A Silver-Promoted Domino Pd-Catalyzed Tandem Amination/Direct Arylation: Access to Polycyclic Heteroaromatics

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Supporting Information

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General Experimental Procedures. Unless otherwise noted, reactions were carried out under an atmosphere of nitrogen or argon in flame – dried glassware with magnetic stirring. Air and/or moisture-sensitive liquids were transferred *via* syringe. Where required, solutions were degassed by bubbling of argon or nitrogen through a needle. Organic solutions were concentrated by rotary evaporation at 25 – 60 °C at 15-30 torr (house vacuum). Analytical thin layer chromatography (TLC) was performed using plates cut from aluminum sheets (silica gel 60 F_{254} from EMD chemicals). Visualization was achieved under a 254 nm UV light or by immersion in an ethanolic solution of anisaldehyde, followed by treatment with a heat gun. Column chromatography was carried out as "Flash Chromatography" as reported by Still[1] using Ultra Pure 230-400 mesh silica gel purchased from Silicycle. The result of ACD/IUPAC Name v8.05 was obtained using the ACD/I-Lab service.

Materials. $Pd_2(dba)_3$ was purchased from Strem Chemicals and used as received. Ligands were purchased from Strem and recrystallized from ethanol before use. All other reagents were obtained from commercial sources and used without further purifications. Toluene was distilled under nitrogen from sodium/benzophenone

(1) Still, W. C.; Khan, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

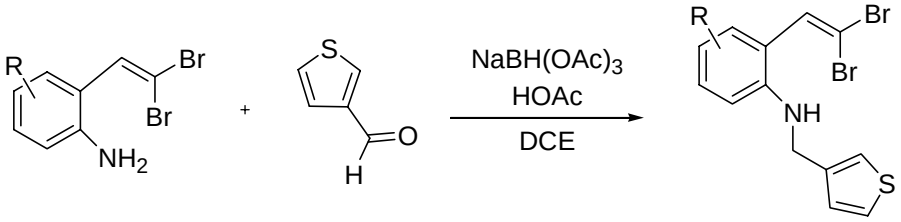
immediately before use. Dichloroethane was distilled under nitrogen from CaH_2. Dichloromethane was passed through a column of activated alumina under nitrogen. *gem*-dibromoaniline substrates were synthesized as previously described,[2] and all characterization was consistent wih the literature.

Instrumentation. Melting points were taken on a Fisher-Johns melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer Spectrum 1000 FT-IR spectrometer as a $CHCl_3$ solution on an NaCl plate or on a Perkin-Elmer Specrum 100 FT-IR spectrometer as a solid sample. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded at 23 °C on Varian Mercury 400 or Mercury 300 spectrometers. Recorded shifts are reported in parts per million (δ) downfield from tetramethylsilane and a referenced to samples of TMS in the solvent. Data are represented as follows: Chemical shift, mutiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, sx = sextet, sp = septet, m = multiplet, br = broad), coupling constant (*J*, Hz) and integration. High resolution mass spectra were obtained using a SI2 Micromass 70-250S (double focussing) mass spectrometer (EI) or a ABI/Sciex Qstar mass spectrometer (ESI).

(2) Fang, Y.-Q.; Lautens, M. *Org. Lett.* **2005**, *7*, 3549.

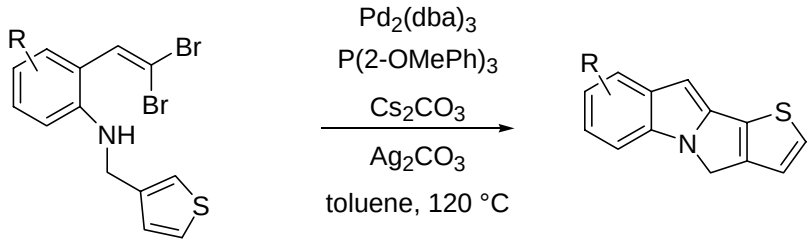
Experimental Procedures

General procedure for the reductive amination (synthesis of starting materials).



The requisite *gem*-dibromovinyl aniline (1.0 equiv) and aldehyde (1.0 equiv) were added to a round bottom flask and dichloroethane (3.5 mL/mmol) was added. Sodium triacetoxyborohydride (1.4 equiv) and acetic acid (1.0 equiv) were added, and the reaction was stirred overnight at room temperature. Sodium hydroxide (10% aqueous solution) was added, and the reaction was stirred for 20 minutes then extracted with Et_2O, washed with H_2O and brine, dried ($MgSO_4$) and concentrated. Products were purified by column chromatography.

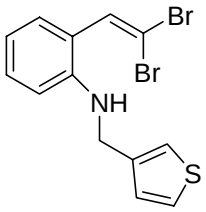
General procedure for the cyclization



The requisite *gem*-dibromoaniline (0.134 mmol) and Cs_2CO_3 (110 mg, 0.268 mmol, 2.0 equiv) were placed in a Biotage microwave vial. Toluene (9 mL) was added, and the suspension was degassed for 10 minutes. $Pd_2(dba)_3$ (3.7 mg, 0.0040 mmol, 3 mol %), $P(2\text{-}OMePh)_3$ (5.8 mg, 0.016 mmol, 12 mol %) and silver carbonate (18.5 mg, 0.63 mmol, 0.5 equiv) were added, and the suspension was degassed for an additional 10 minutes, at which point the vial was sealed with a teflon cap and placed in an oil bath preheated to 120 °C and stirred overnight. The reaction was cooled to room temperature and filtered through a pad of silica, washing with EtOAc. The filtrate was concentrated, and the residue purified by column chromatography or as described.

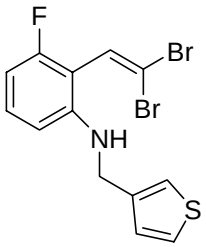
Starting Materials

[2-(2,2-Dibromo-vinyl)]-N-(3-thienylmethyl)aniline (**1a**).



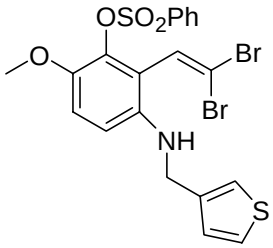
The general procedure was followed (4.0 mmol scale). The product was purified by column chromatography eluting with 2 % Et_2O/pentane to give 1.33 g (89 %) as a white solid. **IR** ($CDCl_3$) 3412, 3099, 3072, 2983, 2840, 1600, 1575, 1504, 1455, 1410, 1388, 1314, 1254, 1157, 1117, 1076, 1046, 932, 875, 855, 831, 770, 746, 692. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.33 (dd, *J* = 4.9, 3.0 Hz, 1H), 7.30-7.18 (m, 4H), 7.08 (dd, *J* = 4.9, 1.1 Hz, 1H), 6.76 (td, *J* = 7.7, 1.0 Hz, 1H), 4.38 (d, *J* = 8.2 Hz, 2H), 3.97 (br s, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 145.0, 140.3, 134.3, 130.1, 129.5, 127.3, 126.6, 122.0, 117.5, 111.4, 93.7, 43.9. **MS EI** *m/z* (rel. intensity) 375(12), 373(22), 371(12), 213(15), 212(30), 97(100). **HRMS** Calculated for $C_{13}H_{11}Br_2NS$: 370.8979, Found 370.8977. mp = 92-93°C (pentane/Et_2O).

2-(2,2-dibromovinyl)-3-fluoro-N-(3-thienylmethyl)aniline (**1b**).



The general procedure was followed (2.0 mmol scale). The product was purified by column chromatography eluting with 2 % Et_2O/pentane to give 576 mg (73 %) as a white solid. **IR** ($CDCl_3$) 3426, 3099, 2985, 2841, 1621, 1580, 1506, 1470, 1412, 1388, 1319, 1236, 1188, 1151, 1113, 1047, 980, 956, 874, 831, 797, 767, 719, 685. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.33 (dd, *J* = 4.9, 3.0 Hz, 1H), 1H), 7.19-7.12 (m, 3H), 7.07 (dd, *J* = 5.0, 1.1 Hz), 6.48-6.41 (m, 2H), 4.40 (d, *J* = 5.6 Hz, 2H), 4.14 (br s, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 159.9 (d, *J* = 245 Hz), 146.3 (d, *J* = 6 Hz), 140.0, 130.9 (d, *J* = 11 Hz), 129.2 (d, *J* = 2 Hz), 127.1, 126.7, 122.0, 109.9 (d, *J* = 19 Hz), 106.6 (d, *J* = 3 Hz), 104.4 (d, *J* = 22 Hz), 97.4 (d, *J* = 2 Hz), 44.0. **^{19}F NMR** (282 MHz, $CDCl_3$) δ = -112.6. **MS EI** *m/z* (rel. intensity) 391(14), 231(14), 230(30), 97(100). **HRMS** Calculated for $C_{13}H_{10}Br_2FNS$: 338.8885, Found: 388.8882 . mp = 108-109 °C (pentane/Et_2O).

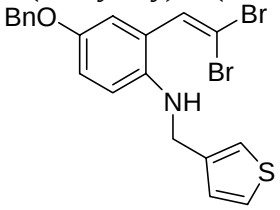
2-(2,2-dibromovinyl)-6-methoxy-3-[(3-thienylmethyl)amino]phenyl benzenesulfonate (**1c**).



The general procedure was followed (2.63 mmol scale). The product was purified by column chromatography eluting with 25 % EtOAc/hexanes to give 1.09 g (74 %) as a white solid. **IR** ($CDCl_3$) 3423, 3099, 3058, 2991, 2929, 2837, 1575, 1505, 1460, 1448, 1437, 1416, 1372, 1317, 1279, 1198, 1176, 1164, 1106, 1090, 994, 967, 926, 910, 847, 780, 753, 729, 687. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.98 (m, 2H), 7.67 (m, 1H), 7.57 (m, 2H), 7.32 (dd, *J* = 4.9, 3.0 Hz, 1H), 7.17 (dd, *J* = 2.8, 1.1 Hz, 1H), 7.05 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.00 (s, 1H), 6.83 (d, *J* = 9.0 Hz, 1H), 6.51 (d, *J* = 9.0 Hz, 1H), 4.33 (d, *J* = 4.5 Hz, 2H), 3.85 (t, *J* = 4.5 Hz, 1H), 3.55 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 144.5, 140.3, 139.7, 137.8, 136.6, 134.0, 130.7, 129.2, 128.4, 127.1, 126.6, 121.8, 118.5, 114.8, 110.0, 97.6, 56.6, 44.4. **MS EI** *m/z* (rel. intensity) 560(25), 558(45), 556(24), 392(12), 390(24), 288(12), 339(28), 337(28), 258(28), 242(35), 240(33),

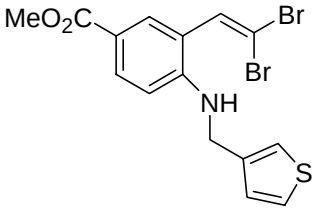
97(100), 77(21). **HRMS** Calculated for $C_{20}H_{17}Br_2NO_4S_2$: 556.8966, Found: 563.8954 . mp = 133-134 °C (hexanes/EtOAc).

4-(benzyloxy)-2-(2,2-dibromovinyl)-N-(3-thienylmethyl)aniline (**1d**).



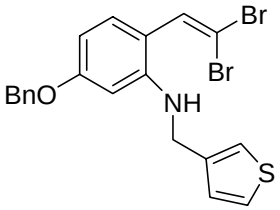
The general procedure was followed (2.0 mmol scale). The product was purified by column chromatography eluting with 5 % EtOAc/hexanes to give 736 mg (77 %) as a yellow solid. **IR** ($CDCl_3$) 3413, 3031, 2853, 1504, 1453, 1415, 1378, 1304, 1290, 1215, 1167, 1118, 1079, 1066, 1022, 855, 831, 807, 777, 733, 695. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.43-7.27 (m, 7H), 7.18-7.17 (m, 1H), 7.07 (dd, *J* = 4.9, 1.1 Hz, 1H), 7.00 (d, *J* = 2.9 Hz, 1H), 6.89 (dd, *J* = 8.8, 2.9 Hz, 1H), 6.63 (d, *J* = 8.9 Hz, 1H), 5.01 (s, 2H), 4.32 (s, 2H), 3.67 (br s, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 151.1, 140.5, 139.7, 137.6, 134.0, 128.8, 128.1, 127.8, 127.4, 126.5, 123.1, 122.0, 117.3, 116.3, 113.1, 93.5, 44.6. **MS EI** *m/z* (rel. intensity) 479(11), 390(13), 388(25), 386(13), 97(100), 91(24). **HRMS** Calculated for $C_{20}H_{17}Br_2NOS$: 476.9398, Found 476.9403. mp = 68-70°C (hexanes/EtOAc).

methyl 3-(2,2-dibromovinyl)-4-[(3-thienylmethyl)amino]benzoate (**1e**).



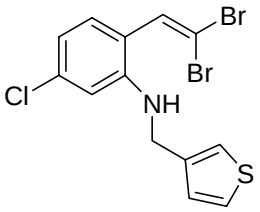
The general procedure was followed (3.0 mmol scale). The product was purified by column chromatography eluting with 10 % EtOAc/hexanes to give 923 mg (71 %) as a brown oil. **IR** ($CDCl_3$) 3368, 3097, 2988, 1698, 1602, 1573, 1518, 1434, 1287, 1233, 1192, 1127, 986, 927, 822, 765. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.94-7.92 (m, 1H), 7.90 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.34 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.24 (s, 1H), 7.19 (dd, *J* = 2.9, 1.2 Hz, 1H), 7.06 (dd, *J* = 5.0, 1.3 Hz, 1H), 6.64 (d, *J* = 8.6 Hz, 1H), 4.45 (s, 3H), 3.86 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 167.1, 148.4, 139.2, 133.3, 132.1, 131.5, 127.0, 126.9, 122.3, 121.1, 118.7, 110.2, 95.5, 52.0, 43.5. **MS EI** *m/z* (rel. intensity) 434(11), 433(22), 432(11), 270(17), 97(100). **HRMS** Calculated for $C_{15}H_{13}Br_2NO_2S$: 428.9034, Found 428.9026.

5-(benzyloxy)-2-(2,2-dibromovinyl)-N-(3-thienylmethyl)aniline (**1f**).



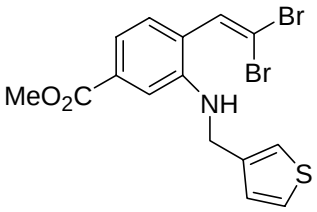
The general procedure was followed (3.0 mmol scale). The product was purified by column chromatography eluting with 5 % EtOAc/hexanes to give 0.95 g (67 %) as a brown oil. **IR** ($CDCl_3$) 3430, 3105, 2989, 2857, 1602, 1576, 1512, 152, 1438, 1384, 1355, 1305, 1259, 1217, 1199, 1158, 1120, 1064, 1023, 994, 937, 908, 854, 811, 795, 777, 704, 691. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.41-7.30 (m, 6H), 7.23-7.21 (m, 2H), 7.17 (m, 1H), 7.06 (dd, *J*= 5.0, 1.1 Hz, 1H), 6.39 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.30 (d, *J* = 2.4 Hz, 1H), 5.01 (s, 2H), 4.33 (s, 2H), 3.98 (br s, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 160.7, 146.4, 139.9, 137.2, 133.7, 130.6, 128.8, 128.2, 127.8, 127.3, 126.6, 122.2, 115.3, 103.2, 98.7. 92.6, 70.2, 43.8. **MS EI** *m/z* (rel. intensity) 479(26), 477(12), 320(18), 319(97), 318(17), 228(100), 97(59), 91(91). **HRMS** Calculated for $C_{20}H_{17}Br_2NOS$: 476.9398, Found 476.9401.

5-chloro-2-(2,2-dibromovinyl)-N-(3-thienylmethyl)aniline (**1g**).



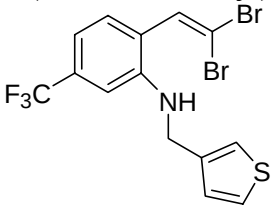
The general procedure was followed (1.36 mmol scale). The product was purified by column chromatography eluting with 5 % EtOAc/hexanes to give 465 mg (84 %) as a yellow solid. **IR** ($CDCl_3$) 3420, 3093, 2990, 2846, 1594, 1568, 1499, 1463, 1446, 1409, 1388, 1310, 1280, 1256, 1239, 1181, 1150, 1128, 1076, 1062, 909, 887, 858, 800, 773, 753, 719, 688. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.33 (dd, *J* = 4.9, 3.0 Hz, 1H), 7.26 – 7.22 (m, 2H), 7.17-7.13(m, 2H), 7.06 (dd, *J* = 4.9, 1.1 Hz, 1H), 6.58 (d, *J* = 8.7 Hz, 1H), 4.36 (d, *J* =5.4 Hz, 2H), 3.98 (t, *J* = 4.9 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 143.6, 139.8, 133.0, 129.1, 127.1, 126.8, 123.2, 122.2, 122.1, 112.5, 95.0, 43.9. **MS EI** *m/z* (rel. intensity) 408(17), 406(23), 246(19), 97(100). **HRMS** Calculated for $C_{13}H_{10}Br_2ClNS$: 404.8589, Found 404.8593. mp = 104-105°C (hexanes/EtOAc).

methyl 4-(2,2-dibromovinyl)-3-[(3-thienylmethyl)amino] (**1h**).



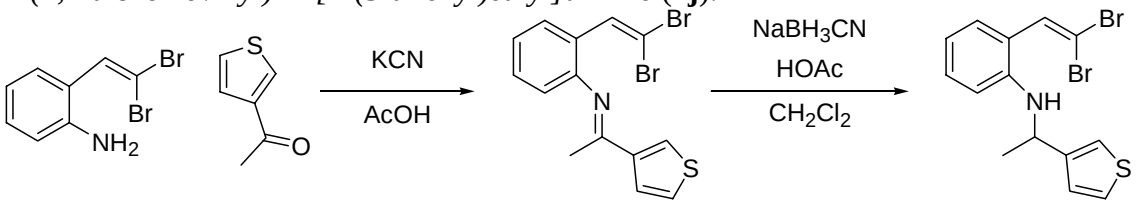
The general procedure was followed (2.0 mmol scale). The product was purified by column chromatography eluting with 10 % EtOAc/hexanes to give 657 mg (76 %) as a yellow oil. **IR** ($CDCl_3$) 3403, 3099, 2948, 2833, 1716, 1607, 1571, 1514, 1435, 1299, 1243, 1110, 1008, 875, 759, 725. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.42 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.38-7.33 (m, 3H), 7.28 (s, 1H). 7.22 (m, 1H), 7.10 (dd, *J* = 5.0, 1.1 Hz, 1H), 4.43 (d, *J* = 5.5 Hz, 2H), 4.00 (t, *J* = 5.4 Hz, 1H), 3.89 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 167.3, 145.0, 139.6, 133.5, 131.5, 129.5, 127.3, 126.7, 126.2, 122.4, 118.6, 112.1, 95.0, 52.4, 43.7. **MS EI** *m/z* (rel. intensity) 433(25), 431(61), 429(30), 352(22), 350(36), 348(11), 271(37), 270(76), 269(12), 224(14), 222(15), 210(19), 97(100). **HRMS** Calculated for $C_{15}H_{13}Br_2NO_2S$: 428.9034, Found 428.9042.

2-(2,2-dibromovinyl)-5-trifluoromethyl-N-(3-thienylmethyl)aniline (**1i**).



The general procedure was followed (2.0 mmol scale). The product was purified by column chromatography eluting with 5 % EtOAc/hexanes to give 690 mg (78 %) as a brown oil. **IR** ($CDCl_3$) 3417, 3099, 2853, 1615, 1579, 1515, 1463, 1435, 1328, 1282, 1255, 1266, 1122, 1083, 932, 868, 763, 745, 667. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.37-7.32 (m, 2H), 7.28-7.24 (m, 1H), 7.22-7.21 (m, 1H), 7.09 (d, *J* = 5.0 Hz, 1H), 6.99 (d, *J* = 7.8 Hz, 1H), 6.88 (s, 1H), 4.40 (d, *J* = 5.4 Hz, 2H), 4.11 (br s, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 145.1, 139.2, 133.1, 132.0 (q, *J* = 32 Hz), 129.9, 127.2, 126.9, 125.0 (q, *J* = 1 Hz), 124.4 (q, *J* = 273 Hz), 122.6, 113.9 (q, *J* = 4 Hz), 107.6 (q, *J* = 4 Hz), 95.5, 43.6. **^{19}F NMR** (282 MHz, $CDCl_3$) δ = -63.4. **MS EI** *m/z* (rel. intensity) 443(15), 441(32), 439(16), 362(12), 360(17), 281(19), 180(48), 97(100). **HRMS** Calculated for $C_{14}H_{10}Br_2F_3NS$: 438.8853, Found 438.8831.

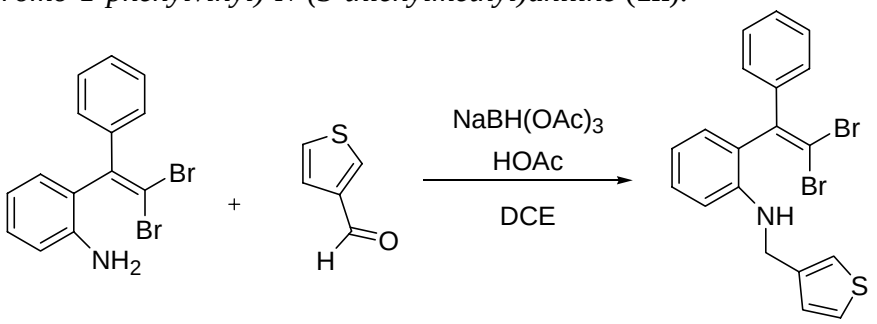
2-(2,2-dibromovinyl)-N-[1-(3-thienyl)ethyl]aniline (**1j**).



The imine *(2-(2,2-dibromovinyl)-N-[(1E)-1-(3-thienyl)ethylidene]aniline)* was prepared as follows: The *gem*-bromoaniline (554 mg, 2.0 mmol), ketone (252 mg, 2.0 mmol) and potassium cyanide (130 mg, 2.0 mmol) were dissolved in acetic acid in a round bottom flask and stirred under an atmosphere of nitrogen overnight. The imine precipitated from solution as a white solid, which was isolated by filtration and washed with methanol to give 351 mg (46 %) of the product as a white solid. **IR** ($CDCl_3$) 3096, 3007, 1625, 1593, 1565, 1519, 1495, 1468, 1444, 1423, 1410, 1388, 1360, 1297, 1271, 1223, 1185, 1159, 1090, 1070, 1042, 951, 913, 905, 883, 874, 855, 840, 829, 804, 786, 753, 737, 711, 674. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.81 (dd, *J* = 2.9, 1.1 Hz, 1H), 7.75-7.70 (m, 2H), 7.38-7.26 (m, 3H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.72 (d, *J* = 7.9 Hz, 1H), 2.16 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 162.5, 149.2, 143.4, 134.9, 129.5, 129.1, 127.6, 127.0, 126.2, 123.4, 119.6, 90.0, 18.8. **MS ESI** *m/z* (rel. intensity) 388(17), 386(34), 384(16), 280(13), 278(25), 276(12), 198(8), 196(9), 118(45), 117(100). **HRMS** Calculated for $C_{14}H_{12}Br_2NS$: 383.9051, Found 383.9039. mp = 111-112 °C (AcOH).

The imine was reduced to the title compound as follows: the imine (300 mg, 0.78 mmol) was dissolved in dichloromethane (4 mL). Sodium cyanoborohydride (122 mg, 1.95 mmol, 2.5 equiv) was added, and then acetic acid was added in 50 μL increments until the reaction was deemed complete by TLC (about 200 μL of acetic acid were added over 2 h). The reaction was quenched by the addition of sodium hydroxide (10 % aqueous solution), extracted with Et_2O, washed with water, dried ($MgSO_4$), filtered and concentrated. The crude product was purified by chromatography eluting with 1 % Et_2O/pentane to give 250 mg (83%) of the title compound as a colourless oil. **IR** ($CDCl_3$) 3409, 2968, 1601, 1578, 1503, 1458, 1415, 1372, 1316, 1260, 1172, 1129, 1082, 1049, 936, 906, 875, 859, 832, 782, 746, 679. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.31-7.24 (m, 3H), 7.17-7.11 (m, 2H), 7.05 (dd, *J* = 5.0, 1.2 Hz, 1H), 6.71 (td, *J* = 7.4, 0.7 Hz, 1H), 6.55 (d, *J* = 8.2 Hz, 1H), 4.66 (q, *J* = 6.4 Hz, 1H), 3.85 (br s, 1H), 1.58 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 146.2, 144.3, 134.4, 130.0, 129.5, 126.4, 126.2, 121.9, 120.4, 117.2, 112.2, 93.6, 49.6, 23.9. **MS EI** *m/z* (rel. intensity) 389(22), 387(50), 385(23), 374(20), 372(47), 370(21), 309(13), 308(92), 307(14), 306(92), 277(17), 275(10), 226(19), 212(35), 198(36), 197(22), 196(35), 195(18), 117(45), 116(21), 111(100), 110(12), 90(12), 89(19). **HRMS** Calculated for $C_{14}H_{13}Br_2NS$: 384.9135, Found 384.9144.

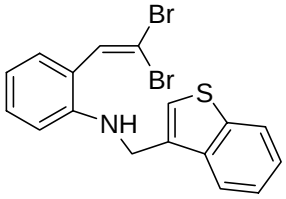
2-(2,2-dibromo-1-phenylvinyl)-N-(3-thienylmethyl)aniline (**1k**).



The *gem*-dibromohalovinyl aniline was preapred using an analagous method to that of Fang.[3] **IR** ($CDCl_3$) 3454, 3378, 3051, 3017, 1615, 1572, 1489, 1451, 1300, 1154, 1028, 948, 834, 776, 747, 697, 619, 606. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.44-7.40 (m, 2H), 7.36-7.28 (m, 3H), 7.14 (td, *J* = 7.9, 1.6 Hz, 1H), 7.07 (dd, *J* = 7.7, 1.5 Hz, 1H), 6.77 (td, *J* = 7.5, 1.0 Hz, 1H), 6.72 (d, *J* = 8.1 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 145.2, 142.2, 139.6, 129.39, 129.37, 128.6, 128.33, 128.26, 128.1, 118.9, 116.5, 92.1. **MS EI** *m/z* (rel. intensity) 355(3), 353(6), 251(3), 274(39), 273(15), 272(40), 271(10) 194(17), 193(100), 192(10), 165(21). **HRMS** Calculated for $C_{14}H_{11}Br_2N$: 350.9292, Found 350.9295. mp = 99-101°C (hexanes/EtOAc).

For the reductive amination, the general procedure was followed (2.0 mmol scale). The product was purified by column chromatography eluting with 2 % Et_2O/pentane to give 710 mg (79 %) as a brown oil. **IR** ($CDCl_3$) 3408, 3052, 1612, 1576, 1496, 1453, 1428, 1375, 1304, 1250, 1159, 1112, 1069, 1042, 1018, 940, 876, 835, 814, 745, 721. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.42-7.36 (m, 2H), 7.35-7.24 (m, 4H), 7.19 (td, *J* = 7.8, 1.5 Hz, 1H), 7.11 (dd, *J* = 7.6, 1.5 Hz, 1H), 6.99 (m, 1H), 6.89 (dd, *J* = 5.0, 1.1 Hz, 1H), 6.74 (td, *J* = 7.5, 0.9 Hz, 1H), 6.65 (d, *J* = 8.2 Hz, 1H), 4.34 (d, *J* = 5.6 Hz, 2H), 4.20 (t, *J* = 5.4 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 145.4, 144.1, 140.4, 129.8, 129.6, 129.0, 128.57, 128.55, 128.0, 127.1, 126.4, 117.5, 111.7, 92.8, 43.8. **MS EI** *m/z* (rel. intensity) 451(3), 449(6), 447(3), 370(8), 368(10), 290(17), 289(53), 288(11), 273(15), 271(15), 165(13), 98(11), 97(100). **HRMS** Calculated for $C_{19}H_{15}Br_2NS$: 446.9292, Found 446.9301.

N-(1-benzothien-3-ylmethyl)-2-(2,2-dibromovinyl)aniline (**3a**).

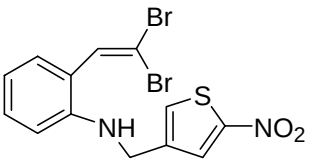


The general procedure was followed (2.0 mmol scale). The product was purified by column chromatography eluting with 2 % Et_2O/pentane to give 700 mg (83 %) as a pale brown solid. **IR** ($CDCl_3$) 3422, 3058, 2833, 1601, 1576, 1506, 1456, 1426, 1378, 1305, 1256, 1162, 1116, 1062, 1045, 1014, 933, 876, 837, 814, 748, 727. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.91-7.88 (m, 1H), 7.83-7.80 (m, 1H), 7.45-7.36 (m, 2H), 7.34-7.21 (m, 5H), 6.78 (t, *J* = 7.6 Hz, 1H), 6.73 (d, *J* = 8.3 Hz, 1H), 4.61 (s, 2H), 4.01 (br s, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 145.0, 141.2, 138.1, 134.2, 133.5, 130.2, 129.6, 124.9, 124.5, 124.0,123.3, 122.2, 121.9,

(3) Fang, Y.Q.; Lautens, M. *J. Org. Chem.* **2008**, *73*, 538.

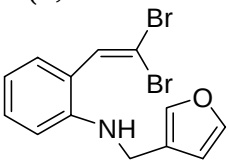
117.7, 111.5, 93.9, 42.9. **MS EI** *m/z* (rel. intensity) 423(15), 262(15), 148(13), 147(100). **HRMS** Calculated for $C_{17}H_{13}Br_2NS$: 420.9135, Found 420.9133. mp = 115-117°C (hexanes/EtOAc).

2-(2,2-dibromovinyl)-N-[(5-nitro-3-thienyl)methyl]aniline (**3b**).



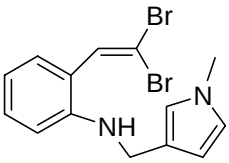
The general procedure was followed (2.0 mmol scale). The product was purified by column chromatography eluting with 2 % Et_2O/pentane to give 595 mg (71 %) as a yellow oil. **IR** ($CDCl_3$) 3416, 3091, 1600, 1578, 1498, 1457, 1400, 1323, 1260, 1193, 1163, 1122, 1078, 985, 937, 907, 874, 812, 746, 729. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.88 (d, *J* = 1.8 Hz, 1H), 7.40-7.39 (m, 1H), 7.33 (s, 1H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.21 (td, *J* = 8.1, 1.2 Hz, 1H), 6.80 (t, *J* = 7.5 Hz, 1H), 6.54 (d, *J* = 8.2 Hz, 1H), 4.39 (d, *J* = 5.6 Hz, 2H), 4.12 (t, *J* = 4.8 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 152.6, 144.2, 140.9, 134.2, 130.2, 129.8, 128.8, 128.3, 122.4, 118.2, 111.3, 94.3, 43.7. **MS EI** *m/z* (rel. intensity) 420(22), 418(39), 416(21), 339(12), 337(15), 259(21), 258(91), 257(34), 212(11), 211(13), 210(19), 197(32), 195(31), 142(100), 130(21), 116(23), 96(45), 89(19), 70(13). **HRMS** Calculated for $C_{17}H_{13}Br_2NS$: 415.8830, Found 415.8832.

2-(2,2-dibromovinyl)-N-(3-furylmethyl)aniline (**3c**).



The general procedure was followed (2.0 mmol scale). The product was purified by column chromatography eluting with 2 % Et_2O/pentane to give 482 mg (68 %) as a brown oil. **IR** ($CDCl_3$) 3407, 1653, 1049, 1025, 1001, 821, 760. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.42-7.41 (m, 2H), 7.29-7.21 (m, 3H), 6.76 (td, *J* = 7.4, 0.9 Hz, 1H), 6.71 (d, *J* = 8.2 Hz, 1H), 6.41 (t, *J* = 1.2 Hz, 1H), 4.21 (d, *J* = 4.9 Hz, 2H), 3.80 (br s, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 145.0, 143.7, 140.3, 134.3, 130.1, 129.5, 123.3, 122.1, 117.6, 111.3, 110.4, 93.6, 39.5. **MS EI** *m/z* (rel. intensity) 359(23), 357(47), 355(24), 278(18), 276(23), 197(64), 196(84), 195(12), 168(35), 167(20), 116(11), 81(100). **HRMS** Calculated for $C_{13}H_{11}Br_2NO$: 354.9207, Found 354.9195.

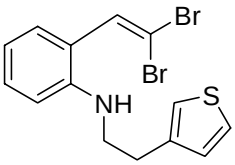
2-(2,2-dibromovinyl)-N-[(1-methyl-1H-pyrrol-3-yl)methyl]aniline (**3d**).



1-methyl-1-*H*-pyrrole-3-carbaldehyde was prepared according to the method of Griengl.[4] The general procedure was followed (0.86 mmol scale). The product was purified by column chromatography eluting with 30 % EtOAc/hexane to give 38 mg (12 %) as a yellow oil. **IR** ($CDCl_3$) 3416, 2937, 2849, 1601, 1576, 1502, 1456, 1437, 1420, 1309, 1257, 1217, 1201, 1186, 1164, 1118, 1050, 999, 936, 876, 859, 816, 791, 770, 745, 697, 671. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.30-7.22 (m, 3H), 6.79-6.70 (m, 2H), 6.6 (m, 1H), 6.57 (t, *J* = 2.5 Hz, 1H), 6.14 (t, *J* = 2.0 Hz, 1H), 4.17 (s, 2H), 3.73 (br s, 1H), 3.64 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 145.7, 134.5, 130.3, 129.6, 122.4, 121.71, 121.68, 120.5, 117.0, 111.3, 108.4, 93.2, 41.7, 36.5. **MS EI** *m/z* (rel. intensity) 372(9), 370(19), 368(7), 198(11), 196(12), 117(66), 94(100). **HRMS** Calculated for $C_{14}H_{14}Br_2N_2$: 367.9524, Found 367.9506.

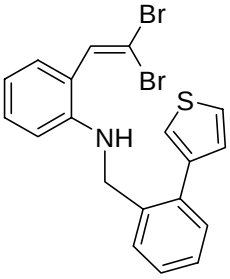
(4) Purkarthofer, T.; Gruber, K.; Fechter, M.H.; Griengl, H. *Tetrahedron* **2005**, *61*, 7661.

2-(2,2-dibromovinyl)-N-[2-(3-thienyl)ethyl]aniline (**5a**).



Thiophen-3-yl-acetaldehyde was prepared according to the method of Bold et al.[5] The aldehyde unstable and must be prepared directly before use. The general procedure was followed (2.0 mmol scale). The product was purified by column chromatography eluting with 2 % Et_2O/pentane to give 463 mg (60 %) as a colourless oil. **IR** ($CDCl_3$) 3403, 2920, 2851, 1602, 1578, 1506, 1456, 1317, 1259, 1181, 1162, 1122, 1077, 1049, 923, 875, 853, 835, 775, 747, 667. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.32 (dd, *J* = 4.9, 2.9 Hz, 1H), 7.26-7.22 (m, 2H), 7.13 (s, 1H), 7.05-7.04 (m, 1H), 6.98 (dd, *J* = 4.9, 1.3 Hz, 1H), 6.73 (td, *J* = 7.6, 1.1 Hz, 1H), 6.69 (d, *J* = 8.2 Hz, 1H), 3.63 (br s, 1H), 3.41 (q, *J* = 6.7 Hz, 2H), 2.98 (t, *J* = 6.9 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 145.0, 139.5, 134.2, 130.1, 129.5, 128.3, 126.4, 122.1, 121.8, 117.2, 111.2, 93.6, 44.4, 30.1. **MS EI** *m/z* (rel. intensity) 390(50), 388(100), 386(48), 308(11), 306(20), 304(10), 290(17), 130 (12), 111(14). **HRMS** Calculated for $C_{14}H_{13}Br_2NS$: 385.9208, Found 385.9201.

2-(2,2-dibromovinyl)-N-[2-(3-thienyl)benzyl]aniline (**5b**).

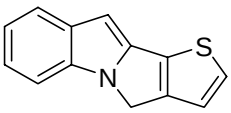


2-thiophen-3-yl benzaldehyde was prepared according to the method of Snieckus.[6] The general procedure was followed (3.0 mmol scale). The product was purified by column chromatography eluting with 2 % EtOAc/hexanes to give 814 mg of a white solid, which was recrystallized from hexanes/EtOAc to give 620 mg (83 %) as a white solid. **IR** ($CDCl_3$) 3411, 3102, 1592, 1575, 1502, 1451, 1425, 1354, 1324, 1201, 1183, 1156, 1126, 1097, 1078, 1045, 986, 939, 894, 875, 843, 814, 792, 750. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.49-7.44 (m, 1H), 7.41-7.30 (m, 5H), 7.26-7.24 (m, 1H), 7.20-7.15 (m, 2H), 7.12 (s, 1H), 6.72 (t, *J* = 7.4 Hz, 1H), 6.56 (d, *J* = 8.2 Hz, 1H), 4.34 (d, *J* = 5.6 Hz, 2H), 3.80 (t, *J* = 5.1 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 144.9, 141.3, 136.7, 136.4, 134.1, 130.7, 130.1, 129.5, 129.4, 128.8, 128.1, 127.9, 126.1, 123.1, 122.0, 117.4, 111.3, 93.6, 46.9. **MS EI** *m/z* (rel. intensity) 449(18), 288(44), 173(100). **HRMS** Calculated for $C_{19}H_{15}Br_2NS$: 446.9292, Found 446.9279. mp = 90-91°C (hexanes/EtOAc).

(5) Bold, G.; Floershiemer, A.; Furet, P.; Guagnano, V.; Masuya, K.; Vaupel, A.; Scoepfer, J. International Patent 047273A1, 2005.

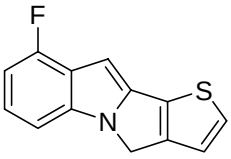
[6] Chamoin, S.; Houldworth, S.; Kruse, C.G.; Iwema Bakker, W.; Snieckus, V.*Tetrahedron Lett.* **1998**, *39*, 4179.

4H-thieno[2',3':3,4]pyrrolo[1,2-a]indole (**2a**).



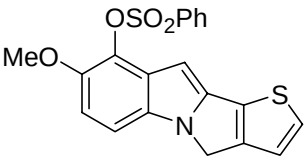
The general procedure was followed (0.13 mmol scale). The product was purified by column chromatography eluting with 1 % Et_2O/pentane to give 25.2 mg (90 %) as a white solid. **IR** (solid) 3100, 3042, 2921, 1911, 1610, 1574, 1561, 1459, 1446, 1352, 1334, 1305, 1274, 1185, 1151, 1105, 1090, 1006, 981, 920, 874, 830, 794, 781, 727, 707. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.62 (d, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 4.9 Hz, 1H), 7.29 (dd, *J* = 8.0, 0.6 Hz, 1H), 7.17 (td, *J* = 7.1, 1.1 Hz, 1H), 7.10-7.04 (m, 2H), 6.41 (d, *J* = 0.6 Hz, 1H), 4.93 (s, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 146.3, 139.8, 134.6, 134.2, 132.5, 128.4, 121.6, 121.4, 121.3, 119.4, 108.5, 90.4, 47.0. **MS EI** *m/z* (rel. intensity) 212(24), 211(100), 210(89), 209(11). **HRMS** Calculated for $C_{13}H_9NS$: 211.0456, Found 211.0452. mp = 153-155°C (pentane/Et_2O).

9-fluoro-4H-thieno[2',3':3,4]pyrrolo[1,2-a]indole (**2b**).



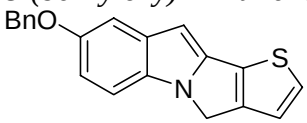
The general procedure was followed (0.13 mmol scale). The product was purified by column chromatography eluting with 1 % Et_2O/pentane to give 26.6 mg (87 %) as a white solid. **IR** (solid) 2958, 2903, 1698, 1621, 1559, 1540, 1487, 1431, 1337, 1267, 1228, 1187, 1144, 994, 956, 826, 772, 739. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.38 (d, *J* = 4.9 Hz, 1H), 7.12-7.05 (m, 3H), 6.79-6.73 (m, 1H), 6.48 (s, 1H), 4.94 (s, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 157.0 (d, *J* = 247 Hz), 146.9, 140.0, 137.2 (d, *J* = 12 Hz), 133.9, 129.1, 122.2 (d, *J* = 8 Hz), 121.6, 121.3, 104.9 (d, *J* = 3 Hz), 104.7 (d, *J* = 19 Hz), 86.6, 47.4. **^{19}F NMR** (282 MHz, $CDCl_3$) δ = -122.2. **MS EI** *m/z* (rel. intensity) 230(19), 229(100), 228(83), 93(10). **HRMS** Calculated for $C_{13}H_8FNS$: 229.0361, Found 229.0359. mp = 128-129°C (pentane/Et_2O).

8-methoxy-4H-thieno[2',3':3,4]pyrrolo[1,2-a]indol-9-yl benzenesulfonate (**2c**).



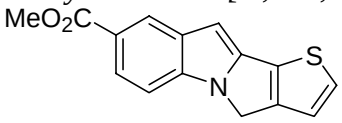
The general procedure was followed (0.13 mmol scale). The product was purified by column chromatography eluting with 35 % EtOAc/hexanes to give 48.5 mg (91 %) as a white solid. **IR** (solid) 3107, 2919, 1633, 1489, 1474, 1450, 1430, 1347, 1333, 1286, 1235, 1193, 1171, 1082, 1054, 997, 965, 923, 842, 814, 791, 750, 738. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.99 (d, *J* = 7.9 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.55-7.50 (m, 2H), 7.37 (d, *J* = 4.9 Hz, 1H), 7.10-7.06 (m, 2H), 6.77 (d, *J* = 8.7 Hz, 1H), 6.33 (s, 1H), 4.88 (s, 2H), 3.55 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 146.9, 145.5, 141.7, 137.2, 133.9, 133.6, 131.4, 131.1, 129.1, 128.7, 128.6, 128.3, 121.2, 108.7, 107.4, 88.1, 57.0, 47.3. **MS EI** *m/z* (rel. intensity) 398(8), 397(27), 258(12), 256(100), 228(18), 213(31), 185(9), 184(10). **HRMS** Calculated for $C_{20}H_{15}NO_4S$: 397.0443, Found 397.0441. mp = 189-191°C (pentane/Et_2O).

8-(benzyloxy)-4H-thieno[2',3':3,4]pyrrolo[1,2-a]indole (**2d**).



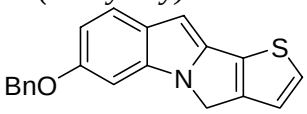
The general procedure was followed (0.13 mmol scale). The product was purified by column chromatography eluting with 4 % Et_2O/pentane to give 34.0 mg (80 %) as a white solid. **IR** (solid) 2916, 1616, 1575, 1493, 1465, 1454, 1436, 1333, 1288, 1242, 1220, 1158, 1135, 1008, 951, 865, 846, 804, 763, 735, 713. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.50-7.46 (m, 2H), 7.42-7.38 (m, 2H), 7.37-7.29 (m, 2H), 7.20 (d, *J* = 6.0 Hz, 1H), 7.18 (s, 1H), 7.07 (d, *J* = 4.9 Hz, 1H), 6.91 (dd, *J* = 8.8, 2.2 Hz, 1H), 6.33 (s, 1H), 5.12 (s, 2H), 4.90 (s, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 153.4, 146.5, 140.7, 138.0, 134.6, 133.2, 130.5, 128.7, 128.4, 128.0, 127.8, 121.5, 112.4, 109.3, 105.7, 90.5, 71.2, 47.4. **MS EI** *m/z* (rel. intensity) 317(8), 227(13), 226(30), 198(11) 84(100). **HRMS** Calculated for $C_{13}H_9NS$: 317.0874, Found 317.0859. mp = 174-176°C (sublimes).

methyl 4H-thieno[2',3':3,4]pyrrolo[1,2-a]indole-8-carboxylate (**2e**).



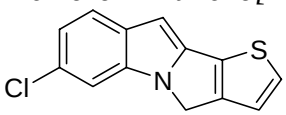
The general procedure was followed (0.13 mmol scale). The product was purified by column chromatography eluting with 10 % Et_2O/pentane to give 26.2 mg (73 %) as a brown solid. **IR** (solid) 3088, 3072, 2941, 1696, 1610, 1568, 1472, 1454, 1432, 1333, 1307, 1255, 1192, 1147, 1088, 972, 910, 801, 790, 760, 743. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 8.37 (d, *J* = 1.4 Hz, 1H), 7.89 (dd, *J* = 8.5, 1.4 Hz, 1H), 7.40 (d, *J* = 4.9 Hz, 1H), 7.29 (d, *J* = 8.6 Hz, 1H), 7.10 (d, *J* = 4.9 Hz, 1H), 6.49 (s, 1H), 4.96 (s, 2H), 3.93 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 168.4, 146.8, 141.4, 137.3, 133.9, 132.4, 129.5, 124.6, 123.4, 121.64, 121.60, 108.2, 91.9, 52.0, 47.5. **MS EI** *m/z* (rel. intensity) 270(19), 269(100), 268(19), 238(24), 211(12), 210(66), 209(20). **HRMS** Calculated for $C_{15}H_{11}NO_2S$: 269.0511, Found 269.0513. mp = 195°C (decomposes).

7-(benzyloxy)-4H-thieno[2',3':3,4]pyrrolo[1,2-a]indole (**2f**).



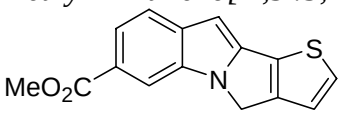
The general procedure was followed (0.13 mmol scale). The product was purified by column chromatography eluting with 5 % Et_2O/pentane to give 34.5 mg (81 %) as a brown solid. **IR** (solid) 3103, 3067, 2926, 1615, 1581, 1561, 1499, 1483, 1464, 1455, 1434, 1387, 1373, 1361, 1341, 1275, 1241, 1222, 1195, 1183, 1136, 1111, 1026, 1000, 985, 945, 918, 876, 856, 808, 775, 747, 700, 667. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.50-7.37 (m, 3H), 7.42-7.37 (m, 2H), 7.35-7.30 (m, 2H), 7.06 (d, *J* = 4.9 Hz, 1H), 6.85 (d, *J* = 2.3 Hz, 1H), 6.82 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.34 (d, *J* = 0.8 Hz, 1H), 5.14 (s, 2H), 4.87 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 155.6, 145.8, 139.2, 137.7, 135.5, 134.6, 128.8, 128.1, 128.0, 127.8, 127.2, 122.4, 121.5, 109.8, 94.2, 90.5, 70.9, 47.1. **MS EI** *m/z* (rel. intensity) 318(10), 317(37), 228(10), 227(25), 226(100), 198(15), 197(10), 91(15). **HRMS** Calculated for $C_{20}H_{15}NOS$: 317.0874, Found 317.0871. mp = 168-170°C (sublimes).

7-chloro-4H-thieno[2',3':3,4]pyrrolo[1,2-a]indole (**2g**).



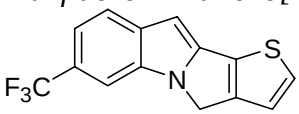
The general procedure was followed (0.13 mmol scale). The product was purified by column chromatography eluting with 8 % EtOAc/hexanes to give 30.3 mg (92 %) as a yellow solid. **IR** (solid) 3110, 2924, 2854, 1728, 1570, 1445, 1376, 1356, 1320, 1275, 1232, 1209, 1177, 1163, 1148, 1083, 1058, 983, 908, 872, 843, 781, 707, 672. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.56 (d, *J* = 1.9 Hz, 1H), 7.38 (d, *J* = 4.9 Hz, 1H), 7.19 (d, *J* = 8.6 Hz, 1H), 7.13-7.07 (m, 2H), 6.34 (s, 1H), 4.91 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 146.9, 134.1, 133.8, 133.3, 129.2, 128.6, 125.2, 121.8, 121.6, 121.1, 109.5, 90.3, 47.5. **MS EI** *m/z* (rel. intensity) 247(33), 246(29), 245(99), 244(51), 211(14), 210(100), 209(18). **HRMS** Calculated for $C_{13}H_8ClNS$: 245.0066, Found 245.0064. mp = 133-134°C (EtOAc/hexanes).

methyl 4H-thieno[2',3':3,4]pyrrolo[1,2-a]indole-7-carboxylate (**2h**).



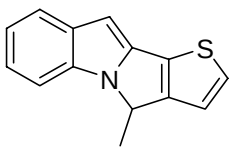
The general procedure was followed (0.13 mmol scale). The product was purified by column chromatography eluting with 5-10 % EtOAc/hexanes to give 31.7 mg (88 %) as a white solid. **IR** (solid) 3103, 2947, 2853, 1708, 1617, 150, 1484, 1465, 1433, 1365, 1346, 1282, 1247, 1208, 1186, 1099, 975, 915, 877, 834, 774, 734, 667. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 8.05 (s, 1H), 7.77 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.42 (d, *J* = 4.9 Hz, 1H), 7.12 (d, *J* = 4.9 Hz, 1H), 6.45 (s, 1H), 5.00 (s, 2H), 3.95 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 168.4, 147.6, 143.3, 136.7, 134.1, 133.8, 129.8, 122.9, 121.7, 121.0, 120.9, 110.8, 91.1, 52.1, 47.6. **MS EI** *m/z* (rel. intensity) 270(17), 269(93), 254(11), 238(41), 211(18), 210(100), 209(29). **HRMS** Calculated for $C_{15}H_{11}NO_2S$: 269.0511, Found 269.0504. mp = 155-156°C (EtOAc/hexanes).

7-trifluoro-4H-thieno[2',3':3,4]pyrrolo[1,2-a]indole (**2i**).



The general procedure was followed (0.13 mmol scale). The product was purified by column chromatography eluting with 1-2 % EtOAc/hexanes to give 32.2 mg (86 %) as a white solid. **IR** (solid) 3099, 1560, 1504, 1491, 1468, 1433, 1348, 1318, 1291, 1268, 1151, 1100, 1058, 918, 867, 818, 762, 734, 711, 669, 655. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.67 (d, *J* = 8.3 Hz, 1H), 7.56 (s, 1H), 7.42 (d, *J* = 4.9 Hz, 1H), 7.31 (d, *J* = 8.3 Hz, 1H), 7.12 (d, *J* = 4.9 Hz, 1H), 6.46 (s, 1H), 4.99 (s, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 147.3, 142.6, 135.2, 133.7, 129.8, 127.0 (q, *J* = 21 Hz), 125.5, (q, *J* = 271 Hz), 123.4 (q, *J* = 32 Hz), 121.8, 121.6, 116.3 (q, *J* = 4 Hz), 106.1 (q, *J* = 4 Hz), 90.9, 47.5. **^{19}F NMR** δ = -60.9. **MS EI** *m/z* (rel. intensity) 280(20), 279(100), 278(69), 211(12), 210(76), 84(11). **HRMS** Calculated for $C_{14}H_8F_3NS$: 279.0330, Found 279.0327. mp = 130°C (decomp.).

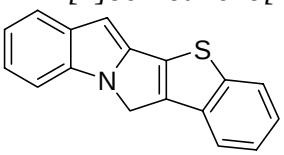
4-methyl-4H-thieno[2',3':3,4]pyrrolo[1,2-a]indole (**2j**).



The general procedure was followed (0.13 mmol scale). The product was purified by column chromatography eluting with 1 % Et_2O/pentane to give 25.0 mg (83 %) as a white solid. **IR** (solid) 3099, 3051, 2982, 2932, 1573, 1562, 1477, 1450, 1431, 1352, 1333, 1305, 1269, 1232, 1203, 1184, 1151, 1136, 1096, 1084, 1046, 1008,

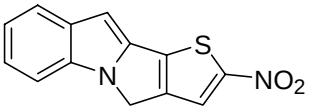
920, 882, 844, 818, 781, 746, 737, 723, 688, 668. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.63 (d, *J* = 7.9 Hz, 1H), 7.35 (dd, *J* = 8.1, 0.7 Hz, 1H), 7.32 (d, *J* = 4.9 Hz, 1H), 7.17 (td, *J* = 7.1, 1.1 Hz, 1H), 7.07 (td, *J* = 8.1, 1.0 Hz, 1H), 7.03 (d, *J* = 4.9 Hz, 1H), 6.39 (s, 1H), 5.23 (q, *J* = 6.7 Hz, 1H), 1.73 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 152.7, 138.9, 134.1, 133.1, 132.9, 128.4, 121.6, 121.4, 120.7, 119.2, 108.7, 90.3, 55.5, 19.8. **MS EI** *m/z* (rel. intensity) 226(25), 225(77), 224(67), 223(93), 222(29), 211(12), 210(100), 111(11). **HRMS** Calculated for $C_{14}H_{11}NS$: 225.0612, Found 225.0610. mp = 116-117°C (Et_2O/pentane).

12H-[1]benzothieno[2',3':3,4]pyrrolo[1,2-a]indole (**4a**).



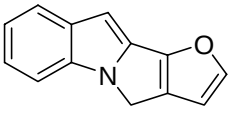
The general procedure was followed (0.13 mmol scale). The product was purified by column chromatography eluting with 1-2 % Et_2O/pentane to give 27.4 mg (78 %) as a white solid. **IR** (solid) 2921, 2851, 1558, 1456, 1418, 1332, 1307, 1260, 1222, 1191, 1147, 1102, 1013, 973, 902, 771, 733, 724. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.89 (d, *J* = 7.9 Hz, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.43 (t, *J* = 6.9 Hz, 1H), 7.37-7.32 (m, 2H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.10 (t, *J* = 7.8 Hz, 1H), 6.52 (s, 1H), 5.12 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 144.0, 140.3, 140.1, 135.0, 134.4, 133.7, 132.6, 125.2, 124.3, 123.9, 122.0, 121.9, 121.0, 119.6, 108.6, 92.0, 46.8. **MS EI** *m/z* (rel. intensity) 262(8), 261(31), 260(36), 235(52), 138(25), 137(100), 136(25), 135(100). **HRMS** Calculated for $C_{17}H_{11}NS$: 261.0612, Found 261.0616. mp = 191-192°C (sublimes).

2-nitro-4H-thieno[2',3':3,4]pyrrolo[1,2-a]indole (**4b**).



The general procedure was followed (0.13 mmol scale), but the reaction was heated for 40 h instead of heating overnight. The product was purified by column chromatography eluting with 10 % Et_2O/pentane to give 17.3 mg (50 %) as a red solid. **IR** (solid) 3097, 1567, 1558, 1508, 1485, 1476, 1312, 1298, 1269, 1178, 1150 ,1134, 1082, 1035, 780, 750, 730. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.98 (s, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.37-7.25 (m, 2H), 7.15 (td, *J* = 8.0, 1.2 Hz, 1H), 6.71 (s, 1H), 5.02 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 142.5, 141.1, 136.8, 135.3, 132.5, 123.7, 123.4, 122.7, 120.6, 109.2, 95.3, 47.1. **MS EI** *m/z* (rel. intensity) 256(10), 226(14), 225(18), 224(100), 223(30), 210(15), 192(20). **HRMS** Calculated for $C_{13}H_8N_2O_2S$: 256.0306, Found 256.0302. mp = 175-176°C.

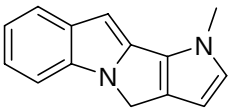
4H-furo[2',3':3,4]pyrrolo[1,2-a]indole (**4c**).



The general procedure was followed (0.13 mmol scale). The product was purified by column chromatography eluting with 2 % Et_2O/pentane to give 19.8 mg (72 %) as a yellow solid. **IR** (solid) 3051, 2922, 2860, 2359, 1625, 1462, 1422, 1371, 1337, 1310, 1286, 1194, 1130, 1076, 1032, 1008, 765, 743, 683. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.61 (d, *J* = 7.9 Hz, 1H), 7.51 (d, *J* = 1.8 Hz, 1H), 7.28 (d, *J* = 8.1 Hz, 1H), 7.17 (td, *J* = 7.1, 1.1 Hz, 1H), 7.06 (td, *J* = 8.0, 1.1 Hz, 1H), 6.57 (d, *J* = 1.8 Hz, 1H), 6.39 (d, *J* = 0.7 Hz, 1H), 4.79 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 152.0, 146.7, 135.4, 132.4, 128.6, 122.1, 121.8, 119.6, 108.4, 108.2, 89.5, 44.6. **MS EI** *m/z* (rel. intensity) 196(14),

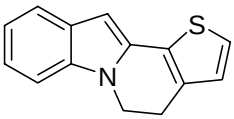
195(100), 194(22), 168(12), 167(95), 166(35), 140(17), 139(19). **HRMS** Calculated for $C_{13}H_9NO$: 195.0684, Found 195.0678. mp = 92-93°C.

1-methyl-1,4-dihydropyrrolo[2',3':3,4]pyrrolo[1,2-a]indole (**4d**).



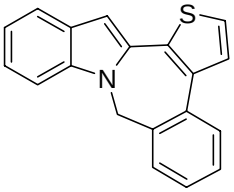
The general procedure was followed (0.13 mmol scale). The product was purified by recrystallization from Et_2O/pentane to give 15.2 mg (55 %) as a white solid. **IR** (solid) 3098, 3046, 2924, 1621, 1548, 1496, 1476, 1451, 1404, 1380, 1339, 1322, 1300, 1269, 1227, 1190, 1147, 1106, 1058, 1013, 986, 923, 843, 777, 768, 744, 736, 717, 686. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.56 (d, *J* = 7.8 Hz, 1H), 7.25 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.12 (td, *J* = 7.1, 1.1 Hz, 1H), 7.03 (td, *J* = 7.9, 1.1 Hz, 1H), 6.64 (d, *J* = 2.6 Hz, 1H), 6.22 (s, 1H), 6.15 (d, *J* = 2.6 Hz, 1H), 4.78 (s, 2H), 3,84 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 137.2, 135.2, 133.0, 131.0, 128.5, 125.9, 121.2, 121.0, 119.1, 108.3, 103.7, 87.1, 45.4, 35.3. **MS EI** *m/z* (rel. intensity) 208(98), 207(100), 206(12), 192(15). **HRMS** Calculated for $C_{14}H_{12}N_2$: 208.1000, Found 208.1005. mp = 178-180 °C (sublimes).

4,5-dihydrothieno[2',3':3,4]pyrido[1,2-a]indole (**6a**).



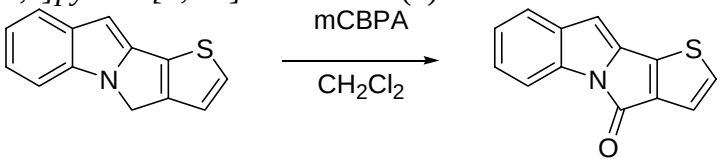
The general procedure was followed (0.13 mmol scale). The product was purified column chromatography eluting with 1% Et_2O/pentane to give 24.9 mg (83 %) as a white solid. **IR** (solid) 3045, 2897, 1909, 1871, 1794, 1651, 1601, 1579, 1507, 1453, 1429, 1384, 1345, 1323, 11304, 1240, 1213, 1198, 1151, 1110, 1088, 1040, 1006, 988, 961, 917, 894, 878, 825, 775, 744, 731, 709. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.58 (d, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.22-7.16 (m, 2H), 7.08 (td, *J* = 7.4, 1.0 Hz, 1H), 6.94 (d, *J* = 5.0 Hz, 1H), 6.59 (s, 1H), 4.25 (t, *J* = 6.8 Hz, 2H), 3.15 (t, *J* = 6.8 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 136.7, 133.4, 132.5, 129.2, 129.0, 127.1, 123.8, 121.8, 120.5, 119.9, 108.9, 96.0, 40.6, 25.2. **MS EI** *m/z* (rel. intensity) 226(19), 225(100), 224(42), 223(29). **HRMS** Calculated for $C_{14}H_{11}NS$: 225.0612, Found 226.0613. mp = 104-106 °C (Et_2O/pentane).

5H-indolo[1,2-b]thieno[2,3-d][2]benzazepine (**6b**).



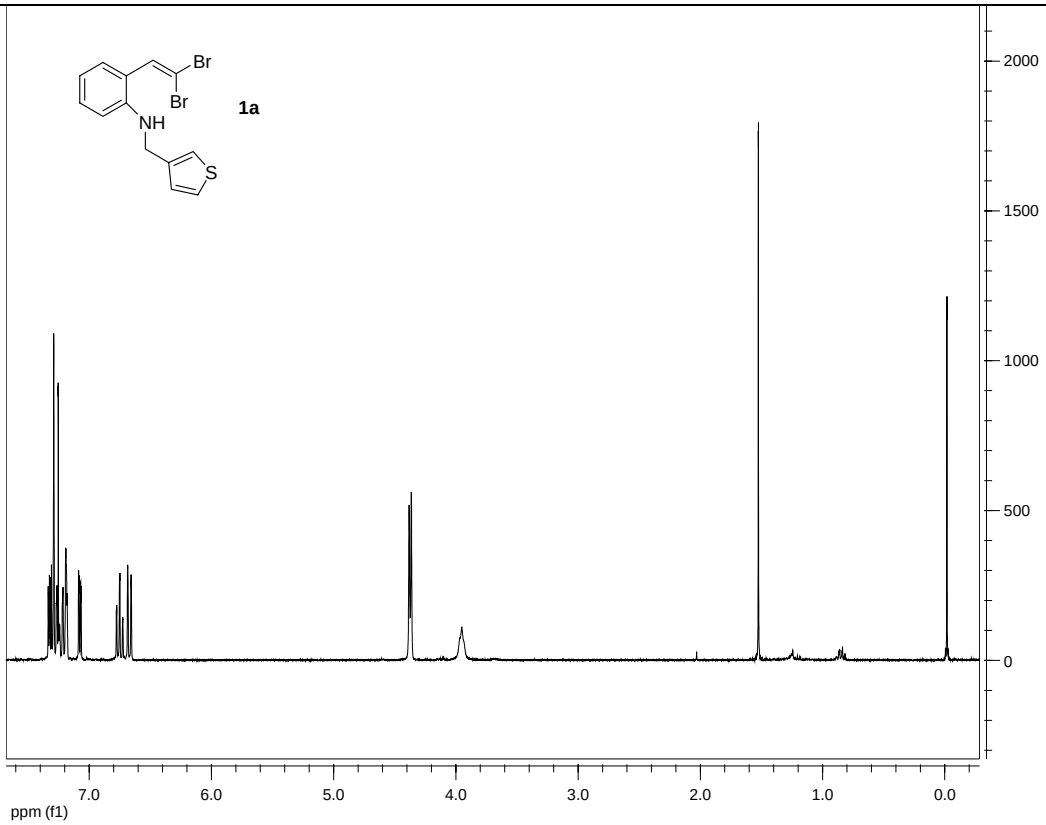
The general procedure was followed (0.096 mmol scale). The product was purified column chromatography eluting with 1% Et_2O/pentane to give 10.8 mg (54 %) as a white solid. **IR** (solid) 3052, 2908, 1456, 1442, 1413, 1354, 1336, 1313, 1267, 1244, 1158, 1132, 1110, 1089, 1065,1012, 885, 835, 824, 767, 745, 718. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.62-7.59 (m, 2H), 7.54 (d, *J* = 8.1 Hz, 1H), 7.48 (dd, *J* = 7.2, 1.4 Hz, 1H), 7.44-7.36 (m, 3H), 7.32 (td, *J* = 7.4, 1.6 Hz, 1H), 7.28-7.22 (m, 1H), 7.09 (td, *J* = 7.5, 0.8 Hz, 1H), 6.69 (s, 1H), 5.16 (s, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 137.2, 136.4, 135.7, 135.6, 134.0, 132.2, 129.0, 128.8, 128.7,128.7, 128.1, 125.5, 122.10, 121.07, 120.1. 109.1. 99.8, 48.0. **MS EI** *m/z* (rel. intensity) 287(100), 254(30). **HRMS** Calculated for $C_{19}H_{13}NS$: 287.0769, Found 287.0768. mp = 189-190 °C (Et_2O/pentane).

4H-thieno[2',3':3,4]pyrrolo[1,2-a]indol-4-one (**7**).



The tetracycle (40 mg, 0.4 mmol) was dissolved in CH_2Cl_2 (8 mL). mCPBA (57-86% w/w, 245 mg, 0.8-1.2 mmol, 2-3 equiv) was added, and the reaction stirred overnight under nitrogen. Et_2O was added, and the solution was washed with water and brine, dried ($MgSO_4$), filtered and concentrated. The product was purified column chromatography eluting with 1% Et_2O/pentane to give 55 mg (61 %) as a brown solid. **IR** (solid) 3094, 1663, 1615, 1596, 1559, 1487, 1451, 1412, 1314, 1179, 1082, 1027, 905, 867, 832, 779, 744, 730, 705, 689. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.56 (d, *J* = 6.9 Hz, 1H), 7.39 (td, *J* = 7.7, 1.2 Hz, 1H), 7.28 (s, 1H), 7.16-7.12 (m, 2H), 7.04 (d, *J* = 5.3 Hz, 1H), 6.91 (d, *J* = 5.3 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 176.5, 143.2, 139.2, 133.4, 131.0, 130.6, 128.8, 126.3, 124.1, 121.7, 116.4, 110.5. **MS EI** *m/z* (rel. intensity) 226(14), 225(100), 196(10), 149(14), 86(12), 84(19). **HRMS** Calculated for $C_{13}H_7NOS$: 225.0248, Found 225.0251. mp = 174-175 °C (sublimes).

Spectra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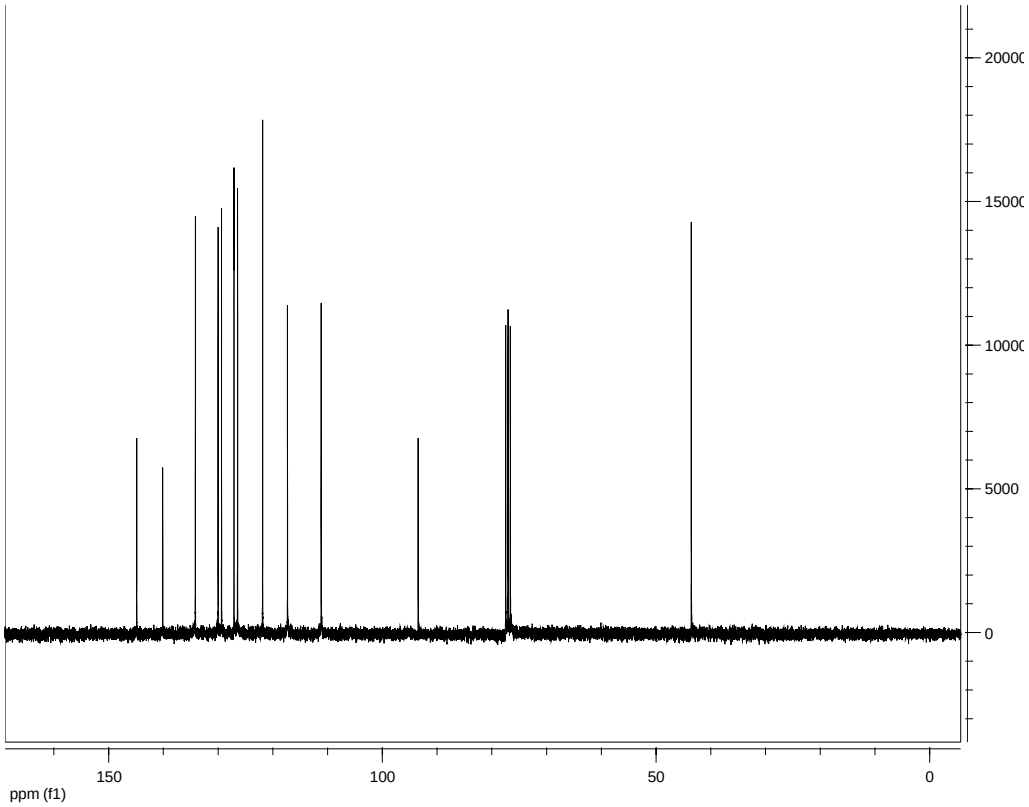
0.0
ppm (f1)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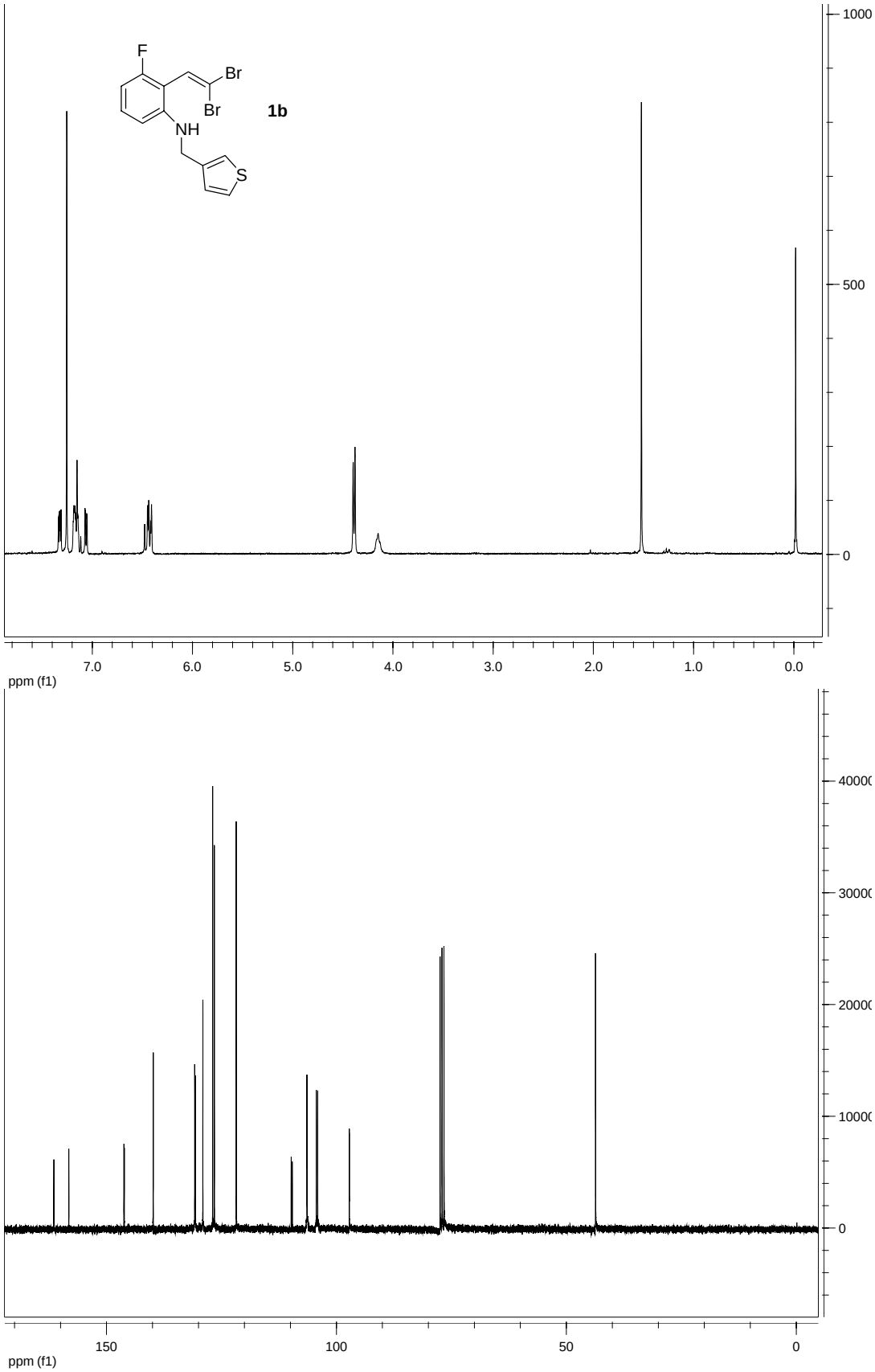
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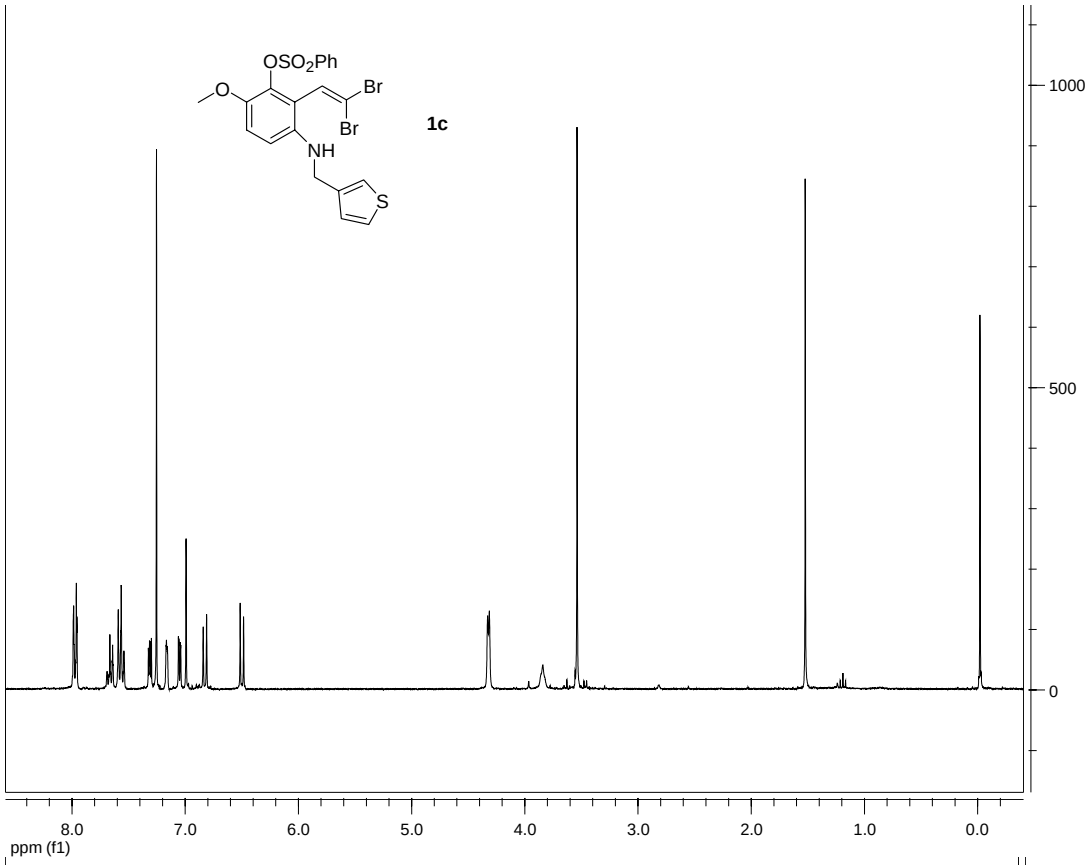
ppm (f1)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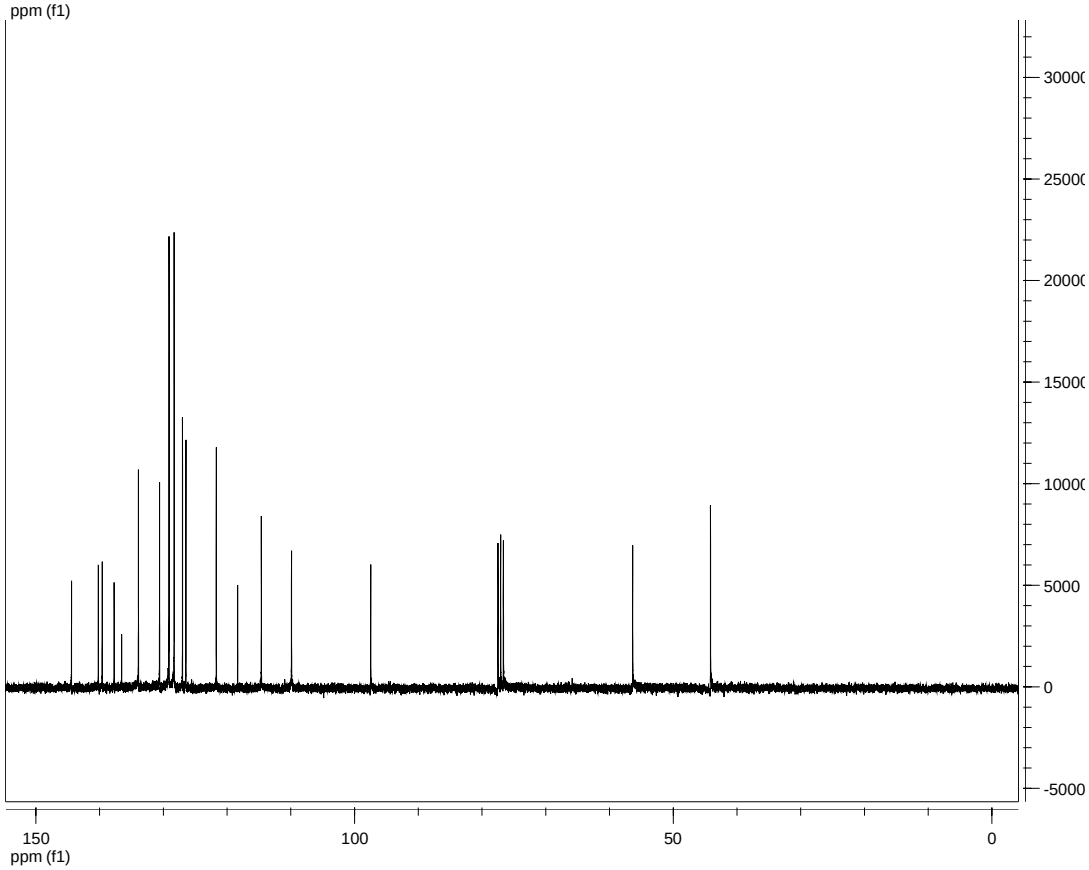
ppm (f1)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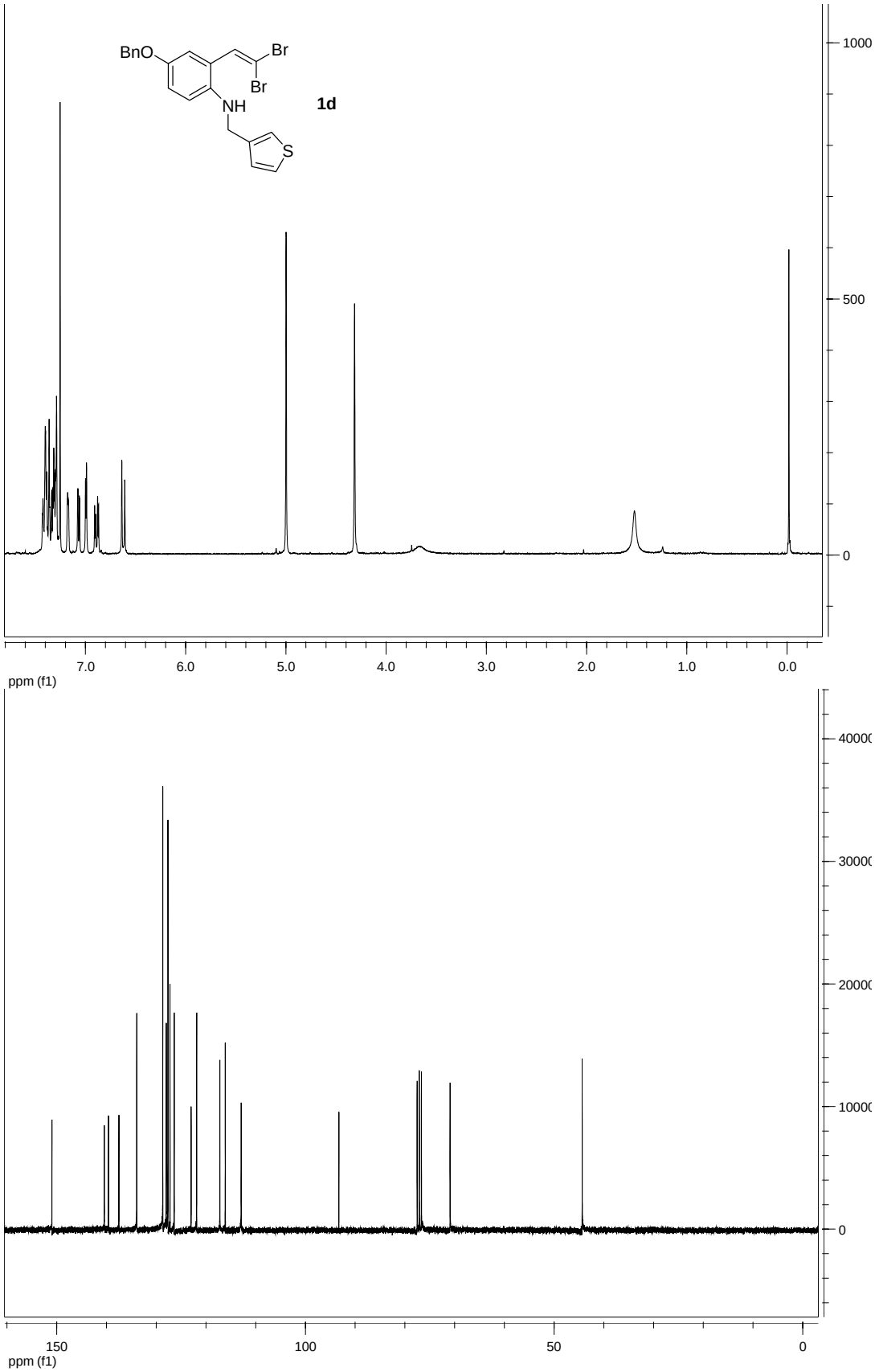
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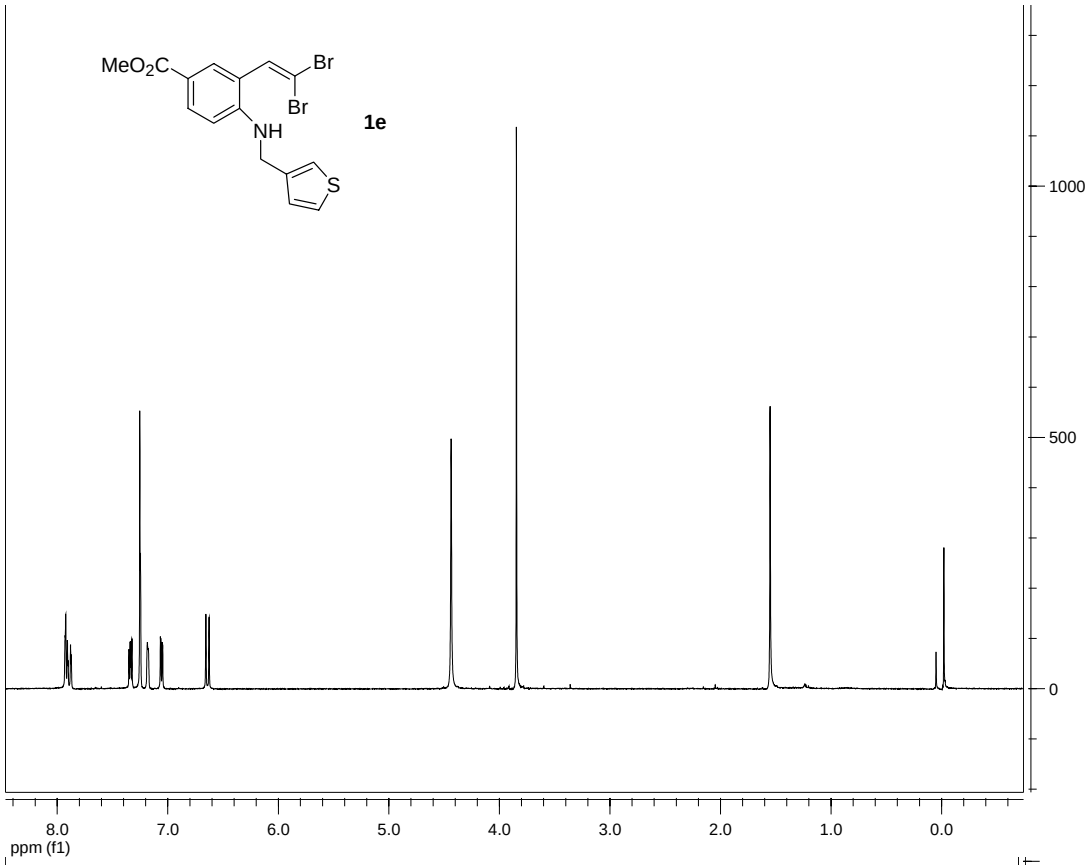
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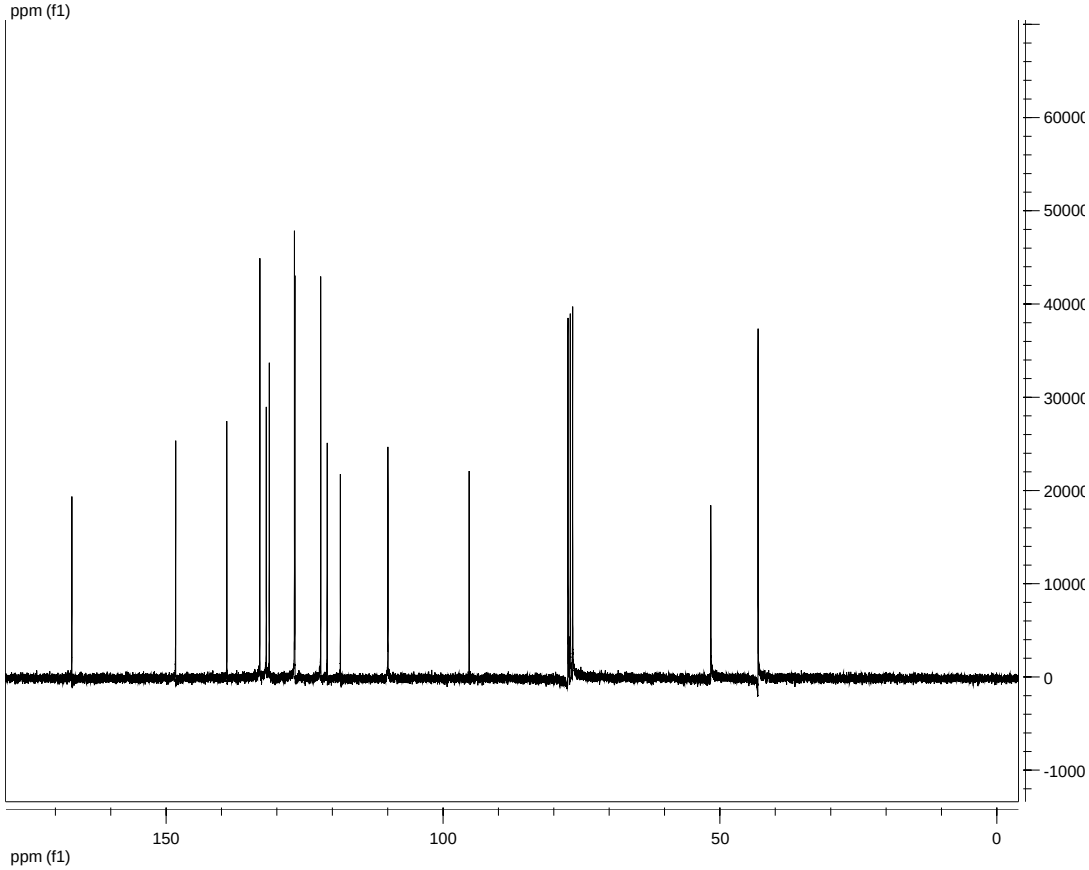
ppm (f1)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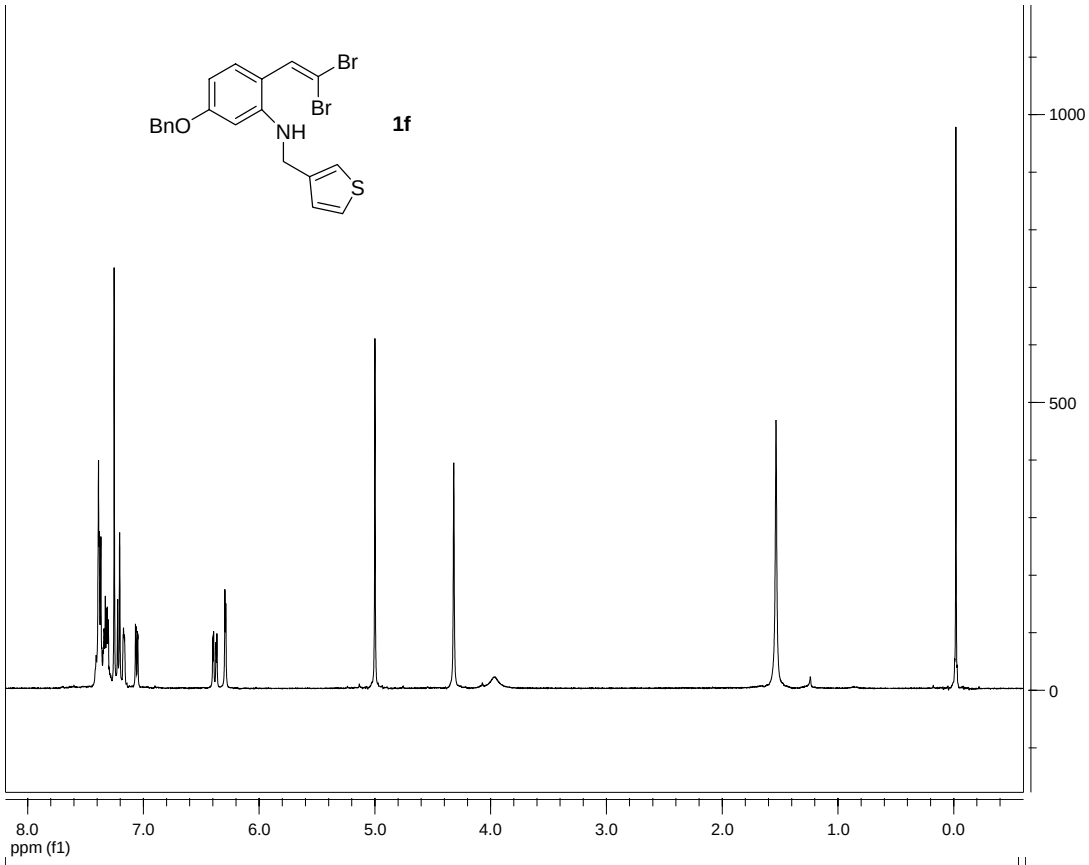
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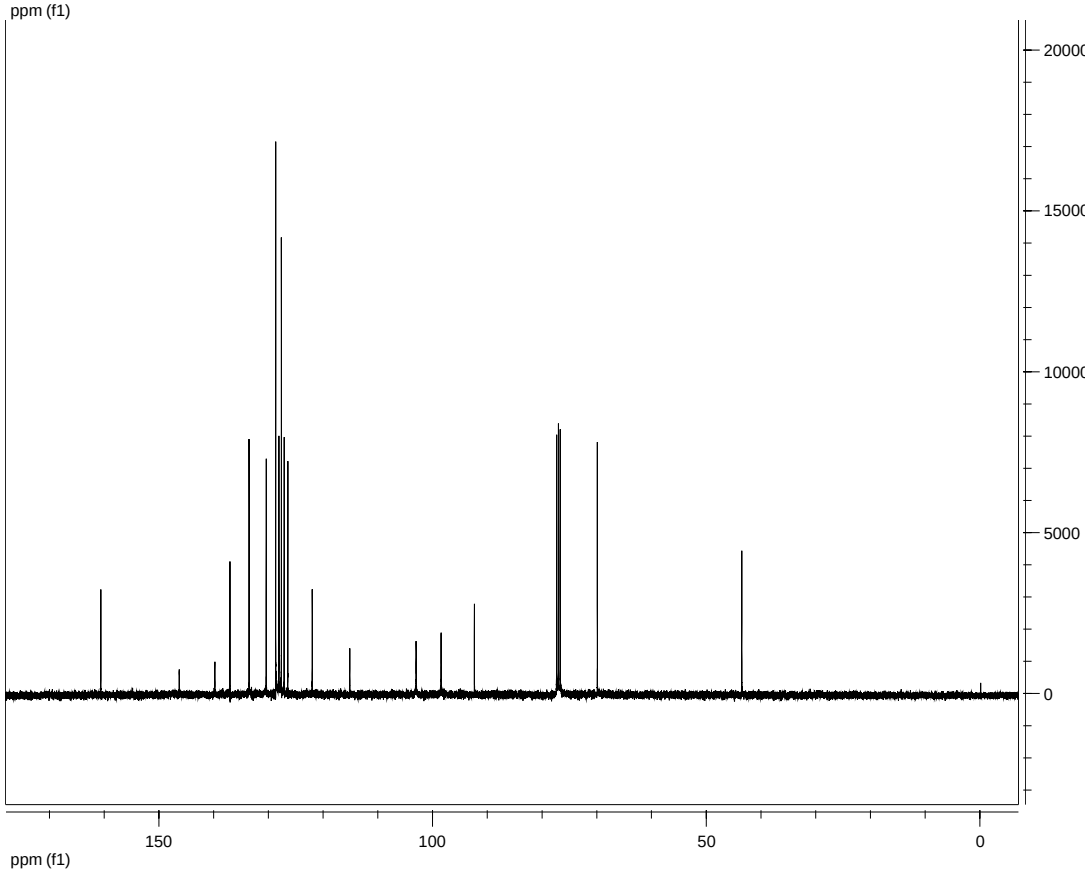
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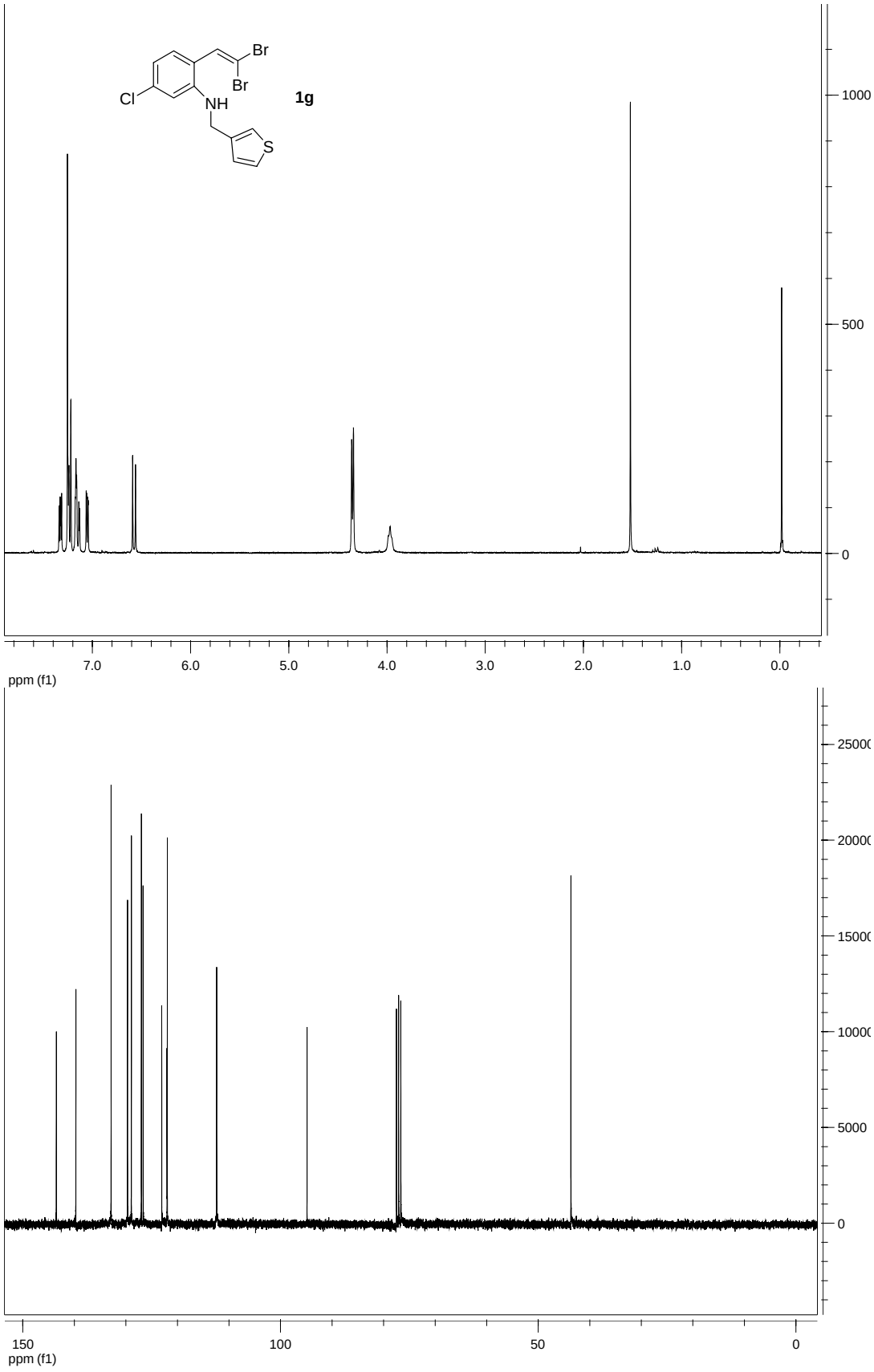
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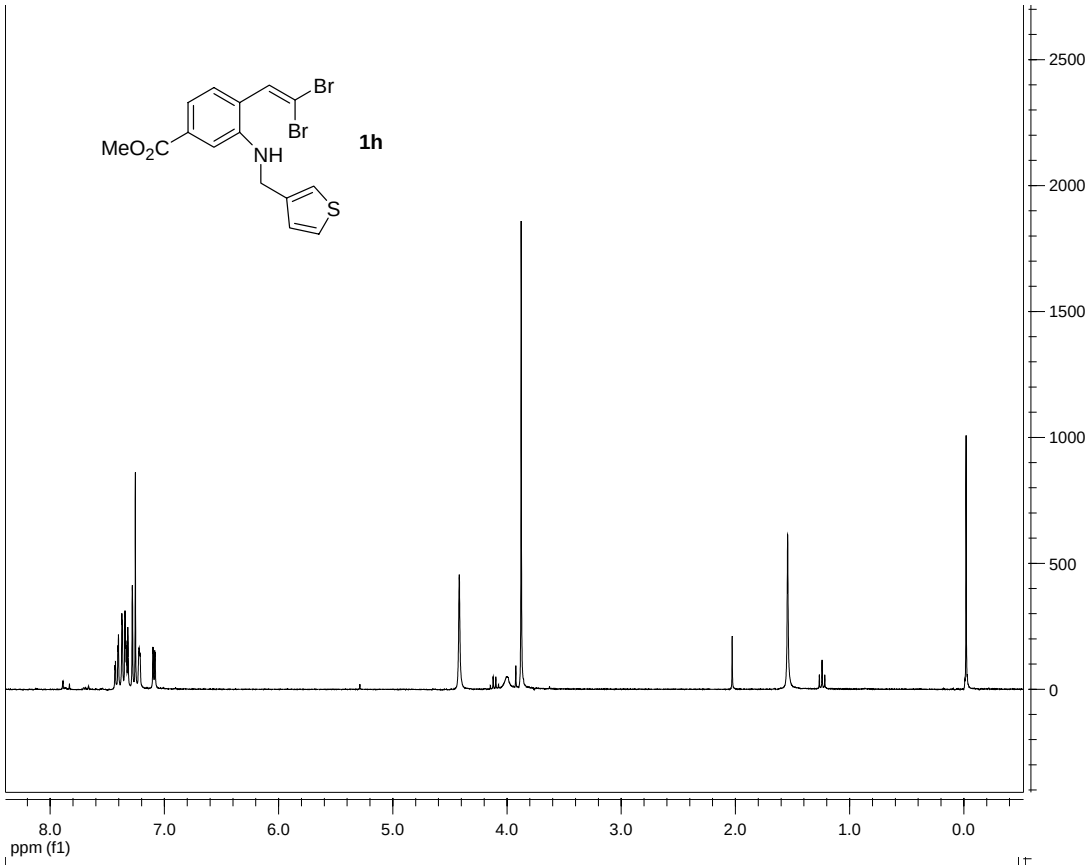
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Br
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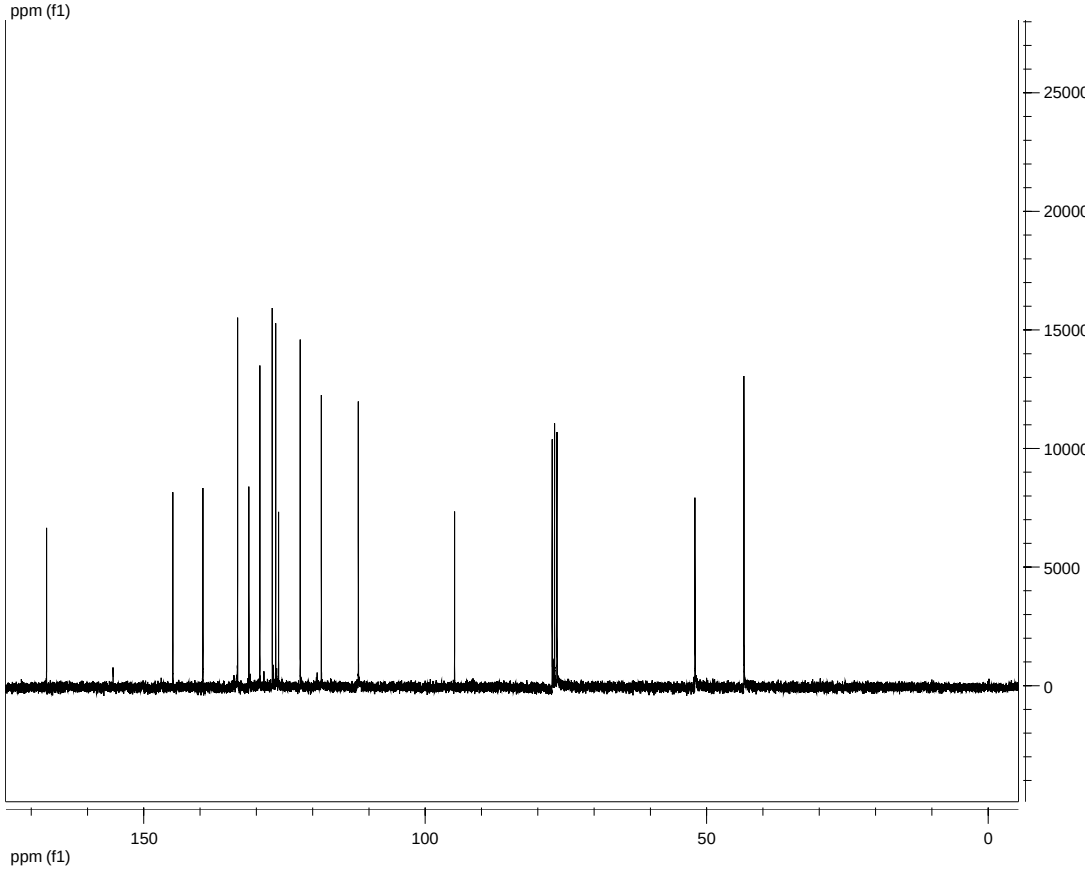
ppm (f1)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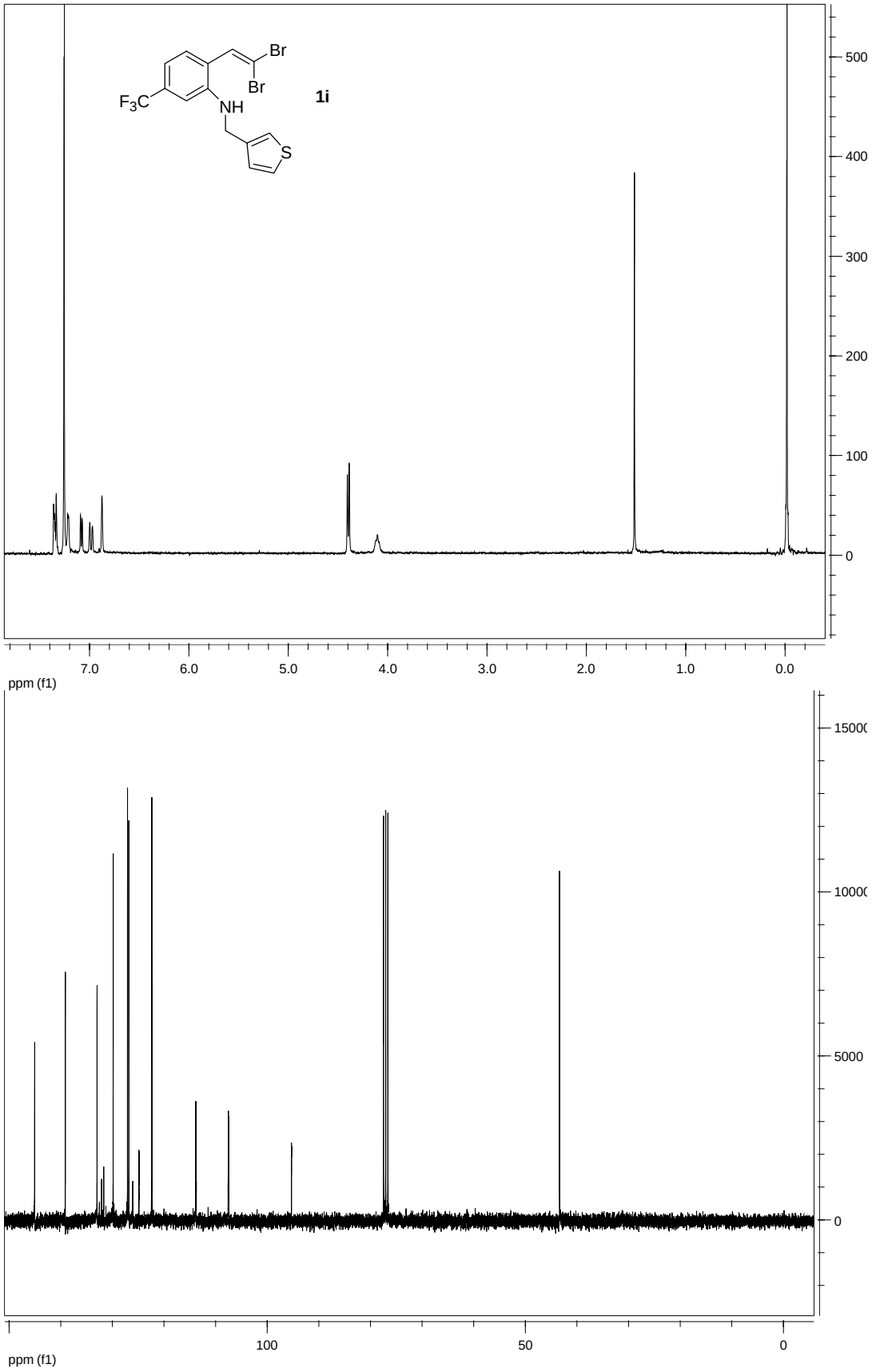
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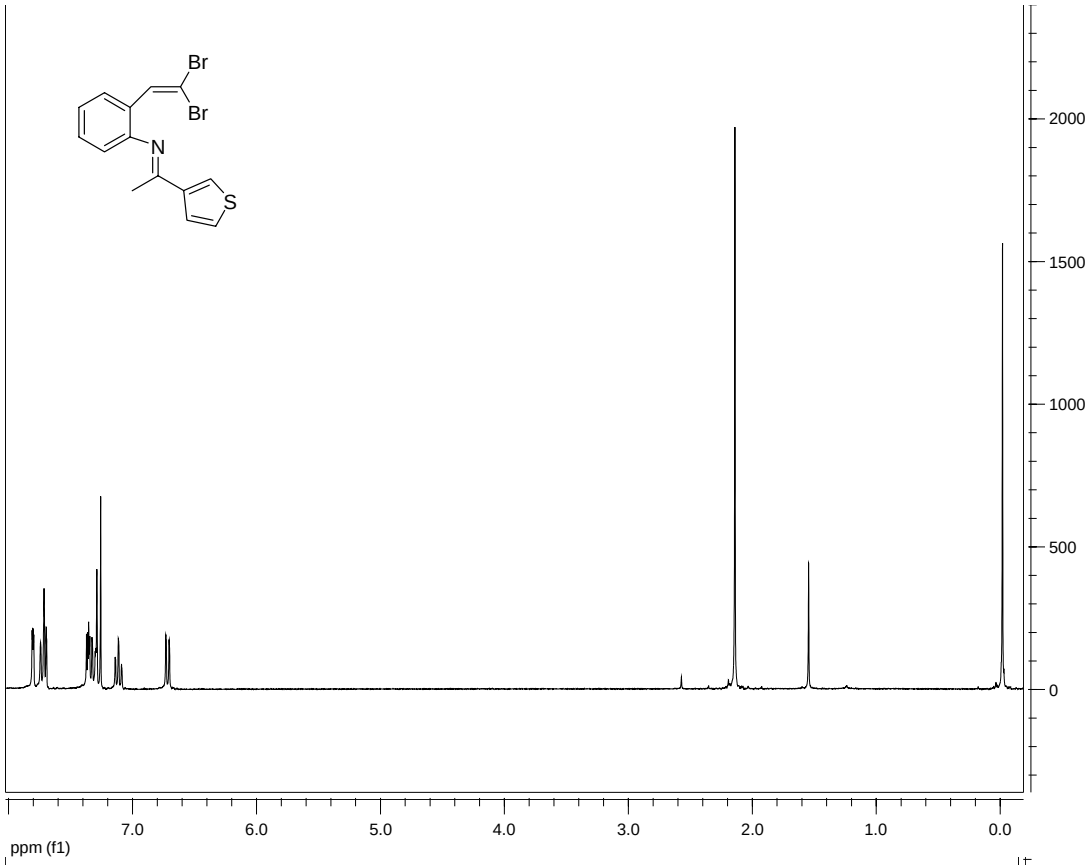
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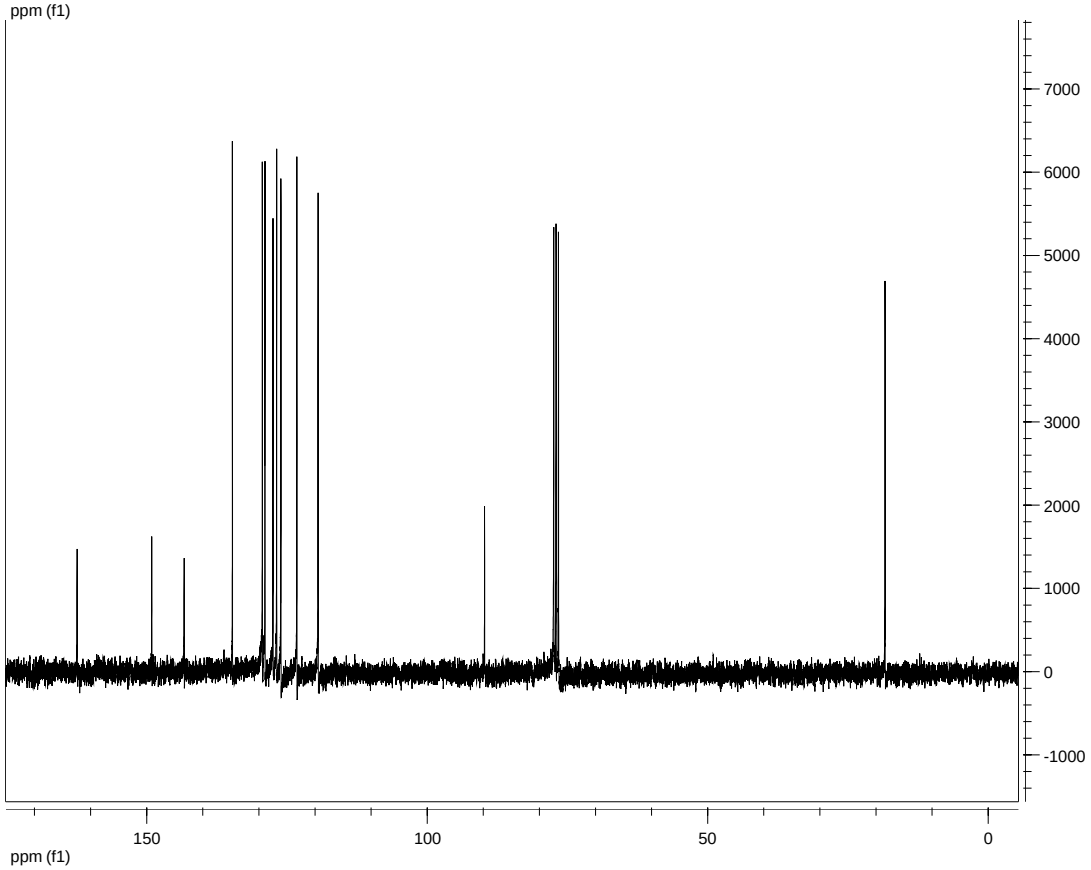
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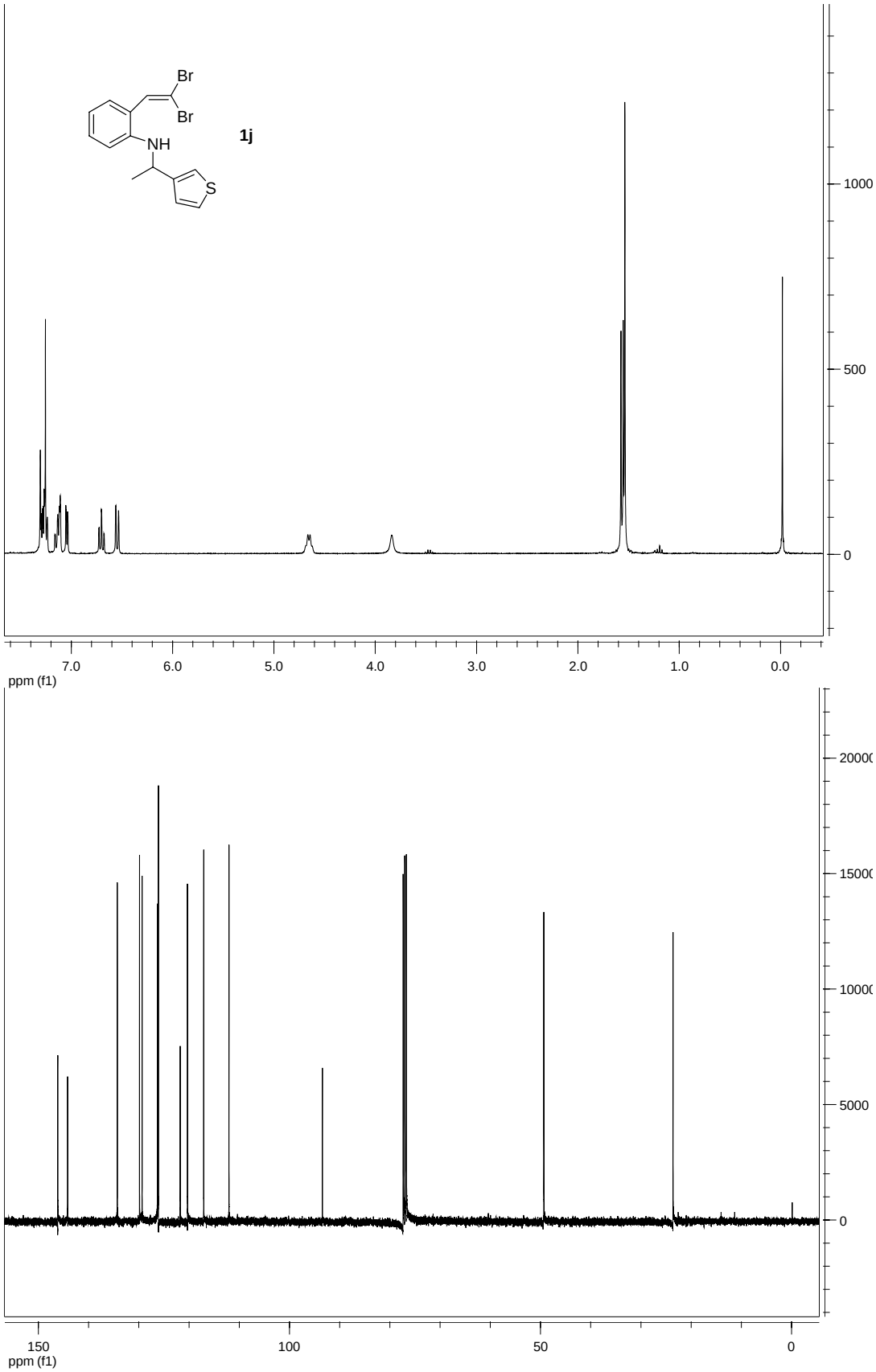
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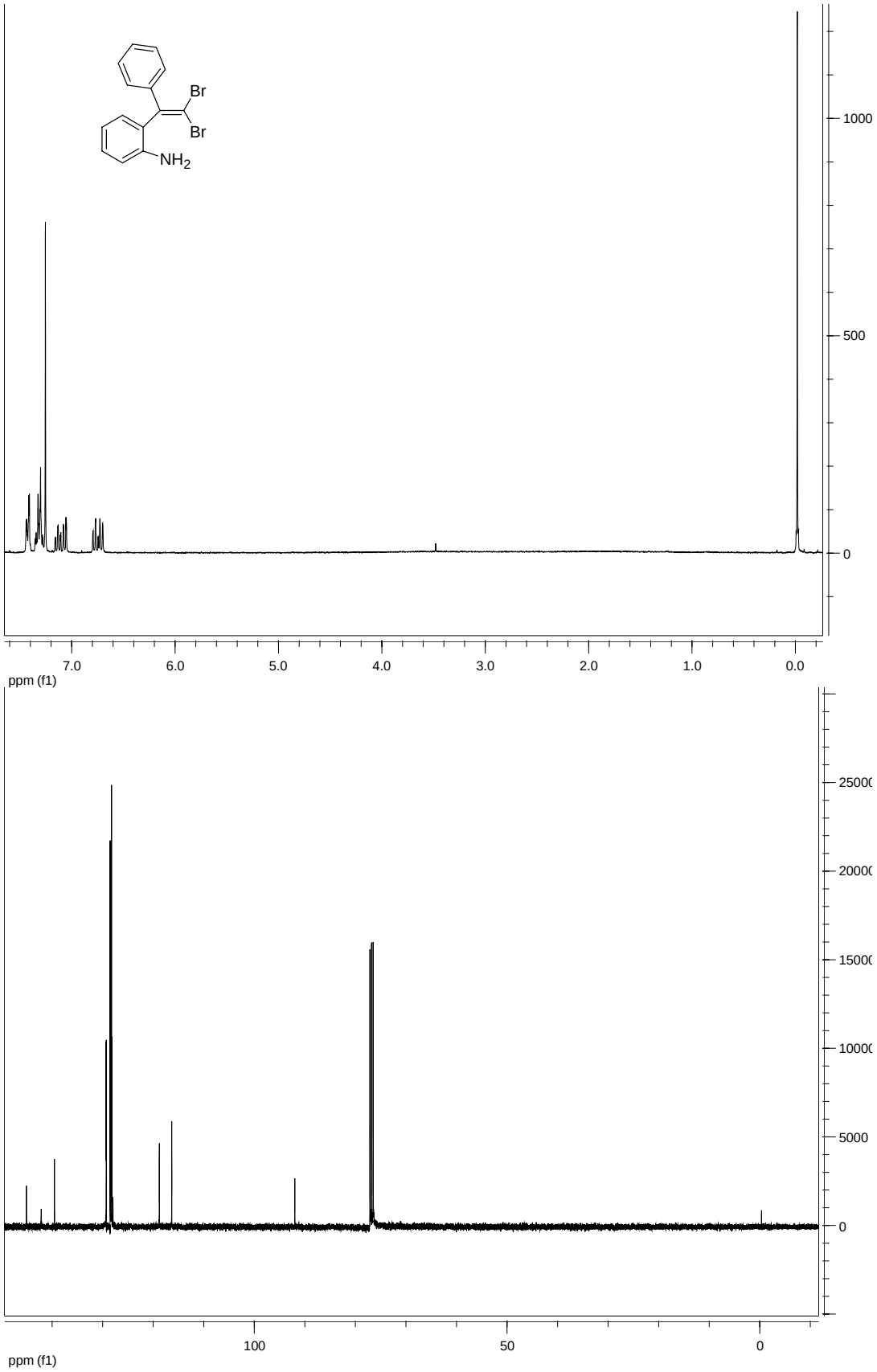
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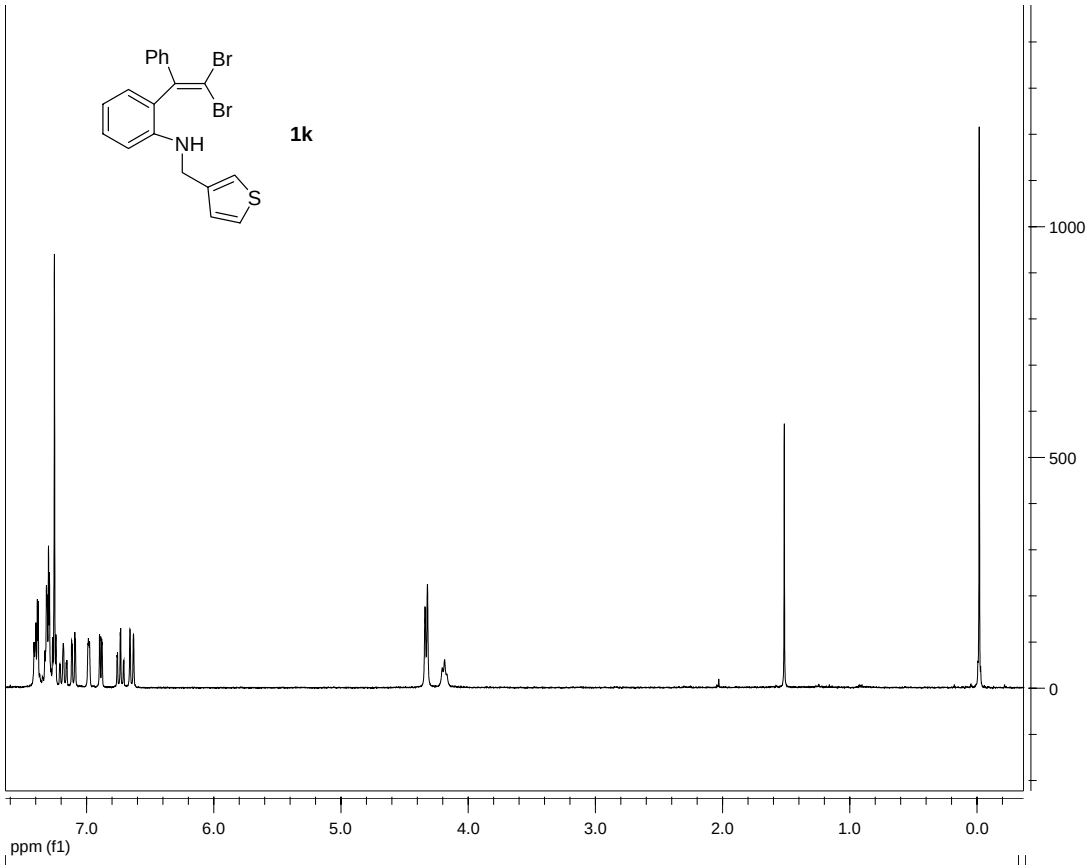
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Br
NH
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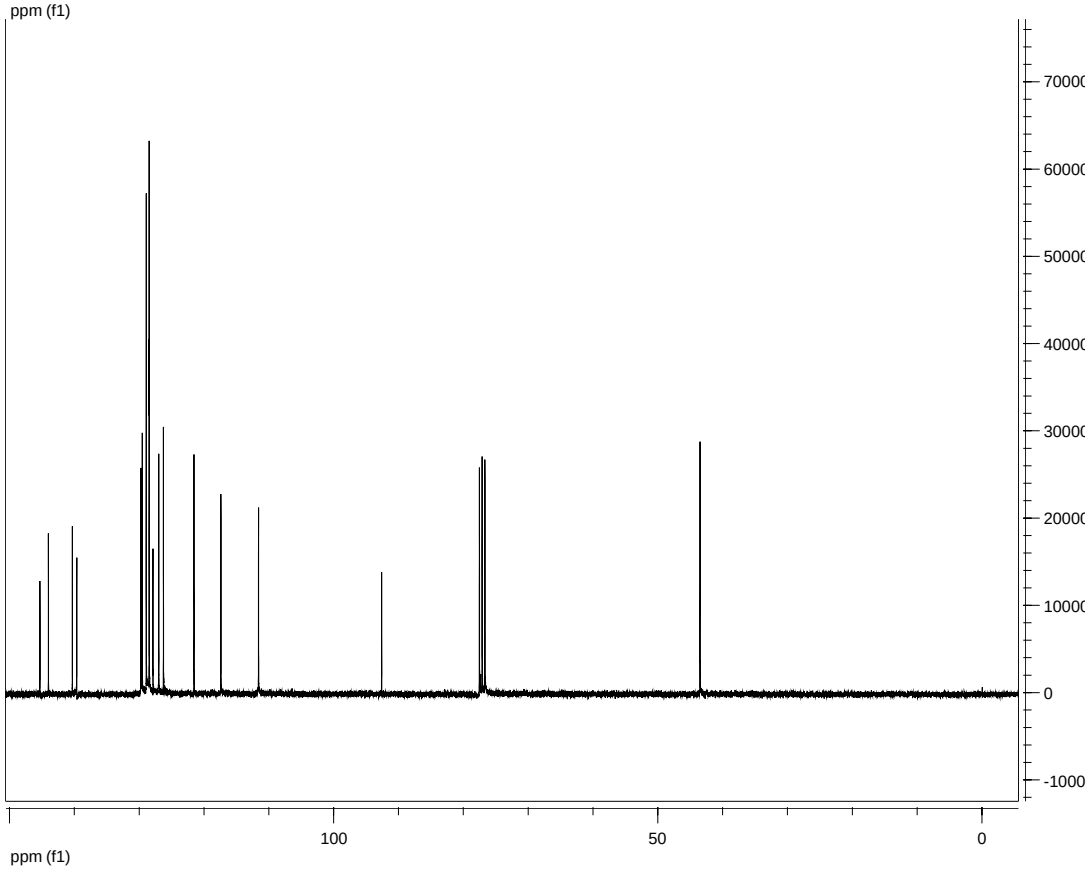
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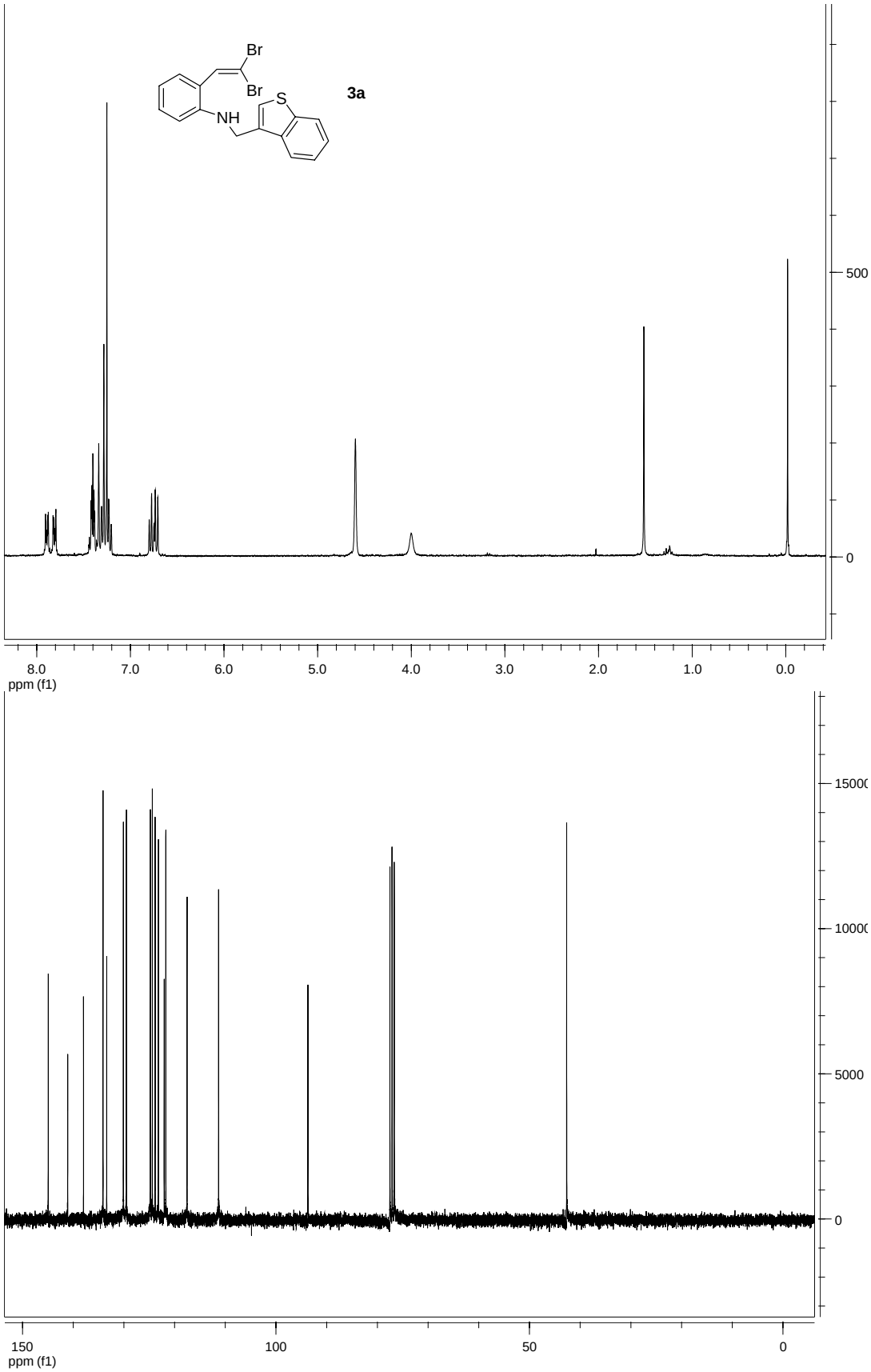
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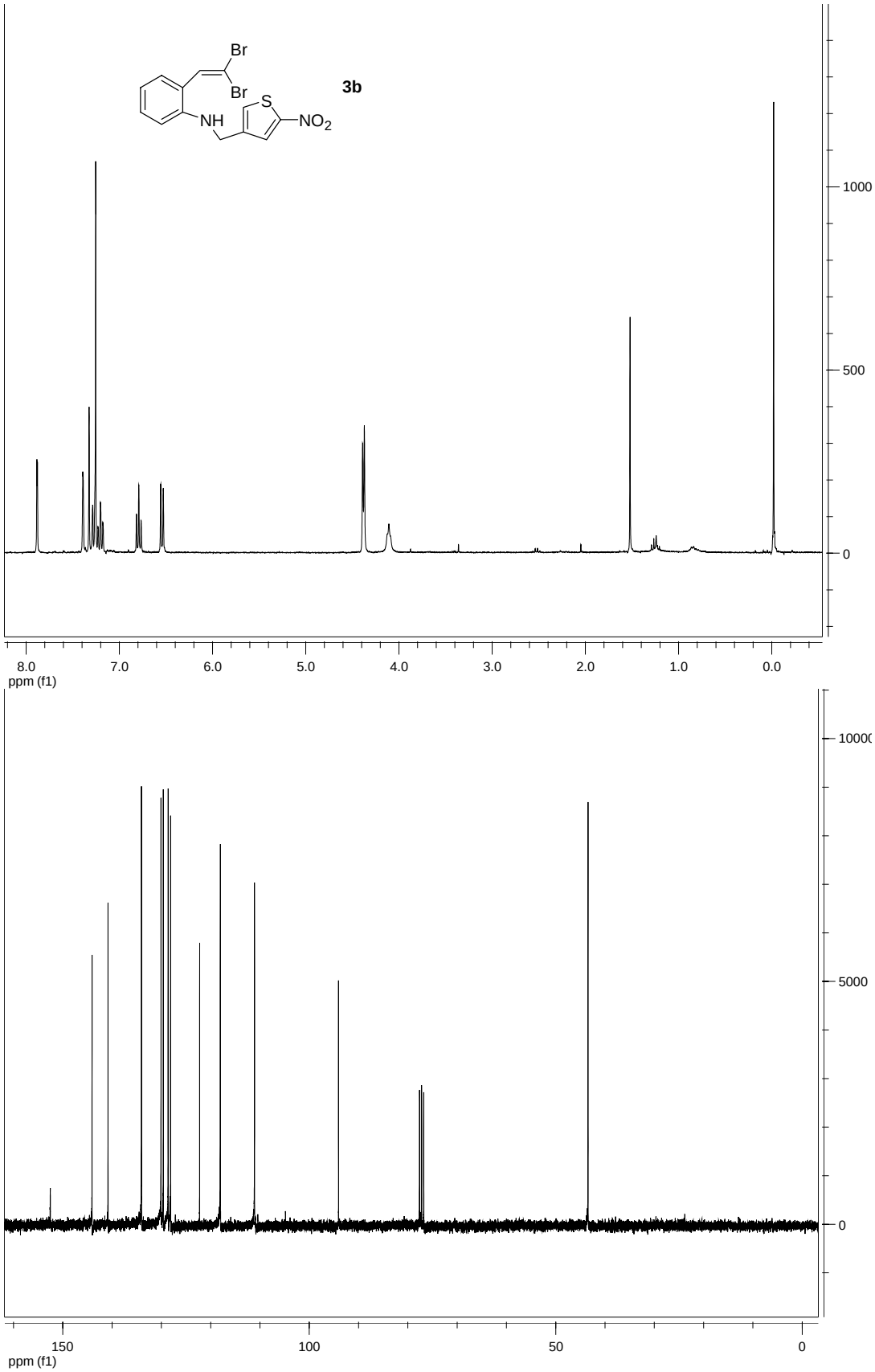
ppm (f1)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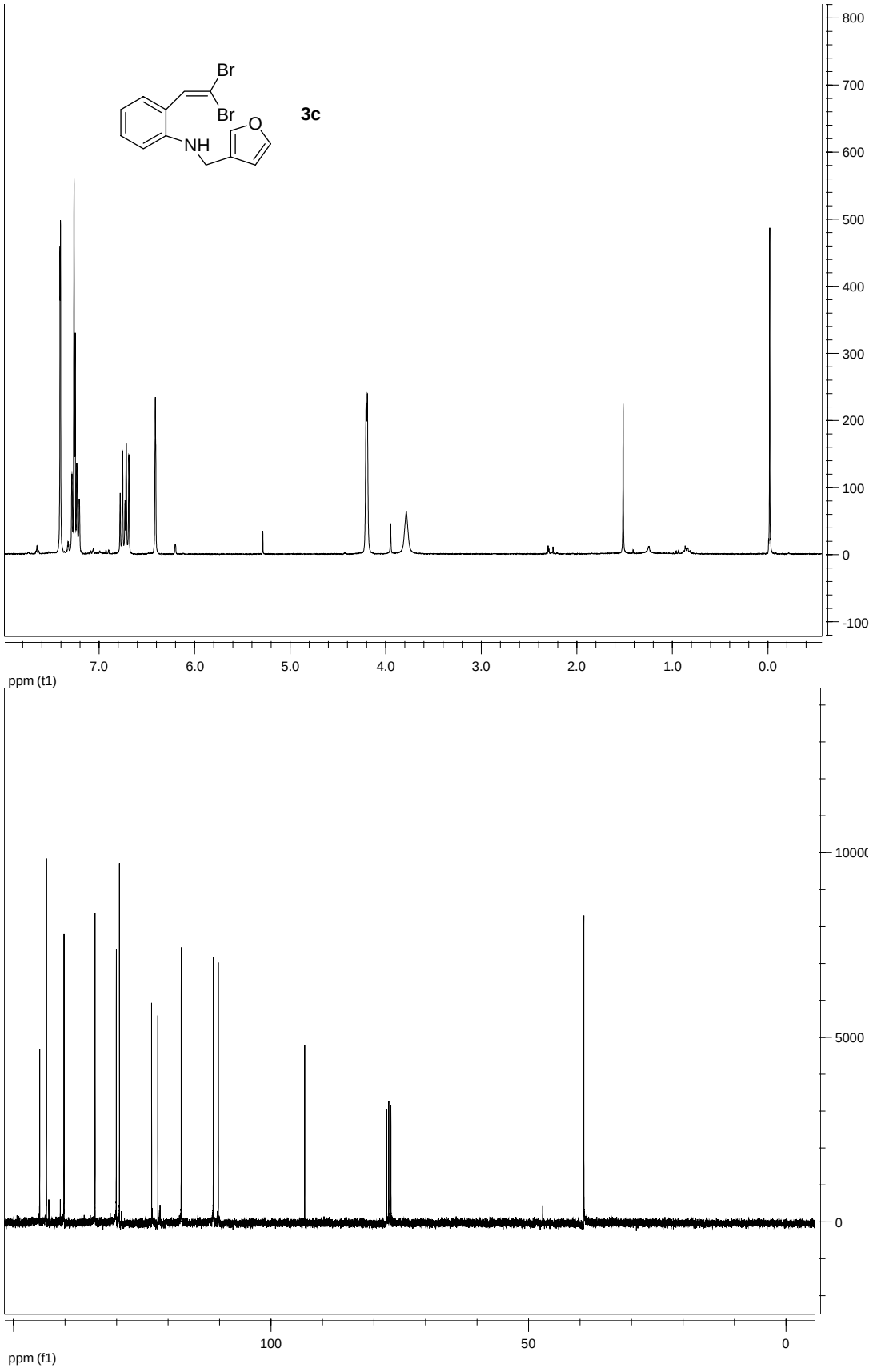
ppm (f1)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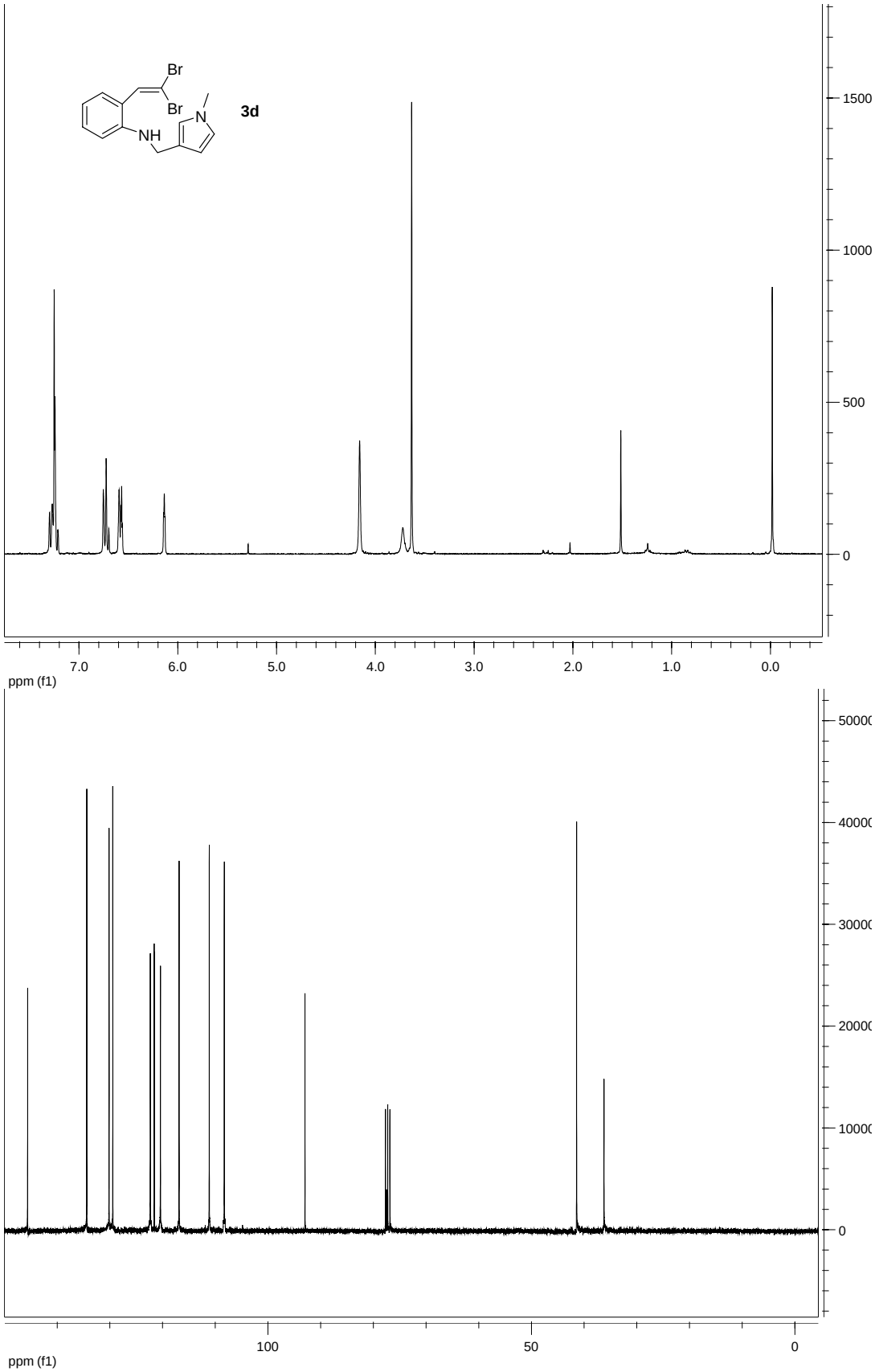
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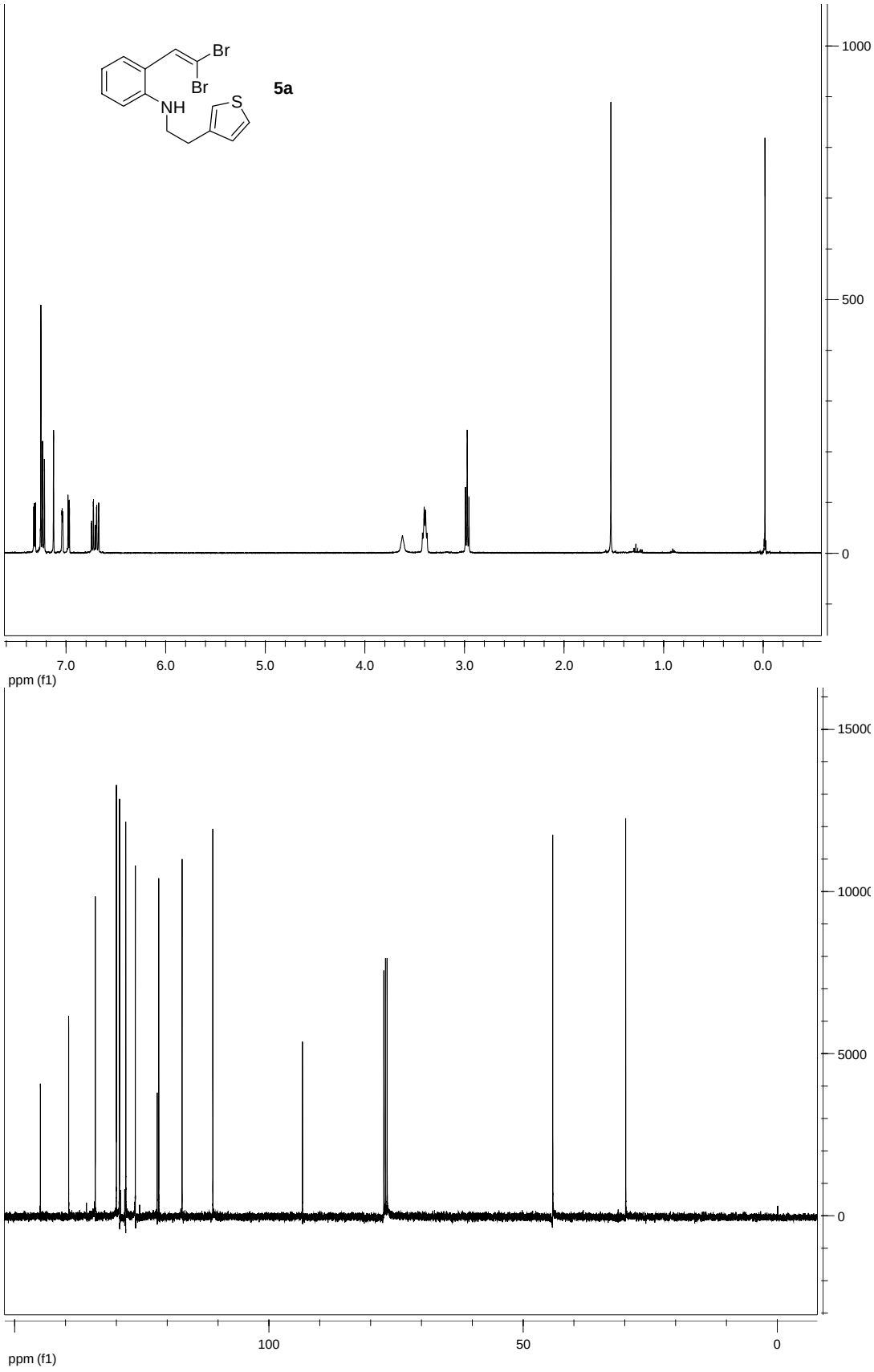
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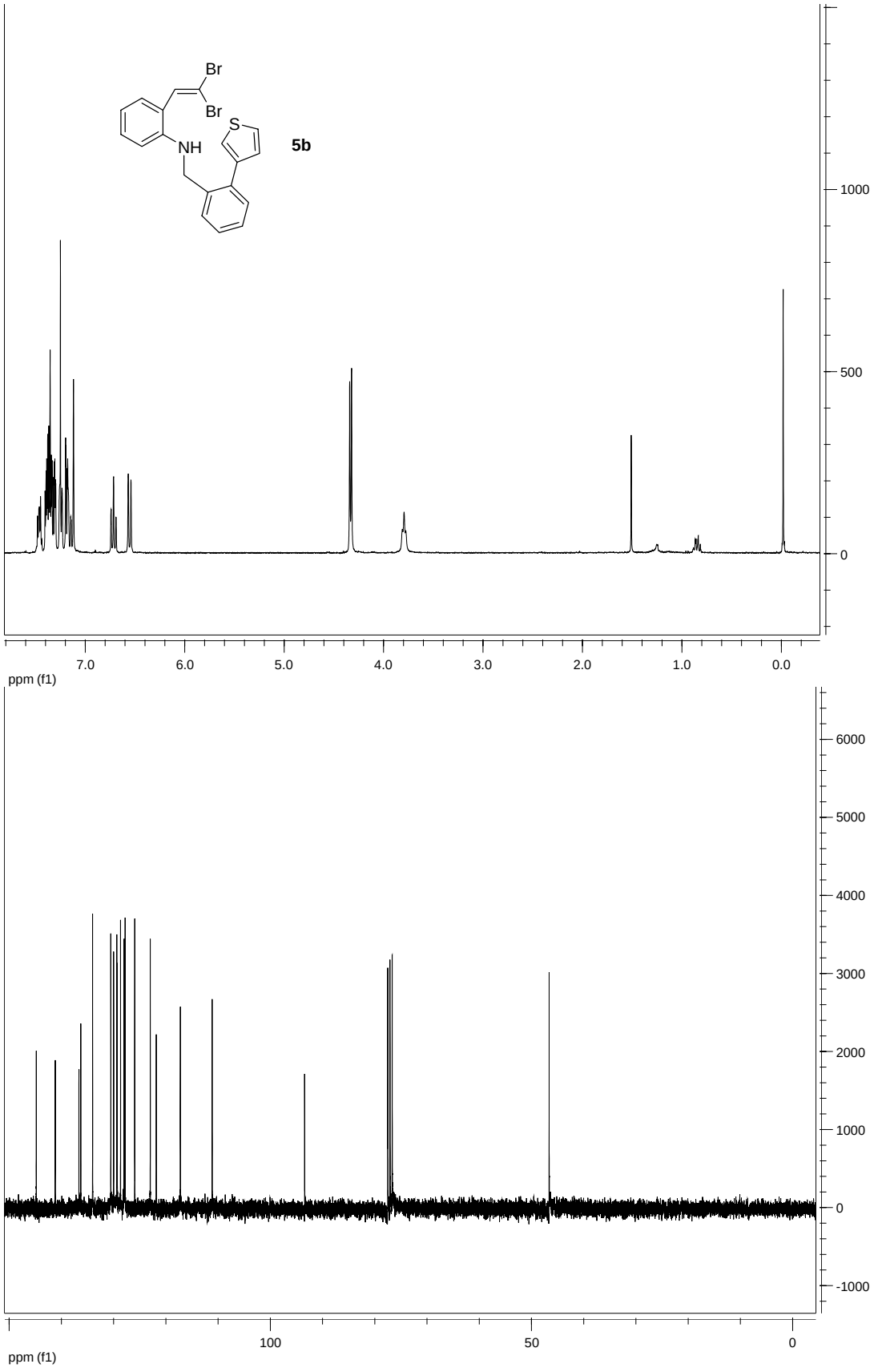
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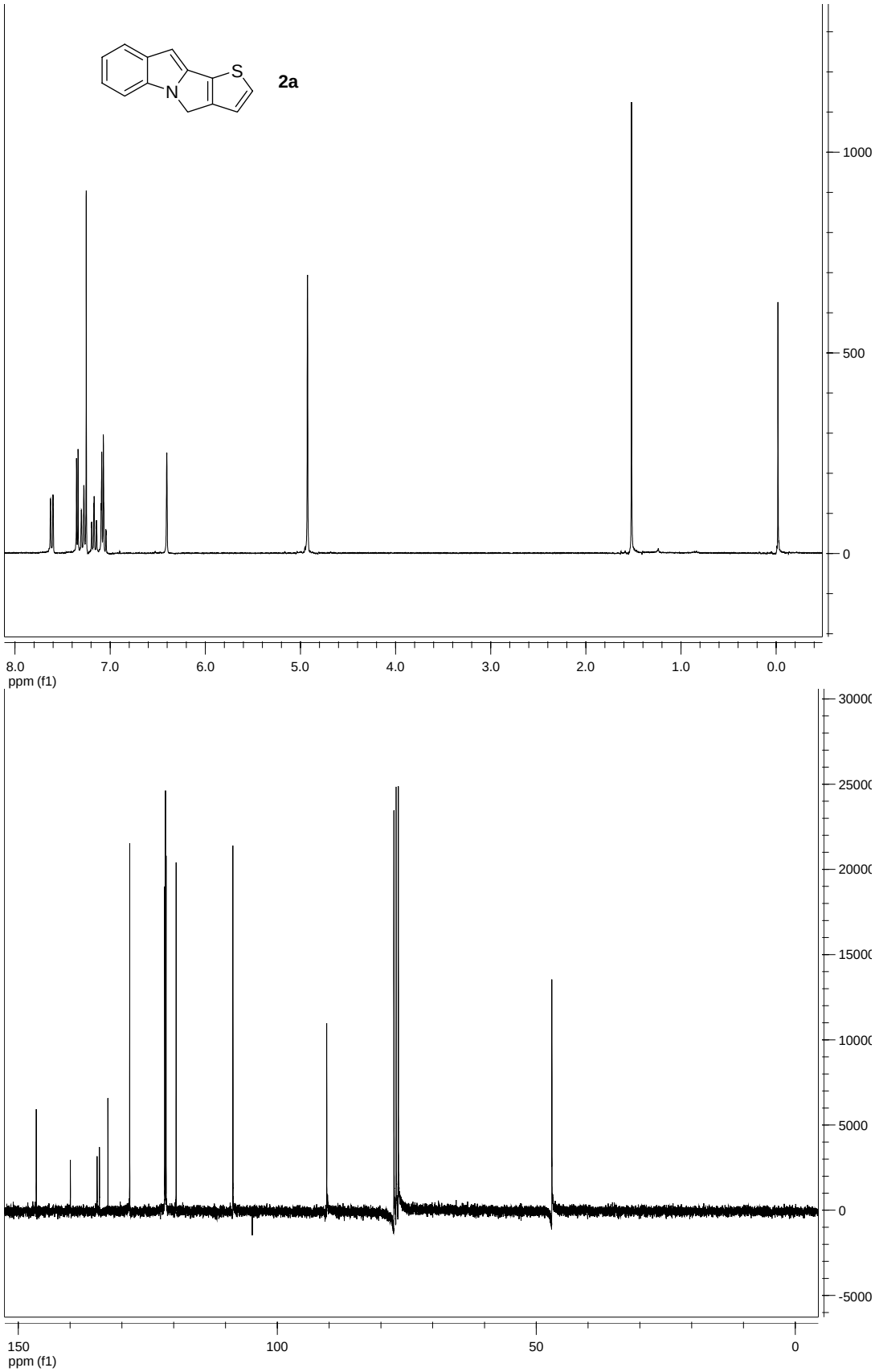
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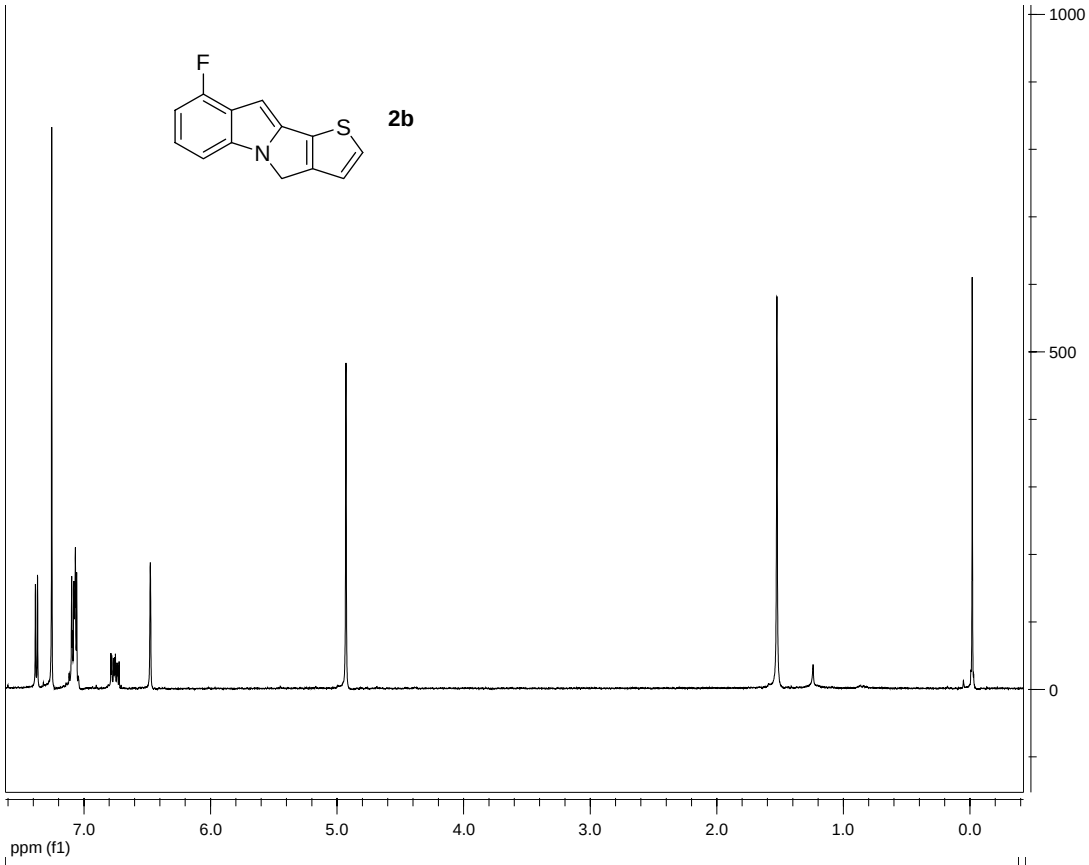
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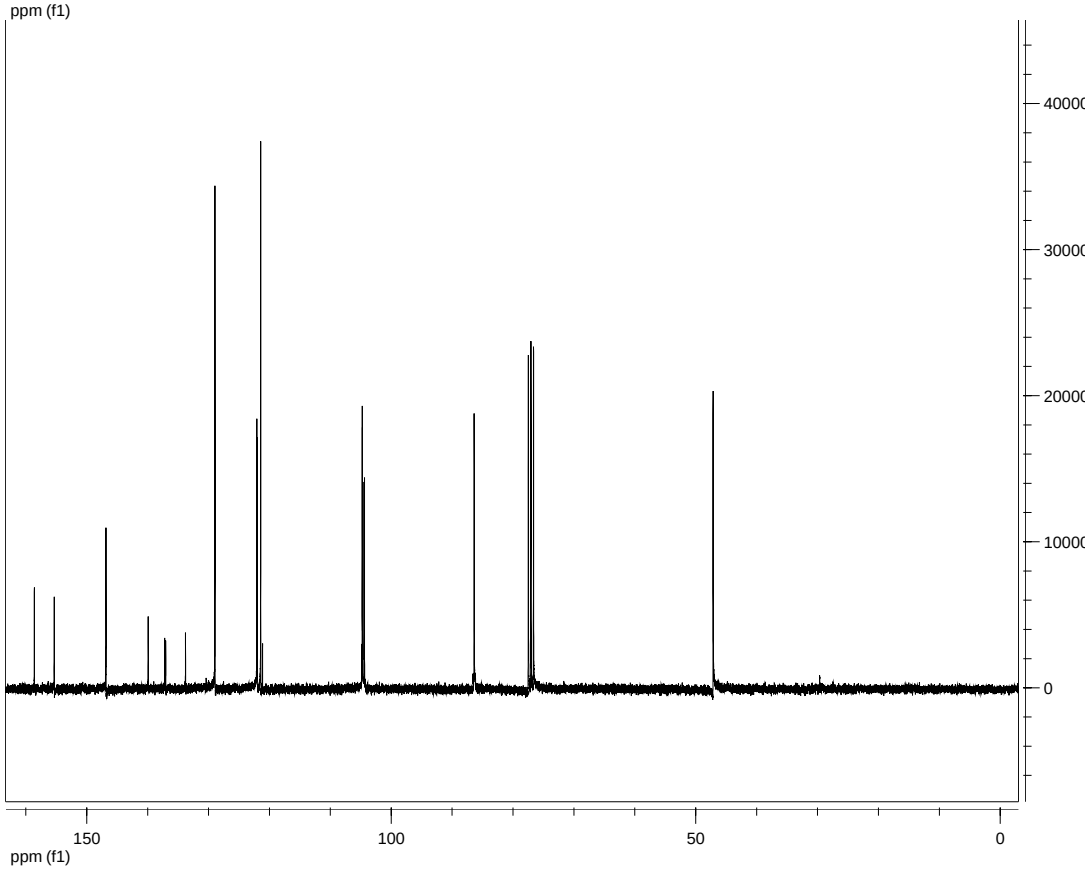
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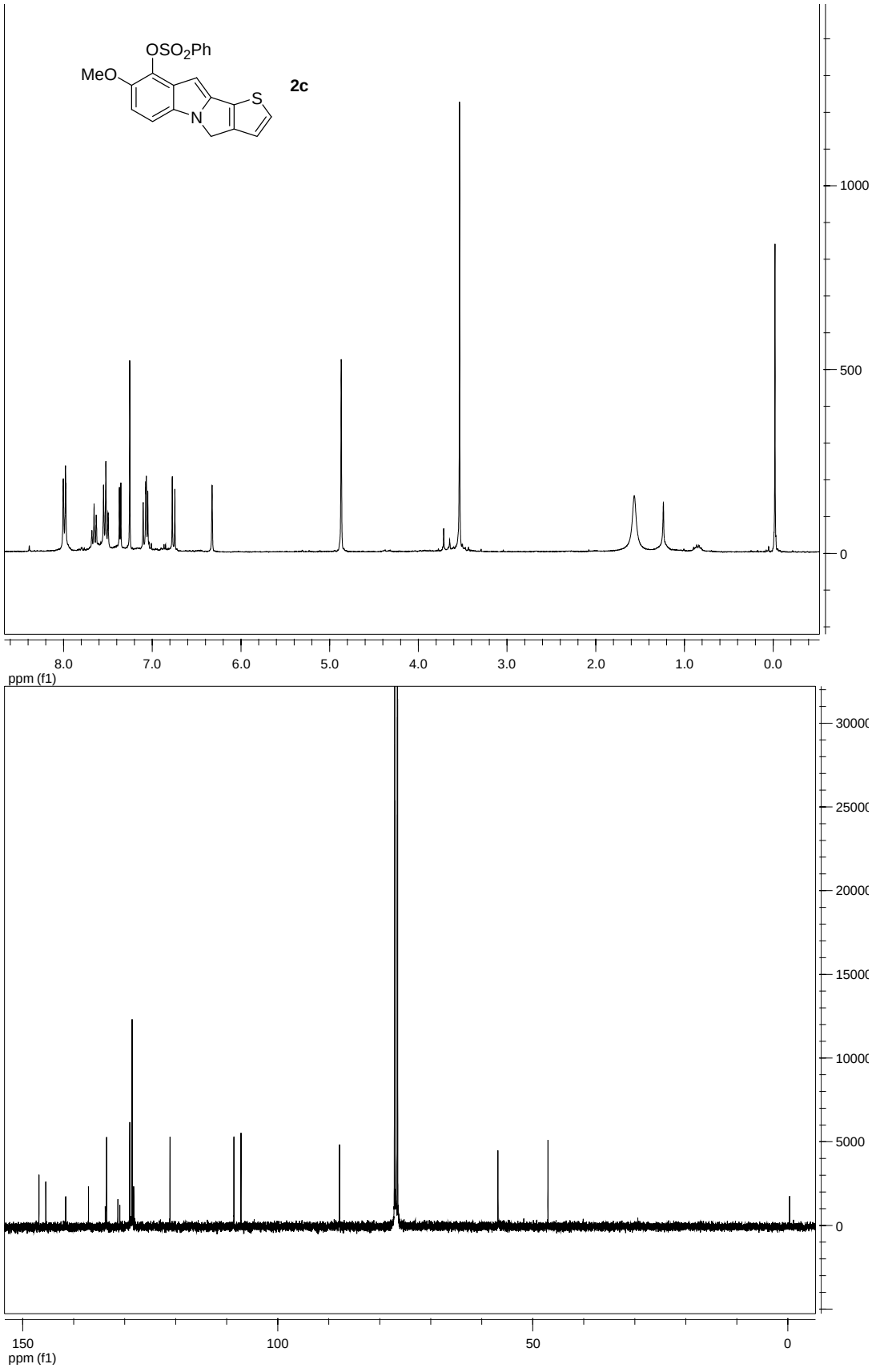
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2.0
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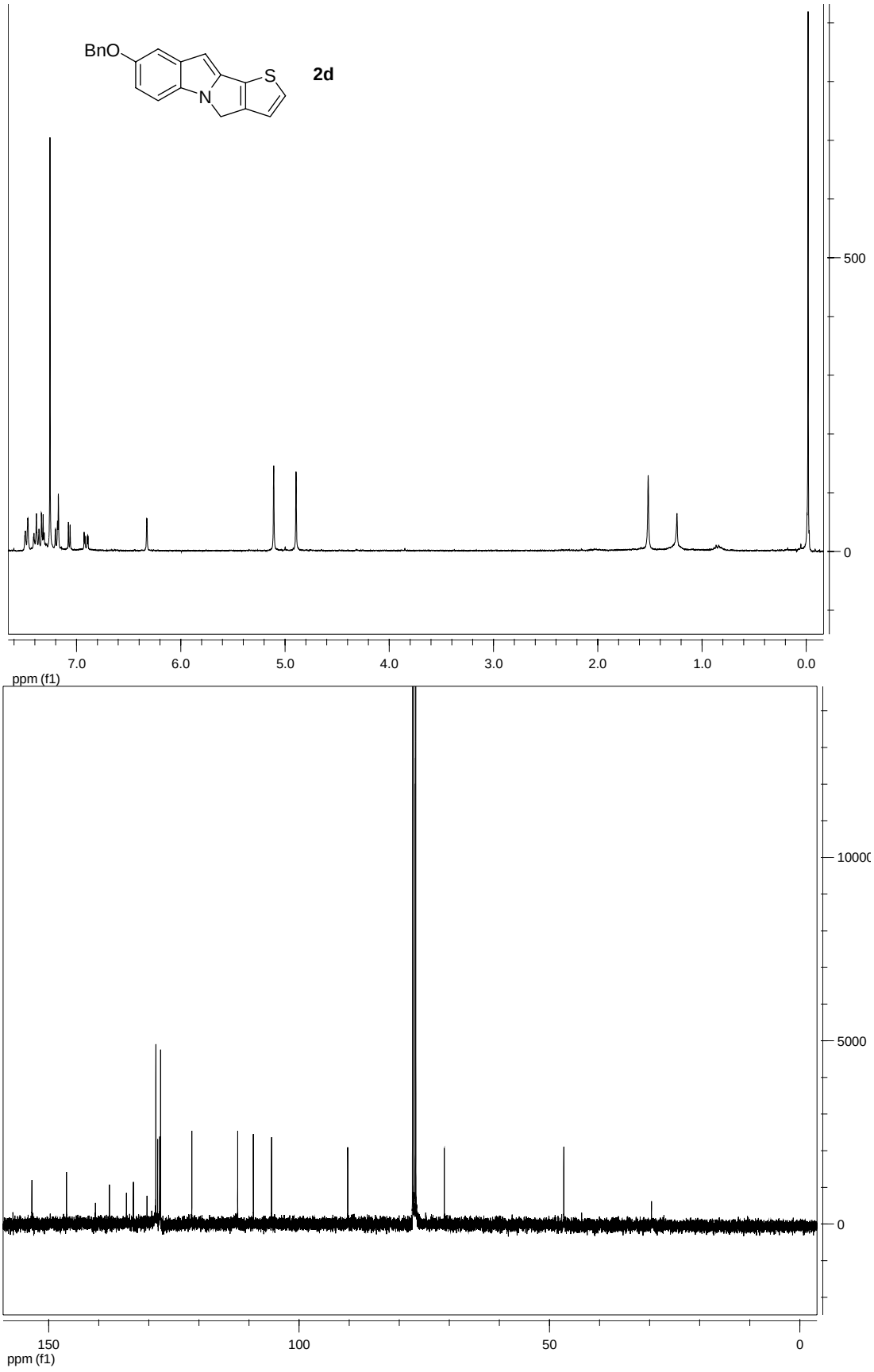
ppm (f1)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N
2d
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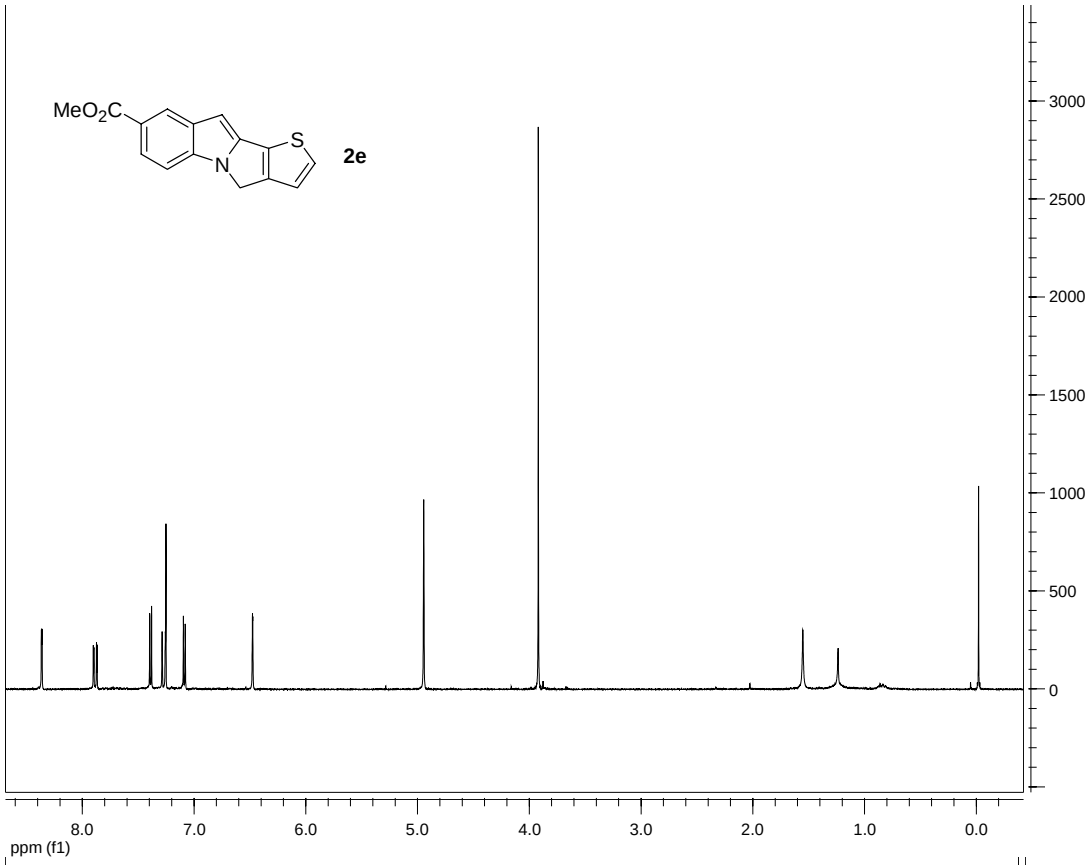
ppm (f1)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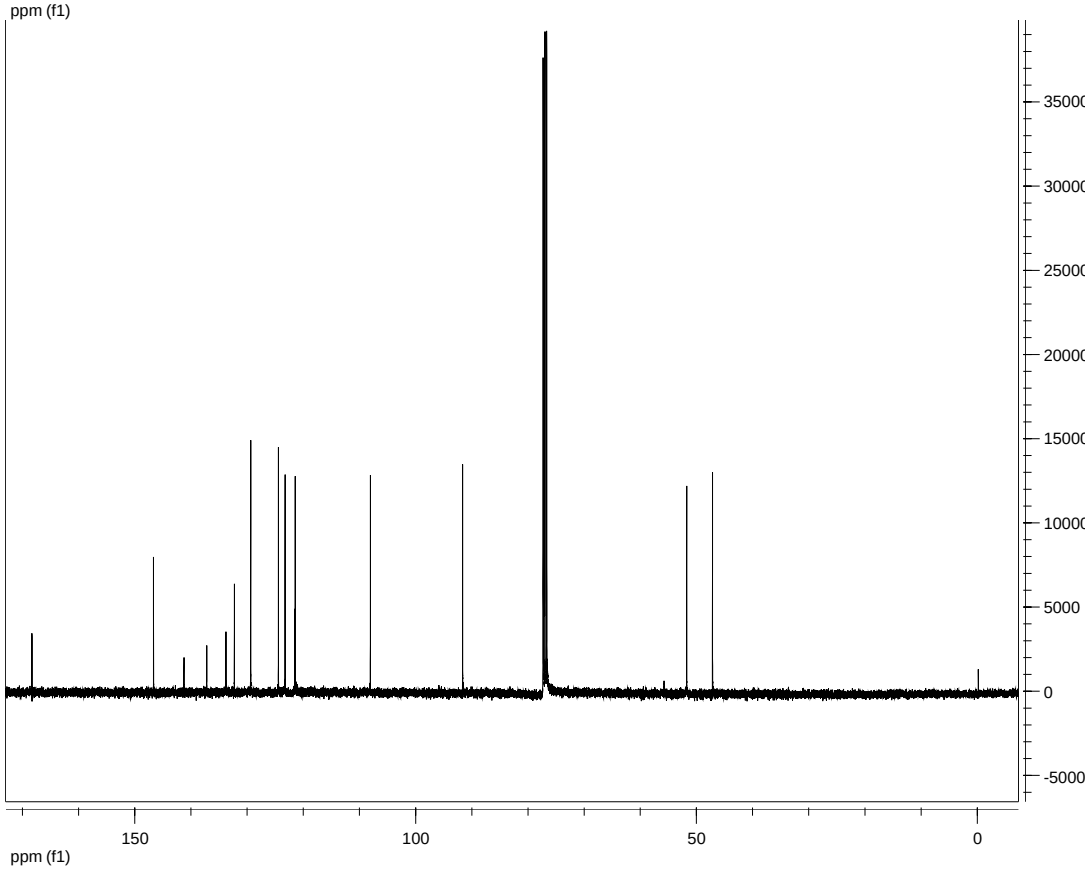
ppm (f1)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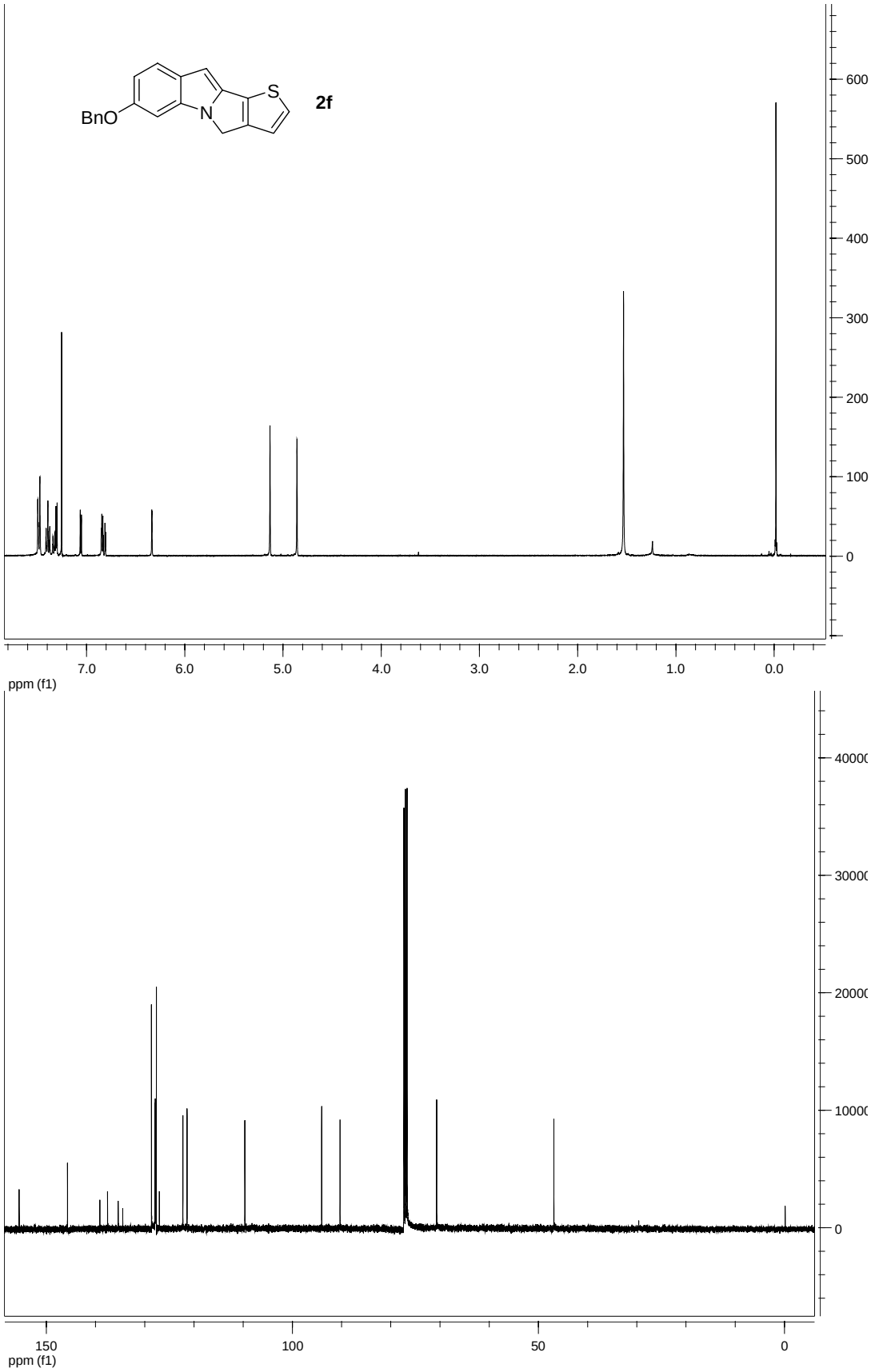
ppm (f1)


BnO
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S
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4.0
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ppm (f1)
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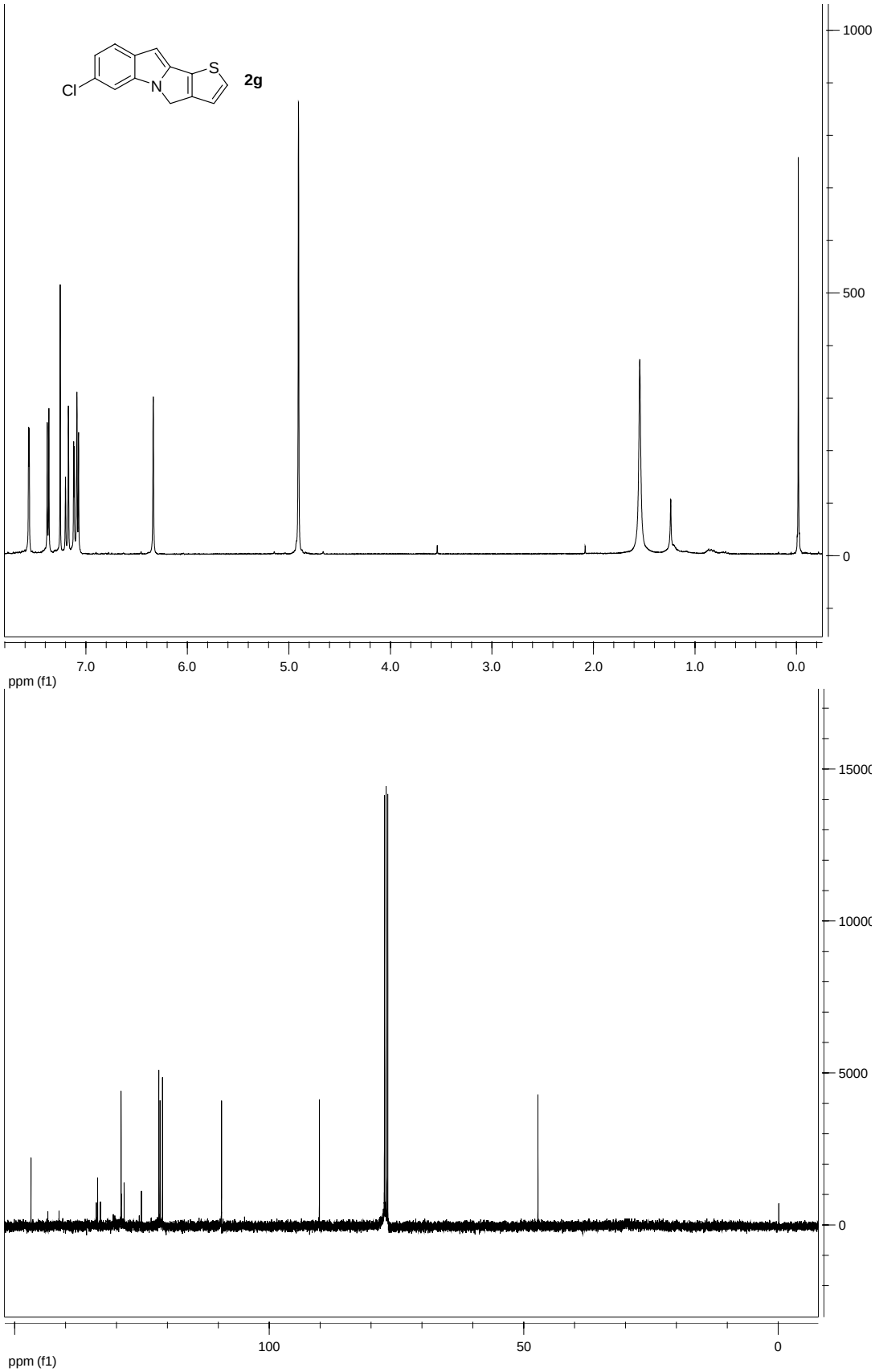
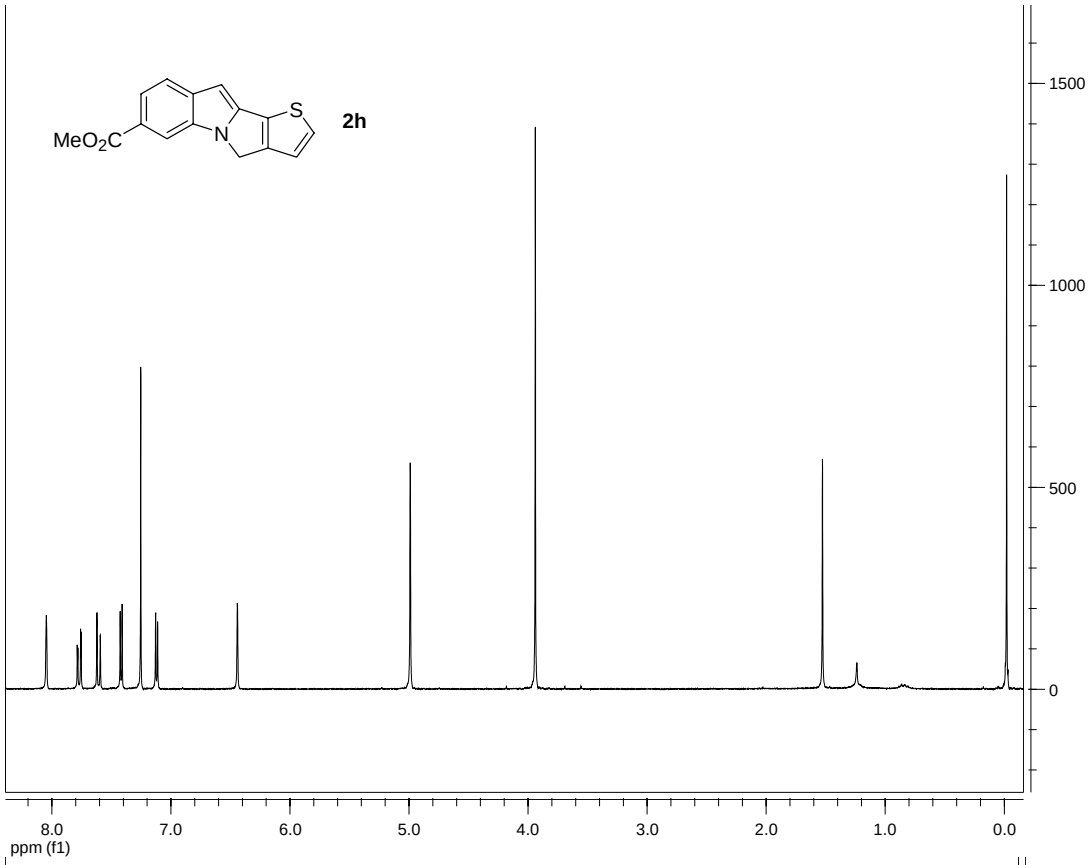
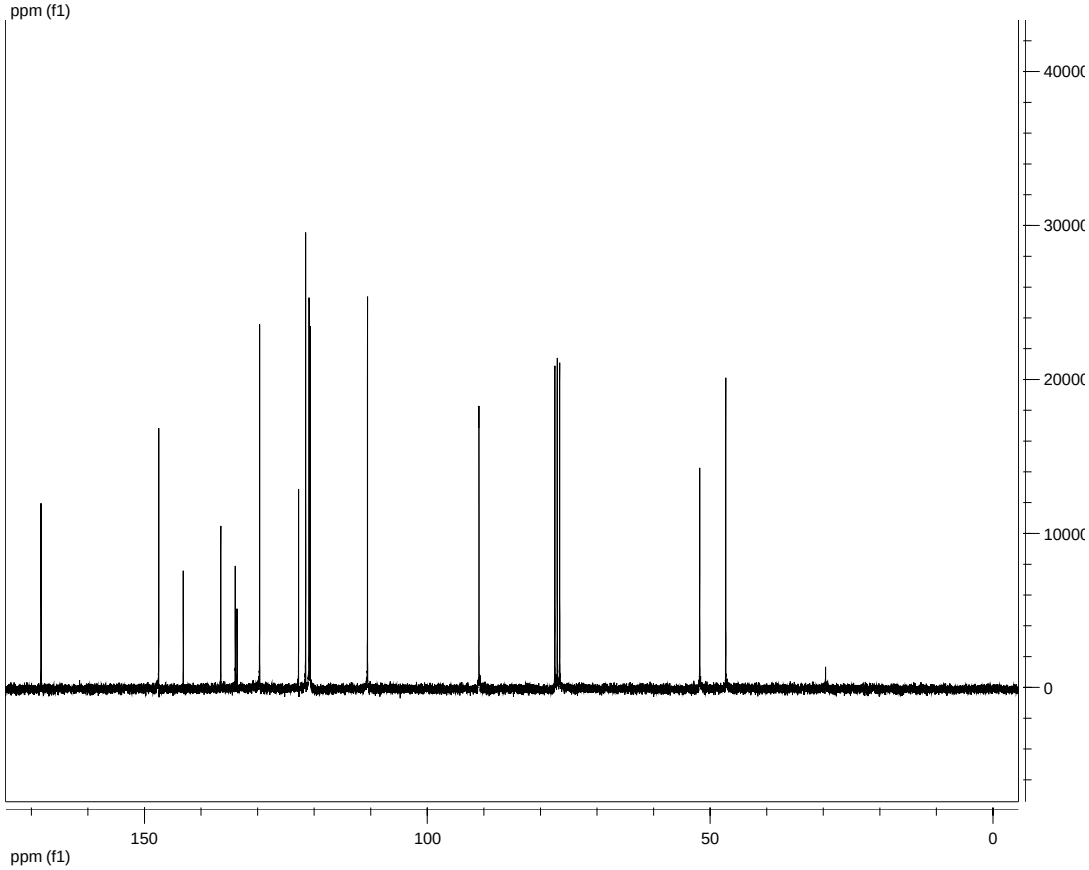
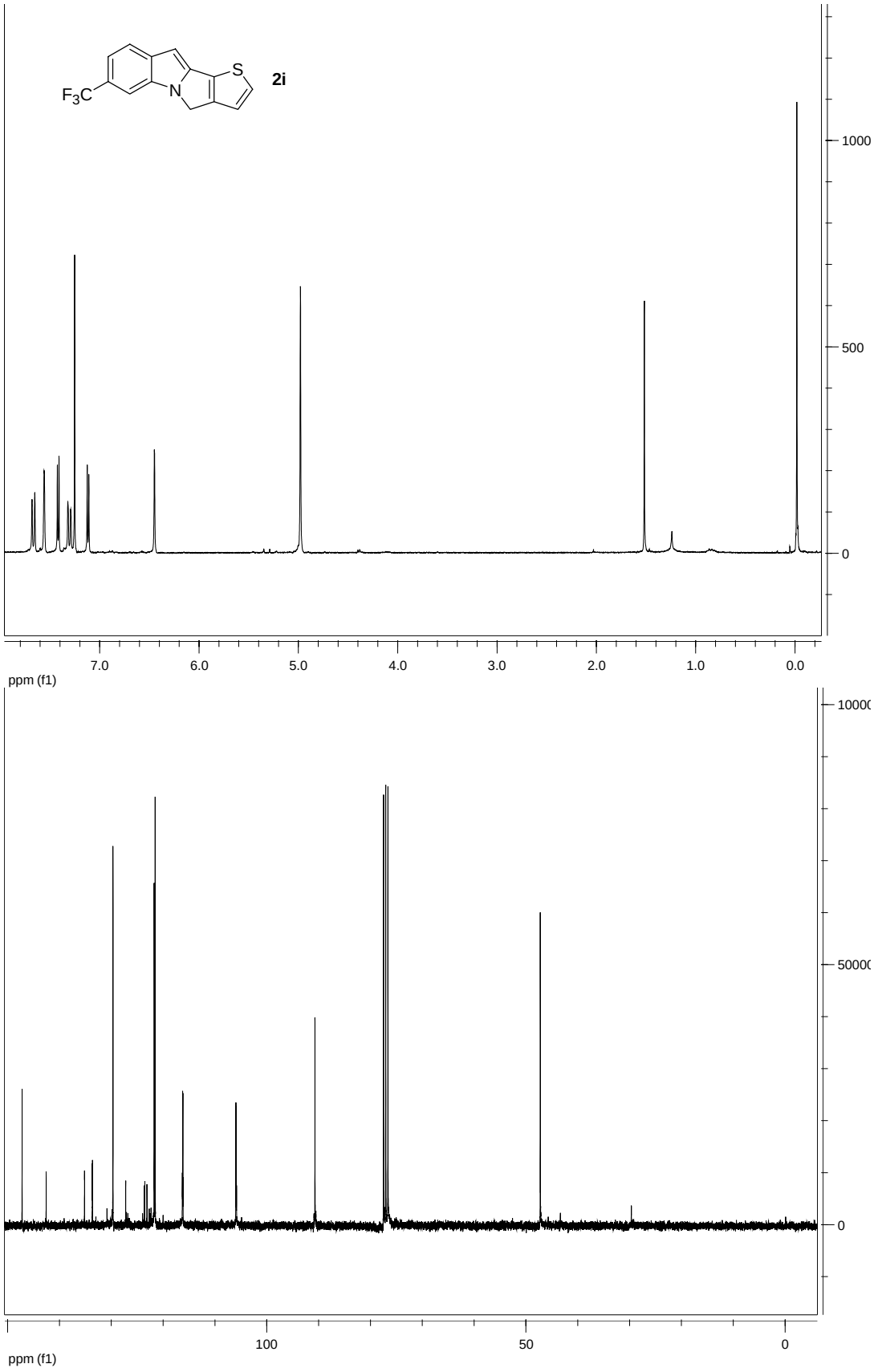
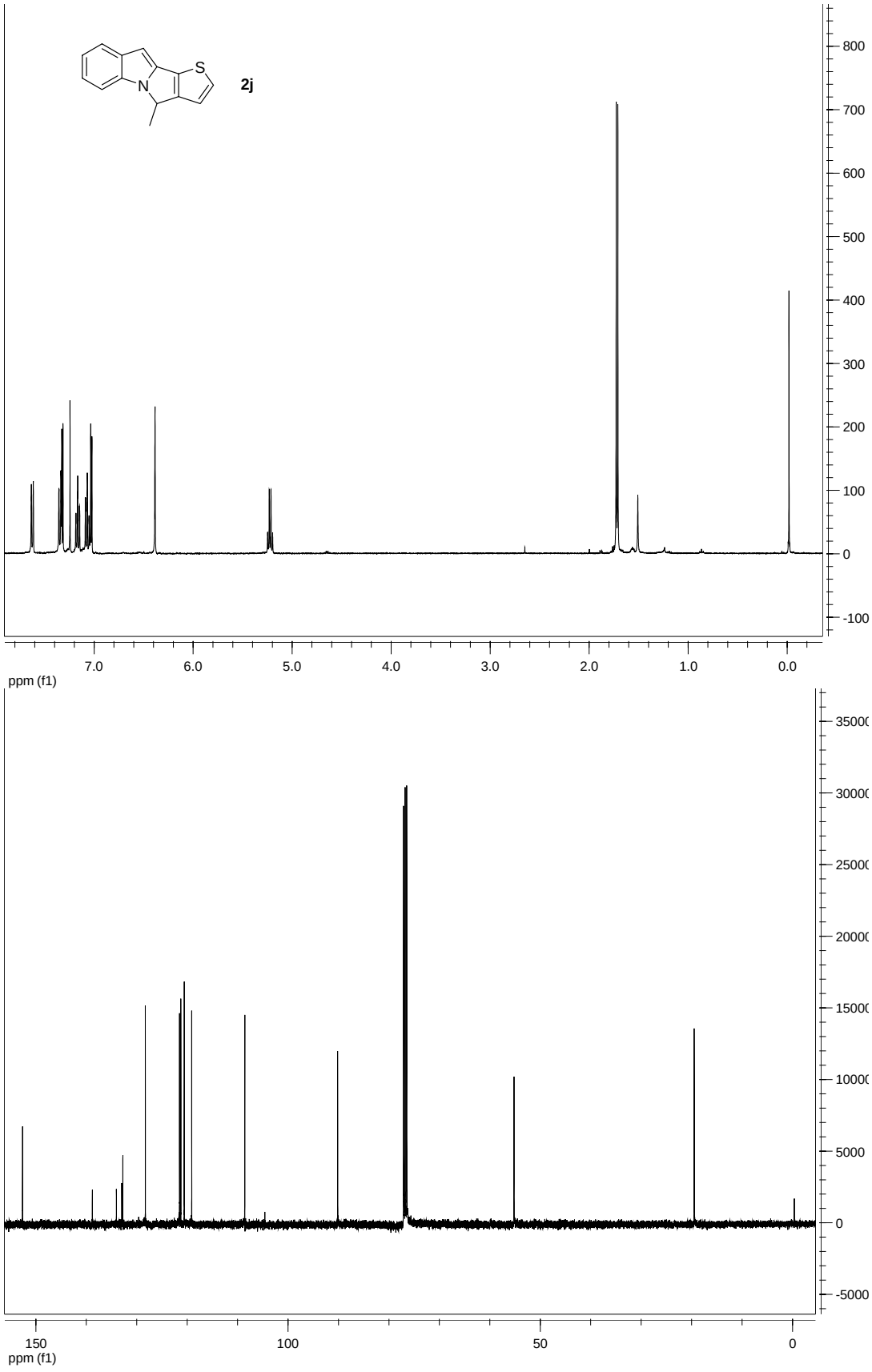
0
ppm (f1)

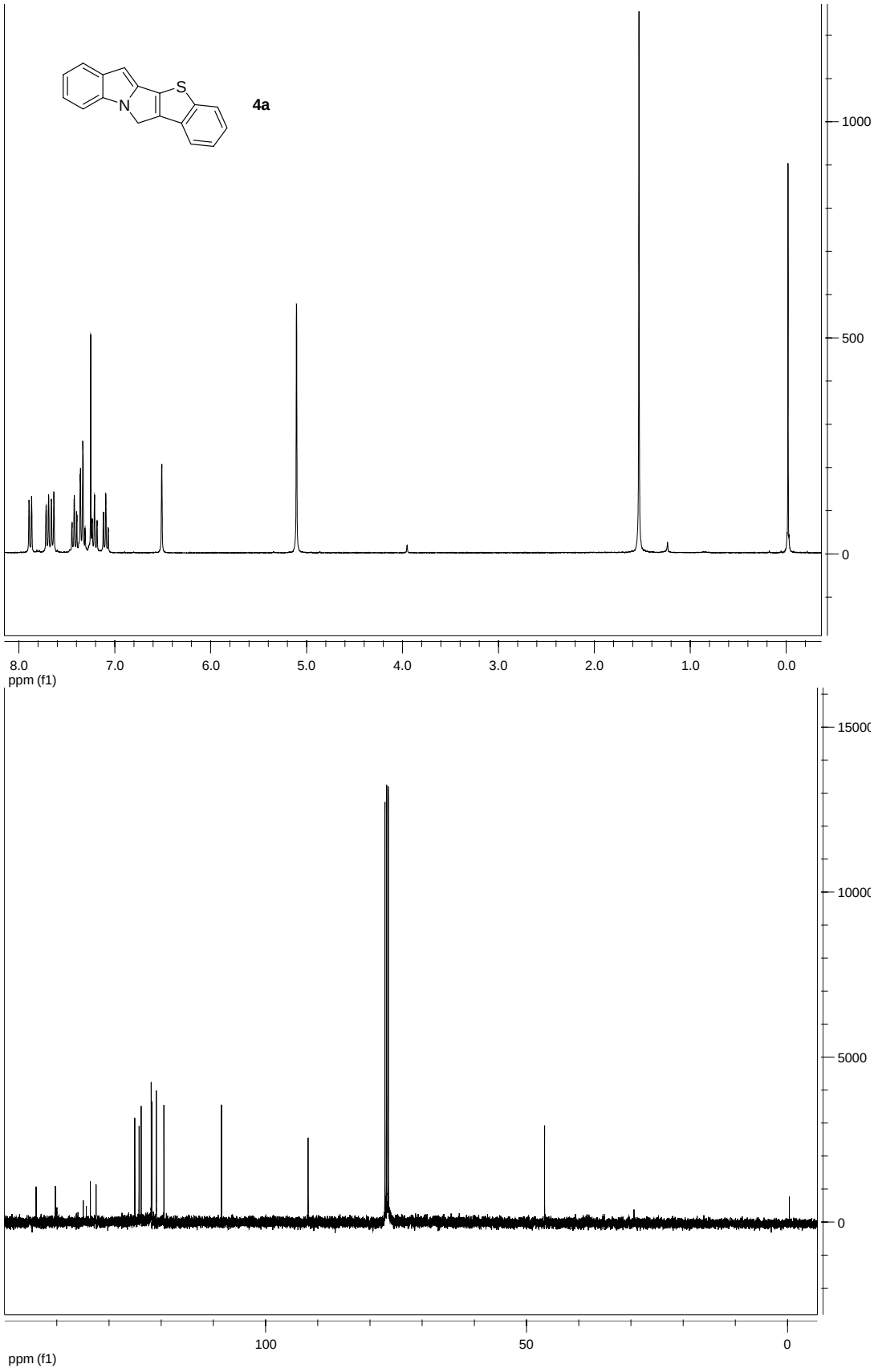

Cl
N
S
2g
1000
500
0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)
15000
10000
5000
0
100
50
0
ppm (f1)

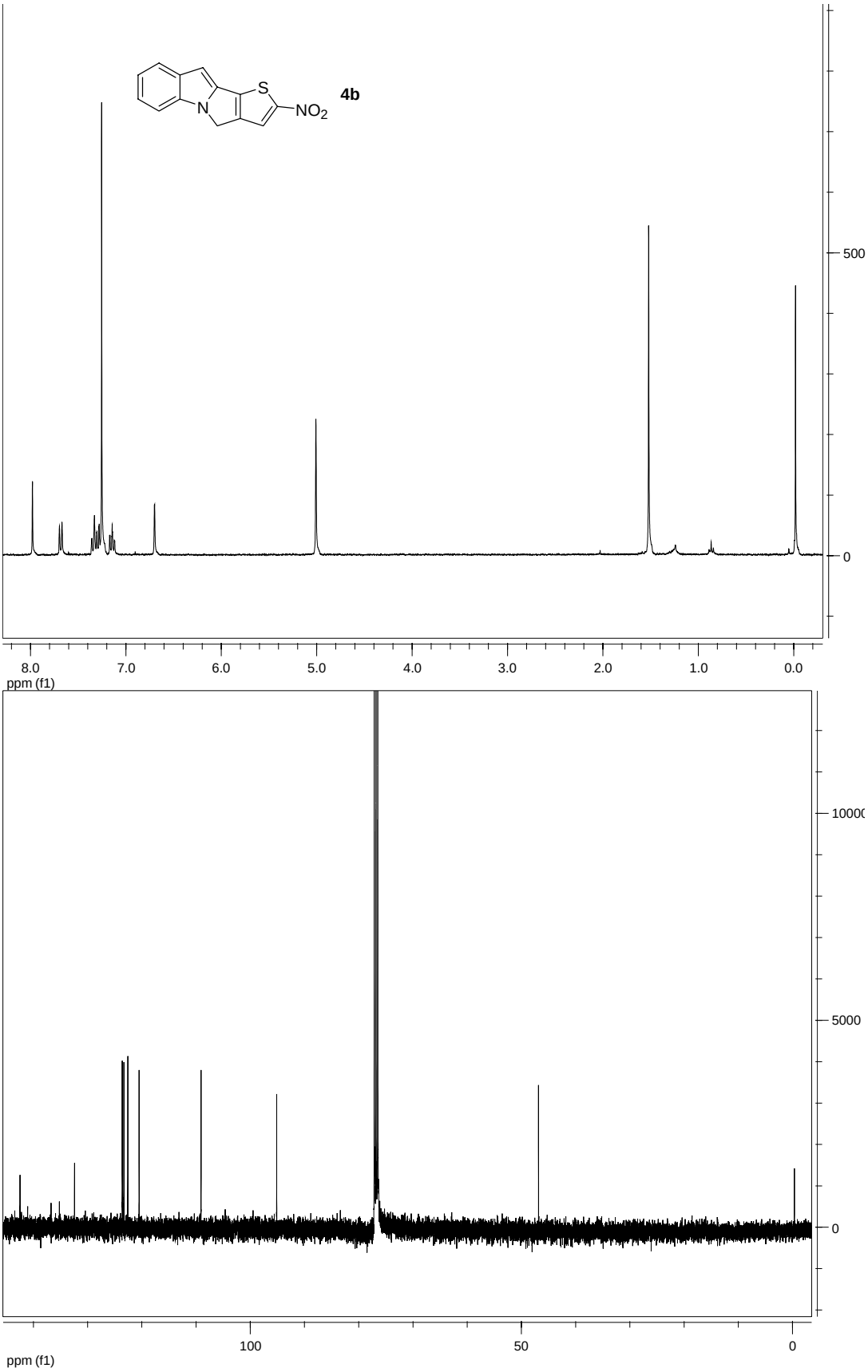

MeO2C
N
S
2h
1500
1000
500
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

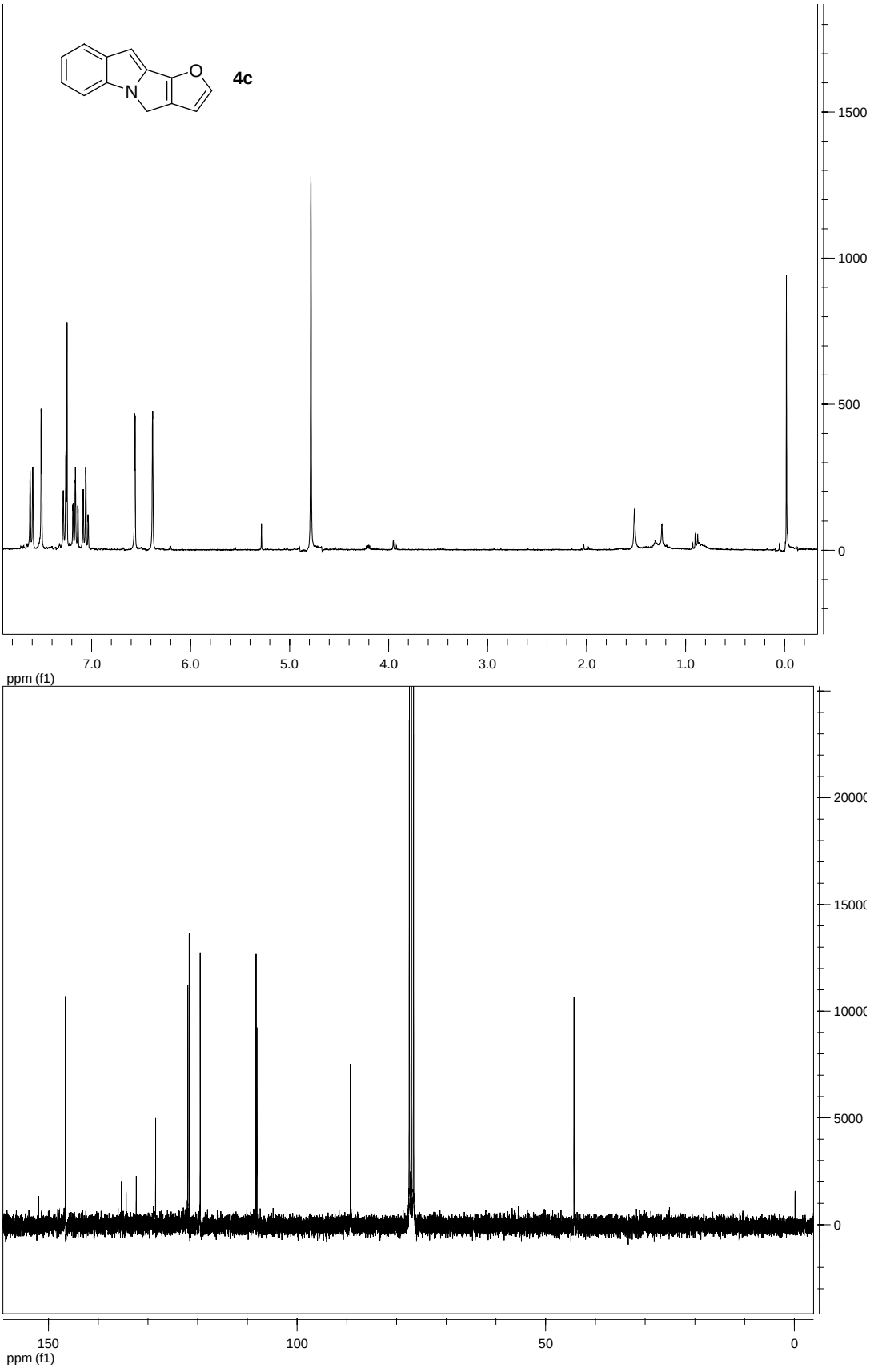

40000
30000
20000
10000
0
150
100
50
0
ppm (f1)

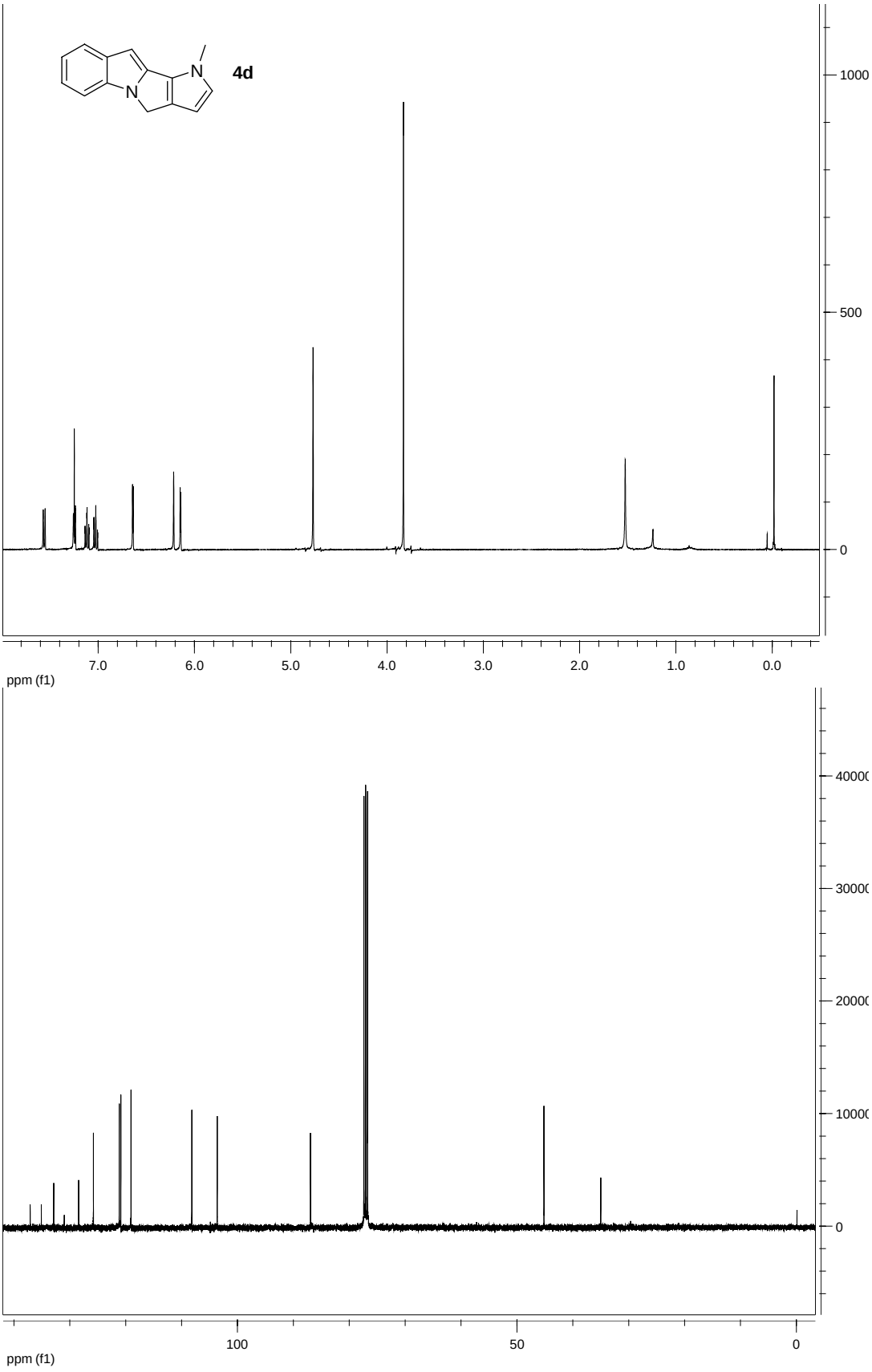

F3C
N
S
2i
1000
500
0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)
10000
50000
0
100
50
0
ppm (f1)

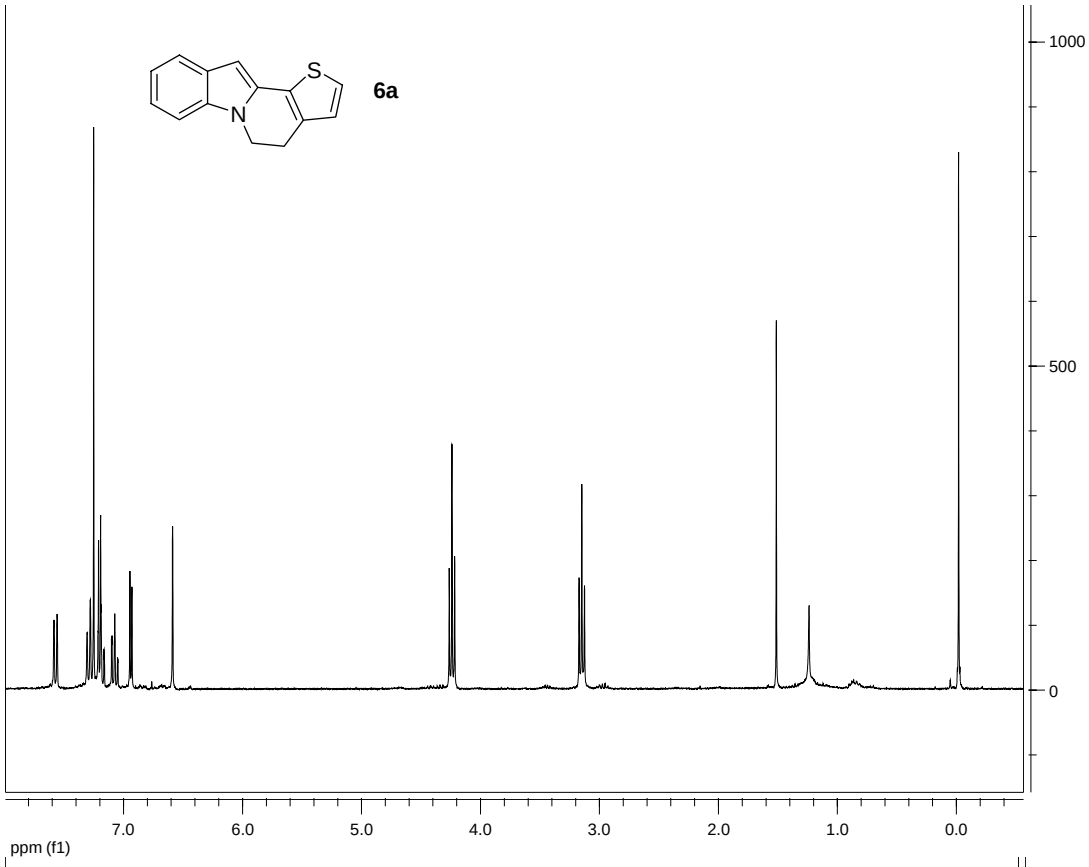

S
N
2j
800
700
600
500
400
300
200
100
0
-100
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)
35000
30000
25000
20000
15000
10000
5000
0
-5000
150
100
50
0
ppm (f1)

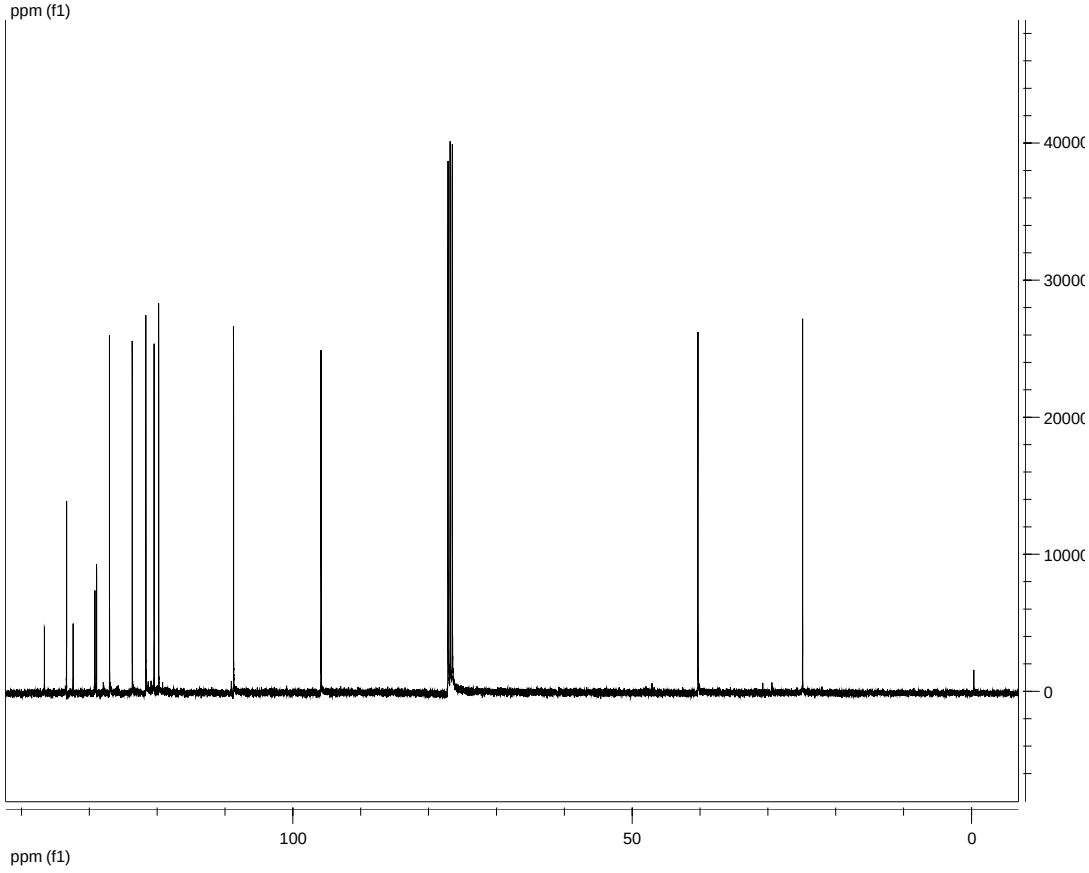

S
N
4a
1000
500
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)
15000
10000
5000
0
100
50
0
ppm (f1)

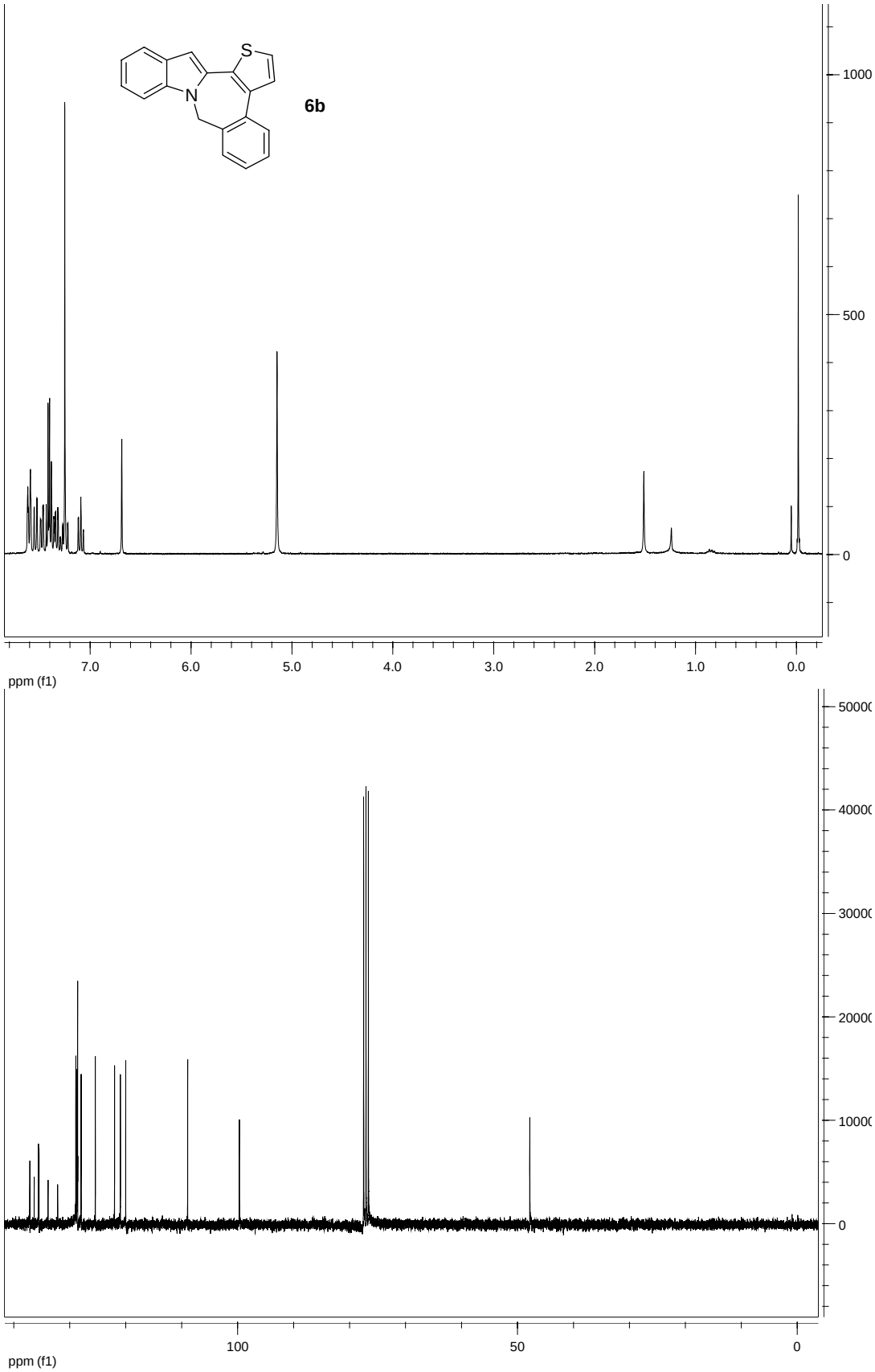

S
N
NO2
4b
500
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)
10000
5000
0
100
50
0
ppm (f1)

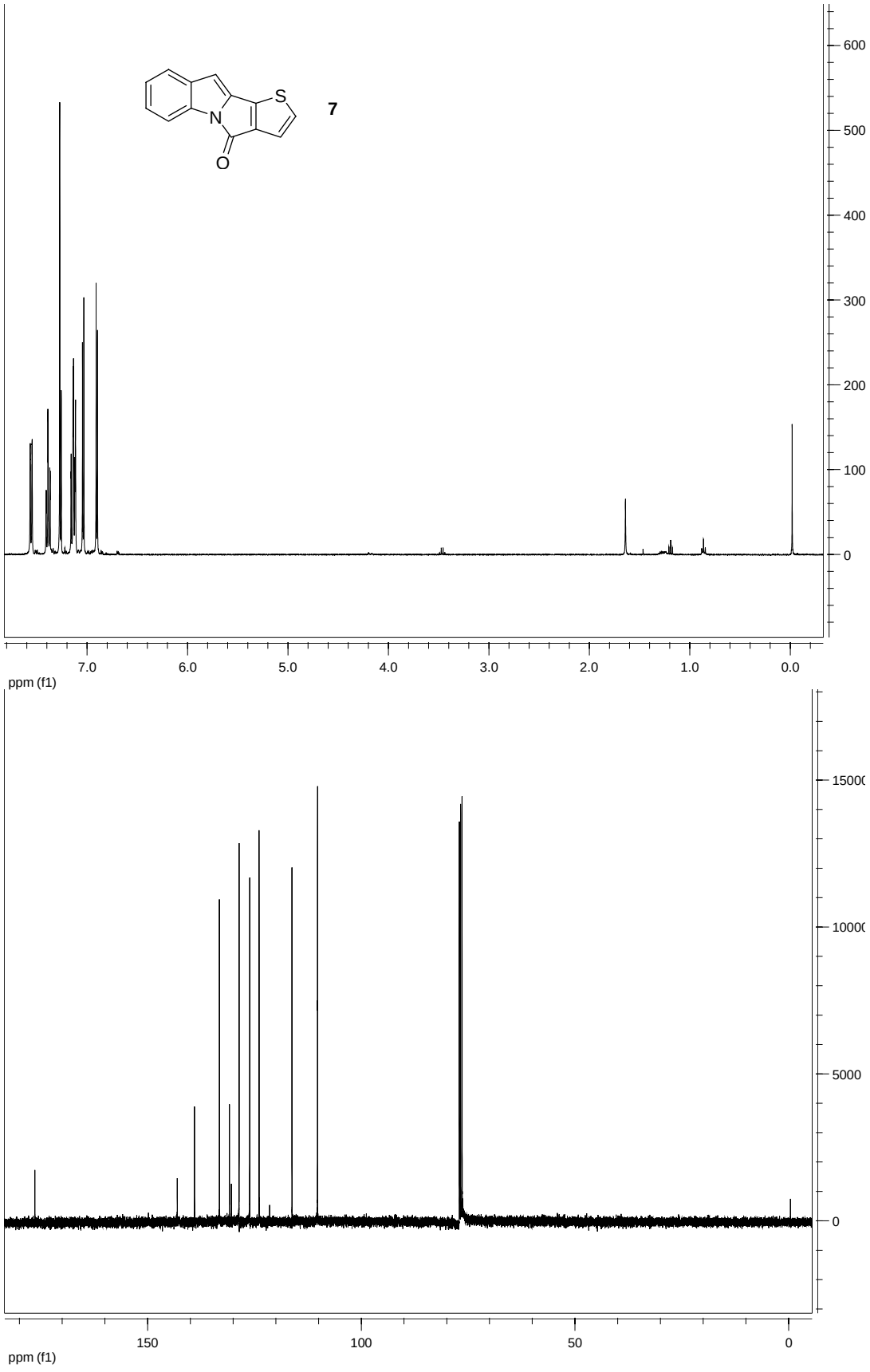

4c
O
N
1500
1000
500
0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)
2000
1500
1000
5000
0
150
100
50
0
ppm (f1)


4d
N
N
1000
500
0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)
40000
30000
20000
10000
0
100
50
0
ppm (f1)


S
N
6a
1000
500
0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


4000
3000
2000
1000
0
100
50
0
ppm (f1)


S
N
6b
1000
500
0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)
50000
40000
30000
20000
10000
0
100
50
0
ppm (f1)


S
N
O
7
600
500
400
300
200
100
0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)
1500
1000
5000
0
150
100
50
0
ppm (f1)