Metal-Free Construction of Primary Sulfonamide through Three Diverse Salts

Ming Wang, Qiaoling Fan, and Xuefeng Jiang*

Shanghai Key Laboratory of Green Chemistry and Chemical Process, School of Chemistry and Molecular Engineering, East China Normal University, 3663 North Zhongshan Road, Shanghai 200062, P. R. China

E-mail: xfjiang@chem.ecnu.edu.cn

Supporting Information

Table of Contents

I. General Information S2

II. General procedure for the sulfonamide synthesis S2

III. Characterization of sulfonamide products S3

IV. The ^{31}P NMR in different reaction times S19

V. The kinetic studies S20

VI. X-Ray crystal structures S24

X. References S25

XI. NMR spectra S26

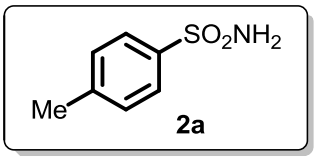
I. General Information.

^{1}H and ^{13}C NMR spectra were recorded on 400 MHz NMR spectrometers (Bruker AVANCE) using $CDCl_3$. Chemical shifts are reported in parts per million (ppm). Chemical shifts for protons are reported in parts per million relative to chloroform, dichloromethane or DMSO ($CHCl_3$ δ 7.26, $(CH_3)_2CO$ δ 2.05, DMSO δ 2.50). Chemical shifts for carbon are reported in parts per million relative to chloroform, dichloromethane or DMSO ($CHCl_3$ δ 77.0, $(CH_3)_2CO$ δ 29.84, DMSO δ 39.52). Data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz), integration. Mass spectra were recorded on a Shimadzu GCMS-QP2010 Ultra. IR spectra were recorded on TENSOR (27) Series FT-IR 241.Spectrometers. aryldiazonium salts **1** were prepared adopting reported procedures from corresponding aryl amines.[1]

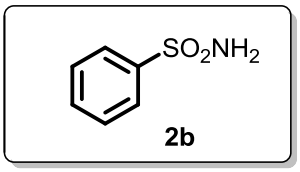
II. General procedure for the sulfonamide synthesis

Under a N_2 atmosphere, aryldiazonium salts **1a** (257.4 mg, 1.25 mmol), NaN_3 (32.5 mg, 0.5 mmol), PPh_3(157.4 mg, 0.6 mmol), $Na_2S_2O_5$ (190.1 mg, 1.0 mmol), TBAB (241.7 mg, 0.75 mmol) and MeCN/H_2O = 1/2 (1 mL), the reaction was stirred at 80 ^{o}C for 12 h, and water (5 mL) was added. The solution was extracted with ethyl acetate and organic layers were combined, dried over sodium sulfate. After evaporation of solvent, the residue was purified by column chromatography to give the corresponding products **2** or **3**.

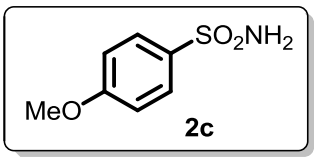
III. Characterization of sulfonamide products



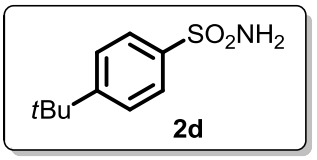
4-Methylbenzenesulfonamide (**2a**): Prepared following general procedure using aryldiazonium salts **1a** (257.4 mg, 1.25 mmol), NaN_3 (32.5 mg, 0.5 mmol), PPh_3(157.4 mg, 0.6 mmol), $Na_2S_2O_5$ (190.1 mg, 1.0 mmol), TBAB (241.7 mg, 0.75 mmol) and MeCN/H_2O = 1/2 (1 mL), the reaction was stirred at 80 ^oC for 12 h giving **2a** in 90% yield as a white solid by column chromatography (PE/EA = 5/1 to 2/1). ^1H NMR (400 MHz, d_6-DMSO) δ 7.71 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H), 7.27 (s, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 141.8, 141.4, 129.3, 125.6, 20.9; **IR** (KBr) v 3348, 3270, 1598, 1500, 1309, 1175, 1021, 917, 835, 669 cm^{-1}; **HRMS** (EI) for $C_7H_9NO_2S$ Calculated: 171.0354, found: 171.0353.



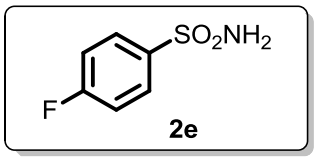
Benzenesulfonamide (**2b**). Prepared following general procedure using aryldiazonium salts **1b** (239.9 mg, 1.25 mmol), NaN_3 (32.5 mg, 0.5 mmol), PPh_3(157.4 mg, 0.6 mmol), $Na_2S_2O_5$ (190.1 mg, 1.0 mmol), TBAB (241.7 mg, 0.75 mmol) and MeCN/H_2O = 1/2 (1 mL), the reaction was stirred at 80 ^oC for 12 h giving **2b** in 72% yield as a white solid by column chromatography (PE/EA = 5/1 to 2/1). **^1H NMR** (400 MHz, d_6-acetone) δ 7.91 (d, J = 7.0 Hz, 2H), 7.72 – 7.43 (m, 3H), 6.59 (s, 2H); **^{13}C NMR** (100 MHz, d_6-acetone) δ 145.0, 132.8, 129.7, 126.8; **IR** (KBr) v 3353, 3258, 1448, 1344, 1160, 1091, 756, 688, 537 cm^{-1}; **HRMS** (EI) for $C_6H_7NO_2S$ Calculated: 157.0197, found: 157.0200.



4-Methoxybenzenesulfonamide (**2c**). Prepared following general procedure using aryldiazonium salts **1c** (277.4 mg, 1.25 mmol), NaN_3 (32.5 mg, 0.5 mmol), PPh_3(157.4 mg, 0.6 mmol), $Na_2S_2O_5$ (190.1 mg, 1.0 mmol), TBAB (241.7 mg, 0.75 mmol) and MeCN/H_2O = 1/2 (1 mL), the reaction was stirred at 80 ^oC for 12 h giving **2c** in 91% yield as a white solid by column chromatography (PE/EA = 4/1 to 1/1). **^{1}H NMR** (400 MHz, d_6-acetone) δ 7.83 (d, J = 8.9 Hz, 2H), 7.06 (d, J = 8.9 Hz, 2H), 6.43 (s, 2H), 3.87 (s, 3H); **^{13}C NMR** (100 MHz, d_6-acetone) δ 163.2, 137.0, 128.9, 114.7, 56.0; **IR** (KBr) v 3348, 3270, 2980, 1598, 1500, 1309, 1157, 917, 835, 669 cm^{-1}; **HRMS** (EI) for $C_7H_9NO_3S$ Calculated: 187.0303, found: 187.0306.

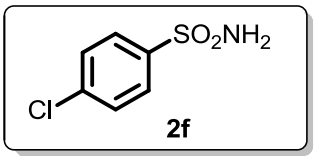


4-(tert-Butyl)benzenesulfonamide (**2d**). Prepared following general procedure using aryldiazonium salts **1d** (310 mg, 1.25 mmol), $Na_2S_2O_5$ (190.1 mg, 1.0 mmol), NaN_3 (32.5 mg, 0.5 mmol), PPh_3(157.4 mg, 0.6 mmol), TBAB (241.7 mg, 0.75 mmol) and MeCN/H_2O = 1/2 (1 mL), the reaction was stirred at 80 ^oC for 12 h giving **2d** in 84% yield as a white solid by column chromatography (PE/EA = 5/1 to 2/1). **^{1}H NMR** (400 MHz, d_6-acetone) δ 7.85 (dd, J = 16.2, 14.0 Hz, 2H), 7.60 (d, J = 8.6 Hz, 2H), 6.50 (s, 2H), 1.34 (s, 9H); **^{13}C NMR** (100 MHz, d_6-acetone) δ 156.1, 142.2, 126.7, 126.5, 35.5, 31.3; **IR** (KBr) v 3363, 3268, 2963, 1568, 1500, 1364, 1166, 1113, 924, 832, 632 cm^{-1}; **HRMS** (EI) for $C_7H_9NO_3S$ Calculated: 213.0823, found: 213.0825.



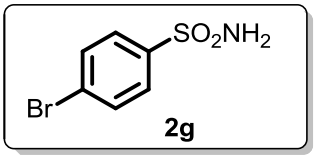
2e

4-Fluorobenzenesulfonamide (**2e**). Prepared following general procedure using aryldiazonium salts **1e** (262.4 mg, 1.25 mmol), $Na_2S_2O_5$ (190.1 mg, 1.0 mmol), NaN_3 (32.5 mg, 0.5 mmol), PPh_3(157.4 mg, 0.6 mmol), TBAB (241.7 mg, 0.75 mmol) and MeCN/H_2O = 1/2 (1 mL), the reaction was stirred at 80 ^oC for 12 h giving **2e** in 75% yield as a white solid by column chromatography (PE/EA = 5/1 to 2/1). **^{1}H NMR** (400 MHz, d_6-acetone) δ 7.96 (dd, *J* = 8.8, 5.2 Hz, 2H), 7.33 (t, *J* = 8.8 Hz, 2H), 6.65 (s, 2H); **^{13}C NMR** (100 MHz, d_6-acetone) δ 164.3 (d, *J* = 250.6 Hz), 141.3 (d, *J* = 3.2 Hz), 129.7 (d, *J* = 9.3 Hz), 116.6 (d, *J* = 22.7 Hz); **^{19}F NMR** (376 MHz, d_6-acetone) δ 68.3; **IR** (KBr) v 3362, 3261, 1587, 1493, 1292, 1177, 1100, 913, 840, 669 cm^{-1}; **HRMS** (EI) for $C_6H_6NO_2SF$ Calculated: 175.0103, found: 175.0106.



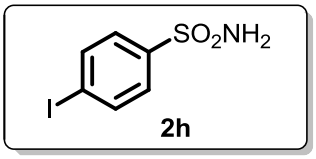
2f

4-Chlorobenzenesulfonamide (**2f**). Prepared following general procedure using aryldiazonium salts **2f** (282.9 mg, 1.25 mmol), $Na_2S_2O_5$ (190.1 mg, 1.0 mmol), NaN_3 (32.5 mg, 0.5 mmol), PPh_3(157.4 mg, 0.6 mmol), TBAB (241.7 mg, 0.75 mmol) and MeCN/H_2O = 1/2 (1 mL), the reaction was stirred at 80 ^oC for 12 h giving **2f** in 60% yield as a white solid by column chromatography (PE/EA = 5/1 to 2/1). **^{1}H NMR** (400 MHz, d_6-acetone) δ 7.90 (d, *J* = 8.5 Hz, 2H), 7.61 (d, *J* = 8.5 Hz, 2H), 6.72 (s, 2H); **^{13}C NMR** (100 MHz, d_6-acetone) δ 144.0, 138.3, 129.9, 128.8; **IR** (KBr) v 3333, 3240, 1572, 1475, 1331, 1150, 1089, 823, 756, 626 cm^{-1}; **HRMS** (EI) for $C_6H_6NO_2SCl$ Calculated: 190.9808, found: 190.9807.



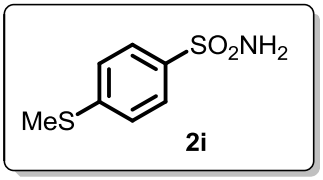
2g

4-Bromobenzenesulfonamide (**2g**). Prepared following general procedure using aryldiazonium salts **1g** (338.5 mg, 1.25 mmol), $Na_2S_2O_5$ (190.1 mg, 1.0 mmol), NaN_3 (32.5 mg, 0.5 mmol), PPh_3(157.4 mg, 0.6 mmol), TBAB (241.7 mg, 0.75 mmol) and MeCN/H_2O = 1/2 (1 mL), the reaction was stirred at 80 ^oC for 12 h giving **2g** in 70% yield as a white solid by column chromatography (PE/EA = 5/1 to 2/1). **^{1}H NMR** (400 MHz, *d_6*-acetone) δ 7.83 (d, *J* = 8.6 Hz, 2H), 7.76 (d, *J* = 8.6 Hz, 2H), 6.71 (s, 2H); **^{13}C NMR** (100 MHz, *d_6*-acetone) δ 144.4, 132.9, 128.9, 126.7; **IR** (KBr) v 3329, 3239, 3117, 1575, 1391, 1310, 1148, 1091, 818, 742, 613 cm^{-1}; **HRMS** (EI) for $C_6H_6NO_2SBr$ Calculated: 234.9303, found: 234.9305.

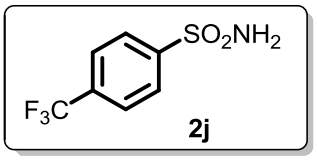


2h

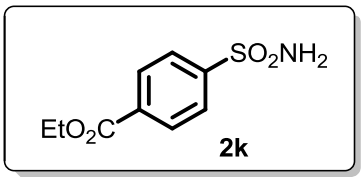
4-Iodobenzenesulfonamide (**2h**). Prepared following general procedure using aryldiazonium salts **1h** (397.3 mg, 1.25 mmol), $Na_2S_2O_5$ (190.1 mg, 1.0 mmol), NaN_3 (32.5 mg, 0.5 mmol), PPh_3(157.4 mg, 0.6 mmol), TBAB (241.7 mg, 0.75 mmol) and MeCN/H_2O = 1/2 (1 mL), the reaction was stirred at 80 ^oC for 12 h giving **2h** in 52% yield as a white solid by column chromatography (PE/EA = 5/1 to 2/1).**^{1}H NMR** (400 MHz, *d_6*-acetone) δ 8.04 – 7.92 (m, 2H), 7.73 – 7.63 (m, 2H), 6.72 (s, 2H); **^{13}C NMR** (100 MHz, *d_6*-acetone) δ 144.9, 138.9, 128.6, 99.1. **IR** (KBr) v 3362, 3256, 2924, 1384, 1300, 1150, 1093, 816, 730, 533 cm^{-1}; **HRMS** (EI) for $C_6H_6NO_2SI$ Calculated: 282.9164, found: 282.9160.



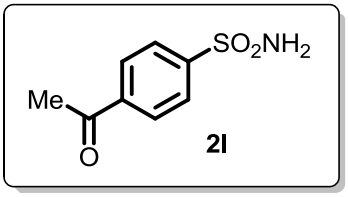
4-(Methylthio)benzenesulfonamide (**2i**). Prepared following general procedure using aryldiazonium salts **1i** (297.5 mg, 1.25 mmol), $Na_2S_2O_5$ (190.1 mg, 1.0 mmol), NaN_3 (32.5 mg, 0.5 mmol), PPh_3(157.4 mg, 0.6 mmol), TBAB (241.7 mg, 0.75 mmol) and MeCN/H_2O = 1/2 (1 mL), the reaction was stirred at 80 ^oC for 12 h giving **2i** in 88% yield as a brown solid by column chromatography (PE/EA = 4/1 to 2/1). **^{1}H NMR** (400 MHz, d_6-acetone) δ 7.79 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 6.55 (s, 2H), 2.56 (s, 3H); **^{13}C NMR** (100 MHz, d_6-acetone) δ 145.3, 141.1, 127.3, 126.0, 14.6; **IR** (KBr) v 3335, 3244, 1305, 1160, 904, 810, 756, 536 cm^{-1}; **HRMS** (EI) for $C_7H_9NO_2S_2$Calculated: 203.0075, found: 203.0073.



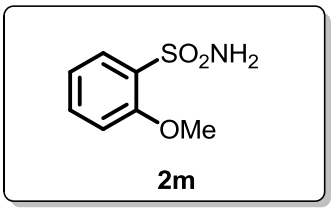
4-(Trifluoromethyl)benzenesulfonamide (**2j**). Prepared following general procedure using aryldiazonium salts **1j** (325 mg, 1.25 mmol), $Na_2S_2O_5$ (190.1 mg, 1.0 mmol), NaN_3 (32.5 mg, 0.5 mmol), PPh_3(157.4 mg, 0.6 mmol), TBAB (241.7 mg, 0.75 mmol) and MeCN/H_2O = 1/2 (1 mL), the reaction was stirred at 80 ^oC for 12 h giving **2j** in 52% yield, as a white solid by column chromatography (PE/EA = 5/1 to 2/1). **^{1}H NMR** (400 MHz, d_6-acetone) δ 8.12 (d, *J* = 8.2 Hz, 2H), 7.94 (d, *J* = 8.3 Hz, 2H), 6.86 (s, 2H); ^{13}C NMR (100 MHz, d_6-acetone) δ 148.71, 133.7 (q, *J* = 32.6 Hz), 127.8, 127.0 (q, *J* = 3.8 Hz), 124.6 (q, *J* = 271.9 Hz); **^{19}F NMR** (376 MHz, d_6-acetone) δ 113.97; **IR** (KBr) v 3382, 3260, 1565, 1406, 1326, 1125, 1112, 838, 713, 611, 532 cm^{-1}; **HRMS** (EI) for $C_7H_6NO_2SF_3$ Calculated: 225.0071, found: 225.0074.



Ethyl 4-sulfamoylbenzoate (**2k**). Prepared following general procedure using aryldiazonium salts **1k** (329.9 mg, 1.25 mmol), $Na_2S_2O_5$ (190.1 mg, 1.0 mmol), NaN_3 (32.5 mg, 0.5 mmol), PPh_3(157.4 mg, 0.6 mmol), TBAB (241.7 mg, 0.75 mmol) and MeCN/H_2O = 1/2 (1 mL), the reaction was stirred at 80 ^oC for 12 h giving **11i** in 78% yield as a white solid by column chromatography (PE/EA = 4/1 to 1/1). **^{1}H NMR** (400 MHz, d_6-acetone) δ 8.17 (d, *J* = 8.6 Hz, 2H), 8.02 (d, *J* = 8.5 Hz, 2H), 6.80 (s, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, d_6-acetone) δ 165.7, 149.0, 134.5, 130.6, 127.3, 62.1, 14.5; **IR** (KBr) v 3320, 3246, 1704, 1576, 1403, 1370, 1283, 1162, 1135, 855, 764, 690, 537 cm^{-1}; **HRMS** (EI) for $C_9H_{11}NO_4S$ Calculated: 229.0405, found: 229.0405.

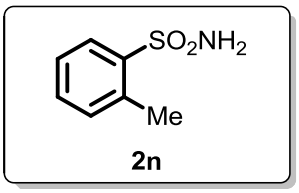


4-Acetylbenzenesulfonamide (**2l**). Prepared following general procedure using aryldiazonium salts **1l** (292.4 mg, 1.25 mmol)，$Na_2S_2O_5$ (190.1 mg, 1.0 mmol), NaN_3 (32.5 mg, 0.5 mmol), PPh_3(157.4 mg, 0.6 mmol), TBAB (241.7 mg, 0.75 mmol) and MeCN/H_2O = 1/2 (1 mL), the reaction was stirred at 80 ^oC for 12 h giving **2l** in 51% yield as a white solid by column chromatography (PE/EA = 4/1 to 2/1). **^{1}H NMR** (400 MHz, d_6-acetone) δ 8.15 (d, *J* = 8.4 Hz, 2H), 8.01 (d, *J* = 8.4 Hz, 2H), 6.81 (s, 2H), 2.65 (s, 3H); **^{13}C NMR** (100 MHz, d_6-acetone) δ 197.3, 148.6, 140.4, 129.6, 127.1, 27.0; **IR** (KBr) v 3310, 3215, 3098, 1668, 1401, 1406, 1350, 1159, 840, 785, 600 cm^{-1}; **HRMS** (EI) for $C_8H_9NO_3S$ Calculated: 199.0303, found: 199.0306.



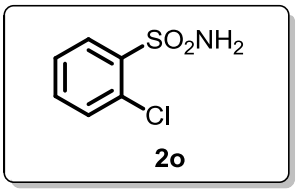
2m

2-Methoxybenzenesulfonamide (**2m**). Prepared following general procedure using aryldiazonium salts **1m** (277.4 mg, 1.25 mmol), $Na_2S_2O_5$ (190.1 mg, 1.0 mmol), NaN_3 (32.5 mg, 0.5 mmol), PPh_3(157.4 mg, 0.6 mmol), TBAB (241.7 mg, 0.75 mmol) and MeCN/H_2O = 1/2 (1 mL), the reaction was stirred at 80 ^oC for 12 h giving **2m** in 82% yield as a white solid by column chromatography (PE/EA = 3/1 to 1/1). **^{1}H NMR** (400 MHz, d_6-acetone) δ 7.81 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.64 – 7.53 (m, 1H), 7.22 (d, *J* = 8.3 Hz, 1H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.31 (s, 2H), 3.99 (s, 3H); **^{13}C NMR** (100 MHz, d_6-acetone) δ 157.2, 134.6, 132.5, 128.7, 120.8, 113.2, 56.5; **IR** (KBr) v 3375, 3265, 1589, 1481, 1300, 1150, 901, 801, 760 cm^{-1}; **HRMS** (EI) for $C_7H_9NO_3S$ Calculated: 187.0303, found: 187.0304.

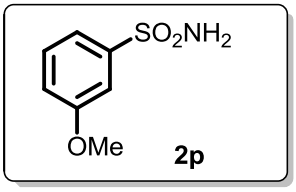


2n

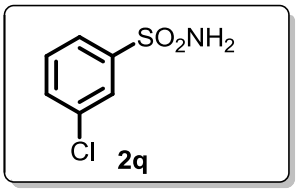
2-Methylbenzenesulfonamide (**2n**). Prepared following general procedure using aryldiazonium salts **1n** (257.4 mg, 1.25 mmol), $Na_2S_2O_5$ (190.1 mg, 1.0 mmol), NaN_3 (32.5 mg, 0.5 mmol), PPh_3(157.4 mg, 0.6 mmol), TBAB (241.7 mg, 0.75 mmol) and MeCN/H_2O = 1/2 (1 mL), the reaction was stirred at 80 ^oC for 12 h giving **2n** in 70% yield as a white solid by column chromatography (PE/EA = 5/1 to 2/1). **^{1}H NMR** (400 MHz, d_6-acetone) δ 7.95 (d, *J* = 7.8 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.36 (dd, *J* = 15.3, 7.5 Hz, 2H), 6.58 (s, 2H), 2.67 (s, 3H); **^{13}C NMR** (100 MHz, d_6-acetone) δ 143.0, 137.2, 133.0, 132.8, 128.3, 126.8, 20.3; **IR** (KBr) v 3381, 3260, 1560, 1472, 1314, 1152, 1069, 921, 766, 595 cm^{-1}; **HRMS** (EI) for $C_7H_9NO_2S$ Calculated:171.0354, found: 171.0354.



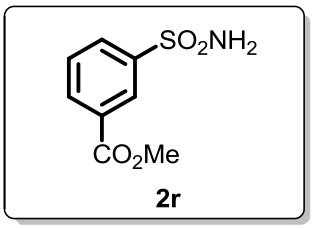
2-Chlorobenzenesulfonamide (**2o**). Prepared following general procedure using aryldiazonium salts **1o** (282.9 mg, 1.25 mmol), $Na_2S_2O_5$ (190.1 mg, 1.0 mmol), NaN_3 (32.5 mg, 0.5 mmol), PPh_3(157.4 mg, 0.6 mmol), TBAB (241.7 mg, 0.75 mmol) and MeCN/H_2O = 1/2 (1 mL), the reaction was stirred at 80 ^oC for 12 h giving **2o** in 62% yield as a white solid by column chromatography (PE/EA = 5/1 to 2/1). **^{1}H NMR** (400 MHz, d_6-acetone) δ 8.11 – 8.04 (m, 1H), 7.67 – 7.59 (m, 2H), 7.57 – 7.48 (m, 1H), 6.78 (s, 2H); **^{13}C NMR** (100 MHz, d_6-acetone) δ 142.0, 134.2, 132.3, 131.9, 130.2, 128.1; **IR** (KBr) v 3357, 3255, 1560, 1454, 1338, 1192, 1042, 913, 766, 590 cm^{-1}; **HRMS** (EI) for $C_6H_6NO_2SCl$ Calculated: 190.9808, found: 190.9805.



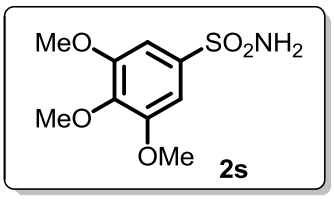
3-Methoxybenzenesulfonamide (**2p**)**.** Prepared following general procedure using aryldiazonium salts **1p** (277.4 mg, 1.25 mmol), $Na_2S_2O_5$ (190.1 mg, 1.0 mmol), NaN_3 (32.5 mg, 0.5 mmol), PPh_3(157.4 mg, 0.6 mmol), TBAB (241.7 mg, 0.75 mmol) and MeCN/H_2O = 1/2 (1 mL), the reaction was stirred at 80 ^oC for 12 h giving **2p** in 92% yield as a white solid by column chromatography (PE/EA = 4/1 to 1/1). **^{1}H NMR** (500 MHz, d_6-acetone) δ 7.49 – 7.45 (m, 2H), 7.43 (dd, *J* = 2.6, 1.1 Hz, 1H), 7.20 – 7.08 (m, 1H), 6.56 (s, 2H), 3.86 (s, 3H); **^{13}C NMR** (125 MHz, d_6-acetone) δ 160.7, 146.3, 130.8, 118.8, 118.5, 111.9, 55.9; **IR** (KBr) v 3342, 3266, 1600, 1492, 1300, 1256, 1172, 1103, 1028, 906, 800, 691cm^{-1}; **HRMS** (EI) for $C_7H_9NO_3S$ Calculated: 187.0303, found: 187.0301.



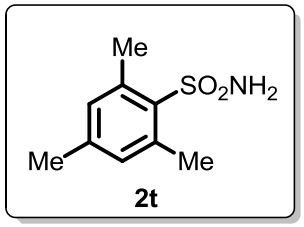
3-Chlorobenzenesulfonamide (**2q**). Prepared following general procedure using aryldiazonium salts **1q** (282.9 mg, 1.25 mmol), $Na_2S_2O_5$ (190.1 mg, 1.0 mmol), NaN_3 (32.5 mg, 0.5 mmol), PPh_3(157.4 mg, 0.6 mmol), TBAB (241.7 mg, 0.75 mmol) and MeCN/H_2O = 1/2 (1 mL), the reaction was stirred at 80 ^oC for 12 h giving **2q** in 72% yield as a white solid by column chromatography (PE/EA = 5/1 to 2/1). **^{1}H NMR** (400 MHz, d_6-acetone) δ 7.93 – 7.80 (m, 2H), 7.70 – 7.57 (m, 2H), 6.78 (s, 2H); **^{13}C NMR** (100 MHz, d_6-acetone) δ 146.9, 135.0, 132.7, 131.7, 126.8, 125.4; **IR** (KBr) v 3332, 3243, 1552, 1422, 1350, 1182, 1078, 901, 793, 677 cm^{-1}; **HRMS** (EI) for $C_6H_6NO_2SCl$ Calculated: 190.9808, found: 190.9805.



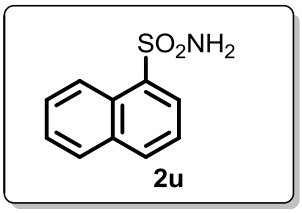
Methyl 3-sulfamoylbenzoate (**2r**). Prepared following general procedure using aryldiazonium salts **1r** (312.4 mg, 1.25 mmol), $Na_2S_2O_5$ (190.1 mg, 1.0 mmol), NaN_3 (32.5 mg, 0.5 mmol), PPh_3(157.4 mg, 0.6 mmol), TBAB (241.7 mg, 0.75 mmol) and MeCN/H_2O = 1/2 (1 mL), the reaction was stirred at 80 ^oC for 12 h giving **2r** in 54% yield as a white solid by column chromatography (PE/EA = 5/1 to 2/1). **^{1}H NMR** (400 MHz, d_6-acetone) δ 8.49 (s, 1H), 8.20 (d, J = 7.8 Hz, 1H), 8.14 (d, J = 7.9 Hz, 1H), 7.73 (t, J = 7.8 Hz, 1H), 6.79 (s, 2H), 3.94 (s, 3H); **^{13}C NMR** (100 MHz, d_6-acetone) δ 166.1, 145.7, 133.3, 131.9, 131.1, 130.4, 127.7, 52.8; **IR** (KBr) v 3289, 3238, 1704, 1598, 1443, 1300,1168, 1075, 967, 752, 681cm^{-1}; **HRMS** (EI) for $C_8H_9NO_4S$ Calculated: 215.0252, found: 215.0249.



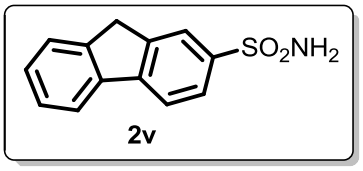
3,4,5-Trimethoxybenzenesulfonamide (**2s**). Prepared following general procedure using aryldiazonium salts **1s** (353.5 mg, 1.25 mmol), $Na_2S_2O_5$ (190.1 mg, 1.0 mmol), NaN_3 (32.5 mg, 0.5 mmol), PPh_3(157.4 mg, 0.6 mmol), TBAB (241.7 mg, 0.75 mmol) and MeCN/H_2O = 1/2 (1 mL), the reaction was stirred at 80 ^oC for 12 h giving **2s** in 85% yield as a brown solid by column chromatography (PE/EA = 3/1 to 1/1). **^{1}H NMR** (400 MHz, *d_6*-acetone) δ 7.19 (s, 2H), 6.51 (s, 2H), 3.87 (s, 6H), 3.78 (s, 3H)；**^{13}C NMR** (100 MHz, *d_6*-acetone) δ 154.2, 141.9, 140.1, 104.5, 60.7, 56.7; **IR** (KBr) v 3361, 3263, 1590, 1409, 1314, 1232, 1128, 990, 931, 842, 619cm^{-1}; **HRMS** (EI) for $C_9H_{13}NO_5S$ Calculated: 247.0514, found: 247.0515.



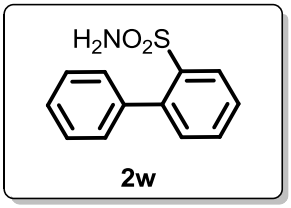
2,4,6-Trimethylbenzenesulfonamide (**2t**). Prepared following general procedure using aryldiazonium salts **1t** (292.5 mg, 1.25 mmol), $Na_2S_2O_5$ (190.1 mg, 1.0 mmol), NaN_3 (32.5 mg, 0.5 mmol), PPh_3(157.4 mg, 0.6 mmol), TBAB (241.7 mg, 0.75 mmol) and MeCN/H_2O = 1/2 (1 mL), the reaction was stirred at 80 ^oC for 12 h giving **2t** in 71% yield as a brown solid by column chromatography (PE/EA = 5/1 to 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.97 (s, 2H), 4.79 (s, 2H), 2.65 (s, 6H), 2.30 (s, 3H)；**^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.2, 138.2, 135.9, 131.9, 22.9, 20.9；**IR** (KBr) v 3342, 3202, 1384, 1010, 1005, 824, 764, 658 cm^{-1}; **HRMS** (EI) for $C_9H_{13}NO_2S$ Calculated: 199.0667, found: 199.0670.



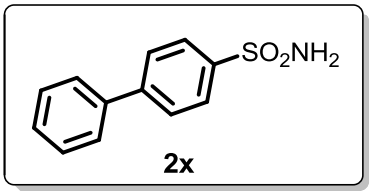
Naphthalene-1-sulfonamide (**2u**). Prepared following general procedure using aryldiazonium salts **1u** (302.4 mg, 1.25 mmol), $Na_2S_2O_5$ (190.1 mg, 1.0 mmol), NaN_3 (32.5 mg, 0.5 mmol), PPh_3(157.4 mg, 0.6 mmol), TBAB (241.7 mg, 0.75 mmol) and MeCN/H_2O = 1/2 (1 mL), the reaction was stirred at 80 ^oC for 12 h giving **2u** in 58% yield as a white solid by column chromatography (PE/EA = 5/1 to 2/1). **^{1}H NMR** (400 MHz, *d*$_6$-acetone) δ 8.78 (d, *J* = 8.4 Hz, 1H), 8.27 (d, *J* = 7.3 Hz, 1H), 8.16 (d, *J* = 8.2 Hz, 1H), 8.05 (d, *J* = 7.9 Hz, 1H), 7.76 – 7.55 (m, 3H), 6.84 (s, 2H); **^{13}C NMR** (100 MHz, *d*$_6$-acetone) δ 140.0, 135.1, 134.1, 129.7, 128.9, 128.4, 127.8, 127.5, 126.0, 125.1; **IR** (KBr) v 3380, 3280, 1567, 1325, 1131, 979, 887, 767 cm^{-1}; **HRMS** (EI) for $C_{10}H_9NO_2S$ Calculated: 207.0354, found: 207.0356.



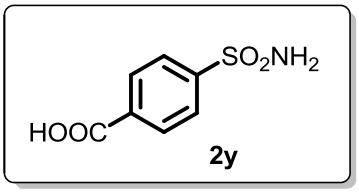
9*H*-Fluorene-2-sulfonamide (**2v**). Prepared following general procedure using aryldiazonium salts **1v** (350 mg, 1.25 mmol), $Na_2S_2O_5$ (190.1 mg, 1.0 mmol), NaN_3 (32.5 mg, 0.5 mmol), PPh_3(157.4 mg, 0.6 mmol), TBAB (241.7 mg, 0.75 mmol) and MeCN/H_2O = 1/2 (1 mL), the reaction was stirred at 80 ^oC for 12 h giving **2v** in 65% yield as a brown solid by column chromatography (PE/EA = 5/1 to 2/1). **^{1}H NMR** (400 MHz, *d*$_6$-acetone) δ 8.08 (s, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 6.8 Hz, 1H), 7.93 (d, *J* = 7.4 Hz, 1H), 7.65 (d, *J* = 7.2 Hz, 1H), 7.48 – 7.37 (m, 2H), 4.03 (s, 2H)； **^{13}C NMR** (100 MHz, *d*$_6$-acetone) δ 145.8, 145.2, 144.6, 143.3, 140.9, 128.9, 127.9, 126.1, 125.9, 123.8, 121.6, 120.8, 37.4; **IR** (KBr) v 3360, 3256, 1547, 1331, 1144, 1159, 1072, 771, 737, 586 cm^{-1};**HRMS** (EI) for $C_{13}H_{11}NO_2S$ Calculated: 245.0511, found: 245.0512.



[1,1'-Biphenyl]-2-sulfonamide (**2w**). Prepared following general procedure using aryldiazonium salts **1w** (335 mg, 1.25 mmol), $Na_2S_2O_5$ (190.1 mg, 1.0 mmol), NaN_3 (32.5 mg, 0.5 mmol), PPh_3(157.4 mg, 0.6 mmol), TBAB (241.7 mg, 0.75 mmol) and MeCN/H_2O = 1/2 (1 mL), the reaction was stirred at 80 ^oC for 12 h giving **2w** in 64% yield as a white solid by column chromatography (PE/EA = 5/1 to 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.13 (dd, *J* = 5.8, 4.8 Hz, 1H), 7.63 – 7.56 (m, 1H), 7.53 – 7.42 (m, 6H), 7.39 – 7.31 (m, 1H), 4.20 (s, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.7, 140.0, 138.9, 132.2(0), 132.1(6), 129.5, 128.5, 128.4, 127.8, 127.5; **IR** (KBr) v 3349, 3267, 1588, 1295, 1171, 916, 820, 730, 656 cm^{-1};**HRMS** (EI) for $C_{12}H_{11}NO_2S$ Calculated: 233.0511, found: 233.0509.

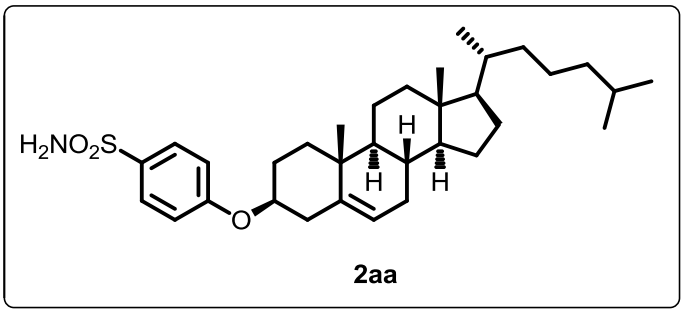


[1,1'-biphenyl]-4-sulfonamide (**2x**). Prepared following general procedure using aryldiazonium salts **1x** (335 mg, 1.25 mmol), $Na_2S_2O_5$ (190.1 mg, 1.0 mmol), NaN_3 (32.5 mg, 0.5 mmol), PPh_3(157.4 mg, 0.6 mmol), TBAB (241.7 mg, 0.75 mmol) and MeCN/H_2O = 1/2 (1 mL), the reaction was stirred at 80 ^oC for 12 h giving **2x** in 81% yield as a white solid by column chromatography (PE/EA = 5/1 to 2/1). **^{1}H NMR** (400 MHz, d_6-acetone) δ 7.98 (d, *J* = 8.3 Hz, 2H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.73 (d, *J* = 7.3 Hz, 2H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.43 (t, *J* = 7.3 Hz, 1H); **^{13}C NMR** (100 MHz, d_6-acetone) δ 145.3, 143.8, 140.2, 129.9, 129.1, 128.1, 128.0, 127.5; **IR** (KBr) v 3345, 3257, 1536, 1295, 1159, 906, 840, 750, 691 cm^{-1};**HRMS** (EI) for $C_{12}H_{11}NO_2S$ Calculated: 233.0511, found: 233.0508.



2y

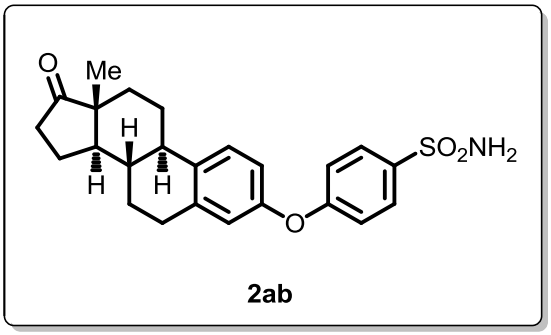
4-sulfamoylbenzoic acid (**2y**). Prepared following general procedure using aryldiazonium salts **1y** (294.9 mg, 1.25 mmol), $Na_2S_2O_5$ (190.1 mg, 1.0 mmol), NaN_3 (32.5 mg, 0.5 mmol), PPh_3(157.4 mg, 0.6 mmol), TBAB (241.7 mg, 0.75 mmol) and MeCN/H_2O = 1/2 (1 mL), the reaction was stirred at 80 ^oC for 12 h giving **2y** in 60% yield as a white solid by column chromatography (DCM/MeOH = 20/1 to 10/1). **^{1}H NMR** (500 MHz, d_6-DMSO) δ 13.38 (s, 1H), 8.15 – 8.07 (m, 2H), 7.97 – 7.89 (m, 2H), 7.53 (s, 2H); **^{13}C NMR** (125 MHz, d_6-DMSO) δ 166.3, 147.7, 133.6, 130.0, 125.9; **IR** (KBr) v 3359, 3260, 1688, 1577, 1287, 1159, 864, 727, 688 cm^{-1};**HRMS** (EI) for $C_7H_7NO_4S$ Calculated: 201.0096, found: 201.0091.



2aa

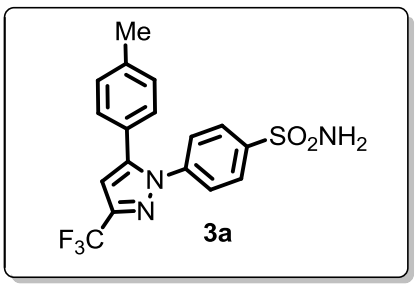
4-(((3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl)oxy)benzenesulfonamide (**2aa**). Prepared following general procedure using aryldiazonium salts **1aa** (720.7 mg, 1.25 mmol), $Na_2S_2O_5$ (190.1 mg, 1.0 mmol), NaN_3 (32.5 mg, 0.5 mmol), PPh_3(157.4 mg, 0.6 mmol), TBAB (241.7 mg, 0.75 mmol) and MeCN/H_2O = 1/2 (1 mL), the reaction was stirred at 80 ^oC for 12 h giving **2aa** in 72% yield as a white solid by column chromatography (PE/EA = 2/1 to 1/1) . **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.75 (d, *J* = 8.6 Hz, 2H), 6.62 (d, *J* = 8.6 Hz, 2H), 5.36 (d, *J* = 4.7 Hz, 1H), 4.01 – 3.79 (m, 1H), 3.11 (s, 2H), 2.53 – 2.29 (m, 2H), 2.09 – 0.77 (m, 38H), 0.69 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.7, 140.6, 140.1, 122.0, 117.9, 116.4, 78.4, 56.8, 56.2, 50.2, 42.3, 39.8, 39.5, 38.9, 37.2, 36.8, 36.2, 35.8, 31.9, 31.9, 28.4, 28.2, 28.0, 24.3, 23.8, 22.8, 22.6, 21.1, 19.4, 18.7, 11.9; **HRMS** (EI) for $C_{33}H_{51}NO_3S$

Calculated: 541.3590, found: 541.3582.



