Electronic Supplementary Material (ESI) for ChemComm.

Cu(II)-Catalyzed Sulfide Construction: Both Aryl Groups Utilization of Intermolecular and Intramolecular Diaryliodonium Salt

Ming Wang, Jianpeng Wei, Qiaoling Fan and Xuefeng Jiang*

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

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

Supporting Information

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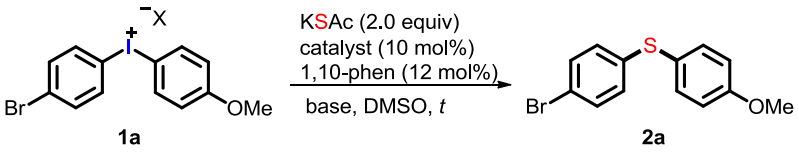
General Information.

^{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 or DMSO ($CHCl_3$ = δ 7.26, DMSO = δ 2.50). Chemical shifts for carbon are reported in parts per million relative to chloroform or DMSO ($CHCl_3$ = δ 77.0, DMSO = δ 39.52). Data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz), integration. Mass spectra were recorded on a Shimadzu GCMS-QP2010 Ultra. IR spectra were recorded on TENSOR (27) Series FT-IR Spectrometers. Diaryliodonium salts **1** and **3** were prepared adopting reported procedures.[1]

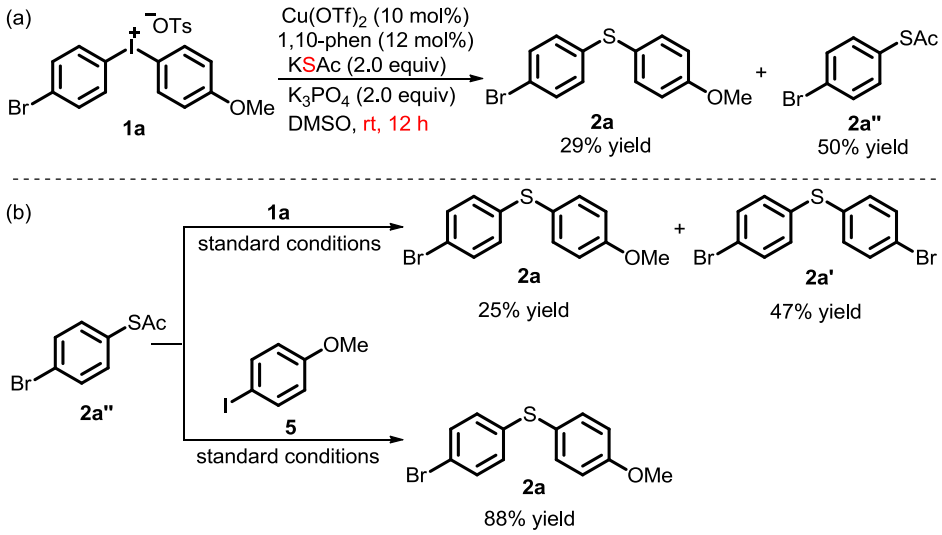
Table S1. Conditions optimization



1a **2a**

Entry	X	Catalyst	Base (equiv)	*t* (^{o}C)	Yield[%][a]
1	BF_4	$Cu(OTf)_2$	K_2CO_3 (2)	100	48
2	BF_4	$Cu(OTf)_2$	Cs_2CO_3 (2)	100	31
3	BF_4	$Cu(OTf)_2$	$NaHCO_3$ (2)	100	42
4	BF_4	$Cu(OTf)_2$	K_3PO_4 (3)	100	54
5	BF_4	$Cu(OTf)_2$	K_3PO_4 (1)	100	26
7	BF_4	$Cu(OTf)_2$	K_3PO_4 (2)	100	77
8	BF_4	$Cu(OTf)_2$	K_3PO_4 (2)	120	62
9	BF_4	$Cu(OTf)_2$	K_3PO_4 (2)	130	50
10	OTs	CuI	K_3PO_4 (2)	100	44
11	OTs	CuBr	K_3PO_4 (2)	100	45
12	OTs	$CuBr_2$	K_3PO_4 (2)	100	53
13[b]	OTs	$Cu(OTf)_2$	K_3PO_4 (2)	100	58

[a] Isolated yields. [b] Without 1,10-Phen.

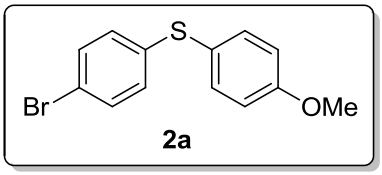


Scheme S1. Mechanistic study.

General procedure for sulfur-iodine exchange of diaryliodonium salts

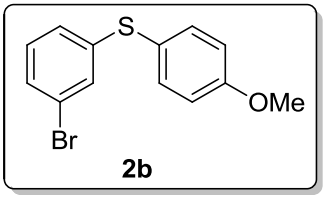
Under a N_2 atmosphere, $Cu(OTf)_2$ (3.6 mg, 0.01 mmol), 1,10-phen (2.2 mg, 0.012 mmol), K_3PO_4 (42.5 mg, 0.2 mmol), KSAc (22.8 mg, 0.2 mmol), diaryliodonium salts **1** or **3**(0.1 mmol) and dry DMSO (1 mL) were added to a flame-dried Schlenk tube. The resulting mixture was stirred at 80-100 ^oC, until TLC analysis indicated complete consumption of the diaryliodonium salts. Water (5 mL) was added and the solution was extracted with ethyl acetate, organic layers were combined, dried over sodium sulfate. After evaporation of solvent, the residue was purified by column chromatography to give the corresponding products **2** or **4**.

Characterization of sulfur-iodine exchange products



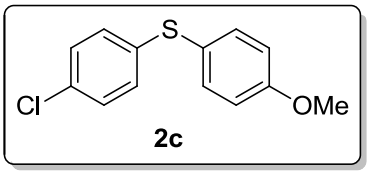
(4-Bromophenyl)(4-methoxyphenyl)sulfane (**2a**): Prepared following general procedure using $Cu(OTf)_2$ (3.6 mg, 0.01 mmol), 1,10-phen (2.2 mg, 0.012 mmol), K_3PO_4 (42.5 mg, 0.2 mmol), KSAc (22.8 mg, 0.2 mmol), diaryliodonium salts **1a** (56.1 mg, 0.1 mmol) and dry DMSO (1 mL), the reaction was stirred at 100 ^oC for 12 h giving **2a** (25.7 mg) in 87% yield as a

colorless oil by column chromatography (PE:EA = 50:1 to 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.9 Hz, 2H), 7.34 (d, *J* = 8.6 Hz, 2H), 7.02 (d, *J* = 8.6 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 3.83 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.2, 138.2, 135.6, 131.9, 129.5, 123.6, 119.4, 115.2, 55.4; **IR** (KBr) ν 3415, 2935, 1589, 1492, 1470, 1249, 1096, 1080, 810 cm^{-1}; **HRMS** (EI) for $C_{13}H_{11}OSBr$ Calculated: 293.9714, found: 293.9718.



2b

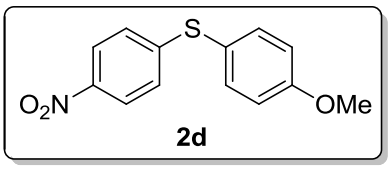
(3-Bromophenyl)(4-methoxyphenyl)sulfane (**2b**): Prepared following general procedure using $Cu(OTf)_2$ (3.6 mg, 0.01 mmol), 1,10-phen (2.2 mg, 0.012 mmol), K_3PO_4 (42.5 mg, 0.2 mmol), KSAc (22.8 mg, 0.2 mmol), diaryliodonium salts **1b** (56.1 mg, 0.1 mmol) and dry DMSO (1 mL), the reaction was stirred at 100 °C for 12 h giving **2b** (20.7 mg) in 70% yield as a colorless oil by column chromatography (PE:EA = 50:1 to 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.4 Hz, 2H), 7.19-7.12 (m, 2H), 7.01-6.92 (m, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 3.73 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.4, 141.6, 136.1, 130.2, 129.9, 128.5, 126.0, 123.0, 122.7, 115.3, 55.4; **IR** (KBr) ν 3448, 2961, 1590, 1492, 1460, 1260, 1181, 1027, 837, 777, 532 cm^{-1}; **HRMS** (EI) for $C_{13}H_{11}OSBr$ Calculated: 293.9714, found: 293.9718.



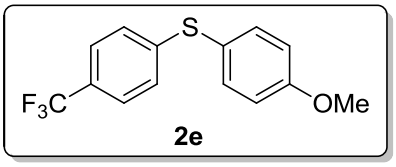
2c

(4-Chlorophenyl)(4-methoxyphenyl)sulfane (**2c**): Prepared following general procedure using $Cu(OTf)_2$ (3.6 mg, 0.01 mmol), 1,10-phen (2.2 mg, 0.012 mmol), K_3PO_4 (42.5 mg, 0.2 mmol), KSAc (22.8 mg, 0.2 mmol), diaryliodonium salts **1c** (51.7 mg, 0.1 mmol) and dry DMSO (1 mL), the reaction was stirred at 100 °C for 12 h giving **2c** (16.8 mg) in 67% yield as a colorless oil by column chromatography (PE:EA = 50:1 to 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.3 Hz, 2H), 7.22 (d, *J* = 7.1 Hz, 2H), 7.10 (d, *J* = 7.1 Hz, 2H), 6.93 (d, *J* = 7.3 Hz, 2H), 3.82 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.1, 137.4, 135.5, 131.6, 129.3, 129.0, 123.8, 115.2, 55.4; **IR** (KBr) ν 3414, 2964, 1587, 1492, 1473,

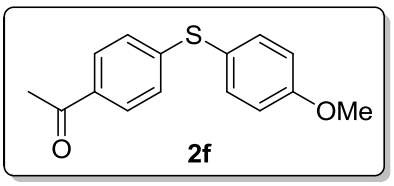
1247, 1175, 1109, 1026, 836, 816, 524 cm^{-1}; **HRMS** (EI) for $C_{13}H_{11}OSCl$ Calculated: 250.0219, found: 250.0222.



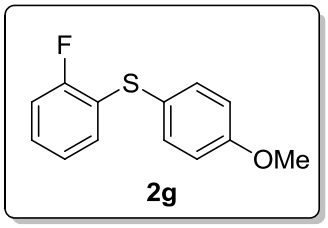
(4-Methoxyphenyl)(4-nitrophenyl)sulfane (**2d**): Prepared following general procedure using $Cu(OTf)_2$ (3.6 mg, 0.01 mmol), 1,10-phen (2.2 mg, 0.012 mmol), K_3PO_4 (42.5 mg, 0.2 mmol), KSAc (22.8 mg, 0.2 mmol), diaryliodonium salts **1d** (52.7 mg, 0.1 mmol) and dry DMSO (1 mL), the reaction was stirred at 100 °C for 12 h giving **2d** (17.0 mg) in 65% yield as a colorless oil by column chromatography (PE:EA = 20:1 to 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.2 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 8.2 Hz, 2H), 3.86 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.1, 150.1, 145.0, 137.2, 125.6, 124.0, 120.1, 115.7, 55.5; **IR** (KBr) ν 3448, 3090, 1592, 1575, 1512, 1494, 1340, 1254, 1180, 1024, 852, 841, 740, 522 cm^{-1}; **HRMS** (EI) for $C_{13}H_{11}NO_3S$ Calculated: 261.0460, found: 261.0457.



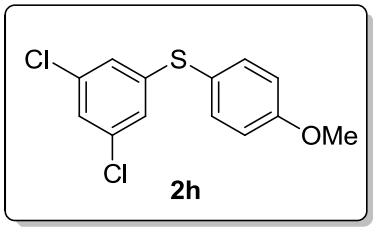
(4-Methoxyphenyl)(4-(trifluoromethyl)phenyl)sulfane (**2e**): Prepared following general procedure using $Cu(OTf)_2$ (3.6 mg, 0.01 mmol), 1,10-phen (2.2 mg, 0.012 mmol), K_3PO_4 (42.5 mg, 0.2 mmol), KSAc (22.8 mg, 0.2 mmol), diaryliodonium salts **1e** (55.0 mg, 0.1 mmol) and dry DMSO (1 mL), the reaction was stirred at 100 °C for 12 h giving **2e** (19.9 mg) in 70% yield as a white solid by column chromatography (PE:EA = 50:1 to 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 13.9, 8.4 Hz, 4H), 7.15 (d, *J* = 8.1 Hz, 2H), 6.96 (d, *J* = 8.5 Hz, 2H), 3.85 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.7, 144.9, 136.7, 127.4, 127.0, 126.4, 125.63 (q, *J* = 3.8 Hz), 121.7, 115.4, 55.4; **IR** (KBr) ν 3448, 2973, 1603, 1590, 1494, 1401, 1330, 1257, 1172, 1113, 832, 532 cm^{-1}; **HRMS** (EI) for $C_{14}H_{11}OSF_3$ Calculated: 284.0483, found: 284.0479.



1-(4-((4-Methoxyphenyl)thio)phenyl)ethanone (**2f**): Prepared following general procedure using $Cu(OTf)_2$ (3.6 mg, 0.01 mmol), 1,10-phen (2.2 mg, 0.012 mmol), K_3PO_4 (42.5 mg, 0.2 mmol), KSAc (22.8 mg, 0.2 mmol), diaryliodonium salts **1f** (52.4 mg, 0.1 mmol) and dry DMSO (1 mL), the reaction was stirred at 100 °C for 12 h giving **2f** (13.7 mg) in 53% yield as a colorless oil by column chromatography (PE:EA = 50:1 to 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.6 Hz, 2H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.09 (d, *J* = 8.6 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 2.53 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.1, 160.7, 146.9, 136.8, 133.9, 128.8, 125.9, 121.5, 115.4, 55.4, 26.4; **IR** (KBr) ν 3444, 2361, 1678, 1590, 1492, 1249, 1179, 1030, 828, cm^{-1}; **HRMS** (EI) for $C_{15}H_{14}O_2S$ Calculated: 258.0715, found: 258.0714.

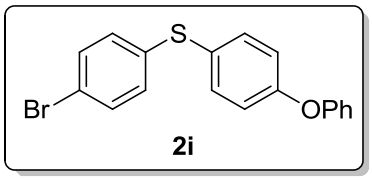


(2-fluorophenyl)(4-methoxyphenyl)sulfane (**2g**): Prepared following general procedure using $Cu(OTf)_2$ (3.6 mg, 0.01 mmol), 1,10-phen (2.2 mg, 0.012 mmol), K_3PO_4 (42.5 mg, 0.2 mmol), KSAc (22.8 mg, 0.2 mmol), diaryliodonium salts **1g** (50.0 mg, 0.1 mmol) and dry DMSO (1 mL), the reaction was stirred at 100 °C for 12 h giving **2g** (18.5 mg) in 79% yield as a colorless oil by column chromatography (PE:EA = 50:1 to 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.8 Hz, 2H), 7.19-7.11 (m, 1H), 7.08-6.97 (m, 3H), 6.91 (d, *J* = 8.9 Hz, 2H), 3.82 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.00\157.56 (*J* = 244 Hz), 159.0, 134.5, 131.4, 129.46\129.44 (*J* = 2 Hz), 126.70\126.63 (*J* = 7 Hz), 123.49\123.45 (*J* = 4 Hz), 121.6, 114.57\114.36 (*J* = 21 Hz), 114.1, 54.3; **IR** (KBr) ν 3440, 2384, 1589, 1566, 1389, 1235, 1162, 1020, 815 cm^{-1}; **MS** (EI) m/z = 234 (100), 219 (55), 127 (10), 96 (10).



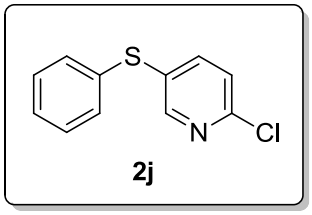
(3,5-dichlorophenyl)(4-methoxyphenyl)sulfane (**2h**): Prepared following general procedure using $Cu(OTf)_2$ (3.6 mg, 0.01 mmol), 1,10-phen (2.2 mg, 0.012 mmol),

K_3PO_4 (42.5 mg, 0.2 mmol), KSAc (22.8 mg, 0.2 mmol), diaryliodonium salts **1h** (55.1 mg, 0.1 mmol) and dry DMSO (1 mL), the reaction was stirred at 100 °C for 12 h giving **2h** (20.2 mg) in 71% yield as a white solid by column chromatography (PE:EA = 50:1 to 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.9 Hz, 2H), 7.09-7.06 (m, 1H), 6.95 (d, *J* = 8.9 Hz, 2H), 6.93-6.90 (m, 2H), 3.86 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.8, 143.4, 136.7, 135.2, 125.3, 124.7, 121.2, 115.5, 55.4; **IR** (KBr) ν 3420, 2972, 1590, 1505, 1472, 1255, 1188, 1123, 1054, 857, 520 cm^{-1}; **MS** (EI) m/z = 284 (100), 269 (50), 206 (30), 171 (25), 139 (10), 96 (5).



2i

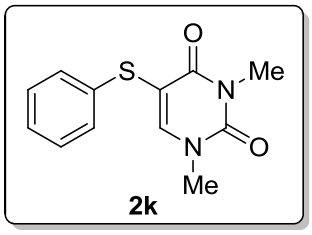
(4-Bromophenyl)(4-phenoxyphenyl)sulfane (**2i**): Prepared following general procedure using $Cu(OTf)_2$ (3.6 mg, 0.01 mmol), 1,10-phen (2.2 mg, 0.012 mmol), K_3PO_4 (42.5 mg, 0.2 mmol), KSAc (22.8 mg, 0.2 mmol), diaryliodonium salts **1i** (62.3 mg, 0.1 mmol) and dry DMSO (1 mL), the reaction was stirred at 100 °C for 12 h giving **2i** (23.2 mg) in 65% yield as a white solid by column chromatography (PE:EA = 50:1 to 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41-7.34 (m, 6H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.12-7.08 (m, 2H), 7.05 (dd, *J* = 8.6, 0.9 Hz, 2H), 6.99-6.96 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.9, 156.4, 136.9, 134.7, 132.1, 130.6, 129.9, 127.2, 124.0, 120.2, 119.5, 119.3; **IR** (KBr) ν 3414, 1584, 1487, 1385, 1278, 1258, 1108, 1022, 833, 815, 754, 692, 482 cm^{-1}; **HRMS** (EI) for $C_{18}H_{13}OSBr$ Calculated: 355.9870, found: 355.9872.



2j

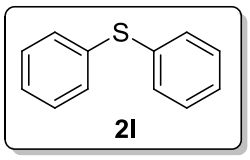
2-chloro-5-(phenylthio)pyridine (**2j**): Prepared following general procedure using $Cu(OTf)_2$ (3.6 mg, 0.01 mmol), 1,10-phen (2.2 mg, 0.012 mmol), K_3PO_4 (42.5 mg, 0.2 mmol), KSAc (22.8 mg, 0.2 mmol), diaryliodonium salts **1j** (46.6 mg, 0.1 mmol) and dry DMSO (1 mL), the reaction was stirred at 100 °C for 12 h giving **2j** (12.0 mg) in 54% yield as a colorless oil by column chromatography (PE:EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 2.4 Hz, 1H), 7.52 (dd, *J* = 8.3, 2.5 Hz, 1H), 7.41-7.30 (m, 5H), 7.24 (d, *J* = 8.3 Hz, 1H); **^{13}C NMR** (100 MHz,

$CDCl_3$) δ 149.5, 148.8, 139.3, 132.3, 131.9, 131.0, 128.6, 127.2, 123.6; **IR** (KBr) ν 3425, 3022, 1680, 1510, 1423, 1317, 1298, 1094, 1022, 852, 810 cm^{-1}; **MS** (EI) m/z = 221 (100), 184 (30), 115 (20), 109 (15), 77 (40).



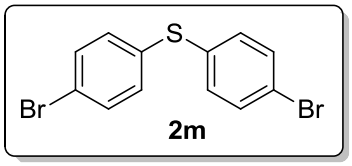
2k

1,3-Dimethyl-5-(phenylthio)pyrimidine-2,4(1H,3H)-dione (**2k**): Prepared following general procedure using $Cu(OTf)_2$ (3.6 mg, 0.01 mmol), 1,10-phen (2.2 mg, 0.012 mmol), K_3PO_4 (42.5 mg, 0.2 mmol), KSAc (22.8 mg, 0.2 mmol), diaryliodonium salts **1k** (49.2 mg, 0.1 mmol) and dry DMSO (1 mL), the reaction was stirred at 100 °C for 12 h giving **2k** (17.9 mg) in 72% yield as a white solid by column chromatography (PE:EA = 5:1 to 3:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.38-7.17 (m, 5H), 3.45 (s, 3H), 3.40 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.8, 151.6, 147.4, 135.2, 129.2, 128.9, 126.9, 106.3, 37.3, 28.7; **IR** (KBr) ν 3448, 2361, 1716, 1642, 1614, 1439, 1347, 770, 737, 689 cm^{-1}; **HRMS** (EI) for $C_{12}H_{12}N_2O_2S$ Calculated: 248.0619, found: 248.0616.



2l

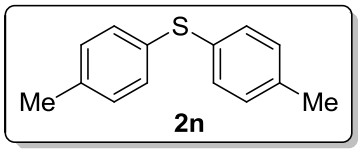
Diphenylsulfane (**2l**): Prepared following general procedure using $Cu(OTf)_2$ (3.6 mg, 0.01 mmol), 1,10-phen (2.2 mg, 0.012 mmol), K_3PO_4 (42.5 mg, 0.2 mmol), KSAc (22.8 mg, 0.2 mmol), diaryliodonium salts **1l** (36.8 mg, 0.1 mmol) and dry DMSO (1 mL), the reaction was stirred at 100 °C for 12 h giving **2l** (10.6 mg) in 57% yield as a colorless oil by column chromatography (PE to PE:EA = 50:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42-7.23 (m, 10H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 135.8, 131.1, 129.2, 127.0; **MS** (EI) m/z = 186 (100), 152 (20), 109 (15), 92 (25), 77 (28).



2m

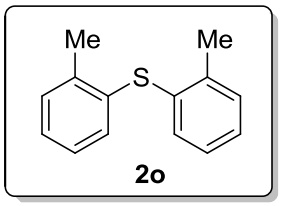
Bis(4-bromophenyl)sulfane (**2m**): Prepared following general procedure using $Cu(OTf)_2$ (3.6 mg, 0.01 mmol), 1,10-phen (2.2 mg, 0.012 mmol), K_3PO_4 (42.5 mg, 0.2 mmol), KSAc (22.8 mg, 0.2 mmol), diaryliodonium salts **1m** (52.6 mg, 0.1 mmol) and dry DMSO (1 mL), the reaction was stirred at 100

°C for 12 h giving **2m** (22.7 mg) in 66% yield as a white solid by column chromatography (PE to PE:EA = 50:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.6 Hz, 4H), 7.19 (d, *J* = 8.6 Hz, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 133.5, 131.6, 131.4, 120.5; **MS** (EI) m/z = 344 (100), 265 (45), 184 (95), 152 (15), 139 (18), 92 (50), 75 (10).



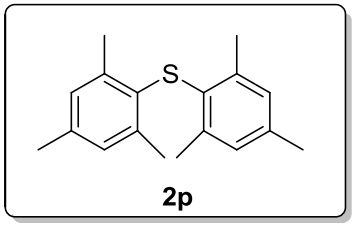
2n

Di-*p*-tolylsulfane (**2n**): Prepared following general procedure using $Cu(OTf)_2$ (3.6 mg, 0.01 mmol), 1,10-phen (2.2 mg, 0.012 mmol), K_3PO_4 (42.5 mg, 0.2 mmol), KSAc (22.8 mg, 0.2 mmol), diaryliodonium salts **1n** (39.6 mg, 0.1 mmol) and dry DMSO (1 mL), the reaction was stirred at 100 °C for 12 h giving **2n** (15.6 mg) in 73% yield as a colorless oil by column chromatography (PE to PE:EA = 50:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.1 Hz, 4H), 7.02 (d, *J* = 8.0 Hz, 4H), 2.24 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 135.9, 131.6, 130.0, 128.9, 20.0; **MS** (EI) m/z = 214 (100), 121 (5), 91 (20), 65 (12).



2o

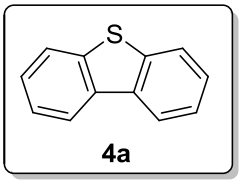
Di-*o*-tolylsulfane (**2o**): Prepared following general procedure using $Cu(OTf)_2$ (3.6 mg, 0.01 mmol), 1,10-phen (2.2 mg, 0.012 mmol), K_3PO_4 (42.5 mg, 0.2 mmol), KSAc (22.8 mg, 0.2 mmol), diaryliodonium salts **1o** (39.6 mg, 0.1 mmol) and dry DMSO (1 mL), the reaction was stirred at 100 °C for 12 h giving **2o** (14.8 mg) in 69% yield as a colorless oil by column chromatography (PE to PE:EA = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-6.89 (m, 8H), 2.31 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.9, 133.2, 130.1, 129.4, 126.1, 125.7, 19.4; **MS** (EI) m/z = 214 (100), 123 (10), 91 (25), 65 (10).



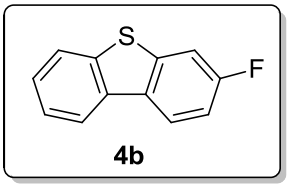
2p

Dimesitylsulfane (**2p**): Prepared following general procedure using $Cu(OTf)_2$ (3.6 mg, 0.01 mmol), 1,10-phen (2.2 mg, 0.012 mmol), K_3PO_4 (42.5 mg, 0.2

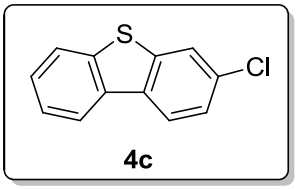
mmol), KSAc (22.8 mg, 0.2 mmol), diaryliodonium salts **1p** (45.2 mg, 0.1 mmol) and dry DMSO (1 mL), the reaction was stirred at 100 °C for 12 h giving **2p** (11.9 mg) in 44% yield as a colorless oil by column chromatography (PE to PE:EA = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (s, 4H), 2.24 (s, 6H), 2.19 (s, 12H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.3, 136.5, 131.1, 129.3, 21.6, 20.8; **MS** (EI) m/z = 270 (90), 150 (100), 104 (20), 76 (10).



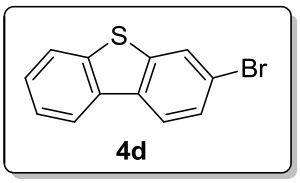
Dibenzo[b,d]thiophene (**4a**): Prepared following general procedure using $Cu(OTf)_2$ (3.6 mg, 0.01 mmol), 1,10-phen (2.2 mg, 0.012 mmol), K_3PO_4 (42.5 mg, 0.2 mmol), KSAc (22.8 mg, 0.2 mmol), diaryliodonium salts **3a** (45.0 mg, 0.1 mmol) and dry DMSO (1 mL), the reaction was stirred at 100 °C for 6 h giving **4a** (13.8 mg) in 75% yield as a white solid by column chromatography (PE to PE:EA = 50:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21-8.12 (m, 2H), 7.91-7.82 (m, 3H), 7.52-7.43 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.4, 134.5, 125.7, 123.3, 121.8, 120.5; **MS** (EI) m/z = 184 (100), 152 (15), 139 (20), 92 (12), 79 (9).



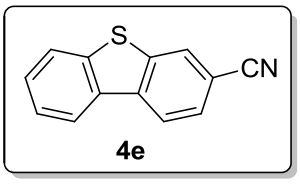
3-Fluorodibenzo[b,d]thiophene (**4b**): Prepared following general procedure using $Cu(OTf)_2$ (3.6 mg, 0.01 mmol), 1,10-phen (2.2 mg, 0.012 mmol), K_3PO_4 (42.5 mg, 0.2 mmol), KSAc (22.8 mg, 0.2 mmol), diaryliodonium salts **3b** (46.8 mg, 0.1 mmol) and dry DMSO (1 mL), the reaction was stirred at 100 °C for 6 h giving **4b** (18.4 mg) in 91% yield as a white solid by column chromatography (PE to PE:EA = 50:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15-8.01 (m, 2H), 7.84 (d, *J* = 6.8 Hz, 1H), 7.54 (d, *J* = 8.7 Hz, 1H), 7.49-7.39 (m, 2H), 7.19 (t, *J* = 8.7 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.05/160.61 (*J* = 244 Hz), 140.75/140.65 (*J* = 10 Hz), 139.2, 134.8, 131.9, 126.38, 124.66, 122.79, 122.62/122.53(*J* = 9 Hz), 121.27, 112.99/112.76 (*J* = 23 Hz), 109.35/ 109.10 (*J* = 25 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.41; **HRMS** (EI) for $C_{12}H_7SF$ Calculated: 202.0252, found: 202.0251.



3-Chlorodibenzo[b,d]thiophene (**4c**): Prepared following general procedure using $Cu(OTf)_2$ (3.6 mg, 0.01 mmol), 1,10-phen (2.2 mg, 0.012 mmol), K_3PO_4 (42.5 mg, 0.2 mmol), KSAc (22.8 mg, 0.2 mmol), diaryliodonium salts **3c** (46.3 mg, 0.1 mmol) and dry DMSO (1 mL), the reaction was stirred at 80 °C for 6 h giving **4c** (19.2 mg) in 88% yield as a white solid by column chromatography (PE to PE:EA = 50:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15-7.63 (m, 4H), 7.50-7.29 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.6, 139.4, 134.7, 134.1, 132.5, 127.0, 125.1, 124.7, 122.8, 122.5, 122.3, 121.6; **HRMS** (EI) for $C_{12}H_7SCl$ Calculated: 217.9957, found: 217.9953.

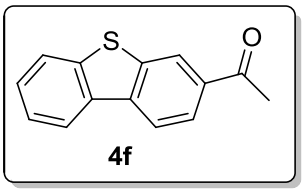


3-Bromodibenzo[b,d]thiophene (**4d**): Prepared following general procedure using $Cu(OTf)_2$ (3.6 mg, 0.01 mmol), 1,10-phen (2.2 mg, 0.012 mmol), K_3PO_4 (42.5 mg, 0.2 mmol), KSAc (22.8 mg, 0.2 mmol), diaryliodonium salts **3d** (50.7 mg, 0.1 mmol) and dry DMSO (1 mL), the reaction was stirred at 80 °C for 6 h giving **4d** (17.9 mg) in 68% yield as a white solid by column chromatography (PE to PE:EA = 50:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12-8.02 (m, 1H), 8.00-7.91 (m, 2H), 7.86-7.79 (m, 1H), 7.54 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.51-7.41 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.0, 139.3, 134.8, 134.4, 127.7, 127.1, 125.4, 124.7, 122.8, 122.6, 121.6, 120.3; **HRMS** (EI) for $C_{12}H_7SBr$ Calculated: 261.9452, found: 261.9455.



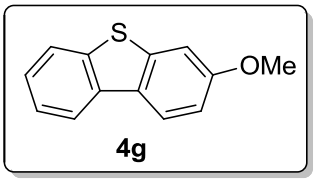
Dibenzo[b,d]thiophene-3-carbonitrile (**4e**): Prepared following general procedure using $Cu(OTf)_2$ (3.6 mg, 0.01 mmol), 1,10-phen (2.2 mg, 0.012 mmol), K_3PO_4 (42.5 mg, 0.2 mmol), KSAc (22.8 mg, 0.2 mmol), diaryliodonium salts **3e** (45.3 mg, 0.1 mmol) and dry DMSO (1 mL), the reaction was stirred at 80 °C for 6 h giving **4e** (17.4 mg) in 83% yield as a white solid by column chromatography (PE:EA = 50:1 to 30:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20-8.07 (m, 3H), 7.88 (d, *J* = 7.6 Hz, 1H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.59-7.48 (m, 2H); **^{13}C NMR** (100 MHz,

$CDCl_3$) δ 140.7, 139.7, 138.9, 134.1, 128.4, 127.4, 127.0, 125.1, 123.0, 122.5, 122.0, 119.0, 109.8; **HRMS** (EI) for $C_{13}H_7NS$ Calculated: 209.0299, found: 209.0297.



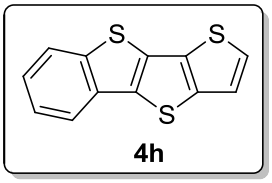
4f

1-(Dibenzo[b,d]thiophen-3-yl)ethanone (**4f**): Prepared following general procedure using $Cu(OTf)_2$ (3.6 mg, 0.01 mmol), 1,10-phen (2.2 mg, 0.012 mmol), K_3PO_4 (42.5 mg, 0.2 mmol), KSAc (22.8 mg, 0.2 mmol), diaryliodonium salts **3f** (47.0 mg, 0.1 mmol) and dry DMSO (1 mL), the reaction was stirred at 80 °C for 6 h giving **4f** (17.9 mg) in 79% yield as a white solid by column chromatography (PE to PE:EA = 50:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 8.20-8.13 (m, 2H), 8.02 (d, *J* = 8.2 Hz, 1H), 7.87 (d, *J* = 7.4 Hz, 1H), 7.55-7.44 (m, 2H), 2.69 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.4, 141.2, 139.5, 139.2, 135.4, 134.6, 127.9, 124.8, 124.3, 123.5, 123.0, 122.5, 121.5, 26.8; **IR** (KBr) ν 3448, 1678, 1596, 1394, 1278, 1253, 1233, 837, 767, 738, 663, 598 cm^{-1}; **HRMS** (EI) for $C_{14}H_{10}OS$ Calculated: 226.0452, found: 226.0454.



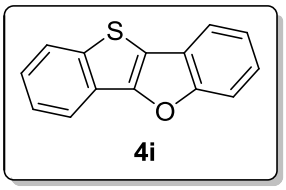
4g

3-Methoxydibenzo[b,d]thiophene (**4g**): Prepared following general procedure using $Cu(OTf)_2$ (3.6 mg, 0.01 mmol), 1,10-phen (2.2 mg, 0.012 mmol), K_3PO_4 (42.5 mg, 0.2 mmol), KSAc (22.8 mg, 0.2 mmol), diaryliodonium salts **3g** (48.0 mg, 0.1 mmol) and dry DMSO (1 mL), the reaction was stirred at 100 °C for 6 h giving **4g** (15.4 mg) in 72% yield as a white solid by column chromatography (PE:EA = 50:1 to 30:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07-7.99 (m, 2H), 7.84-7.76 (m, 1H), 7.46-7.36 (m, 2H), 7.33 (d, *J* = 2.3 Hz, 1H), 7.06 (dd, *J* = 8.7, 2.4 Hz, 1H), 3.91 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.1, 140.0, 137.6, 134.5, 128.1, 124.5, 123.4, 121.6, 121.2, 119.7, 112.4, 104.9, 54.6; **HRMS** (EI) for $C_{13}H_{10}OS$ Calculated: 214.0452, found: 214.0450.



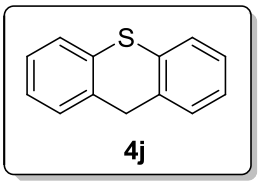
4h

Benzothiophene[4,5]thieno[3,2-b]thiophene (4h): Prepared following general procedure using $Cu(OTf)_2$ (3.6 mg, 0.01 mmol), 1,10-phen (2.2 mg, 0.012 mmol), K_3PO_4 (42.5 mg, 0.2 mmol), KSAc (22.8 mg, 0.2 mmol), diaryliodonium salts **3h** (49.0 mg, 0.1 mmol) and dry DMSO (1 mL), the reaction was stirred at 100 °C for 6 h giving **4h** (7.9 mg) in 32% yield as a white solid by column chromatography (PE to PE:EA = 50:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.47 -7.40 (m, 2H), 7.40-7.33 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.7, 141.6, 136.6, 133.6, 131.6, 129.6, 127.0, 125.0, 124.5, 124.0, 120.9, 120.7; **IR** (KBr) ν 3437, 2924, 1607, 1447, 1384, 1186, 1128, 1015, 748, 641 cm^{-1}; **HRMS** (EI) for $C_{12}H_6S_3$ Calculated: 245.9632, found: 245.9635.



4i

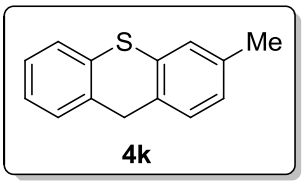
Benzo[4,5]thieno[3,2-b]benzofuran (**4i**): Prepared following general procedure using $Cu(OTf)_2$ (3.6 mg, 0.01 mmol), 1,10-phen (2.2 mg, 0.012 mmol), K_3PO_4 (42.5 mg, 0.2 mmol), KSAc (22.8 mg, 0.2 mmol), diaryliodonium salts **3i** (46.8 mg, 0.1 mmol) and dry DMSO (1 mL), the reaction was stirred at 80 °C for 6 h giving **4i** (14.1 mg) in 63% yield as a white solid by column chromatography (PE to PE:EA = 50:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05-7.99 (m, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.77-7.71 (m, 1H), 7.68-7.63 (m, 1H), 7.49 (td, *J* = 7.6, 1.0 Hz, 1H), 7.42-7.32 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.8, 152.0, 141.0, 124.2, 123.9(4), 123.9(2), 123.9(1), 123.4, 123.1, 122.3, 118.7, 118.6, 117.6, 111.6; **IR** (KBr) ν 3414, 2962, 2924, 1617, 1441, 1392, 1297, 1260, 1120, 1018, 815, 738, 725, 434 cm^{-1}; **HRMS** (EI) for $C_{14}H_8OS$ Calculated: 224.0296, found: 224.0294.



4j

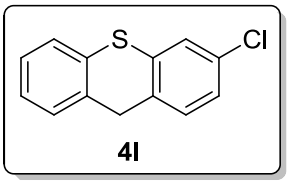
9H-Thioxanthene (**4j**): Prepared following general procedure using $Cu(OTf)_2$ (3.6 mg, 0.01 mmol), 1,10-phen (2.2 mg, 0.012 mmol), K_3PO_4 (42.5 mg, 0.2 mmol), KSAc (22.8 mg, 0.2 mmol), diaryliodonium salts **3j** (46.4 mg, 0.1 mmol) and dry DMSO (1 mL), the reaction was stirred at 100 °C for 6 h giving **4j** (16.7 mg) in 84%

yield as a white solid by column chromatography (PE to PE:EA = 50:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41-7.29 (m, 2H), 7.28-7.19 (m, 2H), 7.15-7.03 (m, 4H), 3.76 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.2, 133.9, 128.0, 126.9, 126.6(4), 126.5(5), 39.3; **HRMS** (EI) for $C_{13}H_{10}S$ Calculated: 198.0503, found: 198.0502.



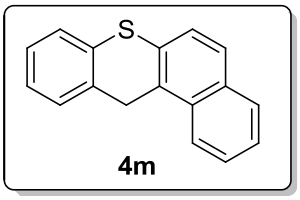
4k

3-Methyl-9H-thioxanthene (**4k**): Prepared following general procedure using $Cu(OTf)_2$ (3.6 mg, 0.01 mmol), 1,10-phen (2.2 mg, 0.012 mmol), K_3PO_4 (42.5 mg, 0.2 mmol), KSAc (22.8 mg, 0.2 mmol), diaryliodonium salts **3k** (47.8 mg, 0.1 mmol) and dry DMSO (1 mL), the reaction was stirred at 100 °C for 6 h giving **4k** (16.6 mg) in 78% yield as a white solid by column chromatography (PE to PE:EA = 50:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48-7.42 (m, 1H), 7.35-7.27 (m, 2H), 7.24-7.16 (m, 3H), 7.03 (dd, *J* = 7.7, 0.9 Hz, 1H), 3.84 (s, 2H), 2.34 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.5, 136.3, 134.0, 133.6, 133.2, 127.9, 127.7, 127.4, 127.4, 126.9, 126.5, 126.45, 38.7, 20.9; **IR** ν 3415, 3047, 1638, 1617, 1461, 1441, 1410, 1120, 1055, 808, 747, 609 cm^{-1}; **HRMS** (EI) for $C_{14}H_{12}S$ Calculated: 212.0660, found: 212.0663.

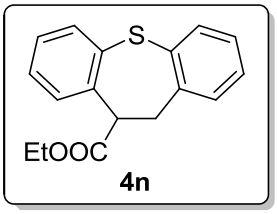


4l

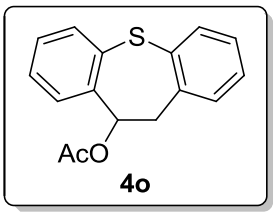
3-Chloro-9H-thioxanthene (**4l**): Prepared following general procedure using $Cu(OTf)_2$ (3.6 mg, 0.01 mmol), 1,10-phen (2.2 mg, 0.012 mmol), K_3PO_4 (42.5 mg, 0.2 mmol), KSAc (22.8 mg, 0.2 mmol), diaryliodonium salts **3l** (49.9 mg, 0.1 mmol) and dry DMSO (1 mL), the reaction was stirred at 100 °C for 6 h giving **4l** (14.4 mg) in 62% yield as a white solid by column chromatography (PE to PE:EA = 50:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45-7.42 (m, 2H), 7.34-7.29 (m, 1H), 7.25-7.15 (m, 4H), 3.82 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 135.8(1), 135.8(0), 134.7, 133.1, 132.1, 128.8, 128.0, 126.9, 126.7, 126.6, 126.6, 38.6; **IR** ν 3417, 1637, 1620, 1577, 1458, 1412, 1384, 1186, 1097, 805, 752 cm^{-1}; **HRMS** (EI) for $C_{13}H_9SCl$ Calculated: 232.0113, found: 232.0111.



12H-Benzo[a]thioxanthene (**4m**): Prepared following general procedure using $Cu(OTf)_2$ (3.6 mg, 0.01 mmol), 1,10-phen (2.2 mg, 0.012 mmol), K_3PO_4 (42.5 mg, 0.2 mmol), KSAc (22.8 mg, 0.2 mmol), diaryliodonium salts **3m** (51.4 mg, 0.1 mmol) and dry DMSO (1 mL), the reaction was stirred at 100 °C for 6 h giving **4m** (19.1 mg) in 77% yield as a white solid by column chromatography (PE to PE:EA = 50:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.5 Hz, 1H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.69 (d, *J* = 8.6 Hz, 1H), 7.63-7.42 (m, 5H), 7.28-7.18 (m, 3H), 4.30 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 135.5, 134.0, 132.6, 131.3(7), 131.3(5), 130.6, 128.9, 128.3, 126.7, 126.6(2), 126.5(7), 126.4(8), 125.2, 125.1, 122.4, 33.5; **IR** ν 3437, 3059, 2924, 1618, 1588, 1469, 1384, 1164, 1118, 807, 750, 739 cm^{-1}; **HRMS** (EI) for $C_{17}H_{12}S$ Calculated: 248.0660, found: 248.0658.

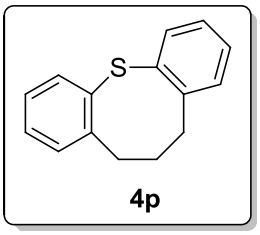


Ethyl 10,11-dihydrodibenzo[b,f]thiepine-10-carboxylate (**4n**): Prepared following general procedure using $Cu(OTf)_2$ (3.6 mg, 0.01 mmol), 1,10-phen (2.2 mg, 0.012 mmol), K_3PO_4 (42.5 mg, 0.2 mmol), KSAc (22.8 mg, 0.2 mmol), diaryliodonium salts **3n** (52.8 mg, 0.1 mmol) and dry DMSO (1 mL), the reaction was stirred at 100 °C for 6 h giving **4n** (14.8 mg) in 52% yield as a colorless oil by column chromatography (PE:EA = 50:1 to 30:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53-7.45 (m, 2H), 7.23-7.08 (m, 6H), 4.56 (dd, *J* = 9.5, 3.7 Hz, 1H), 4.25-4.00 (m, 2H), 3.69 (dd, *J* = 15.2, 9.5 Hz, 1H), 3.57 (dd, *J* = 15.2, 3.7 Hz, 1H), 1.18 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.2, 139.7, 138.8, 134.8, 134.6, 131.9, 131.4, 130.6, 130.2, 127.9, 127.7, 127.3, 126.7, 61.0, 48.8, 35.7, 14.1; **IR** ν 3438, 3061, 2979, 1705, 1473, 1443, 1219, 1159, 1036, 758 cm^{-1}; **HRMS** (EI) for $C_{17}H_{16}O_2S$ Calculated: 284.0871, found: 284.0872.



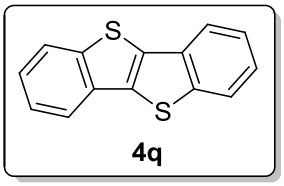
4o

10,11-Dihydrodibenzo[b,f]thiepin-10-yl acetate (**4o**): Prepared following general procedure using $Cu(OTf)_2$ (3.6 mg, 0.01 mmol), 1,10-phen (2.2 mg, 0.012 mmol), K_3PO_4 (42.5 mg, 0.2 mmol), KSAc (22.8 mg, 0.2 mmol), diaryliodonium salts **3o** (51.4 mg, 0.1 mmol) and dry DMSO (1 mL), the reaction was stirred at 60 °C for 6 h giving **4o** (18.4 mg) in 68% yield as a colorless oil by column chromatography (PE:EA = 50:1 to 30:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.2 Hz, 1H), 7.50 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.32 – 7.08 (m, 6H), 6.48 (dd, *J* = 8.9, 3.3 Hz, 1H), 3.67 (dd, *J* = 14.3, 3.3 Hz, 1H), 3.59 (dd, *J* = 14.3, 8.9 Hz, 1H), 2.06 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.2, 139.1, 138.2, 135.3, 134.3, 131.5, 131.4, 131.1, 130.6, 128.3, 128.1, 127.5, 126.9, 72.0, 37.9, 21.2; **IR** ν 3448, 3062, 2927, 1733, 1474, 1433, 1371, 1236, 1025, 758 cm^{-1}; **HRMS** (EI) for $C_{16}H_{14}O_2S$ Calculated: 270.0715, found: 270.0713.



4p

6,7-Dihydro-5H-dibenzo[b,g]thiocine (**4p**): Prepared following general procedure using $Cu(OTf)_2$ (3.6 mg, 0.01 mmol), 1,10-phen (2.2 mg, 0.012 mmol), K_3PO_4 (42.5 mg, 0.2 mmol), KSAc (22.8 mg, 0.2 mmol), diaryliodonium salts **3p** (49.2 mg, 0.1 mmol) and dry DMSO (1 mL), the reaction was stirred at 100 °C for 6 h giving **4p** (17.7 mg) in 78% yield as a colorless oil by column chromatography (PE:EA = 50:1 to 30:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.32-7.15 (m, 4H), 7.13-7.06 (m, 2H), 6.85 (td, *J* = 7.7, 1.8 Hz, 1H), 2.91-2.84 (m, 2H), 2.81-2.73 (m, 2H), 2.16-1.85 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.7, 144.8, 142.7, 139.5, 134.6, 131.9, 129.7, 129.3, 128.3, 127.7, 127.2, 127.0, 100.7, 40.7, 33.8, 31.0; **HRMS** (EI) for $C_{15}H_{14}S$ Calculated: 226.0816, found: 226.0814.

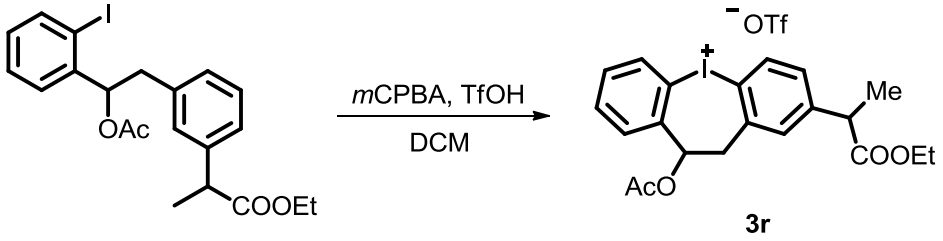


4q

Benzo[b]benzo[4,5]thieno[2,3-d]thiophene (**4q**): Prepared following general procedure using $Cu(OTf)_2$ (3.6 mg, 0.01 mmol), 1,10-phen (2.2 mg, 0.012 mmol), K_3PO_4 (42.5 mg,

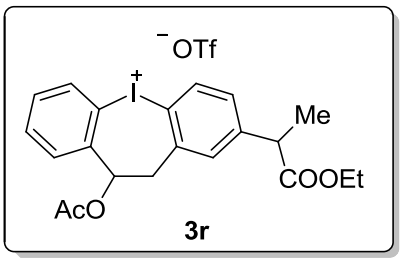
0.2 mmol), KSAc (22.8 mg, 0.2 mmol), diaryliodonium salts **3p** (48.4 mg, 0.1 mmol) and dry DMSO (1 mL), the reaction was stirred at 100 °C for 3 h giving **4p** (17.1 mg) in 71% yield as a white solid by column chromatography (PE to PE:EA = 50:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95-7.84 (m, 4H), 7.50-7.37 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.3, 133.5, 133.1, 125.0, 124.9, 124.1, 121.6; **HRMS** (EI) for $C_{14}H_8S_2$ Calculated: 240.0067, found: 240.0069.

General procedure for the synthesis of 3r



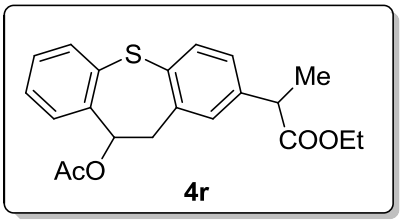
3r

*m*CPBA (75% active oxidant, 101.2 mg, 0.44 mmol) was added to the solution of aryl iodide (186.6 mg, 0.4 mmol) in DCM (4 mL). The resulting solution was cooled to 0 °C and TfOH (120.0 mg, 0.8 mmol) was added dropwise. After 20 min of stirring at 0 °C, the reaction mixture was warmed to room tempurature for 30 min. The latter solution was concentrated, and purified by column chromatography to provide product **3r** (199.1 mg) in 81% yield as a colorless oil by column chromatography (DCM:MeOH = 50:1 to 20:1).



10-Acetoxy-2-(1-carboxyethyl)-10,11-dihydrodibenzo[b,f]iodepin-5-ium (**3r**): 81% yield, dr = 1:1, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.0 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.45 (d, *J* = 6.5 Hz, 1H), 7.39-7.29 (m, 2H), 7.22 (dd, *J* = 8.3, 1.9 Hz, 1H), 6.38 (dd, *J* = 9.1, 5.8 Hz, 1H), 4.21-3.97 (m, 2H), 3.83-3.54 (m, 3H), 2.15 (s, 3H), 1.46 (d, *J* = 7.2 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.3 (173.2), 169.84 (169.77), 146.0, 138.2(4), 138.1(5),

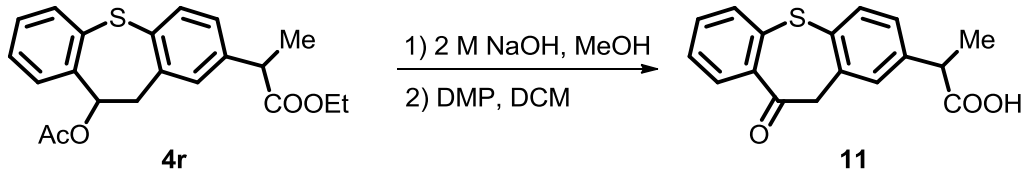
137.12, 136.3 (136.2), 134.34 (134.27), 132.7, 131.8 (131.7), 131.19, 129.4 (129.3), 117.8 (117.7), 112.6 (112.5), 71.4 (71.3), 61.29 (61.27), 45.2, 40.6, 21.0, 18.6(18.4), 14.0; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -78.26; **HRMS** (ESI) for $C_{21}H_{22}O_4I$ $[M\text{-}TfO^-]^+$ Calculated: 465.0563, found: 465.0564.



4r

Ethyl 2-(10-acetoxy-10,11-dihydrodibenzo[b,f] thiepin-2-yl)propanoate (**4r**): Prepared following general procedure using $Cu(OTf)_2$ (3.6 mg, 0.01 mmol), 1,10-phen (2.2 mg, 0.012 mmol), K_3PO_4 (42.5 mg, 0.2 mmol), KSAc (22.8 mg, 0.2 mmol), diaryliodonium salts **3r** (61.4 mg, 0.1 mmol) and dry DMSO (1 mL), the reaction was stirred at 80 °C for 4 h giving **4r** (23.7 mg) in 64% yield (dr = 1:1) as a colorless oil by column chromatography (PE:EA = 20:1 to 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47-7.36 (m, 2H), 7.24-6.92 (m, 5H), 6.43-6.34 (m, 1H), 4.13-3.89 (m, 2H), 3.62-3.54 (m, 2H), 3.51-3.40 (m, 1H), 1.98 (s, 3H), 1.38 (d, *J* = 7.2 Hz, 3H), 1.13 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.11 (173.05), 169.16 (169.11), 140.00 (139.97), 138.28 (138.25), 137.29 (137.22), 133.13 (133.11), 132.77 (132.73), 130.70 (130.67), 130.38 (130.32), 130.08 (130.02), 128.80 (128.72), 127.06 (127.04), 126.53 (126.50), 125.10 (124.99), 70.91 (70.86), 59.84 (59.82), 44.12 (44.08), 36.89 (36.81), 20.1, 17.56 (17.52), 13.1; **IR** ν 3448, 2931, 1733, 1605, 1435, 1372, 1235, 1183, 1072, 1028, 803, 757 cm^{-1}; **HRMS** (EI) for $C_{21}H_{22}O_4S$ Calculated: 370.1239, found: 370.1238.

General procedure for the synthesis of 11

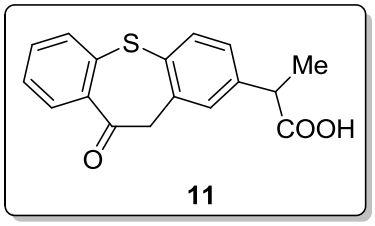


4r **11**

2 M aqueous NaOH (1 mL) was added to a solution of **4r** (23.7 mg, 0.064 mmol) in

MeOH (1 mL). After 8 h of stirring at room temperature, the reaction was quenched with 1 M HCl (2 ml) and diluted with DCM. The organic layer was separated, and the aqueous layer was extracted with DCM. The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was used in next step directly.

The crude product of last step was dissolved in DCM (2 mL), Dess-Martin periodinane (27.1 mg, 0.064 mmol) was added. The mixture was stirred at room temperature for 2 h. The resulting solution was filtered and concentrated under reduced pressure. The residue was purified by column chromatography to provide product **11** (16.4 mg) in 86% yield as a white solid by column chromatography (PE:EA = 1:1 to 1:2).



11

2-(10-oxo-10,11-Dihydrodibenzo[b,f]thiepin-2-yl) propanoic acid (**11**): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.64-7.55 (m, 2H), 7.45-7.38 (m, 2H), 7.35-7.28 (m, 1H), 7.16 (dd, *J* = 8.0, 1.9 Hz, 1H), 4.36 (s, 2H), 3.73 (q, *J* = 7.2 Hz, 1H), 1.49 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.4, 179.1, 141.9, 140.2, 138.0, 136.1, 133.6, 132.6, 131.6, 131.5, 130.9, 128.7, 126.9, 126.5, 51.1, 44.9, 18.1; **IR** ν 3445, 2985, 1705, 1770, 1588, 1459, 1428, 1382, 1285, 1232, 1206, 1158, 1074, 756 cm^{-1}; **HRMS** (EI) for $C_{17}H_{14}O_3S$ Calculated: 298.0664, found: 298.0670.

X-Ray Crystal Structures

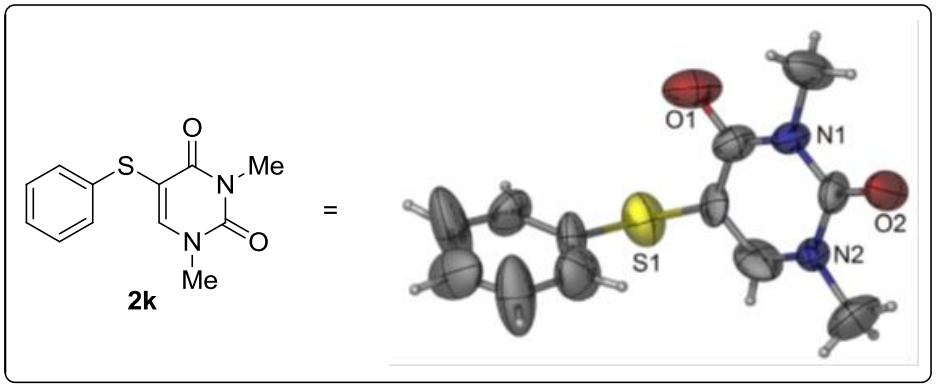
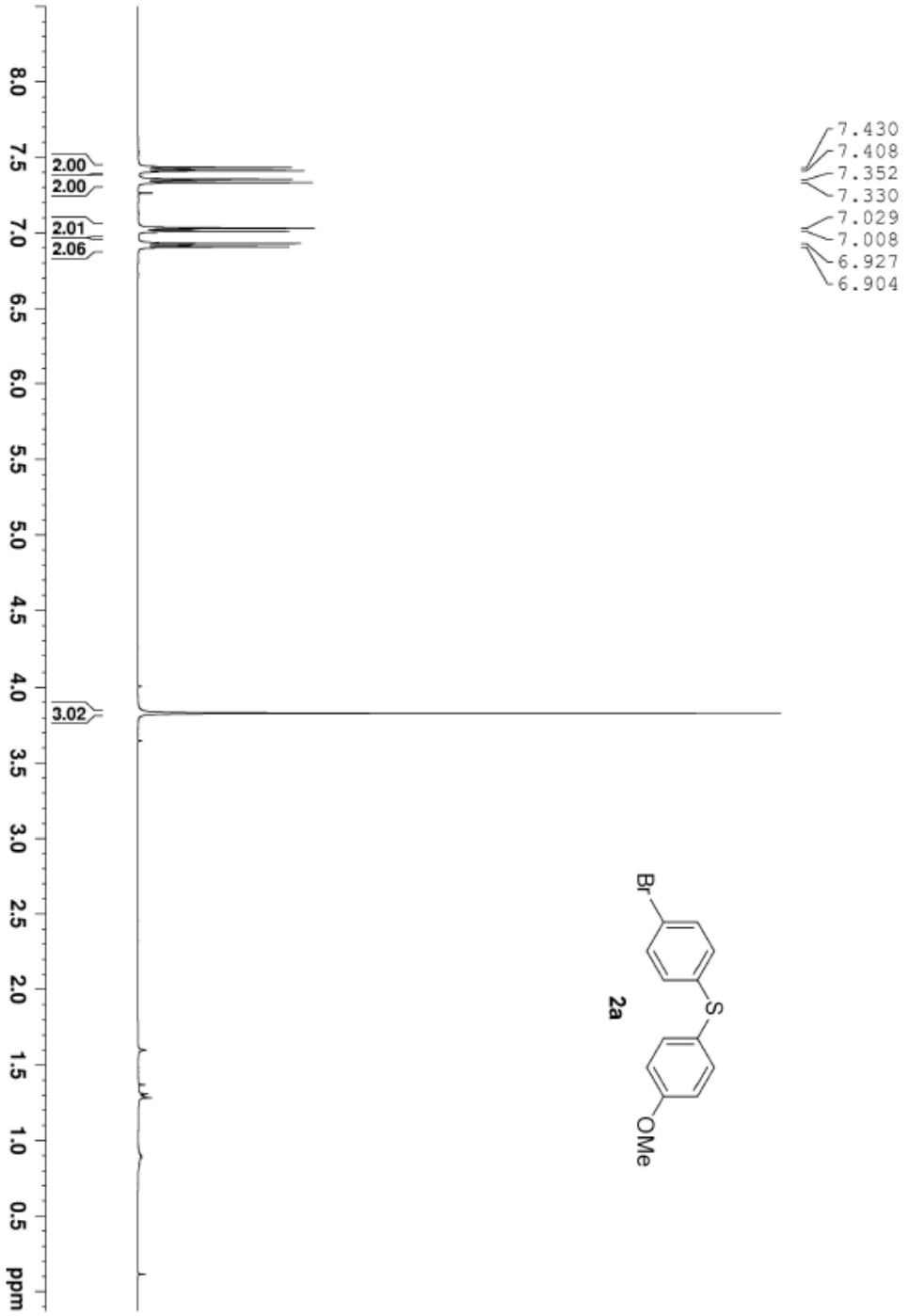


Table S2. Sample and crystal data for 2k (CCDC 1428271)**.**

Bond precision	C-C = 0.0231 A	
	Wavelength=0.71073	
Cell	a = 11.3868(17)	α = 90°
	b = 11.3868(17)	β = 90°
	c = 37.476(6)	γ = 90°
Temperature	296 K	
Volume	4859.4(13)	
Space group	P41	
Sum formula	C12 H12 N2 O2 S	
Mr	248.30	
Dx,g cm^{-3}	1.358	
Z	16	
Mu (mm-1)	0.257	
F000	2080.0	
F000'	2082.81	
h,k,lmax	13,13,44	
Nref	8573	
Tmin,Tmax	0.922,0.946	
Correction method= # Reported T Limits	Tmin=0.922 Tmax=0.946	
AbsCorr = MULTI-SCAN		
Data completeness	1.97/1.00	
R(reflections)	0.1085(4278)	
wR2(reflections)	0.3296(8573)	
S	1.038	
Npar	616	

References

(1) (*a*) M. Bielawski, M. Zhu and B. Olofsson, *Adv. Synth. Catal.* 2007, **349**, 2610. (*b*) T. Dohi, M. Ito, K. Morimoto, Y. Minamitsuji, N. Takenaga and Y. Kita, *Chem. Commun.*, 2007, 4152; (*c*) M. Bielawski, D. Aili and B. Olofsson, *J. Org. Chem.* 2008, **73**, 4602; (*d*) E. A. Merritt, V. M. T. Carneiro, L. F. Silva Jr. and B. Olofsson, *J. Org. Chem.* 2010, **75**, 7416; (*e*) D. Zhu, Q. Liu, B. Luo, M. Chen, R. Pi, P. Huang and S. Wen, *Adv. Synth. Catal.*, 2013, **355**, 2172; (*f*) B. Luo, Q. Cui, H. Luo, Y. Hu, P. Huang, S. Wen, *Adv. Synth. Catal*. **2016**, *358*, 2733.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3.02
8.0
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7.0
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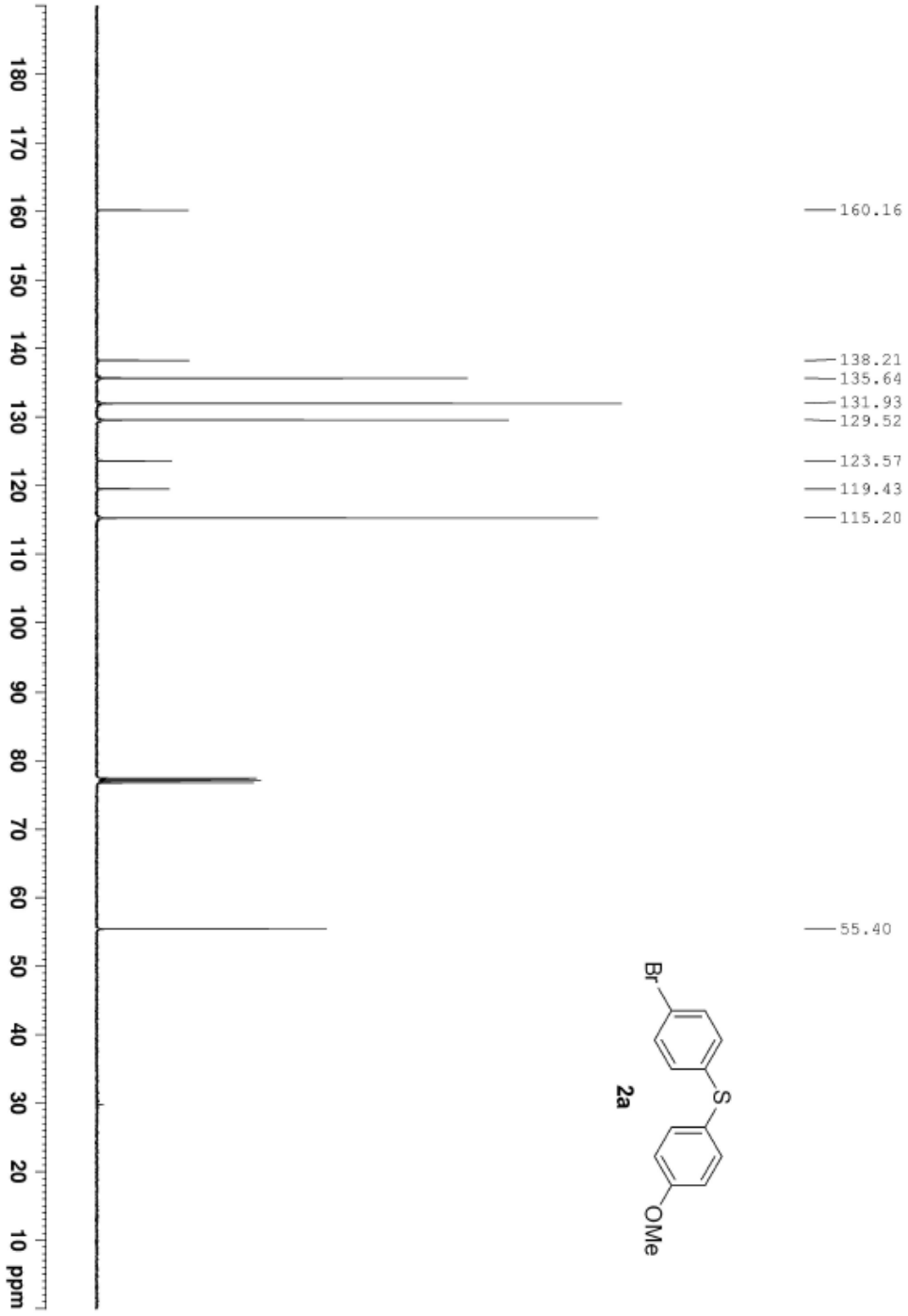
Br
S
OMe
2a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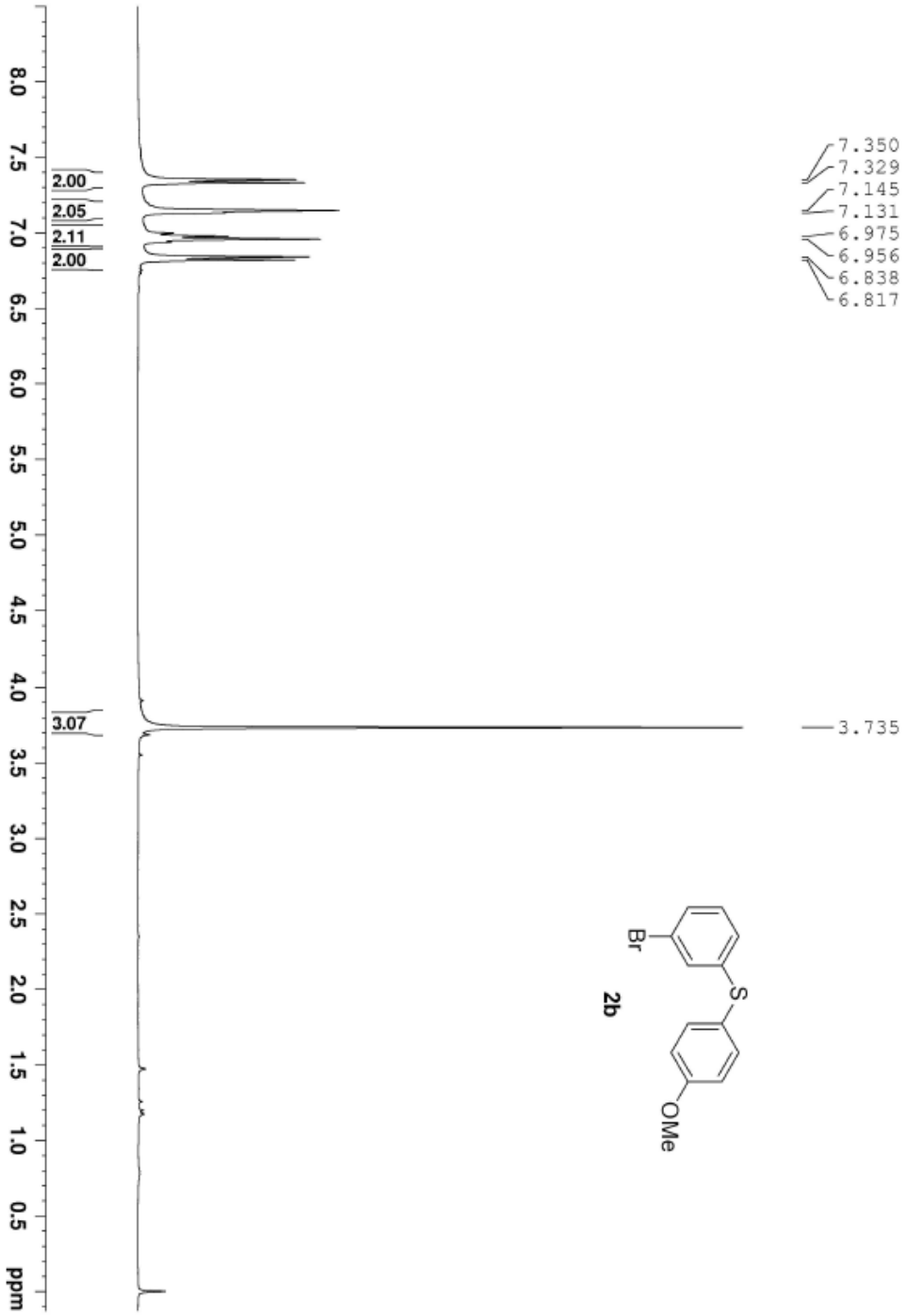
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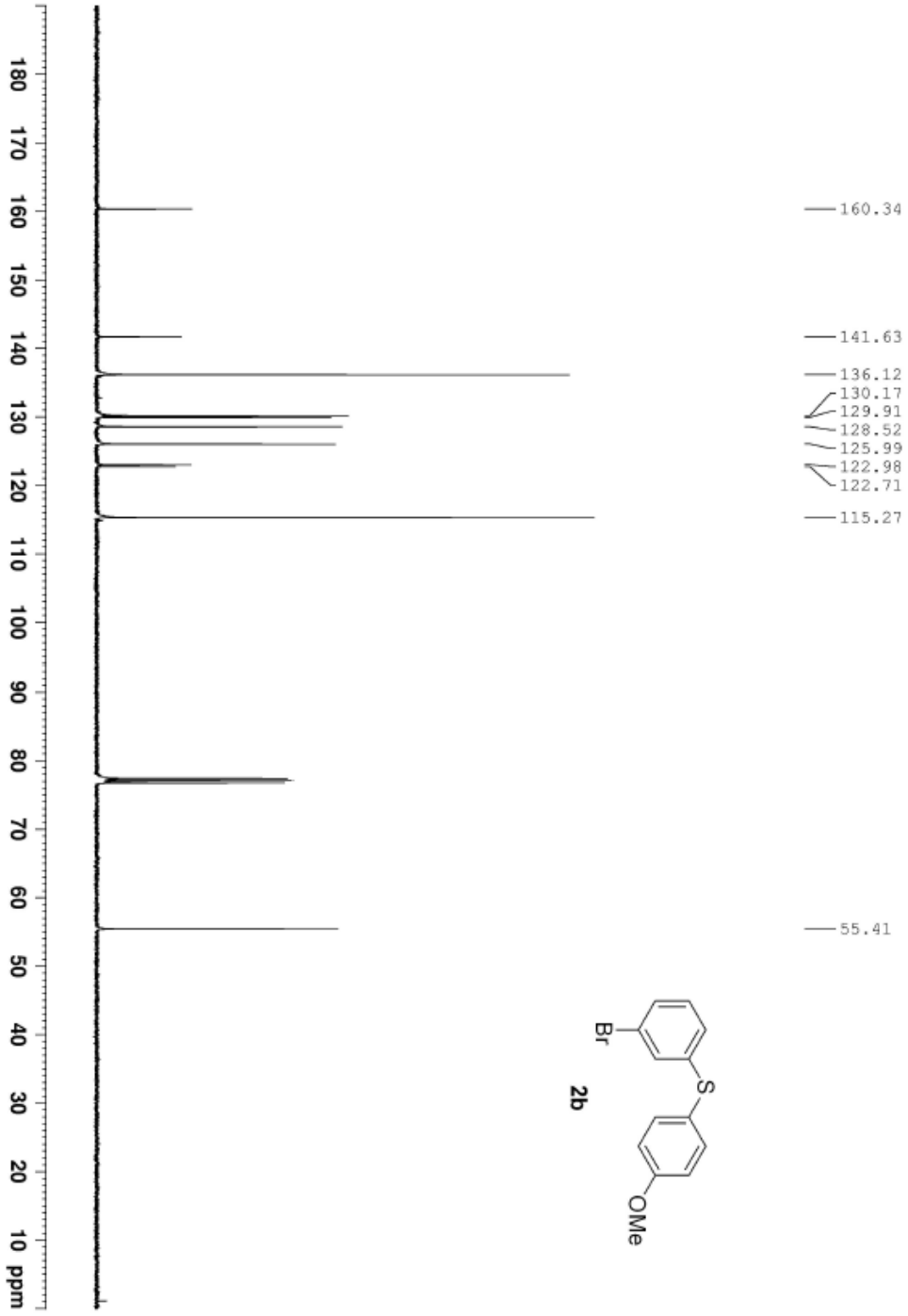
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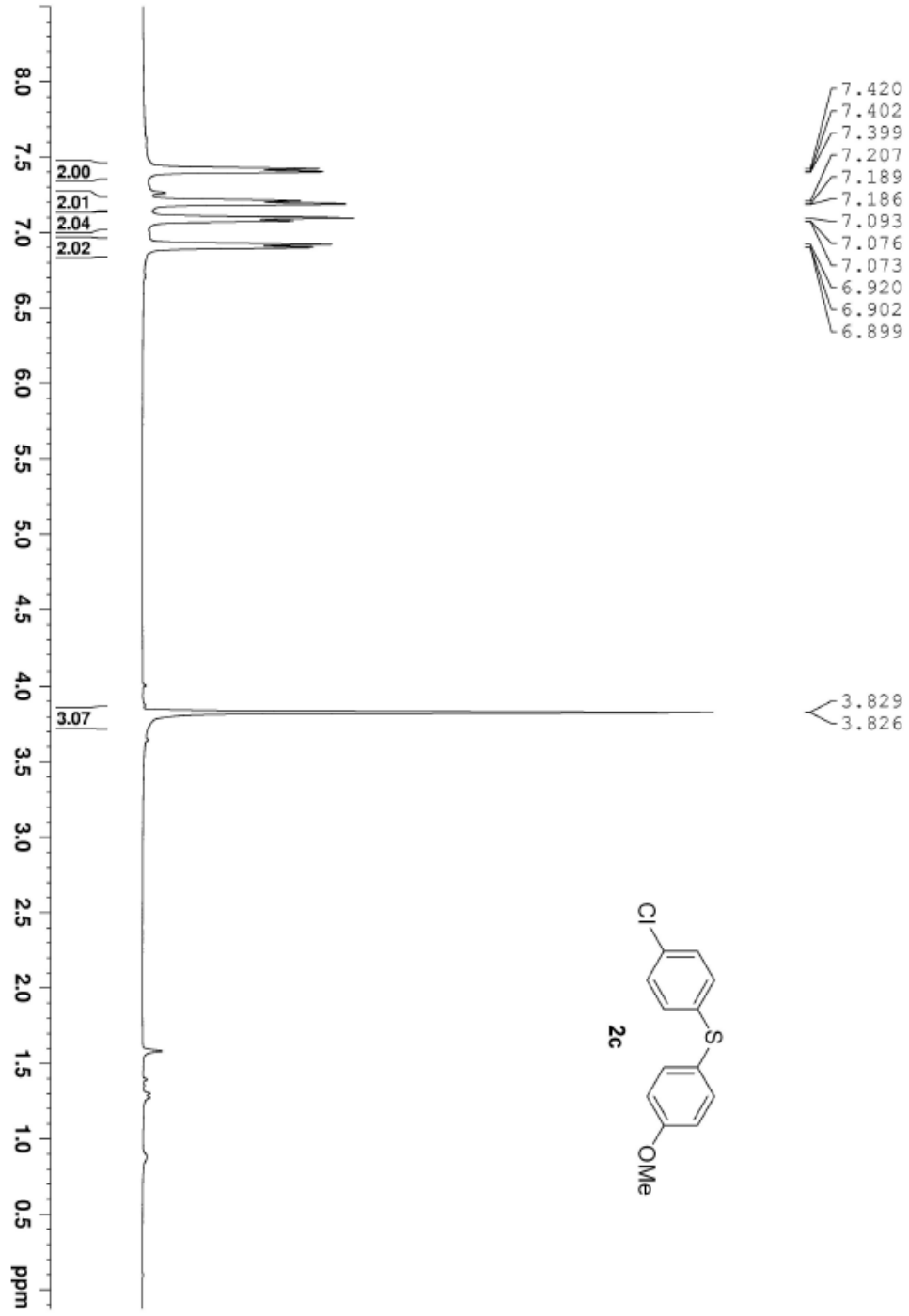
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OMe
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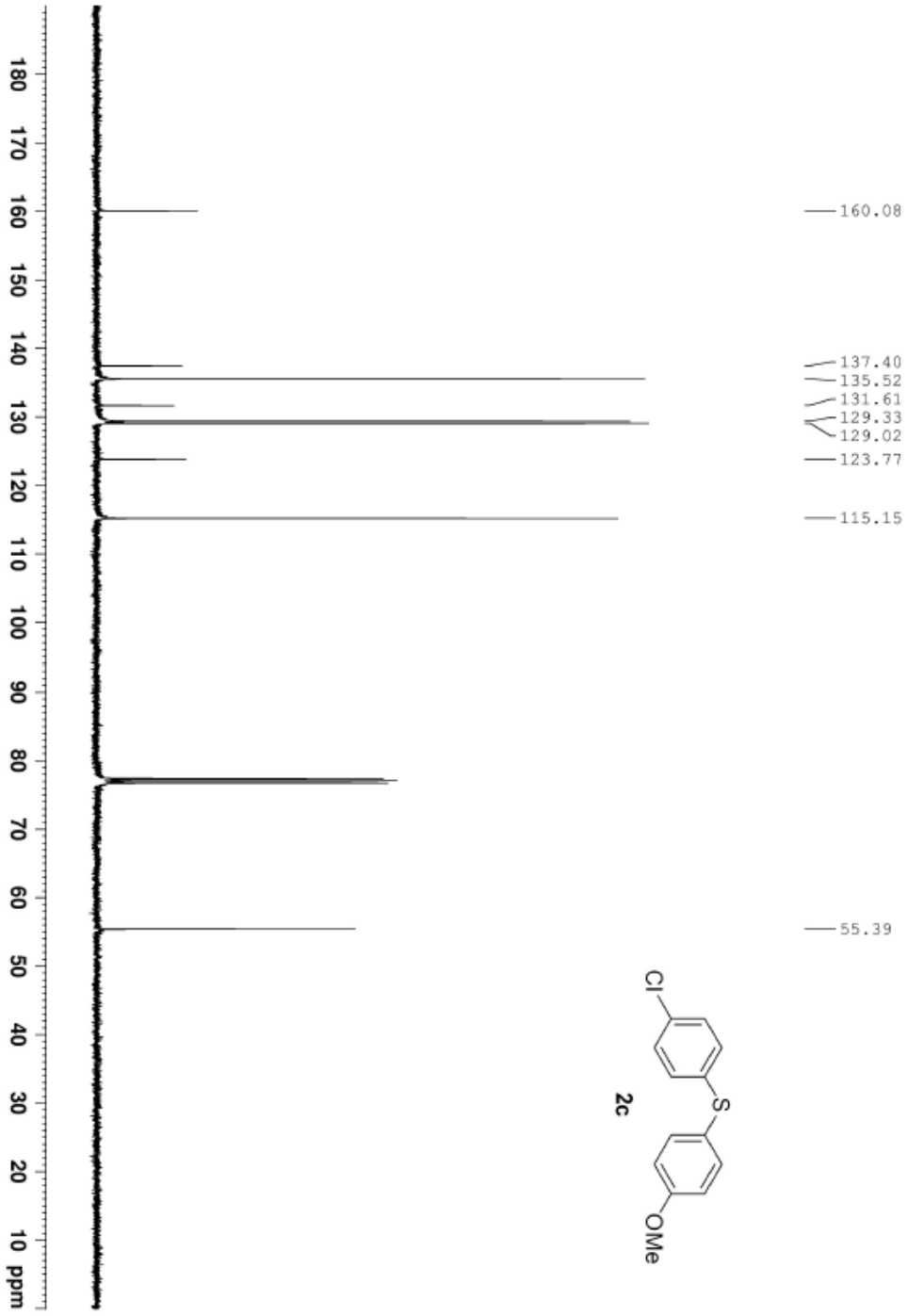
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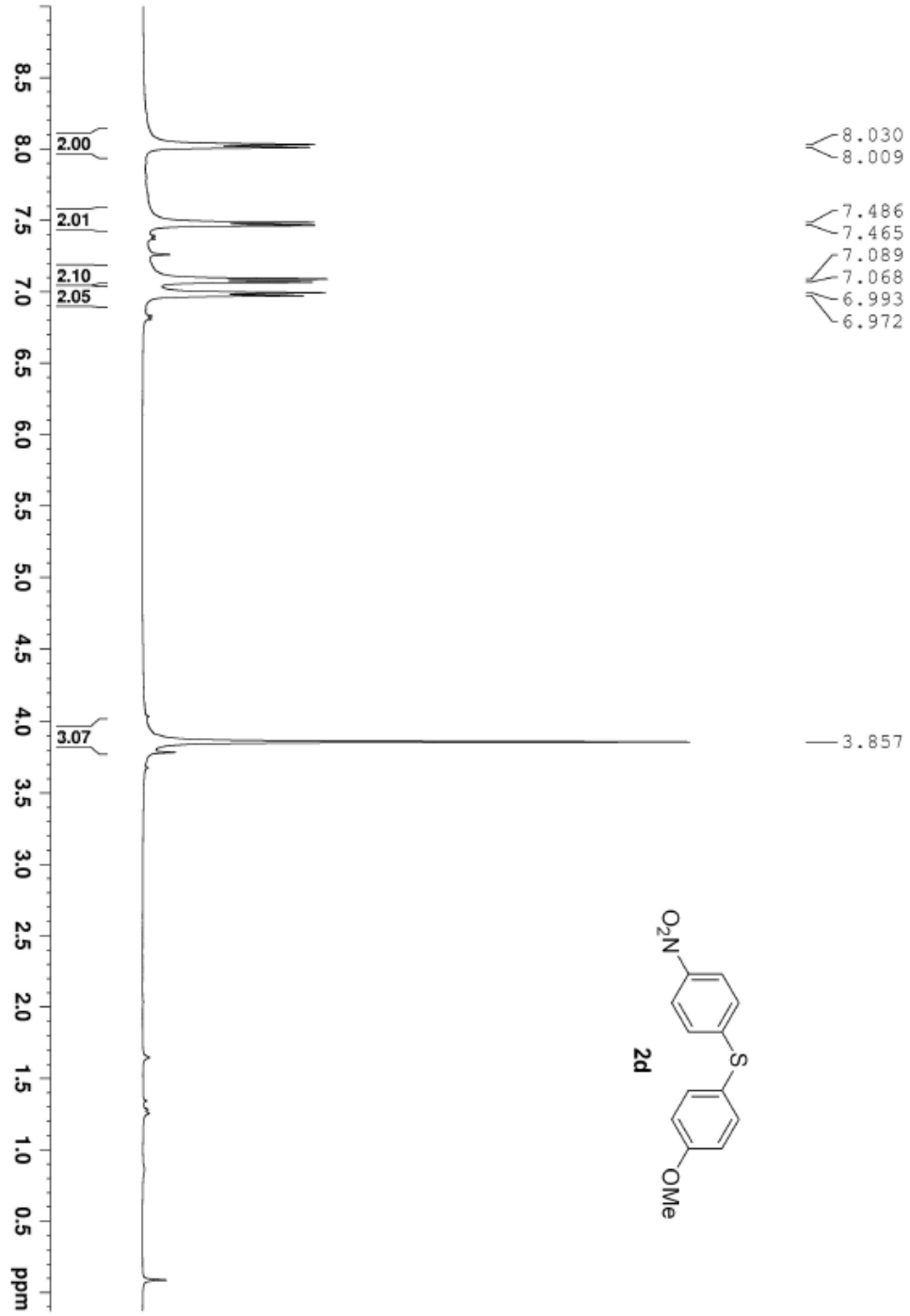
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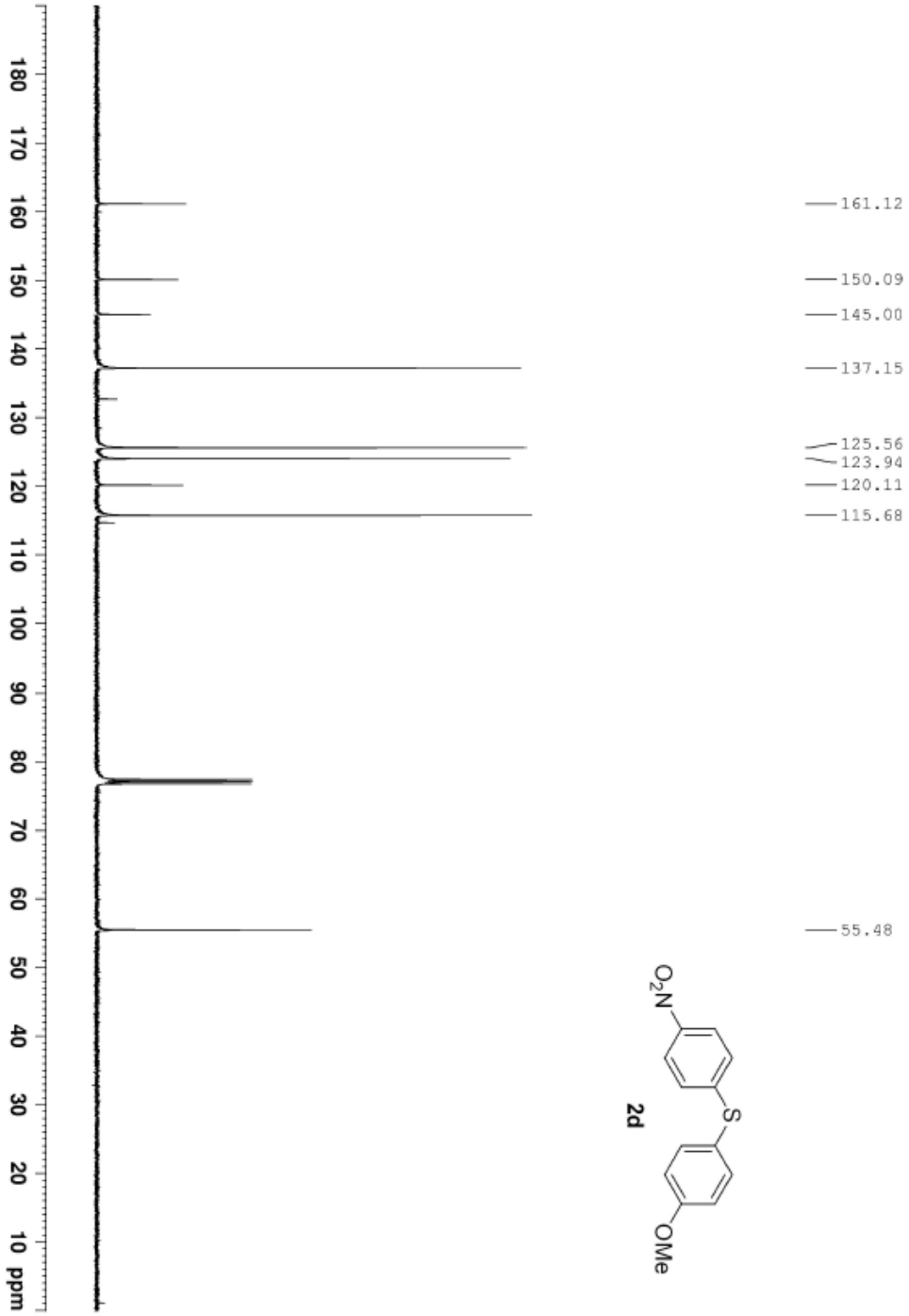
S
OMe
2d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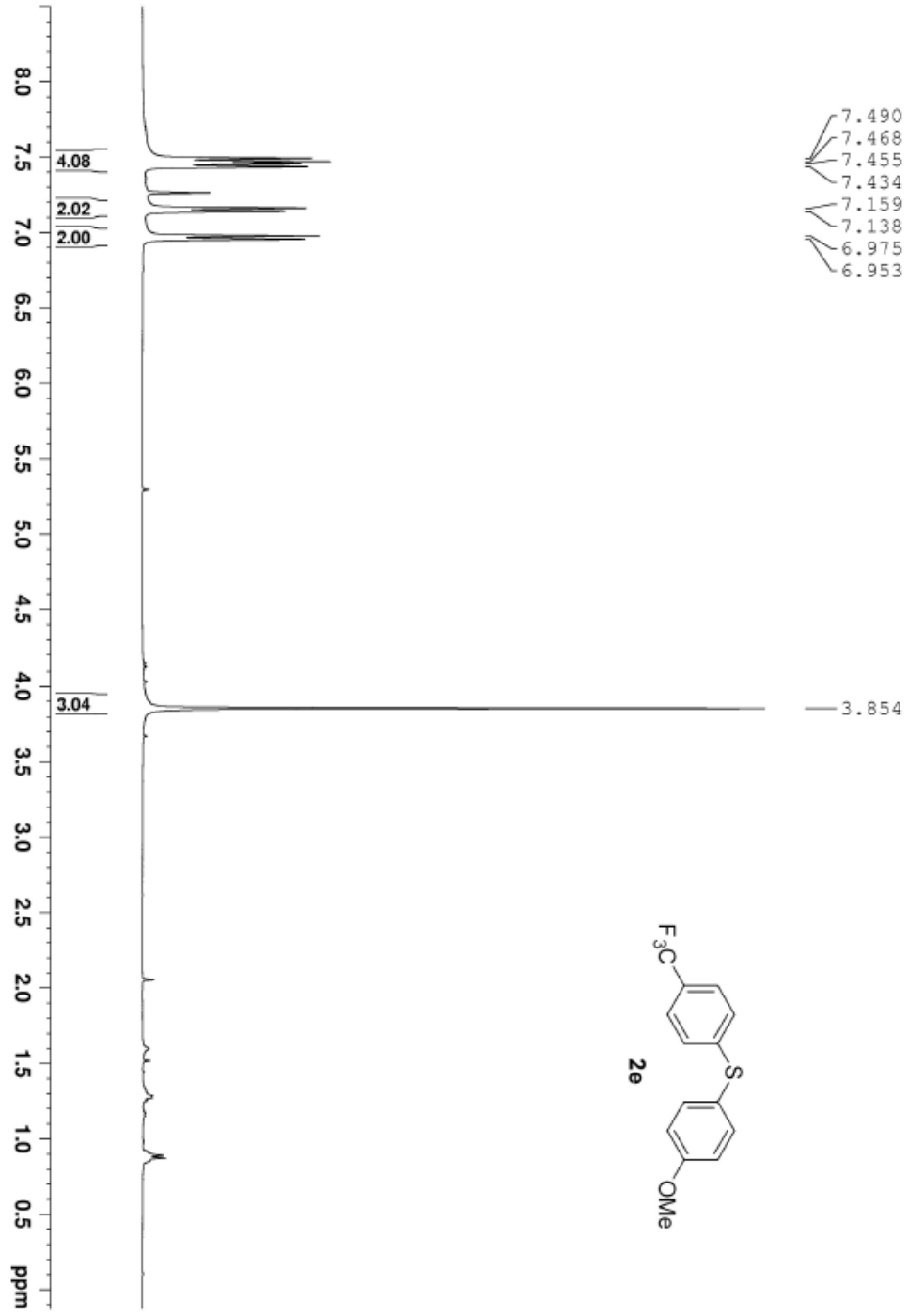
ppm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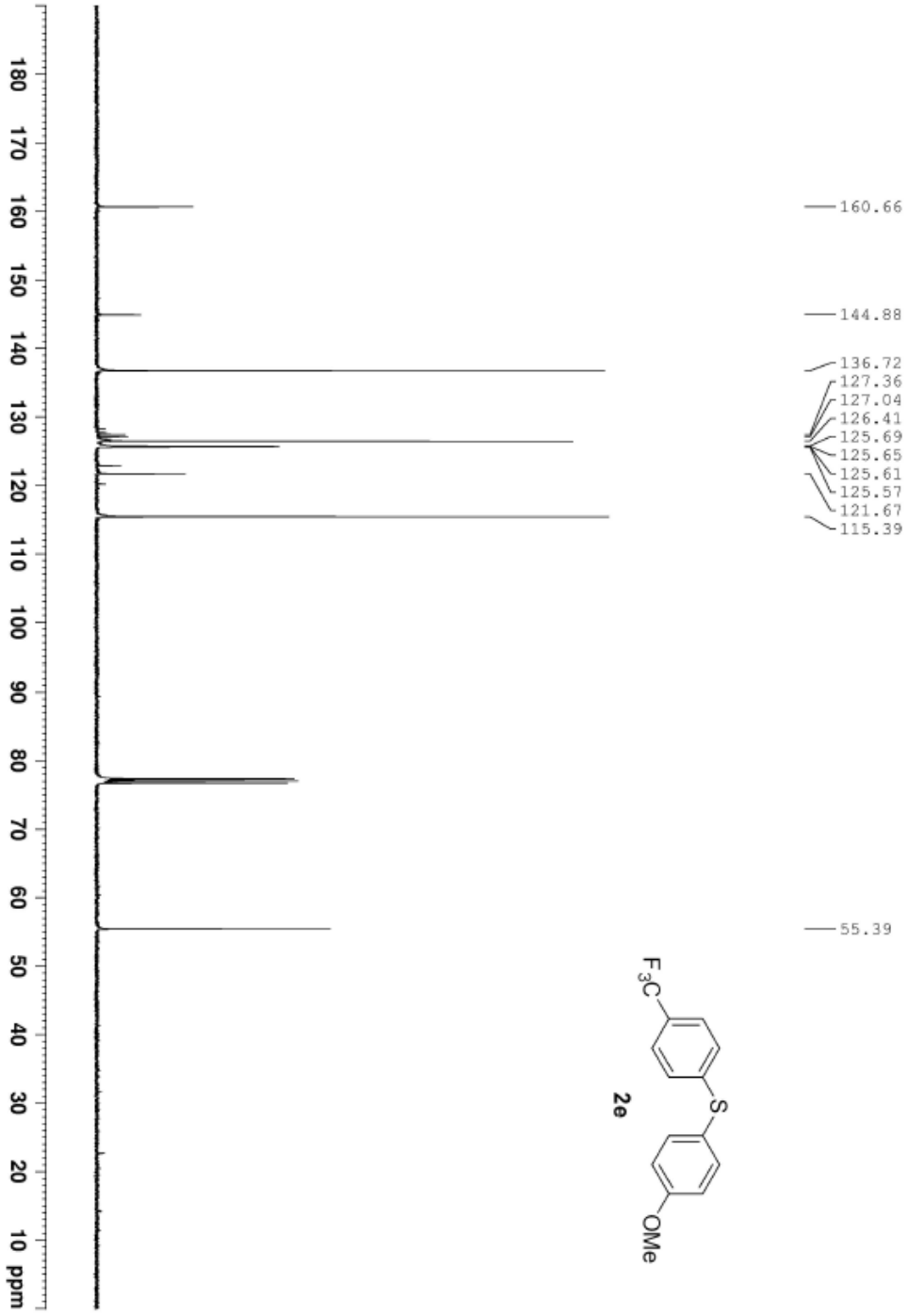
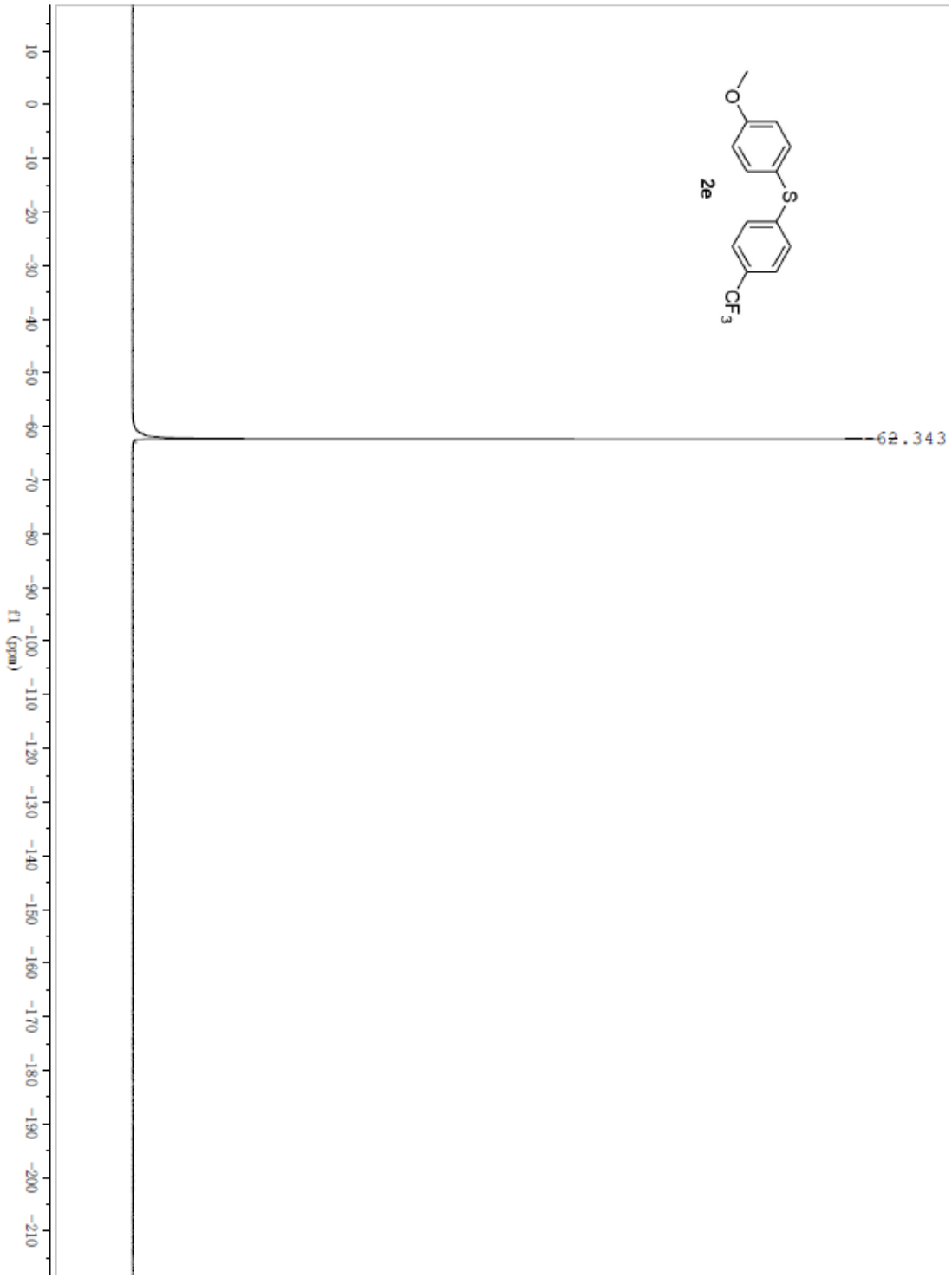
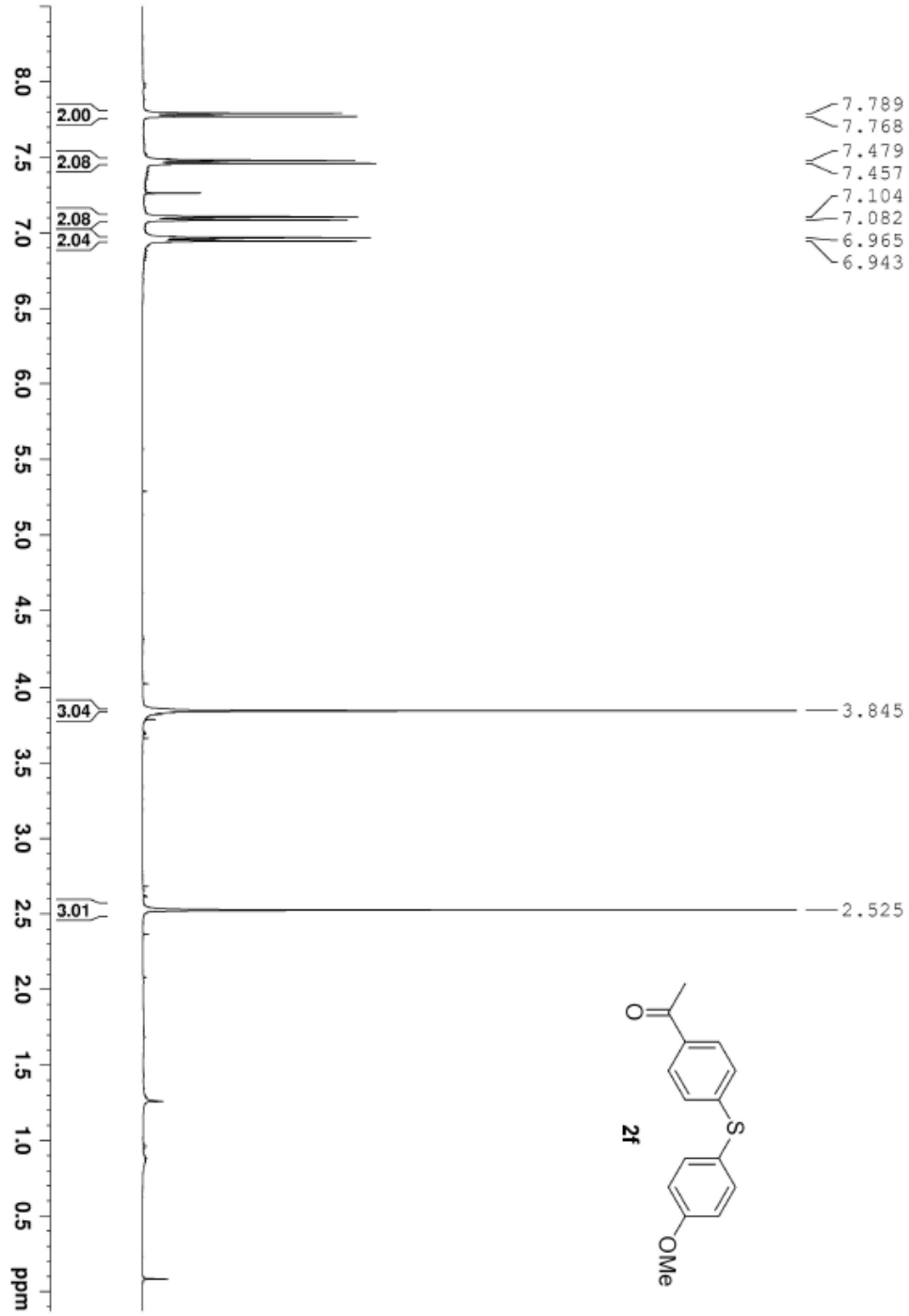
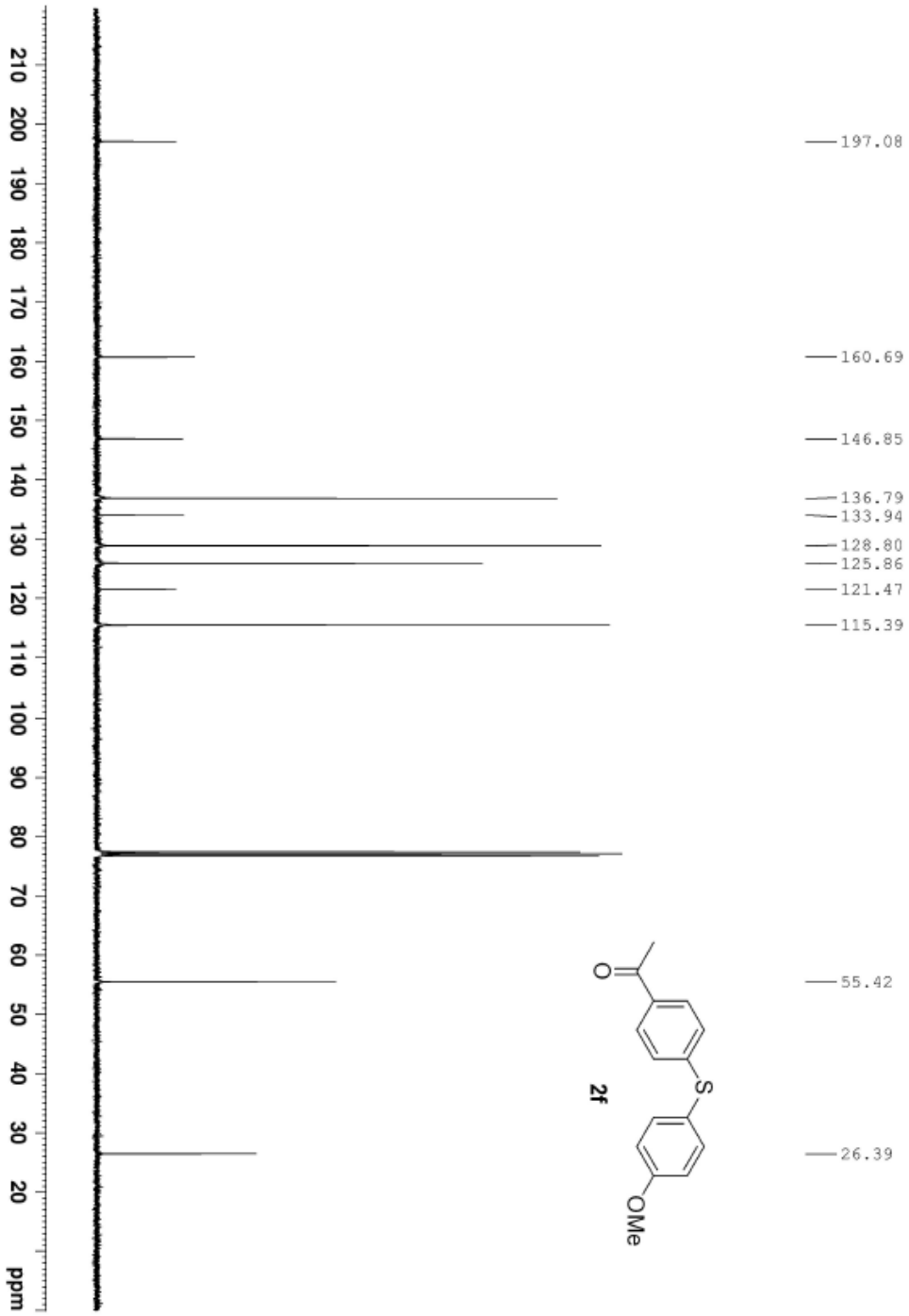
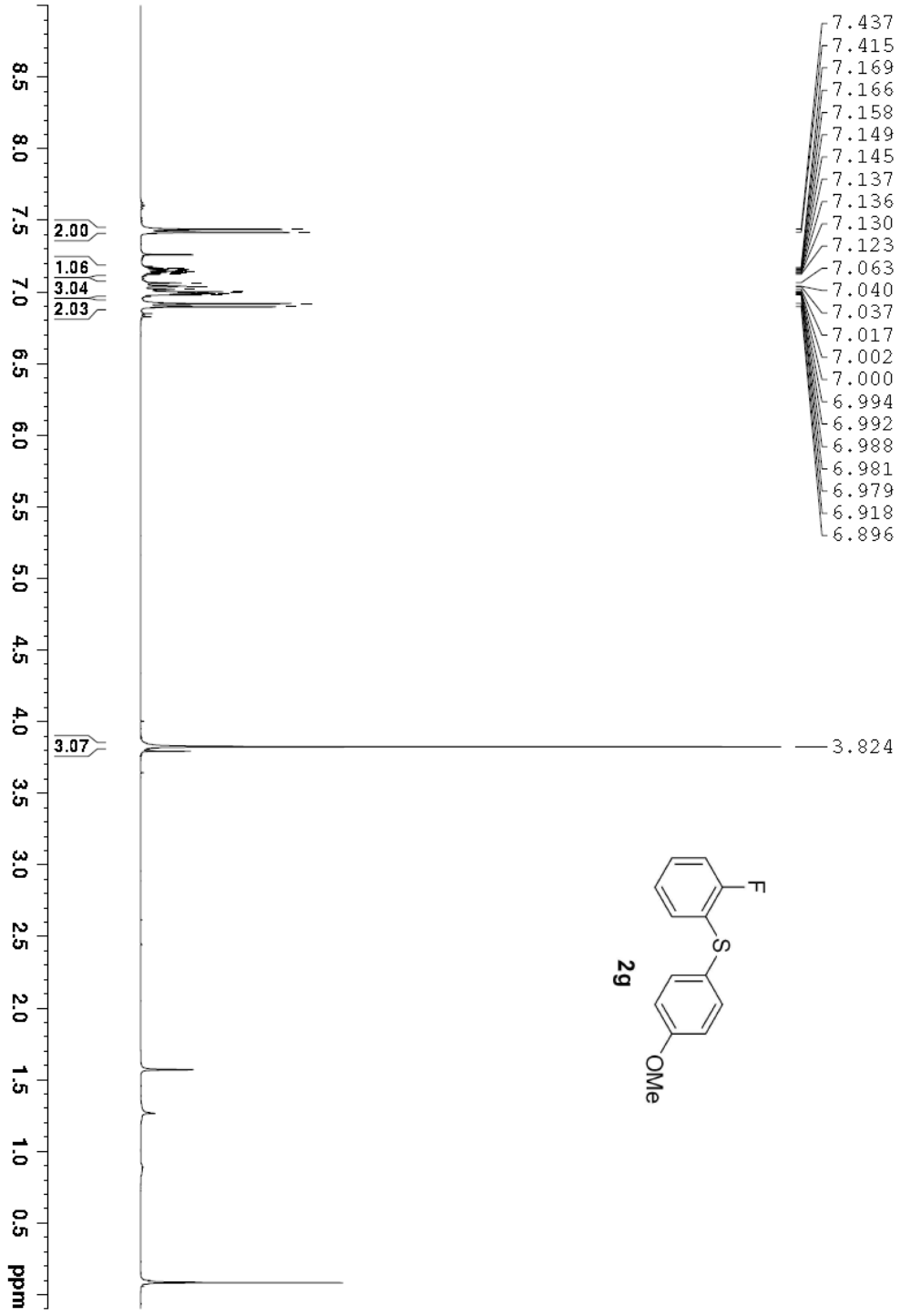
7.468
7.455
7.434
7.159
7.138
6.975
6.953
3.854
4.08
2.02
2.00
3.04
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
F3C
S
OMe
2e

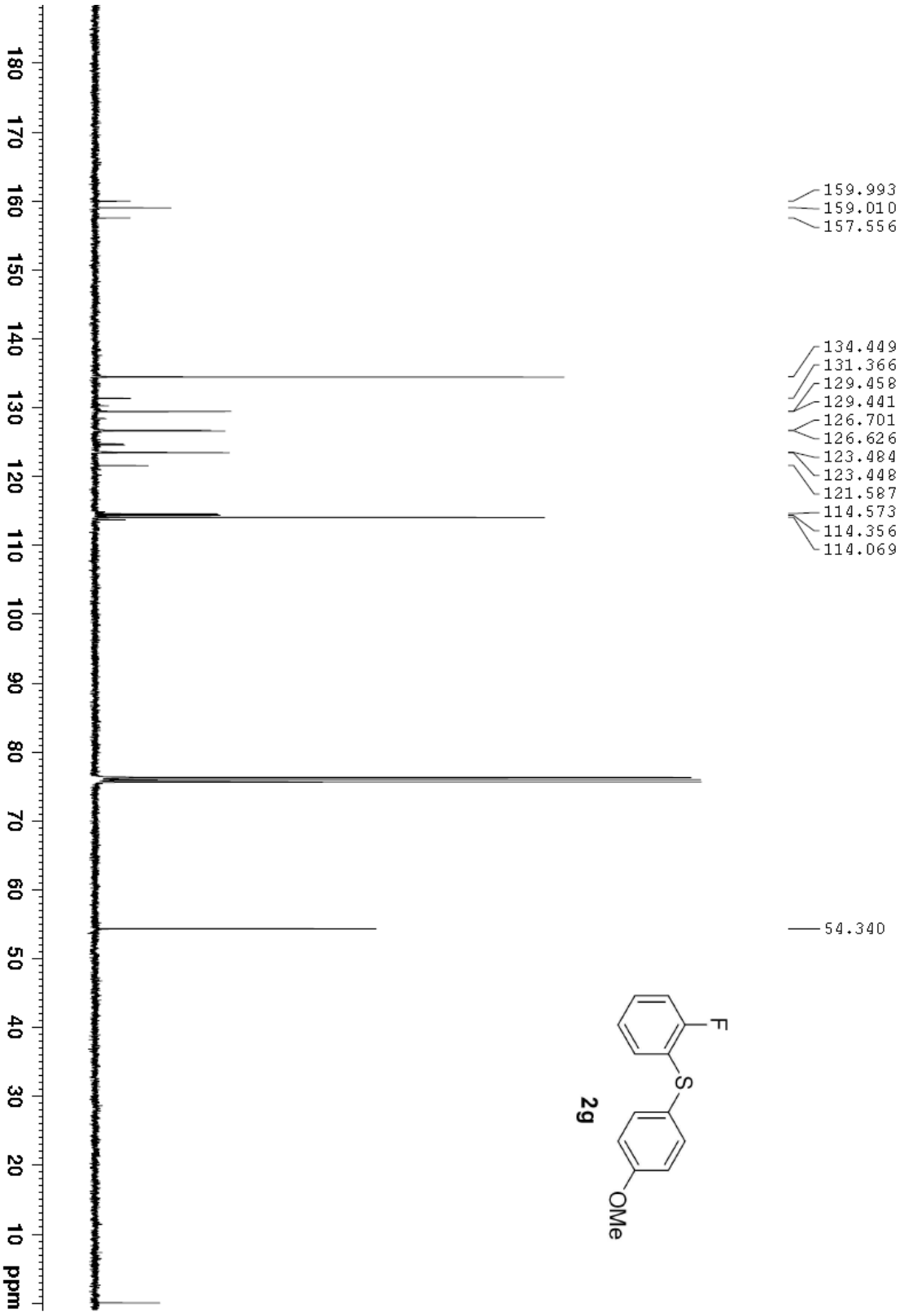

160.66
144.88
136.72
127.36
127.04
126.41
125.69
125.65
125.61
125.57
121.67
115.39
55.39
F3C
S
OMe
2e
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

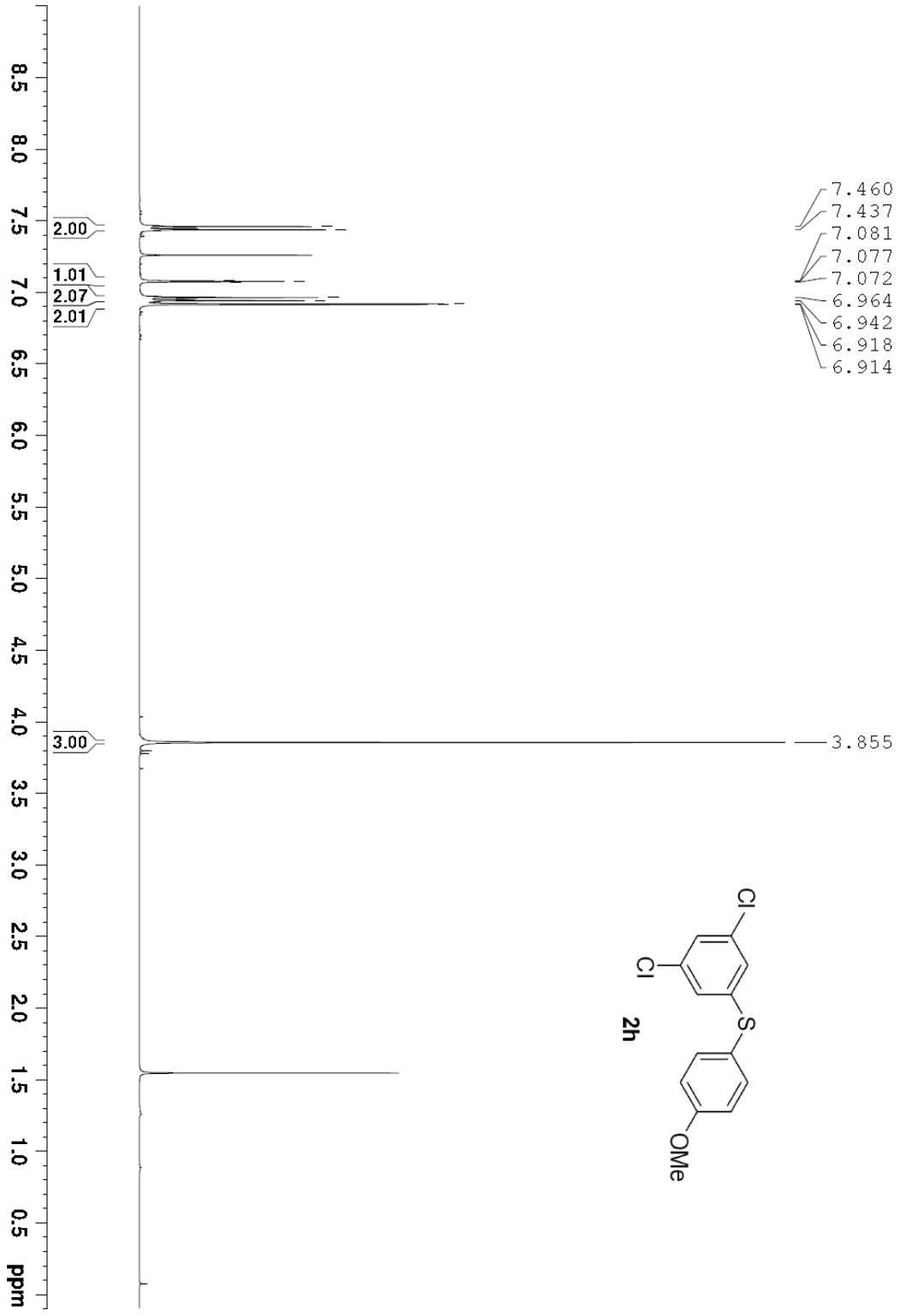

-62.343
2e
f1 (ppm)

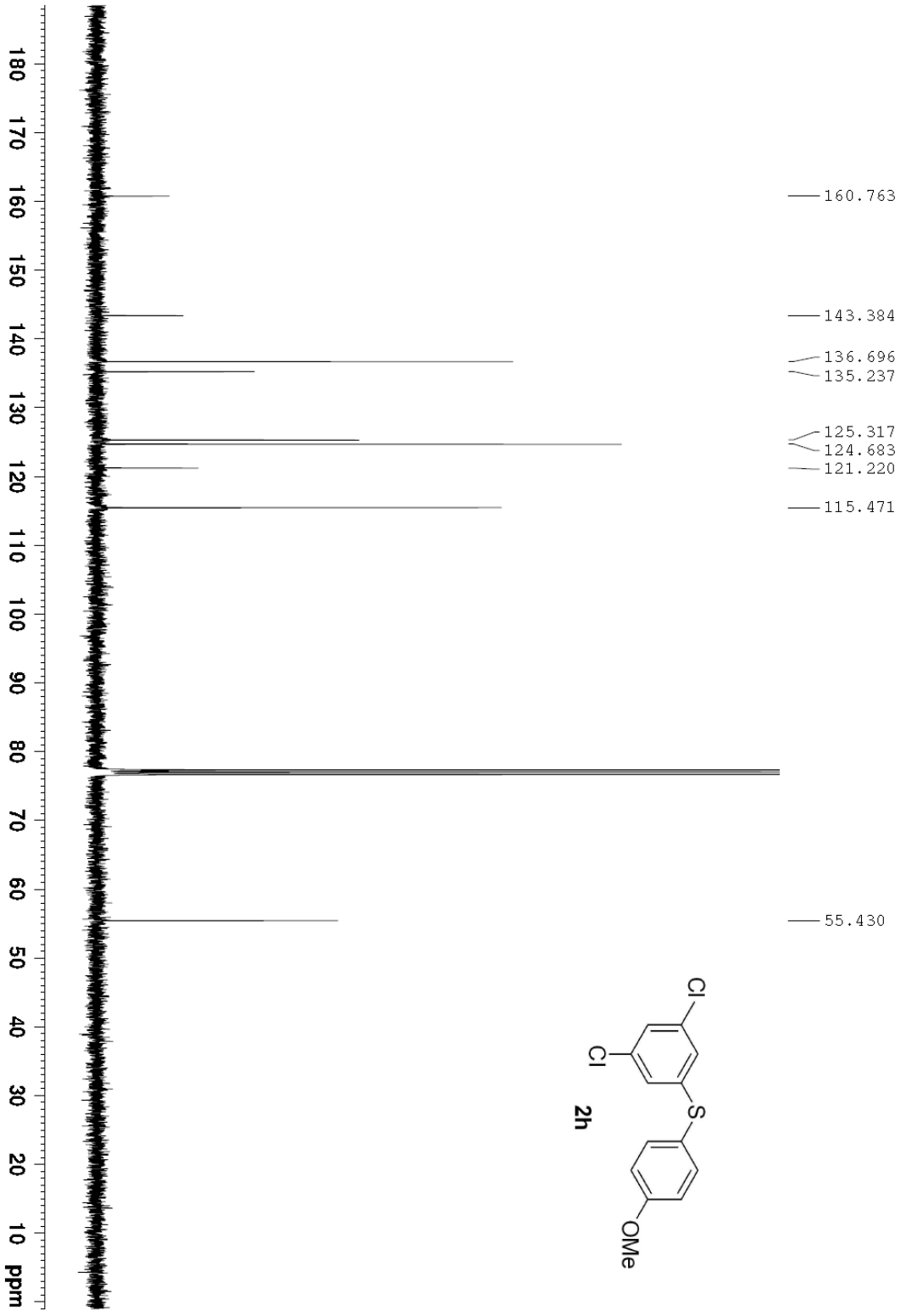

8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
2.08
2.08
2.04
3.04
3.01
7.789
7.768
7.479
7.457
7.104
7.082
6.965
6.943
3.845
2.525
O
S
OMe
2f

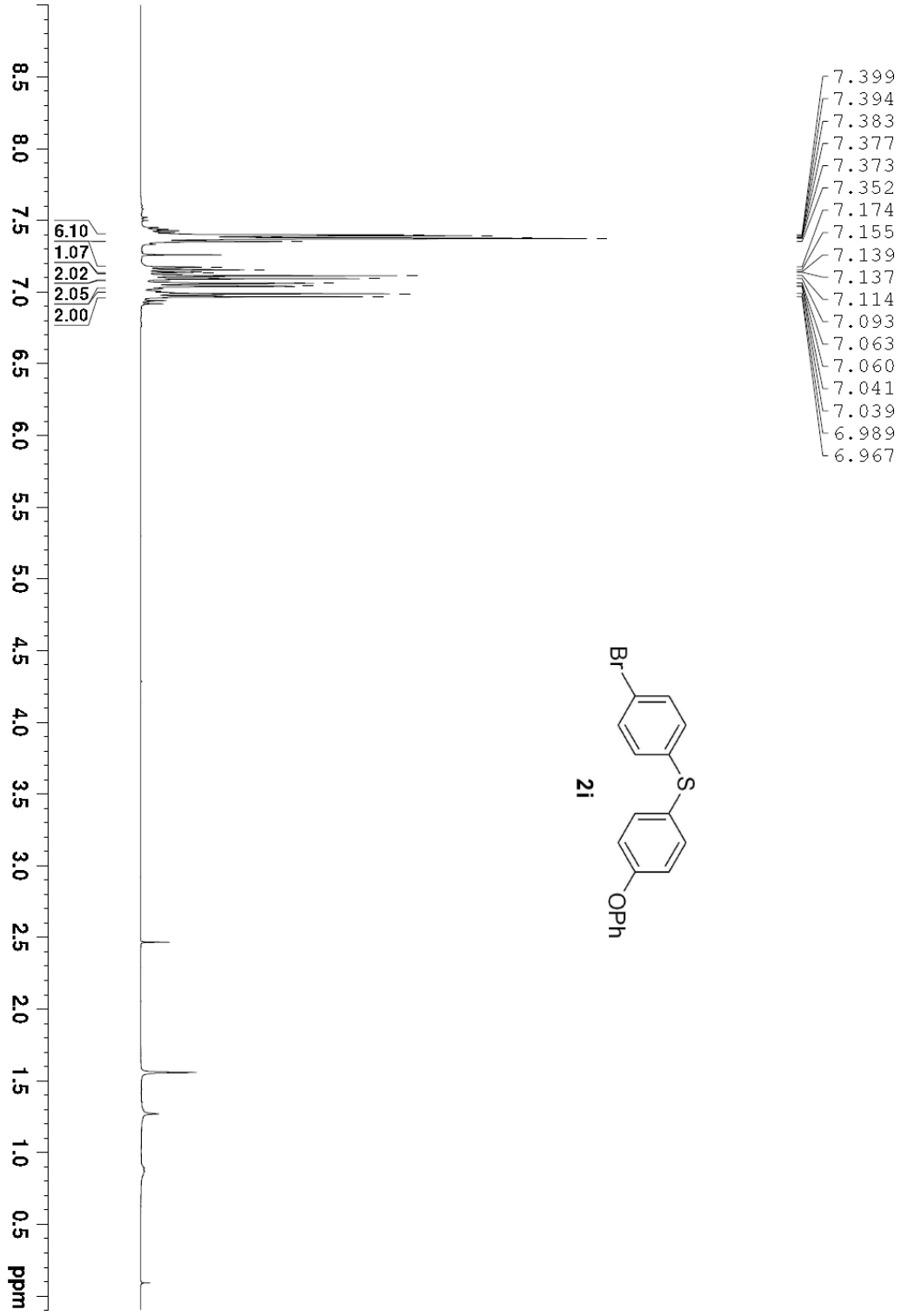

197.08
160.69
146.85
136.79
133.94
128.80
125.86
121.47
115.39
55.42
26.39
O
S
OMe
2f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

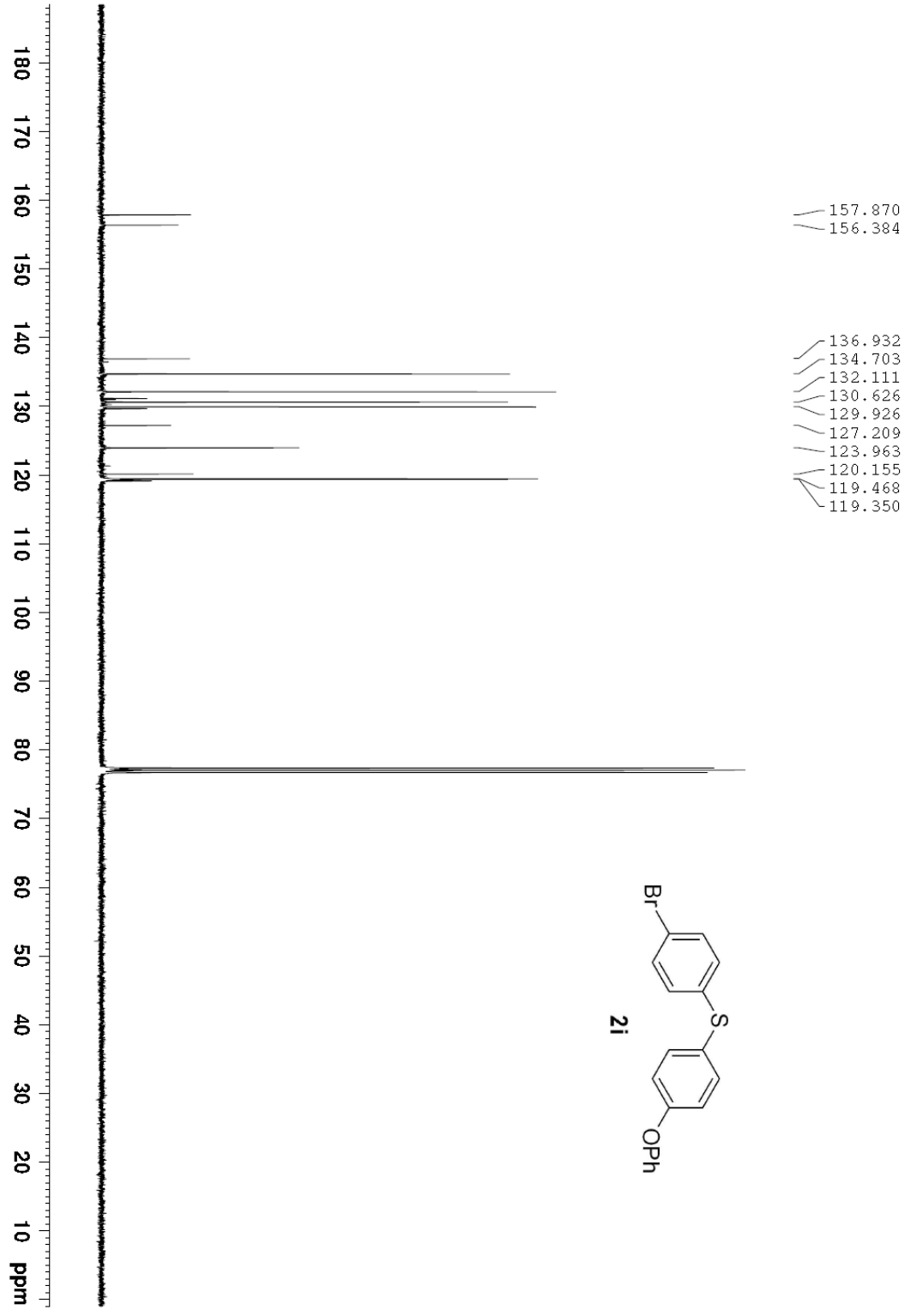

7.437
7.415
7.169
7.166
7.158
7.149
7.145
7.137
7.136
7.130
7.123
7.063
7.040
7.037
7.017
7.002
7.000
6.994
6.992
6.988
6.981
6.979
6.918
6.896
3.824
2.00
1.06
3.04
2.03
3.07
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
F
S
OMe
2g

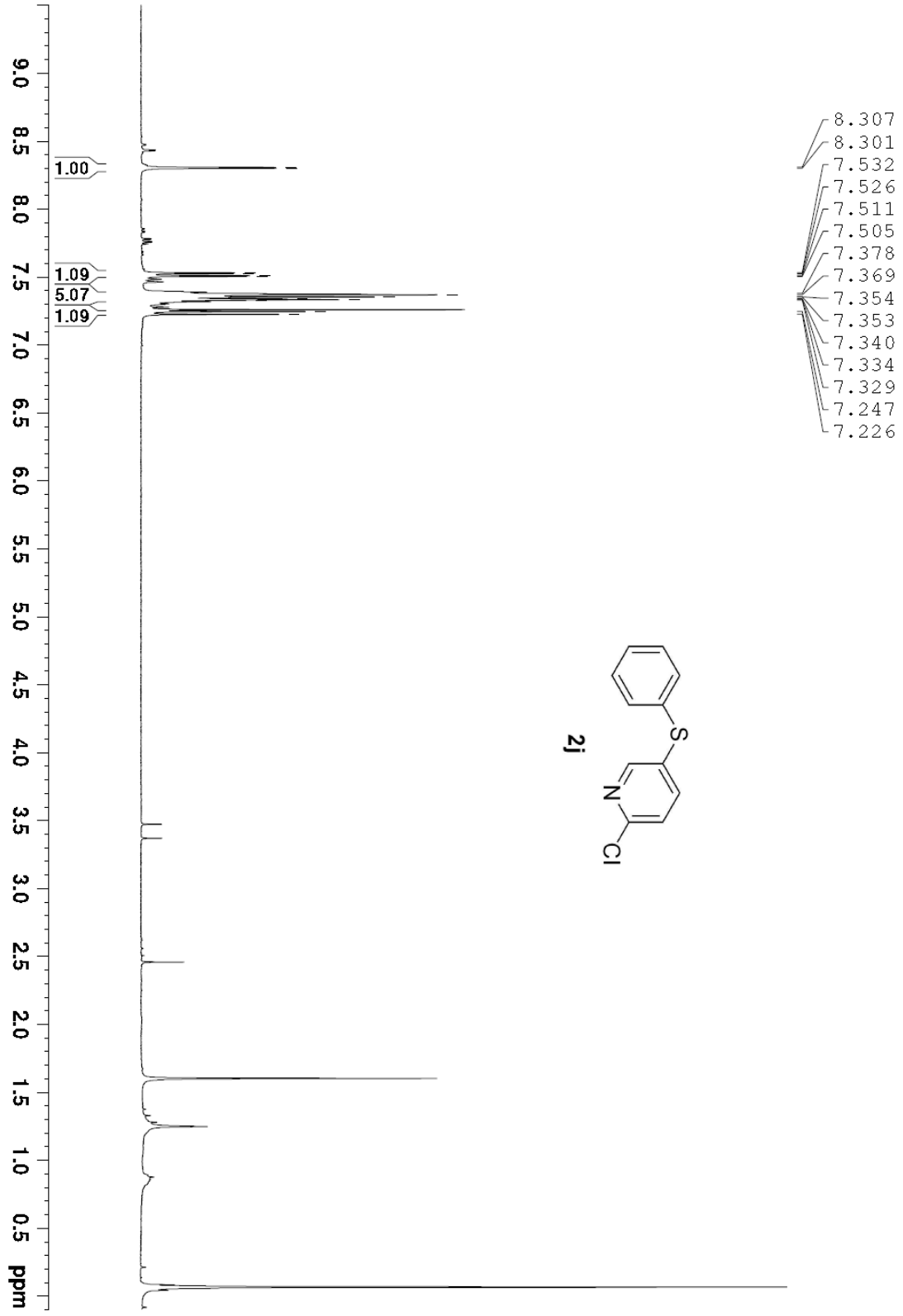

159.993
159.010
157.556
134.449
131.366
129.458
129.441
126.701
126.626
123.484
123.448
121.587
114.573
114.356
114.069
54.340
F
S
OMe
2g
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

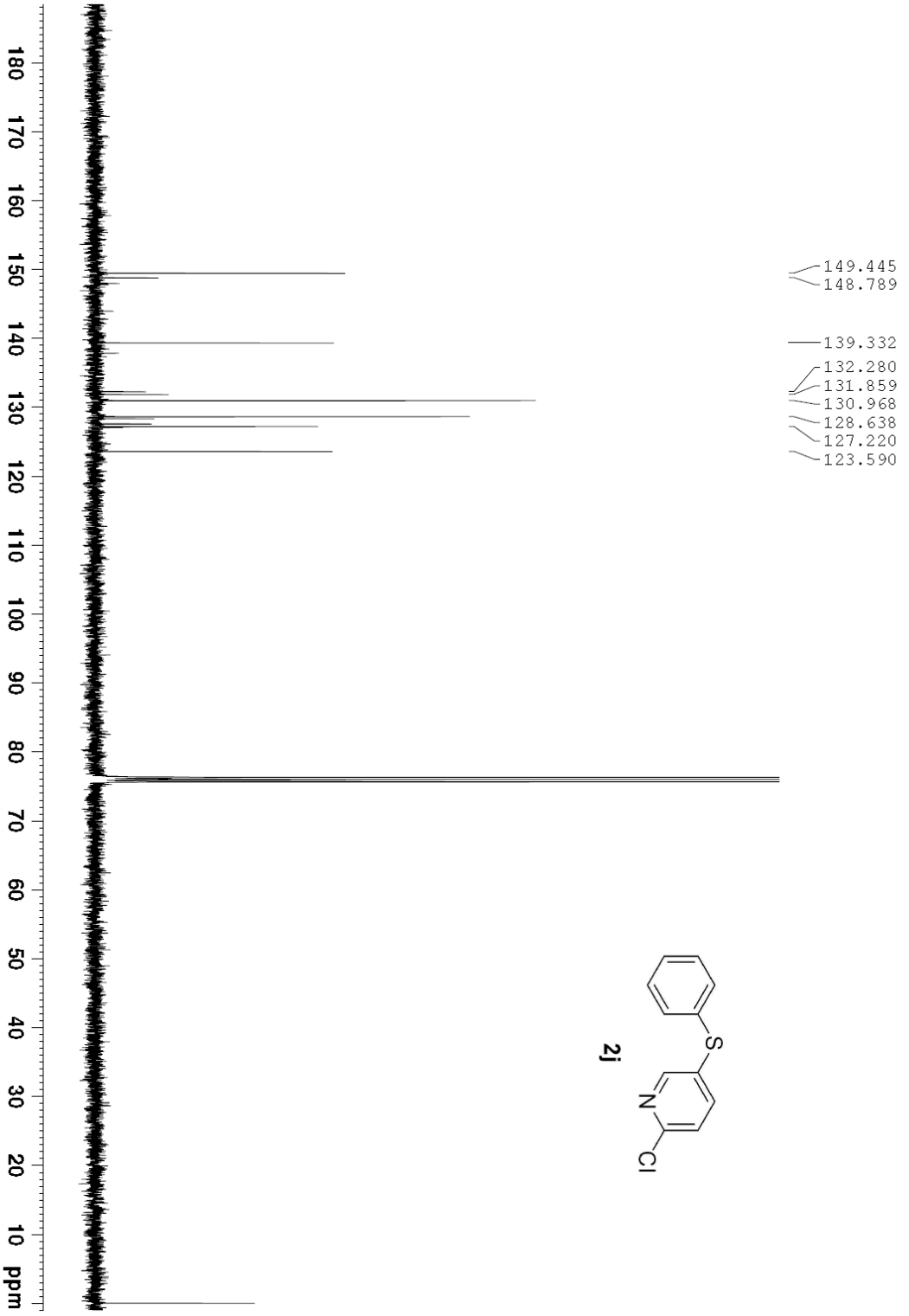

7.460
7.437
7.081
7.077
7.072
6.964
6.942
6.918
6.914
3.855
2.00
1.01
2.07
2.01
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
Cl
Cl
S
OMe
2h

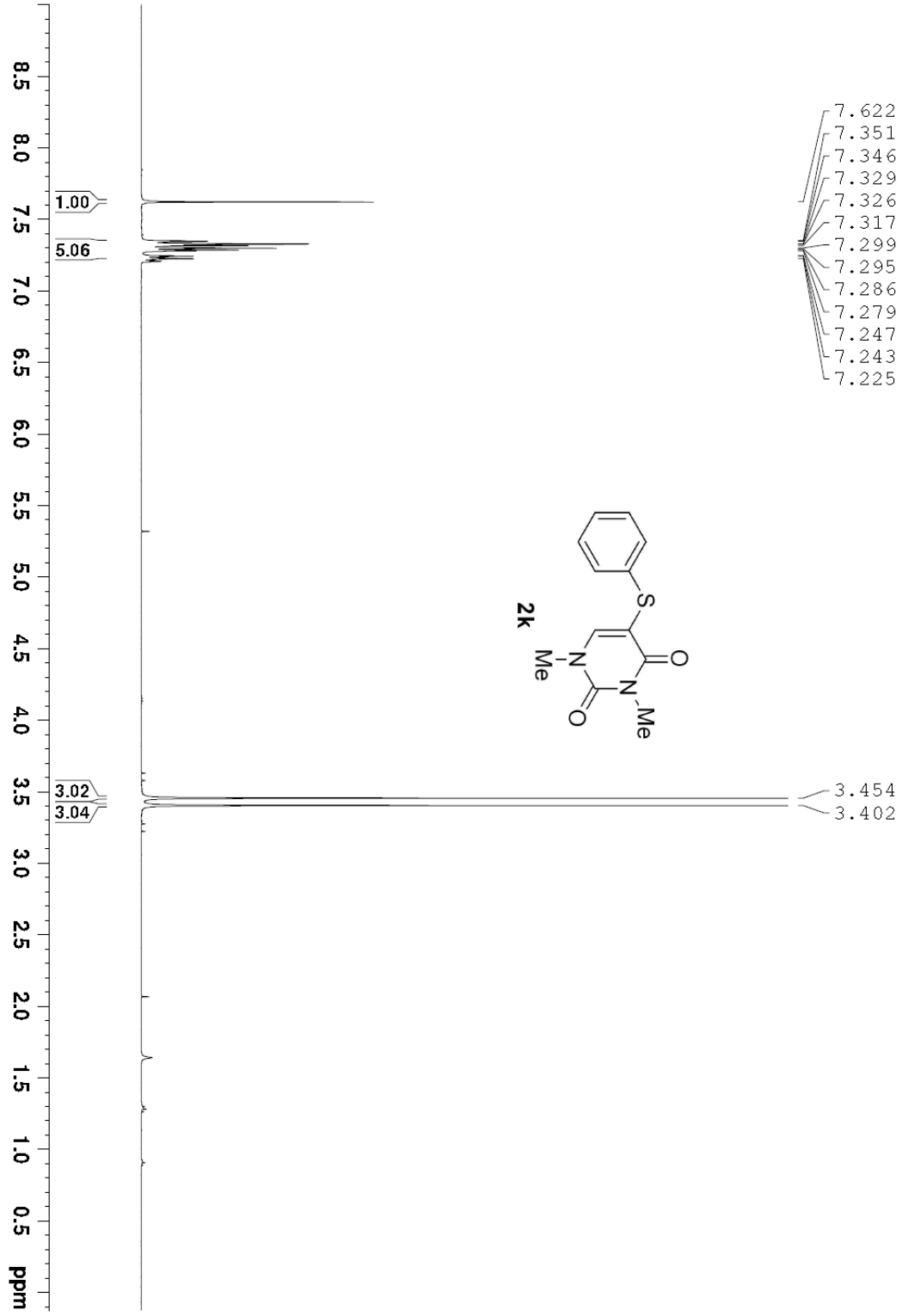

160.763
143.384
136.696
135.237
125.317
124.683
121.220
115.471
55.430
Cl
Cl
S
OMe
2h
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

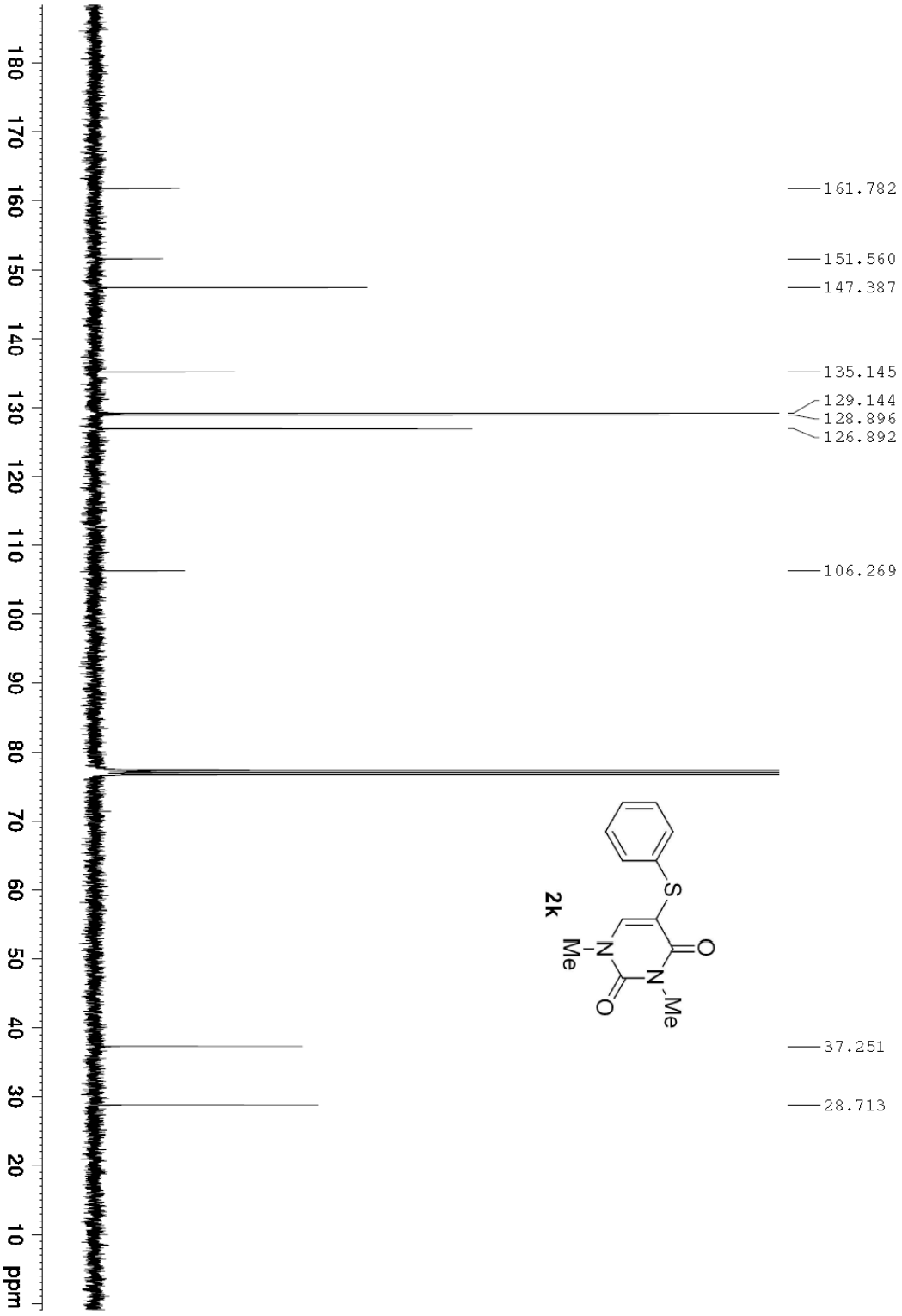

7.399
7.394
7.383
7.377
7.373
7.352
7.174
7.155
7.139
7.137
7.114
7.093
7.063
7.060
7.041
7.039
6.989
6.967
6.10
1.07
2.02
2.05
2.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
Br
S
OPh
2i

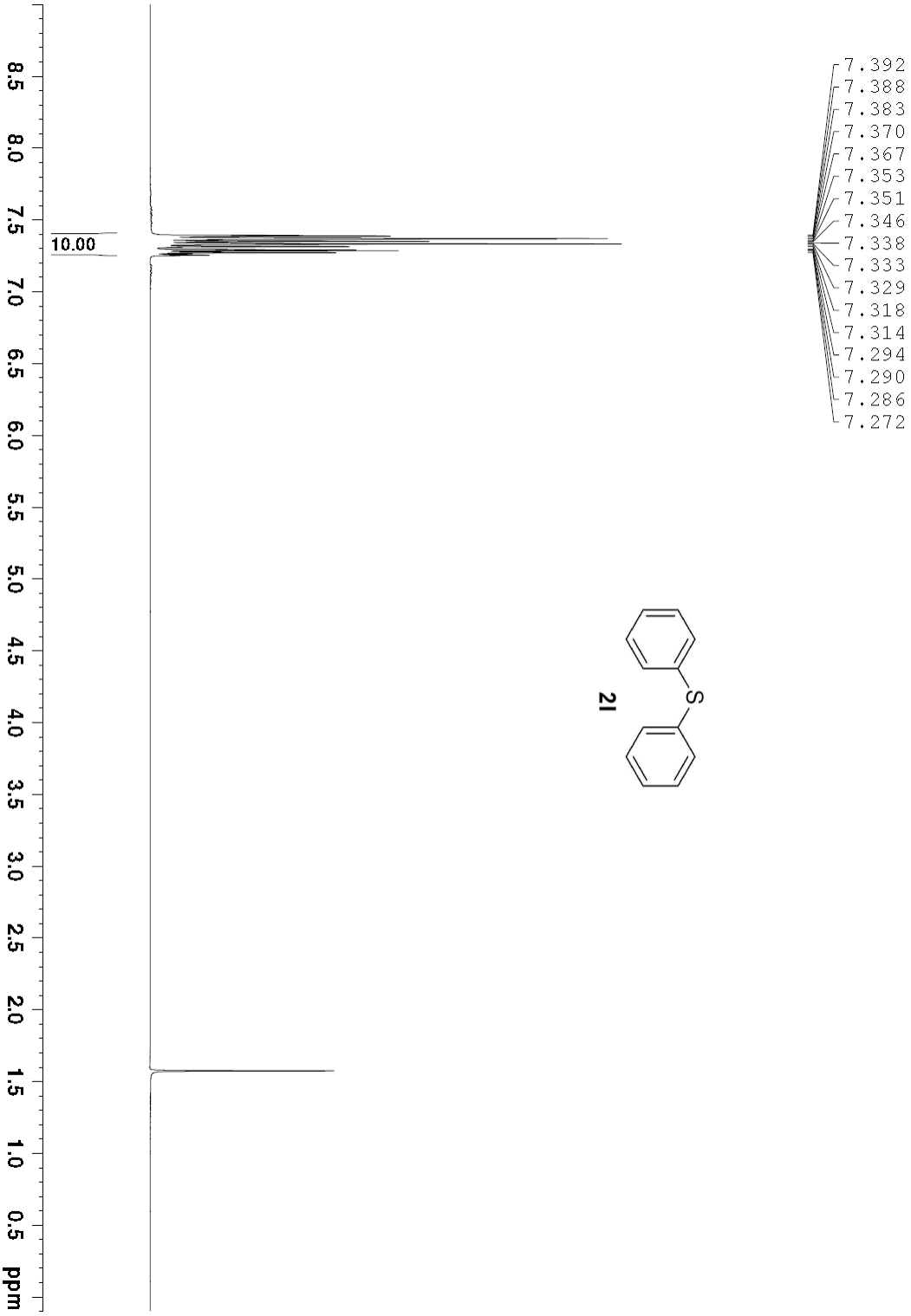

157.870
156.384
136.932
134.703
132.111
130.626
129.926
127.209
123.963
120.155
119.468
119.350
Br
S
OPh
2i
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

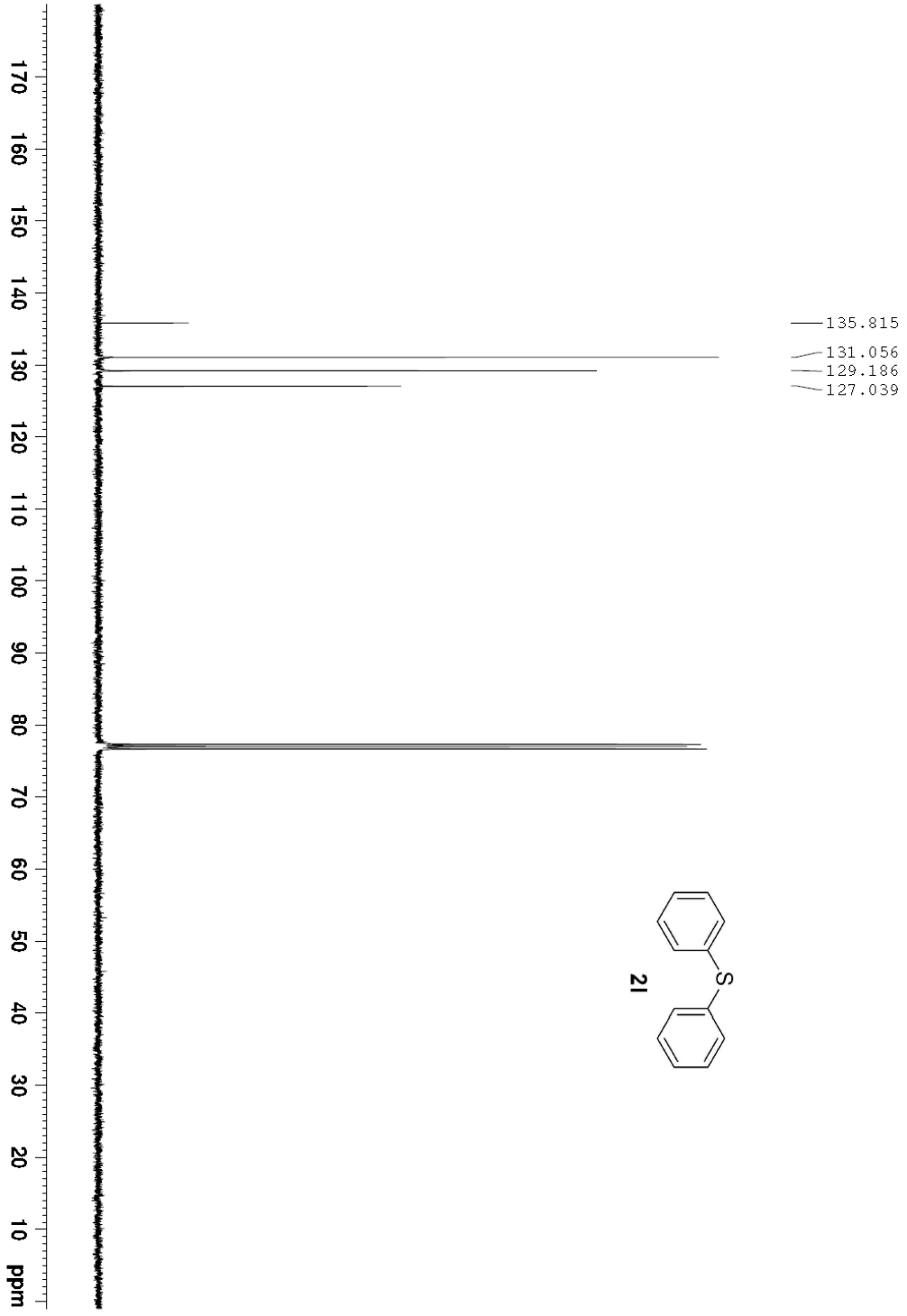

8.307
8.301
7.532
7.526
7.511
7.505
7.378
7.369
7.354
7.353
7.340
7.334
7.329
7.247
7.226
1.00
1.09
5.07
1.09
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
S
N
Cl
2j

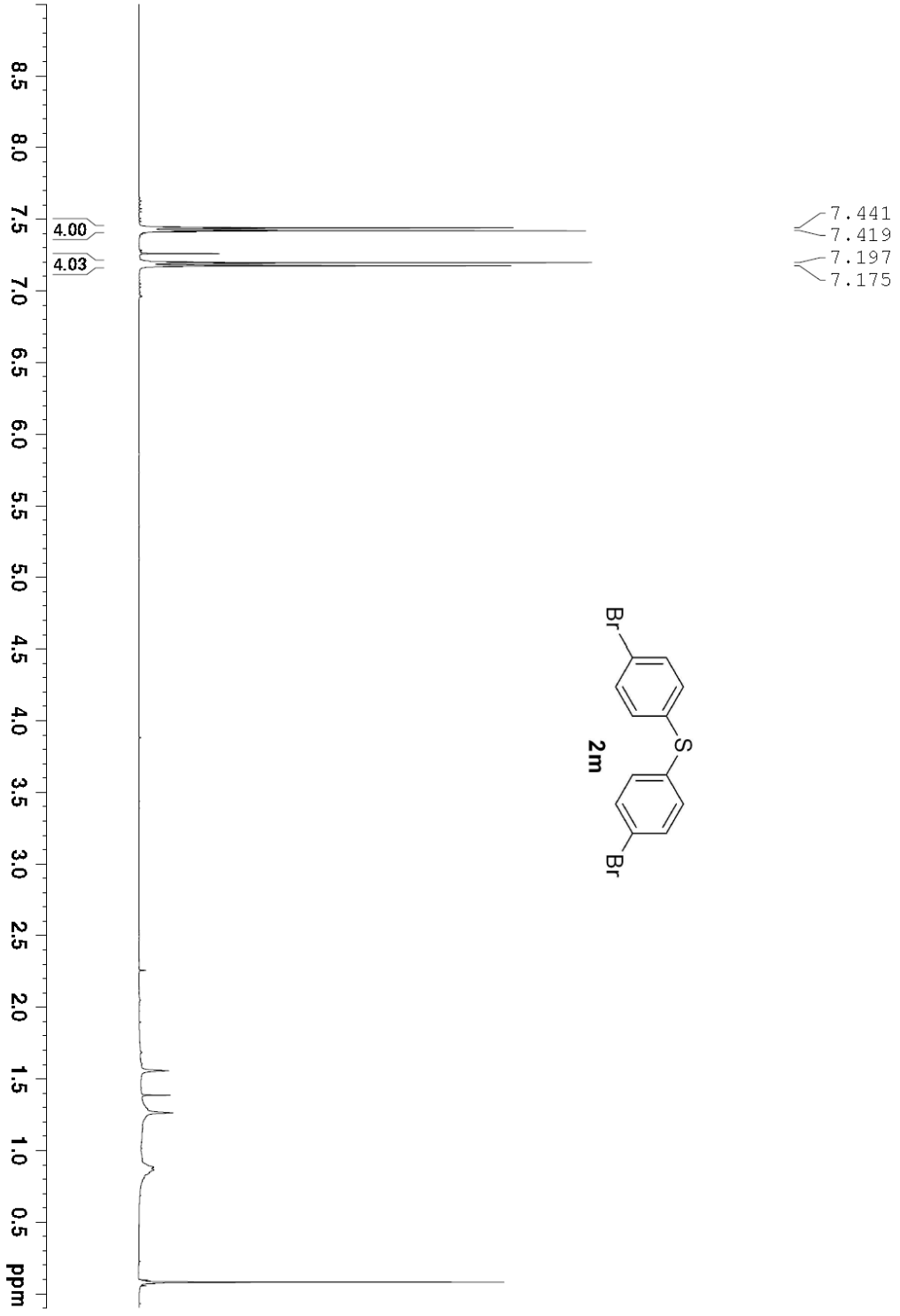

149.445
148.789
139.332
132.280
131.859
130.968
128.638
127.220
123.590
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
S
N
Cl
2j

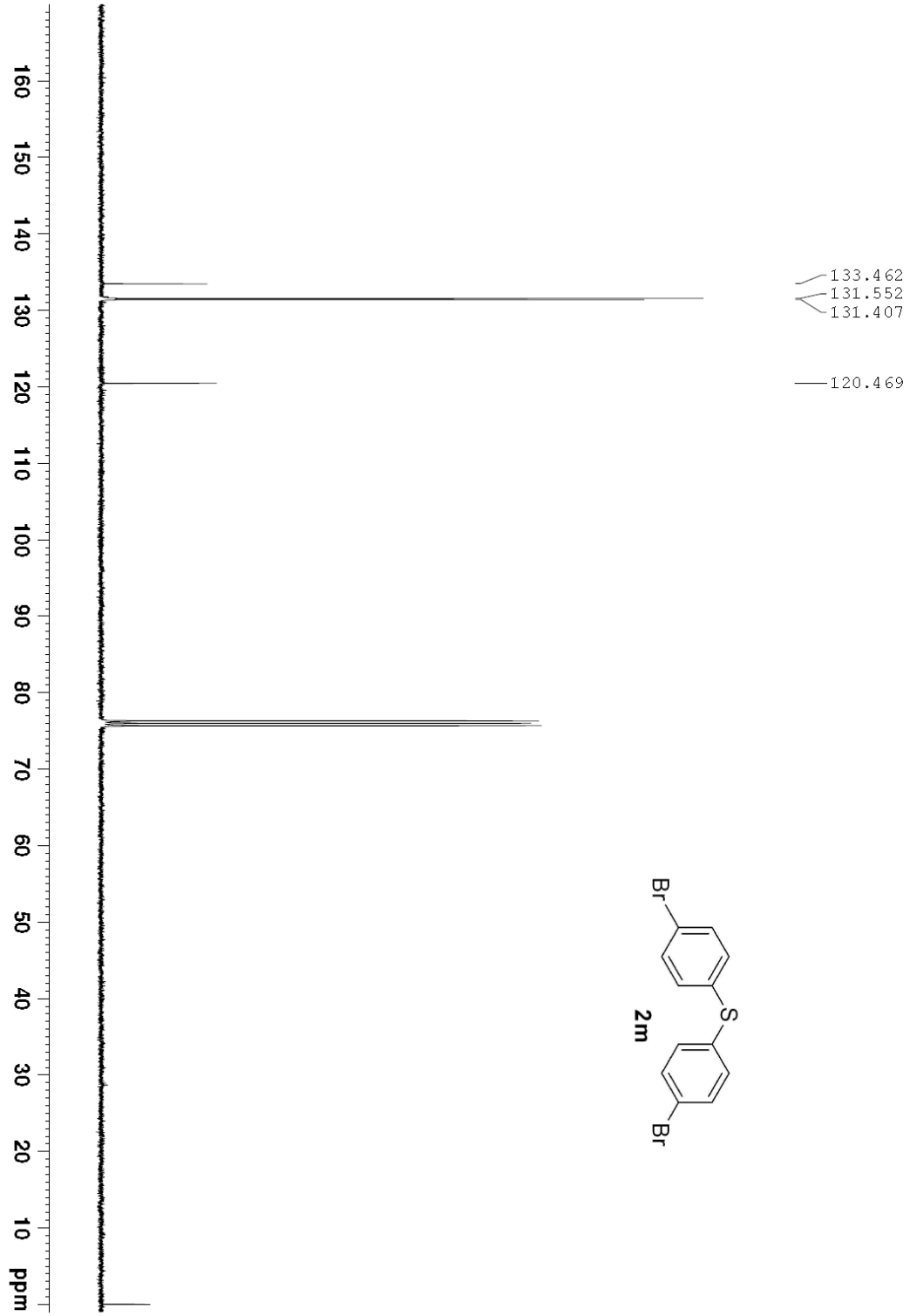

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
5.06
3.02
3.04
7.622
7.351
7.346
7.329
7.326
7.317
7.299
7.295
7.286
7.279
7.247
7.243
7.225
3.454
3.402
2k
S
N
Me
O
N
Me
O

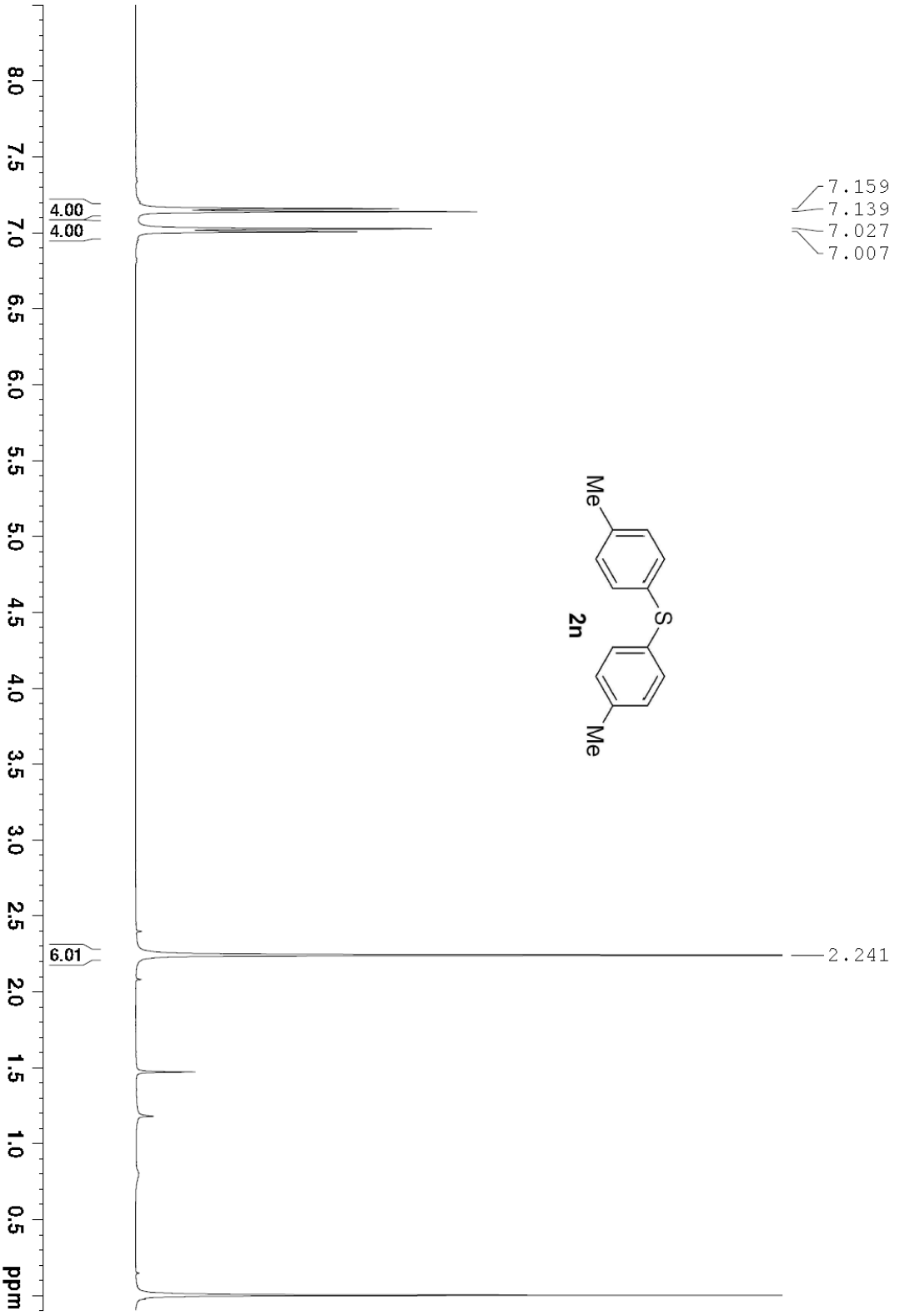

161.782
151.560
147.387
135.145
129.144
128.896
126.892
106.269
37.251
28.713
2k
Me
Me
S
O
O
N
N
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

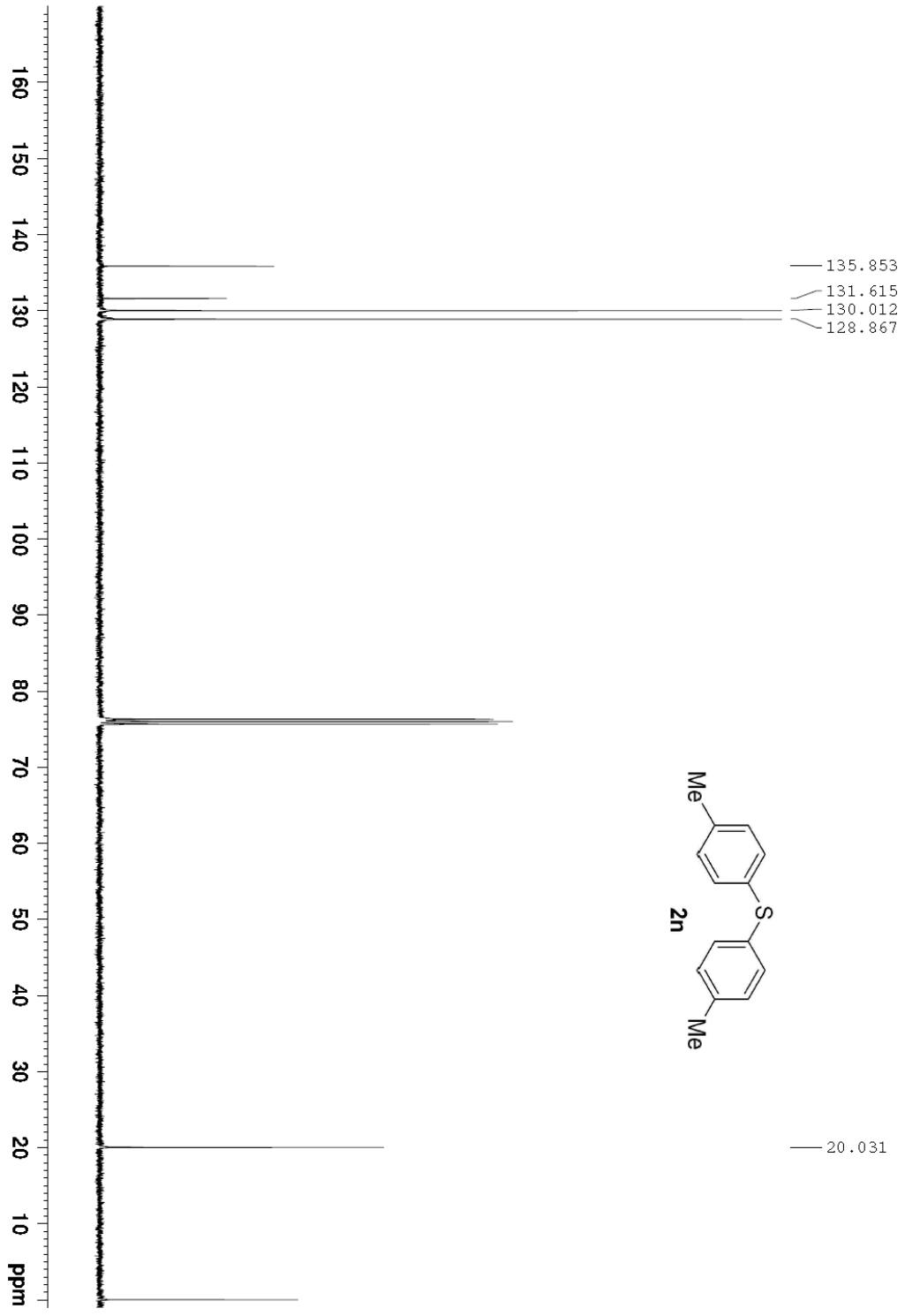

7.392
7.388
7.383
7.370
7.367
7.353
7.351
7.346
7.338
7.333
7.329
7.318
7.314
7.294
7.290
7.286
7.272
10.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
S
2l

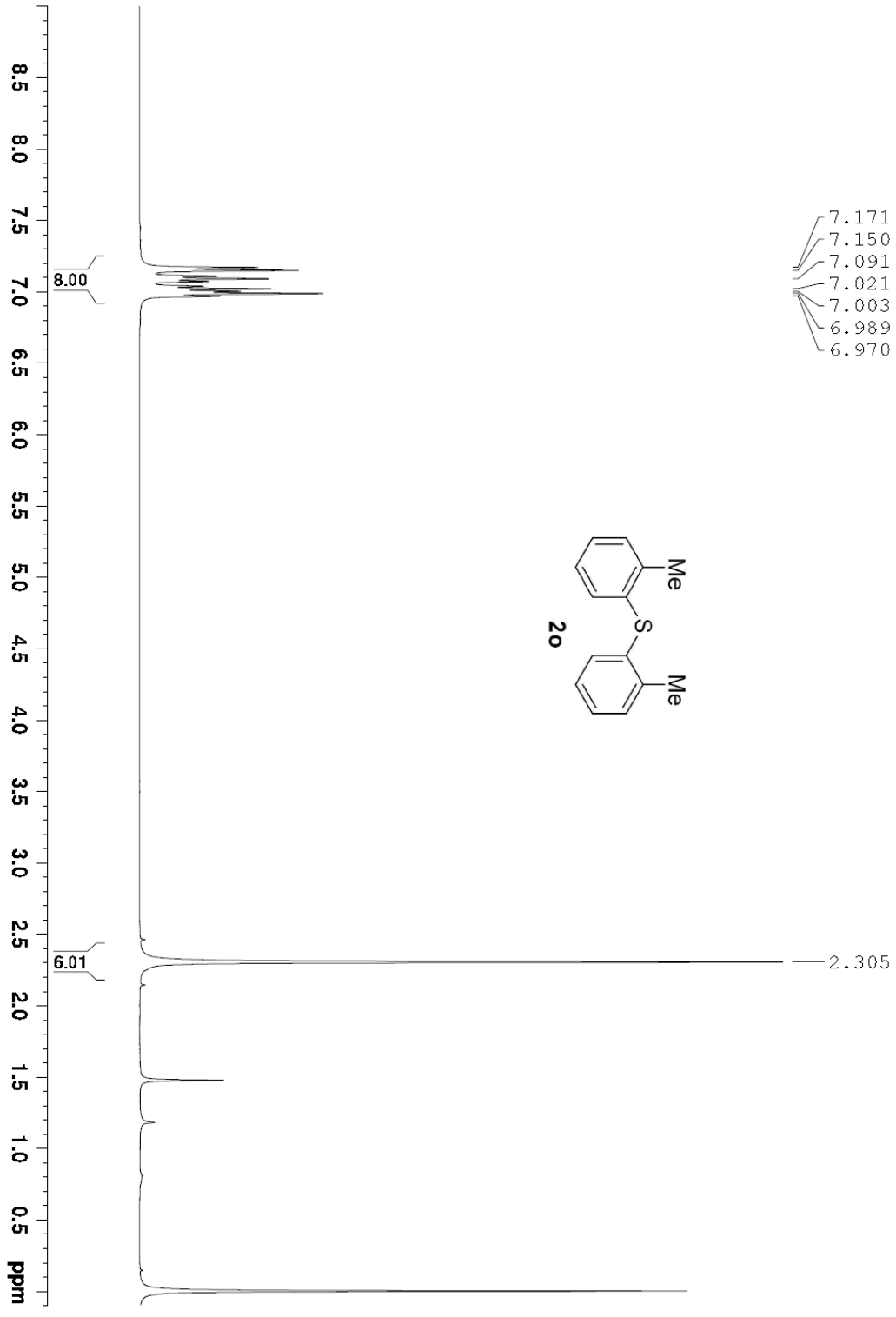

135.815
131.056
129.186
127.039
2l
S
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

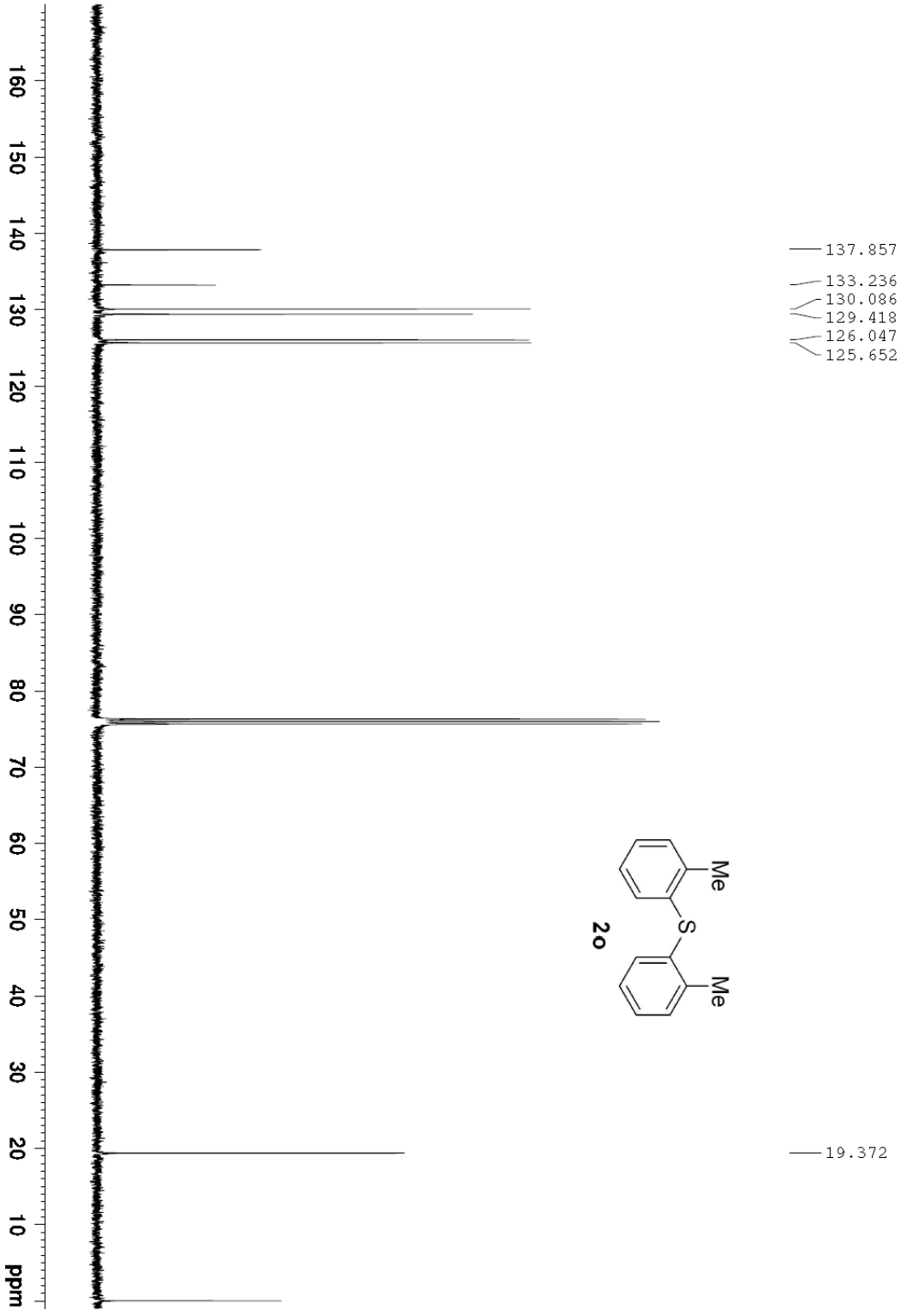

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.00
4.03
7.441
7.419
7.197
7.175
Br
S
Br
2m

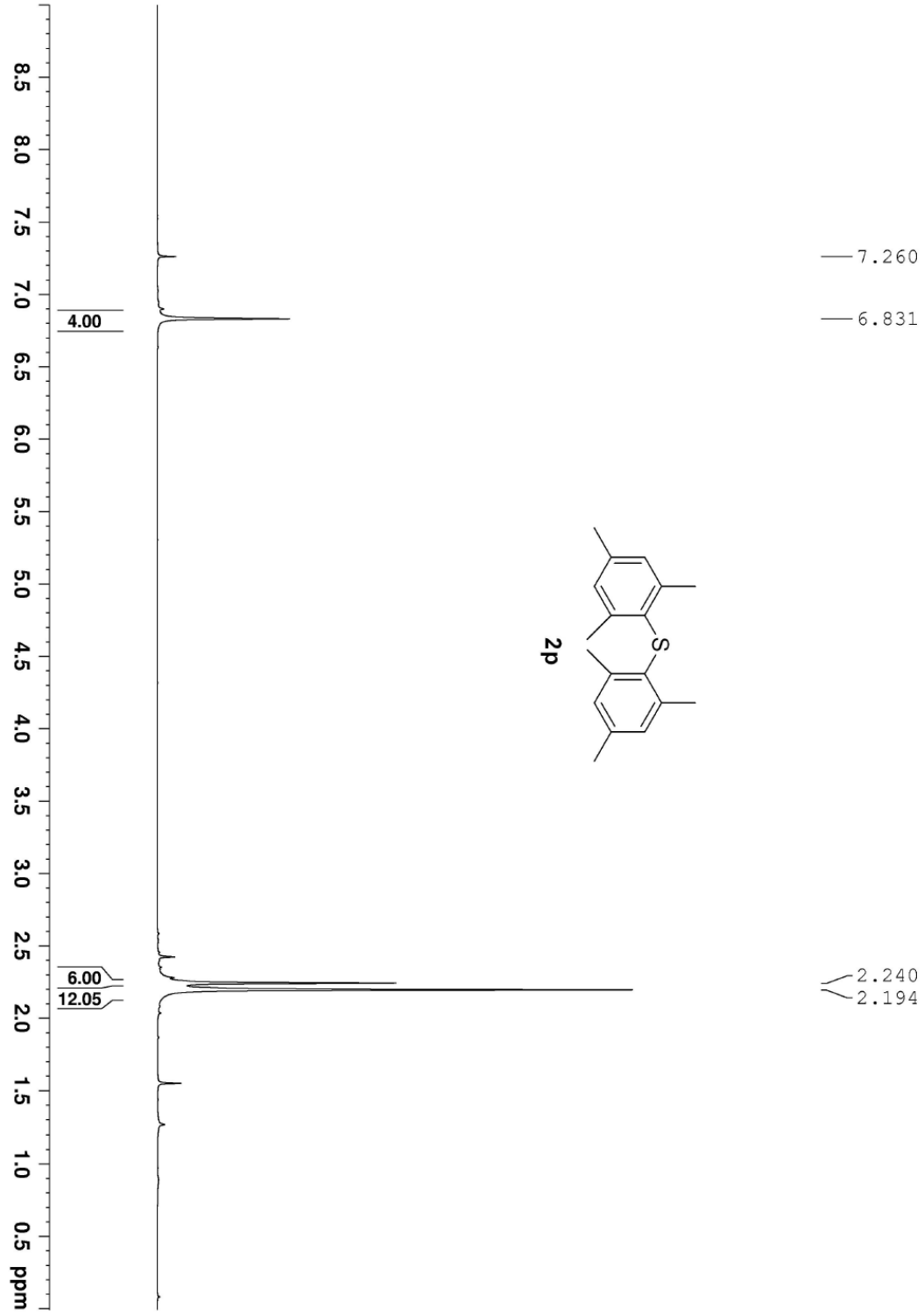

133.462
131.552
131.407
120.469
Br
S
Br
2m
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

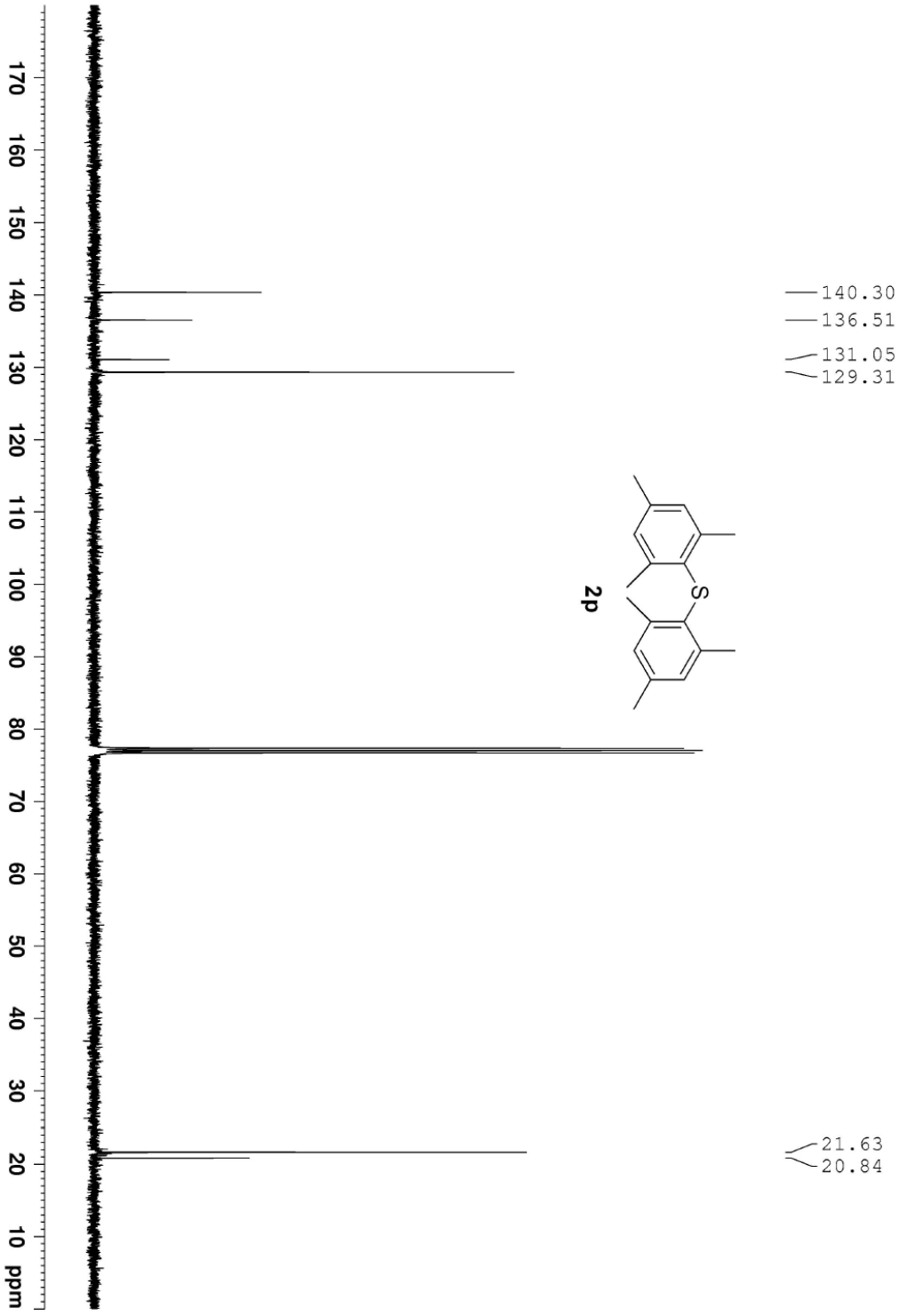

8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.00
4.00
6.01
7.159
7.139
7.027
7.007
2.241
Me
S
Me
2n

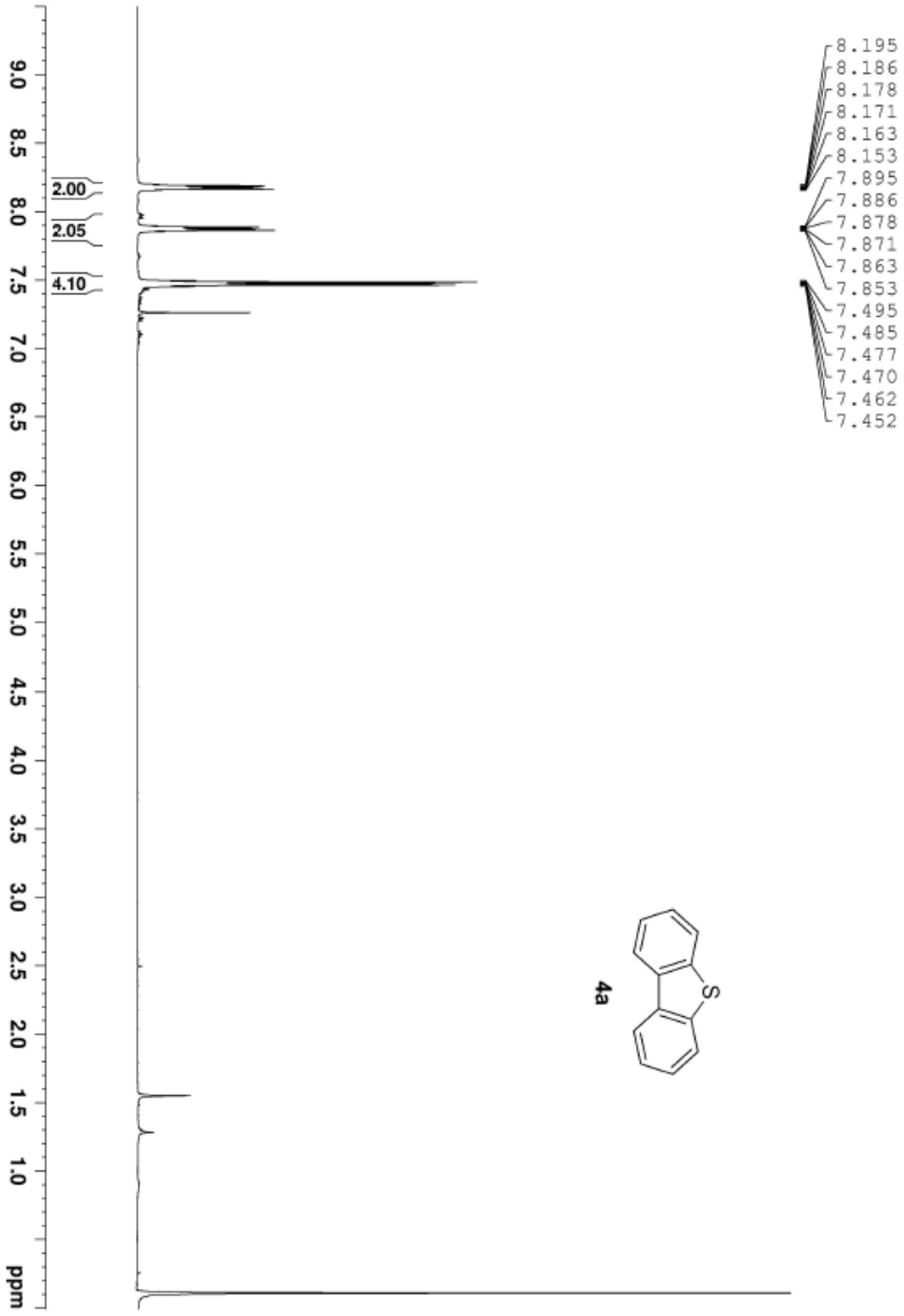

135.853
131.615
130.012
128.867
20.031
Me
S
Me
2n
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

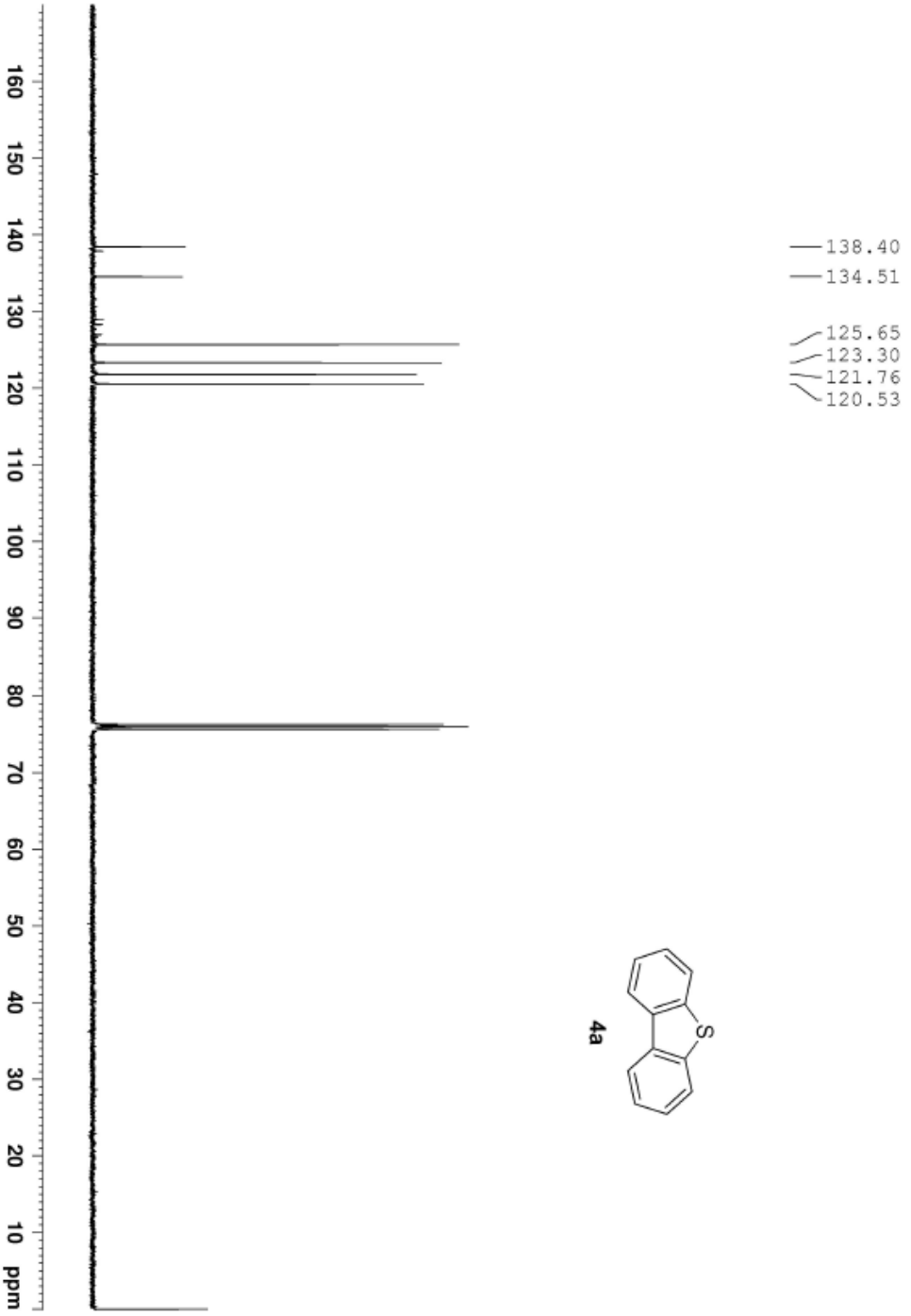

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
8.00
6.01
7.171
7.150
7.091
7.021
7.003
6.989
6.970
2.305
Me
S
Me
2o

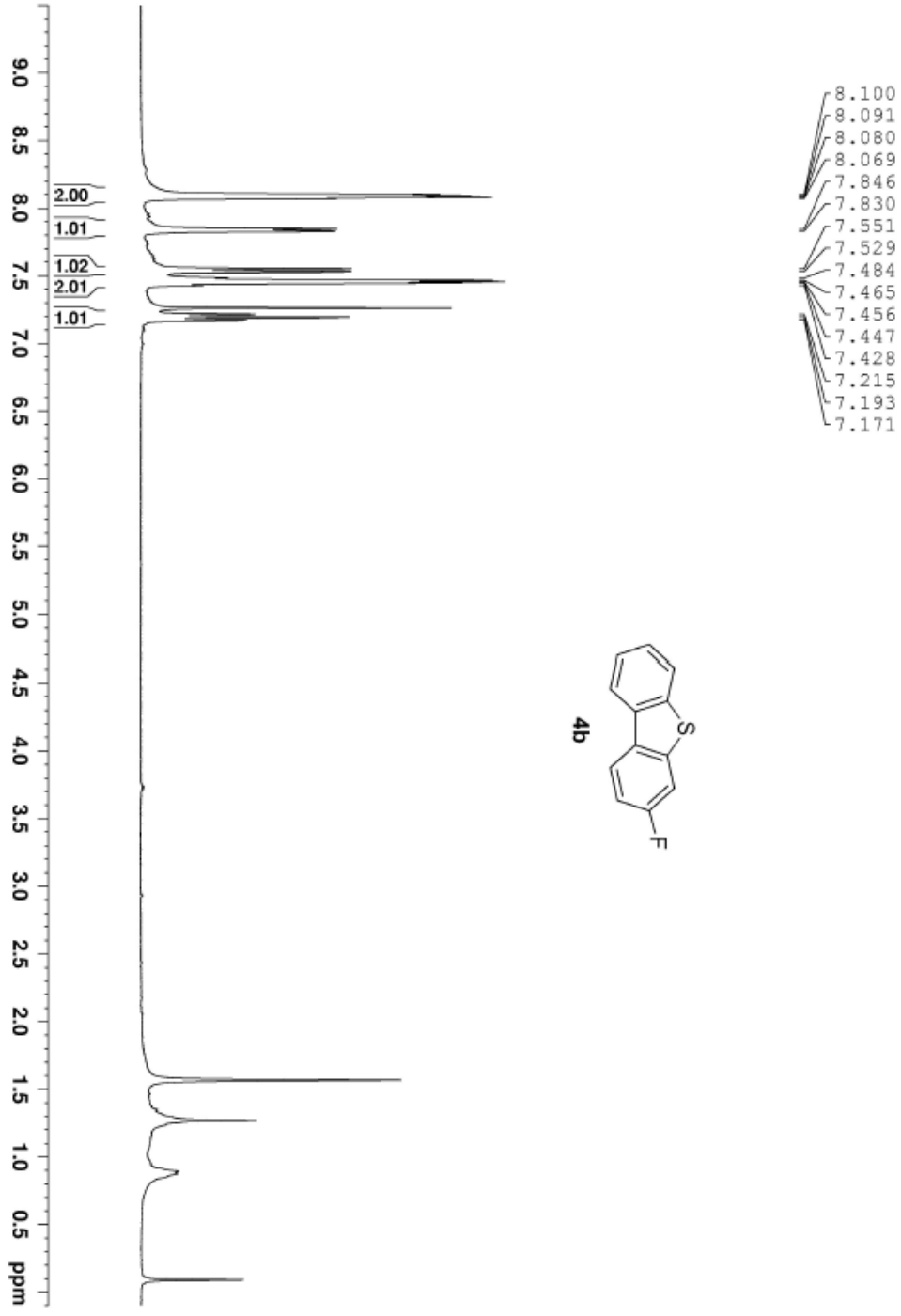

137.857
133.236
130.086
129.418
126.047
125.652
19.372
Me
S
Me
2o
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

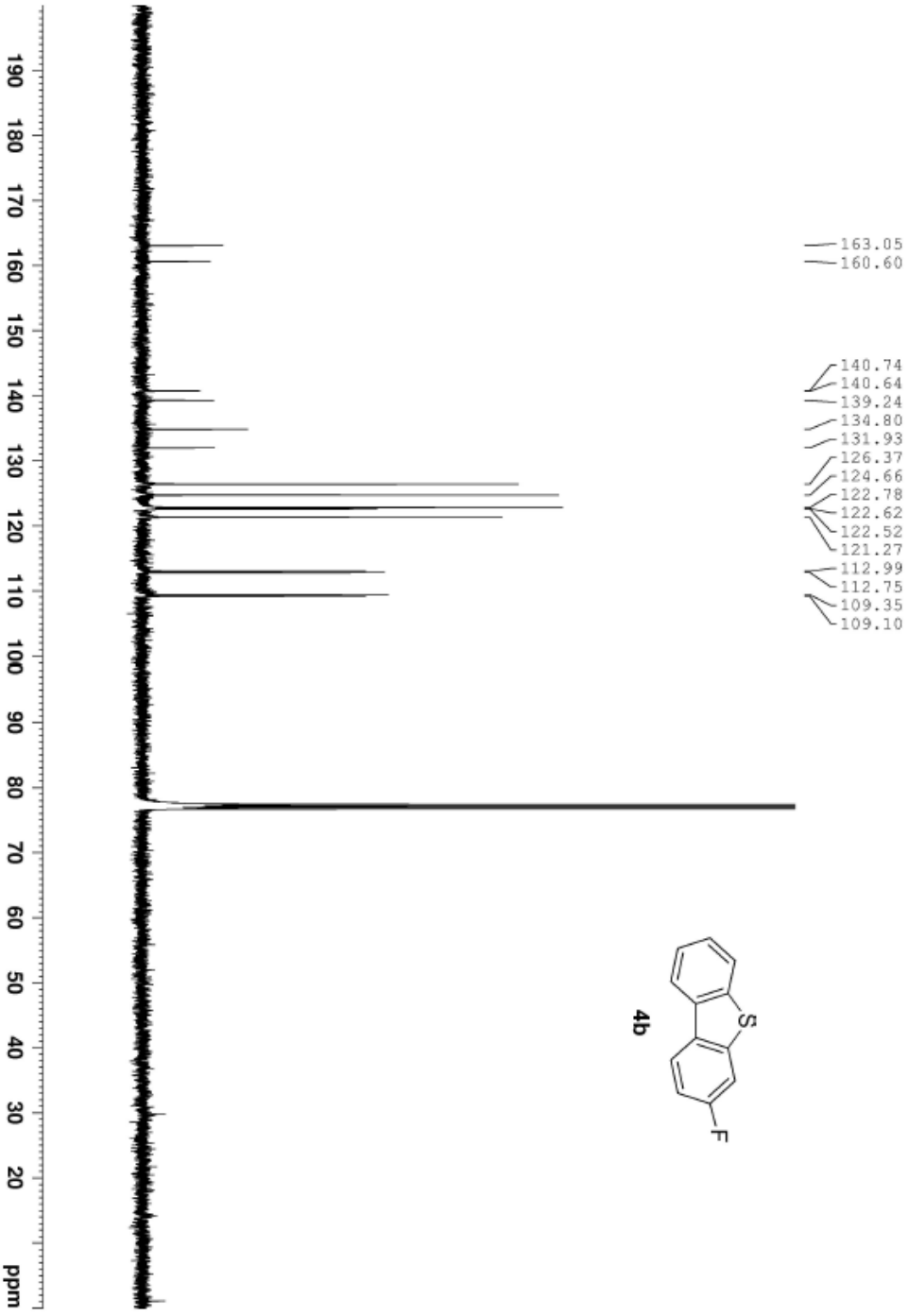

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.00
6.00
12.05
7.260
6.831
2.240
2.194
S
2p

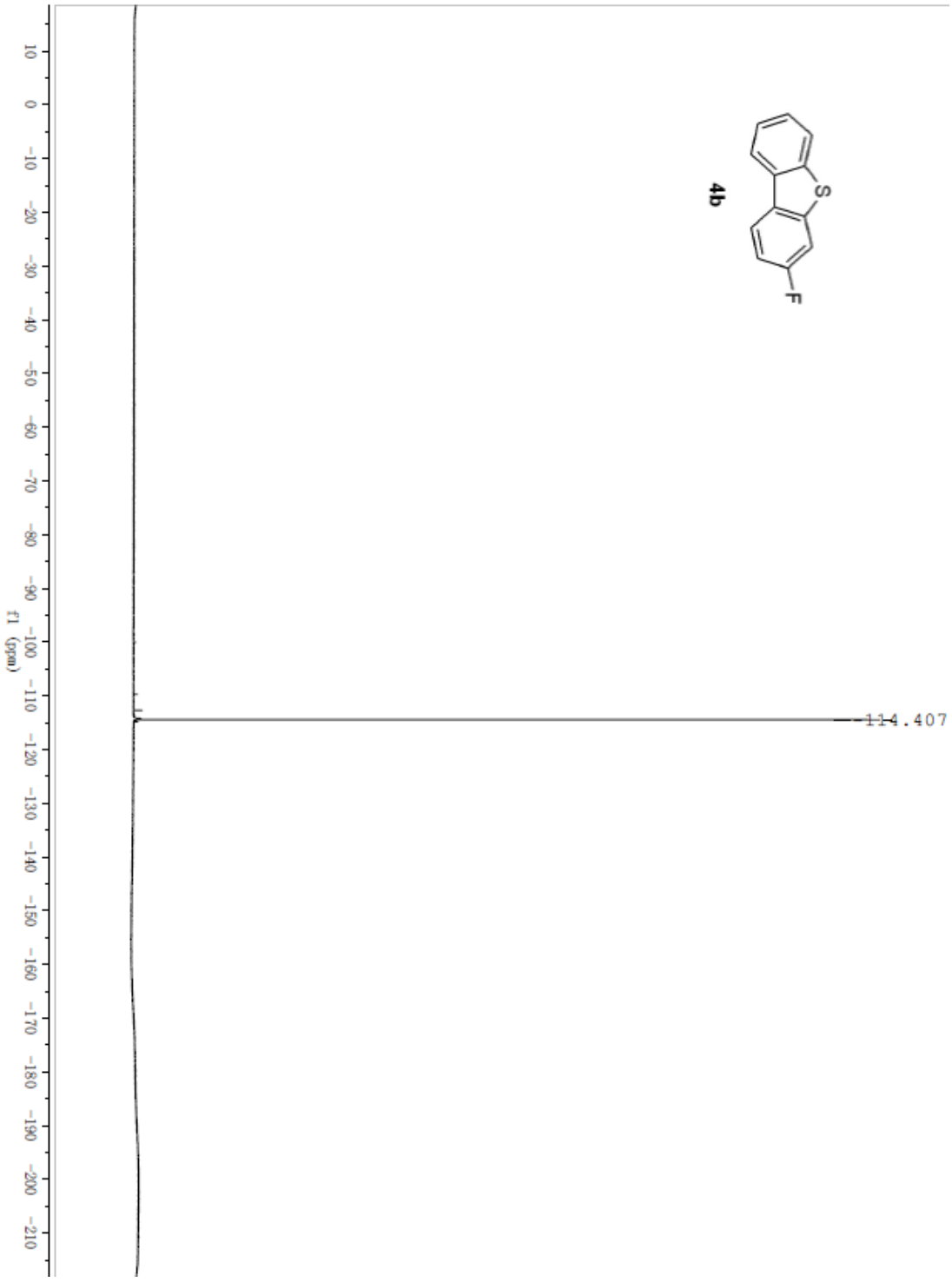

140.30
136.51
131.05
129.31
21.63
20.84
2p
S
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

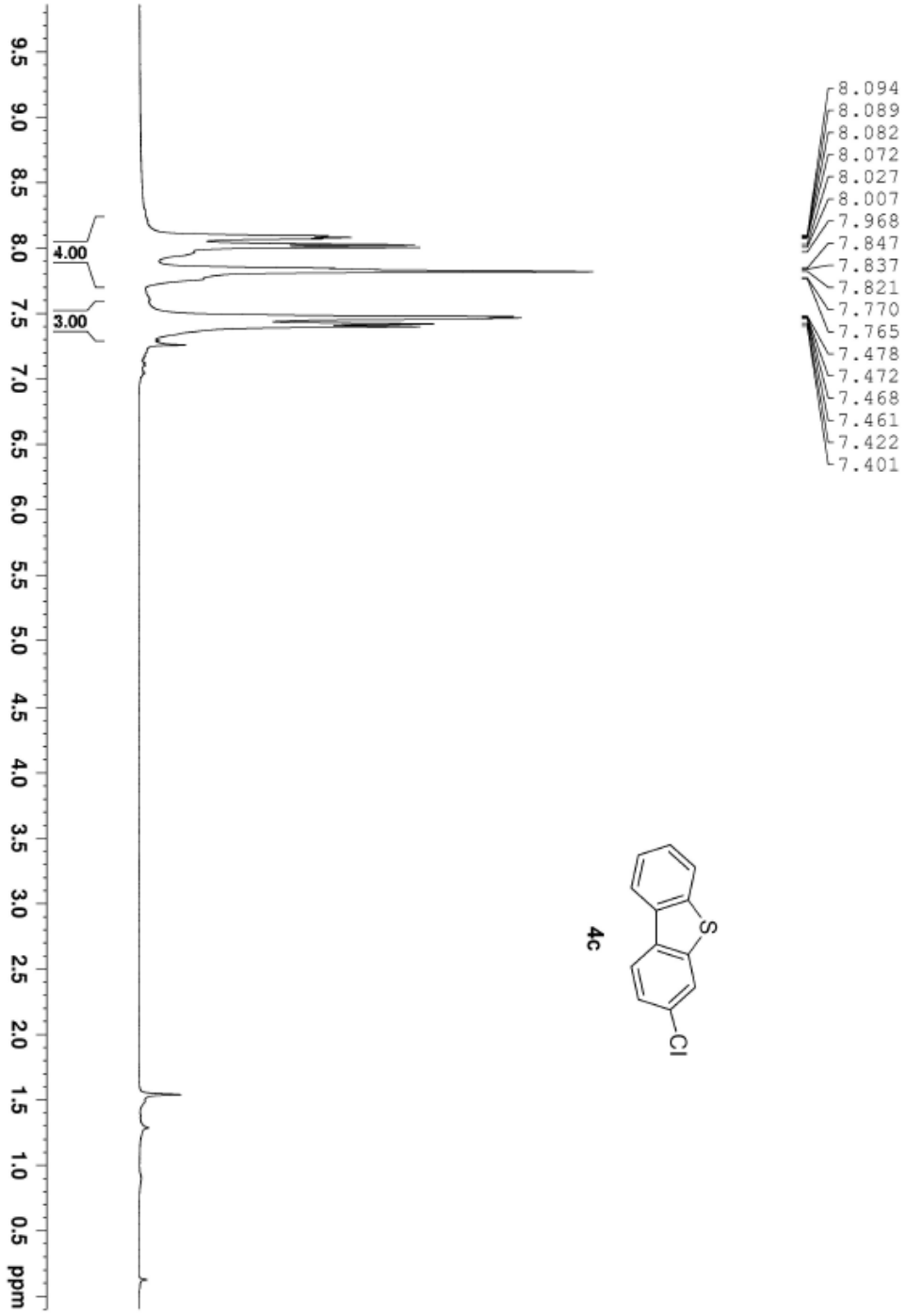

8.195
8.186
8.178
8.171
8.163
8.153
7.895
7.886
7.878
7.871
7.863
7.853
7.495
7.485
7.477
7.470
7.462
7.452
2.00
2.05
4.10
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
S
4a


160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
138.40
134.51
125.65
123.30
121.76
120.53
S
4a


8.100
8.091
8.080
8.069
7.846
7.830
7.551
7.529
7.484
7.465
7.456
7.447
7.428
7.215
7.193
7.171
2.00
1.01
1.02
2.01
1.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
S
F
4b


163.05
160.60
140.74
140.64
139.24
134.80
131.93
126.37
124.66
122.78
122.62
122.52
121.27
112.99
112.75
109.35
109.10
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm
S
F
4b


4b
S
F
-114.407
f1 (ppm)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210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8.007
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7.847
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7.821
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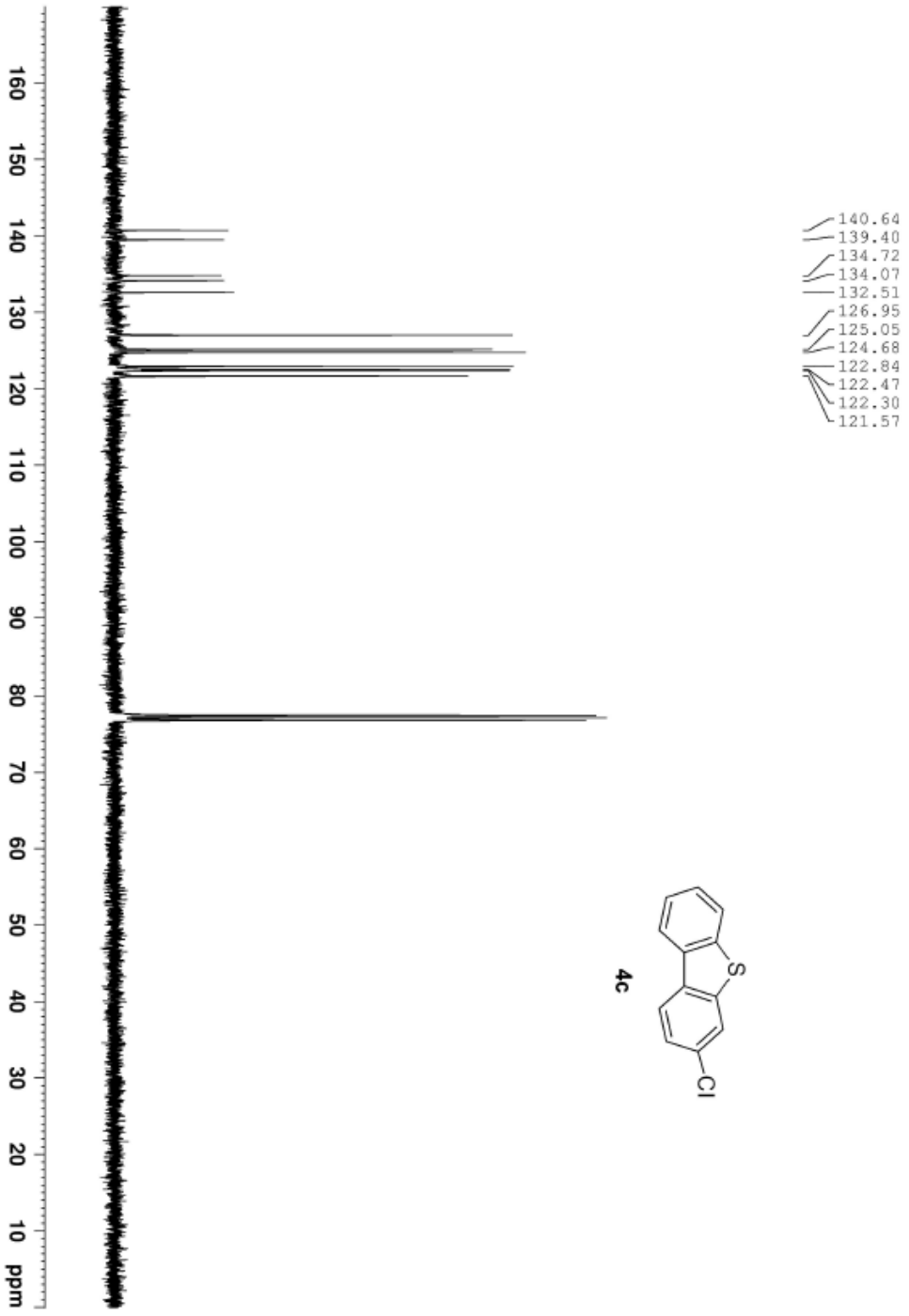
7.765
7.478
7.472
7.468
7.461
7.422
7.401
4.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
S
Cl

4c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10
ppm
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126.95
125.05
124.68
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122.47
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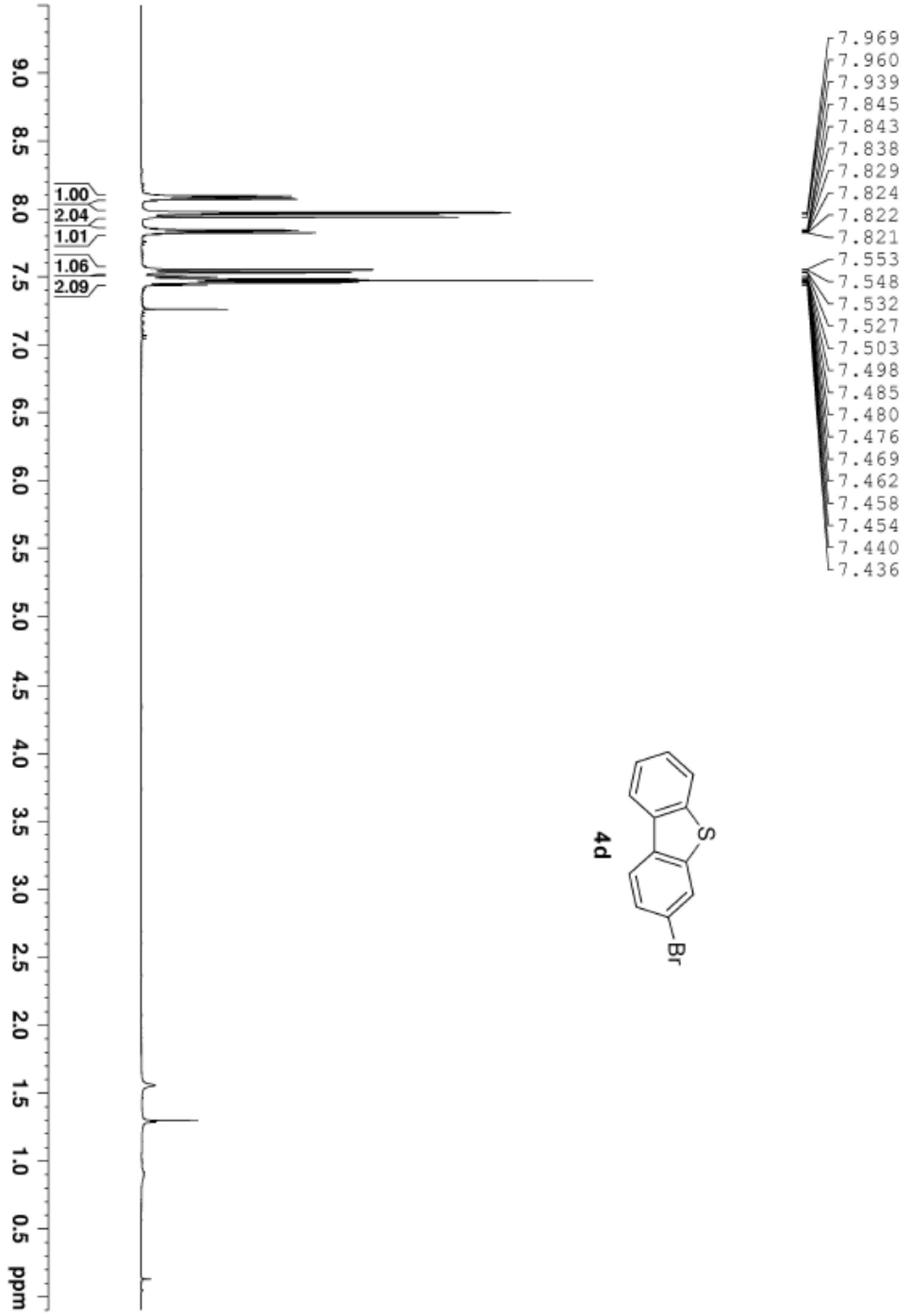
S
Cl
4c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7.822
7.821
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7.548
7.532
7.527
7.503
7.498
7.485
7.480
7.476
7.469
7.462
7.458
7.454
7.440
7.436
1.00
2.04
1.01
1.06
2.09
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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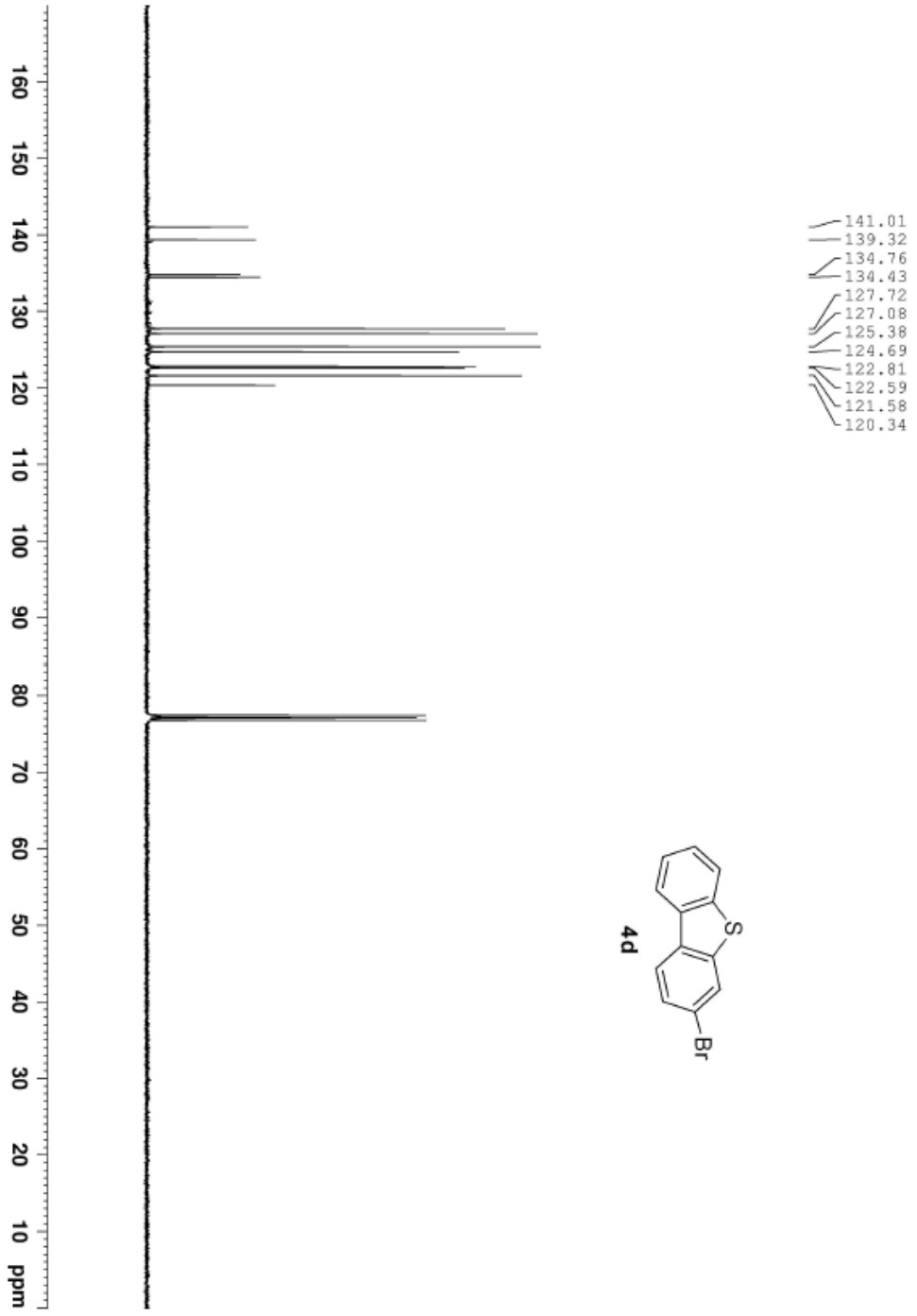
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
S
Br
4d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124.69
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122.59
121.58
120.34
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120
110
100
90
80
70
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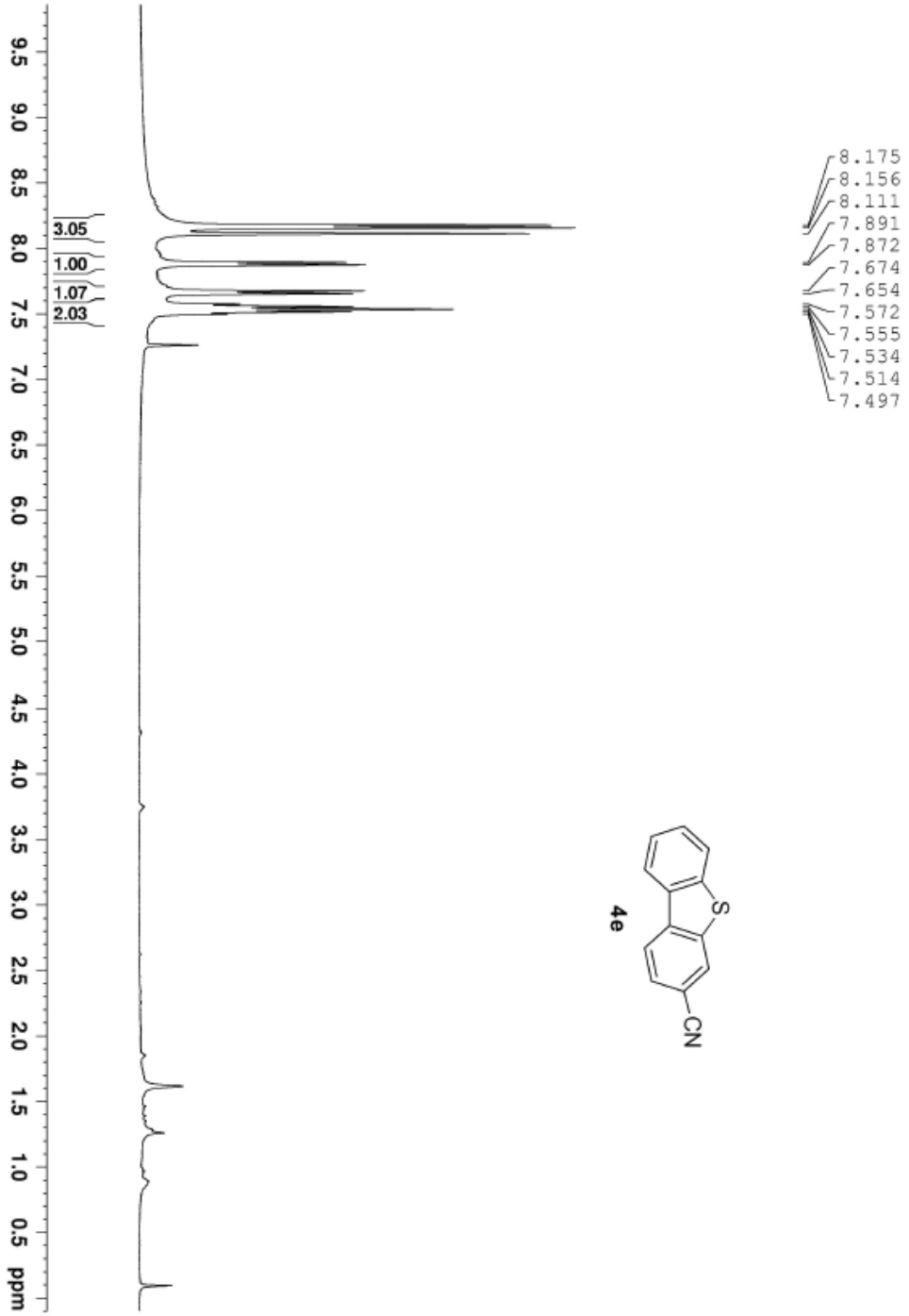
50
40
30
20
10
ppm
S
Br
4d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8.111
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7.674
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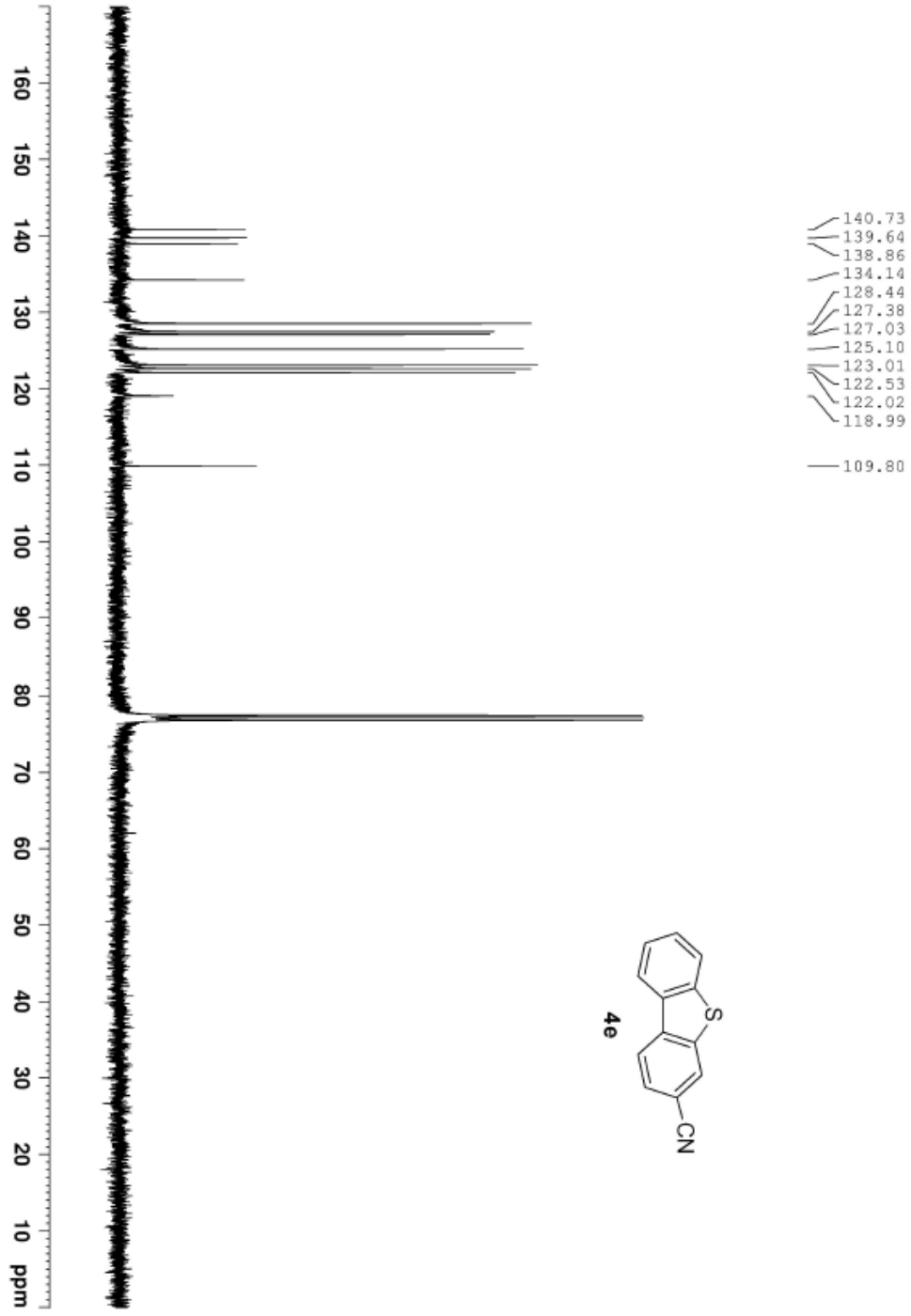
7.572
7.555
7.534
7.514
7.497
3.05
1.00
1.07
2.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
S
CN
4e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10
ppm
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127.03
125.10
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122.02
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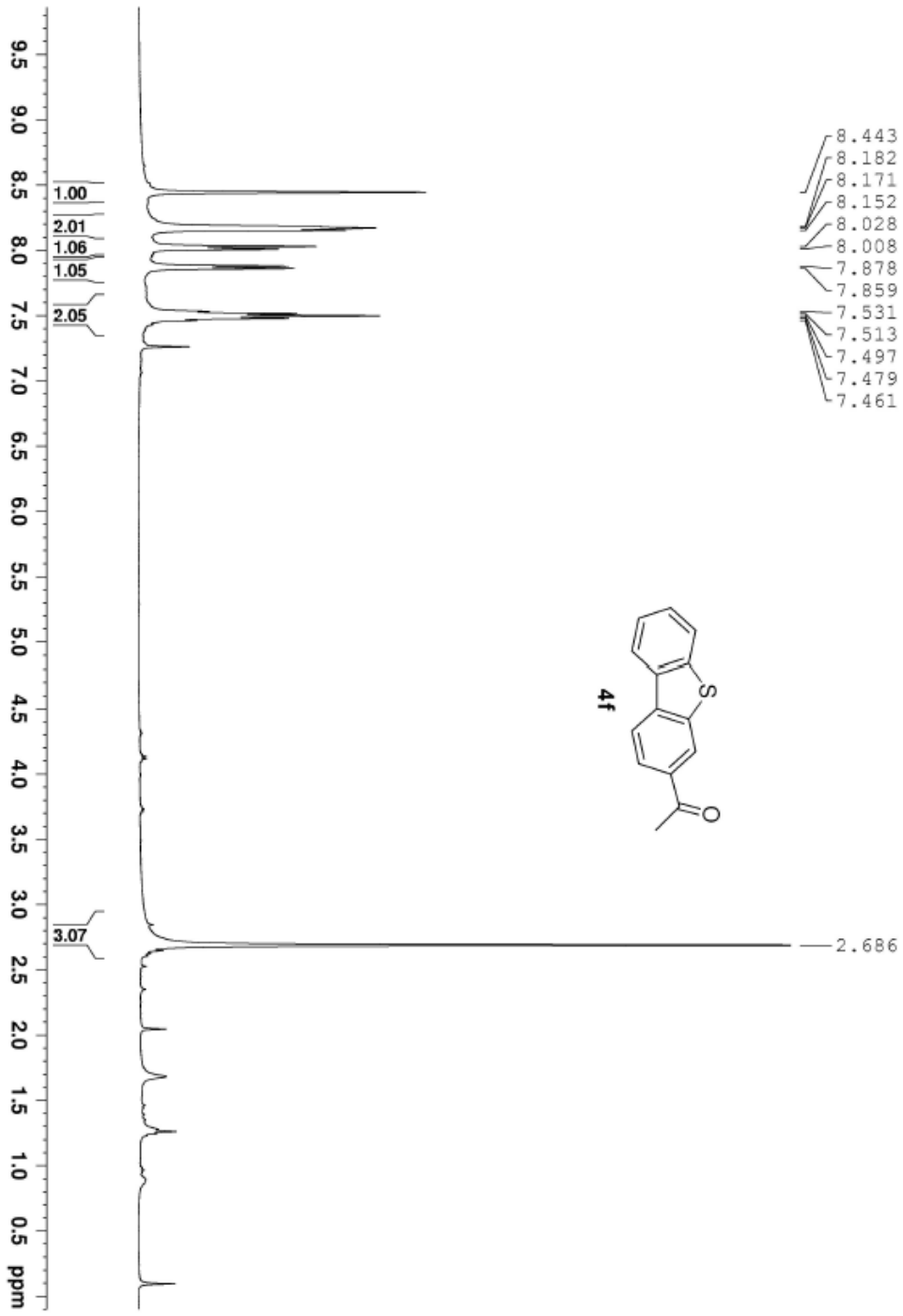
109.80
S
CN
4e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5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
2.01
1.06
1.05
2.05
3.07
8.443
8.182
8.171
8.152
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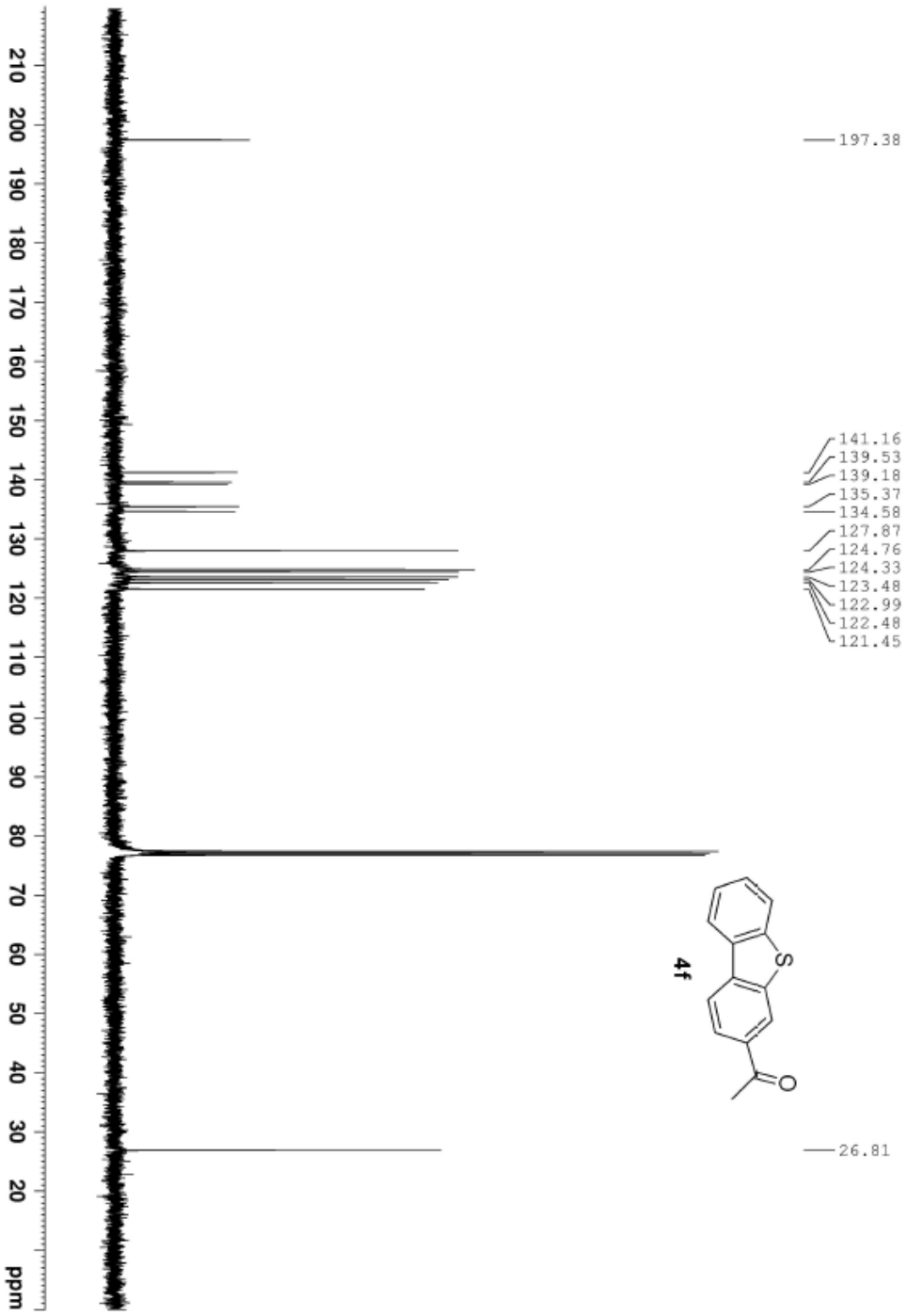
7.859
7.531
7.513
7.497
7.479
7.461
2.686
S
O
4f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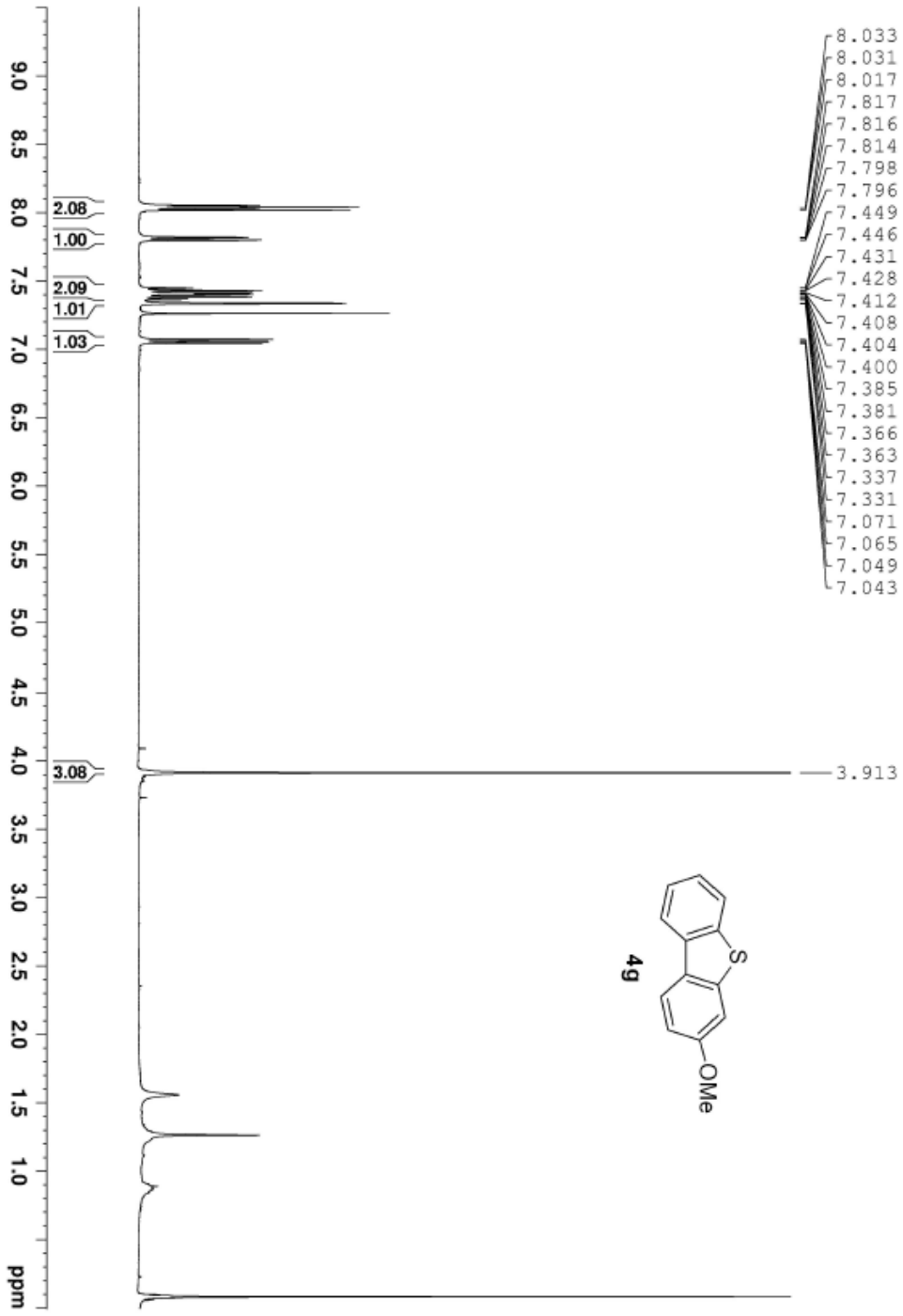
139.53
139.18
135.37
134.58
127.87
124.76
124.33
123.48
122.99
122.48
121.45
26.81
4f
S
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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7.814
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7.796
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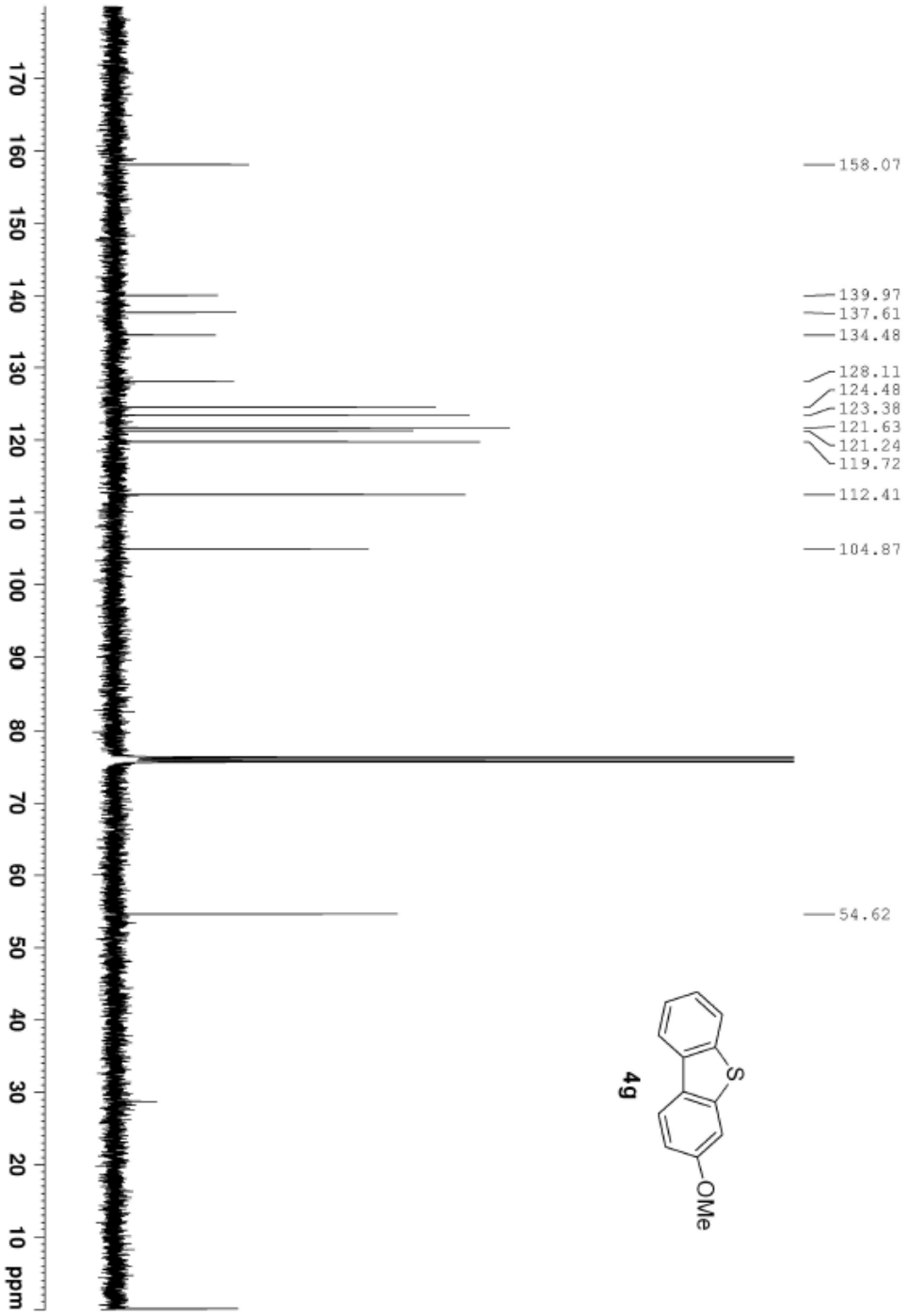
7.446
7.431
7.428
7.412
7.408
7.404
7.400
7.385
7.381
7.366
7.363
7.337
7.331
7.071
7.065
7.049
7.043
3.913
2.08
1.00
2.09
1.01
1.03
3.08
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
S
OMe
4g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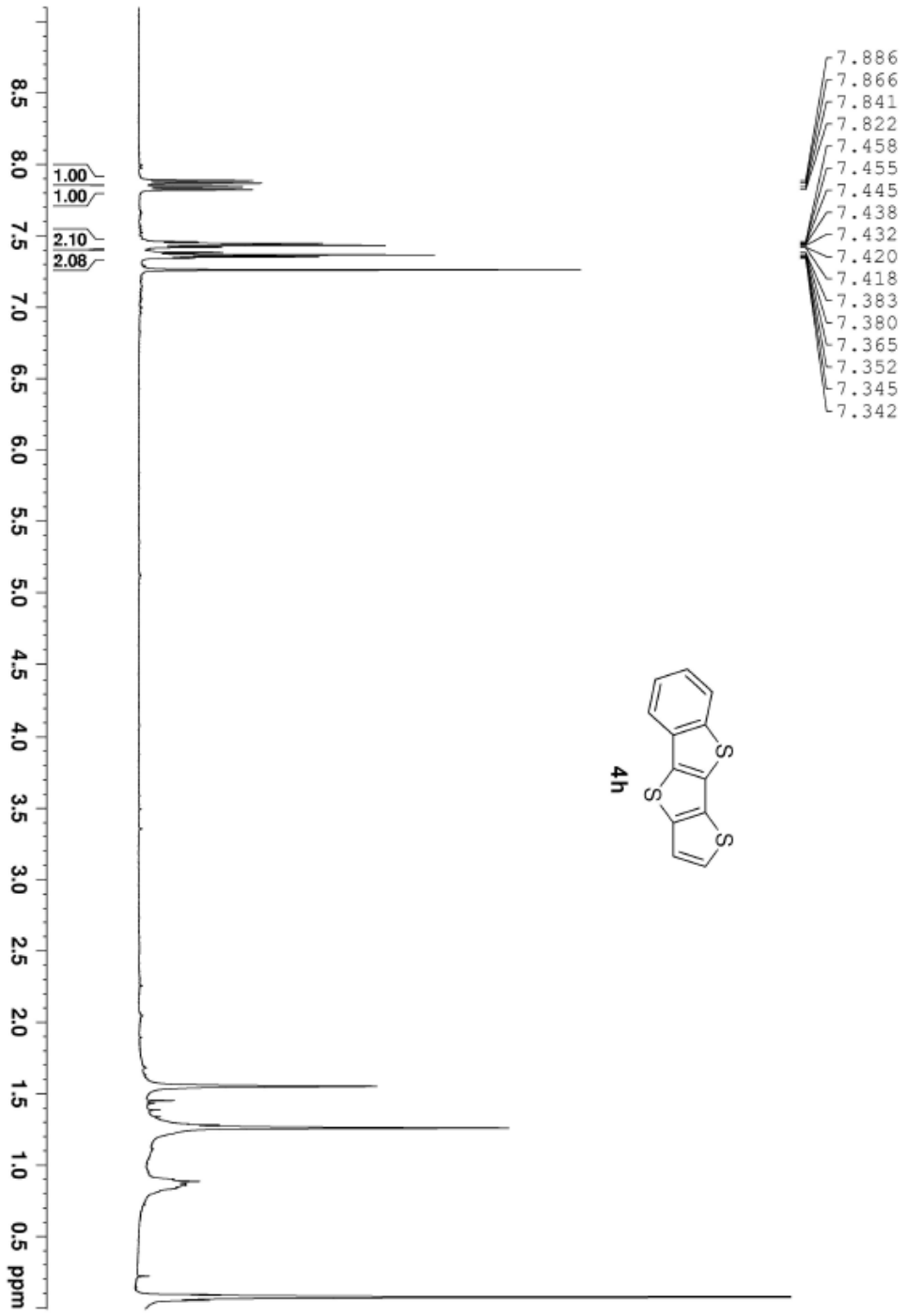
139.97
137.61
134.48
128.11
124.48
123.38
121.63
121.24
119.72
112.41
104.87
54.62
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
S
OMe
4g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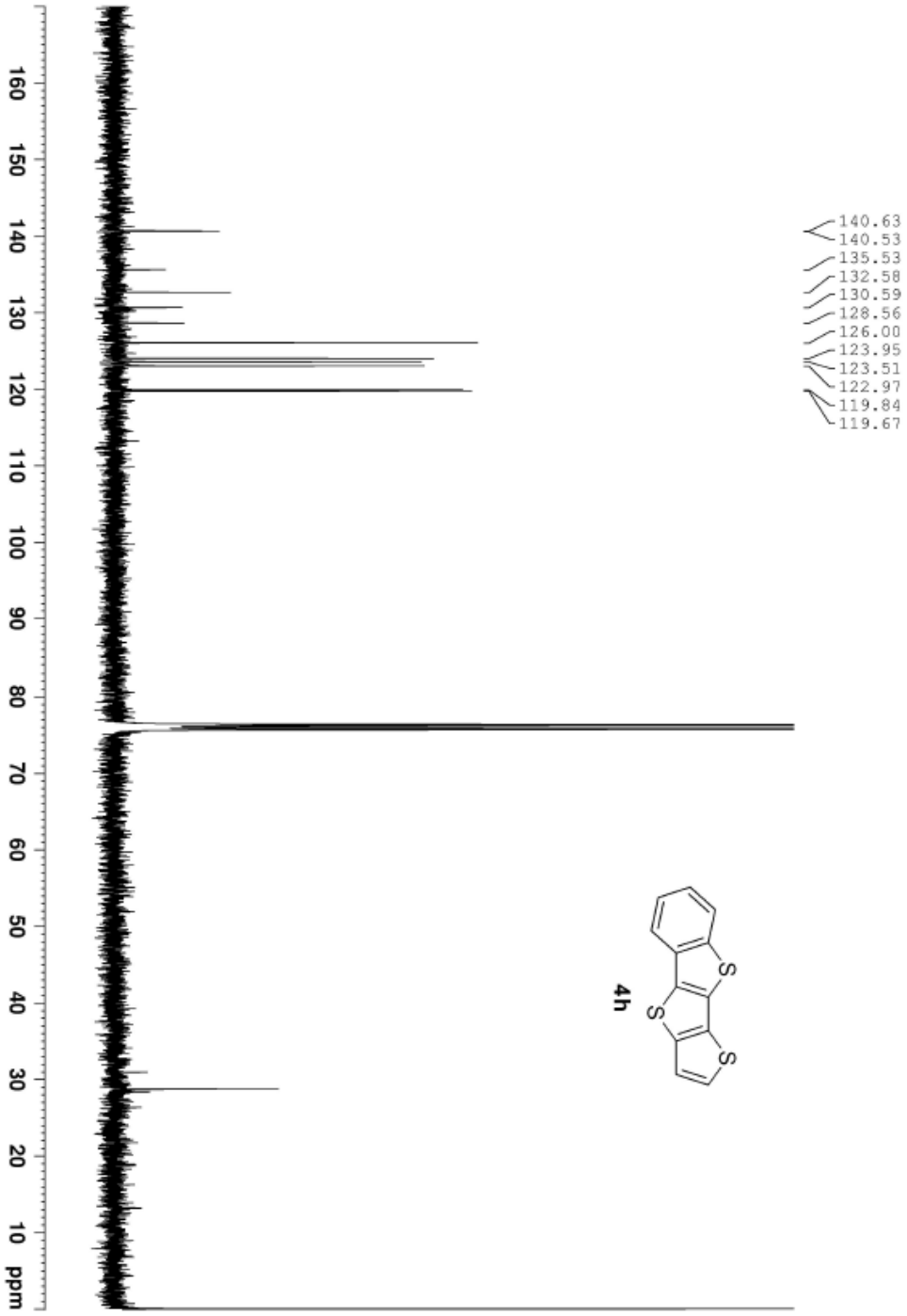
7.438
7.432
7.420
7.418
7.383
7.380
7.365
7.352
7.345
7.342
1.00
1.00
2.10
2.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
S
S
S
4h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150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
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140.53
135.53
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130.59
128.56
126.00
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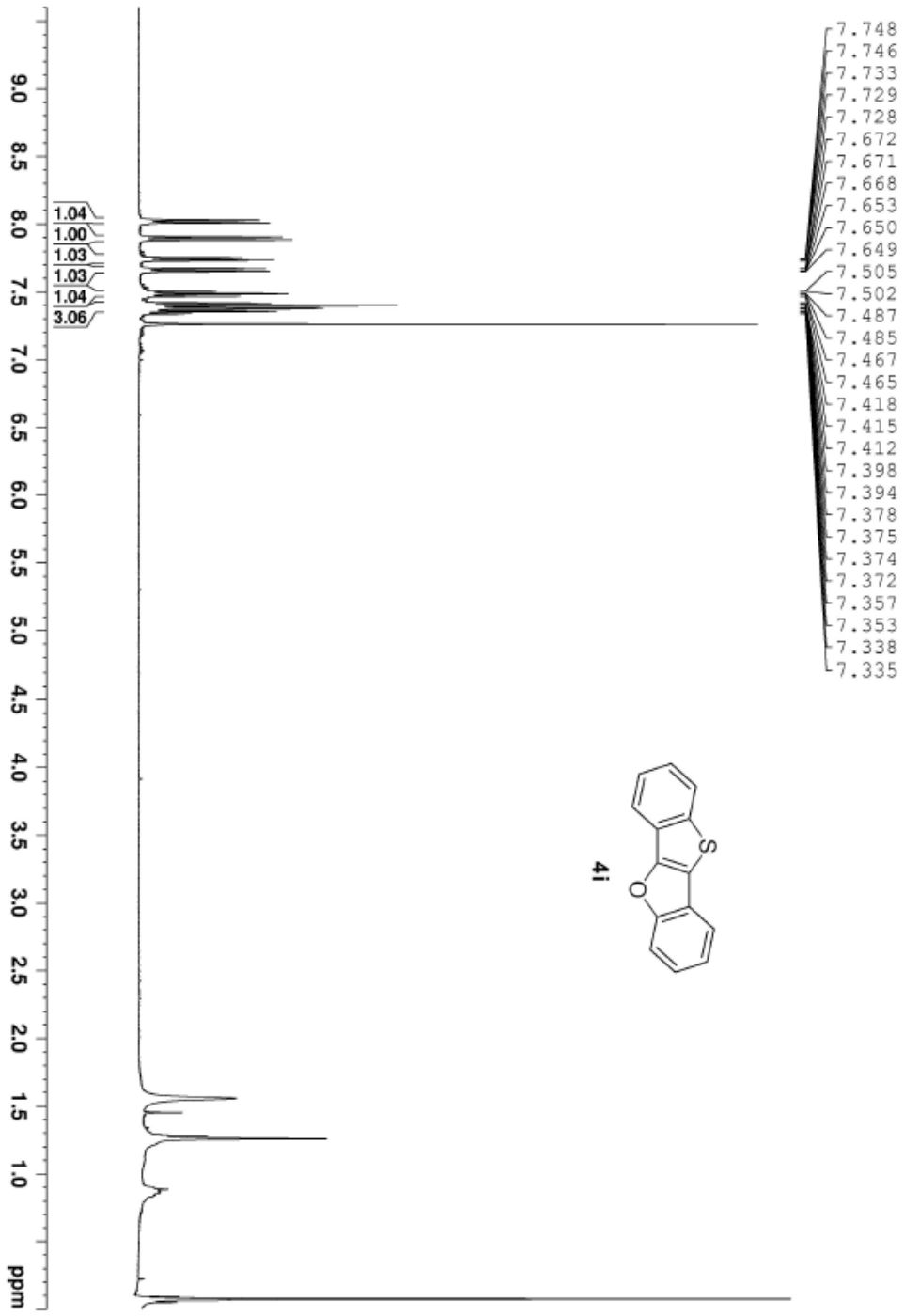
123.51
122.97
119.84
119.67
S
S
S
4h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7.728
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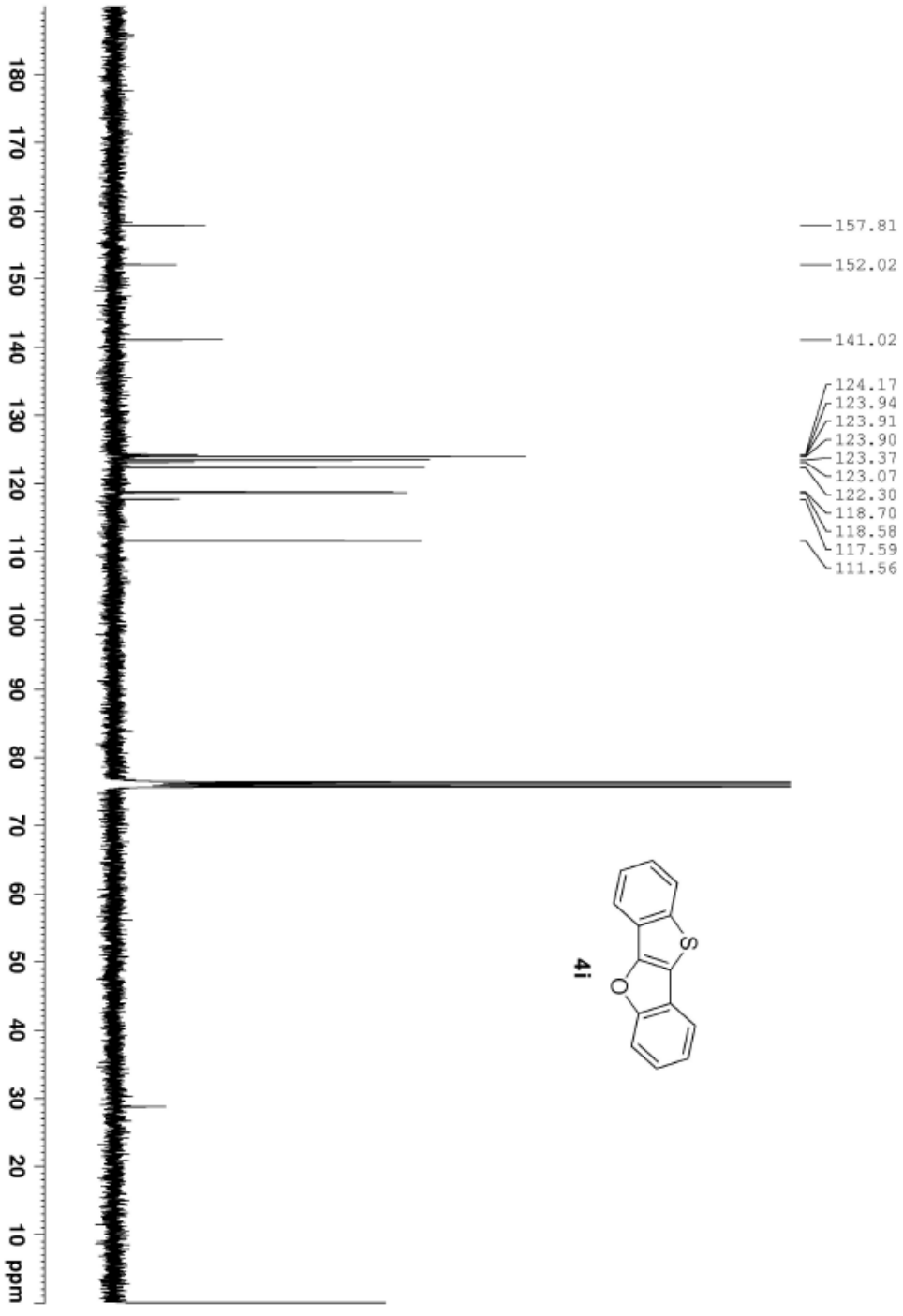
7.671
7.668
7.653
7.650
7.649
7.505
7.502
7.487
7.485
7.467
7.465
7.418
7.415
7.412
7.398
7.394
7.378
7.375
7.374
7.372
7.357
7.353
7.338
7.335
1.04
1.00
1.03
1.03
1.04
3.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
S
O
4i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123.94
123.91
123.90
123.37
123.07
122.30
118.70
118.58
117.59
111.56
S
O
4i
180
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150
140
130
120
110
100
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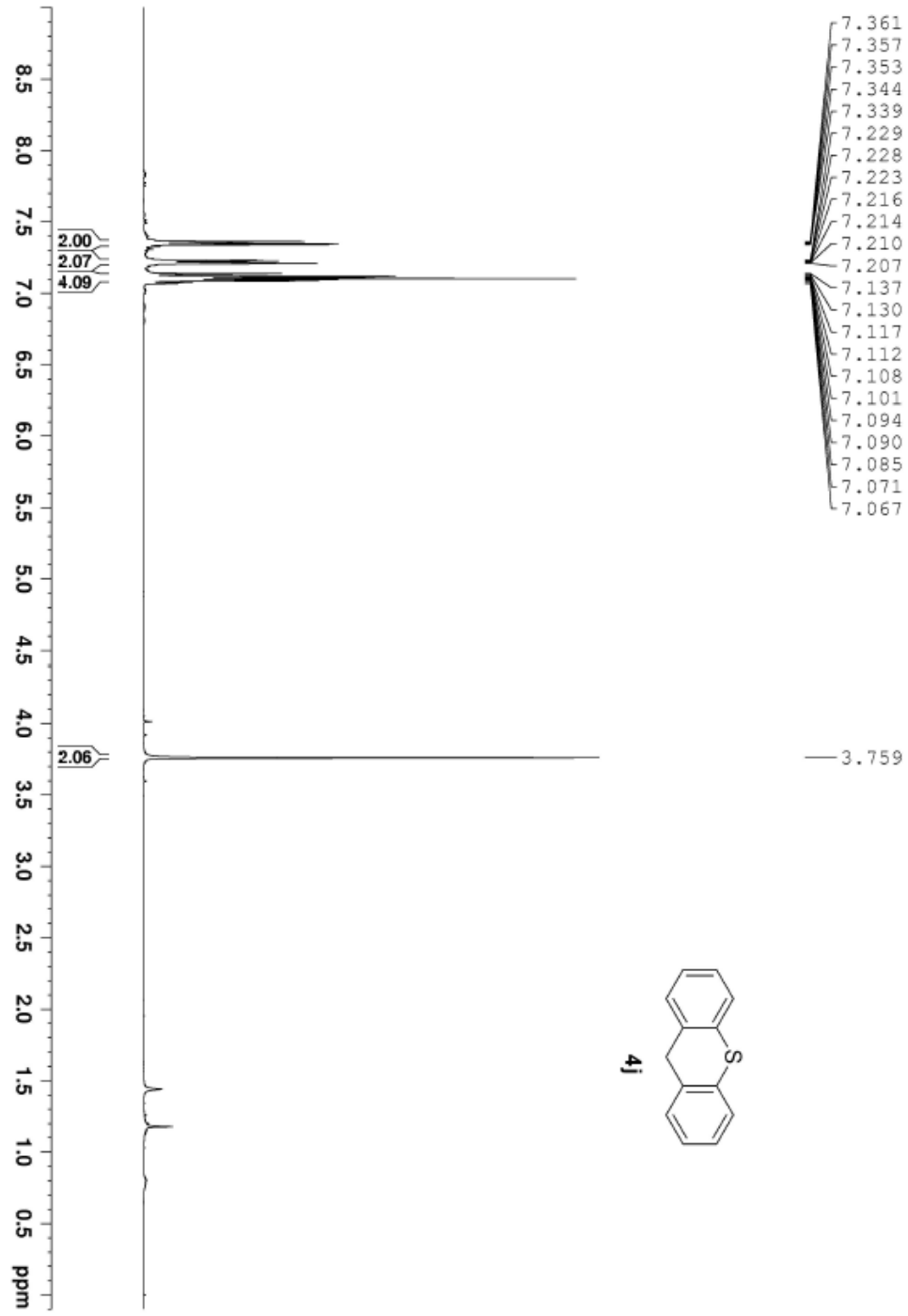
80
70
60
50
40
30
20
10
ppm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7.339
7.229
7.228
7.223
7.216
7.214
7.210
7.207
7.137
7.130
7.117
7.112
7.108
7.101
7.094
7.090
7.085
7.071
7.067
3.759
2.00
2.07
4.09
2.06
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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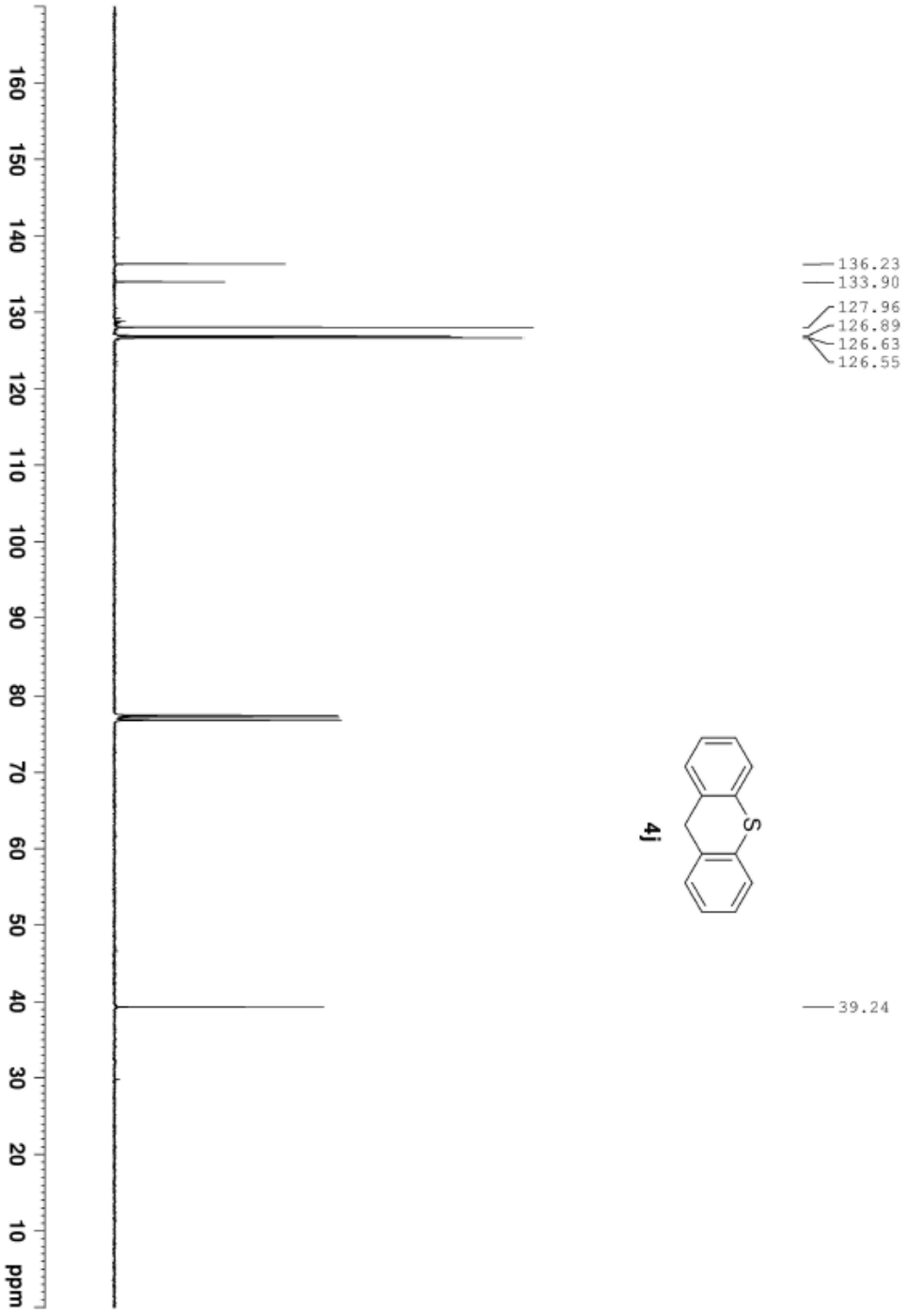
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
S
4j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133.90
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126.89
126.63
126.55
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S
4j
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150
140
130
120
110
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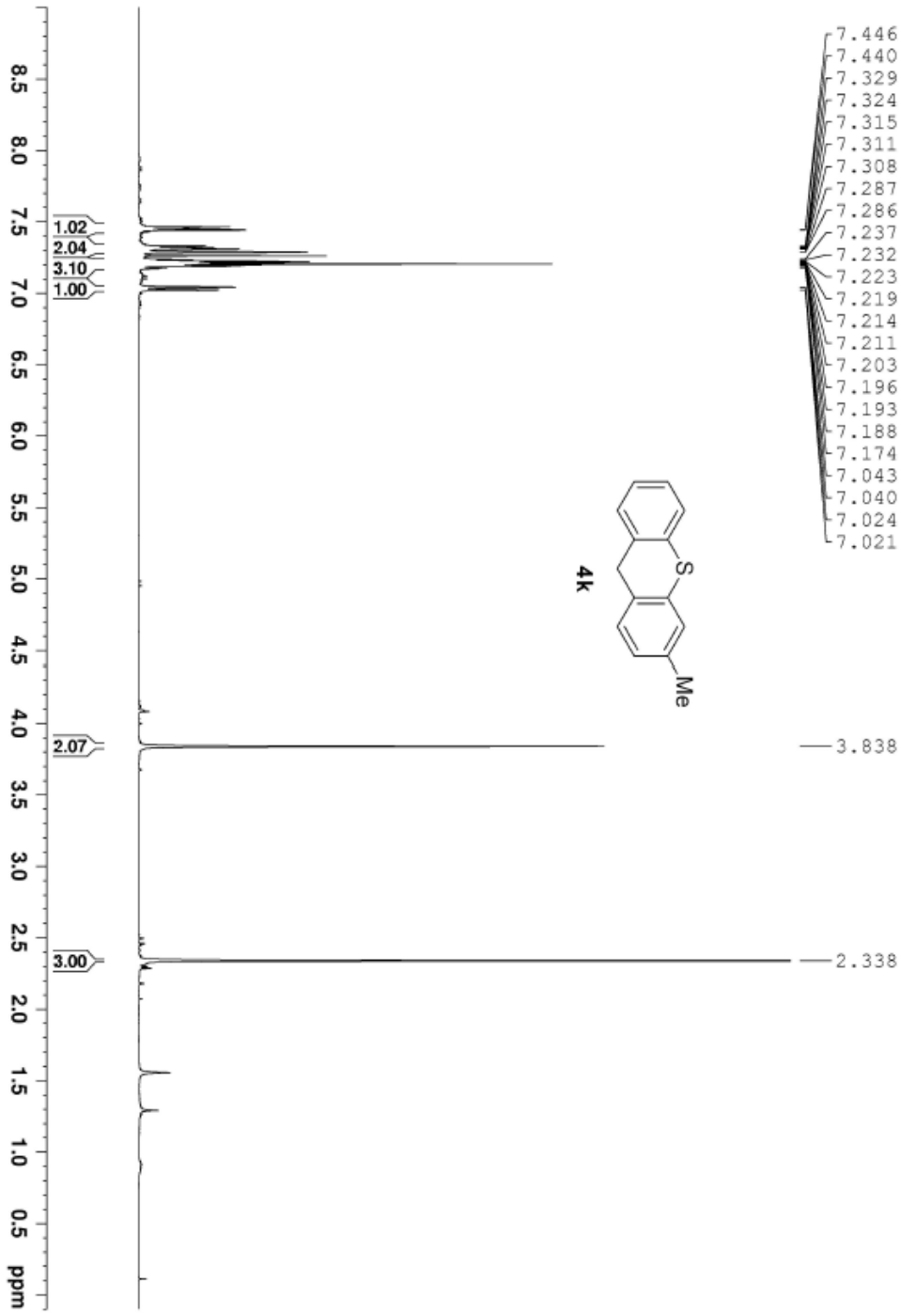
90
80
70
60
50
40
30
20
10
ppm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7.237
7.232
7.223
7.219
7.214
7.211
7.203
7.196
7.193
7.188
7.174
7.043
7.040
7.024
7.021
4k
S
Me
1.02
2.04
3.10
1.00
2.07
3.00
3.838
2.338
8.5
8.0
7.5
7.0
6.5
6.0
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4.5
4.0
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2.0
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1.0
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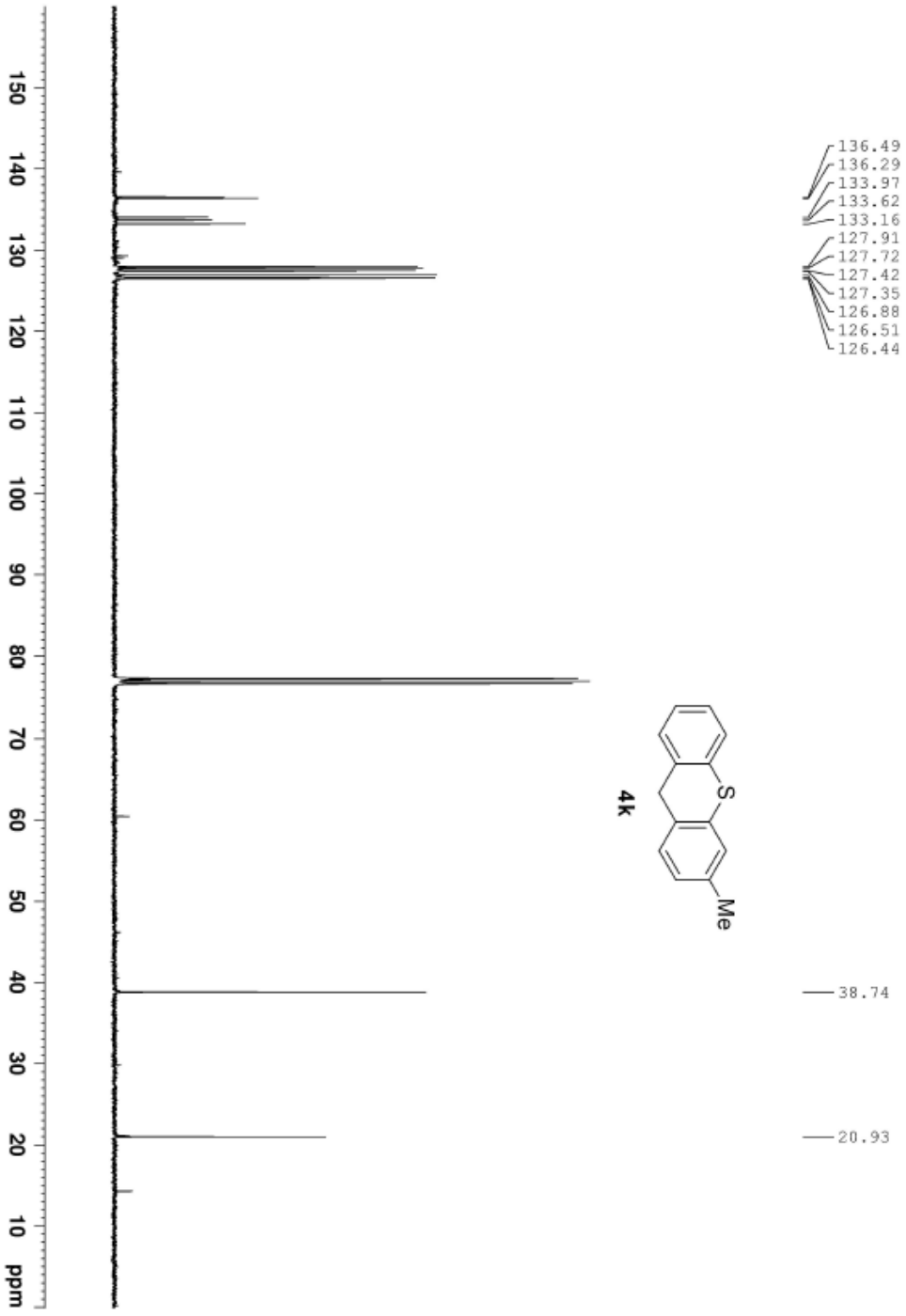
ppm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127.42
127.35
126.88
126.51
126.44
S
Me
4k
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70
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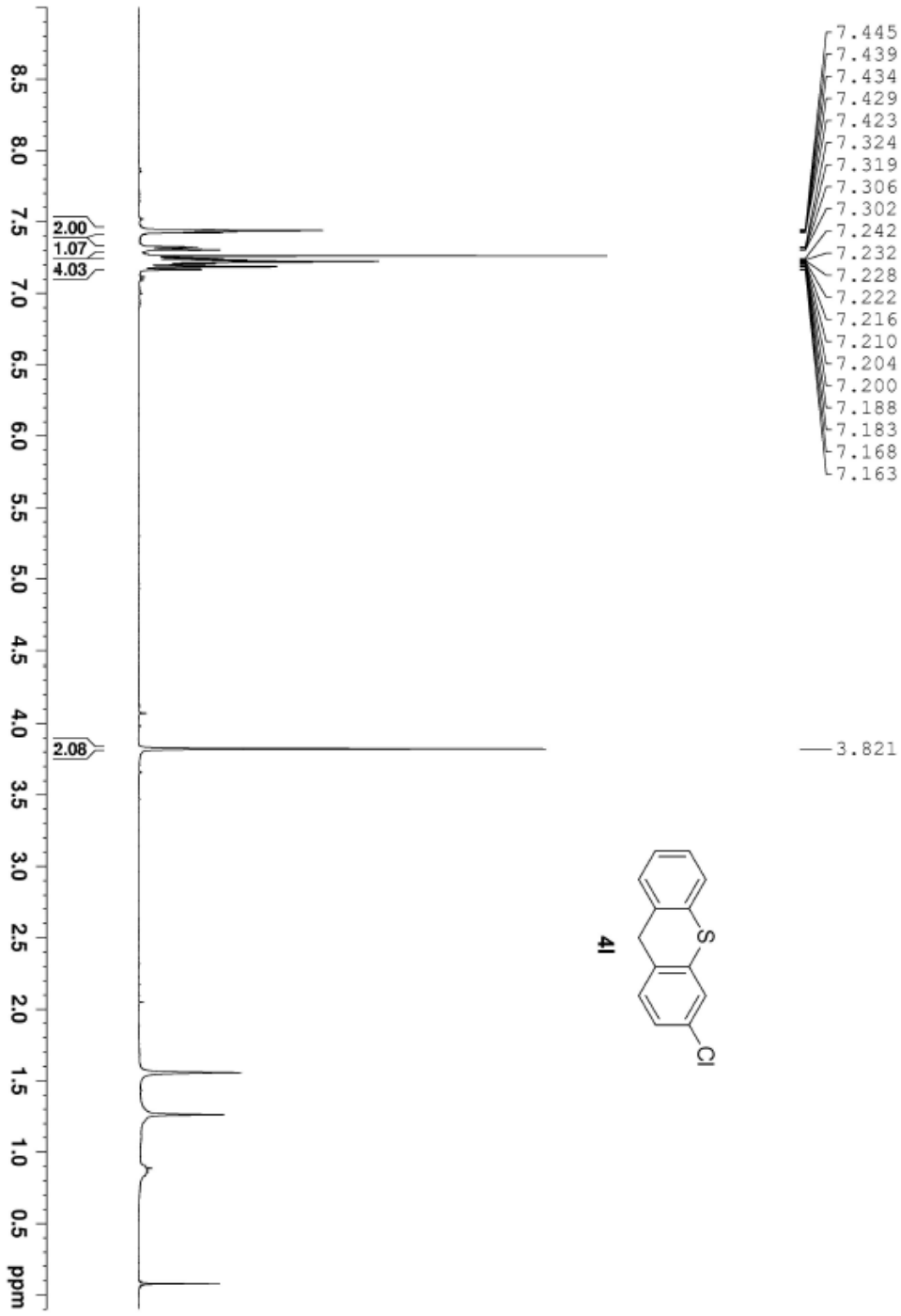
30
20
10
ppm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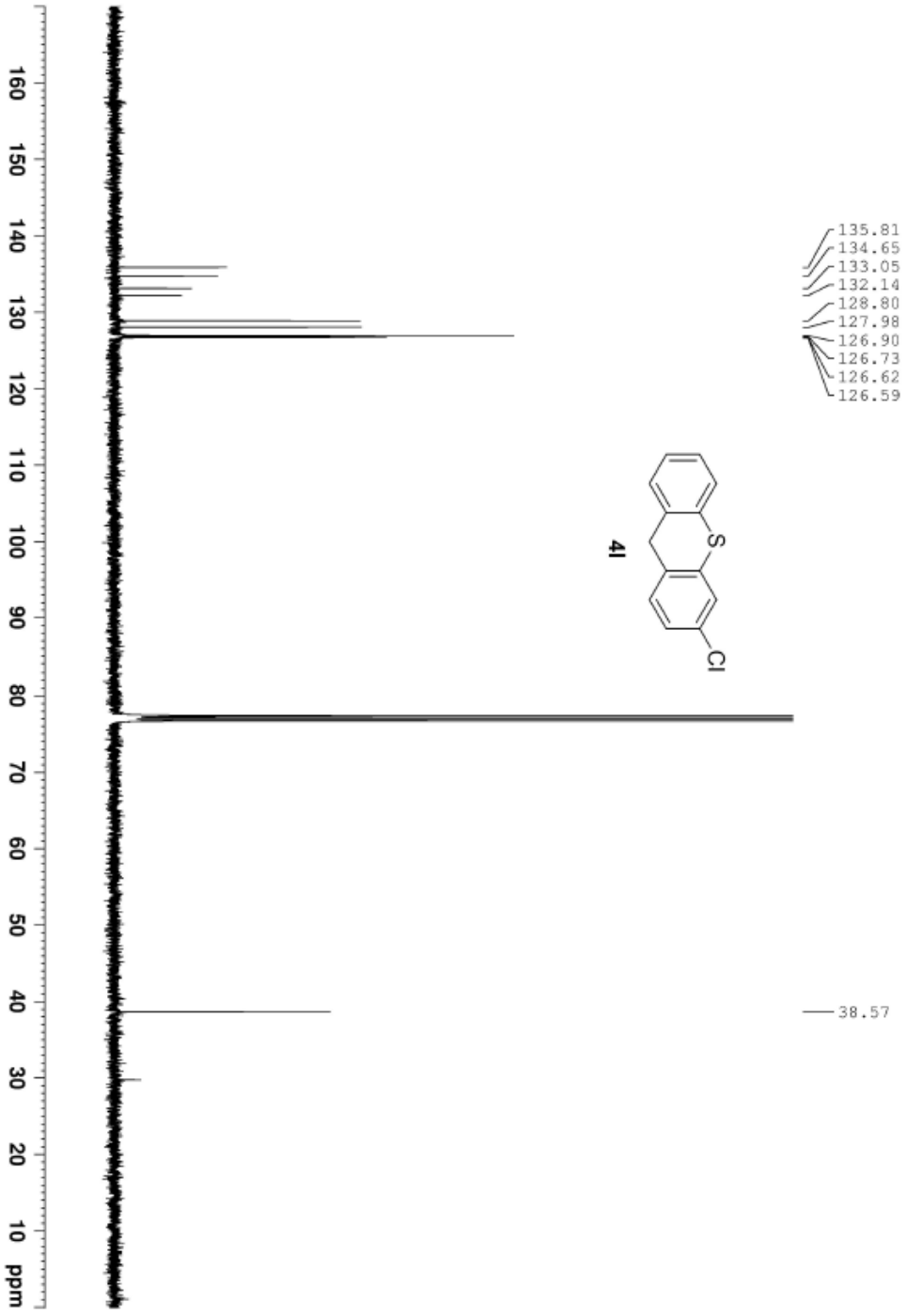
7.242
7.232
7.228
7.222
7.216
7.210
7.204
7.200
7.188
7.183
7.168
7.163
3.821
2.00
1.07
4.03
2.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
S
Cl
4l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127.98
126.90
126.73
126.62
126.59
38.57
4l
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Cl
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150
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130
120
110
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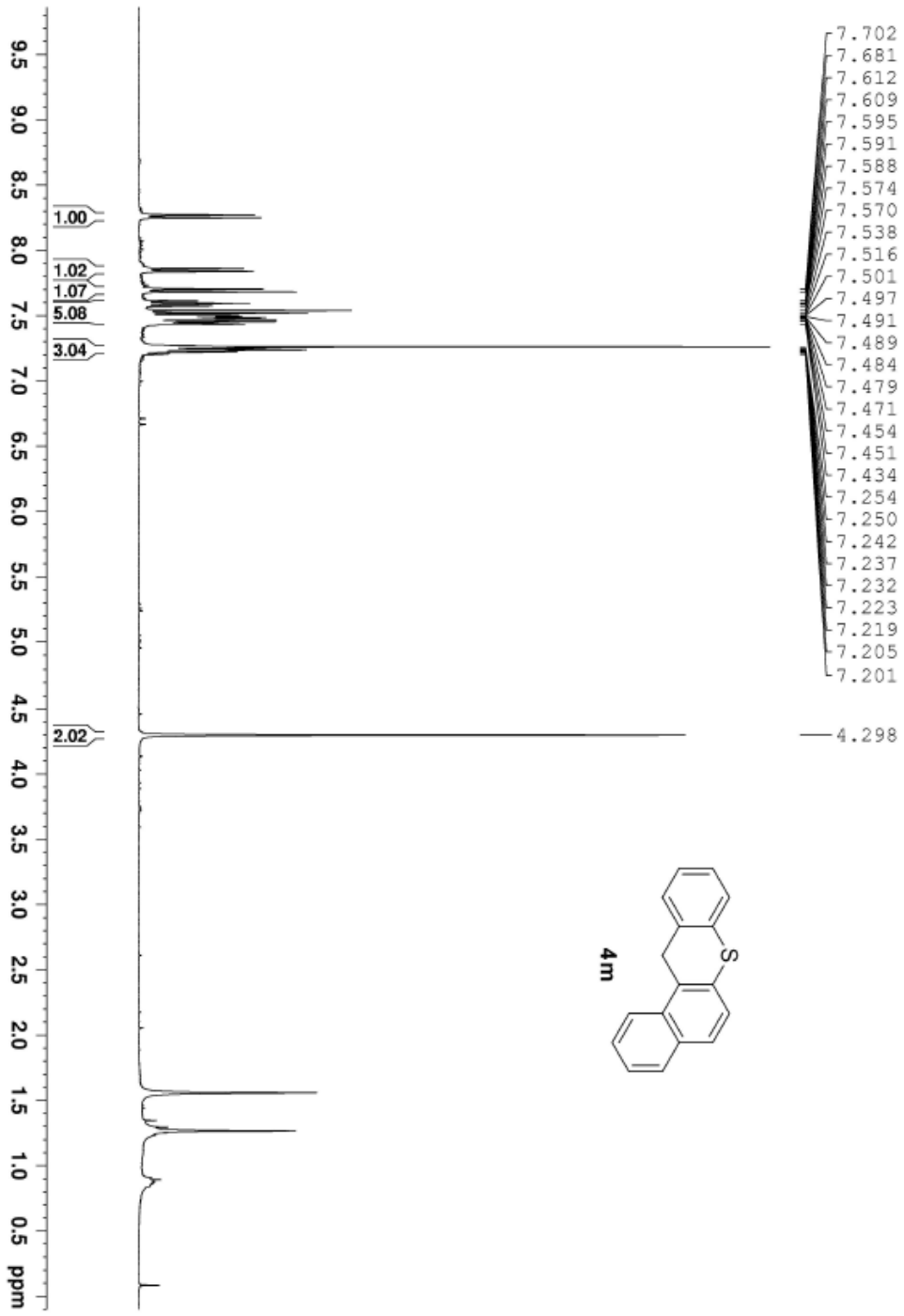
90
80
70
60
50
40
30
20
10
ppm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7.538
7.516
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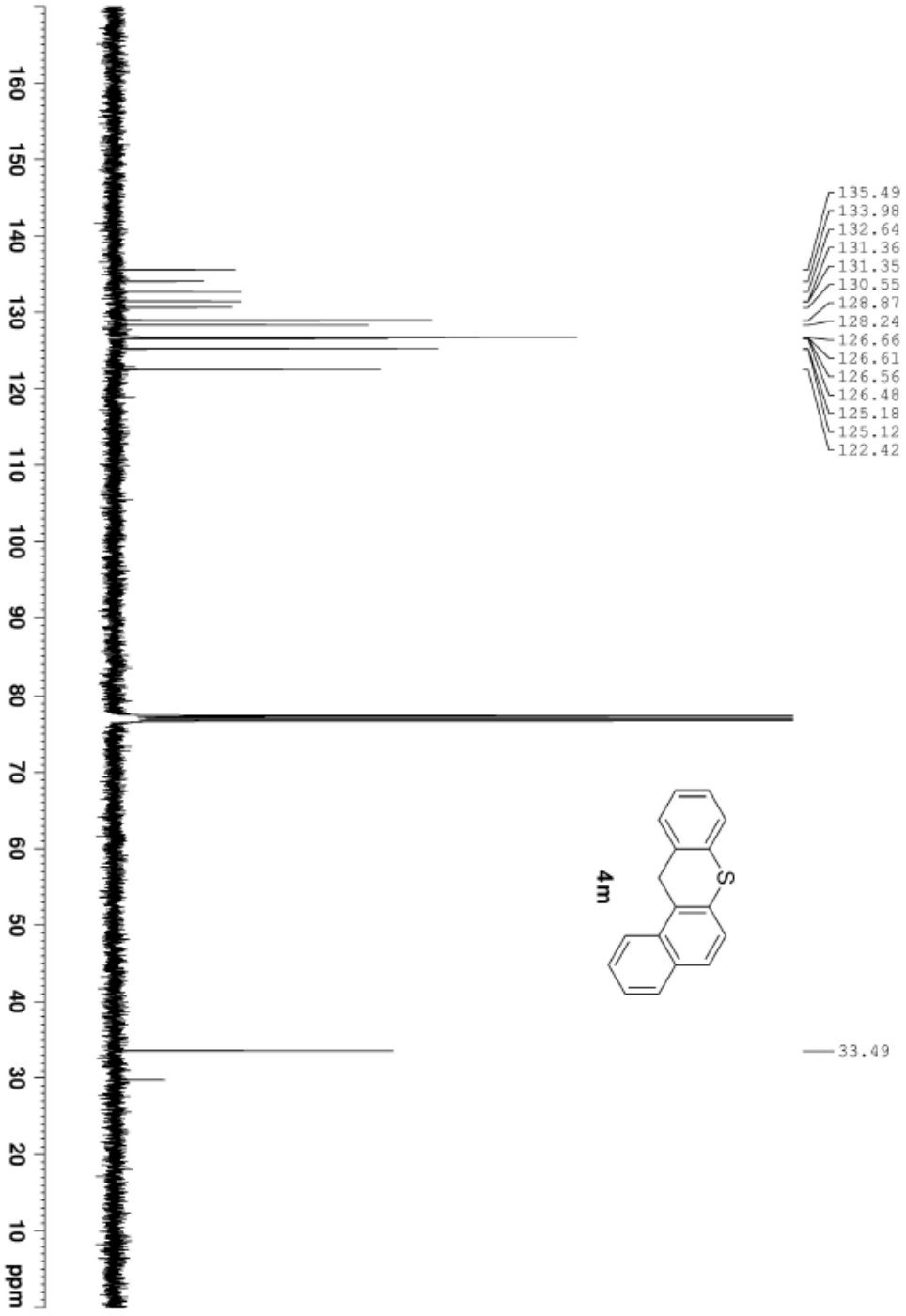
7.497
7.491
7.489
7.484
7.479
7.471
7.454
7.451
7.434
7.254
7.250
7.242
7.237
7.232
7.223
7.219
7.205
7.201
4.298
1.00
1.02
1.07
5.08
3.04
2.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
S
4m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150
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120
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90
80
70
60
50
40
30
20
10
ppm
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131.35
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128.24
126.66
126.61
126.56
126.48
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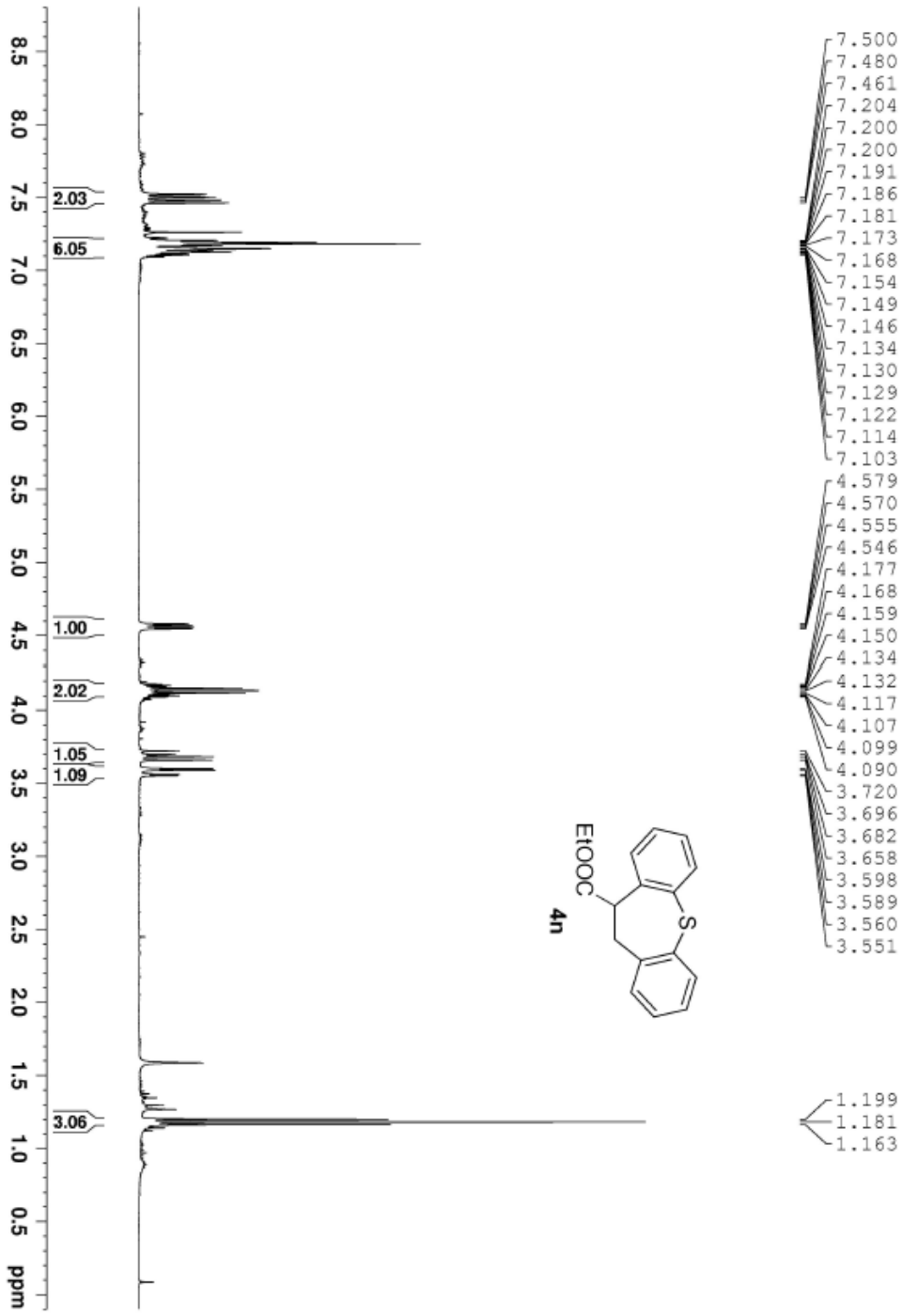
125.12
122.42
33.49
4m
S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6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.03
6.05
1.00
2.02
1.05
1.09
3.06
7.500
7.480
7.461
7.204
7.200
7.200
7.191
7.186
7.181
7.173
7.168
7.154
7.149
7.146
7.134
7.130
7.129
7.122
7.114
7.103
4.579
4.570
4.555
4.546
4.177
4.168
4.159
4.150
4.134
4.132
4.117
4.107
4.099
4.090
3.720
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3.682
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3.598
3.589
3.560
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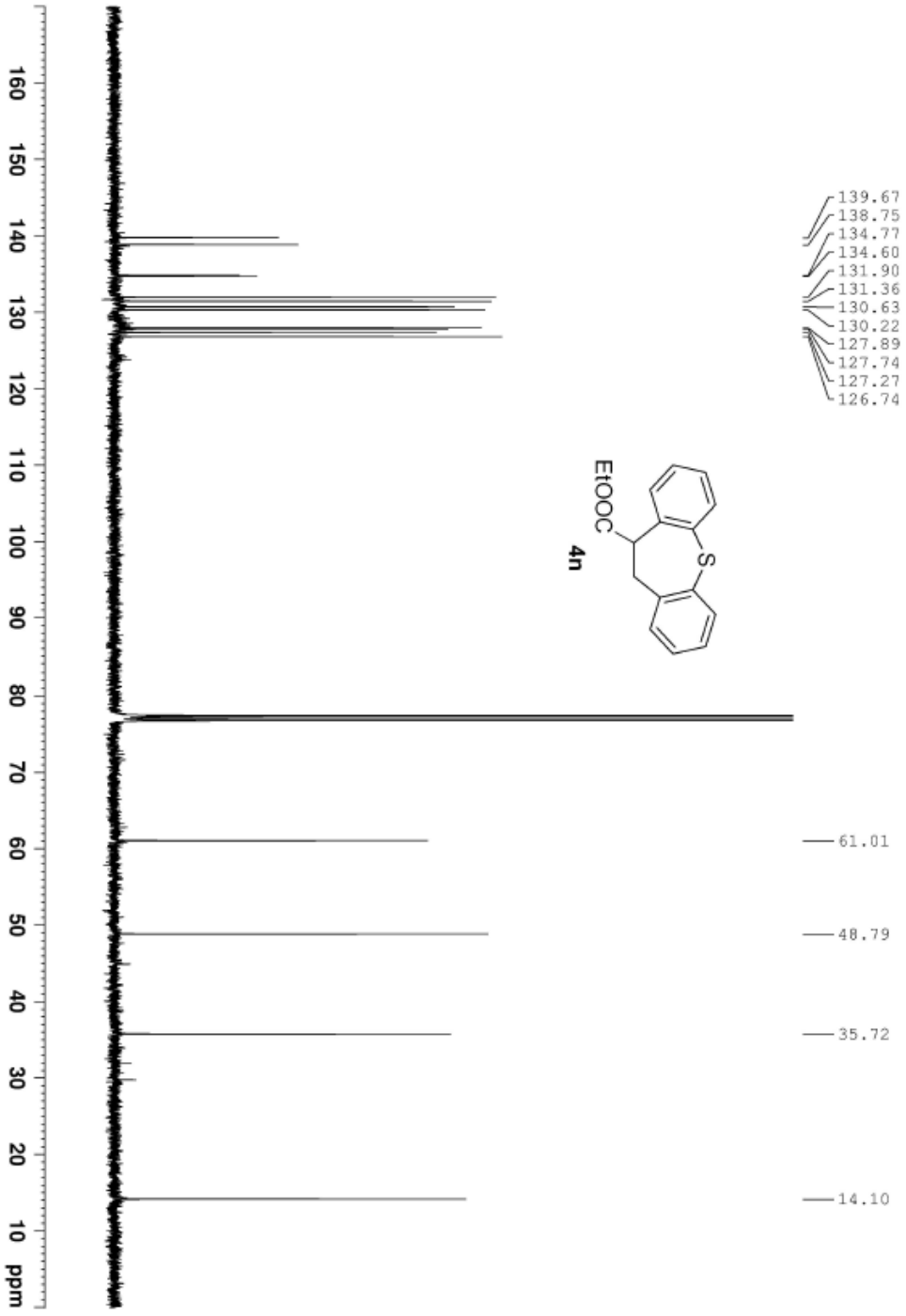
1.181
1.163
EtOOC
S
4n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80
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60
50
40
30
20
10
ppm
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134.77
134.60
131.90
131.36
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127.74
127.27
126.74
EtOOC
S
4n
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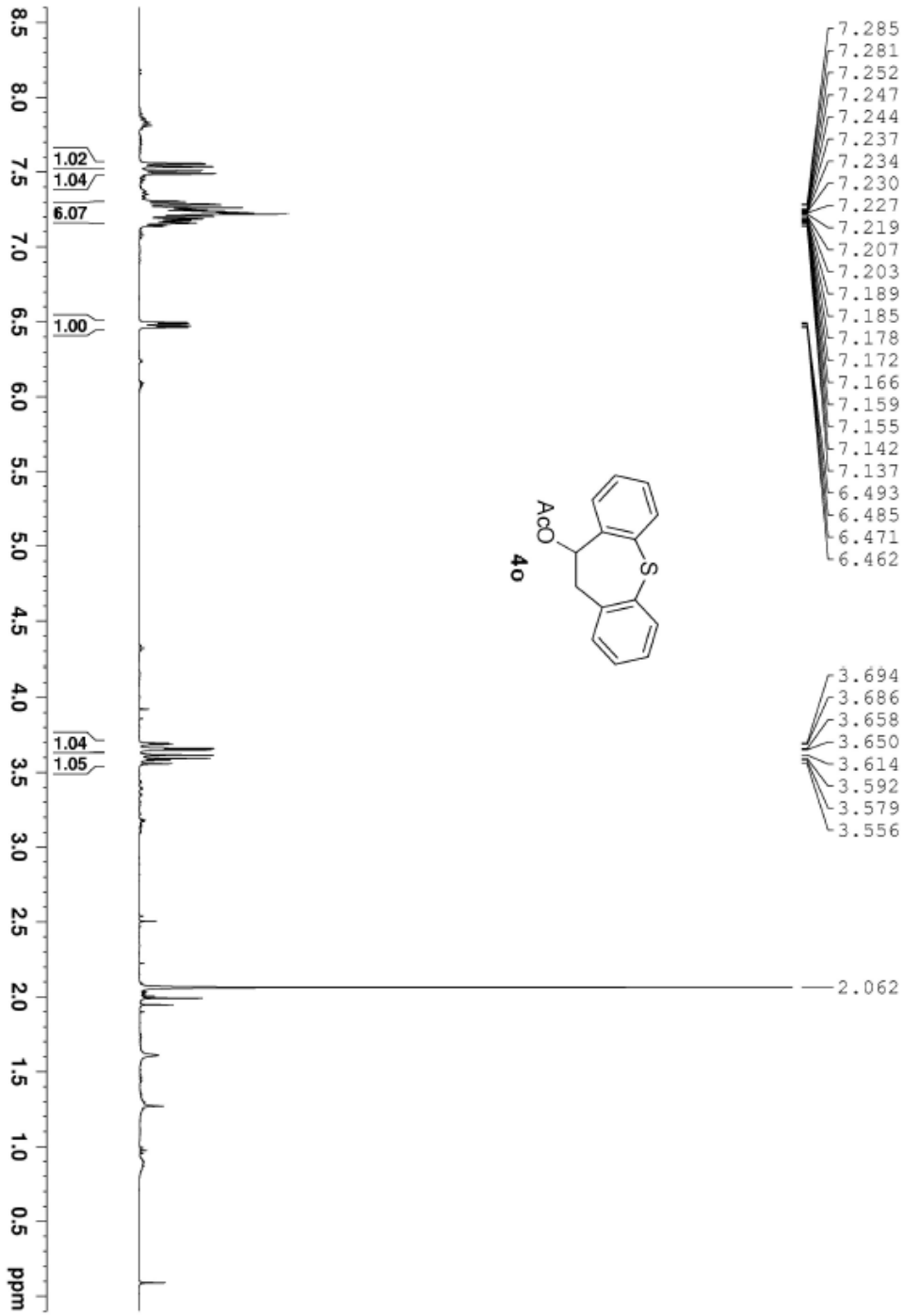
48.79
35.72
14.10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6.0
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5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.02
1.04
6.07
1.00
1.04
1.05
7.285
7.281
7.252
7.247
7.244
7.237
7.234
7.230
7.227
7.219
7.207
7.203
7.189
7.185
7.178
7.172
7.166
7.159
7.155
7.142
7.137
6.493
6.485
6.471
6.462
AcO
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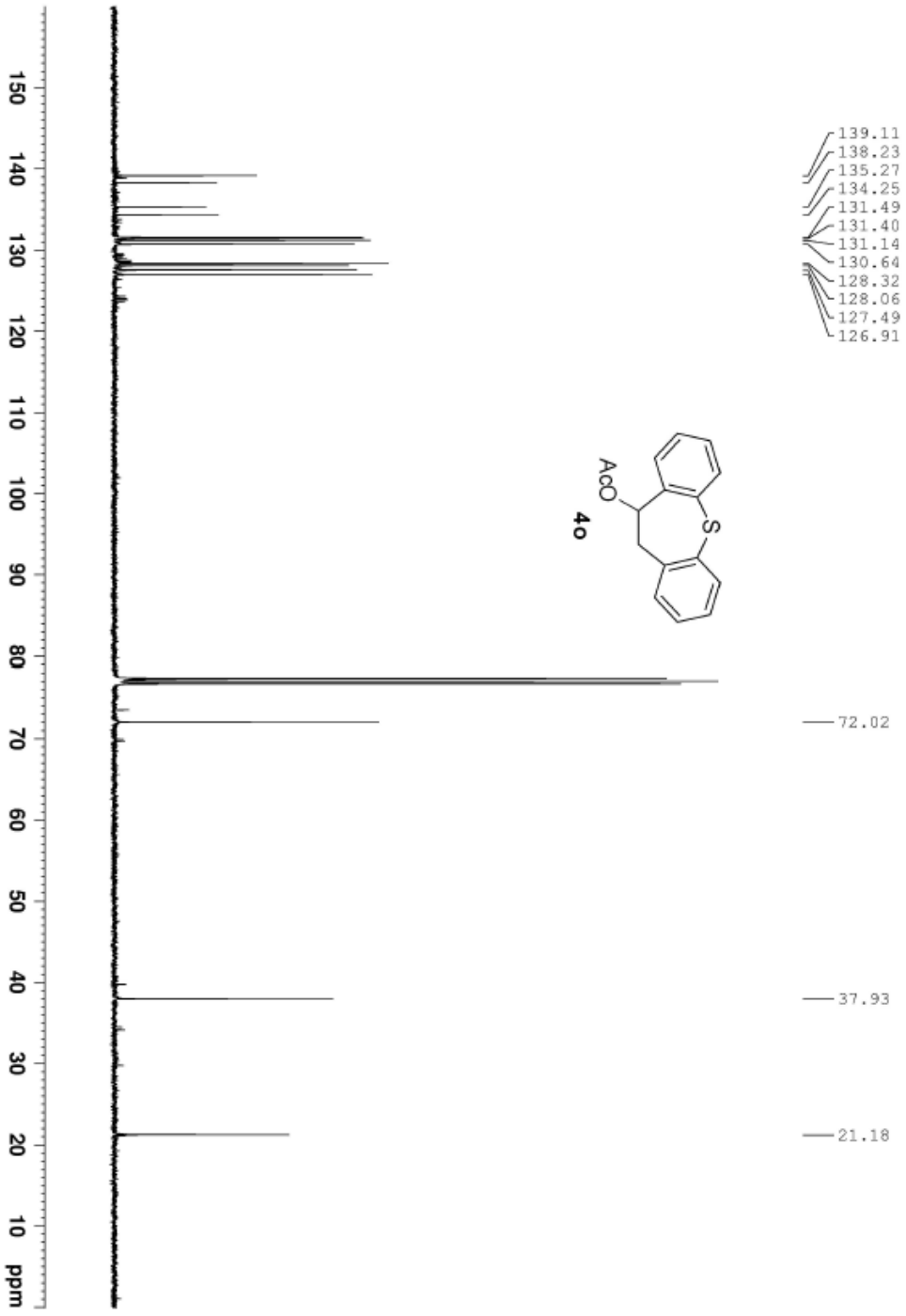
2.062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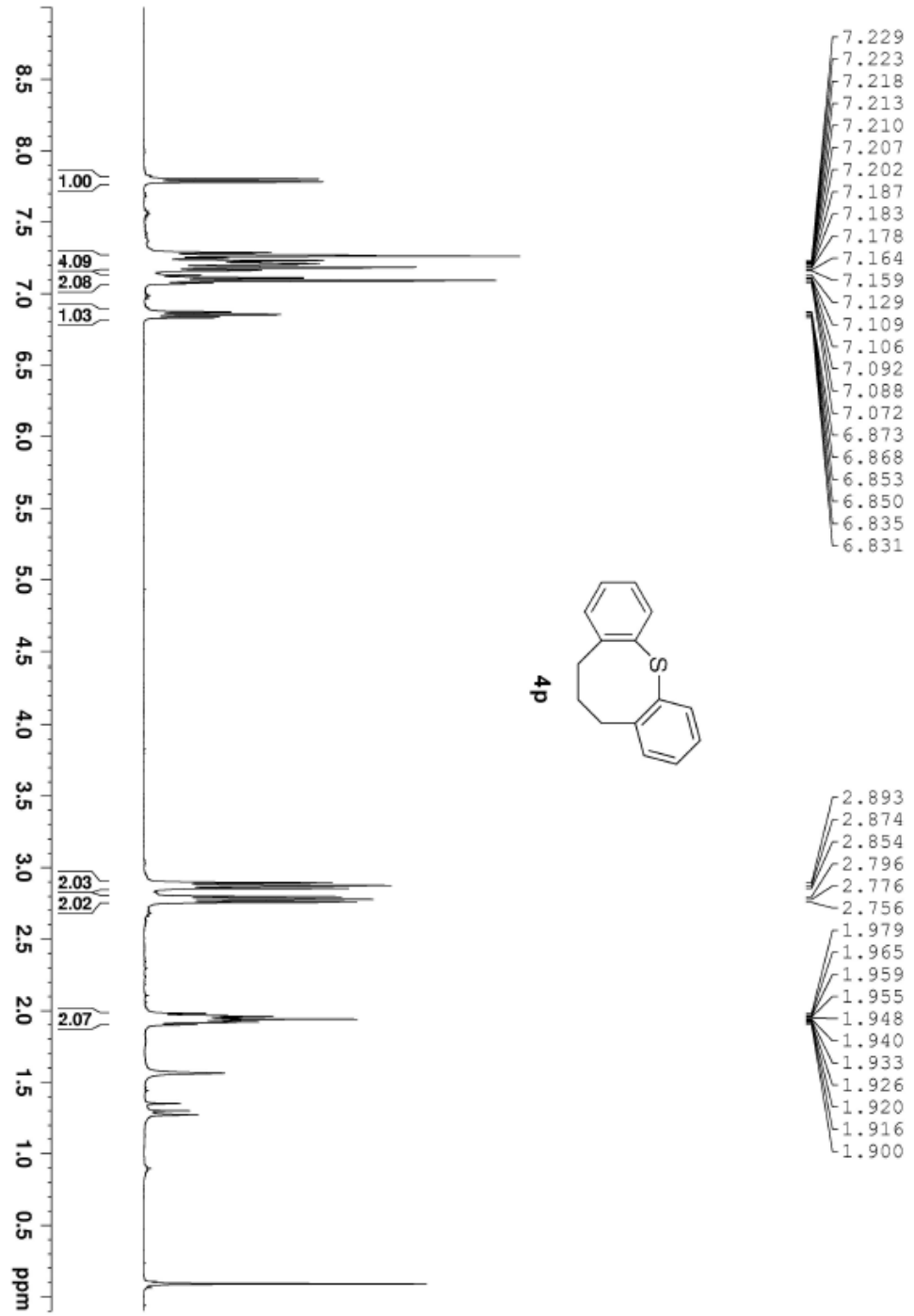
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
139.11
138.23
135.27
134.25
131.49
131.40
131.14
130.64
128.32
128.06
127.49
126.91
AcO
S
4o
72.02
37.93
21.18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5.0
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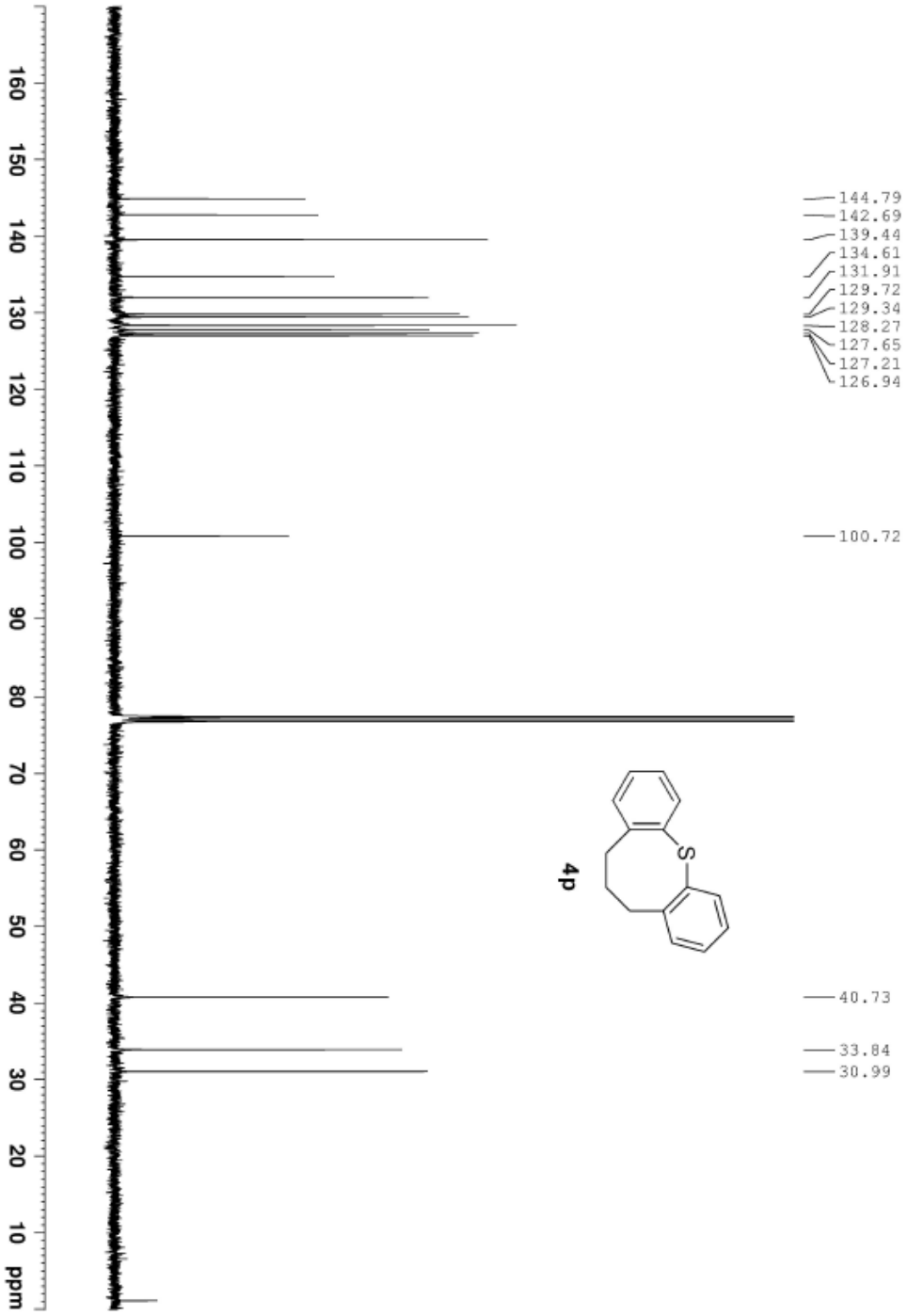
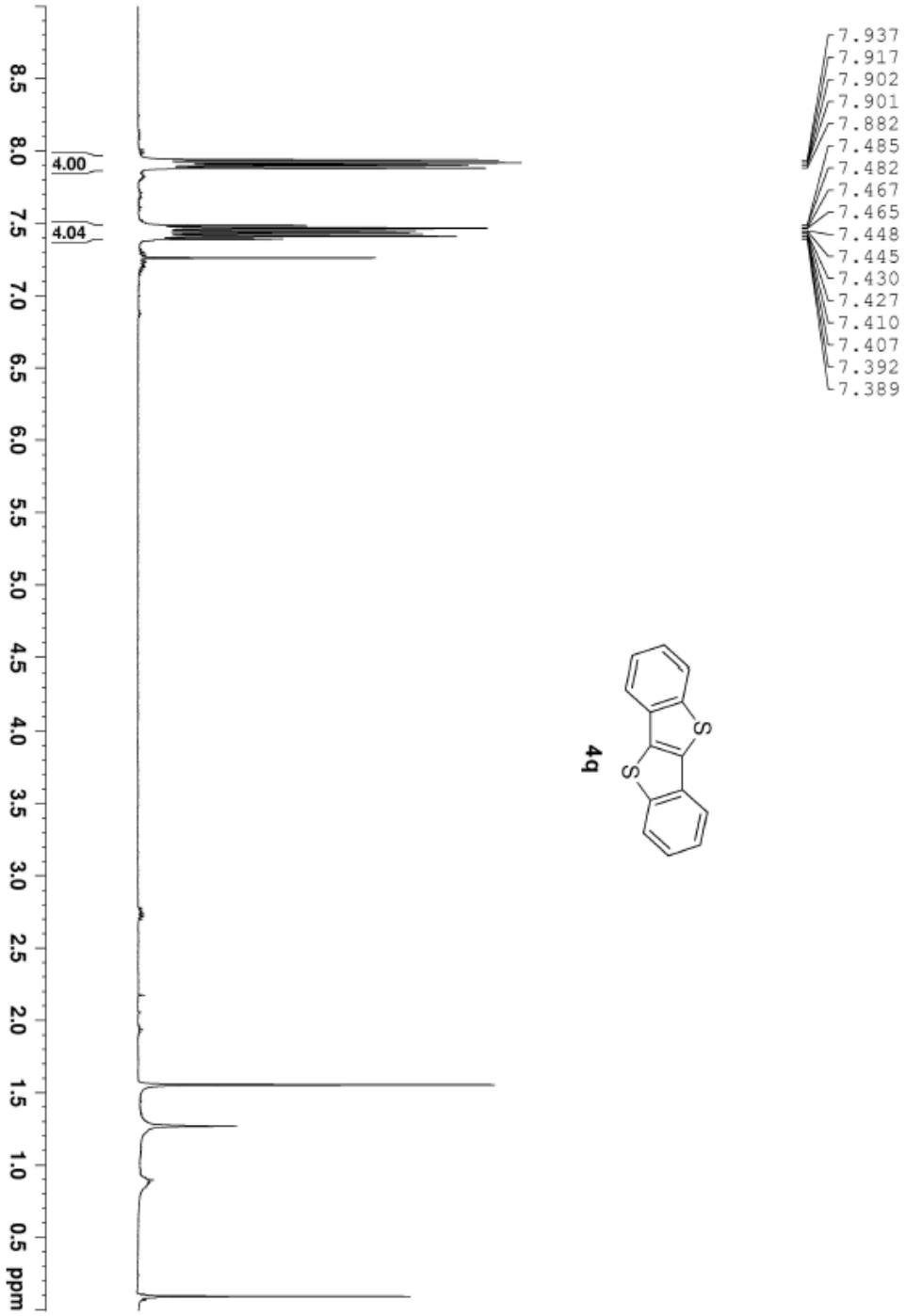
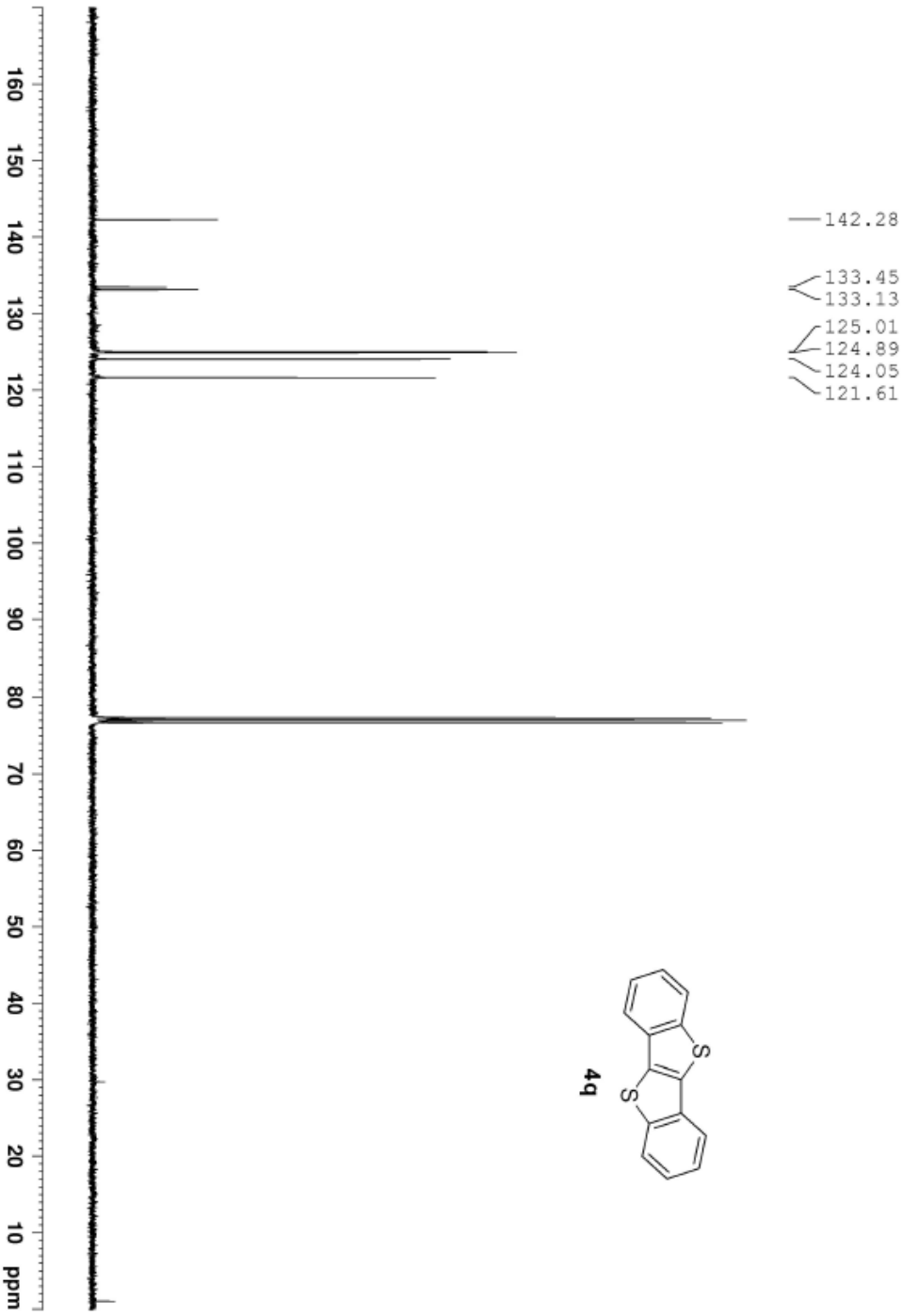
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
4.09
2.08
1.03
2.03
2.02
2.07
7.229
7.223
7.218
7.213
7.210
7.207
7.202
7.187
7.183
7.178
7.164
7.159
7.129
7.109
7.106
7.092
7.088
7.072
6.873
6.868
6.853
6.850
6.835
6.831
S
4p
2.893
2.874
2.854
2.796
2.776
2.756
1.979
1.965
1.959
1.955
1.948
1.940
1.933
1.926
1.920
1.916
1.900

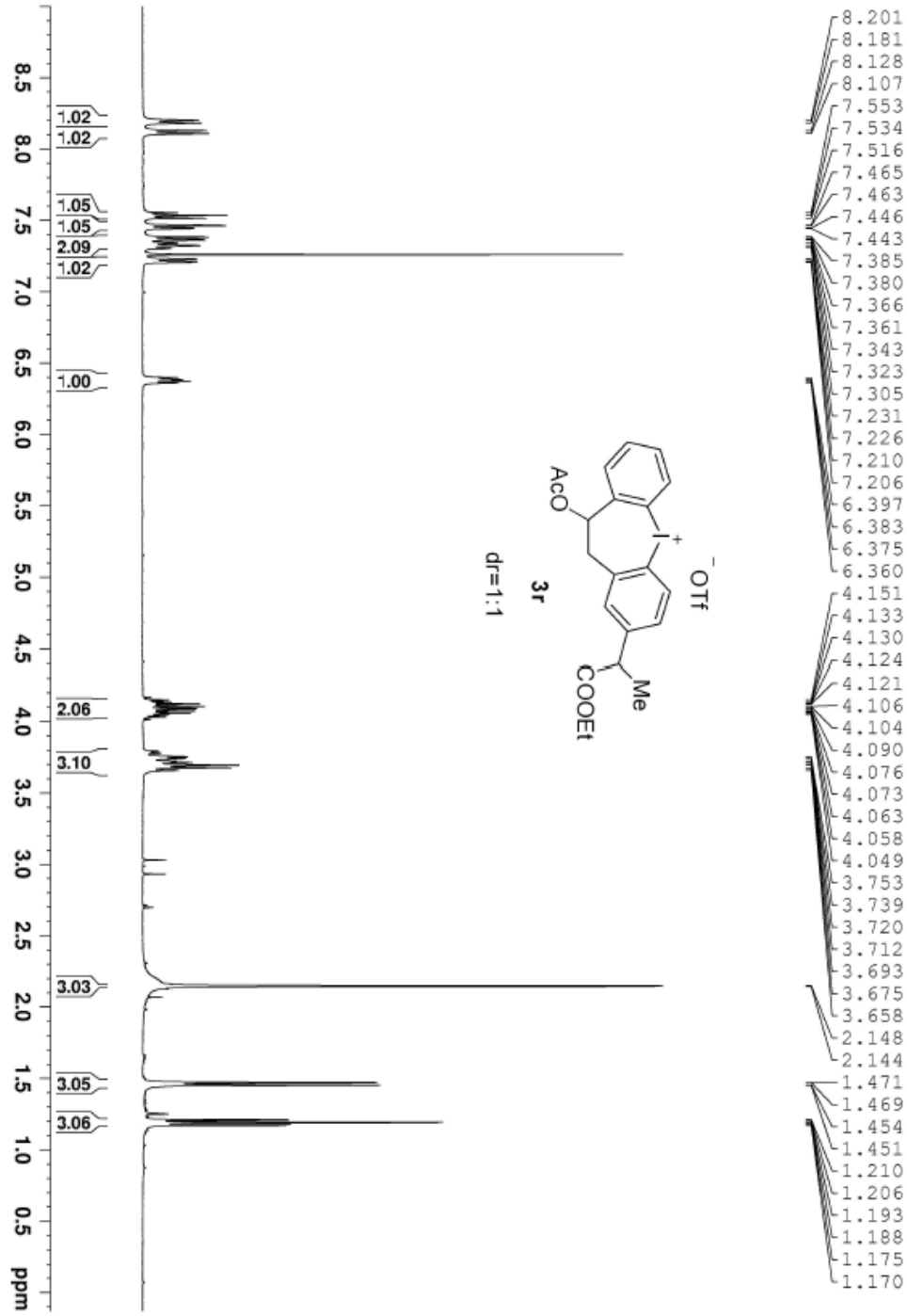

144.79
142.69
139.44
134.61
131.91
129.72
129.34
128.27
127.65
127.21
126.94
100.72
40.73
33.84
30.99
4p
S
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

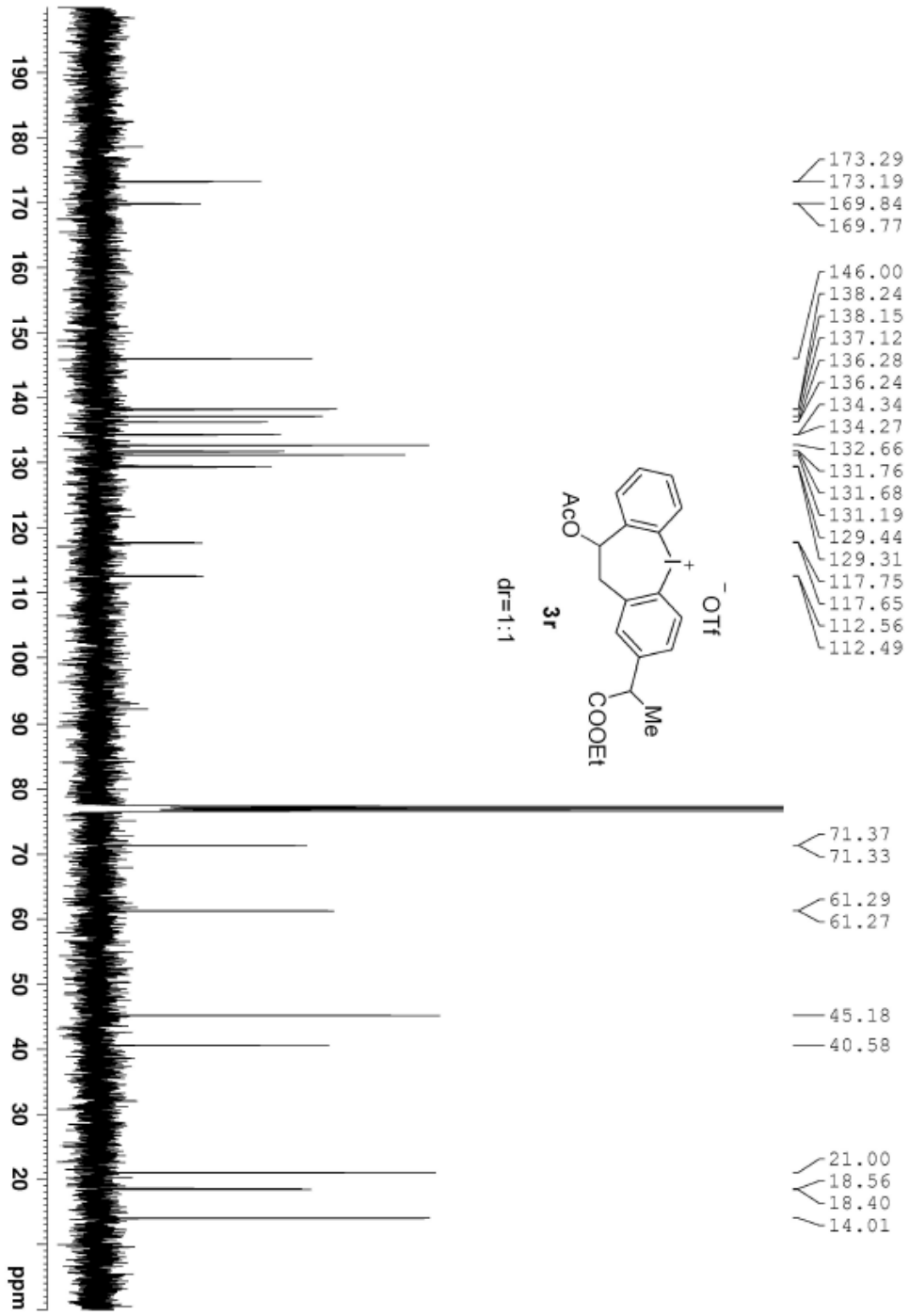

7.937
7.917
7.902
7.901
7.882
7.485
7.482
7.467
7.465
7.448
7.445
7.430
7.427
7.410
7.407
7.392
7.389
4.00
4.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
S
S

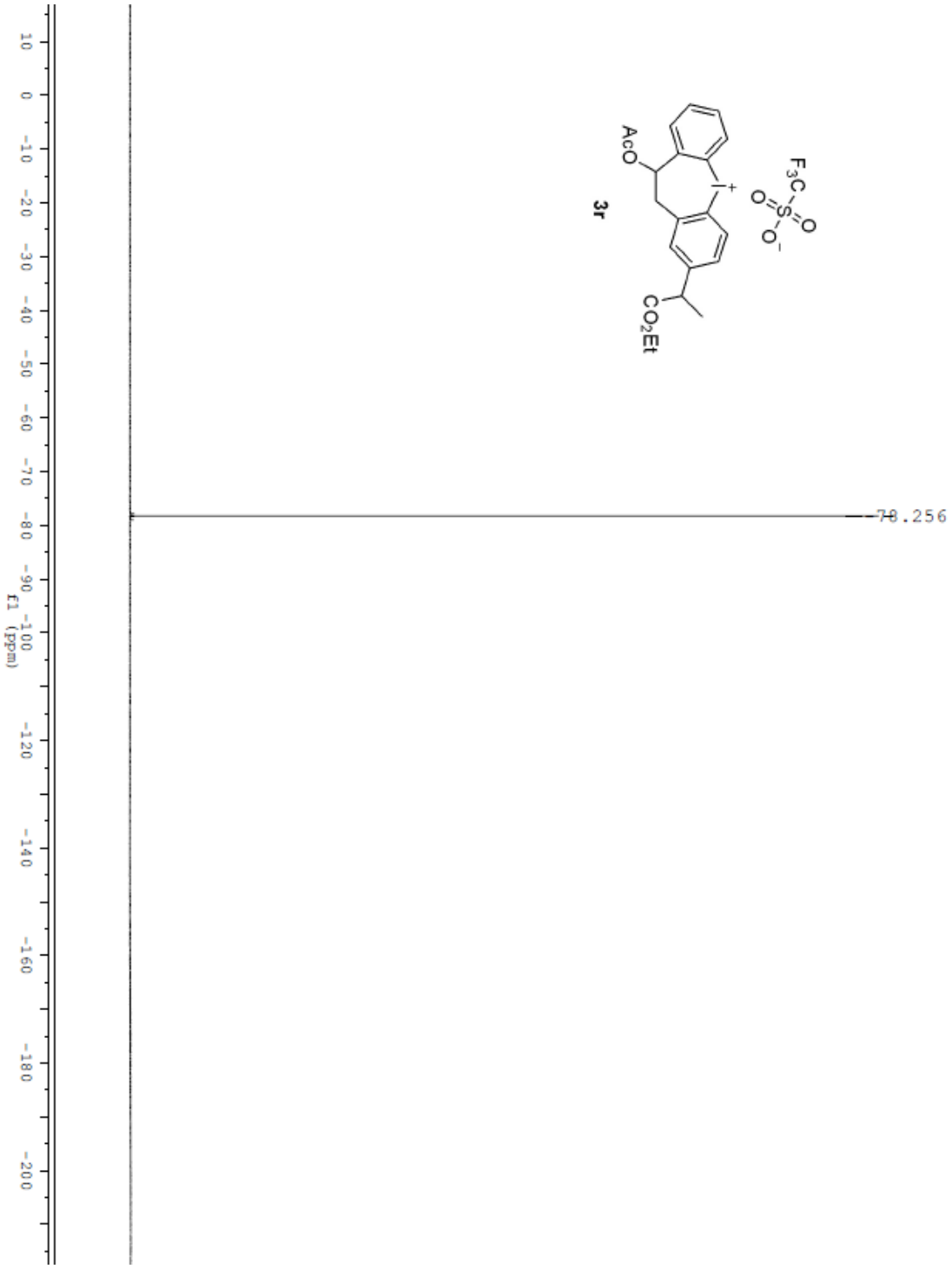
4q

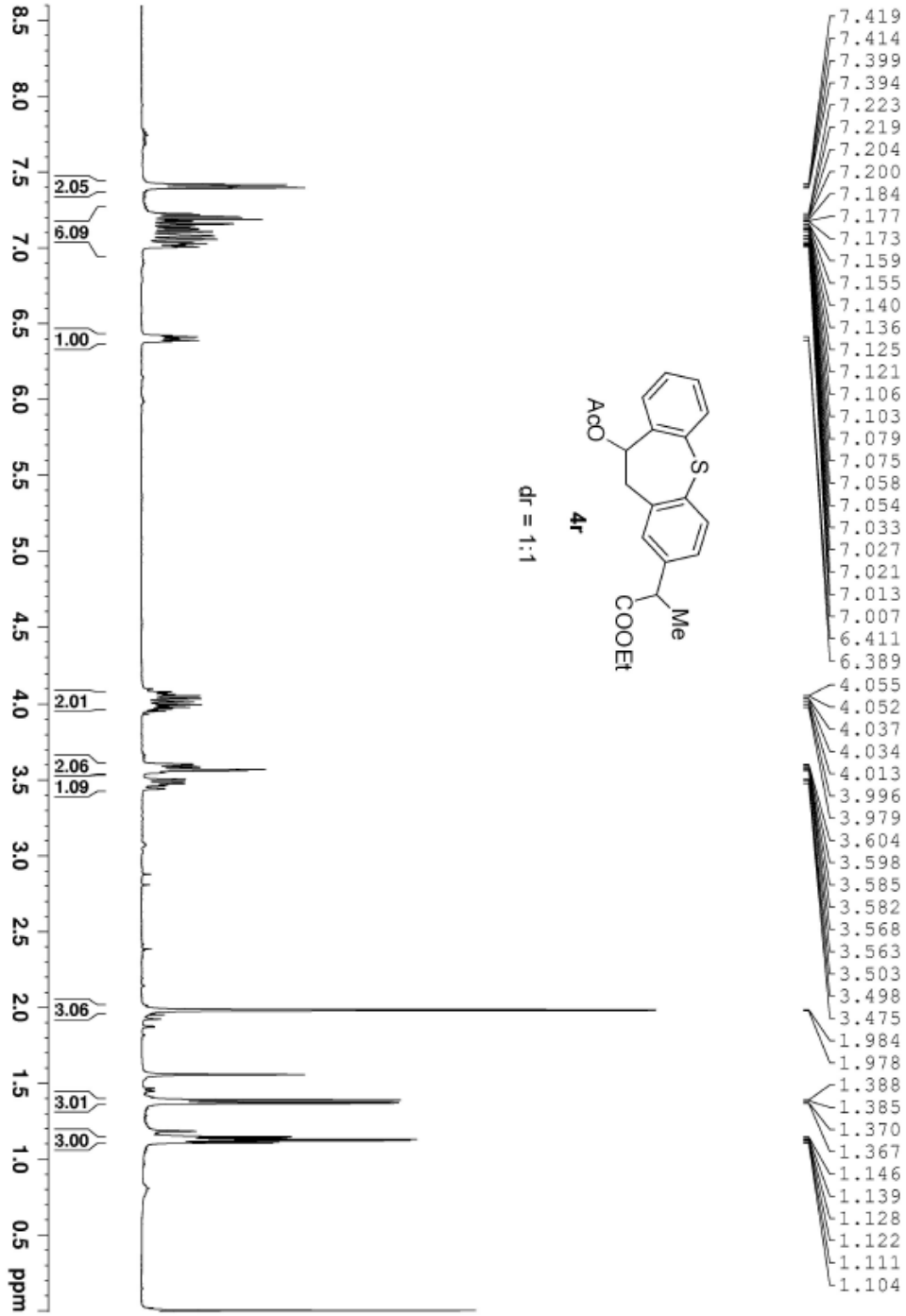

142.28
133.45
133.13
125.01
124.89
124.05
121.61
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
S
S

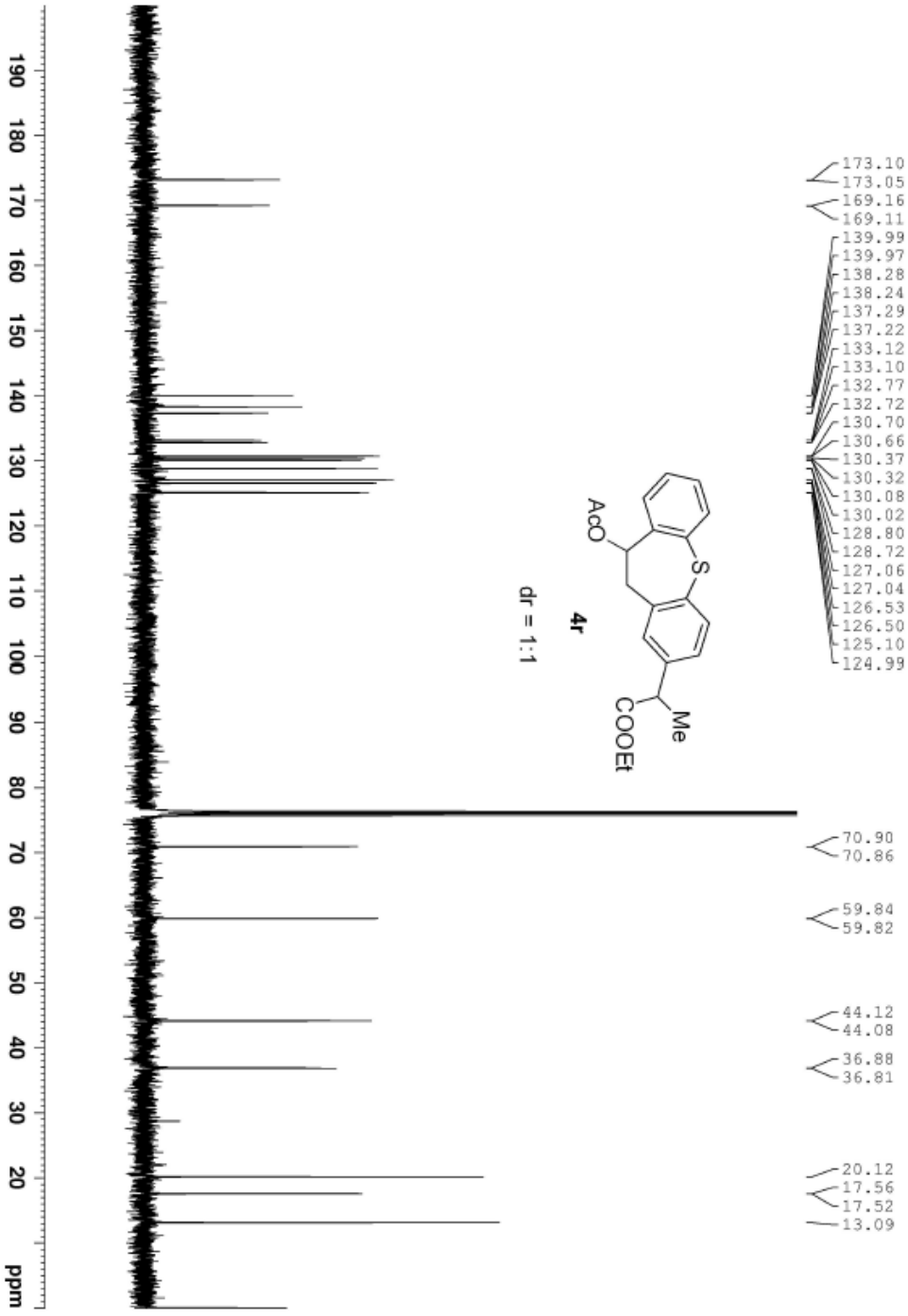
4q

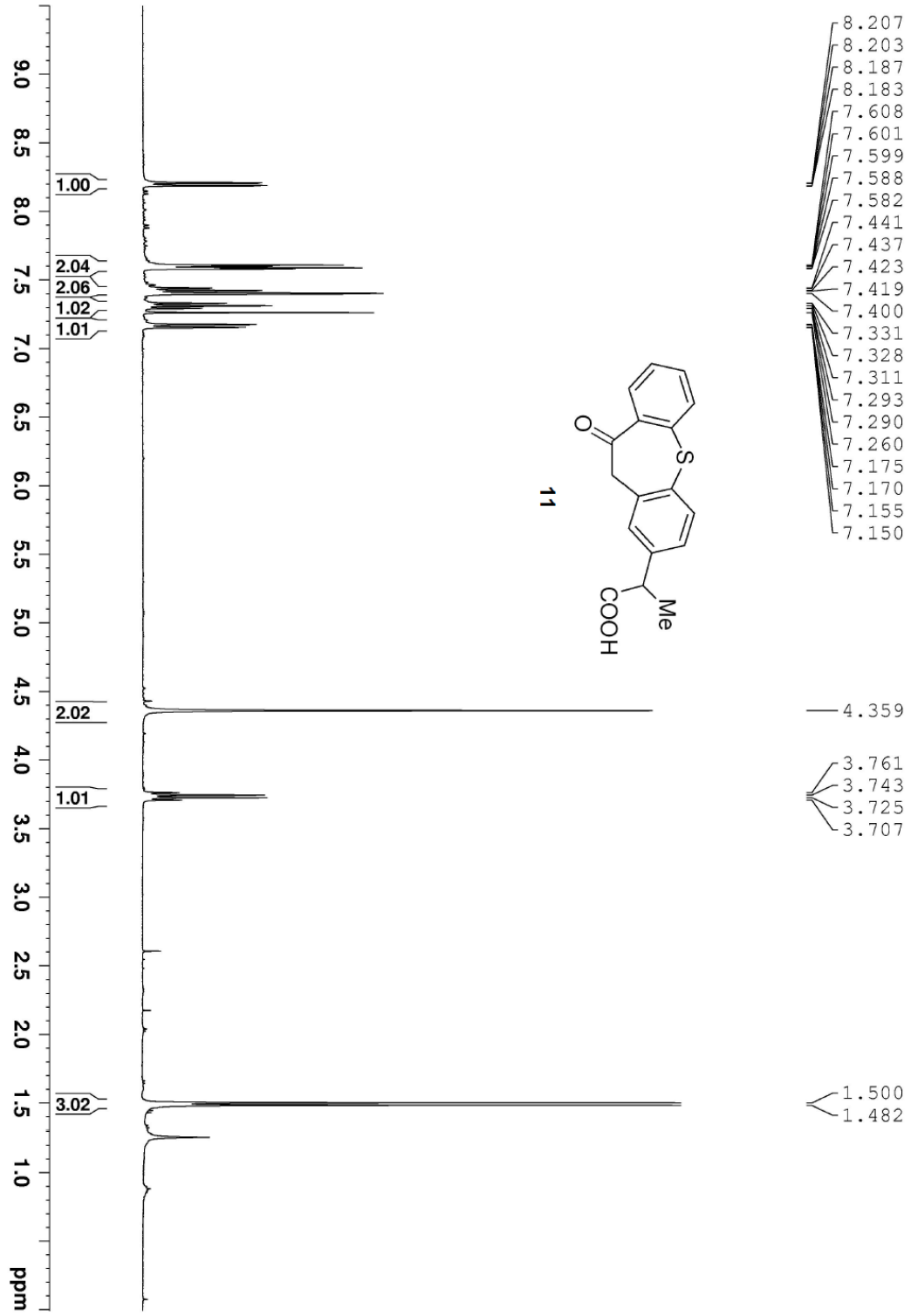

8.201
8.181
8.128
8.107
7.553
7.534
7.516
7.465
7.463
7.446
7.443
7.385
7.380
7.366
7.361
7.343
7.323
7.305
7.231
7.226
7.210
7.206
6.397
6.383
6.375
6.360
4.151
4.133
4.130
4.124
4.121
4.106
4.104
4.090
4.076
4.073
4.063
4.058
4.049
3.753
3.739
3.720
3.712
3.693
3.675
3.658
2.148
2.144
1.471
1.469
1.454
1.451
1.210
1.206
1.193
1.188
1.175
1.170
AcO
I+
OTf-
Me
COOEt
3r
dr=1:1
1.02
1.02
1.05
1.05
2.09
1.02
1.00
2.06
3.10
3.03
3.05
3.06
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

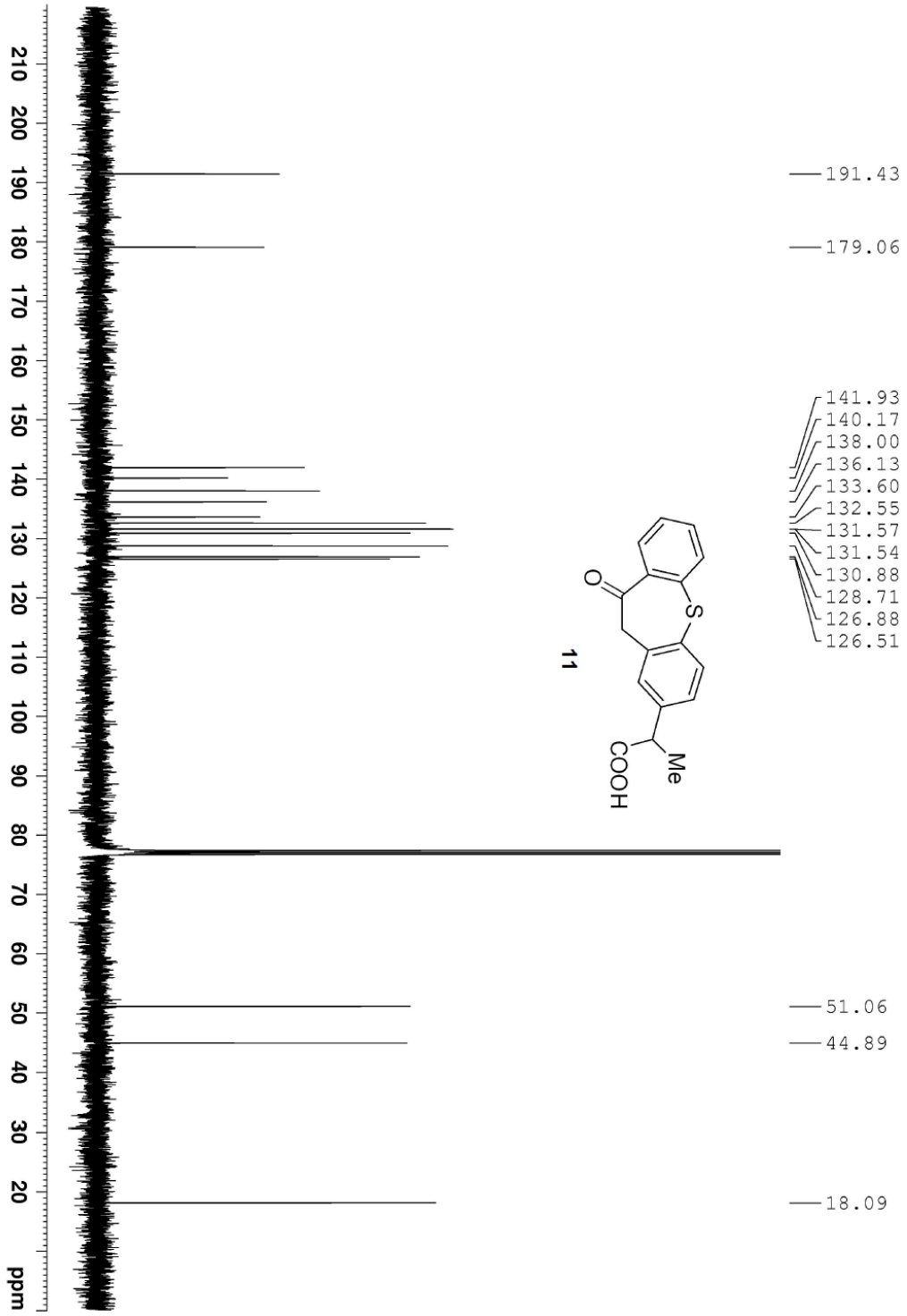

173.29
173.19
169.84
169.77
146.00
138.24
138.15
137.12
136.28
136.24
134.34
134.27
132.66
131.76
131.68
131.19
129.44
129.31
117.75
117.65
112.56
112.49
71.37
71.33
61.29
61.27
45.18
40.58
21.00
18.56
18.40
14.01
AcO
OTf
COOEt
Me
3r
dr=1:1
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


AcO
CO2Et
F3C
O
S
O
O
I+
3r
-78.256
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)


7.419
7.414
7.399
7.394
7.223
7.219
7.204
7.200
7.184
7.177
7.173
7.159
7.155
7.140
7.136
7.125
7.121
7.106
7.103
7.079
7.075
7.058
7.054
7.033
7.027
7.021
7.013
7.007
6.411
6.389
4.055
4.052
4.037
4.034
4.013
3.996
3.979
3.604
3.598
3.585
3.582
3.568
3.563
3.503
3.498
3.475
1.984
1.978
1.388
1.385
1.370
1.367
1.146
1.139
1.128
1.122
1.111
1.104
AcO
S
Me
COOEt
4r
dr = 1:1
2.05
6.09
1.00
2.01
2.06
1.09
3.06
3.01
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


173.10
173.05
169.16
169.11
139.99
139.97
138.28
138.24
137.29
137.22
133.12
133.10
132.77
132.72
130.70
130.66
130.37
130.32
130.08
130.02
128.80
128.72
127.06
127.04
126.53
126.50
125.10
124.99
AcO
S
Me
COOEt
4r
dr = 1:1
70.90
70.86
59.84
59.82
44.12
44.08
36.88
36.81
20.12
17.56
17.52
13.09
ppm


8.207
8.203
8.187
8.183
7.608
7.601
7.599
7.588
7.582
7.441
7.437
7.423
7.419
7.400
7.331
7.328
7.311
7.293
7.290
7.260
7.175
7.170
7.155
7.150
4.359
3.761
3.743
3.725
3.707
1.500
1.482
1.00
2.04
2.06
1.02
1.01
2.02
1.01
3.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
11
O
S
Me
COOH


191.43
179.06
141.93
140.17
138.00
136.13
133.60
132.55
131.57
131.54
130.88
128.71
126.88
126.51
51.06
44.89
18.09
O
S
Me
COOH
11
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm