Electronic Supplementary Material (ESI) for Green Chemistry.

General sulfone construction via sulfur dioxide surrogate control

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Supporting Information

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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 (δ 7.26). Chemical shifts for carbon are reported in parts per million relative to chloroform (δ 77.0). 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.

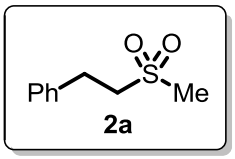
II. General procedure for the alkyl alkyl sulfones synthesis

Under a N_2 atmosphere, alkyl bromide **1** (0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), $PO(OR^2)_3$ (1.5 mmol), KI (166.0 mg, 1.0 mmol), TBAI (92.3 mg, 0.25 mmol), Cs_2CO_3 (325.8 mg, 1.0 mmol) and DMSO (2 mL) were added to a Schlenk tube. The reaction was stirred at 80 ^{o}C for 15 h, and water (25 mL) was added. The solution was extracted with ethyl acetate and organic layers were combined, dried over Na_2SO_4. After evaporation of solvent, the residue was purified by column chromatography to give the corresponding products **2**.

III. General procedure for the aryl alkyl sulfones synthesis

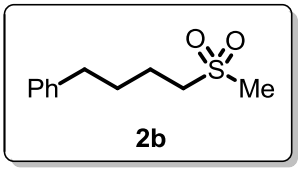
Under a N_2 atmosphere, alkyl iodide **1** (0.5 mmol), $Na_2S_2O_4$ (261.2 mg, 1.5 mmol), $PO(OR^2)_3$ (1.5 mmol), $PdCl_2$dppf (0.7 mg, 0.001 mmol), TBAB (241.8 mg, 0.75 mmol) and DMSO (5 mL) were added to a Schlenk tube. The reaction was stirred at 120 ^{o}C for 15 h, and water (25 mL) was added. The solution was extracted with ethyl acetate and organic layers were combined, dried over Na_2SO_4. After evaporation of solvent, the residue was purified by column chromatography to give the corresponding products **3**.

IV. Characterization of the products



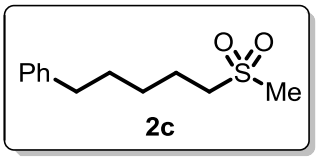
2a

(2-(methylsulfonyl)ethyl)benzene (**2a**): Prepared following general procedure using alkyl bromide **1a** (92.5 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), $PO(OMe)_3$ (210.1 mg, 1.5 mmol), KI (166.0 mg, 1.0 mmol), TBAI (92.3 mg, 0.25 mmol), Cs_2CO_3 (325.8 mg, 1.0 mmol) and DMSO (2 mL), the reaction was stirred at 80 ^oC for 15 h giving **2a** in 71% yield (65.4 mg) as a white solid by column chromatography (PE/EA = 2/1). **^{1}H NMR**(400 MHz, $CDCl_3$) δ 7.28 – 7.15 (m, 5H), 3.25 – 3.21 (m, 2H), 3.11 – 3.07 (m, 2H), 2.74 (s, 3H). **^{13}C NMR**(100 MHz, $CDCl_3$) δ 137.3, 128.9, 128.3, 127.1, 56.1, 40.9, 28.5; **IR** ν 2924, 1600, 1494, 1456, 1433, 1311, 1265, 1149, 1020, 823, 738, 696 cm^{-1}; **HRMS** (EI) for $C_9H_{12}O_2S$ Calculated: 184.0558, found: 184.0559.



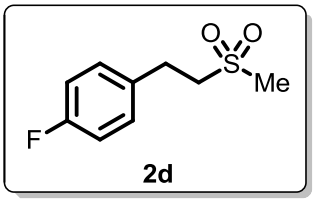
2b

(4-(methylsulfonyl)butyl)benzene (**2b**). Prepared following general procedure using alkyl bromide **1b** (106.6 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), $PO(OMe)_3$ (210.1 mg, 1.5 mmol), KI (166.0 mg, 1.0 mmol), TBAI (92.3 mg, 0.25 mmol), Cs_2CO_3 (325.8 mg, 1.0 mmol) and DMSO (2 mL), the reaction was stirred at 80 ^oC for 15 h giving **2b** in 66% yield (69.8 mg) as a white solid by column chromatography (PE/EA 2/1). **^{1}H NMR**(400 MHz, $CDCl_3$) δ 7.25 – 7.17 (m, 2H), 7.16 – 7.06 (m, 3H), 2.98 – 2.88 (m, 2H), 2.78 (s, 3H), 2.59 (t, *J* = 7.4 Hz, 2H), 1.86 – 1.65 (m, 4H). **^{13}C NMR**(100 MHz, $CDCl_3$) δ 141.0, 128.4, 128.2, 126.0, 54.5, 40.3, 35.2, 29.9, 21.9; **IR** ν 2920, 1498, 1363, 1317, 1298, 1136, 746, 732 cm^{-1}; **HRMS** (EI) for $C_{11}H_{16}O_2S$ Calculated: 212.0871, found: 212.0869.



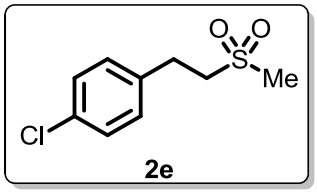
2c

(5-(methylsulfonyl)pentyl)benzene (**2c**). Prepared following general procedure using alkyl bromide **1c** (113.6 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), $PO(OMe)_3$ (210.1 mg, 1.5 mmol), KI (166.0 mg, 1.0 mmol), TBAI (92.3 mg, 0.25 mmol), Cs_2CO_3 (325.8 mg, 1.0 mmol) and DMSO (2 mL), the reaction was stirred at 80 ^oC for 15 h giving **2c** in 61% yield (69.1 mg) as a white solid by column chromatography (PE/EA = 2/1). **^{1}H NMR**(400 MHz, $CDCl_3$) δ 7.23 – 7.17 (m, 2H), 7.13 – 7.05 (m, 3H), 2.93 – 2.86 m, 2H), 2.78 (s, 3H), 2.55 (t, *J* = 7.6 Hz, 2H), 1.83 – 1.71 (m, 2H), 1.64 – 1.54 (m, 2H), 1.47 – 1.32 (m, 2H). **^{13}C NMR**(100 MHz, $CDCl_3$) δ 141.8, 128.2, 125.7, 54.5, 40.3, 35.3, 30.6, 27.7, 22.1. **IR** v 3026, 2858, 1494, 1454, 1290, 1136, 1080, 962, 748 cm^{-1}; **HRMS** (EI) for $C_{12}H_{18}O_2S$ Calculated: 214.0664, found: 214.0662.



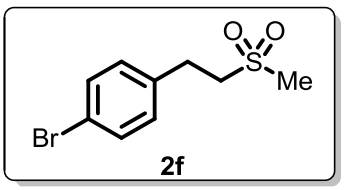
2d

1-fluoro-4-(2-(methylsulfonyl)ethyl)benzene (**2d**). Prepared following general procedure using alkyl bromide **1d** (101.5 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), $PO(OMe)_3$ (210.1 mg, 1.5 mmol), KI (166.0 mg, 1.0 mmol), TBAI (92.3 mg, 0.25 mmol), Cs_2CO_3 (325.8 mg, 1.0 mmol) and DMSO (2 mL), the reaction was stirred at 80 ^oC for 15 h giving **2d** in 64% yield (65.0 mg) as a white solid by column chromatography (PE/EA 2/1). **^{1}H NMR**(400 MHz, $CDCl_3$) δ 7.22 – 7.15 (m, 2H), 7.04 – 6.95 (m, 2H), 3.30 – 3.22 (m, 2H), 3.15 – 3.09 (m, 2H), 2.82 (s, 3H). **^{13}C NMR**(100 MHz, $CDCl_3$) δ 161.7 (d, *J* = 244.2 Hz), 133.0 (d, *J* = 3.3 Hz), 129.8 (d, *J* = 8.0 Hz), 115.7 (*J* = 21.4 Hz), 55.9, 40.9, 27.5. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.3. **IR** v 2933, 1510, 1413, 1319, 1294, 1247, 1128, 966, 717, 700, cm^{-1}; **HRMS** (EI) for $C_9H_{11}FO_2S$ Calculated: 202.0464, found: 202.0462.



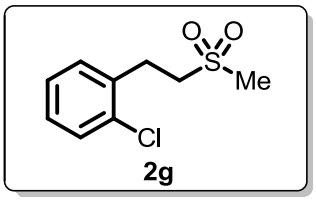
2e

1-chloro-4-(2-(methylsulfonyl)ethyl)benzene (**2e**). Prepared following general procedure using alkyl bromide **1e** (109.8 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), $PO(OMe)_3$ (210.1 mg, 1.5 mmol), KI (166.0 mg, 1.0 mmol), TBAI (92.3 mg, 0.25 mmol), Cs_2CO_3 (325.8 mg, 1.0 mmol) and DMSO (2 mL), the reaction was stirred at 80 ^oC for 15 h giving **2e** in 78% yield (85.5 mg) as a white solid by column chromatography (PE/EA 2/1). **^{1}H NMR**(400 MHz, $CDCl_3$) δ 7.25 – 7.19 (m, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 3.23 – 3.17 (m, 2H), 3.08 – 3.02 (m, 2H), 2.77 (s, 3H). **^{13}C NMR**(100 MHz, $CDCl_3$) δ 135.7, 132.8, 129.7, 128.9, 55.6, 40.9, 27.6. **IR** ν 2933, 1494, 1409, 1319, 1296, 1247, 141, 972, 702, 648 cm^{-1}; **HRMS** (EI) for $C_9H_{11}ClO_2S$ Calculated: 218.0168, found: 218.0171.



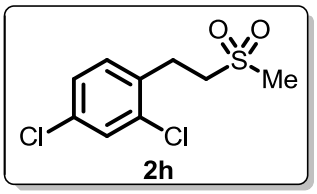
2f

1-bromo-4-(2-(methylsulfonyl)ethyl)benzene (**2f**). Prepared following general procedure using alkyl bromide **1f** (132.0 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), $PO(OMe)_3$ (210.1 mg, 1.5 mmol), KI (166.0 mg, 1.0 mmol), TBAI (92.3 mg, 0.25 mmol), Cs_2CO_3 (325.8 mg, 1.0 mmol) and DMSO (2 mL), the reaction was stirred at 80 ^oC for 15 h giving **2f** in 79% yield (103.9 mg) as a white solid by column chromatography (PE/EA 2/1). **^{1}H NMR**(400 MHz, $CDCl_3$) δ 7.47 – 7.40 (m, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 3.29 – 3.24 (m, 2H), 3.13 – 3.07 (m, 2H), 2.84 (s, 3H). **^{13}C NMR**(100 MHz, $CDCl_3$) δ 136.3, 131.9, 130.0, 120.9, 55.6, 40.9, 27.7. **IR** ν 2934, 1712, 1487, 1406, 1305, 1230, 1143, 1180, 1118, 1070, 846, 812, 621 cm^{-1}; **HRMS** (EI) for $C_9H_{11}BrO_2S$ Calculated: 261.9663, found: 261.9666.



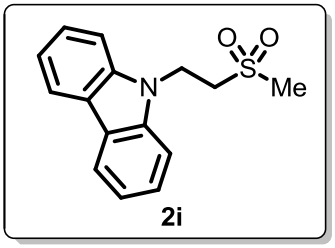
2g

1-chloro-2-(2-(methylsulfonyl)ethyl)benzene (**2g**). Prepared following general procedure using alkyl bromide **1g** (109.8 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), $PO(OMe)_3$ (210.1 mg, 1.5 mmol), KI (166.0 mg, 1.0 mmol), TBAI (92.3 mg, 0.25 mmol), Cs_2CO_3 (325.8 mg, 1.0 mmol) and DMSO (2 mL), the reaction was stirred at 80 ^oC for 15 h giving **2g** in 76% yield (83.2 mg) as a white solid by column chromatography (PE/EA 2/1). **^{1}H NMR**(400 MHz, $CDCl_3$) δ 7.34 – 7.11 (m, 4H), 3.29 – 3.13 (m, 4H), 2.81 (s, 3H). **^{13}C NMR**(100 MHz, $CDCl_3$) δ 134.9, 133.7, 130.7, 129.7, 128.7, 127.3, 53.8, 40.6, 27.0. **IR** v 3026, 1363, 1224, 1141, 962, 702 cm^{-1}; **HRMS** (EI) for $C_9H_{11}ClO_2S$ Calculated: 218.0168, found: 218.0165.



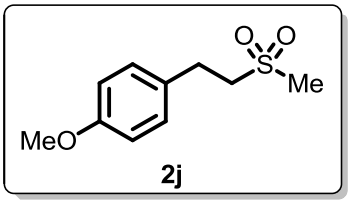
2h

2,4-dichloro-1-(2-(methylsulfonyl)ethyl)benzene (**2h**). Prepared following general procedure using alkyl bromide **1h** (127.0 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), $PO(OMe)_3$ (210.1 mg, 1.5 mmol), KI (166.0 mg, 1.0 mmol), TBAI (92.3 mg, 0.25 mmol), Cs_2CO_3 (325.8 mg, 1.0 mmol) and DMSO (2 mL), the reaction was stirred at 80 ^oC for 15 h giving **2h** in 81% yield (102.5 mg) as a white solid by column chromatography (PE/EA = 2/1). **^{1}H NMR**(400 MHz, $CDCl_3$) δ 7.31 (d, $\underline{J}$ = 1.9 Hz, 1H), 7.20 – 7.12 (m, 2H), 3.25 – 3.10 (m, 4H), 2.84 (s, 3H). **^{13}C NMR**(100 MHz, $CDCl_3$) δ 134.3, 133.7, 133.5, 131.5 , 129.4, 127.5, 53.5, 40.7, 26.3. **IR** v 3026, 1456, 1417, 1224, 1139, 966, 817, 702 cm^{-1}; **HRMS** (EI) for $C_9H_{10}Cl_2O_2S$ Calculated: 251.9779, found: 251.9776.



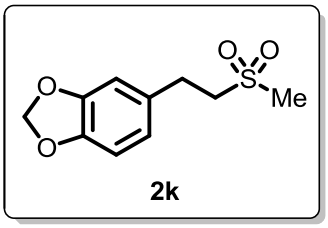
2i

9-(2-(methylsulfonyl)ethyl)-9H-carbazole (**2i**). Prepared following general procedure using alkyl bromide **1i** (137.1 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), $PO(OMe)_3$ (210.1 mg, 1.5 mmol), KI (166.0 mg, 1.0 mmol), TBAI (92.3 mg, 0.25 mmol), Cs_2CO_3 (325.8 mg, 1.0 mmol) and DMSO (2 mL), the reaction was stirred at 80 ^oC for 15 h giving **2i** in 86% yield (117.3 mg) as a white solid by column chromatography (PE/EA = 2/1). **^{1}H NMR**(400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.8 Hz, 2H), 7.46 – 7.35 (m, 4H), 7.23 – 7.18 (m, 2H), 4.76 (t, *J* = 6.7 Hz, 2H), 3.42 (t, *J* = 6.7 Hz, 2H), 2.50 (s, 3H). **^{13}C NMR**(100 MHz, $CDCl_3$) δ 139.5, 126.2, 123.2, 120.6, 119.9, 108.4, 52.6, 41.6, 36.6. **IR** ν 3028, 1217, 1136, 746, 721 cm^{-1}; **HRMS** (EI) for $C_{15}H_{15}NO_2S$ Calculated: 273.0823, found: 273.0825.



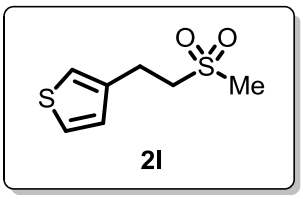
2j

1-methoxy-4-(2-(methylsulfonyl)ethyl)benzene (**2j**). Prepared following general procedure using alkyl bromide **1j** (107.5 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), $PO(OMe)_3$ (210.1 mg, 1.5 mmol), KI (166.0 mg, 1.0 mmol), TBAI (92.3 mg, 0.25 mmol), Cs_2CO_3 (325.8 mg, 1.0 mmol) and DMSO (2 mL), the reaction was stirred at 80 ^oC for 15 h giving **2j** in 74% yield (79.0 mg) as a white solid by column chromatography (PE/EA = 2/1). **^{1}H NMR**(400 MHz, $CDCl_3$) δ 7.16 (d, *J* = 8.6 Hz, 2H), 6.91 – 6.84 (m, 2H), 3.80 (s, 3H),3.31 – 3.25 (m, 2H), 3.14 – 3.09 (m, 2H), 2.81 (s, 3H). **^{13}C NMR**(100 MHz, $CDCl_3$) δ 158.5, 129.3, 129.2, 114.2, 56.3, 55.2, 40.9, 27.7. **IR** ν 3026, 1514, 1249, 1138, 1122, 817, 775 cm^{-1}; **HRMS** (EI) for $C_{10}H_{14}O_3S$ Calculated: 214.0664, found: 214.0662.



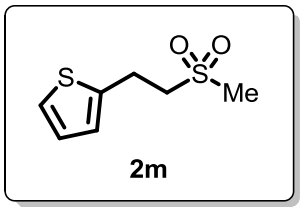
2k

5-(2-(methylsulfonyl)ethyl)benzo[d][1,3]dioxole (**2k**). Prepared following general procedure using alkyl bromide **1k** (114.5 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), $PO(OMe)_3$ (210.1 mg, 1.5 mmol), KI (166.0 mg, 1.0 mmol), TBAI (92.3 mg, 0.25 mmol), Cs_2CO_3 (325.8 mg, 1.0 mmol) and DMSO (2 mL), the reaction was stirred at 80 ^oC for 15 h giving **2k** in 69% yield (79.0 mg) as a white solid by column chromatography (PE/EA = 2/1). **^{1}H NMR**(400 MHz, $CDCl_3$) δ 6.76 – 6.63 (m, 3H), 5.91 (s, 2H), 3.26 – 3.20 (m, 2H), 3.08 – 3.01 (m, 2H), 2.81 (s, 3H). **^{13}C NMR**(100 MHz, $CDCl_3$) δ 147.9, 146.5, 130.9, 121.3, 108.6, 108.4, 100.9, 56.1, 40.8, 28.1. **IR** ν 3026, 1411, 1361, 1303, 1238, 1139, 1120, 1029, 812, 732 cm^{-1}; **HRMS** (EI) for $C_{10}H_{12}O_4S$ Calculated: 228.0456, found: 228.0459.



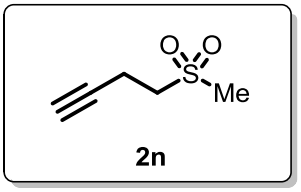
2l

3-(2-(methylsulfonyl)ethyl)thiophene (**2l**). Prepared following general procedure using alkyl bromide **1l** (95.5 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), $PO(OMe)_3$ (210.1 mg, 1.5 mmol), KI (166.0 mg, 1.0 mmol), TBAI (92.3 mg, 0.25 mmol), Cs_2CO_3 (325.8 mg, 1.0 mmol) and DMSO (2 mL), the reaction was stirred at 80 ^oC for 15 h giving **2l** in 68% yield (64.8 mg) as a white solid by column chromatography (PE/EA = 2/1). **^{1}H NMR**(400 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 4.9, 2.9 Hz, 1H), 7.09 – 7.05 (m, 1H), 6.96 (dd, *J* = 4.9, 1.1 Hz, 1H), 3.32 – 3.26 (m, 2H), 3.21 – 3.14 (m, 2H), 2.79 (s, 3H).**^{13}C NMR**(100 MHz, $CDCl_3$) δ 137.3, 127.4, 126.5, 121.8, 55.2, 40.8, 23.1. **IR** ν 3025, 1491, 1363, 1222, 1141, 860, 763, 702 cm^{-1}; **HRMS** (EI) for $C_7H_{10}O_2S_2$ Calculated: 190.0122, found: 190.0119.



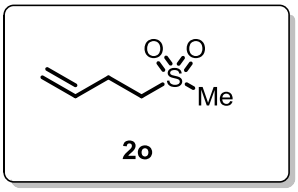
2m

2-(2-(methylsulfonyl)ethyl)thiophene (**2m**). Prepared following general procedure using alkyl bromide **1m** (95.5 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), $PO(OMe)_3$ (210.1 mg, 1.5 mmol), KI (166.0 mg, 1.0 mmol), TBAI (92.3 mg, 0.25 mmol), Cs_2CO_3 (325.8 mg, 1.0 mmol) and DMSO (2 mL), the reaction was stirred at 80 ^oC for 15 h giving **2m** in 66% yield (62.9 mg) as a white solid by column chromatography (PE/EA = 2/1). **^{1}H NMR**(400 MHz, $CDCl_3$) δ 7.18 (dd, *J* = 5.1, 1.1 Hz, 1H), 6.96 – 6.88 (m, 2H), 3.41 – 3.30 (m, 4H), 2.81 (s, 3H). **^{13}C NMR**(100 MHz, $CDCl_3$) δ 139.4, 127.1, 125.8, 124.5, 56.0, 40.9, 23.0. **IR** ν 3026, 1363, 1296, 1222, 1138, 1070, 769cm^{-1}; **HRMS** (EI) for $C_7H_{10}O_2S_2$ Calculated: 190.0122, found: 190.0123.



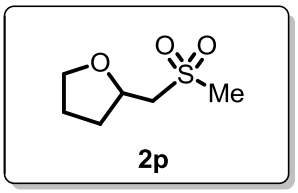
2n

4-(methylsulfonyl)but-1-yne (**2n**). Prepared following general procedure using alkyl bromide **1n** (66.5 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), $PO(OMe)_3$ (210.1 mg, 1.5 mmol), KI (166.0 mg, 1.0 mmol), TBAI (92.3 mg, 0.25 mmol), Cs_2CO_3 (325.8 mg, 1.0 mmol) and DMSO (2 mL), the reaction was stirred at 80 ^oC for 15 h giving **2n** in 61% yield (40.3 mg) as a colorless liquid by column chromatography (PE/EA = 2/1). **^{1}H NMR**(400 MHz, $CDCl_3$) δ 3.20 (t, *J* = 7.1 Hz, 2H), 3.01 (s, 3H), 2.78 (td, J = 7.1, 2.7 Hz, 2H), 2.13 (t, J = 2.7 Hz, 1H). **^{13}C NMR**(100 MHz, $CDCl_3$) δ 79.7, 71.2, 53.3, 41.5, 13.2. **IR** (film) ν 3302, 2924, 2848, 1419, 1363, 1305, 1126, 763 cm^{-1}; **HRMS** (EI) for $C_5H_8O_2S$ Calculated: 132.0245, found: 132.0247.



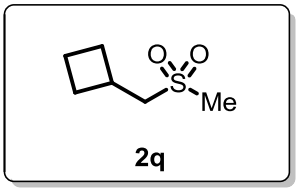
2o

4-(methylsulfonyl)but-1-ene (**2o**). Prepared following general procedure using alkyl bromide **1o** (67.5 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), $PO(OMe)_3$ (210.1 mg, 1.5 mmol), KI (166.0 mg, 1.0 mmol), TBAI (92.3 mg, 0.25 mmol), Cs_2CO_3 (325.8 mg, 1.0 mmol) and DMSO (2 mL), the reaction was stirred at 80 ^oC for 15 h giving **2o** in 47% yield (31.3 mg) as a colorless liquid by column chromatography (PE/EA = 2/1). **^{1}H NMR**(400 MHz, $CDCl_3$) δ 5.74 – 5.86 (m, 1H), 5.21 – 5.06 (m, 2H), 3.13 – 3.02 (m, 2H), 2.89 (s, 3H), 2.62 – 2.54 (m, 2H). **^{13}C NMR**(100 MHz, $CDCl_3$) δ 133.6, 117.5, 53.8, 40.7, 26.5. **IR** (film) v 3018, 2931, 1643, 1444, 1417, 1363, 1238, 765 cm^{-1}; **HRMS** (EI) for $C_5H_{10}O_2S$ Calculated: 134.0402, found: 134.0403.



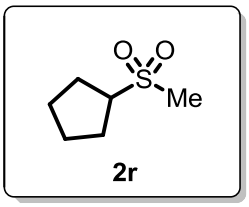
2p

2-((methylsulfonyl)methyl)tetrahydrofuran (**2p**)**.** Prepared following general procedure using alkyl bromide **1p** (82.5 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), $PO(OMe)_3$ (210.1 mg, 1.5 mmol), KI (166.0 mg, 1.0 mmol), TBAI (92.3 mg, 0.25 mmol), Cs_2CO_3 (325.8 mg, 1.0 mmol) and DMSO (2 mL), the reaction was stirred at 80 ^oC for 15 h giving **2p** in 55% yield (44.4 mg) as a colorless liquid by column chromatography (PE/EA = 2/1). **^{1}H NMR**(400 MHz, $CDCl_3$) δ 4.29 (td, *J* = 9.2, 2.8 Hz, 1H), 4.01 – 3.67 (m, 2H), 3.25 – 2.94 (m, 5H), 2.06 – 2.20 (m, 1H), 2.02 – 1.79 (m, 2H), 1.52 – 1.67 (m, 1H). **^{13}C NMR**(100 MHz, $CDCl_3$) δ 73.2, 68.3, 59.8, 42.3, 31.3, 25.1. **IR** (film) v 2983, 2931, 2873, 1643, 1417, 1240, 103, 767, 698 cm^{-1}; **HRMS** (ESI) for $C_6H_{12}O_3S$ $[M+H]^+$ Calculated: 165.0580, found: 165.0577.



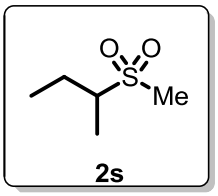
2q

((methylsulfonyl)methyl)cyclobutane (**2q**). Prepared following general procedure using alkyl bromide **1q** (74.5 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), $PO(OMe)_3$ (210.1 mg, 1.5 mmol), KI (166.0 mg, 1.0 mmol), TBAI (92.3 mg, 0.25 mmol), Cs_2CO_3 (325.8 mg, 1.0 mmol) and DMSO (2 mL), the reaction was stirred at 80 ^oC for 15 h giving **2q** in 76% yield (56.1 mg) as a colorless liquid by column chromatography (PE/EA = 2/1). **^{1}H NMR**(400 MHz, $CDCl_3$) δ 3.08 (d, *J* = 7.3 Hz, 2H), 2.92 – 2.77 (m, 4H), 2.27 – 2.14 (m, 2H), 2.03 – 1.79 (m, 4H). **^{13}C NMR**(100 MHz, $CDCl_3$) δ 60.5, 40.9, 29.4, 28.3, 18.9. **IR** (film) v 3020, 2083, 2933, 2643, 1413, 1238, 1109, 854, 769 cm^{-1}; **HRMS** (EI) for $C_6H_{12}O_2S$ Calculated: 148.0558, found: 148.0557.



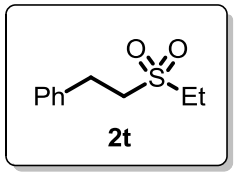
2r

(methylsulfonyl)cyclopentane (**2r**). Prepared following general procedure using alkyl bromide **1r** (74.5 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), $PO(OMe)_3$ (210.1 mg, 1.5 mmol), KI (166.0 mg, 1.0 mmol), TBAI (92.3 mg, 0.25 mmol), Cs_2CO_3 (325.8 mg, 1.0 mmol) and DMSO (2 mL), the reaction was stirred at 80 ^oC for 15 h giving **2r** in 63% yield (46.8 mg) as a white solid by column chromatography (PE/EA = 2/1). **^{1}H NMR**(400 MHz, $CDCl_3$) δ 3.42 – 3.31 (m, 1H), 2.82 (s, 3H), 2.08 – 1.92 (m, 4H), 1.84 – 1.56 (m, 4H). **^{13}C NMR**(100 MHz, $CDCl_3$) δ 62.4, 39.0, 26.7, 25.8. **IR** v 3018, 2974, 2872, 1643, 1448, 1415, 964, 819, 759 cm^{-1}; **HRMS** (ESI) for $C_6H_{13}O_2S$ $[M+H]^+$ Calculated: 149.0636, found: 149.0628.



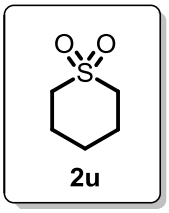
2s

2-(methylsulfonyl)butane (**2s**). Prepared following general procedure using alkyl bromide **1s** (68.5 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), $PO(OMe)_3$ (210.1 mg, 1.5 mmol), KI (166.0 mg, 1.0 mmol), TBAI (92.3 mg, 0.25 mmol), Cs_2CO_3 (325.8 mg, 1.0 mmol) and DMSO (2 mL), the reaction was stirred at 80 ^oC for 15 h giving **2s** in 56% yield (38.2 mg) as a colorless liquid by column chromatography (PE/EA = 2/1). **^{1}H NMR**(400 MHz, $CDCl_3$) δ 2.88 – 2.74 (m, 4H), 2.12 – 1.98 (m, 1H), 1.60 – 1.41 (m, 1H), 1.36 (dd, *J* = 6.9, 2.0 Hz, 3H), 1.03 (td, *J* = 7.5, 2.0 Hz, 3H). **^{13}C NMR**(100 MHz, $CDCl_3$) δ 60.4, 37.1, 22.4, 12.5, 11.0. **IR** (film) v 2981, 2933, 2879, 1417, 1242, 758 cm^{-1}; **GC-MS** (EI) for $C_5H_{12}O_2S$ Calculated: 136.0, found: 136.0.



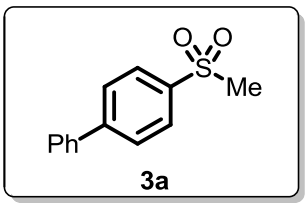
2t

(2-(ethylsulfonyl)ethyl)benzene (**2t**). Prepared following general procedure using alkyl bromide **1a** (92.5 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), $PO(OEt)_3$ (210.1 mg, 1.5 mmol), KI (166.0 mg, 1.0 mmol), TBAI (92.3 mg, 0.25 mmol), Cs_2CO_3 (325.8 mg, 1.0 mmol) and DMSO (2 mL), the reaction was stirred at 120 ^oC for 15 h giving **2t** in 51% yield (50.1 mg) as a white solid by column chromatography (PE/EA = 2/1). **^{1}H NMR**(400 MHz, $CDCl_3$) δ 7.27 – 7.12 (m, 5H), 3.19 – 3.01 (m, 4H), 2.84 (q, *J* = 7.5 Hz, 2H), 1.28 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR**(100 MHz, $CDCl_3$) δ 137.5, 128.7, 128.2, 126.9, 53.0, 47.3, 27.8, 6.4. **IR** v 2983, 1450, 1417, 765, 725, 696 cm^{-1}; **HRMS** (EI) for $C_{10}H_{14}O_2S$ Calculated: 198.0715, found: 198.0717.



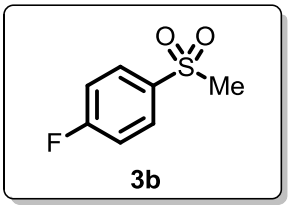
2u

tetrahydro-2H-thiopyran 1,1-dioxide (**2u**). Prepared following general procedure using alkyl bromide **1u** (115.0 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), KI (166.0 mg, 1.0 mmol), TBAI (92.3 mg, 0.25 mmol), Cs_2CO_3 (325.8 mg, 1.0 mmol) and DMSO (2 mL), the reaction was stirred at 80 ^oC for 15 h giving **2u** in 82% yield (55.0 mg) as a colorless liquid by column chromatography (PE/EA = 2/1). **^{1}H NMR**(400 MHz, $CDCl_3$) δ 3.07 – 2.88 (m, 4H), 2.17 – 1.99 (m, 4H), 1.72 – 1.53 (m, 2H). **^{13}C NMR**(100 MHz, $CDCl_3$) δ 52.0, 24.1, 23.7. **IR** (film) v 2937, 1446, 964, 935, 763 cm^{-1}; **HRMS** (EI) for $C_5H_{10}O_2S$ Calculated: 134.0402, found: 134.0401.



3a

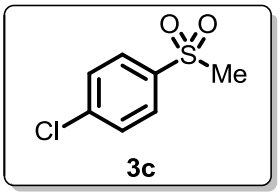
4-(methylsulfonyl)-1,1'-biphenyl (**3a**). Prepared following general procedure using alkyl iodide **1a'** (140.0 mg, 0.5 mmol), $Na_2S_2O_4$ (261.2 mg, 1.5 mmol), $PO(OMe)_3$ (210.1 mg, 1.5 mmol), $PdCl_2$dppf (0.7 mg, 0.001 mmol), TBAB (241.8 mg, 0.75 mmol) and DMSO (5 mL), the reaction was stirred at 120 ^oC for 15 h giving **3a** in 82% yield (95.5 mg) as a white solid by column chromatography (PE/EA = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 – 7.89 (m, 2H), 7.71 – 7.65 (m, 2H), 7.55 – 7.50 (m, 2H), 7.44 – 7.31 (m, 3H), 3.01 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.6, 139.0, 129.0, 128.6, 127.9, 127.8, 127.3, 44.5 (One resonance was not observed due to overlapping resonances). **IR** v3018, 2980, 1643, 1448, 1415, 966, 788, 761, 748 cm^{-1}; **HRMS** (EI) for $C_{13}H_{12}O_2S$ Calculated: 232.0558, found: 232.0560.



3b

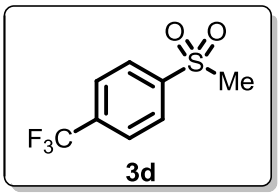
1-fluoro-4-(methylsulfonyl)benzene (**3b**). Prepared following general procedure using alkyl iodide **1b'** (111.1 mg, 0.5 mmol), $Na_2S_2O_4$ (261.2 mg, 1.5 mmol),

$PO(OMe)_3$ (210.1 mg, 1.5 mmol), $PdCl_2$dppf (0.7 mg, 0.001 mmol), TBAB (241.8 mg, 0.75 mmol) and DMSO (5 mL), the reaction was stirred at 120 ^oC for 15 h giving **3b** in 84% yield (72.4 mg) as a white solid by column chromatography (PE/EA = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 – 7.84 (m, 2H), 7.24 – 7.13 (m, 2H), 2.99 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.6 (d, *J* = 254.5 Hz), 136.5 (d, *J* = 3.2 Hz), 130.1 (d, *J* = 9.6 Hz), 116.5 (d, *J* = 2.3 Hz), 44.5. **^{19}F NMR** (376 MHz, CDCl3) δ -103.5. **IR** v 2983, 1591, 1417, 964, 817, 765 cm^{-1}; **HRMS** (EI) for $C_7H_7FO_2S$ Calculated: 174.0151, found: 174.0149.



3c

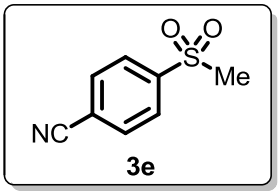
1-chloro-4-(methylsulfonyl)benzene (**3c**). Prepared following general procedure using alkyl iodide **1c'** (119.3 mg, 0.5 mmol), $Na_2S_2O_4$ (261.2 mg, 1.5 mmol), $PO(OMe)_3$ (210.1 mg, 1.5 mmol), $PdCl_2$dppf (0.7 mg, 0.001 mmol), TBAB (241.8 mg, 0.75 mmol) and DMSO (5 mL), the reaction was stirred at 120 ^oC for 15 h giving **3c** in 88% yield (83.5 mg) as a white solid by column chromatography (PE/EA = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 – 7.83 (m, 2H), 7.56 – 7.49 (m, 2H), 3.04 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.3, 138.8, 129.5, 128.8, 44.4. **IR** v 3014, 2922, 2873, 2850, 1643, 1581, 1448, 1417, 1392, 825, 765 cm^{-1}; **HRMS** (EI) for $C_7H_7ClO_2S$ Calculated: 189.9855, found: 189.9858.



3d

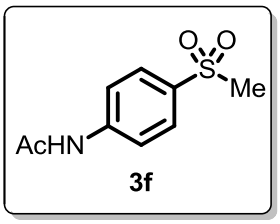
1-(methylsulfonyl)-4-(trifluoromethyl)benzene (**3d**). Prepared following general procedure using alkyl iodide **1d'** (136.0 mg, 0.5 mmol), $Na_2S_2O_4$ (261.2 mg, 1.5 mmol), $PO(OMe)_3$ (210.1 mg, 1.5 mmol), $PdCl_2$dppf (0.7 mg, 0.001 mmol), TBAB (241.8 mg, 0.75 mmol) and DMSO (5 mL), the reaction was stirred at 120 ^oC for 15 h giving **3d** in 81% yield (90.5 mg) as a white solid by column chromatography (PE/EA = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.2 Hz, 2H), 7.83 (d, *J* = 8.3 Hz, 2H), 3.08 (s, 3H). **^{13}C**

NMR (100 MHz, $CDCl_3$) δ 143.8, 135.3 (d, *J* = 33.0 Hz), 128.0, 126.5 (q, *J* = 3.7 Hz), 123.0 (q, *J* = 271.5 Hz), 44.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.2. **IR** v 3016, 1417, 1402, 1060, 842, 763 cm^{-1}; **HRMS** (EI) for $C_8H_7F_3O_2S$ Calculated: 224.0119, found: 224.0122.



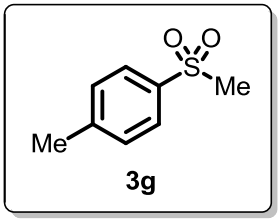
3e

4-(methylsulfonyl)benzonitrile (**3e**). Prepared following general procedure using alkyl iodide **1e'** (114.5 mg, 0.5 mmol), $Na_2S_2O_4$ (261.2 mg, 1.5 mmol), $PO(OMe)_3$ (210.1 mg, 1.5 mmol), $PdCl_2$dppf (0.7 mg, 0.001 mmol), TBAB (241.8 mg, 0.75 mmol) and DMSO (5 mL), the reaction was stirred at 120 ^oC for 15 h giving **3e** in 65% yield (58.9 mg) as a white solid by column chromatography (PE/EA = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.4 Hz, 2H), 7.88 (d, *J* = 8.4 Hz, 2H), 3.08 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.2, 133.1, 128.0, 117.4, 116.9, 44.1. **IR** v 3010, 2261, 1417, 1363, 1138, 831, 798, 754 cm^{-1}; **HRMS** (EI) for $C_8H_7NO_2S$ Calculated: 181.0197, found: 181.0199.



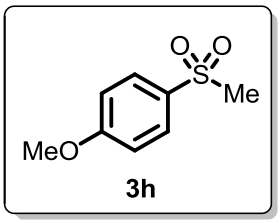
3f

N-(4-(methylsulfonyl)phenyl)acetamide (**3f**). Prepared following general procedure using alkyl iodide **1f'** (130.5 mg, 0.5 mmol), $Na_2S_2O_4$ (261.2 mg, 1.5 mmol), $PO(OMe)_3$ (210.1 mg, 1.5 mmol), $PdCl_2$dppf (0.7 mg, 0.001 mmol), TBAB (241.8 mg, 0.75 mmol) and DMSO (5 mL), the reaction was stirred at 120 ^oC for 15 h giving **3f** in 55% yield (58.5 mg) as a white solid by column chromatography (PE/EA = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.6 Hz, 2H), 7.72 (d, *J* = 8.6 Hz, 2H), 7.51 (s, 1H), 3.04 (s, 3H), 2.23 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.6, 142.7, 135.2, 128.7, 119.5, 44.6, 24.8. **IR** v 3026, 1683, 1643, 1587, 1529, 1417, 1363, 1224, 964, 821, 765 cm^{-1};**HRMS** (EI) for $C_9H_{11}NO_3S$ Calculated: 213.0460, found: 213.0461.



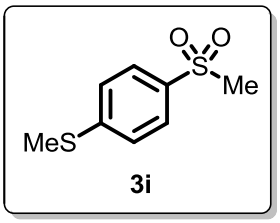
3g

1-methyl-4-(methylsulfonyl)benzene (**3g**). Prepared following general procedure using alkyl iodide **1g'** (109.2 mg, 0.5 mmol), $Na_2S_2O_4$ (261.2 mg, 1.5 mmol), $PO(OMe)_3$ (210.1 mg, 1.5 mmol), $PdCl_2$dppf (0.7 mg, 0.001 mmol), TBAB (241.8 mg, 0.75 mmol) and DMSO (5 mL), the reaction was stirred at 120 ^oC for 15 h giving **3g** in 82% yield (69.0 mg) as a white solid by column chromatography (PE/EA = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 3.01 (s, 3H), 2.43 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.5, 137.5, 129.8, 127.2, 44.5, 21.5. **IR** v 3018, 1593, 1448, 1417, 1363, 952, 819, 759cm^{-1}; **HRMS** (EI) for $C_8H_{10}O_2S$ Calculated: 170.0402, found: 170.0399.



3h

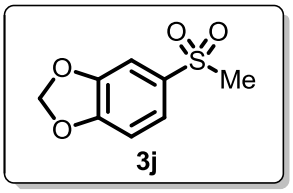
1-methoxy-4-(methylsulfonyl)benzene (**3h**). Prepared following general procedure using alkyl iodide **1h'** (117.1 mg, 0.5 mmol), $Na_2S_2O_4$ (261.2 mg, 1.5 mmol), $PO(OMe)_3$ (210.1 mg, 1.5 mmol), $PdCl_2$dppf (0.7 mg, 0.001 mmol), TBAB (241.8 mg, 0.75 mmol) and DMSO (5 mL), the reaction was stirred at 120 ^oC for 15 h giving **3h** in 67% yield (62.1 mg) as a white solid by column chromatography (PE/EA = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 – 7.78 (m, 2H), 7.02 – 6.93 (m, 2H), 3.84 (s, 3H), 2.99 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.5, 132.0, 129.3, 114.3, 55.6, 44.6. **IR** v 3018, 2446, 1417, 1363, 1224, 763 cm^{-1}; **HRMS** (EI) for $C_8H_{10}O_3S$ Calculated: 186.0351, found: 186.0350.



3i

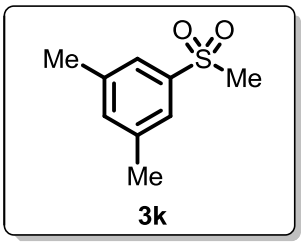
methyl(4-(methylsulfonyl)phenyl)sulfane (**3i**). Prepared following general procedure using alkyl iodide **1i'** (125.1 mg, 0.5 mmol), $Na_2S_2O_4$ (261.2 mg, 1.5 mmol), $PO(OMe)_3$ (210.1 mg, 1.5 mmol), $PdCl_2$dppf (0.7 mg,

0.001 mmol), TBAB (241.8 mg, 0.75 mmol) and DMSO (5 mL), the reaction was stirred at 120 ^{o}C for 15 h giving **3i** in 88% yield (89.4 mg) as a white solid by column chromatography (PE/EA = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.6 Hz, 2H), 7.31 (d, *J* = 8.6 Hz, 2H), 3.01 (s, 3H), 2.50 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.0, 136.0, 127.4, 125.3, 44.5, 14.6. **IR** v 3018, 2924, 2873, 1643, 1577, 1419, 1394, 1363, 1224, 825, 765 cm^{-1}; **HRMS** (EI) for $C_8H_{10}O_2S_2$ Calculated: 202.0122, found: 202.0121.



3j

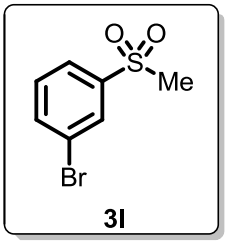
5-(methylsulfonyl)benzo[d][1,3]dioxole (3j). Prepared following general procedure using alkyl iodide **1j'** (124.0 mg, 0.5 mmol), $Na_2S_2O_4$ (261.2 mg, 1.5 mmol), $PO(OMe)_3$ (210.1 mg, 1.5 mmol), $PdCl_2$dppf (0.7 mg, 0.001 mmol), TBAB (241.8 mg, 0.75 mmol) and DMSO (5 mL), the reaction was stirred at 120 ^{o}C for 15 h giving **3j** in 88% yield (88.1 mg) as a white solid by column chromatography (PE/EA = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.30 (d, *J* = 1.8 Hz, 1H), 6.90 (d, *J* = 8.2 Hz, 1H), 6.08 (s, 2H), 3.00 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.2, 148.3, 133.9, 123.2, 108.5, 107.4, 102.5, 44.7. **IR** v 3010, 1500, 1477, 1363, 1224, 1020, 925, 761 cm^{-1}; **HRMS** (EI) for $C_8H_8O_4S$ Calculated: 200.0143, found: 200.0140.



3k

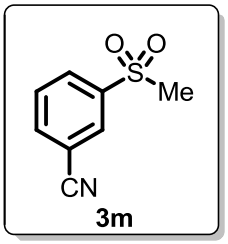
1,3-dimethyl-5-(methylsulfonyl)benzene (3k). Prepared following general procedure using alkyl iodide **1k'** (116.0 mg, 0.5 mmol), $Na_2S_2O_4$ (261.2 mg, 1.5 mmol), $PO(OMe)_3$ (210.1 mg, 1.5 mmol), $PdCl_2$dppf (0.7 mg, 0.001 mmol), TBAB (241.8 mg,

0.75 mmol) and DMSO (5 mL), the reaction was stirred at 120 ^{o}C for 15 h giving **3k** in 88% yield (80.9 mg) as a white solid by column chromatography (PE/EA = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (s, 2H), 7.25 (s, 1H), 3.02 (s, 3H), 2.38 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.2, 139.3, 135.2, 124.7, 44.4, 21.1. **IR** ν 2960, 1608, 1404, 1315, 1290, 1149, 1105, 1020, 956, 869, 858 cm^{-1}; **HRMS** (EI) for $C_9H_{12}O_2S$ Calculated: 184.0558, found: 184.0555.



3l

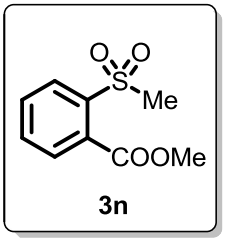
1-bromo-3-(methylsulfonyl)benzene (3l). Prepared following general procedure using alkyl iodide **1l'** (141.5 mg, 0.5 mmol), $Na_2S_2O_4$ (261.2 mg, 1.5 mmol), $PO(OMe)_3$ (210.1 mg, 1.5 mmol), $PdCl_2$dppf (0.7 mg, 0.001 mmol), TBAB (241.8 mg, 0.75 mmol) and DMSO (5 mL), the reaction was stirred at 120 ^{o}C for 15 h giving **3l** in 76% yield (88.5 mg) as a white solid by column chromatography (PE/EA = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 – 8.05 (m, 1H), 7.86 (ddd, *J* = 7.8, 1.7, 1.0 Hz, 1H), 7.76 (ddd, *J* = 8.0, 1.9, 1.0 Hz, 1H), 7.47 – 7.42 (m, 1 H), 3.05 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.2, 136.7, 130.8, 130.2, 125.8, 123.2, 44.3. **IR** ν 3016, 1568, 1411, 1363, 1224, 964, 952, 792, 767, 732 cm^{-1}; **HRMS** (EI) for $C_7H_7BrO_2S$ Calculated: 233.9350, found: 233.9351.



3m

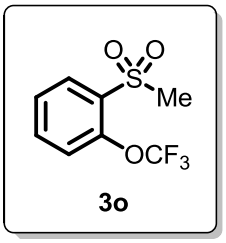
3-(methylsulfonyl)benzonitrile (3m). Prepared following general procedure using alkyl iodide **1m'** (114.5 mg, 0.5 mmol), $Na_2S_2O_4$ (261.2 mg, 1.5 mmol), $PO(OMe)_3$ (210.1 mg, 1.5 mmol), $PdCl_2$dppf (0.7 mg, 0.001 mmol), TBAB (241.8 mg, 0.75 mmol) and DMSO (5 mL), the reaction was stirred at 120 ^{o}C for 15 h giving **3m** in 57% yield (51.2 mg) as a white solid by

column chromatography (PE/EA = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 – 8.23 (m, 1H), 8.20 – 8.15 (m, 1H), 7.96 – 7.92 (m, 1H), 7.74 (dd, *J* = 10.0, 5.7 Hz, 1H), 3.10 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.0, 136.8, 131.3, 131.1, 130.5, 116.8, 114.0, 44.2. **IR** v 3066, 3010, 1415, 1363, 132, 1224, 1170, 975, 964, 802, 756 cm^{-1}; **HRMS** (EI) for $C_8H_7NO_2S$ Calculated: 181.0197, found: 181.0195.



3n

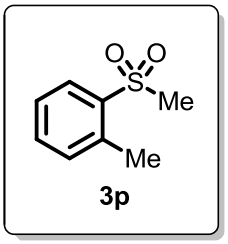
methyl 2-(methylsulfonyl)benzoate (3n). Prepared following general procedure using alkyl iodide **1n'** (131.0 mg, 0.5 mmol), $Na_2S_2O_4$ (261.2 mg, 1.5 mmol), $PO(OMe)_3$ (210.1 mg, 1.5 mmol), $PdCl_2$dppf (0.7 mg, 0.001 mmol), TBAB (241.8 mg, 0.75 mmol) and DMSO (5 mL), the reaction was stirred at 120 ^{o}C for 15 h giving **3n** in 73% yield (77.9 mg) as a white solid by column chromatography (PE/EA = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (dd, *J* = 6.4, 1.6 Hz, 1H), 7.74 – 7.63 (m, 3H), 3.97 (s, 3H), 3.35 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.3, 139.0, 133.4, 132.9, 131.1, 129.7, 129.5, 53.1, 44.7. **IR** v 3022, 1419, 1363, 1224, 1058, 952, 827, 783, 742 cm^{-1};**HRMS** (EI) for $C_9H_{10}O_4S$ Calculated: 214.0300, found:214.0299.



3o

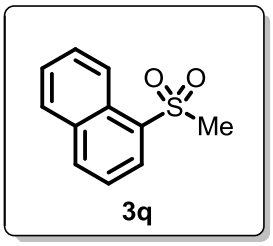
1-(methylsulfonyl)-2-(trifluoromethoxy)benzene (3o). Prepared following general procedure using alkyl iodide **1o'** (144.0 mg, 0.5 mmol), $Na_2S_2O_4$ (261.2 mg, 1.5 mmol), $PO(OMe)_3$ (210.1 mg, 1.5 mmol), $PdCl_2$dppf (0.7 mg, 0.001 mmol), TBAB (241.8 mg, 0.75 mmol) and DMSO (5 mL), the reaction was stirred at 120 ^{o}C for 15 h giving **3o** in 46% yield (55.6 mg) as a white solid by column chromatography (PE/EA = 5/1). **^{1}H NMR** (400 MHz,

$CDCl_3$) δ 8.09 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.72 – 7.67 (m, 1H), 7.51 – 7.39 (m, 2H), 3.20 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.7 (q, *J* = 1.6 Hz), 135.5, 132.4, 130.4, 126.8, 120.1 (q, *J* = 259.8 Hz), 120.0 (d, *J* = 2 Hz), 43.7. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -56.2. **IR** v 3014, 2922, 1589, 1444, 1363, 1224, 1068, 954, 921 786, 767 cm^{-1};**HRMS** (EI) for $C_8H_7F_3O_3S$ Calculated: 240.0068, found: 240.0071.



3p

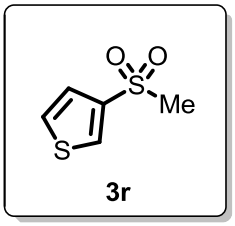
1-methyl-2-(methylsulfonyl)benzene (3p). Prepared following general procedure using alkyl iodide **1p'** (109.0 mg, 0.5 mmol), $Na_2S_2O_4$ (261.2 mg, 1.5 mmol), $PO(OMe)_3$ (210.1 mg, 1.5 mmol), $PdCl_2$dppf (0.7 mg, 0.001 mmol), TBAB (241.8 mg, 0.75 mmol) and DMSO (5 mL), the reaction was stirred at 120 ^oC for 15 h giving **3p** in 48% yield (40.6 mg) as a white solid by column chromatography (PE/EA = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.53 – 7.47 (m, 1H), 7.39 – 7.30 (m, 2H), 3.06 (s, 3H), 2.69 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.5, 137.4, 133.6, 132.6, 129.1, 126.6, 43.5, 20.1. **IR** v 3012, 2927, 1595, 1450, 1417, 1363, 1224, 1062, 806, 775, 705 cm^{-1};**HRMS** (EI) for $C_8H_{10}O_2S$ Calculated: 170.0402, found: 170.0404.



3q

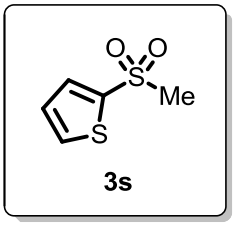
1-(methylsulfonyl)naphthalene (3q). Prepared following general procedure using alkyl iodide **1q'** (127.0 mg, 0.5 mmol), $Na_2S_2O_4$ (261.2 mg, 1.5 mmol), $PO(OMe)_3$ (210.1 mg, 1.5 mmol), $PdCl_2$dppf (0.7 mg, 0.001 mmol), TBAB (241.8 mg, 0.75 mmol) and DMSO (5 mL), the reaction was stirred at 120 ^oC for 15 h giving **3q** in 73% yield (74.8 mg) as a white solid by column chromatography (PE/EA = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.74 – 8.67 (m, 1H), 8.31 (dd, *J* = 7.3, 1.2 Hz, 1H), 8.10 (d, *J* =

8.2 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.72 – 7.68 (m, 1H), 7.62 – 7.58 (m, 2H), 3.20 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 135.4, 135.0, 134.0, 129.4, 129.2, 128.6, 128.4, 126.9, 124.3, 123.7, 44.1. **IR** v 3014, 1448, 1419, 1363, 1224, 1139, 960, 806, 754 cm^{-1}; **HRMS** (EI) for $C_{11}H_{10}O_2S$ Calculated: 206.0402, found: 206.0401.



3r

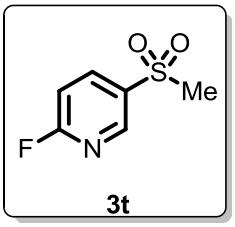
3-(methylsulfonyl)thiophene (3r). Prepared following general procedure using alkyl iodide **1r'** (105.0 mg, 0.5 mmol), $Na_2S_2O_4$ (261.2 mg, 1.5 mmol), $PO(OMe)_3$ (210.1 mg, 1.5 mmol), $PdCl_2$dppf (0.7 mg, 0.001 mmol), TBAB (241.8 mg, 0.75 mmol) and DMSO (5 mL), the reaction was stirred at 120 ^oC for 15 h giving **3r** in 78% yield (62.8 mg) as a white solid by column chromatography (PE/EA = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 3.0, 1.2 Hz, 1H), 7.46 (dd, *J* = 5.1, 3.1 Hz, 1H), 7.40 (dd, *J* = 5.1, 1.2 Hz, 1H), 3.08 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.0, 131.8, 128.5, 125.4, 44.7. **IR** v 3120, 3099, 3026, 1419, 1363, 1224, 960, 817, 777 cm^{-1}; **HRMS** (EI) for $C_5H_6O_2S_2$ Calculated: 161.9809, found: 161.9807.



3s

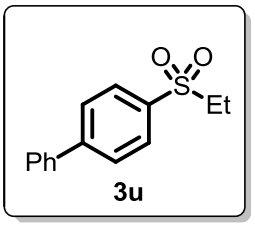
2-(methylsulfonyl)thiophene (3s). Prepared following general procedure using alkyl iodide **1s'** (105.0 mg, 0.5 mmol), $Na_2S_2O_4$ (261.2 mg, 1.5 mmol), $PO(OMe)_3$ (210.1 mg, 1.5 mmol), $PdCl_2$dppf (0.7 mg, 0.001 mmol), TBAB (241.8 mg, 0.75 mmol) and DMSO (5 mL), the reaction was stirred at 120 ^oC for 15 h giving **3s** in 78% yield (62.8 mg) as a white solid by column chromatography (PE/EA = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 4.4 Hz, 2H), 7.15 – 7.11 (m, 1H), 3.16 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.5, 133.6, 133.3, 127.8, 45.9. **IR** v 3107, 1406, 1298, 1224, 1070, 1018, 956, 852,

763, 736, 651 cm^{-1};**HRMS** (EI) for $C_5H_6O_2S_2$ Calculated: 161.9809, found: 161.9806.



3t

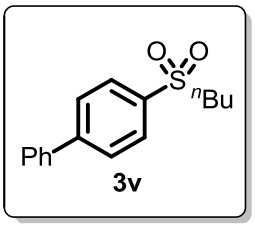
2-fluoro-5-(methylsulfonyl)pyridine (3t). Prepared following general procedure using alkyl iodide **1t'** (111.5 mg, 0.5 mmol), $Na_2S_2O_4$ (261.2 mg, 1.5 mmol), $PO(OMe)_3$ (210.1 mg, 1.5 mmol), $PdCl_2$dppf (0.7 mg, 0.001 mmol), TBAB (241.8 mg, 0.75 mmol) and DMSO (5 mL), the reaction was stirred at 120 ^oC for 15 h giving **3t** in 52% yield (45.4 mg) as a white solid by column chromatography (PE/EA = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 2.5 Hz, 1H), 8.33 (ddd, *J* = 8.7, 7.1, 2.6 Hz, 1H), 7.15 (dd, *J* = 8.6, 2.8 Hz, 1H), 3.13 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.8 (d, *J* =246.9 Hz), 148.6 (d, *J* = 17.2 Hz), 141.0 (d, *J* = 9.7 Hz), 135.1 (d, *J* = 4.7 Hz), 110.7 (d, *J* = 37.8 Hz), 44.9. **IR** v 3061, 3034, 3016, 1589, 1573, 1469, 1365, 1263, 1251, 1224, 1016, 962, 839, 756 cm^{-1}; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -58.8. **HRMS** (EI) for $C_6H_6FNO_2S$ Calculated: 175.0103, found: 175.0106.



3u

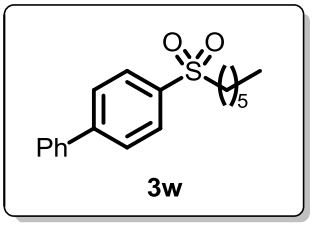
4-(ethylsulfonyl)-1,1'-biphenyl (3u). Under a N_2 atmosphere, alkyl iodide **1u'** (56.0 mg, 0.2 mmol), $Na_2S_2O_5$ (76.0 mg, 1.5 mmol), $PO(OEt^2)_3$ (109.3 mg, 0.6 mmol), Mn (32.9 mg, 0.6mmol), $PdCl_2$dppf (7.3 mg, 0.01 mmol), TBAB (97.2 mg, 0.3 mmol) and DMSO (2 mL), the reaction was stirred at 120 ^oC for 15 h giving **3u** in 84% yield (41.5 mg) as a white solid by column chromatography (PE/EA = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.1 Hz, 2H), 7.76 (d, *J* = 8.1 Hz, 2H), 7.61 (d, *J* = 7.2 Hz, 2H), 7.48 – 7.42 (m, 3H), 3.16 (q, *J* = 7.3 Hz, 2H), 1.31 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ

146.5, 139.0, 137.0, 129.0, 128.6, 128.6, 127.8, 127.3, 50.6, 7.4. **IR** v 3012, 2920, 1593, 1450, 1398, 1363, 1224, 1089, 960, 786 cm^{-1};**HRMS** (EI) for $C_{14}H_{14}O_2S$ Calculated: 246.0715, found: 246.0713.



3v

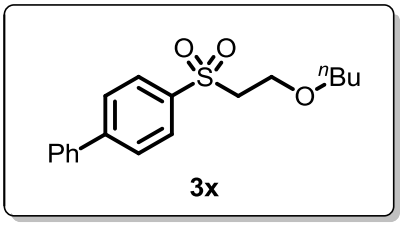
4-(butylsulfonyl)-1,1'-biphenyl (3v). Under a N_2 atmosphere, alkyl iodide **1a'** (56.0 mg, 0.2 mmol), $Na_2S_2O_5$ (76.0 mg, 1.5 mmol), $PO(O^nBu^2)_3$ (159.8 mg, 0.6 mmol), Mn (32.9 mg, 0.6mmol), $PdCl_2$dppf (7.3 mg, 0.01 mmol), TBAB (97.2 mg, 0.3 mmol) and DMSO (2 mL), the reaction was stirred at 120 ^oC for 15 h giving **3v** in 80% yield (43.6 mg) as a white solid by column chromatography (PE/EA = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.65 – 7.58 (m, 2H), 7.52 – 7.39 (m, 3H), 3.19 – 3.05 (m, 2H), 1.80 – 1.69 (m, 2H), 1.47 – 1.35 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.5, 139.0, 137.6, 129.0, 128.6, 128.5, 127.8, 127.3, 56.1, 24.6, 21.5, 13.4. **IR** v 3012, 1593, 1446, 1419, 1365, 1224, 1155, 960, 856, 779 cm^{-1};**HRMS** (EI) for $C_{16}H_{18}O_2S$ Calculated: 274.1028, found: 274.1032.



3w

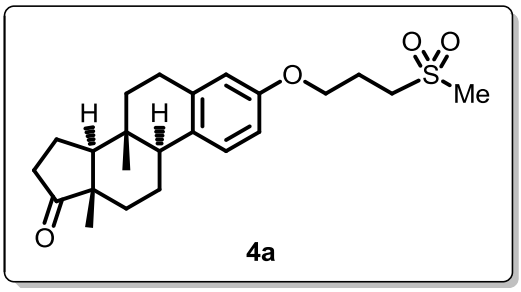
4-(hexylsulfonyl)-1,1'-biphenyl (3w). Under a N_2 atmosphere, alkyl iodide **1a'** (56.0 mg, 0.2 mmol),, $Na_2S_2O_5$ (76.0 mg, 1.5 mmol), Trihexyl phosphate (210.3 mg, 0.6 mmol), Mn (32.9 mg, 0.6mmol), $PdCl_2$dppf (7.3 mg, 0.01 mmol), TBAB (97.2 mg, 0.3 mmol) and DMSO (2 mL), the reaction was stirred at 120 ^oC for 15 h giving **3w** in 66% yield (39.9 mg) as a white solid by column chromatography (PE/EA = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 – 7.93 (m, 2H), 7.80 – 7.72 (m, 2H), 7.65 – 7.57 (m, 2H), 7.52 – 7.39 (m, 3H), 3.18 – 3.04 (m, 2H), 1.80 – 1.69 (m, 2H), 1.45 – 1.17 (m, 6H),

0.86 (t, *J* = 7.0 Hz, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.4, 139.0, 137.7, 129.0, 128.5, 128.5, 127.7, 127.3, 56.3, 31.1, 27.8, 22.5, 22.2, 13.8. **IR** v 3061, 2924, 2870, 1595, 1562, 1481, 1419, 1363, 1222, 1091, 1004, 958, 777, 727, 673 cm^{-1}; **HRMS** (EI) for $C_{18}H_{22}O_2S$ Calculated: 302.1341, found: 302.1337.



3x

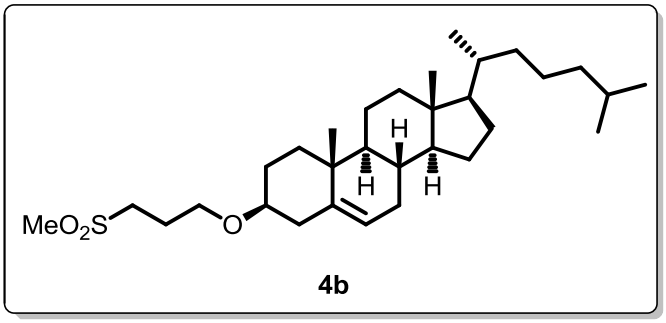
4-((2-butoxyethyl)sulfonyl)-1,1'-biphenyl (3x). Under a N_2 atmosphere, alkyl iodide **1a'** (56.0 mg, 0.2 mmol), $Na_2S_2O_5$ (76.0 mg, 1.5 mmol), Tris(2-butoxyethyl) phosphate (239.1 mg, 0.6 mmol), Mn (32.9 mg, 0.6mmol), $PdCl_2$dppf (7.3 mg, 0.01 mmol), TBAB (97.2 mg, 0.3 mmol) and DMSO (2 mL), the reaction was stirred at 120 ^oC for 15 h giving **3x** in 48% yield (30.3 mg) as a white solid by column chromatography (PE/EA = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 – 7.88 (m, 2H), 7.72 – 7.65 (m, 2H), 7.58 – 7.52 (m, 2H), 7.46 – 7.34 (m, 3H), 3.74 (t, *J* = 6.2 Hz, 2H), 3.38 (t, *J* = 6.2 Hz, 2H), 3.25 (t, *J* = 6.6 Hz, 2H), 1.33 – 1.26 (m, 2H), 1.17 – 1.10 (m, 2H), 0.75 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.5, 139.1, 138.4, 129.0, 128.5, 127.6, 127.3, 71.0, 64.0, 56.4, 31.4, 29.6, 19.0, 13.7. **IR** v 3012, 2960, 2868, 1595, 1481, 1448, 1419, 1363, 1224, 1087, 1006, 958, 761 cm^{-1}; **HRMS** (EI) for $C_{18}H_{22}O_3S$ Calculated: 318.1290, found: 318.1294.



4a

(8R,9S,13S,14S)-8,13-dimethyl-3-(3-(methylsulfonyl)propoxy)-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[a]phenanthren-17(14H)-one (4a). Prepared following general procedure using alkyl iodide **1a"** (78.3 mg, 0.2 mmol), thiourea dioxide (64.8 mg, 0.6

mmol), $PO(OMe)_3$ (84.0 mg, 0.6 mmol), KI (66.4 mg, 0.4 mmol), TBAI (36.9 mg, 0.1 mmol), Cs_2CO_3 (130.4 mg, 0.4 mmol) and DMSO (2 mL), the reaction was stirred at 80 ^oC for 15 h giving **4a** in 72% yield (56.5 mg) as a white solid by column chromatography (PE/EA = 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.6 Hz, 1H), 6.72 – 6.58 (m, 2H), 4.07 (t, *J* = 5.8 Hz, 2H), 3.30 – 3.19 (m, 2H), 2.94 (s, 3H), 2.92- 2.85 (m, 2H), 2.49 (dd, *J* = 18.7, 8.6 Hz, 1H), 2.42 – 1.89 (m, 8H), 1.68 – 1.36 (m, 6H), 0.90 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.2, 137.8, 132.5, 126.3, 114.4, 112.0, 65.3, 51.7, 50.2, 47.8, 43.8, 40.7, 38.2, 35.7, 31.4, 29.5, 26.3, 25.8, 22.6, 21.4, 13.7. **IR** v 3012, 2927, 2873, 1498, 1450, 1363, 1242, 1224, 1153, 966, 781, 754 cm^{-1}; **HRMS** (EI) for $C_{23}H_{32}O_4S$ Calculated: 390.1865, found: 390.1862.



4b

(3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-3-(3-(methylsulfonyl)propoxy)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthrene (4b). Prepared following general procedure using alkyl iodide **1b"** (98.3 mg, 0.2 mmol), thiourea dioxide (64.8 mg, 0.6 mmol), $PO(OMe)_3$ (84.0 mg, 0.6 mmol), KI (66.4 mg, 0.4 mmol), TBAI (36.9 mg, 0.1 mmol), Cs_2CO_3 (130.4 mg, 0.4 mmol) and DMSO (2 mL), the reaction was stirred at 80 ^oC for 15 h giving **4b** in 63% yield (63.8 mg) as a white solid by column chromatography (PE/EA 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.34 (s, 1H), 3.58 (t, J = 5.6 Hz, 2H), 3.19 – 3.07 (m, 3H), 2.90 (s, 3H), 2.32 (dd, *J* = 13.0, 2.6 Hz, 1H), 2.23 – 1.75 (m, 8H), 1.63 – 1.20 (m, 12H), 1.21 – 0.95 (m, 12H), 0.90 (d, *J* = 6.5 Hz, 3H), 0.85 (dd, *J* = 6.6, 1.5 Hz, 6H), 0.67 (s, 3H). **^{13}C NMR** (101 MHz, CDCl3) δ 140.5, 121.7, 79.2, 65.3, 56.7, 56.1, 52.2, 50.1, 42.2, 40.6, 39.7, 39.4, 39.0, 37.1, 36.8, 36.1, 35.7, 31.8, 31.8, 28.3, 28.1, 27.9, 24.2,

23.7, 23.4, 22.7, 22.5, 21.0, 19.3, 18.6, 11.8. **IR** v 2929, 2866, 1448, 1419, 1365, 1224 1153, 962, 754 cm^{-1}; **HRMS** (ESI) for $C_{31}H_{54}O_3S$ $[M+K]^+$ Calculated: 545.3425, found: 545.3415.

V. X-Ray Crystal Structures

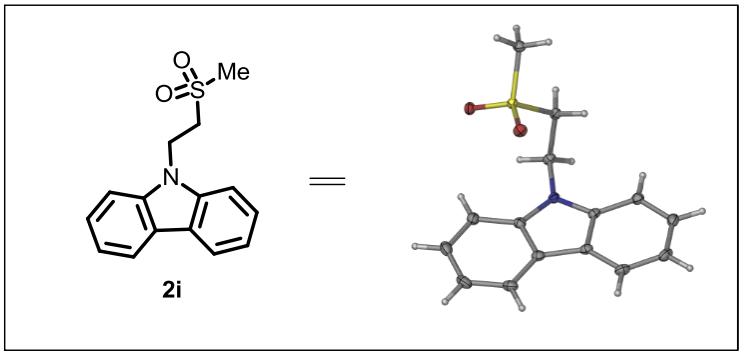
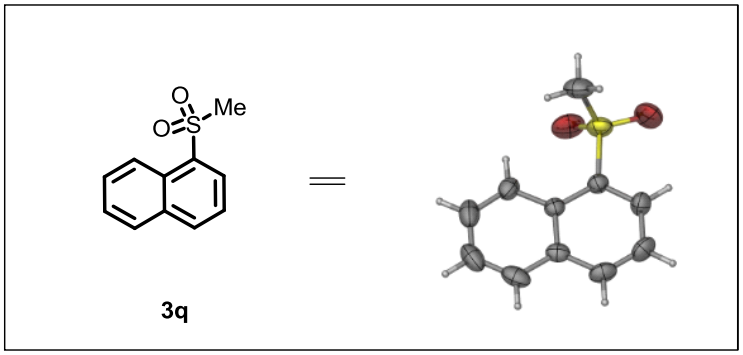


Table S2. Sample and crystal data for **2i** (CCDC 1921692)**.**

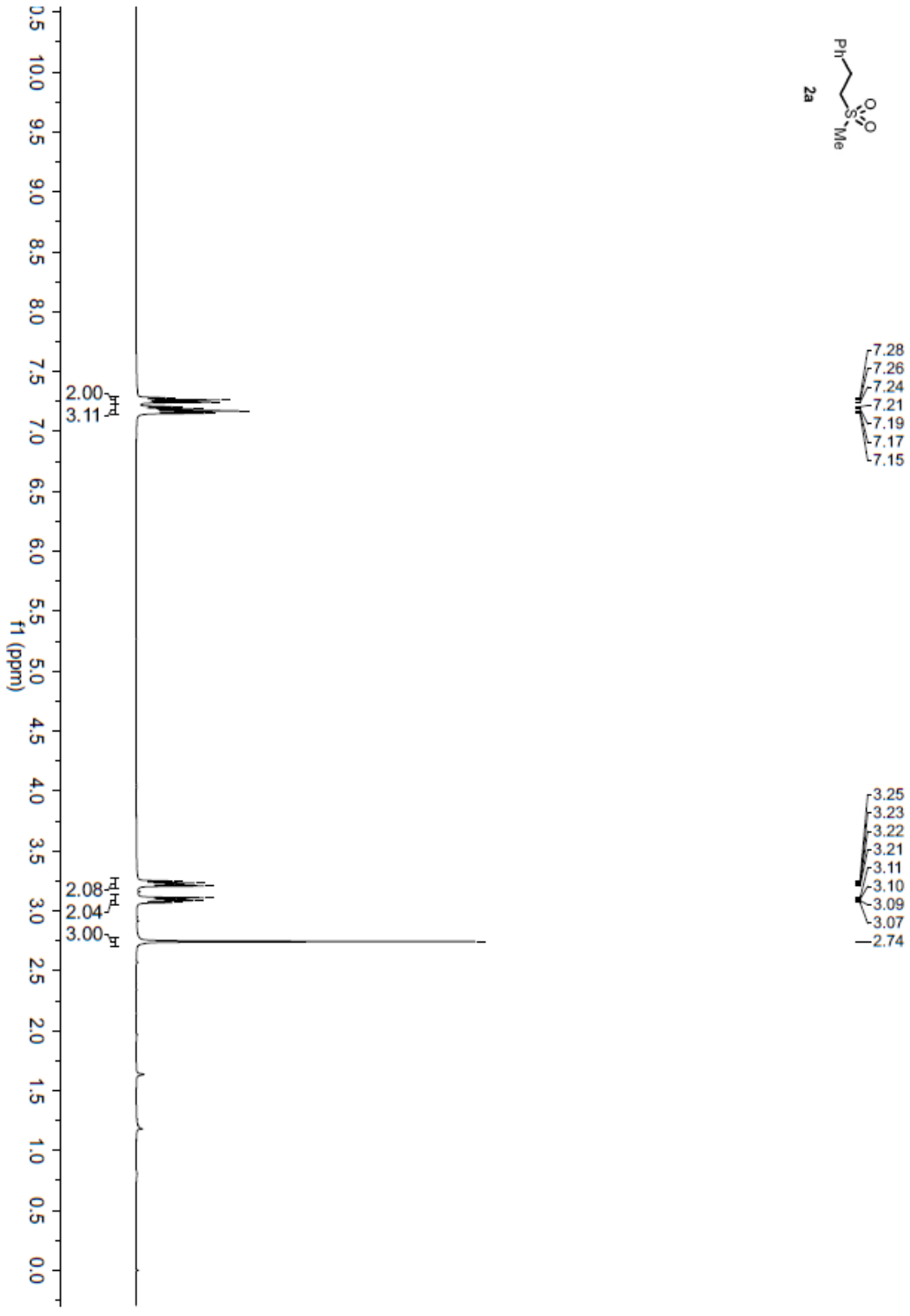
Bond precision	C-C = 0.0019 A
	Wavelength = 1.54184
Cell	a = 5.7433 (1) α = 90°
	b =12.4290(1) β = 97.685(1)
	c = 18.1643 (2) γ = 90°
Temperature	293 K
Volume	1284.98(3)
Space group	P 1 21/c 1
Sum formula	C15 H15 N O2 S
Mr	273.34
Dx,g cm^{-3}	1.413
Z	4
Mu (mm-1)	2.213
F000	576
h,k,lmax	6, 15, 22
Nref	2576
Tmin,Tmax	0.341, 1.000
Correction method= # Reported T Limits	Tmin = 0.341 Tmax = 1.000
AbsCorr = MULTI-SCAN	
Data completeness	0.979
Theta(max)	74.515
R(reflections)	0.0340(2441)
wR2(reflections)	0.882 (2576)
S	1.072
Npar	173



3q

Table S2. Sample and crystal data for **3q** (CCDC 1921697)**.**

Bond precision	C-C = 0.0021 A
	Wavelength = 1.54184
Cell	a =11.2374(1) α = 90°
	b =10.3578(1) β = 90
	c = 16.9587(1) γ = 90°
Temperature	293 K
Volume	1973.90(3)
Space group	P 1 21/c 1
Sum formula	C11 H10 O2 S
Mr	206.25
Dx,g cm^{-3}	1.388
Z	8
Mu (mm-1)	2.664
F000	864.0
h,k,lmax	14, 12, 21
Nref	1999
Tmin,Tmax	0.176, 1.000
Correction method= # Reported T Limits	Tmin = 0.176 Tmax = 1.000
AbsCorr = MULTI-SCAN	
Data completeness	0.993
Theta(max)	74.393
R(reflections)	0.0340(1913)
wR2(reflections)	0.0927 (1999)
S	1.031
Npar	129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S
Me
2a
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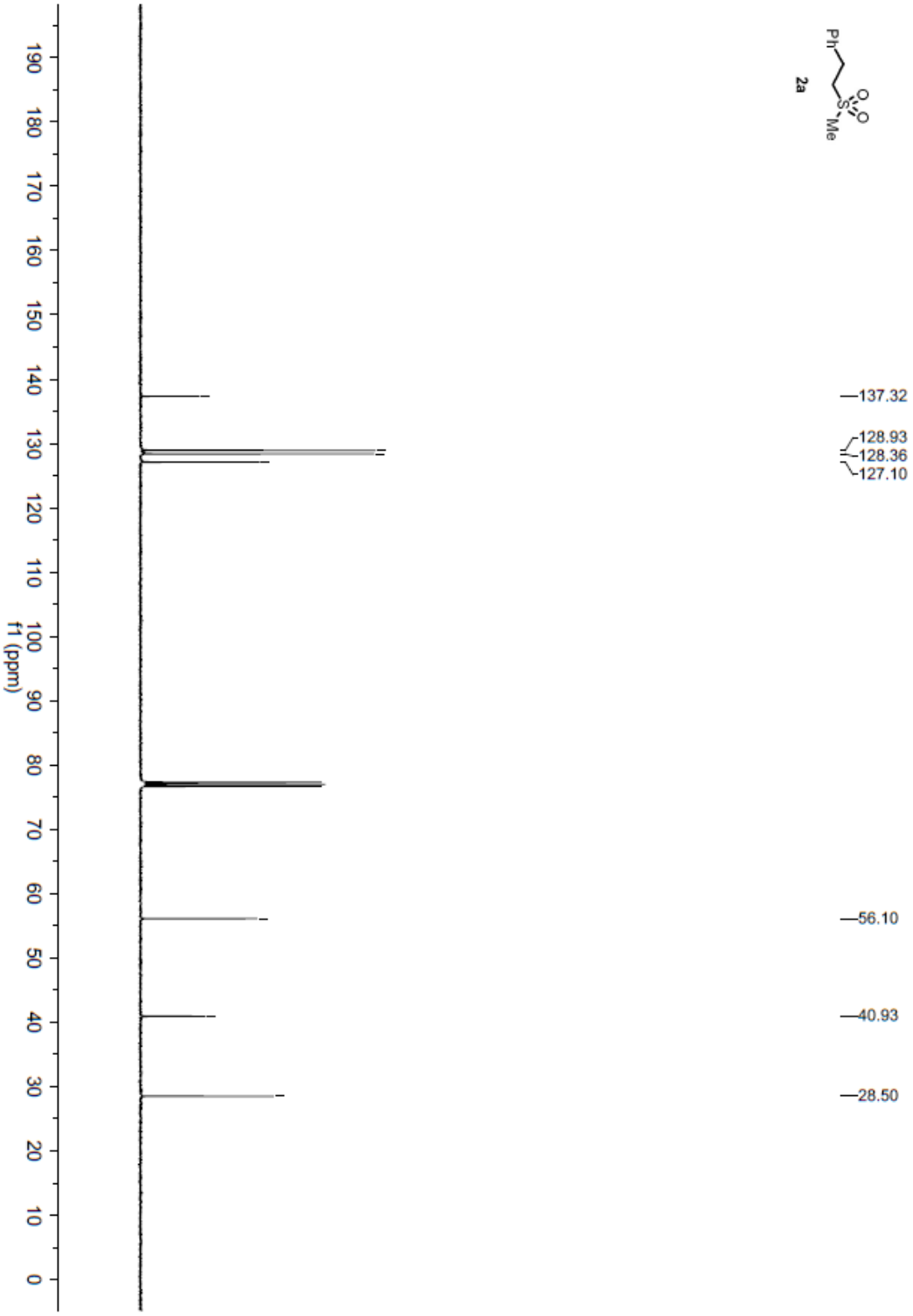
7.26
7.24
7.21
7.19
7.17
7.15
3.25
3.23
3.22
3.21
3.11
3.10
3.09
3.07
2.74
2.00
3.11
2.08
2.04
3.00
f1 (ppm)


Ph
S
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O
Me
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40.93
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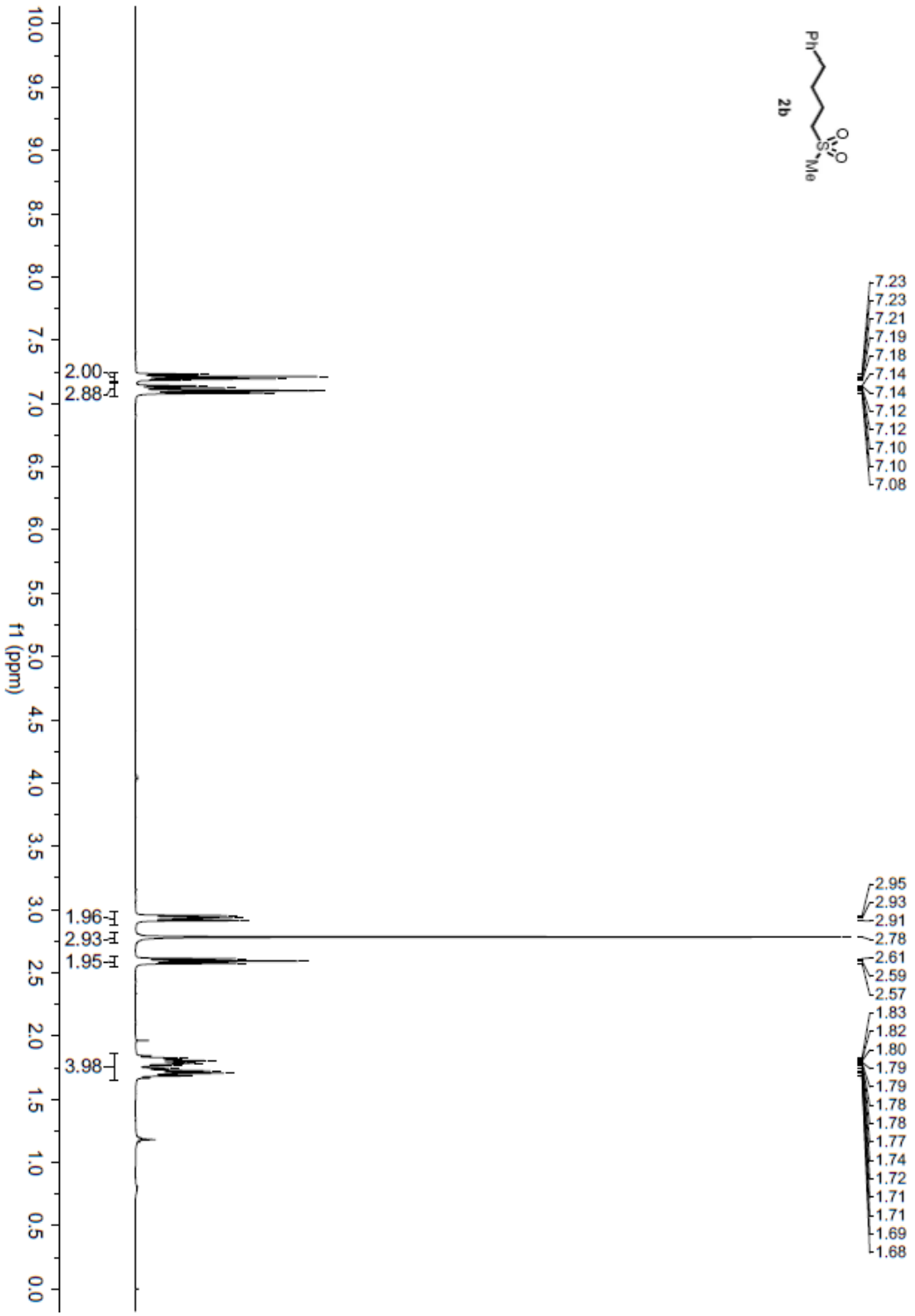
40
30
20
10
0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S
Me
2b
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7.23
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7.19
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7.14
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7.12
7.10
7.10
7.08
2.95
2.93
2.91
2.78
2.61
2.59
2.57
1.83
1.82
1.80
1.79
1.79
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1.95
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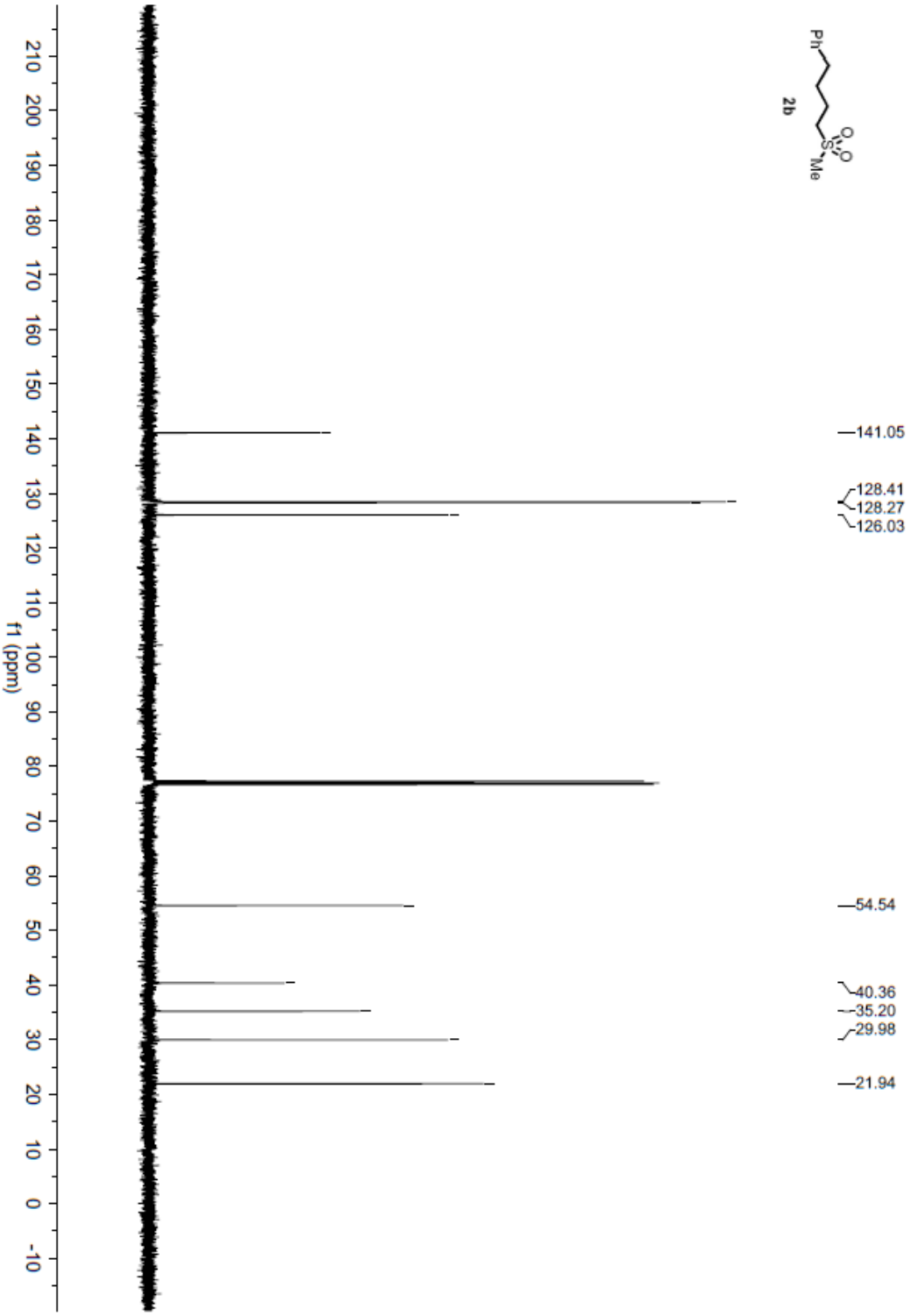
f1 (ppm)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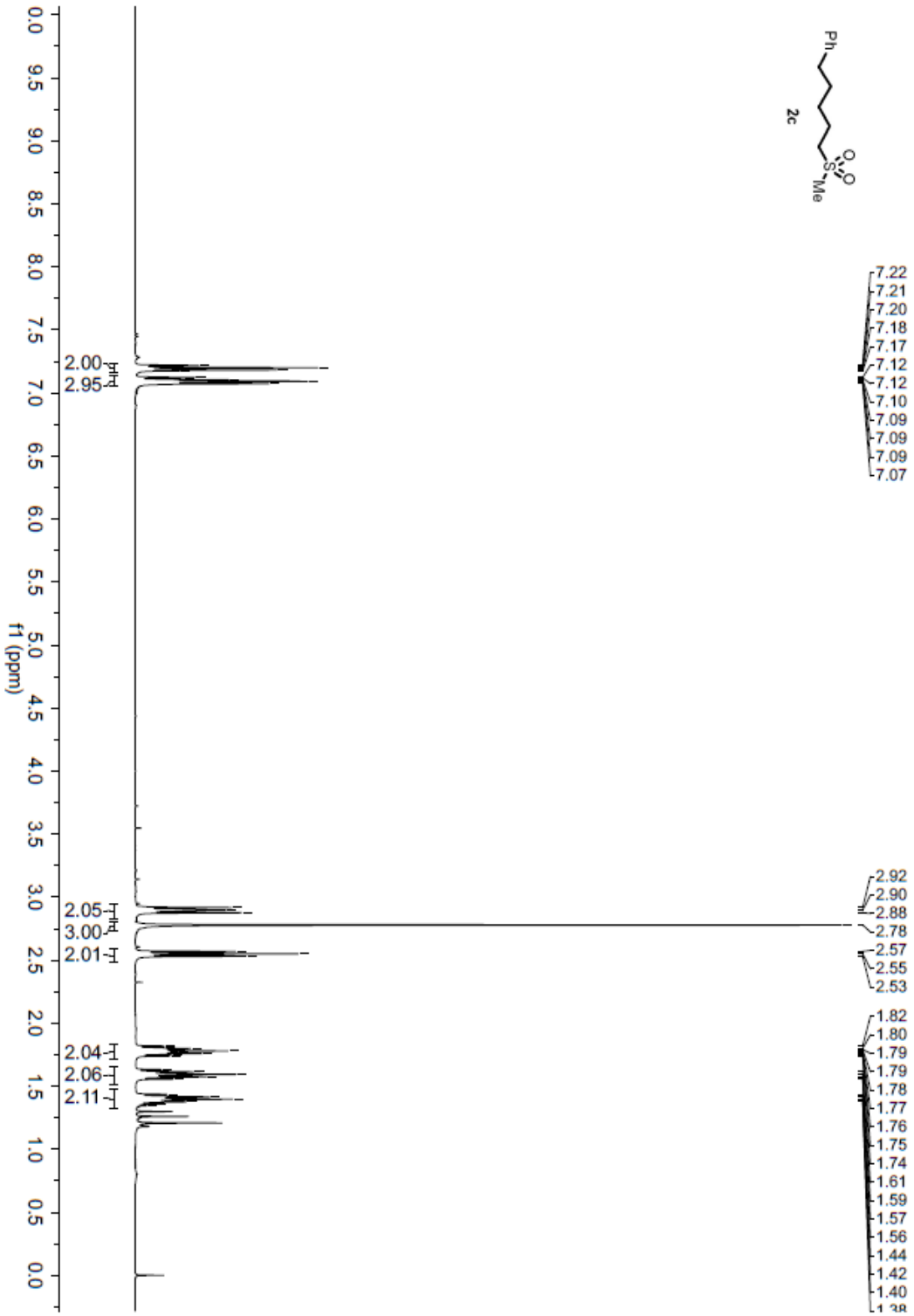
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7.09
7.07
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2.55
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1.79
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1.78
1.77
1.76
1.75
1.74
1.61
1.59
1.57
1.56
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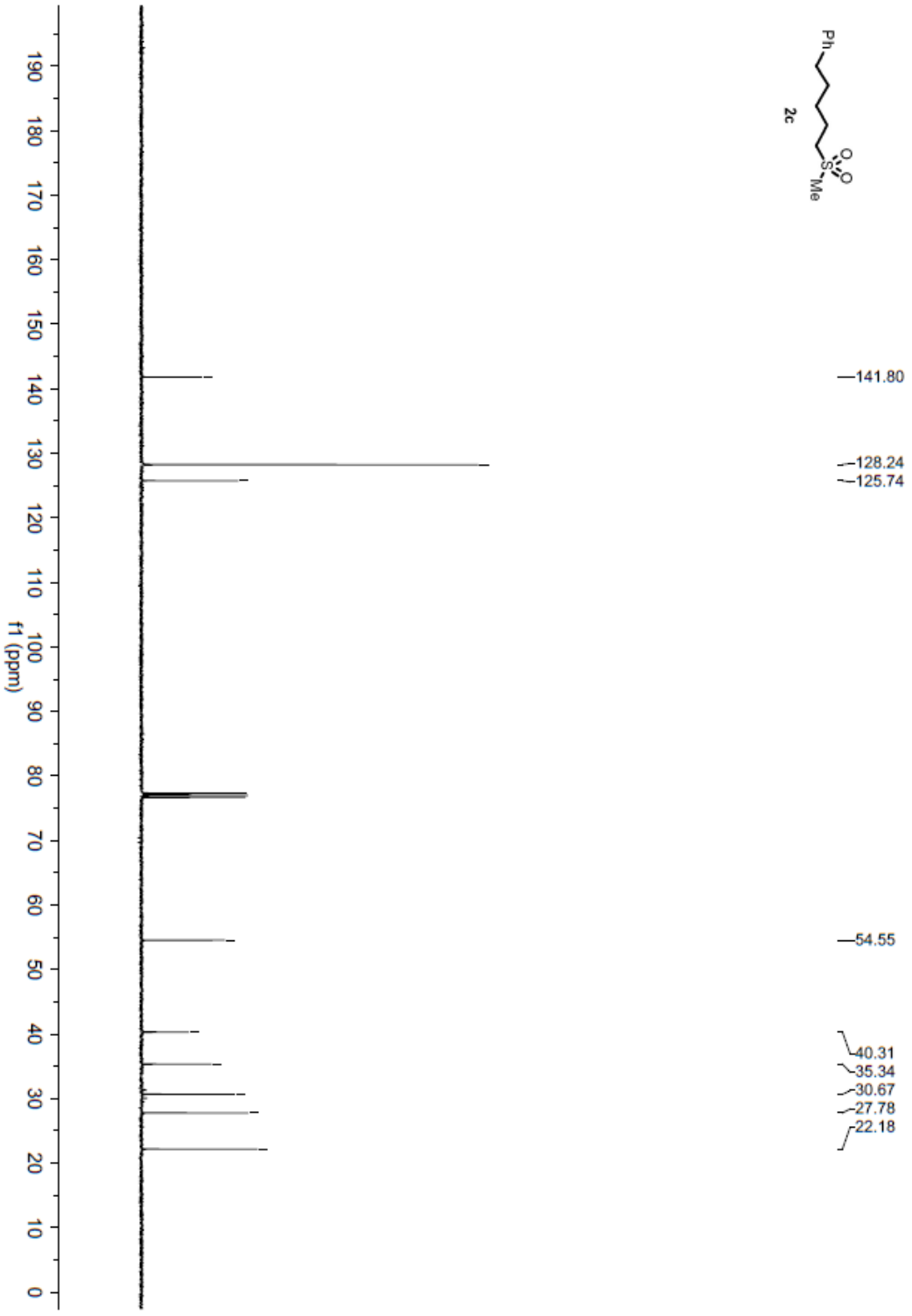
f1 (ppm)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Me
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22.18
f1 (ppm)
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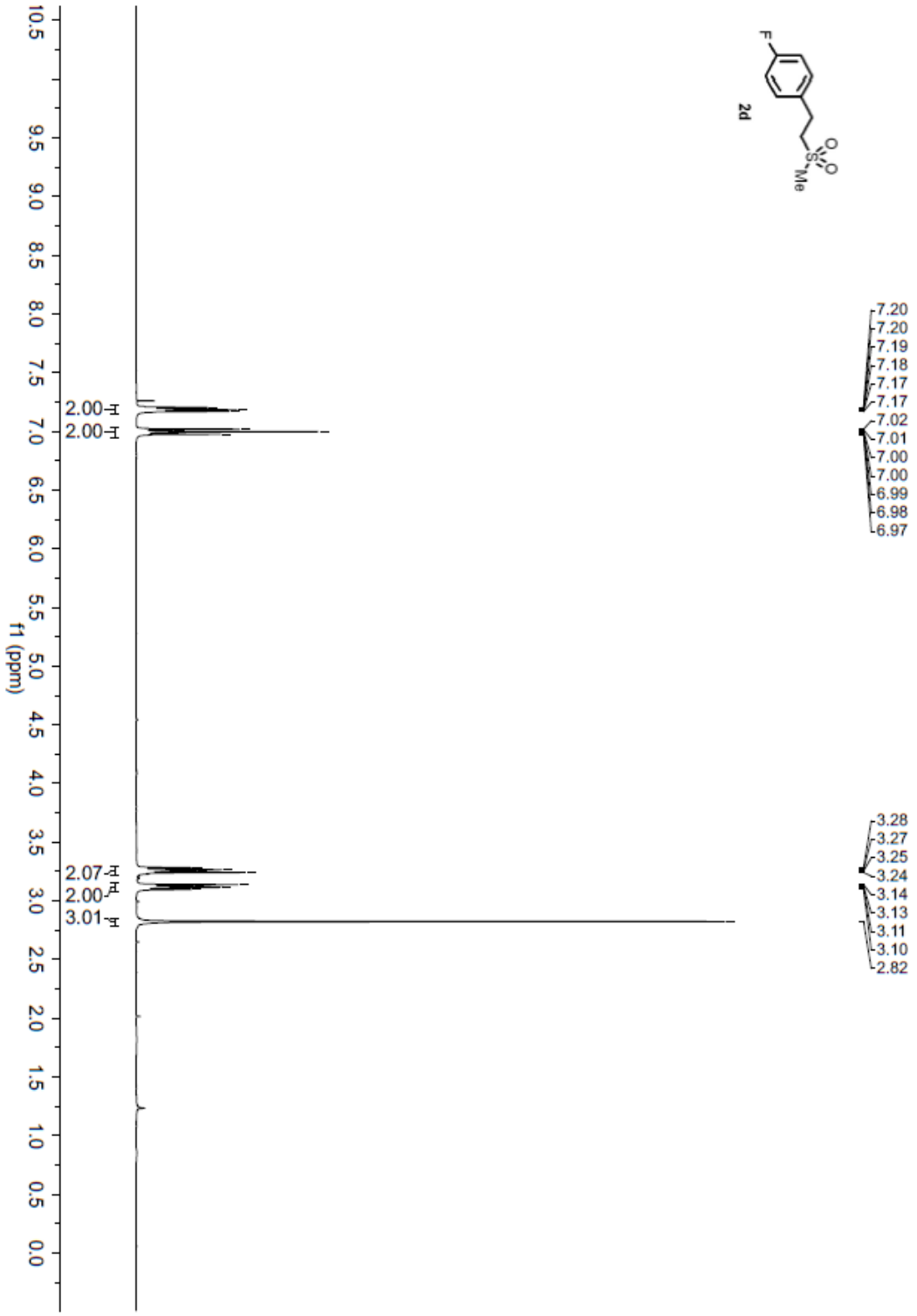
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O
S
Me
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7.17
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7.00
7.00
6.99
6.98
6.97
3.28
3.27
3.25
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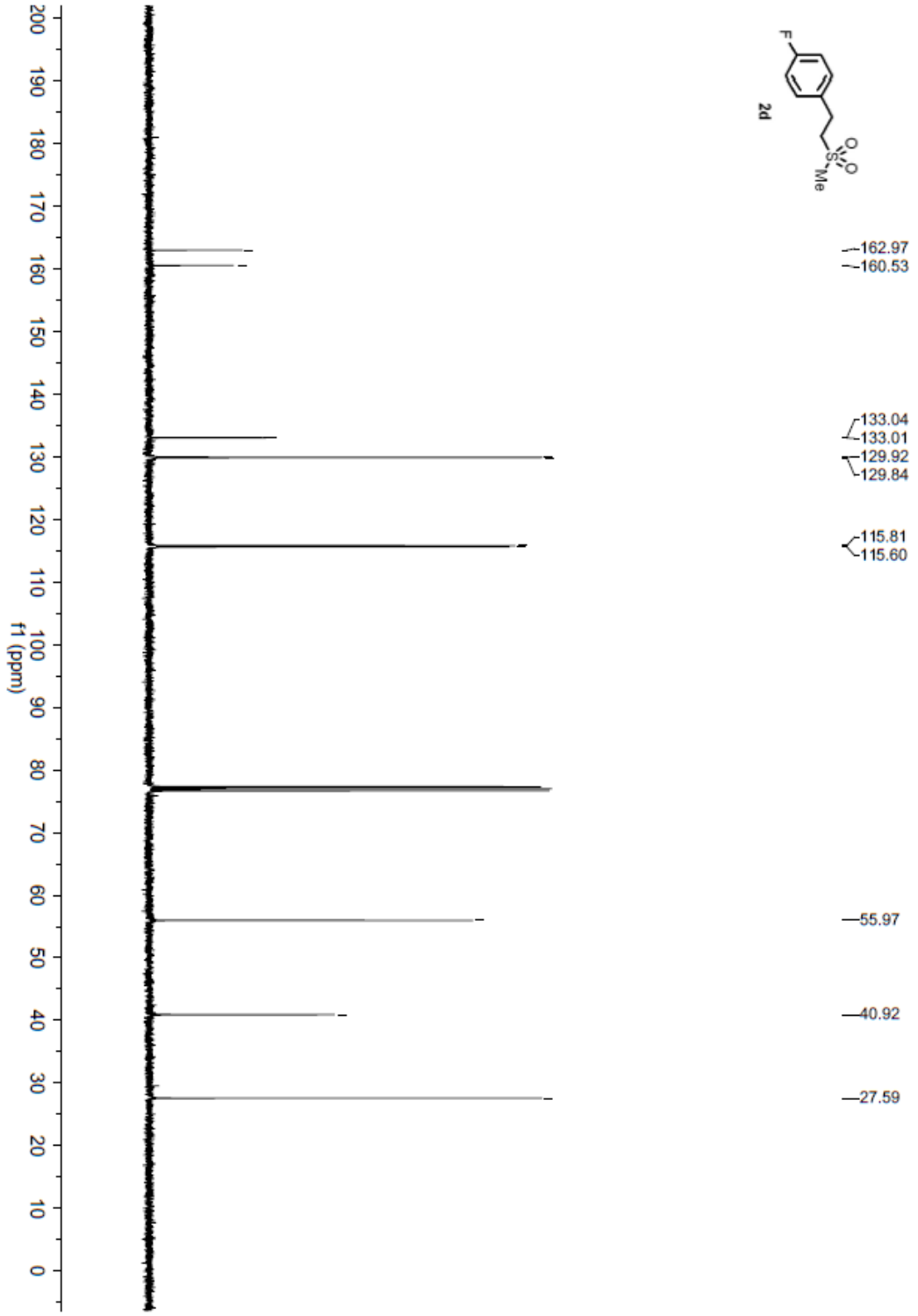
3.10
2.82
2.00
2.00
2.07
2.00
3.01
f1 (ppm)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O
S
Me
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f1 (ppm)
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150
140
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30
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10
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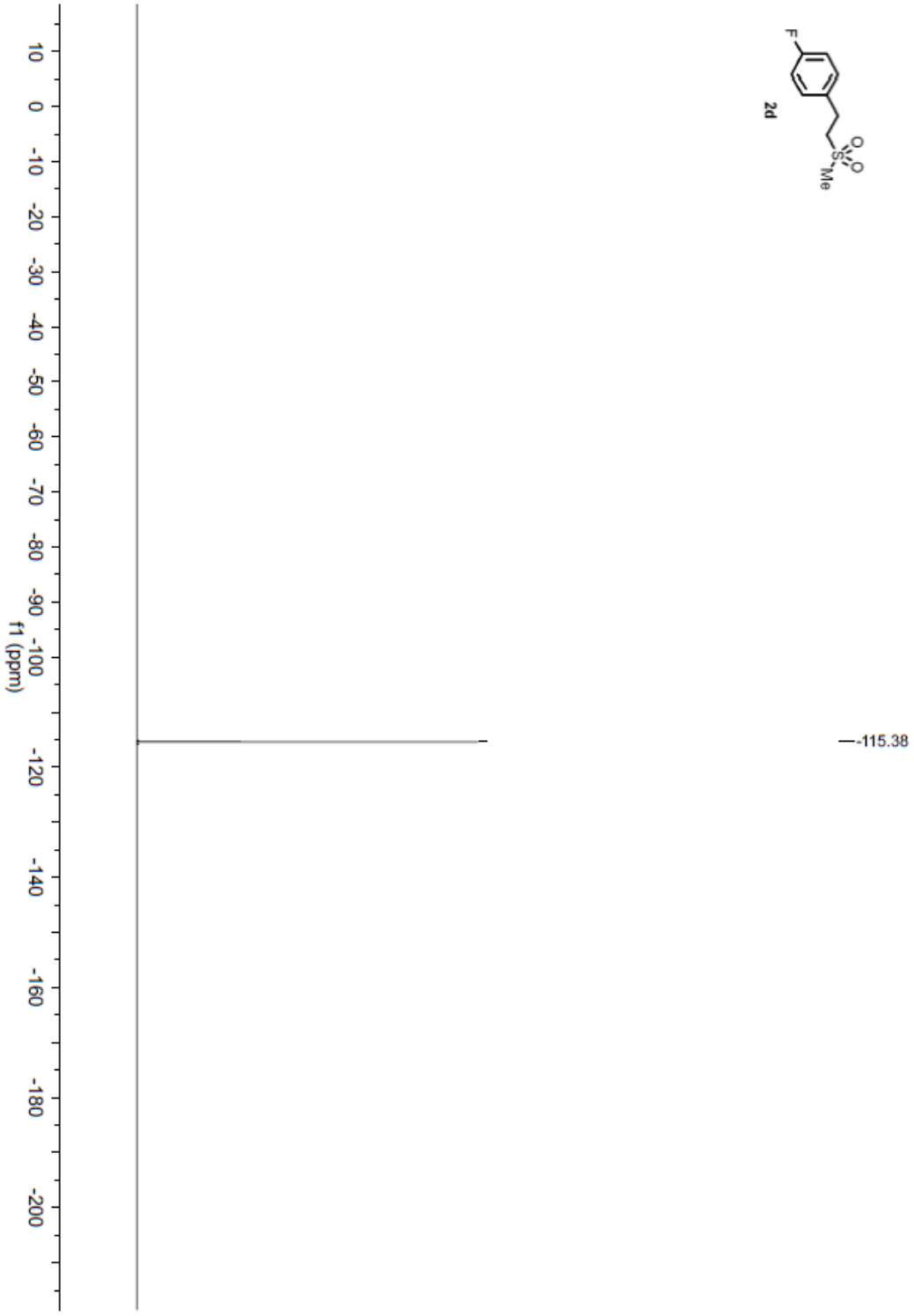
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O
S
Me
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-20
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-40
-50
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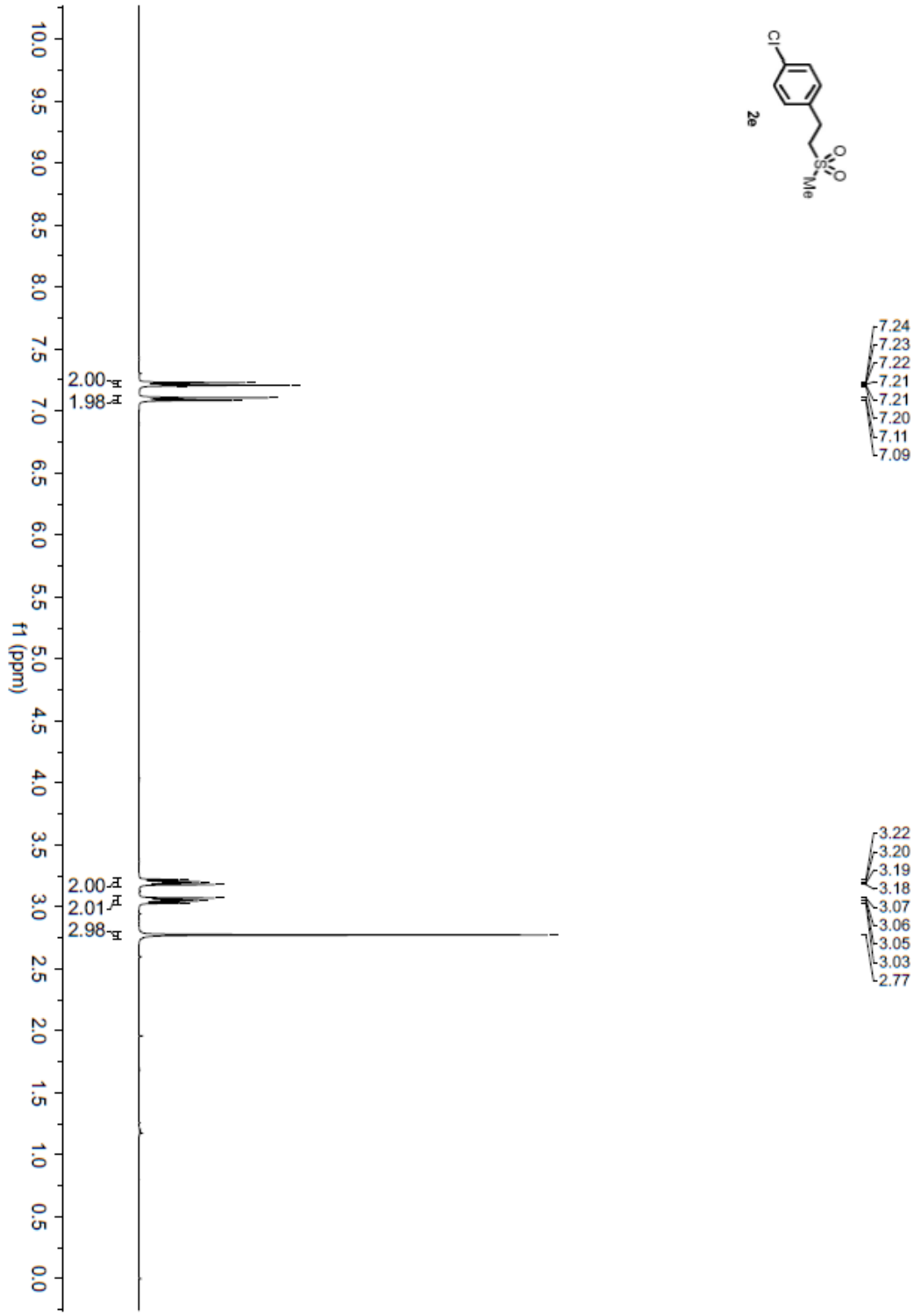
-120
-140
-160
-180
-200
f1 (ppm)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Me
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3.20
3.19
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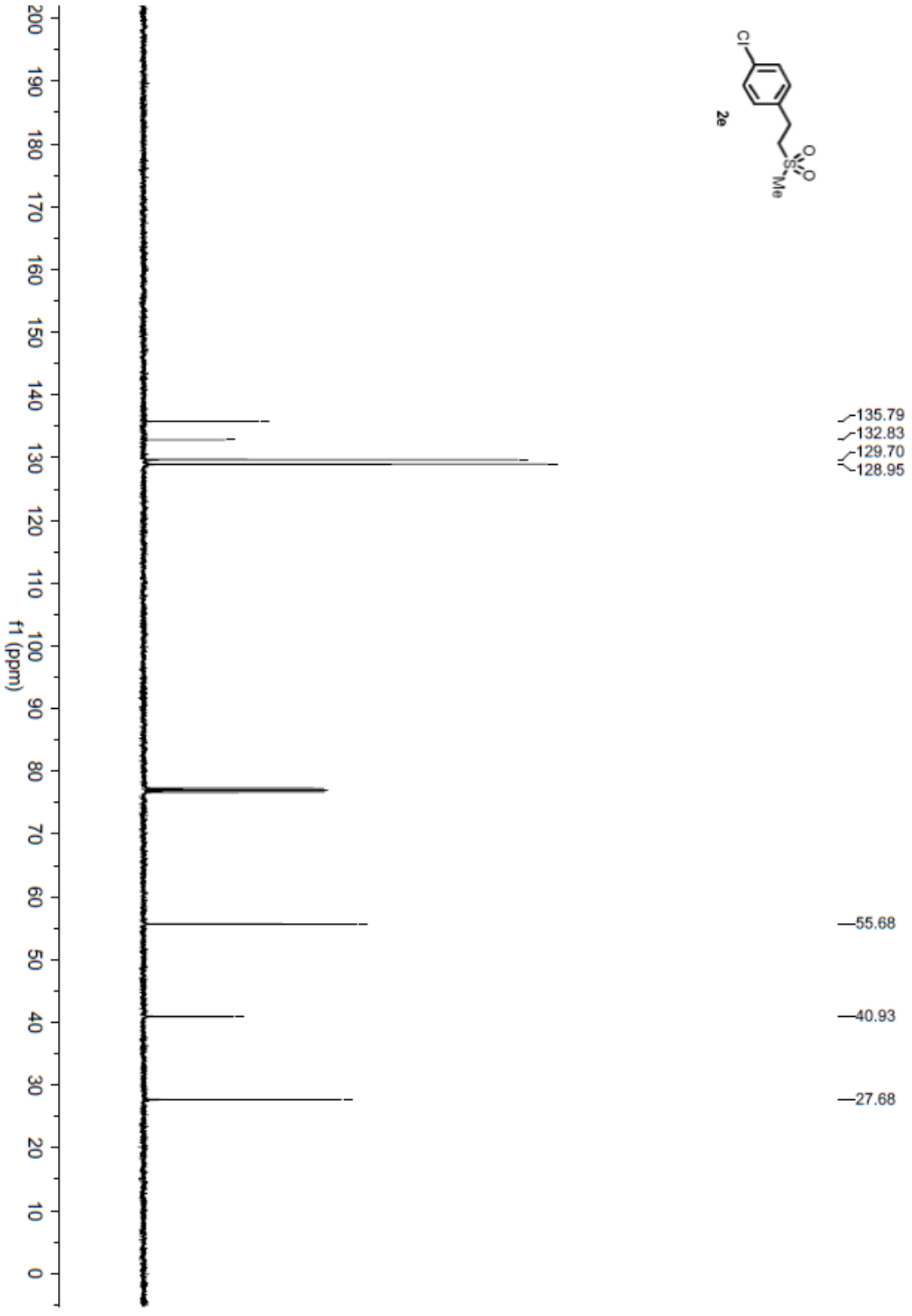
1.98
2.00
2.01
2.98
f1 (ppm)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10
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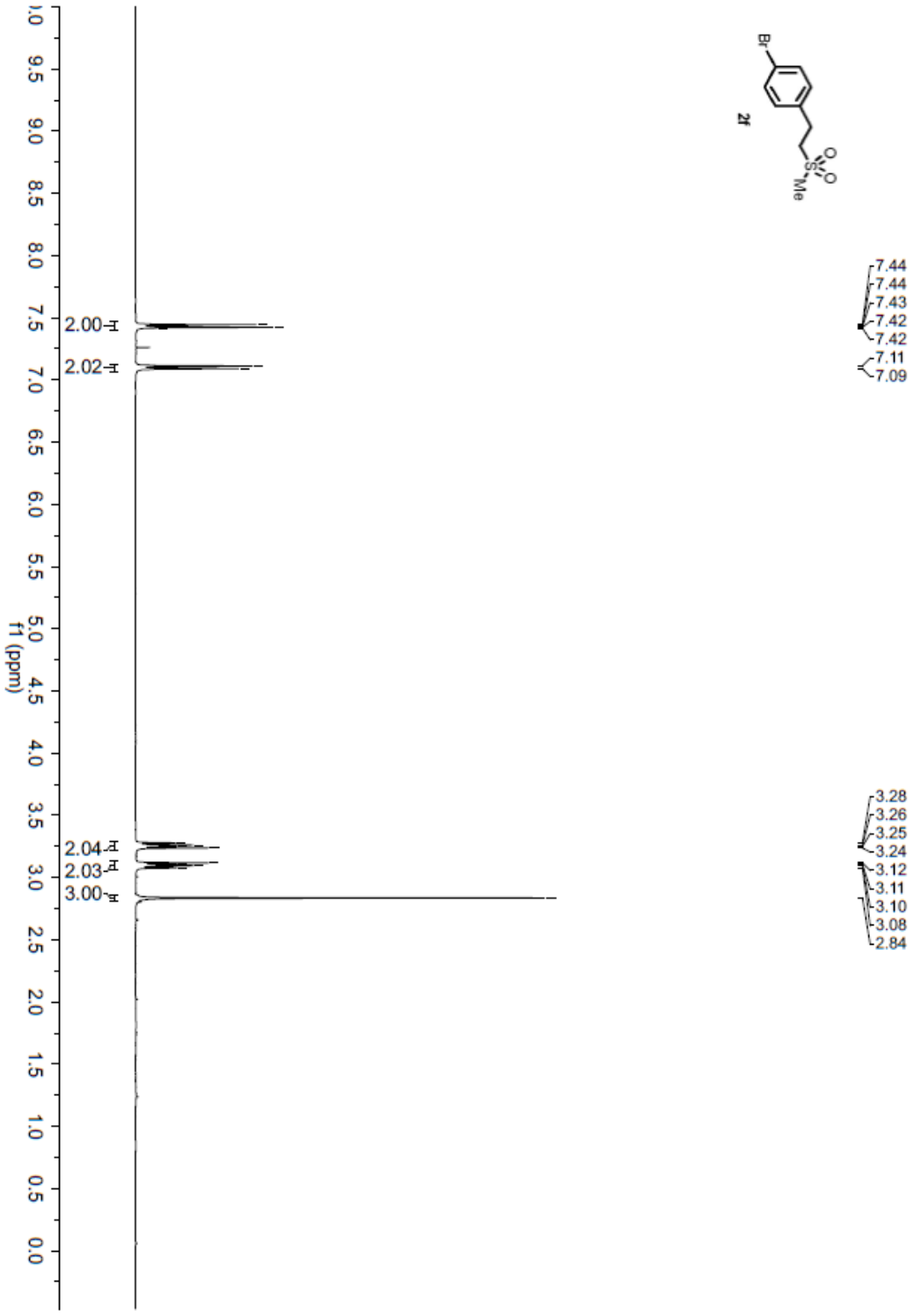
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S
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3.25
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2.04
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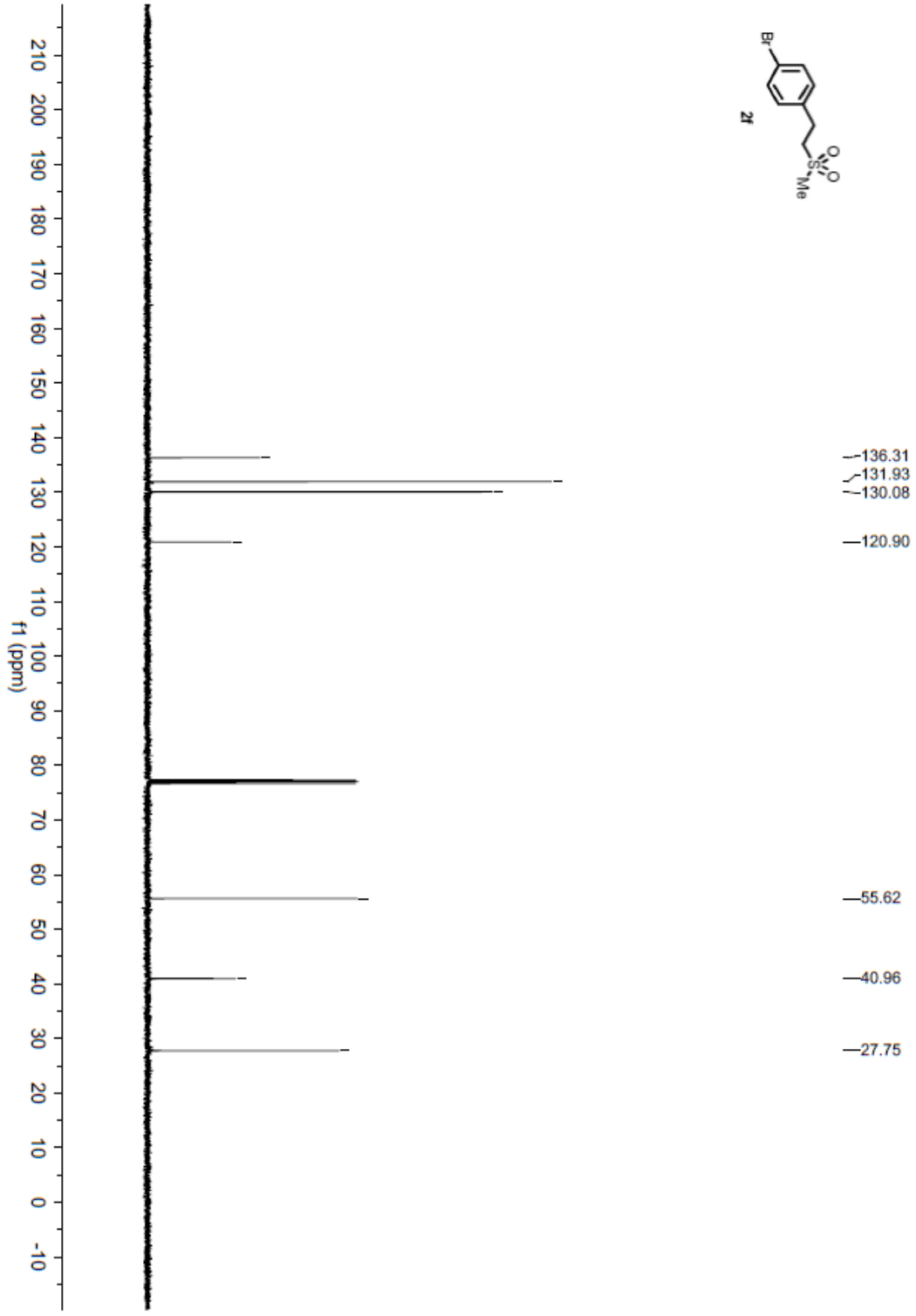
3.00
f1 (ppm)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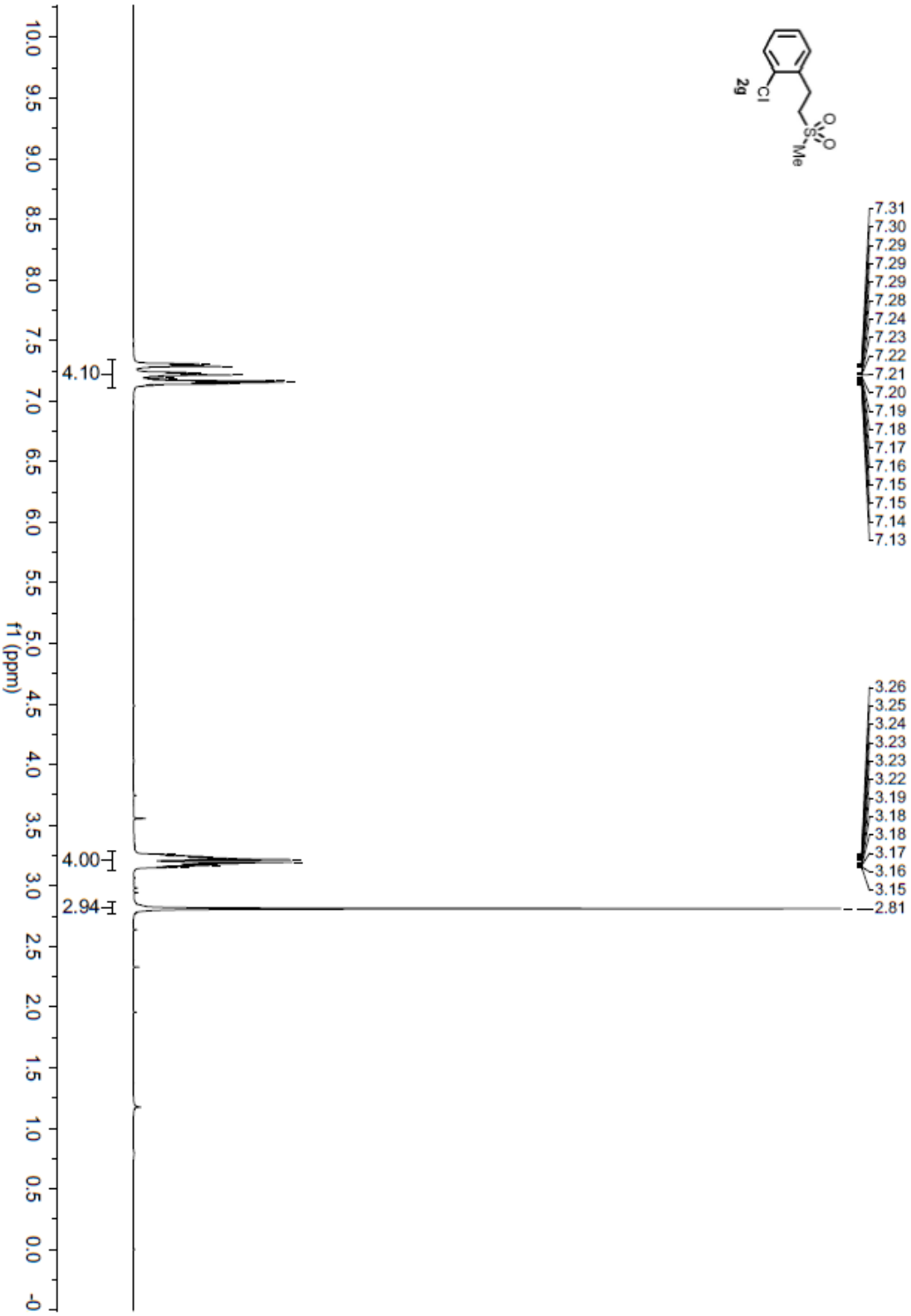
f1 (ppm)
2f


2g
Cl
S
Me
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7.29
7.29
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7.24
7.23
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7.20
7.19
7.18
7.17
7.16
7.15
7.15
7.14
7.13
3.26
3.25
3.24
3.23
3.23
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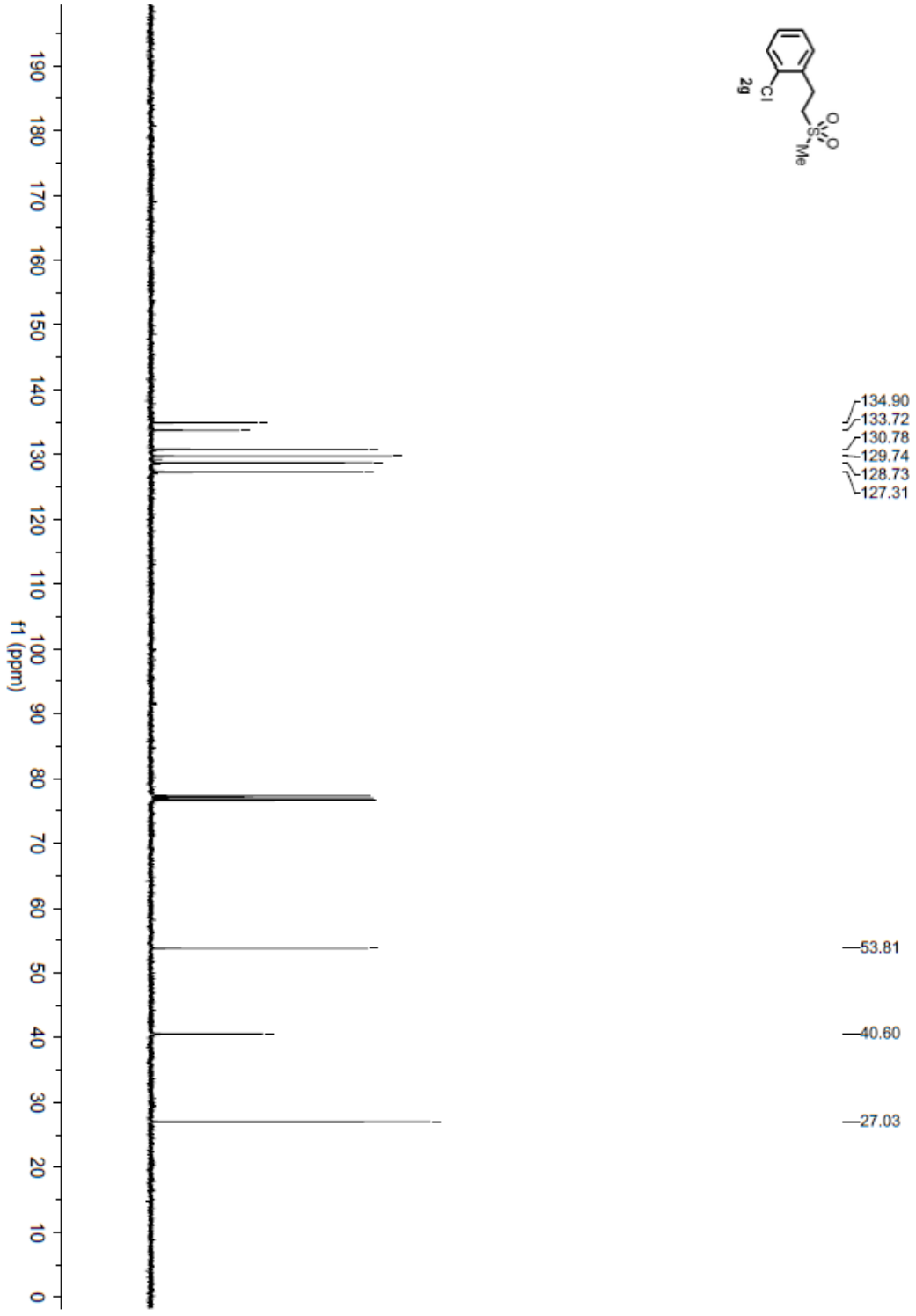
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27.03
f1 (ppm)
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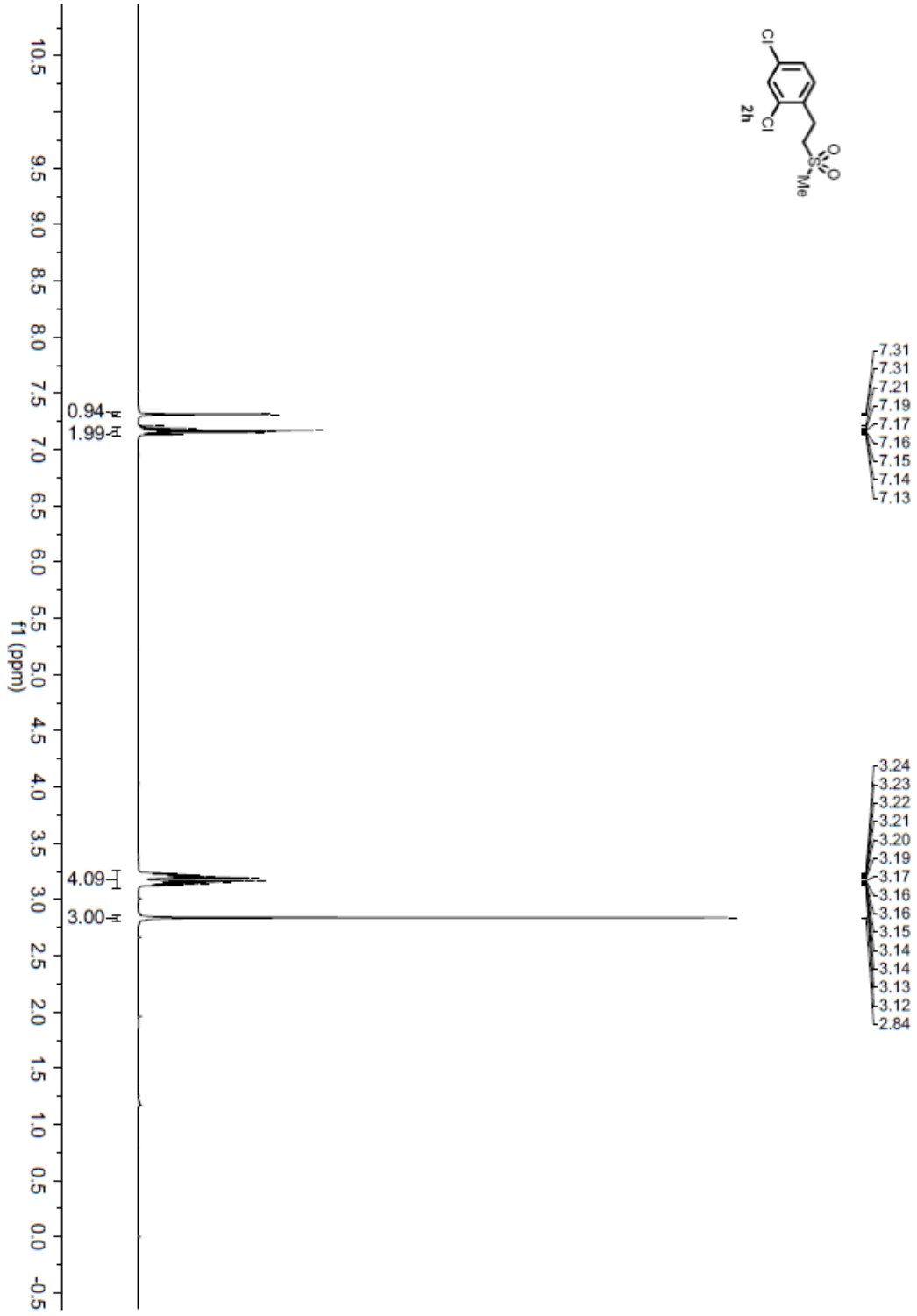
Cl
Cl
2h
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O
S
Me
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7.31
7.21
7.19
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7.16
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7.13
3.24
3.23
3.22
3.21
3.20
3.19
3.17
3.16
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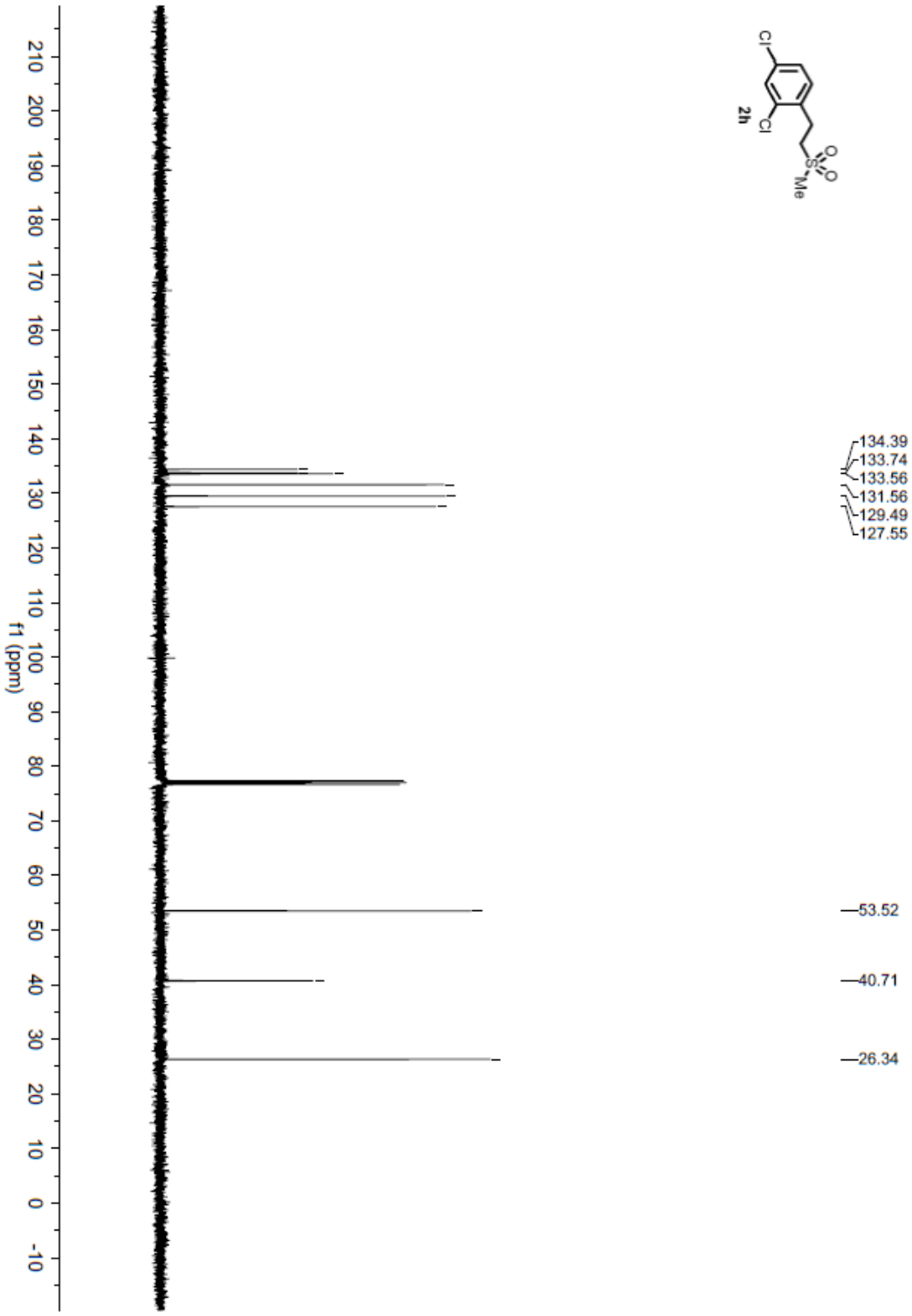
3.00
f1 (ppm)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30
20
10
0
-10
134.39
133.74
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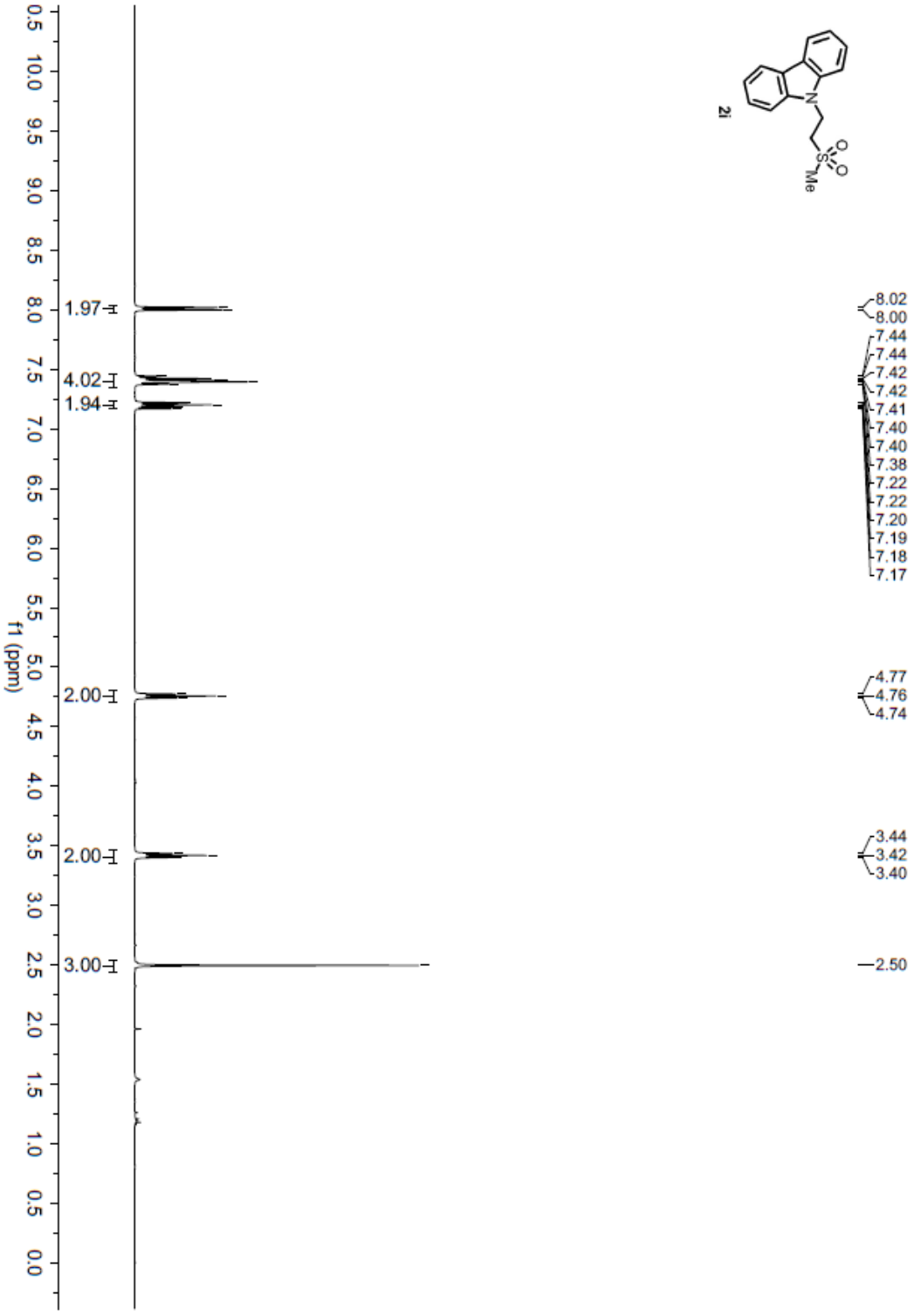
131.56
129.49
127.55
53.52
40.71
26.34
Cl
Cl
2h
O
O
S
Me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O
Me
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7.41
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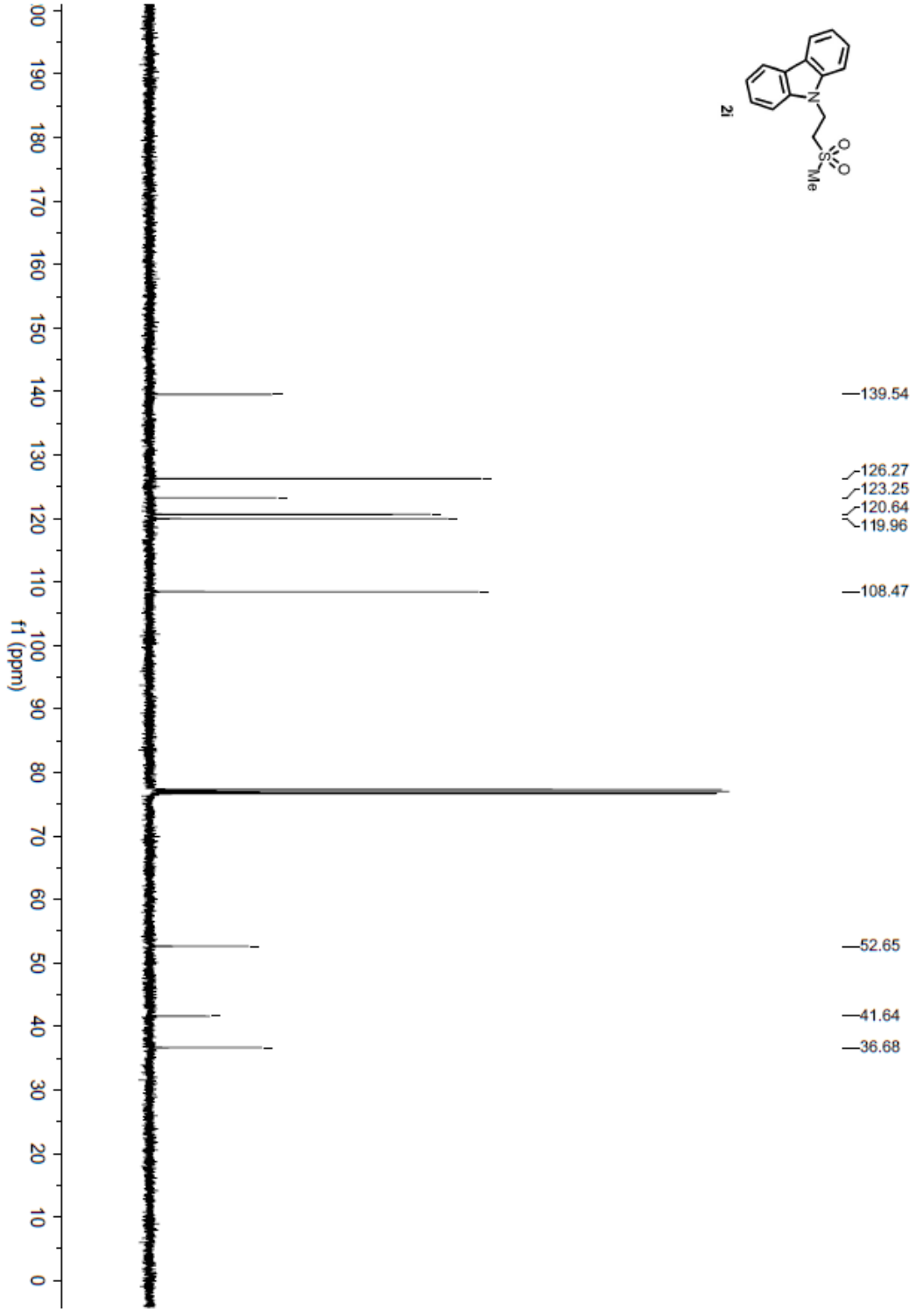
7.38
7.22
7.22
7.20
7.19
7.18
7.17
4.77
4.76
4.74
3.44
3.42
3.40
2.50
1.97
4.02
1.94
2.00
2.00
3.00
f1 (ppm)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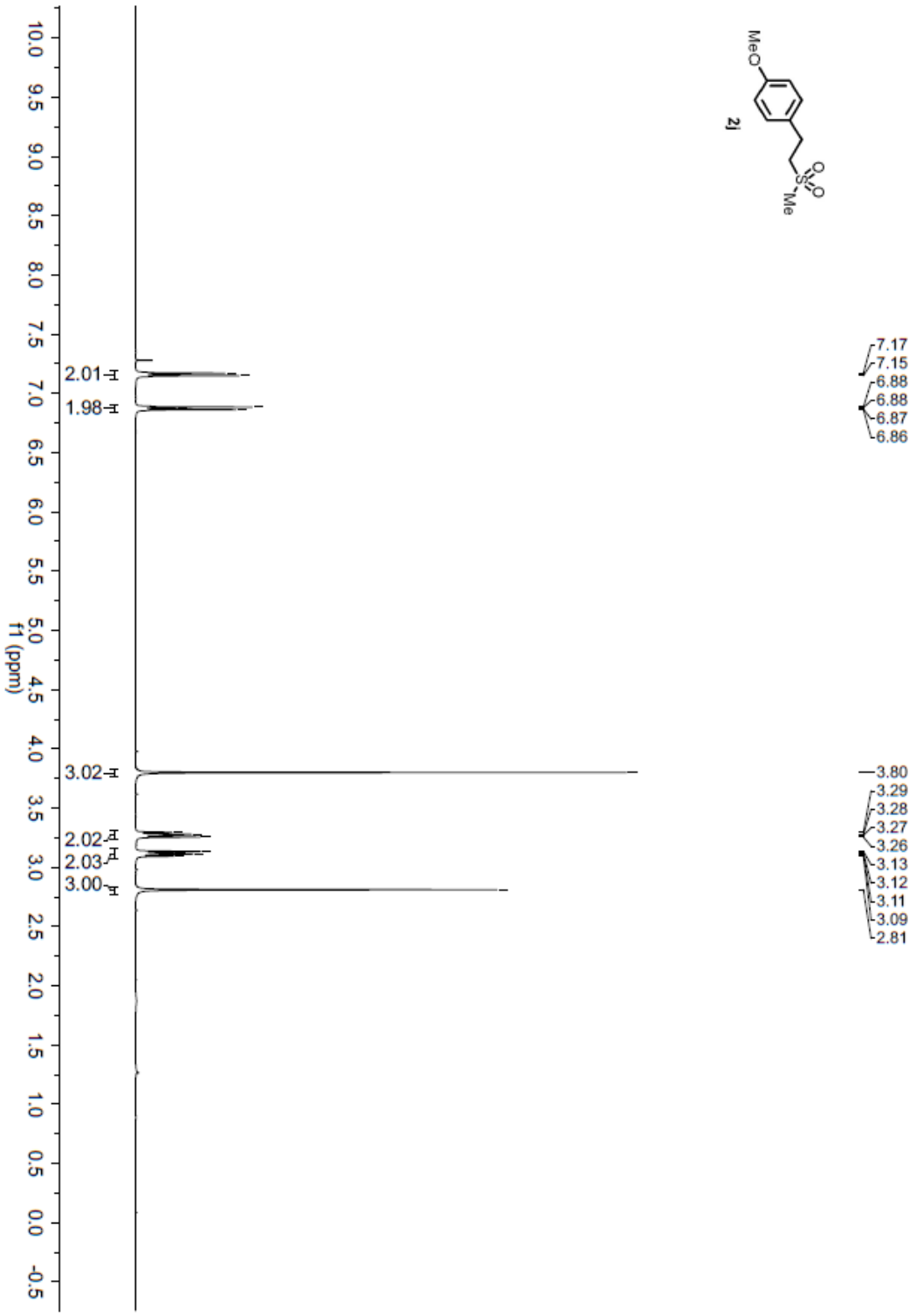
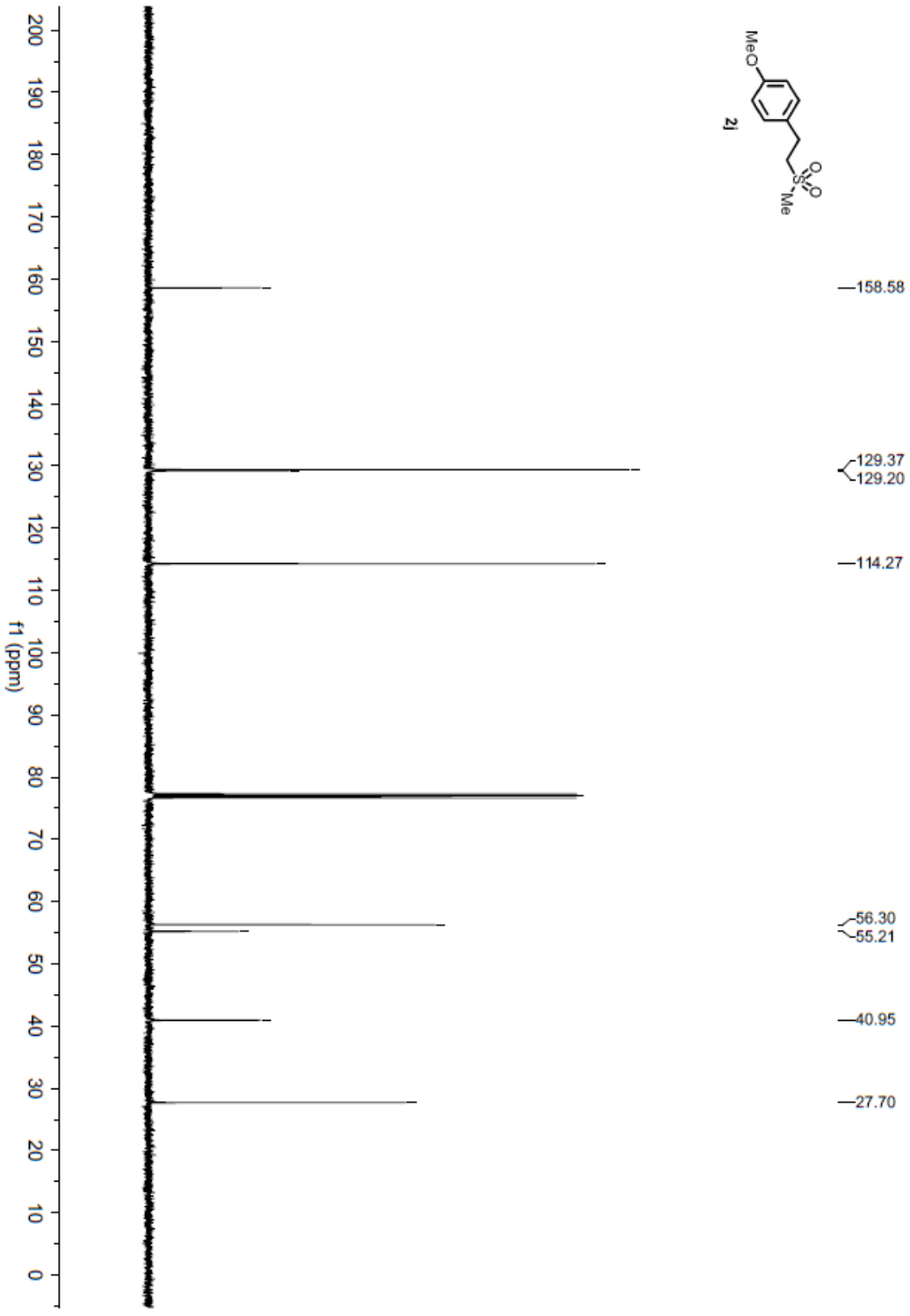
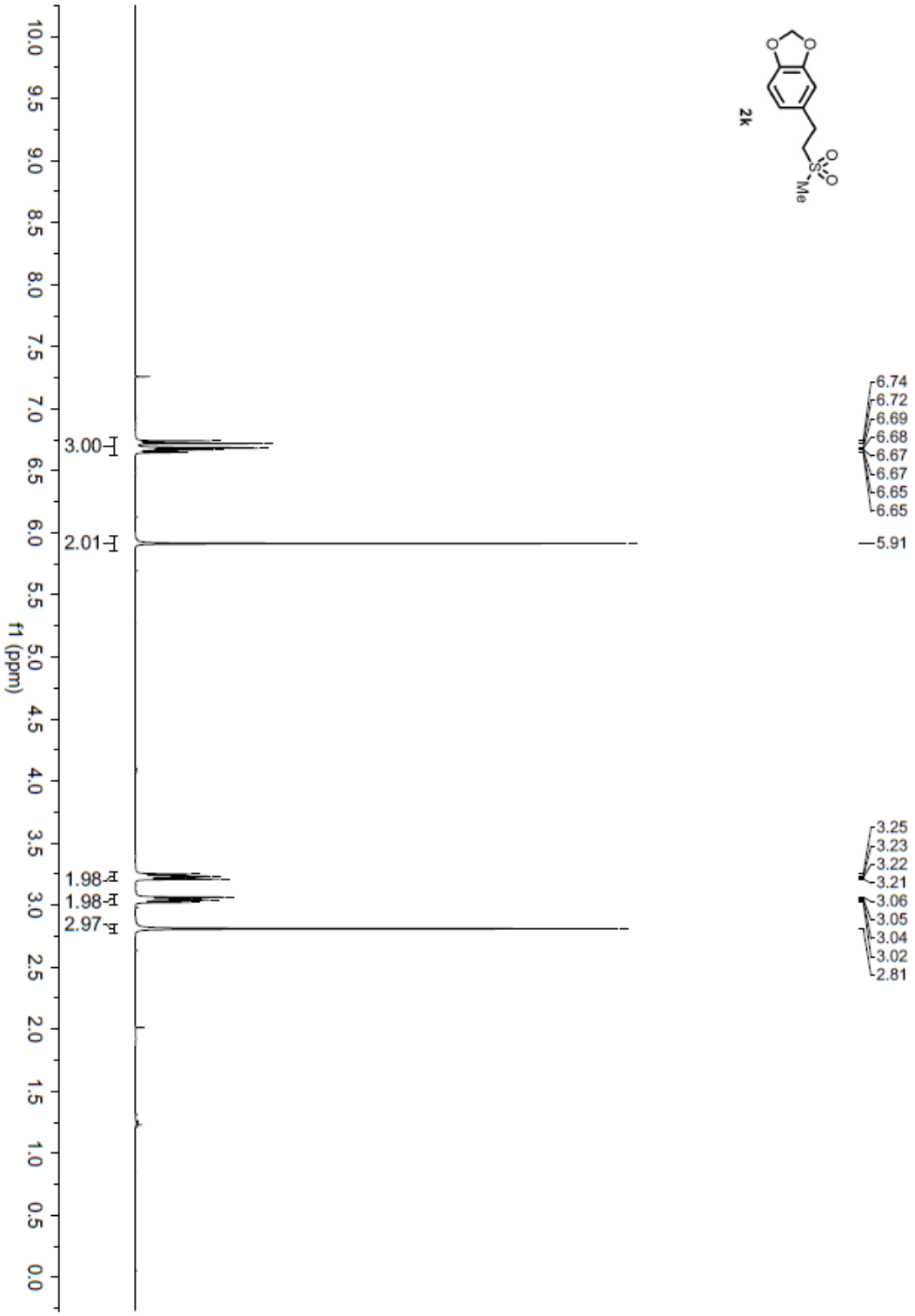
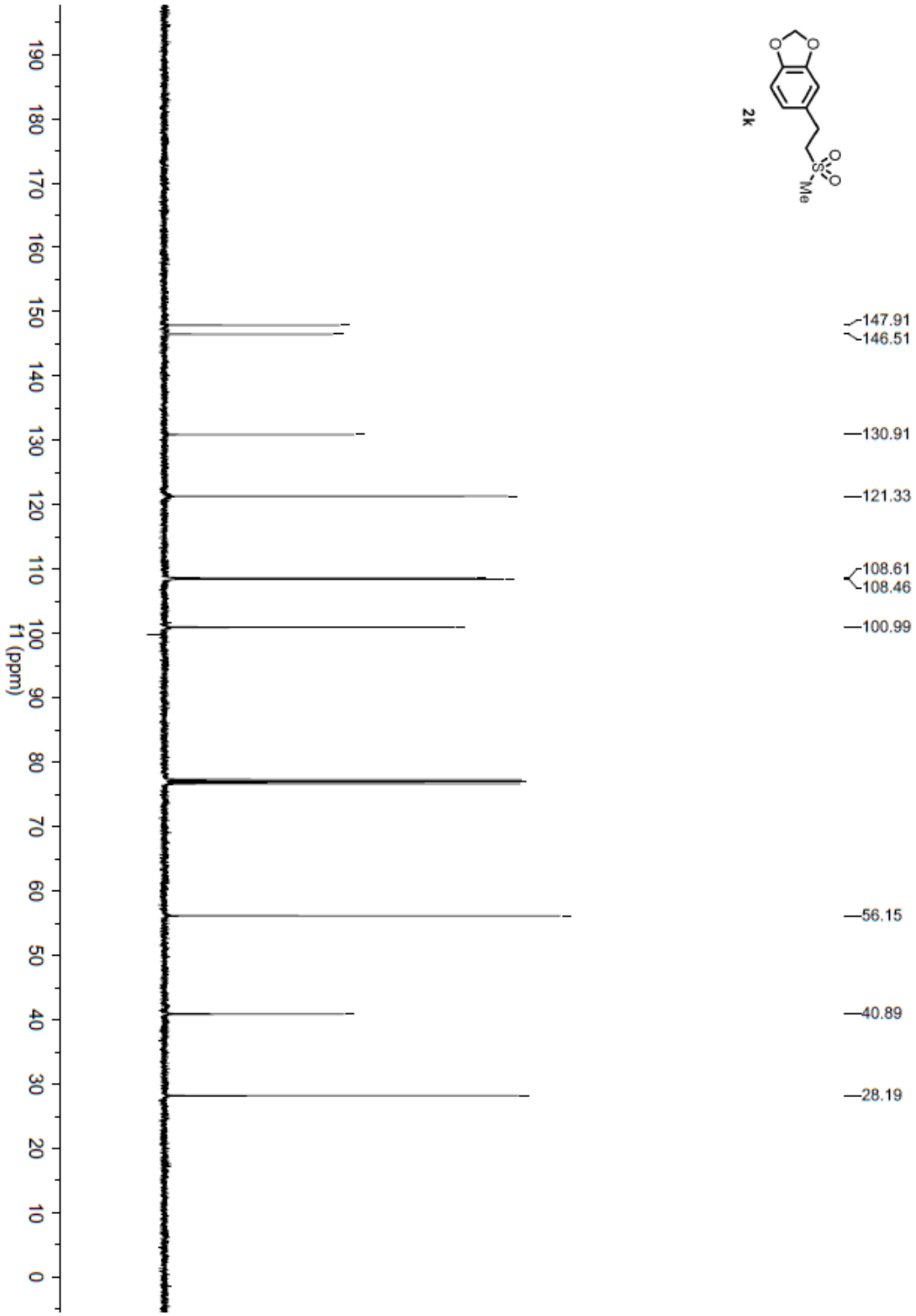
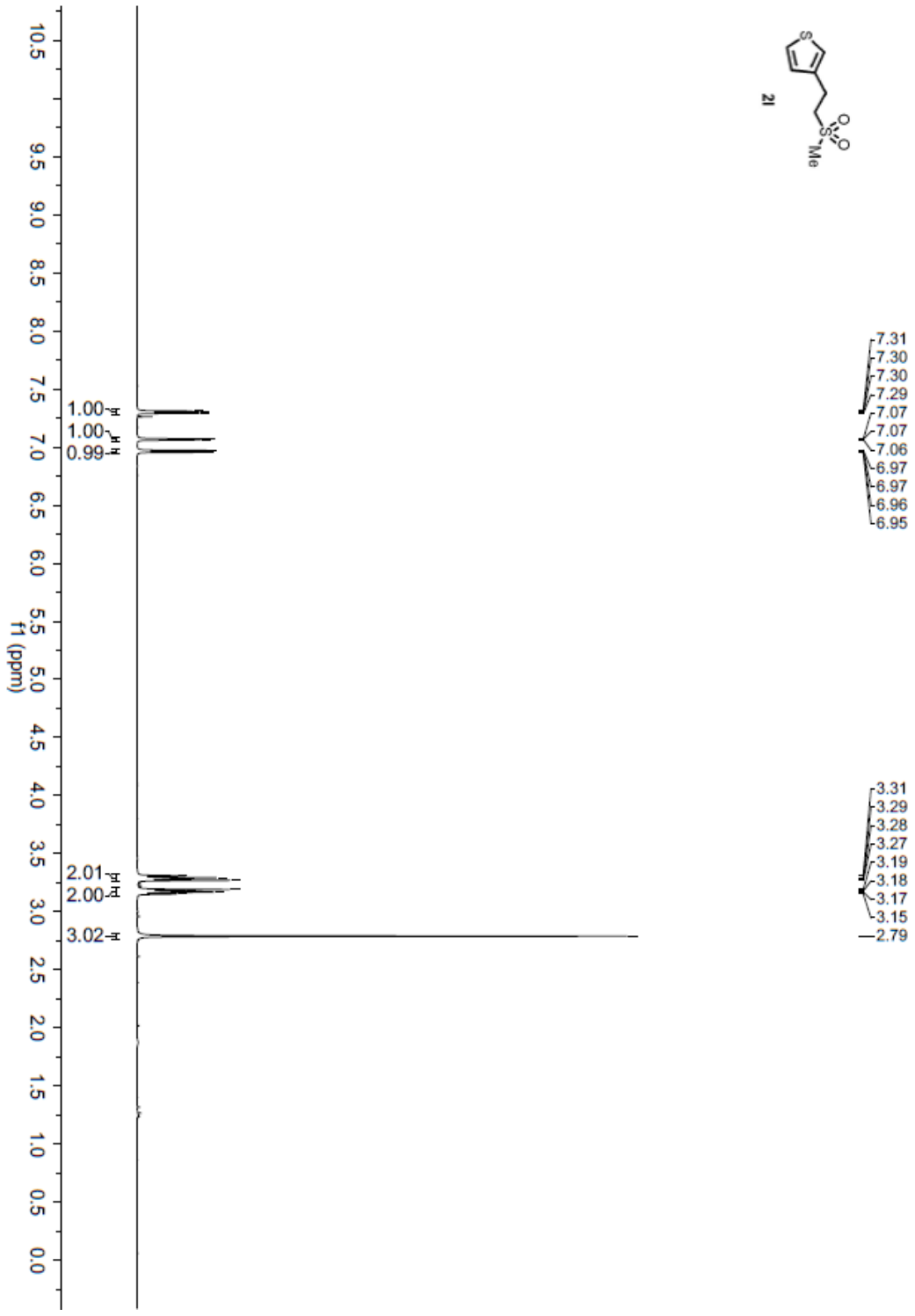
36.68
f1 (ppm)

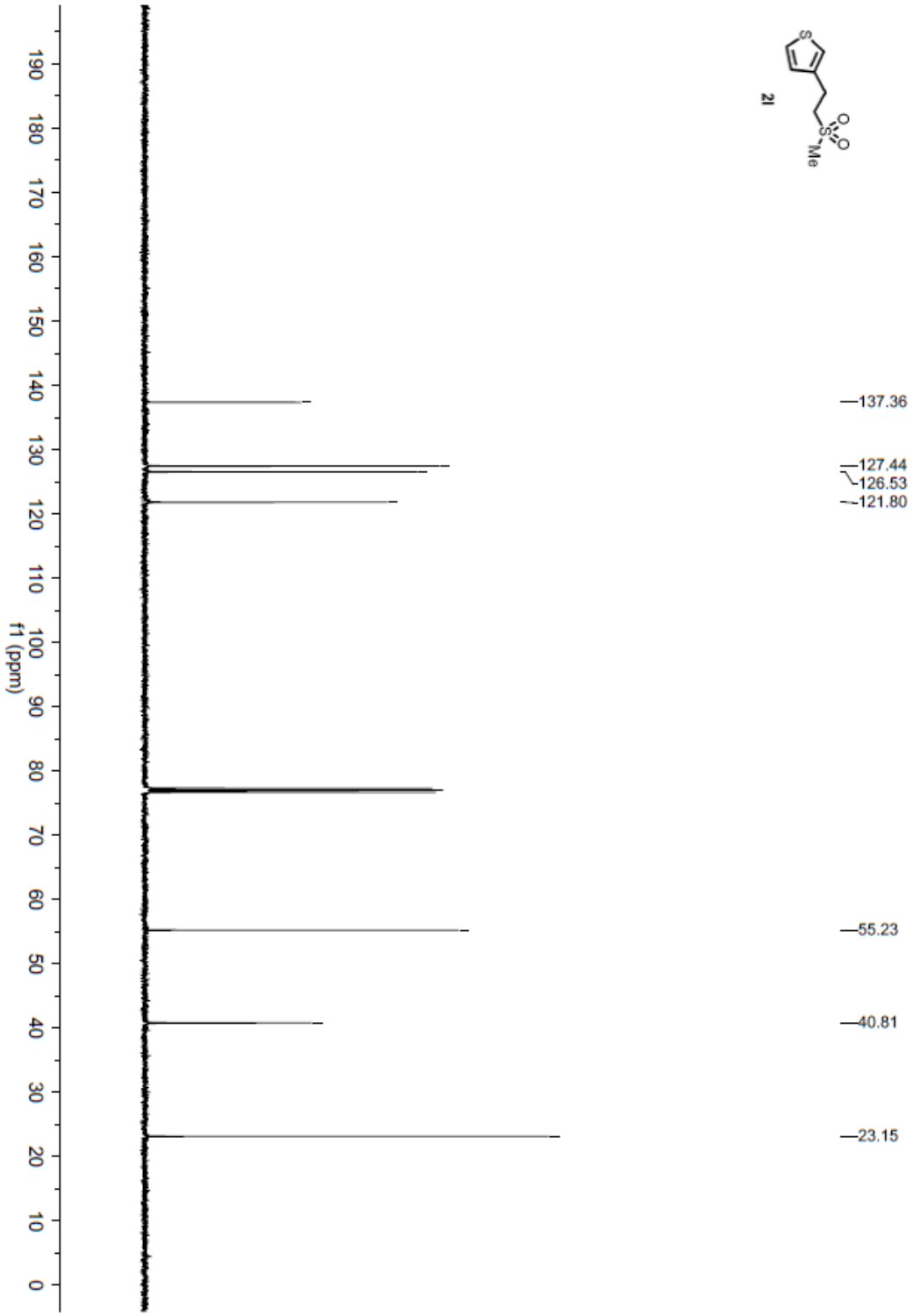

2j
MeO
O
O
S
Me
7.17
7.15
6.88
6.88
6.87
6.86
3.80
3.29
3.28
3.27
3.26
3.13
3.12
3.11
3.09
2.81
2.01
1.98
3.02
2.02
2.03
3.00
f1 (ppm)

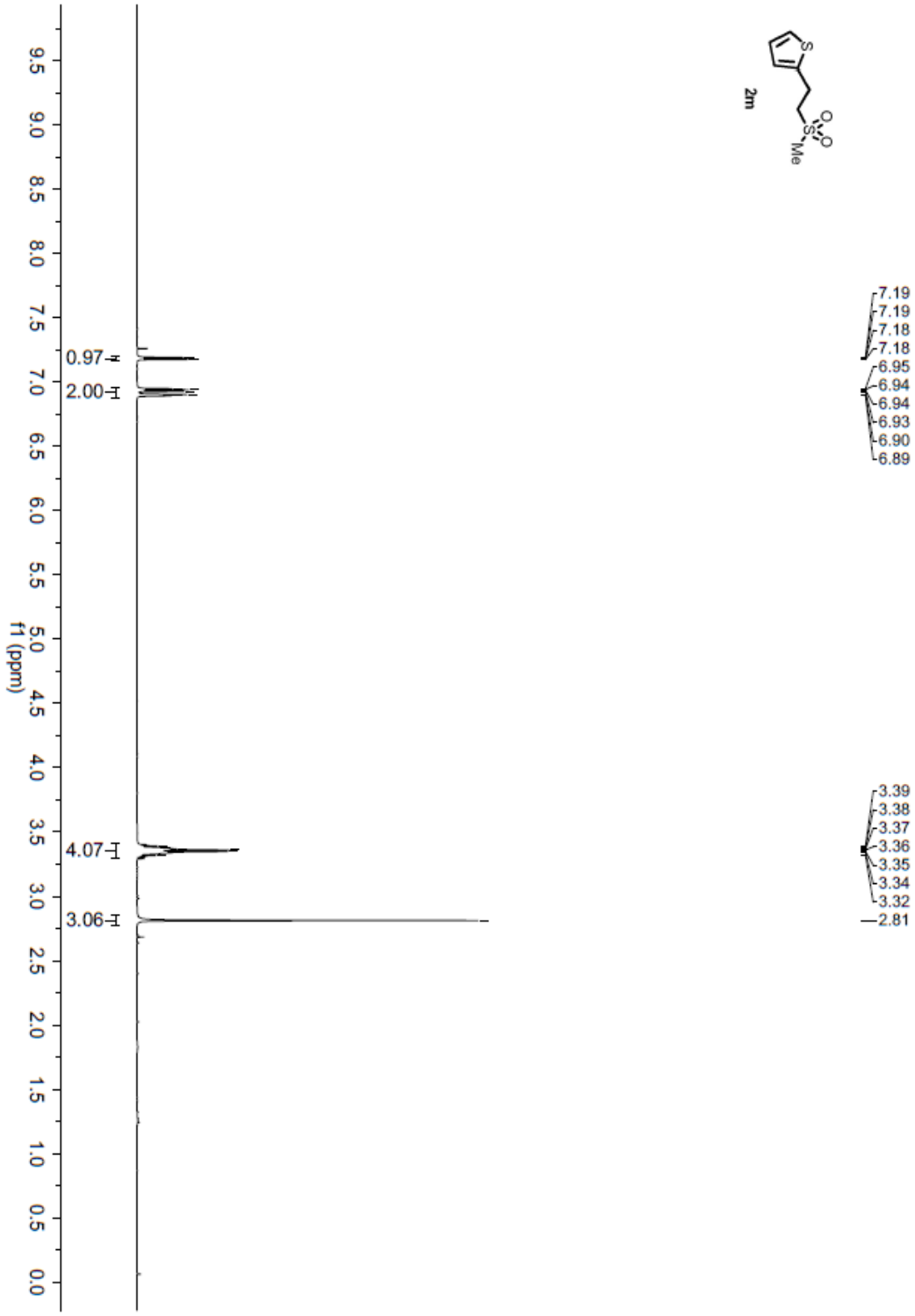

MeO
O
O
S
Me
2j
158.58
129.37
129.20
114.27
56.30
55.21
40.95
27.70
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

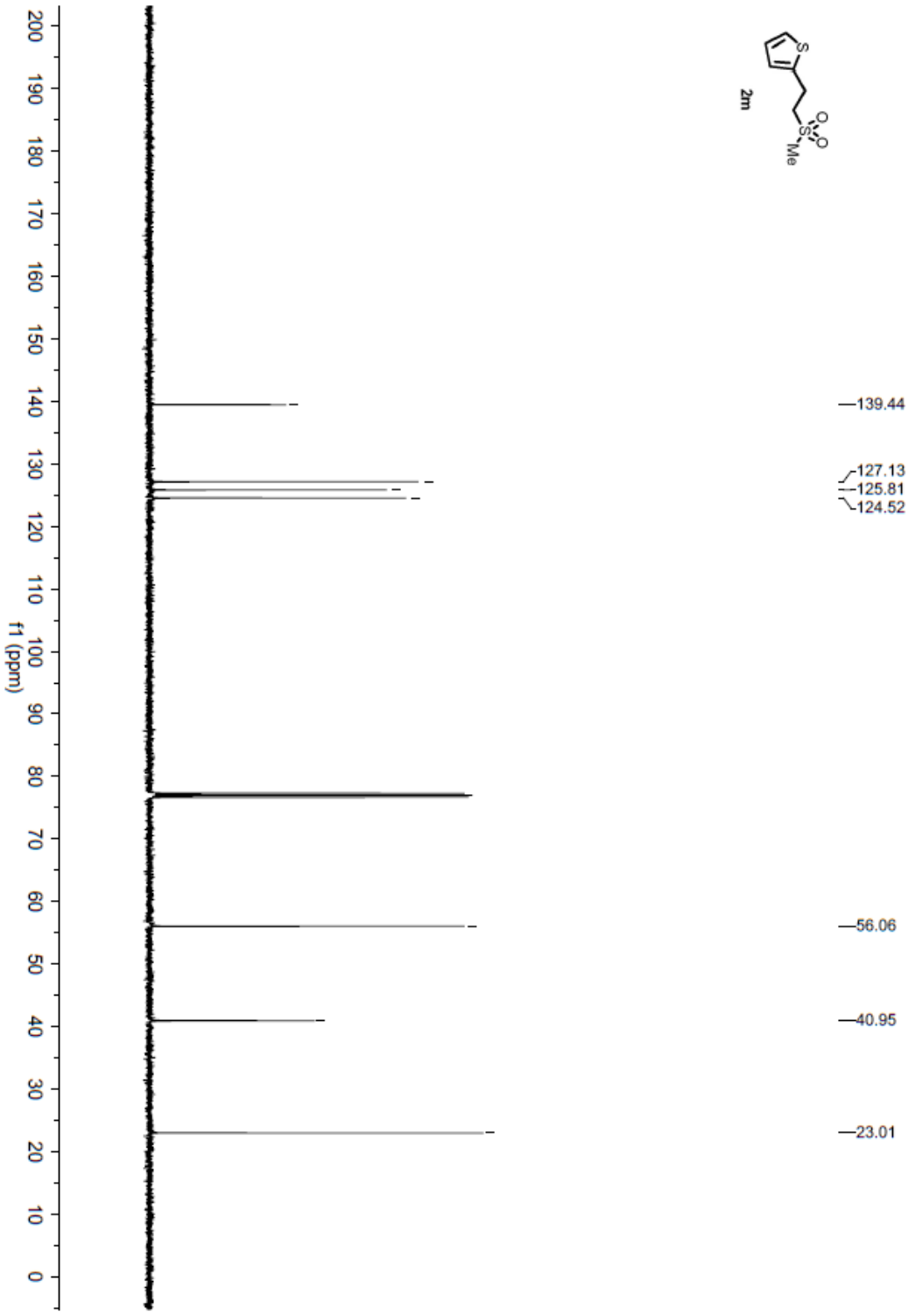

2k
6.74
6.72
6.69
6.68
6.67
6.67
6.65
6.65
5.91
3.25
3.23
3.22
3.21
3.06
3.05
3.04
3.02
2.81
3.00
2.01
1.98
1.98
2.97
f1 (ppm)

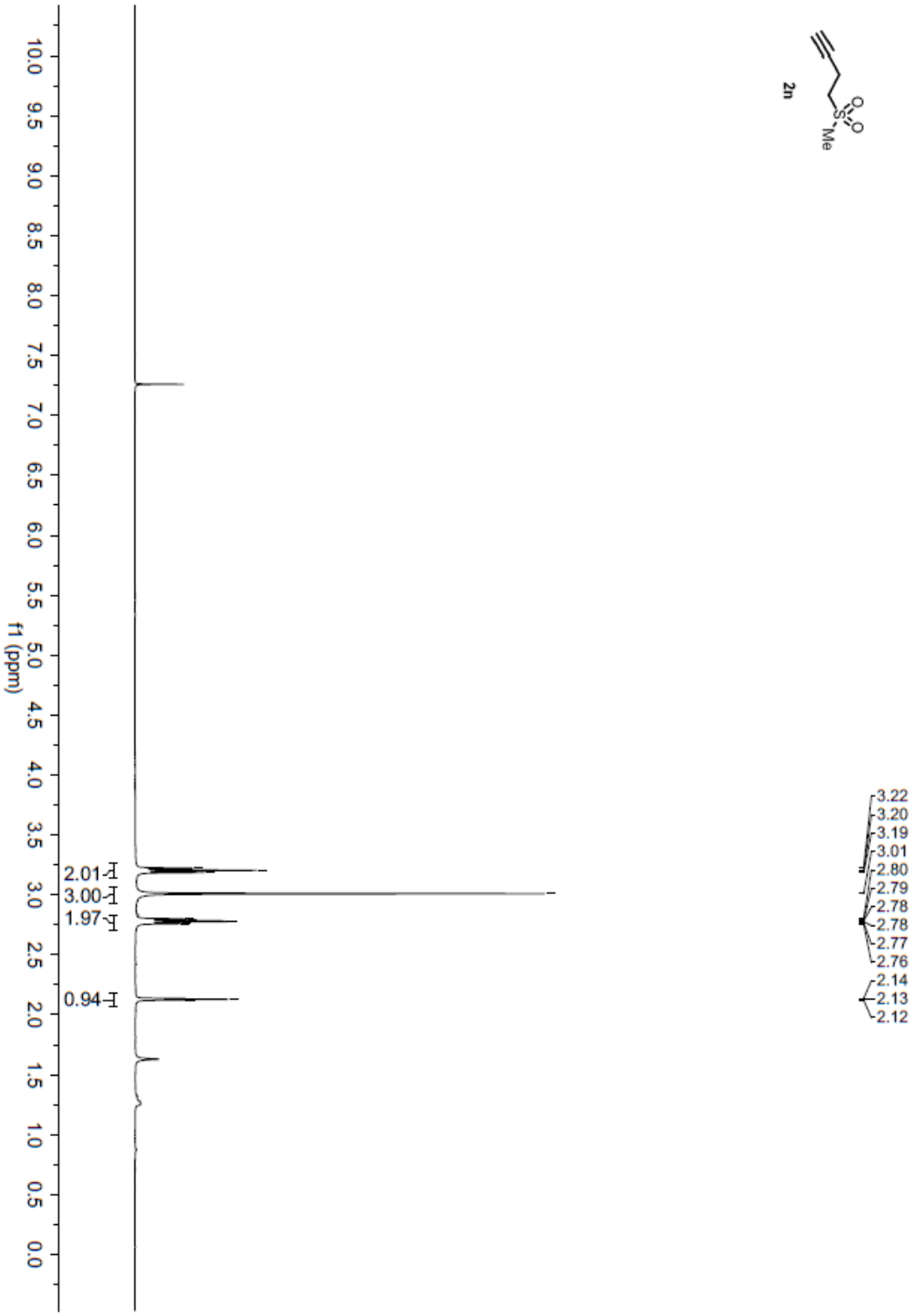

2k
147.91
146.51
130.91
121.33
108.61
108.46
100.99
56.15
40.89
28.19
f1 (ppm)

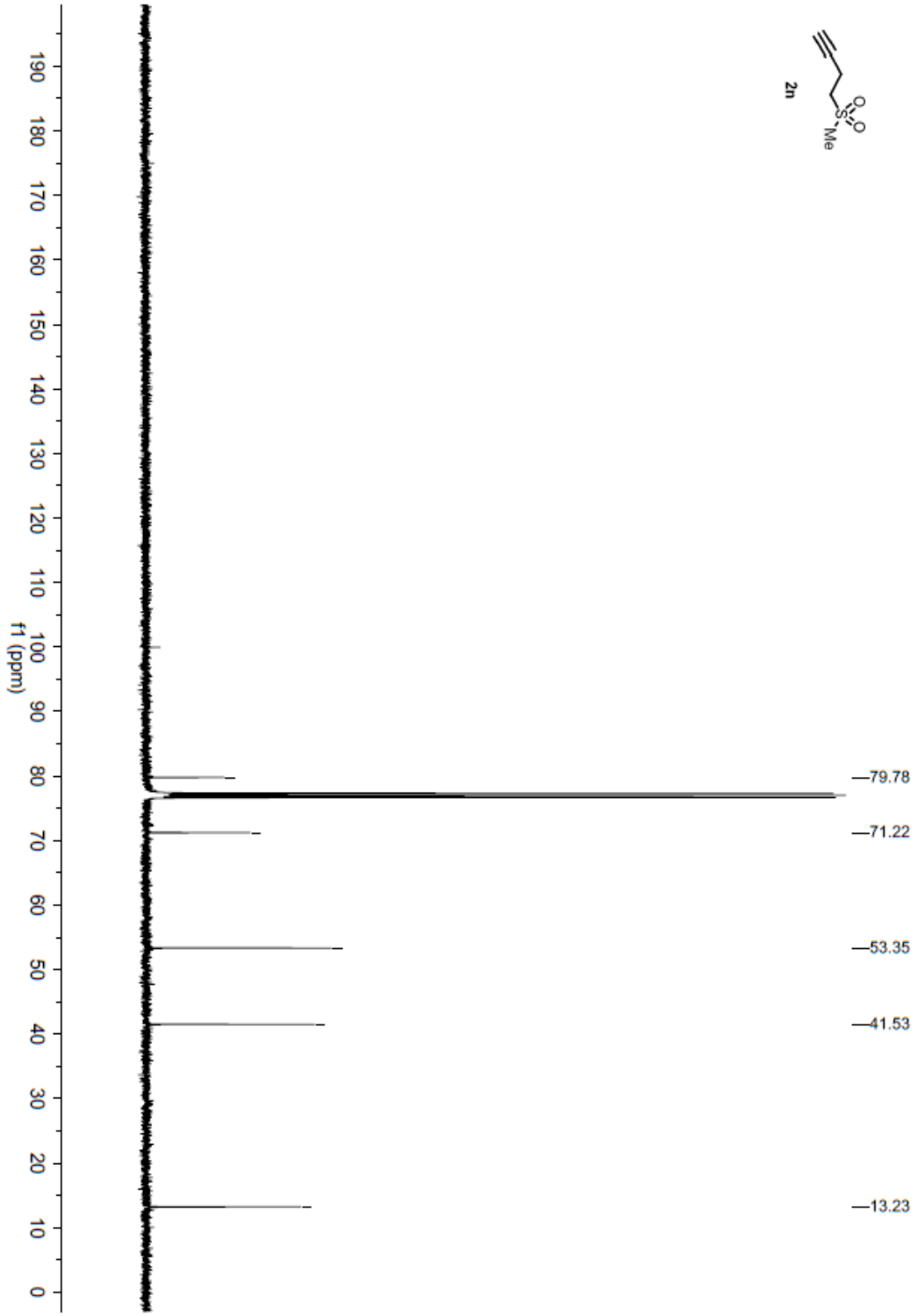

2l
7.31
7.30
7.30
7.29
7.07
7.07
7.06
6.97
6.97
6.96
6.95
3.31
3.29
3.28
3.27
3.19
3.18
3.17
3.15
2.79
1.00
1.00
0.99
2.01
2.00
3.02
f1 (ppm)

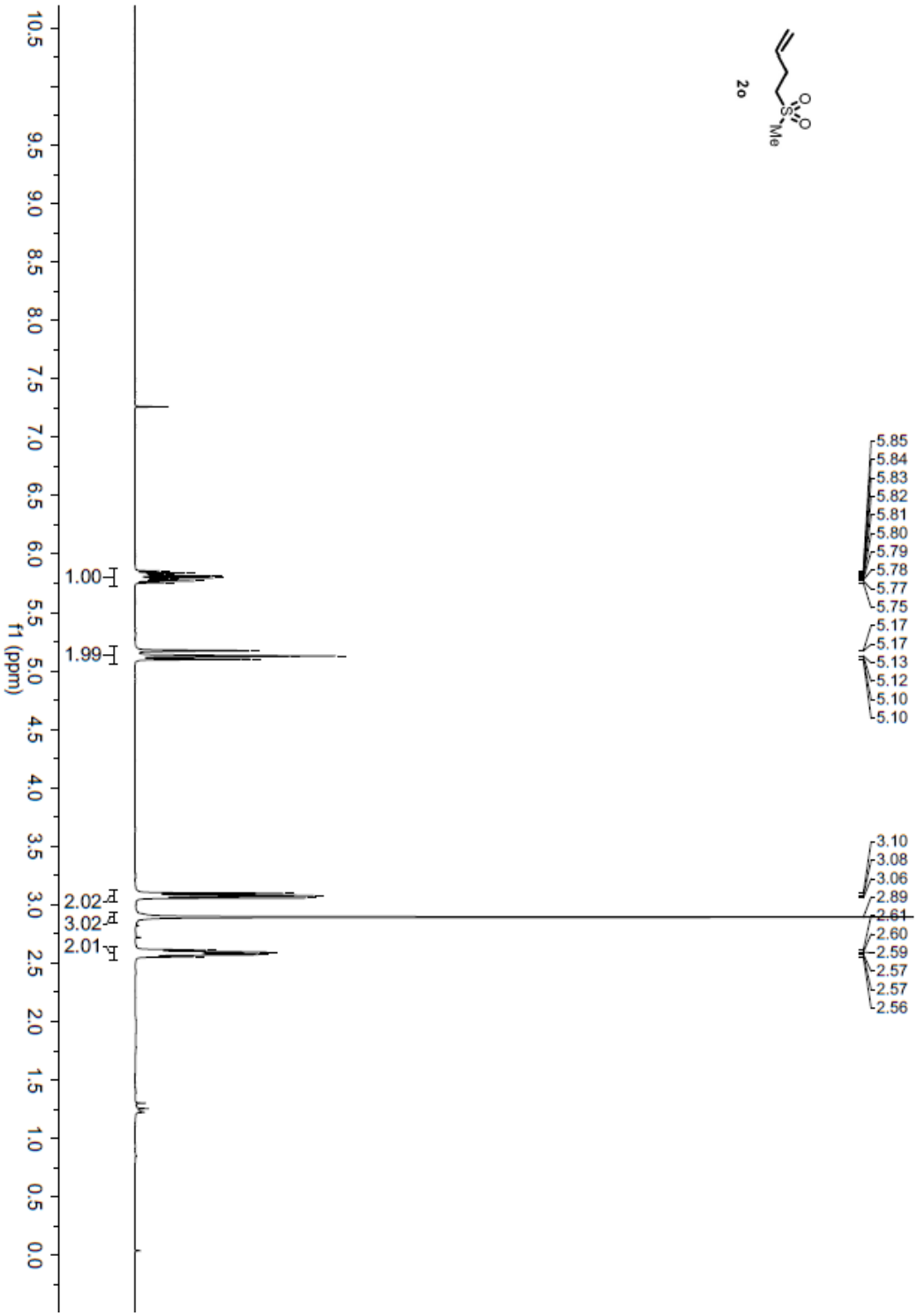

2l
137.36
127.44
126.53
121.80
55.23
40.81
23.15
f1 (ppm)

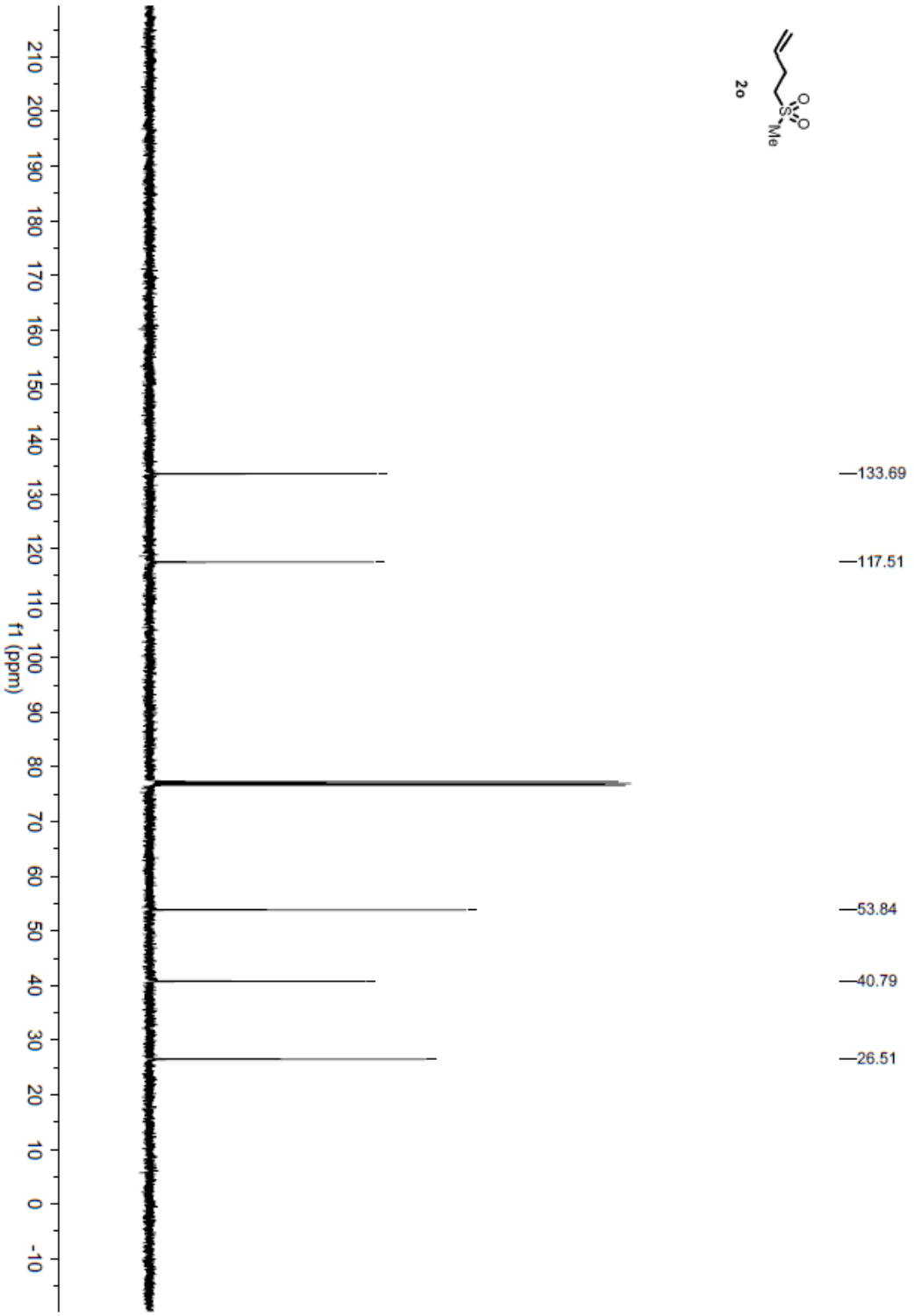

2m
7.19
7.19
7.18
7.18
6.95
6.94
6.94
6.93
6.90
6.89
3.39
3.38
3.37
3.36
3.35
3.34
3.32
2.81
0.97
2.00
4.07
3.06
f1 (ppm)

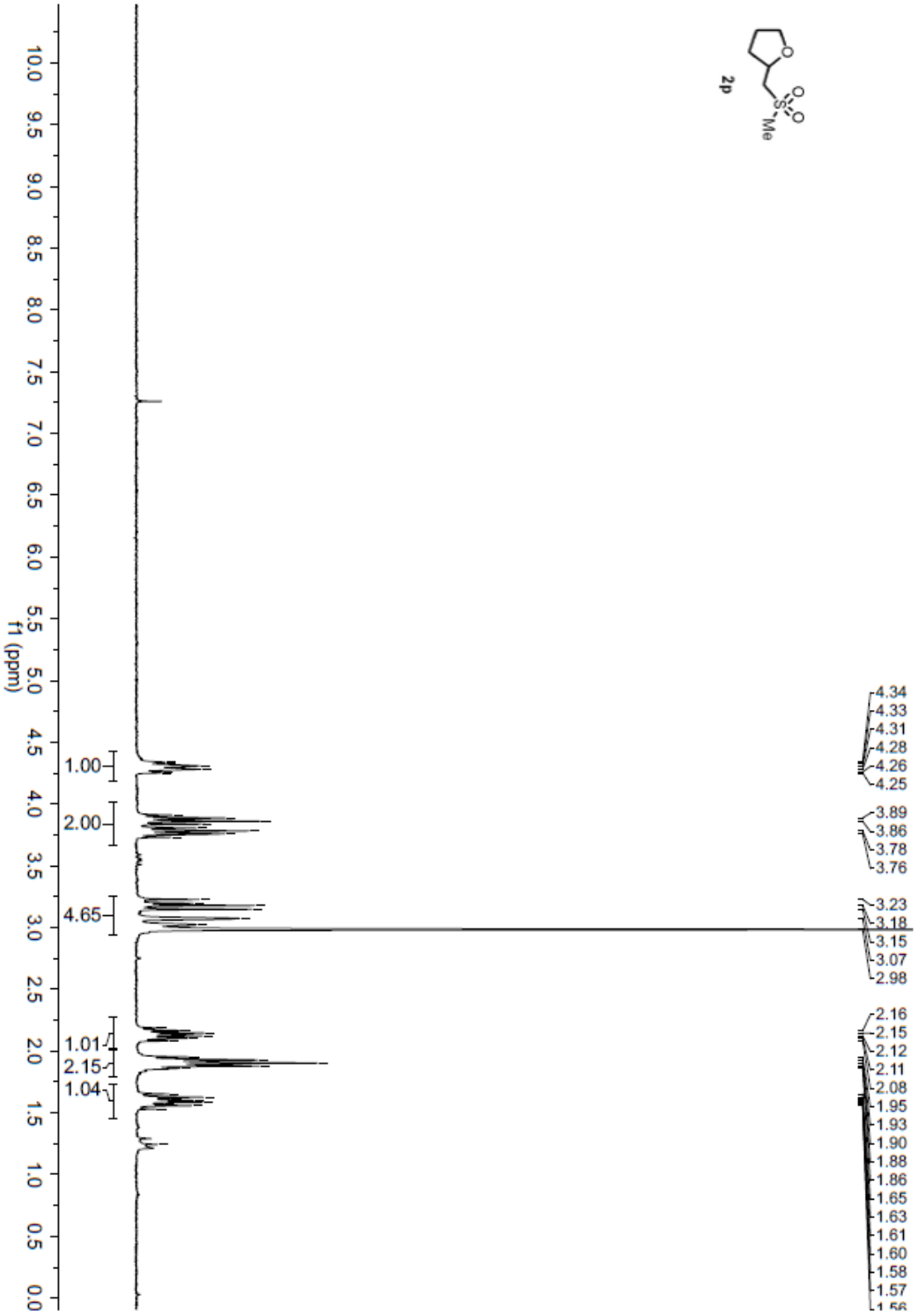

2m
139.44
127.13
125.81
124.52
56.06
40.95
23.01
f1 (ppm)

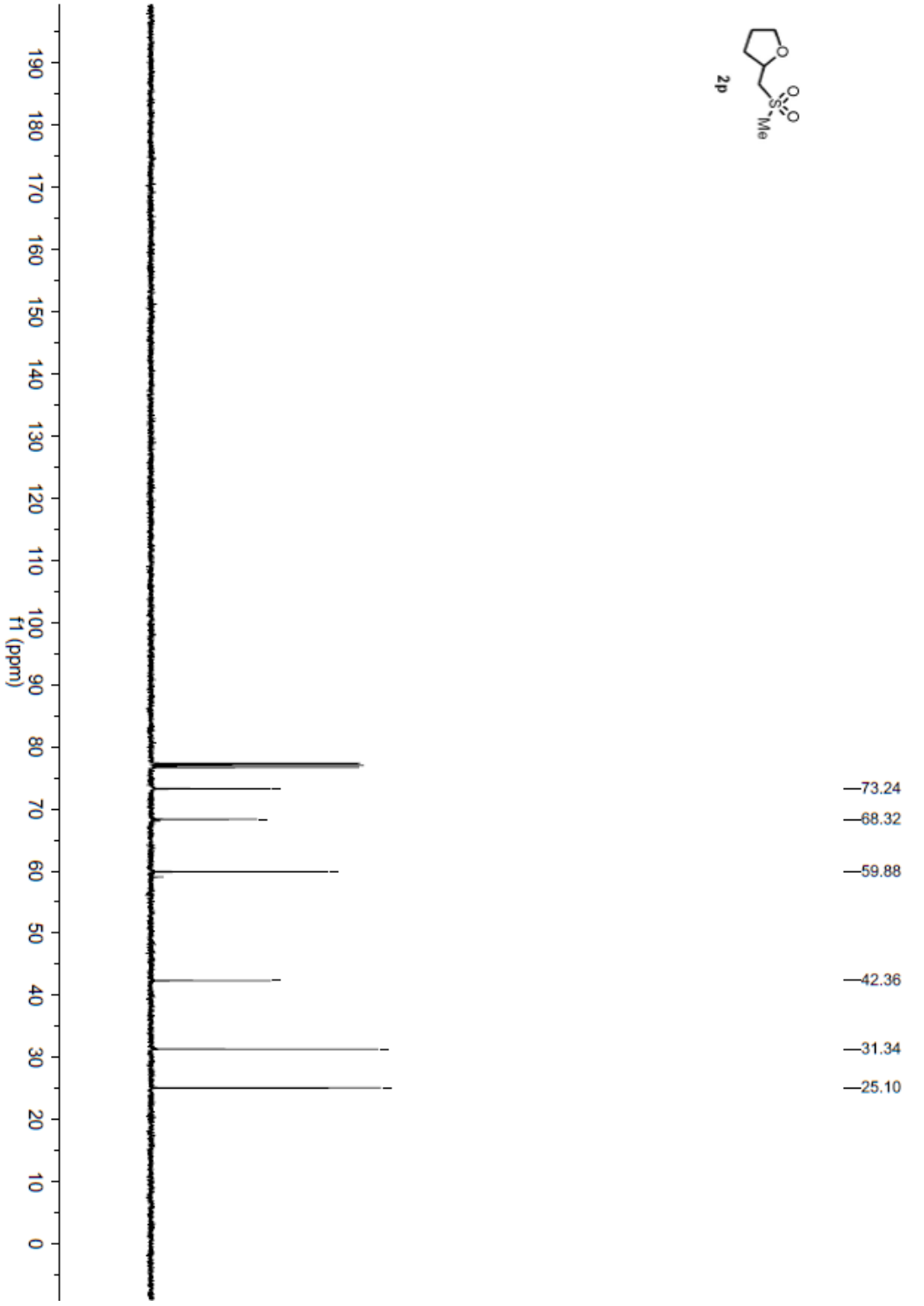

2n
Me
3.22
3.20
3.19
3.01
2.80
2.79
2.78
2.78
2.77
2.76
2.14
2.13
2.12
2.01
3.00
1.97
0.94
f1 (ppm)

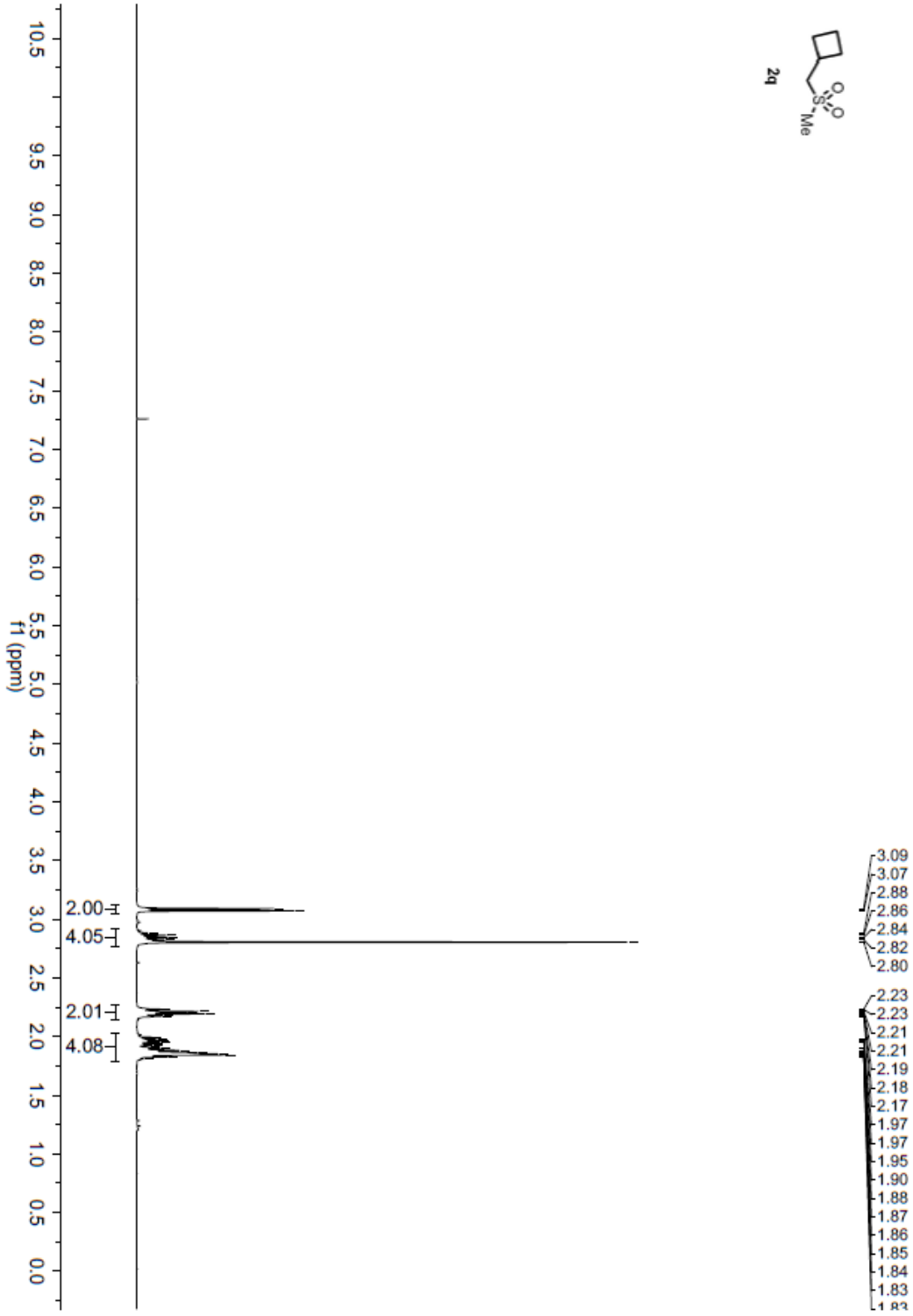

2n
Me
79.78
71.22
53.35
41.53
13.23
f1 (ppm)

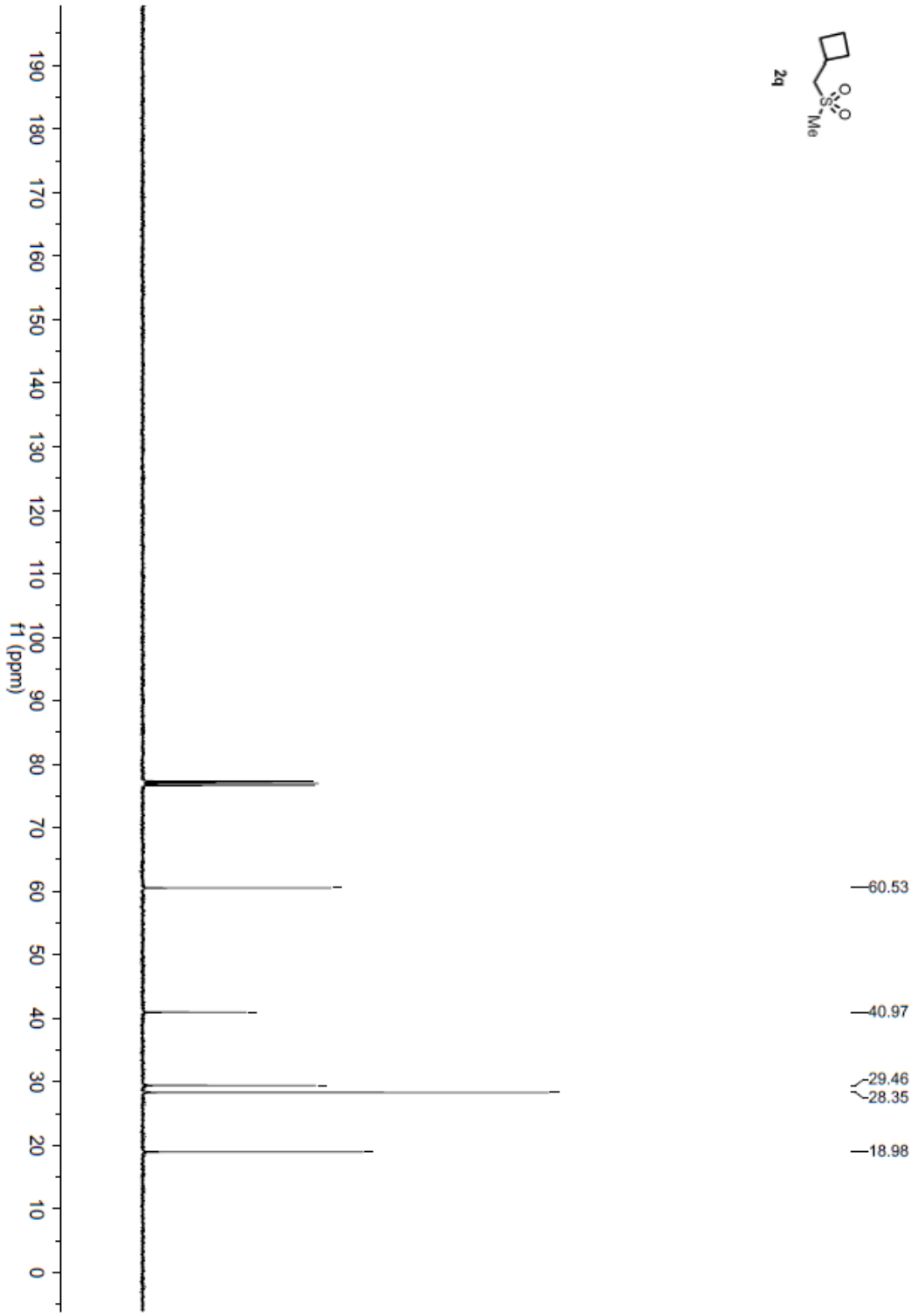

2o
Me
5.85
5.84
5.83
5.82
5.81
5.80
5.79
5.78
5.77
5.75
5.17
5.17
5.13
5.12
5.10
5.10
3.10
3.08
3.06
2.89
2.61
2.60
2.59
2.57
2.57
2.56
1.00
1.99
2.02
3.02
2.01
f1 (ppm)

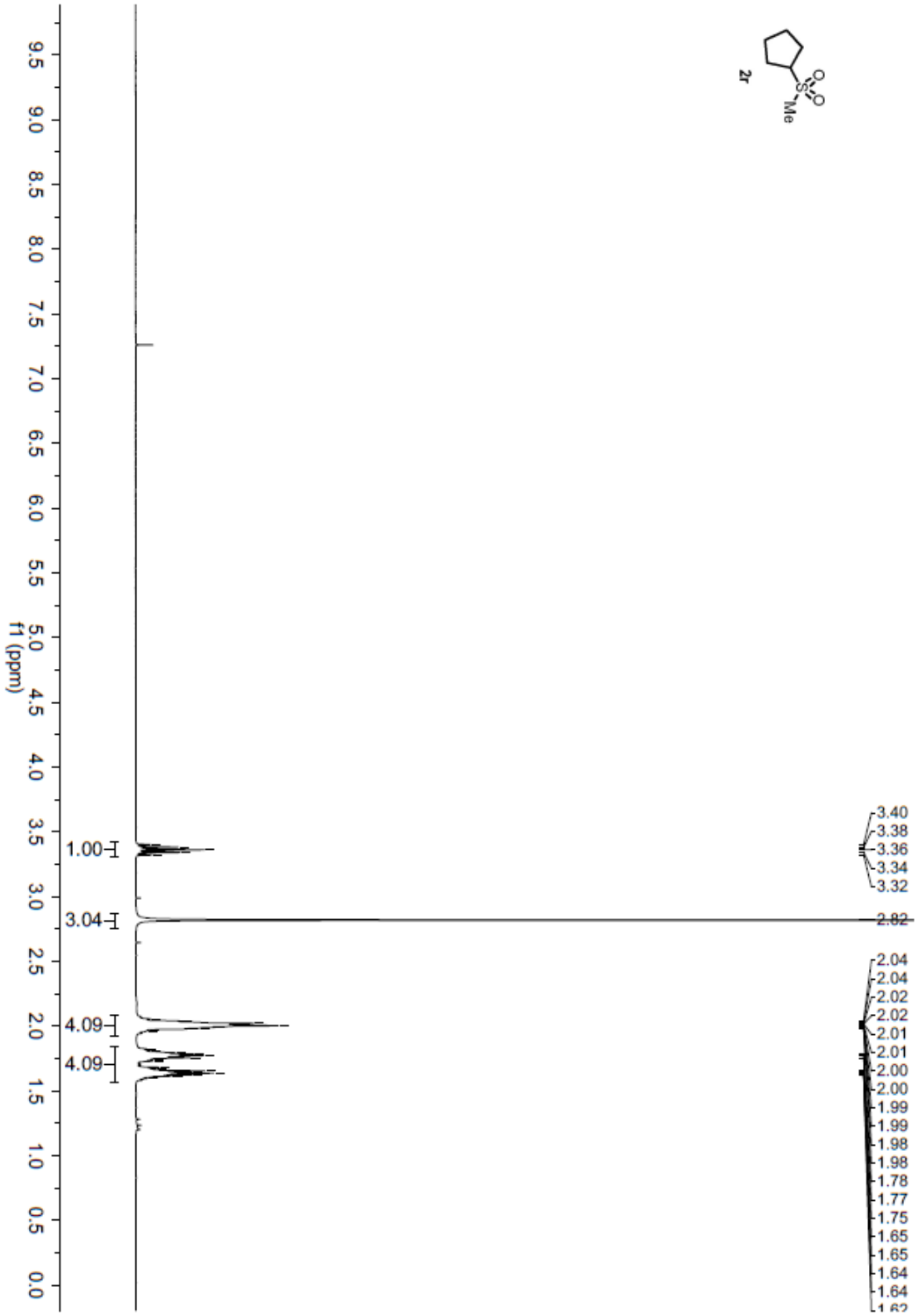

2o
Me
133.69
117.51
53.84
40.79
26.51
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

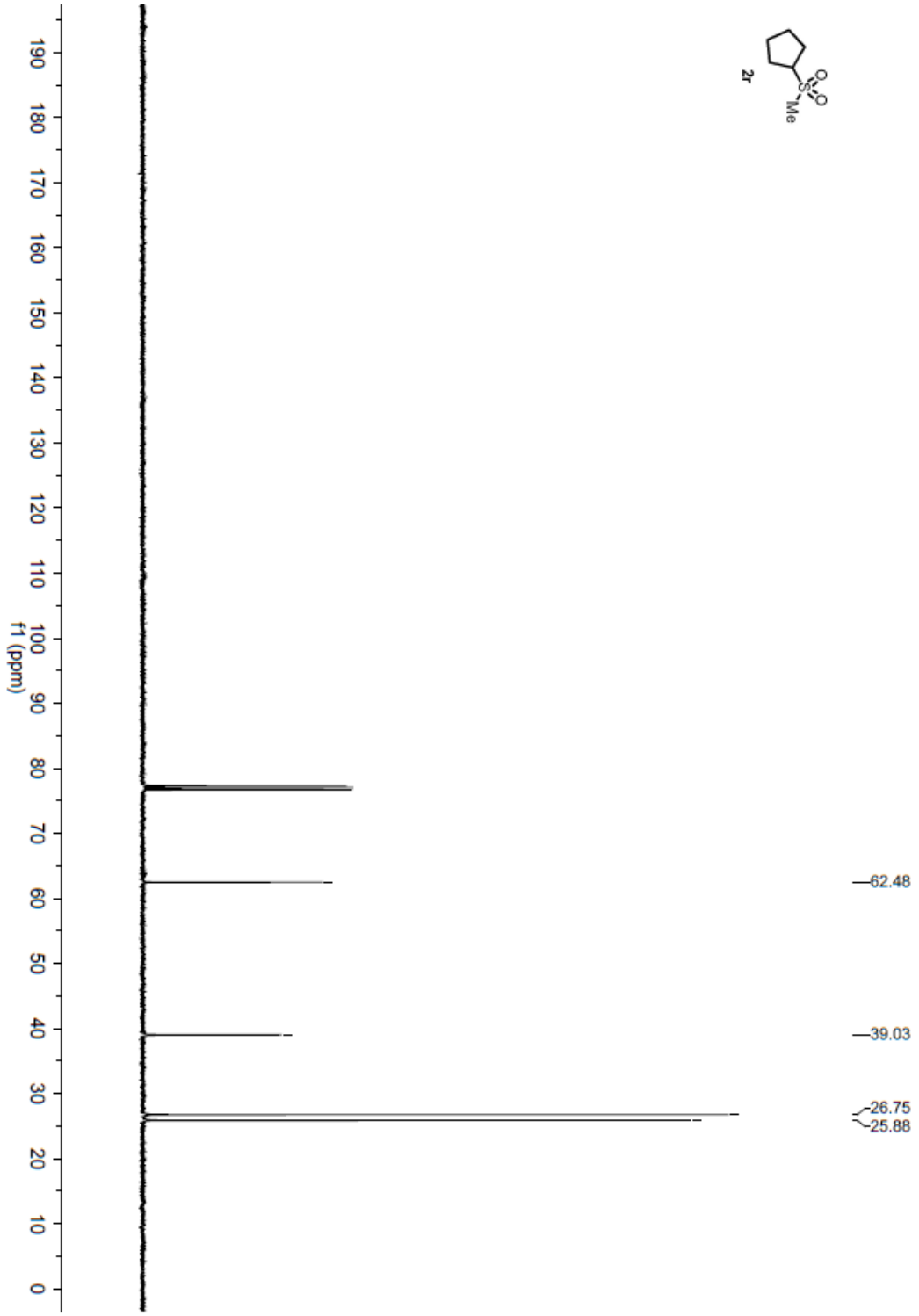

2p
f1 (ppm)
1.00
2.00
4.65
1.01
2.15
1.04
4.34
4.33
4.31
4.28
4.26
4.25
3.89
3.86
3.78
3.76
3.23
3.18
3.15
3.07
2.98
2.16
2.15
2.12
2.11
2.08
1.95
1.93
1.90
1.88
1.86
1.65
1.63
1.61
1.60
1.58
1.57

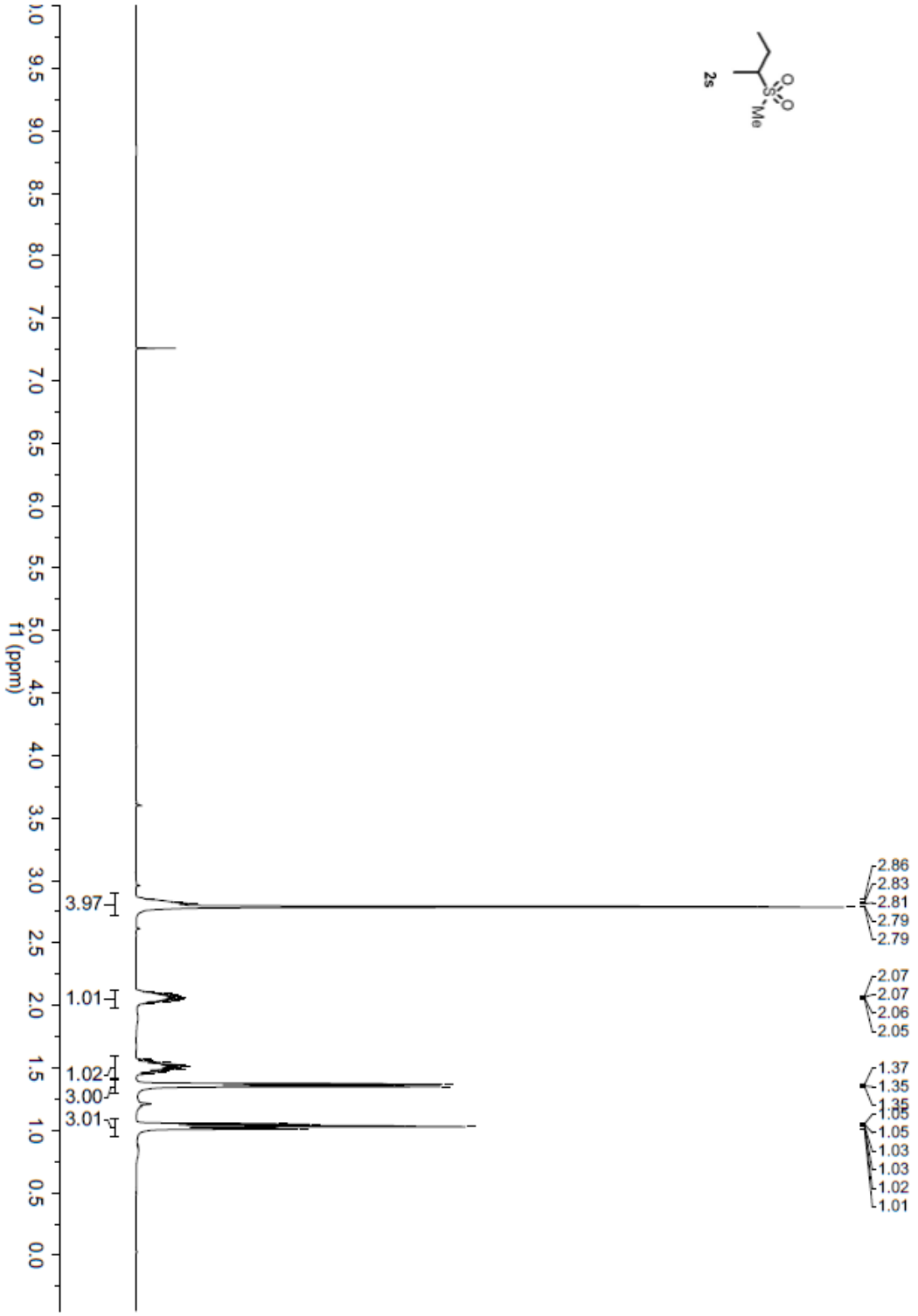

2p
O
O
O
S
Me
73.24
68.32
59.88
42.36
31.34
25.10
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

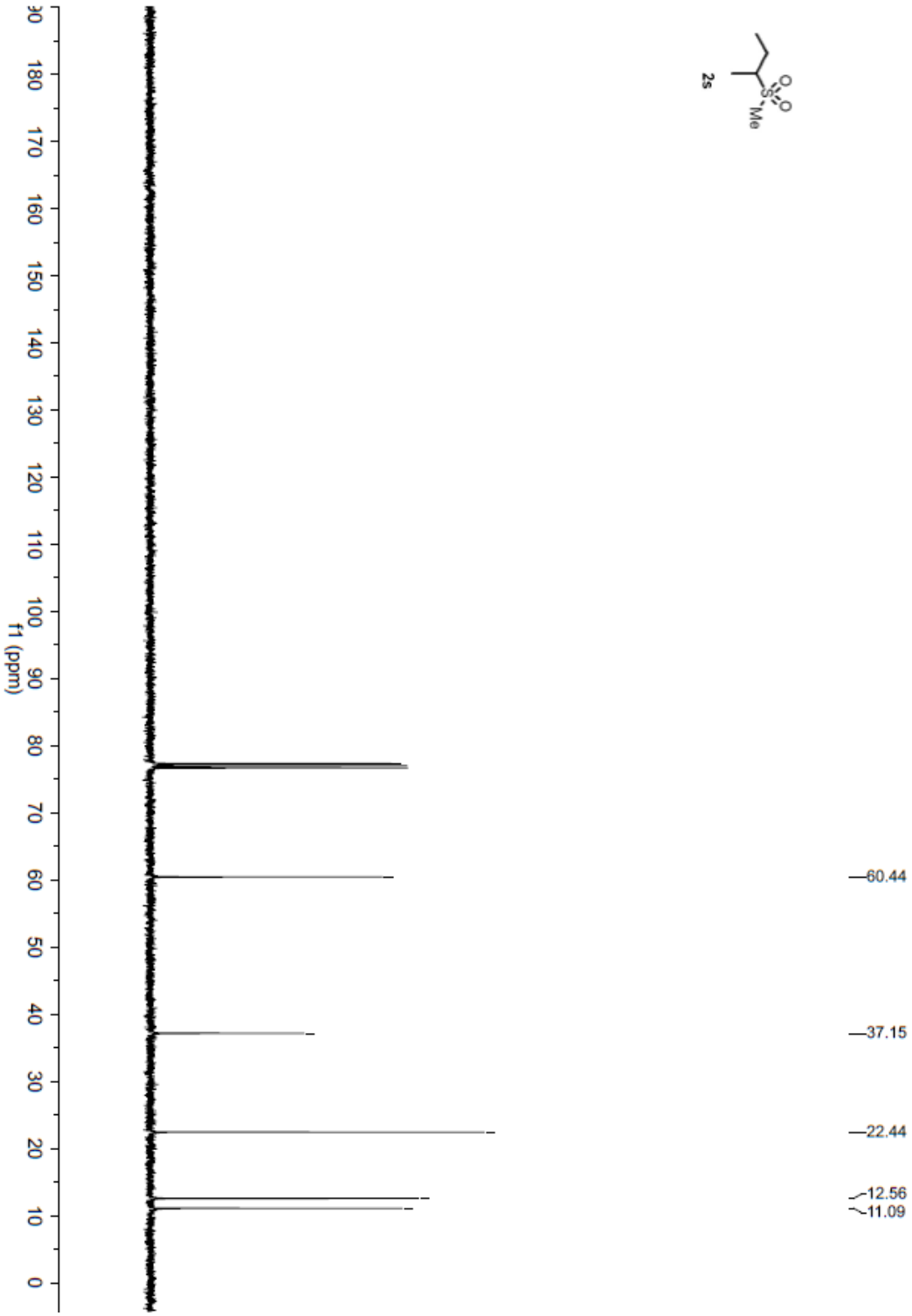

2q
Me
f1 (ppm)
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
2.00
4.05
2.01
4.08
3.09
3.07
2.88
2.86
2.84
2.82
2.80
2.23
2.23
2.21
2.21
2.19
2.18
2.17
1.97
1.97
1.95
1.90
1.88
1.87
1.86
1.85
1.84
1.83

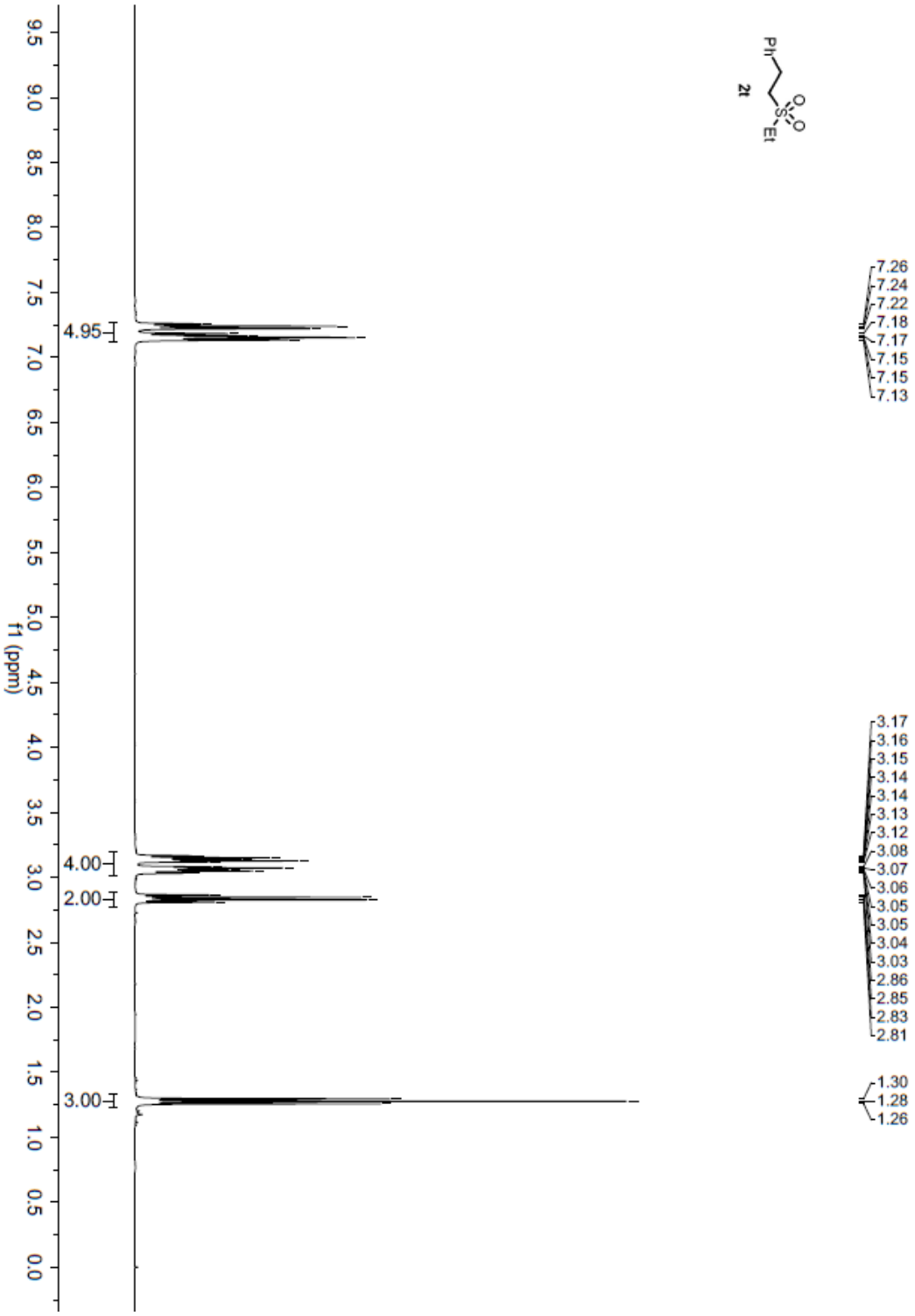

2q
O
O
S
Me
60.53
40.97
29.46
28.35
18.98
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

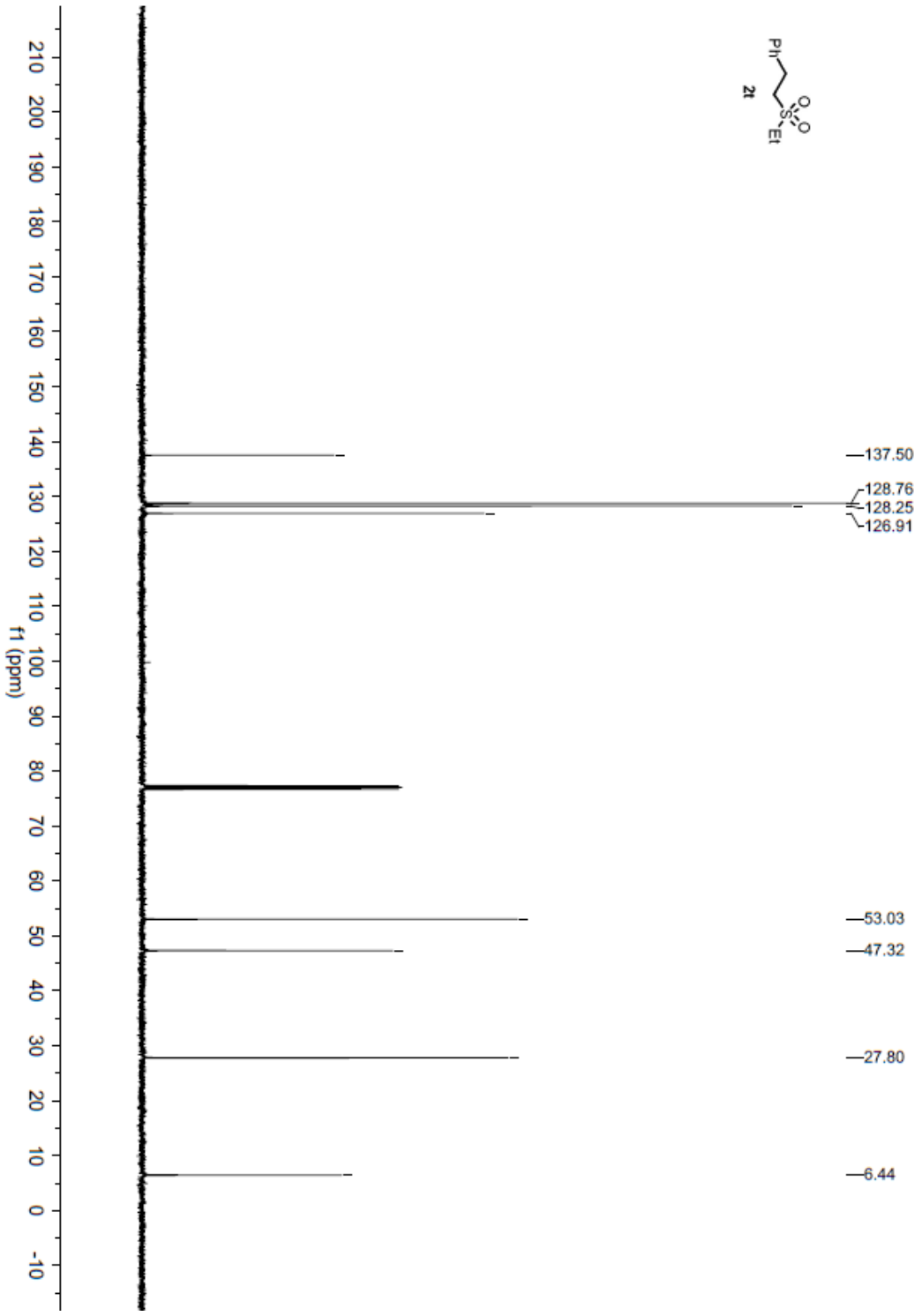

2r
O
O
S
Me
f1 (ppm)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1.00
3.04
4.09
4.09
3.40
3.38
3.36
3.34
3.32
2.82
2.04
2.04
2.02
2.02
2.01
2.01
2.00
2.00
1.99
1.99
1.98
1.98
1.78
1.77
1.75
1.65
1.65
1.64
1.64

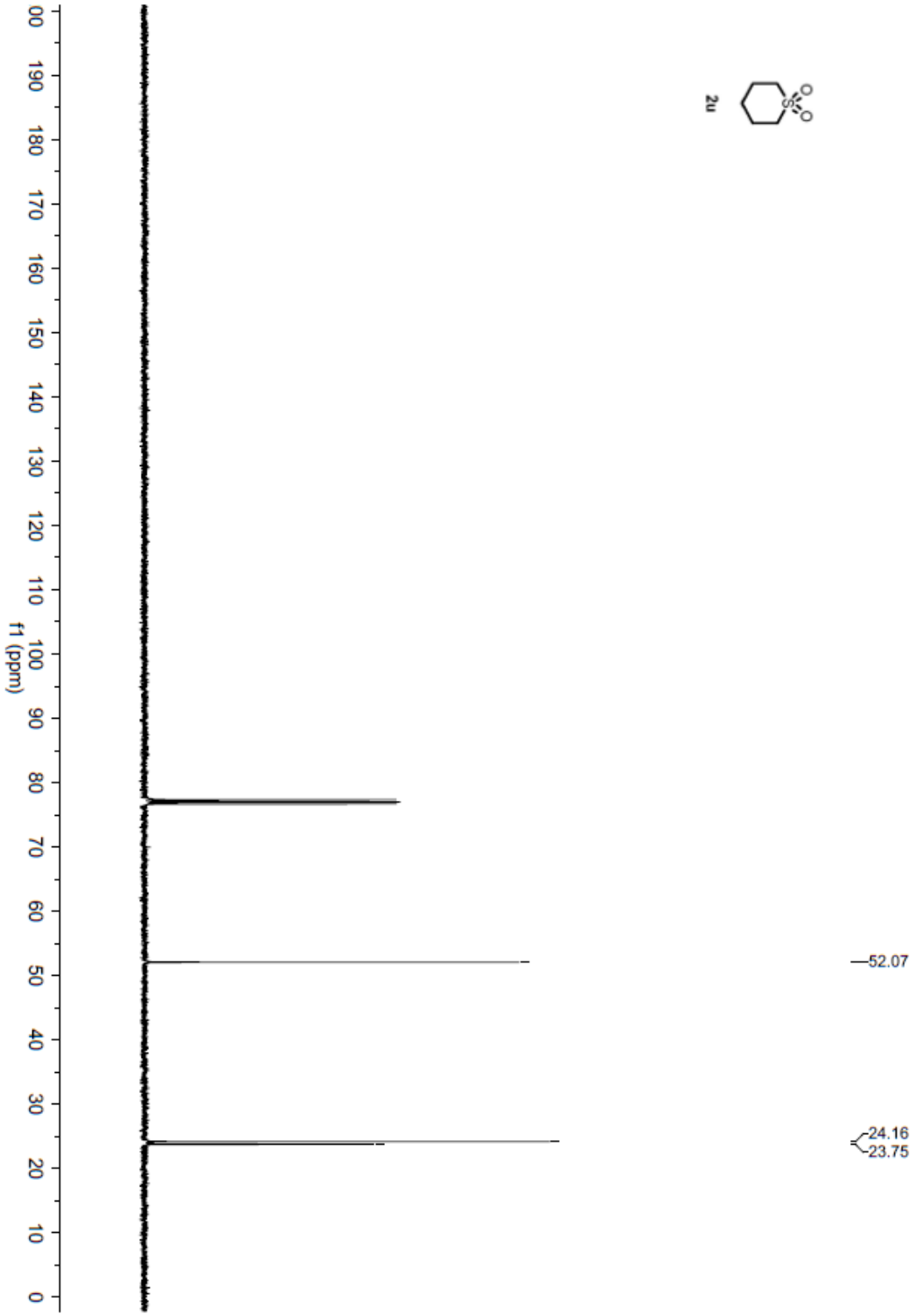

2r
Me
62.48
39.03
26.75
25.88
f1 (ppm)

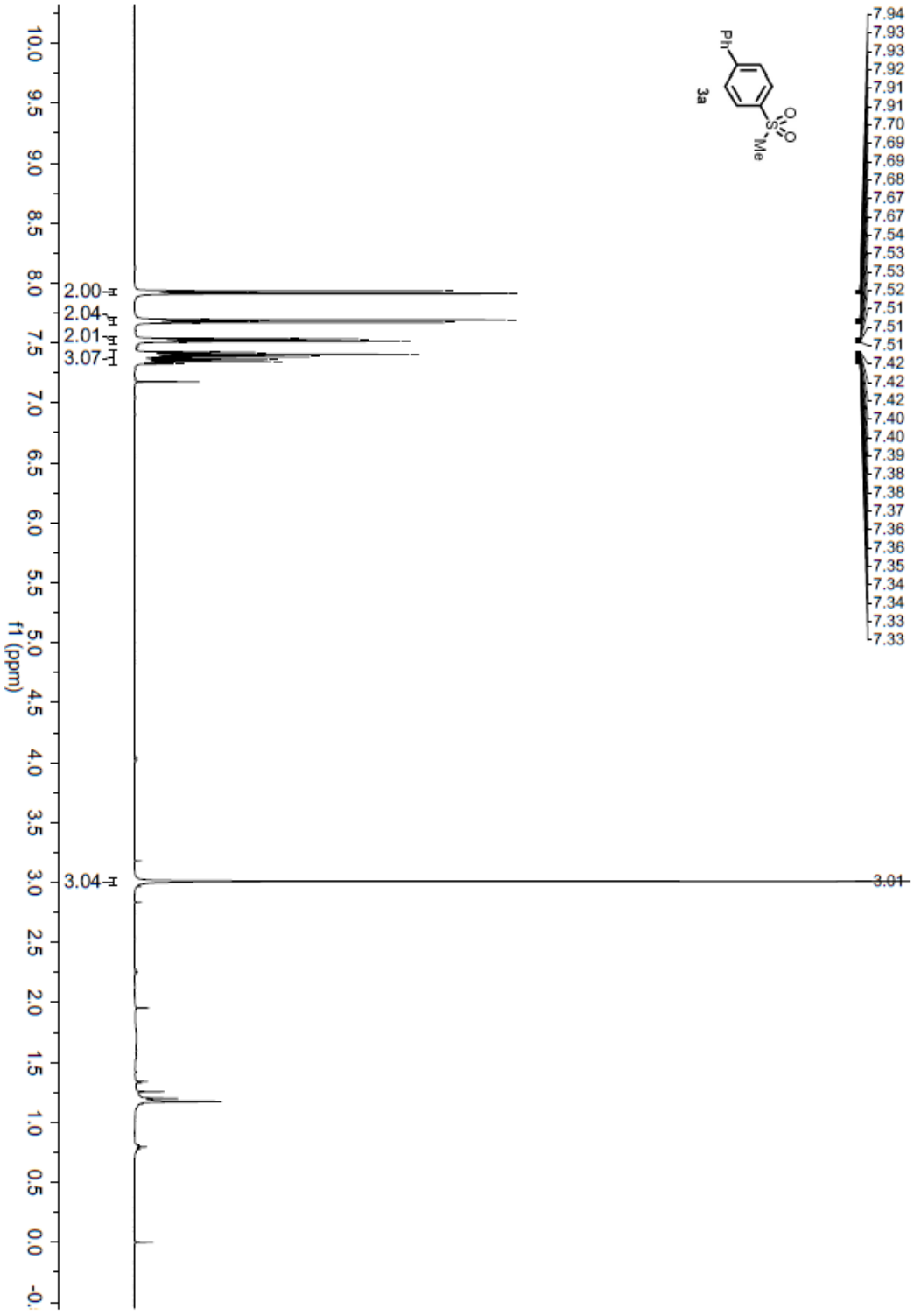

2s
O
O
S
Me
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
3.97
1.01
1.02
3.00
3.01
2.86
2.83
2.81
2.79
2.79
2.07
2.07
2.06
2.05
1.37
1.35
1.35
1.05
1.05
1.03
1.03
1.02
1.01

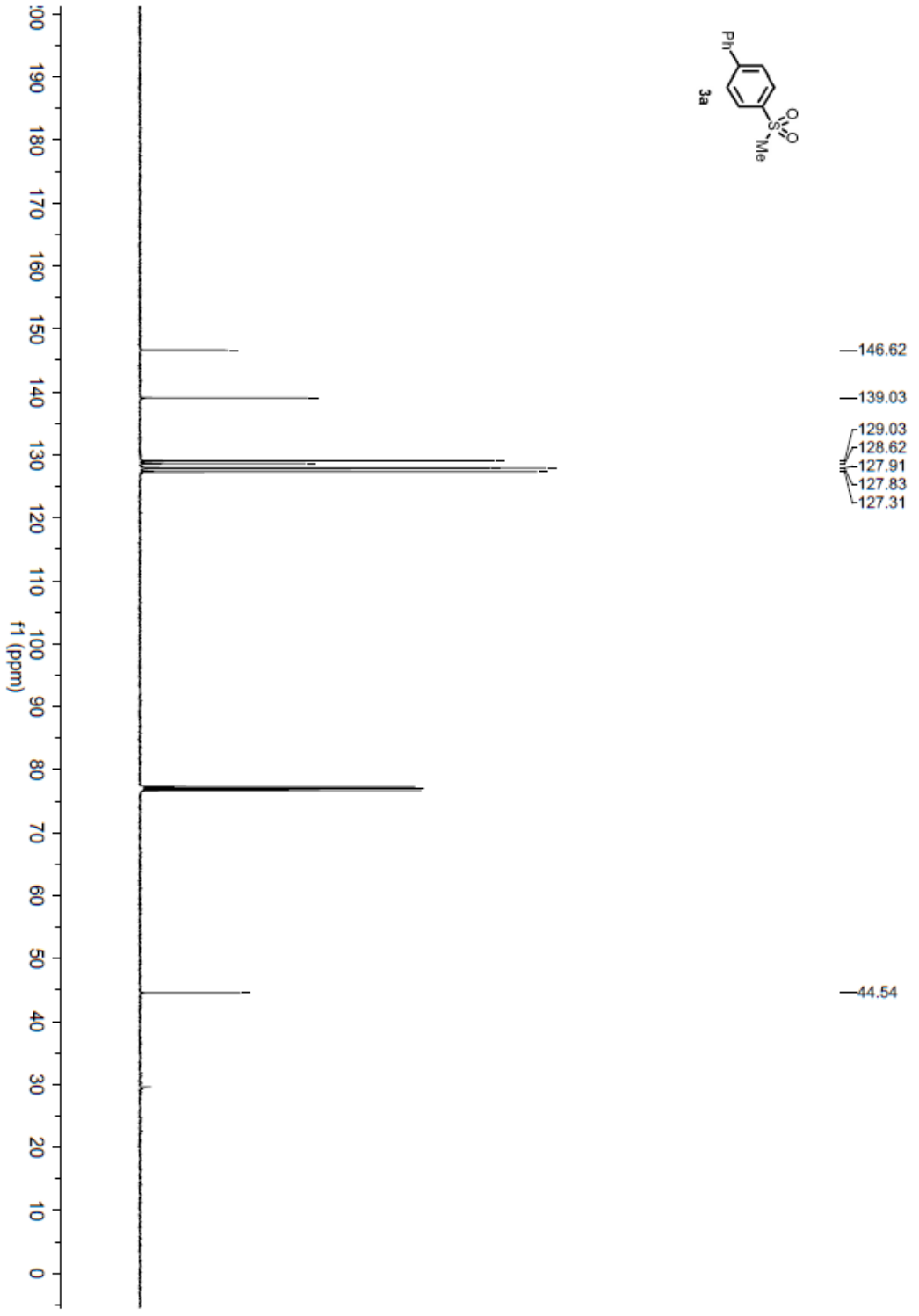

2s
Me
60.44
37.15
22.44
12.56
11.09
f1 (ppm)

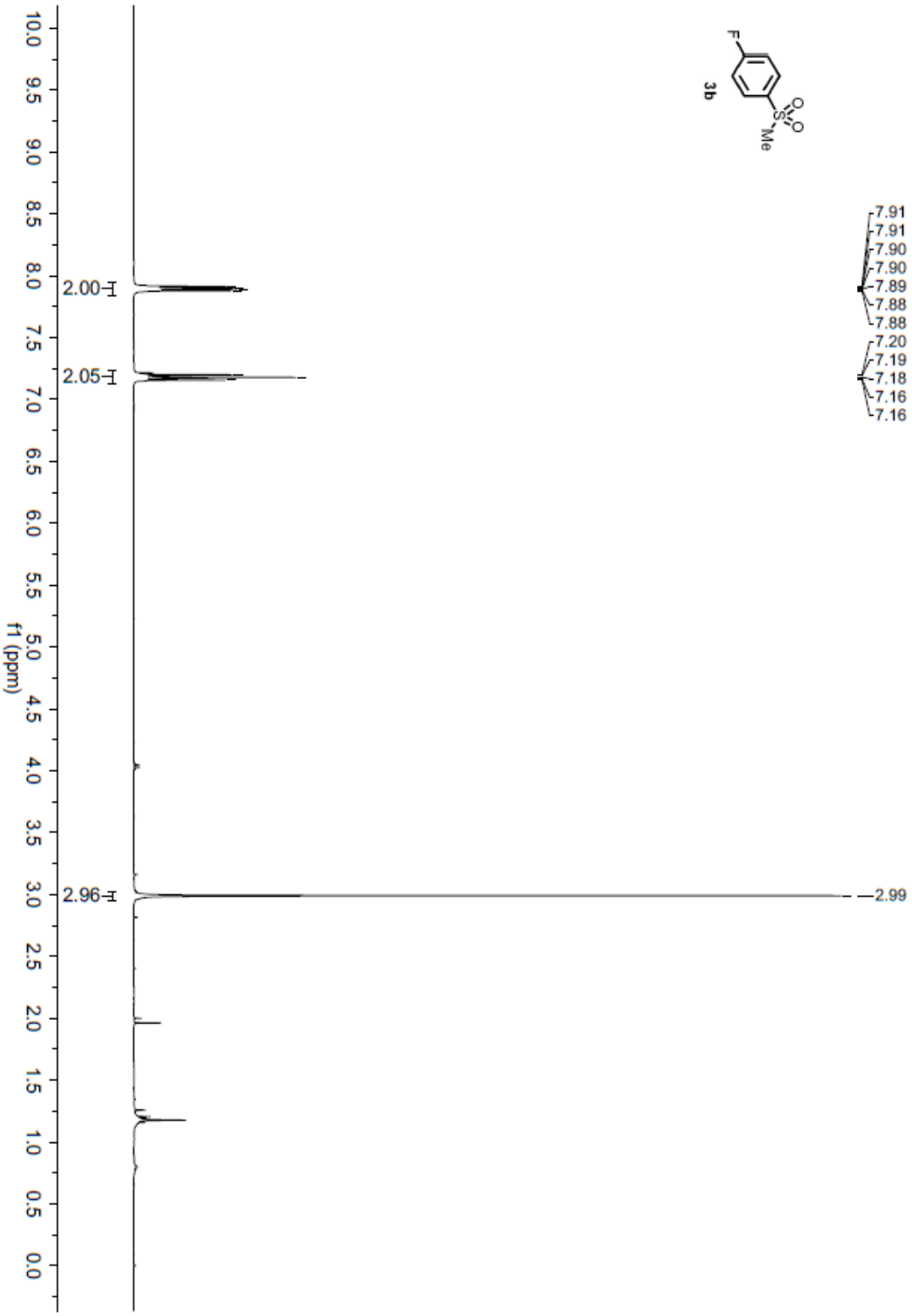

2t
7.26
7.24
7.22
7.18
7.17
7.15
7.15
7.13
3.17
3.16
3.15
3.14
3.14
3.13
3.12
3.08
3.07
3.06
3.05
3.05
3.04
3.03
2.86
2.85
2.83
2.81
1.30
1.28
1.26
4.95
4.00
2.00
3.00
f1 (ppm)

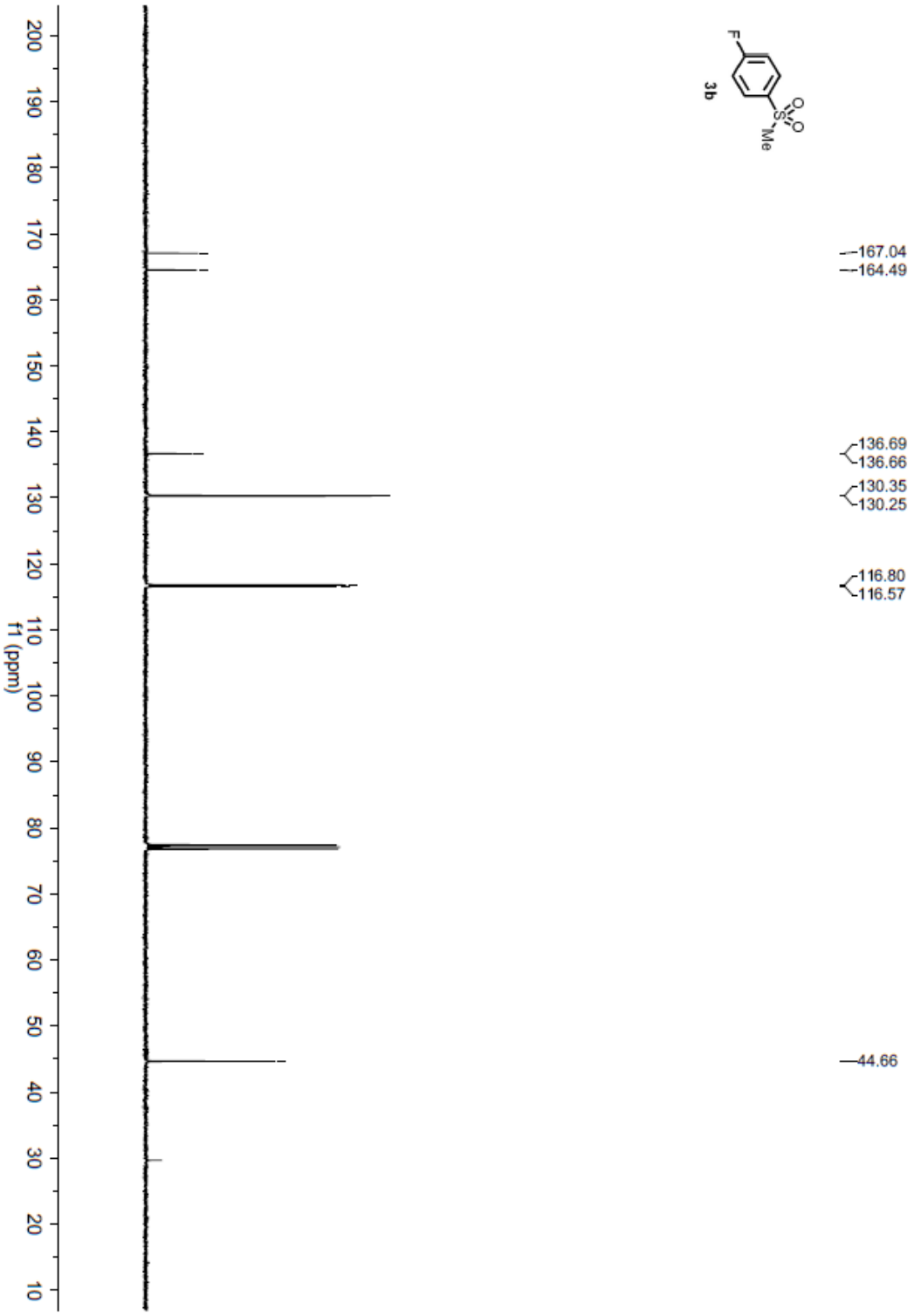

2t
Ph
O
S
O
Et
137.50
128.76
128.25
126.91
53.03
47.32
27.80
6.44
f1 (ppm)

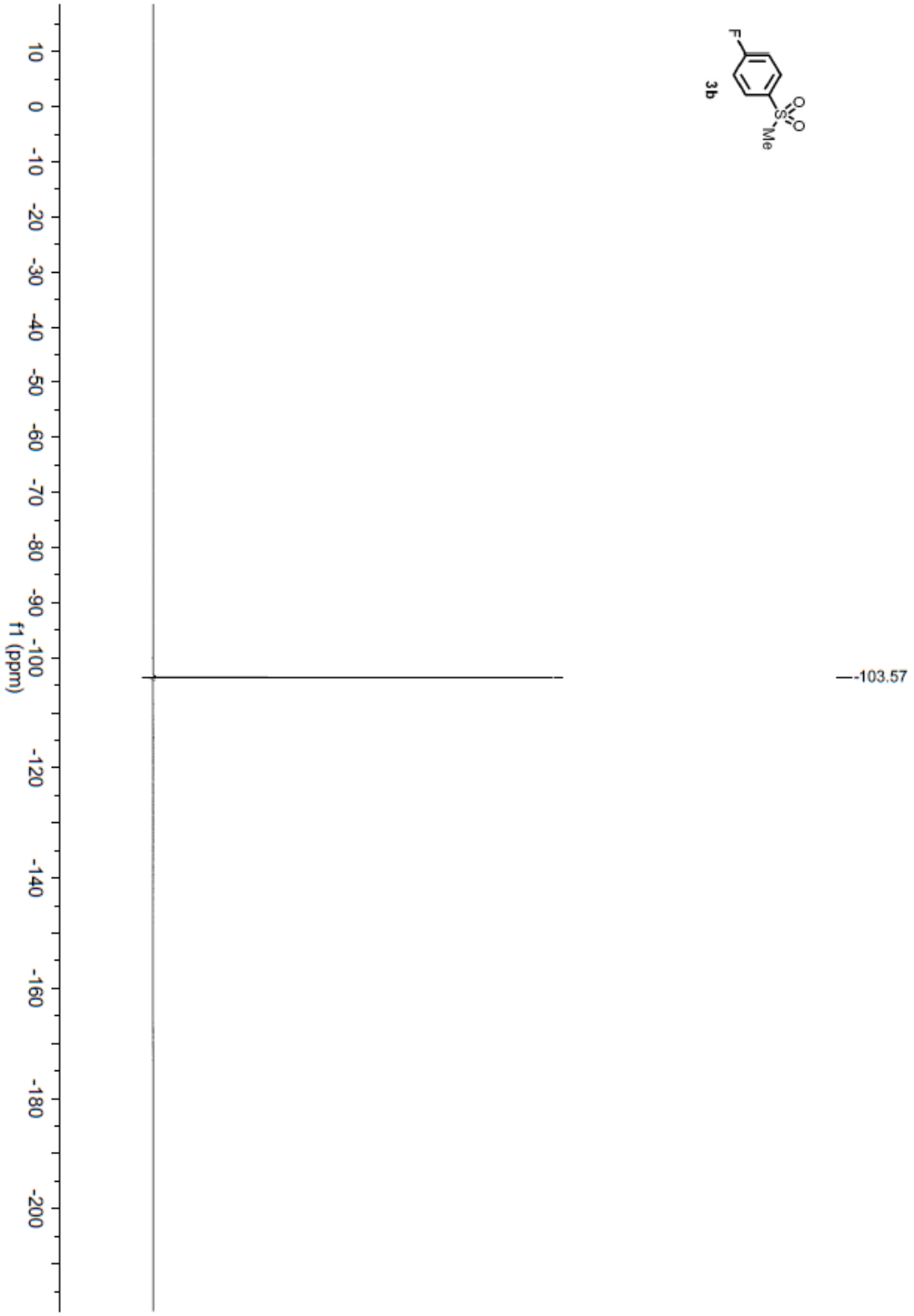

2u
52.07
24.16
23.75
f1 (ppm)

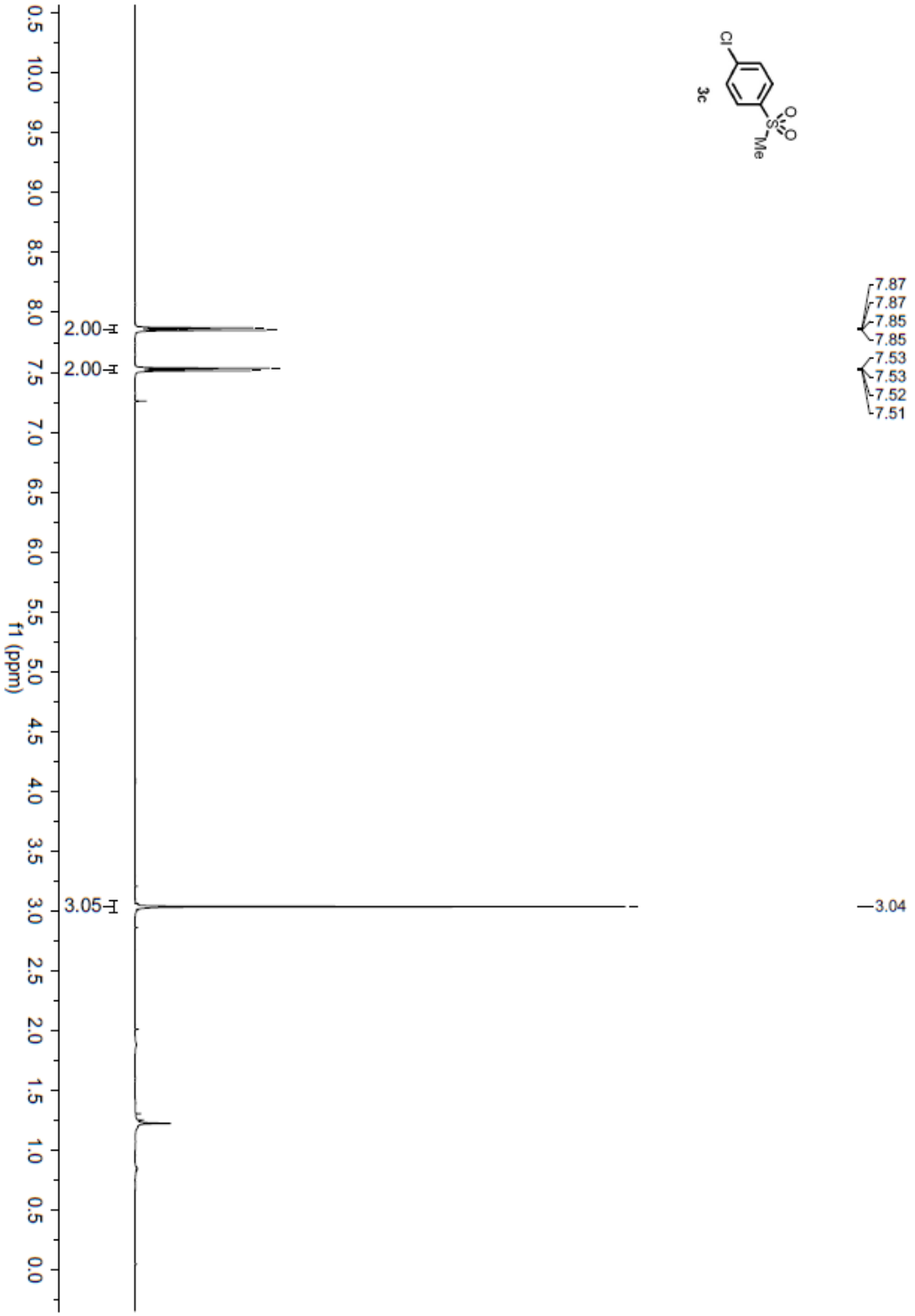

Ph
S
O
O
Me
3a
7.94
7.93
7.93
7.92
7.91
7.91
7.70
7.69
7.69
7.68
7.67
7.67
7.54
7.53
7.53
7.52
7.51
7.51
7.51
7.42
7.42
7.42
7.40
7.40
7.39
7.38
7.38
7.37
7.36
7.36
7.35
7.34
7.34
7.33
7.33
2.00
2.04
2.01
3.07
3.04
3.01
f1 (ppm)

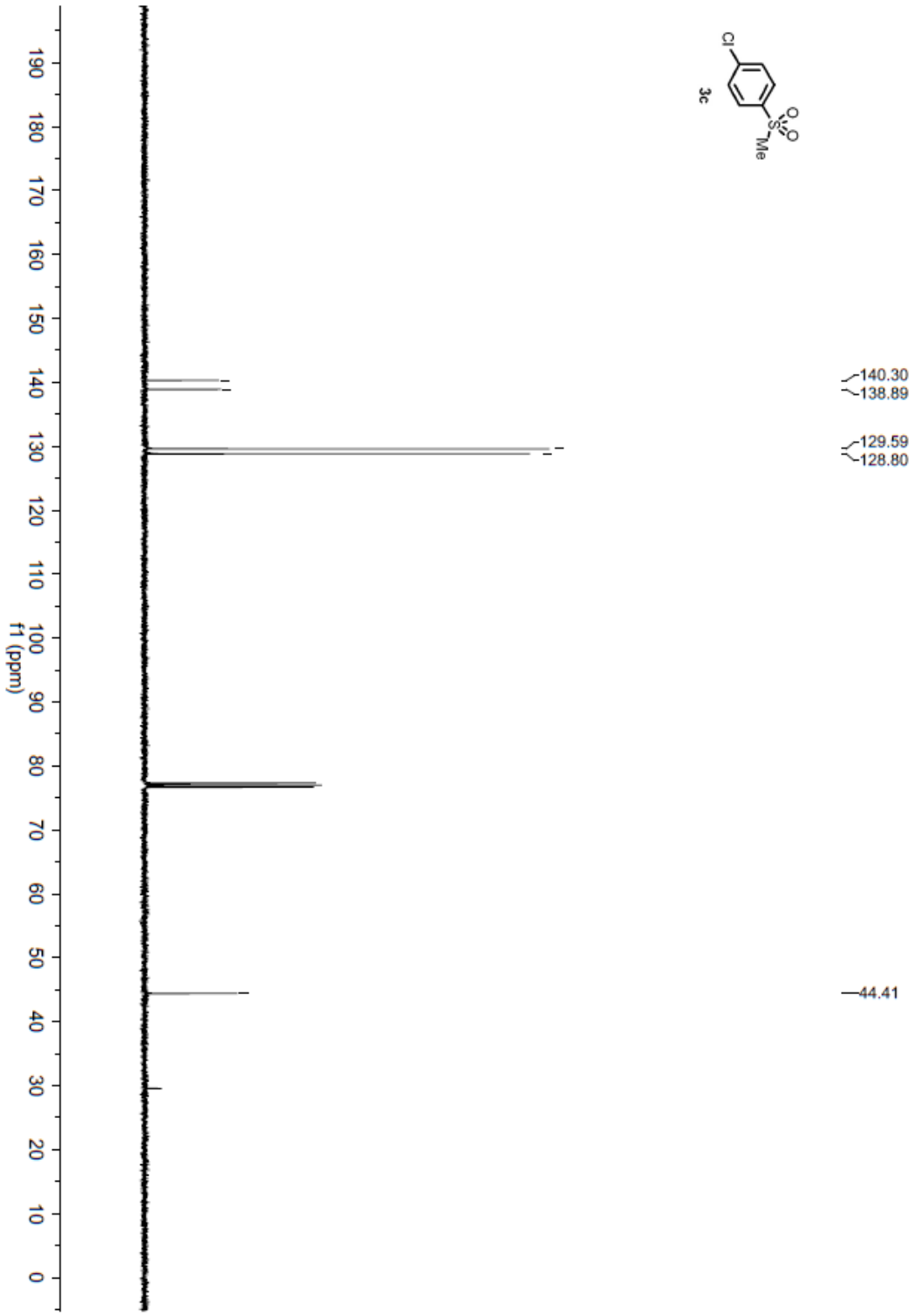

Ph
S
O
O
Me
3a
146.62
139.03
129.03
128.62
127.91
127.83
127.31
44.54
f1 (ppm)

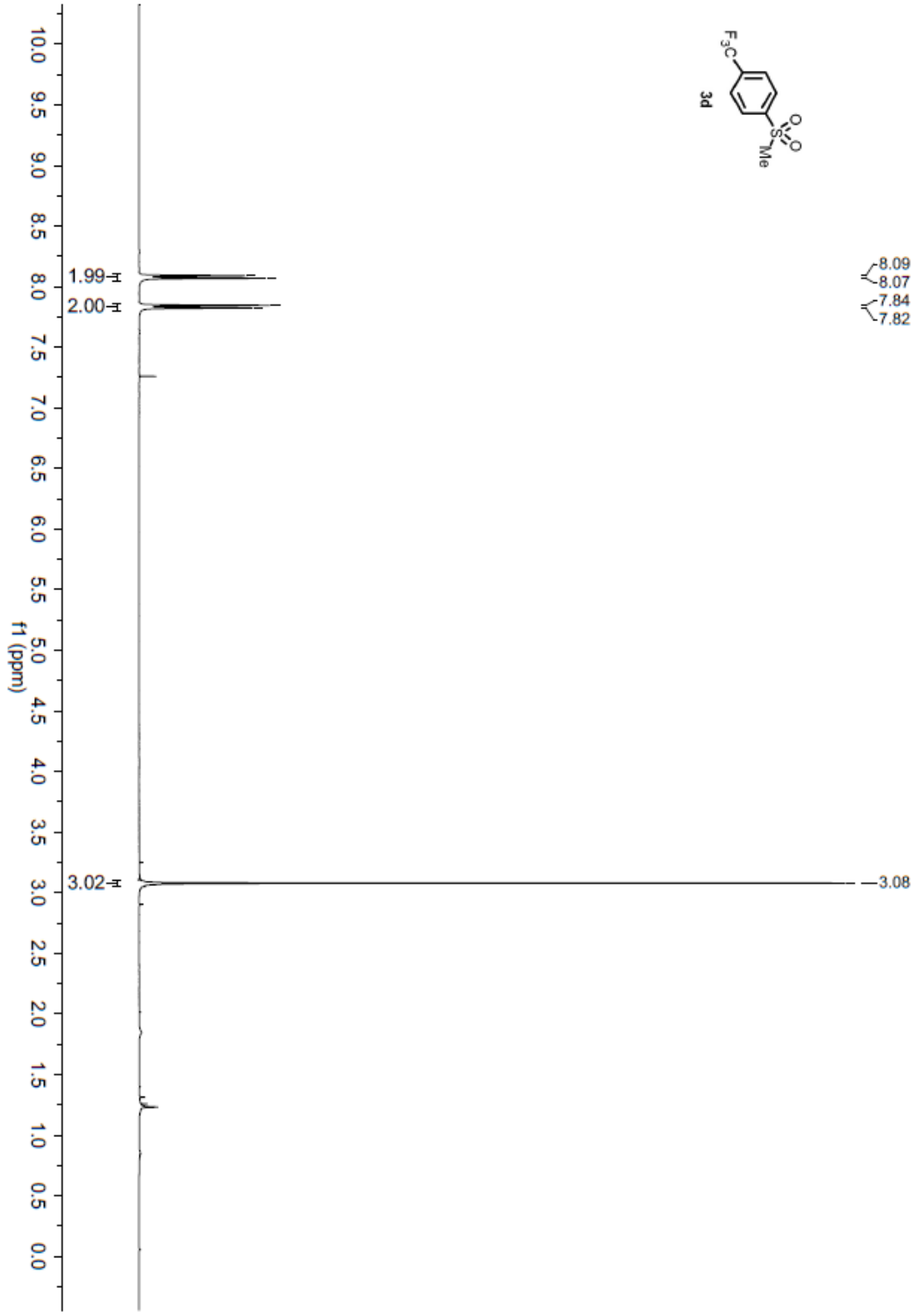

3b
F
O
O
S
Me
7.91
7.91
7.90
7.90
7.89
7.88
7.88
7.20
7.19
7.18
7.16
7.16
2.00
2.05
2.96
2.99
f1 (ppm)

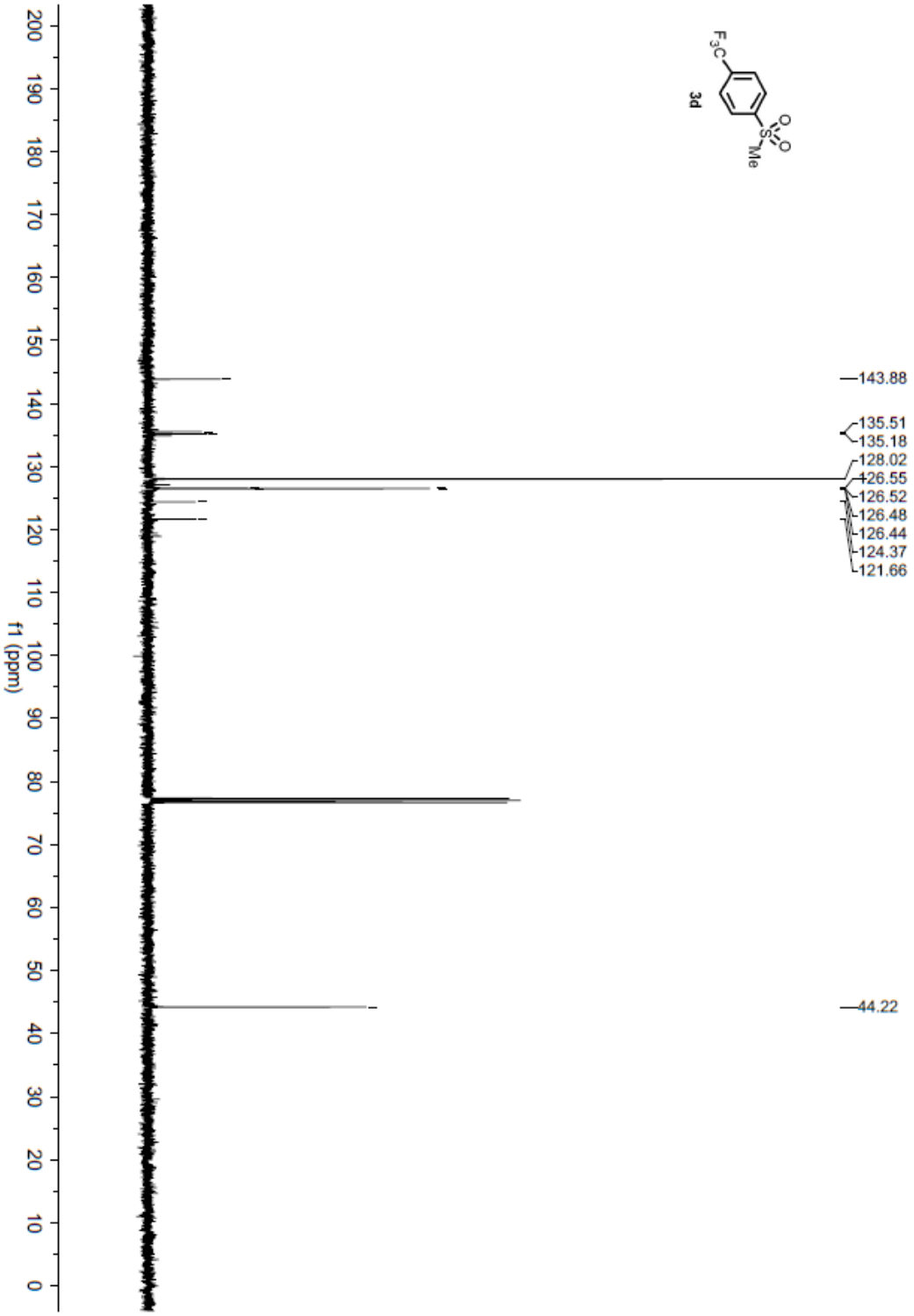

3b
F
O
O
S
Me
167.04
164.49
136.69
136.66
130.35
130.25
116.80
116.57
44.66
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

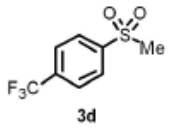

10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)
-103.57
F
O
O
S
Me
3b


3c
Cl
S
O
O
Me
7.87
7.87
7.85
7.85
7.53
7.53
7.52
7.51
3.04
2.00
2.00
3.05
f1 (ppm)


Cl
O
O
S
Me
3c
140.30
138.89
129.59
128.80
44.41
f1 (ppm)

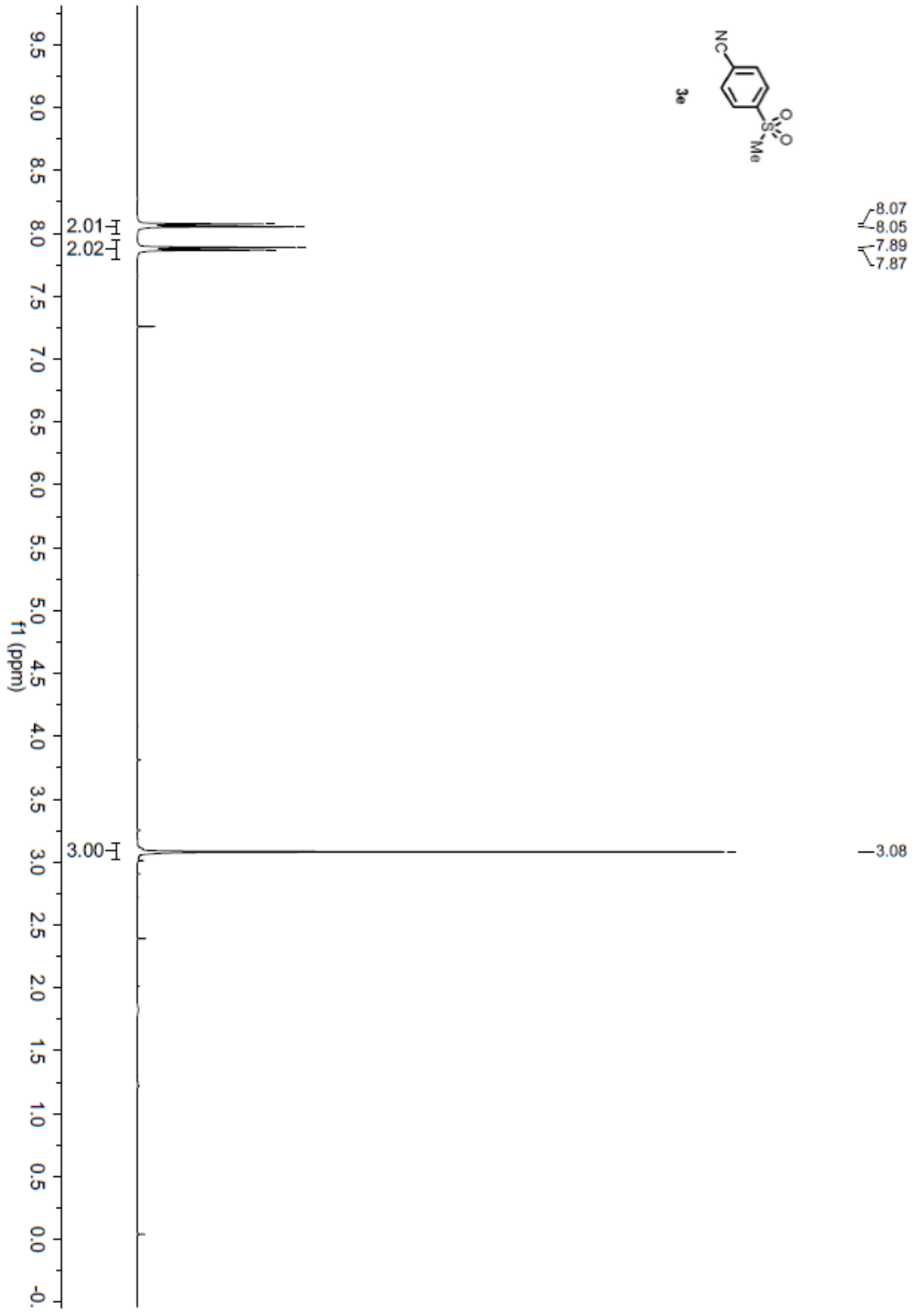

3d
F3C
O
O
S
Me
8.09
8.07
7.84
7.82
3.08
1.99
2.00
3.02
f1 (ppm)

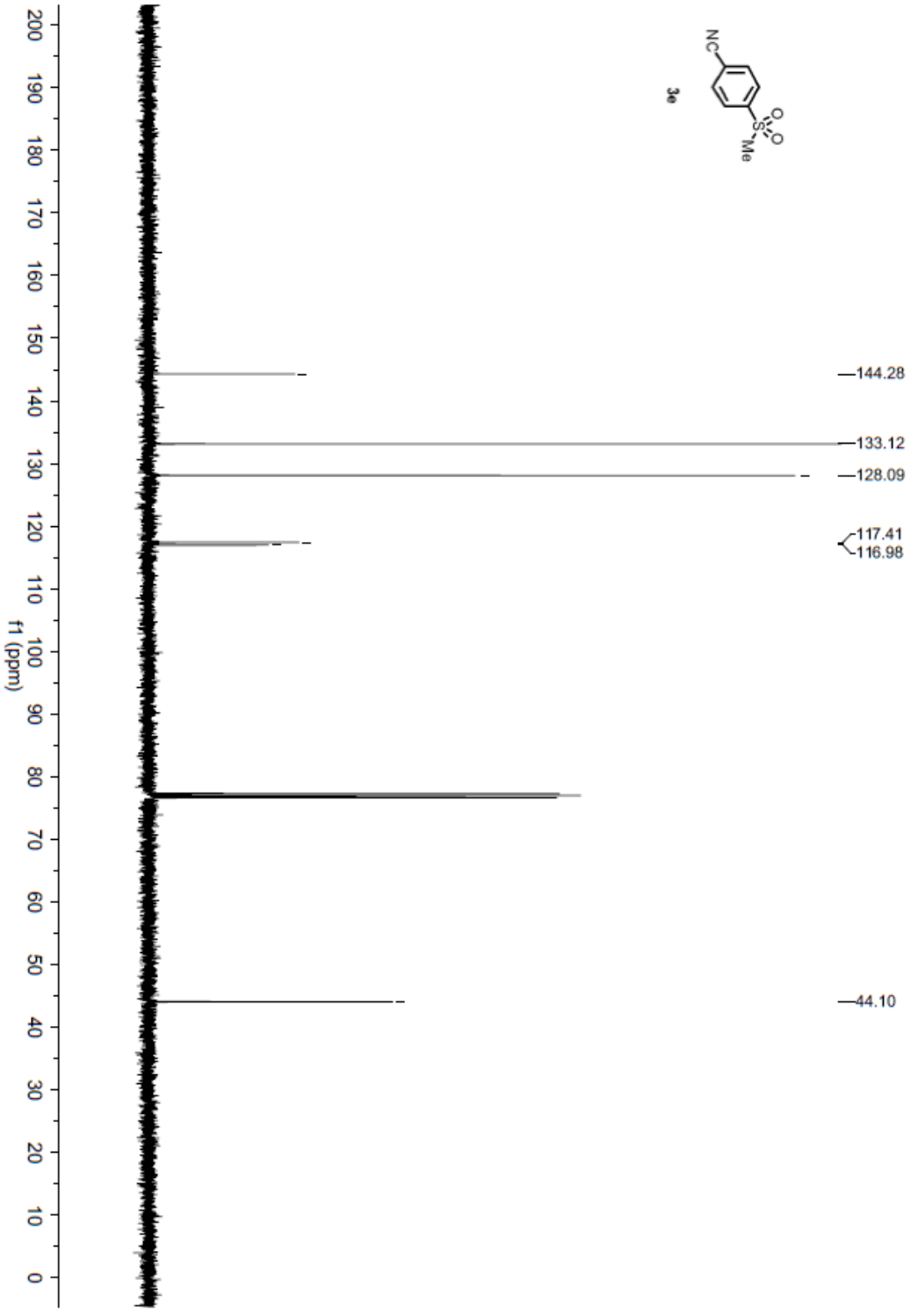

3d
143.88
135.51
135.18
128.02
126.55
126.52
126.48
126.44
124.37
121.66
44.22
f1 (ppm)

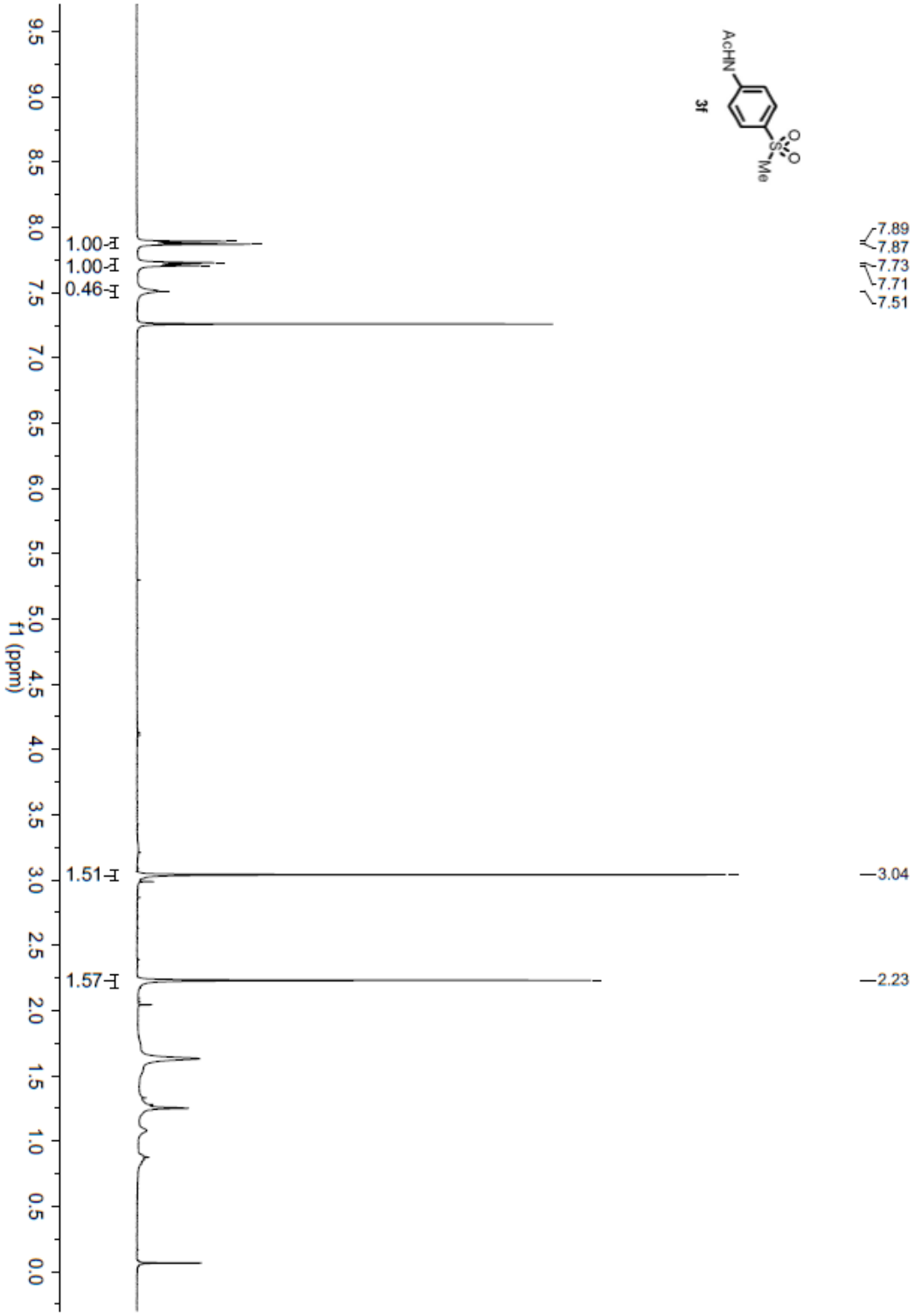

O
O
S
Me
F3C

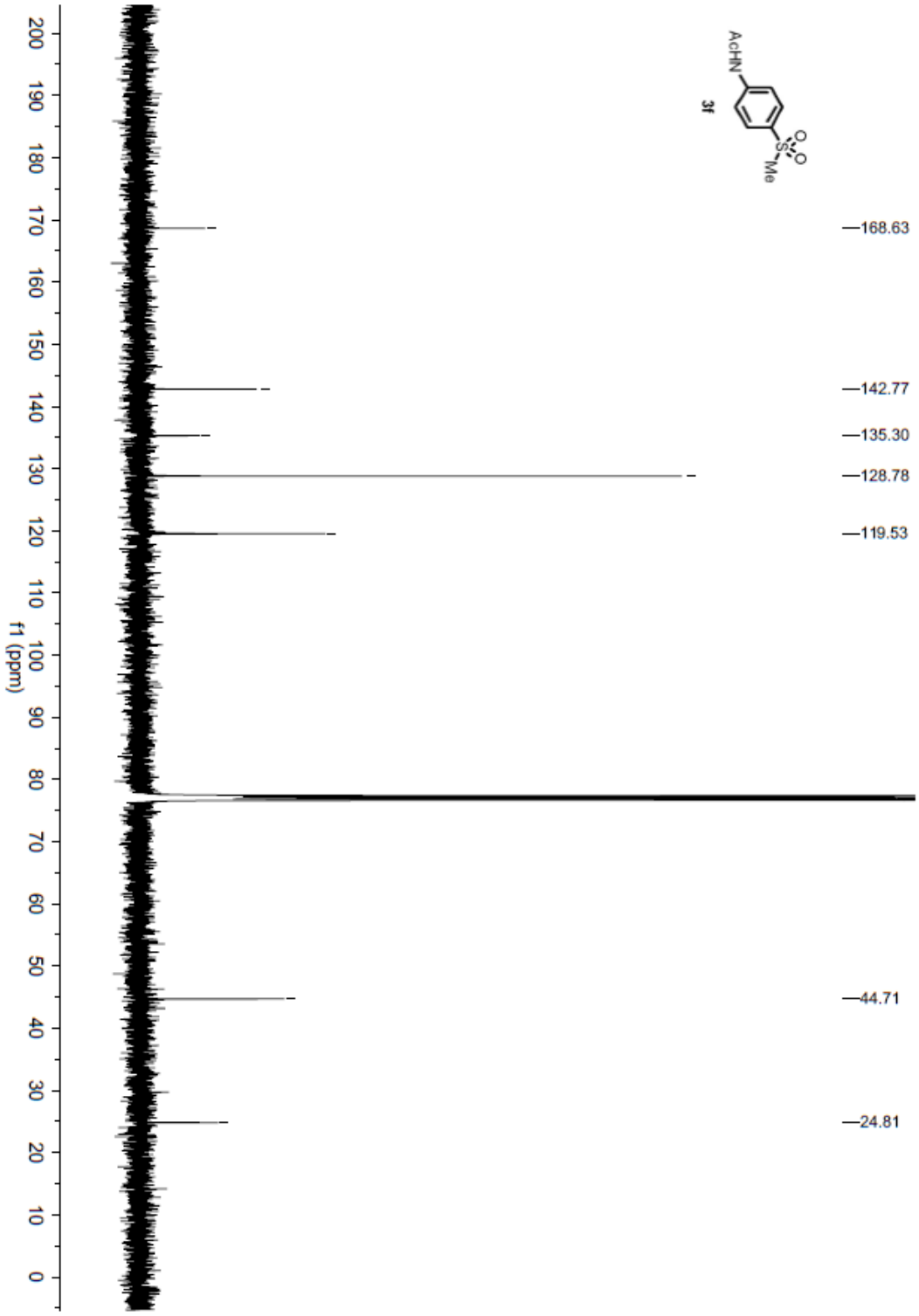
3d

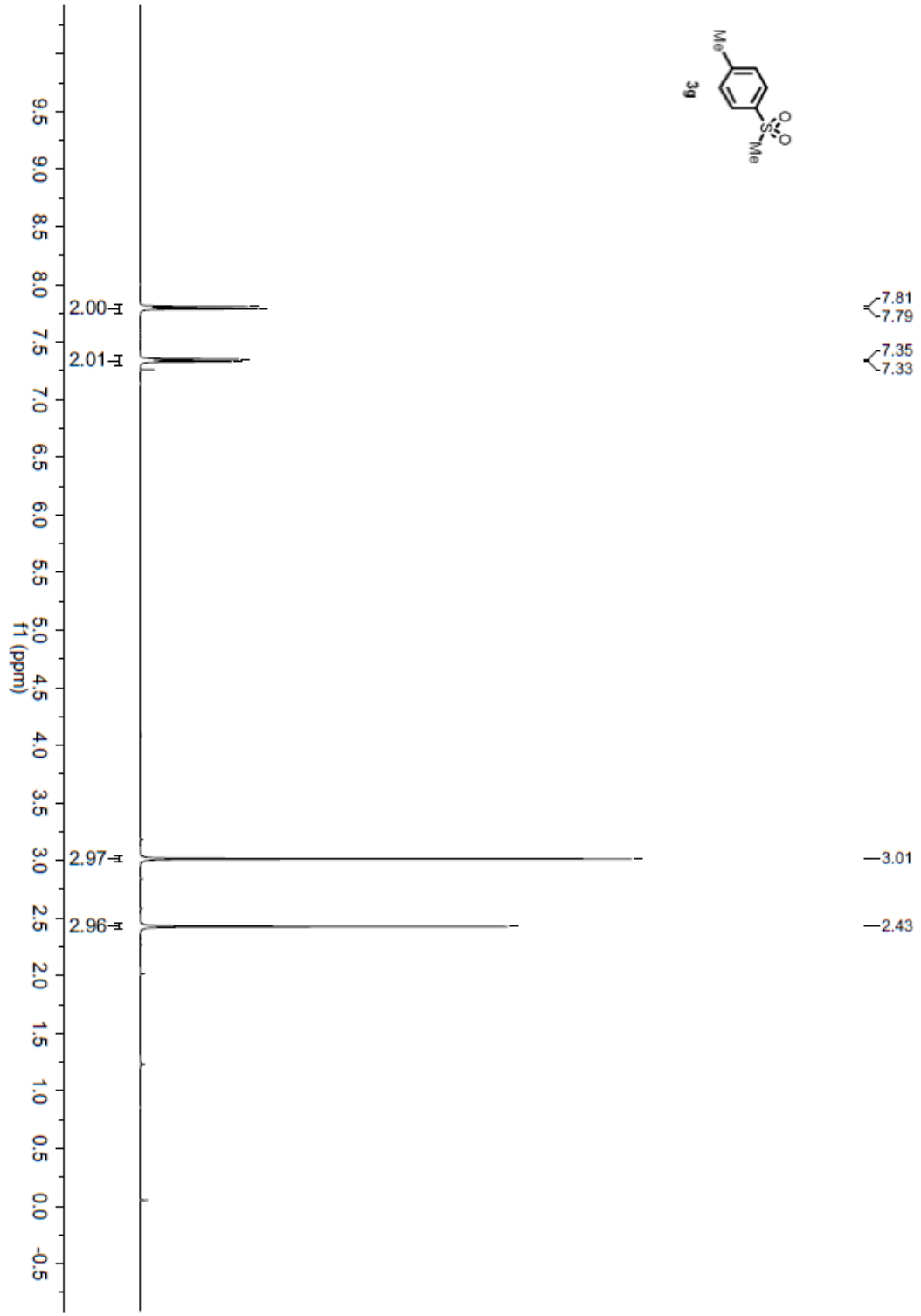
-63.24
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

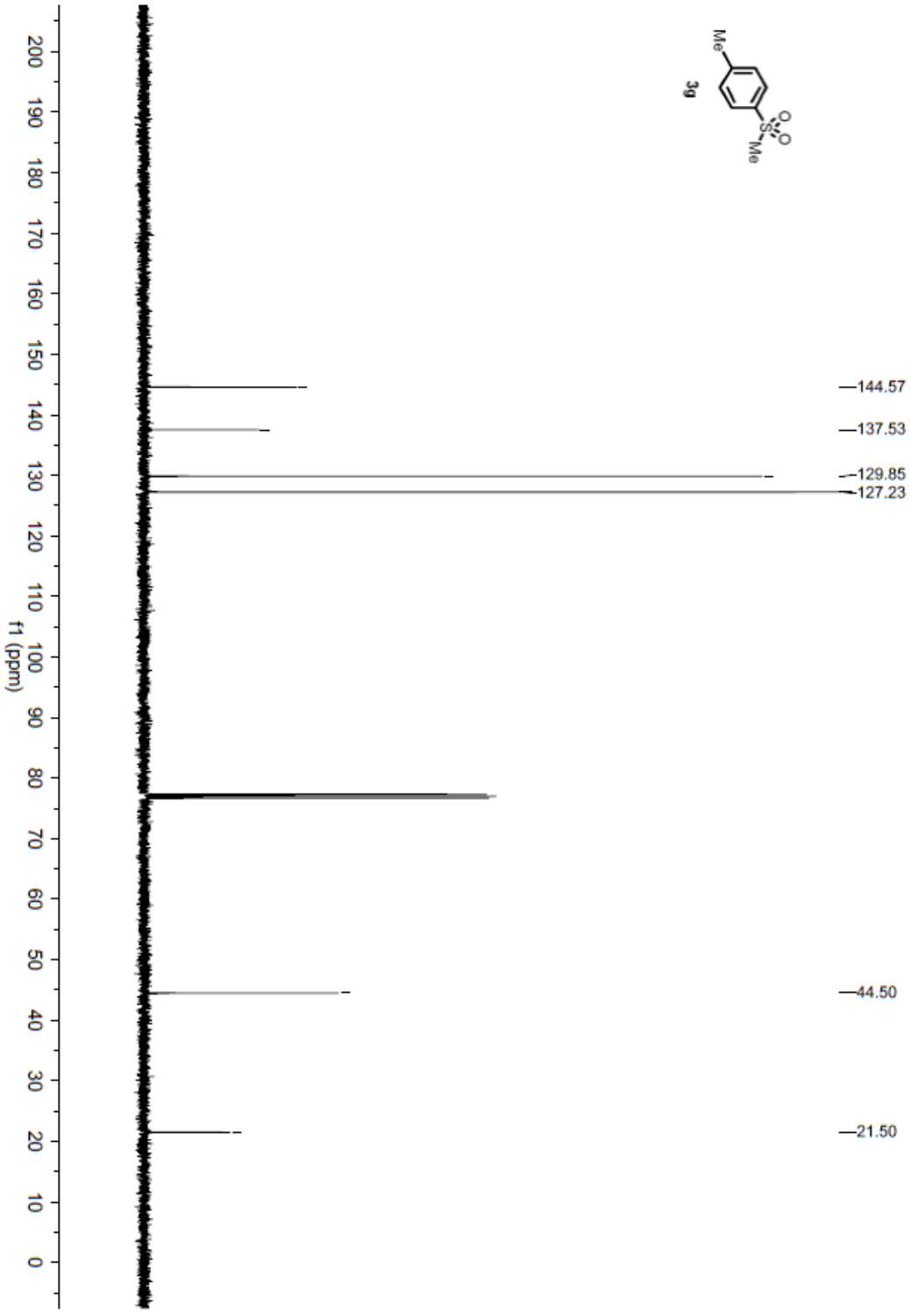

3e
NC
O
O
S
Me
8.07
8.05
7.89
7.87
3.08
2.01
2.02
3.00
f1 (ppm)

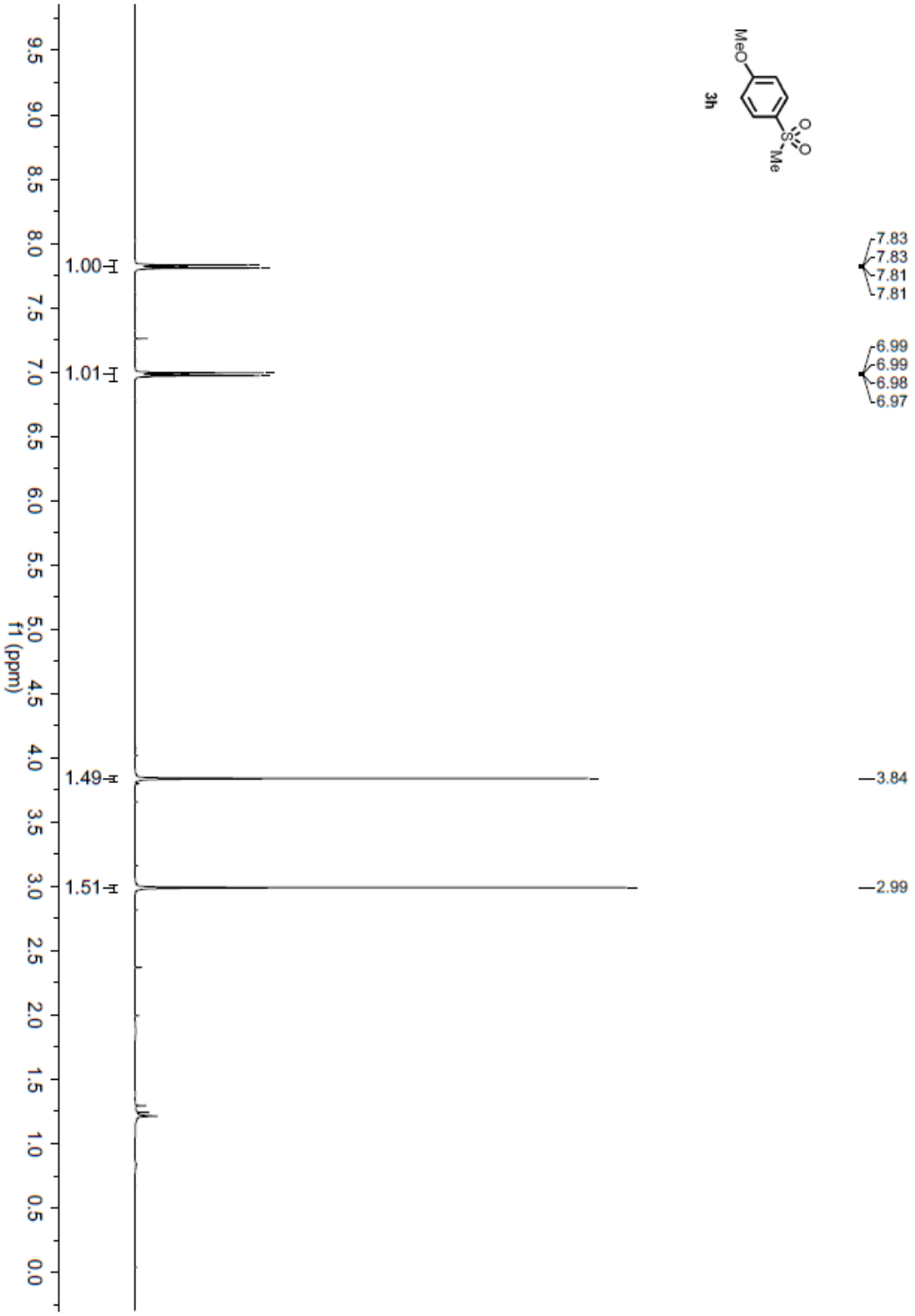

NC
S
O
O
Me
3e
144.28
133.12
128.09
117.41
116.98
44.10
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

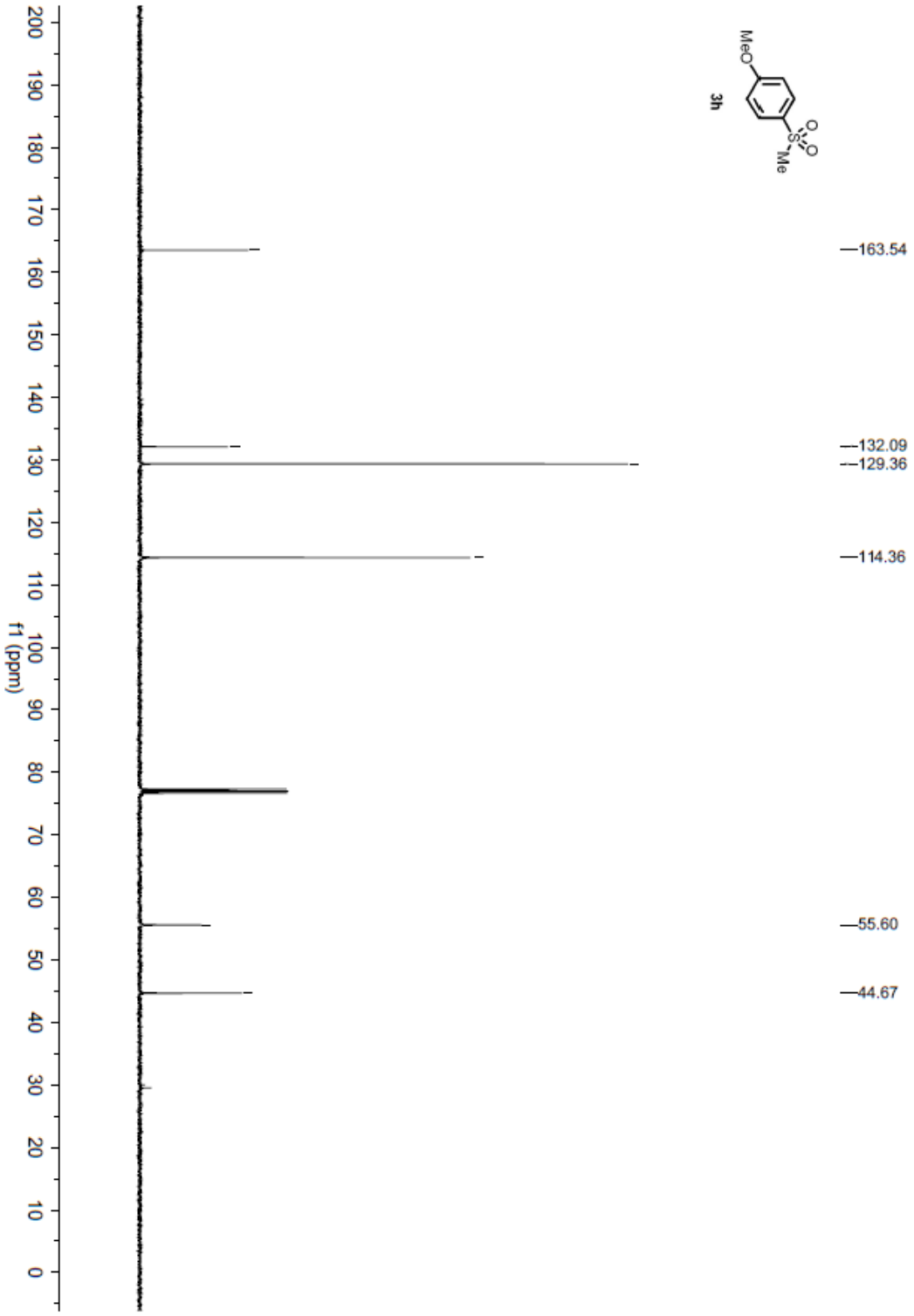

AcHN
3f
S
O
O
Me
7.89
7.87
7.73
7.71
7.51
3.04
2.23
1.00
1.00
0.46
1.51
1.57
f1 (ppm)

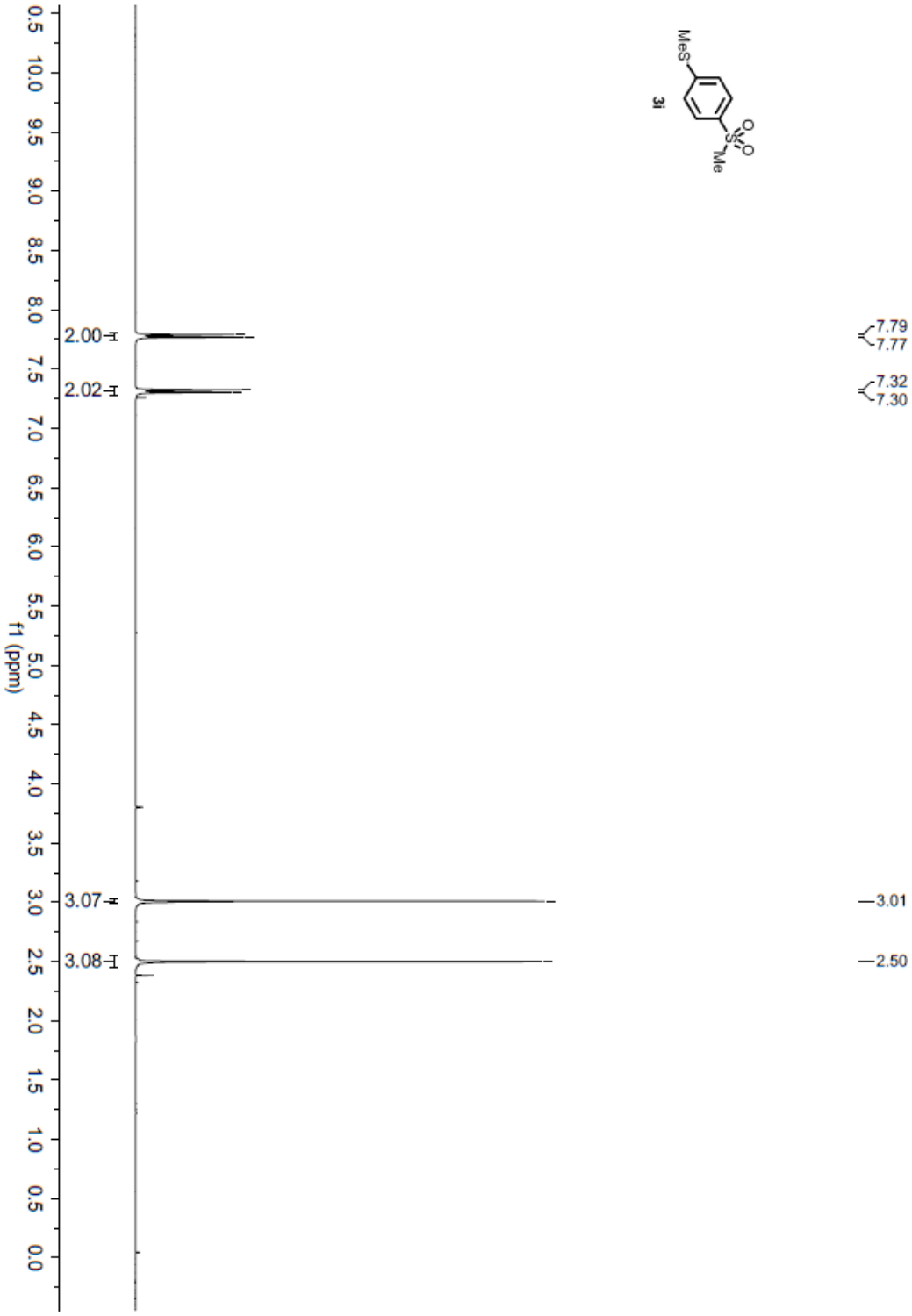

AcHN
S
O
O
Me
3f
168.63
142.77
135.30
128.78
119.53
44.71
24.81
f1 (ppm)

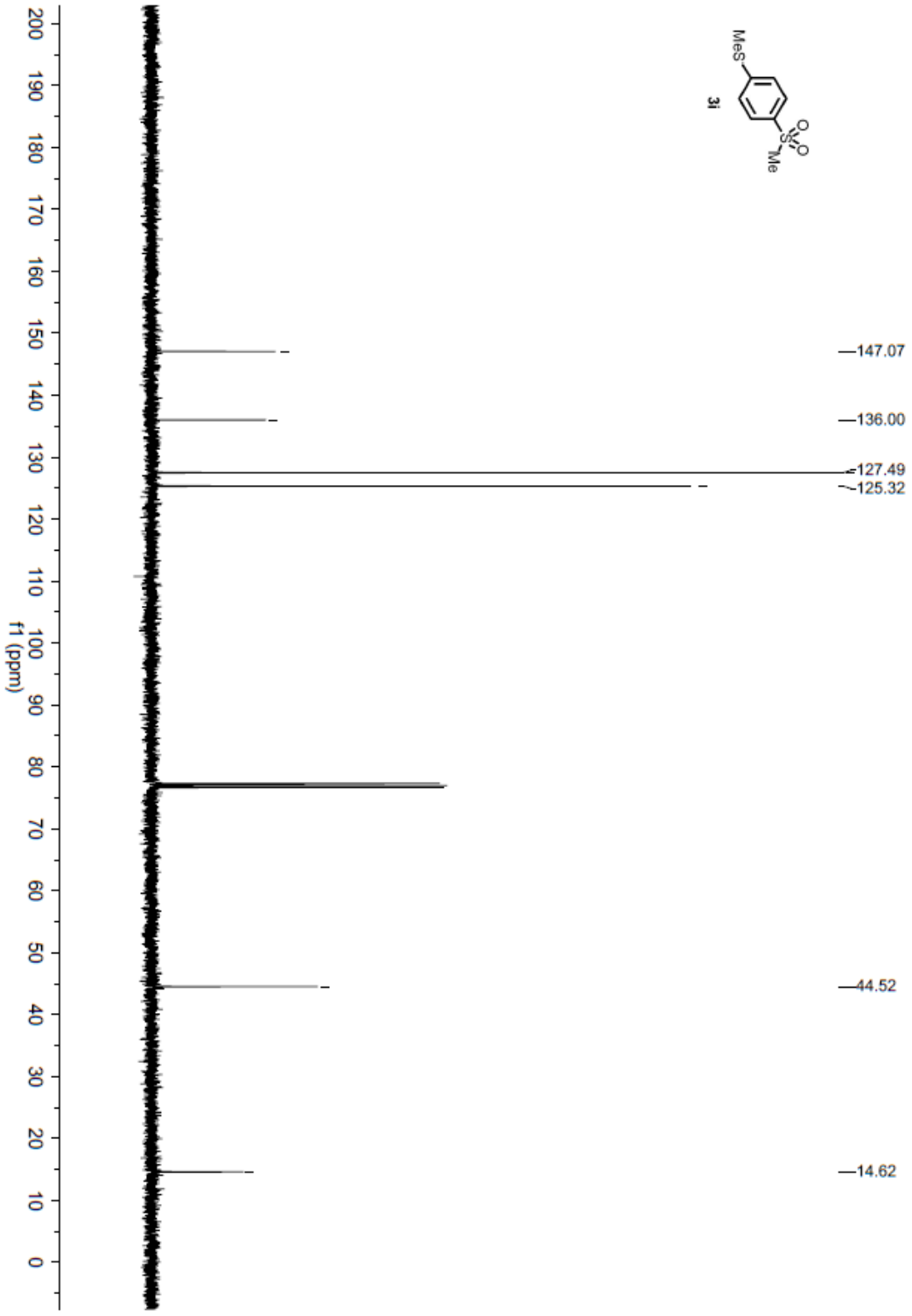

3g
Me
S
O
O
Me
2.00
2.01
2.97
2.96
7.81
7.79
7.35
7.33
3.01
2.43
f1 (ppm)

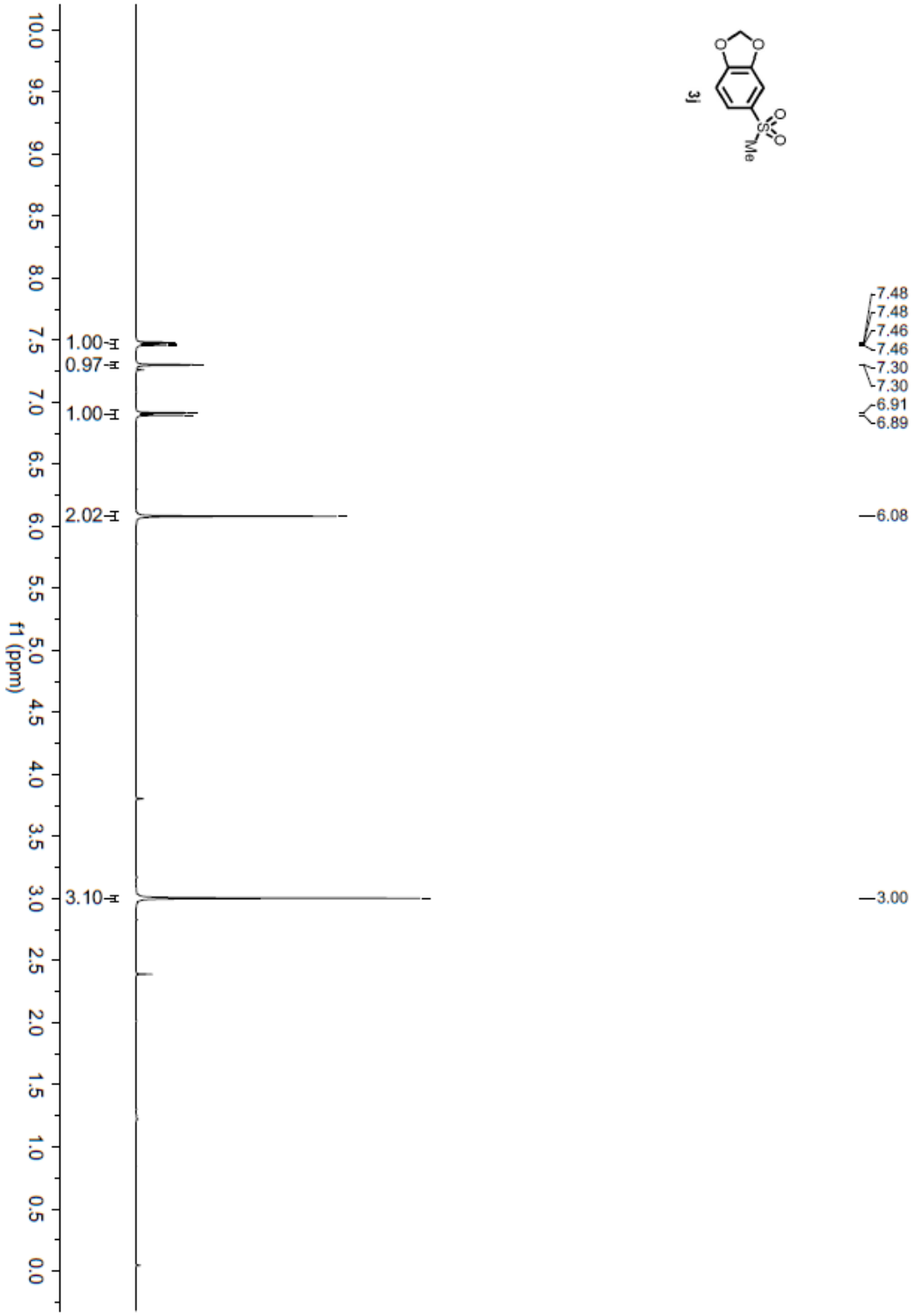

3g
Me
S
O
O
Me
144.57
137.53
129.85
127.23
44.50
21.50
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

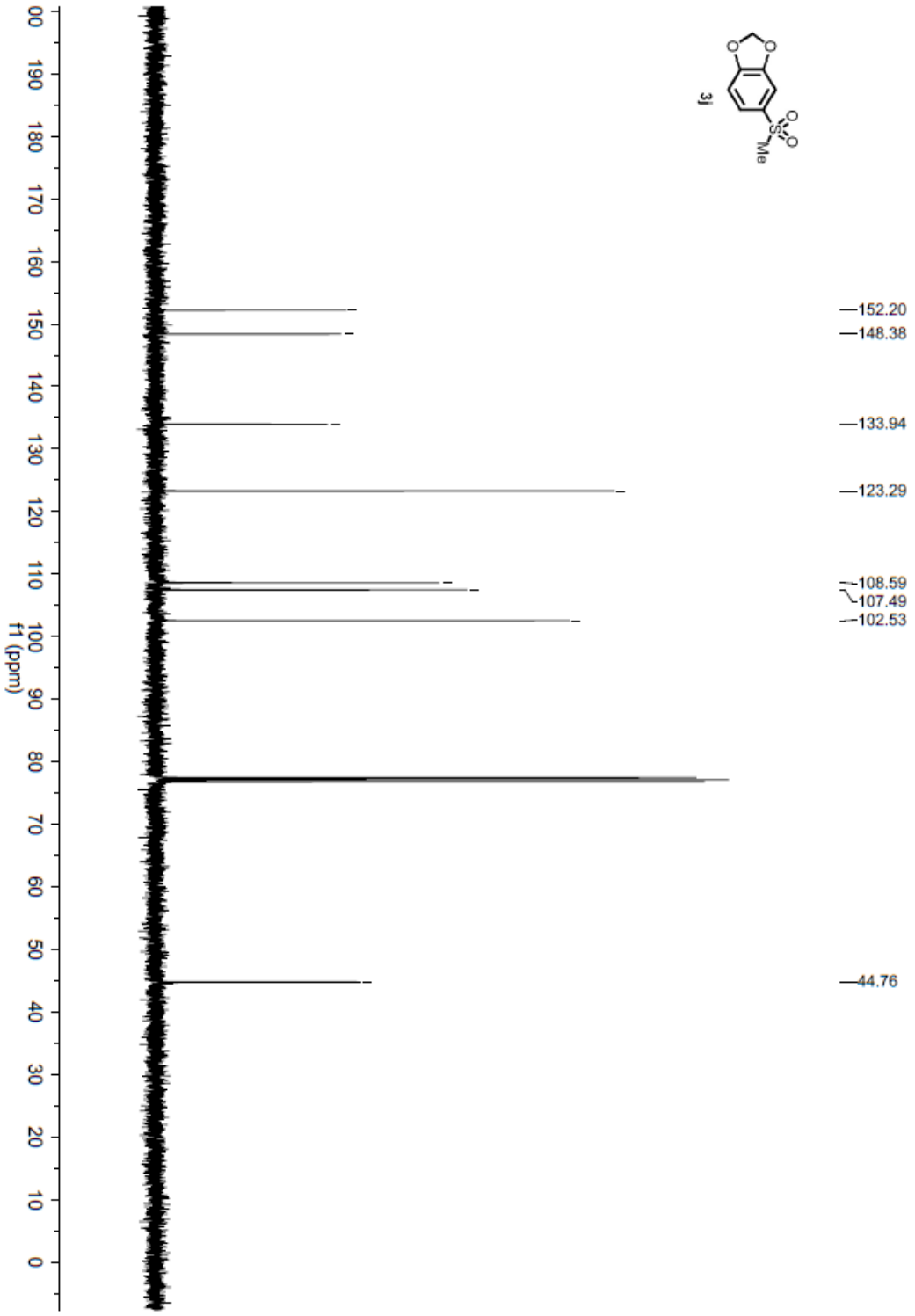

MeO
3h
O
O
S
Me
7.83
7.83
7.81
7.81
6.99
6.99
6.98
6.97
3.84
2.99
1.00
1.01
1.49
1.51
f1 (ppm)

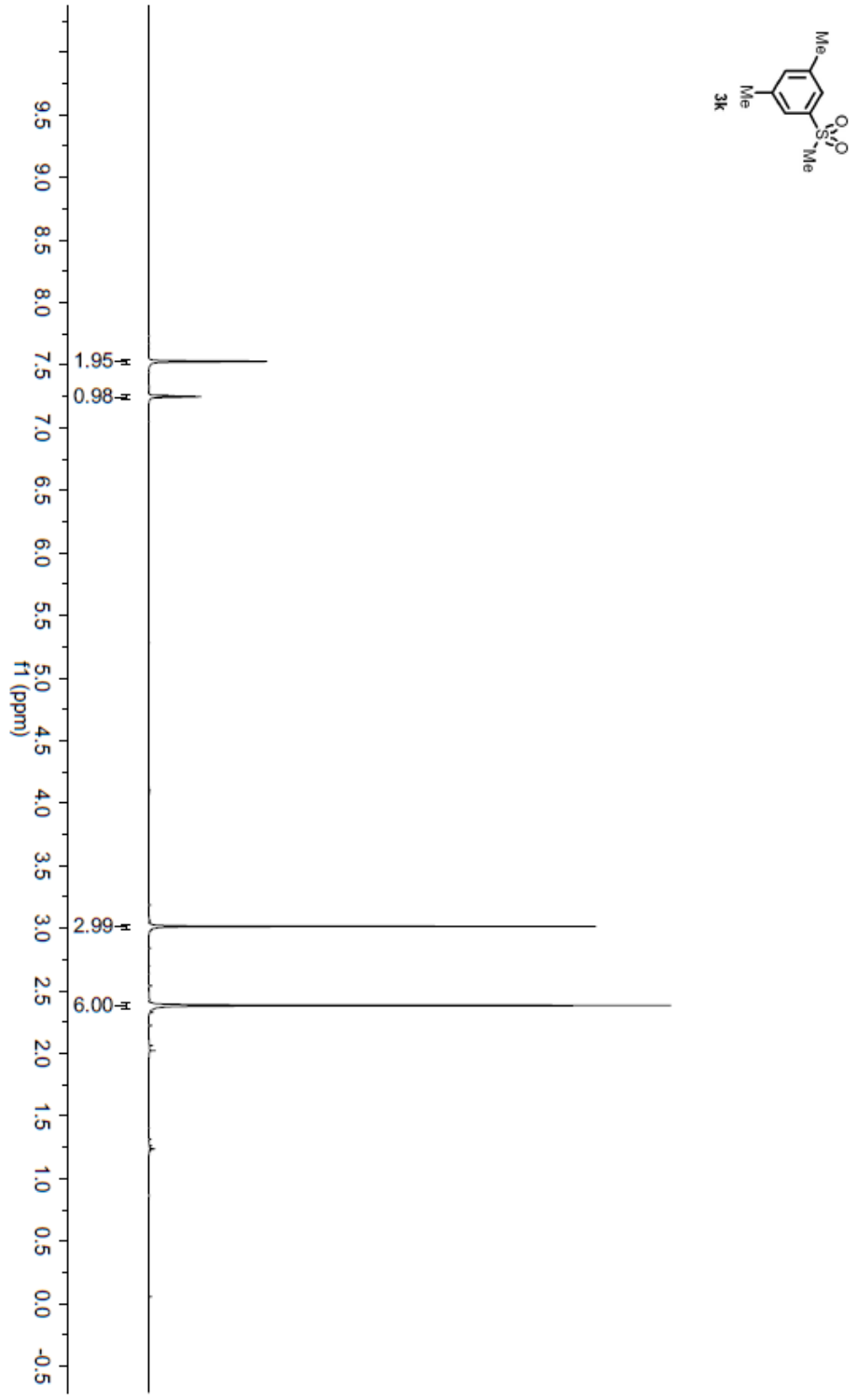

MeO
O
O
S
Me
3h
163.54
132.09
129.36
114.36
55.60
44.67
f1 (ppm)

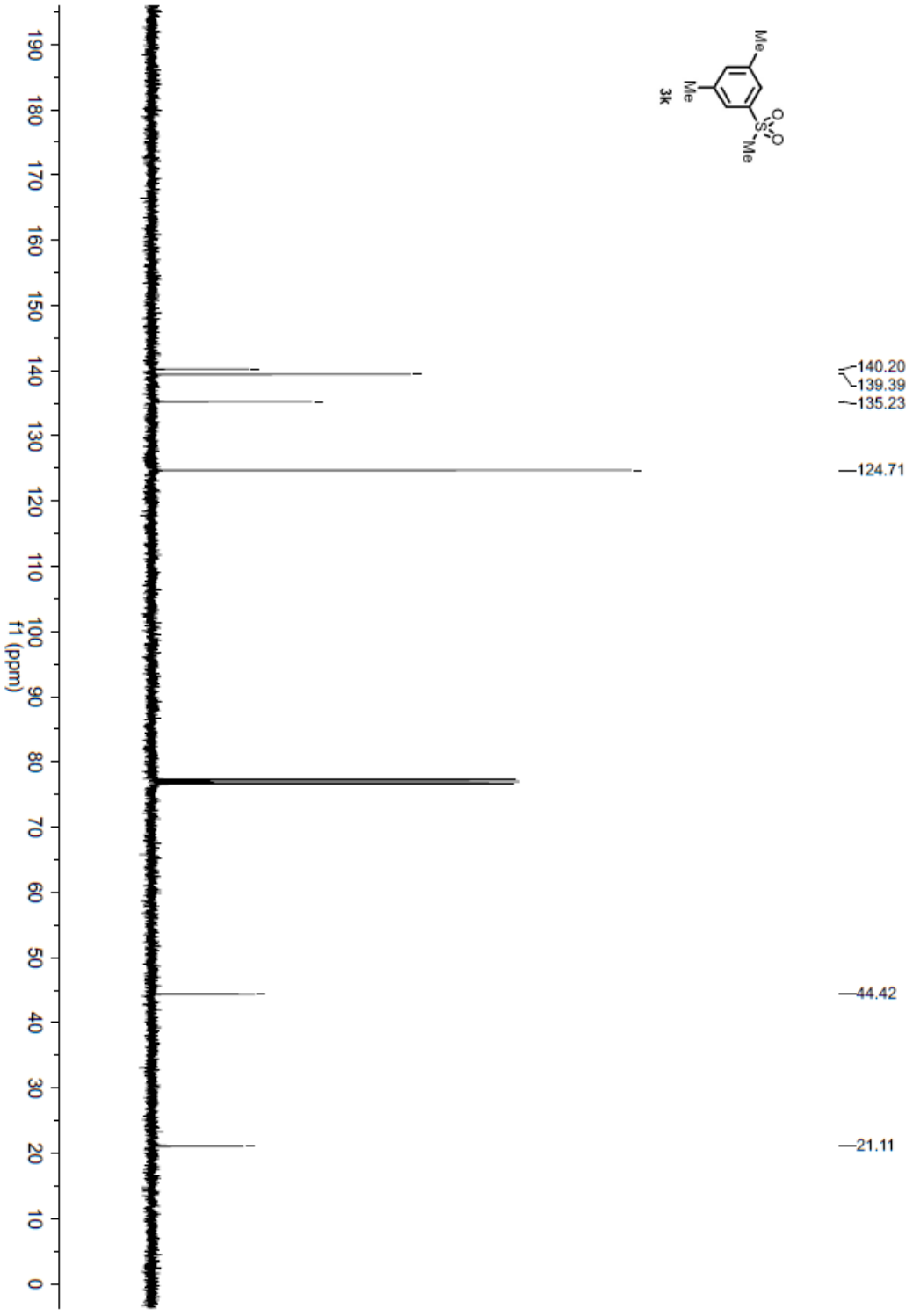

MeS
O
O
S
Me
3i
7.79
7.77
7.32
7.30
3.01
2.50
2.00
2.02
3.07
3.08
f1 (ppm)

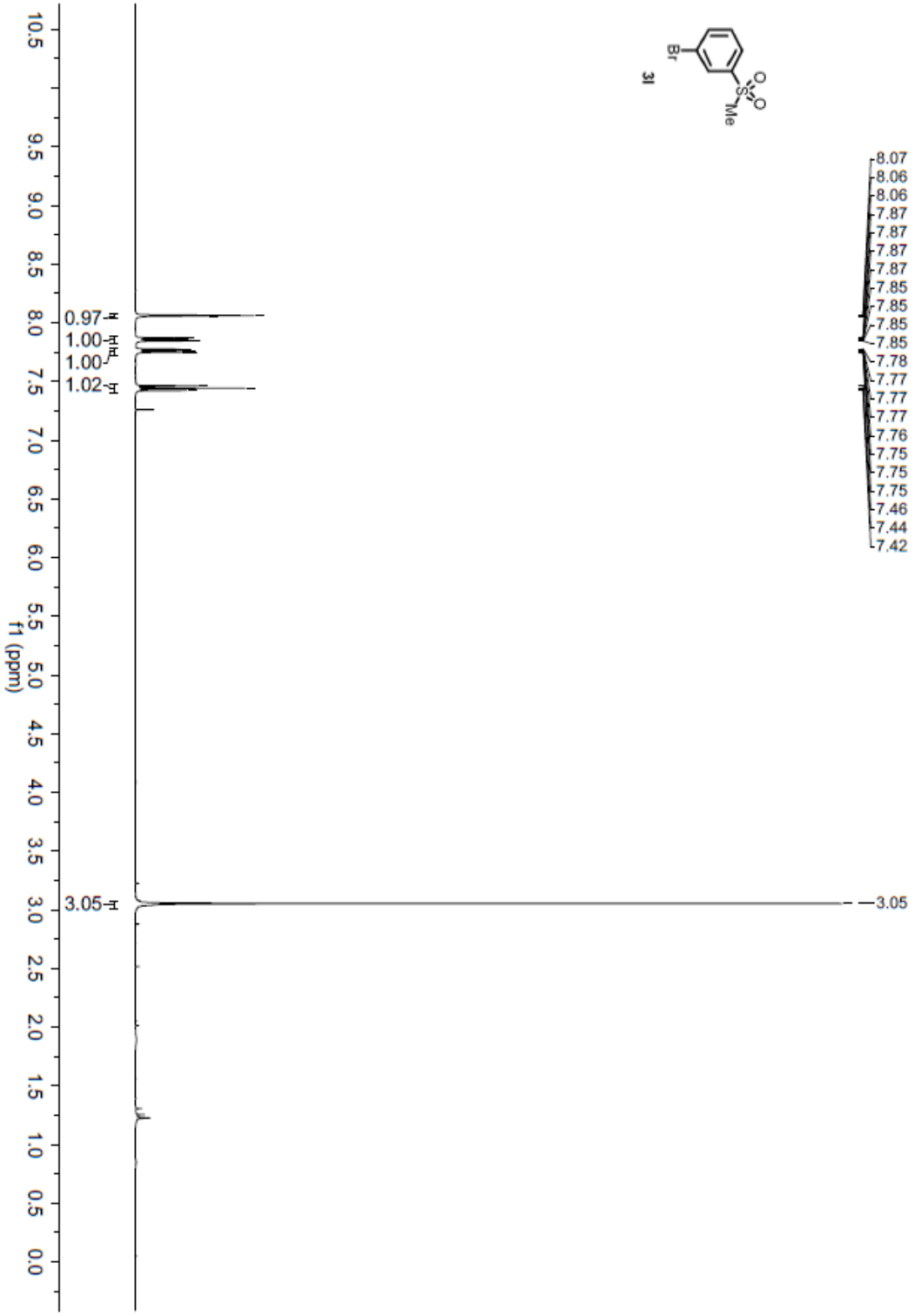

MeS
O
O
S
Me
3i
147.07
136.00
127.49
125.32
44.52
14.62
f1 (ppm)

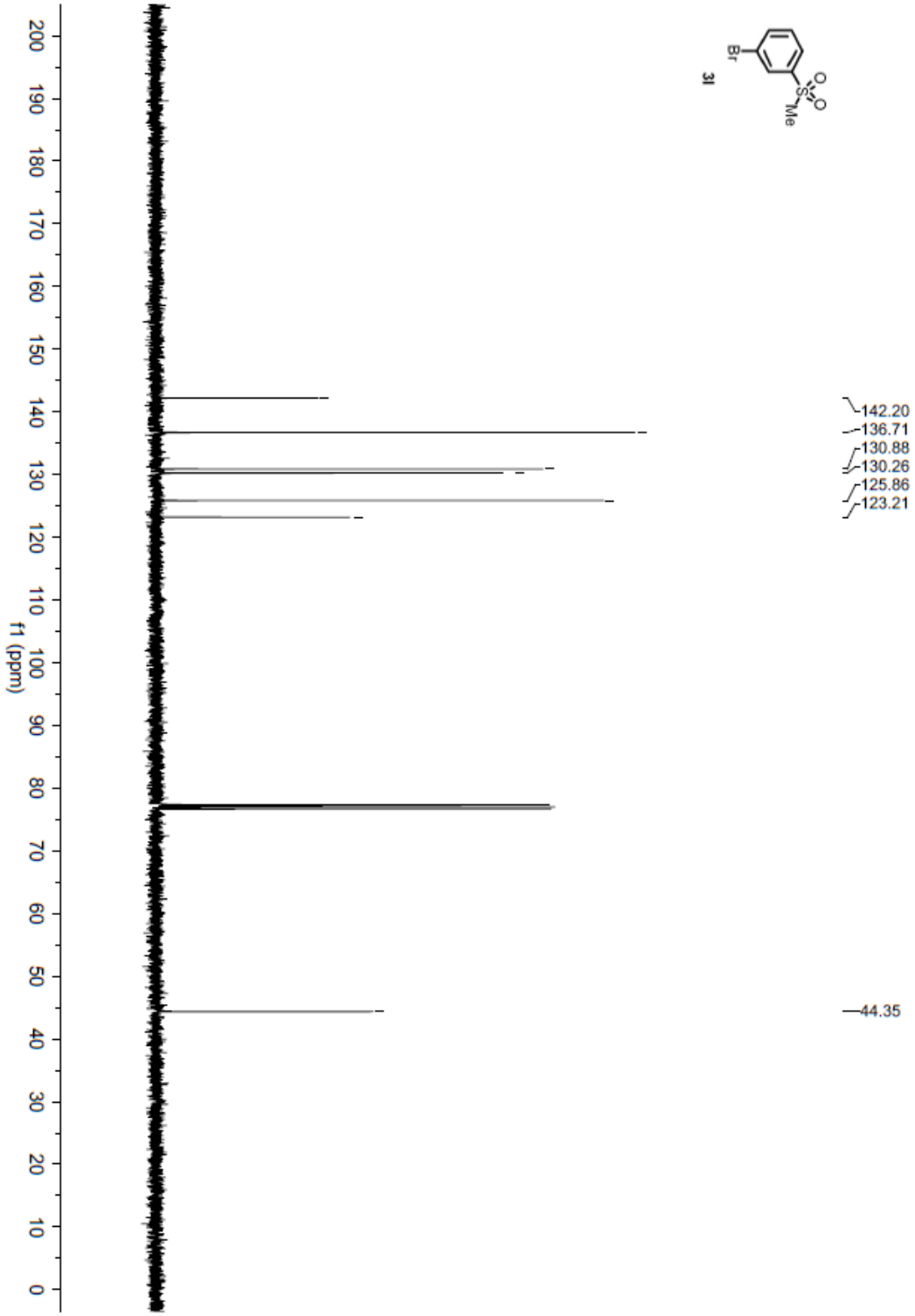

3j
Me
7.48
7.48
7.46
7.46
7.30
7.30
6.91
6.89
6.08
3.00
1.00
0.97
1.00
2.02
3.10
f1 (ppm)

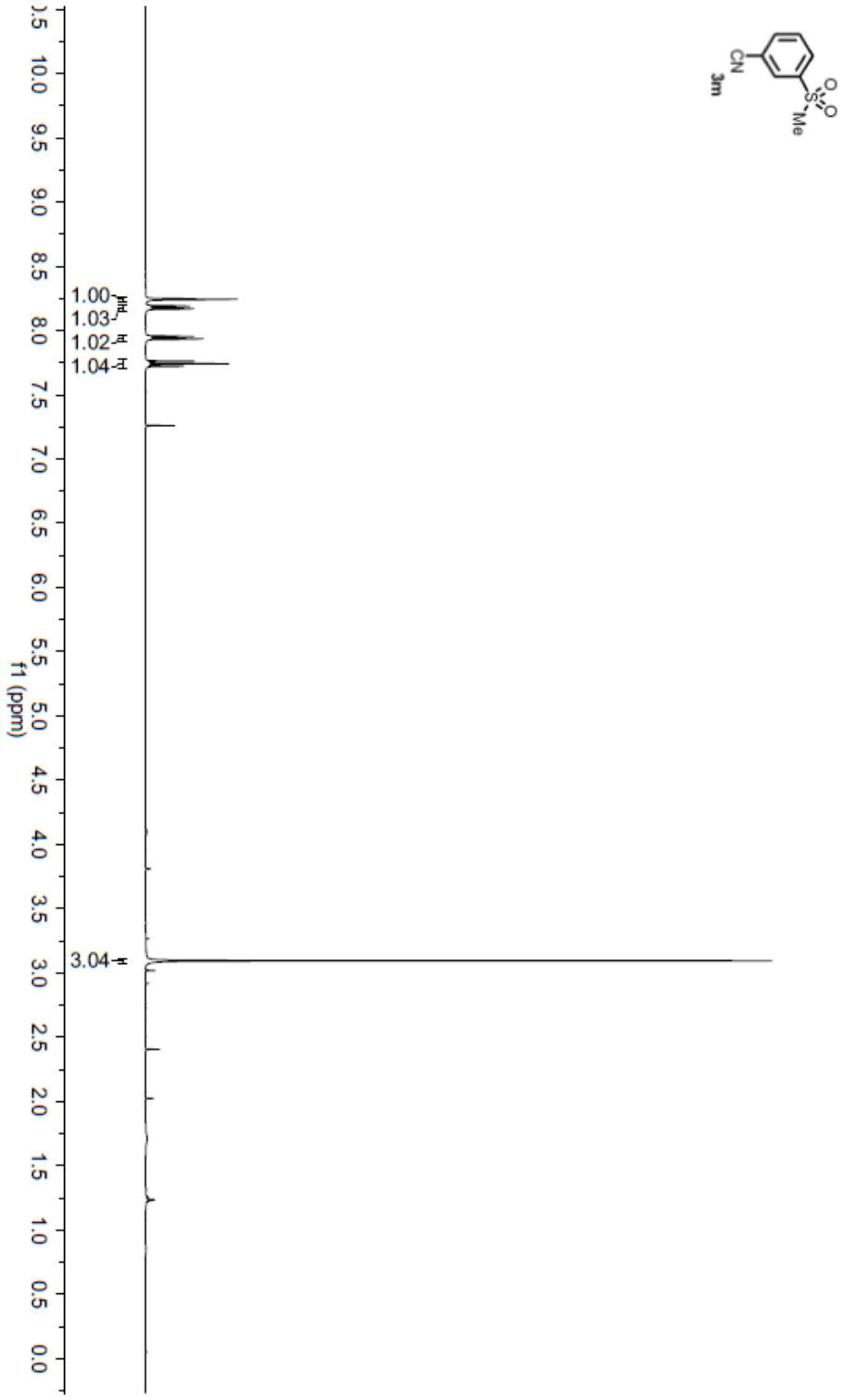

3j
O
O
O
S
O
Me
152.20
148.38
133.94
123.29
108.59
107.49
102.53
44.76
f1 (ppm)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

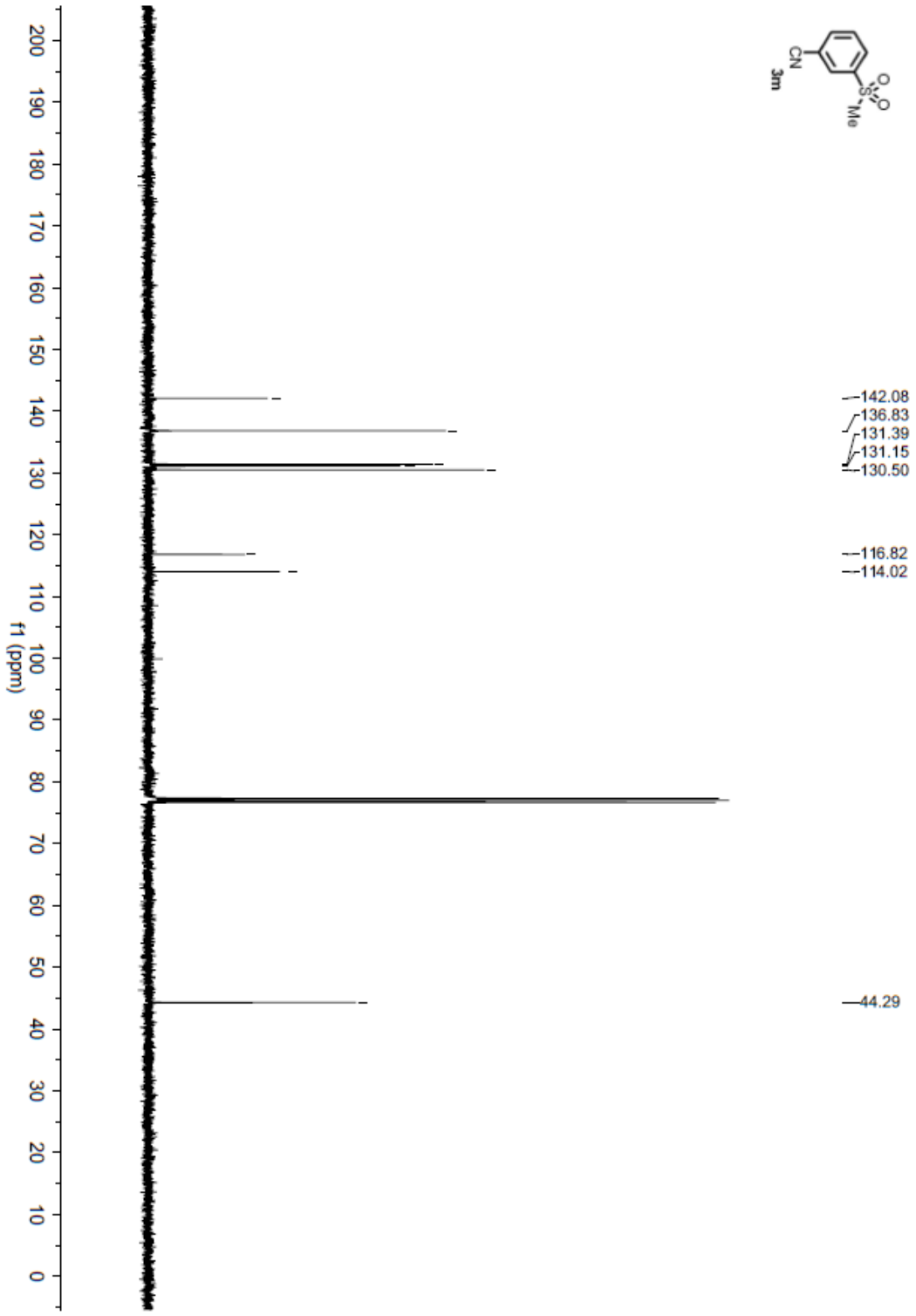

1.95
0.98
2.99
6.00
f1 (ppm)
Me
Me
Me
3k

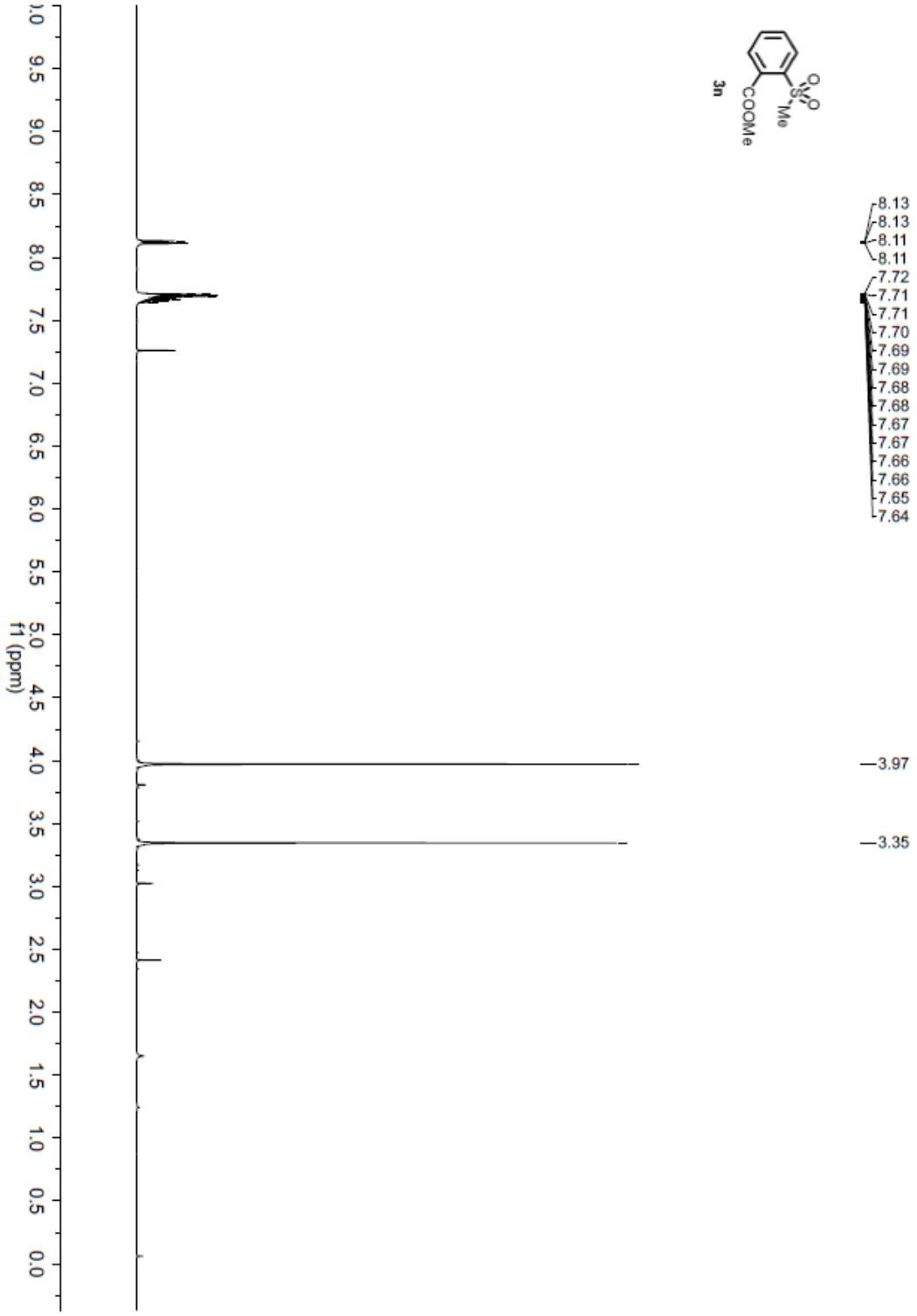

Me
Me
3k
Me
O
O
S
140.20
139.39
135.23
124.71
44.42
21.11
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

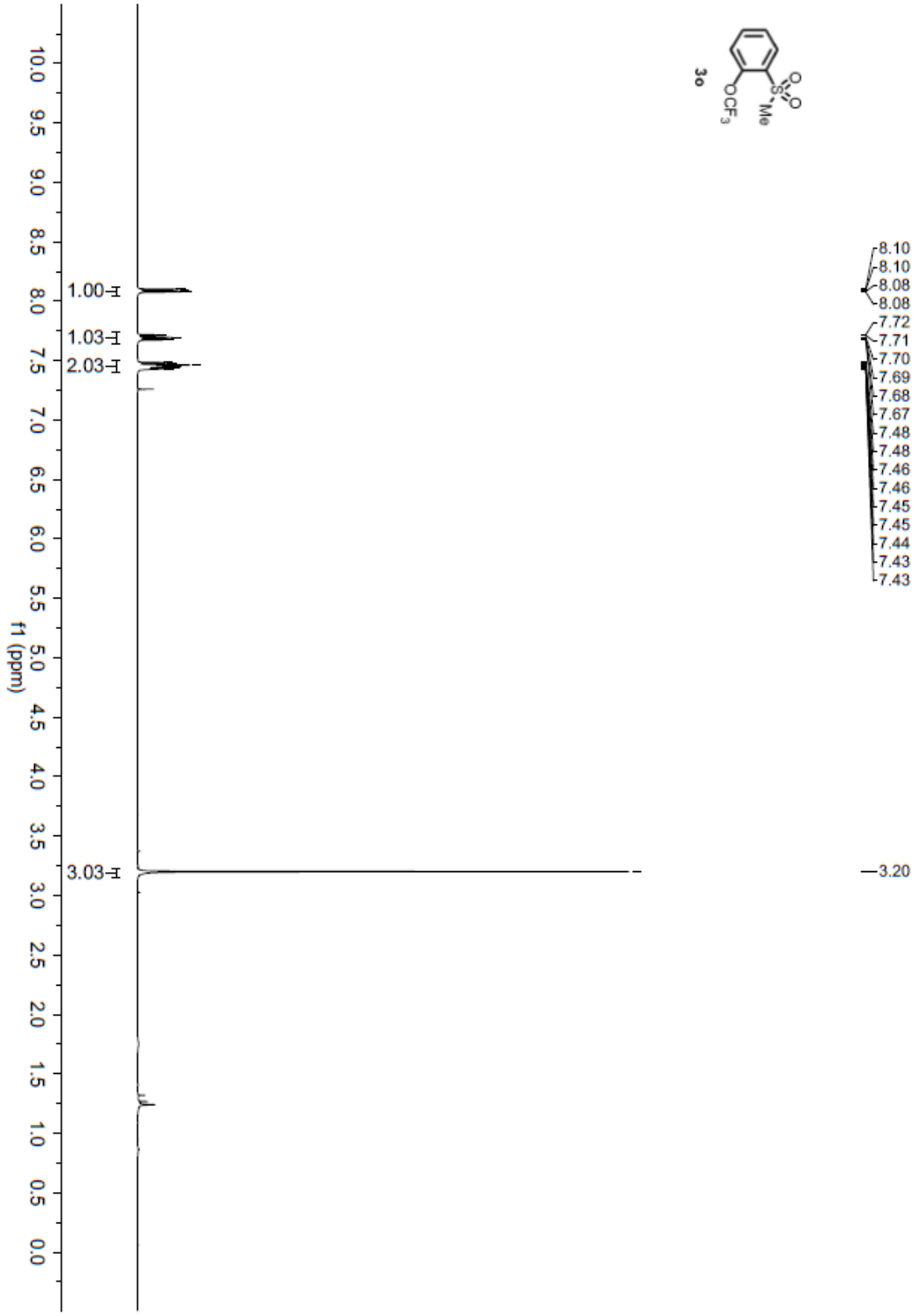

3l
Br
S
O
O
Me
8.07
8.06
8.06
7.87
7.87
7.87
7.87
7.85
7.85
7.85
7.85
7.78
7.77
7.77
7.77
7.76
7.75
7.75
7.75
7.46
7.44
7.42
3.05
0.97
1.00
1.00
1.02
3.05
f1 (ppm)

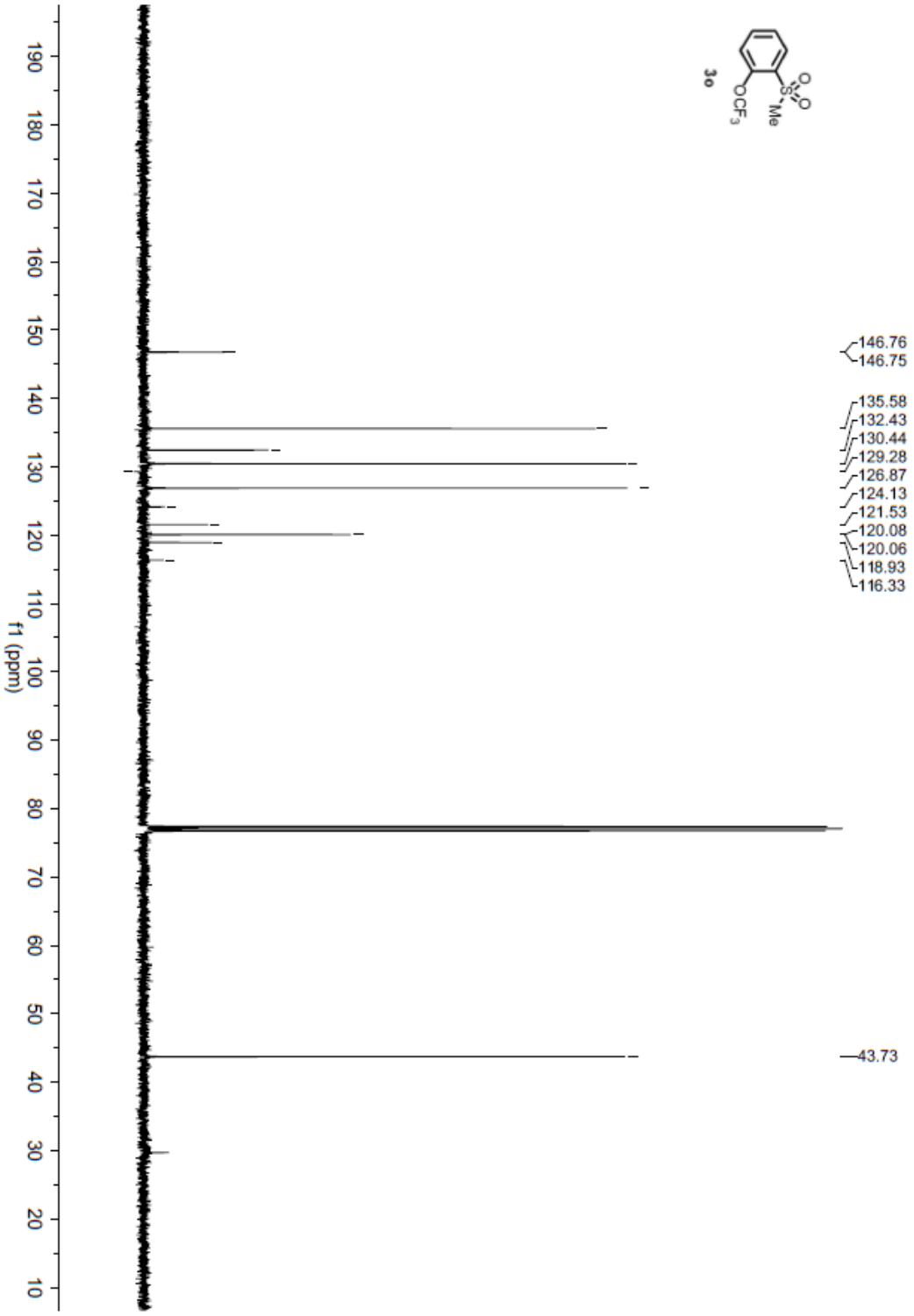

3l
Br
S
O
O
Me
142.20
136.71
130.88
130.26
125.86
123.21
44.35
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

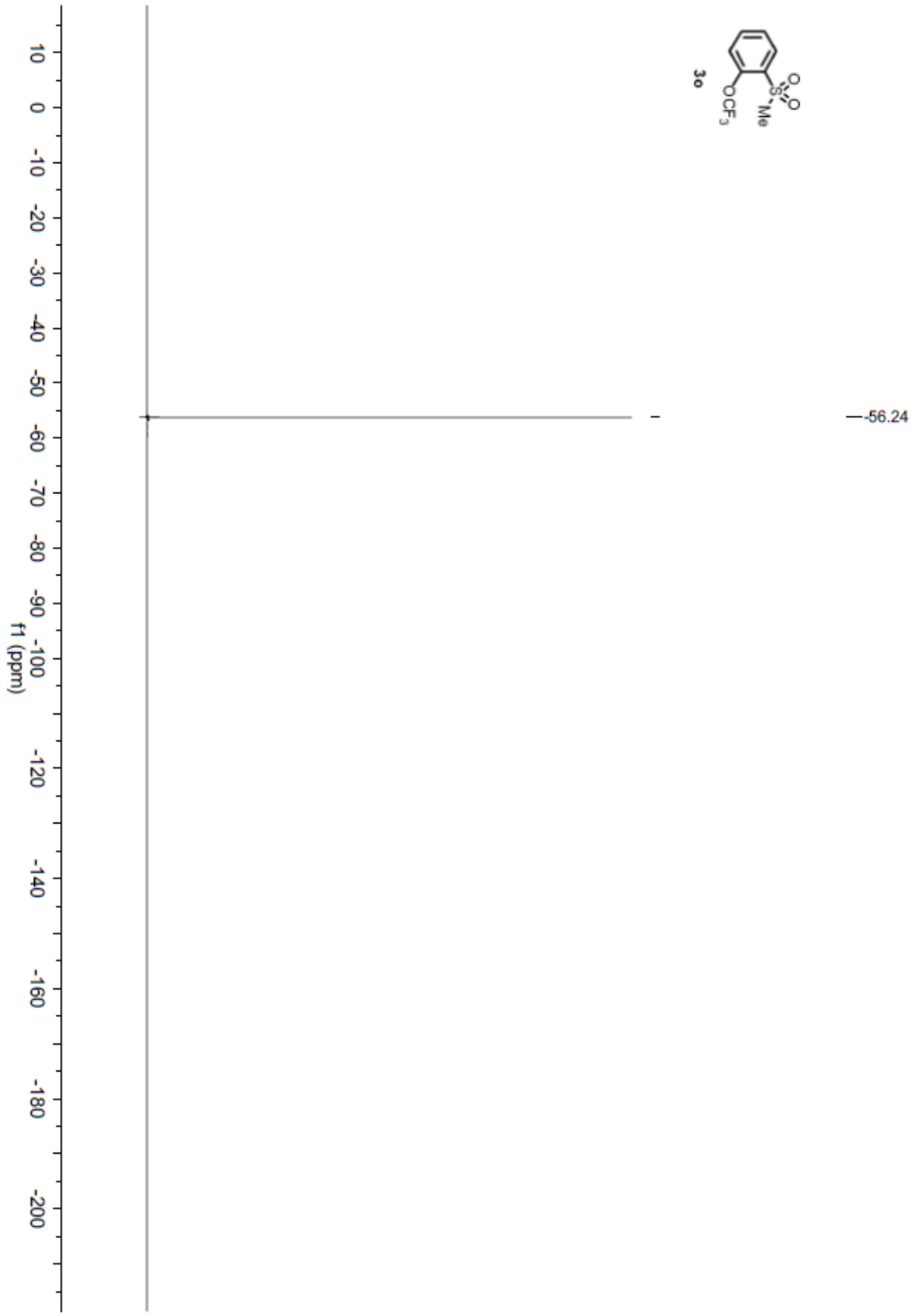

3m
CN
S
O
O
Me
1.00
1.03
1.02
1.04
3.04
f1 (ppm)

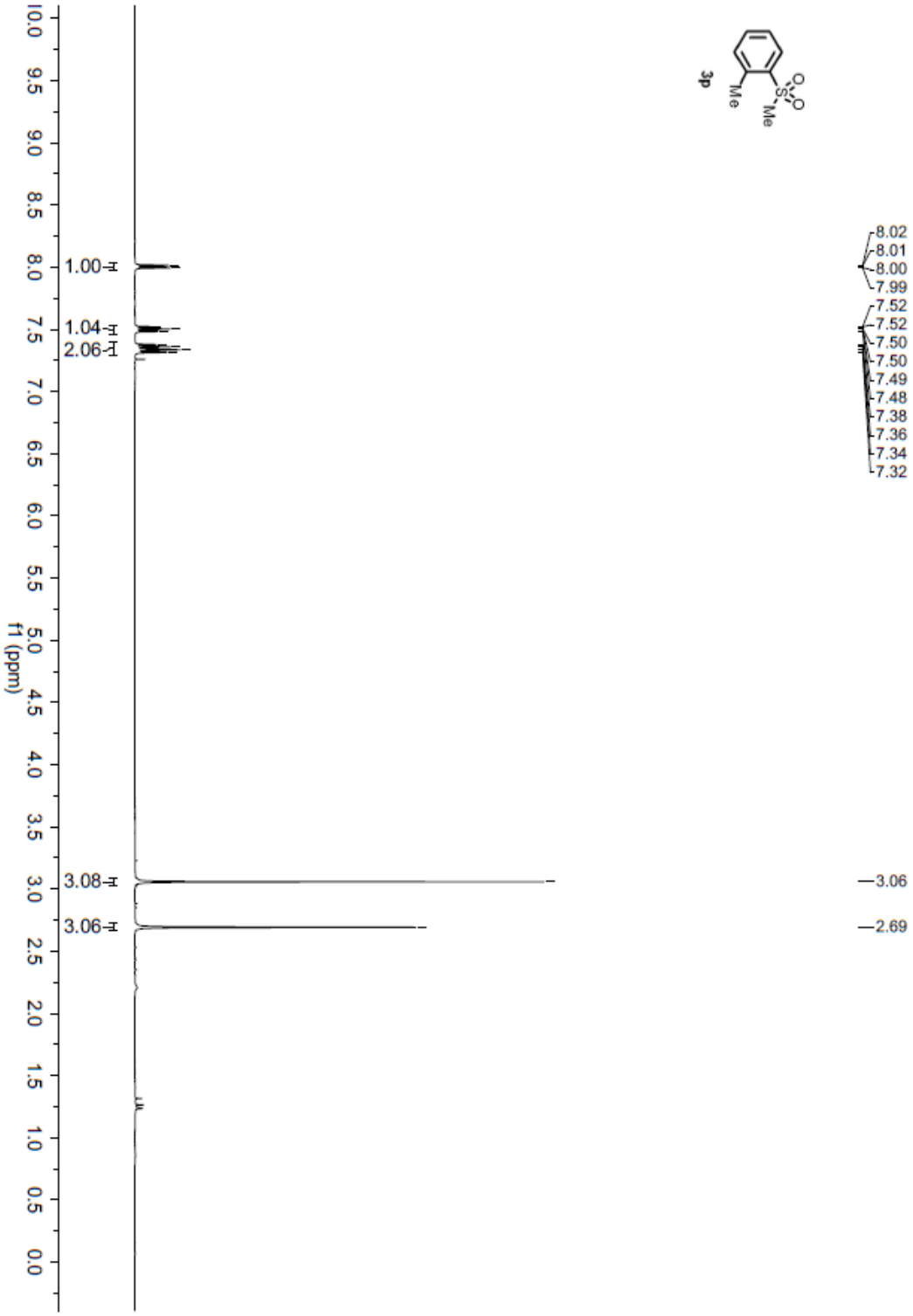

3m
142.08
136.83
131.39
131.15
130.50
116.82
114.02
44.29
f1 (ppm)

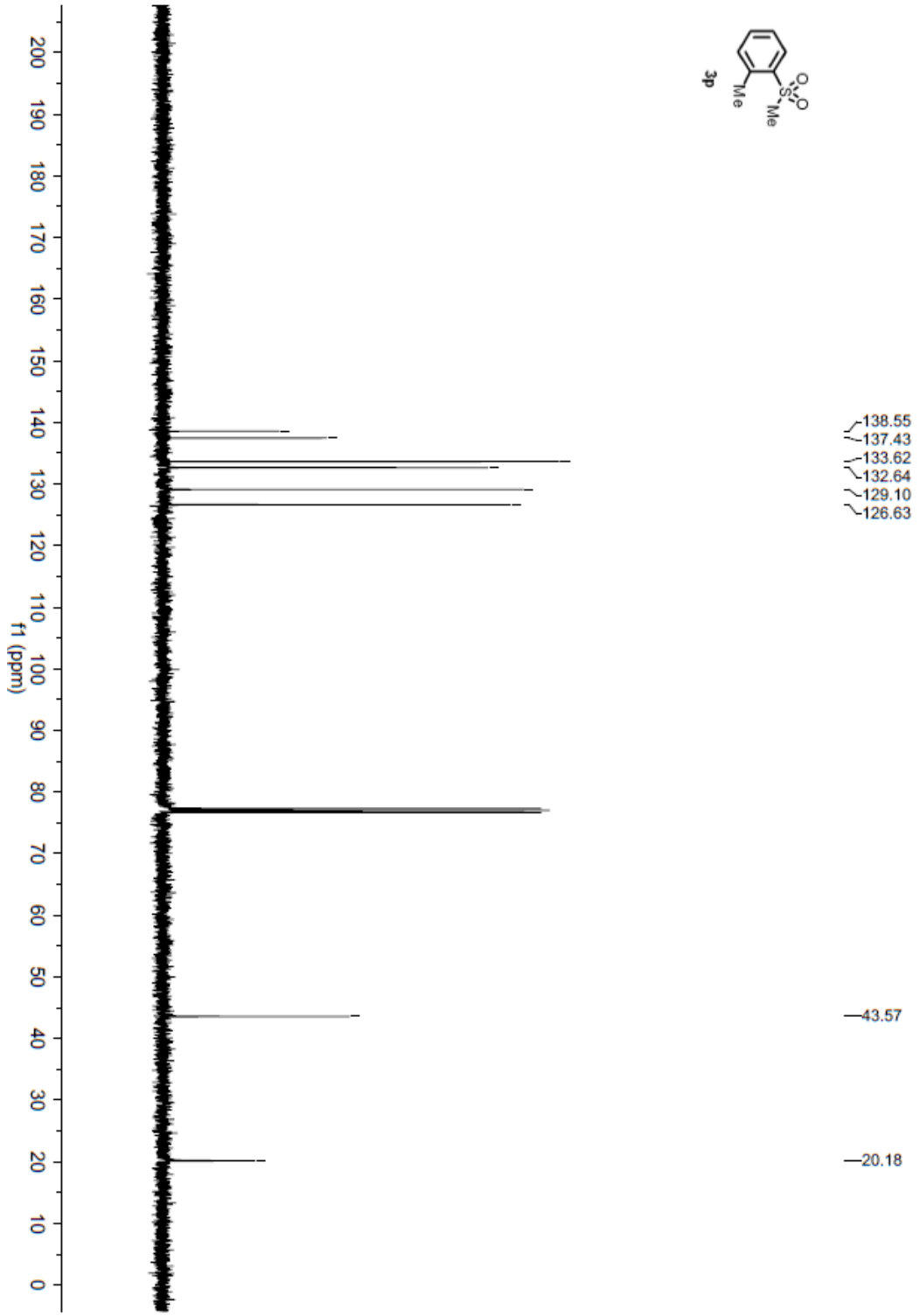

8.13
8.13
8.11
8.11
7.72
7.71
7.71
7.70
7.69
7.69
7.68
7.68
7.67
7.67
7.66
7.66
7.65
7.64
3.97
3.35
f1 (ppm)
3n

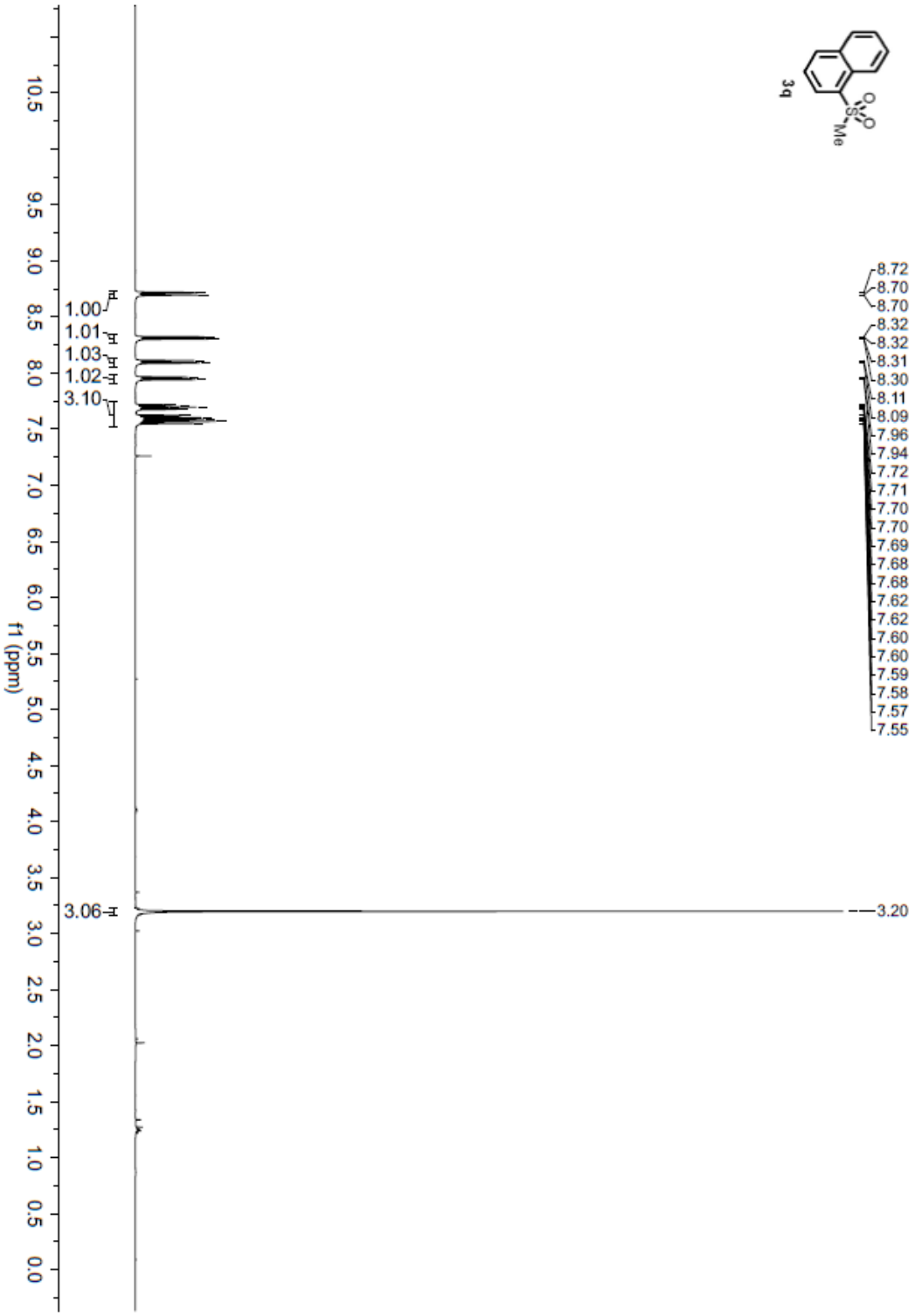

3o
OCF3
S
O
O
Me
8.10
8.10
8.08
8.08
7.72
7.71
7.70
7.69
7.68
7.67
7.48
7.48
7.46
7.46
7.45
7.45
7.44
7.43
7.43
3.20
1.00
1.03
2.03
3.03
f1 (ppm)

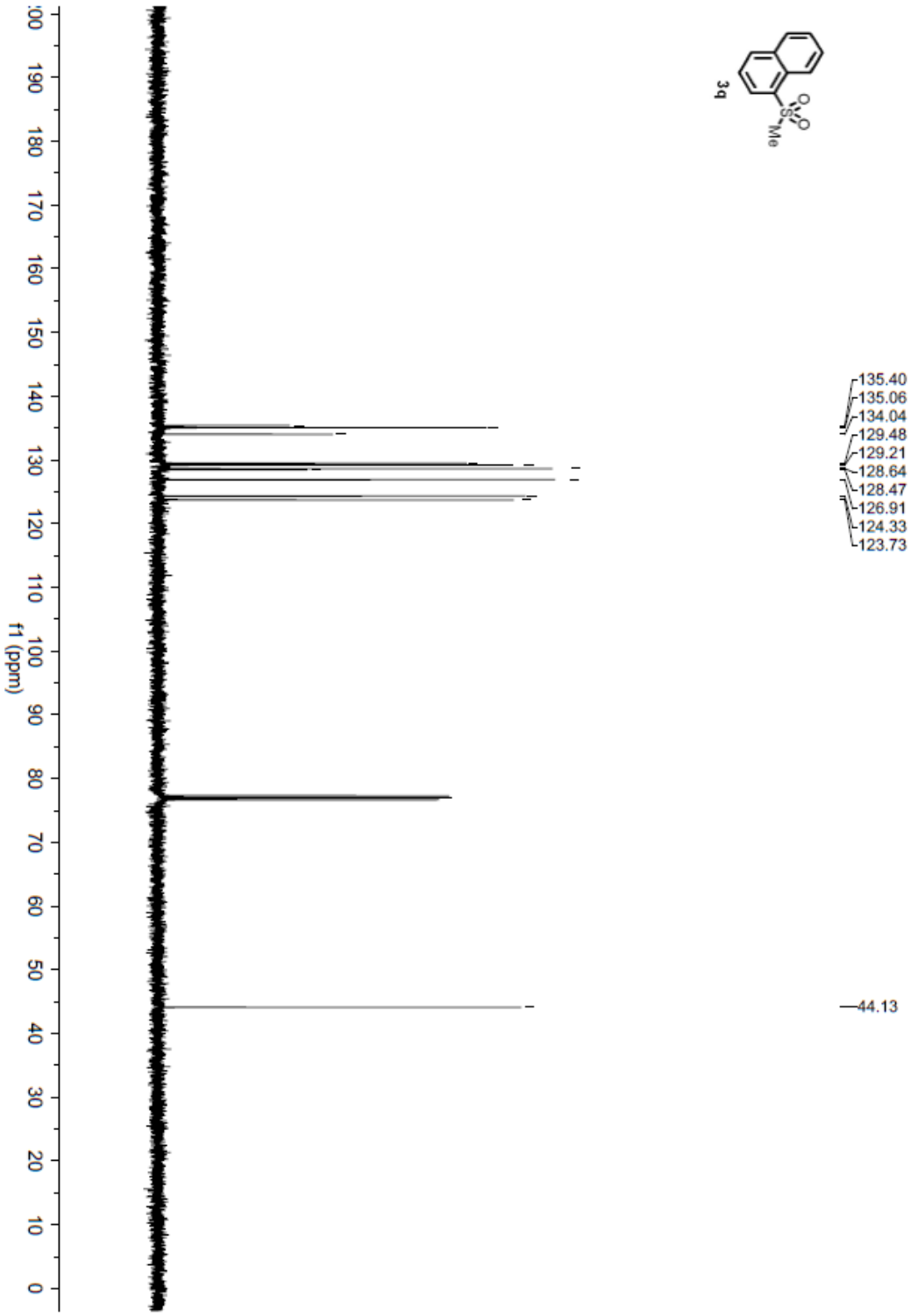

3o
146.76
146.75
135.58
132.43
130.44
129.28
126.87
124.13
121.53
120.08
120.06
118.93
116.33
43.73
f1 (ppm)

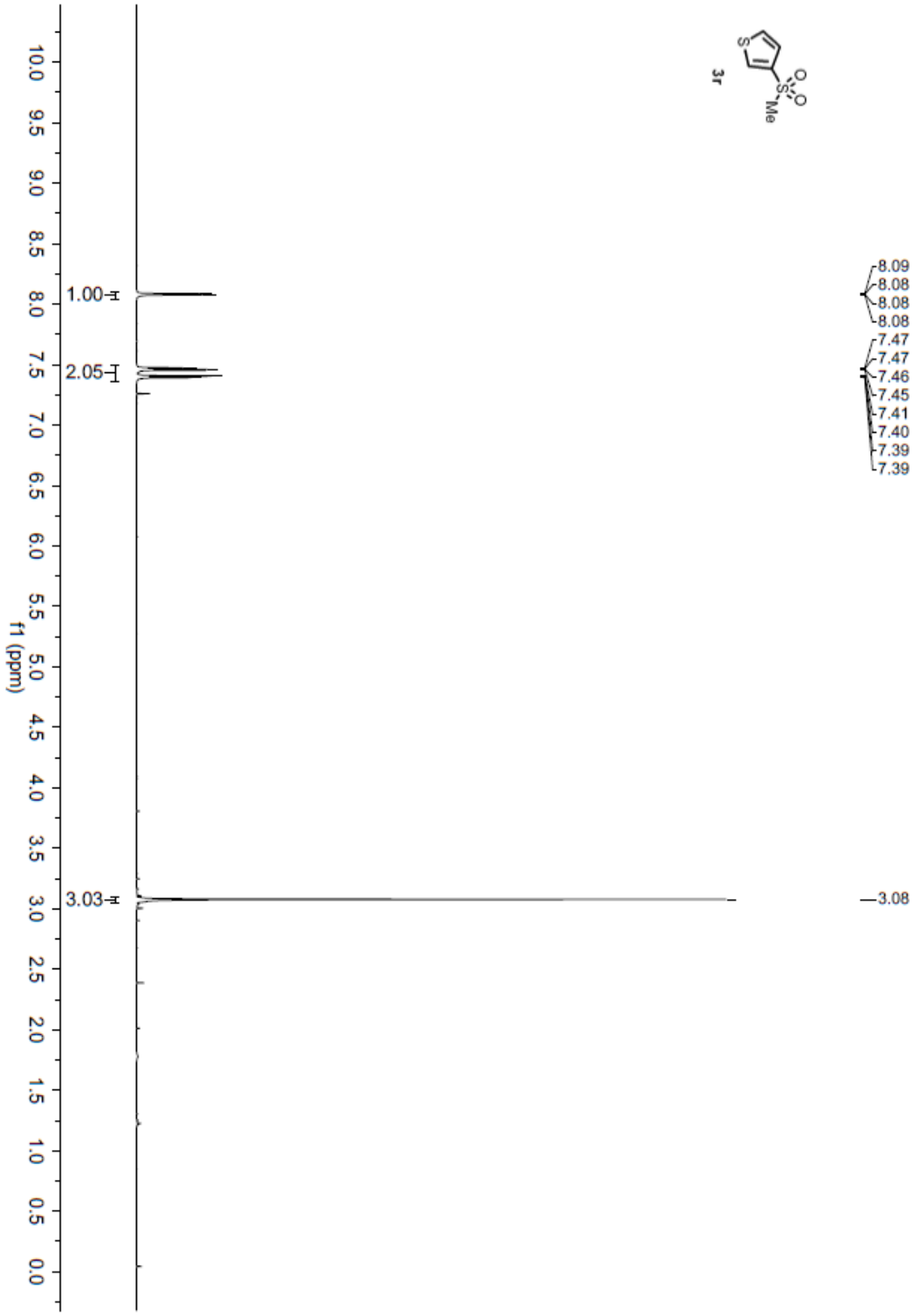

-56.24
3o
f1 (ppm)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

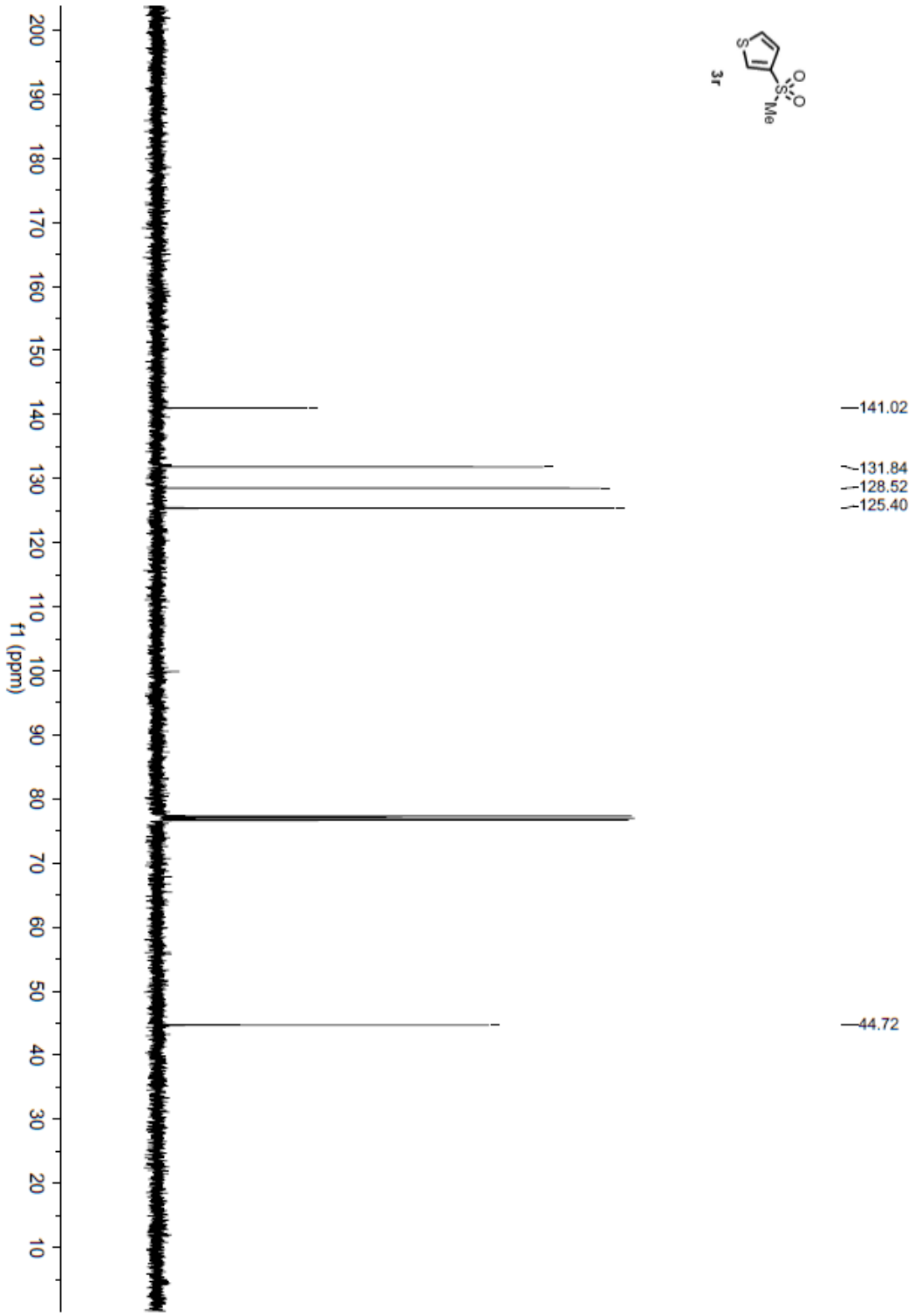

3p
Me
S
O
O
Me
8.02
8.01
8.00
7.99
7.52
7.52
7.50
7.50
7.49
7.48
7.38
7.36
7.34
7.32
3.06
2.69
1.00
1.04
2.06
3.08
3.06
f1 (ppm)

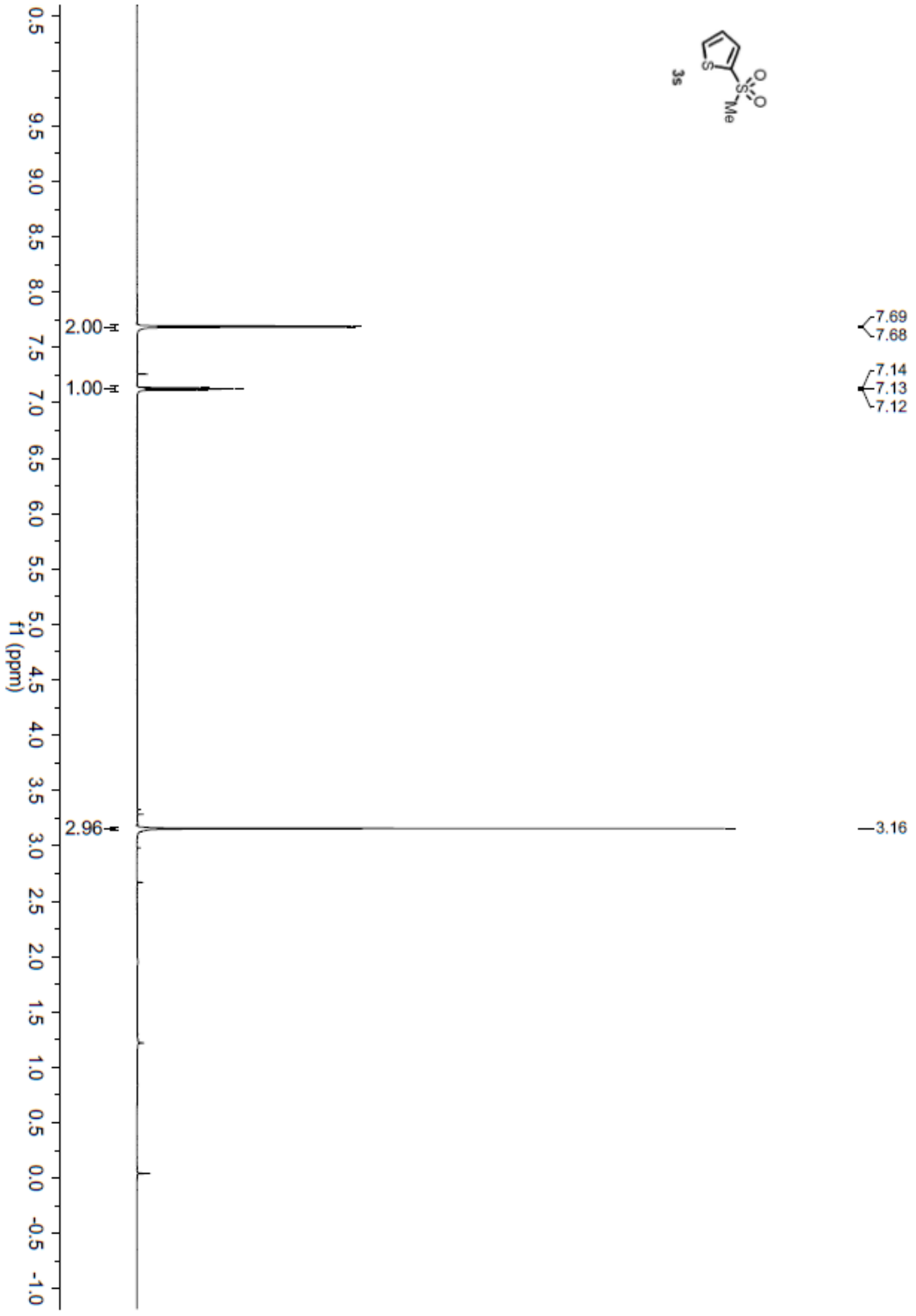

3p
Me
S
O
O
Me
138.55
137.43
133.62
132.64
129.10
126.63
43.57
20.18
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

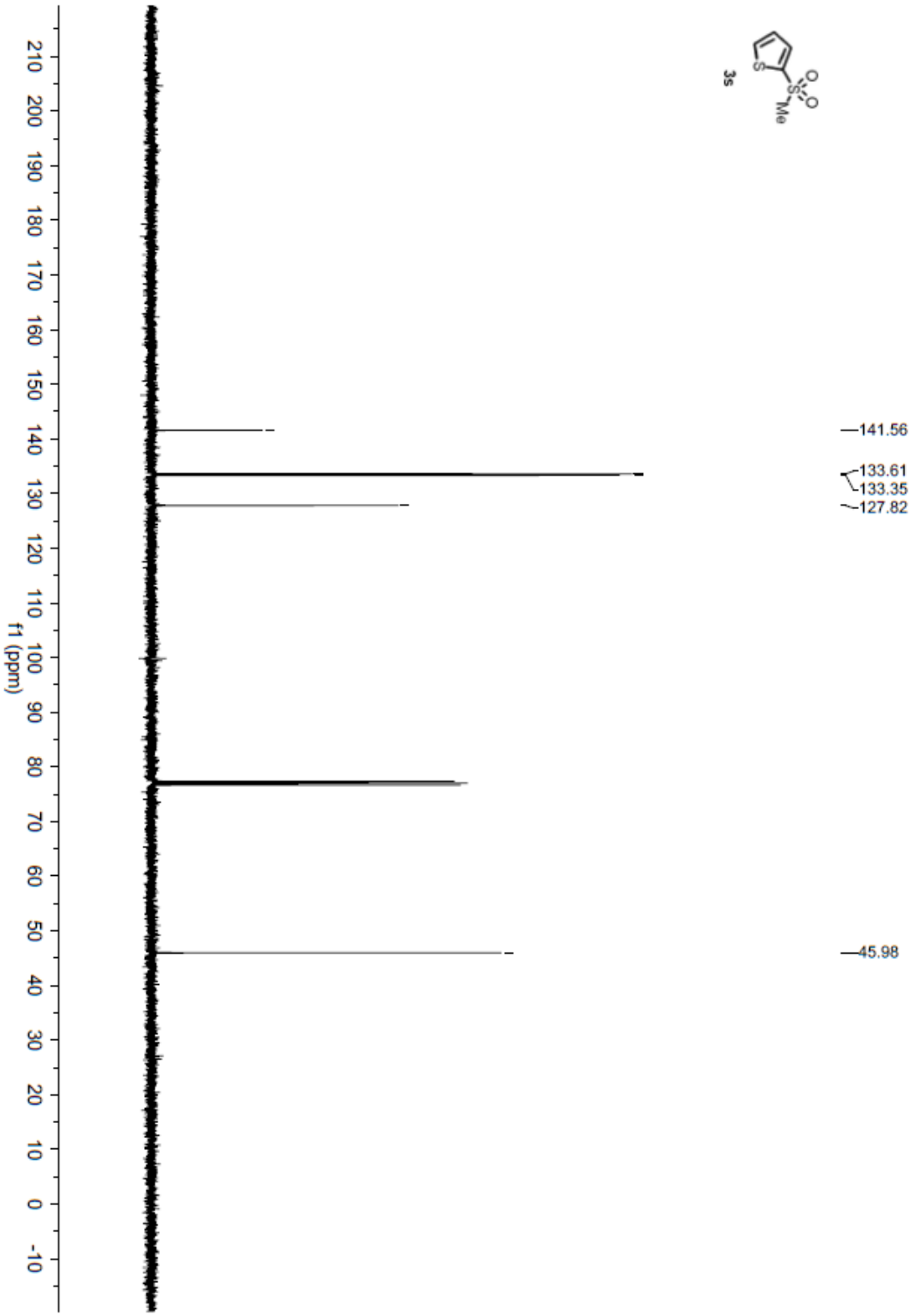

3q
8.72
8.70
8.70
8.32
8.32
8.31
8.30
8.11
8.09
7.96
7.94
7.72
7.71
7.70
7.70
7.69
7.68
7.68
7.62
7.62
7.60
7.60
7.59
7.58
7.57
7.55
1.00
1.01
1.03
1.02
3.10
3.06
3.20
f1 (ppm)

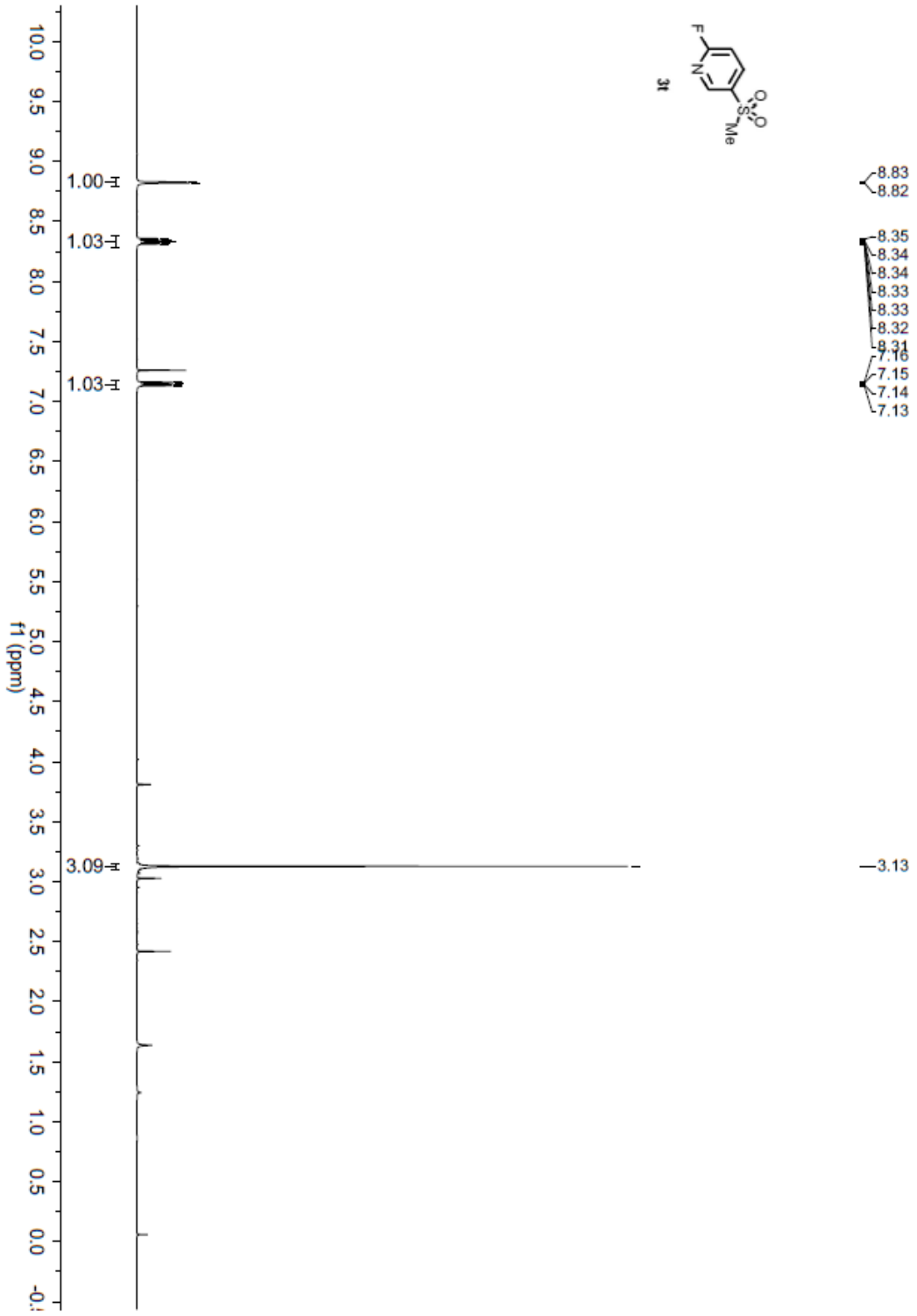

3q
135.40
135.06
134.04
129.48
129.21
128.64
128.47
126.91
124.33
123.73
44.13
f1 (ppm)

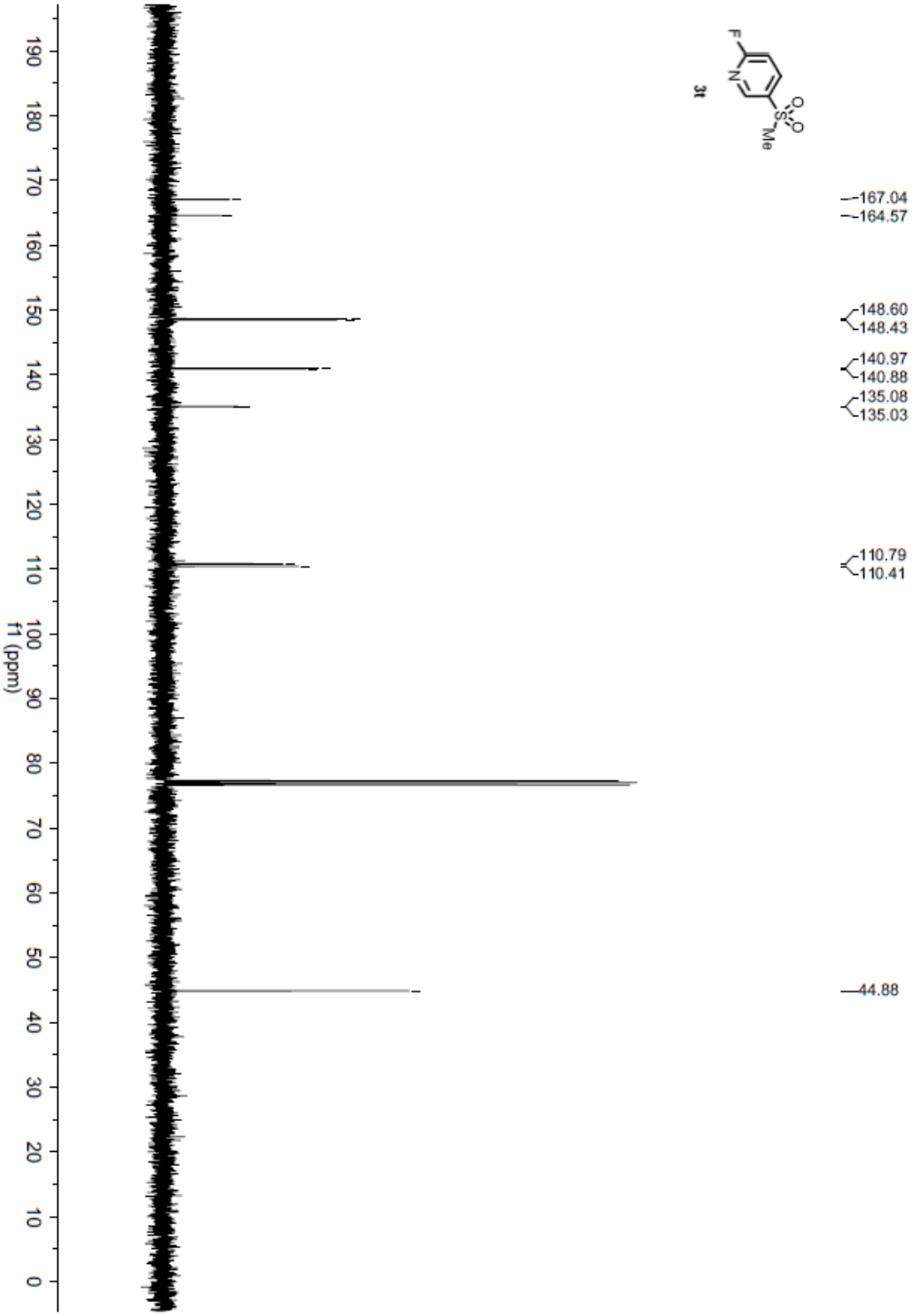

3r
8.09
8.08
8.08
8.08
7.47
7.47
7.46
7.45
7.41
7.40
7.39
7.39
3.08
1.00
2.05
3.03
f1 (ppm)

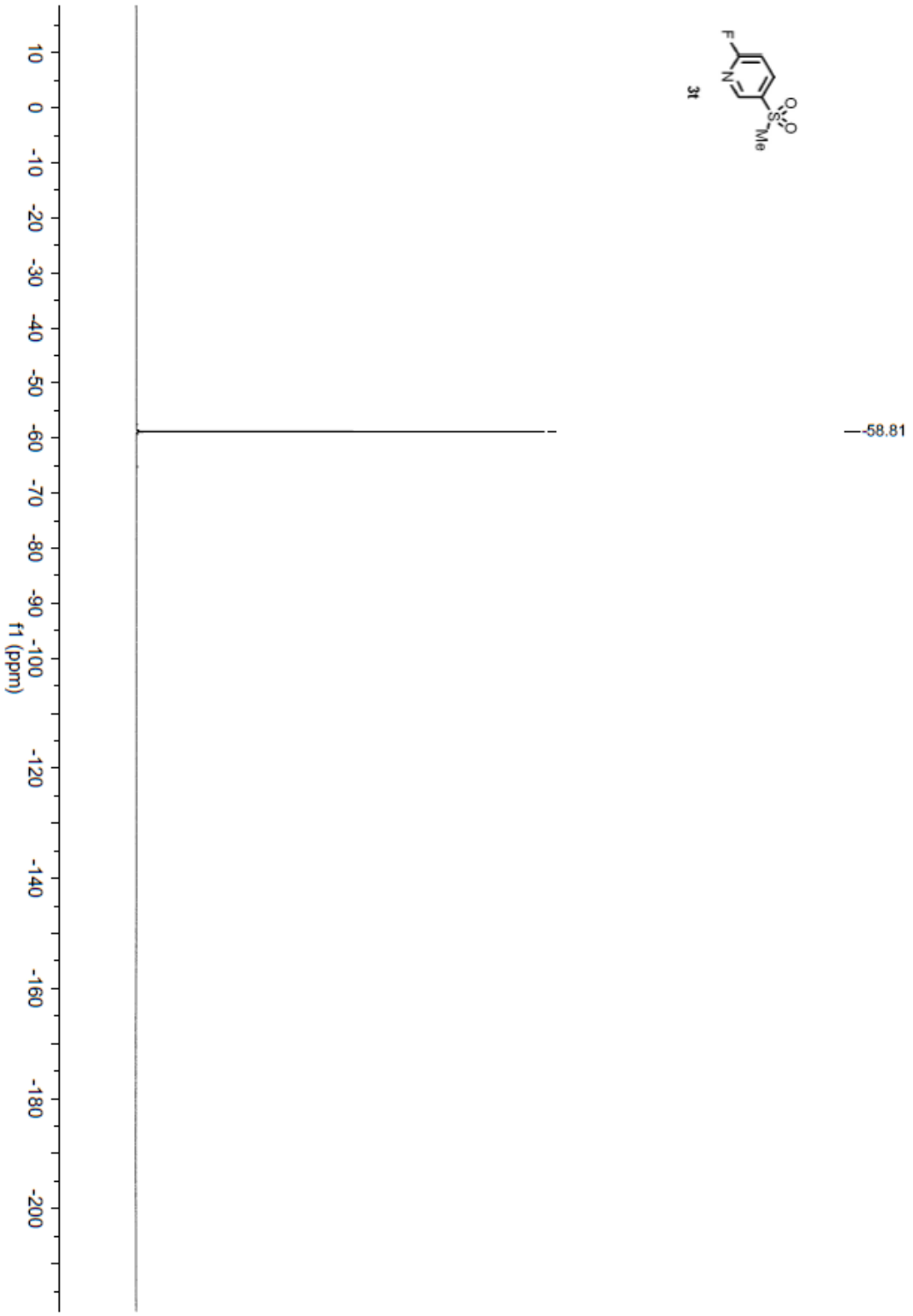

3r
141.02
131.84
128.52
125.40
44.72
f1 (ppm)

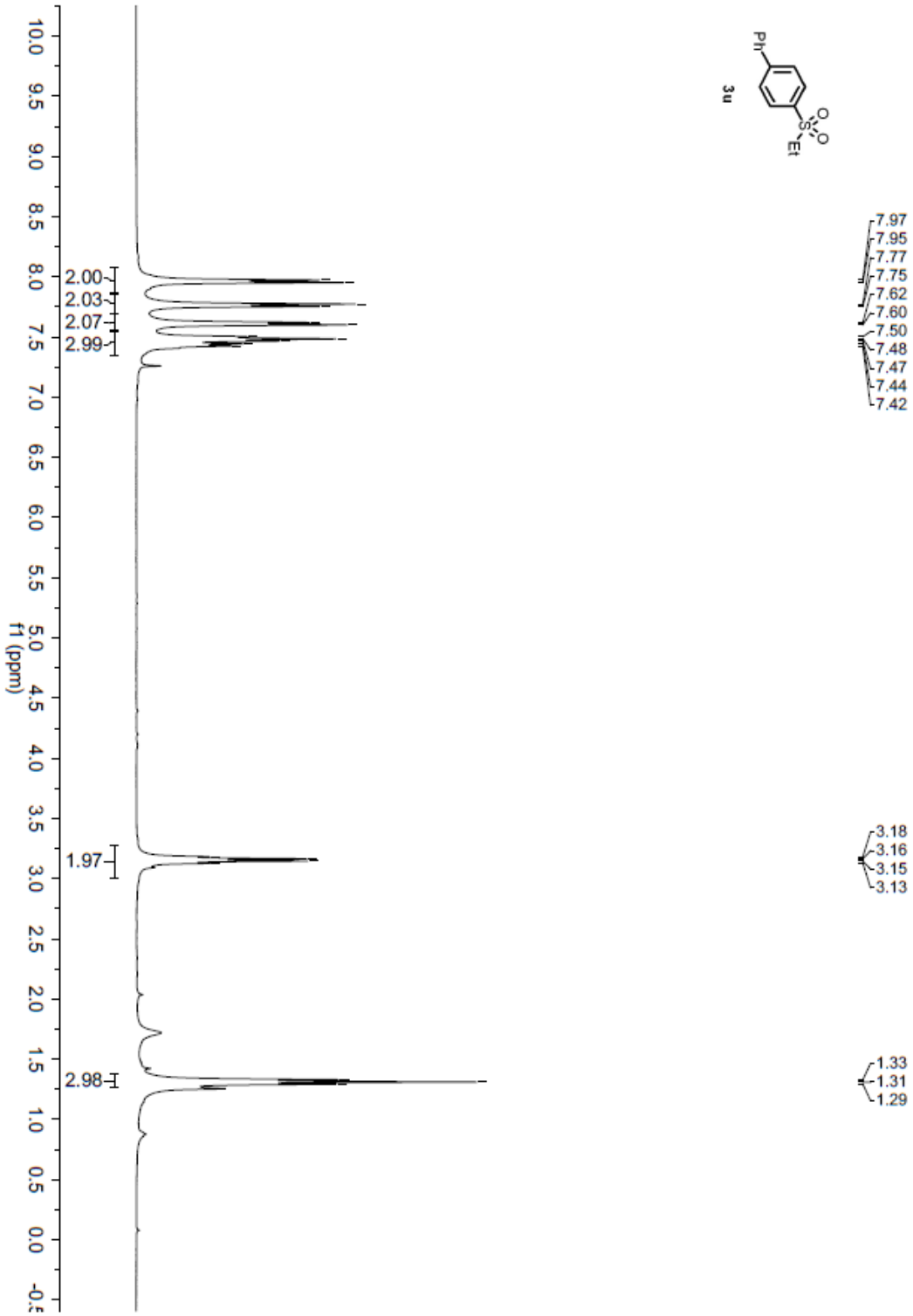

3s
O
O
S
Me
S
2.00
1.00
2.96
7.69
7.68
7.14
7.13
7.12
3.16
f1 (ppm)
0.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

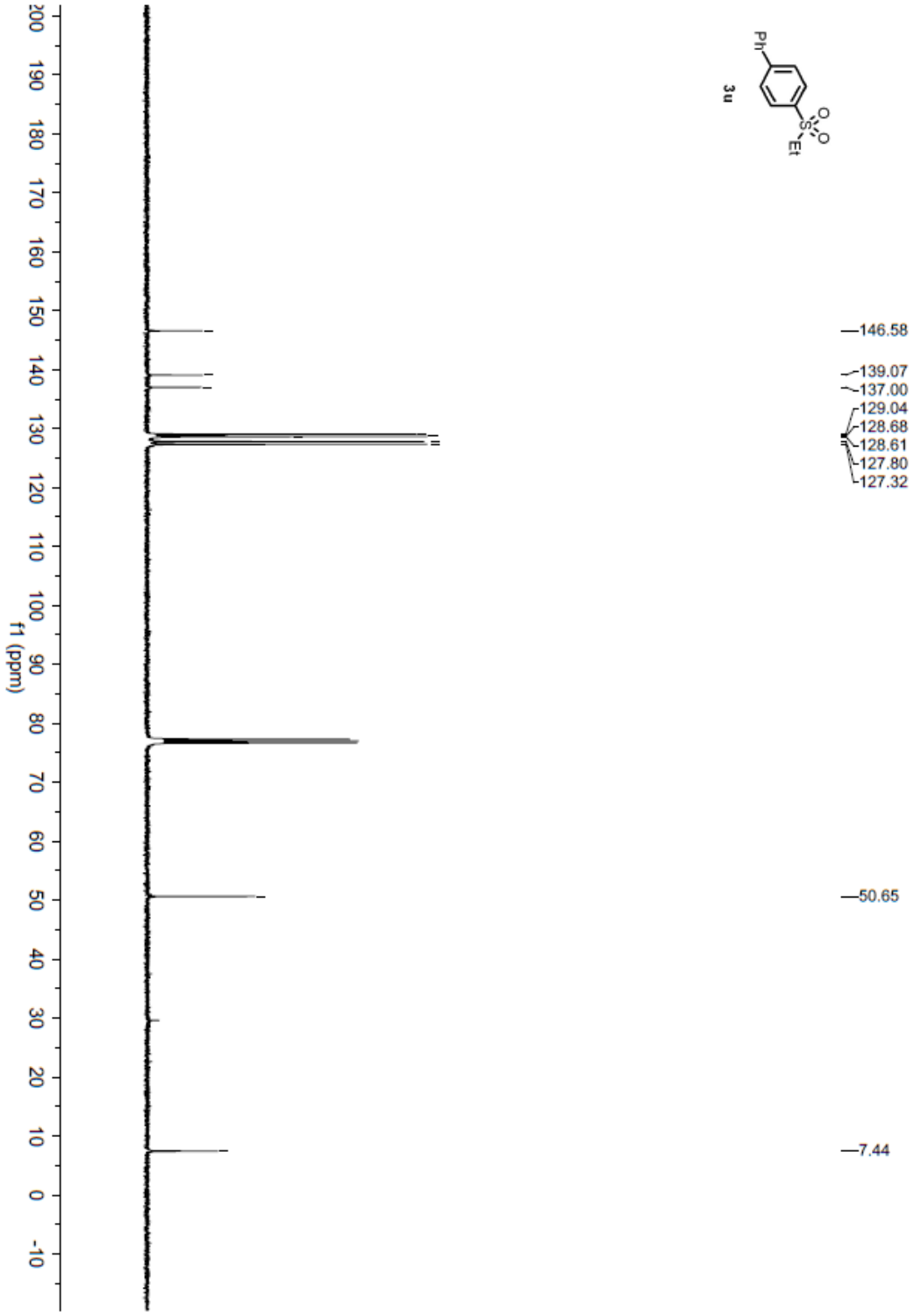

3s
141.56
133.61
133.35
127.82
45.98
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

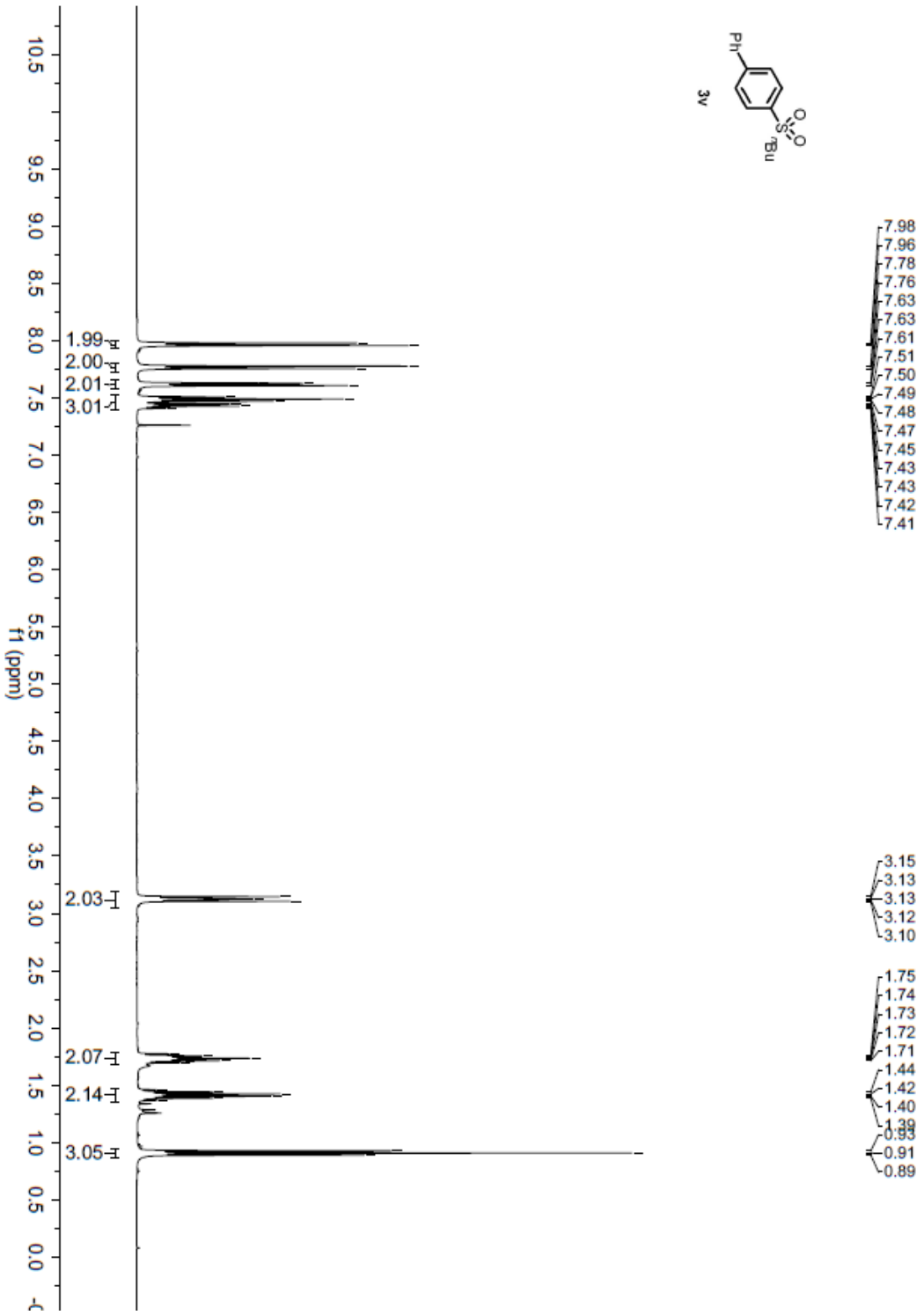

3t
F
N
S
O
O
Me
1.00
1.03
1.03
3.09
8.83
8.82
8.35
8.34
8.34
8.33
8.33
8.32
8.31
7.16
7.15
7.14
7.13
3.13
f1 (ppm)

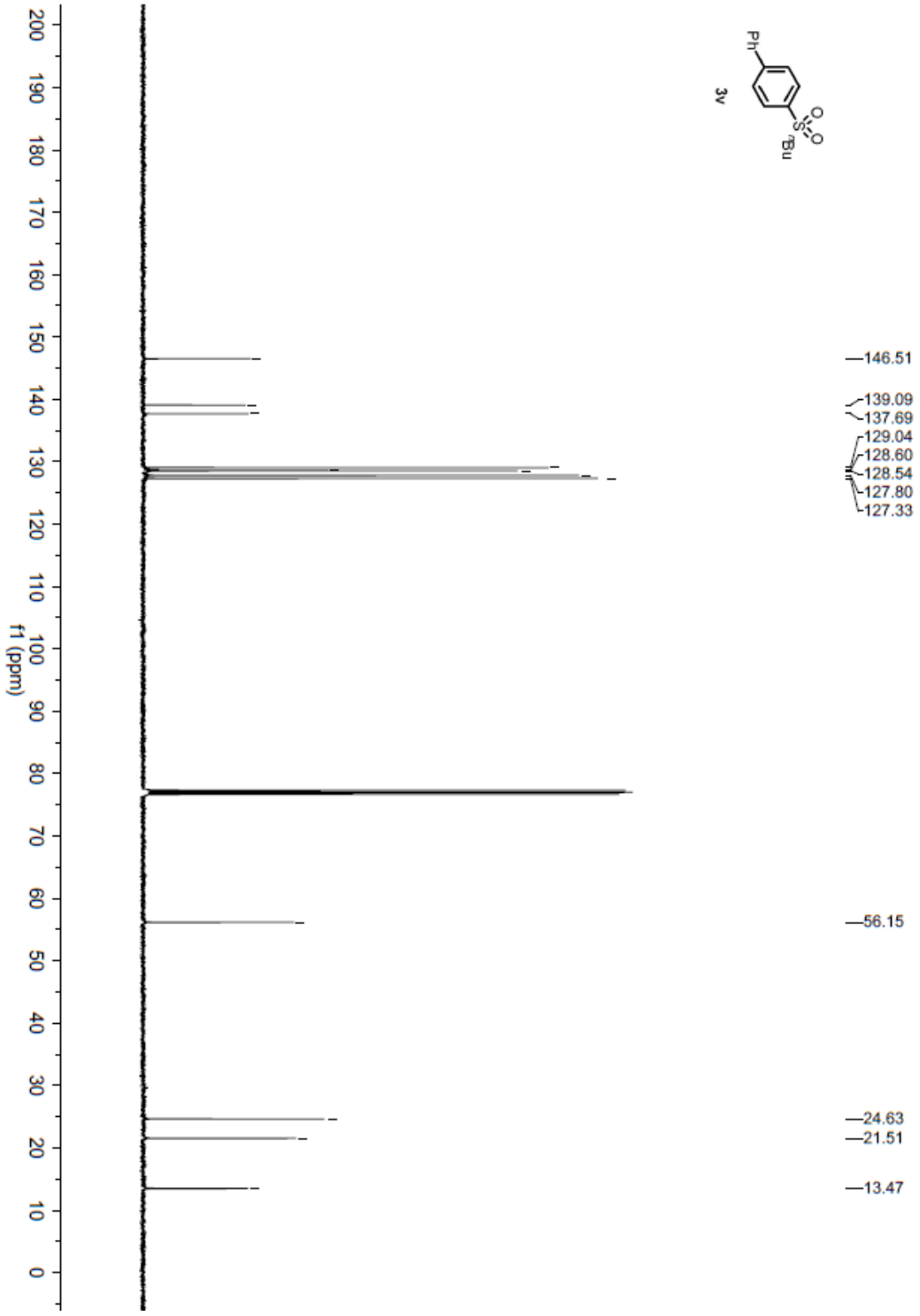

3t
F
N
O
O
S
Me
167.04
164.57
148.60
148.43
140.97
140.88
135.08
135.03
110.79
110.41
44.88
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

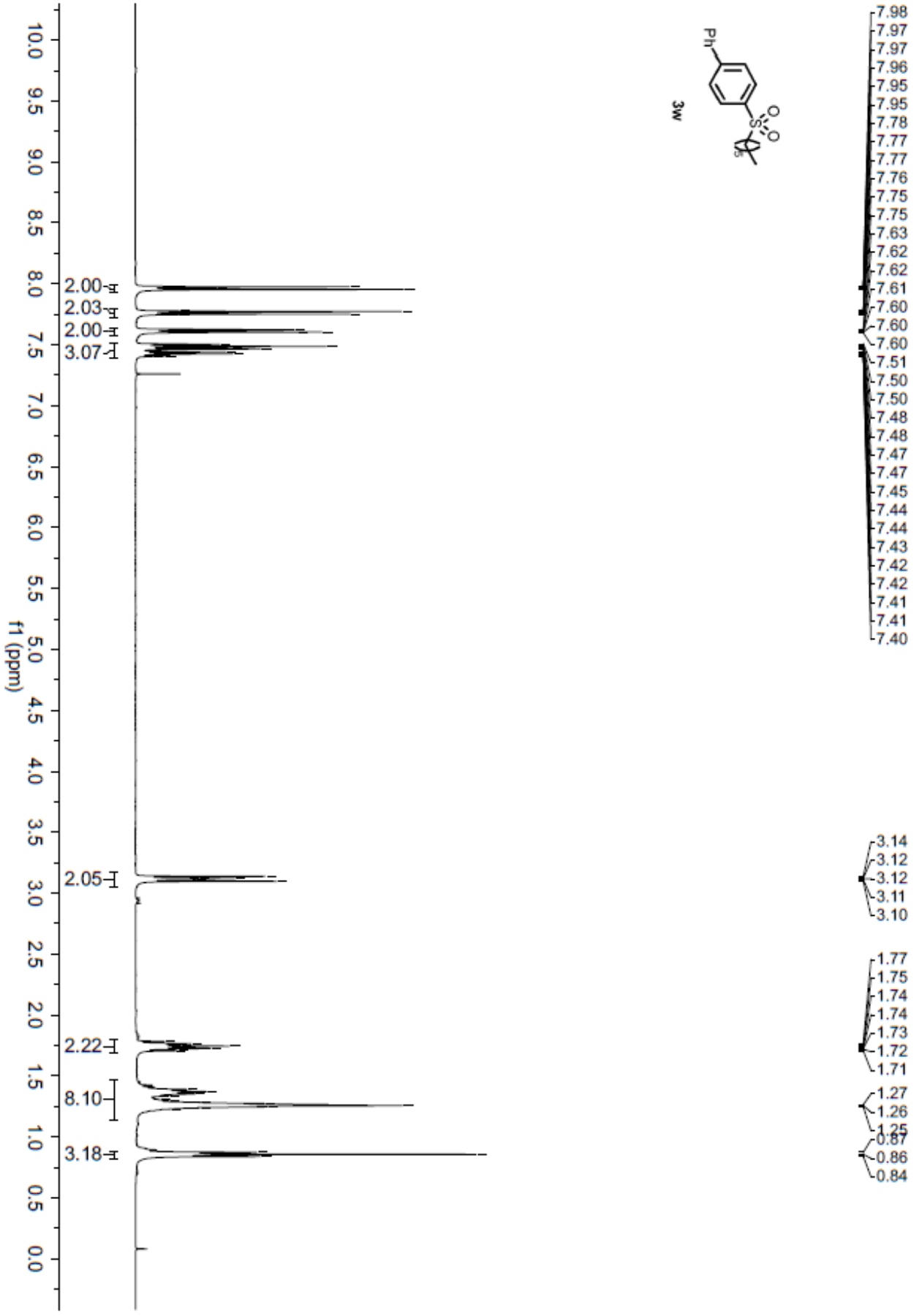

-58.81
3t
F
N
O
O
S
Me
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

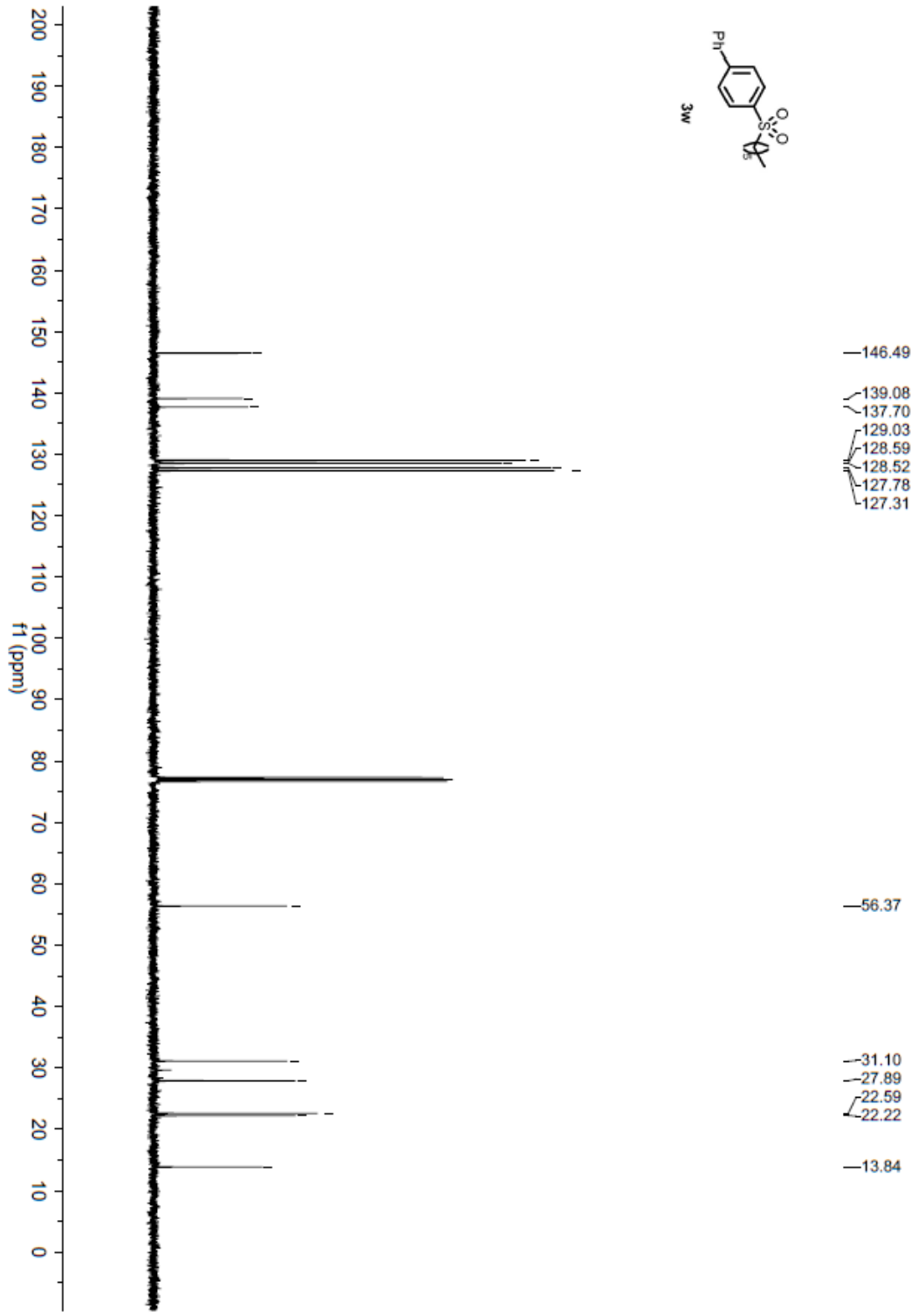

3u
Ph
O
O
S
Et
7.97
7.95
7.77
7.75
7.62
7.60
7.50
7.48
7.47
7.44
7.42
3.18
3.16
3.15
3.13
1.33
1.31
1.29
2.00
2.03
2.07
2.99
1.97
2.98
f1 (ppm)

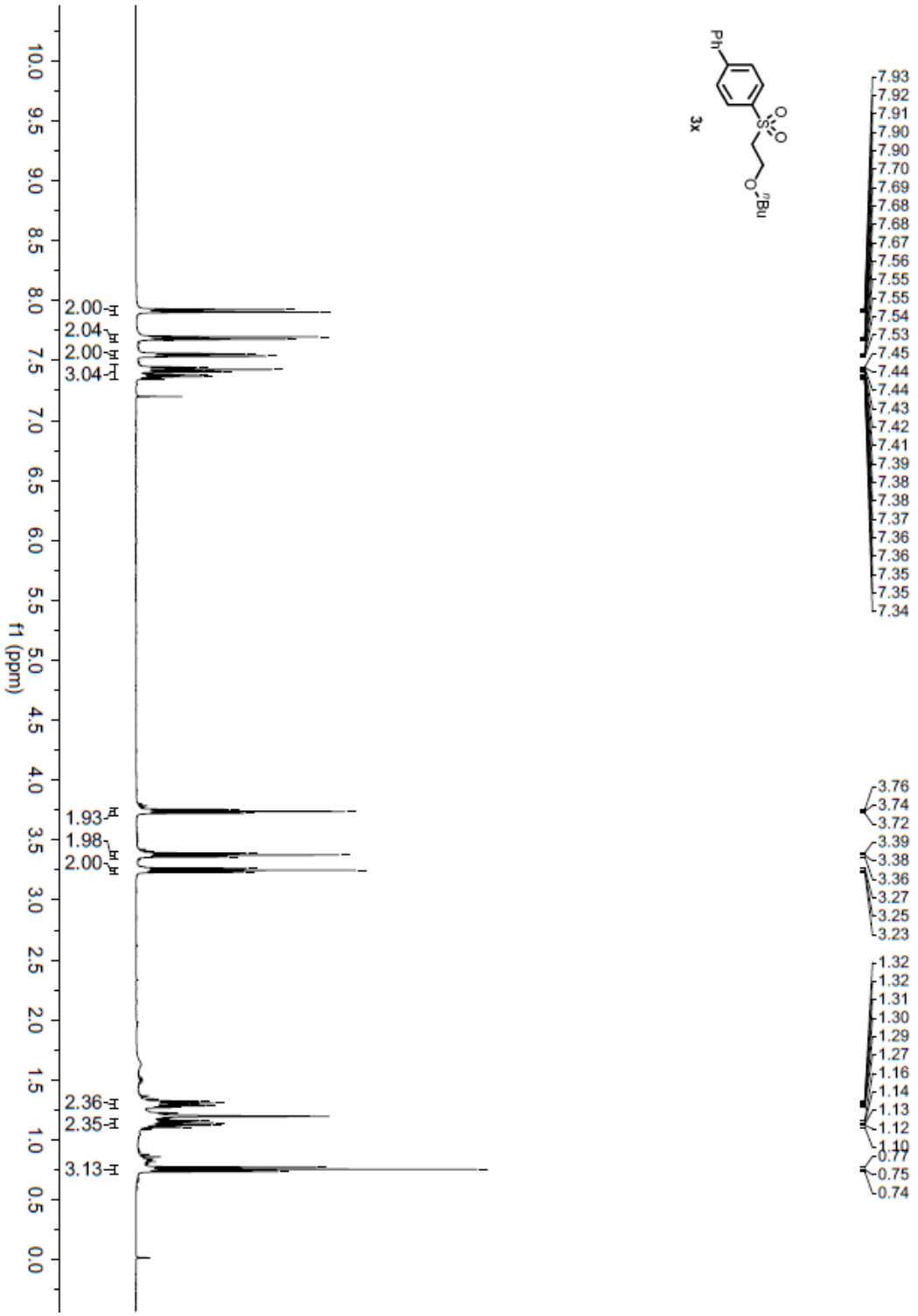

Ph
O
O
S
Et
3u
146.58
139.07
137.00
129.04
128.68
128.61
127.80
127.32
50.65
7.44
f1 (ppm)

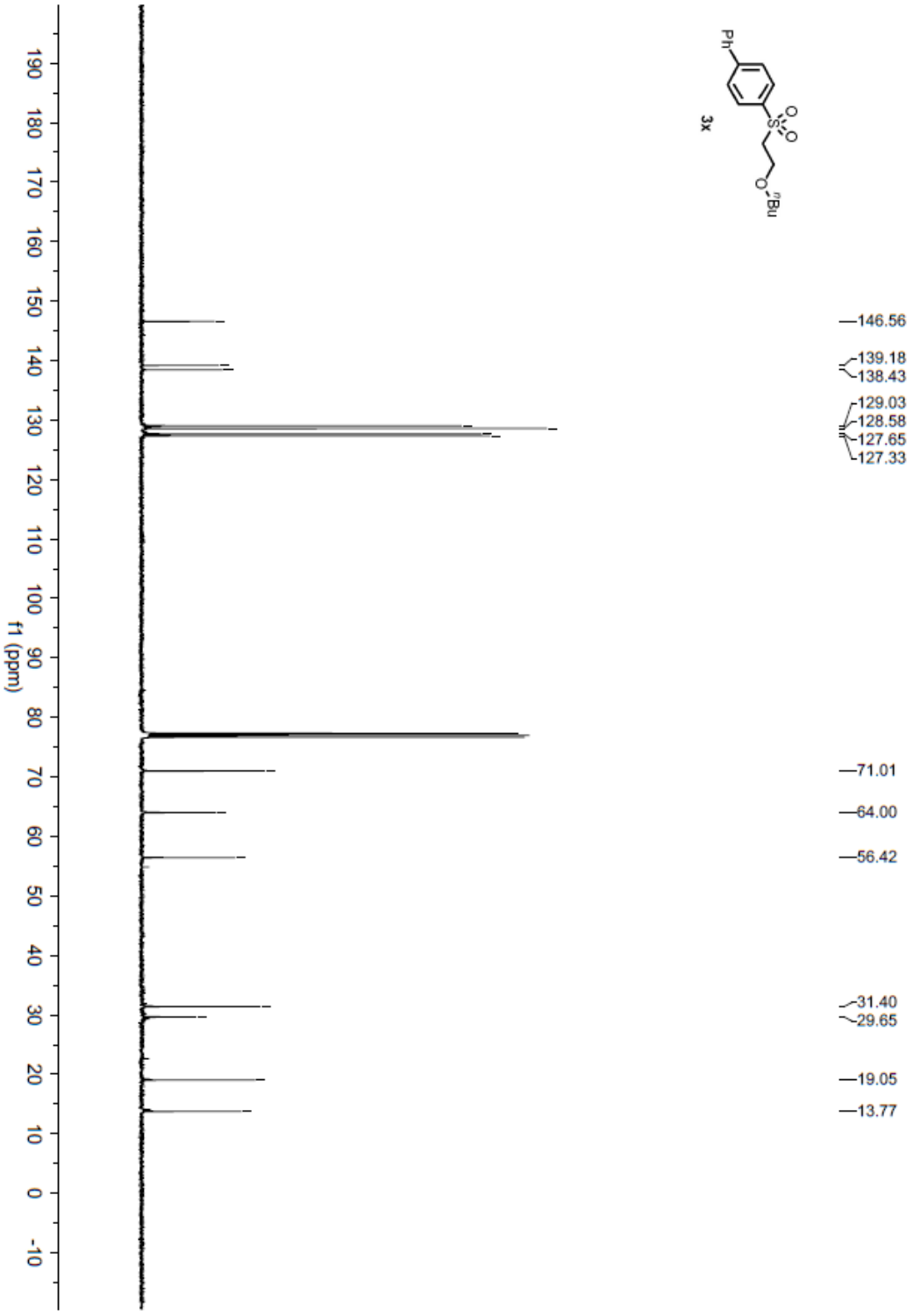

3v
Ph
O
O
S
tBu
f1 (ppm)
1.99
2.00
2.01
3.01
2.03
2.07
2.14
3.05
7.98
7.96
7.78
7.76
7.63
7.63
7.61
7.51
7.50
7.49
7.48
7.47
7.45
7.43
7.43
7.42
7.41
3.15
3.13
3.13
3.12
3.10
1.75
1.74
1.73
1.72
1.71
1.44
1.42
1.40
0.93
0.91
0.89

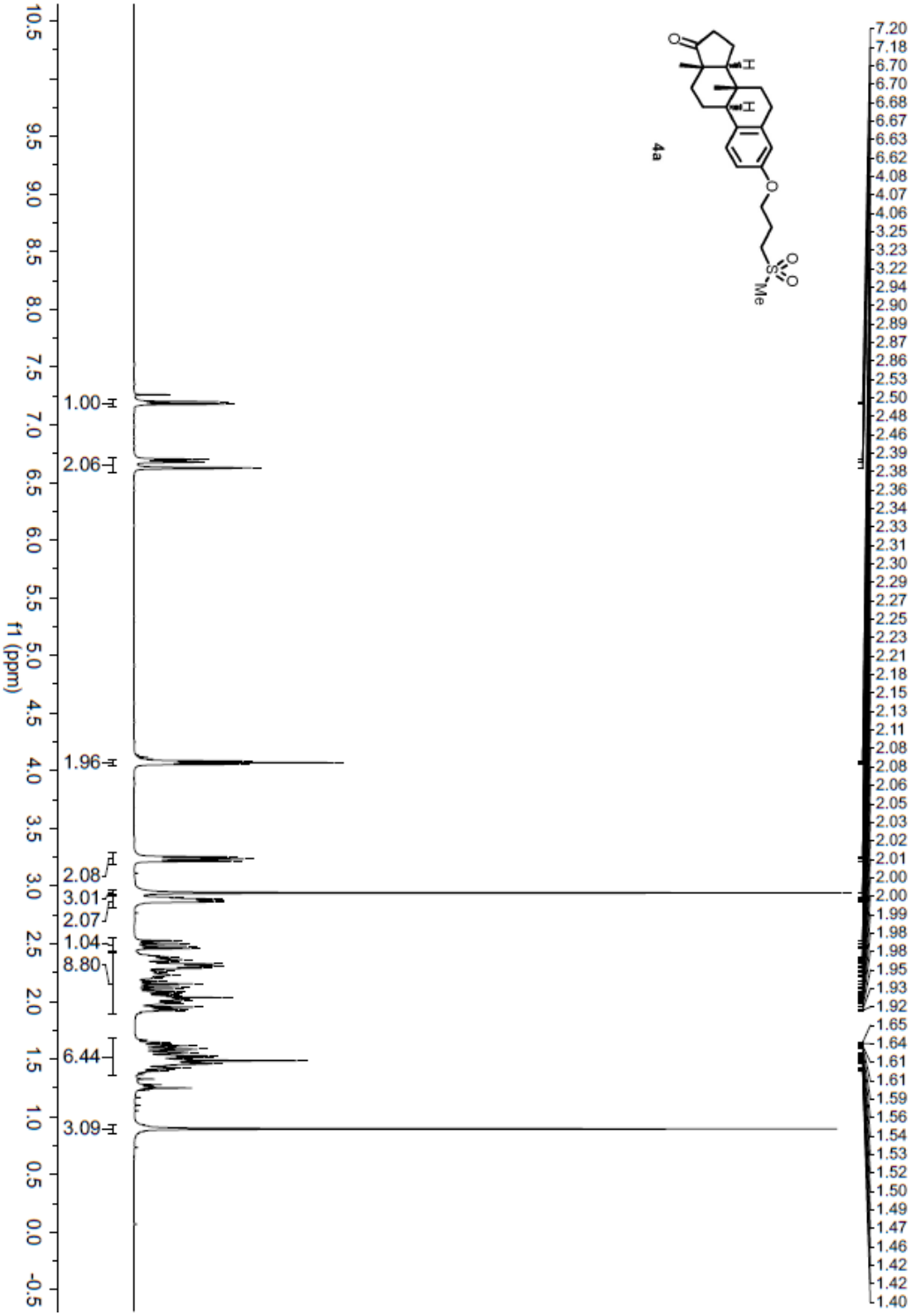

Ph
O
S
O
nBu
3v
146.51
139.09
137.69
129.04
128.60
128.54
127.80
127.33
56.15
24.63
21.51
13.47
f1 (ppm)

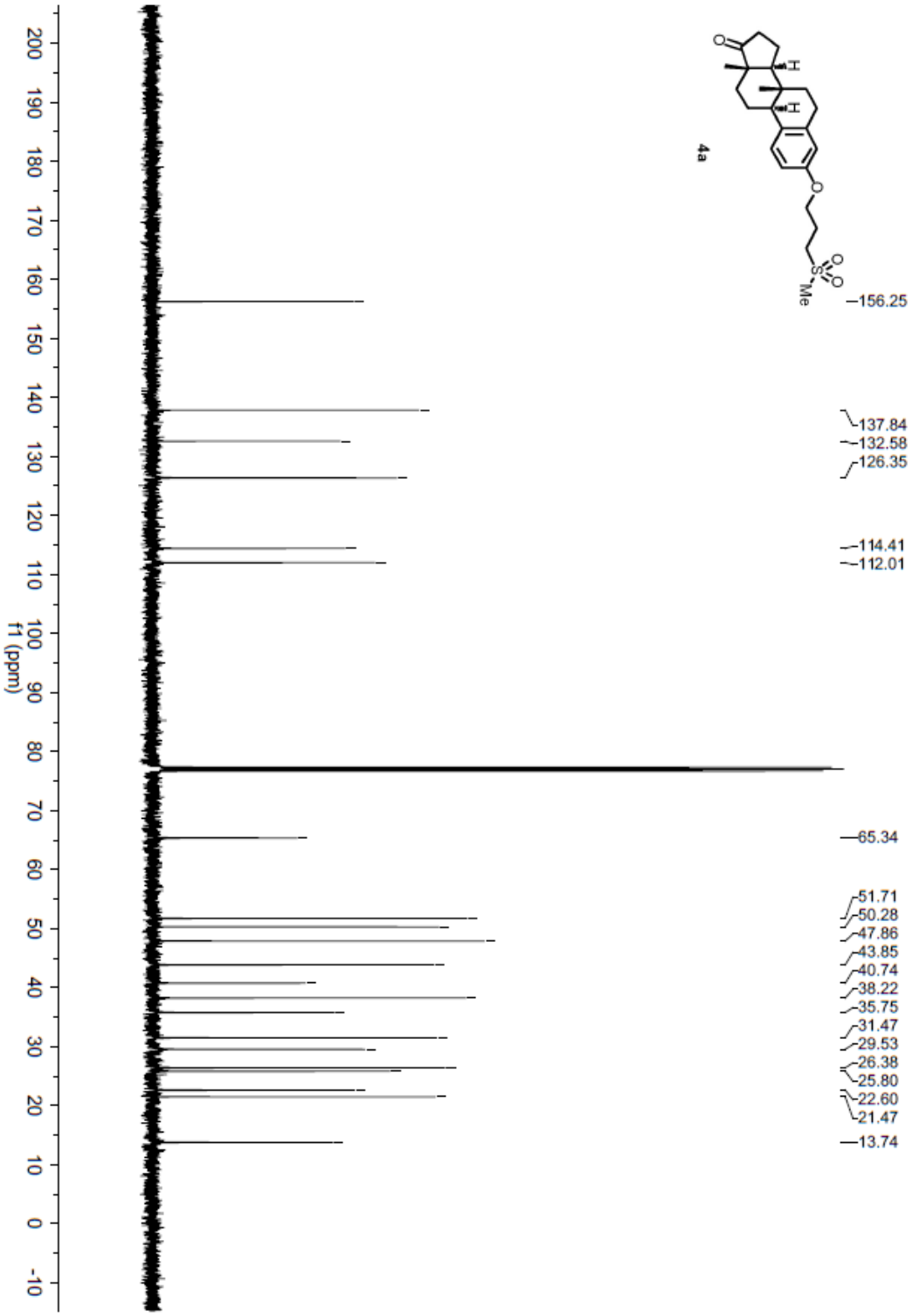

3w
Ph
O
O
S
7.98
7.97
7.97
7.96
7.95
7.95
7.78
7.77
7.77
7.76
7.75
7.75
7.63
7.62
7.62
7.61
7.60
7.60
7.60
7.51
7.50
7.50
7.48
7.48
7.47
7.47
7.45
7.44
7.44
7.43
7.42
7.42
7.41
7.41
7.40
3.14
3.12
3.12
3.11
3.10
1.77
1.75
1.74
1.74
1.73
1.72
1.71
1.27
1.26
1.25
0.87
0.86
0.84
2.00
2.03
2.00
3.07
2.05
2.22
8.10
3.18
f1 (ppm)

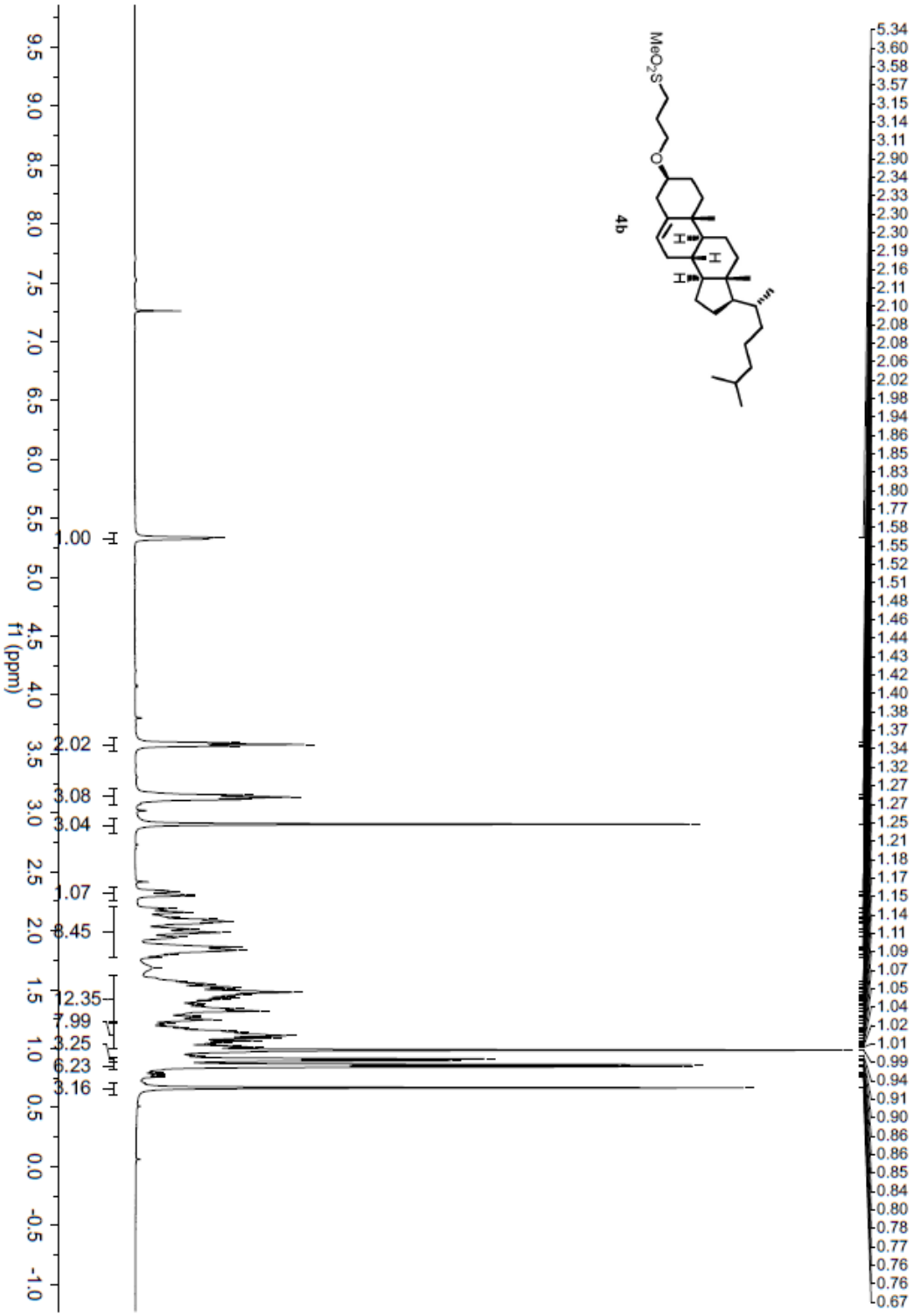

Ph
3w
146.49
139.08
137.70
129.03
128.59
128.52
127.78
127.31
56.37
31.10
27.89
22.59
22.22
13.84
f1 (ppm)

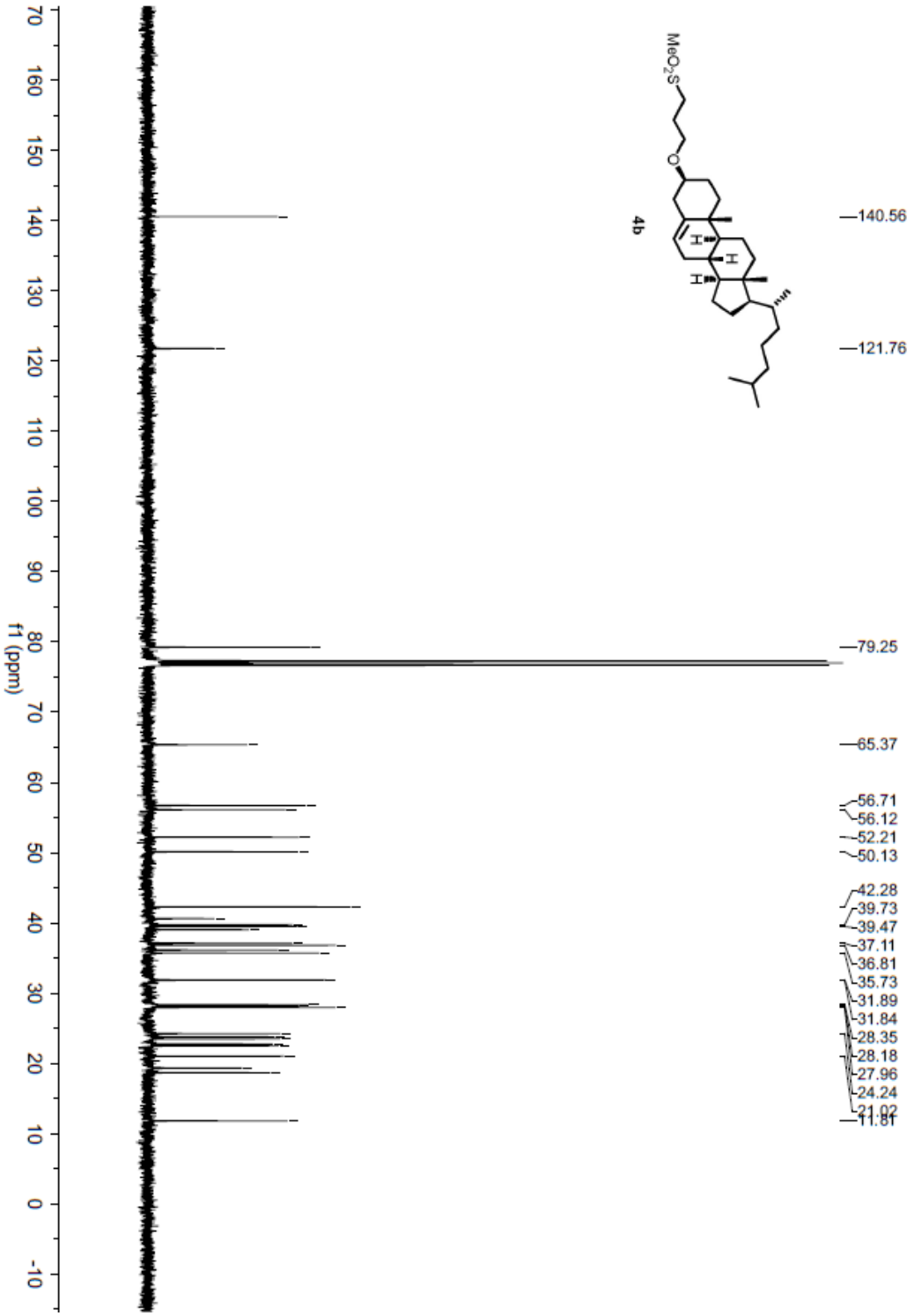

Ph
O
O
S
O
nBu
3x
7.93
7.92
7.91
7.90
7.90
7.70
7.69
7.68
7.68
7.67
7.56
7.55
7.55
7.54
7.53
7.45
7.44
7.44
7.43
7.42
7.41
7.39
7.38
7.38
7.37
7.36
7.36
7.35
7.35
7.34
3.76
3.74
3.72
3.39
3.38
3.36
3.27
3.25
3.23
1.32
1.32
1.31
1.30
1.29
1.27
1.16
1.14
1.13
1.12
1.10
0.77
0.75
0.74
2.00
2.04
2.00
3.04
1.93
1.98
2.00
2.36
2.35
3.13
f1 (ppm)


Ph
O
O
S
O
nBu
3x
146.56
139.18
138.43
129.03
128.58
127.65
127.33
71.01
64.00
56.42
31.40
29.65
19.05
13.77
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


4a
f1 (ppm)
1.00
2.06
1.96
2.08
3.01
2.07
1.04
8.80
6.44
3.09


4a
156.25
137.84
132.58
126.35
114.41
112.01
65.34
51.71
50.28
47.86
43.85
40.74
38.22
35.75
31.47
29.53
26.38
25.80
22.60
21.47
13.74
f1 (ppm)


MeO2S
O
H
H
H
4b
f1 (ppm)
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 -0.5 -1.0
1.00
2.02
3.08
3.04
1.07
8.45
12.35
7.99
3.25
6.23
3.16
5.34 3.60 3.58 3.57 3.15 3.14 3.11 2.90 2.34 2.33 2.30 2.30 2.19 2.16 2.11 2.10 2.08 2.08 2.06 2.02 1.98 1.94 1.86 1.85 1.83 1.80 1.77 1.58 1.55 1.52 1.51 1.48 1.46 1.44 1.43 1.42 1.40 1.38 1.37 1.34 1.32 1.27 1.27 1.25 1.21 1.18 1.17 1.15 1.14 1.11 1.09 1.07 1.05 1.04 1.02 1.01 0.99 0.94 0.91 0.90 0.86 0.86 0.85 0.84 0.80 0.78 0.77 0.76 0.76 0.67


f1 (ppm)
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
MeO2S
O
4b
140.56
121.76
79.25
65.37
56.71
56.12
52.21
50.13
42.28
39.73
39.47
37.11
36.81
35.73
31.89
31.84
28.35
28.18
27.96
24.24
21.02
11.81