SUPPORTING INFORMATION

Regiocontrolled Halogen Dance of 2,5-Dibromopyrroles Using Equilibrium between Dibromopyrrolyllithiums

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Table of Contents

1. General

Analytical thin layer chromatography (TLC) was performed on Wako 70 F_{254} glass sheets precoated with a 0.25 mm thickness of silica gel. Melting points (mp) 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}). ^{1}H NMR (400 MHz) and $^{13}C\{^{1}H\}$ NMR (100 MHz) spectra were measured on JEOL ECZ400 spectrometer. Chemical shifts for ^{1}H 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, benzene-d_5: δ 7.16 ppm, acetone-d_5: δ 2.05 ppm, DMSO-d_5: δ 2.50 ppm), and coupling constants are given in hertz (Hz). The following abbreviations are used for spin multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, and br = broad. Chemical shifts for $^{13}C\{^{1}H\}$ NMR are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 77.16 ppm, benzene-d_6: δ 128.06 ppm, acetone-d_6: δ 29.84 ppm, DMSO-d_6: δ 39.52 ppm). High-resolution mass spectroscopy (HRMS) was performed on a JEOL JMS T100LP AccuTOF LC-Plus [electrospray ionization (ESI)] with a JEOL MS-5414DART attachment.

2. Materials

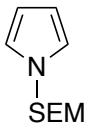
Unless otherwise stated, all reactions were conducted in a flame-dried glassware under an inert atmosphere of nitrogen. All workup and purification procedures were carried out with reagent-grade solvents in air. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Flash column chromatography was performed on Wakogel® 60N (63–212 μm, Wako Pure Chemical Industries, Ltd.) or High-efficiency irregular silica (25–40 μm, Santai Science Inc.). Recycling preparative SEC–HPLC was performed with LC-9201 (Japan Analytical Industry Co., Ltd.) equipped with preparative SEC columns (JAI-GEL-1H and JAI-GEL-2H). Anhydrous THF (>99.5%, water content: <30 ppm) was purchased from FUJIFILM Wako Pure Chemical Corporation and further dried by passing through a solvent purification system (Glass Contour) prior to use. LDA (2.0 M in THF/heptane/ethylbenzene) was purchased from Sigma-Aldrich Co. and used as received. *n*-BuLi (1.6 M in *n*-hexane) was purchased from Kanto Chemical Co. and used as received. Freshly prepared $ZnCl_2$·TMEDA[1] and $Pd(PPh_3)_4$[2] were used in the following experiments.

1 (a) M. Isobe, S. Kondo, N. Nagasawa and T. Goto, *Chem. Lett.*, 1977, **6**, 679–682; (b) K. Snégaroff, S. Komagawa, F. Chevallier, P. C. Gros, S. Golhen, T. Roisnel, M. Uchiyama and F. Mongin, *Chem. Eur. J.*, 2010, **16**, 8191–8201.

2 D. R. Coulson, *Inorg. Synth.*, 1972, **13**, 121–124.

3. Halogen Dance of *N*-Substituted 2,5-Dibromopyrroles (Scheme 2 and Table 1)

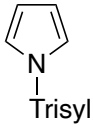
3.1 Synthesis of *N*-Substituted Pyrroles



S1a

1-((2-(Trimethylsilyl)ethoxy)methyl)-1*H*-pyrrole (S1a)

A flame-dried 100-mL round-bottomed flask equipped with a Teflon-coated magnetic stirring bar, a three-way stopcock, and a rubber septum was charged with NaH (60% in oil, 1.206 g, 30.1 mmol, 3.0 equiv) and DMF (25.0 mL). After the suspension was cooled to 0 °C, and pyrrole (0.6720 g, 10.0 mmol, 1.0 equiv) was added to the flask. To the suspension was added SEMCl (2.782 g, 15.0 mmol, 1.5 equiv) dropwise at 0 °C. After stirring at room temperature for 1 h, the resulting mixture was treated with saturated aqueous ammonium chloride (15 mL). After being partitioned, the aqueous layer was extracted with diethyl ether (50 mL) four times. The combined organic extracts were washed twice with brine (100 mL), dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude product, which was purified by silica gel column chromatography (hexane/diethyl ether = 10:1) followed by preparative SEC–HPLC to provide the title compound as a colorless oil (1.126 g, 5.70 mmol, 57%), whose ^{1}H NMR spectral data was identical to that reported in the literature.[3] R_f = 0.34 (hexane/diethyl ether = 10:1); IR (ATR, cm^{-1}): 2955, 2896, 1496, 1409, 1377, 1272, 1249, 1100, 1075, 918, 859, 835, 724, 694, 612; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.78 (dd, 2H, *J* = 2.0, 2.0 Hz), 6.20 (dd, 2H, *J* = 2.0, 2.0 Hz), 5.20 (s, 2H), 3.45 (t, 2H, *J* = 8.1 Hz), 0.89 (t, 2H, *J* = 8.1 Hz), –0.02 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 121.1, 109.2, 78.5, 65.8, 17.8, –1.3; HRMS (DART/TOF) *m/z*: $[M + H]^+$ calcd for $C_{10}H_{20}NOSi$, 198.1314; found, 198.1314.



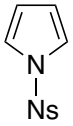
S1g

1-((2,4,6-Triisopropylphenyl)sulfonyl)-1*H*-pyrrole (S1g)

A flame-dried 200-mL round-bottomed flask equipped with a Teflon-coated magnetic stirring bar, a three-way stopcock, and a rubber septum was charged with NaH (60% in oil, 2.407 g, 60.2 mmol, 3.0 equiv) and DMF (50.0 mL). After the suspension was cooled to 0 °C, pyrrole (1.343 g, 20.0 mmol, 1.0 equiv) was added to the flask. To the suspension was added 2,4,6-triisopropylbenzenesulfonyl chloride (6.056 g, 20.0 mmol, 1.0 equiv) portionwise at 0 °C. After stirring at room temperature for 30 min, the resulting mixture was treated with saturated aqueous ammonium chloride (25 mL) and water (100 mL). After being partitioned, the aqueous layer was extracted with diethyl ether (100 mL) four times. The combined organic extracts were washed twice with brine (150 mL), dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude product, which was purified by silica gel column chromatography (hexane/CH_2Cl_2 = 7:3) to provide the title compound as a colorless solid (5.099 g, 15.3 mmol, 76%). R_f =

3 J. M. Muchowski and D. R. Solas, *J. Org. Chem.*, 1984, **49**, 203–205.

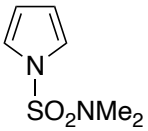
0.35 (hexane/CH_2Cl_2 = 7:3); mp 91–92 °C; IR (ATR, cm^{-1}): 2962, 2928, 2869, 1599, 1465, 1457, 1427, 1373, 1344, 1183, 1171, 1078, 1059, 1040, 886, 741, 729, 674, 640, 627; ^1H NMR (400 MHz, $CDCl_3$): δ 7.19 (s, 2H), 7.08 (dd, 2H, *J* = 2.4, 2.4 Hz), 6.26 (dd, 2H, *J* = 2.4, 2.4 Hz), 4.16 (sept, 2H, *J* = 6.8 Hz), 2.90 (sept, 1H, *J* = 7.1 Hz), 1.25 (d, 6H, *J* = 7.1 Hz), 1.17 (d, 12H, *J* = 6.8 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 154.7, 151.6, 131.1, 124.4, 119.9, 112.1, 34.4, 29.6, 24.7, 23.6; HRMS (DART/TOF) *m/z*: $[M + H]^+$ calcd for $C_{19}H_{28}NO_2S$, 334.1841; found, 334.1835.



S1h

1-((2-Nitrophenyl)sulfonyl)-1*H*-pyrrole (S1h)

A flame-dried 300-mL round-bottomed flask equipped with a Teflon-coated magnetic stirring bar, a three-way stopcock, and a rubber septum was charged with NaH (60% in oil, 0.5612 g, 15.0 mmol, 1.5 equiv) and THF (50.0 mL). After the suspension was cooled to 0 °C, pyrrole (0.6701 g, 9.99 mmol, 1.0 equiv) was added to the flask. To the suspension was added 2-nitrobenzenesulfonyl chloride (2.659 g, 12.0 mmol, 1.2 equiv) portionwise at 0 °C. After stirring at room temperature for 20 h, the resulting mixture was treated with saturated aqueous ammonium chloride (50 mL). After being partitioned, the aqueous layer was extracted with diethyl ether (50 mL) three times. The combined organic extracts were washed twice with brine (100 mL), dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude product, which was purified by silica gel column chromatography (hexane/methyl acetate = 7:3) to provide the title compound as a pale yellow solid (759.9 mg, 3.01 mmol, 30%), whose ^1H NMR and ^{13}C NMR spectral data were identical to those reported in the literature.[4] R_f = 0.30 (hexane/methyl acetate = 7:3); mp 63–64 °C; IR (ATR, cm^{-1}): 3144, 3091, 1587, 1544, 1459, 1440, 1378, 1189, 1174, 1126, 1062, 1033, 932, 851, 775, 752, 732, 655; ^1H NMR (400 MHz, $CDCl_3$): δ 7.78–7.73 (m, 2H), 7.70–7.63 (m, 2H), 7.25 (dd, 2H, *J* = 2.3, 2.3 Hz), 6.39 (dd, 2H, *J* = 2.3, 2.3 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 147.8, 135.1, 132.8, 132.5, 129.6, 124.9, 121.8, 114.1; HRMS (DART/TOF) *m/z*: $[M + H]^+$ calcd for $C_{10}H_9N_2O_4S$, 253.0283; found, 253.0291.



S1i

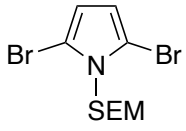
***N*,*N*-Dimethyl-1*H*-pyrrole-1-sulfonamide (S1i)**

A flame-dried 200-mL round-bottomed flask equipped with a Teflon-coated magnetic stirring bar, a three-way stopcock, and a rubber septum was charged with NaH (60% in oil, 2.392 g, 59.8 mmol, 3.0 equiv) and DMF (50.0 mL). After the suspension was cooled to 0 °C, pyrrole (1.330 g, 19.8 mmol, 1.0 equiv) was added to the flask. To the suspension was added *N*,*N*-dimethylsulfamoyl chloride (2.895 g, 20.2 mmol, 1.0 equiv)

4 R. Fuchigami, K. Namba and K. Tanino, *Tetrahedron Lett.*, 2012, **53**, 5725–5728.

dropwise at 0 °C. After stirring at room temperature for 40 min, the resulting mixture was treated with saturated aqueous ammonium chloride (25 mL) and water (100 mL). After being partitioned, the aqueous layer was extracted with diethyl ether (100 mL) four times. The combined organic extracts were washed twice with brine (150 mL), dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude product, which was purified by silica gel column chromatography (hexane/diethyl ether = 20:1) to provide the title compound as a colorless solid (2.688 g, 15.4 mmol, 78%), whose ^{1}H NMR and ^{13}C NMR spectral data were identical to those reported in the literature.[5] R_f = 0.34 (hexane/diethyl ether = 7:3); mp 50–51 °C; IR (ATR, cm^{-1}): 3140, 1470, 1417, 1373, 1267, 1183, 1165, 1061, 1034, 958, 737, 720, 629; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 (dd, 2H, *J* = 2.2, 2.2 Hz), 6.31 (dd, 2H, *J* = 2.2, 2.2 Hz), 2.79 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 121.0, 111.9, 38.4; HRMS (DART/TOF) *m/z*: $[M + H]^+$ calcd for $C_6H_{11}N_2O_2S$, 175.0541; found, 175.0534.

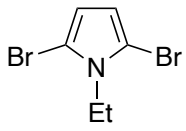
3.2 Synthesis of *N*-Substituted 2,5-Dibromopyrroles



1a

2,5-Dibromo-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-pyrrole (1a)

A flame-dried 100-mL Schlenk tube equipped with a Teflon-coated magnetic stirring bar and a rubber septum was charged with 1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-pyrrole (**S1a**) (0.9858 g, 5.00 mmol, 1.0 equiv) and THF (25.0 mL). The solution was cooled to –78 °C. NBS (1.780 g, 10.0 mmol, 2.0 equiv) was added portionwise to the solution for 10 min. After stirring at –78 °C for 1.5 h, the mixture was treated with saturated aqueous sodium thiosulfate (20 mL). After being partitioned, the aqueous layer was extracted with diethyl ether (100 mL). The combined organic extracts were washed with water (50 mL), dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude product, which was purified by silica gel column chromatography (hexane/CH_2Cl_2 = 100:1) to provide the title compound as a colorless oil (1.533 g, 4.32 mmol, 86%). R_f = 0.38 (hexane/CH_2Cl_2 = 10:1); IR (ATR, cm^{-1}): 2953, 2896, 1524, 1458, 1427, 1367, 1262, 1249, 1112, 1086, 919, 858, 835, 752, 737, 695, 666; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.22 (s, 2H), 5.34 (s, 2H), 3.58 (t, 2H, *J* = 8.2 Hz), 0.92 (t, 2H, *J* = 8.2 Hz), –0.01 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 112.9, 102.0, 74.8, 66.2, 17.9, –1.3; HRMS (DART/TOF) *m/z*: $[M + H]^+$ calcd for $C_{10}H_{18}{}^{79}Br^{81}BrNOSi$, 355.9504; found, 355.9507.

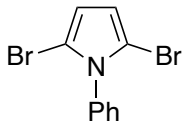


1b

2,5-Dibromo-1-ethyl-1*H*-pyrrole (1b)

5 Q. Yu, X. Li, X. Wang and J. Liu, *Aust. J. Chem.*, 2018, **71**, 95–101.

A flame-dried 100-mL Schlenk tube equipped with a Teflon-coated magnetic stirring bar and a rubber septum was charged with 1-ethyl-1*H*-pyrrole (0.4782 g, 5.03 mmol, 1.0 equiv) and THF (25.0 mL). The solution was cooled to –78 °C. NBS (1.789 g, 10.1 mmol, 2.0 equiv) was added portionwise to the solution for 5 min. After stirring at –78 °C for 4 h, the mixture was warmed up to room temperature and stirred for 2.5 h. The resulting mixture was treated with saturated aqueous sodium thiosulfate (30 mL). After being partitioned, the aqueous layer was extracted with diethyl ether (20 mL) three times. The combined organic extracts were washed with brine (20 mL), dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude product, which was purified by silica gel column chromatography (hexane/Et_3N = 100:1) to provide the title compound as a colorless oil (1.019 g, 4.01 mmol, 80%). R_f = 0.60 (hexane/Et_3N = 100:1); IR (ATR, cm^{-1}): 2977, 2936, 1738, 1516, 1462, 1422, 1378, 1356, 1277, 1257, 1114, 1089, 901, 740; ^1H NMR (400 MHz, $CDCl_3$): δ 6.17 (s, 2H), 4.05 (q, 2H, *J* = 7.2 Hz), 1.28 (t, 3H, *J* = 7.2 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 111.7, 100.3, 42.4, 15.6; HRMS (DART/TOF) *m/z*: $[M + H]^+$ calcd for $C_6H_8{}^{79}Br^{81}BrN$, 253.9003; found, 253.9009.

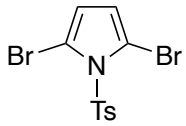


1c

2,5-Dibromo-1-phenyl-1*H*-pyrrole (1c)

A flame-dried 200-mL round-bottomed flask equipped with a Teflon-coated magnetic stirring bar, a three-way stopcock, and a rubber septum was charged with 1-phenyl-1*H*-pyrrole (1.431 g, 10.0 mmol, 1.0 equiv) and DMF (27.0 mL). The solution was cooled to 0 °C. NBS (3.559 g, 20.0 mmol, 2.0 equiv) in DMF (13.0 mL) was added dropwise to the solution for 2 min. After stirring at 0 °C for 30 min, the resulting mixture was treated with hexane (40 mL) and water (120 mL). After being partitioned, the aqueous layer was extracted with hexane (50 mL) three times. The combined organic extracts were dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude product, which was purified by silica gel column chromatography (hexane) to provide the title compound as a colorless oil (2.912 g, 9.68 mmol, 97%), whose ^1H NMR spectral data was identical to that reported in the literature.[6] R_f = 0.42 (hexane); IR (ATR, cm^{-1}): 1597, 1517, 1498, 1454, 1423, 1307, 1157, 1074, 1037, 903, 800, 766, 748, 694, 668, 659, 649, 641, 630, 617; ^1H NMR (400 MHz, $CDCl_3$): δ 7.53–7.47 (m, 3H), 7.28–7.24 (m, 2H), 6.32 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 137.8, 129.18, 129.15, 129.0, 112.6, 102.4; HRMS (DART/TOF) *m/z*: $[M + H]^+$ calcd for $C_{10}H_8{}^{79}Br_2N$, 299.9024; found, 299.9012.

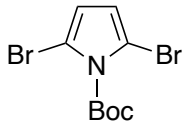
6 F. Faigl, S. Deák, Z. Mucsi, T. Hergert, L. Balázs, B. Sándor, B. Balázs, T. Holczbauer, M. Nyerges and B. Mátravölgyi, *Tetrahedron*, 2016, **72**, 5444–5455.



1d

2,5-Dibromo-1-tosyl-1*H*-pyrrole (1d)

A flame-dried 300-mL round-bottomed flask equipped with a Teflon-coated magnetic stirring bar, a three-way stopcock, and a rubber septum was charged with 1-tosyl-1*H*-pyrrole (**S1d**) (4.434 g, 20.0 mmol, 1.0 equiv) and DMF (40.0 mL). NBS (9.259 g, 52.0 mmol, 2.6 equiv) in DMF (20.0 mL) was added dropwise to the solution for 7 min. After stirring at room temperature for 30 min, the resulting mixture was treated with saturated aqueous sodium thiosulfate (50 mL). After being partitioned, the aqueous layer was extracted with diethyl ether (50 mL) five times. The combined organic extracts were washed with brine (100 mL), dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude product, which was purified by silica gel column chromatography (hexane/diethyl ether = 7:3) to provide the title compound as a colorless solid (4.814 g, 12.7 mmol, 63%). R_f = 0.55 (hexane/diethyl ether = 7:3); mp 96–98 °C; IR (ATR, cm^{-1}): 1388, 1238, 1197, 1182, 1137, 1095, 812, 781, 666; ^1H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, 2H, *J* = 7.8 Hz), 7.34 (d, 2H, *J* = 7.8 Hz), 6.29 (s, 2H), 2.44 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 146.0, 135.4, 130.1, 127.9, 118.8, 101.8, 21.8; HRMS (DART/TOF) *m/z*: $[M + H]^+$ calcd for $C_{11}H_{10}{}^{79}Br^{81}BrNO_2S$, 379.8779; found, 379.8773.



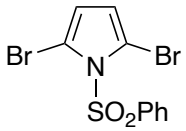
1e

***tert*-Butyl 2,5-dibromo-1*H*-pyrrole-1-carboxylate (1e)**

A 300-mL round-bottomed flask equipped with a Teflon-coated magnetic stirring bar, a three-way stopcock, and a rubber septum was charged with *tert*-butyl 1*H*-pyrrole-1-carboxylate (1.672 g, 10.0 mmol, 1.0 equiv) and THF (66.0 mL). The solution was cooled to –78 °C. NBS (3.555 g, 20.0 mmol, 2.0 equiv) was added portionwise to the solution for 5 min. After stirring at –78 °C for 1 h, the mixture was warmed up to 0 °C and stirred for 2 h. The resulting mixture was treated with saturated aqueous sodium thiosulfate (30 mL). After being partitioned, the aqueous layer was extracted with diethyl ether (30 mL) three times. The combined organic extracts were washed with brine (50 mL) three times, dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude product, which was purified by silica gel column chromatography (hexane/diethyl ether = 49:1) to provide the title compound as a colorless solid (1.158 g, 6.02 mmol, 60%), whose ^1H NMR and ^{13}C NMR spectral data were identical to those reported in the literature.[7] R_f = 0.36 (hexane/diethyl ether = 20:1); mp 75–77 °C; IR (ATR, cm^{-1}): 2982, 1762, 1435, 1372, 1356, 1303, 1279, 1263, 1155, 1078, 994, 907, 844, 778, 622; ^1H NMR (400 MHz, $CDCl_3$): δ 6.25 (s,

7 S. Martina, V. Enkelmann, G. Wegner and A. D. Schlueter, *Synthesis*, 1991, 613–615.

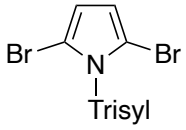
2H), 1.65 (s, 9H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 147.3, 116.3, 100.4, 86.5, 28.0; HRMS (DART/TOF) *m/z*: $[M + H]^+$ calcd for $C_9H_{12}{}^{79}Br_2NO_2$, 323.9235; found, 323.9231.



1f

2,5-Dibromo-1-(phenylsulfonyl)-1*H*-pyrrole (1f)

A flame-dried 200-mL round-bottomed flask equipped with a Teflon-coated magnetic stirring bar, a three-way stopcock, and a rubber septum was charged with 1-(phenylsulfonyl)-1*H*-pyrrole (2.074 g, 10.0 mmol, 1.0 equiv) and DMF (20.0 mL). NBS (4.625 g, 26.0 mmol, 2.6 equiv) in DMF (10.0 mL) was added dropwise to the solution for 3 min. After stirring at room temperature for 40 min, the resulting mixture was treated with saturated aqueous sodium thiosulfate (30 mL). After being partitioned, the aqueous layer was extracted with diethyl ether (75 mL) three times. The combined organic extracts were washed with brine (150 mL) three times, dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude product, which was purified by silica gel column chromatography (hexane/diethyl ether = 5:1) to provide the title compound as a colorless solid (2.444 g, 6.70 mmol, 67%), whose ^{1}H NMR spectral data was identical to that reported in the literature.[8] R_f = 0.41 (hexane/CH_2Cl_2 = 100:1); mp 98–99 °C; IR (ATR, cm^{-1}): 1550, 1448, 1385, 1236, 1195, 1179, 1166, 1140, 1097, 1067, 890, 776, 760, 724, 687; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06–8.02 (m, 2H), 7.69–7.64 (m, 1H), 7.59–7.54 (m, 2H), 6.31 (s, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 138.4, 134.7, 129.5, 127.8, 119.0, 101.9; HRMS (DART/TOF) *m/z*: $[M + H]^+$ calcd for $C_{10}H_8{}^{79}Br_2NO_2S$, 363.8643; found, 363.8649.



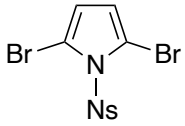
1g

2,5-Dibromo-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole (1g)

A flame-dried 200-mL round-bottomed flask equipped with a Teflon-coated magnetic stirring bar, a three-way stopcock, and a rubber septum was charged with 1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole (**S1g**) (5.001 g, 15.0 mmol, 1.0 equiv) and DMF (30.0 mL). The solution was cooled to 0 °C. To the solution was added NBS (5.868 g, 33.0 mmol, 2.2 equiv) in DMF (15.0 mL) dropwise for 5 min at 0 °C. After stirring at room temperature for 30 min, the resulting mixture was treated with saturated aqueous sodium thiosulfate (45 mL). After being partitioned, the aqueous layer was extracted with diethyl ether (100 mL) four times. The combined organic extracts were washed with brine (200 mL) three times, dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude product, which was purified by silica gel column chromatography (hexane/CH_2Cl_2 = 7:3) to provide the title compound as a colorless solid

8 T. Fukuda, T. Ohta, E.-i. Sudo and M. Iwao, *Org. Lett.*, 2010, **12**, 2734–2737.

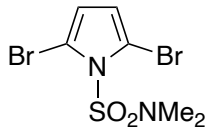
(5.760 g, 11.7 mmol, 78%). R_f = 0.50 (hexane/CH_2Cl_2 = 7:3); mp 88–90 °C; IR (ATR, cm^{-1}): 2962, 2928, 2873, 1599, 1539, 1460, 1433, 1383, 1363, 1243, 1186, 1140, 1107, 1072, 883, 840, 769, 722, 662, 645, 629, 621; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 (s, 2H), 6.27 (s, 2H), 4.09 (sept, 2H, *J* = 6.6 Hz), 2.92 (sept, 1H, *J* = 6.8 Hz), 1.26 (d, 6H, *J* = 6.8 Hz), 1.14 (d, 12H, *J* = 6.6 Hz); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.3, 151.2, 132.6, 124.0, 117.0, 101.3, 34.4, 29.6, 24.3, 23.6; HRMS (DART/TOF) *m/z*: [M + H]$^+$ calcd for $C_{19}H_{26}{}^{79}Br^{81}BrNO_2S$, 492.0031; found, 492.0034.



1h

2,5-Dibromo-1-((2-nitrophenyl)sulfonyl)-1*H*-pyrrole (1h)

A flame-dried 300-mL round-bottomed flask equipped with a Teflon-coated magnetic stirring bar, a three-way stopcock, and a rubber septum was charged with 1-((2-nitrophenyl)sulfonyl)-1*H*-pyrrole (**S1h**) (3.551 g, 14.1 mmol, 1.0 equiv) and DMF (28.2 mL). NBS (6.506 g, 36.6 mmol, 2.6 equiv) in DMF (14.1 mL) was added dropwise to the solution for 5 min. After stirring at room temperature for 40 min, the resulting mixture was treated with saturated aqueous sodium thiosulfate (50 mL). After being partitioned, the aqueous layer was extracted with diethyl ether (100 mL) three times. The combined organic extracts were washed with water (100 mL) three times, dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude product, which was purified by silica gel column chromatography (hexane/CH_2Cl_2 = 1:1) to provide the title compound as a pale green solid (2.410 g, 5.88 mmol, 42%). R_f = 0.47 (hexane/CH_2Cl_2 = 1:1); mp 113–115 °C; IR (ATR, cm^{-1}): 1545, 1441, 1395, 1359, 1234, 1193, 1152, 1127, 1077, 853, 784, 742, 732, 654, 607; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (dd, 1H, *J* = 8.0, 1.2 Hz), 7.85–7.72 (m, 3H), 6.41 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 147.9, 135.4, 132.9, 132.7, 131.0, 125.5, 118.8, 103.1; HRMS (DART/TOF) *m/z*: [M + H]$^+$ calcd for $C_{10}H_7{}^{79}Br_2N_2O_4S$, 408.8493; found, 408.8502.



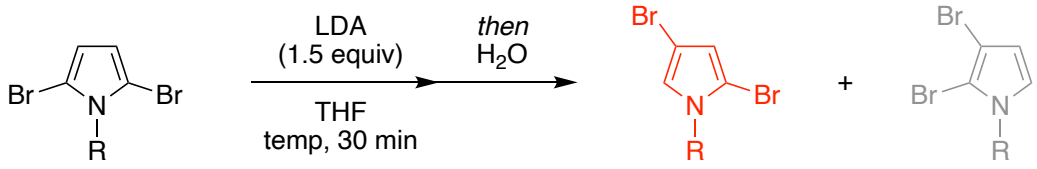
1i

2,5-Dibromo-*N*,*N*-dimethyl-1*H*-pyrrole-1-sulfonamide (1i)

A flame-dried 200-mL round-bottomed flask equipped with a Teflon-coated magnetic stirring bar, a three-way stopcock, and a rubber septum was charged with *N*,*N*-dimethyl-1*H*-pyrrole-1-sulfonamide (**S1i**) (3.489 g, 20.0 mmol, 1.0 equiv) and DMF (40.0 mL). NBS (9.229 g, 51.9 mmol, 2.6 equiv) in DMF (20.0 mL) was added dropwise to the solution for 5 min. After stirring at room temperature for 30 min, the resulting mixture was treated with saturated aqueous sodium thiosulfate (60 mL). After being partitioned, the aqueous layer was extracted with diethyl ether (150 mL) three times. The combined organic extracts were washed twice with brine (200 mL), dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced

pressure to give a crude product, which was purified by silica gel column chromatography (hexane/diethyl ether = 7:3) to provide the title compound as a colorless solid (3.329 g, 10.0 mmol, 50%), whose ^{1}H NMR and ^{13}C NMR spectral data were identical to those reported in the literature.[9] R_f = 0.33 (hexane/diethyl ether = 7:3); mp 62–63 °C; IR (ATR, cm^{-1}): 1436, 1418, 1393, 1271, 1232, 1192, 1130, 1073, 987, 967, 892, 788, 778, 716; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.33 (s, 2H), 3.00 (s, 6H); ^{1}H NMR (400 MHz, benzene-d_6): δ 5.91 (s, 2H), 2.27 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 117.7, 101.7, 38.6; ^{13}C{^{1}H} NMR (100 MHz, benzene-d_6): δ 117.7, 101.8, 37.8; HRMS (DART/TOF) *m/z*: $[M + H]^+$ calcd for $C_6H_9{}^{79}Br^{81}BrN_2O_2S$, 332.8731; found, 332.8730.

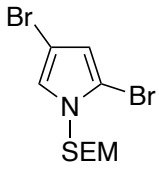
3.3 Halogen Dance of *N*-Substituted 2,5-Dibromopyrroles



1 **2** **3**

General Procedure

A flame-dried 20-mL Schlenk tube equipped with a Teflon-coated magnetic stirring bar and a rubber septum was charged with 2,5-dibromopyrrole **1** (0.300 mmol, 1.0 equiv) and THF (3.0 mL). After the solution was cooled to 0 °C or –78 °C, LDA (2.0 M, 225 µL, 0.45 mmol, 1.5 equiv) was added to the Schlenk tube and stirred for 30 min. The reaction mixture was treated with water (3 mL) and extracted with diethyl ether (3 mL) three times. The combined organic extracts were washed with brine (3 mL), dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude product, which was purified by silica gel column chromatography.



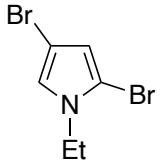
2a

2,4-Dibromo-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-pyrrole (2a)

The yield of 2,4-dibromopyrrole **2a** was determined to be 63% by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane (30.7 mg, 0.183 mmol) as an internal standard by comparing relative values of integration for the peak observed at 5.19 ppm (two protons for **2a**) with that of 1,1,2,2-tetrachloroethane observed at 5.96 ppm. The title compound was obtained as a colorless oil (31.9 mg, 0.0898 mmol, 30%) from 2,5-dibromo-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-pyrrole (**1a**) (106.6 mg, 0.300 mmol) according to the general procedure. R_f = 0.44 (hexane/CH_2Cl_2 = 7:3); IR (ATR, cm^{-1}): 2954, 2892, 1519, 1465, 1441, 1278, 1249, 1173, 1088, 1039, 917, 859, 835, 780, 749, 697, 604; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.86 (d, 1H, *J* =

9 J. Liu, C. Li, Y. Hu, X. Sun, K. Ma and Y. Liu, CN110372563, 2019.

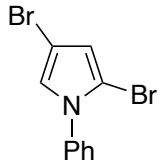
2.0 Hz), 6.20 (d, 1H, *J* = 2.0 Hz), 5.19 (s, 2H), 3.51 (t, 2H, *J* = 8.4 Hz), 0.90 (t, 2H, *J* = 8.4 Hz), –0.00 (s, 9H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 122.4, 114.0, 102.2, 97.0, 76.8, 66.2, 17.8, –1.3; HRMS (DART/TOF) *m/z*: $[M + H]^+$ calcd for $C_{10}H_{18}{}^{79}Br^{81}BrNOSi$, 355.9504; found, 355.9511.



2b

2,4-Dibromo-1-ethyl-1*H*-pyrrole (2b)

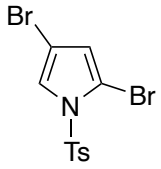
The yield of 2,4-dibromopyrrole **2b** was determined to be 36% by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane (26.4 mg, 0.157 mmol) as an internal standard by comparing relative values of integration for the peak observed at 6.15 ppm (one proton for **2b**) with that of 1,1,2,2-tetrachloroethane observed at 5.96 ppm. The title compound was obtained as a colorless oil (14.8 mg, 0.0583 mmol, 29%) from 2,5-dibromo-1-ethyl-1*H*-pyrrole (**1b**) (76.5 mg, 0.301 mmol) according to the general procedure. R_f = 0.35 (hexane); IR (ATR, cm^{-1}): 1462, 1294, 954, 771, 605; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.73 (d, 1H, *J* = 2.2 Hz), 6.15 (d, 1H, *J* = 2.2 Hz), 3.90 (q, 2H, *J* = 7.5 Hz), 1.35 (t, 3H, *J* = 7.5 Hz); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 120.9, 112.8, 101.4, 95.5, 43.8, 16.3; HRMS (DART/TOF) *m/z*: $[M + H]^+$ calcd for $C_6H_8{}^{79}Br^{81}BrN$, 253.9003; found, 253.8997.



2c

2,4-Dibromo-1-phenyl-1*H*-pyrrole (2c)

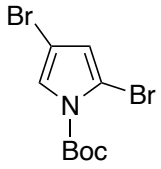
The yield of 2,4-dibromopyrrole **2c** was determined to be 60% by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane (28.6 mg, 0.170 mmol) as an internal standard by comparing relative values of integration for the peak observed at 6.34 ppm (one proton for **2c**) with that of 1,1,2,2-tetrachloroethane observed at 5.96 ppm. The title compound was obtained as a colorless oil (41.4 mg, 0.138 mmol, 46%) from 2,4-dibromo-1-phenyl-1*H*-pyrrole (**1c**) (90.9 mg, 0.302 mmol) according to the general procedure. R_f = 0.34 (hexane); IR (ATR, cm^{-1}): 3133, 1597, 1498, 1443, 1381, 1319, 1184, 1136, 1062, 1027, 964, 920, 780, 764, 737, 694, 604; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49–7.39 (m, 3H), 7.35–7.31 (m, 2H), 6.91 (d, 1H, *J* = 2.0 Hz), 6.34 (d, 1H, *J* = 2.0 Hz); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 138.8, 129.2, 128.4, 126.6, 123.4, 114.6, 102.2, 97.2; HRMS (DART/TOF) *m/z*: $[M + H]^+$ calcd for $C_{10}H_8{}^{81}Br_2N$, 303.8983; found, 303.8982.



2d

2,4-Dibromo-1-tosyl-1*H*-pyrrole (2d)

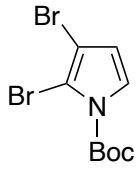
The yields of 2,4-dibromopyrrole **2d** and 2,3-dibromopyrrole **3d** were determined to be 59% and 9%, respectively, by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane (33.7 mg, 0.201 mmol) as an internal standard by comparing relative values of integration for the peaks observed at 6.28 ppm (one proton for **2d**) and 6.36 ppm (one proton for **3d**) with that of 1,1,2,2-tetrachloroethane observed at 5.96 ppm. The title compound was obtained as a colorless solid (61.0 mg, 0.161 mmol, 54%) from 2,5-dibromo-1-tosyl-1*H*-pyrrole (**1d**) (113.9 mg, 0.300 mmol) according to the general procedure. R_f = 0.54 (hexane/CH_2Cl_2 = 1:1); mp 83–85 °C; IR (ATR, cm^{-1}): 2923, 2852, 1597, 1530, 1441, 1383, 1221, 1192, 1176, 1134, 1092, 1061, 1006, 811, 671; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, 2H, *J* = 8.8 Hz), 7.48 (d, 1H, *J* = 2.2 Hz), 7.34 (d, 2H, *J* = 8.8 Hz), 6.28 (d, 1H, *J* = 2.2 Hz), 2.44 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 146.2, 134.5, 130.2, 128.1, 123.2, 119.9, 100.64, 100.59, 21.8; HRMS (DART/TOF) *m/z*: [M + H]$^+$ calcd for $C_{11}H_{10}{}^{79}Br^{81}BrNO_2S$, 379.8779; found, 379.8772.



2e

***tert*-Butyl 2,4-dibromo-1*H*-pyrrole-1-carboxylate (2e)**

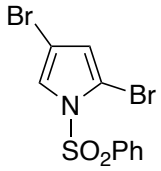
The yields of 2,4-dibromopyrrole **2e** and 2,3-dibromopyrrole **3e** were determined to be 57% and 7%, respectively, by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane (28.3 mg, 0.169 mmol) as an internal standard by comparing relative values of integration for the peaks observed at 7.33 ppm (one proton for **2e**) and 7.35 ppm (one proton for **3e**) with that of 1,1,2,2-tetrachloroethane observed at 5.96 ppm. The title compound was obtained as a colorless oil (47.1 mg, 0.145 mmol, 48%) from *tert*-butyl 2,5-dibromo-1*H*-pyrrole-1-carboxylate (**1e**) (97.4 mg, 0.300 mmol) according to the general procedure. The title compound was isolated from its regioisomer **3e** using silica gel column chromatography and ^{1}H NMR analysis of fractions. R_f = 0.32 (hexane/CH_2Cl_2 = 9:1); IR (ATR, cm^{-1}): 2977, 1766, 1753, 1452, 1396, 1371, 1321, 1302, 1287, 1260, 1232, 1153, 1074, 1021, 916, 845, 797; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (d, 1H, *J* = 2.0 Hz), 6.31 (d, 1H, *J* = 2.0 Hz), 1.61 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 147.0, 122.6, 119.3, 119.3, 101.0, 100.1, 85.8, 28.0; HRMS (DART/TOF) *m/z*: [M + H]$^+$ calcd for $C_9H_{12}{}^{79}Br^{81}BrNO_2$, 325.9214; found, 325.9216.



3e

***tert*-Butyl 2,3-dibromo-1*H*-pyrrole-1-carboxylate (3e)**

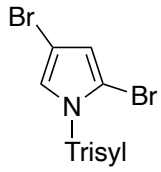
The title compound was obtained as a colorless oil (4.2 mg, 0.013 mmol, 4%) from *tert*-butyl 2,5-dibromo-1*H*-pyrrole-1-carboxylate (**1e**) (97.4 mg, 0.300 mmol) according to the general procedure. R_f = 0.32 (hexane/CH_2Cl_2 = 9:1); IR (ATR, cm^{-1}): 2984, 1762, 1749, 1532, 1458, 1372, 1314, 1275, 1257, 1153, 1080, 1007, 919, 842, 720; ^1H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, 1H, J = 3.8 Hz), 6.29 (d, 1H, J = 3.8 Hz), 1.62 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 147.2, 123.1, 114.2, 106.6, 102.3, 85.8, 28.1; HRMS (DART/TOF) *m/z*: $[M + H]^+$ calcd for $C_9H_{12}{}^{79}Br^{81}BrNO_2$, 325.9214; found, 325.9223.



2f

2,4-Dibromo-1-(phenylsulfonyl)-1*H*-pyrrole (2f)

The yields of 2,4-dibromopyrrole **2f** and 2,3-dibromopyrrole **3f** were determined to be 60% and 11%, respectively, by ^1H NMR analysis using 1,1,2,2-tetrachloroethane (33.3 mg, 0.198 mmol) as an internal standard by comparing relative values of integration for the peaks observed at 6.30 ppm (one proton for **2f**) and 6.38 ppm (one proton for **3f**) with that of 1,1,2,2-tetrachloroethane observed at 5.96 ppm. The products were identified by comparing the ^1H NMR spectrum of the crude product with that reported in the literature.[8] The title compound decomposed immediately after purification by silica gel column chromatography.

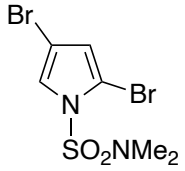


2g

2,4-Dibromo-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole (2g)

The yields of 2,4-dibromopyrrole **2g** and 2,3-dibromopyrrole **3g** were determined to be 58% and 29%, respectively, by ^1H NMR analysis using 1,1,2,2-tetrachloroethane (21.0 mg, 0.125 mmol) as an internal standard by comparing relative values of integration for the peaks observed at 6.24 ppm (one proton for **2g**) and 6.37 ppm (one proton for **3g**) with that of 1,1,2,2-tetrachloroethane observed at 5.96 ppm. The title compound was obtained as a colorless solid (80.5 mg, 0.164 mmol, 55%) from 2,5-dibromo-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole (**1g**) (147.3 mg, 0.300 mmol) according to the general procedure. R_f = 0.65 (hexane/CH_2Cl_2 = 1:1); mp 58–59 °C; IR (ATR, cm^{-1}): 2962, 2928, 2871, 1599, 1527, 1462, 1437,

1378, 1351, 1219, 1174, 1131, 1059, 1002, 914, 884, 796, 668; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, 1H, J = 1.8 Hz), 7.18 (s, 2H), 6.24 (d, 1H, J = 1.8 Hz), 4.03 (sept, 2H, J = 6.8 Hz), 2.92 (sept, 1H, J = 6.8 Hz), 1.26 (d, 6H, J = 6.8 Hz), 1.14 (d, 12H, J = 6.8 Hz); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.5, 151.8, 130.4, 124.3, 122.2, 118.4, 100.5, 99.2, 34.4, 29.8, 24.4, 23.6; HRMS (DART/TOF) *m/z*: $[M + H]^+$ calcd for $C_{19}H_{26}{}^{79}Br^{81}BrNO_2S$, 492.0031; found, 492.0035.



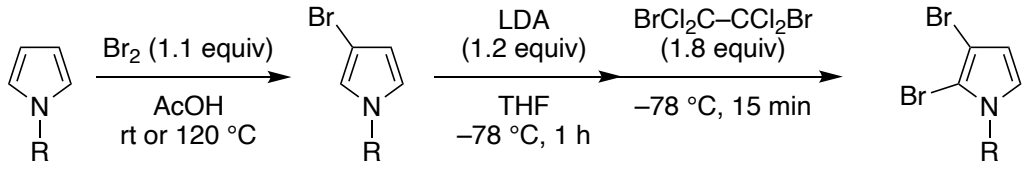
2i

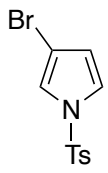
2,4-Dibromo-*N*,*N*-dimethyl-1*H*-pyrrole-1-sulfonamide (2i)

The yields of 2,4-dibromopyrrole **2i** and 2,3-dibromopyrrole **3i** were determined to be 87% and 6%, respectively, by ^{1}H NMR analysis using benzene-d_6 and 1,1,2,2-tetrachloroethane (33.4 mg, 0.199 mmol) as a solvent and an internal standard by comparing relative values of integration for the peaks observed at 5.96 ppm (one proton for **2i**) and 5.89 ppm (one proton for **3i**) with that of 1,1,2,2-tetrachloroethane observed at 4.91 ppm. The title compound was obtained as a colorless solid (76.7 mg, 0.231 mmol, 76%) from 2,5-dibromo-*N*,*N*-dimethyl-1*H*-pyrrole-1-sulfonamide (**1i**) (100.5 mg, 0.303 mmol) according to the general procedure. R_f = 0.47 (hexane/CH_2Cl_2 = 1:1); mp 38–39 °C; IR (ATR, cm^{-1}): 2919, 1527, 1438, 1419, 1392, 1221, 1175, 1136, 1063, 1009, 969, 913, 800, 724; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (d, 1H, J = 2.4 Hz), 6.36 (d, 1H, J = 2.4 Hz), 2.96 (s, 6H); ^{1}H NMR (400 MHz, benzene-d_6): δ 7.11 (d, 1H, J = 2.4 Hz), 5.97 (d, 1H, J = 2.4 Hz), 2.08 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 124.5, 119.1, 99.8, 99.0, 38.5; ^{13}C{^{1}H} NMR (100 MHz, benzene-d_6): δ 124.6, 119.1, 100.1, 99.2, 37.7; HRMS (DART/TOF) *m/z*: $[M + H]^+$ calcd for $C_6H_9{}^{79}Br^{81}BrN_2O_2S$, 332.8731; found, 332.8726.

4. Isomerization of Dibromopyrrolyllithiums Facilitated by the Sulfamoyl Group (Scheme 4)

4.1 Synthesis of *N*-Substituted 2,3-Dibromopyrroles[8]

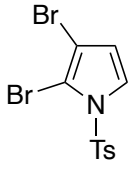




S2d

3-Bromo-1-tosyl-1*H*-pyrrole (S2d)

A 100-mL round-bottomed flask equipped with a Teflon-coated magnetic stirring bar, a three-way stopcock, and a rubber septum was charged with 1-tosyl-1*H*-pyrrole (671.4 mg, 3.03 mmol, 1.0 equiv) and acetic acid (15.0 mL). Br_2 (509.1 mg, 3.19 mmol, 1.1 equiv) in acetic acid (7.5 mL) was added dropwise to the flask for 10 min. After stirring at room temperature for 3 h, the flask was equipped with a reflux condenser and the resulting mixture was heated at 120 °C for 1.5 h, at which time the reaction mixture was treated with saturated aqueous sodium thiosulfate (30 mL). After being partitioned, the aqueous layer was extracted with ethyl acetate (15 mL) four times. The combined organic extracts were washed with water (50 mL) three times, dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude product, which was purified by silica gel column chromatography (hexane/CH_2Cl_2 = 9:1) to provide the title compound as a colorless solid (378.9 mg, 1.26 mmol, 42%), whose ^{1}H NMR and ^{13}C NMR spectral data were identical to those reported in the literature.[10] R_f = 0.45 (hexane/CH_2Cl_2 = 1:1); mp 67–68 °C; IR (ATR, cm^{-1}): 3144, 1596, 1528, 1458, 1375, 1224, 1191, 1172, 1092, 1054, 909, 812, 771, 703, 672; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, 2H, *J* = 8.4 Hz), 7.31 (d, 2H, *J* = 8.4 Hz), 7.15 (dd, 1H, *J* = 2.0, 1.6 Hz), 7.07 (dd, 1H, *J* = 3.2, 2.0 Hz), 6.28 (dd, 1H, *J* = 3.2, 1.6 Hz), 2.42 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 145.7, 135.6, 130.3, 127.2, 121.3, 119.8, 116.3, 102.2, 21.8; HRMS (DART/TOF) *m/z*: $[M + H]^+$ calcd for $C_{11}H_{11}{}^{79}BrNO_2S$, 299.9694; found, 299.9702.



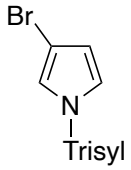
3d

2,3-Dibromo-1-tosyl-1*H*-pyrrole (3d)

A flame-dried 20-mL Schlenk tube equipped with a Teflon-coated magnetic stirring bar and a rubber septum under argon was charged with THF (3.0 mL). The Schlenk tube was cooled to –78 °C and LDA (2.0 M, 0.36 mL, 0.72 mmol, 1.2 equiv) was added to the Schlenk tube. After stirring at –78 °C for 10 min, 3-bromo-1-tosyl-1*H*-pyrrole (**S2d**) (181.9 mg, 0.606 mmol, 1.0 equiv) in THF (1.2 mL) was added to the Schlenk tube. After stirring at –78 °C for 1 h, 1,2-dibromo-1,1,2,2-tetrachloroethane (353.8 mg, 1.09 mmol, 1.8 equiv) in THF (1.2 mL) was added dropwise to the Schlenk tube and the resulting mixture was stirred at –78 °C for 1.5 h, at which time the reaction mixture was treated with water (5 mL). After being partitioned, the aqueous layer was extracted with diethyl ether (5 mL) three times. The combined organic extracts were washed with brine (5 mL), dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude product, which was purified by silica gel column chromatography (hexane/CH_2Cl_2 = 9:1) to provide the title compound as a colorless solid (86.9 mg, 0.229 mmol, 38%). R_f = 0.52 (hexane/CH_2Cl_2 = 1:1); mp 111–112 °C; IR (ATR, cm^{-1}): 1596, 1527, 1493, 1446, 1381, 1269, 1192, 1176, 1129, 1082, 985, 898, 812, 719, 702, 670; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, 2H, *J* = 8.8 Hz), 7.49 (d, 1H, *J* = 3.8 Hz), 7.34 (d, 2H, *J* = 8.8 Hz), 6.36 (d, 1H, *J* = 3.8 Hz), 2.44 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 146.2,

10 C. Zonta, F. Fabris and O. De Lucchi, *Org. Lett.*, 2005, **7**, 1003–1006.

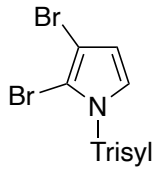
134.5, 130.2, 128.2, 124.0, 115.0, 107.0, 101.7, 21.9; HRMS (DART/TOF) *m/z*: $[M + H]^+$ calcd for $C_{11}H_{10}{}^{79}Br^{81}BrNO_2S$, 379.8779; found, 379.8787.



S2g

3-Bromo-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole (S2g)

A 200-mL round-bottomed flask equipped with a Teflon-coated magnetic stirring bar, a three-way stopcock, and a rubber septum was charged with 1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole (**1g**) (1.695 g, 5.08 mmol, 1.0 equiv) and acetic acid (25.0 mL). Br_2 (852.1 mg, 5.33 mmol, 1.1 equiv) in acetic acid (12.5 mL) was added dropwise to the flask for 10 min. After stirring at room temperature for 2 h, the three-way stopcock was replaced with a reflux condenser and the resulting mixture was heated at 120 °C for 1 h, at which time the reaction mixture was treated with saturated aqueous sodium thiosulfate (30 mL). After being partitioned, the aqueous layer was extracted with ethyl acetate (25 mL) three times. The combined organic extracts were washed with water (100 mL) three times, dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude product, which was purified by silica gel column chromatography (hexane/CH_2Cl_2 = 4:1) to provide the title compound as a colorless solid (1.008 g, 2.44 mmol, 48%). R_f = 0.58 (hexane/CH_2Cl_2 = 1:1); mp 79–80 °C; IR (ATR, cm^{-1}): 2962, 2930, 2871, 1600, 1464, 1427, 1377, 1348, 1224, 1192, 1174, 1050, 950, 910, 885, 761, 668; ^1H NMR (400 MHz, $CDCl_3$): δ 7.20 (s, 2H), 7.05–7.02 (m, 2H), 6.27 (dd, 1H, *J* = 3.2, 2.0 Hz), 4.09 (sept, 2H, *J* = 6.8 Hz), 2.92 (sept, 1H, *J* = 6.9 Hz), 1.26 (d, 6H, *J* = 6.9 Hz), 1.18 (d, 12H, *J* = 6.8 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 155.2, 151.9, 130.3, 124.6, 120.5, 119.0, 114.7, 100.7, 34.4, 29.8, 24.8, 23.6; HRMS (DART/TOF) *m/z*: $[M + H]^+$ calcd for $C_{19}H_{27}{}^{79}BrNO_2S$, 412.0946; found, 412.0962.

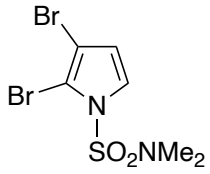


3g

2,3-Dibromo-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole (3g)

A flame-dried 100-mL Schlenk tube equipped with a Teflon-coated magnetic stirring bar and a rubber septum was charged with THF (10.0 mL). The solution was cooled to –78 °C and LDA (2.0 M, 1.2 mL, 2.4 mmol, 1.2 equiv) was added to the Schlenk tube. After stirring at –78 °C for 10 min, 3-bromo-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole (**S2g**) (831.0 mg, 2.02 mmol, 1.0 equiv) in THF (4.0 mL) was added to the Schlenk tube. After stirring at –78 °C for 1 h, 1,2-dibromo-1,1,2,2-tetrachloroethane (1.167 g, 3.58 mmol, 1.8 equiv) in THF (3.0 mL) was added dropwise to the Schlenk tube and the resulting mixture was stirred at –78 °C for 1.5 h, at which time the reaction mixture was treated with water (10 mL). After being

partitioned, the aqueous layer was extracted with diethyl ether (10 mL) three times. The combined organic extracts were washed with brine (10 mL), dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude product, which was purified by silica gel column chromatography (hexane/CH_2Cl_2 = 19:1) to provide the title compound as a colorless solid (523.8 mg, 1.07 mmol, 53%). R_f = 0.37 (hexane/CH_2Cl_2 = 7:3); mp 69–71 °C; IR (ATR, cm^{-1}): 2962, 2928, 2871, 1599, 1524, 1462, 1428, 1364, 1351, 1275, 1194, 1173, 1128, 984, 884, 716, 667; ^1H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, 1H, *J* = 3.8 Hz), 7.18 (s, 2H), 6.37 (d, 1H, *J* = 3.8 Hz), 4.03 (sept, 2H, *J* = 6.8 Hz), 2.92 (sept, 1H, *J* = 6.8 Hz), 1.26 (d, 6H, *J* = 6.8 Hz), 1.13 (d, 12H, *J* = 6.8 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 155.5, 151.8, 130.3, 124.3, 122.8, 113.5, 105.2, 101.6, 34.4, 29.7, 24.4, 23.6; HRMS (DART/TOF) *m/z*: $[M + H]^+$ calcd for $C_{19}H_{26}{}^{79}Br_2NO_2S$, 490.0051; found, 490.0073.



3i

2,3-Dibromo-*N*,*N*-dimethyl-1*H*-pyrrole-1-sulfonamide (3i)

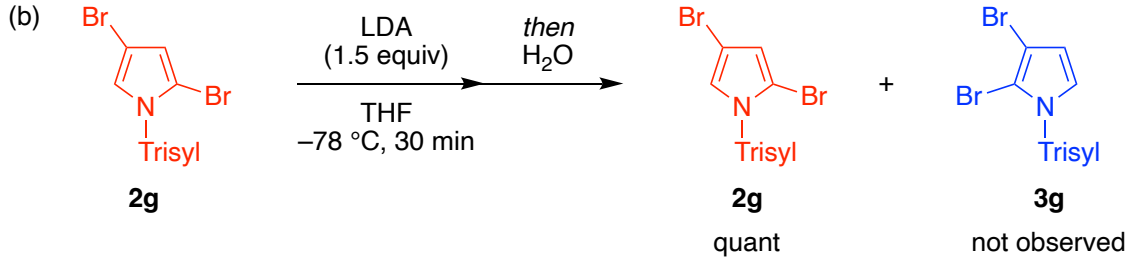
A 200-mL round-bottomed flask equipped with a Teflon-coated magnetic stirring bar, a three-way stopcock, and a rubber septum was charged with *N*,*N*-dimethyl-1*H*-pyrrole-1-sulfonamide (**S1i**) (857.4 mg, 4.92 mmol, 1.0 equiv) and acetic acid (25.0 mL). Br_2 (826.1 mg, 5.17 mmol, 1.1 equiv) in acetic acid (12.5 mL) was added dropwise to the flask for 5 min. After stirring at room temperature for 2 h, the reaction mixture was treated with saturated aqueous sodium thiosulfate (30 mL). After being partitioned, the aqueous layer was extracted with diethyl ether (25 mL) three times. The combined organic extracts were washed with water (100 mL) three times, dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude product. The crude product was purified by silica gel column chromatography (hexane/diethyl ether = 10:1) to provide the corresponding 3-bromopyrrole as a colorless oil (1.048 g), which was used for the next reaction without further purification. R_f = 0.23 (hexane/diethyl ether = 10:1).

A flame-dried 100-mL Schlenk tube equipped with a Teflon-coated magnetic stirring bar and a rubber septum under argon was charged with THF (20.5 mL). The solution was cooled to –78 °C and LDA (2.0 M, 2.5 mL, 5.0 mmol) was added to the Schlenk tube. After stirring at –78 °C for 10 min, the crude bromide (1.048 g) was added to the Schlenk tube. After stirring at –78 °C for 1 h, 1,2-dibromo-1,1,2,2-tetrachloroethane (2.465 g, 7.57 mmol) in THF (4.0 mL) was added dropwise to the Schlenk tube and the resulting mixture was stirred at –78 °C for 1.5 h, at which time the reaction mixture was treated with water (10 mL). After being partitioned, the aqueous layer was extracted with diethyl ether (20 mL) three times. The combined organic extracts were washed with brine (20 mL), dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude product, which was purified by silica gel column chromatography (hexane/diethyl ether = 9:1) to provide the title compound as a colorless solid (536.3 mg, 1.62 mmol, 33% over 2 steps). R_f = 0.39 (hexane/diethyl ether = 1:1); mp 43–44 °C; IR (ATR, cm^{-1}): 2923, 2853, 1391, 1272, 1194, 1173, 1129, 989, 971, 725; ^1H NMR (400 MHz, $CDCl_3$): δ 7.28 (d, 1H, *J* = 3.6 Hz), 6.32 (d, 1H, *J* =

3.6 Hz), 2.95 (s, 6H); ^{1}H NMR (400 MHz, benzene-d_6): δ 6.93 (d, 1H, J = 3.6 Hz), 5.89 (d, 1H, J = 3.6 Hz), 2.10 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 125.4, 113.6, 106.2, 101.1, 38.6; ^{13}C{^{1}H} NMR (100 MHz, benzene-d_6): δ 125.4, 113.4, 106.2, 101.4, 37.6; HRMS (DART/TOF) *m/z*: [M + H]$^+$ calcd for $C_6H_9{}^{79}Br^{81}BrN_2O_2S$, 332.8731; found, 332.8726.

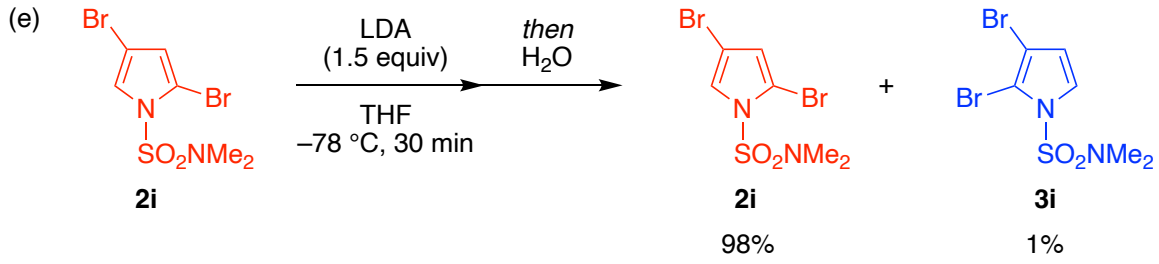
4.2 Isomerization Behavior of 2,4- and 2,3-Dibromopyrroles

Isomerization Behavior of 2,4-Dibromo-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole



A flame-dried 20-mL Schlenk tube equipped with a Teflon-coated magnetic stirring bar and a rubber septum was charged with 2,4-dibromo-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole (**2g**) (99.2 mg, 0.202 mmol, 1.0 equiv) and THF (2.0 mL). After the solution was cooled to –78 °C, LDA (2.0 M, 0.15 mL, 0.30 mmol, 1.5 equiv) was added to the Schlenk tube and stirred for 30 min. The reaction mixture was treated with water (2 mL) and extracted with diethyl ether (3 mL) three times. The combined organic extracts were washed with brine (3 mL), dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude product. The recovery yield of 2,4-dibromopyrrole **2g** was determined to be quantitative by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane (23.7 mg, 0.141 mmol) as an internal standard by comparing relative values of integration for the peak observed at 6.24 ppm (one proton for **2g**) with that of 1,1,2,2-tetrachloroethane observed at 5.96 ppm.

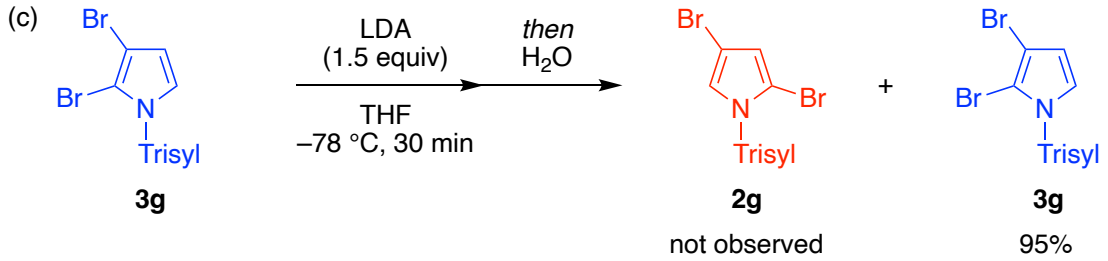
Isomerization Behavior of 2,4-Dibromo-*N*,*N*-dimethyl-1*H*-pyrrole-1-sulfonamide



A flame-dried 20-mL Schlenk tube equipped with a Teflon-coated magnetic stirring bar and a rubber septum was charged with 2,4-dibromo-*N*,*N*-dimethyl-1*H*-pyrrole-1-sulfonamide (**2i**) (67.2 mg, 0.202 mmol, 1.0 equiv) and THF (2.0 mL). After the solution was cooled to –78 °C, LDA (2.0 M, 0.15 mL, 0.30 mmol, 1.5 equiv) was added to the Schlenk tube and stirred for 30 min. The reaction mixture was treated with water (2 mL) and extracted with diethyl ether (3 mL) three times. The combined organic extracts were washed with brine (3 mL), dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude product. The yields of 2,4-dibromopyrrole **2i** and 2,3-dibromopyrrole **3i** were determined to

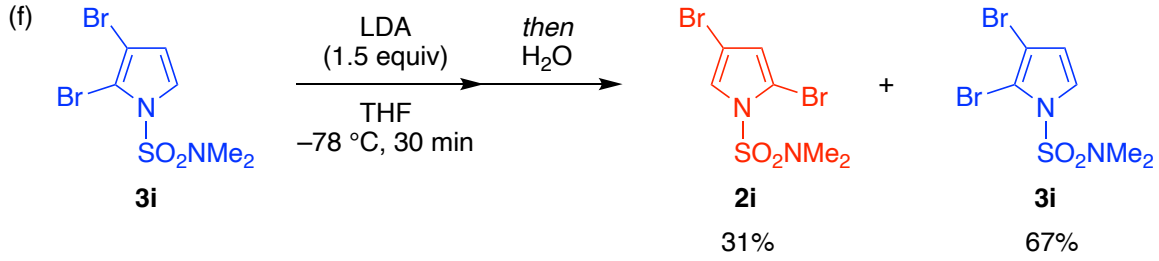
be 98% and 1%, respectively, by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane (23.7 mg, 0.141 mmol) as an internal standard by comparing relative values of integration for the peaks observed at 6.36 ppm (one proton for **2i**) and 6.32 ppm (one proton for **3i**) with that of 1,1,2,2-tetrachloroethane observed at 5.96 ppm.

Isomerization Behavior of 2,3-Dibromo-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole



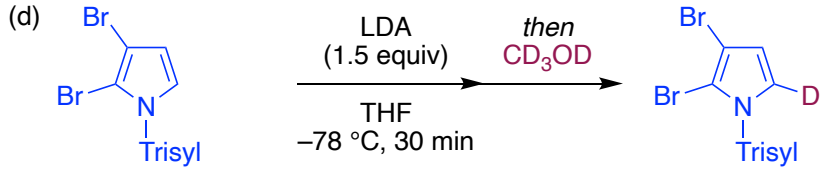
A flame-dried 20-mL Schlenk tube equipped with a Teflon-coated magnetic stirring bar and a rubber septum was charged with 2,3-dibromo-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole (**3g**) (98.0 mg, 0.199 mmol, 1.0 equiv) and THF (2.0 mL). After the solution was cooled to –78 °C, LDA (2.0 M, 0.15 mL, 0.30 mmol, 1.5 equiv) was added to the Schlenk tube and stirred for 30 min. The reaction mixture was treated with water (2 mL) and extracted with diethyl ether (3 mL) three times. The combined organic extracts were washed with brine (3 mL), dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude product. The recovery yield of 2,4-dibromopyrrole **3g** was determined to be 95% by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane (23.0 mg, 0.137 mmol) as an internal standard by comparing relative values of integration for the peak observed at 6.37 ppm (one proton for **3g**) with that of 1,1,2,2-tetrachloroethane observed at 5.96 ppm.

Isomerization Behavior of 2,3-Dibromo-*N*,*N*-dimethyl-1*H*-pyrrole-1-sulfonamide



A flame-dried 20-mL Schlenk tube equipped with a Teflon-coated magnetic stirring bar and a rubber septum was charged with 2,3-dibromo-*N*,*N*-dimethyl-1*H*-pyrrole-1-sulfonamide (**3i**) (66.7 mg, 0.201 mmol, 1.0 equiv) and THF (2.0 mL). After the solution was cooled to –78 °C, LDA (2.0 M, 0.15 mL, 0.30 mmol, 1.5 equiv) was added to the Schlenk tube and stirred for 30 min. The reaction mixture was treated with water (2 mL) and extracted with diethyl ether (3 mL) three times. The combined organic extracts were washed with brine (3 mL), dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude product. The yields of 2,4-dibromopyrrole **2i** and 2,3-dibromopyrrole **3i** were determined to be 31% and 67%, respectively, by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane (21.8 mg, 0.130 mmol) as an internal standard by comparing relative values of integration for the peaks observed at 6.36 ppm (one proton for **2i**) and 6.32 ppm (one proton for **3i**) with that of 1,1,2,2-tetrachloroethane observed at 5.96 ppm.

4.3 Deuteration of *N*-Trisyl-2,3-dibromopyrrole through Deprotolithiation

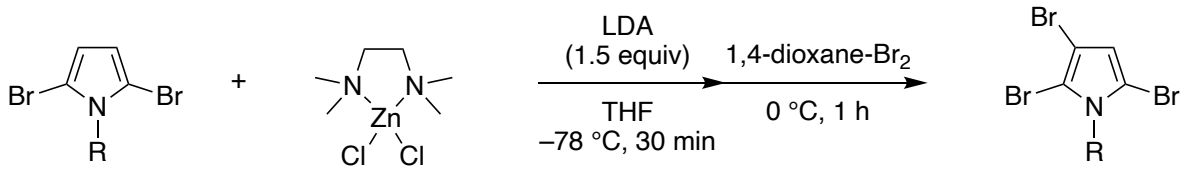


3g **3g**-*d*

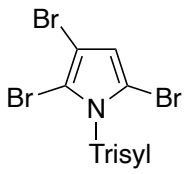
86%D

A flame-dried 20-mL Schlenk tube equipped with a Teflon-coated magnetic stirring bar and a rubber septum was charged with 2,3-dibromopyrrole **3g** (98.2 mg, 0.200 mmol, 1.0 equiv) and THF (2.0 mL). After the solution was cooled to –78 °C, LDA (2.0 M, 0.15 mL, 0.30 mmol, 1.5 equiv) was added to the Schlenk tube. The reaction mixture was stirred at –78 °C for 30 min and treated with CD_3OD (0.30 mL). The resulting mixture was extracted with diethyl ether (3 mL) three times. The combined organic extracts were washed with brine (3 mL), dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude product. The yields of 2,3-dibromopyrrole **3g** and deuterated 2,3-dibromopyrrole **3g**-*d* were determined to be 13% and 86%, respectively, by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane (22.2 mg, 0.132 mmol) as an internal standard by comparing relative values of integration for the peaks observed at 7.52 ppm (one proton for **3g**) and 6.37 ppm (one proton for **3g**-*d*) with that of 1,1,2,2-tetrachloroethane observed at 5.96 ppm. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (s, 2H), 6.37 (s, 1H), 4.03 (sept, 2H, J = 6.6 Hz), 2.92 (sept, 1H, J = 7.0 Hz), 1.26 (d, 6H, J = 7.0 Hz), 1.13 (d, 12H, J = 6.6 Hz); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.0, 151.8, 130.6, 124.3, 122.6 (t, $^1J_{C–D}$ = 29.7 Hz), 113.3, 105.2, 101.58, 34.4, 29.7, 24.4, 23.6.

4.4 Synthesis of *N*-Substituted 2,3,5-Tribromopyrroles



1 (1.5 equiv) **6**

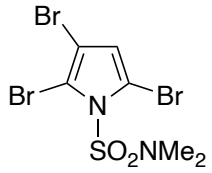


6g

2,3,5-Tribromo-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole (6g)

A flame-dried 20-mL Schlenk tube equipped with a Teflon-coated magnetic stirring bar and a rubber septum was charged with 2,5-dibromopyrrole **1g** (146.1 mg, 0.298 mmol, 1.0 equiv), $ZnCl_2$·TMEDA (114.0 mg,

0.452 mmol, 1.5 equiv), and THF (3.0 mL). After the solution was cooled to –78 °C, LDA (2.0 M, 225 μL, 0.45 mmol, 1.5 equiv) was added to the Schlenk tube and stirred for 30 min. The reaction mixture was treated with 1,4-dioxane-bromine complex (115.1 mg, 0.464 mmol, 1.6 equiv). After stirring at 0 °C for 2 h, the reaction mixture was treated with saturated aqueous sodium thiosulfate (3 mL) and saturated aqueous ammonium chloride (3 mL). The mixture was partitioned and the aqueous layer was extracted with diethyl ether (3 mL) three times. The combined organic extracts were washed with brine (3 mL), dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude product, which was purified by silica gel column chromatography (hexane/CH_2Cl_2 = 19:1) to provide the title compound as a colorless solid (95.9 mg, 0.168 mmol, 57%). R_f = 0.63 (hexane/CH_2Cl_2 = 1:1); mp 112–113 °C; IR (ATR, cm^{-1}): 2963, 2929, 2873, 1599, 1524, 1460, 1430, 1385, 1363, 1231, 1187, 1154, 1108, 1037, 1014, 939, 883, 792, 665; ^1H NMR (400 MHz, $CDCl_3$): δ 7.17 (s, 2H), 6.41 (s, 1H), 4.04 (sept, 2H, *J* = 6.8 Hz), 2.92 (sept, 1H, *J* = 7.0 Hz), 1.26 (d, 6H, *J* = 7.0 Hz), 1.15 (d, 12H, *J* = 6.8 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 155.7, 151.4, 132.1, 124.2, 118.8, 105.8, 103.3, 101.9, 34.5, 29.6, 24.3, 23.6; HRMS (DART/TOF) *m/z*: [M + H]$^+$ calcd for $C_{19}H_{25}{}^{79}Br_2{}^{81}BrNO_2S$, 569.9136; found, 569.9160.



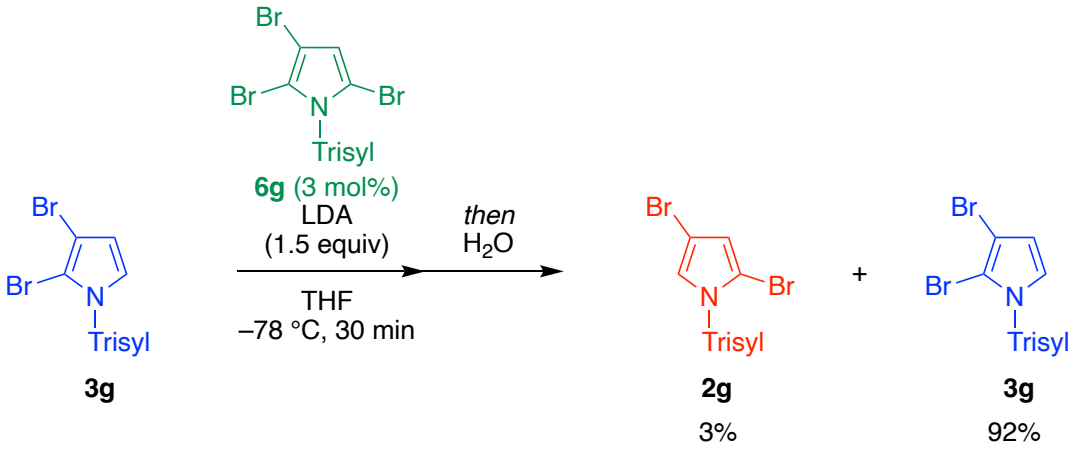
6i

2,3,5-Tribromo-*N*,*N*-dimethyl-1*H*-pyrrole-1-sulfonamide (6i)

A flame-dried 20-mL Schlenk tube equipped with a Teflon-coated magnetic stirring bar and a rubber septum was charged with 2,5-dibromopyrrole **1i** (98.0 mg, 0.295 mmol, 1.0 equiv), $ZnCl_2$·TMEDA (111.4 mg, 0.441 mmol, 1.5 equiv), and THF (3.0 mL). After the solution was cooled to –78 °C, LDA (2.0 M, 225 μL, 0.45 mmol, 1.5 equiv) was added to the Schlenk tube and stirred for 30 min. The reaction mixture was treated with 1,4-dioxane-bromine complex (241.3 mg, 0.973 mmol, 3.3 equiv). After stirring at 0 °C for 2 h, the reaction mixture was treated with saturated aqueous sodium thiosulfate (3 mL) and saturated aqueous ammonium chloride (3 mL). The mixture was partitioned and the aqueous layer was extracted with diethyl ether (3 mL) three times. The combined organic extracts were washed with brine (3 mL), dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude product, which was purified by silica gel column chromatography (hexane/diethyl ether = 9:1) to provide the title compound as a colorless solid (80.9 mg, 0.197 mmol, 67%). R_f = 0.29 (hexane/diethyl ether = 4:1); mp 43–44 °C; IR (ATR, cm^{-1}): 1524, 1456, 1438, 1423, 1398, 1279, 1229, 1192, 1155, 1111, 1019, 971, 795, 722, 607; ^1H NMR (400 MHz, $CDCl_3$): δ 6.47 (s, 1H), 3.02 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 119.6, 106.4, 103.6, 102.2, 38.7; HRMS (DART/TOF) *m/z*: [M + H]$^+$ calcd for $C_6H_8{}^{79}Br{}^{81}Br_2N_2O_2S$, 412.7816; found, 412.7829.

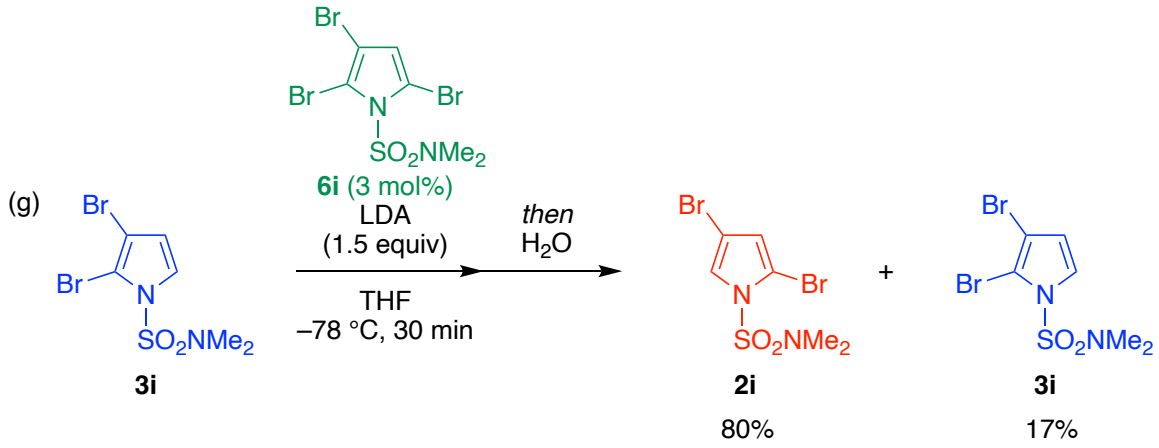
4.5 Effect of 2,3,5-Tribromopyrroles on Isomerization Behavior of 2,3-Dibromopyrroles

Reaction of *N*-Trisyl-2,3-dibromopyrrole



A flame-dried 20-mL Schlenk tube equipped with a Teflon-coated magnetic stirring bar and a rubber septum was charged with 2,3-dibromopyrrole **3g** (98.5 mg, 0.200 mmol, 1.0 equiv) and THF (2.0 mL). The solution was cooled to –78 °C. LDA (2.0 M, 0.15 mL, 0.30 mmol, 1.5 equiv) was added to the Schlenk tube. After stirring at –78 °C for 5 min, 2,3,5-tribromopyrrole **6g** (3.5 mg, 6.1 μmol, 3 mol%) was added to the to the solution. After stirring at –78 °C for 25 min, the reaction mixture was treated with water (2 mL) and extracted with diethyl ether (3 mL) three times. The combined organic extracts were washed with brine (3 mL), dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude product. The yields of 2,4-dibromopyrrole **2g** and 2,3-dibromopyrrole **3g** were determined to be 3% and 92%, respectively, by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane (36.8 mg, 0.219 mmol) as an internal standard by comparing relative values of integration for the peaks observed at 6.24 ppm (one proton for **2g**) and 6.37 ppm (one proton for **3g**) with that of 1,1,2,2-tetrachloroethane observed at 5.96 ppm.

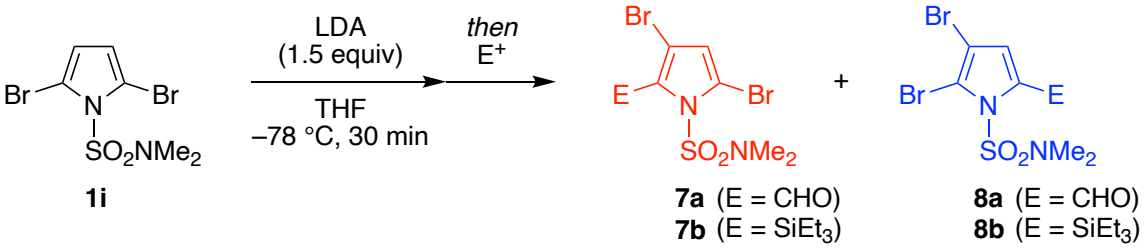
Reaction of *N*-Sulfamoyl-2,3-dibromopyrrole



A flame-dried 20-mL Schlenk tube equipped with a Teflon-coated magnetic stirring bar and a rubber septum was charged with 2,3-dibromopyrrole **3i** (66.7 mg, 0.201 mmol, 1.0 equiv) and THF (2.0 mL). The solution was cooled to –78 °C. LDA (2.0 M, 0.15 mL, 0.30 mmol, 1.5 equiv) was added to the Schlenk tube. After

stirring at –78 °C for 5 min, 2,3,5-tribromopyrrole **6i** (2.6 mg, 6.3 μmol, 3 mol%) was added to the to the solution. After stirring at –78 °C for 25 min, the reaction mixture was treated with water (2 mL) and extracted with diethyl ether (3 mL) three times. The combined organic extracts were washed with brine (3 mL), dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude product. The yields of 2,4-dibromopyrrole **2i** and 2,3-dibromopyrrole **3i** were determined to be 80% and 17%, respectively, by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane (28.4 mg, 0.169 mmol) as an internal standard by comparing relative values of integration for the peaks observed at 6.36 ppm (one proton for **2i**) and 6.32 ppm (one proton for **3i**) with that of 1,1,2,2-tetrachloroethane observed at 5.96 ppm.

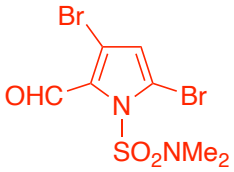
5 Regiocontrolled Synthesis of 2,4- and 2,3-Dibromopyrroles (Table 2)



1i

7a (E = CHO)
7b (E = $SiEt_3$)

8a (E = CHO)
8b (E = $SiEt_3$)

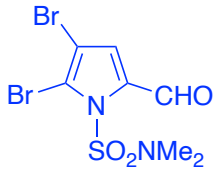


7a

3,5-Dibromo-2-formyl-*N*,*N*-dimethyl-1*H*-pyrrole-1-sulfonamide (7a)

A flame-dried 20-mL Schlenk tube equipped with a Teflon-coated magnetic stirring bar and a rubber septum was charged with 2,5-dibromopyrrole **1i** (101.7 mg, 0.306 mmol, 1.0 equiv) and THF (3.0 mL). After the solution was cooled to –78 °C, LDA (2.0 M, 225 μL, 0.45 mmol, 1.5 equiv) was added to the Schlenk tube and stirred at –78 °C for 30 min. To the Schlenk tube was added ethyl formate (47.5 μL, 0.590 mmol, 1.9 equiv). After stirring at –78 °C for 22 h, the resulting mixture was treated with saturated aqueous ammonium chloride (3 mL). After being partitioned, the aqueous layer was extracted with diethyl ether (3 mL) three times. The combined organic extracts were washed with brine (3 mL), dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude product. The yields of 2,4-dibromopyrrole **7a** and 2,3-dibromopyrrole **8a** were determined to be 66% and 5%, respectively, by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane (34.7 mg, 0.207 mmol) as an internal standard by comparing relative values of integration for the peaks observed at 10.01 ppm (one proton for **7a**) and 10.08 ppm (one proton for **8a**) with that of 1,1,2,2-tetrachloroethane observed at 5.96 ppm. The crude product was purified by silica gel column chromatography (hexane/diethyl ether = 1:1) to provide 2,4-dibromopyrrole **7a** as a colorless solid (70.3 mg, 0.195 mmol, 64%). R_f = 0.26 (hexane/diethyl ether = 1:1); mp 83–84 °C; IR (ATR, cm^{-1}): 1660, 1430, 1409, 1395, 1180, 1134, 1063, 975, 784, 726; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.01 (s, 1H), 6.56 (s, 1H), 3.01 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 180.1, 133.3, 121.7, 110.9, 110.6, 38.8; HRMS

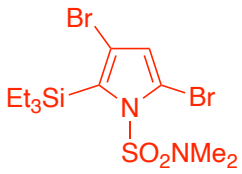
(DART/TOF) *m/z*: $[M + H]^+$ calcd for $C_7H_9{}^{79}Br^{81}BrN_2O_3S$, 360.8680; found, 360.8663.



8a

2,3-Dibromo-5-formyl-*N*,*N*-dimethyl-1*H*-pyrrole-1-sulfonamide (8a)

A flame-dried 20-mL Schlenk tube equipped with a Teflon-coated magnetic stirring bar and a rubber septum was charged with 2,5-dibromopyrrole **1i** (98.1 mg, 0.295 mmol, 1.0 equiv) and THF (3.0 mL). After the solution was cooled to –78 °C, LDA (2.0 M, 225 µL, 0.45 mmol, 1.5 equiv) was added to the Schlenk tube and stirred at –78 °C for 30 min. To the Schlenk tube was added DMF (45.0 µL, 0.585 mmol, 2.0 equiv). After stirring at –78 °C for 1 h, the mixture was warmed up to –40 °C and stirred for 21 h. The resulting mixture was treated with saturated aqueous ammonium chloride (3 mL). After being partitioned, the aqueous layer was extracted with diethyl ether (3 mL) three times. The combined organic extracts were washed with brine (3 mL), dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude product. The yield of 2,3-dibromopyrrole **8a** was determined to be 49% by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane (32.1 mg, 0.191 mmol) as an internal standard by comparing relative values of integration for the peak observed at 10.08 ppm (one proton for **8a**) with that of 1,1,2,2-tetrachloroethane observed at 5.96 ppm. The crude product was purified by silica gel column chromatography (hexane/diethyl ether = 1:1) to provide 2,3-dibromopyrrole **8a** as a colorless solid (42.0 mg, 0.117 mmol, 39%). R_f = 0.26 (hexane/diethyl ether = 1:1); mp 89–90 °C; IR (ATR, cm^{-1}): 1668, 1425, 1406, 1388, 1175, 1063, 965, 796, 723; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.08 (s, 1H), 7.20 (s, 1H), 3.00 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 180.6, 137.7, 121.7, 110.8, 107.9, 38.7; HRMS (DART/TOF) *m/z*: $[M + H]^+$ calcd for $C_7H_9{}^{79}Br^{81}BrN_2O_3S$, 360.8680; found, 360.8691.

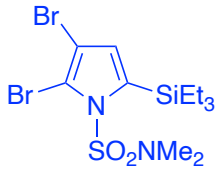


7b

3,5-Dibromo-*N*,*N*-dimethyl-2-(triethylsilyl)-1*H*-pyrrole-1-sulfonamide (7b)

A flame-dried 20-mL Schlenk tube equipped with a Teflon-coated magnetic stirring bar and a rubber septum was charged with 2,5-dibromopyrrole **1i** (99.9 mg, 0.301 mmol, 1.0 equiv) and THF (3.0 mL). After the solution was cooled to –78 °C, LDA (2.0 M, 225 µL, 0.45 mmol, 1.5 equiv) was added to the Schlenk tube and stirred at –78 °C for 30 min. To the Schlenk tube was added TESOTf (122.5 µL, 0.542 mmol, 1.8 equiv). After stirring at –78 °C for 1 h, the mixture was warmed up to –40 °C and stirred for 21 h. The resulting mixture was treated with saturated aqueous ammonium chloride (3 mL). After being partitioned, the aqueous layer was extracted with diethyl ether (3 mL) three times. The combined organic extracts were washed with brine (3 mL), dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to

give a crude product. The yields of 2,4-dibromopyrrole **7b** and 2,3-dibromopyrrole **8b** were determined to be 91% and 3%, respectively, by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane (32.9 mg, 0.196 mmol) as an internal standard by comparing relative values of integration for the peaks observed at 6.42 ppm (one proton for **7b**) and 6.51 ppm (one proton for **8b**) with that of 1,1,2,2-tetrachloroethane observed at 5.96 ppm. The crude product was purified by silica gel column chromatography (hexane/diethyl ether = 9:1) to provide 2,4-dibromopyrrole **7b** as a colorless oil (119.4 mg, 0.268 mmol, 89%). R_f = 0.31 (hexane/diethyl ether = 9:1); IR (ATR, cm^{-1}): 1379, 1175, 1115, 1019, 972, 727, 699, 615; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.41 (s, 1H), 2.86 (s, 6H), 1.01–0.93 (m, 15H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 137.8, 122.7, 114.6, 106.0, 38.1, 8.0, 5.7; HRMS (DART/TOF) *m/z*: $[M + H]^+$ calcd for $C_{12}H_{23}{}^{79}Br^{81}BrN_2O_2SSi$, 446.9596; found, 446.9585.

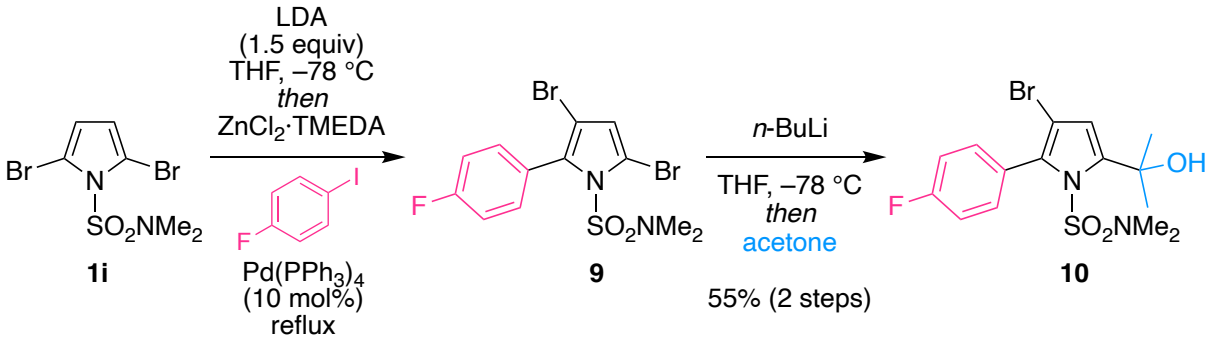


8b

2,3-Dibromo-*N*,*N*-dimethyl-5-(triethylsilyl)-1*H*-pyrrole-1-sulfonamide (8b)

A flame-dried 20-mL Schlenk tube equipped with a Teflon-coated magnetic stirring bar and a rubber septum was charged with 2,5-dibromopyrrole **1i** (99.9 mg, 0.301 mmol, 1.0 equiv) and THF (3.0 mL). After the solution was cooled to –78 °C, LDA (2.0 M, 225 μL, 0.45 mmol, 1.5 equiv) was added to the Schlenk tube and stirred at –78 °C for 30 min. To the Schlenk tube was added TESCl (90.0 μL, 0.537 mmol, 1.8 equiv). After stirring at –78 °C for 1 h, the mixture was warmed up to 0 °C and stirred for 21 h. The resulting mixture was treated with saturated aqueous ammonium chloride (3 mL). After being partitioned, the aqueous layer was extracted with diethyl ether (3 mL) three times. The combined organic extracts were washed with brine (3 mL), dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude product. The yields of 2,4-dibromopyrrole **7b** and 2,3-dibromopyrrole **8b** were determined to be 2% and 96%, respectively, by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane (32.7 mg, 0.195 mmol) as an internal standard by comparing relative values of integration for the peaks observed at 6.42 ppm (one proton for **7b**) and 6.50 ppm (one proton for **8b**) with that of 1,1,2,2-tetrachloroethane observed at 5.96 ppm. The crude product was purified by silica gel column chromatography (hexane/diethyl ether = 9:1) to provide 2,3-dibromopyrrole **8b** as a colorless oil (101.4 mg, 0.227 mmol, 76%). R_f = 0.33 (hexane/diethyl ether = 9:1); IR (ATR, cm^{-1}): 1377, 1177, 1157, 1134, 1035, 974, 727, 706, 632; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.50 (s, 1H), 2.94 (s, 6H), 0.95–0.90 (m, 9H), 0.88–0.81 (m, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 138.8, 126.3, 106.8, 105.5, 38.1, 7.7, 4.4; HRMS (DART/TOF) *m/z*: $[M + H]^+$ calcd for $C_{12}H_{23}{}^{79}Br^{81}BrN_2O_2SSi$, 446.9596; found, 446.9578.

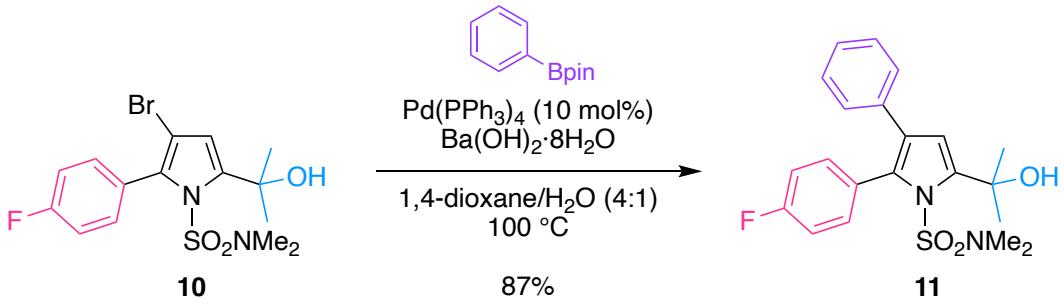
6 Formal Synthesis of Atorvastatin through Halogen Dance (Scheme 5)



3-Bromo-2-(4-fluorophenyl)-5-(2-hydroxypropan-2-yl)-*N*,*N*-dimethyl-1*H*-pyrrole-1-sulfonamide (10)

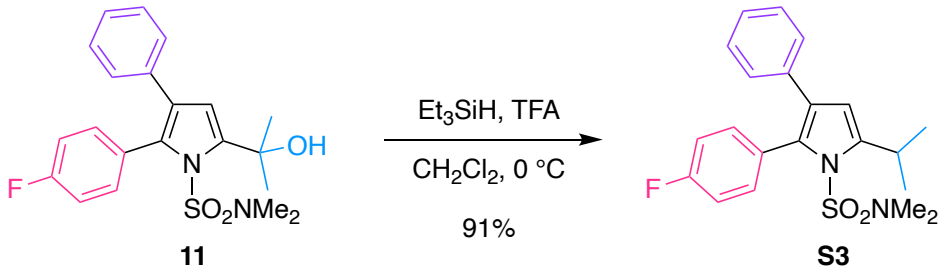
A flame-dried 100-mL Schlenk tube equipped with a Teflon-coated magnetic stirring bar and a rubber septum under argon was charged with 2,5-dibromopyrrole **1i** (995.3 mg, 3.00 mmol, 1.0 equiv) and THF (30.0 mL). The solution was cooled to –78 °C. LDA (2.0 M, 2.25 mL, 4.5 mmol, 1.5 equiv) was added to the Schlenk tube. After stirring at –78 °C for 30 min, $ZnCl_2$·TMEDA (1.135 g, 4.50 mmol, 1.5 equiv) was added to the solution. After stirring at –78 °C for 10 min, 1-fluoro-4-iodobenzene (1.999 g, 9.00 mmol, 3.0 equiv) and $Pd(PPh_3)_4$ (346.0 mg, 0.299 mmol, 10 mol%) were added to the solution. The resulting mixture was heated at 70 °C for 17 h, at which time the reaction mixture was treated with water (15 mL). After being partitioned, the aqueous layer was extracted with diethyl ether (50 mL) three times. The combined organic extracts were washed with brine (100 mL), dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude product. The crude product was purified by silica gel column chromatography (hexane/ethyl acetate = 4:1 to 7:3) to provide the corresponding arylated pyrrole **9** as a colorless solid (991.3 mg), which was used for the next reaction without further purification. R_f = 0.17 (hexane/ethyl acetate = 4:1).

A flame-dried 50-mL round-bottomed flask equipped with a Teflon-coated magnetic stirring bar, a three-way stopcock, and a rubber septum was charged with arylated pyrrole **9** (991.3 mg) and THF (23.0 mL). The solution was cooled to –78 °C and *n*-BuLi (1.59 M, 1.61 mL, 2.56 mmol) was added dropwise to the Schlenk tube. After stirring at –78 °C for 10 min, acetone (515 μL, 6.99 mmol) was added to the solution. After stirring at –78 °C for 2 h, the reaction mixture was treated with water (15 mL). After being partitioned, the aqueous layer was extracted with diethyl ether (15 mL) three times. The combined organic extracts were washed with brine (30 mL), dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude product, which was purified by silica gel column chromatography (hexane/ethyl acetate = 4:1) to provide the title compound as a colorless solid (671.6 mg, 1.66 mmol, 55% over 2 steps). R_f = 0.30 (hexane/ethyl acetate = 7:3); mp 76–78 °C; IR (ATR, cm^{-1}): 3549, 2985, 2941, 1608, 1520, 1492, 1368, 1349, 1336, 1289, 1226, 1183, 1162, 1105, 974, 957, 840, 815, 728, 627; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41–7.36 (m, 2H), 7.17–7.12 (m, 2H), 6.33 (s, 1H), 4.80 (s, 1H), 2.37 (s, 6H), 1.71 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 163.1 (d, $^1J_{C–F}$ = 249 Hz), 145.4, 133.6 (d, $^3J_{C–F}$ = 8.6 Hz), 132.9, 126.7 (d, $^4J_{C–F}$ = 2.9 Hz), 115.2 (d, $^2J_{C–F}$ = 22.1 Hz), 114.2, 103.3, 69.3, 36.8, 31.0; HRMS (DART/TOF) *m/z*: [M – OH]$^+$ calcd for $C_{15}H_{17}{}^{79}BrFN_2O_2S$, 387.0178; found, 387.0187.



2-(4-Fluorophenyl)-5-(2-hydroxypropan-2-yl)-*N*,*N*-dimethyl-3-phenyl-1*H*-pyrrole-1-sulfonamide (11)

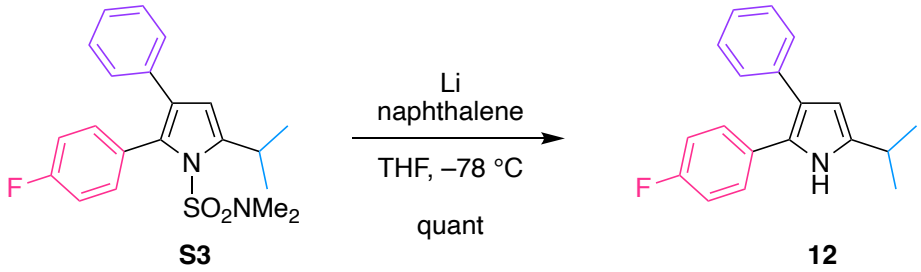
A 50-mL round-bottomed flask equipped with a Teflon-coated magnetic stirring bar and a reflux condenser was charged with tertiary alcohol **10** (609.5 mg, 1.50 mmol, 1.0 equiv), phenylboronic acid pinacol ester (460.1 mg, 2.25 mmol, 1.5 equiv), $Ba(OH_2)·8H_2O$ (2.835 g, 8.99 mmol, 6.0 equiv), $Pd(PPh_3)_4$ (174.4 mg, 0.151 mmol, 0.10 equiv), 1,4-dioxane (12 mL), and water (3.0 mL). The flask was placed in a preheated oil bath and heated at 100 °C for 4 h, at which time the reaction mixture was treated with saturated aqueous ammonium chloride (25 mL). The resulting mixture was extracted with diethyl ether (25 mL) three times. The combined organic extracts were washed with brine (50 mL) three times, dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude product, which was purified by silica gel column chromatography (hexane/ethyl acetate = 4:1) to provide the title compound as a colorless solid (523.9 mg, 1.30 mmol, 87%). R_f = 0.30 (hexane/ethyl acetate = 7:3); mp 154–155 °C; IR (ATR, cm^{-1}): 3552, 2982, 2936, 1603, 1526, 1506, 1486, 1447, 1364, 1344, 1224, 1175, 1160, 1075, 1030, 973, 856, 841, 768, 730, 699, 617; ^1H NMR (400 MHz, $CDCl_3$): δ 7.36–7.30 (m, 2H), 7.19–7.11 (m, 3H), 7.08–7.02 (m, 2H), 7.00–6.95 (m, 2H), 6.45 (s, 1H), 4.96 (s, 1H), 2.36 (s, 6H), 1.77 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 162.8 (d, $^1J_{C–F}$ = 247 Hz), 145.0, 134.0 (d, $^3J_{C–F}$ = 8.7 Hz), 134.2, 131.2, 128.3, 128.2, 127.8 (d, $^4J_{C–F}$ = 2.8 Hz), 126.7, 126.3, 115.2 (d, $^2J_{C–F}$ = 22.1 Hz), 112.8, 69.2, 36.6, 31.1; HRMS (DART/TOF) *m/z*: $[M – OH]^+$ calcd for $C_{21}H_{22}FN_2O_2S$, 385.1386; found, 385.1388.



2-(4-Fluorophenyl)-5-isopropyl-*N*,*N*-dimethyl-3-phenyl-1*H*-pyrrole-1-sulfonamide (S3)

A flame-dried 20-mL Schlenk tube equipped with a Teflon-coated magnetic stirring bar and a rubber septum was charged with diarylated pyrrole **11** (483.0 mg, 1.20 mmol, 1.0 equiv) and anhydrous CH_2Cl_2 (6.0 mL). The solution was cooled to 0 °C. Triethylsilane (0.95 mL, 6.0 mmol, 5.0 equiv) was added to the Schlenk tube. After stirring at 0 °C for 5 min, trifluoroacetic acid (275 μL, 3.60 mmol, 3.0 equiv) was added to the solution. After stirring at 0 °C for 2 h, the reaction mixture was treated with saturated aqueous sodium hydrogen carbonate (6 mL). After being partitioned, the aqueous layer was extracted with CH_2Cl_2 (6 mL)

three times. The combined organic extracts were washed with brine (10 mL), dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude product, which was purified by silica gel column chromatography (hexane/CH_2Cl_2 = 7:3) to provide the title compound as a colorless solid (421.6 mg, 1.09 mmol, 91%). R_f = 0.33 (hexane/CH_2Cl_2 = 1:1); mp 155–156 °C; IR (ATR, cm^{-1}): 2976, 2926, 1602, 1534, 1509, 1462, 1417, 1382, 1267, 1225, 1173, 1158, 1135, 1090, 1063, 960, 833, 816, 767, 728, 716, 697, 633; ^1H NMR (400 MHz, $CDCl_3$): δ 7.35–7.29 (m, 2H), 7.18–7.09 (m, 3H), 7.05–6.99 (m, 4H), 6.28 (d, 1H, J = 1.2 Hz), 3.62 (sept, 1H, J = 6.5 Hz), 2.46 (s, 6H), 1.34 (d, 6H, J = 6.5 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 162.7 (d, $^1J_{C–F}$ = 247 Hz), 146.2, 134.9, 133.9 (d, $^3J_{C–F}$ = 8.7 Hz), 129.9, 128.8 (d, $^4J_{C–F}$ = 2.9 Hz), 128.2, 126.5, 126.4, 115.0 (d, $^2J_{C–F}$ = 21.0 Hz), 109.6, 37.0, 27.7, 24.0 (one aromatic carbon signal is missing because of overlapping); HRMS (DART/TOF) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{24}FN_2O_2S$, 387.1543; found, 387.1557.



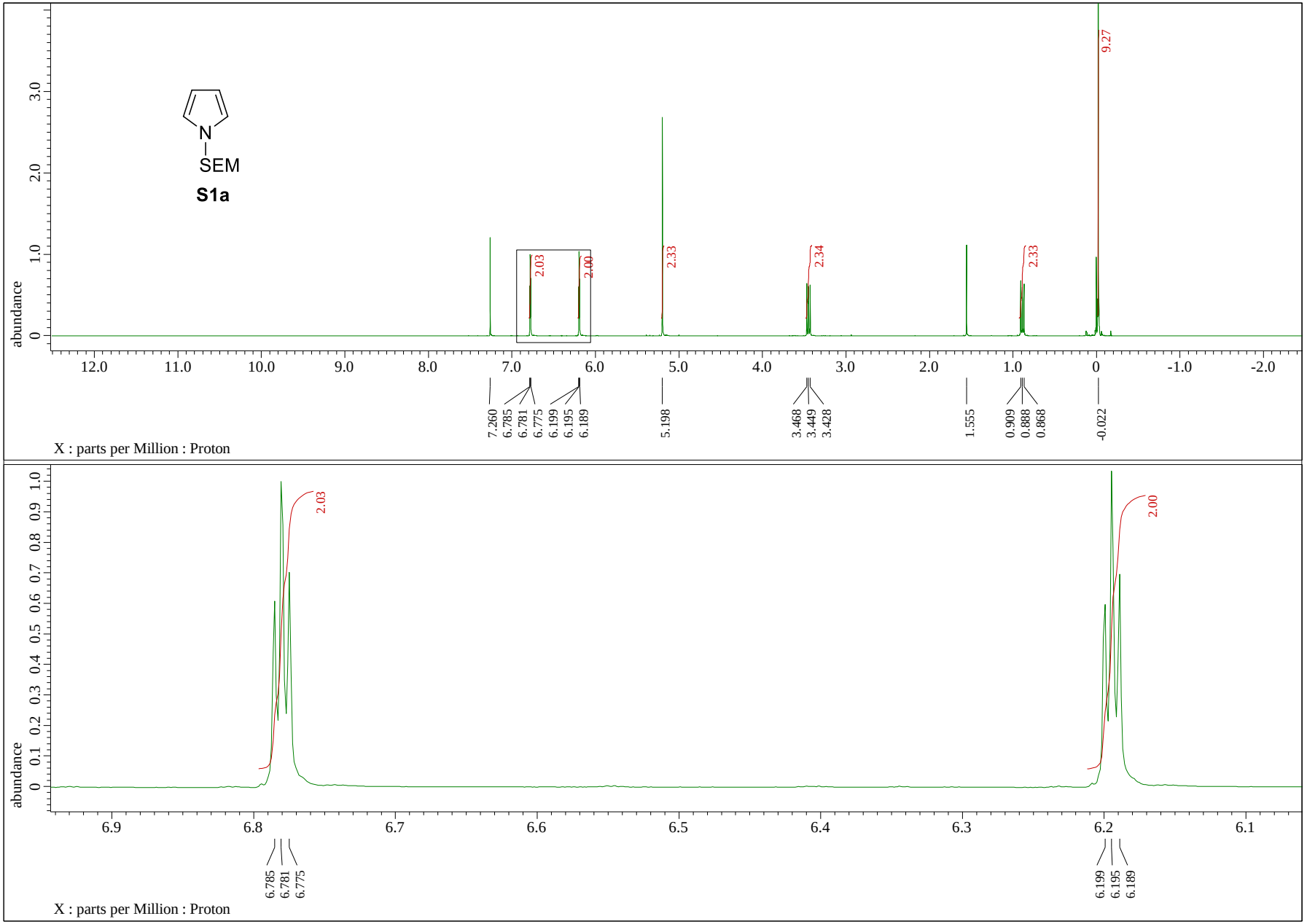
S3 **12**

2-(4-Fluorophenyl)-5-isopropyl-3-phenyl-1*H*-pyrrole (12)

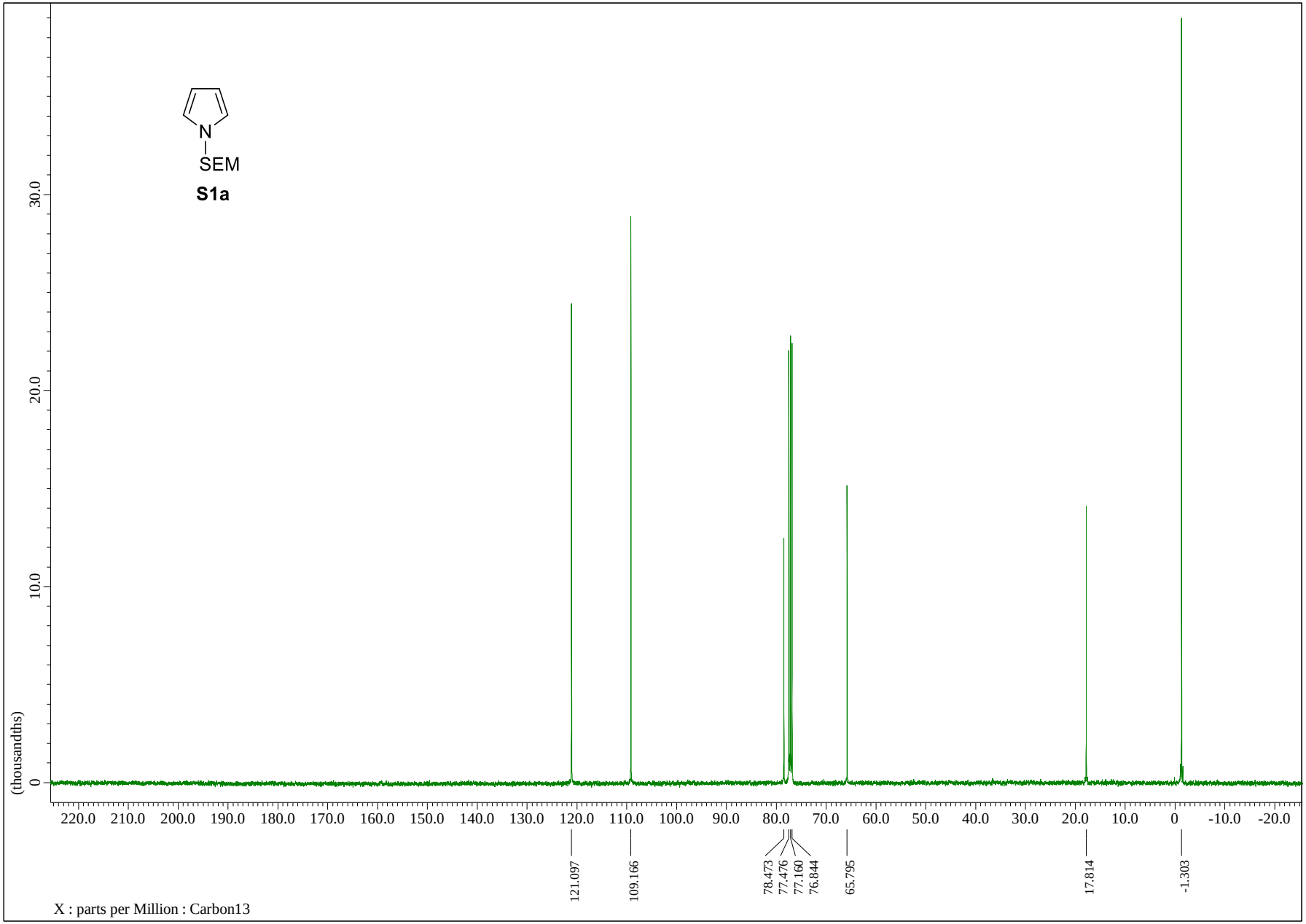
A flame-dried 50-mL Schlenk tube equipped with a Teflon-coated magnetic stirring bar and a rubber septum was charged with naphthalene (319.9 mg, 2.50 mmol, 5.0 equiv) and lithium wire (69.1 mg, 9.96 mmol, 20 equiv). After the addition of THF (10.0 mL), the mixture was cooled to –78 °C and diarylated pyrrole **S3** (194.0 mg, 0.502 mmol, 1.0 equiv) was added to the Schlenk tube. After stirring at –78 °C for 5 h, the reaction mixture was treated with water (10 mL). After being partitioned, the aqueous layer was extracted with CH_2Cl_2 (10 mL) three times. The combined organic extracts were washed with brine (20 mL), dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude product. The crude product was purified by silica gel column chromatography (hexane, then hexane/ethyl acetate = 10:1) to provide the title compound as a colorless solid (142.0 mg, 0.508 mmol, quant), whose ^1H NMR and ^{13}C NMR spectral data were identical to those reported in the literature.[11] R_f = 0.32 (hexane/ethyl acetate = 10:1); mp 85–87 °C; IR (ATR, cm^{-1}): 3455, 3424, 3064, 2964, 2930, 2871, 1603, 1524, 1509, 1437, 1338, 1223, 1158, 1094, 1072, 954, 838, 813, 764, 700; ^1H NMR (400 MHz, $CDCl_3$): δ 7.90 (br s, 1H), 7.34–7.22 (m, 6H), 7.19–7.14 (m, 1H), 7.02–6.95 (m, 2H), 6.12 (d, 1H, J = 3.2 Hz), 2.98 (sept, 1H, J = 6.9 Hz), 1.33 (d, 6H, J = 6.9 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 161.8 (d, $^1J_{C–F}$ = 244 Hz), 139.5, 136.8, 129.9 (d, $^4J_{C–F}$ = 2.9 Hz), 129.2 (d, $^3J_{C–F}$ = 7.6 Hz), 128.4, 125.74, 125.69, 121.8, 115.7 (d, $^2J_{C–F}$ = 22.0 Hz), 106.1, 27.2, 22.7 (one aromatic carbon signal is missing because of overlapping); HRMS (DART/TOF) *m/z*: $[M + H]^+$ calcd for $C_{19}H_{19}FN$, 280.1502; found, 280.1511.

11 A. Kondoh, A. Iino, S. Ishikawa, T. Aoki and M. Terada, *Chem.Eur. J.*, 2018, **24**, 15246–15253.

^{1}H NMR (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



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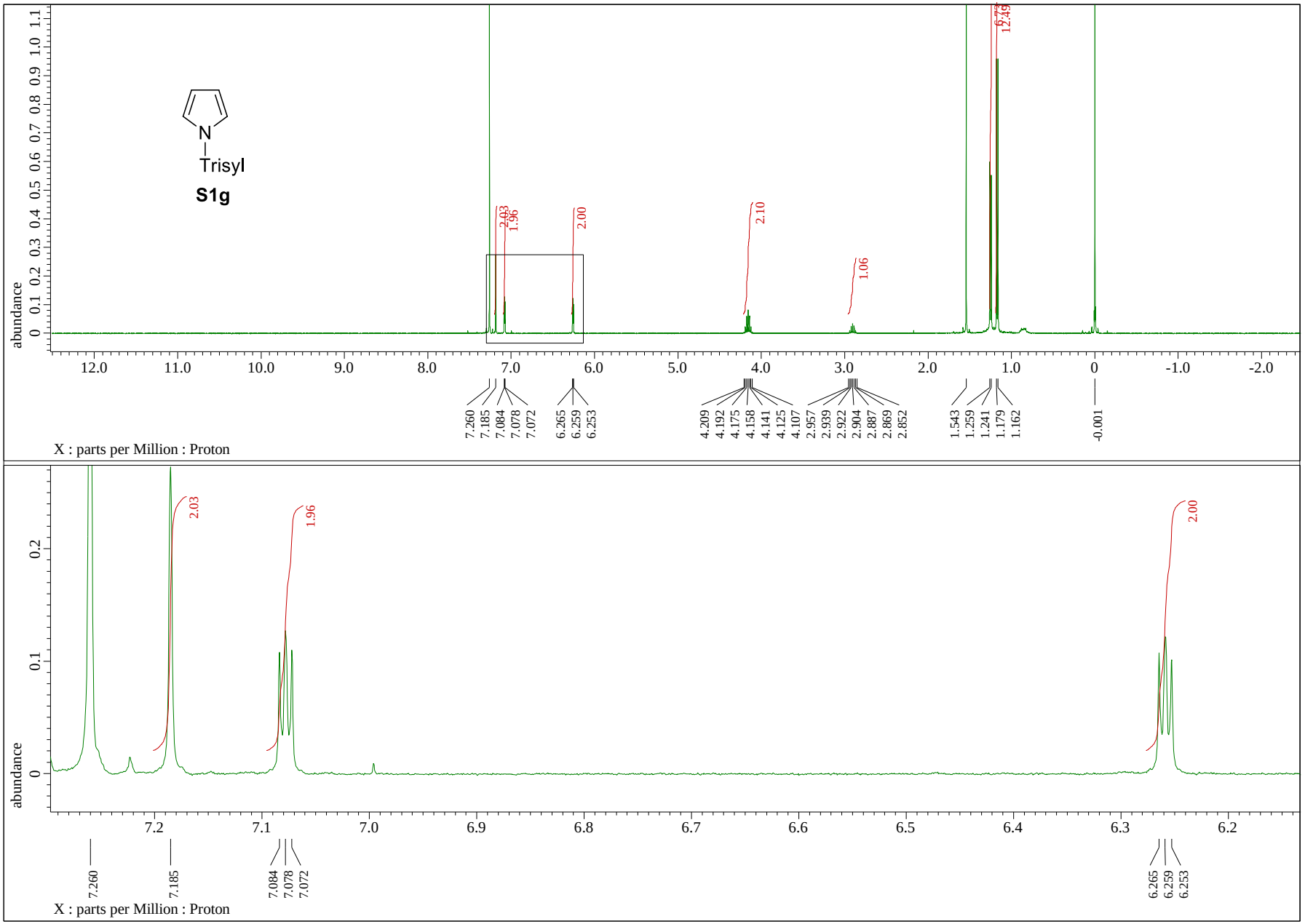

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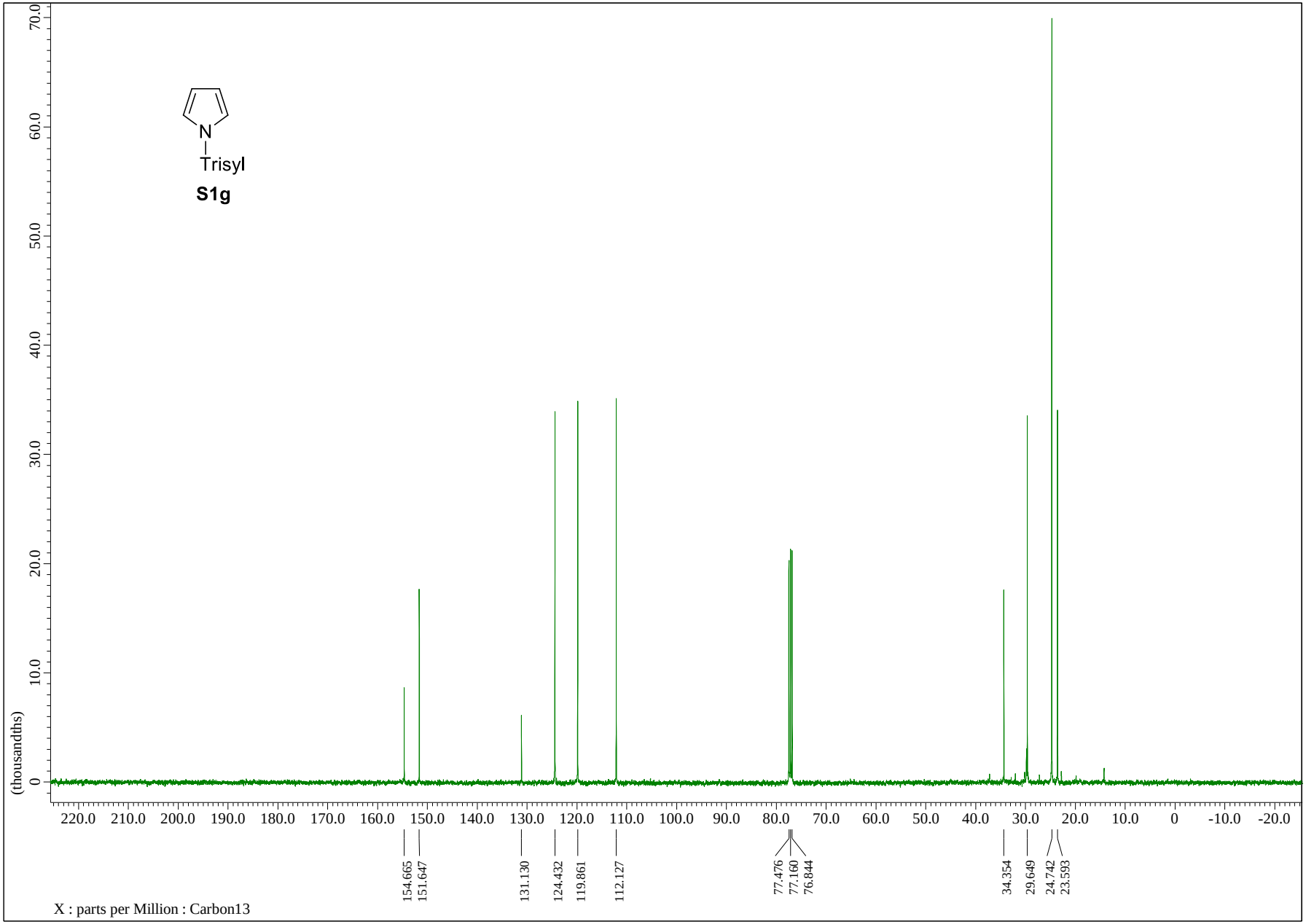

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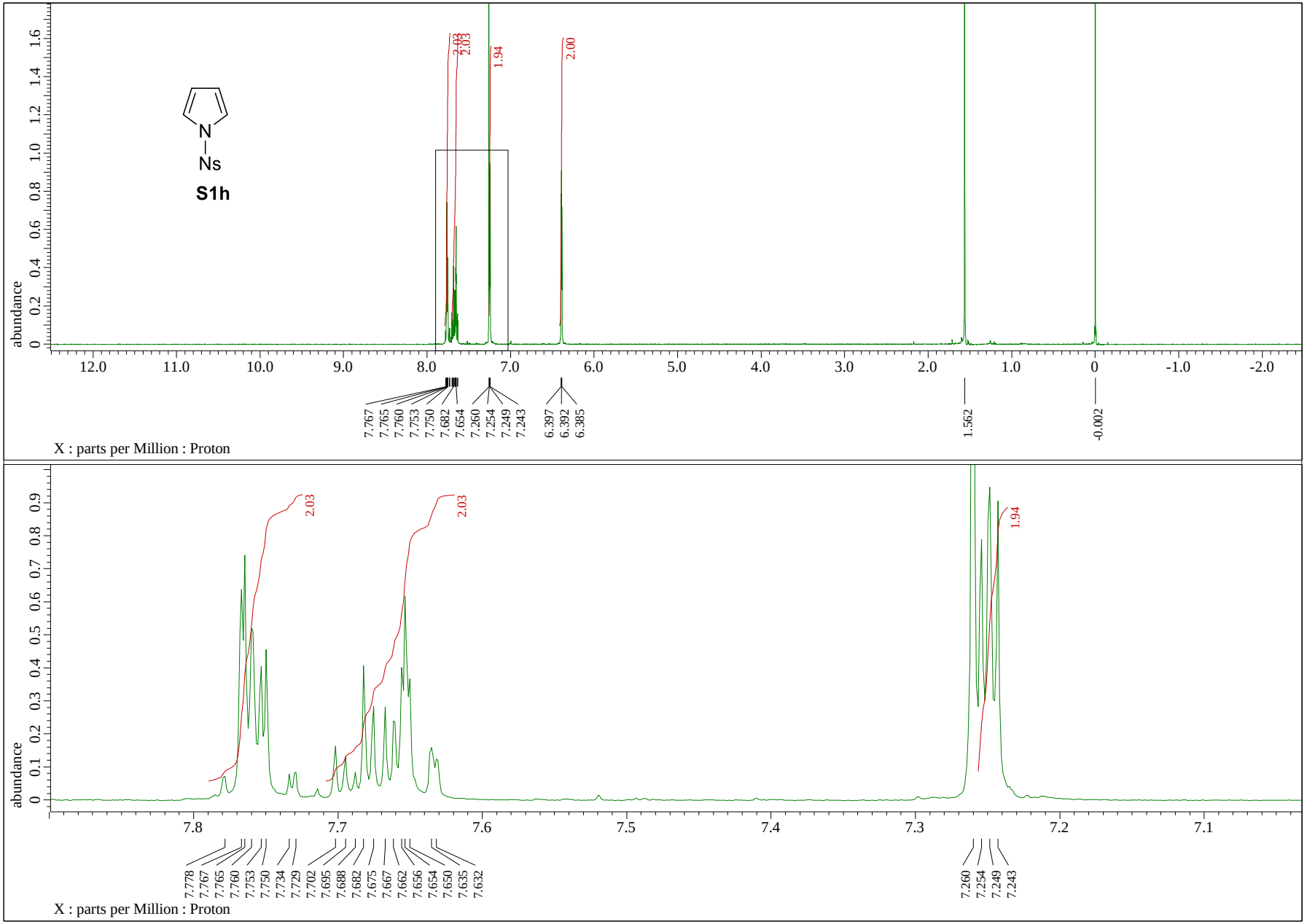

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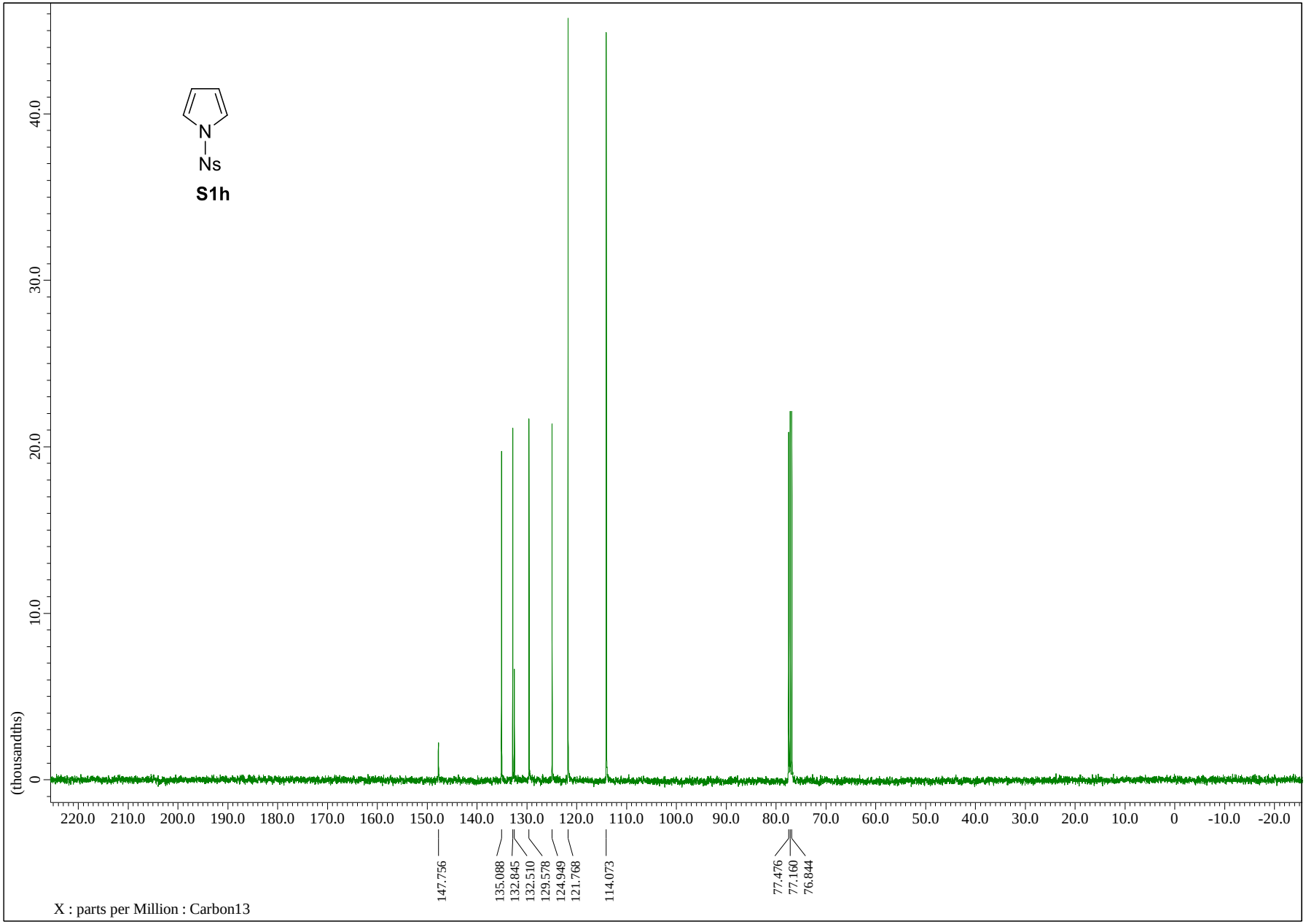

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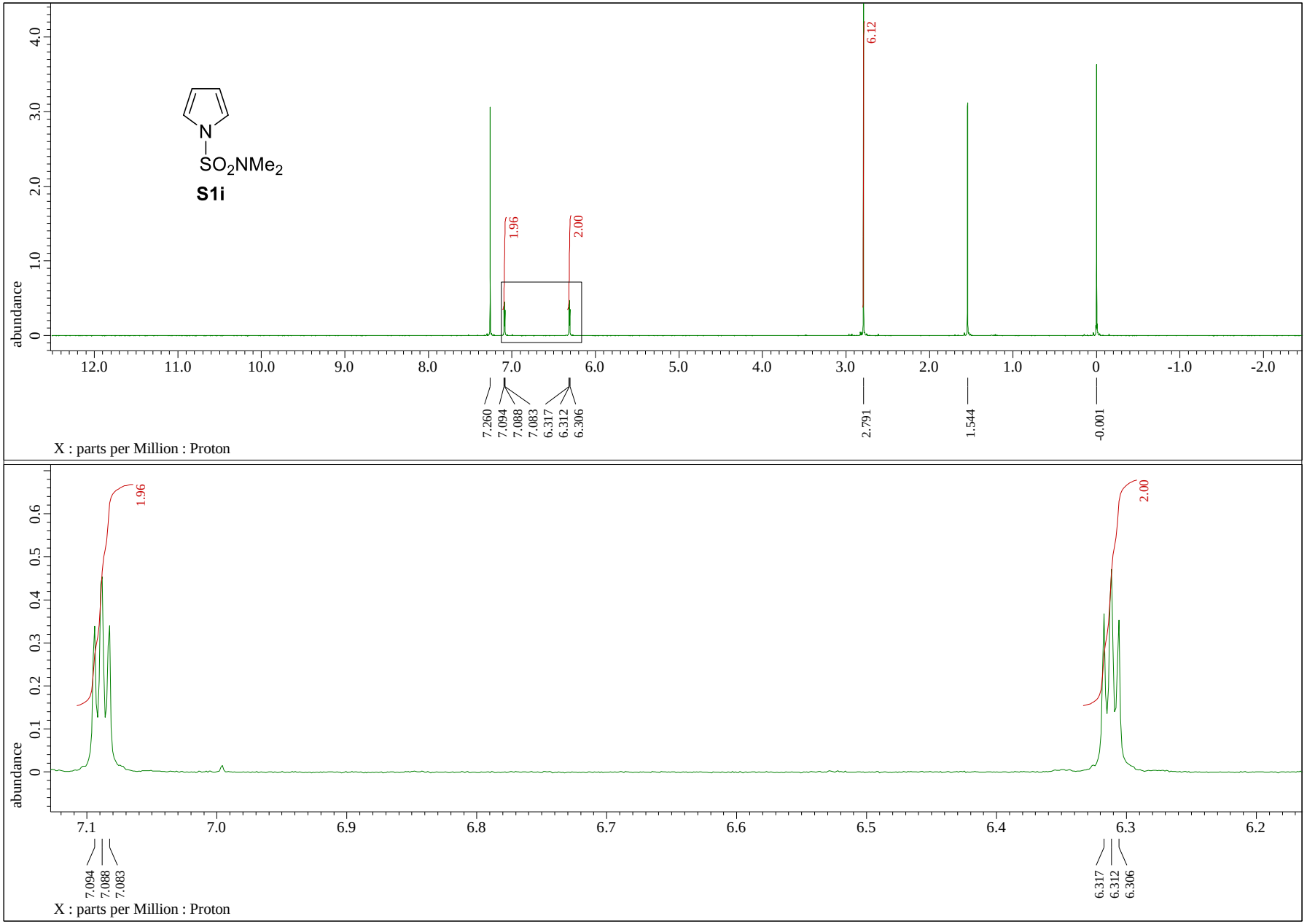

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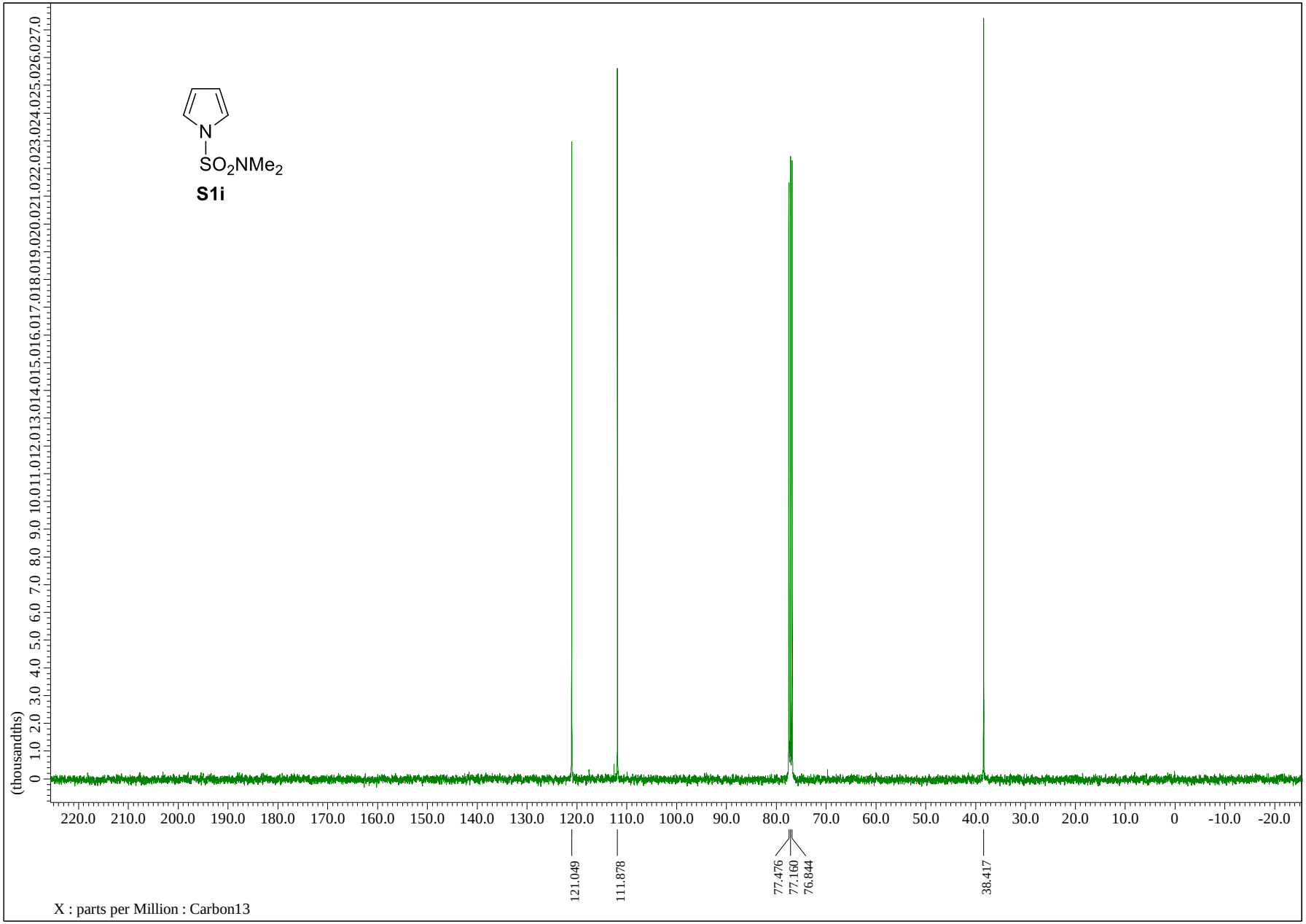

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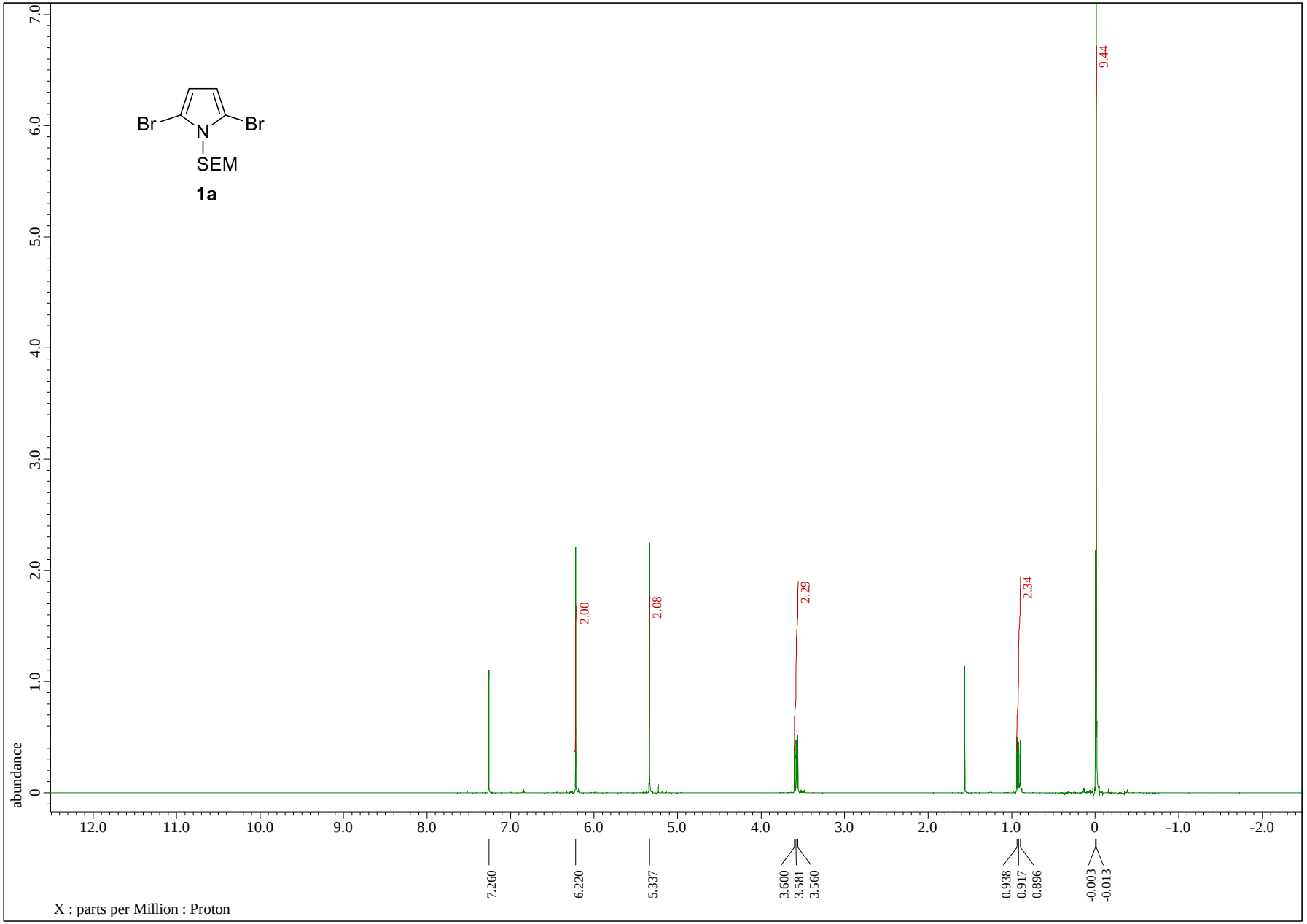

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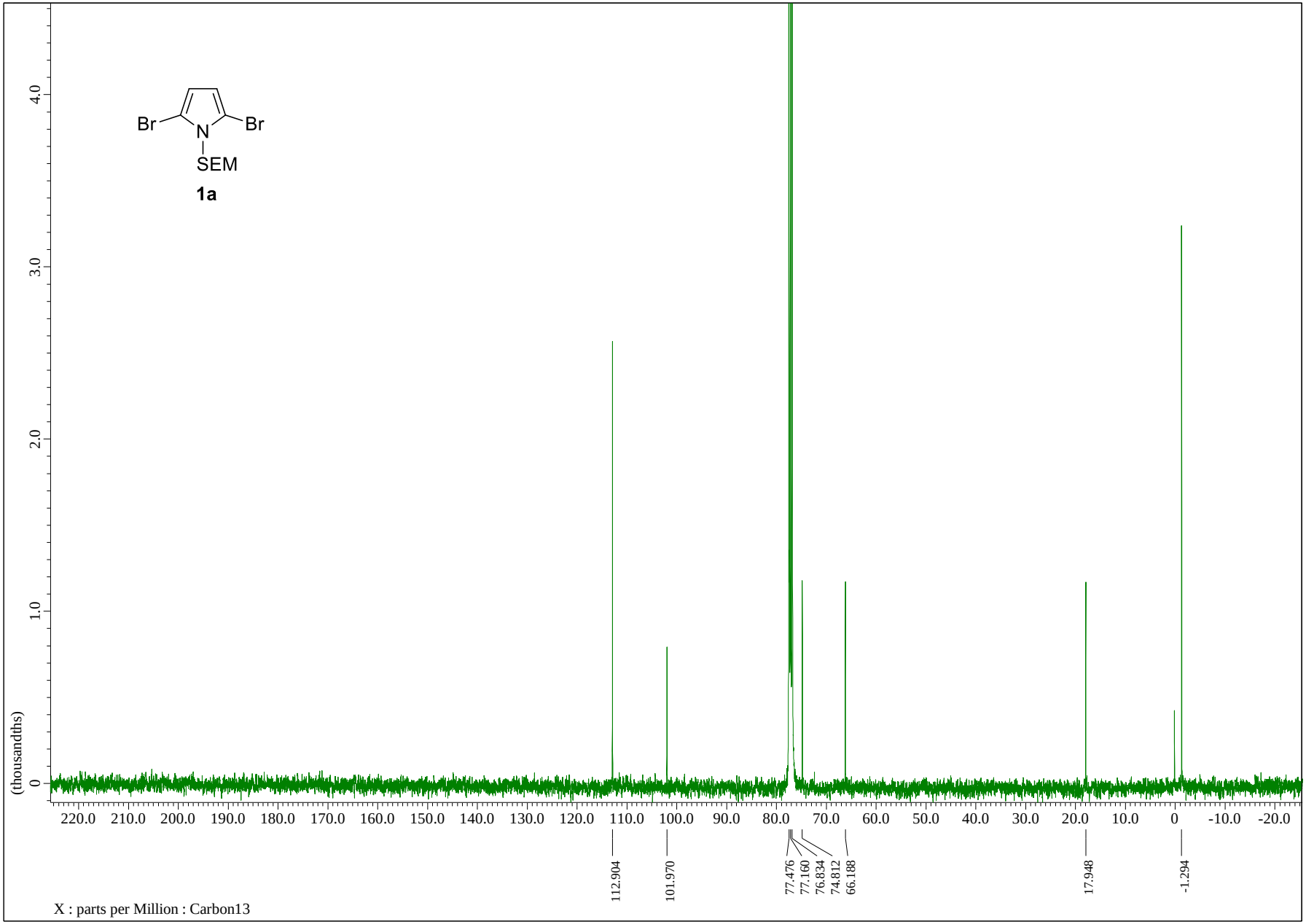

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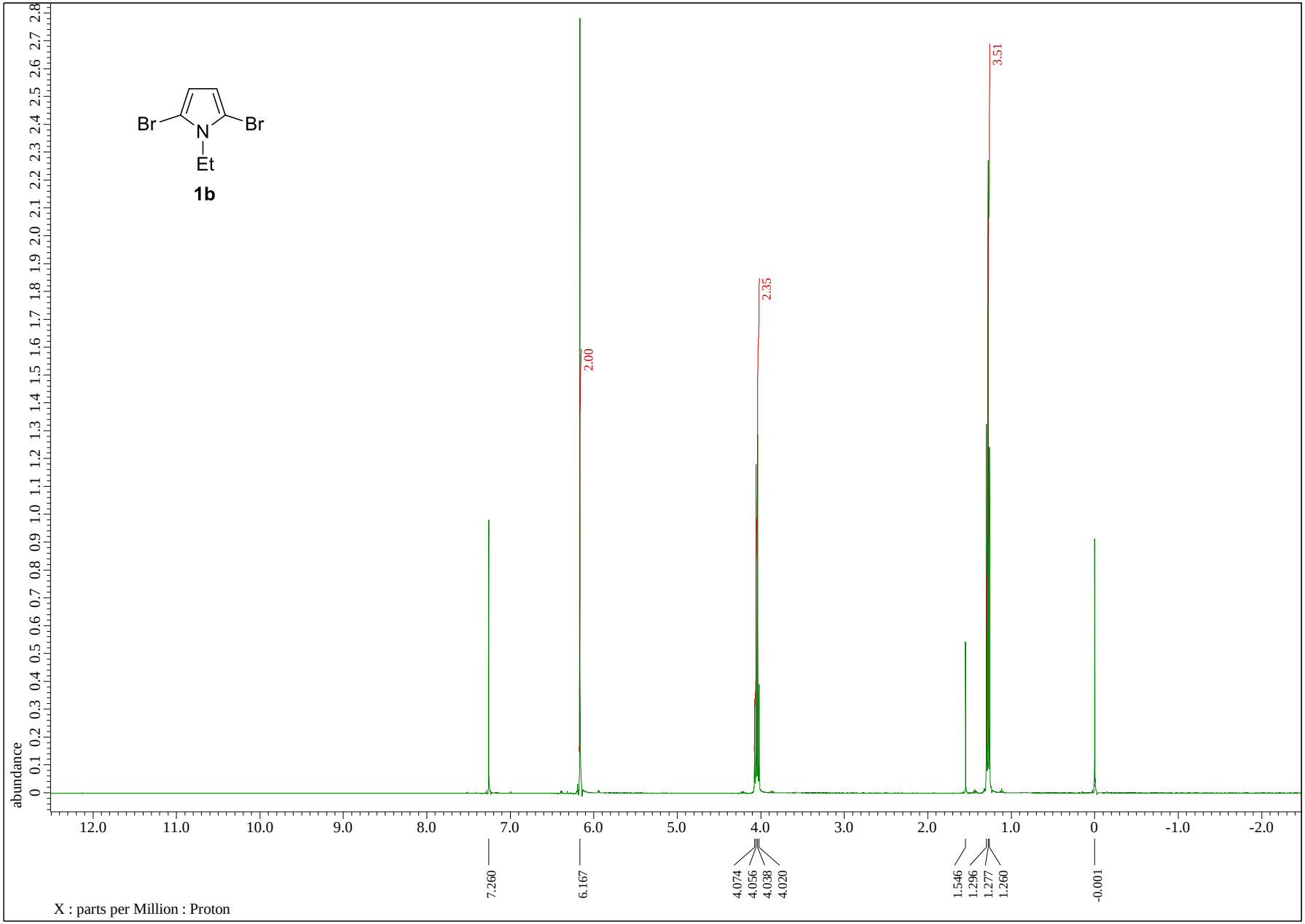

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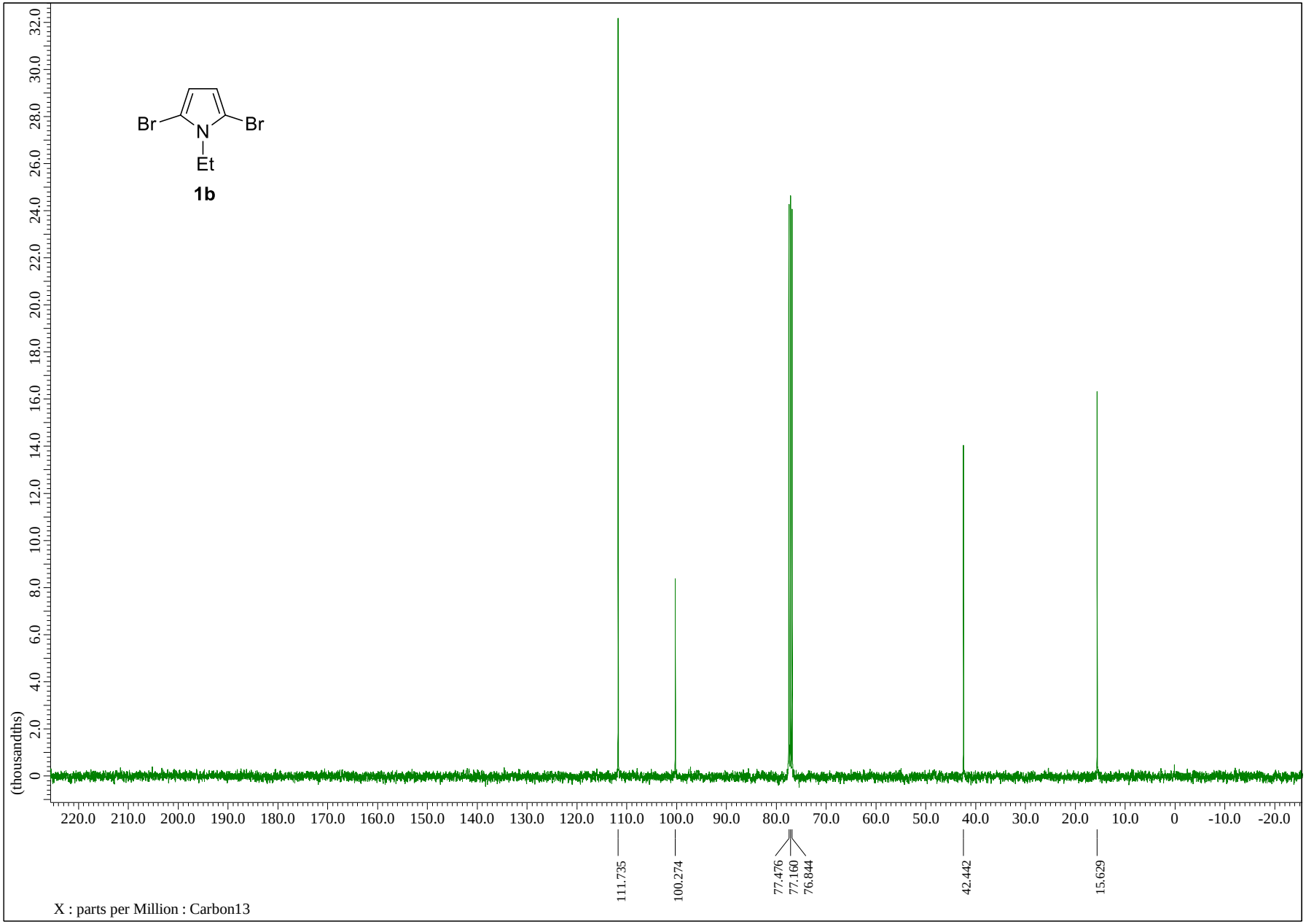

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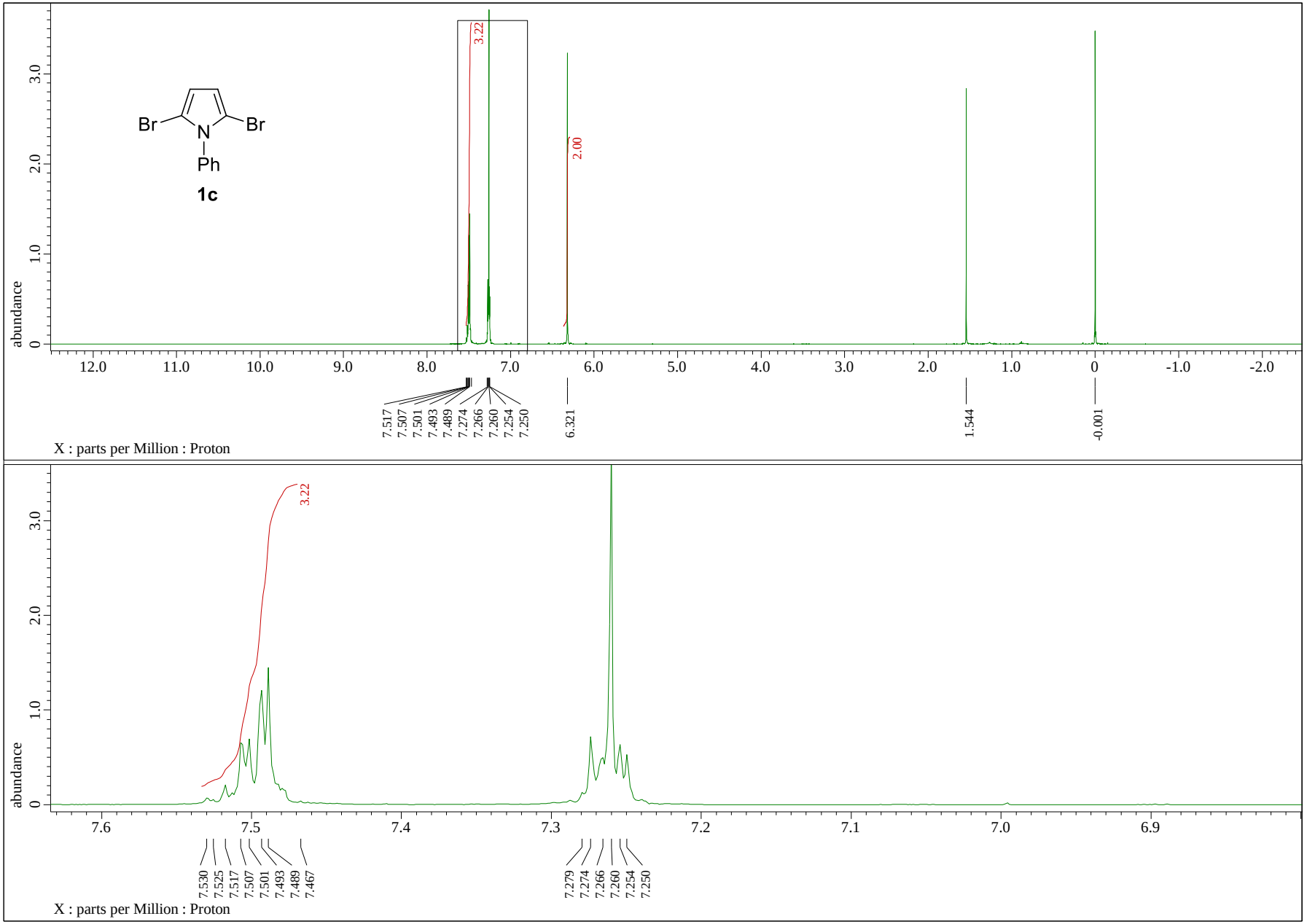

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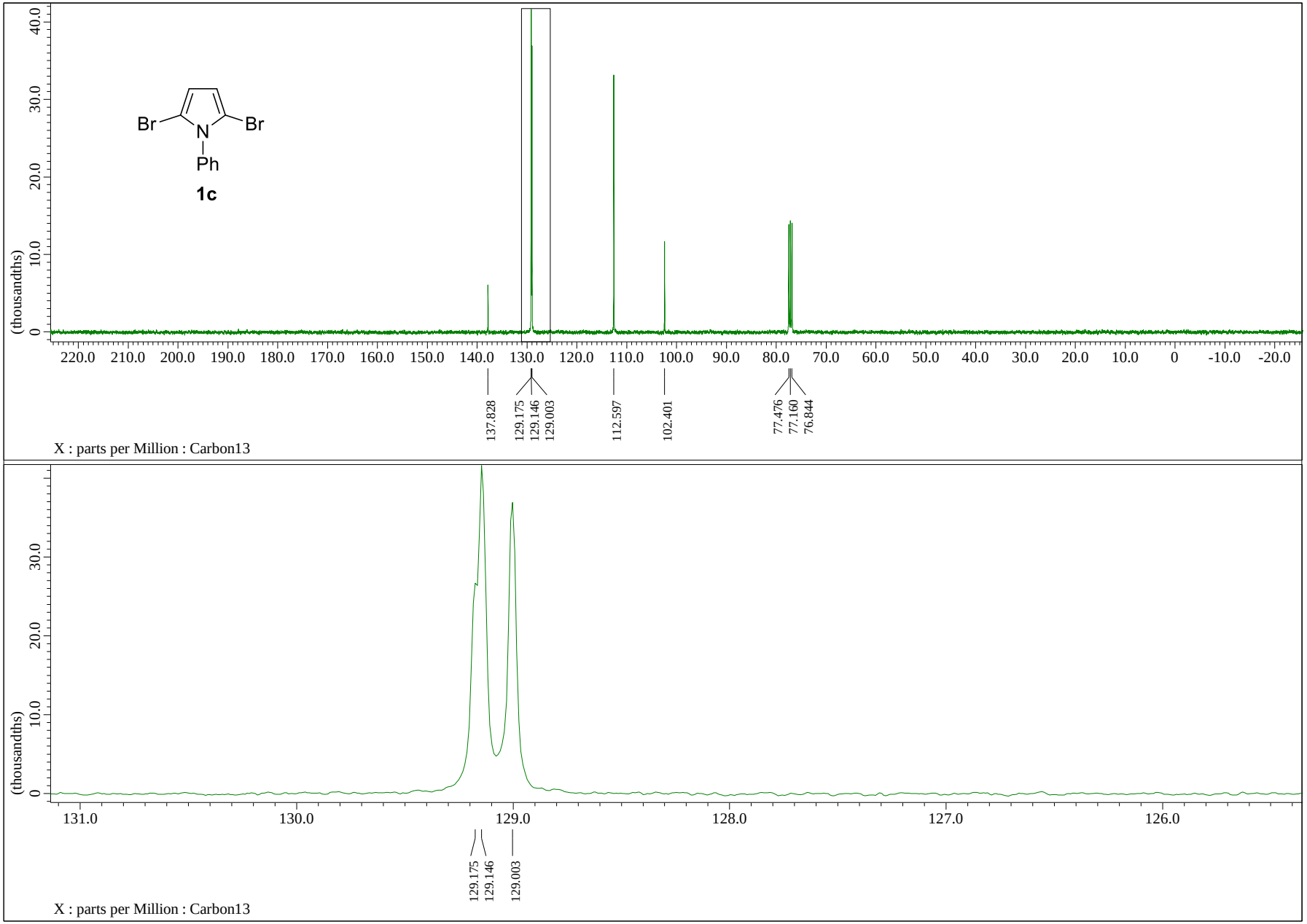

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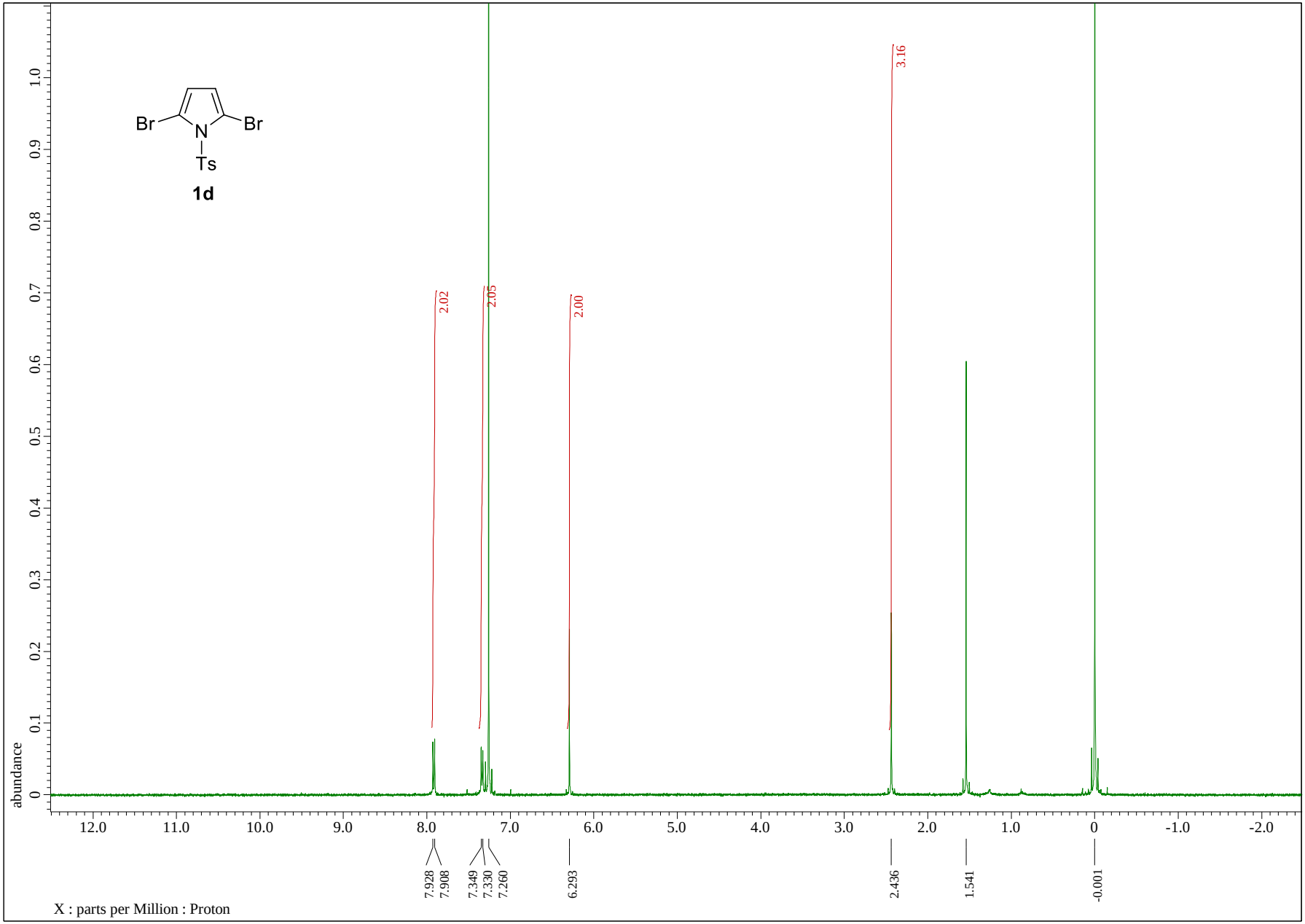

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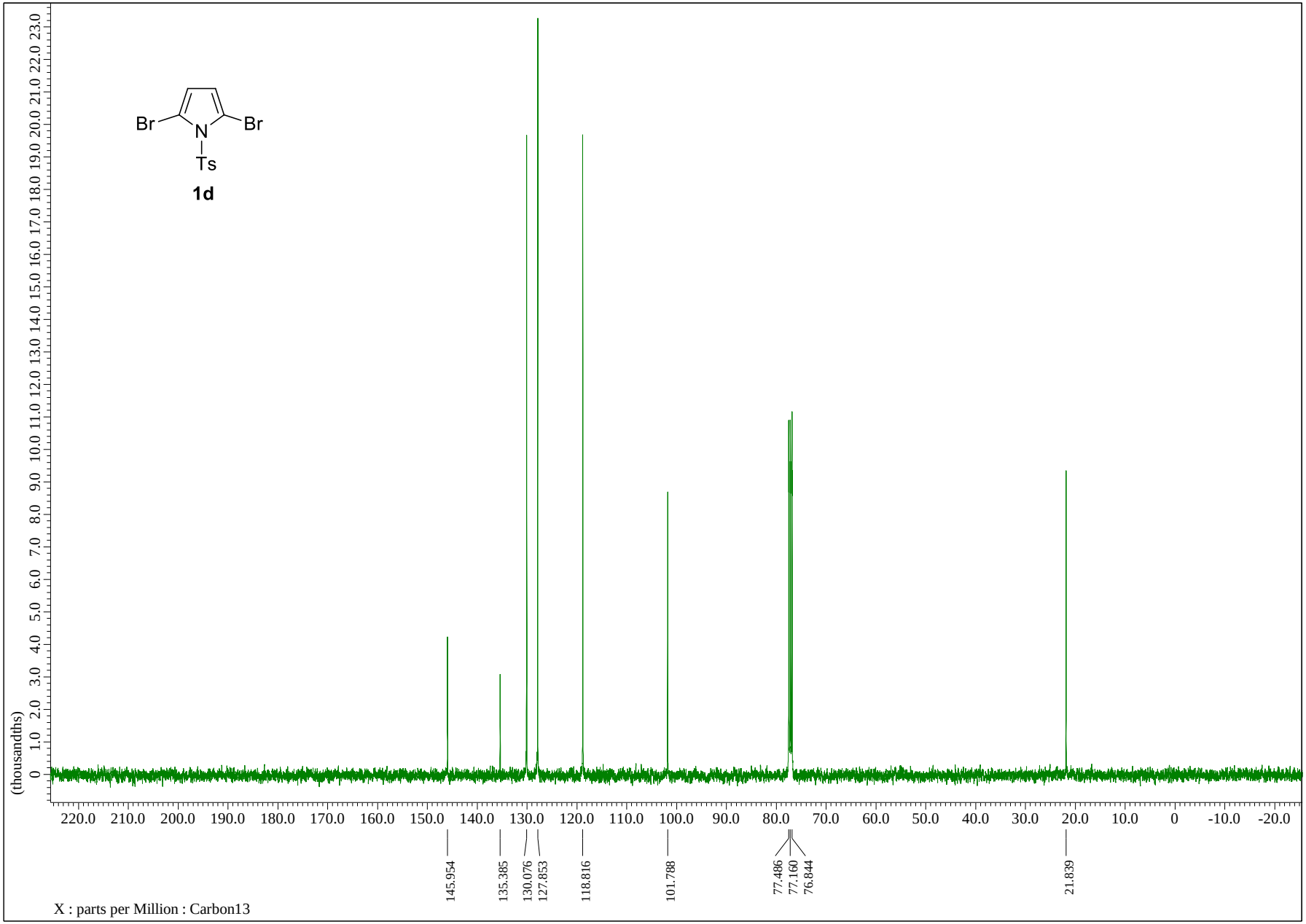

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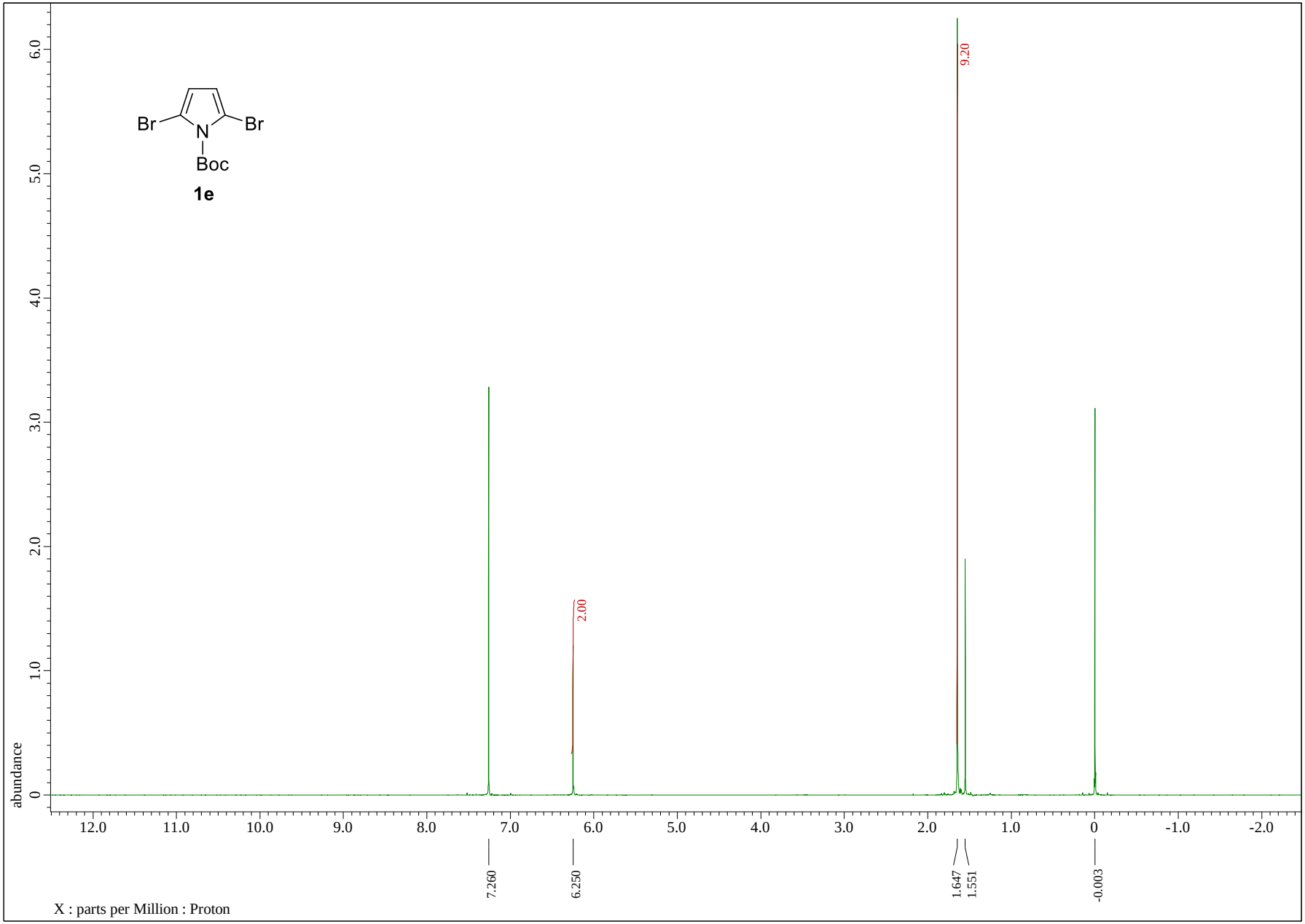

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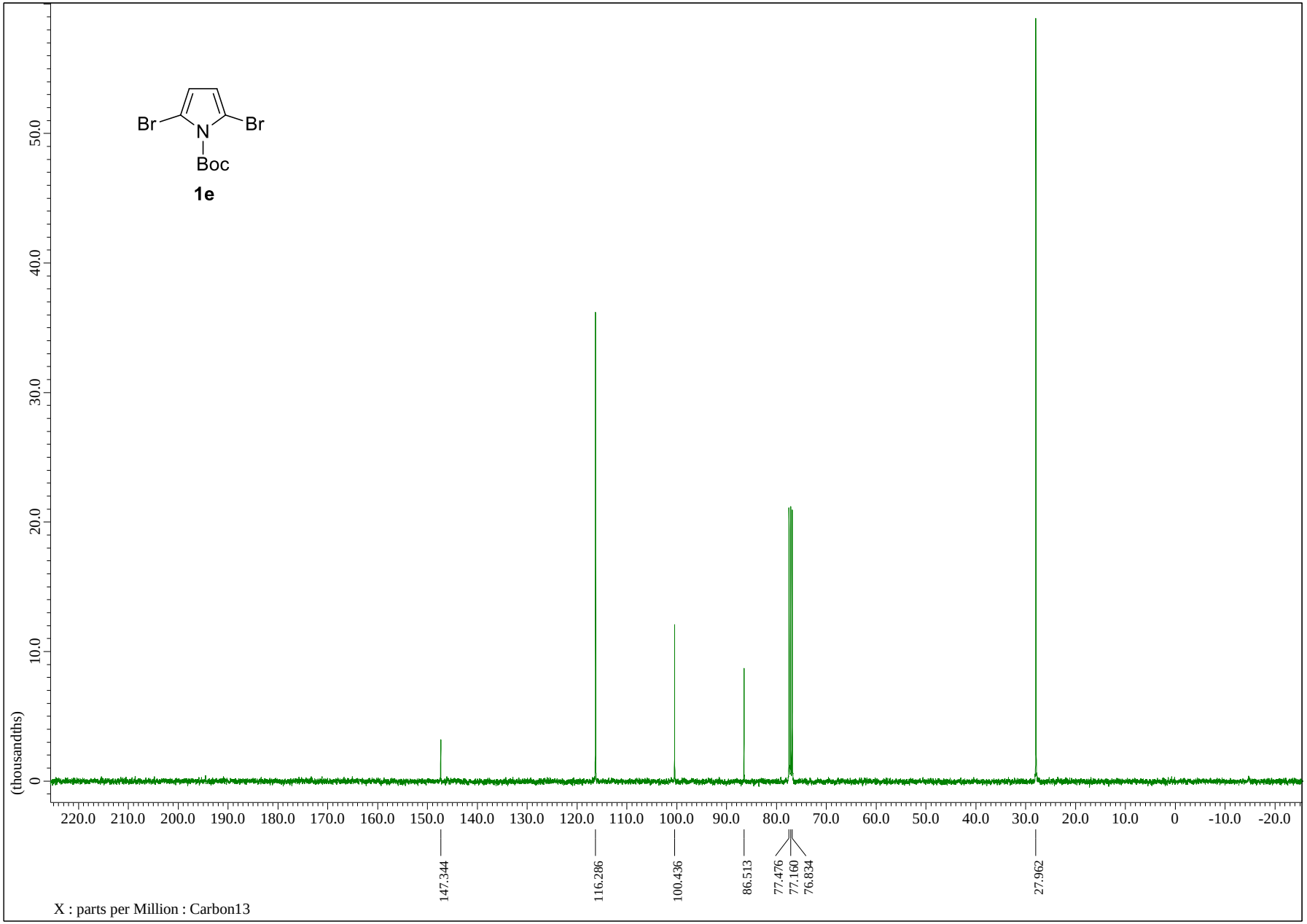

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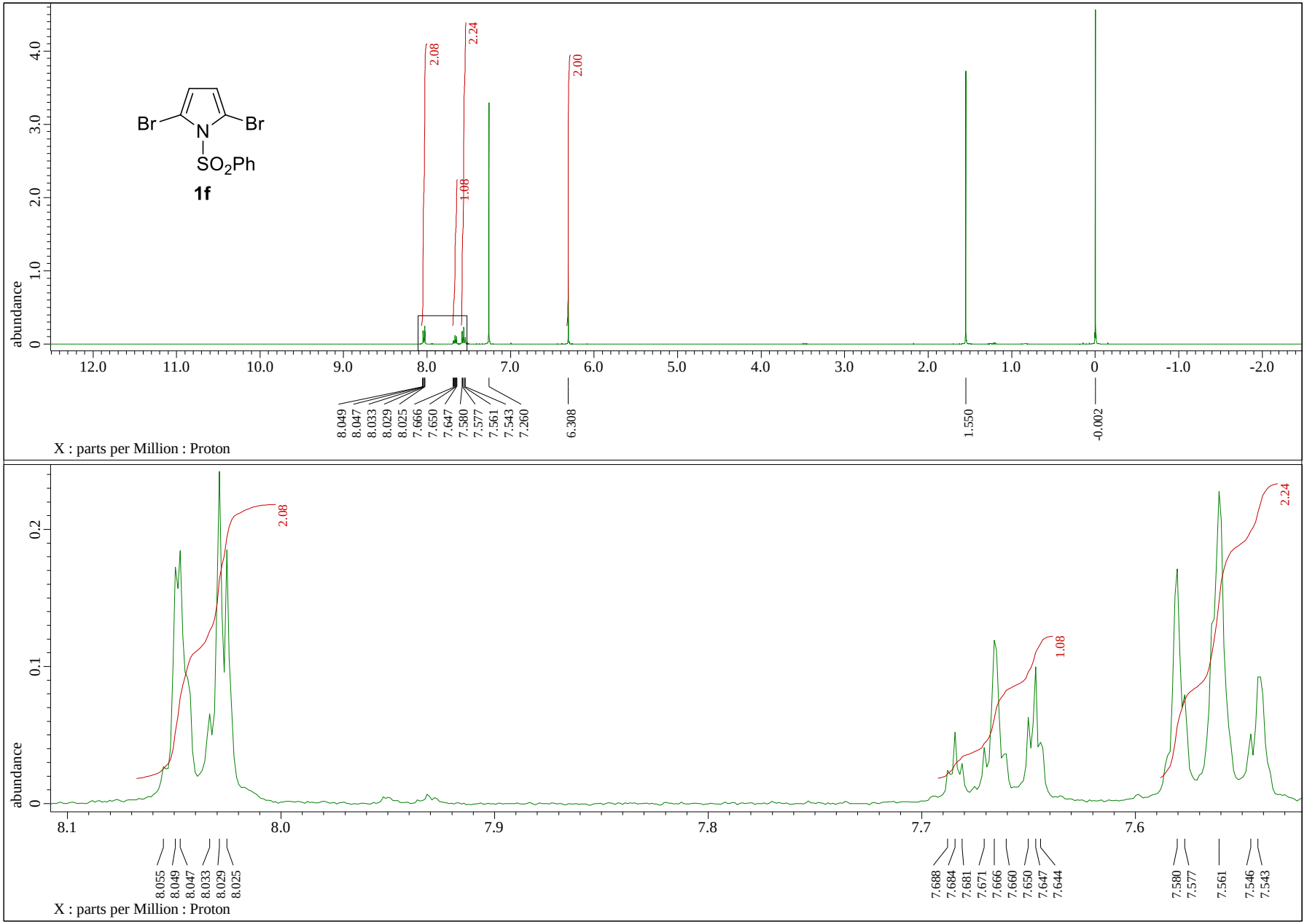

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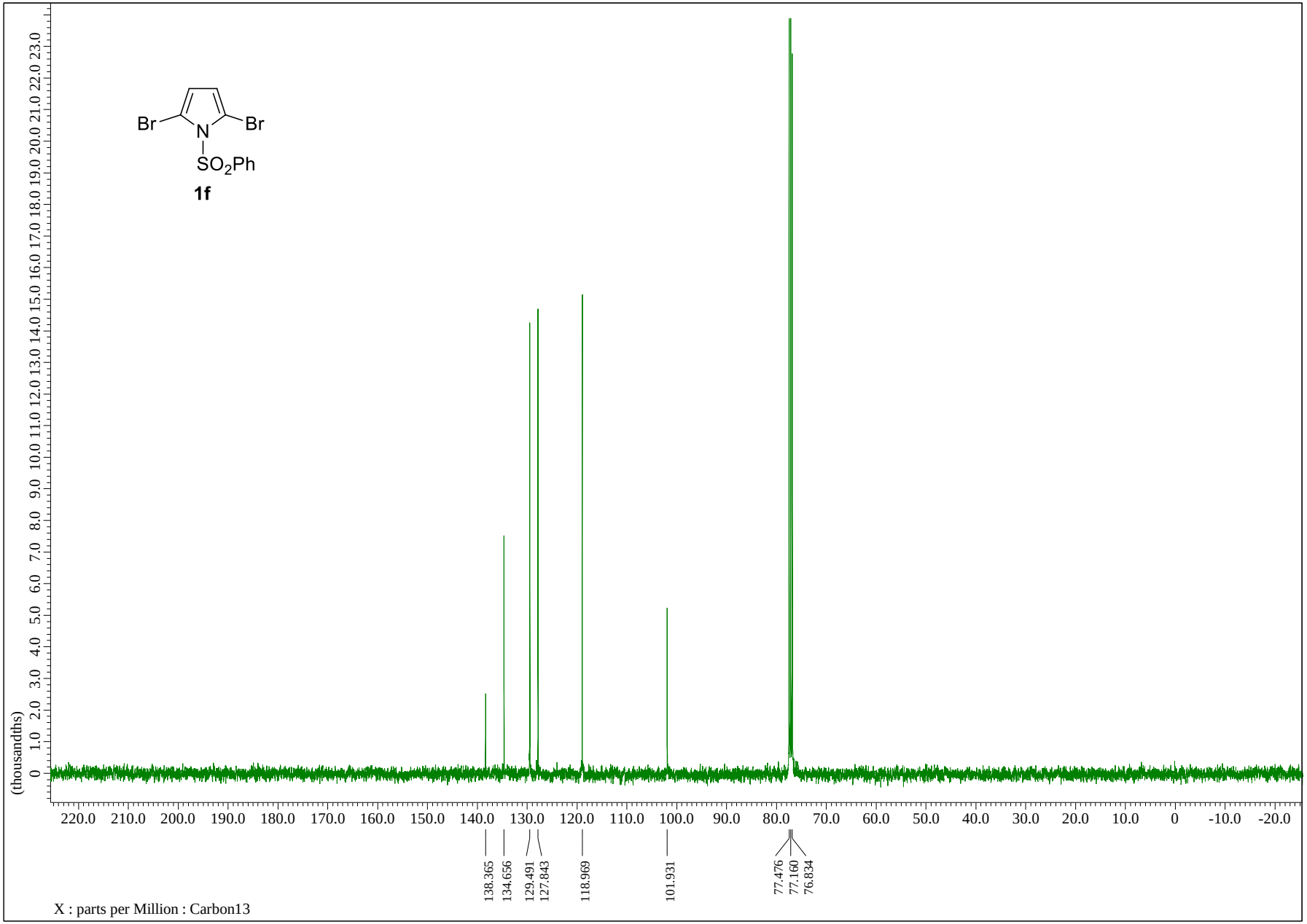

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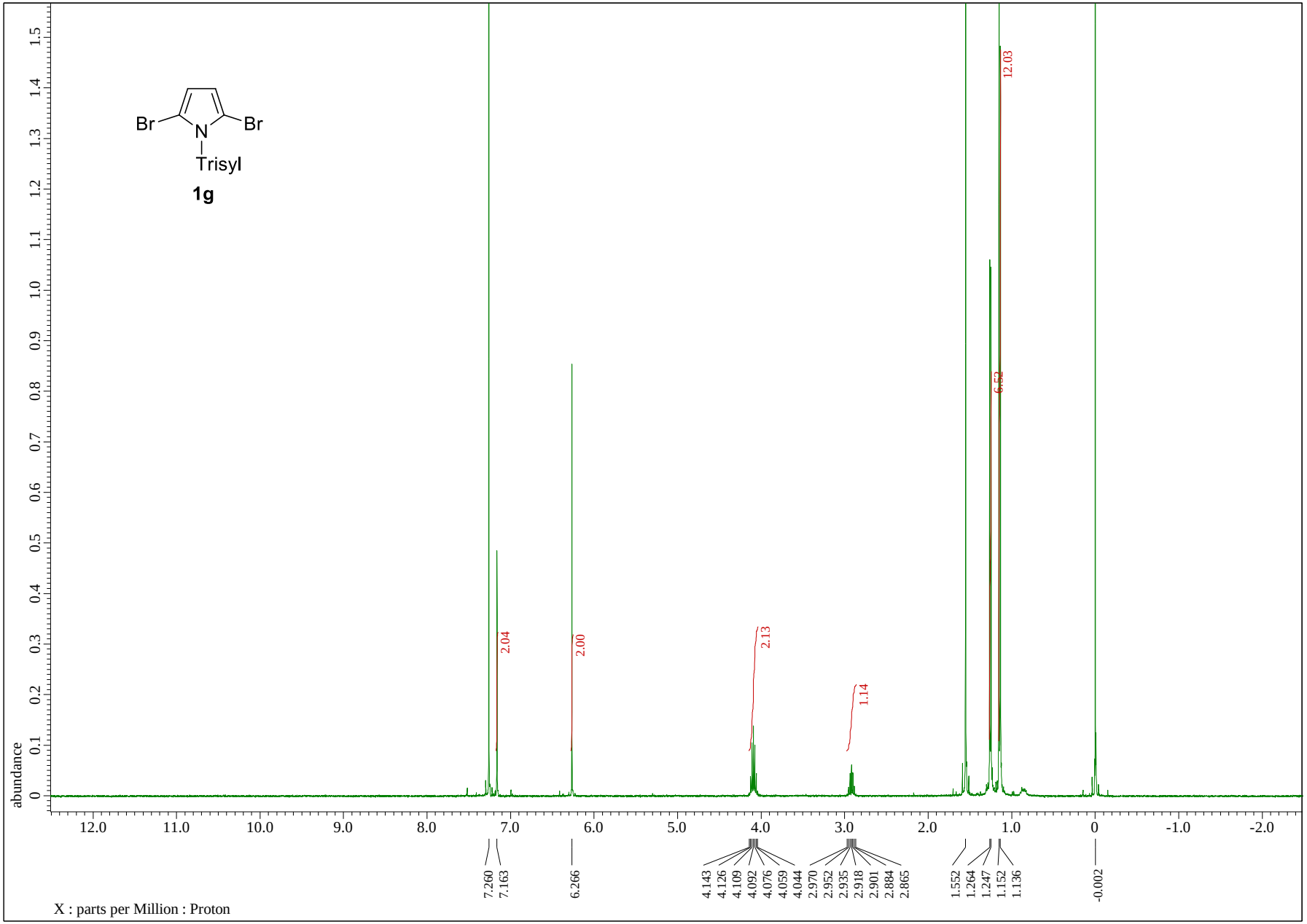

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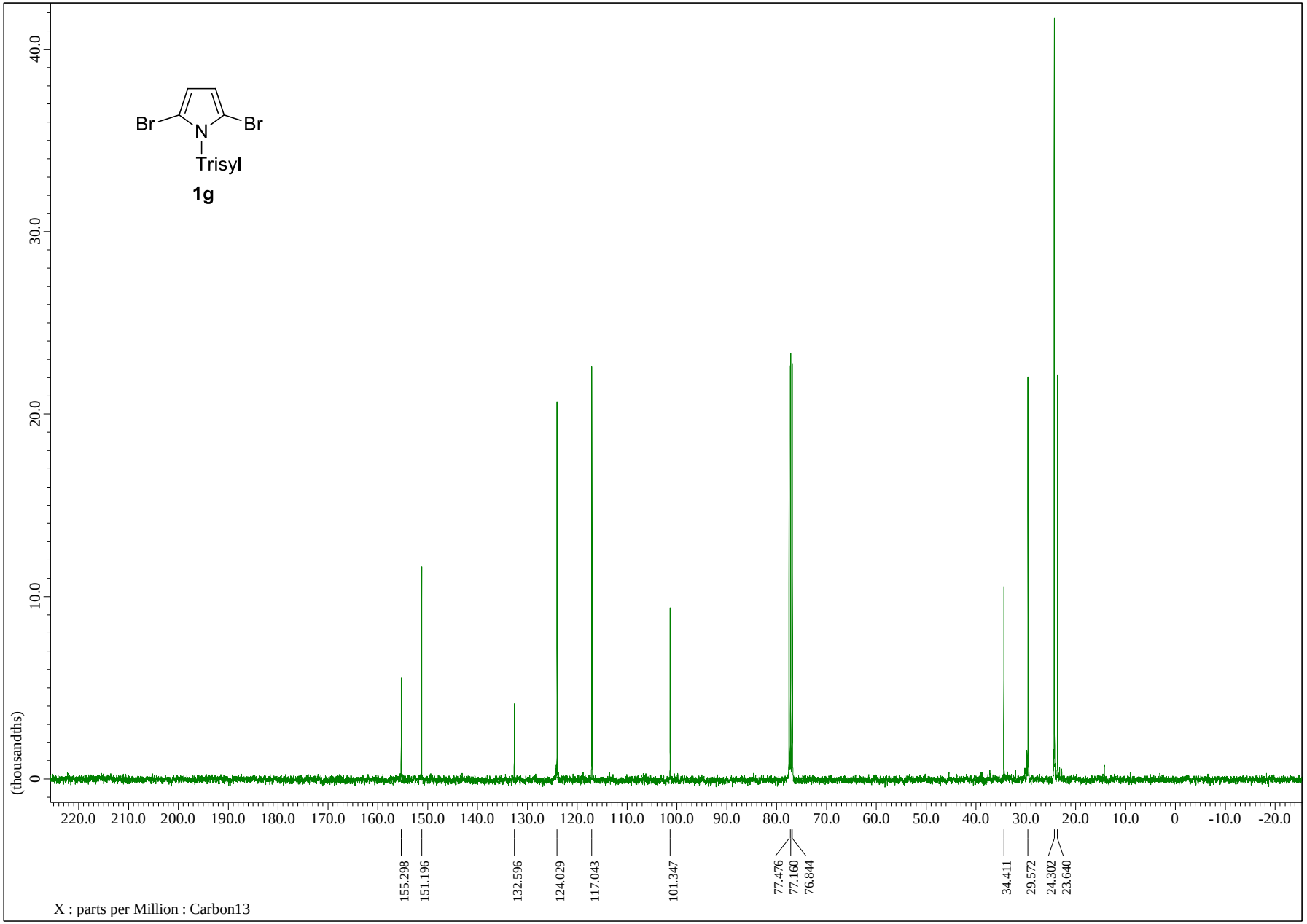

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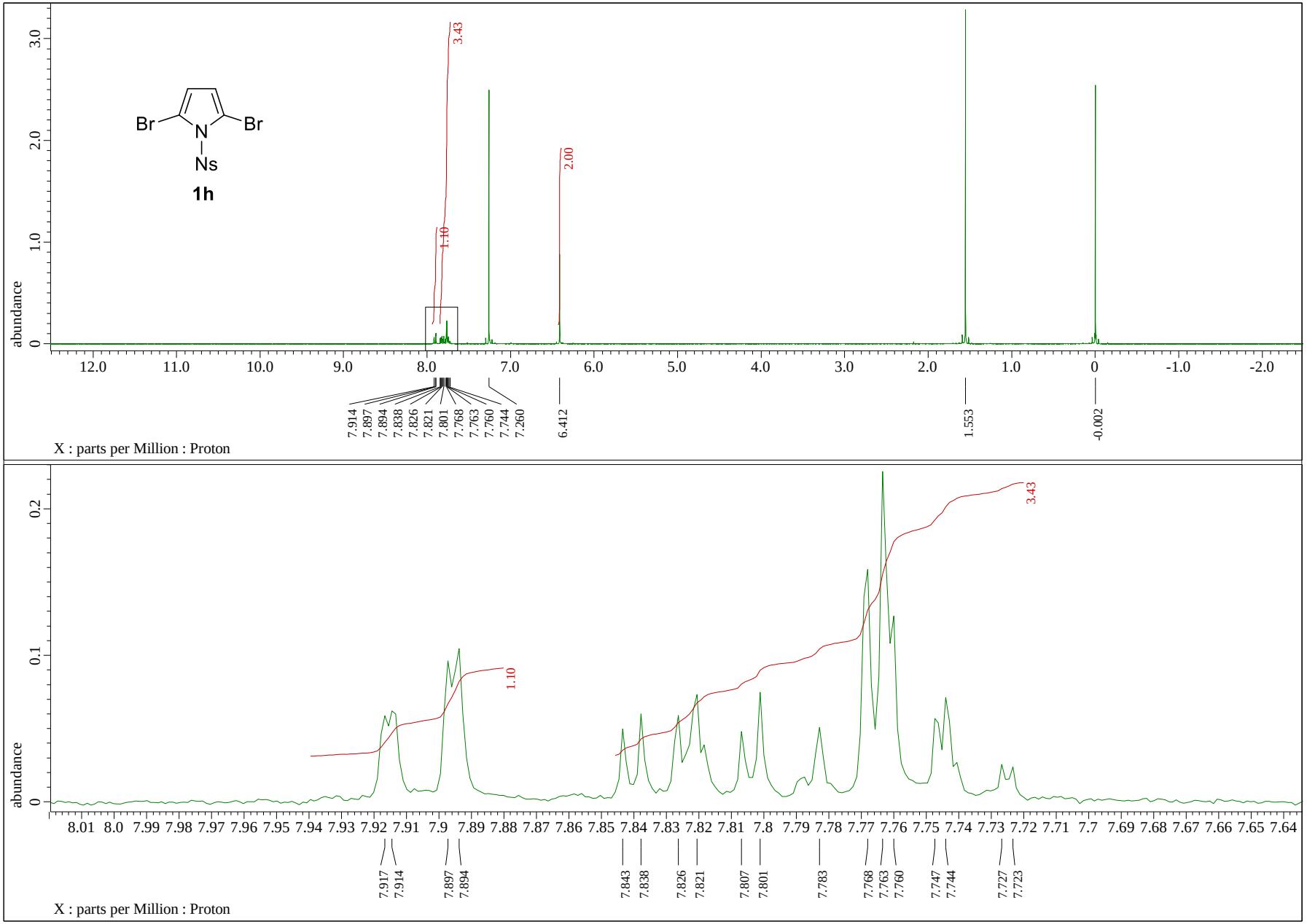

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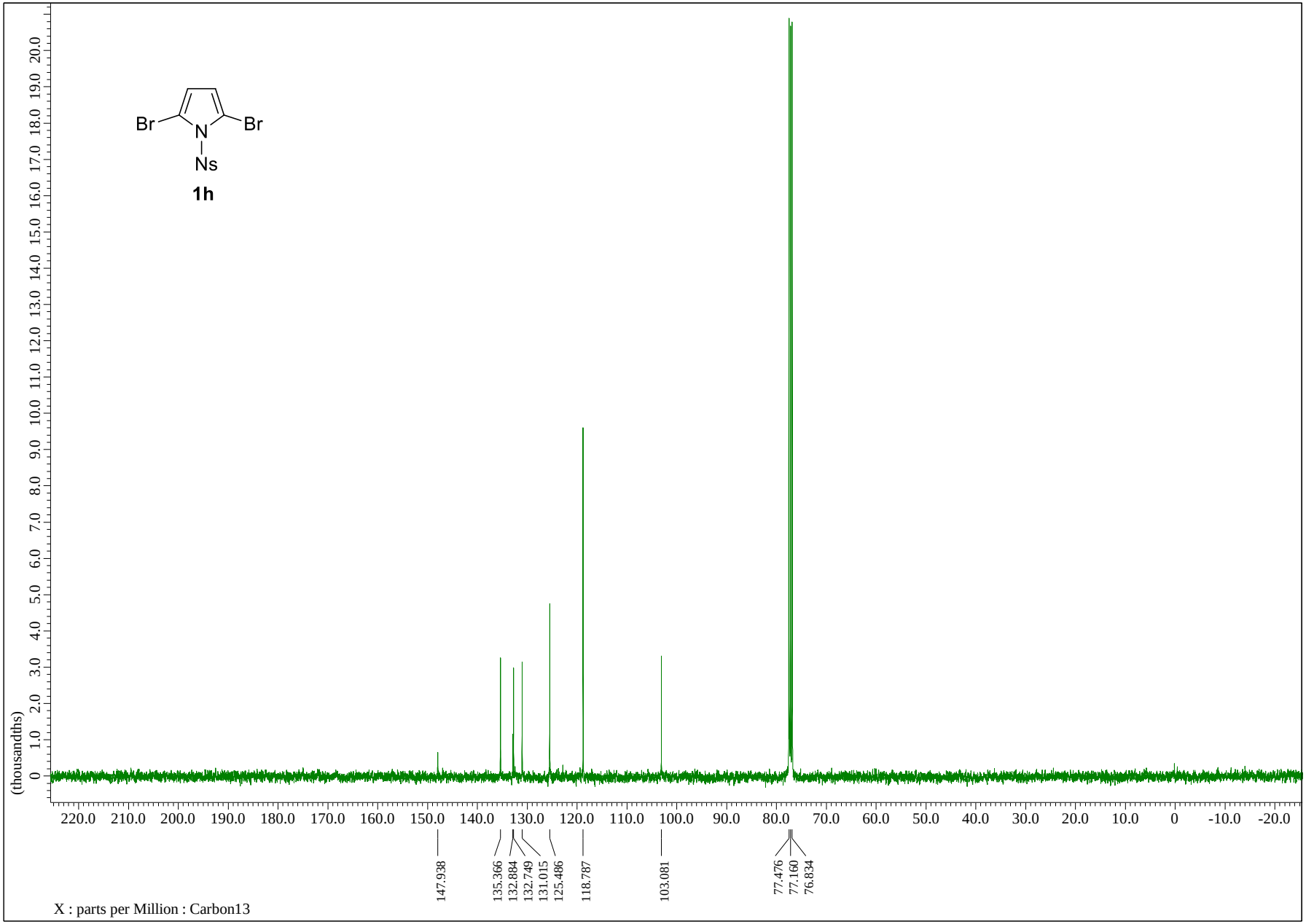

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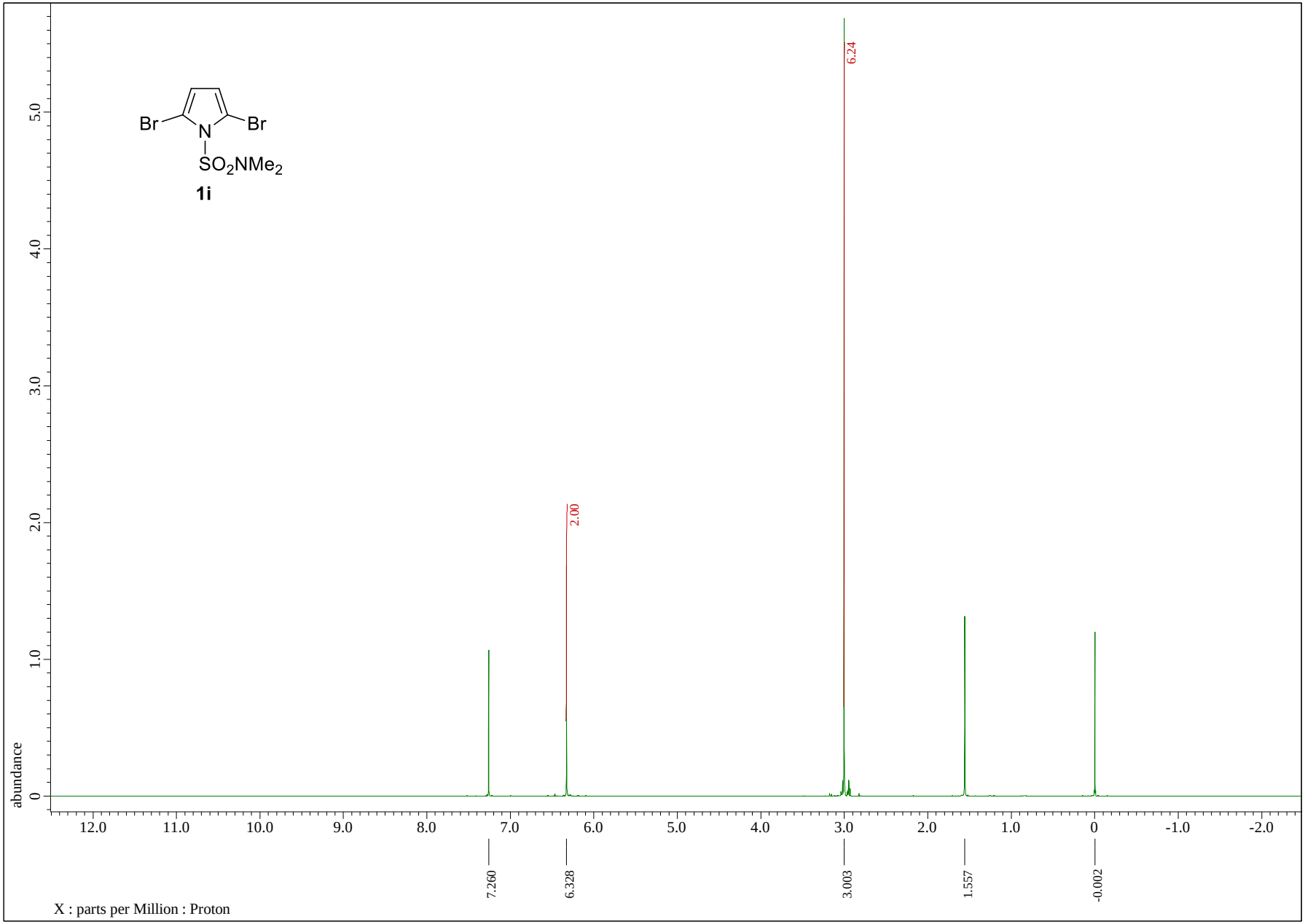

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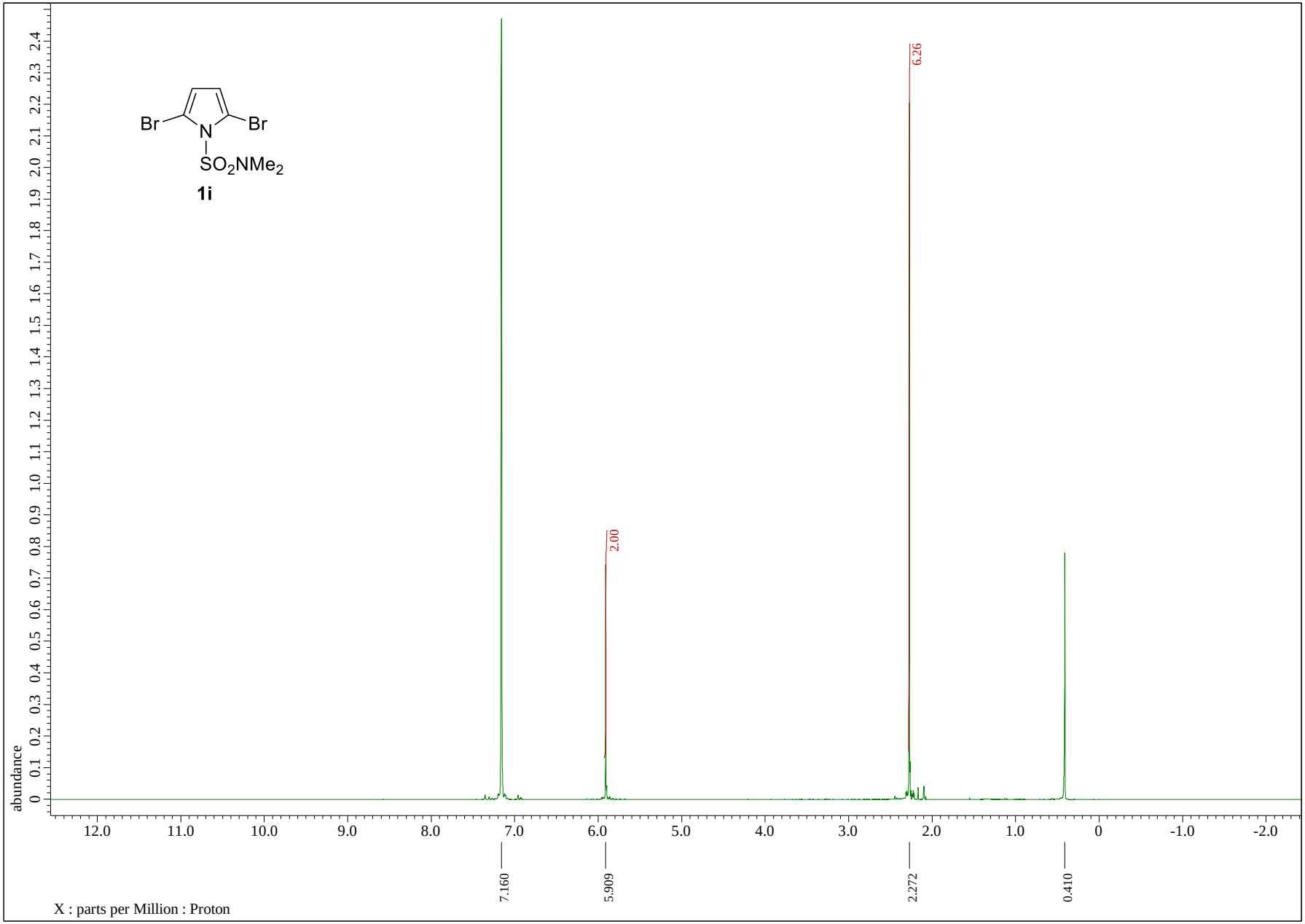

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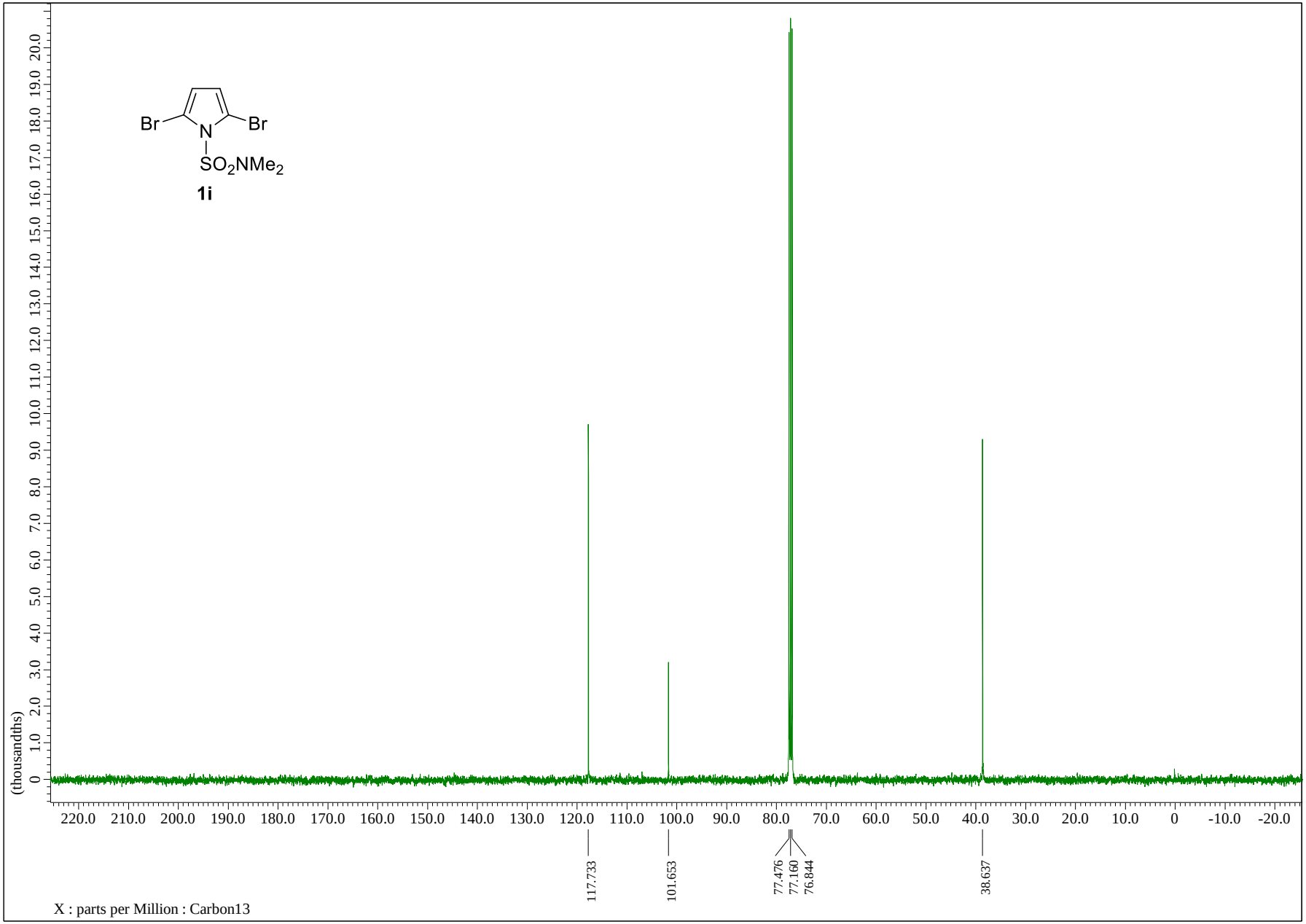

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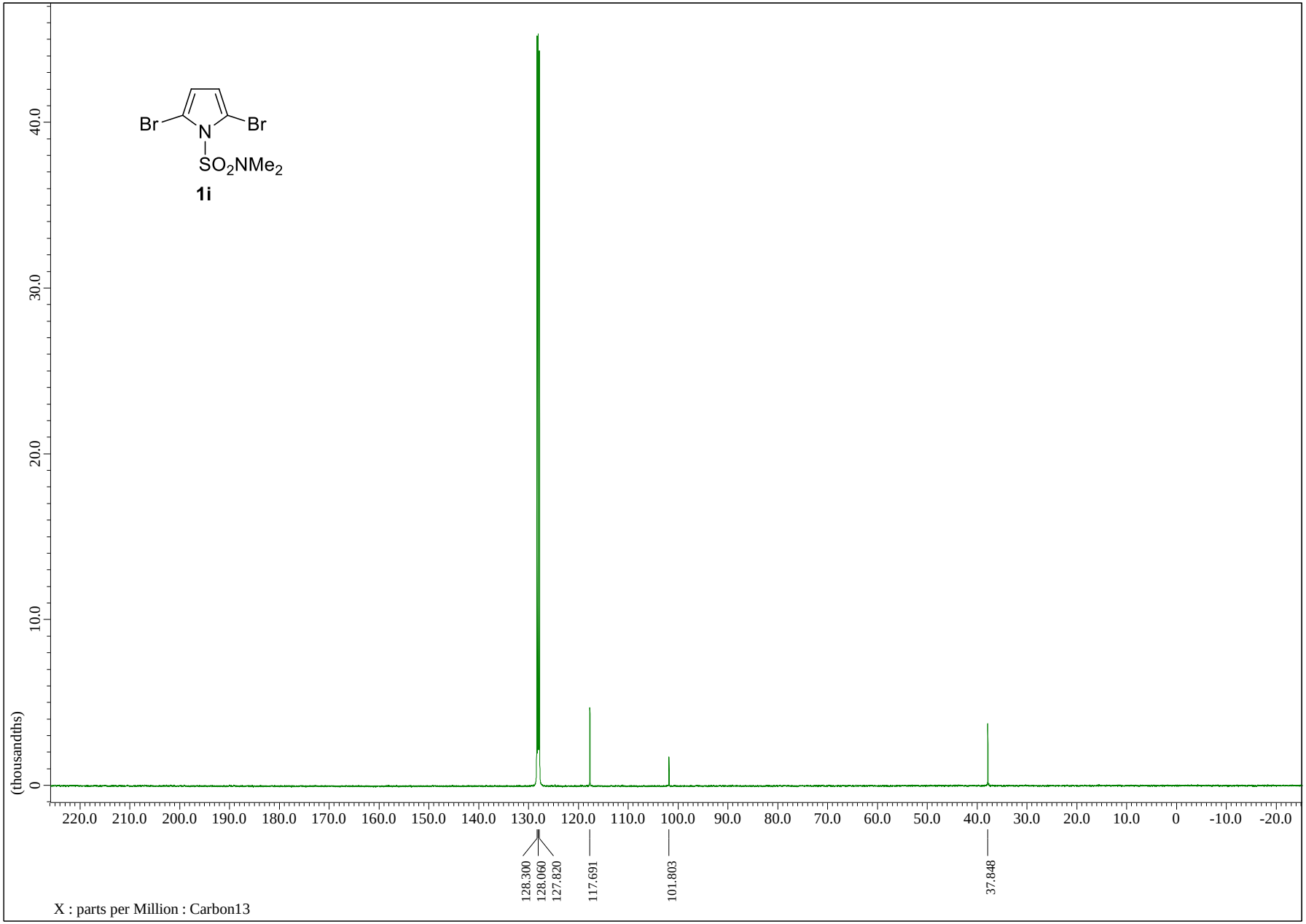

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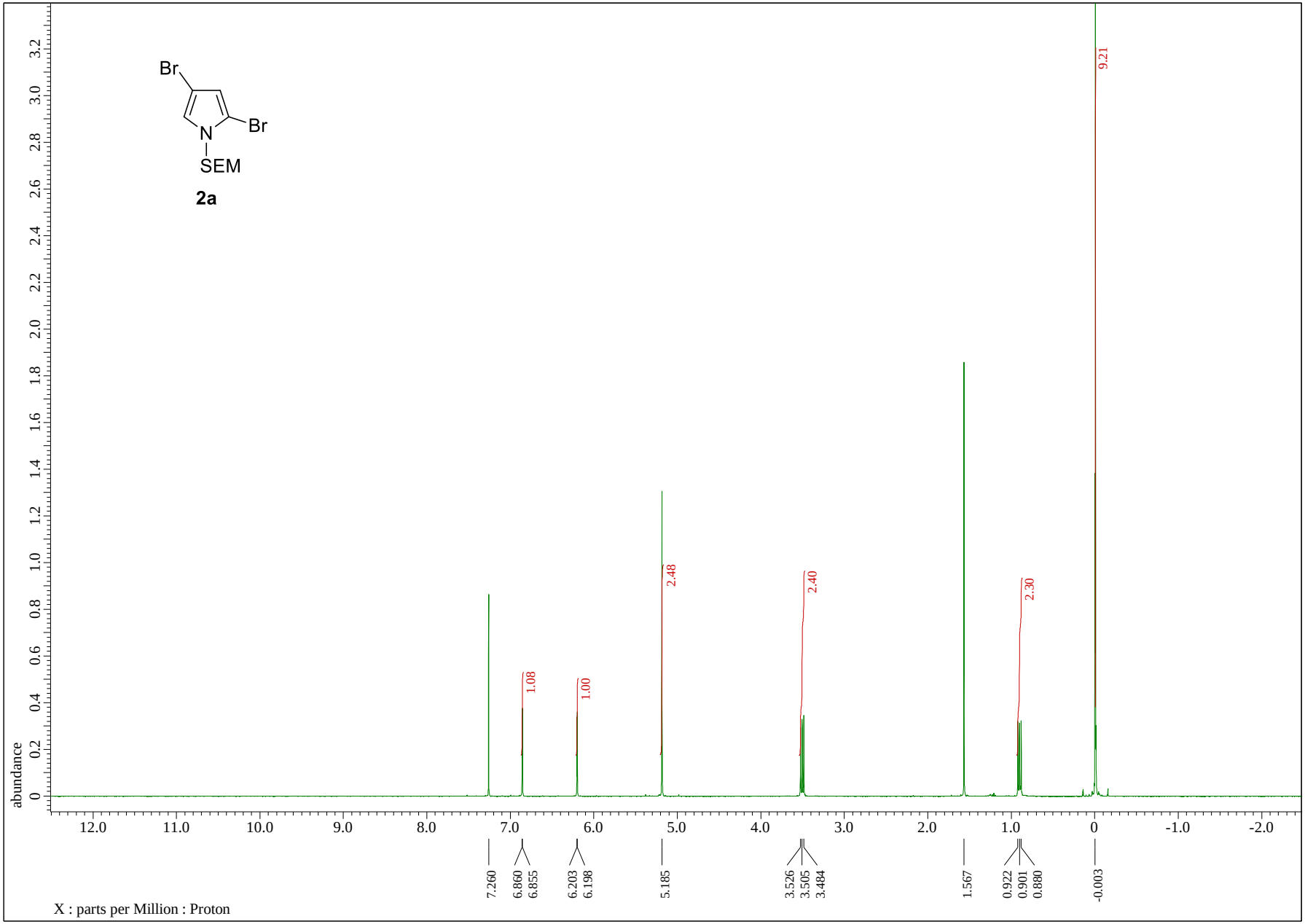

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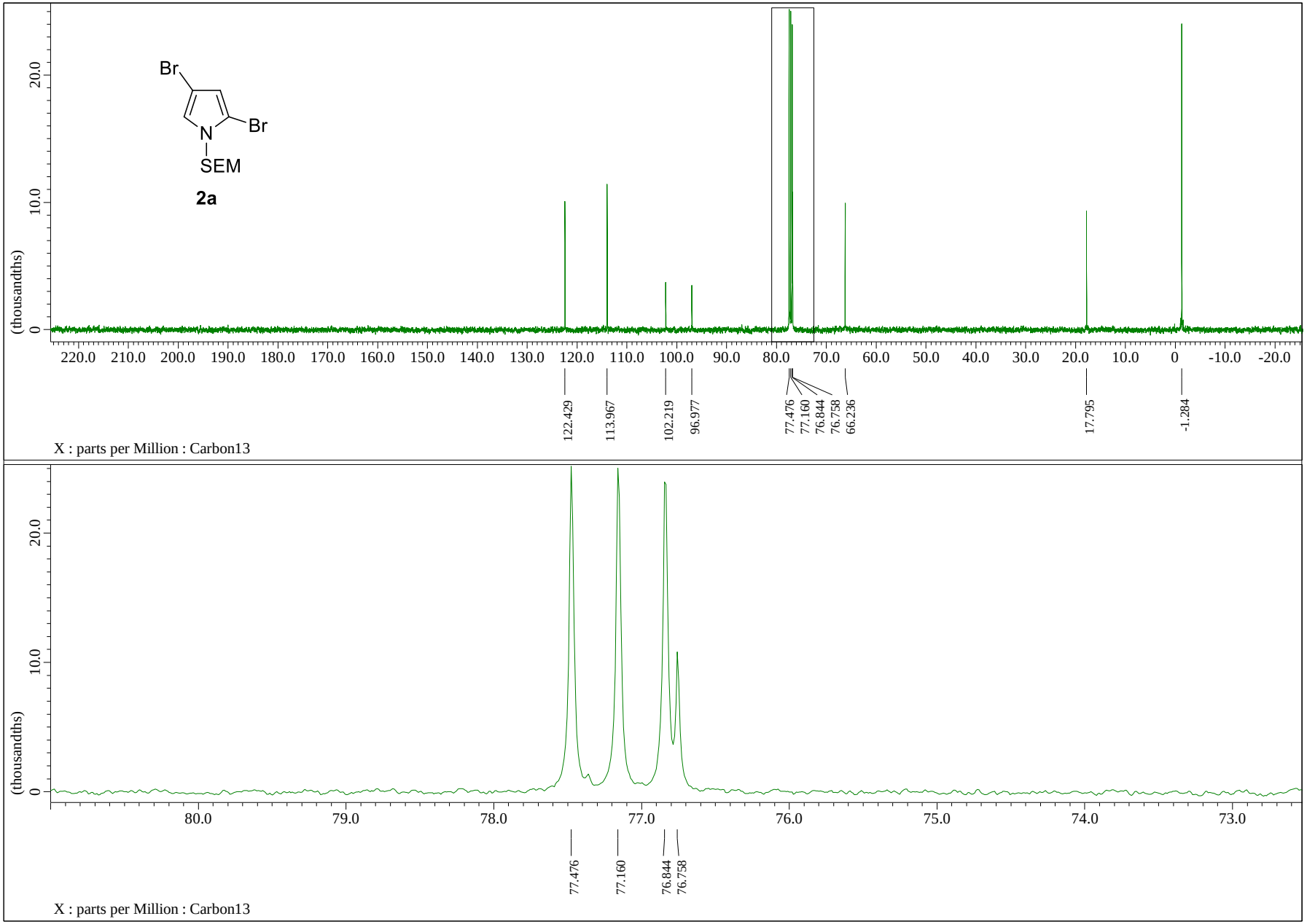

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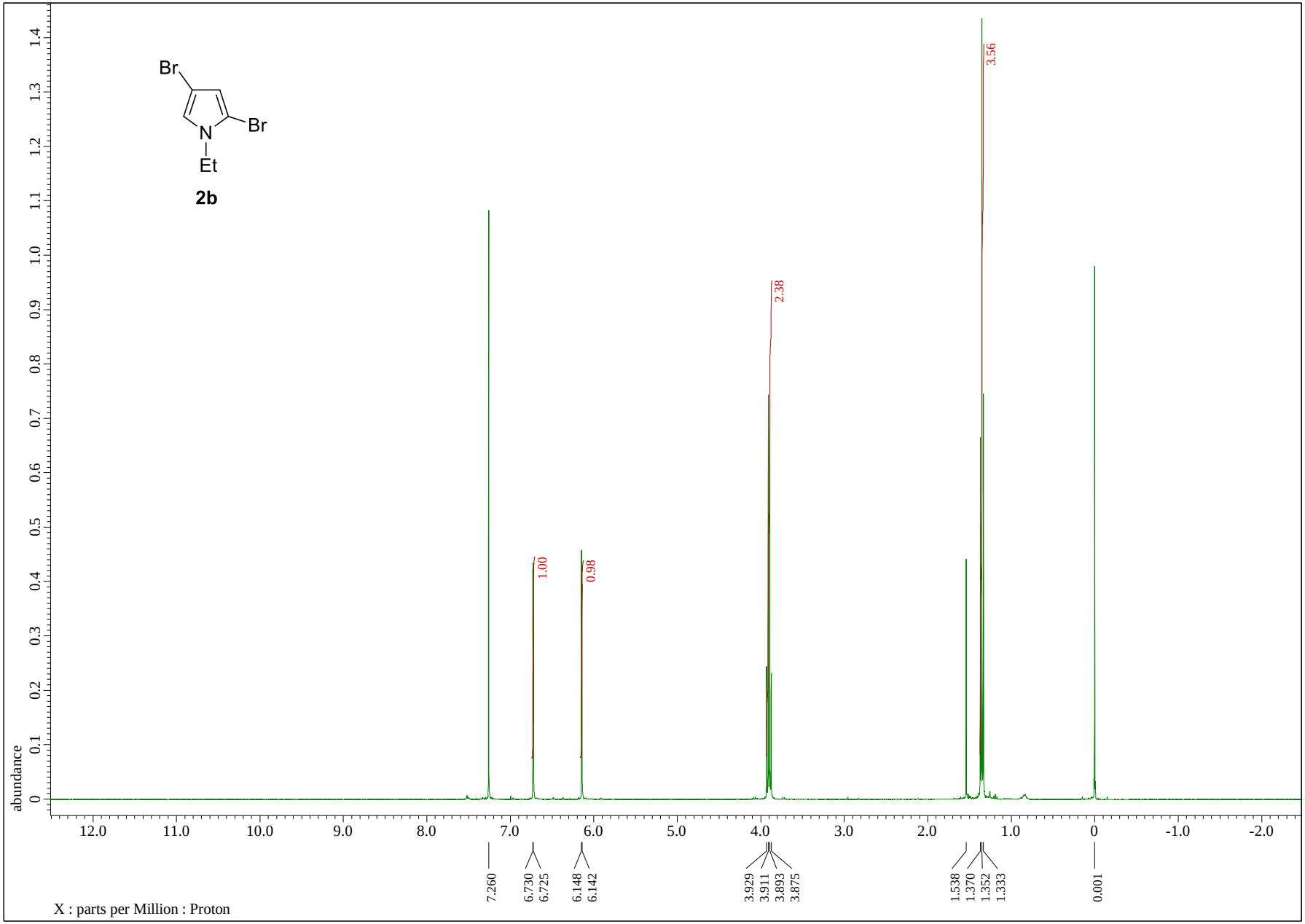
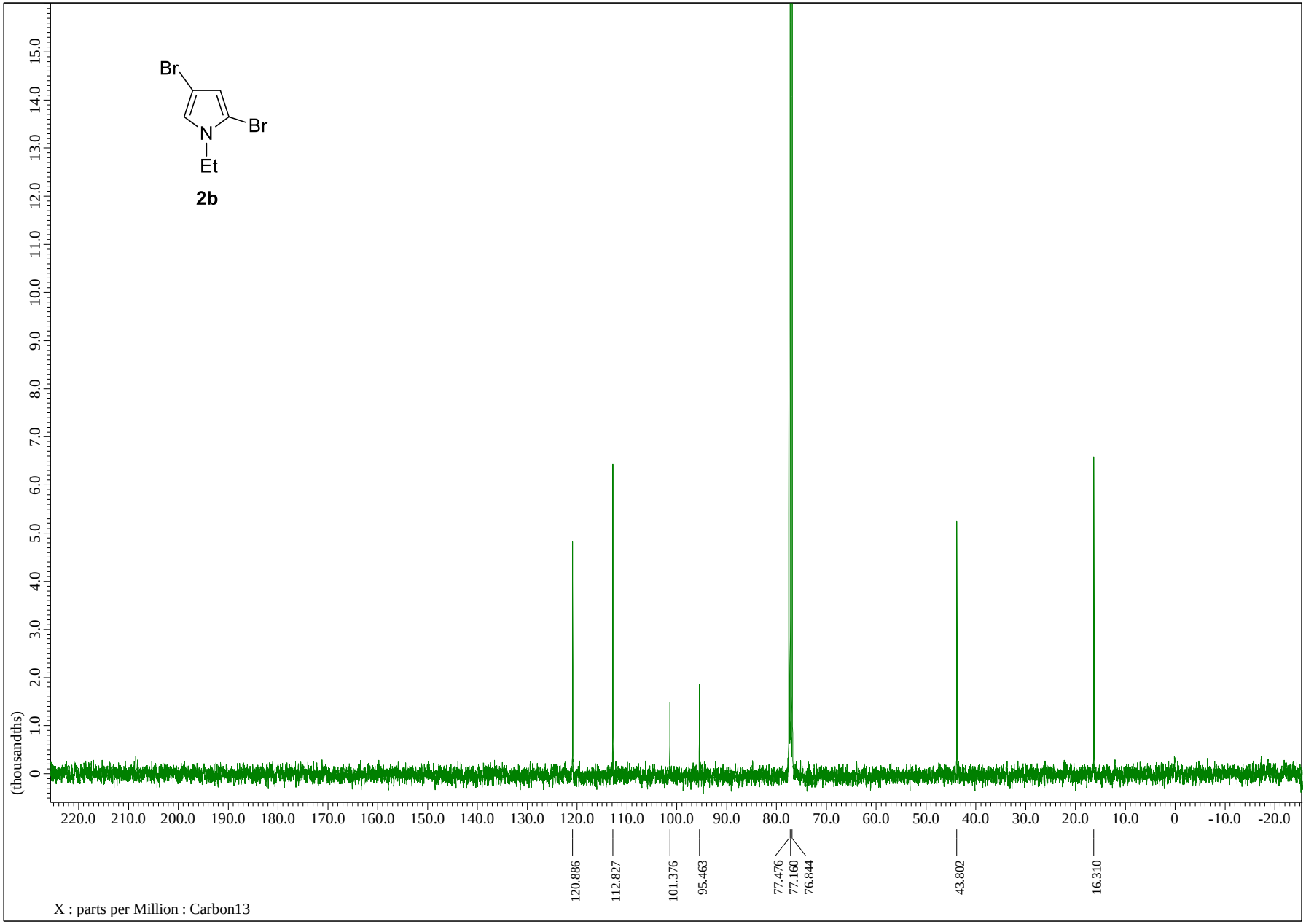


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



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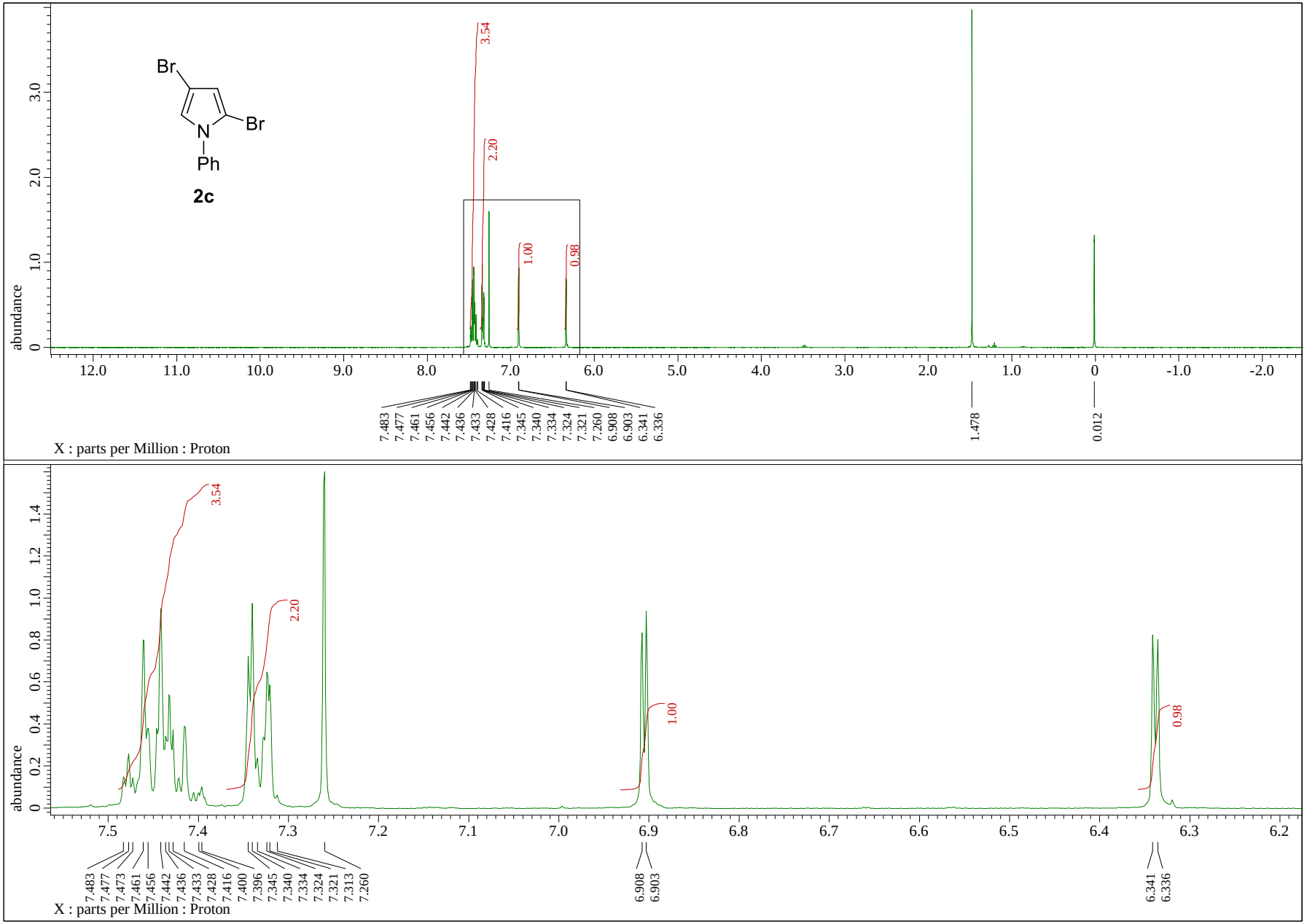

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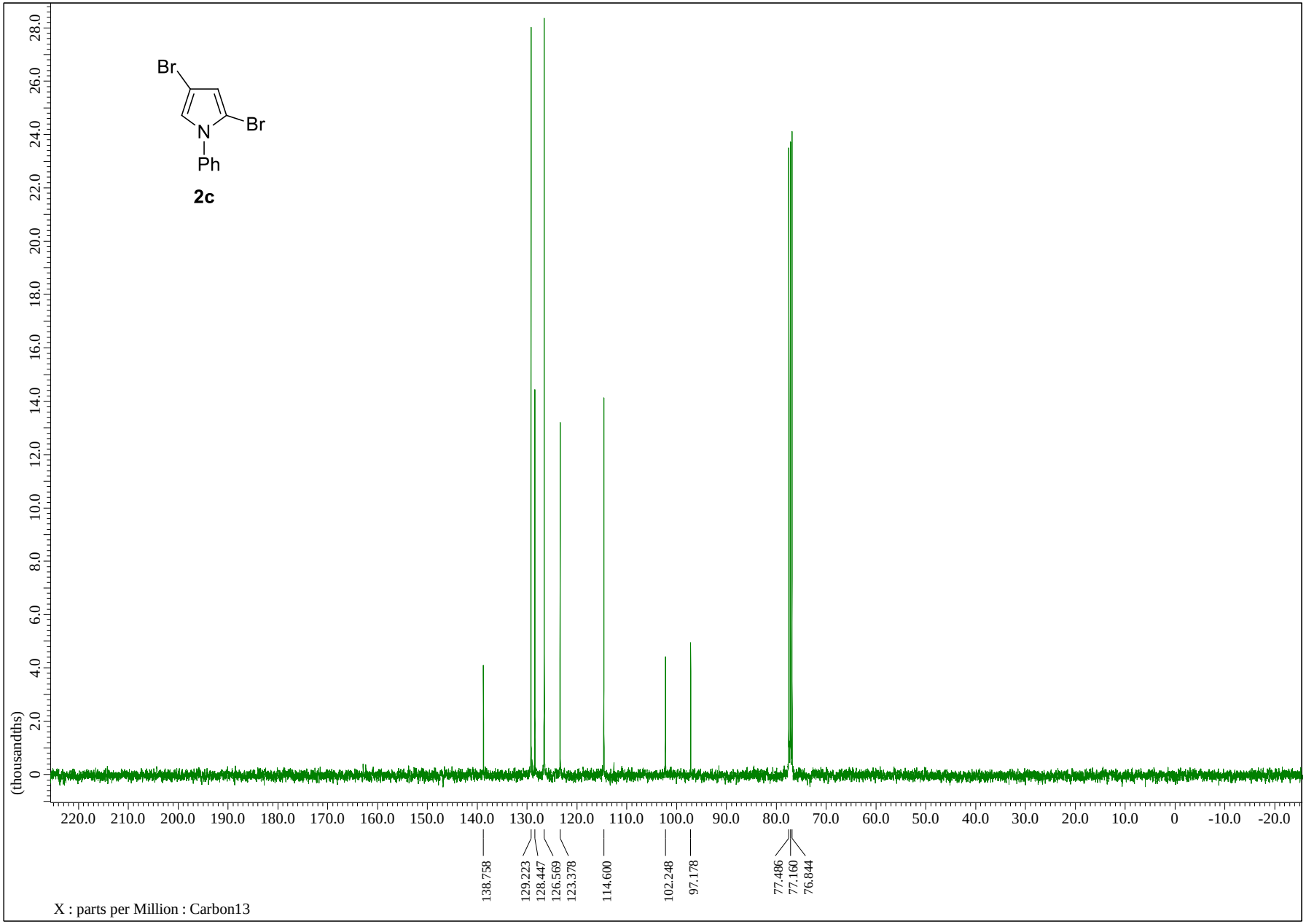

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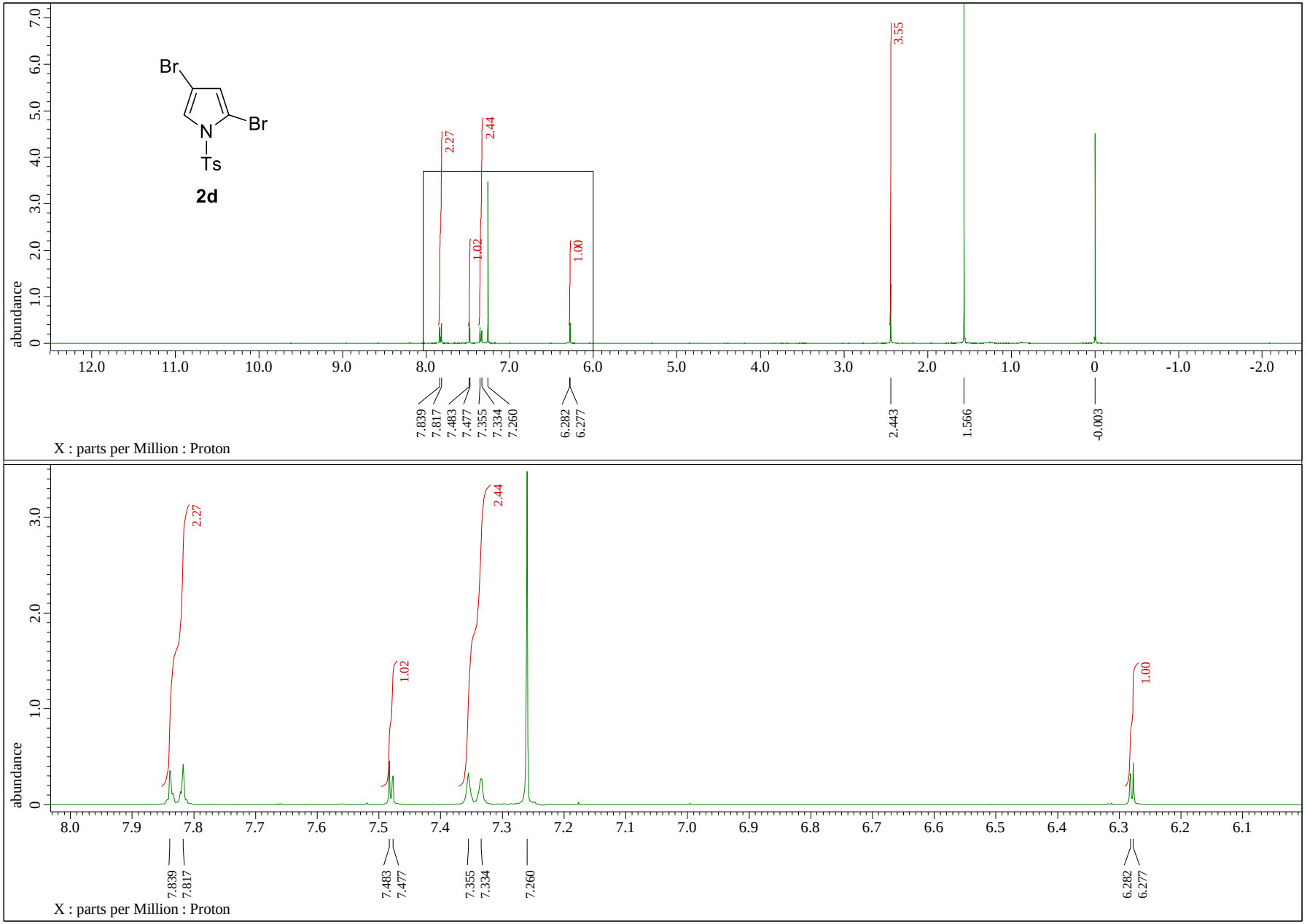

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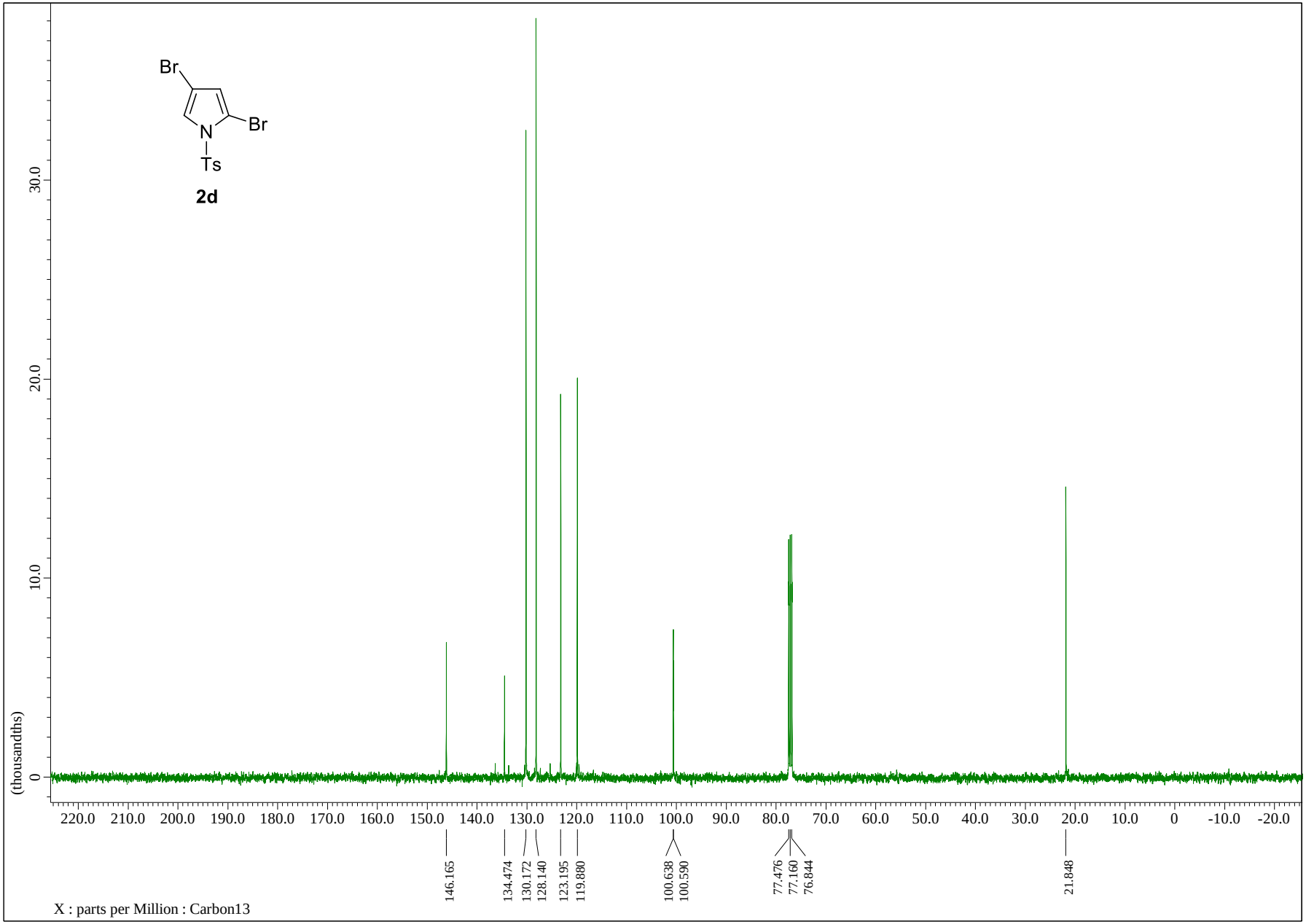
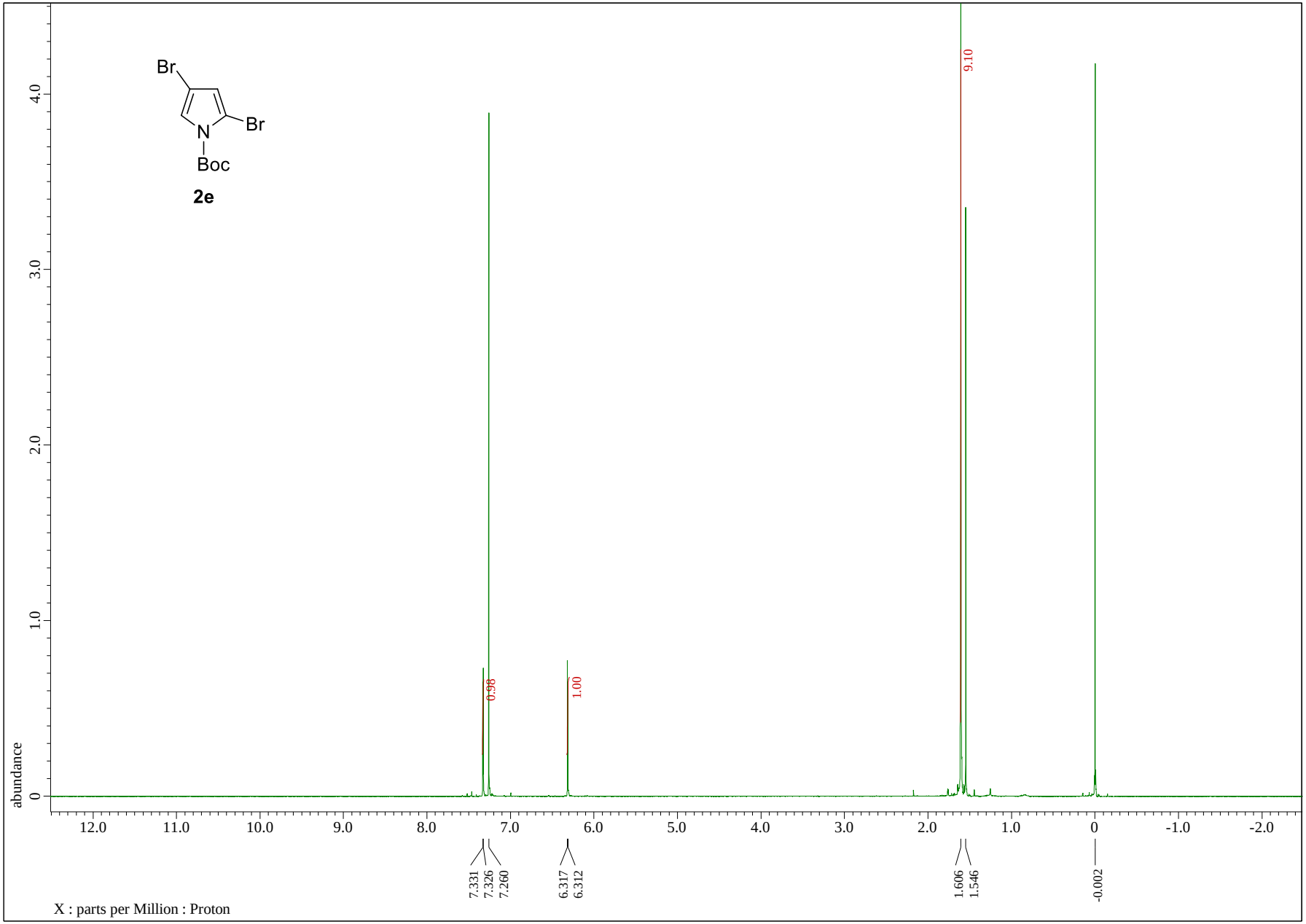
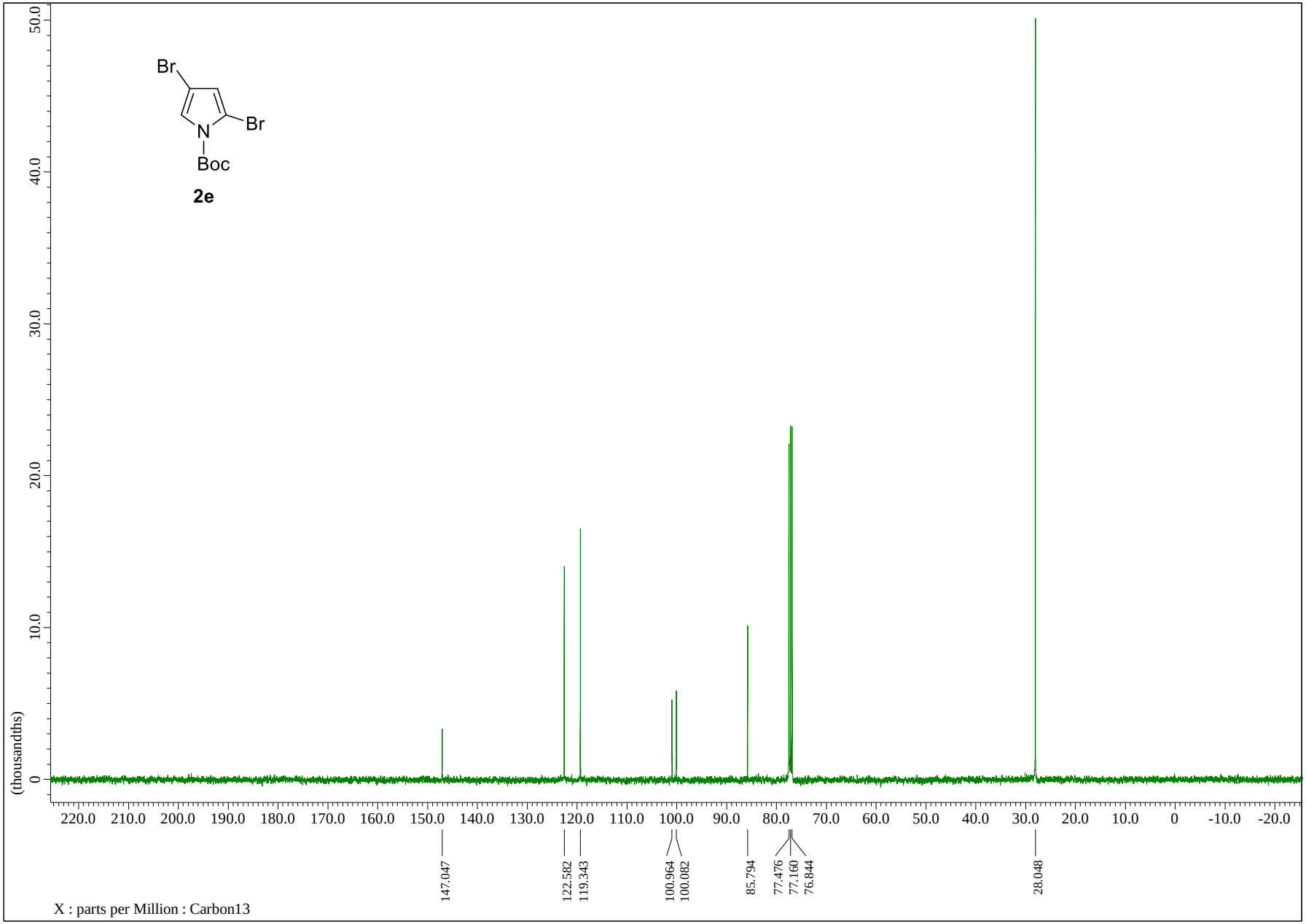


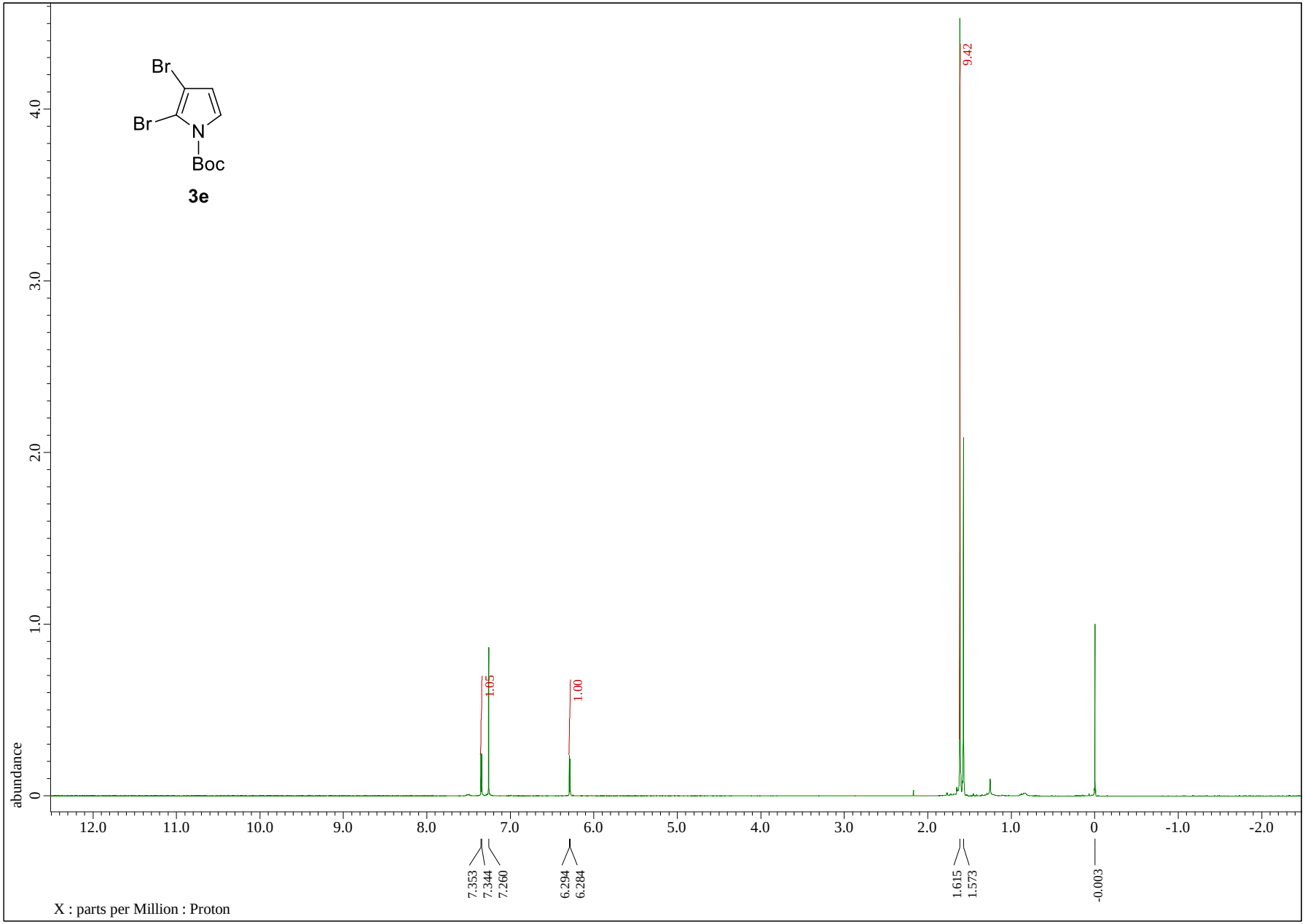
^{1}H NMR (400 MHz, $CDCl_3$)



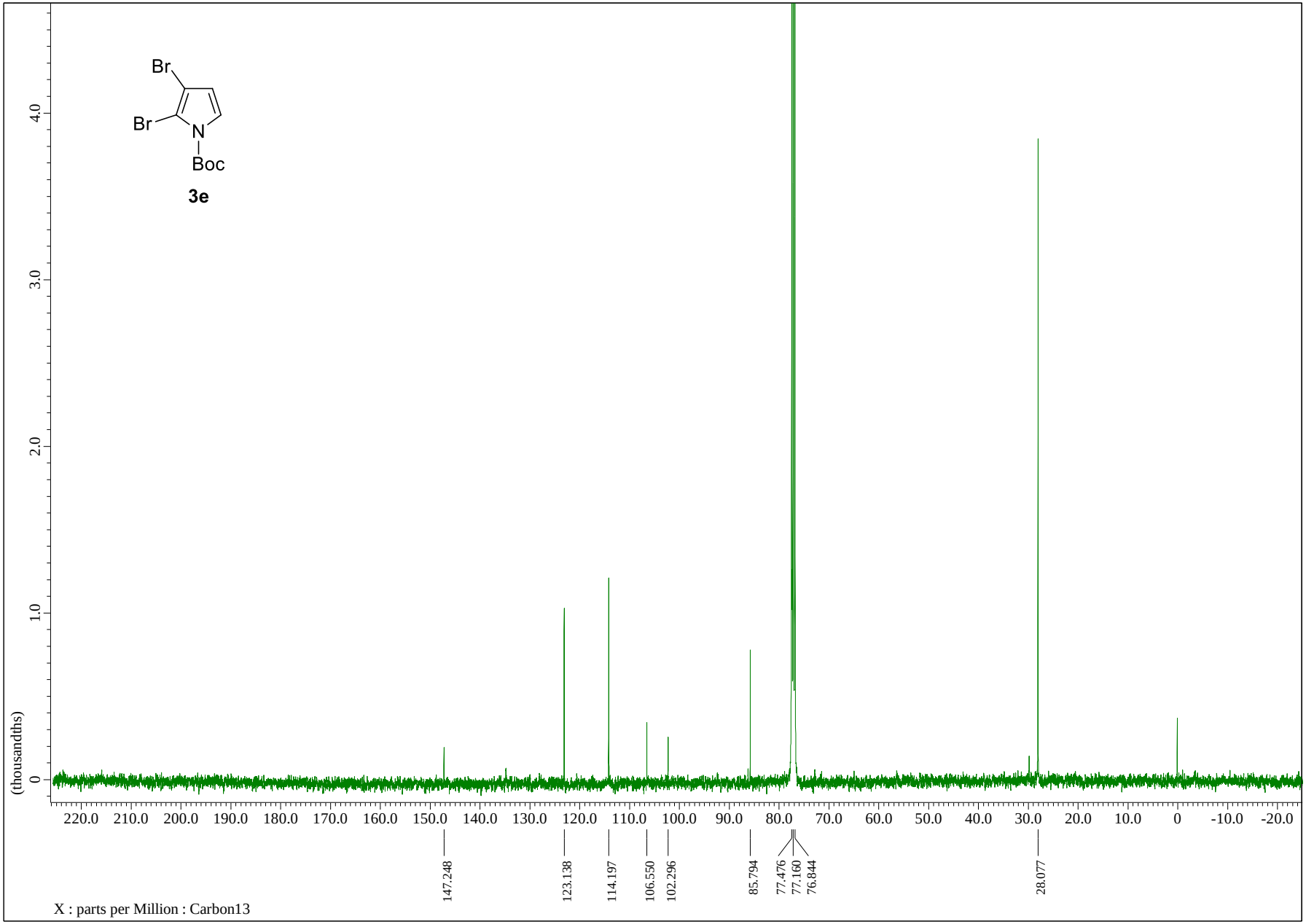
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



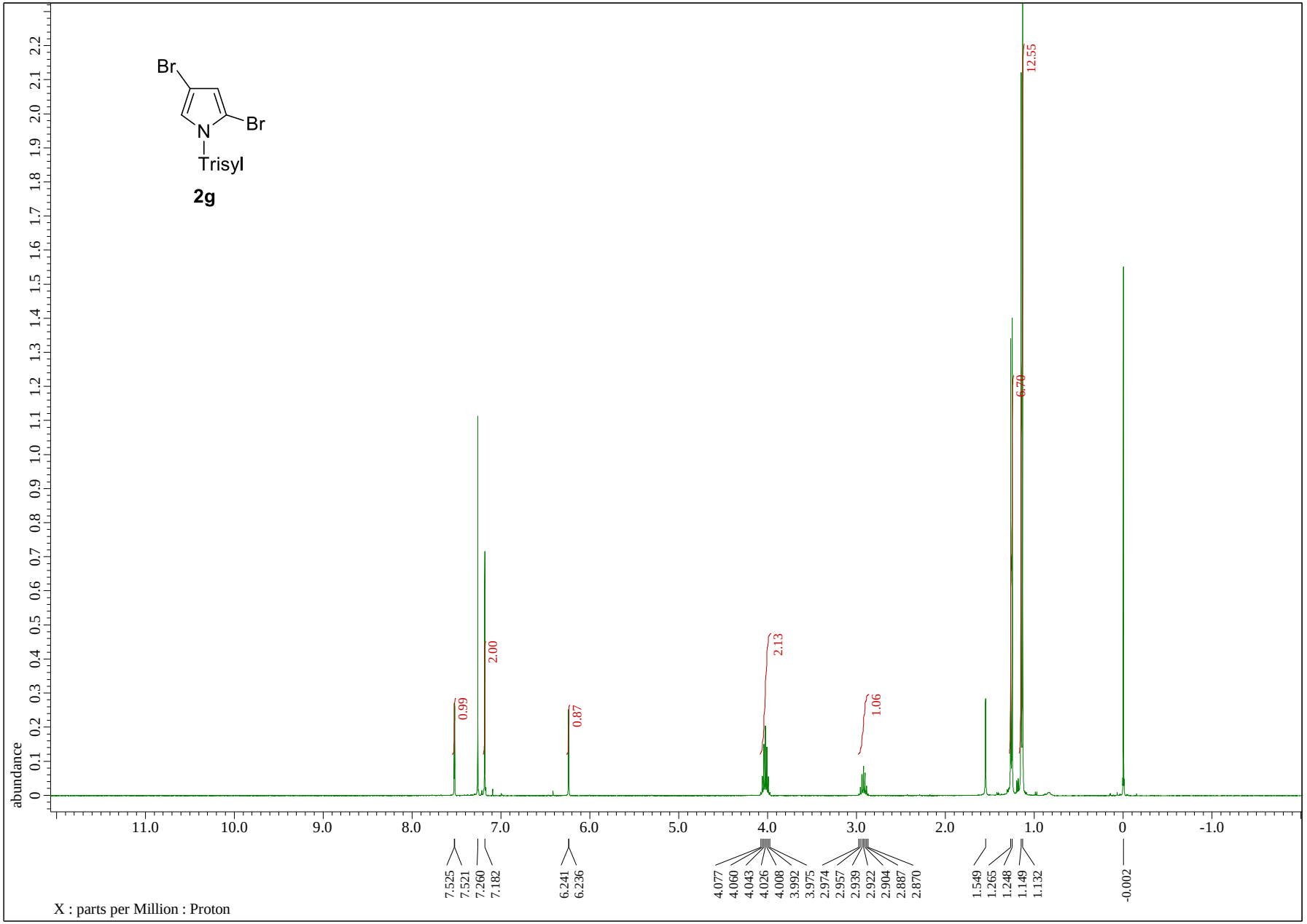
^{1}H NMR (400 MHz, $CDCl_3$)



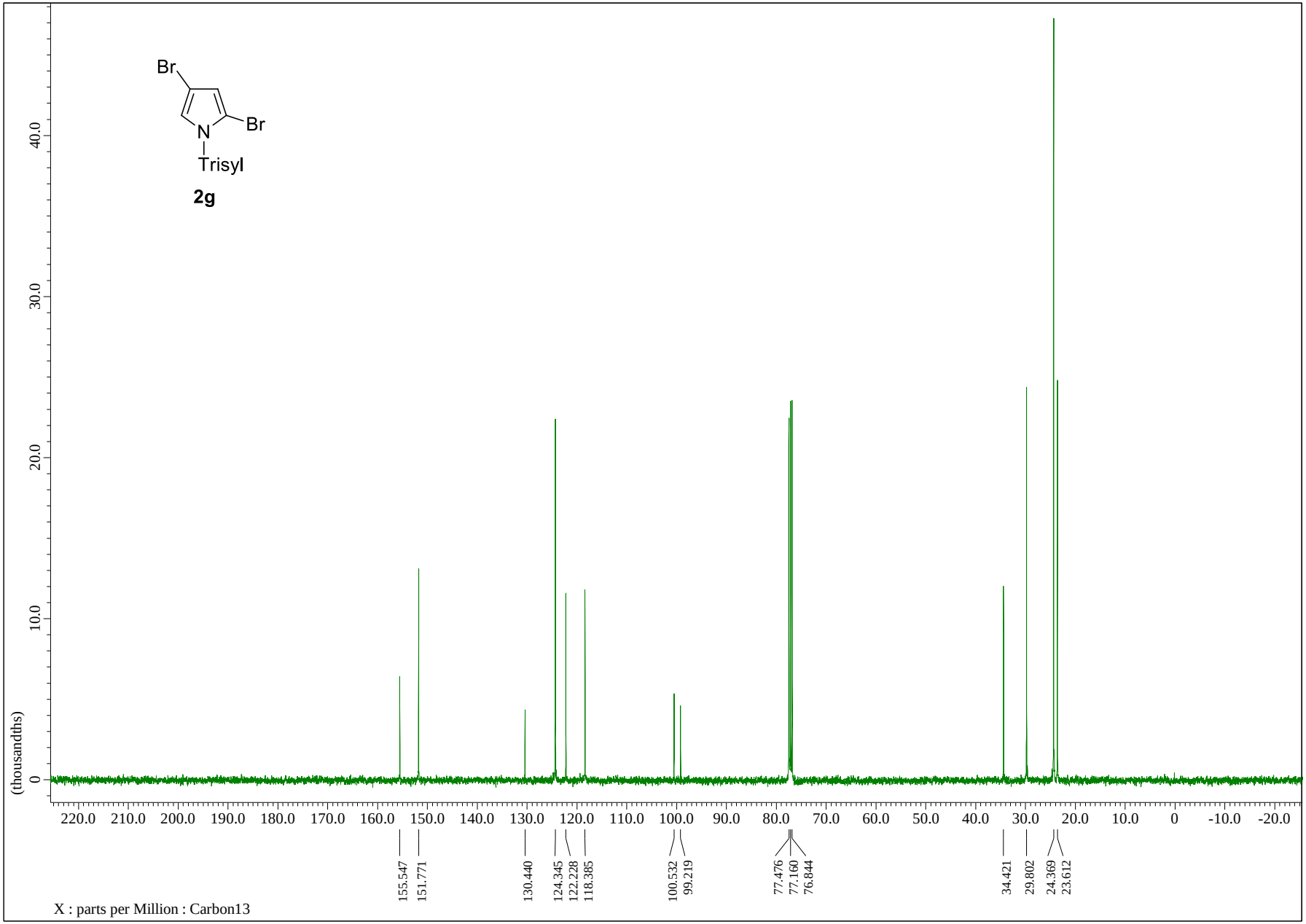
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



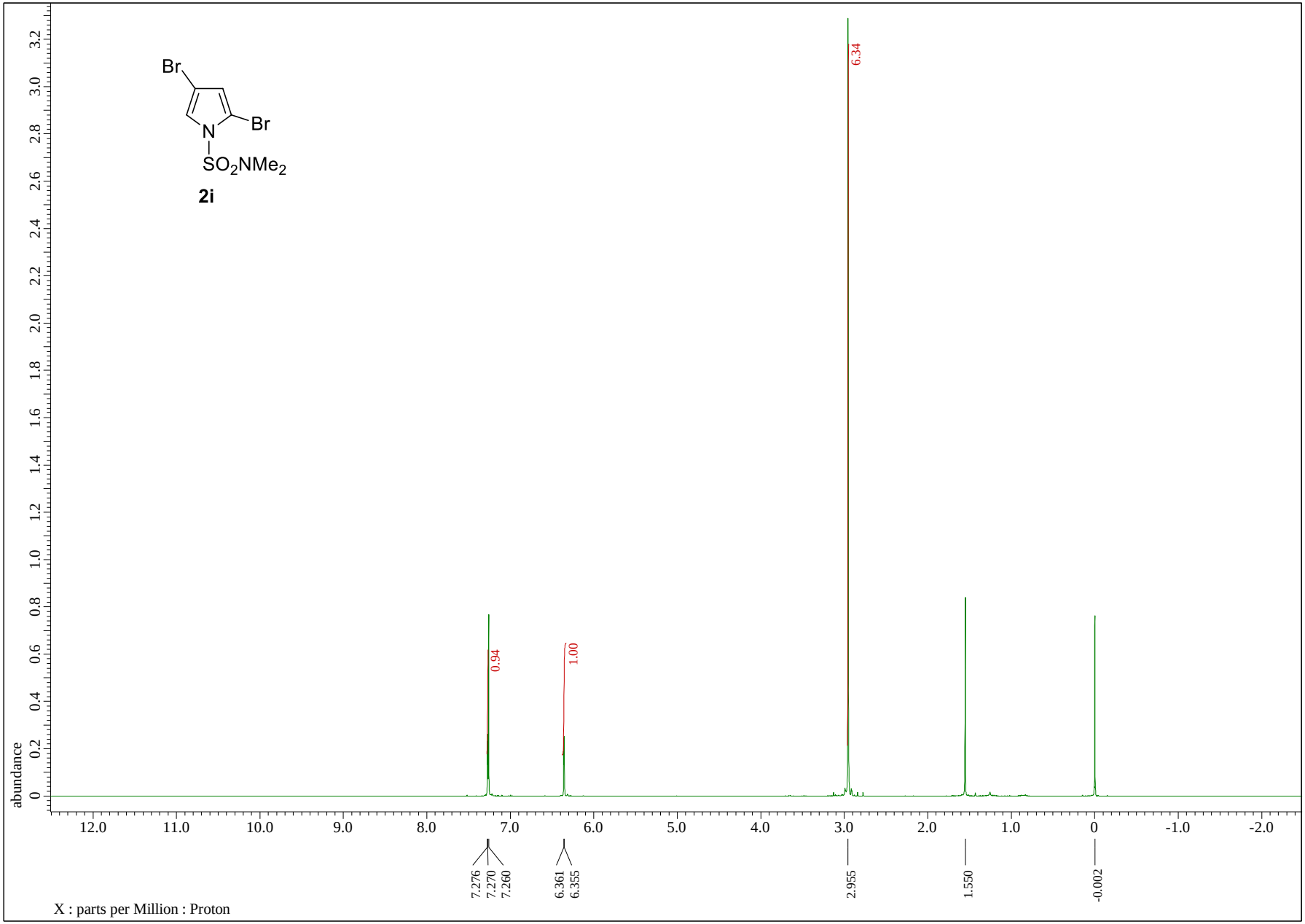
^{1}H NMR (400 MHz, $CDCl_3$)



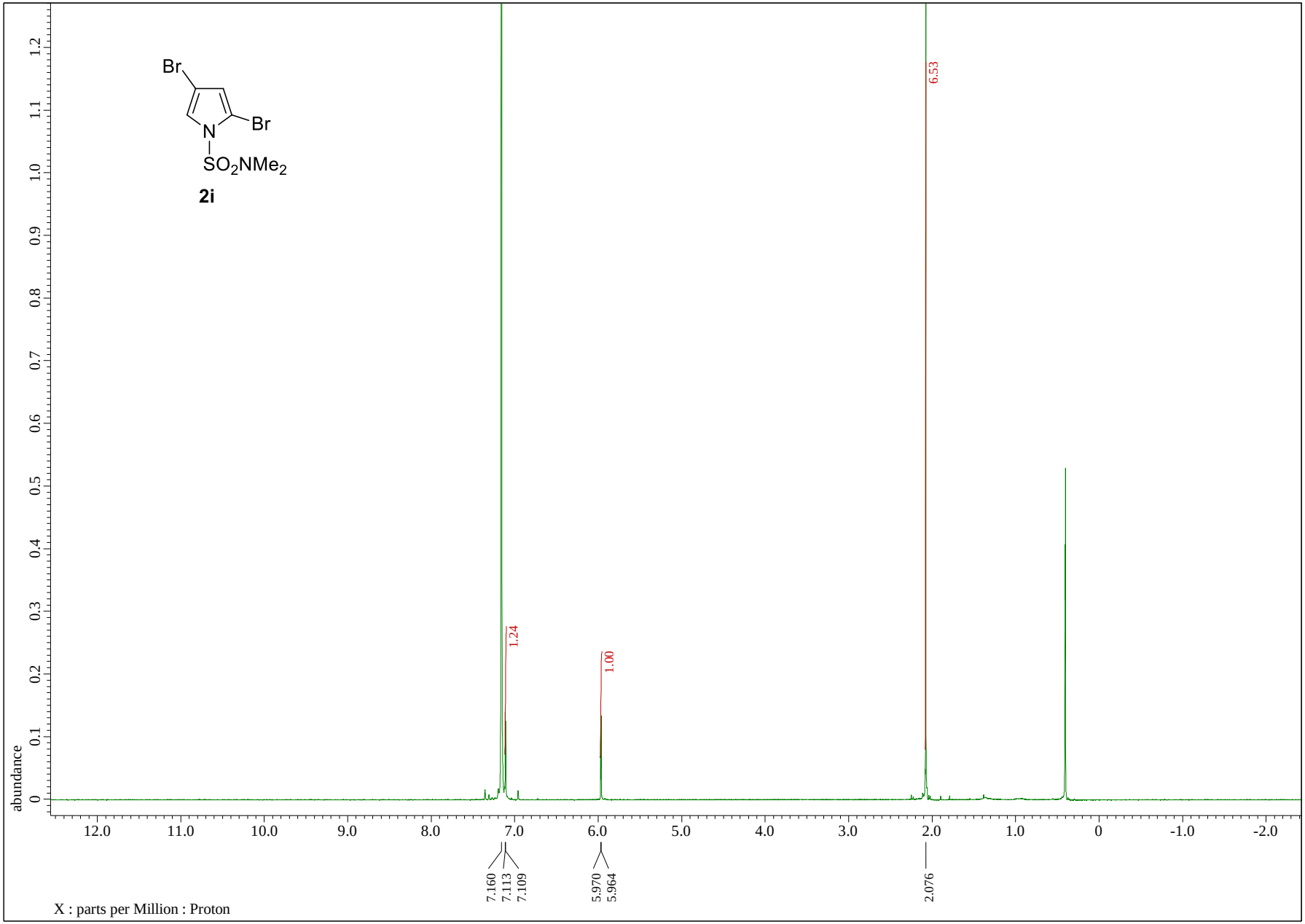
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



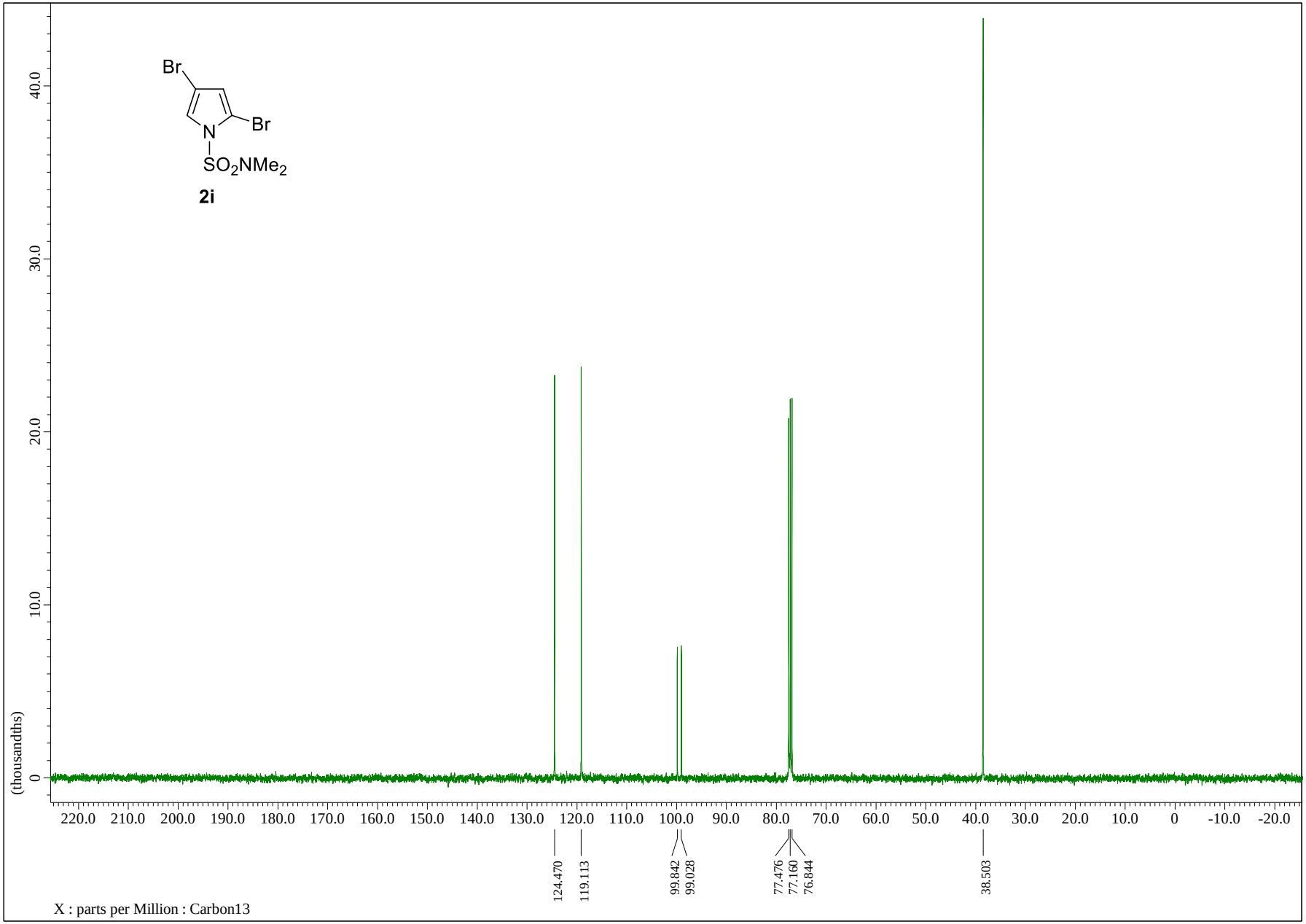
^{1}H NMR (400 MHz, $CDCl_3$)



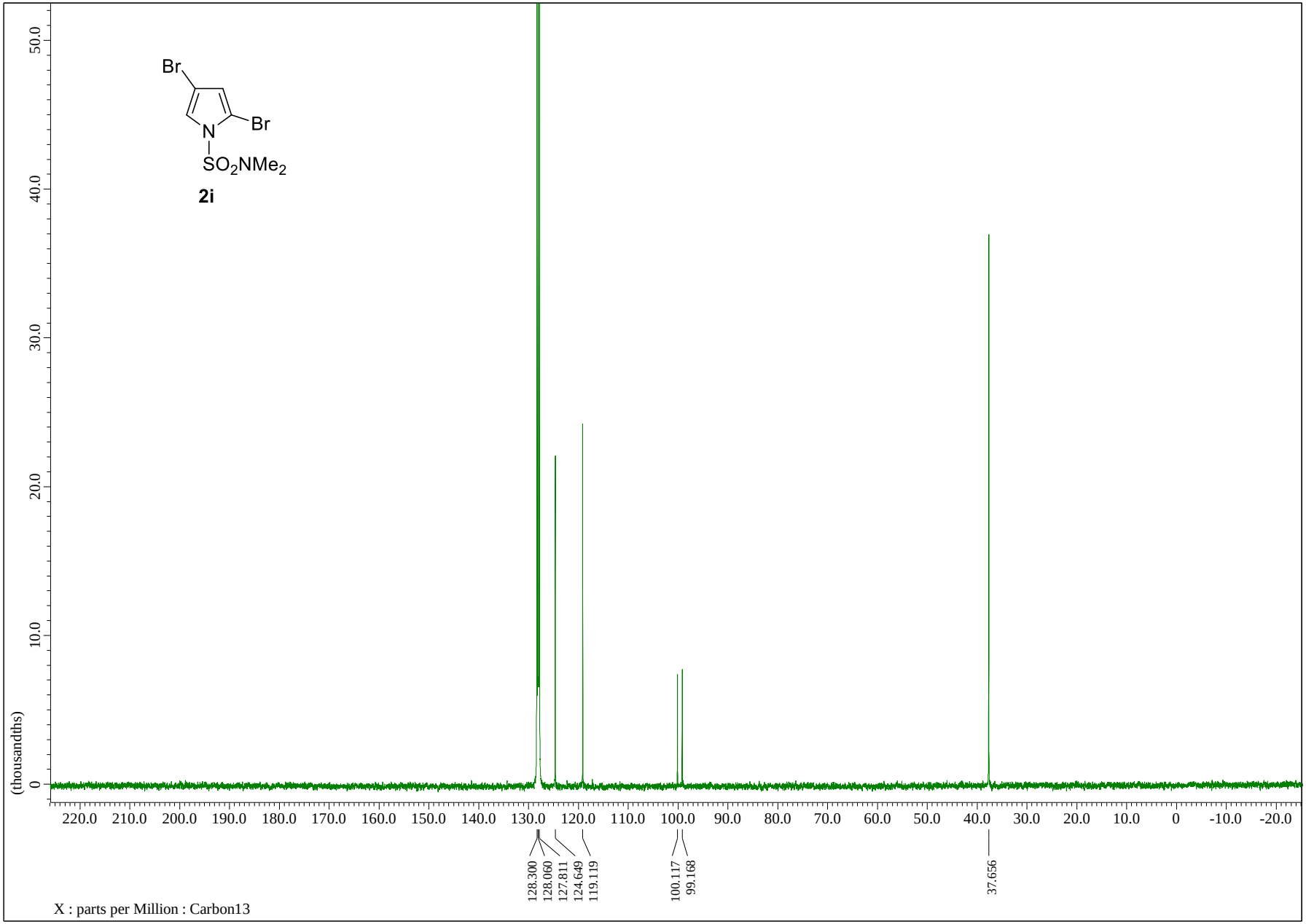
^{1}H NMR (400 MHz, benzene-d_6)



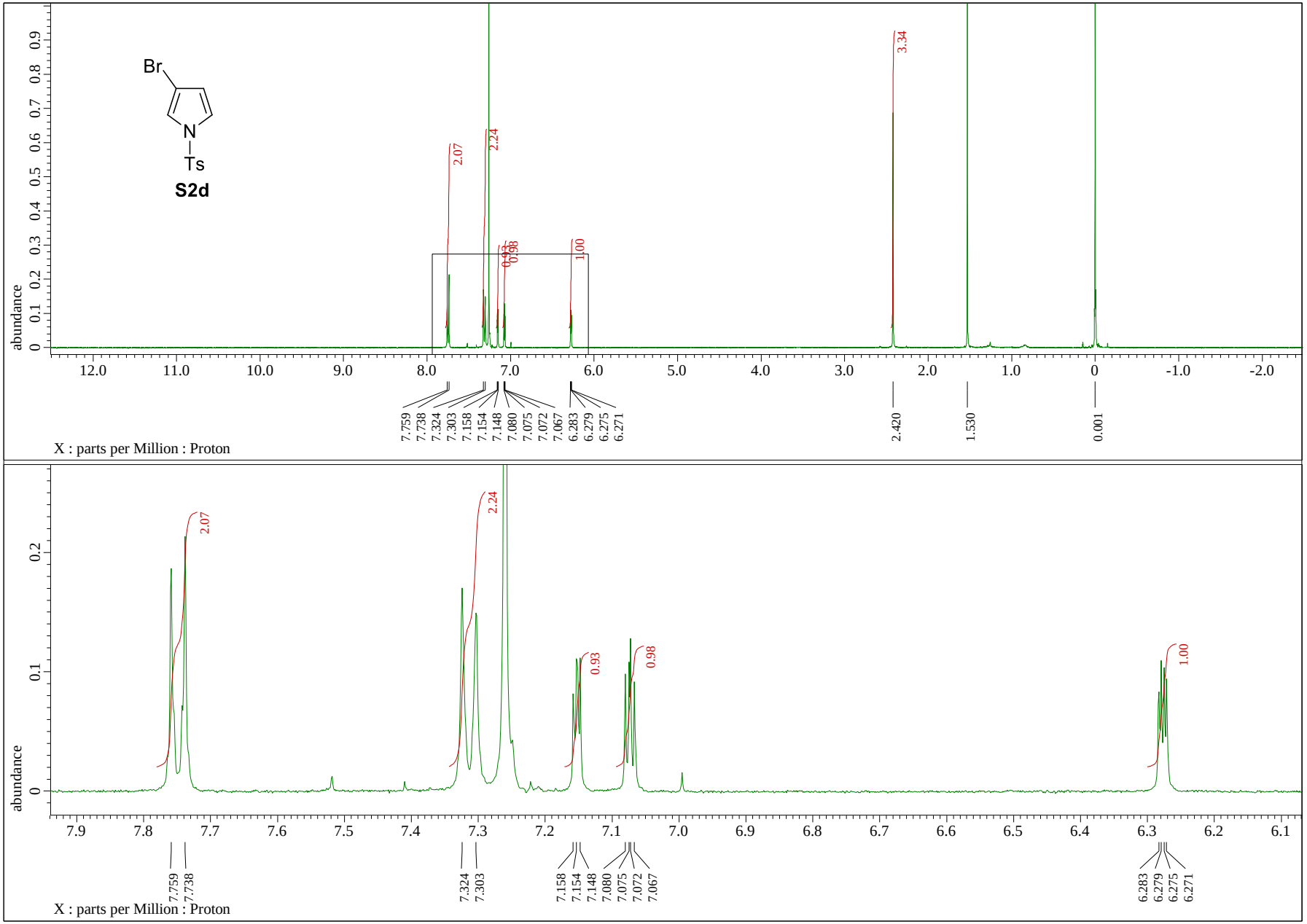
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



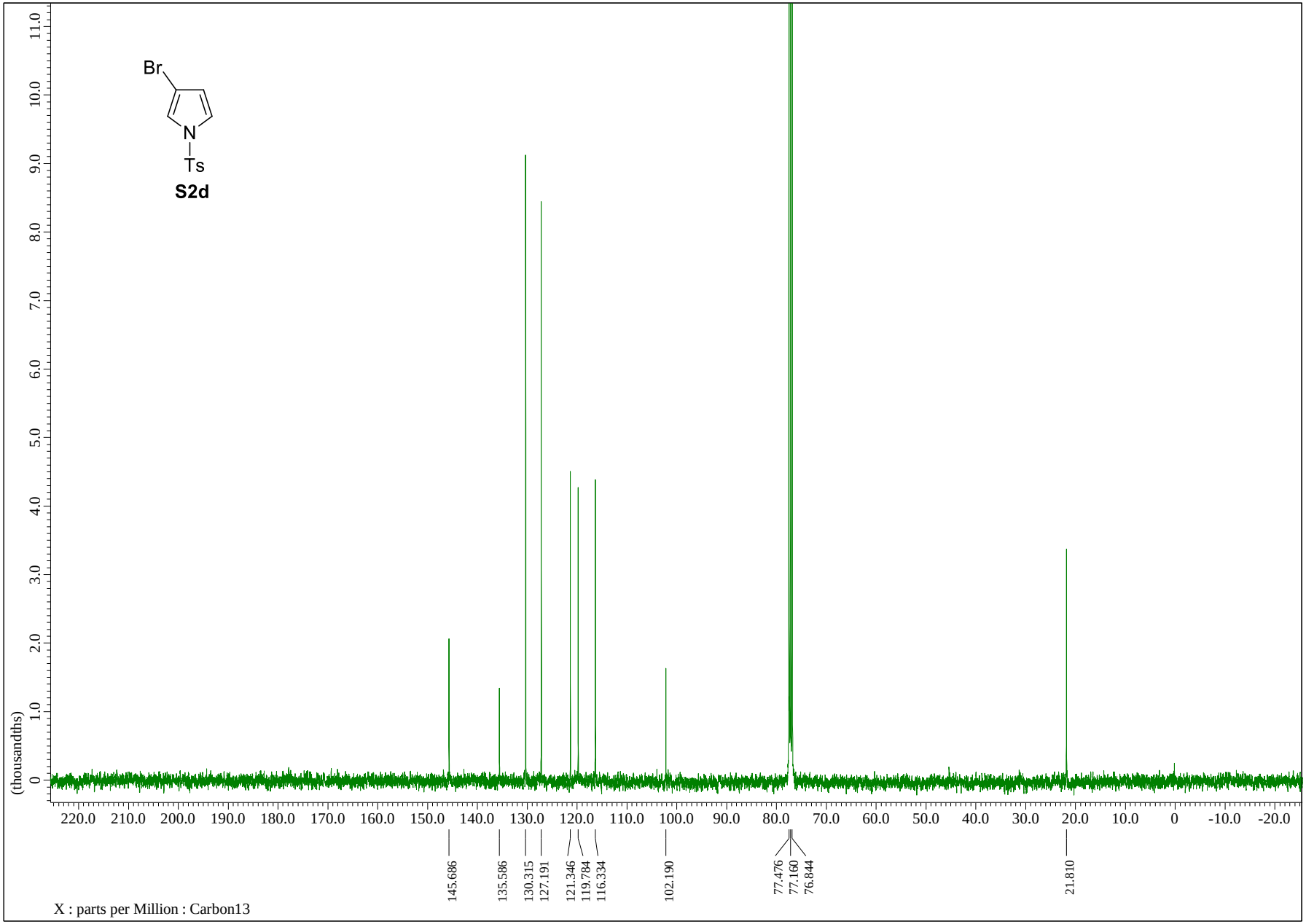
$^{13}C\{^{1}H\}$ NMR (100 MHz, benzene-d_6)



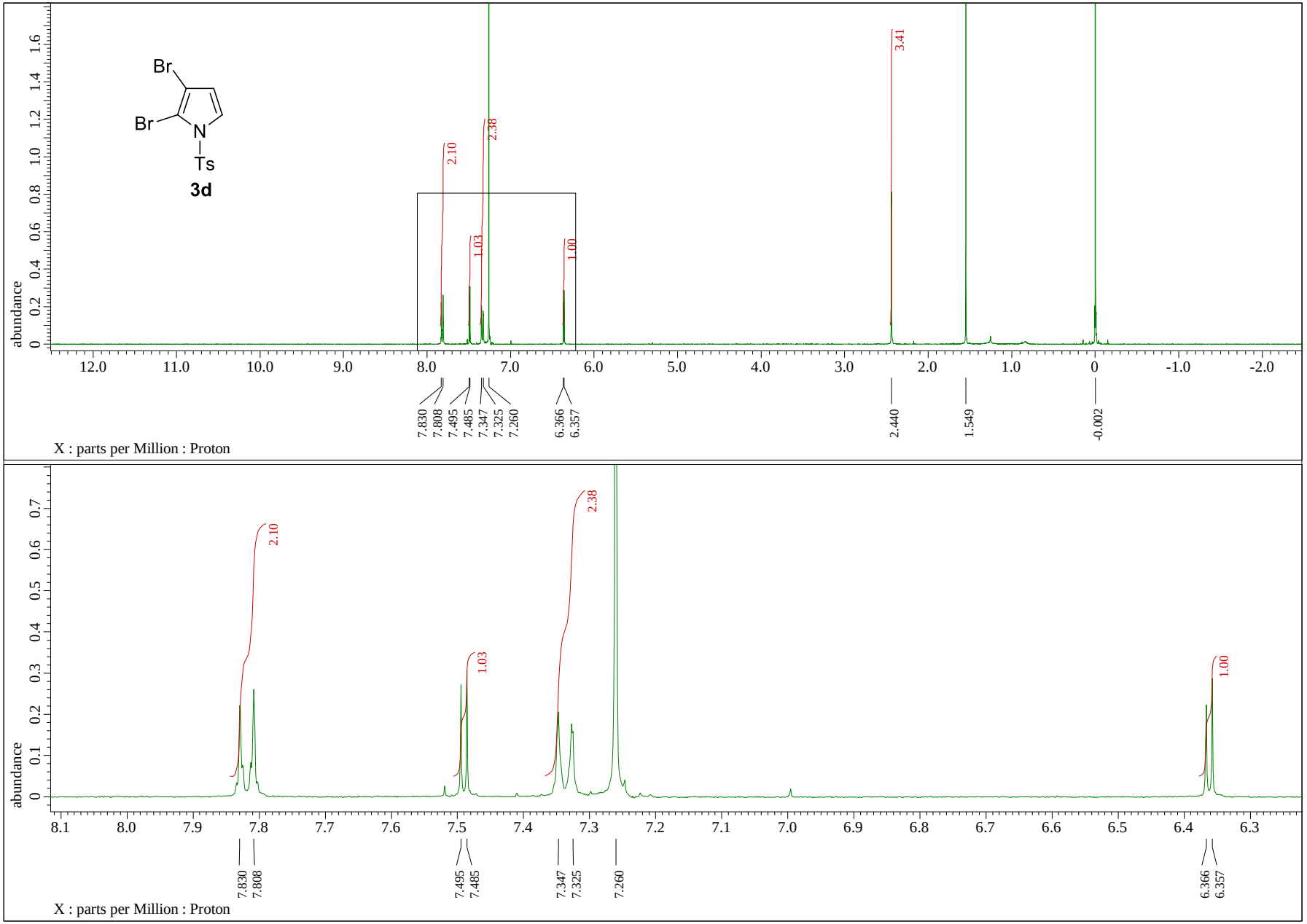
^{1}H NMR (400 MHz, $CDCl_3$)



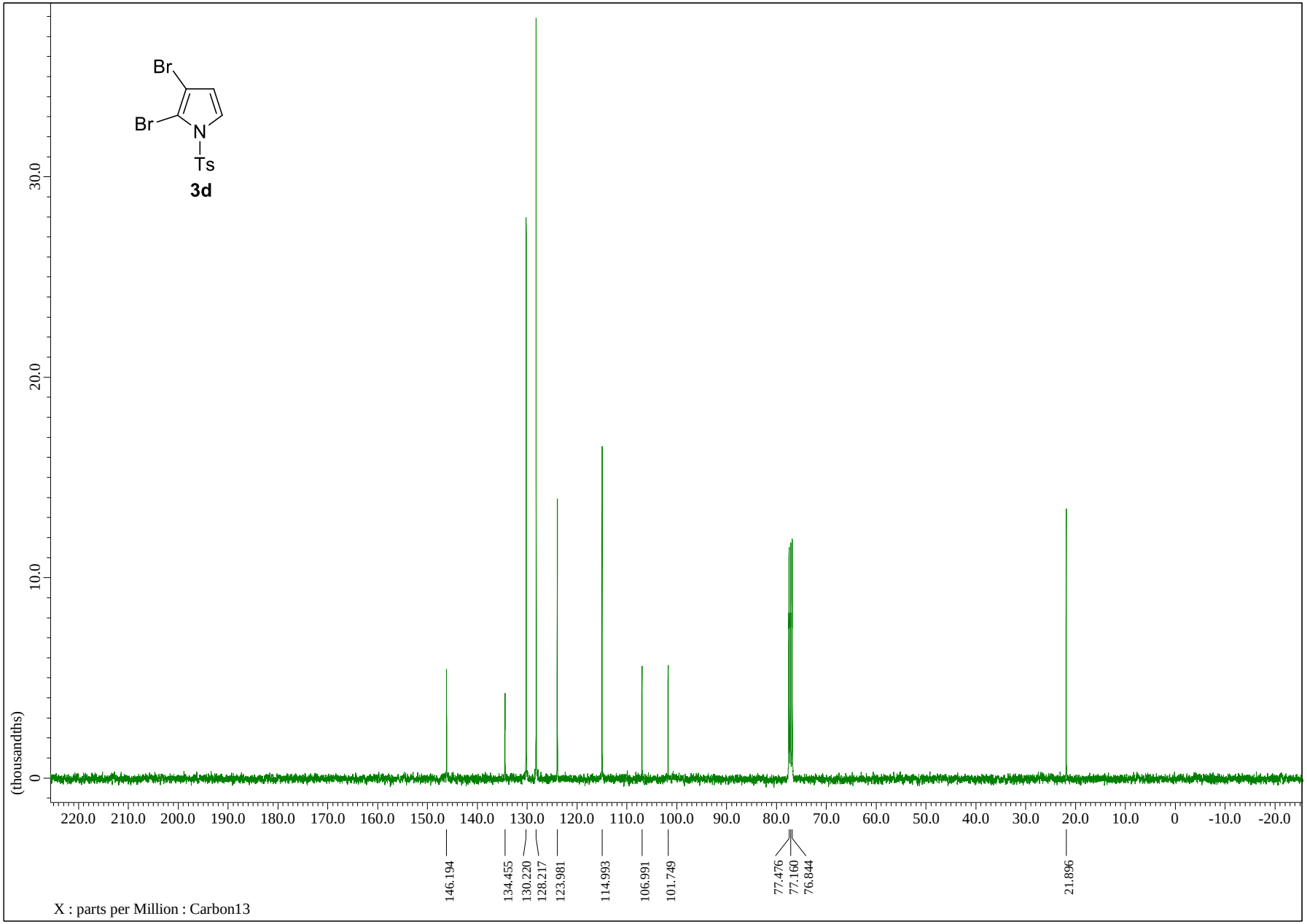
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



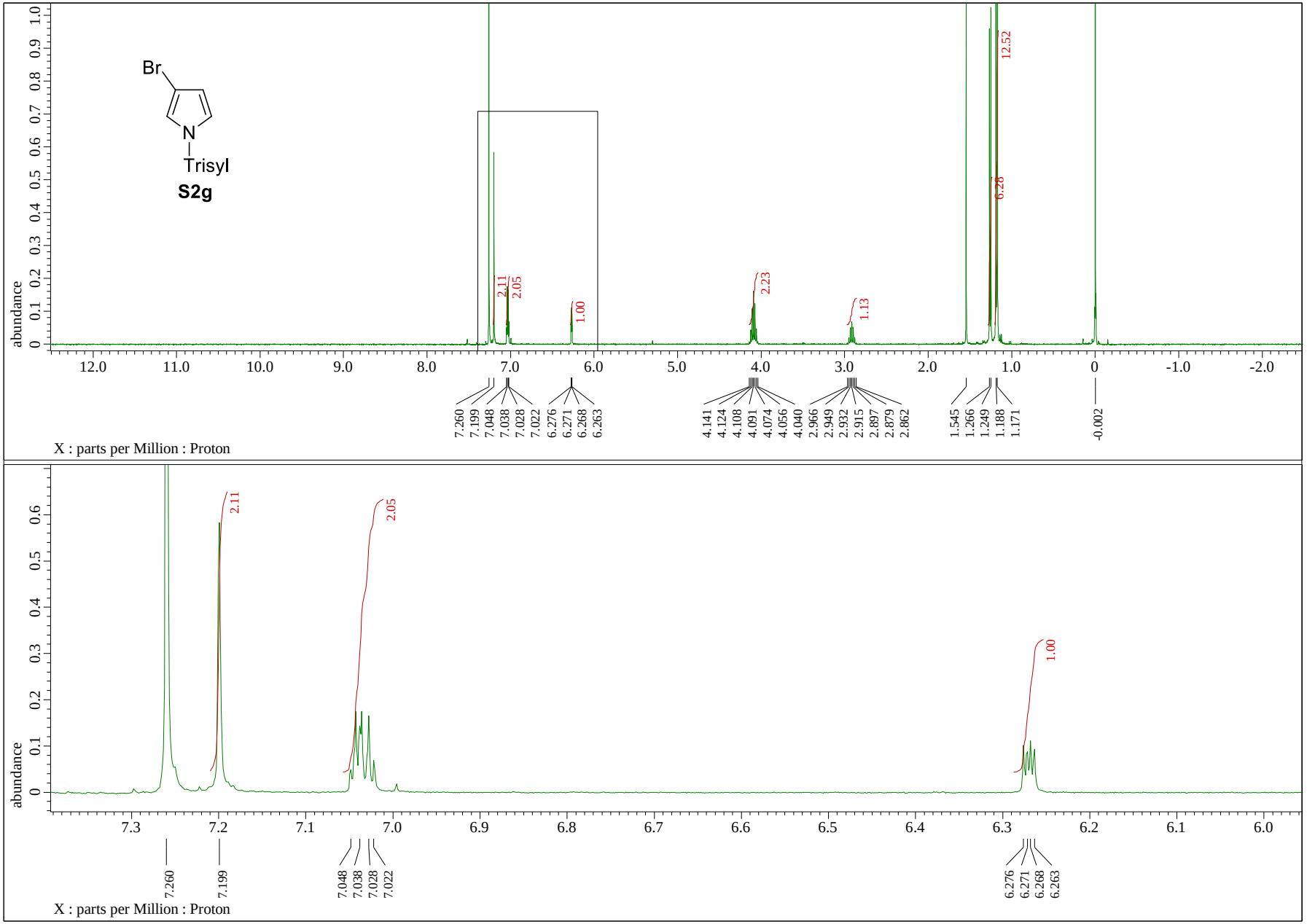
^{1}H NMR (400 MHz, $CDCl_3$)



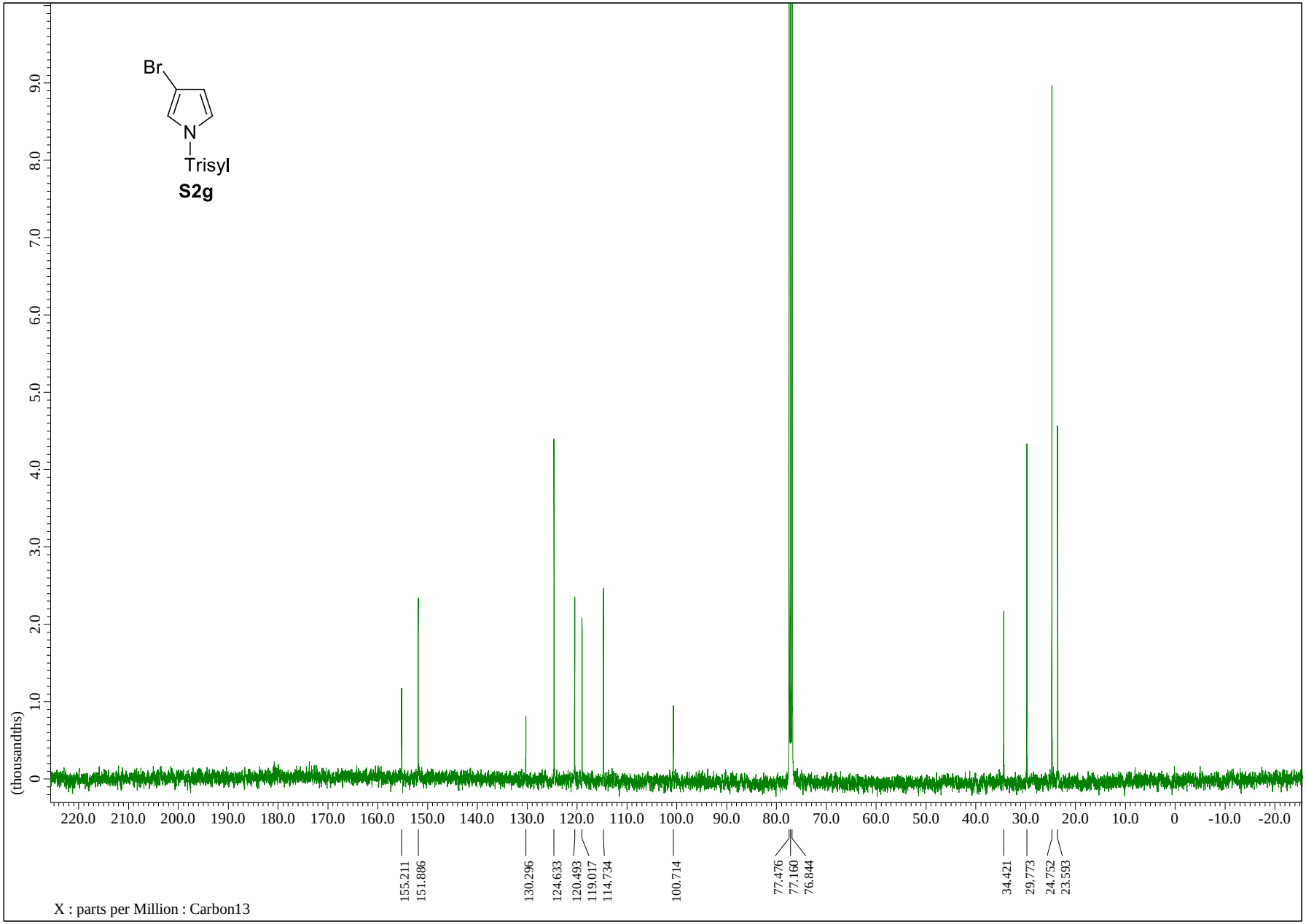
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



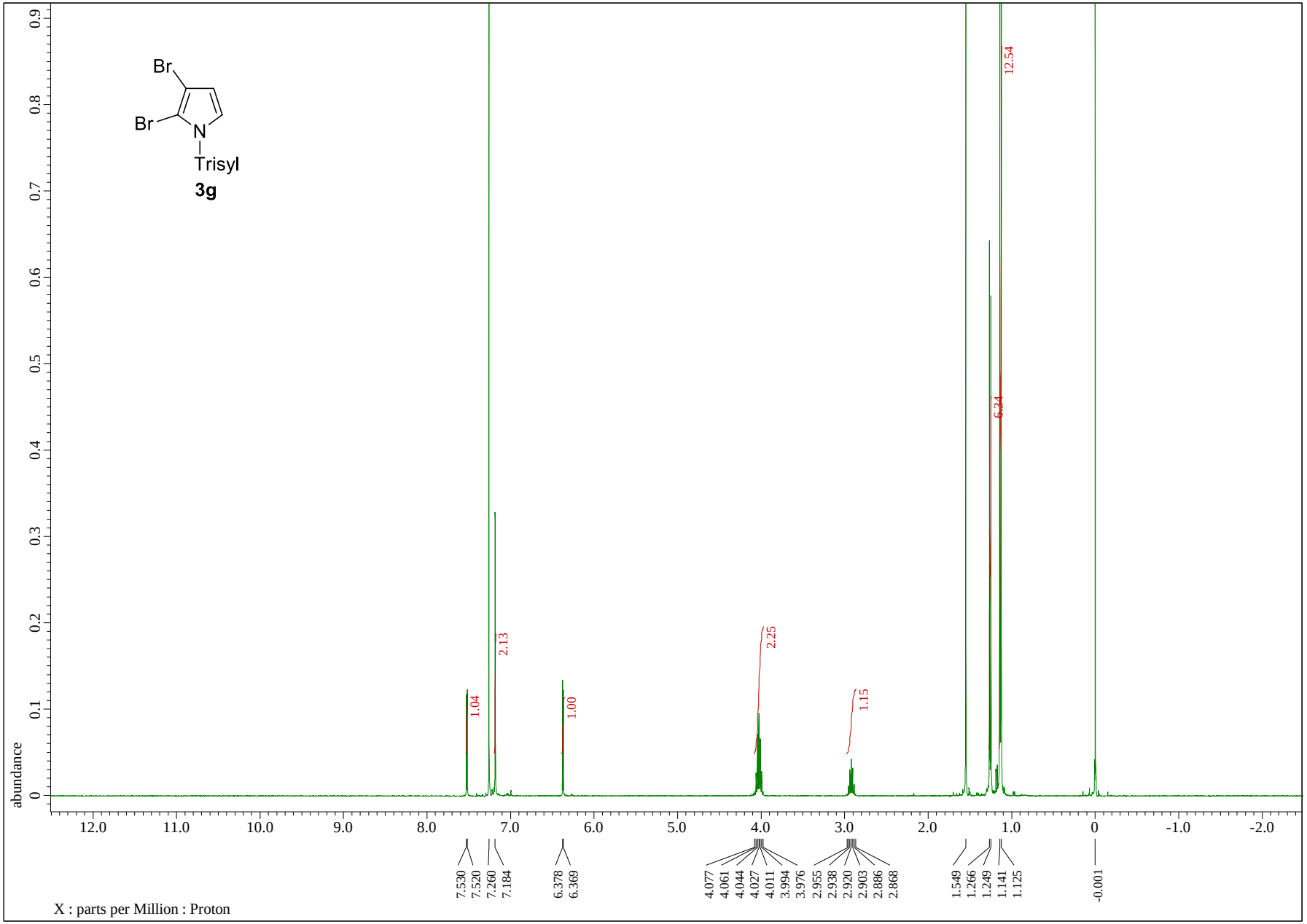
^{1}H NMR (400 MHz, $CDCl_3$)



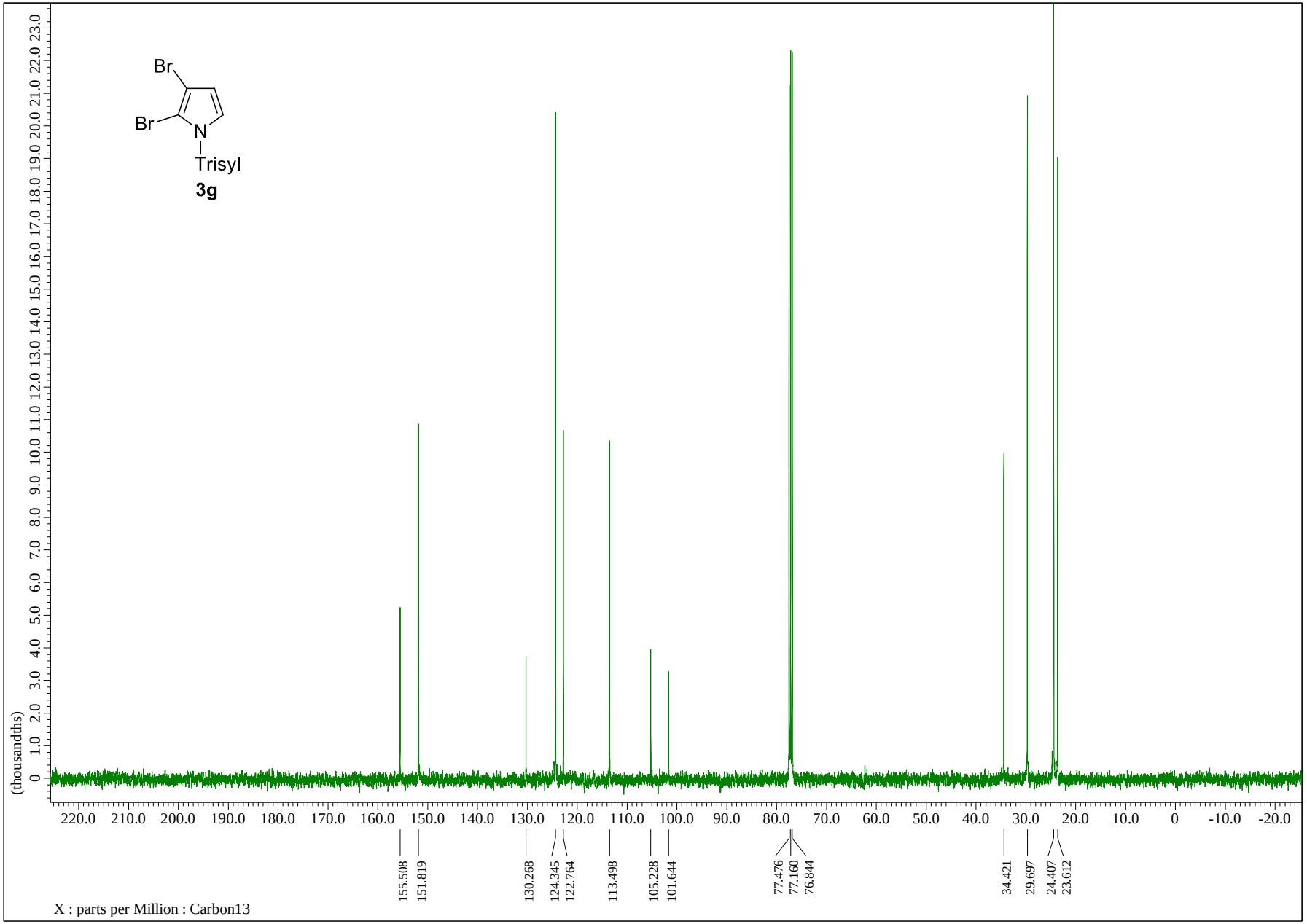
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



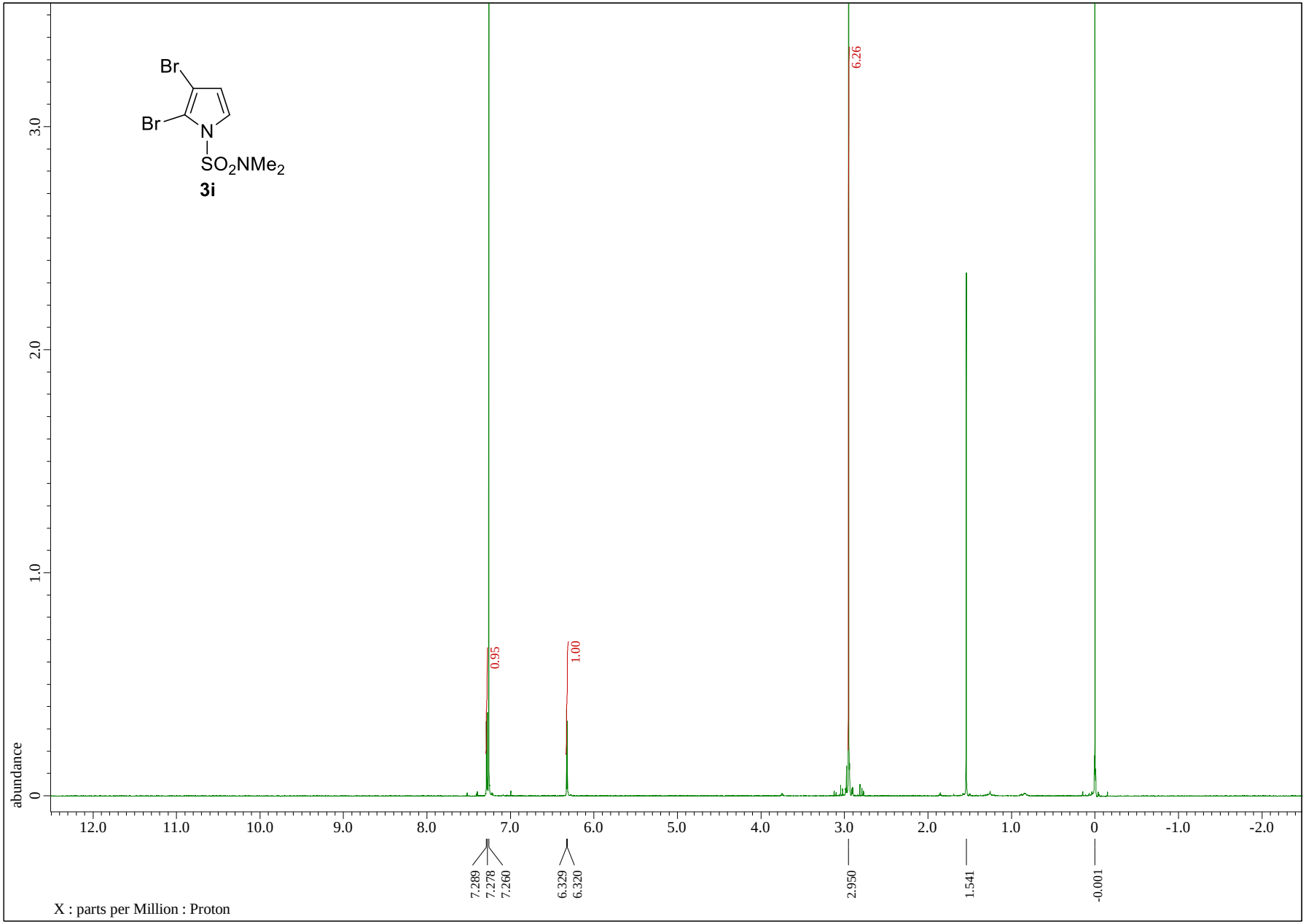
^{1}H NMR (400 MHz, $CDCl_3$)



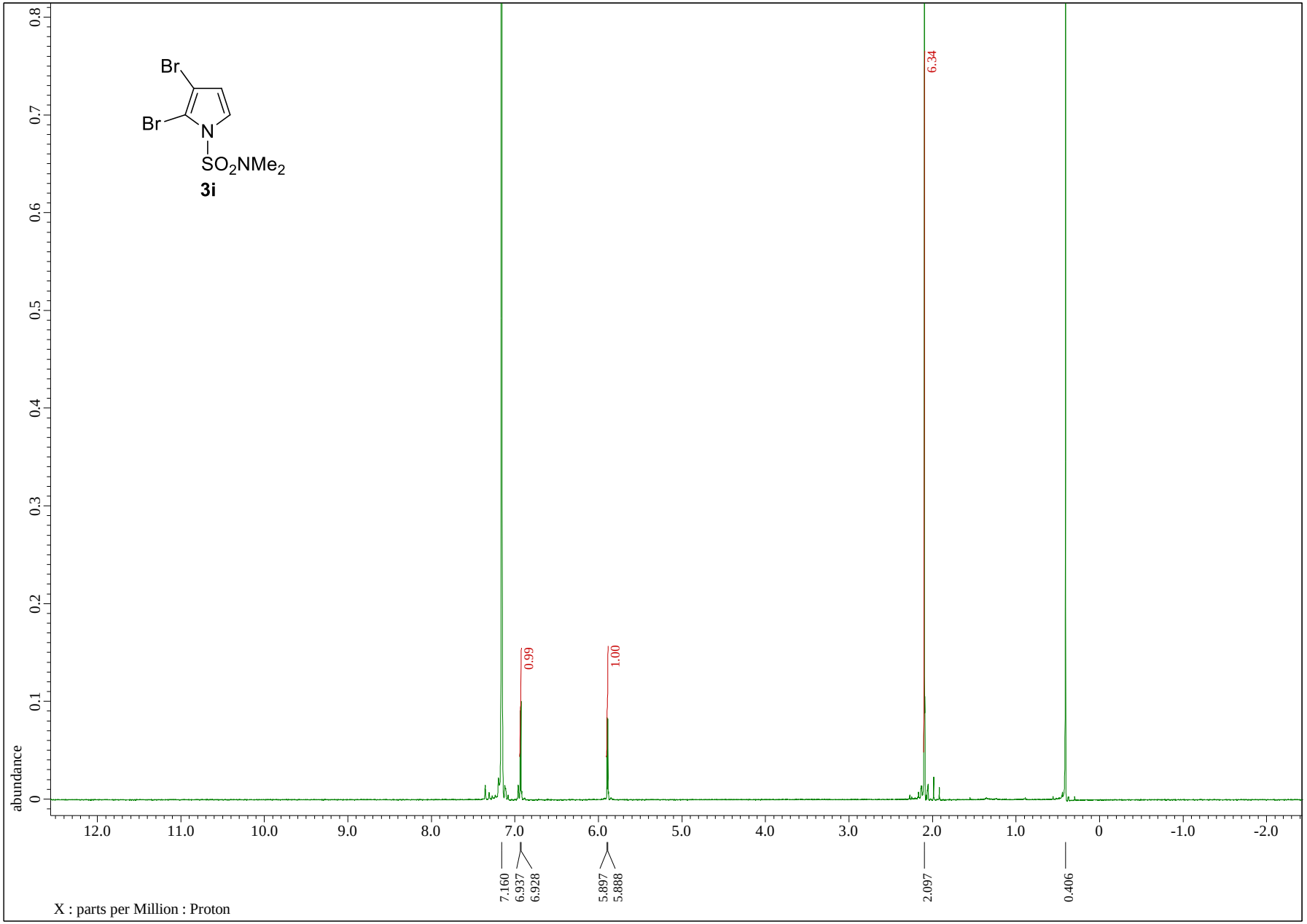
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



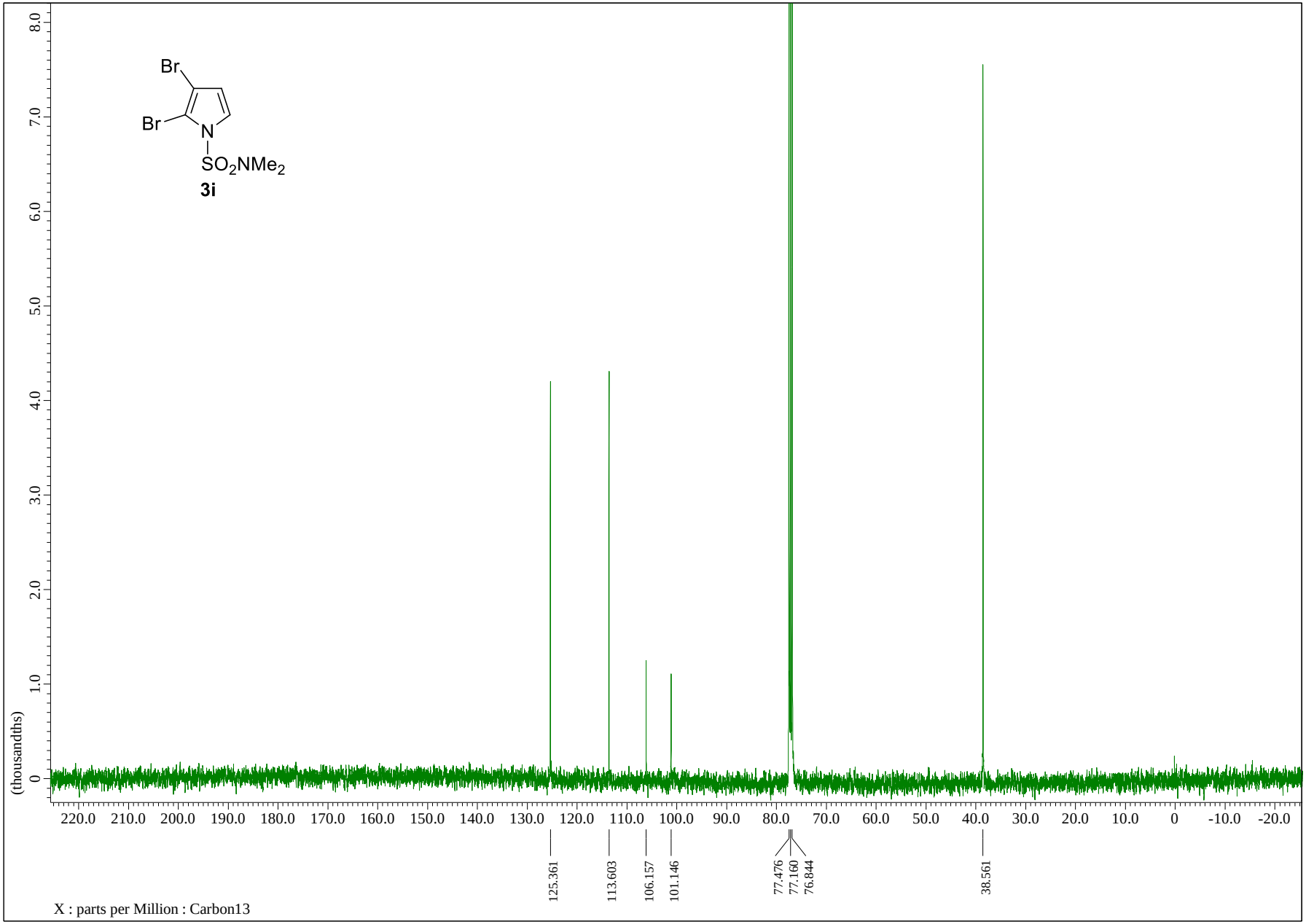
^{1}H NMR (400 MHz, $CDCl_3$)



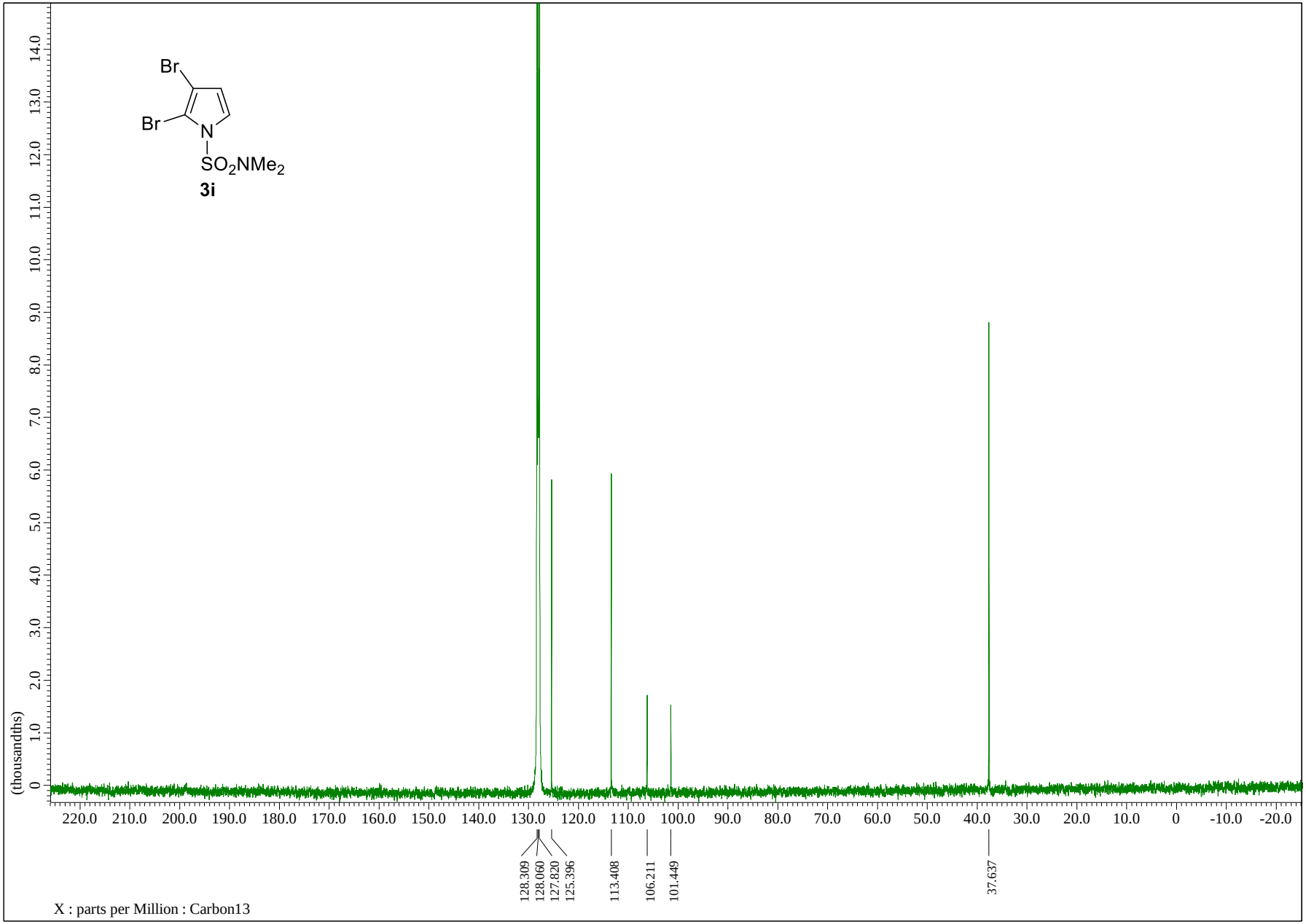
^{1}H NMR (400 MHz, benzene-d_6)



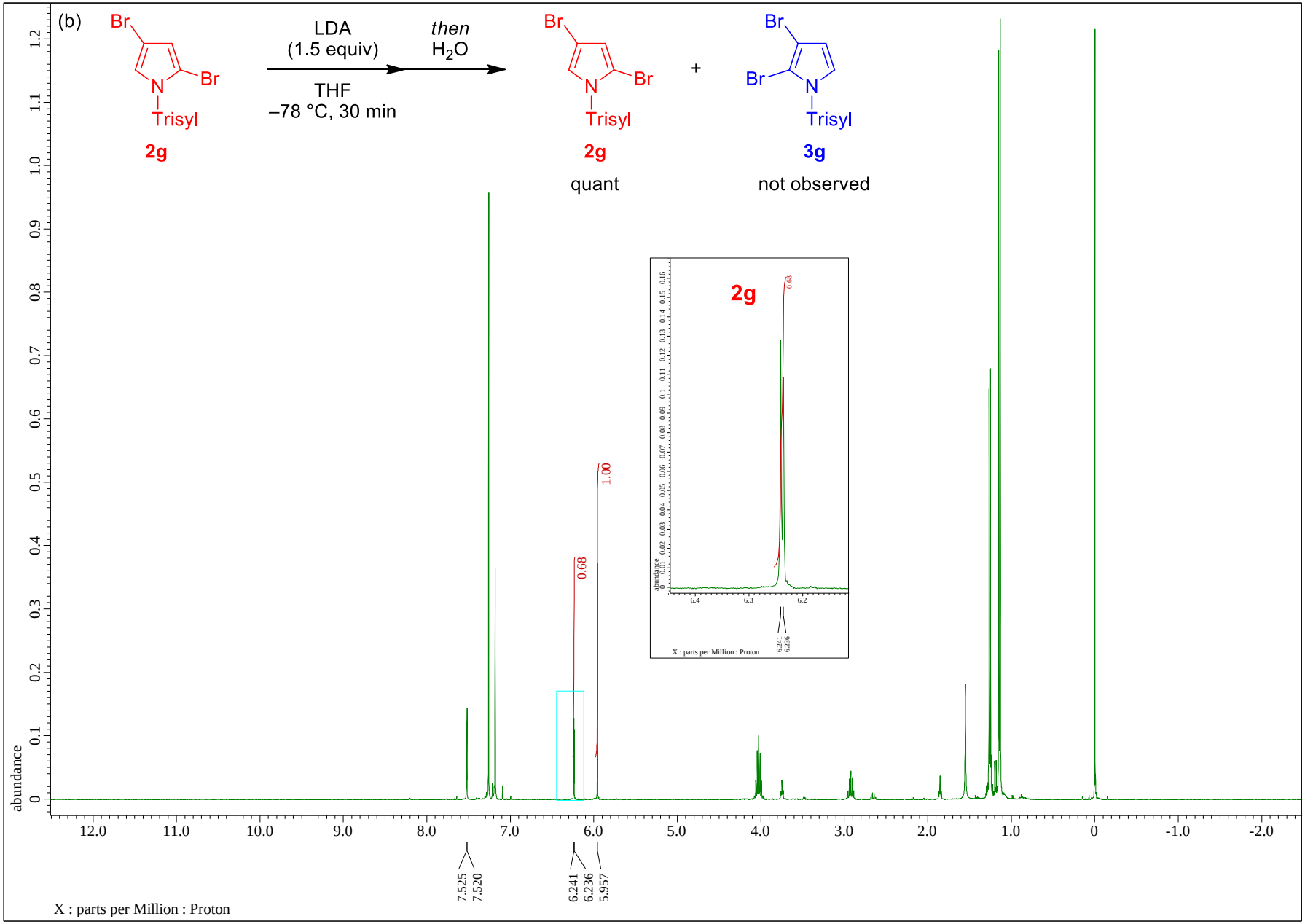
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



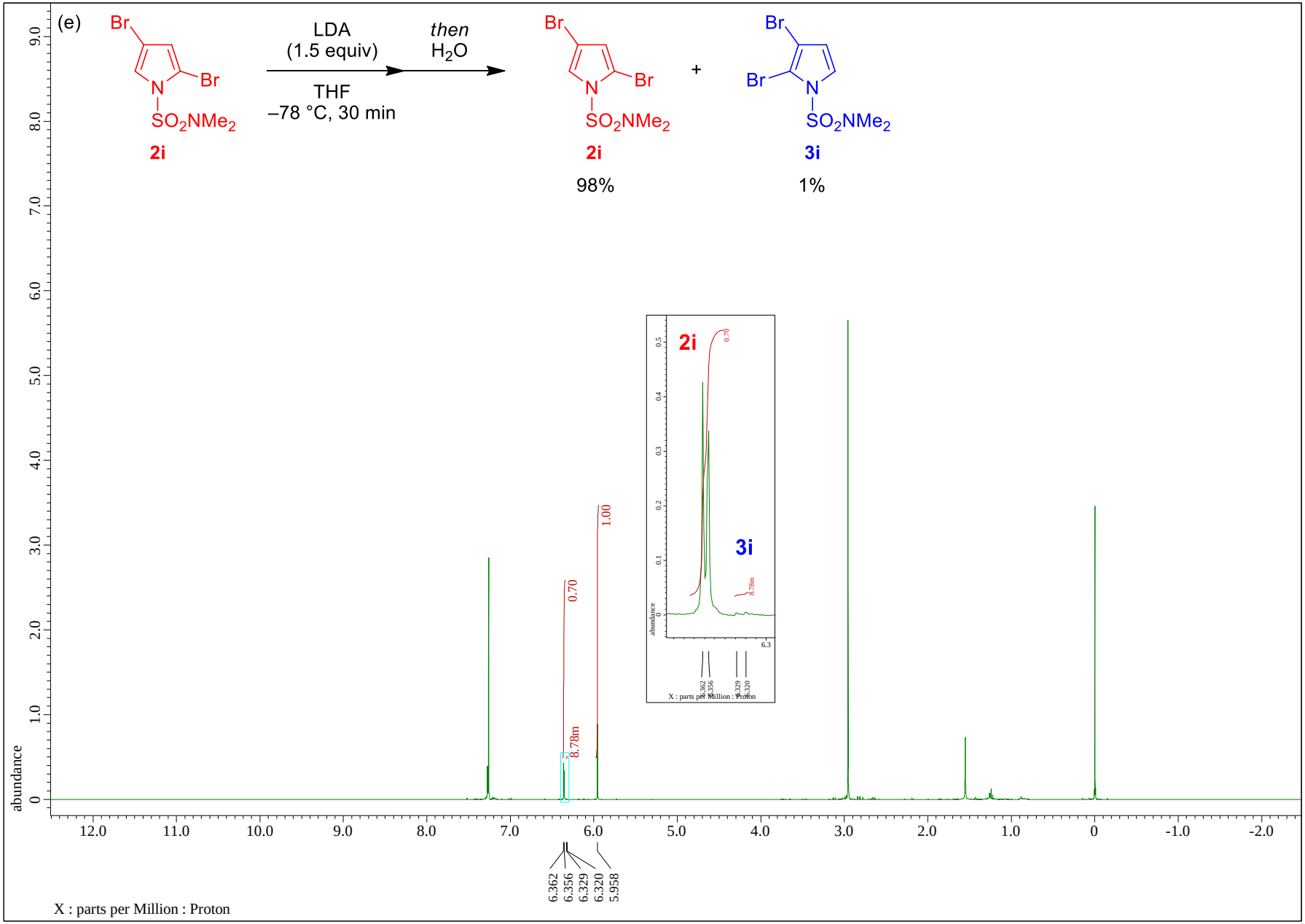
$^{13}C\{^{1}H\}$ NMR (100 MHz, benzene-d_6)



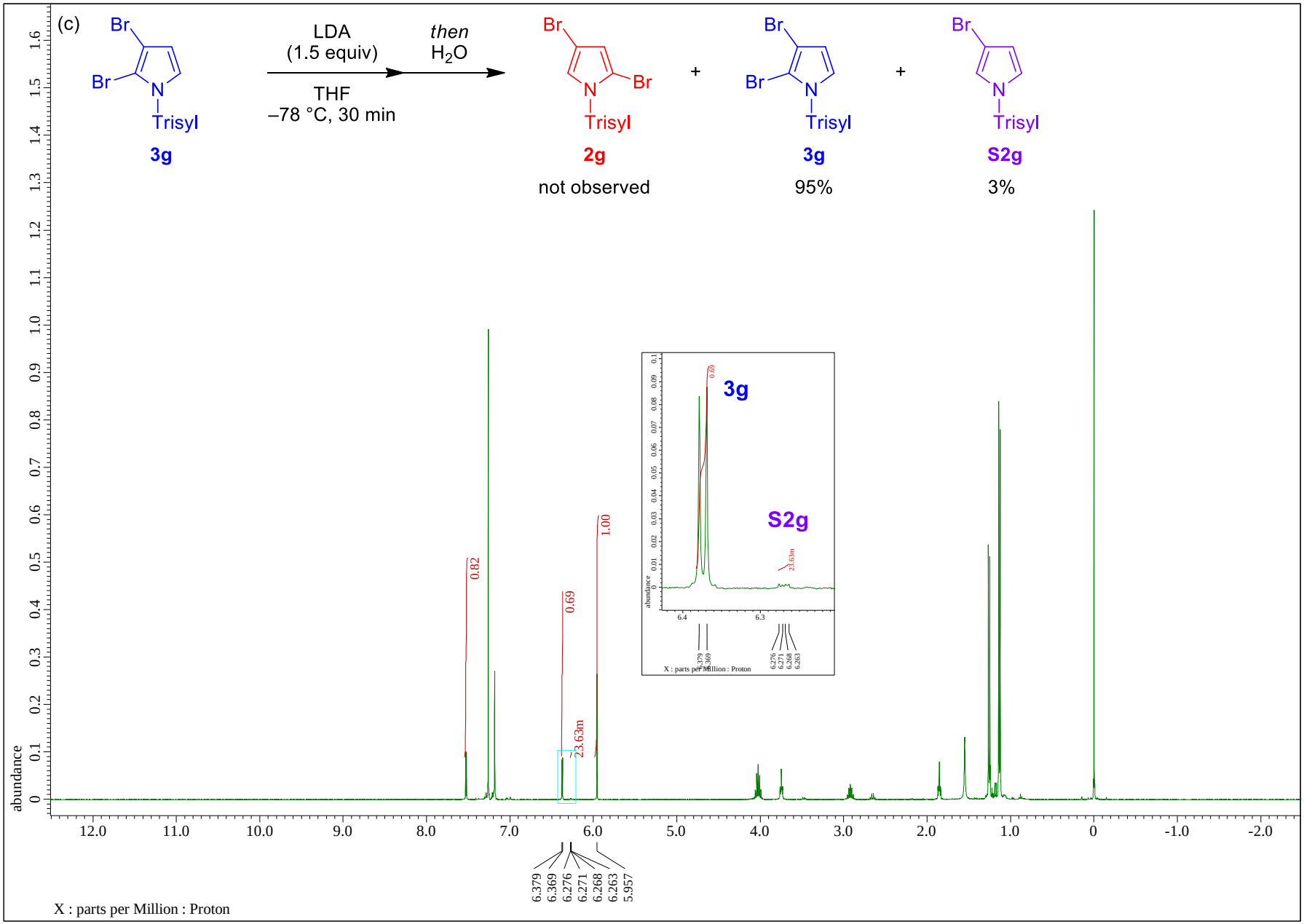
^{1}H NMR (400 MHz, $CDCl_3$)



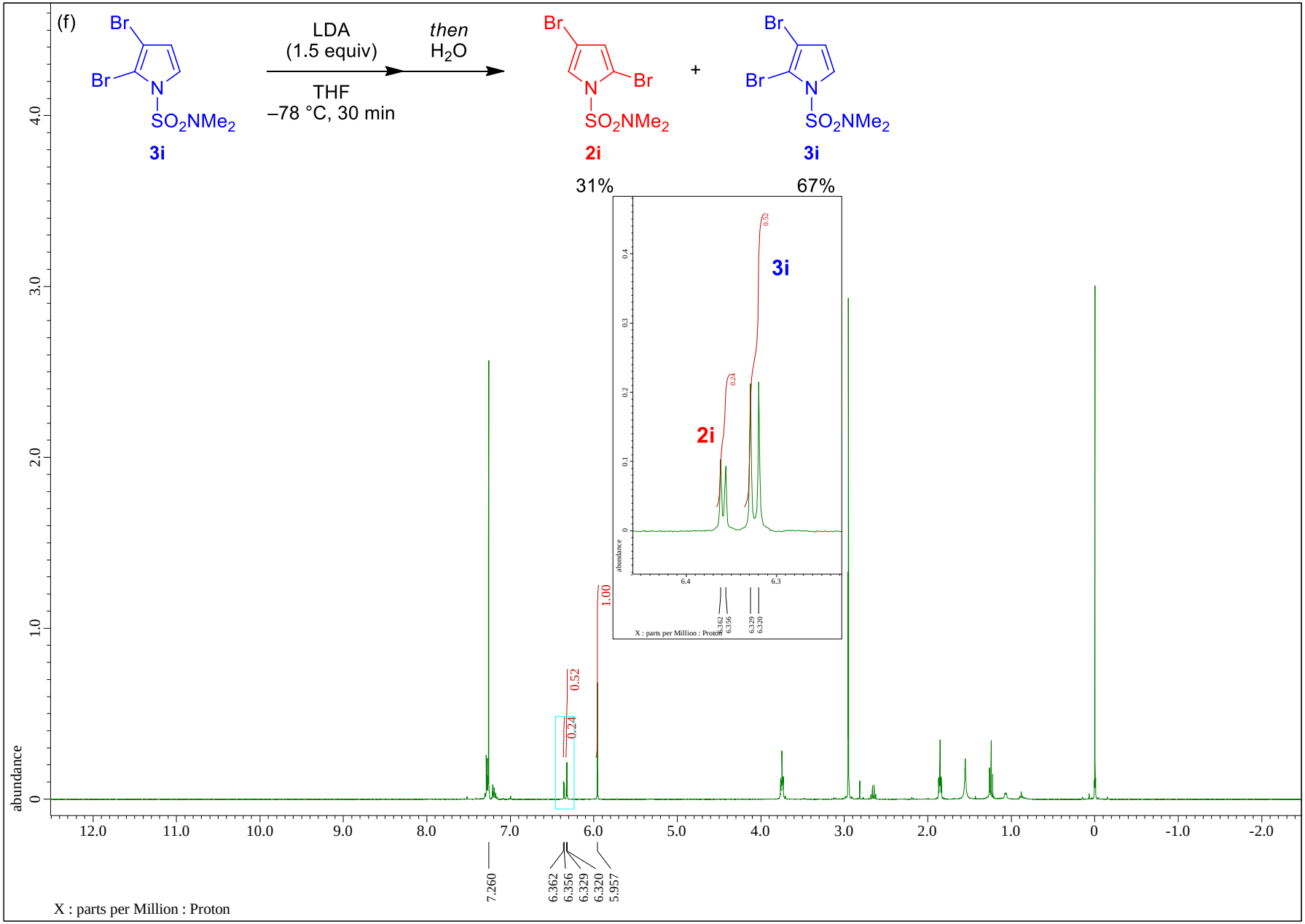
^{1}H NMR (400 MHz, $CDCl_3$)



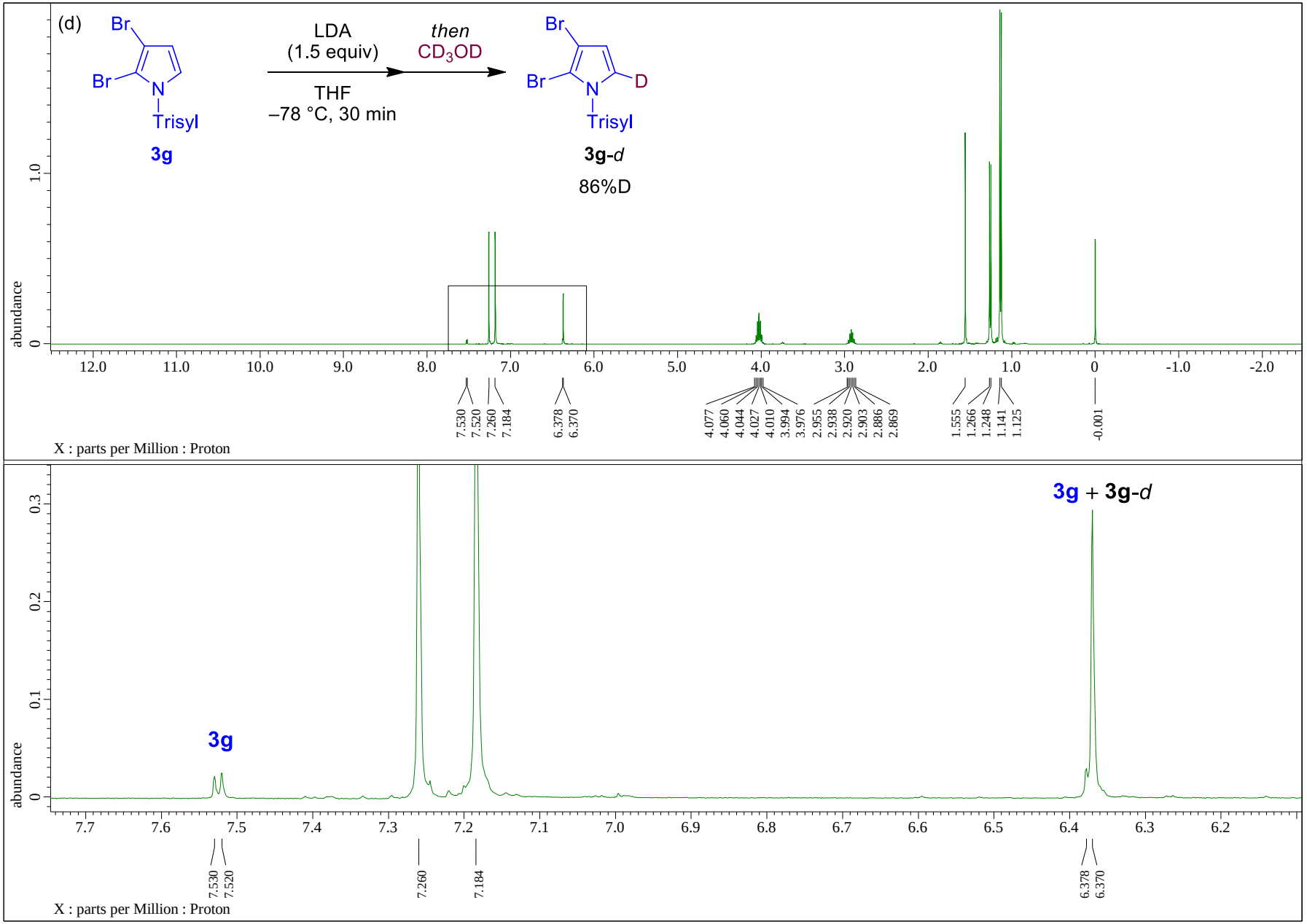
^{1}H NMR (400 MHz, $CDCl_3$)



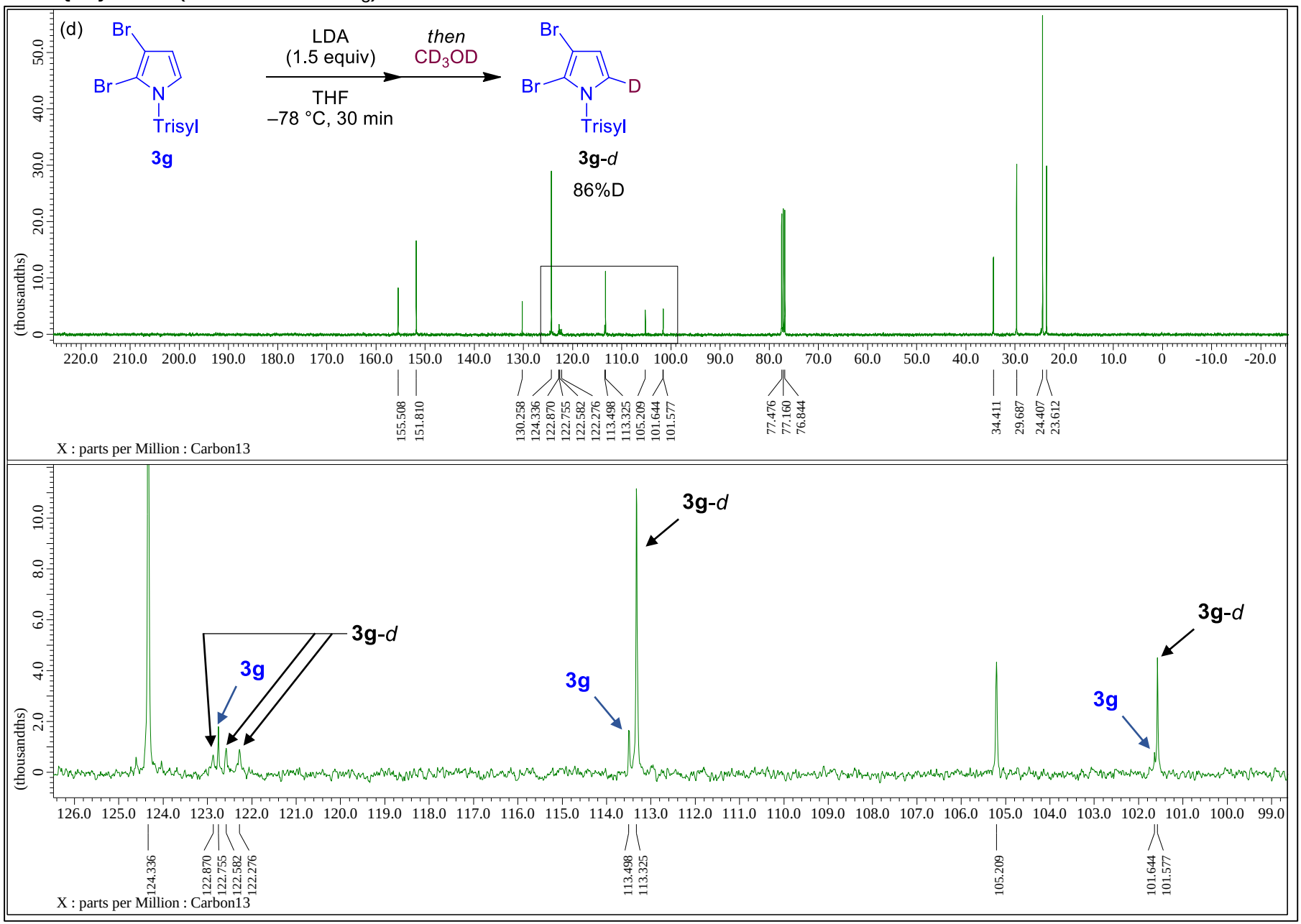
^{1}H NMR (400 MHz, $CDCl_3$)



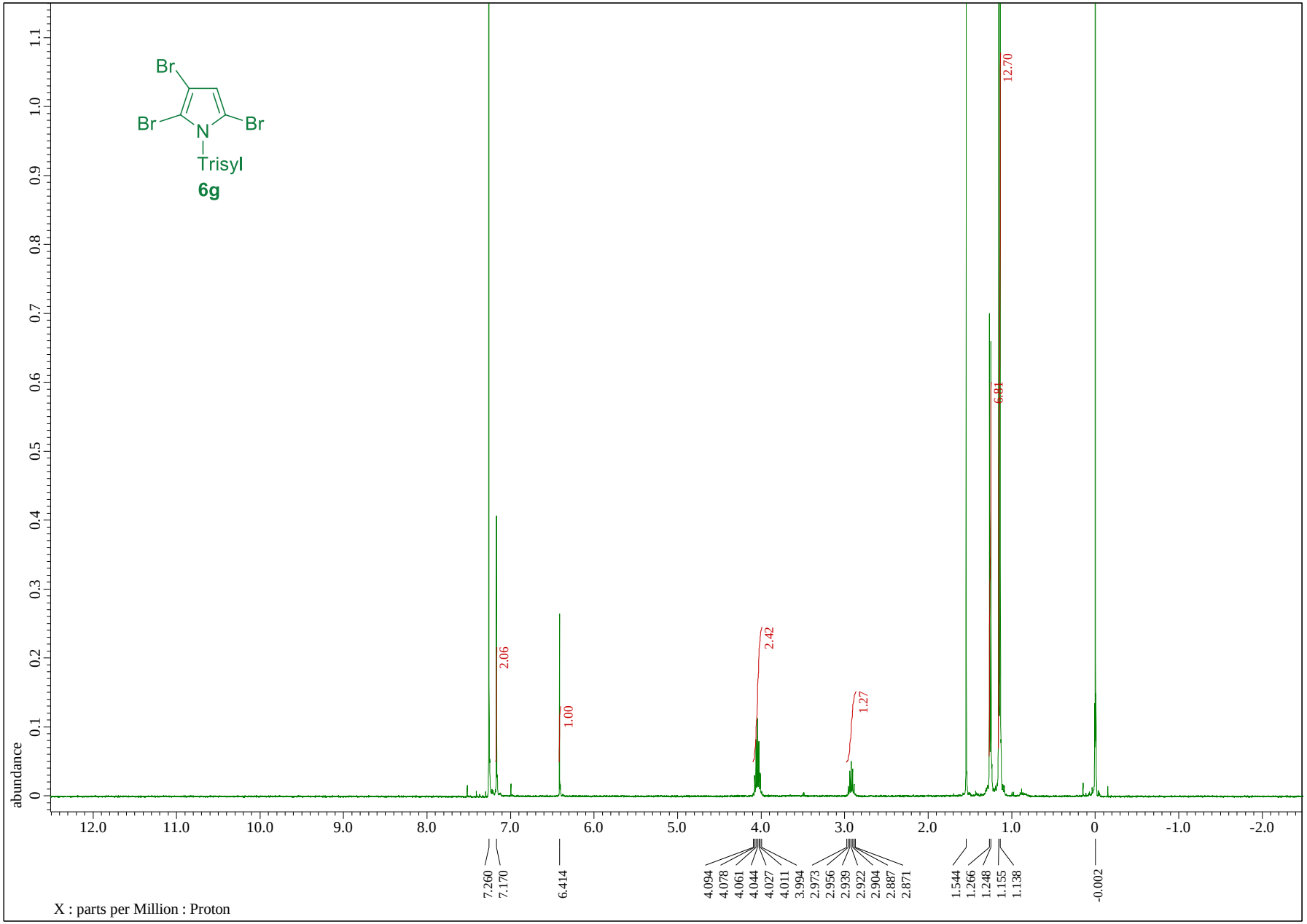
^{1}H NMR (400 MHz, $CDCl_3$)



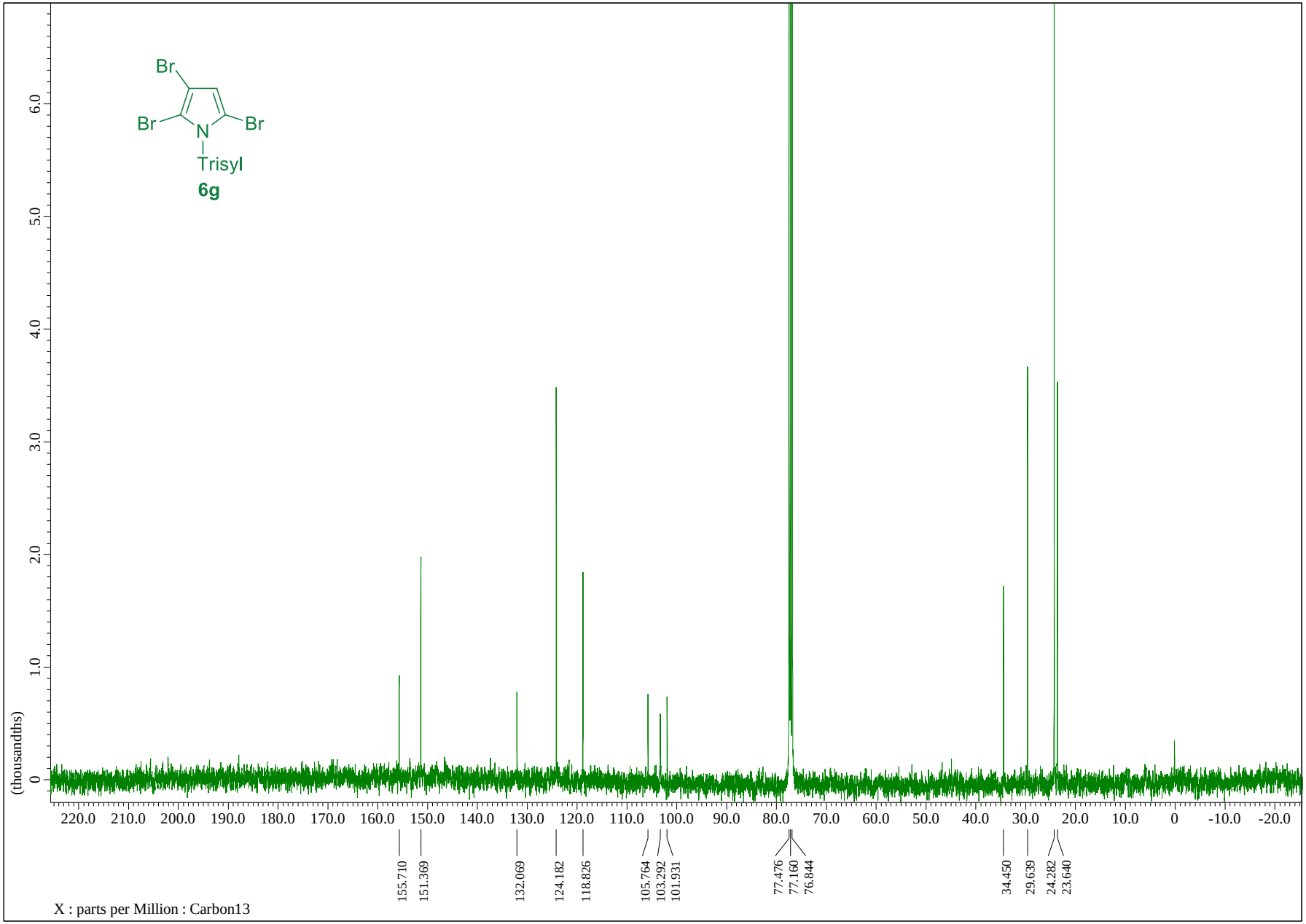
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



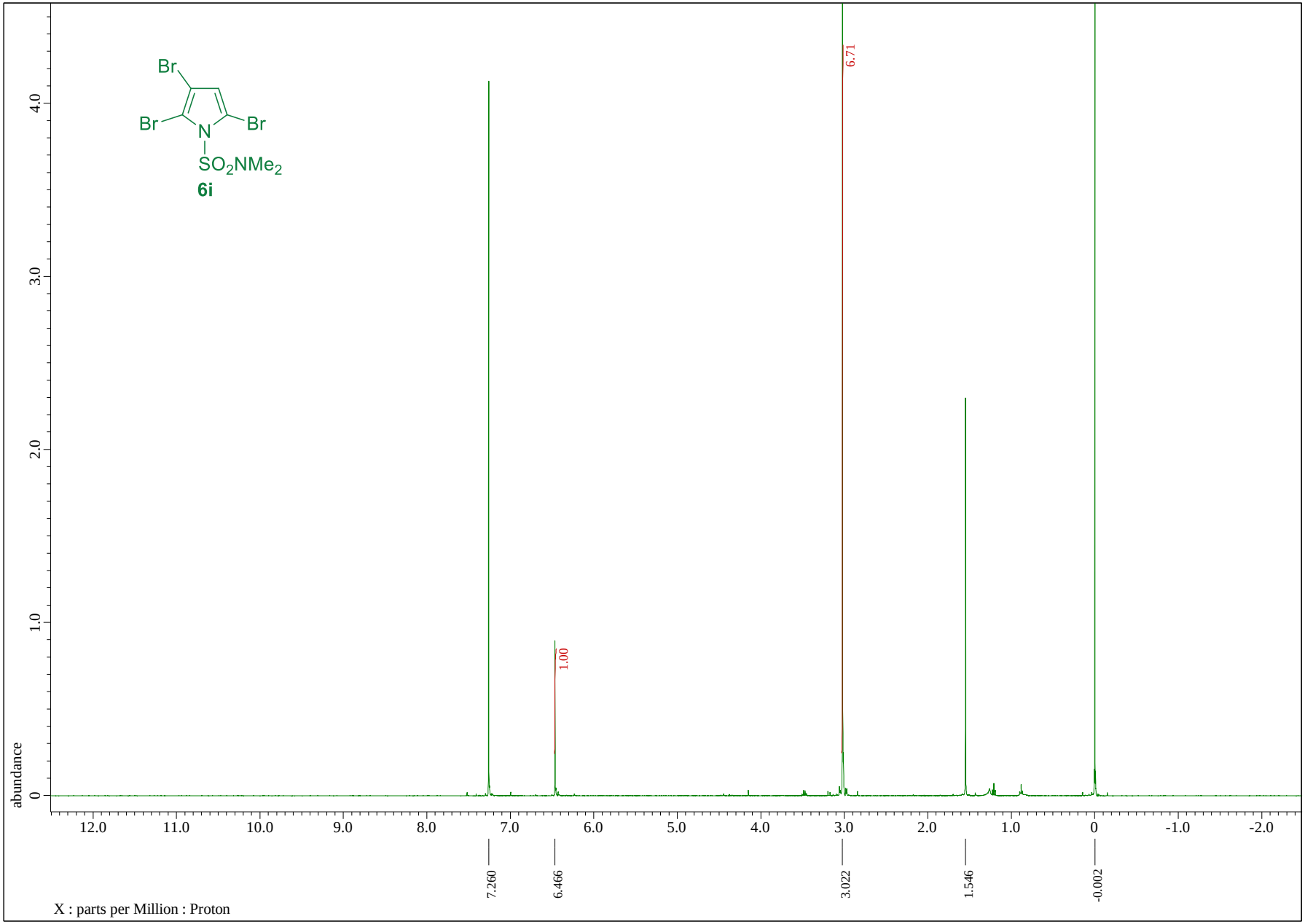
^{1}H NMR (400 MHz, $CDCl_3$)



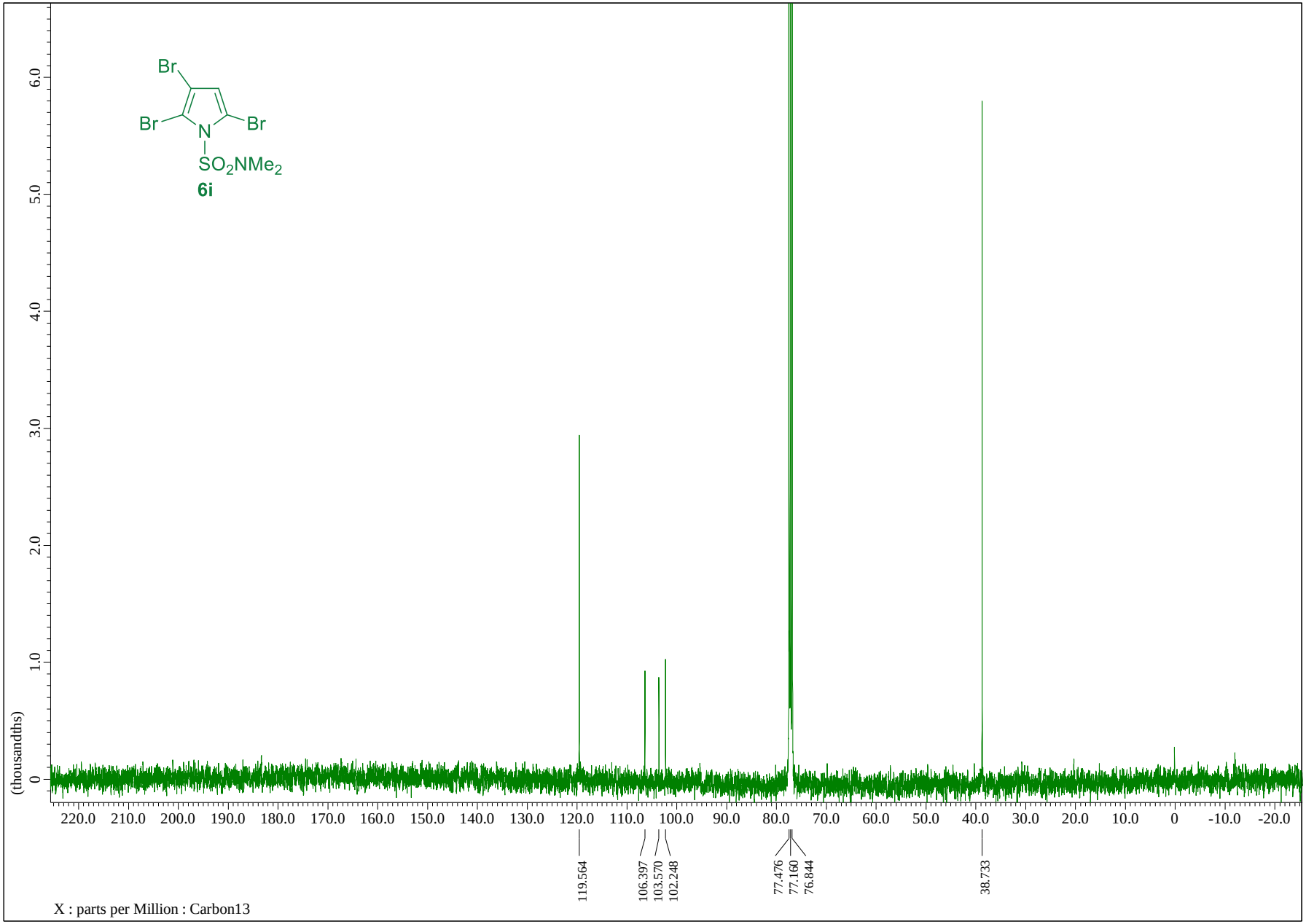
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



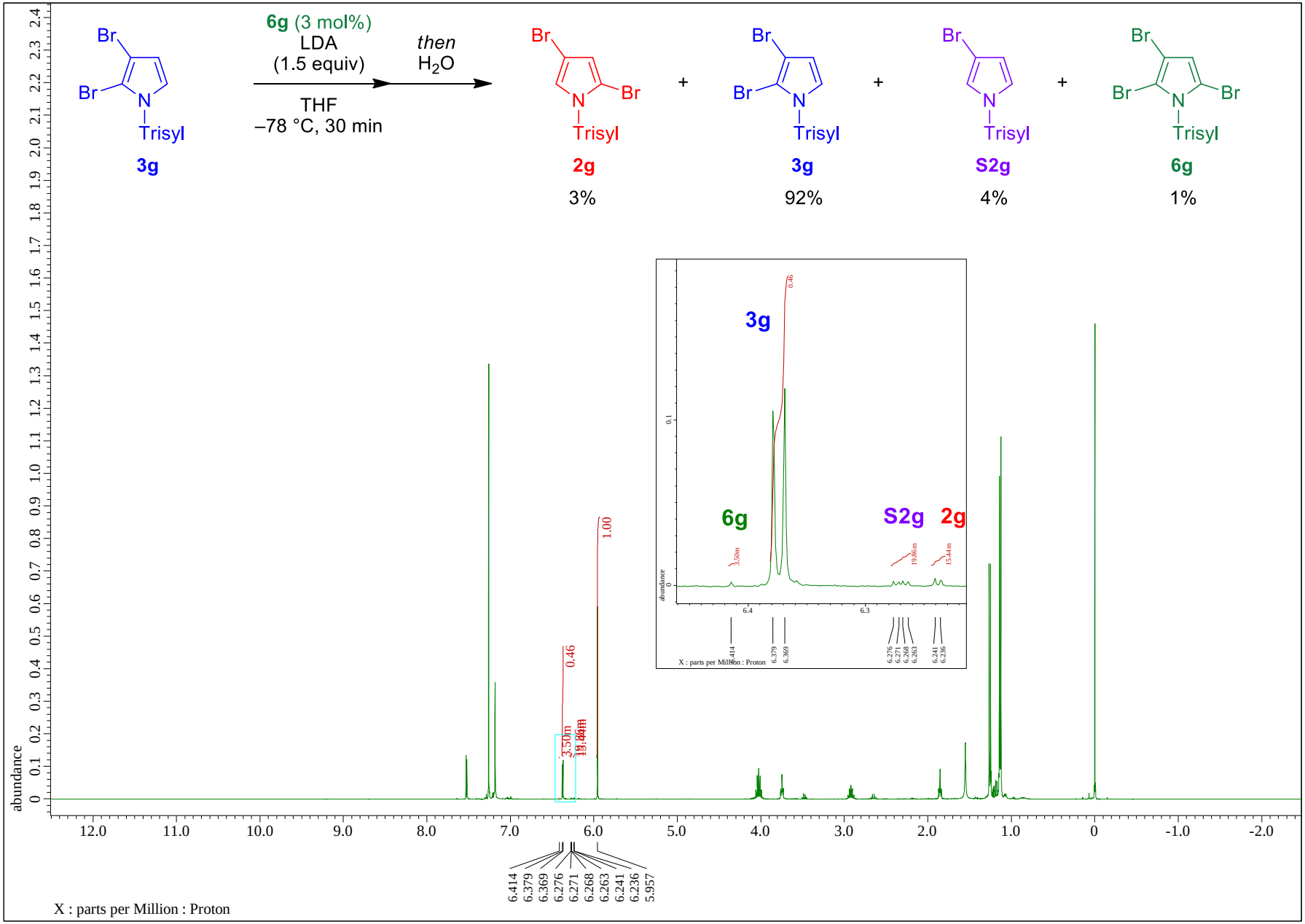
^{1}H NMR (400 MHz, $CDCl_3$)



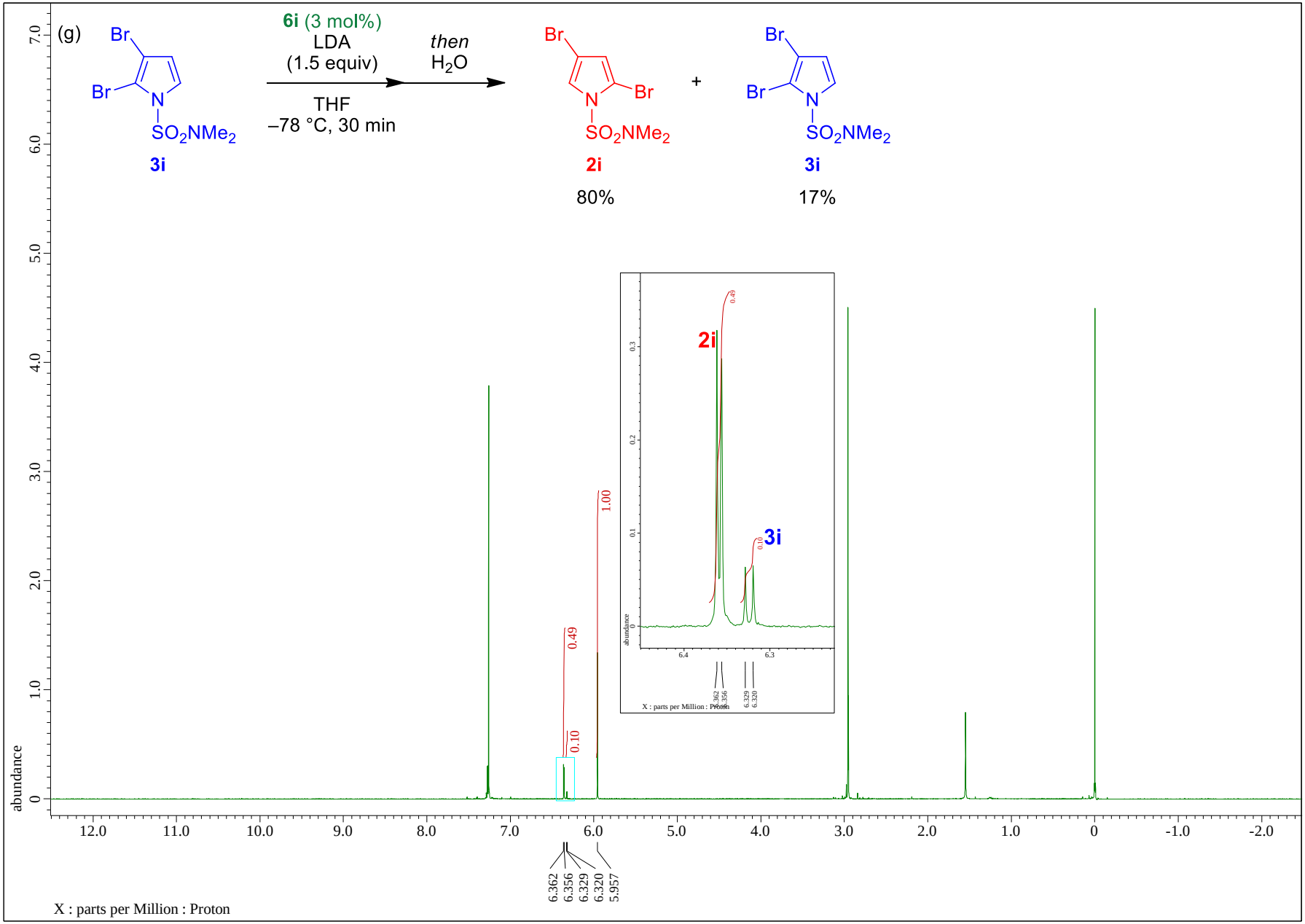
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



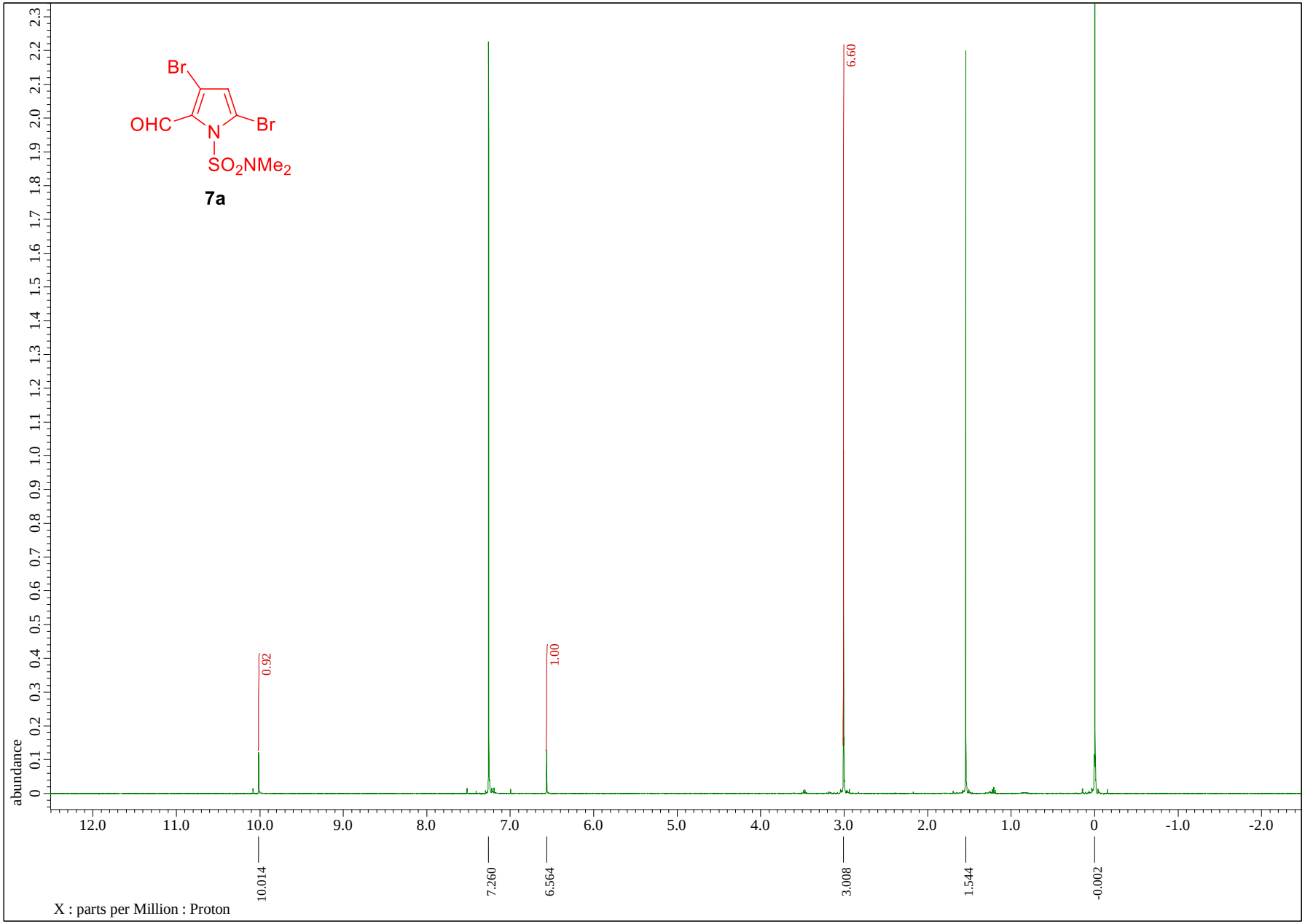
^{1}H NMR (400 MHz, $CDCl_3$)



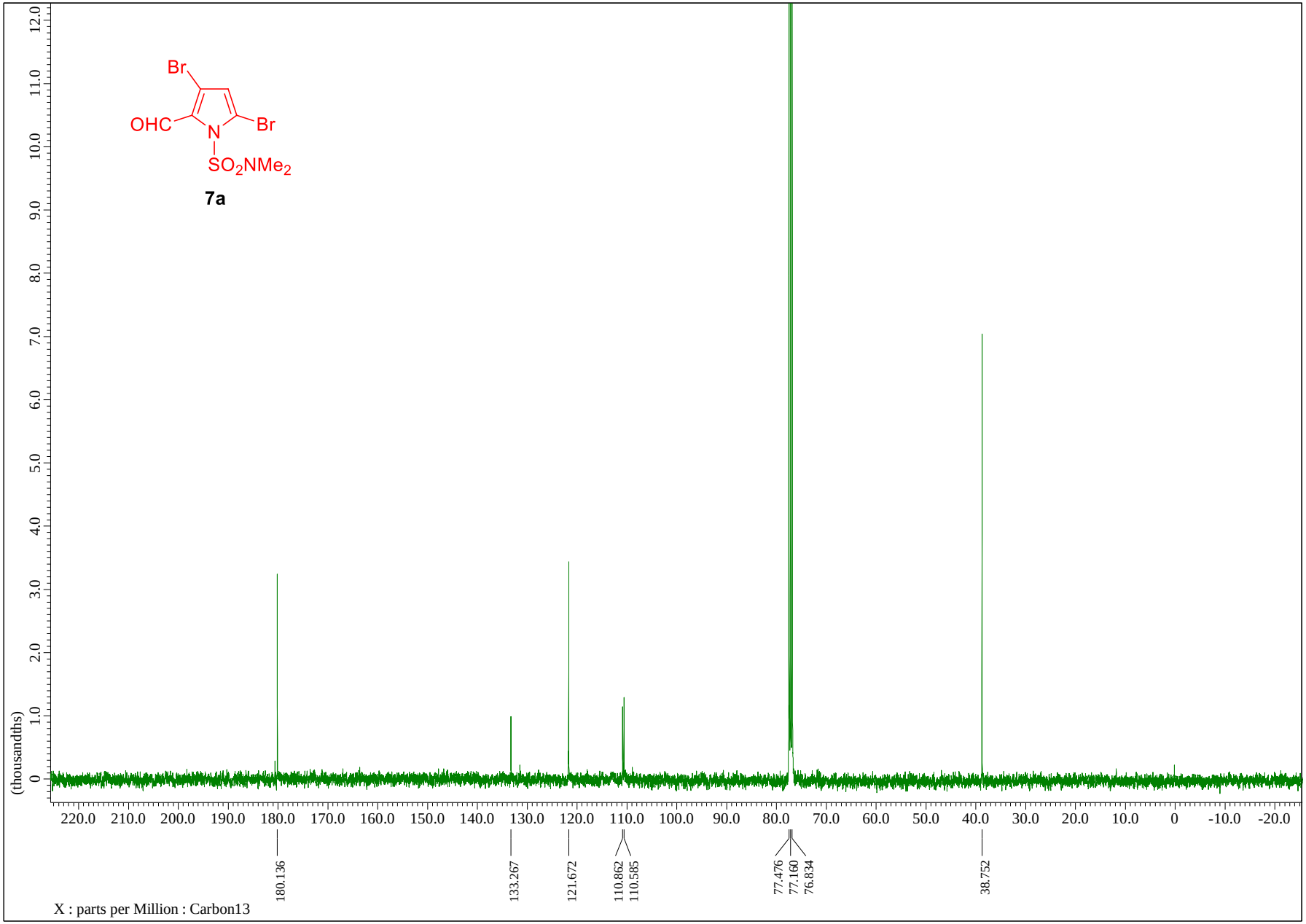
^{1}H NMR (400 MHz, $CDCl_3$)



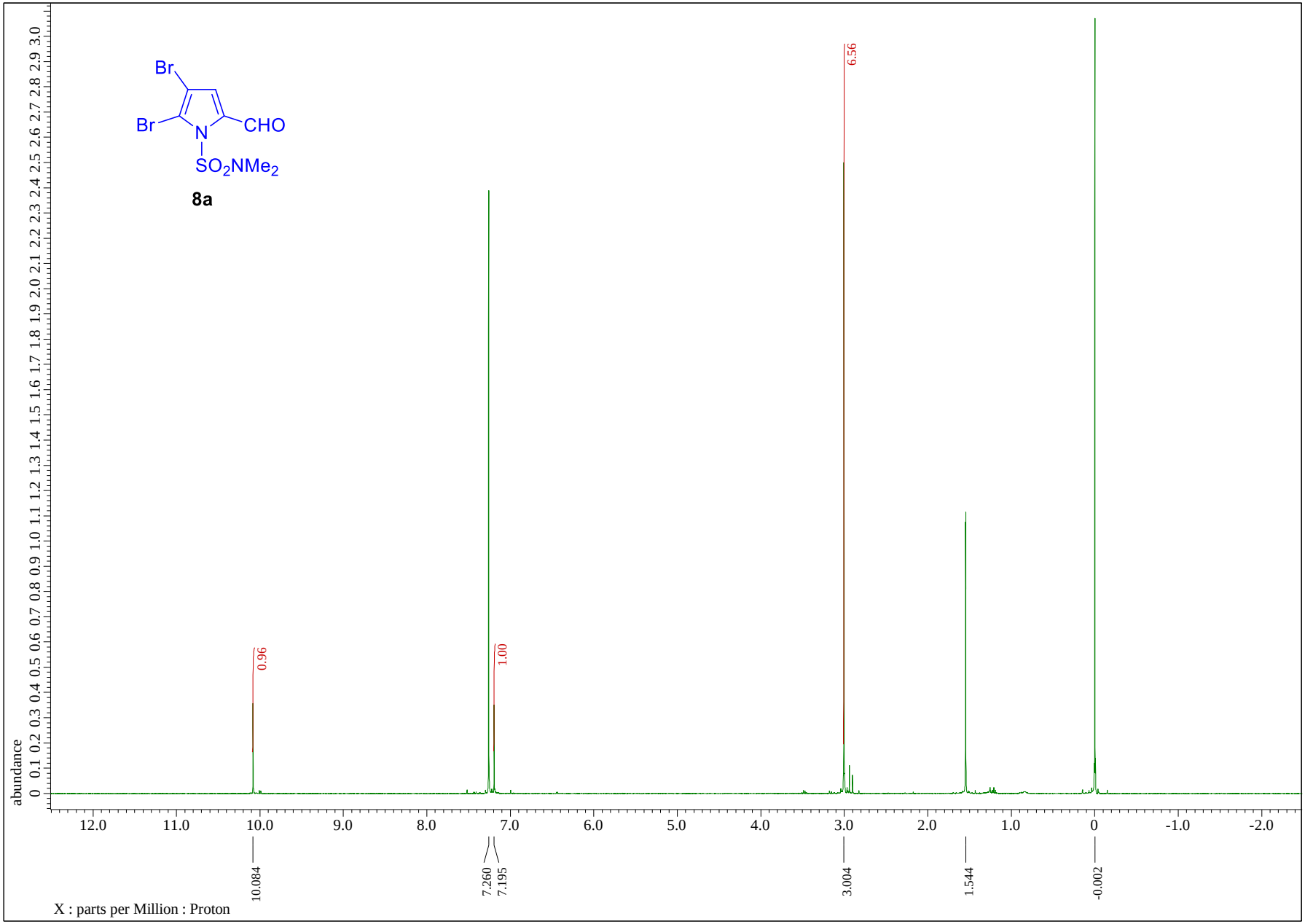
^{1}H NMR (400 MHz, $CDCl_3$)



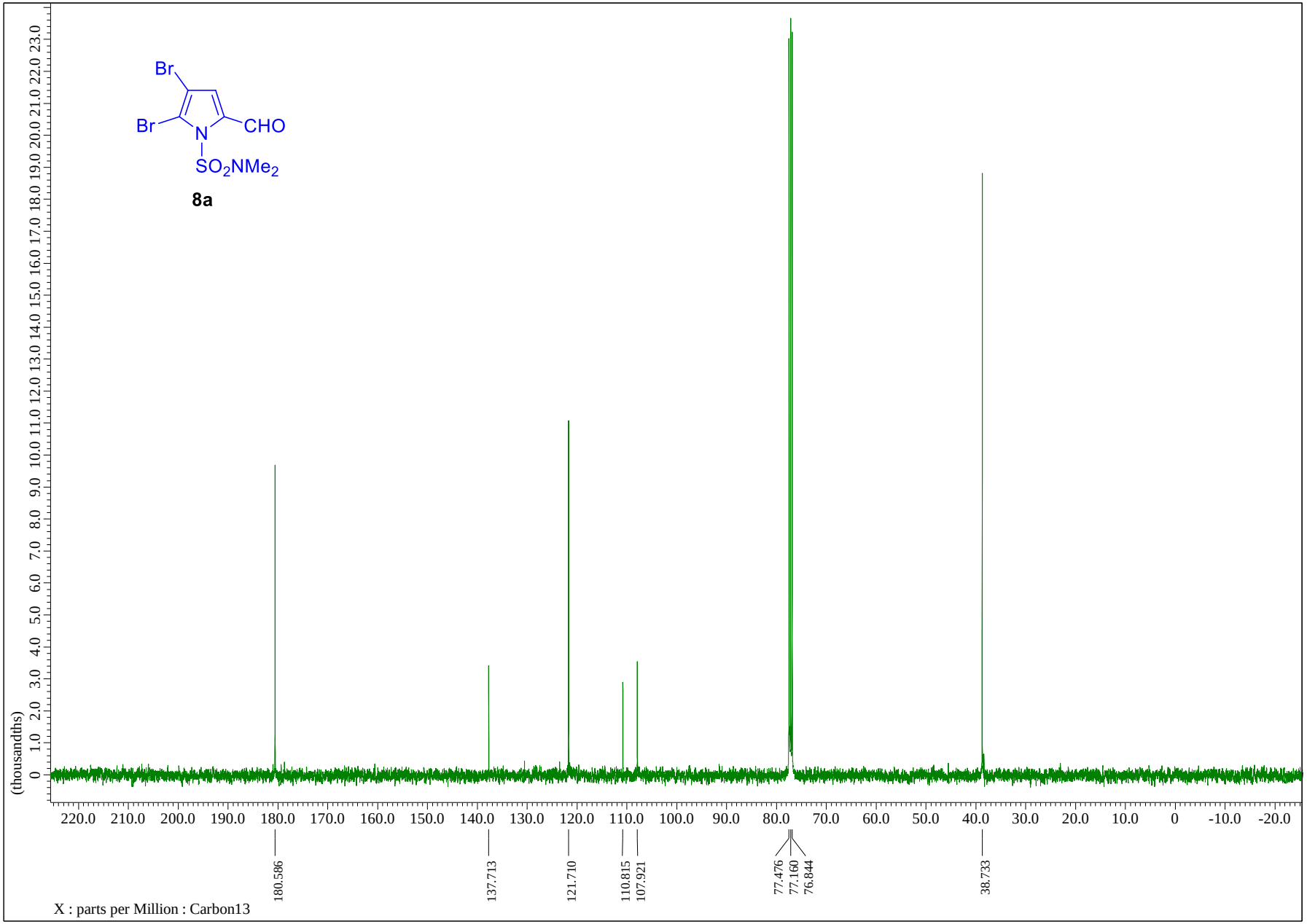
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



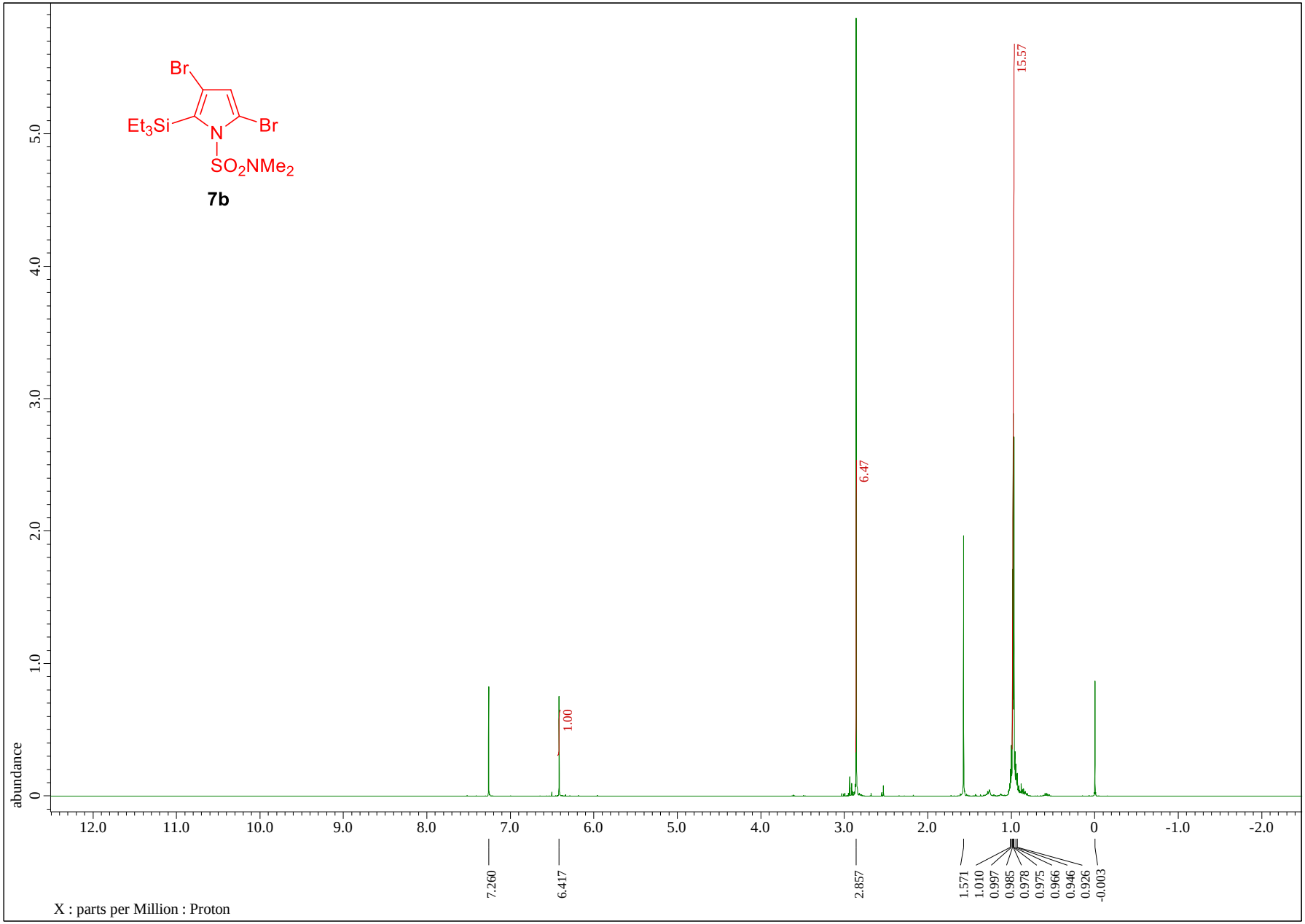
^{1}H NMR (400 MHz, $CDCl_3$)



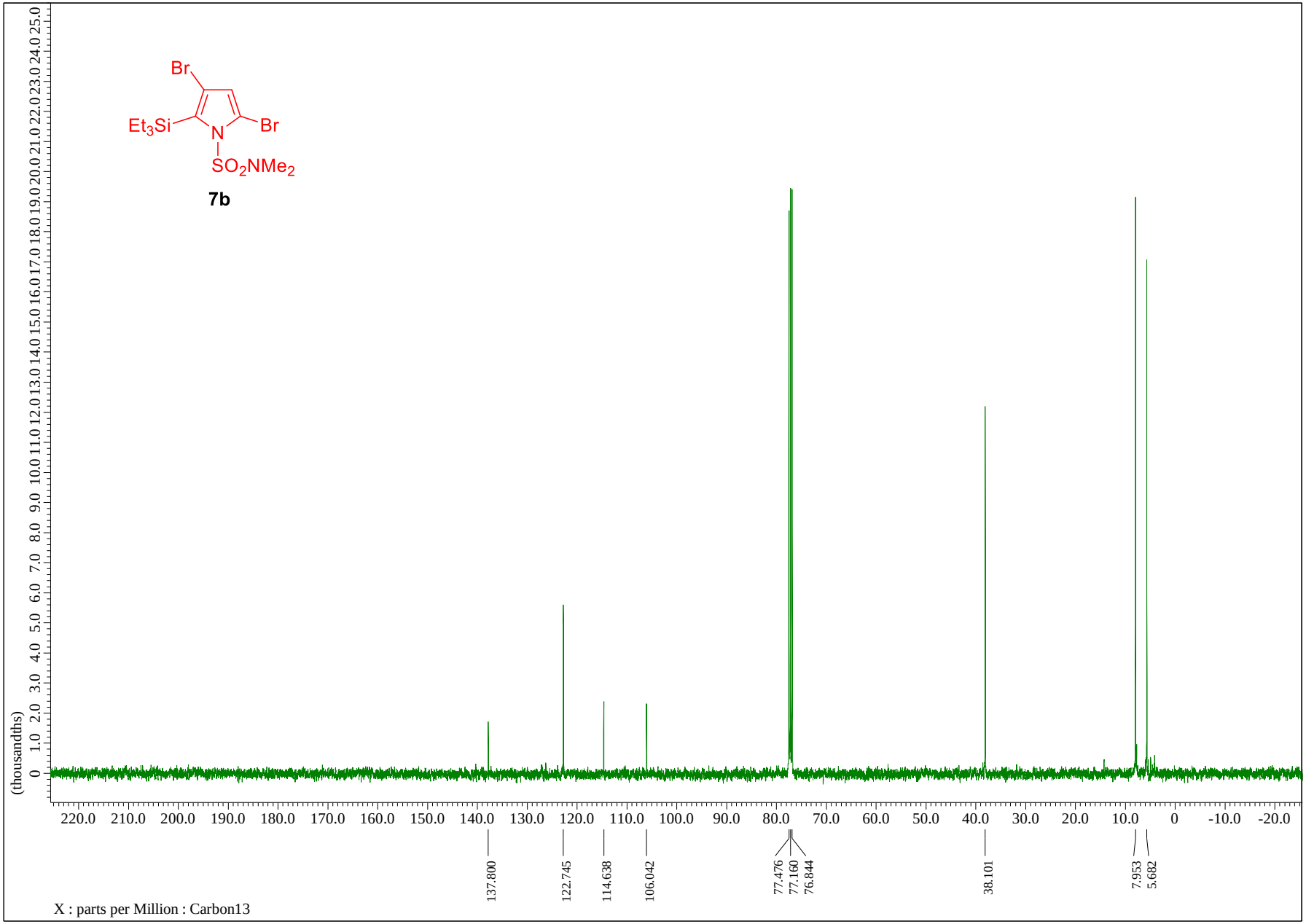
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



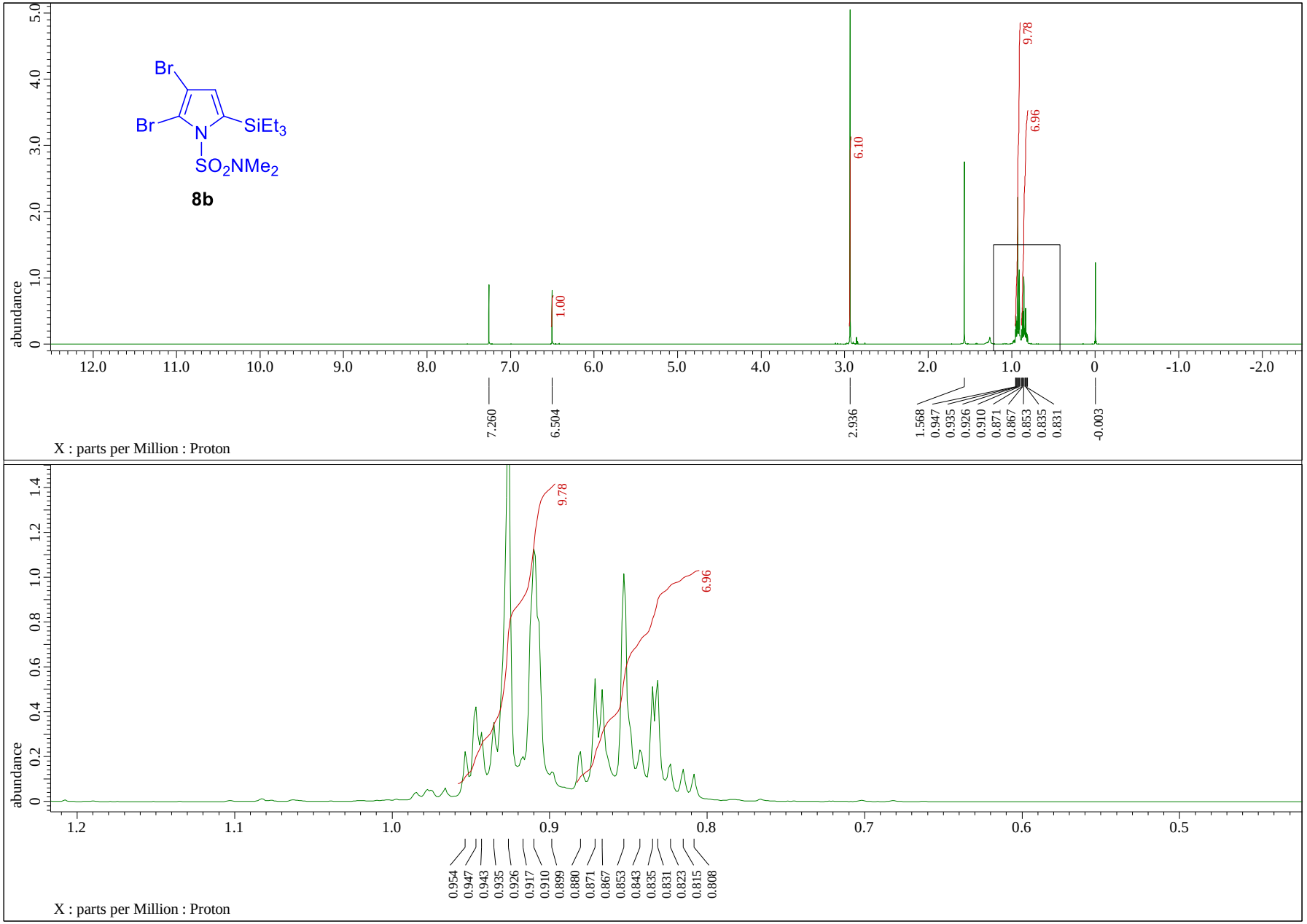
^{1}H NMR (400 MHz, $CDCl_3$)



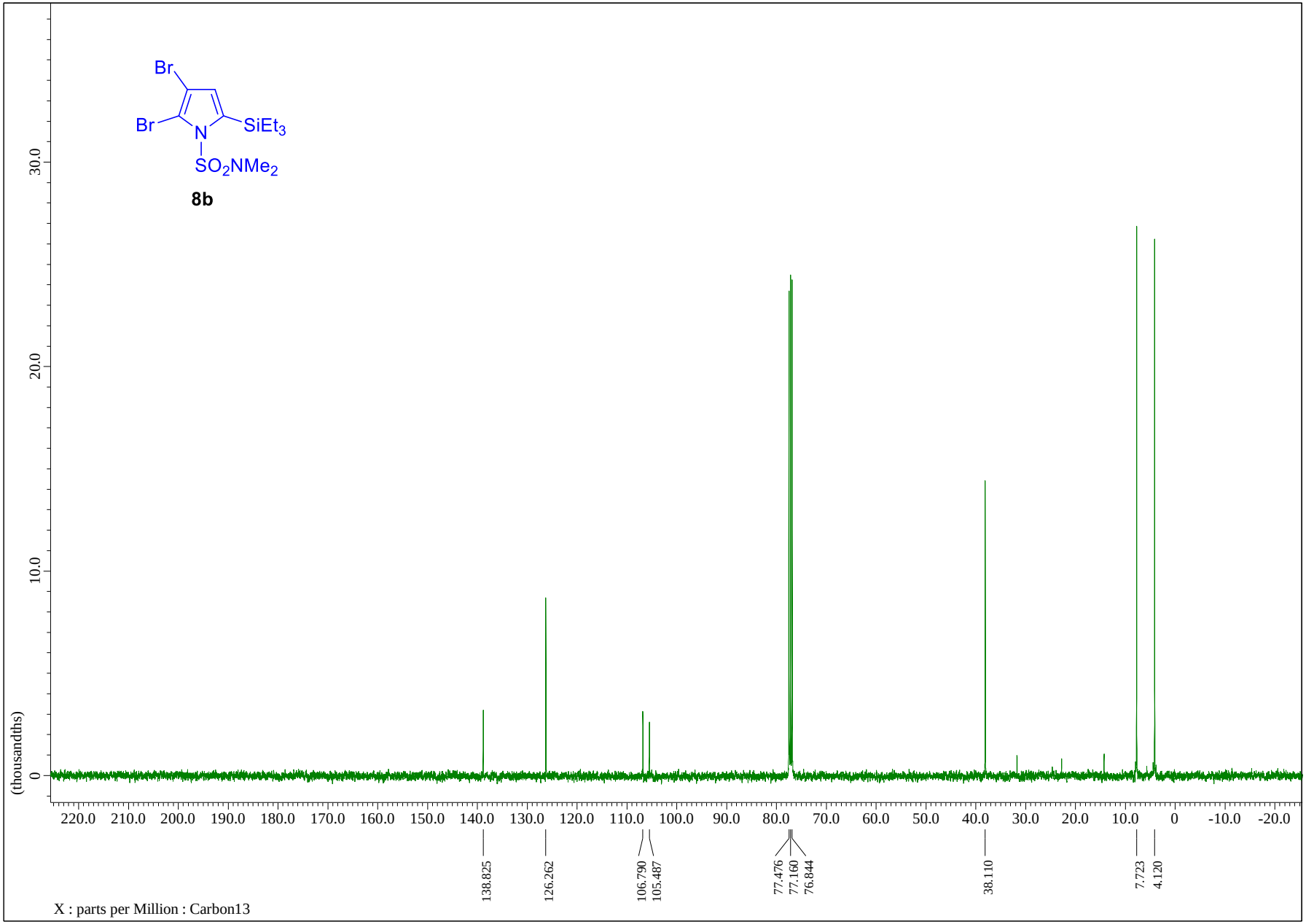
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



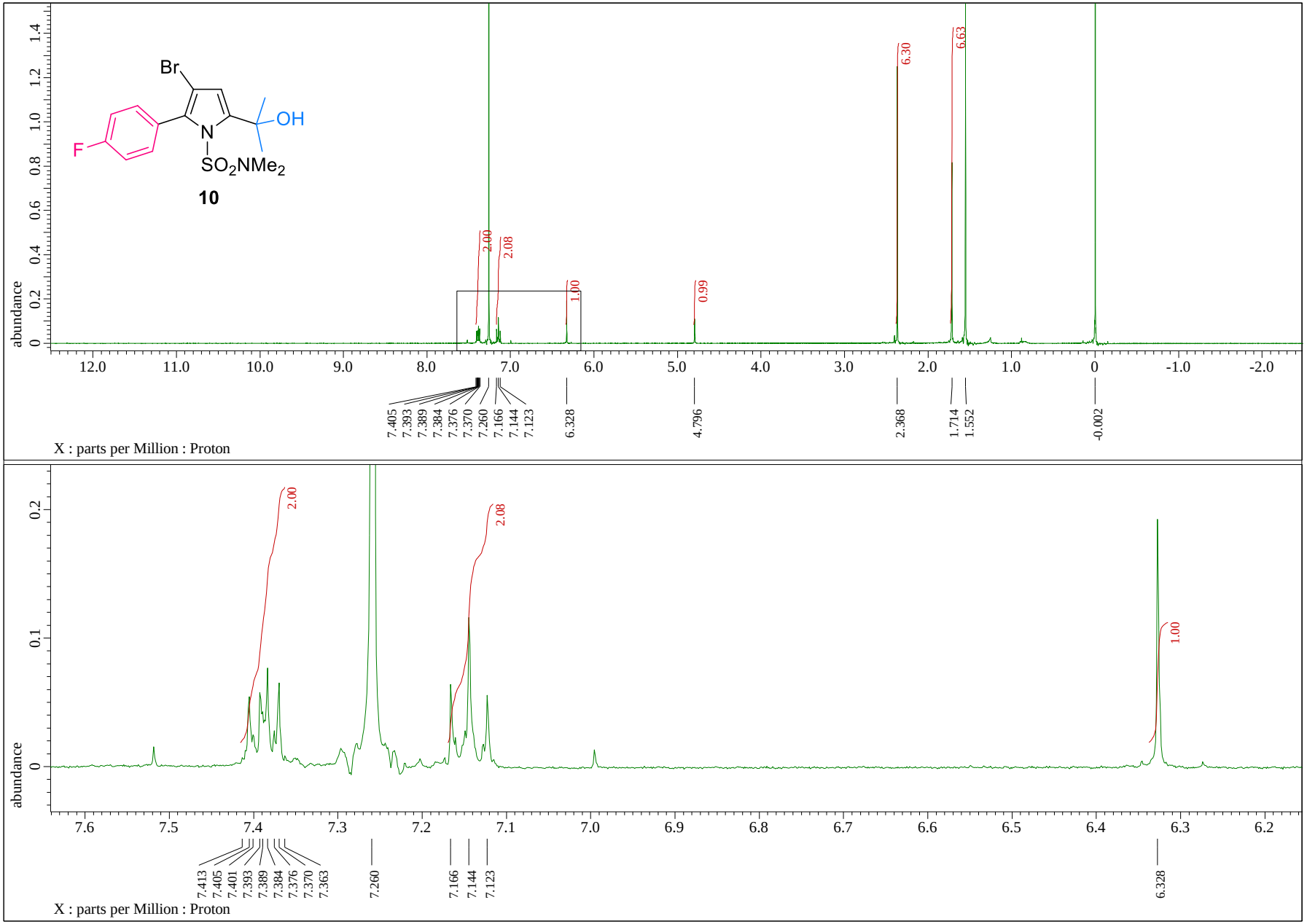
^{1}H NMR (400 MHz, $CDCl_3$)



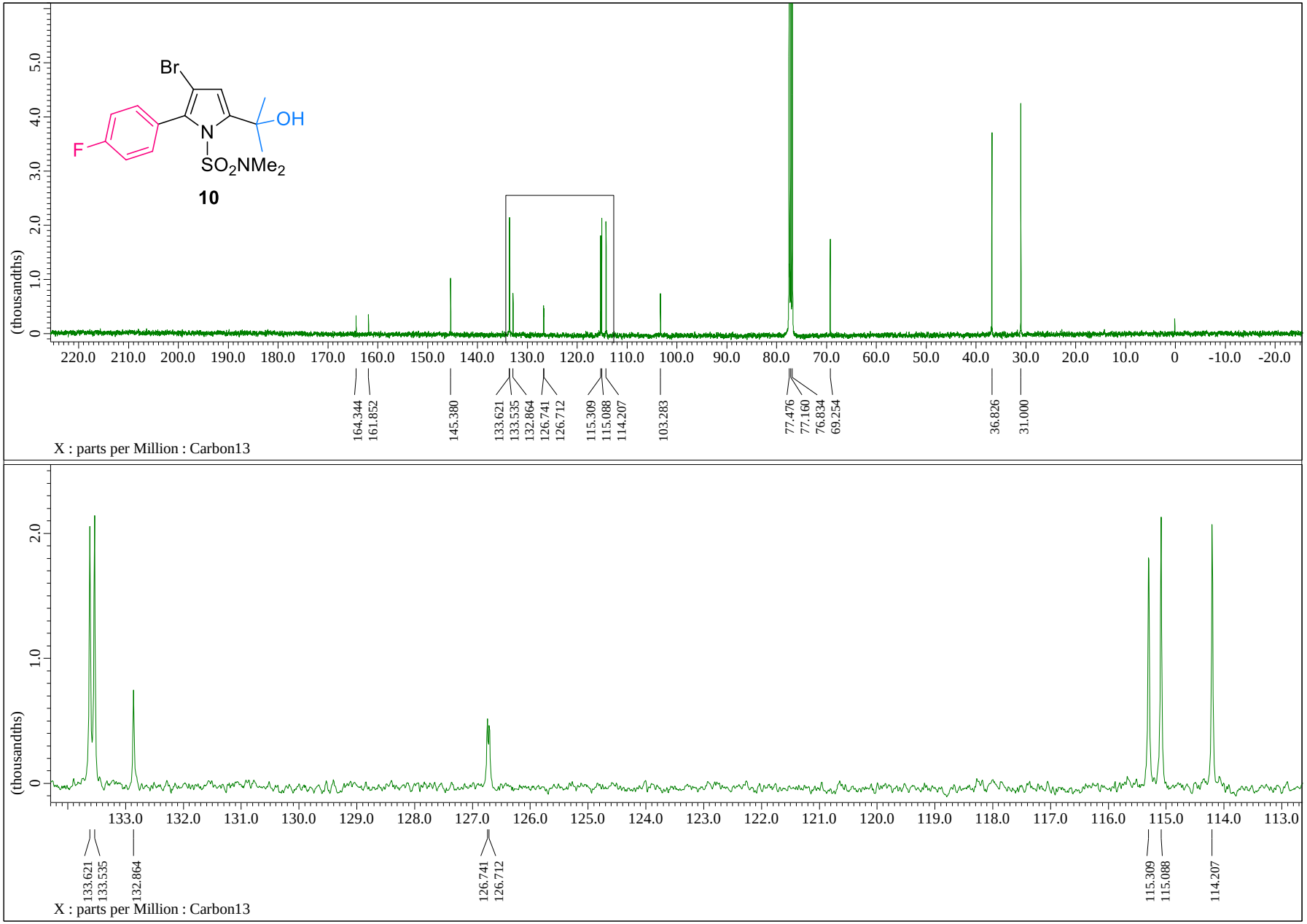
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



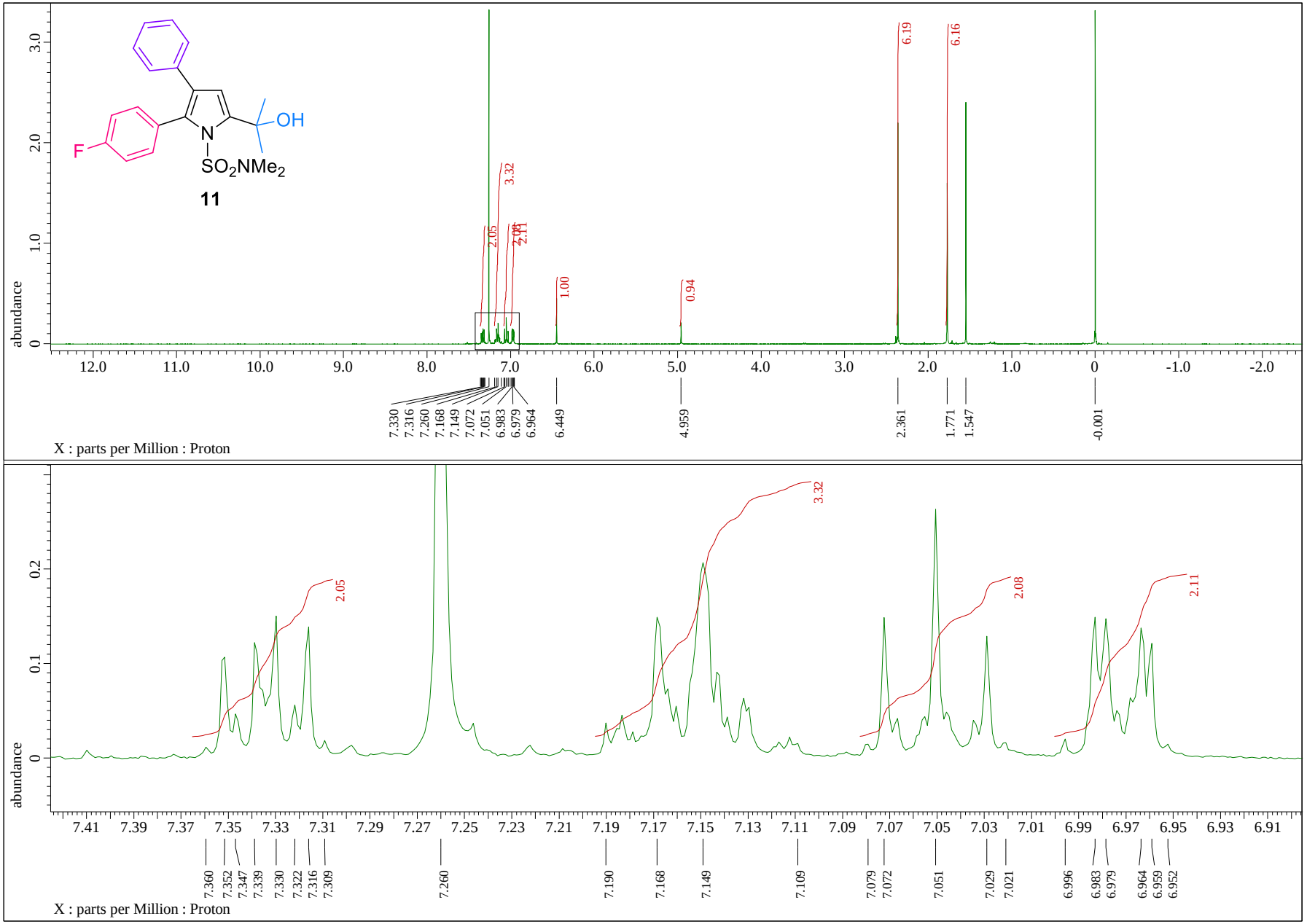
^{1}H NMR (400 MHz, $CDCl_3$)



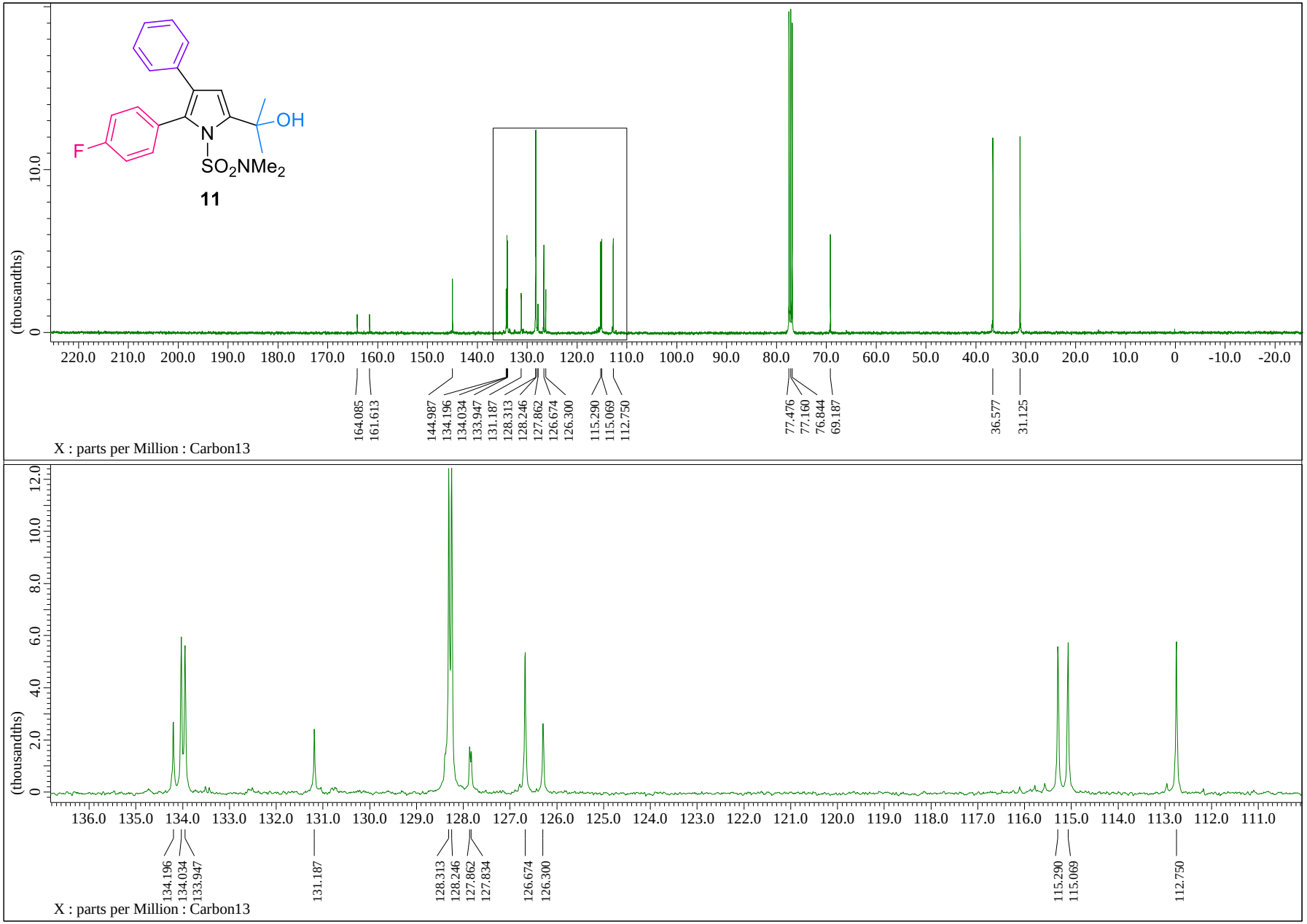
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



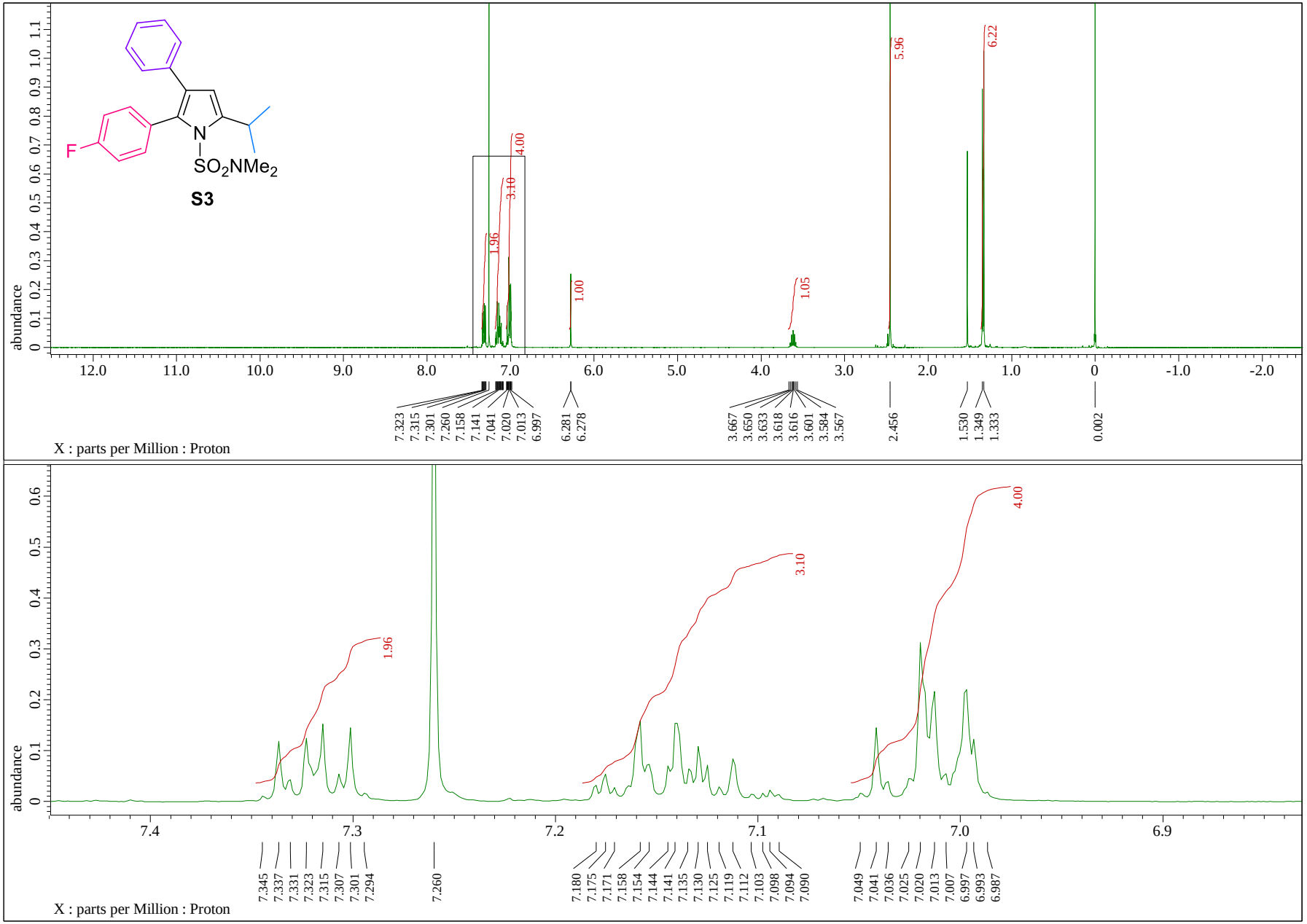
^{1}H NMR (400 MHz, $CDCl_3$)



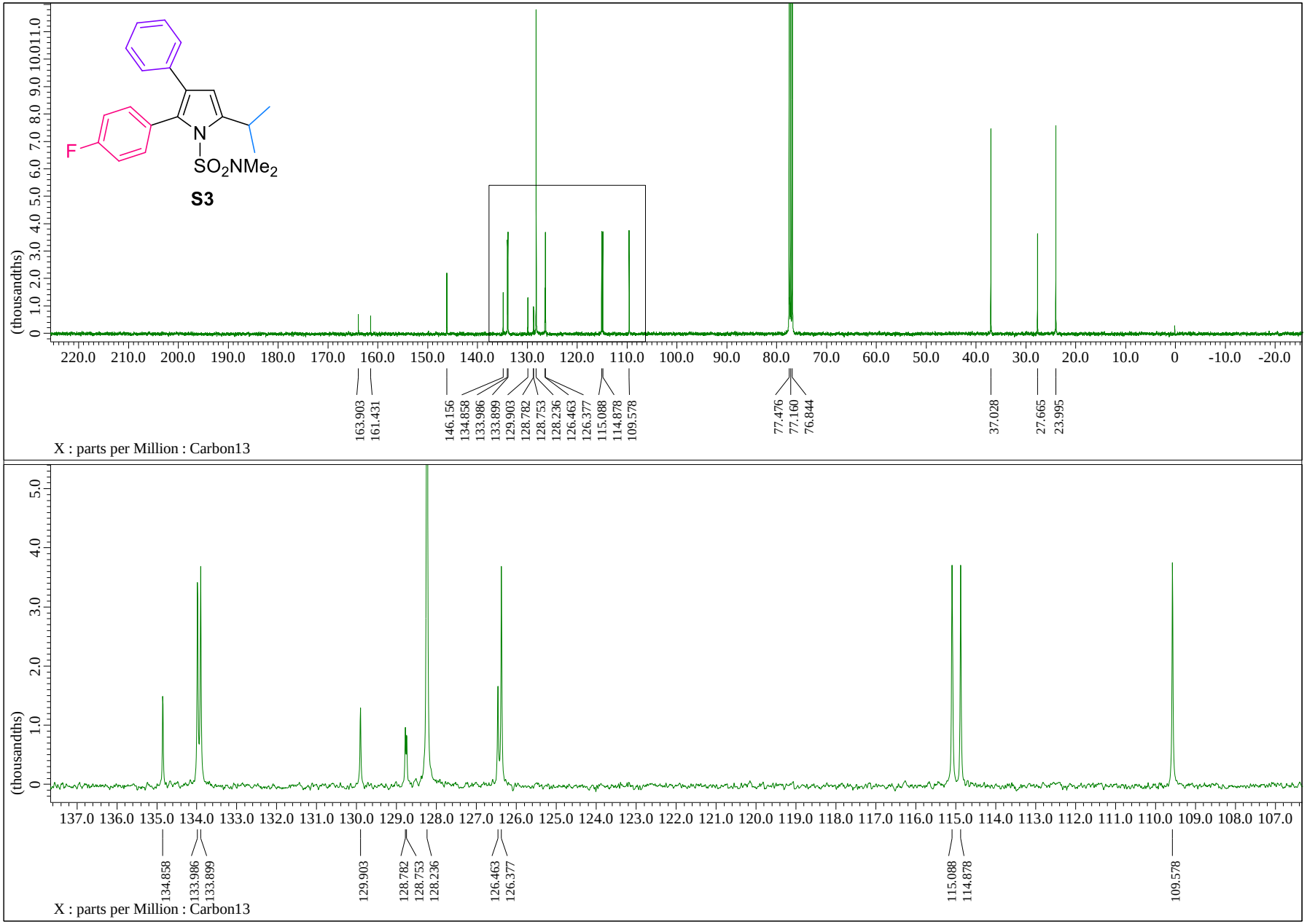
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



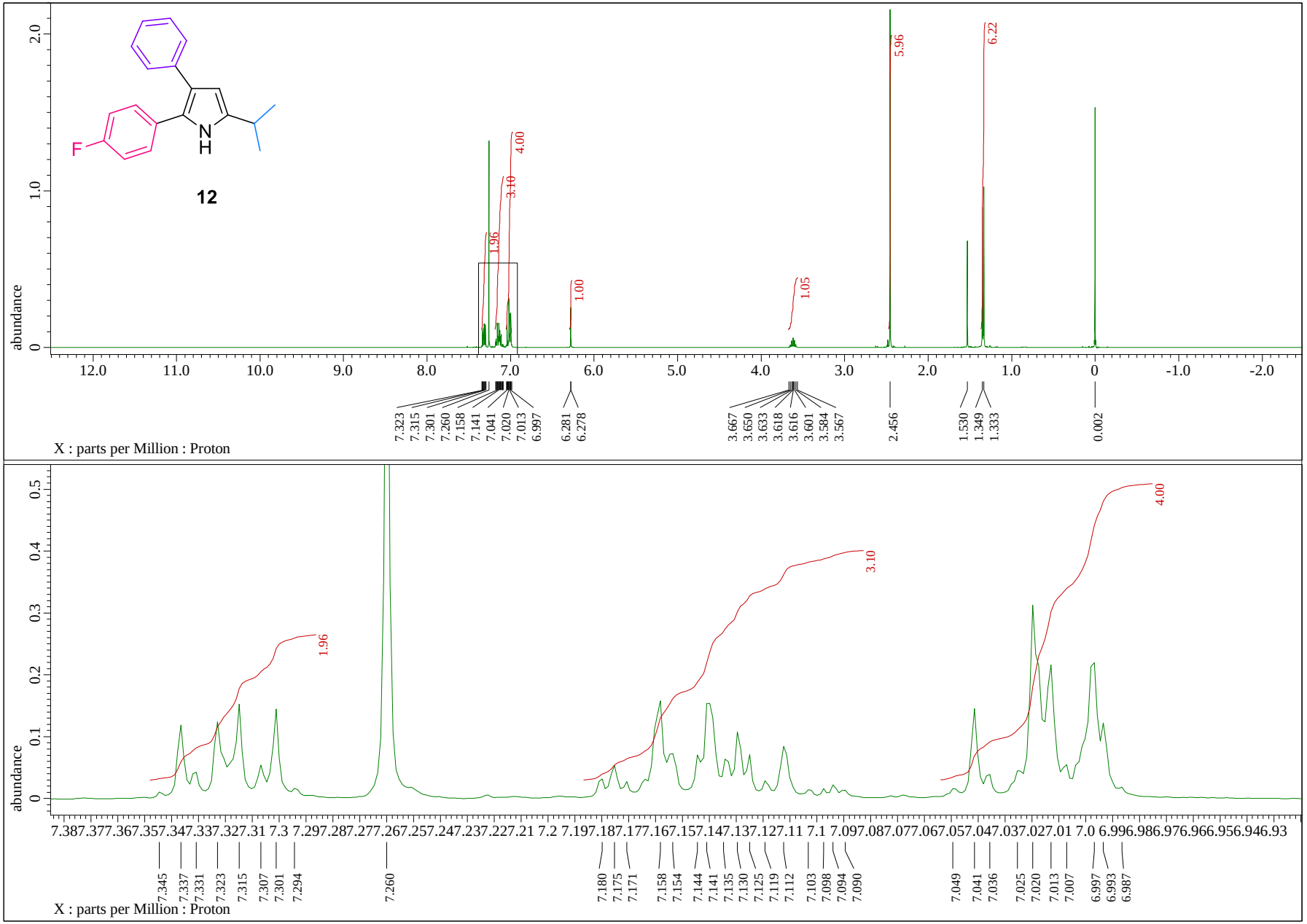
^{1}H NMR (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)