2ab

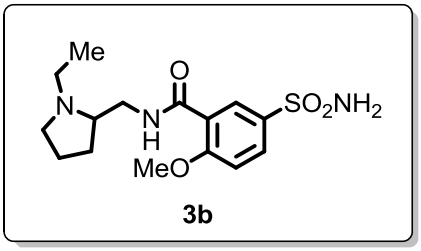
4-(((8S,9R,13R,14R)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)oxy)benzenesulfonamide (**2ab**). Prepared following general procedure using aryldiazonium salts **1ab** (575.3 mg, 1.25 mmol), $Na_2S_2O_5$ (190.1 mg, 1.0 mmol), NaN_3 (32.5 mg, 0.5 mmol), PPh_3(157.4 mg, 0.6 mmol), TBAB (241.7 mg, 0.75 mmol) and MeCN/H_2O = 1/2 (1 mL), the reaction was stirred at 80 ^oC for 12 h giving **2ab** in 78% yield as a white solid by column chromatography (PE/EA = 2/1 to 1/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 9.3, 2.2 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 1H), 7.03 (dd, *J* = 9.2, 2.2 Hz, 2H), 6.86 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.80 (d, *J* = 6.5 Hz, 1H), 5.19 (s, 2H), 2.92 (dd, *J* = 10.4, 4.6 Hz, 2H), 2.53 (dd, *J* = 19.1, 8.6 Hz, 1H), 2.49 – 2.39 (m, 1H), 2.32 (td, *J* = 10.8, 3.7 Hz, 1H), 2.23 – 2.13 (m, 1H), 2.07 (ddd, *J* = 13.4, 10.7, 5.5 Hz, 2H), 1.98 (dd, *J* = 12.5, 3.3 Hz, 1H), 1.72 – 1.41 (m, 6H), 0.95 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.7, 152.9, 138.8, 136.5, 135.4, 128.6, 127.0, 120.2, 117.5, 117.4, 50.3, 47.9, 44.1, 38.0, 35.8, 31.5, 29.4, 26.3, 25.8, 21.5, 13.8; **IR** (KBr) v 3573, 3505, 2926, 1725, 1591, 1165, 1489, 1327, 1261, 1156, 921, 838, 543 cm^{-1};**HRMS** (EI) for $C_{24}H_{27}NO_4S$ Calculated: 425.1661, found: 425.1664.



3a

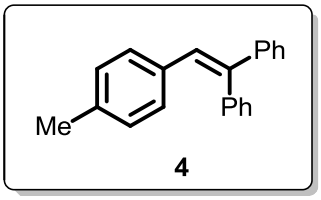
Celecoxib (**3a**). Prepared following general procedure using aryldiazonium salts **1ba** (520.1 mg, 1.25 mmol), $Na_2S_2O_5$ (190.1 mg, 1.0 mmol), NaN_3 (32.5 mg, 0.5 mmol), PPh_3(157.4 mg, 0.6 mmol), TBAB (241.7 mg, 0.75 mmol) and MeCN/H_2O = 1/2 (1 mL), the reaction was stirred at 80 ^oC for

12 h giving **3a** in 72% yield as a white solid by column chromatography (DCM/MeOH = 30/1 to 20/1). **^{1}H NMR** (400 MHz, d_6-DMSO) δ 7.89 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 8.8 Hz, 4H), 7.18 – 7.24 (m, 5H), 2.32 (s, 3H); **^{13}C NMR** (100 MHz, d_6-DMSO) δ 145.3, 144.0, 142.2 (q, *J* = 37.7 Hz), 141.1, 139.1, 129.4, 128.8, 126.8, 126.0, 121.3 (q, *J* = 269.9 Hz), 106.1, 20.8; **^{19}F NMR** (376 MHz, d_6-DMSO) δ -60.85; **IR** (KBr) v 3341, 3233, 1348, 1274, 1165, 1135, 981, 845, 792, 633 cm^{-1}; **HRMS** (EI) for $C_{17}H_{14}N_3O_2SF_3$ Calculated: 381.0759, found: 381.0762.



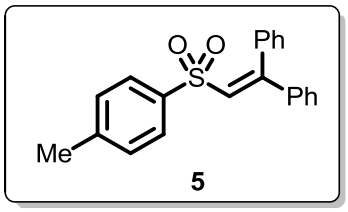
3b

Sulpiride (**3b**). Prepared following general procedure using aryldiazonium salts **1bb** (470.1 mg, 1.25 mmol), $Na_2S_2O_5$ (190.1 mg, 1.0 mmol), NaN_3 (32.5 mg, 0.5 mmol), PPh_3(157.4 mg, 0.6 mmol), TBAB (241.7 mg, 0.75 mmol) and MeCN/H_2O = 1/2 (1 mL), the reaction was stirred at 80 ^{o}C for 12 h giving **3b** in 60% yield as a white solid by column chromatography (DCM/MeOH = 20/1 to 10/1). **^{1}H NMR** (400 MHz, d_6-DMSO) δ 8.43 – 8.32 (m, 1H), 8.28 (d, *J* = 2.4 Hz, 1H), 7.89 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.38 – 7.25 (m, 3H), 3.97 (s, 3H), 3.60 – 3.44 (m, 1H), 3.24 – 3.04 (m, 2H), 2.82 (dq, *J* = 14.6, 7.3 Hz, 1H), 2.57 (d, *J* = 8.1 Hz, 1H), 2.26 – 2.06 (m, 2H), 1.87 - 1.75 (m, 1H), 1.64 – 1.42 (m, 3H), 1.06 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, d_6-DMSO) δ 163.5, 159.2, 136.4, 129.9, 128.7, 122.7, 112.6, 62.0, 56.6, 53.2, 47.6, 41.7, 28.2, 22.5, 14.1; **IR** (KBr) v 3385, 3209, 2968, 1644, 1547, 1480, 1365, 1160, 1091, 933, 827, 575 cm^{-1}; **HRMS** (EI) for $C_{15}H_{23}N_3O_4S$ Calculated: 341.1409, found: 341.1422.



4

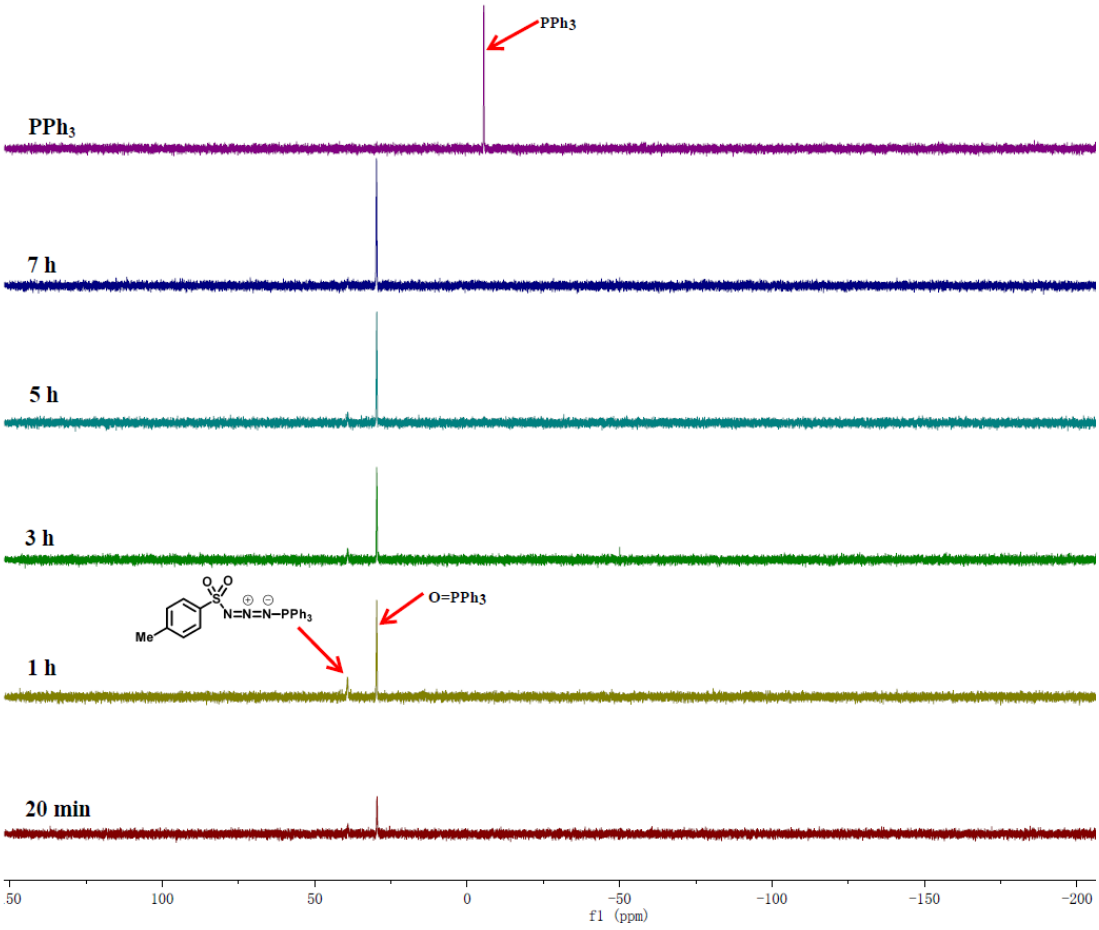
(2-(*p*-Tolyl)ethene-1,1-diyl)dibenzene (**4**). Prepared following general procedure using aryldiazonium salts **1a** (257.4 mg, 1.25 mmol), $Na_2S_2O_5$ (190.1 mg, 1.0 mmol), NaN_3 (32.5 mg, 0.5 mmol), PPh_3(157.4 mg, 0.6 mmol), TBAB (241.7 mg, 0.75 mmol), 1,1-diphenylethylene(135.2 mg, 0.75 mmol) and MeCN/H_2O = 1/2 (1 mL), the reaction was stirred at 80 ^oC for 12 h giving **4** in 15% yield as an oil by column chromatography (PE to PE/EA = 50/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38– 7.27 (m, 8H), 7.25 – 7.21 (m, 2H), 6.98 – 6.90 (m, 5H), 2.28 (s, 3H)； **^{13}C NMR** (125 MHz, $CDCl_3$) δ 143.5, 141.7, 140.6, 136.6, 134.5, 130.4, 129.4, 128.7, 128.6, 128.2, 128.1, 127.5, 127.3(2), 127.2(9), 21.2; **HRMS** (EI) for $C_{21}H_{18}$ Calculated: 270.1409, found: 270.1410.



5

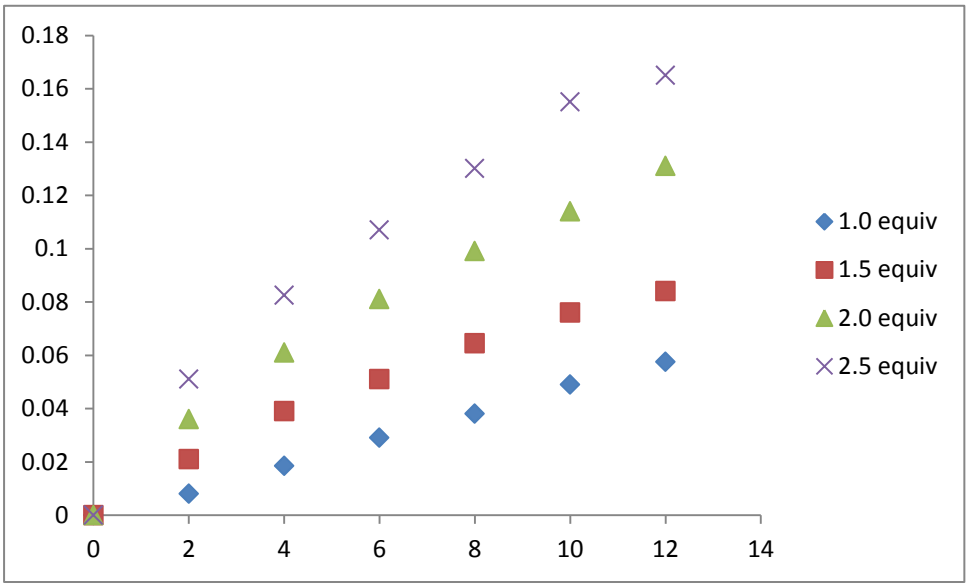
(2-Tosylethene-1,1-diyl)dibenzene (**5**). Following the same procedure with compound **4** to give **5** in 8% yield as a brown oil by column chromatography (PE/EA = 20/1 to 10/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.3 Hz, 2H), 7.37 (td, *J* = 7.2, 5.2 Hz, 2H), 7.30 (t, *J* = 7.7 Hz, 4H), 7.20 (d, *J* = 7.2 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 7.0 Hz, 2H), 6.99 (s, 1H), 2.38 (s, 3H)； **^{13}C NMR** (125 MHz, $CDCl_3$) δ 154.7, 143.7, 139.2, 138.6, 135.5, 130.2, 129.7, 129.3, 128.9, 128.8, 128.5, 128.2, 127.8, 127.7, 21.5. **HRMS** (EI) for $C_{21}H_{18}O_2S$ Calculated: 334.1028, found: 334.1024.

IV. The ^{31}P NMR in different reaction times

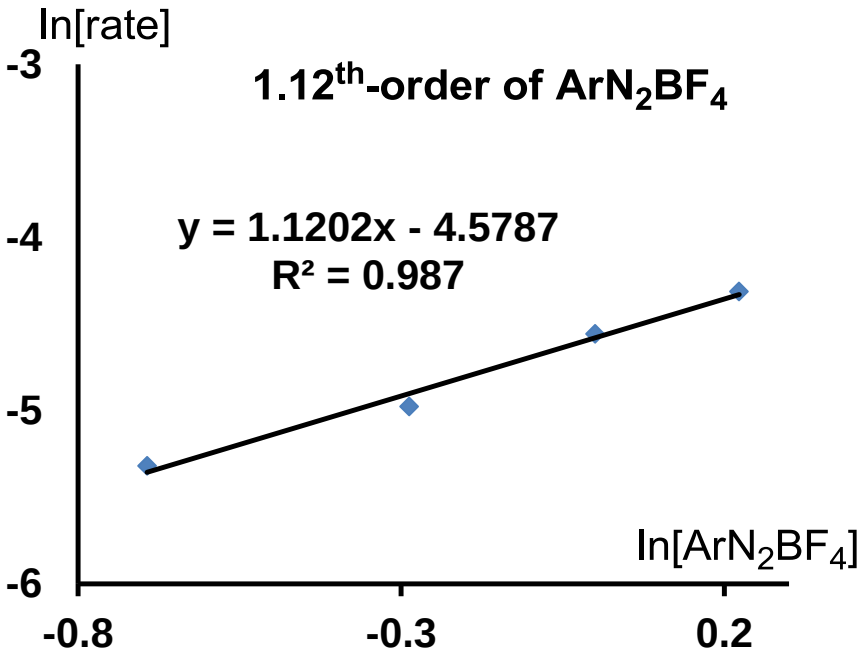


V. The kinetic studies

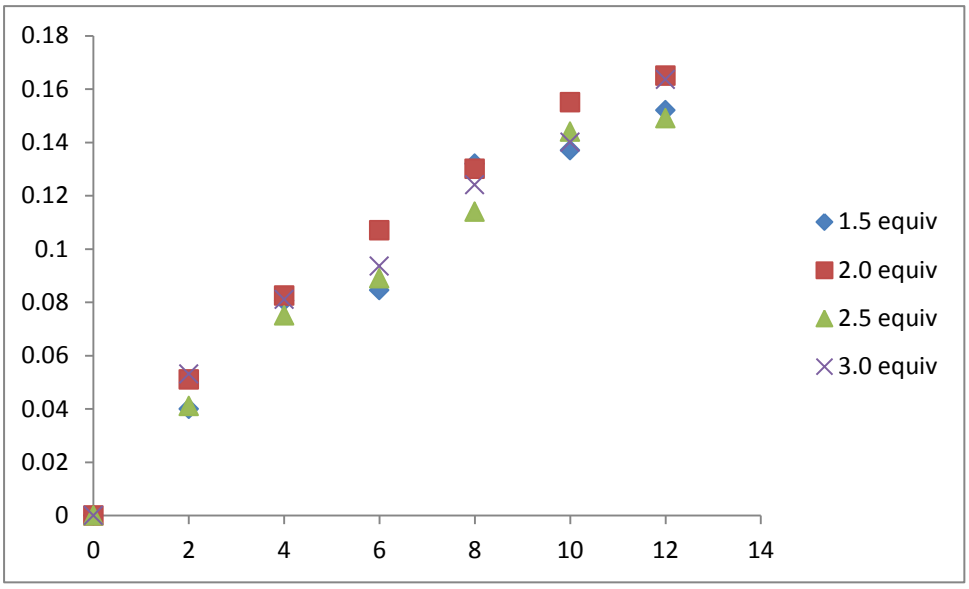
(1) Rates for varying ArN_2BF_4 (**1a**)

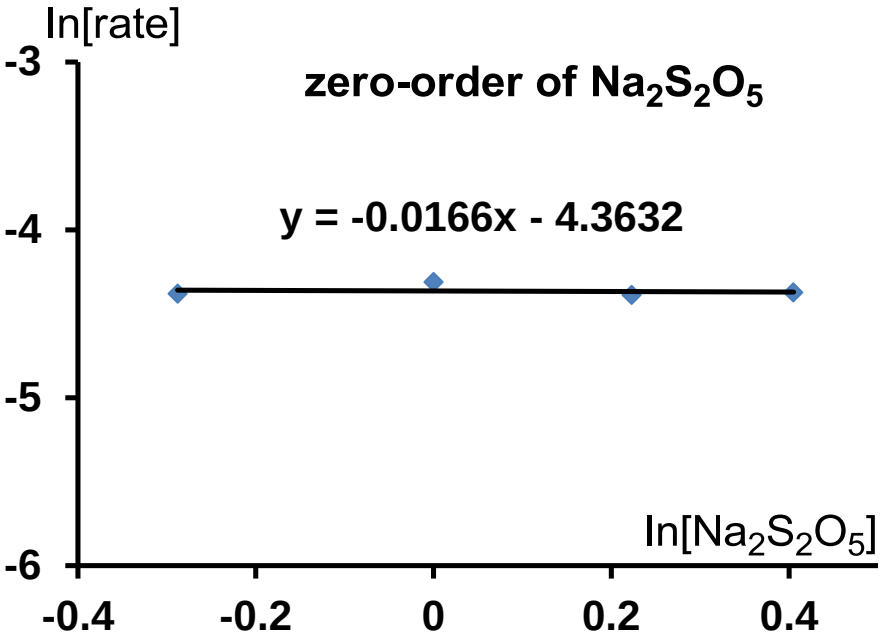


Rate = [product]/[time]

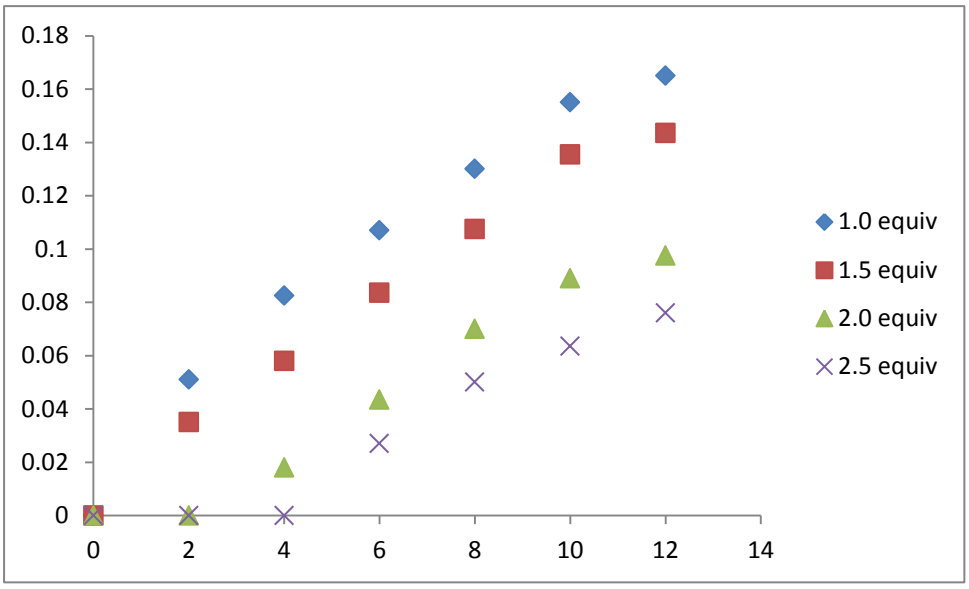


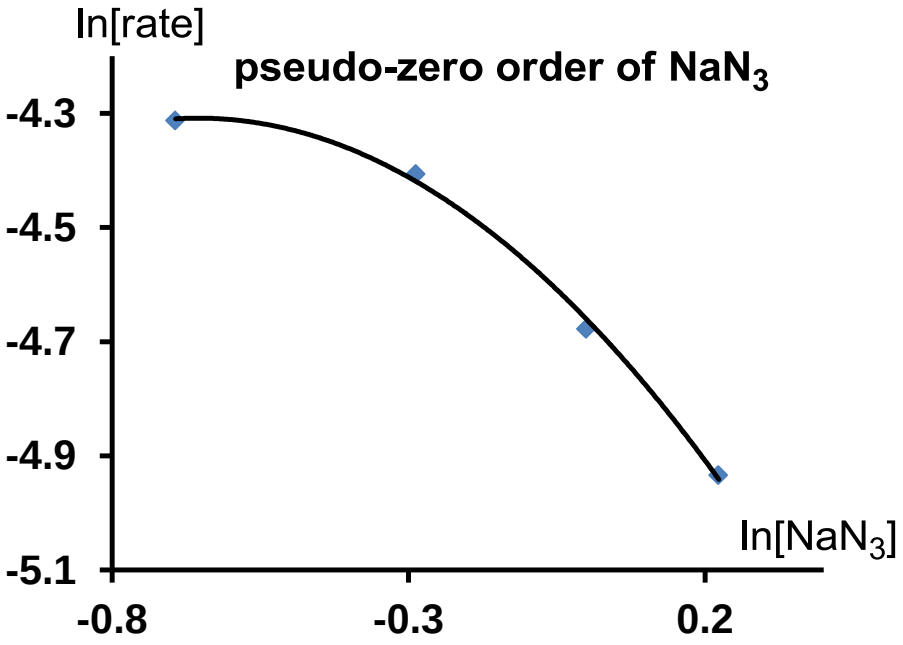
(2) Rates for varying $Na_2S_2O_5$



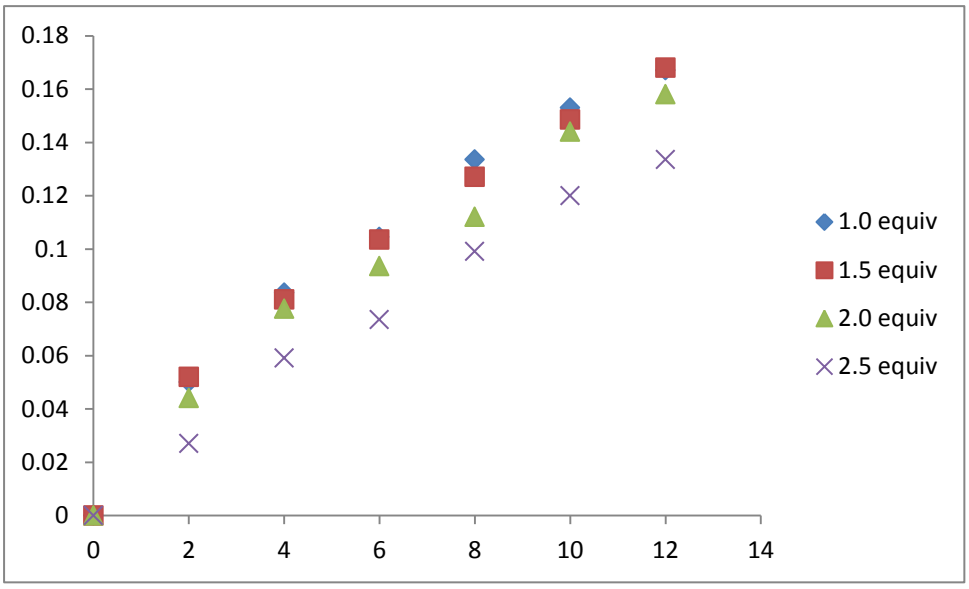


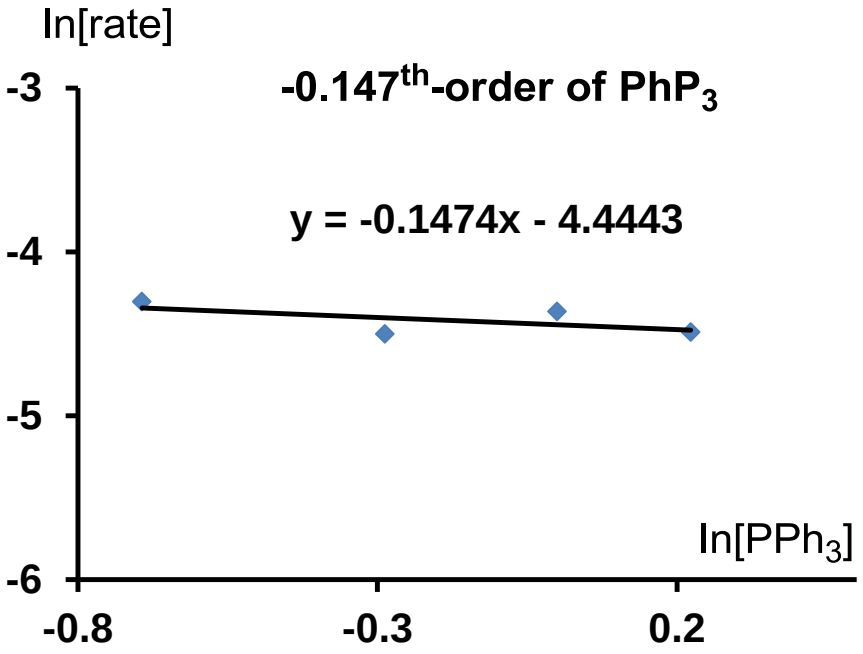
(3) Rates for varying NaN_3





(4) Rates for varying PPh_3





VI. X-Ray Crystal Structures

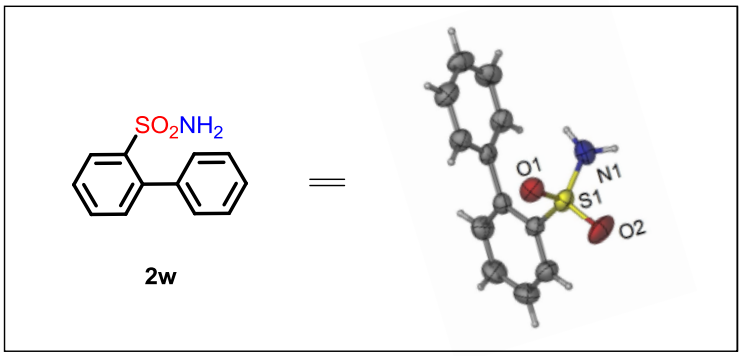
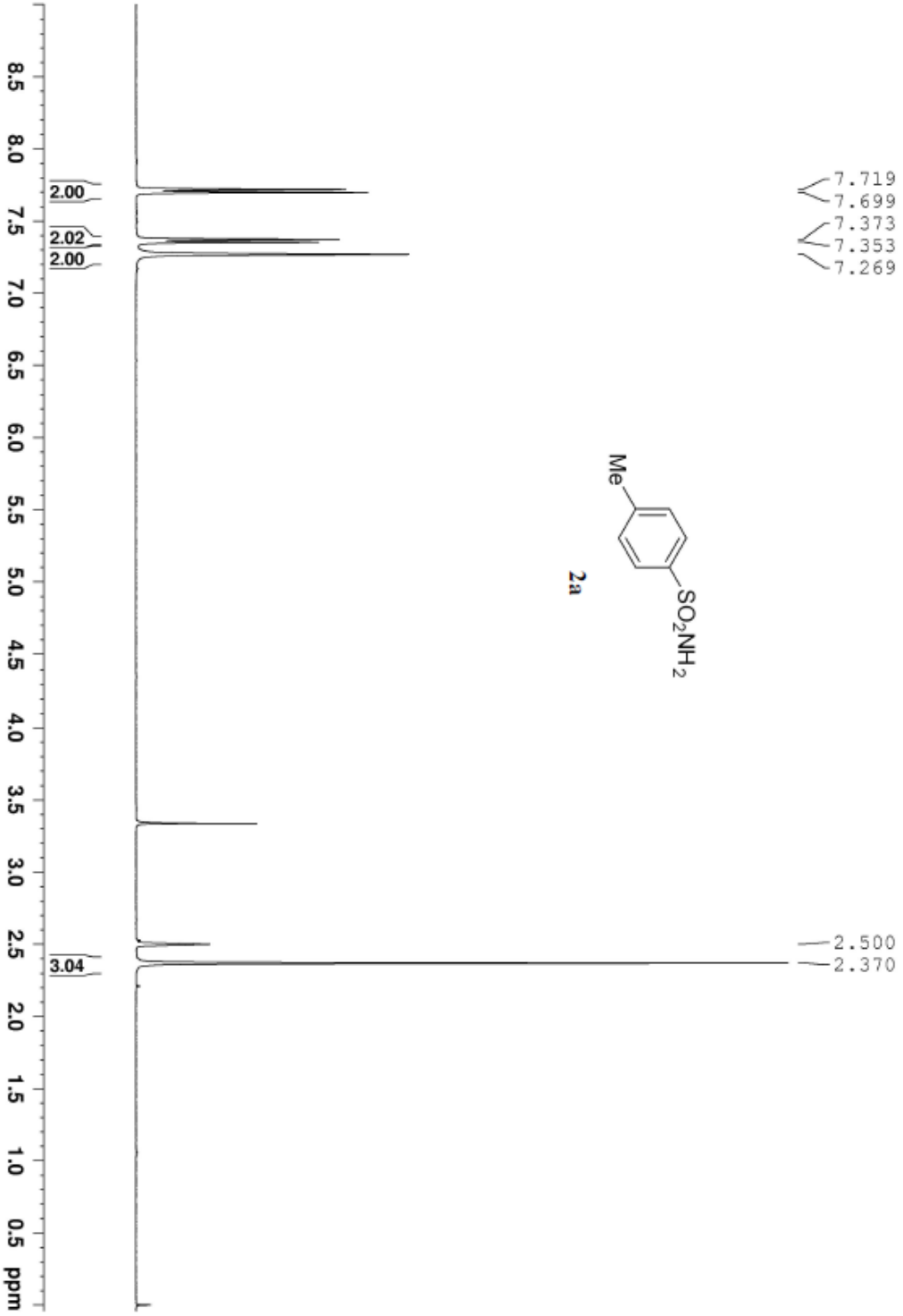


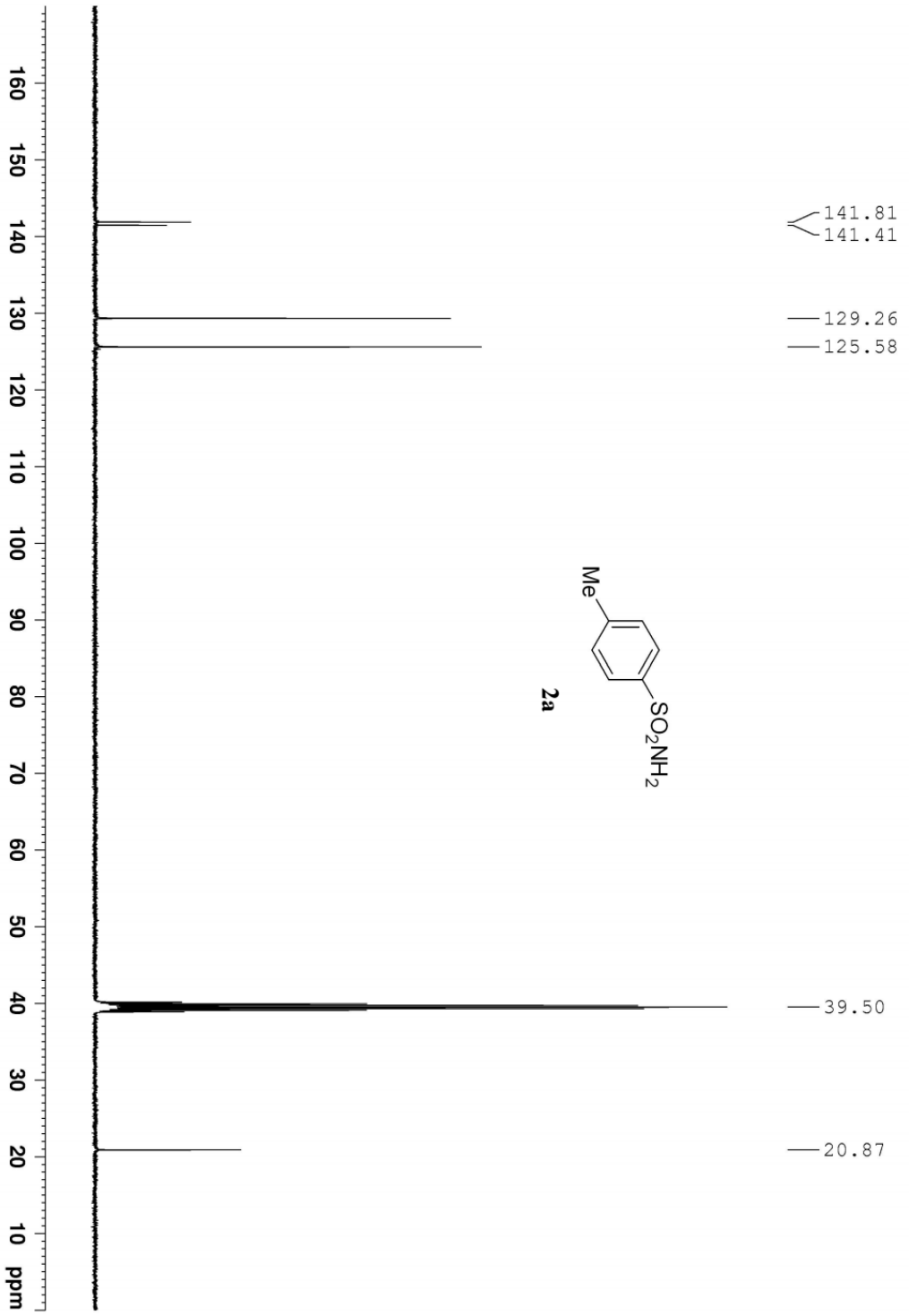
Table S2. Sample and crystal data for **2w** (CCDC 1868563)**.**

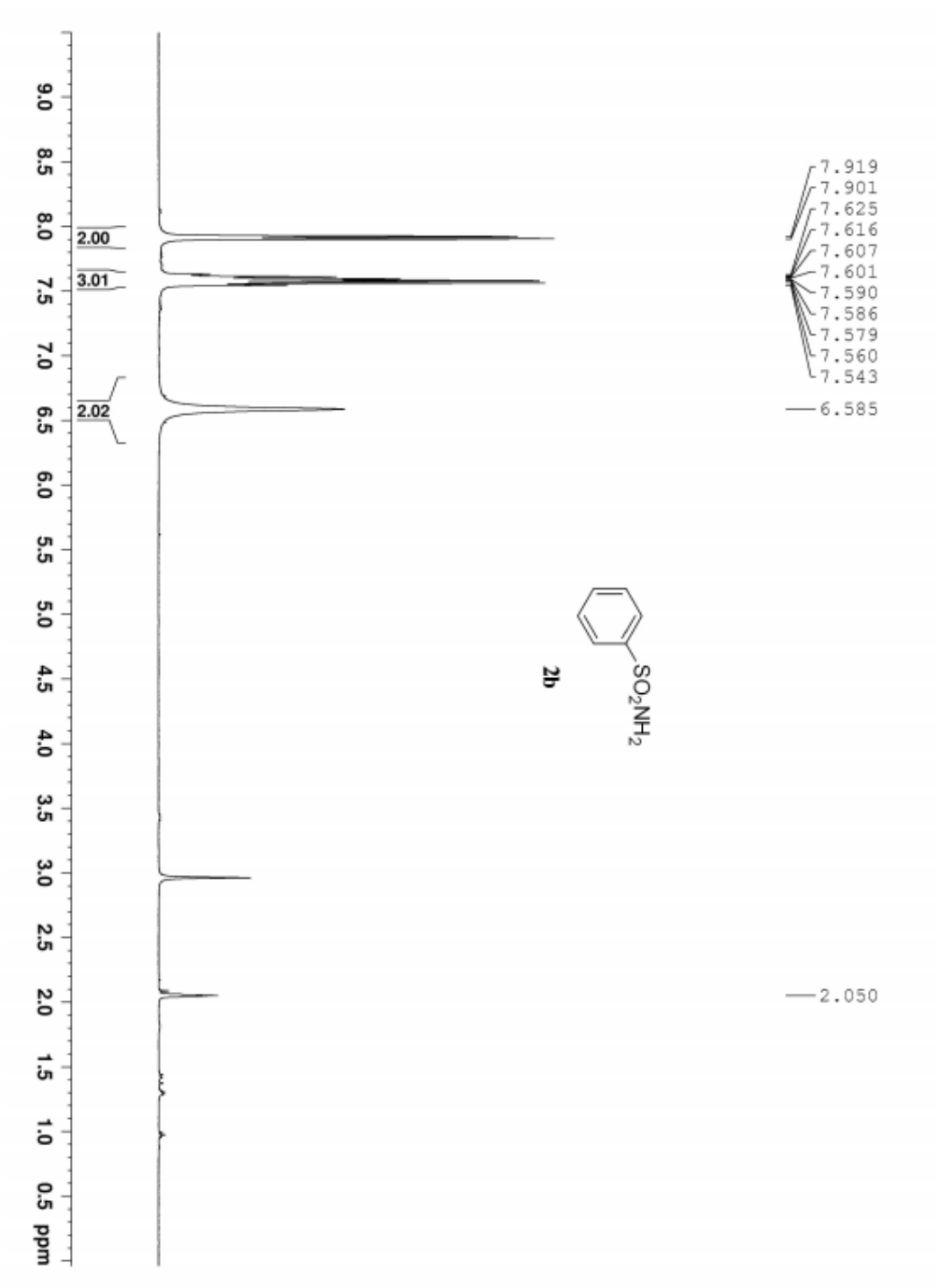
Bond precision	C-C = 0.0027 A
	Wavelength = 1.54184
Cell	a = 11.1231 (2) α = 90°
	b = 11.9525(2) β = 99.993(2)
	c = 8.5577 (1) γ = 90°
Temperature	293 K
Volume	1120.48(3)
Space group	P 1 21/c 1
Sum formula	C12 H11 N O2 S
Mr	233.28
Dx,g cm^{-3}	1.383
Z	4
Mu (mm-1)	2.441
F000	488.0
h,k,lmax	13, 14, 10
Nref	1960
Tmin,Tmax	0.276, 1.000
Correction method= # Reported T Limits	Tmin = 0.276 Tmax = 1.000
AbsCorr = MULTI-SCAN	
Data completeness	0.980
Theta(max)	67.062
R(reflections)	0.0395(1824)
wR2(reflections)	0.1078 (1960)
S	1.041
Npar	146

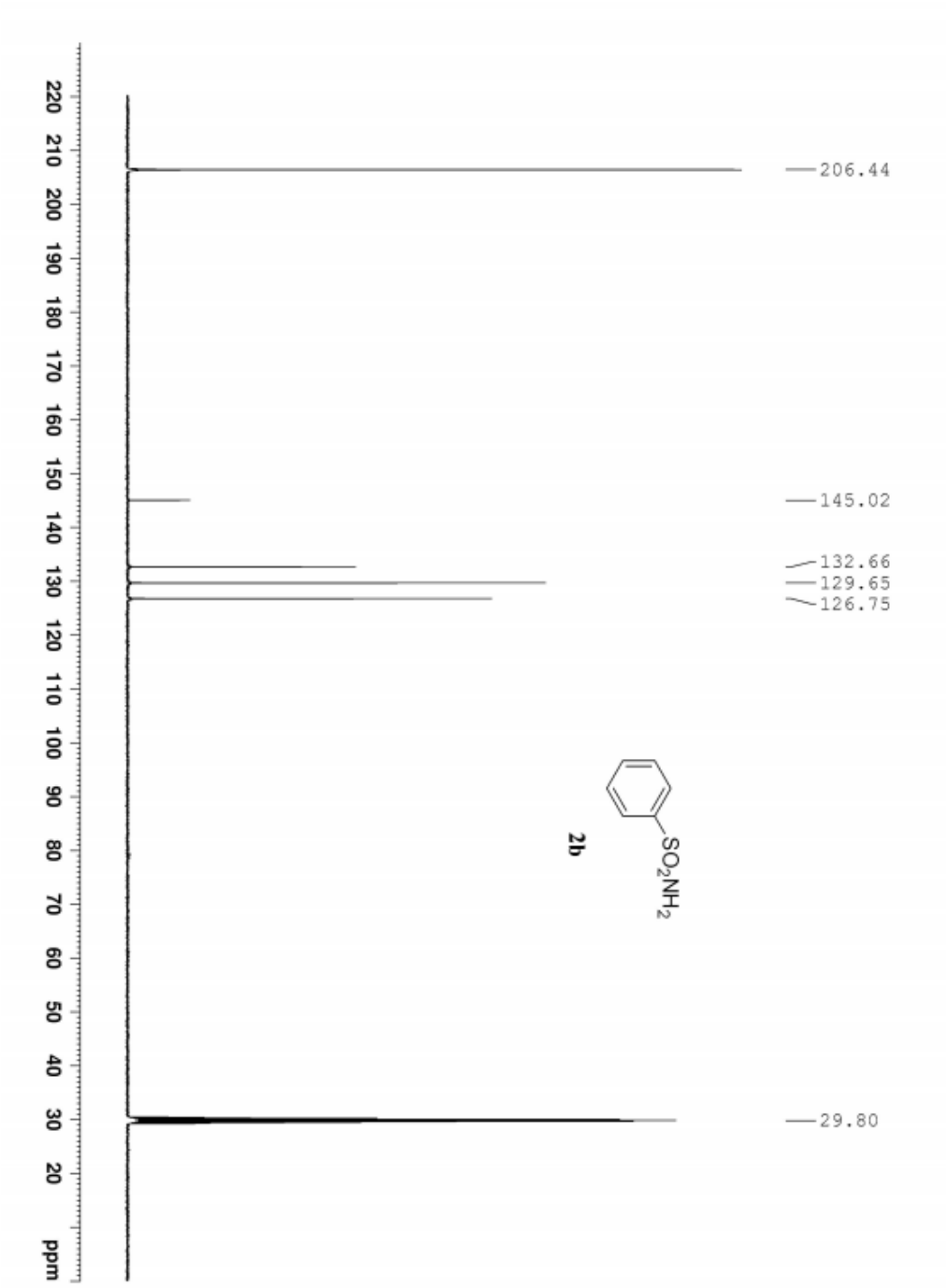
X. References

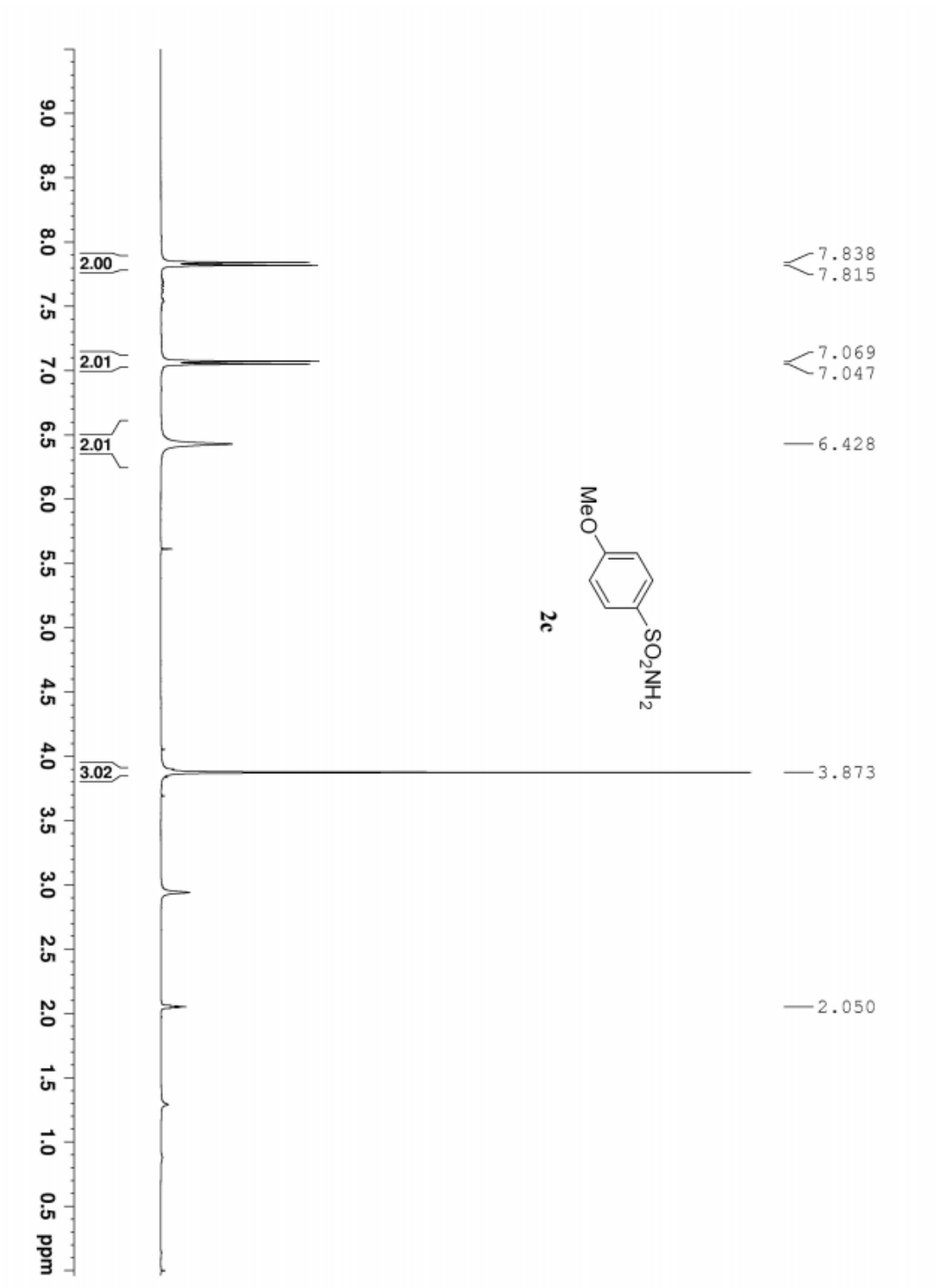
(1) (a) J. Wu, Y. Gu, X. Leng, Q. Shen, *Angew. Chem. Int. Ed.* **2015**, *54*, 7648; (b) G. Danoun, B. Bayarmagnai, M. F. Gruenberg, L. J. Goossen, *Chem. Sci.* **2014**, 5, 1312.

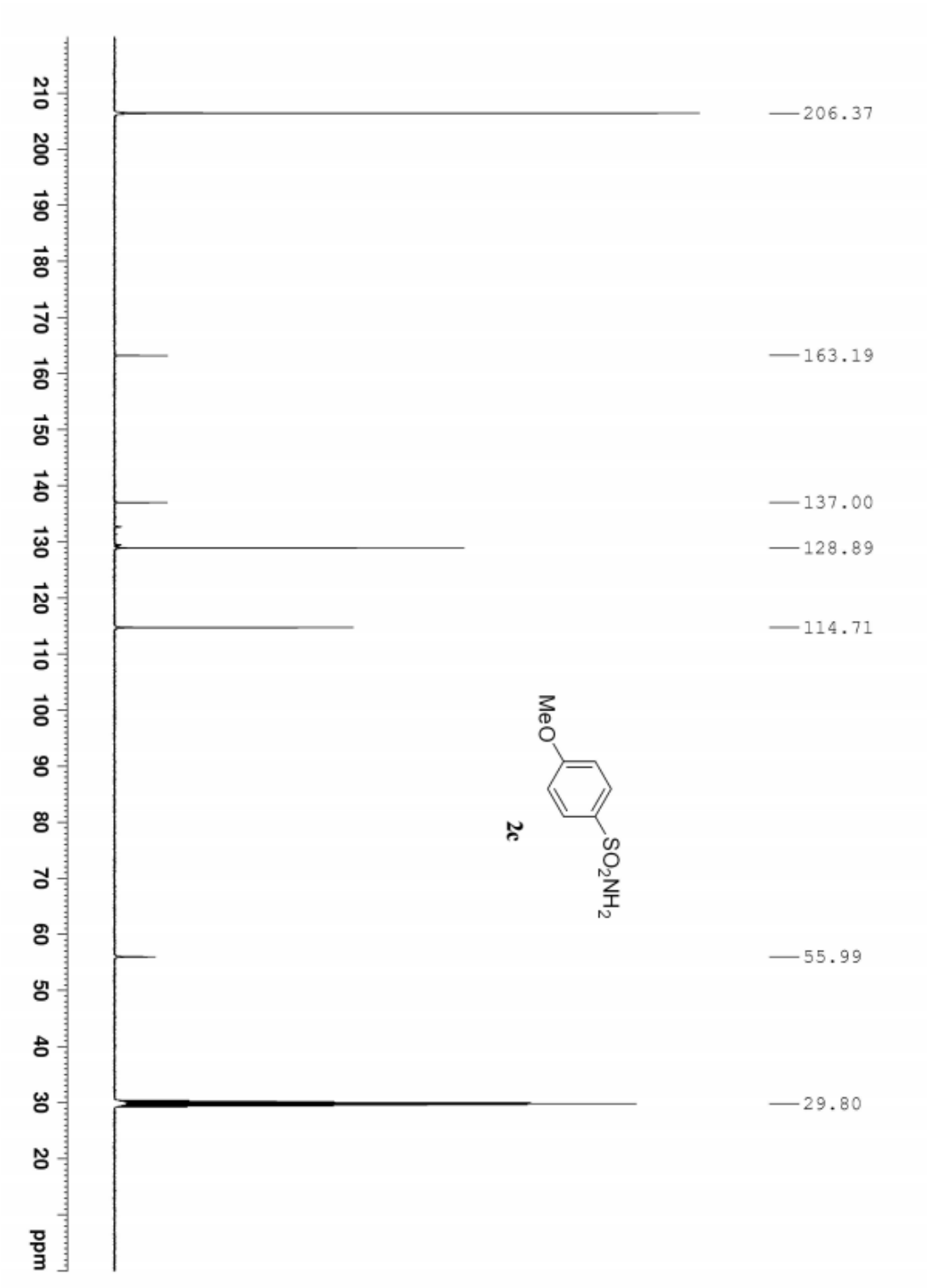

7.719
7.699
7.373
7.353
7.269
2.500
2.370
2.00
2.02
2.00
3.04
Me
SO2NH2
2a
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

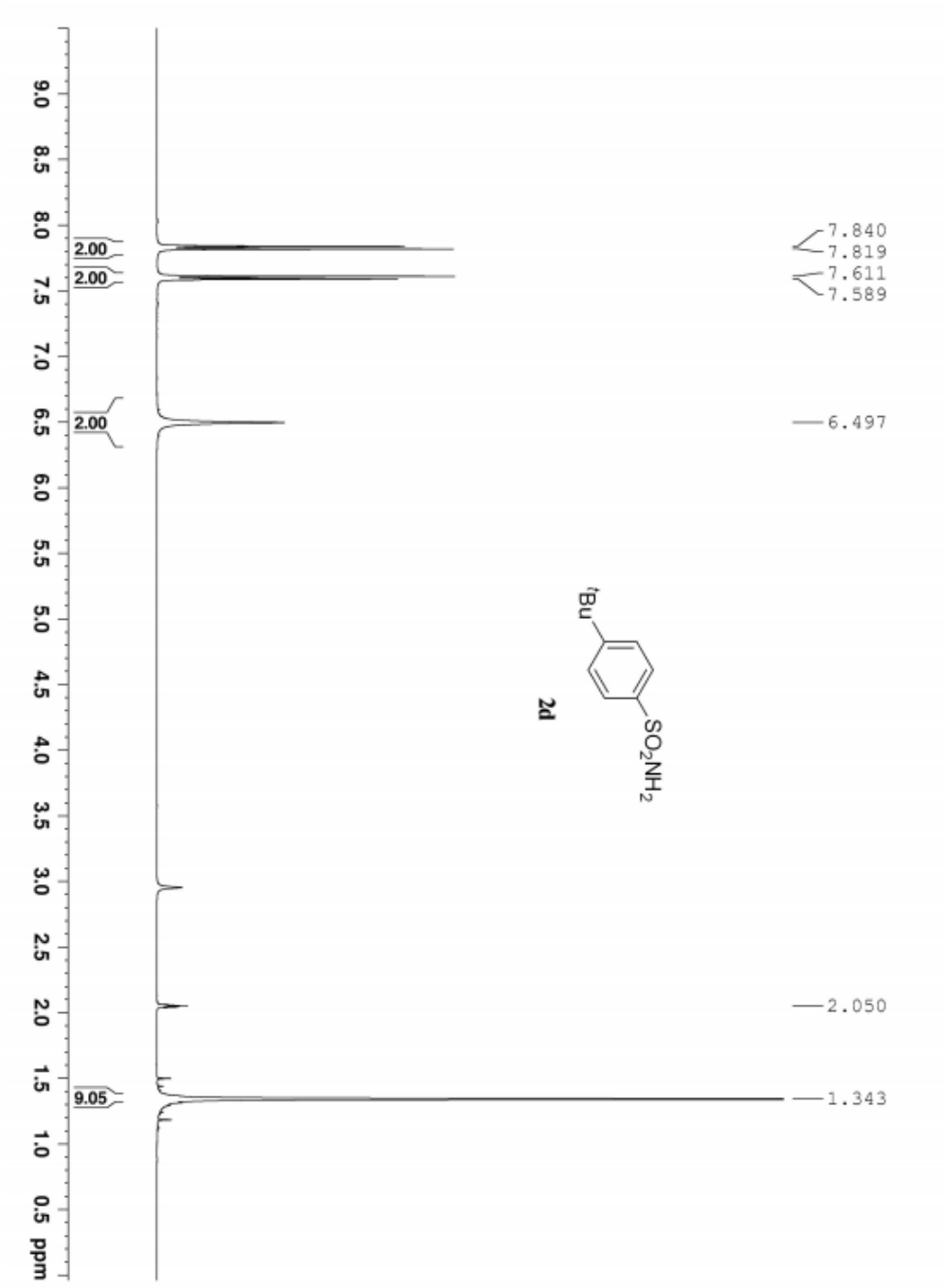

141.81
141.41
129.26
125.58
39.50
20.87
Me
SO2NH2
2a
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

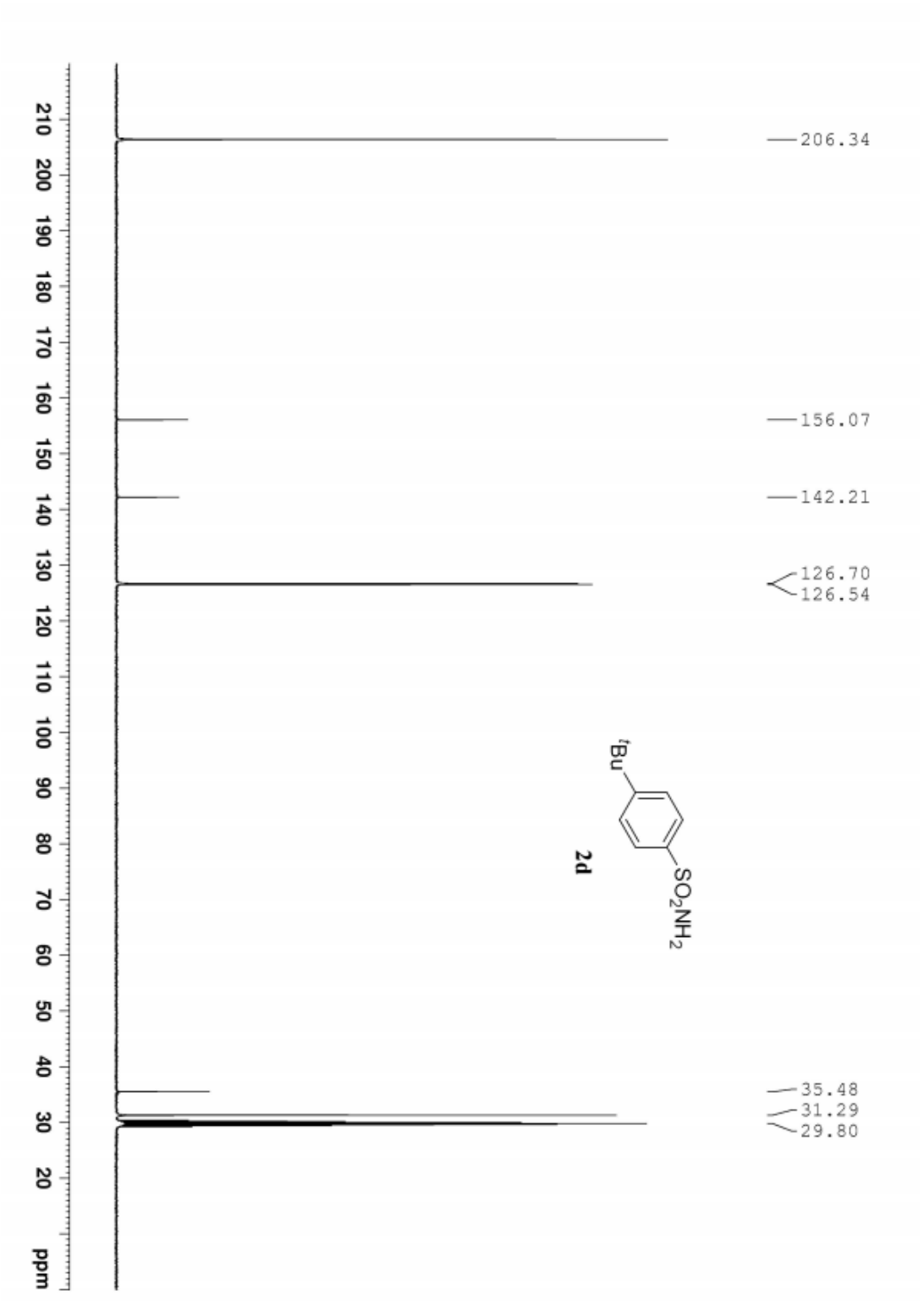

7.919
7.901
7.625
7.616
7.607
7.601
7.590
7.586
7.579
7.560
7.543
6.585
2.050
2.00
3.01
2.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
SO2NH2
2b

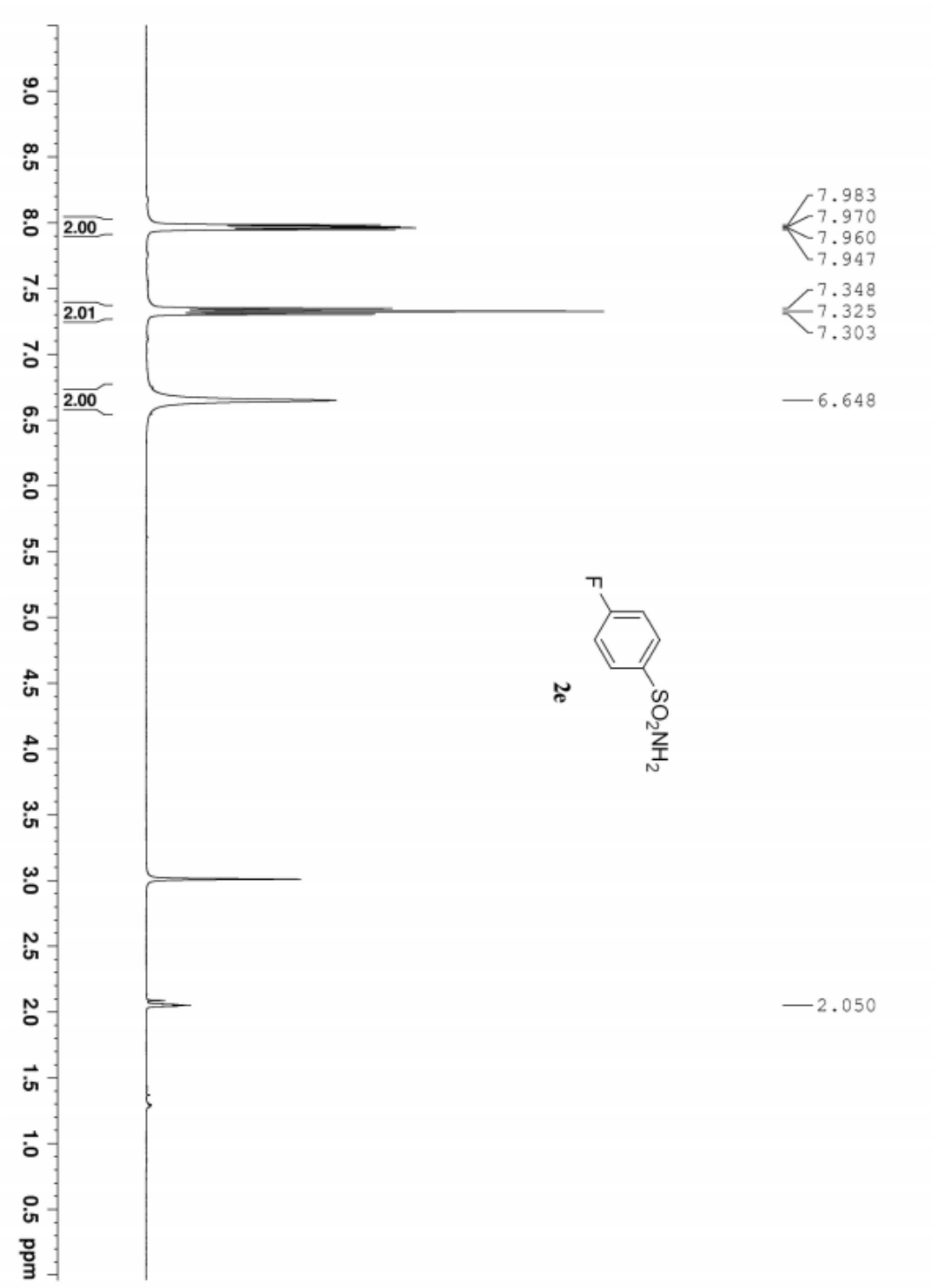

206.44
145.02
132.66
129.65
126.75
29.80
SO2NH2
2b
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

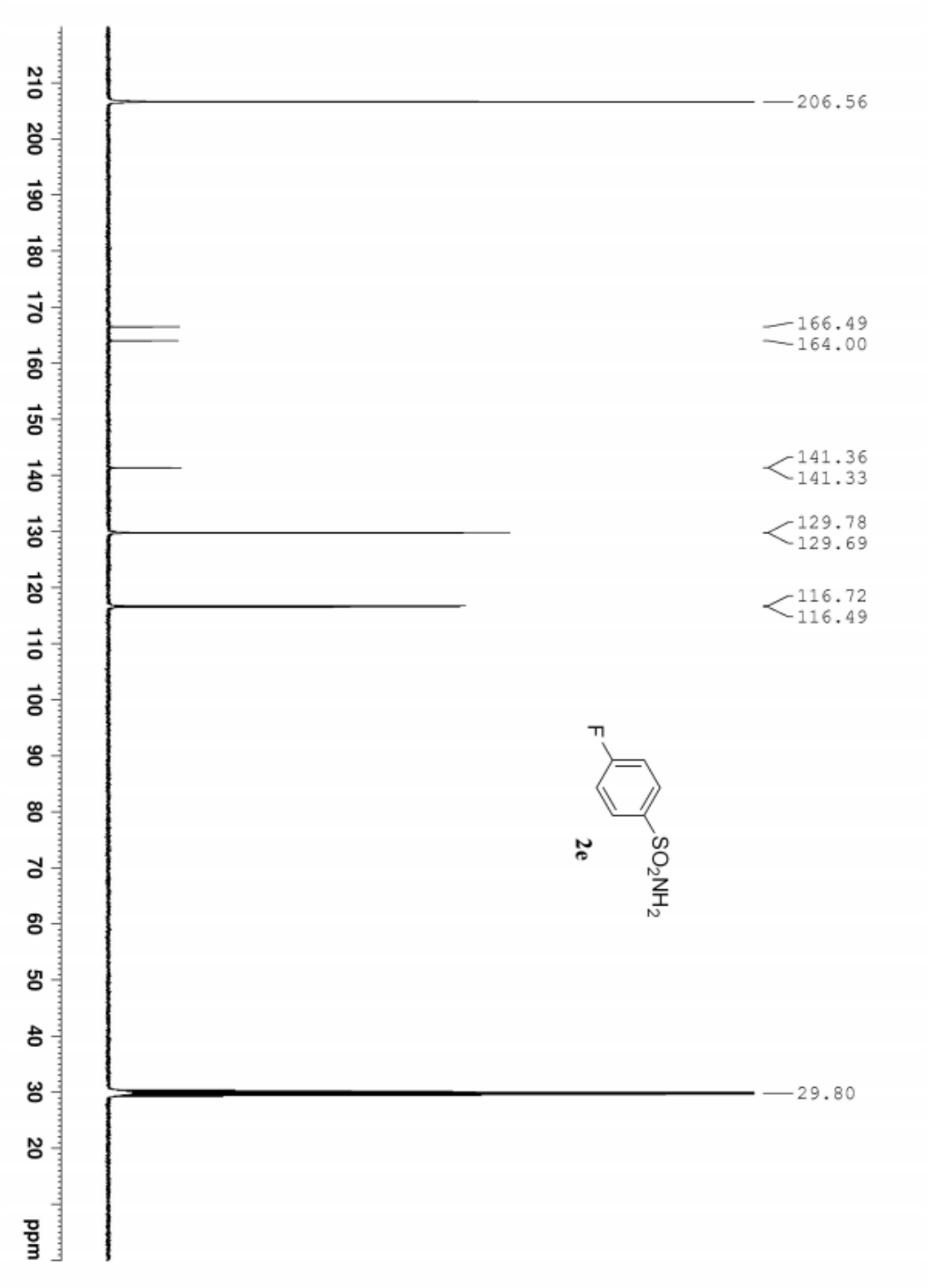

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
2.01
2.01
3.02
7.838
7.815
7.069
7.047
6.428
3.873
2.050
MeO
SO2NH2
2c

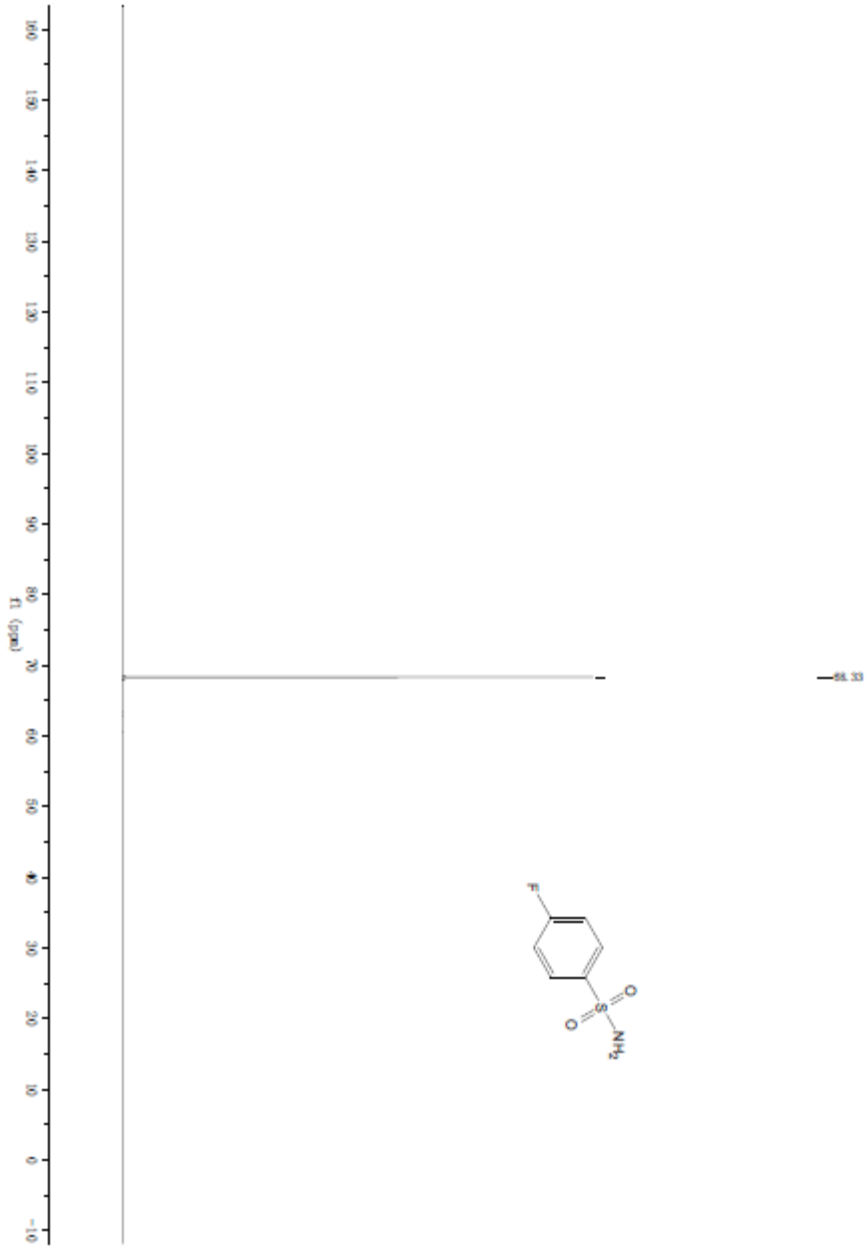

206.37
163.19
137.00
128.89
114.71
55.99
29.80
MeO
SO2NH2
2c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

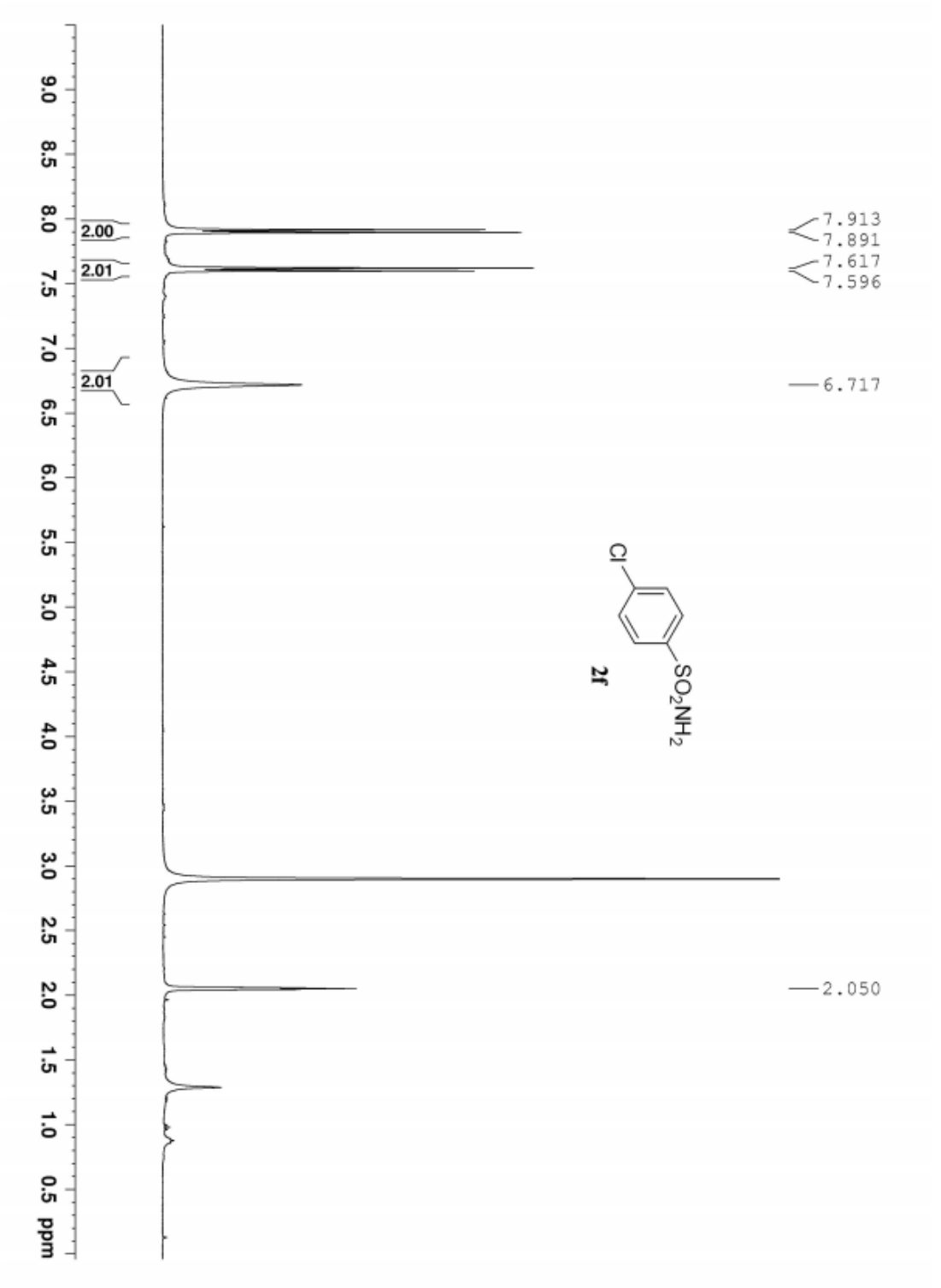

7.840
7.819
7.611
7.589
6.497
2.050
1.343
2.00
2.00
2.00
9.05
tBu
SO2NH2
2d
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

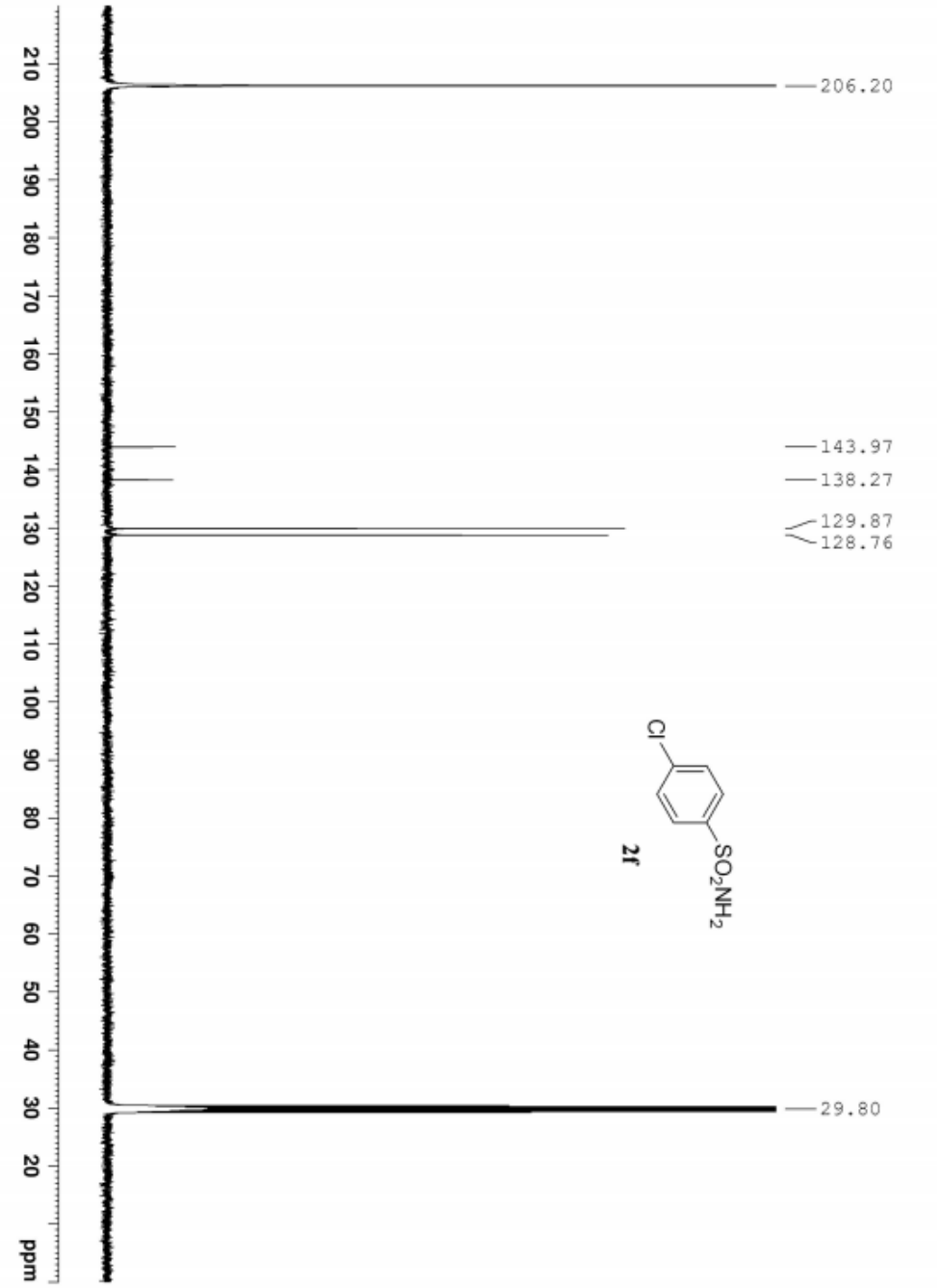

206.34
156.07
142.21
126.70
126.54
35.48
31.29
29.80
tBu
SO2NH2
2d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

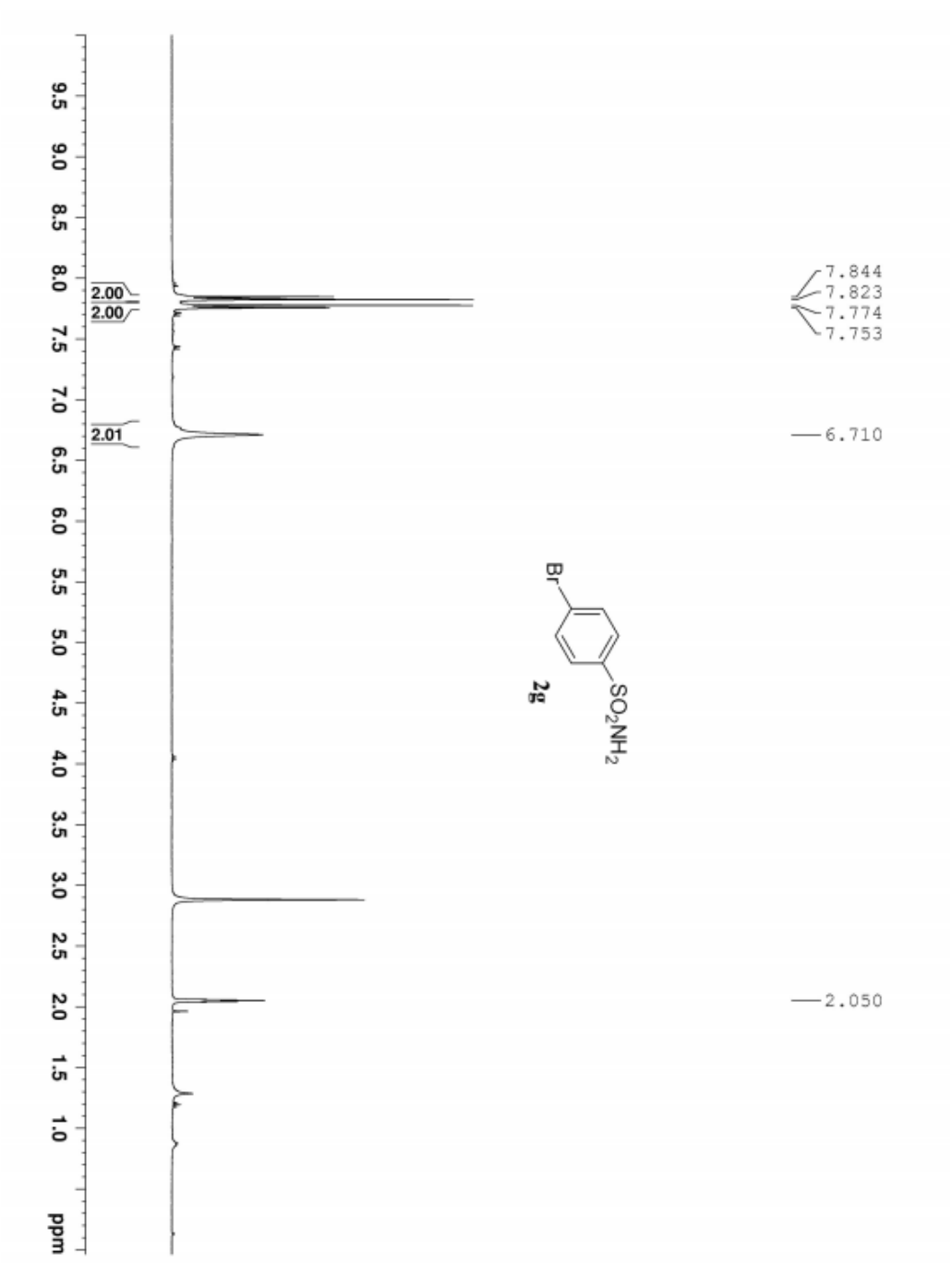

7.983
7.970
7.960
7.947
7.348
7.325
7.303
6.648
2.050
2.00
2.01
2.00
F
SO2NH2
2e
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

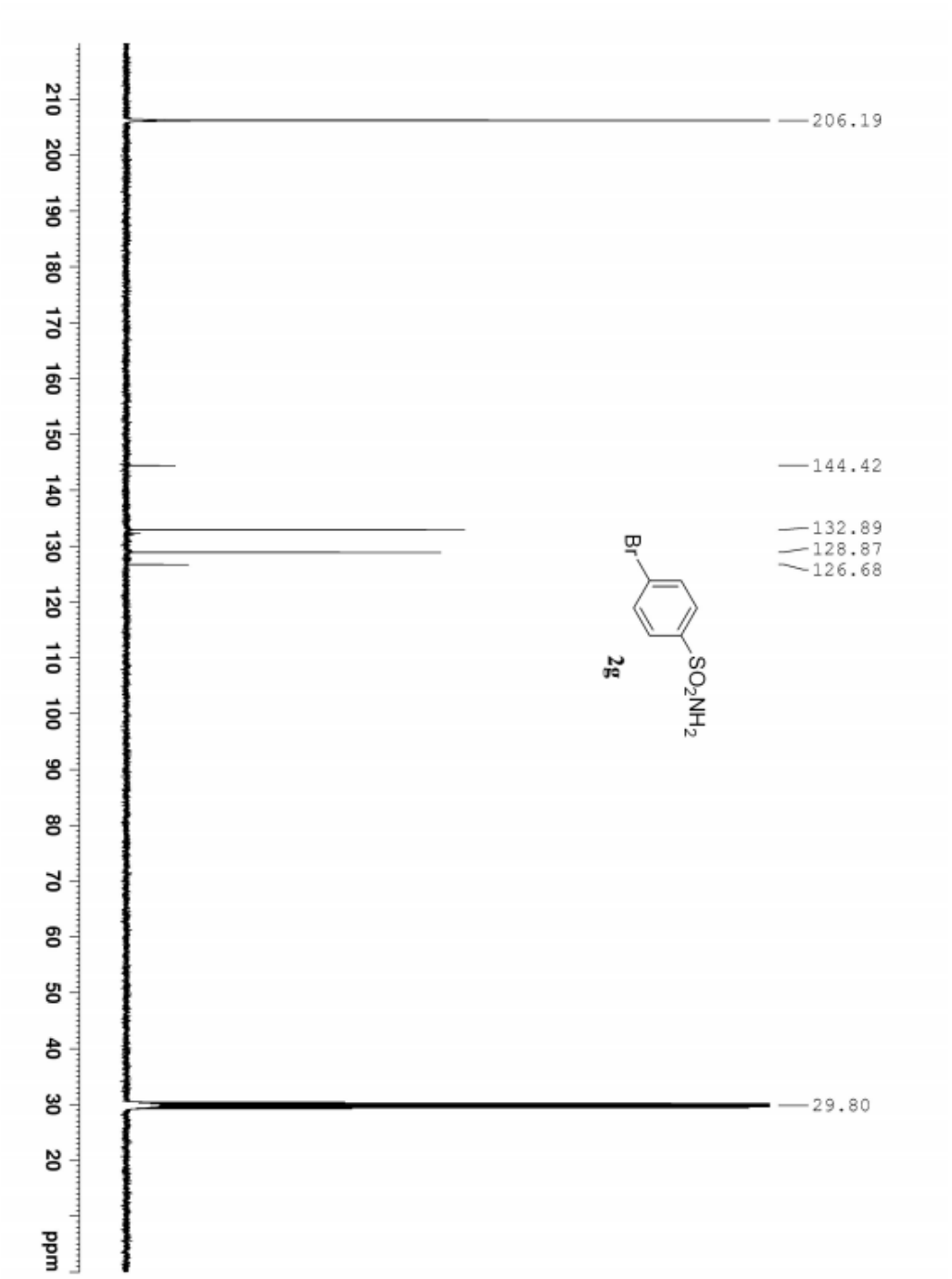

206.56
166.49
164.00
141.36
141.33
129.78
129.69
116.72
116.49
29.80
F
SO2NH2
2e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

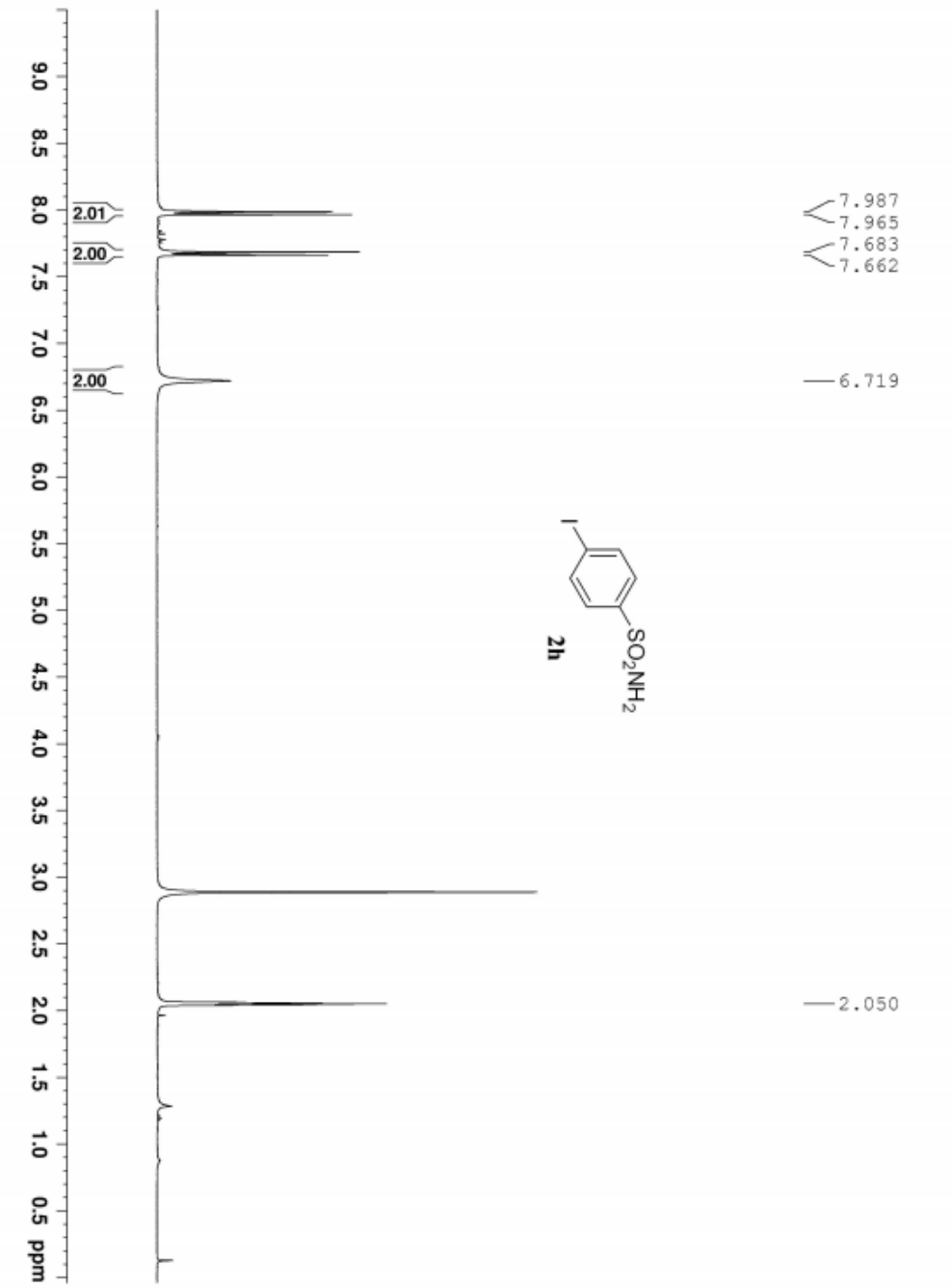

f1 (ppm)
65.33
F
S
O
O
NH2

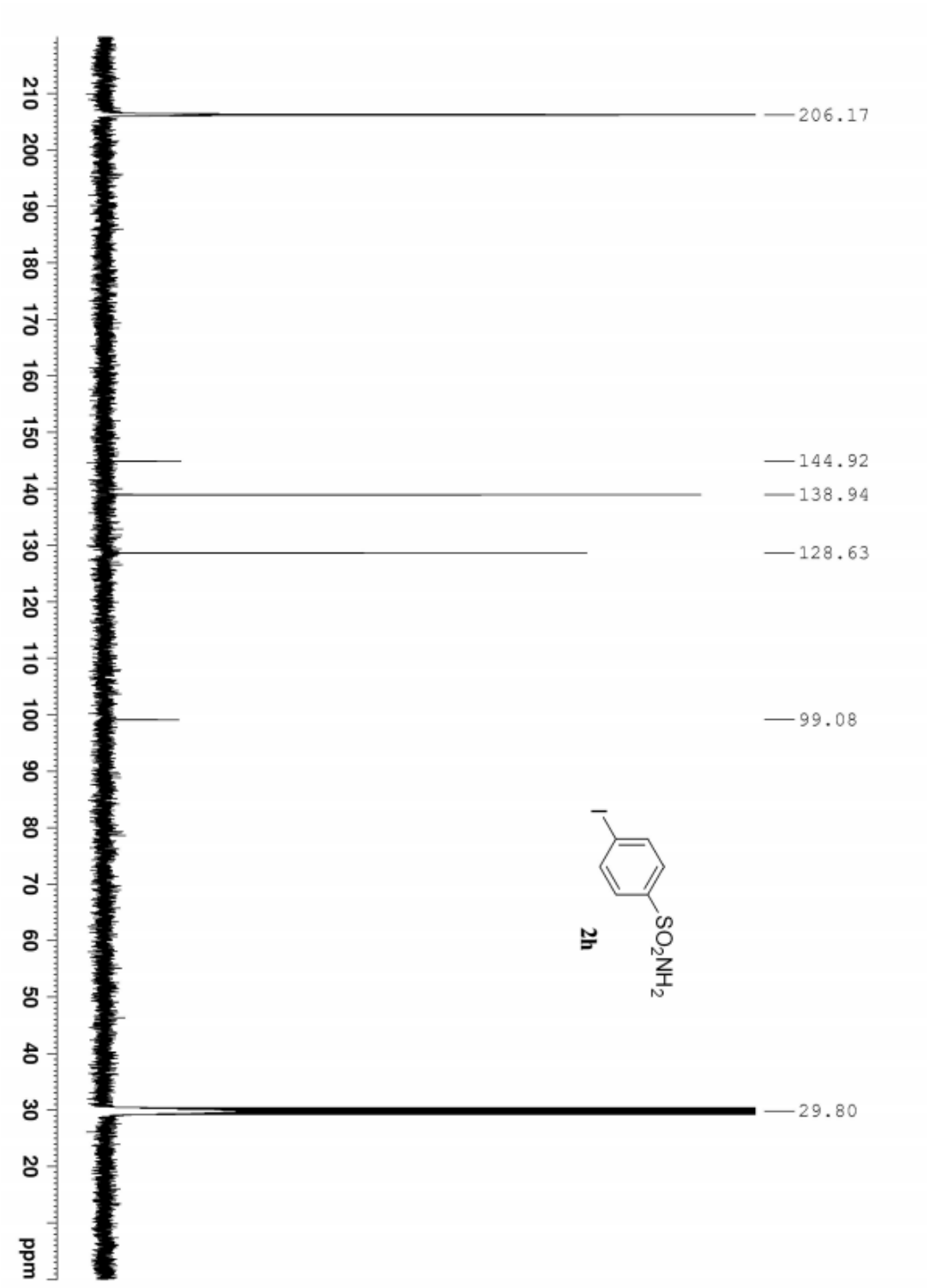

7.913
7.891
7.617
7.596
6.717
2.050
2.00
2.01
2.01
Cl
SO2NH2
2f
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

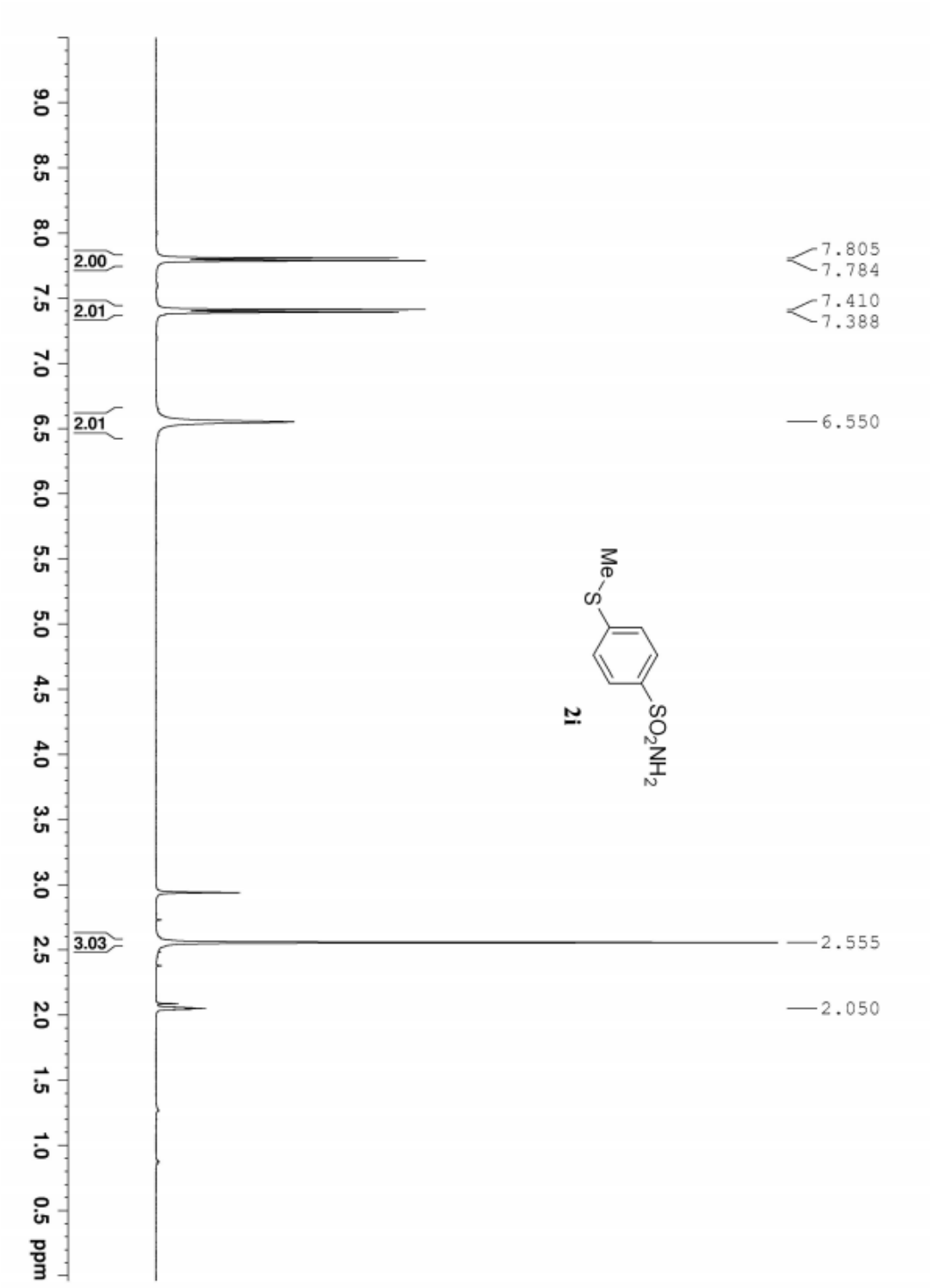

206.20
143.97
138.27
129.87
128.76
29.80
Cl
SO2NH2
2f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

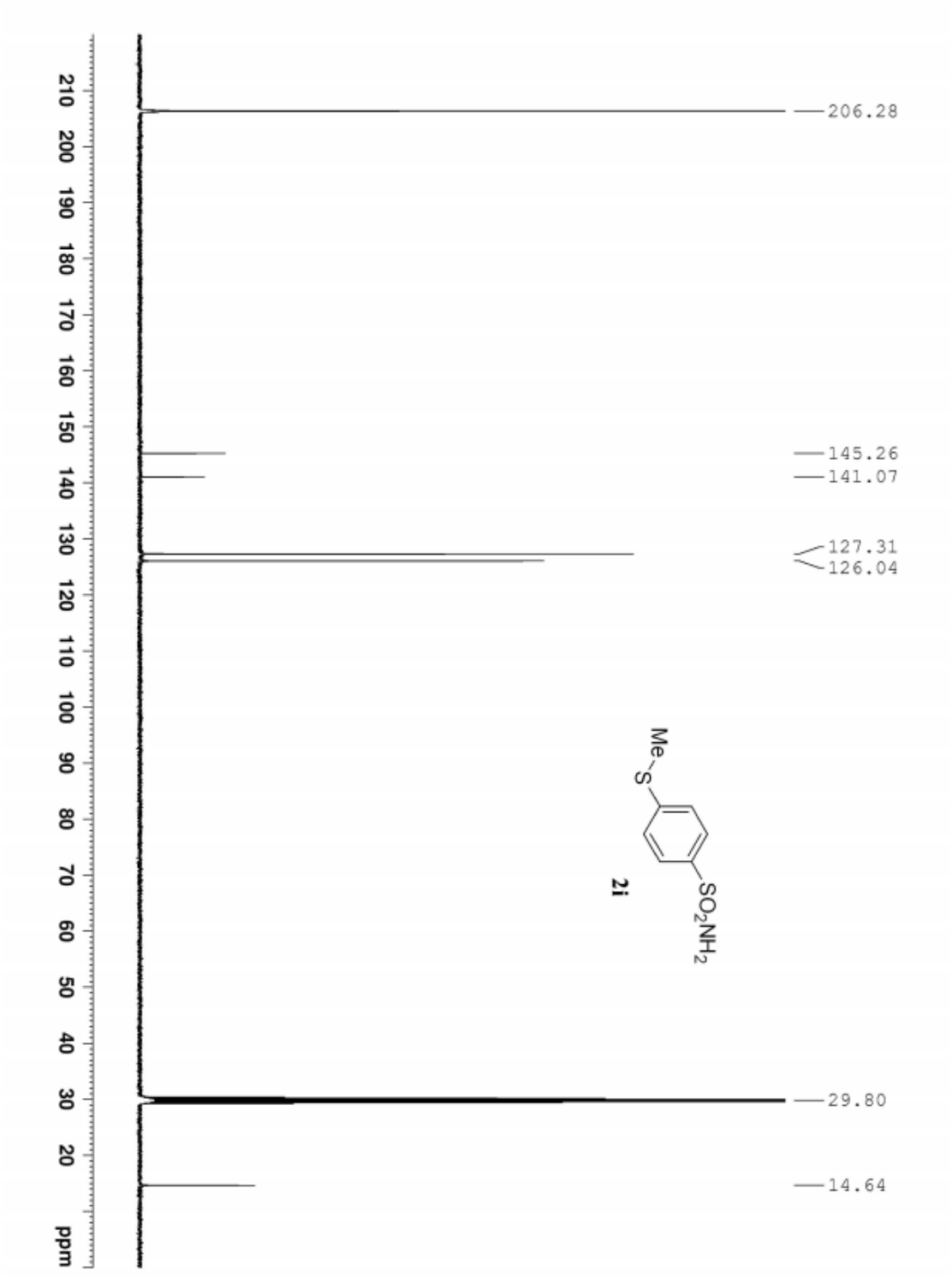

7.844
7.823
7.774
7.753
6.710
2.050
2.00
2.00
2.01
Br
SO2NH2
2g
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
ppm

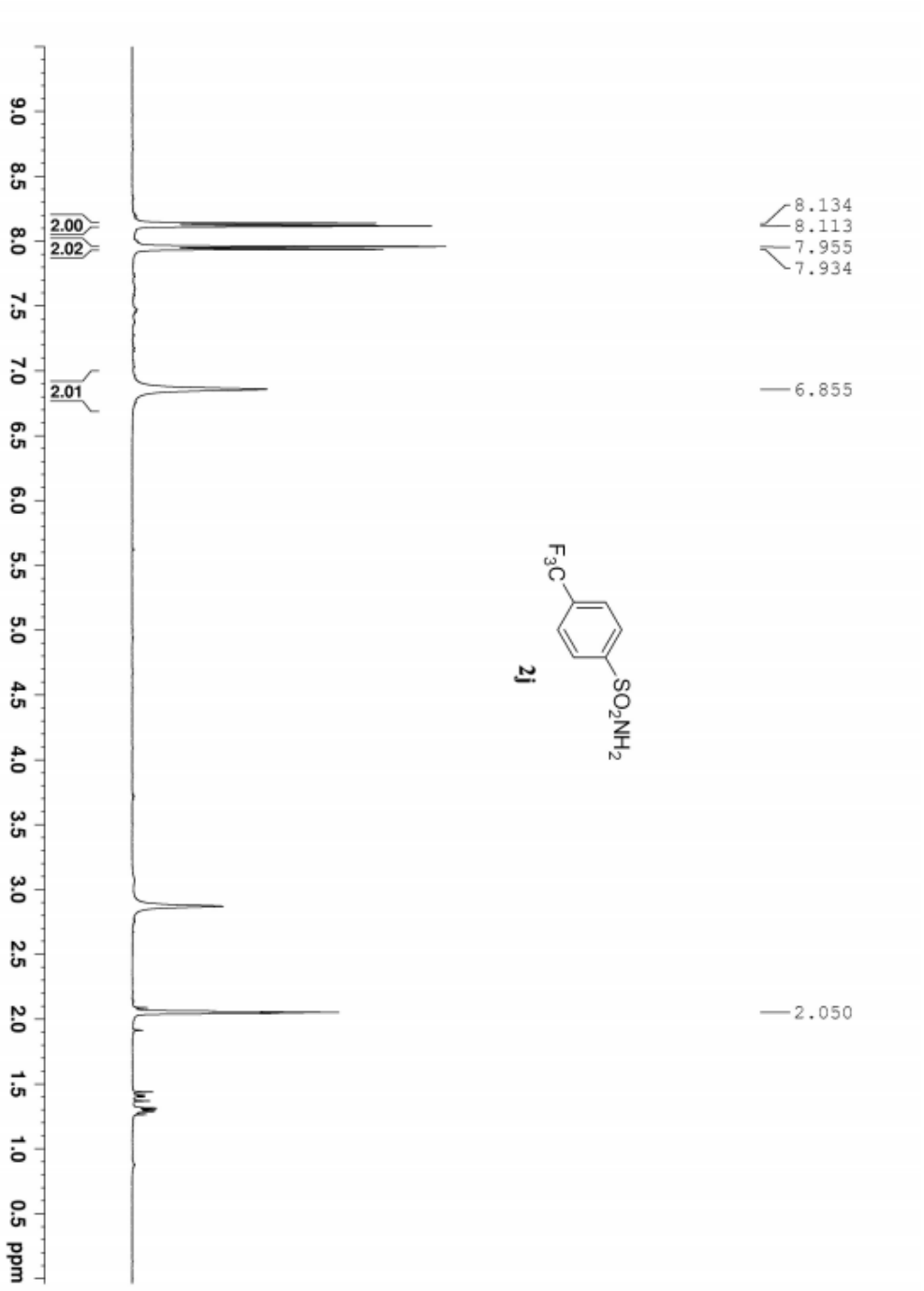

206.19
144.42
132.89
128.87
126.68
29.80
Br
SO2NH2
2g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

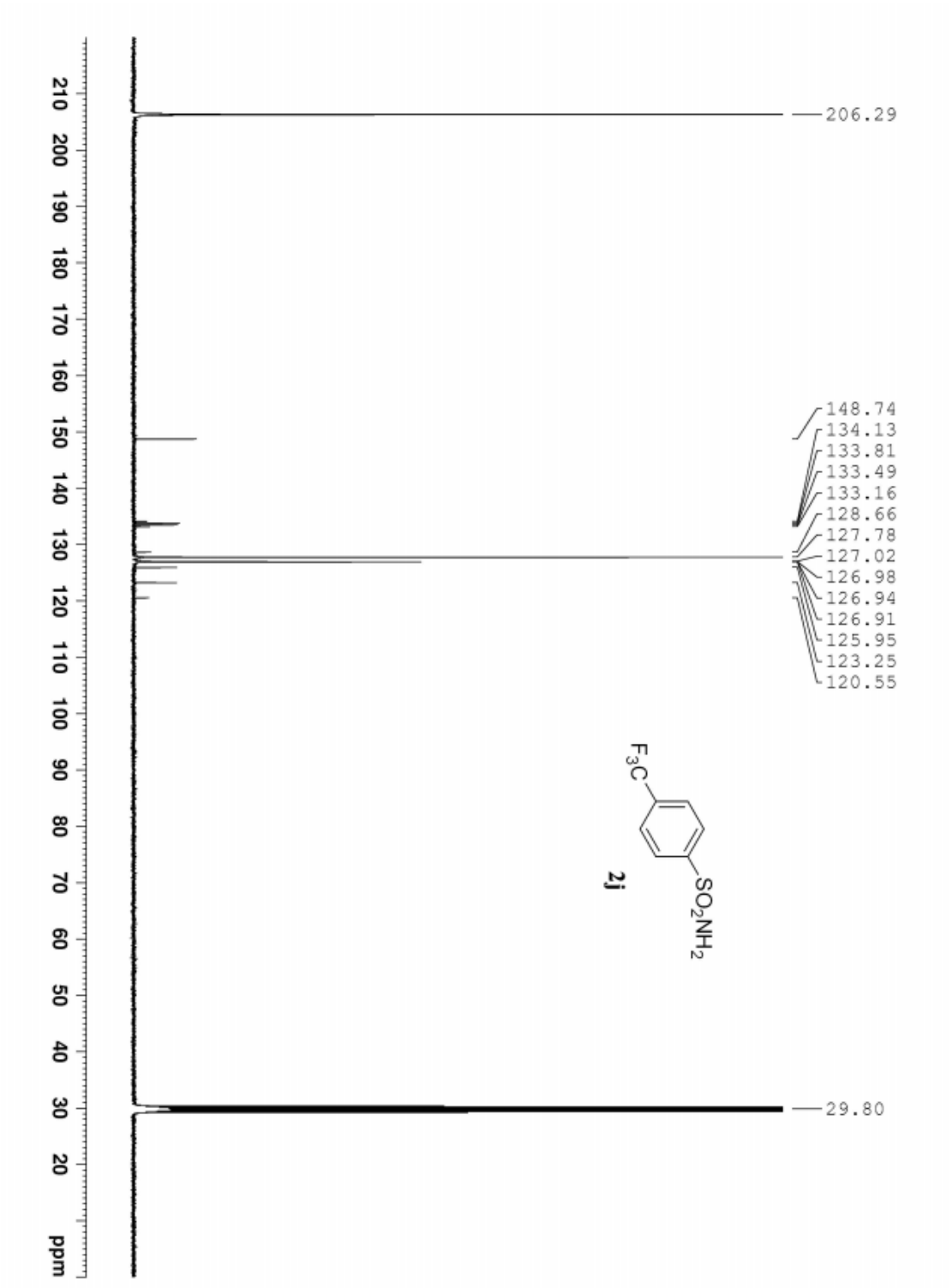

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.01
2.00
2.00
7.987
7.965
7.683
7.662
6.719
2.050
I
SO2NH2
2h


206.17
144.92
138.94
128.63
99.08
29.80
I
SO2NH2
2h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


7.805
7.784
7.410
7.388
6.550
2.555
2.050
2.00
2.01
2.01
3.03
Me
S
SO2NH2
2i
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 ppm

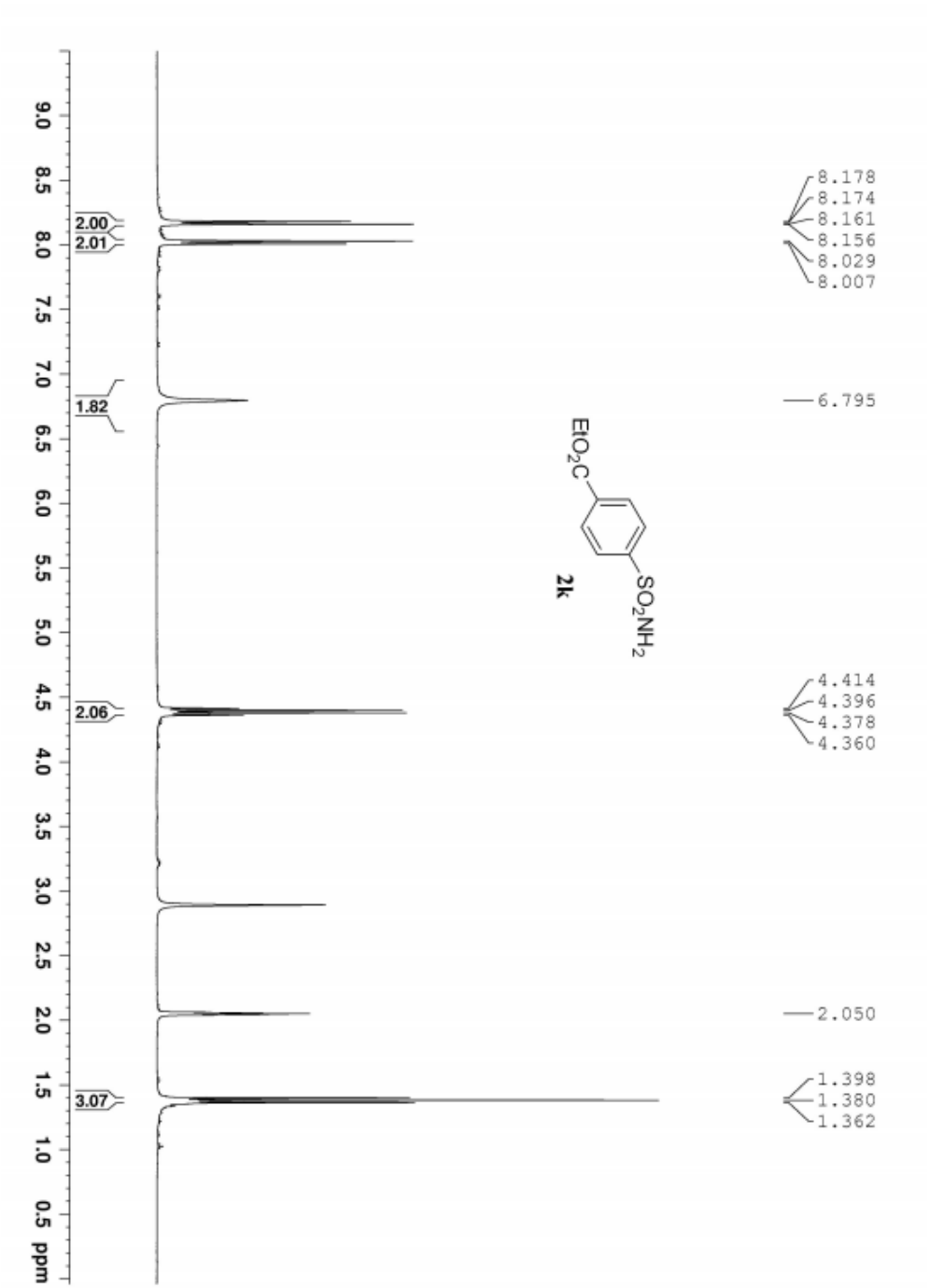

206.28
145.26
141.07
127.31
126.04
29.80
14.64
Me
S
SO2NH2
2i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

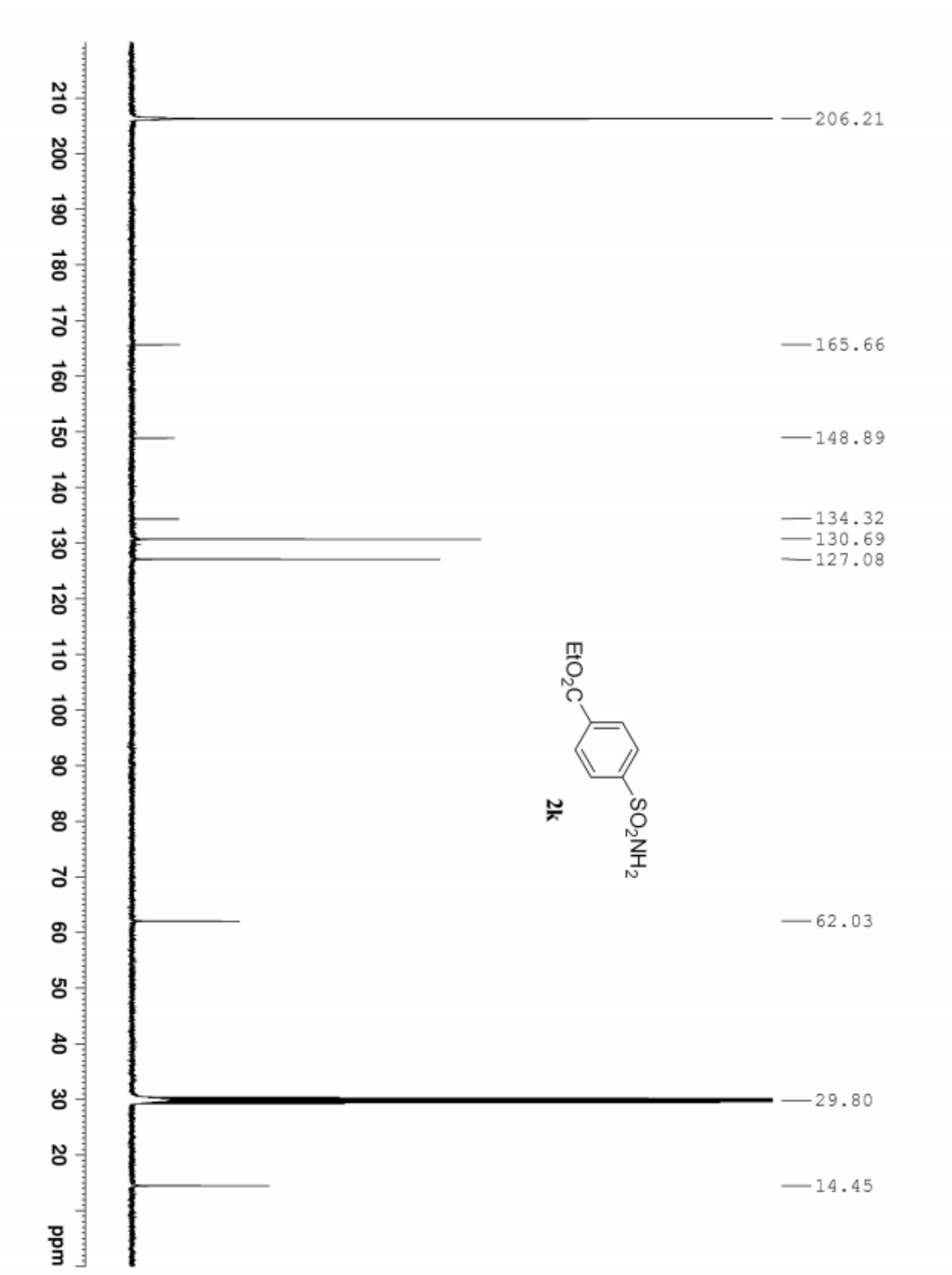

8.134
8.113
7.955
7.934
6.855
2.050
2.00
2.02
2.01
F3C
SO2NH2
2j
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

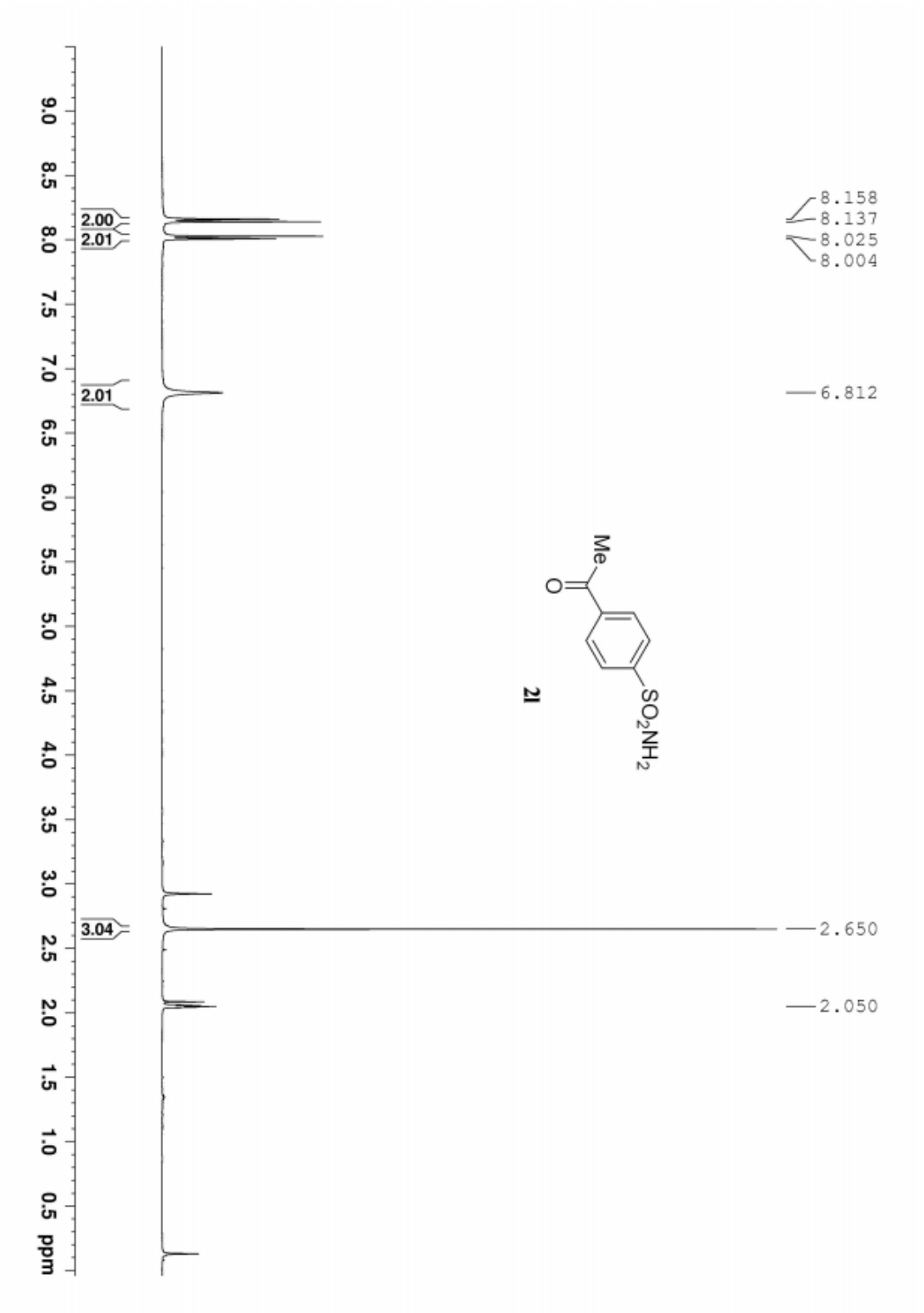

206.29
148.74
134.13
133.81
133.49
133.16
128.66
127.78
127.02
126.98
126.94
126.91
125.95
123.25
120.55
29.80
F3C
SO2NH2
2j
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

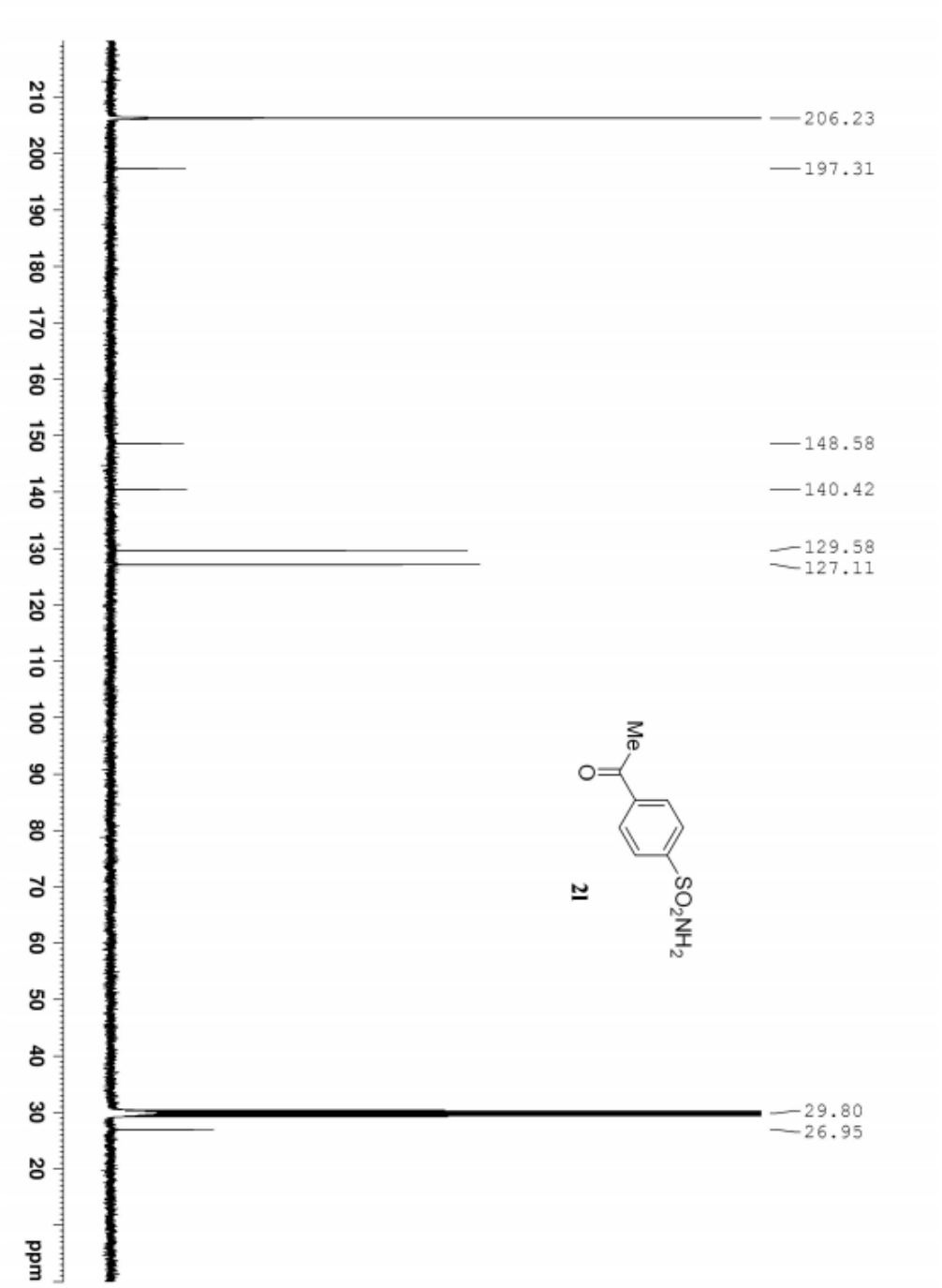
-113.97
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
F
F
F
O
S
O
NH2

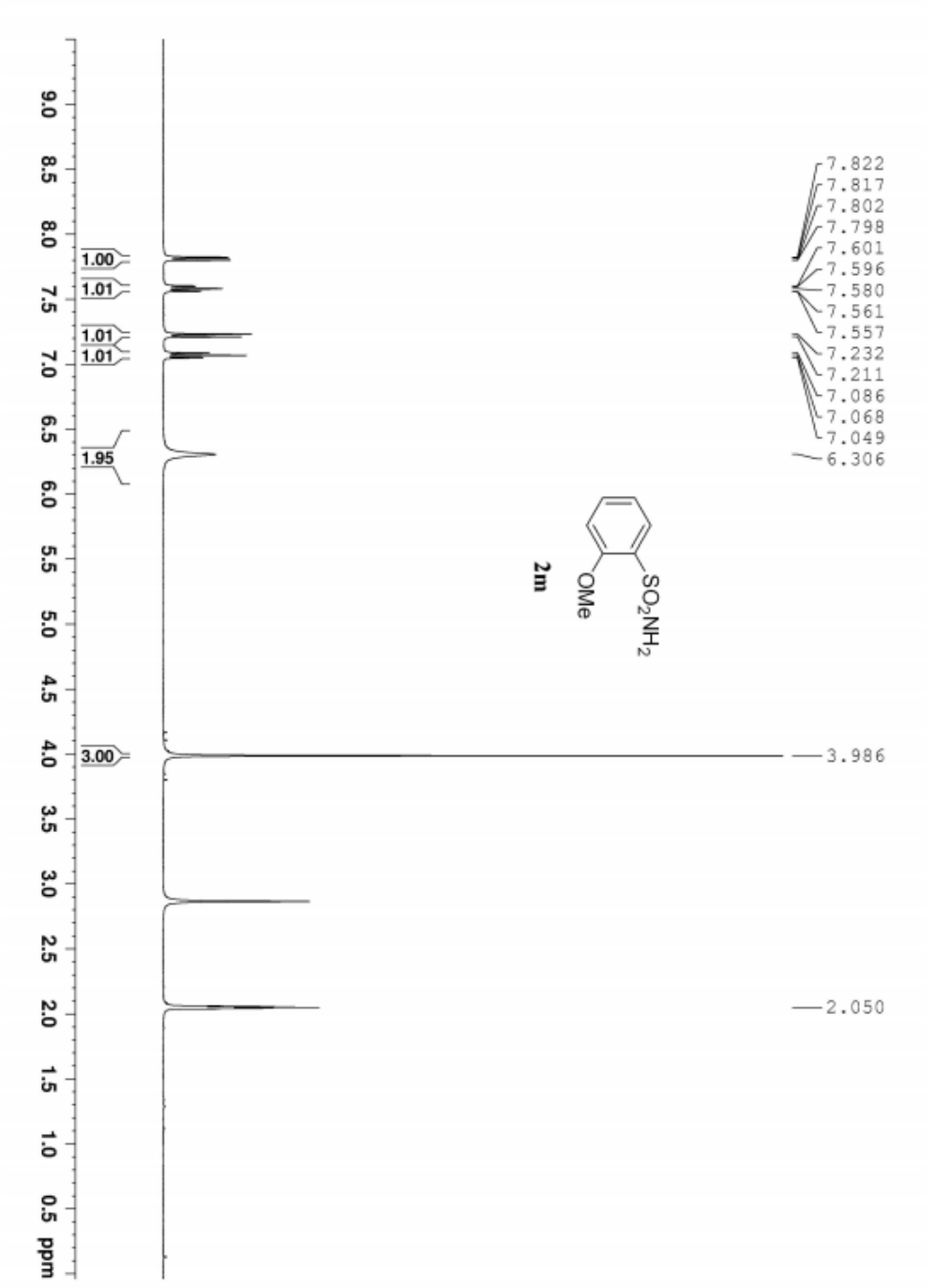
2j

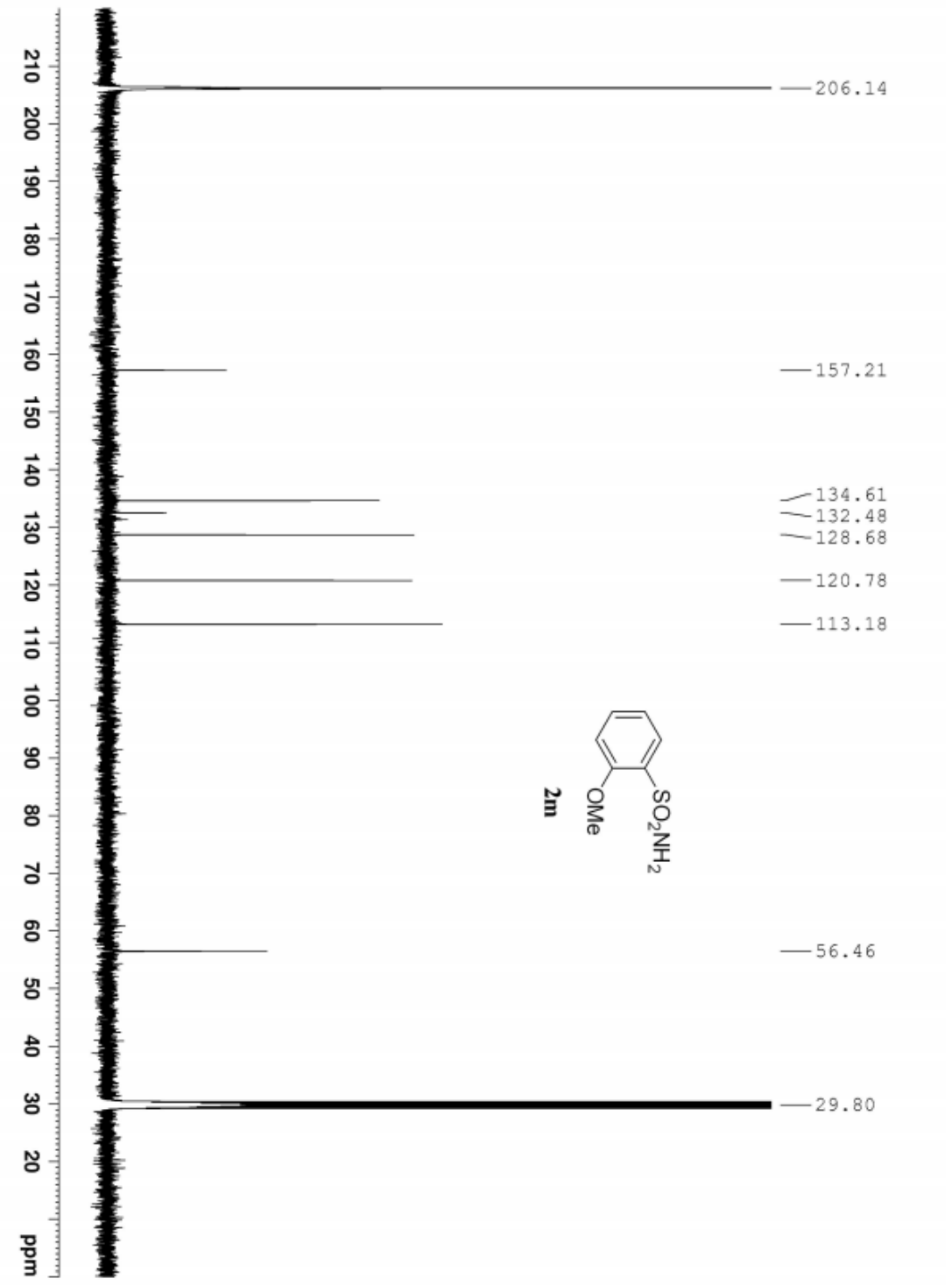

8.178
8.174
8.161
8.156
8.029
8.007
6.795
4.414
4.396
4.378
4.360
2.050
1.398
1.380
1.362
2.00
2.01
1.82
2.06
3.07
EtO2C
SO2NH2
2k
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

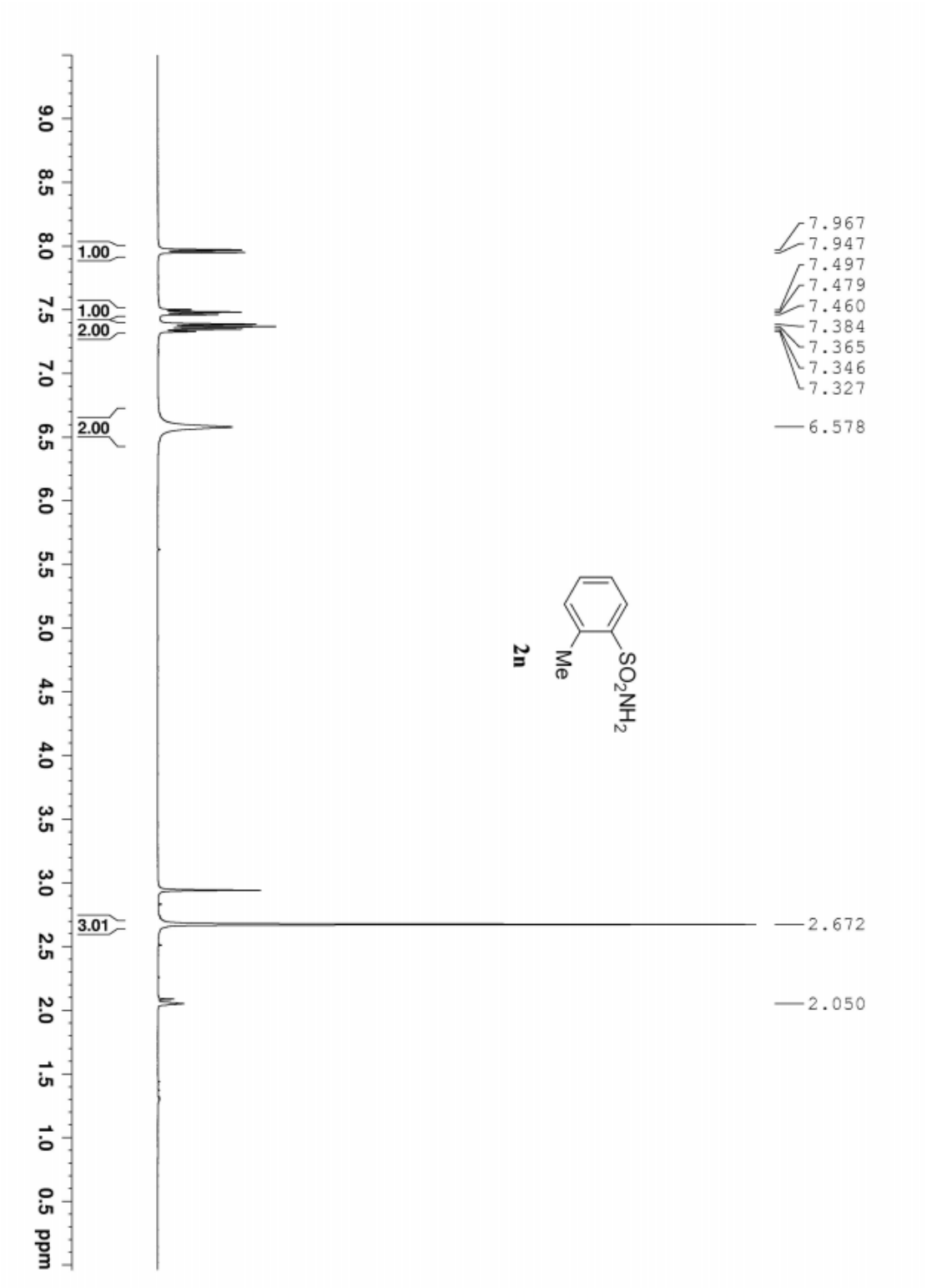

206.21
165.66
148.89
134.32
130.69
127.08
62.03
29.80
14.45
EtO2C
SO2NH2
2k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
ppm

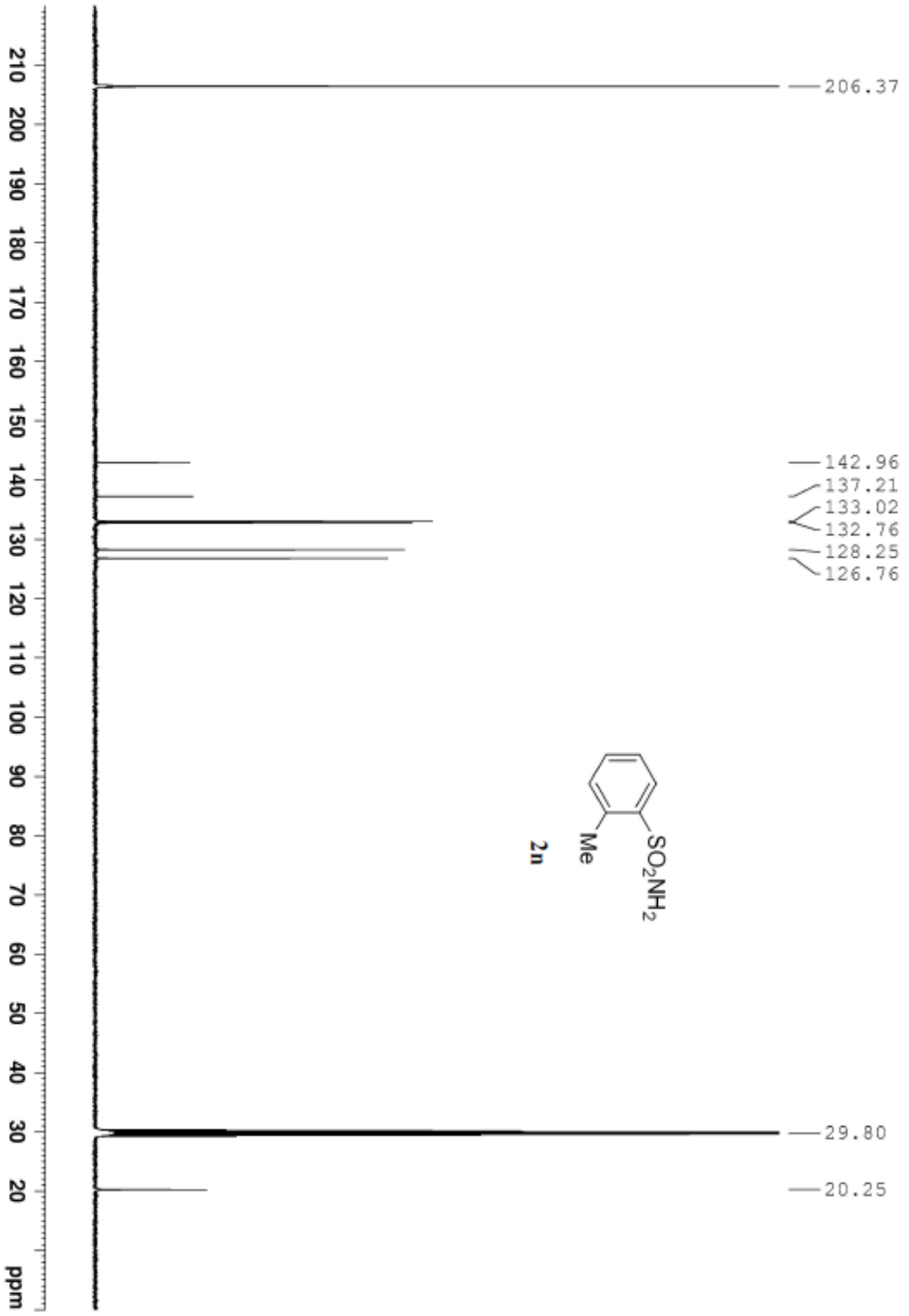

8.158
8.137
8.025
8.004
6.812
2.650
2.050
2.00
2.01
2.01
3.04
Me
O
SO2NH2
2l
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

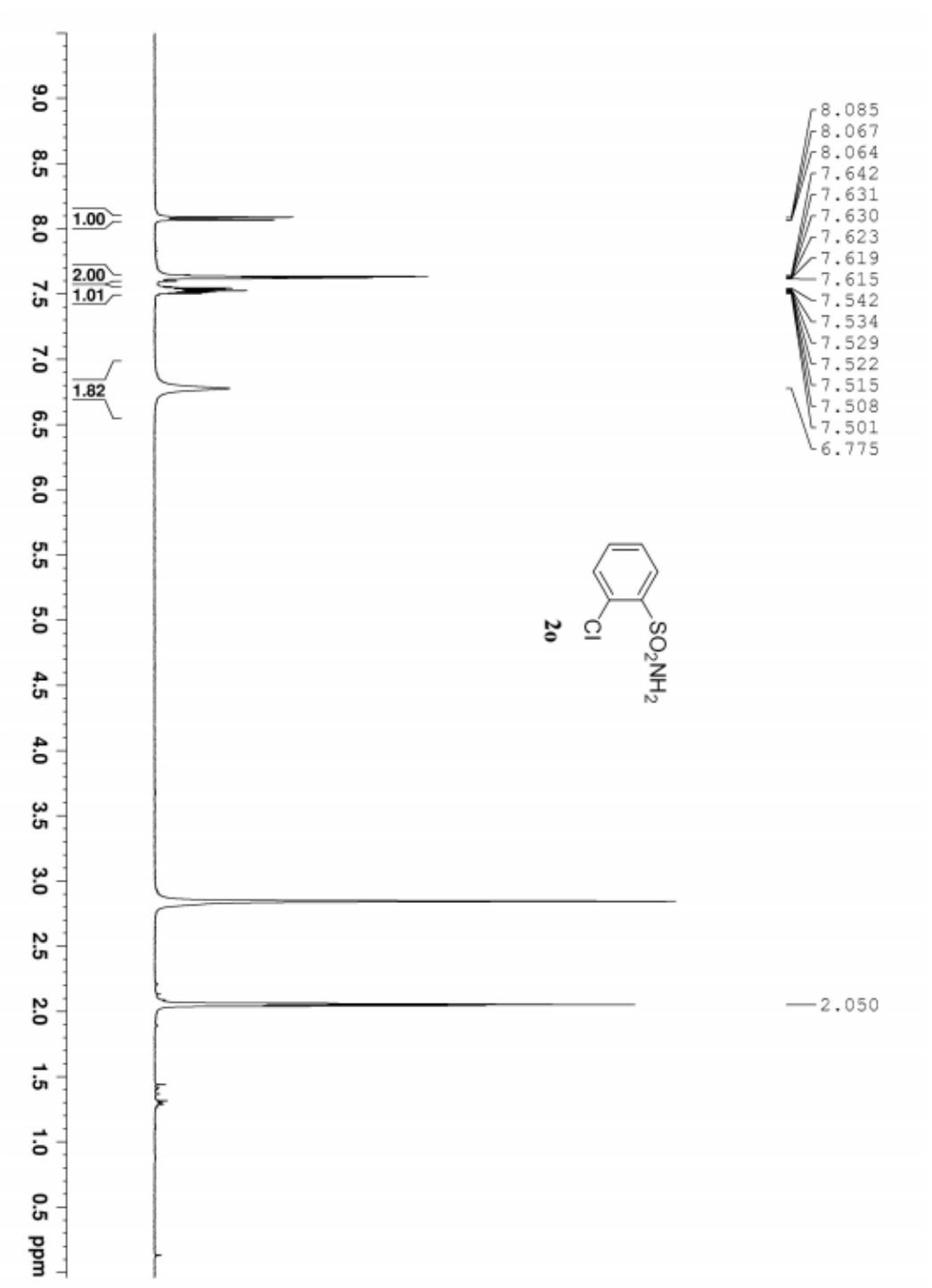

206.23
197.31
148.58
140.42
129.58
127.11
29.80
26.95
Me
O
SO2NH2
21
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

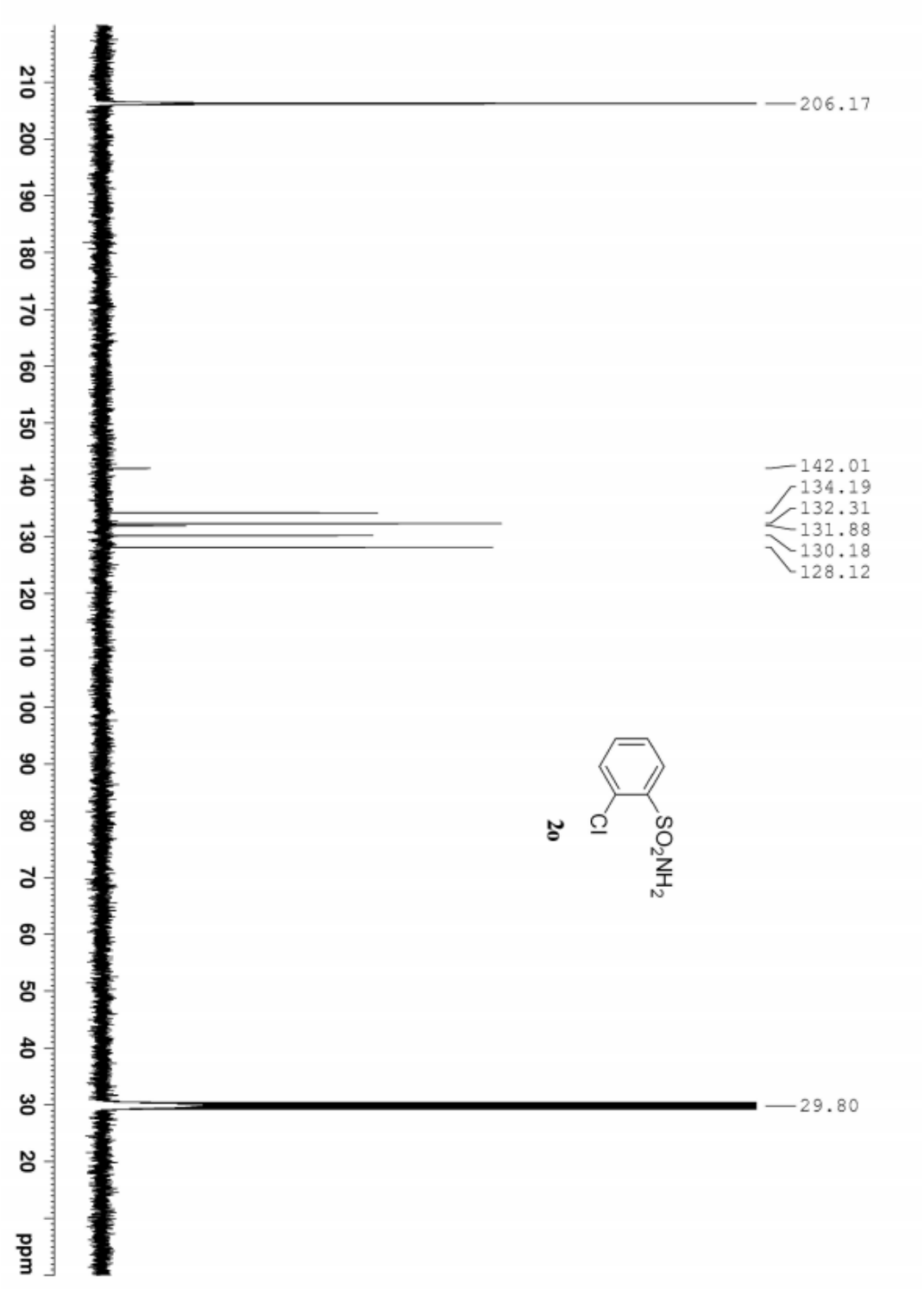

7.822
7.817
7.802
7.798
7.601
7.596
7.580
7.561
7.557
7.232
7.211
7.086
7.068
7.049
6.306
3.986
2.050
1.00
1.01
1.01
1.01
1.95
3.00
OMe
SO2NH2
2m
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

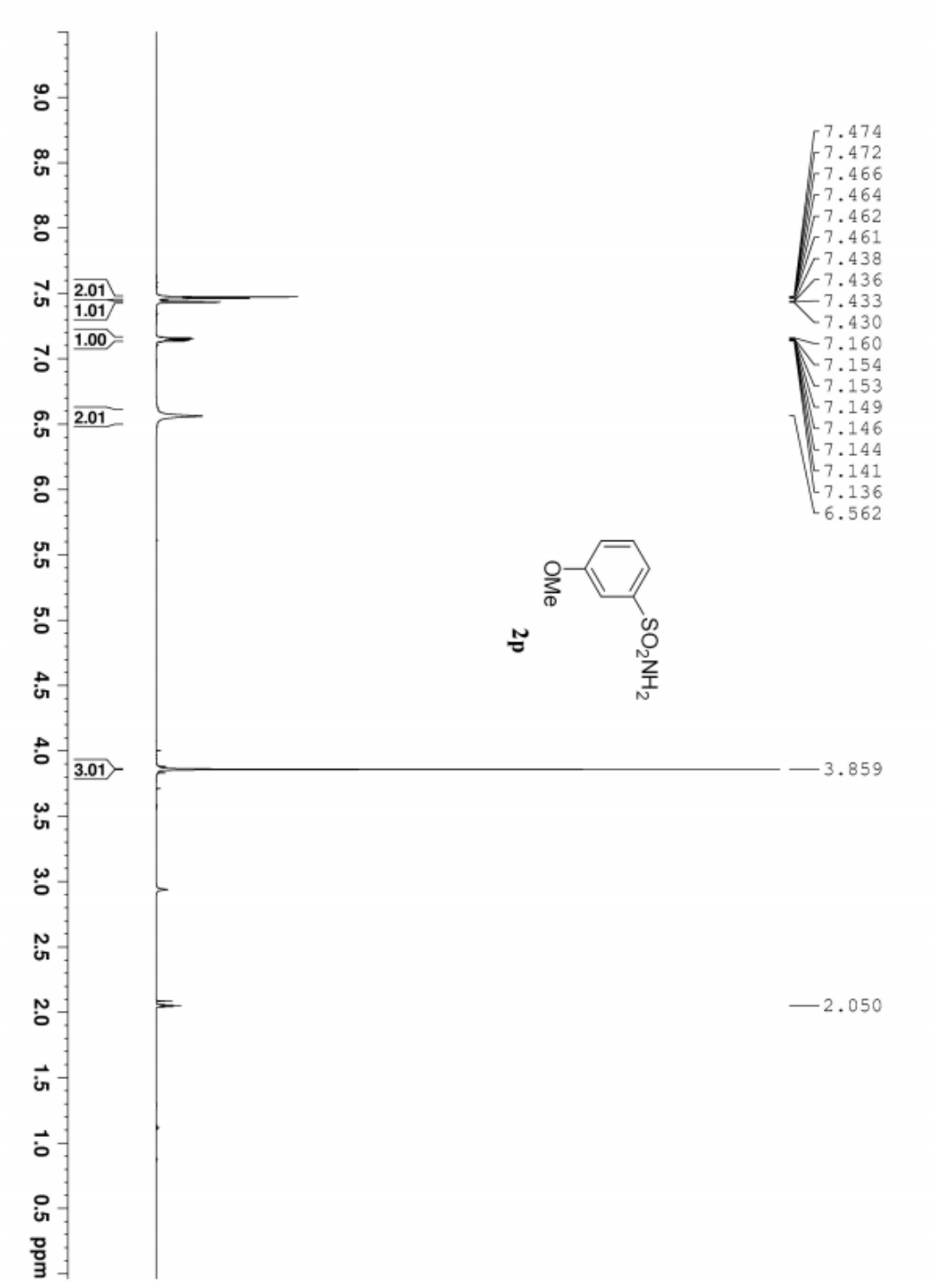

206.14
157.21
134.61
132.48
128.68
120.78
113.18
56.46
29.80
OMe
SO2NH2
2m
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

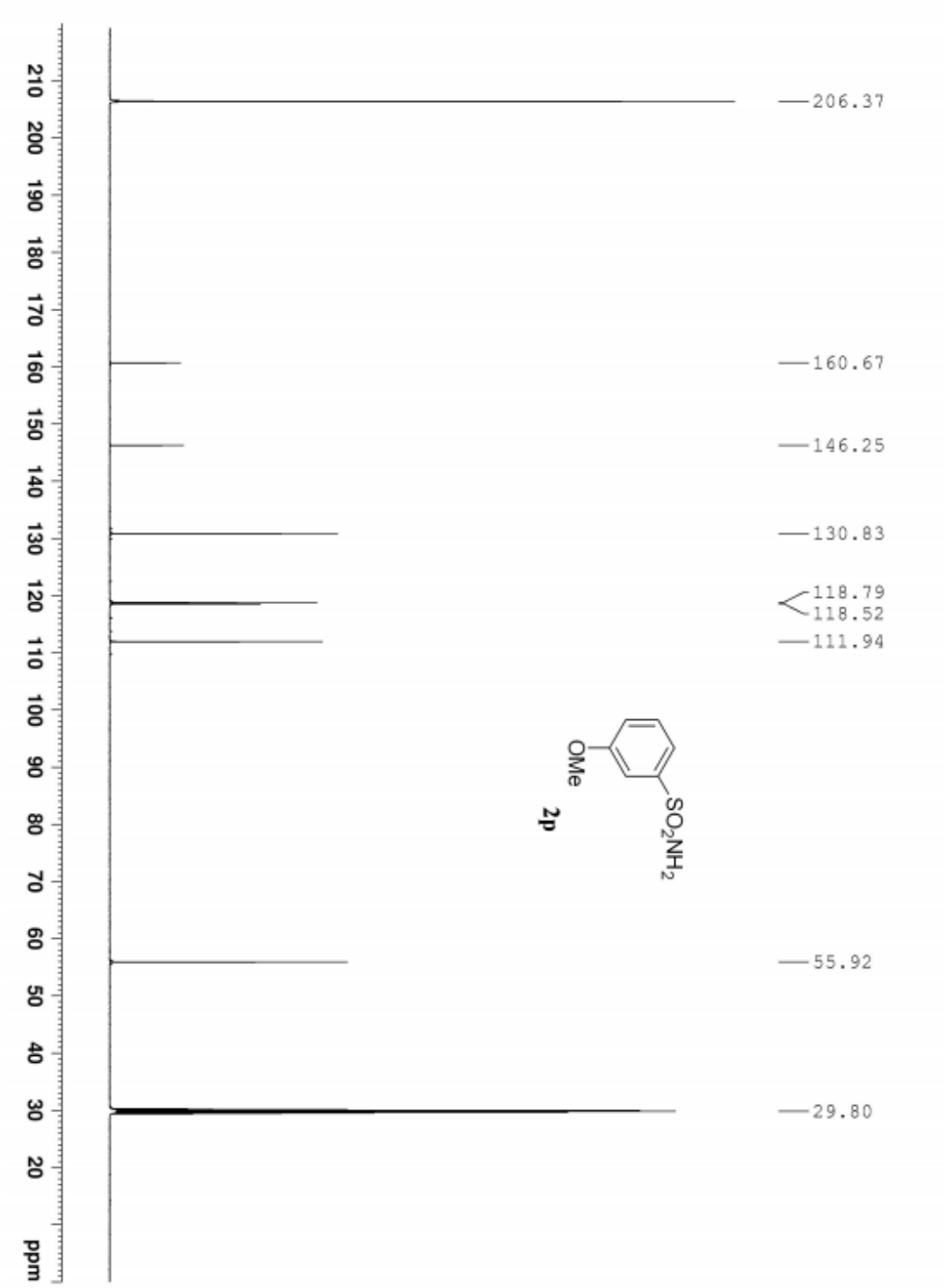

7.967
7.947
7.497
7.479
7.460
7.384
7.365
7.346
7.327
6.578
2.672
2.050
1.00
1.00
2.00
2.00
3.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
Me
SO2NH2
2n

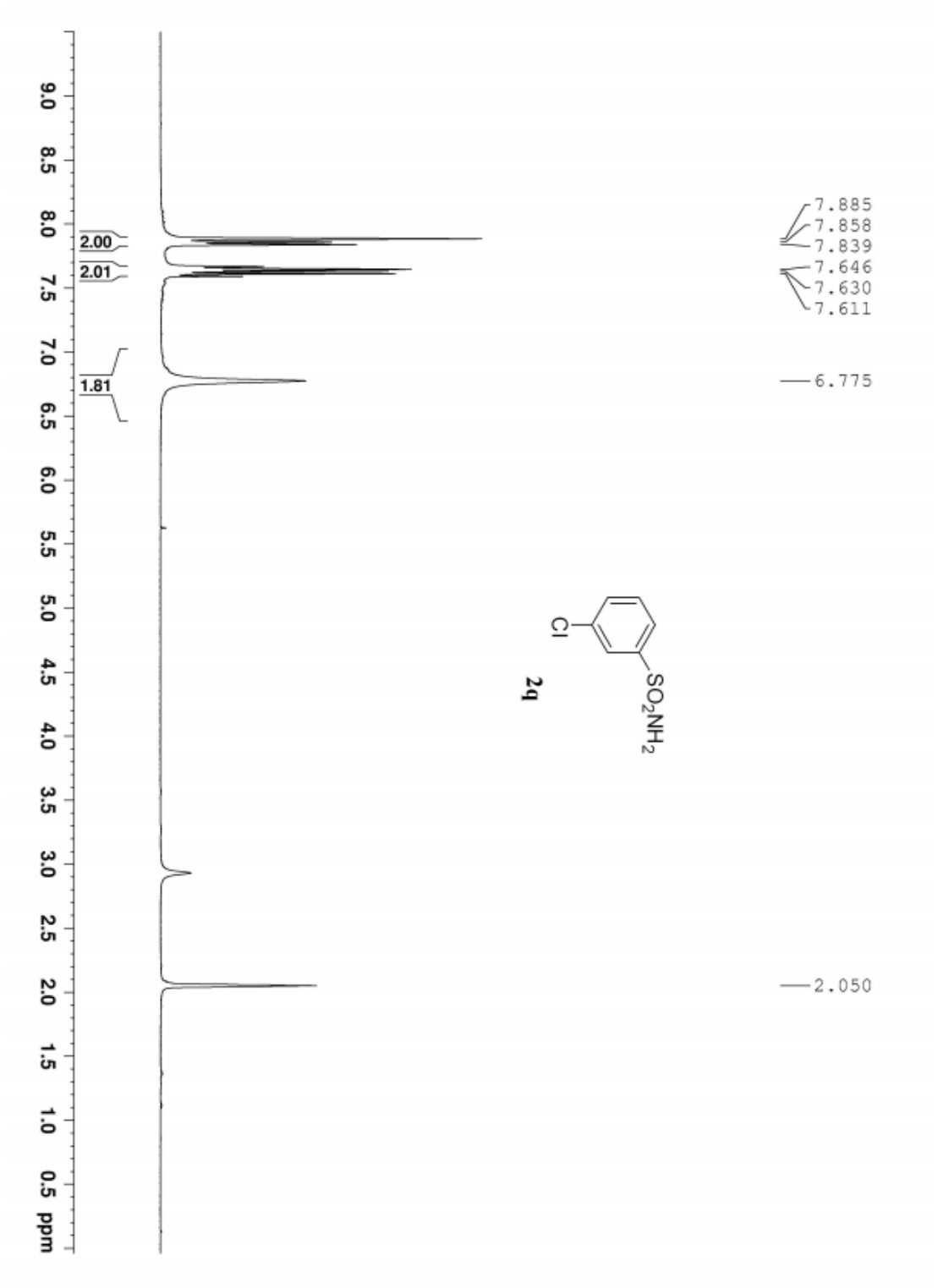

206.37
142.96
137.21
133.02
132.76
128.25
126.76
29.80
20.25
Me
SO2NH2
2n
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
ppm

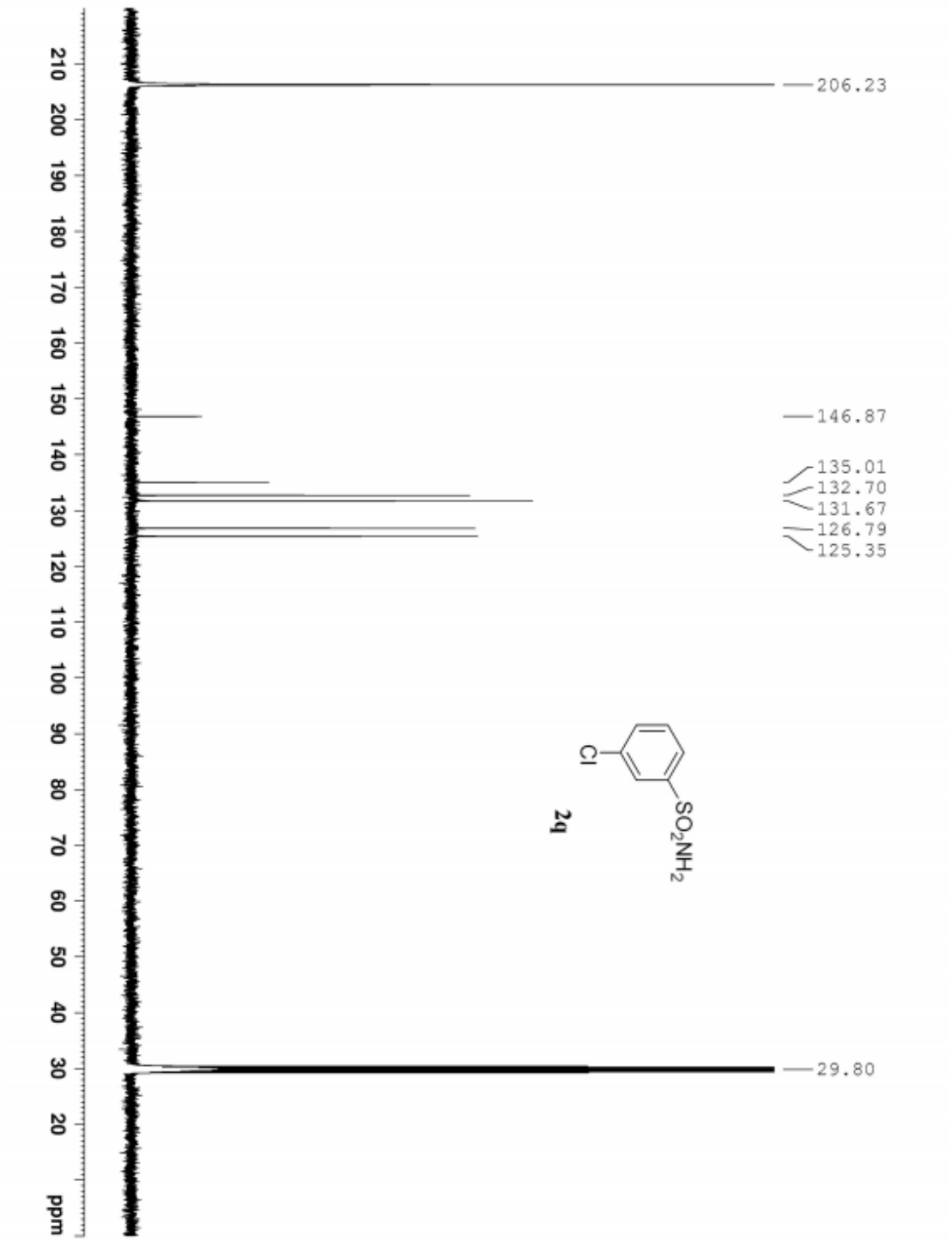

8.085
8.067
8.064
7.642
7.631
7.630
7.623
7.619
7.615
7.542
7.534
7.529
7.522
7.515
7.508
7.501
6.775
1.00
2.00
1.01
1.82
2.050
Cl
SO2NH2
2o
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

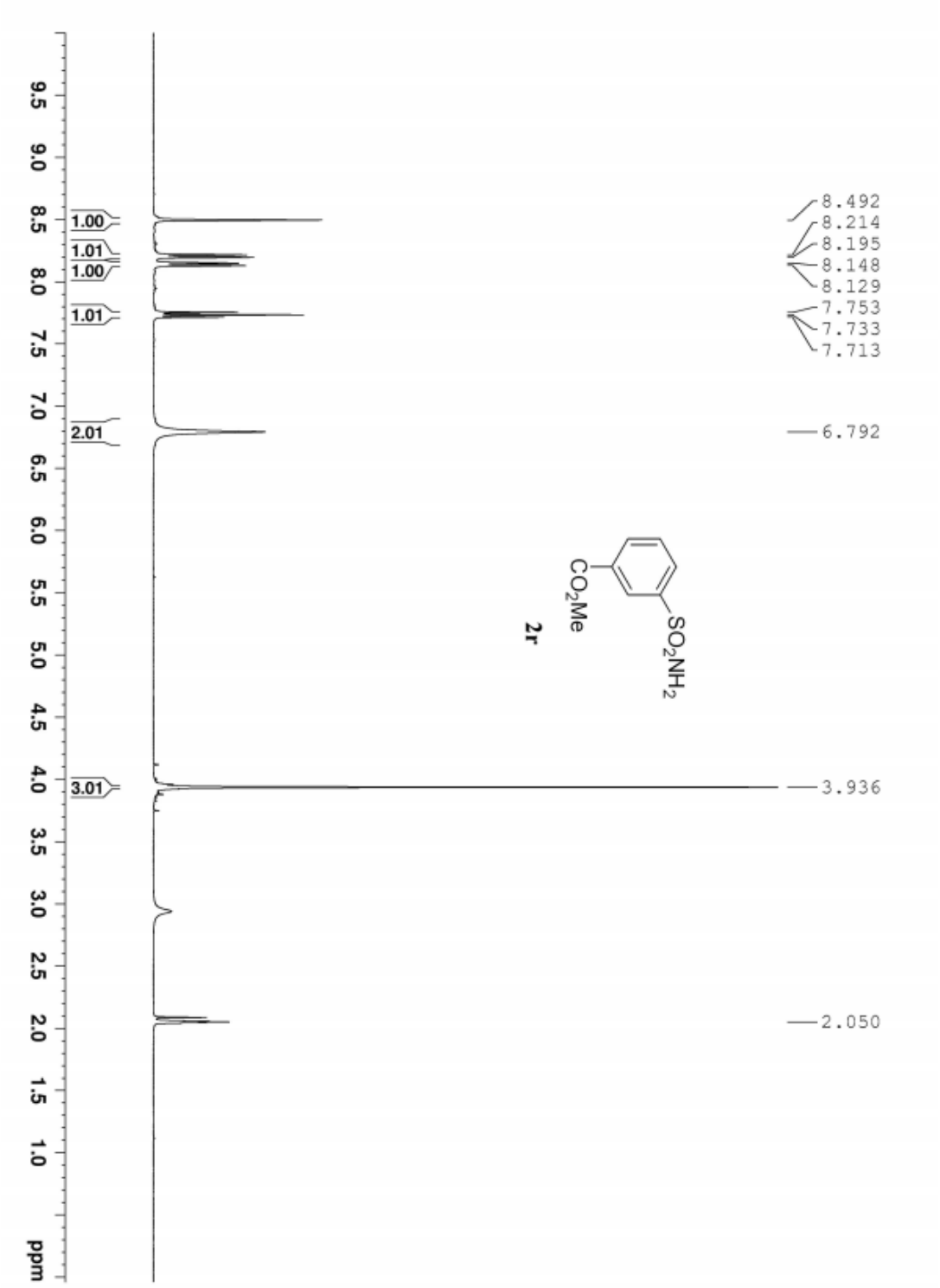

206.17
142.01
134.19
132.31
131.88
130.18
128.12
29.80
Cl
SO2NH2
2o
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

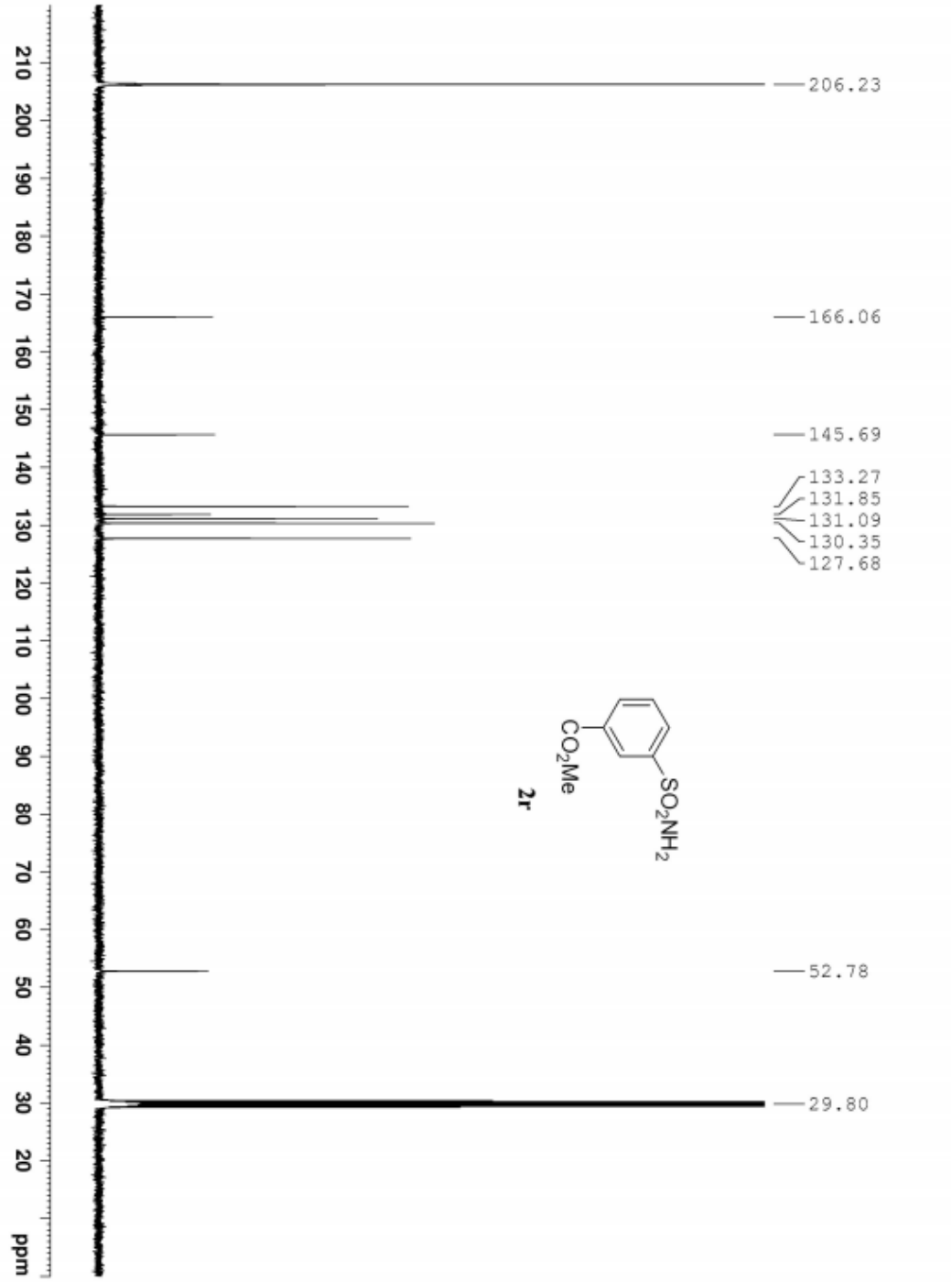

7.474
7.472
7.466
7.464
7.462
7.461
7.438
7.436
7.433
7.430
7.160
7.154
7.153
7.149
7.146
7.144
7.141
7.136
6.562
OMe
SO2NH2
2p
2.01
1.01
1.00
2.01
3.01
3.859
2.050
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

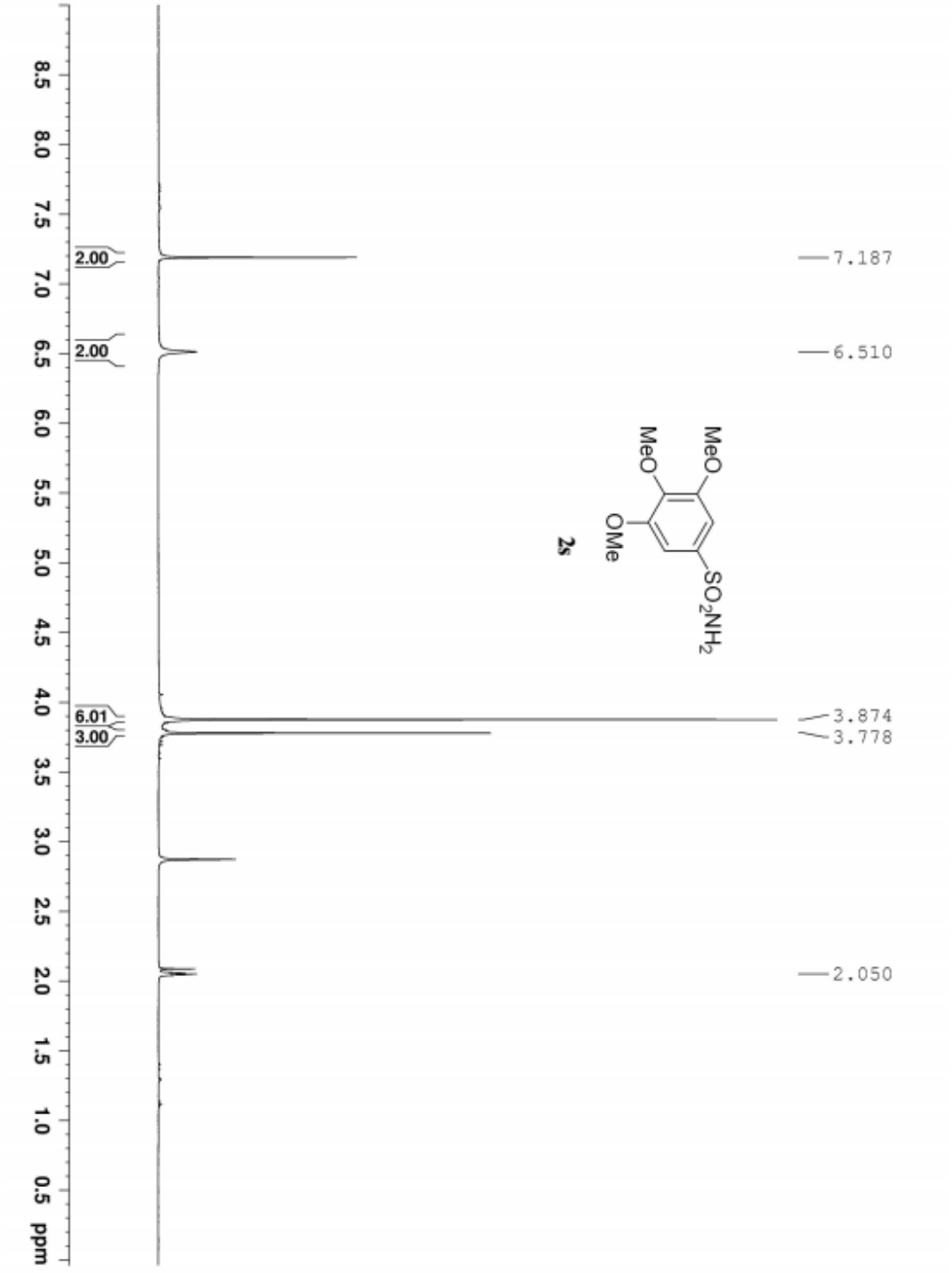

206.37
160.67
146.25
130.83
118.79
118.52
111.94
55.92
29.80
OMe
SO2NH2
2p
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

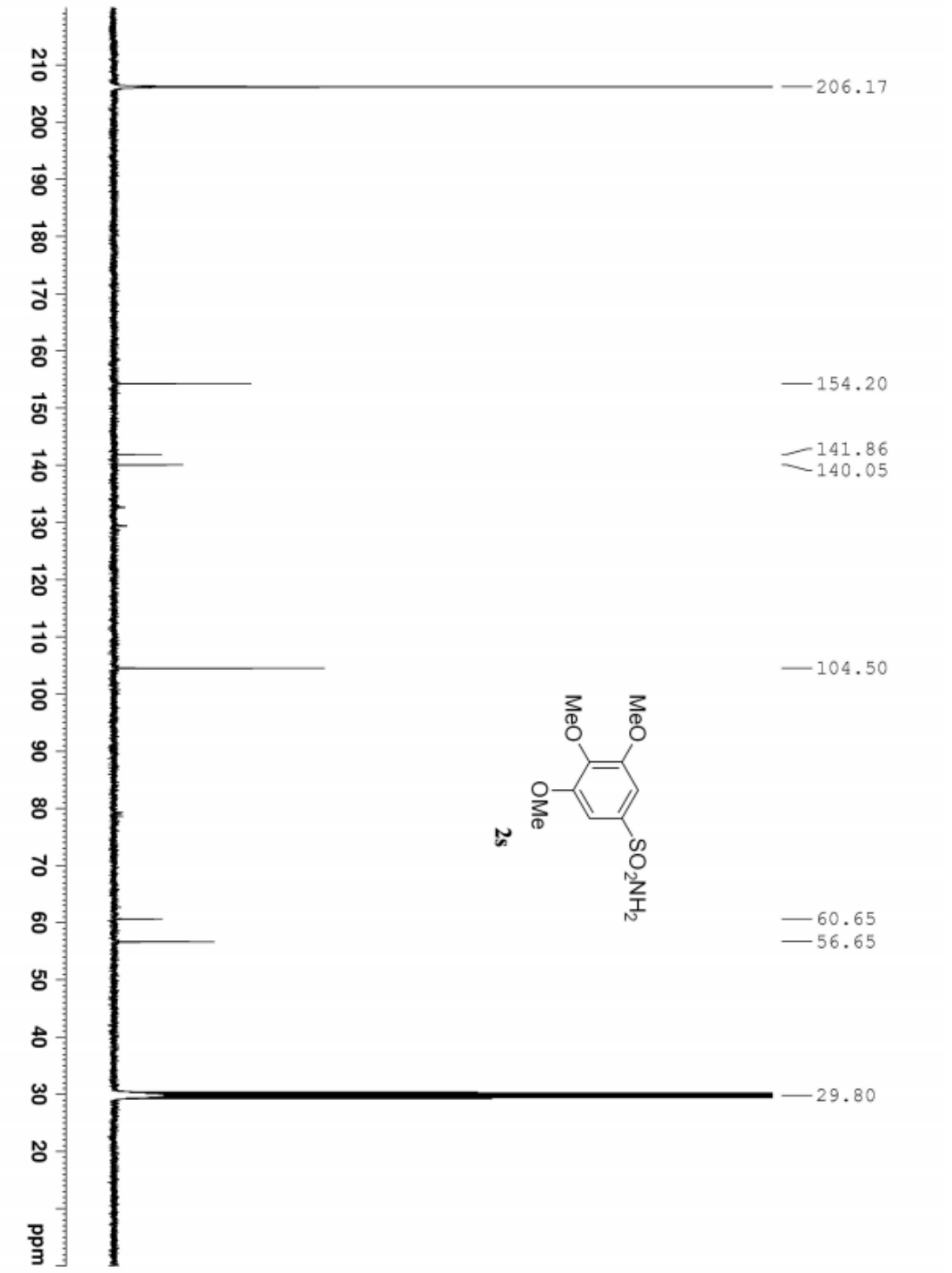

7.885
7.858
7.839
7.646
7.630
7.611
6.775
2.050
2.00
2.01
1.81
Cl
SO2NH2
2q
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

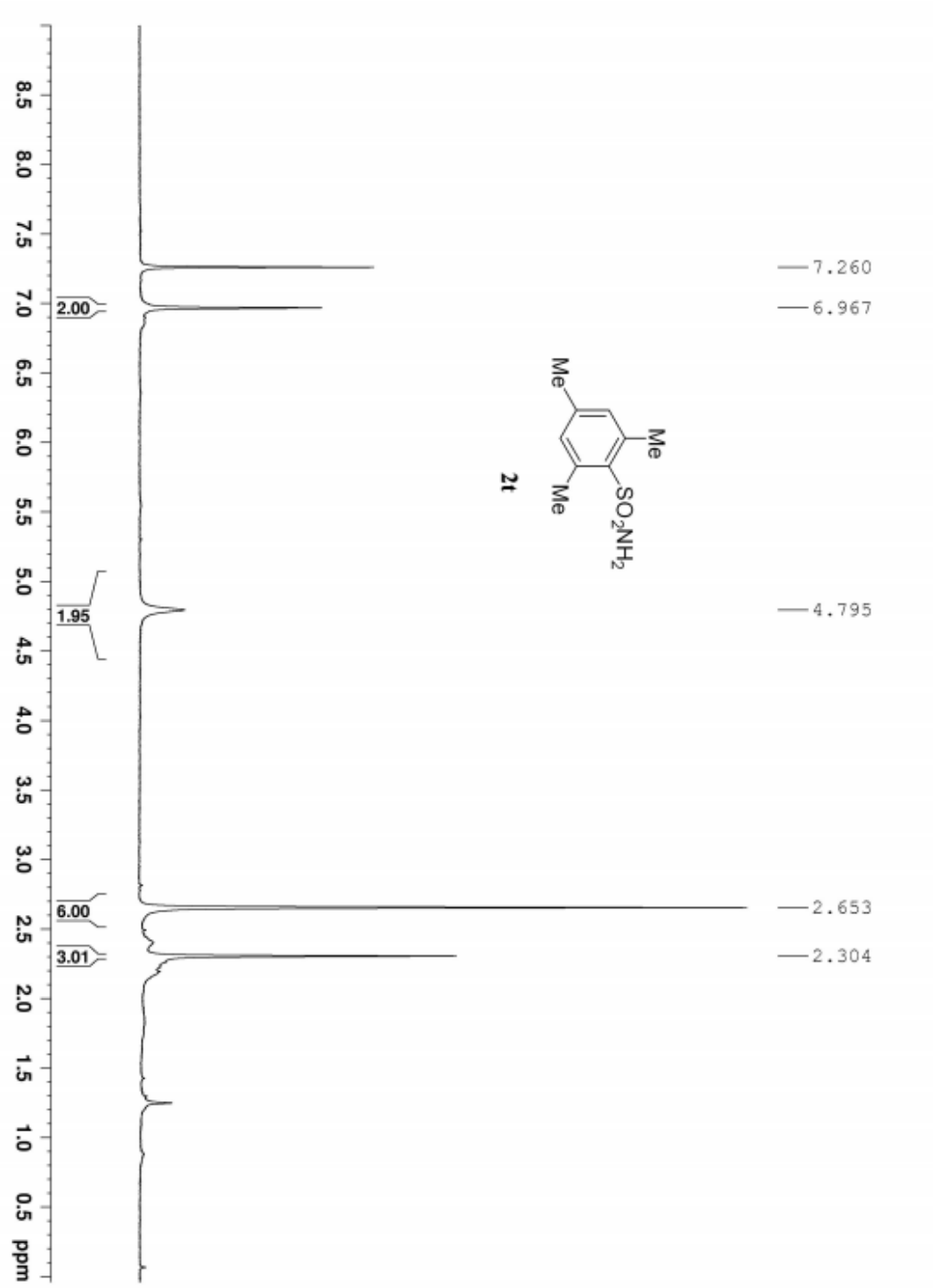

206.23
146.87
135.01
132.70
131.67
126.79
125.35
29.80
Cl
SO2NH2
2q
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

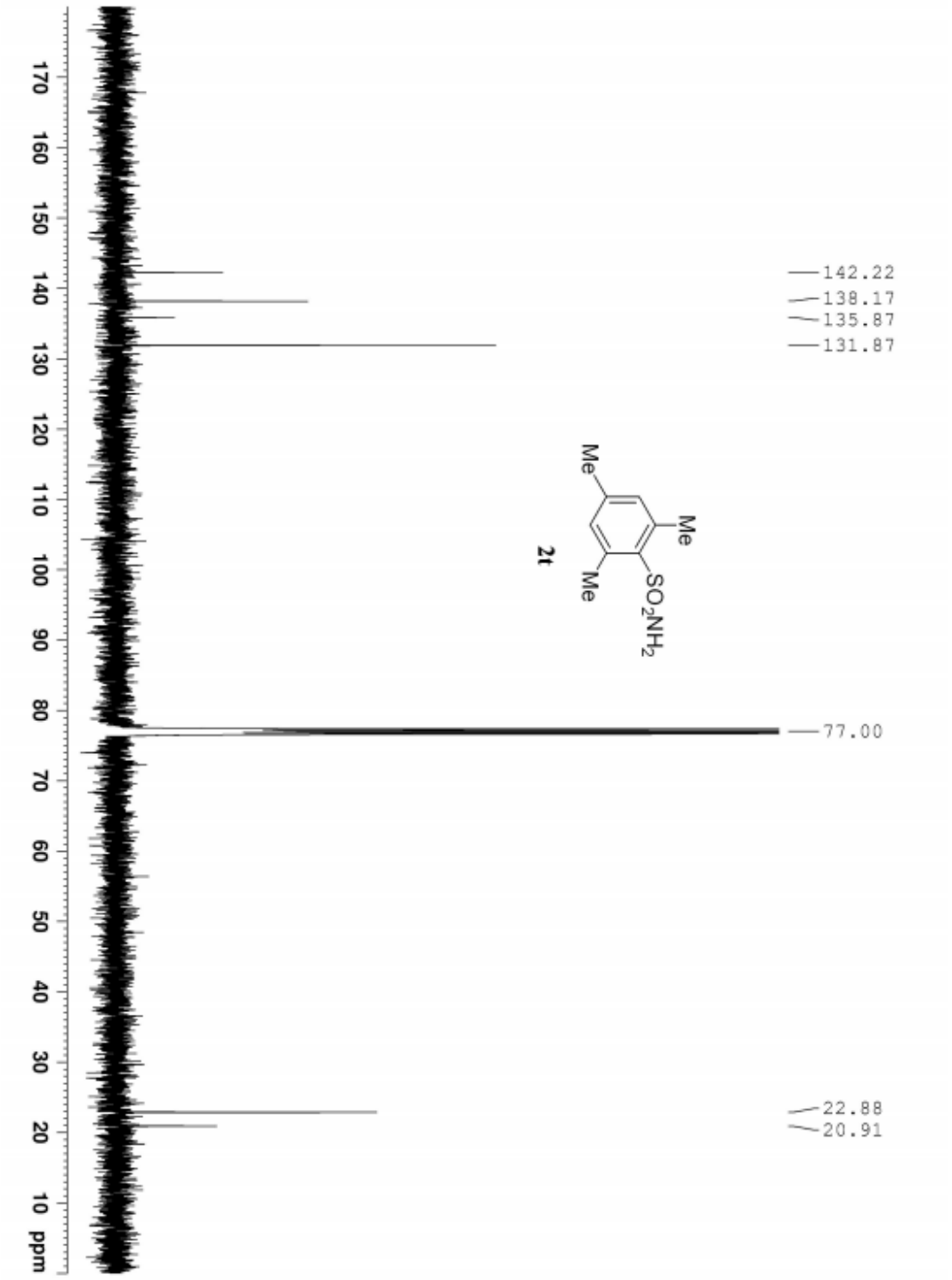

8.492
8.214
8.195
8.148
8.129
7.753
7.733
7.713
6.792
3.936
2.050
1.00
1.01
1.00
1.01
2.01
3.01
CO2Me
SO2NH2
2r
ppm

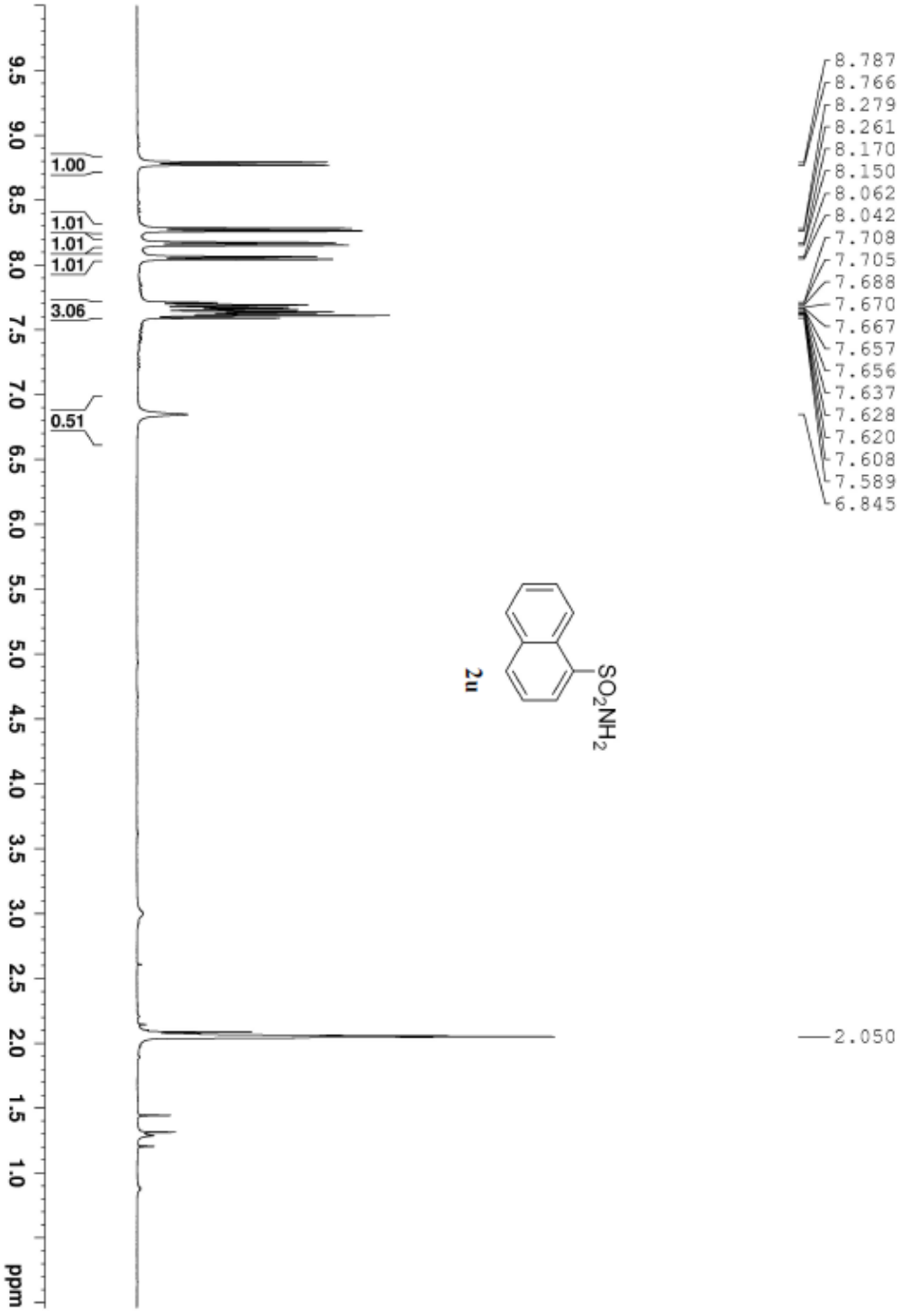

206.23
166.06
145.69
133.27
131.85
131.09
130.35
127.68
52.78
29.80
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm
CO2Me
SO2NH2
2r

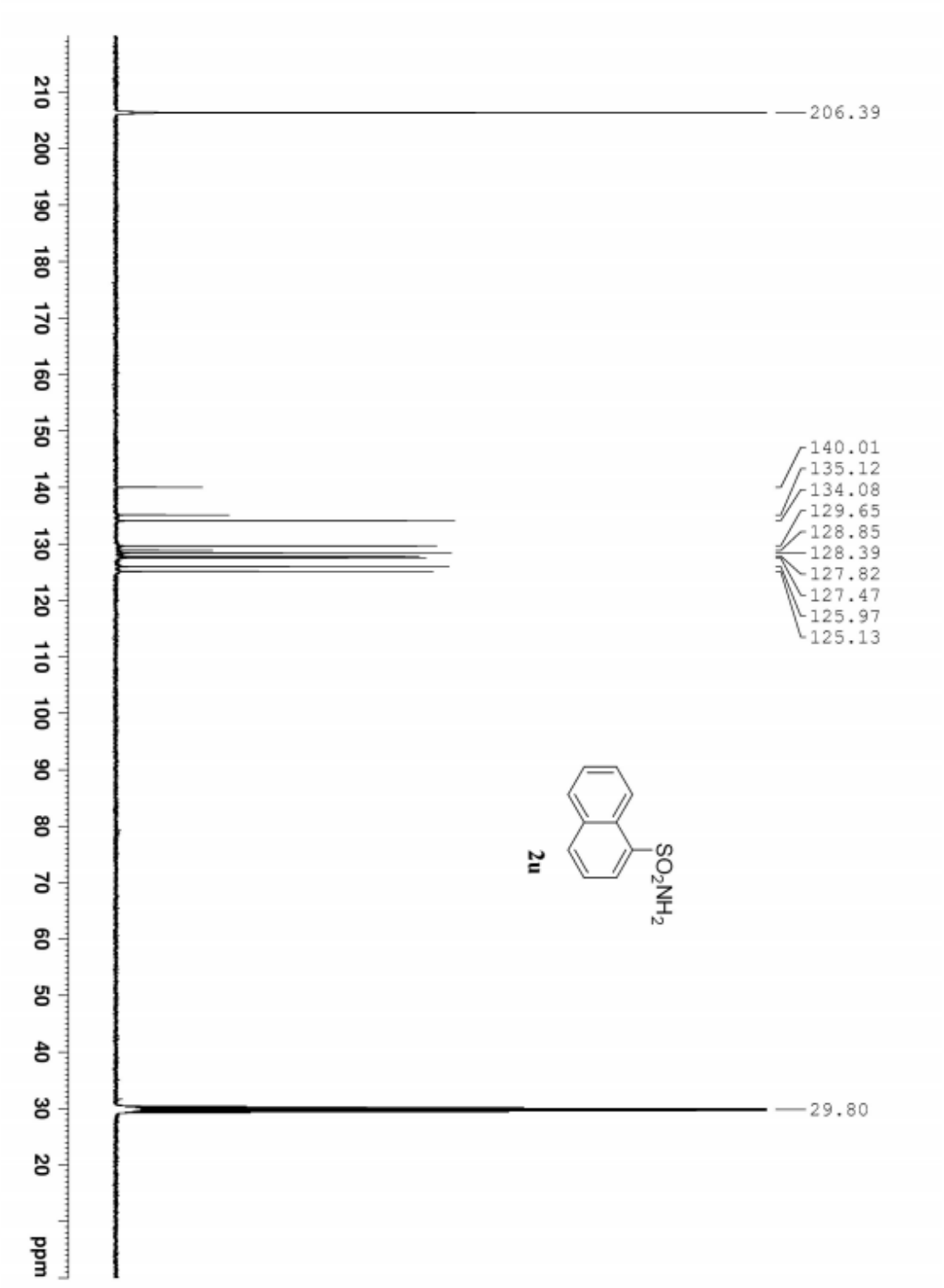

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
2.00
6.01
3.00
7.187
6.510
3.874
3.778
2.050
MeO
MeO
OMe
SO2NH2
2s

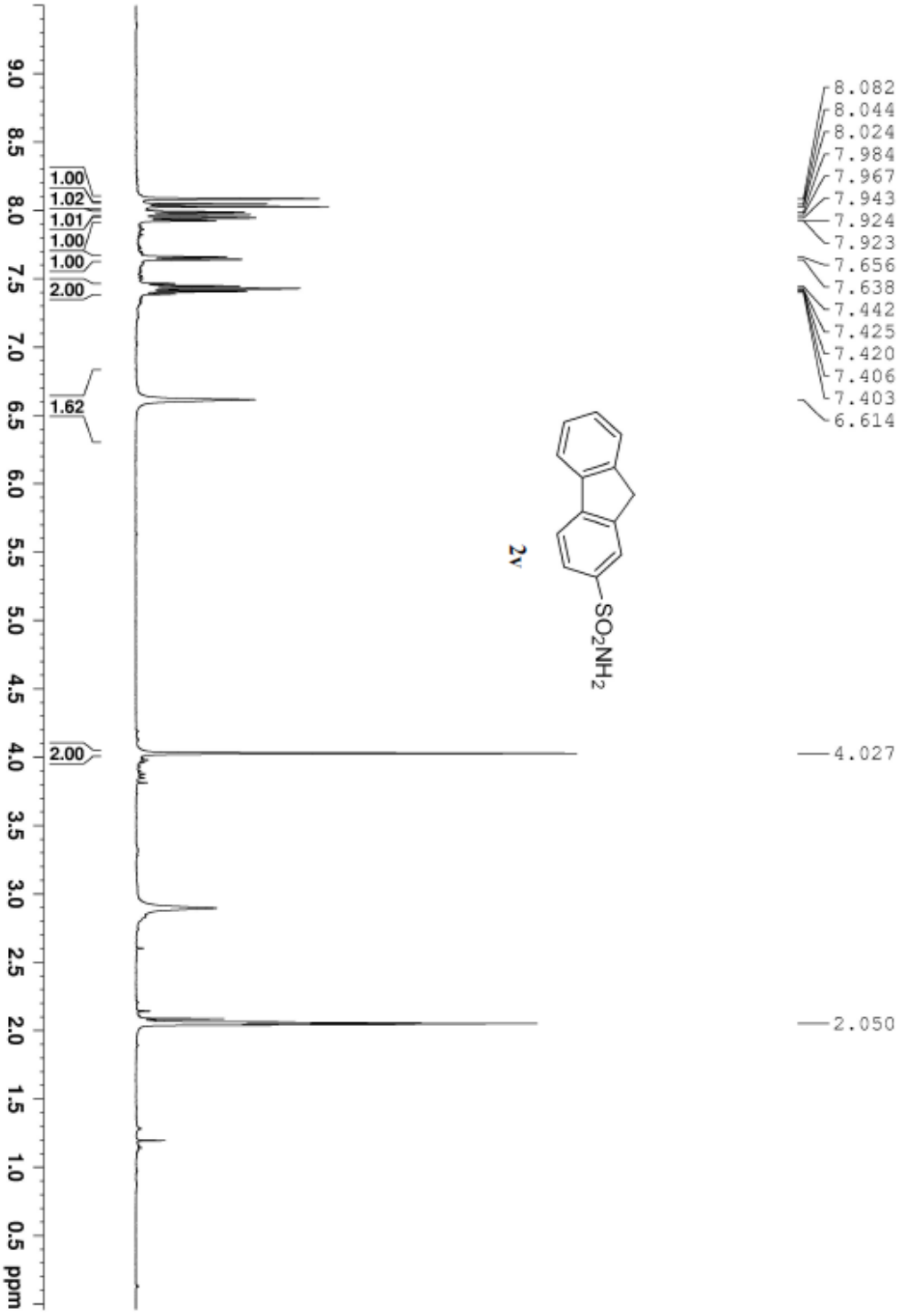

206.17
154.20
141.86
140.05
104.50
60.65
56.65
29.80
MeO
MeO
OMe
SO2NH2
2s
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
ppm

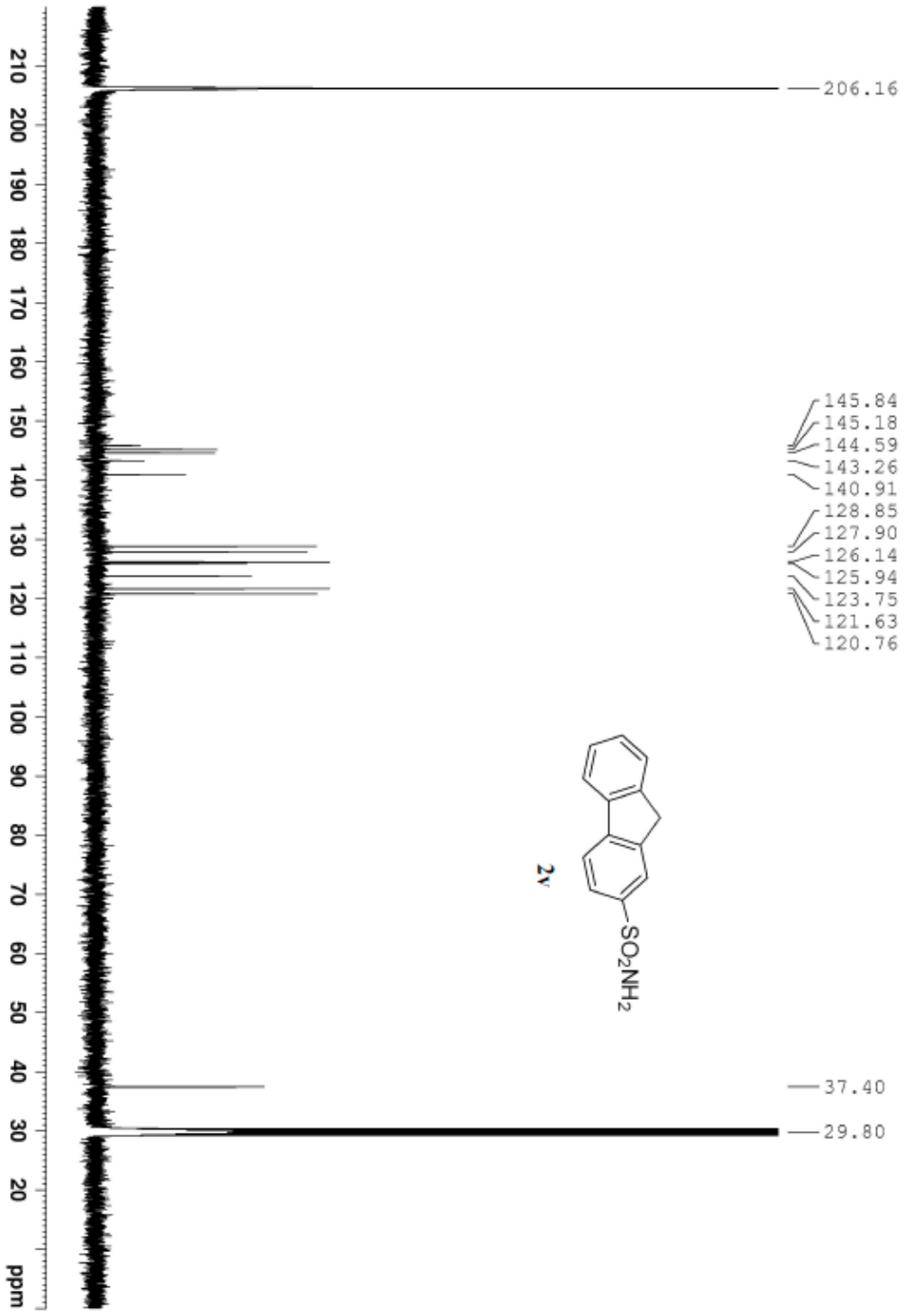

7.260
6.967
4.795
2.653
2.304
2.00
1.95
6.00
3.01
Me
Me
Me
SO2NH2
2t
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

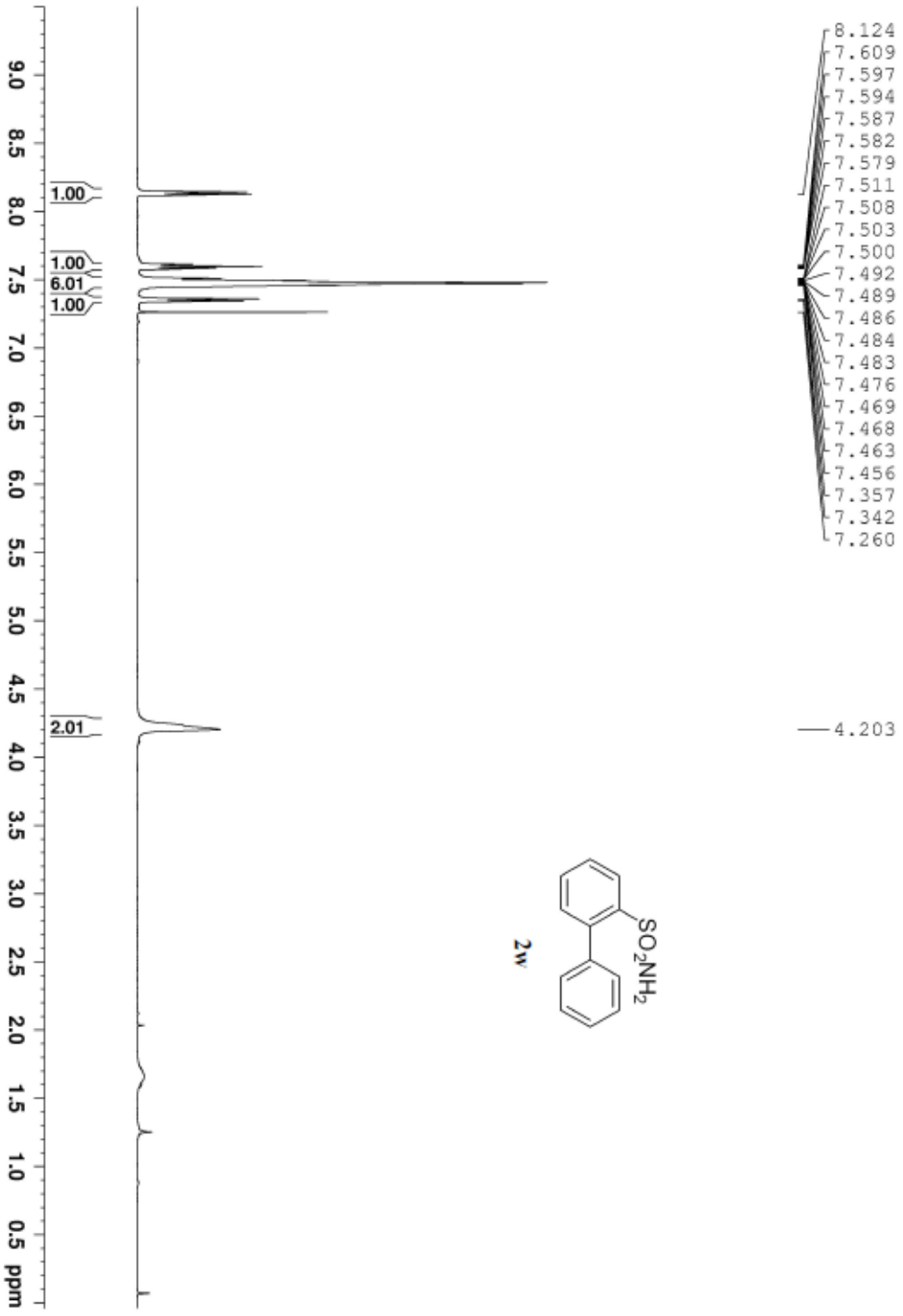

142.22
138.17
135.87
131.87
77.00
22.88
20.91
Me
Me
Me
SO2NH2
2t
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

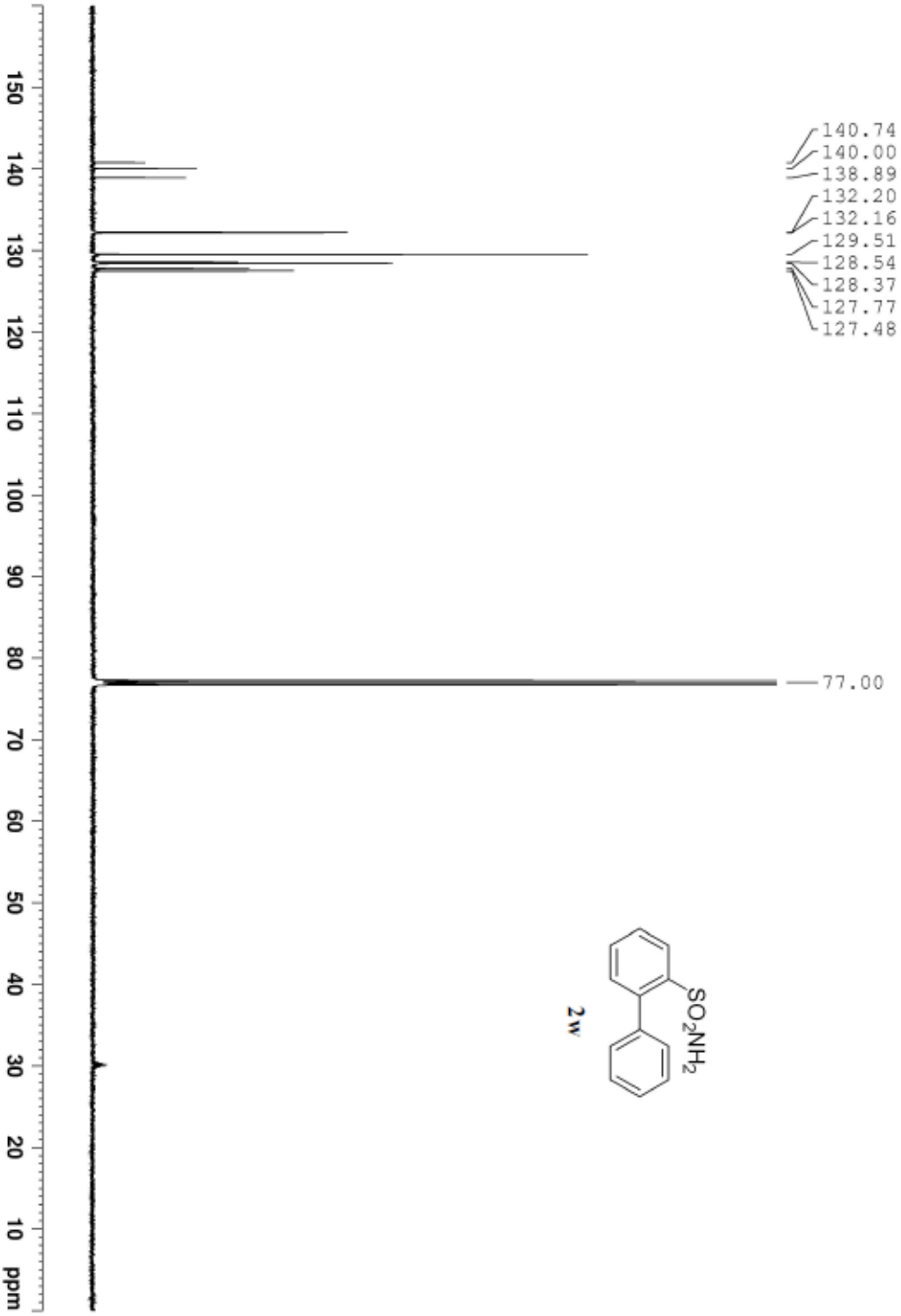

8.787
8.766
8.279
8.261
8.170
8.150
8.062
8.042
7.708
7.705
7.688
7.670
7.667
7.657
7.656
7.637
7.628
7.620
7.608
7.589
6.845
2.050
1.00
1.01
1.01
1.01
3.06
0.51
ppm
2u
SO2NH2

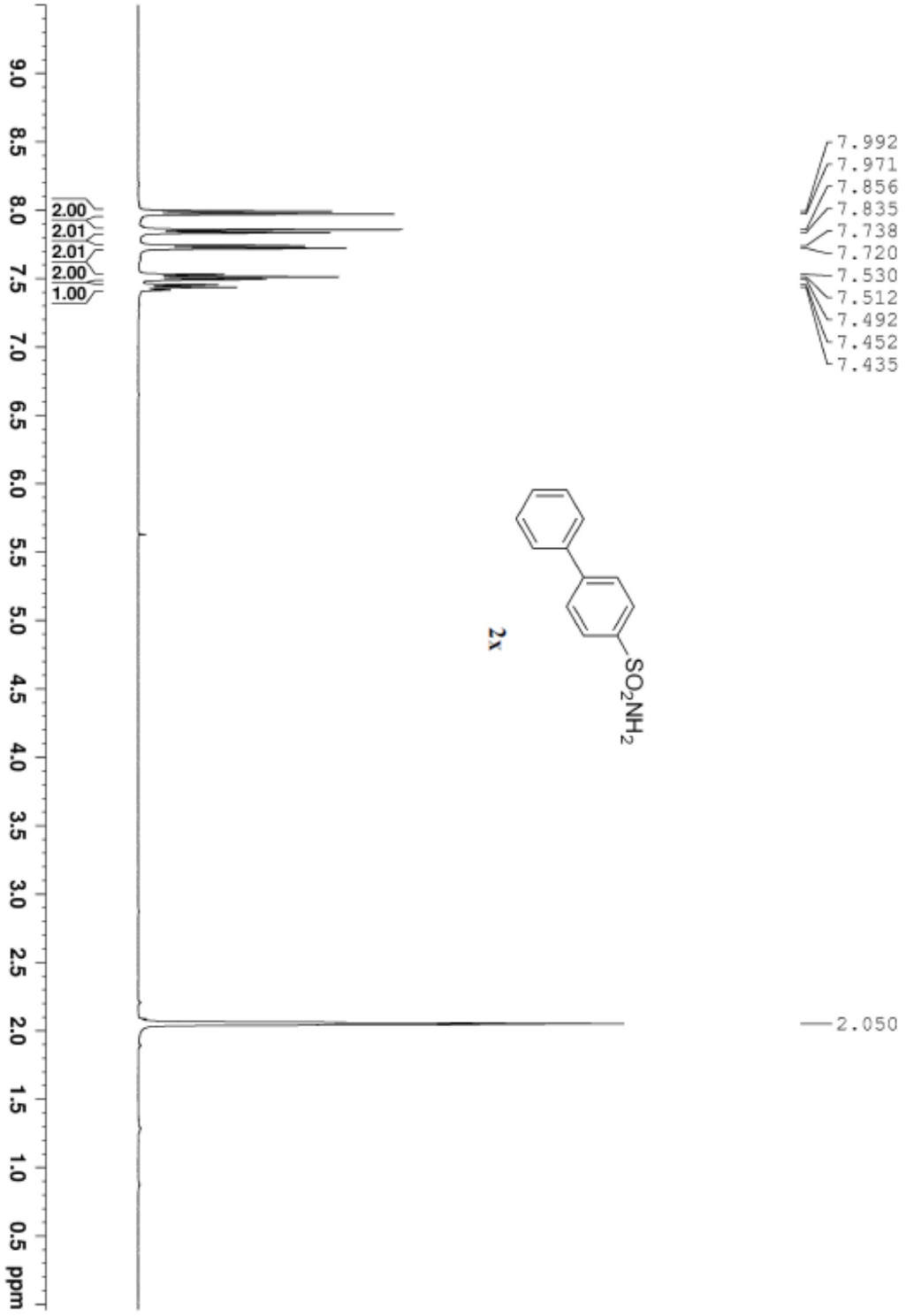

206.39
140.01
135.12
134.08
129.65
128.85
128.39
127.82
127.47
125.97
125.13
29.80
SO2NH2
2u
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

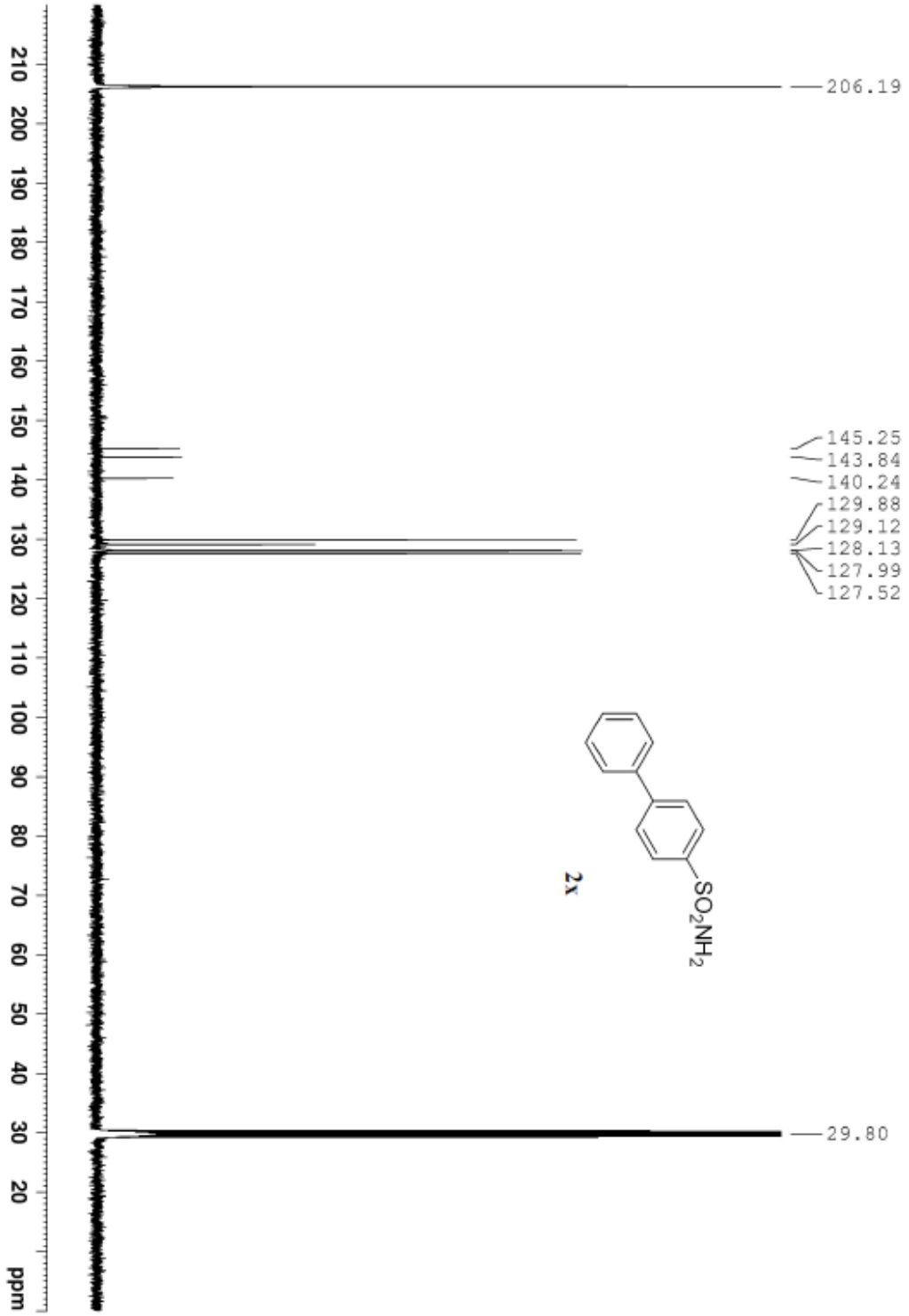

8.082
8.044
8.024
7.984
7.967
7.943
7.924
7.923
7.656
7.638
7.442
7.425
7.420
7.406
7.403
6.614
1.00
1.02
1.01
1.00
1.00
2.00
1.62
2.00
4.027
2.050
2v
SO2NH2
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

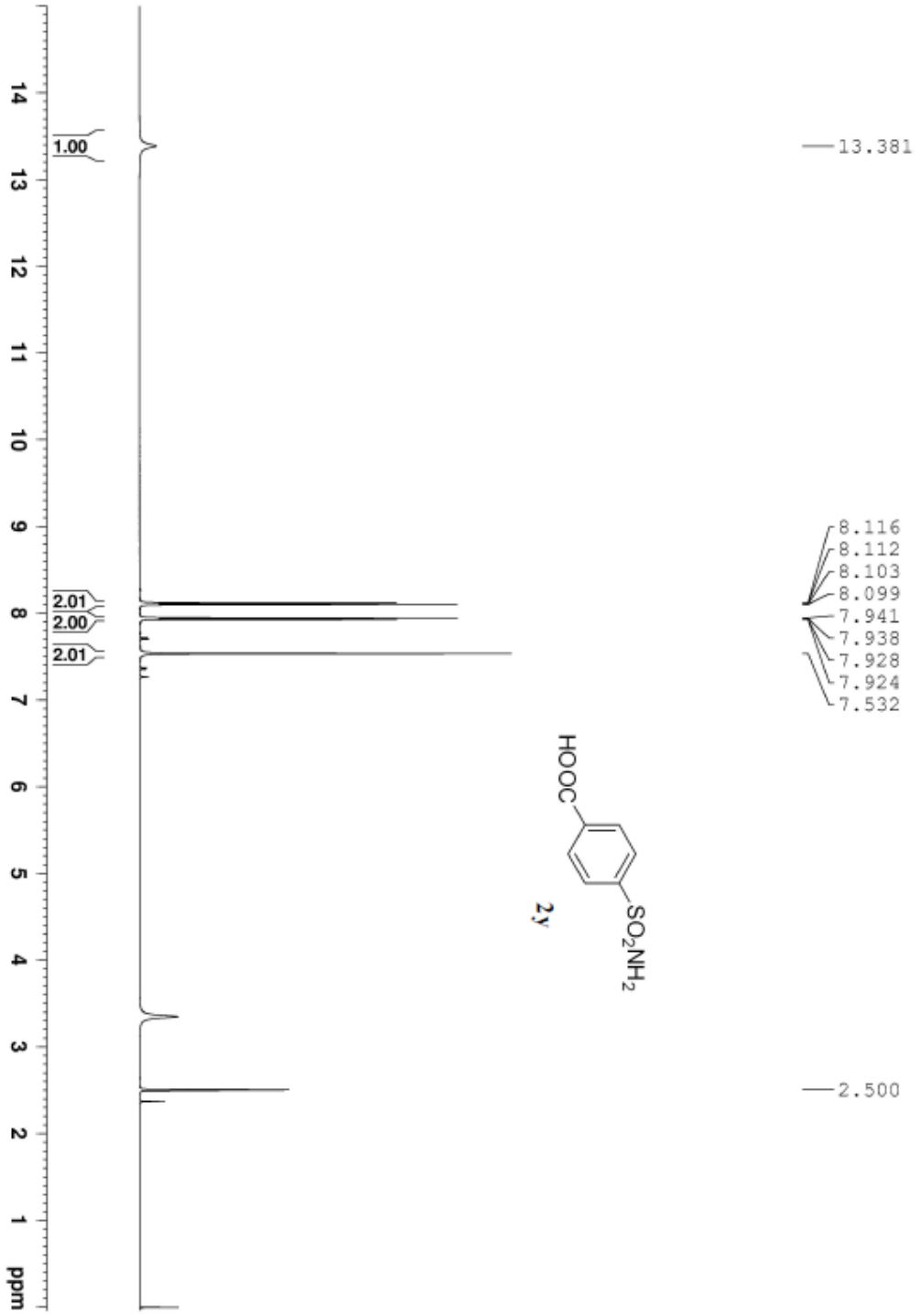

206.16
145.84
145.18
144.59
143.26
140.91
128.85
127.90
126.14
125.94
123.75
121.63
120.76
37.40
29.80
2v
SO2NH2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

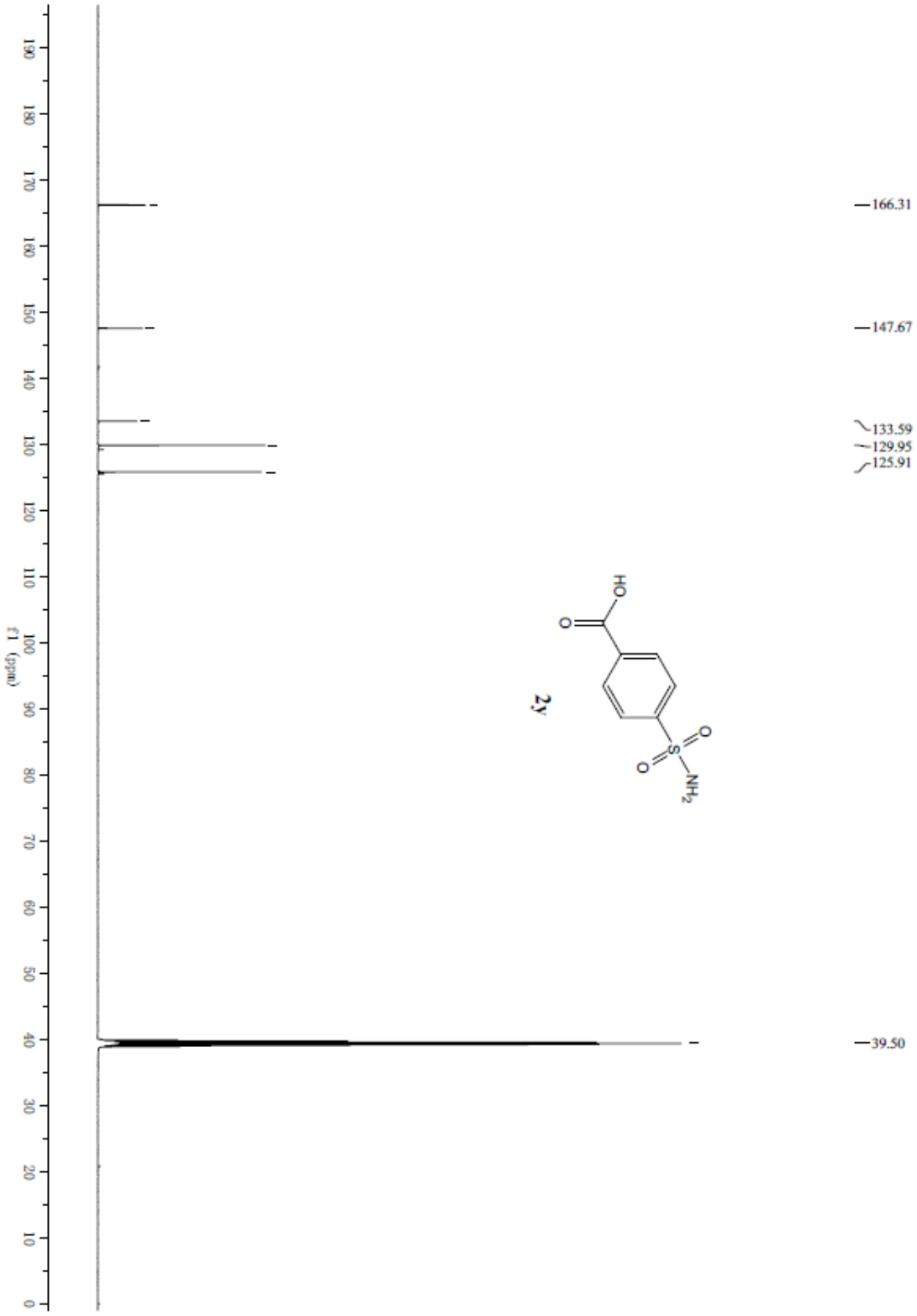

8.124
7.609
7.597
7.594
7.587
7.582
7.579
7.511
7.508
7.503
7.500
7.492
7.489
7.486
7.484
7.483
7.476
7.469
7.468
7.463
7.456
7.357
7.342
7.260
4.203
1.00
1.00
6.01
1.00
2.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
SO2NH2
2w

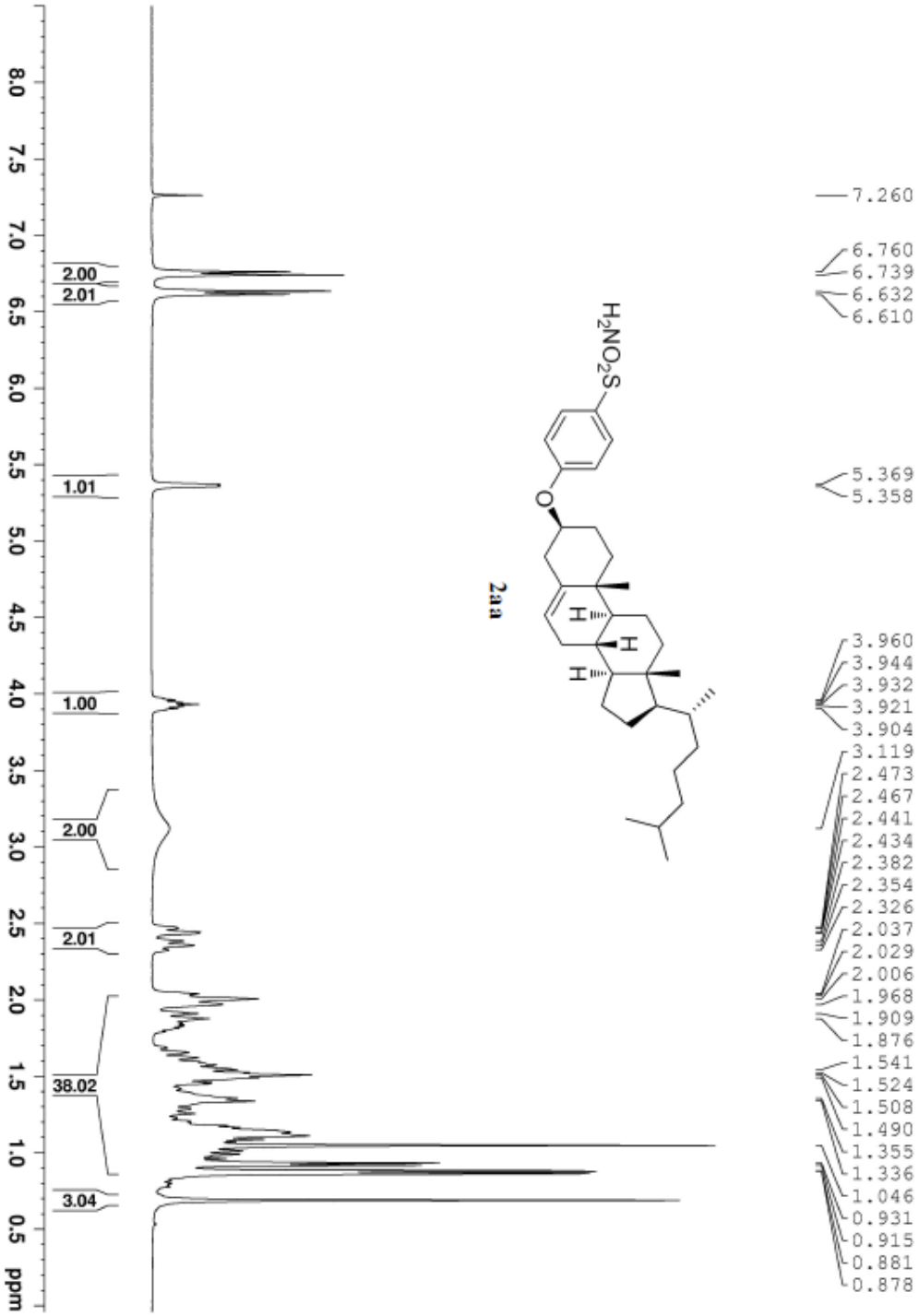

140.74
140.00
138.89
132.20
132.16
129.51
128.54
128.37
127.77
127.48
77.00
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
SO2NH2
2w

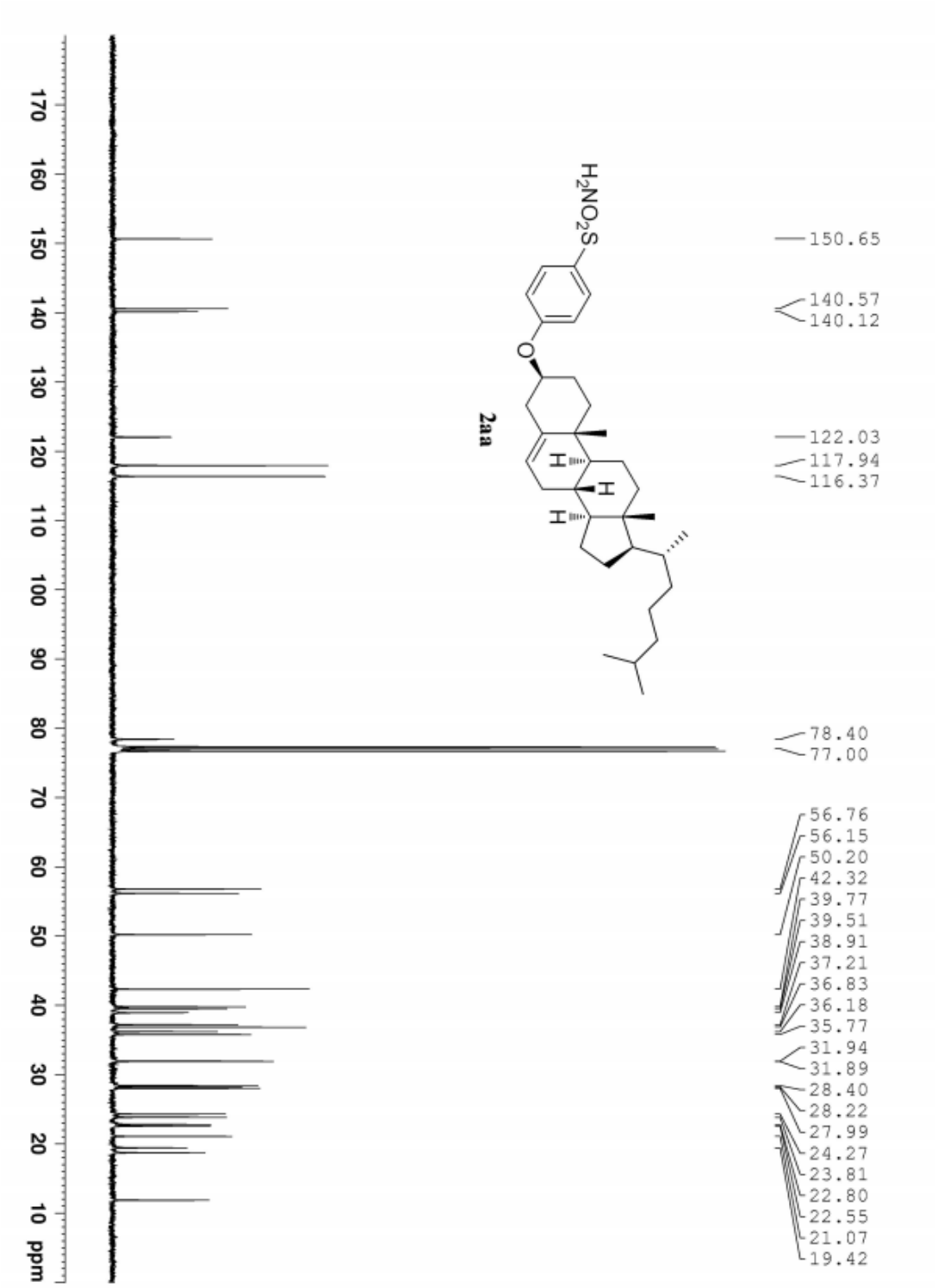

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
2.01
2.01
2.00
1.00
7.992
7.971
7.856
7.835
7.738
7.720
7.530
7.512
7.492
7.452
7.435
2.050
2x
SO2NH2

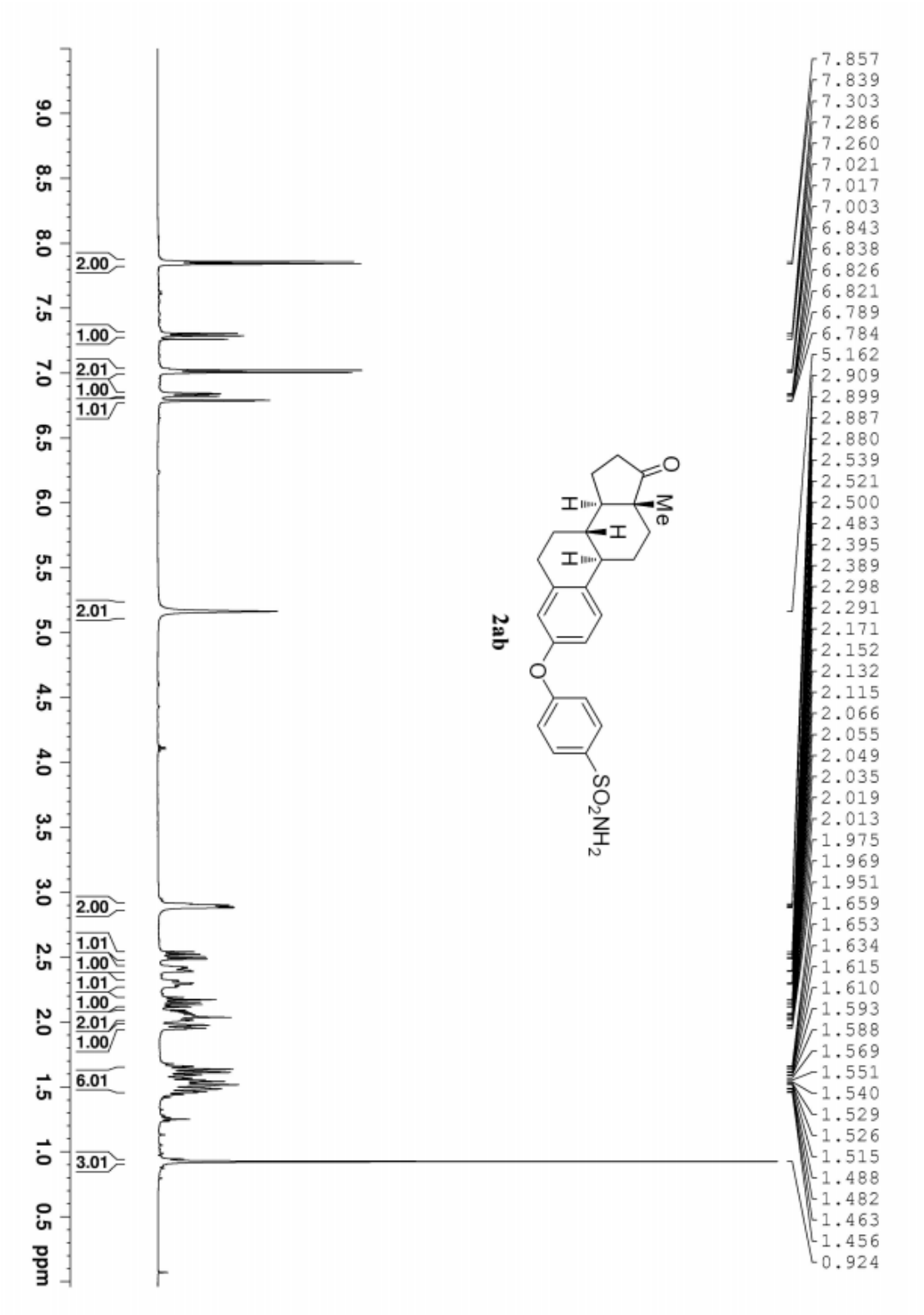

206.19
145.25
143.84
140.24
129.88
129.12
128.13
127.99
127.52
29.80
2x
SO2NH2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

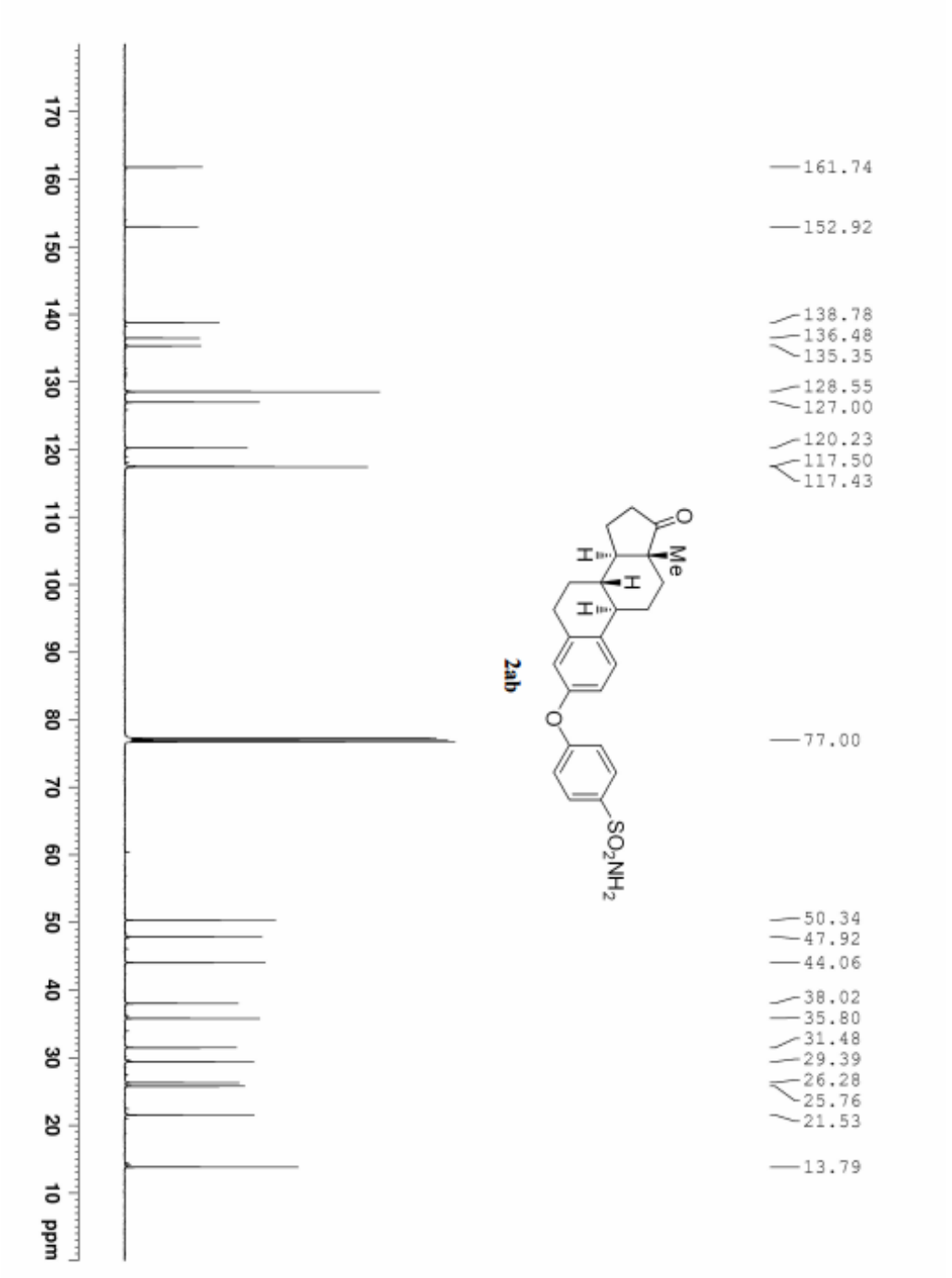

13.381
8.116
8.112
8.103
8.099
7.941
7.938
7.928
7.924
7.532
2.500
1.00
2.01
2.00
2.01
HOOC
SO2NH2
2y
ppm

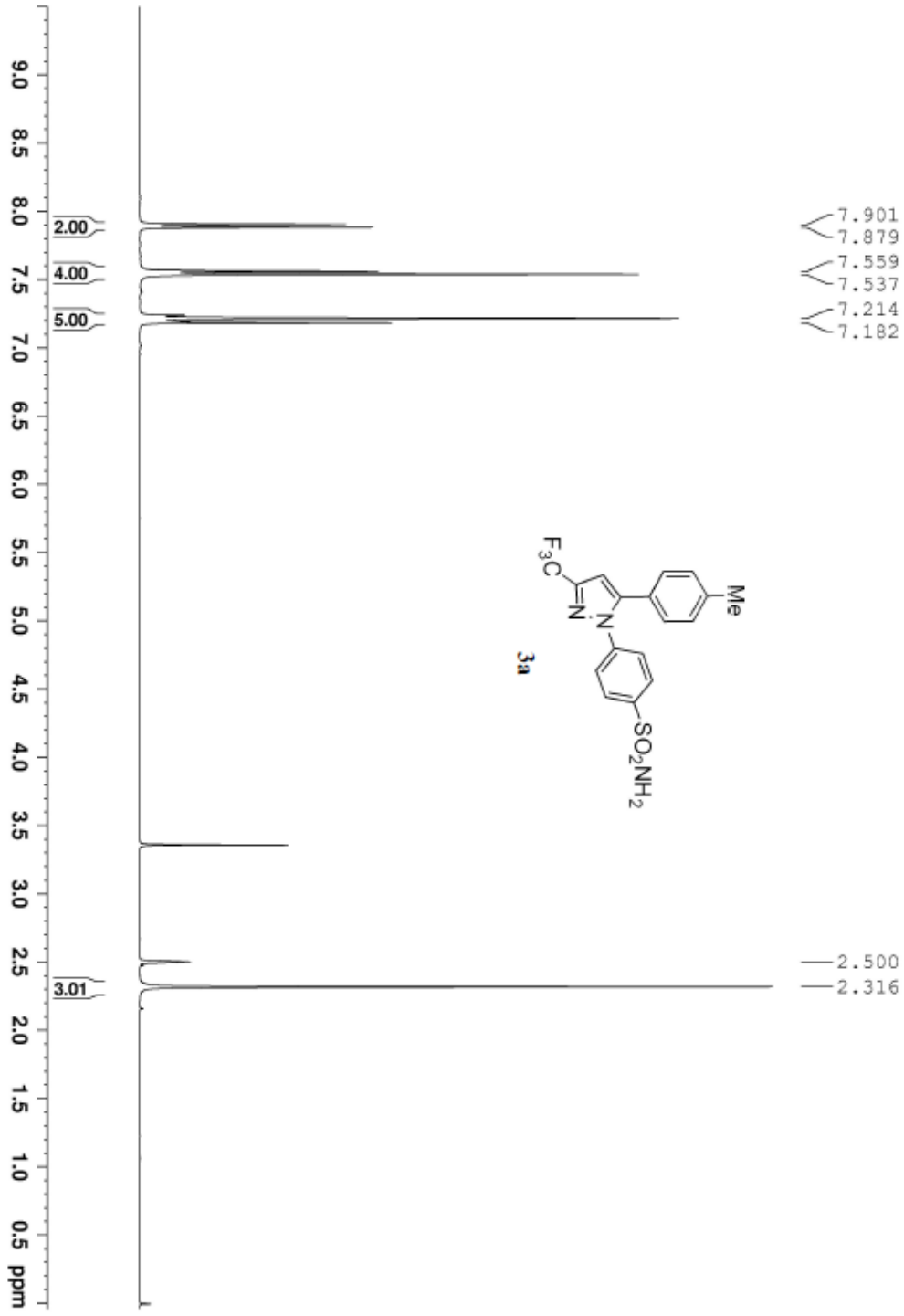

166.31
147.67
133.59
129.95
125.91
39.50
f1 (ppm)
2y
HO
O
O
S
O
NH2

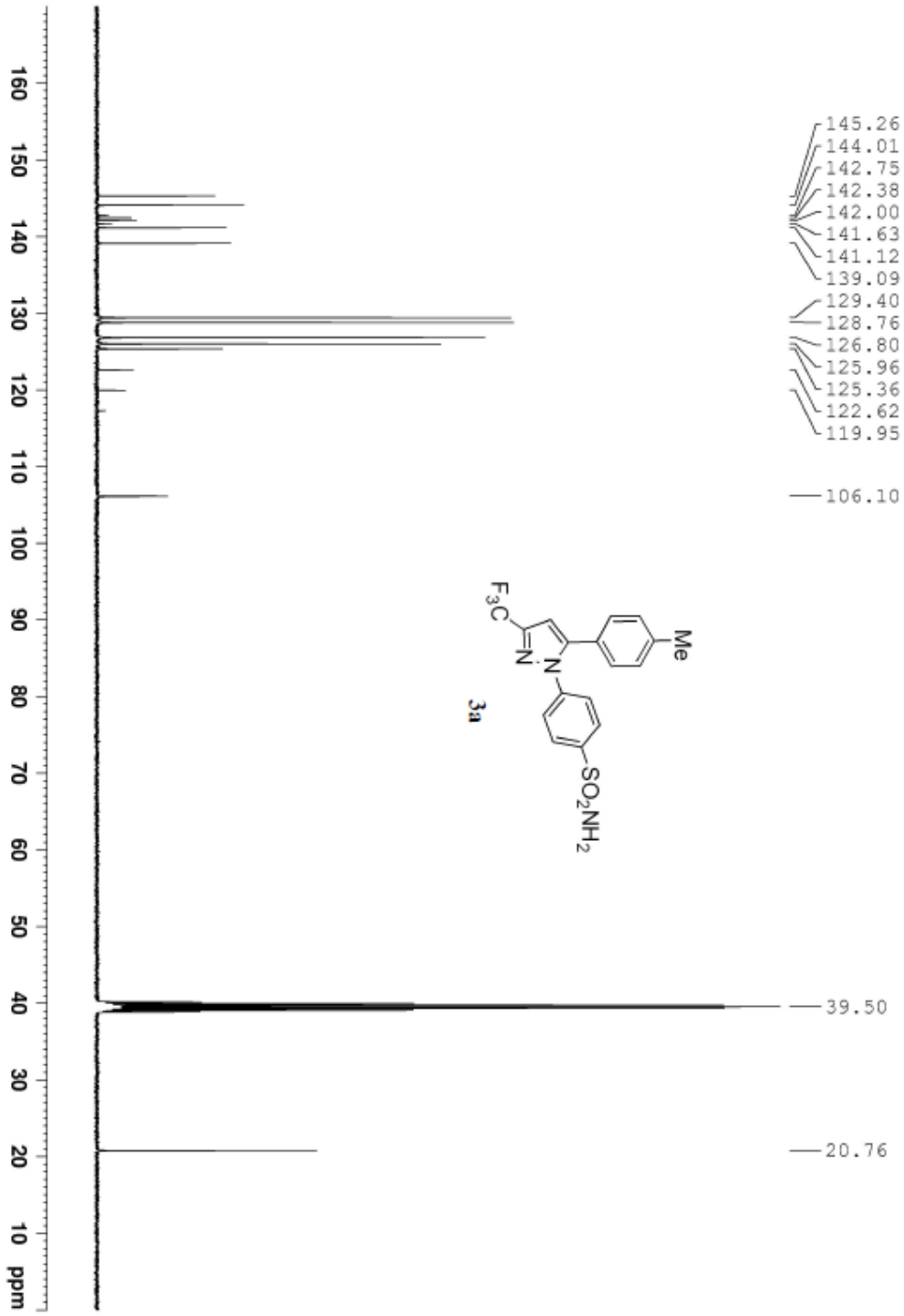

7.260
6.760
6.739
6.632
6.610
5.369
5.358
3.960
3.944
3.932
3.921
3.904
3.119
2.473
2.467
2.441
2.434
2.382
2.354
2.326
2.037
2.029
2.006
1.968
1.909
1.876
1.541
1.524
1.508
1.490
1.355
1.336
1.046
0.931
0.915
0.881
0.878
2.00
2.01
1.01
1.00
2.00
2.01
38.02
3.04
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
H2NO2S
O
H
H
H
2aa

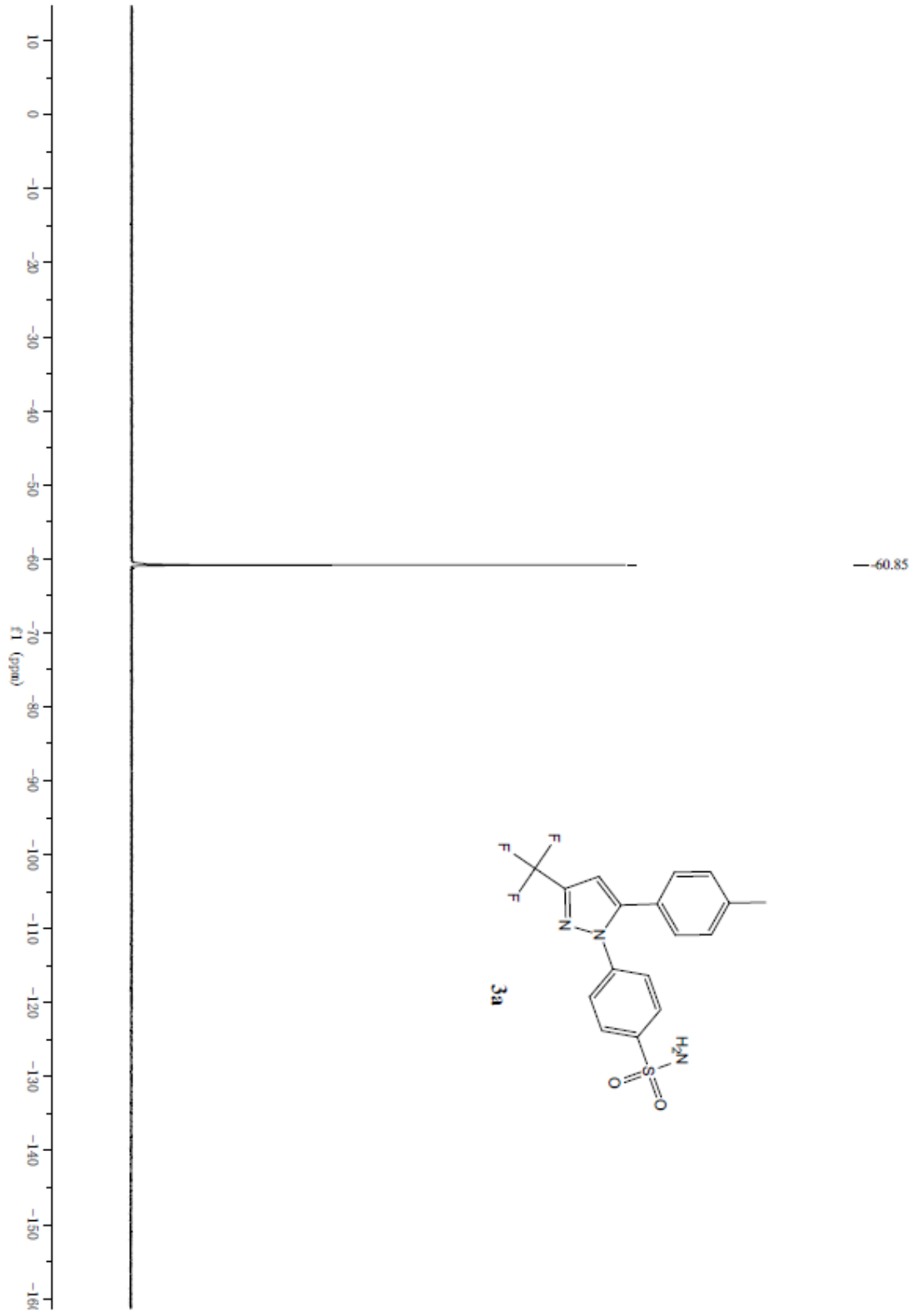

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
H_2NO_2S
O
H
H
H
2aa
150.65
140.57
140.12
122.03
117.94
116.37
78.40
77.00
56.76
56.15
50.20
42.32
39.77
39.51
38.91
37.21
36.83
36.18
35.77
31.94
31.89
28.40
28.22
27.99
24.27
23.81
22.80
22.55
21.07
19.42

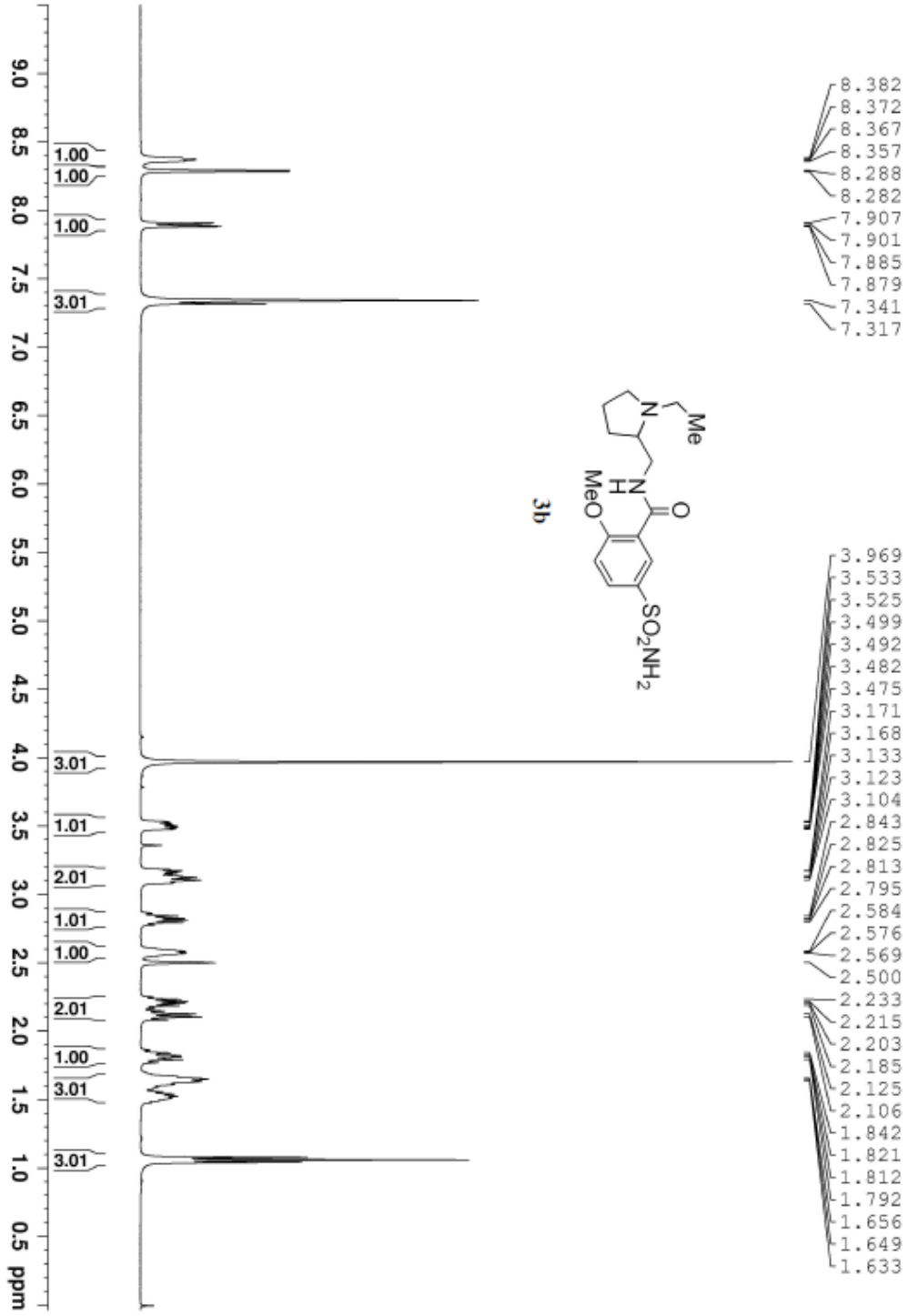

7.857
7.839
7.303
7.286
7.260
7.021
7.017
7.003
6.843
6.838
6.826
6.821
6.789
6.784
5.162
2.909
2.899
2.887
2.880
2.539
2.521
2.500
2.483
2.395
2.389
2.298
2.291
2.171
2.152
2.132
2.115
2.066
2.055
2.049
2.035
2.019
2.013
1.975
1.969
1.951
1.659
1.653
1.634
1.615
1.610
1.593
1.588
1.569
1.551
1.540
1.529
1.526
1.515
1.488
1.482
1.463
1.456
0.924
O
Me
H
H
H
O
SO2NH2
2ab
2.00
1.00
2.01
1.00
1.01
2.01
2.00
1.01
1.00
1.01
1.00
2.01
1.00
6.01
3.01
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
ppm


161.74
152.92
138.78
136.48
135.35
128.55
127.00
120.23
117.50
117.43
77.00
50.34
47.92
44.06
38.02
35.80
31.48
29.39
26.28
25.76
21.53
13.79
O
Me
H
H
H
O
SO2NH2
2ab
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

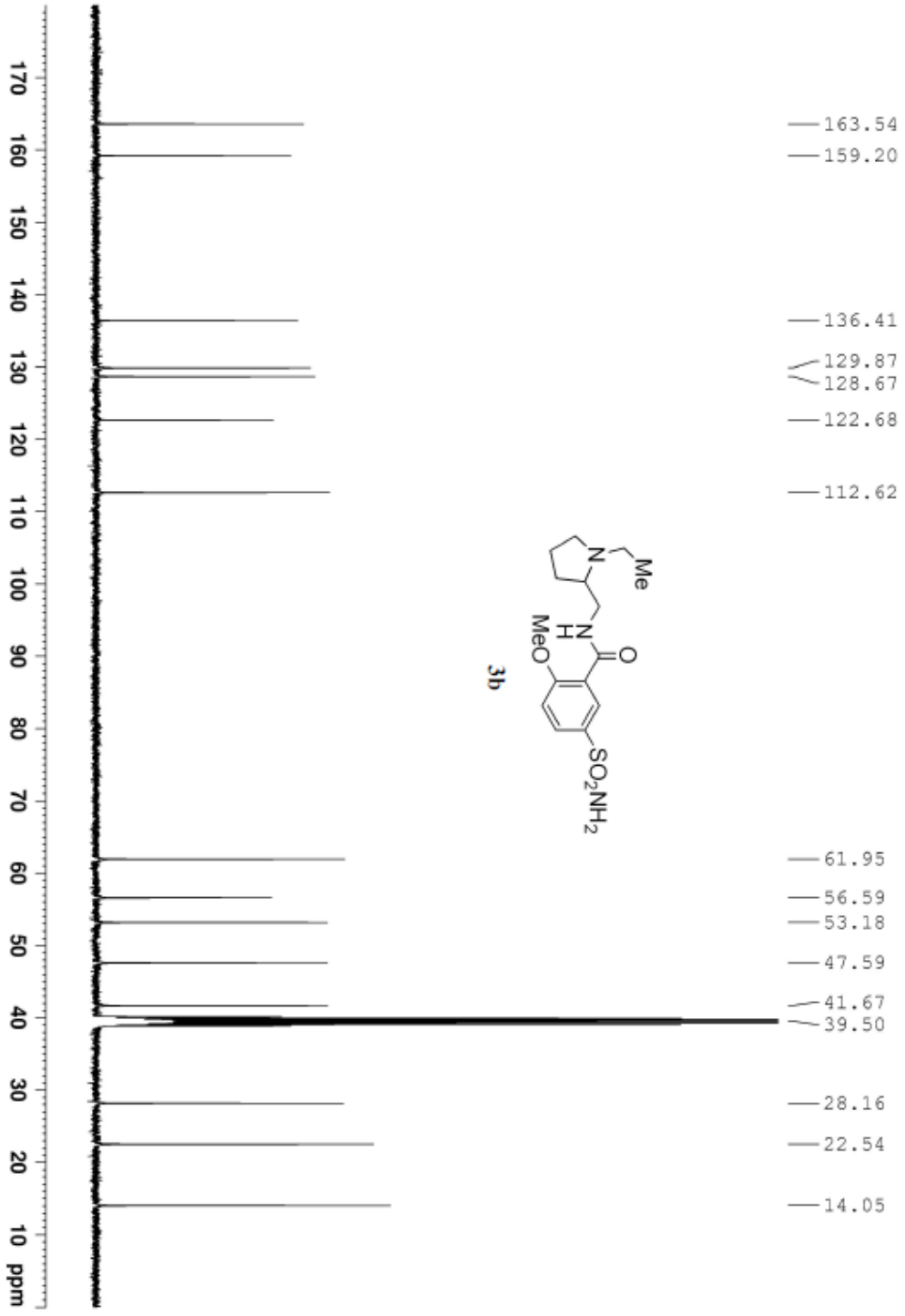

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
4.00
5.00
3.01
7.901
7.879
7.559
7.537
7.214
7.182
2.500
2.316
F3C
N
N
Me
SO2NH2
3a

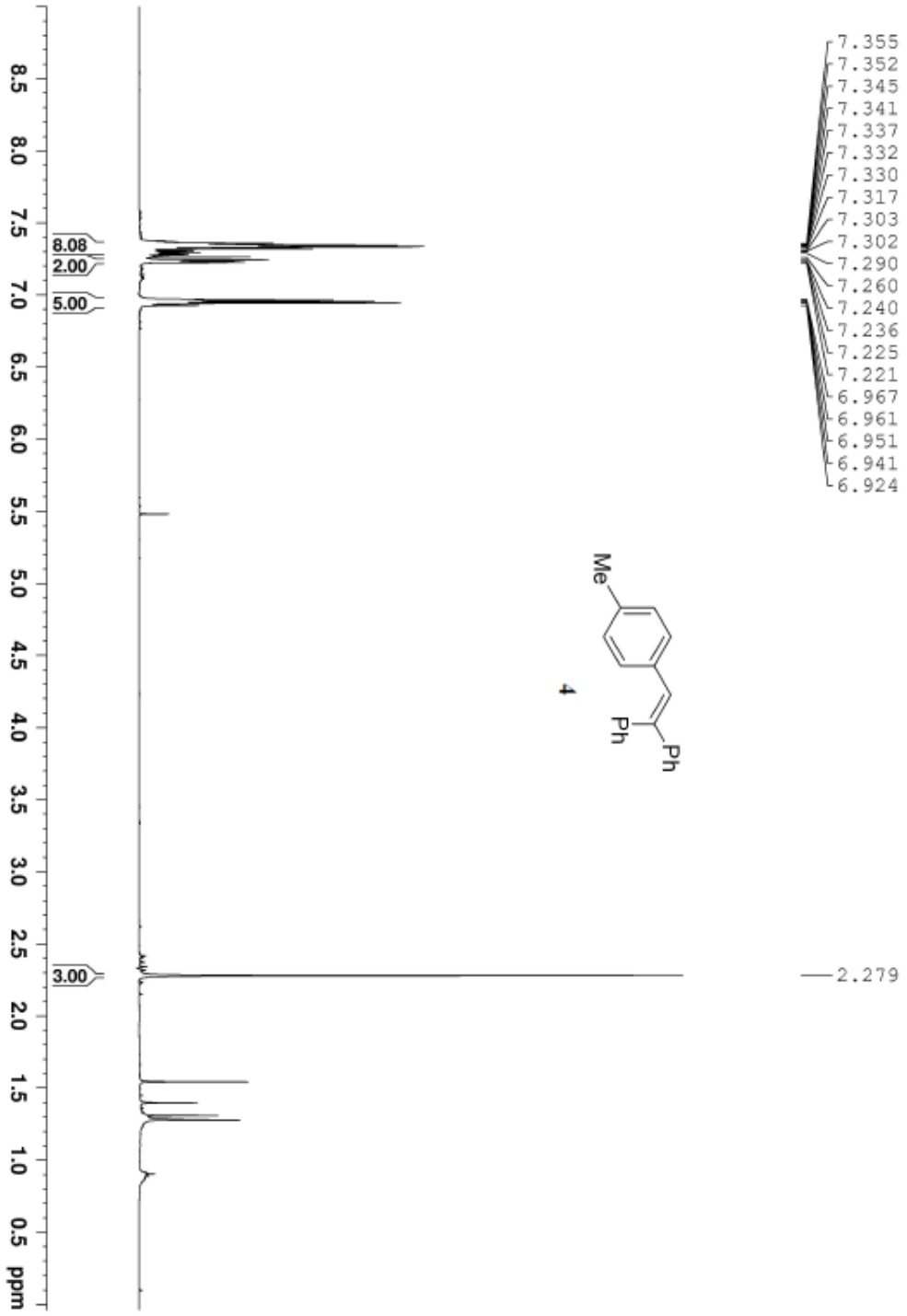

145.26
144.01
142.75
142.38
142.00
141.63
141.12
139.09
129.40
128.76
126.80
125.96
125.36
122.62
119.95
106.10
39.50
20.76
Me
F_3C
N
N
SO_2NH_2
3a
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

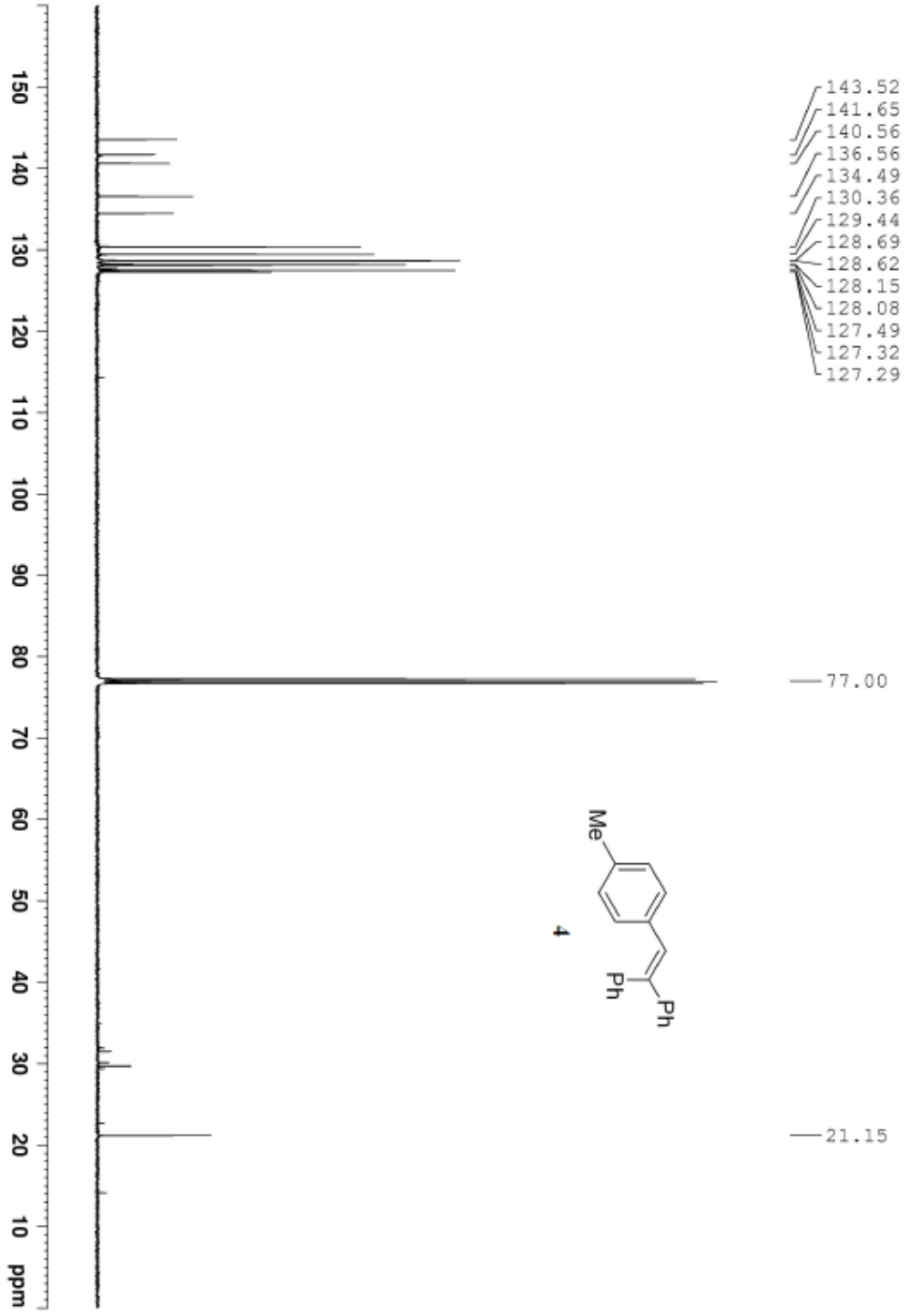

10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)
-60.85
F
F
F
N
N
H2N
S
O
O
3a

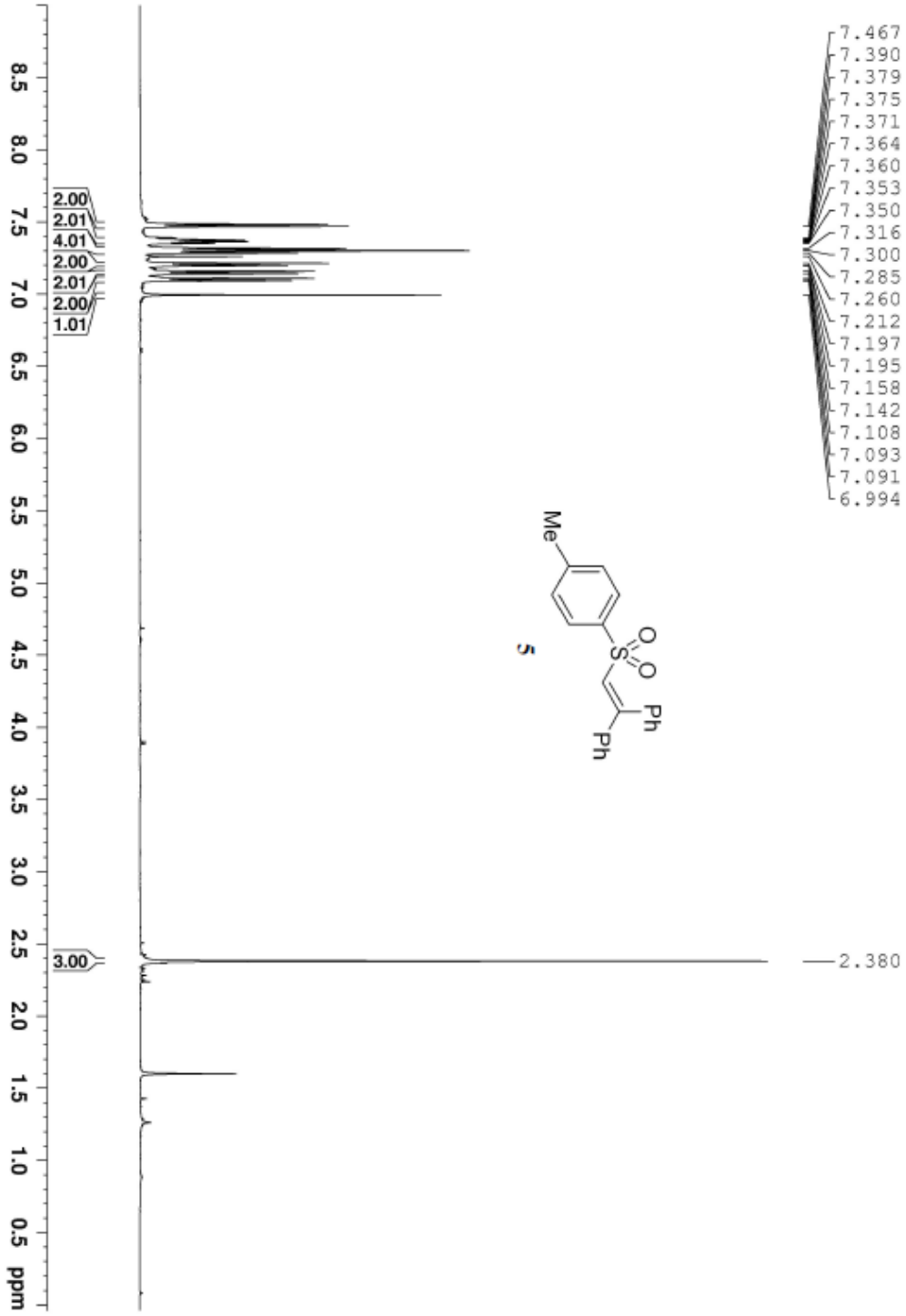

8.382
8.372
8.367
8.357
8.288
8.282
7.907
7.901
7.885
7.879
7.341
7.317
3.969
3.533
3.525
3.499
3.492
3.482
3.475
3.171
3.168
3.133
3.123
3.104
2.843
2.825
2.813
2.795
2.584
2.576
2.569
2.500
2.233
2.215
2.203
2.185
2.125
2.106
1.842
1.821
1.812
1.792
1.656
1.649
1.633
1.00
1.00
1.00
3.01
3.01
1.01
2.01
1.01
1.00
2.01
1.00
3.01
3.01
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
ppm
Me
N
N
H
MeO
O
SO2NH2

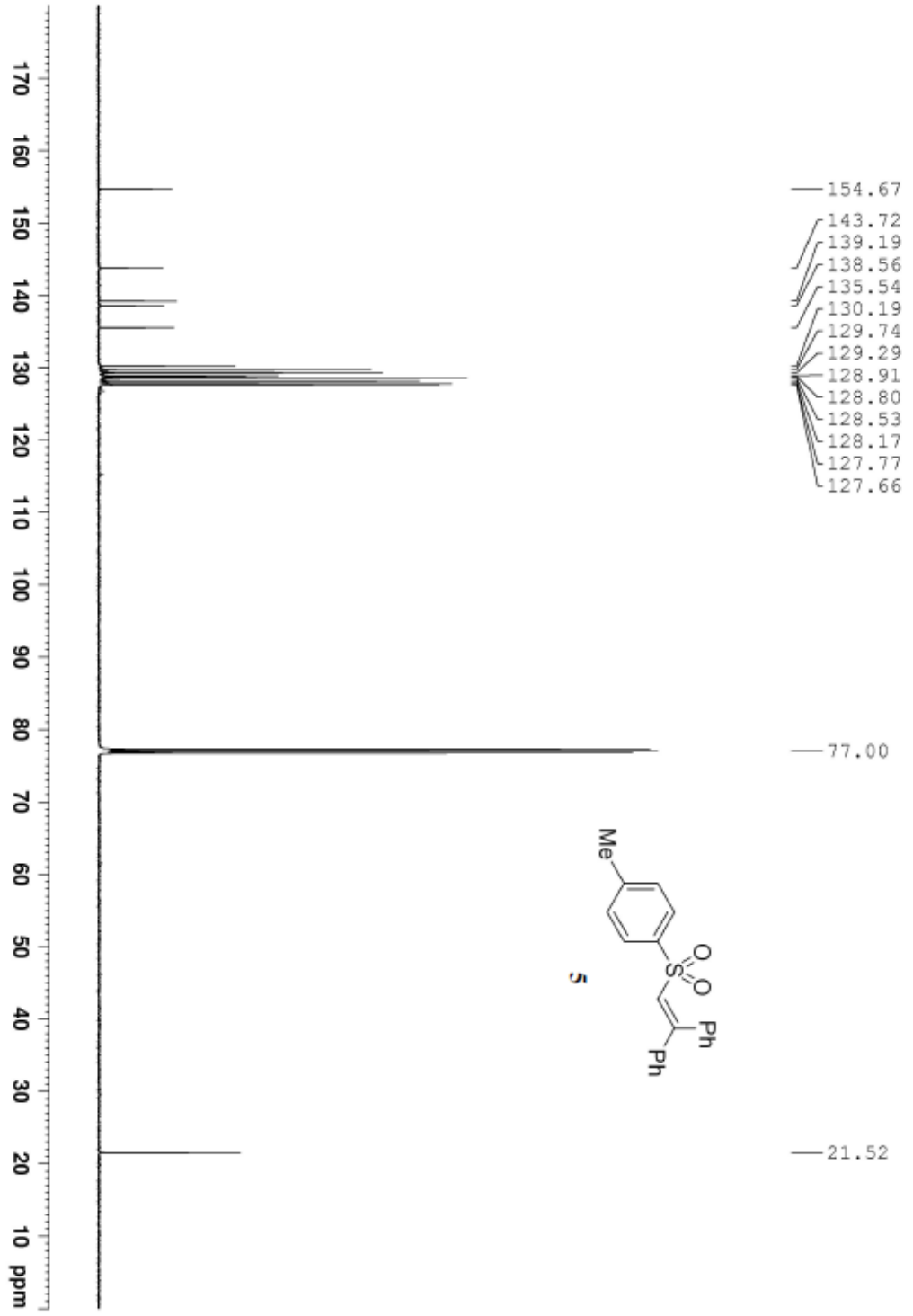
3b


163.54
159.20
136.41
129.87
128.67
122.68
112.62
61.95
56.59
53.18
47.59
41.67
39.50
28.16
22.54
14.05
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
Me
N
N
H
O
MeO
SO2NH2
3b


7.355
7.352
7.345
7.341
7.337
7.332
7.330
7.317
7.303
7.302
7.290
7.260
7.240
7.236
7.225
7.221
6.967
6.961
6.951
6.941
6.924
8.08
2.00
5.00
3.00
2.279
Me
Ph
Ph
4
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
ppm


143.52
141.65
140.56
136.56
134.49
130.36
129.44
128.69
128.62
128.15
128.08
127.49
127.32
127.29
77.00
21.15
Me
Ph
Ph
4
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.467
7.390
7.379
7.375
7.371
7.364
7.360
7.353
7.350
7.316
7.300
7.285
7.260
7.212
7.197
7.195
7.158
7.142
7.108
7.093
7.091
6.994
2.380
2.00
2.01
4.01
2.00
2.01
2.00
1.01
3.00
Me
O
O
S
Ph
Ph
5
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
ppm


154.67
143.72
139.19
138.56
135.54
130.19
129.74
129.29
128.91
128.80
128.53
128.17
127.77
127.66
77.00
21.52
Me
O
O
S
Ph
Ph
5
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm