, 133.64, 132.82, 131.53, 128.91, 128.23, 127.42 (q, $J_{C\text{-}F}$ = 276.9 Hz, 1C), 127.02, 119.27, 46.63, 38.72, 31.04, 28.93 (q, $J_{C\text{-}F}$ = 28.8 Hz, 1C), 26.54 (q, $J_{C\text{-}F}$ = 3.3 Hz, 1C), 24.99. ^{19}F NMR (282 MHz, $CDCl_3$) δ -66.62 (t, J = 10.4 Hz, 3F). IR (thin film, NaCl) 1682, 1601, 1259, 1136, 743 cm^{-1}. HRMS (APCI/ESI) m/z calc'd for $C_{16}H_{18}F_3O$ $[M+H]^+$: 283.1304, found: 283.1305.



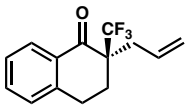
(*R*)-2-allyl-2-fluoro-3,4-dihydronaphthalen-1(2*H*)-one (5c)[14,15]**:** 20.3 mg, 99% yield; colorless oil; R_f = 0.28 (10:1 Hexane:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (dd, J = 7.8, 1.4 Hz, 1H), 7.52 (app td, J = 7.5, 1.5 Hz, 1H), 7.35 (app td, J = 7.5, 1.1 Hz, 1H), 7.28 – 7.24 (m, 1H), 5.95 – 5.84 (m, 1H), 5.25 – 5.07 (m, 2H), 3.19 – 3.07 (m, 1H), 3.02 (ddd, J = 17.3, 9.6, 5.3 Hz, 1H), 2.77 – 2.66 (m, 1H), 2.64 – 2.49 (m, 1H), 2.48 – 2.26 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.12 (d, $J_{C\text{-}F}$ = 17.6 Hz, 1C), 142.82, 134.20, 130.97 (d, $J_{C\text{-}F}$ = 4.1 Hz, 1C), 128.87, 128.40, 128.39, 127.23, 120.01, 95.11 (d, $J_{C\text{-}F}$ = 185.0 Hz, 1C), 38.09 (d, $J_{C\text{-}F}$ = 23.5 Hz, 1C), 32.01 (d, $J_{C\text{-}F}$ = 22.6 Hz, 1C), 26.01 (d, $J_{C\text{-}F}$ = 10.1 Hz, 1C). ^{19}F NMR (282 MHz, $CDCl_3$) δ -159.85 – -160.09 (m, 1F). IR (thin film, NaCl) 1678, 1602, 1221, 930, 741 cm^{-1}. HRMS (APCI/ESI) m/z calc'd for $C_{13}H_{14}FO$ $[M+H]^+$: 205.1023, found: 205.1023.



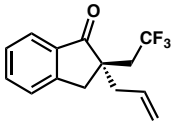
(*R*)-2-(2-chloroallyl)-2-fluoro-3,4-dihydronaphthalen-1(2*H*)-one (5d): 22.9 mg, 96% yield; colorless oil; R_f = 0.43 (10:1 Hexane:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (dd, J = 7.8, 1.3 Hz, 1H), 7.54 (app td, J = 7.5, 1.5 Hz, 1H), 7.36 (app t, J = 7.8 Hz, 1H), 7.28 (d, J = 7.8 Hz, 1H), 5.45 (d, J = 1.2 Hz, 1H), 5.39 (d, J = 0.7 Hz, 1H), 3.24 – 3.01 (m, 3H), 2.90 (dd, J = 27.4, 15.3 Hz, 1H), 2.60 – 2.42 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.92 (d, $J_{C\text{-}F}$ = 18.5 Hz, 1C), 142.94, 134.78 (d, $J_{C\text{-}F}$ = 2.6 Hz, 1C), 134.41, 130.74, 128.88, 128.60 (d, $J_{C\text{-}F}$ = 1.2 Hz, 1C), 127.31, 118.62 (d, $J_{C\text{-}F}$ = 1.1 Hz, 1C), 94.03 (d, $J_{C\text{-}F}$ = 185.8 Hz, 1C), 42.67 (d, $J_{C\text{-}F}$ = 24.4 Hz, 1C), 31.69 (d, $J_{C\text{-}F}$ = 22.3 Hz, 1C), 26.00 (d, $J_{C\text{-}F}$ = 9.9 Hz, 1C). ^{19}F NMR (282 MHz, $CDCl_3$) δ -158.17 – -158.43 (m, 1F). IR (thin film, NaCl) 1680, 1631, 1602, 1223, 743 cm^{-1}. HRMS (APCI/ESI) m/z calc'd for $C_{13}H_{13}ClFO$ $[M+H]^+$: 239.0633, found: 239.0633.



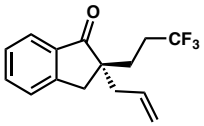
(*S*)-2-(2-fluoroallyl)-2-methyl-3,4-dihydronaphthalen-1(2*H*)-one (5e): 20.0 mg, 92% yield; colorless oil; R_f = 0.53 (10:1 Hexane:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (dd, J = 7.9, 1.4 Hz, 1H), 7.47 (app td, J = 7.4, 1.5 Hz, 1H), 7.31 (app t, J = 7.5 Hz, 1H), 7.23 (d, J = 7.7 Hz, 1H), 4.64 (dd, J = 17.2, 2.6 Hz, 1H), 4.32 (dd, J = 49.5, 2.6 Hz, 1H), 3.09 – 2.94 (m, 2H), 2.66 (dd, J = 20.5, 14.6 Hz, 1H), 2.50 (dd, J = 25.1, 14.6 Hz, 1H), 2.17 (dddd, J = 14.4, 9.1, 5.2, 1.3 Hz, 1H), 2.04 (dddd, J = 13.8, 6.0, 5.0, 1.1 Hz, 1H), 1.26 (d, J = 0.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.14, 164.07 (d, $J_{C\text{-}F}$ = 157.8 Hz, 1C), 143.28, 133.41, 131.34, 128.81, 128.28, 126.86, 93.85 (d, $J_{C\text{-}F}$ = 20.2 Hz, 1C), 44.26 (d, $J_{C\text{-}F}$ = 3.3 Hz, 1C), 39.39 (d, $J_{C\text{-}F}$ = 25.7 Hz, 1C), 33.30 (d, $J_{C\text{-}F}$ = 1.8 Hz, 1C), 25.48, 21.94 (d, $J_{C\text{-}F}$ = 1.5 Hz, 1C). ^{19}F NMR (282 MHz, $CDCl_3$) δ -88.59 – -88.99 (m, 1F). IR (thin film, NaCl) 1680, 1601, 1222, 741 cm^{-1}. HRMS (APCI/ESI) m/z calc'd for $C_{14}H_{16}FO$ $[M+H]^+$: 219.1180, found: 219.1185.



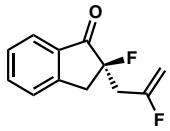
(*R*)-2-allyl-2-(trifluoromethyl)-3,4-dihydronaphthalen-1(2*H*)-one (5f)[9]: 22.8 mg, 90% yield; colorless oil; R_f = 0.36 (10:1 Hexane:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.51 (app td, *J* = 7.5, 1.5 Hz, 1H), 7.34 (app t, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 7.9 Hz, 1H), 5.87 – 5.65 (m, 1H), 5.21 – 5.11 (m, 2H), 3.10 (dt, *J* = 17.5, 6.7 Hz, 1H), 3.02 (dt, *J* = 17.3, 6.1 Hz, 1H), 2.76 (dd, *J* = 14.3, 7.3 Hz, 1H), 2.59 (dd, *J* = 14.3, 2.6 Hz, 1H), 2.43 – 2.25 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.89, 143.09, 134.20, 131.84, 131.57 (d, *J* = 1.5 Hz), 128.88, 128.50, 127.18, 126.57 (q, $J_{C\text{-}F}$ = 285.3 Hz, 1C), 120.08, 53.58 (q, $J_{C\text{-}F}$ = 22.3 Hz, 1C), 35.56 (q, $J_{C\text{-}F}$ = 2.2 Hz, 1C), 26.47 (q, $J_{C\text{-}F}$ = 2.0 Hz, 1C), 24.71. ^{19}F NMR (282 MHz, $CDCl_3$) δ -69.26 (s, 3F). IR (thin film, NaCl) 1688, 1601, 1161, 741cm^{-1}.



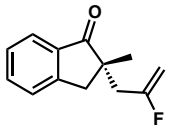
(*R*)-2-allyl-2-(2,2,2-trifluoroethyl)-2,3-dihydro-1*H*-inden-1-one (5g): 21.8 mg, 86% yield; colorless oil; R_f = 0.40 (10:1 Hexane:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.7 Hz, 1H), 7.62 (app td, *J* = 7.5, 1.2 Hz, 1H), 7.45 (d, *J* = 7.7 Hz, 1H), 7.40 (app t, *J* = 7.4 Hz, 1H), 5.58 – 5.47 (m, 1H), 5.19 – 4.96 (m, 2H), 3.36 (d, *J* = 17.6 Hz, 1H), 3.14 (d, *J* = 17.6 Hz, 1H), 2.64 – 2.48 (m, 2H), 2.45 (dd, *J* = 13.7, 6.7 Hz, 1H), 2.34 (dd, *J* = 13.7, 8.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.28, 152.43, 135.55, 135.38, 131.99, 127.87, 126.60 (q, $J_{C\text{-}F}$ = 278.7 Hz, 1C), 126.59, 124.51, 119.93, 49.03 (d, $J_{C\text{-}F}$ = 1.7 Hz, 1C), 42.44, 39.20 (q, $J_{C\text{-}F}$ = 27.7 Hz, 1C), 36.24 (q, $J_{C\text{-}F}$ = 1.9 Hz, 1C). ^{19}F NMR (282 MHz, $CDCl_3$) δ -59.71 (t, *J* = 11.3 Hz, 3F). IR (thin film, NaCl) 1715, 1608, 1258, 1122 cm^{-1}. HRMS (FAB$^+$) m/z calc'd for $C_{14}H_{14}F_3O$ [M+H]$^{l+}$: 255.0991, found: 255.0995.



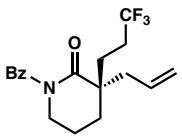
(*R*)-2-allyl-2-(3,3,3-trifluoropropyl)-2,3-dihydro-1*H*-inden-1-one (5h): 24.8 mg, 92% yield; colorless oil; R_f = 0.41 (10:1 Hexane:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (app dt, *J* = 7.6, 0.9 Hz, 1H), 7.62 (app td, *J* = 7.5, 1.2 Hz, 1H), 7.45 (app dt, *J* = 7.7, 0.9 Hz, 1H), 7.39 (app t, *J* = 7.6 Hz, 1H), 5.53 (dddd, *J* = 16.8, 10.1, 8.0, 6.7 Hz, 1H), 5.12 (dq, *J* = 16.9, 1.5 Hz, 1H), 5.03 (dd, *J* = 10.1, 1.0 Hz, 1H), 3.17 (dd, *J* = 17.4, 0.9 Hz, 1H), 2.91 (d, *J* = 17.4 Hz, 1H), 2.42 (ddt, *J* = 13.7, 6.6, 1.3 Hz, 1H), 2.34 (ddt, *J* = 13.7, 8.1, 1.0 Hz, 1H), 2.16 – 1.90 (m, 3H), 1.86 – 1.74 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.23, 152.52, 136.37, 135.51, 132.76, 127.92, 127.09 (q, $J_{C\text{-}F}$ = 276.0 Hz, 1C), 126.67, 124.31, 119.33, 50.95, 41.37, 37.27, 31.54 – 27.19 (m, 2C). ^{19}F NMR (282 MHz, $CDCl_3$) δ -66.65 (t, *J* = 10.3 Hz, 3F). IR (thin film, NaCl) 1709, 1608, 1256, 1150 cm^{-1}. HRMS (APCI/ESI) m/z calc'd for $C_{15}H_{16}F_3O$ [M+H]$^+$: 269.1148, found: 269.1158.



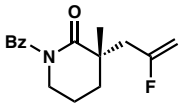
(*R*)-2-fluoro-2-(2-fluoroallyl)-2,3-dihydro-1*H*-inden-1-one (5i): 20.0 mg, 96% yield; colorless oil; R_f = 0.30 (5:1 Hexane:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (ddd, *J* = 7.7, 1.3, 0.7 Hz, 1H), 7.67 (App td, *J* = 7.5, 1.3 Hz, 1H), 7.50 – 7.40 (m, 2H), 4.71 (dd, *J* = 17.0, 3.0 Hz, 1H), 4.48 (dd, *J* = 49.1, 3.0 Hz, 1H), 3.61 (ddt, *J* = 17.8, 13.7, 0.7 Hz, 1H), 3.40 (dd, *J* = 23.7, 17.8 Hz, 1H), 3.00 (ddd, *J* = 22.5, 15.1, 10.7 Hz, 1H), 2.77 – 2.63 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.64 (d, $J_{C\text{-}F}$ = 17.6 Hz, 1C), 160.59 (dd, $J_{C\text{-}F}$ = 257.4, 7.6 Hz, 1C), 150.61 (d, $J_{C\text{-}F}$ = 3.4 Hz, 1C), 136.67, 133.63 (d, $J_{C\text{-}F}$ = 1.2 Hz, 1C), 128.49, 126.85 (d, $J_{C\text{-}F}$ = 1.2 Hz, 1C), 125.33, 95.17 (dd, $J_{C\text{-}F}$ = 18.7, 1.3 Hz, 1C), 94.75 (dd, $J_{C\text{-}F}$ = 188.4, 2.4 Hz, 1C), 37.73 (dd, $J_{C\text{-}F}$ = 24.6, 2.3 Hz, 1C), 37.28 (t, $J_{C\text{-}F}$ = 27.1 Hz, 1C). ^{19}F NMR (282 MHz, $CDCl_3$) δ -92.01 – -92.40 (m, 1F), -154.37 – -154.65 (m, 1F). IR (thin film, NaCl) 1732, 1608, 1227, 730 cm^{-1}. HRMS (APCI/ESI) m/z calc'd for $C_{12}H_{11}F_2O$ $[M+H]^+$: 209.0772, found: 209.0770.



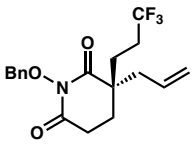
(*S*)-2-(2-fluoroallyl)-2-methyl-2,3-dihydro-1*H*-inden-1-one (5j): 21.8 mg, 97% yield; colorless oil; R_f = 0.33 (10:1 Hexane:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (dt, *J* = 7.6, 1.0 Hz, 1H), 7.60 (app td, *J* = 7.4, 1.2 Hz, 1H), 7.44 (dt, *J* = 7.7, 1.0 Hz, 1H), 7.38 (app td, *J* = 7.4, 0.9 Hz, 1H), 4.58 (ddd, *J* = 17.3, 2.8, 0.7 Hz, 1H), 4.30 (ddd, *J* = 49.6, 2.8, 0.7 Hz, 1H), 3.36 (d, *J* = 17.3 Hz, 1H), 2.93 (d, *J* = 17.3 Hz, 1H), 2.58 – 2.45 (m, 2H), 1.25 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.74, 164.02 (d, $J_{C\text{-}F}$ = 258.2 Hz, 1C), 152.63, 135.20, 127.66, 126.76, 124.62, 93.46 (d, $J_{C\text{-}F}$ = 19.9 Hz, 1C), 47.85 (d, $J_{C\text{-}F}$ = 2.8 Hz, 1C), 43.62 – 34.74 (m, 2C), 24.19. ^{19}F NMR (282 MHz, $CDCl_3$) δ -91.35 – -91.74 (m, 1F). IR (thin film, NaCl) 1732, 1608, 1227, 730 cm^{-1}. HRMS (APCI/ESI) m/z calc'd for $C_{13}H_{14}FO$ $[M+H]^+$: 205.1023, found: 205.1022.



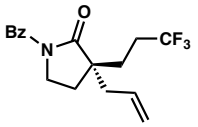
(*R*)-3-allyl-1-benzoyl-3-(3,3,3-trifluoropropyl)piperidin-2-one (5k): 27.4 mg, 94% yield; colorless oil; R_f = 0.37 (3:1 Hexane:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 – 7.47 (m, 3H), 7.40 – 7.38 (m, 2H), 5.72 (ddt, *J* = 17.4, 10.2, 7.3 Hz, 1H), 5.22 – 5.15 (m, 2H), 3.84 – 3.71 (m, 2H), 2.55 (ddt, *J* = 13.9, 7.2, 1.2 Hz, 1H), 2.38 (ddt, *J* = 13.9, 7.5, 1.2 Hz, 1H), 2.21 – 1.93 (m, 5H), 1.93 – 1.86 (m, 2H), 1.84 – 1.77 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.21, 175.61, 136.46, 132.11, 131.79, 128.44 (2C), 127.47 (2C), 127.23 (q, $J_{C\text{-}F}$ = 276.9 Hz, 1C), 120.09, 47.20, 46.09, 41.13, 31.62, 29.32, 29.13 (q, $J_{C\text{-}F}$ = 28.8 Hz, 1C), 19.41. ^{19}F NMR (282 MHz, $CDCl_3$) δ -66.53 (t, *J* = 10.5 Hz, 3F). IR (thin film, NaCl) 2950, 1682, 1258, 1149 cm^{-1}; HRMS (APCI/ESI) m/z calc'd for $C_{18}H_{21}F_3NO_2$ $[M+H]^+$: 340.1519, found: 340.1519.



(*S*)-1-benzoyl-3-(2-fluoroallyl)-3-methylpiperidin-2-one (5l): 23.5 mg, 85% yield; colorless oil; R_f = 0.52 (3:1 Hexane:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 2H), 7.49 – 7.44 (m, 1H), 7.41 – 7.35 (m, 2H), 4.67 (ddd, *J* = 17.3, 2.7, 0.7 Hz, 1H), 4.32 (ddd, *J* = 49.7, 2.7, 0.5 Hz, 1H), 4.00 – 3.84 (m, 1H), 3.79 – 3.62 (m, 1H), 2.76 (dd, *J* = 19.4, 14.6 Hz, 1H), 2.41 (ddd, *J* = 24.8, 14.6, 0.8 Hz, 1H), 2.19 – 1.95 (m, 3H), 1.93 – 1.75 (m, 1H), 1.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.80 (d, $J_{C\text{-}F}$ = 289.8 Hz, 1C), 163.47 (d, $J_{C\text{-}F}$ = 258.1 Hz, 1C), 136.47, 131.55, 128.28 (2C), 127.52 (2C), 94.42 (d, $J_{C\text{-}F}$ = 20.0 Hz, 1C), 47.16, 43.60 (d, $J_{C\text{-}F}$ = 3.1 Hz, 1C), 41.10 (d, $J_{C\text{-}F}$ = 25.5 Hz, 1C), 33.28 (d, $J_{C\text{-}F}$ = 1.9 Hz, 1C), 25.83 (d, $J_{C\text{-}F}$ = 1.5 Hz, 1C), 19.72. ^{19}F NMR (282 MHz, $CDCl_3$) δ -89.31 – 89.70 (m, 1F). IR (thin film, NaCl) 2942, 1697, 1672, 1277, 1144 cm^{-1}. HRMS (APCI/ESI) m/z calc'd for $C_{16}H_{19}FNO_2$ $[M+H]^+$: 276.1394, found: 276.1397.

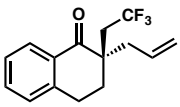
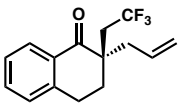
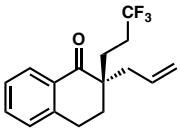
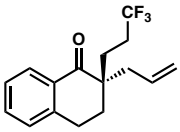
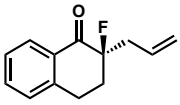
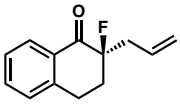
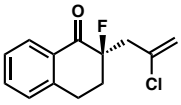
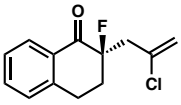
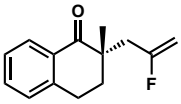
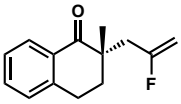
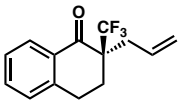
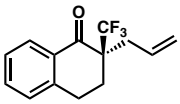
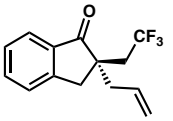
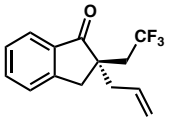
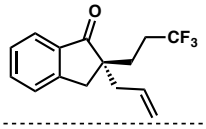
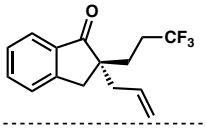
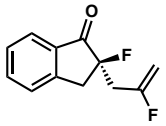
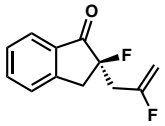
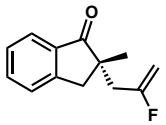
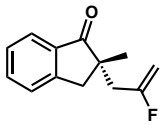
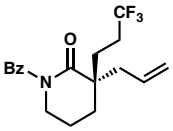
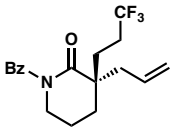
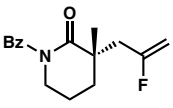
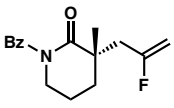
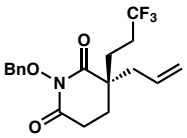
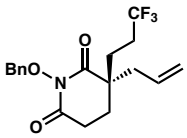
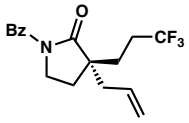
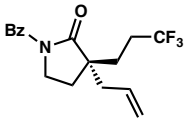


(*R*)-3-allyl-1-(benzyloxy)-3-(3,3,3-trifluoropropyl)piperidine-2,6-dione (5m): 33.0 mg, 93% yield; colorless oil; R_f = 0.24 (3:1 Hexane:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.46 (m, 2H), 7.40 – 7.34 (m, 3H), 5.61 (ddt, *J* = 17.4, 10.1, 7.4 Hz, 1H), 5.25 – 5.06 (m, 2H), 5.02 (s, 2H), 2.83 – 2.70 (m, 2H), 2.39 (ddt, *J* = 14.2, 7.3, 1.2 Hz, 1H), 2.30 (ddt, *J* = 14.2, 7.4, 1.1 Hz, 1H), 2.09 – 1.94 (m, 2H), 1.90 – 1.80 (m, 2H), 1.78 – 1.66 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.63, 167.45, 133.67, 131.03, 130.38 (2C), 129.45, 128.54 (2C), 126.88 (q, $J_{C\text{-}F}$ = 275.9 Hz, 1C), 120.75, 78.04, 45.18, 39.76, 29.22, 28.75 (q, $J_{C\text{-}F}$ = 29.2Hz, 1C), 27.76 (q, *J* = 3.0 Hz, 1C), 25.35. ^{19}F NMR (282 MHz, $CDCl_3$) δ -66.56 (t, *J* = 10.1 Hz, 3F). IR (thin film, NaCl) 1741, 1702, 1258, 1184 cm^{-1}. HRMS (APCI/ESI) m/z calc'd for $C_{18}H_{21}F_3NO_3$ $[M+H]^+$: 356.1468, found: 356.1470.



(*R*)-3-allyl-1-benzoyl-3-(3,3,3-trifluoropropyl)pyrrolidin-2-one (5n): 26.7 mg, 82% yield; colorless oil; R_f = 0.35 (5:1 Hexane:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.51 (m, 3H), 7.45 – 7.39 (m, 2H), 5.76 (dddd, *J* = 17.1, 10.2, 7.8, 7.0 Hz, 1H), 5.29 – 5.16 (m, 2H), 3.96 – 3.85 (m, 2H), 2.38 (ddt, *J* = 13.8, 7.0, 1.3 Hz, 1H), 2.34 – 2.28 (m, 1H), 2.28 – 2.06 (m, 3H), 1.95 (ddd, *J* = 13.3, 8.3, 6.4 Hz, 1H), 1.86 – 1.81 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.93, 170.74, 134.18, 132.23, 131.91, 128.90 (2C), 128.00 (2C), 127.0 (q, $J_{C\text{-}F}$ = 276.9 Hz, 1C), 120.39, 48.44, 42.96, 39.93, 28.94 (q, $J_{C\text{-}F}$ = 29.2 Hz, 1C), 28.02 (q, $J_{C\text{-}F}$ = 3.0 Hz, 1C), 27.60. ^{19}F NMR (282 MHz, $CDCl_3$) δ -66.60 (t, *J* = 10.4 Hz, 3F). IR (thin film, NaCl) 1738, 1678, 1305, 1258, 1138 cm^{-1}. HRMS (APCI/ESI) m/z calc'd for $C_{17}H_{19}F_3NO_2$ $[M+H]^+$: 326.1362, found: 326.1352.

Methods for the Determination of Enantiomeric Excess (ee) & Optical Rotation:

	products	assigned as	assay conditions	ee (%)	$[\alpha]_D^{25}$ (c = 1, $CHCl_3$)
5a			SFC, Chiralcel OD-H 0% IPA isocratic, 2.5 mL/min t (major) = 9.21 t (minor) = 8.65	90	-21.307
5b			SFC, Chiralcel OD-H 1% IPA isocratic, 2.5 mL/min t (major) = 5.71 t (minor) = 8.86	92	+0.267
5c			SFC, Chiralcel OJ-H 0% IPA isocratic, 2.5 mL/min t (major) = 6.38 t (minor) = 5.98	93	-28.692
5d			SFC, Chiralpak AD-H 3% IPA isocratic, 2.5 mL/min t (major) = 9.73 t (minor) = 11.11	95	-32.885
5e			SFC, Chiralpak IC 5% IPA isocratic, 2.5 mL/min t (major) = 4.78 t (minor) = 4.21	85	-9.688
5f			SFC, Chiralpak AD-H 5% IPA isocratic, 2.5 mL/min t (major) = 2.72 t (minor) = 3.04	64	-31.191
5g			SFC, Chiralpak AS-H 0% IPA isocratic, 2.5 mL/min t (major) = 2.81 t (minor) = 2.55	90	-25.986
5h			SFC, Chiralpak AD-H 3% IPA isocratic, 2.5 mL/min t (major) = 3.85 t (minor) = 3.16	87	-28.049
5i			SFC, Chiralpak AD-H 5% IPA isocratic, 2.5 mL/min t (major) = 2.98 t (minor) = 3.54	79	-85.633
5j			SFC, Chiralpak IC 3% IPA isocratic, 2.5 mL/min t (major) = 8.09 t (minor) = 7.23	74	-58.663
5k			SFC, Chiralpak AD-H 5% IPA isocratic, 2.5 mL/min t (major) = 6.15 t (minor) = 4.63	89	-5.691
5l			SFC, Chiralpak AD-H 5% IPA isocratic, 2.5 mL/min t (major) = 9.04 t (minor) = 11.38	97	-65.009
5m			SFC, Chiralcel OJ-H 3% IPA isocratic, 2.5 mL/min t (major) = 10.67 t (minor) = 9.86	89	+3.302
5n			SFC, Chiralpak AD-H 10% IPA isocratic, 2.5 mL/min t (major) = 2.28 t (minor) = 3.25	79	-14.268

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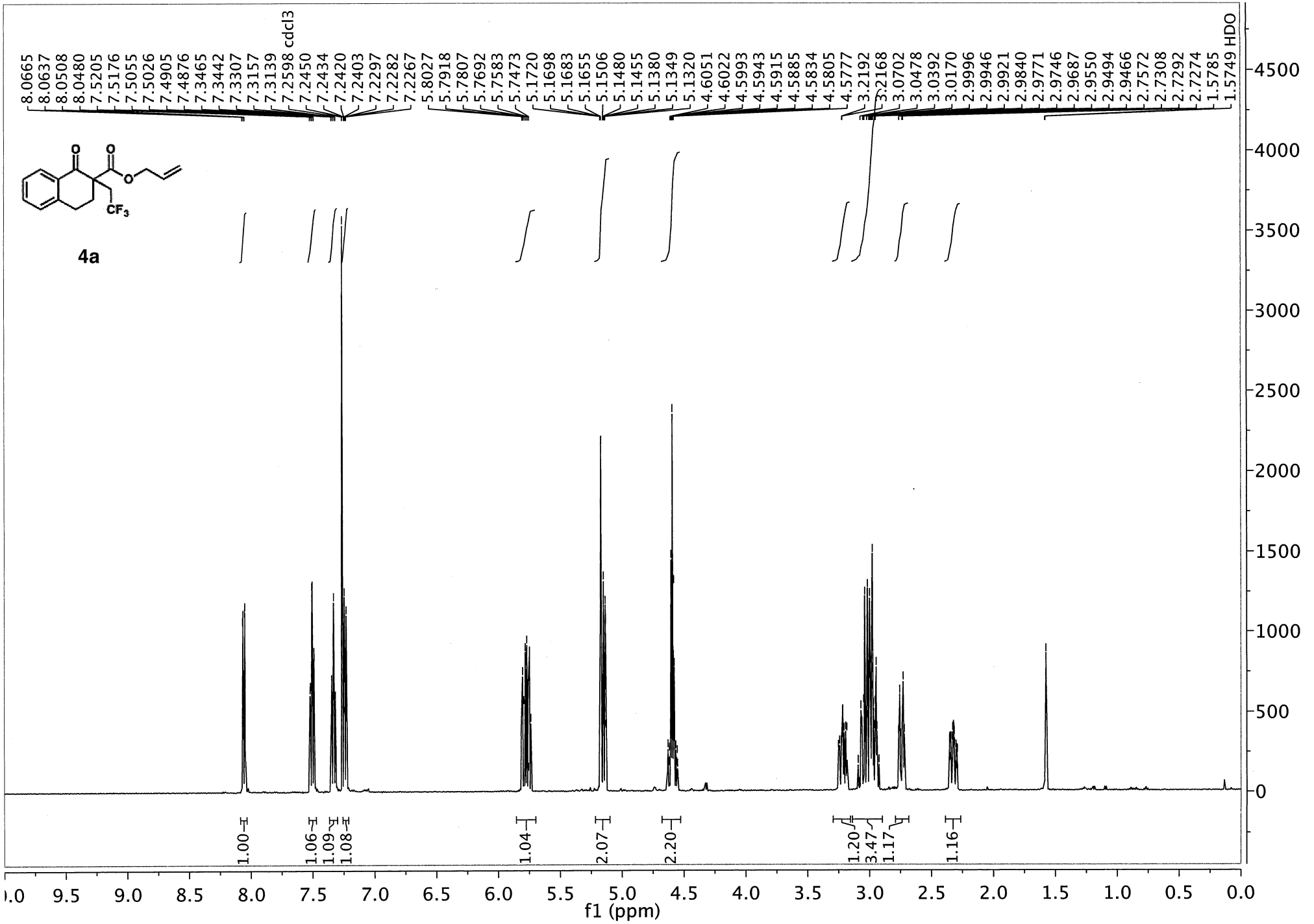
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O
CF3
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1.06
1.09
1.08
1.04
2.07
2.20
1.20
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1.17
1.16
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1500
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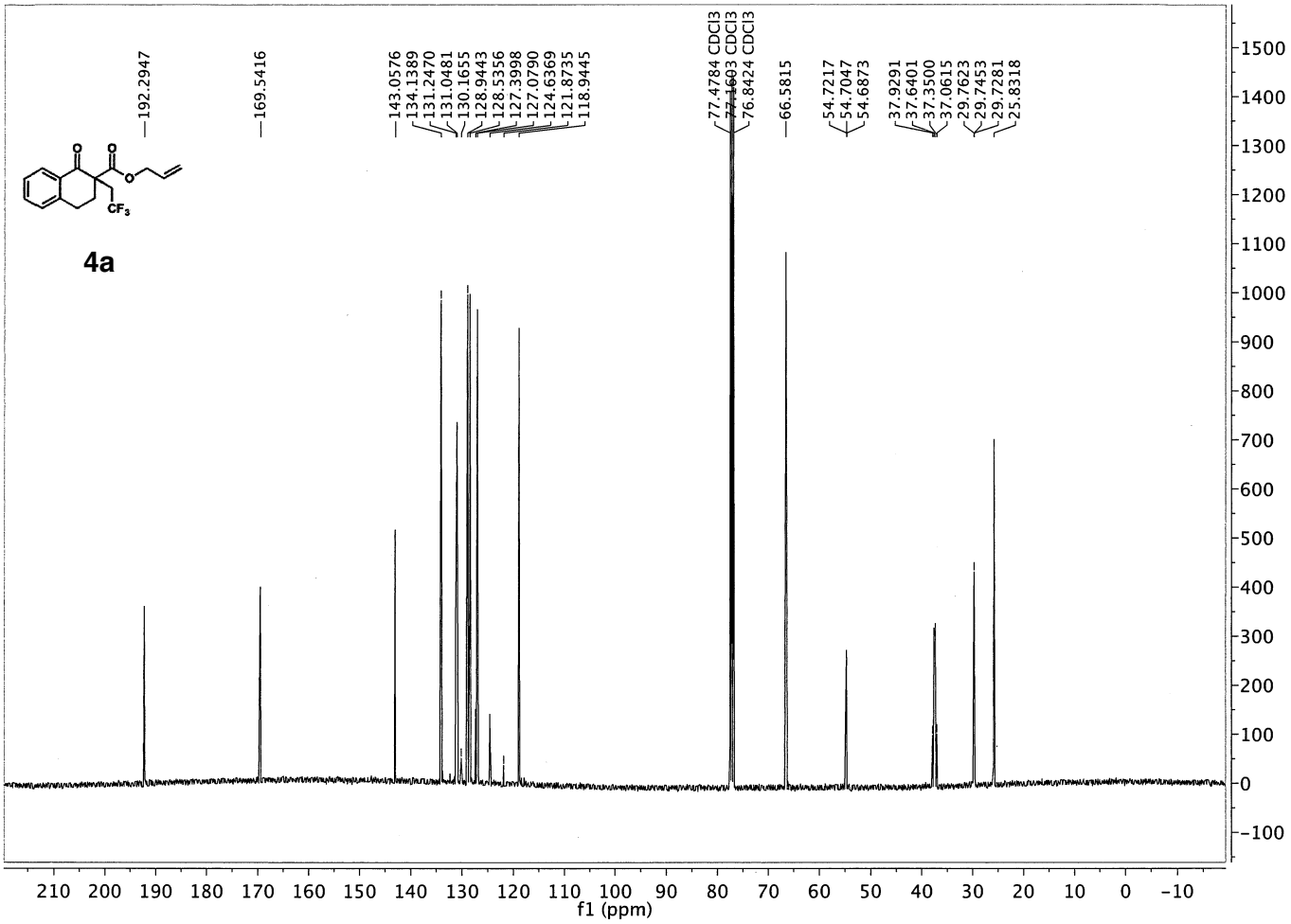
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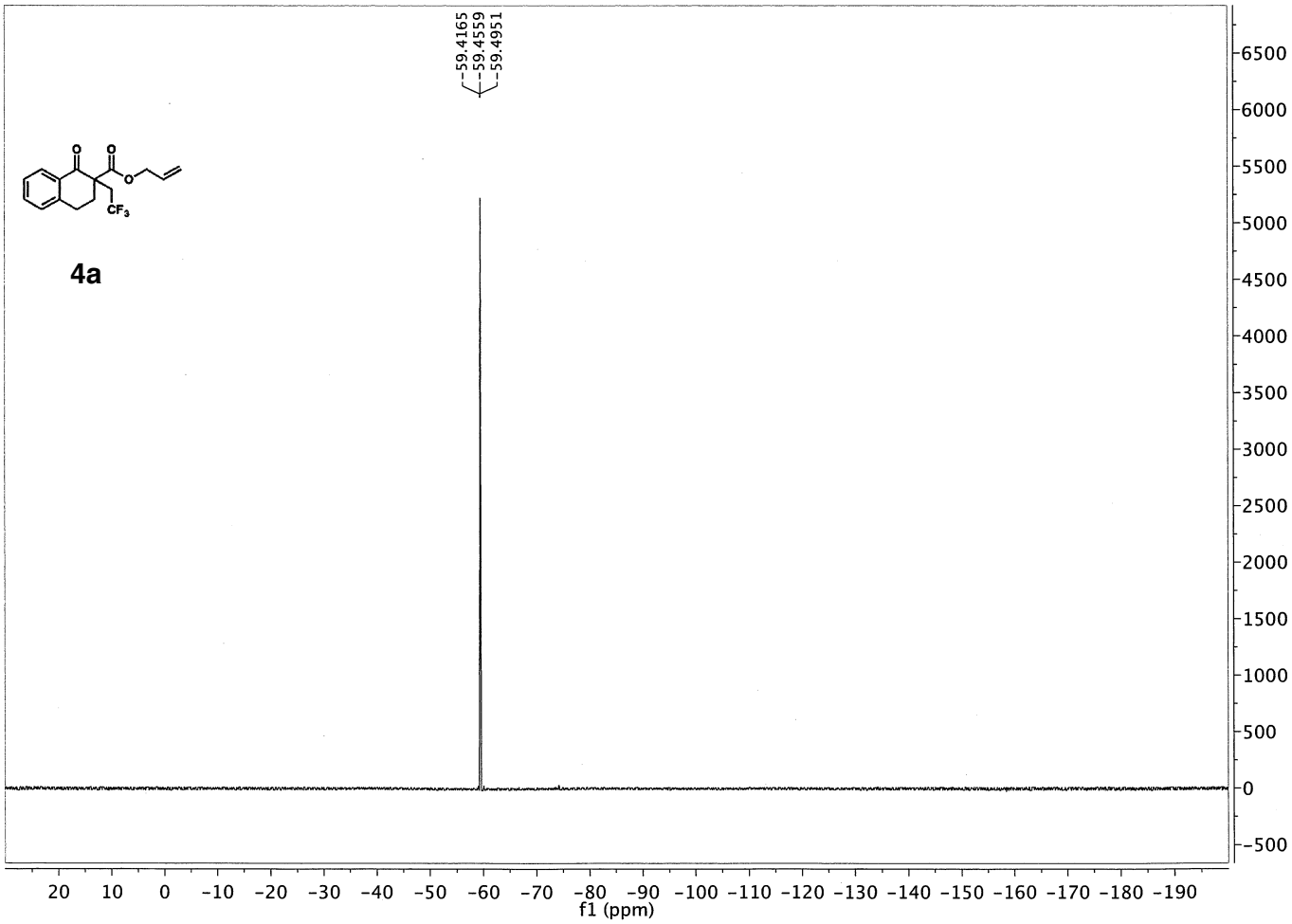
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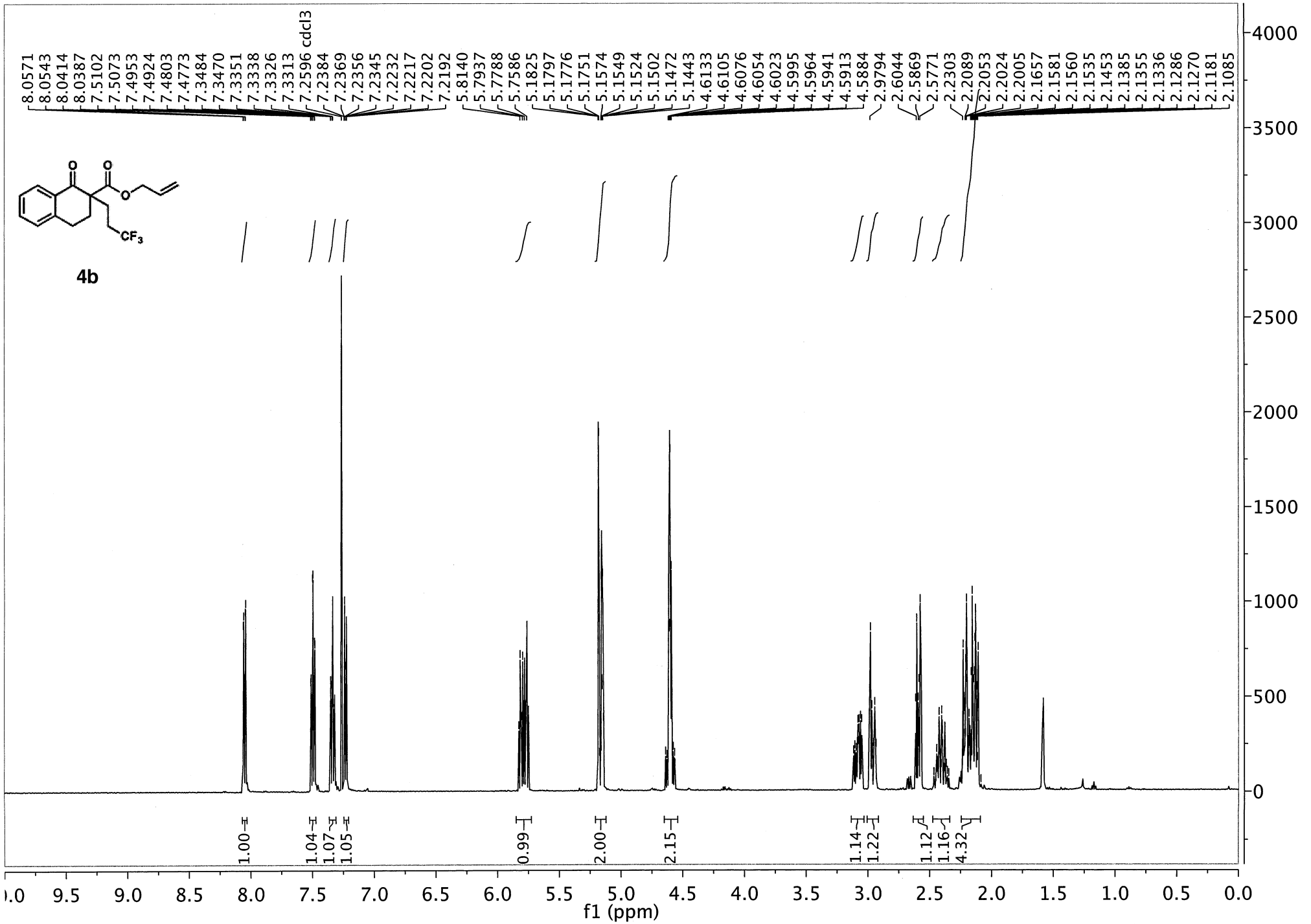
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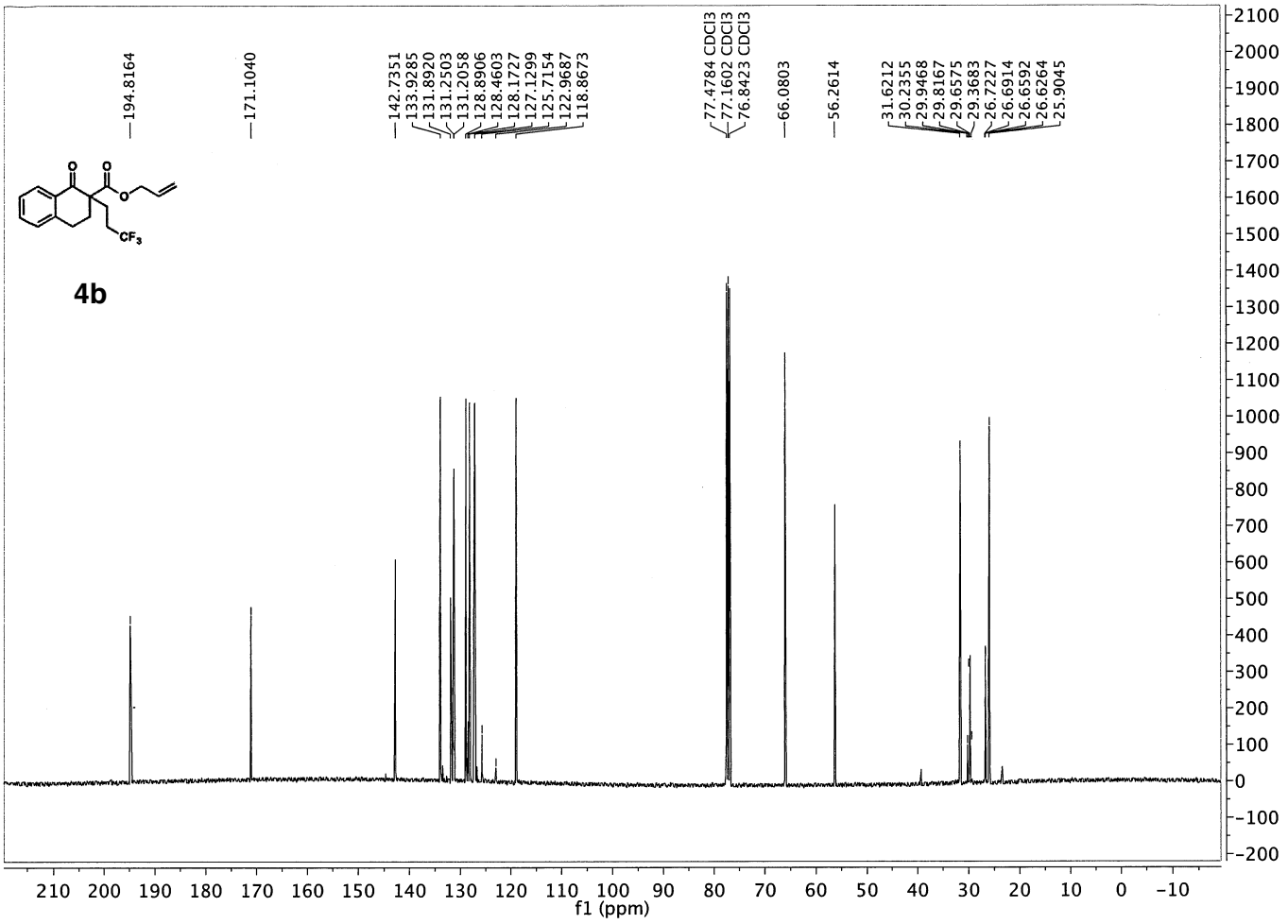
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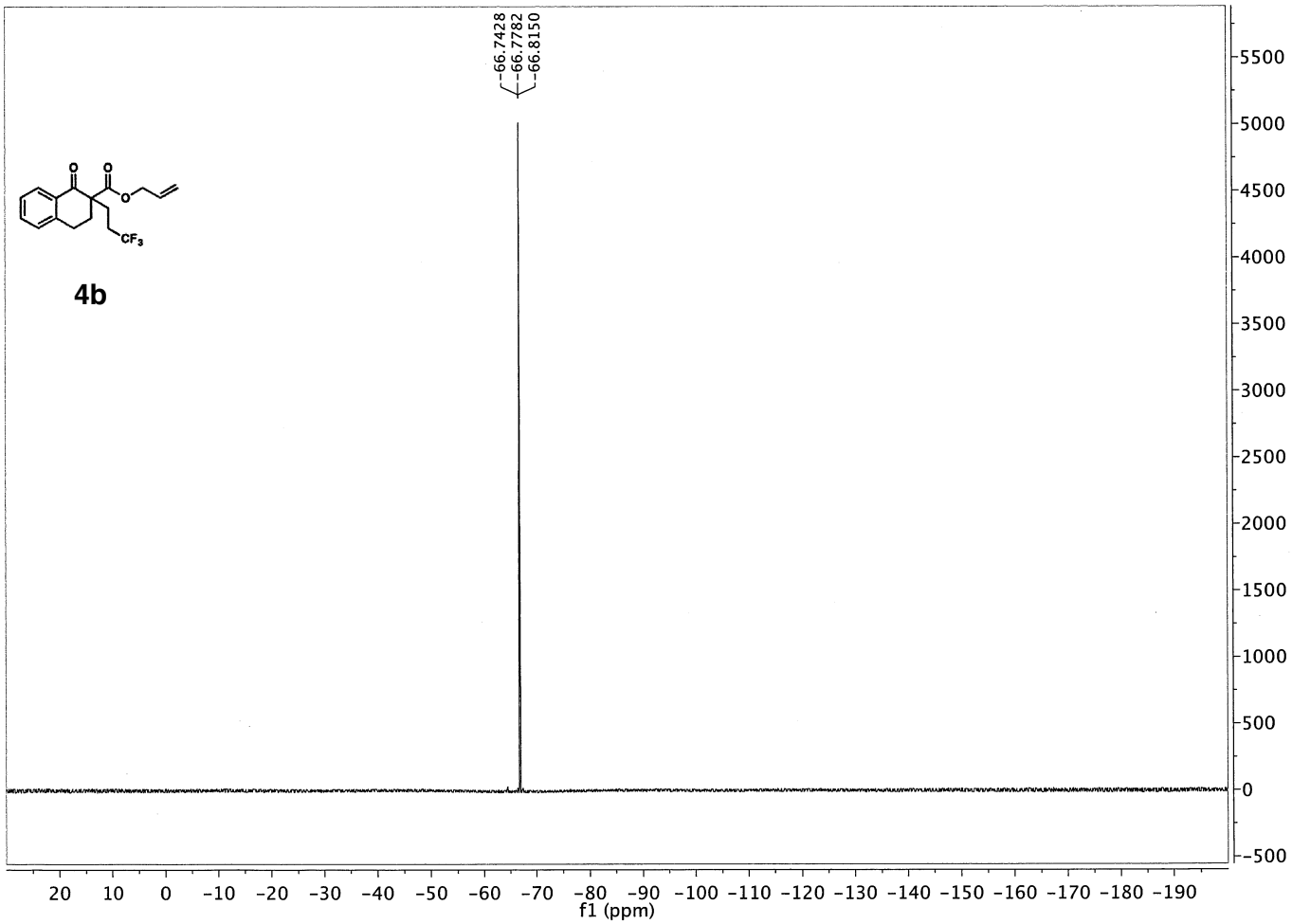
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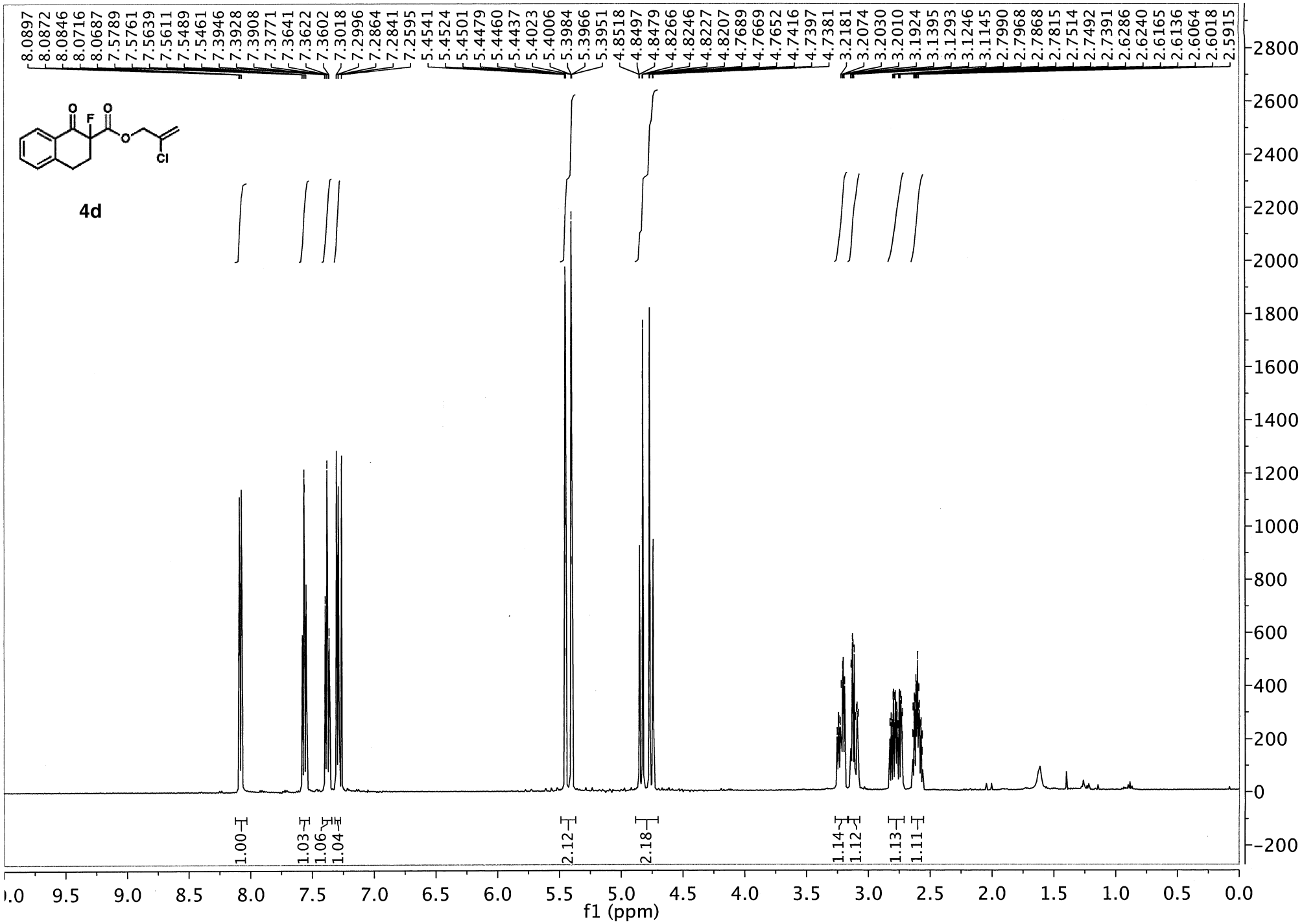
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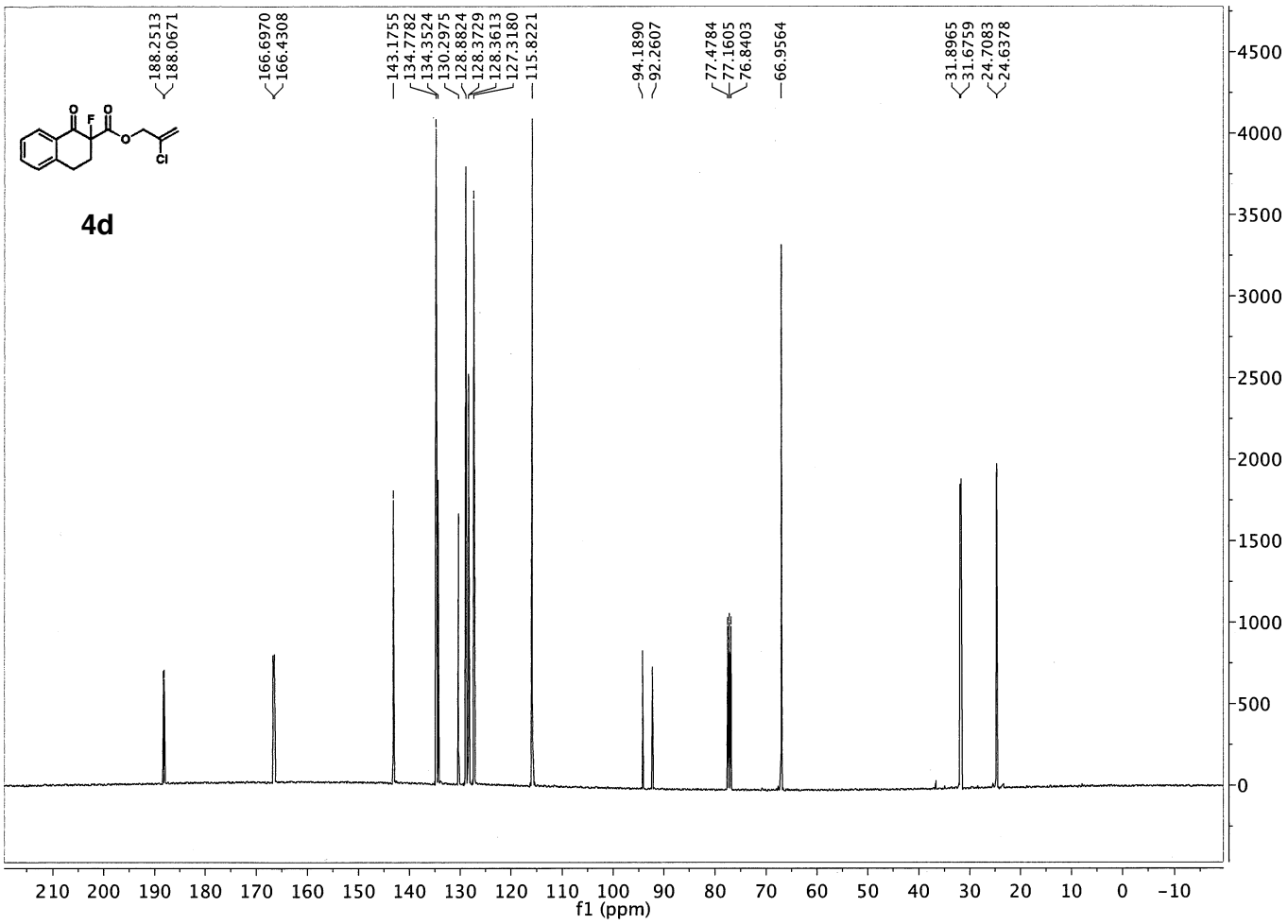
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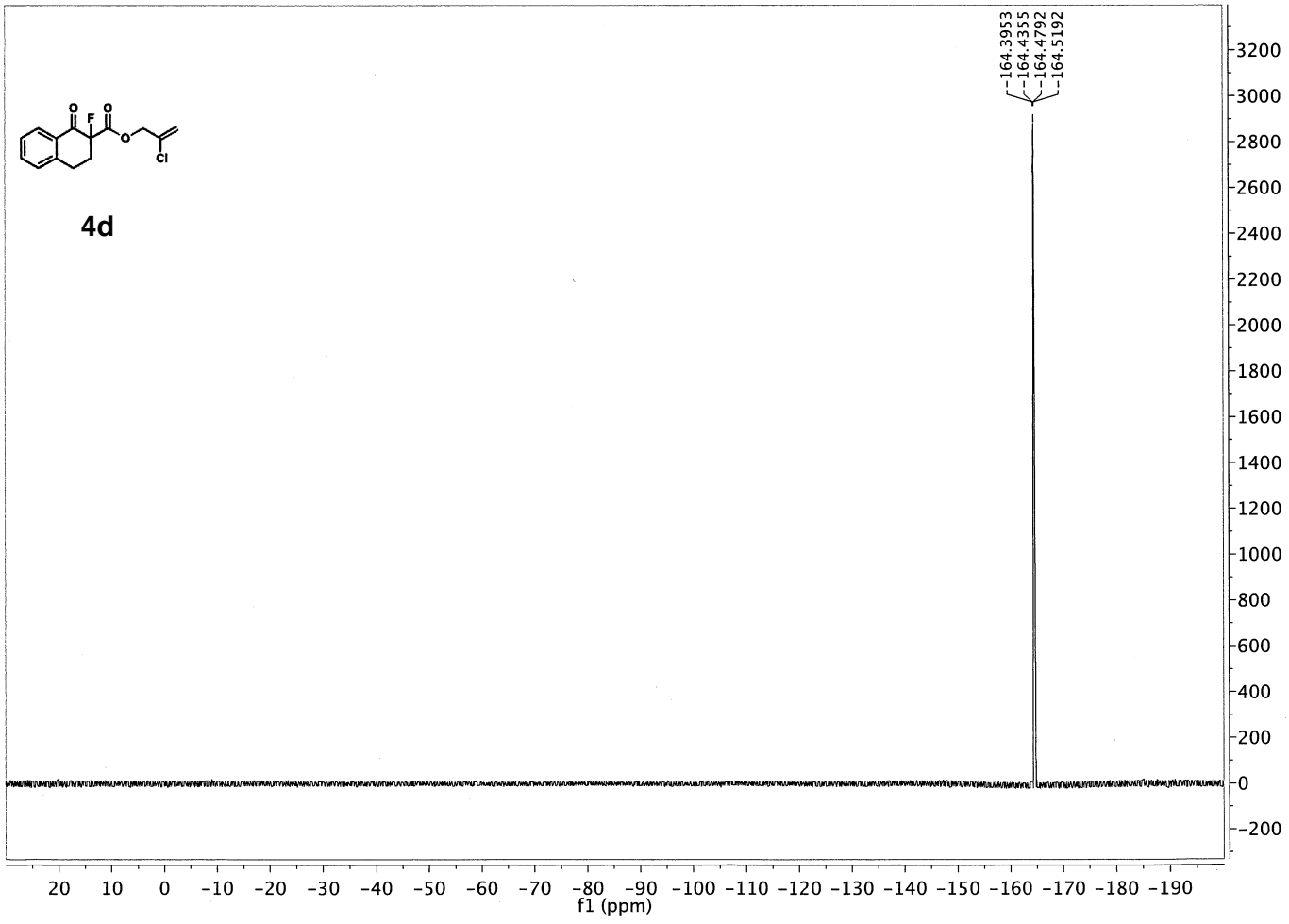
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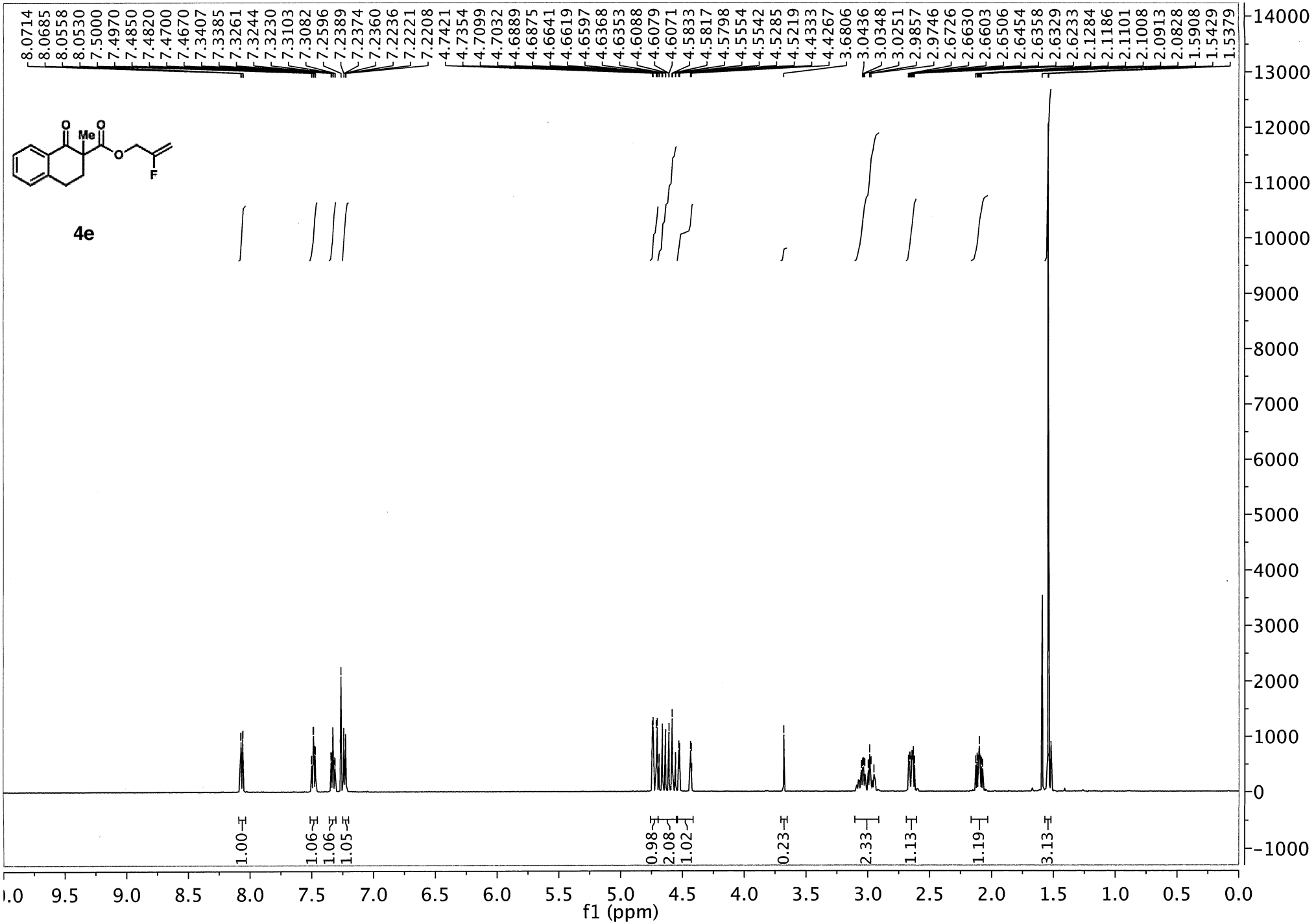
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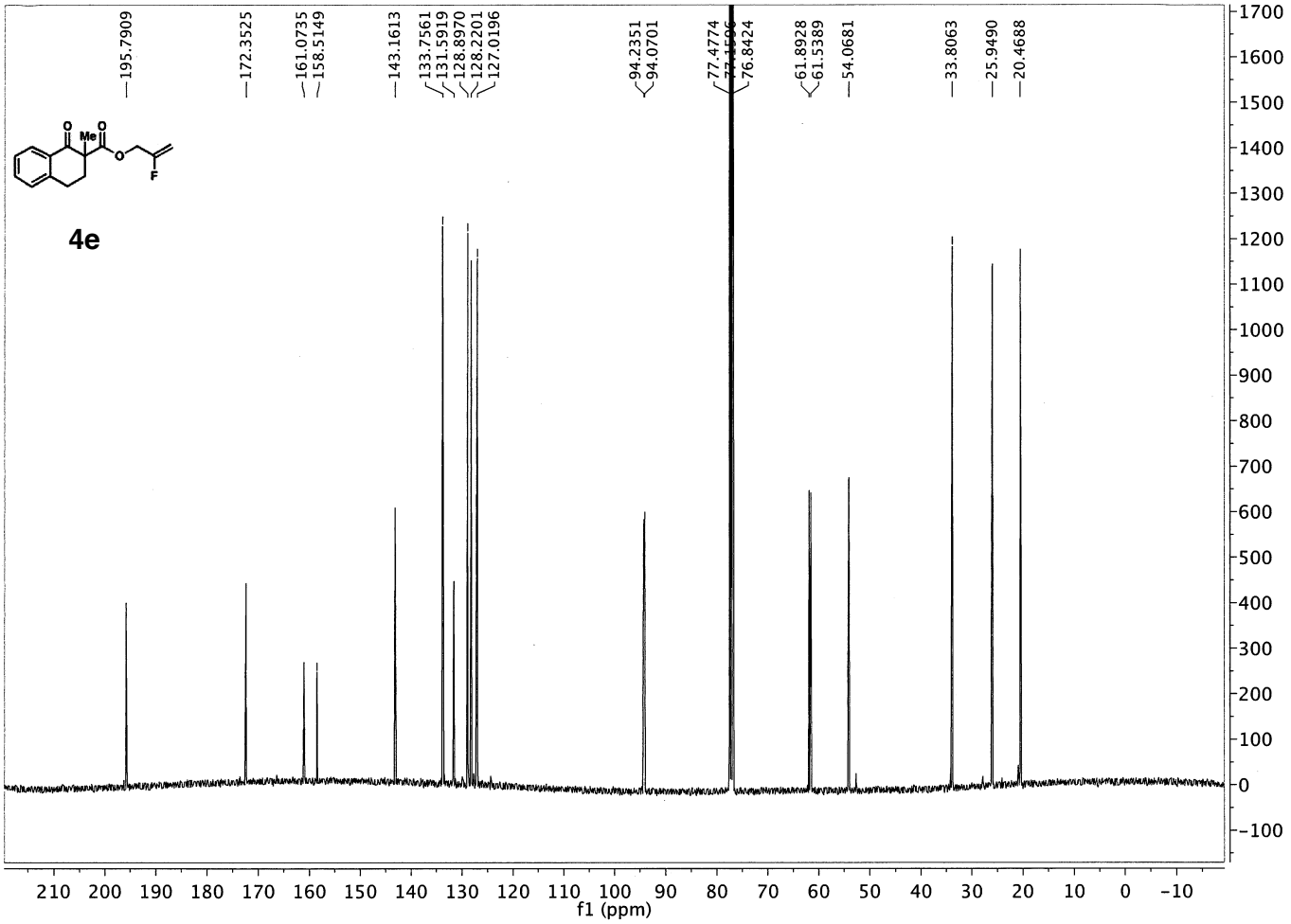
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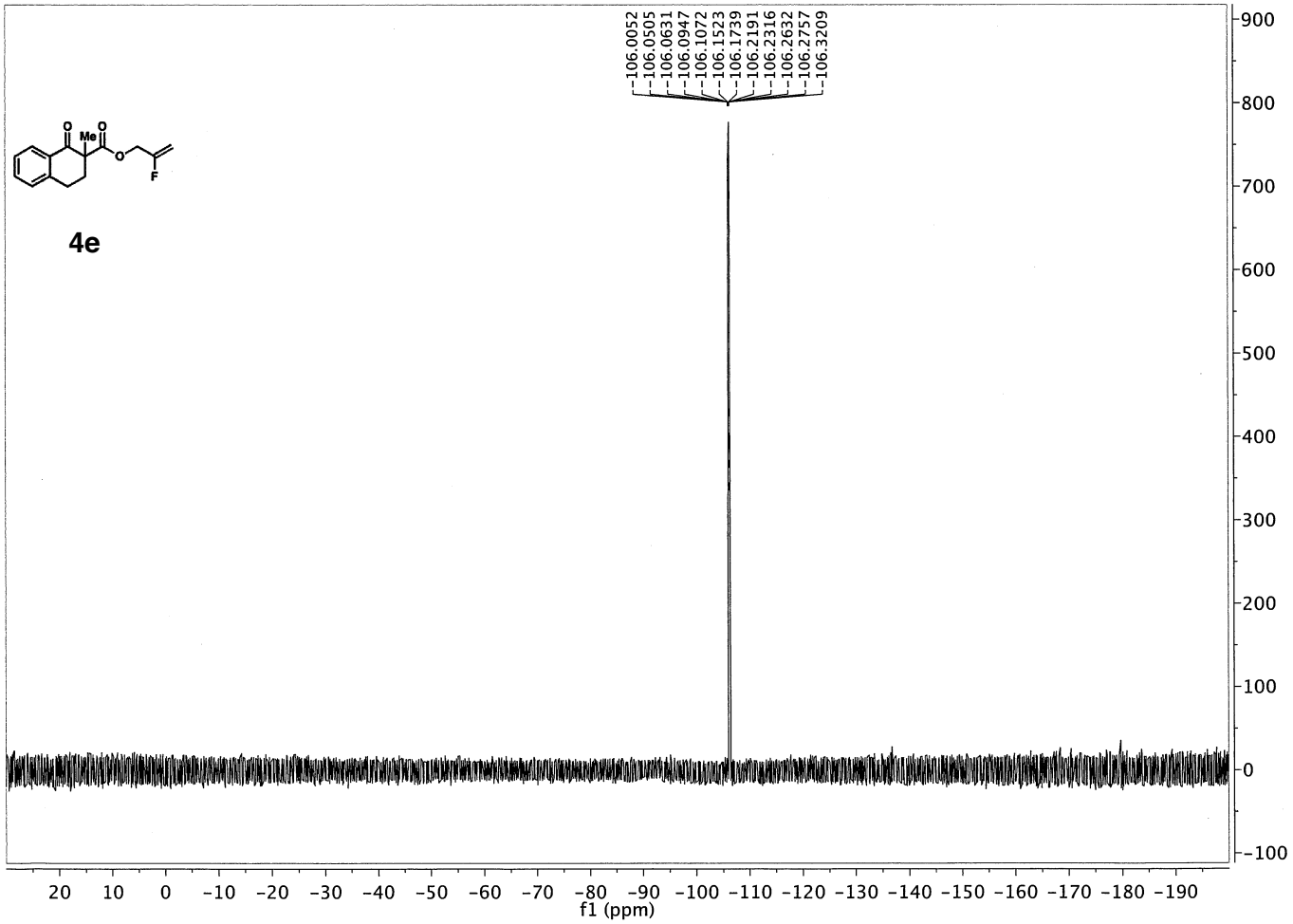
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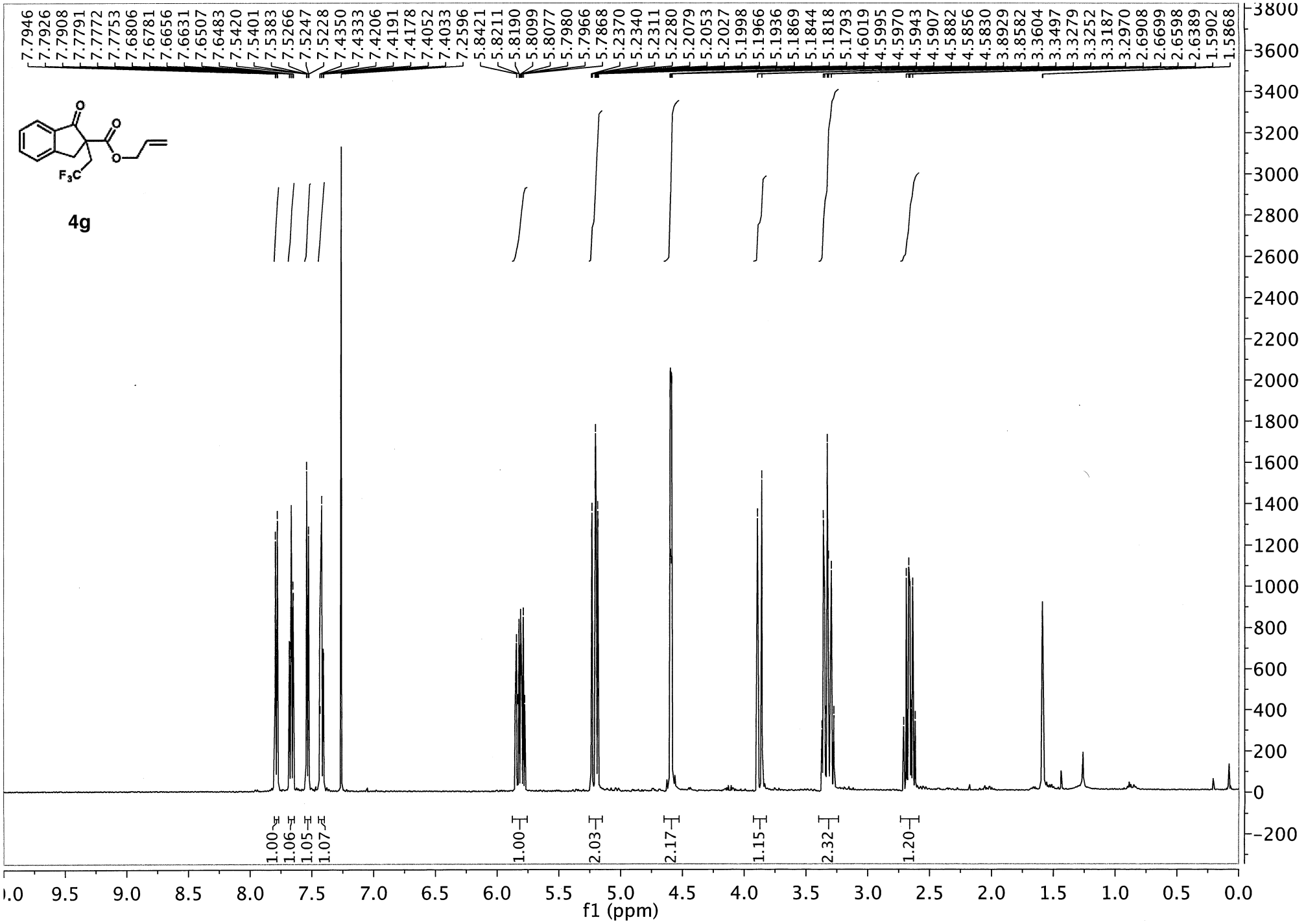
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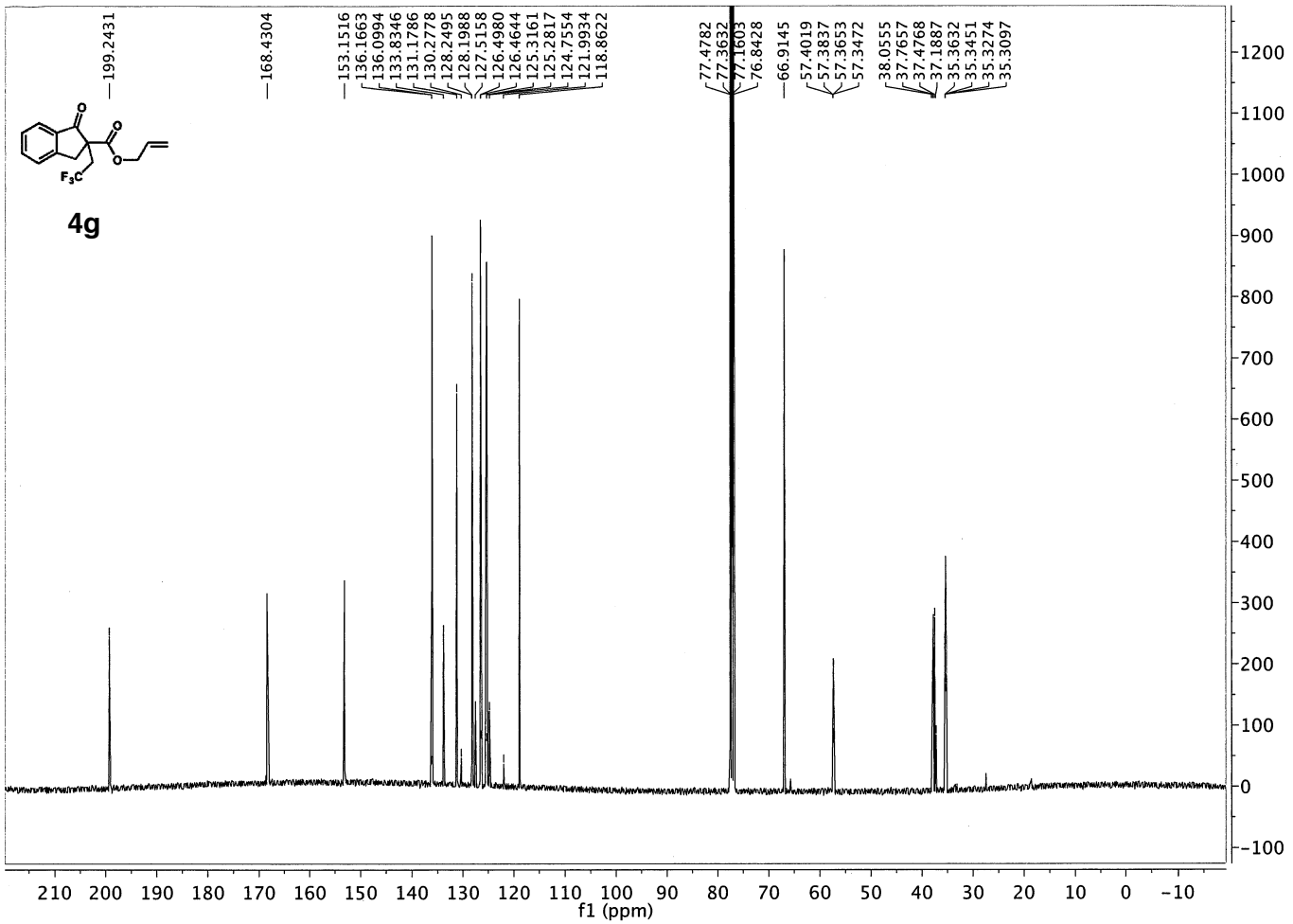
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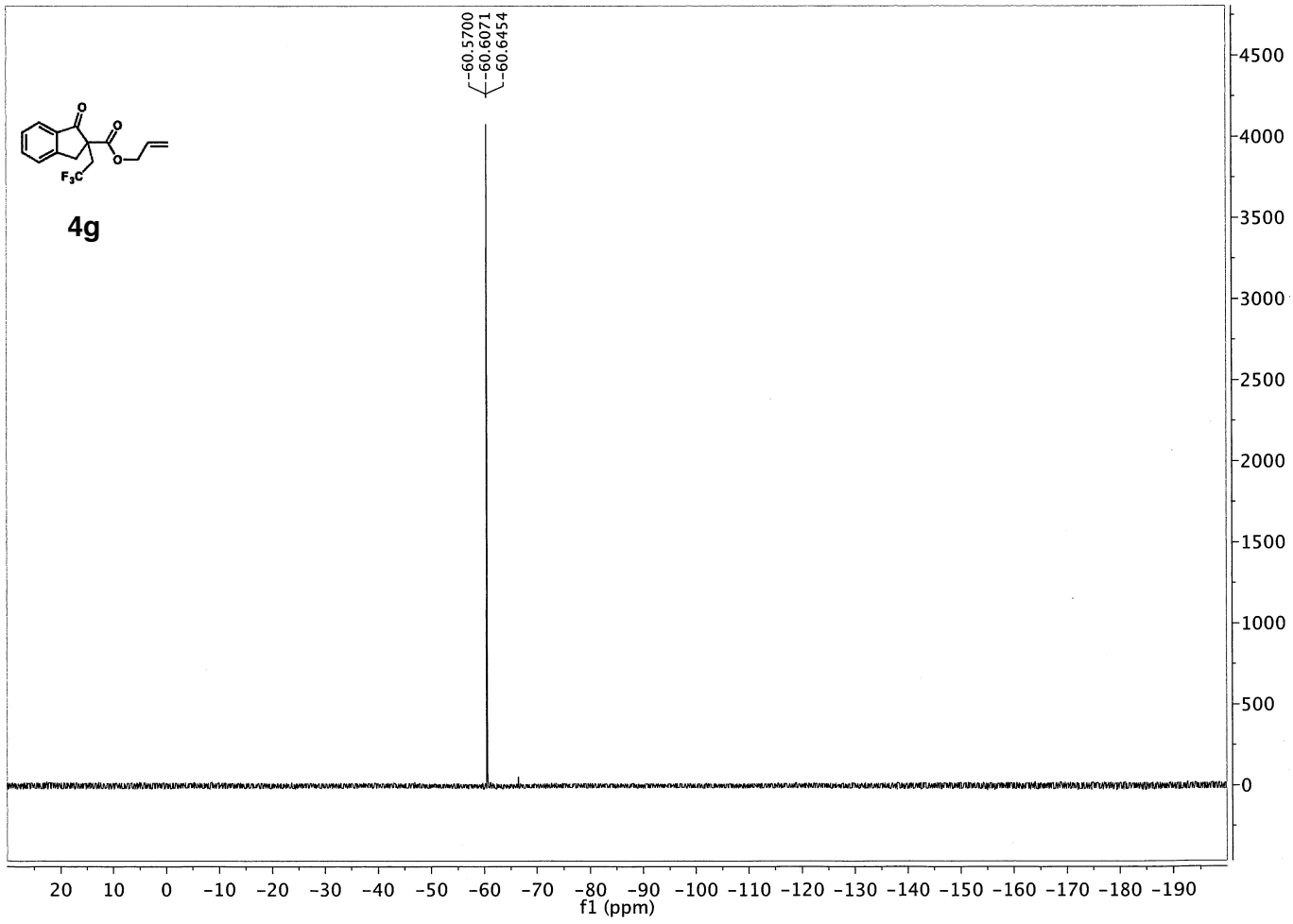
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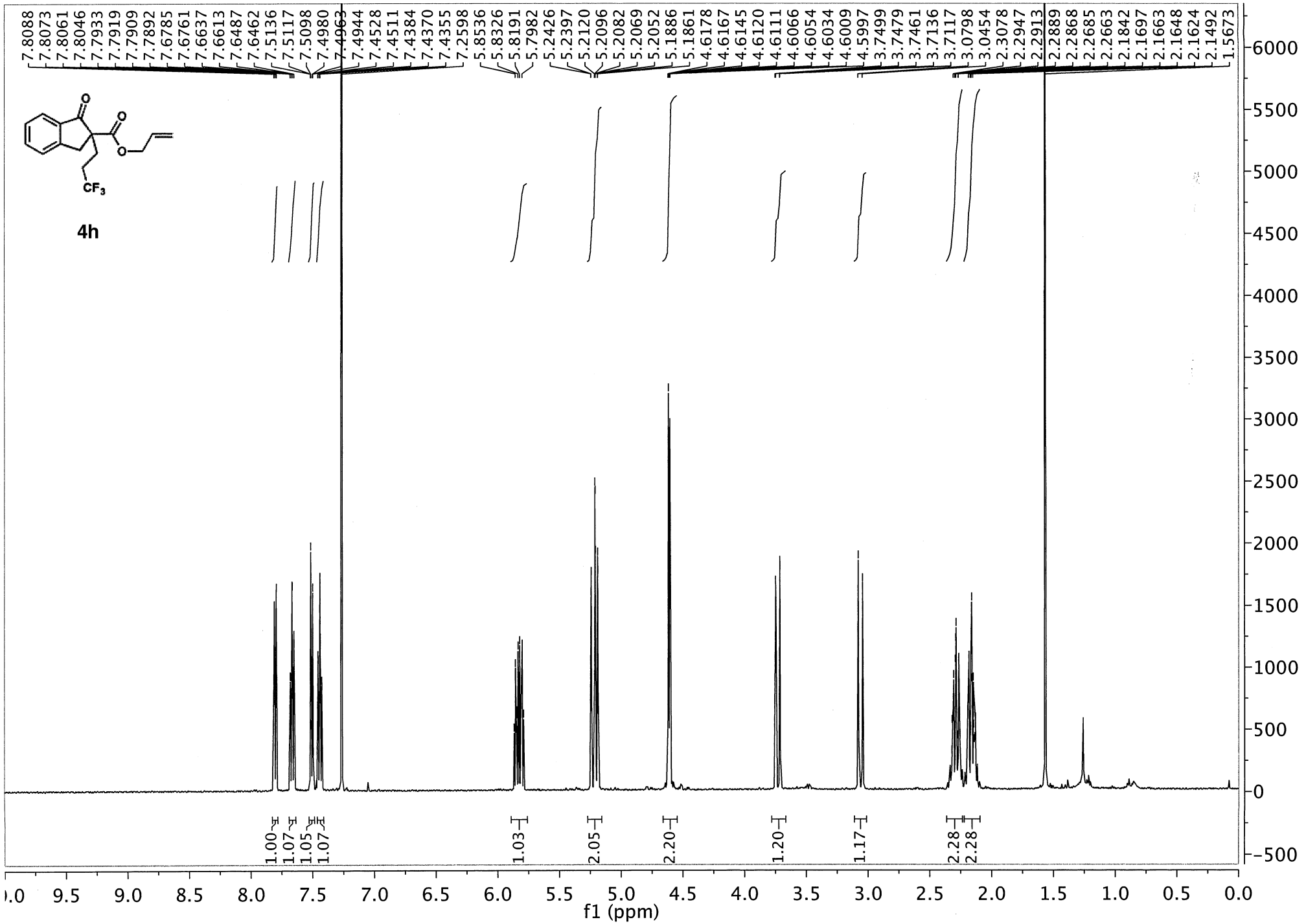
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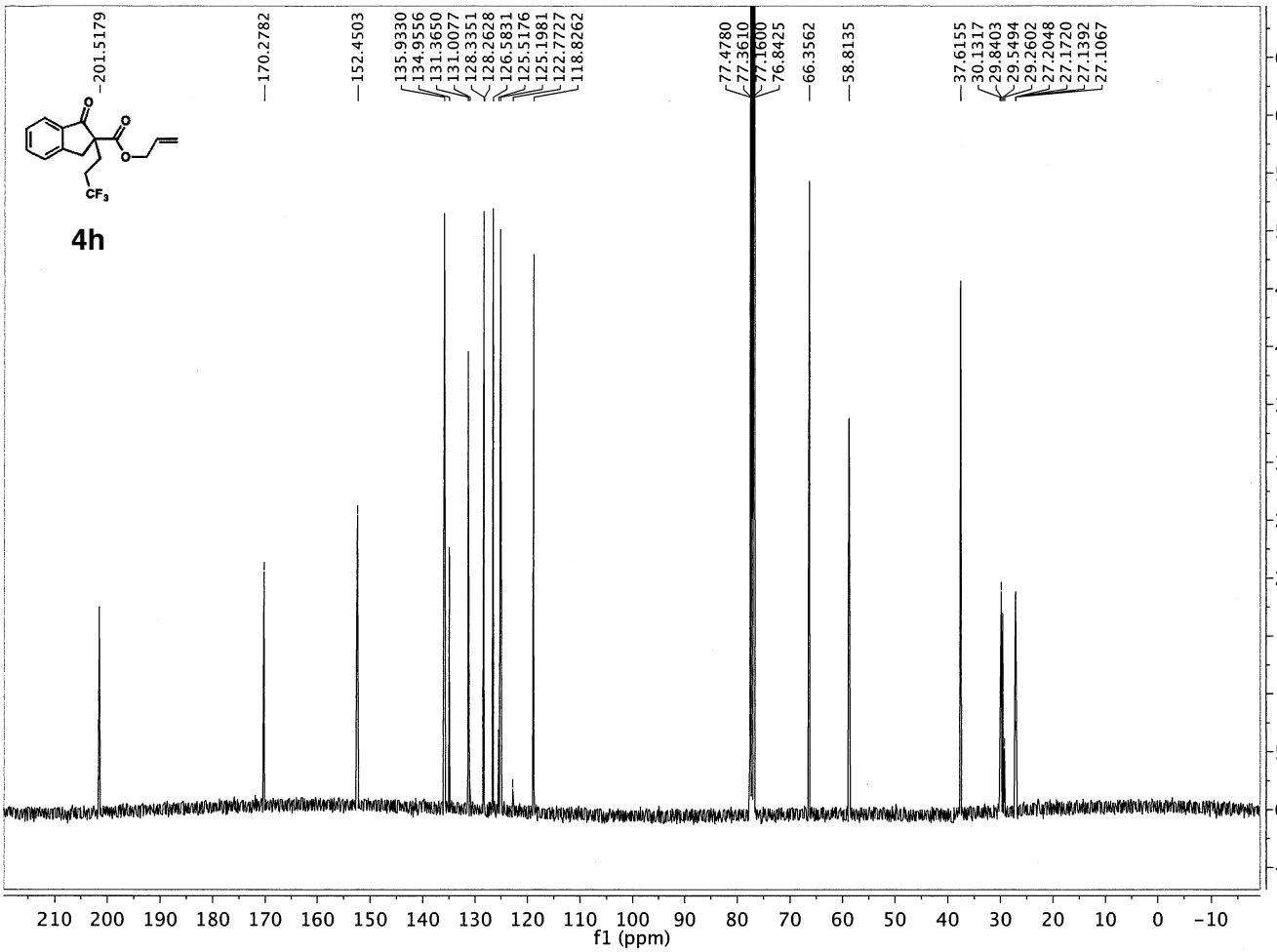
f1 (ppm)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128.2628
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125.5176
125.1981
122.7727
118.8262
77.4780
77.3610
77.1600
76.8425
66.3562
58.8135
37.6155
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29.2602
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27.1720
27.1392
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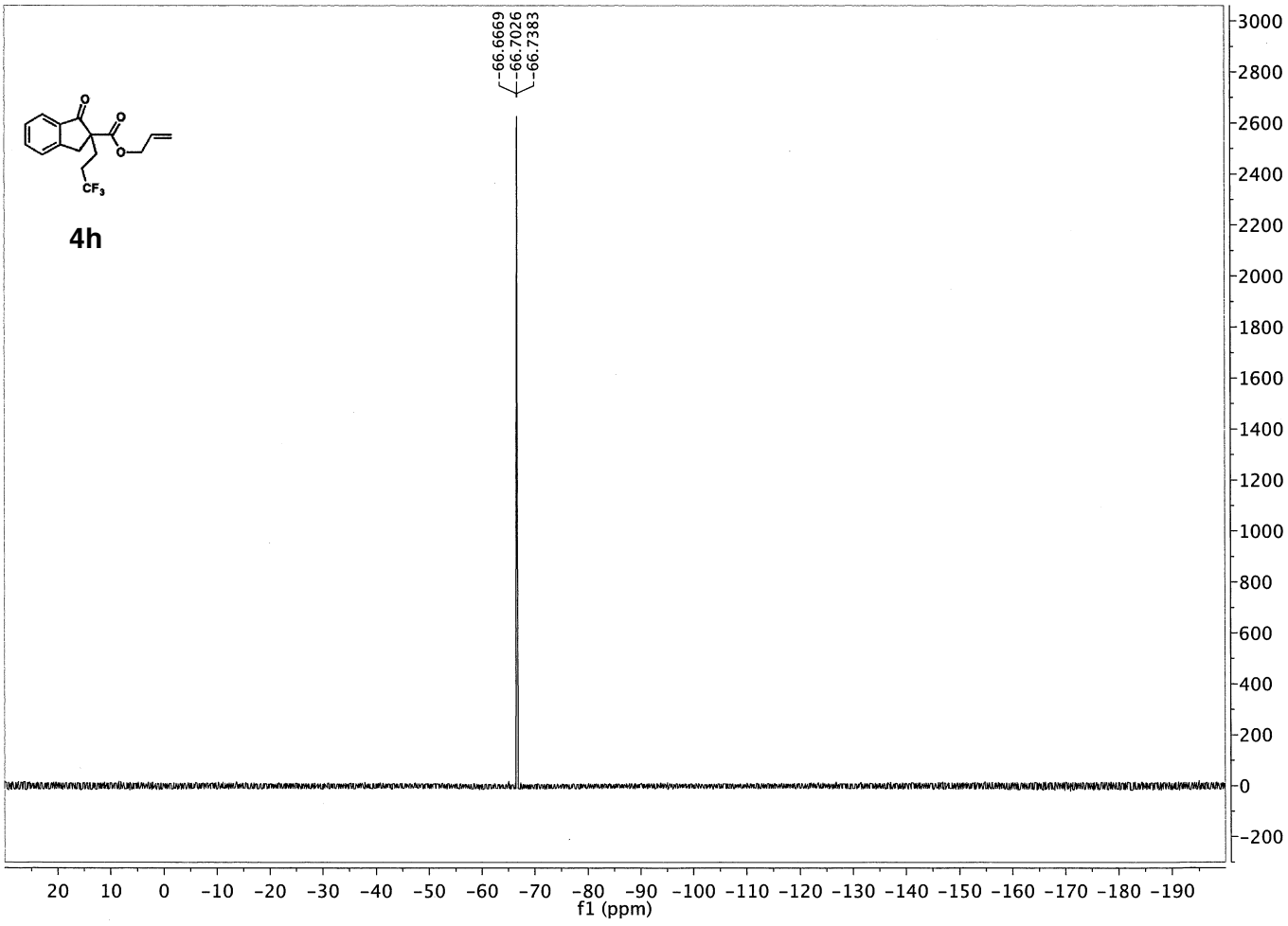
4h
f1 (ppm)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66.7383
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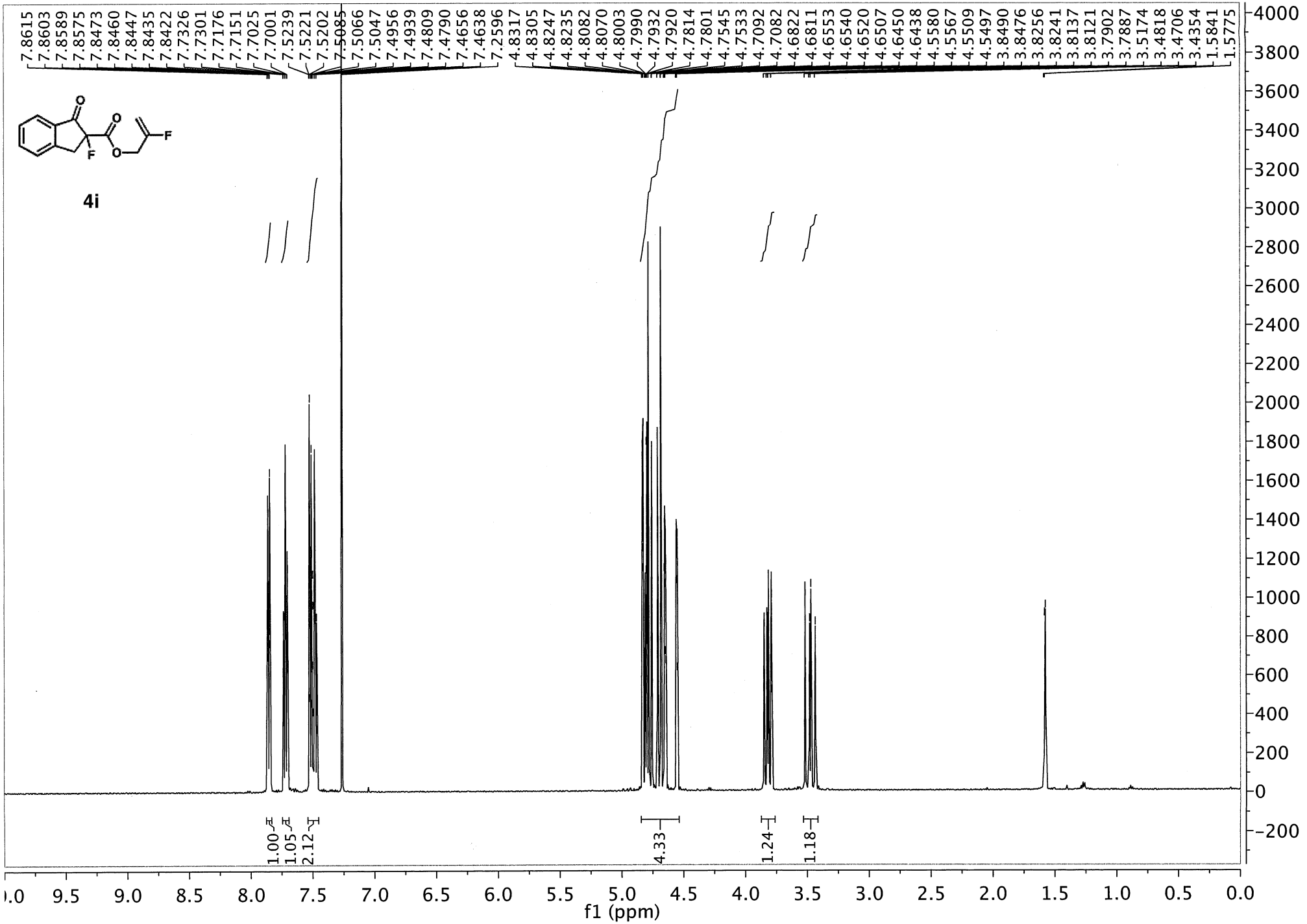
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7.8422
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7.7301
7.7176
7.7151
7.7025
7.7001
7.5239
7.5221
7.5202
7.5085
7.5066
7.5047
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7.4809
7.4790
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4.8305
4.8247
4.8235
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4.7990
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4.7801
4.7545
4.7533
4.7092
4.7082
4.6822
4.6811
4.6553
4.6540
4.6520
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4.6450
4.6438
4.5580
4.5567
4.5509
4.5497
3.8490
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3.8256
3.8241
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3.4818
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1.24
1.18
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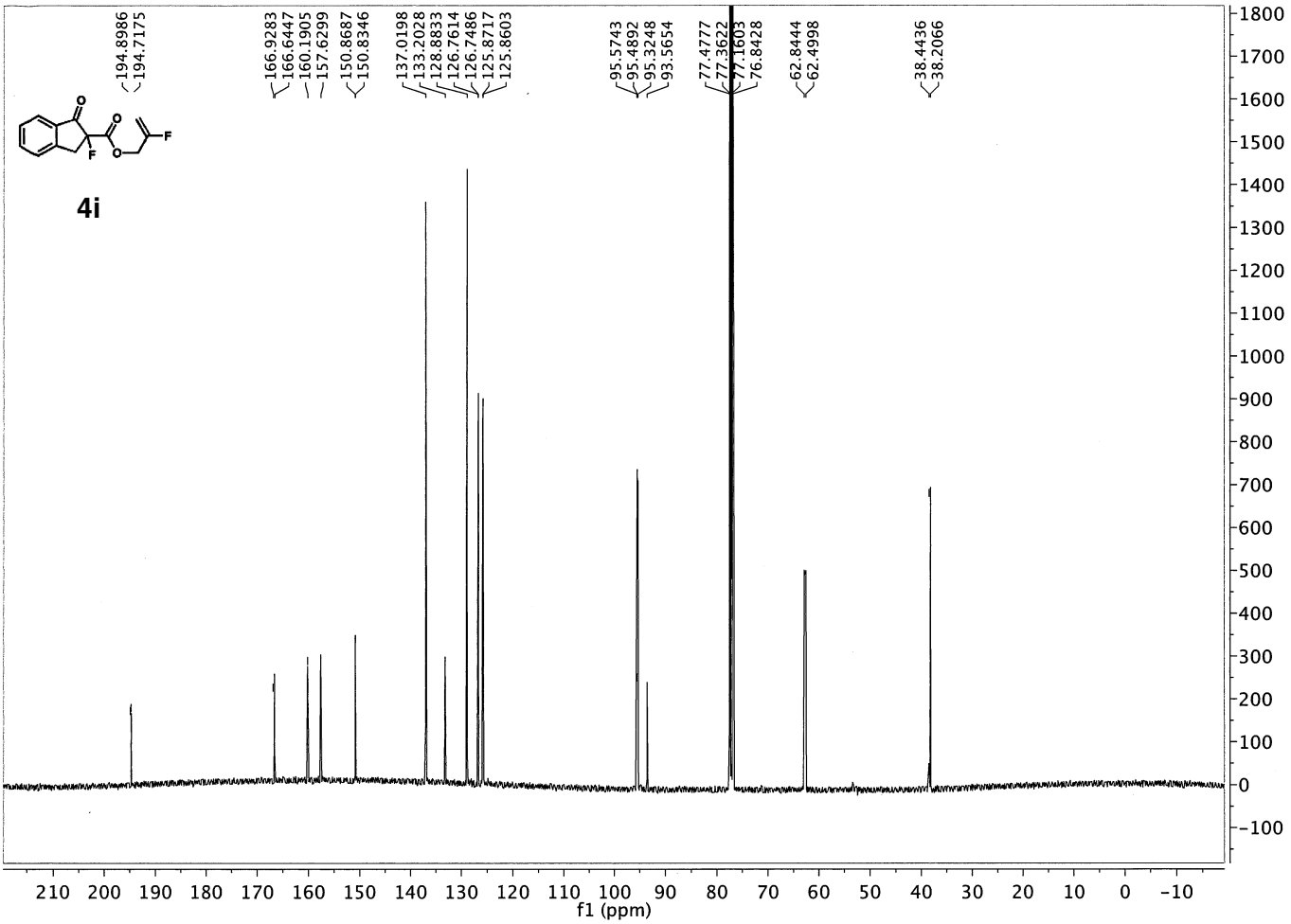
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128.8833
126.7614
126.7486
125.8717
125.8603
95.5743
95.4892
95.3248
93.5654
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38.4436
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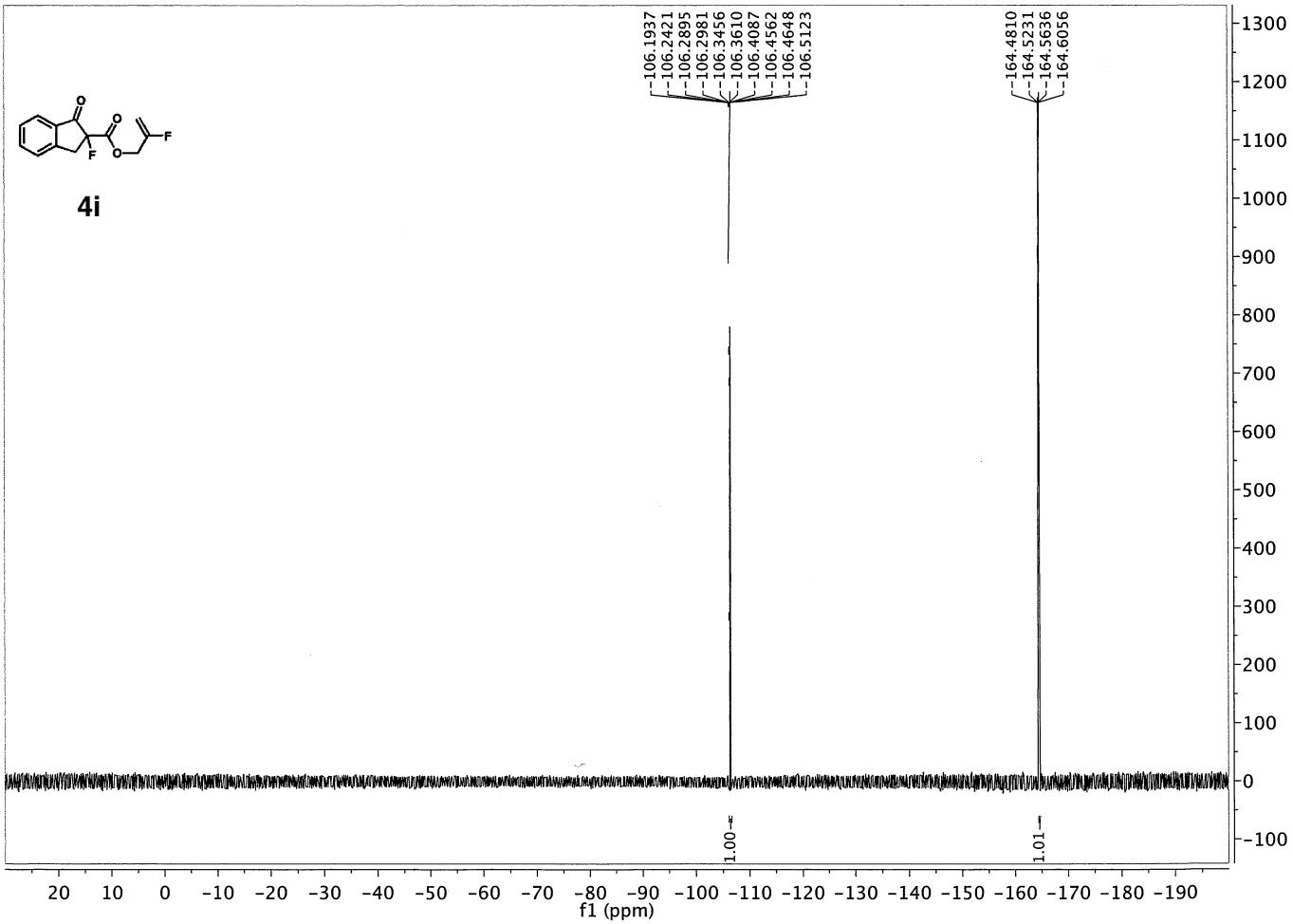
4i
f1 (ppm)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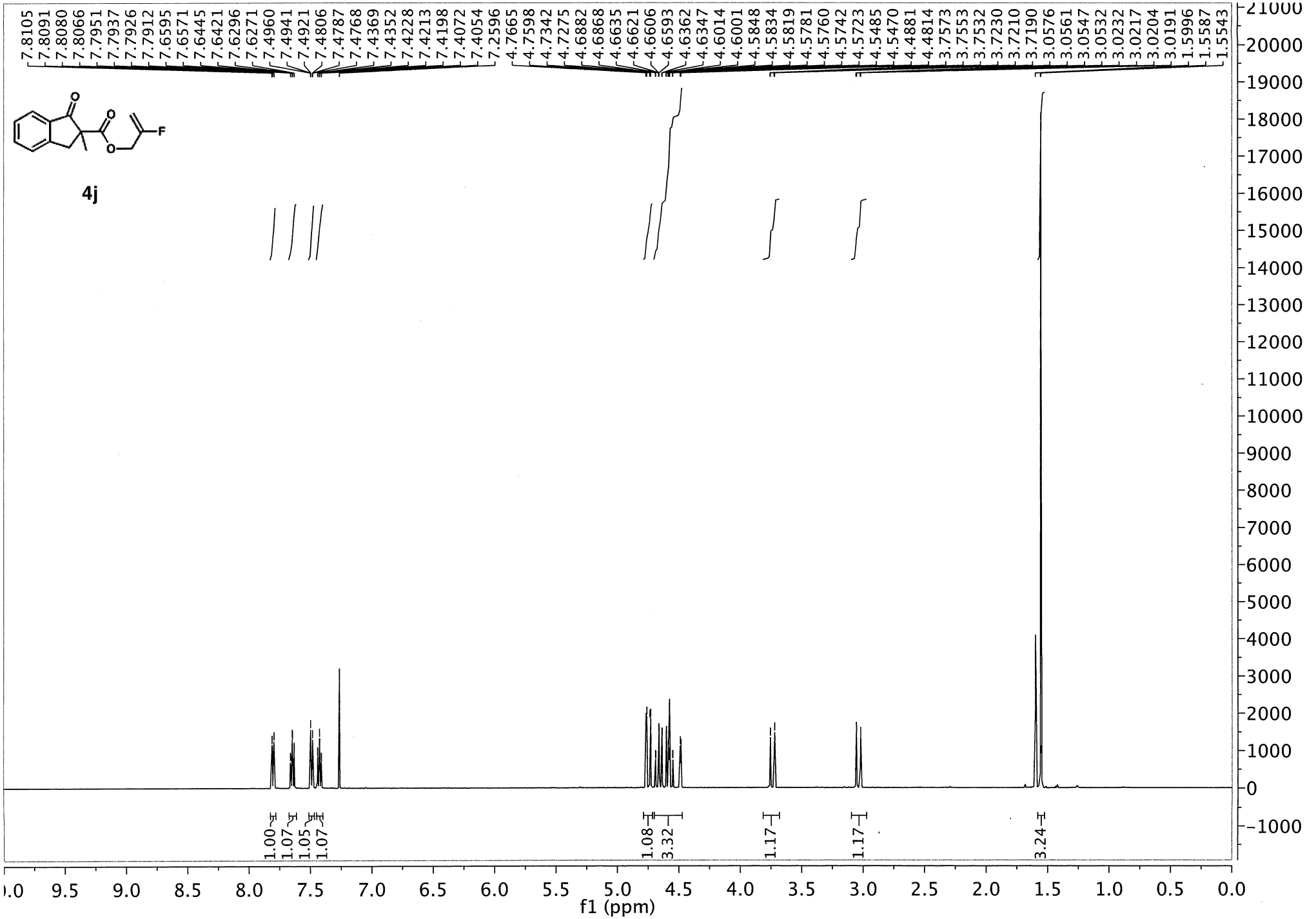
f1 (ppm)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4.7342
4.7275
4.6882
4.6868
4.6635
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4.6593
4.6362
4.6347
4.6014
4.6001
4.5848
4.5834
4.5819
4.5781
4.5760
4.5742
4.5723
4.5485
4.5470
4.4881
4.4814
3.7573
3.7553
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3.7230
3.7210
3.7190
3.0576
3.0561
3.0547
3.0532
3.0232
3.0217
3.0204
3.0191
1.5996
1.5587
1.5543
O
O
O
F
4j
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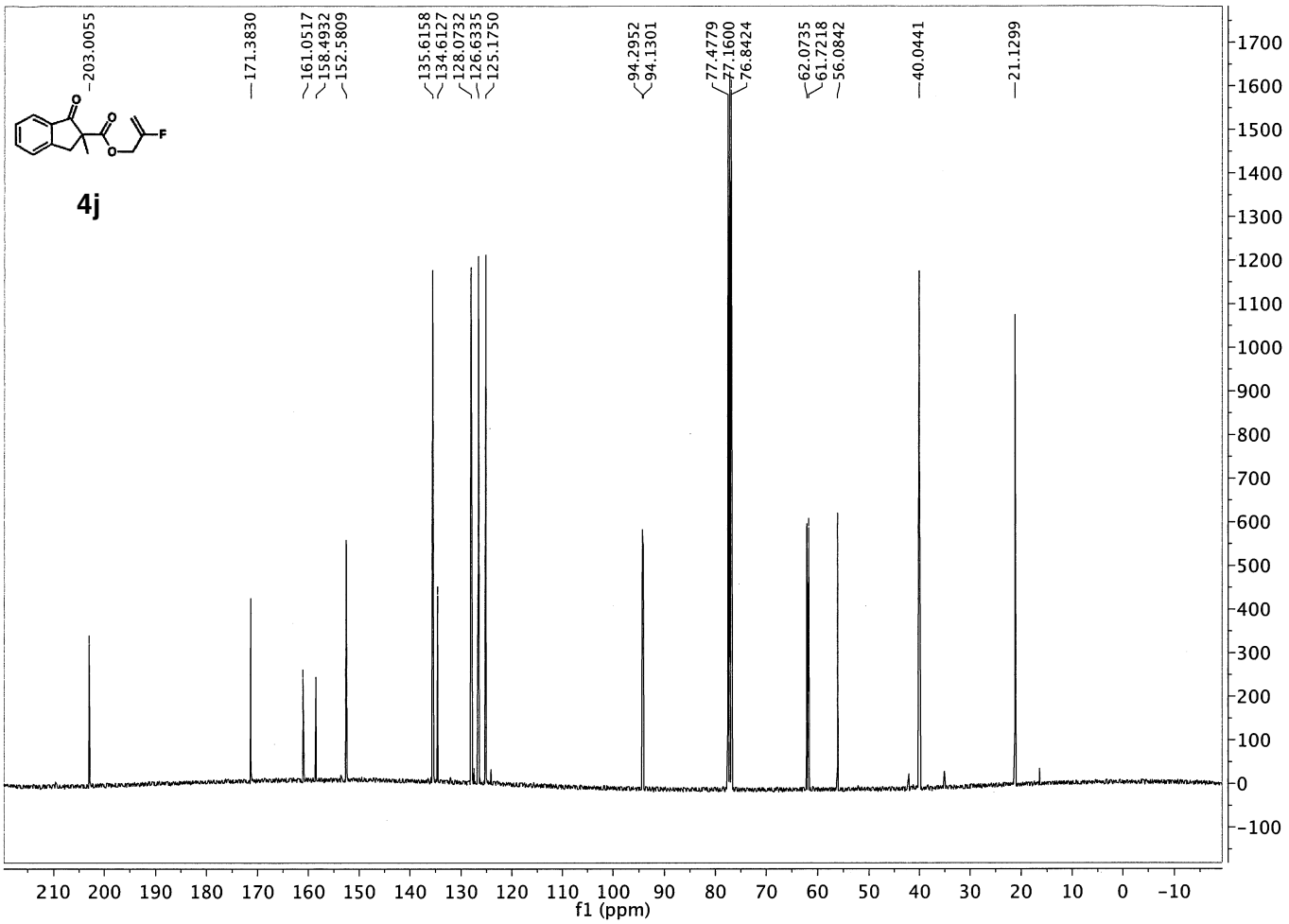
1.07
1.05
1.07
1.08
3.32
1.17
1.17
3.24
f1 (ppm)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56.0842
40.0441
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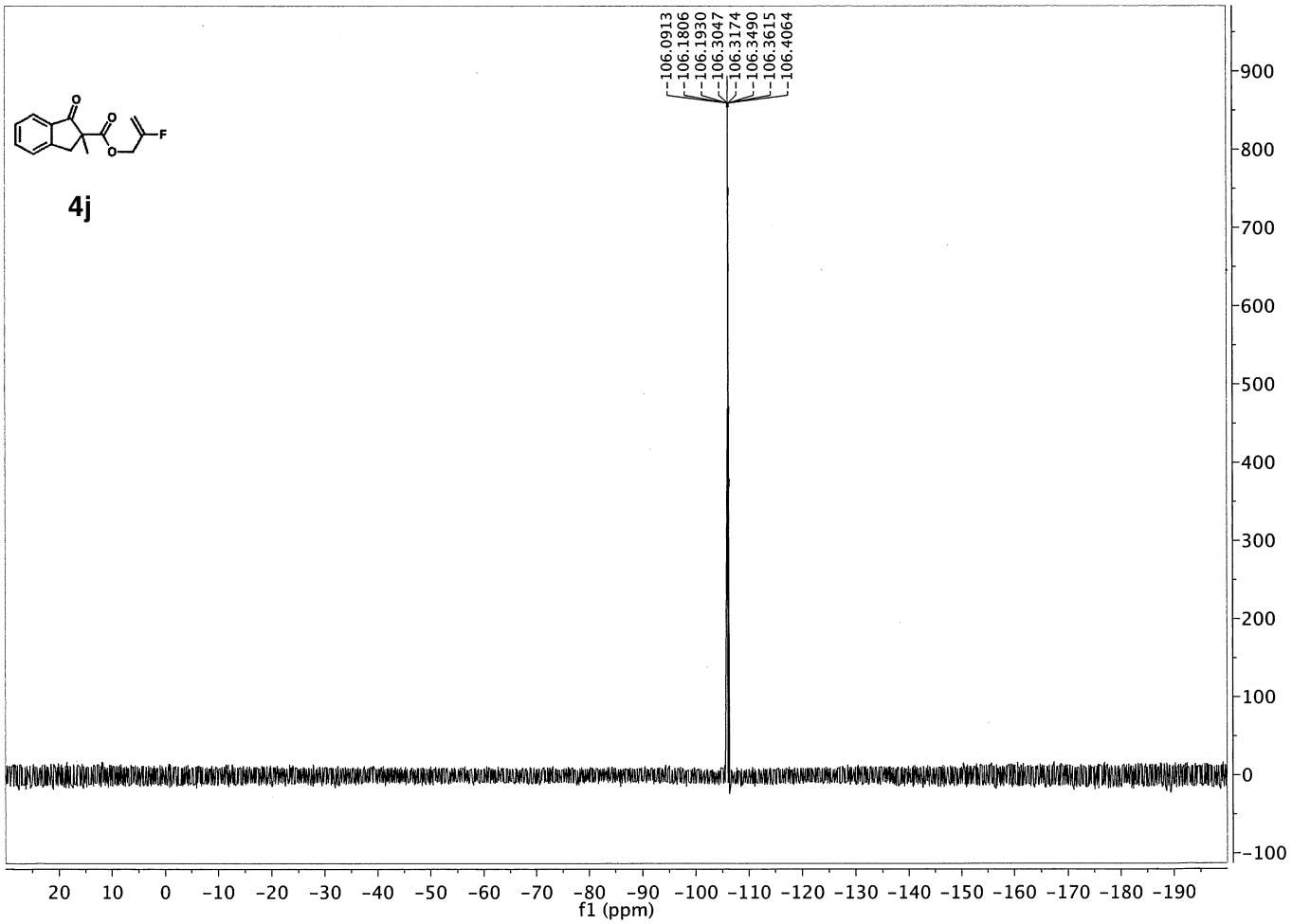
f1 (ppm)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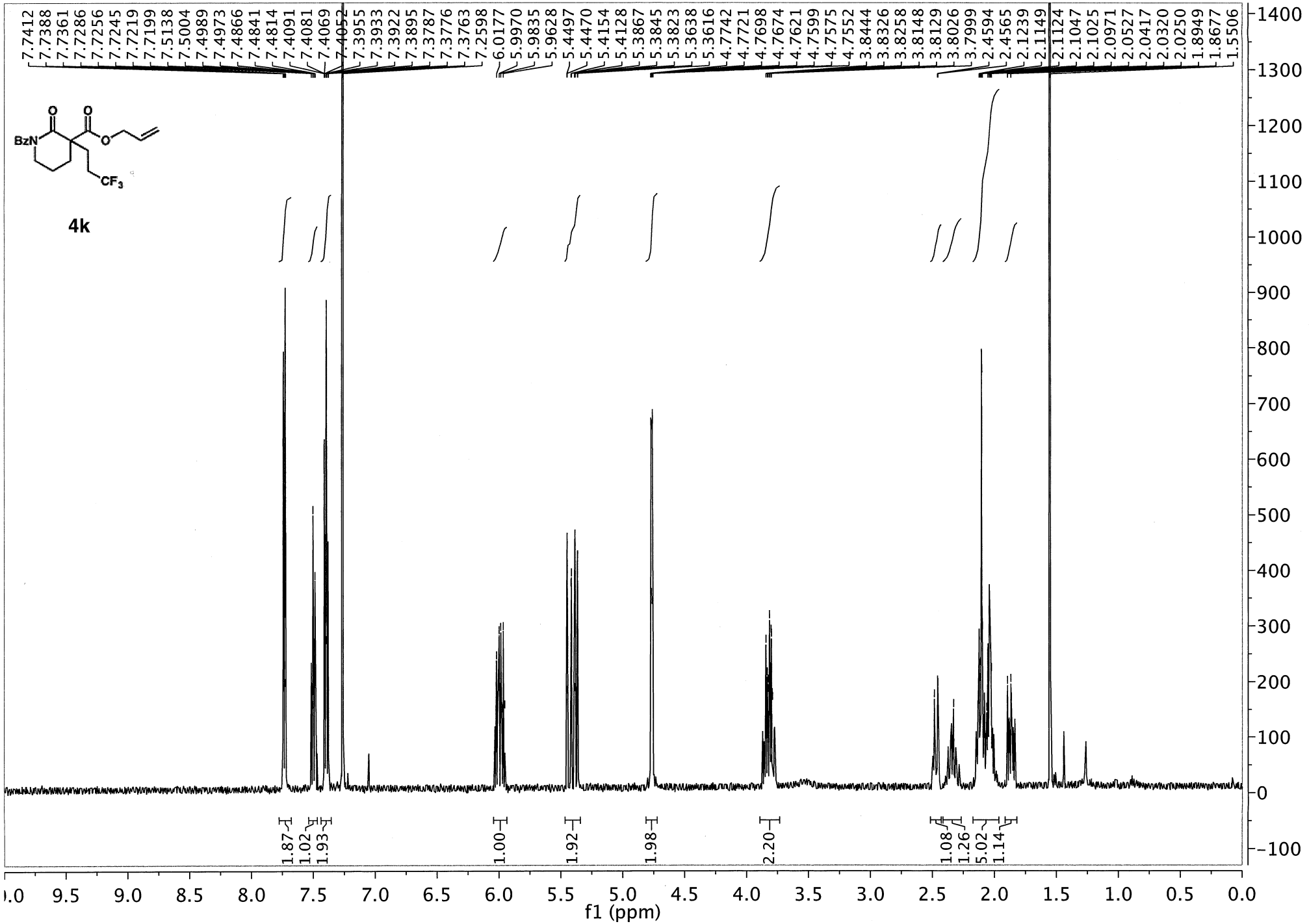
4j
f1 (ppm)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7.4973
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7.4841
7.4814
7.4091
7.4081
7.4069
7.4052
7.3955
7.3933
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7.3895
7.3787
7.3776
7.3763
7.2598
6.0177
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5.9835
5.9628
5.4497
5.4470
5.4154
5.4128
5.3867
5.3845
5.3823
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5.3616
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4.7575
4.7552
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3.8129
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3.7999
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2.1149
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2.1047
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2.0527
2.0417
2.0320
2.0250
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1.5506
BzN
O
O
O
CF3
4k
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1.98
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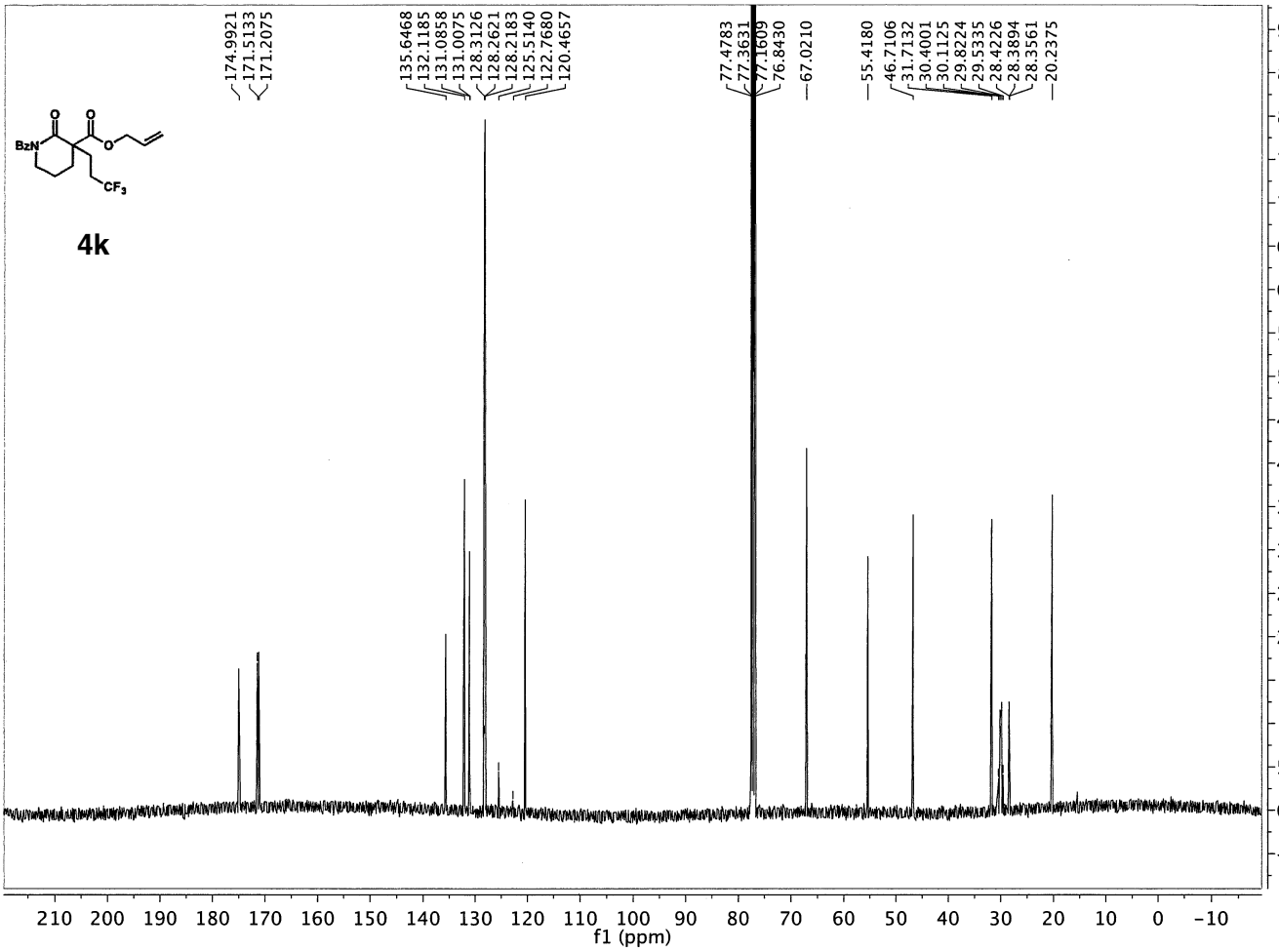
1.08
1.26
5.02
1.14
f1 (ppm)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46.7106
31.7132
30.4001
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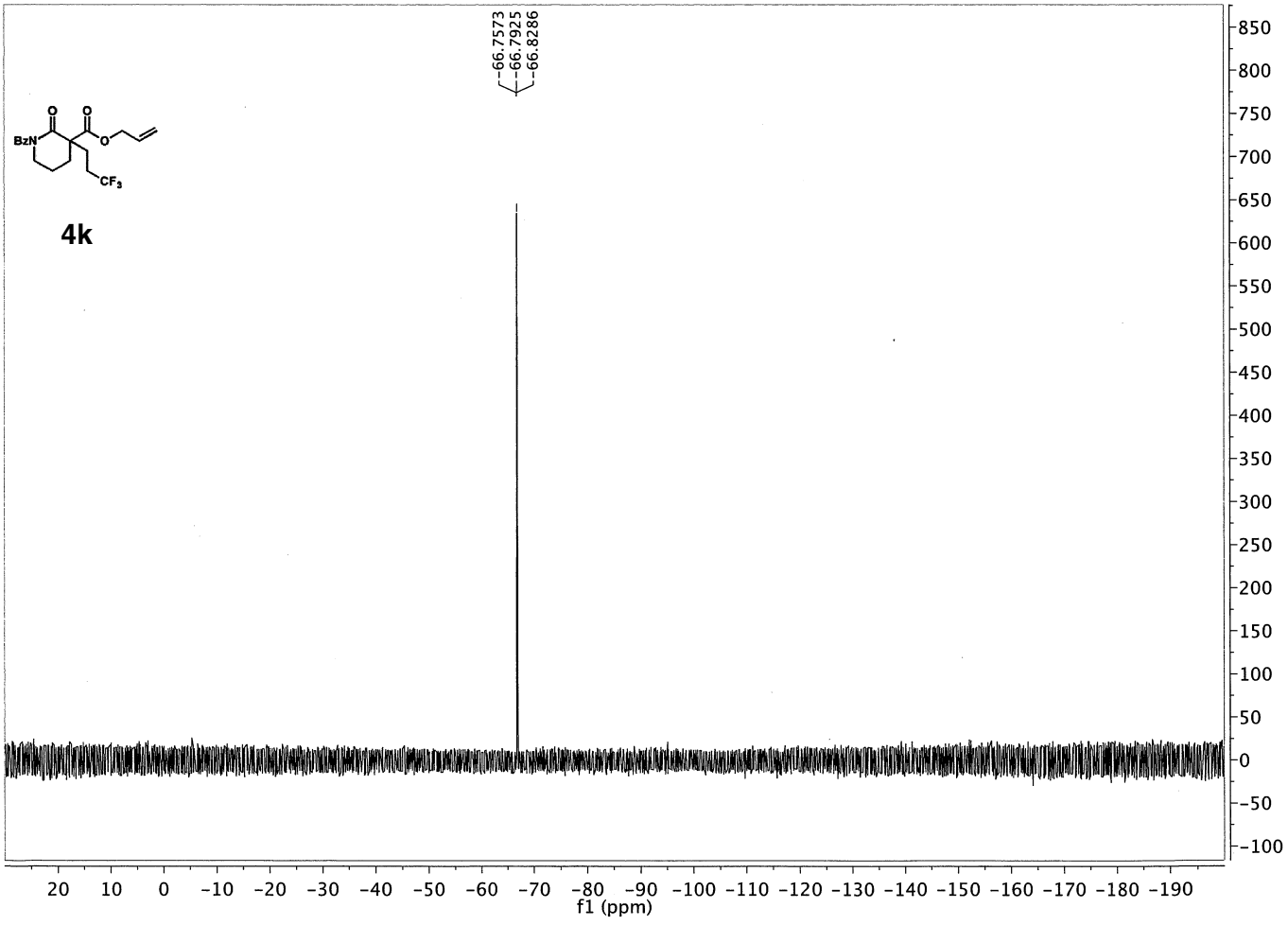
20.2375
BzN
CF3
4k
f1 (ppm)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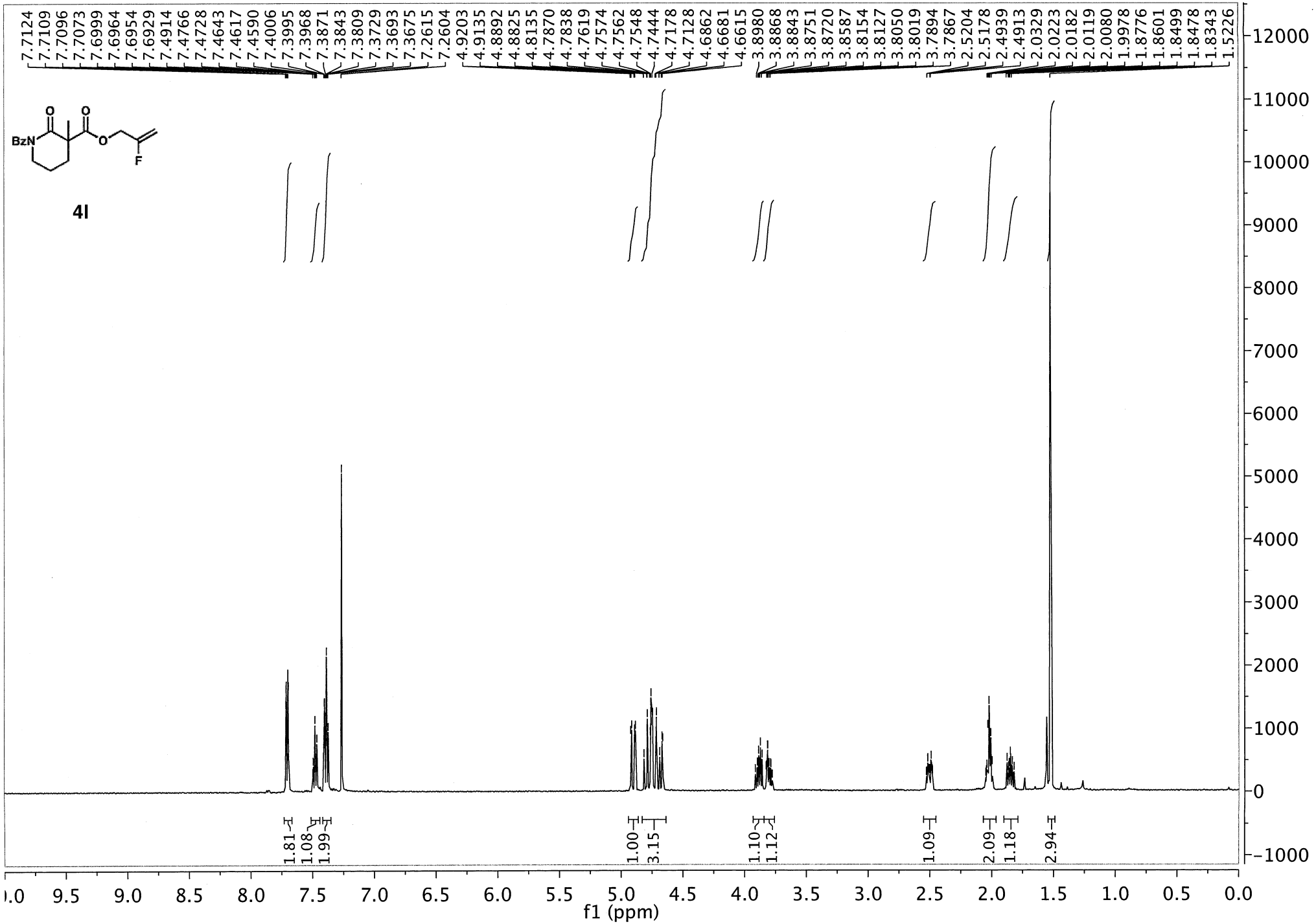
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7.3843
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7.3729
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7.3675
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O
O
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1.08
1.99
1.00
3.15
1.10
1.12
1.09
2.09
1.18
2.94
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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1.0
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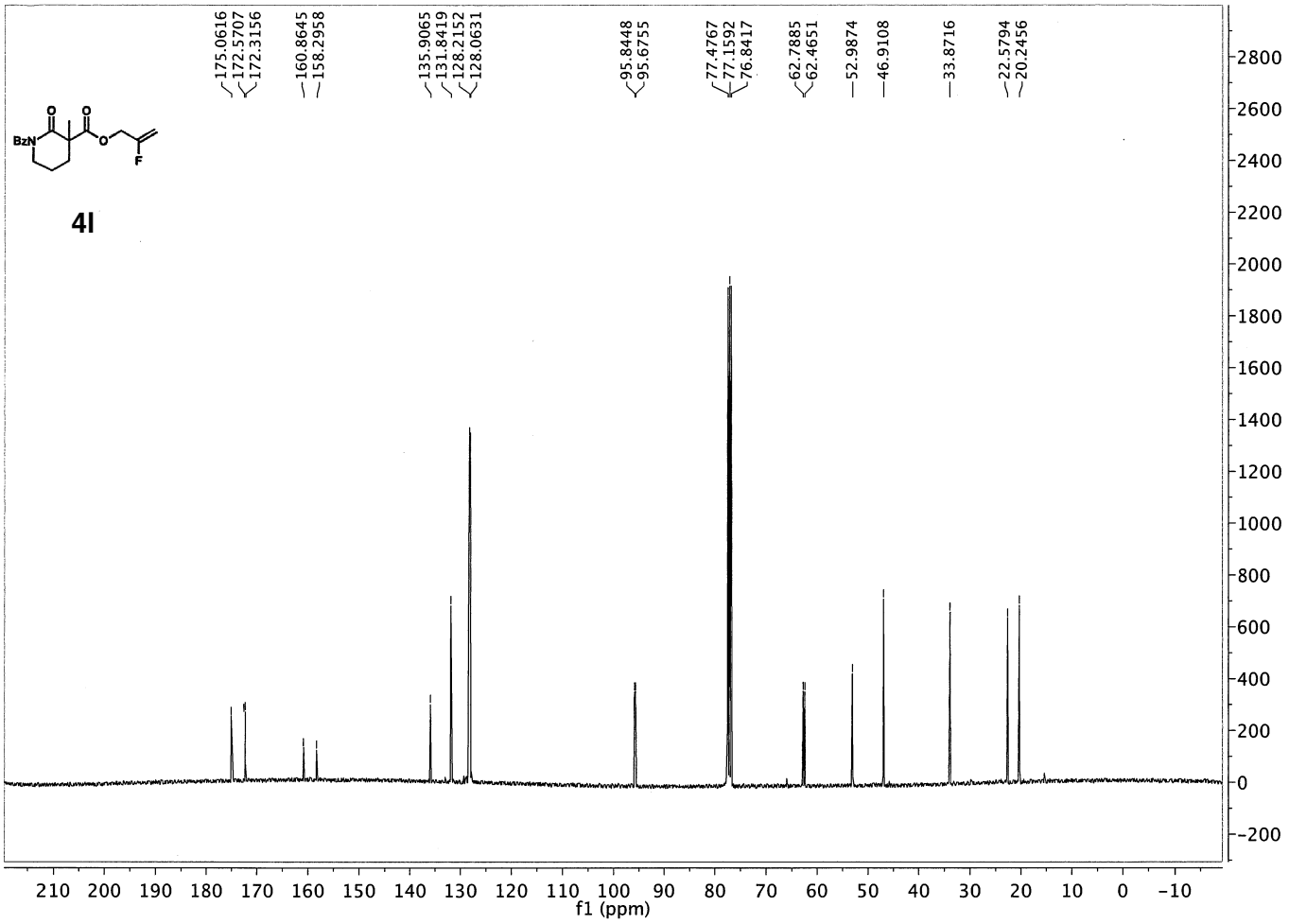
0.0
f1 (ppm)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77.4767
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76.8417
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62.4651
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20.2456
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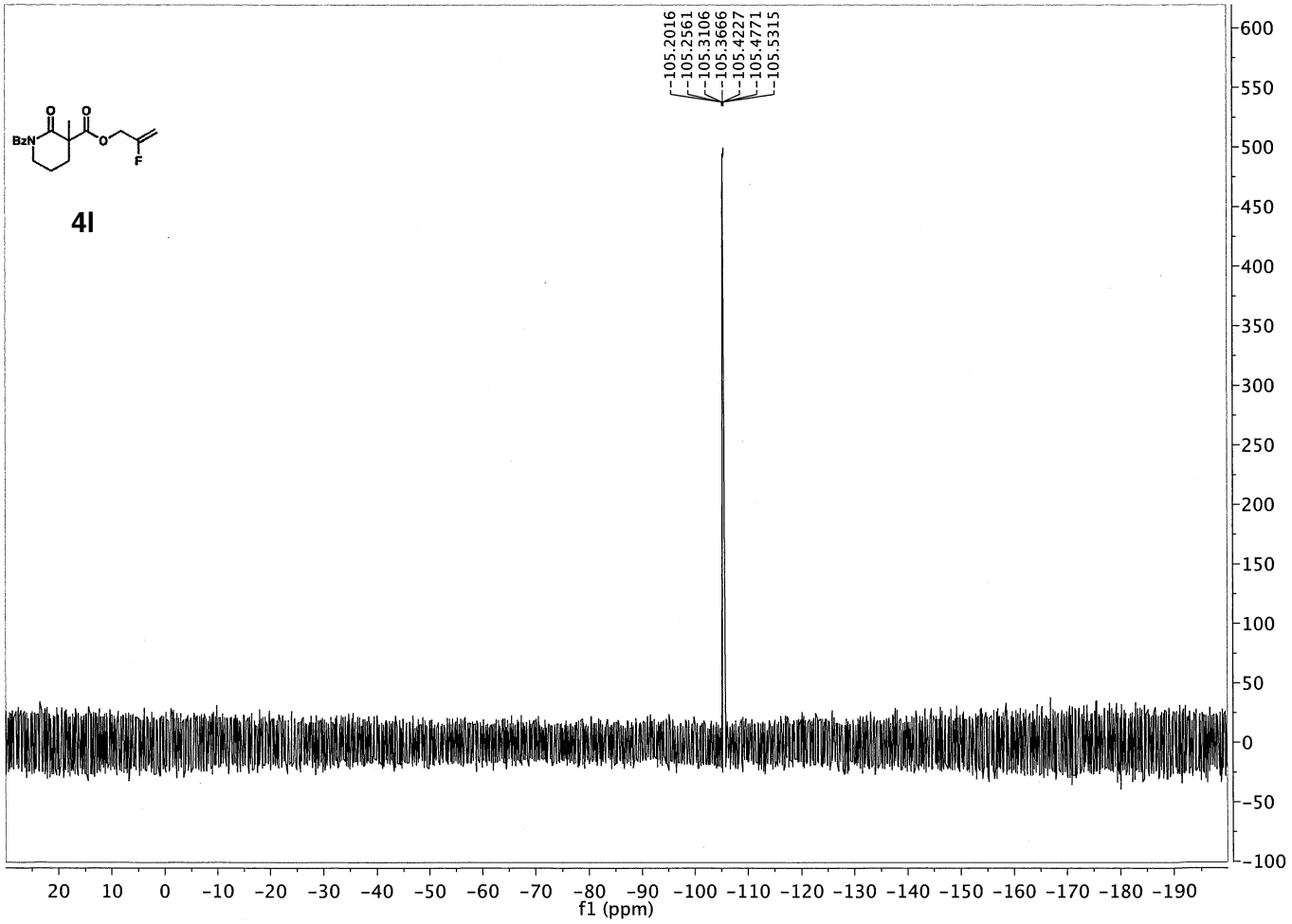
O
F
4l
f1 (ppm)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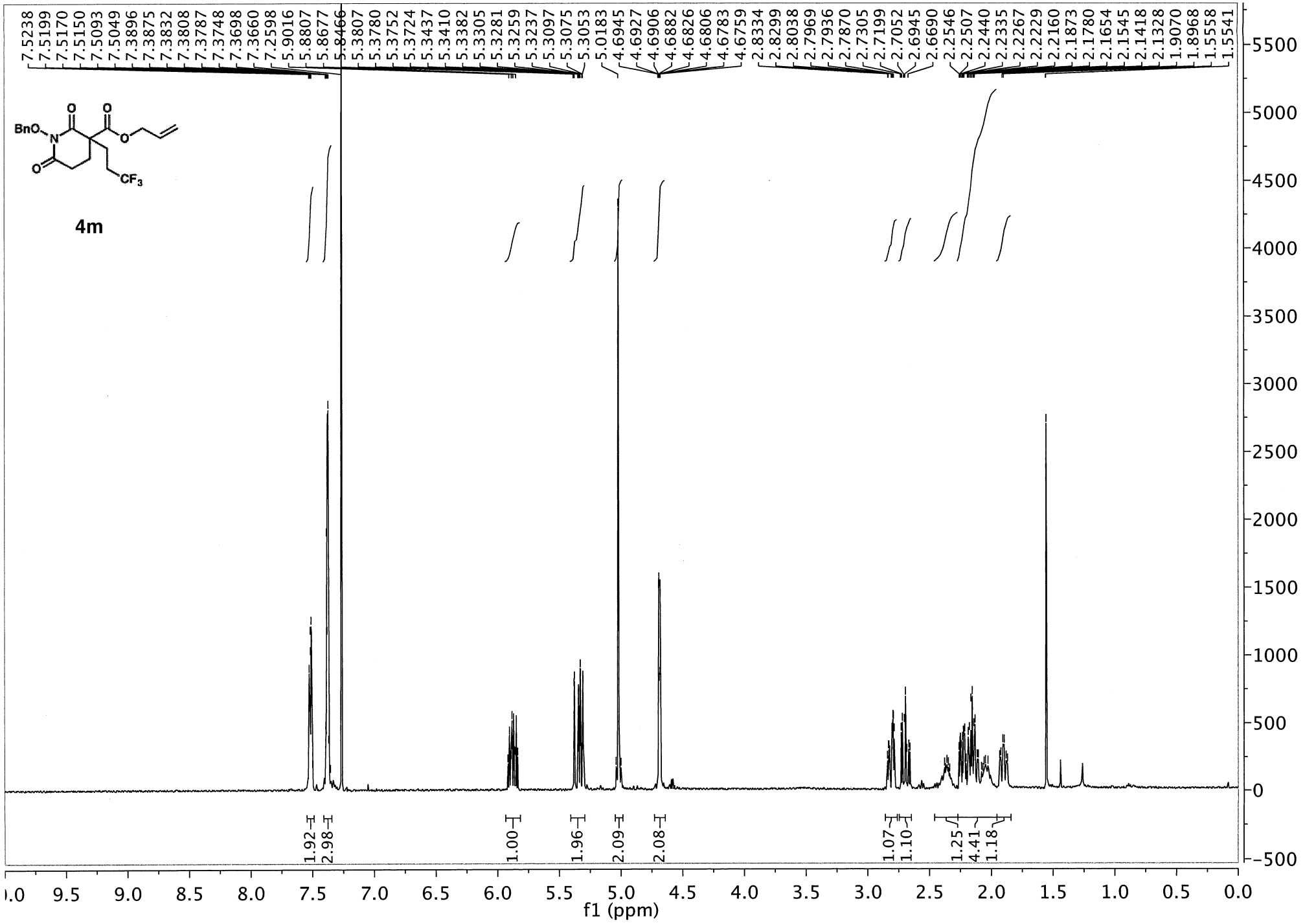
F
4l
f1 (ppm)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7.2598
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5.3281
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2.1328
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1.5541
BnO
N
O
O
O
O
CF3
4m
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2.08
1.07
1.10
1.25
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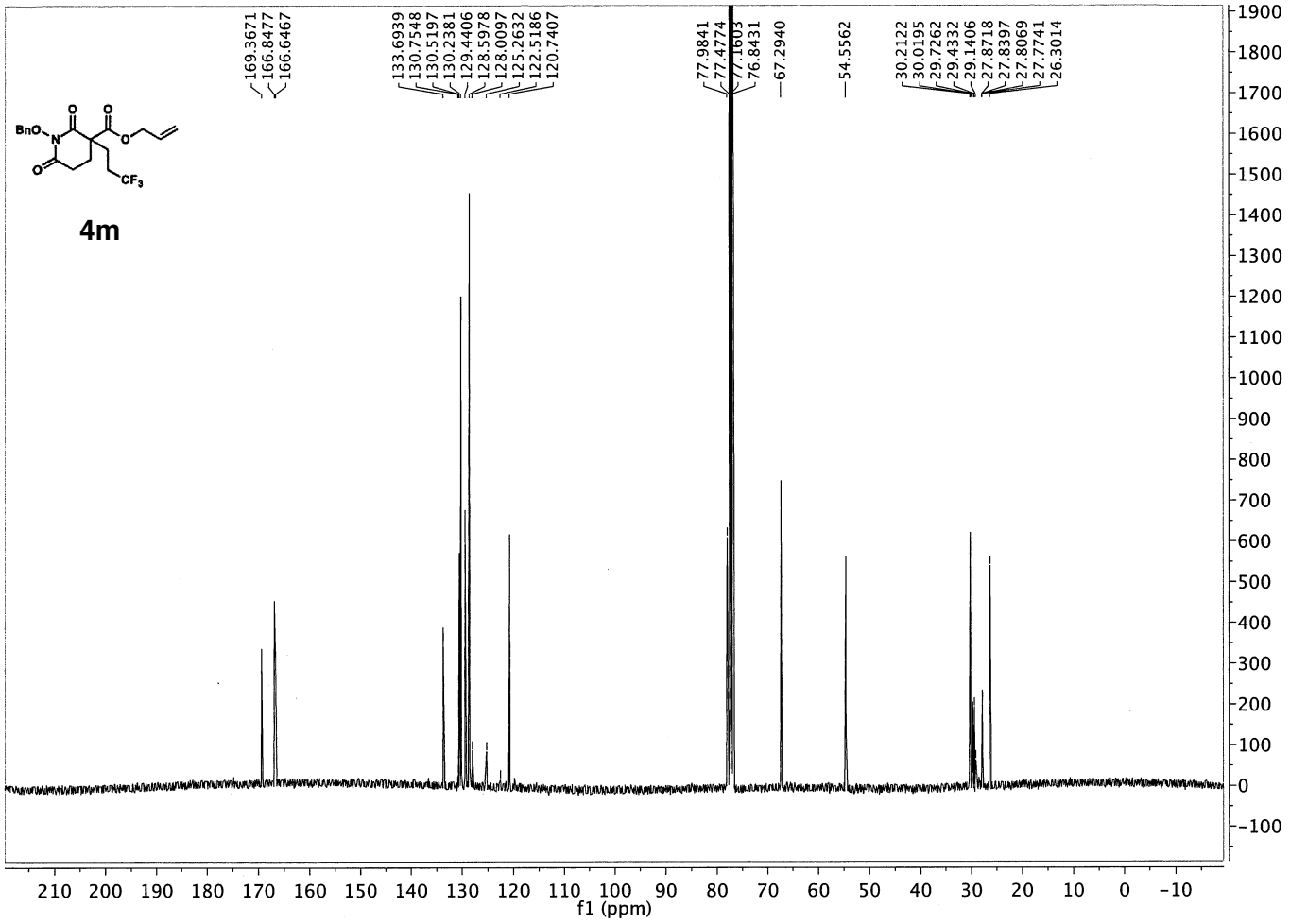
1.18
f1 (ppm)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76.8431
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30.0195
29.7262
29.4332
29.1406
27.8718
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BnO
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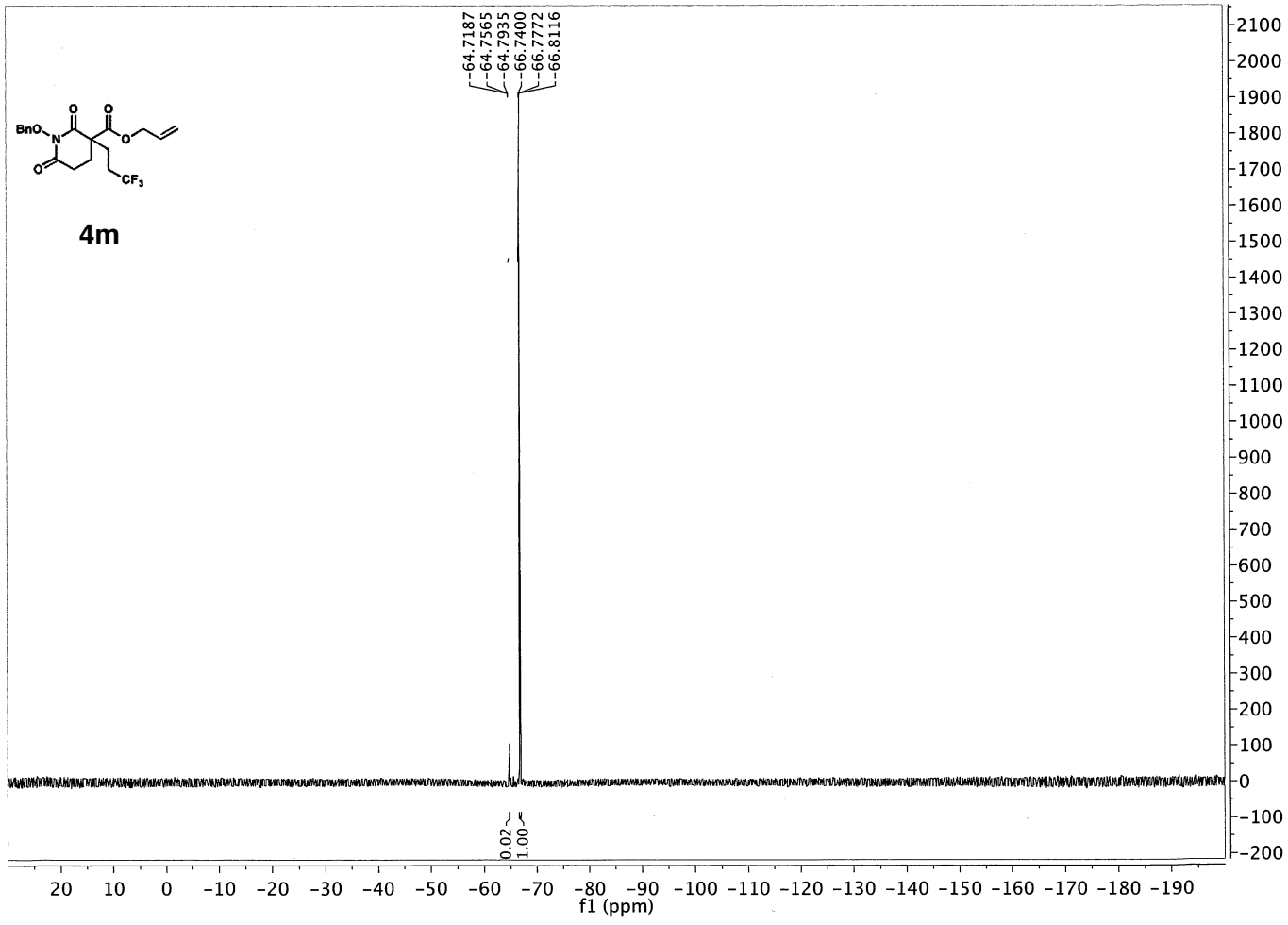
O
O
O
CF3
4m
f1 (ppm)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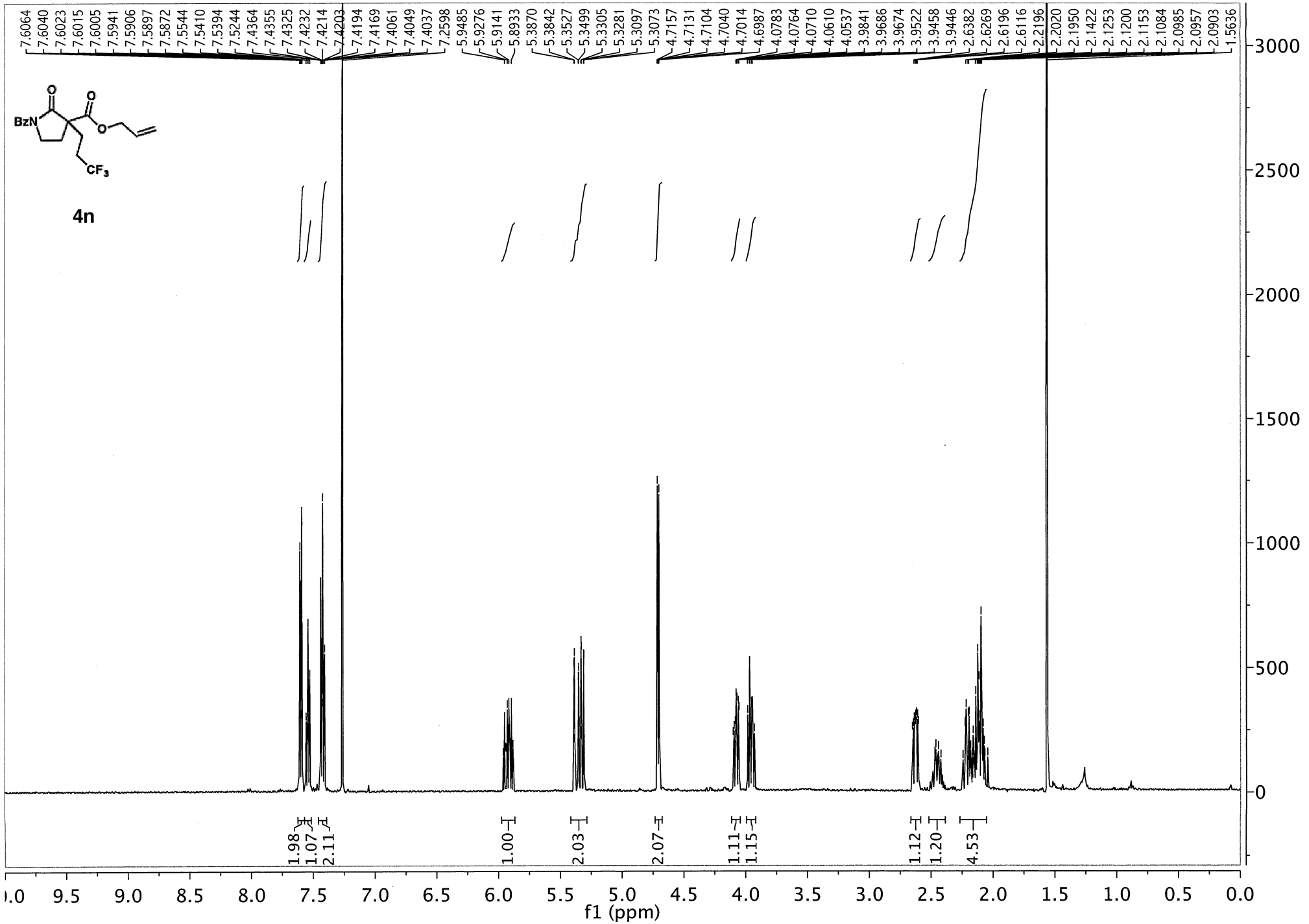
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2.0903
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O
O
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CF3
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2.11
1.00
2.03
2.07
1.11
1.15
1.12
1.20
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2500
2000
1500
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8.5
8.0
7.5
7.0
6.5
6.0
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1.5
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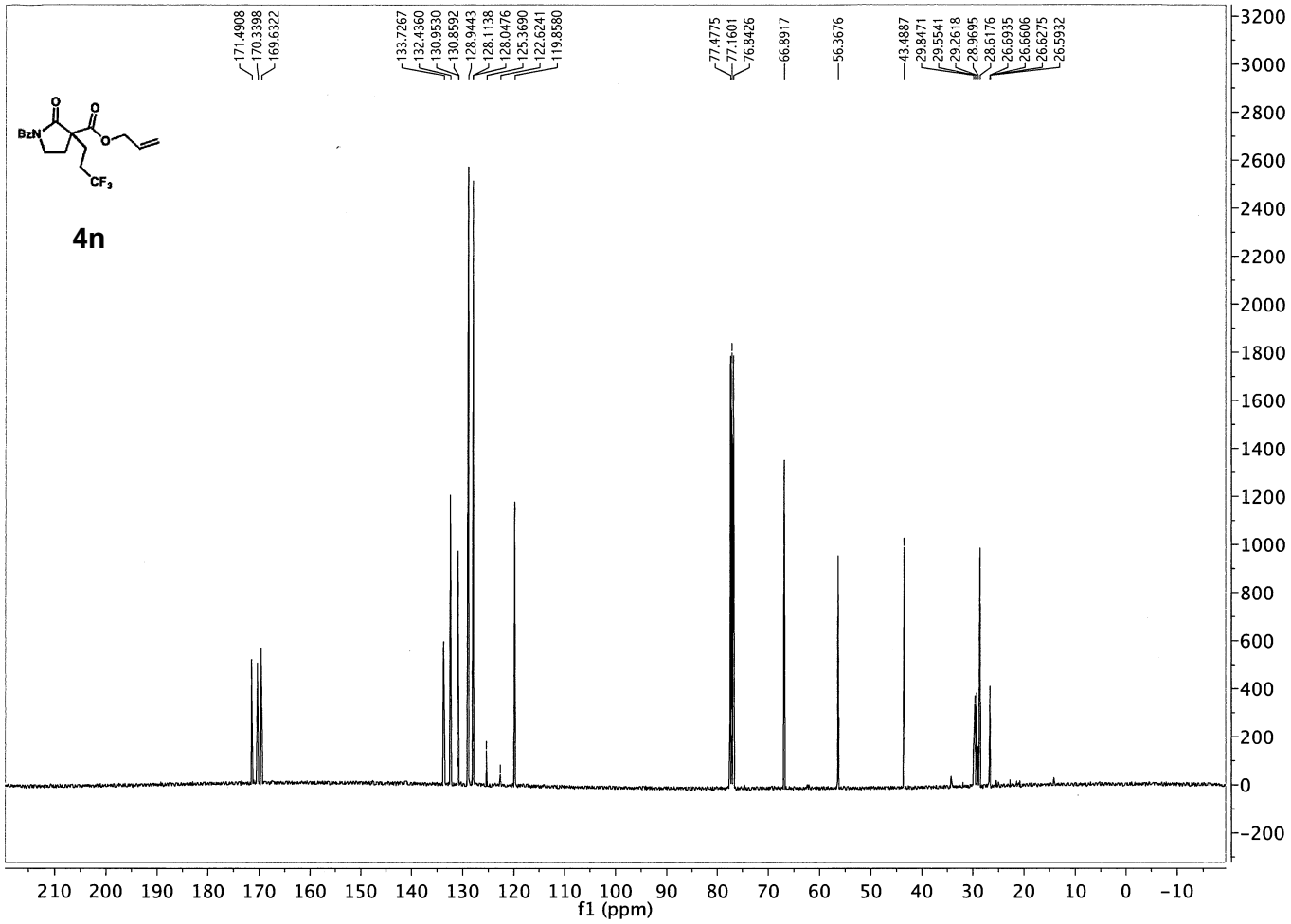
0.0
f1 (ppm)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29.8471
29.5541
29.2618
28.9695
28.6176
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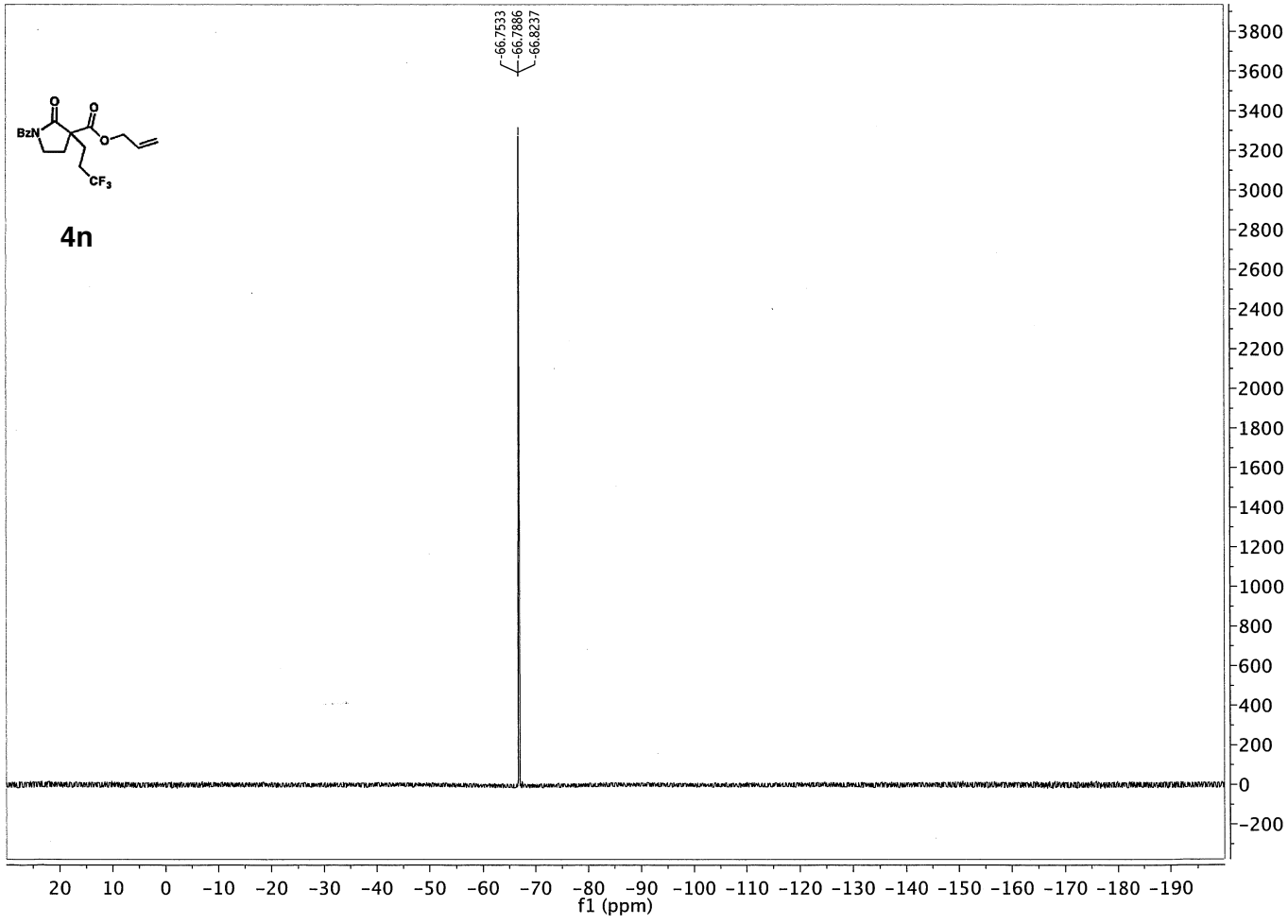
26.6606
26.6275
26.5932
BzN
CF3
4n
f1 (ppm)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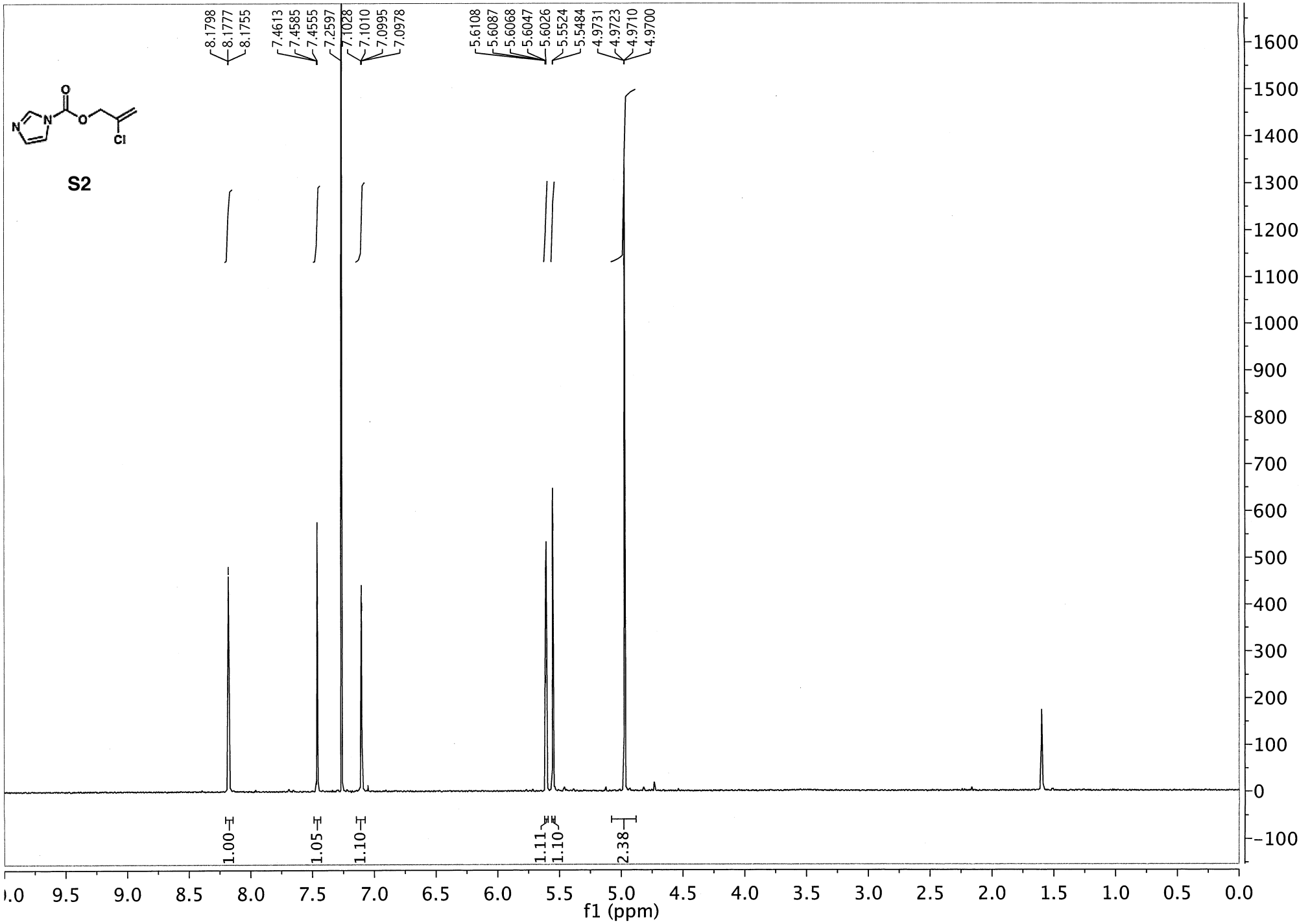
f1 (ppm)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5.6087
5.6068
5.6047
5.6026
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5.5484
4.9731
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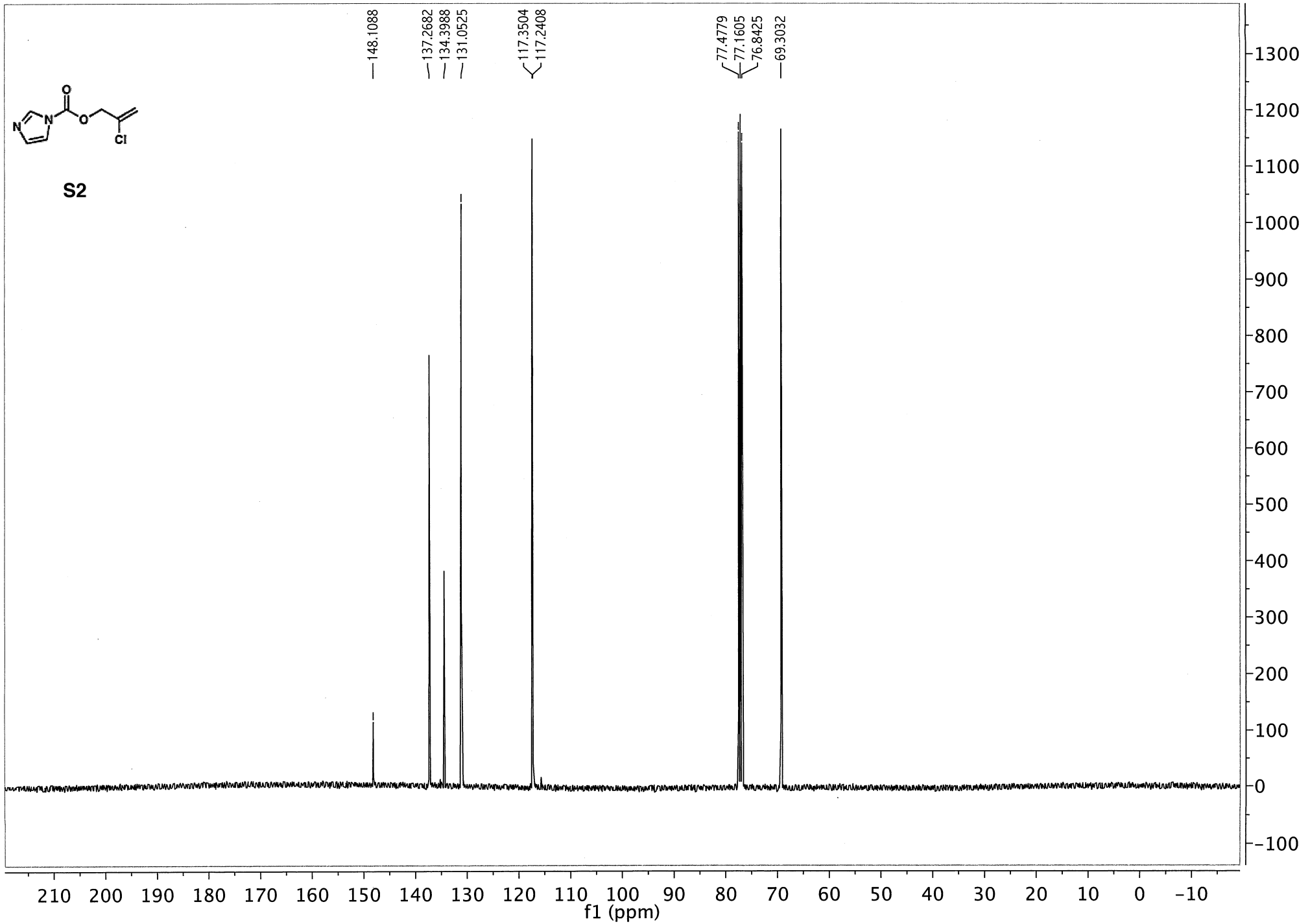
4.9700
S2
1.00
1.05
1.10
1.11
1.10
2.38
f1 (ppm)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O
Cl
S2
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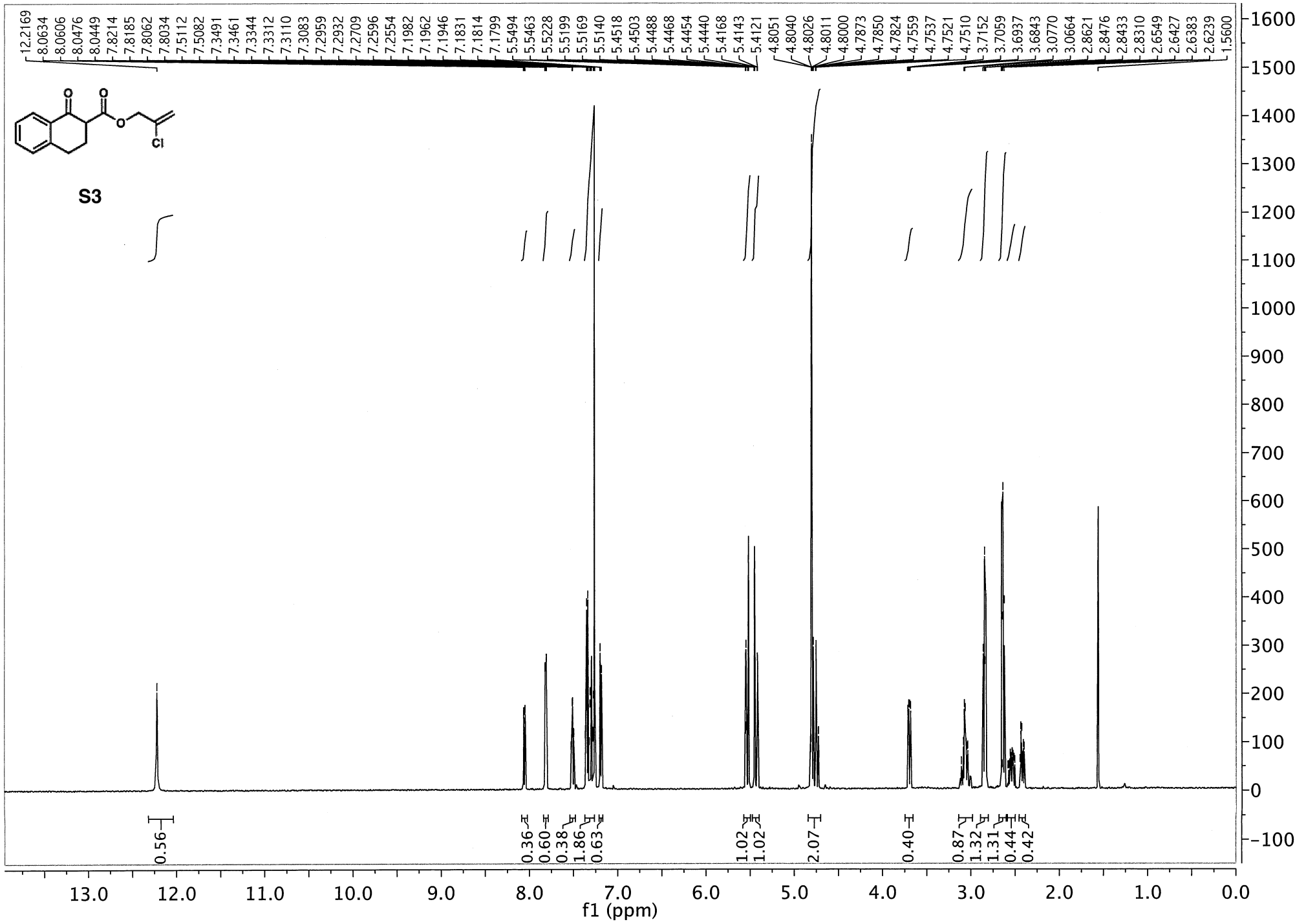
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.3491
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7.3312
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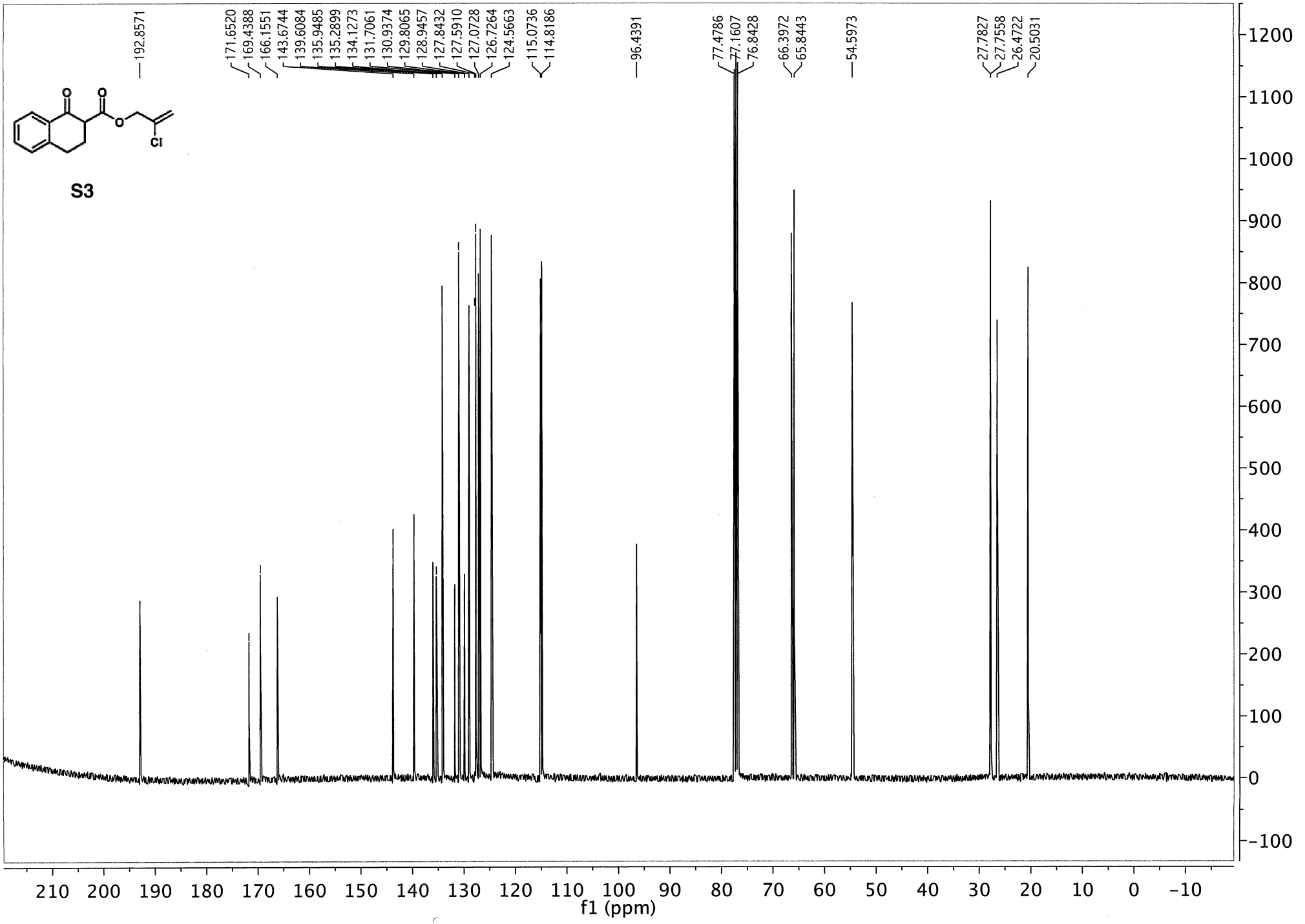
7.3083
7.2959
7.2932
7.2709
7.2596
7.2554
7.1982
7.1962
7.1946
7.1831
7.1814
7.1799
5.5494
5.5463
5.5228
5.5199
5.5169
5.5140
5.4518
5.4503
5.4488
5.4468
5.4454
5.4440
5.4168
5.4143
5.4121
4.8051
4.8040
4.8026
4.8011
4.8000
4.7873
4.7850
4.7824
4.7559
4.7537
4.7521
4.7510
3.7152
3.7059
3.6937
3.6843
3.0770
3.0664
2.8621
2.8476
2.8433
2.8310
2.6549
2.6427
2.6383
2.6239
1.5600
O
O
O
Cl
S3
0.56
0.36
0.60
0.38
1.86
0.63
1.02
1.02
2.07
0.40
0.87
1.32
1.31
0.44
0.42
f1 (ppm)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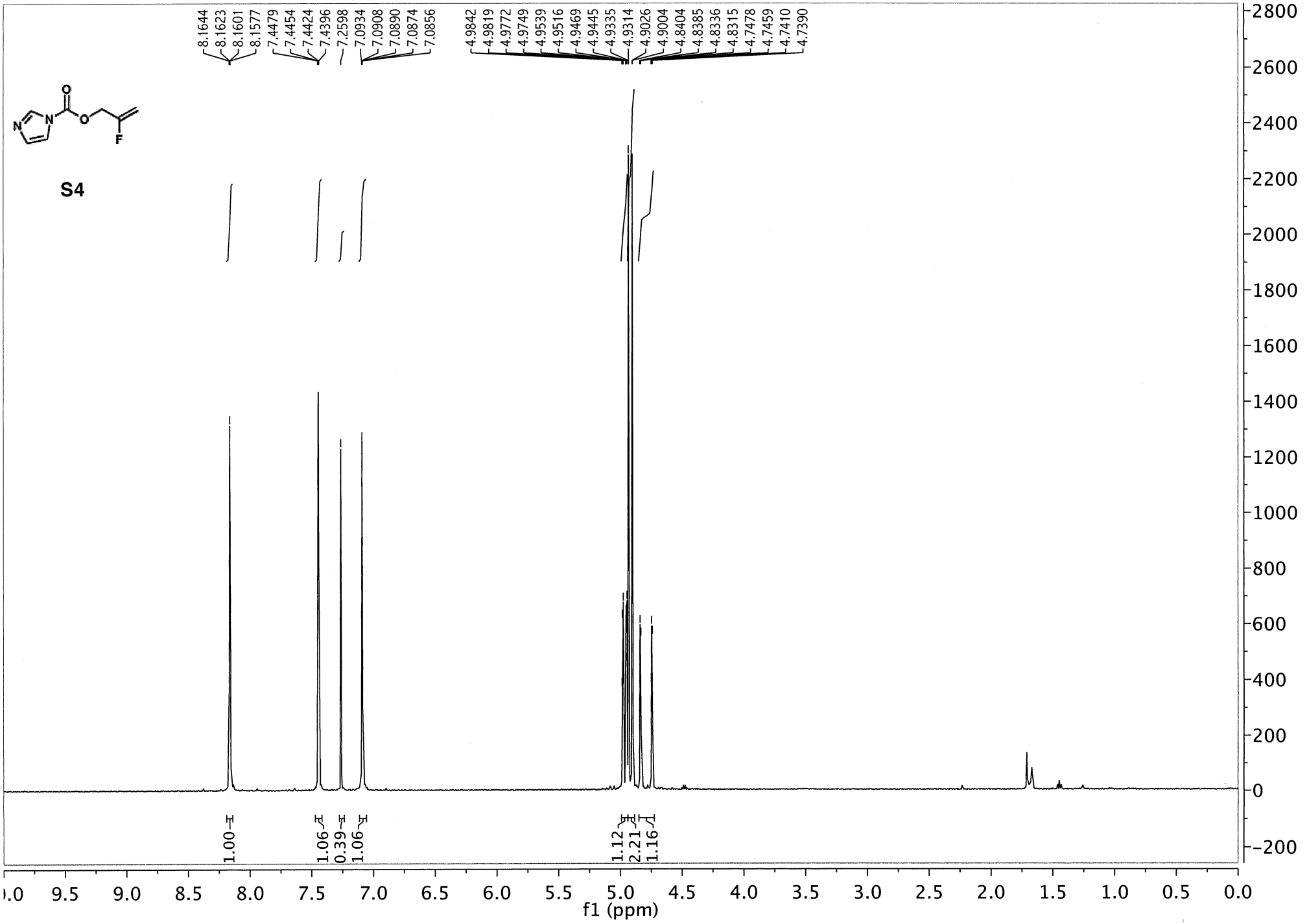
131.7061
130.9374
129.8065
128.9457
127.8432
127.5910
127.0728
126.7264
124.5663
115.0736
114.8186
96.4391
77.4786
77.1607
76.8428
66.3972
65.8443
54.5973
27.7827
27.7558
26.4722
20.5031
O
O
O
Cl
S3
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.4424
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7.2598
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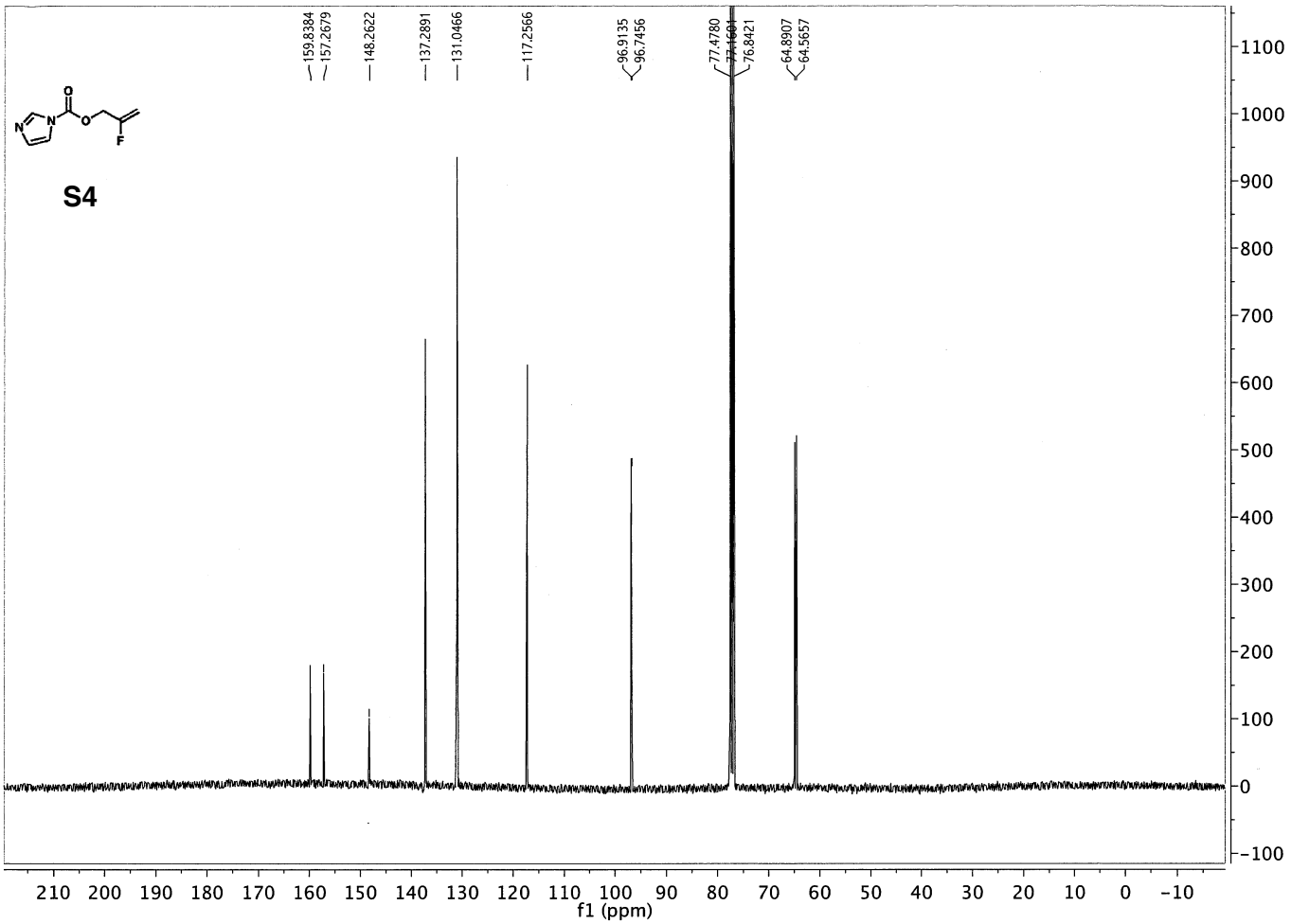
7.0908
7.0890
7.0874
7.0856
4.9842
4.9819
4.9772
4.9749
4.9539
4.9516
4.9469
4.9445
4.9335
4.9314
4.9026
4.9004
4.8404
4.8385
4.8336
4.8315
4.7478
4.7459
4.7410
4.7390
O
N
O
F
S4
1.00
1.06
0.39
1.06
1.12
2.21
1.16
f1 (ppm)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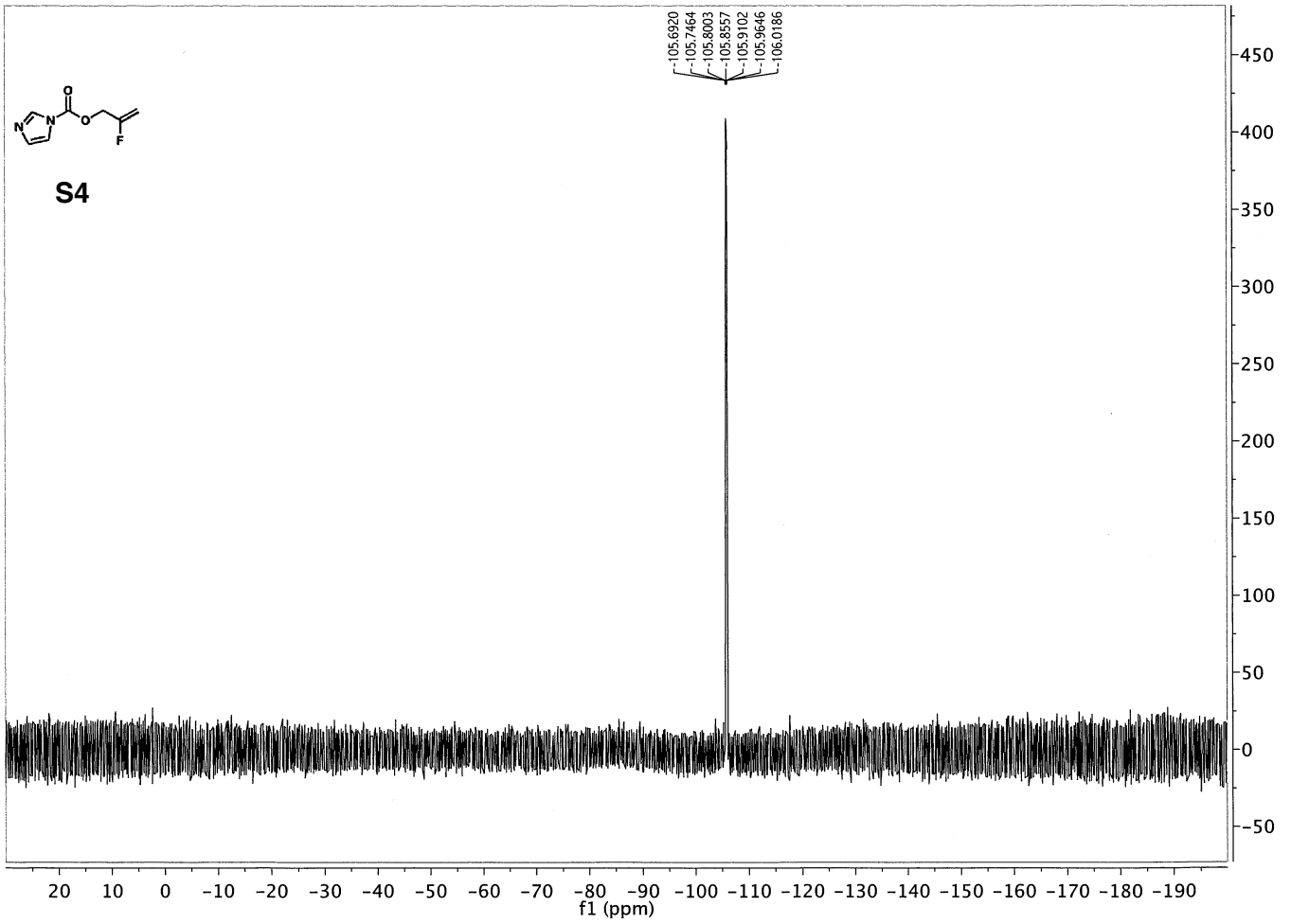
157.2679
148.2622
137.2891
131.0466
117.2566
96.9135
96.7456
77.4780
77.1604
76.8421
64.8907
64.5657
S4
f1 (ppm)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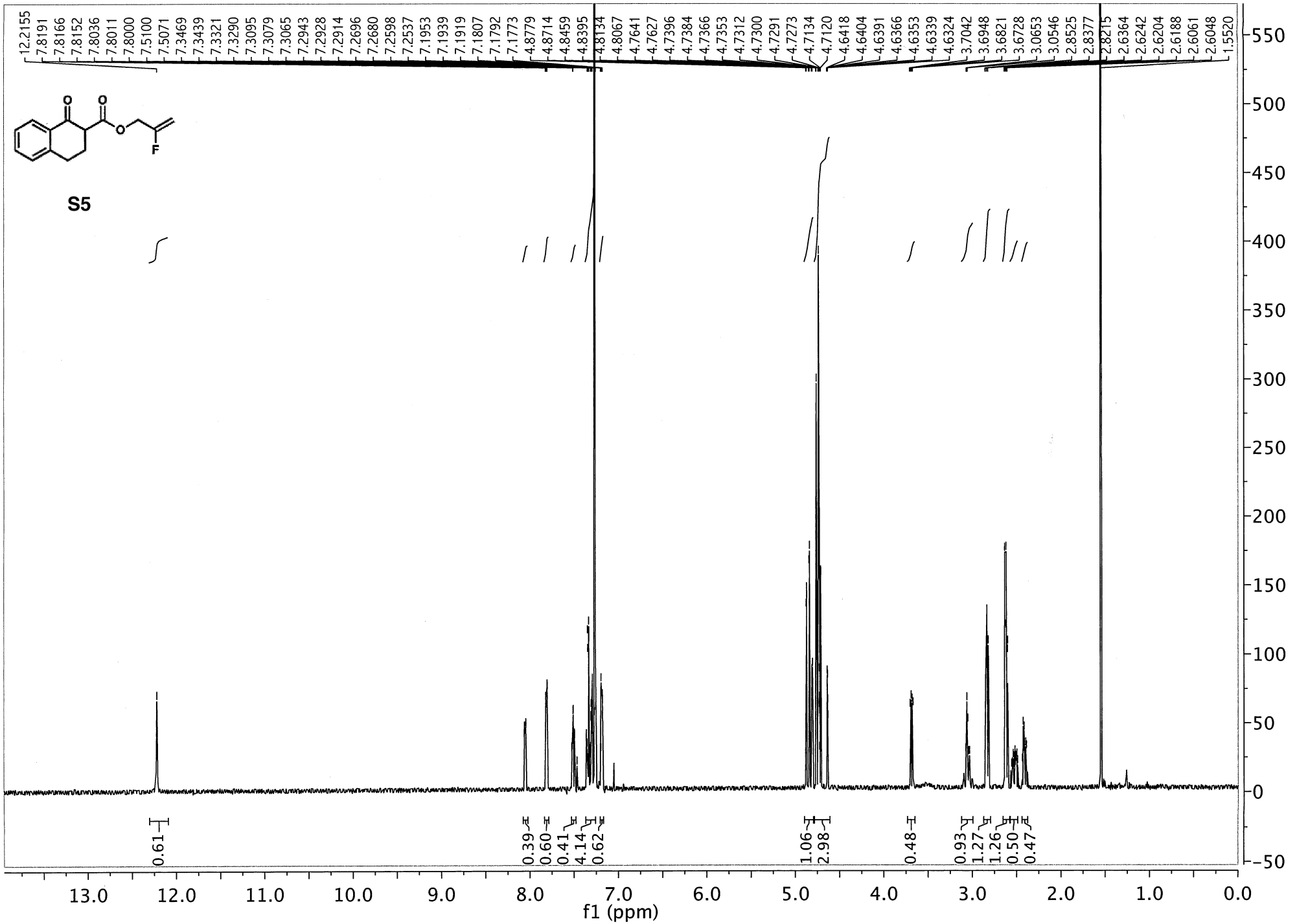
-105.9646
-106.0186
S4
f1 (ppm)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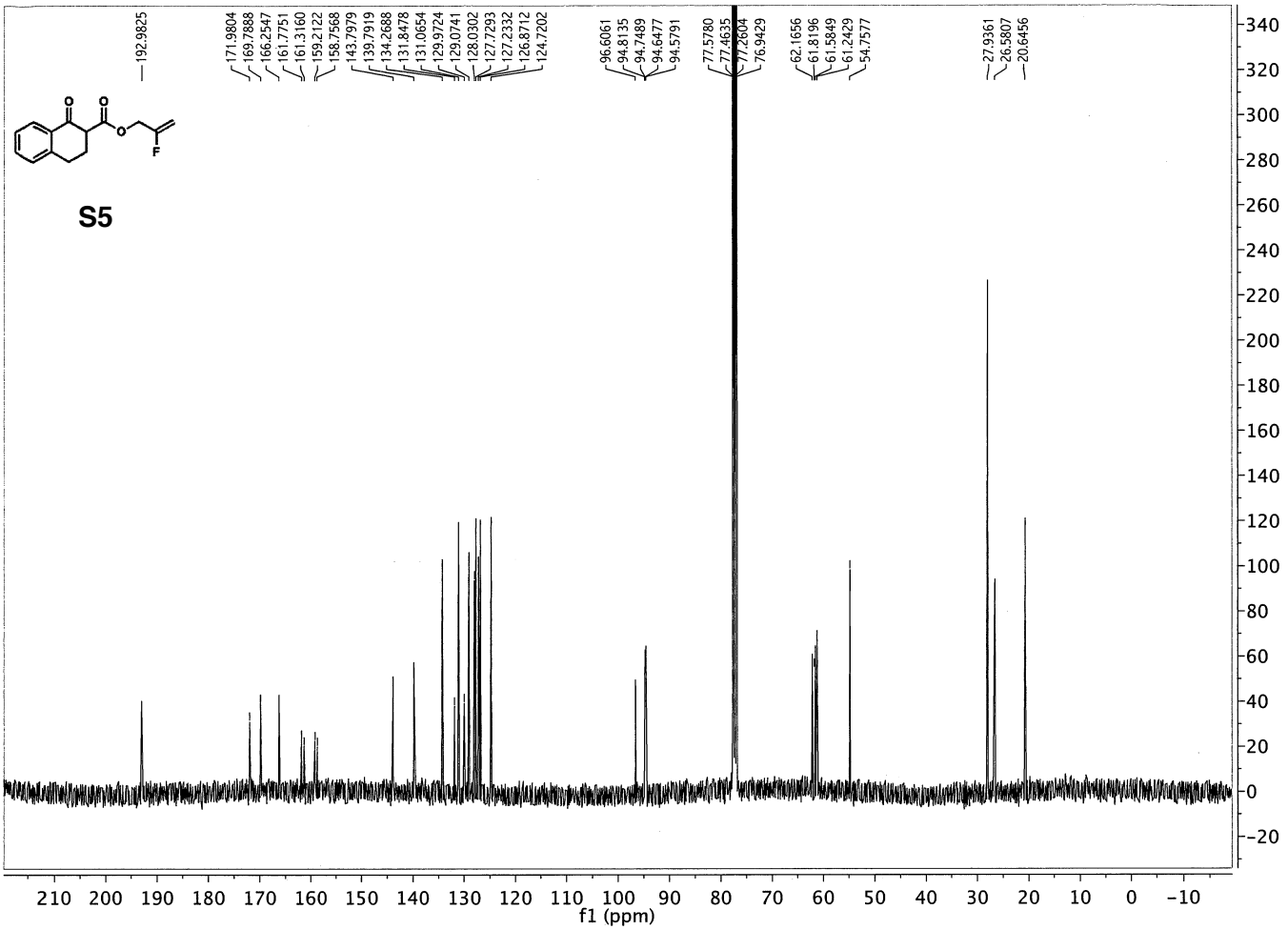
7.3321
7.3290
7.3095
7.3079
7.3065
7.2943
7.2928
7.2914
7.2696
7.2680
7.2598
7.2537
7.1953
7.1939
7.1919
7.1807
7.1792
7.1773
4.8779
4.8714
4.8459
4.8395
4.8134
4.8067
4.7641
4.7627
4.7396
4.7384
4.7366
4.7353
4.7312
4.7300
4.7291
4.7273
4.7134
4.7120
4.6418
4.6404
4.6391
4.6366
4.6353
4.6339
4.6324
3.7042
3.6948
3.6821
3.6728
3.0653
3.0546
2.8525
2.8377
2.8215
2.6364
2.6242
2.6204
2.6188
2.6061
2.6048
1.5520
O
O
O
F
S5
0.61
0.39
0.60
0.41
4.14
0.62
1.06
2.98
0.48
0.93
1.27
1.26
0.50
0.47
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)
550
500
450
400
350
300
250
200
150
100
50
0
-50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143.7979
139.7919
134.2688
131.8478
131.0654
129.9724
129.0741
128.0302
127.7293
127.2332
126.8712
124.7202
96.6061
94.8135
94.7489
94.6477
94.5791
77.5780
77.4635
77.2804
76.9429
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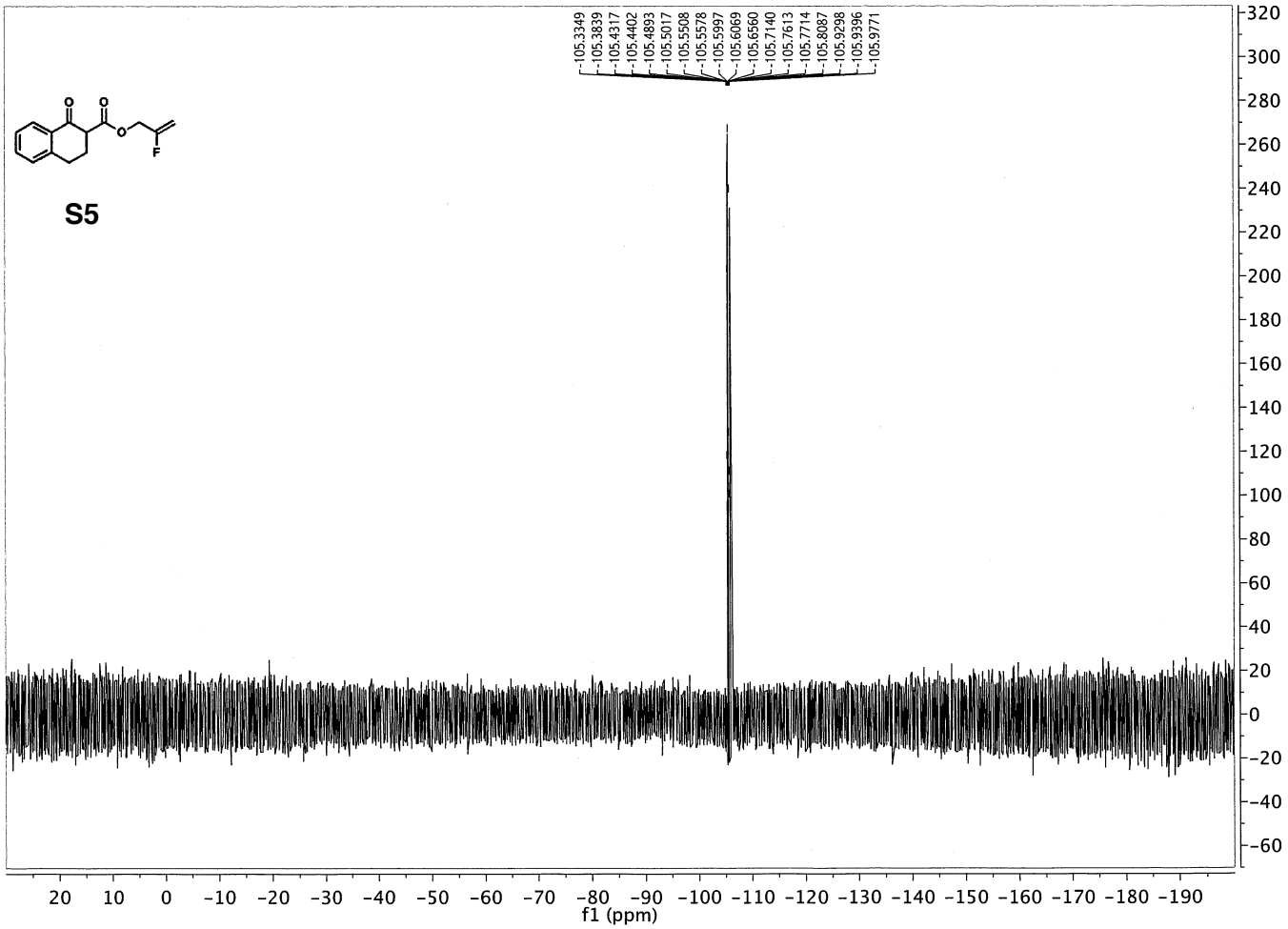
61.8196
61.5849
61.2429
54.7577
27.9361
26.5807
20.6456
S5
f1 (ppm)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-105.6069
-105.6560
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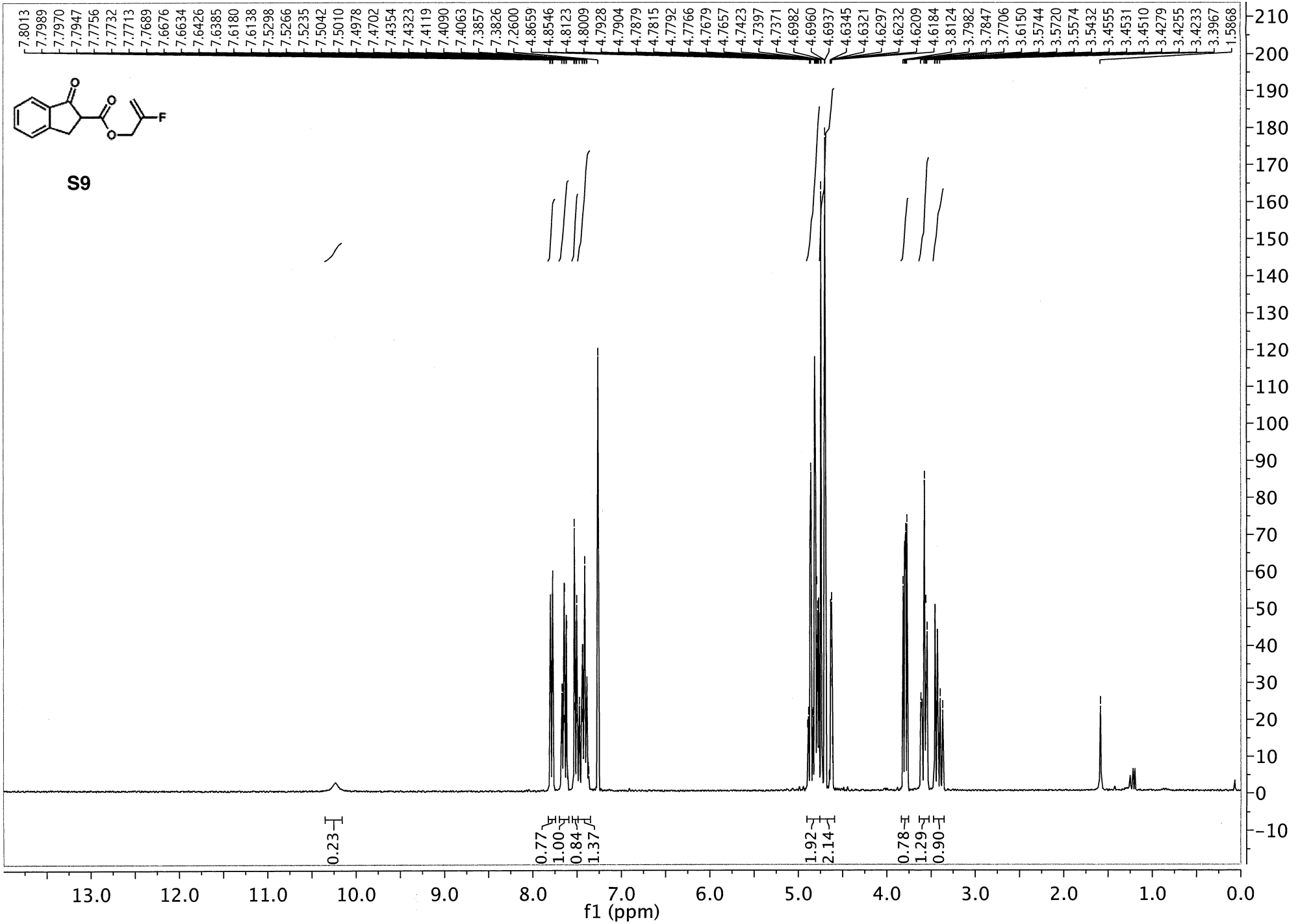
-105.7714
-105.8087
-105.9298
-105.9396
-105.9771
S5
f1 (ppm)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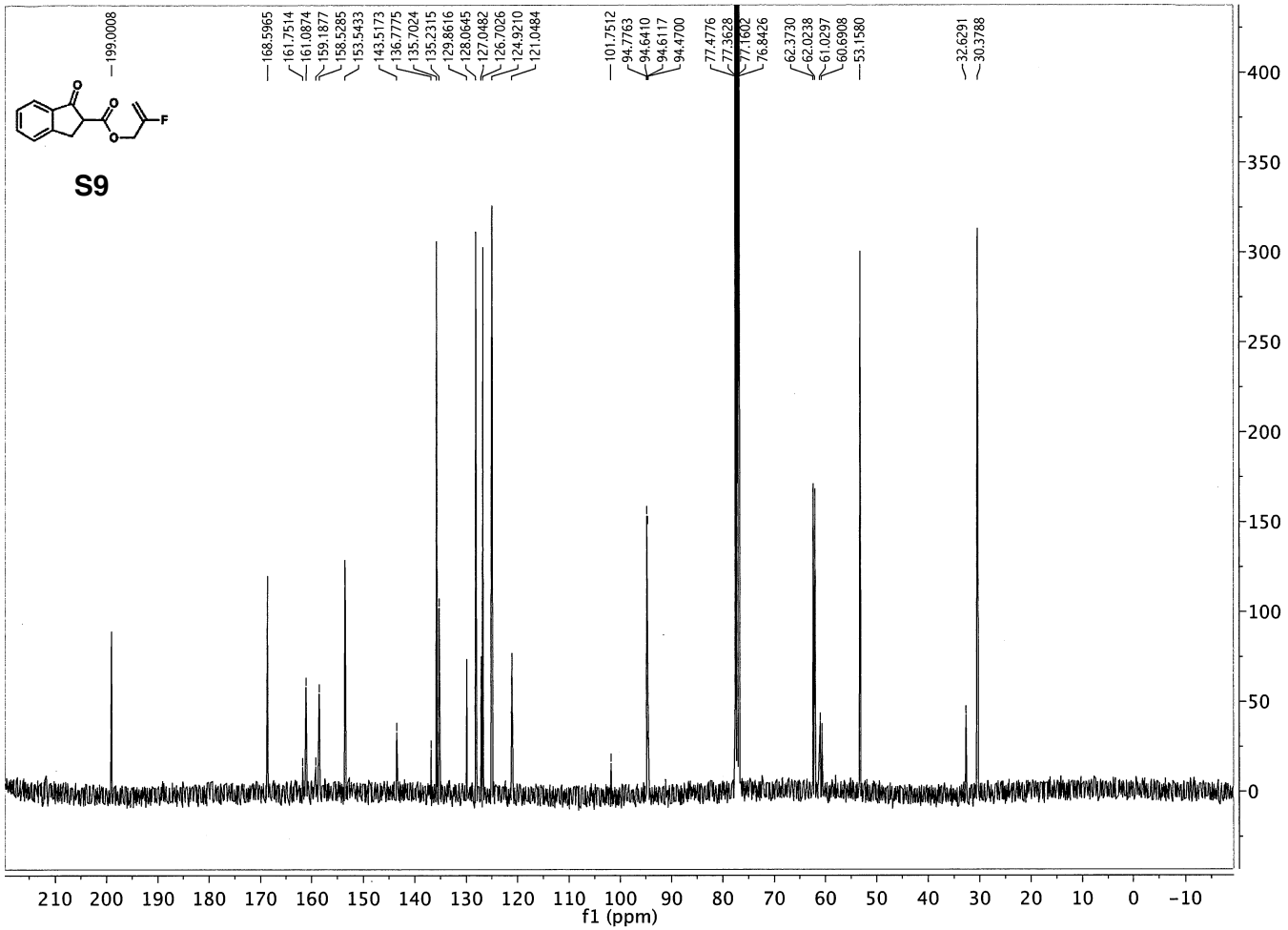
7.7970
7.7947
7.7756
7.7732
7.7713
7.7689
7.6676
7.6634
7.6426
7.6385
7.6180
7.6138
7.5298
7.5266
7.5235
7.5042
7.5010
7.4978
7.4702
7.4354
7.4323
7.4119
7.4090
7.4063
7.3857
7.3826
7.2600
4.8659
4.8546
4.8123
4.8009
4.7928
4.7904
4.7879
4.7815
4.7792
4.7766
4.7679
4.7657
4.7423
4.7397
4.7371
4.6982
4.6960
4.6937
4.6345
4.6321
4.6297
4.6232
4.6209
4.6184
3.8124
3.7982
3.7847
3.7706
3.6150
3.5744
3.5720
3.5574
3.5432
3.4555
3.4531
3.4510
3.4279
3.4255
3.4233
3.3967
1.5868
O
O
O
F
S9
0.23
0.77
1.00
0.84
1.37
1.92
2.14
0.78
1.29
0.90
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10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161.0874
159.1877
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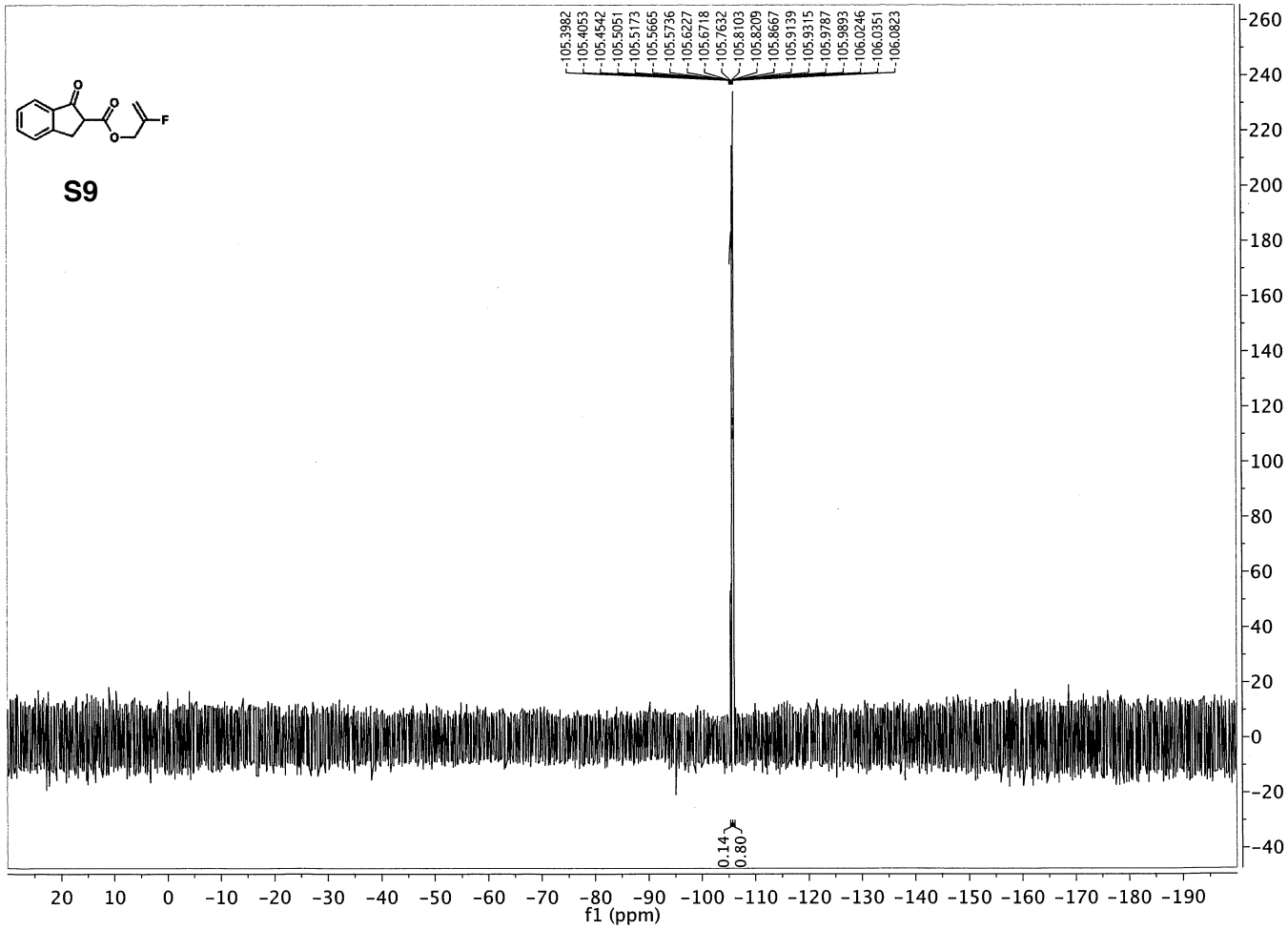
153.5433
143.5173
136.7775
135.7024
135.2315
129.8616
128.0645
127.0482
126.7026
124.9210
121.0484
101.7512
94.7763
94.6410
94.6117
94.4700
77.4776
77.3628
77.1602
76.8426
62.3730
62.0238
61.0297
60.6908
53.1580
32.6291
30.3788
S9
f1 (ppm)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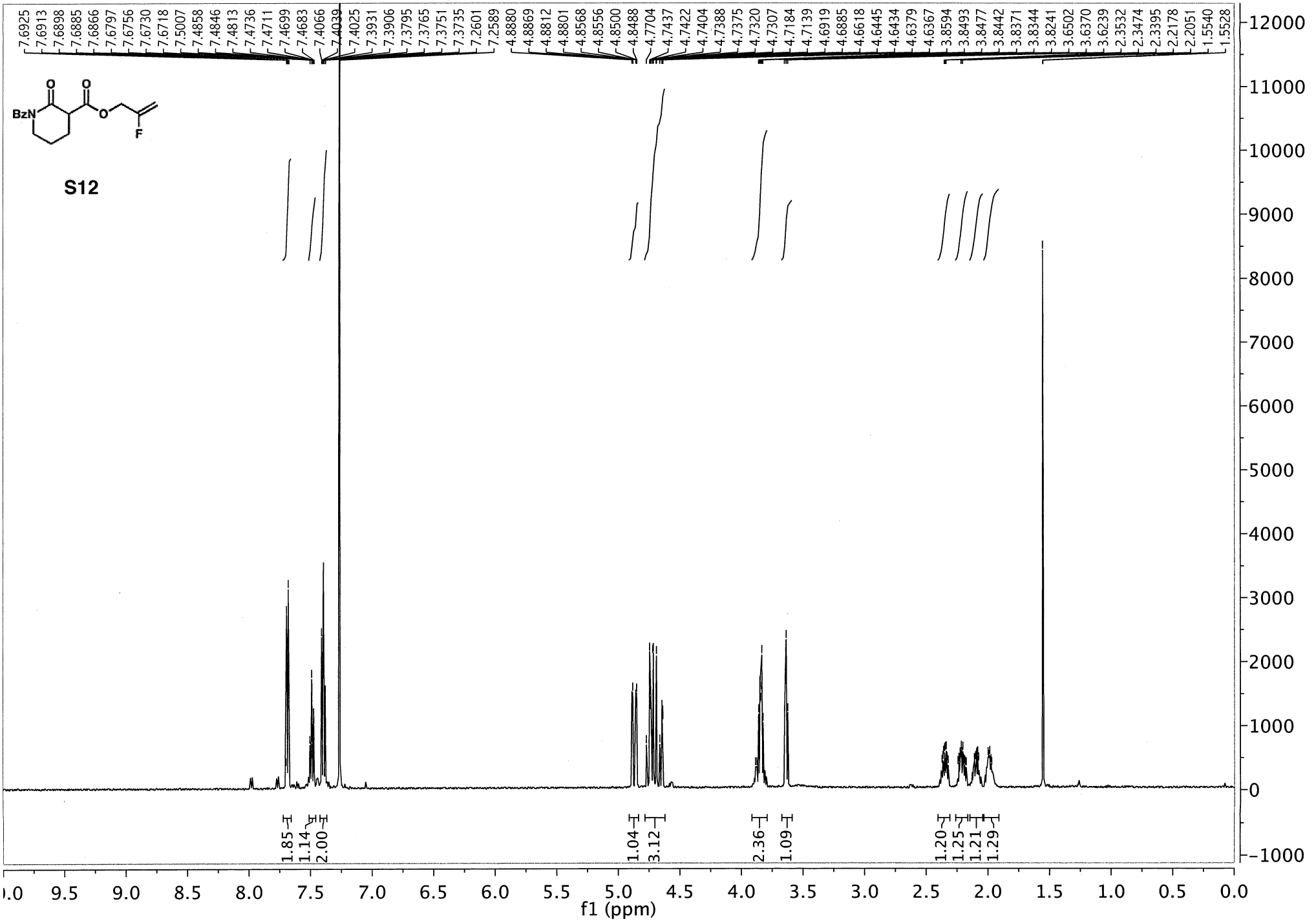
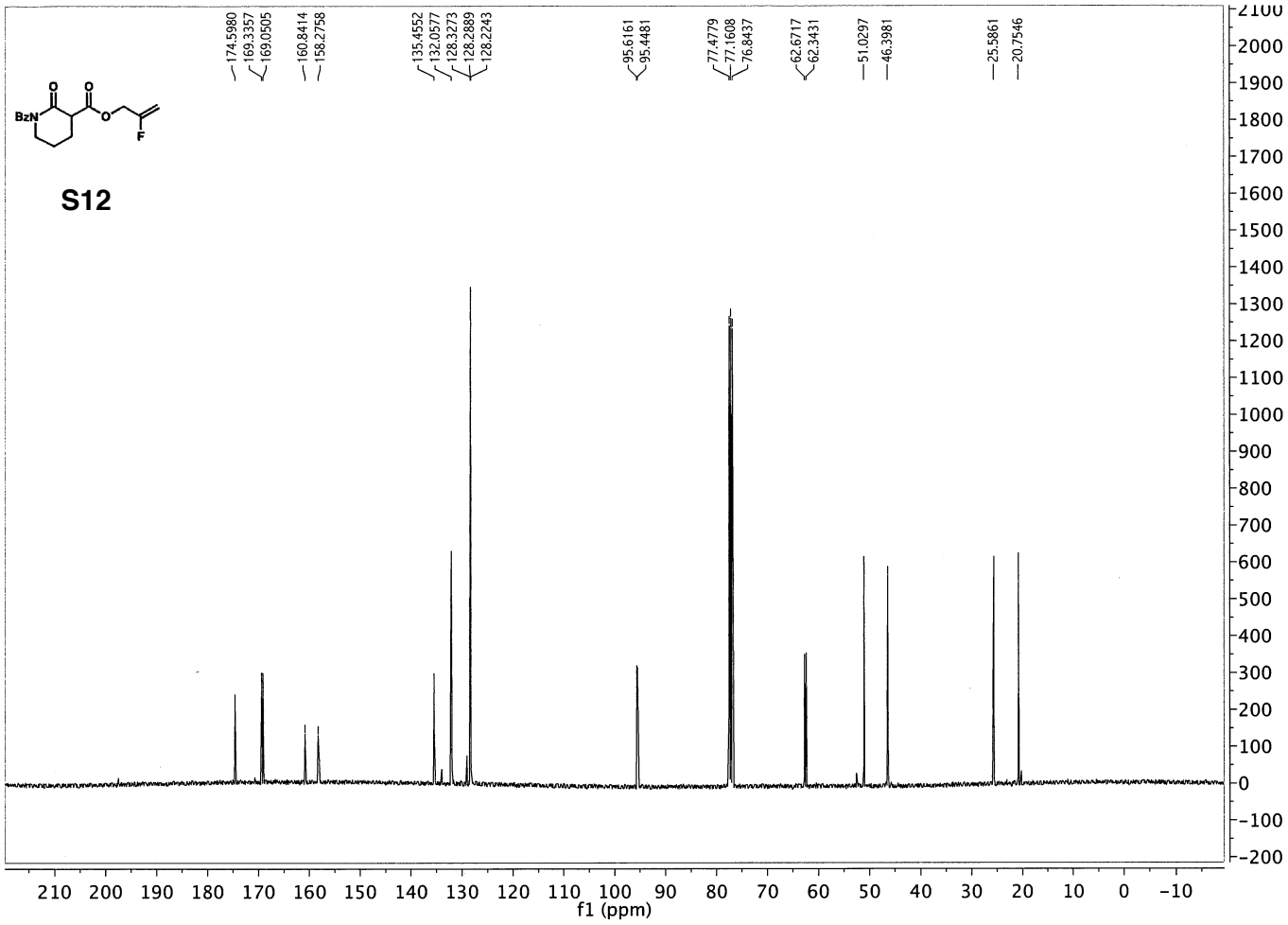
105.5736
105.6227
105.6718
105.7632
105.8103
105.8209
105.8667
105.9139
105.9315
105.9787
105.9893
106.0246
106.0351
106.0823
0.14
0.80
S9
f1 (ppm)


BzN
O
O
O
F
S12
7.6925 7.6913 7.6898 7.6885 7.6866 7.6797 7.6756 7.6730 7.6718 7.5007 7.4858 7.4846 7.4813 7.4736 7.4711 7.4699 7.4683 7.4066 7.4039 7.4025 7.3931 7.3906 7.3795 7.3765 7.3751 7.3735 7.2601 7.2589
4.8880 4.8869 4.8812 4.8801 4.8568 4.8556 4.8500 4.8488 4.7704 4.7437 4.7422 4.7404 4.7388 4.7375 4.7320 4.7307 4.7184 4.7139 4.6919 4.6885 4.6618 4.6445 4.6434 4.6379 4.6367
3.8594 3.8493 3.8477 3.8442 3.8371 3.8344 3.8241 3.6502 3.6370 3.6239 2.3532 2.3474 2.3395 2.2178 2.2051 1.5540 1.5528
1.85 1.14 2.00 1.04 3.12 2.36 1.09 1.20 1.25 1.21 1.29
f1 (ppm)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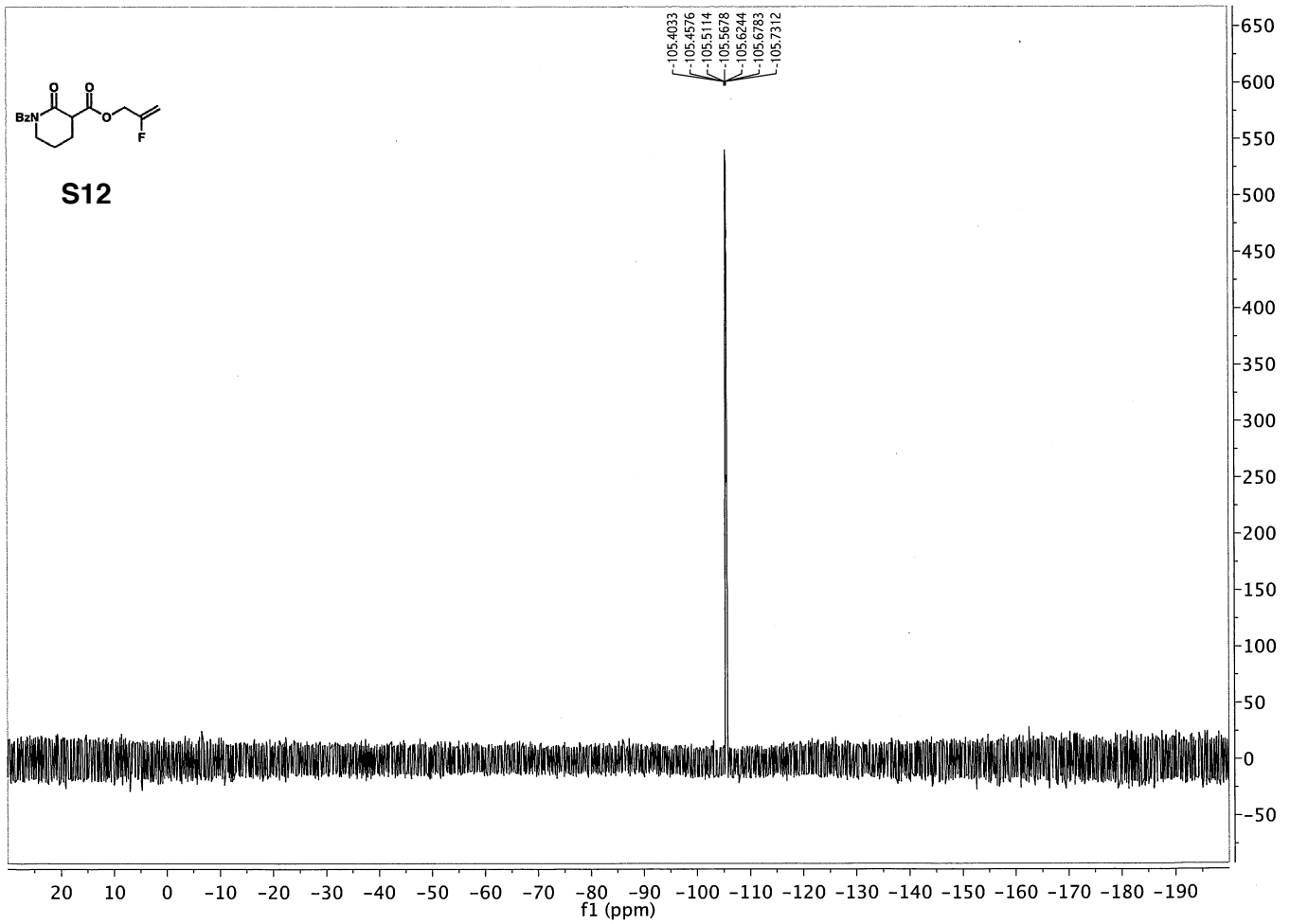
132.0577
128.3273
128.2889
128.2243
95.6161
95.4481
77.4779
77.1608
76.8437
62.6717
62.3431
51.0297
46.3981
25.5861
20.7546
BzN
O
O
O
F
f1 (ppm)

S12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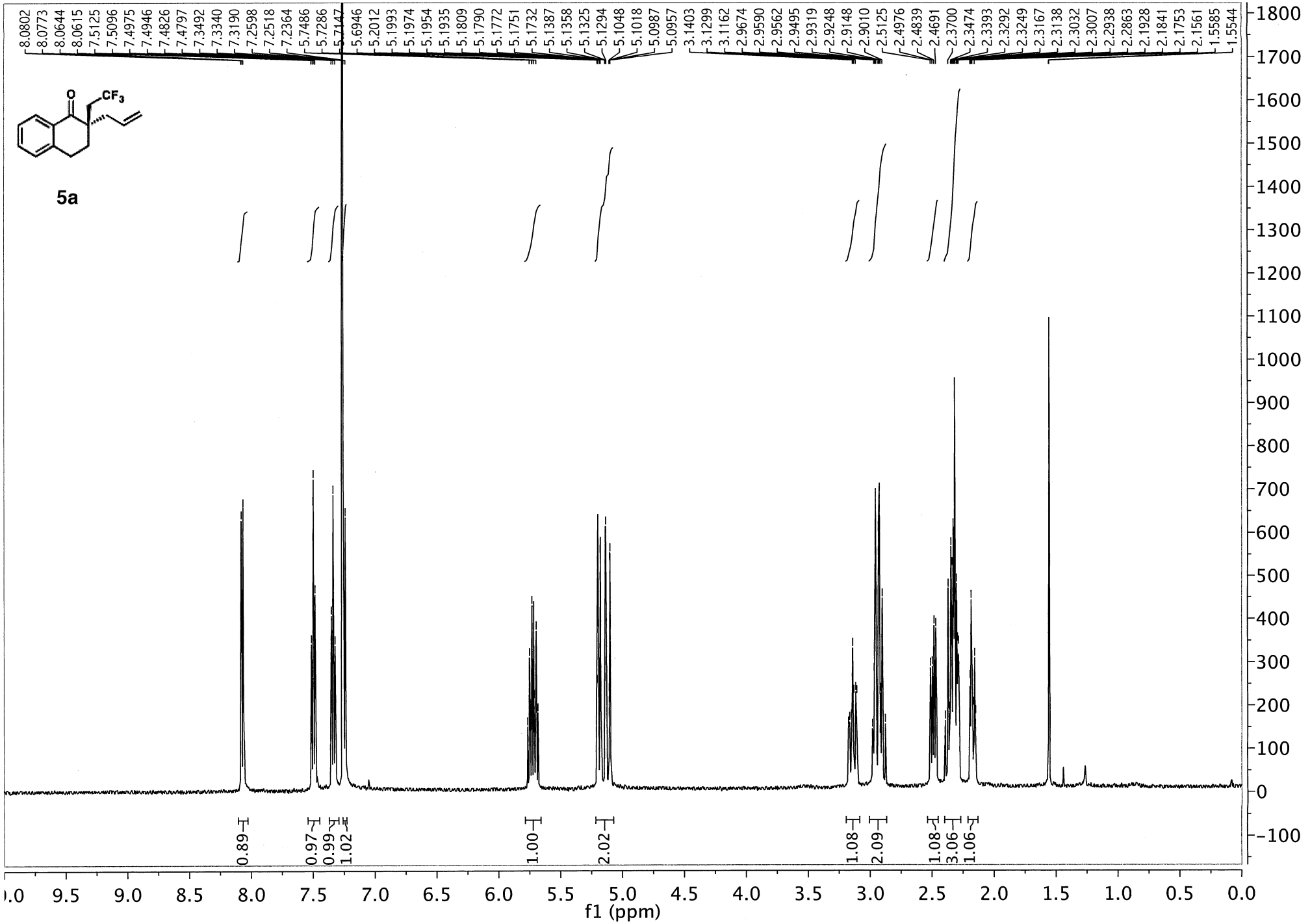
-105.5678
-105.6244
-105.6783
-105.7312
BzN
O
O
O
F
f1 (ppm)

S12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8.0644
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7.4975
7.4946
7.4826
7.4797
7.3492
7.3340
7.3190
7.2598
7.2518
7.2364
5.7486
5.7286
5.7147
5.6946
5.2012
5.1993
5.1974
5.1954
5.1935
5.1809
5.1790
5.1772
5.1751
5.1732
5.1387
5.1358
5.1325
5.1294
5.1048
5.1018
5.0987
5.0957
3.1403
3.1299
3.1162
2.9674
2.9590
2.9562
2.9495
2.9319
2.9248
2.9148
2.9010
2.5125
2.4976
2.4839
2.4691
2.3700
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2.3393
2.3292
2.3249
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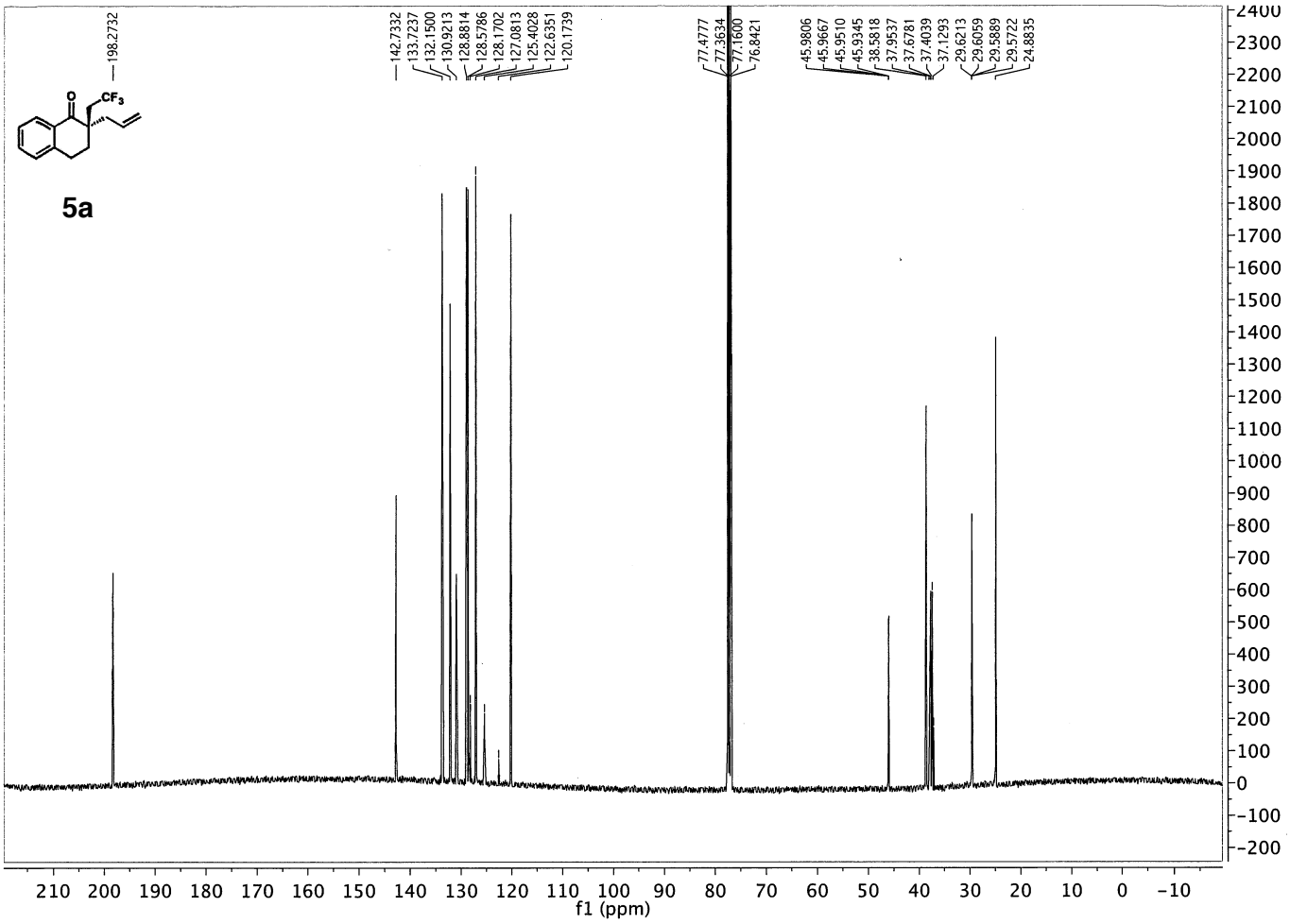
2.3138
2.3032
2.3007
2.2938
2.2863
2.1928
2.1841
2.1753
2.1561
1.5585
1.5544
O
CF3
5a
0.89
0.97
0.99
1.02
1.00
2.02
1.08
2.09
1.08
3.06
1.06
f1 (ppm)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128.5786
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127.0813
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122.6351
120.1739
77.4777
77.3634
77.1600
76.8421
45.9806
45.9667
45.9510
45.9345
38.5818
37.9537
37.6781
37.4039
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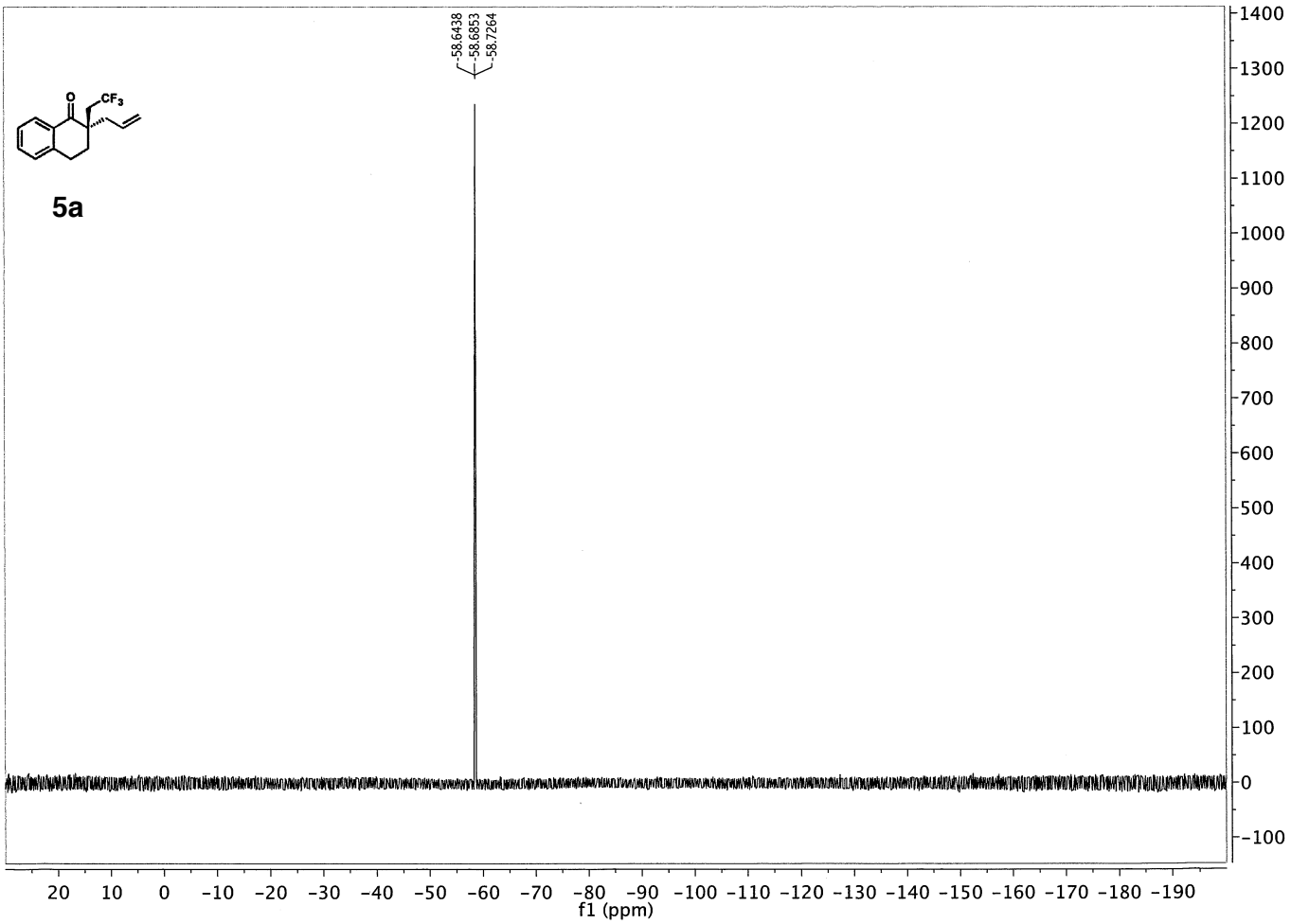
29.6213
29.6059
29.5889
29.5722
24.8835
CF3
O
5a
f1 (ppm)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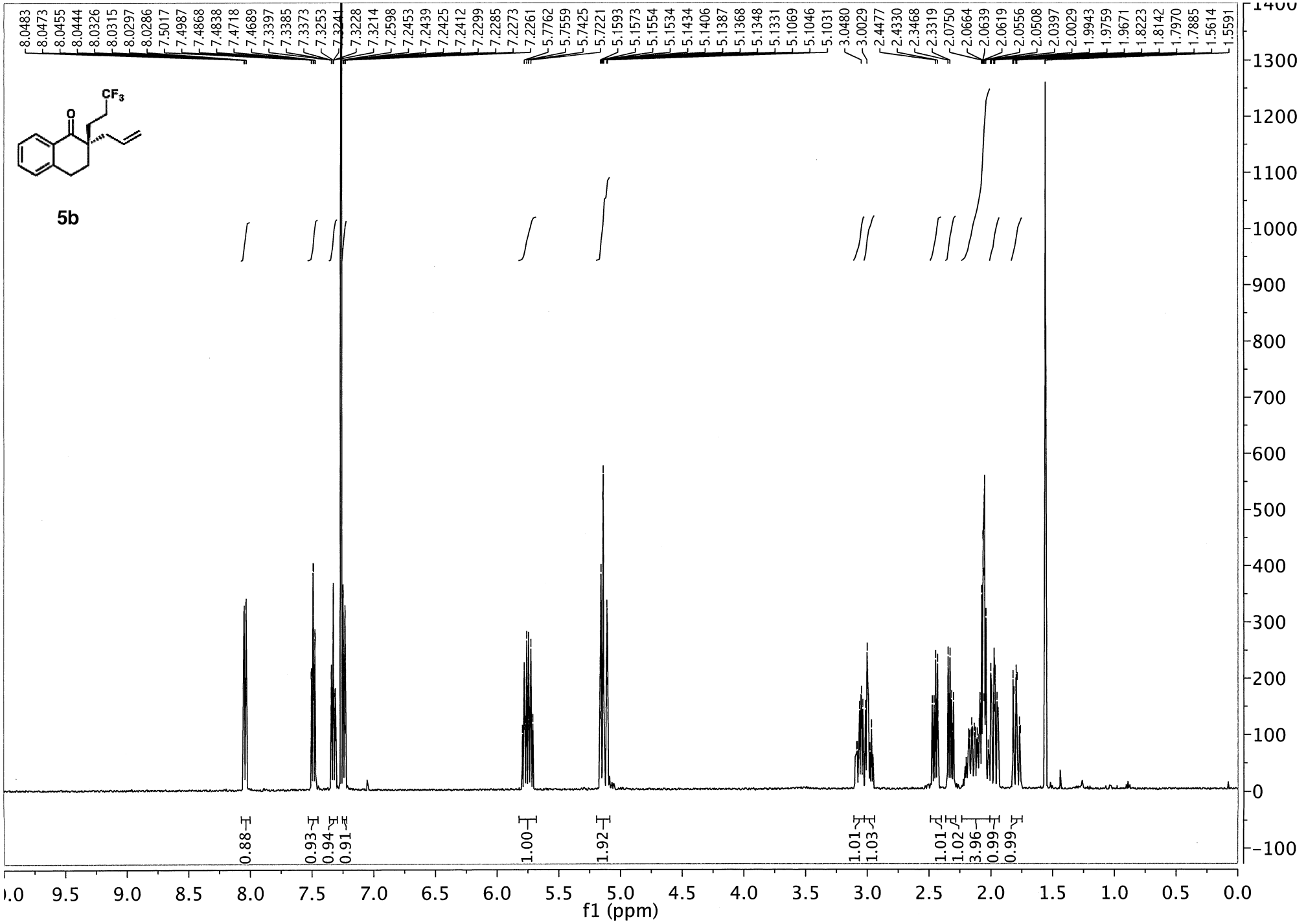
CF3
O
5a
f1 (ppm)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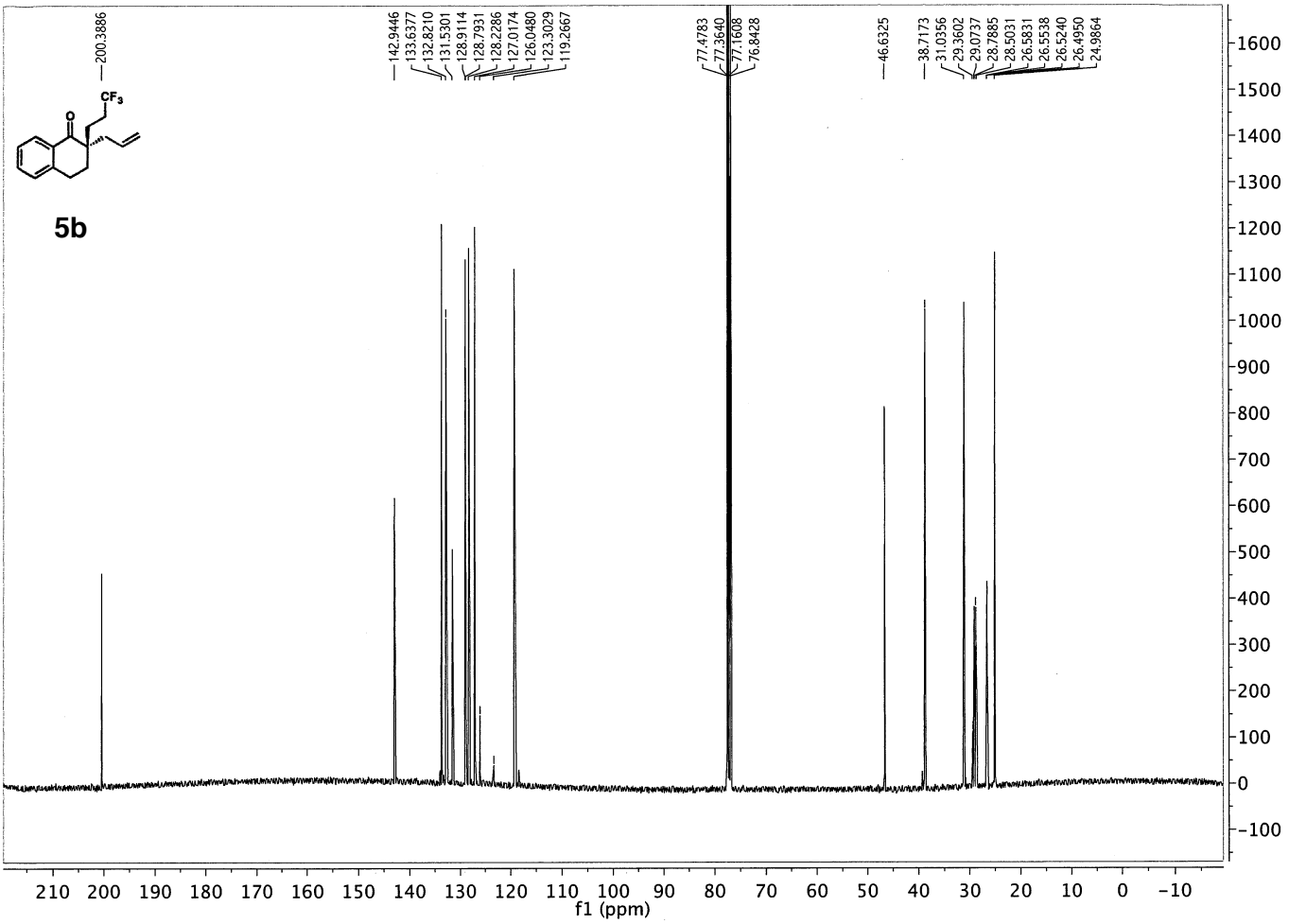
8.0297
8.0286
7.5017
7.4987
7.4868
7.4838
7.4718
7.4689
7.3397
7.3385
7.3373
7.3253
7.3241
7.3228
7.3214
7.2598
7.2453
7.2439
7.2425
7.2412
7.2299
7.2285
7.2273
7.2261
5.7762
5.7559
5.7425
5.7221
5.1593
5.1573
5.1554
5.1534
5.1434
5.1406
5.1387
5.1368
5.1348
5.1331
5.1069
5.1046
5.1031
3.0480
3.0029
2.4477
2.4330
2.3468
2.3319
2.0750
2.0664
2.0639
2.0619
2.0556
2.0508
2.0397
2.0029
1.9943
1.9759
1.9671
1.8223
1.8142
1.7970
1.7885
1.5614
1.5591
CF3
O
5b
0.88
0.93
0.94
0.91
1.00
1.92
1.01
1.03
1.01
1.02
3.96
0.99
0.99
f1 (ppm)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126.0480
123.3029
119.2667
77.4783
77.3640
77.1608
76.8428
46.6325
38.7173
31.0356
29.3602
29.0737
28.7885
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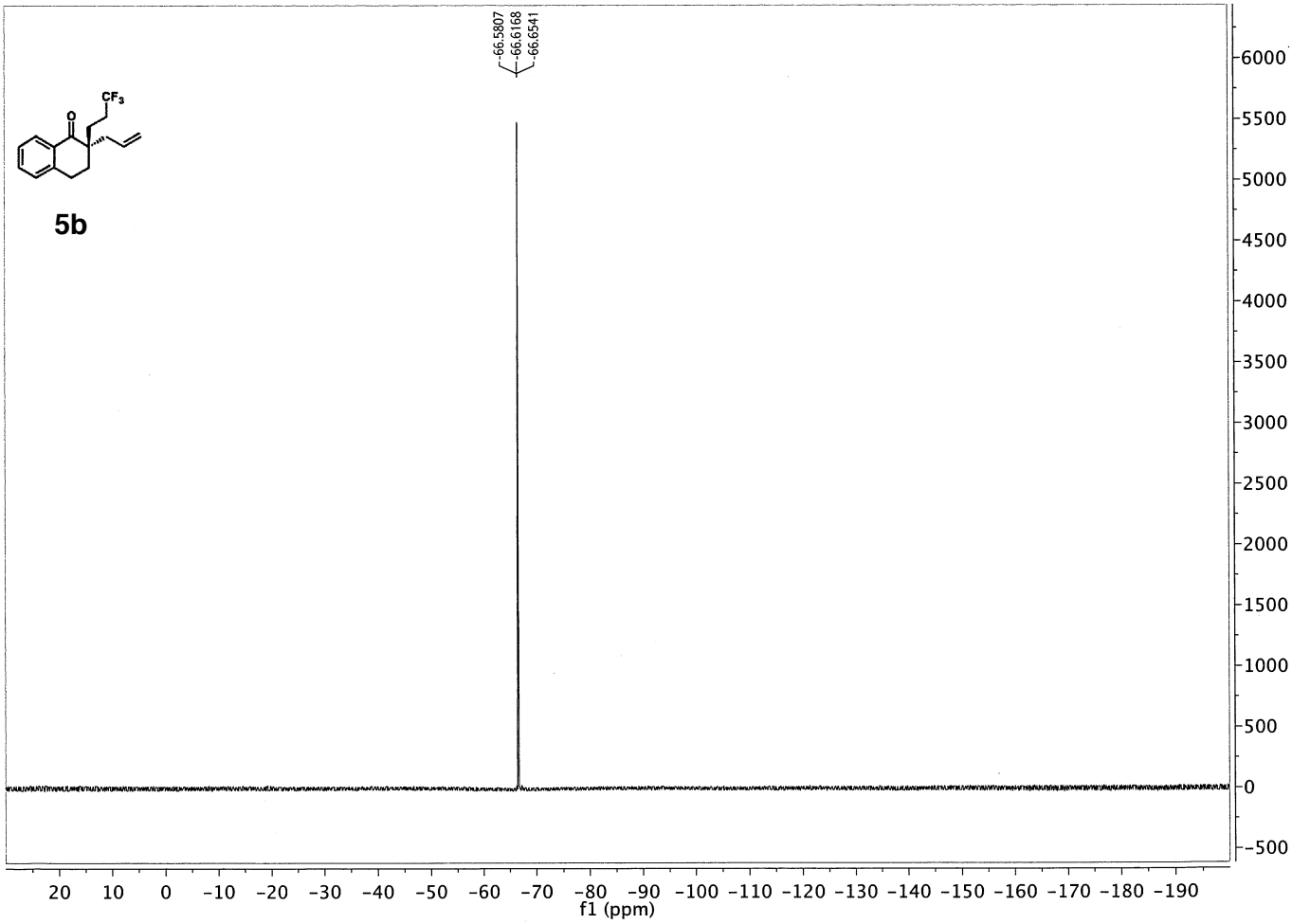
26.5831
26.5538
26.5240
26.4950
24.9864
CF3
O
5b
f1 (ppm)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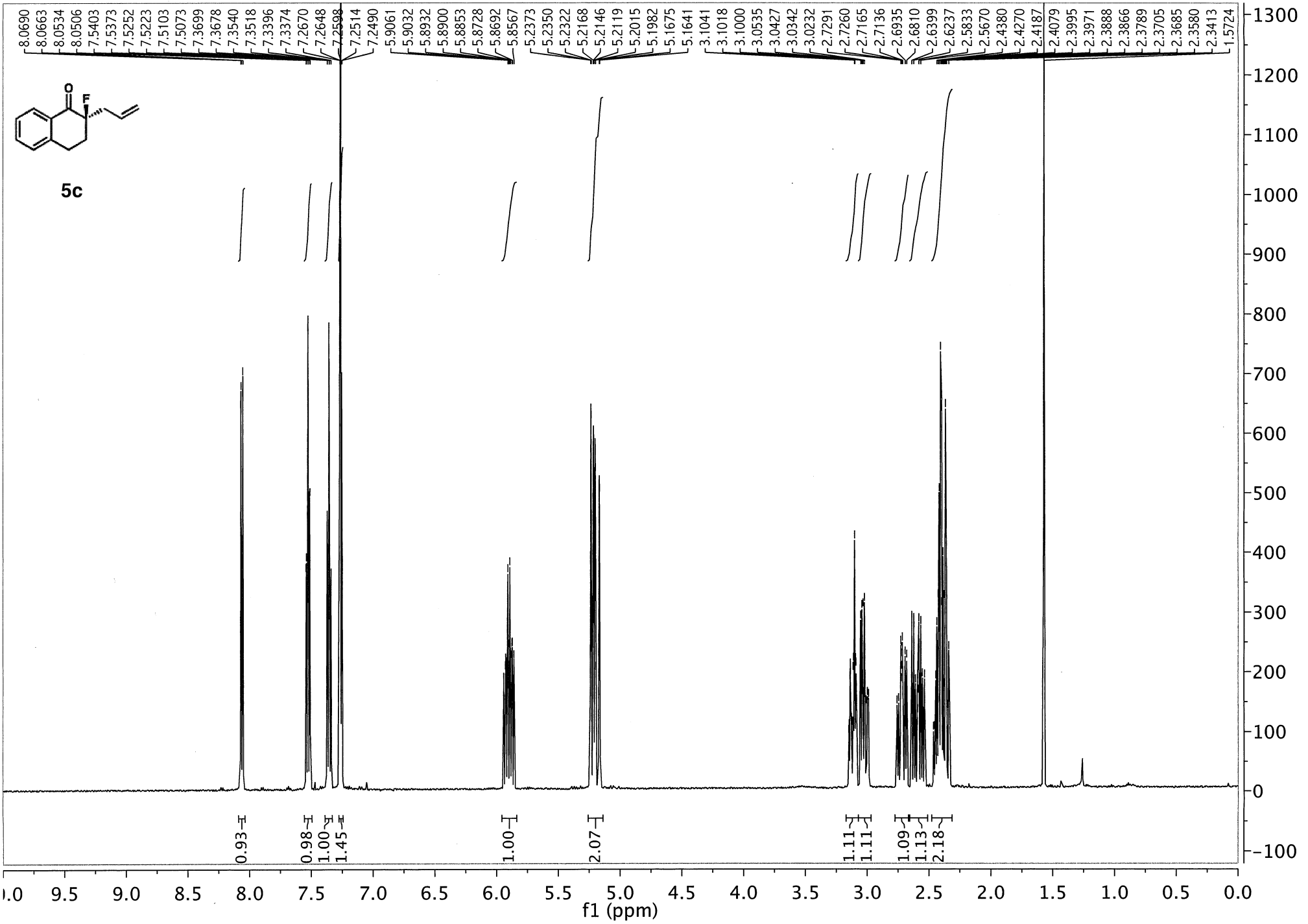
CF3
O
5b
f1 (ppm)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7.5103
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7.3699
7.3678
7.3540
7.3518
7.3396
7.3374
7.2670
7.2648
7.2598
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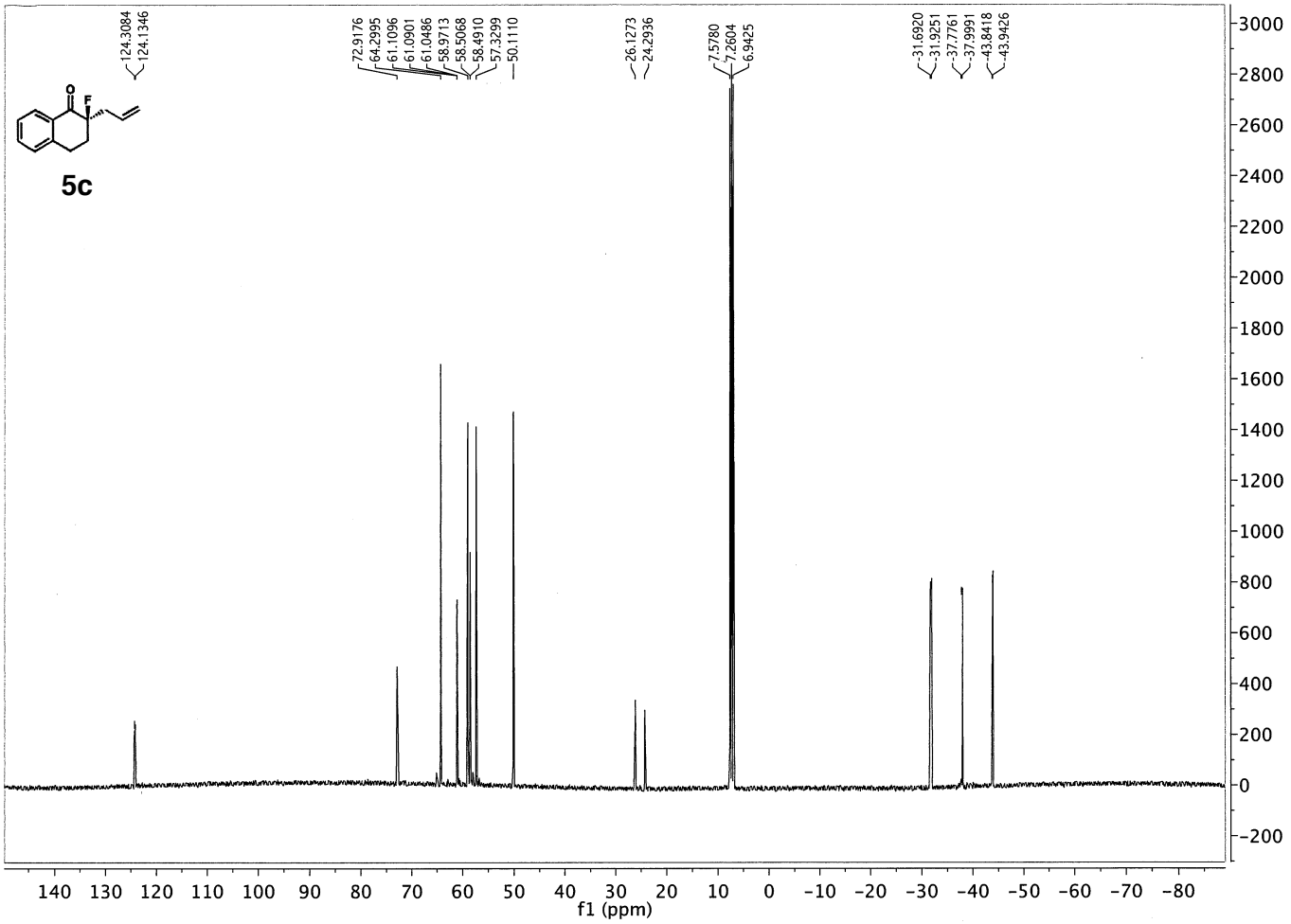
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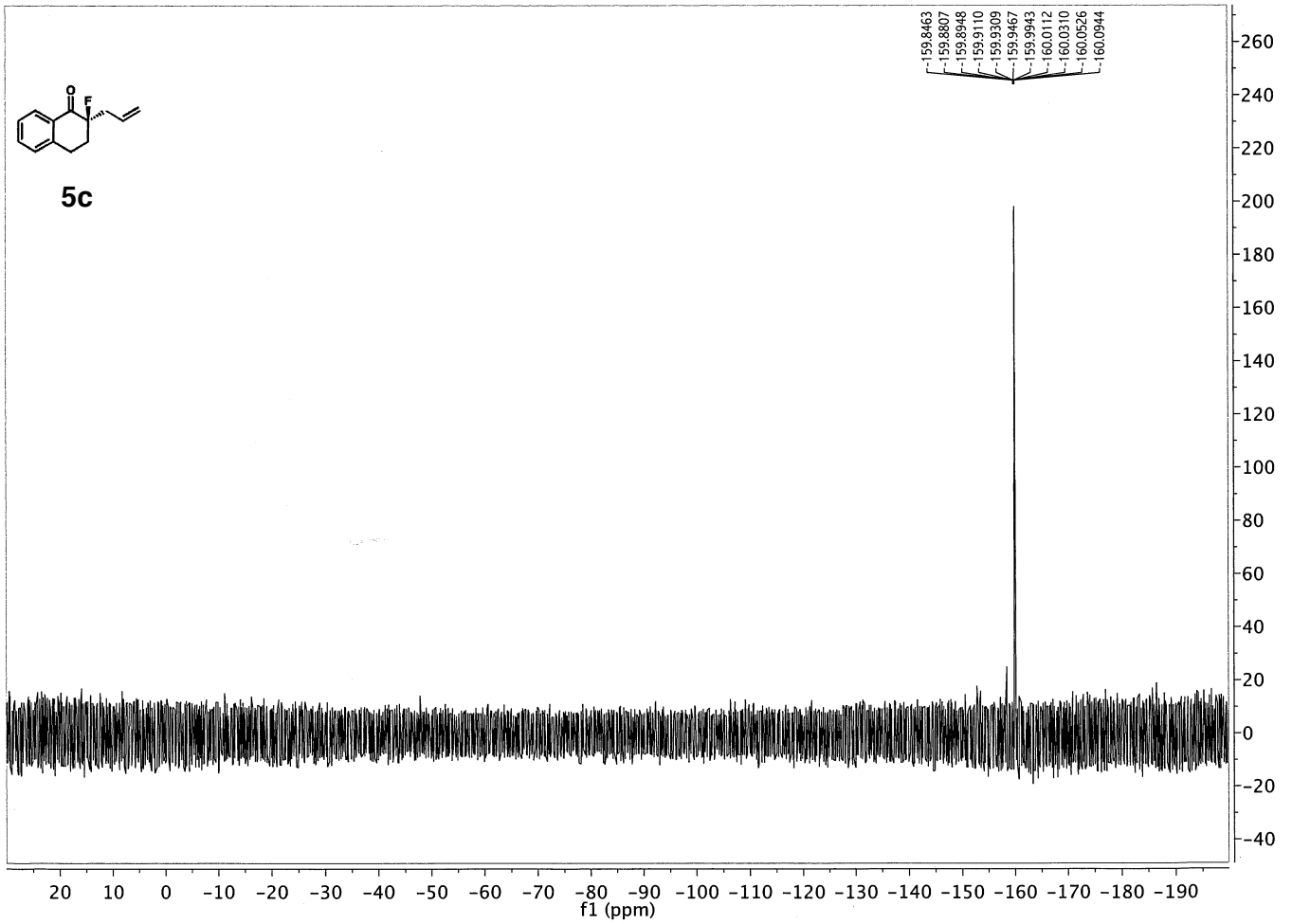
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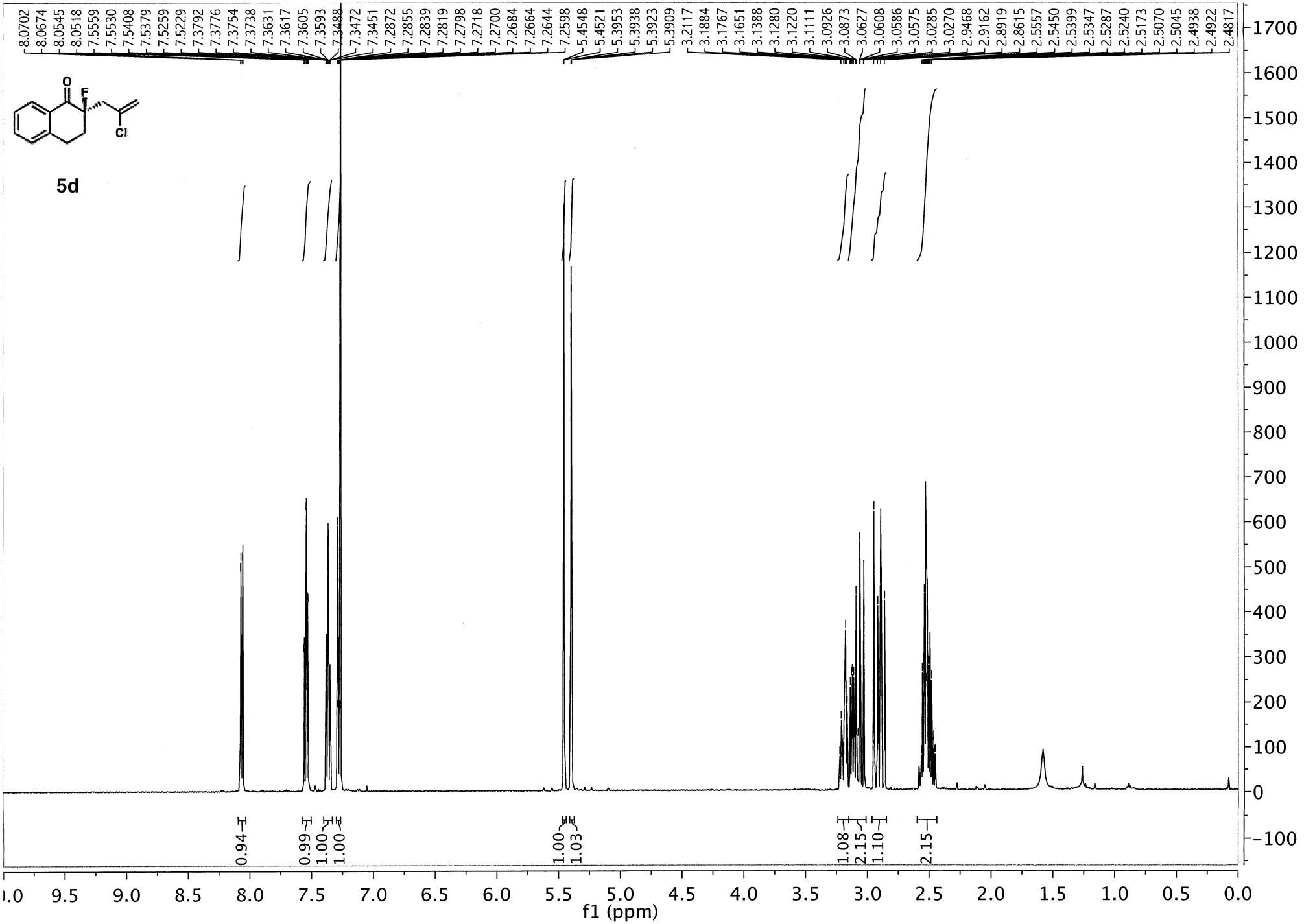
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O
F
Cl
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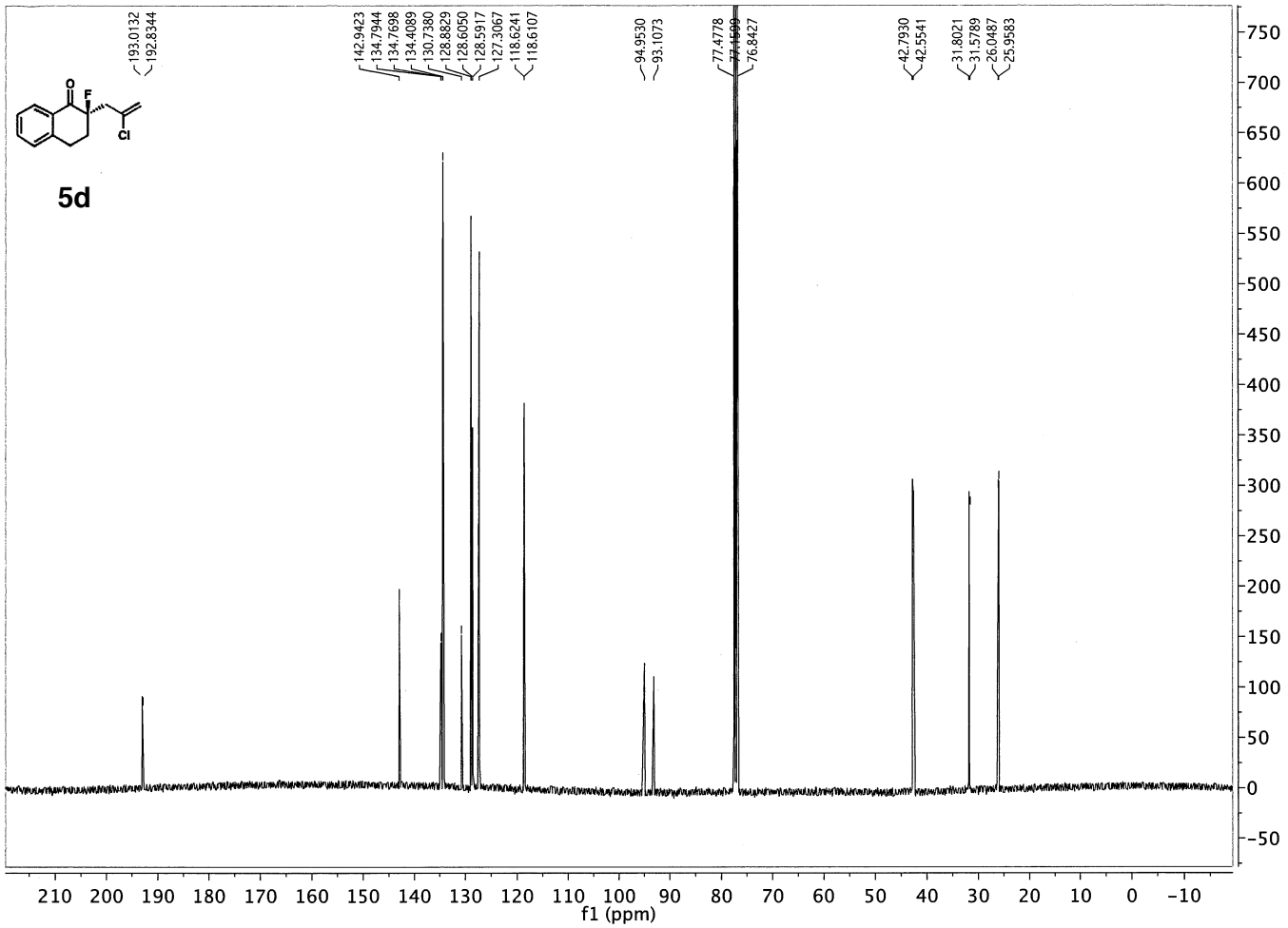
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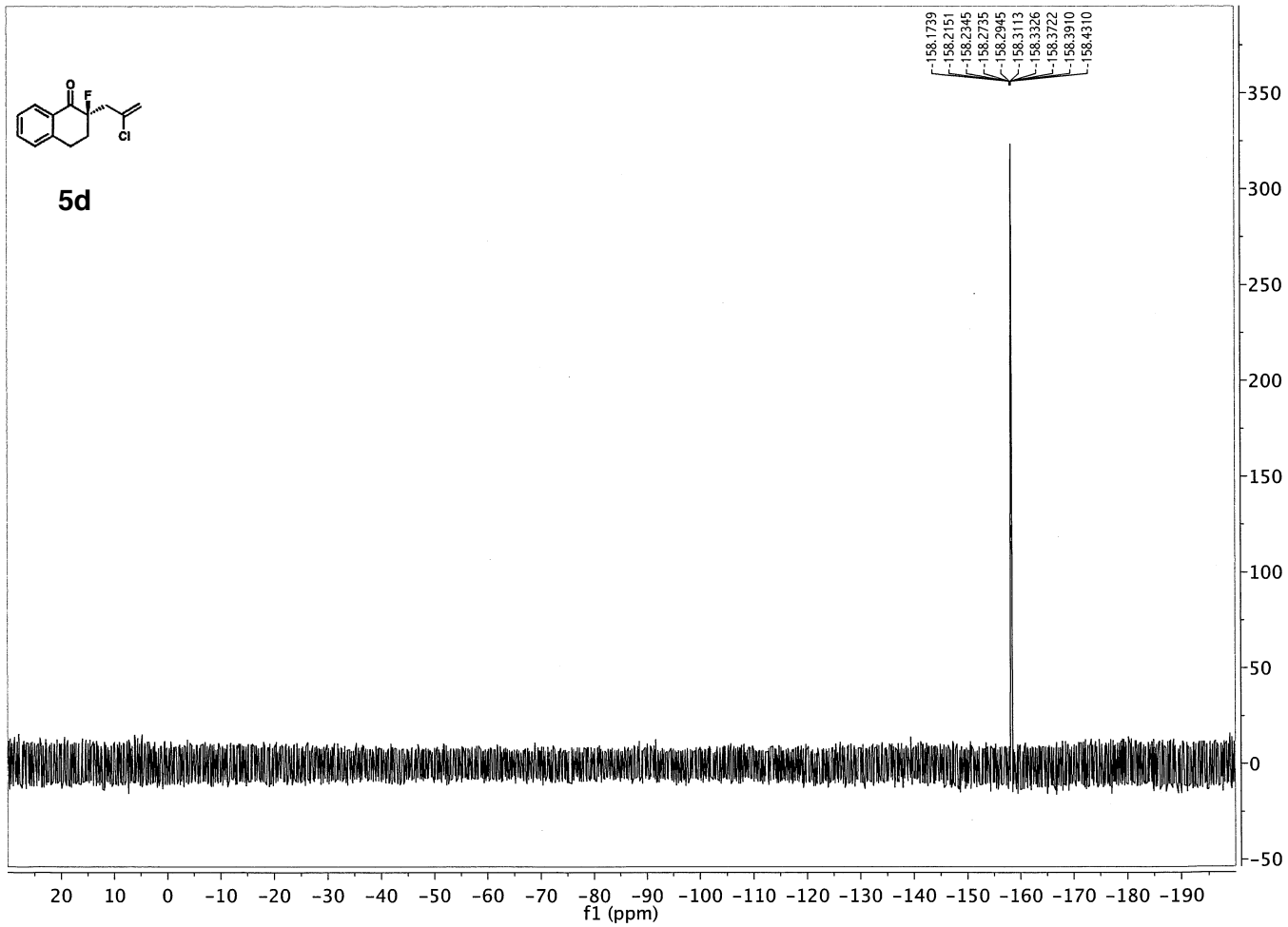
Cl
5d
f1 (ppm)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Cl
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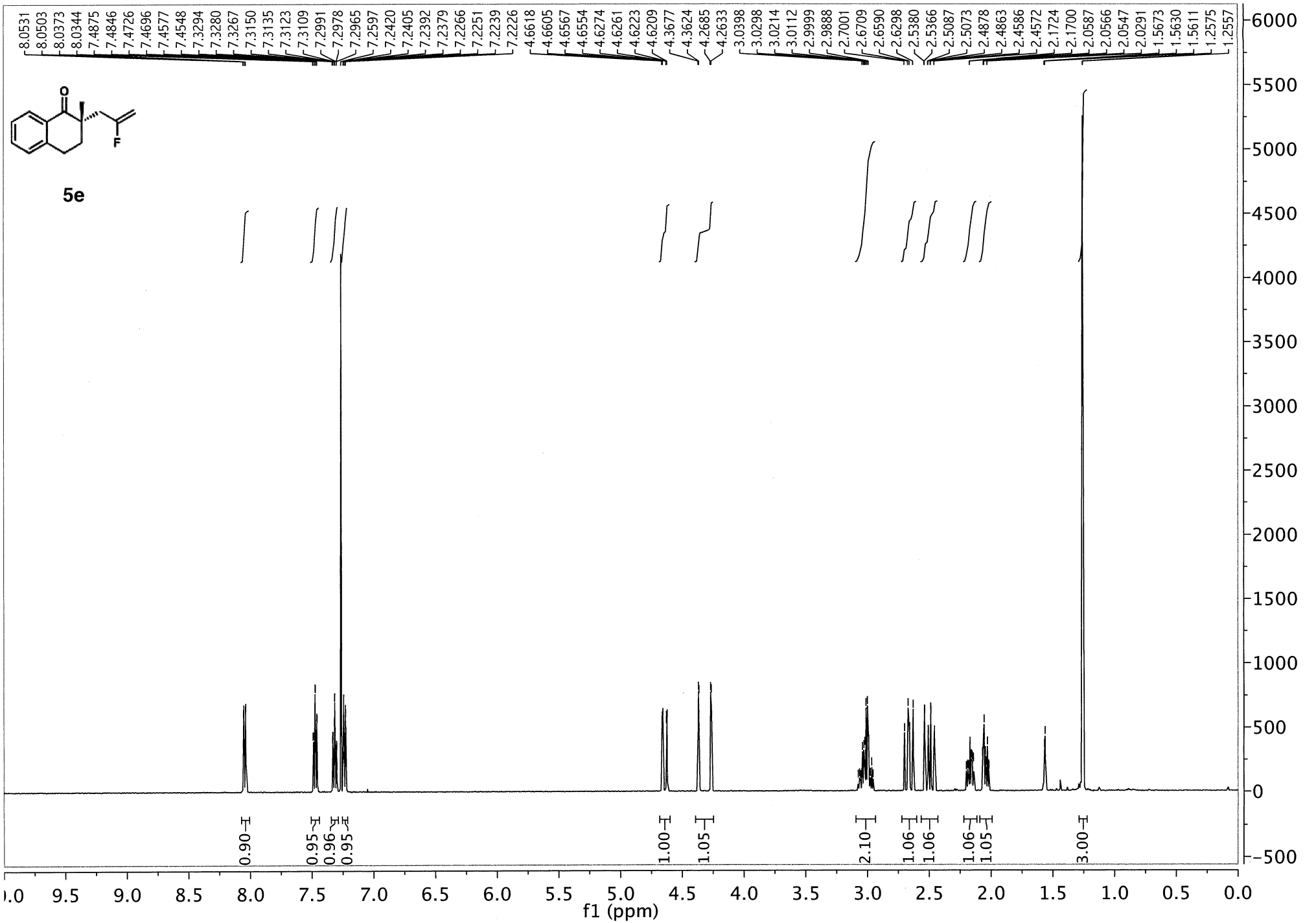
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1.2575
1.2557
O
F
5e
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0.95
0.96
0.95
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1.05
2.10
1.06
1.06
1.06
1.05
3.00
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
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9.0
8.5
8.0
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7.0
6.5
6.0
5.5
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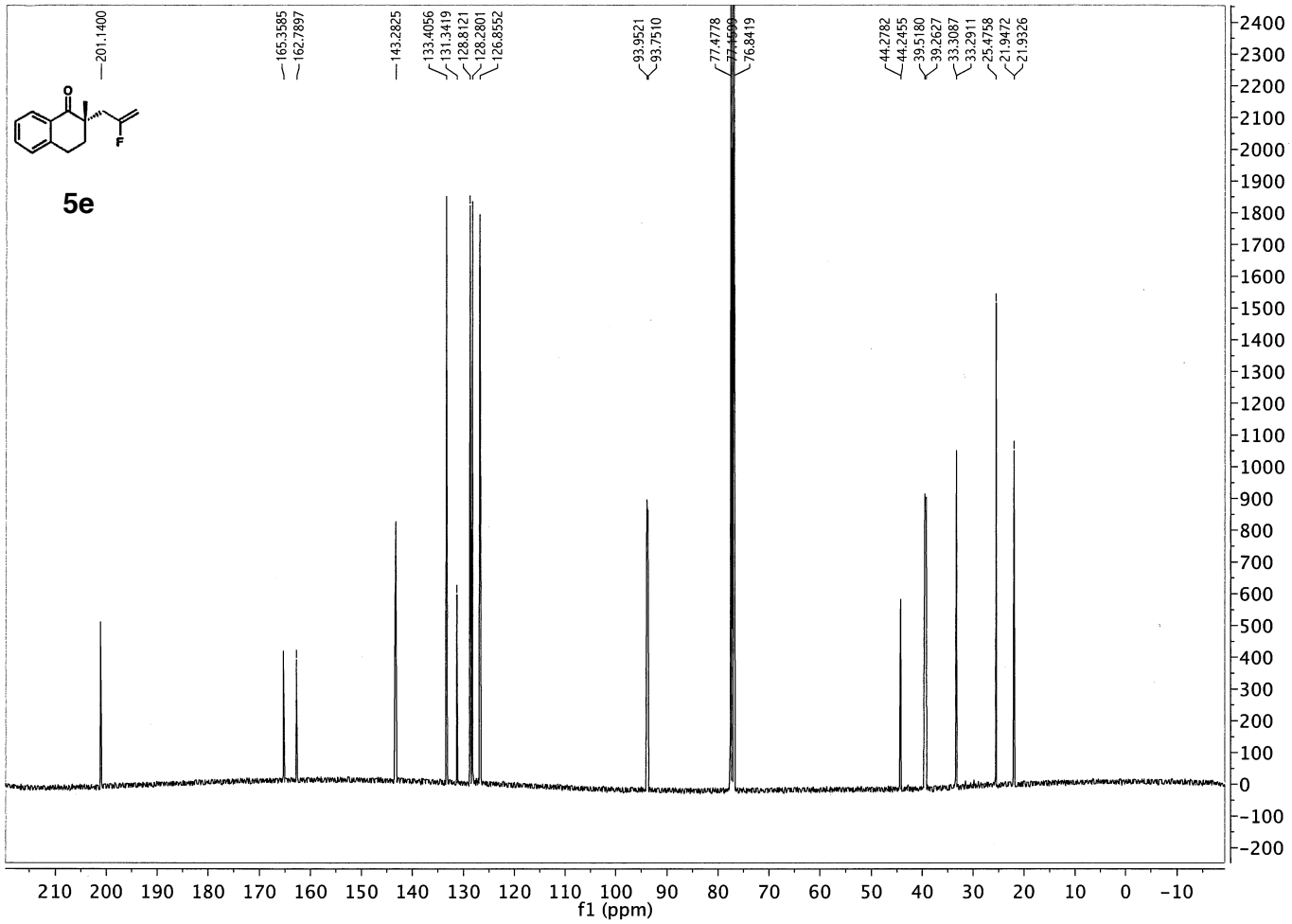
0.0
f1 (ppm)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77.1599
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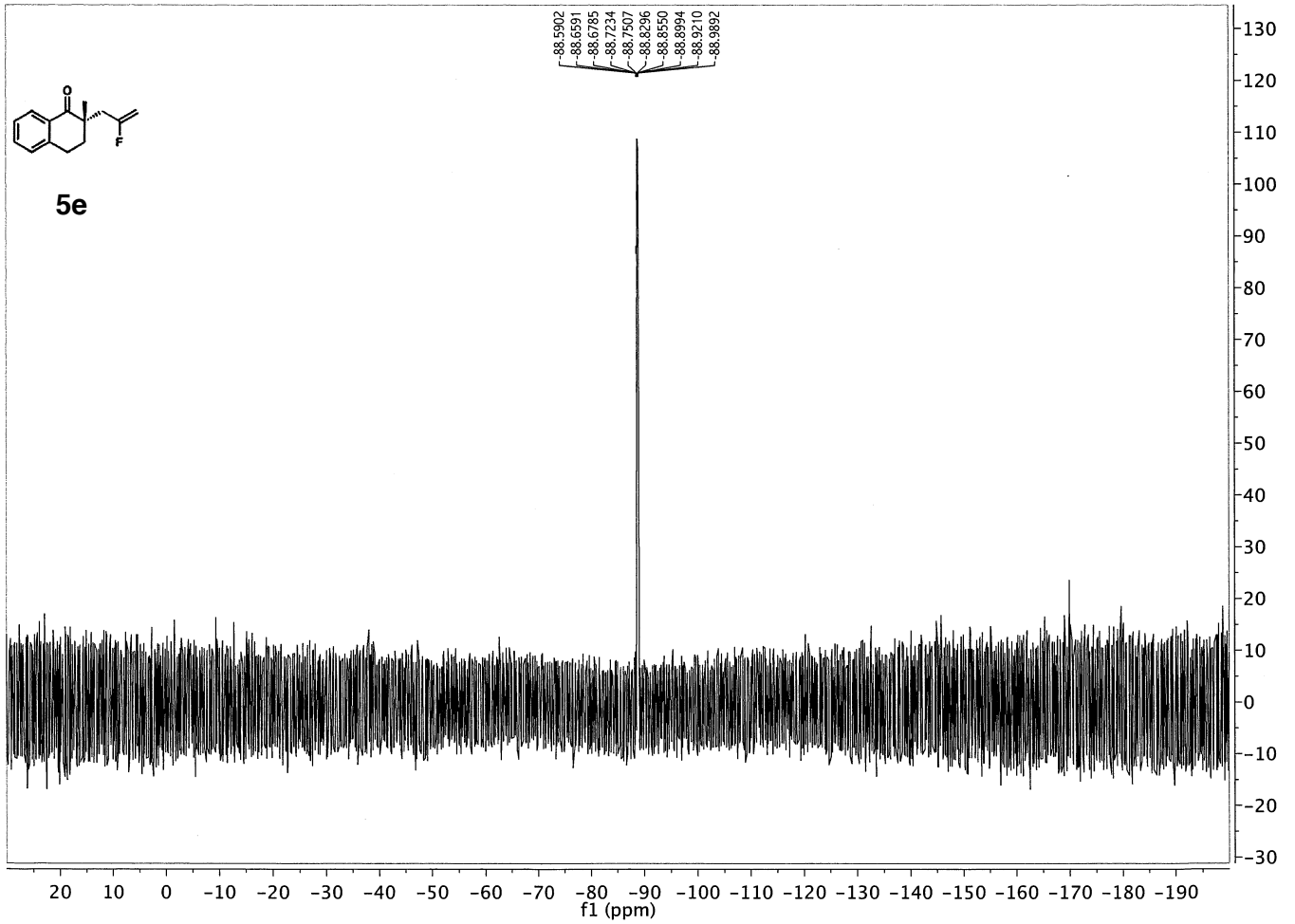
5e
f1 (ppm)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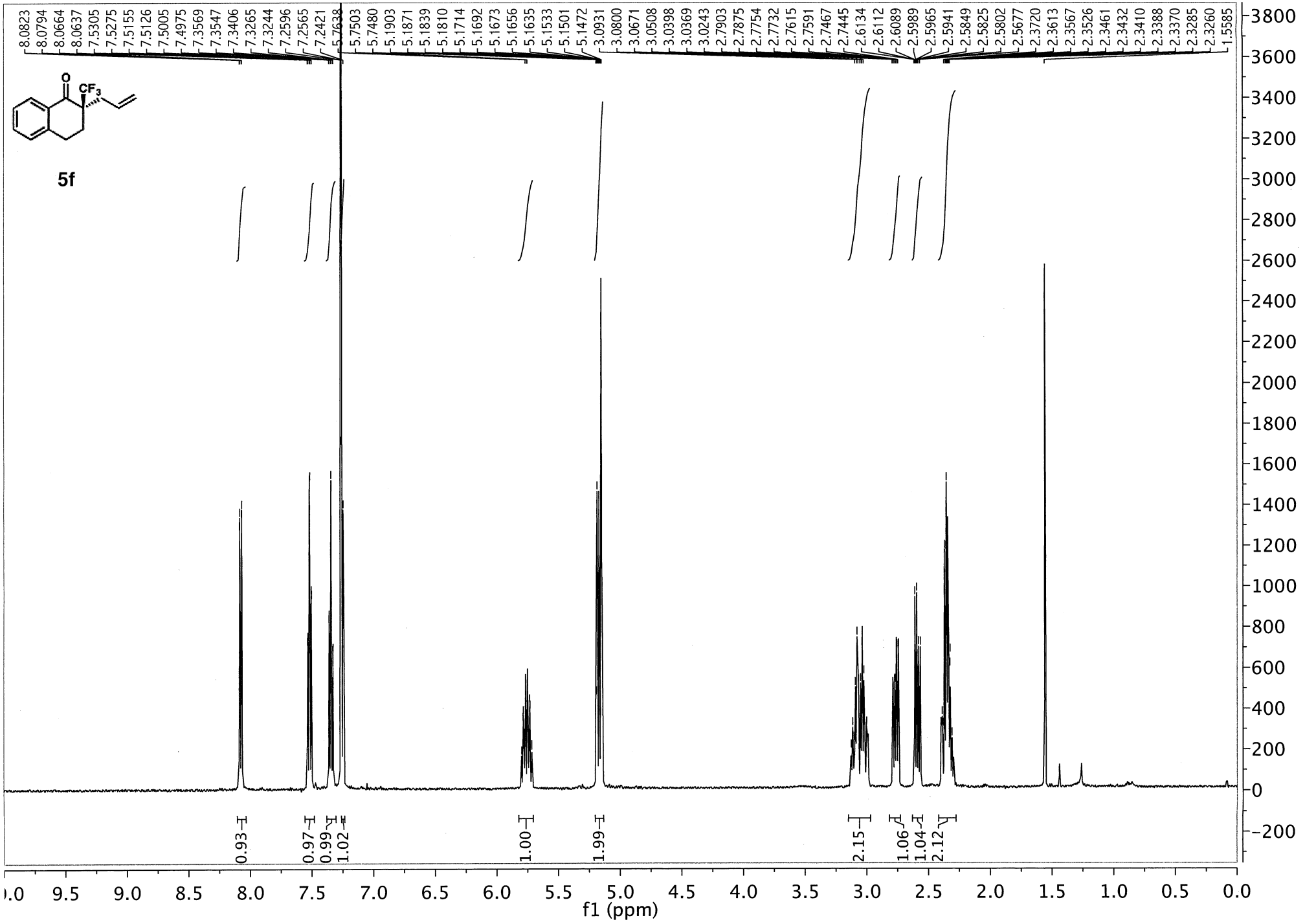
f1 (ppm)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7.2421
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5.1839
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O
CF3
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1.06
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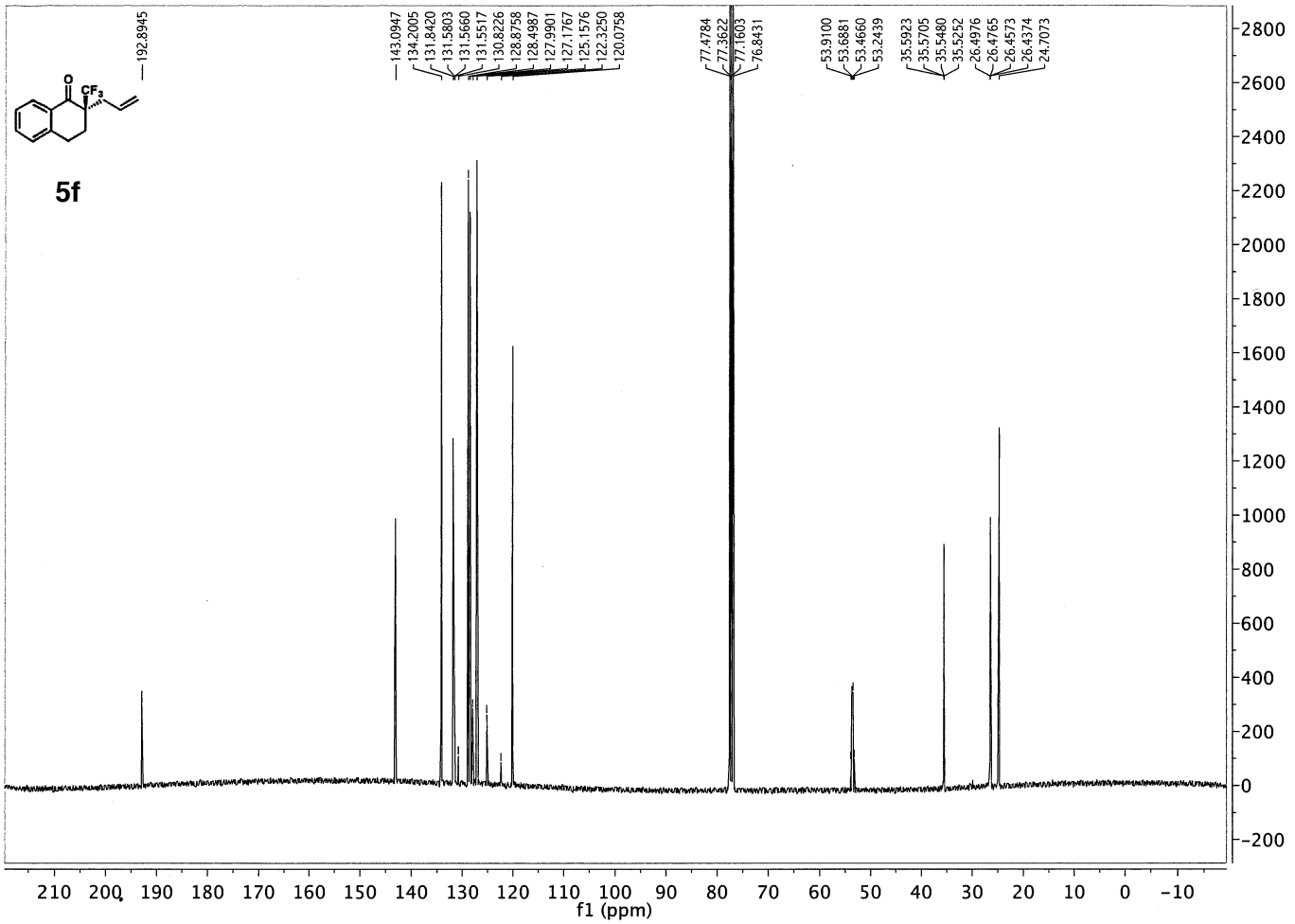
2.12
f1 (ppm)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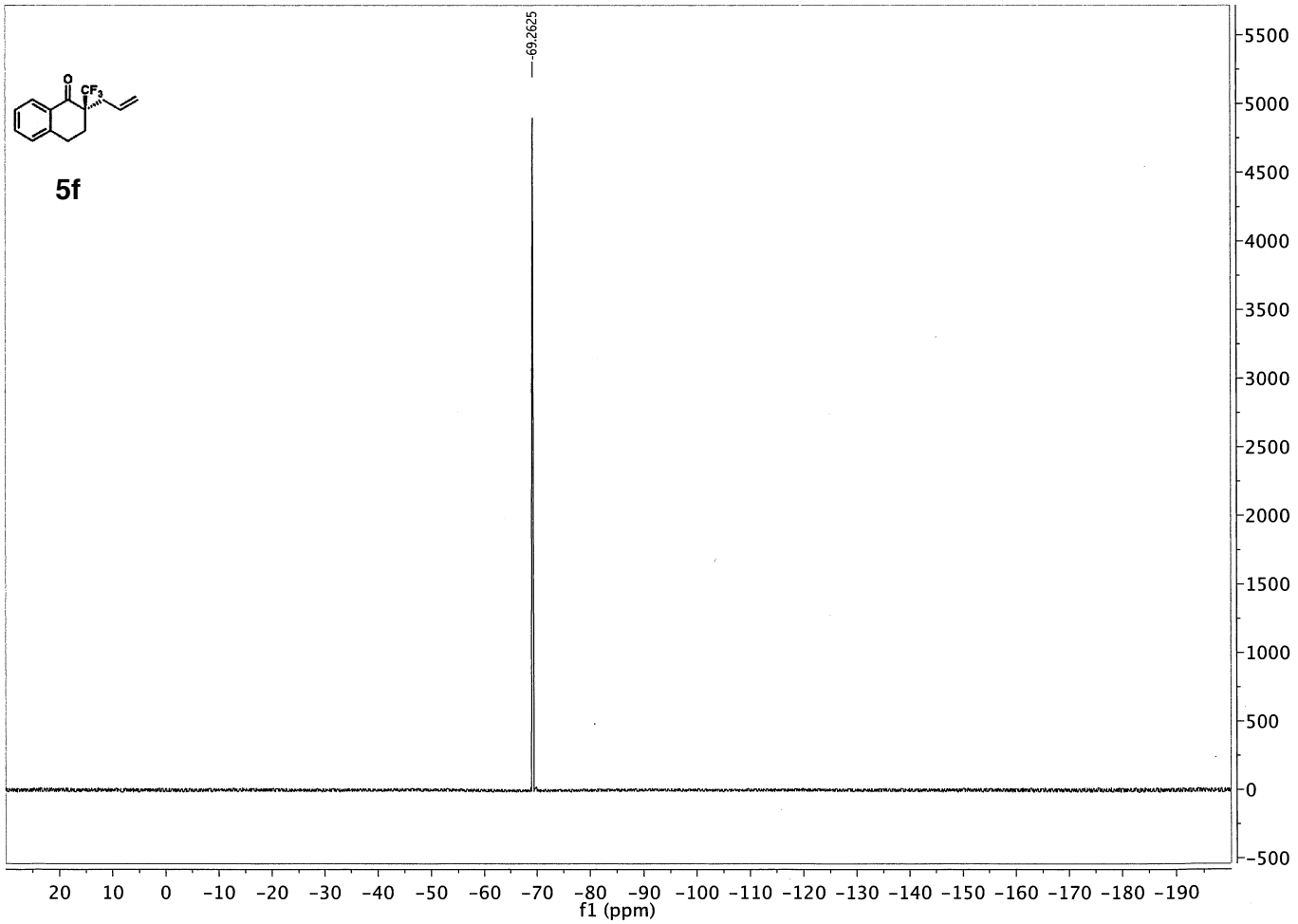
CF3
5f
f1 (ppm)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CF3
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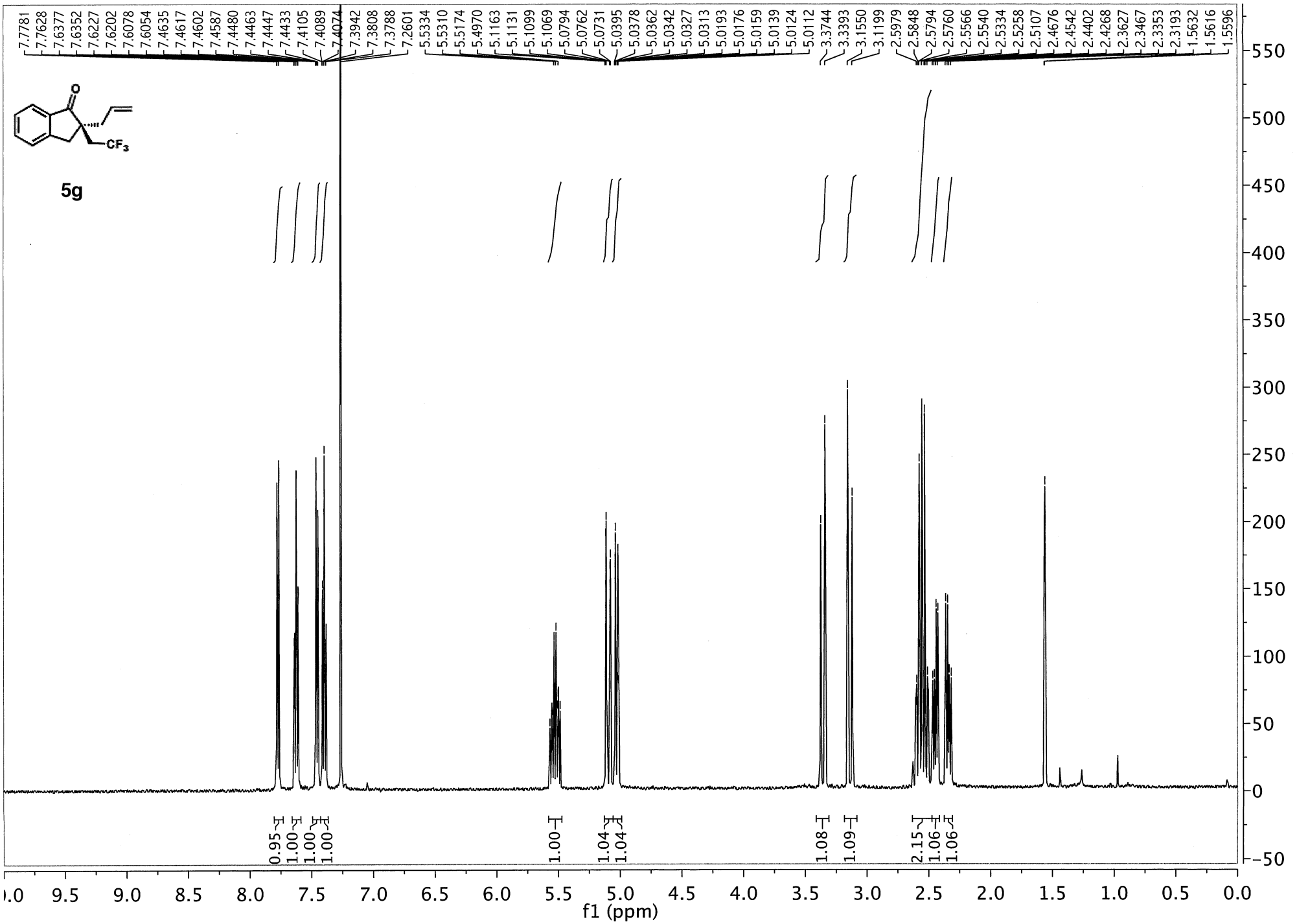
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O
CF3
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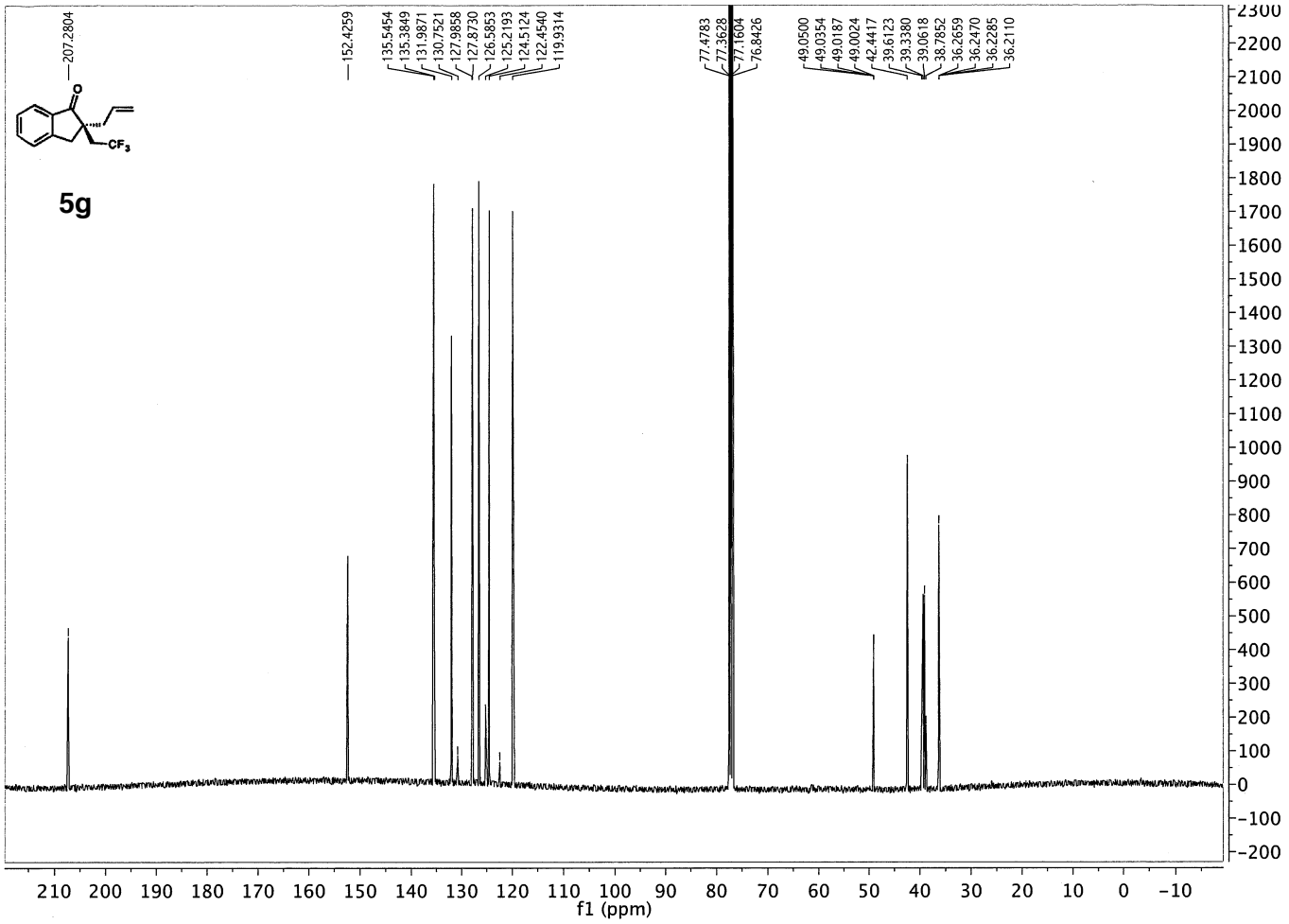
1.06
f1 (ppm)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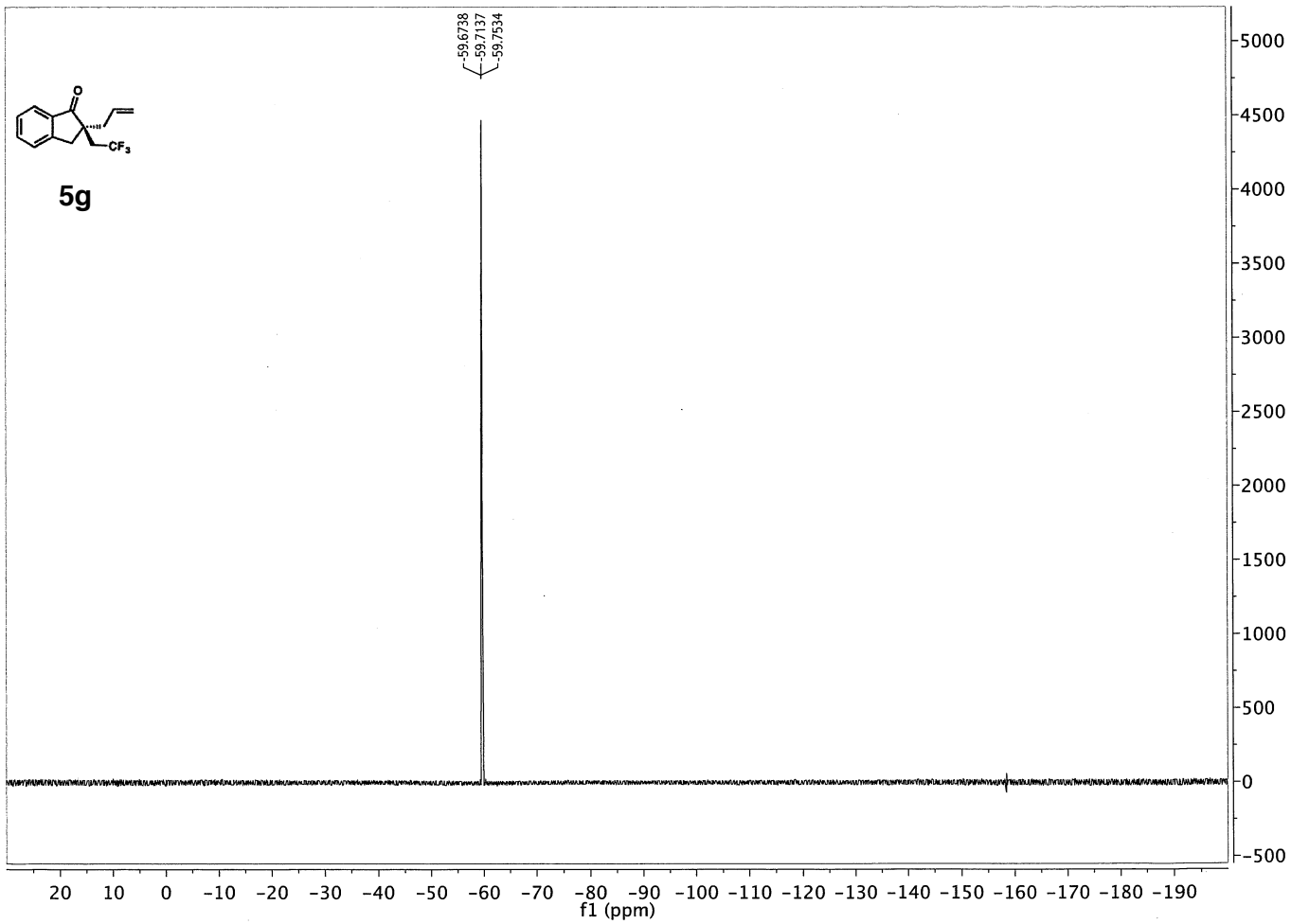
f1 (ppm)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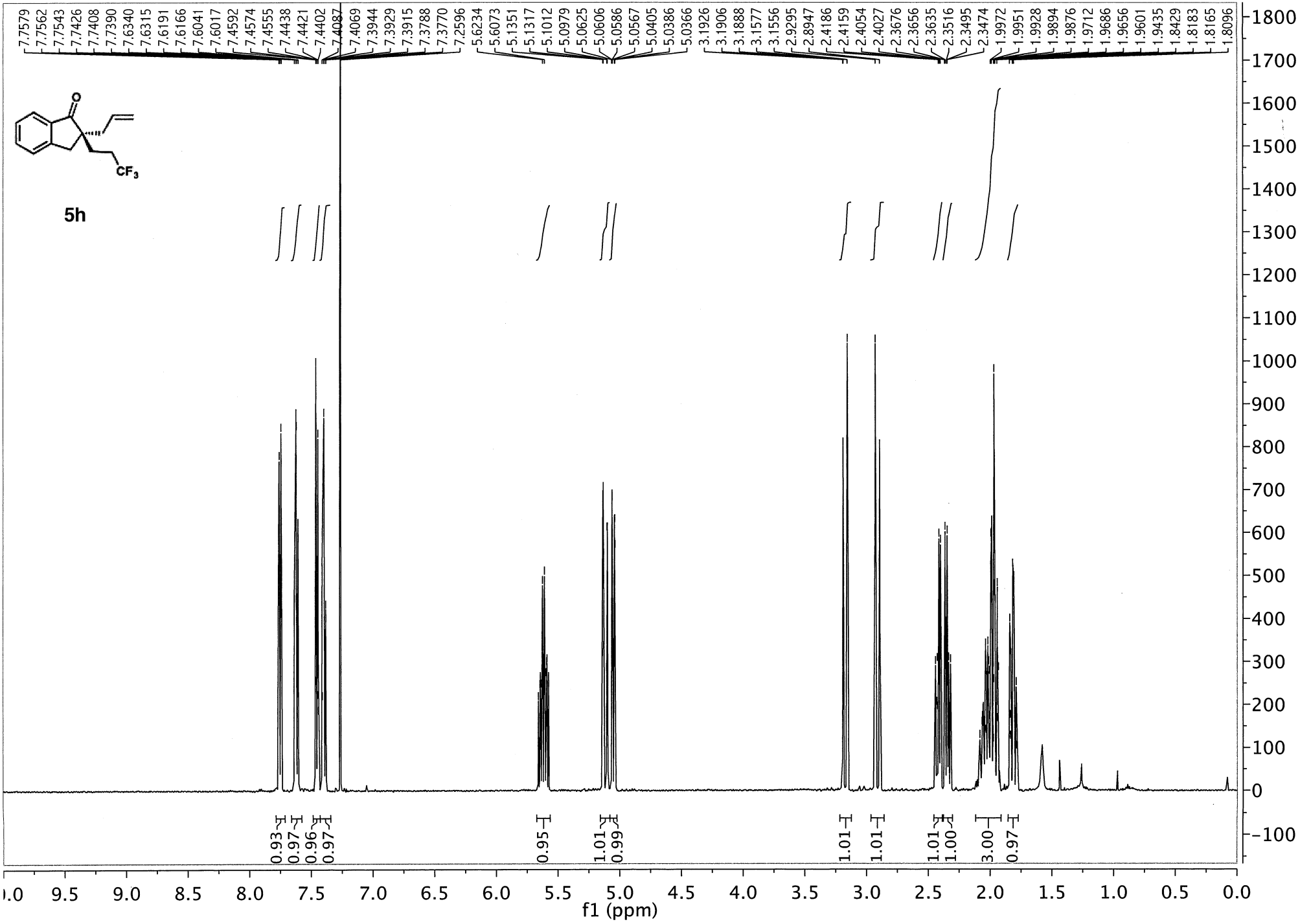
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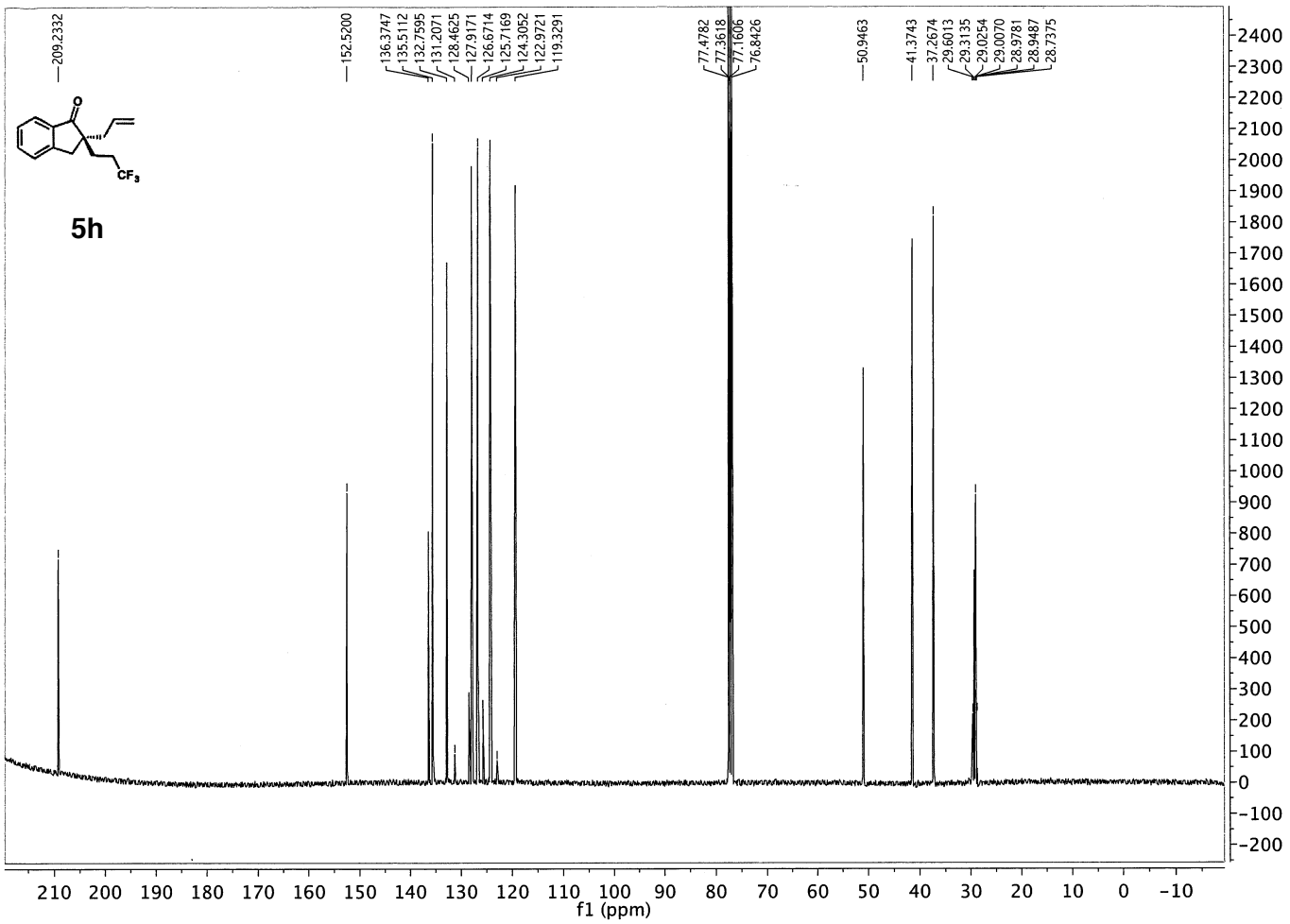
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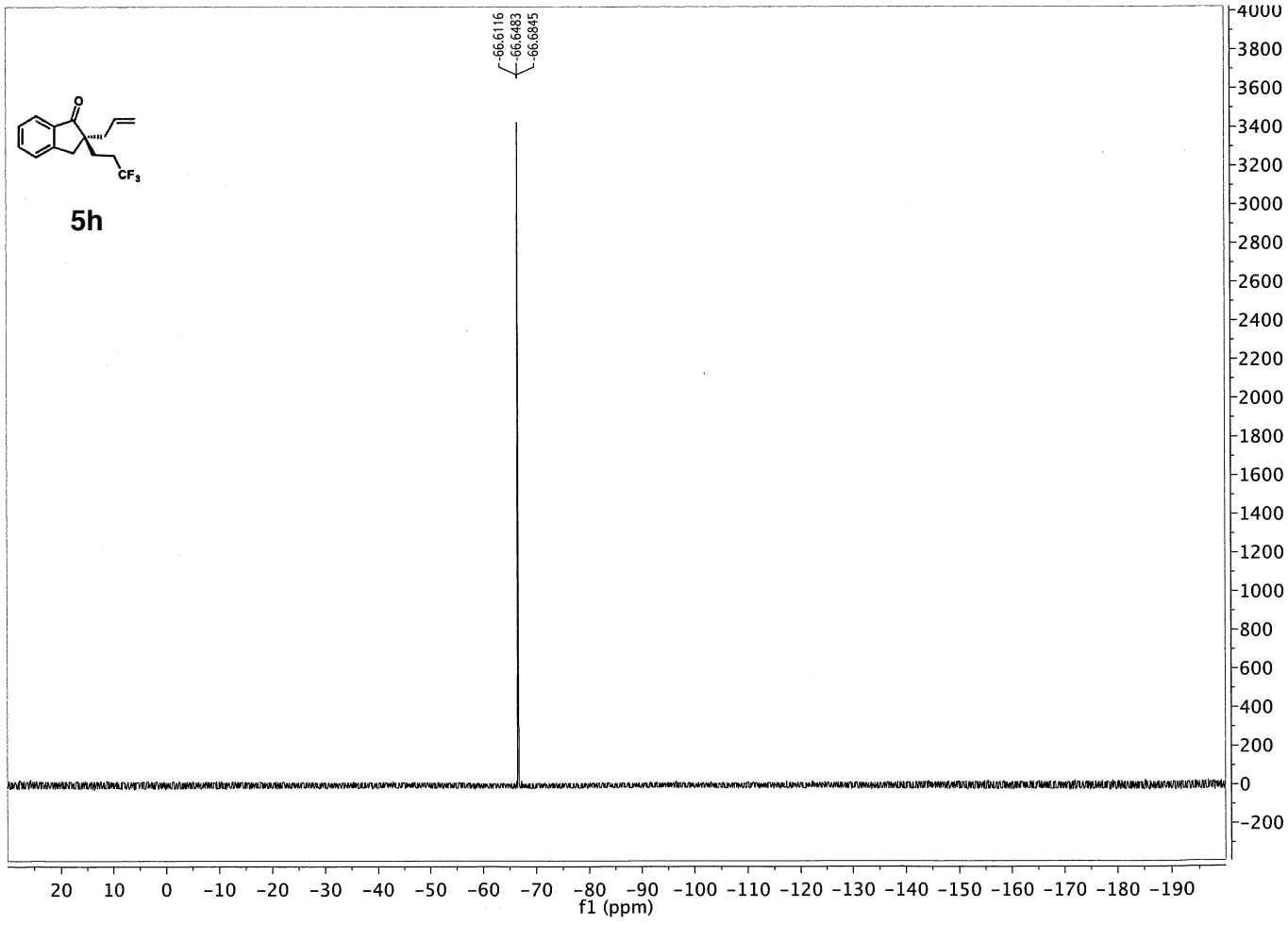
O
CF3
5h
f1 (ppm)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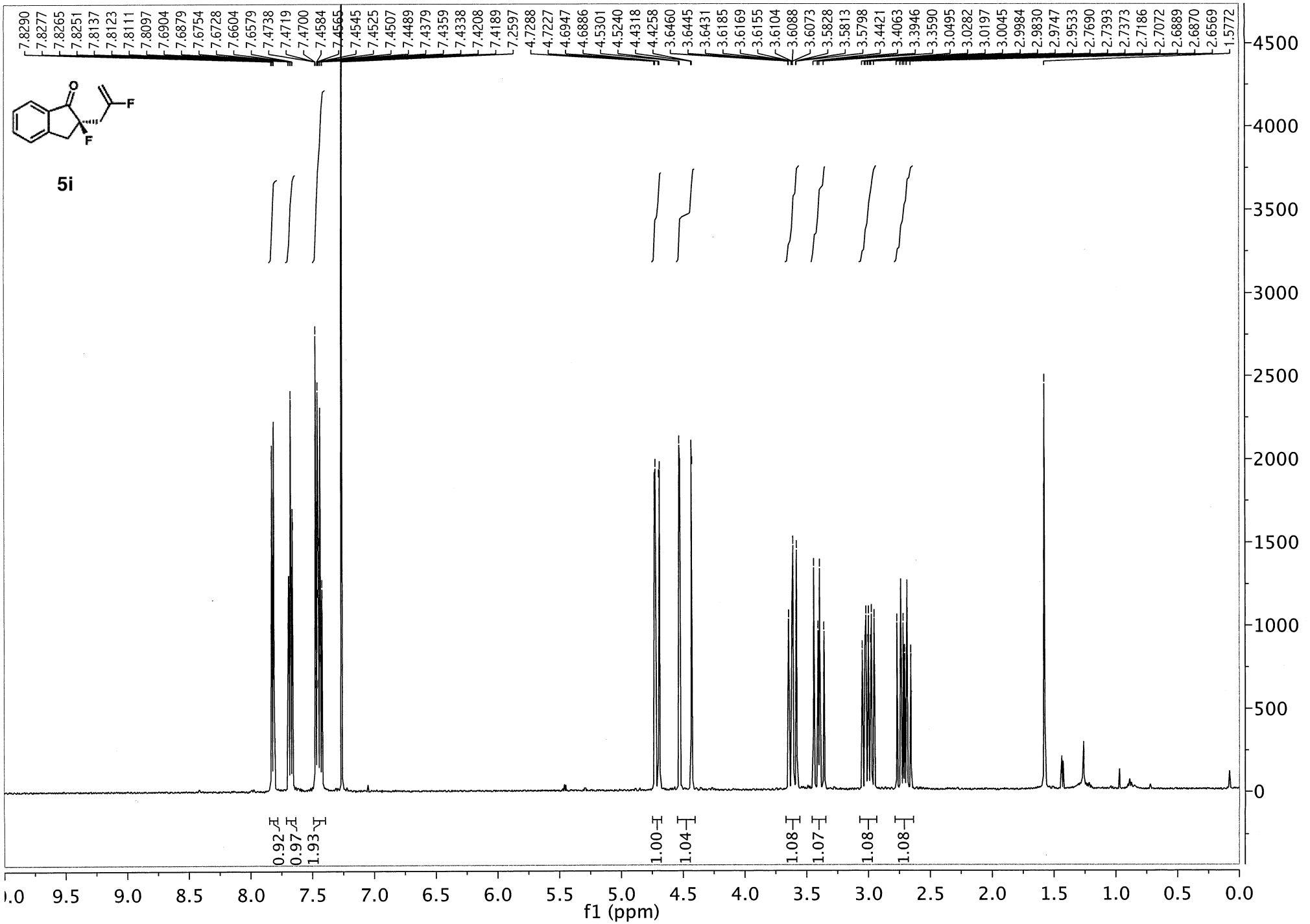
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O
F
F
5i
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1.08
1.07
1.08
1.08
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3000
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2000
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1000
500
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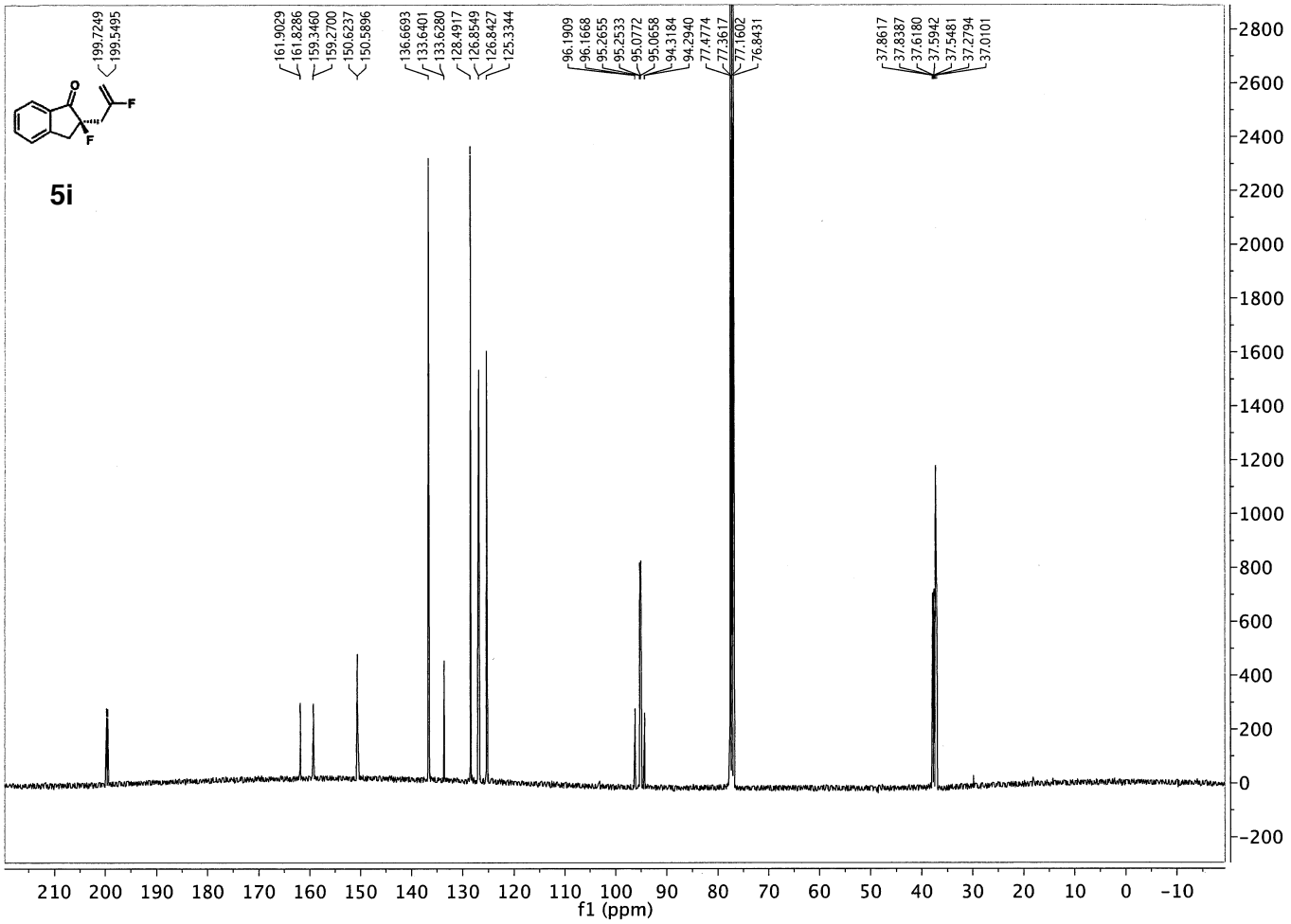
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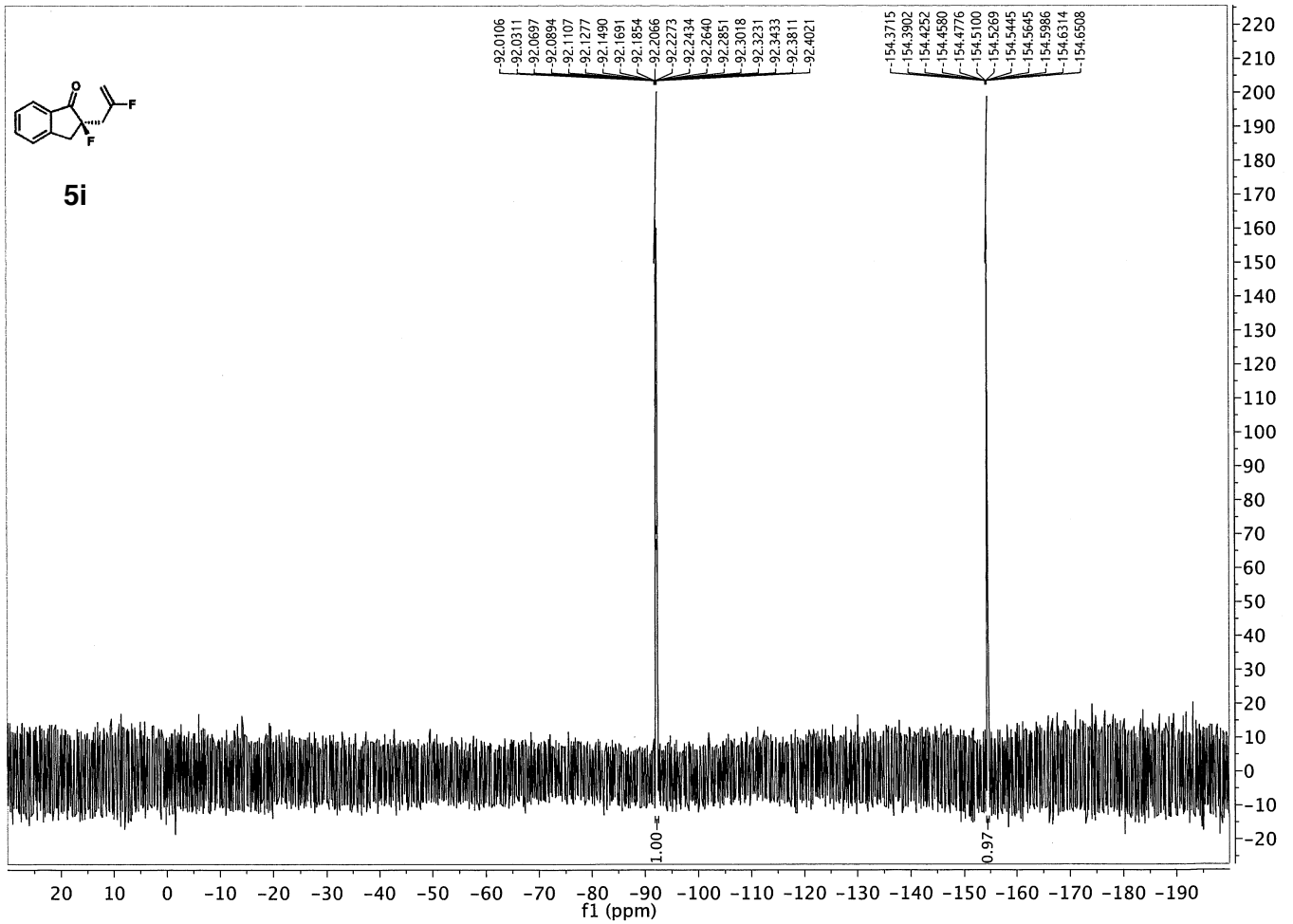
F
F
5i
f1 (ppm)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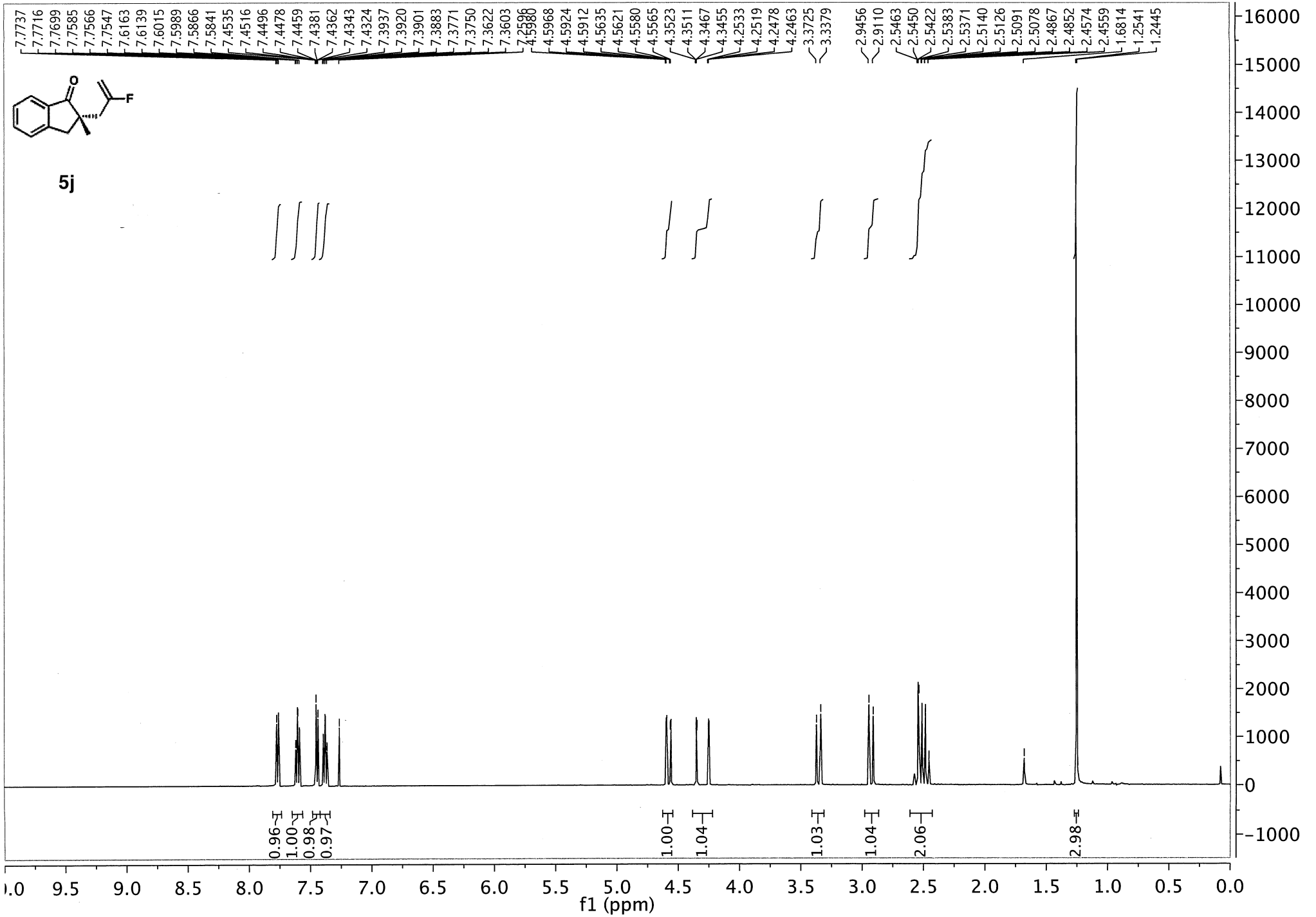
O
F
F
5i
1.00
0.97
f1 (ppm)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O
F
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1.00
0.98
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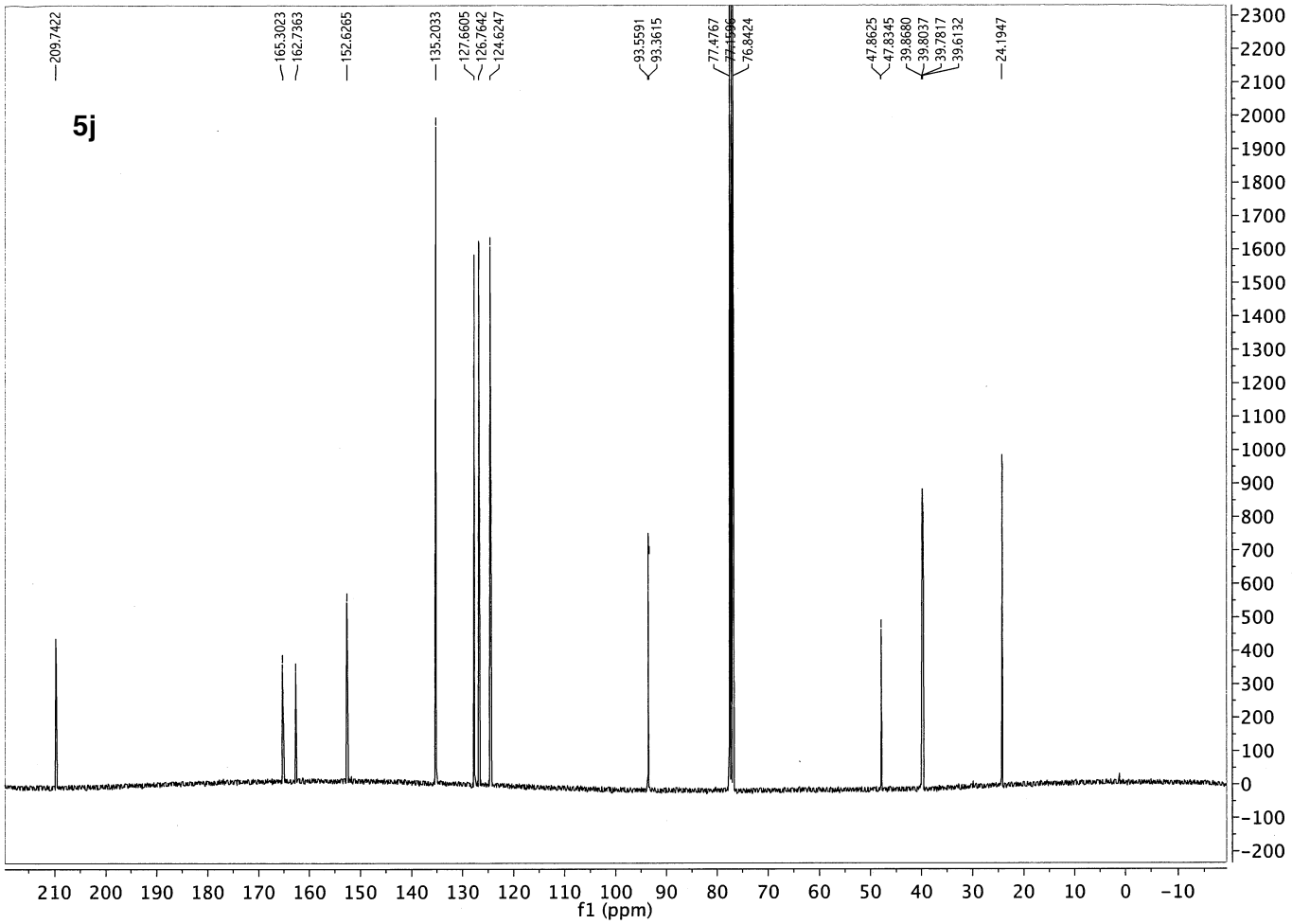
1.00
1.04
1.03
1.04
2.06
2.98
f1 (ppm)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77.4767
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39.8680
39.8037
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39.6132
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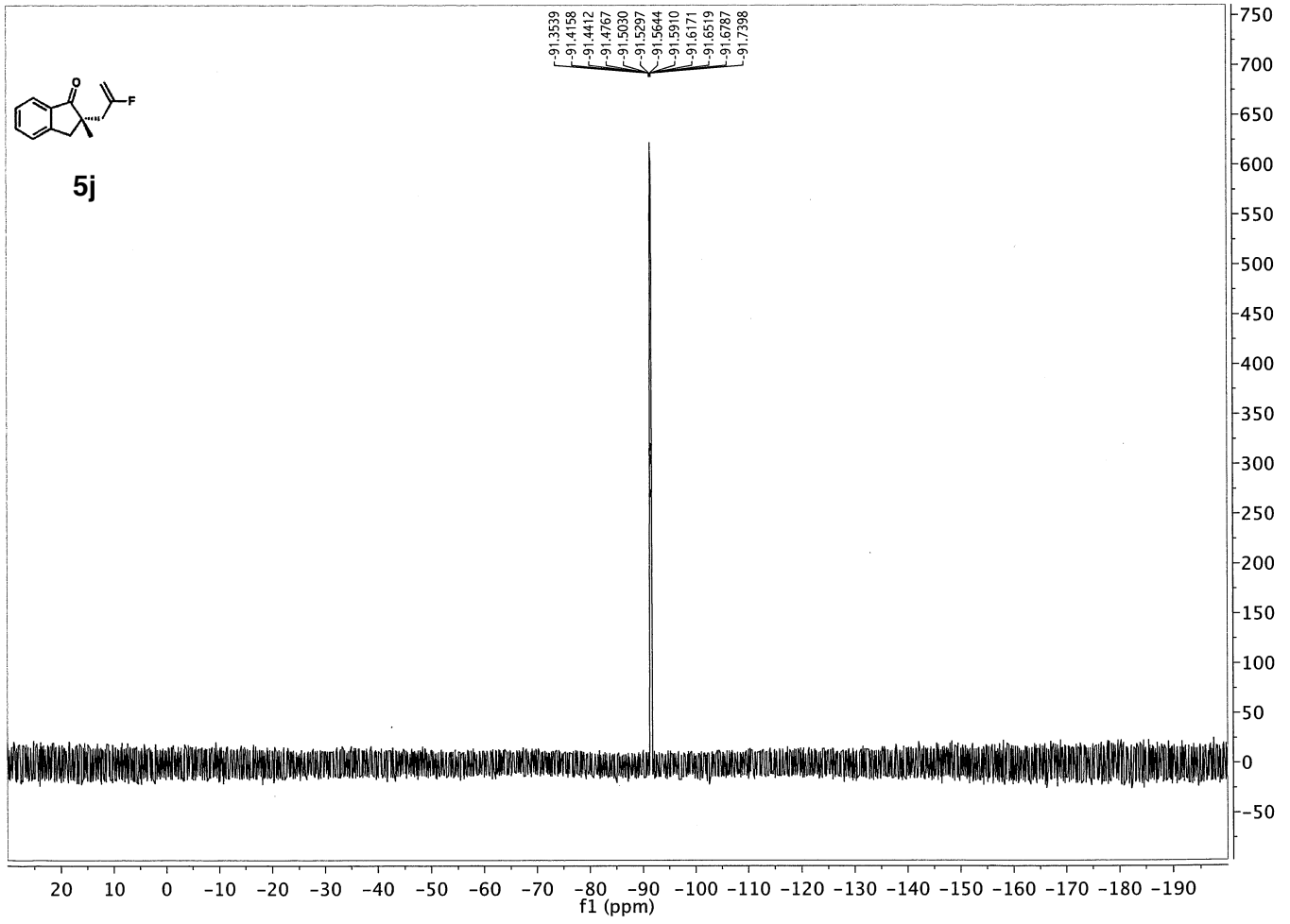
f1 (ppm)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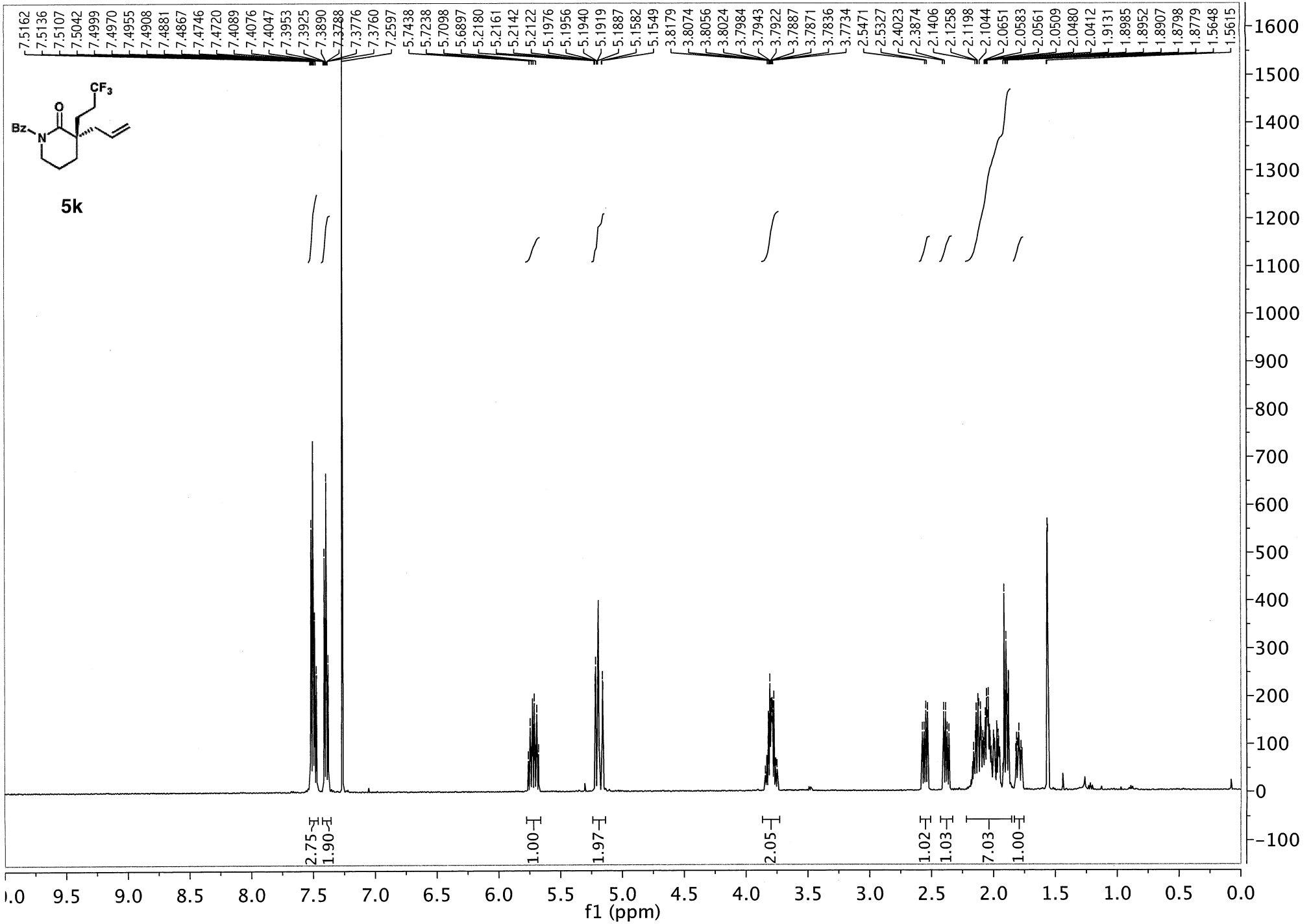
91.6787
91.7398
O
F
5j
f1 (ppm)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7.4955
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7.4867
7.4746
7.4720
7.4089
7.4076
7.4047
7.3953
7.3925
7.3890
7.3788
7.3776
7.3760
7.2597
5.7438
5.7238
5.7098
5.6897
5.2180
5.2161
5.2142
5.2122
5.1976
5.1956
5.1940
5.1919
5.1887
5.1582
5.1549
3.8179
3.8074
3.8056
3.8024
3.7984
3.7943
3.7922
3.7887
3.7871
3.7836
3.7734
2.5471
2.5327
2.4023
2.3874
2.1406
2.1258
2.1198
2.1044
2.0651
2.0583
2.0561
2.0509
2.0480
2.0412
1.9131
1.8985
1.8952
1.8907
1.8798
1.8779
1.5648
1.5615
CF3
O
Bz
N
5k
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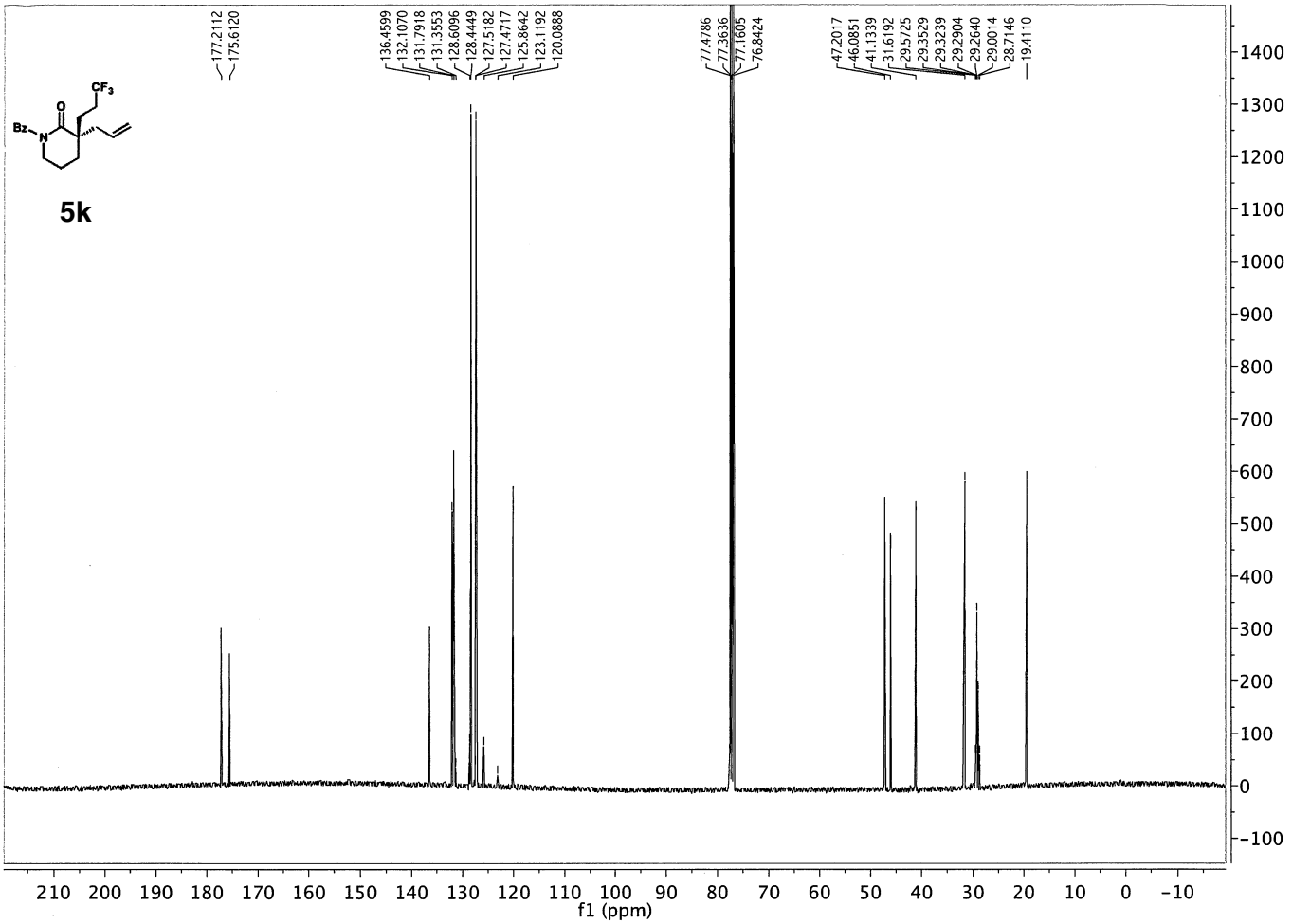
1.90
1.00
1.97
2.05
1.02
1.03
7.03
1.00
f1 (ppm)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123.1192
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77.4786
77.3636
77.1605
76.8424
47.2017
46.0851
41.1339
31.6192
29.5725
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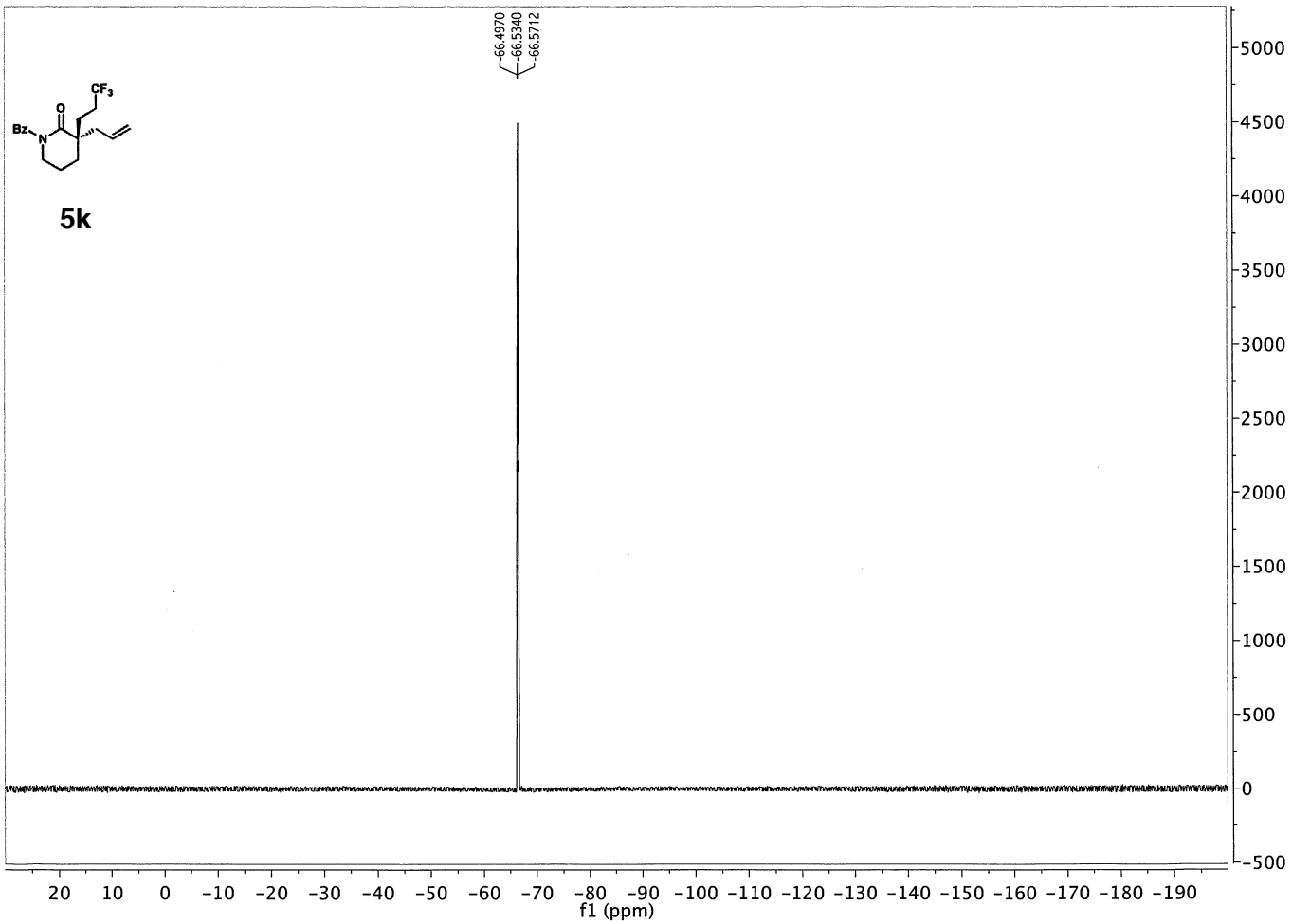
19.4110
Bz
CF3
5k
f1 (ppm)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Bz
CF3
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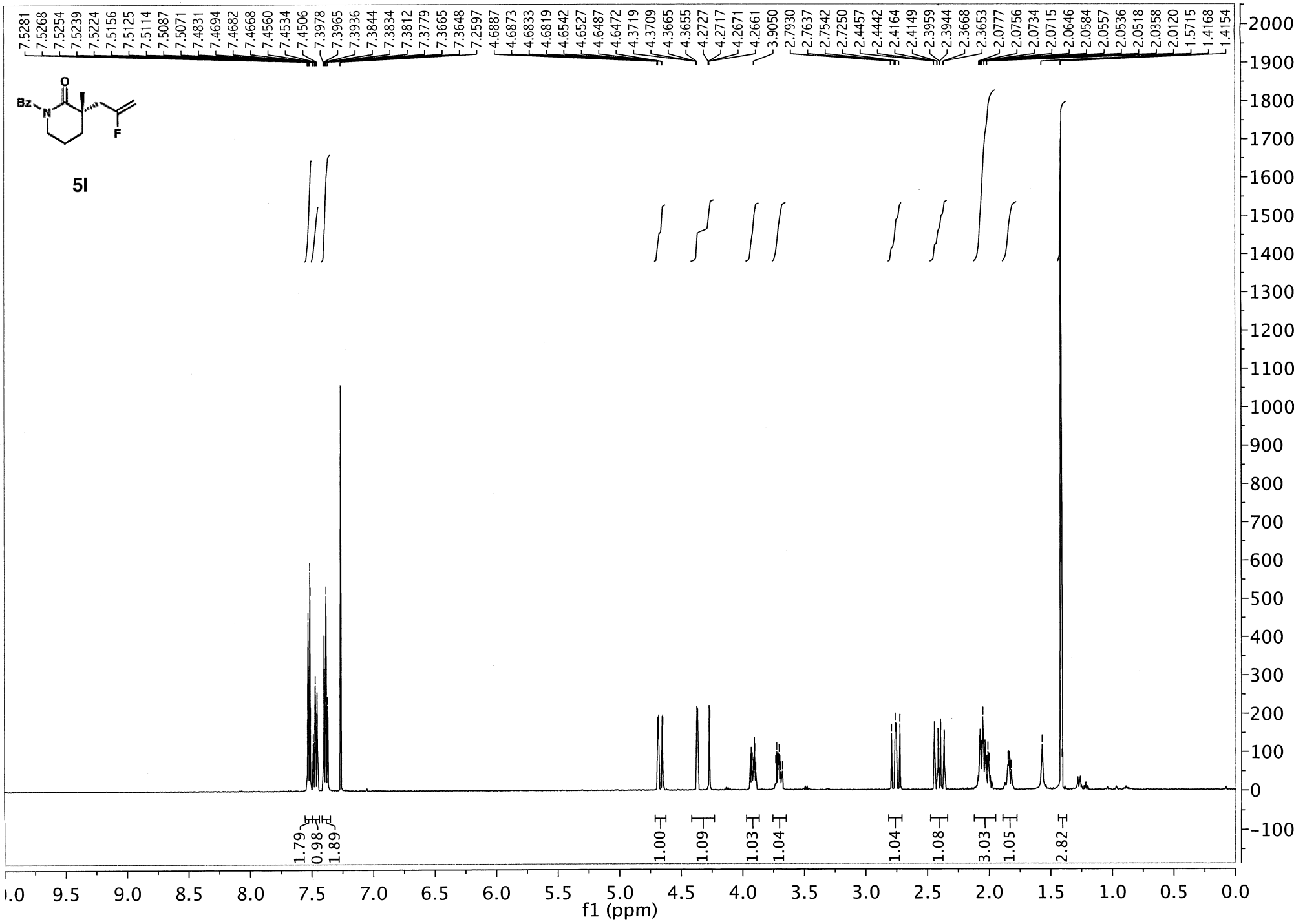
f1 (ppm)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7.4694
7.4682
7.4668
7.4560
7.4534
7.4506
7.3978
7.3965
7.3936
7.3844
7.3834
7.3812
7.3779
7.3665
7.3648
7.2597
4.6887
4.6873
4.6833
4.6819
4.6542
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4.6472
4.3719
4.3709
4.3665
4.3655
4.2727
4.2717
4.2671
4.2661
3.9050
2.7930
2.7637
2.7542
2.7250
2.4457
2.4442
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2.4149
2.3959
2.3944
2.3668
2.3653
2.0777
2.0756
2.0734
2.0715
2.0646
2.0584
2.0557
2.0536
2.0518
2.0358
2.0120
1.5715
1.4168
1.4154
Bz
N
O
F
5l
1.79
0.98
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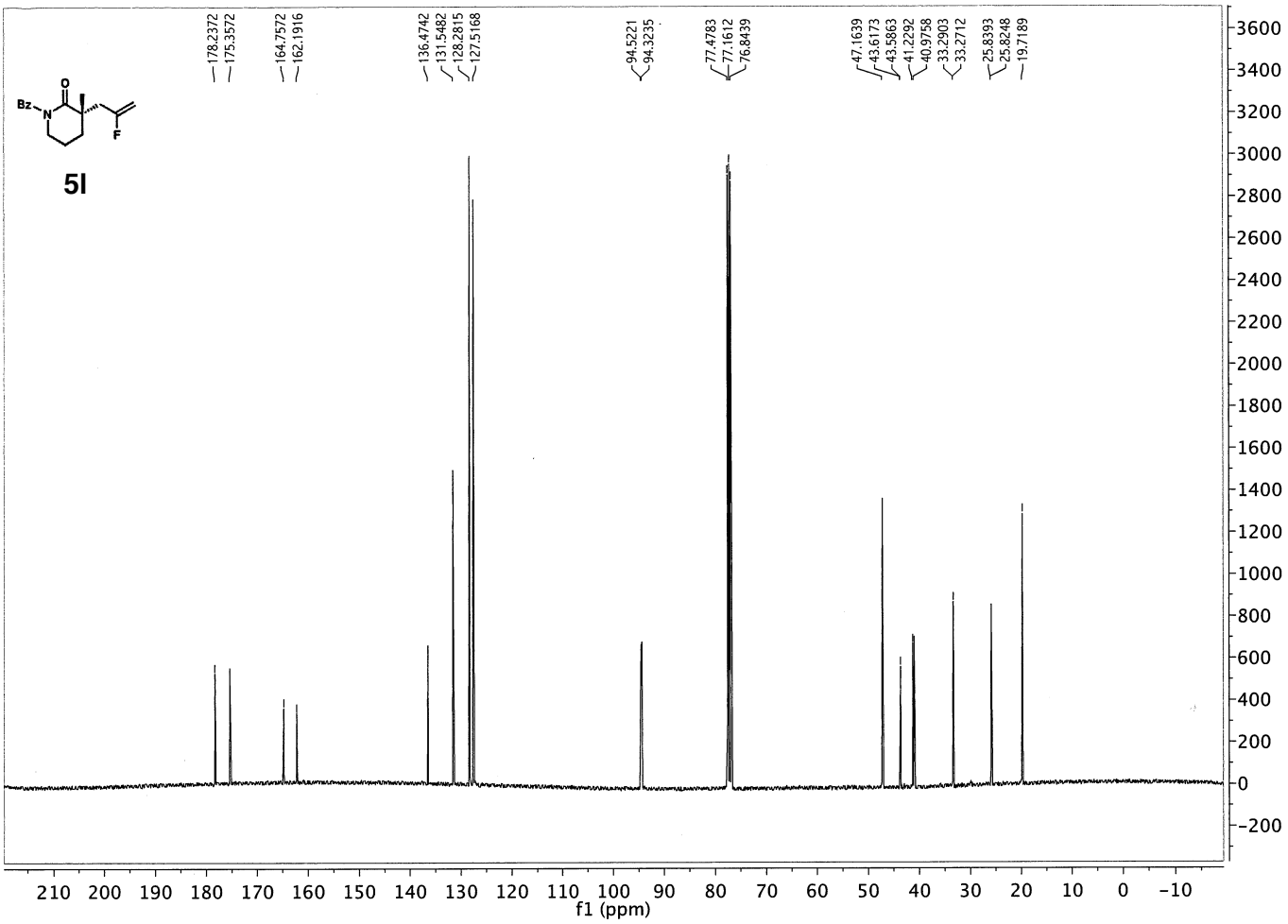
1.09
1.03
1.04
1.04
1.08
3.03
1.05
2.82
f1 (ppm)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76.8439
47.1639
43.6173
43.5863
41.2292
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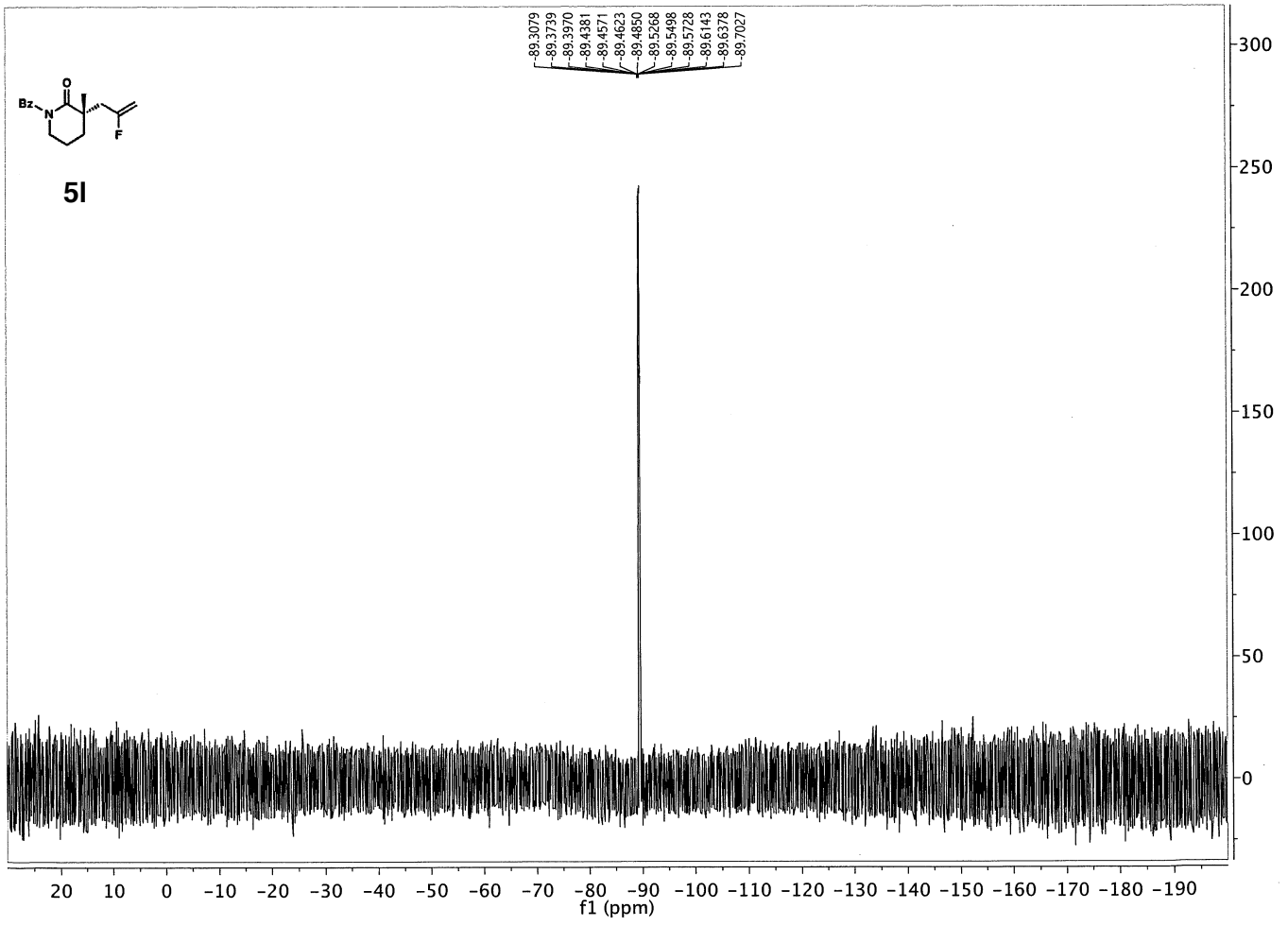
33.2712
25.8393
25.8248
19.7189
Bz
N
O
F
5l
f1 (ppm)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Bz
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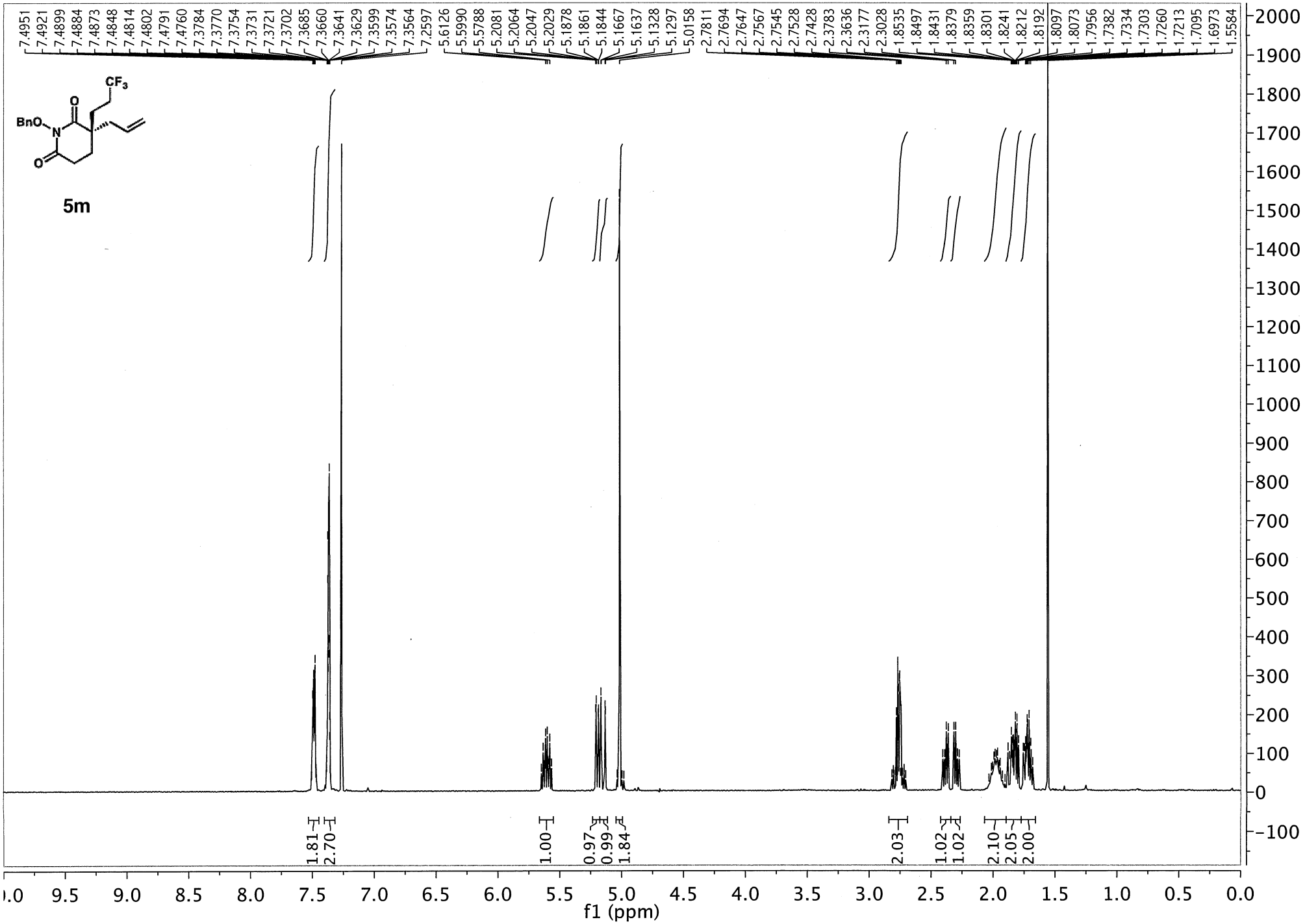
O
F
5l
f1 (ppm)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7.4873
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7.4760
7.3784
7.3770
7.3754
7.3731
7.3721
7.3702
7.3685
7.3660
7.3641
7.3629
7.3599
7.3574
7.3564
7.2597
5.6126
5.5990
5.5788
5.2081
5.2064
5.2047
5.2029
5.1878
5.1861
5.1844
5.1667
5.1637
5.1328
5.1297
5.0158
2.7811
2.7694
2.7647
2.7567
2.7545
2.7528
2.7428
2.3783
2.3636
2.3177
2.3028
1.8535
1.8497
1.8431
1.8379
1.8359
1.8301
1.8241
1.8212
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1.8097
1.8073
1.7956
1.7382
1.7334
1.7303
1.7260
1.7213
1.7095
1.6973
1.5584
CF3
O
BnO
N
O
5m
1.81
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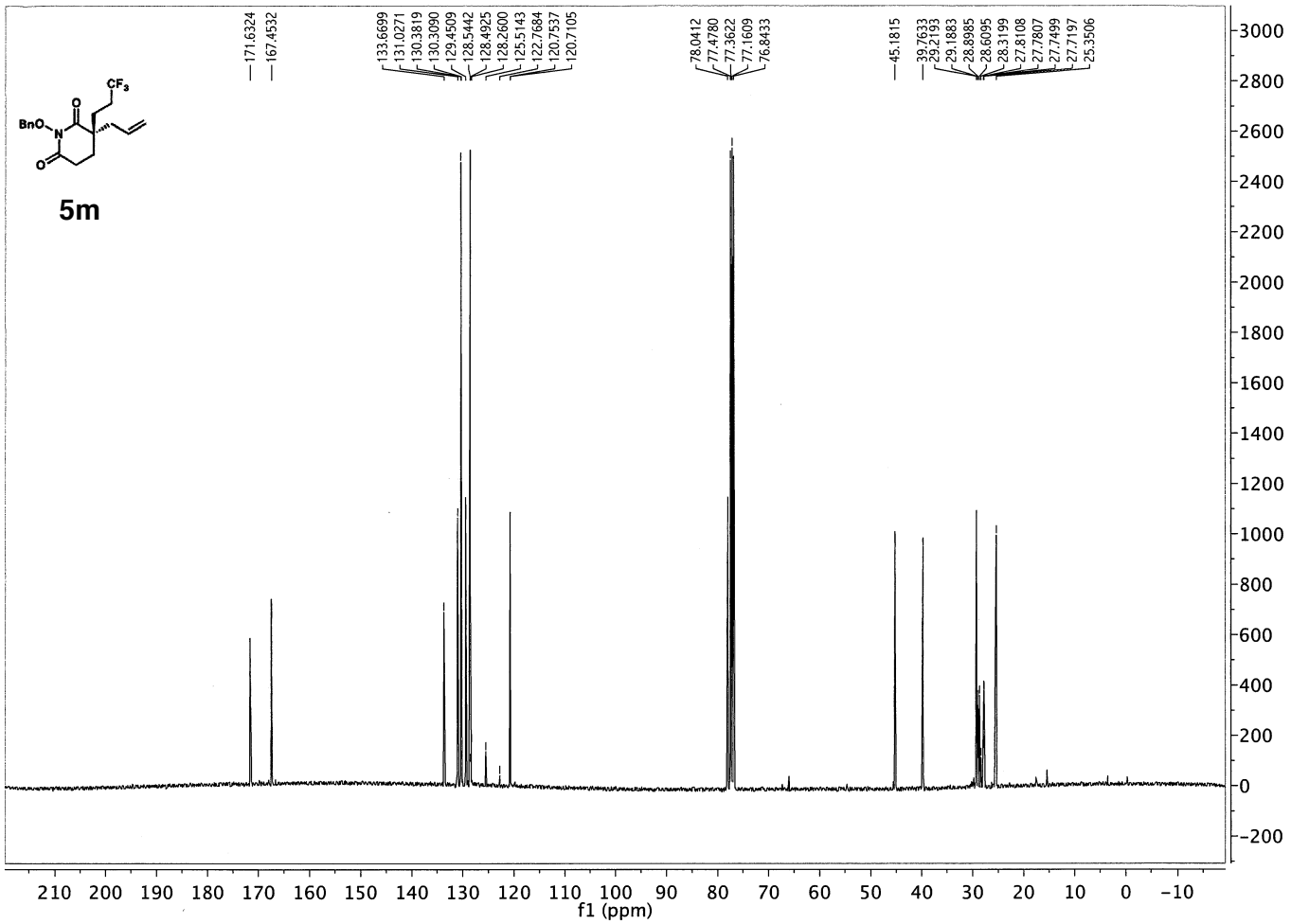
0.97
0.99
1.84
2.03
1.02
1.02
2.10
2.05
2.00
f1 (ppm)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120.7537
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78.0412
77.4780
77.3622
77.1609
76.8433
45.1815
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28.6095
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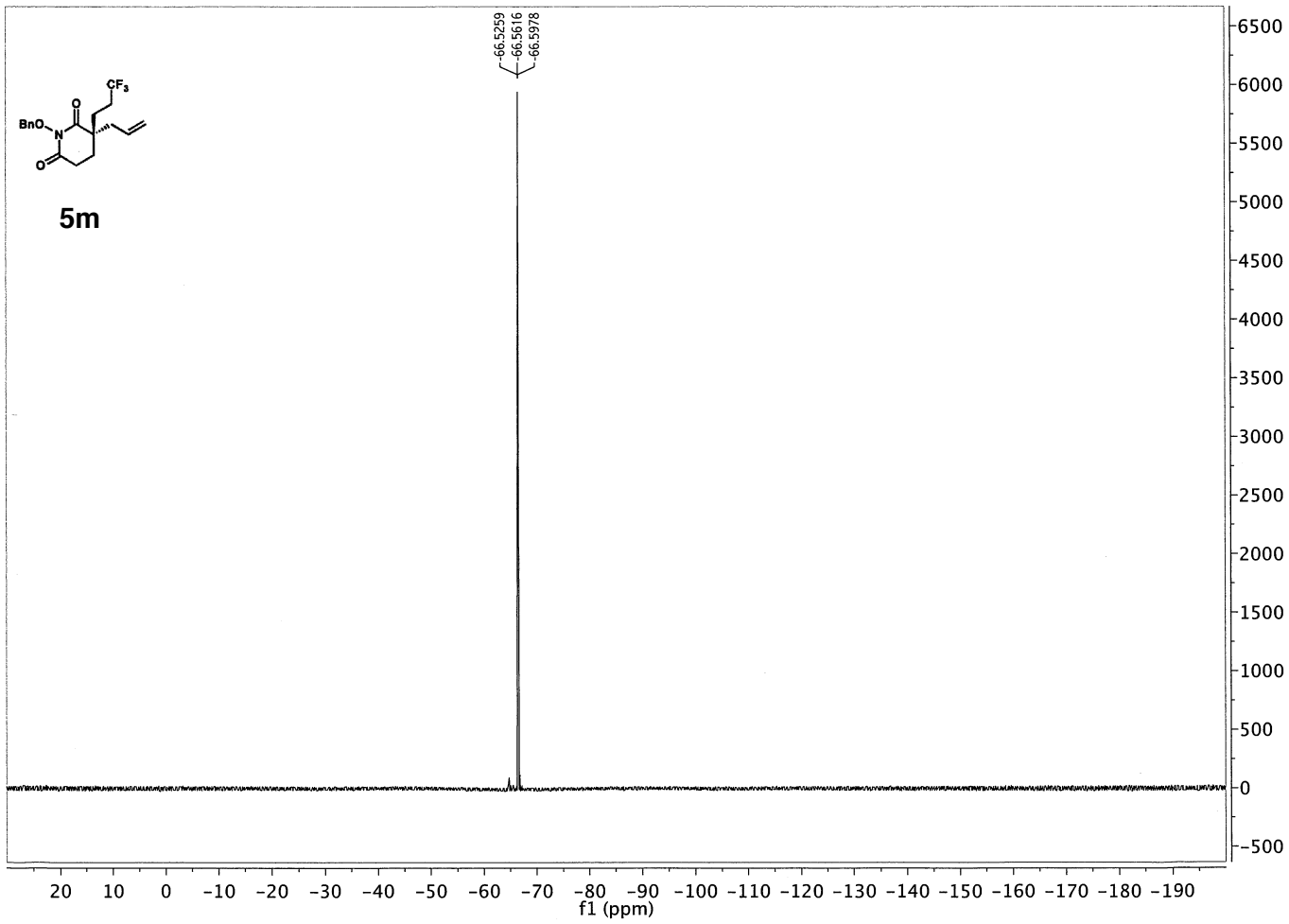
25.3506
BnO
N
O
CF3
5m
f1 (ppm)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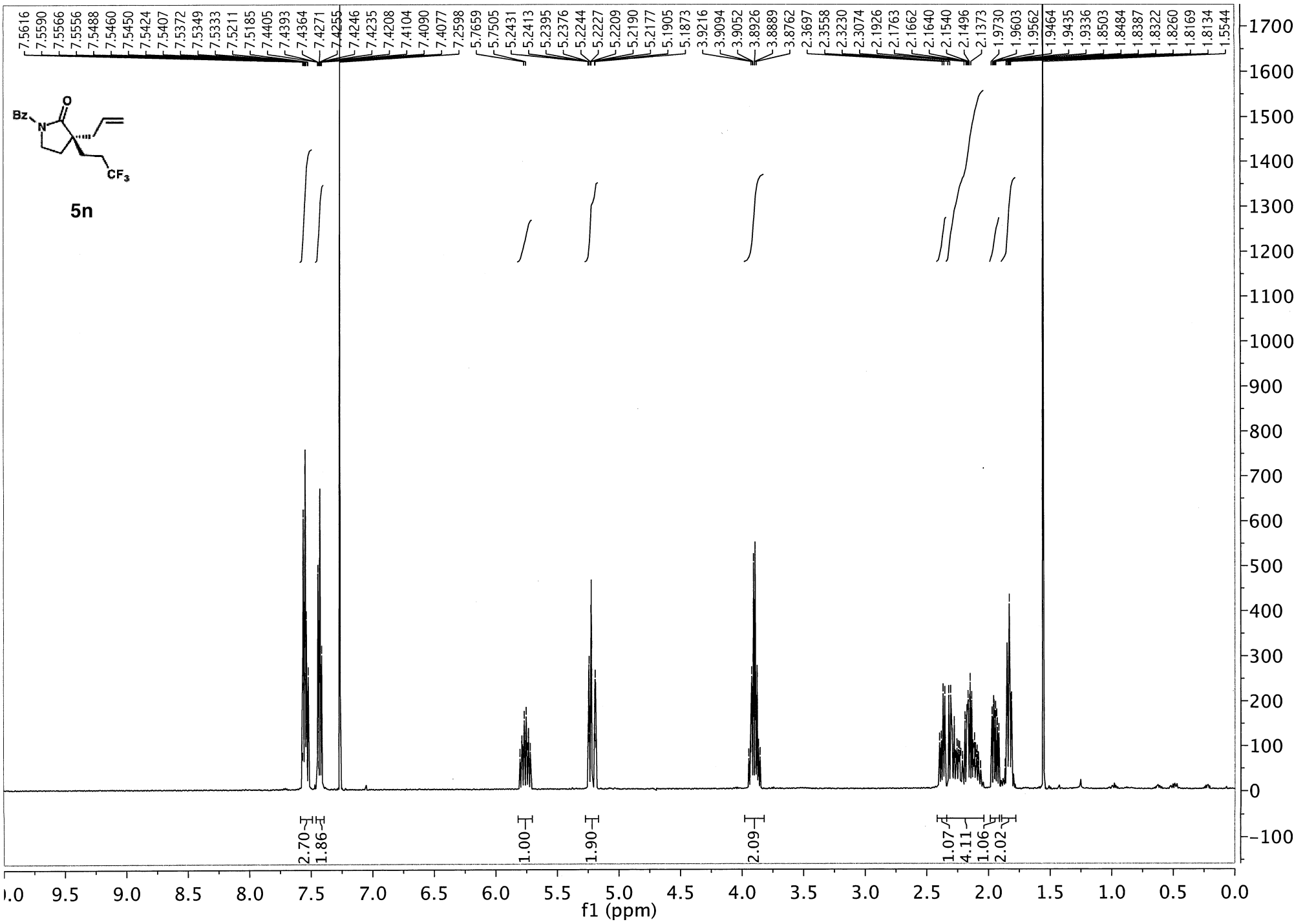
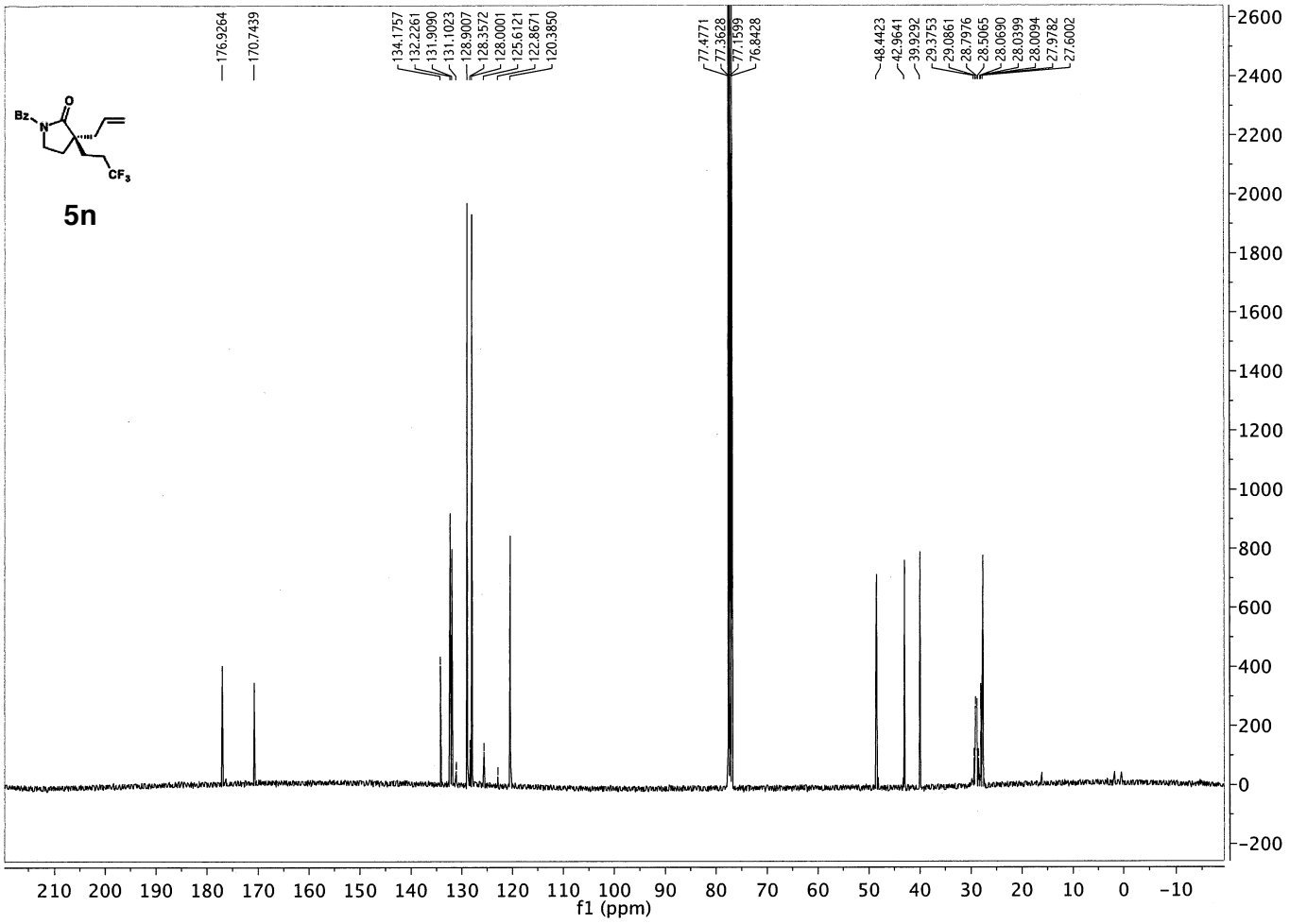
BnO
N
O
CF3
5m
f1 (ppm)


Bz
N
O
CF3
5n
f1 (ppm)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120.3850
77.4771
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76.8428
48.4423
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28.7976
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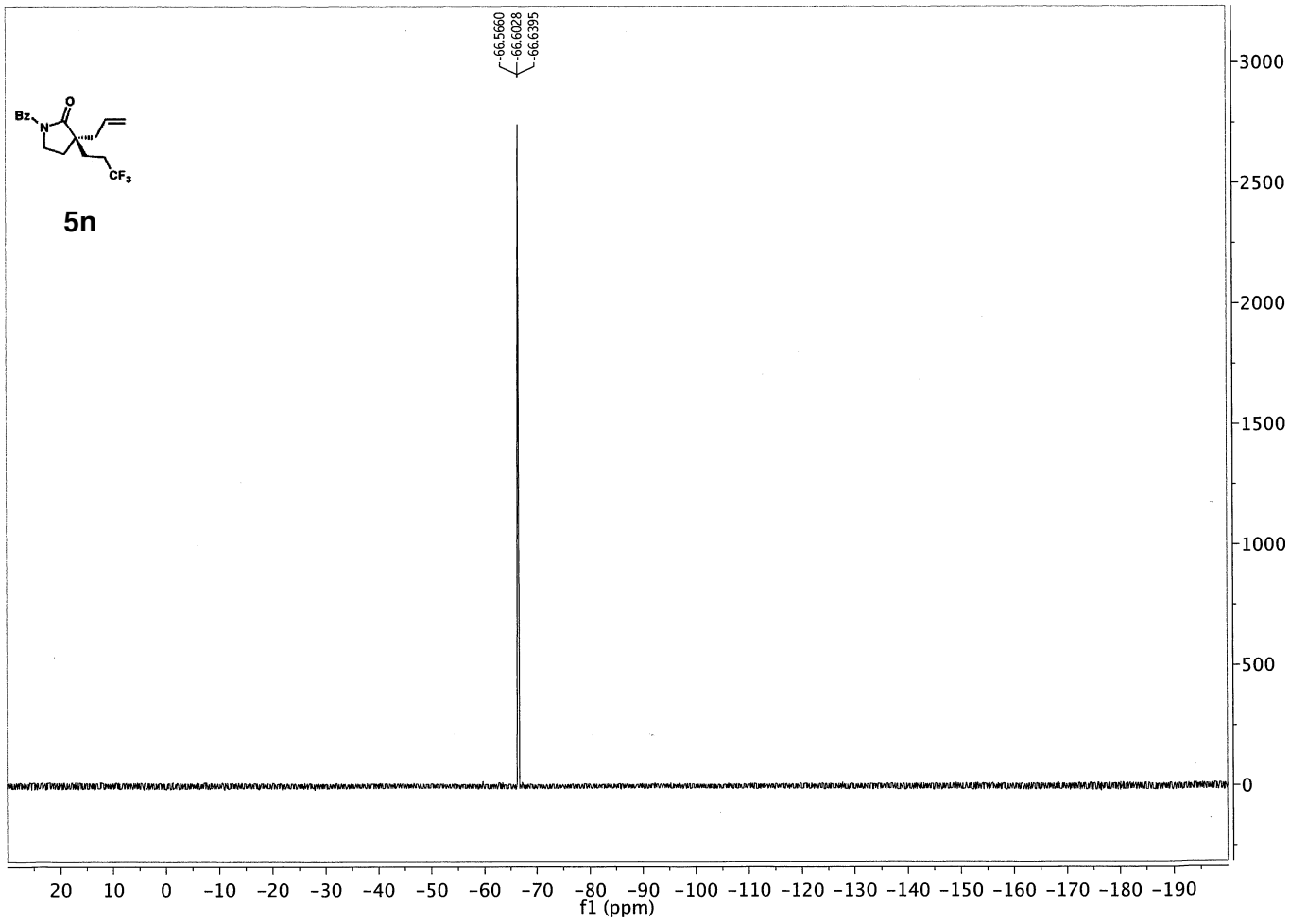
Bz
O
N
CF3
5n
f1 (ppm)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Bz
O
N
CF3
5n
f1 (ppm)