Iodolium Salts as Halogen-Bond Donor Catalysts in the Nazarov Cyclization: The Molecular Oxygen Enigma

Avery J. To and Graham K. Murphy*

Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada, N2L 3G1
E-mail: graham.murphy@uwaterloo.ca

New Journal of Chemistry, 2022

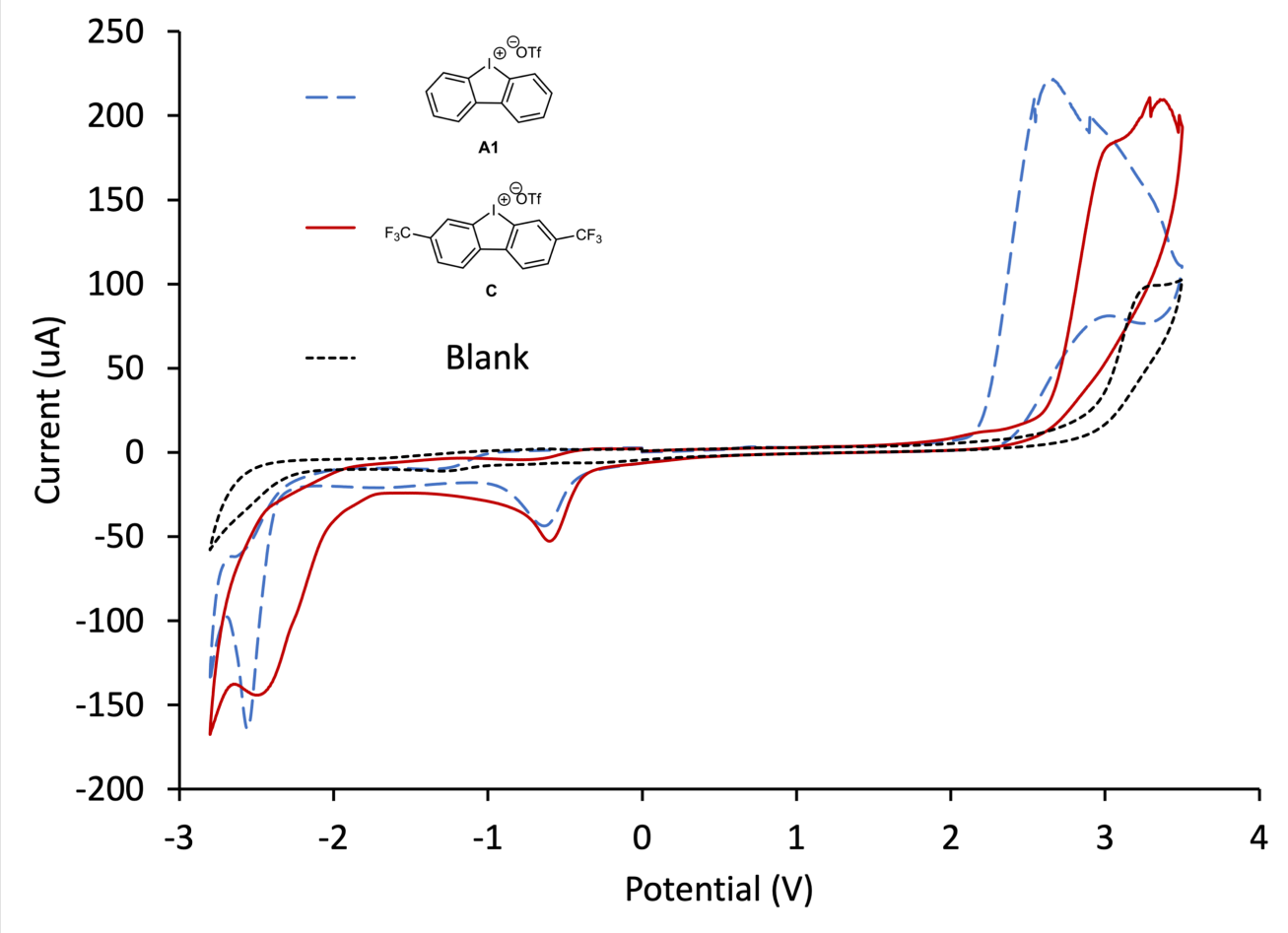
Table of Contents

1 General Experimental and Characterization Details:

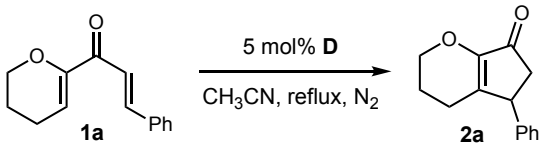
Reactions were carried out in oven-dried glassware and cooled under a nitrogen atmosphere or with a drying tube packed with Drierite to exclude water. Solvents were dried and purified using a JC Meyer solvent purification system and were used without further purification (exceptions listed below). Acetone was dried with 4Å molecular sieves, DMF was stored over 4Å molecular sieves overnight before distillation onto fresh sieves, ACN was stirred with flame dried K_2CO_3 overnight before sequential drying with 4Å molecular sieves (2x), and $CHCl_3$ was washed with water before sequential drying with 4Å molecular sieves (2x). Transfer of anhydrous solvents and reagents was accomplished with oven-dried needles. *m*CPBA was flamed dried under vacuum prior to use. Organolithiums were titrated prior to use with benzylbenzamide.[1] Thin layer chromatography was performed on glass plates pre-coated with 0.25 mm Kieselgel 60 F254 (Silicycle). Flash chromatography columns were packed with 230-400 mesh silica gel (Silicycle). Proton NMR spectra (^{1}H NMR) were recorded at 300 and are reported (ppm) relative to the residual solvent peak. Carbon NMR spectra (^{13}C NMR) were recorded at 75 MHz and are reported (ppm) relative to the center line of the residual solvent peak. Fluorine NMR spectra (^{19}F NMR) were recorded at 282 MHz and are reported (ppm) relative to the peak of trifluoroacetic acid. Phosphorus NMR spectra (^{31}P NMR) were recorded 122 MHz All coupling constants (J) are reported in hertz (Hz). Singlet = s, broad singlet = br. s, doublet = d, triplet = t, quartet = q, quintet = qu., sextet = sex, multiplet = m. All literature known compounds matched the spectral data found in the literature. High resolution mass spectroscopy was performed on a Thermo Fisher Scientific Q-Exactive hybrid mass spectrometer. Accurate mass determinations were performed at a mass resolution of 70,000. Samples were infused at 10 μL/min in 1:1 CH_3OH/H_2O + 0.1% formic acid.

2 Cyclic Voltammetry:

The cyclic voltammograms were collected with WaveNano potentiostat (Pine Research Instrumentation) in a conventional three-electrode configuration system: a platinum button working electrode (1.6 mm diameter), a platinum wire counter electrode and a platinum wire. A 0.1 mM solution of *n*-Bu_4NPF_6 in acetonitrile were used as the electrolyte and solvent respectively. The solution was deoxygenated by bubbling nitrogen through the solution for 5 min prior to each measurement. Data was collected at ambient temperature with a scan rate of 100 mV/s.



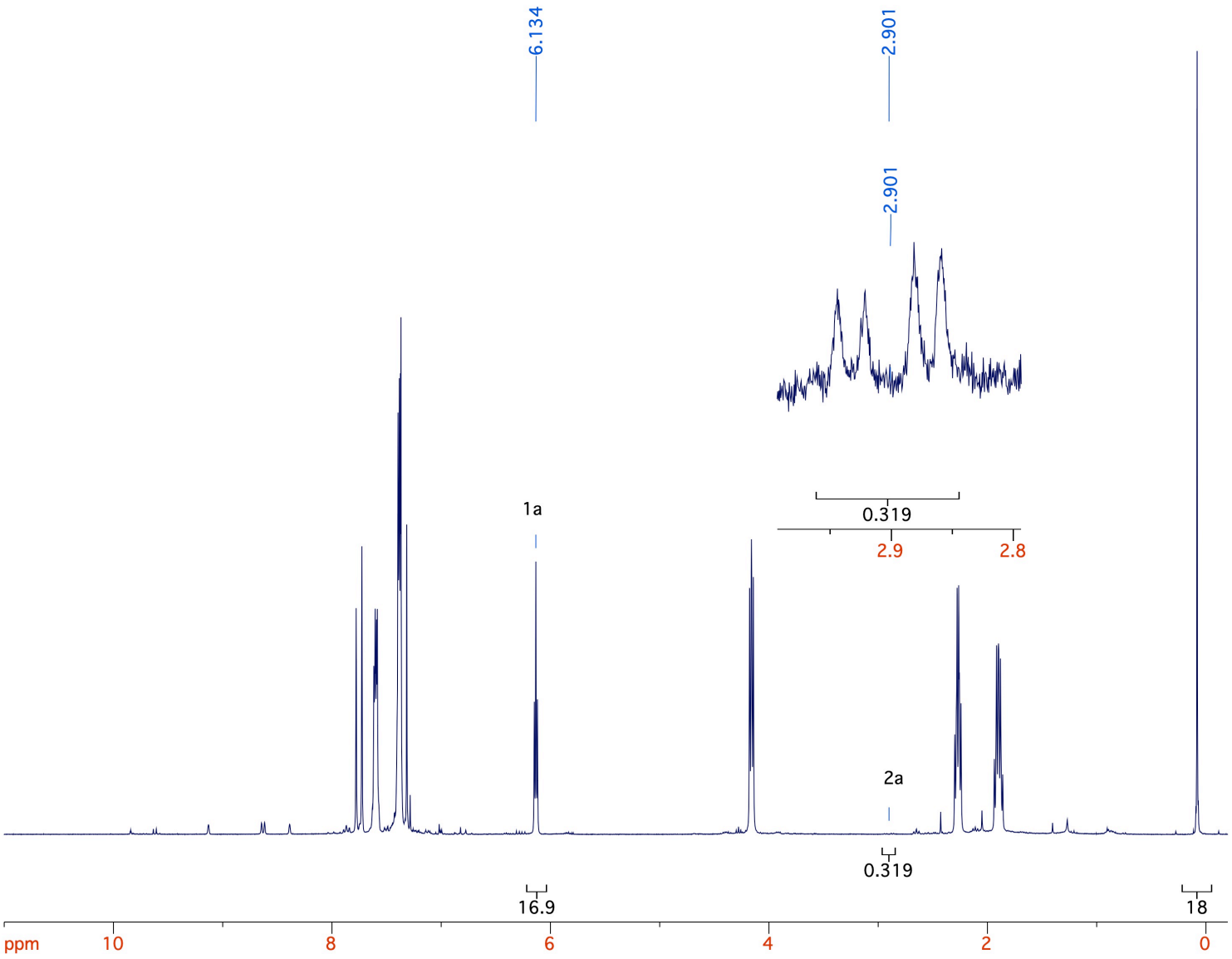
3 Select Quantitative NMR experiments (3µL of hexamethyldisiloxane):



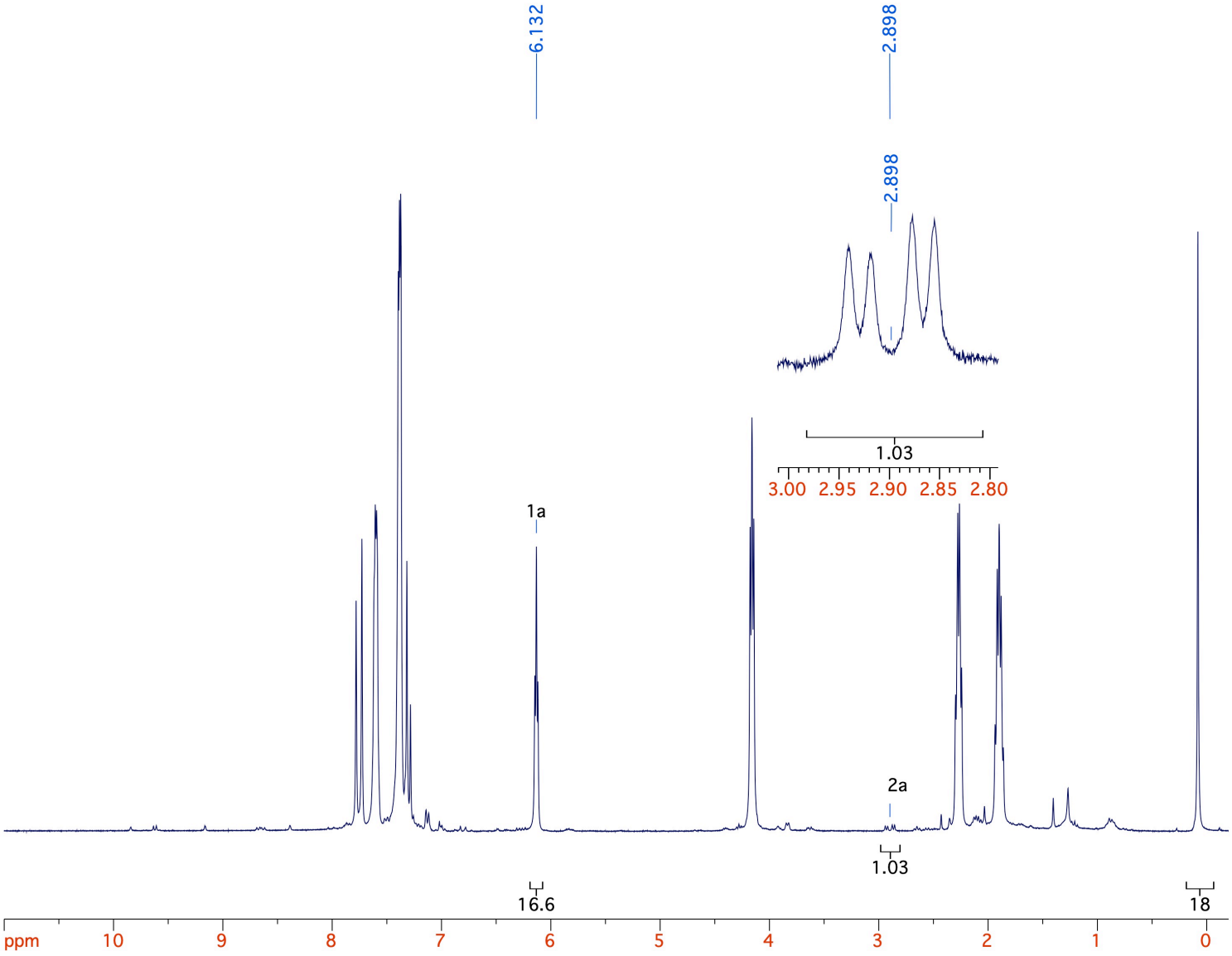
(3)

a) using 46 mol% H_2O 2% (95% of **1a**)
b) using 92 mol% H_2O 6% (94% of **1a**)
c) using 141 mol% H_2O 3% (95% of **1a**)

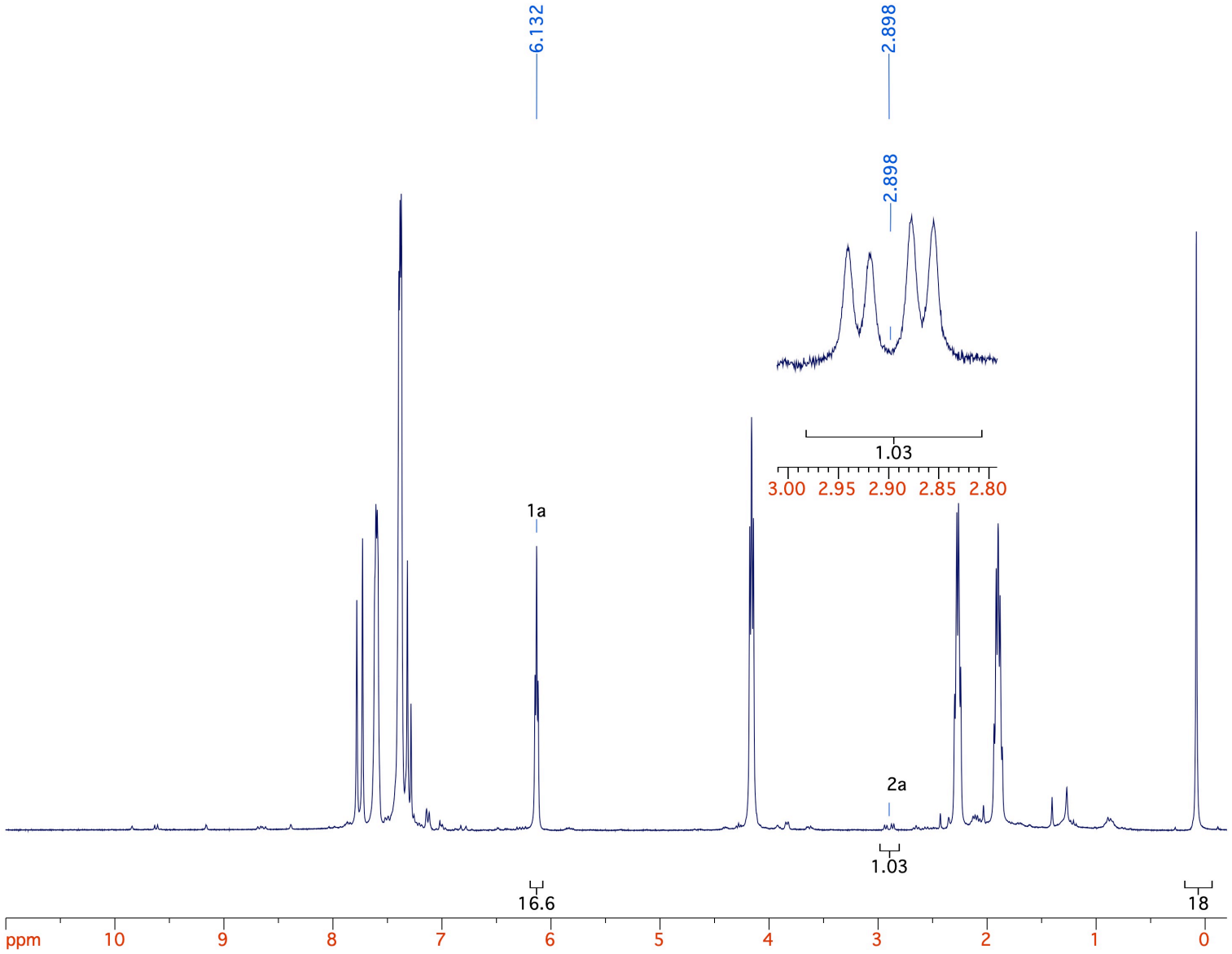
Scale of **1a**: 0.25 mmol
Conditions a):

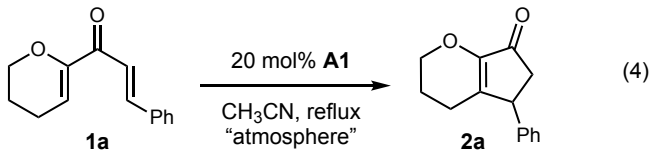


Conditions b):



Conditions c):

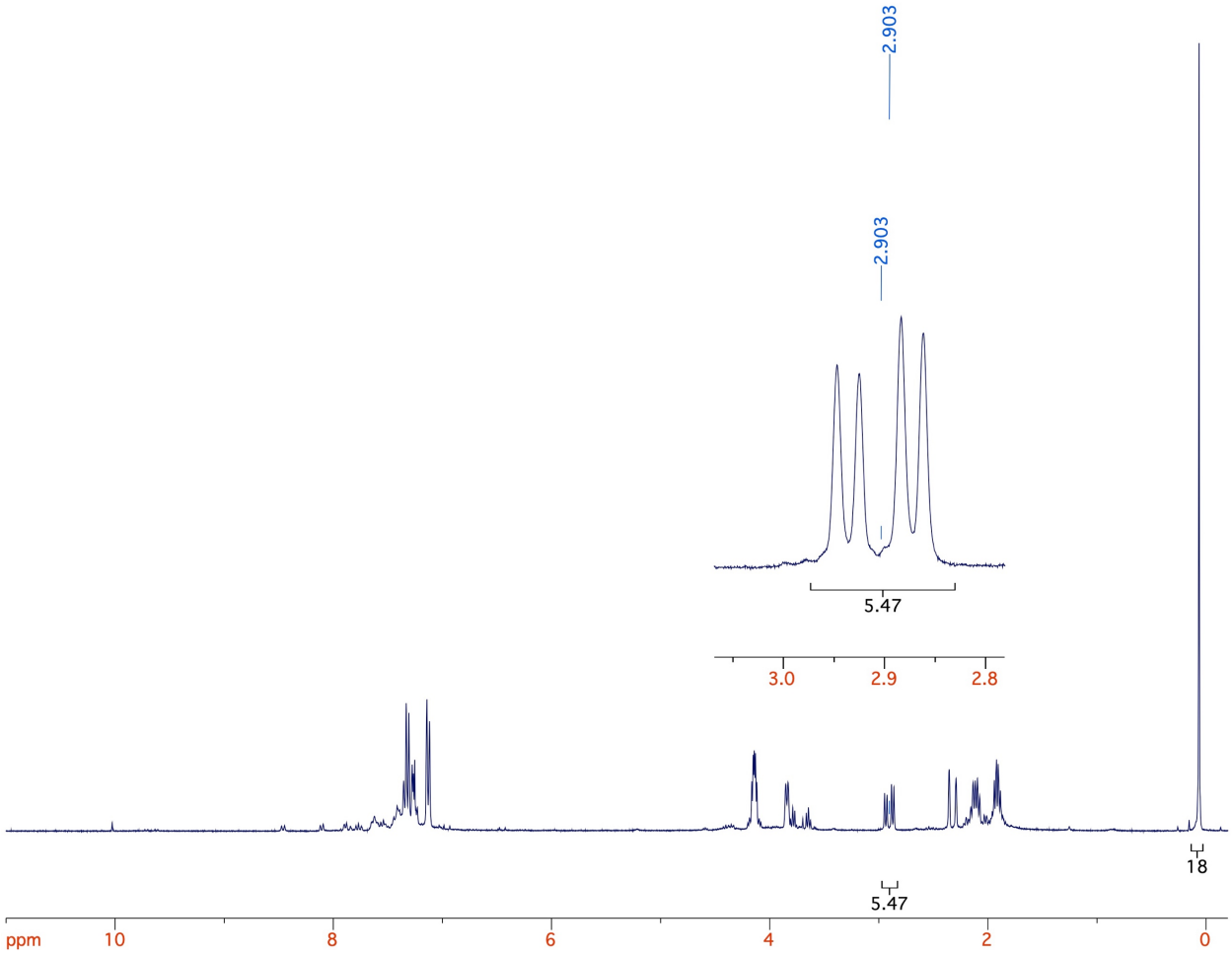


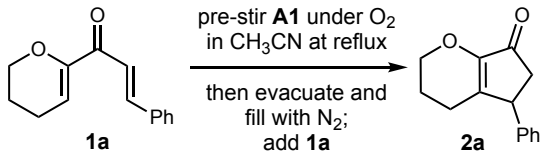


(4)

a) Under argon, 1 h, 0% **2a**;
b) then expose to atmosphere, 1 h, 77% **2a**

Scale of **1a**: 0.1 mmol

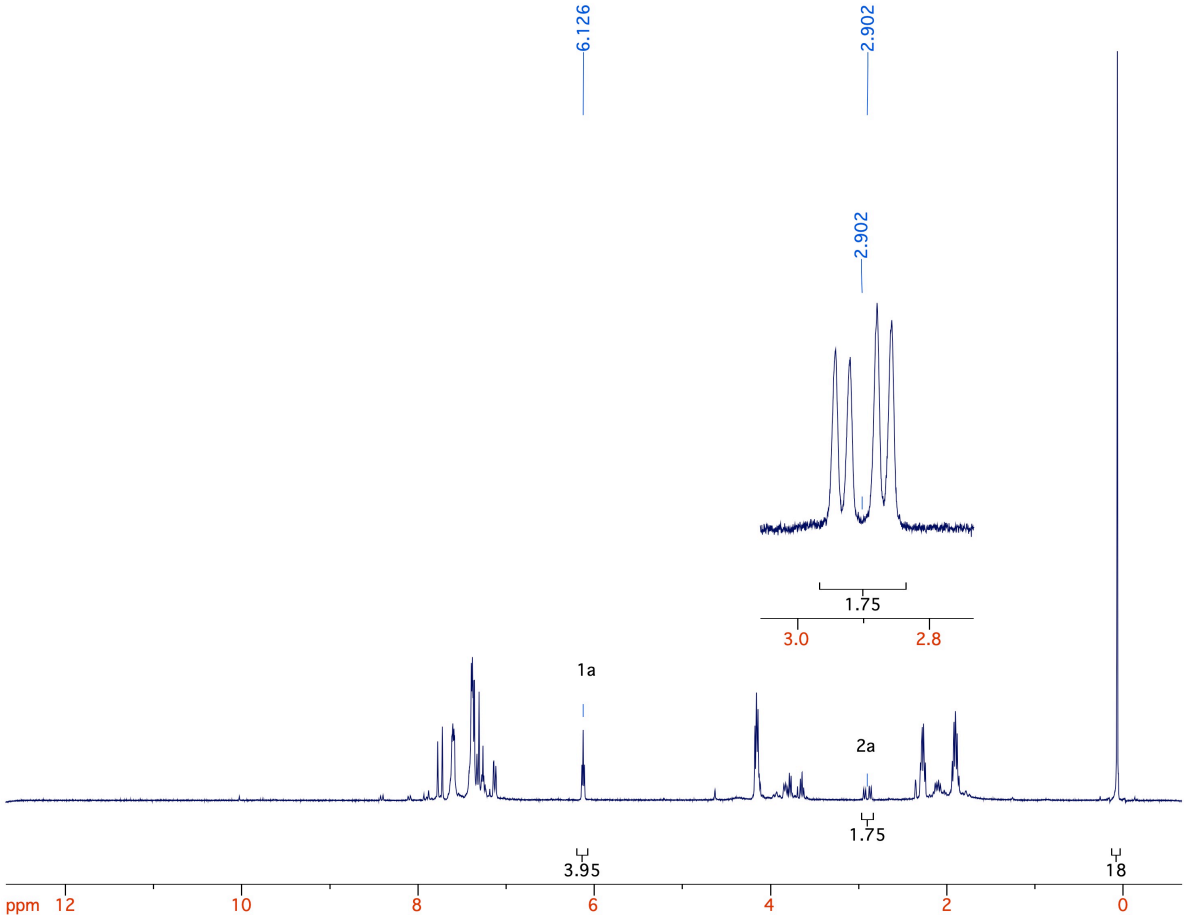




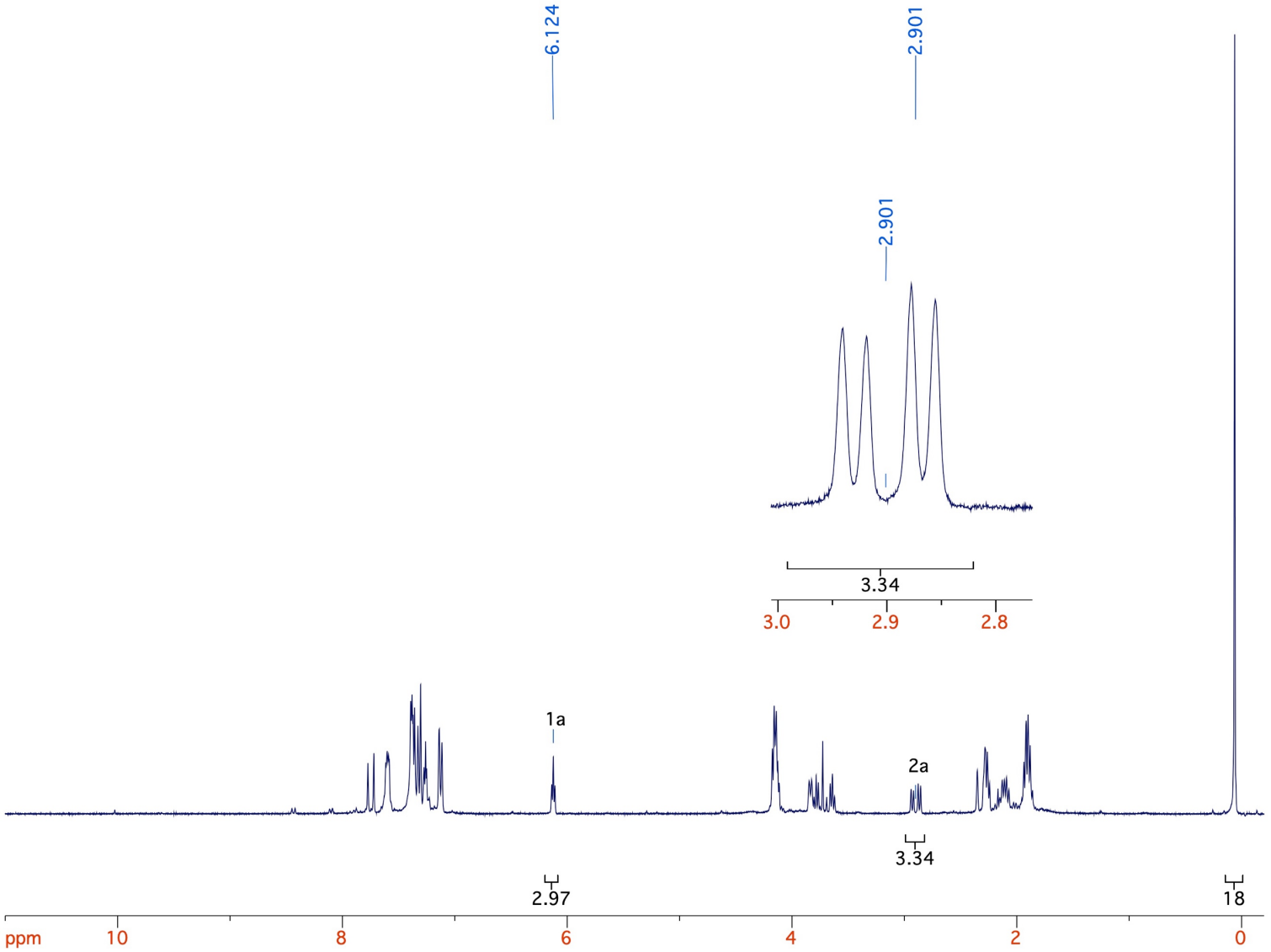
(5)

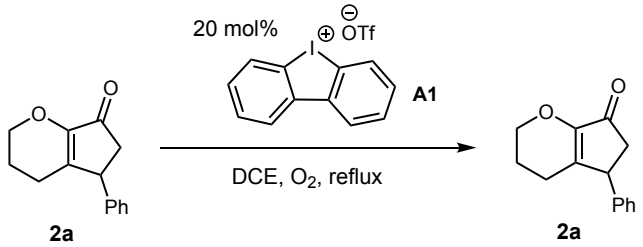
a) 20 mol% **A1**, 25% **2a**
b) 40 mol% **A1**, 47% **2a**

Scale of **1a**: 0.1 mmol
Condition a):

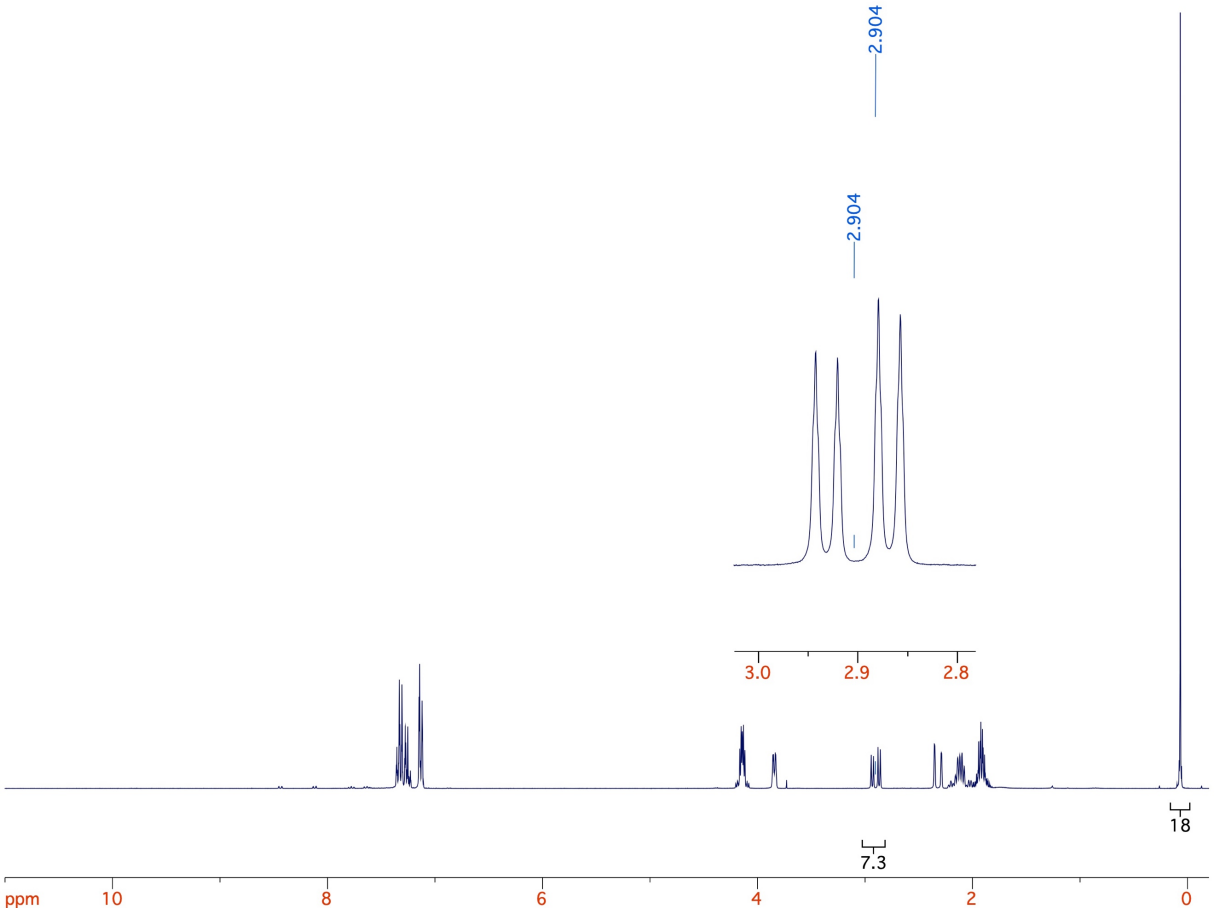


Condition b):

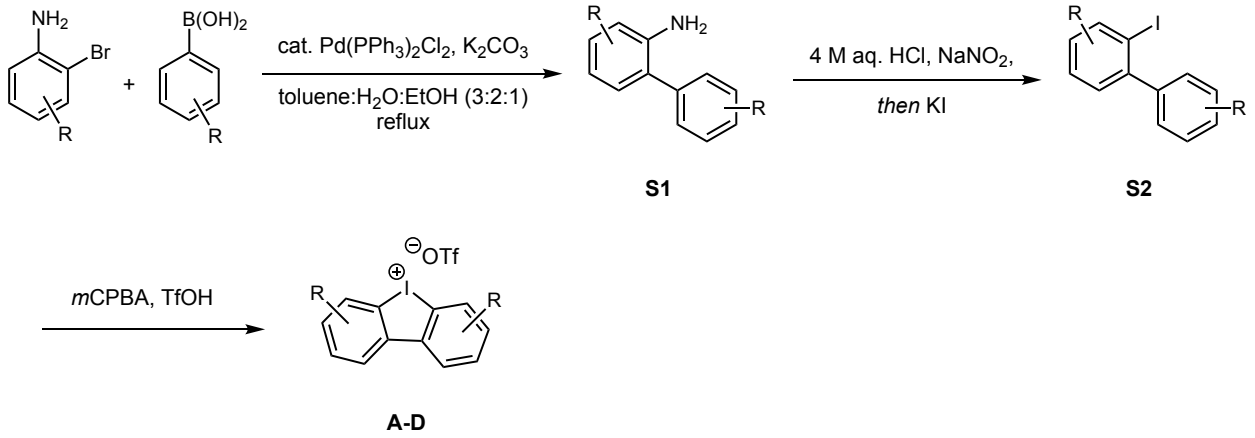




Scale of **2a**: 0.1 mmol



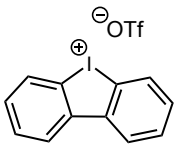
4 Preparation of Diaryliodonium salts:



General Procedure A1) To a flame-dried round bottom flask with a stir bar was added aniline (1.0 equiv.), boronic acid (1.0 equiv.), K_2CO_3 (3.0 equiv.), toluene:water:ethanol (3:2:1, 0.6 M), and bis(triphenylphosphine)palladium chloride (5 mol%) in succession. A water condenser was installed and the atmosphere was purged and backfilled with N_2. The reaction was refluxed until aniline was shown to be fully consumed by TLC analysis. Once complete, the reaction was cooled and the EtOH was removed under reduced pressure. The residue was then dissolved in EtOAc or Et_2O and washed with water, brine, dried over anhydrous $MgSO_4$, and the solvent removed under reduced pressure. The reaction mixture was purified by column chromatography over silica gel to afford anilines, **S1**.

General Procedure A2) To a round bottom flask with a stir bar was added **S1** (1.0 equiv.) and THF (0.4 M) followed by 4 M aq. HCl (10 equiv.) and stirred at 0 °C. To the stirring solution was added $NaNO_2$ (1.5 equiv., 1.2 M in DI H_2O) dropwise and stirred for 20 min, before adding KI (3.0 equiv., 2.5 M in H_2O) dropwise, warming to room temperature and stirring overnight. Following the specified reaction time an equal volume of ethyl acetate was added and the aqueous layer extracted thrice, the combined organic layers were then washed with 1 M $Na_2S_2O_3$ until clear, water, brine, dried with anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography over silica gel to give iodoarenes, **S2**.

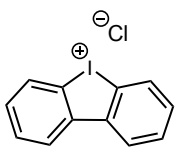
General Procedure A3) To a round bottom flask with a stir bar was added iodoarene, **S2** (1 equiv.), DCM (0.4 M), *m*CPBA (1.5 equiv.) followed by dropwise addition of triflic acid (3.0 equiv.) all at room temperature. The reaction was stirred until disappearance of the iodoarene is observed by TLC. Solvent was removed under reduced pressure and the residue resuspended in diethyl ether and stirred for 30 min. The suspension was filtered, and the filter cake was washed three times with diethyl ether to obtain **A-D**.



A1

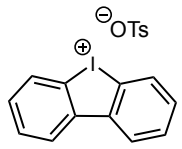
Dibenzo[*b*,*d*]iodol-5-ium trifluoromethanesulfonate (**A1**):[2] 2-bromoaniline (2 g, 11.6 mmol, 1 equiv.) and phenylboronic acid (1.70 g, 14.0 mmol, 1.2 equiv.) were treated with general procedure A and purified by column chromatography with 5% ethyl acetate in hexanes to afford **S1-A1** (1.79 g, 10.6 mmol, 91%) as a white solid. R_f = 0.18 (5% ethyl acetate in hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52-7.46 (m, 4H), 7.43-7.36 (m, 1H), 7.26-7.17 (m, 2H), 6.88 (td, *J* = 7.4, 1.0 Hz, 1H), 6.80 (d, *J* = 7.9 Hz, 1H), 3.78 (br. s, 2H).[3] **S1-A1** (1.73 g, 10.2 mmol, 1 equiv.) was then treated with general procedure B and isolated by column chromatography eluting with hexanes to obtain **S2-A1** (2.40 g, 8.57 mmol, 84%) as a clear oil. R_f = 0.58 (10% ethyl acetate in hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.9 Hz, 1H), 7.46-7.30 (m, 7H), 7.04 (t, *J* = 7.6 Hz, 1H).[4] **S2-A1** (1.5 g, 5.36 mmol, 1 equiv.) was cyclized according to general

procedure C with *m*CPBA (1.63 g, 8.04 mmol, 85%, 1.5 equiv.) and triflic acid (1.42 mL, 16.1 mmol, 3 equiv.) for 1.75 hours to obtain **A1** (2.18 g, 5.09 mmol, 95%) as an off-white/grey solid following recrystallization from ACN. ^{1}H-NMR (300 MHz; DMSO-d_6) δ 8.49 (dd, *J* = 7.9, 1.3 Hz, 2H), 8.21 (dd, *J* = 8.2, 0.9 Hz, 2H), 7.88-7.83 (m, 2H), 7.71 (ddd, *J* = 8.3, 7.3, 1.2 Hz, 2H). ^{13}C NMR (76 MHz; DMSO-d_6) δ 141.7, 131.1, 130.7, 130.6, 127.0, 121.6.



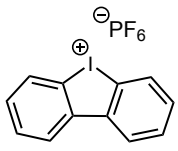
A2

Dibenzo[*b*,*d*]iodol-5-ium chloride (A2):[5] Dibenzo[*b*,*d*]iodol-5-ium trifluoromethanesulfonate (**A1**) (250 mg, 0.58 mmol, 1.0 equiv.) was stirred with 1 mL of formic acid and 1 mL of brine at room temperature for 30 min. The resulting salt was filtered was washed with water (3x) and ether (3x) to afford a white salt (165 mg, 0.52 mmol, 90%). ^{1}H-NMR (300 MHz; DMSO-d_6): δ 8.57 (d, *J* = 7.6 Hz, 2H), 8.43 (dd, *J* = 7.8, 1.0 Hz, 2H), 7.83-7.78 (m, 2H), 7.69-7.63 (m, 2H). ^{13}C NMR (76 MHz; DMSO-d_6) δ 141.3, 130.6, 130.4, 130.3, 126.3, 124.1.



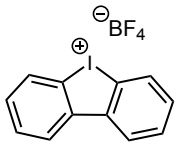
A3

Dibenzo[*b*,*d*]iodol-5-ium 4-methylbenzenesulfonate (A3):[6] 2-iodo-1,1'-biphenyl (280 mg, 1.0 mmol, 1.0 equiv.) and *m*CPBA (304 mg, 1.5 mmol, 85%, 1.5 equiv.) were dissolved in 10 mL of DCM and TsOH (571 mg, 3.0 mmol, 3.0 equiv.) was added and stirred for 1.5 hours. The solvent was removed and the solid suspended in diethyl ether for 10 min at 0 °C. Filtration of the solution afforded **A3** (381 mg, 0.85 mmol, 85%) as a white powder. ^{1}H-NMR (300 MHz; DMSO-d_6): δ 8.48 (dd, *J* = 7.9, 1.2 Hz, 2H), 8.26 (dd, *J* = 8.2, 0.8 Hz, 2H), 7.88-7.82 (m, 2H), 7.73-7.68 (m, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 2.32-2.23 (m, 3H). ^{13}C NMR (76 MHz; DMSO-d_6) δ 145.4, 141.8, 137.8, 131.0, 130.7 (2C), 128.1, 127.0, 125.5, 121.7, 20.8.



A4

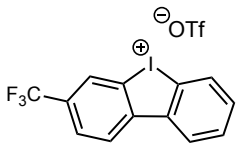
Dibenzo[*b*,*d*]iodol-5-ium hexafluorophosphate(V) (A4): **A1** (250 mg, 0.58 mmol, 1.0 equiv.) was stirred with 2 mL of DCM and 5 mL of sat. KPF_6 in water for 6 hours. The resulting solid was filtered to obtained product **A4** (240 mg, 0.57 mmol, 97%). ^{1}H-NMR (300 MHz; CD_3OD): δ 8.39 (dd, *J* = 7.8, 1.0 Hz, 2H), 8.13 (d, *J* = 8.3 Hz, 2H), 7.90-7.85 (m, 2H), 7.74-7.68 (m, 2H). ^{13}C NMR (75 MHz; CD_3OD) δ 143.7, 132.5, 132.4, 131.6, 128.4, 121.4. ^{19}F NMR (282 MHz; CD_3OD): δ -74.8 (d, *J* = 707 Hz). ^{31}P NMR (122 MHz; CD_3OD): δ -146.3 (apparent sex, *J* = 711 Hz). HRMS-ESI calcd for $C_{12}H_8I$ $[M]^+$ 278.9665, found 278.9669.



A5

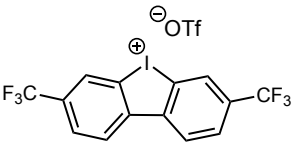
Dibenzo[*b*,*d*]iodol-5-ium tetrafluoroborate (A5): 2-iodo-1,1'-biphenyl (**S2-A1**) (100 mg, 0.36 mmol, 1.0 equiv.) and *m*CPBA (110 mg, 0.54 mmol, 85%, 1.5 equiv.) were dissolved in 2 mL of DCM. The solution was cooled to 0 °C and $BF_3 \cdot OEt_2$ (112 μL, 0.89 mmol, 2.5 equiv.) was added dropwise. The reaction was stirred for 30 min before the solvent was removed and the residue redissolved in diethyl ether to precipitate the salt over 20 min at 0 °C. Isolation via filtration afforded **A5** (123 mg, 0.34 mmol, 93%) as a white solid. ^{1}H-NMR (300 MHz; CD_3OD): δ 8.40 (dd, *J* = 7.9, 1.1 Hz, 2H), 8.14 (dd, *J* = 8.4, 0.5 Hz, 2H), 7.91-7.85 (m, 2H), 7.74-7.69 (m, 2H). ^{13}C NMR (75 MHz; CD_3OD) δ 143.8, 132.5, 132.4, 131.6, 128.4, 121.4. ^{19}F NMR (282 MHz; CD_3OD): δ -154.8. HRMS-ESI calcd for $C_{12}H_8I$ $[M]^+$ 278.9665, found 278.9663.

Dibenzo[*b*,*d*]iodol-5-ium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (A6) was prepared according to Heinen et. al.[7]



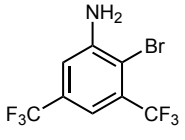
B

3-(trifluoromethyl)dibenzo[*b*,*d*]iodol-5-ium trifluoromethanesulfonate (**B**): 2-bromo-5-(trifluoromethyl)aniline (1.5 g, 6.25 mmol, 1 equiv.) and phenylboronic acid (0.762 g, 6.25 mmol, 1.0 equiv.) were treated with general procedure A and purified by column chromatography with 5% ethyl acetate in hexanes to afford **S1-B** (1.08 g, 4.55 mmol, 73%) as white solid. R_f = 0.20 (5% ethyl acetate in hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57-7.43 (m, 5H), 7.27 (d, *J* = 7.9 Hz, 1H), 7.13 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.04 (s, 1H), 3.96 (br. s, 2H). ^{13}C NMR (75 MHz; $CDCl_3$) δ 144.1, 138.3, 130.9, 130.7 (q, *J* = 32.0 Hz), 130.7 (q, *J* = 1.3 Hz), 129.2 (2C), 128.9 (2C), 128.0, 124.5 (q, *J* = 272.2 Hz), 115.0 (q, *J* = 3.9 Hz), 112.0 (q, *J* = 3.9 Hz). ^{19}F NMR (282 MHz; $CDCl_3$) δ -61.9.[8] **S1-B** (0.980 g, 4.22 mmol, 1 equiv.) was then treated with general procedure B and isolated by column chromatography eluting with hexanes to obtain **S2-B** (1.40 g, 4.22 mmol, 95%) as a clear oil. R_f = 0.61 (hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.72-7.67 (m, 1H), 7.52-7.42 (m, 4H), 7.37-7.34 (m, 2H). ^{13}C NMR (75 MHz; $CDCl_3$) *δ* 150.4 (q, *J* = 1.2 Hz), 143.2, 136.4 (q, *J* = 3.8 Hz), 131.0 (q, *J* = 32.9 Hz), 130.2, 129.1 (2C), 128.4, 128.3 (2C), 125.1 (q, *J* = 3.6 Hz), 123.1 (q, *J* = 272.7 Hz), 98.4. ^{19}F NMR (283 MHz; $CDCl_3$) δ -62.58. **S2-B** (0.100 g, 0.29 mmol, 1 equiv.) was cyclized according to general procedure C with *m*CPBA (0.087 g, 0.43 mmol, 85%, 1.5 equiv.) and triflic acid (76 µL, 0.86 mmol, 3 equiv.) for 45 min to obtain **B** (0.127 g, 0.26 mmol, 89%) as a white solid following recrystallization from ACN. ^{1}H-NMR (300 MHz; CD_3OD): δ 8.60 (d, *J* = 8.4 Hz, 1H), 8.52 (d, *J* = 7.6 Hz, 1H), 8.47 (s, 1H), 8.19 (dd, *J* = 8.8, 3.2 Hz, 2H), 7.95 (t, *J* = 7.7 Hz, 1H), 7.81 (t, *J* = 8.0 Hz, 1H). ^{13}C NMR (76 MHz; MeOD) δ 147.2, 142.1, 133.5, 133.2 (q, *J* = 33.6 Hz), 132.5, 131.6, 129.2 (q, *J* = 3.6 Hz), 129.2, 128.8 (q, *J* = 4.4 Hz), 128.8, 124.5 (q, *J* = 272.3 Hz), 122.6, 121.7 (q, *J* = 318.7 Hz), 121.4. ^{19}F NMR (282 MHz; CD_3OD): δ -63.4, -79.5. HRMS-ESI calcd for $C_{13}H_7F_3I$ $[M]^+$ 346.9539, found 346.9546.



C

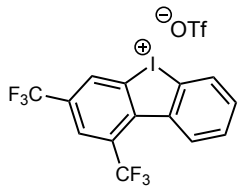
3,7-bis(trifluoromethyl)dibenzo[*b*,*d*]iodol-5-ium trifluoromethanesulfonate (**C**): 2-bromo-5-(trifluoromethyl)aniline (1.50 g, 6.25 mmol, 1.0 equiv.) and (4-(trifluoromethyl)phenyl)boronic acid (1.20 g, 6.25 mmol, 1.0 equiv.) were treated with general procedure A and purified by column chromatography with a gradient from 5% to 10% ethyl acetate in hexanes to afford **S1-C** (1.58 g, 5.18 mmol, 83%) as a yellow oil. R_f = 0.79 (10% ethyl acetate in hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 1H), 7.09 (d, *J* = 8.1 Hz, 1H), 7.02 (s, 1H), 3.92 (br. s, 2H). ^{13}C NMR (75 MHz; $CDCl_3$): δ 144.0, 142.1, 131.6 (q, *J* = 32.1 Hz), 130.9, 130.2 (q, 32.4 Hz), 129.5 (2C), 129.1, 126.2 (q, *J* = 3.7 Hz, 2C), 124.2 (q, *J* = 272.1 Hz, 2C), 115.3 (q, *J* = 3.8 Hz), 112.3 (q, *J* = 3.9 Hz). ^{19}F NMR (282 MHz; $CDCl_3$): δ -62.0, -62.3. **S1-C** (1.53 g, 5.01 mmol, 1 equiv.) was then treated with general procedure B and isolated by column chromatography eluting with hexanes to obtain **S2-C** (1.76 g, 4.23 mmol, 85%) as a clear oil. R_f = 0.56 (hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.75-7.69 (m, 3H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 1H). ^{19}F NMR (282 MHz; CDCl3): δ -62.0, -62.1.[9] **S2-C** (0.500 g, 1.20 mmol, 1 equiv.) was cyclized according to general procedure C with *m*CPBA (0.365 g, 1.80 mmol, 85%, 1.5 equiv.) and triflic acid (318 µL, 3.60 mmol, 3 equiv.) for 5 h to obtain **C** (0.526 g, 0.932 mmol, 78%) as a white solid following recrystallization from ACN. ^{1}H-NMR (300 MHz; CD_3OD): δ 8.72 (d, *J* = 8.5 Hz, 1H), 8.50 (s, 1H), 8.25 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (75 MHz; CD_3OD) δ 146.0, 134.3 (q, *J* = 33.7 Hz), 129.8, 129.5 (q, *J* = 3.6 Hz), 128.8 (q, *J* = 4.2 Hz), 124.5 (q, *J* = 272.3 Hz), 122.9, 121.7 (q, *J* = 318.4 Hz). ^{19}F NMR (282 MHz; CD_3OD): δ -63.5, -79.5. HRMS-ESI calcd for $C_{14}H_6F_6I$ $[M]^+$ 414.9413, found 414.9410.



S3

2-bromo-3,5-bis(trifluoromethyl)aniline (S3):[10] A 50 mL RBF with a stir bar was charged with 3,5-bis(trifluoromethyl)aniline (1 mL, 6.44 mmol, 1 equiv.), chloroform (20 mL), cooled to 0 °C and bromine (365 µL, 7.09 mmol, 1.1 equiv.) added dropwise. Stirring for 1 hour was followed by quenching with sat. aq. $NaHCO_3$. The organic layer was partitioned and washed three times with sat. aq. $NaHCO_3$, water, brine, dried with $MgSO_4$ and concentrated under reduced pressure. Purification of the residue with flash column chromatography using 10% ethyl acetate in hexanes provided a yellow oil **S3** (1.52 g, 4.94 mmol, 77%). R_f

= 0.23 (10% ethyl acetate in hexanes). ^{1}H-NMR (300 MHz; $CDCl_3$): δ 7.28 (dd, *J* = 1.4, 0.5 Hz, 1H), 7.14 (dd, *J* = 1.5, 0.5 Hz, 1H), 4.63 (s, 2H). ^{13}C NMR (75 MHz; $CDCl_3$) *δ* 146.5, 132.0 (q, *J* = 29.7 Hz), 130.8 (q, *J* = 31.7 Hz), 123.4 (q, *J* = 272.4 Hz), 122.8 (q, *J* = 273.7 Hz), 114.8 (q, *J* = 3.5 Hz), 113.6—113.3 (m), 109.2. ^{19}F NMR (283 MHz; $CDCl_3$) δ -63.1, -63.4.



D

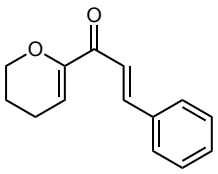
1,3-bis(trifluoromethyl)dibenzo[*b*,*d*]iodol-5-ium trifluoromethanesulfonate (**D**): 2-bromo-3,5-(trifluoromethyl)aniline (500 mg, 1.60 mmol, 1.0 equiv.) and phenylboronic acid (244 mg, 2.00 mmol, 1.25 equiv.) were treated with general procedure A and purified by column chromatography with 10% ethyl acetate in hexanes to afford **S1-D** (321 mg, 1.06 mmol, 66%) as a faintly yellow clear oil. R_f = 0.11 (10% ethyl acetate in hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57-7.45 (m, 3H), 7.42 (s, 1H), 7.30 (d, *J* = 6.9 Hz, 2H), 7.17 (s, 1H), 3.82 (br. s, 2H). ^{13}C NMR (75 MHz; $CDCl_3$): δ 146.6, 134.1, 131.0 (q, *J* = 33.0 Hz), 130.7 (q, *J* = 30.0 Hz), 129.8, 129.1 (2C), 128.8 (2C), 128.7, 123.7 (q, *J* = 272.3 Hz), 123.6 (q, *J* = 274.3 Hz), 114.5 (q, *J* = 3.5 Hz), 112.0 (qq, *J* = 5.6, 3.9 Hz). ^{19}F NMR (282 MHz; $CDCl_3$): δ -57.7, -62.6. **S1-D** (654 mg, 2.14 mmol, 1 equiv.) was then treated with general procedure B and isolated by column chromatography eluting with hexanes to obtain **S2-D** (548 mg) as a clear oil in a mixture with the presumed chlorinated product. R_f = 0.56 (hexanes). This product was carried forward to the next step. **S2-D** (0.548 g, 1.32 mmol, 1 equiv.) was cyclized according to general procedure C with *m*CPBA (0.375 g, 1.98 mmol, 85%, 1.5 equiv.) and triflic acid (349 μL, 3.95 mmol, 3 equiv.) for 4 h to obtain **D** (416 mg, 0.74 mmol, 56%) as a white solid following recrystallization from ACN. ^{1}H-NMR (300 MHz; CD_3OD): δ 8.84 (s, 1H), 8.73 (d, *J* = 8.4 Hz, 1H), 8.57 (s, 1H), 8.34 (dd, *J* = 8.2, 1.1 Hz, 1H), 8.03-7.98 (m, 1H), 7.90-7.85 (m, 1H). ^{13}C NMR (75 MHz; CD_3OD) δ 145.0, 139.7, 134.0, 133.1 (q, *J* = 3.6 Hz), 132.6 (q, *J* = 8.4 Hz), 132.6, 132.1 (q, *J* = 34.9 Hz), 132.1, 130.9 (q, *J* = 33.5 Hz), 128.40—128.05 (m), 124.7, 124.6 (q, *J* = 273.7 Hz), 123.8 (q, *J* = 272.5 Hz), 122.3, 121.7 (q, *J* = 318.6 Hz). ^{19}F NMR (282 MHz; CD_3OD) δ -58.2, -62.5, -78.3. HRMS-ESI calcd for $C_{14}H_6F_6I$ $[M]^+$ 414.9413, found 414.9411.

5 Preparation of Substrates

The preparation of the required cinnamaldehydes was based on the procedure outlined in Morack, T., et al., *Angew. Chem. Int. Ed.* **2019,** *58*, 1208.[11] Spectra were consistent with literature. 2-iodoxybenzoic acid was prepared according to literature procedure.[12]

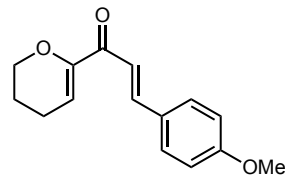
5.1 General Procedure B: Preparation of dihydropyran substrates

To appropriately size oven-dried round bottom flask and stir bar was added THF (1M) and dihydropyran (1.0 equiv.) under N_2 atmosphere. The round bottom flask was cooled to -78 °C and *t*BuLi (1.1 equiv. in pentane) was added dropwise. The mixture was warmed to 0 °C for 30 min before cooling -78 °C and adding aldehyde (2M in THF, 1.0 equiv.) dropwise, before again warming to 0 °C for 1 hr. The reaction was quenched with sat. NH_4Cl and diluted with Et_2O. The aqueous layer was separated and extracted (3x) with Et_2O, the combined organic layers were washed with water (3x), brine, dried with $MgSO_4$ and rotary evaporated to an oil. The crude residue was dissolved in DMSO (0.5M), IBX (1.1 equiv.) was added in one portion and the solution stirred until starting material was consumed by TLC. Dilution of the reaction mixture with Et_2O and water, separation of the layers, extraction (3x) of aqueous layer with Et_2O, sequential washing of the combined organic layers with water and brine, drying with $MgSO_4$ and rotary evaporation yielded a crude oil which was purified by column chromatography.



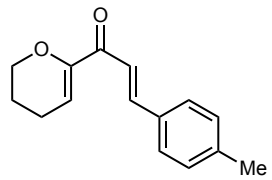
1a

(*E*)-1-(3,4-dihydro-2*H*-pyran-6-yl)-3-phenylprop-2-en-1-one (1b):[13] Dihydropyran (456 μL, 5.0 mmol, 1.0 equiv.) in THF (5.0 mL, 1M) was treated with *t*BuLi (3.99 mL, 5.50 mmol, 1.38 M, 1.1 equiv.), (*E*)-cinnamaldehyde (629 mg, 5.0 mmol, 1.0 equiv.) in 1.67 mL of THF, IBX (1.54 g, 5.5 mmol, 1.1 equiv.), DMSO (10 mL, 0.5 M) following General Procedure B to obtain **1a** (511 mg, 2.38 mmol, 48%) as a yellow oil after column chromatographic purification with 15% ethyl acetate in hexanes. R_f = 0.28 (15% ethyl acetate in hexanes). ^{1}H-NMR (300 MHz; $CDCl_3$): δ 7.73 (d, *J* = 15.8 Hz, 1H), 7.59-7.56 (m, 2H), 7.38-7.29 (m, 4H), 6.10 (t, *J* = 4.3 Hz, 1H), 4.15-4.13 (m, 2H), 2.24 (td, *J* = 6.3, 4.4 Hz, 2H), 1.91-1.83 (m, 2H). ^{13}C NMR (76 MHz; $CDCl_3$): δ 185.4, 151.9, 143.8, 135.0, 130.4, 128.9, 128.5, 120.5, 110.8, 66.4, 21.6, 21.0.



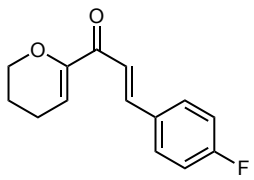
1b

(*E*)-1-(3,4-dihydro-2*H*-pyran-6-yl)-3-(4-methoxyphenyl)prop-2-en-1-one (1b):[14] Dihydropyran (137 μL, 1.5 mmol, 1.0 equiv.) in THF (1.5 mL, 1M) was treated with *t*BuLi (1.20 mL, 1.65 mmol, 1.38 M, 1.1 equiv.), (*E*)-4-methoxycinnamaldehyde (243 mg, 1.5 mmol, 1.0 equiv.) in 470 μL of THF, IBX (462 mg, 1.65 mmol, 1.1 equiv.), DMSO (3 mL, 0.5 M) following General Procedure B to obtain **1b** (218 mg, 0.89 mmol, 60%) as a yellow oil after column chromatographic purification with 20% ethyl acetate in hexanes. R_f = 0.24 (20% ethyl acetate in hexanes). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.66 (d, *J* = 15.8 Hz, 1H), 7.52-7.47 (m, 2H), 7.18 (d, *J* = 15.7 Hz, 1H), 6.87-6.82 (m, 2H), 6.05 (t, *J* = 4.3 Hz, 1H), 4.11-4.07 (m, 2H), 3.76 (s, 3H), 2.19 (td, *J* = 6.3, 4.4 Hz, 2H), 1.86-1.79 (m, 2H). ^{13}C-NMR (76 MHz, $CDCl_3$): 185.2, 161.4, 151.9, 143.4, 130.1, 127.6, 118.0, 114.2, 110.1, 66.2, 55.2, 21.5, 20.8.



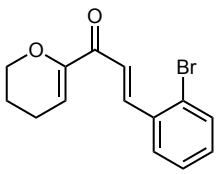
1c

(*E*)-1-(3,4-dihydro-2*H*-pyran-6-yl)-3-(*p*-tolyl)prop-2-en-1-one (1c): Dihydropyran (137 μL, 1.5 mmol, 1.0 equiv.) in THF (1.5 mL, 1M) was treated *t*BuLi (0.971 mL, 1.65 mmol, 1.7 M, 1.1 equiv.), (*E*)-4-methylcinnamaldehyde (219 mg , 1.5 mmol, 1.0 equiv.) in 750 μL of THF, IBX (462 mg, 1.65 mmol, 1.1 equiv.), DMSO (3 mL, 0.5 M) following General Procedure B to obtain **1c** (129 mg, 0.57 mmol, 38%) as a yellow solid after column chromatographic purification with 20% ethyl acetate in hexanes. R_f = 0.23 (20% ethyl acetate in hexanes). ^{1}H-NMR (300 MHz; $CDCl_3$): δ 7.75 (d, *J* = 15.8 Hz, 1H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 15.7 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.13 (t, *J* = 4.3 Hz, 1H), 4.19-4.15 (m, 2H), 2.39 (s, 3H), 2.28 (td, *J* = 6.3, 4.4 Hz, 2H), 1.95-1.87 (m, 2H). ^{13}C NMR (76 MHz; $CDCl_3$) δ 185.5, 152.0, 143.9, 140.8, 132.3, 129.6, 128.5, 119.5, 110.4, 66.4, 21.6, 21.5, 20.9. HRMS-ESI calcd for $C_{15}H_{17}O_2$ $[M+H]^+$ 229.1223, found 229.1222.



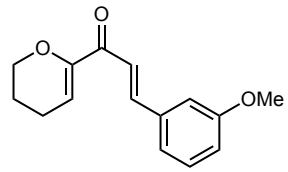
1d

(*E*)-1-(3,4-dihydro-2*H*-pyran-6-yl)-3-(4-fluorophenyl)prop-2-en-1-one (1d): Dihydropyran (365 μL, 4.0 mmol, 1.0 equiv.) in THF (4.0 mL, 1M), was treated with *t*BuLi (3.06 mL, 4.4 mmol, 1.44 M, 1.1 equiv.), (*E*)-4-fluorocinnamaldehyde (600 mg, 4.0 mmol, 1 equiv.) in 4.0 mL of THF, IBX (1.20 g, 4.4 mmol, 1.1 equiv.), DMSO (8 mL, 0.5 M) following General Procedure B to obtain **1d** (405 mg, 1.76 mmol, 44%) as a pale yellow solid after column chromatographic purification with 15% ethyl acetate in hexanes. R_f = 0.33 (20% ethyl acetate in hexanes). ^{1}H-NMR (300 MHz; $CDCl_3$): δ 7.69 (d, *J* = 15.8 Hz, 1H), 7.61-7.54 (m, 2H), 7.25 (dd, *J* = 15.8, 0.5 Hz, 1H), 7.10-7.02 (m, 2H), 6.10 (t, *J* = 4.3 Hz, 1H), 4.16-4.12 (m, 2H), 2.25 (td, *J* = 6.3, 4.4 Hz, 2H), 1.92-1.85 (m, 2H). ^{13}C NMR (76 MHz; $CDCl_3$) *δ* 185.3, 164.2 (d, *J* = 251.3 Hz), 152.0, 142.6, 131.4 (d, *J* = 3.3 Hz), 130.4 (d, *J* = 8.6 Hz), 120.3 (d, *J* = 2.5 Hz), 116.1 (d, *J* = 21.9 Hz), 110.8, 66.5, 21.7, 21.0. ^{19}F NMR (283 MHz; $CDCl_3$) δ -109.4. HRMS-ESI calcd for $C_{14}H_{14}FO_2$ $[M+H]^+$ 233.0972, found 233.0971.



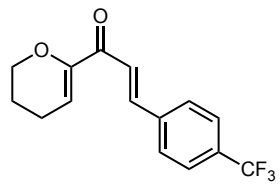
1e

(*E*)-3-(2-bromophenyl)-1-(3,4-dihydro-2*H*-pyran-6-yl)prop-2-en-1-one (1e): Dihydropyran (86 μL, 0.94 mmol, 1.0 equiv.) in THF (1.5 mL, 1M), was treated with *t*BuLi (749 μL, 1.03 mmol, 1.38 M, 1.1 equiv.), (*E*)-2-bromocinnamaldehyde (198 mg, 0.94 mmol, 1.0 equiv.) in 750 μL of THF, IBX (289 mg, 1.03 mmol, 1.1 equiv.), DMSO (2.0 mL, 0.5 M) following General Procedure B to obtain **1e** (117 mg, 0.40 mmol, 42%) as a yellow solid after column chromatographic purification with 20% ethyl acetate in hexanes. R_f = 0.38 (20% ethyl acetate in hexanes. ^{1}H-NMR (300 MHz; $CDCl_3$): δ 8.06 (d, *J* = 15.8 Hz, 1H), 7.67 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.59 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.33-7.17 (m, 3H), 6.11 (t, *J* = 4.3 Hz, 1H), 4.16-4.12 (m, 2H), 2.25 (td, *J* = 6.3, 4.4 Hz, 2H), 1.92-1.85 (m, 2H). ^{13}C NMR (76 MHz; $CDCl_3$) *δ* 185.1, 151.8, 142.0, 135.1, 133.5, 131.2, 127.9, 127.6, 125.9, 123.5, 111.2, 66.4, 21.6, 21.0. HRMS-ESI calcd for $C_{14}H_{14}BrO_2$ $[M+H]^+$ 293.0172, found 293.0170.



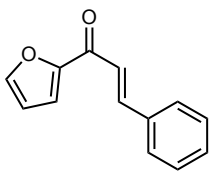
1f

(*E*)-1-(3,4-dihydro-2*H*-pyran-6-yl)-3-(3-methoxyphenyl)prop-2-en-1-one (1f): Dihydropyran (109 μL, 1.2 mmol, 1.0 equiv.) in THF (3.0 mL, 0.43 M), was treated with *t*BuLi (917 μL, 1.32 mmol, 1.44 M, 1.1 equiv.), (*E*)-3-methoxycinnamaldehyde (195 mg, 1.2 mmol, 1.0 equiv.) in 1.2 mL of THF, IBX (370 mg, 1.32 mmol, 1.1 equiv.), DMSO (3.0 mL, 0.43 M) following General Procedure B to obtain **1f** (123 mg, 0.50 mmol, 42%) as a yellow oil after column chromatographic purification with 20% ethyl acetate in hexanes. R_f = 0.28 (20% ethyl acetate in hexanes). ^{1}H-NMR (300 MHz; $CDCl_3$): δ 7.73 (d, *J* = 15.8 Hz, 1H), 7.35-7.28 (m, 2H), 7.23-7.20 (m, 1H), 7.14-7.12 (m, 1H), 6.96 (ddd, *J* = 8.1, 2.5, 0.9 Hz, 1H), 6.14 (t, *J* = 4.3 Hz, 1H), 4.20-4.16 (m, 2H), 3.86 (s, 3H), 2.29 (td, *J* = 6.3, 4.4 Hz, 2H), 1.96-1.88 (m, 2H). ^{13}C NMR (76 MHz; $CDCl_3$) δ 185.3, 159.9, 151.9, 143.7, 136.4, 129.8, 121.2, 120.8, 116.2, 113.3, 110.8, 66.4, 55.3, 21.6, 20.9. HRMS-ESI calcd for $C_{15}H_{17}O_3$ $[M+H]^+$ 245.1172, found 245.1171.



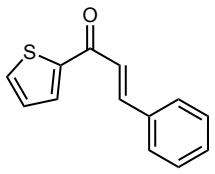
1g

(*E*)-1-(3,4-dihydro-2*H*-pyran-6-yl)-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (1g): Dihydropyran (182 μL, 2.0 mmol, 1.0 equiv.) in THF (4.0 mL, 0.5 M), was treated with *t*BuLi (1.53 μL, 2.2 mmol, 1.44 M, 1.1 equiv.), (*E*)-4-trifluoromethylcinnamaldehyde (400 mg, 2.0 mmol, 1.0 equiv.) in 4.0 mL of THF, IBX (616 mg, 2.2 mmol, 1.1 equiv.), DMSO (4.0 mL, 0.5 M) following General Procedure B to obtain **1g** (238 mg, 0.84 mmol, 42%) as a dark yellow oil after column chromatographic purification with 5% ethyl acetate in hexanes. R_f = 0.13 (20% ethyl acetate in hexanes). ^{1}H-NMR (300 MHz; $CDCl_3$): δ 7.66-7.53 (m, 5H), 7.34 (d, *J* = 15.9 Hz, 1H), 6.09 (t, *J* = 4.3 Hz, 1H), 4.10-4.07 (m, 2H), 2.19 (td, *J* = 6.2, 4.5 Hz, 2H), 1.86-1.78 (m, 2H). ^{13}C NMR (76 MHz; $CDCl_3$) *δ* 151.6, 141.4, 138.3, 131.4 (q, *J* = 32.6 Hz), 128.4, 125.6 (q, *J* = 3.8 Hz), 123.8 (q, *J* = 272.1 Hz), 122.7, 111.3, 66.3, 21.1 (d, *J* = 45.1 Hz), 20.8. ^{19}F NMR (282 MHz; $CDCl_3$) δ -62.9. HRMS-ESI calcd for $C_{15}H_{14}F_3O_2$ $[M+H]^+$ 283.0940, found 283.0938.



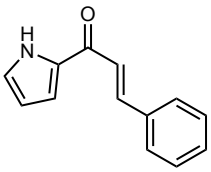
1h

(*E*)-1-(furan-2-yl)-3-phenylprop-2-en-1-one (1h):[15] 1-(furan-2-yl)ethan-1-one (251 μL, 2.50 mmol, 1 equiv.) was added to a solution of ethanol (5.0 mL), aqueous NaOH (250 μL, 0.25 mmol, 1M, 10 mol%), and benzaldehyde (254 μL, 2.50 mmol, 1.0 equiv.). The solution was stirred at room temperature for 20.5 hrs. The ethanol was removed under reduced pressure, the residue redissolved in ether, and the organic layer washed with water (3x), brine (1x), dried with $MgSO_4$ and the solvent removed under reduced pressure. Column chromatographic purification with 15% ethyl acetate in hexanes gave **1h** (295 mg, 1.49 mmol, 59%) as a white solid. R_f = 0.25 (15% ethyl acetate in hexanes). ^{1}H-NMR (300 MHz; $CDCl_3$): δ 7.88 (d, *J* = 15.8 Hz, 1H), 7.66-7.63 (m, 3H), 7.48-7.39 (m, 4H), 7.33 (dd, *J* = 3.6, 0.6 Hz, 1H), 6.59 (dd, *J* = 3.6, 1.7 Hz, 1H). ^{13}C NMR (76 MHz; $CDCl_3$) δ 178.1, 153.8, 146.6, 144.1, 134.8, 130.7, 129.1, 128.6, 121.3, 117.6, 112.7.



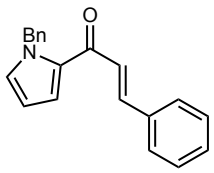
1i

(*E*)-3-phenyl-1-(thiophen-2-yl)prop-2-en-1-one (1i):[16] 1-(thiophen-2-yl)ethan-1-one (270 μL, 2.50 mmol, 1 equiv.) was added to a solution of ethanol (5.0 mL), aqueous NaOH (250 μL, 0.25 mmol, 1M, 10 mol%), and benzaldehyde (254 μL, 2.50 mmol, 1 equiv.). The solution was stirred at room temperature for 20.5 hrs. The ethanol was removed under reduced pressure, the residue redissolved in ether, and the organic layer washed with water (3x), brine (1x), dried with $MgSO_4$ and the solvent removed under reduced pressure. Column chromatographic purification with 15% ethyl acetate in hexanes gave **1i** (390 mg, 1.88 mmol, 75%) as a white solid. R_f = 0.29 (15% ethyl acetate in hexanes). ^{1}H-NMR (300 MHz; $CDCl_3$): δ 7.89-7.84 (m, 2H), 7.70-7.64 (m, 3H), 7.45-7.40 (m, 4H), 7.19 (dd, *J* = 4.7, 4.0 Hz, 1H). ^{13}C NMR (76 MHz; $CDCl_3$) *δ* 182.1, 145.6, 144.2, 134.8, 134.0, 131.9, 130.7, 129.1, 128.6, 128.4, 121.7.



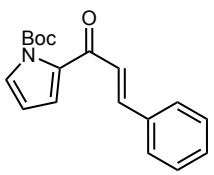
1j

(*E*)-3-phenyl-1-(1*H*-pyrrol-2-yl)prop-2-en-1-one (1j):[17] 1-(1*H*-pyrrol-2-yl)ethan-1-one (273 mg, 2.50 mmol, 1 equiv.) was added to a solution of ethanol (5.0 mL), aqueous NaOH (250 μL, 0.25 mmol, 1M, 10 mol%), and benzaldehyde (254 μL, 2.50 mmol, 1 equiv.). The solution was stirred at room temperature for 48 hrs. The ethanol was removed under reduced pressure, the residue redissolved in ether, and the organic layer washed with water (3x), brine (1x), dried with $MgSO_4$ and the solvent removed under reduced pressure. Column chromatographic purification with 25% ethyl acetate in hexanes gave **1j** (434 mg, 1.88 2.20 mmol, 88%) as a yellow solid. R_f = 0.27 (25% ethyl acetate in hexanes). ^{1}H-NMR (300 MHz; $CDCl_3$): δ 9.99 (s, 1H), 7.85 (d, *J* = 15.7 Hz, 1H), 7.66-7.63 (mm, 2H), 7.46-7.35 (m, 4H), 7.14 (td, *J* = 2.7, 1.2 Hz, 1H), 7.10 (ddd, *J* = 3.8, 2.4, 1.3 Hz, 1H), 6.36 (dt, *J* = 3.8, 2.5 Hz, 1H). ^{13}C NMR (76 MHz; $CDCl_3$) *δ* 179.0, 142.4, 135.2, 133.3, 130.3, 129.0, 128.5, 125.6, 122.1, 116.5, 111.1.



1k

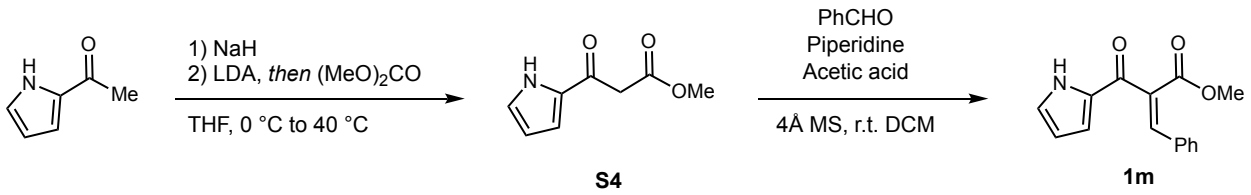
(*E*)-1-(1-benzyl-1*H*-pyrrol-2-yl)-3-phenylprop-2-en-1-one (1k): (*E*)-3-phenyl-1-(1*H*-pyrrol-2-yl)prop-2-en-1-one **1j** (197 mg, 1.00 mmol, 1 equiv.), potassium hydroxide (213 mg, 3.80 mmol, 3.8 equiv.), and DMSO (1.0 mL, 1.0 M) were stirred at room temperature for 0.75 hours. After this time benzyl bromide (202 μL, 1.70 mmol, 1.7 equiv.) was added and stirred until complete by TLC. Upon completion of the reaction, equal volumes of Et_2O and water were added, the phases were separated, and the aqueous layer extracted 3x with Et_2O. The combined organic layers were subsequently washed with water, brine, dried with $MgSO_4$, and the solvent removed under reduced pressure. Column chromatographic purification with 7.5 % ethyl acetate in hexanes gave **1k** (252 mg, 0.88 mmol, 88%) as a white solid. R_f = 0.39 (10% ethyl acetate in hexanes). ^{1}H-NMR (300 MHz; $CDCl_3$): δ 7.74 (d, *J* = 15.6 Hz, 1H), 7.64-7.61 (m, 2H), 7.46-7.39 (m, 4H), 7.37-7.27 (m, 3H), 7.23-7.17 (m, 3H), 7.01 (dd, *J* = 2.3, 1.8 Hz, 1H), 6.30 (dd, *J* = 4.1, 2.5 Hz, 1H), 5.74 (s, 2H). ^{13}C NMR (75 MHz; $CDCl_3$): *δ* 179.7, 141.8, 138.4, 135.4, 131.7, 131.3, 130.1, 129.0, 128.8, 128.3, 127.5, 127.2, 123.7, 120.0, 109.1, 52.9. HRMS-ESI calcd for $C_{20}H_{18}NO$ $[M+H]^+$ 288.1383, found 288.1382.



1l

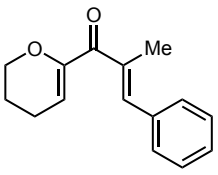
***tert*-butyl 2-cinnamoyl-1*H*-pyrrole-1-carboxylate (1l):**[18] (*E*)-3-phenyl-1-(1*H*-pyrrol-2-yl)prop-2-en-1-one **1j** (100 mg, 0.51 mmol, 1 equiv.) was dissolved in 1 mL of THF at room temperature. To this solution was added triethylamine (141 μL, 1.01 mmol, 2.0 equiv.), Boc_2O (500 μL, 2 M in THF, 1.01 mmol, 2.0 equiv.), DMAP (6 mg, 0.051 mmol, 10 mol%) and stirred for 24 hours. The solvent was removed under vacuum and the residue redissolved in ether. The organic layer was washed sequentially with water and brine before drying with $MgSO_4$ and removing solvent under reduce pressure. The residue was plugged through silica with 40% ethyl acetate in hexanes to afford **1l** (150 mg, 0.50 mmol, 99%**)** as a yellow solid. R_f = 0.66 (20% ethyl acetate in hexanes). ^{1}H-NMR (300 MHz; $CDCl_3$): δ 7.65 (d, *J* = 15.9 Hz, 1H), 7.59-7.56 (m, 2H), 7.42-7.39 (m, 3H), 7.11 (d, *J* = 16.0 Hz, 1H),

6.84 (dd, J = 3.5, 1.6 Hz, 1H), 6.23 (dd, J = 3.3, 3.3 Hz, 1H), 1.55 (s, 9H). ^{13}C NMR (76 MHz; $CDCl_3$) δ 182.8, 148.9, 143.6, 134.9, 134.2, 130.5, 129.1, 128.4, 127.3, 125.7, 120.7, 110.4, 85.1, 27.7.



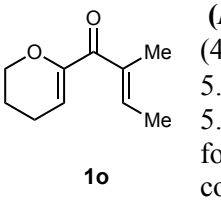
S4 **1m**

Methyl (*Z*)-3-phenyl-2-(1*H*-pyrrole-2-carbonyl)acrylate (1m):[19] 2-acetylpyrrole (546 mg, 5.0 mmol, 1.0 equiv.) was added to a round bottom flask at 0 °C containing NaH (220 mg, 60% in mineral oil, 5.5 mmol, 1.1 equiv.) and THF (15 mL) and stirred for 30 minutes. Freshly prepared LDA (nBuLi: 2.43 mL, 5.5 mmol, 1.1 equiv; diisopropylamine: 771 µL, 5.5 mmol, 1.1 equiv.) in THF (10 mL) was cannulaed into the reaction flask over 10 minutes at -78 °C. After an additional 10 minutes $(MeO)_2CO$ was added and the reaction warmed to 0 °C stirred for 1 hour then 40 °C for 4 hours. The reaction was cooled to rt and quenched with sat. ammonium chloride. The reaction mixture was extracted 3x with DCM, and the collected organic layers were washed with water, brine, dried with $MgSO_4$ and isolated under reduced pressure. Column chromatographic purification with 25% ethyl acetate in hexanes gave **S4** (294 mg, 1.50 mmol, 30%) a yellow oil. R_f = 0.16 (25% ethyl acetate in hexanes). ^{1}H-NMR (300 MHz; $CDCl_3$): δ 10.56 (s, 1H), 7.06-7.04 (m, J = 1.1 Hz, 1H), 6.92 (ddd, J = 3.9, 2.5, 1.4 Hz, 1H), 6.21 (ddd, J = 3.9, 2.4, 2.4 Hz, 1H), 3.79 (s, 2H), 3.66 (s, 3H). ^{13}C-NMR (76 MHz, $CDCl_3$): δ 181.8, 168.1, 131.0, 126.8, 118.4, 110.8, 52.3, 44.7. **S4** (250 mg, 1.5 mmol, 1.0 equiv.) was dissolved in 5 ml of DCM to which was added benzaldehyde (182 µL, 1.8 mmol, 1.2 equiv.), acetic acid (26 µL, 0.45 mmol, 30 mol%), pyrrolidine (37 µL, 0.45 mmol, 30 mol%), 4 Å molecule sieves (420 mg) and was stirred overnight. The reaction was diluted with DCM and washed with dilute HCl, water and brine before drying the organic layer with $MgSO_4$ and removing solvent under reduced pressure. The residue was purified with 20% ethyl acetate in hexanes to **1m** (148 mg, 0.58 mmol, 48%) as an oil. R_f = 0.2 (20% ethyl acetate in hexanes). ^{1}H-NMR (300 MHz; $CDCl_3$): δ 9.86 (br. s, 1H), 7.96 (s, 1H), 7.44-7.41 (m, 2H), 7.30-7.22 (m, 3H), 7.10 (ddd, J = 2.7, 2.7, 1.2 Hz, 1H), 6.72 (ddd, J = 3.8, 2.4, 1.4 Hz, 1H), 6.19 (ddd, J = 3.9, 2.4, 2.4 Hz, 1H), 3.81 (s, 3H).



1n

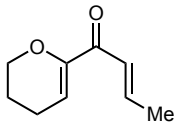
(*E*)-1-(3,4-dihydro-2*H*-pyran-6-yl)-2-methyl-3-phenylprop-2-en-1-one (1n):[13] Dihydropyran (456 µL, 5.0 mmol, 1.0 equiv.) in THF (10 mL, 0.5 M) was treated with *t*BuLi (4.17 mL, 5.5 mmol, 1.32 M, 1.1 equiv.), (*E*)-2-methyl-3-phenylacrylaldehyde (698 µL mg, 5.0 mmol, 1 equiv.) in 5.0 mL of THF, IBX (1.50 mg, 5.5 mmol, 1.1 equiv.) in DMSO (10 mL, 0.5 M) following General Procedure B to obtain **1n** (604 mg, 2.90 mmol, 53%) as a yellow oil after column chromatographic purification with 10% ethyl acetate in hexanes. Rf = 0.27 (20% ethyl acetate in hexanes). ^{1}H-NMR (300 MHz; $CDCl_3$): δ 7.42-7.41 (m, 4H), 7.38-7.30 (m, 1H), 7.28-7.24 (m, 1H), 5.83 (t, J = 4.1 Hz, 1H), 4.18 (t, J = 5.1 Hz, 2H), 2.30-2.24 (m, 2H), 2.15 (s, 3H), 1.97-1.88 (m, 2H). ^{13}C NMR (76 MHz; $CDCl_3$) δ 193.3, 151.0, 138.6, 135.6, 135.5, 129.3, 128.1, 128.4, 112.9, 66.1, 21.3, 20.6, 14.5.



1o

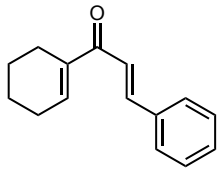
(*E*)-1-(3,4-dihydro-2*H*-pyran-6-yl)-2-methylbut-2-en-1-one (1o):[13] Dihydropyran (456 µL, 5.0 mmol, 1.0 equiv.) in THF (10 mL, 0.5 M) was treated with *t*BuLi (4.17 mL, 5.5 mmol, 1.32 M, 1.1 equiv.), (*E*)-2-methylbut-2-enal (483 µL, 5.0 mmol, 1.0 equiv.) in 5.0 mL of THF, then IBX (1.50 mg, 5.5 mmol, 1.1 equiv.) in DMSO (10 mL, 0.5 M) following General Procedure B to obtain **1o** (375 mg, 2.26 mmol, 45%) as a clear oil after column chromatographic purification with 15% ethyl acetate in hexanes. Rf = 0.26 (15% ethyl acetate in hexanes). ^{1}H-NMR (300 MHz; $CDCl_3$): δ 6.32-6.23 (m, 1H), 5.39 (t, J = 4.1 Hz, 1H), 3.87-

3.83 (m, 2H), 1.99-1.94 (m, 2H), 1.66-1.59 (m, 8H). ^{13}C NMR (76 MHz; $CDCl_3$) δ 192.3, 150.7, 137.2, 135.6, 111.3, 65.7, 21.1, 20.2, 13.8, 11.8.



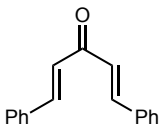
1p

(*E*)-1-(3,4-dihydro-2*H*-pyran-6-yl)but-2-en-1-one (1p):[20] Dihydropyran (456 μL, 5.0 mmol, 1 equiv) in THF (10 mL, 0.5 M) was treated with *t*BuLi (4.17 mL, 5.5 mmol, 1.32 M, 1.1 equiv.), (*E*)-but-2-enal (414 μL mg, 5.0 mmol, 1.0 equiv.) in 5.0 mL of THF, and IBX (1.50 mg, 5.5 mmol, 1.1 equiv.) in DMSO (10 mL, 0.5 M) following General Procedure B to obtain **1p** (337 mg, 2.20 mmol, 55%) as a clear oil after column chromatographic purification with 10% ether in pentanes. R_f = 0.13 (10% ether in pentanes). ^{1}H-NMR (300 MHz; $CDCl_3$): δ 6.97 (dq, *J* = 14.7, 7.3 Hz, 1H), 6.67-6.61 (m, 1H), 5.97 (t, *J* = 4.1 Hz, 1H), 4.07 (t, *J* = 5.1 Hz, 2H), 2.19 (app. q, *J* = 5.4 Hz, 2H), 1.89 (m, 5H). ^{13}C NMR (76 MHz; $CDCl_3$) δ 185.0, 151.3, 143.5, 125.5, 110.6, 66.0, 21.3, 20.6, 18.2.



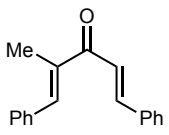
1q

(*E*)-1-(cyclohex-1-en-1-yl)-3-phenylprop-2-en-1-one (1q):[21] *n*BuLi (0.957 mL, 2.30 M, 2.20 mmol, 1.1 equiv.) was added to diisopropyl amine (339 μL, 2.4 mmol, 1.2 equiv.) in 5 mL of THF at -78 °C. After stirring for 5 minutes 1-(cyclohex-1-en-1-yl)ethan-1-one (248 mg, 2.00 mmol, 1.0 equiv.) in 1.0 mL of THF was added dropwise and stirred for 15 minutes at which point benzaldehyde (213 μL, 2.1 mmol, 1.05 equiv.) was added dropwise and the resulting mixture was warmed to 0 °C. After an additional 1.5 hrs mesyl chloride (170 μL, 2.20 mmol, 1.1 equiv.), triethyl amine (836 μL, 6.00 mmol, 3.0 equiv.) and DMAP (269 mg, 2.20 mmol, 1.1 equiv.) were added sequentially and the reaction was warmed to room temperature and stirred for 4 hrs. The reaction was diluted with equal volumes of sat. ammonium chloride and DCM. The layers were separated and the aqueous extracted 3x with DCM. The combined organic layers were washed twice with 3 M HCl, sat. $NaHCO_3$, water, brine and dried with MgSO4. The residue was purified by column chromatography with 10% ethyl acetate in hexanes to afford **1q** (112 mg, 0.53 mmol, 26%) as a yellow solid. R_f = 0.37 (10% ethyl acetate in hexanes). ^{1}H-NMR (300 MHz; $CDCl_3$): δ 7.61 (d, *J* = 15.7 Hz, 1H), 7.57-7.53 (m, 2H), 7.38-7.33 (m, 3H), 7.29 (d, *J* = 15.7 Hz, 1H), 7.01 (tt, *J* = 3.8, 1.8 Hz, 1H), 2.37-2.26 (m, 4H), 1.72-1.59 (m, 4H). ^{13}C NMR (76 MHz; $CDCl_3$) δ 190.9, 142.4, 140.3, 140.1, 135.3, 130.0, 128.8, 128.1, 121.4, 26.2, 23.6, 22.0, 21.6.



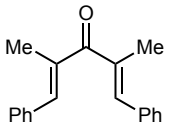
1r

(1*E*,4*E*)-1,5-diphenylpenta-1,4-dien-3-one (1r):[22] Acetone (0.50 mL, 6.76 mmol, 1.0 equiv.), benzaldehyde (1.55 mL, 15.2 mmol, 2.3 equiv.), and NaOH (2.0 mL, 1.0 M aq.) were heated to 40 °C for 1.5 hrs after which the ethyl acetate was added and the organic layer washed with water (3x), brine (1x), dried with $MgSO_4$, and rotary evaporated to a solid. Recrystallization from ethanol afforded **1r** (673 mg, 2.87 mmol, 43%) as a yellow solid. R_f = 0.42 (15% ethyl acetate in hexanes). ^{1}H-NMR (300 MHz; $CDCl_3$): δ 7.75 (d, *J* = 16.0 Hz, 2H), 7.65-7.59 (m, 4H), 7.43-7.37 (m, 6H), 7.15-7.07 (m, 2H). ^{13}C NMR (76 MHz; $CDCl_3$) δ 189.0, 143.4, 134.9, 130.6, 129.0, 128.5, 125.5.



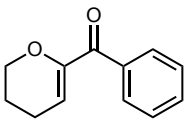
1s

(1*E*,4*E*)-2-methyl-1,5-diphenylpenta-1,4-dien-3-one (1s):[23] (*E*)-3-methyl-4-phenylbut-3-en-2-one (320 mg, 2.0 mmol, 1.0 equiv.) and benzaldehyde (224 μL, 2.2 mmol, 1.1 equiv.) were stirred at room temperature in NaOH in ethanol (2.0 mL, 1 M, 1.0 equiv.) for 13.5 hrs. The reaction was then evaporated to dryness under reduce pressure, then dissolved in equal volumes of water and ethyl acetate. The layers were separated and the aqueous layer extracted (3x) with ethyl acetate, the combined organic layers were subsequently washed with water, brine, dried with $MgSO_4$, and rotary evaporated. Column chromatographic purification with 5% ethyl acetate in hexanes gave **1s** (434 mg, 1.78 mmol, 89%) as a yellow oil. R_f = 0.40 (5% ethyl acetate in hexanes). ^{1}H-NMR (300 MHz; $CDCl_3$): δ 7.74 (d, *J* = 15.7 Hz, 1H), 7.66-7.61 (m, 3H), 7.51-7.35 (m, 9H), 2.22 (d, *J* = 1.4 Hz, 3H). ^{13}C NMR (76 MHz; $CDCl_3$) δ 192.8, 143.5, 138.8, 138.6, 136.1, 135.2, 130.3, 129.9, 129.0, 128.6, 128.6, 128.4, 122.1, 13.9.



1t

(1*E*,4*E*)-2,4-dimethyl-1,5-diphenylpenta-1,4-dien-3-one (1t):[24] 3-pentanone (615 μL, 5.82 mmol, 1 equiv.), benzaldehyde (1213 μL, 11.9 mmol, 2.04 equiv.), potassium hydroxide (690 mg in 2 mL DI water, 12.3 mmol, 2.1 equiv.) in MeOH (4 mL, 1.5 M) were stirred at reflux for 24 hours. The reaction was cooled to room temperature, acidified to pH =1 with 2 M HCl. The reaction mixture was extracted 3x with DCM, and the collected organic layers were washed with sat. $NaHCO_3$, water, brine, dried with $MgSO_4$ and isolated under reduced pressure as a yellow oil. Recrystallization from MeOH afford the white flakey solid **1t** (220 mg, 0.84 mmol, 14%). R_f = 0.69 (15% ethyl acetate in hexanes). ^{1}H-NMR (300 MHz; $CDCl_3$): δ 7.47-7.39 (m, 8H), 7.37-7.31 (m, 2H), 7.23 (d, *J* = 1.2 Hz, 2H), 2.23 (d, *J* = 1.4 Hz, 6H). ^{13}C NMR (75 MHz; $CDCl_3$): δ 202.2, 139.1, 137.0, 136.1, 129.7, 128.6, 128.4, 15.1.

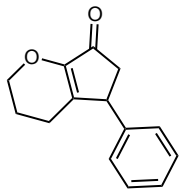


1u

(3,4-dihydro-2*H*-pyran-6-yl)(phenyl)methanone (1u):[25] Dihydropyran (365 μL, 4.0 mmol, 1.0 equiv.) in THF (4 mL, 0.5 M) was treated with *t*BuLi (3.06 mL, 4.4 mmol, 1.44 M, 1.1 equiv.), benzaldehyde (404 μL, 4.0 mmol, 1.0 equiv.) in 4.0 mL of THF then IBX (1.20 g, 4.4 mmol, 1.1 equiv.) in DMSO (8 mL, 0.5 M) following General Procedure B to obtain **1u** (316 mg, 1.68 mmol, 42%) as a yellow oil after column chromatographic purification with 20% ethyl acetate in hexanes. Rf = 0.36 (20% ethyl acetate in hexanes). ^{1}H-NMR (300 MHz; $CDCl_3$): δ 7.62-7.59 (m, 2H), 7.37-7.32 (m, 1H), 7.27-7.22 (m, 2H), 5.65 (t, *J* = 4.2 Hz, 1H), 4.02-3.98 (m, 2H), 2.08 (td, *J* = 6.3, 4.3 Hz, 2H), 1.77-1.69 (m, 2H). ^{13}C NMR (76 MHz; $CDCl_3$) *δ* 190.5, 150.9, 136.8, 131.6, 128.9, 127.6, 115.2, 66.0, 21.0, 20.5.

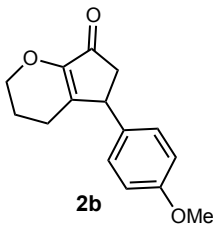
6 Nazarov Products

General Procedure C (GP-C): To an oven dried 10 mL round bottom flask, stir bar and water condenser cooled with a drying tube, was added substrate **1** (0.25 mmol, 1 equiv.), catalyst (**D**) (5 mol%, 0.0125 mmol) and acetonitrile (0.1 M, 2.5 mL). The reaction mixture was lowered into a pre-heated oil bath and refluxed until disappearance of substrate was observed by TLC. Removal of solvent under reduced pressure and flash chromatography to yield the pure products.



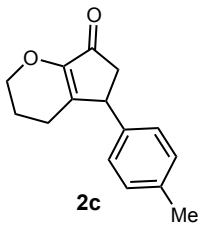
2a

5-phenyl-3,4,5,6-tetrahydrocyclopenta[*b*]pyran-7(2*H*)-one (2a):[13] Divinylketone **1a** (54 mg, 0.25 mmol, 1.0 equiv.) was treated with GP-C for 7.5 hours and purified with 25% ethyl acetate in hexanes to obtain **2a** as a yellow oil (42 mg, 0.20 mmol, 78%). Trial #2, 61%; Trial #3, 71%; average = 70%. R_f = 0.19 (25% ethyl acetate in hexanes). ^{1}H-NMR (300 MHz; $CDCl_3$): δ 7.36-7.23 (m, 3H), 7.14 (d, *J* = 7.8 Hz, 2H), 4.20-4.08 (m, 2H), 3.85 (d, *J* = 6.6 Hz, 1H), 2.90 (dd, *J* = 18.9, 6.6 Hz, 1H), 2.32 (d, *J* = 19.0 Hz, 1H), 2.22-2.01 (m, 2H), 1.99-1.84 (m, 2H). ^{13}C NMR (76 MHz; $CDCl_3$) *δ* 200.3, 151.5, 147.7, 141.7, 129.0, 127.2, 127.1, 67.0, 43.7, 43.0, 22.3, 21.5.



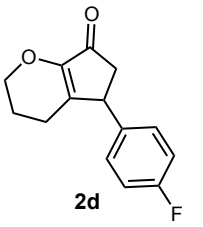
2b

5-(4-methoxyphenyl)-3,4,5,6-tetrahydrocyclopenta[*b*]pyran-7(2*H*)-one (2b): Divinylketone **1b** (61 mg, 0.25 mmol, 1.0 equiv.) was treated with GP-C for 5 hours and purified with 30% ethyl acetate in hexanes obtained **2b** as a pale yellow solid (38 mg, 0.16 mmol, 62%). R_f = 0.21 (30% ethyl acetate in hexanes). ^{1}H-NMR (300 MHz; $CDCl_3$): δ 7.05-7.01 (m, 2H), 6.87-6.82 (m, 2H), 4.18-4.06 (m, 2H), 3.80-3.76 (m, 4H), 2.86 (dd, *J* = 19.0, 6.6 Hz, 1H), 2.26 (ddt, *J* = 19.0, 1.8, 0.8 Hz, 1H), 2.17-2.00 (m, 2H), 1.97-1.82 (m, 2H). ^{13}C NMR (76 MHz; $CDCl_3$) *δ* 200.3, 158.8, 151.4, 147.8, 133.7, 128.2, 114.5, 67.0, 55.4, 43.2, 43.0, 22.3, 21.6. HRMS-ESI calcd for $C_{15}H_{17}O_3$ $[M+H]^+$ 245.1172, found 245.1171.



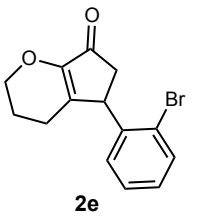
2c

5-(*p*-tolyl)-3,4,5,6-tetrahydrocyclopenta[*b*]pyran-7(2*H*)-one (2c): Divinylketone **1c** (57 mg, 0.25 mmol, 1.0 equiv.) was treated with GP-C for 6.67 hours and purified with 20% ethyl acetate in hexanes to obtain **2c** as a yellow solid (32 mg, 0.14 mmol, 56%). R_f = 0.13 (20% ethyl acetate in hexanes). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.16-7.14 (m, 2H), 7.05-7.01 (m, 2H), 4.21-4.08 (m, 2H), 3.82 (dq, *J* = 6.6, 1.6 Hz, 1H), 2.89 (ddt, *J* = 19.0, 6.6, 0.7 Hz, 1H), 2.35-2.27 (m, 4H), 2.18-2.09 (m, 2H), 2.00-1.84 (m, 2H). ^{13}C-NMR (76 MHz, $CDCl_3$): δ 200.30, 151.48, 147.67, 138.72, 136.90, 129.75, 127.07, 67.02, 43.37, 43.13, 22.29, 21.58, 21.13. HRMS-ESI calcd for $C_{15}H_{17}O$ $[M+H]^+$ 229.1223, found 229.1223.



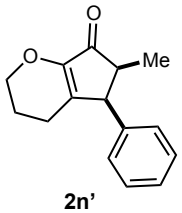
2d

5-(4-fluorophenyl)-3,4,5,6-tetrahydrocyclopenta[*b*]pyran-7(2*H*)-one (2d): Divinylketone **1d** (58 mg, 0.25 mmol, 1.0 equiv.) was treated with GP-C for 26.5 hours and purified with 20% ethyl acetate in hexanes obtained **2d** as a yellow oil (33 mg, 0.14 mmol, 57%). R_f = 0.11 (20% ethyl acetate in hexanes). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.12-7.05 (m, 2H), 7.04-6.96 (m, 2H), 4.19-4.06 (m, 2H), 3.82 (dq, *J* = 6.7, 1.6 Hz, 1H), 3.84-3.81 (dd, *J* = 19.0, 6.7 Hz, 1H), 2.29-2.22 (m, 1H), 2.18-1.99 (m, 2H), 1.99-1.81 (m, 2H). ^{13}C NMR (76 MHz; $CDCl_3$): δ 199.9, 162.2 (d, *J* = 245.6 Hz), 151.7, 147.0, 137.5 (d, *J* = 3.2 Hz), 128.7 (d, *J* = 7.9 Hz), 116.0 (d, *J* = 21.3 Hz), 67.0, 43.1, 43.0, 22.2, 21.5. ^{19}F NMR (282 MHz; $CDCl_3$): δ -115.5. HRMS-ESI calcd for $C_{14}H_{14}O_2F$ $[M+H]^+$ 233.0972, found 233.0971.

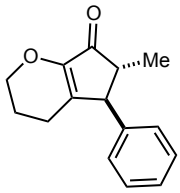


2e

5-(2-bromophenyl)-3,4,5,6-tetrahydrocyclopenta[*b*]pyran-7(2*H*)-one (2e): Divinylketone **1e** (73 mg, 0.25 mmol, 1.0 equiv.) was treated with GP-C for 8 hours, additional catalyst (7 mg, 0.0125 mmol) was added and stirred for another hour. Starting material remained partially unconsumed. Purification with 20% ethyl acetate in hexanes obtained **2e** as a pale yellow solid (31 mg, 0.11 mmol, 44%). R_f = 0.16 (20% ethyl acetate in hexanes). ^{1}H NMR (300 MHz, $CDCl_3$): 7.58 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.28 (td, *J* = 7.5, 1.3 Hz, 1H), 7.14-7.08 (m, 1H), 6.99 (dd, *J* = 7.7, 1.5 Hz, 1H), 4.44 (br. d, 1H), 4.22-4.10 (m, 2H), 2.96 (dd, *J* = 19.0, 6.7 Hz, 1H), 2.27-2.14 (m, 3H), 1.99-1.90 (m, 2H). ^{13}C NMR (76 MHz; $CDCl_3$) *δ* 199.6, 152.3, 146.1, 140.9, 133.3, 128.7, 128.3, 67.1, 42.0, 22.4, 21.6. HRMS-ESI calcd for $C_{14}H_{14}O_2Br$ $[M+H]^+$ 293.0172, found 293.0174.



2n'



2n"

Divinylketone **1n** (57 mg, 0.25 mmol, 1.0 equiv.) was treated with GP-C for 0.5 hours and purified with 20% ethyl acetate in hexanes obtained combined **2n'** and **2n''** (23.1 mg, 0.10 mmol, 41%) as a clear oil.

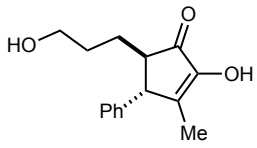
Divinylketone **1n** (57 mg, 0.25 mmol, 1.0 equiv.) was treated with GP-C modified to include 20 mol% of catalyst for 0.25 hours and purified with 20% ethyl acetate in hexanes obtained combined **2n'** (18.2 mg, 0.080 mmol, 32%) and **2n''** (5.1 mg, 0.022 mmol, 8.9%) as a clear oils.

***Cis*-6-methyl-5-phenyl-3,4,5,6-tetrahydrocyclopenta[*b*]pyran-7(2*H*)-one (2n'):**[13] R_f = 0.23 (20% ethyl acetate in hexanes). ^{1}H-NMR (300 MHz; $CDCl_3$): δ 7.36-7.24 (m, 3H), 7.06-7.04 (m, 2H), 4.28-4.14 (m, 2H), 4.04 (ddd, *J* = 6.6, 1.3, 1.3 Hz, 1H), 2.83-2.72 (m, 1H), 2.21 (t, *J* = 6.4 Hz, 2H), 2.04-1.92 (m, 2H),

0.71 (d, J = 7.6 Hz, 3H). ^{13}C NMR (76 MHz; $CDCl_3$) δ 203.1, 151.7, 145.0, 138.8, 129.0, 128.6, 127.3, 67.2, 49.0, 43.4, 22.7, 21.8, 12.4.

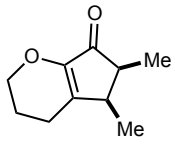
***Trans*-6-methyl-5-phenyl-3,4,5,6-tetrahydrocyclopenta[*b*]pyran-7(2*H*)-one (2n'')**:[26] R_f = 0.29 (20% ethyl acetate in hexanes). ^{1}H-NMR (300 MHz; $CDCl_3$): δ 7.37-7.24 (m, 3H), 7.15-7.12 (m, 2H), 4.16 (dd, J = 5.8, 4.6 Hz, 2H), 3.34 (ddd, J = 1.9, 1.9, 1.9 Hz, 1H), 2.30-2.21 (m, 1H), 2.10 (t, J = 6.0 Hz, 2H), 1.97-1.89 (m, 2H), 1.27 (d, J = 7.4 Hz, 3H). ^{13}C NMR (76 MHz; $CDCl_3$) δ 202.7, 150.9, 145.4, 141.3, 129.1, 127.5, 127.3, 67.1, 53.4, 49.5, 22.2, 21.7, 15.0.

Room temperature experiment for the isolation of 4:

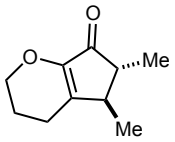


4

Divinylketone **1n** (57 mg, 0.25 mmol, 1.0 equiv.) was treated with GP-C at room temperature for 23 hours and purified with 20-50% ethyl acetate in hexanes to isolate **4** (7.9 mg, 0.032 mmol, 13%) as a clear oil. %). R_f = 0.32 (50% ethyl acetate in hexanes). ^{1}H-NMR (300 MHz; $CDCl_3$): δ 7.35-7.23 (m, 4H), 7.14-7.11 (m, 2H), 5.92 (s, 1H), 3.60 (t, J = 6.0 Hz, 2H), 3.42 (t, J = 1.4 Hz, 1H), 2.35 (t, J = 5.7 Hz, 1H), 1.91-1.82 (m, 1H), 1.77 (dd, J = 1.2, 0.8 Hz, 3H), 1.72-1.63 (m, 5H). ^{13}C NMR (76 MHz; $CDCl_3$) δ 204.5, 148.7, 145.0, 141.5, 129.1, 127.7, 127.4, 62.7, 53.2, 52.9, 30.1, 27.5, 12.7. HRMS-ESI calcd for $C_{15}H_{19}O_3$ $[M+H]^+$ 247.1340, found 247.1329.



2o'

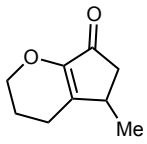


2o''

Divinylketone **1o** (42 mg, 0.25 mmol, 1.0 equiv.) was treated with GP-C for 1.3 hours and purified with 20% ethyl acetate in hexanes obtained **2o'** (12.4 mg, 0.16 mmol, 30%) and **2o''** (8.1 mg, 0.16 mmol, 19%) as a clear oils.

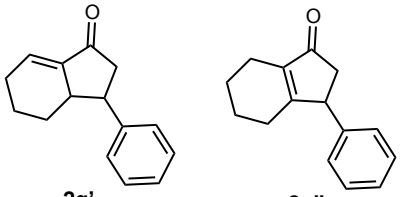
***Cis*-5,6-dimethyl-3,4,5,6-tetrahydrocyclopenta[*b*]pyran-7(2*H*)-one (2o')**:[13] R_f = 0.17 (20% ethyl acetate in hexanes). ^{1}H-NMR (300 MHz; $CDCl_3$): δ 4.19-4.12 (m, 1H), 4.06-3.99 (m, 1H), 2.82 (dq, J = 6.9, 6.9 Hz, 1H), 2.55-2.36 (m, J = 7.1 Hz, 2H), 2.21 (ddd, J = 18.7, 5.5, 5.5 Hz, 1H), 1.99-1.91 (m, 2H), 1.10 (d, J = 7.6 Hz, 3H), 1.05 (d, J = 7.3 Hz, 3H).

***Trans*-5,6-dimethyl-3,4,5,6-tetrahydrocyclopenta[*b*]pyran-7(2*H*)-one (2o'')**:[13] R_f = 0.22 (20% ethyl acetate in hexanes). ^{1}H-NMR (300 MHz; $CDCl_3$): δ 4.15-4.04 (m, 2H), 2.41 (ddd, J = 18.8, 6.4, 6.4 Hz, 1H), 2.29-2.13 (m, 2H), 1.99-1.85 (m, 3H), 1.18 (dd, J = 7.1, 4.2 Hz, 6H).



2p

5-methyl-3,4,5,6-tetrahydrocyclopenta[*b*]pyran-7(2*H*)-one (2p):[27] Divinylketone **1p** (38 mg, 0.25 mmol, 1.0 equiv.) was treated with GP-C for 9.75 hours and purified with 50% ethyl acetate in hexanes to obtain **2p** as a clear oil (15 mg, 0.099 mmol, 39%). R_f = 0.18 (50% ethyl acetate in hexanes). ^{1}H-NMR (300 MHz; $CDCl_3$): δ 4.14-3.99 (m, 2H), 2.77-2.67 (m, 1H), 2.59 (dd, J = 18.6, 6.2 Hz, 1H), 2.42 (ddd, J = 18.8, 6.7, 6.7 Hz, 1H), 2.19 (ddd, J = 18.8, 5.7, 5.7 Hz, 1H), 1.97-1.89 (m, 3H), 1.15 (d, J = 7.0 Hz, 3H). ^{13}C NMR (76 MHz; $CDCl_3$) δ 200.2, 150.6, 149.6, 66.8, 41.7, 32.1, 21.9, 21.6, 19.4.

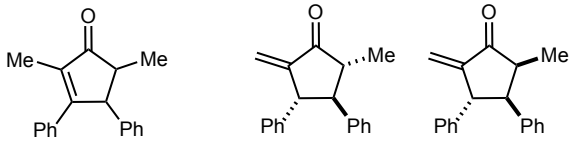


2q' **2q"**

Divinylketone **1q** (53 mg, 0.25 mmol, 1.0 equiv.) was treated with GP-C for 20 hours after which another 5 mol% of catalyst was added. After an additional 8 hours no change was apparent by TLC and the reaction was purified with 5% ethyl acetate in hexanes to obtain divinylketone **1q** (30 mg, 0.14 mmol, 57%), **2q'** (10 mg, 0.0.47 mmol, 19%) and **2q''** (5.2 mg, 0.024 mmol, 10%) as yellow solids.

3-phenyl-2,3,3a,4,5,6-hexahydro-1*H*-inden-1-one (2q'):[28] R_f = 0.14 (5% ethyl acetate in hexanes). ^{1}H-NMR (300 MHz; $CDCl_3$): δ 7.41-7.34 (m, 2H), 7.31-7.26 (m, 3H), 6.81 (ddd, *J* = 3.3, 3.3, 3.3 Hz, 1H), 2.83 (ddd, *J* = 12.5, 10.7, 7.0 Hz, 1H), 2.73-2.64 (m, 2H), 2.55 (dd, *J* = 17.8, 12.5 Hz, 1H), 2.43-2.30 (m, 1H), 2.28-2.15 (m, 1H), 2.08-2.00 (m, *J* = 4.3 Hz, 1H), 1.93-1.86 (m, 1H), 1.51 (dddd, *J* = 13.6, 13.6, 10.5, 6.4, 3.1 Hz, 1H), 1.21-1.08 (m, 1H). ^{13}C NMR (76 MHz; $CDCl_3$) δ 204.7, 141.8, 141.2, 133.1, 128.8, 127.3, 127.0, 48.3, 46.2, 45.9, 27.2, 25.6, 21.7.

3-phenyl-2,3,4,5,6,7-hexahydro-1*H*-inden-1-one (2q''):[28] R_f = 0.06 (5% ethyl acetate in hexanes). ^{1}H-NMR (300 MHz; $CDCl_3$): δ 7.35-7.21 (m, 3H), 7.10-7.07 (m, 2H), 3.84-3.82 (m, 1H), 2.90 (dd, *J* = 18.8, 6.9 Hz, 1H), 2.36 (dd, *J* = 18.8, 2.3 Hz, 1H), 2.25-2.22 (m, 2H), 2.07-2.04 (m, 2H), 1.72-1.61 (m, 4H). ^{13}C NMR (76 MHz; $CDCl_3$) δ 208.4, 175.4, 142.1, 139.4, 129.1, 127.4, 127.1, 48.2, 45.1, 26.6, 22.3, 21.8, 20.3.

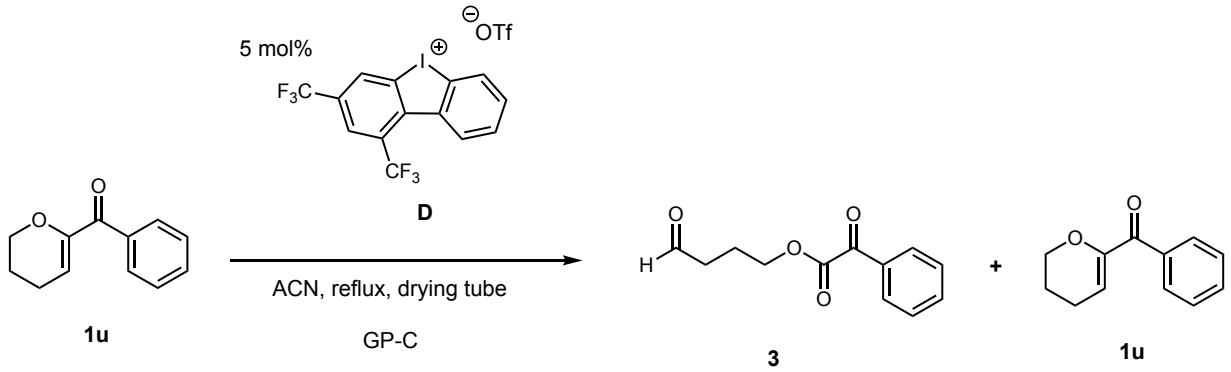


2t' **2t"-major** **2t"-minor**

Divinylketone **1t** (66 mg, 0.25 mmol, 1.0 equiv.) was treated with GP-C for 0.5 hours and purified with 5% ethyl acetate in hexanes obtained **2t'** (27.4 mg, 0.10 mmol, 42%, 1:4 *anti*:*syn*) and **2t''** (4.5 mg, 0.017 mmol, 7%, 1:4.2 mix of epimers) as oils.

2,5-dimethyl-3,4-diphenylcyclopent-2-en-1-one (2t'):[29] R_f = 0.18 (5% ethyl acetate in hexanes). ^{1}H-NMR (300 MHz; $CDCl_3$): δ 7.42-7.01 (m, 20H, syn and anti), 4.63 (dq, *J* = 7.1, 1.5 Hz, 1H, syn), 4.00 (dq, *J* = 2.3, 2.3 Hz, 1H, anti), 2.94 (dq, *J* = 7.4, 7.4 Hz, 1H, syn), 2.43 (dq, *J* = 7.4, 2.9 Hz, 1H, anti), 2.11 (d, *J* = 1.7 Hz, 3H, syn), 2.05 (d, *J* = 2.0 Hz, 3H, anti), 1.38 (d, *J* = 7.4 Hz, 3H, anti), 0.78 (d, *J* = 7.5 Hz, 3H, syn). ^{13}C NMR (76 MHz; $CDCl_3$) *δ* 211.5 (syn), 211.0 (anti), 167.1 (anti), 166.3 (syn), 142.1 (anti), 139.3 (syn), 137.1 (syn), 136.8 (anti), 135.8 (syn), 135.3 (anti), 129.1, 129.0, 129.0, 128.9, 128.8, 128.5, 128.4, 128.4, 128.3, 127.7, 126.9, 126.7, 56.5 (anti), 52.7 (syn), 51.4 (anti), 45.6 (syn), 15.4 (anti), 12.4 (syn), 10.3 (syn), 10.2 (anti).

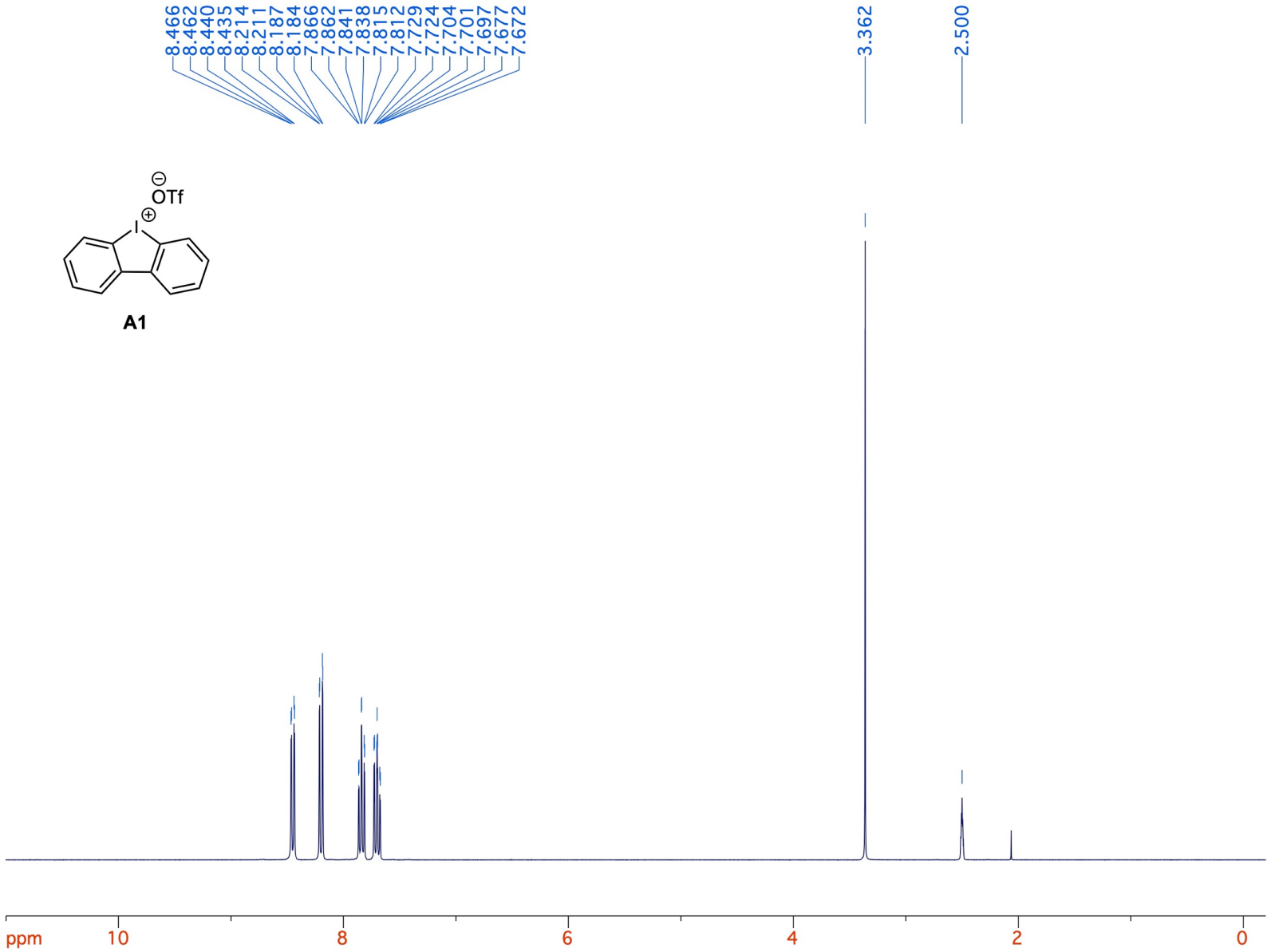
2-methyl-5-methylene-3,4-diphenylcyclopentan-1-one (2t''):[30] R_f = 0.10 (5% ethyl acetate in hexanes). ^{1}H-NMR (300 MHz; $CDCl_3$): δ 7.31-7.04 (m, 20H, major and minor), 6.34-6.33 (m, 1H, minor), 6.26 (d, *J* = 3.1 Hz, 1H, major), 5.24-5.23 (m, 1H, minor), 5.05 (d, *J* = 2.6 Hz, 1H, major), 4.35-4.33 (m, 1H, minor), 3.95-3.90 (m, 1H, major), 3.67-3.61 (m, 1H, minor), 2.90-2.82 (m, 2H, major and minor), 2.70-2.60 (m, 1H, major), 1.15 (d, *J* = 6.7 Hz, 3H, major), 0.87 (d, *J* = 7.4 Hz, 3H, minor).

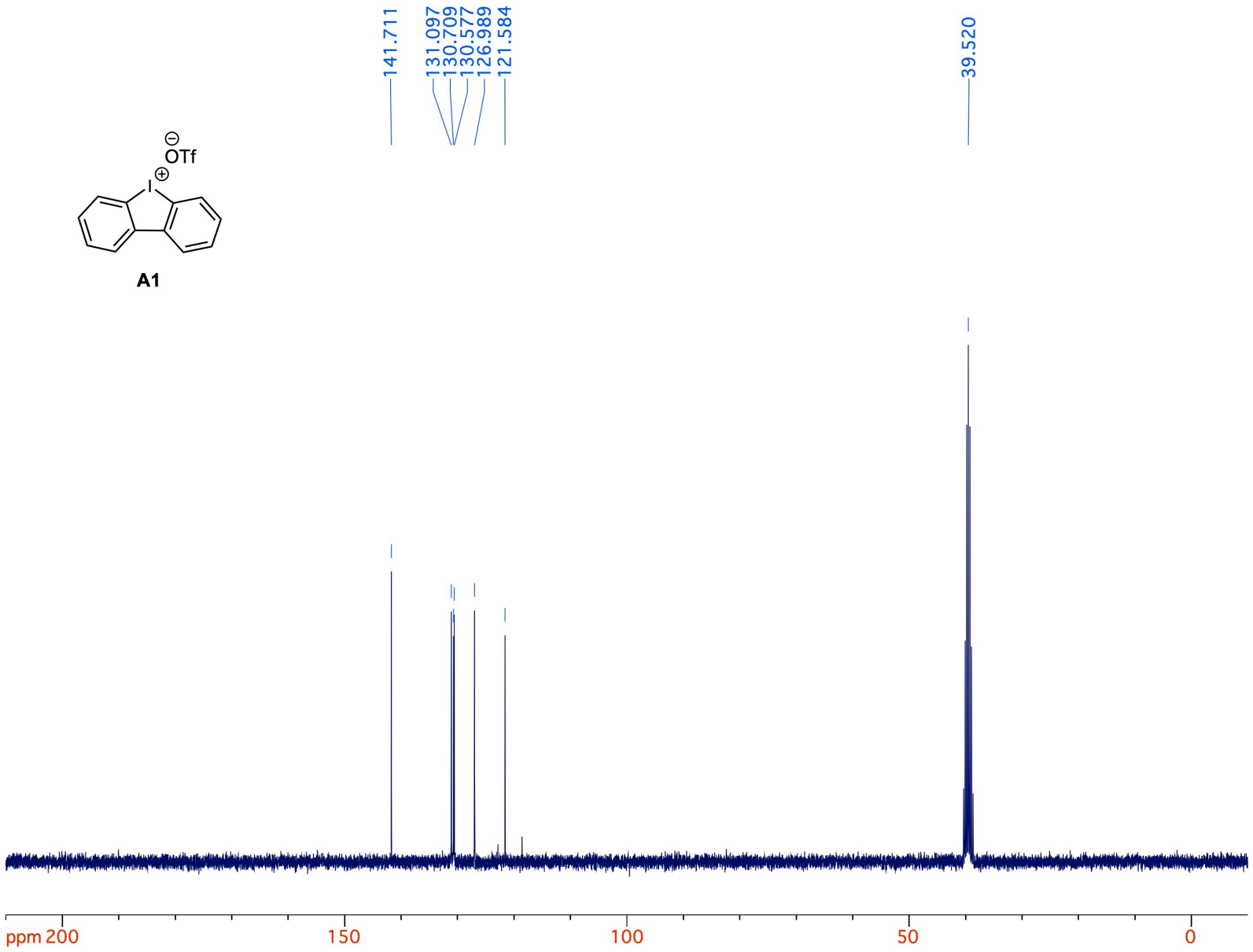


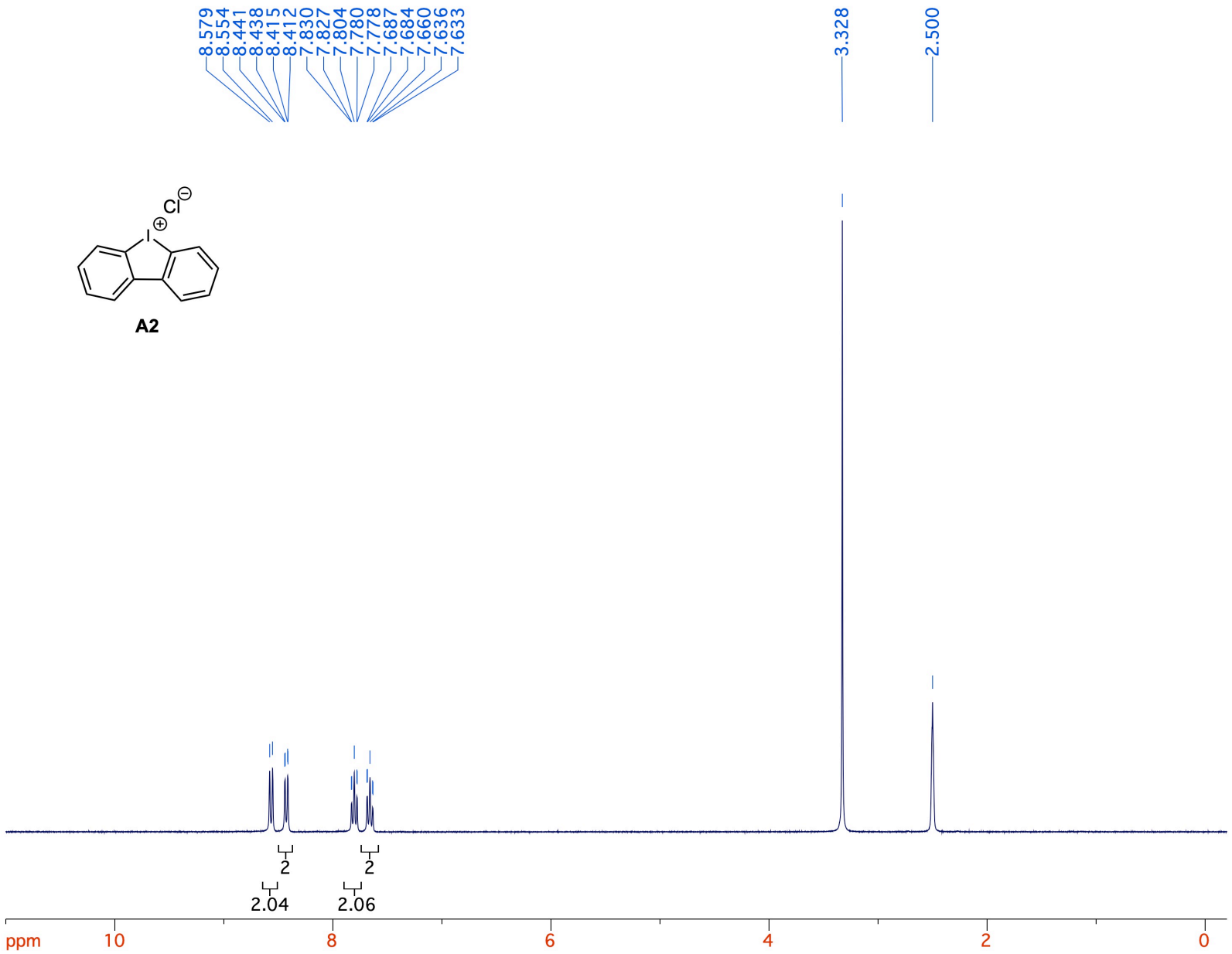
4-oxobutyl 2-oxo-2-phenylacetate (1u): Unsaturated ketone **1u** (47 mg, 0.25 mmol, 1.0 equiv.) was treated with GP-C for 23 hours and purified with 25% ethyl acetate in hexanes to obtain **3** as a clear oil (3.0 mg, 0.014 mmol, 5.4%). R_f = 0.22 (25% ethyl acetate in hexanes). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.82 (t, *J* = 0.9 Hz, 1H), 8.03-7.99 (m, 2H), 7.68 (tt, *J* = 7.4, 1.6 Hz, 1H), 7.56-7.50 (m, 2H), 4.43 (t, *J* = 6.4 Hz, 2H), 2.65 (td, *J* = 7.1, 0.9 Hz, 2H), 2.12 (tt, *J* = 6.8, 6.8 Hz, 2H). ^{13}C-NMR (76 MHz, $CDCl_3$): δ 200.6, 186.0, 163.6, 135.0, 132.4, 130.0, 129.0, 65.0, 40.1, 21.1.

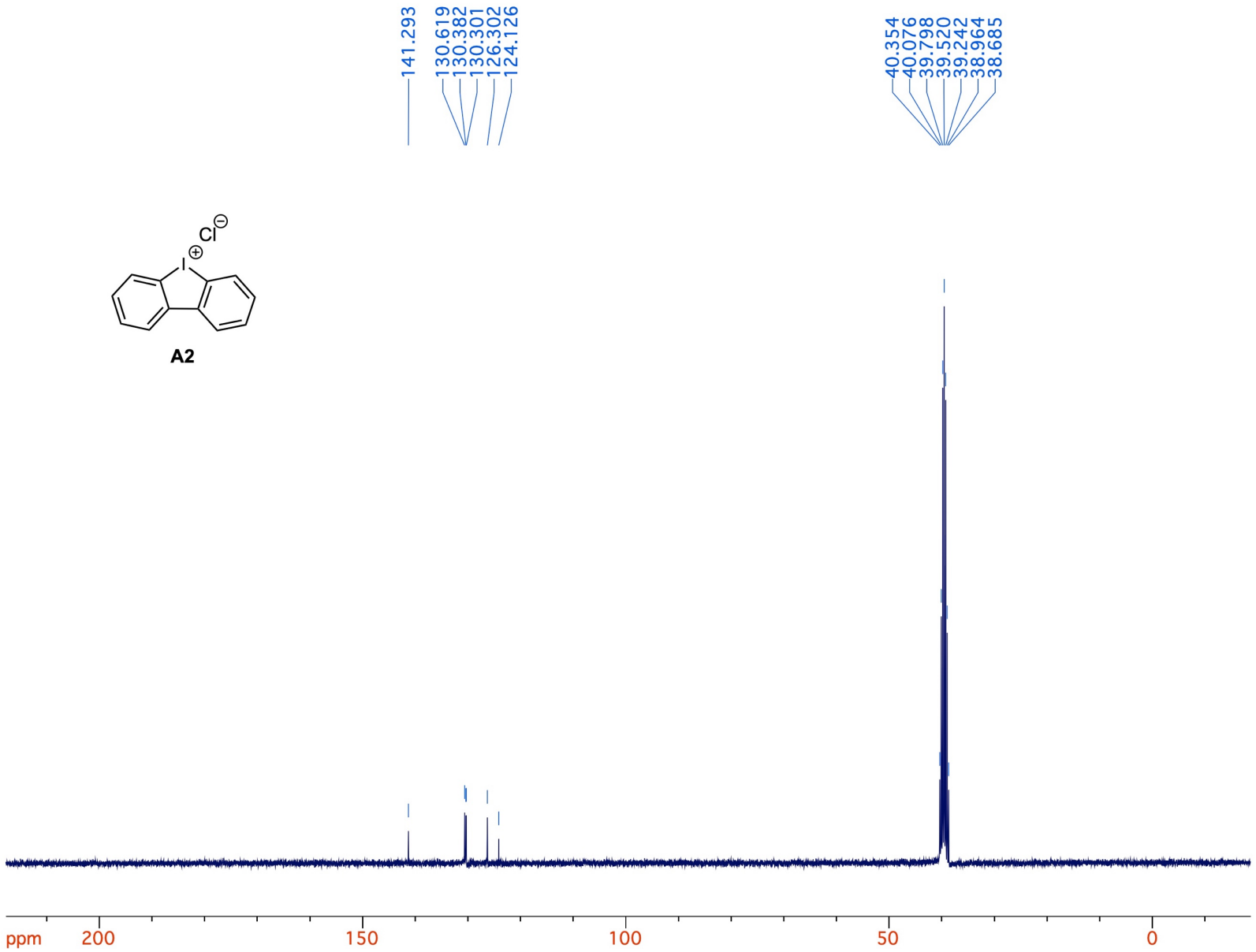
References:

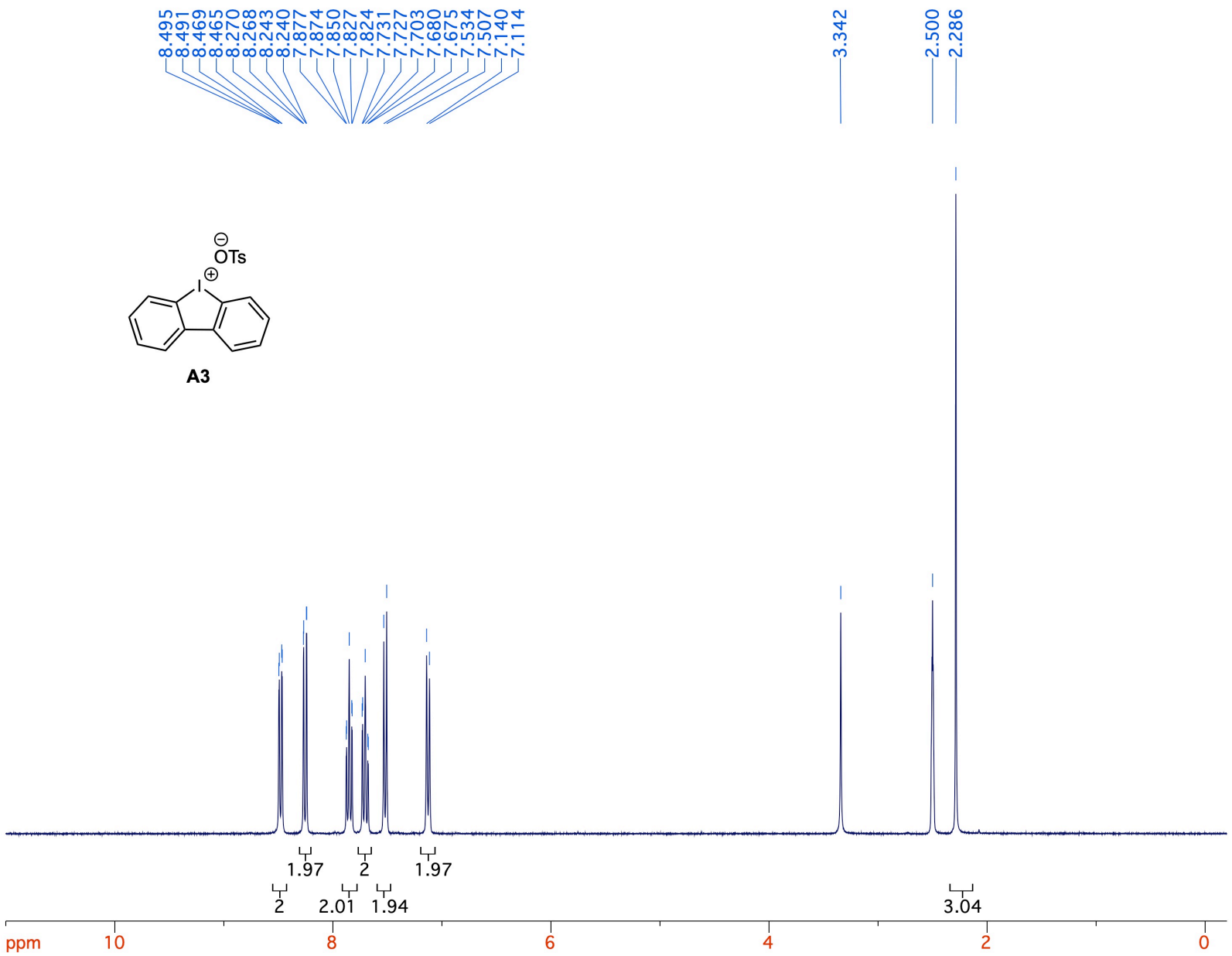
[1] A. F. Burchat, J. M. Chong, N. Nielsen, *J. Organomet. Chem.* **1997**, *542*, 281-283.
[2] D. Zhu, Q. Liu, B. Luo, M. Chen, R. Pi, P. Huang, S. Wen, *Adv. Synth. Catal.* **2013**, *355*, 2172-2178.
[3] W. P. Hong, A. V. Iosub, S. S. Stahl, *J. Am. Chem. Soc.* **2013**, *135*, 13664-13667.
[4] C. Poriel, Y. Ferrand, S. Juillard, P. Le Maux, G. Simonneaux, *Tetrahedron* **2004**, *60*, 145-158.
[5] P. S. Postnikov, O. A. Guselnikova, M. S. Yusubov, A. Yoshimura, V. N. Nemykin, V. V. Zhdankin, *J. Org. Chem.* **2015**, *80*, 5783-5788.
[6] M. Elsherbini, W. J. Moran, *Org. Biomol. Chem.* **2021**, *19*, 4706-4711.
[7] F. Heinen, E. Engelage, C. J. Cramer, S. M. Huber, *J. Am. Chem. Soc.* **2020**, *142*, 8633-8640.
[8] T. Pirali, F. Zhang, A. H. Miller, J. L. Head, D. McAusland, M. F. Greaney, *Angew. Chem. Int. Ed.* **2012**, *51*, 1006-1009.
[9] C. D. Zhu, D. Wang, D. Y. Wang, Y. Zhao, W. Y. Sun, Z. Z. Shi, *Angew. Chem. Int. Ed.* **2018**, *57*, 8848-8853.
[10] A. A. Ageshina, G. A. Chesnokov, M. A. Topchiy, I. V. Alabugin, M. S. Nechaev, A. F. Asachenko, *Org. Biomol. Chem.* **2019**, *17*, 4523-4534.
[11] T. Morack, C. Mück-Lichtenfeld, R. Gilmour, *Angew. Chem. Int. Ed.* **2019**, *58*, 1208-1212.
[12] M. Frigerio, M. Santagostino, S. Sputore, *J. Org. Chem.* **1999**, *64*, 4537-4538.
[13] G. X. Liang, S. N. Gradl, D. Trauner, *Org. Lett.* **2003**, *5*, 4931-4934.
[14] F. De Simone, J. Andrès, R. Torosantucci, J. Waser, *Org. Lett.* **2009**, *11*, 1023-1026.
[15] T. Maji, A. Karmakar, O. Reiser, *J. Org. Chem.* **2011**, *76*, 736-739.
[16] J. Wang, C. Liu, J. Yuan, A. Lei, *Angew. Chem. Int. Ed.* **2013**, *52*, 2256-2259.
[17] C. E. Diaz-Uribe, W. Vallejo, W. Castellar, J. Trilleras, S. Ortiz, A. Rodriguez-Serrano, X. Zarate, J. Quiroga, *Rsc Adv.* **2015**, *5*, 71565-71572.
[18] S. Son, G. C. Fu, *J. Am. Chem. Soc.* **2007**, *129*, 1046-1047.
[19] M. Fujiwara, M. Kawatsura, S. Hayase, M. Nanjo, T. Itoh, *Adv. Synth. Catal.* **2009**, *351*, 123-128.
[20] J. Z. Hamilton, N. T. Kadunce, M. D. McDonald, L. Rios, A. R. Matlin, *Tetrahedron Lett.* **2015**, *56*, 6622-6624.
[21] F. Richter, H.-H. Otto, *Liebigs Ann. Chem.* **1990**, *1990*, 7-14.
[22] A. Iwata, H. Tang, A. Kunai, J. Ohshita, Y. Yamamoto, C. Matui, *J. Org. Chem.* **2002**, *67*, 5170-5175.
[23] S. Silwal, R. J. Rahaim, *J. Org. Chem.* **2014**, *79*, 8469-8476.
[24] M. Tejeda-Serrano, S. Sanz-Navarro, F. Blake, A. Leyva-Pérez, *Synthesis* **2020**, *52*, 2031-2037.
[25] C. D. L. Baker, J. Fawcett, C. D. Insley, D. S. Messenger, C. L. Newland, H. L. Overend, A. B. Patel, M. Shah, B. Vara, D. Virdee, B. J. Rawlings, *Chem. Commun.* **2005**, 1883-1885.
[26] M. Vogler, L. Süsse, J. H. W. LaFortune, D. W. Stephan, M. Oestreich, *Organometallics* **2018**, *37*, 3303-3313.
[27] K. Murugan, S. Srimurugan, C. Chen, *Chem. Commun.* **2010**, *46*, 1127-1129.
[28] Y.-K. Wu, F. G. West, *J. Org. Chem.* **2010**, *75*, 5410-5413.
[29] N. Paul, S. Kaladevi, A. J. Beneto, S. Muthusubramanian, N. Bhuvanesh, *Tetrahedron* **2012**, *68*, 6892-6901.
[30] Y. Kwon, R. McDonald, F. G. West, *Angew. Chem. Int. Ed.* **2013**, *52*, 8616-8619.

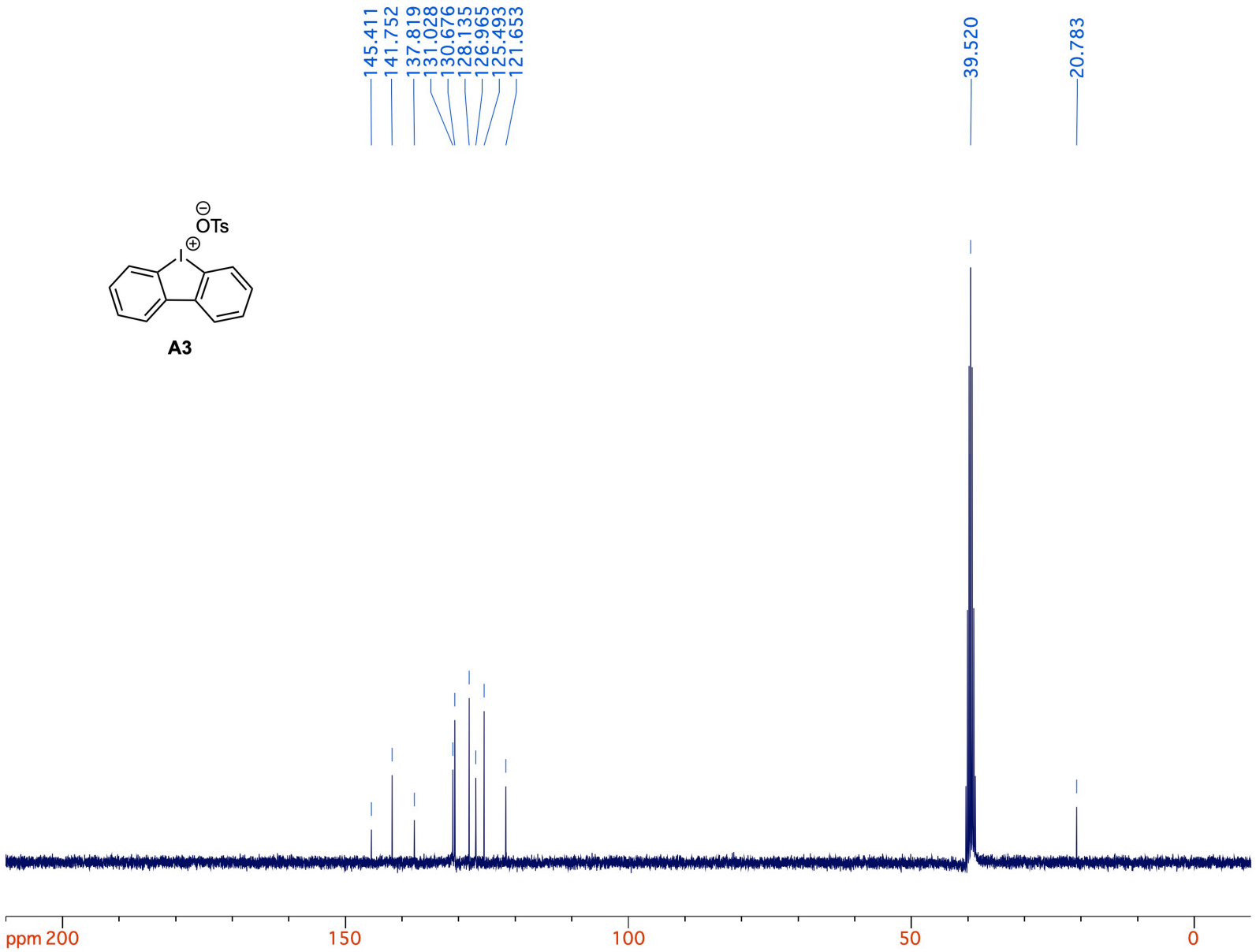

8.466
8.462
8.440
8.435
8.214
8.211
8.187
8.184
7.866
7.862
7.841
7.838
7.815
7.812
7.729
7.724
7.704
7.701
7.697
7.677
7.672
3.362
2.500
OTf
I
A1
ppm
10
8
6
4
2
0

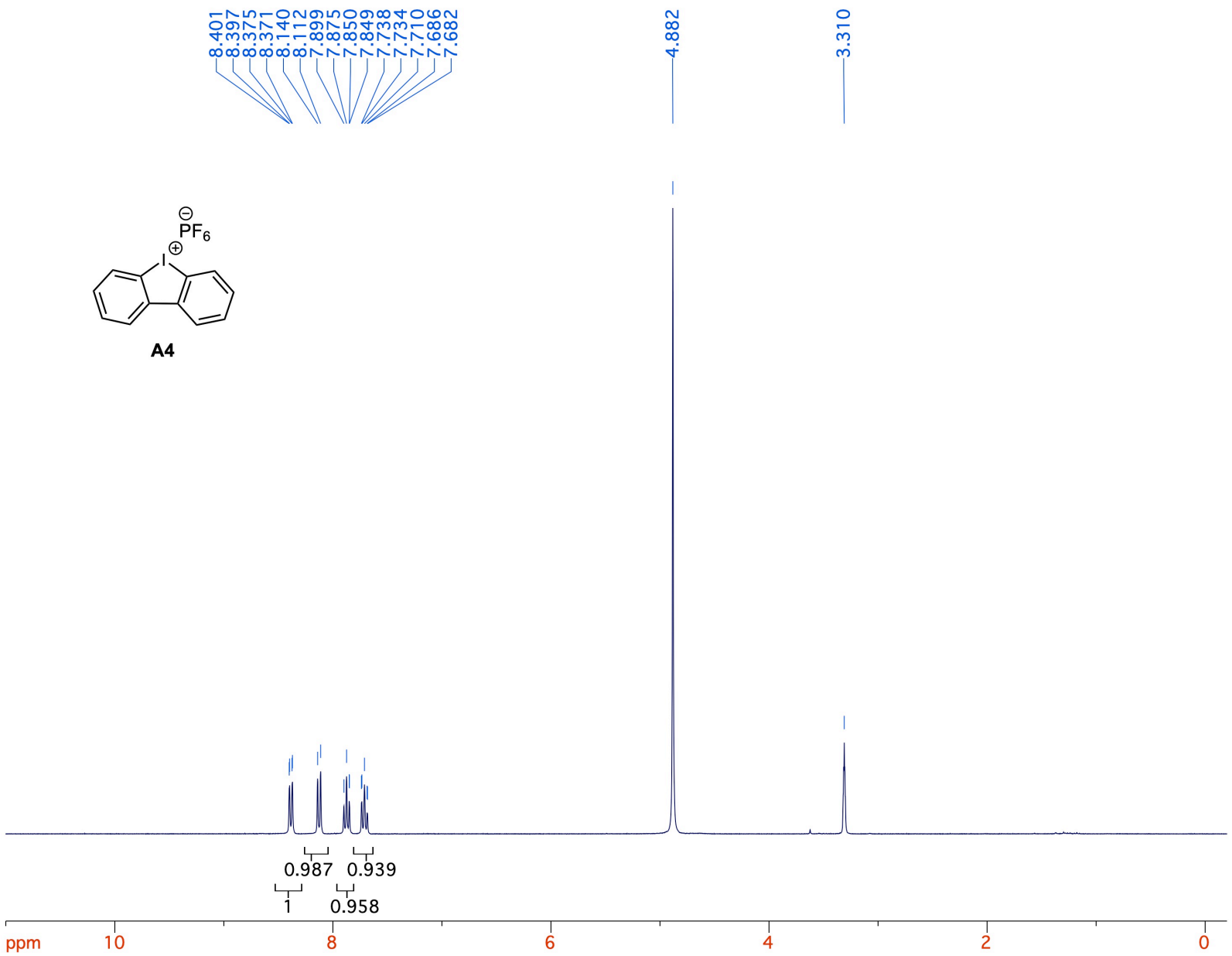

141.711
131.097
130.709
130.577
126.989
121.584
39.520
OTf
A1
ppm 200
150
100
50
0

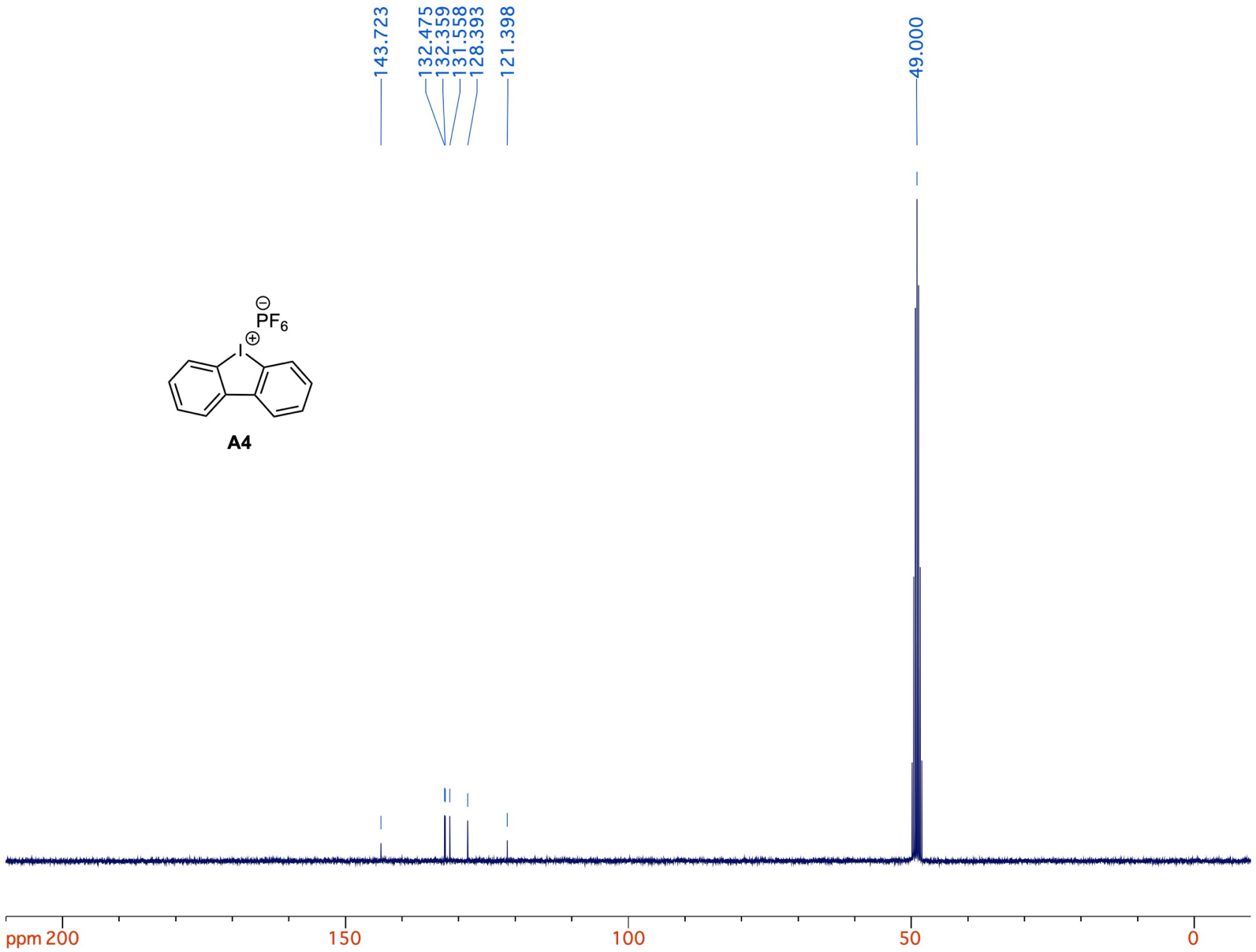

8.579
8.554
8.441
8.438
8.415
8.412
7.830
7.827
7.804
7.780
7.778
7.687
7.684
7.660
7.636
7.633
3.328
2.500
Cl
I
A2
2
2
2.04
2.06
ppm
10
8
6
4
2
0

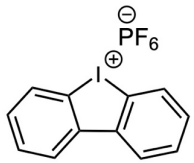

141.293
130.619
130.382
130.301
126.302
124.126
40.354
40.076
39.798
39.520
39.242
38.964
38.685
Cl
I
A2
ppm
200
150
100
50
0


8.495
8.491
8.469
8.465
8.270
8.268
8.243
8.240
7.877
7.874
7.850
7.827
7.824
7.731
7.727
7.703
7.680
7.675
7.534
7.507
7.140
7.114
3.342
2.500
2.286
OTs
A3
1.97
2
1.97
2
2.01
1.94
3.04
ppm
10
8
6
4
2
0

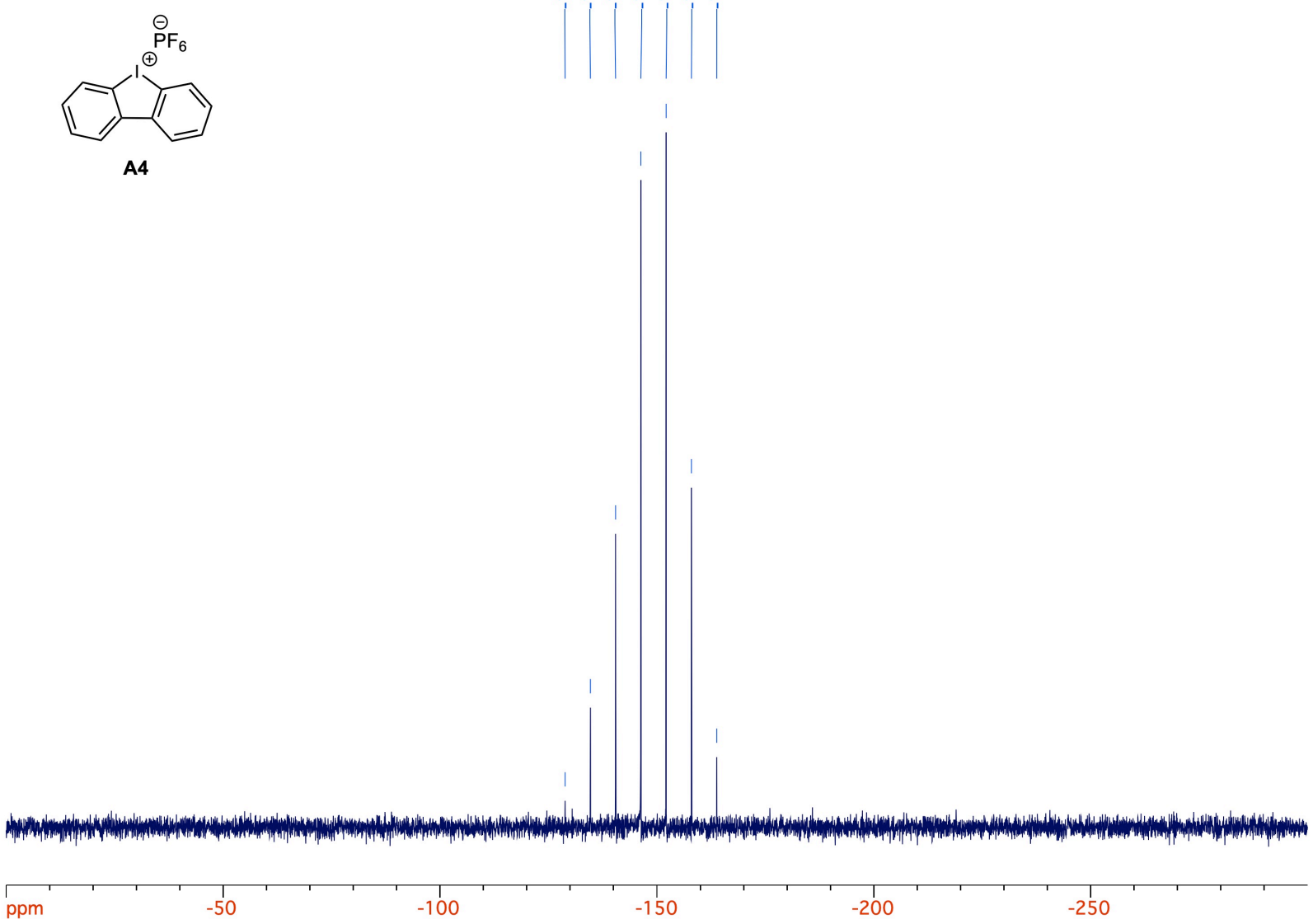

145.411
141.752
137.819
131.028
130.676
128.135
126.965
125.493
121.653
39.520
20.783
OTs
I
A3
ppm 200
150
100
50
0

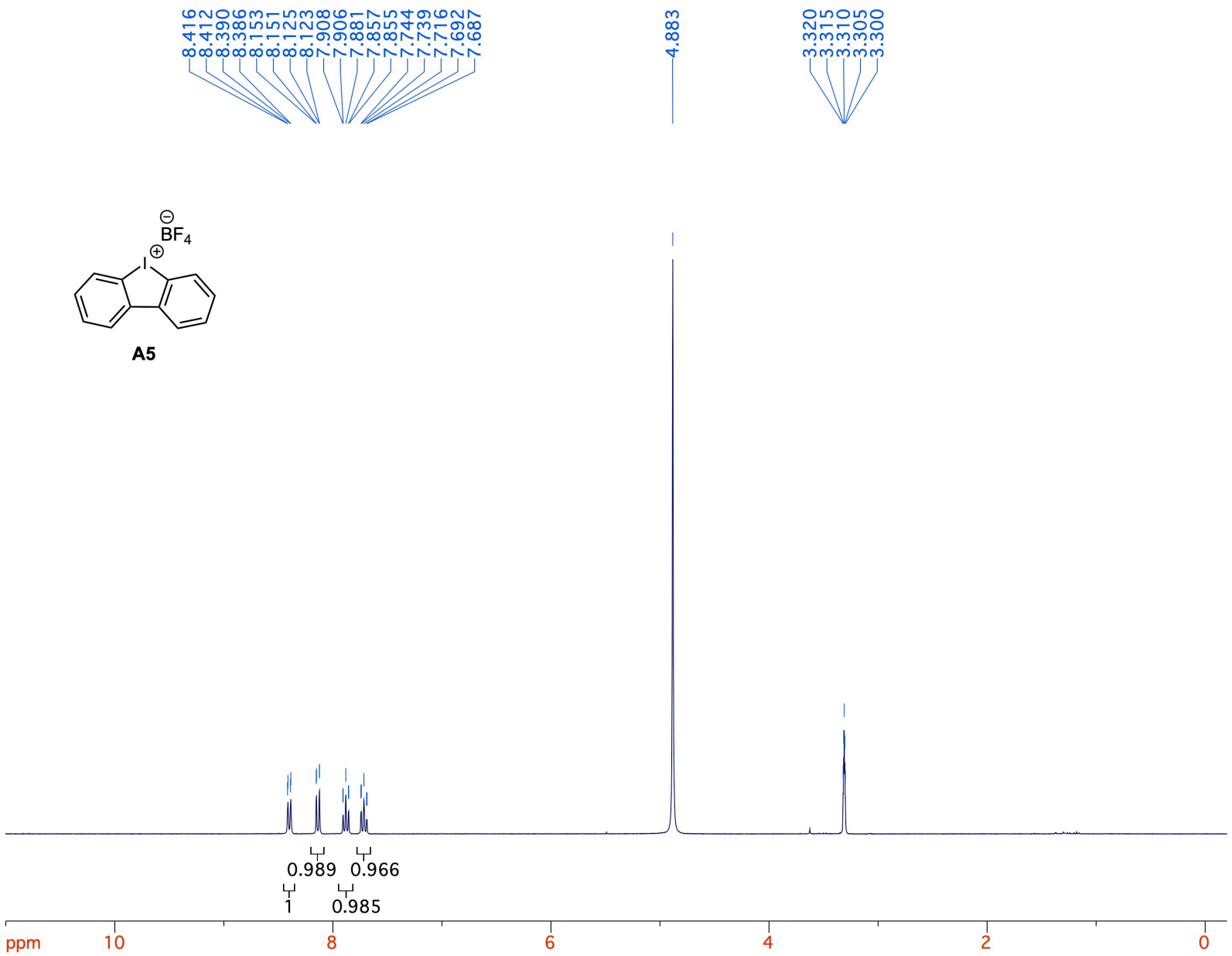

8.401
8.397
8.375
8.371
8.140
8.112
7.899
7.875
7.850
7.849
7.738
7.734
7.710
7.686
7.682
4.882
3.310
PF6
A4
0.987
0.939
1
0.958
ppm
10
8
6
4
2
0

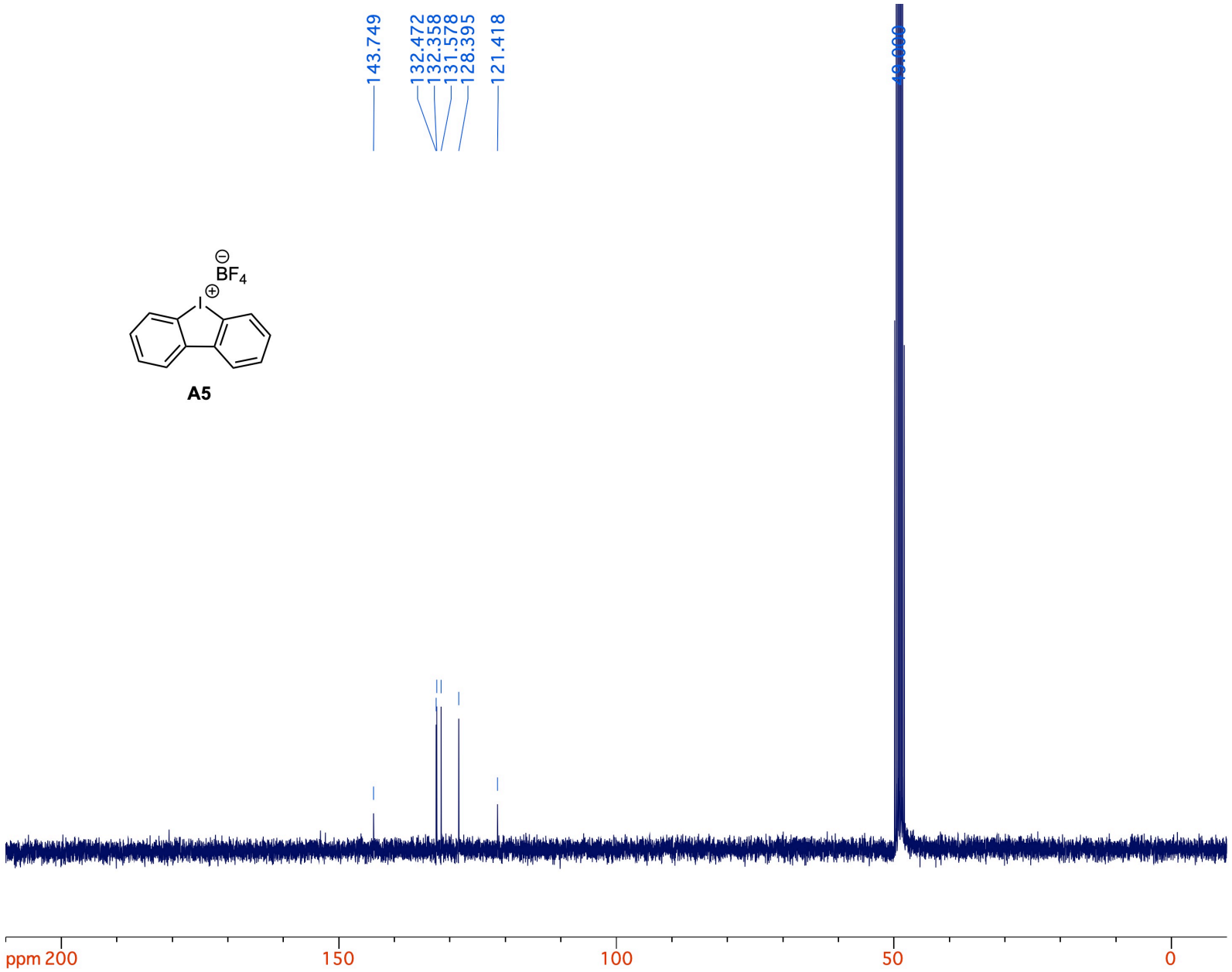

143.723
132.475
132.359
131.558
128.393
121.398
49.000
PF6
A4
ppm 200
150
100
50
0

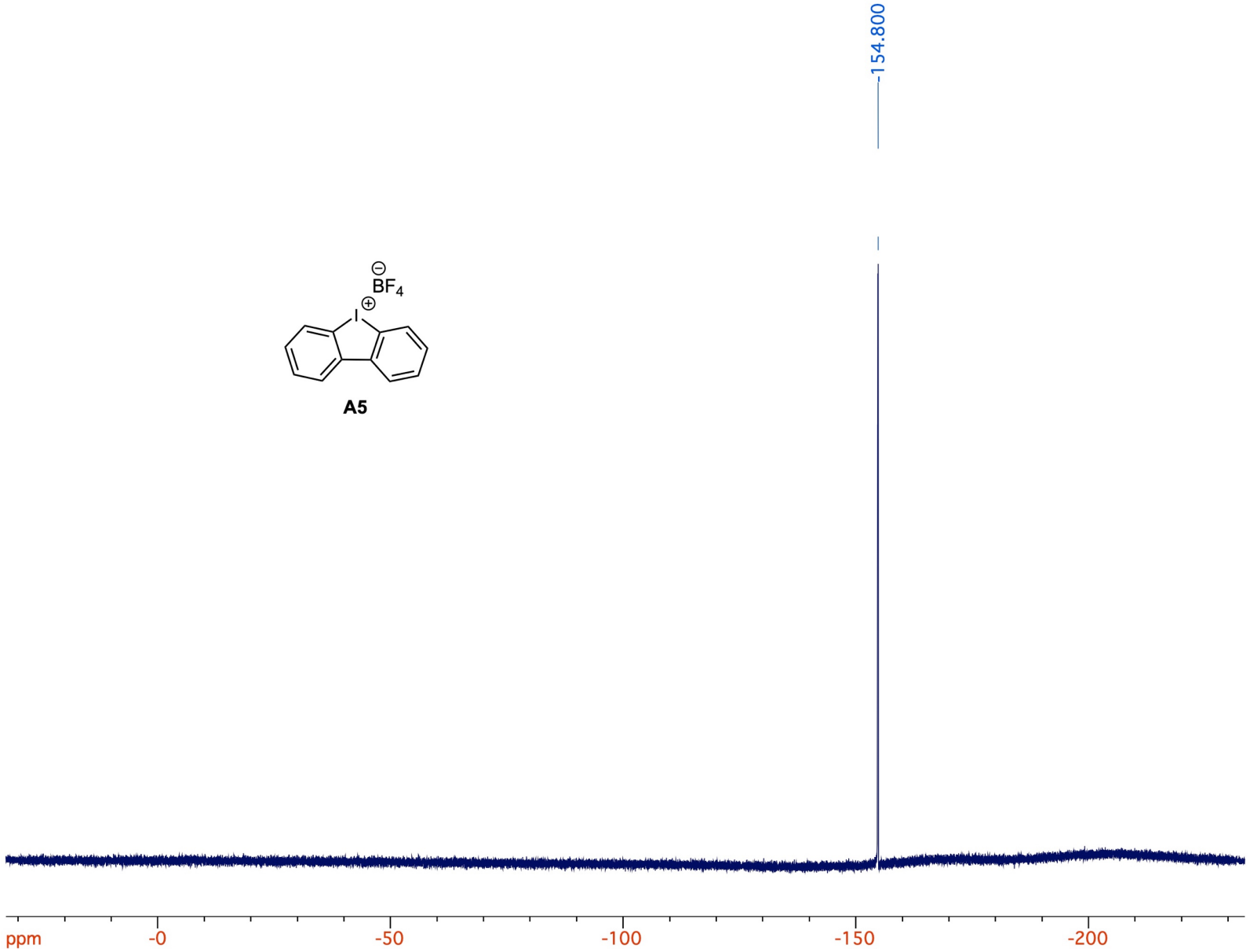


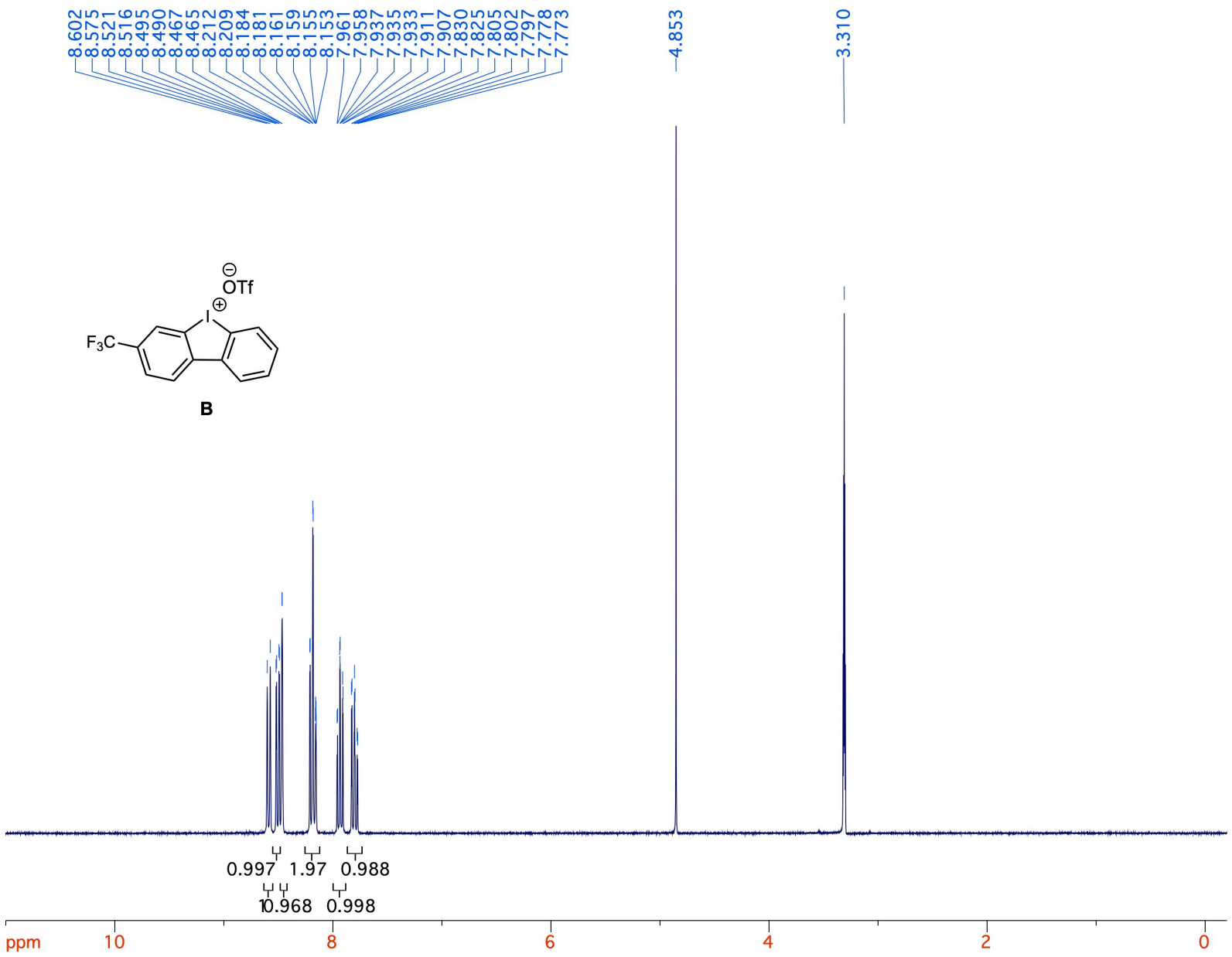
A4

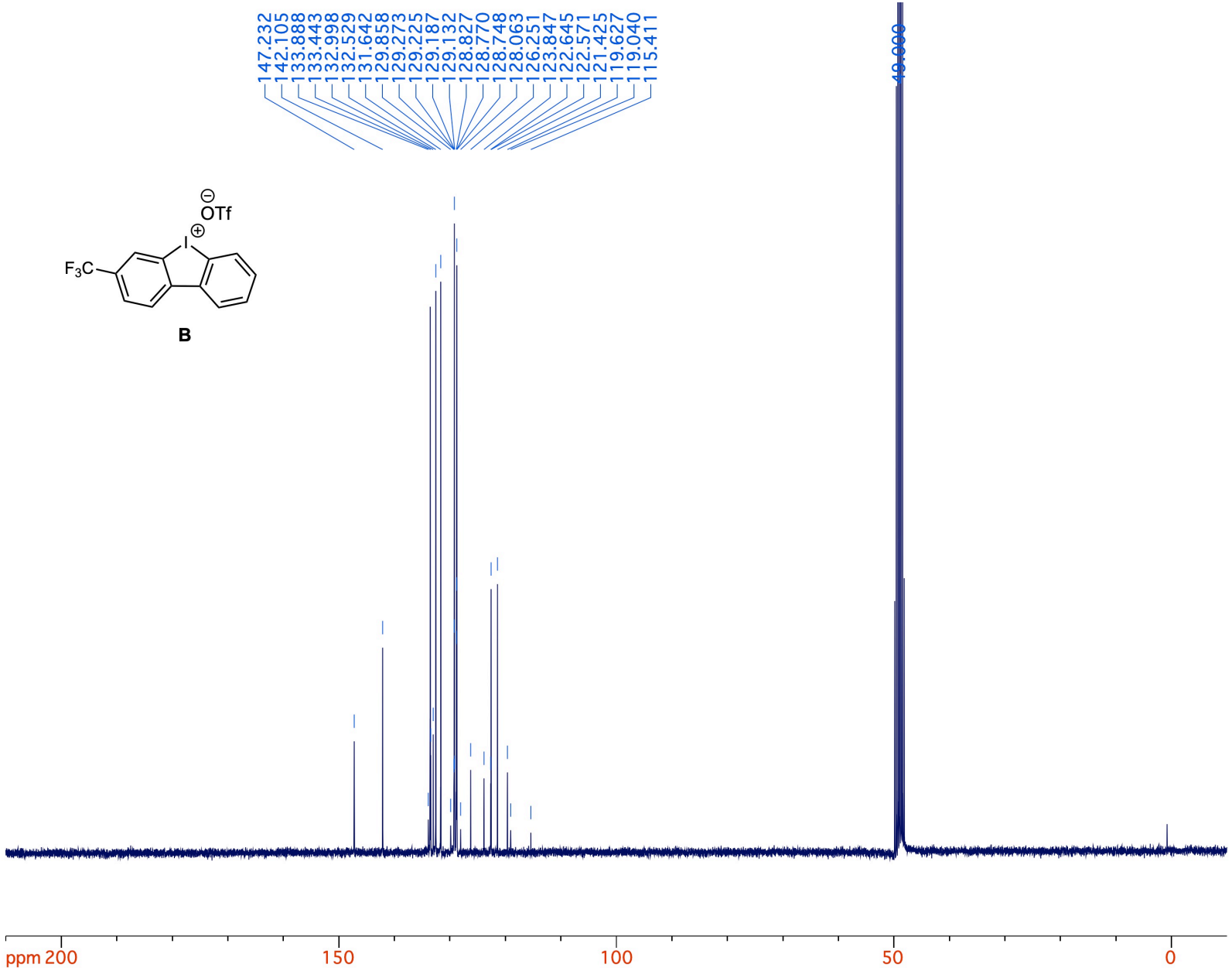

128.846
134.674
140.475
146.300
152.129
157.959
163.790
PF6
A4
ppm
-50
-100
-150
-200
-250

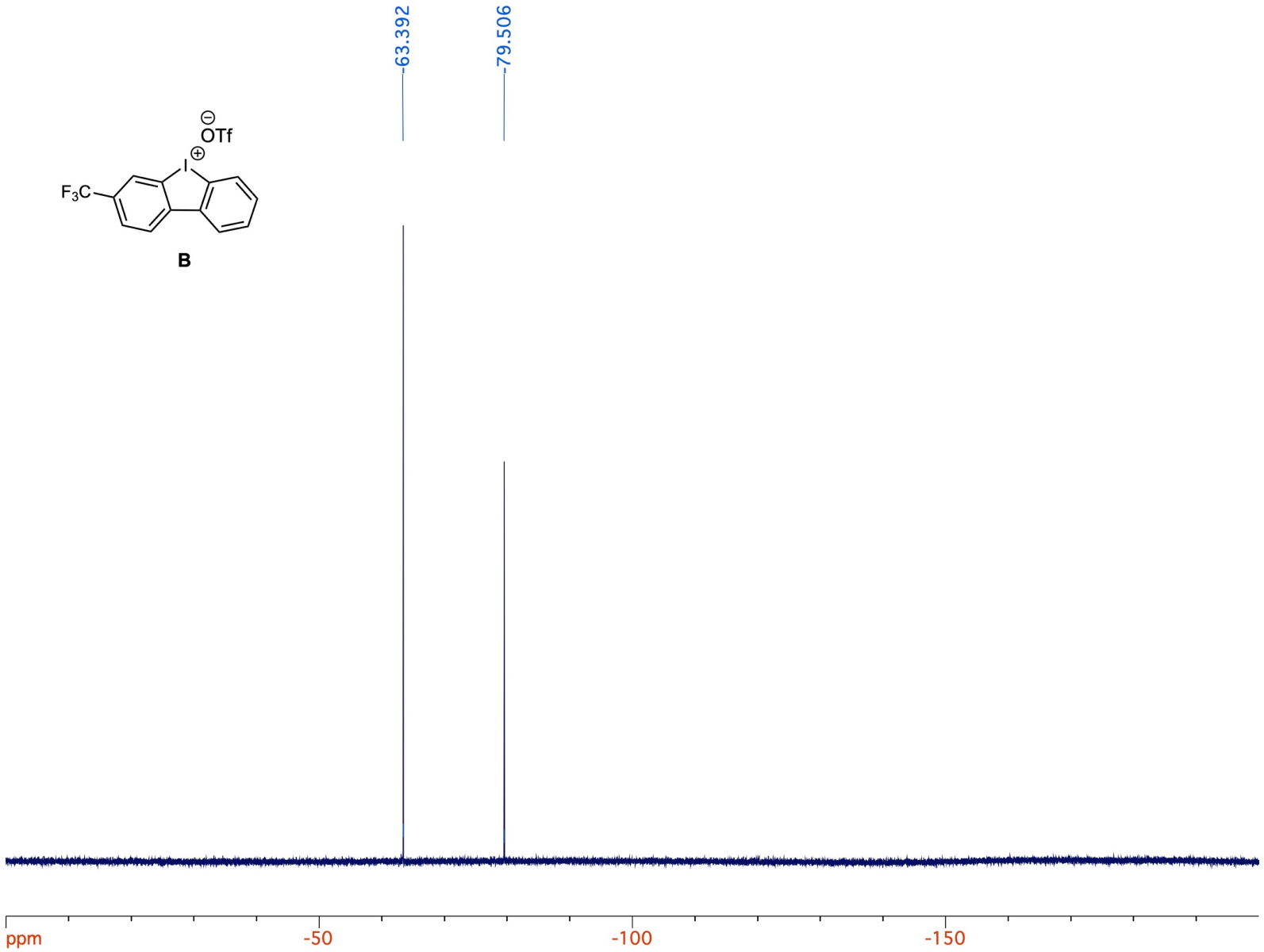

8.416
8.412
8.390
8.386
8.153
8.151
8.125
8.123
7.908
7.906
7.881
7.857
7.855
7.744
7.739
7.716
7.692
7.687
4.883
3.320
3.315
3.310
3.305
3.300
BF4
A5
0.989
0.966
1
0.985
ppm
10
8
6
4
2
0

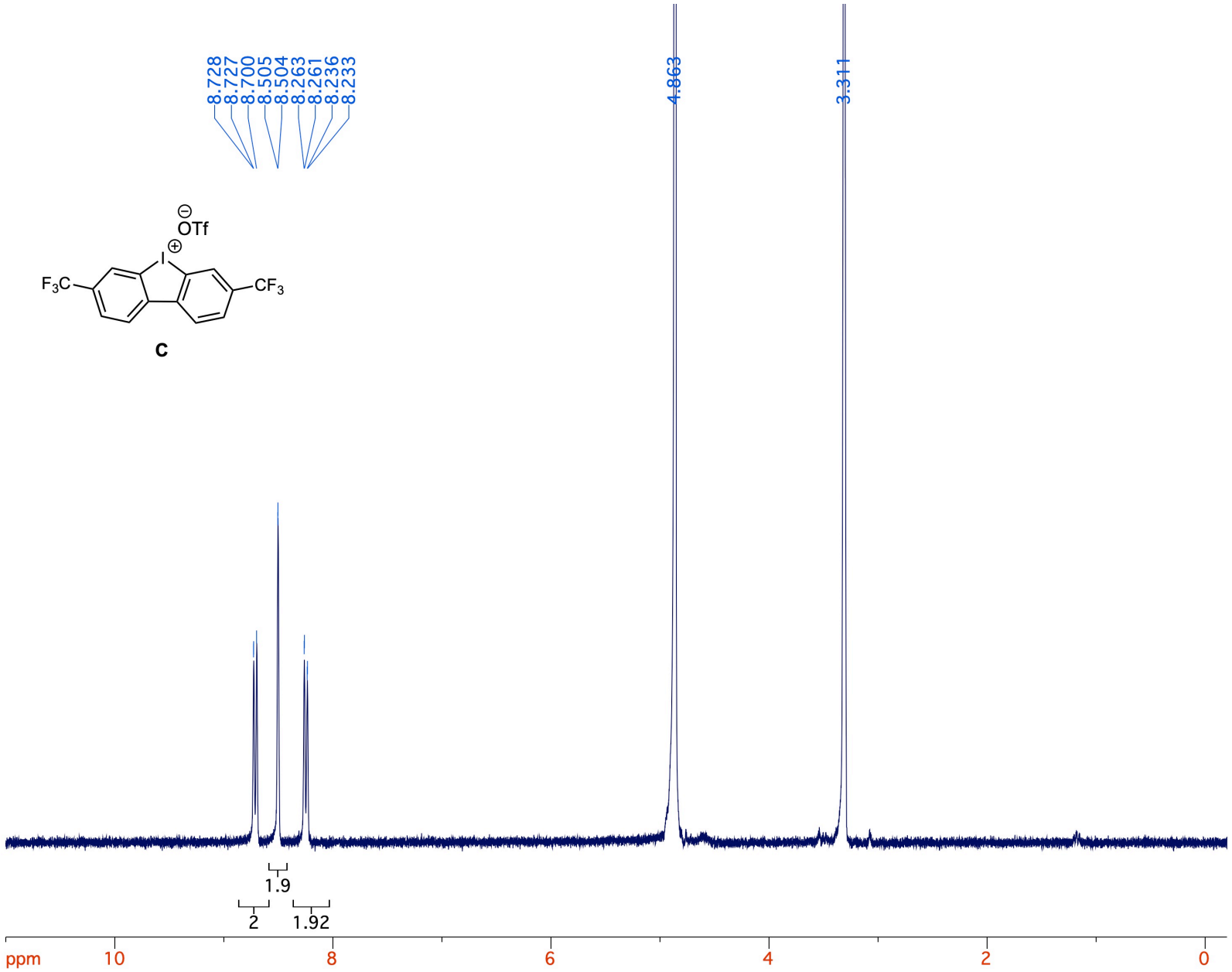

143.749
132.472
132.358
131.578
128.395
121.418
49.000
BF4
A5
ppm 200
150
100
50
0

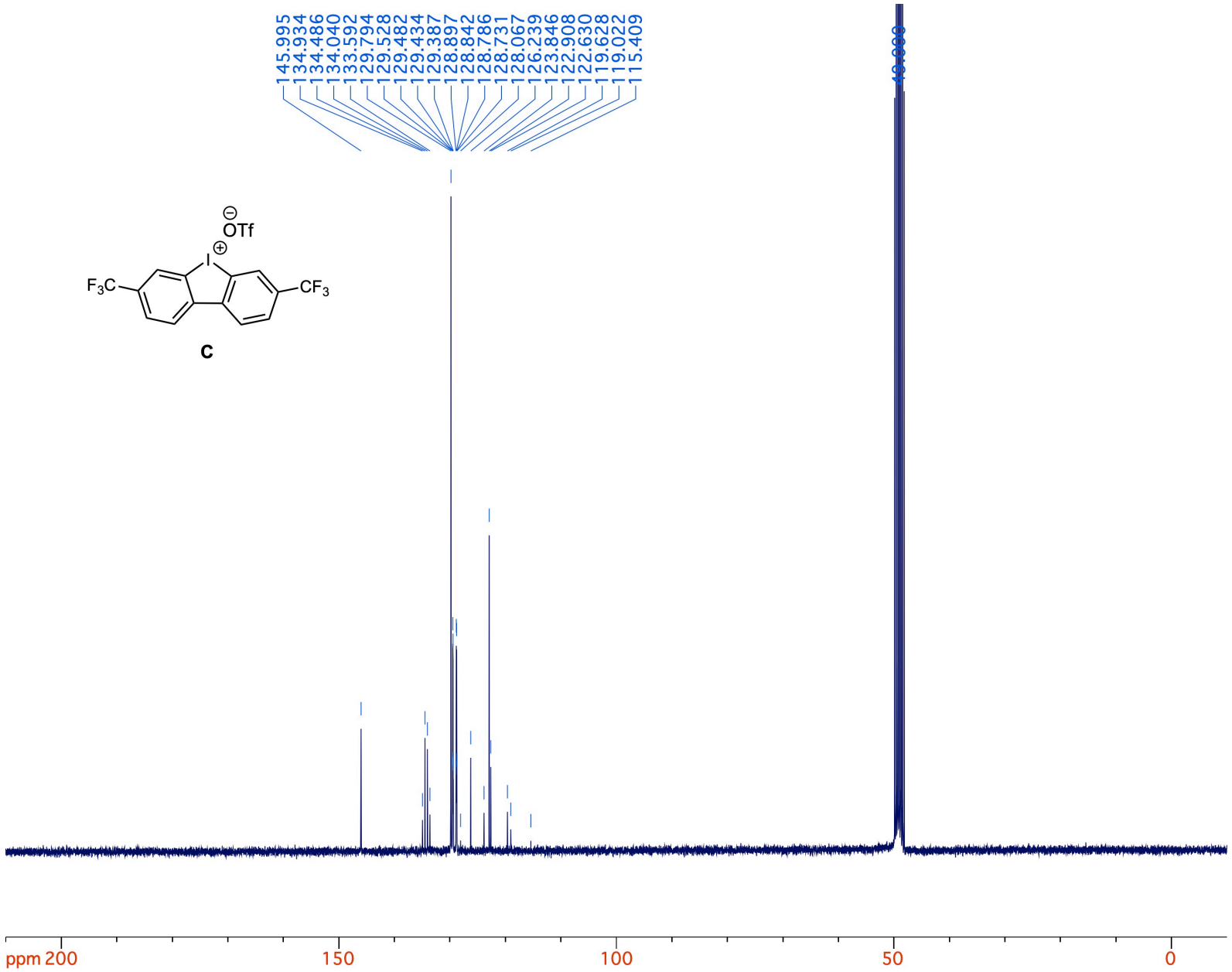

-154.800
BF4
A5
ppm
-0
-50
-100
-150
-200

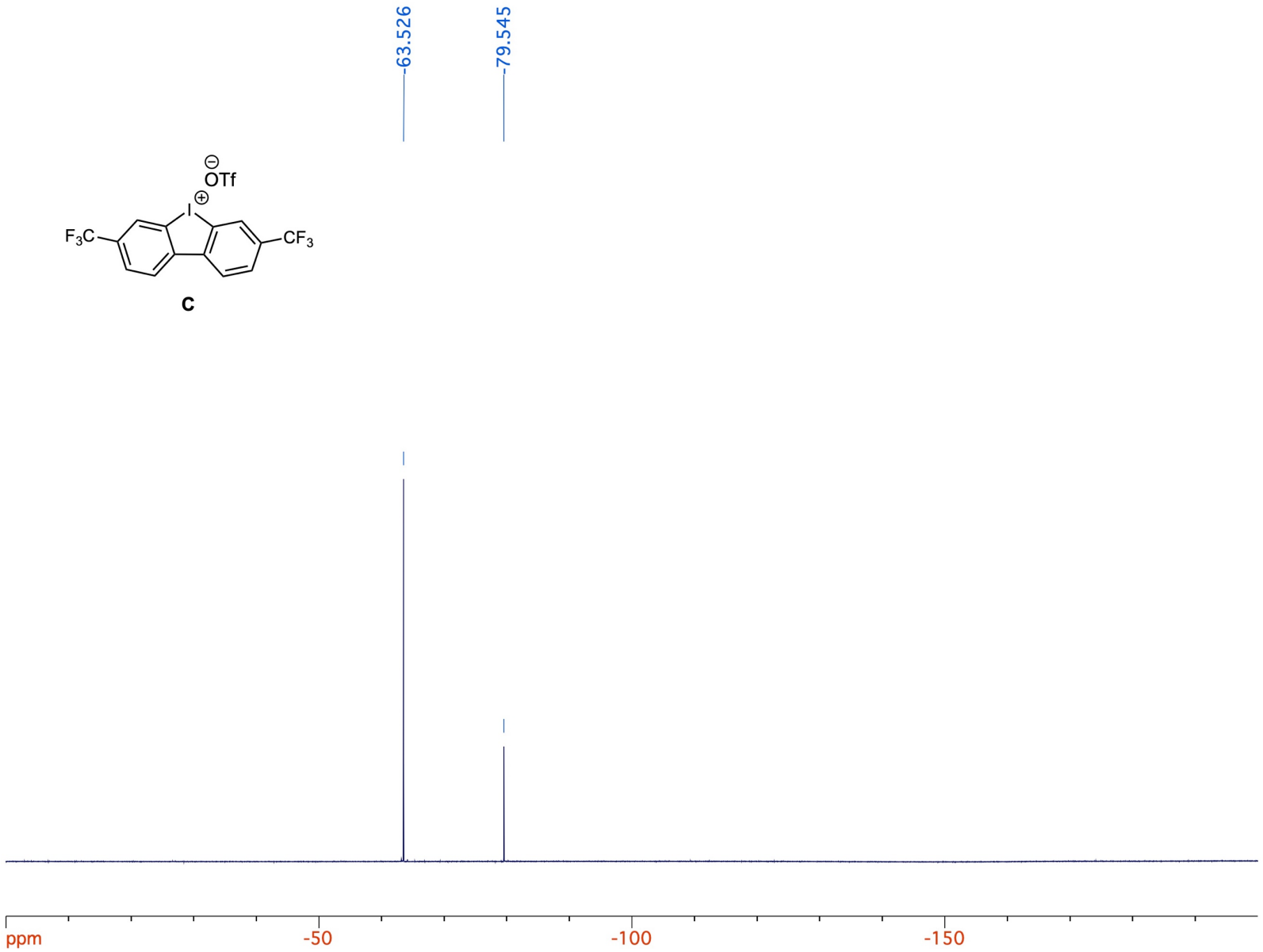

8.602
8.575
8.521
8.516
8.495
8.490
8.467
8.465
8.212
8.209
8.184
8.181
8.161
8.159
8.155
8.153
7.961
7.958
7.937
7.935
7.933
7.911
7.907
7.830
7.825
7.805
7.802
7.797
7.778
7.773
4.853
3.310
OTf
I
F3C
B
0.997
1.97
0.988
1
0.968
0.998
ppm
10
8
6
4
2
0

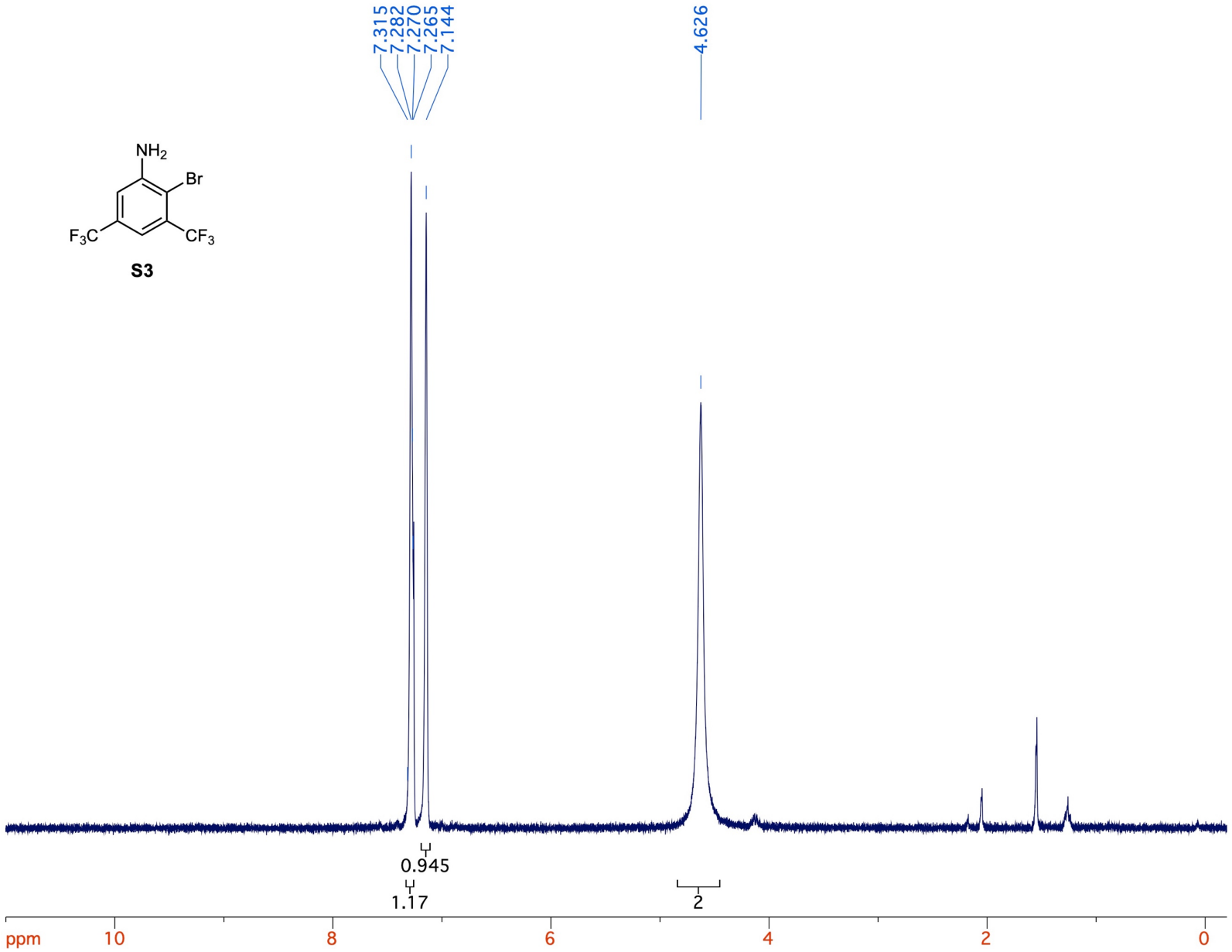

147.232
142.105
133.888
133.443
132.998
132.529
131.642
129.858
129.273
129.225
129.187
129.132
128.827
128.770
128.748
128.063
126.251
123.847
122.645
122.571
121.425
119.627
119.040
115.411
49.000
OTf
I
F3C
B
ppm 200
150
100
50
0

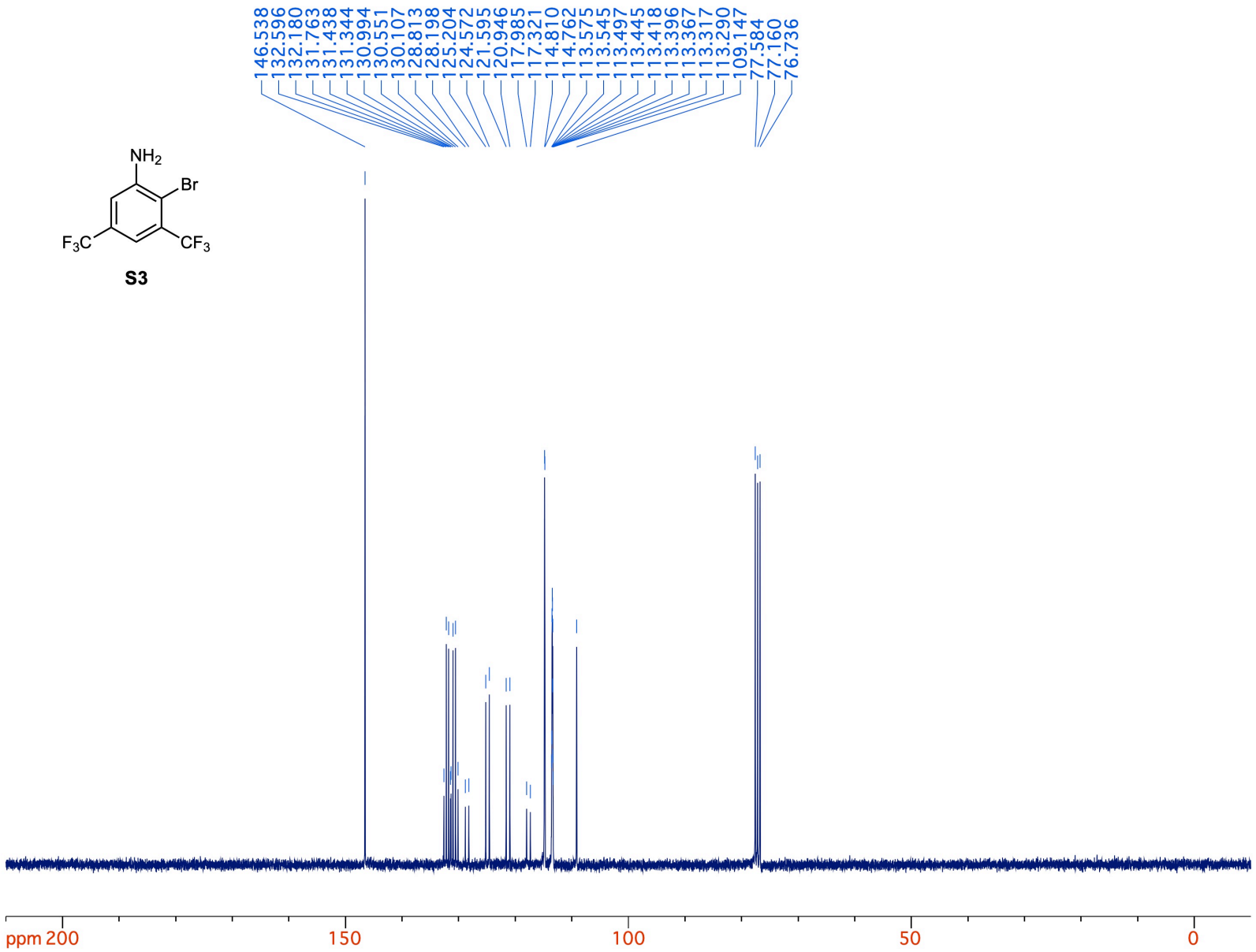

63.392
79.506
OTf
F3C
B
ppm
-50
-100
-150

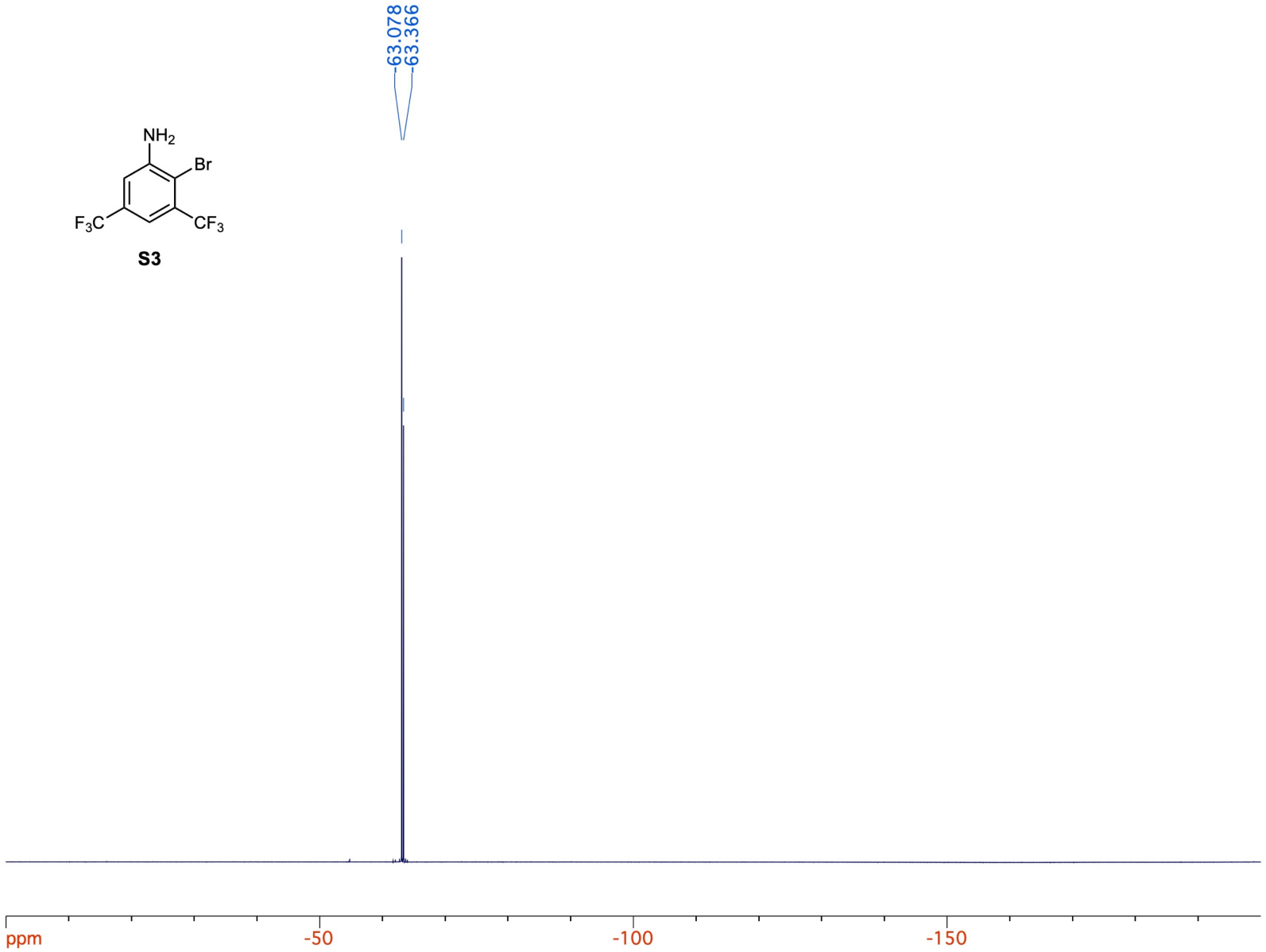

8.728
8.727
8.700
8.505
8.504
8.263
8.261
8.236
8.233
4.863
3.311
OTf
F3C
CF3
c
1.9
2
1.92
ppm
10
8
6
4
2
0

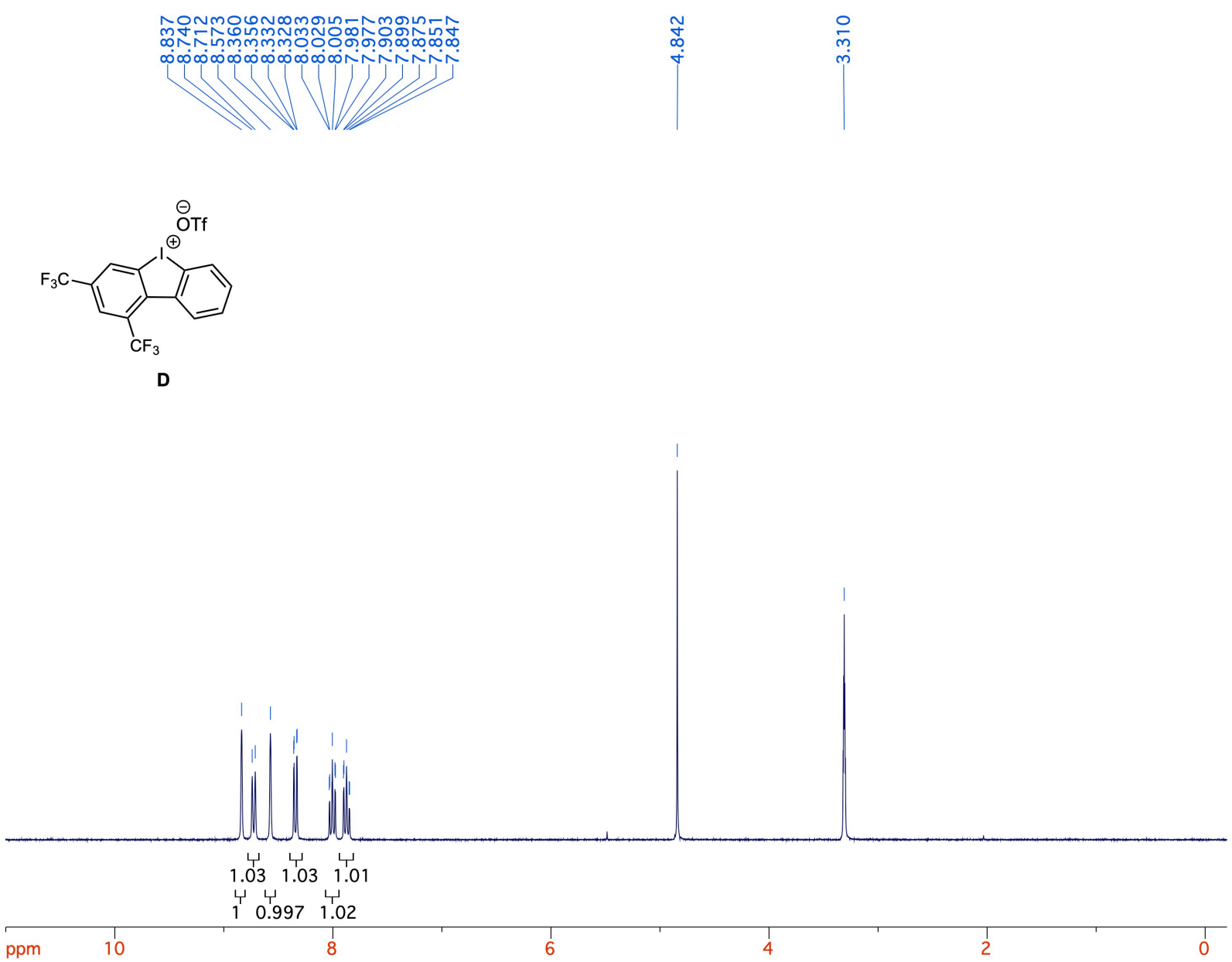

145.995
134.934
134.486
134.040
133.592
129.794
129.528
129.482
129.434
129.387
128.897
128.842
128.786
128.731
128.067
126.239
123.846
122.908
122.630
119.628
119.022
115.409
49.000
OTf
F3C
CF3
C
ppm 200
150
100
50
0


63.526
79.545
OTf
I
F3C
CF3
c
ppm
-50
-100
-150

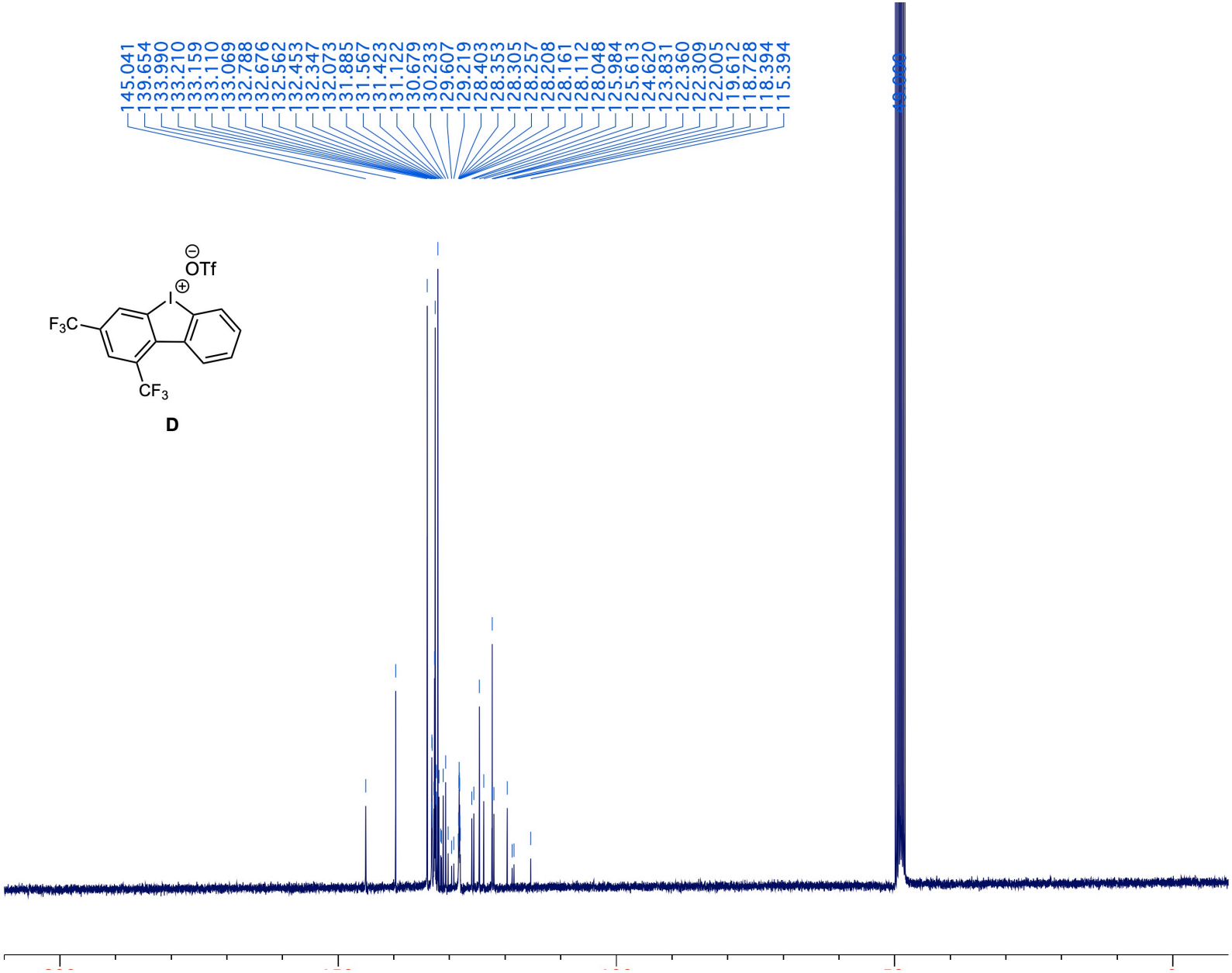

7.315
7.282
7.270
7.265
7.144
4.626
NH2
Br
F3C
CF3
S3
0.945
1.17
2
ppm
10
8
6
4
2
0


146.538
132.596
132.180
131.763
131.438
131.344
130.994
130.551
130.107
128.813
128.198
125.204
124.572
121.595
120.946
117.985
117.321
114.810
114.762
113.575
113.545
113.497
113.445
113.418
113.396
113.367
113.317
113.290
109.147
77.584
77.160
76.736
NH2
Br
F3C
CF3
S3
ppm 200
150
100
50
0

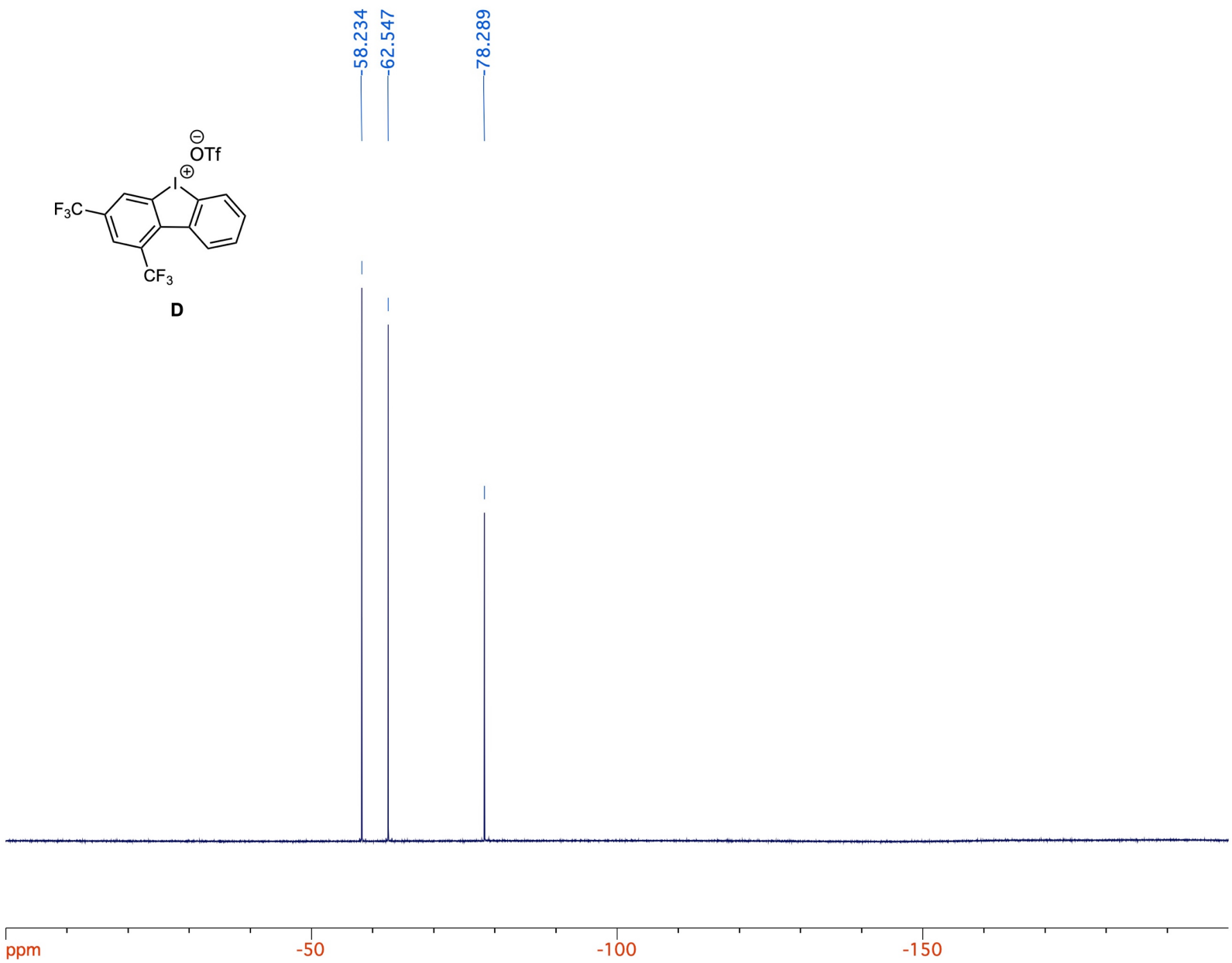

63.078
63.366
NH2
Br
F3C
CF3
S3
ppm
-50
-100
-150

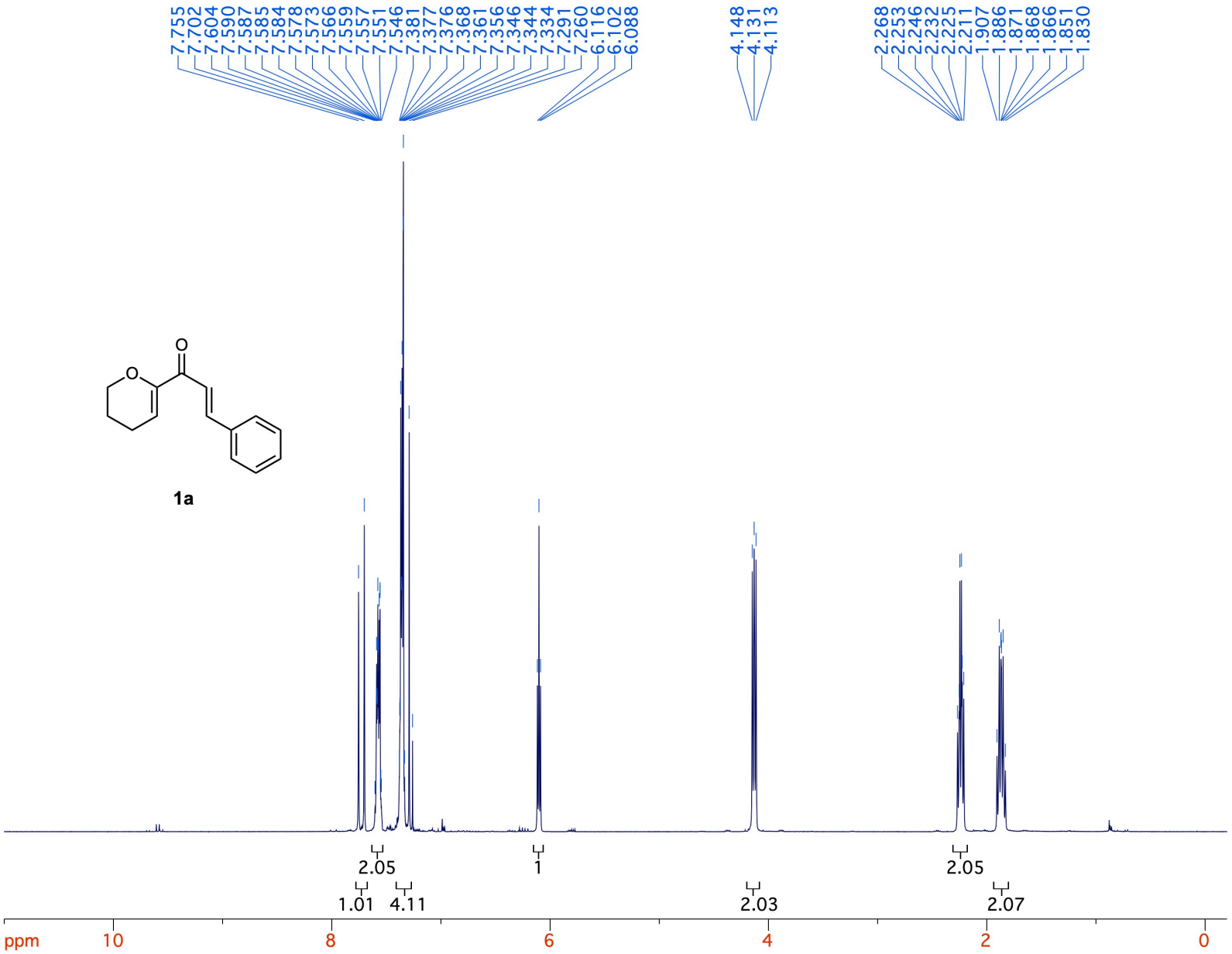

8.837
8.740
8.712
8.573
8.360
8.356
8.332
8.328
8.033
8.029
8.005
7.981
7.977
7.903
7.899
7.875
7.851
7.847
4.842
3.310
OTf
I
F3C
CF3
1.03
1.03
1.01
1
0.997
1.02
ppm
10
8
6
4
2
0

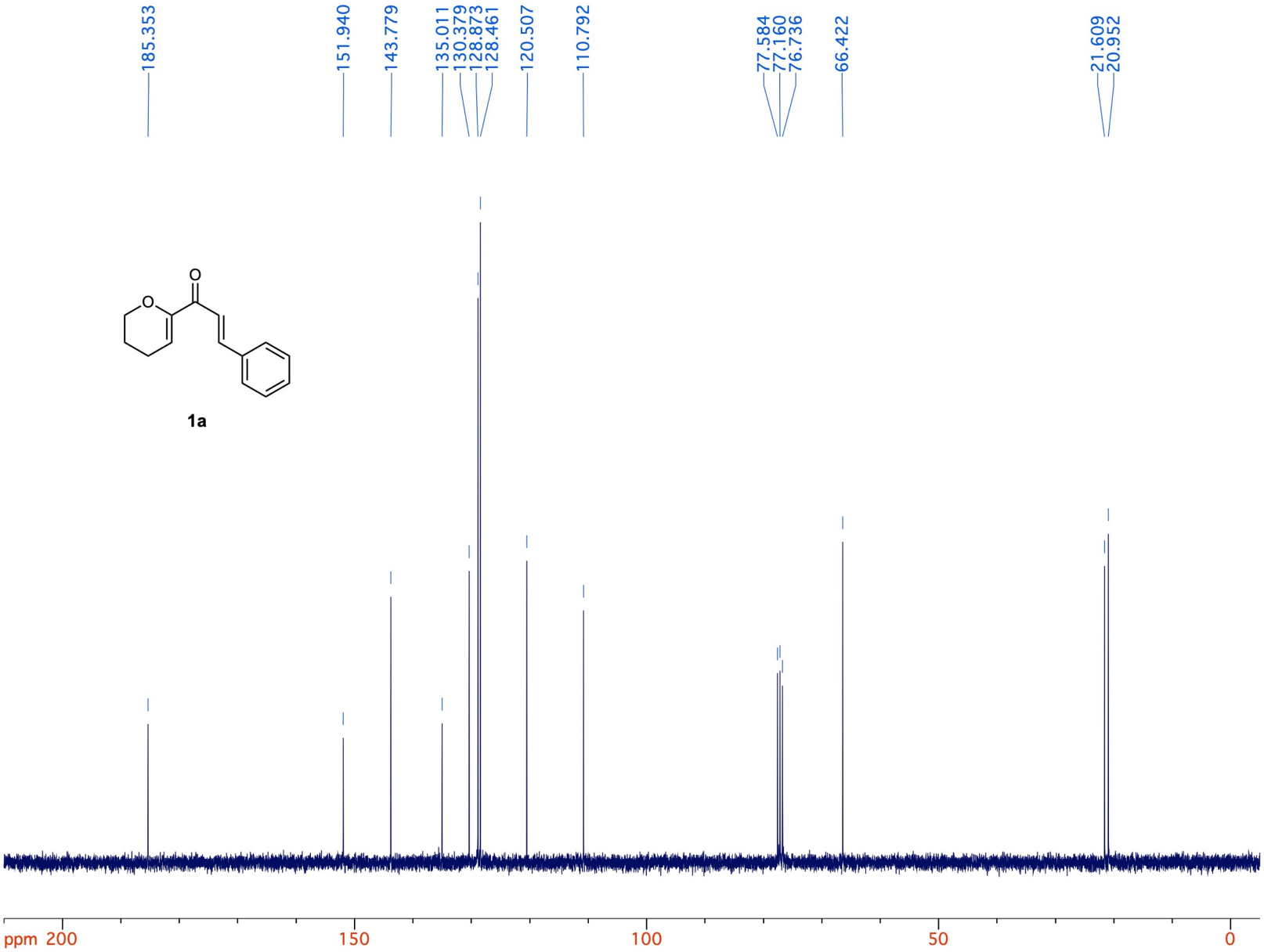
D

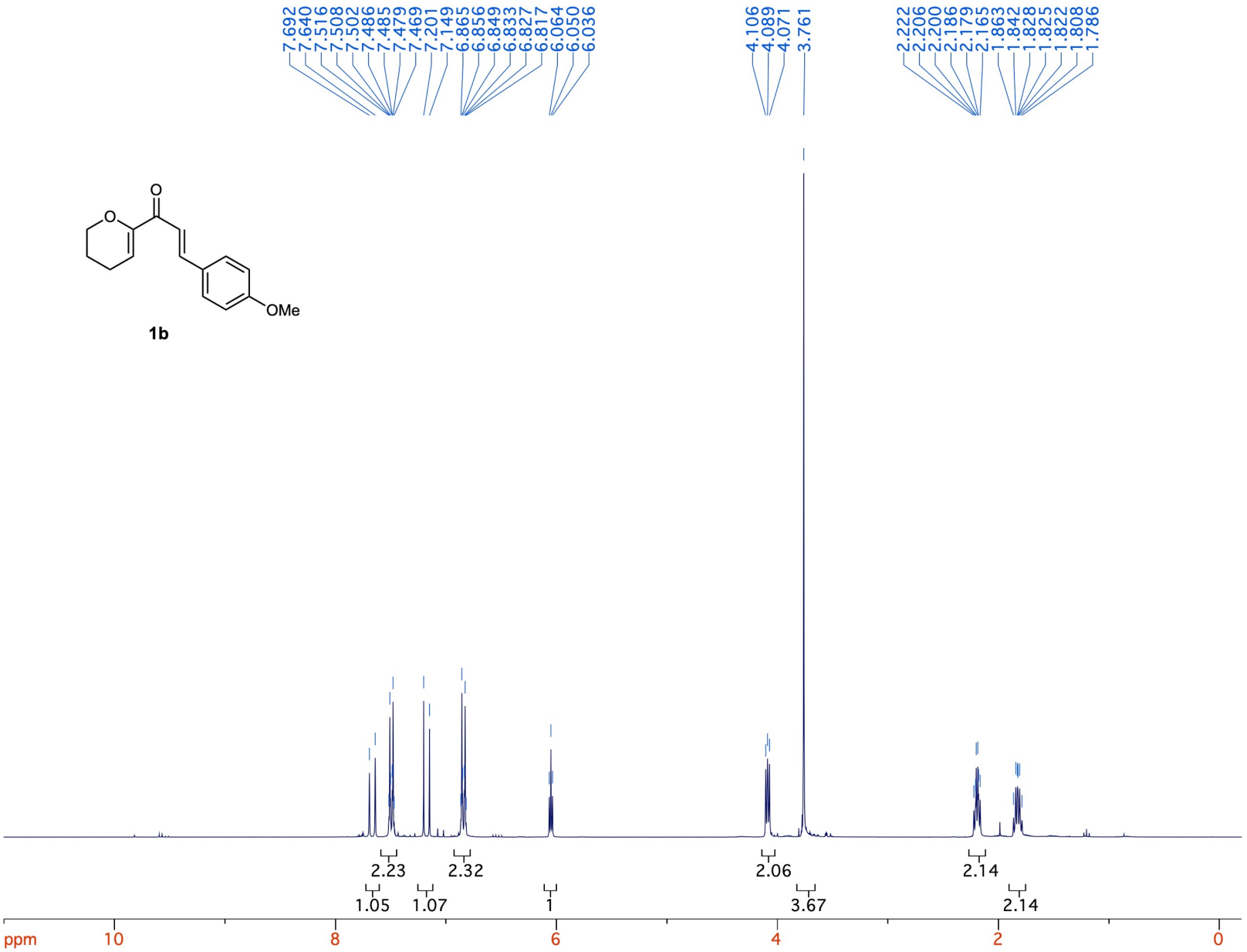

145.041
139.654
133.990
133.210
133.159
133.110
133.069
132.788
132.676
132.562
132.453
132.347
132.073
131.885
131.567
131.423
131.122
130.679
130.233
129.607
129.219
128.403
128.353
128.305
128.257
128.208
128.161
128.112
128.048
125.984
125.613
124.620
123.831
122.360
122.309
122.005
119.612
118.728
118.394
115.394
OTf
I
F3C
CF3

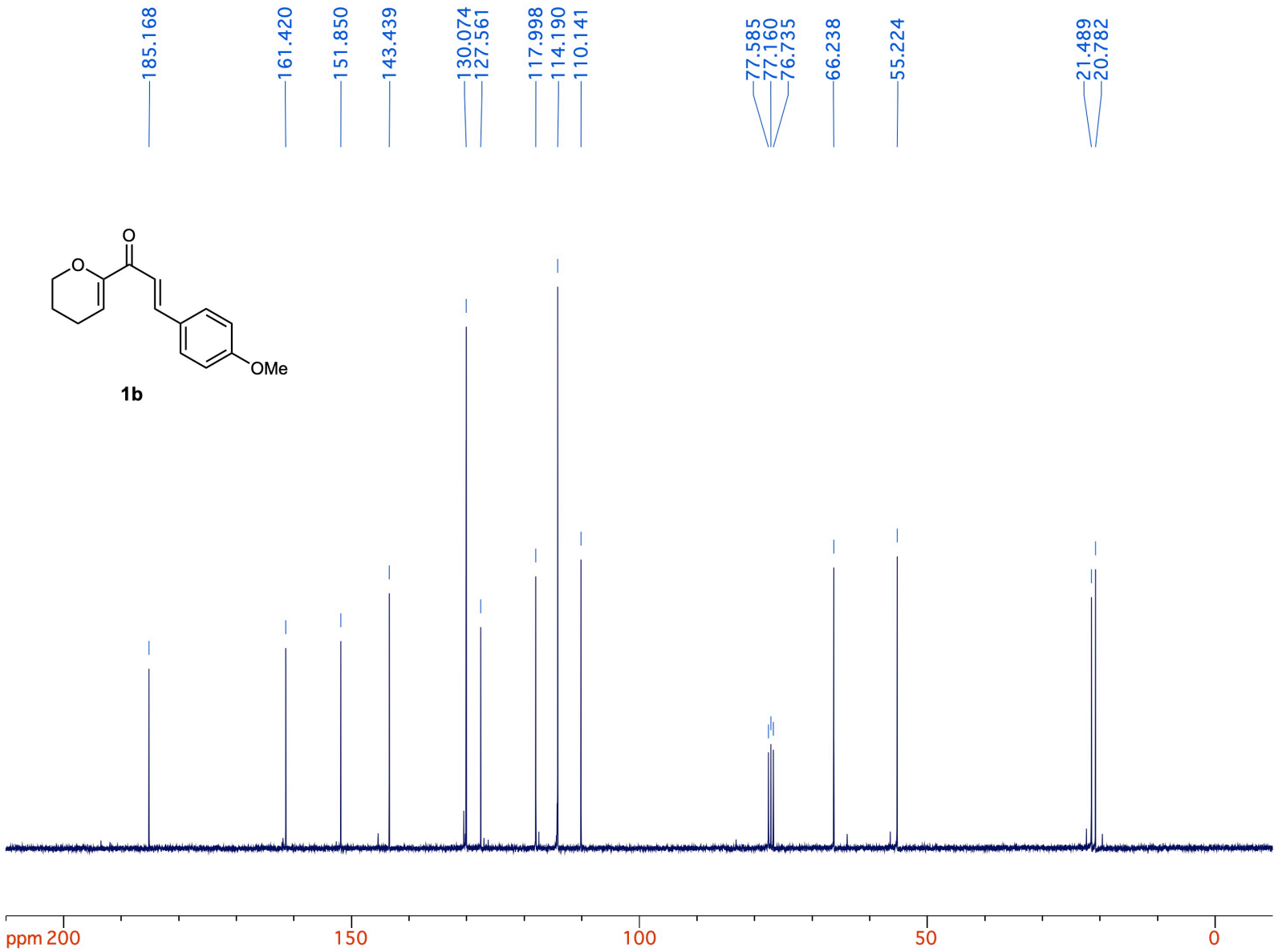
D

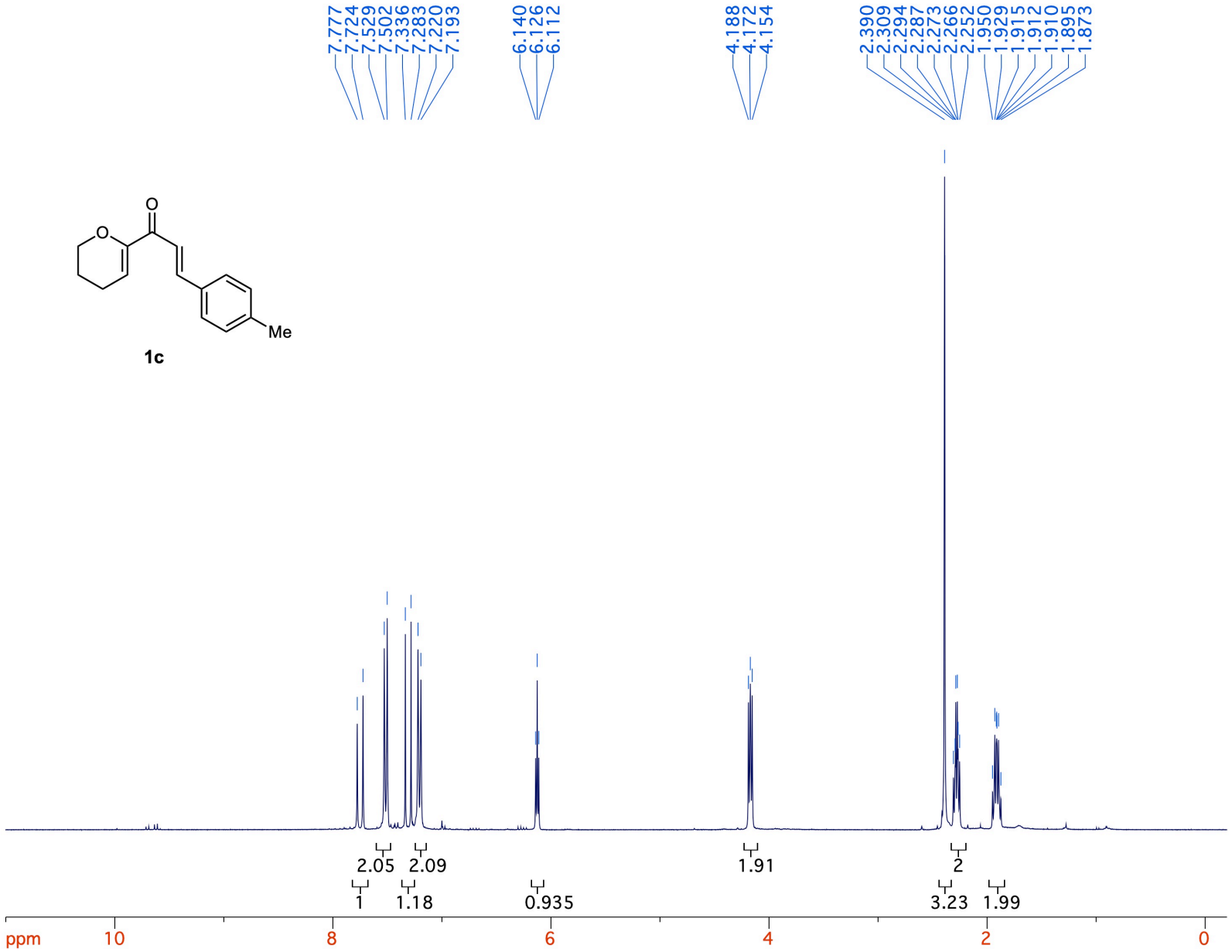

58.234
62.547
78.289
OTf
I
F3C
CF3
D
ppm
-50
-100
-150

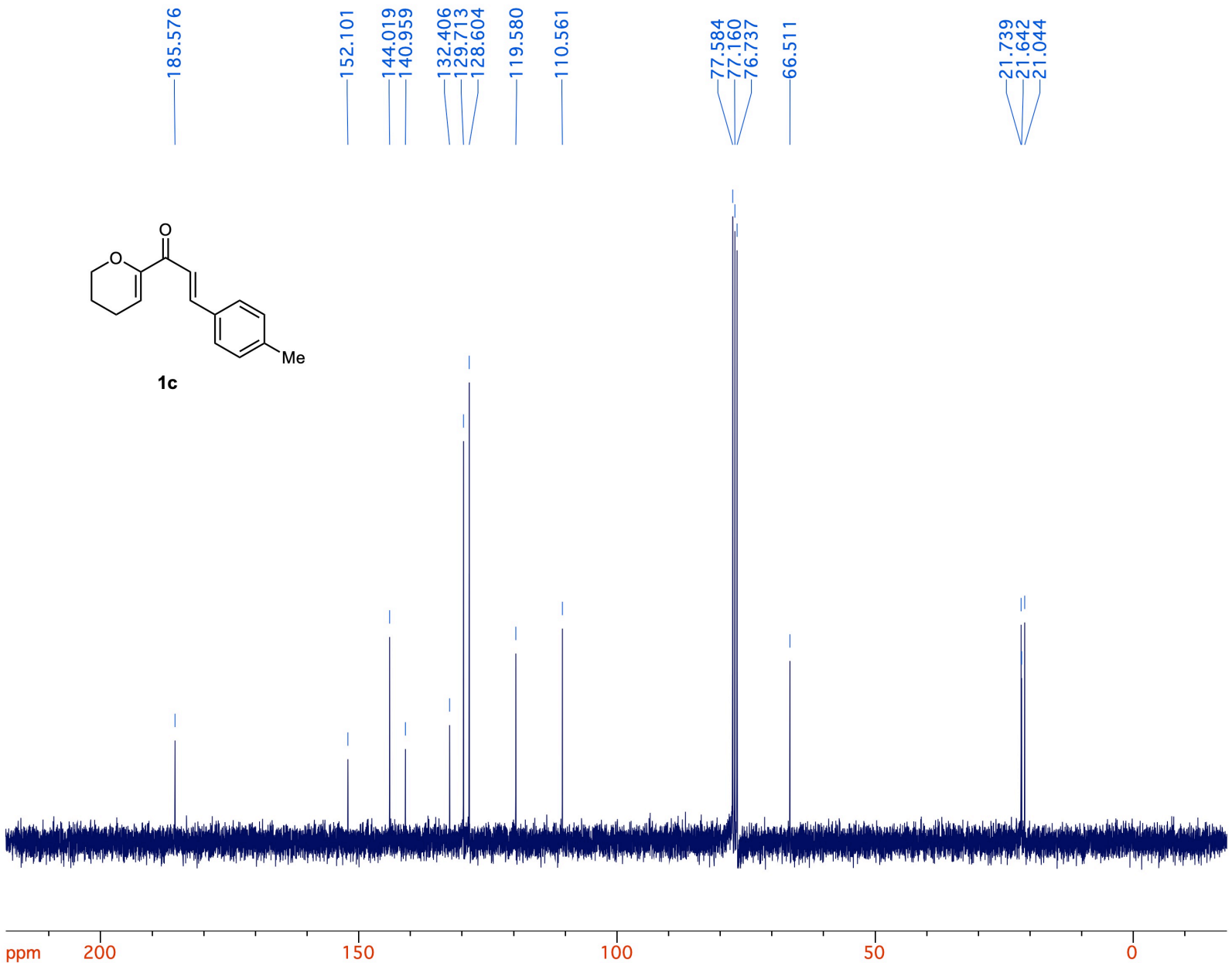

7.755
7.702
7.604
7.590
7.587
7.585
7.584
7.578
7.573
7.566
7.559
7.557
7.551
7.546
7.381
7.377
7.376
7.368
7.361
7.356
7.346
7.344
7.334
7.291
7.260
6.116
6.102
6.088
4.148
4.131
4.113
2.268
2.253
2.246
2.232
2.225
2.211
1.907
1.886
1.871
1.868
1.866
1.851
1.830
O
O
1a
2.05
1
2.05
1.01
4.11
2.03
2.07
ppm
10
8
6
4
2
0

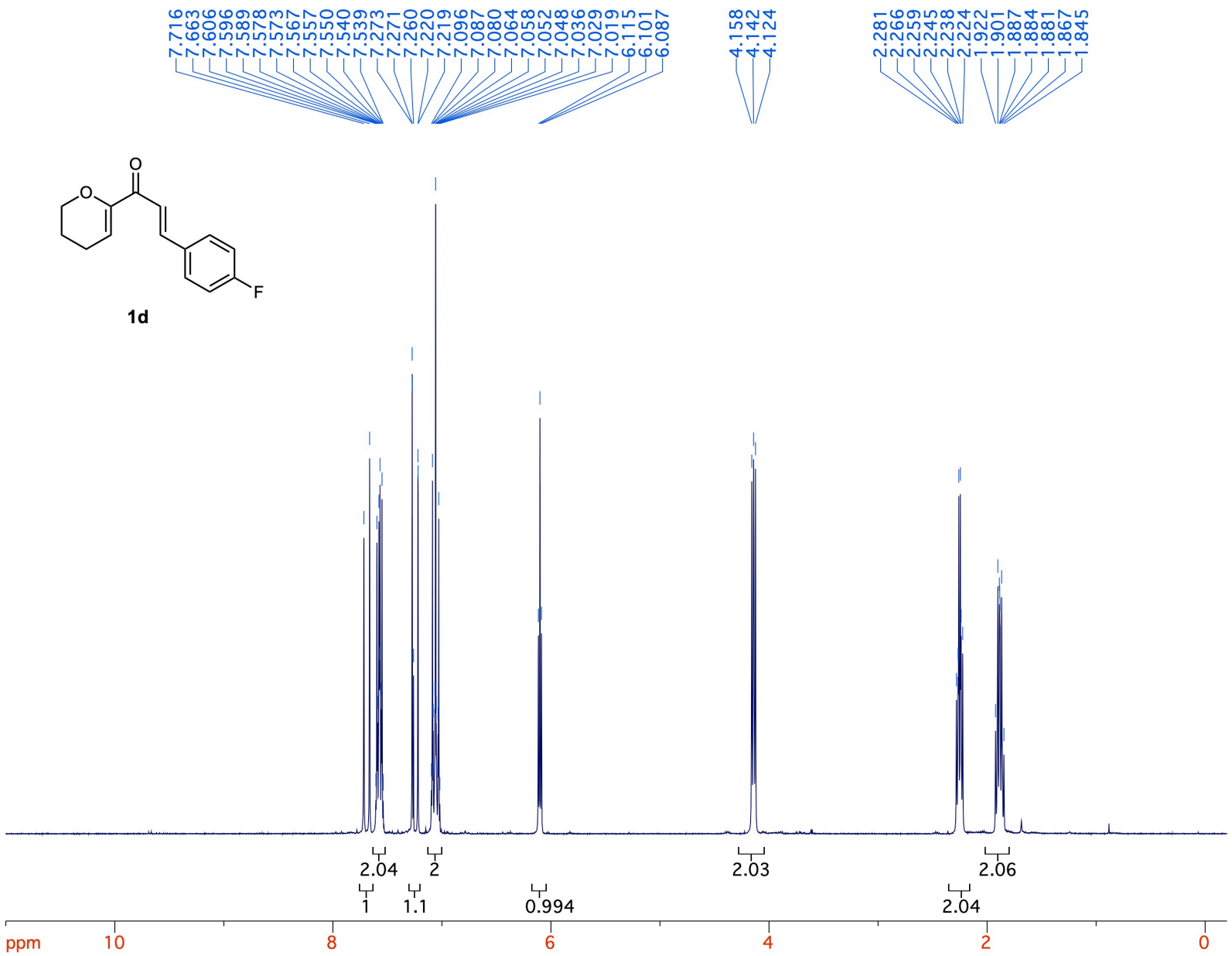

185.353
151.940
143.779
135.011
130.379
128.873
128.461
120.507
110.792
77.584
77.160
76.736
66.422
21.609
20.952
O
O
1a
ppm 200
150
100
50
0

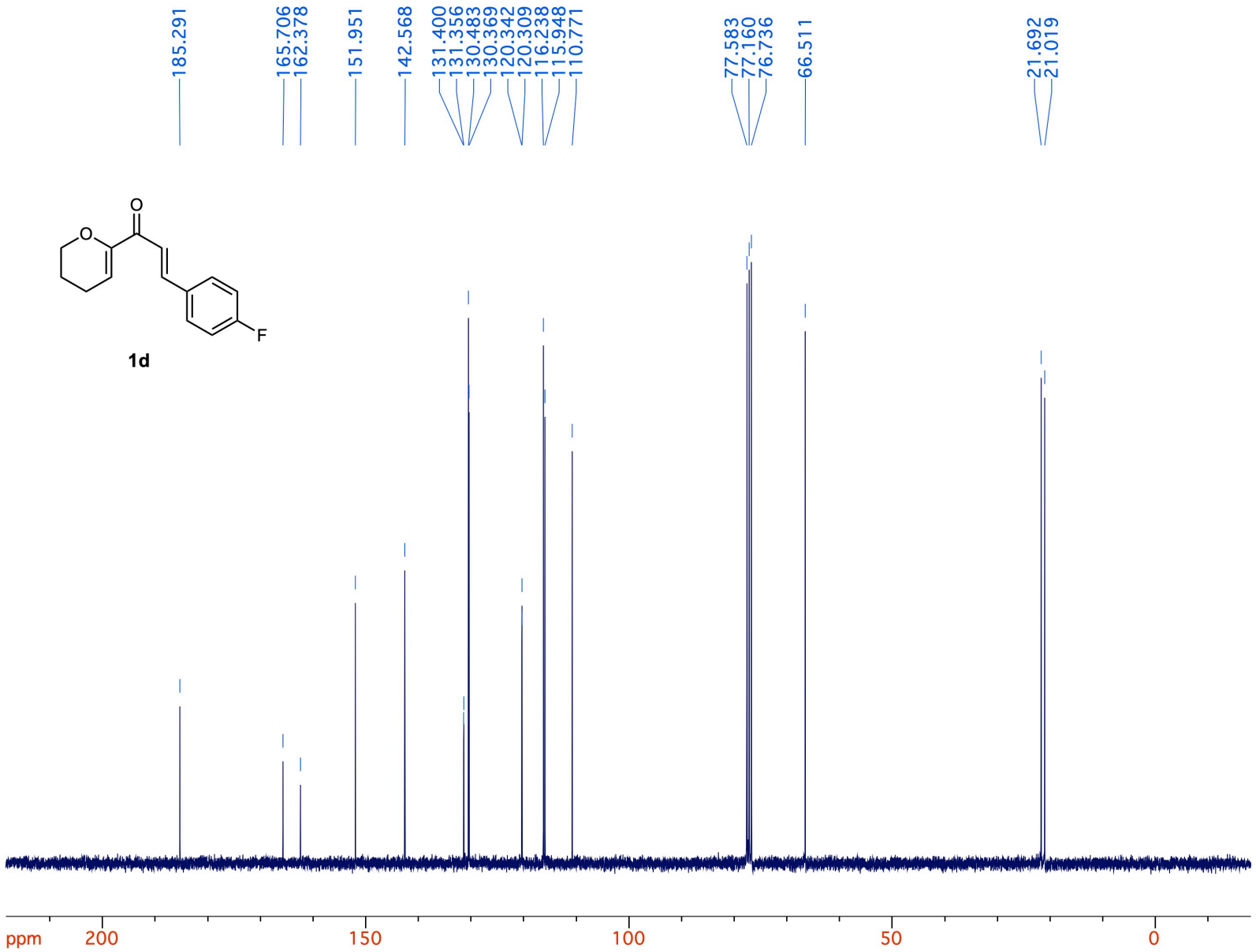

7.692
7.640
7.516
7.508
7.502
7.486
7.485
7.479
7.469
7.201
7.149
6.865
6.856
6.849
6.833
6.827
6.817
6.064
6.050
6.036
4.106
4.089
4.071
3.761
2.222
2.206
2.200
2.186
2.179
2.165
1.863
1.842
1.828
1.825
1.822
1.808
1.786
O
O
OMe
1b
2.23
2.32
2.06
2.14
1.05
1.07
1
3.67
2.14
ppm
10
8
6
4
2
0

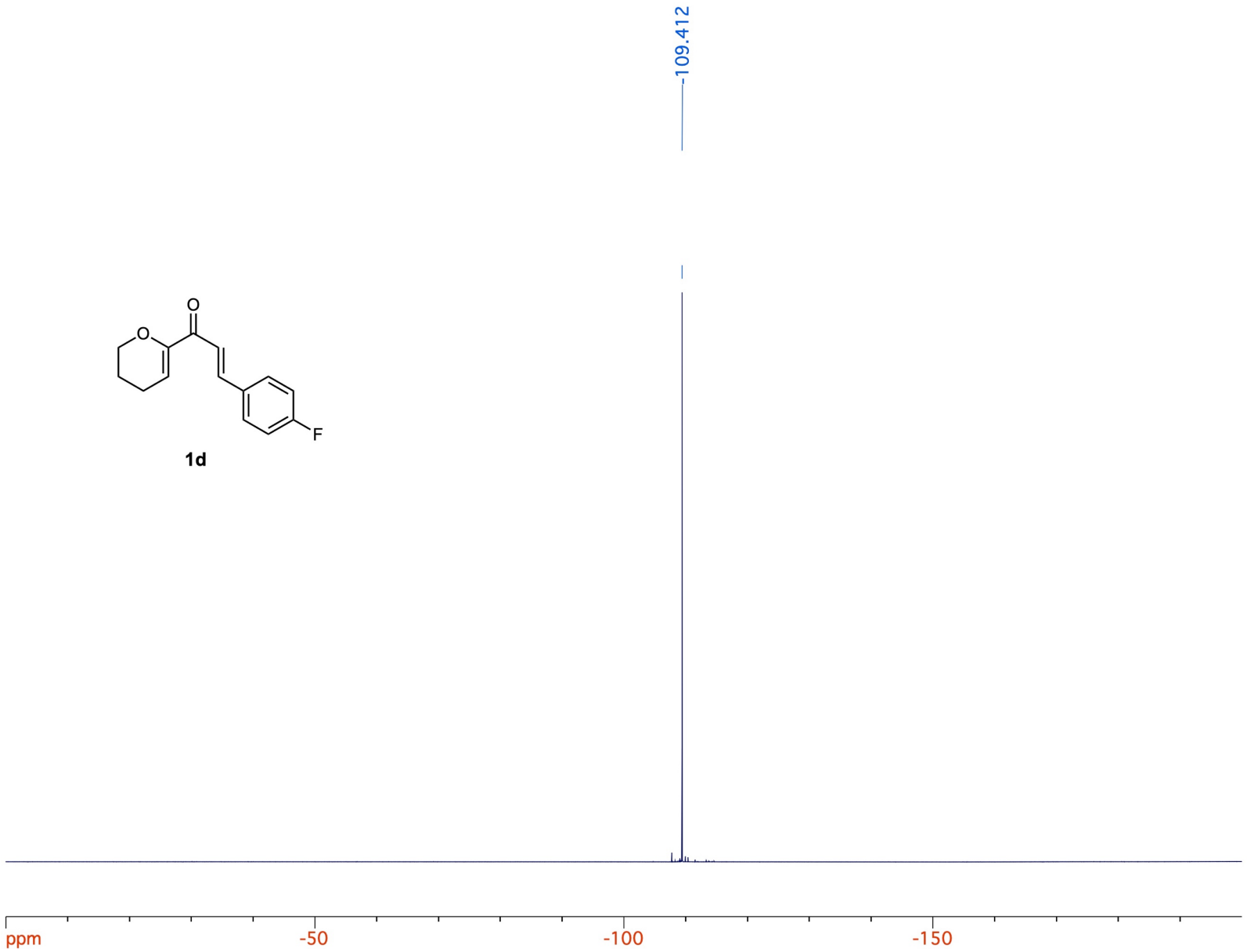

185.168
161.420
151.850
143.439
130.074
127.561
117.998
114.190
110.141
77.585
77.160
76.735
66.238
55.224
21.489
20.782
O
O
OMe
1b
ppm 200
150
100
50
0

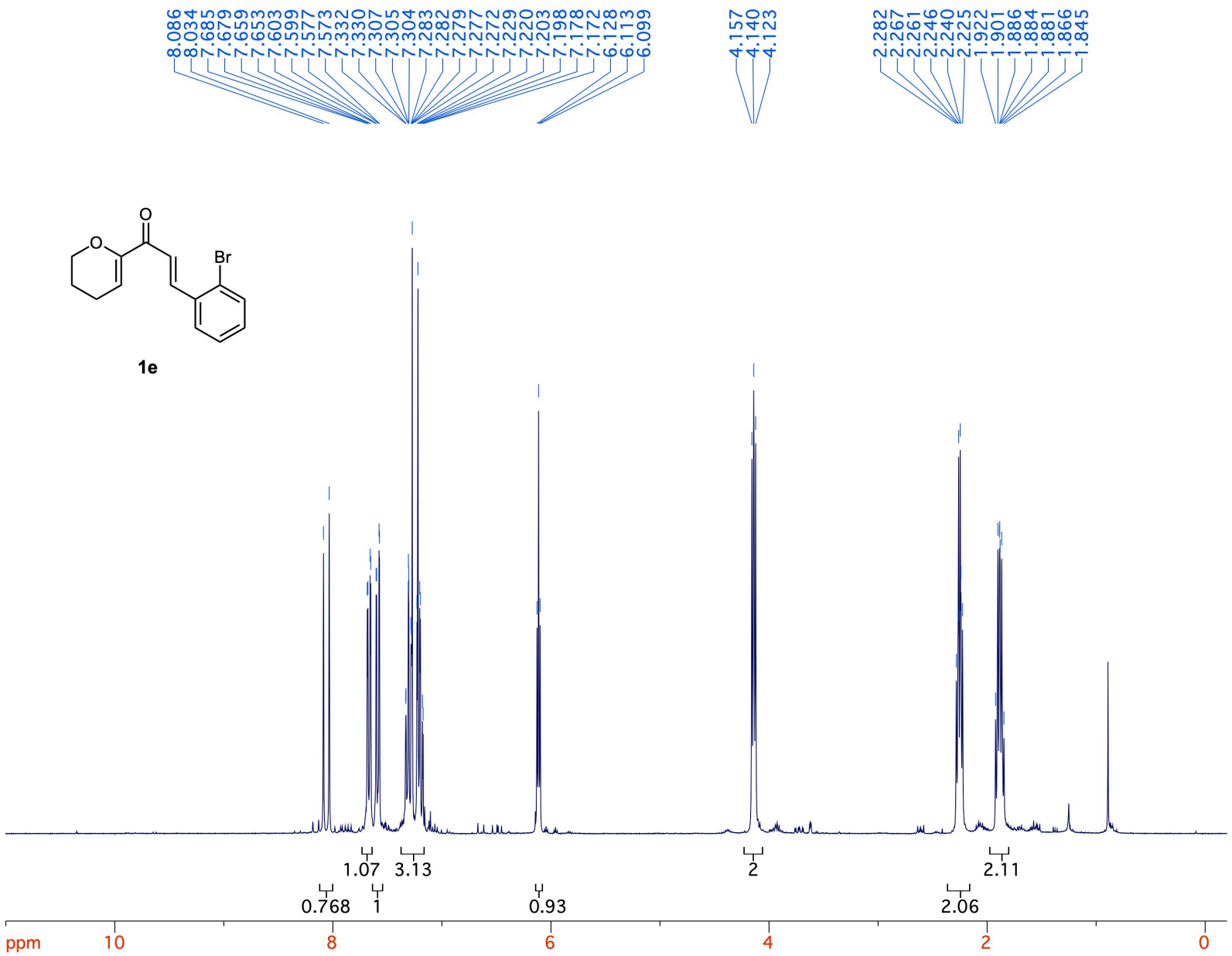

7.777
7.724
7.529
7.502
7.336
7.283
7.220
7.193
6.140
6.126
6.112
4.188
4.172
4.154
2.390
2.309
2.294
2.287
2.273
2.266
2.252
1.950
1.929
1.915
1.912
1.910
1.895
1.873
O
O
Me
1c
2.05
2.09
1.91
2
1
1.18
0.935
3.23
1.99
ppm
10
8
6
4
2
0

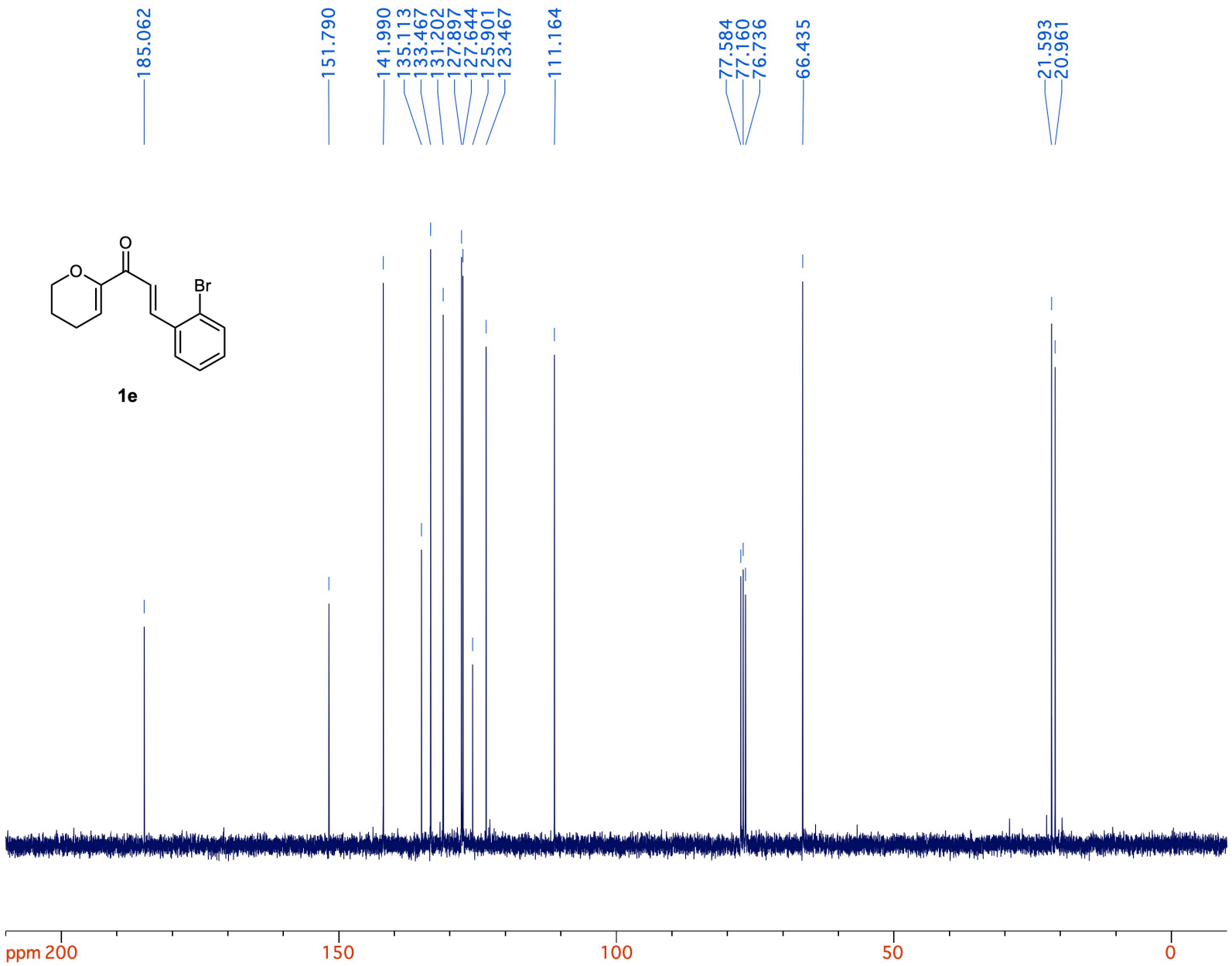

185.576
152.101
144.019
140.959
132.406
129.713
128.604
119.580
110.561
77.584
77.160
76.737
66.511
21.739
21.642
21.044
O
O
Me
1c
ppm
200
150
100
50
0

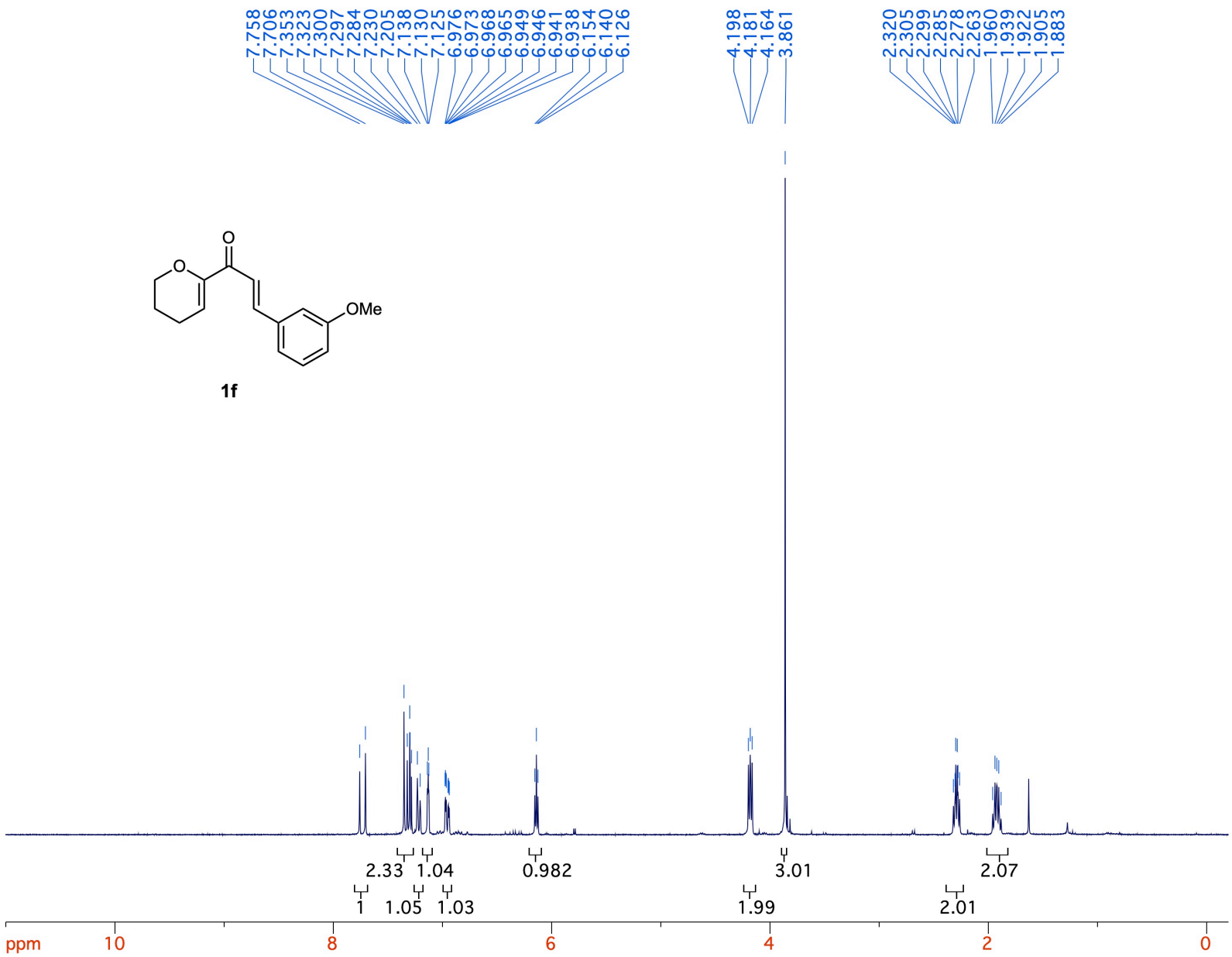

7.716
7.663
7.606
7.596
7.589
7.578
7.573
7.567
7.557
7.550
7.540
7.539
7.273
7.271
7.260
7.220
7.219
7.096
7.087
7.080
7.064
7.058
7.052
7.048
7.036
7.029
7.019
6.115
6.101
6.087
4.158
4.142
4.124
2.281
2.266
2.259
2.245
2.238
2.224
1.922
1.901
1.887
1.884
1.881
1.867
1.845
O
O
F
1d
2.04
2
2.03
2.06
1
1.1
0.994
2.04
ppm
10
8
6
4
2
0

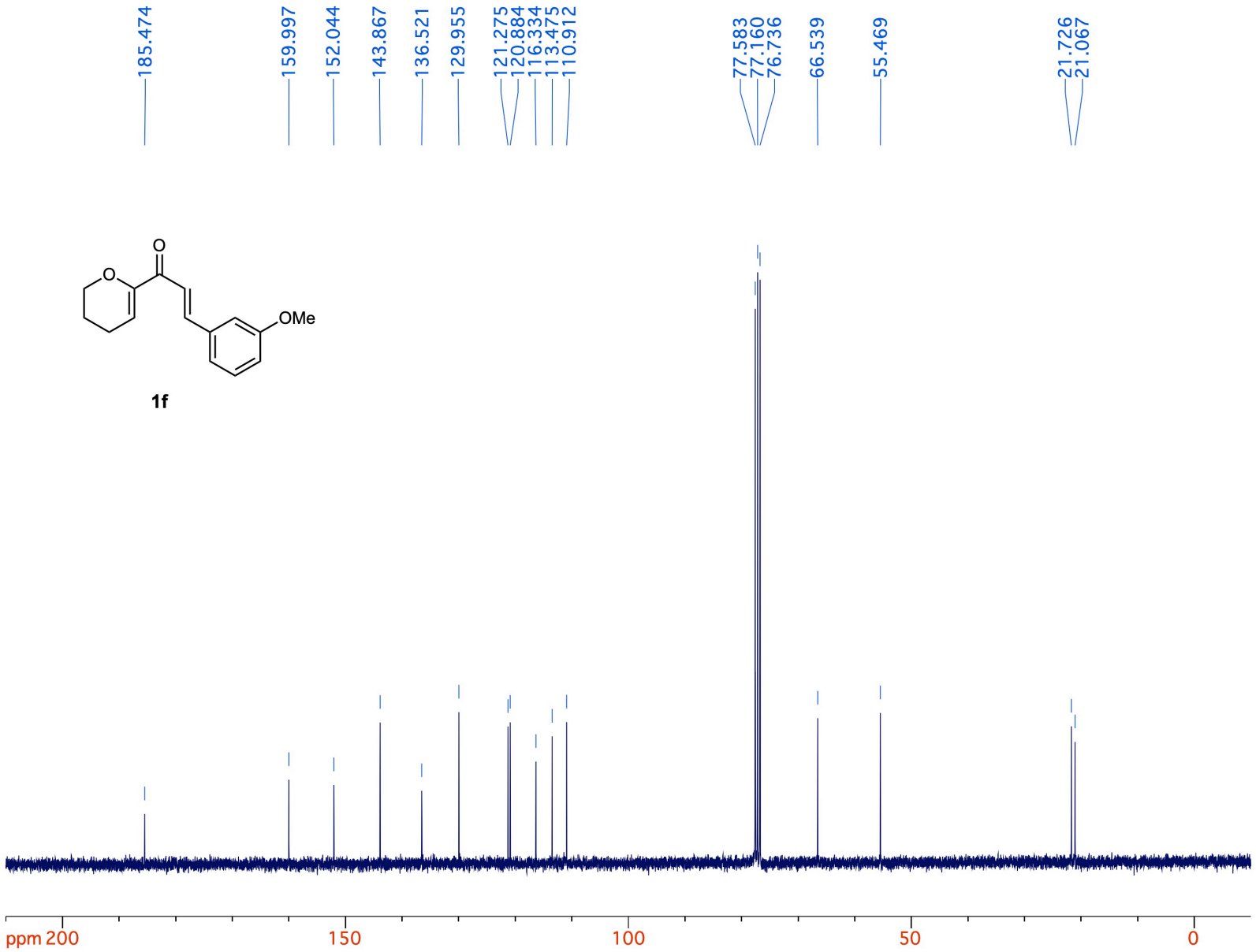

185.291
165.706
162.378
151.951
142.568
131.400
131.356
130.483
130.369
120.342
120.309
116.238
115.948
110.771
77.583
77.160
76.736
66.511
21.692
21.019
O
O
F
1d
ppm
200
150
100
50
0

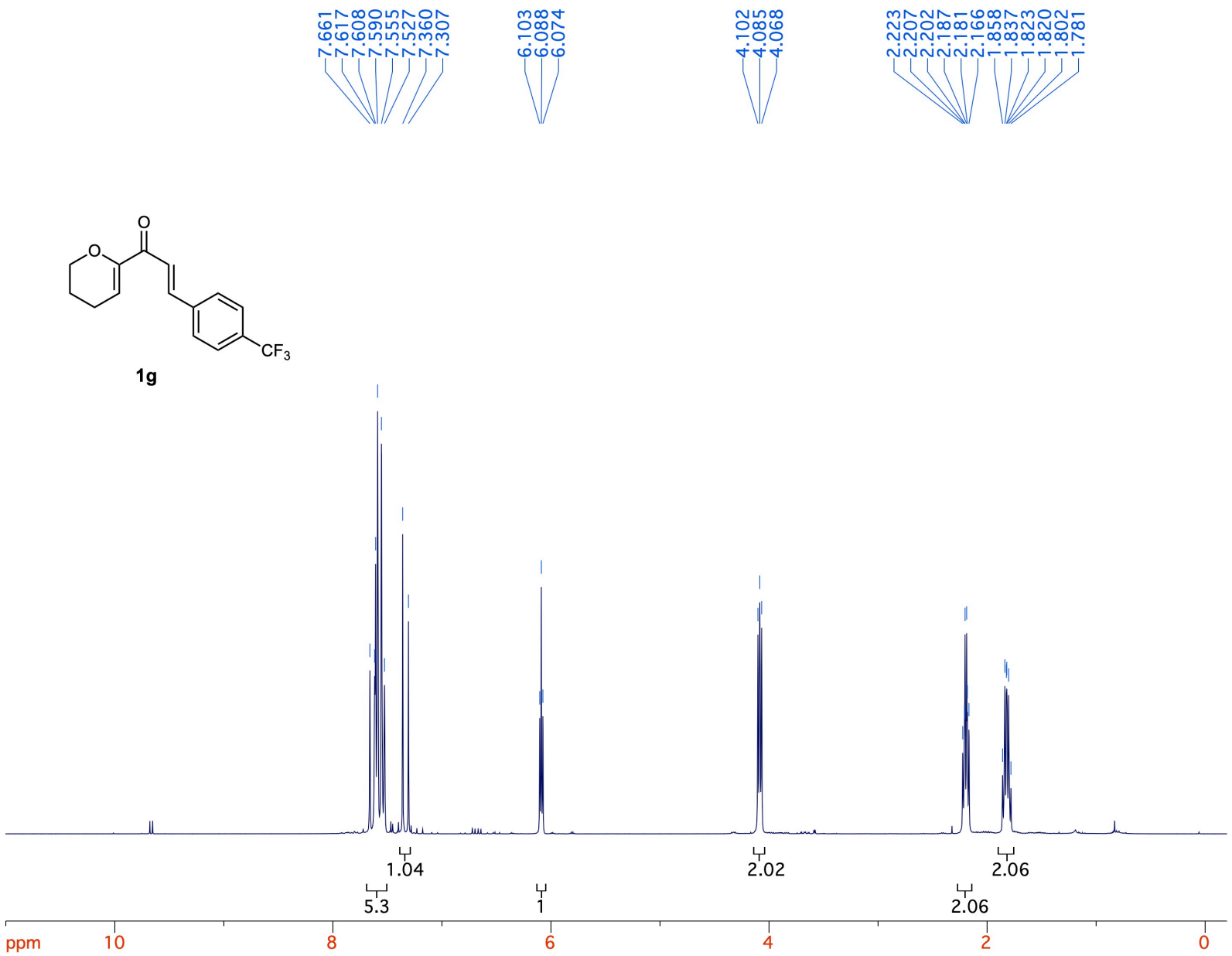

-109.412
O
O
F
1d
ppm
-50
-100
-150

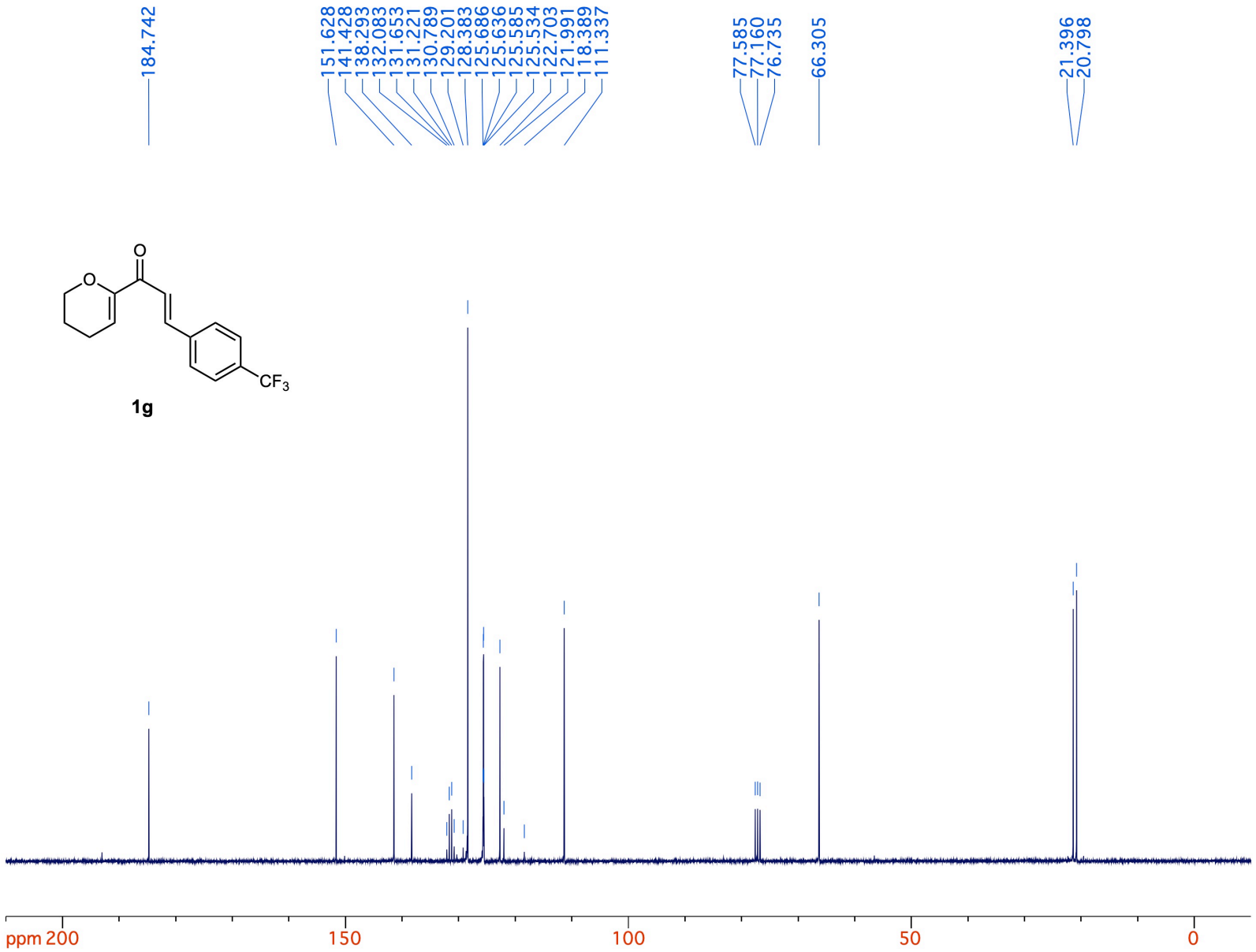

8.086
8.034
7.685
7.679
7.659
7.653
7.603
7.599
7.577
7.573
7.332
7.330
7.307
7.305
7.304
7.283
7.282
7.279
7.277
7.272
7.229
7.220
7.203
7.198
7.178
7.172
6.128
6.113
6.099
4.157
4.140
4.123
2.282
2.267
2.261
2.246
2.240
2.225
1.922
1.901
1.886
1.884
1.881
1.866
1.845
O
O
Br
1e
1.07
3.13
2
2.11
0.768
1
0.93
2.06
ppm
10
8
6
4
2
0

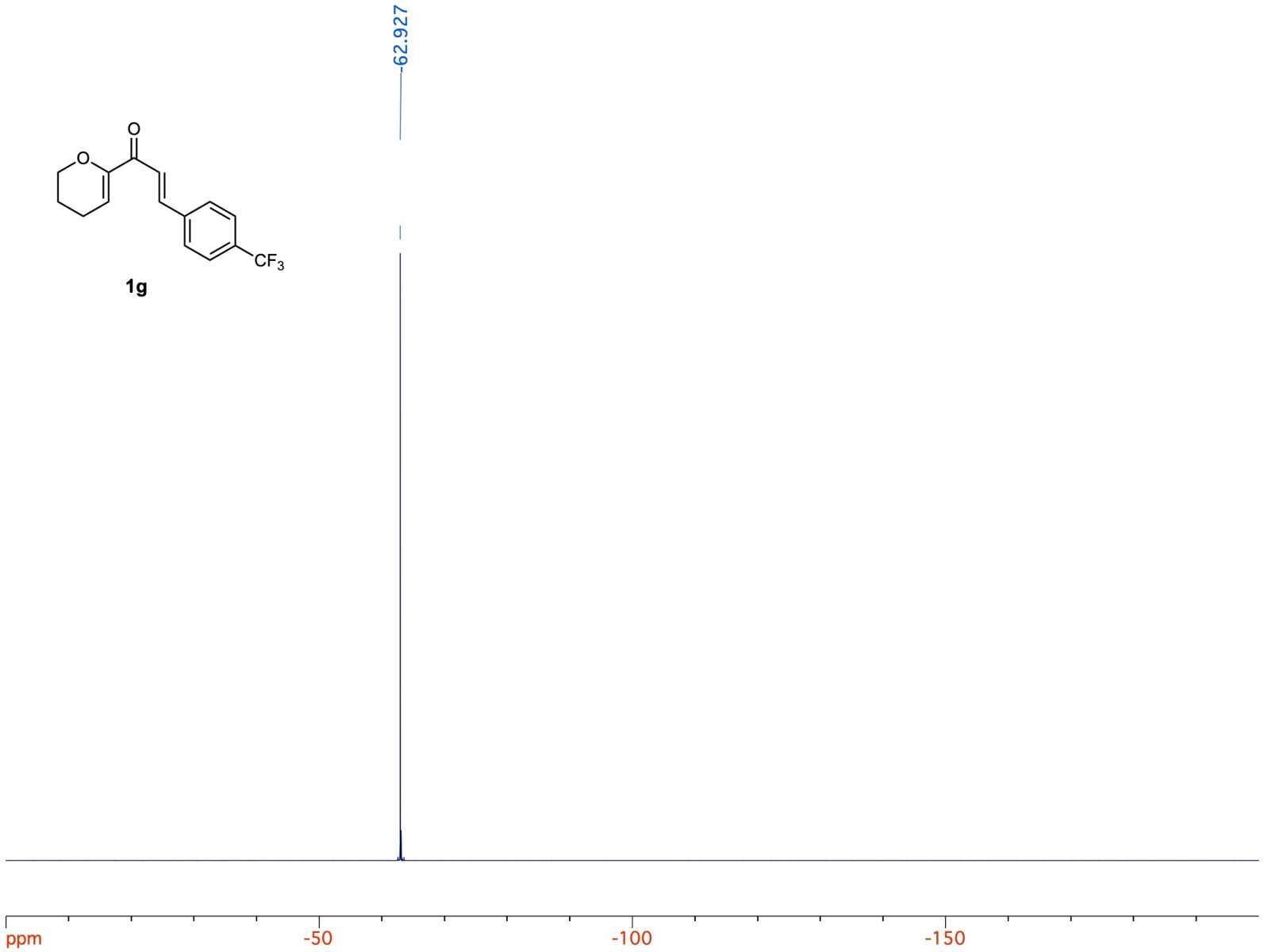

185.062
151.790
141.990
135.113
133.467
131.202
127.897
127.644
125.901
123.467
111.164
77.584
77.160
76.736
66.435
21.593
20.961
O
O
Br
1e
ppm 200
150
100
50
0

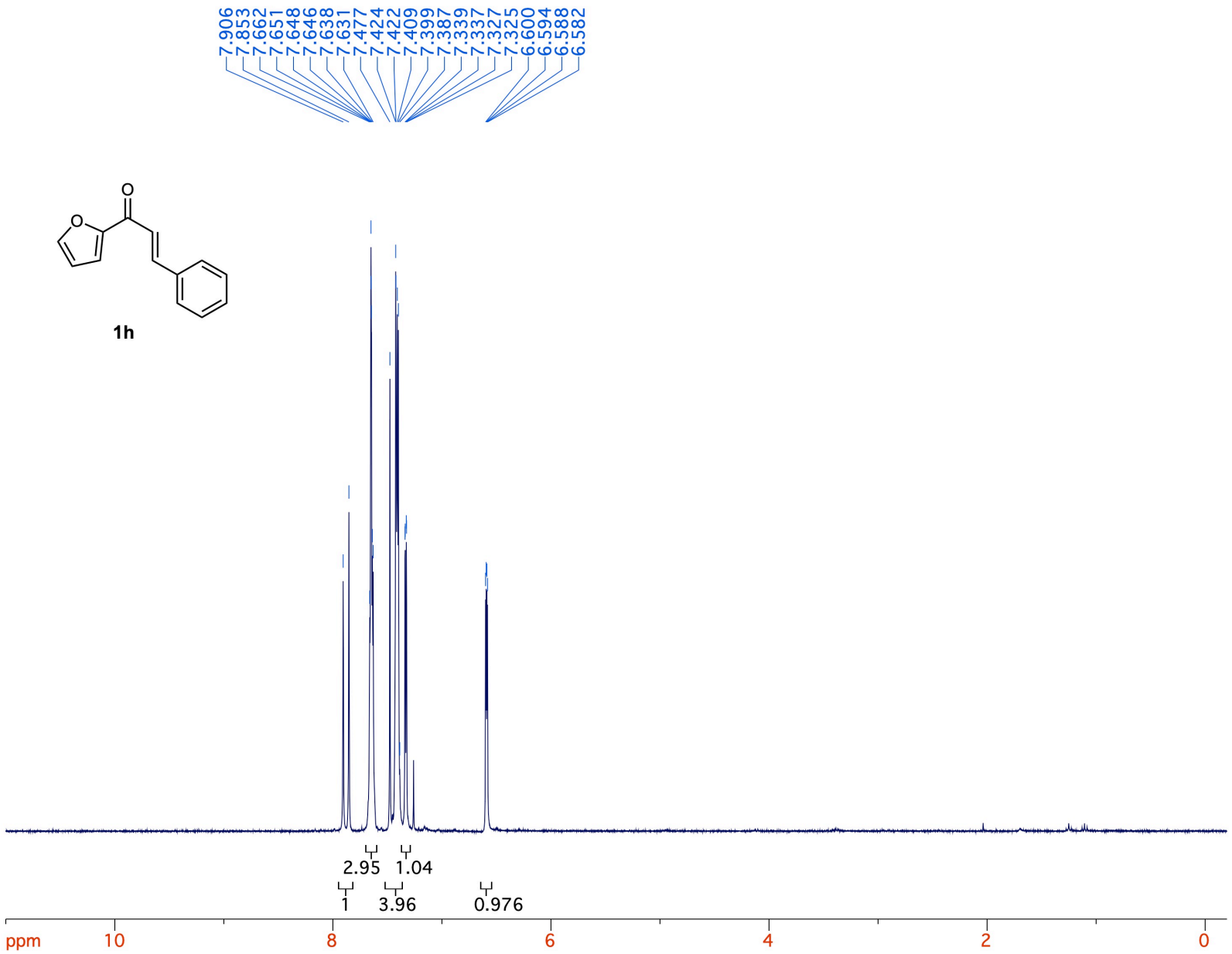

7.758
7.706
7.353
7.323
7.300
7.297
7.284
7.230
7.205
7.138
7.130
7.125
6.976
6.973
6.968
6.965
6.949
6.946
6.941
6.938
6.154
6.140
6.126
4.198
4.181
4.164
3.861
2.320
2.305
2.299
2.285
2.278
2.263
1.960
1.939
1.922
1.905
1.883
O
O
OMe
1f
2.33
1.04
0.982
3.01
2.07
1
1.05
1.03
1.99
2.01
ppm
10
8
6
4
2
0

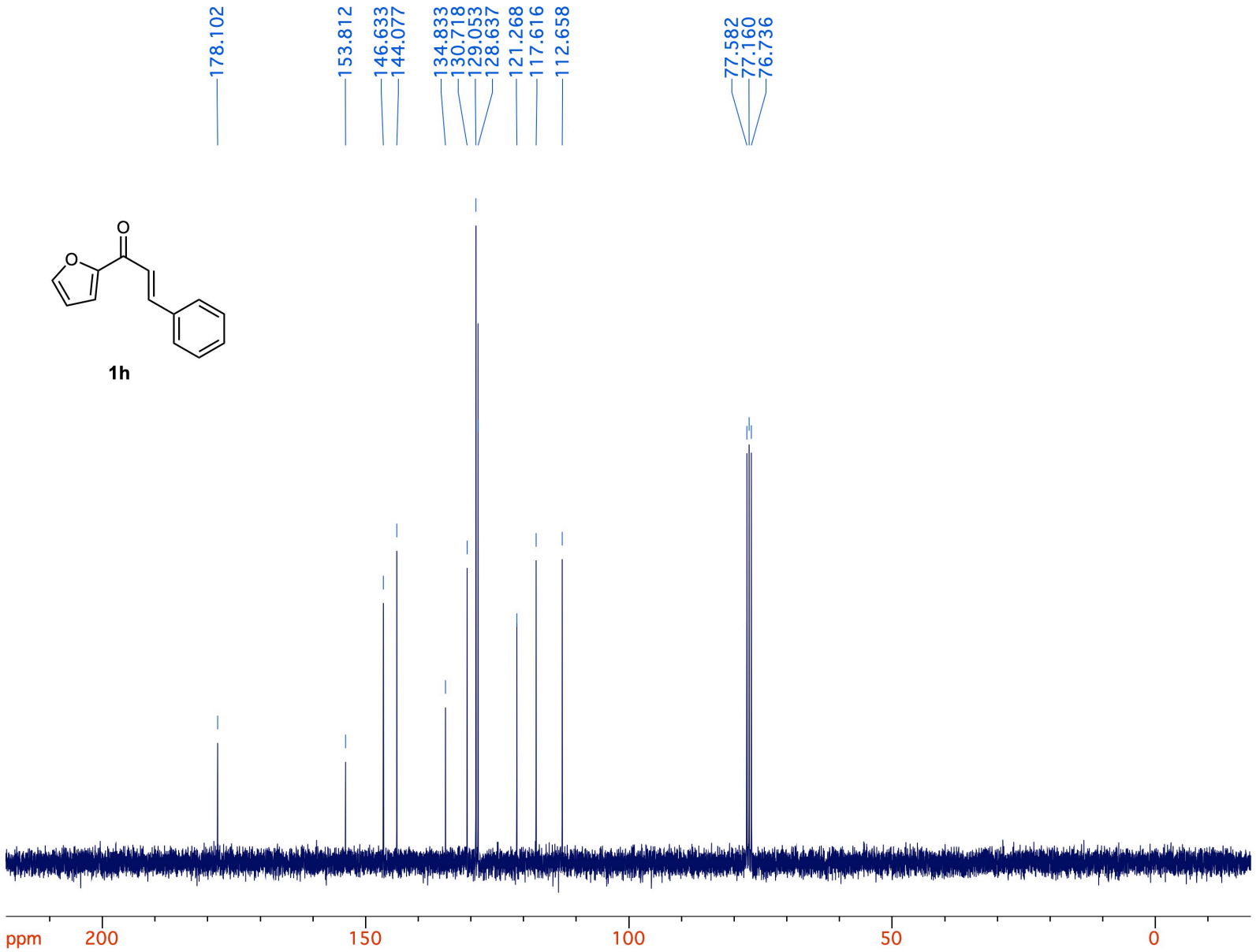

185.474
159.997
152.044
143.867
136.521
129.955
121.275
120.884
116.334
113.475
110.912
77.583
77.160
76.736
66.539
55.469
21.726
21.067
O
O
OMe
1f
ppm 200
150
100
50
0

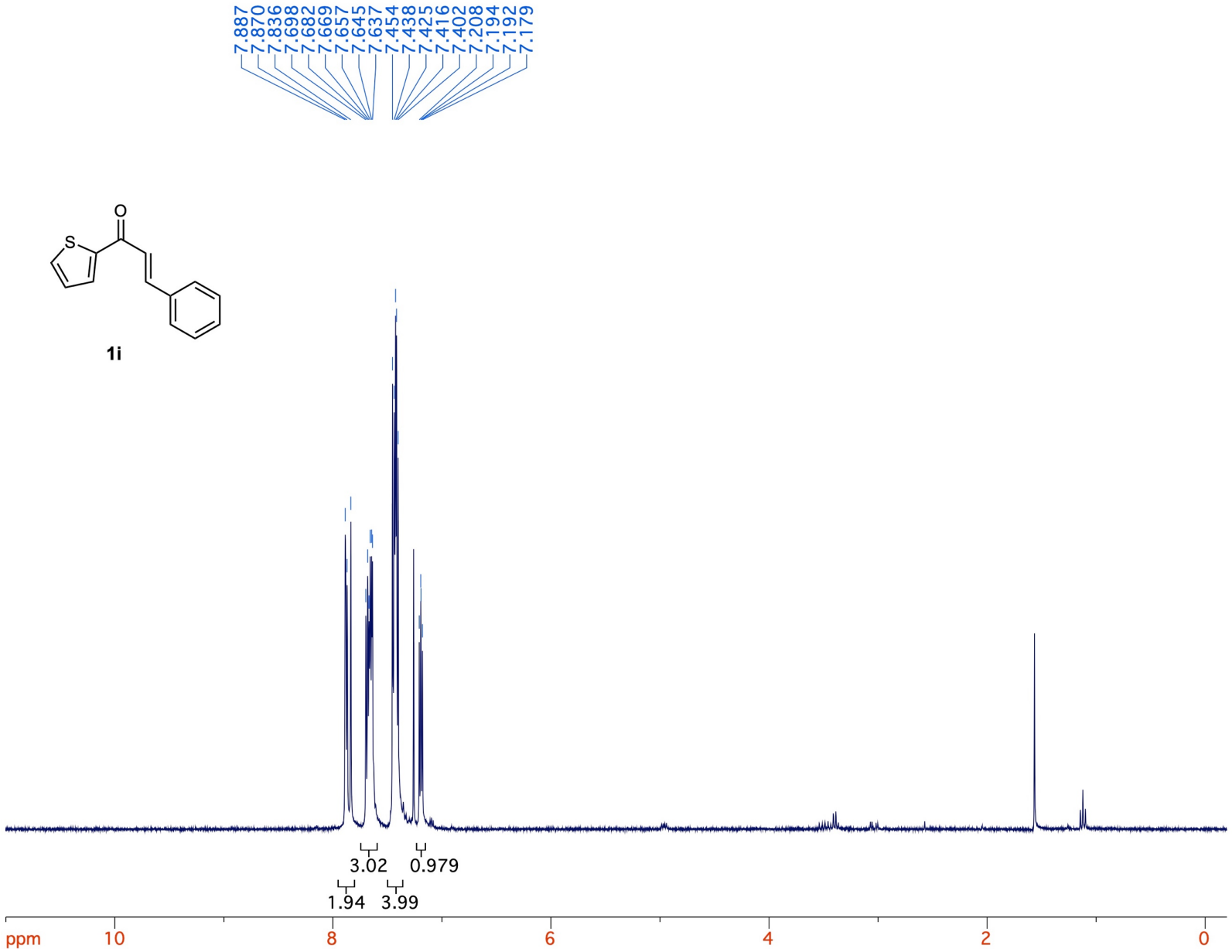

7.661
7.617
7.608
7.590
7.555
7.527
7.360
7.307
6.103
6.088
6.074
4.102
4.085
4.068
2.223
2.207
2.202
2.187
2.181
2.166
1.858
1.837
1.823
1.820
1.802
1.781
O
O
CF3
1g
1.04
2.02
2.06
5.3
1
2.06
ppm
10
8
6
4
2
0

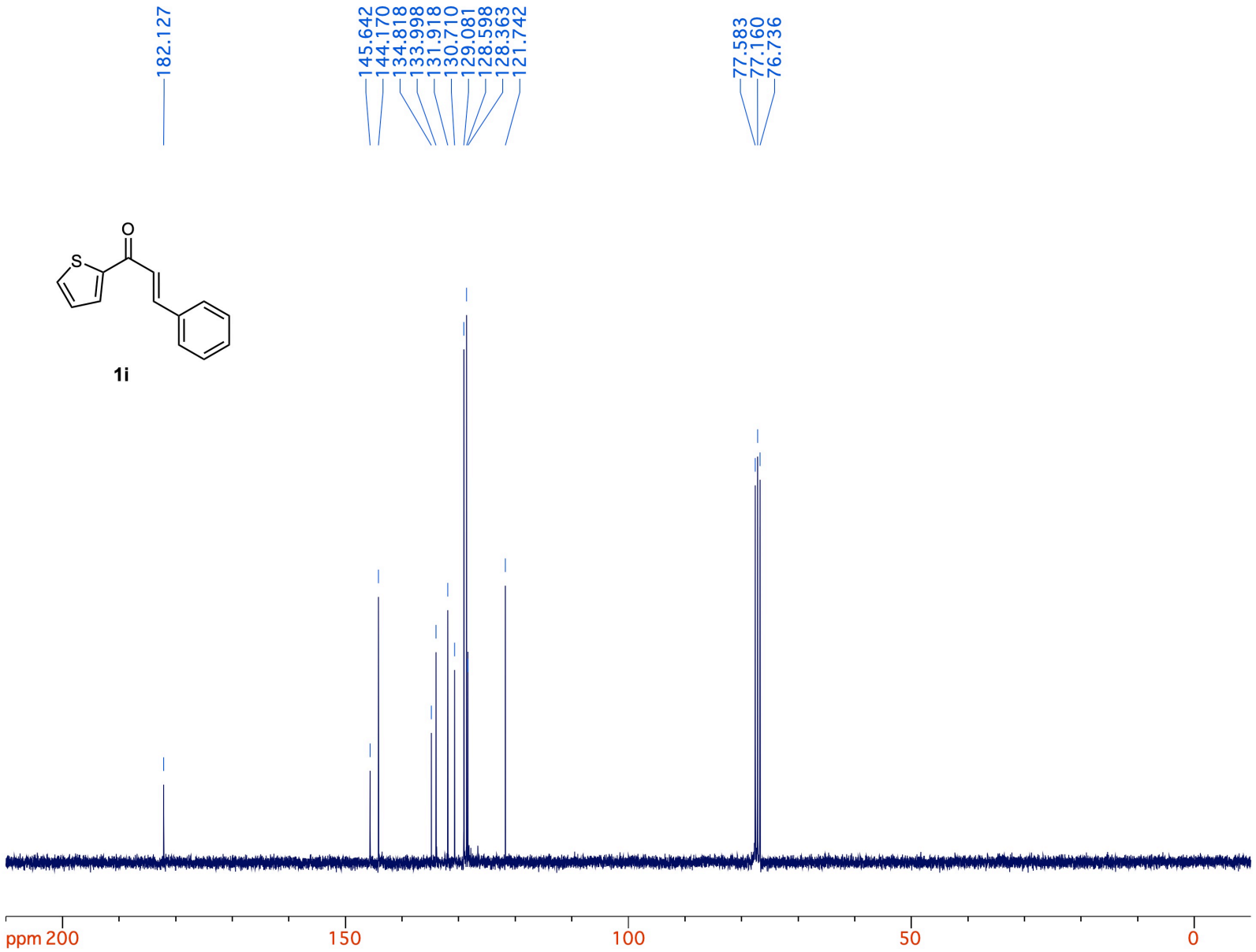

184.742
151.628
141.428
138.293
132.083
131.653
131.221
130.789
129.201
128.383
125.686
125.636
125.585
125.534
122.703
121.991
118.389
111.337
77.585
77.160
76.735
66.305
21.396
20.798
O
O
CF3
1g
ppm 200
150
100
50
0

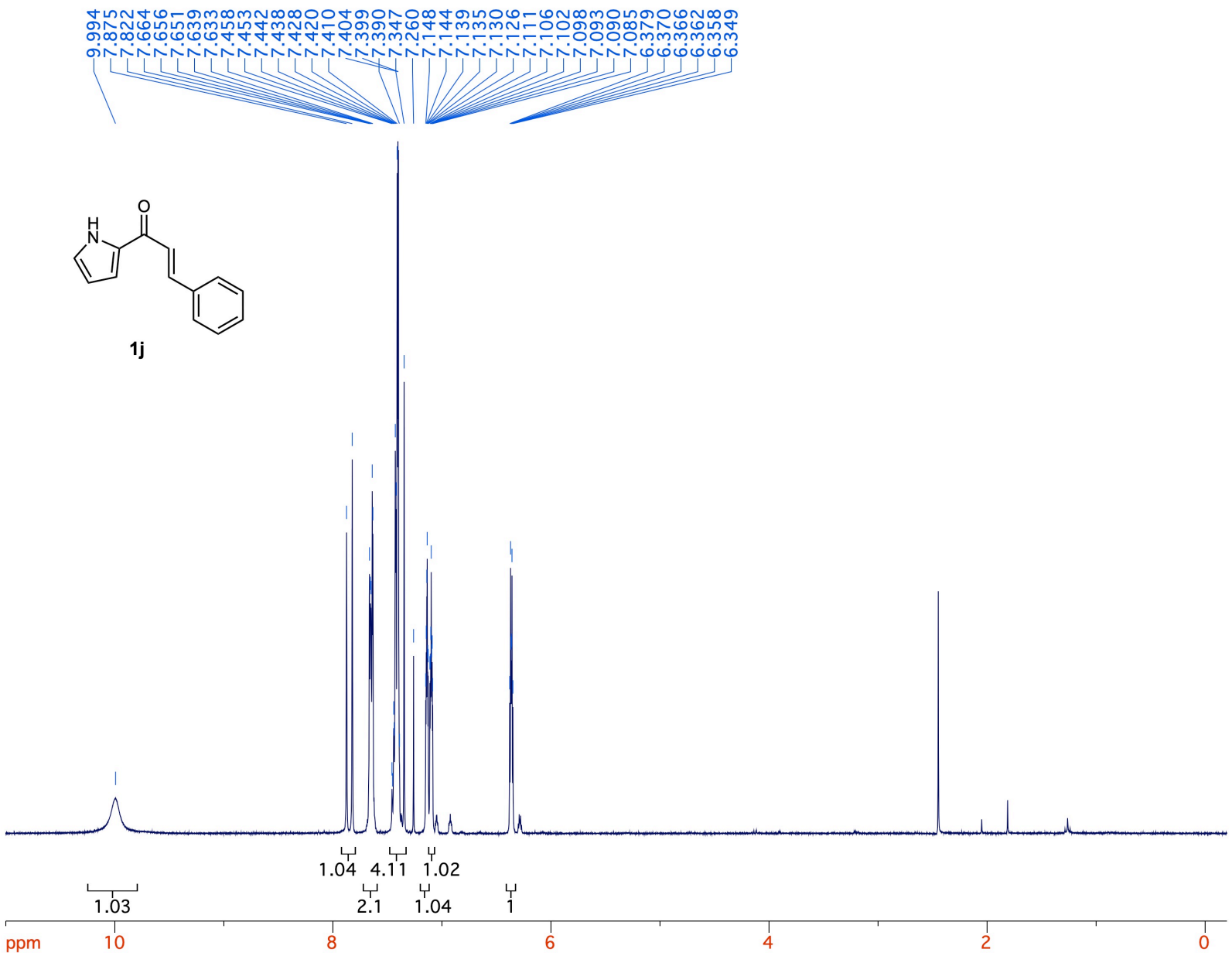

62.927
O
O
CF3
1g
ppm
-50
-100
-150

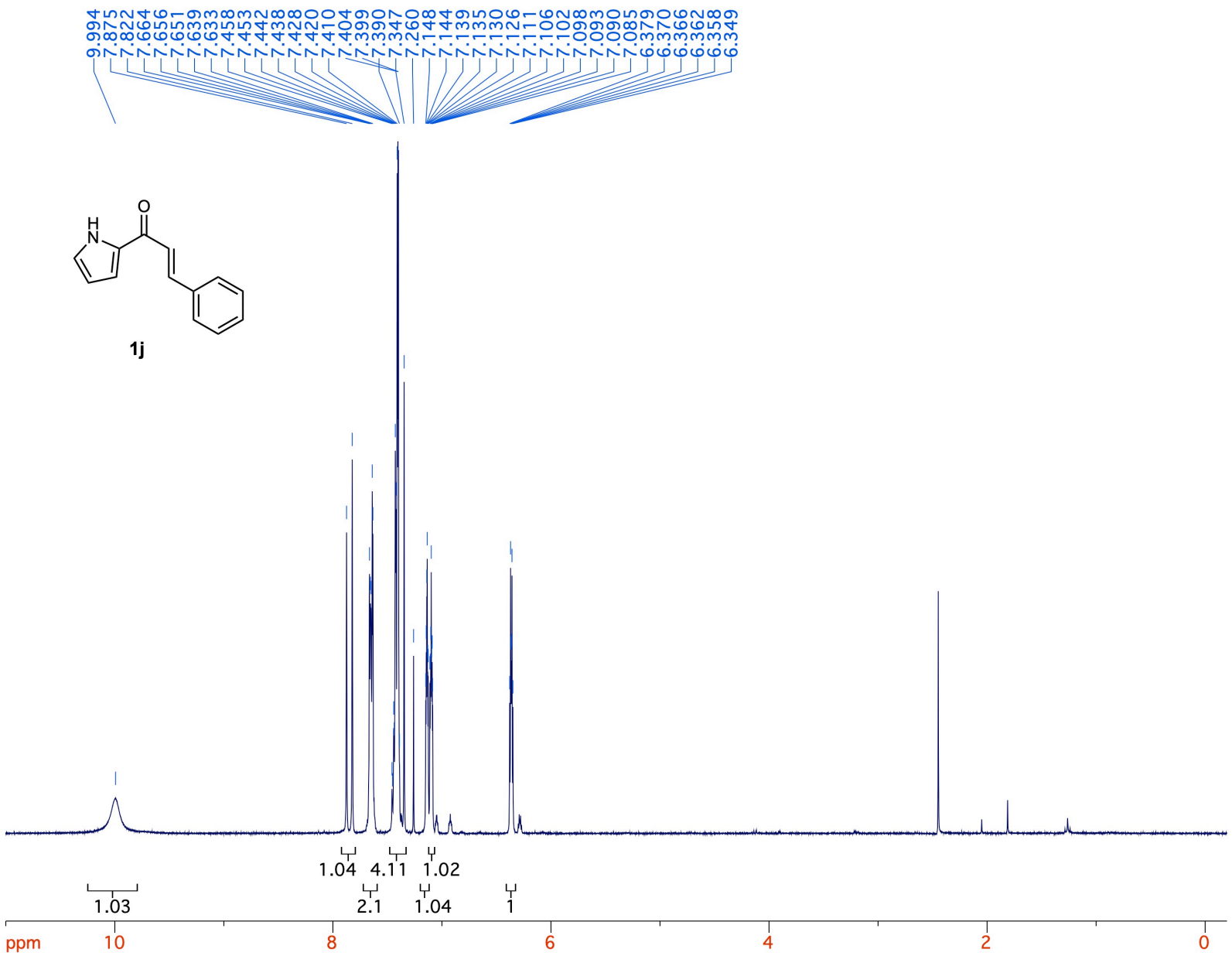

7.906
7.853
7.662
7.651
7.648
7.646
7.638
7.631
7.477
7.424
7.422
7.409
7.399
7.387
7.339
7.337
7.327
7.325
6.600
6.594
6.588
6.582
O
O
1h
2.95
1.04
1
3.96
0.976
ppm
10
8
6
4
2
0

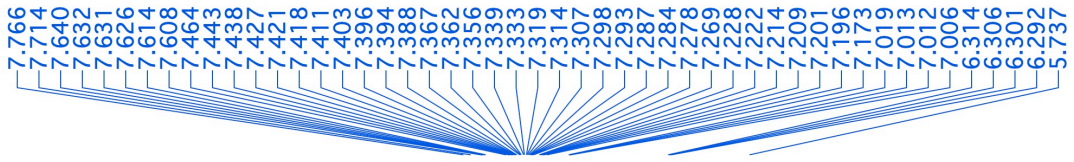

178.102
153.812
146.633
144.077
134.833
130.718
129.053
128.637
121.268
117.616
112.658
77.582
77.160
76.736
O
O
1h
ppm
200
150
100
50
0

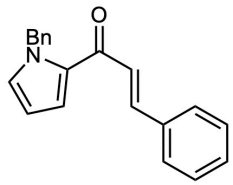

7.887
7.870
7.836
7.698
7.682
7.669
7.657
7.645
7.637
7.454
7.438
7.425
7.416
7.402
7.208
7.194
7.192
7.179
O
S
1i
3.02
0.979
1.94
3.99
ppm
10
8
6
4
2
0


182.127
145.642
144.170
134.818
133.998
131.918
130.710
129.081
128.598
128.363
121.742
77.583
77.160
76.736
O
S
1i
ppm 200
150
100
50
0


9.994
7.875
7.822
7.664
7.656
7.651
7.639
7.633
7.458
7.453
7.442
7.438
7.428
7.420
7.410
7.404
7.399
7.390
7.347
7.260
7.148
7.144
7.139
7.135
7.130
7.126
7.111
7.106
7.102
7.098
7.093
7.090
7.085
6.379
6.370
6.366
6.362
6.358
6.349
O
H
N
1j
1.04
4.11
1.02
1.03
2.1
1.04
1
ppm
10
8
6
4
2
0

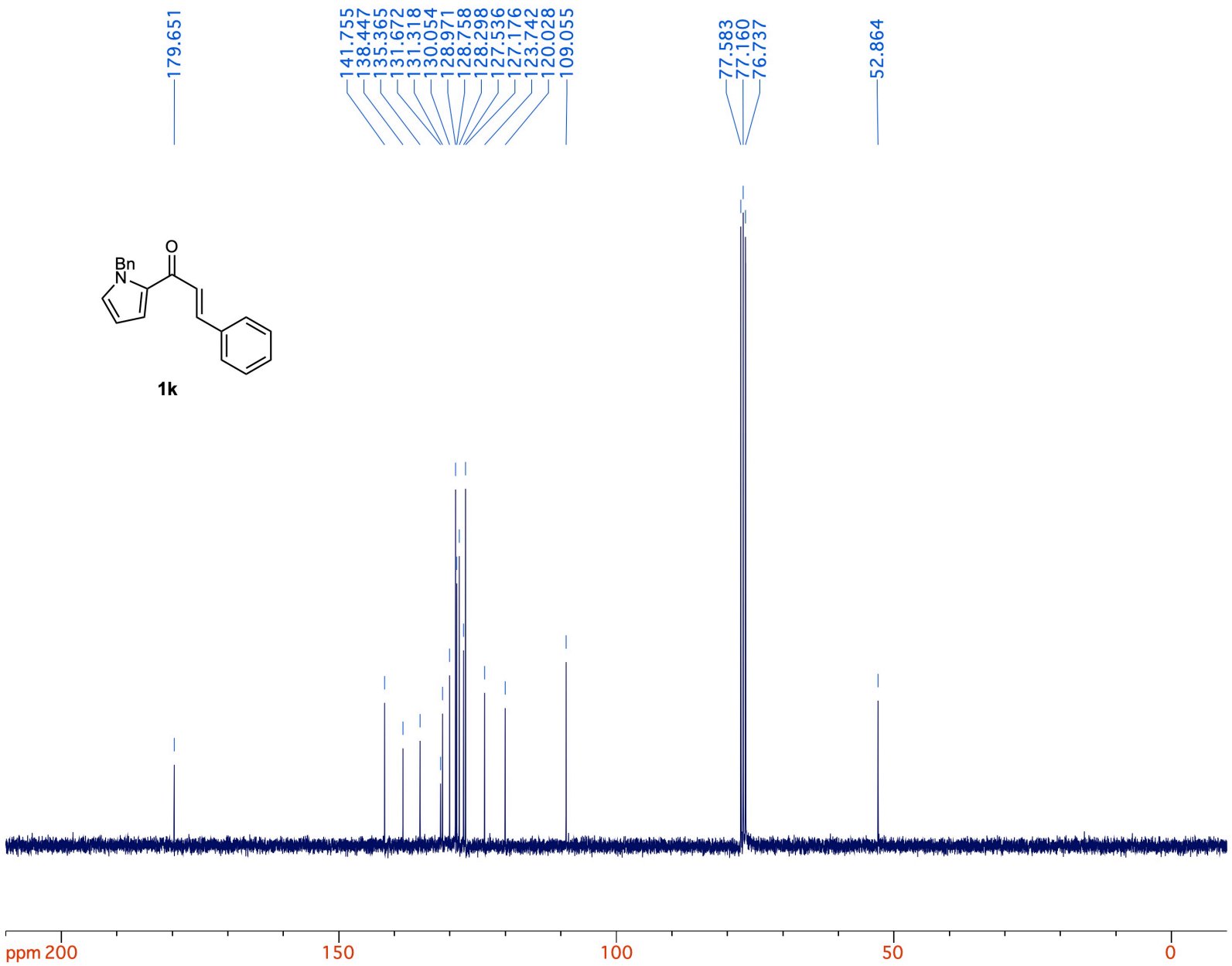

9.994
7.875
7.822
7.664
7.656
7.651
7.639
7.633
7.458
7.453
7.442
7.438
7.428
7.420
7.410
7.404
7.399
7.390
7.347
7.260
7.148
7.144
7.139
7.135
7.130
7.126
7.111
7.106
7.102
7.098
7.093
7.090
7.085
6.379
6.370
6.366
6.362
6.358
6.349
O
H
N
1j
1.04
4.11
1.02
1.03
2.1
1.04
1
ppm
10
8
6
4
2
0

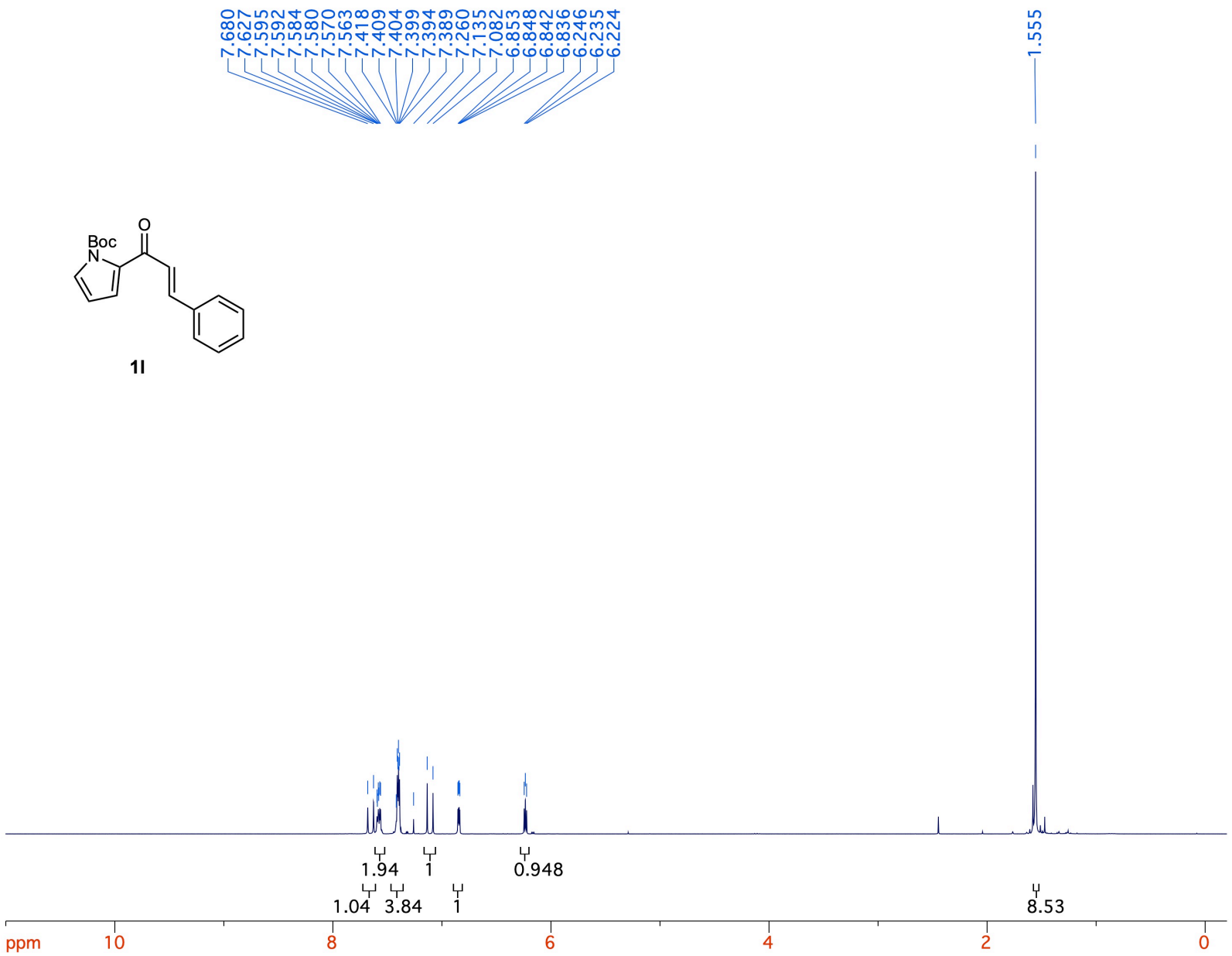

7.766
7.714
7.640
7.632
7.631
7.626
7.614
7.608
7.464
7.443
7.438
7.427
7.421
7.418
7.411
7.403
7.396
7.394
7.388
7.367
7.362
7.356
7.339
7.333
7.319
7.314
7.307
7.298
7.293
7.287
7.284
7.278
7.269
7.228
7.222
7.214
7.209
7.201
7.196
7.173
7.019
7.013
7.012
7.006
6.314
6.306
6.301
6.292
5.737


Bn
N
O

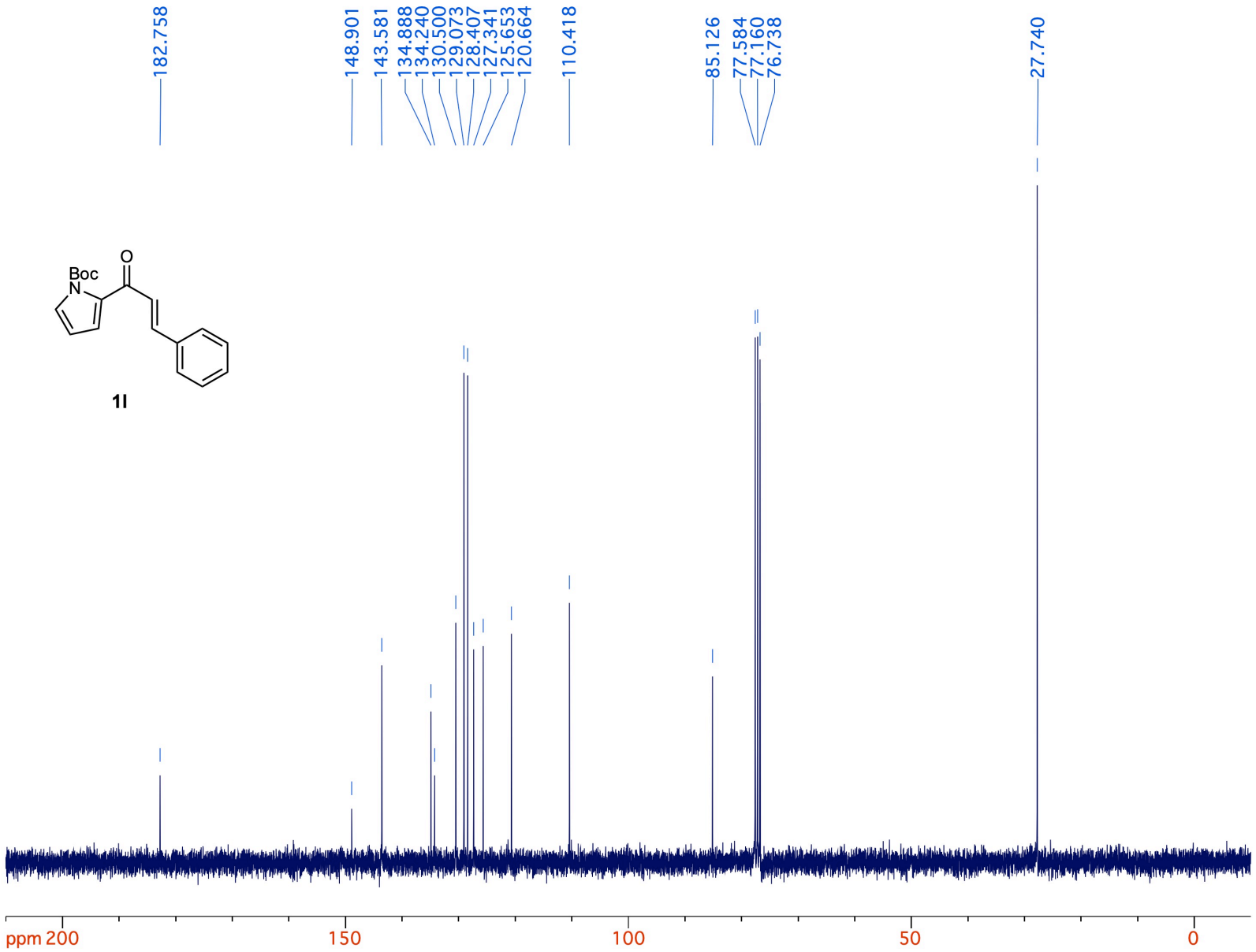
1k

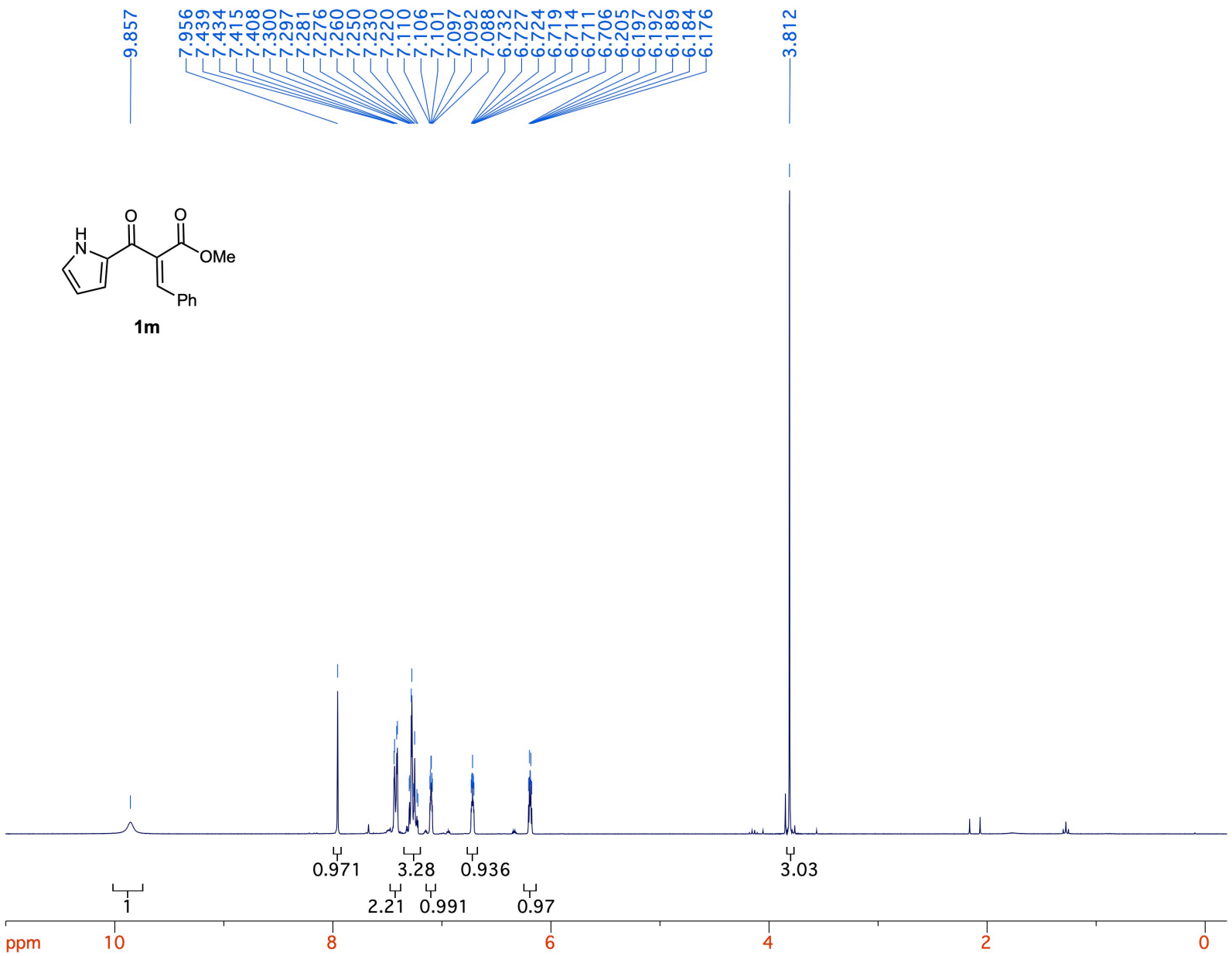
2
3.25
0.982
1.97
13.92
3.02
0.963
ppm
10
8
6
4
2
0

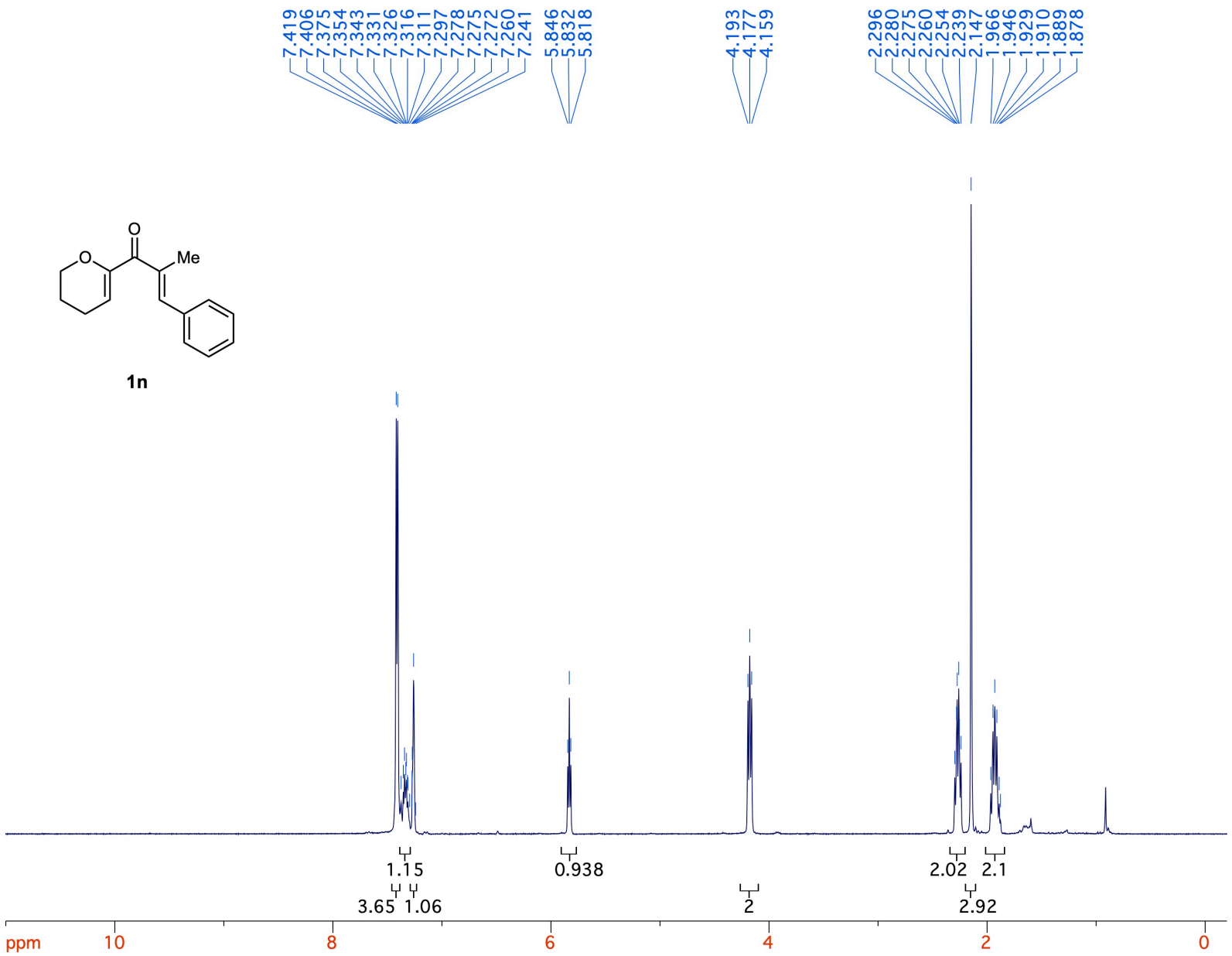

179.651
141.755
138.447
135.365
131.672
131.318
130.054
128.971
128.758
128.298
127.536
127.176
123.742
120.028
109.055
77.583
77.160
76.737
52.864
Bn
N
O
1k
ppm 200
150
100
50
0

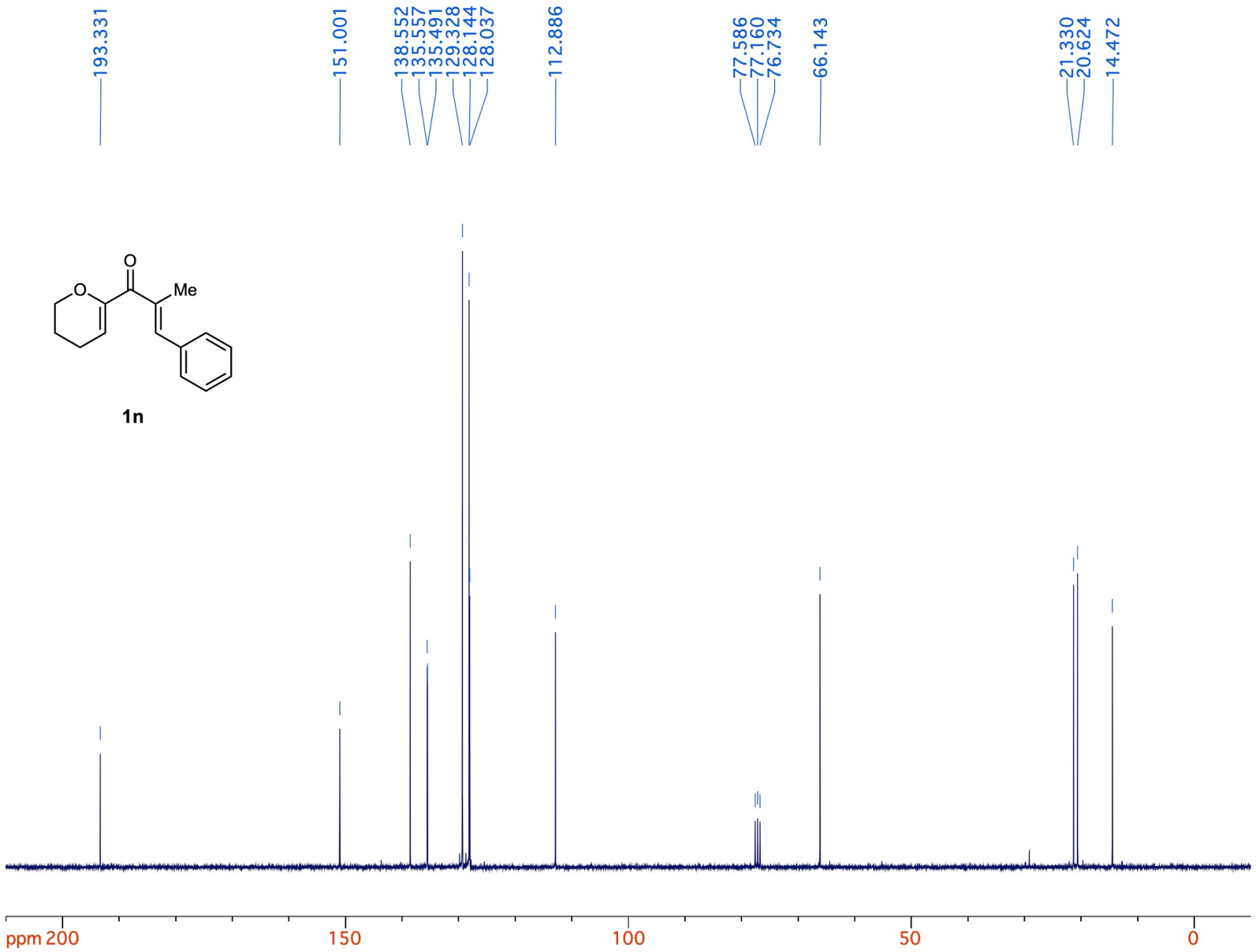

7.680
7.627
7.595
7.592
7.584
7.580
7.570
7.563
7.418
7.409
7.404
7.399
7.394
7.389
7.260
7.135
7.082
6.853
6.848
6.842
6.836
6.246
6.235
6.224
1.555
Boc
N
O
1.94
1
0.948
1.04
3.84
1
8.53
ppm
10
8
6
4
2
0

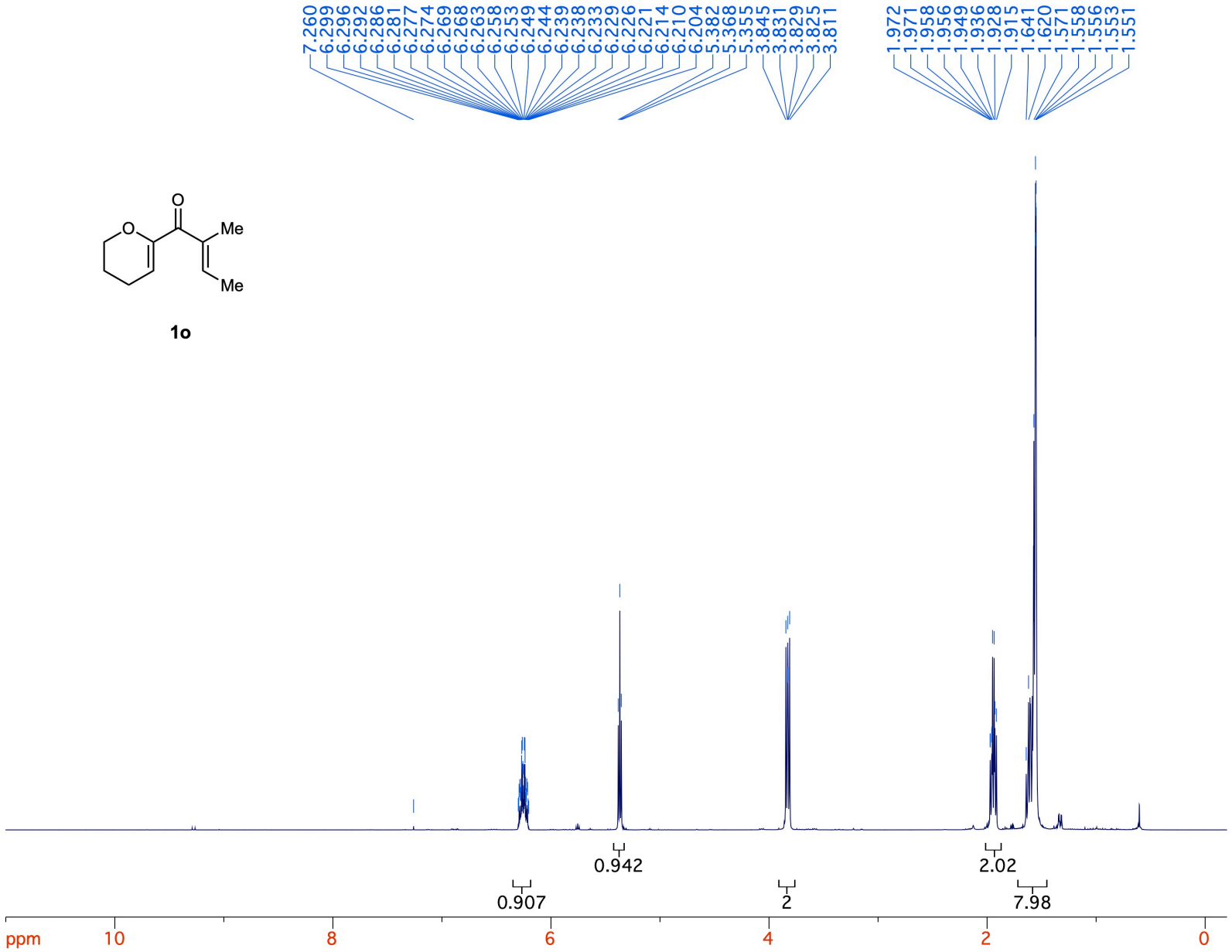
1l

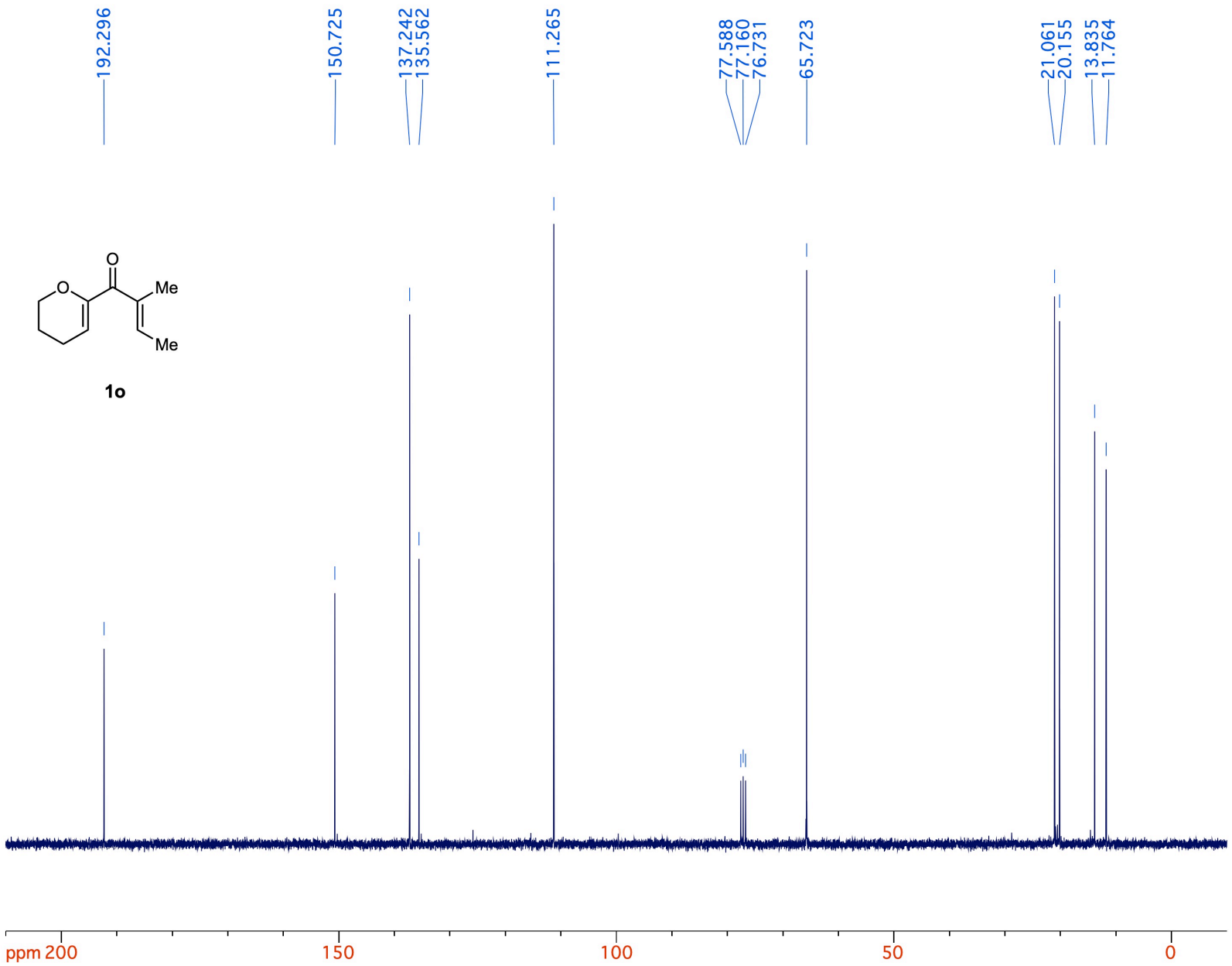

182.758
148.901
143.581
134.888
134.240
130.500
129.073
128.407
127.341
125.653
120.664
110.418
85.126
77.584
77.160
76.738
27.740
Boc
N
O
1l
ppm 200
150
100
50
0

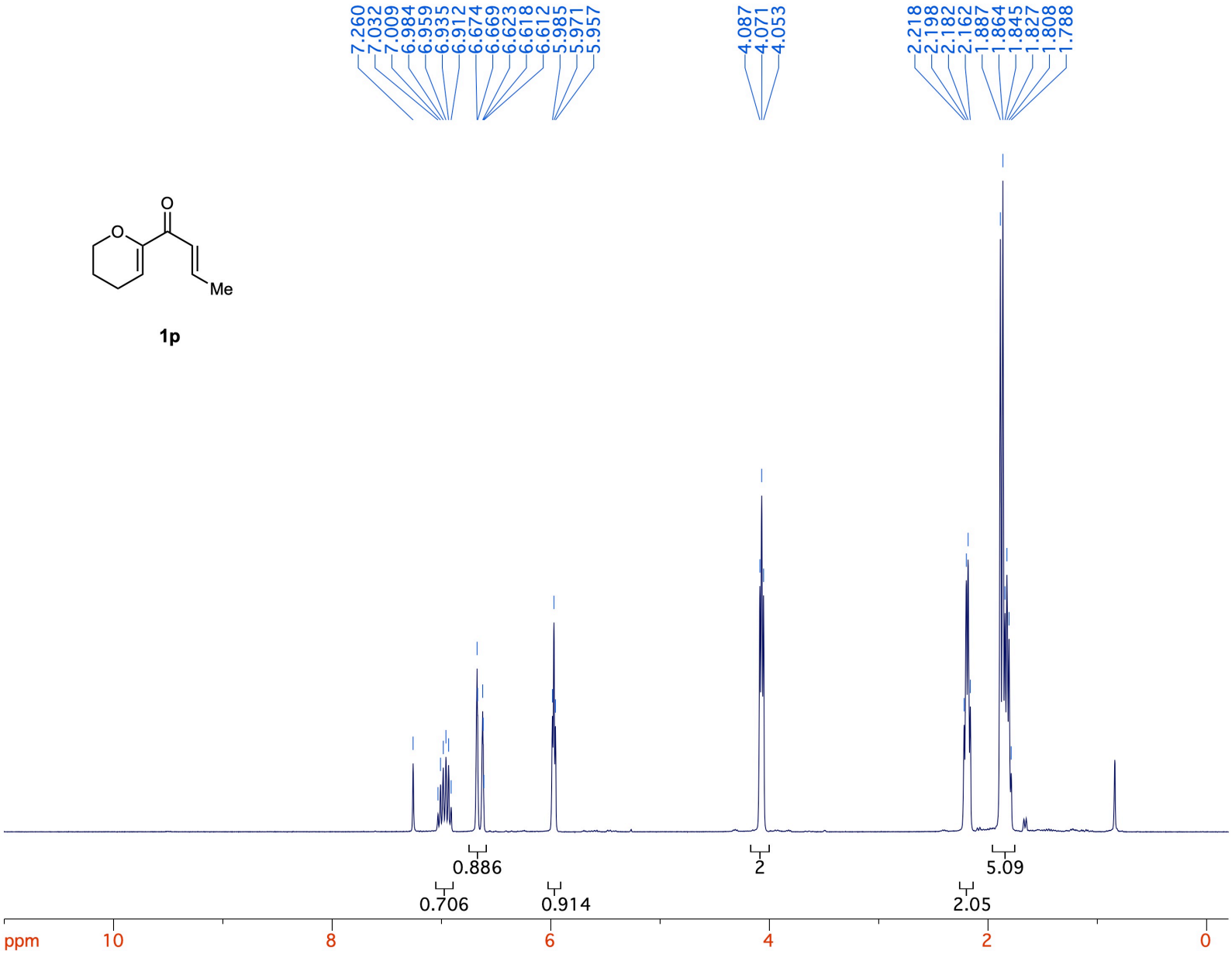

9.857
7.956
7.439
7.434
7.415
7.408
7.300
7.297
7.281
7.276
7.260
7.250
7.230
7.220
7.110
7.106
7.101
7.097
7.092
7.088
6.732
6.727
6.724
6.719
6.714
6.711
6.706
6.205
6.197
6.192
6.189
6.184
6.176
3.812
O
O
H
N
OMe
Ph
1m
0.971
3.28
0.936
3.03
1
2.21
0.991
0.97
ppm
10
8
6
4
2
0

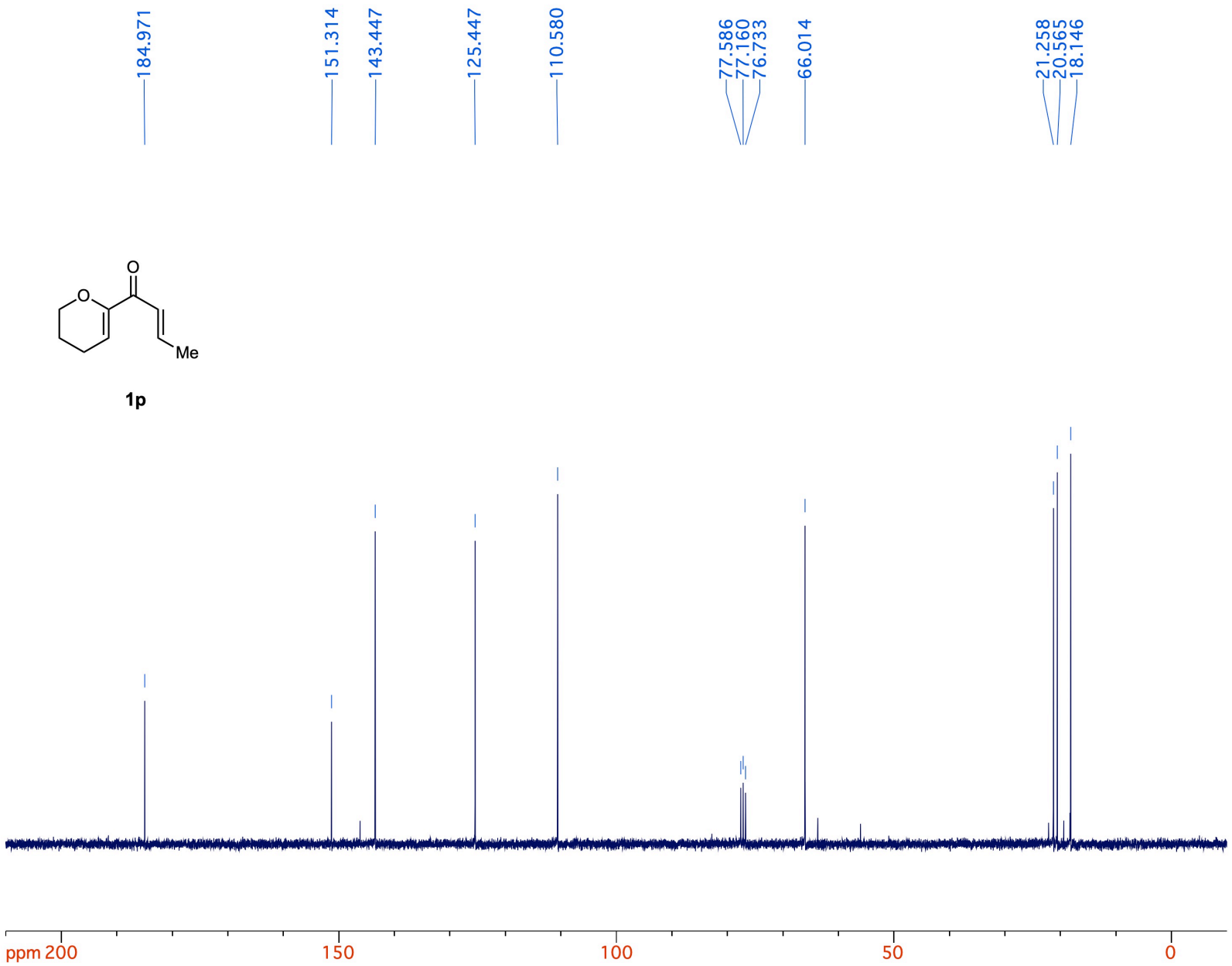

7.419
7.406
7.375
7.354
7.343
7.331
7.326
7.316
7.311
7.297
7.278
7.275
7.272
7.260
7.241
5.846
5.832
5.818
4.193
4.177
4.159
2.296
2.280
2.275
2.260
2.254
2.239
2.147
1.966
1.946
1.929
1.910
1.889
1.878
O
O
Me
1n
1.15
0.938
2.02
2.1
3.65
1.06
2
2.92
ppm
10
8
6
4
2
0

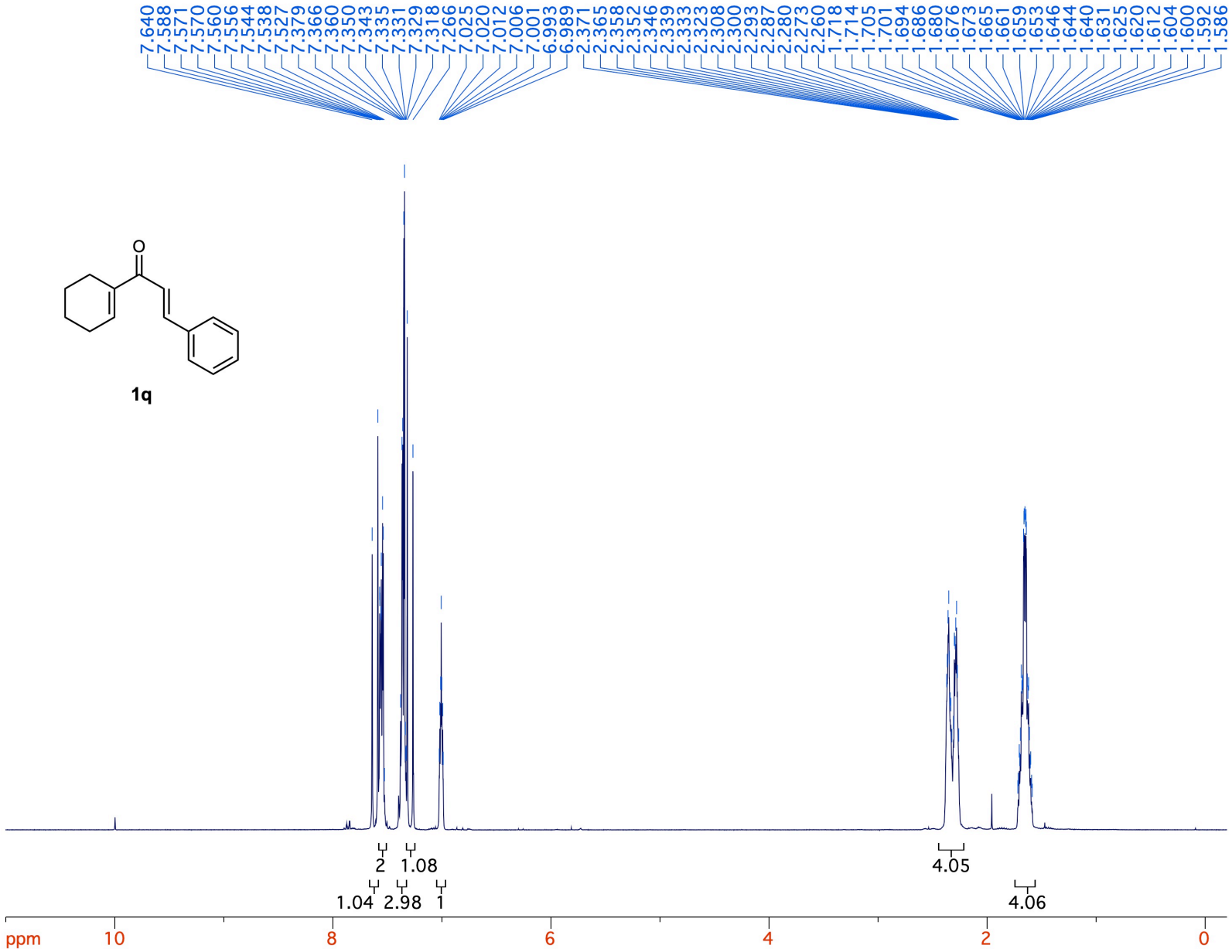

193.331
151.001
138.552
135.557
135.491
129.328
128.144
128.037
112.886
77.586
77.160
76.734
66.143
21.330
20.624
14.472
O
O
Me
1n
ppm 200
150
100
50
0

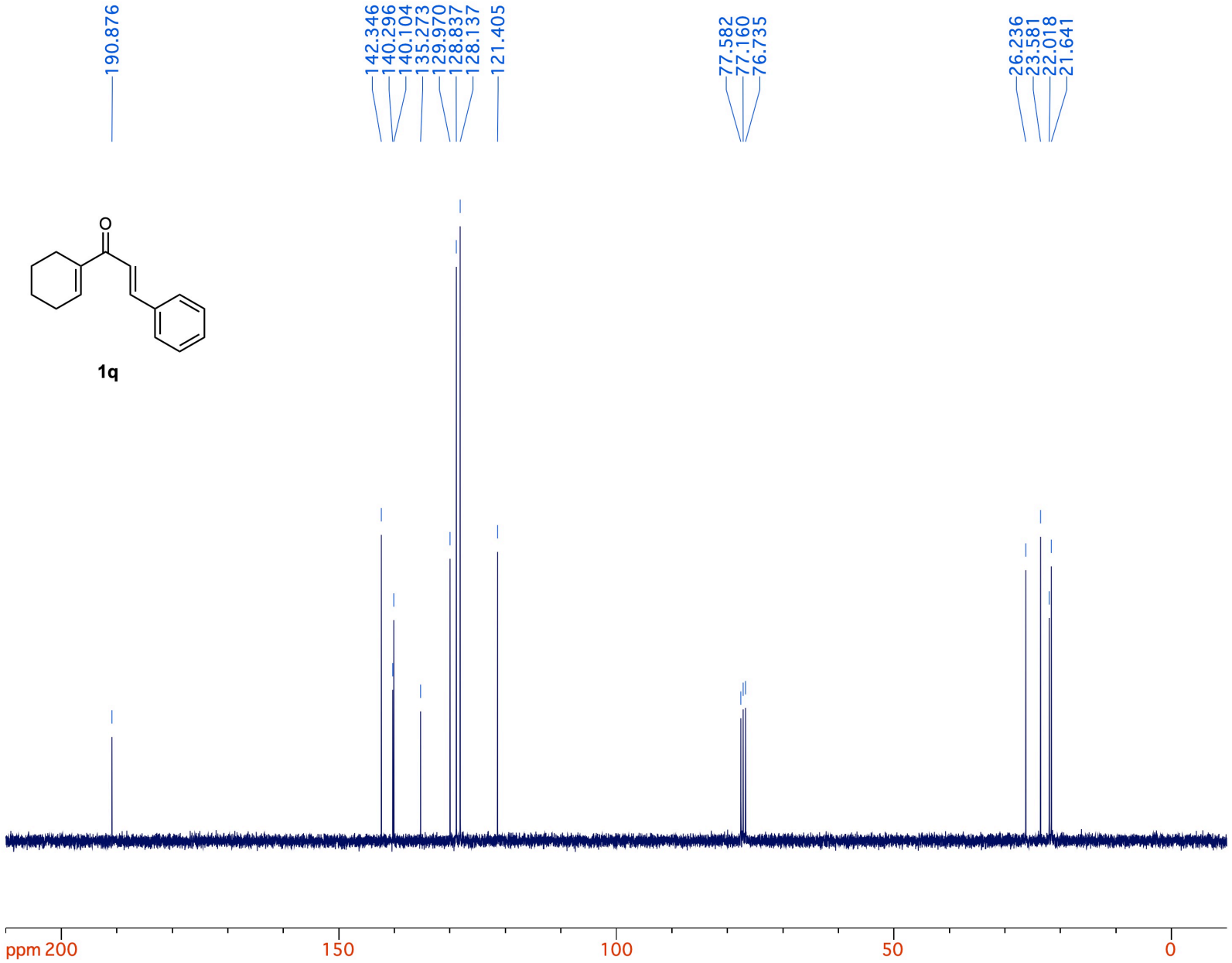

7.260
6.299
6.296
6.292
6.286
6.281
6.277
6.274
6.269
6.268
6.263
6.258
6.253
6.249
6.244
6.239
6.238
6.233
6.229
6.226
6.221
6.214
6.210
6.204
5.382
5.368
5.355
3.845
3.831
3.829
3.825
3.811
1.972
1.971
1.958
1.956
1.949
1.936
1.928
1.915
1.641
1.620
1.571
1.558
1.556
1.553
1.551
O
O
Me
Me
1o
0.942
2.02
0.907
2
7.98
ppm
10
8
6
4
2
0

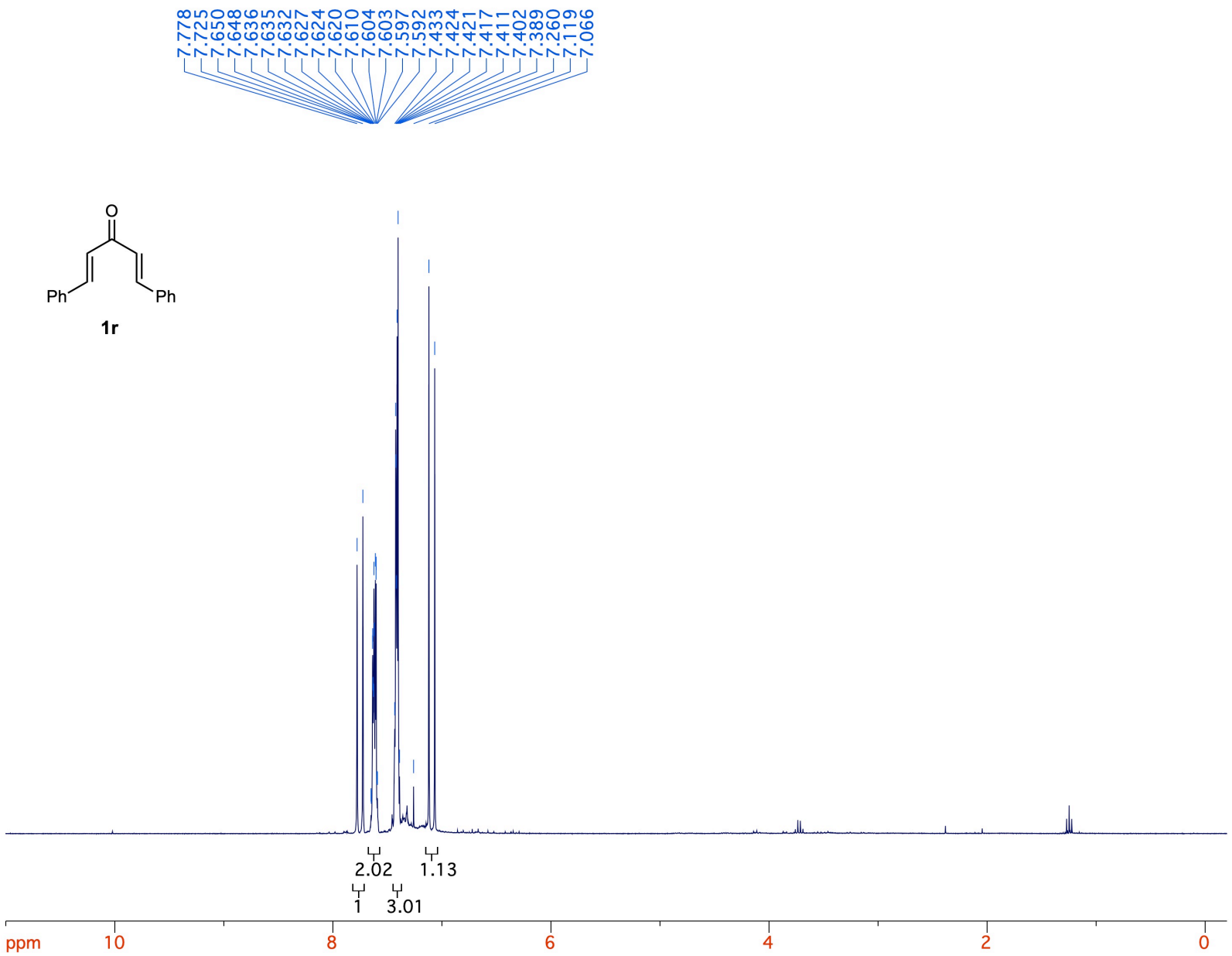

192.296
150.725
137.242
135.562
111.265
77.588
77.160
76.731
65.723
21.061
20.155
13.835
11.764
O
O
Me
Me
1o
ppm 200
150
100
50
0

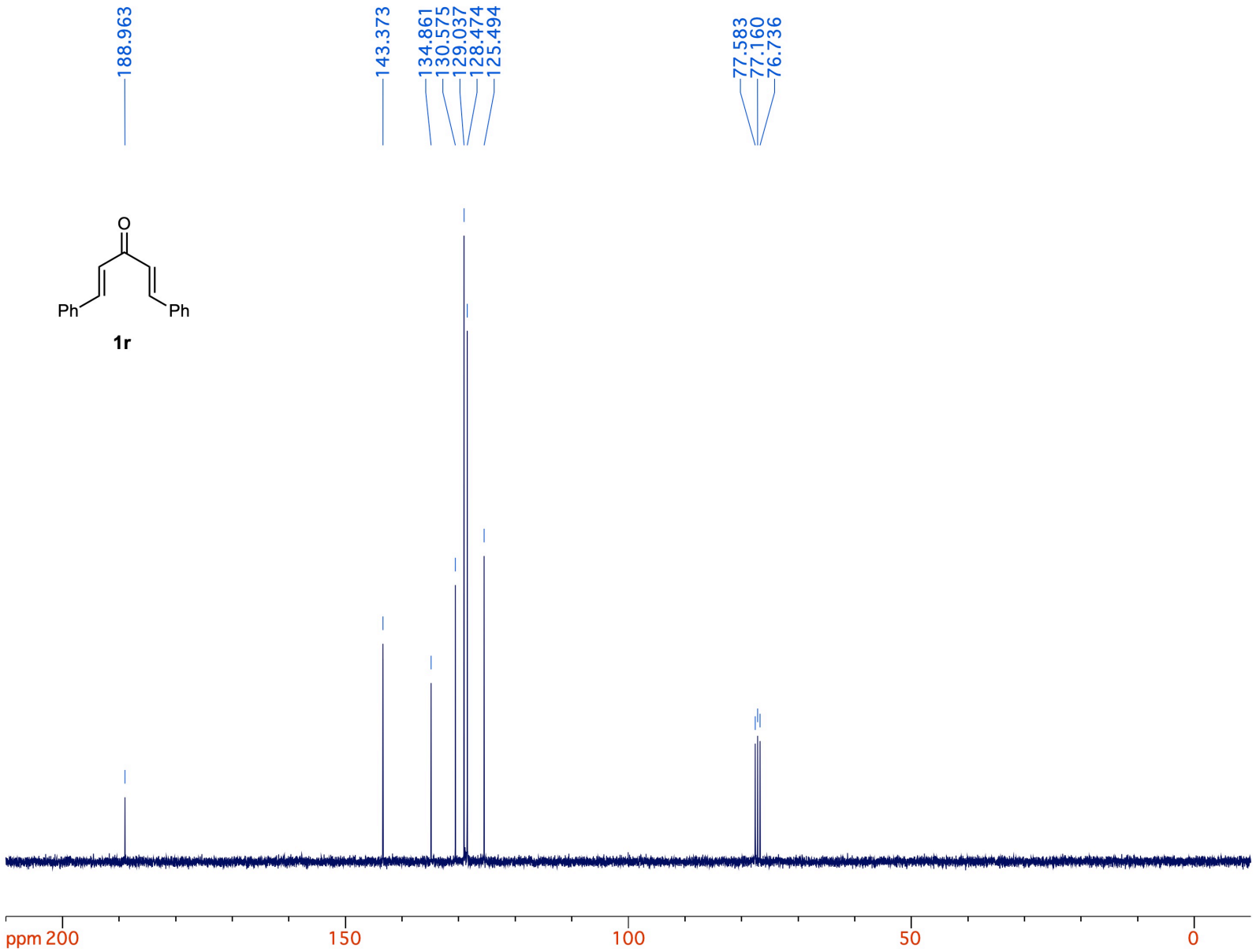

7.260
7.032
7.009
6.984
6.959
6.935
6.912
6.674
6.669
6.623
6.618
6.612
5.985
5.971
5.957
4.087
4.071
4.053
2.218
2.198
2.182
2.162
1.887
1.864
1.845
1.827
1.808
1.788
O
O
Me
1p
0.886
2
5.09
0.706
0.914
2.05
ppm
10
8
6
4
2
0

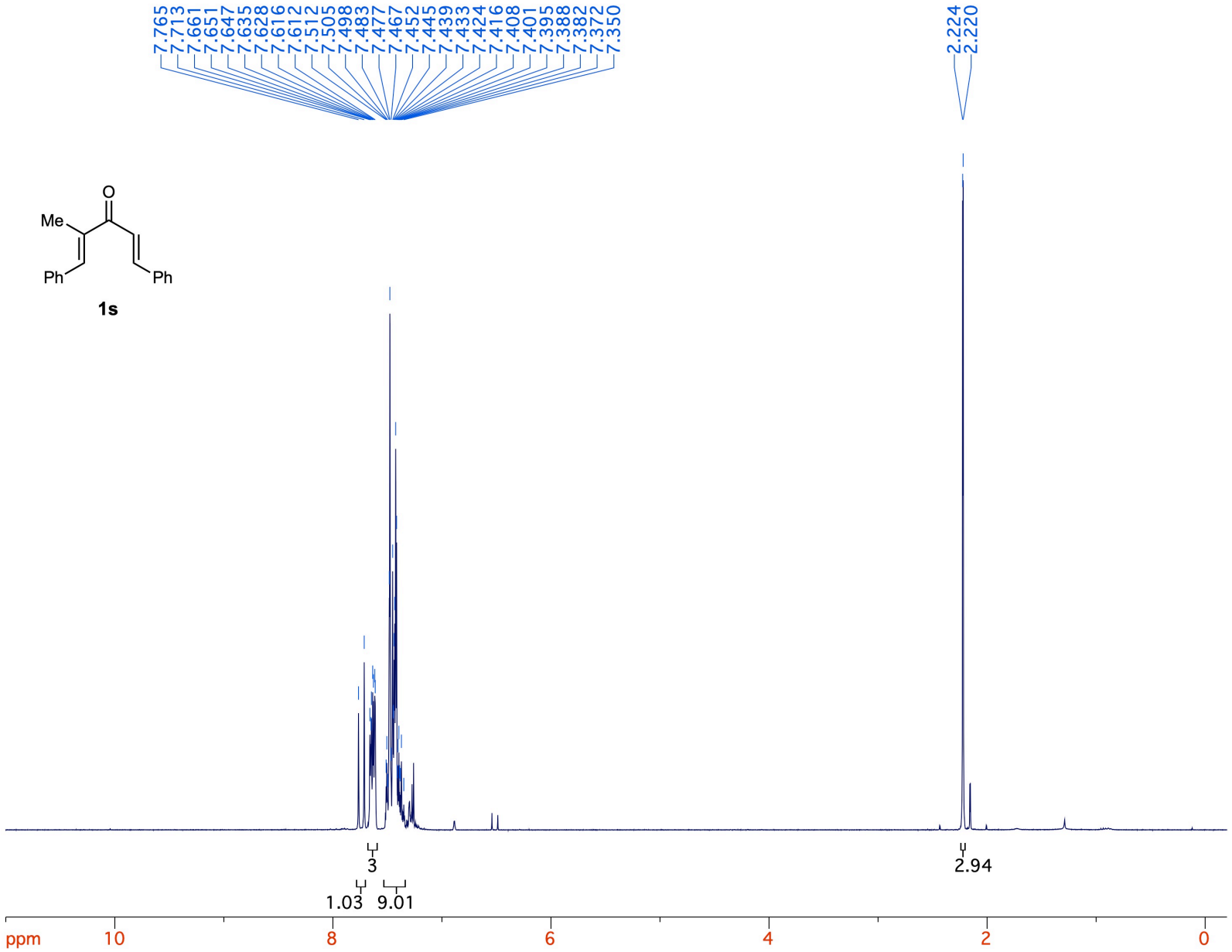

184.971
151.314
143.447
125.447
110.580
77.586
77.160
76.733
66.014
21.258
20.565
18.146
O
O
Me
1p
ppm 200
150
100
50
0

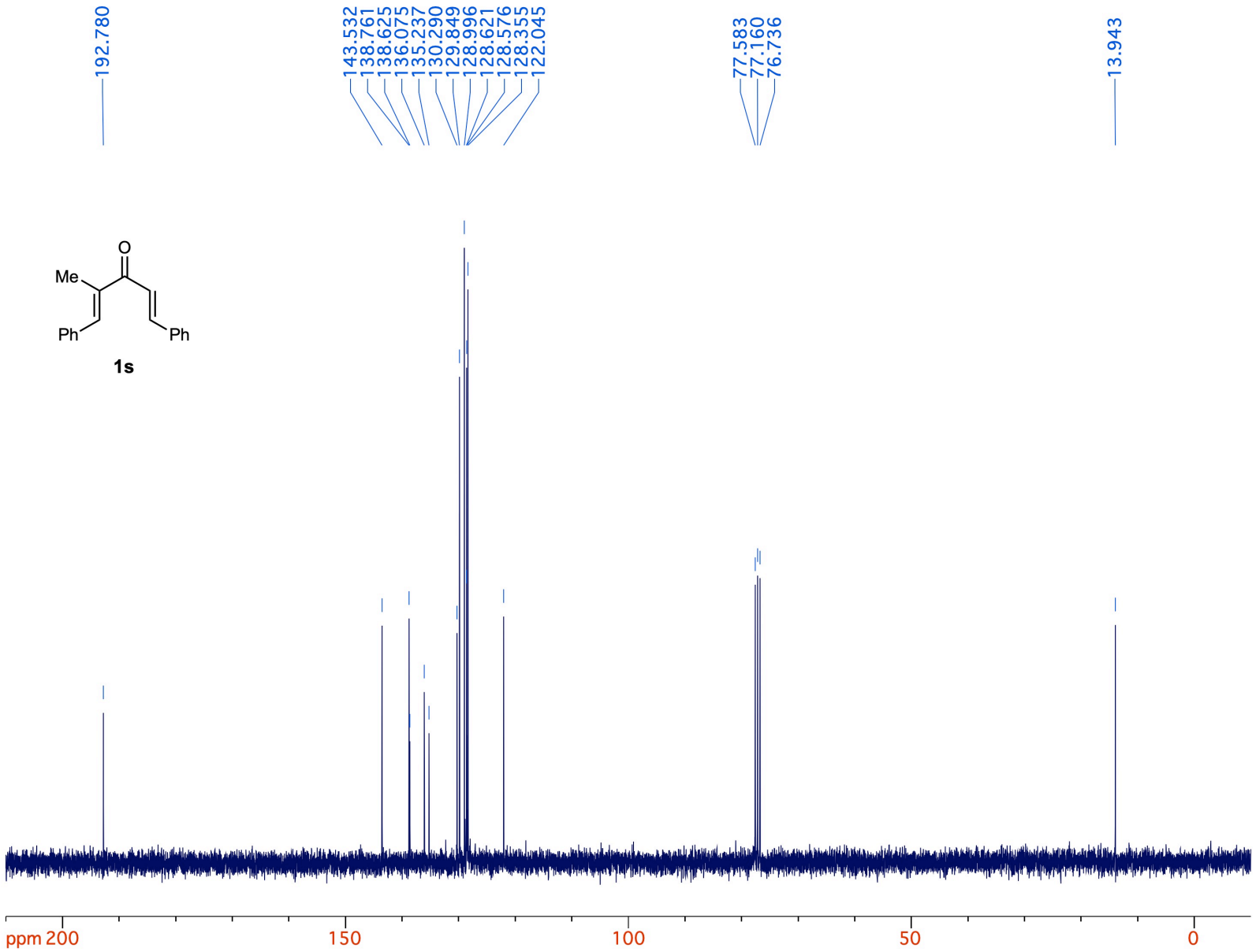

7.640
7.588
7.571
7.570
7.560
7.556
7.544
7.538
7.527
7.379
7.366
7.360
7.350
7.343
7.335
7.331
7.329
7.318
7.266
7.025
7.020
7.012
7.006
7.001
6.993
6.989
2.371
2.365
2.358
2.352
2.346
2.339
2.333
2.323
2.308
2.300
2.293
2.287
2.280
2.273
2.260
1.718
1.714
1.705
1.701
1.694
1.686
1.680
1.676
1.673
1.665
1.661
1.659
1.653
1.646
1.644
1.640
1.631
1.625
1.620
1.612
1.604
1.600
1.592
1.586
O
1q
2
1.08
4.05
1.04
2.98
1
4.06
ppm
10
8
6
4
2
0

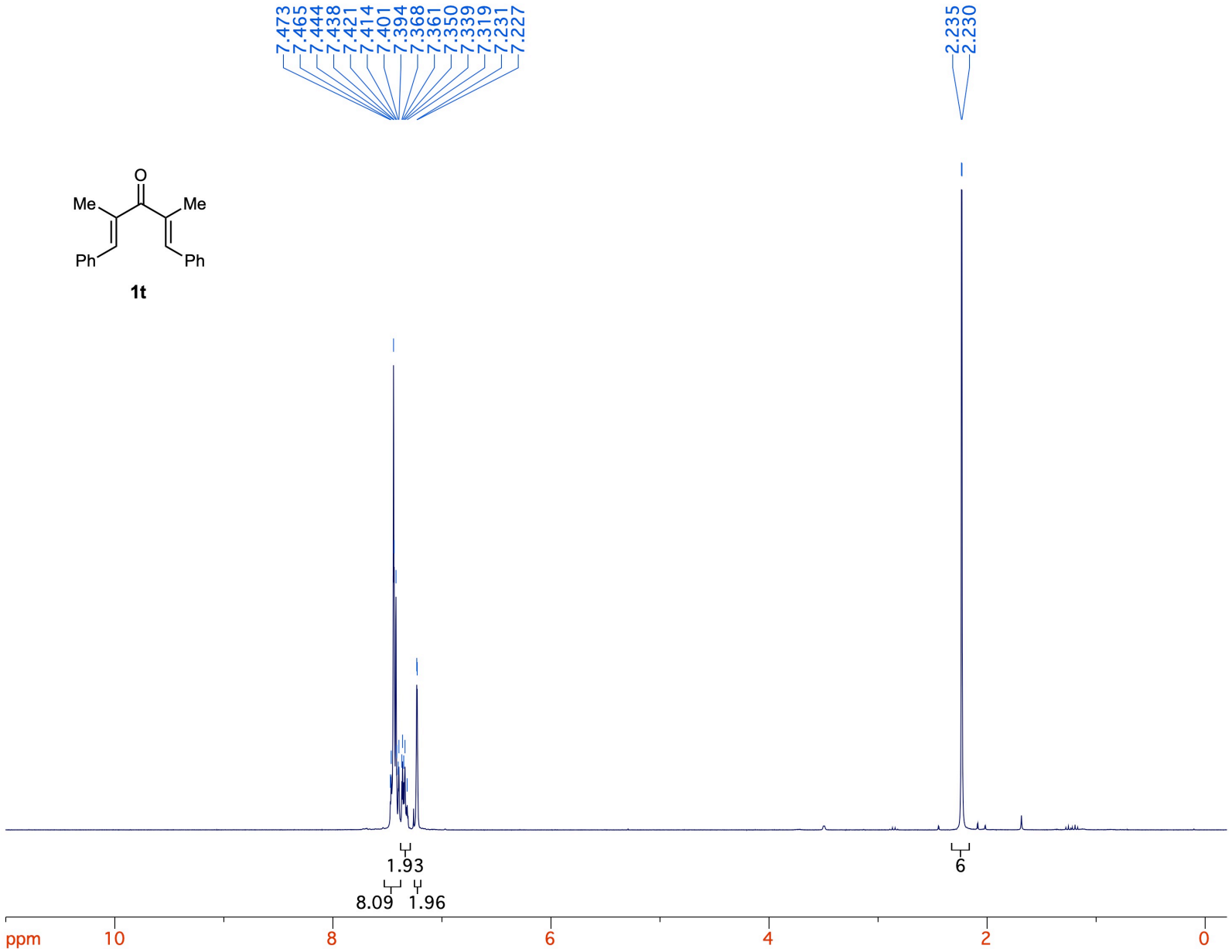

190.876
142.346
140.296
140.104
135.273
129.970
128.837
128.137
121.405
77.582
77.160
76.735
26.236
23.581
22.018
21.641
O
1q
ppm 200
150
100
50
0

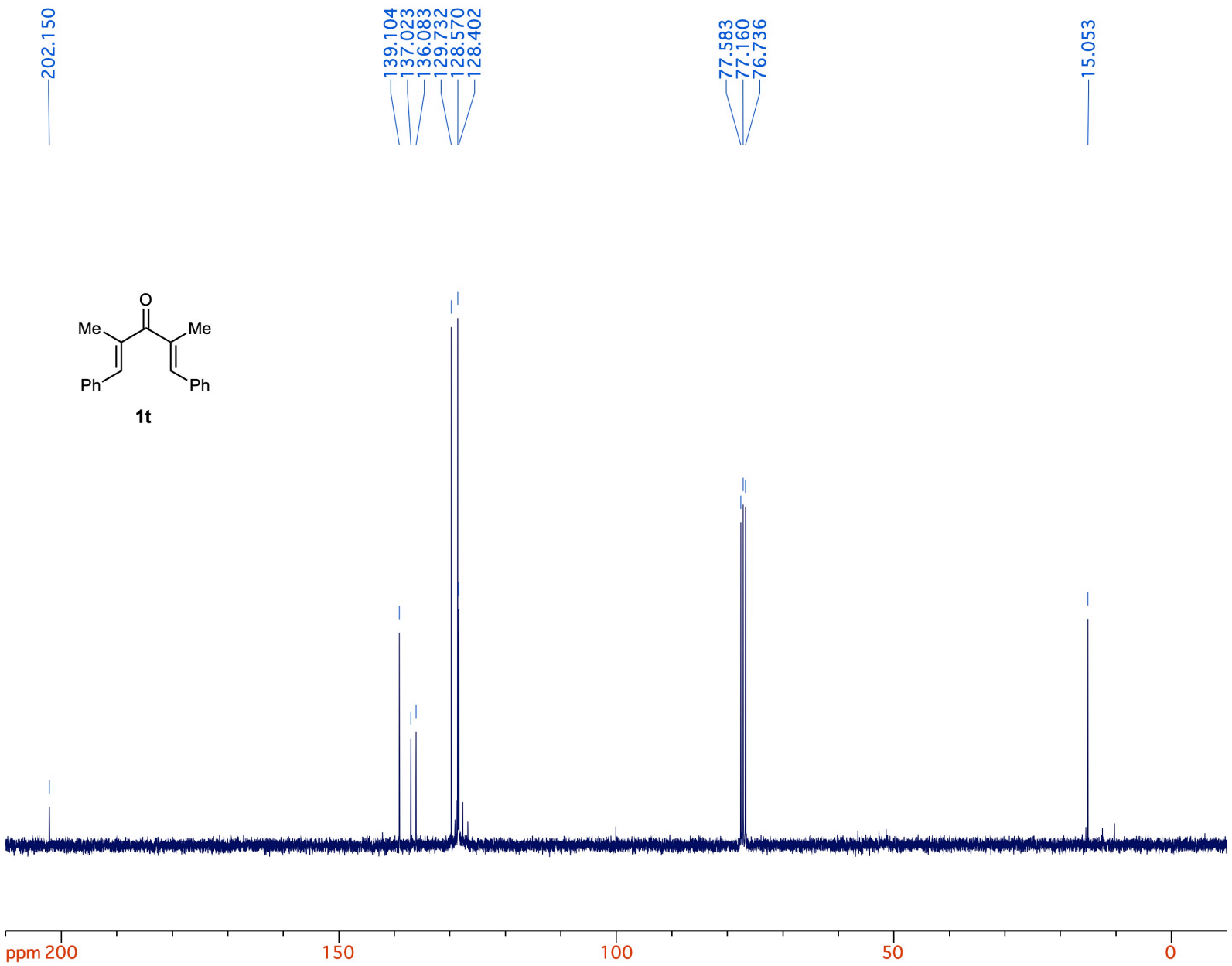

7.778
7.725
7.650
7.648
7.636
7.635
7.632
7.627
7.624
7.620
7.610
7.604
7.603
7.597
7.592
7.433
7.424
7.421
7.417
7.411
7.402
7.389
7.260
7.119
7.066
O
Ph
Ph
1r
2.02
1.13
1
3.01
ppm
10
8
6
4
2
0

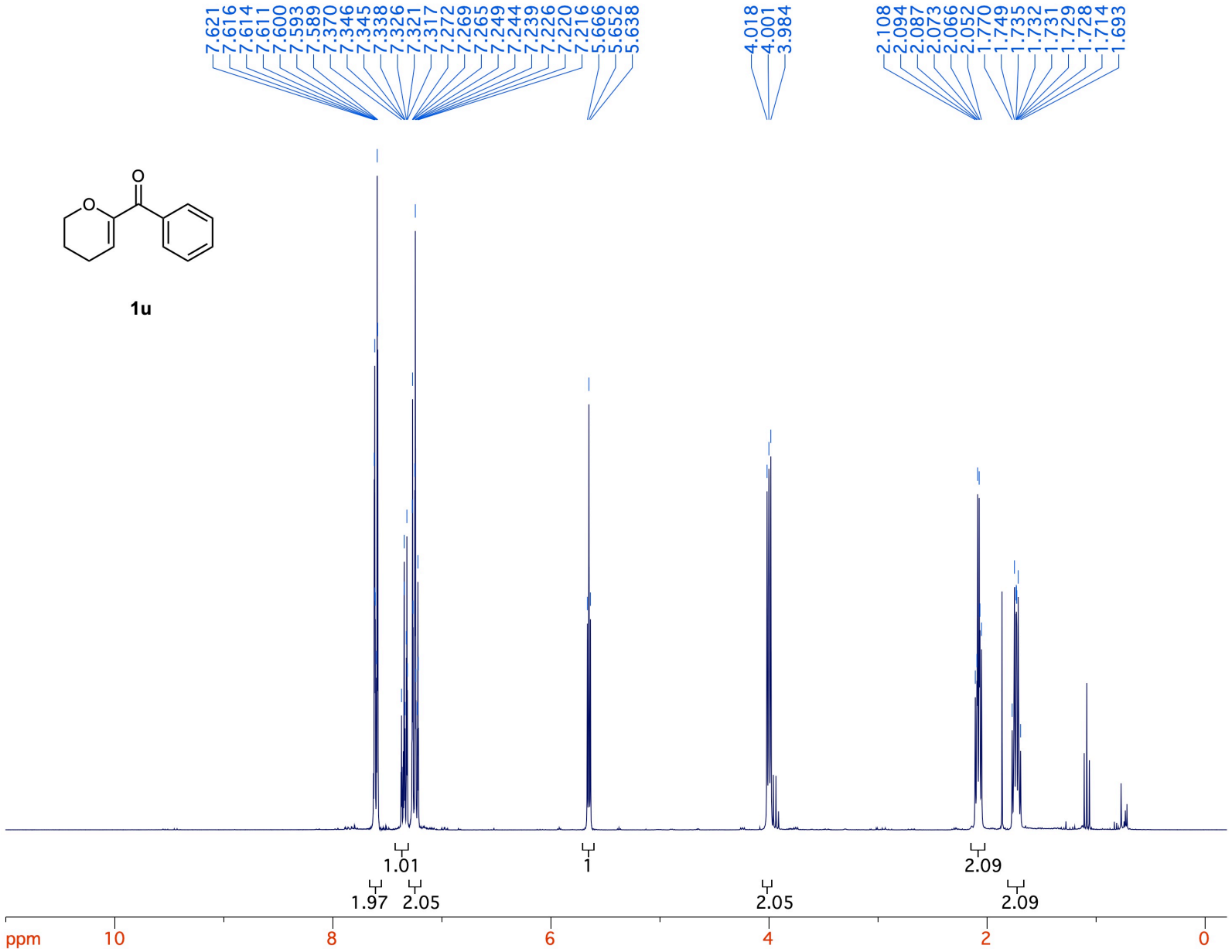

188.963
143.373
134.861
130.575
129.037
128.474
125.494
77.583
77.160
76.736
O
Ph
Ph
1r
ppm 200
150
100
50
0

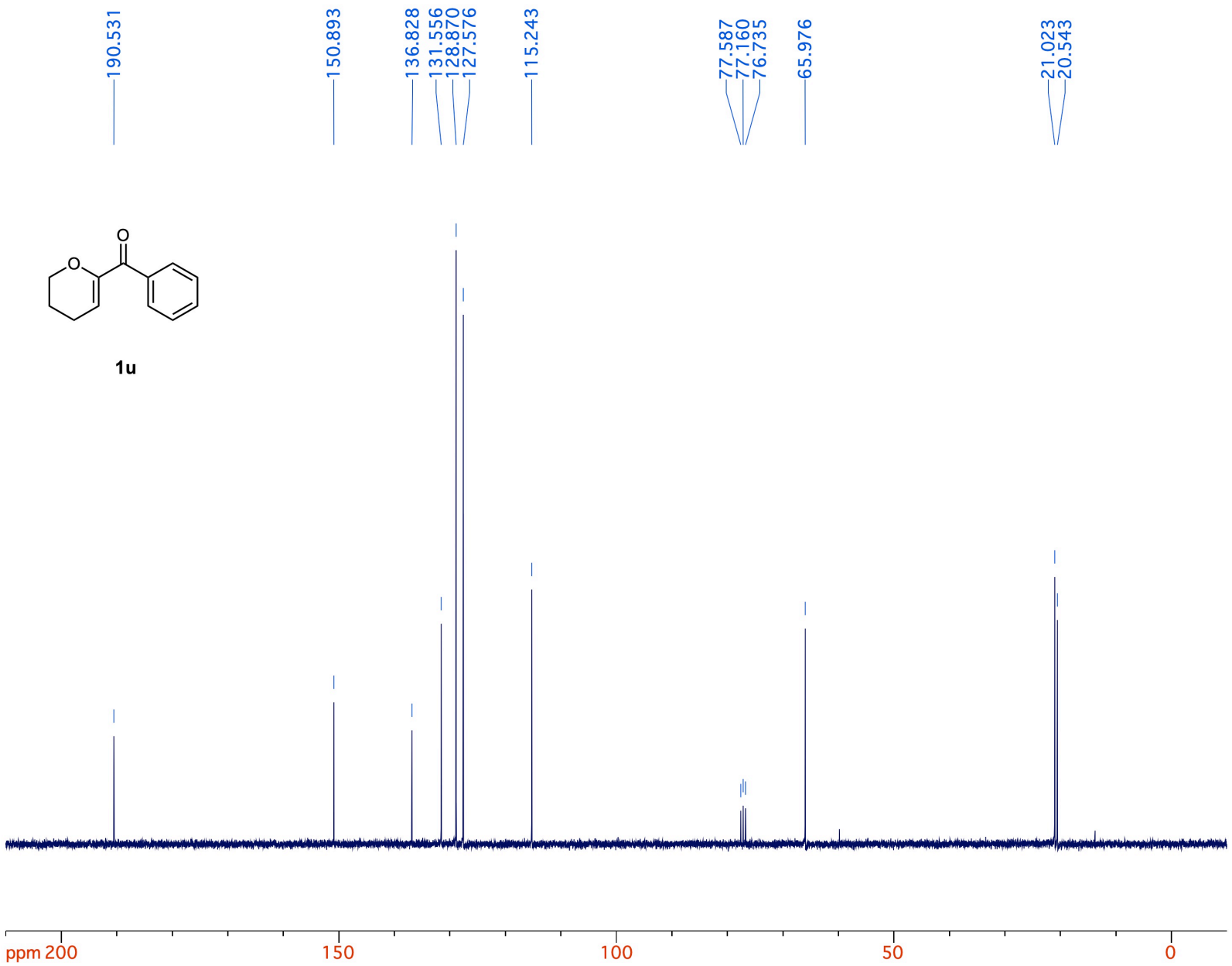

7.765
7.713
7.661
7.651
7.647
7.635
7.628
7.616
7.612
7.512
7.505
7.498
7.483
7.477
7.467
7.452
7.445
7.439
7.433
7.424
7.416
7.408
7.401
7.395
7.388
7.382
7.372
7.350
2.224
2.220
O
Me
Ph
Ph
1s
3
1.03
9.01
2.94
ppm
10
8
6
4
2
0

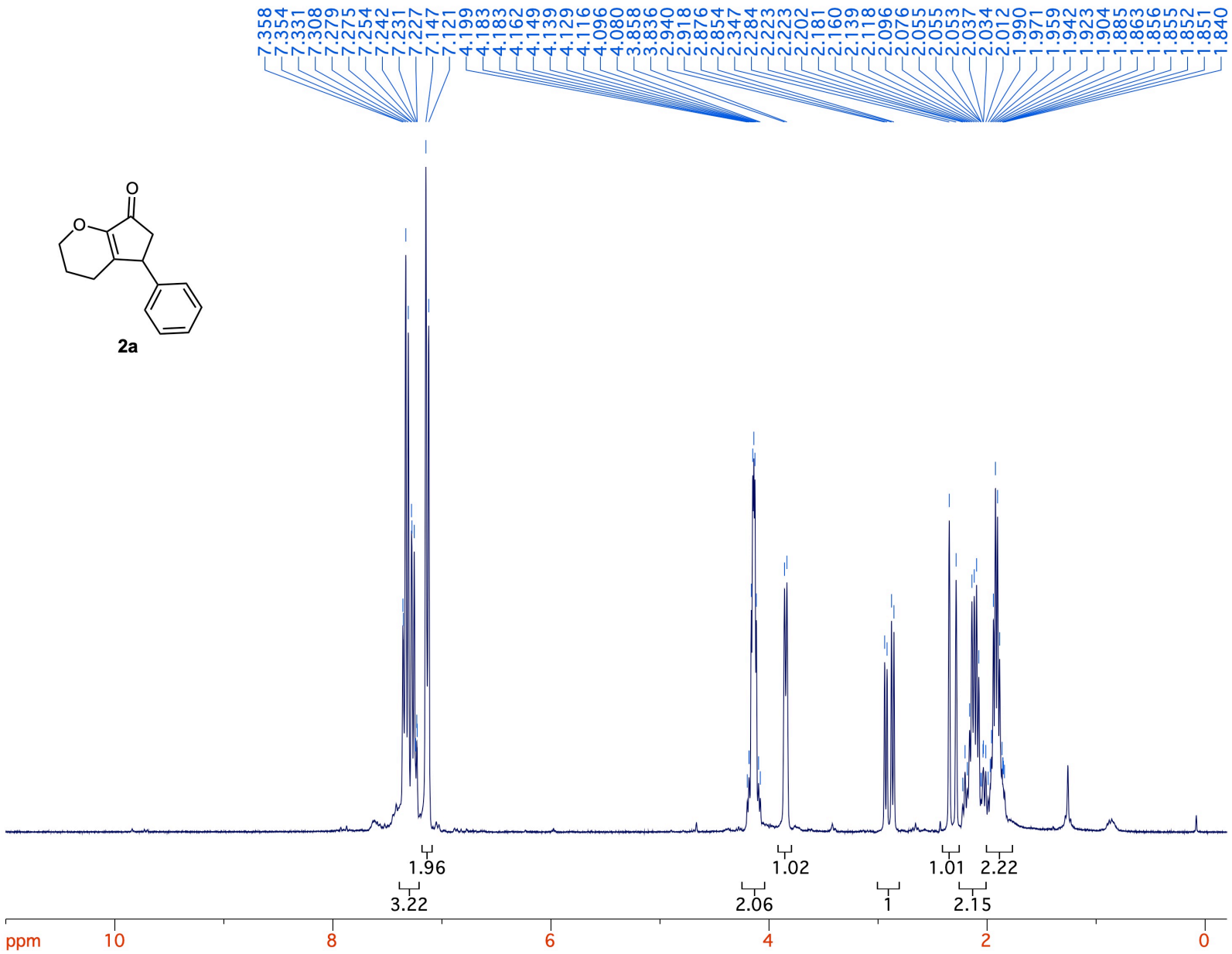

192.780
143.532
138.761
138.625
136.075
135.237
130.290
129.849
128.996
128.621
128.576
128.355
122.045
77.583
77.160
76.736
13.943
O
Me
Ph
Ph
1s
ppm 200
150
100
50
0

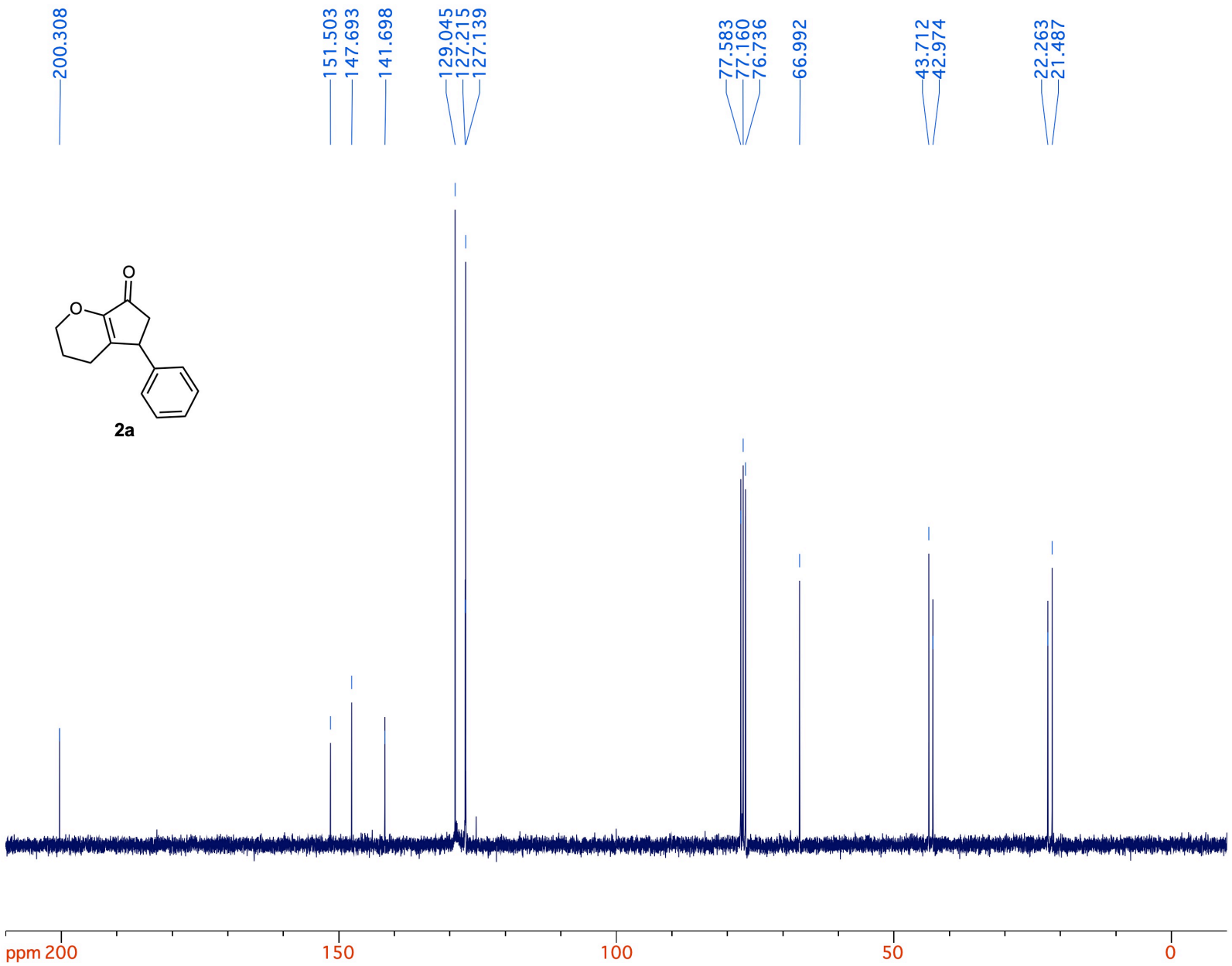

7.473
7.465
7.444
7.438
7.421
7.414
7.401
7.394
7.368
7.361
7.350
7.339
7.319
7.231
7.227
2.235
2.230
O
Me
Me
Ph
Ph
1t
1.93
8.09
1.96
6
ppm
10
8
6
4
2
0

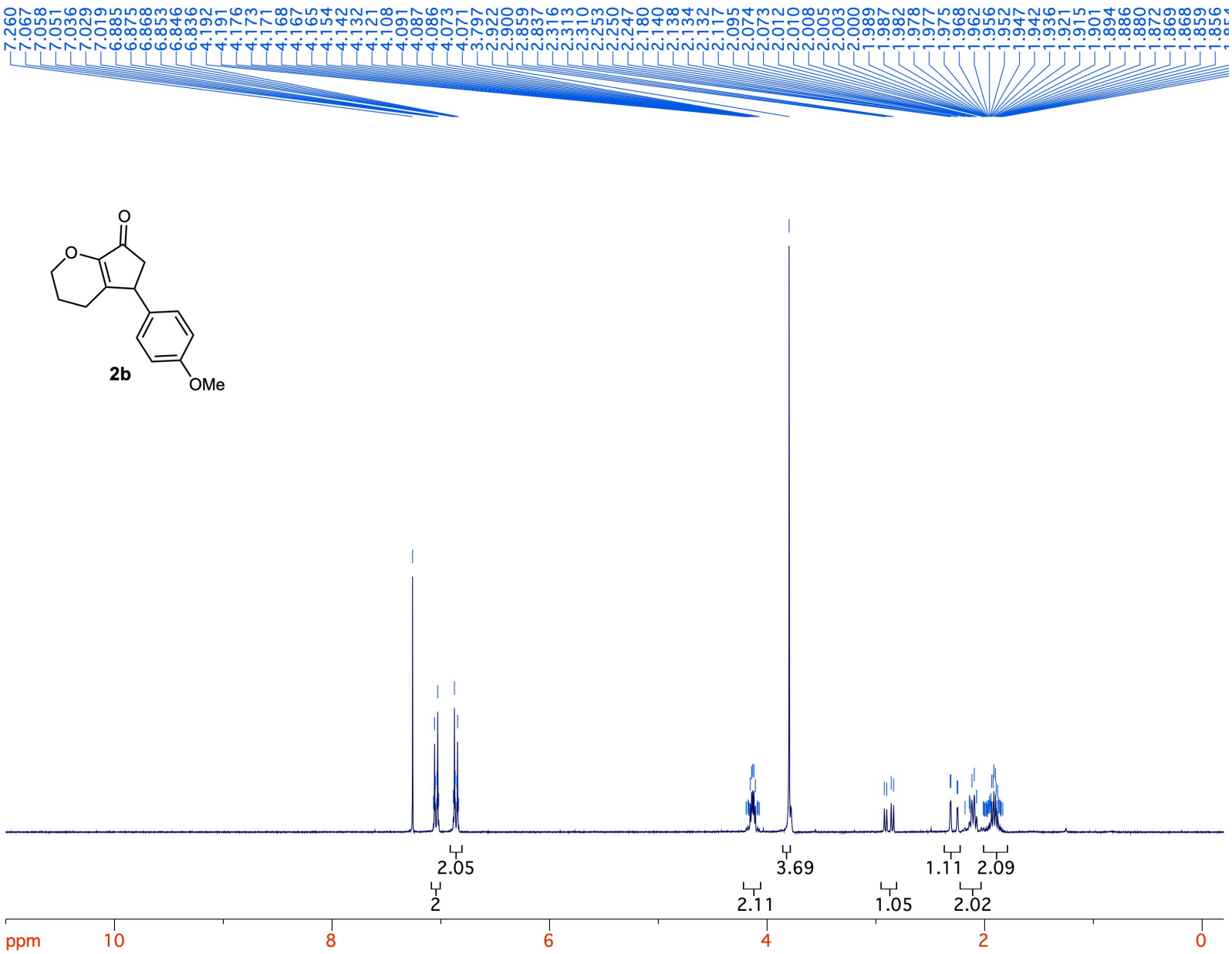

202.150
139.104
137.023
136.083
129.732
128.570
128.402
77.583
77.160
76.736
15.053
O
Me
Me
Ph
Ph
1t
ppm 200
150
100
50
0

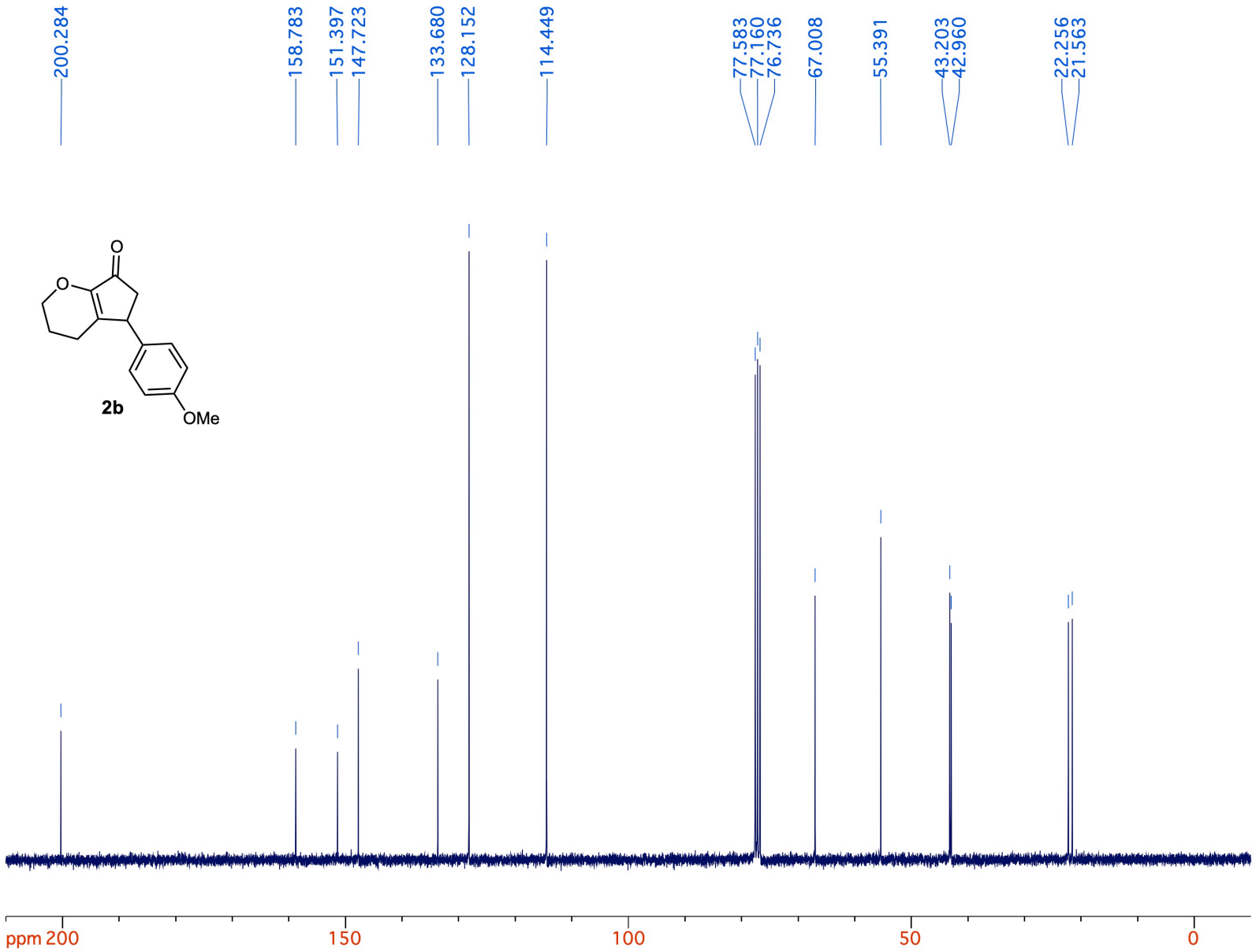

7.621
7.616
7.614
7.611
7.600
7.593
7.589
7.370
7.346
7.345
7.338
7.326
7.321
7.317
7.272
7.269
7.265
7.249
7.244
7.239
7.226
7.220
7.216
5.666
5.652
5.638
4.018
4.001
3.984
2.108
2.094
2.087
2.073
2.066
2.052
1.770
1.749
1.735
1.732
1.731
1.729
1.728
1.714
1.693
O
O
1u
1.01
1
2.09
1.97
2.05
2.05
2.09
ppm
10
8
6
4
2
0

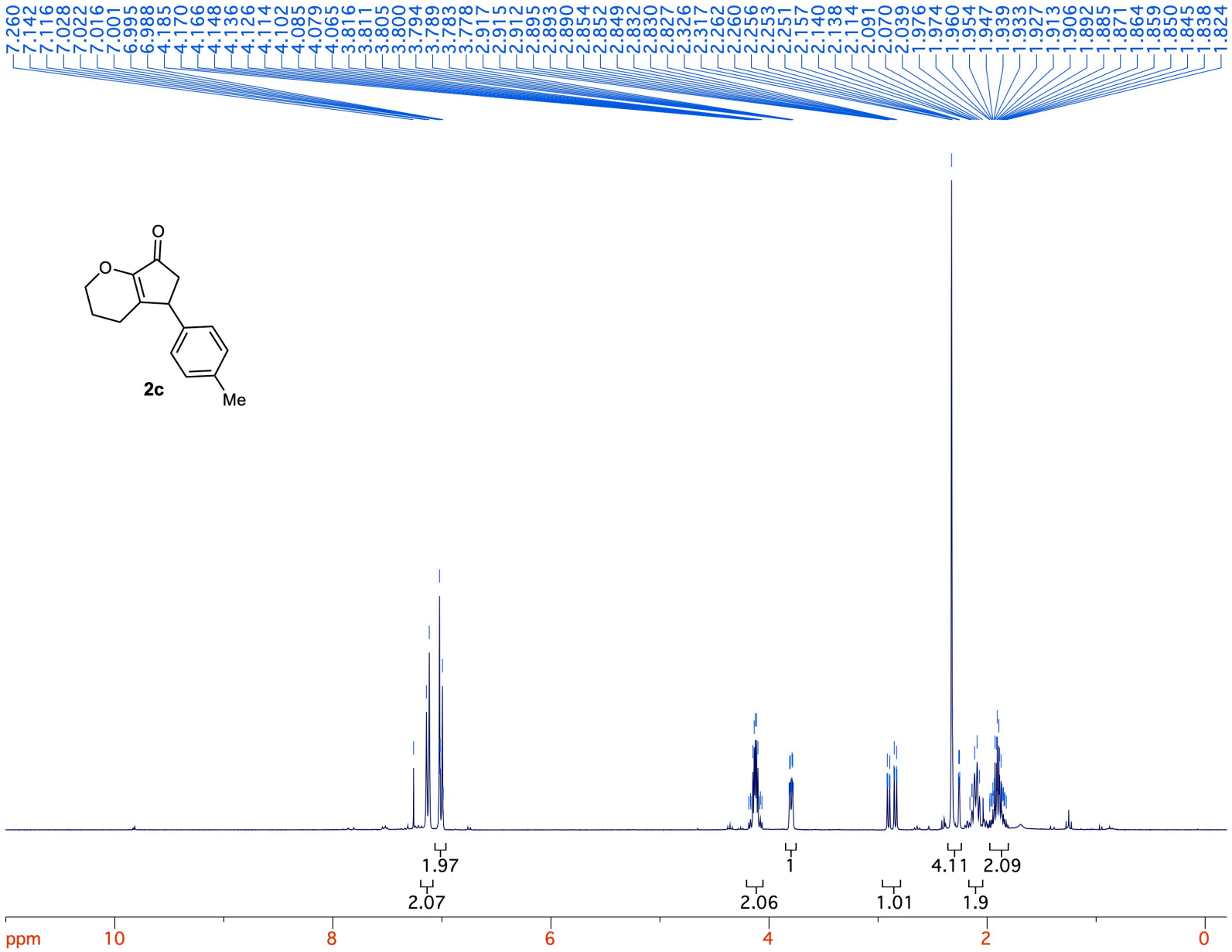

190.531
150.893
136.828
131.556
128.870
127.576
115.243
77.587
77.160
76.735
65.976
21.023
20.543
O
O
1u
ppm 200
150
100
50
0

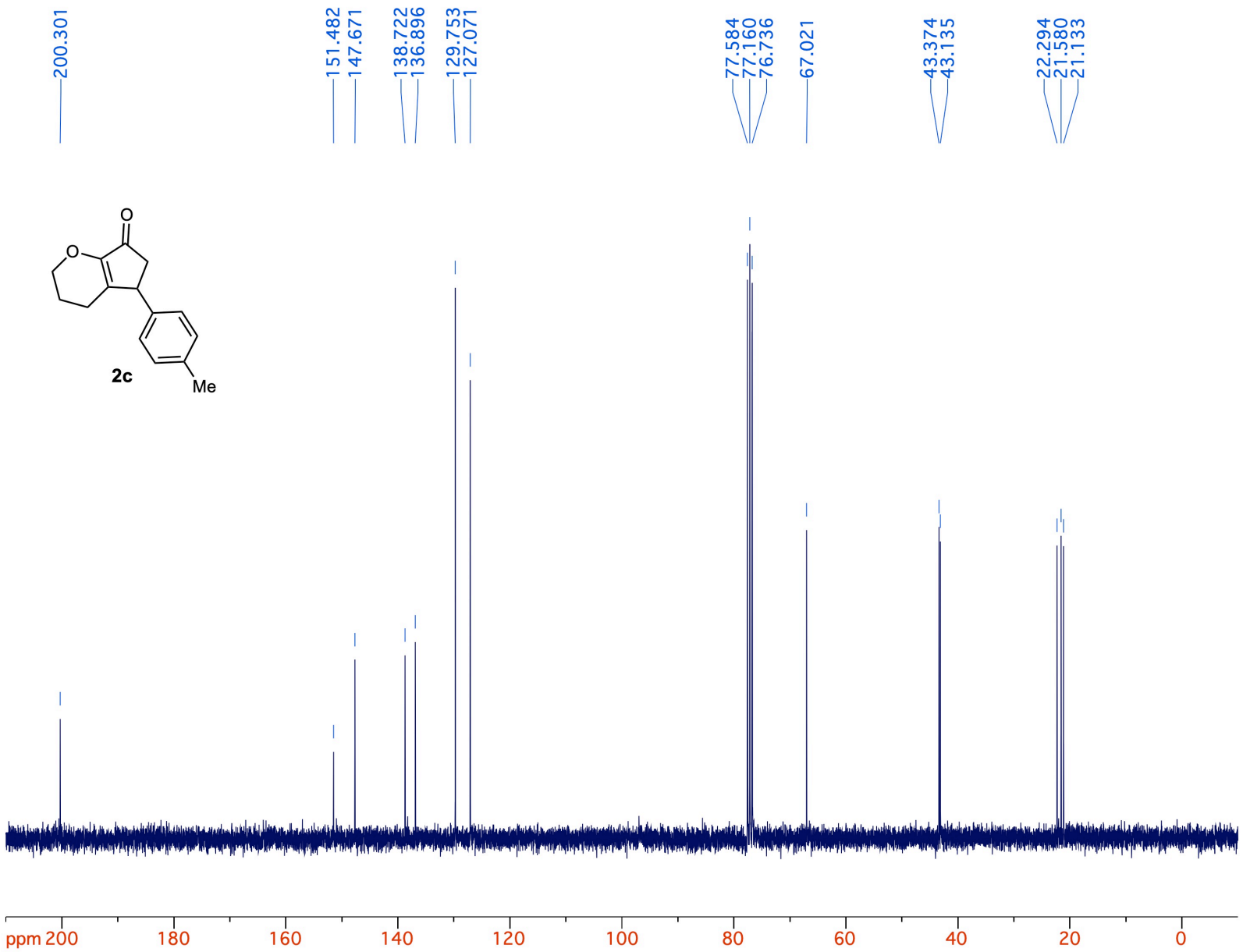

7.358
7.354
7.331
7.308
7.279
7.275
7.254
7.242
7.231
7.227
7.147
7.121
4.199
4.183
4.162
4.149
4.139
4.129
4.116
4.096
4.080
3.858
3.836
3.940
2.918
2.876
2.854
2.347
2.284
2.223
2.223
2.202
2.181
2.160
2.139
2.118
2.096
2.076
2.055
2.055
2.053
2.037
2.034
2.012
1.990
1.971
1.959
1.942
1.923
1.904
1.885
1.863
1.856
1.855
1.852
1.851
1.840
O
O
2a
1.96
1.02
1.01
2.22
3.22
2.06
1
2.15
ppm
10
8
6
4
2
0

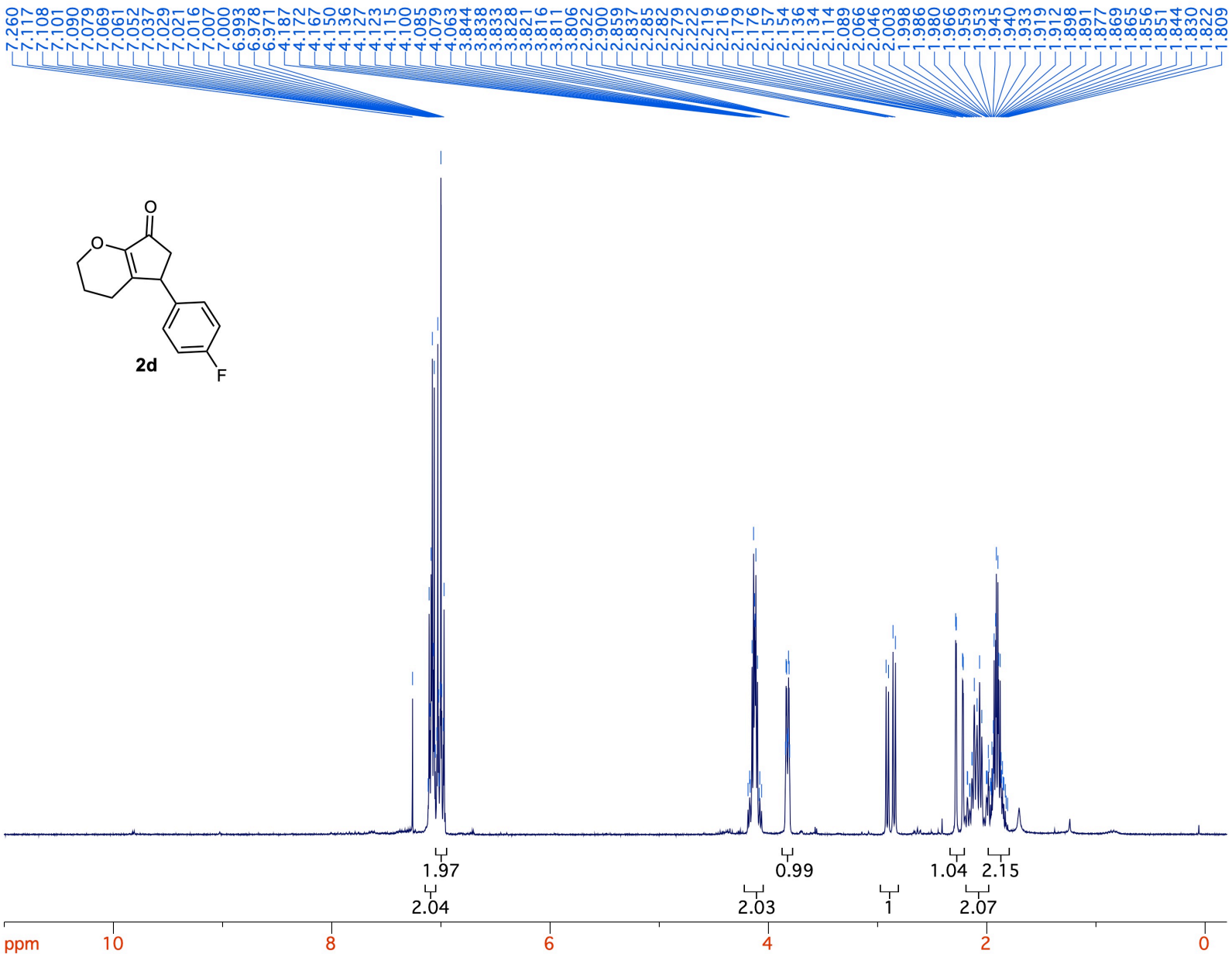

200.308
151.503
147.693
141.698
129.045
127.215
127.139
77.583
77.160
76.736
66.992
43.712
42.974
22.263
21.487
O
O
2a
ppm 200
150
100
50
0

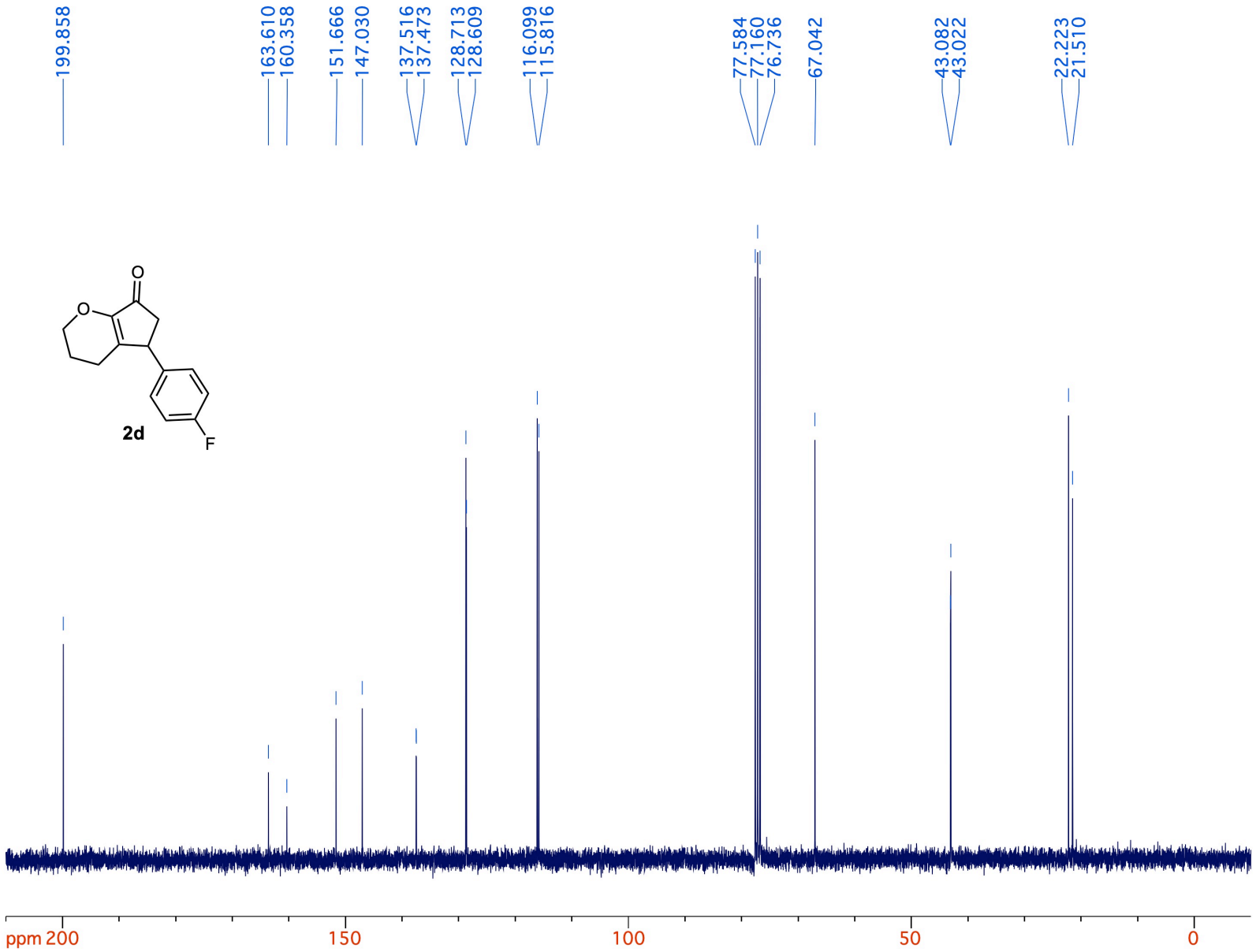

7.260
7.067
7.058
7.051
7.036
7.029
7.019
6.885
6.875
6.868
6.853
6.846
6.836
4.192
4.191
4.176
4.173
4.171
4.168
4.167
4.165
4.154
4.142
4.132
4.121
4.108
4.091
4.087
4.086
4.073
4.071
3.797
3.922
2.900
2.859
2.837
2.316
2.313
2.310
2.253
2.250
2.247
2.180
2.140
2.138
2.134
2.132
2.117
2.095
2.074
2.073
2.012
2.010
2.008
2.005
2.003
2.000
1.989
1.987
1.982
1.978
1.977
1.975
1.968
1.962
1.956
1.952
1.947
1.942
1.936
1.921
1.915
1.901
1.894
1.886
1.880
1.872
1.869
1.868
1.859
O
O
2b
OMe
2.05
3.69
1.11
2.09
2
2.11
1.05
2.02
ppm
10
8
6
4
2
0

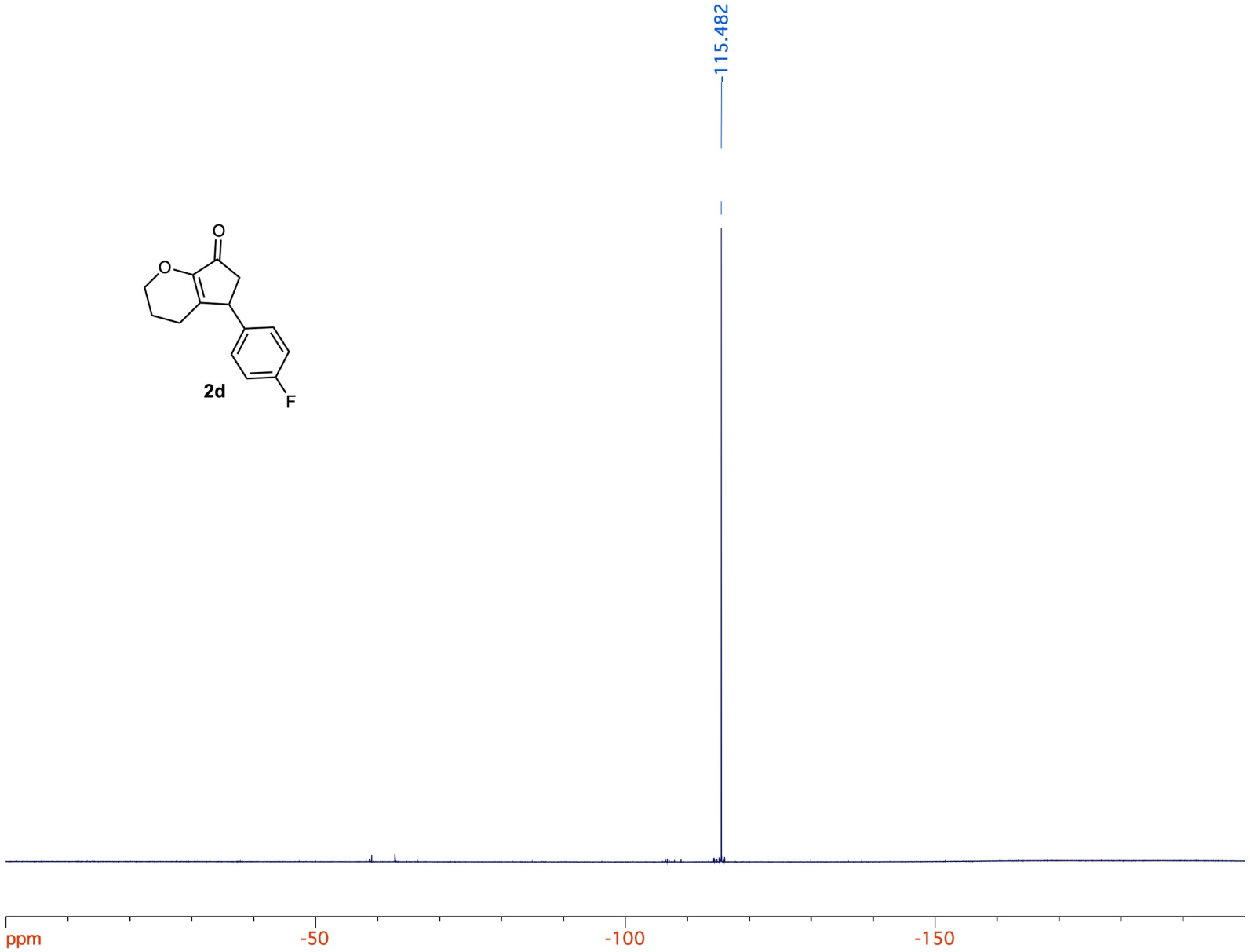

200.284
158.783
151.397
147.723
133.680
128.152
114.449
77.583
77.160
76.736
67.008
55.391
43.203
42.960
22.256
21.563
O
O
2b
OMe
ppm 200
150
100
50
0

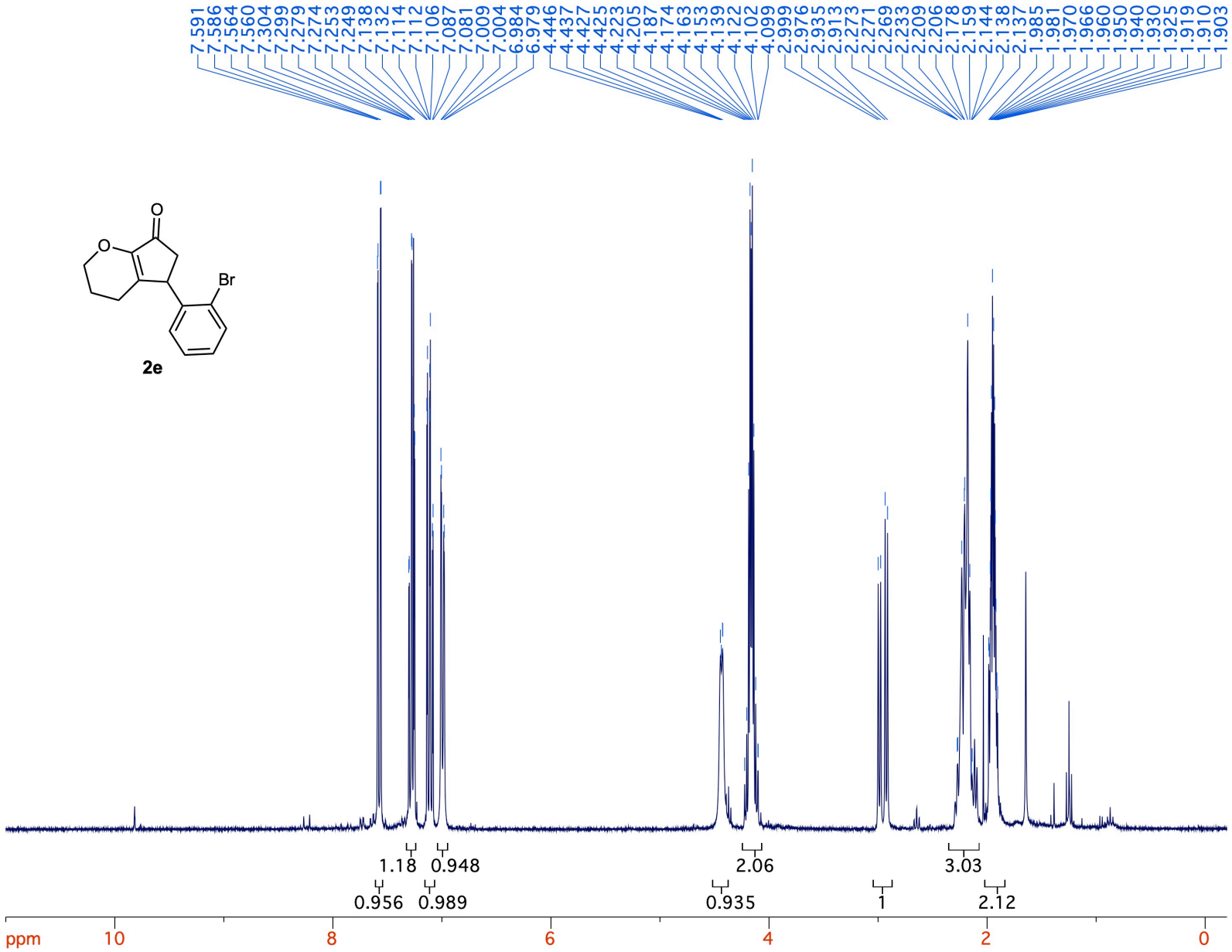

7.260
7.142
7.116
7.028
7.022
7.016
7.001
6.995
6.988
4.185
4.170
4.166
4.148
4.136
4.126
4.114
4.102
4.085
4.079
4.065
3.816
3.811
3.805
3.800
3.794
3.789
3.783
3.778
2.917
2.915
2.912
2.895
2.893
2.890
2.854
2.852
2.849
2.832
2.830
2.827
2.326
2.317
2.262
2.260
2.256
2.253
2.251
2.157
2.140
2.138
2.114
2.091
2.070
2.039
1.976
1.974
1.960
1.954
1.947
1.939
1.933
1.927
1.913
1.906
1.892
1.885
1.871
1.864
1.859
1.850
1.845
1.838
1.824
O
O
2c
Me
1.97
2.07
1
2.06
1.01
4.11
1.9
2.09
ppm
10
8
6
4
2
0

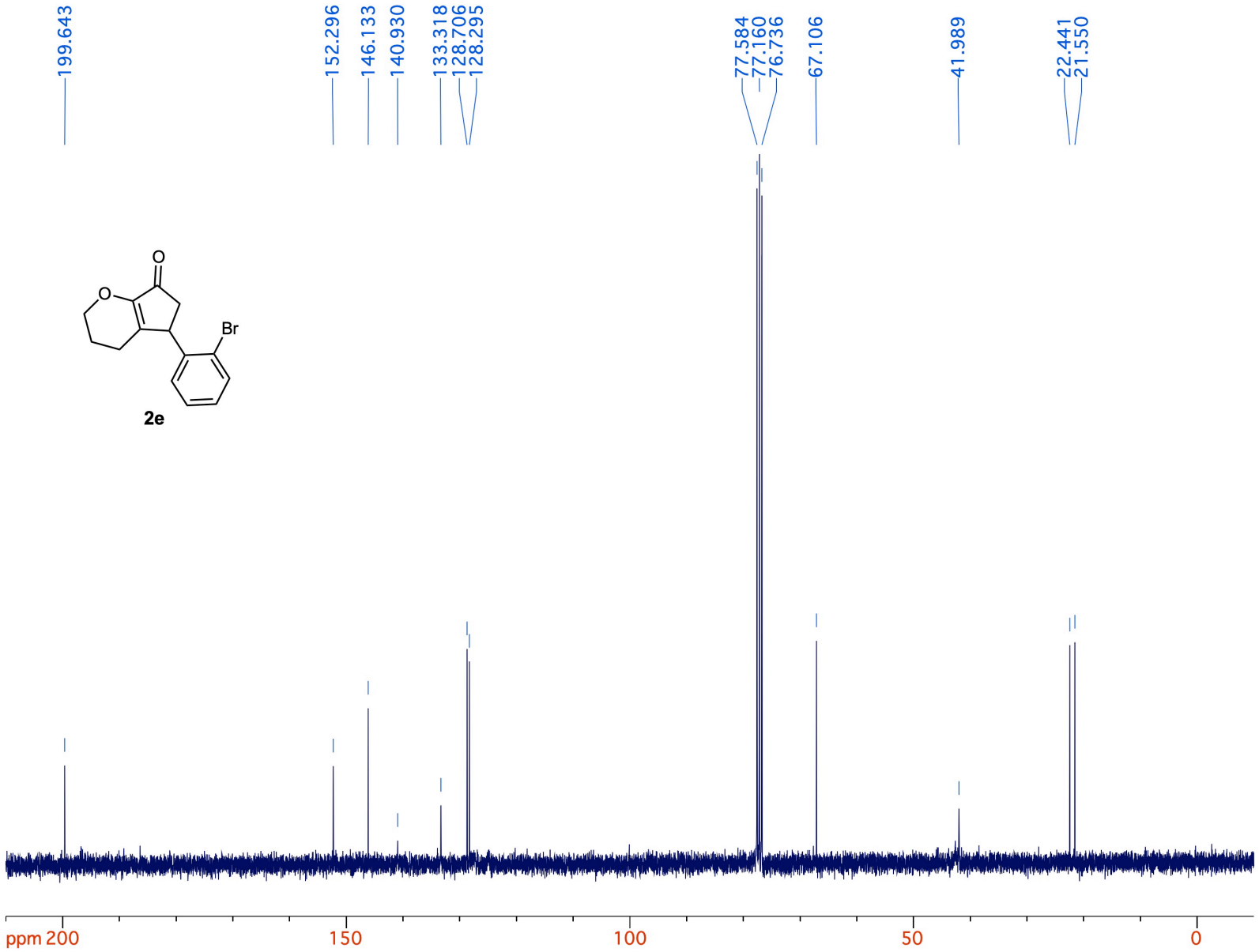

200.301
151.482
147.671
138.722
136.896
129.753
127.071
77.584
77.160
76.736
67.021
43.374
43.135
22.294
21.580
21.133
O
O
2c
Me
ppm 200
180
160
140
120
100
80
60
40
20
0

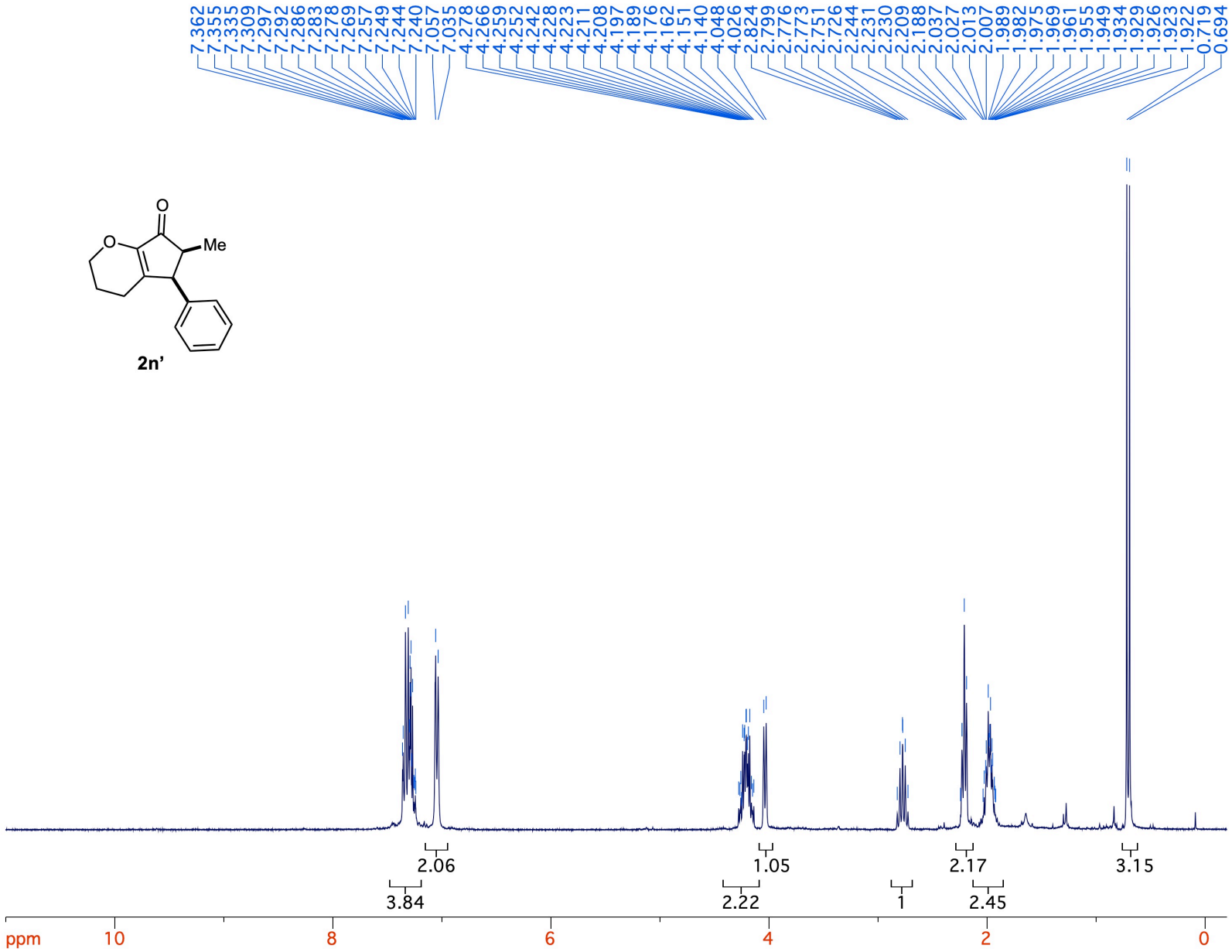

7.260
7.117
7.108
7.101
7.090
7.079
7.069
7.061
7.052
7.037
7.029
7.021
7.016
7.007
7.000
6.993
6.978
6.971
4.187
4.172
4.167
4.150
4.136
4.127
4.123
4.115
4.100
4.085
4.079
4.063
3.844
3.838
3.833
3.828
3.821
3.816
3.811
3.806
2.922
2.900
2.859
2.837
2.285
2.282
2.279
2.222
2.219
2.216
2.179
2.176
2.157
2.154
2.136
2.134
2.114
2.089
2.066
2.046
2.003
1.998
1.986
1.980
1.966
1.959
1.953
1.945
1.940
1.933
1.919
1.912
1.898
1.891
1.877
1.869
1.865
1.856
1.851
1.844
1.830
1.822
1.809
O
O
F
2d
1.97
2.04
0.99
2.03
1
1.04
2.15
2.07
ppm
10
8
6
4
2
0

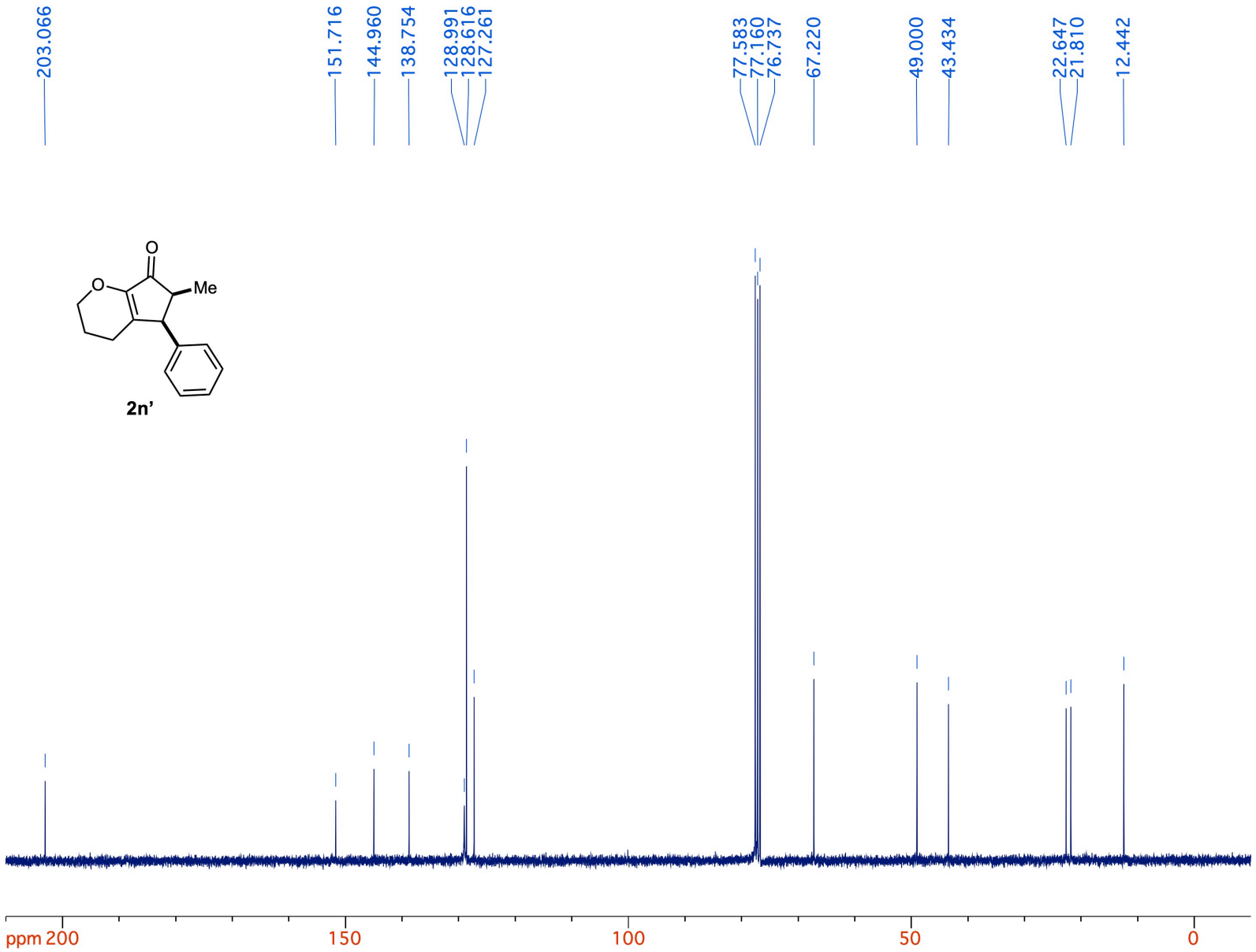

199.858
163.610
160.358
151.666
147.030
137.516
137.473
128.713
128.609
116.099
115.816
77.584
77.160
76.736
67.042
43.082
43.022
22.223
21.510
O
O
F
2d
ppm 200
150
100
50
0

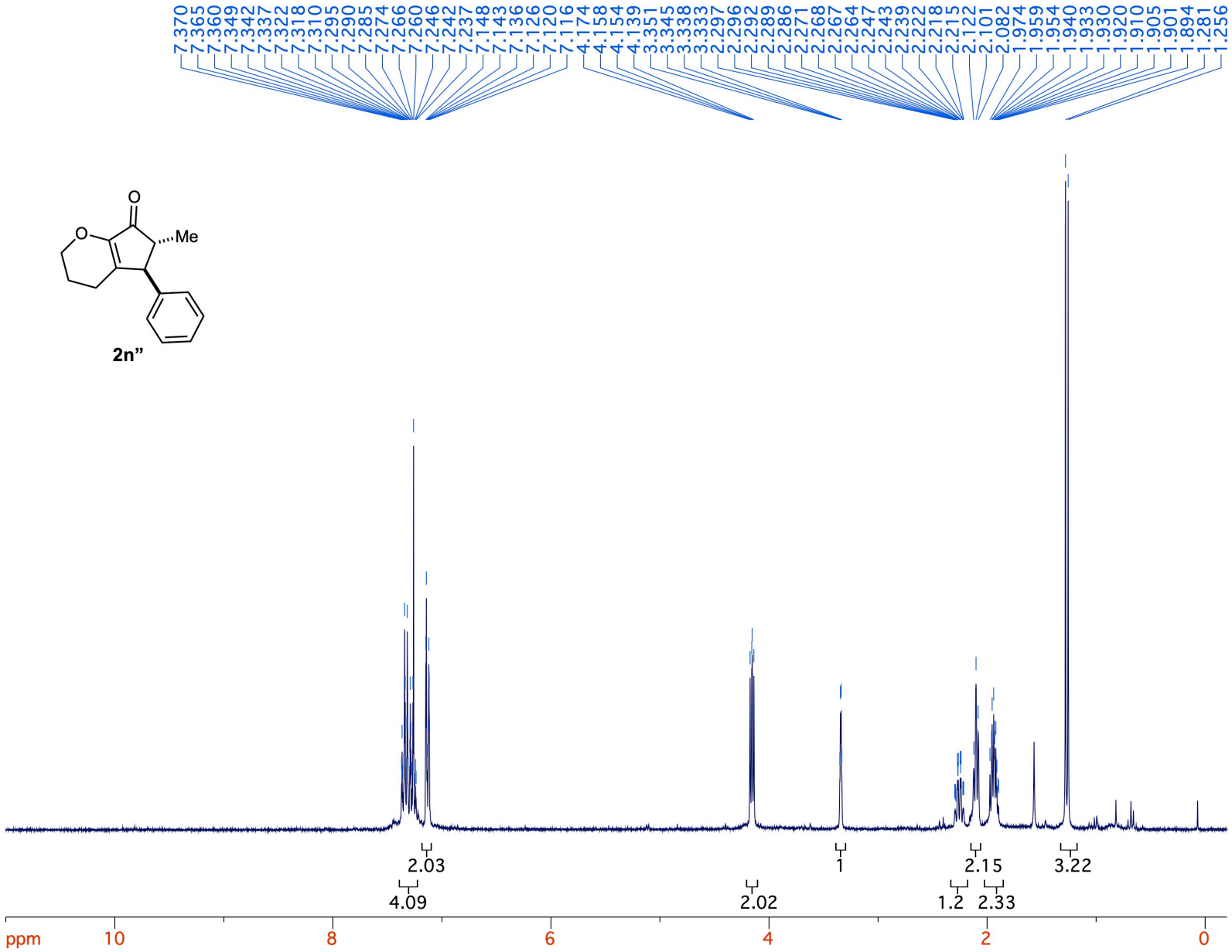

-115.482
O
O
F
2d
ppm
-50
-100
-150

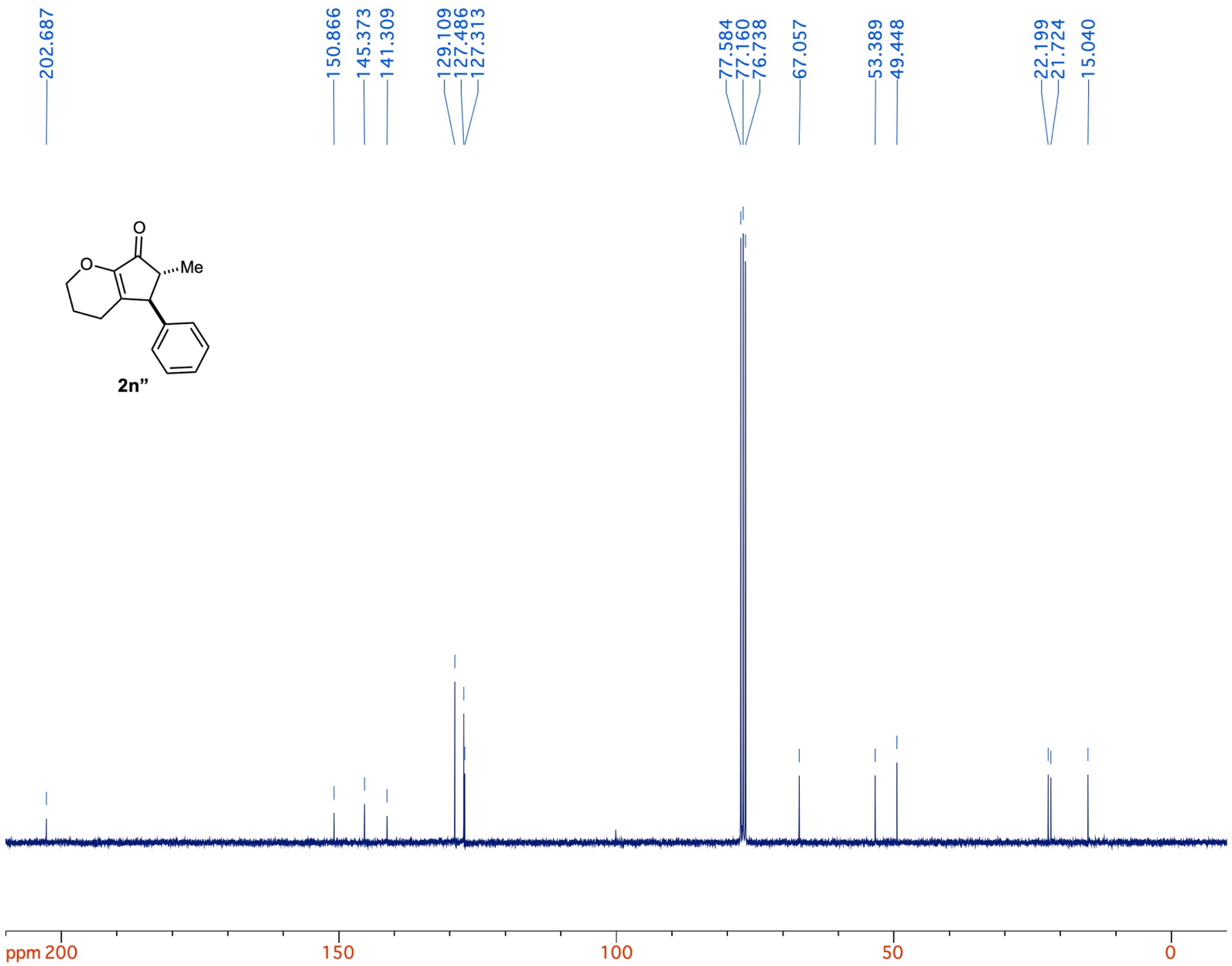

7.591
7.586
7.564
7.560
7.304
7.299
7.279
7.274
7.253
7.249
7.138
7.132
7.114
7.112
7.106
7.087
7.081
7.009
7.004
6.984
6.979
4.446
4.437
4.427
4.425
4.223
4.205
4.187
4.174
4.163
4.153
4.139
4.122
4.102
4.099
2.999
2.976
2.935
2.913
2.273
2.271
2.269
2.233
2.209
2.206
2.178
2.159
2.144
2.138
2.137
1.985
1.981
1.970
1.966
1.960
1.950
1.940
1.930
1.925
1.919
1.910
1.903
O
O
Br
2e
1.18
0.948
2.06
3.03
0.956
0.989
0.935
1
2.12
ppm
10
8
6
4
2
0

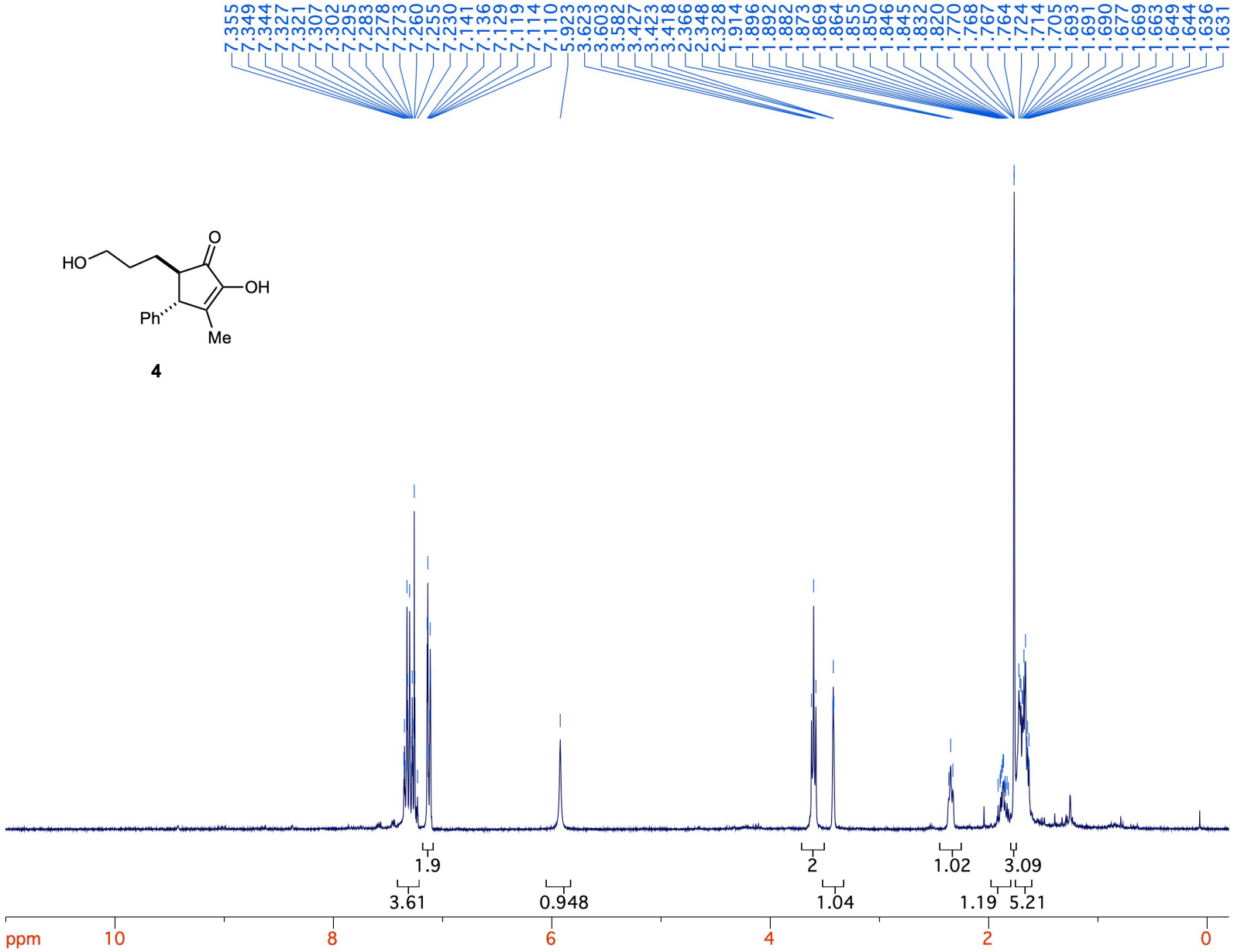

199.643
152.296
146.133
140.930
133.318
128.706
128.295
77.584
77.160
76.736
67.106
41.989
22.441
21.550
O
O
Br
2e
ppm 200
150
100
50
0

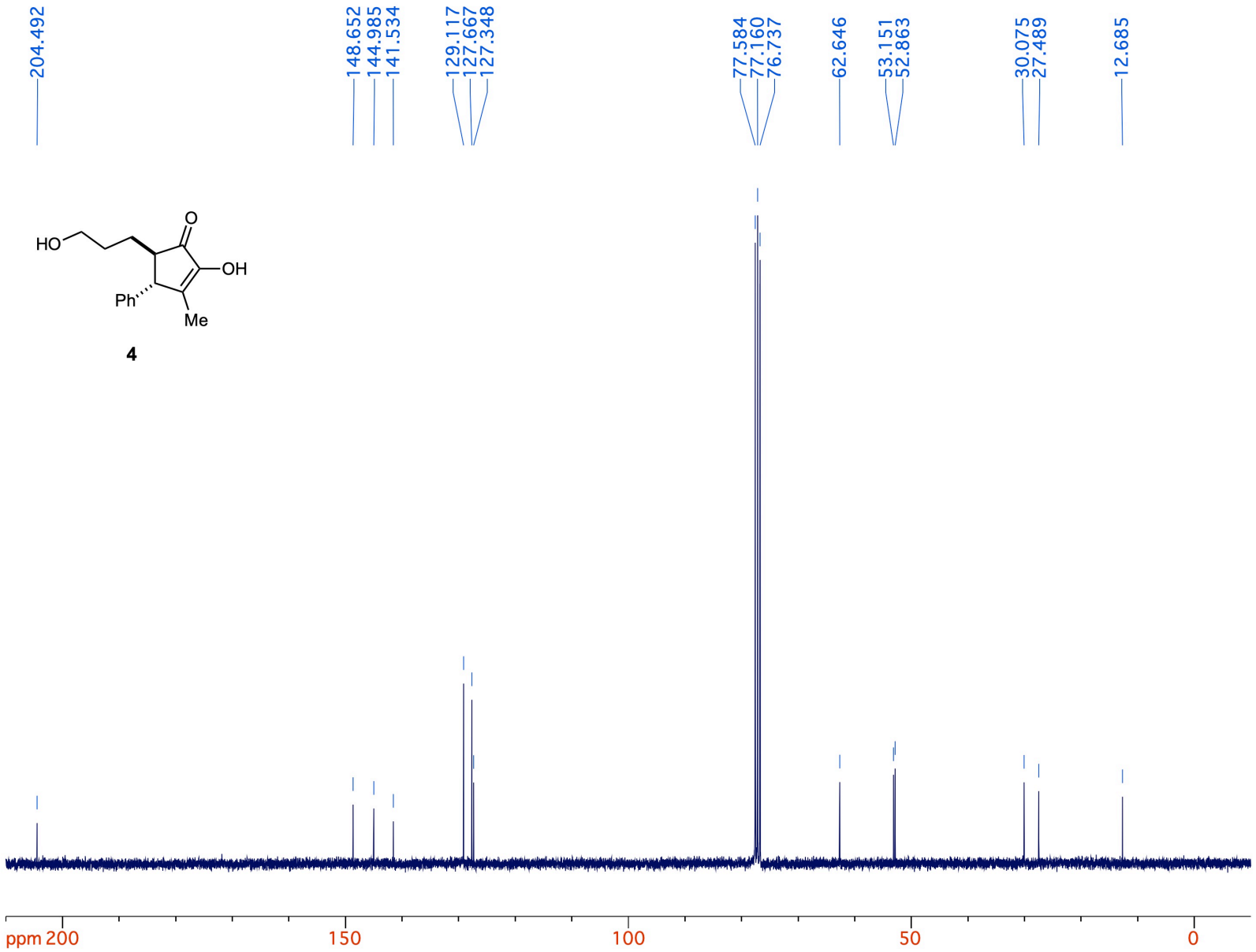

7.362
7.355
7.335
7.309
7.297
7.292
7.286
7.283
7.278
7.269
7.257
7.249
7.244
7.240
7.057
7.035
4.278
4.266
4.259
4.252
4.242
4.228
4.223
4.211
4.208
4.197
4.189
4.176
4.162
4.151
4.140
4.048
4.026
2.824
2.799
2.776
2.773
2.751
2.726
2.244
2.231
2.230
2.209
2.188
2.037
2.027
2.013
2.007
1.989
1.982
1.975
1.969
1.961
1.955
1.949
1.934
1.929
1.926
1.923
1.922
0.719
0.694
O
O
Me
2n'
2.06
1.05
2.17
3.15
3.84
2.22
1
2.45
ppm
10
8
6
4
2
0

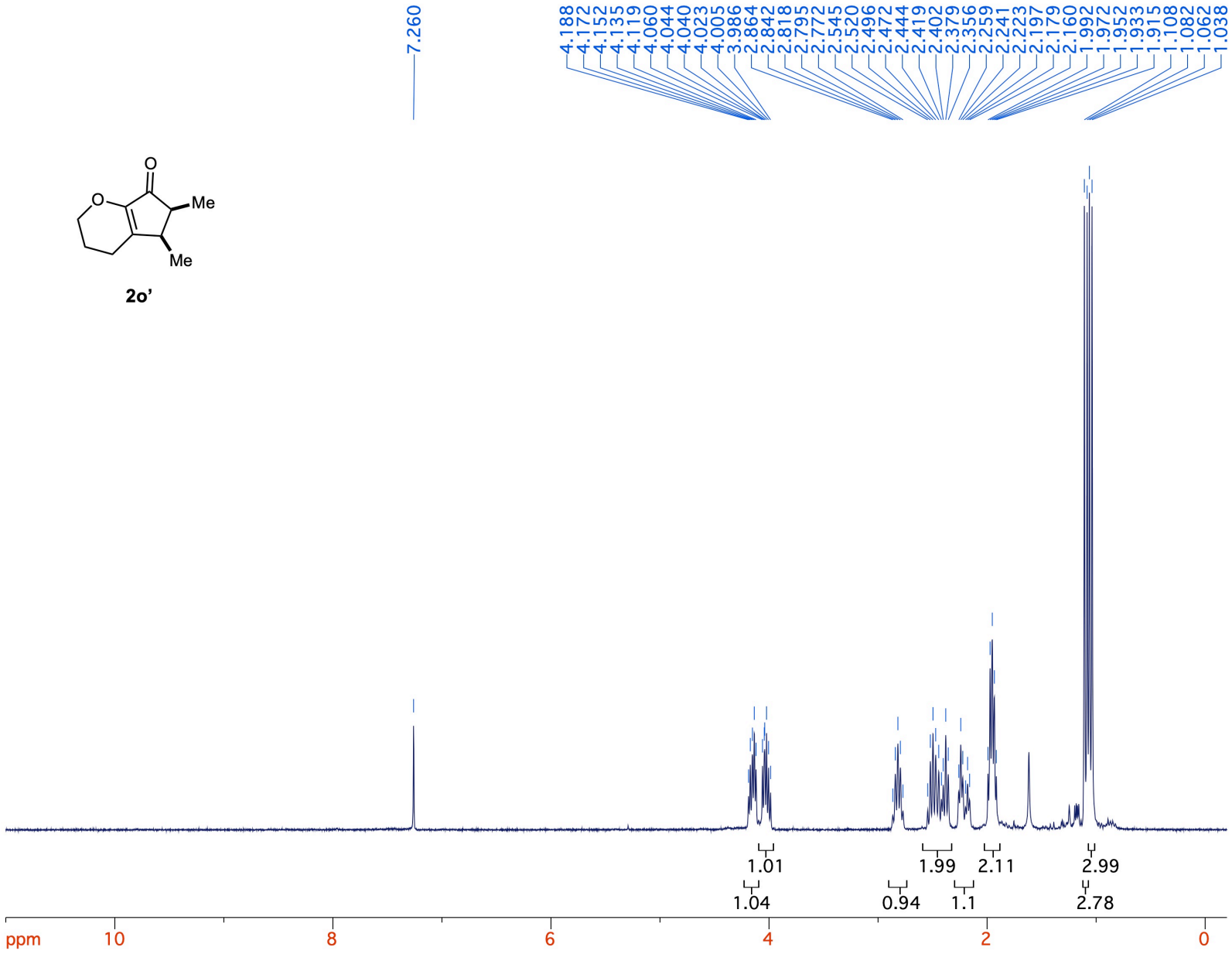

203.066
151.716
144.960
138.754
128.991
128.616
127.261
77.583
77.160
76.737
67.220
49.000
43.434
22.647
21.810
12.442
O
O
Me
2n'
ppm 200
150
100
50
0


7.370
7.365
7.360
7.349
7.342
7.337
7.322
7.318
7.310
7.295
7.290
7.285
7.274
7.266
7.260
7.246
7.242
7.237
7.148
7.143
7.136
7.126
7.120
7.116
4.174
4.158
4.154
4.139
3.351
3.345
3.338
3.333
3.297
2.296
2.292
2.289
2.286
2.271
2.268
2.267
2.264
2.247
2.243
2.239
2.222
2.218
2.215
2.122
2.101
2.082
1.974
1.959
1.954
1.940
1.933
1.930
1.920
1.910
1.905
1.901
1.894
1.281
1.256
O
O
Me
2n”
2.03
1
2.15
3.22
4.09
2.02
1.2
2.33
ppm
10
8
6
4
2
0

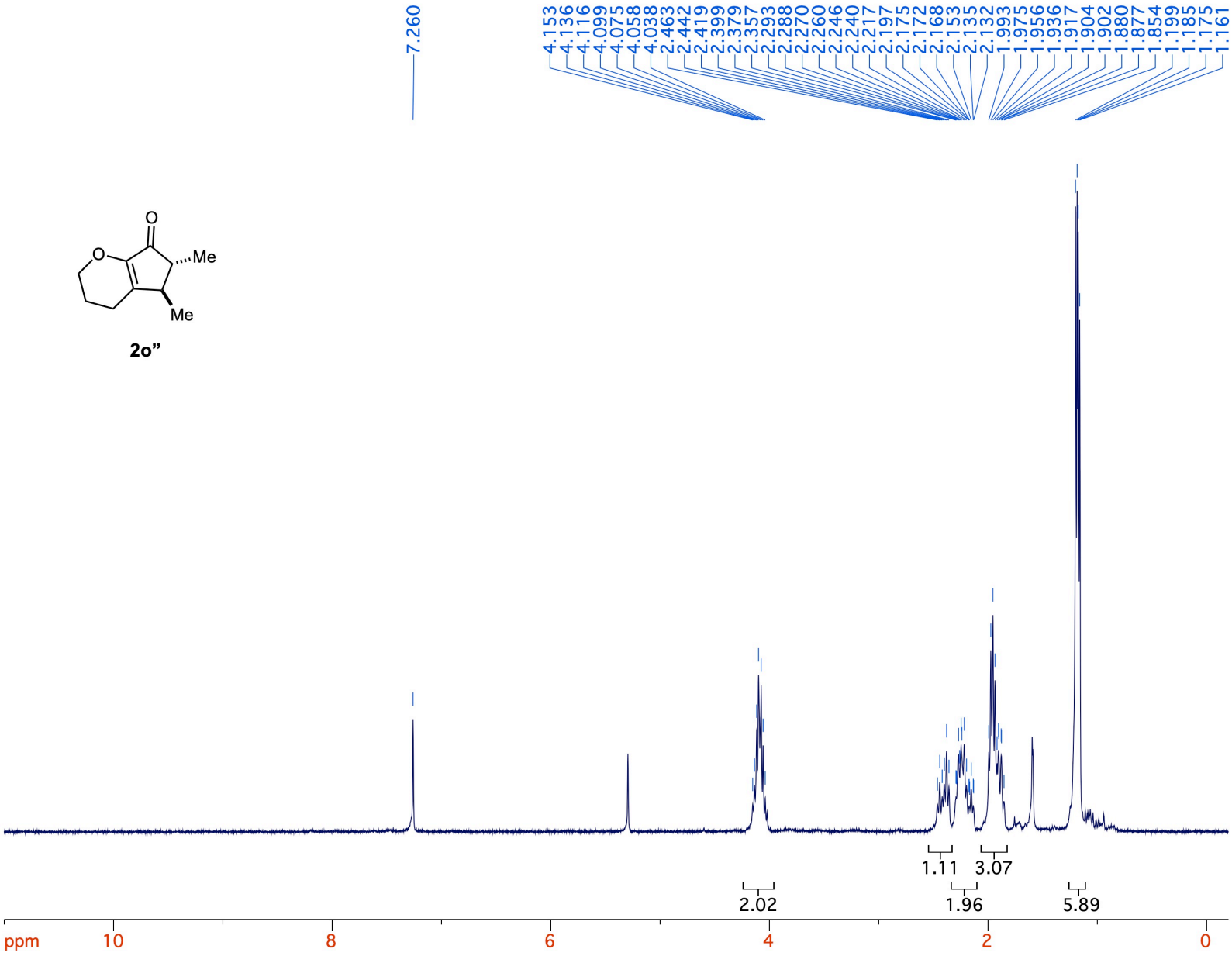

202.687
150.866
145.373
141.309
129.109
127.486
127.313
77.584
77.160
76.738
67.057
53.389
49.448
22.199
21.724
15.040
O
O
Me
2n”
ppm 200
150
100
50
0


7.355
7.349
7.344
7.327
7.321
7.307
7.302
7.295
7.283
7.278
7.273
7.260
7.255
7.230
7.141
7.136
7.129
7.119
7.114
7.110
5.923
3.623
3.603
3.582
3.427
3.423
3.418
2.366
2.348
2.328
1.914
1.896
1.892
1.882
1.873
1.869
1.864
1.855
1.850
1.846
1.845
1.832
1.820
1.770
1.768
1.767
1.764
1.724
1.714
1.705
1.693
1.691
1.690
1.677
1.669
1.663
1.649
1.644
1.636
1.631
HO
O
OH
Ph
Me
4
1.9
3.61
0.948
2
1.04
1.02
1.19
3.09
5.21
ppm
10
8
6
4
2
0

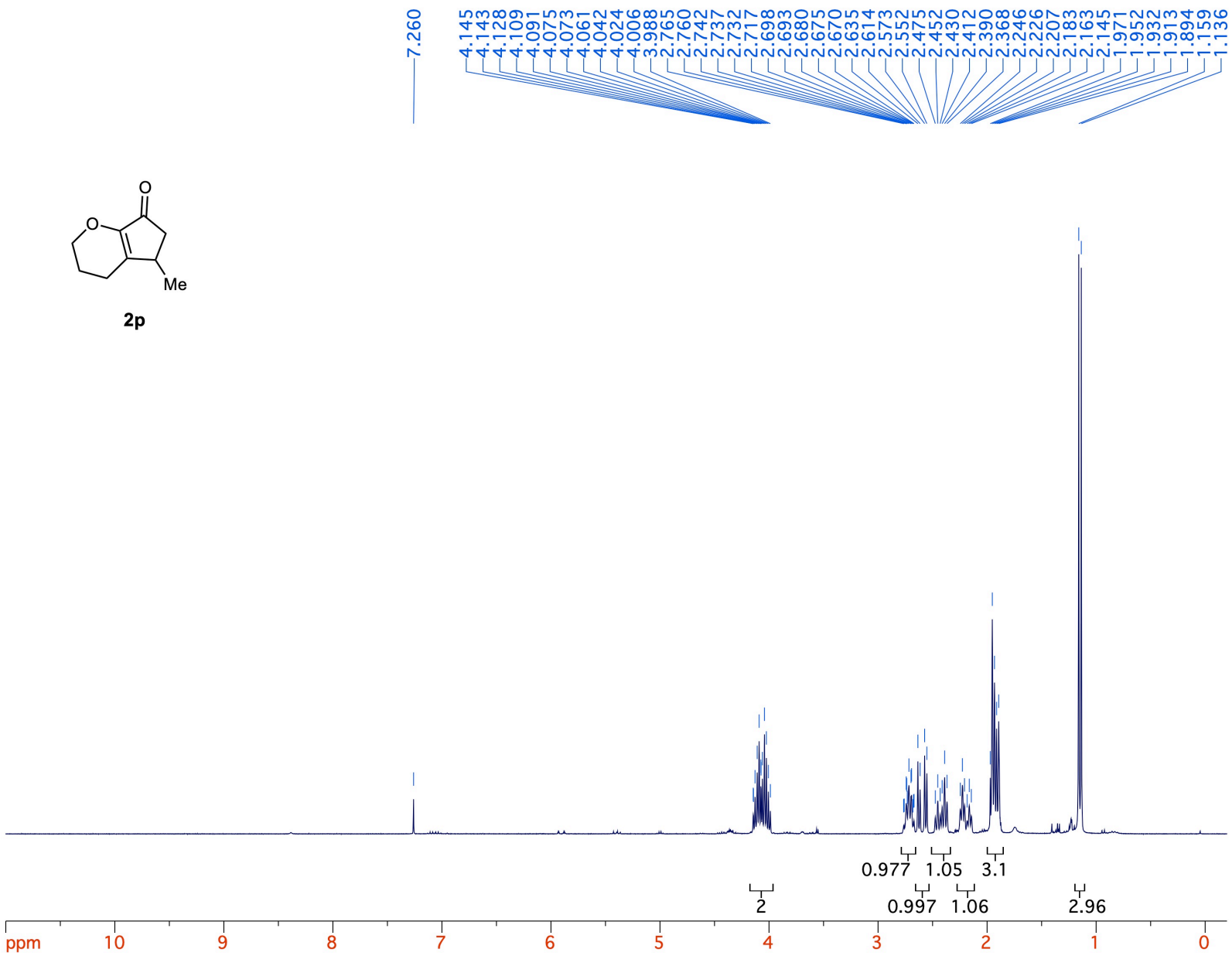

204.492
148.652
144.985
141.534
129.117
127.667
127.348
77.584
77.160
76.737
62.646
53.151
52.863
30.075
27.489
12.685
HO
O
OH
Ph
Me
4
ppm 200
150
100
50
0

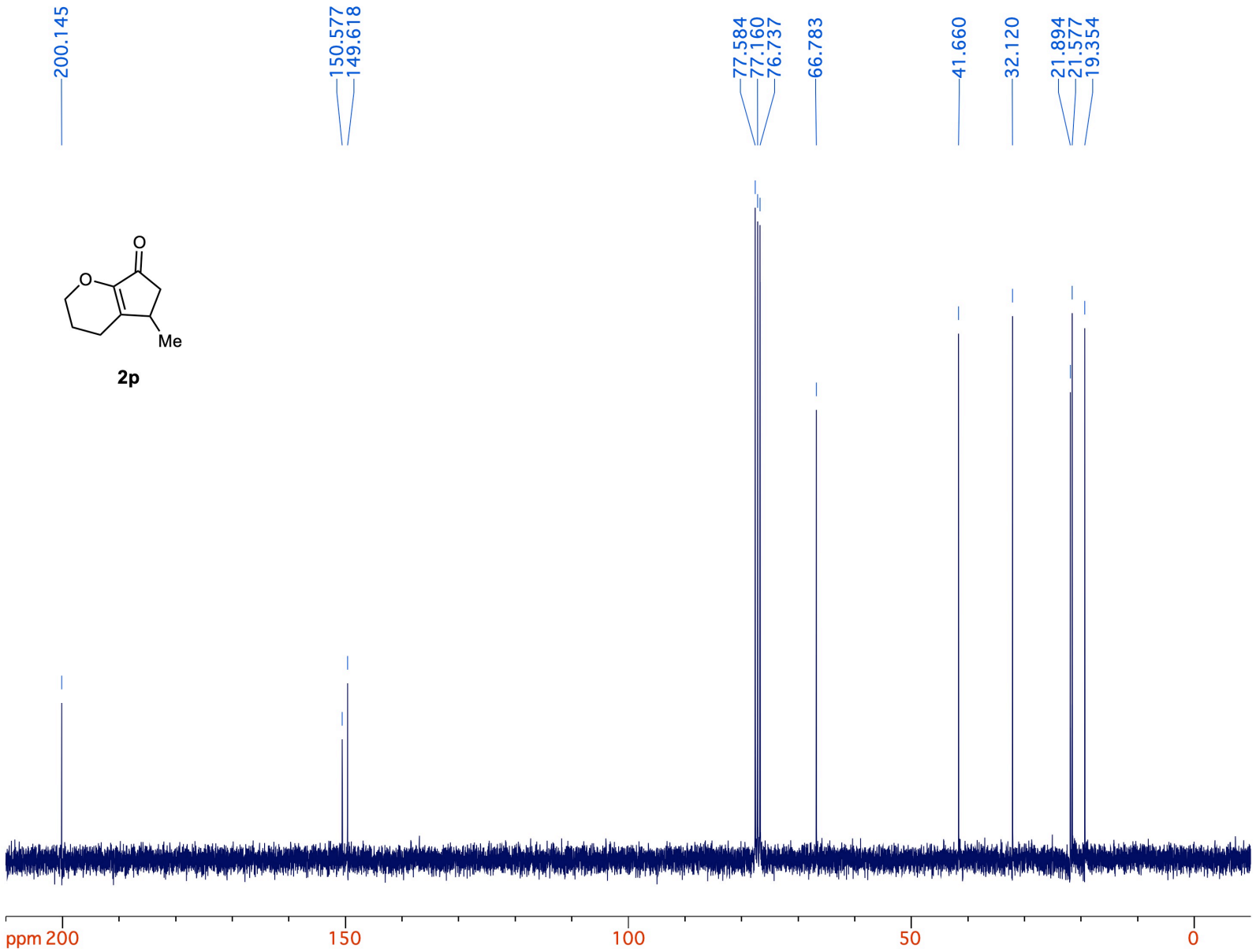

7.260
4.188
4.172
4.152
4.135
4.119
4.060
4.044
4.040
4.023
4.005
3.986
2.864
2.842
2.818
2.795
2.772
2.545
2.520
2.496
2.472
2.444
2.419
2.402
2.379
2.356
2.259
2.241
2.223
2.197
2.179
2.160
1.992
1.972
1.952
1.933
1.915
1.108
1.082
1.062
1.038
O
O
Me
Me
1.01
1.99
2.11
2.99
1.04
0.94
1.1
2.78
ppm
10
8
6
4
2
0

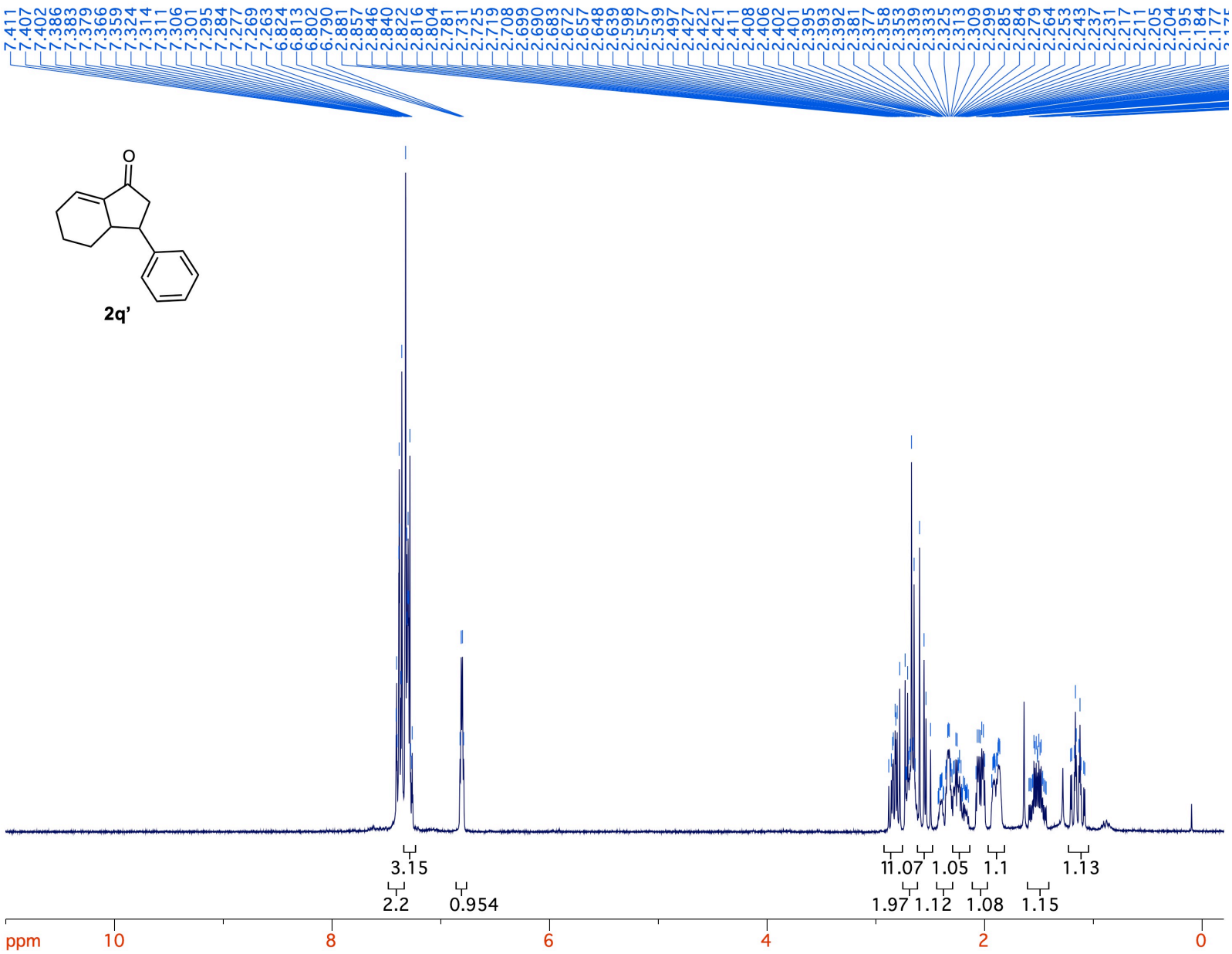
2o'

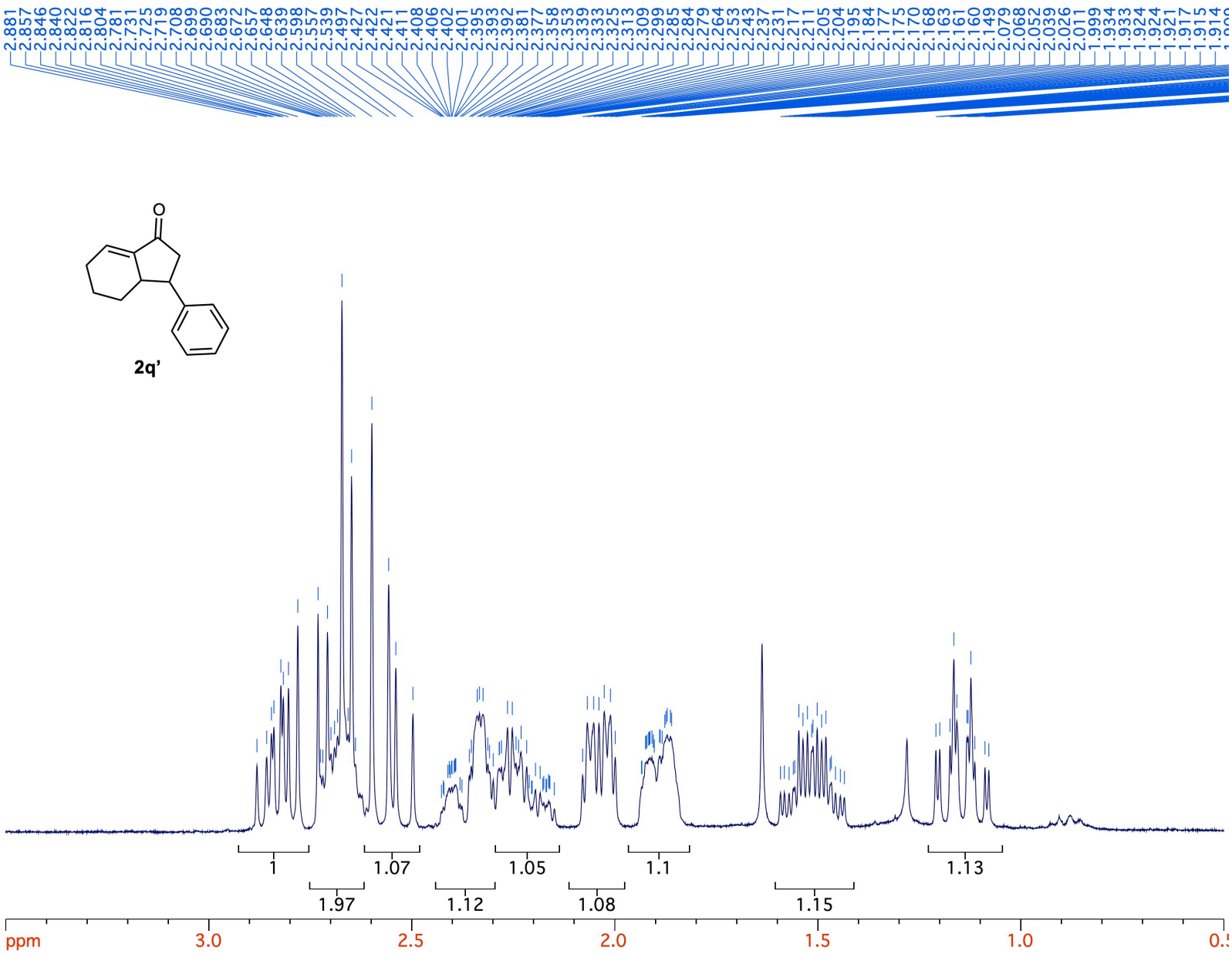

7.260
4.153
4.136
4.116
4.099
4.075
4.058
4.038
2.463
2.442
2.419
2.399
2.379
2.357
2.293
2.288
2.270
2.260
2.246
2.240
2.217
2.197
2.175
2.172
2.168
2.153
2.135
2.132
1.993
1.975
1.956
1.936
1.917
1.904
1.902
1.880
1.877
1.854
1.199
1.185
1.175
1.161
O
O
Me
Me
1.11
3.07
2.02
1.96
5.89
ppm
10
8
6
4
2
0

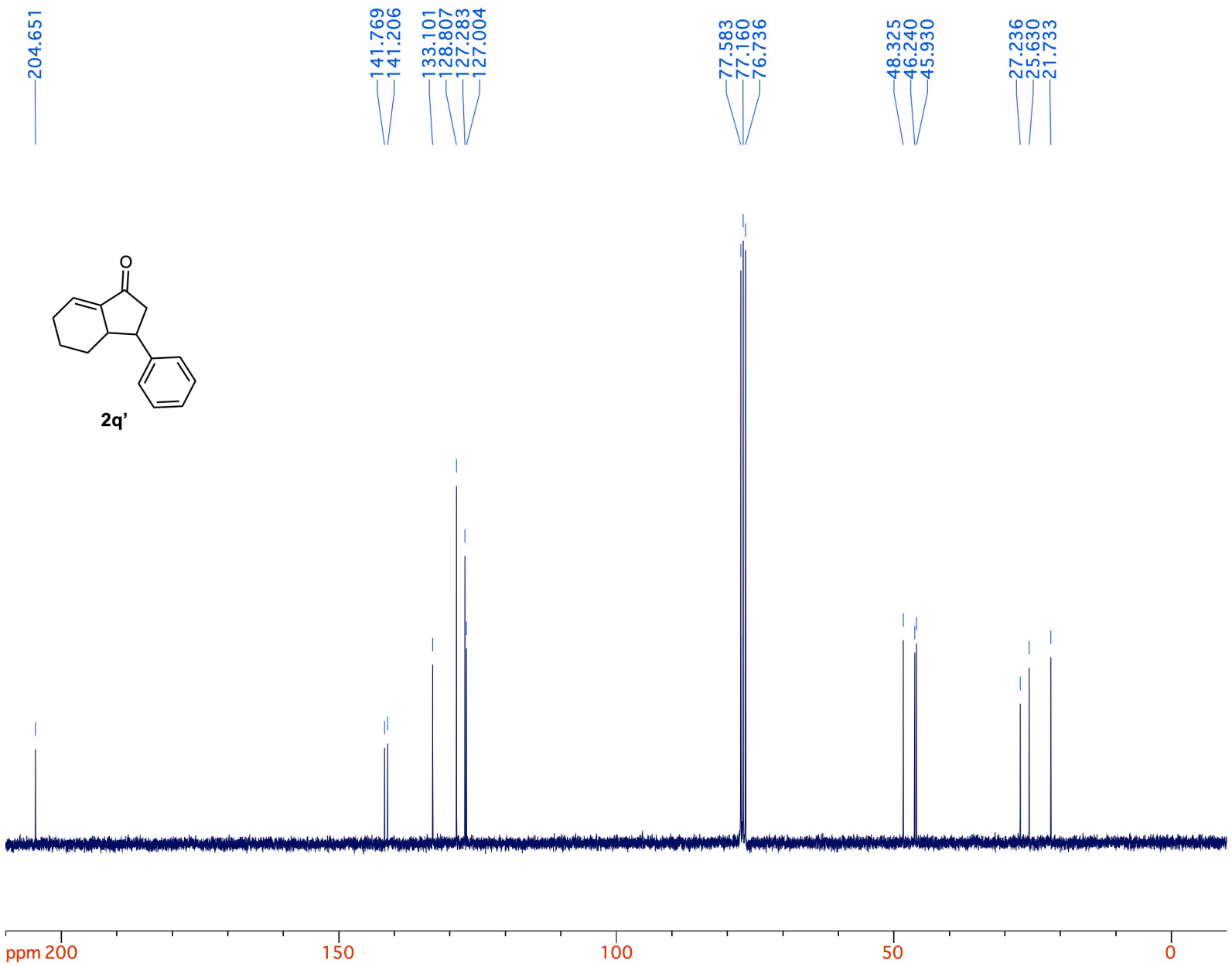
2o”

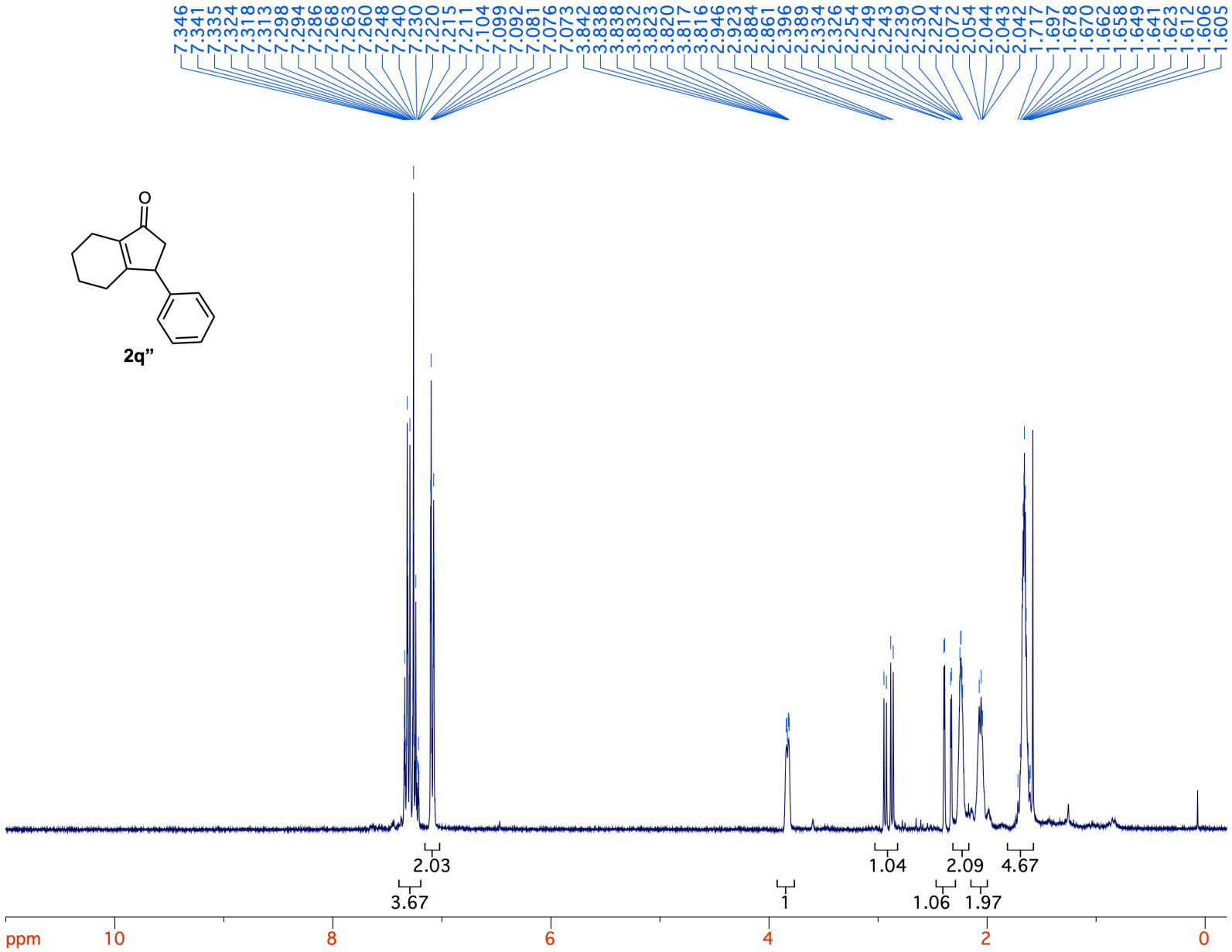

7.260
4.145
4.143
4.128
4.109
4.091
4.075
4.073
4.061
4.042
4.024
4.006
3.988
3.765
2.760
2.742
2.737
2.732
2.717
2.698
2.693
2.680
2.675
2.670
2.635
2.614
2.573
2.552
2.475
2.452
2.430
2.412
2.390
2.368
2.246
2.226
2.207
2.183
2.163
2.145
1.971
1.952
1.932
1.913
1.894
1.159
1.136
O
O
Me
2p
0.977
1.05
3.1
2
0.997
1.06
2.96
ppm
10
9
8
7
6
5
4
3
2
1
0

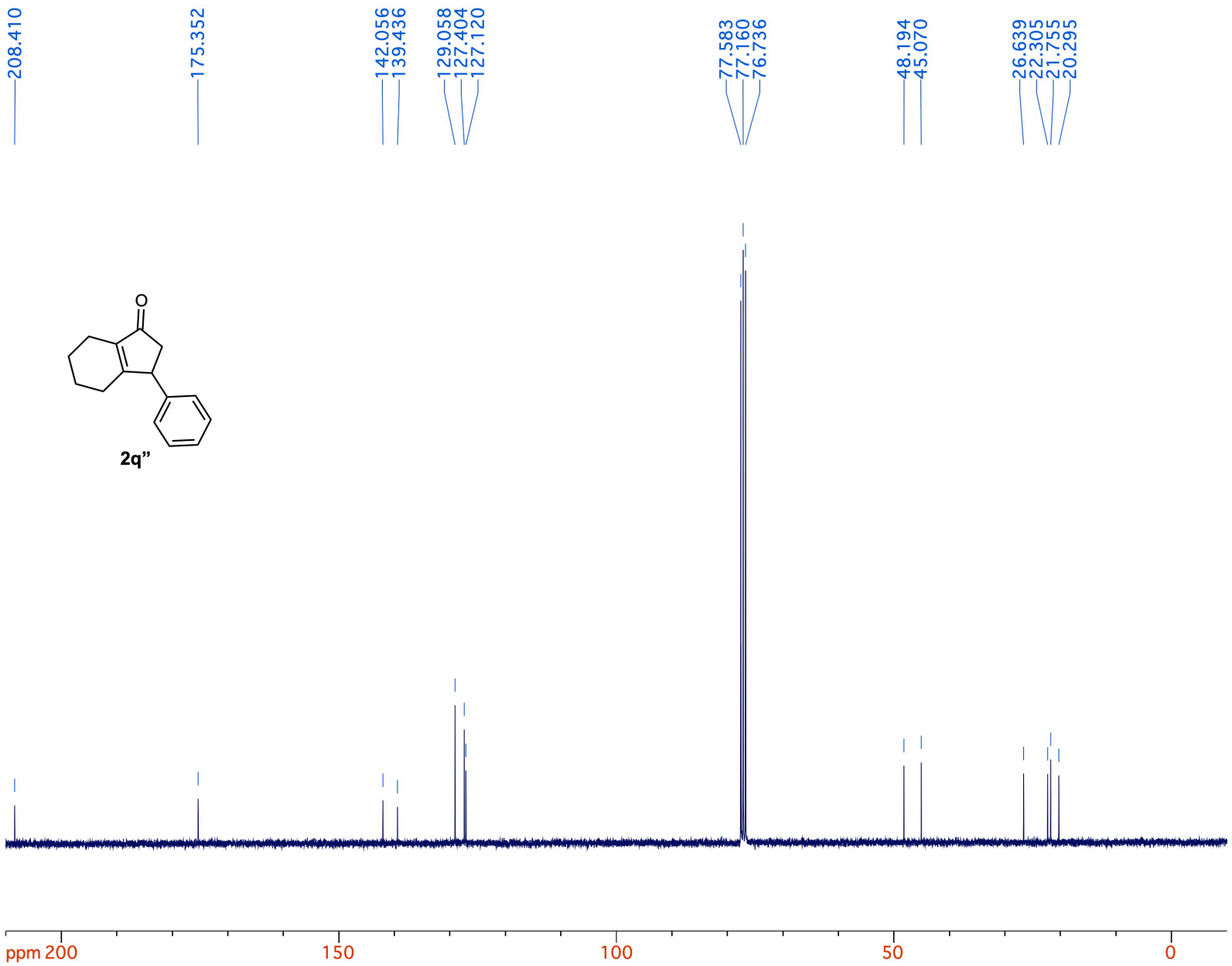

200.145
150.577
149.618
77.584
77.160
76.737
66.783
41.660
32.120
21.894
21.577
19.354
O
O
Me
2p
ppm 200
150
100
50
0

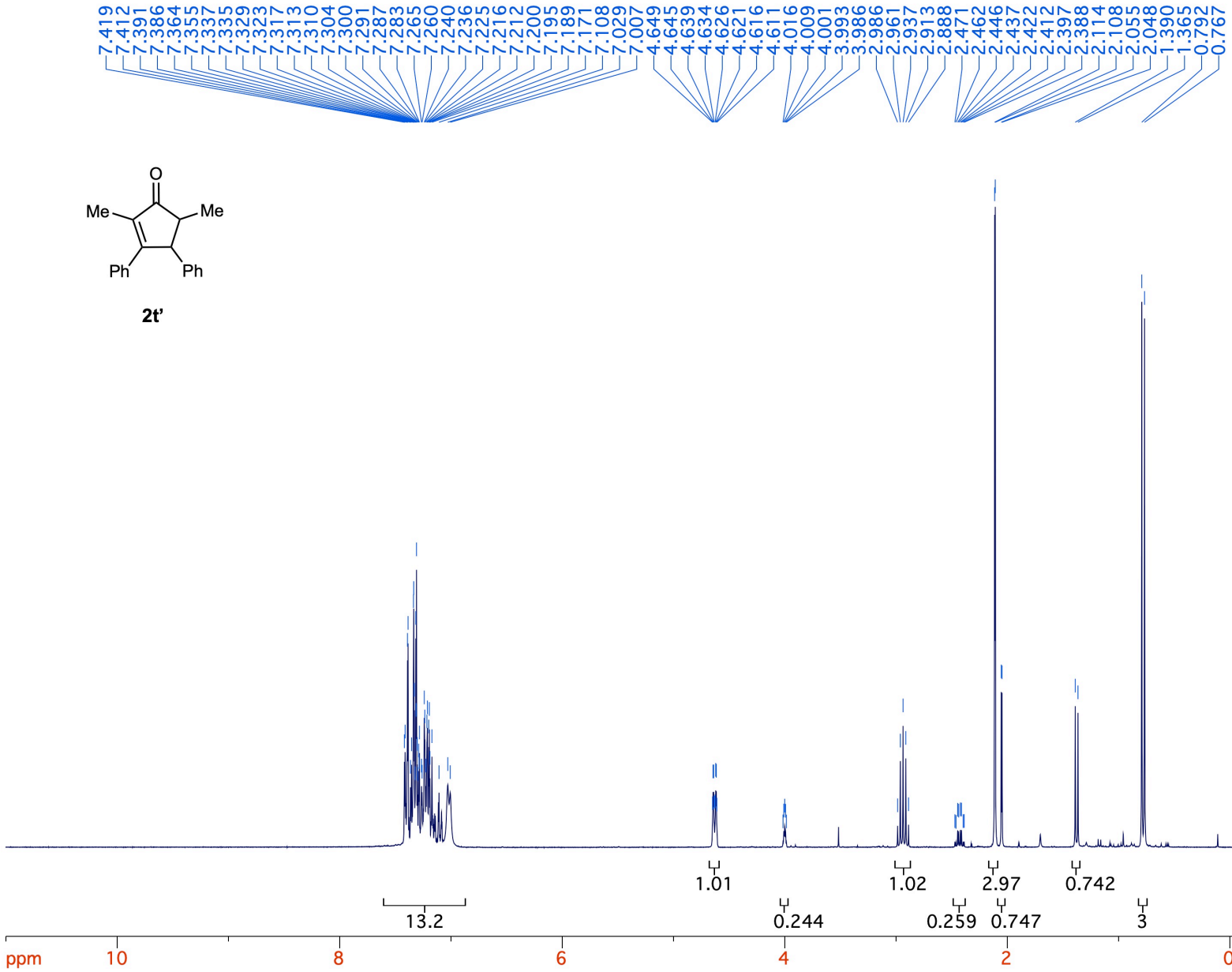

7.411
7.407
7.402
7.386
7.383
7.379
7.366
7.359
7.324
7.314
7.311
7.306
7.301
7.295
7.284
7.277
7.269
7.263
6.824
6.813
6.802
6.790
2.881
2.857
2.846
2.840
2.822
2.816
2.804
2.781
2.731
2.725
2.719
2.708
2.699
2.690
2.683
2.672
2.657
2.648
2.639
2.598
2.557
2.539
2.497
2.427
2.422
2.421
2.411
2.408
2.406
2.402
2.401
2.395
2.393
2.392
2.381
2.377
2.358
2.353
2.339
2.333
2.325
2.313
2.309
2.299
2.285
2.284
2.279
2.264
2.253
2.243
2.237
2.231
2.217
2.211
2.205
2.204
2.195
2.184
2.177
O
2q'
3.15
2.2
0.954
11.07
1.97
1.05
1.12
1.1
1.08
1.13
1.15
ppm
10
8
6
4
2
0

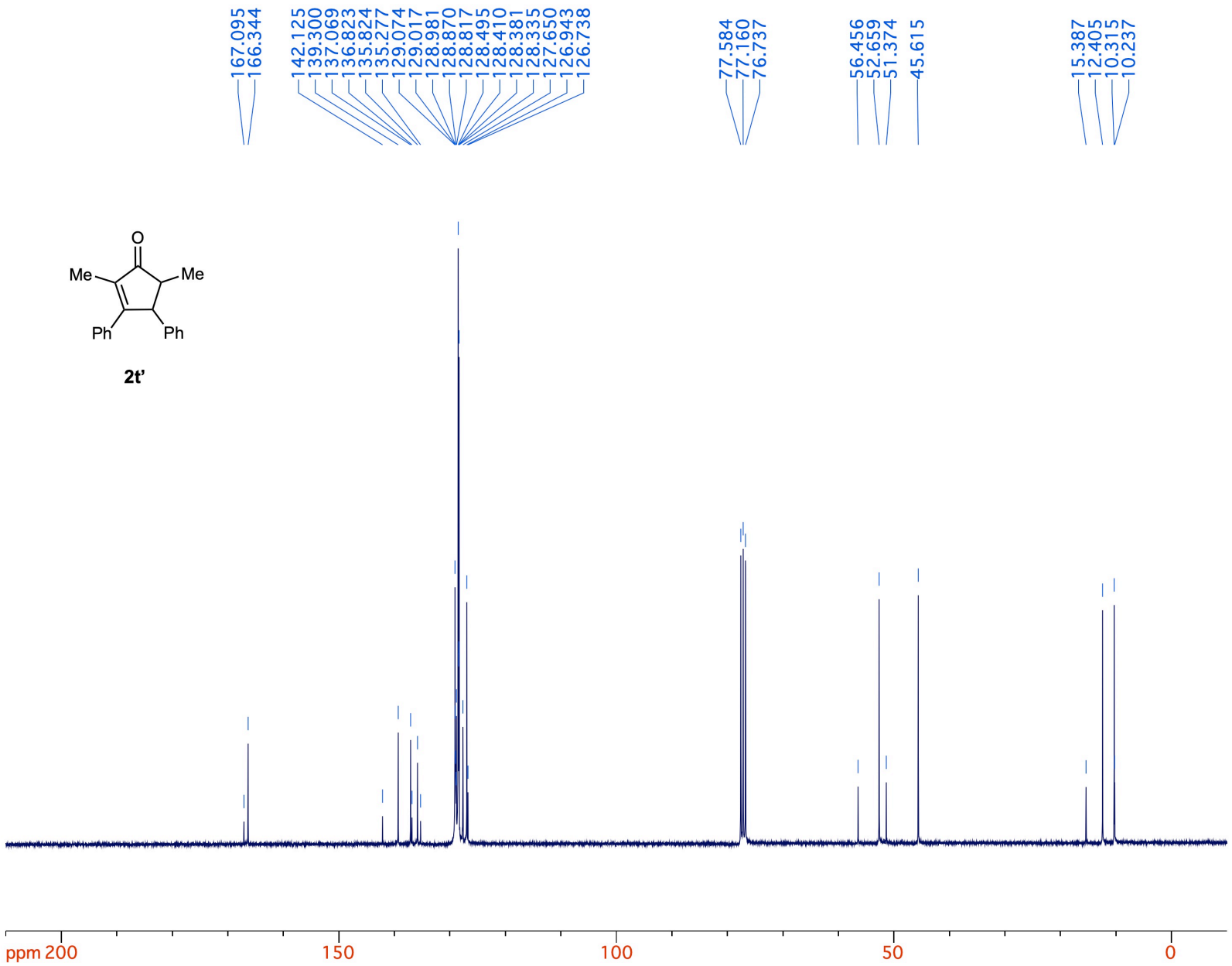

2.881
2.857
2.846
2.840
2.822
2.816
2.804
2.781
2.731
2.725
2.719
2.708
2.699
2.690
2.683
2.672
2.657
2.648
2.639
2.598
2.557
2.539
2.497
2.427
2.422
2.421
2.411
2.408
2.406
2.402
2.401
2.395
2.393
2.392
2.381
2.377
2.358
2.353
2.339
2.333
2.325
2.313
2.309
2.299
2.285
2.284
2.279
2.264
2.253
2.243
2.237
2.231
2.217
2.211
2.205
2.204
2.195
2.184
2.177
2.175
2.170
2.168
2.163
2.161
2.160
2.149
2.079
2.068
2.052
2.039
2.026
2.011
1.999
1.934
1.933
1.924
1.924
1.921
1.917
1.915
1.914
O
2q'
1
1.07
1.05
1.1
1.13
1.97
1.12
1.08
1.15
ppm
3.0
2.5
2.0
1.5
1.0

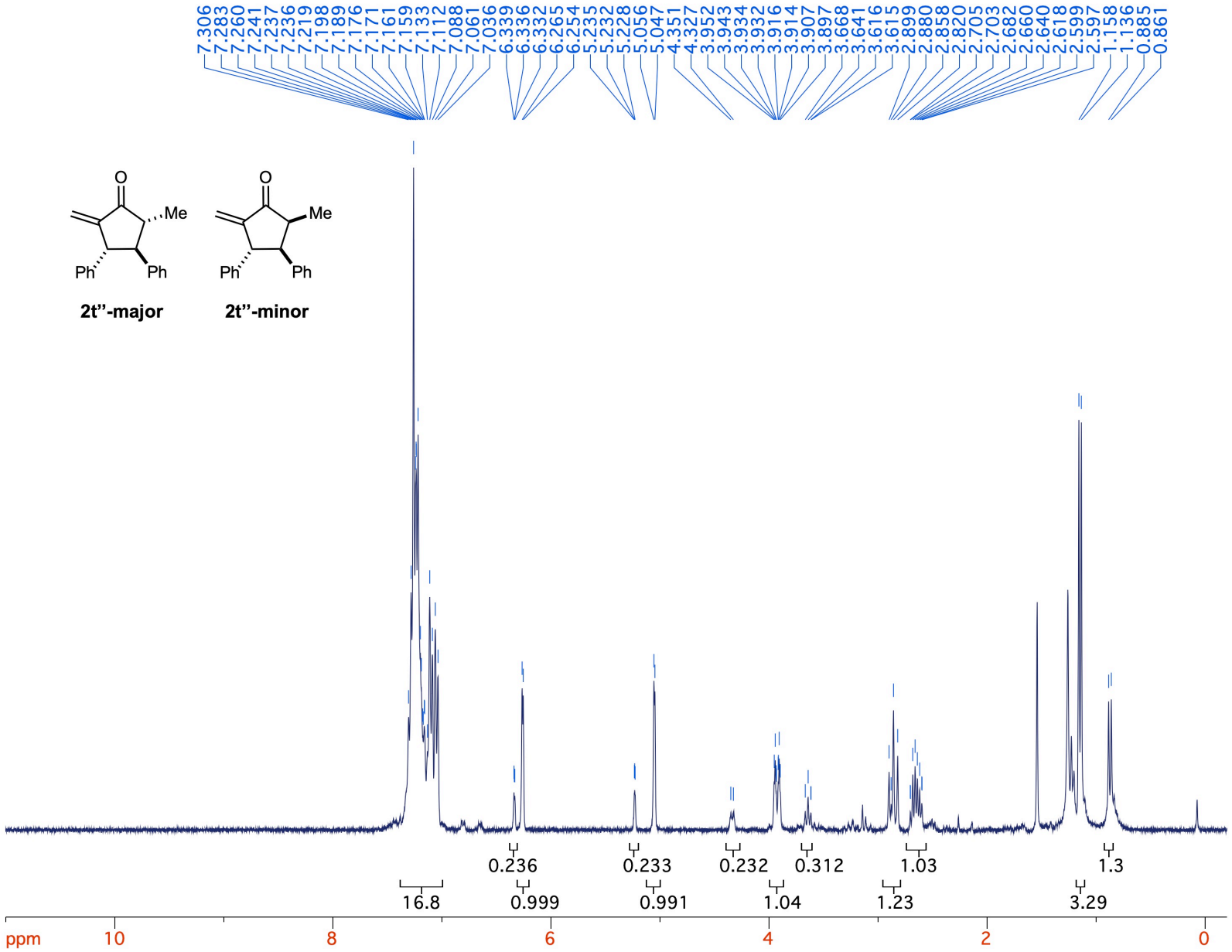

204.651
141.769
141.206
133.101
128.807
127.283
127.004
77.583
77.160
76.736
48.325
46.240
45.930
27.236
25.630
21.733
O
2q'
ppm 200
150
100
50
0

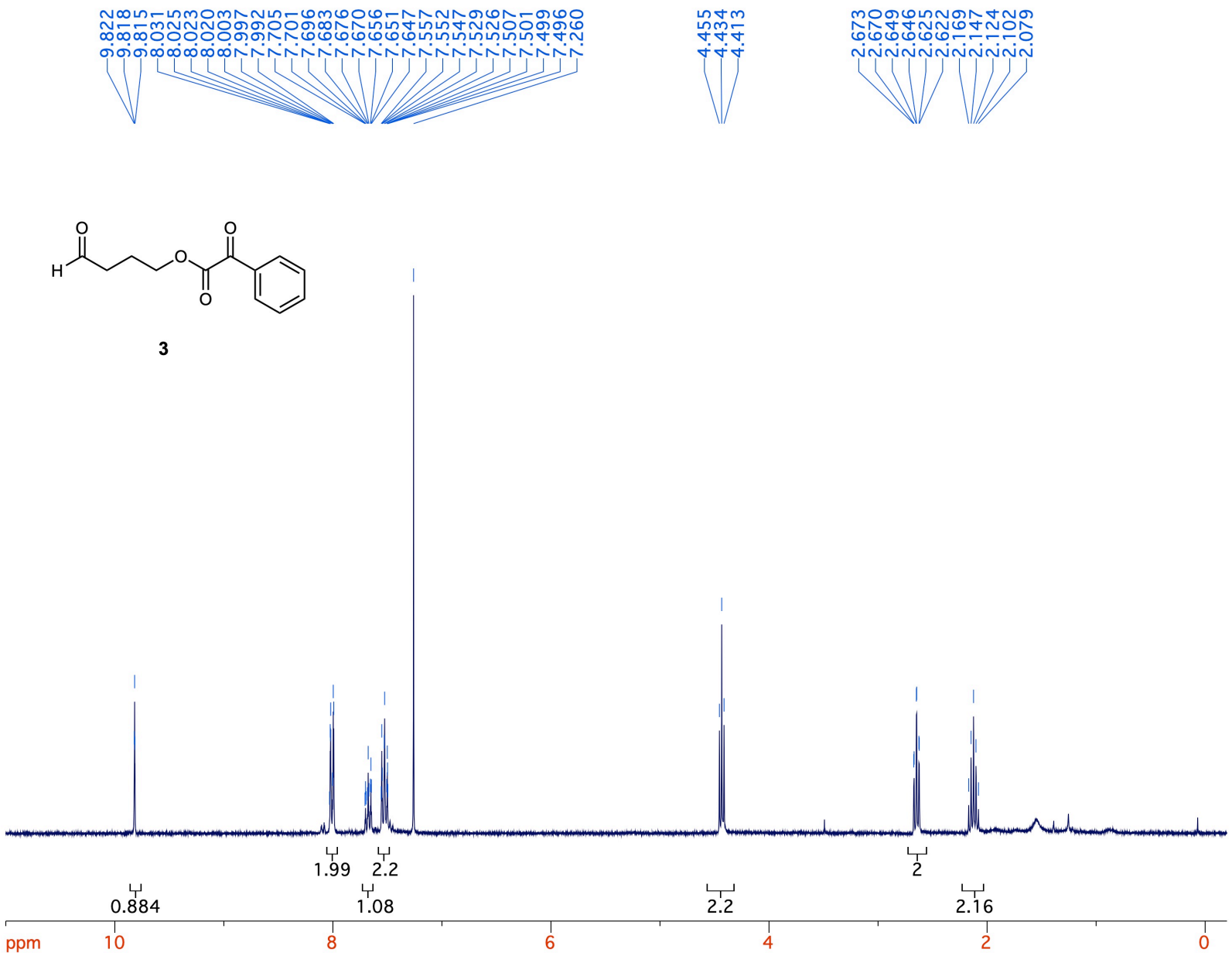

7.346
7.341
7.335
7.324
7.318
7.313
7.298
7.294
7.286
7.268
7.263
7.260
7.248
7.240
7.230
7.220
7.215
7.211
7.104
7.099
7.092
7.081
7.076
7.073
3.842
3.838
3.838
3.832
3.823
3.820
3.817
3.816
2.946
2.923
2.884
2.861
2.396
2.389
2.334
2.326
2.254
2.249
2.243
2.239
2.230
2.224
2.072
2.054
2.044
2.043
2.042
1.717
1.697
1.678
1.670
1.662
1.658
1.649
1.641
1.623
1.612
1.606
1.605
O
2q”
2.03
1.04
2.09
4.67
3.67
1
1.06
1.97
ppm
10
8
6
4
2
0

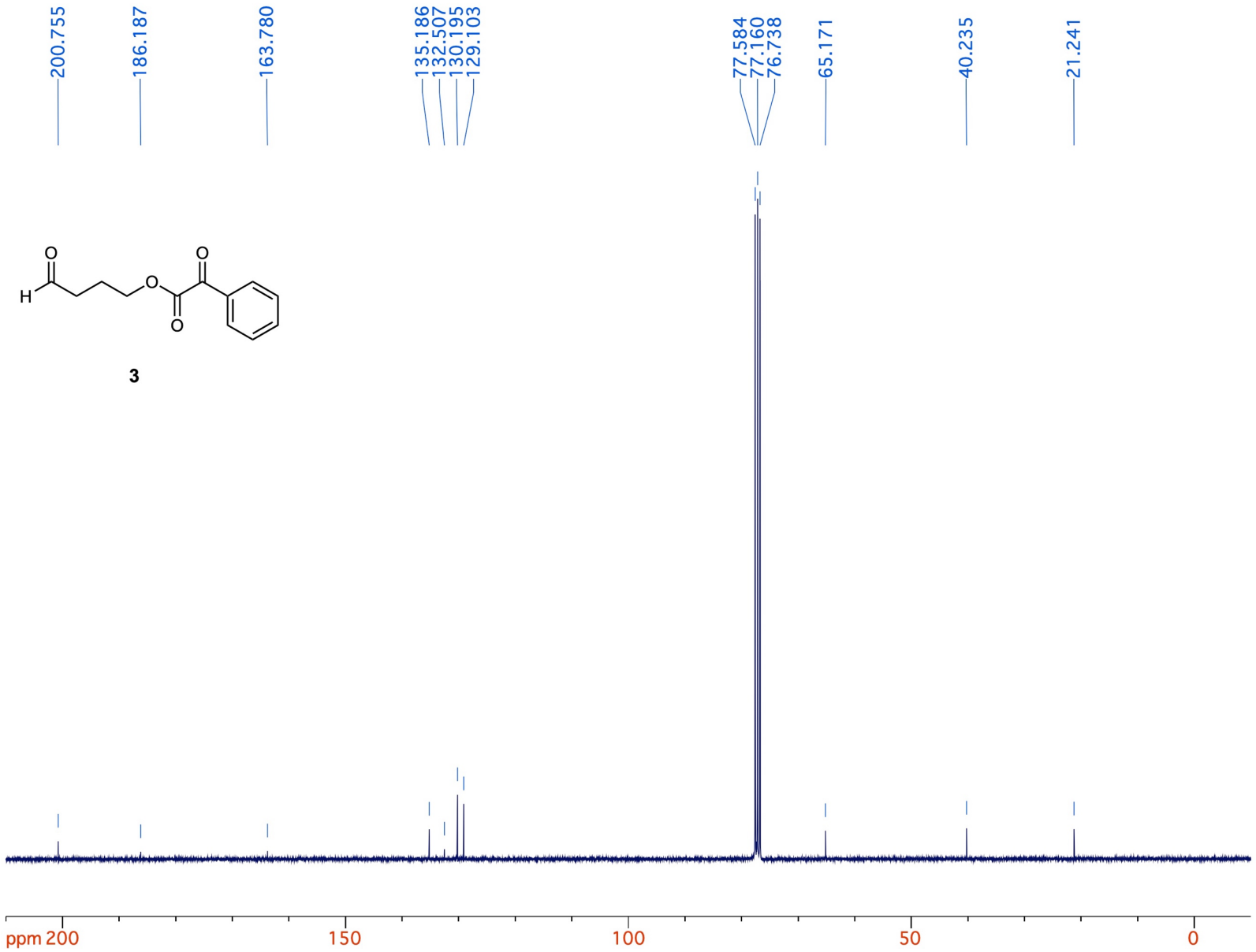

208.410
175.352
142.056
139.436
129.058
127.404
127.120
77.583
77.160
76.736
48.194
45.070
26.639
22.305
21.755
20.295
O
2q”
ppm 200
150
100
50
0


7.419
7.412
7.391
7.386
7.364
7.355
7.337
7.335
7.329
7.323
7.317
7.313
7.310
7.304
7.300
7.291
7.287
7.283
7.265
7.260
7.240
7.236
7.225
7.216
7.212
7.200
7.195
7.189
7.171
7.108
7.029
7.007
4.649
4.645
4.639
4.634
4.626
4.621
4.616
4.611
4.016
4.009
4.001
3.993
3.986
3.986
2.961
2.937
2.913
2.888
2.471
2.462
2.446
2.437
2.422
2.412
2.397
2.388
2.114
2.108
2.055
2.048
1.390
1.365
0.792
0.767
O
Me
Me
Ph
Ph
2t'
1.01
1.02
2.97
0.742
13.2
0.244
0.259
0.747
3
ppm
10
8
6
4
2
0


167.095
166.344
142.125
139.300
137.069
136.823
135.824
135.277
129.074
129.017
128.981
128.870
128.817
128.495
128.410
128.381
128.335
127.650
126.943
126.738
77.584
77.160
76.737
56.456
52.659
51.374
45.615
15.387
12.405
10.315
10.237
O
Me
Me
Ph
Ph
2t'
ppm 200
150
100
50
0


7.306
7.283
7.260
7.241
7.237
7.236
7.219
7.198
7.189
7.176
7.171
7.161
7.159
7.133
7.112
7.088
7.061
7.036
6.339
6.336
6.332
6.265
6.254
5.235
5.232
5.228
5.056
5.047
4.351
4.327
3.952
3.943
3.934
3.932
3.916
3.914
3.907
3.897
3.668
3.641
3.616
3.615
2.899
2.880
2.858
2.820
2.705
2.703
2.682
2.660
2.640
2.618
2.599
2.597
1.158
1.136
0.885
0.861
O
Me
Ph
Ph
2t''-major
O
Me
Ph
Ph
2t''-minor
0.236
0.233
0.232
0.312
1.03
1.3
16.8
0.999
0.991
1.04
1.23
3.29
ppm
10
8
6
4
2
0


9.822
9.818
9.815
8.031
8.025
8.023
8.020
8.003
7.997
7.992
7.705
7.701
7.696
7.683
7.676
7.670
7.656
7.651
7.647
7.557
7.552
7.547
7.529
7.526
7.507
7.501
7.499
7.496
7.260
4.455
4.434
4.413
2.673
2.670
2.649
2.646
2.625
2.622
2.169
2.147
2.124
2.102
2.079
O
H
O
O
O
O
3
1.99
2.2
2
0.884
1.08
2.2
2.16
ppm
10
8
6
4
2
0


200.755
186.187
163.780
135.186
132.507
130.195
129.103
77.584
77.160
76.738
65.171
40.235
21.241
O
H
O
O
O
O
3
ppm 200
150
100
50
0