SUPPORTING INFORMATION

Synthesis of Thieno[3,2-*b*]indoles via Halogen Dance and Ligand-Controlled One-Pot Sequential Coupling Reaction

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1 General

Analytical thin layer chromatography (TLC) was performed on Merck 60 F_{254} aluminum sheets precoated with a 0.25 mm thickness of silica gel. Melting points (m.p.) were measured on a Yanaco MP-J3 and are uncorrected. Infrared (IR) spectra were recorded on a Bruker Alpha with an ATR attachment (Ge) and are reported in wave numbers (cm^{-1}). ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured on a JEOL ECZ400 spectrometer. Chemical shifts for ^1H NMR are reported in parts per million (ppm) downfield from tetramethylsilane with the solvent resonance as the internal standard ($CHCl_3$: δ 7.26 ppm) and coupling constants are in Hertz (Hz). The following abbreviations are used for spin multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad. Chemical shifts for ^{13}C NMR are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 77.16 ppm). High-resolution mass spectra (HRMS) were performed on a JEOL JMS-T100LP AccuTOF LC-Plus (ESI) with a JEOL MS-5414DART attachment.

2 Materials

Unless otherwise stated, all reactions were conducted in flame-dried glassware under an inert atmosphere of nitrogen. All work-up and purification procedures were carried out with reagent solvents in air. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Flash column chromatography was performed on Wakogel® C-300 (45–75 μm, Wako Pure Chemical Industries, Ltd.). Recycling preparative SEC-HPLC was performed with LC-9201 (Japan Analytical Industry Co., Ltd.) equipped with preparative SEC column (JAI-GEL-2H). Anhydrous THF was purchased from Wako Pure Chemical Industries, Ltd. LDA (ca. 1.5 M in THF/ethylbenzene/heptane) was purchased from Tokyo Chemical Industry Co., Ltd (Product number: L0171). Freshly prepared $ZnCl_2$·TMEDA[1] and $Pd(PPh_3)_4$[2] were used in the following experiments.

3 Substituent effects in Negishi coupling (Table 1)

Benzyl (2-(3,5-dibromothiophen-2-yl)phenyl)carbamate (4a).

A flame-dried 20-mL Schlenk tube equipped with a Teflon-coated magnetic stirring bar and a rubber septum was charged with 2,5-dibromothiophene (**2**) (169.6 mg, 0.70 mmol, 1.4 equiv) and anhydrous THF (5.0 mL). The solution was cooled to –78 °C. LDA (1.5 M, 0.43 mL, 0.65 mmol, 1.3 equiv) was added to the Schlenk tube and the resulting mixture was heated to 0 °C. To the red solution was added $ZnCl_2$·TMEDA complex (174.6 mg, 0.69 mmol, 1.4 equiv) at room temperature. After stirring at room temperature for 15 min, *N*-Cbz-2-iodoaniline (176.1 mg, 0.499 mmol, 1.0 equiv) and $Pd(PPh_3)_4$ (28.8 mg, 0.025 mmol, 5 mol%) were added to the orange solution. The resulting mixture was heated at 60 °C for 24 h, at which time the reaction mixture was treated with saturated aqueous ammonium chloride (5 mL). After partitioned, the aqueous layer was extracted twice with diethyl ether (3 mL).

(1) (a) Isobe, M.; Kondo, S.; Nagasawa, N.; Goto, T. *Chem. Lett.* **1977**, *6*, 679–682; b) Snégaroff, K.; Komagawa, S.; Chevallier, F.; Gros, P. C.; Golhen, S.; Roisnel, T.; Uchiyama, M.; Mongin, F. *Chem. Eur. J.* **2010**, *16*, 8191–8201.
(2) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121–124.

The combined organic extracts were washed with brine, dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexane) followed by preparative SEC-HPLC to provide the arylated thiophene **4a** as a yellow oil (37.2 mg, 0.0796 mmol, 16%). R_f = 0.46 (hexane/CH_2Cl_2 = 1:1); IR (ATR, cm^{-1}): 2958, 2924, 2854, 1596, 1503, 1452, 1407, 1389, 1319, 709, 700, 668, 629; ^1H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, 1H, *J* = 7.6 Hz), 7.47–7.42 (m, 1H), 7.42–7.31 (m, 5H), 7.23 (dd, 1H, *J* = 7.6, 1.6 Hz), 7.12 (dd, 1H, *J* = 8.0, 7.2 Hz), 7.06 (s, 1H), 6.61 (br s, 1H), 5.19 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.4, 136.5, 136.0, 135.6, 133.0, 131.8, 130.8, 128.8, 128.6, 128.5, 123.5, 121.0, 120.4, 114.0, 110.9, 67.4; HRMS (DART$^+$) *m/z*: calcd. for $C_{18}H_{14}{}^{81}Br_2NO_2S$, 469.9071 $[M+H]^+$; found, 469.9090.

***tert*-Butyl (2-(3,5-dibromothiophen-2-yl)phenyl)carbamate (4b).**

The title compound was obtained in 23% yield (51.0 mg, 0.118 mmol) as a yellow solid from *N*-Boc-2-iodoaniline (160.7 mg, 0.504 mmol, 1.0 equiv) according to the general procedure. R_f = 0.46 (hexane/CH_2Cl_2 = 1:1); M.p. 67.2–69.4 °C (CH_2Cl_2); IR (ATR, cm^{-1}): 3425, 2978, 2926, 1736, 1582, 1530, 1504, 1453, 1429, 1391, 1367, 1301, 1230, 1154, 816, 752; ^1H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, 1H, *J* = 8.0 Hz), 7.44–7.39 (m, 1H), 7.22 (dd, 1H, *J* = 7.6, 1.6 Hz), 7.09 (ddd, 1H, *J* = 8.0, 7.2, 0.8 Hz), 7.09 (s, 1H), 6.38 (br s, 1H), 1.50 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.8, 137.0, 136.0, 133.0, 131.7, 130.6, 123.0, 120.8, 120.5, 113.8, 110.7, 81.1, 28.4; HRMS (DART$^+$) *m/z*: calcd. for $C_{15}H_{16}{}^{79}Br_2NO_2S$, 431.9263 $[M+H]^+$; found, 431.9278.

2-(3,5-Dibromothiophen-2-yl)aniline (4c).

The title compound was obtained in 53% yield (89.1 mg, 0.268 mmol) as a yellow solid from 2-iodoaniline (110.0 mg, 0.502 mmol, 1.0 equiv) according to the general procedure. R_f = 0.46 (hexane/CH_2Cl_2 = 1:1); M.p. 39.8–41.1 °C (CH_2Cl_2); IR (ATR, cm^{-1}): 2933, 2911, 2850, 1614, 1573, 1528, 1468, 1455, 1434, 1301, 1257, 1158, 1127, 979, 812, 747; ^1H NMR (400 MHz, $CDCl_3$): δ 7.23 (ddd, 1H, *J* = 8.0, 7.6, 0.8 Hz), 7.13 (d, 1H, *J* = 8.0 Hz), 7.05 (s, 1H), 6.82–6.75 (m, 2H), 3.83 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.1, 137.5, 132.8, 132.0, 130.8, 118.3, 116.7, 115.8, 112.8, 109.7; HRMS (DART$^+$) *m/z*: calcd. for $C_{10}H_8{}^{79}Br_2NS$, 331.8744 $[M+H]^+$; found 331.8729.

2-(3,5-Dibromothiophen-2-yl)-*N*-phenylaniline (4d).

The title compound was obtained in 69% yield (140.1 mg, 0.342 mmol) as a yellow solid from *N*-phenyl-2-iodoaniline (147.0 mg, 0.498 mmol, 1.0 equiv) according to the general procedure. R_f = 0.46 (hexane/CH_2Cl_2 = 5:1); M.p. 74.7–77.2 °C (CH_2Cl_2); IR (ATR, cm^{-1}): 2922, 2851, 1591, 1502, 1453, 1305, 980, 857, 746, 690; ^1H NMR (400 MHz, $CDCl_3$): δ 7.34–7.24 (m, 5H), 7.10 (d, 2H, *J* = 7.6 Hz), 7.06 (s, 1H), 7.01–6.91 (m, 2H), 5.64 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.4, 142.2, 137.1, 132.8, 132.4, 130.5, 129.4, 122.2, 120.2, 119.9, 119.8, 116.4, 113.2, 110.3; HRMS (DART$^+$) *m/z*: calcd. for $C_{16}H_{12}{}^{79}Br_2NS$, 407.9057 $[M+H]^+$; found 407.9040.

_N_-Butyl-2-(3,5-dibromothiophen-2-yl)aniline (4e).

The title compound was obtained in 52% yield (108.7 mg, 0.258 mmol) as a yellow oil from *N*-butyl-2-iodoaniline (137.0 mg, 0.498 mmol, 1.0 equiv) according to the general procedure. R_f = 0.50 (hexane/CH_2Cl_2 = 5:1); IR (ATR, cm^{-1}): 3420, 2957, 2926, 2868, 2857, 1603, 1578, 1528, 1501,1456, 1428, 1318, 1301, 980, 813, 744, 525; ^1H NMR (400 MHz, $CDCl_3$): δ 7.32–7.27 (m, 1H), 7.09 (dd, 1H, *J* = 7.6, 1.6 Hz), 7.05 (s, 1H), 6.73–6.67 (m, 2H), 3.77 (br s, 1H), 3.18–3.10 (m, 2H), 1.62–1.52 (m, 2H), 1.39 (tq, 2H, *J* = 7.2, 7.2 Hz), 0.93 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.6, 137.6, 132.8, 132.0, 131.0, 116.2, 116.0, 112.8, 110.7, 110.0, 43.6, 31.6, 20.4, 14.0; HRMS (DART$^+$) *m/z*: calcd. for $C_{14}H_{16}{}^{79}Br_2NS$, 387.9370 $[M+H]^+$; found 387.9352.

_N_-Benzyl-2-(3,5-dibromothiophen-2-yl)aniline (4f).

The title compound was obtained in 58% yield (121.3 mg, 0.288 mmol) as a yellow solid from *N*-benzyl-2-iodoaniline (154.1 mg, 0.498 mmol, 1.0 equiv) according to the general procedure. R_f = 0.29 (hexane/CH_2Cl_2 = 5:1); M.p. 75.4–76.8 °C (CH_2Cl_2); IR (ATR, cm^{-1}): 1602, 1579, 1500, 1453, 1362, 1321, 1296, 1178, 1163, 1130, 980, 813, 746; ^1H NMR (400 MHz, $CDCl_3$): δ 7.38–7.31 (m, 4H), 7.29–7.22 (m, 2H), 7.13 (dd, 1H, *J* = 7.6, 1.6 Hz), 7.05 (s, 1H), 6.76–6.71 (m, 1H), 6.64 (d, 1H, *J* = 8.0 Hz), 4.39 (d, 2H, *J* = 5.6 Hz), 4.28 (t, 1H, *J* = 5.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.2, 139.1, 137.4, 132.8, 132.0, 131.0, 128.8, 127.31, 127.28, 116.8, 116.2, 113.0, 111.1, 110.2, 47.9; HRMS (DART$^+$) *m/z*: calcd. for $C_{17}H_{14}{}^{79}Br_2NS$, 421.9214 $[M+H]^+$; found 421.9227.

4 One-pot Arylation/Intramolecular Amination (Scheme 3 and Table 3)

2-(3-Bromo-5-(*p*-tolyl)thiophen-2-yl)-*N*-phenylaniline (5).

A 10-mL screw-top test tube equipped with a Teflon-coated magnetic stirring bar was charged with dibromothiophene **4d** (81.4 mg, 0.199 mmol, 1.0 equiv), 4-methylphenylboronic acid (32.3 mg, 0.24 mmol, 1.2 equiv), $PdCl_2(dppf)\cdot CH_2Cl_2$ (8.2 mg, 10 μmol, 5.0 mol%), K_3PO_4 (84.9 mg, 0.40 mmol, 2.0 equiv), and 1,4-dioxane (2.0 mL). The reaction mixture was heated at 80 °C for 6 h, at which time the reaction mixture was treated with water (2 mL). After partitioned, the aqueous layer was extracted twice with diethyl ether (2 mL). The combined organic extracts were washed with brine, dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexane/CH_2Cl_2 = 5:1) to give **5** (57.4 mg, 0.137 mmol, 69%) as a yellow oil. R_f = 0.39 (hexane/CH_2Cl_2 = 5:1); IR (ATR, cm^{-1}): 2922, 2852, 1591, 1570, 1516, 1505, 1498, 1472, 1464, 1457, 1308, 808, 746, 692; ^1H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, 2H, *J* = 8.0 Hz), 7.37–7.25 (m, 5H), 7.24 (s, 1H), 7.20 (d, 2H, *J* = 7.6 Hz), 7.12 (dd, 2H, *J* = 8.4, 1.2 Hz), 6.99–6.93 (m, 2H), 5.77 (br s, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.2, 142.5, 142.4, 138.5, 133.8, 132.5, 130.4, 130.1, 129.9, 129.4, 125.9, 125.6, 122.0, 120.8, 120.1, 119.8, 116.2, 111.4, 21.4; HRMS (DART$^+$) *m/z*: calcd. for $C_{23}H_{19}{}^{79}BrNS$, 420.0422 $[M+H]^+$; found 420.0409.

Method A

4-Phenyl-2-(*p*-tolyl)-4*H*-thieno[3,2-*b*]indole (1a).

A 10-mL screw-top test tube equipped with a Teflon-coated magnetic stirring bar was charged with dibromothiophene **4d** (81.3 mg, 0.199 mmol, 1.0 equiv), 4-methylphenylboronic acid (32.7 mg, 0.24 mmol, 1.2 equiv), $PdCl_2(dppf)\cdot CH_2Cl_2$ (8.3 mg, 0.010 mmol, 5.0 mol%), K_3PO_4 (84.9 mg, 0.40 mmol, 2.0 equiv), *t*-$Bu_3P\cdot HBF_4$ (12.0 mg, 0.040 mmol, 20 mol%), NaO*t*-Bu (57.7 mg, 0.60 mmol, 3.0 equiv), and 1,4-dioxane (2.0 mL). The reaction mixture was heated at 125 °C for 5 h, at which time the reaction mixture was treated with water (2 mL). After partitioned, the aqueous layer was extracted twice with diethyl ether. The combined organic extracts were washed with brine, dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexane) to give **1a** (38.5 mg, 0.113 mmol, 57%) as a yellow solid. R_f = 0.43 (hexane/CH_2Cl_2 = 5:1); M.p. 102.1–105.0 °C (CH_2Cl_2); IR (ATR, cm^{-1}): 1596, 1532, 1504, 1451, 1425, 1339, 1212, 1184, 1077, 1067, 801, 743, 699; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79–7.76 (m, 1H), 7.65–7.53 (m, 7H), 7.45–7.41 (m, 1H), 7.30 (s, 1H), 7.27–7.23 (m, 2H), 7.20 (d, 2H, *J* = 8.0 Hz), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.2, 145.2, 140.9, 138.9, 137.7, 132.6, 129.9, 129.7, 126.9, 125.7, 125.3, 123.0, 122.7, 120.6, 119.0, 116.7, 111.0, 107.1, 21.3; HRMS ($DART^+$) *m/z*: calcd. for $C_{23}H_{18}NS$, 340.1160 $[M+H]^+$; found 340.1167.

2,4-Diphenyl-4*H*-thieno[3,2-*b*]indole (1b).

The title compound was obtained in 34% yield (22.1 mg, 0.0679 mmol) as a yellow solid from dibromothiophene **4d** (82.2 mg, 0.201 mmol, 1.0 equiv) according to the general procedure. R_f = 0.49 (hexane/CH_2Cl_2 = 5:1); M.p. 147.7–152.4 °C (CH_2Cl_2); IR (ATR, cm^{-1}): 3054, 2925, 1596, 1529, 1502, 1452, 1421, 1340, 1212, 1069, 812, 752, 698; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80–7.77 (m, 1H), 7.69–7.66 (m, 2H), 7.64–7.53 (m, 5H), 7.45–7.37 (m, 3H), 7.35 (s, 1H), 7.31–7.22 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.9, 145.2, 140.9, 138.8, 135.4, 129.9, 129.1, 127.7, 126.9, 125.7, 125.3, 123.2, 122.6, 120.6, 119.1, 117.2, 111.0, 107.6; HRMS ($DART^+$) *m/z*: calcd. for $C_{22}H_{16}NS$, 326.1003 $[M+H]^+$; found 326.1006.

2-(4-(*tert*-Butyl)phenyl)-4-phenyl-4*H*-thieno[3,2-*b*]indole (1c).

The title compound was obtained in 45% yield (33.7 mg, 0.0883 mmol) as a yellow solid from dibromothiophene **4d** (81.1 mg, 0.198 mmol, 1.0 equiv) according to the general procedure. R_f = 0.49 (hexane/CH_2Cl_2 = 5:1); M.p. 140.2–145.7 °C (CH_2Cl_2); IR (ATR, cm^{-1}): 3059, 2961, 1597, 1531, 1504, 1452, 1426, 1407, 1361, 1340, 1271, 1214, 1113, 832, 806, 744, 699; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81–7.78 (m, 1H), 7.66–7.55 (m, 7H), 7.46–7.41 (m, 3H), 7.33 (s, 1H), 7.31–7.23 (m, 2H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.0, 146.1, 145.2, 140.9, 138.9, 132.6, 129.9, 126.9, 126.0, 125.5, 125.3, 123.0, 122.7, 120.6, 119.0, 116.9, 111.0, 107.2, 34.8, 31.4; HRMS ($DART^+$) *m/z*: calcd. for $C_{26}H_{24}NS$, 382.1629 $[M+H]^+$; found 382.1612.

***N*,*N*-Dimethyl-4-(4-phenyl-4*H*-thieno[3,2-*b*]indol-2-yl)aniline (1d).**

The title compound was obtained in 14% yield (10.4 mg, 0.0282 mmol) as a yellow solid from dibromothiophene **4d** (81.0 mg, 0.198 mmol, 1.0 equiv) according to the general procedure. R_f = 0.57

(hexane/CH_2Cl_2 = 1:1); M.p. 190.0–193.6 °C (CH_2Cl_2); IR (ATR, cm^{-1}): 2922, 1606, 1533, 1506, 1451, 1420, 1358, 1339, 1212, 1192, 817, 801, 747, 700, 671, 649, 637; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75–7.73 (m, 1H), 7.64–7.52 (m, 7H), 7.41 (t, 1H, *J* = 7.6 Hz), 7.23–7.20 (m, 2H), 7.17 (s, 1H), 6.73 (d, 2H, *J* = 8.8 Hz), 3.00 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.3, 147.3, 145.4, 140.6, 139.0, 129.9, 126.8, 125.3, 123.8, 122.9, 122.5, 120.5, 118.7, 115.4, 112.6, 110.9, 105.3, 40.6 (one aromatic carbon signal is missing due to overlapping); HRMS (DART$^+$) *m/z*: calcd. for $C_{24}H_{21}N_2S$, 369.1425 $[M+H]^+$; found 369.1414.

1-(4-(4-Phenyl-4*H*-thieno[3,2-*b*]indol-2-yl)phenyl)ethan-1-one (1e).

The title compound was obtained in 29% yield (21.3 mg, 0.0580 mmol) as a yellow solid from dibromothiophene **4d** (80.7 mg, 0.197 mmol, 1.0 equiv) according to the general procedure. R_f = 0.46 (hexane/CH_2Cl_2 = 1:2); M.p. 171.6–173.9 °C (CH_2Cl_2); IR (ATR, cm^{-1}): 2924, 1678, 1598, 1504, 1451, 1422, 1404, 1357, 1339, 1268, 1193, 836, 809, 746, 700, 648; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, 2H, *J* = 8.4 Hz), 7.81 (d, 1H, *J* = 8.0 Hz), 7.75 (d, 2H, *J* = 8.4 Hz), 7.63–7.60 (m, 4H), 7.55 (d, 1H, *J* = 7.6 Hz), 7.48–7.42 (m, 2H), 7.33–7.23 (m, 2H), 2.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.4, 145.2, 144.0, 141.3, 139.8, 138.6, 135.8, 130.0, 129.3, 127.2, 125.4, 125.3, 123.8, 122.4, 120.8, 119.4, 118.7, 111.2, 108.9, 26.7; HRMS (DART$^+$) *m/z*: calcd. for $C_{24}H_{18}NOS$, 368.1109 $[M+H]^+$; found 368.1107.

2-(3-Methoxyphenyl)-4-phenyl-4*H*-thieno[3,2-*b*]indole (1f).

The title compound was obtained in 57% yield (40.1 mg, 0.113 mmol) as a yellow solid from dibromothiophene **4d** (81.8 mg, 0.200 mmol, 1.0 equiv) according to the general procedure. R_f = 0.22 (hexane/CH_2Cl_2 = 5:1); M.p. 76.1–77.9 °C (CH_2Cl_2); IR (ATR, cm^{-1}): 2929, 1596, 1578, 1527, 1501, 1488, 1452, 1339, 1289, 1260, 1165, 1048, 745; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80–7.77 (m, 1H), 7.65–7.53 (m, 5H), 7.45–7.40 (m, 1H), 7.34 (s, 1H), 7.32–7.19 (m, 5H), 6.87–6.82 (m, 1H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1, 145.7, 145.1, 141.0, 138.8, 136.7, 130.1, 130.0, 127.0, 125.3, 123.2, 122.6, 120.6, 119.1, 118.4, 117.3, 113.3, 111.4, 111.1, 107.8, 55.5; HRMS (DART$^+$) *m/z*: calcd. for $C_{23}H_{18}NOS$, 356.1109 $[M+H]^+$; found 356.1112.

4-Phenyl-2-(3-(trifluoromethyl)phenyl)-4*H*-thieno[3,2-*b*]indole (1g).

The title compound was obtained in 9% yield (7.5 mg, 0.019 mmol) as a yellow solid from dibromothiophene **4d** (82.4 mg, 0.201 mmol, 1.0 equiv) according to the general procedure. R_f = 0.53 (hexane/CH_2Cl_2 = 5:1); M.p. 96.0–97.0 °C (CH_2Cl_2); IR (ATR, cm^{-1}): 2923, 1597, 1528, 1502, 1452, 1327, 1271, 1218, 1166, 1126, 1094, 1073, 795, 745, 694; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91–7.88 (m, 1H), 7.86–7.79 (m, 2H), 7.65–7.58 (m, 4H), 7.57–7.49 (m, 3H), 7.49–7.42 (m, 1H), 7.40 (s, 1H), 7.33–7.23 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.1, 143.8, 141.1, 138.7, 136.2, 131.5 (q, $^2J_{C–F}$ = 32.6 Hz), 130.0, 129.6, 128.8, 127.1, 125.3, 124.14 (q, $^1J_{C–F}$ = 271.2 Hz), 124.11 (q, $^3J_{C–F}$ = 3.8 Hz), 123.6, 122.4, 122.3 (q, $^3J_{C–F}$ = 3.9 Hz), 120.7, 119.2, 117.9, 111.2, 108.5; HRMS (DART$^+$) *m/z*: calcd. for $C_{23}H_{15}F_3NS$, 394.0877 $[M+H]^+$; found 394.0876.

2-(Anthracen-9-yl)-4-phenyl-4*H*-thieno[3,2-*b*]indole (1i).

The title compound was obtained in 28% yield (23.5 mg, 0.0552 mmol) as a yellow solid from dibromothiophene **4d** (81.2 mg, 0.198 mmol, 1.0 equiv) according to the general procedure. R_f = 0.34 (hexane/CH_2Cl_2 = 5:1); M.p. 220.9–222.5 °C (CH_2Cl_2); IR (ATR, cm^{-1}): 3057, 3046, 2925, 1674, 1595, 1527, 1499, 1451, 1437, 1345, 1284, 1213, 736, 699; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56–8.54 (m, 1H), 8.35–8.31 (m, 1H), 8.07–8.00 (m, 4H), 7.87–7.83 (m, 1H), 7.81 (dd, 1H, *J* = 6.0, 3.2 Hz), 7.72–7.66 (m, 3H), 7.57–7.51 (m, 2H), 7.50–7.27 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.5, 140.8, 140.5, 139.0, 132.1, 131.3, 129.9, 129.2, 128.4, 126.82, 126.77, 126.2, 125.4, 125.1, 123.3, 122.7, 120.7, 119.2, 119.0, 114.3, 111.3 (one aromatic carbon signal is missing due to overlapping); HRMS (DART$^+$) *m/z*: calcd. for $C_{30}H_{20}NS$, 426.1316 $[M+H]^+$; found 426.1311.

Method B

2,4-Diphenyl-4*H*-thieno[3,2-*b*]indole (1b).

A 10-mL screw-top test tube equipped with a Teflon-coated magnetic stirring bar was charged with dibromothiophene **4d** (82.7 mg, 0.202 mmol, 1.0 equiv), phenylboronic acid (30.1 mg, 0.24 mmol, 1.2 equiv), $Pd(PPh_3)_4$ (21.5 mg, 0.020 mmol, 10 mol%), K_2CO_3 (196.9 mg, 1.4 mmol, 7.0 equiv), *t*-$Bu_3P{\cdot}HBF_4$ (24.5 mg, 0.080 mmol, 40 mol%), NaO*t*-Bu (59.7 mg, 0.60 mmol, 3.0 equiv), 1,4-dioxane (2.0 mL), and H_2O (0.50 mL). The reaction mixture was heated at 125 °C for 22 h, at which time the reaction mixture was treated with water (2 mL). After partitioned, the aqueous layer was extracted twice with diethyl ether. The combined organic extracts were washed with brine, dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexane) to give **1b** (58.3 mg, 0.179 mmol, 89%) as a yellow solid.

1-(4-(4-Phenyl-4*H*-thieno[3,2-*b*]indol-2-yl)phenyl)ethan-1-one (1e).

The title compound was obtained in 60% yield (43.6 mg, 0.119 mmol) as a yellow solid from dibromothiophene **4d** (81.9 mg, 0.200 mmol, 1.0 equiv) according to the general procedure.

4-Phenyl-2-(3-(trifluoromethyl)phenyl)-4*H*-thieno[3,2-*b*]indole (1g).

The title compound was obtained in 48% yield (36.9 mg, 0.0938 mmol) as a yellow solid from dibromothiophene **4d** (80.0 mg, 0.196 mmol, 1.0 equiv) according to the general procedure.

2-(2-Nitrophenyl)-4-phenyl-4*H*-thieno[3,2-*b*]indole (1h).

The title compound was obtained in 43% yield (31.8 mg, 0.0858 mmol) as an orange solid from dibromothiophene **4d** (82.0 mg, 0.200 mmol, 1.0 equiv) according to the general procedure. R_f = 0.62 (hexane/CH_2Cl_2 = 1:1); M.p. 119.9–122.3 °C (CH_2Cl_2); IR (ATR, cm^{-1}): 3054, 2922, 1722, 1596, 1526, 1500, 1451, 1354, 1340, 746, 699; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81–7.76 (m, 2H), 7.66 (dd, 1H, *J* = 7.8, 1.8 Hz), 7.63–7.54 (m, 6H), 7.50–7.45 (m, 1H), 7.43–7.38 (m, 1H), 7.33–7.22 (m, 2H), 7.13 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.5, 144.6, 141.0, 138.6, 138.1, 132.5, 132.1, 130.0, 129.3, 128.8, 127.1, 125.3, 124.1, 123.8, 122.3, 120.7, 119.4, 119.2, 111.8, 111.2; HRMS (DART$^+$) *m/z*: calcd. for $C_{22}H_{15}N_2O_2S$, 371.0854 $[M+H]^+$; found 371.0851.

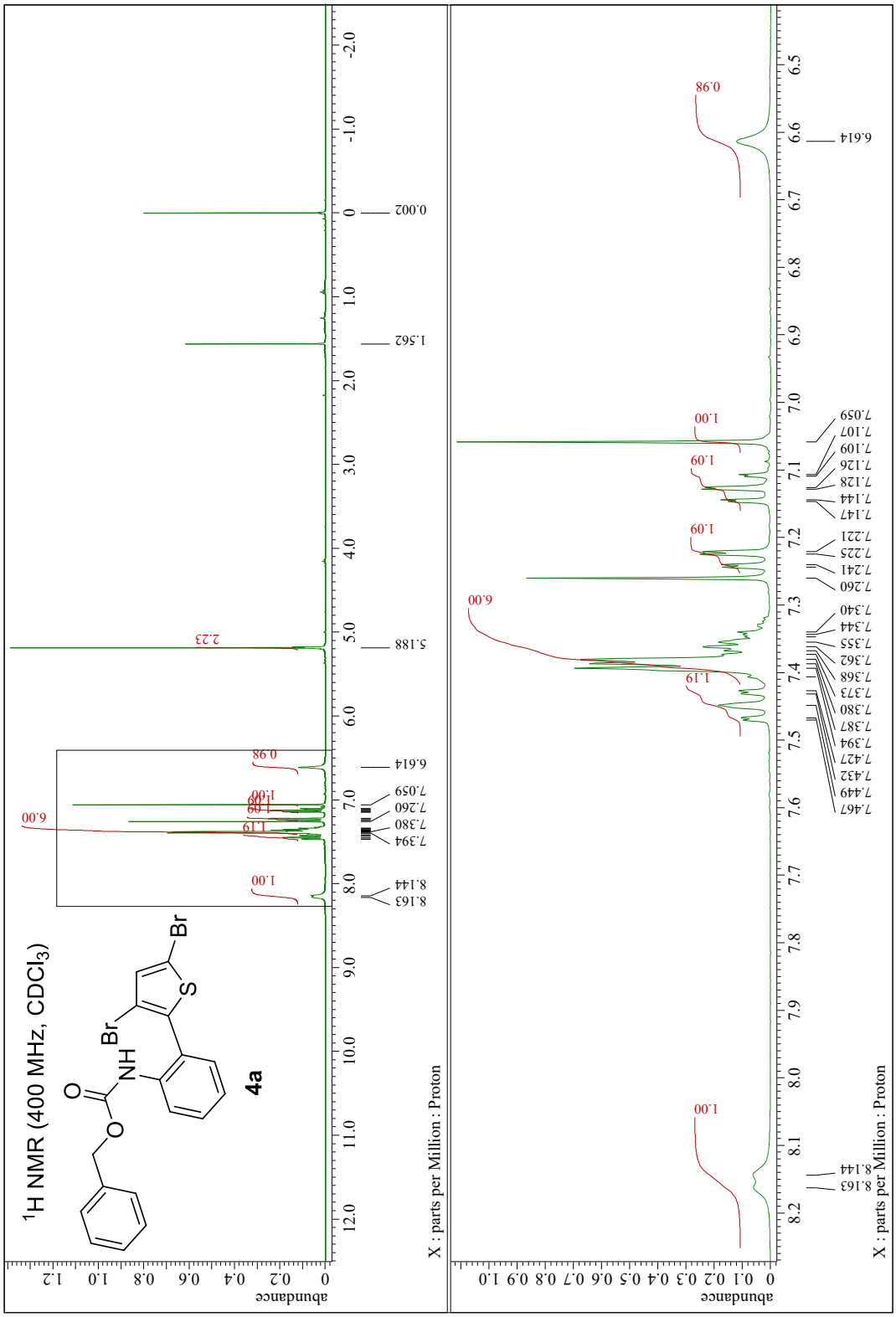
2-(Anthracen-9-yl)-4-phenyl-4*H*-thieno[3,2-*b*]indole (1i).

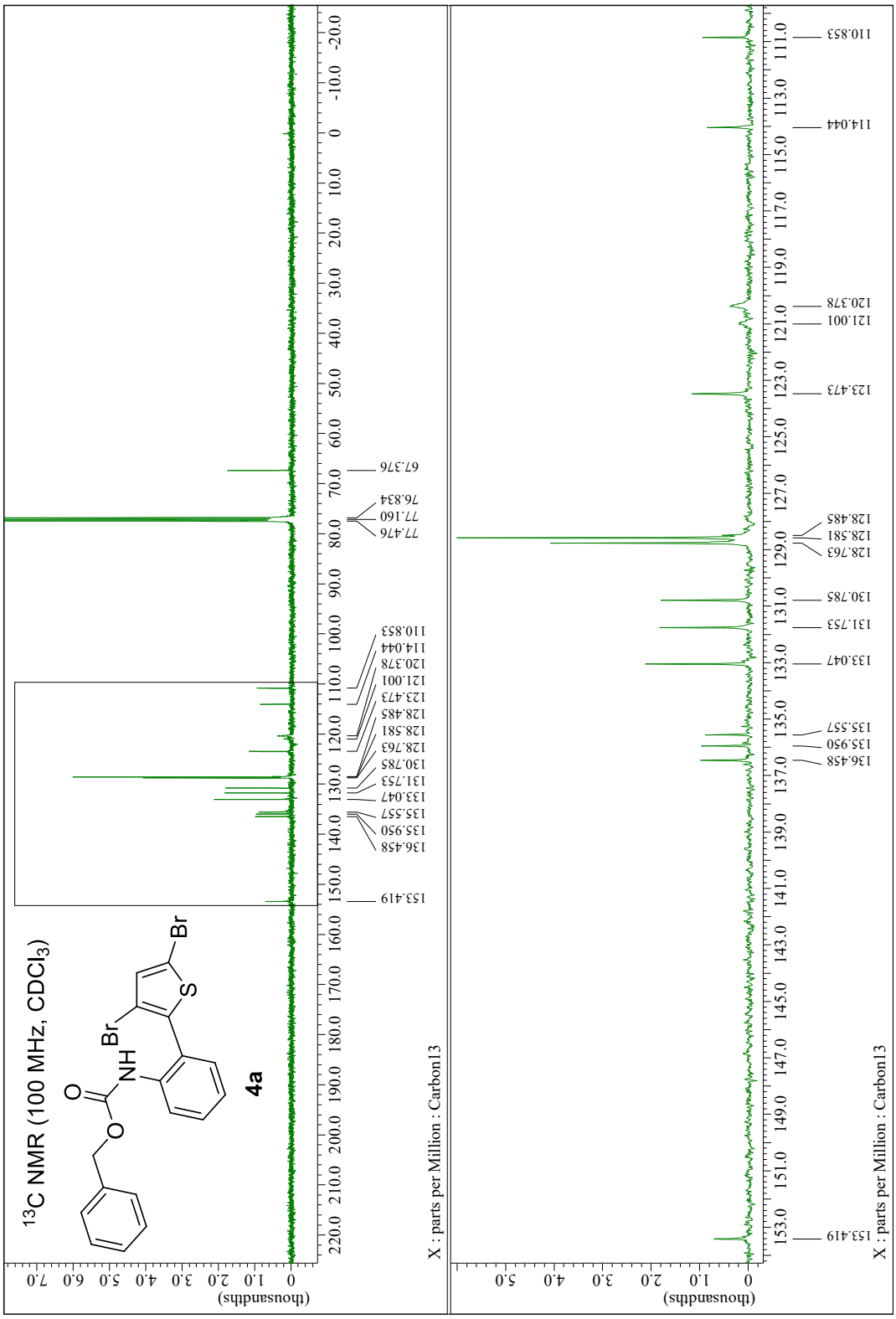
The title compound was obtained in 45% yield (37.9 mg, 0.0891 mmol) as a yellow solid from dibromothiophene **4d** (81.1 mg, 0.198 mmol, 1.0 equiv) according to the general procedure.

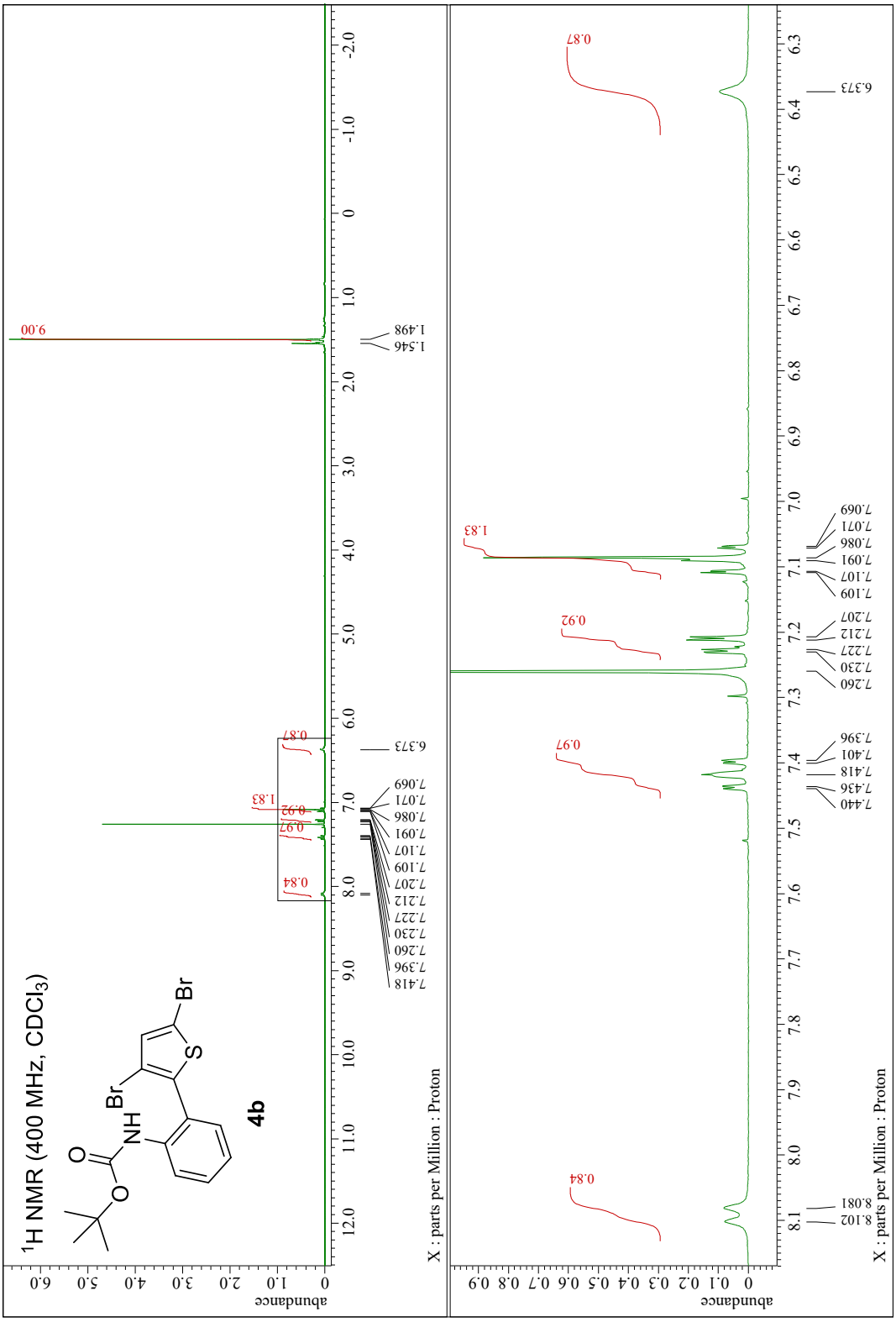
5 Synthesis of Unsymmetrical Indolothienoindole (Scheme 6)

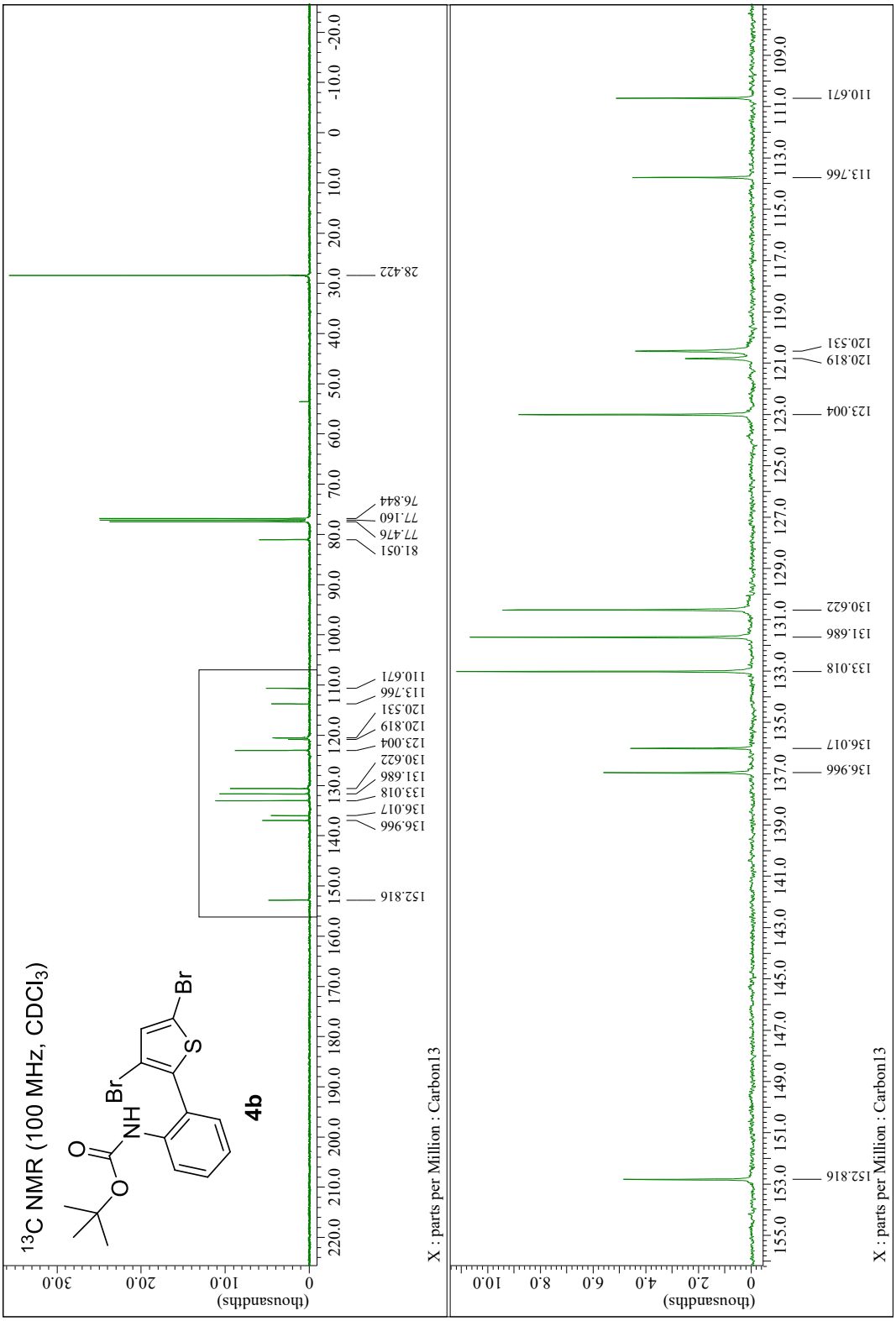
5-Phenyl-5,6-dihydrothieno[3,2-*b*:4,5-*b*']diindole (6).

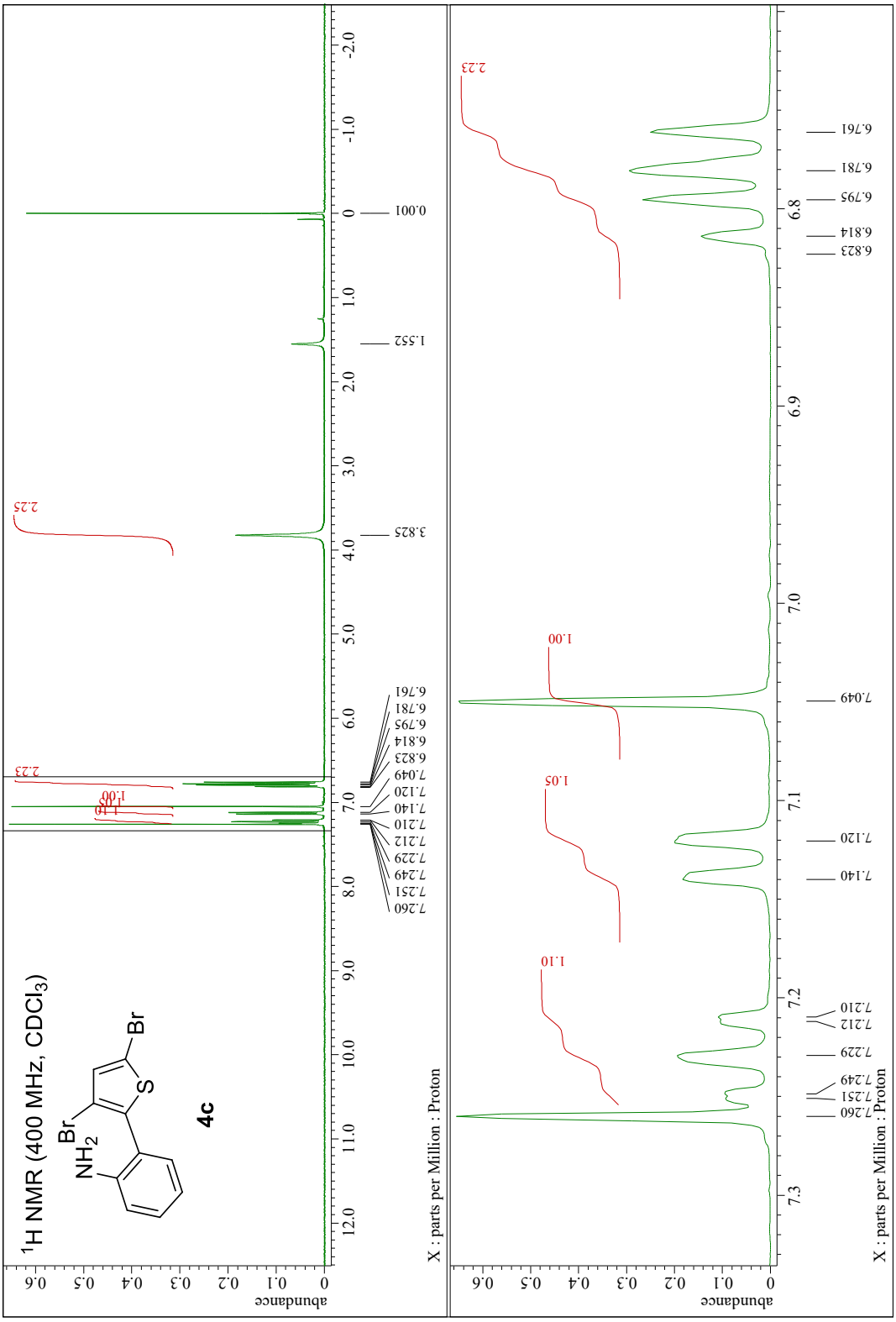
A flame-dried 20-mL Schlenk tube equipped with a Teflon-coated magnetic stirring bar and a rubber septum was charged with **1h** (29.1 mg, 0.0786 mmol, 1.0 equiv), PPh_3 (62.0 mg, 0.236 mmol, 3.0 equiv), and *o*-dichlorobenzene (2.2 mL). The reaction mixture was heated at 200 °C for 24 h, at which time the reaction mixture was purified by silica gel column chromatography (hexane/CH_2Cl_2 = 10:1 to 3:1, gradient) to give **6** (12.2 mg, 0.0360 mmol, 46%) as a yellow solid. R_f = 0.62 (hexane/CH_2Cl_2 = 1:1); M.p. 89.8–92.7 °C ($CHCl_3$); IR (ATR, cm^{-1}): 2958, 2924, 2854, 1596, 1503, 1451, 1407, 1387, 1319, 740, 700, 668, 629; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (br s, 1H), 7.84–7.79 (m, 1H), 7.78–7.75 (m, 1H), 7.72–6.68 (m, 4H), 7.62–7.58 (m, 1H), 7.55–7.50 (m, 1H), 7.41 (dd, 1H, *J* = 7.2, 1.6 Hz), 7.32–7.19 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.5, 140.2, 138.7, 130.5, 129.5, 127.6, 127.4, 125.1, 124.1, 123.4, 123.1, 123.0, 121.0, 120.97, 120.5, 118.9, 118.6, 112.2, 111.0 (one aromatic carbon signal is missing due to overlapping); HRMS (DART$^+$) *m/z*: calcd. for $C_{22}H_{14}N_2S$, 338.0878 $[M]^+$; found 338.0883.

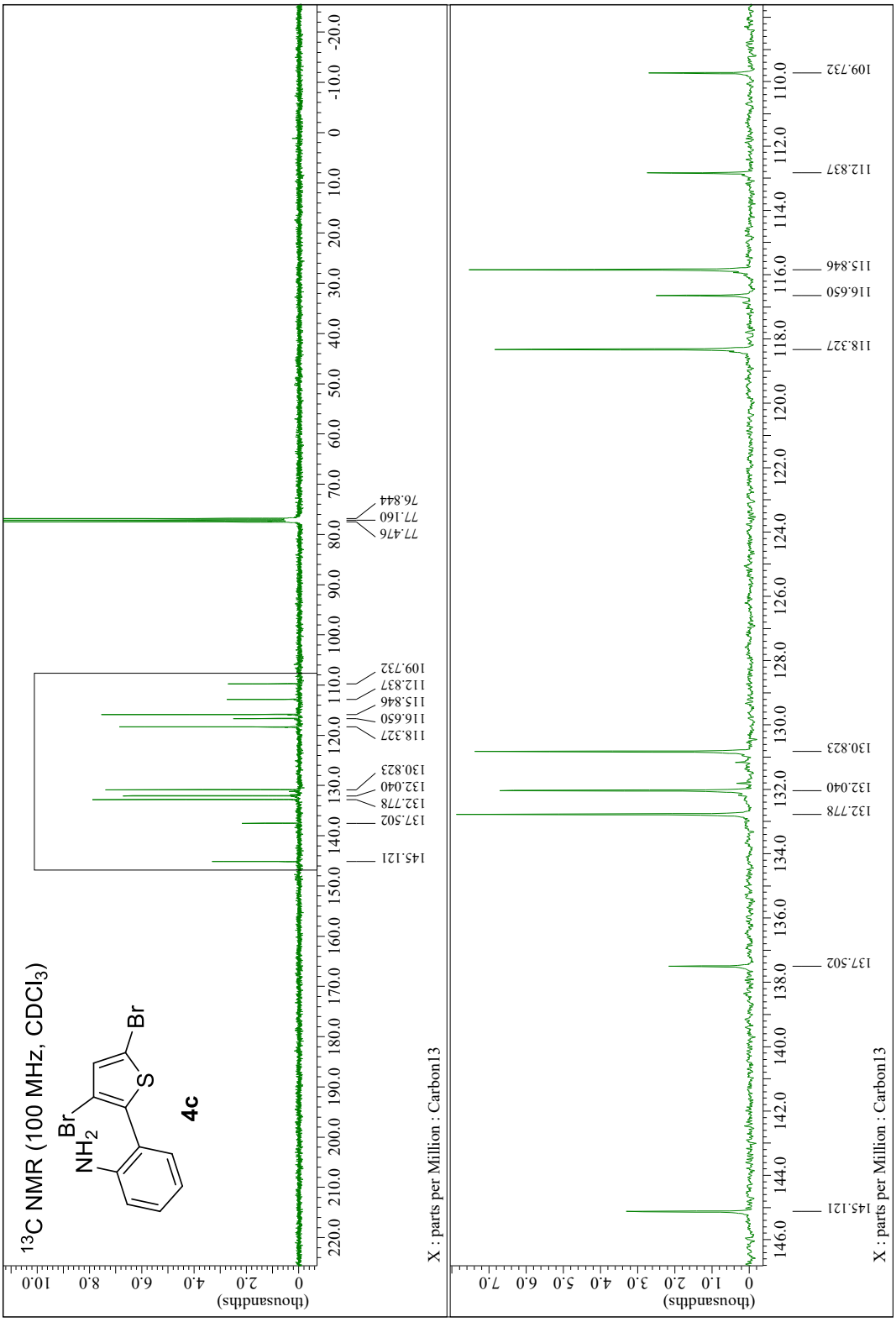

^{1}H NMR (400 MHz, $CDCl_3$)
4a
Br
S
Br
NH
O
O
abundance
X : parts per Million : Proton
8.163
8.144
7.467
7.449
7.432
7.427
7.394
7.387
7.380
7.373
7.368
7.362
7.355
7.340
7.260
7.241
7.225
7.221
7.147
7.144
7.128
7.126
7.109
7.107
7.059
6.614
5.188
2.23
1.562
0.002
6.00
1.19
1.09
1.00
0.98

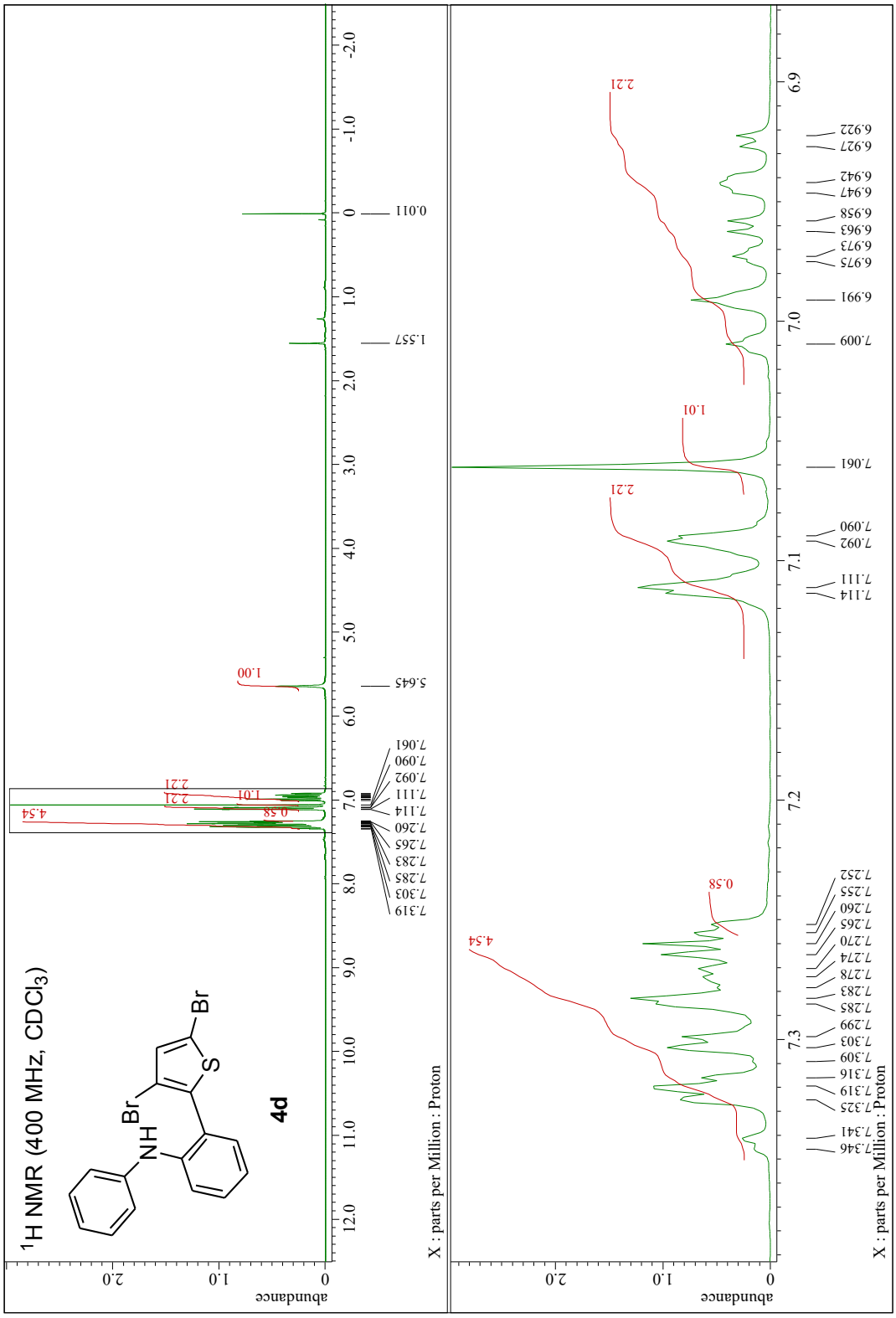

^{13}C NMR (100 MHz, CDCl$_3$)
4a
Br
Br
S
NH
O
O
153.419
136.458
135.950
135.557
133.047
131.753
130.785
128.763
128.581
128.485
123.473
121.001
120.378
114.044
110.853
77.476
77.160
76.834
67.376
X : parts per Million : Carbon13
(thousandths)

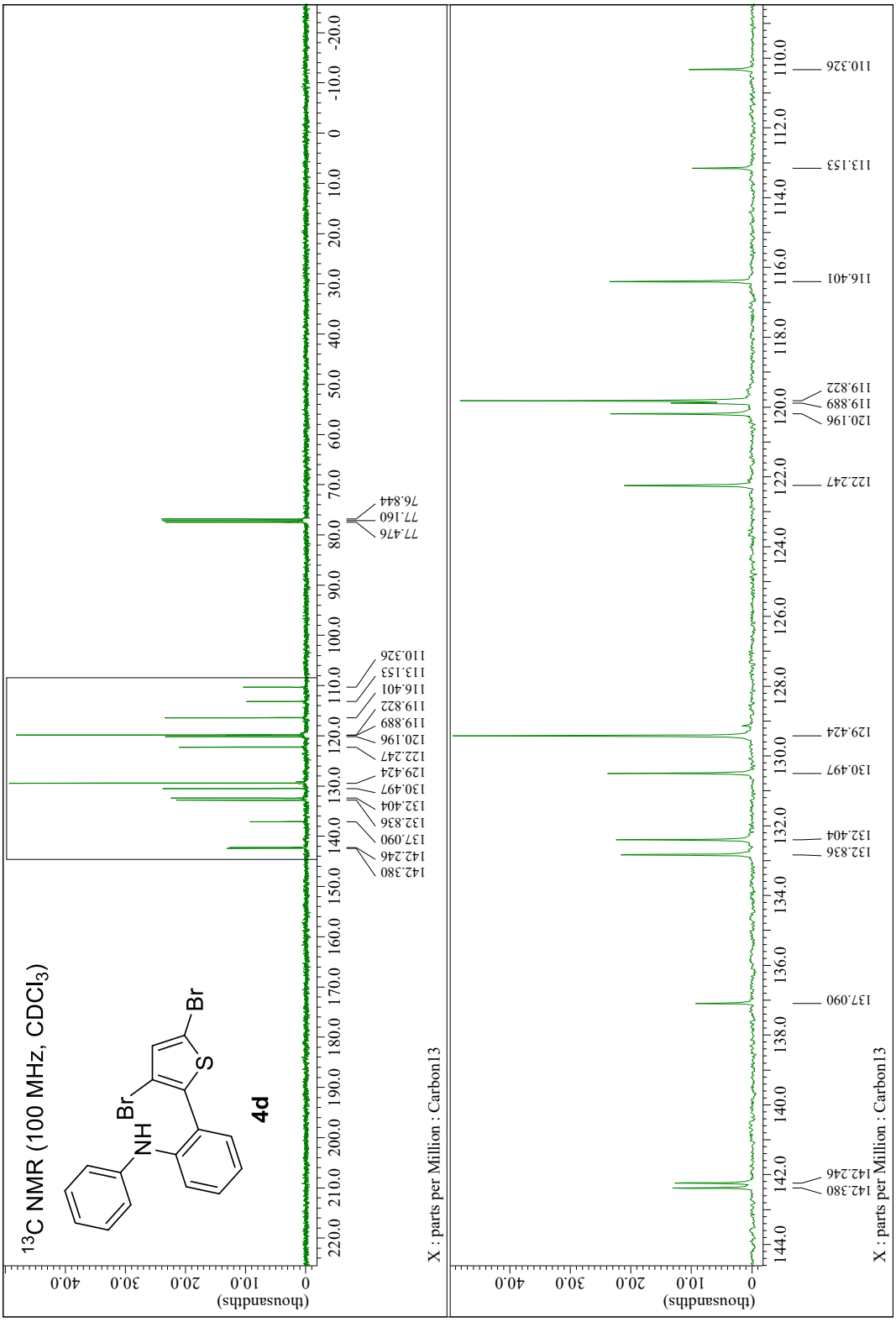

^{1}H NMR (400 MHz, CDCl$_3$)
4b
Br
Br
NH
O
O
S
abundance
X : parts per Million : Proton
9.00
1.546
1.498
6.373
7.418
7.396
7.260
7.230
7.227
7.212
7.207
7.109
7.107
7.091
7.086
7.071
7.069
0.84
0.97
0.92
1.83
0.87
8.102
8.081
7.440
7.436
7.418
7.401
7.396

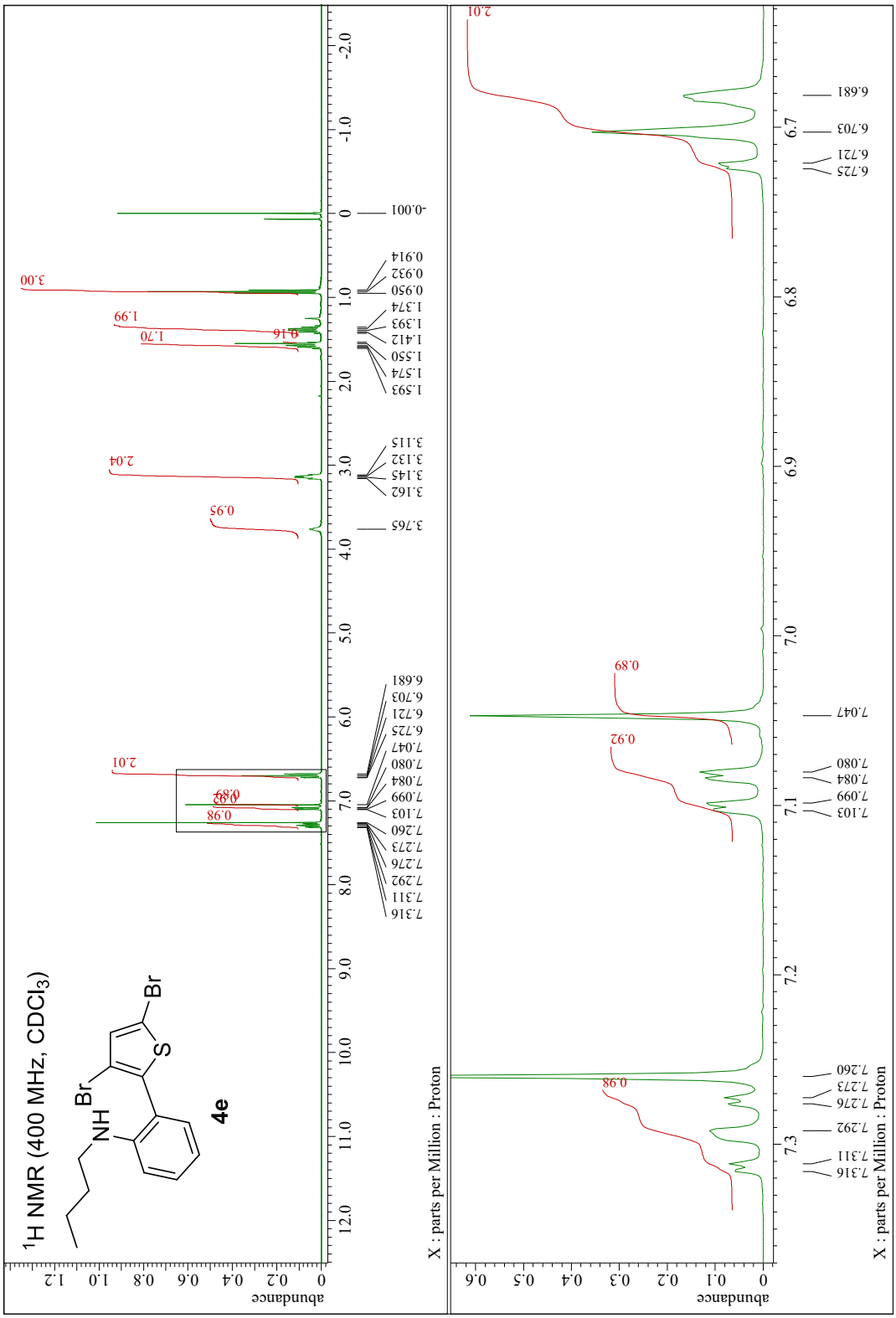

^{13}C NMR (100 MHz, CDCl$_3$)
4b
X : parts per Million : Carbon13
(thousandths)
28.422
76.844
77.160
77.476
81.051
110.671
113.766
120.531
120.819
123.004
130.622
131.686
133.018
136.017
136.966
152.816

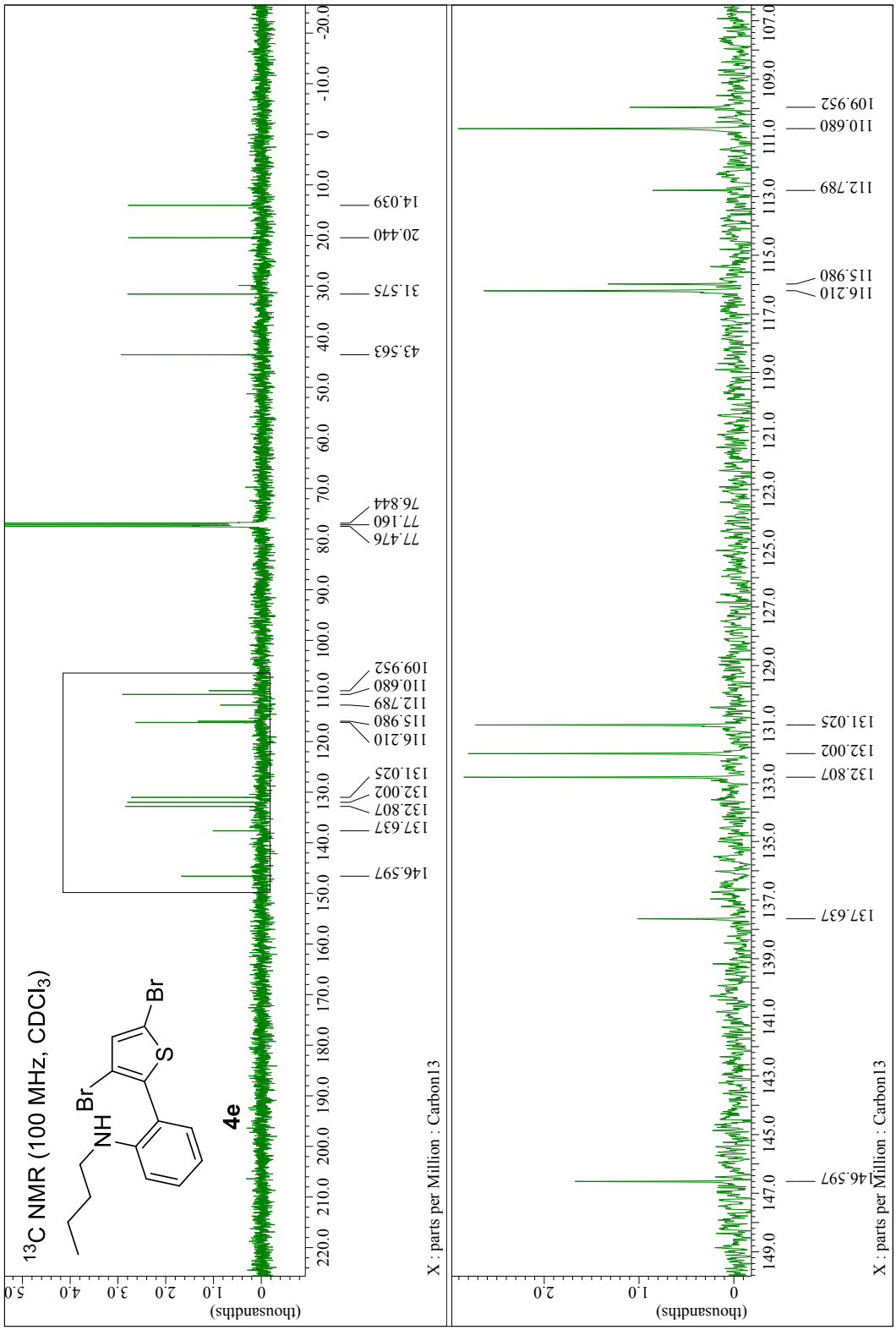

^{1}H NMR (400 MHz, CDCl$_3$)
Br
NH$_2$
S
Br
4c
abundance
X : parts per Million : Proton
2.25
3.825
1.552
0.001
2.23
1.00
1.05
1.10
7.260
7.251
7.249
7.229
7.212
7.210
7.140
7.120
7.049
6.823
6.814
6.795
6.781
6.761


^{13}C NMR (100 MHz, CDCl$_3$)
4c
Br
NH$_2$
Br
S
(thousandths)
X : parts per Million : Carbon13
145.121
137.502
132.778
132.040
130.823
118.327
116.650
115.846
112.837
109.732
77.476
77.160
76.844

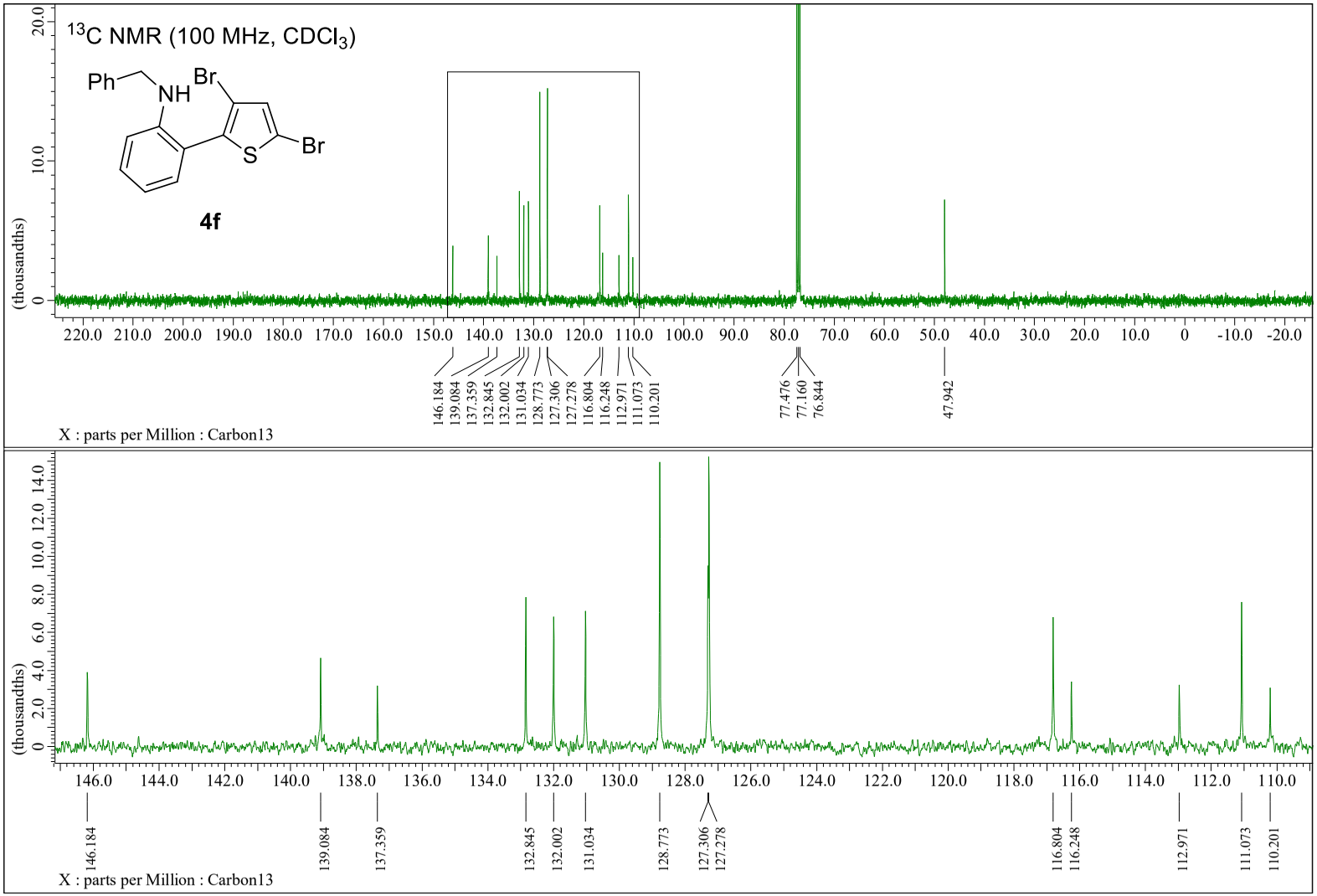

^{1}H NMR (400 MHz, CDCl$_3$)
4d
Br
NH
Br
S
abundance
X : parts per Million : Proton
4.54
0.58
1.01
2.21
1.00
5.645
1.557
0.011
7.319
7.303
7.285
7.283
7.265
7.260
7.114
7.111
7.092
7.090
7.061
6.922
6.927
6.942
6.947
6.958
6.963
6.973
6.975
6.991
7.009
7.252
7.255
7.260
7.265
7.270
7.274
7.278
7.283
7.285
7.299
7.303
7.309
7.316
7.319
7.325
7.341
7.346


^{13}C NMR (100 MHz, CDCl$_3$)
4d
Br
NH
Br
S
142.380
142.246
137.090
132.836
132.404
130.497
129.424
122.247
120.196
119.889
119.822
116.401
113.153
110.326
77.476
77.160
76.844
X : parts per Million : Carbon13
(thousandths)

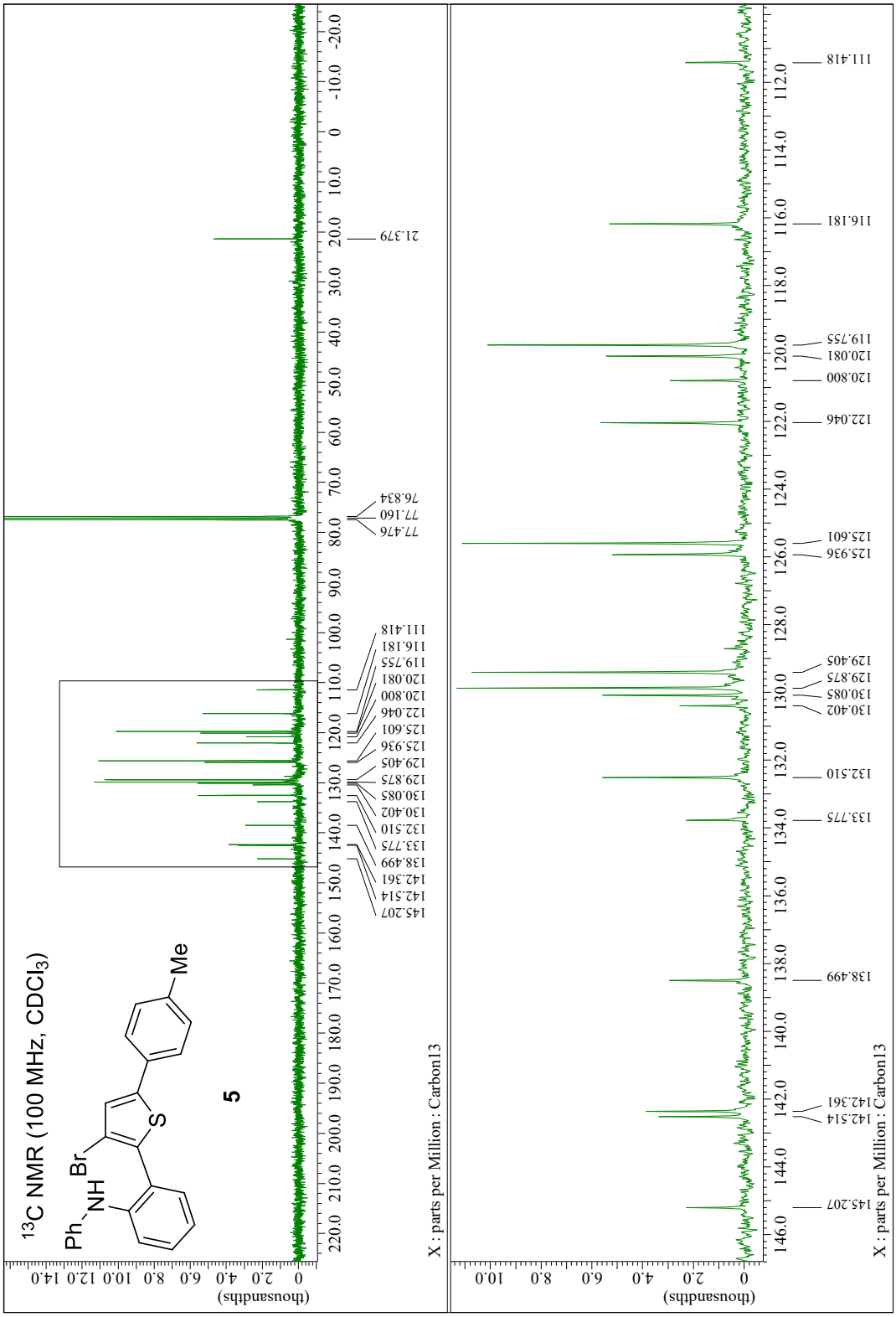

^{1}H NMR (400 MHz, CDCl$_3$)
4e
Br
NH
Br
S
abundance
X : parts per Million : Proton

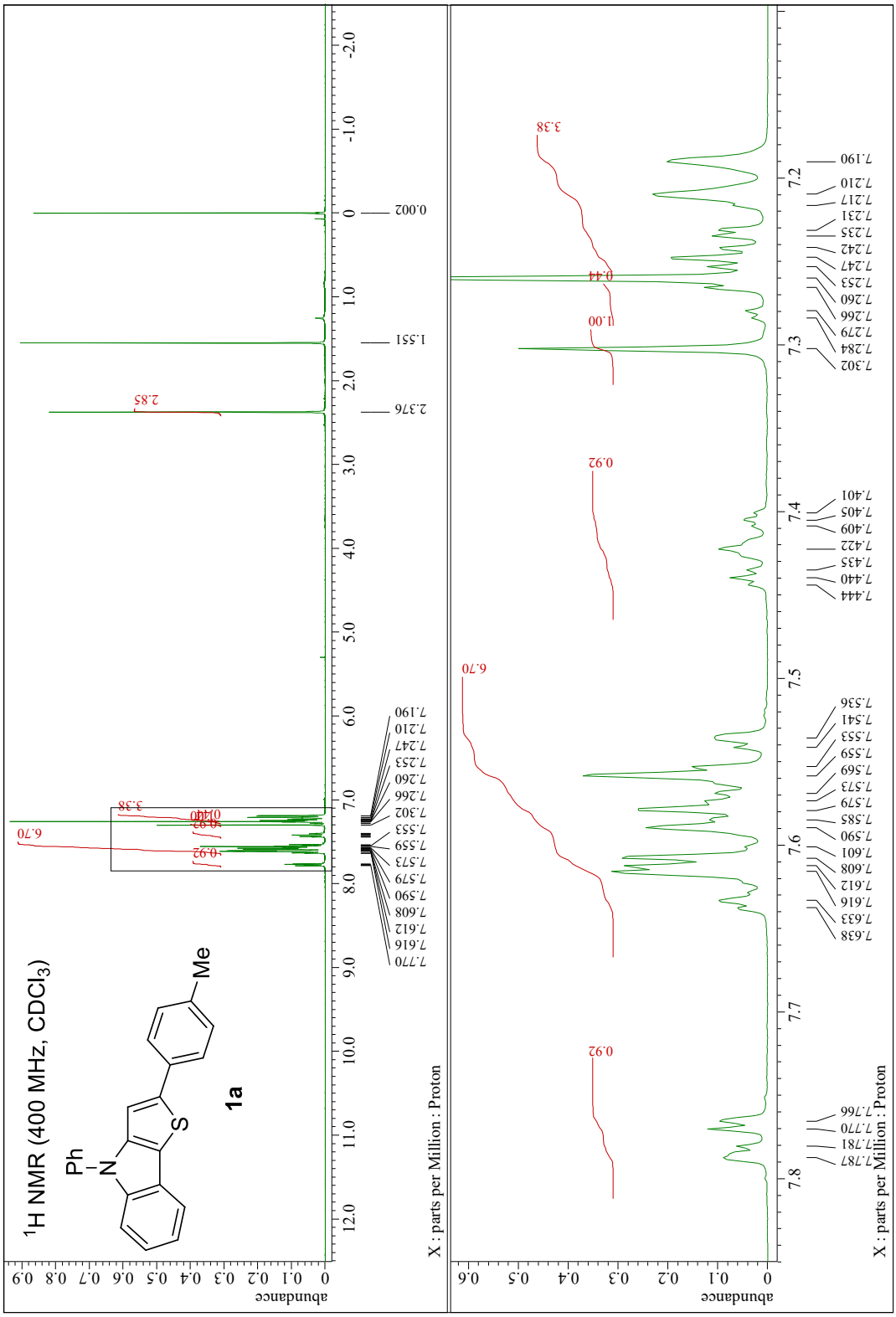

^{13}C NMR (100 MHz, CDCl$_3$)
4e
Br
NH
Br
S
(thousandths)
X : parts per Million : Carbon13
146.597
137.637
132.807
132.002
131.025
116.210
115.980
112.789
110.680
109.952
77.476
77.160
76.844
43.563
31.575
20.440
14.039

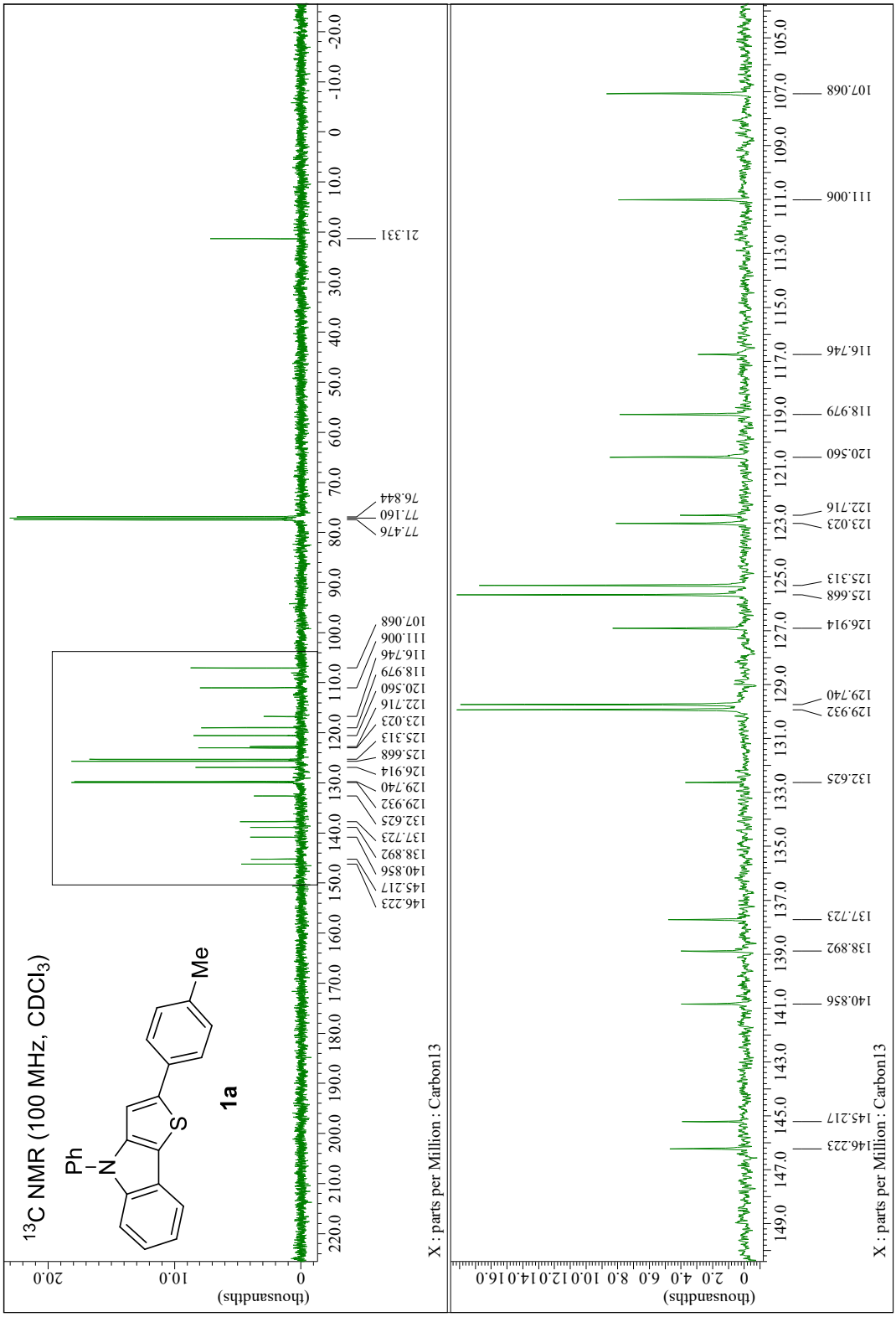
^{1}H NMR (400 MHz, $CDCl_3$)
4f
Ph
NH
Br
Br
S
abundance
X : parts per Million : Proton
4.94
2.36
1.00
1.23
1.07
1.10
1.06
0.99
1.24
1.23
0.004
1.550
4.397
4.383
4.290
4.276
4.264
7.350
7.333
7.314
7.279
7.260
7.246
7.142
7.138
7.123
7.119
7.045
6.758
6.739
6.652
6.632
7.373
7.368
7.350
7.333
7.328
7.314
7.284
7.279
7.260
7.246
7.228
7.225
7.142
7.138
7.123
7.119
7.045
6.758
6.739
6.721
6.719
6.652
6.632

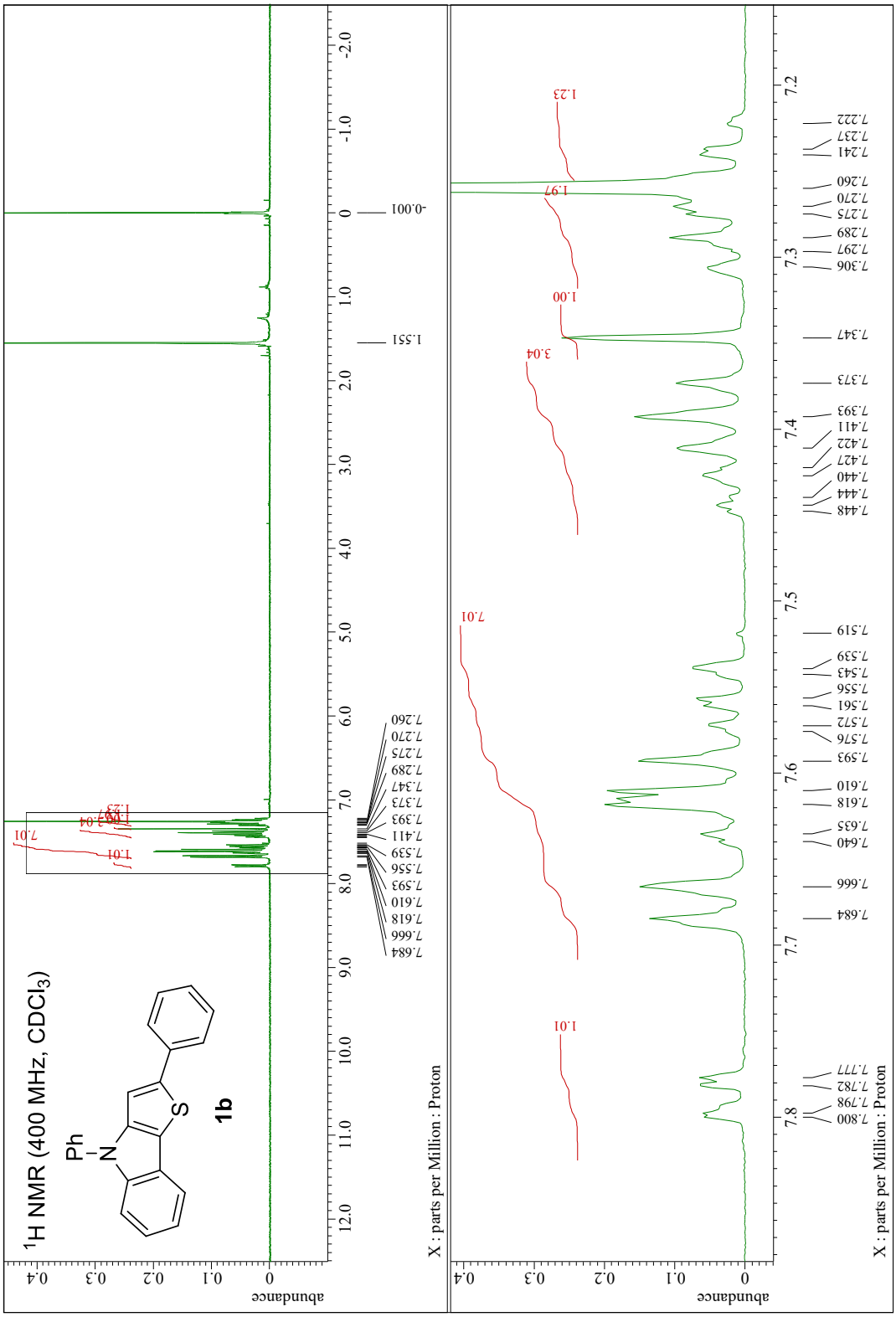

^{13}C NMR (100 MHz, $CDCl_3$)
Ph
NH
Br
Br
S
4f
(thousandths)
X : parts per Million : Carbon13
146.184
139.084
137.359
132.845
132.002
131.034
128.773
127.306
127.278
116.804
116.248
112.971
111.073
110.201
77.476
77.160
76.844
47.942

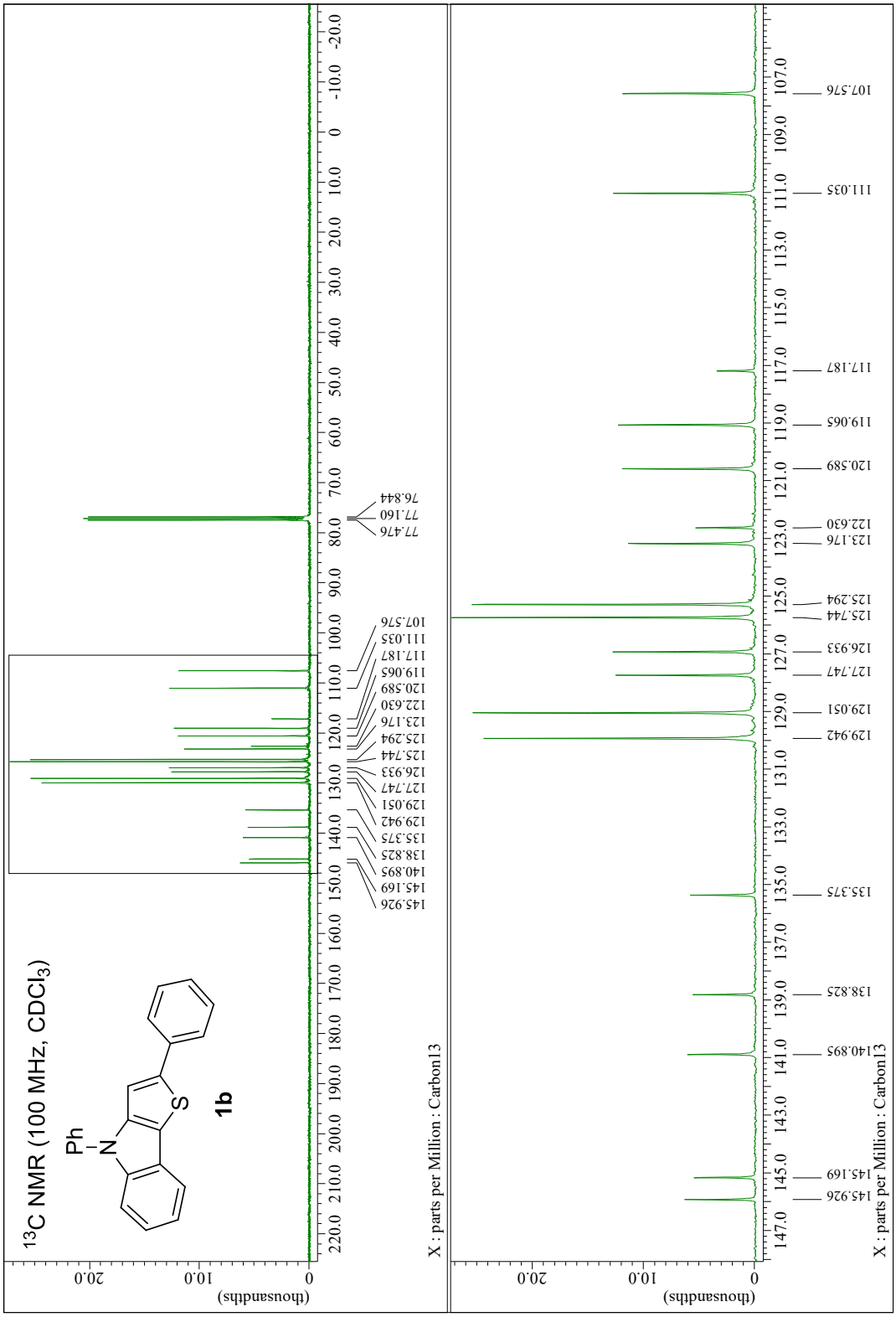
^{1}H NMR (400 MHz, CDCl$_3$)
Ph
NH
Br
S
Me
5
abundance
X : parts per Million : Proton
0.75
1.91
1.97
1.67
4.04
4.06
3.00
0.001
1.555
2.377
5.774
6.968
7.132
7.214
7.237
7.252
7.260
7.270
7.274
7.342
7.346
7.448
7.468
6.987
6.972
6.968
6.953
6.950
6.935
6.932
7.114
7.135
7.132
7.195
7.214
7.237
7.252
7.260
7.270
7.274
7.278
7.287
7.292
7.299
7.313
7.316
7.323
7.326
7.342
7.346
7.364
7.366
7.442
7.448
7.464
7.468
7.473

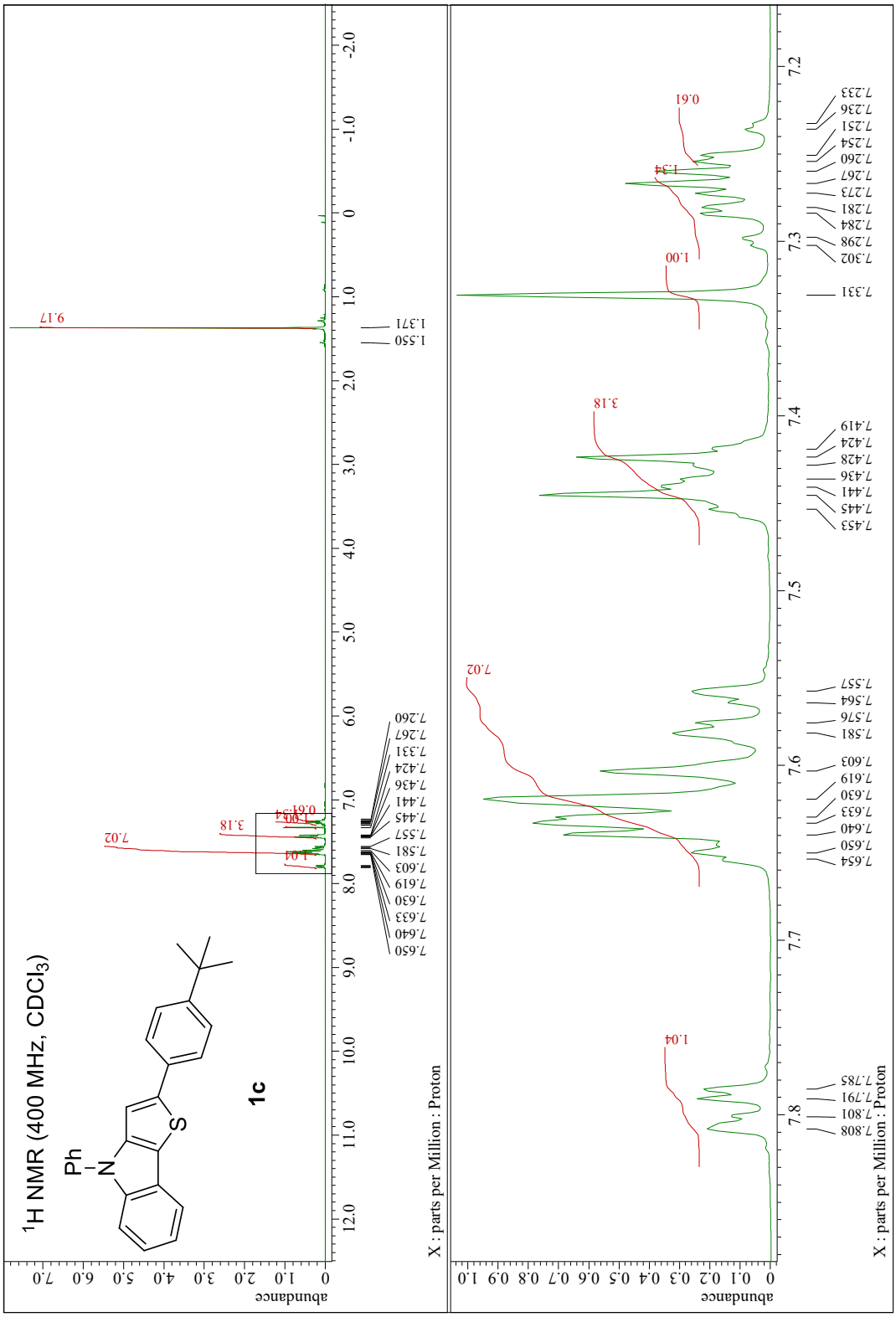

^{13}C NMR (100 MHz, $CDCl_3$)
Ph
NH
Br
S
Me
5
21.379
76.834
77.160
77.476
111.418
116.181
119.755
120.081
120.800
122.046
125.601
125.936
129.405
129.875
130.085
130.402
132.510
133.775
138.499
142.361
142.514
145.207
(thousandths)
X : parts per Million : Carbon13


^{1}H NMR (400 MHz, CDCl$_3$)
Ph
N
S
Me
1a
abundance
X : parts per Million : Proton
6.70
0.92
3.38
0.44
1.00
2.85
2.376
1.551
0.002


^{13}C NMR (100 MHz, $CDCl_3$)
Ph
N
S
Me
1a
21.331
76.844
77.160
77.476
107.068
111.006
116.746
118.979
120.560
122.716
123.023
125.313
125.668
126.914
129.740
129.932
132.625
137.723
138.892
140.856
145.217
146.223
X : parts per Million : Carbon13
(thousandths)


^{1}H NMR (400 MHz, CDCl$_3$)
Ph
N
S
1b
abundance
X : parts per Million : Proton
7.01
1.01
3.04
1.00
1.97
1.23
1.551
-0.001
7.684
7.666
7.640
7.635
7.618
7.610
7.593
7.576
7.572
7.561
7.556
7.543
7.539
7.519
7.448
7.444
7.440
7.427
7.422
7.411
7.393
7.373
7.347
7.306
7.297
7.289
7.275
7.270
7.260
7.241
7.237
7.222
7.800
7.798
7.782
7.777


^{13}C NMR (100 MHz, CDCl$_3$)
Ph
N
S
1b
145.926
145.169
140.895
138.825
135.375
129.942
129.051
127.747
126.933
125.744
125.294
123.176
122.630
120.589
119.065
117.187
111.035
107.576
77.476
77.160
76.844
(thousandths)
X : parts per Million : Carbon13


^{1}H NMR (400 MHz, CDCl$_3$)
Ph
N
S
1c
abundance
X : parts per Million : Proton
9.17
7.02
3.18
1.04
1.00
0.61
1.34
1.550
1.371
7.650
7.640
7.633
7.630
7.619
7.603
7.581
7.557
7.445
7.441
7.436
7.424
7.331
7.267
7.260
7.808
7.801
7.791
7.785
7.654
7.650
7.640
7.633
7.630
7.619
7.603
7.581
7.576
7.564
7.557
7.453
7.445
7.441
7.436
7.428
7.424
7.419
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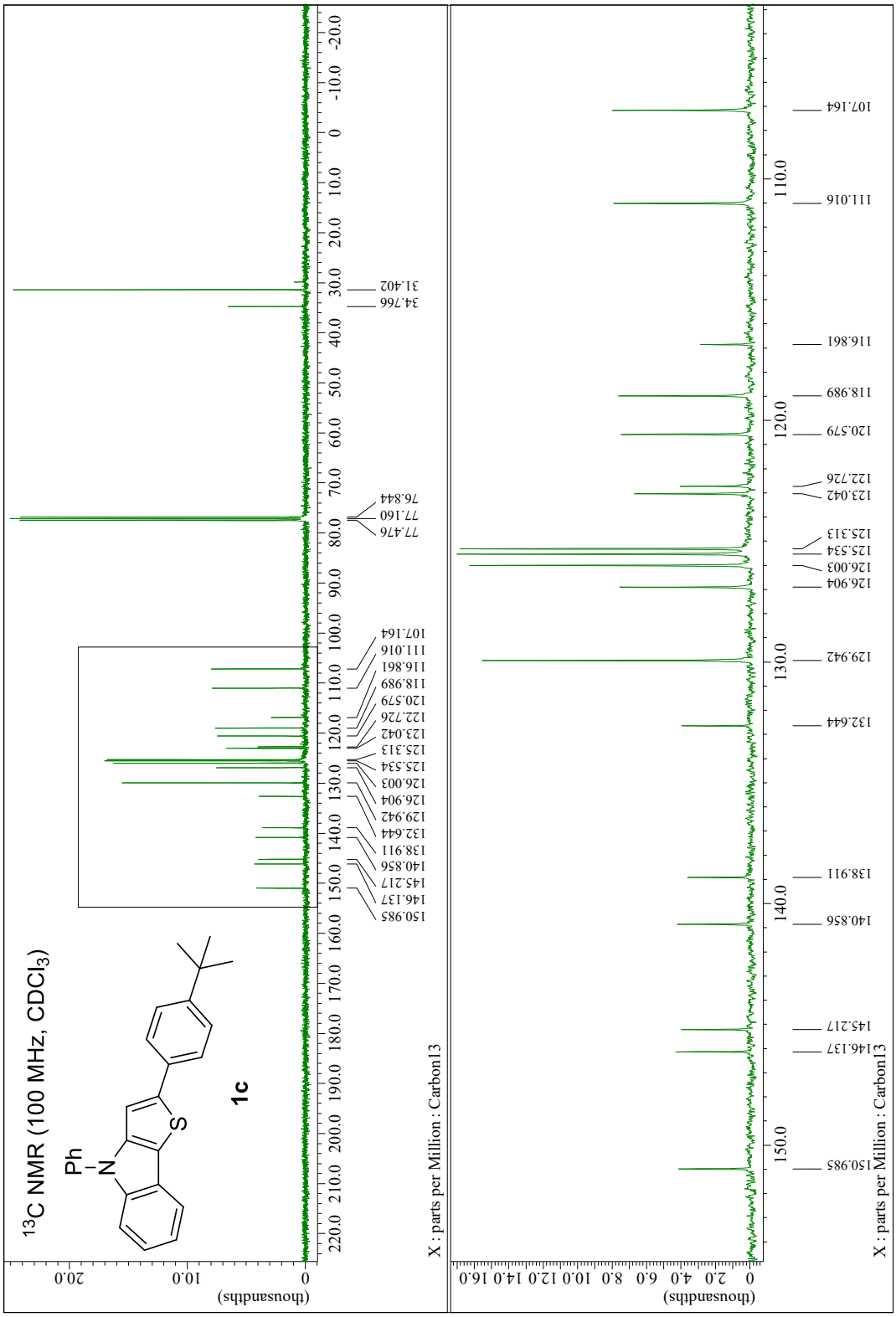
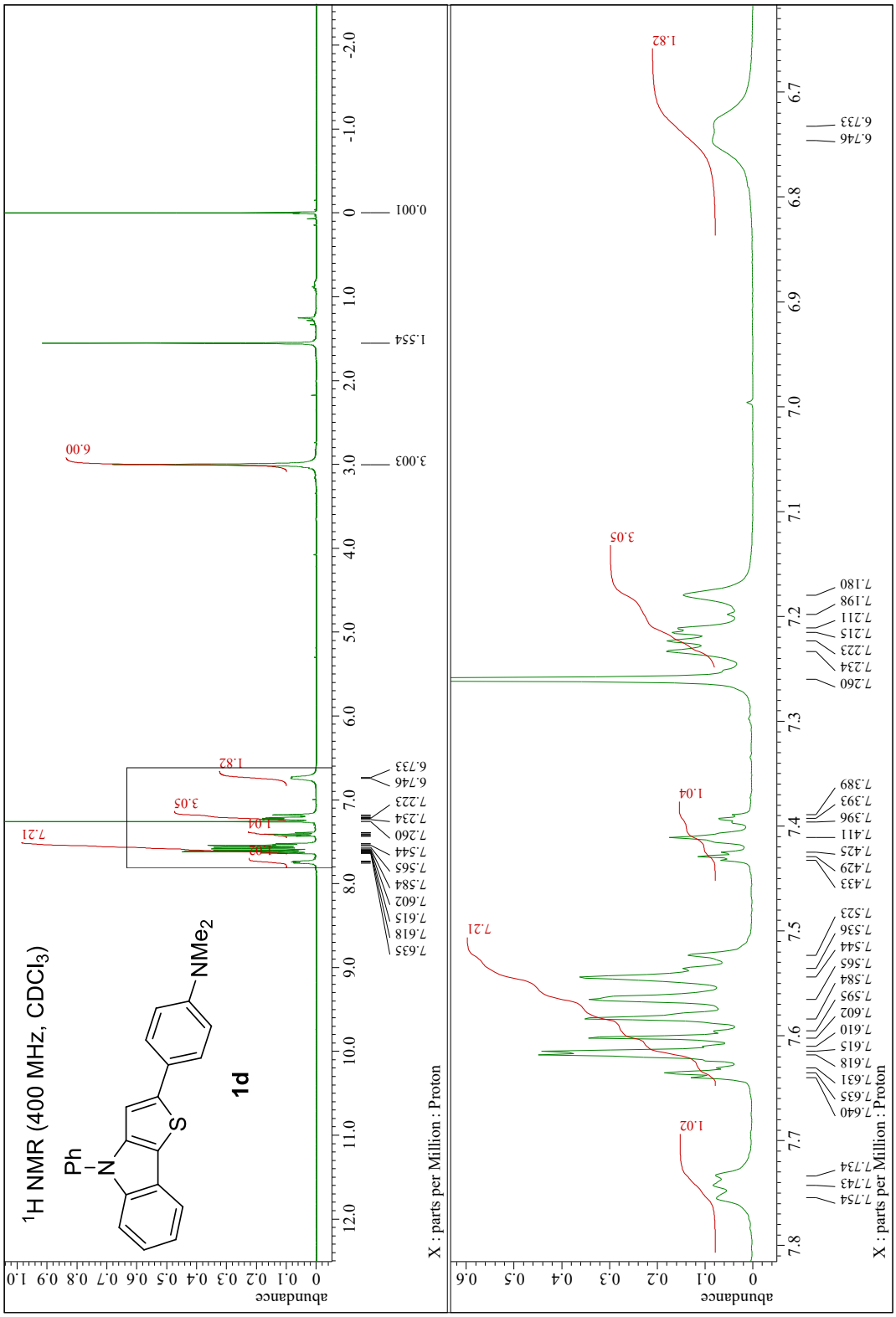
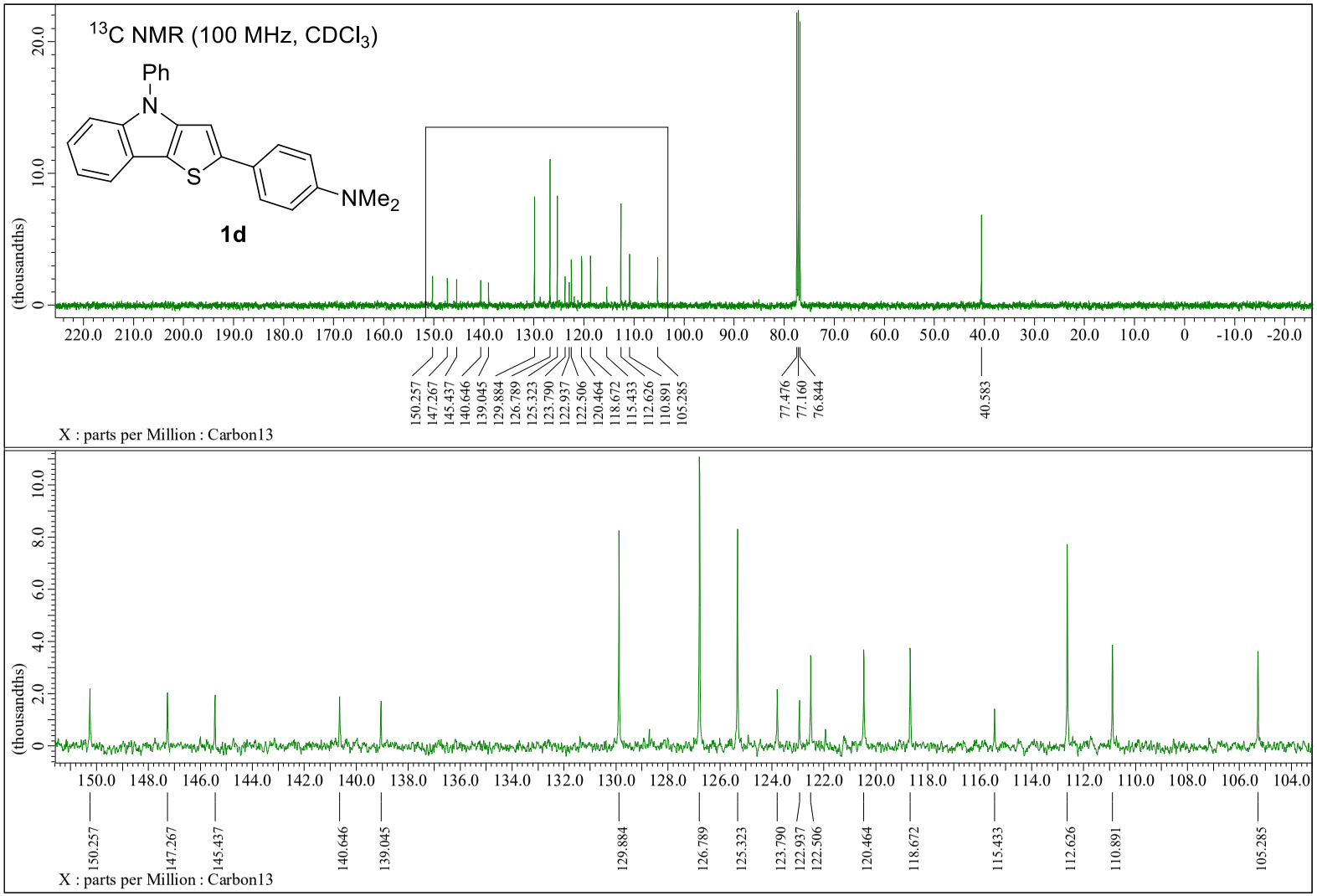
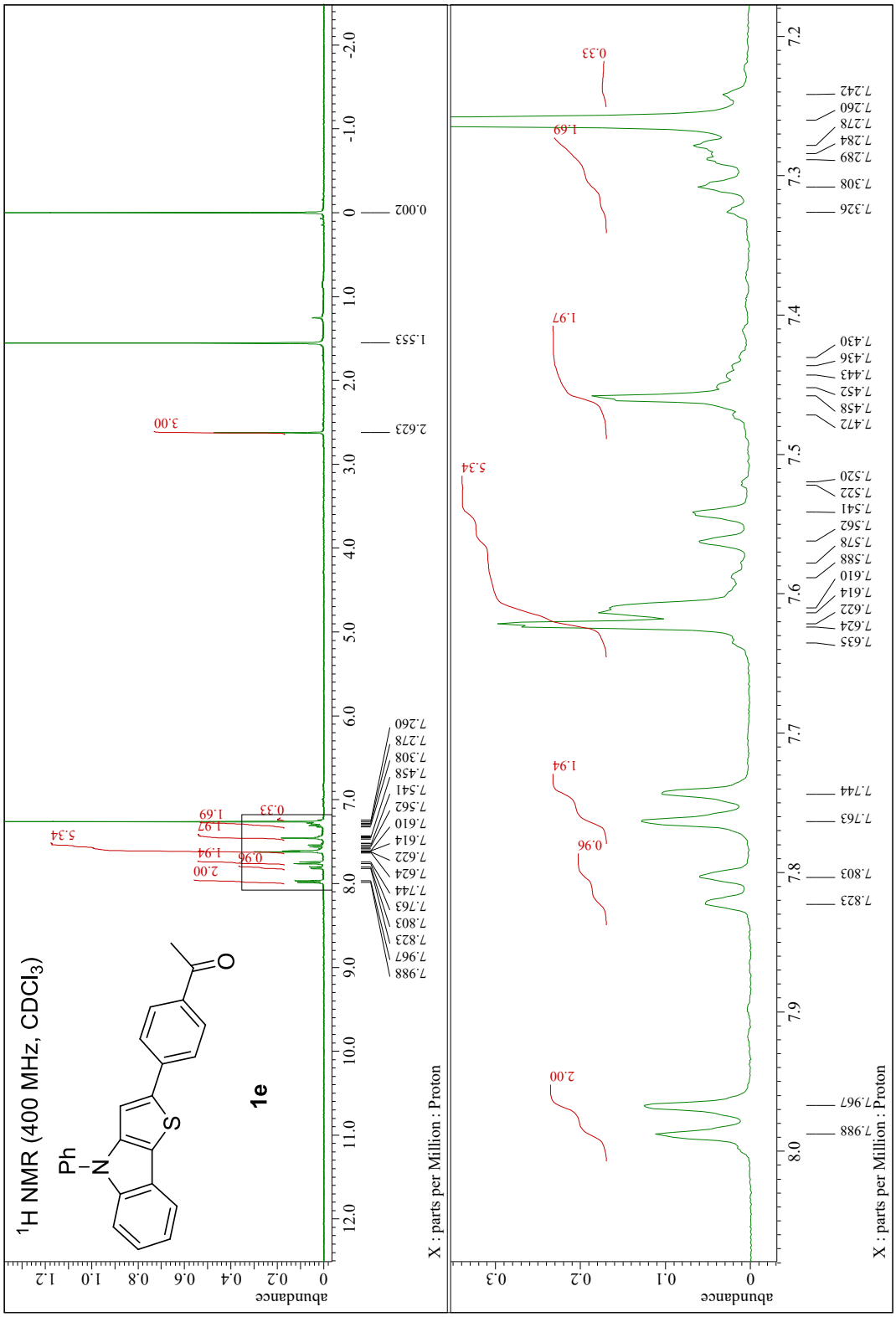
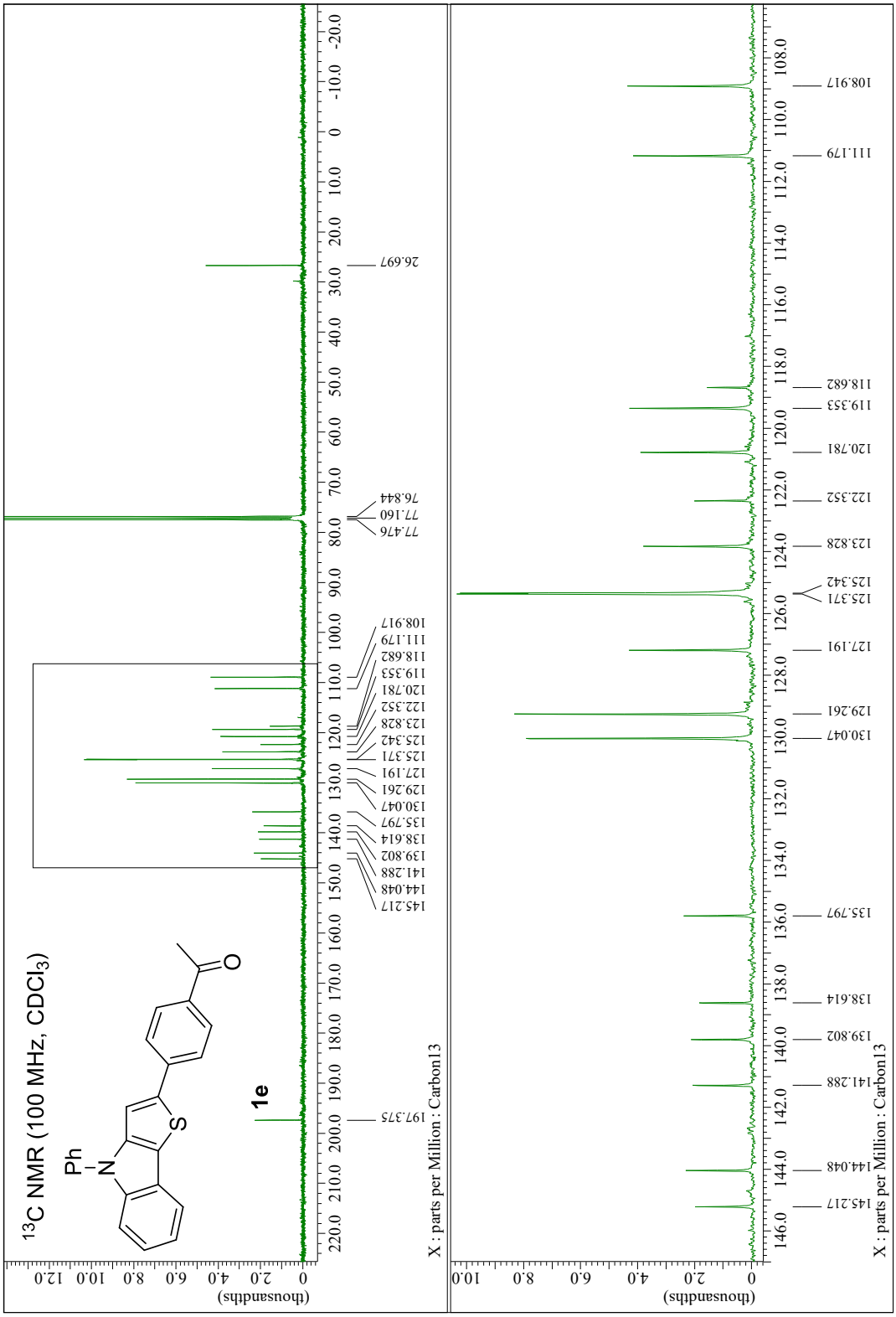
7.267
7.260
7.254
7.251
7.236
7.233

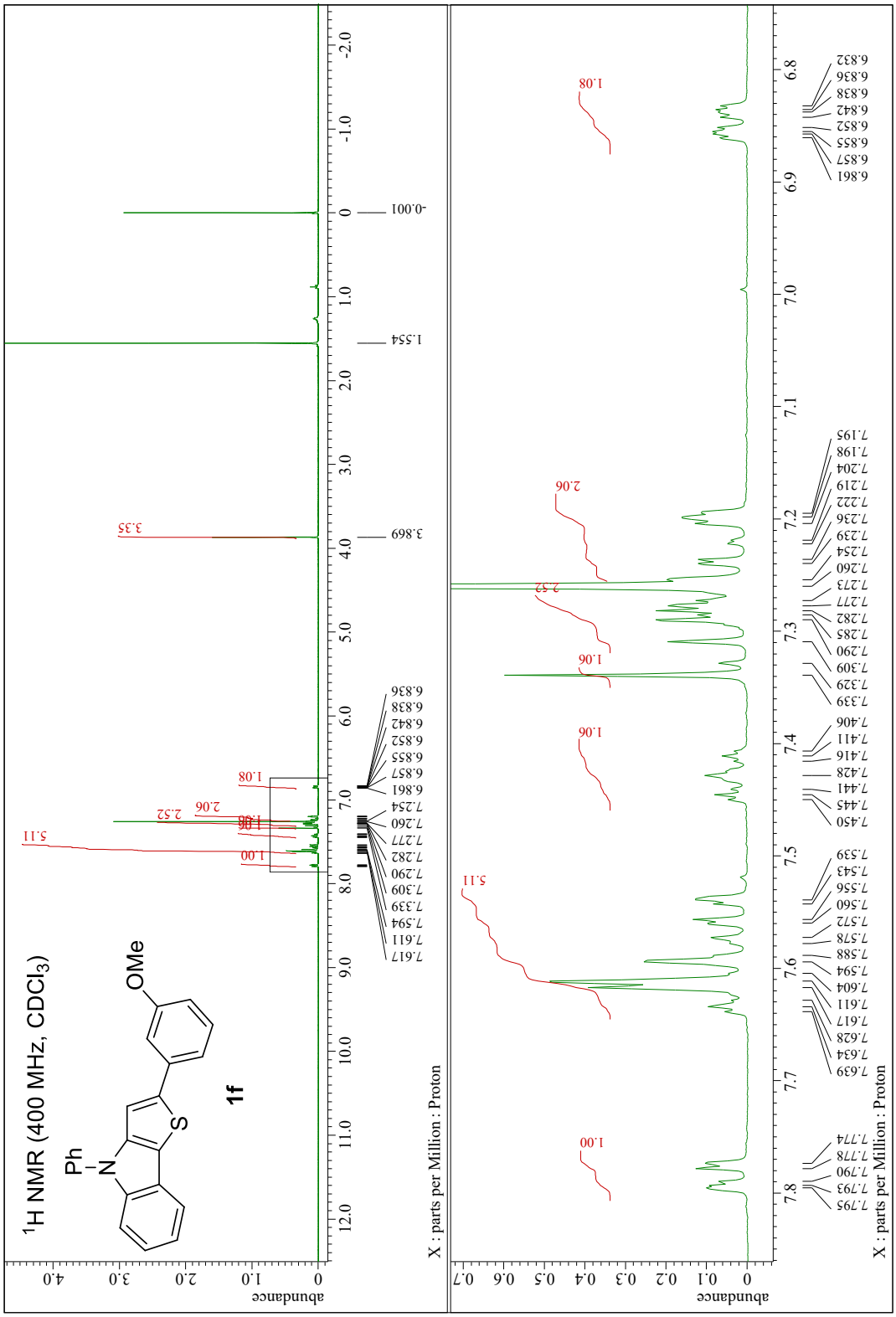

^{13}C NMR (100 MHz, CDCl$_3$)
Ph
N
S
1c
X : parts per Million : Carbon13
(thousandths)
150.985
146.137
145.217
140.856
138.911
132.644
129.942
126.904
126.003
125.534
125.313
123.042
122.726
120.579
118.989
116.861
111.016
107.164
77.476
77.160
76.844
34.766
31.402


^{1}H NMR (400 MHz, CDCl$_3$)
Ph
N
S
NMe$_2$
1d
abundance
X : parts per Million : Proton
7.21
3.05
1.82
1.04
6.00
1.554
3.003
0.001
1.02

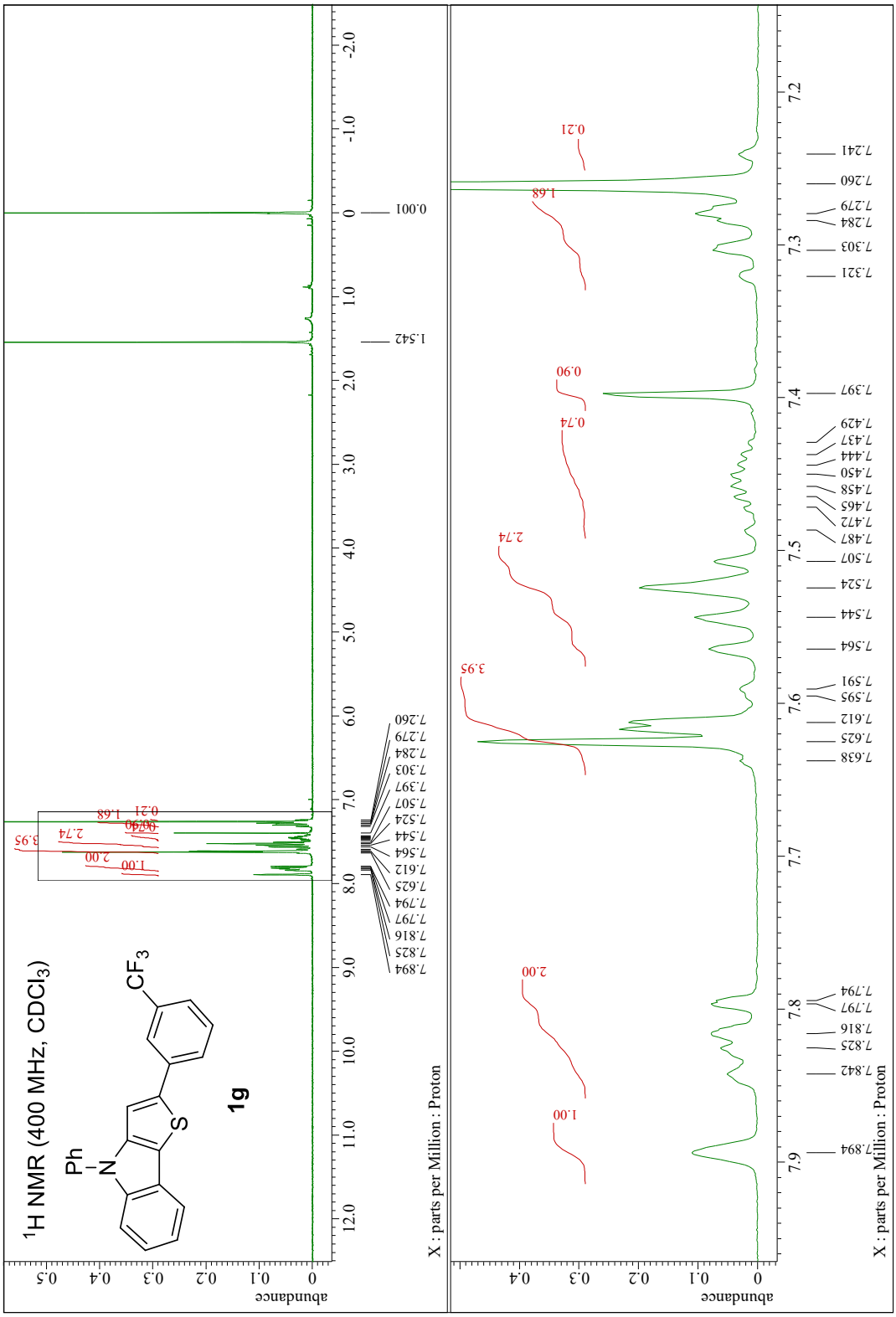

^{13}C NMR (100 MHz, $CDCl_3$)
Ph
N
S
NMe_2
1d
(thousandths)
X : parts per Million : Carbon13
150.257
147.267
145.437
140.646
139.045
129.884
126.789
125.323
123.790
122.937
122.506
120.464
118.672
115.433
112.626
110.891
105.285
77.476
77.160
76.844
40.583

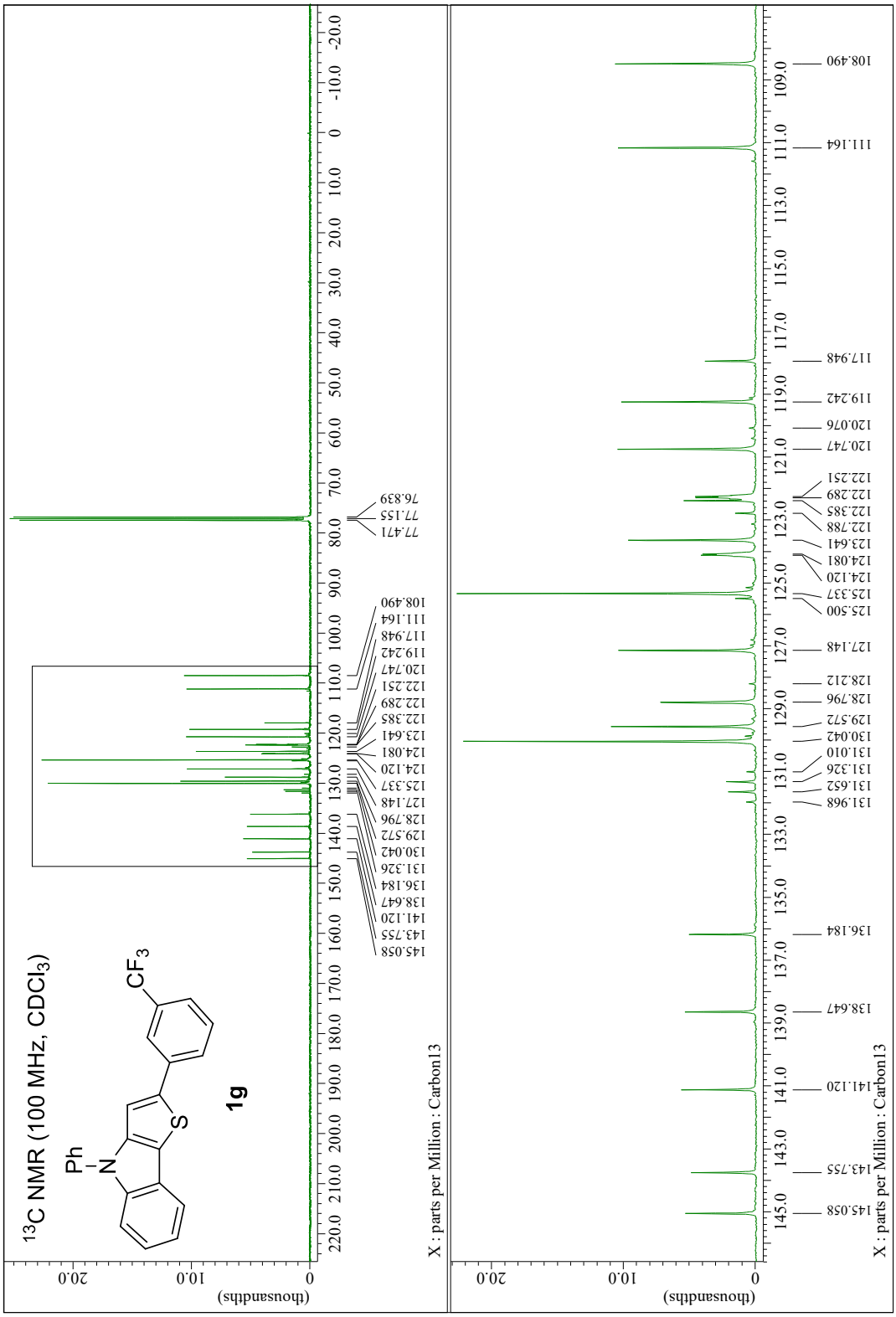

^{1}H NMR (400 MHz, CDCl$_3$)
1e
Ph
N
S
O
abundance
X : parts per Million : Proton
0.002
1.553
2.623
3.00
5.34
0.33
1.69
1.97
0.96
1.94
2.00
7.988
7.967
7.823
7.803
7.763
7.744
7.635
7.624
7.622
7.614
7.610
7.588
7.578
7.562
7.541
7.520
7.522
7.472
7.458
7.452
7.443
7.436
7.430
7.326
7.308
7.289
7.284
7.278
7.260
7.242


^{13}C NMR (100 MHz, CDCl$_3$)
1e
Ph
N
S
O
(thousandths)
X : parts per Million : Carbon13
197.375
145.217
144.048
141.288
139.802
138.614
135.797
130.047
129.261
127.191
125.371
125.342
123.828
122.352
120.781
119.353
118.682
111.179
108.917
77.476
77.160
76.844
26.697

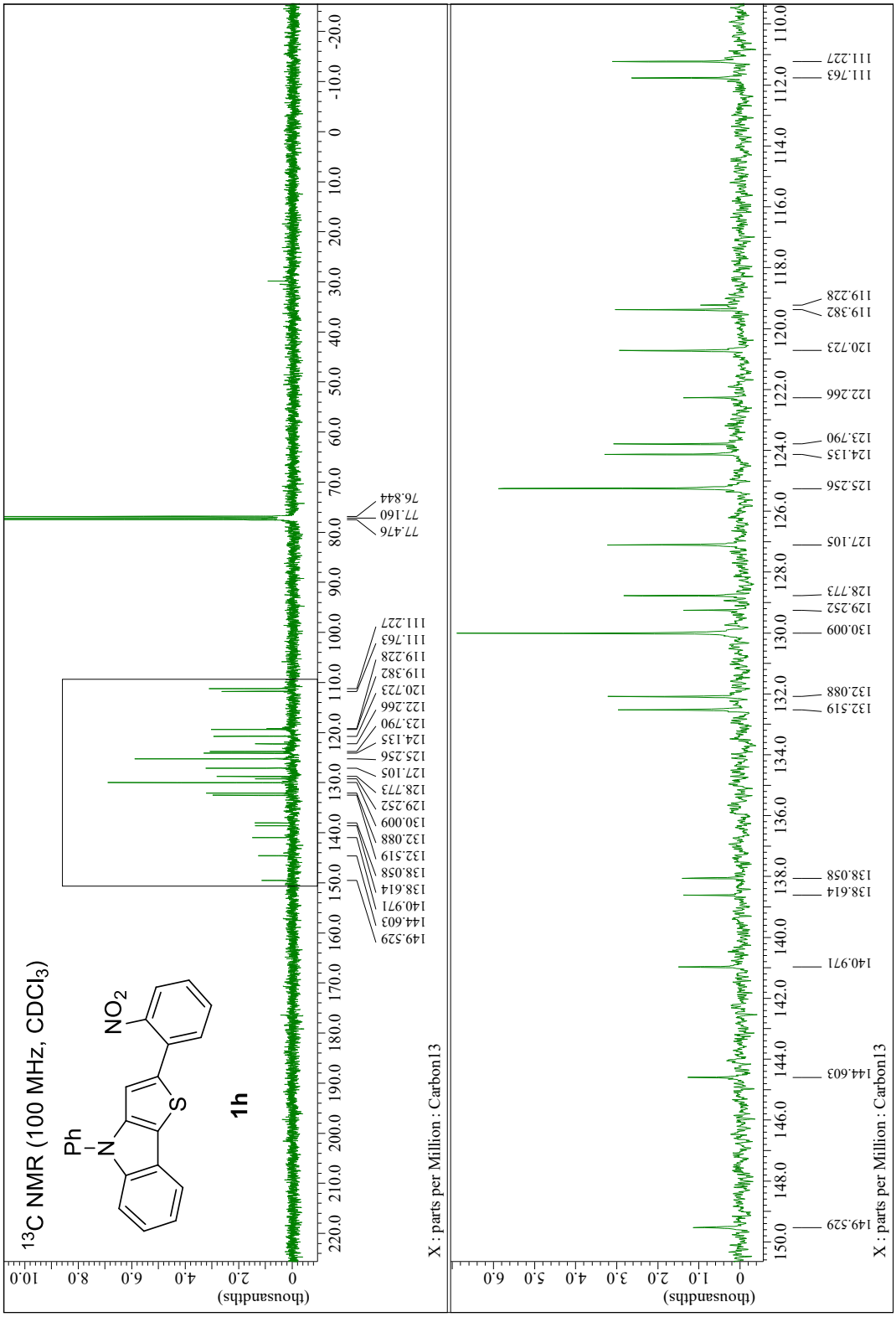

1H NMR (400 MHz, CDCl3)
1f
Ph
N
S
OMe
abundance
X : parts per Million : Proton
5.11
1.00
2.06
2.52
1.06
1.08
3.35
3.869
1.554
-0.001

^{13}C NMR (100 MHz, CDCl$_3$)
Ph
N
S
OMe
1f
160.127
145.744
145.092
140.952
138.834
136.736
130.085
129.970
126.981
125.332
123.234
122.620
120.608
119.084
118.414
113.296
111.399
111.054
107.815
77.476
77.160
76.834
55.484
X : parts per Million : Carbon13
(thousandths)

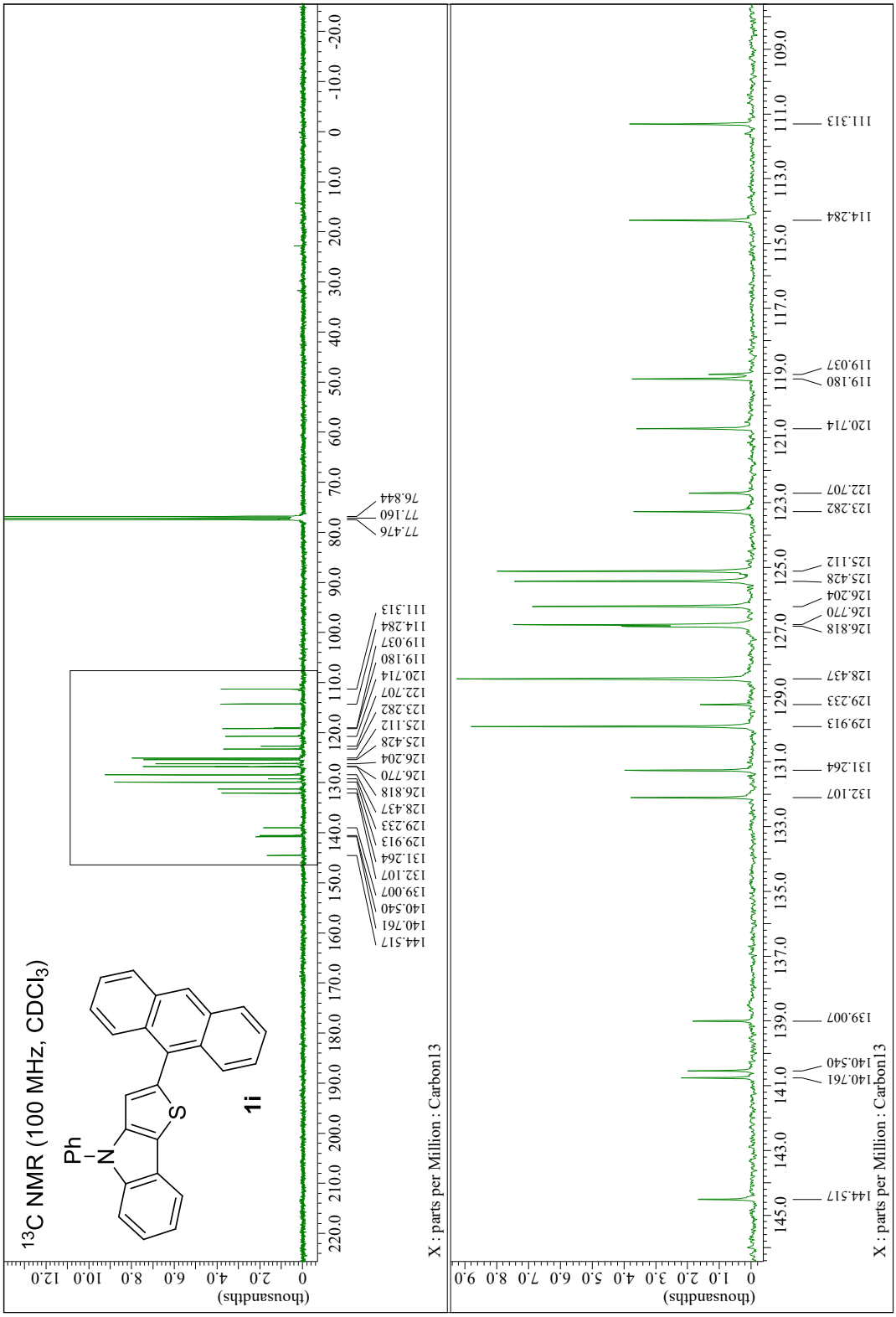

^{1}H NMR (400 MHz, CDCl$_3$)
Ph
N
S
CF$_3$
1g
abundance
X : parts per Million : Proton

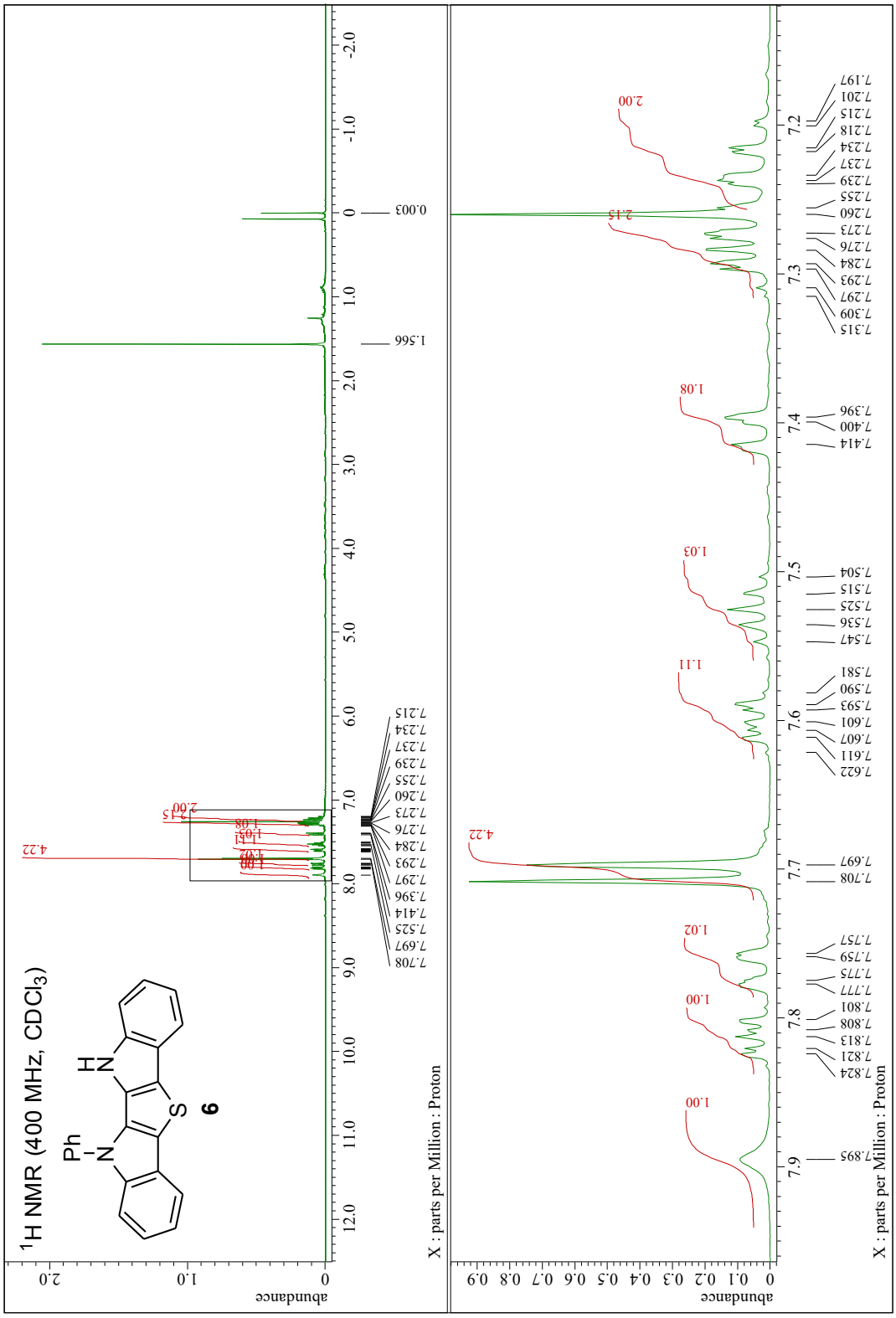

^{13}C NMR (100 MHz, $CDCl_3$)
Ph
N
S
CF_3
1g
(thousandths)
X : parts per Million : Carbon13
145.058
143.755
141.120
138.647
136.184
131.326
130.042
129.572
128.796
127.148
125.337
124.120
124.081
123.641
122.385
122.289
122.251
120.747
119.242
117.948
111.164
108.490
77.471
77.155
76.839

^{1}H NMR (400 MHz, CDCl$_3$)
Ph
N
S
NO$_2$
1h
abundance
X : parts per Million : Proton
6.28
2.08
0.91
1.07
0.98
1.65
0.81
1.00
1.547
0.001
7.785
7.766
7.762
7.652
7.648
7.604
7.601
7.581
7.576
7.567
7.554
7.260
7.251
7.249
7.125


^{13}C NMR (100 MHz, CDCl$_3$)
1h
Ph
N
S
NO$_2$
(thousandths)
X : parts per Million : Carbon13
149.529
144.603
140.971
138.614
138.058
132.519
132.088
130.009
129.252
128.773
127.105
125.256
124.135
123.790
122.266
120.723
119.382
119.228
111.763
111.227
77.476
77.160
76.844

^{1}H NMR (400 MHz, CDCl$_3$)
Ph
N
S
1i
abundance
X : parts per Million : Proton
8.15
2.94
1.68
3.94
0.71
1.00
-0.002
1.551
8.553
8.055
8.036
8.014
7.712
7.708
7.690
7.671
7.561
7.543
7.521
7.482
7.461
7.440
7.418
7.402
7.361
7.345
7.341
7.324
7.321
7.314
7.310
7.295
7.292
7.260
8.341
8.332
8.326
8.318
7.863
7.861
7.858
7.843
7.841
7.826
7.818
7.811
7.803
7.712
7.708
7.690
7.674
7.671
7.561
7.543
7.521
7.498
7.495
7.482
7.474
7.461
7.440
7.426
7.418
7.405
7.402
7.361
7.345
7.341
7.324
7.321
7.314
7.310
7.295
7.292
7.260


^{13}C NMR (100 MHz, CDCl$_3$)
Ph
N
S
1i
(thousandths)
X : parts per Million : Carbon13
77.476
77.160
76.844
144.517
140.761
140.540
139.007
132.107
131.264
129.913
129.233
128.437
126.818
126.770
126.204
125.428
125.112
123.282
122.707
120.714
119.180
119.037
114.284
111.313


^{1}H NMR (400 MHz, CDCl$_3$)
Ph
N
H
N
S
6
abundance
X : parts per Million : Proton
4.22
2.60
2.15
1.08
1.05
1.02
1.00
0.003
1.566
7.708
7.697
7.525
7.414
7.396
7.297
7.293
7.284
7.276
7.273
7.260
7.255
7.239
7.237
7.234
7.215
7.895
7.824
7.821
7.813
7.808
7.801
7.777
7.775
7.759
7.757
7.622
7.611
7.607
7.601
7.593
7.590
7.581
7.547
7.536
7.525
7.515
7.504
7.414
7.400
7.396
7.315
7.309
7.297
7.293
7.284
7.276
7.273
7.260
7.255
7.239
7.237
7.234
7.218
7.215
7.201
7.197

^{13}C NMR (100 MHz, $CDCl_3$)
Ph
N
H
N
S
6
(thousandths)
X : parts per Million : Carbon13
140.511
140.214
138.710
130.459
129.491
127.556
127.412
125.055
124.067
123.387
123.090
123.023
121.001
120.963
120.484
118.883
118.586
112.204
111.025
77.476
77.160
76.844