Rh_2(II)-Catalyzed Ring Expansion of Cyclobutanol-substituted Aryl Azides to Access Medium-Sized *N*-Heterocycles

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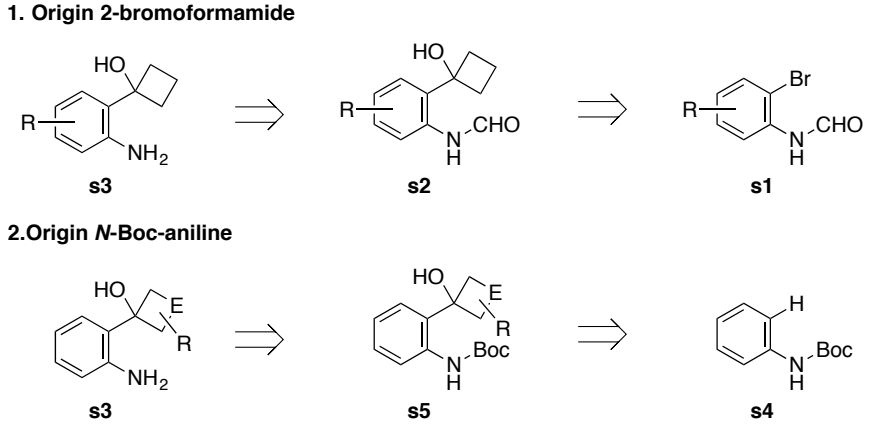
Supporting Information

Contents:

General. ^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature using 500 MHz or 300 MHz spectrometers. The data are reported as follows: chemical shift in ppm from internal tetramethylsilane on the d scale, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. High-resolution mass spectra were obtained by peak matching. Melting points are reported uncorrected. Analytical thin layer chromatography was performed on 0.25 mm silica gel plates with UV254 fluorescent indicator. Liquid chromatography was performed using forced flow (flash chromatography) of the indicated solvent system on 60Å (40 – 60 μm) mesh silica gel (SiO_2). Medium pressure liquid chromatography (MPLC) was performed using pumps to force flow the indicated solvent system down columns that had been packed with 60Å (40 – 60 μm) mesh silica gel (SiO_2). All reactions were carried out under an atmosphere of nitrogen in glassware that was oven-dried. Unless otherwise noted, all reagents were commercially obtained and, where appropriate, purified prior to use. Acetonitrile, methanol, toluene, THF, Et_2O, and CH_2Cl_2 were dried by filtration through alumina according to the procedure of Grubbs.[1] Metal salts were stored in a nitrogen atmosphere dry box.

I. Synthesis of *ortho*-Cyclobutanol Anilines

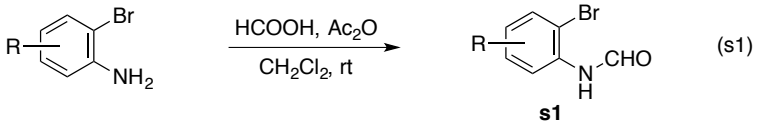
The *ortho*-cyclobutanol anilines for our method development were constructed from either 2-bromoformamide **s1** or *N*-Boc aniline (Scheme s1).



Scheme s1. Strategies to construct the *ortho*-cyclobutanol aniline precursors

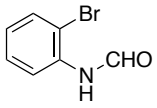
A. General Procedure for Formamide Synthesis

The formamides were prepared following the protocol reported by Takemoto and co-workers.[2]



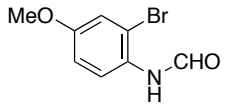
To a mixture of formic acid (3.49 equiv) and acetic anhydride (1.25 equiv) was added a solution of 2-bromoaniline (1.0 equiv) in CH_2Cl_2 and the mixture was stirred at room temperature. After 2 h, the mixture was concentrated under reduced pressure to afford the formamide product as a solid. No additional purification was performed.

B. Characterization Data of Formamides.



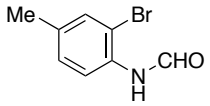
s1a

***N*-(2-Bromophenyl)formamide s1a.**[3] The general procedure was followed by using 2.00 g of 2-bromoaniline (11.6 mmol), 1.52 mL of formic acid and 1.36 mL of Ac_2O to give the product, a white solid, as a 2:1 mixture of rotamers (2.03 g, 88%). The spectral data of **s1a** matched that reported by Sarvari and Sharghi:[3] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (d, *J* = 6.0 Hz, 0.47H), 8.49 (s, 1H), 8.38 (d, *J* = 8.0 Hz, 1H), 7.70 (br s, 1H), 7.60 (d, *J* = 8.0 Hz, 0.52H), 7.55 (dd, *J* = 8.0 Hz, 1.5 Hz, 1H), 7.34 – 7.30 (m, 1.54H), 7.27 – 7.25 (m, 0.69H), 7.07 (t, *J* = 8.0 Hz, 0.5H), 7.02 – 6.99 (m, 1H), only visible signals; ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.5 (CH), 158.6 (CH), 134.8 (C), 133.5 (CH), 132.4 (CH), 128.7 (CH), 128.5 (CH), 126.4 (CH), 125.7 (CH), 122.3 (CH), 119.0 (CH), 114.5 (C), 113.0 (C), only visible signals; ATR-FTIR (thin film): 3259, 3106, 2906, 1702, 1665, 1577, 1595, 1521, 1466, 1401, 1293, 1158, 1045, 908, 739 cm^{-1}.



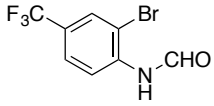
s1b

***N*-(2-Bromo-4-methoxyphenyl)formamide s1b.** The general procedure was followed by using 2.00 g of 2-bromo-4-methoxy aniline (9.9 mmol), 1.30 mL of formic acid and 1.16 mL of Ac_2O to give the product, a brown solid, as a 2:1 mixture of rotamers (2.03 g, 94%): mp = 115 – 117 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (d, *J* = 11.5 Hz, 0.46H), 8.43 (s, 1H), 8.22 (d, *J* = 9.0 Hz, 1H), 7.44 (br s, 1H), 7.27 – 7.26 (m, 0.67H), 7.17 – 7.16 (m, 1H), 7.11 – 7.10 (m, 1H), 6.87 (dd, *J* = 9.0 Hz, 2.5 Hz, 1.51H), 3.80 (s, 1.47H), 3.79 (s, 3H), only visible signals; ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.1 (C), 159.0 (CH), 156.7 (C), 128.1 (C), 123.5 (CH), 121.8 (CH), 118.5 (CH), 117.7 (CH), 114.5 (CH), 113.9 (CH), 55.8 (CH_3) 55.7 (CH_3), only visible signals; ATR-FTIR (thin film): 3247, 2891, 1697, 1662, 1581, 1538, 1488, 1403, 1393, 1294, 1223, 1032, 872, 837, 724 cm^{-1}. HRMS (ESI) m/z calcd for $C_8H_9NO_2Br$ [M + H]$^+$: 229.9816, found 229.9817.



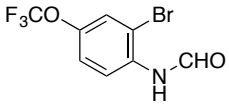
s1c

***N*-(2-Bromo-4-methylphenyl)formamide s1c.**[4] The general procedure was followed by using 1.00 g of 2-bromo-4-methyl aniline (5.4 mmol), 0.71 mL of formic acid and 0.63 mL of Ac_2O to give the product, a brown solid, as a 2:1 mixture of rotamers (1.2 g, quantitative). The spectral data of **s1c** matched that reported by Heinicke and co-workers:[4] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (d, *J* = 11.5 Hz, 0.49H), 8.46 (s, 1H), 8.23 (d, *J* = 8.5 Hz, 1H), 7.59 (br s, 1H), 7.42 (s, 0.49H), 7.37 (s, 1H), 7.13 (t, *J* = 10.0 Hz, 2H), 2.32 (s, 1.65H), 2.30 (s, 3H), only visible signals; ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.8 (CH), 158.8 (CH), 136.8 (C), 135.8 (C), 133.8 (CH), 132.6 (CH), 132.5 (C), 132.3 (C), 129.3 (CH), 129.1 (CH), 122.2 (CH), 119.4 (CH), 114.7 (C), 113.0 (C), 20.6 (CH_3), 20.5 (CH_3), only visible signals; ATR-FTIR (thin film): 3242, 2905, 1694, 1666, 1574, 1505, 1399, 1224, 1038, 863, 816, 732, 672 cm^{-1}.



s1d

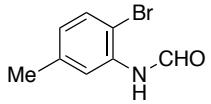
***N*-(2-Bromo-4-trifluoromethylphenyl)formamide s1d.** The general procedure was followed by using 0.894 g of 2-bromo-4-trifluoromethyl aniline (5.40 mmol), 0.49 mL of formic acid and 0.43 mL of Ac_2O to give the product, a white solid, as a mixture of rotamers (0.972 g, 97%): mp = 101 – 103 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.83 (d, *J* = 10.0 Hz, 0.24H), 8.58 (d, *J* = 8.5 Hz, 1H), 8.55 (s, 1H), 7.87 (s, 0.41H), 7.82 (s, 2H), 7.59 (d, *J* = 8.5 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 0.22H), only visible signals; ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.7 (CH), 158.9 (CH), 137.8 (C), 130.8 (C), 129.5 (CH), 127.5 (C), 127.3 (C), 125.9 (CH), 125.8 (CH), 123.0 (q, J_{CF} = 278.4 Hz, C), 121.7 (CH), 117.5 (C), 112.2 (C), only visible signals; ^{19}F NMR (282 MHz, $CDCl_3$) δ –62.8; ATR-FTIR (thin film): 3278, 1705, 1609, 1525, 1397, 1321, 1265, 1120, 1077, 894, 821, 734, 677 cm^{-1}. HRMS (ESI) m/z calcd for $C_8H_6NOF_3Br$ [M + H]$^+$: 267.9587, found 267.9585.



s1e

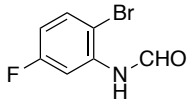
***N*-(2-Bromo-4-trifluoromethoxyphenyl)formamide s1e.** The general procedure was followed by using 1.00 g of 2-bromo-4-trifluoromethoxy aniline (3.91 mmol), 0.51 mL of formic acid and 0.46 mL of Ac_2O to give the product, a white solid, as a mixture of rotamers (1.12 g, quantitative): mp = 110 – 112 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.67 (d, *J* = 10.5 Hz, 0.26 H), 8.50 (d, *J* = 1.0 Hz, 1H), 8.45 (d, *J* = 9.5 Hz, 1H), 7.69 (br s, 1H), 7.51 (s, 0.26H), 7.45 (d, *J* = 2.0 Hz, 1H), 7.29 (d, *J* = 9.0 Hz, 0.26H), 7.21 (d, *J* = 7.5 Hz, 1.3H), only visible signals; ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.3 (CH), 158.8 (CH), 145.1 (C), 133.8 (C), 126.4 (CH), 125.2 (CH), 122.7 (CH), 122.4 (q, J_{CF} = 256.5 Hz, C), 121.5 (CH), 121.2

(CH), 119.6 (CH), 114.7 (C), 112.9 (C), only visible signals; ^{19}F NMR (282 MHz, $CDCl_3$) δ –58.7; ATR-FTIR (thin film): 3190, 3034, 2894, 1659, 1541, 1482, 1396, 1294, 1197, 1163, 1040, 942, 888, 849, 709 cm^{-1}. HRMS (ESI) m/z calcd for $C_8H_6NO_2BrF3$ [M + H]$^+$: 285.9535, found 285.9534.



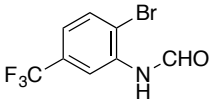
s1g

***N*-(2-Bromo-5-methylphenyl)formamide s1g.** The general procedure was followed by using 1.00 g of 2-bromo 5-methyl aniline (5.37 mmol), 0.71 mL of formic acid and 0.63 mL of Ac_2O to give the product, a brown solid, as a 2:1 mixture of rotamers (1.24 g, quantitative): mp = 97 – 99 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (d, *J* = 11.0 Hz, 0.51H), 8.47 (s, 1H), 8.22 (s, 1H), 7.63 (br s, 1.33H), 7.45 (d, *J* = 8.0 Hz, 0.53H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.07 (s, 0.49H), 6.88 (d, *J* = 8.0 Hz, 0.53H), 6.62 (d, *J* = 8.0 Hz, 1H), 2.33 (s, 1.62H), 2.32 (s, 3.34 H) only visible signals; ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.5 (CH), 158.8 (CH), 138.8 (C), 134.4 (C), 133.1 (CH), 131.9 (CH), 127.3 (CH), 126.6 (CH), 122.8 (CH), 119.7 (CH), 109.7 (C), 21.3 (CH_3), 21.1 (CH_3), only visible signals; ATR-FTIR (thin film): 3239, 2922, 1652, 1581, 1526, 1411, 1291, 1195, 1030, 815, 718, 701 cm^{-1}. HRMS (ESI) m/z calcd for C_8H_9NOBr [M + H]$^+$: 213.9870, found 213.9868.



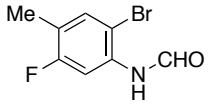
s1h

***N*-(2-Bromo-5-fluorophenyl)formamide s1h.** The general procedure was followed by using 1.00 g of 2-bromo-5-fluoro aniline (5.30 mmol), 0.70 mL of formic acid and 0.62 mL of Ac_2O to give the product, a white solid, as a 4:1 mixture of rotamers (1.05 g, 88%): mp = 133 – 135 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72 (d, *J* = 11.0 Hz, 0.25H), 8.50 (s, 1H), 8.28 (dd, *J* = 10.5 Hz, 2.5 Hz, 1H), 7.70 (br s, 1H), 7.57 – 7.54 (m, 0.29H), 7.50 (dd, *J* = 8.5 Hz, 5.5 Hz, 1H), 7.01 (d, *J* = 9.0 Hz, 0.25H), 6.81 (t, *J* = 8.5 Hz, 0.28H), 6.76 (ddd, *J* = 11.0 Hz, 8.5 Hz, 3.0 Hz, 1H), only visible signals; ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.1 (C), 161. 1 (d, J_{CF} = 31.4 Hz, C), 158.8 (CH), 137.0 (C), 136.0 (d, J_{CF} = 11.4 Hz, C), 134.4 (d, J_{CF} = 9.4 Hz, C), 133.0 (d, J_{CF} = 9.0 Hz, CH), 113.2 (d, J_{CF} = 23.3 HZ, C), 112.6 (d, J_{CF} = 23.4 Hz, CH), 109.7 (d, J_{CF} = 28.3 Hz, CH), 106.7 (d, J_{CF} = 3.6 Hz, C), 106.0 (d, J_{CF} = 27.3 Hz, C), only visible signals; ^{19}F NMR (282 MHz, $CDCl_3$) δ –111.2; ATR-FTIR (thin film): 3261, 3107, 2907, 1668, 1608, 1541, 1427, 1398, 1280, 1133, 1101, 1032, 866, 795, 612 cm^{-1}. HRMS (ESI) m/z calcd for C_7H_6NOFBr [M + H]$^+$: 217.9615, 217.9617 found.



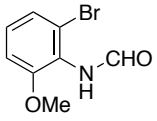
s1i

***N*-(2-Bromo-5-trifluoromethylphenyl)formamide s1i.** The general procedure was followed by using 1.00 g of 2-bromo-5-trifluoromethyl aniline (4.20 mmol), 0.56 mL of formic acid and 0.50 mL of Ac_2O to give the product, a white solid, as a mixture of rotamers (0.916 g, 91%): mp = 96 – 98 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.78 (s, 0.15H), 8.74 (s, 1H), 8.54 (s, 1H), 7.85 (br s, 1H), 7.74 (d, *J* = 7.5 Hz, 0.29H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.50 (s, 0.23H), 7.32 (d, *J* = 8.0 Hz, 0.24H), 7.25 (d, *J* = 6.0 Hz, 0.85H), only visible signals; ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.0 (CH), 158.9 (CH), 135.4 (C), 134.2 (CH), 132.9 (CH), 131.0 (q, J_{CF} = 32.6 Hz, C), 123.4 (q, J_{CF} = 269.9 Hz, C), 122.7 (CH), 122.0 (q, J_{CF} = 4.1 Hz, CH), 118.8 (q, J_{CF} = 4.5 Hz, CH), 116.3 (C), 115.1 (CH), only visible signals; ^{19}F NMR (282 MHz, $CDCl_3$) δ –63.3; ATR-FTIR (thin film): 3289, 2894, 1677, 1586, 1524, 1427, 1325, 1236, 1169, 1119, 1078, 1029, 894, 819, 737 cm^{-1}. HRMS (ESI) m/z calcd for $C_8H_6NOF_3Br$ [M + H]$^+$: 267.9586, found 267.9585.



s1j

***N*-(2-Bromo-5-fluoro-4-methylphenyl)formamide s1j.** The general procedure was followed by using 0.900 g of 2-bromo 5-fluoro 4-methyl aniline (4.20 mmol), 0.58 mL of formic acid and 0.52 mL of Ac_2O to give the product, a brown solid, as a mixture of rotamers (1.02 g, quantitative): mp = 108 – 110 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 (d, *J* = 11.0 Hz, 0.29H), 8.45 (d, *J* = 1.0 Hz, 1H), 8.16 (d, *J* = 11.5 Hz, 1H), 7.69 (br s, 1H), 7.41 (d, *J* = 7.5 Hz, 0.28H), 7.34 (d, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 10.0 Hz, 0.28H), 2.23 (s, 1H), 2.21 (d, *J* = 1.5 Hz, 3.4H), only visible signals; ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.3 (CH), 160.2 (d, J_{CF} = 243.1 Hz, C), 158.8 (CH), 135.3 (d, J_{CF} = 6.4 Hz, CH), 133.9 (d, J_{CF} = 6.0 Hz, CH), 133.4 (d, J_{CF} = 11.4 Hz, C), 122.6 (d, J_{CF} = 19.1 Hz, C), 109.4 (d, J_{CF} = 30.1 Hz, CH), 106.4 (d, J_{CF} = 3.4 Hz, C), 106.3 (CH), 106.1 (CH), 14.0 (CH_3), 13.9 (CH_3); ^{19}F NMR (282 MHz, $CDCl_3$) δ –118.7, –115.2; ATR-FTIR (thin film): 3241, 2906, 1697, 1668, 1619, 1514, 1502, 1405, 1294, 1197, 1170, 1120, 877, 772, 749, 602 cm^{-1}. HRMS (ESI) m/z calcd for C_8H_8NOFBr $[M + H]^+$: 231.9776, found 231.9773.

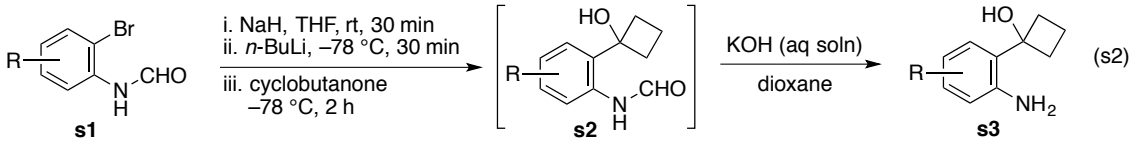


s1k

***N*-(2-Bromo-6-methoxyphenyl)formamide s1k:** The general procedure was followed by using 1.00 g of 2-bromo 6-methoxy aniline (4.50 mmol), 0.65 mL of formic acid and 0.58 mL of Ac_2O to give the product, a brown solid, as a mixture of rotamers (1.13 g, quantitative): mp = 110 – 112 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (d, *J* = 11.0 Hz, 0.39H), 8.40 (br s, 0.12H), 7.27 – 7.25 (m, 0.15H), 7.22 (d, *J* = 8.0 Hz, 0.56H), 7.14 (br s, 0.19H), 7.07 (t, *J* = 9.0 Hz, 0.65H), 7.03 (d, *J* = 8.5 Hz, 0.50H), 6.92 (d, *J* = 8.0 Hz, 0.65H), 6.72 (d, *J* = 8.5 Hz, 0.39H), 6.60 – 6.57 (m, 0.38H), 4.20 (s, 0.67H), 3.85 (d, *J* = 5.5Hz, 2.96H), only visible signals; ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.5 (C), 164.0 (C), 150.0 (C), 127.4 (CH), 125.2 (CH), 124.3 (CH), 118.1 (CH), 111.0 (CH), 109.0 (CH), 108.6 (C), 56.2 (CH_3), 55.9 (CH_3); ATR-FTIR (thin film): 3247, 2891, 1697, 1662, 1581, 1538, 1488, 1403, 1393, 1294, 1223, 1032, 872, 837, 724 cm^{-1}. HRMS (ESI) m/z calcd for $C_8H_9NO_2Br$ $[M + H]^+$: 229.9819, found 229.9817.

C. General Procedure for Synthesis of *o*-Cyclobutanol Anilines from 2-Bromoformamides

The *o*-cyclobutanol formamides were prepared following the protocol reported by Curtin and co-workers.[5] The formyl group was removed through a base-mediated hydrolysis reaction to provide the *o*-cyclobutanol aniline.



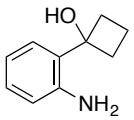
(s2)

To a slurry of NaH (60% dispersion in mineral oil, 1.83 equiv) in THF (6 mL was added dropwise a solution of *N*-(2-bromophenyl) formamide (1.0 equiv) in 4 mL of tetrahydrofuran. The mixture was stirred at room temperature for 20 minutes, then chilled to – 78 °C. To the cold suspension was added dropwise a 2.5 M solution of *n*-butyllithium in hexanes (1.25 equiv). The mixture was stirred at –78 °C. After 30 minutes, cyclobutanone (1.1 equiv) was added dropwise. The mixture was stirred at –78 °C. After 2 hours, the reactives were quenched by adding 20 mL of a saturated aqueous solution of NH_4Cl. The resulting mixture was warmed to room temperature. The mixture was extracted with 3 × 30 mL of ethyl acetate, and the combined organic layers were dried over Na_2SO_4, filtered, and the filtrate was concentrated under reduced pressure. The resulting residue was purified by medium pressure liquid chromatography

(MPLC) to give the title compounds as a mixture of rotational isomers, which were submitted to the next step without characterization.

The mixture of *o*-cyclobutanol formamide rotamers was dissolved in dioxane and treated with a 5% aq soln of KOH. The resulting mixture was heated to reflux, and the reaction progress was monitored using thin layer chromatography until the starting material was completely consumed. After the reaction mixture was cooled to room temperature, it was diluted with water. The resulting mixture was extracted with 3 × 10 mL of EtOAc. The combined organic extracts were washed with brine, dried over $MgSO_4$ and the filtrate was concentrated under reduced pressure. The resulting residue was purified by MPLC to afford the product.

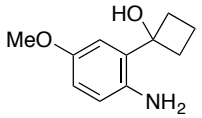
D. Characterization Data of *o*-Cyclobutanol Formamides



s3a

***N*-(2-(1-Hydroxycyclobutyl)phenyl)formamide s2a.** The general procedure was followed by using 0.653 g (17.0 mmol) of NaH, 2.00 g (9.30 mmol) of **s1a**, 4.65 mL (11.6 mmol) of *n*-BuLi and 0.760 mL (10.2 mmol) of cyclobutanone to give the crude material. Purification by MPLC (hexanes:EtOAc 3:1– 1:1) provided **s2a** as a thick yellow oil (0.50 g, 26%), which was submitted to the KOH-mediated hydrolysis step without additional characterization.

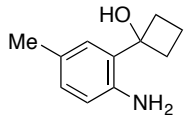
***N*-(2-(1-Hydroxycyclobutyl)phenyl)aniline s3a.**[5] The general procedure was followed by using 0.200 g (1.23 mmol) of **s2a**. Purification by MPLC (5:1 – 3:1 hexanes:EtOAc) afforded the product as a brown solid (0.083 g, 50%): **s3a** was previously reported by Curtin and co-workers:[5] R_f = 0.28 (5:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$ with 1% (v/v) TMS) δ 7.23 (dd, *J* = 7.5 Hz, 1.0 Hz, 1H), 7.12 – 7.09 (m, 1H), 6.74 (dt, *J* = 7.5 Hz, 1.5 Hz, 1H), 6.69 (dd, *J* = 8.0 Hz, 1.5 Hz, 1H), 4.19 (br s, 2H), 2.70 – 2.65 (m, 2H), 2.39 – 2.33 (m, 2H), 2.04 – 1.96 (m, 1H), 1.69 – 1.60 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$ with 1% (v/v) TMS) δ 145.6 (C), 128.8 (CH), 128.1 (C), 125.3 (CH), 117.7 (CH), 116.8 (CH), 77.6 (C), 35.1 (CH_2), 13.7 (CH_2); ATR-FTIR (thin film): 3341, 2925, 2853, 1608, 1494, 1456, 1303, 1122, 746 cm^{-1}.



s3b

***N*-(2-(1-Hydroxycyclobutyl)-4-methoxyphenyl)formamide s2b.** The general procedure was followed by using 0.303 g (7.90 mmol) of NaH, 1.00 g (4.30 mmol) of **s1b**, 2.20 mL (5.40 mmol) of *n*-BuLi and 0.350 mL (4.70 mmol) of cyclobutanone to give the crude material. Purification by MPLC (hexanes:EtOAc 3:1– 1:1) gave the product as a thick yellow oil (0.20 g, 21%), which was submitted to the KOH-mediated hydrolysis step without additional characterization.

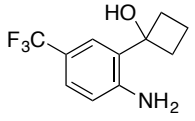
***N*-(2-(1-Hydroxycyclobutyl)-4-methoxyphenyl)aniline s3b.** The general procedure was followed by using 0.300 g (1.30 mmol) of **s2b**. Purification by MPLC (5:1 – 3:1 hexanes:EtOAc) afforded the product as a brown solid (0.280 g, 78%): R_f = 0.13 (5:1 hexanes:EtOAc); mp = 121 – 123 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.84 – 6.83 (m, 1H), 6.70 – 6.67 (m, 1H), 6.64 – 6.62 (m, 1H), 3.85 – 3.75 (m, 5H), 2.64 – 2.59 (m, 2H), 2.38 – 2.31 (m, 2H), 2.02 – 1.95 (m, 1H), 1.69 – 1.60 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.3 (C), 138.9 (C), 130.5 (C), 118.0 (CH), 113.1 (CH), 112.3 (CH), 77.3 (C), 55.9 (CH_3), 35.1 (CH_2), 13.6 (CH_2); ATR-FTIR (thin film): 3400, 3363, 2935, 1766, 1498, 1428, 1286, 1217, 1128, 1048, 815 cm^{-1}. HRMS (EI) m/z calcd for $C_{11}H_{15}NO_2$: 193.1103, found 193.1094.



s3c

***N*-(2-(1-Hydroxycyclobutyl)-4-methylphenyl)formamide s2c.** The general procedure was followed by using 0.164 g (4.30 mmol) of NaH, 0.500 g (2.34 mmol) of **s1c**, 1.20 mL (2.93 mmol) of *n*-BuLi and 0.200 mL (4.70 mmol) of cyclobutanone to give the crude material. Purification by MPLC (hexanes:EtOAc 3:1– 1:1) gave the product as a thick brown oil (0.10 g, 20%), which was submitted to the KOH-mediated hydrolysis step without additional characterization.

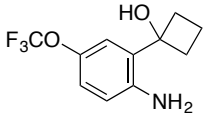
***N*-(2-(1-Hydroxycyclobutyl)-4-methylphenyl)aniline s3c.** The general procedure was followed by using 0.250 g (1.22 mmol) of **s2c**. Purification by MPLC (5:1 – 3:1 hexanes:EtOAc) afforded the product as a brown solid (0.130 g, 60%): R_f = 0.18 (5:1 hexanes:EtOAc); mp = 104 – 106 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.02 (s, 1H), 6.93 (d, *J* = 7.5 Hz, 1H), 6.60 (d, *J* = 8.0 Hz, 1H), 3.98 (br s, 2H), 2.67 – 2.62 (m, 2H), 2.36 – 2.31 (m, 2H), 2.27 (s, 3H), 2.02 – 1.97 (m, 1H), 1.68 – 1.60 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142. 9 (C), 129.1 (CH), 128.6 (C), 127.0 (C), 125.9 (CH), 117.1 (CH), 77.5 (C), 35.1 (CH_2), 20.7 (CH_3), 13.8 (CH_2); ATR-FTIR (thin film): 3367, 2983, 2945, 2860, 1502, 1319, 1290, 1130, 909, 815, 760 cm^{-1}. HRMS (ESI) m/z calcd for $C_{11}H_{14}NO$ $[M – H]^+$: 176.1073, found 176.1075.



s3d

***N*-(2-(1-Hydroxycyclobutyl)-4-trifluoromethylphenyl)formamide s2d.** The general procedure was followed by using 0.211 g (5.50 mmol) of NaH, 0.800 g (3.00 mmol) of **s1d**, 1.50 mL (3.80 mmol) of *n*-BuLi and 0.250 mL (3.30 mmol) of cyclobutanone to give the crude material. Purification by MPLC (hexanes:EtOAc 3:1– 1:1) gave the product as a thick brown oil (0.20 g, 26%), which was submitted to the KOH-mediated hydrolysis step without additional characterization.

***N*-(2-(1-Hydroxycyclobutyl)-4-trifluoromethylphenyl)aniline s3d.** The general procedure was followed by using 0.260 g (1.00 mmol) of **s2d**. Purification by MPLC (5:1 hexanes:EtOAc) afforded the product as a yellow solid (0.160 g, 70%): R_f = 0.33 (5:1 hexanes:EtOAc), mp = 107 – 109 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (s, 1H), 7.33 (d, *J* = 8.5 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 4.16 (br s, 2H), 2.65 – 2.60 (m, 2H), 2.37 – 2.31 (m, 2H), 2.04 – 1.96 (m, 1H), 1.68 – 1.59 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.7 (C), 127.3 (C), 126.0 (q, J_{CF} = 4.0 Hz, CH), 124.8 (q, J_{CF} = 268.5 Hz, C), 122.6 (q, J_{CF} = 3.3 Hz, CH), 118.9 (q, J_{CF} = 32.0 Hz, C), 115.9 (CH), 77.3 (C), 34.9 (CH_2), 13.6 (CH_2); ^{19}F NMR (282 MHz, $CDCl_3$) δ –61.4 ; ATR-FTIR (thin film): 3374, 3203, 2992, 2954, 1622, 1331, 1263, 1176, 1110, 1082, 904 cm^{-1}. HRMS (ESI) m/z calcd for $C_{11}H_{11}NOF_3$ $[M – H]^+$: 230.0799, found 230.0793.

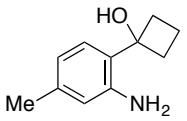


s3e

N-(2-(1-Hydroxycyclobutyl)-4-trifluoromethoxyphenyl)formamide s2e. The general procedure was followed by using 0.246 g (6.40 mmol) of NaH, 1.00 g (3.50 mmol) of **s1e**, 1.80 mL (3.80 mmol) of *n*-BuLi and 0.290 mL (3.30 mmol) of cyclobutanone to give the crude material. Purification by MPLC (hexanes:EtOAc 3:1– 1:1) gave the product as a thick brown oil (0.29 g, 30%), which was submitted to the KOH-mediated hydrolysis step without additional characterization.

***N*-(2-(1-Hydroxycyclobutyl)-4-trifluoromethoxyphenyl)aniline s3e.** The general procedure was followed by using 0.300 g (1.09 mmol) of **s2e**. Purification by MPLC (5:1 hexanes:EtOAc) afforded the product as a yellow solid (0.180 g, 65%): R_f = 0.25 (5:1 hexanes:EtOAc); mp = 116 – 118 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.06 (d, *J* = 2.0 Hz, 1H), 6.98 –

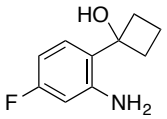
6.96 (m, 1H), 6.61 (d, J = 9.0 Hz, 1H), 4.26 (br s, 2H), 2.62 – 2.57 (m, 2H), 2.37 – 2.31 (m, 2H), 2.03 – 1.95 (m, 1H), 1.67 – 1.58 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.4 (C), 140.6 (C), 129.0 (C), 121.6 (CH), 120.7 (q, J_{CF} = 253.6 Hz, C), 118.8 (CH), 117.0 (CH), 77.1 (C), 35.0 (CH_2), 13.5 (CH_2); ^{19}F NMR (282 MHz, $CDCl_3$) δ –58.8; ATR-FTIR (thin film): 3375, 2990, 1625, 1498, 1249, 1215, 1154, 885, 822 cm^{-1}. HRMS (EI) m/z calcd for $C_{11}H_{12}NO_2F_3$: 247.0813, found 247.0820.



s3g

***N*-(2-(1-Hydroxycyclobutyl))-5-methylphenyl)formamide s2g.** The general procedure was followed by using 0.329 g (8.55 mmol) of NaH, 1.00 g (4.67 mmol) of **s1g**, 2.30 mL (5.84 mmol) of *n*-BuLi and 0.390 mL (5.14 mmol) of cyclobutanone to give the crude material. Purification by MPLC (hexanes:EtOAc 3:1– 1:1) gave the product as a thick brown oil (0.20 g, 21%), which was submitted to the KOH-mediated hydrolysis step without additional characterization.

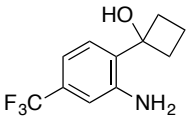
***N*-(2-(1-Hydroxycyclobutyl)-5-methylphenyl)aniline s3g.** The general procedure was followed by using 0.180 g (1.02 mmol) of **s2g**. Purification by MPLC (5:1 hexanes:EtOAc) afforded the product as a brown solid (0.16 g, 75%): R_f = 0.28 (5:1 hexanes:EtOAc); mp = 96 – 98 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (d, J = 8.0 Hz, 1H), 6.56 (d, J = 8.0 Hz, 1H), 6.51 (s, 1H), 4.12 (br s, 2H), 2.66 – 2.61 (m, 2H), 2.34 (q, J = 9.0 Hz, 2H), 2.27 (s, 3H), 2.01 – 1.93 (m, 1H), 1.62 (quin, J = 8.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.5 (C), 138.6 (C), 125. 7 (C), 125.3 (CH), 118.5 (CH), 117.6 (CH), 77.2 (C), 35.1 (CH_2) 21.1 (CH_3), 13.7 (CH_2); ATR-FTIR (thin film): 3418, 3320, 2976, 2934, 2858, 1615, 1510, 1428, 1115, 819, 792 cm^{-1}. HRMS (EI) m/z calcd for $C_{11}H_{15}NO$: 177.11541, found 177.11537.



s3h

***N*-(5-Fluoro-2-(1-hydroxycyclobutyl)phenyl)formamide s2h.** The general procedure was followed by using 0.288 g (7.50 mmol) of NaH, 0.900 g (4.10 mmol) of **s1h**, 2.00 mL (5.10 mmol) of *n*-BuLi and 0.340 mL (4.50 mmol) of cyclobutanone to give the crude material. Purification by MPLC (hexanes:EtOAc 3:1– 1:1) gave the product as a thick brown oil (0.15 g, 18%), which was submitted to the KOH-mediated hydrolysis step without additional characterization.

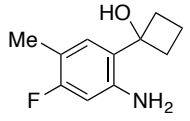
***N*-(5-Fluoro-2-(1-hydroxycyclobutyl)phenyl)aniline s3h.** The general procedure was followed by using 0.215 g (1.03 mmol) of **s2h**. Purification by MPLC (5:1 hexanes:EtOAc) afforded the product as a brown solid (0.130 g, 68%): R_f = 0.25 (5:1 hexanes:EtOAc); mp = 139 – 141 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 (dd, J = 8.0 Hz, 6.0 Hz, 1H), 6.38 (dt, J = 8.5 Hz, 2.5 Hz, 1H), 6.33 (dd, J = 11.0 Hz, 2.5 Hz, 1H), 4.30 (br s, 2H), 2.60 – 2.55 (m, 2H), 2.32 – 2.27 (m, 2H), 2.00 – 1.92 (m, 1H), 1.64 – 1.55 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.0 (d, J_{CF} = 240.8, C), 147.5 (d, J_{CF} = 9.4 Hz, C), 126.7 (d, J_{CF} = 11.0 Hz, CH), 124.0 (C), 103.7 (d, J_{CF} = 20.3 Hz, CH), 103.2 (d, J_{CF} = 24.0 Hz, CH), 77.1 (C), 35.2 (CH_2), 13.7 (CH_2); ^{19}F NMR (282 MHz, $CDCl_3$) δ –115.2; ATR-FTIR (thin film): 3418, 3326, 3230, 2923, 2852, 1622, 1434, 1332, 1162, 1126, 1104, 870, 804, 740 cm^{-1}. HRMS (ESI) m/z calcd for $C_{10}H_{11}NOF$ $[M - H]^+$: 180.0827, found 180.0825.



s3i

N-(2-(1-Hydroxycyclobutyl)-5-trifluoromethylphenyl)formamide s2i. The general procedure was followed by using 0.209 g (5.45 mmol) of NaH, 0.800 g (2.98 mmol) of **s1i**, 1.50 mL (3.73 mmol) of *n*-BuLi and 0.250 mL (3.30 mmol) of cyclobutanone to give the crude material. Purification by MPLC (hexanes:EtOAc 3:1– 1:1) gave the product as a thick brown oil (0.18 g, 23%), which was submitted to the KOH-mediated hydrolysis step without additional characterization.

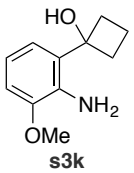
***N*-(2-(1-Hydroxycyclobutyl)-5-trifluoromethylphenyl)aniline s3i.** The general procedure was followed by using 0.263 g (1.02 mmol) of **s2i**. Purification by MPLC (5:1 hexanes:EtOAc) afforded the product as a yellow solid (0.170 g, 70%): R_f = 0.28 (5:1 hexanes:EtOAc); mp = 102 – 104 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (d, J = 8.0 Hz, 1H), 6.96 (d, J = 8.0 Hz, 1H), 6.86 (s, 1H), 4.40 (s, 2H), 2.64 – 2.59 (m, 2H), 2.37 – 2.31 (m, 2H), 2.02 – 1.96 (m, 1H), 1.65 – 1.58 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.0 (C), 130.9 (q, J_{CF} = 31.9 Hz, C), 127.4 (C), 125.7 (CH), 124.1 (q, J_{CF} = 270.5 Hz, C), 114.0 (q, J_{CF} = 4.0 Hz, CH), 112.9 (q, J_{CF} = 3.6 Hz, CH), 77.2 (C), 35.0 (CH_2), 13.6 (CH_2); ^{19}F NMR (282 MHz, $CDCl_3$) δ –63.3; ATR-FTIR (thin film): 3418, 3326, 3230, 2923, 2852, 1622, 1434, 1332, 1162, 1126, 1104, 870, 804, 740 cm^{-1}. HRMS (ESI) m/z calcd for $C_{11}H_{11}NOF_3$ [M – H]$^+$: 230.0783, found 230.0793.



s3j

***N*-(5-Fluoro-2-(1-hydroxycyclobutyl)-3-methylphenyl)formamide s2j.** The general procedure was followed by using 0.174 g (7.10 mmol) of NaH, 0.900 g (3.90 mmol) of **s1j**, 1.90 mL (4.88 mmol) of *n*-BuLi and 0.320 mL (4.30 mmol) of cyclobutanone to give the crude material. Purification by MPLC (hexanes:EtOAc 3:1– 1:1) gave the product as a thick brown oil (0.18 g, 21%), which was submitted to the KOH-mediated hydrolysis step without additional characterization.

***N*-(5-Fluoro-2-(1-hydroxycyclobutyl)-4-methylphenyl)aniline s3j.** The general procedure was followed by using 0.260 g (1.17 mmol) of **s2j**. Purification by MPLC (5:1 hexanes:EtOAc) afforded the product as a red solid (0.14 g, 60%) as a mixture of rotamers: R_f = 0.33 (5:1 hexanes:EtOAc); mp = 114 – 116 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.97 (d, J = 8.5 Hz, 1H), 6.84 (t, J = 8.0 Hz, 0.26H), 6.35 (d, J = 11.0 Hz, 1.21H), 4.13 (s, 2H), 2.82 – 2.76 (m, 0.58H), 2.63 – 2.60 (m, 2H), 2.44 – 2.40 (m, 0.70H), 2.35 – 2.29 (m, 3H), 2.16 (s, 3H), 2.12 (s, 0.90 H), 2.00 – 1.96 (m, 1H), 1.88 – 1.85 (m, 0.37H), 1.66 – 1.57 (m, 1H), 1.27 – 1.24 (m, 0.19H) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.2 (d, J_{CF} = 241.3 Hz, C), 145.0 (d, J_{CF} = 10.0 Hz, C), 130.3 (d, J_{CF} = 8.1 Hz, CH), 128.1 (d, J_{CF} = 6.9 Hz, CH), 124.0 (C), 112.6 (d, J_{CF} = 17.3 Hz, C), 111.8 (CH), 103.4 (d, J_{CF} = 25.0 Hz, CH), 77.1 (C), 37.1 (d, J_{CF} = 5.6 Hz, CH_2), 35.3 (CH_2), 17.0 (CH_2), 13.8 (CH_3), 13.7 (CH_2), only visible signals; ^{19}F NMR (282 MHz, $CDCl_3$) δ –120.0, –119.2; ATR-FTIR (thin film): 3346, 2948, 2867, 1632, 1587, 1509, 1419, 1310, 1141, 1110, 1044, 1023, 882, 782 cm^{-1}. HRMS (ESI) m/z calcd for $C_{11}H_{13}NOF$ [M – H]$^+$: 194.0979, found 194.0981.



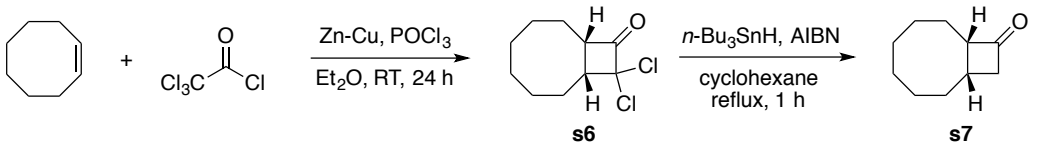
s3k

***N*-(2-(1-Hydroxycyclobutyl-6-methoxy)phenyl)formamide s2k.** The general procedure was followed by using 0.303 g (7.90 mmol) of NaH, 1 g (4.30 mmol) of **s1k**, 2.20 mL (5.40 mmol) of *n*-BuLi and 0.350 mL (4.70 mmol) of

cyclobutanone to give the crude material. Purification by MPLC (hexanes:EtOAc 3:1– 1:1) gave the product as a thick yellow oil (0.14 g, 13%), which was submitted to the KOH-mediated hydrolysis step without additional characterization.

***N*-(2-(1-Hydroxycyclobutyl-6-methoxy)phenyl)aniline s3k.** The general procedure was followed by using 0.225 g (1.02 mmol) of **s2k**. Purification by MPLC (5:1 hexane:EtOAc) afforded the product as a red solid (0.14 g, 70%): R_f = 0.25 (5:1 hexanes:EtOAc); mp = 116 – 118 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.90 (dd, *J* = 8.0 Hz, 1.0 Hz, 1H), 6.79 (dd, *J* = 8.0 Hz, 1.0 Hz, 1H), 6.70 (t, *J* = 8.0 Hz, 1H), 4.36 (s, 2H), 3.86 (s, 3H), 3.85 (s, 1H), 2.70 – 2.65 (m, 2H), 2.40 – 2.31 (m, 2H), 2.02 – 1.95 (m, 1H), 1.68 – 1.59 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.8 (C), 135.0 (C), 128.4 (C), 117.6 (CH), 116.7 (CH), 109.9 (CH), 77.6 (C), 55.7 (CH_3), 35.2 (CH_2), 13.8 (CH_2); ATR-FTIR (thin film): 3478, 3389, 3267, 2985, 2942, 2835, 1615, 1568, 1463, 1439, 1284, 1219, 1122, 1048, 954, 837, 734 cm^{-1}. HRMS (EI) m/z calcd for $C_{11}H_{15}NO_2$: 193.10965, found 193.11028.

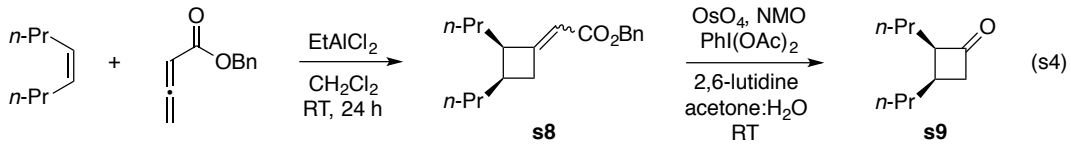
E. General Procedure for Synthesis of Cyclobutanones



(s3)

(1*R*,8*S*)-10,10 dichlorobicyclo[6.2.0]decan-9-one s6.[6] The compound was prepared using the procedure developed by Deprés and co-workers.[6] To a stirred mixture of 0.500 g (4.50 mmol) of commercially available cis-cyclooctene and 0.589 g (9.00 mmol) of Zn-Cu couple under argon was added over 1h a solution of 0.64 mL (6.80 mmol) of $POCl_3$ and 0.76 mL (6.80 mmol) of CCl_3COCl in 10 mL dry ether. After the reaction was stirred for 14 h, the ether solution was separated from the excess couple and added to hexane, and the resulting mixture was partially concentrated under reduced pressure in order to precipitate the zinc chloride. The supernatant was decanted and washed successively with cold water, cold aqueous sodium bicarbonate solution, water, and brine, and then dried over anhydrous $MgSO_4$. Evaporation of the solvent under reduced pressure afforded **s6** as a clear oil (0.460 g, 45%) which was submitted in the next step without further characterization.

(1*S*,8*S*)-[6.2.0]decan-9-one s7.[7] Dechlorination was accomplished following the procedure developed by Montaigne and Ghosez.[7] Under an inert atmosphere of argon, 1.60 mL (5.80 mmol) of freshly distilled Bu_3SnH was heated at reflux. To this solution was added, 0.010 g (0.06 mmol) of AIBN and 0.460 g (2.00 mmol) of **s6** in cyclohexane quickly in one portion and refluxed for 1h. The solution was cooled, concentrated *in vacuo* and purified using MPLC (25:1 hexanes:EtOAc) to give the product as a colorless oil (0.128 g, 42%): R_f = 0.47 (10:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.29 – 3.21 (m, 1H), 3.14 – 3.08 (m, 1H), 2.53 – 2.43 (m, 2H), 1.81 – 1.62 (m, 5H), 1.59 – 1.53 (m, 3H), 1.40 – 1.23 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.2 (C), 62.4 (CH), 52.4 (CH_2), 30.3 (CH_2), 29.8 (CH), 29.7 (CH_2), 28.6 (CH_2), 26.1 (CH_2), 25.4 (CH_2), 22.0 (CH_2); ATR-FTIR (thin film): 2916, 2850, 1773, 1464, 1445, 1208, 1083 cm^{-1}. HRMS (EI) m/z calcd for $C_{10}H_{15}O$: 151.11177, found 151.11230.



(s4)

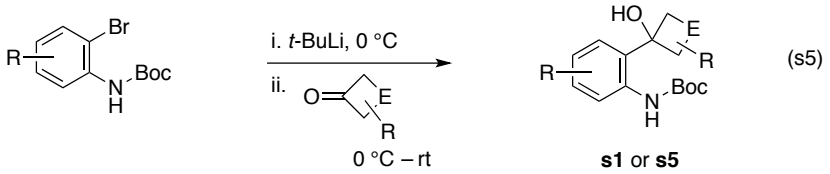
Benzyl 2-(2*R*,3*R*)-2,3-dipropylcyclobutylidene)acetate s8.[8] The compound was prepared using the procedure developed by Snider and Spindell.[8] 0.50 mL (3.20 mmol) of commercially available cis-4 octene was added dropwise to a solution of 0.507 g (2.91 mmol) of benzyl buta-2,3 dienoate and 2.65 mL (2.65 mmol) of $EtAlCl_2$ in 6 mL of CH_2Cl_2. The reaction mixture was stirred for 24 h at 25 °C, diluted with ether, and quenched by slow addition of saturated NaH_2PO_4 solution. A 10% aq soln of hydrochloric acid was added to dissolve the precipitated alumina. The two layers were separated and the aqueous layer was washed with three portions of ether. The combined organic layers were dried over $MgSO_4$ and

concentrated *in vacuo* and purified using MPLC (20:1 hexanes:EtOAc) to give **s8**, a yellow oil, as 12.5:1 (E:Z) mixture of diastereomers (0.641 g, 77%): R_f = 0.81 (10:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 5.66H), 5.70 – 5.59 (m, 1H), 5.63 – 5.62 (m, 0.08H), 5.14 (s, 2.06H), 5.13 (s, 0.20H), 3.16 – 3.10 (m, 1.08H), 3.07 – 3.01 (m, 1.09H), 2.73 – 2.68 (m, 1.14H), 2.45 – 2.38 (m, 1.15H), 1.50 – 1.43 (m, 3.27H), 1.39 – 1.18 (m, 6.07H), 0.93 – 0.88 (m, 6.71H), 0.87 (t, *J* = 7.5 Hz, 0.43H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.6 (C), 166.5 (C), 136.5 (C), 128.5 (CH), 128.3 (CH), 128.1 (CH), 128.0 (CH), 111.5 (CH), 111.0 (CH), 65.5 (CH_2), 48.4 (CH), 47.3 (CH), 37.8 (CH_2), 37.6 (CH_2), 34.4 (CH), 34.2 (CH), 32.6 (CH_2), 32.1 (CH2), 30.9 (CH_2), 30.0 (CH_2), 22.0 (CH_2), 21.3 (CH_2), 20.7 (CH_2), 14.4 (CH_3), 14.2 (CH_3), 14.2 (CH_3); ATR-FTIR (thin film): 2956, 2927, 2871, 1714, 1670, 1456, 1377, 1336, 1260, 1176, 1004 cm^{-1}. HRMS (EI) m/z calcd for $C_{19}H_{26}O_2$: 286.19366, found 286.19328.

(2*R*,3*R*)-2,3-dipropylcyclobutan-1-one s9.[9] The compound was prepared using the procedure developed by Nicolaou and co-workers.[9] To a solution of 0.250 g of cyclobutante **s8** (0.87 mmol) in 10:1 acetone:water (0.1 M) were added 0.20 mL of 2,6-lutidine (1.74 mmol), 0.153 g of 4-methylmorpholine *N*-oxide (1.31 mmol) and 0.11 mL of osmium tetroxide (4% in H_2O, 0.02 mmol). The reaction progress was monitored using TLC. When the starting material had been consumed, 0.420 g of $PhI(OAc)_2$ (1.31 mmol) was added. After stirring for 2 h, the reaction was quenched with saturated aqueous sodium thiosulfate (10 mL). The mixture was extracted with ethyl acetate (3 × 10 mL), washed with saturated aqueous copper sulfate (2 × 20 mL), dried over $MgSO_4$, and concentrated in vacuo. The crude residue was purified by MPLC (49:1 hexanes:EtOAc) to give **s9** as a clear oil (0.097 g, 72%): R_f = 0.78 (10:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.28 – 3.22 (m, 1H), 3.14 – 3.08 (m, 1H), 2.51 – 2.39 (m, 2H), 1.61 – 1.54 (m, 1H), 1.46 – 1.19 (m, 7H), 0.94 (t, *J* = 7.5 Hz, 3H), 0.90 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.0 (C), 61.7 (CH), 50.2 (CH_2), 32.3 (CH_2), 27.4 (CH), 26.4 (CH_2), 21.4 (CH_2), 21.2 (CH_2), 14.1 (CH_3), 14.1 (CH_3); ATR-FTIR (thin film): 2957 , 2928, 2873, 1775, 1465 cm^{-1}. HRMS (ESI) m/z calcd for $C_{10}H_{19}O$ $[M + H]^+$: 155.14398, found 155.14360.

F. General Procedure for Synthesis of *o*-Cyclobutanol Carbamates

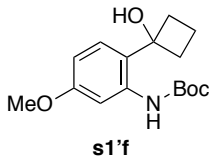
o-Cyclobutanol carbamates were prepared following the protocol reported by Fensome and co-workers.[10]



(s5)

To a cooled (0 °C) 3 M solution of commercially available *N*-Boc aniline (1.0 equiv) in dry Et_2O under an inert atmosphere of argon was dropwise added *t*-butyl lithium (1.9 M in pentane, 2.5 equiv) using a syringe pump. After 3 h, a solution of the cycloalkanone (1.5 equiv) in dry Et_2O was added dropwise. The resulting mixture was allowed to warm to rt. The reactives were quenched through the addition of a saturated aq soln of NH_4Cl. The resulting mixture was diluted with EtOAc. The two layers were separated, and the aqueous layer was extracted 3 additional times with EtOAc (3 × 5 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$ and the filtrate concentrated under reduced pressure. The resulting residue was purified by MPLC to afford the product.

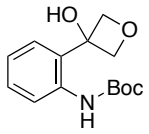
G. Characterization data for *o*-Cyclobutanol Carbamates



s1'f

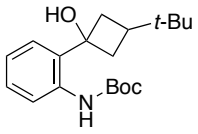
***tert*-Butyl (2-(1-hydroxycyclobutyl)-5-methoxyphenylcarbamate s1'f.** The general procedure was followed at –78 °C using 1.000 g of commercially available *tert*-butyl (2-bromo-5-methoxyphenyl) carbamate (3.31 mmol), 4.36 mL of *t*-

butyl lithium (8.28 mmol) and 0.370 mL of cyclobutanone (4.97 mmol). Purification using MPLC (5:1 hexanes:EtOAc) gave the product as a white sticky solid (0.296 g, 24%): R_f = 0.48 (5:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (br s, 1H), 7.60 (d, *J* = 3.0 Hz, 1H), 7.18 (d, *J* = 8.5 Hz, 1H), 6.53 (dd, *J* = 8.5 Hz, 3.0 Hz, 1H), 3.80 (s, 3H), 2.59 – 2.53 (m, 2H), 2.40 (s, 1H), 2.39 – 2.31 (m, 2H), 2.05 – 1.97 (m, 1H), 1.67 – 1.59 (m, 1H), 1.50 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.8 (C), 153.1 (C), 138.6 (C), 125.8 (CH), 124.9 (C), 108.3 (CH), 107.0 (CH), 80.2 (C), 77.1 (C), 55.4 (CH_3), 35.6 (CH_2), 28.4 (CH_3), 13.8 (CH_2); ATR-FTIR (thin film): 3346, 2978, 2360, 1727, 1703, 1616, 1528, 1239, 876 cm^{-1}. HRMS (ESI) m/z calcd for $C_{16}H_{23}NO_4Na$ [M + Na]$^+$: 316.1517, found 316.1515.



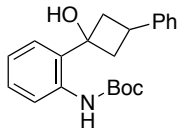
s5b

***tert*-Butyl (2-(1-hydroxyoxetane)phenylcarbamate s5a.** The general procedure was followed by using 0.800 g of *N*-Boc aniline (4.14 mmol), 5.50 ml of *t*-butyl lithium (10.4 mmol) and 0.360 mL of commercially available 3-oxetanone (6.20 mmol). Purification by MPLC (5:1 hexanes:EtOAc) gave the product as a yellow solid (0.420 g, 38%): R_f = 0.53 (1:1 hexanes:EtOAc); mp = 102 – 104 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.0 Hz, 1H), 7.29 – 7.25 (m, 1H), 7.18 (s, 1H), 7.14 – 7.08 (m, 2H), 4.96 (d, *J* = 7.0 Hz, 2H), 4.74 (d, *J* = 7.0 Hz, 3H), 1.47 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.1 (C), 135.6 (C), 133.1 (C), 129.2 (CH), 126.1 (CH), 126.1 (CH), 124.7 (CH), 124.1 (CH), 82.8 (CH_2), 81.1 (C), 75.9 (C), 28.3 (CH_3); ATR-FTIR (thin film): 3360, 2978, 2875, 1698, 1587, 1514, 1450, 1367, 1236, 1155, 1052, 1025, 976, 729 cm^{-1}. HRMS (ESI) m/z calcd for $C_{14}H_{19}NO_4Na$ [M + Na]$^+$: 288.1213, found 288.1212.



s5c

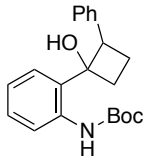
***tert*-Butyl (2-(1-Hydroxy-3-*tert*-butylcyclobutyl)phenylcarbamate s5c.** The general procedure was followed by using 0.300 g of *N*-Boc aniline (1.56 mmol), 2.0 mL of *t*-butyl lithium (5.18 mmol) and 0.290 g of 3-*tert*-butylcyclobutanone (2.39 mmol).[11] Purification by MPLC (15:1 hexanes:EtOAc) gave the product as a yellow sticky solid, as a 2:1 mixture of atropisomers (0.17 g, 33%): R_f = 0.78 (5:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (s, 0.93H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 0.41H), 7.53 (s, 0.42H), 7.37 (dd, *J* = 8.0 Hz, 1.5 Hz, 1H), 7.29 (dt, *J* = 8.0 Hz, 2.0 Hz, 1H), 7.24 (dd, *J* = 8.0 Hz, 2.0 Hz, 0.39 H), 7.18 (dd, *J* = 7.5 Hz, 1.5 Hz, 0.44H), 7.04 – 7.00 (m, 1.43H), 2.56 – 2.47 (m, 2H), 2.26 (d, J = 9.0 Hz, 2H), 2.11 – 2.02 (m, 2H), 1.64 – 1.57 (m, 1H), 1.51 (s, 13.6H), 0.84 (s, 9H), 0.81 (s, 4.51H) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.5 (C), 153.2 (C), 138.0 (C), 136.6 (C), 135.0 (C), 131.8 (C), 128.6 (CH), 128.4 (CH), 125.3 (CH), 124.8 (CH), 123.1 (CH), 122.4 (CH), 122.3 (CH), 121.9 (CH), 80.3 (C), 80.1 (C), 74.1 (C), 71.8 (C), 40.4 (CH), 36.8 (CH_2), 35.5 (CH_2), 30.9 (C), 30.8 (C), 28.4 (CH_3), 26.6 (CH_3), 26.3 (CH_3) (only visible peaks); ATR-FTIR (thin film): 3356, 2956, 2866, 1729, 1704, 1587, 1520, 1450, 1366, 1304, 1236, 1161, 1025, 755 cm^{-1}. HRMS (ESI) m/z calcd for $C_{19}H_{29}NO_3Na$ [M + Na]$^+$: 342.2040, found 342.2045.



s5d

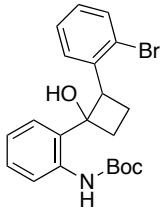
***tert*-Butyl (2-(1-Hydroxy-3-phenylcyclobutyl)phenylcarbamate s5d.** The general procedure was followed by using 0.300 g of *N*-Boc aniline (1.56 mmol), 2.30 mL of *t*-butyl lithium (3.89 mmol) and 0.338 g of 3-phenylcyclobutanone (2.33 mmol).[11] Purification by MPLC (15:1 hexanes:EtOAc) gave the product as a white sticky solid, as a 3:1 mixture of atropisomers (0.15 g, 28%): R_f = 0.68 (5:1 hexanes:EtOAc); mp = 153 – 155 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (s,

1.30H), 7.99 (s, 0.45H), 7.76 (d, *J* = 8.5 Hz, 0.38H), 0.33 (s, 0.43H), 7.49 (dd, *J* = 8.5 Hz, 1.5 Hz, 1.01H), 7.35 – 7.27 (m, 5.81H), 7.24 – 7.18 (m, 2.57H), 7.12 – 7.06 (m, 1.36H), 3.97 (quin, *J* = 8.5 H, 0.40 H), 3.13 – 3.07 (m, 1.82H), 3.04 – 2.97 (m, 1.31H), 2.88 – 2.81 (m, 1.66H), 2.69 – 2.63 (m, 0.86H), 2.57 – 2.51 (m, 1.82H), 1.53 (s, 3.24H), 1.52 (s, 9H) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.7 (C), 153.3 (C), 144.7 (C), 144.1 (C), 137.9 (C), 136.3 (C), 135.4 (C), 131.6 (C), 128.9 (CH), 128.6 (CH), 128.4 (CH), 128.4 (CH), 126.7 (CH), 126.5 (CH), 126.3 (CH), 126.2 (CH), 125.6 (CH), 124.8 (CH), 123.6 (CH), 122.8 (CH), 122.7 (CH), 122.4 (CH), 80.5 (C), 80.3 (C), 75.0 (C), 72.7 (C), 43.2 (CH2), 42.2 (CH2), 34.2 (CH), 30.7 (CH_3), 28.4 (CH_3) only visible peaks; ATR-FTIR (thin film): 3362, 2977, 2930, 1726, 1703, 1586, 1519, 1450, 1367, 1246, 1155, 1048, 1025, 750, 698 cm^{-1}. HRMS (ESI) m/z calcd for $C_{21}H_{25}NO_3Na$ [M + Na]$^+$: 362.1726, found 362.1732.



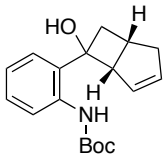
s5e

***tert*-Butyl (2-(1-hydroxycyclobutyl)phenylcarbamate s5e.** The general procedure was followed by using 0.495 g of *N*-Boc aniline (2.56 mmol), 3.40 mL of *t*-butyl lithium (6.40 mmol) and 0.560 g of 2-phenylcyclobutanone (3.84 mmol).[12] Purification by MPLC (15:1 hexanes:EtOAc) gave the product as a white sticky solid (0.370 g, 43%): R_f = 0.78 (5:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.0 Hz, 1H), 7.93 (s, 1H), 7.47 – 7.45 (m, 3H), 7.40 (t, *J* = 8.0 Hz, 2H), 7.31 – 7.27 (m, 2H), 7.05 (dt, *J* = 7.5 Hz, 1.0 Hz, 1H), 4.20 (m, 1H), 2.56 – 2.45 (m, 3H), 2.29 – 2.22 (m, 1H), 2.07 (d, *J* = 1.0 Hz, 1H), 1.52 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.1 (C), 138.4 (C), 137.5 (C), 133.3 (C), 128.8 (CH), 128.8 (CH), 128.5 (CH), 127.2 (CH), 125.2 (CH), 122.5 (CH), 121.8 (CH), 80.2 (C), 80.0 (C), 47.8 (CH), 33.6 (CH_2), 28.4 (CH_3), 21.7 (CH_2); ATR-FTIR (thin film): 3374, 2977, 2360, 2341, 1726, 1585, 1522, 1449, 1392, 1305, 1239, 1161, 1048, 753 cm^{-1}. HRMS (ESI) m/z calcd for $C_{21}H_{25}NO_3Na$ [M + Na]$^+$: 362.1722, found 362.1732.



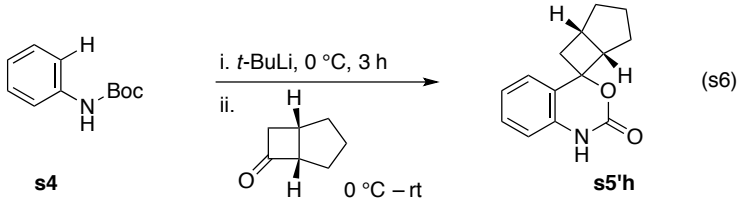
s5f

***tert*-Butyl (2-(1-hydroxycyclobutyl)phenylcarbamate s5f.** The general procedure was followed by using 0.200 g of *N*-Boc aniline (1.04 mmol), 1.40 mL of *t*-butyl lithium (2.60 mmol) and 0.356 g of 2-(2-bromophenyl)cyclobutanone (1.56 mmol).[13] Purification by MPLC (12:1 hexanes:EtOAc) gave the product as a brown solid (0.200 g, 46%): R_f = 0.53 (5:1 hexanes:EtOAc); mp = 196 – 198 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.67 (s, 1H), 7.60 (t, *J* = 8.0 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.28 (t, *J* = 8.0 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 4.56 (t, *J* = 7.5 Hz, 1H), 2.60 – 2.53 (m, 1H), 2.48 – 2.39 (m, 2H), 2.29 – 2.23 (m, 2H), 1.45 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$ δ 153.1 (C), 138.5 (C), 137.3 (C), 133.1 (CH), 132.8 (C), 130.4 (CH), 128.7 (CH), 128.5 (CH), 127.5 (CH), 125.9 (C), 125.7 (CH), 122.6 (CH), 121.7 (CH), 80.8 (C), 80.0 (C), 46.9 (CH), 33.7 (CH_2), 28.3 (CH_3), 22.6 (CH_2); ATR-FTIR (thin film): 3368, 2977, 1704, 1586, 1521, 1448, 1241, 1157, 1048, 1023, 752, 736 cm^{-1}. HRMS (ESI) m/z calcd for $C_{21}H_{24}NO_3NaBr$ [M + Na]$^+$: 440.0829, found 440.0837.



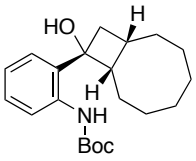
s5g

***tert*-Butyl (2-(1-hydroxycyclobutyl)phenylcarbamate s5g.** The general procedure was followed by using 0.250 g of *N*-Boc aniline (1.30 mmol), 1.50 mL of *t*-butyl lithium (3.30 mmol) and 0.210 mL of commercially available bicyclo[3.2.0]hept-2-en-6 one (1.95 mmol). Purification by MPLC (12:1 hexanes:EtOAc) gave the product, a brown sticky solid, as a mixture of diastereomers (0.17 g, 43%): R_f = 0.58 (7:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.93 (s, 0.10H), 8.27 (d, *J* = 8.0 Hz, 0.11H), 7.85 (d, *J* = 8.0 Hz, 0.86H), 7.49 – 7.48 (m, 0.83H), 7.47 – 7.45 (m, 0.22H), 7.38 – 7.34 (m, 0.27H), 7.32 – 7.25 (m, 2.23H), 7.06 – 7.02 (m, 1H), 7.00 (dd, *J* = 8.0 Hz, 1.5 Hz, 0.10H), 5.99 – 5.95 (m, 1.93H), 5.89 (s, 0.22H), 3.45 – 3.42 (m, 1H), 3.16 – 3.08 (m, 2H), 2.90 (d, *J* = 8.0 Hz, 1H), 2.66 – 2.60 (m, 1H), 2.48 (s, 1H), 2.14 – 2.11 (m, 1H), 1.51 (s, 9H), 1.50 (s, 1.55H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.1 (C), 150.9 (C), 139.2 (C), 136.9 (C), 135.6 (CH), 134.4 (CH), 132.7 (CH), 132.4 (CH), 131.9 (CH), 128.4 (CH), 125.3 (CH), 122.9 (CH), 122.7 (CH), 121.0 (CH), 120.4 (CH), 117.1 (CH), 115.8 (CH), 80.5 (C), 80.0 (C), 77.4 (C), 45.7 (CH), 41.9 (CH_2), 39.8 (CH), 33.4 (CH_2), 28.4 (CH_3), 28.3 (CH_3) only visible peaks; ATR-FTIR (thin film): 3371, 2977, 2928, 1727, 1704, 1585, 1515, 1448, 1238, 1153, 1048, 1024, 748, 726 cm^{-1}. HRMS (ESI) m/z calcd for $C_{18}H_{23}NO_3Na$ [M + Na]$^+$: 324.1571, found 324.1576.



s4 **s5'h**

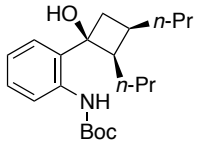
Spiro(2-(1-hydroxycyclobutyl)phenylbenzoxazine s5'h. The general procedure was followed by using 0.200 g of *N*-Boc aniline (1.04 mmol), 1.32 mL of *t*-butyl lithium (2.50 mmol) and 0.170 g of bicyclo[3.2.0]heptan-6-one (1.50 mmol).[14] Purification by MPLC (5:1 hexanes:EtOAc) gave the product as a orange solid (0.07 g, 30%): R_f = 0.30 (3:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.19 (s, 1H), 7.36 (d, *J* = 7.5 Hz, 1H), 7.22 (dt, *J* = 7.5 Hz, 1.5 Hz, 1H), 7.10 (dt, *J* = 7.5 Hz, 1.0 Hz, 1H), 6.87 (d, *J* = 7.5 Hz, 1H), 2.90 – 2.86 (m, 1H), 2.77 – 2.72 (m, 1H), 2.65 (quin, *J* = 7.0 Hz, 1H), 2.21 – 2.06 (m, 3H), 1.91 – 1.86 (m, 1H), 1.70 (dd, *J* = 11.5 Hz, 6.0 Hz, 1H), 1.59 – 1.46 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.0 (C), 133.9 (C), 128.5 (CH), 126.4 (C), 123.6 (CH), 122.6 (CH), 114.3 (CH), 80.5 (C), 52.6 (CH), 37.9 (CH_2), 32.6 (CH_2), 31.4 (CH), 26.9 (CH_2), 25.6 (CH_2); ATR-FTIR (thin film): 3245, 2950, 1708, 1597, 1501, 1353, 1250, 1157, 1073, 1019, 751 cm^{-1}. HRMS (ESI) m/z calcd for $C_{14}H_{16}NO_2$ [M + H]$^+$: 230.1176, found 230.1181.



s5i

***N*-(2-(1-Hydroxycyclobutyl)phenyl)carbamate s5i.** The general procedure was followed by using 0.200 g of *N*-Boc aniline (1.04 mmol), 1.32 mL of *t*-butyl lithium (2.50 mmol) and 0.237 g of bicyclo[6.2.0]decan-9-one (1.50 mmol). Purification by MPLC (15:1 hexanes:EtOAc) gave the product as a white sticky solid (0.12 g, 33%): R_f = 0.54 (5:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz, 1H), 7.79 (br s, 1H), 7.35 – 7.33 (m, 1H), 7.30 – 7.26 (m, 1H), 7.05 – 7.01 (m, 1H), 2.88 – 2.83 (m, 1H), 2.57 – 2.52 (m, 1H), 2.14 (br s, 1H), 1.99 – 1.83 (m, 4H), 1.82 – 1.71 (m, 2H), 1.59 – 1.42 (m, 13H), 1.32 – 1.17 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.1 (C), 137.6 (C), 134.0 (C), 128.3 (CH), 124.4 (CH), 122.6 (CH), 122.4 (CH), 79.9 (C), 75.2 (C), 49.2 (CH), 40.2 (CH_2), 31.5 (CH), 30.2 (CH_2), 29.2 (CH_2), 28.6 (CH_2), 28.4 (CH_3), 25.8 (CH_2), 25.2 (CH_2), 22.6 (CH_2); ATR-FTIR (thin film): 3365, 2975, 2919, 2850, 1729, 1704,

1586, 1519, 1449, 1367, 1245, 1160, 1048, 747 cm^{-1}. HRMS (ESI) m/z calcd for $C_{21}H_{31}NO_3Na$ [M + Na]$^+$: 368.2192, found 368.2202.



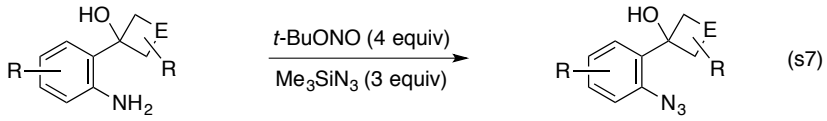
s5j

***N*-(2-(1-Hydroxycyclobutyl)phenyl)carbamate s5j.** The general procedure was followed by using 0.200 g of *N*-Boc aniline (1.04 mmol), 1.32 mL of *t*-butyl lithium (2.50 mmol) and 0.240 g of (2*S*,3*S*)-2,3-dipropylcyclobutan-1-one (1.50 mmol). Purification by MPLC (15:1 hexanes:EtOAc) gave the product as a white sticky solid (0.14 g, 40%): R_f = 0.78 (10:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.93 (s, 1H), 7.31 (dd, *J* = 7.5 Hz, 1.5 Hz, 1H), 7.28 – 7.24 (m, 1H), 7.00 (dt, *J* = 7.5 Hz, 1.0 Hz, 1H), 2.72 – 2.64 (m, 2H), 2.25 (br s, 1H), 2.03 – 1.93 (m, 2H), 1.71 – 1.54 (m, 2H), 1.51 (s, 9H), 1.48 – 1.40 (m, 4H), 1.34 – 1.25 (m, 1H), 1.22 – 1.12 (m, 1H), 1.00 (t, *J* = 7.0 Hz, 3H), 0.91 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.1 (C), 137.6 (C), 133.6 (C), 128.3 (CH), 124.7 (CH), 122.4 (CH), 121.9 (CH), 79.9 (C), 75.9 (C), 46.2 (CH), 39.4 (CH_2), 32.6 (CH_2), 30.4 (CH), 28.4 (CH_3), 27.4 (CH_2), 23.4 (CH_2), 20.8 (CH_2), 14.8 (CH_3), 14.3 (CH_3); ATR-FTIR (thin film): 3365, 2975, 2919, 2850, 1729, 1704, 1586, 1519, 1449, 1367, 1245, 1160, 1048, 747 cm^{-1}. HRMS (EI) m/z calcd for $C_{21}H_{33}NO_3$: 347.24507, found 347.24605.

II. Synthesis of *o*-Cyclobutanol Aryl Azides

A. General Procedure

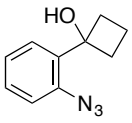
The *o*-cyclobutanol aryl azides were prepared following the protocol reported by Moses and co-workers.[15]



s3 **8** or **10** (s7)

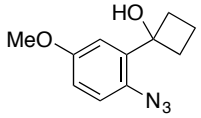
To a cooled solution (0 °C) of o-cyclobutanol aniline **s3** in MeCN (0.2 M), was added dropwise *t*-BuONO (4.0 equiv), Me_3SiN_3 (3.0 equiv). The resulting solution was warmed to room temperature. After 1.5 h, the reaction mixture was concentrated in vacuo. The residue was purified by MPLC (10:1 – 7:1 hexanes:EtOAc) to afford the *ortho*-cyclobutanol aryl azide.

B. Characterization Data for *o*-Cyclobutanol Azides



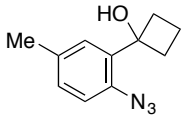
8a

***o*-Cyclobutanol aryl azide 8a.** The general procedure was followed by using 0.155 g of aniline **s3a** (0.950 mmol), 0.450 mL of *t*-BuONO (3.80 mmol), 0.37 mL Me_3SiN_3 (2.85 mmol) in 4.8 mL of MeCN. Purification by MPLC (10:1 hexanes:EtOAc) gave the product as a brown oil (0.150 g, 82%): R_f = 0.52 (5:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 7.5 Hz, 1.5 Hz, 1H), 7.31 (dd, *J* = 7.5 Hz, 1.5 Hz, 1H), 7.17 (dd, *J* = 8.0 Hz, 1.0 Hz, 1H), 7.12 (dt, *J* = 7.5 Hz, 1.5 Hz, 1H), 3.24 (s, 1H), 2.58 – 2.52 (m, 2H), 2.40 – 2.34 (m, 2H), 2.15 – 2.08 (m, 1H), 1.70 – 1.64 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.4 (C), 136.2 (C), 128.8 (CH), 126.4 (CH), 124.7 (CH), 118.8 (CH), 76.8 (C), 35.2 (CH_2), 14.5 (CH_2); ATR-FTIR (thin film): 3397, 2946, 2125, 2087, 1486, 1444, 1293, 1131, 751 cm^{-1}. HRMS (ESI) m/z calcd for $C_{10}H_{12}NO$ [M + H – N_2]$^+$: 162.0923, found 162.0919.



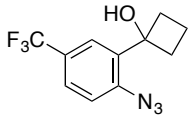
8b

***o*-Cyclobutanol aryl azide 8b.** The general procedure was followed by using 0.152 g of aniline **s3b** (0.790 mmol), 0.380 mL of *t*-BuONO (3.16 mmol), 0.310 mL of Me_3SiN_3 (2.37 mmol) in 3.9 mL of MeCN. Purification by MPLC (10:1 hexanes:EtOAc) gave the product as a brown oil (0.160 g, 94%): R_f = 0.40 (5:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.5 Hz, 1H), 6.91 (d, *J* = 1.0 Hz, 1H), 6.84 (dd, *J* = 8.5 Hz, 1.0 Hz, 1H), 3.81 (s, 3H), 3.16 (br s, 1H), 2.55 – 2.50 (m, 2H), 2.39 – 2.34 (m, 2H), 2.14 – 2.07 (m, 1H), 1.72 – 1.64 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.8 (C), 137.6 (C), 129.6 (C), 119.8 (CH), 113.1 (CH), 113.0 (CH), 76.7 (C), 55.7 (CH_3), 35.2 (CH_2), 14.3 (CH_2); ATR-FTIR (thin film): 3513, 2941, 2836, 2108, 1579, 1485, 1312, 1237, 1038, 803 cm^{-1}. HRMS (ESI) m/z calcd for $C_{11}H_{13}N_3O_2Na$ [M + Na]$^+$: 242.0899, found 242.0905.



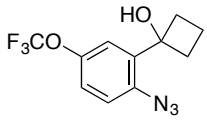
8c

***o*-Cyclobutanol aryl azide 8c.** The general procedure was followed by using 0.150 g of aniline **s3c** (0.84 mmol), 0.40 mL of *t*-BuONO (3.16 mmol), 0.33 mL of Me_3SiN_3 (2.37 mmol) in 3.5 mL of MeCN. Purification by MPLC (10:1 hexanes:EtOAc) gave the product as a brown oil (0.122 g, 72%): R_f = 0.55 (5:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 (s, 1H), 7.12 (s, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 3.09 (s, 1H), 2.57 – 2.52 (m, 2H), 2.39 – 2.36 (m, 2H), 2.35 (s, 3H), 2.15 – 2.08 (m, 1H), 1.72 – 1.64 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.9 (C), 134.5 (C), 134.4 (C), 129.2 (CH), 127.1 (CH), 118.7 (CH), 76.8 (C), 35.2 (CH_2), 21.0 (CH_3), 14.5 (CH_2); ATR-FTIR (thin film): 3417, 2947, 2114, 1492, 1300, 1157, 1137, 910, 807 cm^{-1}. HRMS (ESI) m/z calcd for $C_{11}H_{14}NO$ [M + H – N_2]$^+$: 176.1077, found 176.1075.



8d

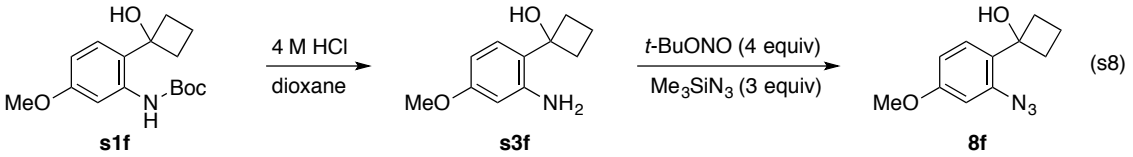
***o*-Cyclobutanol aryl azide 8d.** The general procedure was followed by using 0.232 g of aniline **s3d** (1.00 mmol), 0.480 mL of *t*-BuONO (3.16 mmol), 0.400 mL of Me_3SiN_3 (2.37 mmol) in 5.0 mL of MeCN. Purification by MPLC (10:1 hexanes:EtOAc) gave the product as a brown oil (0.210 g, 80%): R_f = 0.55 (5:1 hexanes:EtOAc; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.5 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 1H), 3.06 (s, 1H), 2.59 – 2.54 (m, 2H), 2.42 – 2.37 (m, 2H), 2.21 – 2.12 (m, 1H), 1.76 – 1.68 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.1 (C), 136.8 (C), 126.8 (q, J_{CF} = 32.5 Hz, C), 125.8 (q, J_{CF} = 3.8 Hz, CH), 123.9 (q, J_{CF} = 269.9 Hz, C), 123.6 (q, J_{CF} = 3.9 Hz, CH), 119.0 (CH), 76.5 (C), 35.0 (CH_2), 14.5 (CH_2); ^{19}F NMR (282 MHz, $CDCl_3$) δ –62.3; ATR-FTIR (thin film): 3383, 2952, 2109, 1614, 1496, 1293, 1272, 1119, 1081, 903, 822 cm^{-1}. HRMS (ESI) m/z calcd for $C_{11}H_{11}NOF_3$ [M + H – N_2]$^+$: 230.0790, found 230.0792.



8e

***o*-Cyclobutanol aryl azide 8e.** The general procedure was followed by using 0.114 g of aniline **s3e** (0.460 mmol), 0.220 mL of *t*-BuONO (1.84 mmol), 0.180 mL of Me_3SiN_3 (1.38 mmol) in 2.31 mL of MeCN. Purification by MPLC (10:1 hexanes:EtOAc) gave the product as a brown oil (0.090 g, 70%): R_f = 0.54 (5:1 hexanes:EtOAc); ^{1}H NMR (500 MHz,

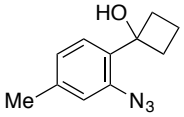
$CDCl_3$) δ 7.19 – 7.16 (m, 3H), 3.14 (s, 1H), 2.55 – 2.49 (m, 2H), 2.40 – 2.35 (m, 2H), 2.17 – 2.09 (m, 1H), 1.74 – 1.65 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.8 (C), 138.1 (C), 136.1 (C), 121.2 (CH), 120.5 (q, J_{CF} = 255.4 Hz, C), 119.8 (CH), 119.7 (CH), 76.4 (C), 35.1 (CH_2), 14.3 (CH_2); ^{19}F NMR (282 MHz, $CDCl_3$) δ –58.5 ; ATR-FTIR (thin film): 3390, 2953, 2118, 1483, 1249, 1208, 1158, 890, 817 cm^{-1}. HRMS (ESI) m/z calcd for $C_{11}H_{11}NO_2F_3$ $[M + H - N_2]^+$: 246.0742, found 246.0742.



s1f **s3f** **8f**

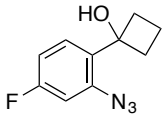
***N*-(2-(1-Hydroxy-3-*tert*-butylcyclobutyl)phenyl)aniline s3f.** *o*-Cyclobutanol carbamate **s3f** (0.500 g, 1.34 mmol) was dissolved in 1 mL of dioxane. To the stirred solution was added dropwise 4 mL of a 4 M solution of HCl in dioxane. The reaction progress was monitored by TLC. When the starting material was consumed, the mixture was neutralized by adding a saturated solution of $NaHCO_3$ (until effervescence stopped). The solution was extracted 3 × 10 mL of EtOAc. The organic layer was dried over Na_2SO_4, filtered, and the filtrate was concentrated *in vacuo* to afford **s3f** as a yellow solid, which was submitted to the next step without further characterization or purification.

***o*-Cyclobutanol aryl azide 8f.** The general procedure was followed by using 0.280 g of aniline **s3'f** (1.03 mmol), 0.490 mL of *t*-BuONO (4.12 mmol), 0.410 mL of Me_3SiN_3 (3.09 mmol) in 5.2 mL of MeCN. Purification by MPLC (10:1 hexanes:EtOAc) gave the product as a brown oil (0.243 g, 79%): R_f = 0.52 (3:1 hexanes:EtOAc); ^1H NMR (500 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.5 Hz, 1H), 6.72 (d, *J* = 2.5 Hz, 1H), 6.66 (dd, *J* = 8.5 Hz, 2.5 Hz, 1H), 3.83 (s, 3H), 2.96 (s, 1H), 2.55 – 2.50 (m, 2H), 2.38 – 2.33 (m, 2H), 2.13 – 2.04 (m, 1H), 1.69 – 1.63 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.9 (C), 138.5 (C), 128.9 (C), 127.3 (CH), 109.4 (CH), 105.2 (CH), 76.4 (C), 55.5 (CH_3), 35.4 (CH_2), 14.4 (CH_2); ATR-FTIR (thin film): 3400, 2915, 2110, 2107, 1608, 1502, 1315, 1229, 1123, 830 cm^{-1}. HRMS (ESI) m/z calcd for $C_{11}H_{13}N_3O_2Na$ $[M + Na]^+$: 242.0898, found 242.0904.



8g

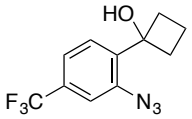
***o*-Cyclobutanol aryl azide 8g.** The general procedure was followed by using 0.178 g of aniline **s3g** (1.01 mmol), 0.480 mL of *t*-BuONO (4.04 mmol), 0.400 mL of Me_3SiN_3 (3.03 mmol) in 5.00 mL of MeCN. Purification by MPLC (10:1 hexanes:EtOAc) gave the product as a brown oil (0.170 g, 80%): R_f = 0.55 (5:1 hexanes:EtOAc); ^1H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 7.5 Hz, 1H), 6.99 (s, 1H), 6.95 – 6.93 (m, 1H), 3.06 (s, 1H), 2.39 – 2.34 (m, 5H), 2.13 – 2.05 (m, 1H), 1.70 – 1.62 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.9 (C), 137.1 (C), 133.4 (C), 126.2 (CH), 125.5 (CH), 119.4 (CH), 76.6 (C), 35.3 (CH_2), 21.1 (CH_3), 14.4 (CH_2); ATR-FTIR (thin film): 3417, 2947, 2114, 1492, 1300, 1157, 1137, 910, 807 cm^{-1}. HRMS (ESI) m/z calcd for $C_{11}H_{14}NO$ $[M + H - N_2]^+$: 176.1074, found 176.1075.



8h

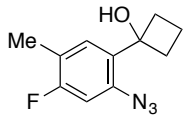
***o*-Cyclobutanol aryl azide 8h.** The general procedure was followed by using 0.183 g of aniline **s3h** (1.01 mmol), 0.480 mL of *t*-BuONO (4.04 mmol), 0.400 mL of Me_3SiN_3 (3.03 mmol) in 5.0 mL of MeCN. Purification by MPLC (10:1 hexanes:EtOAc) gave the product as a yellow oil (0.180 g, 85%): R_f = 0.53 (5:1 hexanes:EtOAc); ^1H NMR (500 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 8.5 Hz, 6.5 Hz, 1H), 6.88 (dd, *J* = 9.0 Hz, 2.0 Hz, 1H), 6.81 (dt, *J* = 8.5 Hz, 2.5 Hz, 1H), 3.03 (s, 1H), 2.54 – 2.48 (m, 2H), 2.38 – 2.33 (m, 2H), 2.15 – 2.07 (m, 1H), 1.70 – 1.62 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ

162.5 (d, J_{CF} = 247.6 Hz, C), 139.1 (d, J_{CF} = 9.1 Hz, C), 132.3 (d, J_{CF} = 3.3 Hz, C), 127.8 (d, J_{CF} = 9.0 Hz, CH), 111.3 (d, J_{CF} = 20.3 Hz, CH), 106.3 (d, J_{CF} = 24.1 Hz, CH), 76.4 (C), 35.3 (CH_2), 14.5 (CH_2); ^{19}F NMR (282 MHz, $CDCl_3$) δ −112.9; ATR-FTIR (thin film): 3394, 2950, 2109, 1593, 1498, 1412, 1292, 1230, 1140, 959, 842, 666 cm^{-1}. HRMS (CI) m/z calcd for $C_{10}H_{11}N_3OF$ $[M + H]^+$: 208.0884, found 208.0886.



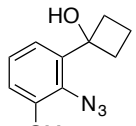
8i

***o*-Cyclobutanol aryl azide 8i.** The general procedure was followed by using 0.233 g of aniline **s3i** (1.01 mmol), 0.480 mL of *t*-BuONO (4.04 mmol), 0.400 mL of Me_3SiN_3 (3.03 mmol) in 5.0 mL of MeCN. Purification by MPLC (10:1 hexanes:EtOAc) gave the product as a yellow oil (0.210 g, 80%): R_f = 0.55 (5:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.5 Hz, 1H), 7.38 (d, *J* = 3.5 Hz, 2H), 3.2 (s, 1H), 2.58 – 2.52 (m, 2H), 2.42 – 2.36 (m, 2H), 2.19 – 2.10 (m, 1H), 1.74 – 1.65 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.7 (C), 138.5 (C), 131.2 (q, J_{CF} = 33.1 Hz, C), 127.0 (CH), 123.5 (q, J_{CF} = 270.3 Hz, C), 121.5 (q, J_{CF} = 3.9 Hz, CH), 115.6 (q, J_{CF} = 3.9 Hz, CH), 76. 5 (C), 35.1 (CH_2), 14.4 (CH_2); ^{19}F NMR (282 MHz, $CDCl_3$) δ −63.2; ATR-FTIR (thin film): 3490, 2924, 2107, 1417, 1328, 1274, 1123, 1086, 902, 871, 834, 656 cm^{-1}. HRMS (ESI) m/z calcd for $C_{11}H_{11}NOF_3$ $[M + H - N_2]^+$: 230.0791, found 230.0793.



8j

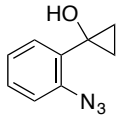
***o*-Cyclobutanol aryl azide 8j.** The general procedure was followed by using 0.197 g of aniline **s3j** (1.01 mmol), 0.480 mL of *t*-BuONO (4.04 mmol), 0.400 mL of Me_3SiN_3 (3.03 mmol) in 5.0 mL of MeCN. Purification by MPLC (10:1 hexanes:EtOAc) gave the product as a yellow oil (0.190 g, 85%) as a mixture of rotamers: R_f = 0.56 (5:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.5 Hz, 1H), 7.1 (t, *J* = 8.0 Hz, 0.19H), 6.84 (d, *J* = 9.5 Hz, 1H), 6.84 (s, 0.11H), 2.97 (s, 1H), 2.69 – 2.65 (m, 0.39H), 2.54 – 2.48 (m, 2H), 2.47 – 2.43 (m, 0.38H), 2.38 – 2.32 (m, 2H), 2.24 (d, *J* = 1.5 Hz, 3H), 2.21 (d, *J* = 2.5 Hz, 0.56H), 2.15 – 2.08 (m, 1H), 1.88 – 1.81 (m, 0.20H), 1.71 – 1.63 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.6 (d, J_{CF} = 244.1 Hz, C), 159.6 (d, J_{CF} = 246.1 Hz, C), 136.2 (d, J_{CF} = 7.3 Hz, C), 131.9 (d, J_{CF} = 2.9 Hz, C), 130.4 (d, J_{CF} = 5.9 Hz, CH), 129.3 (d, J_{CF} = 5.6 Hz, CH), 120.9 (d, J_{CF} = 18.1 Hz, C), 113.9 (d, J_{CF} = 3.5 Hz, CH), 106.0 (d, J_{CF} = 25.8 Hz, CH), 76.4 (C), 37.3 (d, J_{CF} = 4.1 Hz, CH_2), 35.4 (CH_2), 29.7 (C), 17.6 (CH_2), 14.5 (CH_2), 14.4 (d, J_{CF} = 5.4 Hz, CH_2), 14.1 (d, J_{CF} = 3.6 Hz, CH_3), only visible signals; ^{19}F NMR (282 MHz, $CDCl_3$) δ −117.4, −116.7 ; ATR-FTIR (thin film): 3353, 2949, 2106, 1588, 1504, 1313, 1239, 1164, 1134, 1091, 889, 839 cm^{-1}. HRMS (ESI) m/z calcd for $C_{11}H_{13}NOF$ $[M + H - N_2]^+$: 194.0980, found 194.0981.



8k

***o*-Cyclobutanol aryl azide 8k.** The general procedure was followed by using 0.195 g of aniline **s3k** (1.01 mmol), 0.480 mL of *t*-BuONO (4.04 mmol), 0.400 mL of Me_3SiN_3 (3.03 mmol) in 5.0 mL of MeCN. Purification by MPLC (10:1 hexanes:EtOAc) gave the product as a orange oil (0.180 g, 80%): R_f = 0.53 (5:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 – 7.06 (m, 1H), 6.94 (dd, *J* = 8.0 Hz, 1.5 Hz, 1H), 6.84 (dd, *J* = 8.0 Hz, 1.0 Hz, 1H), 3.90 (s, 3H), 3.31 (s, 1H), 2.57 – 2.51 (m, 2H), 2.41 – 2.35 (m, 2H), 2.15 – 2.07 (m, 1H), 1.71 – 1.64 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.5 (C), 138.1 (C), 125.3 (C), 125.2 (CH), 118.1 (CH), 111.3 (CH), 77.1 (C), 56.1 (CH_3), 35.4 (CH_2), 14.5 (CH_2); ATR-

FTIR (thin film): 3543, 2941, 2146, 2118, 2096, 1579, 1455, 1439, 1310, 1261, 1033, 734 cm^{-1}. HRMS (ESI) m/z calcd for $C_{11}H_{13}N_3O_2Na$ $[M + Na]^+$: 242.0899, found 242.0905.

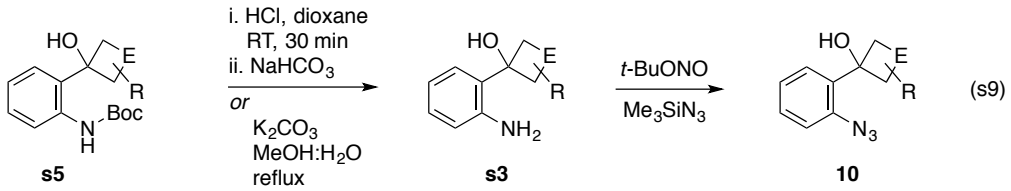


10a

***o*-Cyclopropanol aryl azide 10a.** The general procedure was followed by using 0.0400 g of aniline **s3l** (0.270 mmol),[16] 0.130 mL of *t*-BuONO (1.08 mmol), 0.110 mL of Me_3SiN_3 (0.810 mmol) in 2.0 mL of MeCN. Purification by MPLC (5:1 hexanes:EtOAc) gave the product as a yellow oil (0.03 g, 65%): R_f = 0.56 (5:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.30 (m, 2H), 7.20 (dd, *J* = 8.0 Hz, 1.5 Hz, 1H), 7.11 – 7.07 (m, 1H), 3.18 (s, 1H), 1.16 – 1.13 (m, 2H), 0.94 – 0.91 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.5 (C), 133.2 (C), 129.1 (CH), 128.8 (CH), 124.8 (CH), 118.3 (CH), 55.2 (C), 13.9 (CH_2); ATR-FTIR (thin film): 3391, 2926, 2853, 2360, 2127, 2093, 1491, 1445, 1293, 1225, 753 cm^{-1}. HRMS (ESI) m/z calcd for $C_9H_9N_3ONa$ $[M + Na]^+$: 198.0644, found 198.0646.

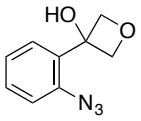
C. General Procedure for Synthesis of *o*-Cyclobutanol Azides from *o*-Cyclobutanol Carbamates

Deprotection of the *N*-Boc carbamate was accomplished following two different strategies reported by Hruby and co-workers and Harigaya and co-workers.[17]



Method A.[17a] The original procedure described by Hruby and co-workers was slightly modified. The *o*-cyclobutanol carbamate was dissolved in 1 mL of dioxane. To the stirred solution was added dropwise a 4 M solution of HCl in dioxane. The reaction progress was monitored by TLC. When the starting material was consumed, the mixture was neutralized by adding a saturated solution of $NaHCO_3$ (until effervescence stopped). The solution was extracted 3 × 10 mL of EtOAc. The organic layer was dried over Na_2SO_4, filtered, and the filtrate was concentrated *in vacuo*. The resulting aniline was submitted to the next step without further characterization or purification.

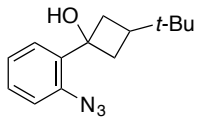
Method B.[17b] The original procedure developed by Harigaya and co-workers was slightly modified. The *o*-cyclobutanol carbamate was dissolved in a 3:1 v:v solution of MeOH and H_2O (1 mL / mmol). To the resulting solution was added K_2CO_3 (3.0 equiv), and the mixture was heated to reflux. The reaction progress was monitored using TLC. Once starting material was consumed, the reaction mixture was cooled to room temperature and was concentrated i*in vacuo*. The resulting mixture was diluted with EtOAc. The organic layer was seperated, dried over Na_2SO_4, filtered and the filtrate was concentrated *in vacuo* and submitted to the next step without further characterization or purification.



10b

***N*-(2-(1-Hydroxyoxetane)phenyl)aniline s3m. Method B** was followed using 0.460 g of **s5b** (1.74 mmol), 0.721 g of K_2CO_3 (5.22 mmol) to give **s3m** as a yellow solid (0.167 g, 58%) which was submitted to the next step without further characterization or purification.

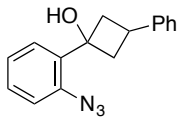
***o*-Oxetane aryl azide 10b.** The general procedure was followed by using 0.167 g of aniline **s3m** (1.01 mmol), 0.480 mL of *t*-BuONO (4.04 mmol), 0.400 mL of Me_3SiN_3 (3.03 mmol) in 5.0 mL of MeCN. Purification by MPLC (5:1 hexanes:EtOAc) gave the product as a yellow oil (0.120 g, 62%): R_f = 0.47 (1:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (dt, *J* = 8.0 Hz, 1.5 Hz, 1H), 7.22 (dd, *J* = 7.5 Hz, 1.5 Hz, 1H), 7.18 – 7.14 (m, 2H), 5.05 (d, *J* = 7.5 Hz, 2H), 4.81 (d, *J* = 7.5 Hz, 2H), 3.62 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.4 (C), 132.4 (C), 129.9 (CH), 127.0 (CH), 125.1 (CH), 118.7 (CH), 82.8 (CH_2), 75.7 (C); ATR-FTIR (thin film): 3352, 2947, 2875, 2121, 2089, 1489, 1287, 972 752 cm^{-1}. HRMS (ESI) m/z calcd for $C_9H_9N_3O_2Na$ $[M + Na]^+$: 214.0593, found 214.0595.



10c

***N*-(2-(1-Hydroxy-3-*tert*-butylcyclobutyl)phenyl)aniline s3n. Method A** was followed using 0.500 g of **s5c** (1.56 mmol), 4 mL of HCl (4 M in dioxane) to give **s3n** as a yellow solid (0.220 g, 64%) which was submitted to the next step without further characterization or purification.

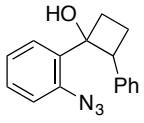
***o*-Cyclobutanol aryl azide 10c.** The general procedure was followed by using 0.220 g of aniline **s3n** (1.01 mmol), 0.480 mL of *t*-BuONO (4.04 mmol), 0.400 mL of Me_3SiN_3 (3.03 mmol) in 5.0 mL of MeCN. Purification by MPLC (10:1 hexanes:EtOAc) gave the product, a yellow oil, as a mixture of atropisomers (0.160 g, 63%): R_f = 0.57 (5:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 7.5 Hz, 1.5 Hz, 0.76H), 7.36 (dt, *J* = 7.5 Hz, 1.5 Hz, 0.78H), 7.31 (dt, *J* = 7.5 Hz, 1.5 Hz, 1H), 7.26 – 7.21 (m, 1.88H), 7.18 – 7.15 (m, 1.75H), 7.12 (dt, *J* = 7.5 Hz, 1.0 Hz, 1H), 3.45 (s, 0.70H), 2.76 (s, 0.88H), 2.64 – 2.57 (m, 0.94H), 2.52 – 2.47 (m, 1.56H), 2.32 – 2.27 (m, 2H), 2.22 – 2.17 (m, 2H), 2.16 – 2.10 (m, 1.64H), 1.63 – 1.55 (m, 0.88H), 0.85 (s, 7.05H), 0.82 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.9 (C), 137.1 (C), 137.0 (C), 135.7 (C), 128.8 (CH), 128.7 (CH), 126.5 (CH), 126.2 (CH), 124.8 (CH), 124.7 (CH), 119.0 (CH), 118.6 (CH), 73.0 (C), 70.8 (C), 40.7 (CH), 36.8 (CH), 36.5 (CH_2), 35.9 (CH_2), 30.9 (C), 30.9 (CH), 26.6 (CH_3), 26.3 (CH_3); ATR-FTIR (thin film): 3393, 2953, 2865, 2125, 2088, 1486, 1293, 1235, 750 cm^{-1}. HRMS (ESI) m/z calcd for $C_{14}H_{20}NO$ $[M + H - N_2]^+$: 218.1540, found 218.1545.



10d

***N*-(2-(1-Hydroxy-3-phenylcyclobutyl)phenyl)aniline s3o. Method A** was followed using 0.500 g of **s5d** (1.47 mmol), 4 mL of HCl (4 M in dioxane) to give **s3o** as a yellow solid (0.230 g, 68%) which was submitted to the next step without further characterization or purification.

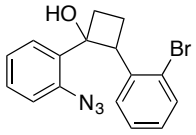
***o*-Cyclobutanol aryl azide 10d.** The general procedure was followed by using 0.230 g of aniline **s3o** (1.01 mmol), 0.480 mL of *t*-BuONO (4.04 mmol), 0.400 mL of Me_3SiN_3 (3.03 mmol) in 5.0 mL of MeCN. Purification by MPLC (10:1 hexanes:EtOAc) gave the product, a yellow oil, as a mixture of atopisomers (0.220 g, 86%): R_f = 0.30 (5:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.0 Hz, 0.58H), 7.42 (t, *J* = 7.5 Hz, 0.60H), 7.36 – 7.27 (m, 6.77H), 7.26 – 7.19 (m, 4.84H), 7.15 (t, *J* = 7.5 Hz, 1H), 4.00 (quin, *J* = 9.0 Hz, 0.93H), 3.61 (s, 0.54H), 3.11 – 3.04 (m, 1.71H), 3.00 (s, 1H), 2.92 – 2.87 (m, 1.94H), 2.66 – 2.57 (m, 3.15H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.1 (C), 144.5 (C), 138.0 (C), 137.2 (C), 136.6 (C), 135.1 (C), 129.1 (CH), 129.0 (CH), 128.4 (CH), 128.4 (CH), 126.8 (CH), 126.6 (CH), 126.5 (CH), 126.3 (CH), 126.2 (CH), 126.0 (CH), 124.9 (CH), 124.9 (CH), 119.1 (CH), 118.7 (CH), 74.1 (C), 71.9 (C), 43.1 (CH_2), 42.4 (CH_2), 34.4 (CH), 30.8 (CH); ATR-FTIR (thin film): 3393, 3025, 2981, 2933, 2122, 2092, 1579, 1486, 1445, 1279, 747, 697 cm^{-1}. HRMS (ESI) m/z calcd for $C_{16}H_{16}NO$ $[M + H - N_2]^+$: 238.1229, found 238.1232.



10e

***N*-(2-(1-Hydroxy-2-phenylcyclobutyl)phenyl)aniline s3p. Method A** was followed using 0.500 g of **s5e** (1.47 mmol), 4 mL of HCl (4 M in dioxane) to give **s3p** as a yellow solid (0.242 g, 72%) which was submitted to the next step without further characterization or purification.

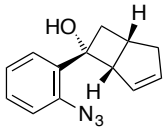
***o*-Cyclobutanol aryl azide 10e.** The general procedure was followed by using 0.242 g of aniline **s3p** (1.01 mmol), 0.480 mL of *t*-BuONO (4.04 mmol), 0.400 mL of Me_3SiN_3 (3.03 mmol) in 5.0 mL of MeCN. Purification by MPLC (10:1 hexanes:EtOAc) gave the product as a yellow oil, (0.180 g, 71%): R_f = 0.61 (5:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 7.41 – 7.36 (m, 4H), 7.34 – 7.31 (m, 1H), 7.29 – 7.25 (m, 1H), 7.17 – 7.13 (m, 2H), 3.95 (t, *J* = 9.0 Hz, 1H), 2.80 (d, *J* = 1.0 Hz, 1H), 2.72 – 2.66 (m, 1H), 2.62 – 2.54 (m, 1H), 2.38 – 2.33 (m, 1H), 2.29 – 2.23 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.4 (C), 137.1 (C), 136.8 (C), 128.9 (CH), 128.7 (CH), 128.3 (CH), 126.8 (CH), 126.8 (CH), 124.8 (CH), 119.0 (CH), 79.6 (C), 49.5 (CH), 32.3 (CH_2), 22.5 (CH_2); ATR-FTIR (thin film): 3542, 2948, 2123, 2089, 1577, 1484, 1444, 1290, 1021, 901, 751, 699 cm^{-1}. HRMS (ESI) m/z calcd for $C_{16}H_{16}NO$ [M + H – N_2]$^+$: 238.1242, found 238.1232.



10f

***N*-(2-(1-Hydroxy-2-arylcyclobutyl)phenyl)aniline s3q. Method A** was followed using 0.500 g of **s5f** (1.20 mmol), 4 mL of HCl (4 M in dioxane) to give **s3q** as a brown solid (0.229 g, 60%) which was submitted to the next step without further characterization or purification.

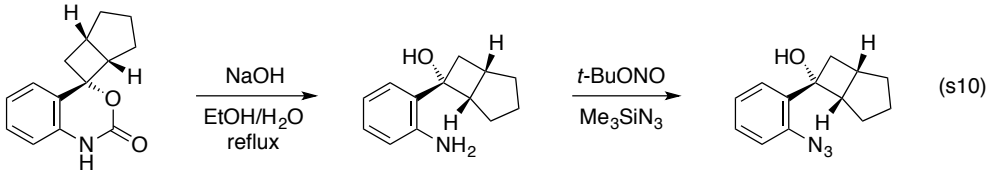
***o*-Cyclobutanol aryl azide 10f.** The general procedure was followed by using 0.321 g of aniline **s3q** (1.01 mmol), 0.480 mL of *t*-BuONO (4.04 mmol), 0.400 mL of Me_3SiN_3 (3.03 mmol) in 5.0 mL of MeCN. Purification by MPLC (10:1 hexanes:EtOAc) gave the product, a yellow oil, as a mixture of atropisomers (0.240 g, 68%): R_f = 0.56 (5:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 7.5 Hz, 1.5 Hz, 1H), 7.67 (dd, *J* = 7.5 Hz, 1.5 Hz, 0.23H), 7.59 (dd, *J* = 8.0 Hz, 1.5 Hz, 1.19H), 7.54 – 7.50 (m, 0.53H), 7.44 – 7.41 (m, 1.23H), 7.40 – 7.35 (m, 1.27H), 7.31 (dt, *J* = 7.5 Hz, 1.5 Hz, 1H), 7.24 – 7.18 (m, 1H), 7.15 – 7.09 (m, 3H), 6.32 – 6.29 (m, 0.22H), 4.32 – 4.28 (m, 1H), 3.18 (t, *J* = 7.5 Hz, 0.46H), 3.10 (d, *J* = 2.0 Hz, 0.92H), 2.85 – 2.79 (m, 1H), 2.56 (quin, *J* = 10.0 Hz, 1H), 2.37 – 2.29 (m, 0.49H), 2.27 – 2.19 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.0 (C), 137.2 (C), 136.3 (C), 133.2 (CH), 132.6 (CH), 131.0 (C), 130.8 (CH), 130.4 (CH), 130.2 (CH), 128.8 (CH), 128.2 (CH), 128.1 (CH), 127.2 (CH), 126.8 (CH), 126.6 (CH), 125.9 (CH), 124.9 (CH), 124.8 (CH), 119.2 (C), 119.1 (CH), 118.7 (CH), 82.9 (C), 80.6 (C), 49.0 (CH), 38.7 (CH_2), 30.4 (CH_2), 28.4 (CH_2), 22.9 (CH_2) only visible peaks; ATR-FTIR (thin film): 3459, 2956, 2924, 2854, 2125, 2093, 1637, 1485, 1281, 751 cm^{-1}. HRMS (ESI) m/z calcd for $C_{16}H_{15}NOBr$ [M + H – N_2]$^+$: 316.0346, found 316.0337.



10g

***N*-(2-(1-Hydroxycyclobutyl)phenyl)aniline s3r. Method A** was followed using 0.500 g of **s5g** (1.66 mmol), 4 mL of HCl (4 M in dioxane) to give **s3r** as a brown solid (0.233 g, 70%) which was submitted to the next step without further characterization or purification.

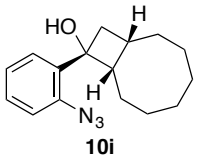
***o*-Cyclobutanol aryl azide 10g.** The general procedure was followed by using 0.297 g of aniline **s3r** (1.01 mmol), 0.480 mL of *t*-BuONO (4.04 mmol), 0.400 mL of Me_3SiN_3 (3.03 mmol) in 5.0 mL of MeCN. Purification by MPLC (10:1 hexanes:EtOAc) gave the product as a yellow oil, (0.120 g, 38%): R_f = 0.54 (5:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.39 (m, 1H), 7.35 – 7.30 (m, 1H), 7.20 – 7.13 (m, 2H), 5.95 – 5.92 (m, 2H), 3.38 – 3.34 (m, 1H), 3.12 – 3.06 (m, 2H), 3.00 – 2.95 (m, 1H), 2.68 (s, 1H), 2.64 – 2.57 (m, 1H), 2.15 – 2.11 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.3 (C), 137.1 (C), 134.8 (CH), 132.9 (CH), 128.7 (CH), 127.0 (CH), 124.7 (CH), 119.0 (CH), 76.0 (C), 46.6 (CH), 41.3 (CH_2), 39.8 (CH), 33.5 (CH_2); ATR-FTIR (thin film): 3459, 3050, 2923, 2123.4, 2089, 1668, 1485, 1292, 1078, 750 cm^{-1}. HRMS (ESI) m/z calcd for $C_{13}H_{14}NO$ $[M + H - N_2]^+$: 200.1082, found 200.1075.



s5'h **s3s** **10h**

***N*-(2-(1-Hydroxycyclobutyl)phenyl)aniline s3s:** The compound was prepared by using the procedure developed by Bali and co-workers.[18] To a solution of 0.500 g of **s5'h** (2.12 mmol) in 8 mL of EtOH was added 4 mL of a 10% aq soln of NaOH. The resulting mixture was heated to reflux, and the reaction progress was monitored using TLC. Once the starting material was consumed, the reaction mixture was cooled to room temperature and concentrated *in vacuo*. The resulting mixture was diluted with water and extracted with 3 × 10 mL of EtOAc. The combined organic phases were washed with saturated brine, dried over $MgSO_4$, filtered and the filtrate was concentrated *in vacuo* to give **s3s** as a yellow solid (0.301 g, 70%) which was submitted to the next step without further characterization or purification.

***o*-Cyclobutanol aryl azide 10h.** The general procedure was followed by using 0.205 g of aniline **s3s** (1.01 mmol), 0.480 mL of *t*-BuONO (4.04 mmol), 0.400 mL of Me_3SiN_3 (3.03 mmol) in 5.0 mL of MeCN. Purification by MPLC (10:1 Hex:EtOAc) gave the product as a yellow oil, (0.150 g, 65%): R_f = 0.52 (5:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (dt, *J* = 7.5 Hz, 1.5 Hz, 1H), 7.23 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 7.18 (dd, *J* = 8.0 Hz, 1.5 Hz, 1H), 7.12 (dt, *J* = 7.5 Hz, 1.0 Hz, 1H), 3.15 (s, 1H), 3.06 – 3.01 (m, 1H), 2.99 – 2.95 (m, 1H), 2.32 – 2.27 (m, 1H), 2.22 (dd, *J* = 13.0 Hz, 6.5 Hz, 1H), 1.60 – 1.41 (m, 4H), 1.38 – 1.27 (m, 1H), 1.11 (dd, *J* = 12.5 Hz, 6.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.4 (C), 133.4 (C), 128.8 (CH), 127.4 (CH), 124.8 (CH), 118.4 (CH), 77.1 (C), 53.1 (CH), 34.2 (CH_2), 32.8 (CH), 32.4 (CH_2), 28.6 (CH_2), 24.8 (CH_2); ATR-FTIR (thin film): 3400, 2944, 2853, 2123, 2085, 1484, 1446, 1277, 1022, 752 cm^{-1}. HRMS (ESI) m/z calcd for $C_{13}H_{16}NO$ $[M + H - N_2]^+$: 202.1229, found 202.1232.

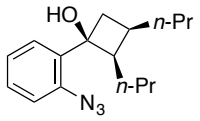


10i

***N*-(2-(1-Hydroxycyclobutyl)phenyl)aniline s3t. Method A** was followed using 0.150 g of **s5i** (0.43 mmol), 2 mL of HCl (4 M in dioxane) to give **s3t** as a brown solid (0.063 g, 60%) which was submitted to the next step without further characterization or purification.

***o*-Cyclobutanol aryl azide 10i.** The general procedure was followed using 0.248 g of aniline **s3t** (1.01 mmol), 0.480 mL of *t*-BuONO (4.04 mmol), 0.400 mL of Me_3SiN_3 (3.03 mmol) in 5.0 mL of MeCN. Purification by MPLC (20:1 Hex:EtOAc) gave the product as a yellow oil, (0.164 g, 60%): R_f = 0.54 (5:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 8.0 Hz, 1.5 Hz, 1H), 7.32 (dt, *J* = 7.5 Hz, 1.5 Hz, 1H), 7.20 (dd, *J* = 8.0 Hz, 1.5 Hz, 1H), 7.14 (dt, *J* = 7.5 Hz, 1.0 Hz, 1H), 3.07 (s, 1H), 2.82 – 2.77 (m, 1H), 2.49 – 2.44 (m, 1H), 2.01 – 1.74 (m, 6H), 1.56 – 1.46 (m, 4H), 1.39 – 1.19 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.3 (C), 134.0 (C), 128.7 (CH), 127.6 (CH), 125.0 (CH), 118.1 (CH), 79.1 (C), 54.0 (CH), 35.3 (CH_2), 32.9 (CH), 31.1 (CH_2), 28.9 (CH_2), 27.7 (CH_2), 26.1 (CH_2), 25.9 (CH_2), 25.2

(CH_2); ATR-FTIR (thin film): 2918, 2849, 2124, 1623, 1485, 1464, 1445, 1277, 1156, 1051, cm^{-1}. HRMS (ESI) m/z calcd for $C_{16}H_{20}NO$ $[M - H - N_2]^+$: 242.1536, found 242.1545.



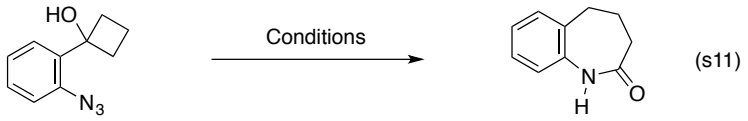
10j

***N*-(2-(1-Hydroxycyclobutyl)phenyl)aniline s3u. Method A** was followed using 0.150 g of **s5i** (0.43 mmol), 2 mL of HCl (4 M in dioxane) to give **s3u** as a yellow solid (0.074 g, 70%) which was submitted to the next step without further characterization or purification.

***o*-Cyclobutanol aryl azide 10j.** The general procedure was followed using 0.250 g of aniline **s3u** (1.01 mmol), 0.480 mL of *t*-BuONO (4.04 mmol), 0.400 mL of Me_3SiN_3 (3.03 mmol) in 5.0 mL of MeCN. Purification by MPLC (20:1 Hex:EtOAc) gave the product as a yellow oil, (0.182 g, 66%): R_f = 0.55 (5:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (dt, *J* = 8.0 Hz, 2.0 Hz, 1H), 7.19 (dd, *J* = 8.0 Hz, 1.5 Hz, 1H), 7.16 – 7.11 (m, 2H), 3.38 (br s, 1H), 2.89 – 2.80 (m, 1H), 2.56 – 2.51 (m, 1H), 2.28 – 2.18 (m, 2H), 1.47 – 1.40 (m, 1H), 1.33 – 1.19 (m, 4H), 1.14 – 1.05 (m, 2H), 0.92 (t, *J* = 7.0 Hz, 3H), 0.87 – 0.81 (m, 1H), 0.78 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.4 (C), 134.2 (C), 128.7 (CH), 127.6 (CH), 124.9 (CH), 118.1 (CH), 78.2 (C), 51.0 (CH), 35.2 (CH_2), 32.8 (CH_2), 32.7 (CH), 29.6 (CH_2), 21.7 (CH_2), 20.6 (CH_2), 14.4 (CH_3), 14.3 (CH_3); ATR-FTIR (thin film): cm^{-1}. HRMS (ESI) m/z calcd for $C_{16}H_{22}N$ $[M - H - N_2O]^+$: 228.1744, found 228.1752.

III. Rh_2(II)-Catalyzed Benzazepine-2-one Formation

A. General Procedure for the Screening of Reaction Conditions



(s11)

8a **9a**

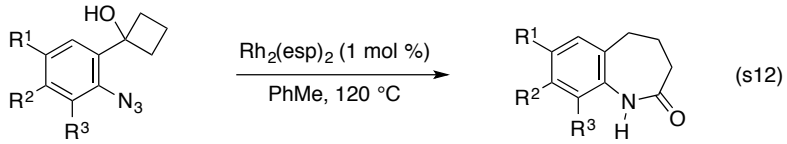
To a 10 mL Schlenk tube, under a nitrogen atmosphere, was added 0.10 mmol of azide followed by the metal salt (1 – 5 mol %) in 1.0 mL of solvent. The Schlenk tube was sealed and heated for 16 h. The reaction mixture was then cooled to room temperature and filtered through a pad of silica gel. The filtrate was concentrated *in vacuo*, and the crude mixture was analyzed using ^{1}H NMR spectroscopy using CH_2Br_2 as an internal standard.

Table s1. Screen of catalyst, catalyst loading, solvent and reaction temperature.

Entry	catalyst	mol %	solvent	T (°C)	**9a** yield, %[a]
1	...	...	PhMe	130	trace
2	$Rh_2(O_2CCH_3)_4$	5	PhMe	100	24
3	$Rh_2(O_2CC_7H_{15})_4$	5	PhMe	100	15
4	$Rh_2(O_2CCF_3)_4$	5	PhMe	100	47
5	$Rh_2(O_2CC_3F_7)_4$	5	PhMe	100	66
6	$Rh_2(esp)_2$	5	PhMe	100	80
7	$Rh_2(esp)_2$	5	PhMe	120	71
8	$Rh_2(esp)_2$	1	PhMe	120	82
9	$RuBr_3 \cdot nH_2O$	1	PhMe	120	23
10	Co(TPP)	5	PhMe	120	trace
11	$[Ir(COD)(OMe)]_2$	5	PhMe	120	23
12	$FeBr_2$	20	PhMe	120	…
13	$FeBr_2$	30	CH_2Cl_2	40	…
14	$FeBr_3$	20	PhMe	120	…
15	$FeBr_3$	30	CH_2Cl_2	40	…

[a] As determined using ^{1}H NMR spectroscopy using CH_2Br_2 as the internal standard.

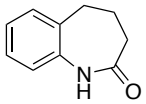
B. Optimized Procedure



8 **9** (s12)

To a 10 mL Schlenk tube, under a nitrogen atmosphere, was added 0.10 mmol of azide followed by 0.001 mmol of $Rh_2(esp)_2$ (1 mol %) in 1.0 mL of toluene. The Schlenk tube was sealed and heated at 120 °C for 16 h. The reaction mixture was then cooled to room temperature and filtered through a pad of silica gel. The filtrate was concentrated *in vacuo*, and the crude mixture was purified by MPLC (7:1 – 3:1 hexanes:EtOAc) to afford the benzazepinone product.

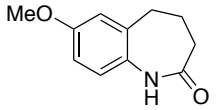
C. Characterization Data for Benzazepine-2-one



9a

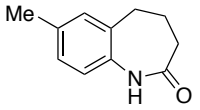
Benzazepine-2-one 9a.[19] The optimized procedure was followed using 0.019 g of azide **8a** (0.10 mmol) and 0.0080 g of $Rh_2(esp)_2$ (1 mol %) in 1.0 mL of toluene. Purification by MPLC (7:1 – 3:1 hexanes:EtOAc) afforded the product as a brown solid (0.0129 g, 80%). The spectral data of **9a** matched that reported by Chen and Gilman:[19] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.26 – 7.22 (m, 2H), 7.14 (td, *J* = 7.5 Hz, 1.0 Hz, 1H), 6.97 (d, *J* = 7.5 Hz, 1H), 2.81 (t, *J* = 7.5 Hz, 2H), 2.36 (t, *J* = 7.5 Hz, 2H), 2.24 (quin, J = 7.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.0 (C), 137.7 (C), 134.4 (C), 129.9 (CH), 127.5 (CH), 125.8 (CH), 121.8 (CH), 32.7 (CH_2), 30.4 (CH_2), 28.4 (CH_2); ATR-FTIR (thin film): 3184, 3061,

2934, 1656, 1490, 1383, 1155, 787 cm^{-1}. The diastereomeric identity of the product was confirmed using X-Ray crystallography.[20]



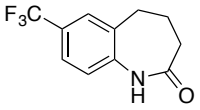
s9b

Benzazepine-2-one 9b.[21] The optimized procedure was followed using 0.030 g of azide **s8b (**0.10 mmol) and 0.0080 g of $Rh_2(esp)_2$ (1 mol %) in 1.0 mL of toluene. Purification by MPLC (7:1 – 3:1 hexanes:EtOAc) afforded product as an orange solid (0.0205 g, 80%). The spectral data of **9b** matched that reported by Crosby and co-workers:[21] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (s, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.76 – 6.74 (m, 1H), 6.52 (d, *J* = 2.0 Hz, 1H), 3.79 (s, 3H), 2.76 (t, *J* = 7.0 Hz, 2H), 2.32 (t, *J* = 7.0 Hz, 2H), 2.21 (quin, *J* = 7.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.0 (C), 159.0 (C), 138.5 (C), 130.6 (CH), 126.5 (C), 111.0 (CH), 107.8 (CH), 55.5 (CH_3), 32.8 (CH_2), 29.5 (CH_2), 28.6 (CH_2); ATR-FTIR (thin film): 3172, 2935, 1661, 1621, 1498, 1381, 1282, 1164, 1050, 890, 737 cm^{-1}.



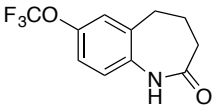
9c

Benzazepine-2-one 9c.[22] The optimized procedure was followed using 0.029 g of azide **8c** (0.10 mmol) and 0.0080 g of $Rh_2(esp)_2$ (1 mol %) in 1.0 mL of toluene. Purification by MPLC (7:1 – 3:1 hexanes:EtOAc) afforded the product as a white solid (0.016 g, 91%). Benzazepinone **9c** was previously reported by Huanming and co-workers:[22] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (br s, 1H), 7.0 (d, J = 5.5 Hz, 2H), 6.86 – 6.85 (m, 1H), 2.76 (t, J = 7.0 Hz, 2H), 2.36 – 2.33 (m, 5H), 2.21 (quin, J = 7.0 Hz, 2H) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.0 (C), 136.0 (C), 135.1 (C), 134.2 (C), 130.5 (CH), 128.0 (CH), 121.7 (CH), 32.7 (CH_2), 30.3 (CH_2), 28.4 (CH_2), 20.9 (CH_3); ATR-FTIR (thin film): 3178, 3041, 2933, 1656, 1504, 1386, 1160, 825 cm^{-1}.



9d

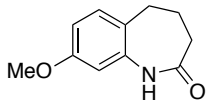
Benzazepine-2-one 9d.[23] The optimized procedure was followed using 0.026 g of azide **8d (**0.10 mmol) and 0.0080 g of $Rh_2(esp)_2$ (1 mol %) in 1.0 mL of toluene. Purification by MPLC (7:1 – 3:1 hexanes:EtOAc) afforded the product as a white solid (0.0169 g, 74%). Benzazepinone **9d** was previously reported by Hoyt and co-workers:[23] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.50 (d, *J* = 7.5 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 1H), 2.86 (t, *J* = 7.0 Hz, 2H), 2.40 (t, *J* = 7.5 Hz, 2H), 2.28 (quin, *J* = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.1 (C), 141.1 (C), 134.7 (C), 127.6 (q, J_{CF} = 32.1 Hz, C), 127.1 (q, J_{CF} = 4.5 Hz, CH), 126.1 (q, J_{CF} = 269.4 Hz, C), 124.7 (q, J_{CF} = 3.6 Hz, CH), 121.8 (CH), 32.9 (CH_2), 30.5 (CH_2), 28.2 (CH_2); ^{19}F NMR (282 MHz, $CDCl_3$) δ –62.6; ATR-FTIR (thin film): 3186, 2949, 1670, 1348, 1259, 1158, 1124, 1078, 932, 846 cm^{-1}.



9e

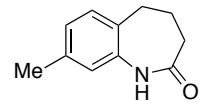
Benzazepine-2-one 9e.[23] The optimized procedure was followed using 0.027 g of azide **8e (**0.10 mmol) and 0.0080 g of $Rh_2(esp)_2$ (1 mol %) in 1.0 mL of toluene. Purification by MPLC (7:1 – 3:1 hexanes:EtOAc) afforded the product as a brown solid (0.0174 g, 71%). Benzazepinone **9e** was previously reported by Hoyt and co-workers:[23] ^{1}H NMR (500 MHz,

$CDCl_3$) δ 8.35 (s, 1H), 7.10 – 7.09 (m, 2H), 7.03 – 7.01 (m, 1H), 2.81 (t, *J* = 7.5 Hz, 2H), 2.37 (t, *J* = 7.5 Hz, 2H), 2.25 (quin, *J* = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.1 (C), 146.4 (C), 136.5 (C), 136.2 (C), 123.0 (CH), 122.5 (CH), 120.5 (q, J_{CF} = 255.2 Hz, C), 120.0 (CH), 32.7 (CH_2), 30.5 (CH_2), 28.1 (CH_2); ^{19}F NMR (282 MHz, $CDCl_3$) δ –58.4; ATR-FTIR (thin film): 3170, 3074, 2943, 1683, 1496, 1380, 1283, 1231, 1205, 1165, 894, 814, 738 cm^{-1}.



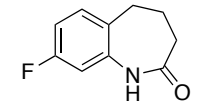
9f

Benzazepine-2-one 9f.[24] The optimized procedure was followed using 0.030 g of azide **8f** (0.10 mmol) and 0.0080 g of $Rh_2(esp)_2$ (1 mol %) in 1.0 mL of toluene. Purification by MPLC (7:1 – 3:1 hexanes:EtOAc) afforded product as a brown solid (0.0229 g, 85%). Benzazepinone **9f** was previously reported by Takashi and co-workers:[24] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (s, 1H), 7.11 (d, *J* = 8.5 Hz, 1H), 6.69 (dd, *J* = 8.0 Hz, 2.5 Hz, 1H), 6.52 (d, *J* = 2.0 Hz, 1H), 3.79 (s, 3H), 2.74 (t, *J* = 7.5 Hz, 2H), 2.36 (t, *J* = 7.5 Hz, 2H), 2.19 (quin, *J* = 7.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.3 (C), 157.4 (C), 135.9 (C), 130.8 (C), 123.1 (CH), 115.2 (CH), 112.2 (CH), 55.5 (CH_3), 32.5 (CH_2), 30.5 (CH_2), 28.2 (CH_2); ATR-FTIR (thin film): 3209, 2935, 1667, 1615, 1509, 1378, 1279, 1162, 1038, 858 cm^{-1}.



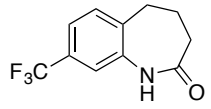
9g

Benzazepine-2-one 9g.[25] The optimized procedure was followed using 0.020 g of azide **8g** (0.10 mmol) and 0.0080 g of $Rh_2(esp)_2$ (1 mol %) in 1.0 mL of toluene. Purification by MPLC (7:1 – 3:1 hexanes:EtOAc) afforded product as a light orange solid (0.0136 g, 80%). Benzazepinone **9g** was previously reported by Huisgen.[25] R_f = 0.56 (1:1 hexanes:EtOAc); mp = 152 – 154 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.10 (d, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 7.0 Hz, 1H), 6.80 (s, 1H), 2.76 (t, *J* = 7.5 Hz, 2H), 2.35 (t, *J* = 7.5 Hz, 2H), 2.33 (s, 3H), 2.21 (quin, *J* = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.3 (C), 137.6 (C), 137.4 (C), 131.2 (C), 129.7 (CH), 126.4 (CH), 122.4 (CH), 32.8 (CH_2), 29.9 (CH_2), 28.5 (CH_2), 21.0 (CH_3); ATR-FTIR (thin film): 3172, 3077, 2940, 1684, 1662, 1512, 1383, 1159, 799 cm^{-1}.



9h

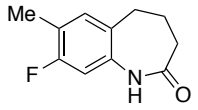
Benzazepine-2-one 9h.[26] The optimized procedure was followed using 0.021 g of azide **8h** (0.10 mmol) and 0.0080 g of $Rh_2(esp)_2$ (1 mol %) in 1.0 mL of toluene. Purification by MPLC (7:1 – 3:1 hexanes:EtOAc) afforded the product as a brown solid (0.0136 g, 78%). Benzazepinone **9h** was previously reported by Altenbach and co-workers:[26] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.16 (dd, *J* = 8.0 Hz, 6.0 Hz, 1H), 6.83 (dt, *J* = 8.0 Hz, 2.5 Hz, 1H), 6.73 (dd, *J* = 9.0 Hz, 2.5 Hz, 1H), 2.27 (t, J_{CF} = 7.5 Hz, 2H), 2.37 (t, *J* = 7.5 Hz, 2H), 2.20 (quin, *J* = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.3 (C), 161.8 (d, J_{CF} = 244.5 Hz, C), 139.1 (d, *J* = 8.9 Hz, C), 130.9 (d, J_{CF} = 9.3 Hz, CH), 129.9 (C), 112.3 (d, J_{CF} = 20.2 Hz, CH), 109.1 (d, J_{CF} = 23.7 Hz, CH), 32.8 (CH_2), 29.7 (CH_2), 28.5 (CH_2); ^{19}F NMR (282 MHz, $CDCl_3$) δ –115.3; ATR-FTIR (thin film): 3187, 3102, 2951, 1663, 1605, 1507, 1483, 1260, 1161, 1151, 998, 834, 705 cm^{-1}.



9i

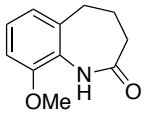
Benzazepine-2-one 9i. The optimized procedure was followed using 0.026 g of azide **8i** (0.10 mmol) and 0.0080 g of $Rh_2(esp)_2$ (1 mol %) in 1.0 mL of toluene. Purification by MPLC (7:1 – 3:1 hexanes:EtOAc) afforded the product as a white solid (0.0197 g, 86%): R_f = 0.30 (1:1 hexanes:EtOAc); mp = 146 – 148 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (s,

1H), 7.39 (d, J = 8.0 Hz, 1H), 7.34 (d, J = 8.0 Hz, 1H), 7.26 (s, 1H), 2.87 (t, J = 7.0 Hz, 2H), 2.38 (t, J = 7.0 Hz, 2H), 2.27 (quin, J = 7.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.0 (C), 138.4 (C), 138.3 (C), 130.5 (CH), 130.1 (q, J_{CF} = 32.8 Hz, C), 123.7 (q, J_{CF} = 270.3 Hz, C), 122.4 (q, J_{CF} = 3.8 Hz, CH), 118.7 (q, J_{CF} = 3.8 Hz, CH), 32.7 (CH_2), 30.4 (CH_2), 28.2 (CH_2); ^{19}F NMR (282 MHz, $CDCl_3$) δ −62.9; ATR-FTIR (thin film): 3190, 2925, 1675, 1327, 1166, 1115, 1076, 987, 828, 672 cm^{-1}. HRMS (ESI) m/z calcd for $C_{11}H_{11}NOF_3$ $[M + H]^+$: 230.0794, found 230.0793.



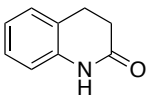
9j

Benzazepine-2-one 9j. The optimized procedure was followed using 0.022 g of azide **8j** (0.10 mmol) and 0.0080 g of $Rh_2(esp)_2$ (1 mol %) in 1.0 mL of toluene. Purification by MPLC (7:1 – 3:1 hexanes:EtOAc) afforded the product as a brown solid (0.0155 g, 80%), as a mixture of rotamers: R_f = 0.48 (1:1 hexanes:EtOAc); mp = 142 – 144 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.00 (d, J = 8.0 Hz, 1H), 6.68 (d, J = 10.0 Hz, 1H), 2.85 (t, J = 7.0 Hz, 0.32H), 2.73 (t, J = 7.0 Hz, 2H), 2.35 (t, J = 7.0 Hz, 2H), 2.26 – 2.17 (m, 5.38H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.2 (C), 159.9 (d, J_{CF} = 242.5 Hz, C), 136.4 (d, J_{CF} = 9.8 Hz, C), 132.3 (d, J_{CF} = 6.0 Hz, CH), 129.7 (d, J_{CF} = 2.9 Hz, C), 129.0 (d, J_{CF} = 5.9 Hz, C), 121.9 (d, J_{CF} = 16.5 Hz, 116.9 (C), 108.9 (d, J_{CF} = 23.4 Hz, CH), 32.9 (CH_2), 32.8 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 28.5 (CH_2), 27.5 (CH_2), 14.6 (CH_3), 14.1 (CH_3); ^{19}F NMR (282 MHz, $CDCl_3$) δ −119.3; ATR-FTIR (thin film): 3192, 2951, 2869, 1667, 1625, 1509, 1495, 1376, 1102, 881, 759 cm^{-1} HRMS (ESI) m/z calcd for $C_{11}H_{13}NOF$ $[M + H]^+$: 194.0983, found 194.0981.



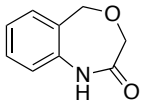
9k

Benzazepine-2-one 9k. The optimized procedure was followed using 0.022 g of azide **8k** (0.10 mmol) and 0.0080 g of $Rh_2(esp)_2$ (1 mol %) in 1.0 mL of toluene. Purification by MPLC (7:1 – 3:1 hexanes:EtOAc) afforded product as a light orange solid (0.0142 g, 74%): R_f = 0.14 (5:1 hexanes:EtOAc); mp = 160 – 162 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (s, 1H), 7.07 (t, J = 7.5 Hz, 1H), 6.80 (t, J = 8.0 Hz, 2H), 3.83 (s, 3H), 2.78 (t, J = 7.5 Hz, 2H), 2.37 (t, J = 7.5 Hz, 2H), 2.23 (quin, J = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.3 (C), 150.1 (C), 134.8 (C), 126.8 (C), 125.5 (CH), 121.7 (CH), 109.1 (CH), 55.6 (CH_3), 33.3 (CH_2), 30.4 (CH_2), 28.5 (CH_2); ATR-FTIR (thin film): 3198, 2968, 2935, 1652, 1602, 1455, 1288, 1084, 787, 771 cm^{-1}. HRMS (ESI) m/z calcd for $C_{11}H_{14}NO_2$ $[M + H]^+$: 192.1019, found 192.1025.



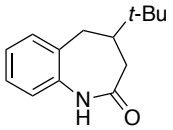
11a

Quinolinone 11a.[27] The optimized procedure was followed using 0.018 g of azide **10a** (0.10 mmol) and 0.0080 g of $Rh_2(esp)_2$ (1 mol %) in 1.0 mL of toluene. Purification by MPLC (7:1 – 3:1 hexanes:EtOAc) afforded product as a white solid (0.0118 g, 80%). The spectral data of **11a** matched that reported by Liu and Hu:[27] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (br s, 1H), 7.19 – 7.16 (m, 2H), 6.99 (t, J = 8.0 Hz, 1H), 6.74 (d, J = 8.0 Hz, 1H), 2.97 (t, J = 7.5 Hz, 2H), 2.64 (t, J = 7.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.4 (C), 137.1 (C), 128.1 (CH), 127.5 (CH), 127.4 (C), 123.3 (CH), 115.2 (CH), 30.8 (CH_2), 25.4 (CH_2); ATR-FTIR (thin film): 3197, 2975, 2914, 1682, 1595, 1492, 1439, 1386, 1282, 1246, 1033, 817, 749 cm^{-1}.



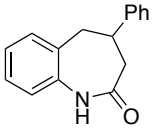
11b

Benzazepine-2-one 11b.[28] The optimized procedure was followed using 0.019 g of azide **10b** (0.10 mmol) and 0.0080 g of $Rh_2(esp)_2$ (1 mol %) in 1.0 mL of toluene. Purification by MPLC (5:1 – 1:1 hexanes:EtOAc) afforded product as a white solid (0.0083 g, 51%). The spectral data of **10b** matched that reported by Ashweek and co–workers:[28] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (br s, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 7.06 (t, *J* = 7.0 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 4.74 (s, 2H), 4.58 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.2 (C), 135.8 (C), 129.2 (CH), 128.7 (C), 128.6 (CH), 123.8 (CH), 119.2 (CH), 73.5 (CH_2), 72.9 (CH_2); ATR-FTIR (thin film): 3192, 3058, 2992, 1657, 1592, 1495, 1447, 1402, 1133, 944, 839 cm^{-1}.



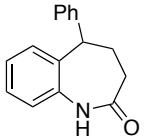
11c

Benzazepine-2-one 11c. The optimized procedure was followed using 0.024 g of azide **10c** (0.10 mmol) and 0.0080 g of $Rh_2(esp)_2$ (1 mol %) in 1.0 mL of toluene. Purification by MPLC (5:1 – 3:1 hexanes:EtOAc) afforded product as a white solid (0.0143 g, 66 %): R_f = 0.29 (3:1 Hexane:EtOAc); mp = 178 – 180 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (br s, 1H), 7.24 – 7.19 (m, 2H), 7.10 (dt, *J* = 7.5 Hz, 1.5 Hz, 1H), 6.95 (dd, *J* = 7.5 Hz, 1.0 Hz, 1H), 2.84 – 2.78 (m, 2H), 2.43 – 2.34 (m, 2H), 2.20 (quin, *J* = 7.0 Hz, 1H), 0.99 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.4 (C), 137.8 (C), 134.1 (C), 130.9 (CH), 127.3 (CH), 125.3 (CH), 121.2 (CH), 51.4 (CH), 34.8 (CH_2), 34.4 (C), 32.4 (CH_2), 27.7 (CH_3); ATR-FTIR (thin film): 3056, 2962, 2360, 1663, 1586, 1491, 1264, 733 cm^{-1}. HRMS (ESI) m/z calcd for $C_{14}H_{20}NO$ $[M + H]^+$: 218.1543, found 218.1545.



11d

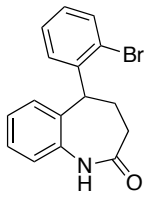
Benzazepine-2-one 11d.[29] The optimized procedure was followed using 0.025 g of azide **10d** (0.10 mmol) and 0.0080 g of $Rh_2(esp)_2$ (1 mol %) in 1.0 mL of toluene. Purification by MPLC (5:1 – 3:1 hexanes:EtOAc) afforded product as a white solid (0.0237 g, quantitative). The spectral data of **11d** matched that reported by Hudson and co–workers:[29] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (br s, 1H), 7.33 – 7.28 (m, 5H), 7.24 – 7.21 (m, 2H), 7.17 (t, *J* = 7.0 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 1H), 3.71 (quin, *J* = 7.5 Hz, 1H), 3.20 (dd, *J* = 14.0 Hz, 7.0 Hz, 1H), 2.91 (dd, *J* = 13.5 Hz, 6.5 Hz, 1H), 2.69 – 2.62 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.1 (C), 145.0 (C), 137.4 (C), 133.0 (C), 130.7 (CH), 128.7 (CH), 127.8 (CH), 126.9 (CH), 126.8 (CH), 125.7 (CH), 121.8 (CH), 46.7 (CH), 39.6 (CH_2), 38.8 (CH_2); ATR-FTIR (thin film): 3195, 3059, 2918, 1664, 1584, 1492, 1380, 1158, 756 cm^{-1}.



11e

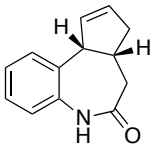
Benzazepine-2-one 11e.[30] The optimized procedure was followed using 0.025 g of azide **10e** (0.10 mmol) and 0.0080 g of $Rh_2(esp)_2$ (1 mol %) in 1.0 mL of toluene. Purification by MPLC (5:1 – 3:1 hexanes:EtOAc) afforded product as a white solid (0.0161 g, 72%). The spectral data of **11e** matched that reported by Ikeda and co–workers:[30] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (br s, 1H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.32 – 7.26 (m, 3H), 7.21 (t, *J* = 8.0 Hz, 1H), 7.04 (t, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.80 (d, *J* =7.5 Hz, 1H), 4.44 – 4.39 (m, 1H), 2.63 – 2.45 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$)

δ 174.6 (C), 140.9 (C), 137.1 (C), 137.0 (C), 128.9 (CH), 128.8 (CH), 128.6 (CH), 127.3 (CH), 127.1 (CH), 125.8 (CH), 121.8 (CH), 45.1 (CH), 33.6 (CH_2), 32.7 (CH_2); ATR-FTIR (thin film): 3198, 3060, 2924, 1665, 1484, 1381, 759, 735 cm^{-1}.



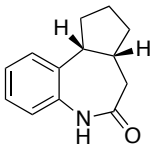
11f

Benzazepine-2-one 11f. The optimized procedure was followed using 0.034 g of azide **s8s (**0.10 mmol) and 0.0080 g of $Rh_2(esp)_2$ (1 mol %) in 1.0 mL of toluene. Purification by MPLC (5:1 – 3:1 hexanes:EtOAc) afforded product as a brown solid (0.0209 g, 66%). R_f = 0.27 (1:1 hexanes:EtOAc); mp = 160 – 162 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 8.0 Hz, 1.5 Hz, 1H), 7.47 – 7.39 (m, 3H), 7.24 – 7.16 (m, 2H), 7.04 – 6.97 (m, 2H), 6.59 (d, *J* = 7.5 Hz, 1H), 4.79 – 4.73 (m, 1H), 2.57 – 2.49 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.3 (C), 140.2 (C), 137.2 (C), 135.6 (C), 133.6 (CH), 129.2 (CH), 128.6 (CH), 128.0 (CH), 127.9 (C), 127.4 (CH), 126.0 (CH), 125.9 (CH), 121.8 (CH), 44.3 (CH), 32.7 (CH_2), 32.6 (CH_2); ATR-FTIR (thin film): 3197, 3060, 2924, 1667, 1486, 1470, 1379, 757, 738 cm^{-1}. HRMS (ESI) m/z calcd for $C_{16}H_{15}NOBr$ $[M + H]^+$: 316.0331, found 316.0337.



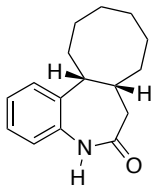
11g

Benzazepine-2-one 11g. The optimized procedure was followed using 0.032 g of azide **10g (**0.10 mmol) and 0.0080 g of $Rh_2(esp)_2$ (1 mol %) in 1.0 mL of toluene. Purification by MPLC (5:1 – 3:1 hexanes:EtOAc) afforded product as a brown solid (0.0175 g, 60%): R_f = 0.24 (1:1 hexanes:EtOAc); mp = 158 – 160 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (br s, 1H), 7.27 – 7.22 (m, 2H), 7.13 (t, *J* = 7.0 Hz, 1H), 6.95 (d, *J* = 7.5 Hz, 1H), 5.90 – 5.89 (m, 1H), 5.78 – 5.76 (m, 1H), 3.68 – 3.58 (m, 2H), 2.74 – 2.61 (m, 3H), 2.27 – 2.23 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.5 (C), 137.0 (C), 136.7 (C), 132.2 (CH), 131.4 (CH), 131.0 (CH), 127.6 (CH), 125.5 (CH), 122.9 (CH), 52.1 (CH), 45.2 (CH), 39.9 (CH_2), 37.8 (CH_2); ATR-FTIR (thin film): 3197, 3050, 2920, 1666, 1583, 1489, 1433, 1391, 1169, 752, 732, 706 cm^{-1}. HRMS (ESI) m/z calcd for $C_{13}H_{14}NO$ $[M + H]^+$: 200.1072, found 200.1075.



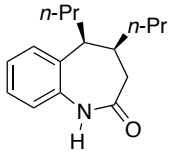
11h

Benzazepine-2-one 11h. The optimized procedure was followed using 0.023 g of azide **10h (**0.10 mmol) and 0.0080 g of $Rh_2(esp)_2$ (1 mol %) in 1.0 mL of toluene. Purification by MPLC (5:1 – 3:1 hexanes:EtOAc) afforded product as a brown solid (0.0147 g, 73%): R_f = 0.12 (3:1 hexanes:EtOAc); mp = 164 – 166 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (br s, 1H), 7.24 – 7.20 (m, 2H), 7.12 (dt, *J* = 7.5 Hz, 1.0 Hz, 1H), 6.96 (dd, *J* = 7.5 Hz, 1.0 Hz, 1H), 3.29 (q, *J* = 7.5 Hz, 1H), 2.91 – 2.83 (m, 1H), 2.52 (dd, *J* = 12.5 Hz, 7.5 Hz, 1H), 2.14 (dd, *J* = 12.5 Hz, 7.5 Hz, 1H), 2.05 – 1.96 (m, 2H), 1.95 – 1.85 (m, 2H), 1.67 – 1.57 (m, 1H), 1.57 – 1.49 (m, 1H) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.2 (C), 137.1 (C), 136.0 (C), 129.6 (CH), 127.2 (CH), 125.4 (CH), 122.5 (CH), 46.3 (CH), 44.5 (CH), 38.4 (CH_2), 31.4 (CH_2), 31.3 (CH_2), 25.0 (CH_2); ATR-FTIR (thin film): cm^{-1}. HRMS (ESI) m/z calcd for $C_{13}H_{16}NO$ $[M + H]^+$: 202.1229, found 200.1232.



11i

Benzazepine-2-one 11i. The optimized procedure was followed using 0.024 g of azide **10i** (0.10 mmol) and 0.0080 g of $Rh_2(esp)_2$ (1 mol %) in 1.0 mL of toluene. Purification by MPLC (5:1 – 3:1 hexanes:EtOAc) afforded product as a white solid (0.0205 g, 95%): R_f = 0.23 (1:1 hexanes:EtOAc); mp = 173 – 175 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (br s, 1H), 7.30 (dd, *J* = 7.5 Hz, 1.5 Hz, 1H), 7.24 – 7.17 (m, 2H), 6.98 (dd, *J* = 7.5 Hz, 1.5 Hz, 1H), 3.10 – 3.05 (m, 1H), 2.89 – 2.82 (m, 1H), 2.33 – 2.29 (m, 1H), 2.19 – 2.11 (m, 1H), 1.91 (t, *J* = 12.0 Hz, 1H), 1.87 – 1.81 (m, 1H), 1.75 – 1.58 (m, 6H), 1.56 – 1.46 (m, 3H), 1.14 – 1.09 (m, 1H) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.9 (C), 137.7 (C), 137.1 (C), 127.5 (CH), 126.9 (CH), 125.5 (CH), 121.7 (CH), 42.8 (CH), 42.3 (CH_2), 41.0 (CH), 29.7 (CH_2), 28.4 (CH_2), 28.3 (CH_2), 26.7 (CH_2), 26.4 (CH_2), 25.3 (CH_2); ATR-FTIR (thin film): 3191, 2918, 2853, 2359, 1667, 1582, 1481, 1443, 1373, 757, 730 cm^{-1}. HRMS (ESI) m/z calcd for $C_{16}H_{22}NO$ $[M + H]^+$: 244.1697, found 244.1701.



11j

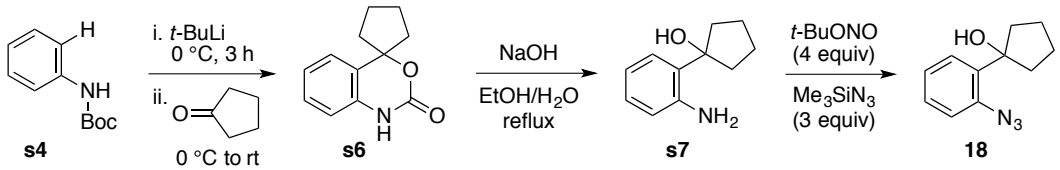
Benzazepine-2-one 11j. The optimized procedure was followed using 0.027 g of azide **10i** (0.10 mmol) and 0.0080 g of $Rh_2(esp)_2$ (1 mol %) in 1.0 mL of toluene. Purification by MPLC (5:1 – 3:1 hexanes:EtOAc) afforded product as a brown solid (0.0160 g, 65%): R_f = 0.27 (2:1 hexanes:EtOAc); mp = 170 – 172 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (br s, 1H), 7.24 – 7.16 (m, 3H), 7.01 – 6.99 (m, 1H), 3.09 (q, *J* = 6.5 Hz, 1H), 2.54 – 2.42 (m, 2H), 1.83 – 1.64 (m, 3H), 1.48 – 1.41 (m, 1H), 1.33 – 1.21 (m, 3H), 1.13 – 1.04 (m, 1H), 0.93 (t, *J* = 7.5 Hz, 3H), 0.90 – 0.80 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.5 (C), 137.8 (C), 135.1 (C), 127.5 (CH), 126.8 (CH), 125.3 (CH), 121.8 (CH), 42.7 (CH), 41.8 (CH), 39.5 (CH_2), 31.3 (CH_2), 30.8 (CH_2), 20.8 (CH_2), 19.5 (CH_2), 14.4 (CH_3), 14.1 (CH_3); ATR-FTIR (thin film): 3196, 2955, 2929, 2870, 1665, 1378, 756 cm^{-1}. HRMS (EI) m/z calcd for $C_{16}H_{23}NO$: 245.17819, found 245.17797.

The diastereomeric identity of the product was confirmed using X-Ray crystallography.[31]

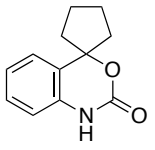
IV. Mechanistic Experiments

A. Synthesis of Mechanism Probes.

The *ortho*-cyclopentanol aryl azide was constructed following the sequence below (Scheme s2).

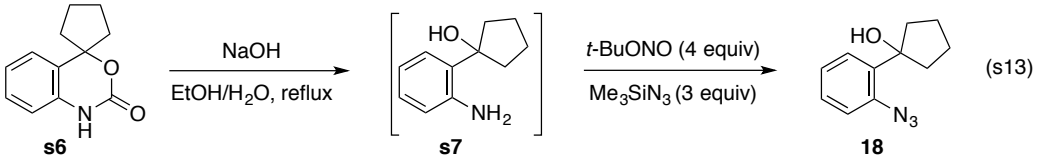


Scheme s2. Synthesis of *ortho*-cyclopentanol aryl azide.



s6

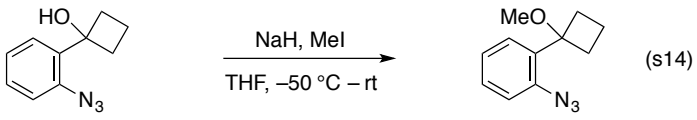
Spiro[4*H*-3,1-benzoxazine-4,1'-cyclopentan]-2(1*H*)-one s6.[32] To a cooled (0 °C) 3 M solution of *N*-Boc aniline (0.800 g, 4.14 mmol) in 1.4 mL of dry Et_2O under an inert atmosphere of argon was dropwise added 5.45 mL of a 1.9 M solution of *t*-butyl lithium in pentane using a syringe pump. After 3 h, a solution of the 0.550 mL of cyclopentanone (6.21 mmol) in 2.0 mL dry Et_2O was added dropwise. The resulting mixture was allowed to warm to rt. The reactives were quenched through the addition of a saturated aq soln of NH_4Cl. The resulting mixture was diluted with EtOAc. The two layers were separated, and the aqueous layer was extracted 3 additional times with EtOAc (3 × 5 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$ and the filtrate concentrated under reduced pressure. The resulting residue was purified by MPLC (2:1 hexanes:EtOAc) to afford the product as a white solid (0.33 g, 40%). The spectral data of **s6** matched that reported by Puwen and Jeffrey:[26] ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.39 (br s, 1H), 7.22 – 7.19 (m, 1H), 7.12 (d, *J* = 7.5 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 2.37 – 2.31 (m, 2H), 2.11 – 1.99 (m, 4H), 1.88 – 1.82 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.4 (C), 134.8 (C), 128.8 (CH), 124.6 (C), 123.3 (CH), 122.9 (CH), 114.6 (CH), 93.2 (C), 39.7 (CH_2), 23.7 (CH_2); ATR-FTIR (thin film): 3096, 2927, 1702, 1596, 1493, 1372, 1262, 1047, 762 cm^{-1}.



s6 **s7** **18**

1-(2-Aminophenyl) cyclopentanol s7. To a solution of 0.330 g of **s6** (1.63 mmol) in 6.0 mL of EtOH was added 3.0 mL of a 10% aq soln of NaOH. The resulting mixture was heated to reflux, and the reaction progress was monitored using TLC. Once the starting material was consumed, the reaction mixture was cooled to room temperature and concentrated *in vacuo*. The resulting mixture was diluted with water and extracted with 3 × 10 mL of EtOAc. The combined organic phases were washed with saturated brine, dried over $MgSO_4$, filtered and the filtrate was concentrated *in vacuo* to give **s7** as a yellow solid (0.230 g, 80%) which was submitted to the next step without further characterization or purification.

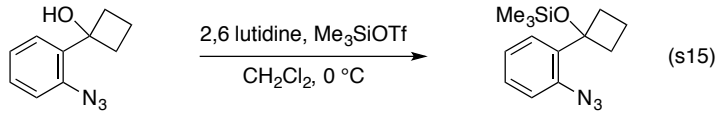
1-(2-Azidophenyl) cyclopentanol 18. To a cooled solution (0 °C) of 0.092 g of 1-(*o*-aminophenyl) cyclopentanol **s7** (0.52 mmol)) in 2.6 mL of MeCN, was added dropwise 0.250 mL of *t*-BuONO (2.08 mmol) and 0.210 mL of Me_3SiN_3 (1.56 mmol). The resulting solution was warmed to room temperature. After 1.5 h, the reaction mixture was concentrated in vacuo. The residue was purified by MPLC (10:1 hexanes:EtOAc) to afford the product as a yellow oil (0.085 g, 80%): R_f = 0.70 (3:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (dd, J = 8.0 Hz, 1.5 Hz, 1H), 7.31 (dt, J = 7.5 Hz, 1.5 Hz, 1H), 7.19 (dd, J = 8.0 Hz, 1.0 Hz, 1H), 7.11 (dt, J = 7.5 Hz, 1.5 Hz, 1H), 2.99 (s, 1H), 2.11 – 2.04 (m, 4H), 2.01 – 1.92 (m, 2H), 1.82 – 1.74 (m, 2H) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.2 (C), 137.1 (C), 128.4 (CH), 126.6 (CH), 124.8 (CH), 118.9 (CH), 82.6 (C), 39.6 (CH_2), 23.5 (CH_2); ATR-FTIR (thin film): 3423, 2951, 2871, 2120, 2084, 1576, 1484, 1443, 1284, 1000, 750 cm^{-1}. HRMS (ESI) m/z calcd for $C_{11}H_{13}N_3ONa$ $[M + Na]^+$: 226.0957, found 226.0959.



8a **21a**

1-Azido-2-(1-methoxycyclobutyl)benzene 21a. A solution of azide alcohol **8a** (0.100 g, 0.53 mmol) in THF (2 mL) was added to a cold (– 50 °C) stirred suspension of 60% NaH (0.030 g, 0.78 mmol) in THF (3 mL). After stirring for 10 min, methyl iodide (0.050 mL, 0.78 mmol) was added. The mixture was allowed to warm to room temperature overnight and

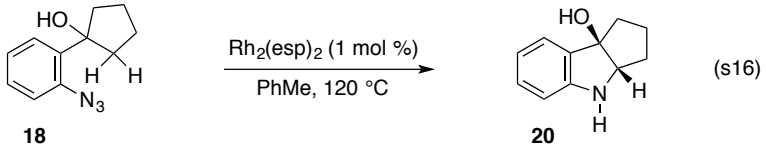
the reactives were quenched through the addition of water. The resulting mixture was extracted with dichloromethane, dried over anhydrous magnesium sulfate, and the filtrate was concentrated *in vacuo*. The resulting residue was purified by MPLC (15:1 hexanes:EtOAc) to provide the compound as a yellow oil (0.054 g, 50%): R_f = 0.66 (5:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.5 Hz, 1H), 7.29 (d, J = 7.5 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 2.93 (s, 3H), 2.54 – 2.42 (m, 4H), 2.10 – 2.01 (m, 1H), 1.72 – 1.64 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.6 (C), 132.7 (C), 129.1 (CH), 129.0 (CH), 123.9 (CH), 119.2 (CH), 81.8 (C), 50.6 (CH_3), 32.4 (CH_2), 14.9 (CH_2) ; ATR-FTIR (thin film): 2983, 2940, 2819, 2121, 2085, 1485, 1443, 1295, 1130, 752 cm^{-1}. HRMS (ESI) m/z calcd for $C_{11}H_{13}N_3ONa$ [M + Na]$^+$: 226.0956, found 226.0958.



8a **21b** (s15)

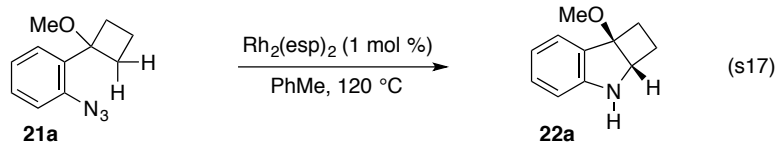
(1-(2-Azidophenyl)cyclobutoxy)trimethylsilane 21b. To a cooled solution (0 °C) of 0.162 g of aryl azide **8a** (0.86 mmol) in 8 mL of CH_2Cl_2 under an Ar atmosphere was added 1.00 mL of 2,6-lutidine (8.60 mmol) followed by the dropwise addition of 0.780 mL of Me_3SiOTf (4.30 mmol). After 3 h, the reaction mixture was passed through a short silica gel column using Et_2O as the eluent, and the filtrate was concentrated *in vacuo*. The resulting residue was purified by MPLC (20:1 hexanes:EtOAc) to give the product as a yellow oil (0.170 g, 75%): R_f = 0.47 (10:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 8.0 Hz, 1H), 2.67 – 2.62 (m, 2H), 2.46 – 2.40 (m, 2H), 1.95 – 1.87 (m, 1H), 1.53 – 1.43 (m, 1H), 0.12 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.2 (C), 135.3 (C), 128.9 (CH), 127.2 (CH), 124.1 (CH), 119.6 (CH), 77.6 (C), 37.3 (CH_2), 14.0 (CH_2), 1.3 (CH_3); ATR-FTIR (thin film): 2953, 2123, 2090, 1487, 1444, 1294, 1249, 1135, 987, 839 cm^{-1}. HRMS (ESI) m/z calcd for $C_{13}H_{19}N_3OSiNa$ [M + Na]$^+$: 284.1195, found 284.1196.

B. Mechanistic experiments



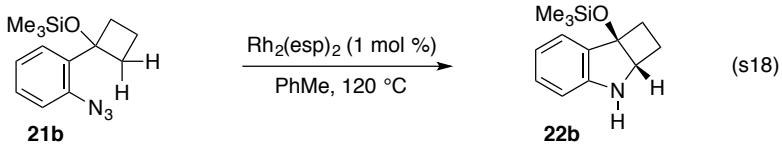
18 **20** (s16)

Tetrahydrocyclopenta indol-ol 20. To a 10 mL Schlenk tube, under a nitrogen atmosphere, was added 0.020 g of azide **18** (0.10 mmol) followed by 0.080 g of $Rh_2(esp)_2$ (0.001 mmol) in 1.0 mL of toluene. The Schlenk tube was sealed and heated at 120 °C for 16 h. The reaction mixture was then cooled to room temperature and filtered through a pad of silica gel. The filtrate was concentrated *in vacuo*, and the crude mixture was purified by MPLC (5:1 – 3:1 hexanes:EtOAc) to afford the product as a brown liquid (0.009 g, 51%): R_f = 0.18 (3:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.26 (m, 1H), 7.13 – 7.10 (m, 1H), 6.76 (t, *J* = 7.0 Hz, 1H), 6.60 (d, *J* = 7.5 Hz, 1H), 4.01 – 3.99 (m, 1H), 3.91 (br s, 1H), 2.15 – 2.04 (m, 4H), 1.81 – 1.76 (m, 1H), 1.69 – 1.64 (m, 1H), 1.59 – 1.48 (m, 1H) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.9 (C), 132.7 (C), 129.6 (CH), 123.9 (CH), 118.8 (CH), 109.6 (CH), 90.7 (C), 71.2 (CH), 41.3 (CH_2), 35.6 (CH_2), 24.7 (CH_2); ATR-FTIR (thin film): 3243, 2946, 2923, 2854, 1713, 1606, 1464, 1314, 1295, 1067, 1056, 756 cm^{-1}. HRMS (ESI) m/z calcd for $C_{11}H_{14}NO$ [M + H]$^+$: 176.1074, found 176.1075.



(s17)

Methoxy-tetrahydrocyclobuta indole 22a. To a 10 mL Schlenk tube, under a nitrogen atmosphere, was added 0.020 g of azide **21a** (0.10 mmol) followed by 0.080 g of $Rh_2(esp)_2$ (0.001 mmol) in 1.0 mL of toluene. The Schlenk tube was sealed and heated at 120 °C for 16 h. The reaction mixture was then cooled to room temperature and filtered through a pad of silica gel. The filtrate was concentrated *in vacuo*, and the crude mixture was purified by MPLC (5:1 – 3:1 hexanes:EtOAc) to afford the product as a brown liquid (0.009 g, 52%): R_f = 0.41 (5:1 hexanes:EtOAc) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.29 (m, 1H), 7.19 (dt, *J* = 7.5 Hz, 1.0 Hz, 1H), 6.88 – 6.85 (dt, *J* = 7.5 Hz, 1H), 6.76 – 6.74 (m, 1H), 4.20 (t, *J* = 6.5 Hz, 1H), 4.03 (br s, 1H), 3.05 (s, 3H), 2.48 – 2.35 (m, 2H), 2.24 – 2.17 (m, 1H), 1.47 – 1.39 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.2 (C), 130.3 (C), 129.7 (CH), 125.1 (CH), 119.7 (CH), 111.9 (CH), 86.3 (C), 59.2 (CH_3), 51.2 (CH), 31.9 (CH_2), 22.5 (CH_2); ATR-FTIR (thin film): 3359, 2922, 2852, 1607, 1464, 1310, 1172, 746 cm^{-1}. HRMS (ESI) m/z calcd for $C_{11}H_{14}NO$ $[M + H]^+$: 176.1075, found 176.1075.



(s18)

Trimethylsilyloxytetrahydrocyclobutaindole 22b. To a 10 mL Schlenk tube, under a nitrogen atmosphere, was added 0.026 g of azide **21b** (0.10 mmol) followed by 0.080 g of $Rh_2(esp)_2$ (0.001 mmol) in 1.0 mL of toluene. The Schlenk tube was sealed and heated at 120 °C for 16 h. The reaction mixture was then cooled to room temperature and filtered through a pad of silica gel. The filtrate was concentrated *in vacuo*, and the crude mixture was purified by MPLC using neutral alumina (15:1 hexanes:EtOAc) to afford the product as a brown liquid (0.012 g, 51%): R_f = 0.84 (10:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 7.5 Hz, 1H), 7.16 (t, *J* = 8.0 Hz, 1H), 6.82 (t, *J* = 7.0 Hz, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 4.09 (dd, *J* = 8.0 Hz, 1.5 Hz, 1H), 4.04 (br s, 1H), 2.45 (dd, *J* = 10.0 Hz, 7.0 Hz, 2H), 2.17 – 2.11 (m, 1H), 1.38 – 1.30 (m, 1H), – 0.04 (s, 9H) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.0 (C), 134.4 (C), 129.4 (CH), 125.4 (CH), 119.5 (CH), 112.0 (CH), 82.4 (C), 63.7 (CH), 35.1 (CH_2), 22.2 (CH_2), 1.26 (CH_3); ATR-FTIR (thin film): 3368, 2953, 2360, 2124, 1608, 1478, 1465, 1250, 1168, 1128, 841 cm^{-1}. HRMS (EI) m/z calcd for $C_{13}H_{20}NOSi$ $[M + H]^+$: 234.1314, found 234.1314.

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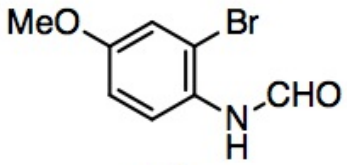
V. Spectral Data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s1b

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MeO
Br
N
H
CHO

s1b

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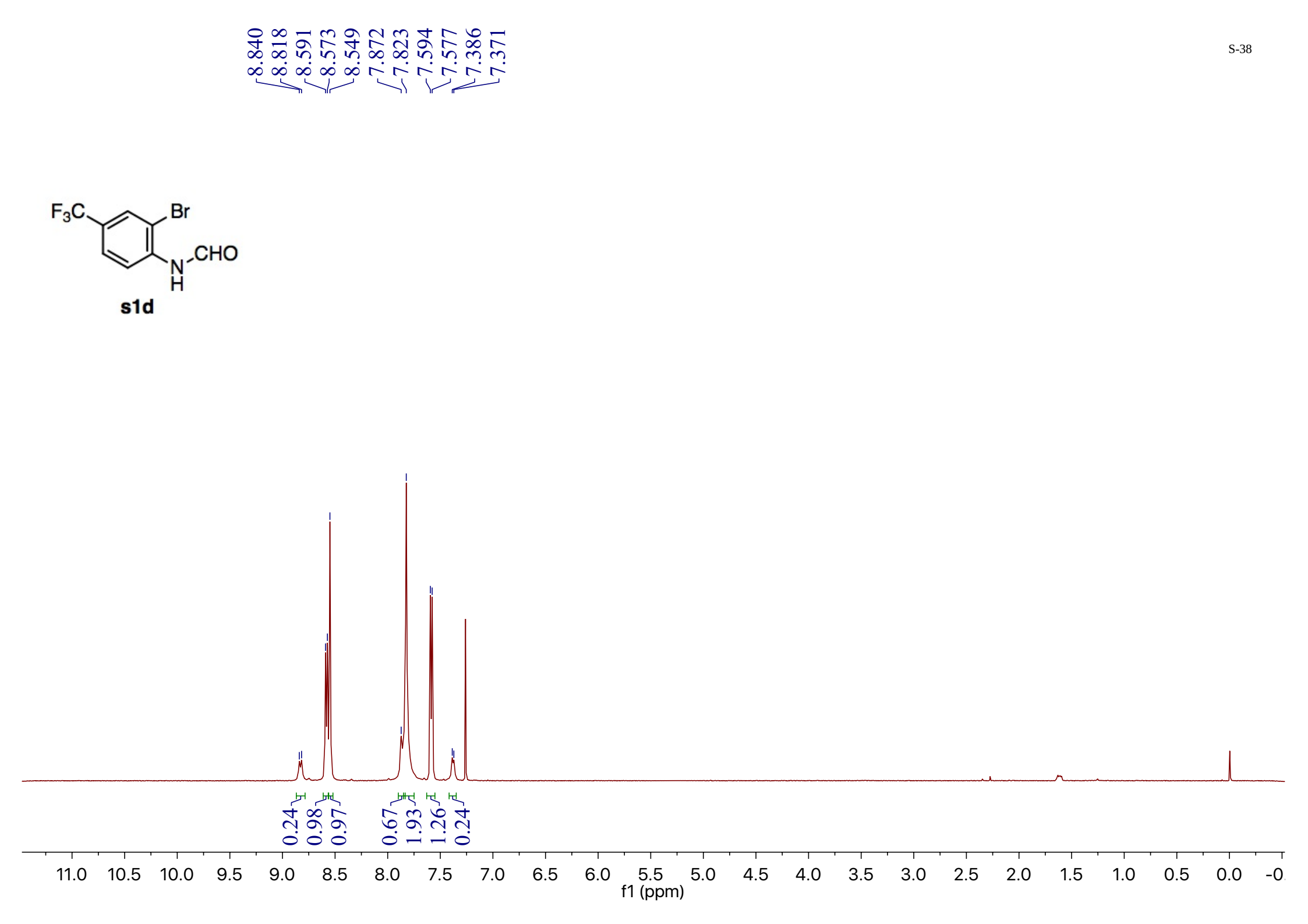
f1 (ppm)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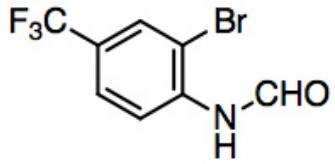
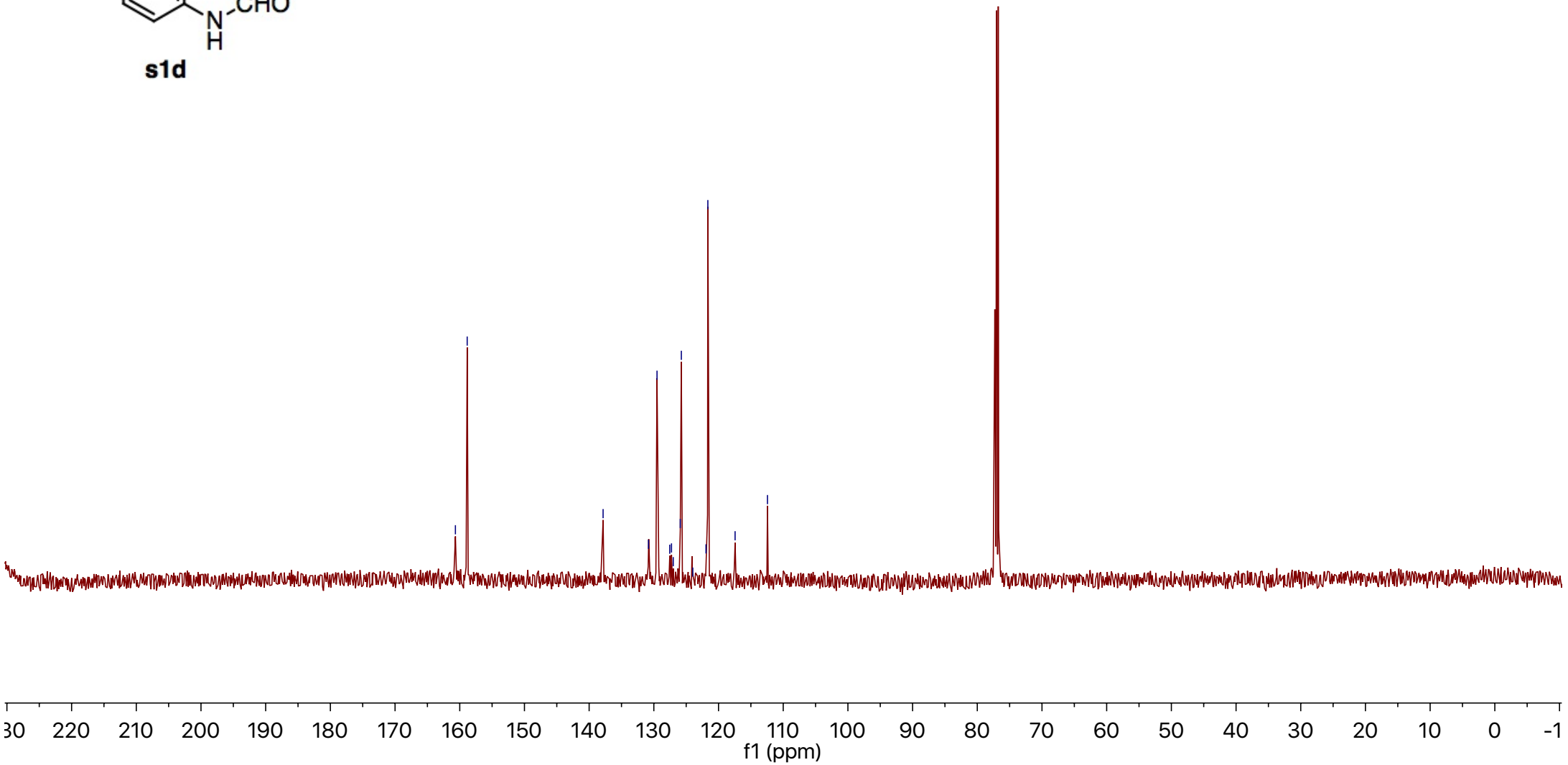
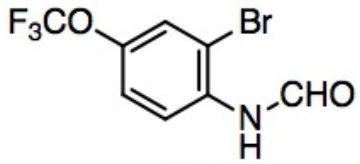


s1d

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CHO

s1e

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f1 (ppm)

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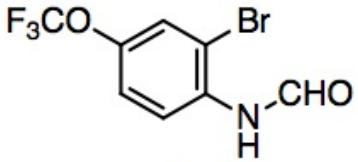
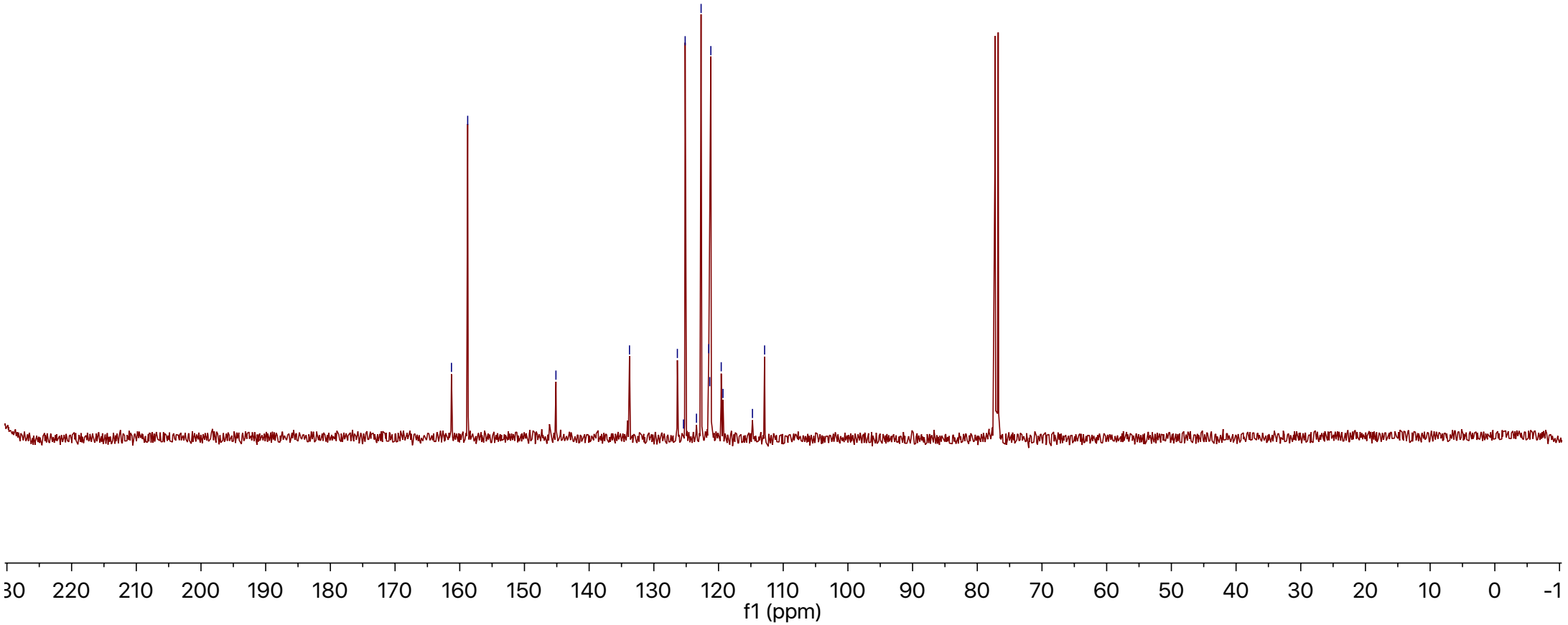
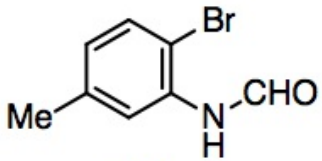
121.187
119.581
119.308
114.754
112.878



s1e

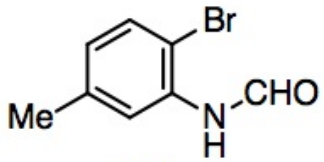



Br
Me
N
H
CHO

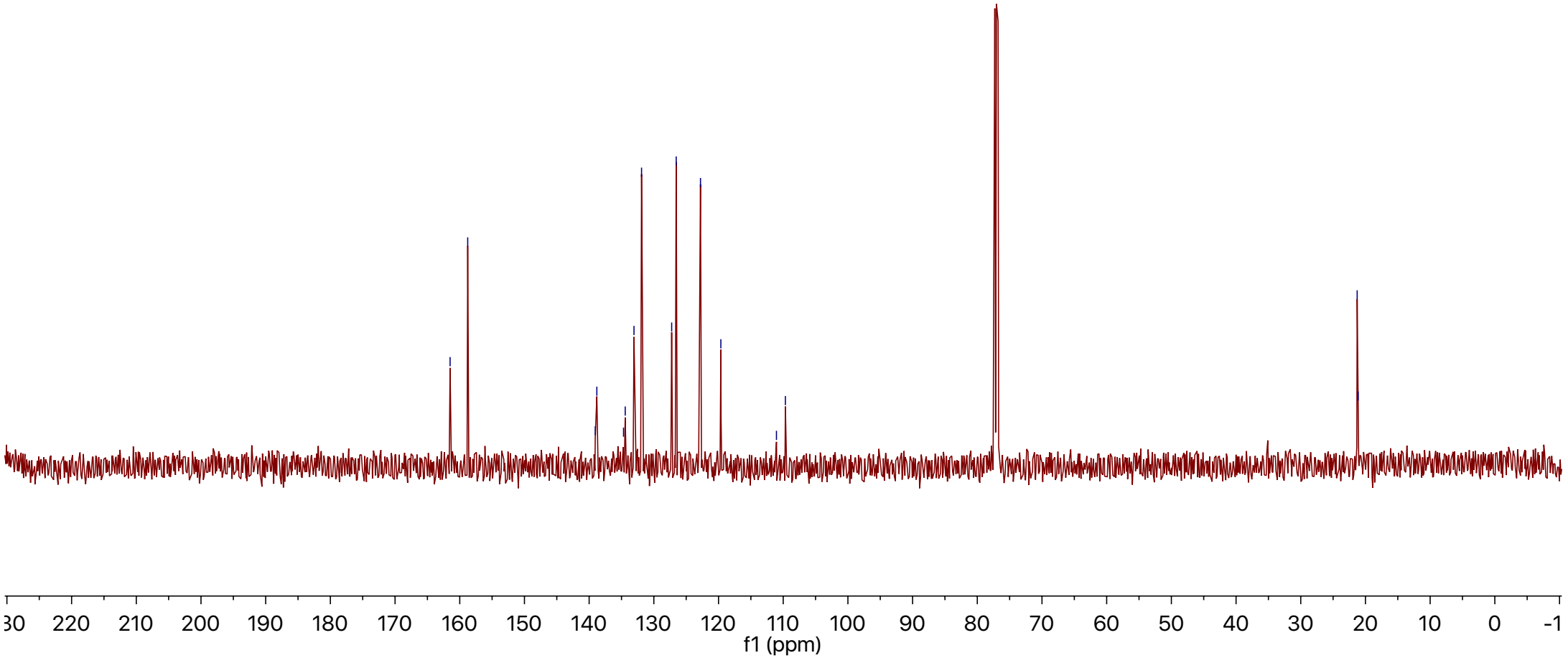
s1g

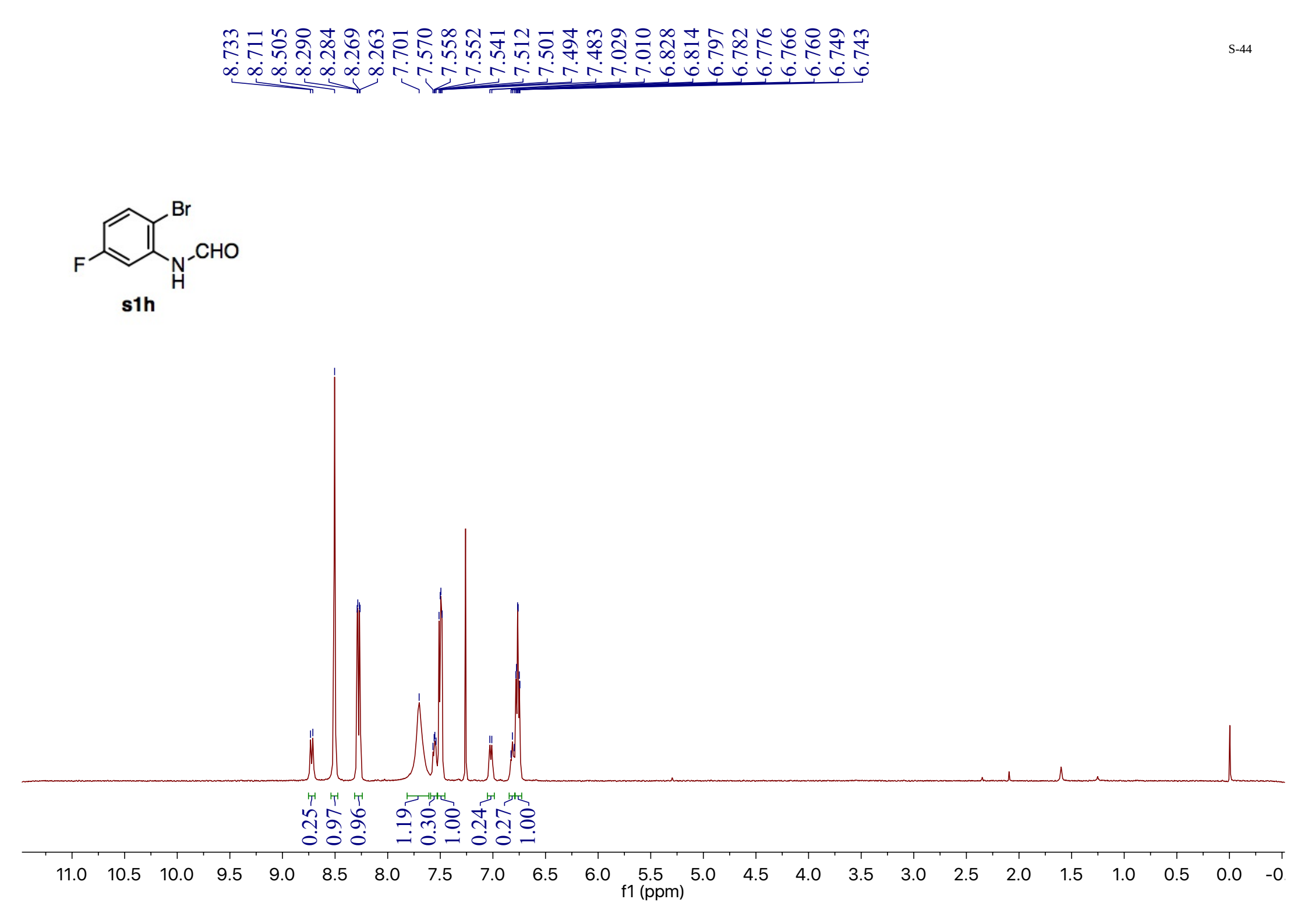
8.696
8.673
8.471
8.222
7.623
7.458
7.442
7.411
7.395
7.067
6.888
6.872
6.830
6.814
2.330
2.324
0.51
1.01
1.01
1.44
0.55
1.04
0.49
0.54
1.06
1.46
3.25
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

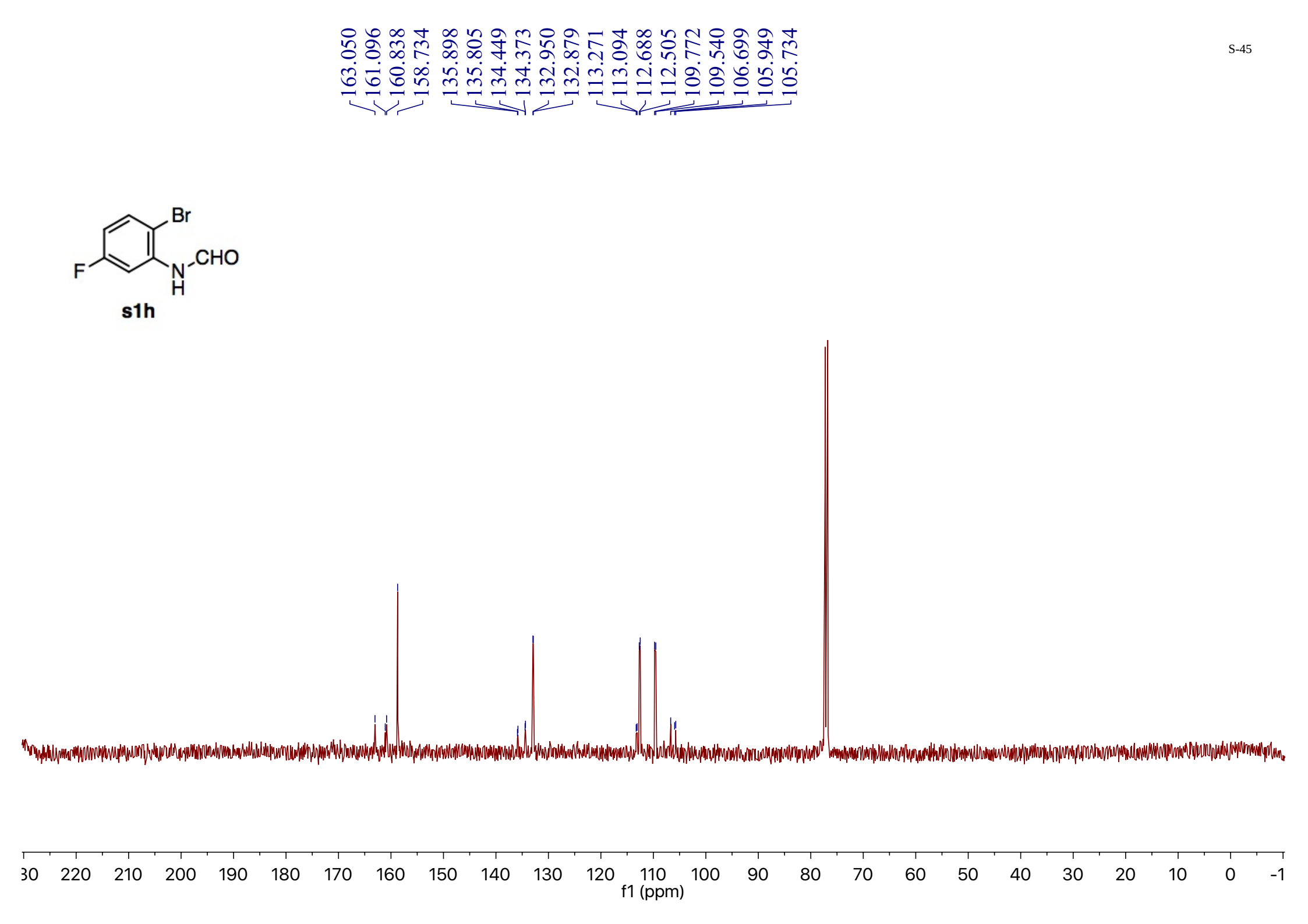
161.494
158.770
139.050
138.809
134.683
134.423
133.067
131.898
127.241
126.542
122.789
119.641
111.045
109.665
21.280
21.134

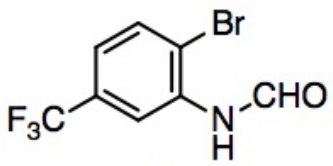


s1g




8.733
8.711
8.505
8.290
8.284
8.269
8.263
7.701
7.570
7.558
7.552
7.541
7.512
7.501
7.494
7.483
7.029
7.010
6.828
6.814
6.797
6.782
6.776
6.766
6.760
6.749
6.743
Br
F
N
H
CHO
s1h
0.25
0.97
0.96
1.19
0.30
1.00
0.24
0.27
1.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

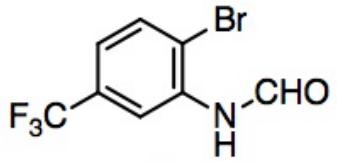

163.050
161.096
160.838
158.734
135.898
135.805
134.449
134.373
132.950
132.879
113.271
113.094
112.688
112.505
109.772
109.540
106.699
105.949
105.734
Br
F
N
H
CHO
s1h
f1 (ppm)


Br
F3C
N
H
CHO

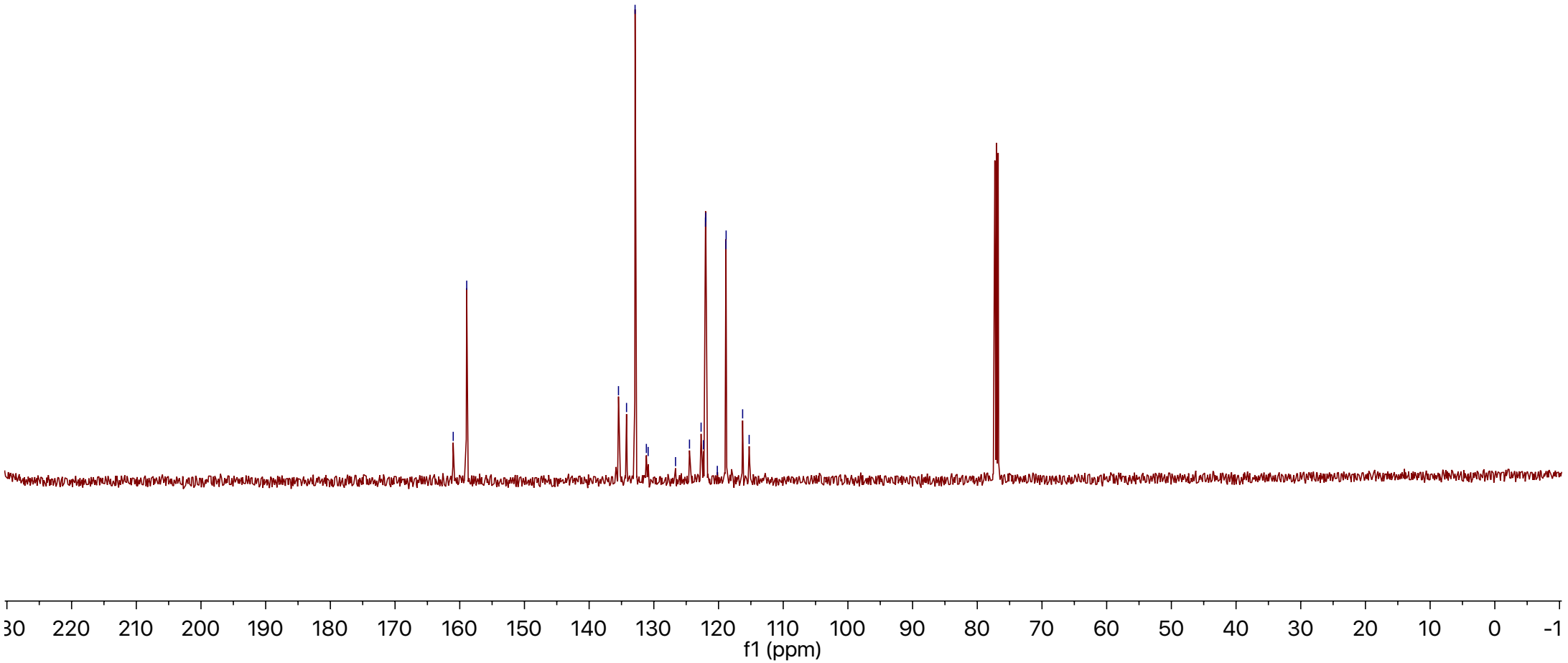
s1i

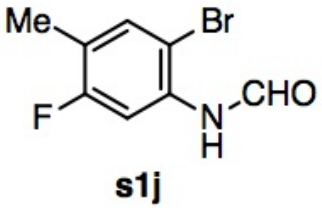
8.777
8.738
7.848
7.748
7.733
7.681
7.665
7.498
7.327
7.312
7.260
7.248
0.12
1.09
1.00
1.17
0.30
1.03
0.23
0.24
1.12
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

161.009
158.924
135.463
134.219
132.900
131.153
130.881
126.645
124.486
122.694
122.322
122.014
121.978
120.186
118.859
118.824
116.273
115.265



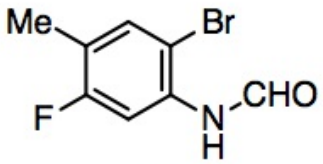
s1i




Me
Br
F
N
H
CHO

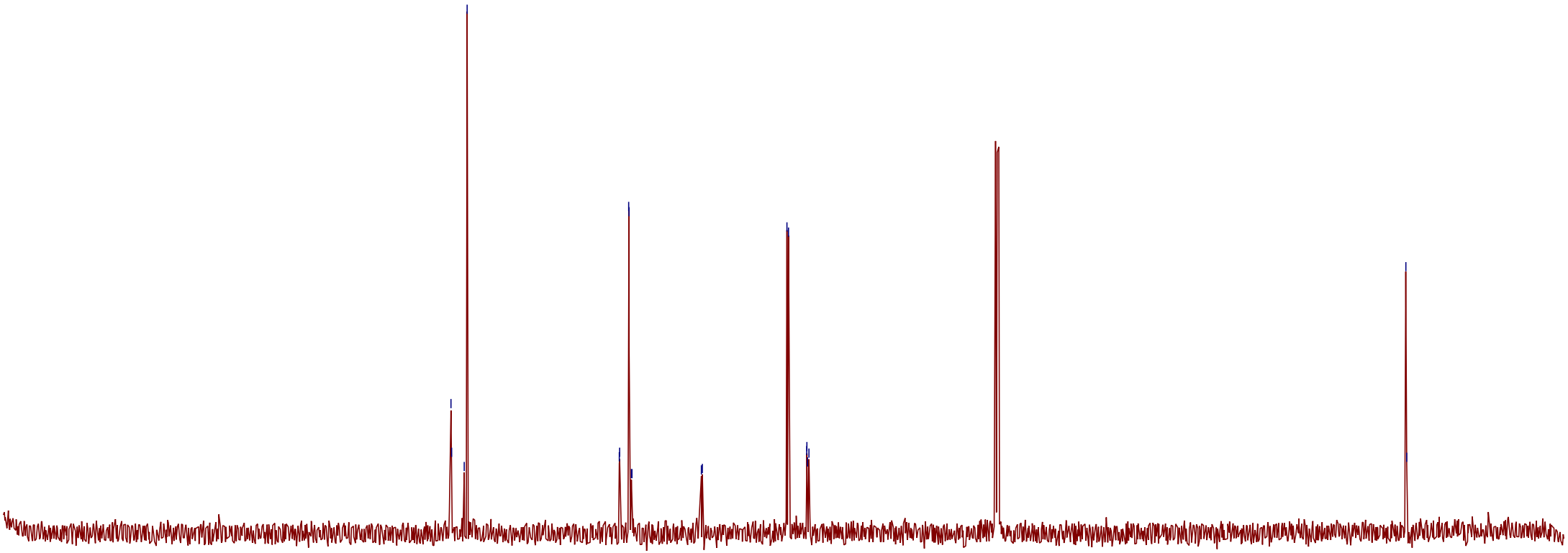
s1j

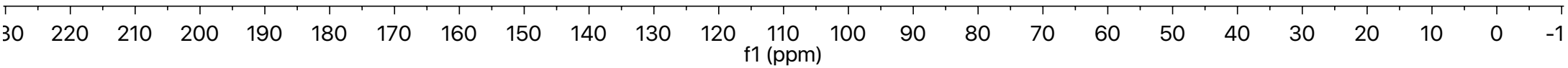
8.643
8.621
8.460
8.456
8.168
8.145
7.690
7.411
7.396
7.349
7.334
6.958
6.938
2.228
2.213
2.209
0.29
1.03
0.99
1.25
0.28
0.99
0.26
0.96
3.22
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

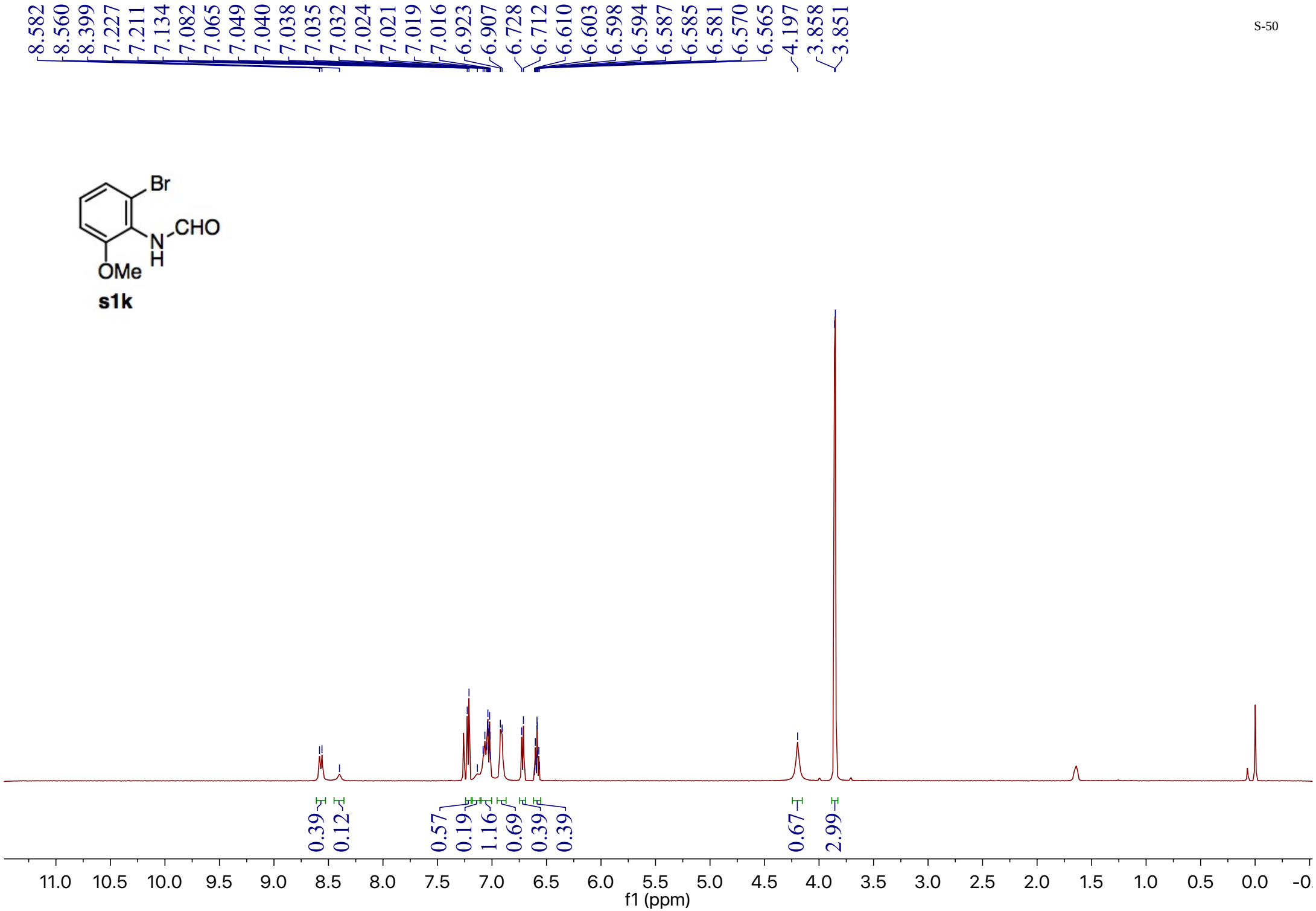


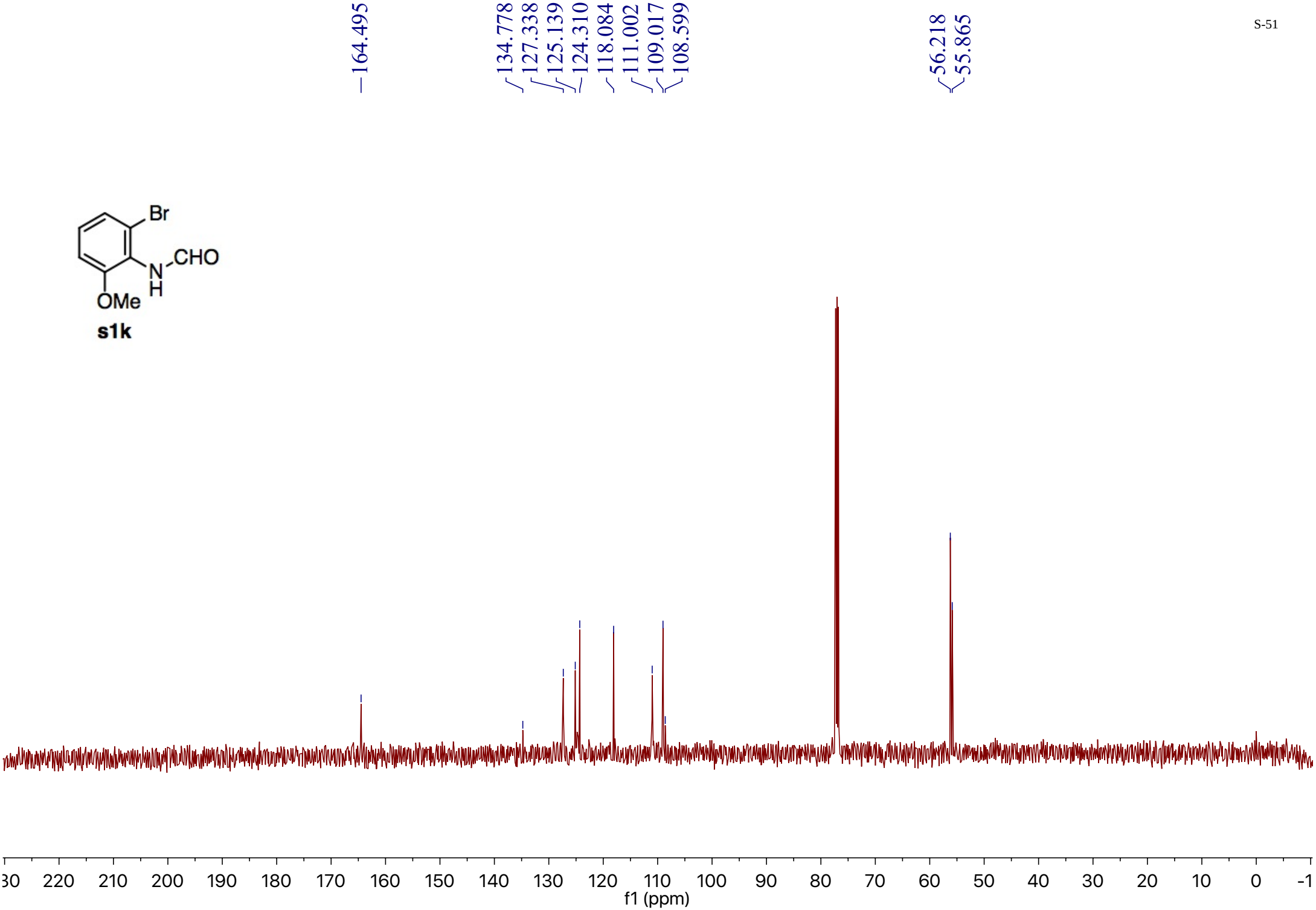
s1j

161.295
161.195
159.250
158.802
135.336
135.285
133.888
133.840
133.472
133.381
122.677
122.524
109.480
109.239
106.430
106.403
106.307
106.087
14.026
13.898

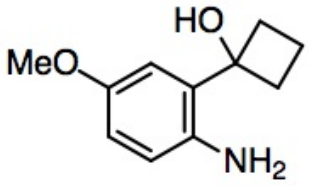




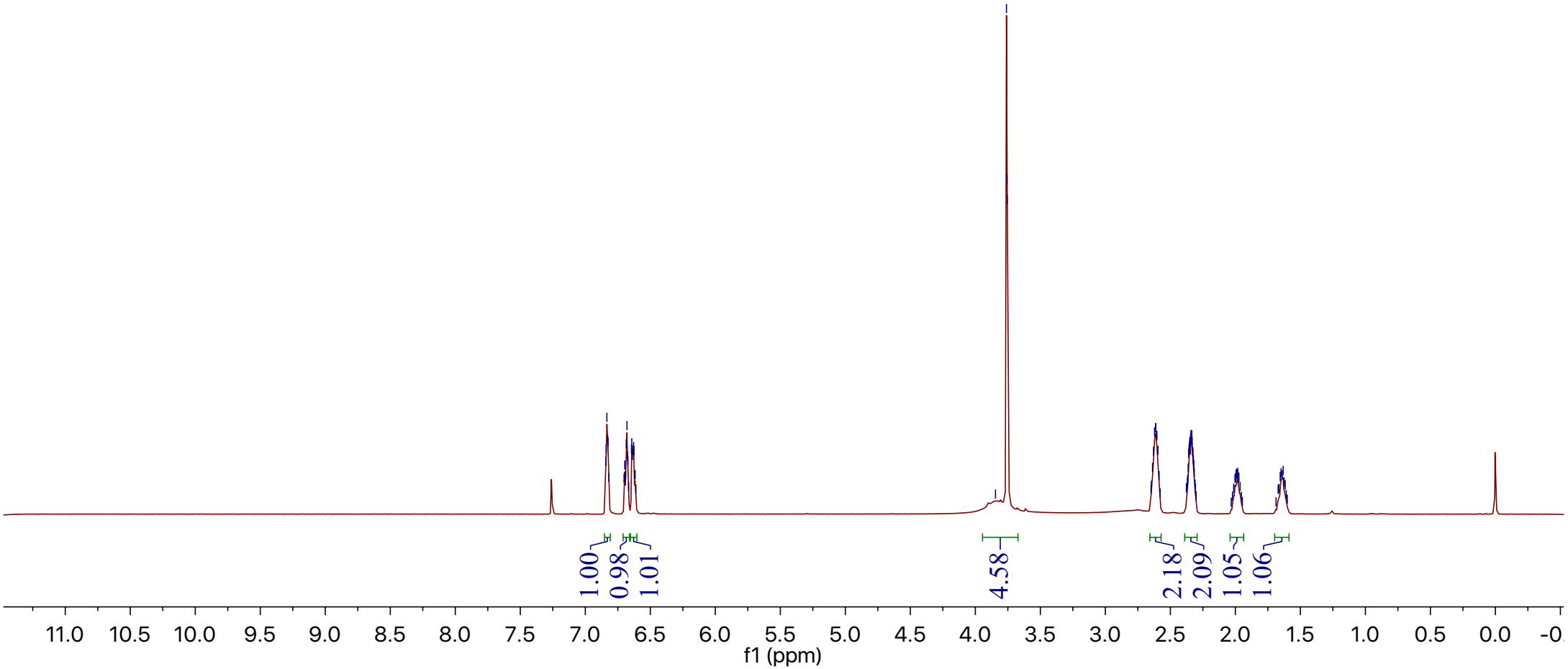

8.582
8.560
8.399
7.227
7.211
7.134
7.082
7.065
7.049
7.040
7.038
7.035
7.032
7.024
7.021
7.019
7.016
6.923
6.907
6.728
6.712
6.610
6.603
6.598
6.594
6.587
6.585
6.581
6.570
6.565
4.197
3.858
3.851
Br
N
H
CHO
OMe
s1k
0.39
0.12
0.57
0.19
1.16
0.69
0.39
0.39
0.67
2.99
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

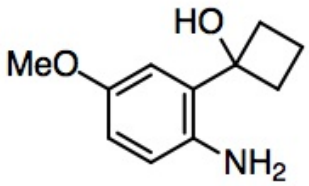

164.495
134.778
127.338
125.139
124.310
118.084
111.002
109.017
108.599
56.218
55.865
Br
N
H
CHO
OMe
s1k
f1 (ppm)

6.842 6.840 6.834 6.828 6.825 6.696 6.685 6.679 6.675 6.672 6.645 6.643 6.637 6.634 6.628 6.626 6.620 6.617 3.761 3.757 3.754 2.637 2.629 2.621 2.614 2.611 2.605 2.604 2.595 2.363 2.360 2.357 2.353 2.351 2.348 2.344 2.341 2.338 2.335 2.332 2.329 2.326 2.323 2.319 2.316 1.994 1.991 1.985 1.981 1.648 1.639 1.632



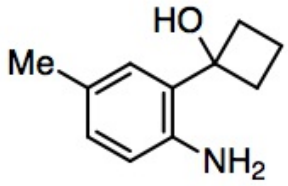
s3b




HO
MeO
NH2

s3b

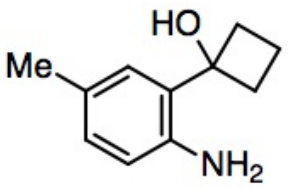
152.283
138.854
130.495
118.025
113.081
112.313
76.847
55.842
35.086
13.618
f1 (ppm)


HO
Me
NH2

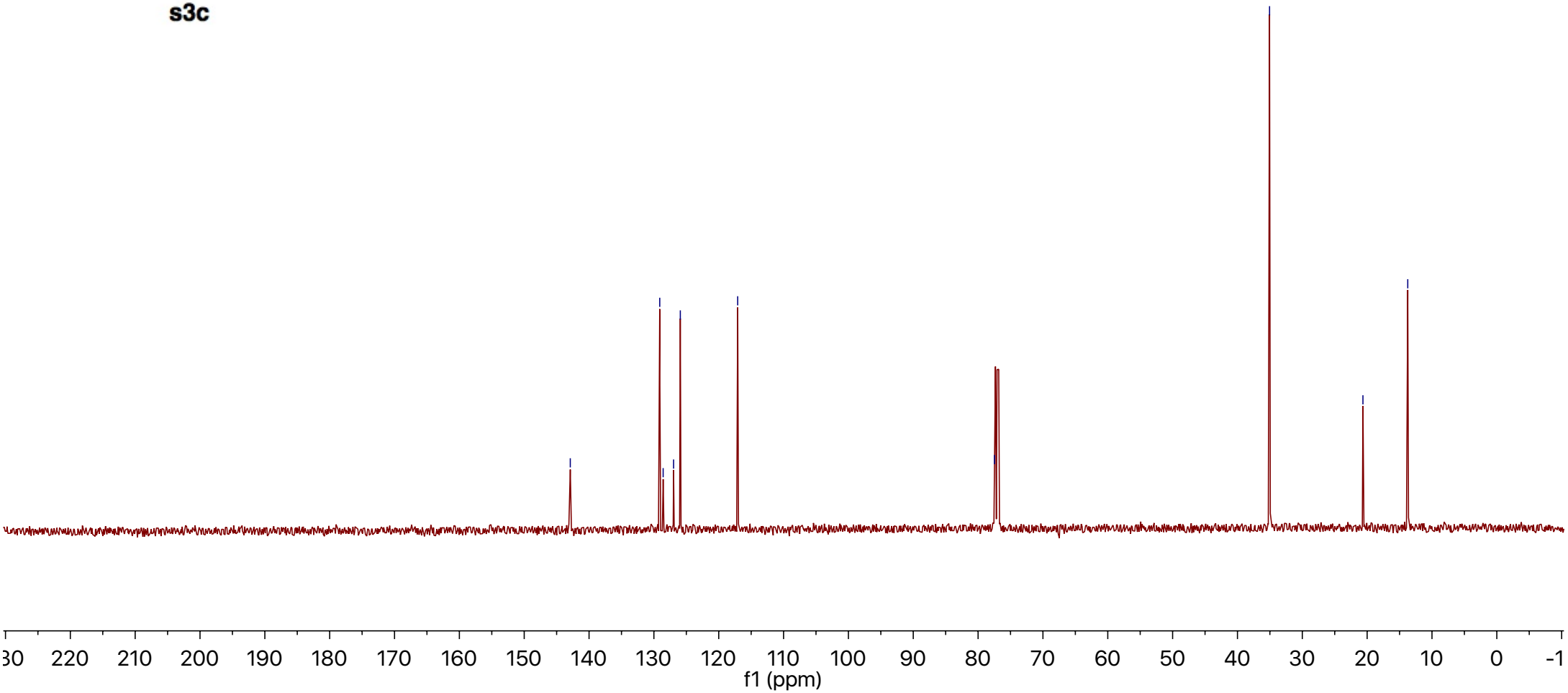
s3c

7.017
6.931
6.916
6.603
6.587
3.977
2.674
2.670
2.665
2.659
2.652
2.645
2.640
2.634
2.628
2.622
2.617
2.363
2.348
2.342
2.329
2.323
2.309
2.305
2.272
2.043
2.035
2.025
2.016
2.006
1.996
1.986
1.984
1.974
1.965
1.956
1.682
1.665
1.648
1.632
1.627
1.616
1.611
1.595
1.00
0.98
0.99
1.76
2.20
2.07
3.24
1.19
1.12
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

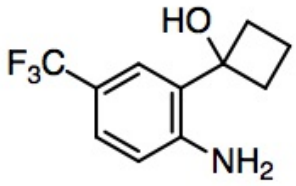
142.895
129.097
128.572
126.961
125.925
117.076
77.479
35.048
20.647
13.735



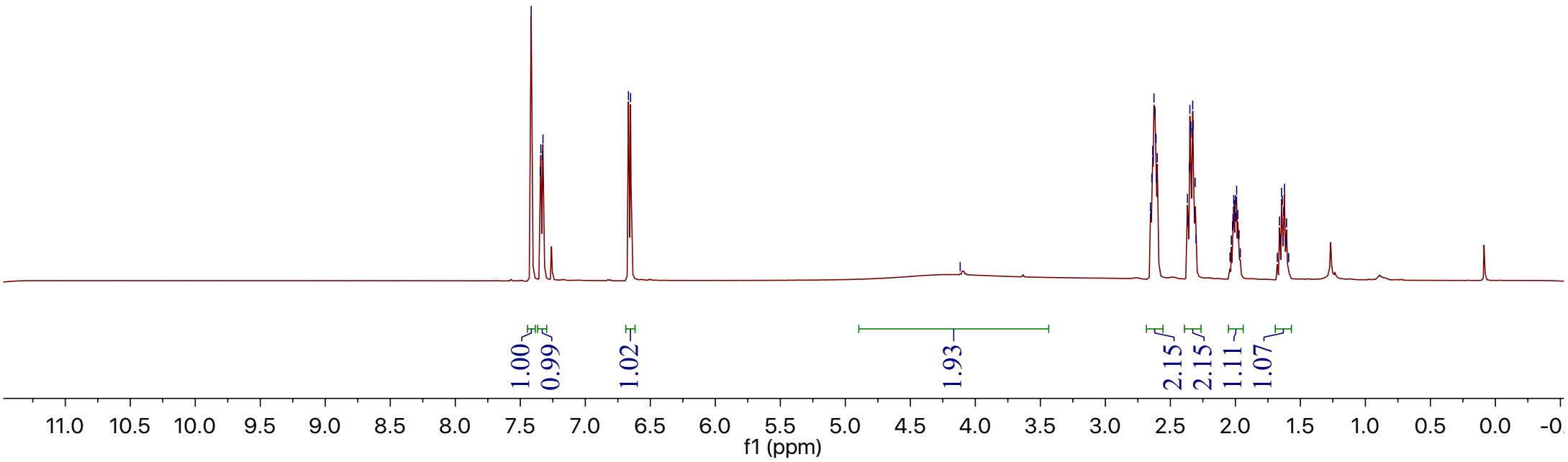
s3c

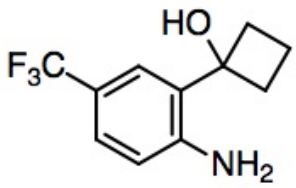


7.416 7.346 7.342 7.330 7.326 6.668 6.652 2.653 2.649 2.643 2.636 2.632 2.626 2.618 2.610 2.606 2.600 2.368 2.362 2.353 2.350 2.347 2.343 2.334 2.328 2.324 2.315 2.309 2.303 2.041 2.031 2.022 2.018 2.013 2.009 2.003 2.000 1.994 1.990 1.981 1.972 1.962 1.677 1.661 1.655 1.645 1.639 1.629 1.622 1.613 1.606 1.590



s3d

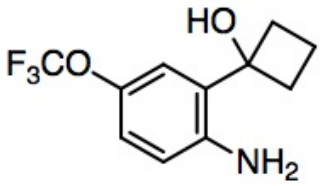



HO
F3C
NH2

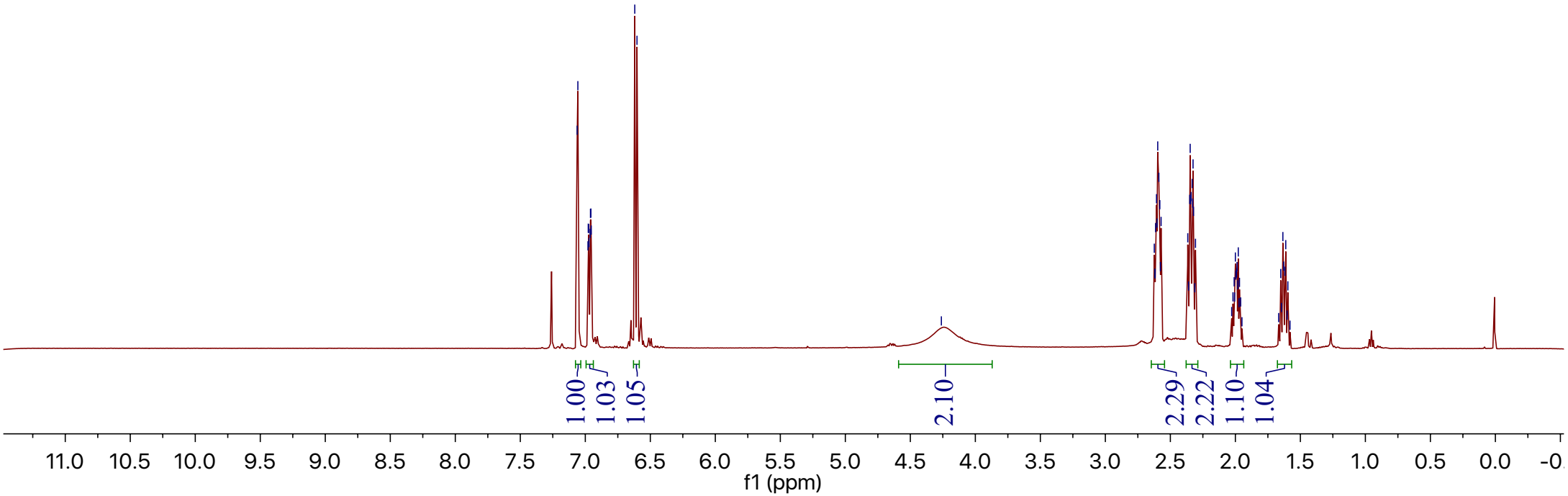
s3d

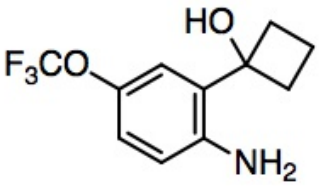
148.713
128.168
127.271
126.022
125.993
125.957
125.925
125.748
123.870
122.642
122.607
122.577
122.551
121.722
119.404
119.148
118.890
118.631
115.869
77.300
34.909
13.562
f1 (ppm)

7.063 7.057 6.980 6.977 6.974 6.972 6.963 6.960 6.957 6.955 6.620 6.602 2.624 2.620 2.617 2.614 2.607 2.603 2.597 2.588 2.581 2.576 2.571 2.366 2.360 2.351 2.347 2.344 2.341 2.332 2.328 2.325 2.322 2.312 2.307 2.018 2.009 2.006 2.000 1.996 1.990 1.987 1.981 1.978 1.968 1.959 1.651 1.635 1.629 1.618 1.612 1.596



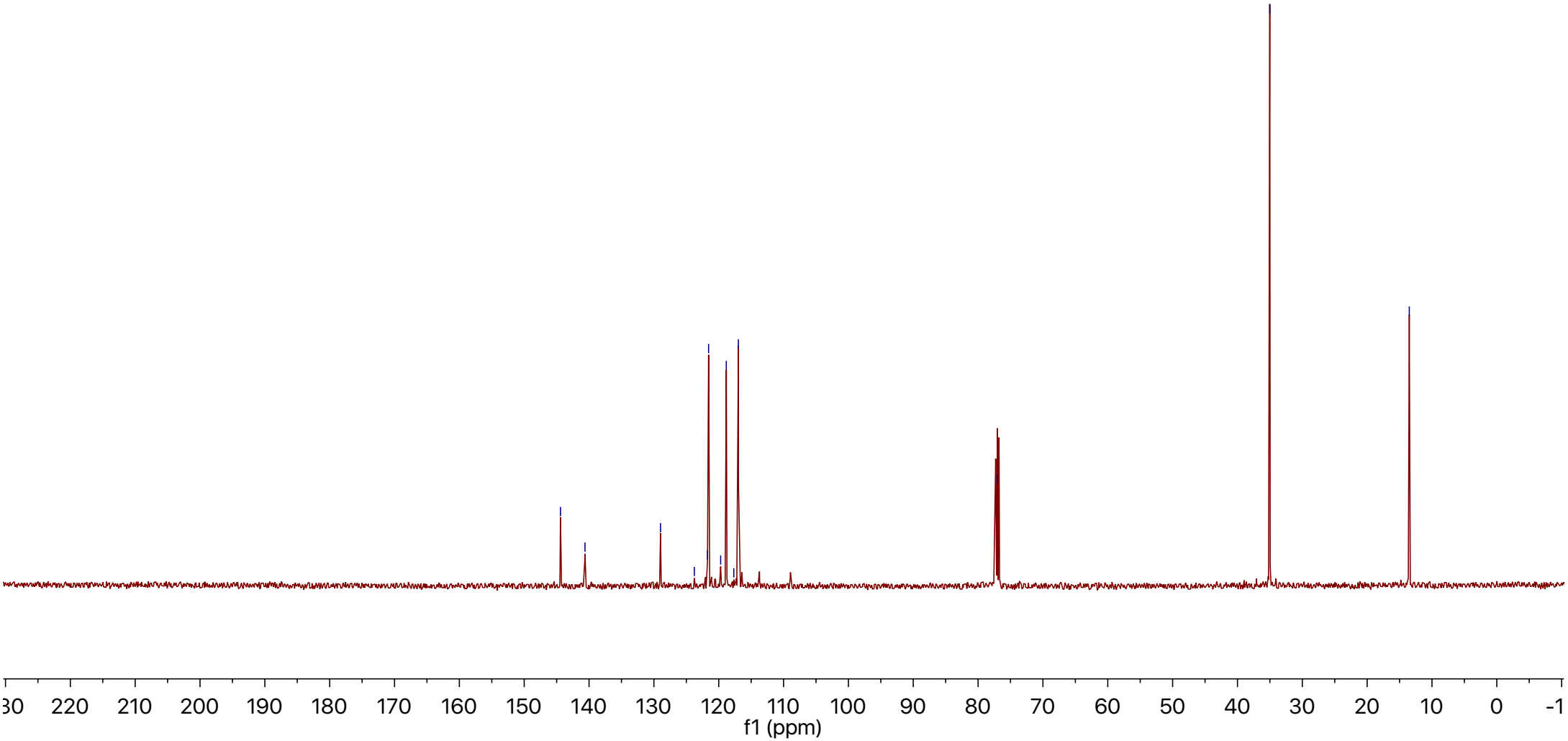
s3e

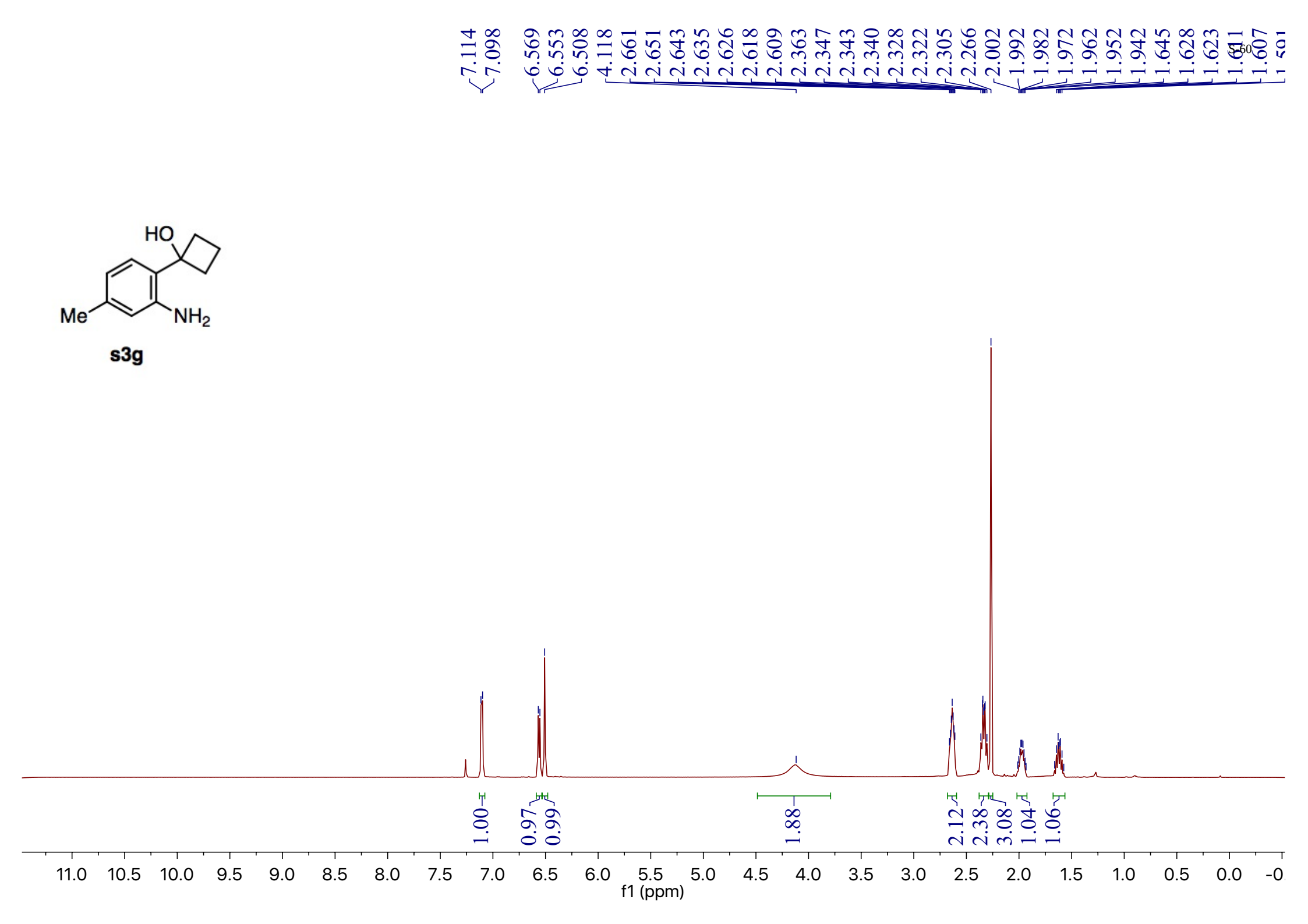




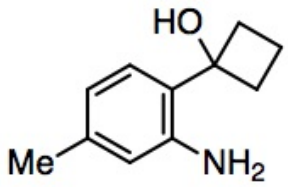
s3e

144.406
140.627
128.978
123.761
121.732
121.564
119.703
118.835
117.674
116.968
77.061
35.012
13.500

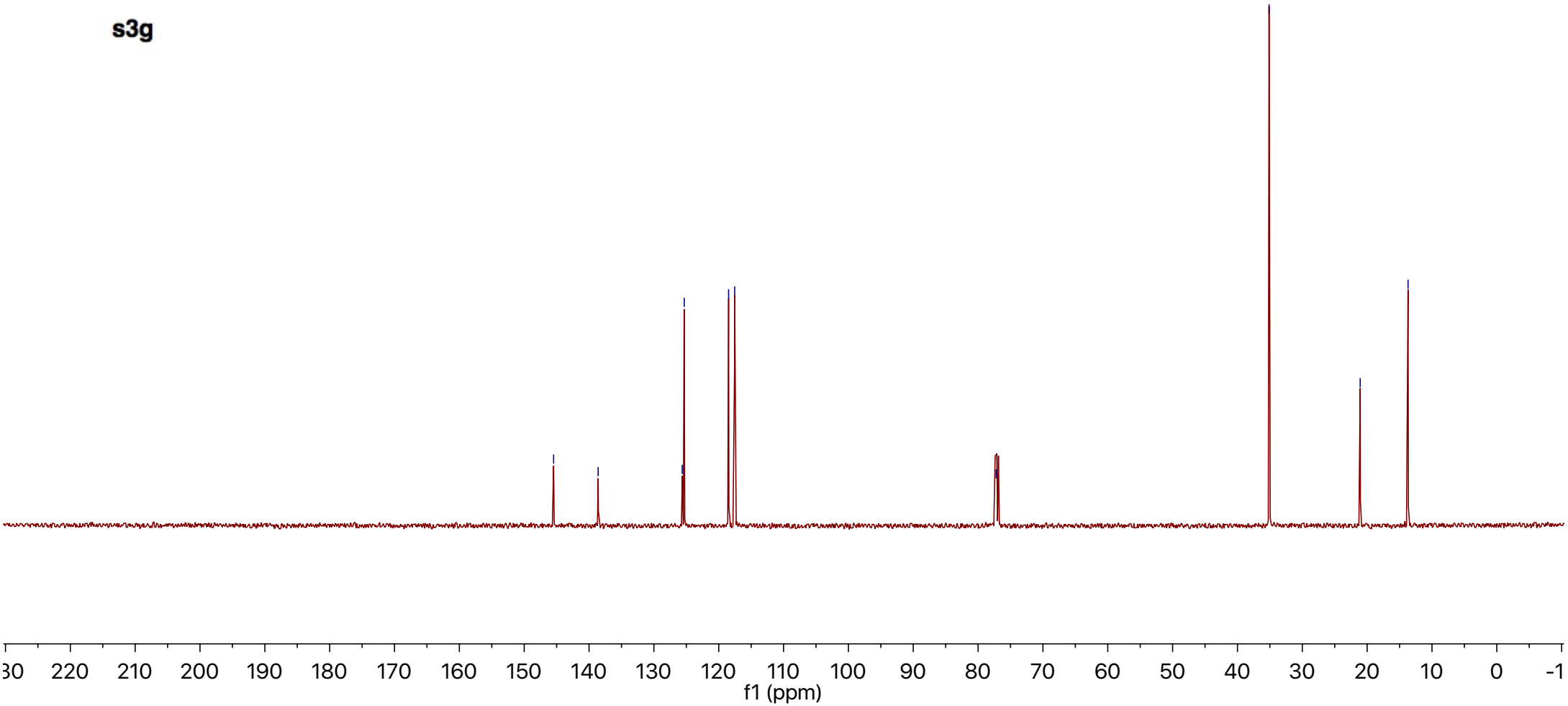


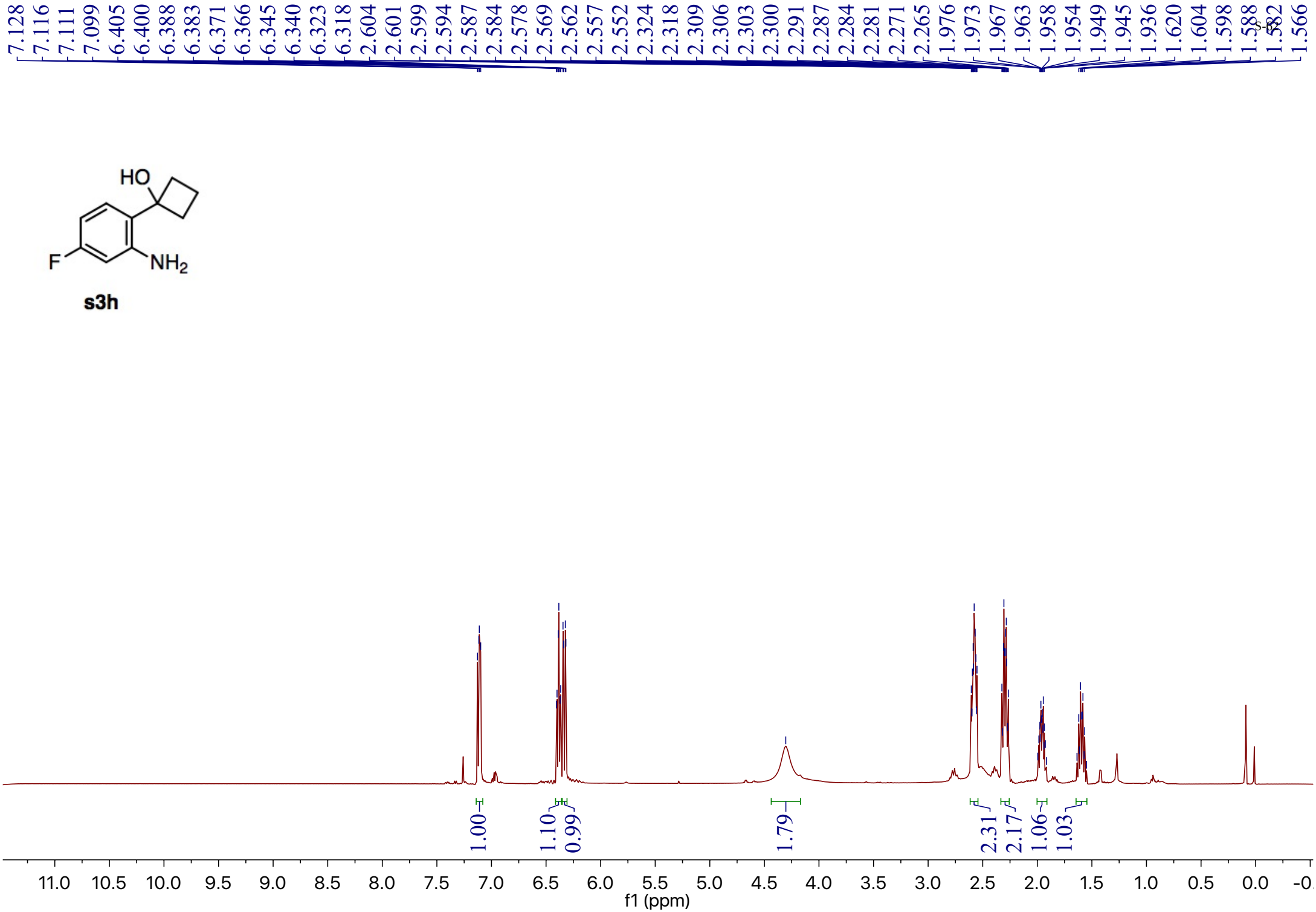

7.114
7.098
6.569
6.553
6.508
4.118
2.661
2.651
2.643
2.635
2.626
2.618
2.609
2.363
2.347
2.343
2.340
2.328
2.322
2.305
2.266
2.002
1.992
1.982
1.972
1.962
1.952
1.942
1.645
1.628
1.623
1.611
1.607
HO
Me
NH2
s3g
1.00
0.97
0.99
1.88
2.12
2.38
3.08
1.04
1.06
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

145.466
138.601
125.627
125.325
118.480
117.537
77.220
35.122
21.072
13.687

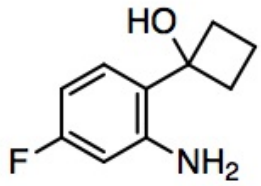


s3g

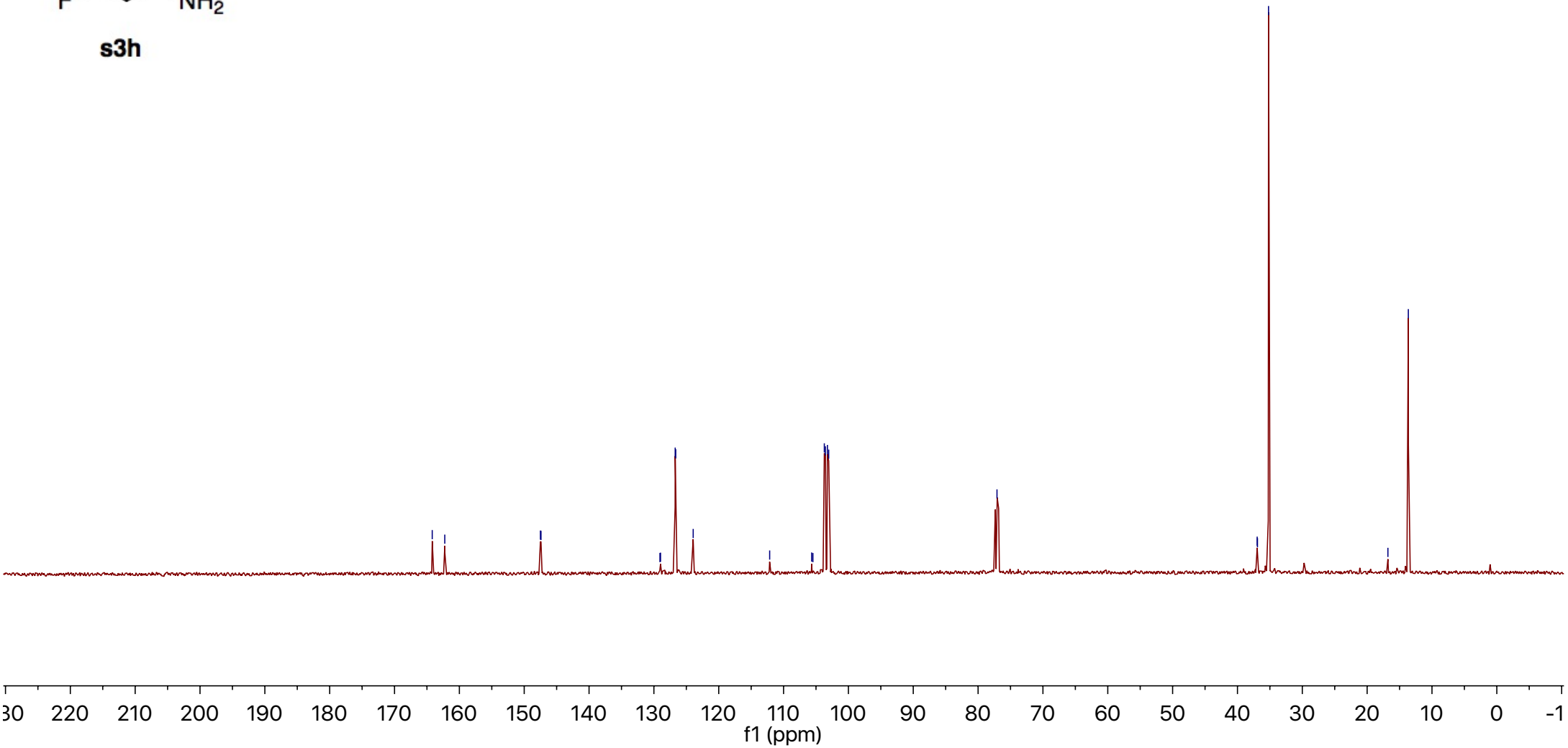


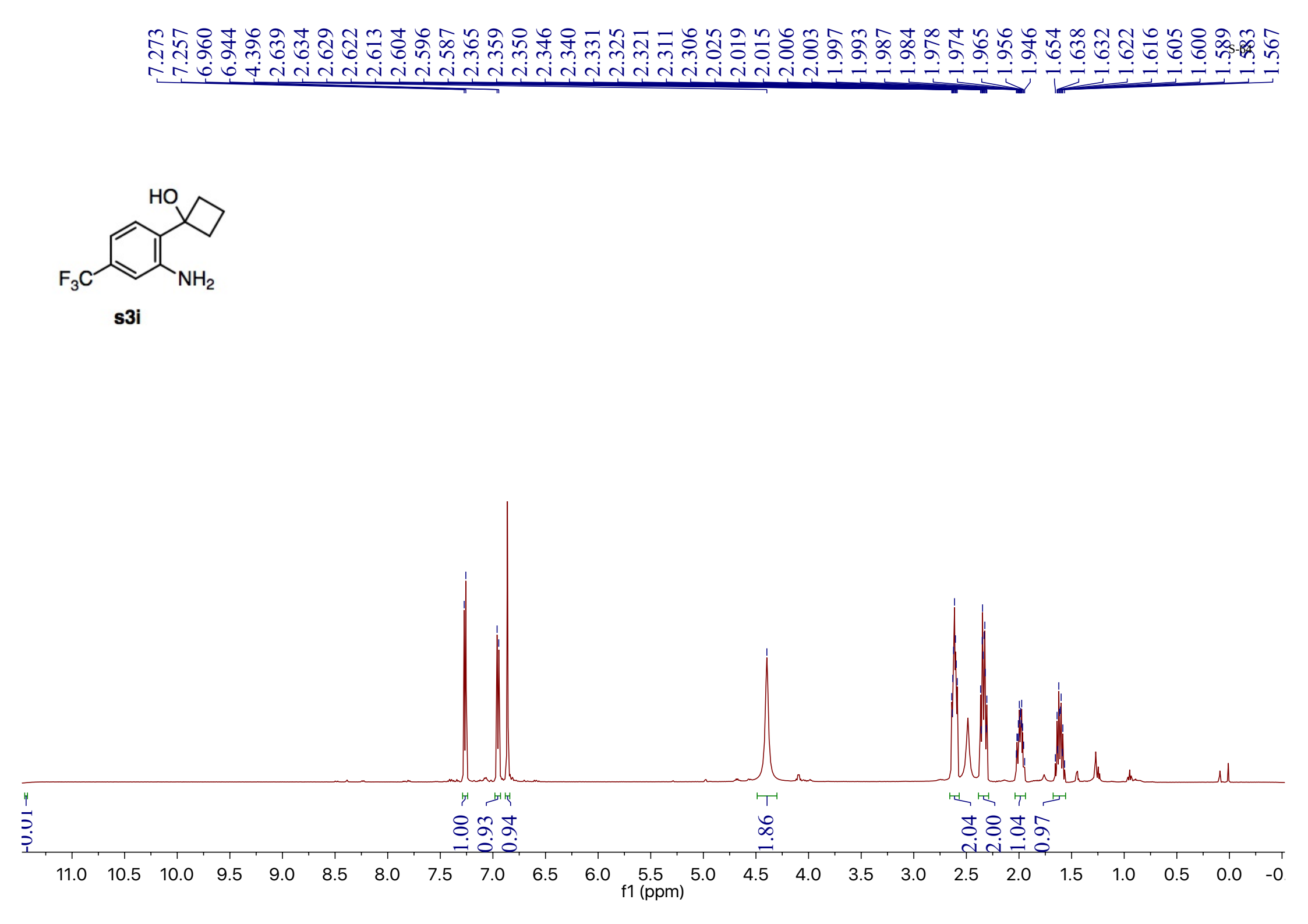

7.128
7.116
7.111
7.099
6.405
6.400
6.388
6.383
6.371
6.366
6.345
6.340
6.323
6.318
2.604
2.601
2.599
2.594
2.587
2.584
2.578
2.569
2.562
2.557
2.552
2.324
2.318
2.309
2.306
2.303
2.300
2.291
2.287
2.284
2.281
2.271
2.265
1.976
1.973
1.967
1.963
1.958
1.954
1.949
1.945
1.936
1.620
1.604
1.598
1.588
1.582
1.566
HO
F
NH2
s3h
1.00
1.10
0.99
1.79
2.31
2.17
1.06
1.03
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

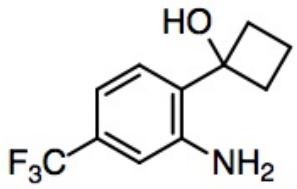
164.185
162.250
147.500
147.413
129.067
128.976
126.715
126.634
123.938
112.144
105.671
105.476
103.716
103.547
103.237
103.042
77.086
36.960
36.916
35.206
16.797
13.646



s3h



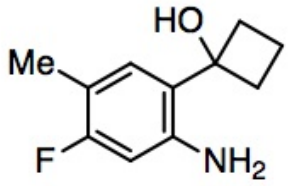

7.273
7.257
6.960
6.944
4.396
2.639
2.634
2.629
2.622
2.613
2.604
2.596
2.587
2.365
2.359
2.350
2.346
2.340
2.331
2.325
2.321
2.311
2.306
2.025
2.019
2.015
2.006
2.003
1.997
1.993
1.987
1.984
1.978
1.974
1.965
1.956
1.946
1.654
1.638
1.632
1.622
1.616
1.605
1.600
1.589
1.583
1.567
HO
F3C
NH2
s3i
1.00
0.93
0.94
1.86
2.04
2.00
1.04
0.97
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


HO
F3C
NH2

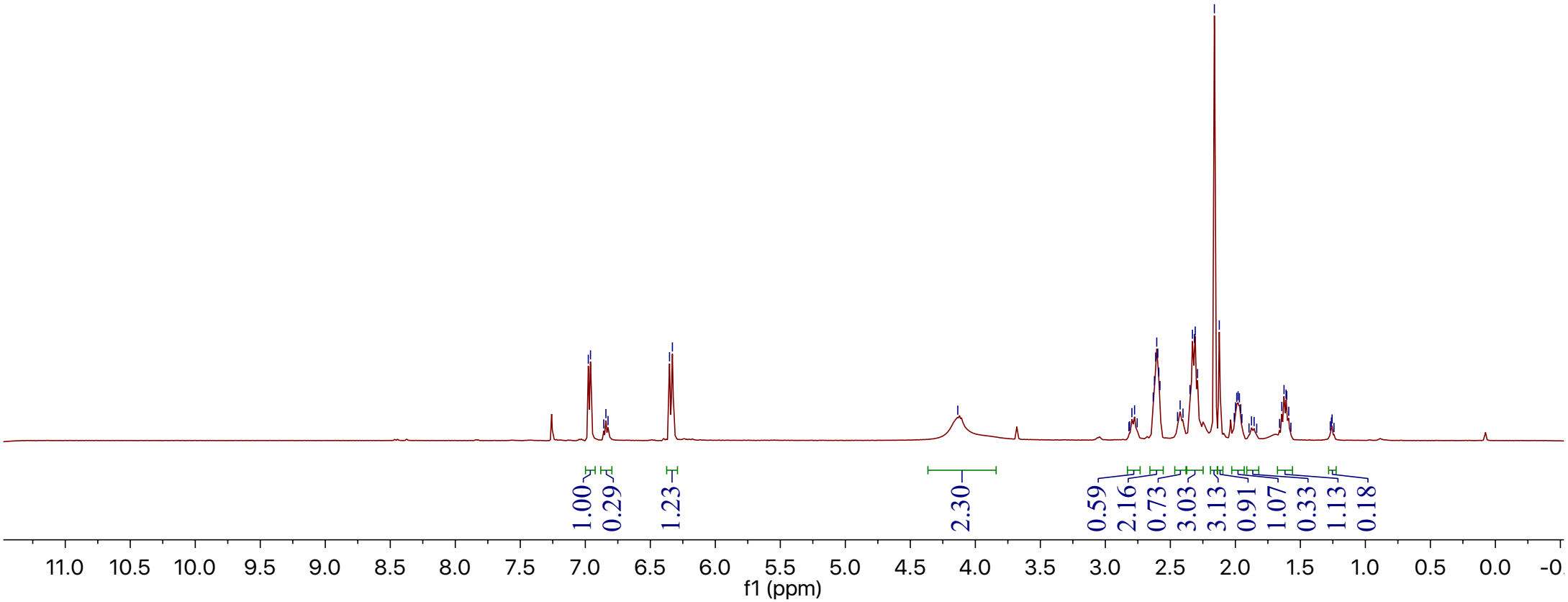
s3i

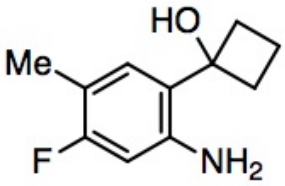
145.991
131.248
131.011
130.739
130.484
127.411
125.698
125.224
123.062
120.898
114.072
114.040
114.007
113.975
112.954
112.920
112.889
112.860
77.147
34.998
13.524
f1 (ppm)

6.977 6.960 6.858 6.842 6.825 6.352 6.330 4.135 2.819 2.814 2.796 2.775 2.755 2.632 2.622 2.613 2.605 2.596 2.589 2.580 2.445 2.425 2.403 2.349 2.330 2.315 2.309 2.291 2.161 2.124 2.009 1.999 1.989 1.979 1.969 1.959 1.950 1.895 1.876 1.856 1.836 1.660 1.643 1.626 1.610 1.605 1.590 1.573 1.270 1.261 1.256 1.242



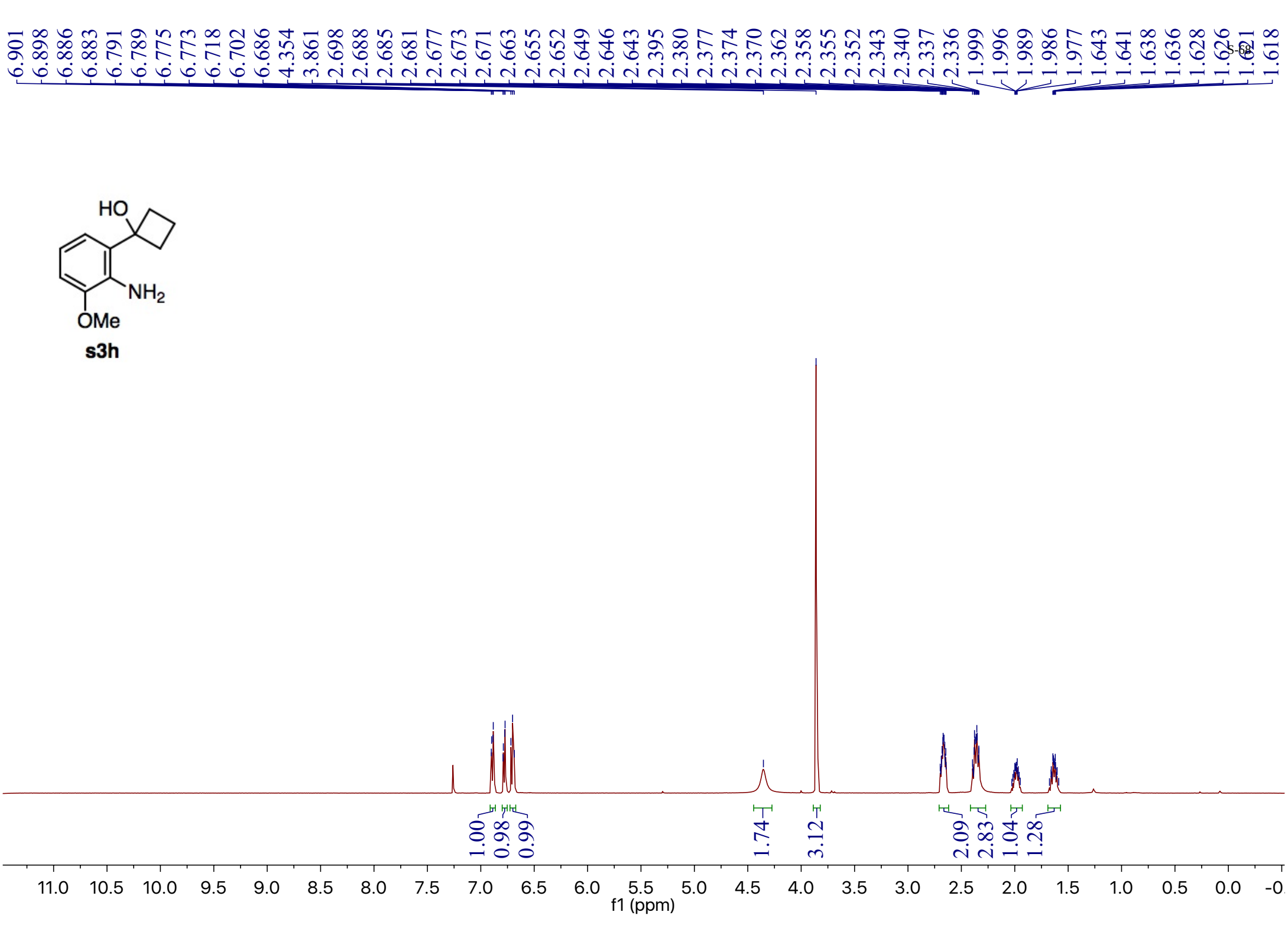
s3j




HO
Me
F
NH2

s3j

162.151
160.221
145.004
144.924
130.355
130.290
128.168
128.113
124.017
112.690
112.552
111.790
103.489
103.289
77.111
37.081
37.036
35.268
16.958
13.766
13.689
f1 (ppm)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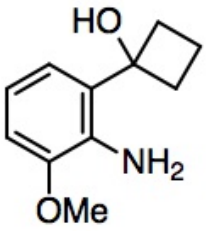
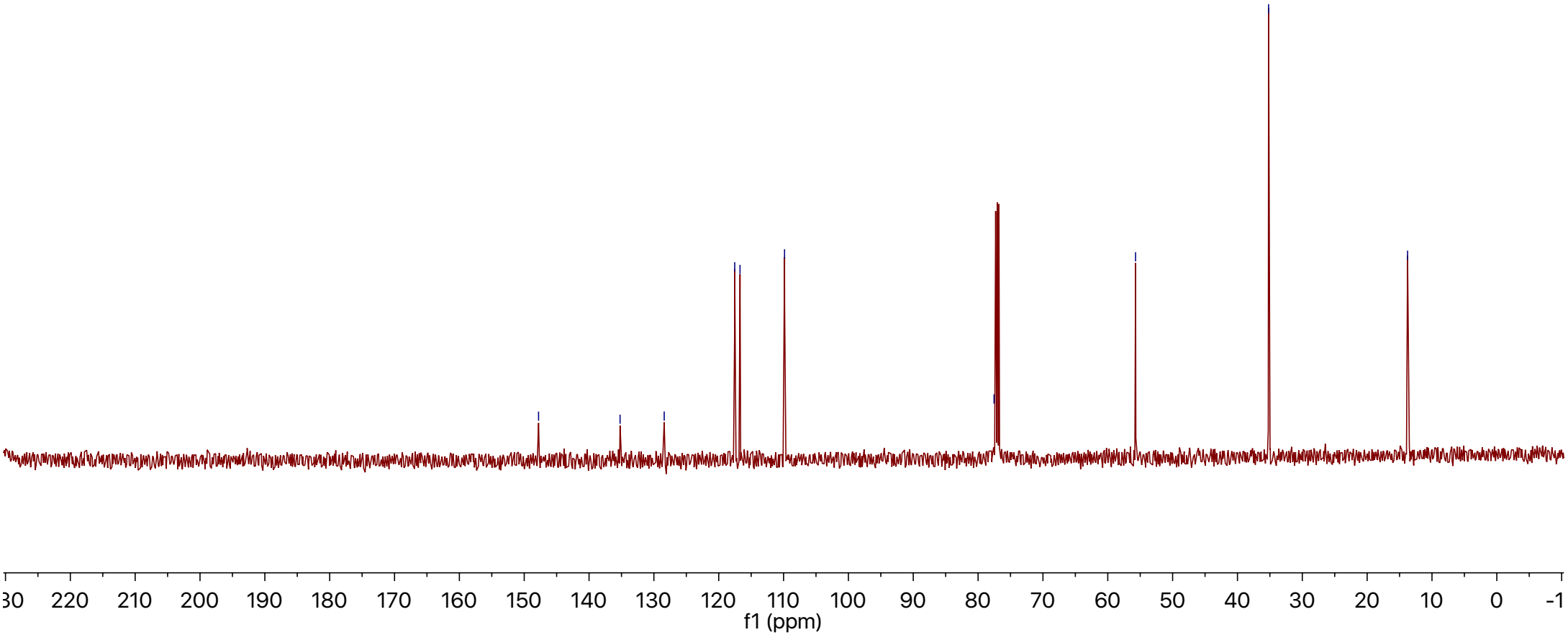
6.898
6.886
6.883
6.791
6.789
6.775
6.773
6.718
6.702
6.686
4.354
3.861
2.698
2.688
2.685
2.681
2.677
2.673
2.671
2.663
2.655
2.652
2.649
2.646
2.643
2.395
2.380
2.377
2.374
2.370
2.362
2.358
2.355
2.352
2.343
2.340
2.337
2.336
1.999
1.996
1.989
1.986
1.977
1.643
1.641
1.638
1.636
1.628
1.626
1.621
1.618
HO
NH2
OMe
s3h
1.00
0.98
0.99
1.74
3.12
2.09
2.83
1.04
1.28
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

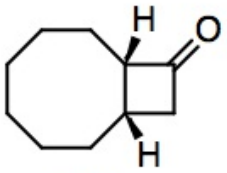
147.787
135.217
128.408
117.533
116.718
109.850
77.542
55.715
35.195
13.762



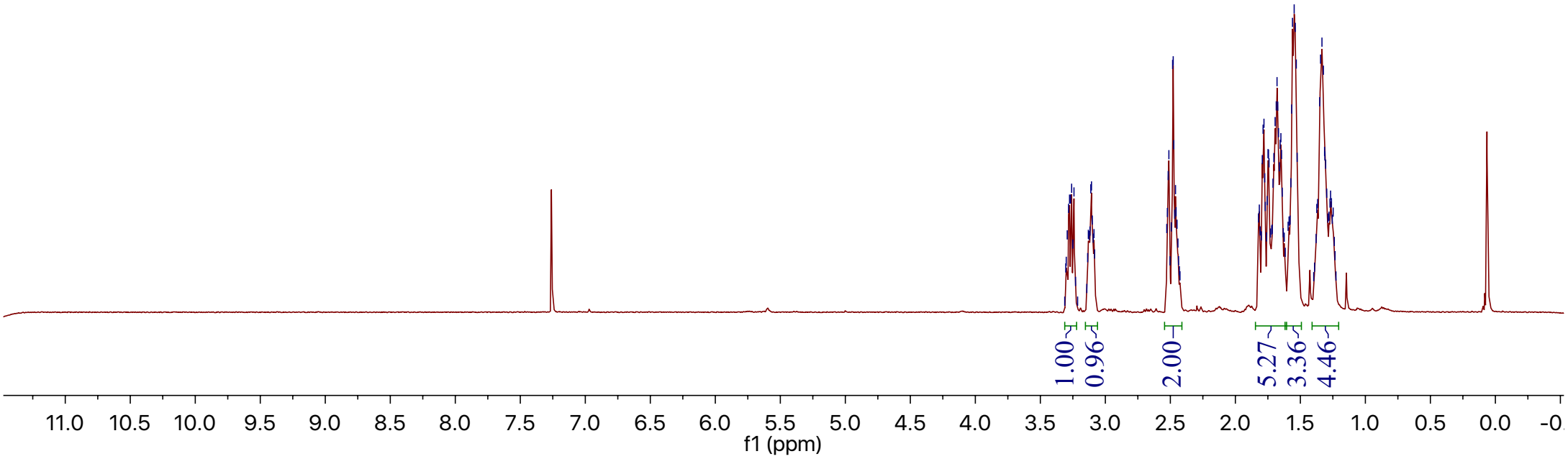
s3h



3.275 3.267 3.259 3.241 3.112 3.107 2.517 2.511 2.483 2.478 2.473 2.460 1.793 1.787 1.780 1.774 1.770 1.755 1.749 1.745 1.741 1.711 1.704 1.694 1.686 1.679 1.674 1.668 1.661 1.655 1.650 1.645 1.640 1.573 1.567 1.560 1.548 1.539 1.531 1.525 1.367 1.351 1.345 1.334 1.323 1.314 1.312 1.305 1.297 1.272 1.268 1.261

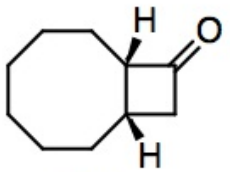


s7

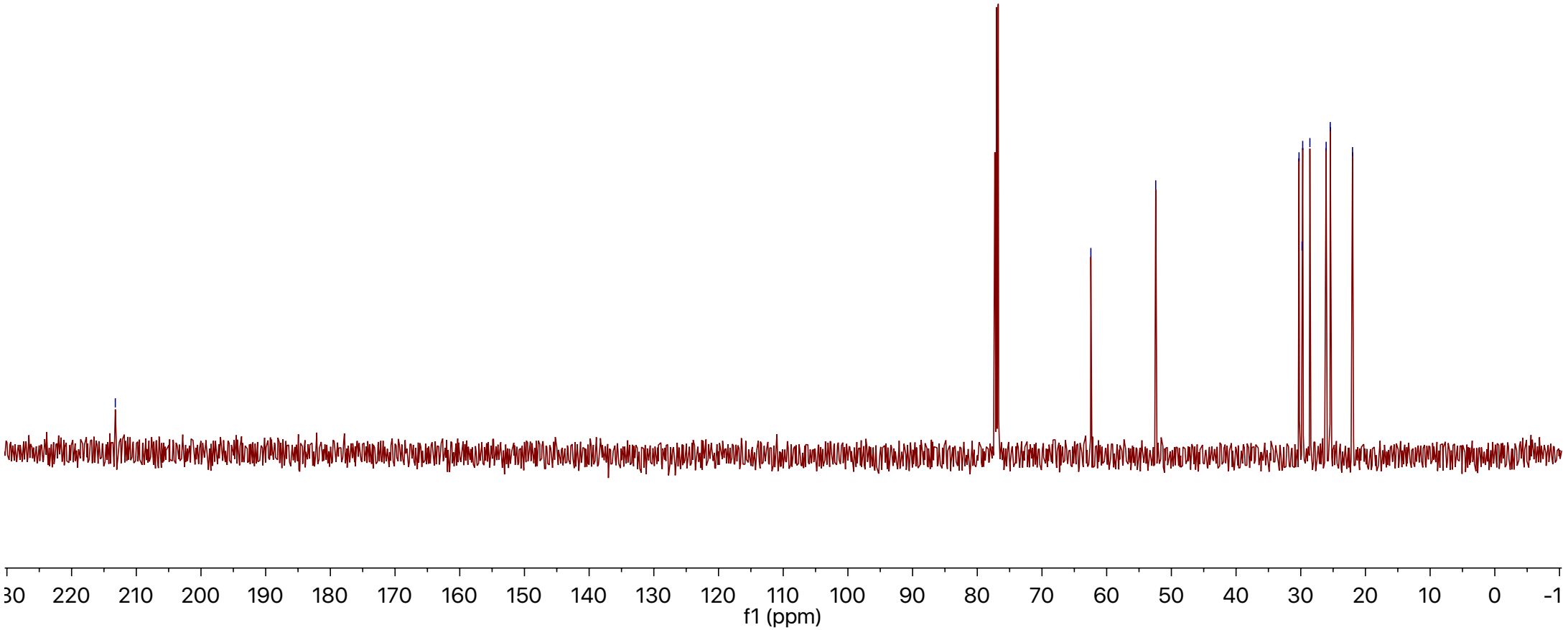


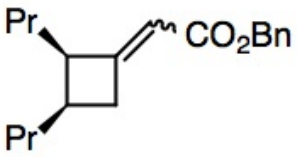
213.242

62.443
52.417
30.268
29.804
29.698
28.587
26.074
25.442
21.996

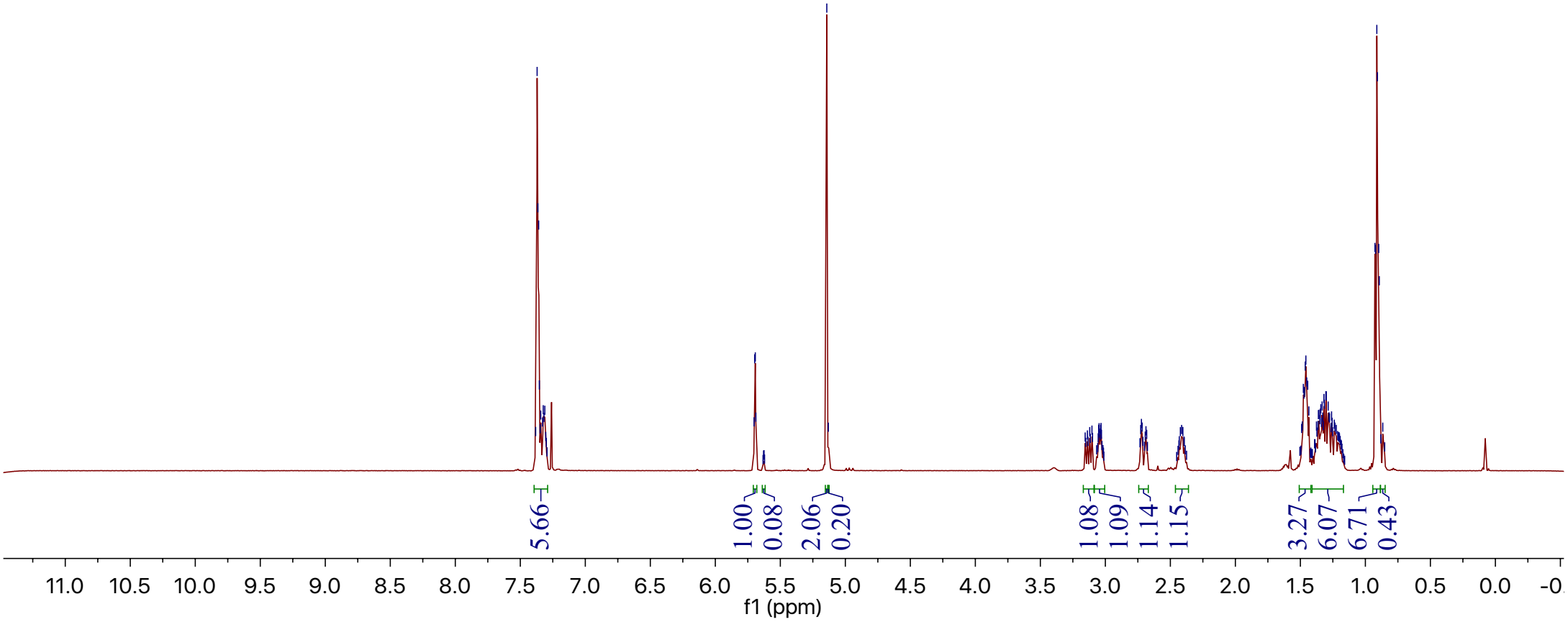


s7

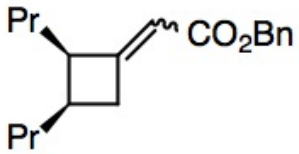



Pr
CO2Bn
Pr

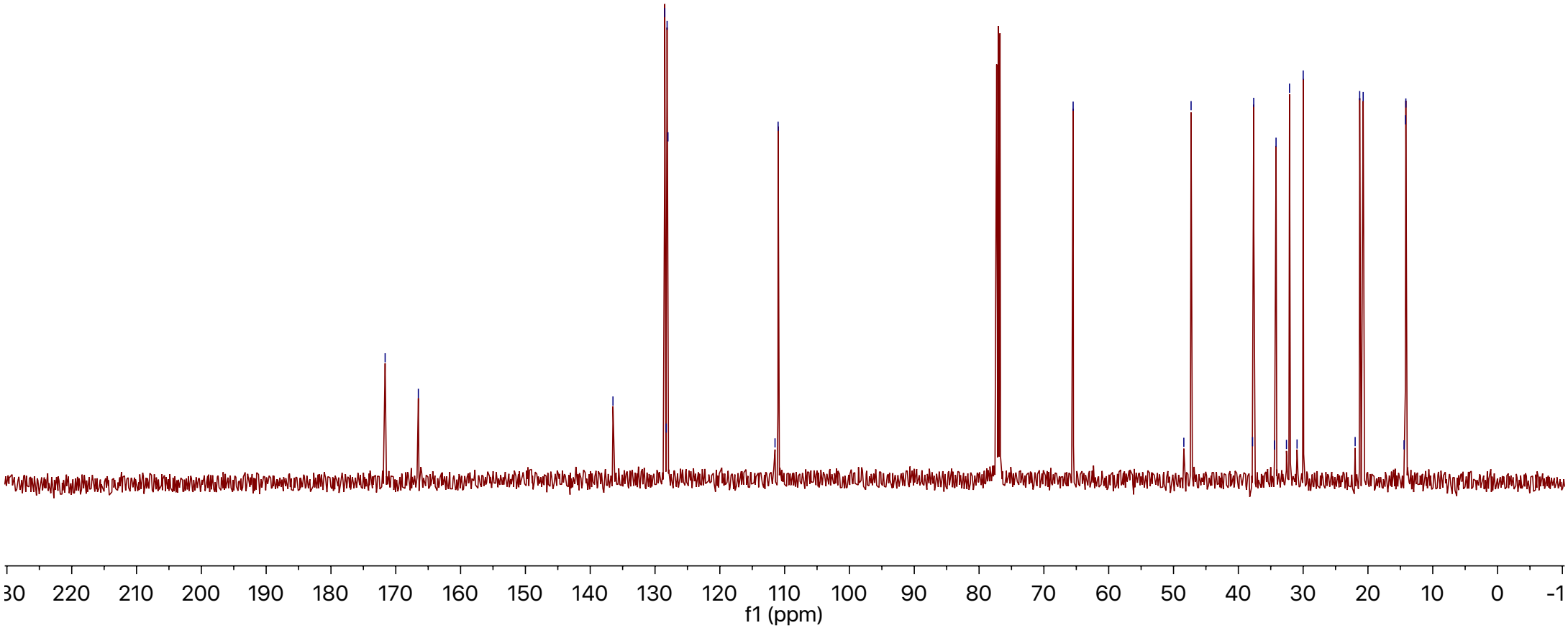
s8


7.371
7.365
7.359
7.354
7.343
7.329
7.324
7.318
7.311
5.702
5.697
5.692
5.688
5.142
2.722
2.717
1.485
1.477
1.472
1.468
1.463
1.458
1.451
1.444
1.435
1.376
1.364
1.361
1.357
1.350
1.347
1.343
1.338
1.333
1.328
1.323
1.319
1.315
1.304
1.301
1.286
1.279
1.276
1.260
1.256
1.239
0.926
0.921
0.912
0.907
0.897
0.893
5.66
1.00
0.08
2.06
0.20
1.08
1.09
1.14
1.15
3.27
6.07
6.71
0.43
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

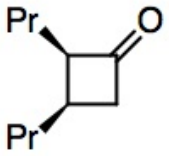
171.643
166.519
136.491
128.496
128.270
128.137
128.005
111.486
111.010
65.487
48.408
47.288
37.803
37.623
34.179
32.101
30.939
29.990
21.976
21.272
20.737
14.212



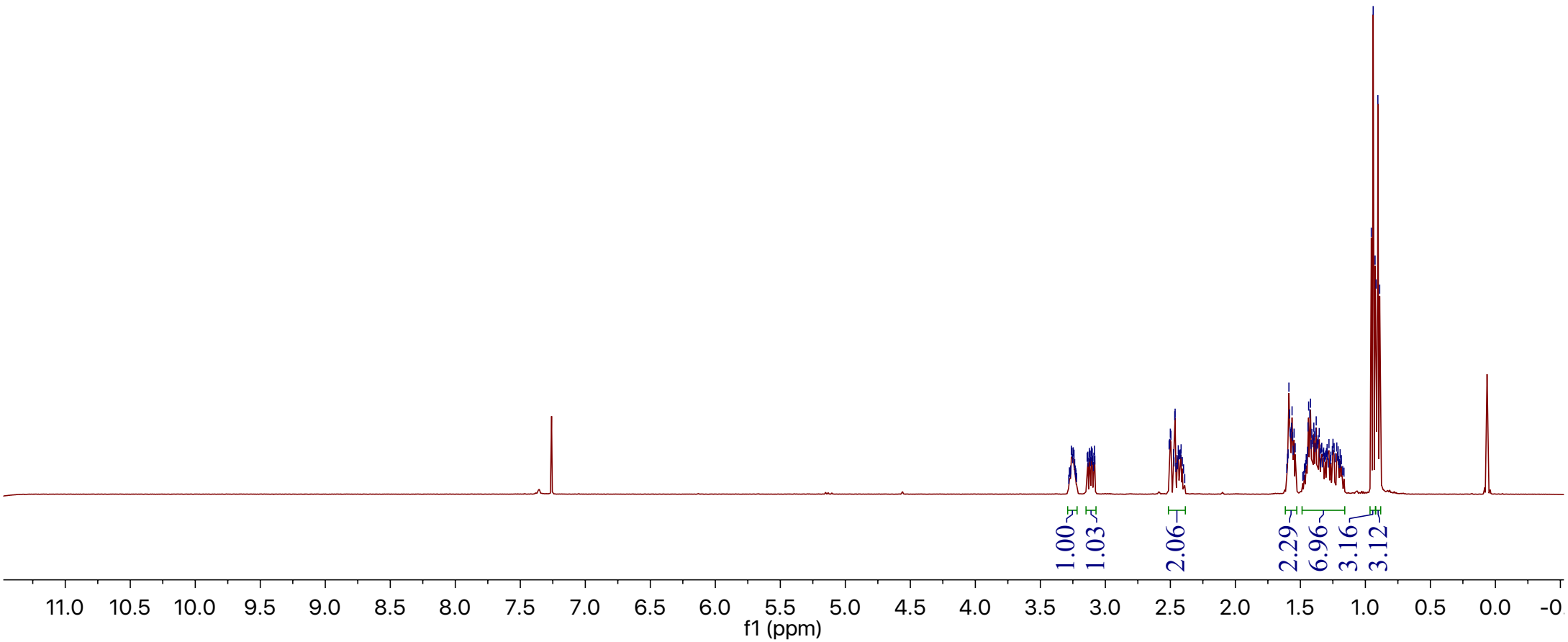
s8



3.262
3.083
2.509
2.505
2.500
2.496
2.466
2.463
2.439
2.417
1.588
1.584
1.579
1.574
1.568
1.564
1.559
1.556
1.548
1.540
1.441
1.436
1.427
1.422
1.418
1.412
1.406
1.403
1.396
1.393
1.387
1.381
1.378
1.372
1.368
1.364
1.355
1.340
1.335
1.294
1.280
1.254
1.249
1.240
1.220
1.210
0.954
0.940
0.925
0.918
0.904
0.890

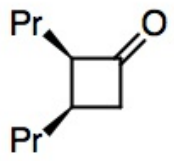


s9

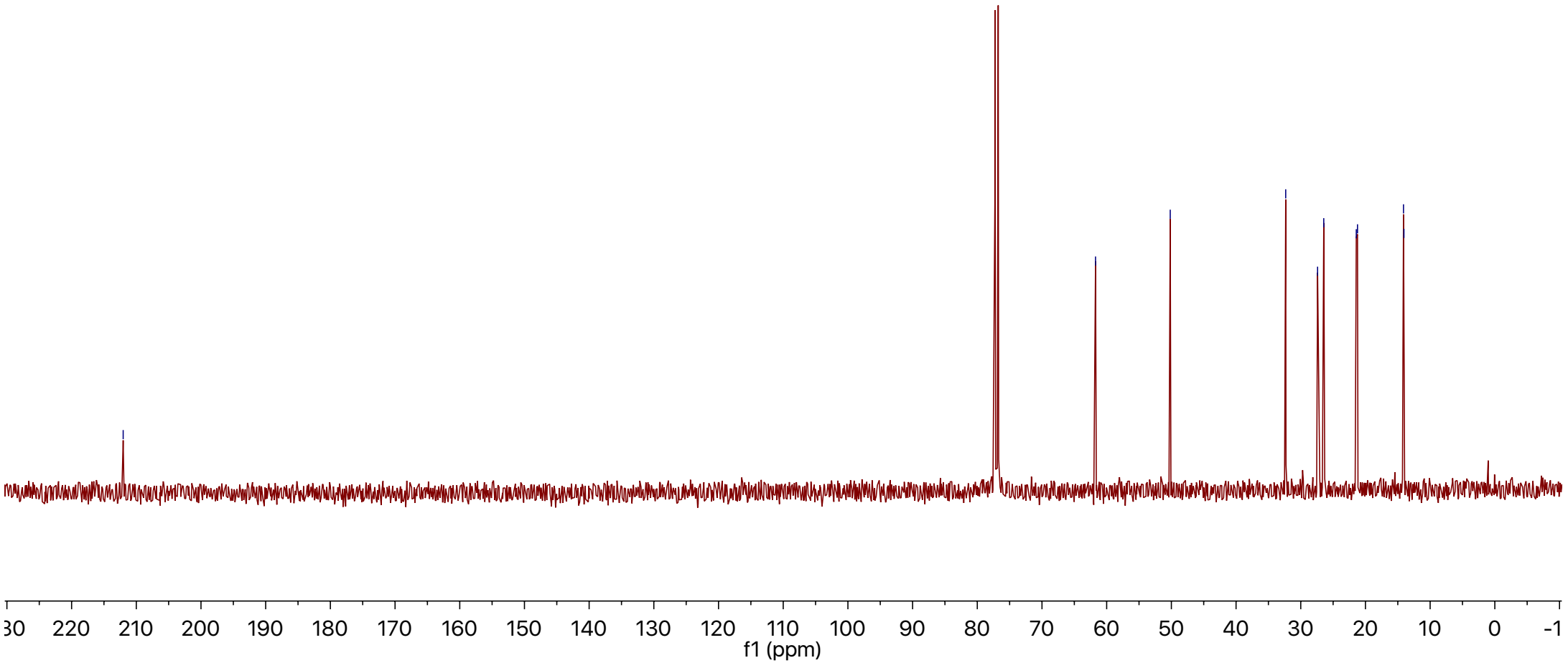


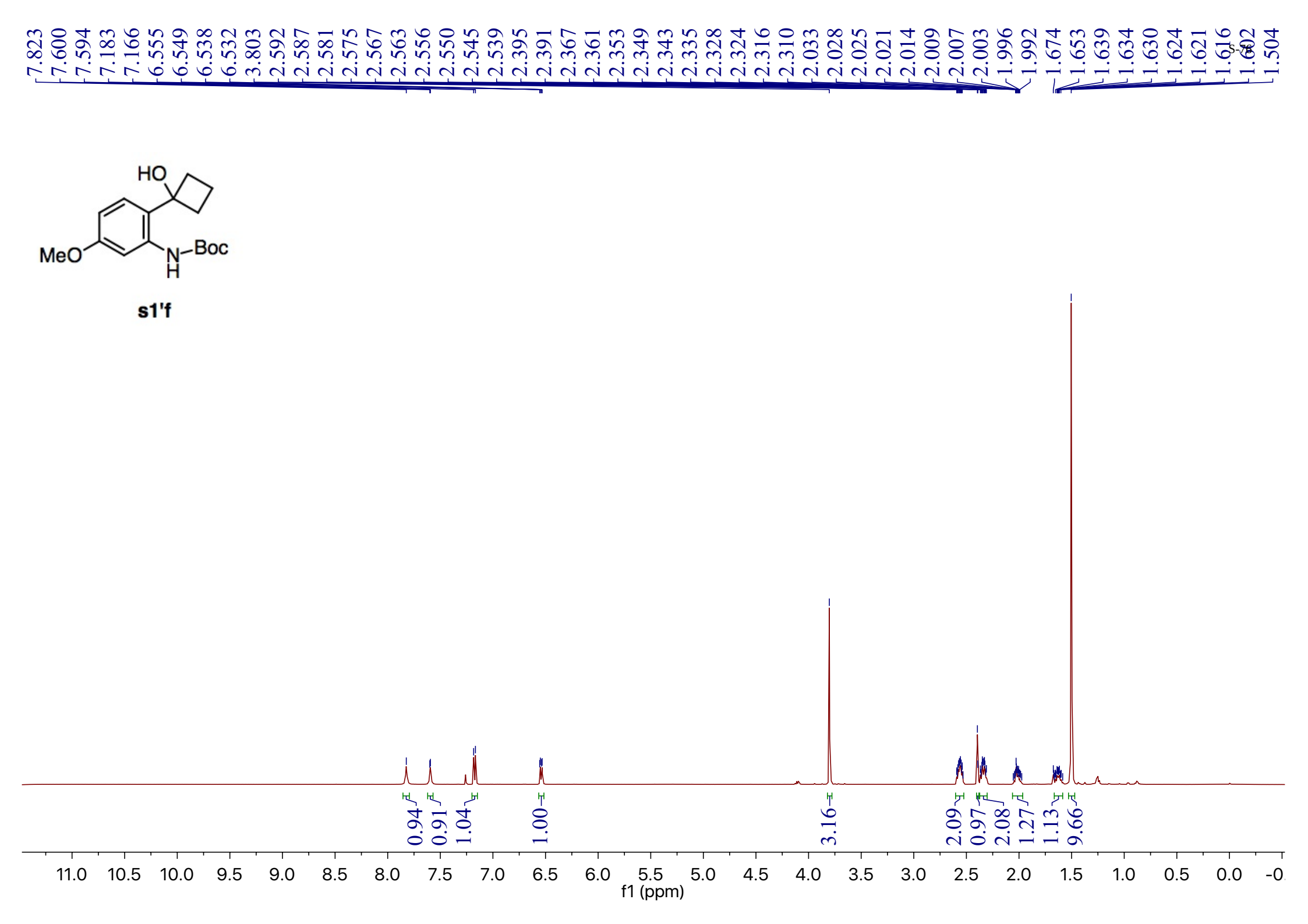
212.027

61.723
50.175
32.326
27.398
26.444
21.417
21.225
14.117
14.049

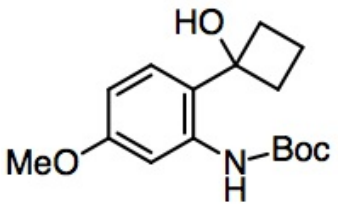


s9

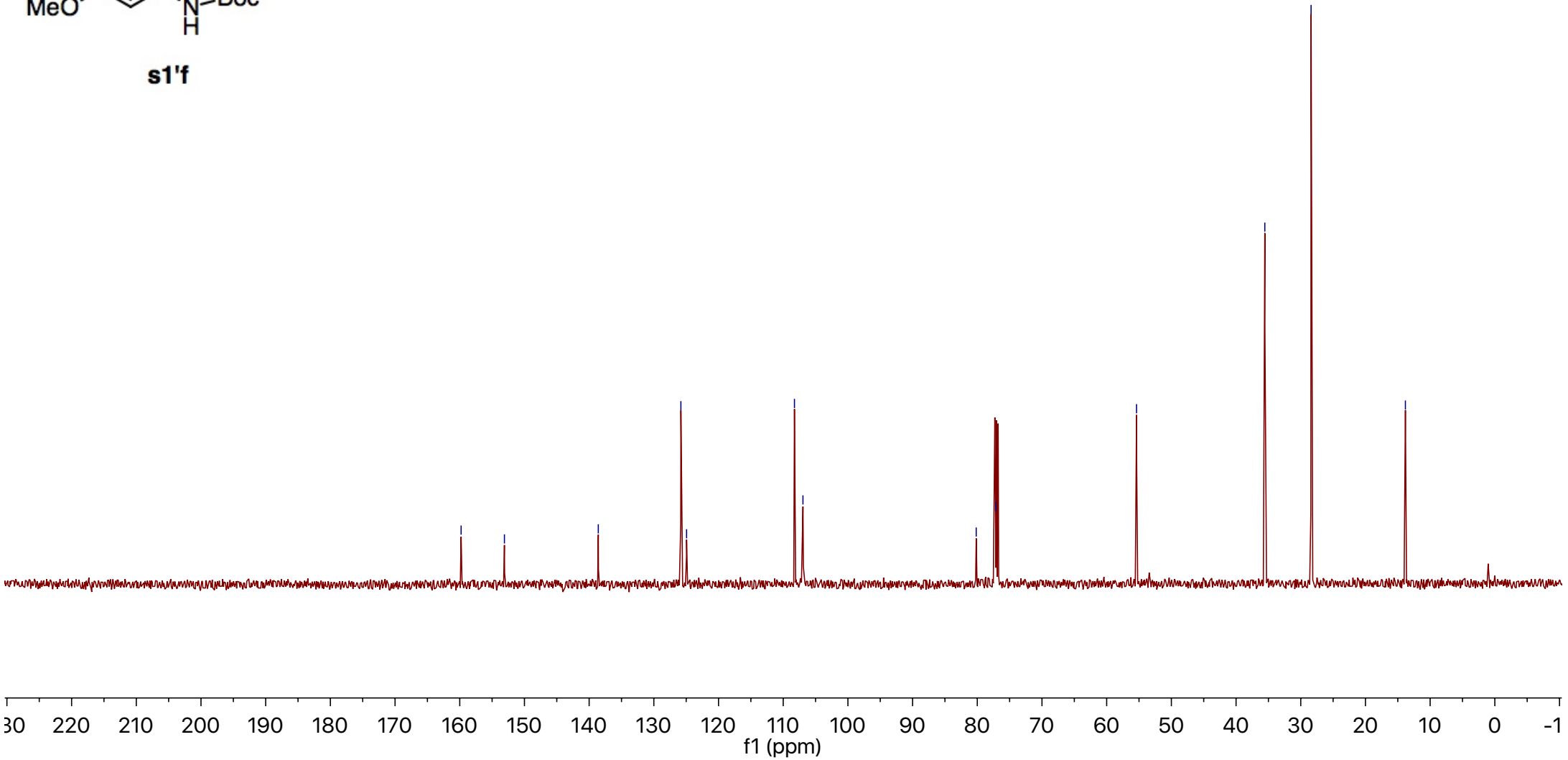


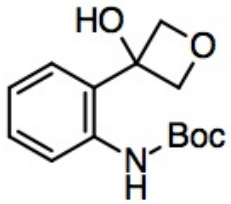

7.823
7.600
7.594
7.183
7.166
6.555
6.549
6.538
6.532
3.803
2.592
2.587
2.581
2.575
2.567
2.563
2.556
2.550
2.545
2.539
2.395
2.391
2.367
2.361
2.353
2.349
2.343
2.335
2.328
2.324
2.316
2.310
2.033
2.028
2.025
2.021
2.014
2.009
2.007
2.003
1.996
1.992
1.674
1.653
1.639
1.634
1.630
1.624
1.621
1.616
1.602
1.504
HO
MeO
N
H
Boc
s1'f
0.94
0.91
1.04
1.00
3.16
2.09
0.97
2.08
1.27
1.13
9.66
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

159.789
153.095
138.586
125.818
124.938
108.262
106.949
80.167
77.172
55.383
35.555
28.403
13.824



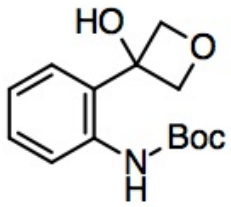
s1'f




HO
O
Boc
N
H

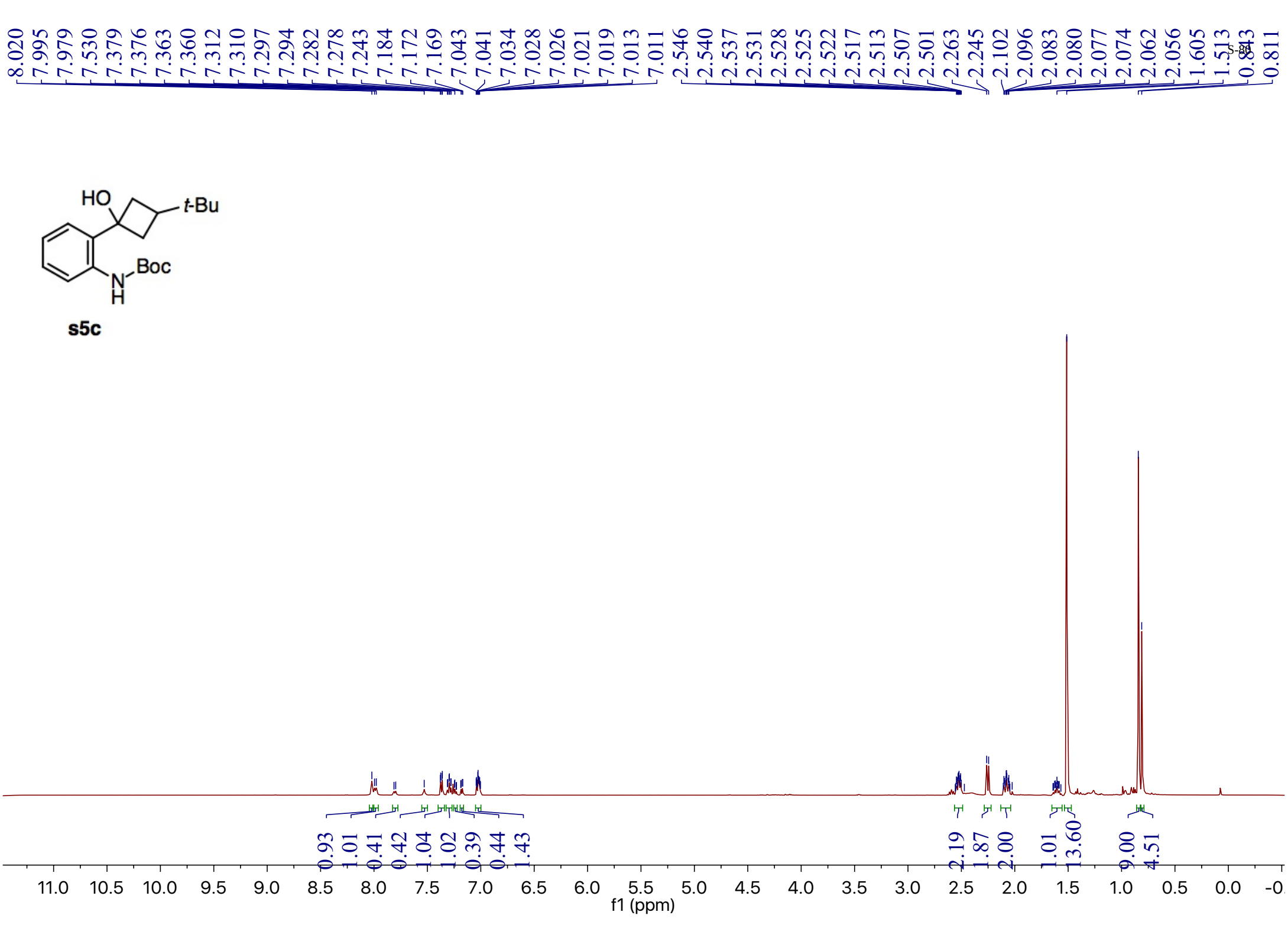
s5b

7.551
7.535
7.286
7.282
7.272
7.269
7.266
7.260
7.256
7.252
7.175
7.142
7.138
7.127
7.123
7.116
7.114
7.102
7.100
7.087
7.084
4.960
4.946
4.746
4.732
1.472
1.00
1.10
0.97
2.13
2.07
3.05
9.48
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


HO
O
Boc
N
H

s5b

154.06
135.57
133.08
129.17
126.12
124.65
124.08
82.82
81.07
75.86
28.31
f1 (ppm)


8.020
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7.979
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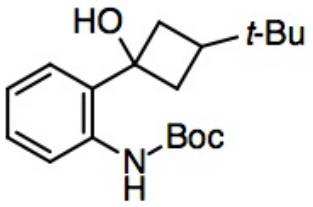
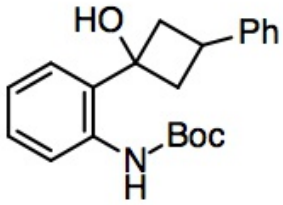
7.379
7.376
7.363
7.360
7.312
7.310
7.297
7.294
7.282
7.278
7.243
7.184
7.172
7.169
7.043
7.041
7.034
7.028
7.026
7.021
7.019
7.013
7.011
2.546
2.540
2.537
2.531
2.528
2.525
2.522
2.517
2.513
2.507
2.501
2.263
2.245
2.102
2.096
2.083
2.080
2.077
2.074
2.062
2.056
1.605
1.513
0.843
0.811
HO
t-Bu
Boc
N
H
s5c
0.93
1.01
0.41
0.42
1.04
1.02
0.39
0.44
1.43
2.19
1.87
2.00
1.01
13.60
9.00
4.51
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


HO
t-Bu
Boc
N
H

s5c

153.465
153.195
138.005
136.617
134.962
131.763
128.589
128.422
125.249
124.766
123.135
122.353
122.266
121.865
80.247
80.085
74.104
71.750
40.443
36.807
35.515
30.937
30.775
28.426
26.598
26.303
f1 (ppm)

8.012 7.498 7.488 7.485 7.473 7.470 7.351 7.347 7.343 7.331 7.317 7.314 7.302 7.288 7.284 7.280 7.270 7.237 7.234 7.223 7.219 7.212 7.209 7.205 7.203 7.196 7.112 7.100 7.097 7.085 7.082 3.119 3.113 3.103 3.101 3.098 3.094 3.085 3.079 3.017 3.002 2.847 2.806 2.662 2.656 2.562 2.557 2.542 2.537 2.518 1.529 1.523



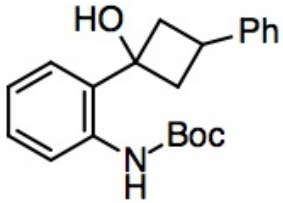
s5d

1.30 0.45 0.38 0.43 1.01 5.81 2.57 1.36 0.40 1.82 1.31 1.66 0.86 1.82 3.24 9.00

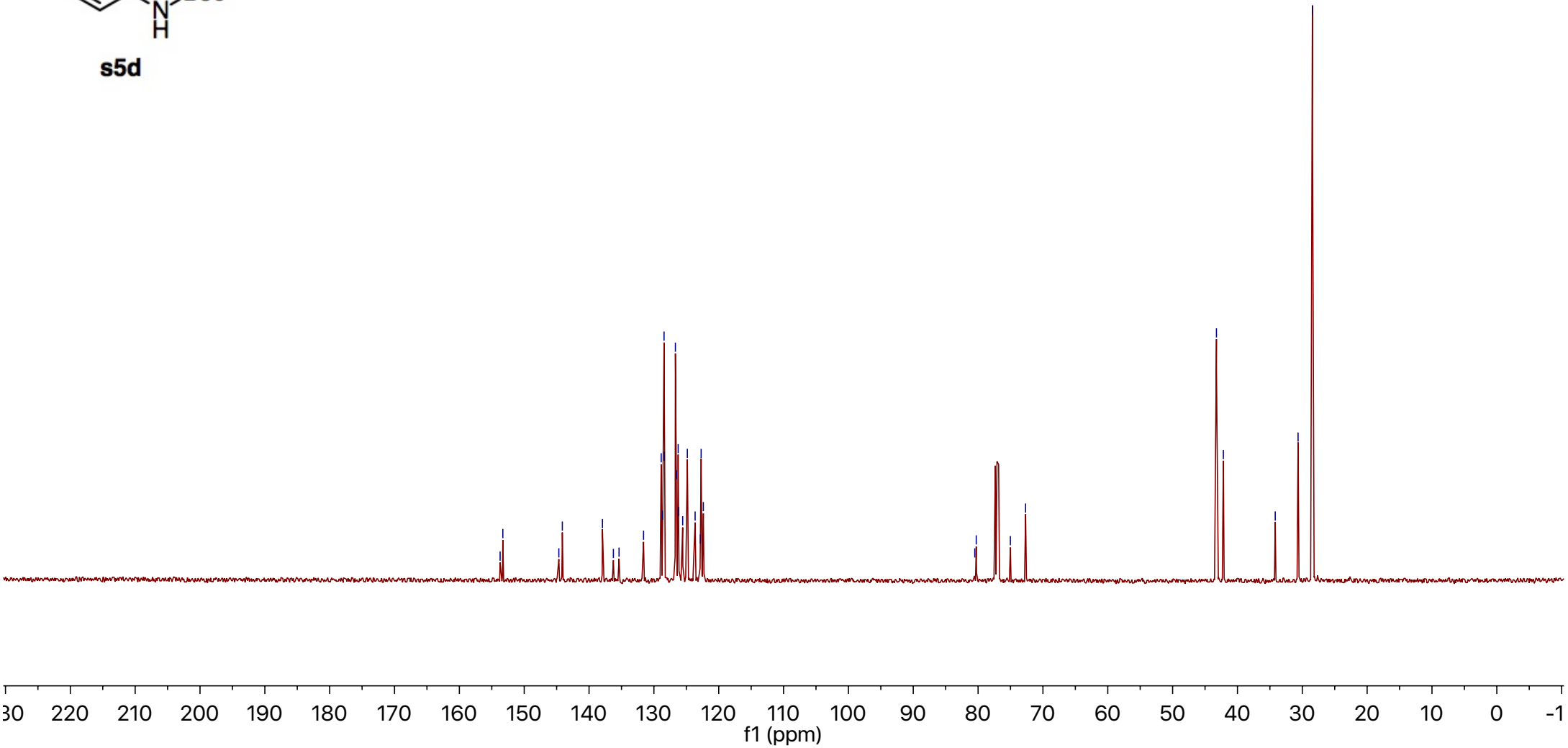
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0

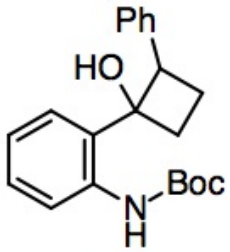
f1 (ppm)

153.716
153.295
144.659
144.120
137.935
136.247
135.376
131.595
128.873
128.644
128.432
128.385
126.684
126.518
126.255
126.163
125.560
124.843
123.643
122.835
122.713
122.372
80.509
80.284
75.024
72.676
43.241
42.175
34.174
30.652
28.442



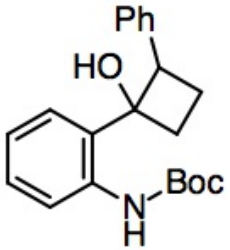
s5d




Ph
HO
Boc
N
H

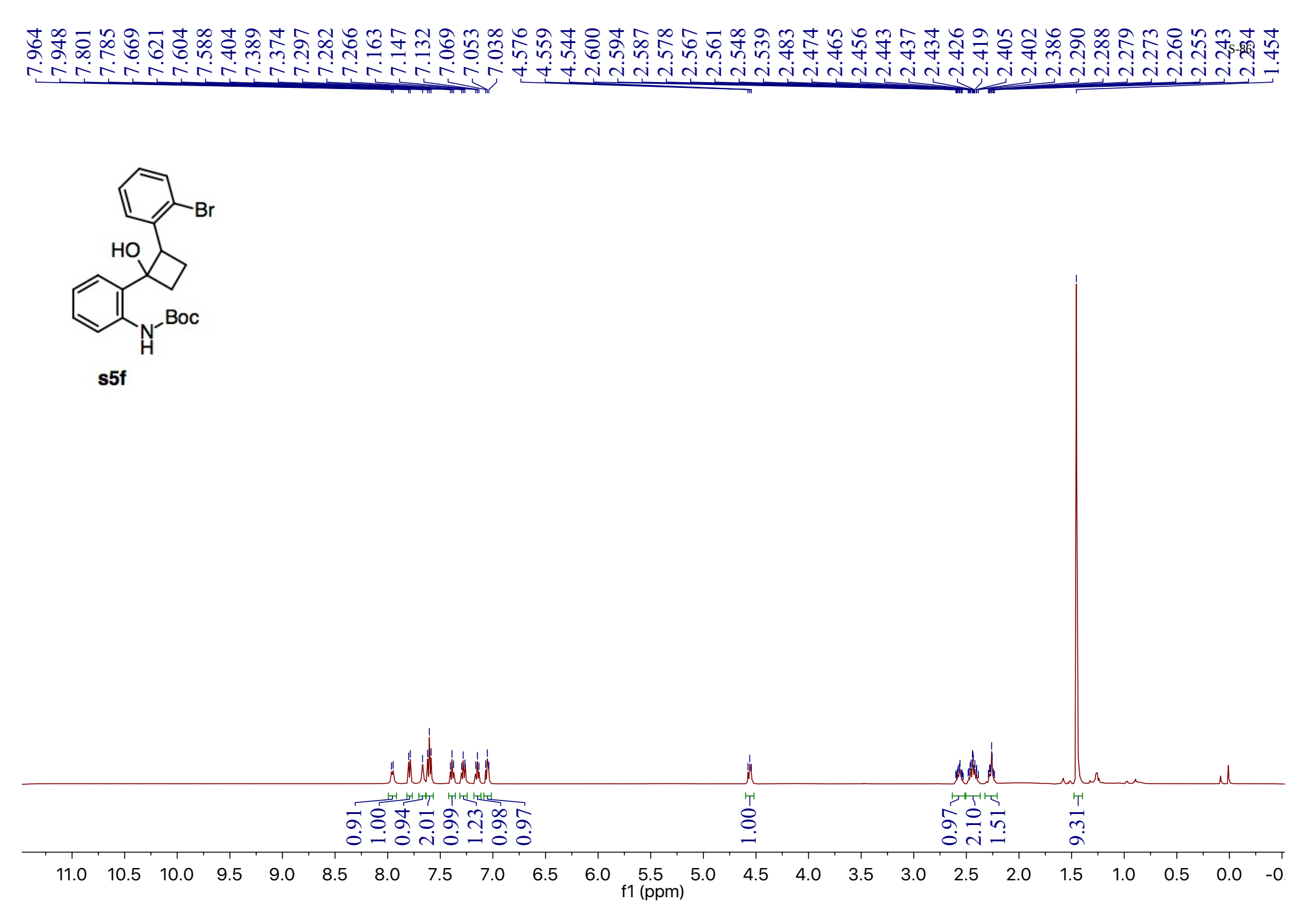
s5e

7.996
7.980
7.932
7.468
7.465
7.462
7.452
7.449
7.446
7.412
7.397
7.381
7.312
7.310
7.306
7.302
7.295
7.291
7.288
7.286
7.282
7.280
7.278
7.274
7.271
7.070
7.067
7.055
7.052
7.039
7.037
4.180
4.163
2.529
2.526
2.523
2.517
2.513
2.507
2.505
2.499
2.494
2.486
2.474
2.468
2.272
2.269
2.264
2.246
2.075
2.073
1.515
0.96
0.94
3.08
2.04
2.29
1.10
1.01
3.13
1.00
1.00
9.21
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


Ph
HO
Boc
N
H

s5e

153.082
138.412
137.509
133.252
128.784
128.753
128.533
127.168
125.198
122.502
121.758
80.206
79.984
47.795
33.626
28.431
21.695
f1 (ppm)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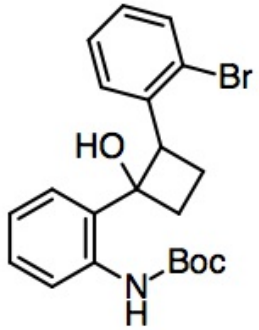
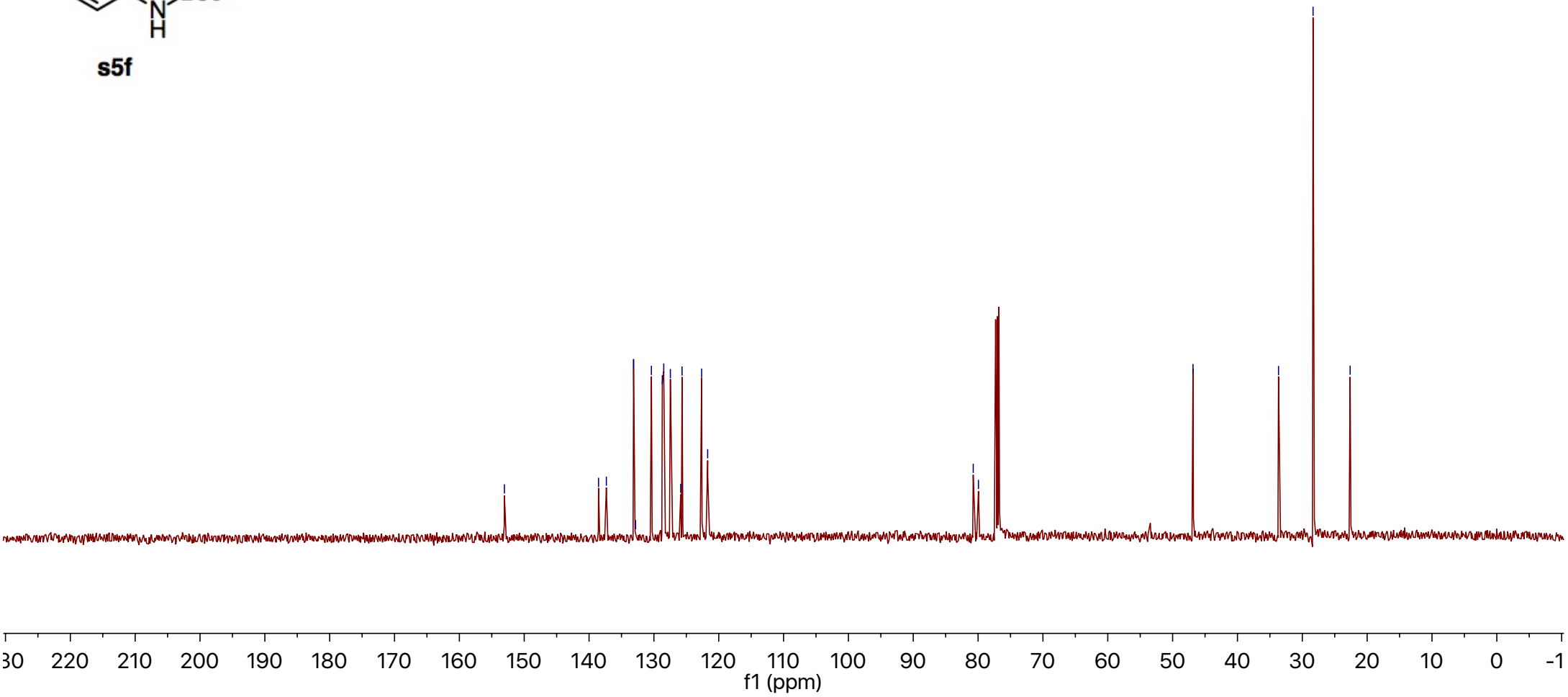
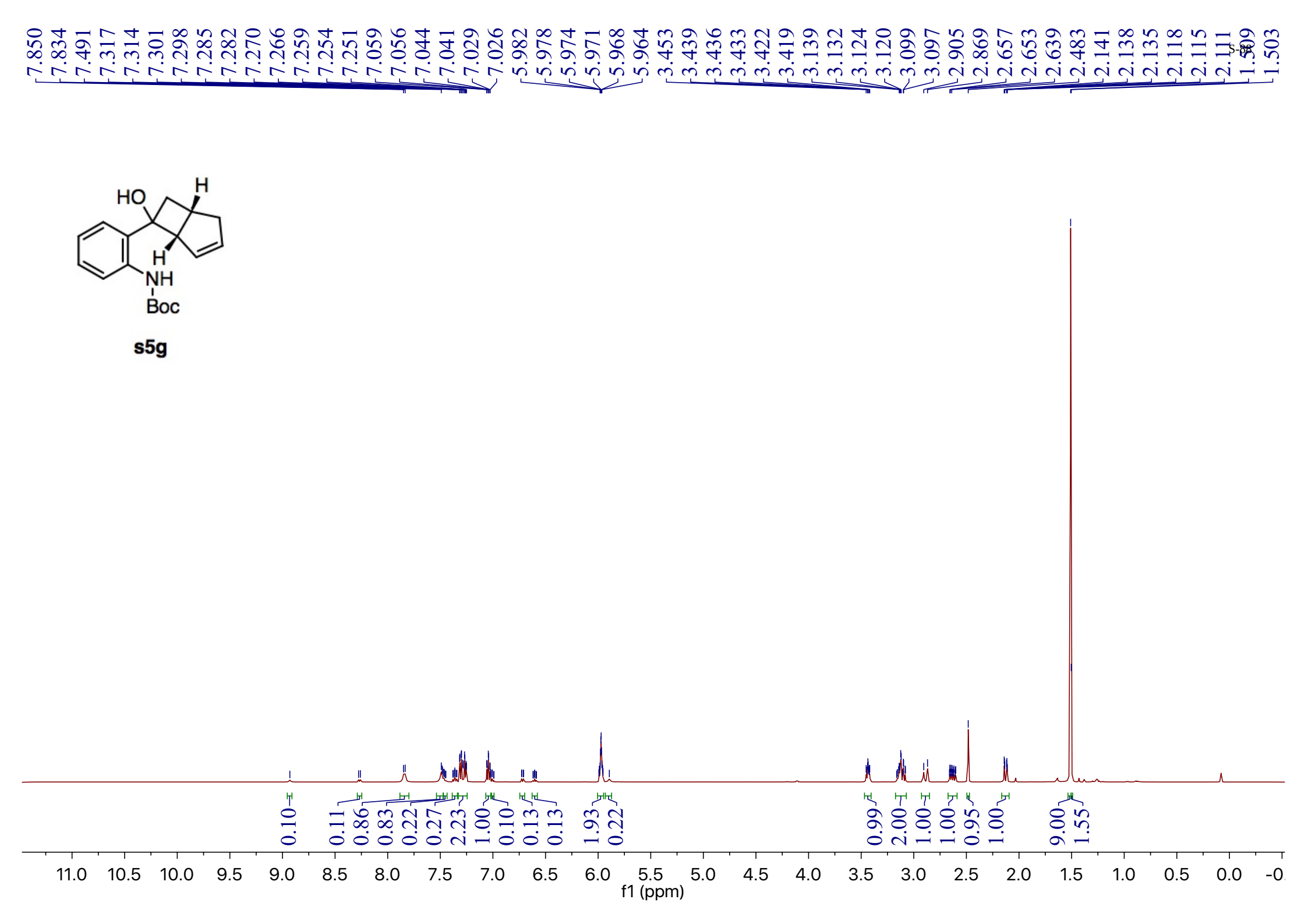
7.948
7.801
7.785
7.669
7.621
7.604
7.588
7.404
7.389
7.374
7.297
7.282
7.266
7.163
7.147
7.132
7.069
7.053
7.038
4.576
4.559
4.544
2.600
2.594
2.587
2.578
2.567
2.561
2.548
2.539
2.483
2.474
2.465
2.456
2.443
2.437
2.434
2.426
2.419
2.405
2.402
2.386
2.290
2.288
2.279
2.273
2.260
2.255
2.243
2.234
1.454
Br
HO
Boc
N
H
s5f
0.91
1.00
0.94
2.01
0.99
1.23
0.98
0.97
1.00
0.97
2.10
1.51
9.31
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

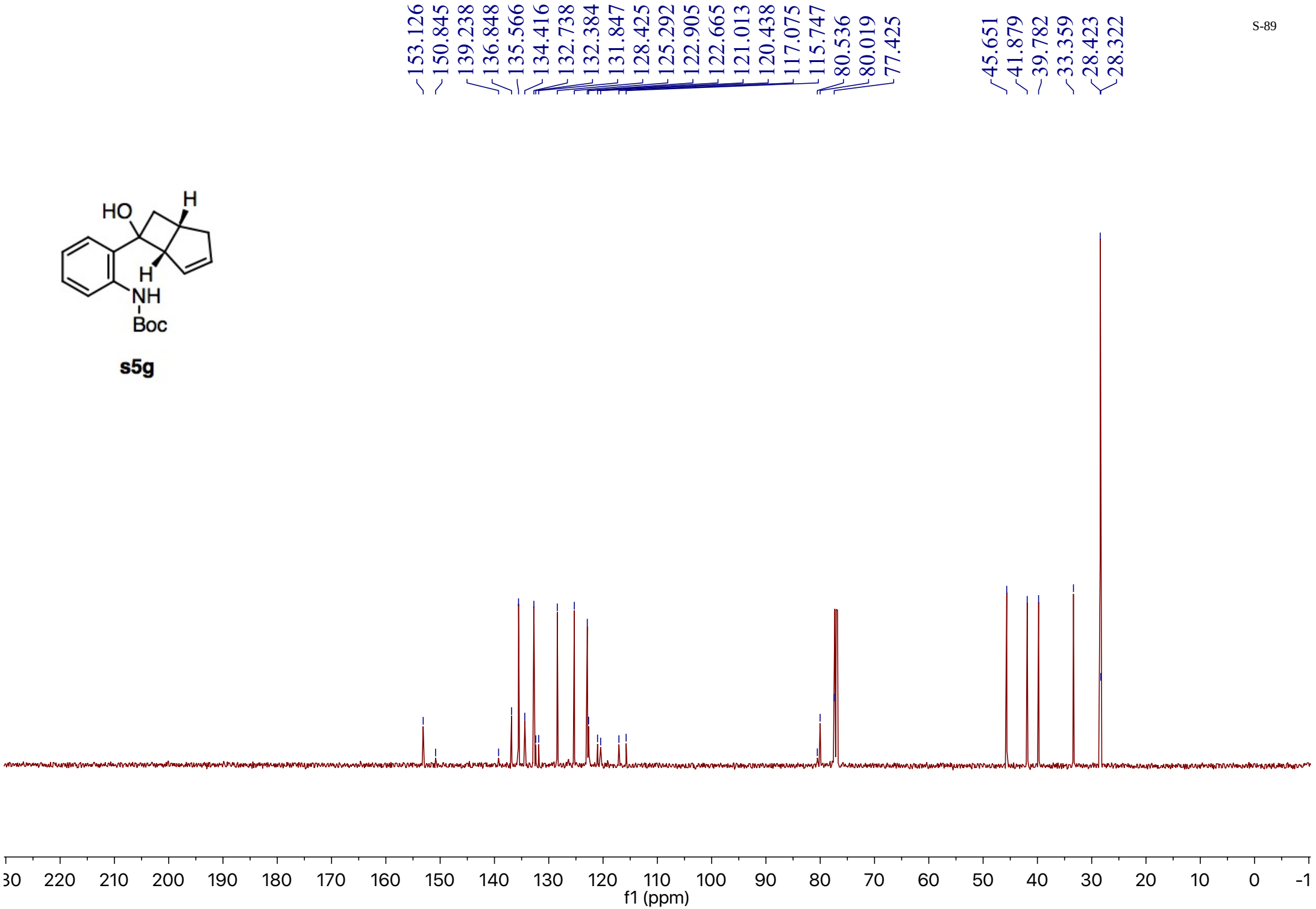
153.055
138.538
137.332
133.132
133.132
132.820
130.386
128.702
128.480
127.459
125.867
125.657
122.636
121.707
80.749
79.947
46.851
33.666
28.341
22.623



s5f




7.850
7.834
7.491
7.317
7.314
7.301
7.298
7.285
7.282
7.270
7.266
7.259
7.254
7.251
7.059
7.056
7.044
7.041
7.029
7.026
5.982
5.978
5.974
5.971
5.968
5.964
3.453
3.439
3.436
3.433
3.422
3.419
3.139
3.132
3.124
3.120
3.099
3.097
2.905
2.869
2.657
2.653
2.639
2.483
2.141
2.138
2.135
2.118
2.115
2.111
1.509
1.503
HO
H
H
NH
Boc
s5g
0.10
0.11
0.86
0.83
0.22
0.27
2.23
1.00
0.10
0.13
0.13
1.93
0.22
0.99
2.00
1.00
1.00
0.95
1.00
9.00
1.55
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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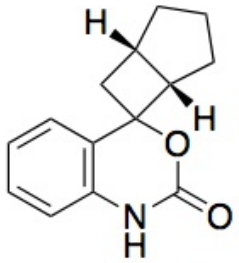
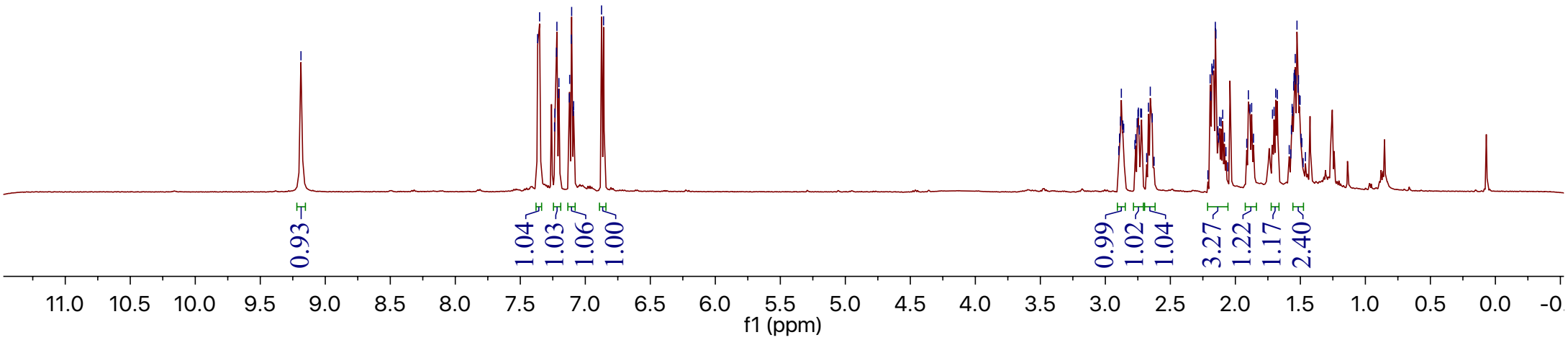
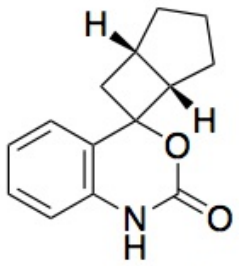
150.845
139.238
136.848
135.566
134.416
132.738
132.384
131.847
128.425
125.292
122.905
122.665
121.013
120.438
117.075
115.747
80.536
80.019
77.425
45.651
41.879
39.782
33.359
28.423
28.322
HO
H
H
NH
Boc
s5g
f1 (ppm)

9.187 7.367 7.352 7.234 7.221 7.218 7.206 7.203 7.123 7.120 7.107 7.105 7.092 7.090 6.875 6.860 2.883 2.877 2.749 2.746 2.728 2.722 2.668 2.654 2.639 2.194 2.189 2.181 2.176 2.167 2.154 2.150 2.097 1.900 1.887 1.875 1.714 1.702 1.689 1.677 1.564 1.560 1.552 1.549 1.545 1.540 1.536 1.526 1.518 1.514 1.507 1.502



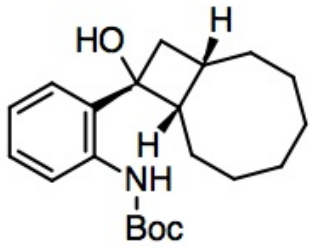
s5'h




H
H
O
N
H
O

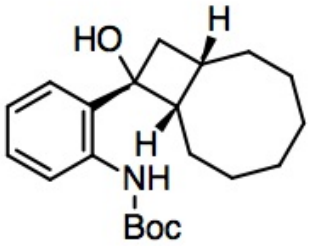
s5'h

153.032
133.845
133.843
128.542
126.354
123.568
122.563
114.308
80.537
52.638
37.930
32.627
31.372
26.933
25.626
f1 (ppm)


HO
H
H
NH
Boc

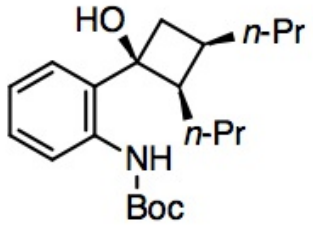
s5i

7.884
7.793
7.354
7.350
7.338
7.335
7.331
7.282
7.278
7.264
7.261
7.031
7.028
7.024
7.013
2.853
2.144
1.940
1.932
1.927
1.923
1.905
1.900
1.895
1.863
1.858
1.853
1.845
1.839
1.834
1.761
1.755
1.749
1.737
1.549
1.545
1.540
1.533
1.504
1.500
1.489
1.482
1.473
1.466
1.300
1.280
1.280
1.263
1.256
1.246
1.237
1.230
0.93
0.95
1.03
1.10
1.02
0.97
0.97
0.98
4.00
1.98
13.30
4.53
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


HO
H
H
NH
Boc

s5i

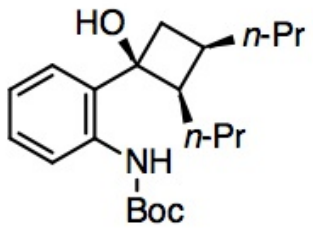
153.105
137.578
133.956
128.314
124.419
122.599
122.394
79.885
75.154
49.163
40.185
31.535
30.191
29.184
28.581
28.427
25.769
25.164
22.626
f1 (ppm)


HO
n-Pr
n-Pr
NH
Boc

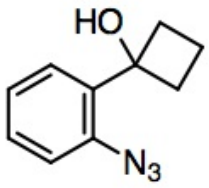
s5j

7.949
7.931
7.315
7.312
7.300
7.297
7.277
7.274
7.262
7.259
7.246
7.243
7.019
7.017
7.004
7.002
6.989
6.987
2.695
2.689
2.676
2.662
2.657
2.251
2.002
1.999
1.986
1.971
1.964
1.950
1.650
1.589
1.508
1.469
1.454
1.450
1.439
1.434
1.423
1.413
1.408
1.312
1.297
1.283
1.192
1.176
1.015
1.001
0.986
0.921
0.907
0.892
1.10
1.04
0.96
1.04
0.96
1.95
0.93
1.97
2.16
9.03
4.29
1.42
1.17
3.00
3.36
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

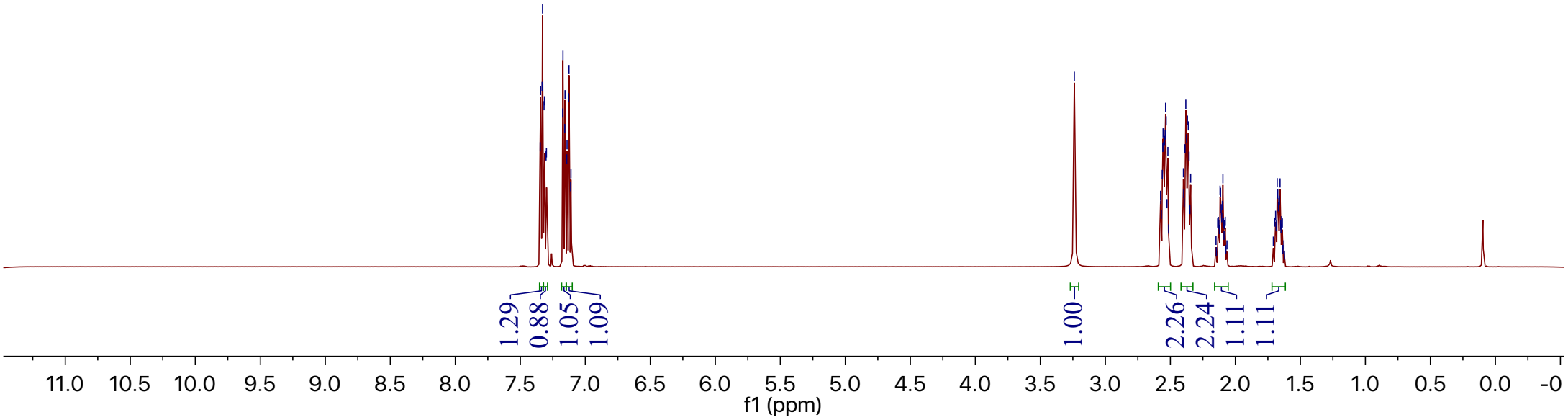
153.069
137.598
133.565
128.300
124.701
122.410
121.902
79.872
75.859
46.166
39.355
32.612
30.429
28.408
27.355
22.360
20.743
14.750
14.277



s5j


HO
N3

8a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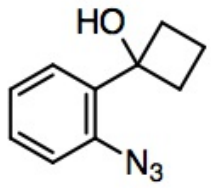
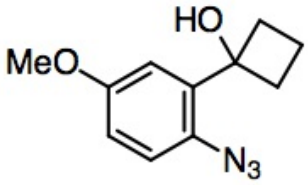
7.317
7.314
7.302
7.299
7.174
7.172
7.158
7.156
7.143
7.140
7.128
7.125
7.113
7.110
3.239
2.575
2.573
2.562
2.558
2.556
2.552
2.550
2.544
2.539
2.537
2.532
2.526
2.519
2.399
2.397
2.393
2.387
2.381
2.375
2.369
2.362
2.356
2.344
2.118
2.114
2.100
2.096
1.678
1.674
1.669
1.666
1.661
1.656
1.29
0.88
1.05
1.09
1.00
2.26
2.24
1.11
1.11
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


HO
N3

8a

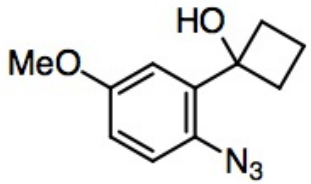
137.372
136.202
128.747
126.367
124.717
118.790
76.728
35.218
14.457
f1 (ppm)


HO
MeO
N3

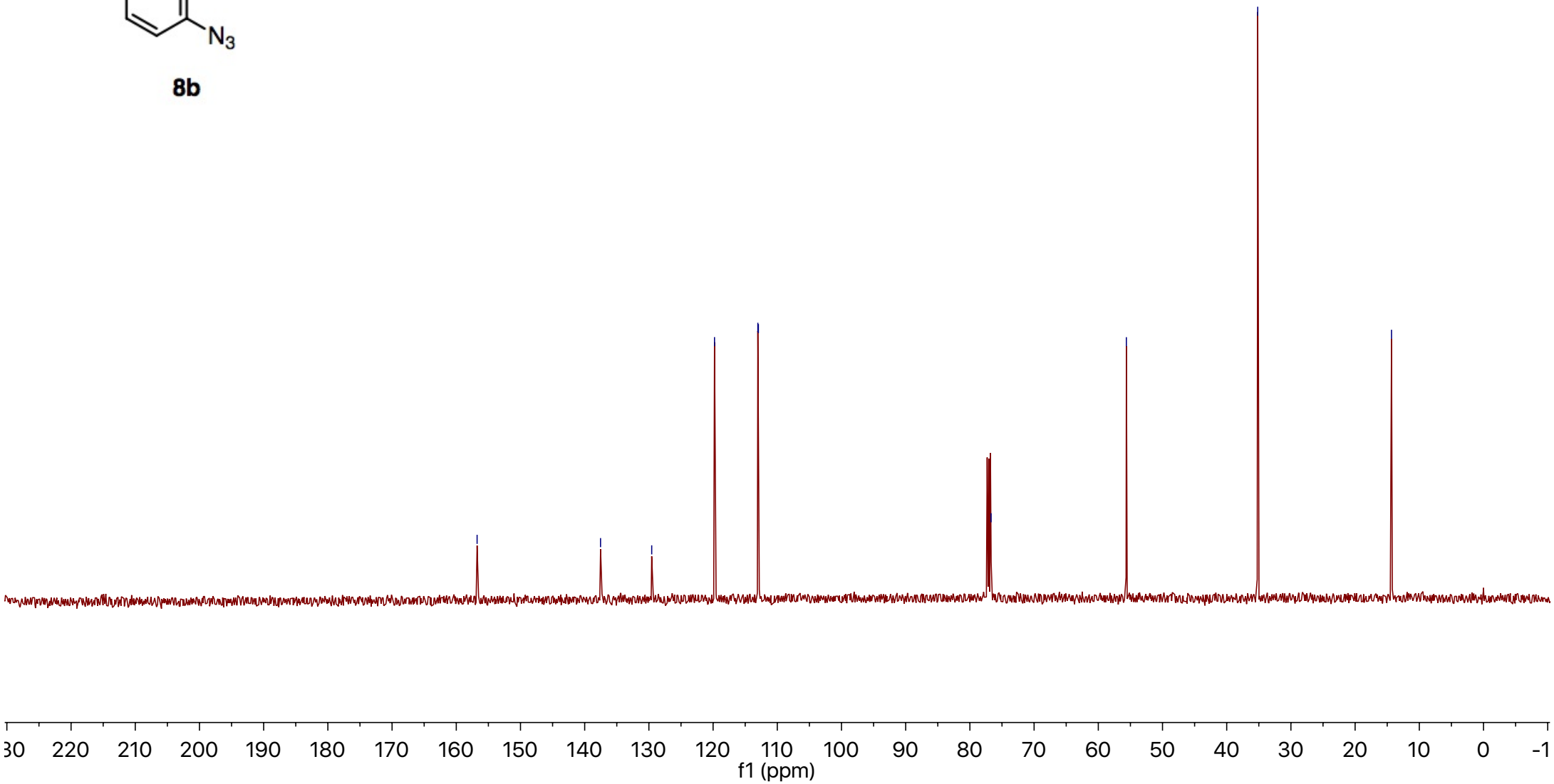
8b

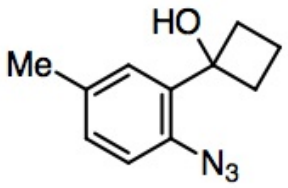
7.101
7.083
6.908
6.902
6.852
6.846
6.835
6.829
3.804
3.182
3.176
2.552
2.549
2.537
2.532
2.526
2.524
2.519
2.511
2.507
2.500
2.496
2.494
2.388
2.381
2.375
2.369
2.364
2.357
2.351
2.350
2.346
2.344
2.337
2.334
2.332
2.110
2.107
2.103
2.097
2.089
2.089
2.085
1.690
1.688
1.685
1.680
1.675
1.673
1.667
1.663
1.651
1.00
1.04
1.04
3.24
0.99
2.22
2.19
1.12
1.17
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

156.756
137.529
129.560
119.777
113.027
112.947
76.707
55.629
35.168
14.328



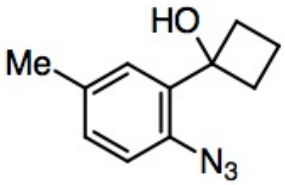
8b




HO
Me
N3

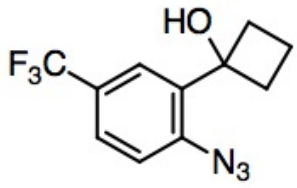
8c

7.145
7.137
7.122
7.118
7.078
7.062
3.094
2.577
2.570
2.564
2.558
2.552
2.546
2.539
2.534
2.526
2.521
2.395
2.388
2.382
2.376
2.370
2.364
2.357
2.345
2.345
2.154
2.141
2.135
2.132
2.128
2.123
2.118
2.113
2.105
2.101
2.088
2.083
2.070
1.719
1.707
1.701
1.696
1.689
1.684
1.678
1.672
1.668
1.661
1.655
1.650
1.638
2.06
1.00
0.96
2.19
5.37
1.06
1.08
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

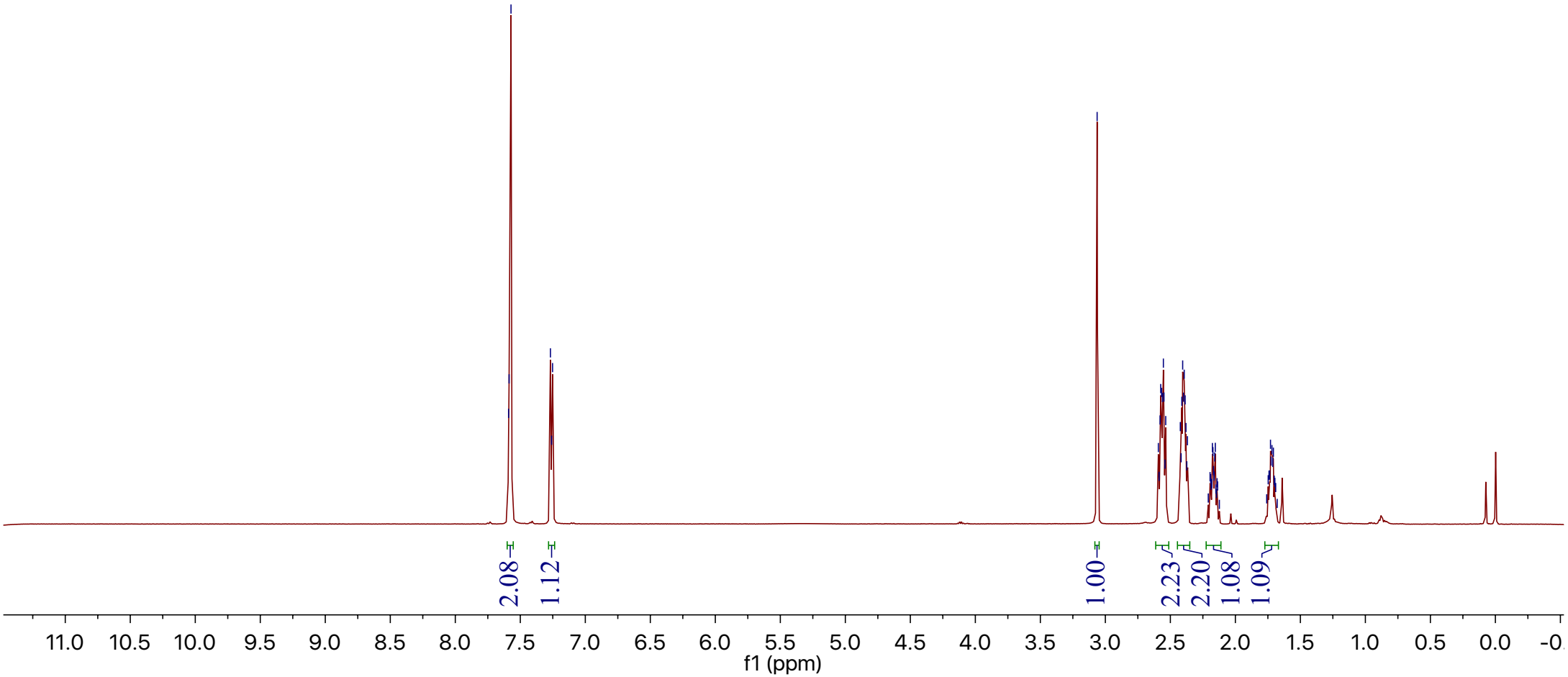

HO
Me
N3

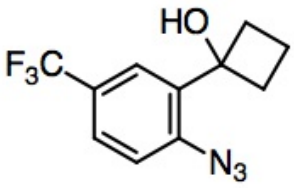
8c

135.946
134.458
134.456
129.176
127.082
118.692
76.767
35.202
21.000
14.449
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


HO
F3C
N3

8d

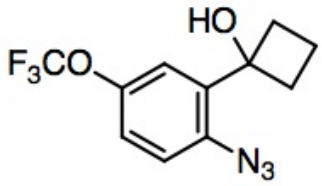

2.08
1.12
1.00
2.23
2.20
1.08
1.09
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)


HO
F3C
N3

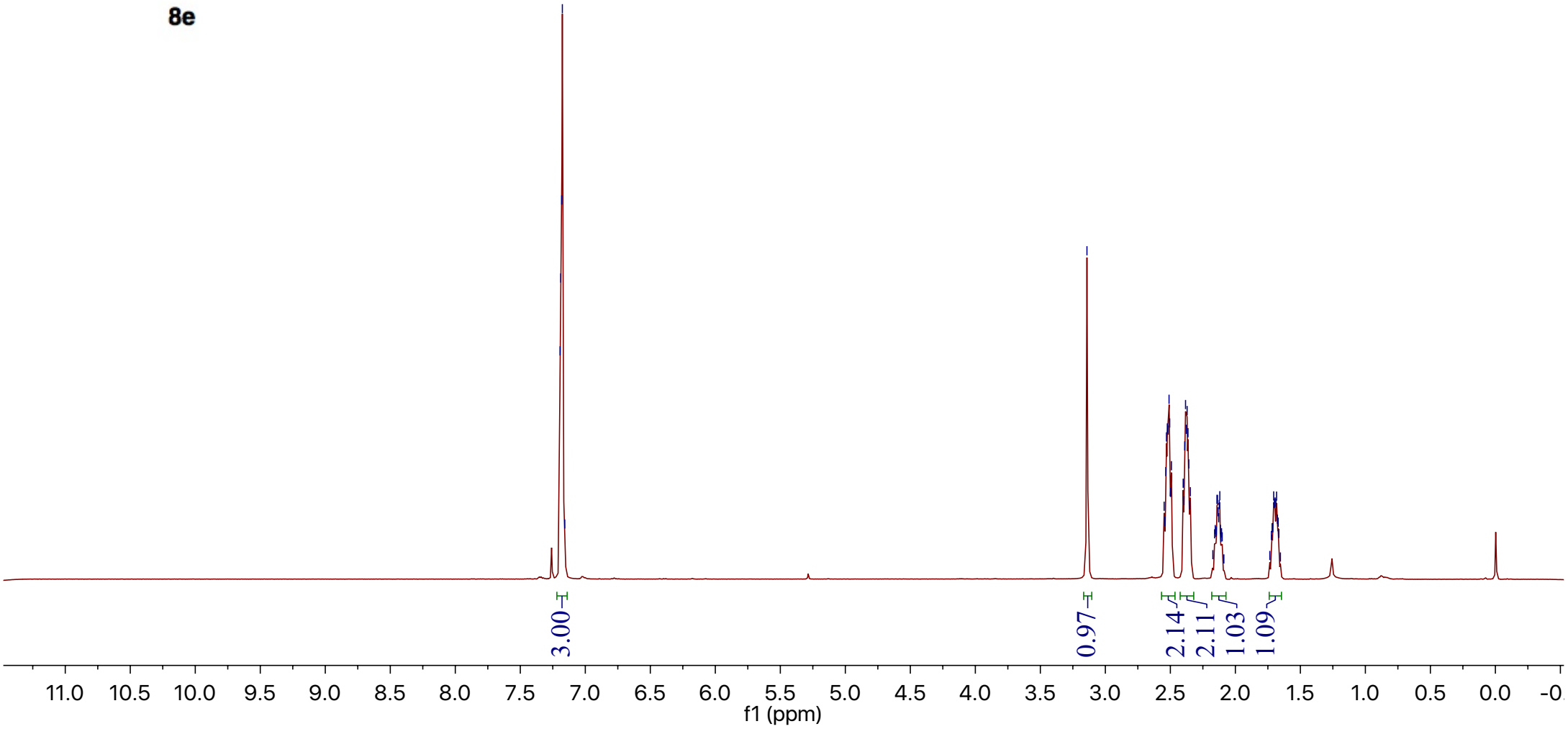
8d

141.131
136.827
127.193
126.934
126.674
126.469
126.413
125.870
125.838
125.808
125.779
124.962
123.679
123.644
123.613
123.584
122.803
120.640
118.986
76.508
35.044
14.458
f1 (ppm)

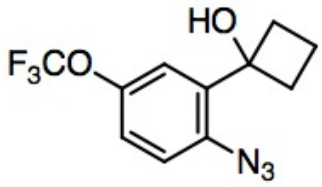
7.194 7.189 7.181 7.177 7.158 3.141 2.548 2.542 2.535 2.530 2.523 2.517 2.510 2.505 2.498 2.492 2.401 2.395 2.390 2.383 2.377 2.371 2.364 2.358 2.351 2.346 2.173 2.160 2.155 2.151 2.146 2.142 2.137 2.133 2.128 2.124 2.120 2.115 2.110 2.106 2.101 1.723 1.717 1.712 1.705 1.700 1.694 1.688 1.683 1.676 1.671 1.665



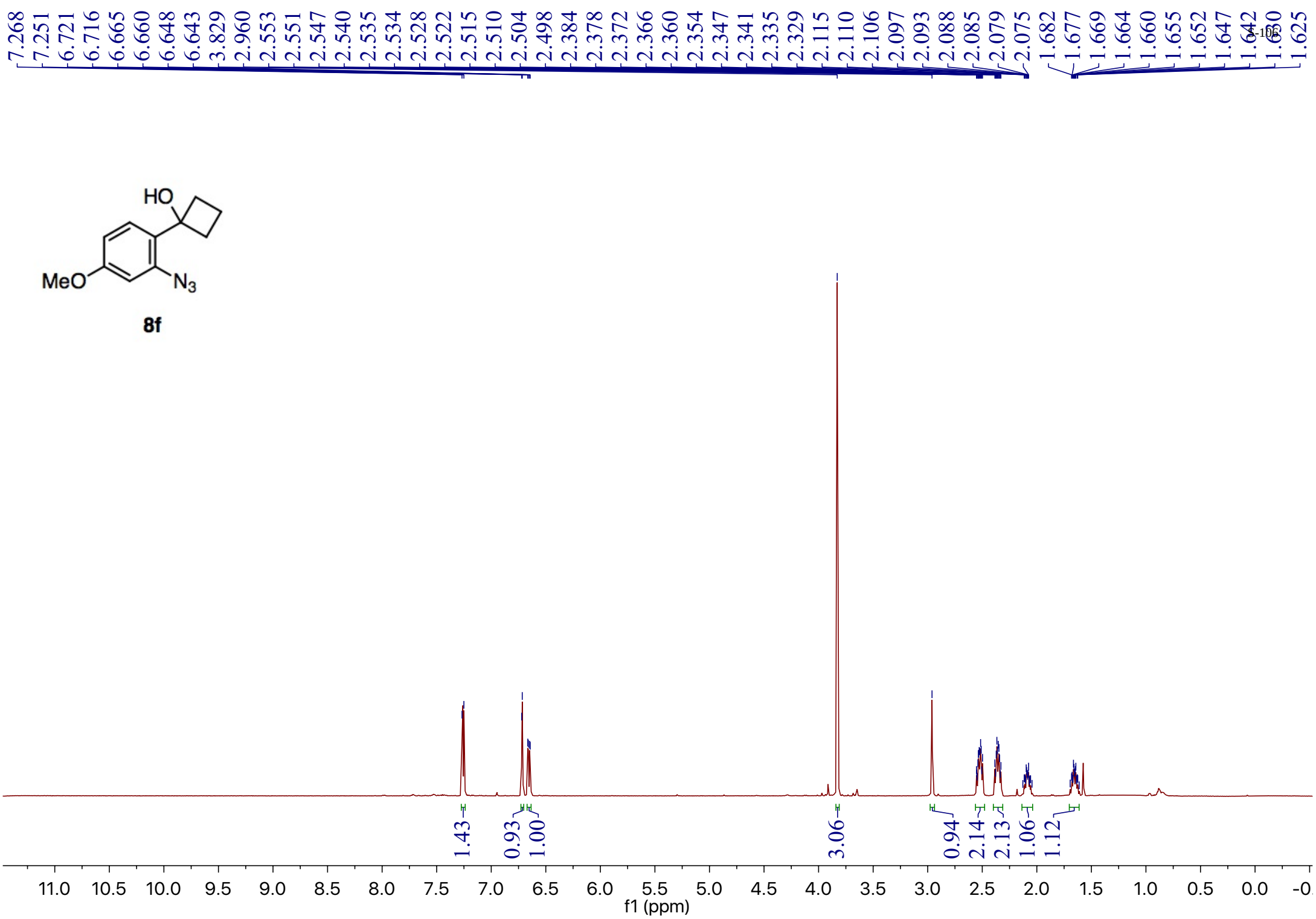
8e



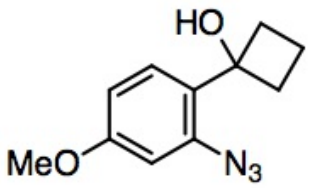
145.785
138.070
136.096
123.512
121.468
121.126
119.816
119.679
119.422
117.377
76.358
35.066
14.306



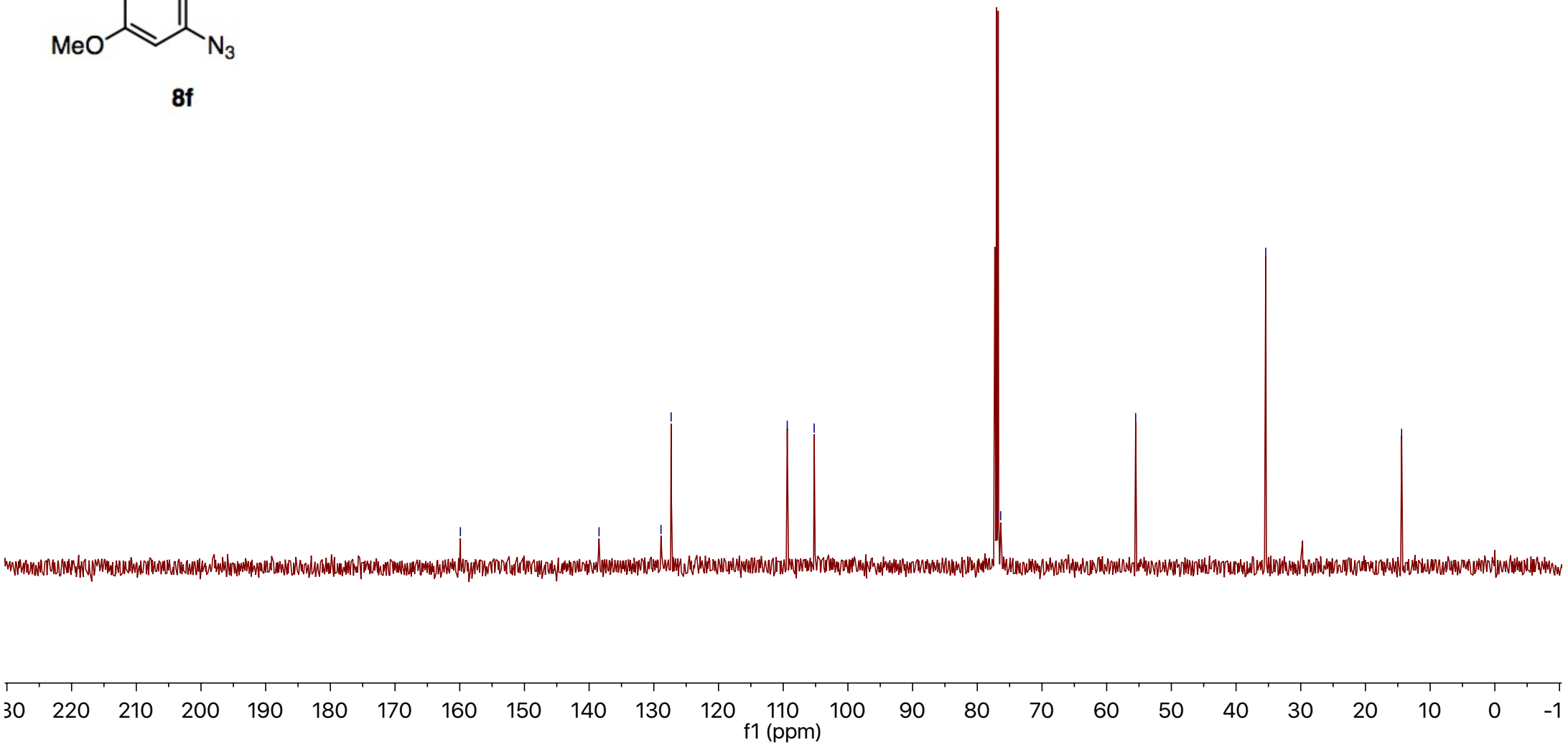
8e

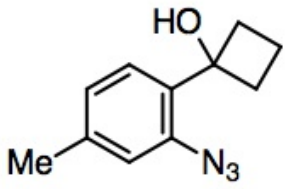

7.268
7.251
6.721
6.716
6.665
6.660
6.648
6.643
3.829
2.960
2.553
2.551
2.547
2.540
2.535
2.534
2.528
2.522
2.515
2.510
2.504
2.498
2.384
2.378
2.372
2.366
2.360
2.354
2.347
2.341
2.335
2.329
2.115
2.110
2.106
2.097
2.093
2.088
2.085
2.079
2.075
1.682
1.677
1.669
1.664
1.660
1.655
1.652
1.647
1.642
1.630
1.625
HO
MeO
N3
8f
1.43
0.93
1.00
3.06
0.94
2.14
2.13
1.06
1.12
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

159.900
138.473
128.890
127.323
109.377
105.210
76.387
55.516
35.409
14.407

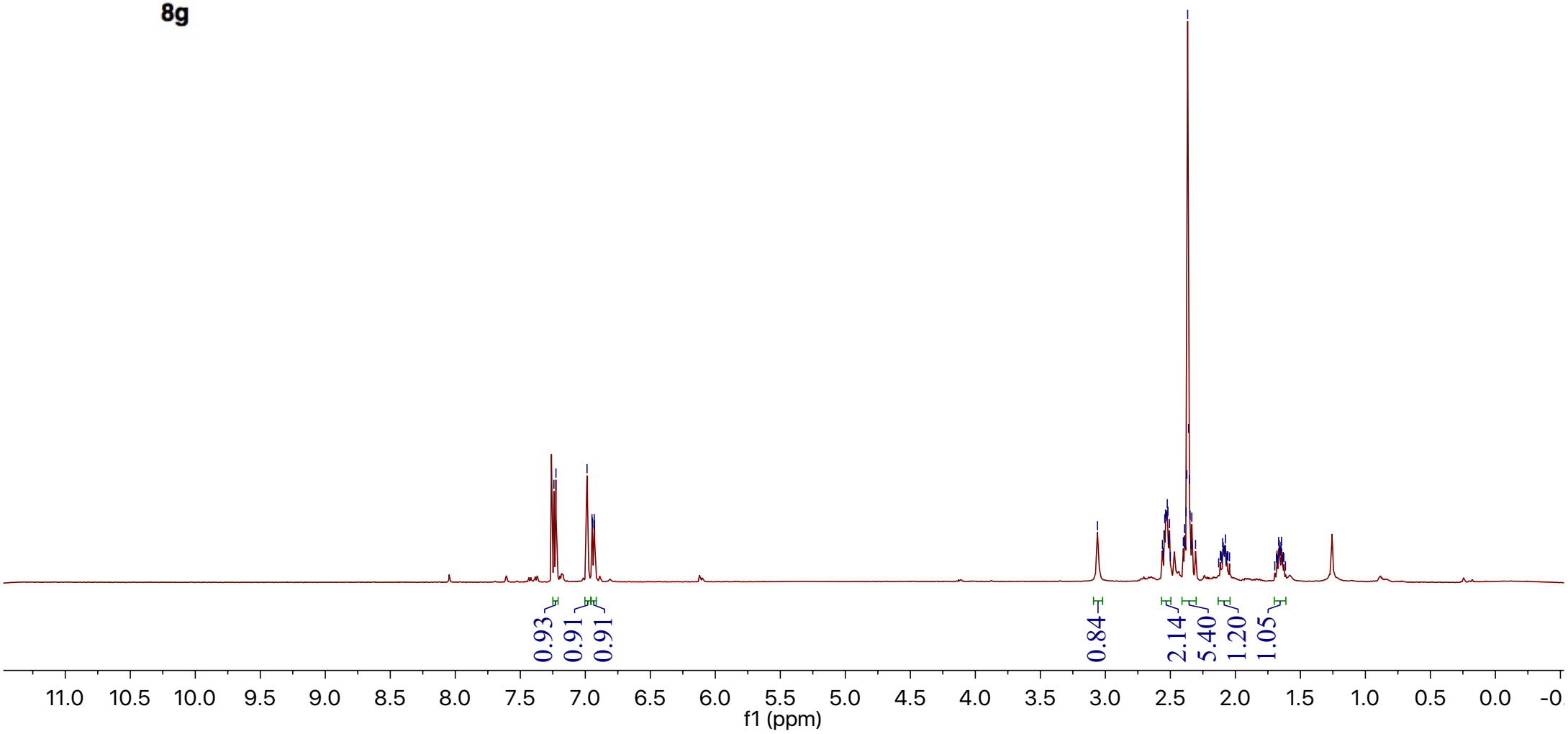


8f

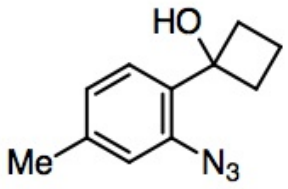



HO
Me
N_3

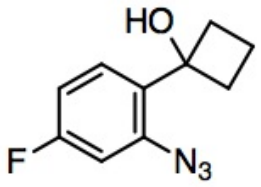
8g


7.241
7.226
6.987
6.949
6.946
6.934
6.931
6.930
3.060
2.561
2.556
2.549
2.543
2.537
2.531
2.524
2.519
2.513
2.506
2.500
2.400
2.391
2.385
2.379
2.373
2.367
2.360
2.354
2.348
2.341
2.335
2.306
2.116
2.110
2.106
2.098
2.094
2.088
2.085
2.080
2.076
2.063
2.058
2.045
1.680
1.667
1.662
1.658
1.654
1.650
1.645
1.632
0.93
0.91
0.91
0.84
2.14
5.40
1.20
1.05
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

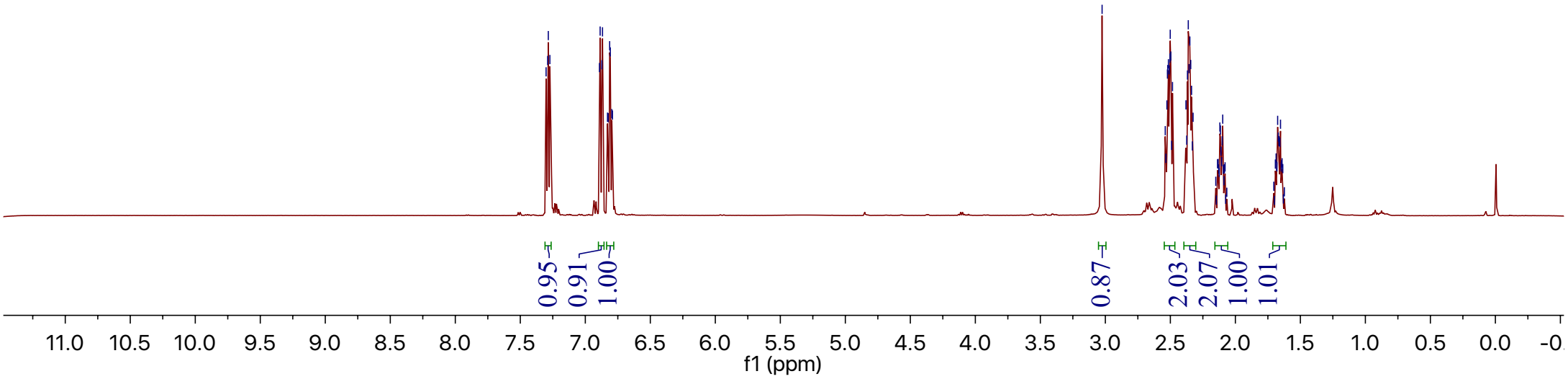
138.911
137.104
133.380
126.207
125.455
119.372
76.538
35.283
21.031
14.348



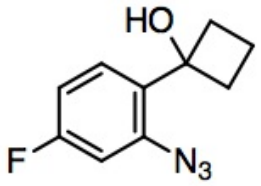
8g


HO
F
N3

8h

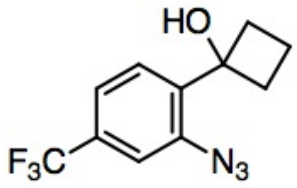

0.95
0.91
1.00
0.87
2.03
2.07
1.00
1.01
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

163.426
161.455
139.147
139.081
132.345
132.330
127.859
127.786
111.412
111.245
106.395
106.197
76.329
35.309
14.483

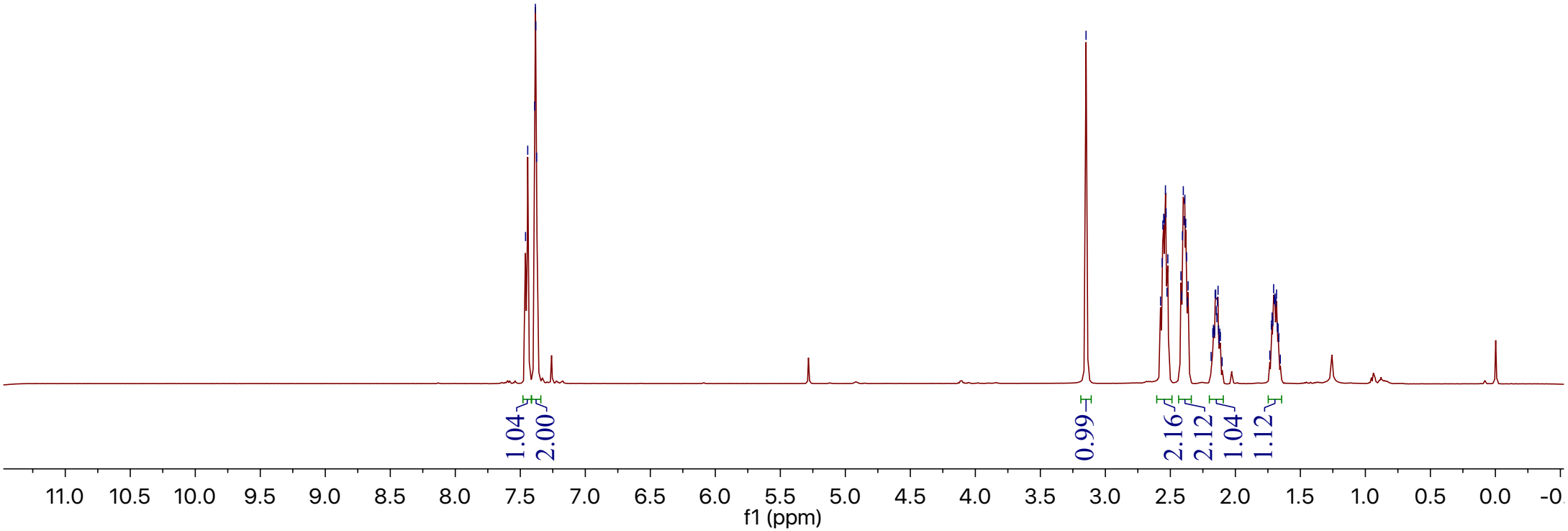


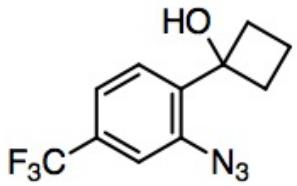
8h

7.460 7.443 7.389 7.384 7.381 7.375 3.148 2.576 2.563 2.558 2.551 2.545 2.538 2.533 2.526 2.519 2.419 2.413 2.407 2.400 2.394 2.388 2.382 2.375 2.369 2.363 2.173 2.169 2.164 2.160 2.155 2.151 2.147 2.142 2.138 2.133 2.128 2.124 2.120 2.115 1.735 1.723 1.717 1.712 1.706 1.701 1.695 1.688 1.683 1.677 1.671 1.666



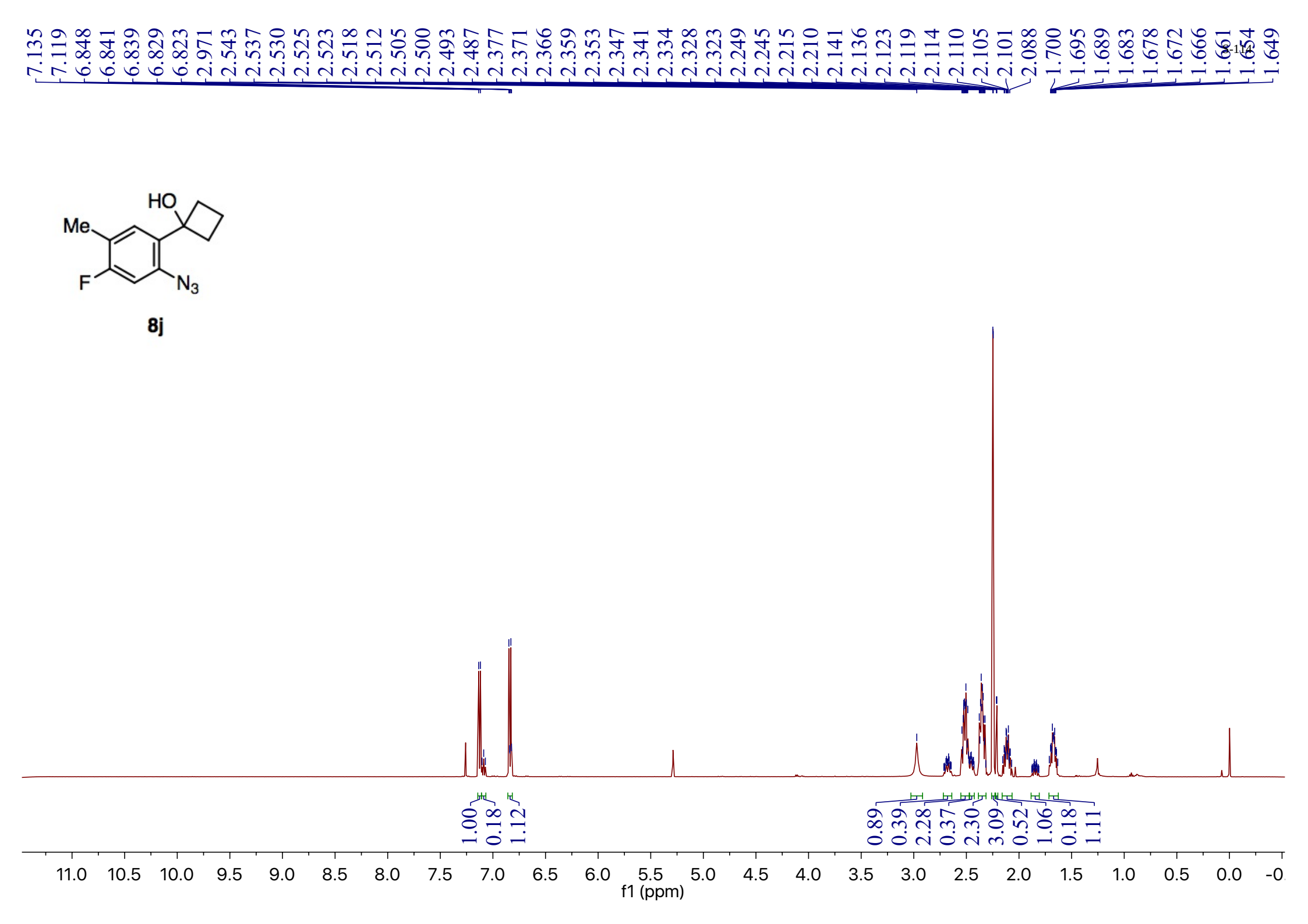
8i



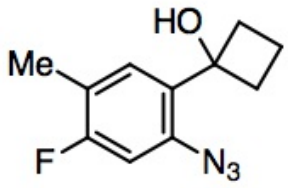

HO
F3C
N3

8i

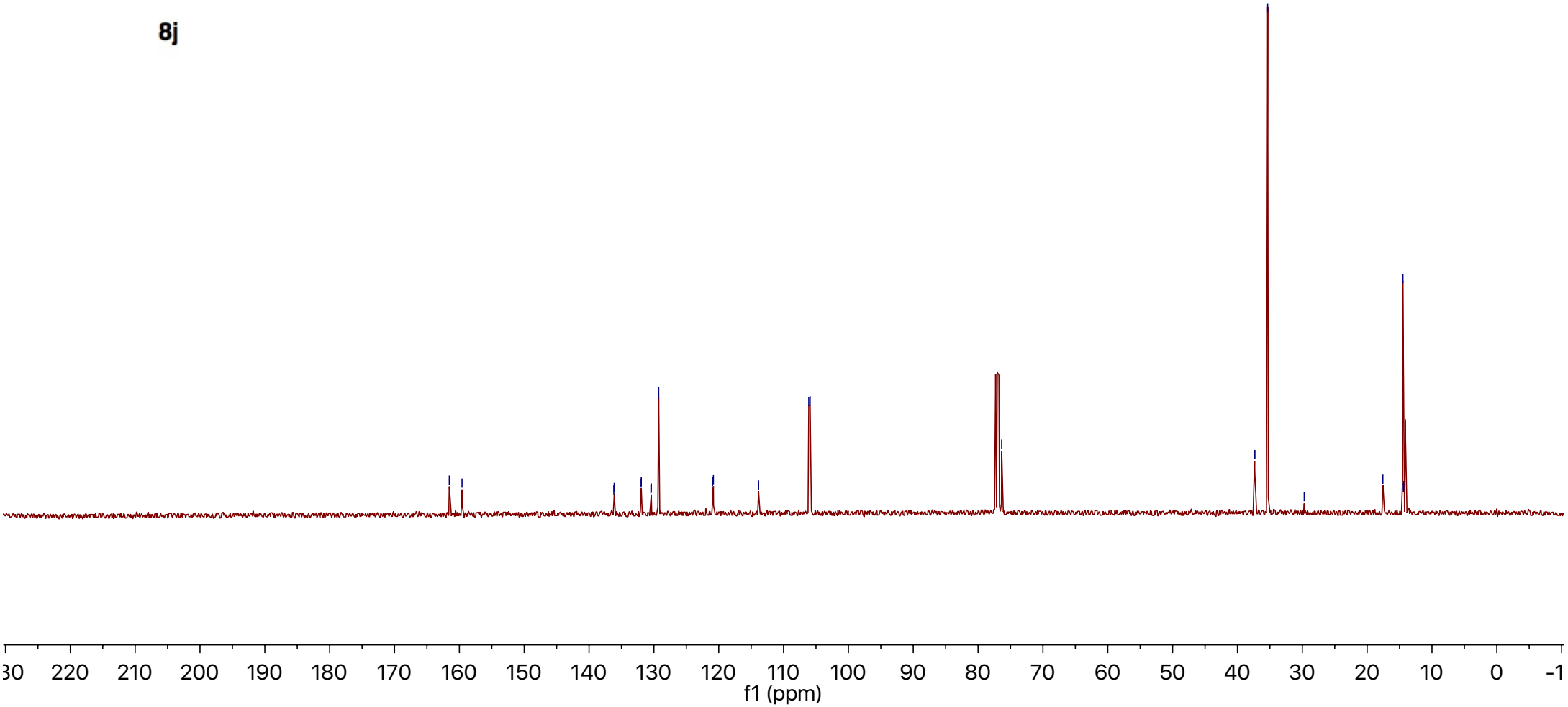
139.716
138.434
131.538
131.274
131.011
130.747
126.976
126.714
124.546
122.383
121.577
121.542
121.512
121.481
120.221
115.679
115.648
115.618
115.587
76.457
35.075
14.396
f1 (ppm)


7.135
7.119
6.848
6.841
6.839
6.829
6.823
2.971
2.543
2.537
2.530
2.525
2.523
2.518
2.512
2.505
2.500
2.493
2.487
2.377
2.371
2.366
2.359
2.353
2.347
2.341
2.334
2.328
2.323
2.249
2.245
2.215
2.210
2.141
2.136
2.123
2.119
2.114
2.110
2.105
2.101
2.088
1.700
1.695
1.689
1.683
1.678
1.672
1.666
1.661
1.654
1.649
HO
Me
F
N3
8j
1.00
0.18
1.12
0.89
0.39
2.28
0.37
2.30
3.09
0.52
1.06
0.18
1.11
f1 (ppm)

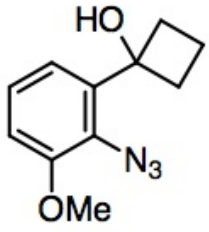
161.554
159.592
136.184
136.119
131.967
131.943
130.459
130.401
129.312
129.261
120.957
120.822
113.881
113.861
106.112
105.905
76.361
37.356
37.321
35.339
29.704
17.573
14.498
14.498
14.408
14.373
14.124
14.113



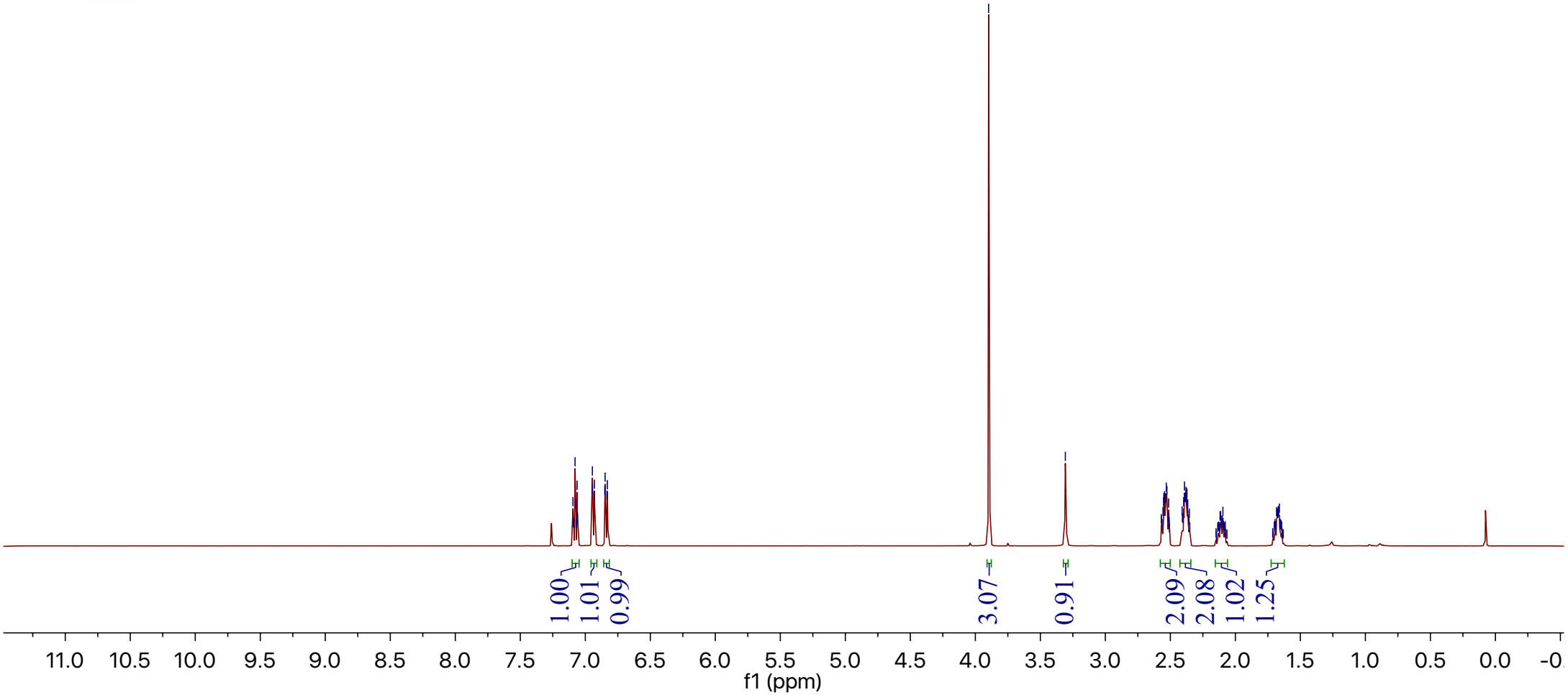
8j



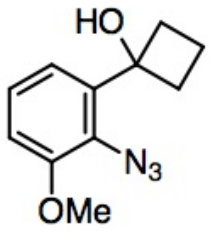
7.095 7.079 7.076 7.063 7.060 6.948 6.946 6.933 6.930 6.850 6.847 6.834 6.831 3.898 3.308 2.570 2.556 2.552 2.550 2.546 2.544 2.538 2.531 2.526 2.520 2.513 2.410 2.407 2.404 2.398 2.392 2.390 2.386 2.384 2.380 2.378 2.374 2.372 2.369 2.366 2.356 2.354 2.118 2.114 2.109 2.096 1.683 1.679 1.674 1.671 1.666 1.661



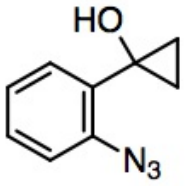
8k



154.441
138.106
125.308
125.127
118.118
111.230
76.997
56.104
35.329
14.469

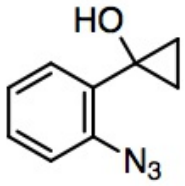


8k


HO
N3

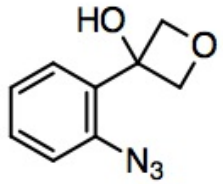
10a

7.354
7.351
7.349
7.346
7.339
7.336
7.324
7.321
7.313
7.311
7.298
7.296
7.199
7.196
7.183
7.180
7.113
7.111
7.098
7.096
7.091
7.083
7.081
7.078
7.074
3.183
1.161
1.150
1.147
1.144
1.136
1.128
0.937
0.927
0.923
0.912
2.03
0.98
1.00
0.84
2.10
2.21
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


HO
N3

10a

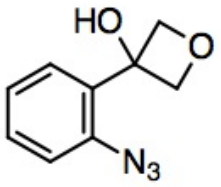
139.530
133.190
129.084
128.779
124.774
118.332
55.221
13.922
f1 (ppm)


HO
O
N3

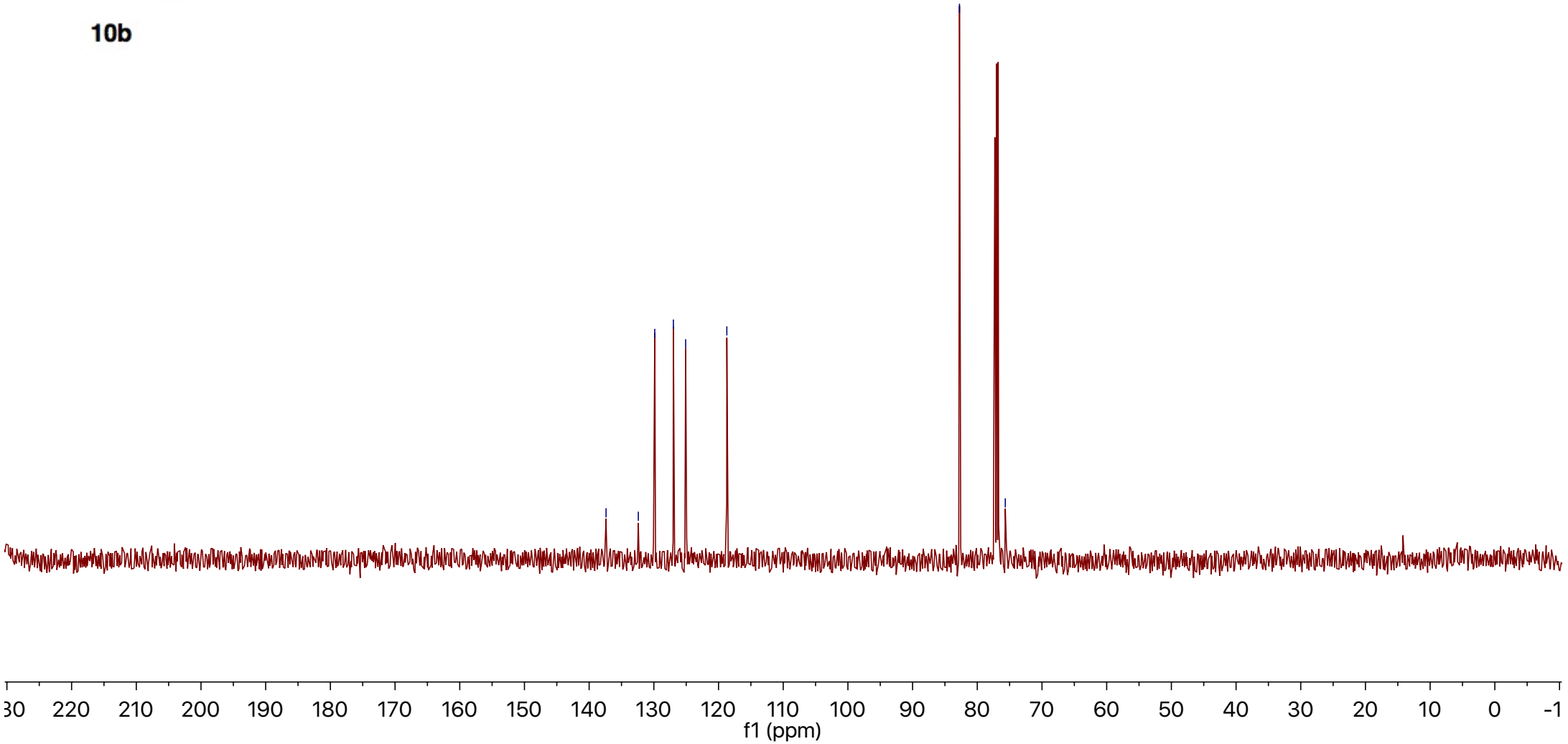
10b

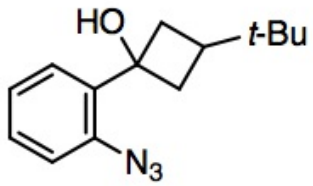
7.387
7.384
7.372
7.369
7.356
7.353
7.228
7.225
7.213
7.210
7.183
7.181
7.167
7.165
7.152
7.150
7.137
7.135
5.055
5.040
4.809
4.794
3.623
1.00
1.01
1.98
2.08
2.08
0.97
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

137.385
132.398
129.855
126.977
125.081
118.714
82.753
75.672



10b

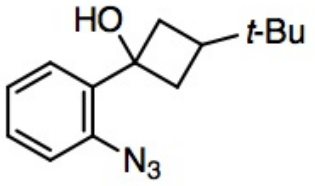



HO
t-Bu
N3

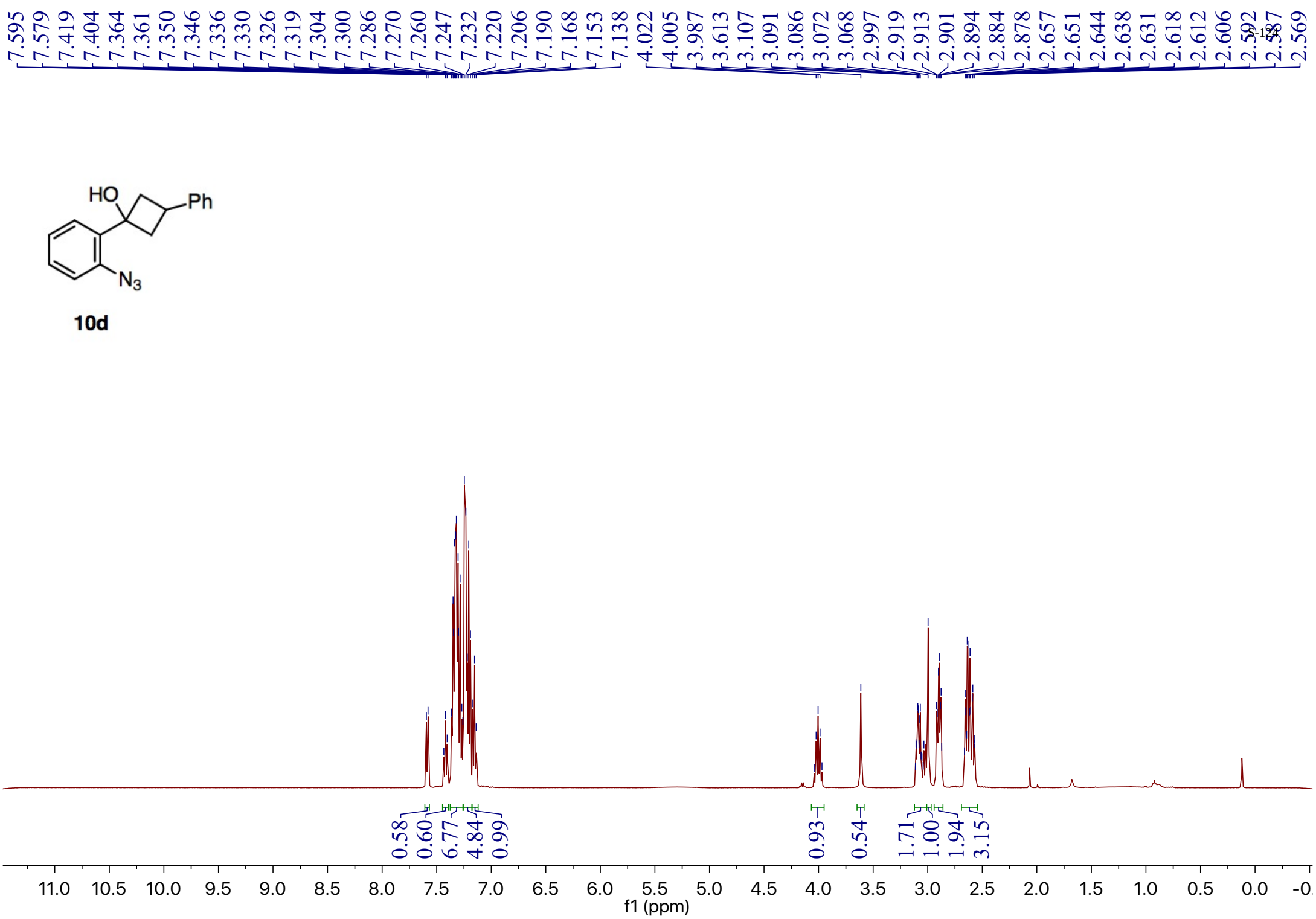
10c

7.487
7.484
7.472
7.469
7.360
7.357
7.310
7.307
7.259
7.254
7.242
7.239
7.232
7.229
7.216
7.213
7.172
7.170
7.166
7.164
7.156
7.154
7.137
7.135
7.122
7.120
3.452
2.758
2.603
2.501
2.498
2.495
2.492
2.476
2.296
2.292
2.290
2.286
2.276
2.270
2.218
2.212
2.198
2.192
2.151
2.132
2.130
2.126
2.124
2.105
0.852
0.815
0.76
0.78
1.02
1.88
1.75
1.00
0.70
0.88
0.94
1.56
2.02
1.99
1.64
0.88
7.05
9.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

137.922
137.142
137.037
135.708
128.768
128.675
126.536
126.221
124.802
124.707
118.971
118.609
73.003
70.759
40.744
36.834
36.537
35.865
30.909
30.850
26.626
26.336



10c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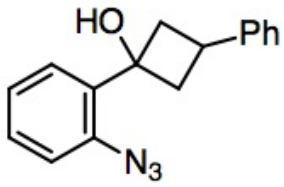
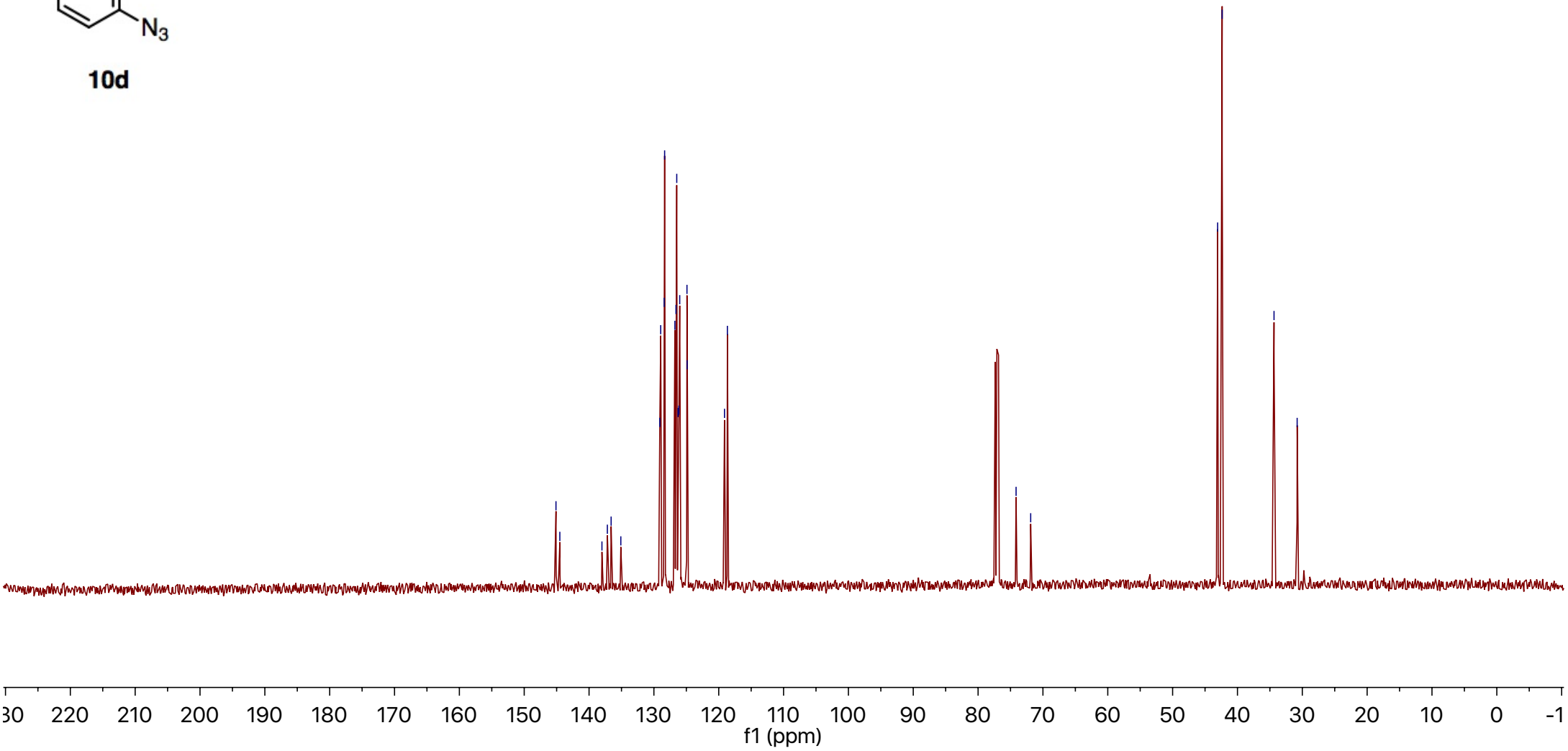
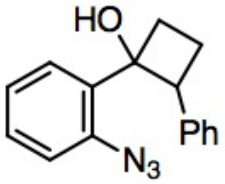
7.579
7.419
7.404
7.364
7.361
7.350
7.346
7.336
7.330
7.326
7.319
7.304
7.300
7.286
7.270
7.260
7.247
7.232
7.220
7.206
7.190
7.168
7.153
7.138
4.022
4.005
3.987
3.613
3.107
3.091
3.086
3.072
3.068
2.997
2.919
2.913
2.901
2.894
2.884
2.878
2.657
2.651
2.644
2.638
2.631
2.618
2.612
2.606
2.592
2.587
2.569
HO
Ph
N3
10d
0.58
0.60
6.77
4.84
0.99
0.93
0.54
1.71
1.00
1.94
3.15
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

145.101
144.507
138.012
137.177
136.595
135.100
129.090
128.949
128.411
128.345
126.762
126.596
126.474
126.278
126.150
126.015
124.899
124.872
119.111
118.665
74.142
71.888
43.056
42.361
34.360
30.794

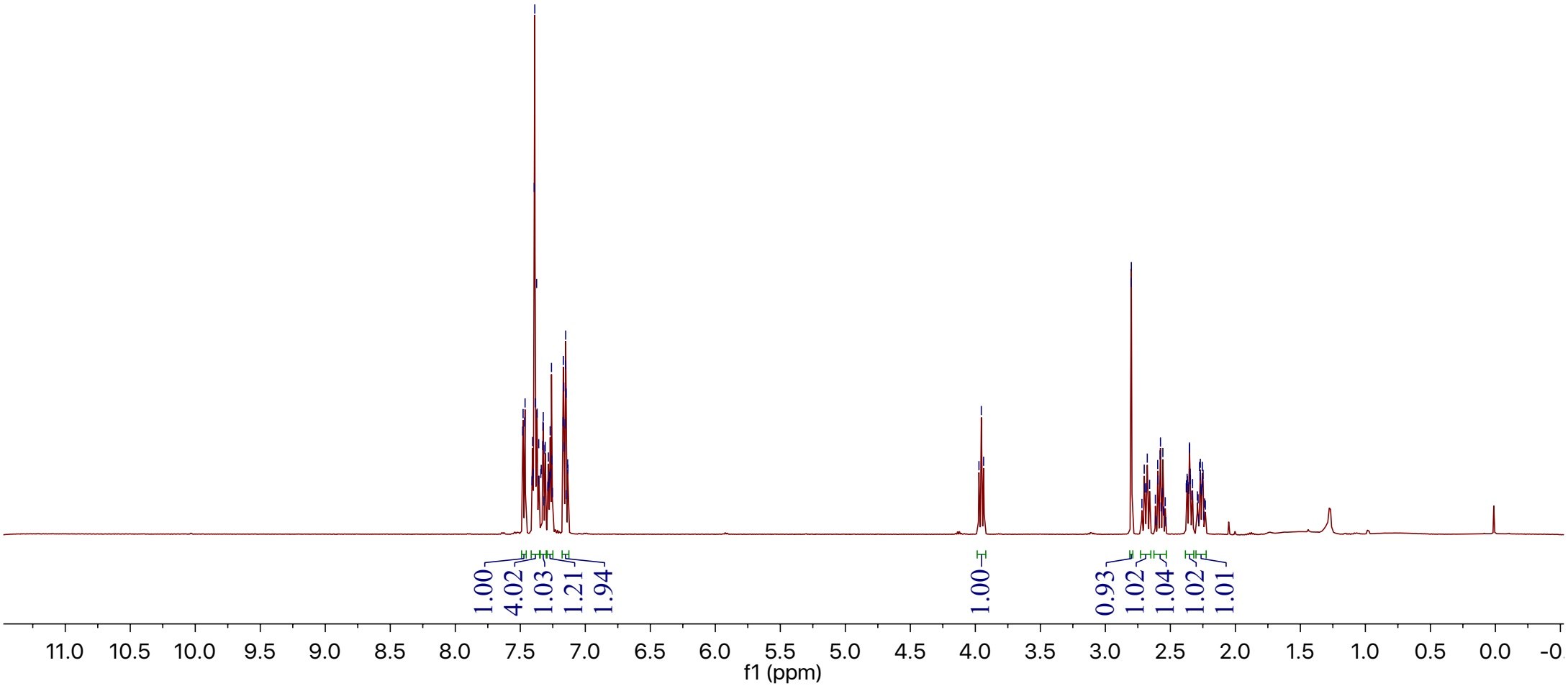


10d

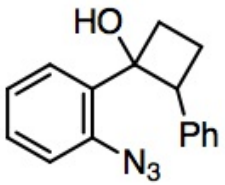



HO
Ph
N3

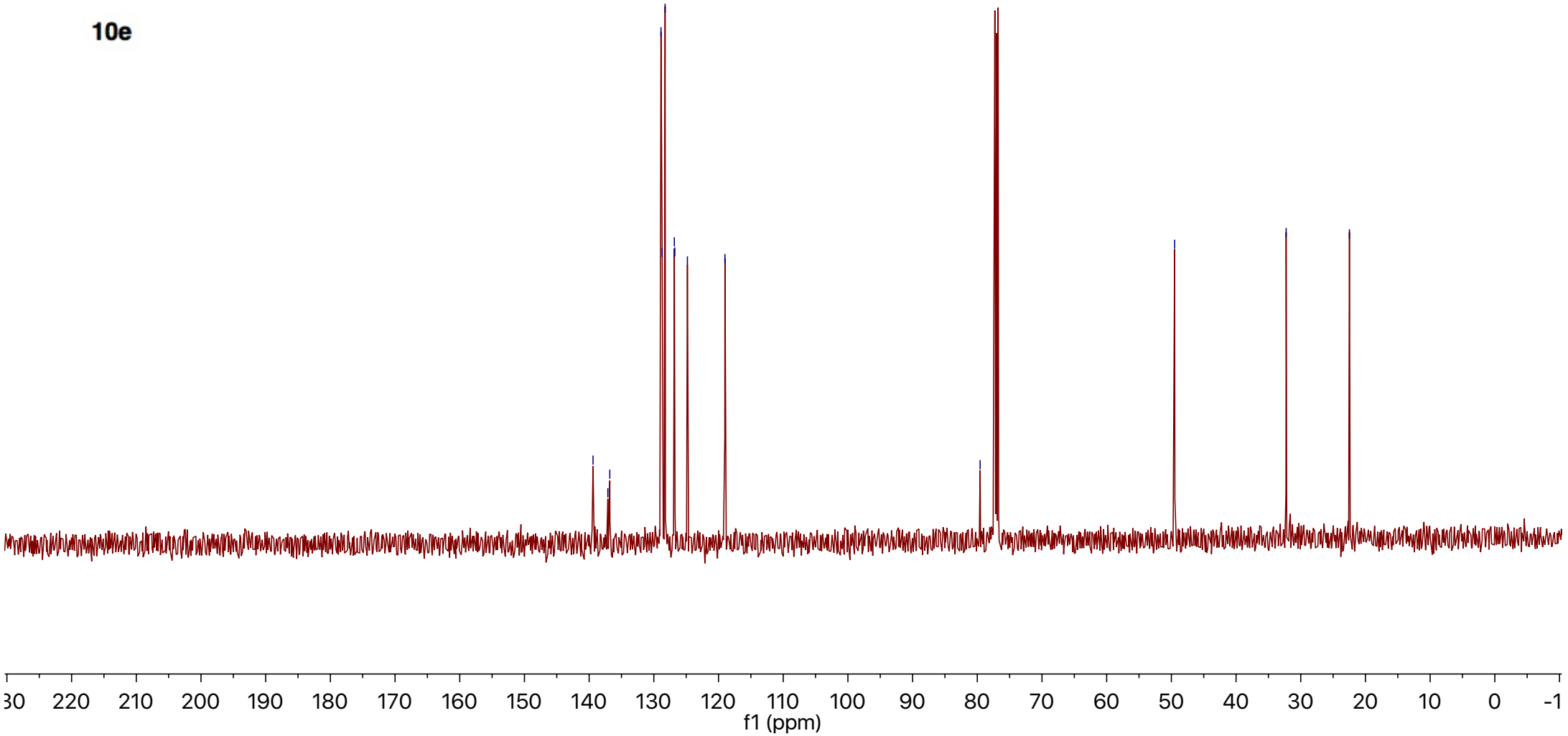
10e

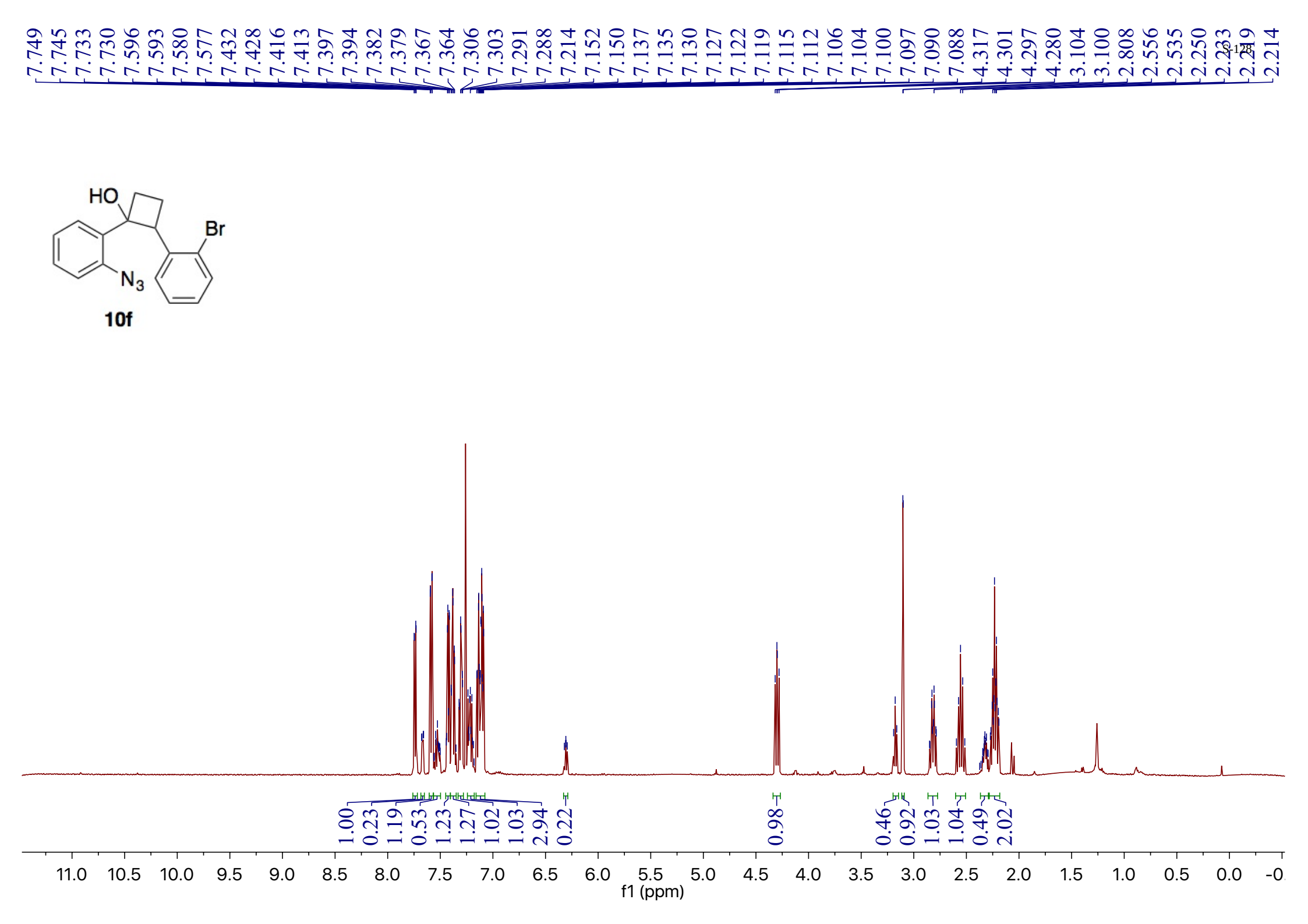

1.00
4.02
1.03
1.21
1.94
1.00
0.93
1.02
1.04
1.02
1.01
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

139.398
137.108
136.805
128.893
128.710
128.256
126.831
126.757
124.810
119.011
79.563
49.492
32.257
22.473



10e

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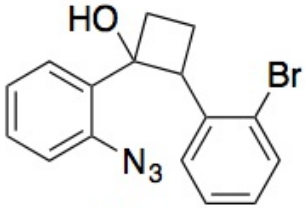
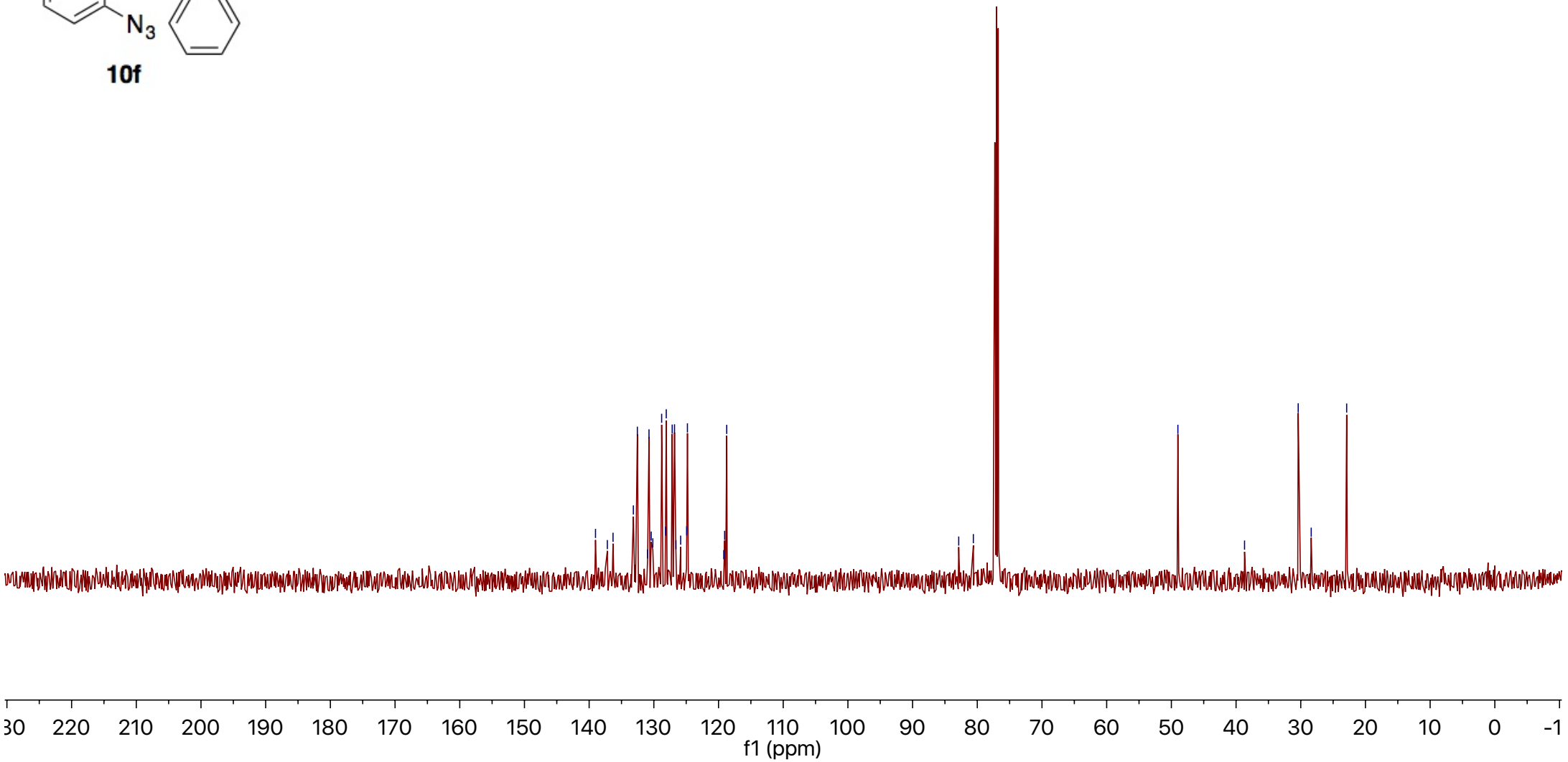
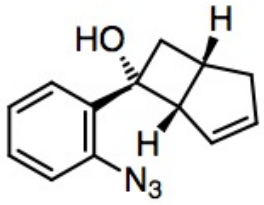
7.745
7.733
7.730
7.596
7.593
7.580
7.577
7.432
7.428
7.416
7.413
7.397
7.394
7.382
7.379
7.367
7.364
7.306
7.303
7.291
7.288
7.214
7.152
7.150
7.137
7.135
7.130
7.127
7.122
7.119
7.115
7.112
7.106
7.104
7.100
7.097
7.090
7.088
4.317
4.301
4.297
4.280
3.104
3.100
2.808
2.556
2.535
2.250
2.233
2.229
2.214
HO
Br
N3
10f
1.00
0.23
1.19
0.53
1.23
1.27
1.02
1.03
2.94
0.22
0.98
0.46
0.92
1.03
1.04
0.49
2.02
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

139.017
137.187
136.307
133.165
132.547
130.968
130.747
130.406
130.155
128.792
128.203
128.079
127.162
126.803
126.586
125.854
124.918
124.808
119.191
119.054
118.734
82.870
80.610
48.992
38.689
30.395
28.383
22.902



10f

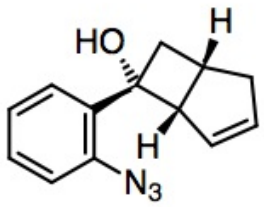



HO
H
H
N3

10g

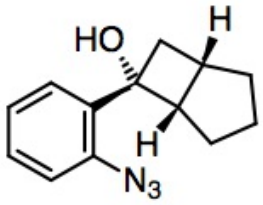
7.406
7.401
7.392
7.386
7.331
7.327
7.322
7.312
7.307
7.200
7.194
7.184
7.178
7.161
7.156
7.149
7.146
7.141
7.132
7.126
5.948
5.941
5.938
5.934
5.929
5.924
3.360
3.353
3.341
3.122
3.110
3.106
3.100
3.083
3.077
2.997
2.992
2.987
2.963
2.958
2.953
2.679
2.626
2.613
2.609
2.140
2.136
2.131
2.121
2.118
2.113
2.108
1.00
1.03
2.01
2.00
1.03
2.11
1.08
0.99
1.10
1.04
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

137.266
137.107
134.826
132.937
128.731
126.990
124.665
118.977
76.016
46.561
41.349
39.772
33.511

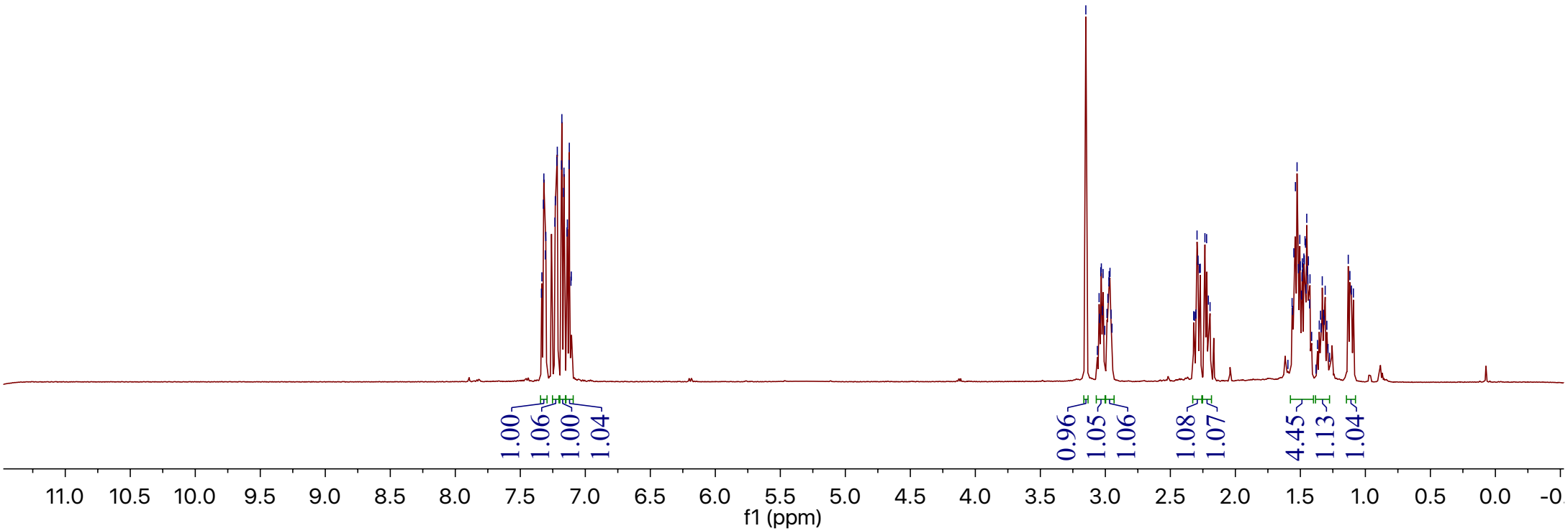


10g

7.334 7.322 7.319 7.307 7.304 7.234 7.231 7.219 7.215 7.183 7.180 7.167 7.164 7.140 7.138 7.125 7.123 7.110 7.108 3.150 3.035 3.031 3.018 2.971 2.964 2.295 2.287 2.277 2.270 2.234 2.221 1.550 1.538 1.525 1.515 1.504 1.501 1.487 1.485 1.482 1.473 1.470 1.464 1.460 1.451 1.446 1.442 1.438 1.426 1.332 1.322 1.119



10h



137.431
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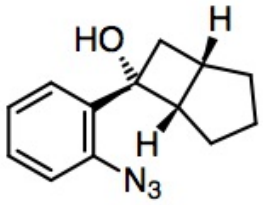
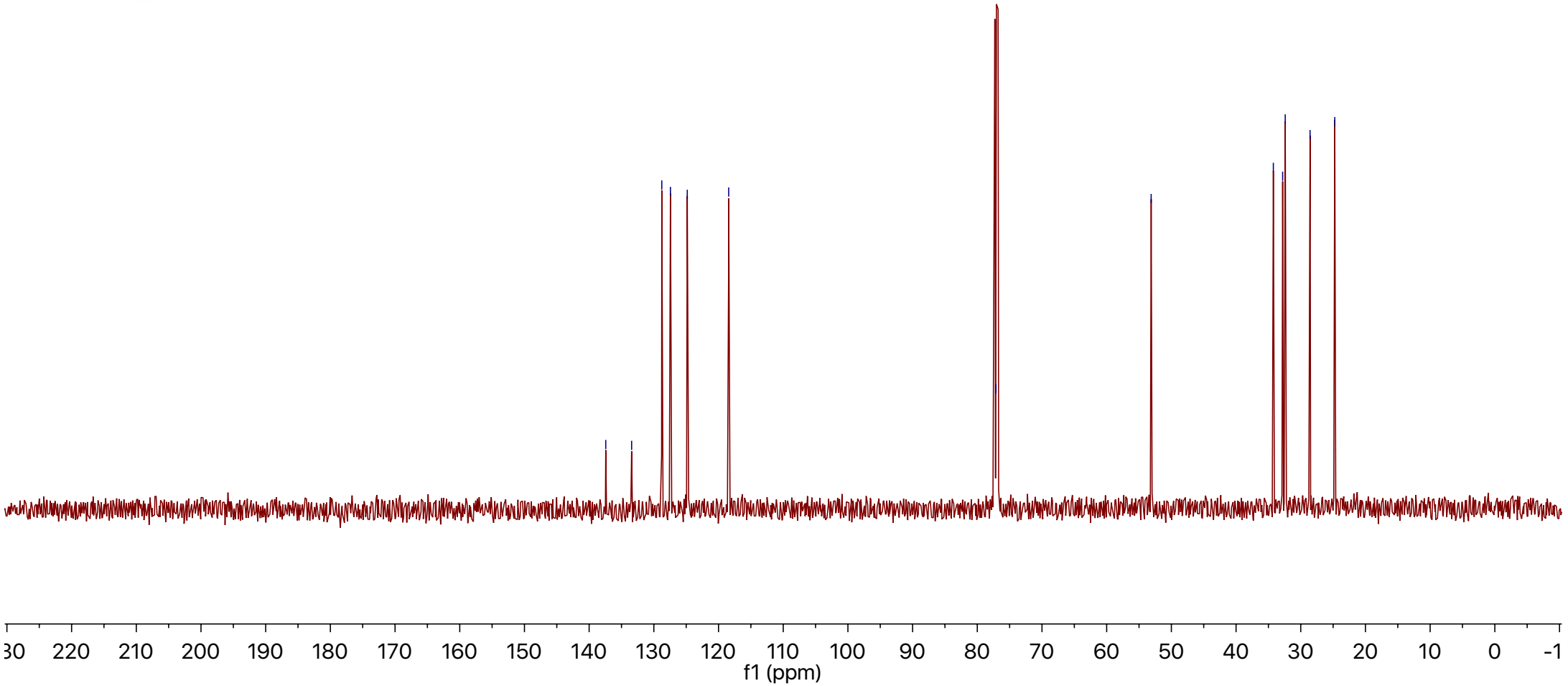
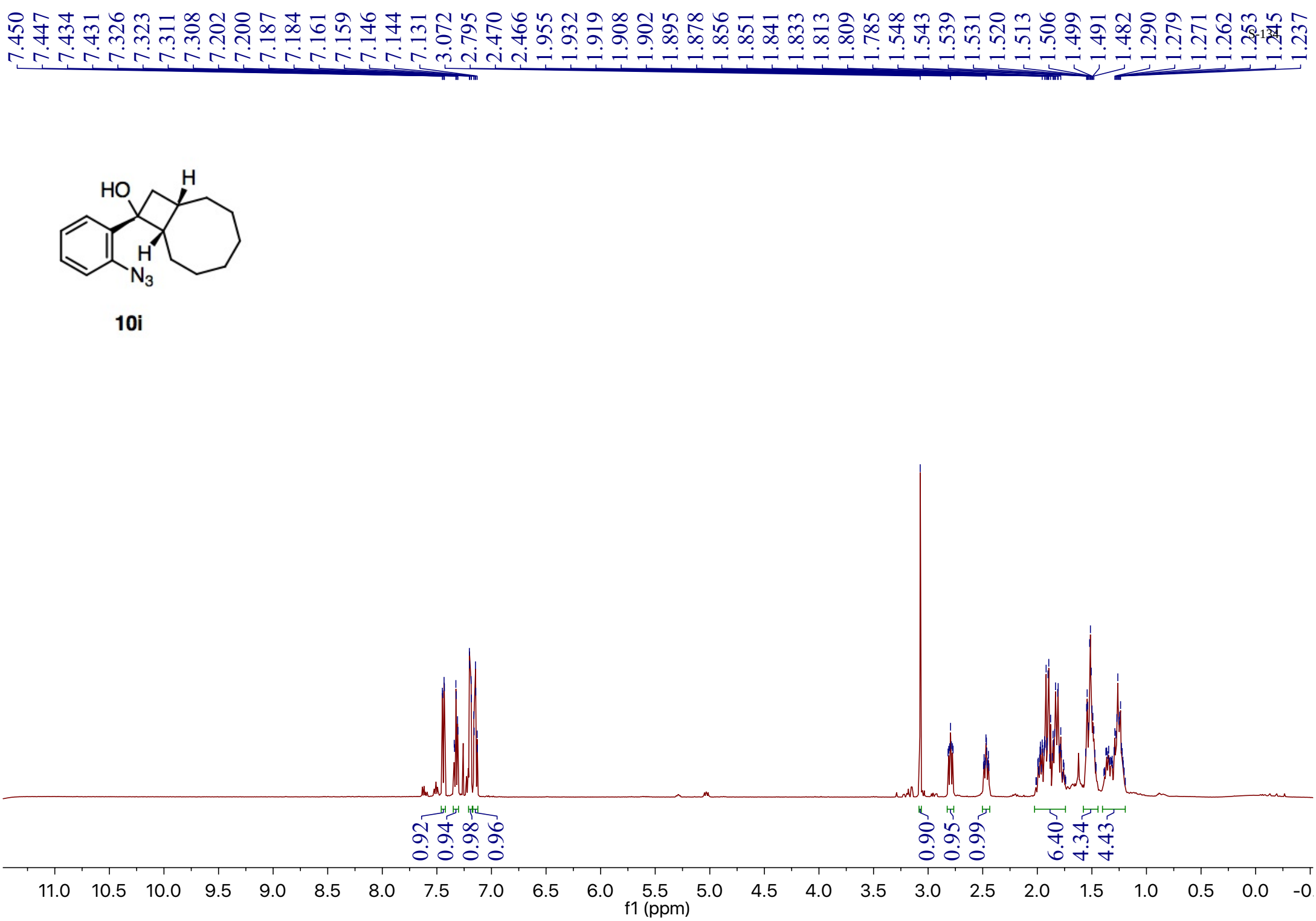
127.432
124.832
118.428
77.112
53.123
34.237
32.796
32.400
28.560
24.744



10h

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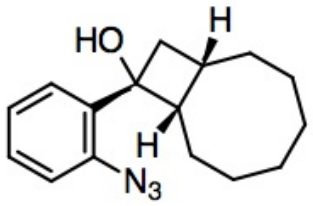
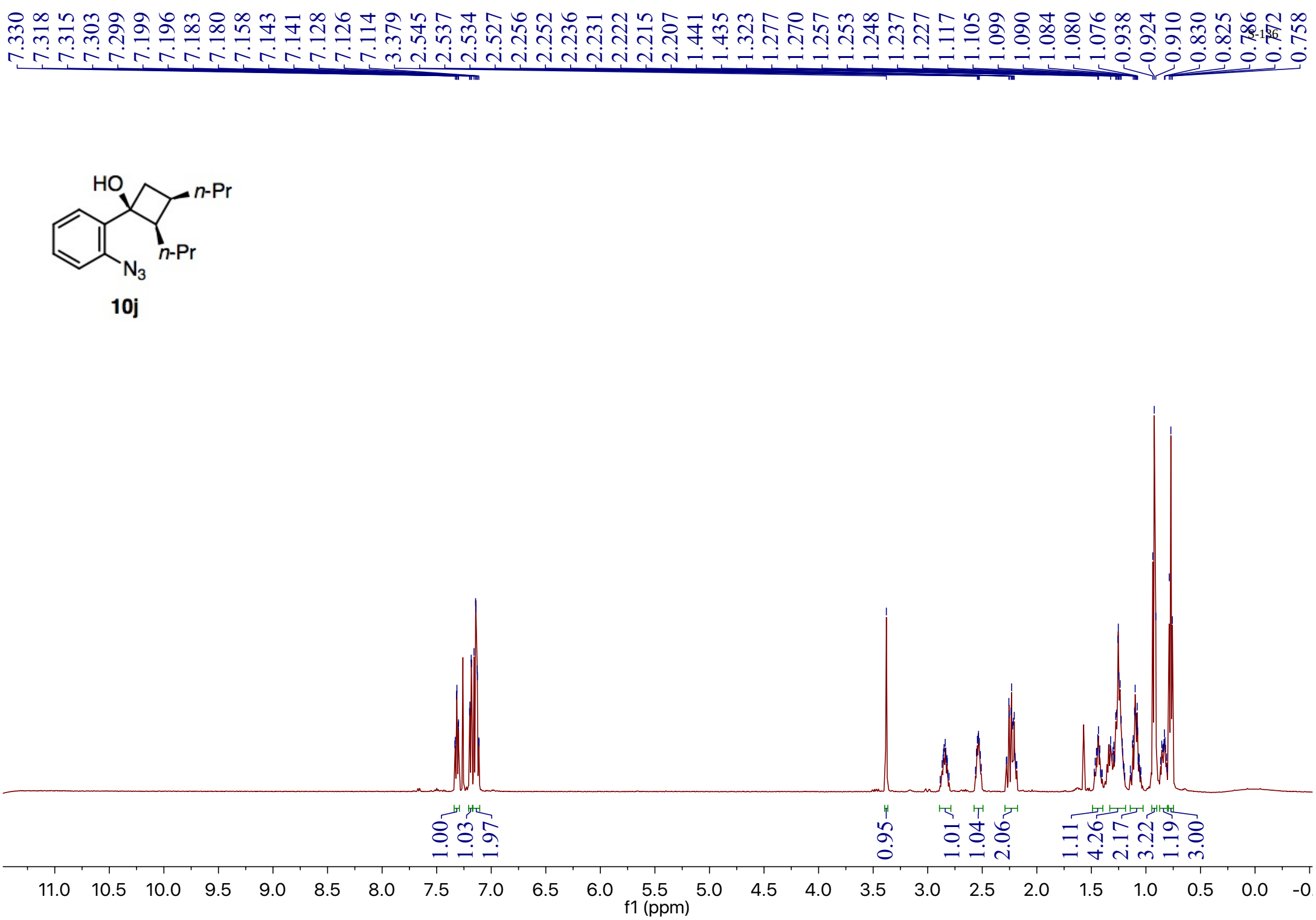
7.447
7.434
7.431
7.326
7.323
7.311
7.308
7.202
7.200
7.187
7.184
7.161
7.159
7.146
7.144
7.131
3.072
2.795
2.470
2.466
1.955
1.932
1.919
1.908
1.902
1.895
1.878
1.856
1.851
1.841
1.833
1.813
1.809
1.785
1.548
1.543
1.539
1.531
1.520
1.513
1.506
1.499
1.491
1.482
1.290
1.279
1.271
1.262
1.253
1.245
1.237
HO
H
H
N3
10i
0.92
0.94
0.98
0.96
0.90
0.95
0.99
6.40
4.34
4.43
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

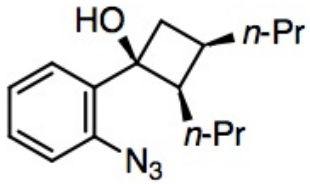
137.333
133.965
128.668
127.558
124.965
118.069
79.068
53.975
35.301
32.918
31.047
28.846
27.667
26.059
25.898
25.209



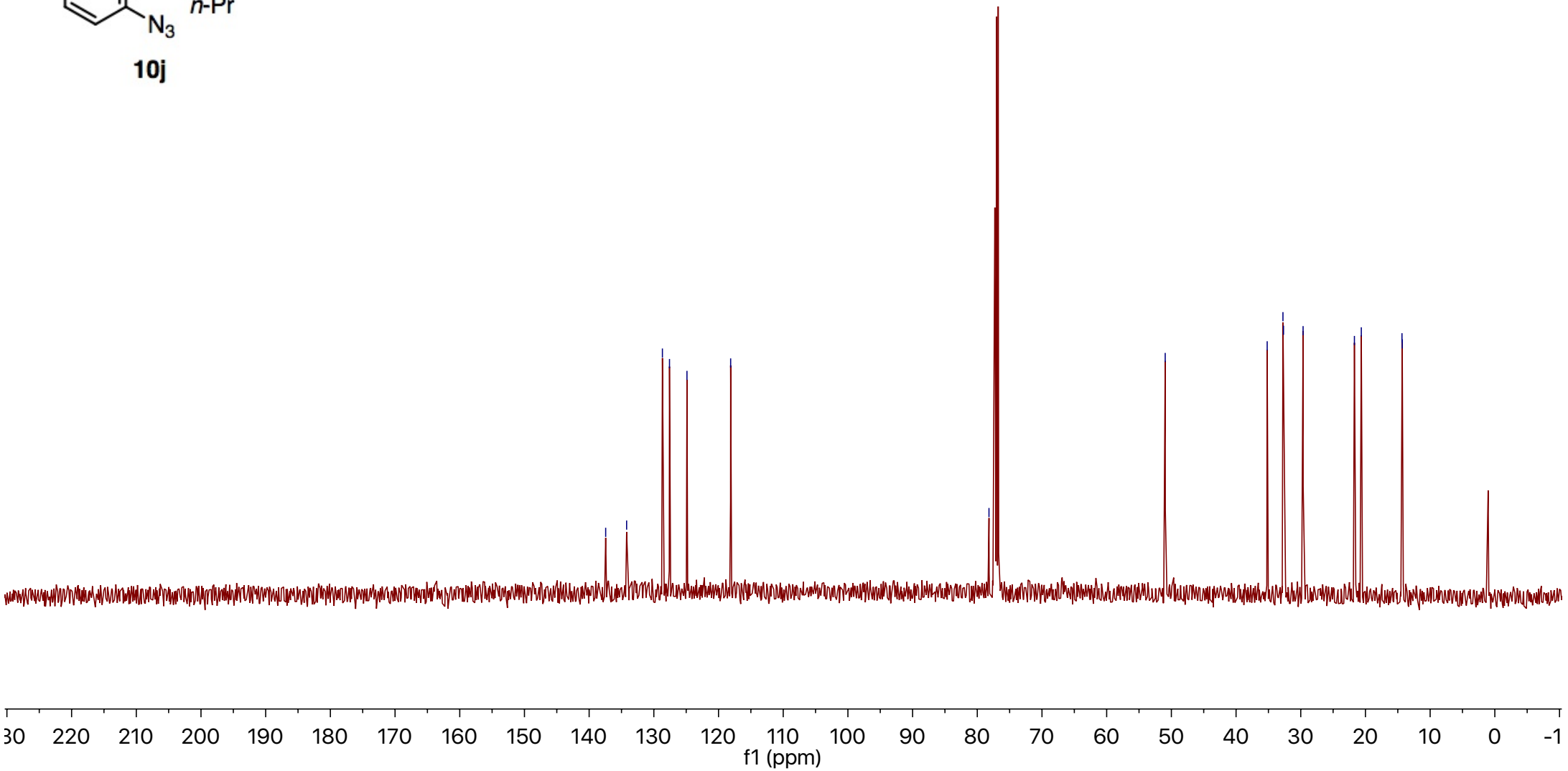
10i

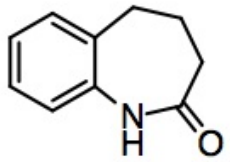

7.330
7.318
7.315
7.303
7.299
7.199
7.196
7.183
7.180
7.158
7.143
7.141
7.128
7.126
7.114
3.379
2.545
2.537
2.534
2.527
2.256
2.252
2.236
2.231
2.222
2.215
2.207
1.441
1.435
1.323
1.277
1.270
1.257
1.253
1.248
1.237
1.227
1.117
1.105
1.099
1.090
1.084
1.080
1.076
0.938
0.924
0.910
0.830
0.825
0.786
0.772
0.758
S-156
HO
n-Pr
n-Pr
N3
10j
1.00
1.03
1.97
0.95
1.01
1.04
2.06
1.11
4.26
2.17
3.22
1.19
3.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

137.444
134.205
128.675
127.579
124.878
118.125
78.193
50.952
35.188
32.752
32.664
29.639
21.705
20.640
14.352
14.310



10j

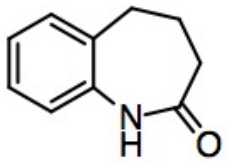




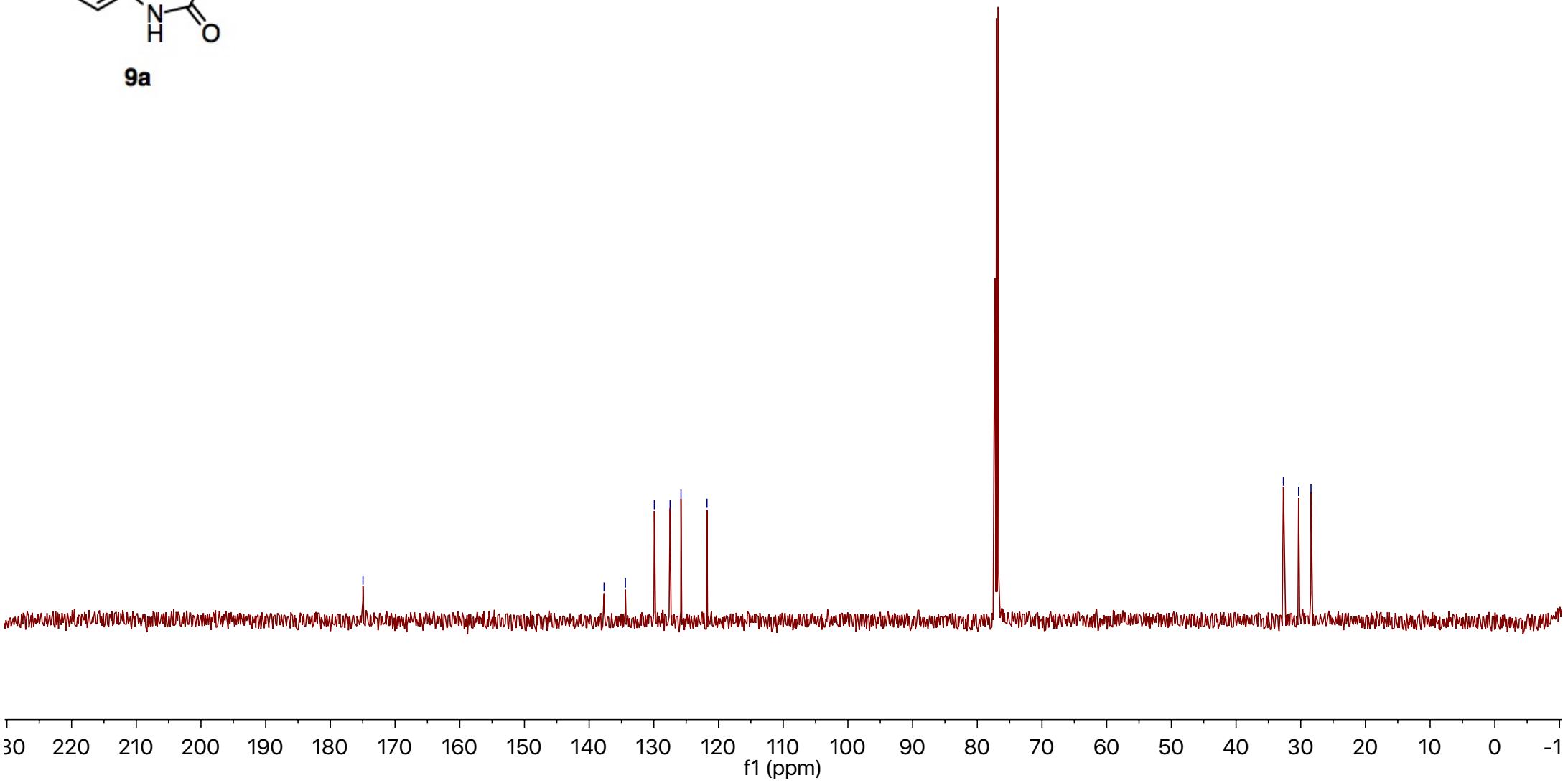
9a

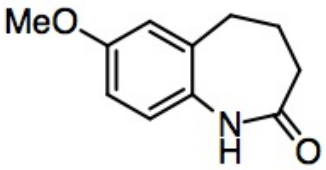
7.552
7.261
7.258
7.252
7.237
7.234
7.230
7.222
7.218
7.156
7.153
7.141
7.138
7.126
7.123
6.975
6.960
2.823
2.808
2.794
2.376
2.361
2.347
2.265
2.251
2.237
2.222
2.207
0.91
2.10
0.98
0.99
2.04
2.06
2.05
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

174.959
137.689
134.397
129.916
127.483
125.802
121.784
32.679
30.331
28.417



9a

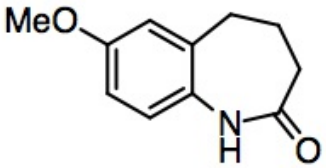



MeO
N
H
O

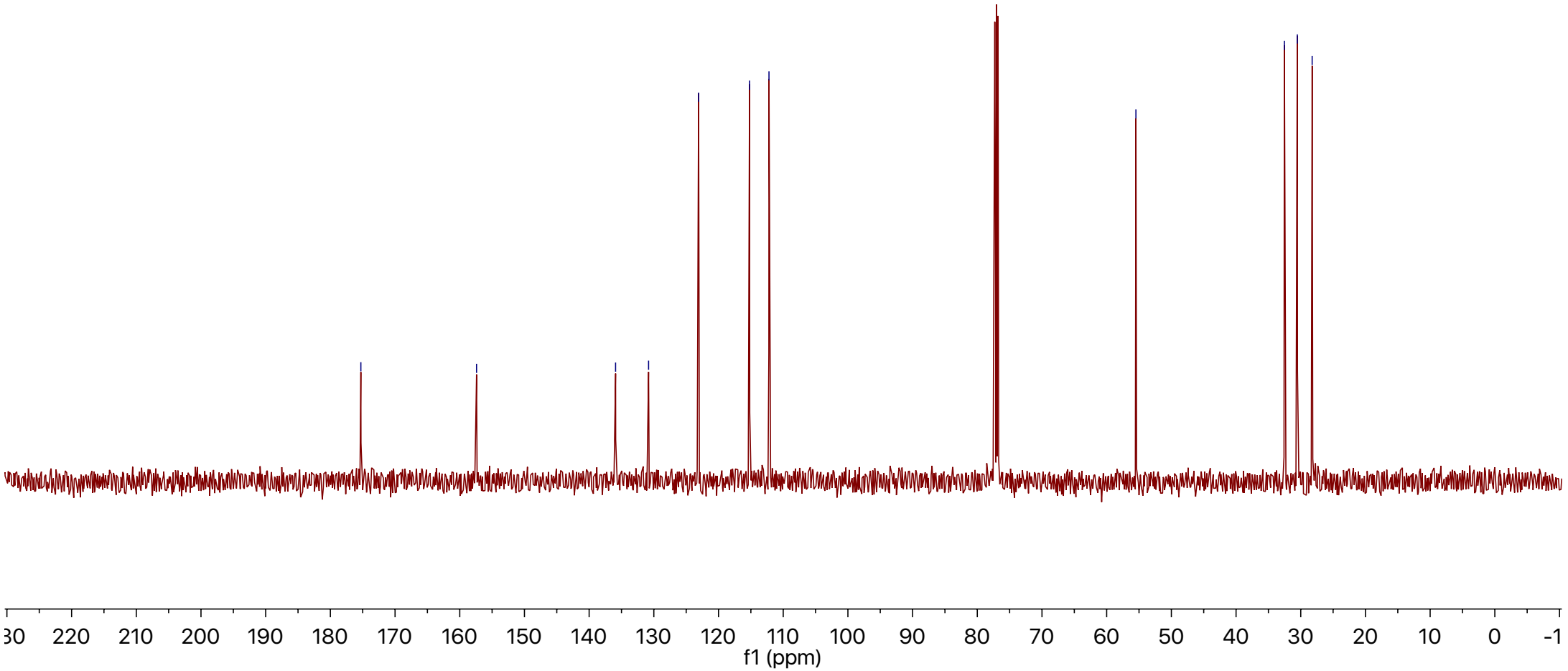
9b

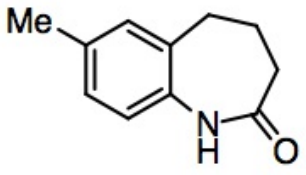
7.949
6.929
6.912
6.756
6.740
6.734
3.794
2.774
2.760
2.746
2.339
2.324
2.310
2.236
2.221
2.207
2.193
2.178
1.00
1.09
2.18
3.30
2.21
2.22
2.23
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

175.286
157.402
135.913
130.812
123.080
115.204
112.199
55.480
32.529
30.532
28.237

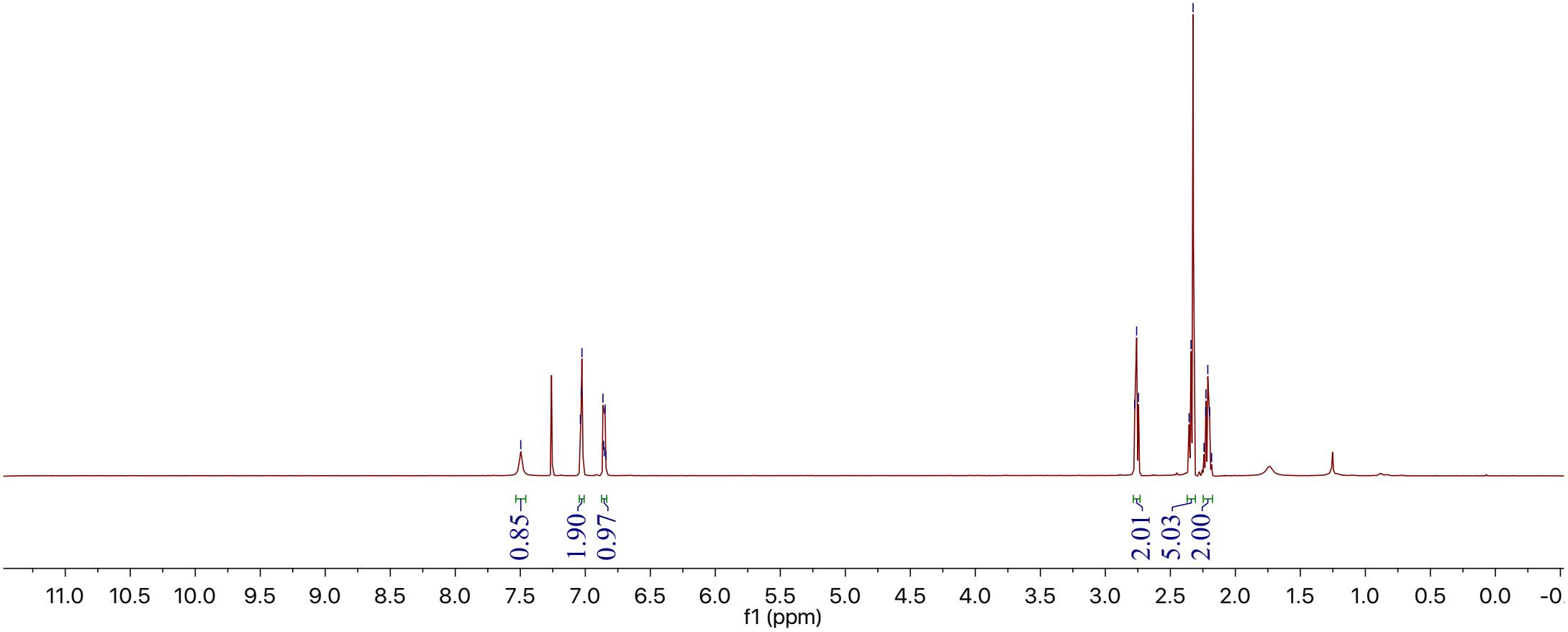


9b




Me
N
H
O

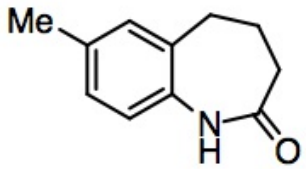
9c


7.496
7.038
7.031
7.026
6.864
6.859
6.854
6.847
6.842
2.774
2.759
2.745
2.356
2.341
2.325
2.241
2.228
2.226
2.212
2.197
2.183
0.85
1.90
0.97
2.01
5.03
2.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

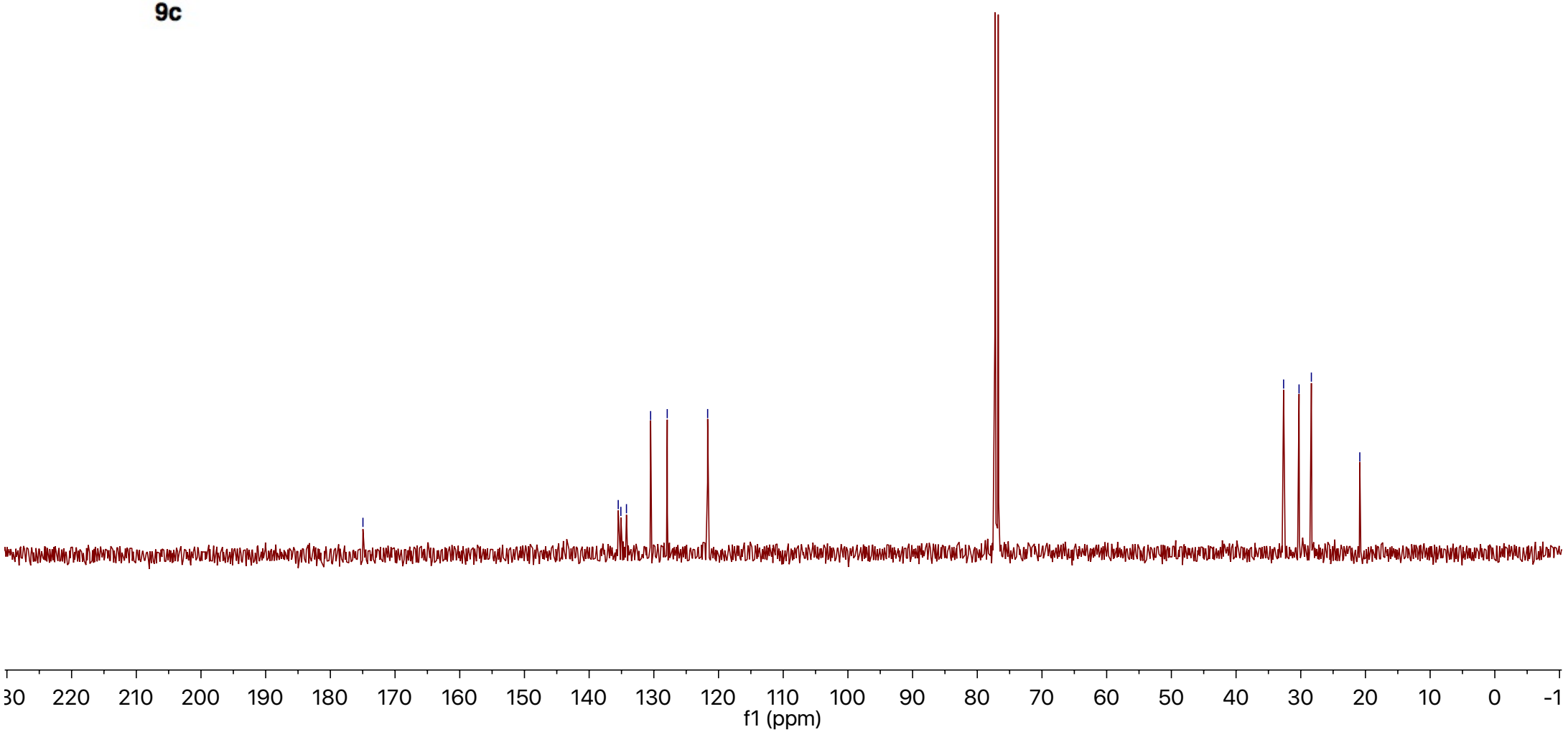
174.965

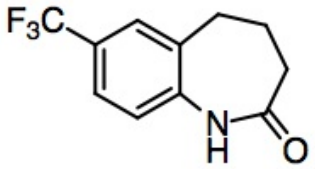
135.503
135.096
134.230
130.497
127.928
121.682

32.649
30.264
28.360
20.873



9c

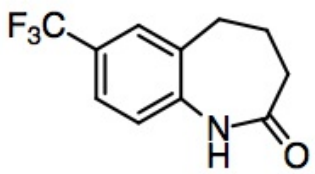



F3C
N
H
O

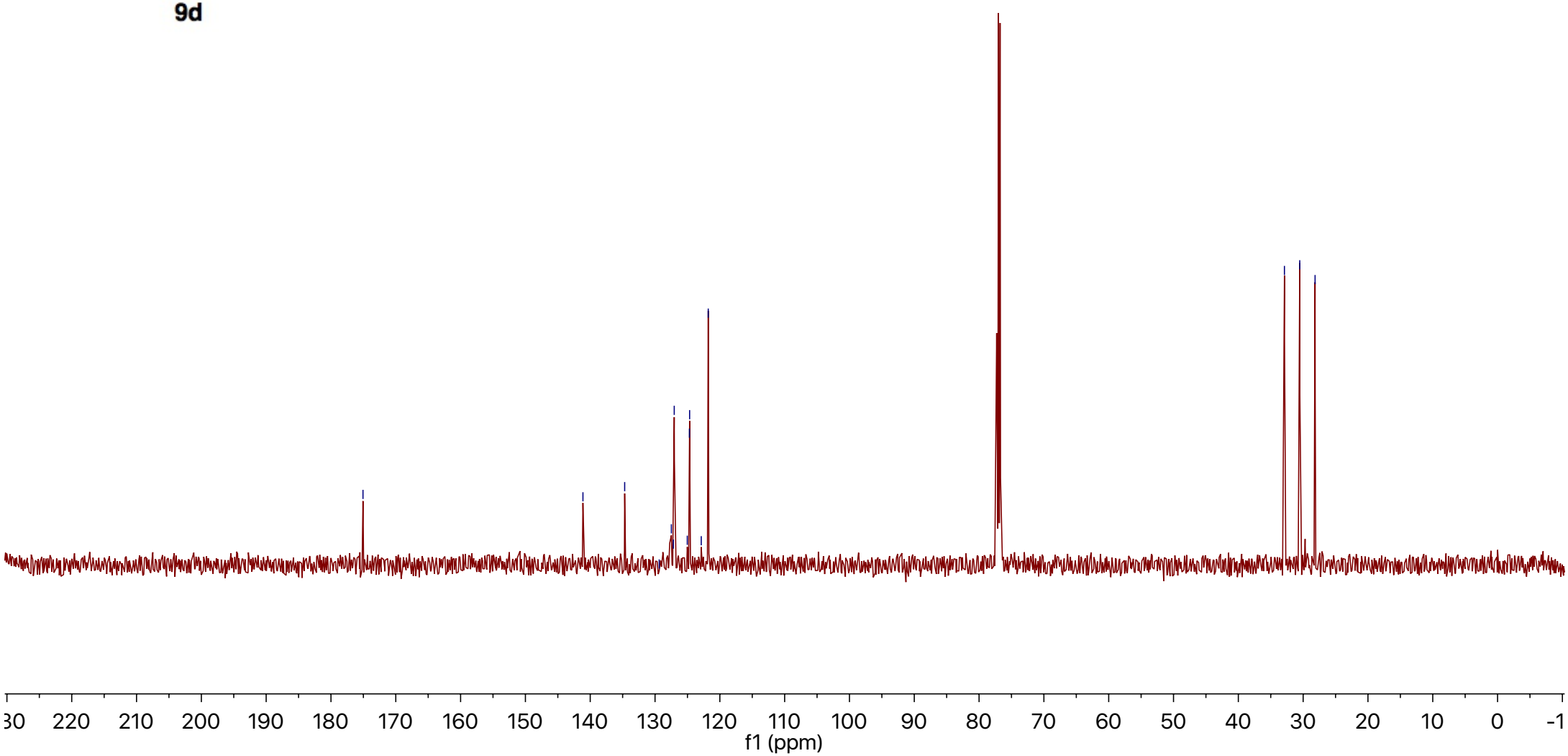
9d

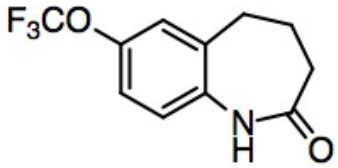
8.368
7.509
7.505
7.490
7.479
7.463
7.099
7.083
2.881
2.867
2.852
2.411
2.397
2.382
2.310
2.295
2.281
2.266
2.252
1.00
2.16
1.09
2.25
2.25
2.24
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

175.061
141.122
134.685
129.358
127.479
127.177
127.036
125.023
124.692
124.663
122.868
121.789
32.886
30.523
28.158



9d

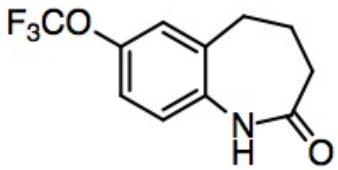



F3CO
N
H
O

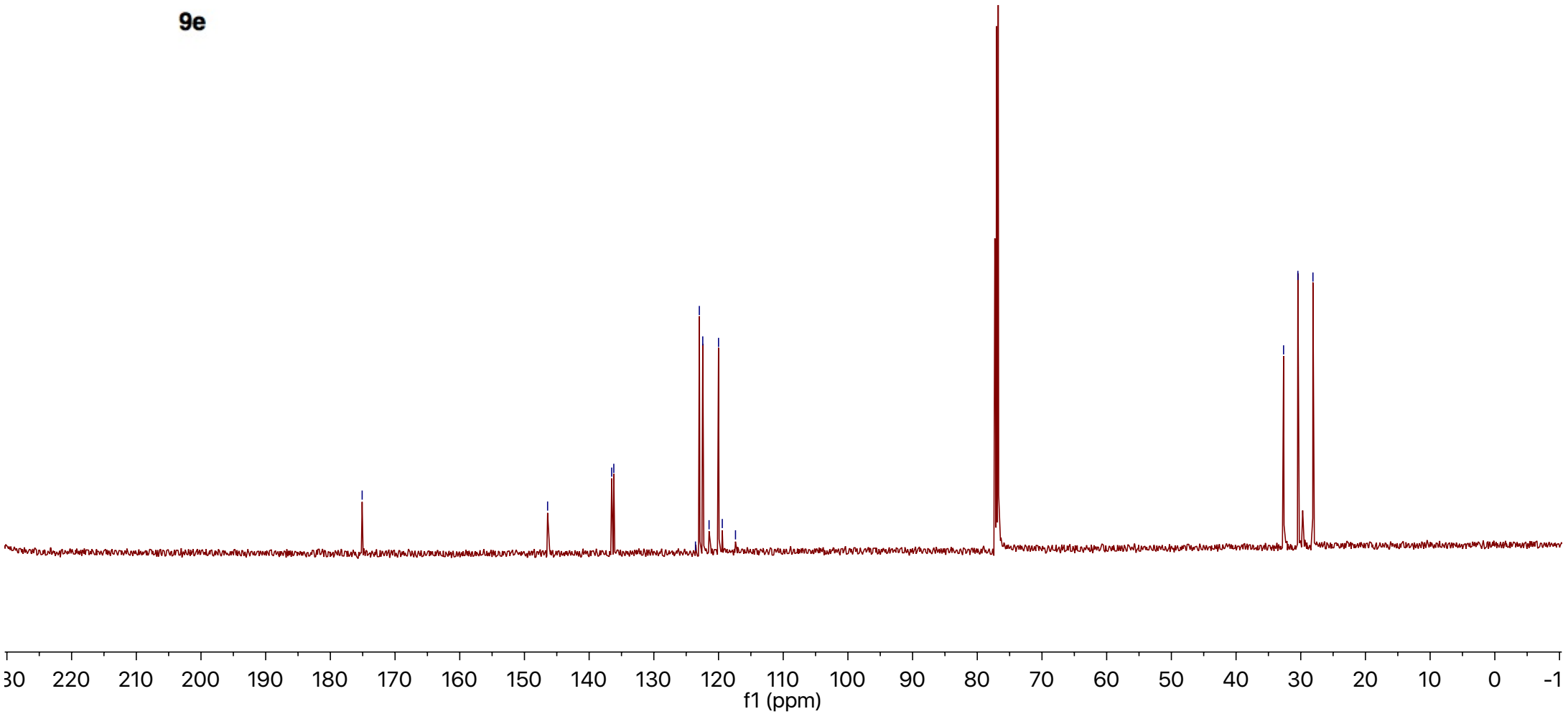
9e

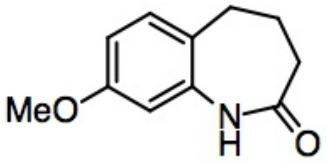
8.346
7.104
7.096
7.089
7.084
7.036
7.029
7.020
7.011
2.823
2.808
2.794
2.387
2.372
2.358
2.282
2.268
2.253
2.239
2.225
1.00
2.03
1.04
2.13
2.18
2.14
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

175.086
146.421
136.513
136.188
123.564
122.967
122.436
121.462
119.997
119.419
117.377
32.653
30.443
28.114



9e

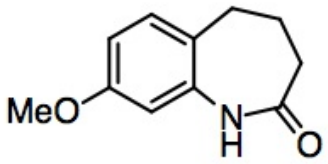



MeO
N
H
O

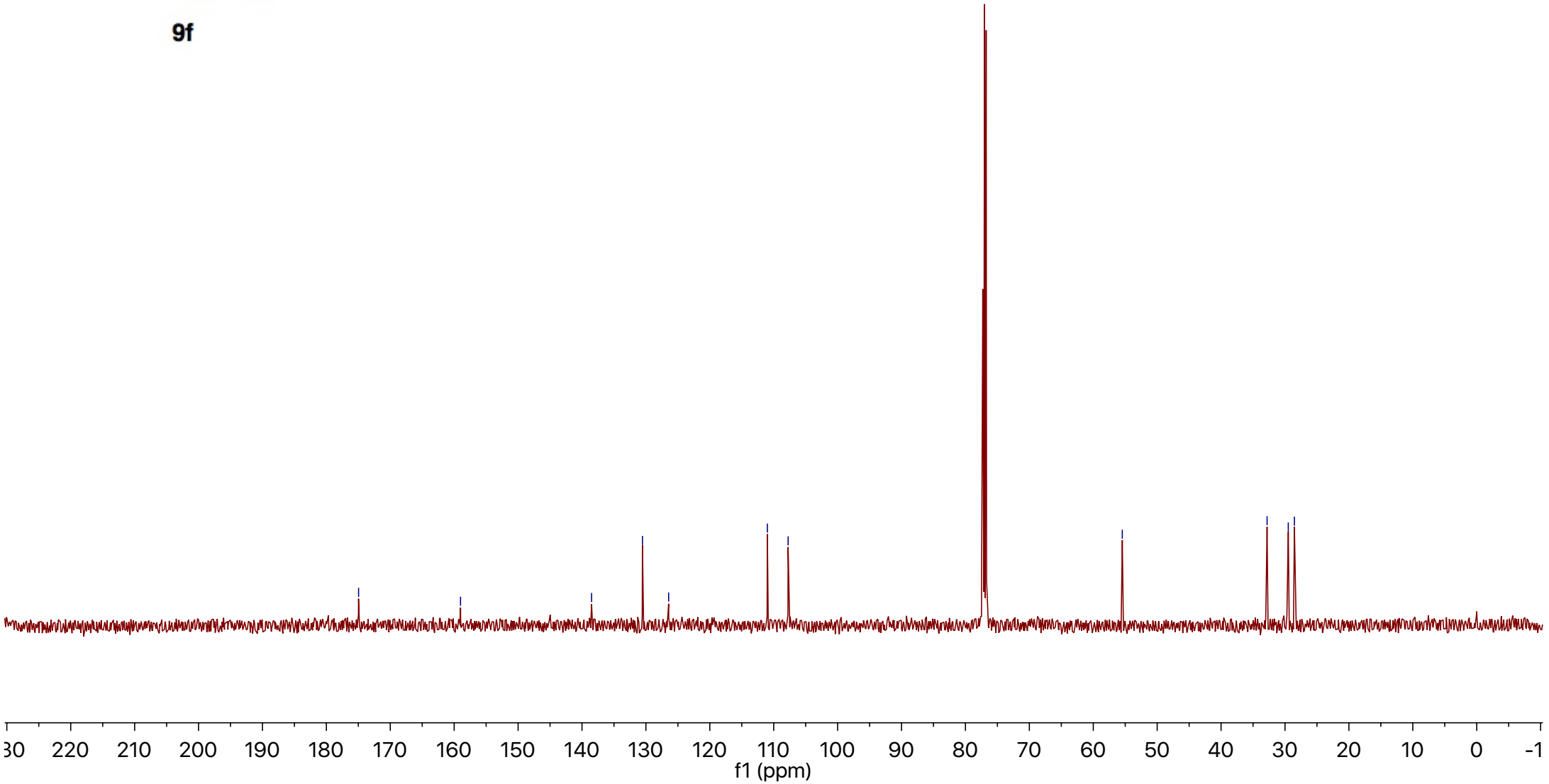
9f

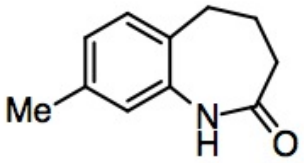
7.375
7.122
7.105
6.699
6.694
6.683
6.678
6.519
6.514
3.791
2.750
2.736
2.721
2.370
2.355
2.341
2.221
2.206
2.192
2.177
2.163
1.00
1.09
1.06
1.07
3.28
2.17
2.24
2.20
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

174.959
159.008
138.500
130.538
126.441
110.995
107.747
55.460
32.803
29.486
28.529



9f

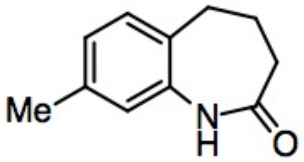



Me
N
H
O

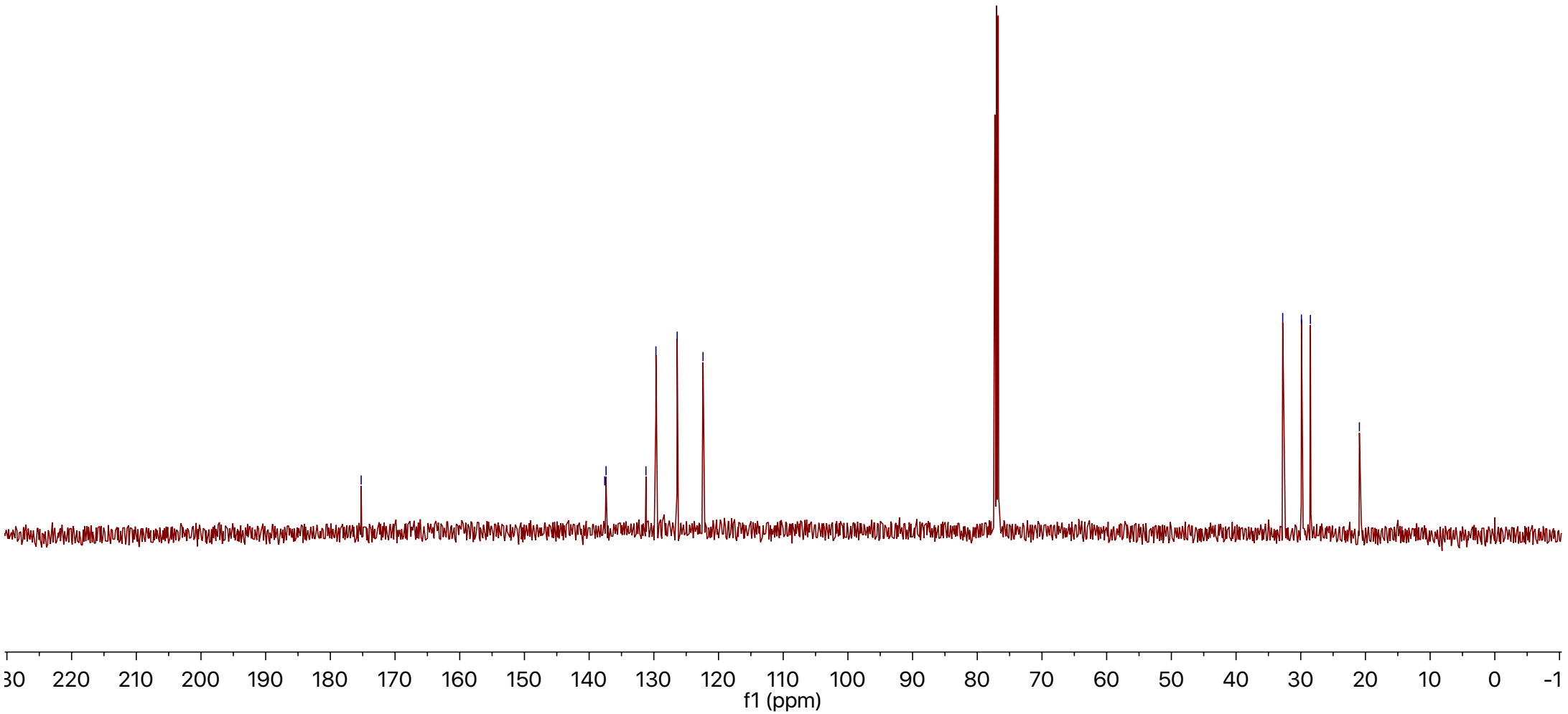
9g

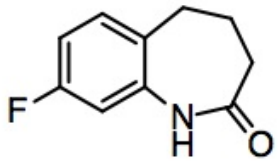
7.758
7.103
7.088
6.950
6.935
6.795
2.775
2.761
2.747
2.367
2.352
2.338
2.325
2.238
2.224
2.209
2.195
2.180
0.93
1.00
0.99
0.99
2.06
5.17
2.11
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

175.238
137.591
137.385
131.218
129.676
126.393
122.397
32.790
29.893
28.507
20.935



9g

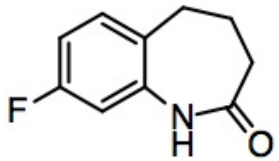



F
N
H
O

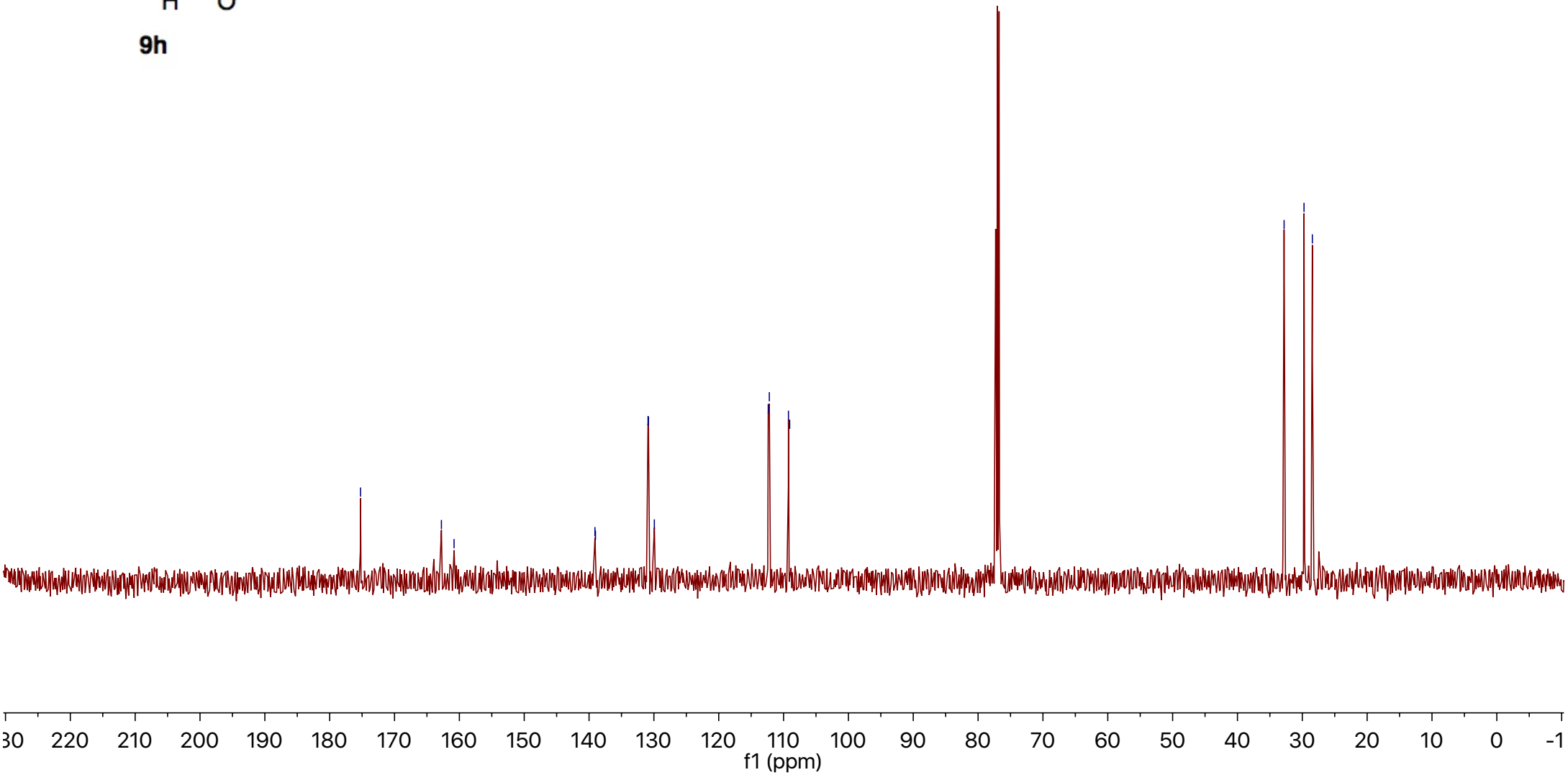
9h

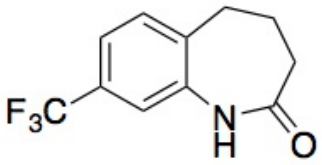
8.221
7.175
7.163
7.158
7.146
6.855
6.850
6.839
6.833
6.822
6.817
6.754
6.749
6.736
6.731
2.785
2.771
2.756
2.383
2.369
2.354
2.249
2.235
2.220
2.205
2.191
1.00
1.09
1.05
1.03
2.13
2.27
2.25
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

175.243
162.770
160.817
139.091
139.012
130.905
130.834
129.929
112.365
112.199
109.245
109.059
32.807
29.733
28.448

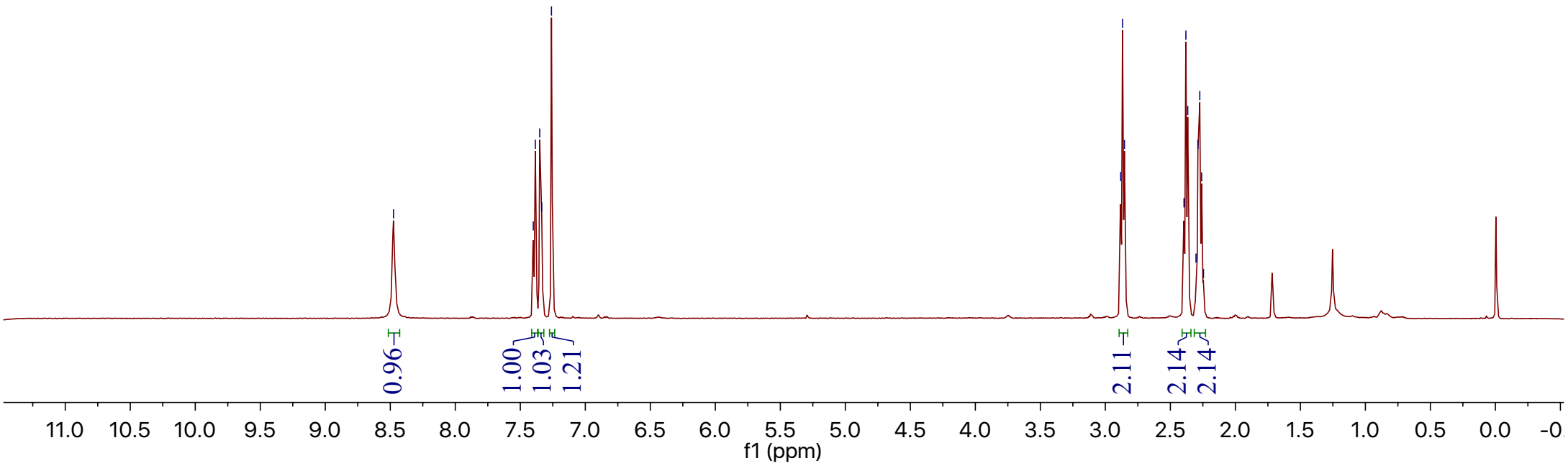


9h

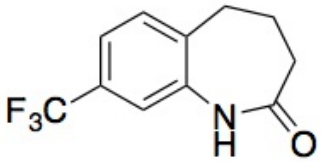



F3C
N
H
O

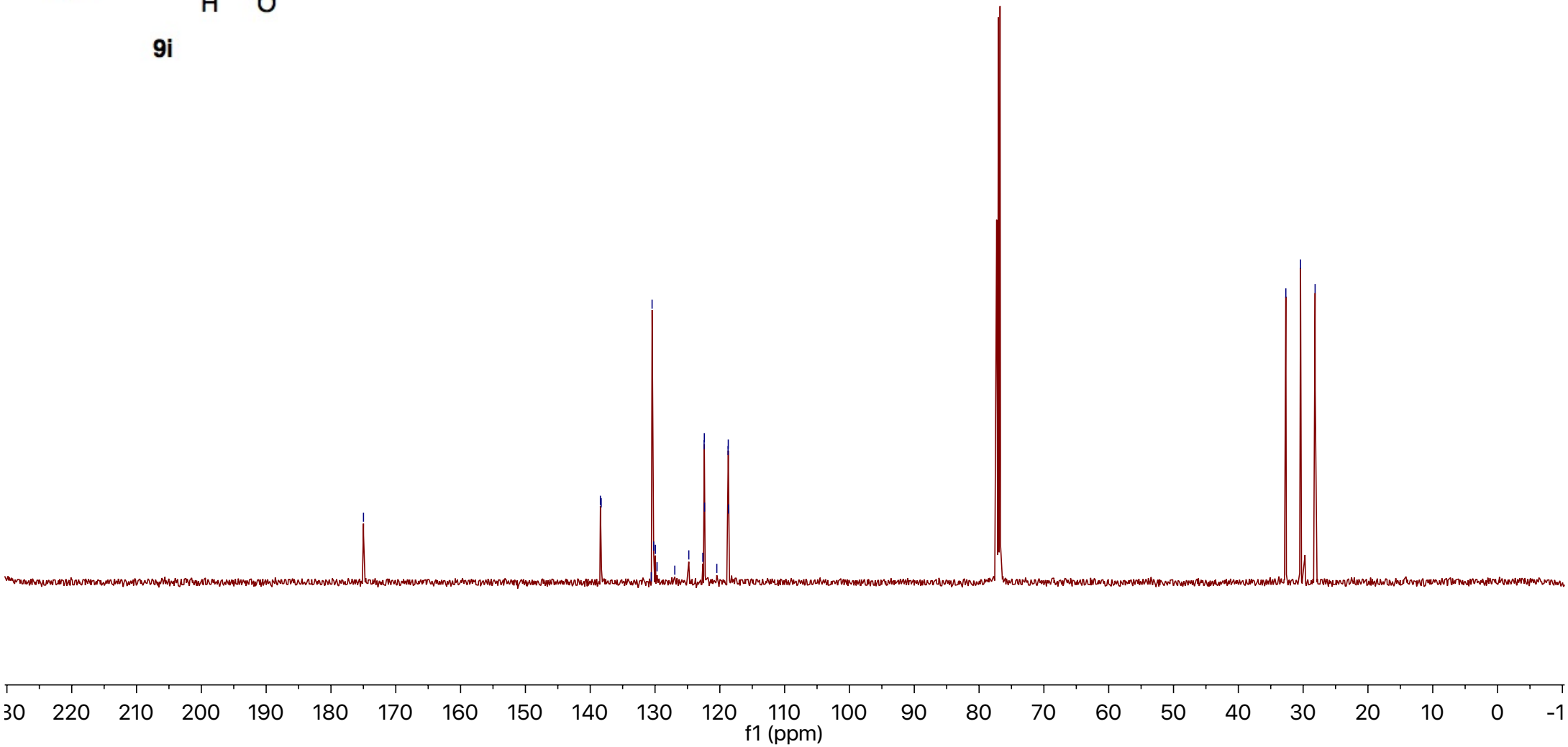
9i

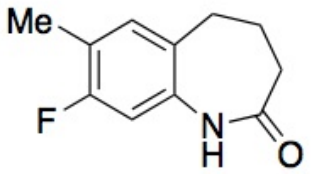

8.475
7.400
7.384
7.351
7.335
7.260
2.882
2.867
2.853
2.395
2.381
2.366
2.303
2.288
2.274
2.259
2.245
0.96
1.00
1.03
1.21
2.11
2.14
2.14
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

174.983
138.430
138.309
130.583
130.454
130.211
129.949
129.688
126.950
124.789
122.627
122.424
122.394
122.365
120.466
118.729
118.699
118.670
32.670
30.401
28.152



9i

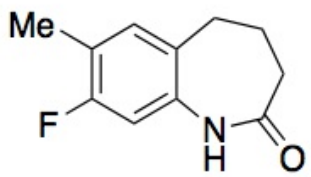



Me
F
N
H
O

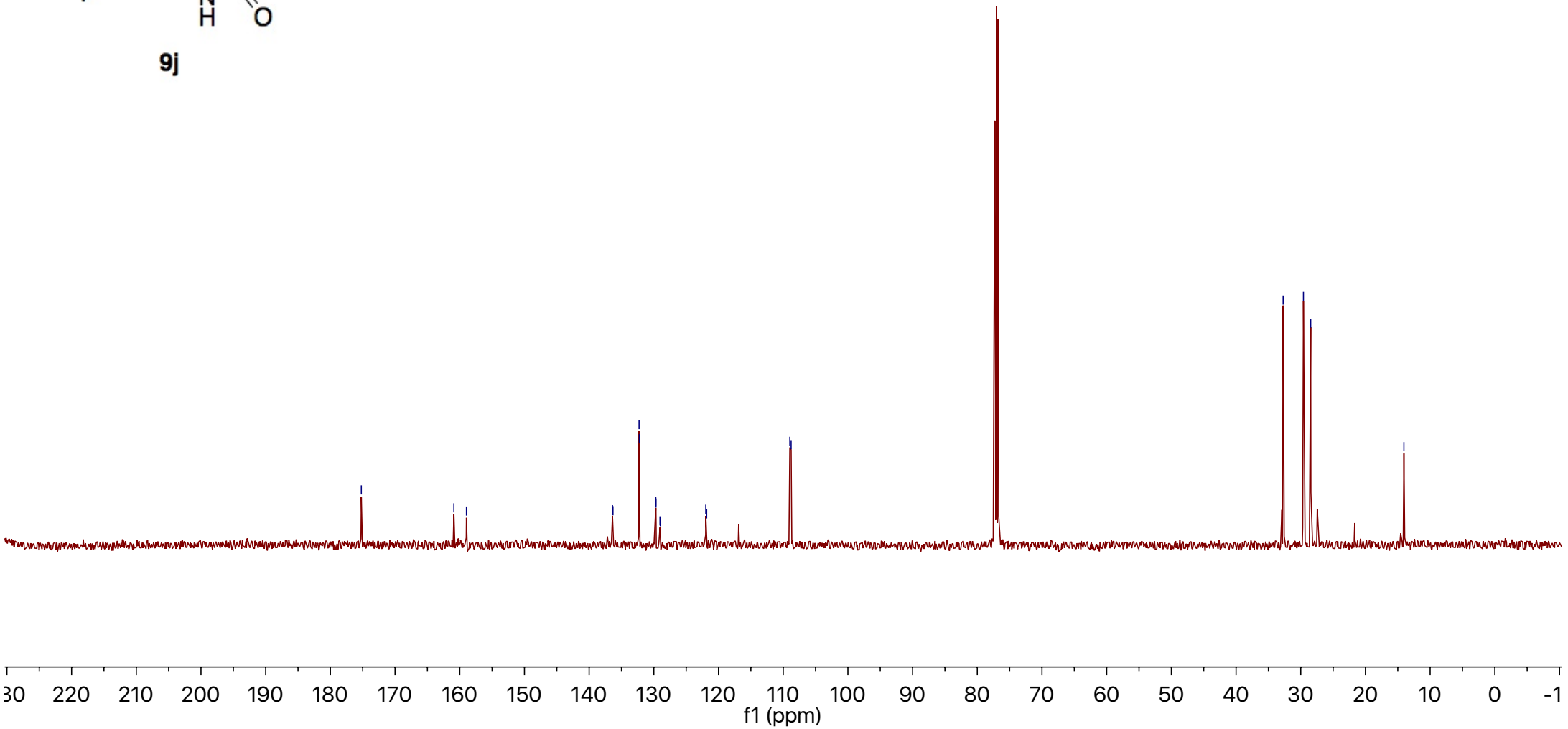
9j

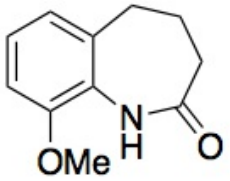
7.926
7.013
6.997
6.690
6.670
2.741
2.726
2.712
2.361
2.346
2.332
2.259
2.254
2.237
2.233
2.226
2.212
2.197
2.182
2.168
0.98
1.00
0.96
1.90
2.18
5.36
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

175.214
160.906
158.966
136.396
136.318
132.281
132.233
129.697
129.674
129.043
128.996
121.968
121.836
108.974
108.779
32.722
29.586
28.463
14.054



9j

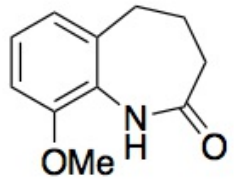



OMe
N
H
O

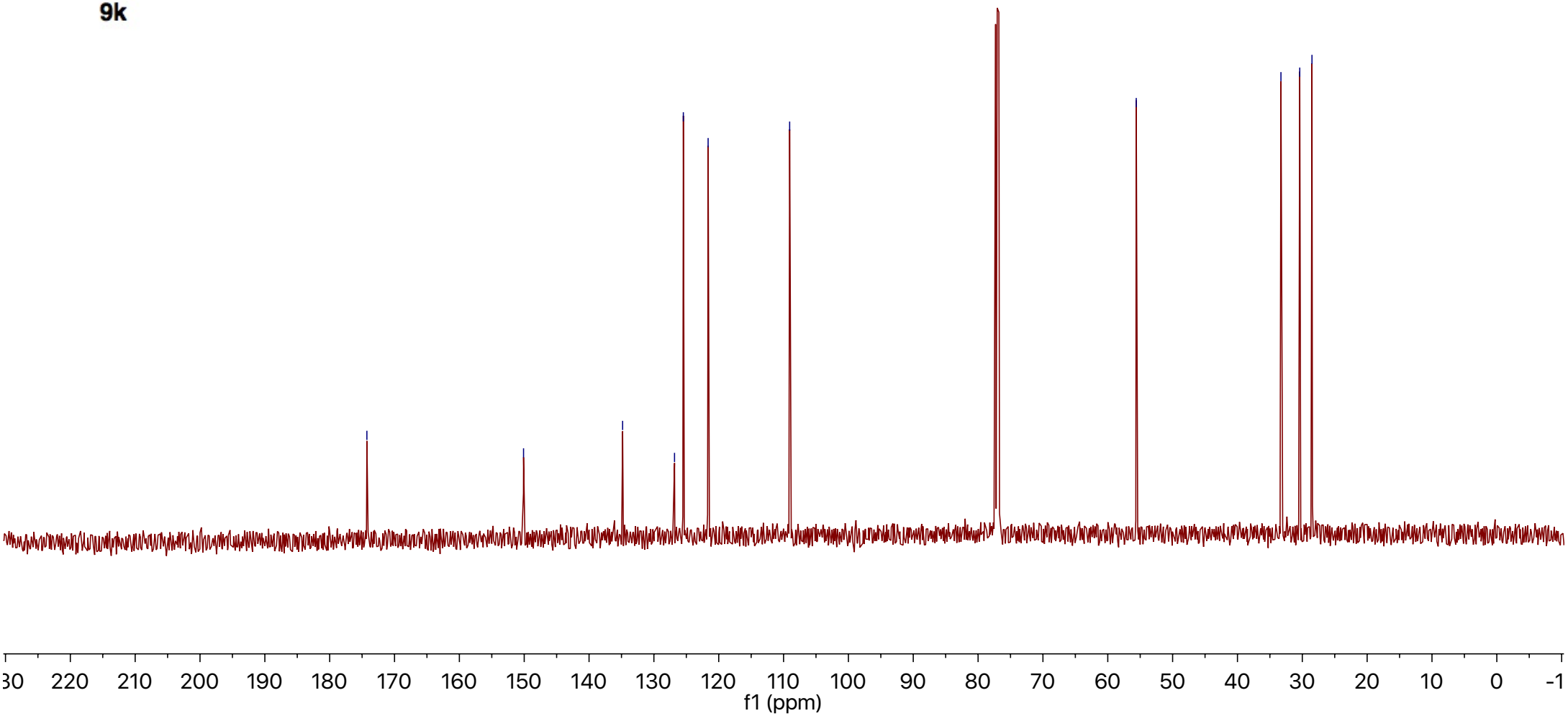
9k

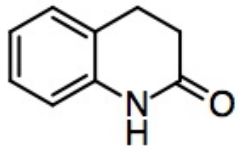
7.223
7.082
7.066
7.051
6.818
6.803
6.787
3.832
2.793
2.779
2.764
2.387
2.373
2.358
2.262
2.248
2.234
2.219
2.204
0.88
1.00
2.01
3.12
2.10
2.11
2.11
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

174.263
150.102
134.823
126.819
125.458
121.637
109.063
55.609
33.293
30.392
28.507



9k

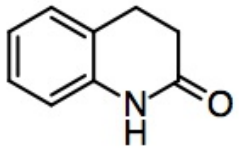




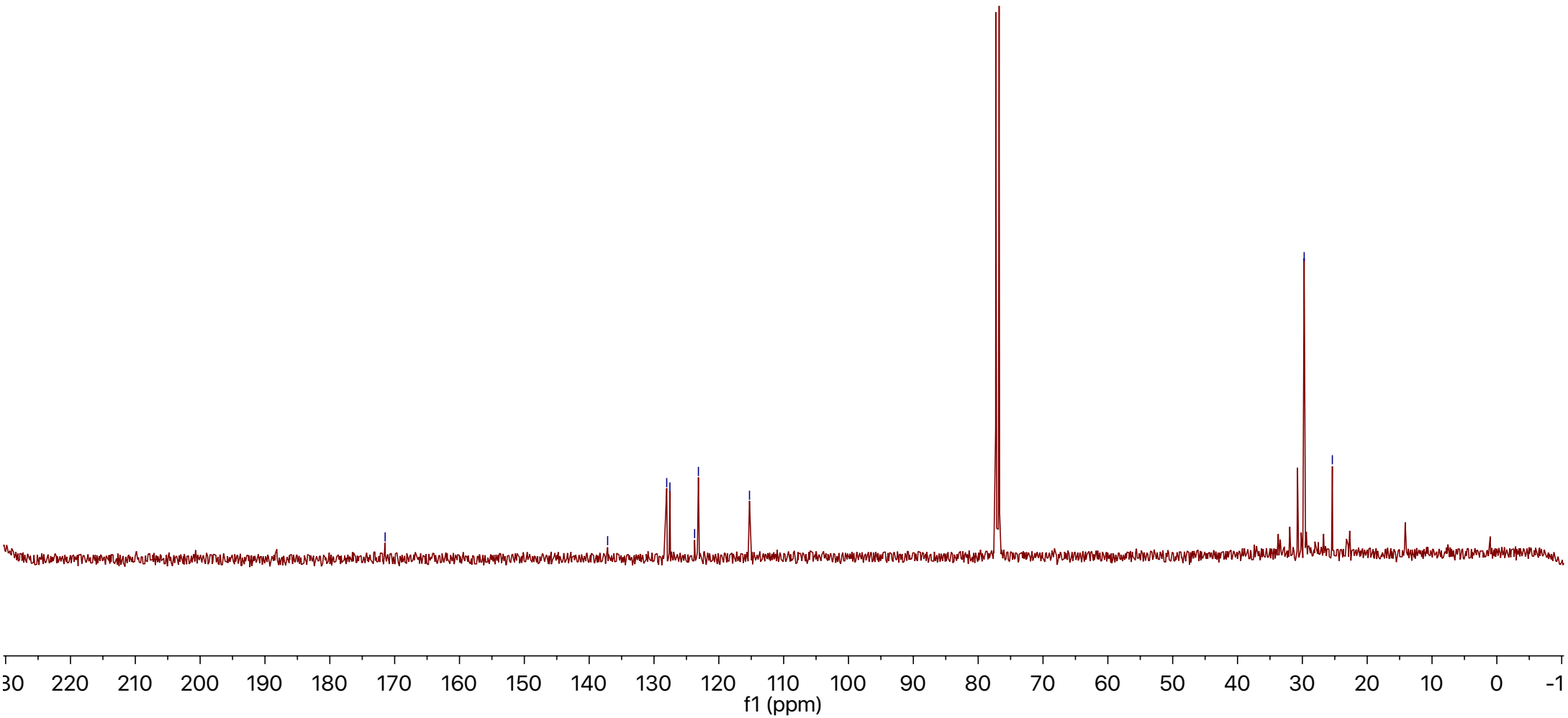
11a

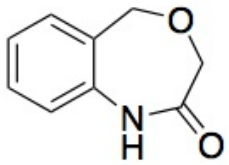
7.658
7.190
7.176
7.161
7.009
6.994
6.979
6.739
6.723
2.988
2.973
2.958
2.657
2.641
2.627
0.74
2.11
1.03
1.06
2.29
2.20
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

171.470
137.152
128.041
127.547
123.736
123.149
115.272
29.719
25.372

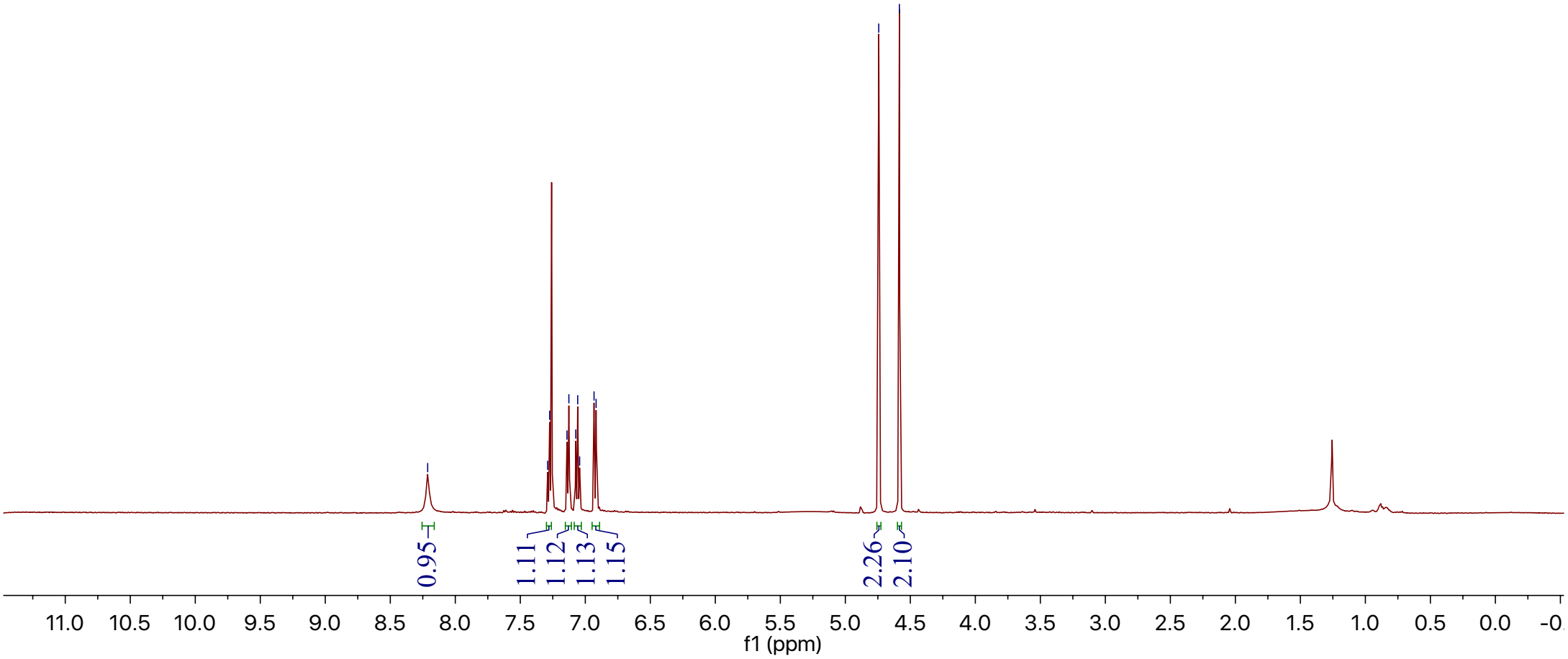


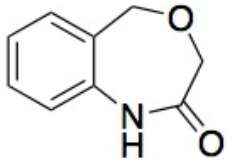
11a





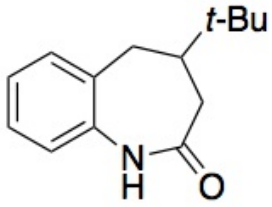
11b


8.212
7.290
7.274
7.141
7.126
7.073
7.058
7.044
6.933
6.917
4.743
4.584
0.95
1.11
1.12
1.13
1.15
2.26
2.10
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)


O
N
H
O

11b

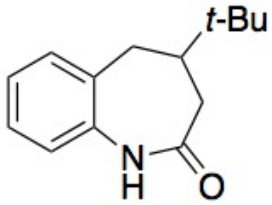
173.159
135.828
129.199
128.714
128.577
123.765
119.206
73.461
72.864
f1 (ppm)


t-Bu
N
H
O

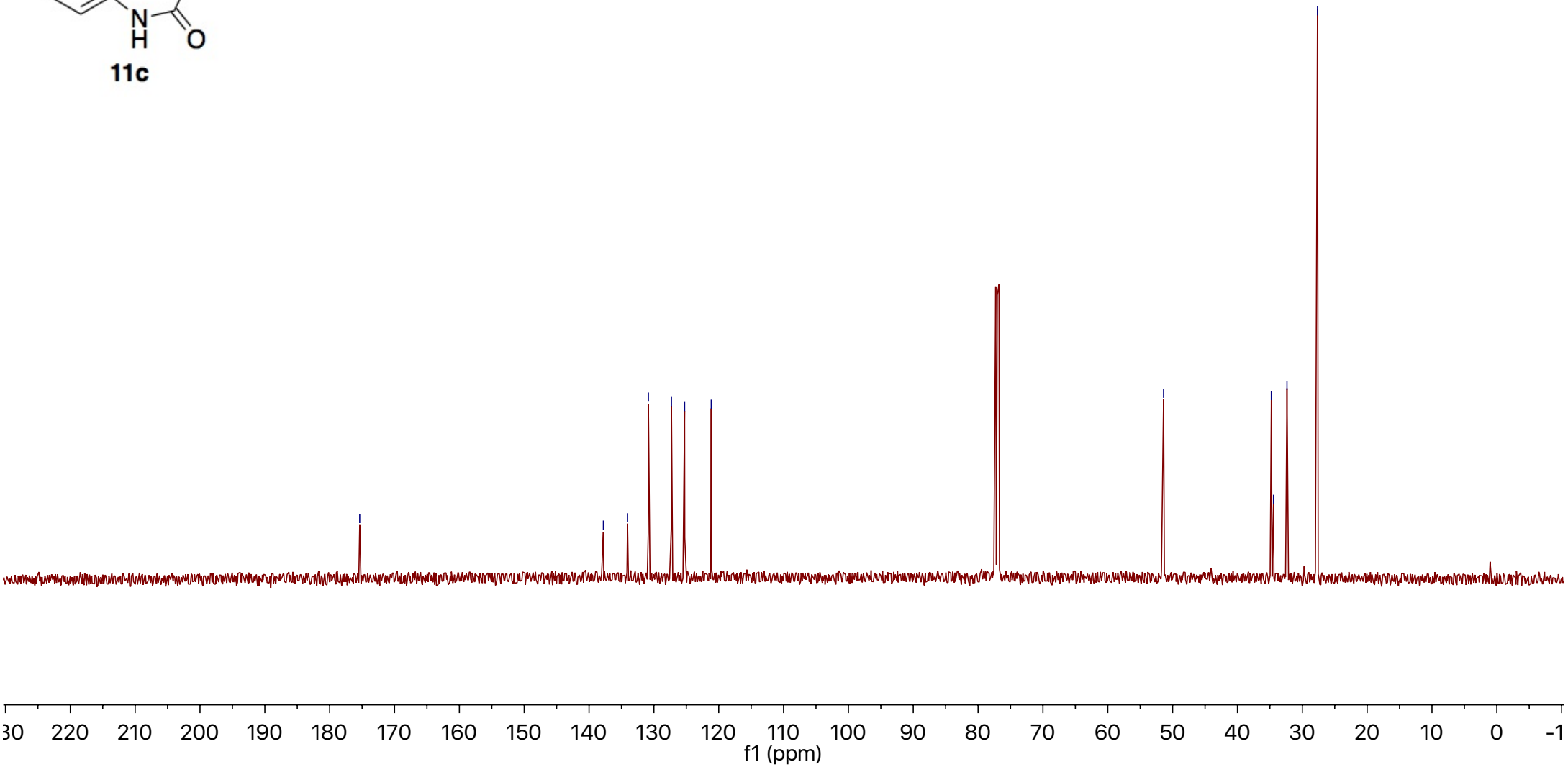
11c

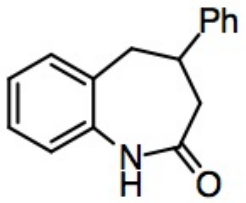
8.085
7.244
7.241
7.227
7.213
7.209
7.197
7.194
7.117
7.114
7.102
7.099
7.087
7.084
6.958
6.955
6.942
6.940
2.827
2.813
2.810
2.799
2.794
2.433
2.420
2.408
2.394
2.383
2.369
2.357
2.343
2.229
2.215
2.201
2.186
2.172
1.00
2.13
1.08
1.04
2.03
2.16
1.09
9.70
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

175.371
137.790
134.067
130.849
127.294
125.263
121.152
51.395
34.776
34.435
32.363
27.655

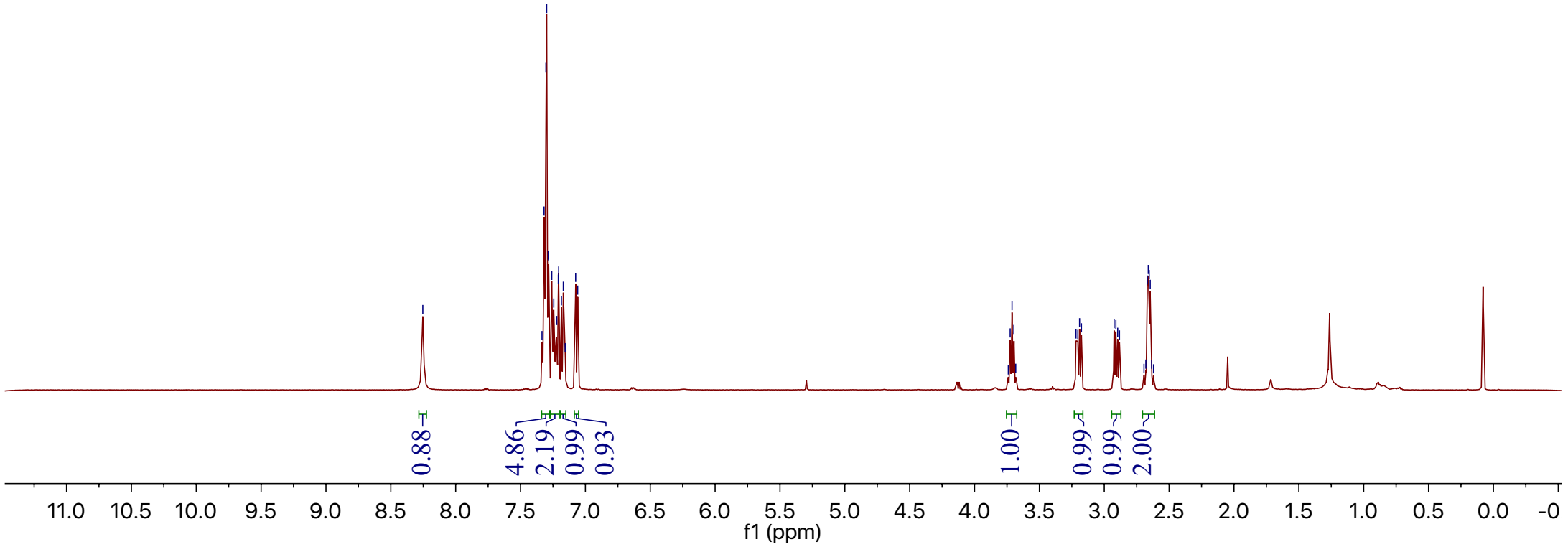


11c

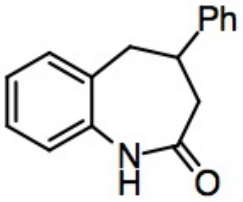



Ph
N
H
O

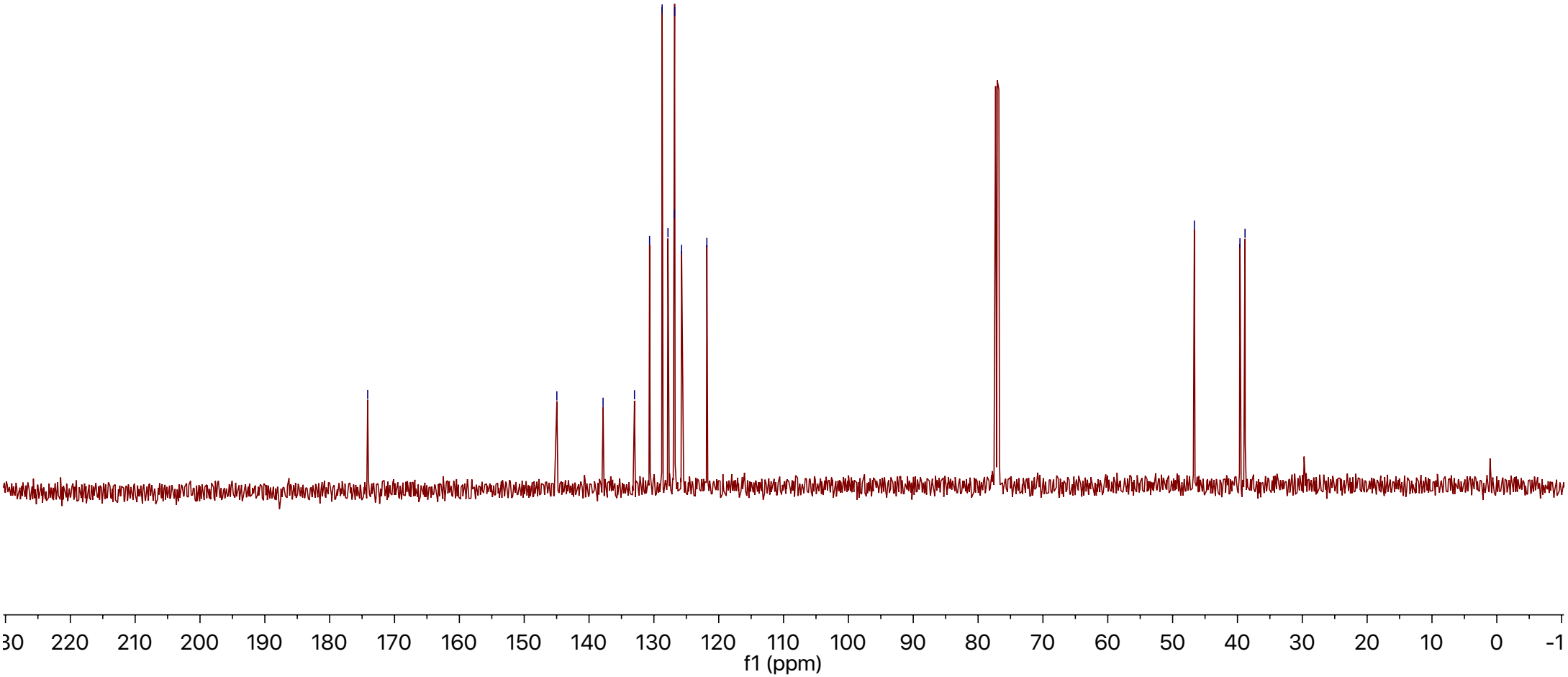
11d

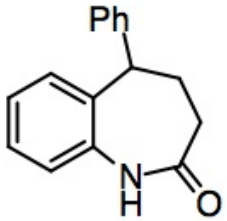

8.253
7.334
7.319
7.304
7.299
7.286
7.283
7.259
7.244
7.221
7.209
7.206
7.185
7.170
7.156
7.075
7.060
3.740
3.725
3.711
3.697
3.682
3.218
3.204
3.190
3.176
2.924
2.910
2.896
2.883
2.694
2.679
2.668
2.660
2.654
2.646
2.635
2.620
0.88
4.86
2.19
0.99
0.93
1.00
0.99
0.99
2.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

174.141
144.967
137.838
132.993
130.667
128.725
127.830
126.854
126.799
125.730
121.830
46.650
39.615
38.831

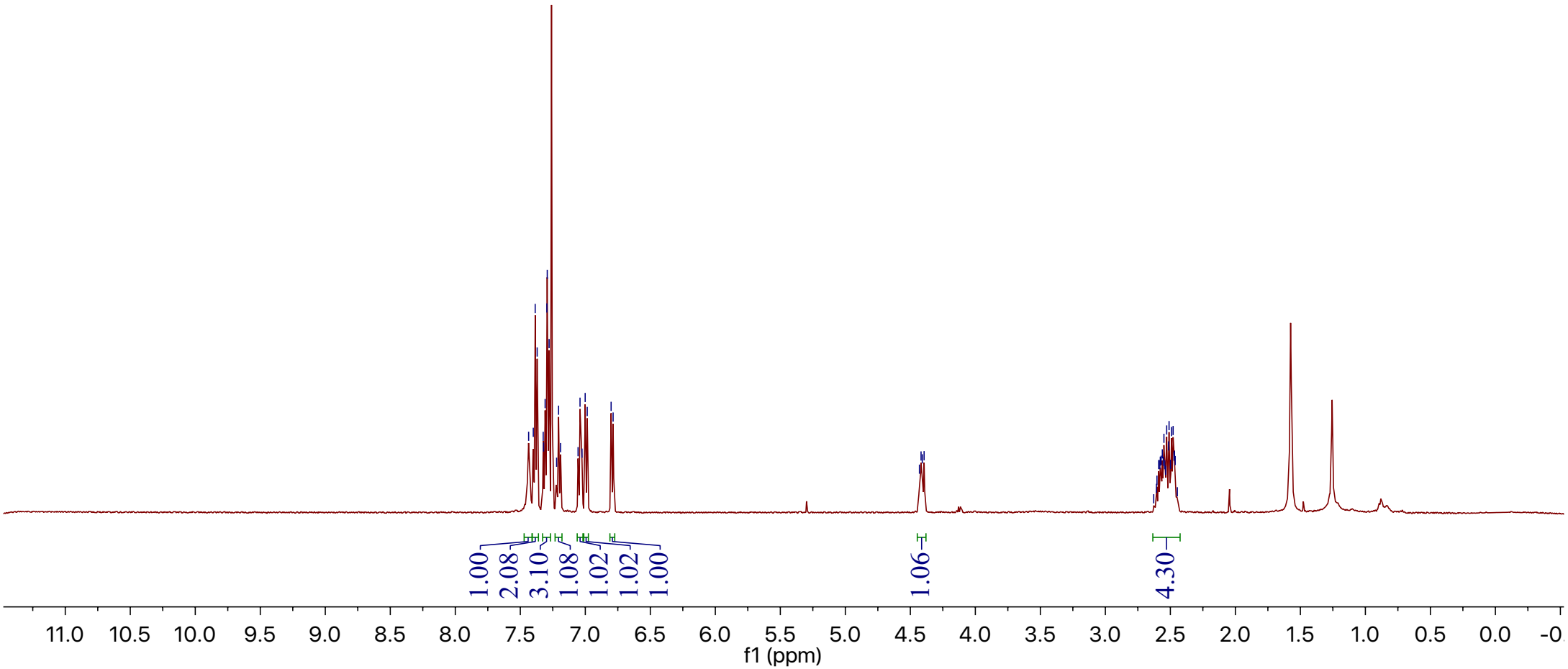


11d

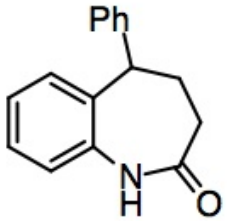



Ph
N
H
O

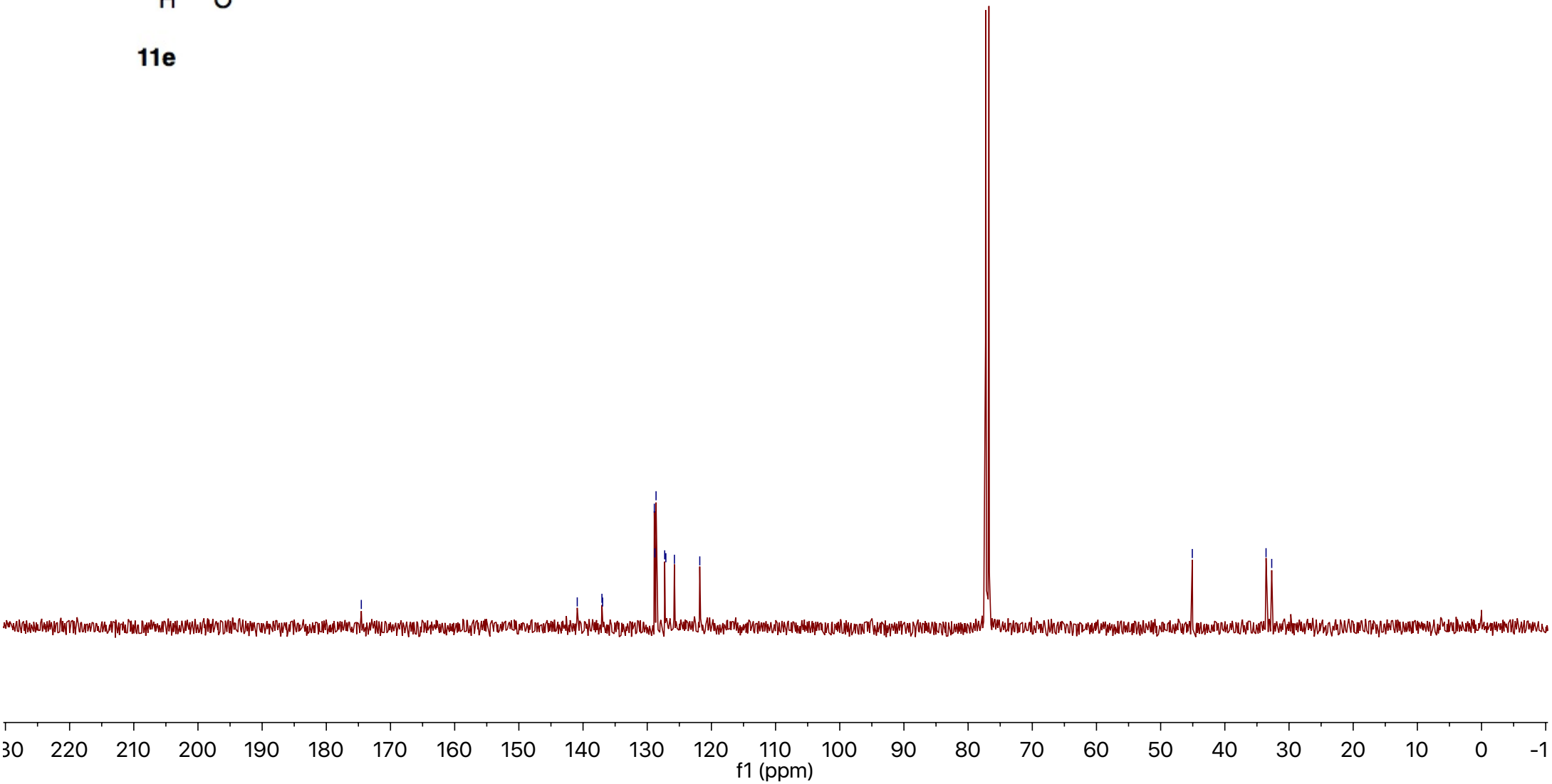
11e


7.436
7.400
7.385
7.370
7.324
7.321
7.309
7.296
7.293
7.278
7.221
7.206
7.190
7.056
7.041
7.025
7.001
6.985
6.801
6.786
4.430
4.418
4.408
4.394
2.603
2.590
2.580
2.577
2.571
2.562
2.555
2.549
2.543
2.536
2.528
2.514
2.510
2.499
2.491
2.479
2.468
1.00
2.08
3.10
1.08
1.02
1.02
1.00
1.06
4.30
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

174.549
140.901
137.055
136.949
128.891
128.809
128.623
127.279
127.095
125.764
121.811
45.066
33.578
32.693

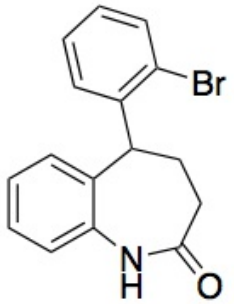


11e

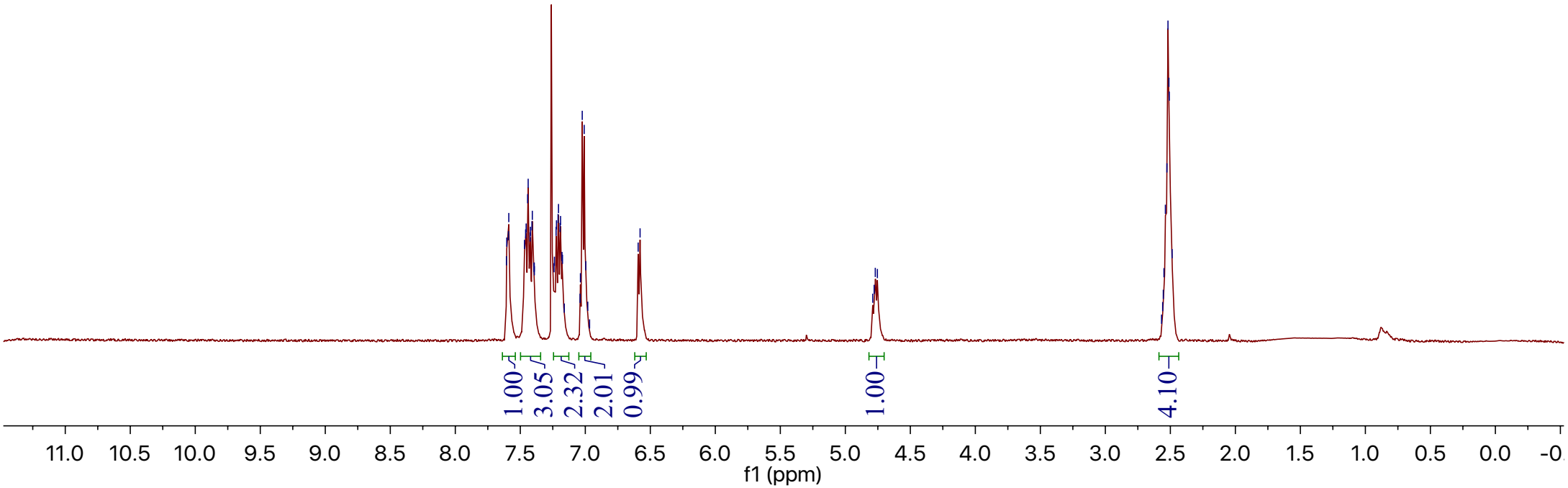


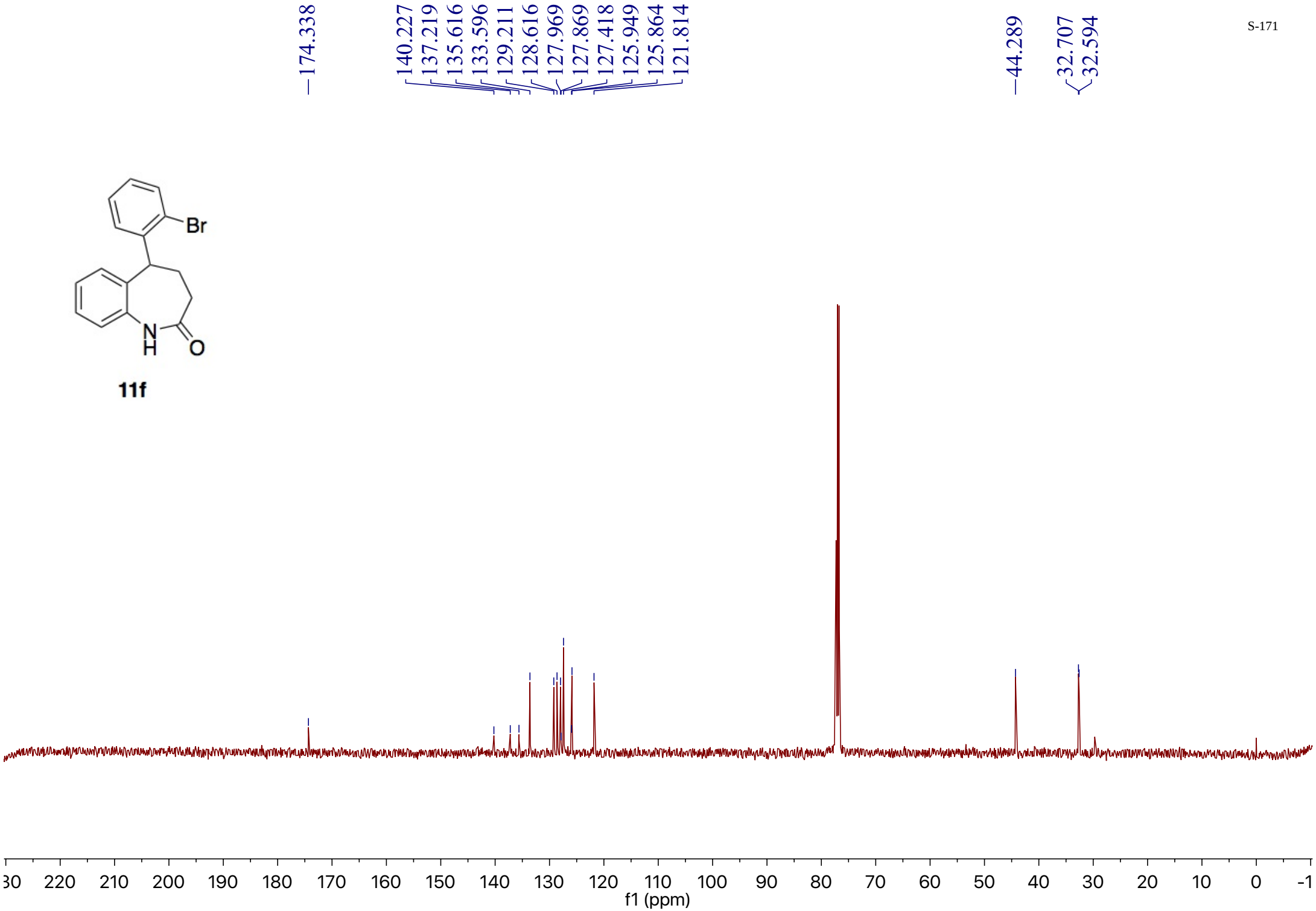
7.607 7.604 7.591 7.588 7.468 7.459 7.455 7.443 7.439 7.425 7.422 7.410 7.408 7.237 7.225 7.222 7.210 7.206 7.194 7.190 7.179 7.175 7.024 7.009 6.996 6.594 6.579 4.789 4.778 4.770 4.753

2.568 2.559 2.554 2.549 2.538 2.527 2.518 2.511 2.508 2.487

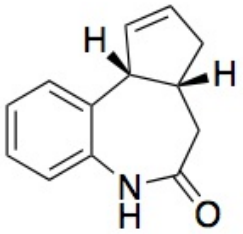


11f

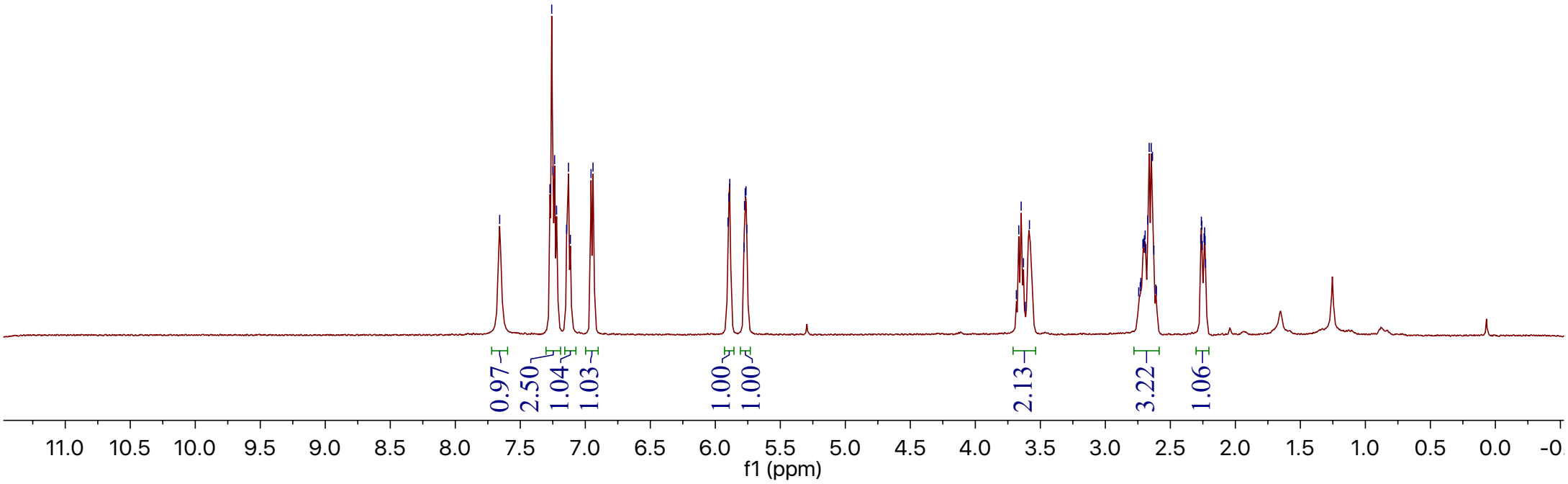


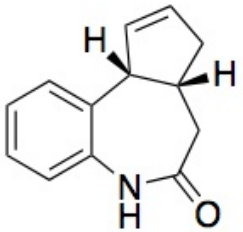

174.338
140.227
137.219
135.616
133.596
129.211
128.616
127.969
127.869
127.418
125.949
125.864
121.814
44.289
32.707
32.594
Br
N
H
O
11f
f1 (ppm)

7.659
7.272
7.258
7.249
7.236
7.221
7.144
7.129
7.115
6.956
6.941
5.903
5.896
5.889
5.780
5.775
5.770
5.764
5.758
3.684
3.666
3.648
3.630
3.617
3.584
2.711
2.705
2.699
2.694
2.689
2.674
2.663
2.647
2.638
2.266
2.262
2.258
2.255
2.241
2.236



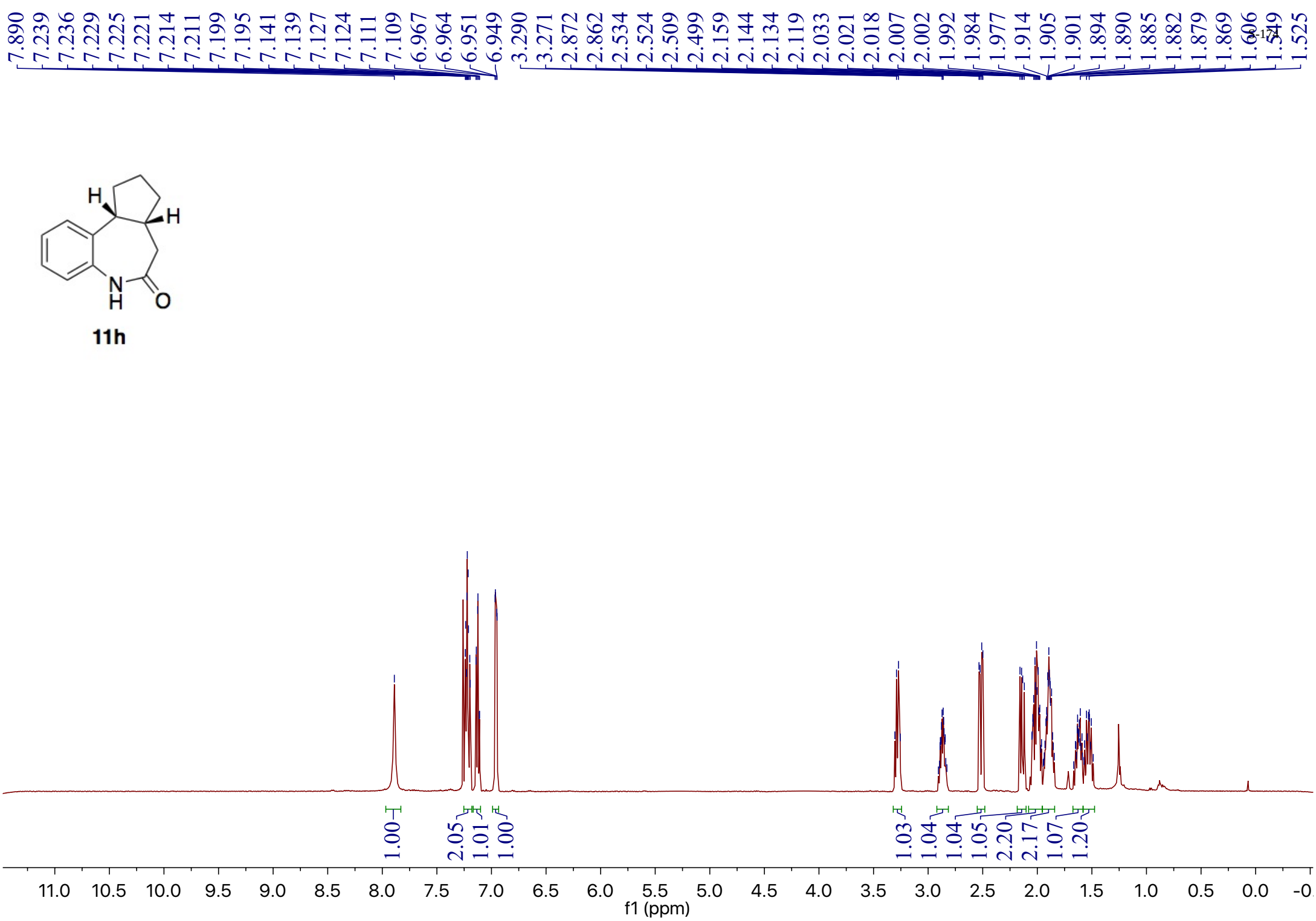
11g




H
H
N
H
O

11g

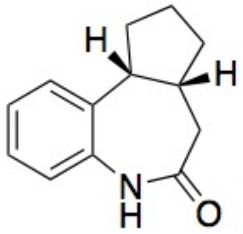
174.517
136.968
136.732
132.166
131.355
130.997
127.600
125.516
122.937
52.113
45.227
39.911
37.793
f1 (ppm)


7.890
7.239
7.236
7.229
7.225
7.221
7.214
7.211
7.199
7.195
7.141
7.139
7.127
7.124
7.111
7.109
6.967
6.964
6.951
6.949
3.290
3.271
2.872
2.862
2.534
2.524
2.509
2.499
2.159
2.144
2.134
2.119
2.033
2.021
2.018
2.007
2.002
1.992
1.984
1.977
1.914
1.905
1.901
1.894
1.890
1.885
1.882
1.879
1.869
1.606
1.519
1.525
H
H
N
H
O
11h
1.00
2.05
1.01
1.00
1.03
1.04
1.04
1.05
2.20
2.17
1.07
1.20
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

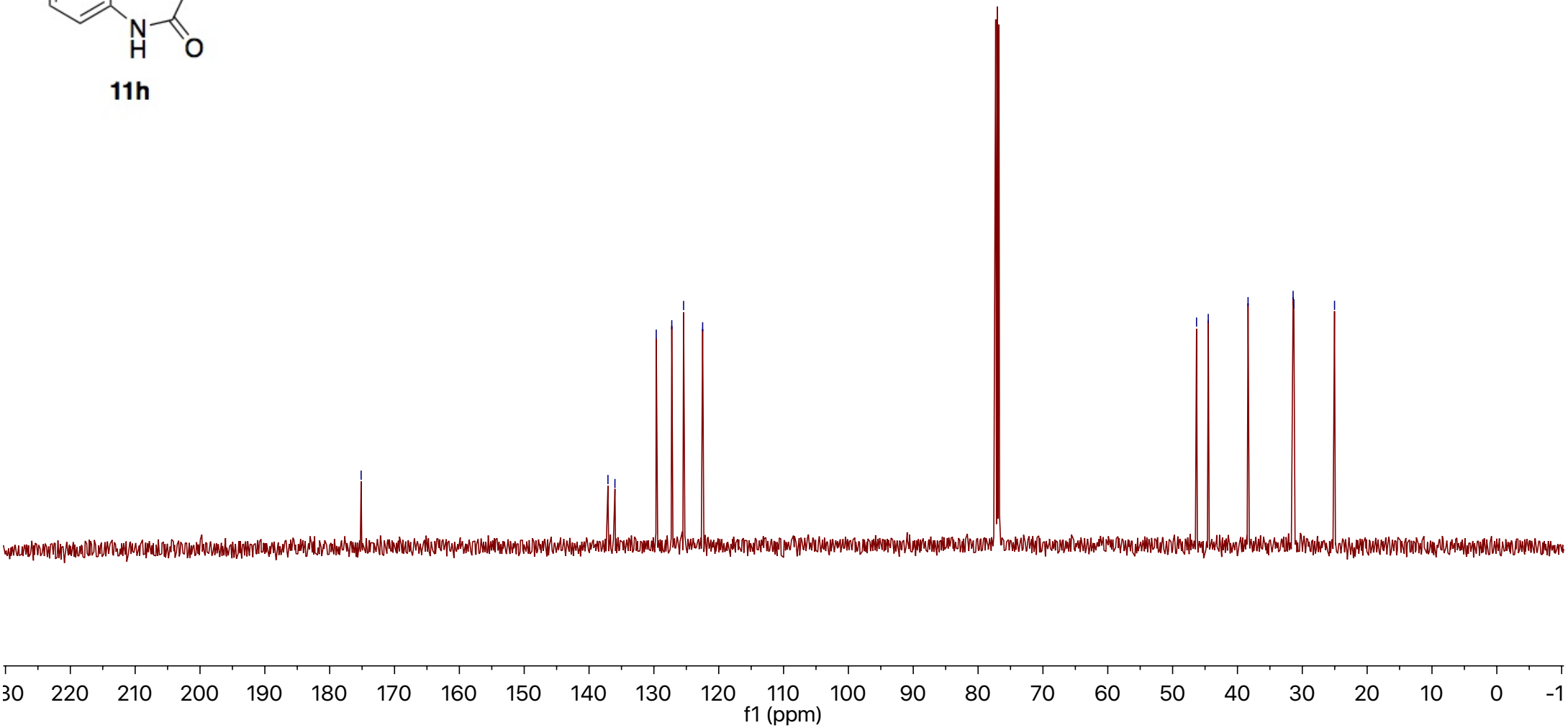
175.149

137.084
136.007
129.637
127.240
125.420
122.481

46.311
44.503
38.366
31.418
31.303
25.029



11h



7.913
7.313
7.310
7.298
7.295
7.225
7.222
7.210
7.207
7.201
7.198
7.186
7.183
6.991
6.988
6.976
6.973
2.307
2.304
2.294
2.290
2.142
2.138
1.938
1.914
1.891
1.730
1.726
1.721
1.718
1.714
1.710
1.700
1.693
1.692
1.683
1.670
1.665
1.659
1.648
1.642
1.635
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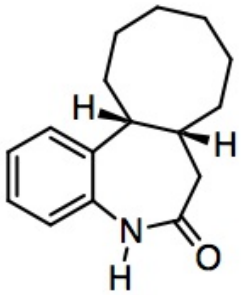
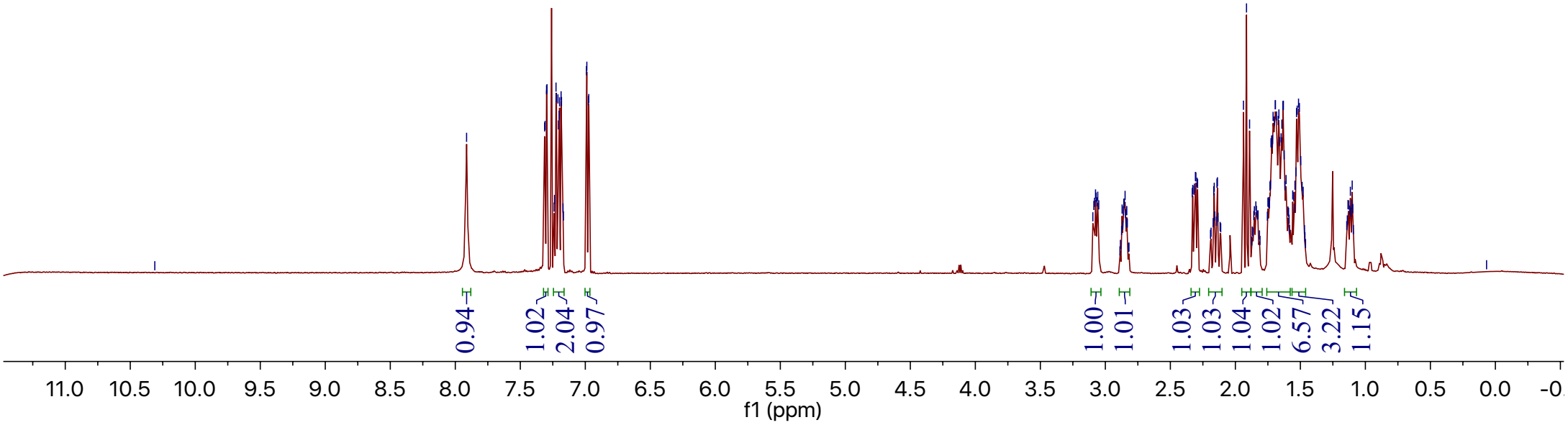
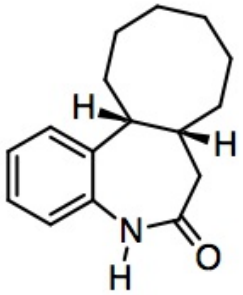
1.625
1.610
1.534
1.530
1.524
1.514
1.507
1.497
1.101



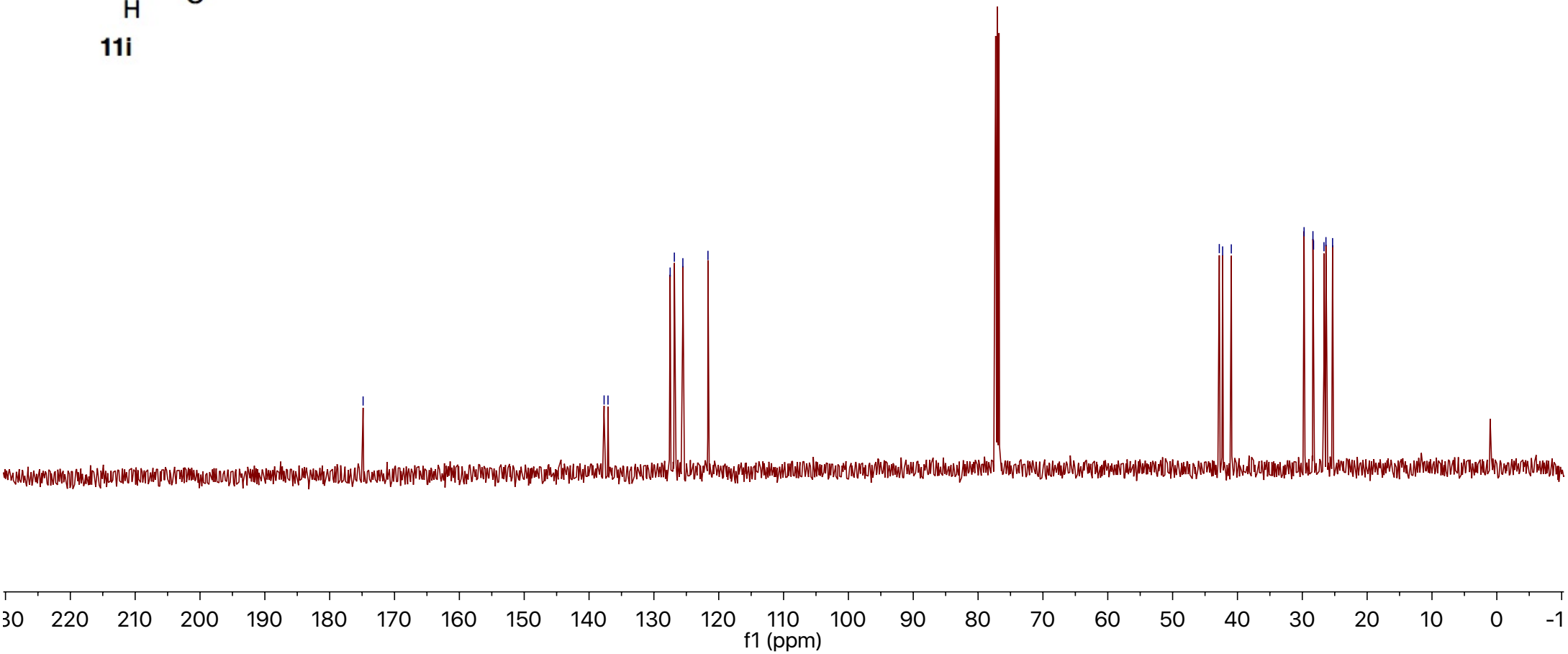
11i

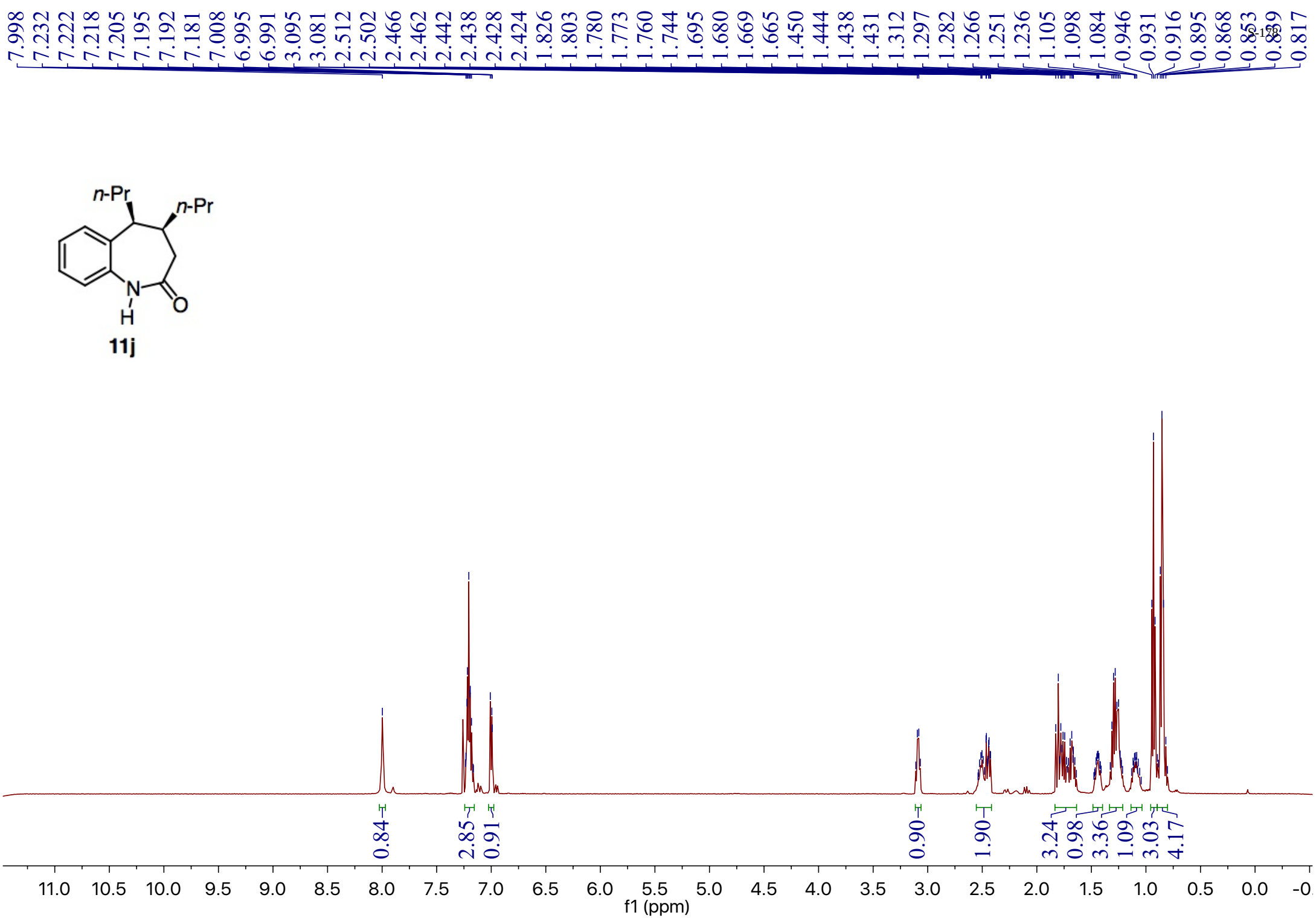


174.847
137.679
137.077
127.494
126.845
125.531
121.660
42.800
42.285
40.949
29.724
28.359
28.264
26.655
26.352
25.327

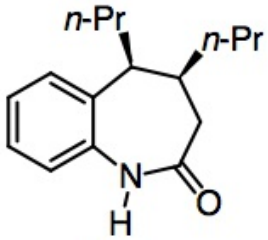


11i

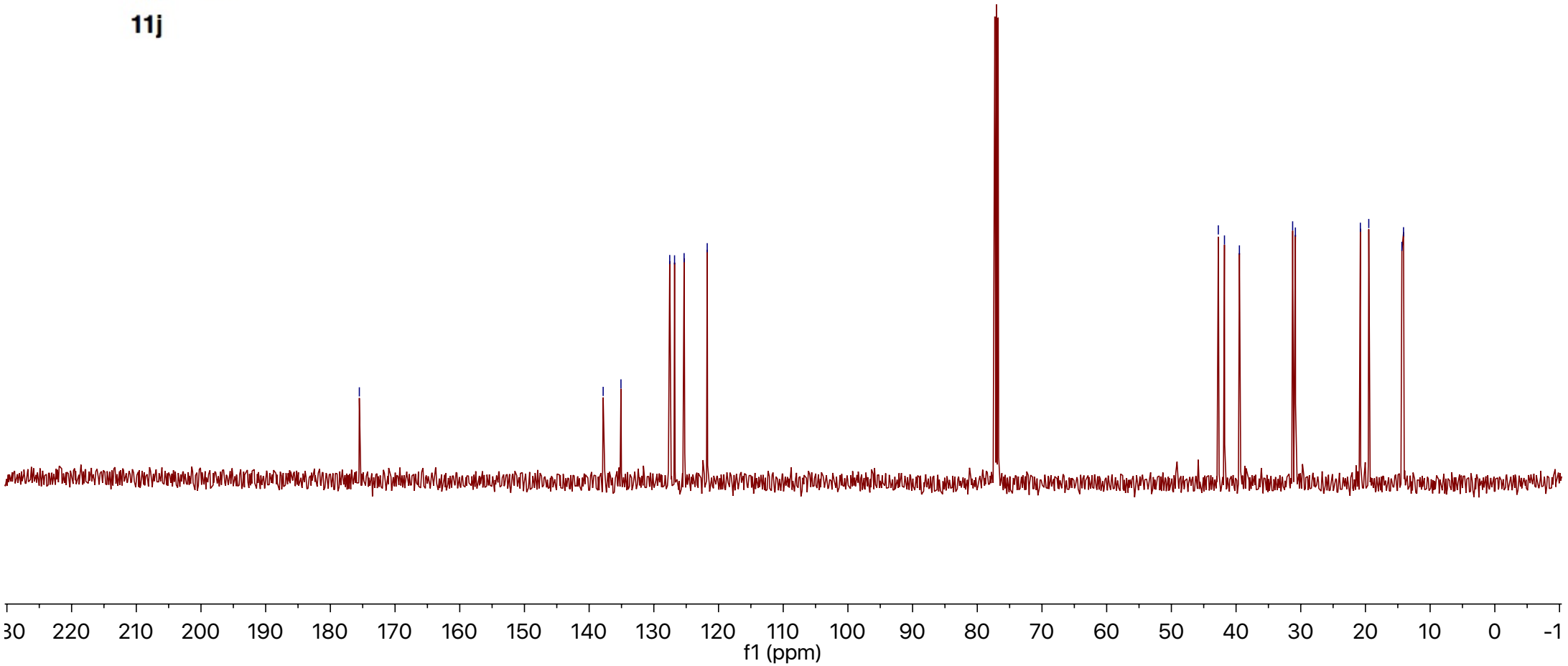


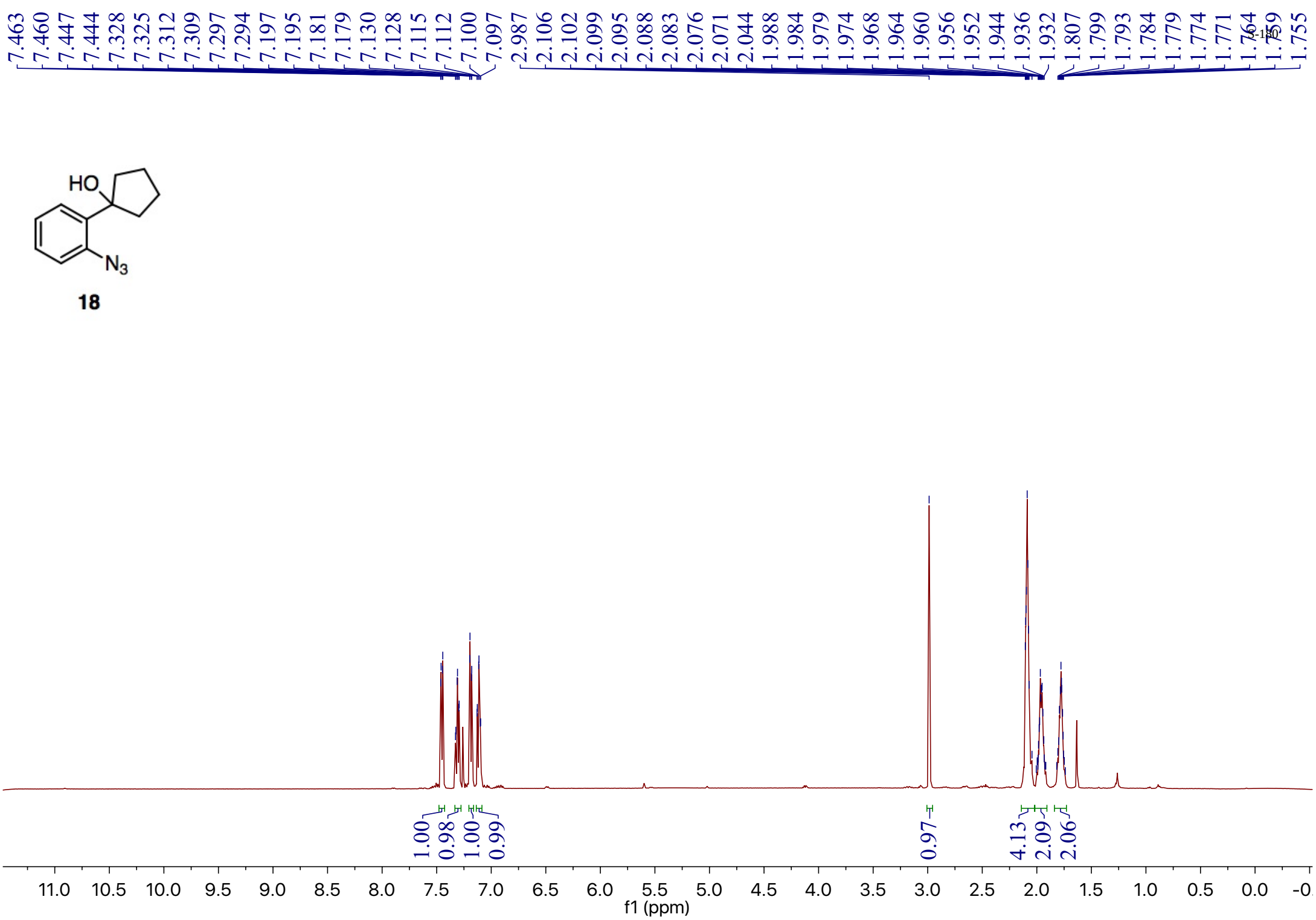

7.998
7.232
7.222
7.218
7.205
7.195
7.192
7.181
7.008
6.995
6.991
3.095
3.081
2.512
2.502
2.466
2.462
2.442
2.438
2.428
2.424
1.826
1.803
1.780
1.773
1.760
1.744
1.695
1.680
1.669
1.665
1.450
1.444
1.438
1.431
1.312
1.297
1.282
1.266
1.251
1.236
1.105
1.098
1.084
0.946
0.931
0.916
0.895
0.868
0.853
0.839
0.817
n-Pr
n-Pr
N
H
O
11j
0.84
2.85
0.91
0.90
1.90
3.24
0.98
3.36
1.09
3.03
4.17
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

175.522
137.833
135.080
127.542
126.796
125.320
121.747
42.741
41.792
39.483
31.254
30.828
20.785
19.486
14.366
14.112



11j

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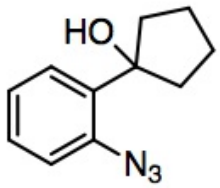
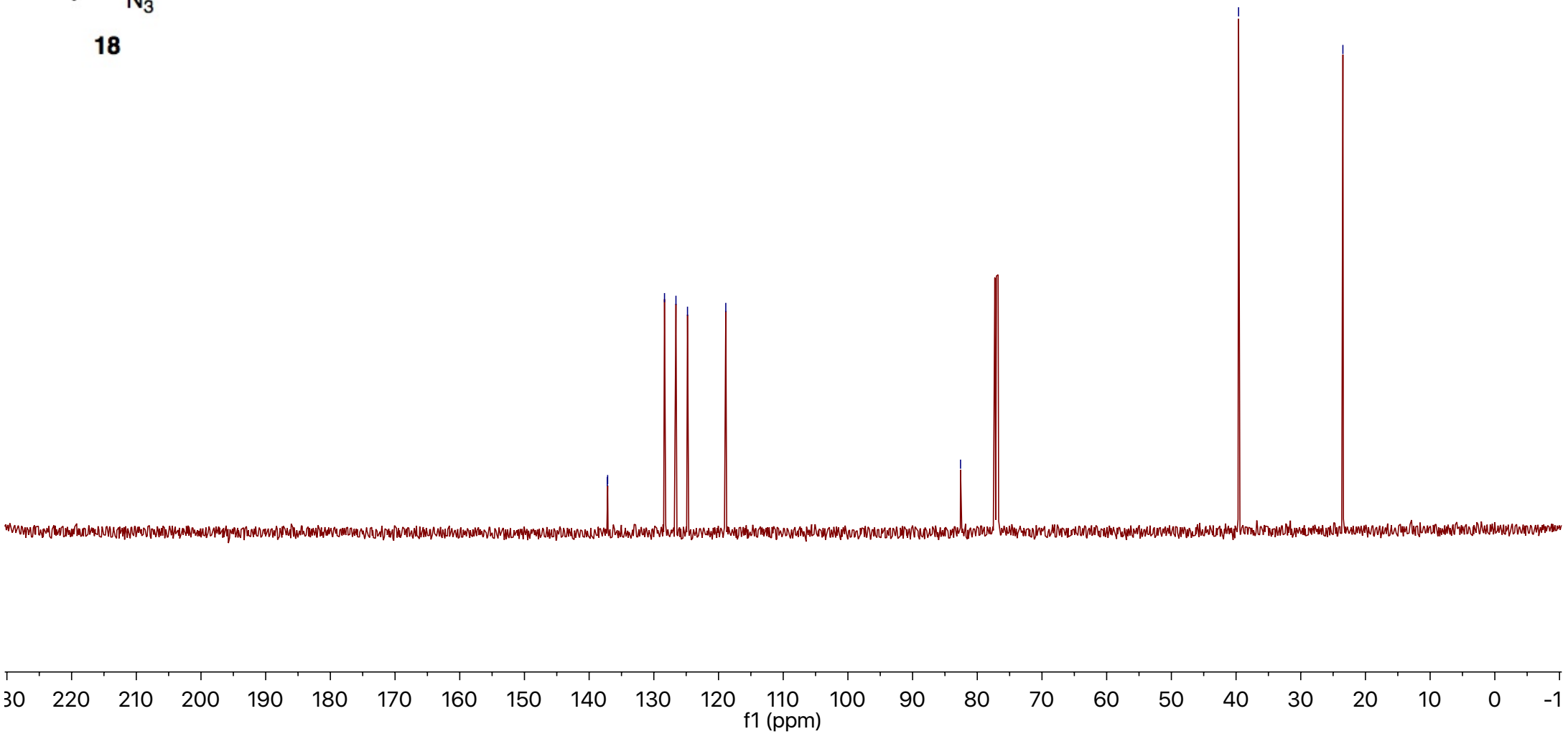
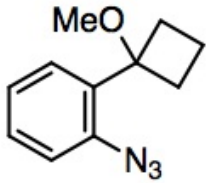
7.460
7.447
7.444
7.328
7.325
7.312
7.309
7.297
7.294
7.197
7.195
7.181
7.179
7.130
7.128
7.115
7.112
7.100
7.097
2.987
2.106
2.102
2.099
2.095
2.088
2.083
2.076
2.071
2.044
1.988
1.984
1.979
1.974
1.968
1.964
1.960
1.956
1.952
1.944
1.936
1.932
1.807
1.799
1.793
1.784
1.779
1.774
1.771
1.764
1.759
1.755
HO
N3
18
1.00
0.98
1.00
0.99
0.97
4.13
2.09
2.06
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

137.193
137.139
128.350
126.580
124.795
118.877
82.589
39.612
23.485

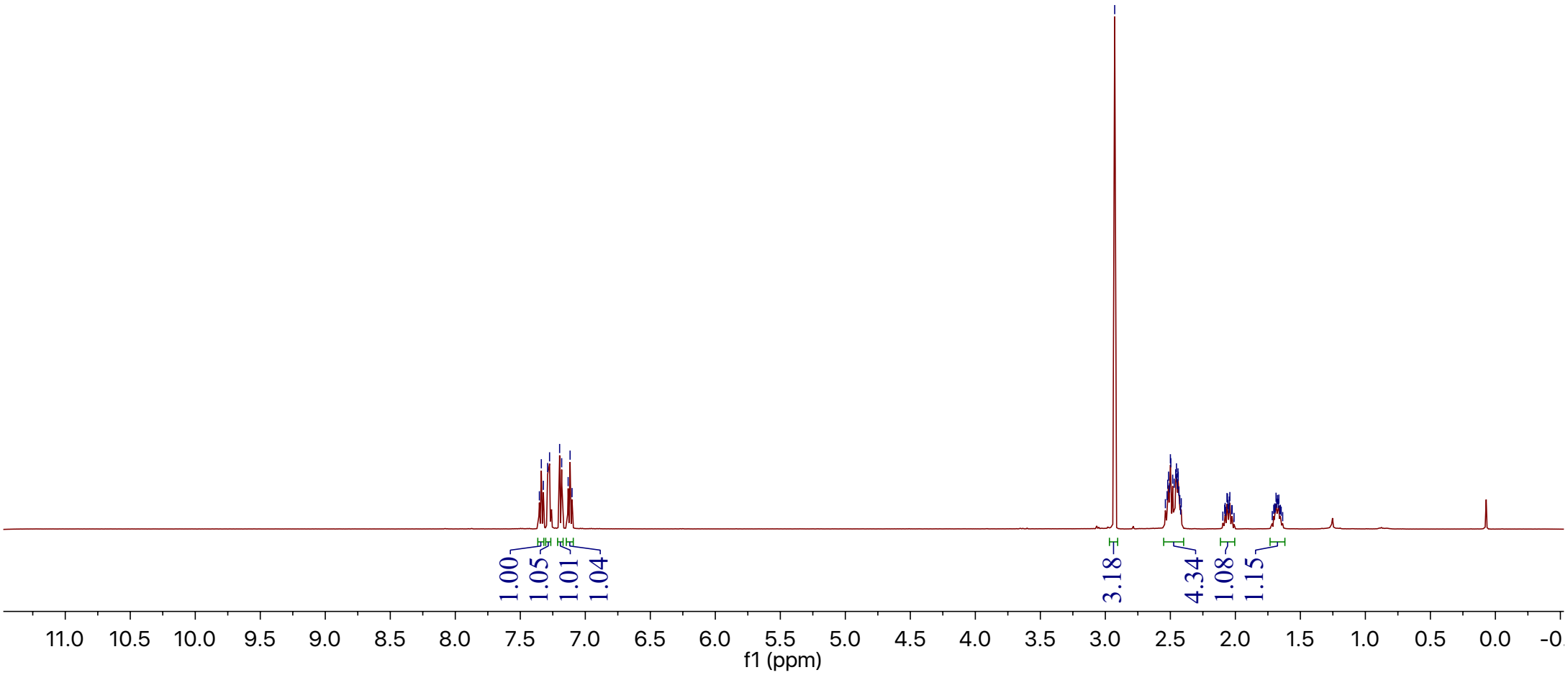


18

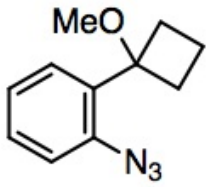



MeO
N3

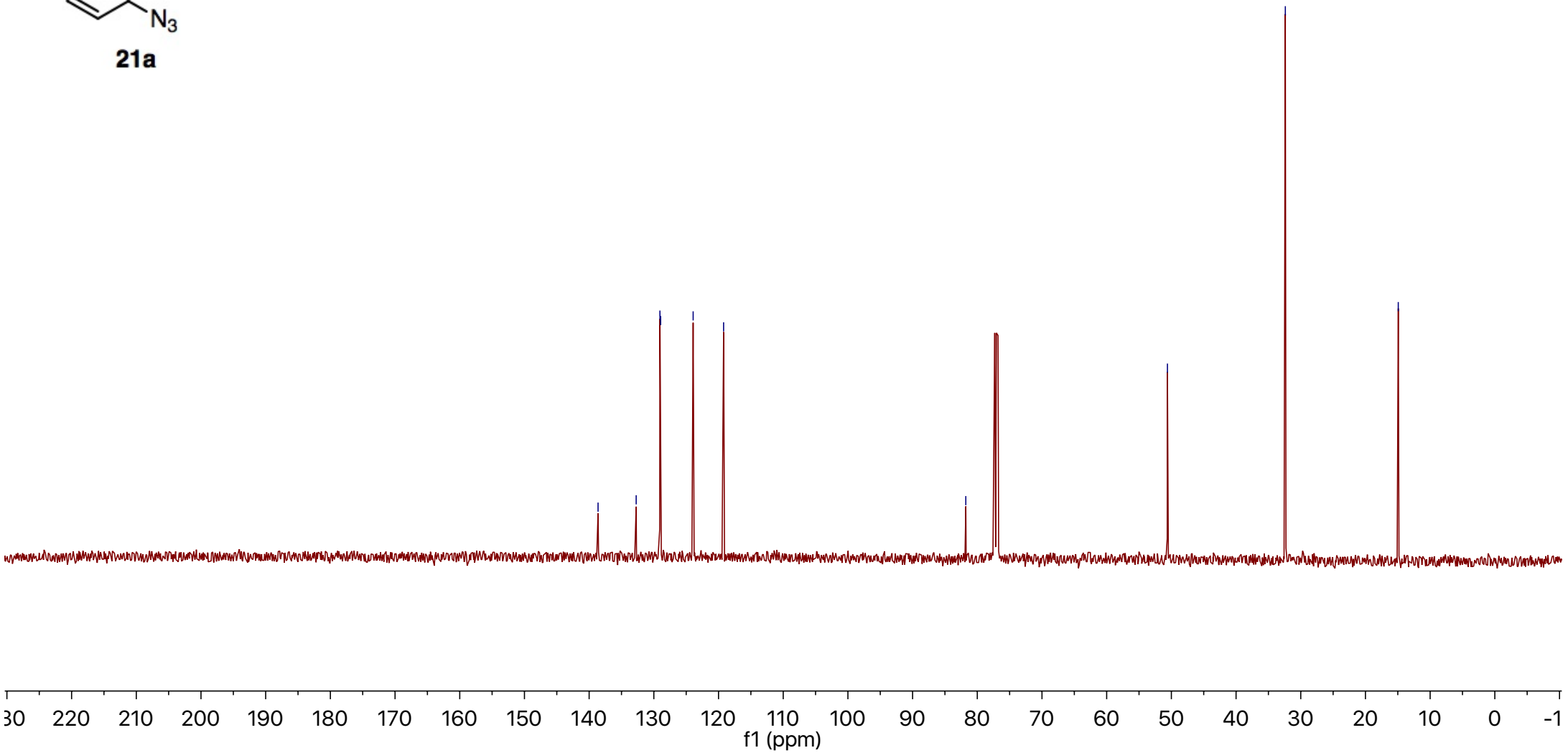
21a

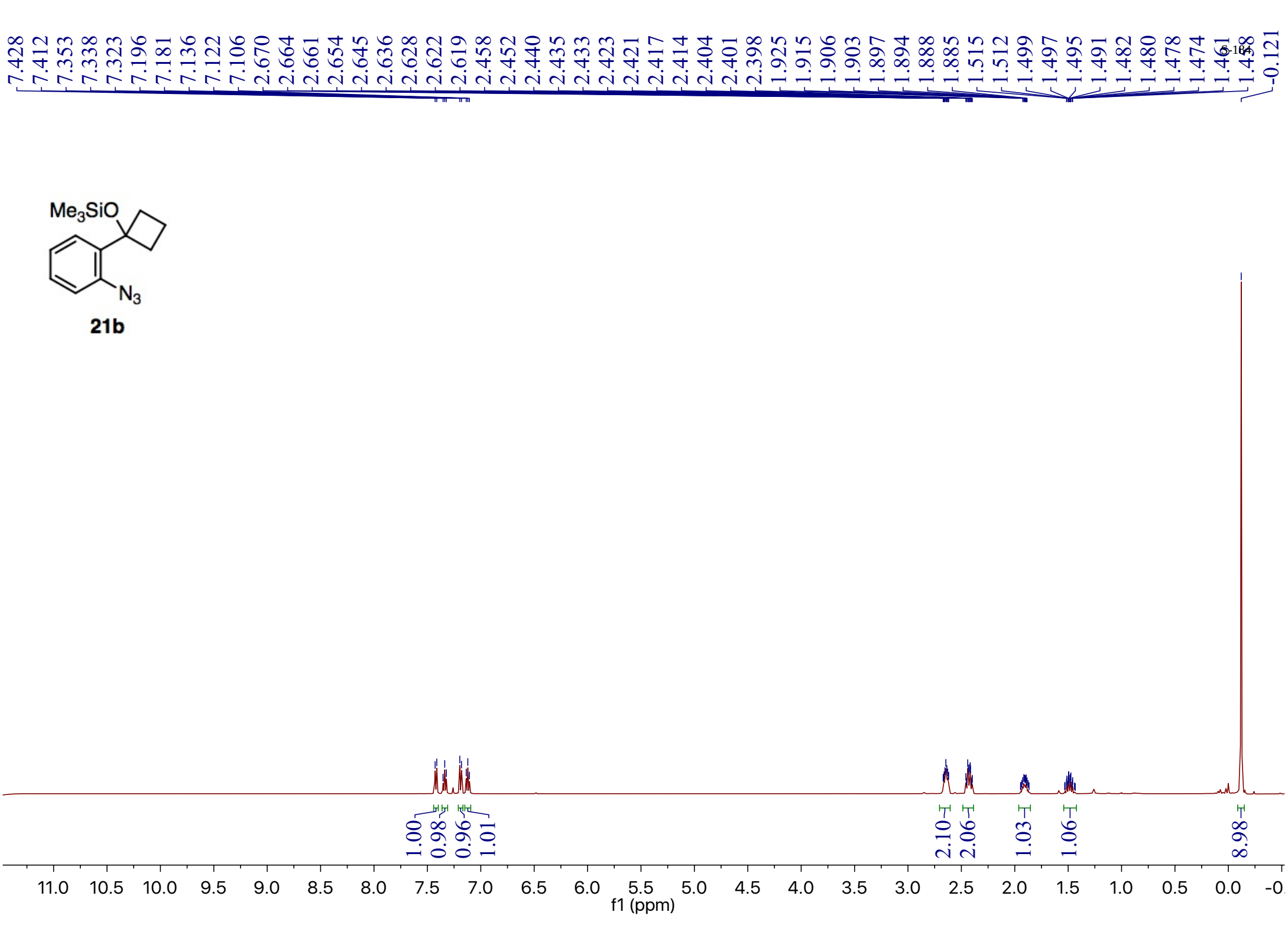

7.353
7.338
7.323
7.290
7.275
7.198
7.182
7.132
7.117
7.102
2.928
2.538
2.525
2.520
2.514
2.506
2.500
2.496
2.482
2.470
2.459
2.453
2.450
2.446
2.441
2.439
2.434
2.427
2.421
2.416
2.082
2.079
2.075
2.065
2.061
2.057
2.050
2.046
2.042
2.028
2.025
1.705
1.698
1.694
1.687
1.682
1.676
1.670
1.665
1.658
1.654
1.648
1.00
1.05
1.01
1.04
3.18
4.34
1.08
1.15
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

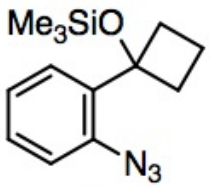
138.621
132.729
129.055
128.947
123.922
119.214
81.775
50.607
32.384
14.926



21a

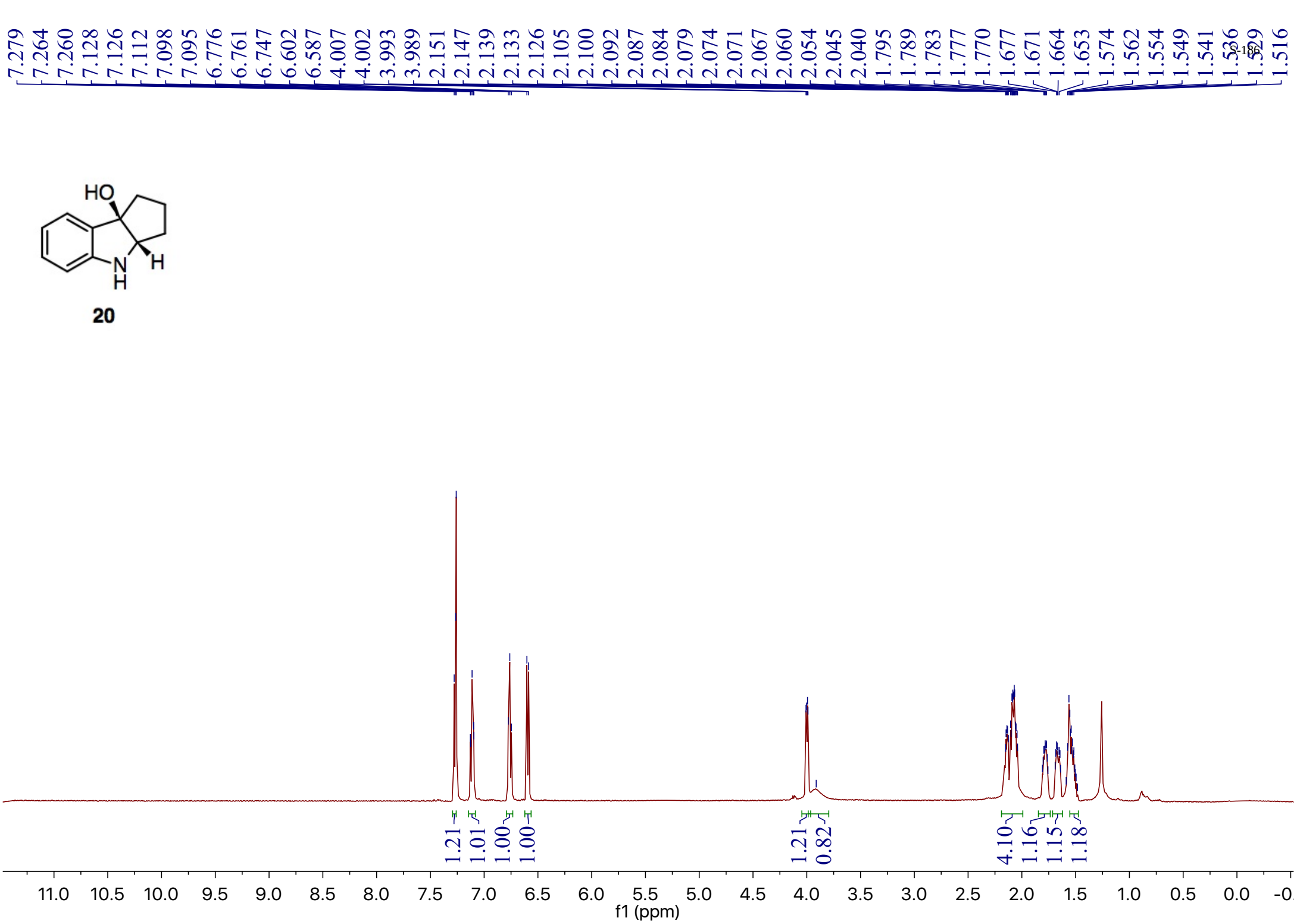



7.428
7.412
7.353
7.338
7.323
7.196
7.181
7.136
7.122
7.106
2.670
2.664
2.661
2.654
2.645
2.636
2.628
2.622
2.619
2.458
2.452
2.440
2.435
2.433
2.423
2.421
2.417
2.414
2.404
2.401
2.398
1.925
1.915
1.906
1.903
1.897
1.894
1.888
1.885
1.515
1.512
1.499
1.497
1.495
1.491
1.482
1.480
1.478
1.474
1.461
1.448
-0.121
6-104
Me3SiO
N3
21b
1.00
0.98
0.96
1.01
2.10
2.06
1.03
1.06
8.98
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

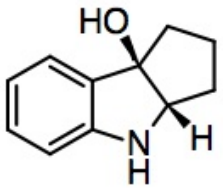

Me3SiO
N3

21b

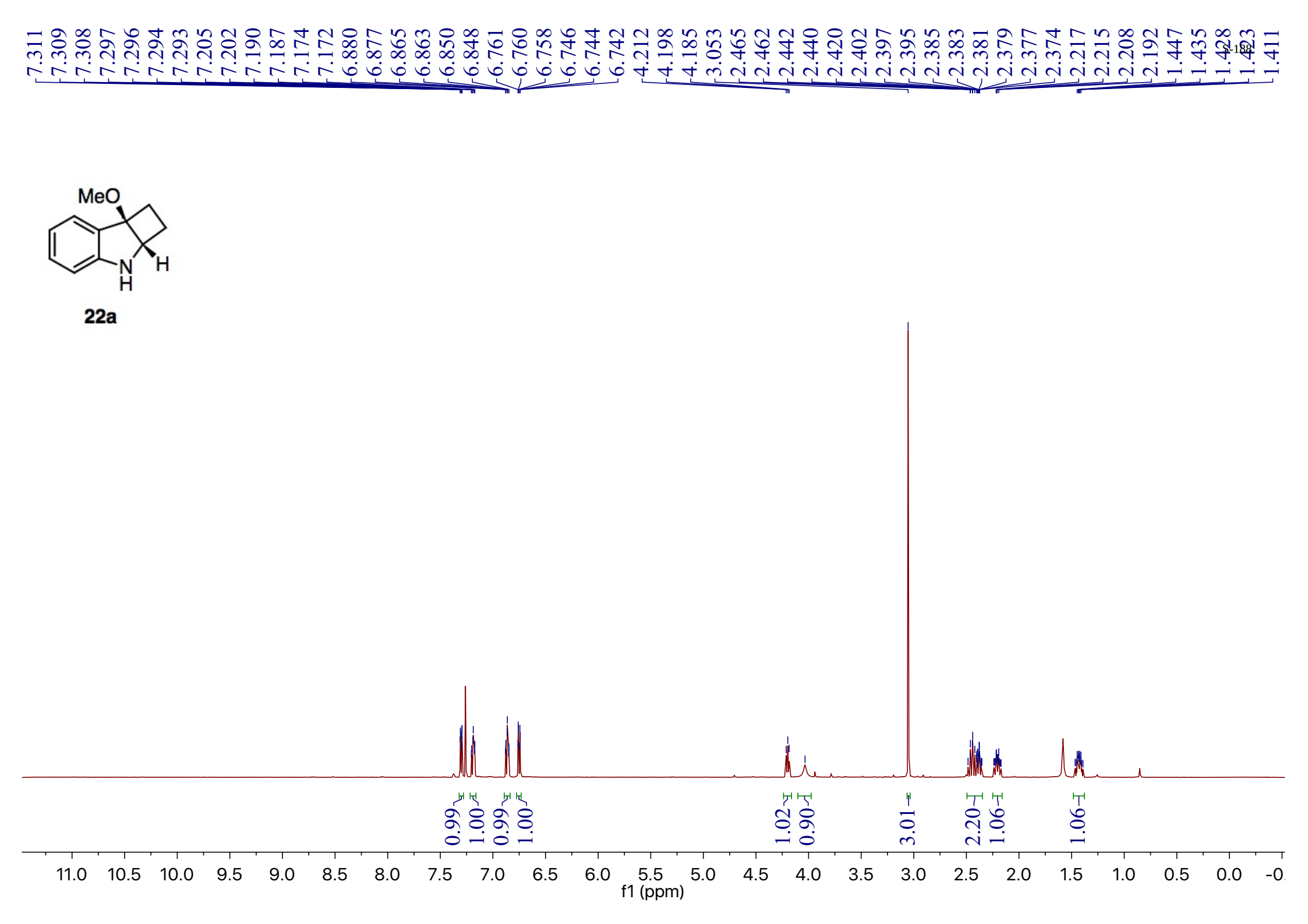
139.225
135.328
128.939
127.153
124.084
119.610
77.619
37.276
14.040
1.303
f1 (ppm)


7.279
7.264
7.260
7.128
7.126
7.112
7.098
7.095
6.776
6.761
6.747
6.602
6.587
4.007
4.002
3.993
3.989
2.151
2.147
2.139
2.133
2.126
2.105
2.100
2.092
2.087
2.084
2.079
2.074
2.071
2.067
2.060
2.054
2.045
2.040
1.795
1.789
1.783
1.777
1.770
1.677
1.671
1.664
1.653
1.574
1.562
1.554
1.549
1.541
1.536
1.529
1.516
3-186
HO
N
H
H
20
1.21
1.01
1.00
1.00
1.21
0.82
4.10
1.16
1.15
1.18
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

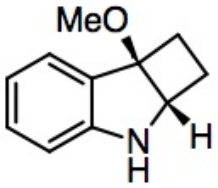
150.871
132.738
129.577
123.907
118.815
109.563
90.743
71.214
41.331
35.581
24.707



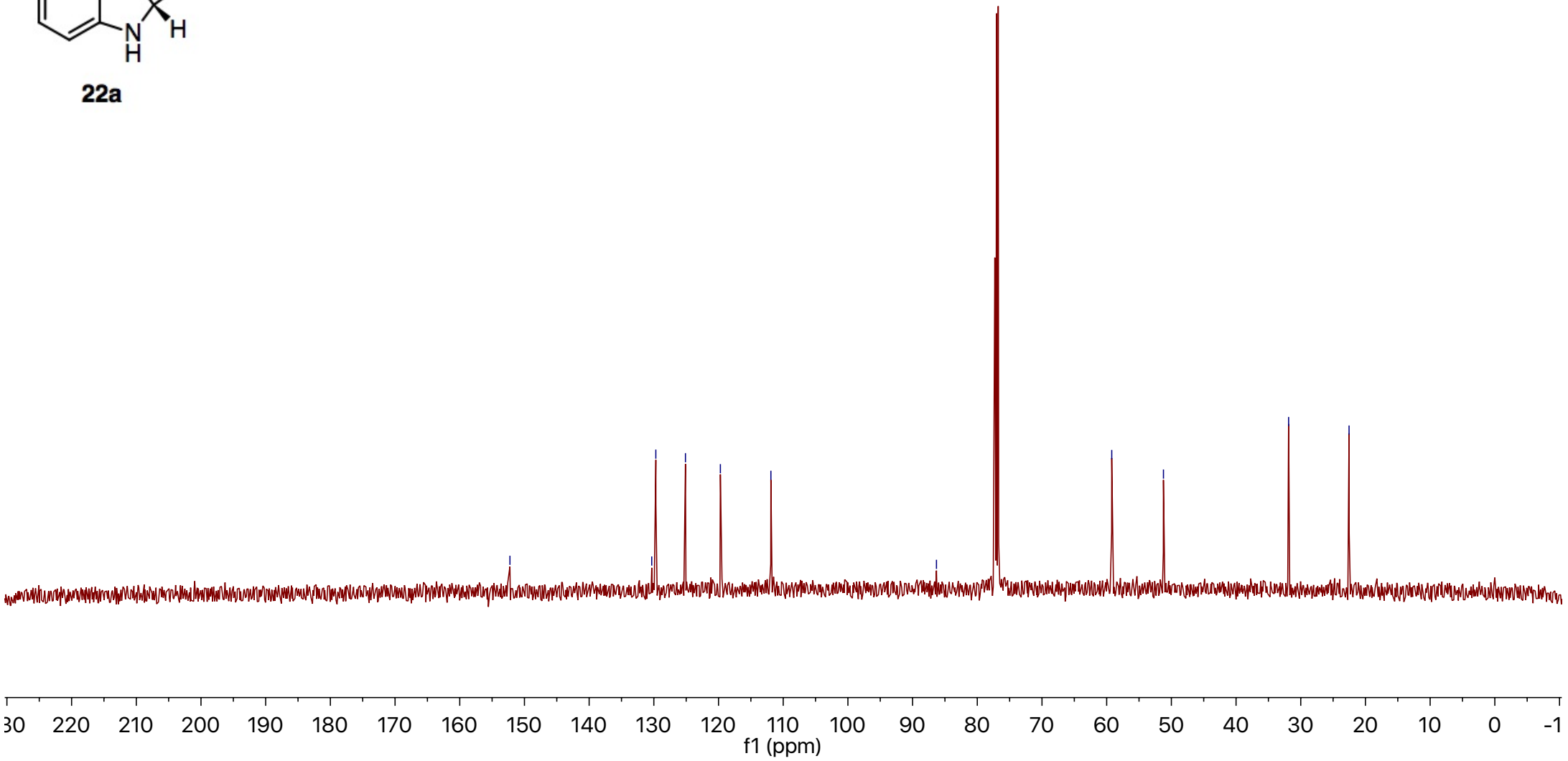
20


7.311
7.309
7.308
7.297
7.296
7.294
7.293
7.205
7.202
7.190
7.187
7.174
7.172
6.880
6.877
6.865
6.863
6.850
6.848
6.761
6.760
6.758
6.746
6.744
6.742
4.212
4.198
4.185
3.053
2.465
2.462
2.442
2.440
2.420
2.402
2.397
2.395
2.385
2.383
2.381
2.379
2.377
2.374
2.217
2.215
2.208
2.192
1.447
1.435
1.428
1.423
1.411
MeO
N
H
H
22a
0.99
1.00
0.99
1.00
1.02
0.90
3.01
2.20
1.06
1.06
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

152.243
130.323
129.691
125.112
119.713
111.904
86.312
59.215
51.222
31.876
22.532



22a




Me3SiO
N
H
H

22b

7.325
7.310
7.170
7.155
7.139
6.838
6.823
6.809
6.737
6.721
4.101
4.089
4.086
4.073
4.043
2.465
2.451
2.445
2.431
2.173
2.159
2.149
2.145
2.142
2.135
2.131
2.120
2.105
1.375
1.363
1.356
1.351
1.343
1.337
1.331
1.324
1.319
1.312
1.300
-0.037
x10
1.07
1.12
0.99
1.00
1.16
0.79
2.34
1.07
1.15
9.20
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

151.016
134.354
129.377
125.414
119.529
111.999
82.379
63.676
35.050
22.165
1.261

22b