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Supporting Information

Synthesis and properties of polythiophene bearing an alkylsulfonic acid ester at the side chain

Aika Kuwayama,[a] Sonoka Yamamoto,[a] Yuma Sakagami,[a]Mizuho Yamagishi,[a] Kentaro Okano,[a] Masaki Horie,[b] Masahiro Funahashi,[c] Atsunori Mori*[ad]

[a]Department of Chemical Science and Engineering, Kobe University, 1-1 Rokkodai, Nada, Kobe 657-8501, Japan, [b]Department of Chemical Engineering, National Tsing Hua University, 101, Sec. 2, Kuang-Fu Road, Hsinchu 30013, Taiwan, [c]Department of Advanced Materials Science, Kagawa University, 2217-20 Hayashi-cho, Takamatsu, Kagawa 761-0396, Japan, and [d]Research Center for Membrane and Film Technology, Kobe University, 1-1 Rokkodai, Nada, Kobe 657-8501, Japan, and

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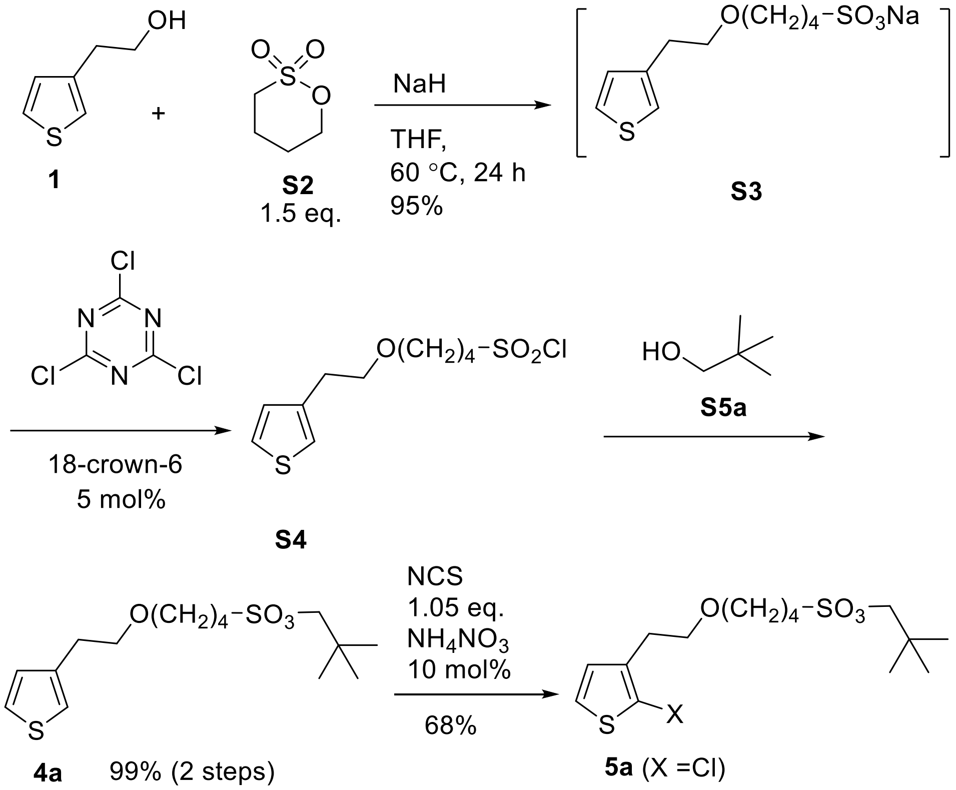


Scheme S1. Preparation of halothiophene derivatives **3** and **4** bearing alkylsulfonate substituent

Experimental section

General. Melting points (mp) were measured on a Yanaco MP-J3 and are uncorrected. Unless specified, all the reactions were carried out under a nitrogen or argon atmosphere using standard Schlenk technique. ^{1}H (400 MHz) and ^{13}C{^{1}H} (100 MHz) NMR spectra were measured on a JEOL ECZ 400 NMR spectrometer. The chemical shifts were expressed in ppm with tetramethylsilane (0 ppm for ^{1}H as an internal standard in $CDCl_3$) or D_2O (4.79 ppm for ^{1}H), DMSO (2.50 ppm for ^{1}H), $CDCl_3$ (77.16 ppm for ^{13}C), DMSO (39.52 ppm for ^{13}C). HRMS spectra were measured by JEOL JMS-T100LP AccuTOF LC-Plus (ESI) with a JEOL MS-5414DART attachment. IR spectra were recorded on Bruker Alpha with an ATR attachment (Ge). HPLC with preparative SEC column (JAI-GEL-1H and JAI-GEL-2H) was performed by JAI LC-9201. SEC analyses were carried out with a standard HPLC system equipped with a UV detector at 40 °C using $CHCl_3$ as an eluent with Shodex KF-405LHQ[1] and Waters e2414 equipped with RI detector Waters 2414 using aqueous 0.1 M sodium sulfate solution as an eluent with the flow rate of 0.7 mL/min with Shodex STANDARD P-82 (Pullulan). Molecular weights and molecular weight distributions were estimated on the basis of the calibration curve obtained by 6 standard polystyrenes. UV-vis-NIR absorption spectra of polymer films were measured with SEC-2001-025-DUVN and JASCO V-670 as a chlorform or aqueous solution (10^{-2} M). Thermal analyses were carried out with RIGAKU Thermo plus EVO2 TG-DTA 8121. Electric conductivities were measured by four-point-probe method on the cast film of the polymer by Loresta-GXII, Nittoseiko Analytech. The thickness of the film was measured with stylus profiler ULVAC DEKTAK 8.

Material. Tetrahydrofuran was purchased from Kanto Chemical Co. Ltd. as an anhydrous grade and passed through alumina and copper columns (Nikko Hansen & Co. Ltd) prior to use[2] or alternatively employed after the distillation from sodium dispersion/benzophenone ketyl.[3] ^{i}PrMgCl·LiCl (**7**) was purchased from Sigma Aldrich Chemical. Co. Ltd as a 1.3 M THF solution.[4] TMPMgCl·LiCl (**5**, chloromagnesium 2,2,6,6-tetramethylpiperidine-1-yl lithium chloride salt) was purchased from Sigma Aldrich Chemical. Co. Ltd as a 1 M THF solution[5] or alternatively prepared by the reaction of ^{i}PrMgCl·LiCl and TMPH (2,2,6,6-tetramethylpiperidine), which was stored as a 1 M solution under an argon atmosphere at room temperature. $NiCl_2(PPh_3)(IPr)$[6] (**7**) was purchased from TCI Co. Ltd. and used as obtained. Ion exchange resin Amberlite IR120B H was kindly donated from Teika Co. Ltd.

Sodium 4-(3-thienylethoxy)-1-butanesulfonate (S3)[7]: To a solution of 3-

thiopheneethanol (**1**, 4.38 mL, 40 mmol) in 116 mL of anhydrous THF was added sodium hydride (60% dispersion in mineral oil) (1.92 g, 60 mmol) at 0 ºC under an argon atmosphere. After stirring at room temperature for 30 min, 1,4-butanesultone (S**2**, 6.11 mL, 60 mmol) was added to the resulting mixture and stirring was continued at 60 ºC for 24 h. After cooling to room temperature, the reaction mixture was filtered and the residue was washed with acetone. The obtained product was dried under reduced pressure at 60 ºC to provide crude product **S3** as a light yellow solid (11.12 g, 39 mmol), which was used for the next reaction without further purification. ^{1}H NMR (DMSO-d_6): δ 7.43 (dd, J = 4.8, 2.8 Hz, 1H), 7.20 (br, 1H), 7.01 (d, J = 4.8 Hz, 1H), 3.54 (t, J = 7.2 Hz, 2H), 3.36 (t, J = 6.4 Hz, 2H), 2.81 (t, J = 6.4 Hz, 2H), 2.35-2.48 (m, 2H), 1.48-1.64 (br, 4H); ^{13}C{^{1}H} NMR (DMSO-d_6): δ 139.4, 128.7, 125.6, 121.3, 70.4, 69.9, 51.2, 30.2, 28.6, 22.0; mp 173.5-175.0 °C. IR (ATR) 2940, 2862, 1430, 1207, 1181, 1113, 917, 744 cm^{-1}.

4-(3-Thienylethoxy)-1-butanesulfonyl chloride (S4): A mixture of sodium 4-(3-thienylethoxy)-1-butanesulfonate (**S3**, 10.16 g, 35 mmol), cyanuryl chloride (6.45 g, 35 mmol), and 18-crown-6 (0.46 g, 1.75 mmol) in 70 mL of acetone was stirred at room temperature for 24 h. The resulting mixture was filtered off and the residue was washed with acetone. The obtained solid was purified by column chromatography on silica gel using hexane/ethyl acetate = 6/1 as an eluent to afford 11.1 g of **S3** as a light yellow solid (77%). The obtained product was employed for the following reaction without further purification or purification by column chromatography on silica gel with hexane/ethyl acetate (6:1, v/v) to provide 4-(3-thienylethoxy)-1-butanesulfonyl chloride as a light yellow oil (7.65 g, 27.1 mmol, 77%). ^{1}H NMR (CDCl$_3$): δ 7.27 (dd, J = 3.2, 4.8 Hz, 1H), 7.01 (dd, J = 3.2, 1.2 Hz, 1H), 6.97 (dd, J = 4.8, 1.2 Hz, 1H), 3.66-3.71 (m, 2H), 3.65 (t, J = 6.8 Hz, 2H), 3.50 (t, J = 5.2 Hz, 2H), 2.90 (t, J = 6.8 Hz, 2H), 2.10-2.16 (m, 2H), 1.74–1.81 (m, 2H); ^{13}C{^{1}H} NMR (CDCl$_3$): δ 139.4, 128.5, 125.7, 121.3, 71.4, 70.0, 65.5, 30.9, 27.7, 22.3. IR (ATR) 2924, 2865, 2854, 1374, 1163, 1110, 735, 633 cm^{-1}. HRMS (DART$^+$) *m/z*: calcd for $C_{10}H_{16}ClO_3S_2$, 283.0229: found, 283.0243.

2,2-Dimethylpropyl 4-(3-thienylethoxy)-1-butanesulfonate (2a): To a solution of 2,2-dimethyl-1-propanol (**S5a**, 0.47 g, 5.3 mmol) and triethylamine (0.72 mL, 5.2 mmol) in 5.1 mL of toluene was added sulfonyl chloride **S4** (1.43 g, 5.1 mmol) at 0 °C and stirring was continued for 24 h. The resulting mixture was poured into water and two phases were separated. The aqueous layer was extracted with diethyl ether. The combined organic extracts were dried over anhydrous sodium sulfate and the solvent was concentrated under reduced pressure to leave a crude oil (99%) The obtained product was employed for the following reaction without further purification. ^{1}H NMR (CDCl$_3$): δ 7.25 (d, *J* = 2.8 Hz, 1H), 6.99–7.02 (m, 1H), 6.97 (dd, *J* = 4.8, 0.8 Hz, 1H), 3.85 (s, 2H), 3.63 (t, *J* = 6.0 Hz, 2H), 3.48 (t, *J* = 5.9 Hz, 2H), 3.13 (dd, *J* = 8.0, 8.0 Hz, 2H), 2.89 (t, *J* = 6.8 Hz, 2H), 1.96 (quint, *J* = 7.8 Hz, 2H), 1.72 (quint, *J* = 7.8 Hz, 2H), 0.99 (s, 9H); ^{13}C{^{1}H} NMR (CDCl$_3$): δ 139.4, 128.6, 125.5, 121.2, 78.6, 71.3, 70.1, 50.1, 31.9, 30.9, 28.3, 26.2, 21.1; IR (ATR) 2960, 2866, 1478, 1352, 1167, 1113, 967, 838, 776 cm^{-1}. HRMS (DART$^+$) *m/z*: calcd for $C_{15}H_{27}O_4S_2$, 335.1351: found, 335.1348.

Methyl 4-(3-thienylethoxy)-1-butanesulfonate (2b): 90% yield. ^{1}H NMR (CDCl$_3$): δ 7.25 (d, *J* = 2.8 Hz, 1H), 7.01 (d, *J* = 2.8 Hz, 1H), 6.97 (d, *J* = 4.8 Hz, 1H), 3.88 (s, 3H), 3.63 (t, *J* = 6.8 Hz, 2H), 3.47 (t, *J* = 5.2 Hz, 2H), 3.13 (dd, *J* = 8.0, 8.0 Hz, 2H), 2.90 (t, *J* = 6.8 Hz, 2H), 1.95 (quint, *J* = 7.8 Hz, 2H), 1.72 (quint, *J* = 7.8 Hz, 2H); ^{13}C{^{1}H} NMR (CDCl$_3$): δ 139.6, 128.5, 125.5, 121.3, 71.3, 70.1, 55.2, 49.7, 30.8, 28.2, 21.0; IR (ATR) 2962, 2919, 2851, 1354, 1260, 1159, 1106, 1017, 994, 796 cm^{-1}. HRMS (DART$^+$) *m/z*: calcd for $C_{11}H_{19}O_4S_2$: 279.0725: found, 279.0711.

Ethyl 4-(3-thienylethoxy)-1-butanesulfonate (2c): 84% yield. ^{1}H NMR (CDCl$_3$): δ 7.25 (d, *J* = 2.8 Hz, 1H), 7.01 (dd, *J* =2.8, 0.8 Hz, 1H,), 6.97 (dd, *J* = 4.8, 0.8 Hz, 1H), 4.27 (q, *J* =7.8 Hz, 2H), 3.63 (t, *J* = 6.8 Hz, 2H), 3.48 (t, *J* = 4.8 Hz, 2H), 3.08–3.14 (m, 2H), 2.90 (t, *J* =6.8 Hz, 2H), 1.94 (m, 2H), 1.72 (m, 2H), 1.40 (t, *J* =7.8 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 139.4, 128.6, 125.5, 121.3, 71.3, 70.1, 66.0, 50.4, 30.8, 28.3, 21.0, 15.3; IR (ATR) 2963, 2873, 2862, 1469, 1351, 1113, 1062, 1026, 945, 909, 826, 773 cm^{-1}. HRMS (DART$^+$) *m/z*: calcd for $C_{12}H_{21}O_4S_2$, 293.0881: found, 293.0895.

2-Methylpropyl 4-(3-thienylethoxy)-1-butanesulfonate (2d): 95% yield. ^{1}H NMR (CDCl$_3$): δ 7.25 (d, *J* =2.8 Hz, 1H), 7.01 (dd, *J* =2.8, 0.8 Hz, 1H), 6.97 (dd, *J* = 4.8, 0.8 Hz, 1H), 3.97 (d, *J* =6.8 Hz, 2H), 3.63 (t, *J* =6.8 Hz, 2H), 3.48 (t, *J* =6.0 Hz, 2H), 3.10-3.14 (m, 2H), 2.90 (t, *J* =6.8 Hz, 2H), 2.03 (quint, *J* =6.8 Hz, 1H), 1.91–1.97 (m, 2H), 1.67–1.76 (m, 2H), 0.98 (d, *J* = 6.8 Hz, 6H); ^{13}C{^{1}H}NMR (CDCl$_3$): δ 139.4, 128.6, 125.4, 121.2, 75.4, 71.3, 70.1, 50.2, 30.9, 28.5, 28.3, 21.1, 18.8; IR (ATR) 2964, 2924, 2871, 2857, 1472, 1353, 1169, 1113, 976, 945, 910, 835, 774 cm^{-1}. HRMS (DART$^+$) *m/z*: calcd for $C_{14}H_{25}O_4S_2$, 321.1194: found, 321.1192.

2,2-Dimethylpropyl 4-(3-(2-chlorothienyl)ethoxy)-1-butanesulfonate (3a): To a solution of **6a** (1.34 g, 4.0 mmol) in 8.0 mL of acetonitrile was added *N*-chlorosuccinimide (0.56 g, 4.2 mmol) and NH_4NO_3 (32.0 mg, 0.4 mmol) at room temperature and stirring was continued at 60 °C for 24 h. The resulting mixture was washed with aq. $Na_2S_2O_3$, sat. ammonium chloride, and brine. The organic solution was dried over anhydrous sodium sulfate. Removal of the solvent under reduced pressure left a crude material, which was purified by column chromatography on silica gel with hexane/ethyl acetate (6:1, vol/vol) to afford 0.99 g of 7a as a light-yellow oil (68%). ^1H NMR ($CDCl_3$) δ 7.04 (d, J = 5.2 Hz, 1H), 6.84 (d, J = 5.2 Hz, 1H), 3.85 (s, 2H), 3.59 (t J = 6.8 Hz, 2H,), 3.47 (t, J = 6.0 Hz, 2H), 3.10-3.14 (m, 2H), 2.85 (t, J = 6.8 Hz, 2H), 1.90-1.98 (m, 2H), 1.68-1.75 (m, 2H), 0.99 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 140.8, 135.7, 128.3, 122.4, 78.6, 70.1, 70.0, 50.1, 31.9, 28.7, 28.3, 26.2, 21.0; IR (ATR) 2960, 2863, 1480, 1352, 1167, 1113, 1053, 1026, 964, 874, 718 cm^{-1}. HRMS (DART$^+$) *m/z*: calcd for $C_{15}H_{26}{}^{35}ClO_4S_2$, 369.0961: found, 369.0966.

Methyl 4-(3-(2-chlorothienyl)ethoxy)-1-butanesulfonate (3b): 50% yield. ^1H NMR ($CDCl_3$) δ 7.05 (d, J =6.0 Hz, 1H), 6.85 (d, J =6.0 Hz, 1H), 3.88 (s, 3H), 3.59 (t, J =6.8 Hz, 2H), 3.47 (t, J =6.0 Hz, 2H), 3.11−3.15 (m, 2H), 2.85 (t, J =6.8 Hz, 2H), 1.90-1.98 (m , 2H), 1.68-1.74 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 135.7, 128.3, 125.8, 122.5, 70.1, 70.0, 55.2, 49.7, 28.7, 28.2, 21.0; IR (ATR) 2971, 2957, 2946, 2862, 1413, 1354, 1171, 991, 825, 722 cm^{-1}. HRMS (DART$^+$) *m/z*: calcd for $C_{11}H_{18}{}^{35}ClO_4S_2$, 313.0335: found, 313.0334.

Ethyl 4-(2-chloro-3-thienylethoxy)-1-butanesulfonate (3c): 76% yield. ^1H NMR ($CDCl_3$) δ 7.04 (d, 1H, J =6.0 Hz), 6.85 (d, 1H, J =6.0 Hz), 4.28 (q, 2H, J =6.8 Hz), 3.59 (t, 2H, J =6.8 Hz), 3.46 (t, 2H, J =6.0 Hz), 3.01–3.13 (m, 2H), 2.84 (t, 2H, J =6.8 Hz), 1.94 (quint, 2H, J =6.8 Hz), 1.70 (quint, 2H, J =6.8 Hz), 1.40 (t, 3H, J =6.8 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 140.2, 135.7, 128.3, 122.4, 70.1, 70.0, 66.0, 50.4, 28.7, 28.2, 21.0, 15.3; IR (ATR) 2960, 2934, 2917, 2868, 1476, 1435, 1407, 1349, 1163, 1108, 1004, 912, 819 cm^{-1}. HRMS (DART$^+$) *m/z*: calcd for $C_{12}H_{20}{}^{35}ClO_4S_2$, 327.0492: found, 327.0507.

2-Methylpropyl 4-(2-chloro-3-thienylethoxy)-1-butanesulfonate (3d): 67% yield. ^1H NMR ($CDCl_3$) δ 7.04 (d, 1H, J =6.0 Hz), 6.84 (d, 1H, J =6.0 Hz), 3.97 (d, 2H, J =6.8 Hz), 3.60 (t, 2H, J =6.8 Hz), 3.46 (t, 2H, J =6.0 Hz), 3.10–3.14 (m, 2H), 2.85 (t, 2H, J =6.8 Hz), 2.02 (quint, 1H, 6.8 Hz), 1.93 (quint, 2H, J =6.8 Hz), 1.71 (quint, 2H, J = 6.8 Hz), 0.99 (d, 6H, J =6.8 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 135.7, 134.4, 128.3, 122.4, 75.5, 70.1, 70.0, 50.2, 28.7, 28.5, 28.3, 21.1, 18.8; IR (ATR) 2959, 2925, 2860, 1469, 1354, 1169, 1115, 1052, 976, 946, 840, 825, 718 cm^{-1}. HRMS (DART$^+$) *m/z*: calcd for $C_{14}H_{24}{}^{35}ClO_4S_2$, 355.0805: found, 355.0801.

Attempted deprotonative polymerization of 3a with TMPMgCl·LiCl and nickel catalyst **8**: To a solution of **7a** in 1.0 mL of THF was added TMPMgCl·LiCl (0.12 mL of 1.0 M THF-toluene solution, 0.12 mmol) dropwise. After stirring for 10 min, nickel catalyst **8** (1.56 mg, 2.0 μmol) was added and further stirring was continiued at 60 °C for 24 h. The reaction was terminated by the addition of 1.0 M hydrochloric acid (0.5 mL) to form a precipitate, which was filtered off. However, little solid material was obtained.

2,2-Dimethylpropyl 4-(2-chloro-5-iodo-3-thienylethoxy)-1-butanesulfonatethiophene (4a): A round-bottomed flask equipped with magnetic stirring bar was added methyl 4-(3-(2-chlorothienyl)ethoxy)-1-butanesulfonate (**5**) (594 mg, 1.9 mmol, 1.0 equiv), *N*-iodosuccinimide (NIS) (427.4 mg, 1.9 mmol, 1.0 equiv), $CHCl_3$ (6.0 mL) and acetic acid (1.5 mL) and stirred at room temperature for 24 h. The reaction mixture was treated with saturated aqueous sodium thiosulfate (1 mL). After partitioned, the aqueous layer was extracted with diethyl ether. The combined organic extracts were washed with saturated aqueous ammonium chloride and brine. Then combined organic layer was dried over sodium sulfate and filtered. The filtrate was concentrated under reduced pressure to give the crude material, which was purified by column chromatography on silica gel with hexane/ethyl acetate (4:1, v/v) as a light yellow oil (673.1 mg, 1.53 mmol, 81%). ^{1}H NMR ($CDCl_3$) δ 7.03 (s, 1H), 3.87 (s, 2H), 3.55 (t, *J* = 6.4 Hz, 2H), 3.46 (t, *J* = 6.0 Hz, 2H), 3.12-3.16 (m, 2H), 2.81 (t, *J* = 6.4 Hz, 2H), 1.95 (quint, *J* = 6.8 Hz, 2H), 1.72 (quint, *J* = 6.8 Hz, 2H), 0.99 (s, 9H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 140.8, 138.1, 138.0, 129.0, 78.7, 70.2, 69.8, 68.6, 50.1, 31.9, 28.4, 28.3, 26.3, 21.0; IR (ATR) 2960, 2869, 1348, 1216, 1167, 1113, 1060, 1026, 967 934, 838, 746, 709, 665 cm^{-1}; HRMS (DART^{+}) *m/z*: calcd. for $C_{15}H_{25}{}^{35}ClIO_4S_2$, 494.9928: found, 494.9956.

Preparation of other chloro(iodo)thiophenes **4b-d** was carried out in a similar manner.

Methyl 4-(2-chloro-5-iodo-3-thienylethoxy)-1-butanesulfonate (4b): 81% yield. ^{1}H NMR ($CDCl_3$) δ 7.03 (s, 1H), 3.89 (s, 3H), 3.55 (t, *J* =6.8 Hz, 2H), 3.46 (t, *J* =6.0 Hz, 2H), 3.11-3.16 (m, 2H), 2.80 (t, *J* =6.8 Hz, 2H), 1.93 (quint, *J* =6.8 Hz, 2H), 1.71 (quint, *J* =6.8 Hz, 2H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 138.0, 135.3, 129., 70.2, 69.8, 68.7, 55.3, 49.7, 28.4, 28.2, 21.0; IR (ATR) 2950, 2935, 2870, 2859, 1461, 1410, 1352, 1160, 1112, 1062, 990, 825, 791 cm^{-1}. HRMS (DART^{+}) *m/z*: calcd. for $C_{11}H_{17}{}^{35}ClIO_4S_2$, 438.9302: found, 438.9287.

Ethyl 4-(2-chloro-5-iodo-3-thienylethoxy)-1-butanesulfonate (4c): 98% yield. ^{1}H NMR ($CDCl_3$) δ 7.03 (s, 1H), 4.29 (q, 2H, *J* =6.8 Hz), 3.55 (t, 2H, *J* =6.8 Hz), 3.45 (t, 2H, *J* =6.0 Hz), 3.10-3.14 m, 2H), 2.80 (t, 2H, *J* =6.0 Hz), 1.94 (quint, 2H, *J* =6.8 Hz), 1.72 (quint, 2H, *J* =6.8 Hz), 1.41 (t, 3H, *J* =6.8 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 138.0, 129.0, 120.3, 70.1, 69.8, 68.6, 66.0, 50.4, 28.4, 28.2, 21.0, 15.3; IR (ATR) 2921, 2866, 1348, 1226, 1168, 1112, 1059, 1004, 917, 826 cm^{-1}. HRMS (DART $^+$) calcd. for $C_{12}H_{19}{}^{35}ClIO_4S_2$, 452.9458: found, 452.9455.

2-Methylpropyl 4-(2-chloro-5-iodo-3-thienylethoxy)-1-butanesulfonate (4d): 94% yield. ^{1}H NMR ($CDCl_3$) δ 7.04 (s, 1H), 3.99 (d, *J* = 6.8 Hz, 2H), 3.56 (t, 2H, *J* =6.8 Hz), 3.47 (t, 2H, *J* =6.0 Hz), 3.12 (dd, 2H, *J* =6.0, 6.0 Hz), 2.80 (t, 2H, *J* =6.8 Hz), 2.04 (quint, 1H, *J* =6.8 Hz), 1.93 (quint, 2H, *J* =6.8 Hz), 1.71 (quint, 2H, *J* =6.8 Hz), 0.99 (d, 6H, *J* =6.8 Hz). ^{13}C{^{1}H} NMR (CDCl3): δ 138.0, 128.8, 113.8, 75.4, 70.0, 69.7, 68.6, 50.0, 28.4, 28.3, 28.1, 20.9, 18.7; IR (ATR) 2978, 2913, 2874, 1352, 1113, 1024, 977, 942, 827, 769 cm^{-1}. HRMS (DART $^+$) calcd. for $C_{14}H_{23}{}^{35}ClIO_4S_2$, 480.9771: found, 480.9784.

Polymerization of 2,2-Dimethylpropyl 4-(2-chloro-5-iodo-3-thienylethoxy)-1-butanesulfonatethiophene (8a): To a screw-capped test tube equipped with a magnetic stirring bar were added chloro(iodo)thiophene **4a** (98.8 mg, 0.2 mmol) and THF (2.0 mL) in a glove box. EtMgCl (90 μL, 2 M THF solution, 0.18 mmol) was added to the resulting mixture and stirring was continued for 10 min to form the corresponding organometallic monomer. Nickel catalyst $NiCl_2(IPr)PPh_3$ (**6**, 3.1 mg, 4.0 μmol) was added to the THF solution of the monomer and the mixture was stirred for 24 h. The reaction was terminated by the addition of 1 M hydrochloric acid to form a dark purple precipitate, which was filtered off and washed repeatedly with methanol and hexane to afford the polymer **8a** (33.2 mg, 50%). The average molecular weight and the PDI value were estimated by SEC analysis to reveal $M_n = 25300$; PDI = 1.33. ^{1}H NMR ($CDCl_3$): δ 7.07 (s, 1H), 3.84 (s, 2H), 3.72 (t, *J* = 6.8 Hz, 2H), 3.53 (t, *J* = 6.0 Hz, 2H), 3.13–3.17 (m, 2H), 3.07–3.10 (m, 2H), 1.97 (quint, *J* = 7.2 Hz, 2H), 1.76 (quint, *J* = 7.2 Hz, 2H), 0.96(s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 136.3, 133.7, 129.4, 122.9, 78.8, 70.8, 70.3, 50.0, 31.9, 30.1, 28.4, 26.3, 21.0; IR (ATR) 2965, 2926, 2870, 2861, 1540, 1512, 1366, 1349, 1278, 1169, 1110, 967, 940, 835 cm^{-1}.

Attempted thermal decomposition of polythiophene 8a: Polythiophene **8a** (5.1 mg) was measured on a glass substrate and placed over a hot plate heated at 200 °C. After standing there for 20 min, it was confirmed to recover **8a** by ^{1}H NMR analysis.

Measurement of TG-DTA indicated 52% of weight loss at 245 °C suggesting the elimination of H–$\mathrm{CH_2SO_3CH_2}$^{t}Bu.

Poly(3-(5-oxa-1-methoxysulfonyl-heptan-7-yl)thiophen-2,5-diyl) (8b): To a solution of **4a** (0.15 mmol) in 1.5 mL of THF was added EtMgCl (0.13 m L of 1.0 M THF solution, 0.13 mmol) dropwise under a nitrogen atmosphere and stirring was continued for 10 min at room temperature. To the resulting mixture $\mathrm{NiCl_2(PPh_3)IPr}$ (**8**, 3.0 μmol) was added to initiate the polymerization. After stirring at room temperature for 24 h, the reaction mixture was poured into a mixture of 0.5 mL of hydrochloric acid and 0.5 mL of methanol to form a precipitate, which was filtered off to leave a red solid. After washing with methanol and hexanes repeatedly, the solid was dried under reduced pressure to afford 70 mg of **8b**, a part of which was dissolved in water accompanied by insoluble material in both of chloroform and water.

Poly(3-(5-oxa-1-ethoxysulfonyl-heptan-7-yl)thiophen-2,5-diyl) (8c): To a solution of **4c** (0.1 mmol) in 1.0 mL of THF was added EtMgCl (0.09 mL of 1.0 M THF solution, 0.09 mmol) dropwise under a nitrogen atmosphere and stirring was continued for 10 min at room temperature. To the resulting mixture $\mathrm{NiCl_2(PPh_3)IPr}$ (**6**, 2.0 μmol) was added to initiate the polymerization. After stirring at 0 °C for 24 h, the reaction mixture was poured into a mixture of 0.5 mL of hydrochloric acid and 0.5 mL of methanol to form a precipitate, which was filtered off to leave a purple solid. After washing with methanol and hexanes repeatedly, the solid was dried under reduced pressure to afford 24 mg of **8c**. The molecular weight (M_n) and the molecular weight distribution (M_w/M_n) was estimated by SEC analysis. ($M_n = 6800$, $M_w/M_n = 1.45$). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 7.08 (s, 1H), 4.25 (q, J = 6.8 Hz, 2H), 3.72 (t, J = 6.4 Hz, 2H), 3.53 (t, J = 6.0 Hz, 2H), 2.99–3.15 (m, 4H), 3.12-3.16 (br, 2H), 1.85-1.99 (m, 2H), 1.69-1.79 (m, 2H), 1.35 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$) δ 136.3, 133.7, 131.9, 129.3, 70.7, 70.2, 66.2, 50.3, 30.0, 28.3, 21.0, 15.3; IR (ATR) 2958, 2956, 2926, 2922, 2852, 1505, 1455, 1346, 1167, 1110, 1100, 1001, 917, 818, 640 cm^{-1}.

Poly(3-(5-oxa-1-(2-methyl)propyloxysulfonyl-heptan-7-yl)thiophen-2,5-diyl) (8d): $M_n = 7800$, $M_w/M_n = 1.45$. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 7.07 (s, 1H), 3.95 (d, J = 6.8 Hz, 2H), 3.72 (t, J =6.8 Hz, 2H), 3.53 (et, J = 6.0 Hz, 2H), 3.02–3.16 (m, 3H), 1.89–2.06 (m, 2H), 1.70–1.81 (m, 2H), 1.69–1.81 (m, 1H), 1.23–1.28 (m, 1H), 0.95 (d, J = 6.8 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $\mathrm{CDCl_3}$) δ 136.3, 133.7, 131.9, 129.4, 75.6, 70.7, 70.2, 50.1, 30.0, 28.5, 28.3, 21.0, 18.8. IR (ATR) 2955, 2926, 2871, 2856, 1508, 1457, 1376, 1356, 1167, 1114, 974, 858, 743 cm^{-1}.

Poly(3-(5-oxa-1-sodiumsulfonato-heptan-7-yl)thiophen-2,5-diyl) (9): To a screw-capped test tube equipped with a magnetic stirring bar was dissolved **8c** (14.5 mg, 50 μmol) in 0.5 mL of DMSO. Sodium iodide (22.4 mg, 0.15 mmol) was then added to the resulting solution. Stirring was further continued for additional at 80 °C for 6 h to form a precipitate, which was filtered off. The residue was washed with hexane/ethanol (1:1, v/v), to afford 12 mg of the corresponding sulfonic acid sodium salt **10** in 96% yield. Attepted measurement of ^{1}H and ^{13}C NMR spectra in D_2O resulted in showing broad signals and little characteristic peaks was observed. IR (ATR) 3400 (br), 2938, 2864, 1683 (w), 1653 8 (w), 1508, 1418, 1176, 1112, 1053, 795, 739 cm^{-1}. SEC analysis (H_2O) M_n = 22000.

Transformation of polythiophene benzenesulfonate (8c) with alkaline metal hydroxide leading to metal salt: To a screw-capped test tube equipped with a magnetic stirring bar was dissolved **8c** (29.0 mg, 0.10 mmol) in 1.0 mL of ethanol. Sodium hydroxide (6.0 mg, 0.15 mmol) was then added to the resulting solution. Stirring was further continued under reflux for additional 6 h to form a precipitate, which was filtered off. The residue was washed with hexane to afford 25.6 mg of the corresponding sulfonic acid sodium salt **9** in 96% yield.

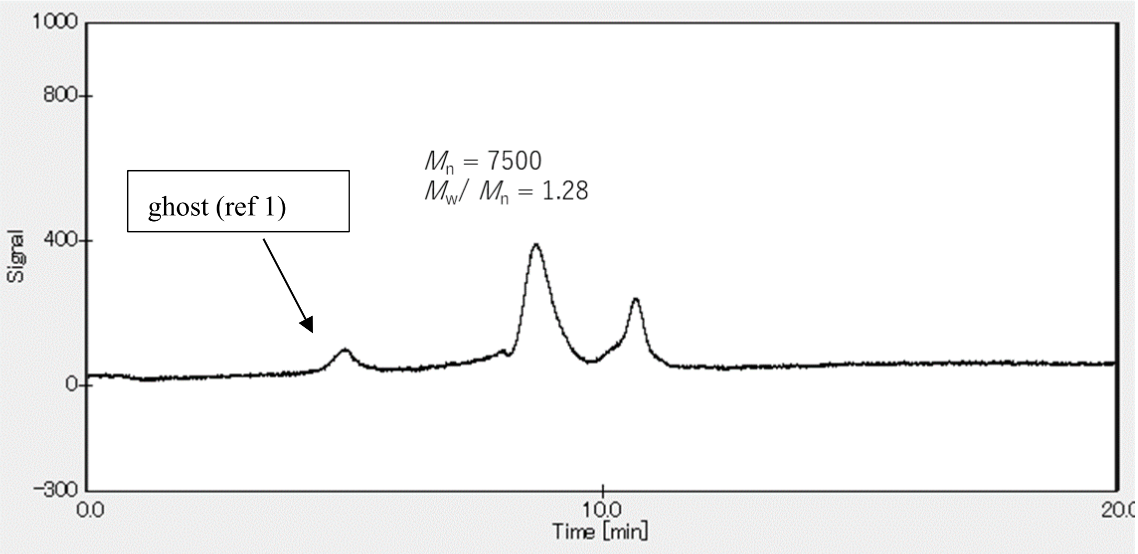
Poly(3-(5-oxa-1-lithiumsulfonato-heptan-7-yl)thiophen-2,5-diyl) (10): The formation of lithium salt was carried out in a similar manner shown above with **8c** (29.0 mg, 0.1 mmol) and lithium hydroxyde (7.1 mg, 0.3 mmol) to afford 22.8 mg of the corresponding sulfonic acid sodium salt **10** in 85% yield. IR (ATR) 3500 (br), 2939, 2864, 1643 (w), 1512, 1454, 1184, 1110, 1059, 835, 797, 733 cm^{-1}. SEC analysis (H_2O) M_n = 22000.

Poly(3-(5-oxa-1-potassiumsulfonato-heptan-7-yl)thiophen-2,5-diyl) (11): The formation of potassium salt was carried out in a similar manner shown above with **8c** (29.0 mg, 0.1 mmol) and potassium hydroxyde (16.8 mg, 0.3 mmol) to afford 28.4 mg of the corresponding sulfonic acid sodium salt **10** in 95% yield. IR (ATR) 3500 (br), 2947, 2865, 1657 8 (w), 1441, 1369, 1183, 1104, 1050, 835 cm^{-1}. SEC analysis (H_2O) M_n = 22000.

Poly(3-(5-oxa-1-hydrogensulfonato-heptan-7-yl)thiophen-2,5-diyl) (12): To an aqueous solution of polythiophene lithium salt (**10**) (1 mg in 1.0 mL of water) was added 30 mg of Amberlite IR120B H at room temperature. The resulting suspension was stirred for 5 min to 24 h and the mixture was filtered off. The filtrate was concentrated under reduced pressure to leave a dark purple solid. IR (ATR) 3500 (br), 2947, 2865, 1657, 1441, 1369, 1183, 1104, 1050, 835 cm^{-1}.

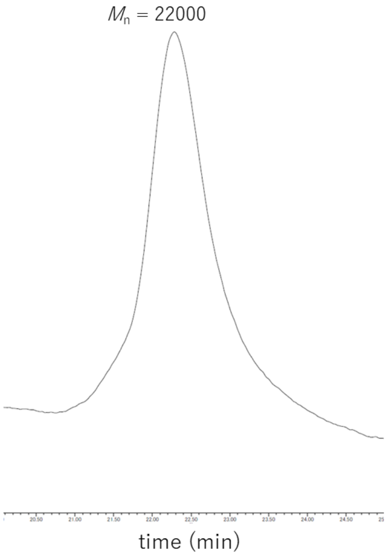
Oxidative polymerization of thiophene 3 with $Fe_2(OTs)_3OH$ (Taycatron AF40E) as an oxidant: To 2.0 mL of THF was added Sodium 4-(3-thienylethoxy)-1-butanesulfonate (**S3**) (29 mg, 0.1 mmol) at room temperature. $Fe_2(OTs)_3OH$ dispersed in 0.55 mL of EtOH (40.5% w/w, 0.4 mmol) was added to the resulting mixture followed by the addition of $Na_2S_2O_8$ (47.6 mg, 0.2 mmo). After stirring at 60 °C for 24 h, the mixture was cast on the glass substrate and subjected to the measurement of conductivity.

SEC profile of 8c

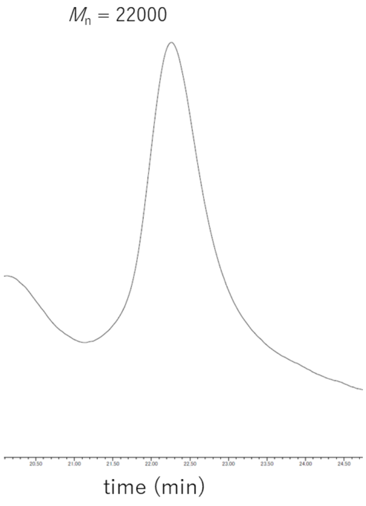


SEC profile of 9–11 using H_2O as an eluent

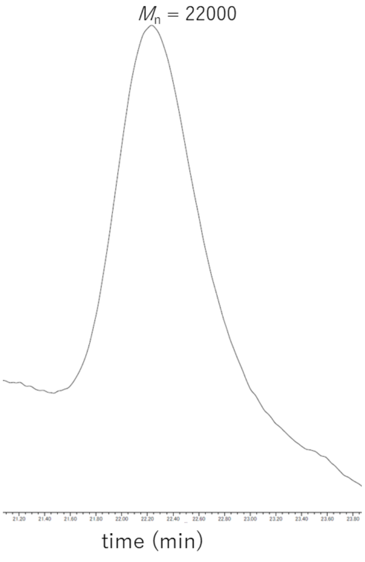
9 (M =Na)



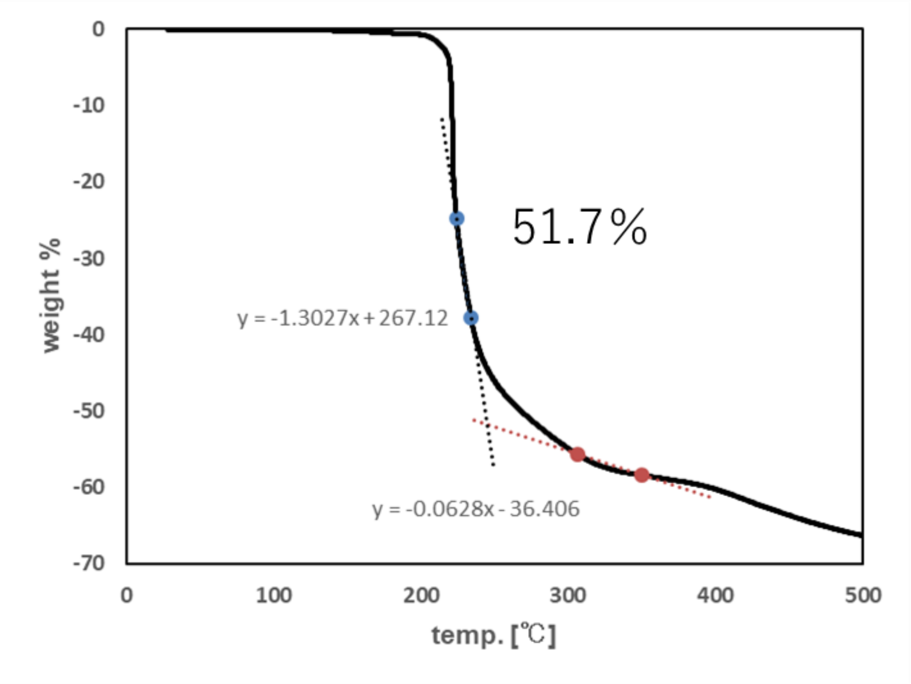
10 (M =Li)



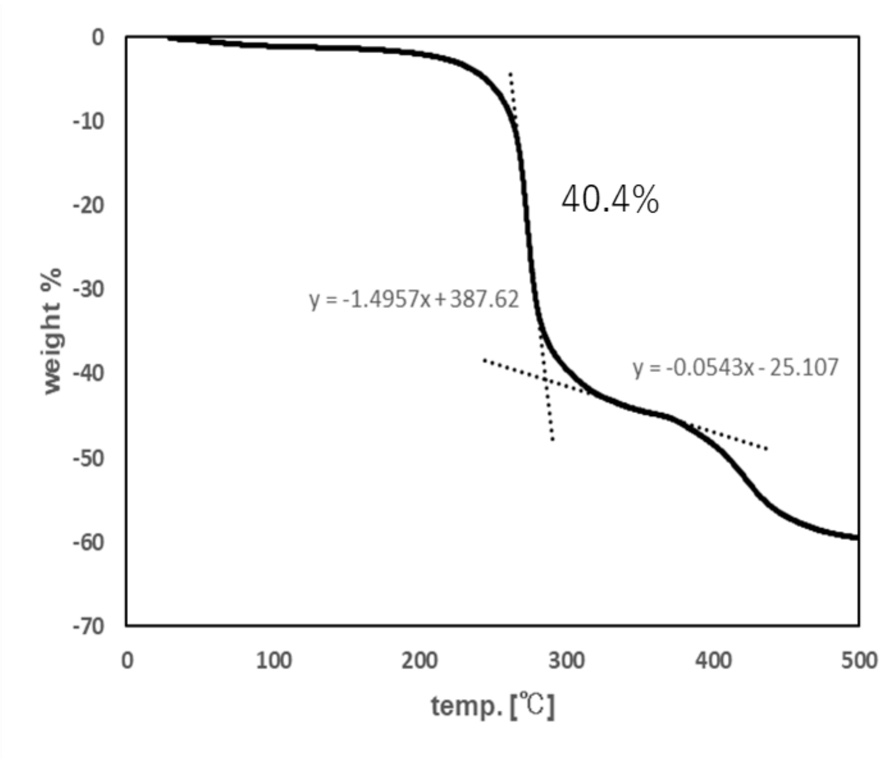
11 (M =K)



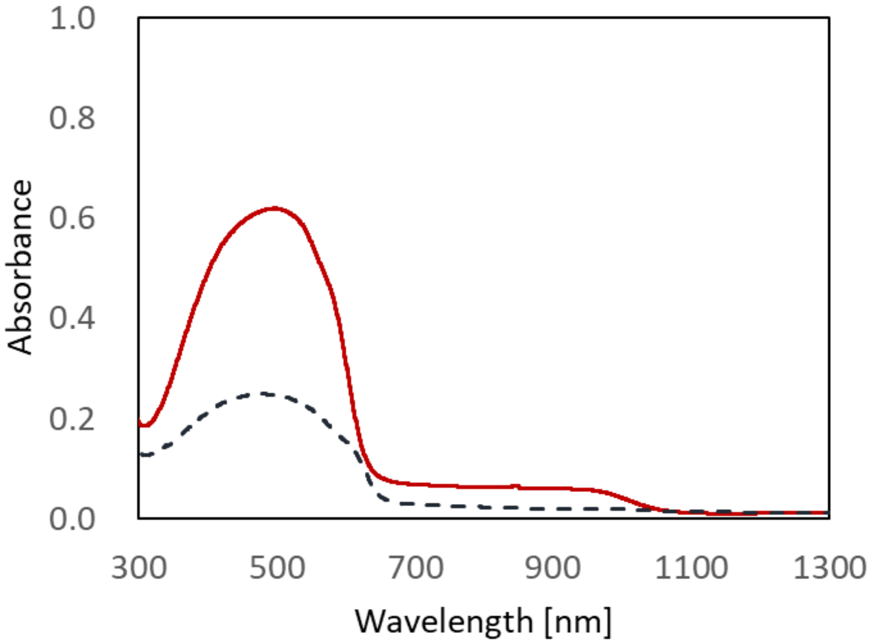
Thermogravimetric analysis of 8a (neopentyl ester)



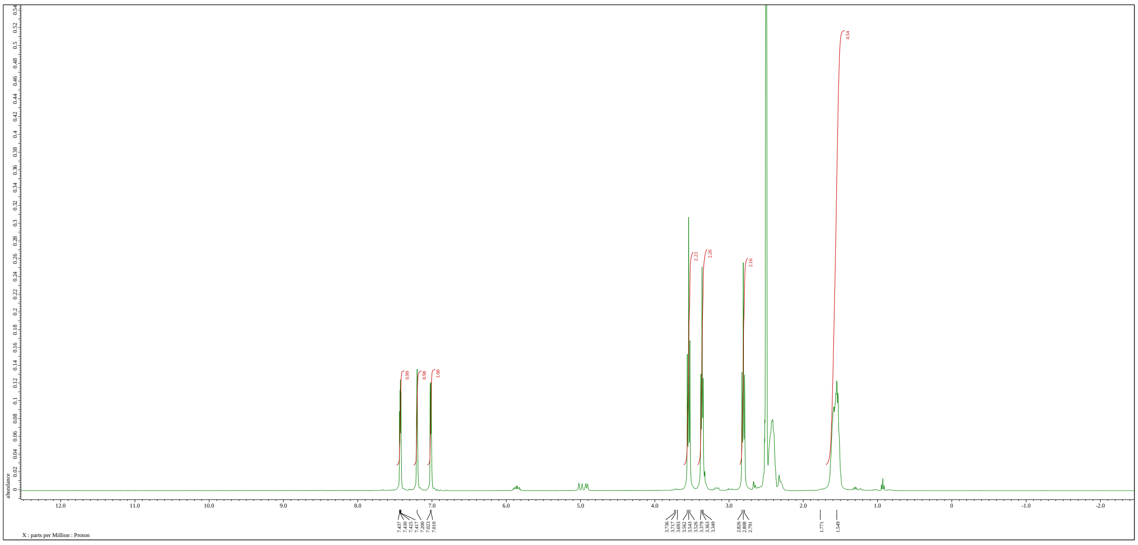
Thermogravimetric analysis (TG) of 8c (ethyl ester)

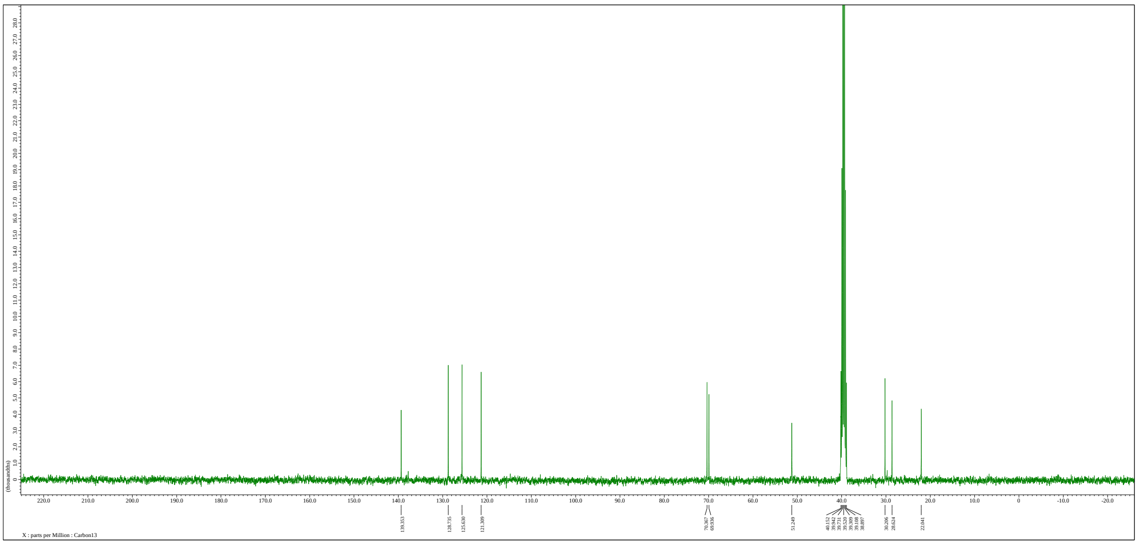


Absorption spectra of 9 in chloroform solution (red) and the thin film (black dotted)

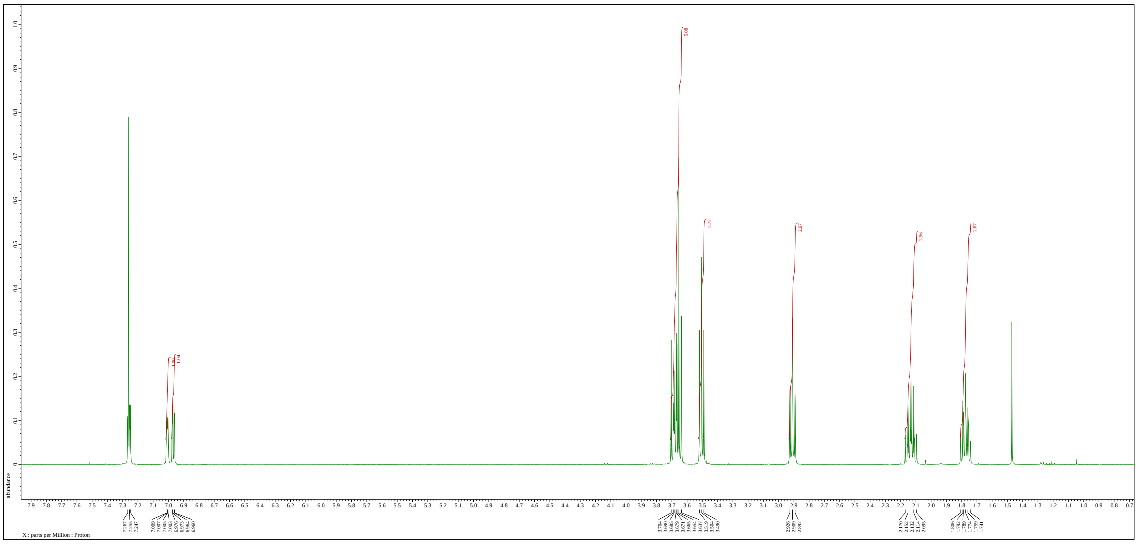


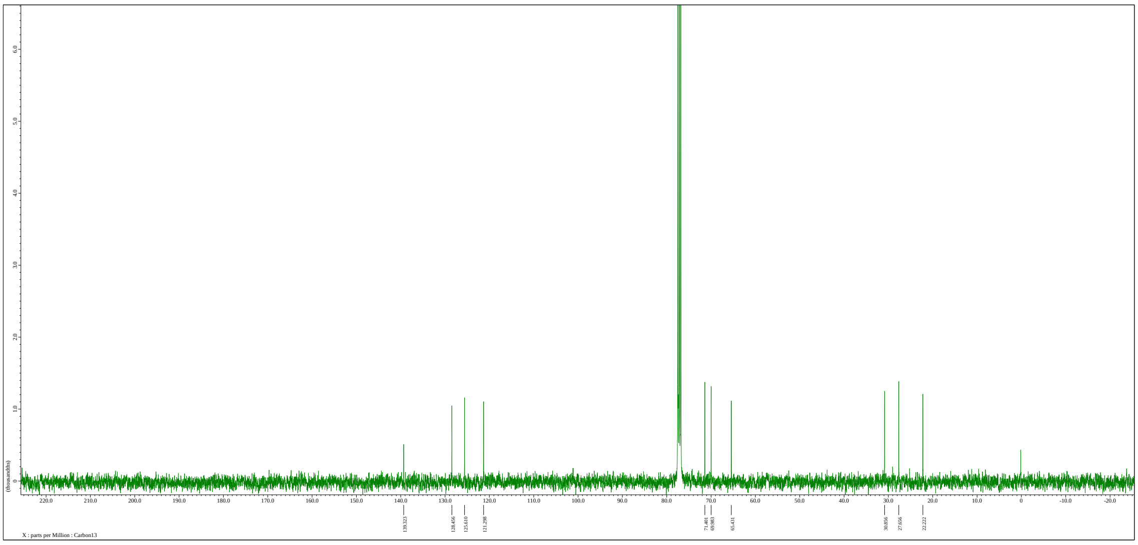
Sodium 4-(3-thienylethoxy)-1-butanesulfonate (S3)



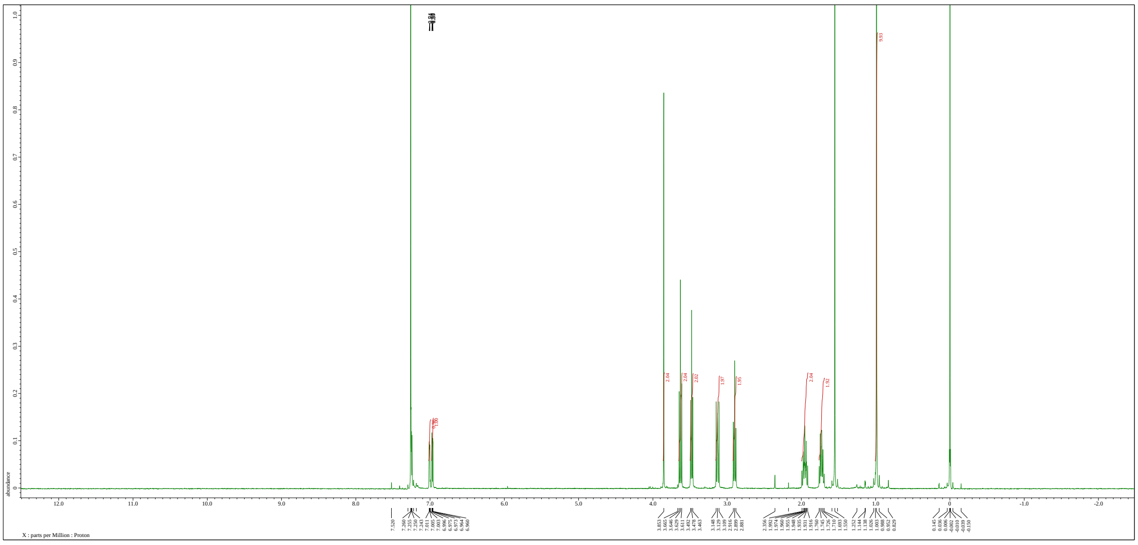


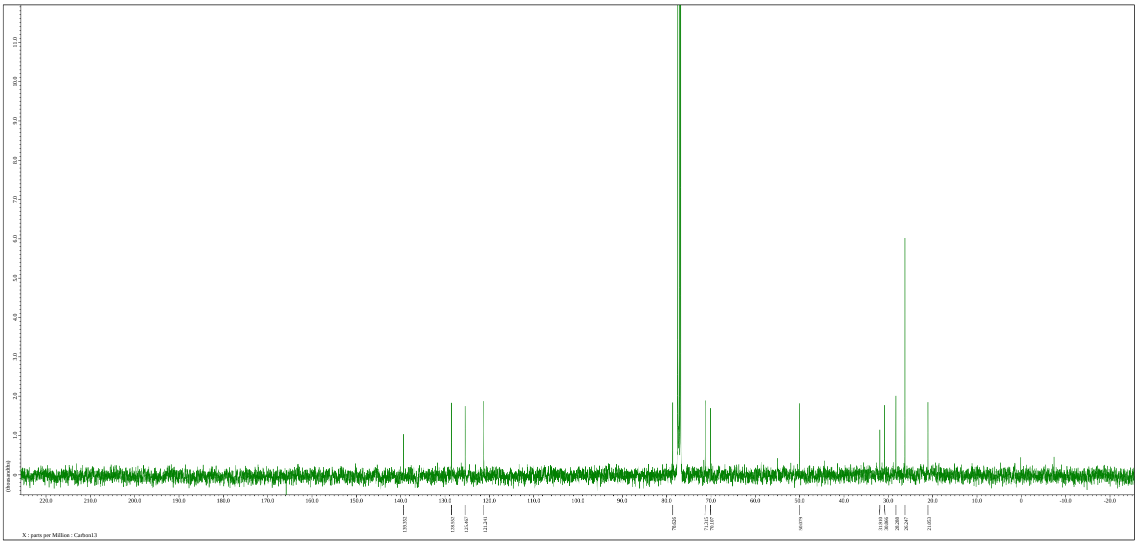
4-(3-Thienylethoxy)-1-butanesulfonyl chloride (S4)



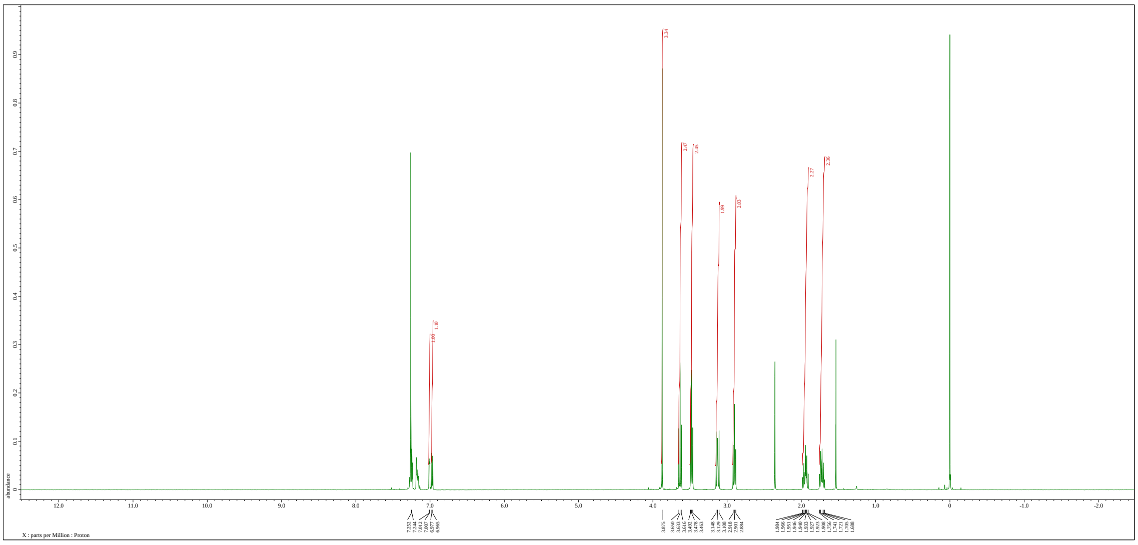


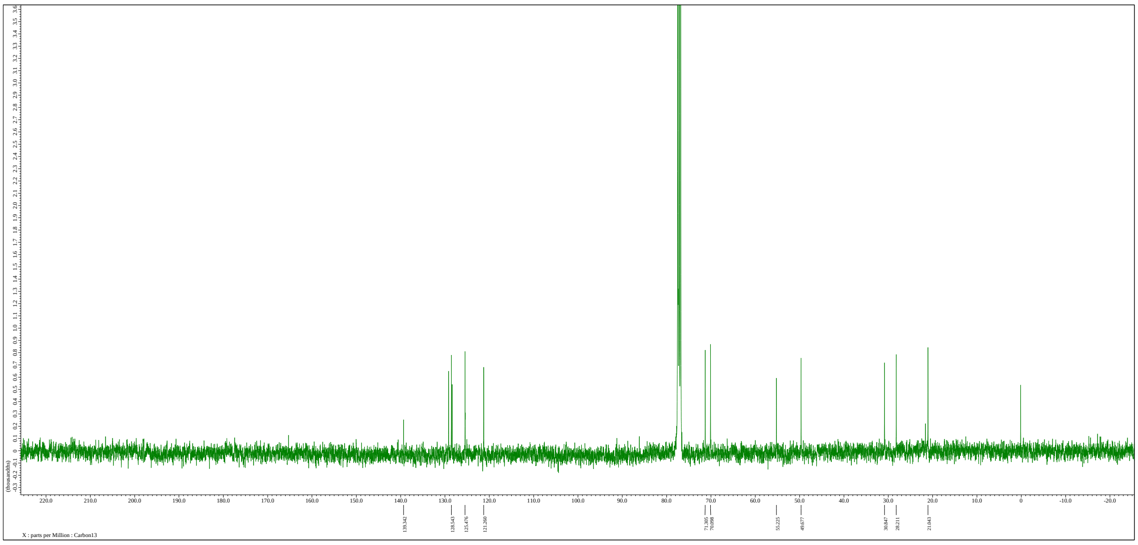
2,2-Dimethylpropyl 4-(3-thienylethoxy)-1-butanesulfonate (2a)



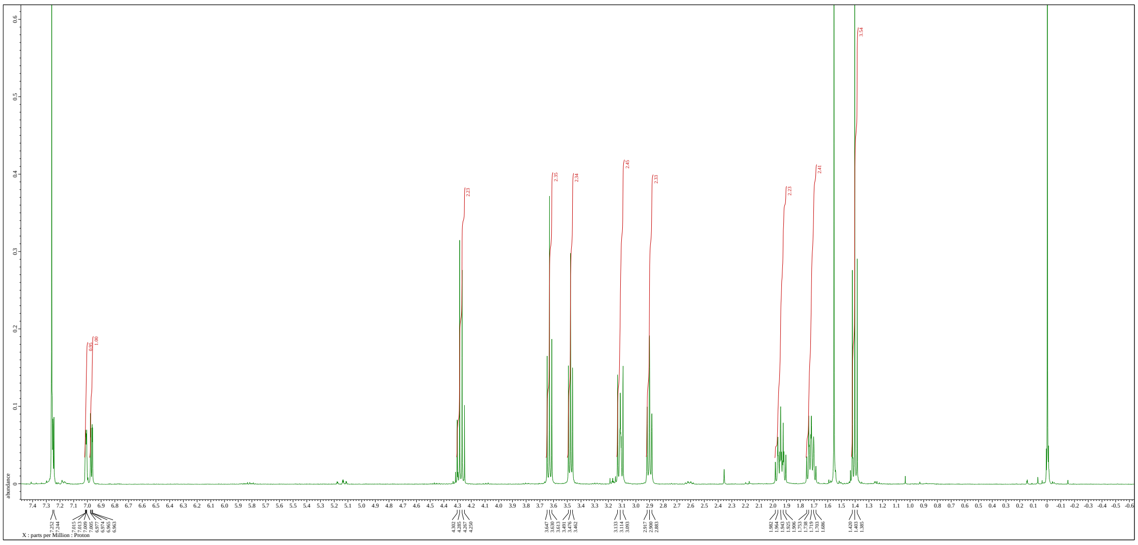


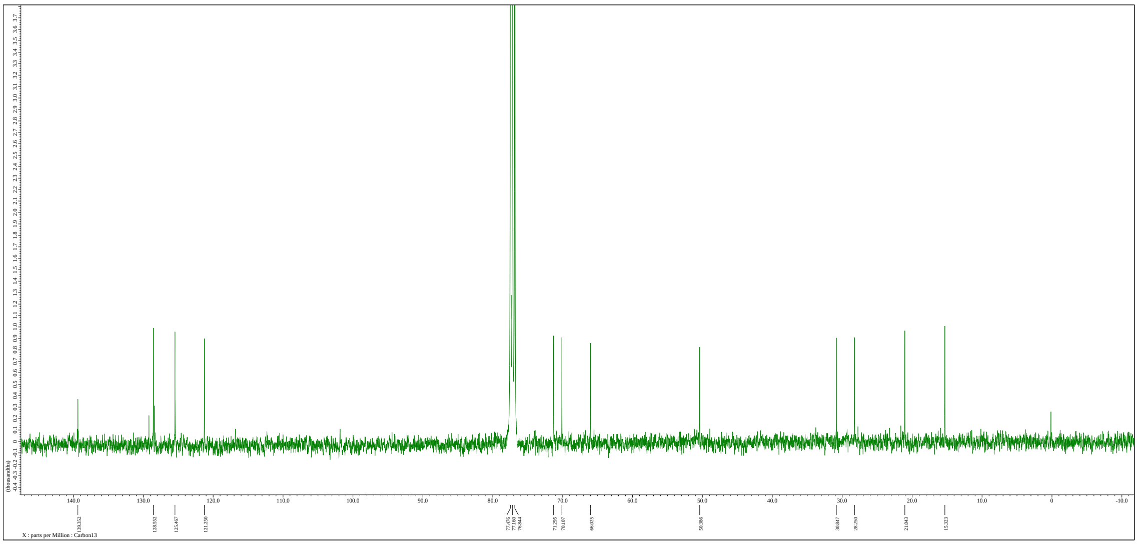
Methyl 4-(3-thienylethoxy)-1-butanesulfonate (2b)



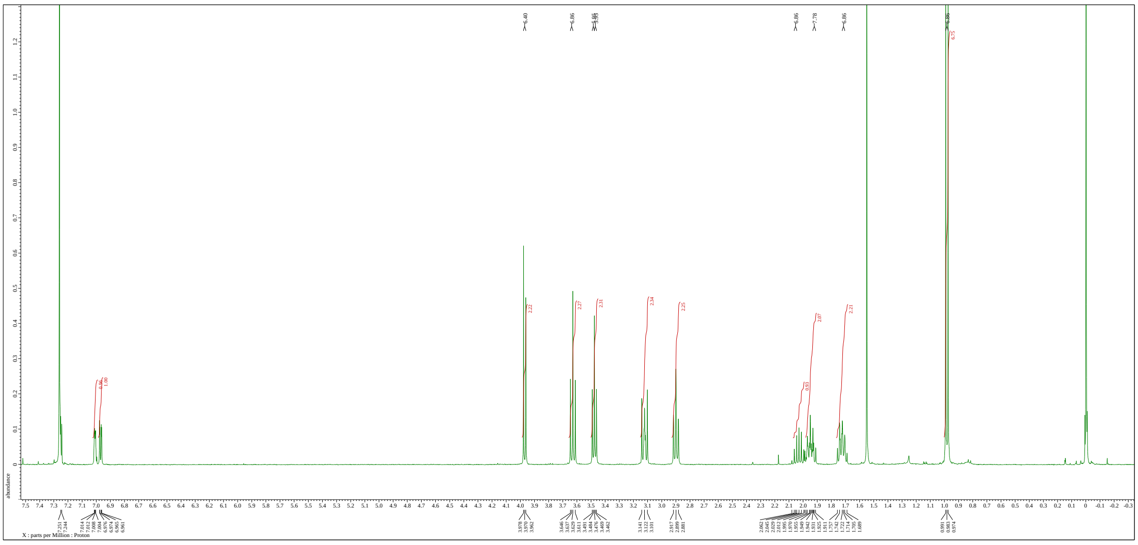


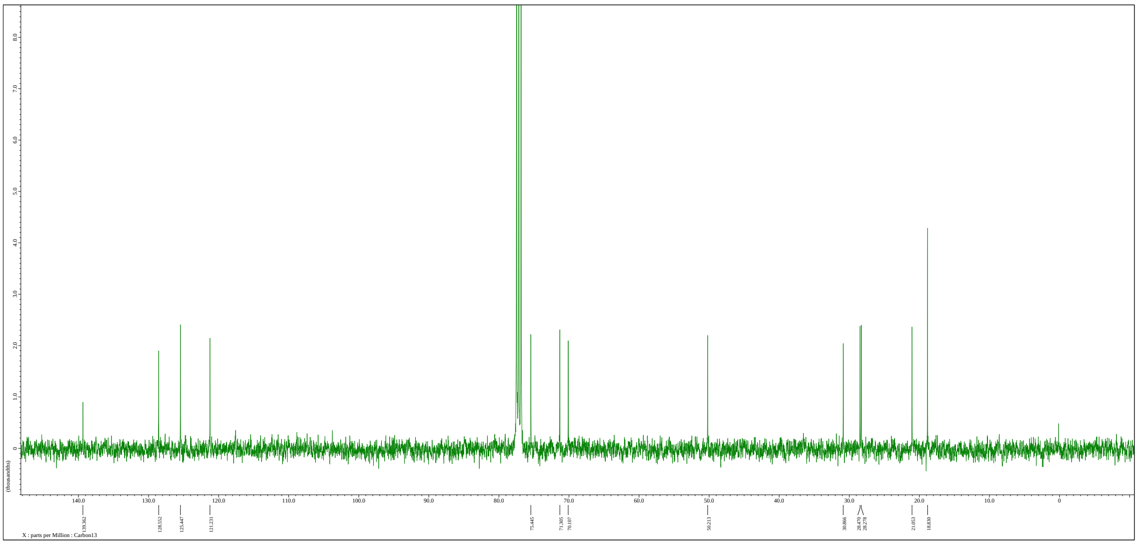
Ethyl 4-(3-thienylethoxy)-1-butanesulfonate (2c)



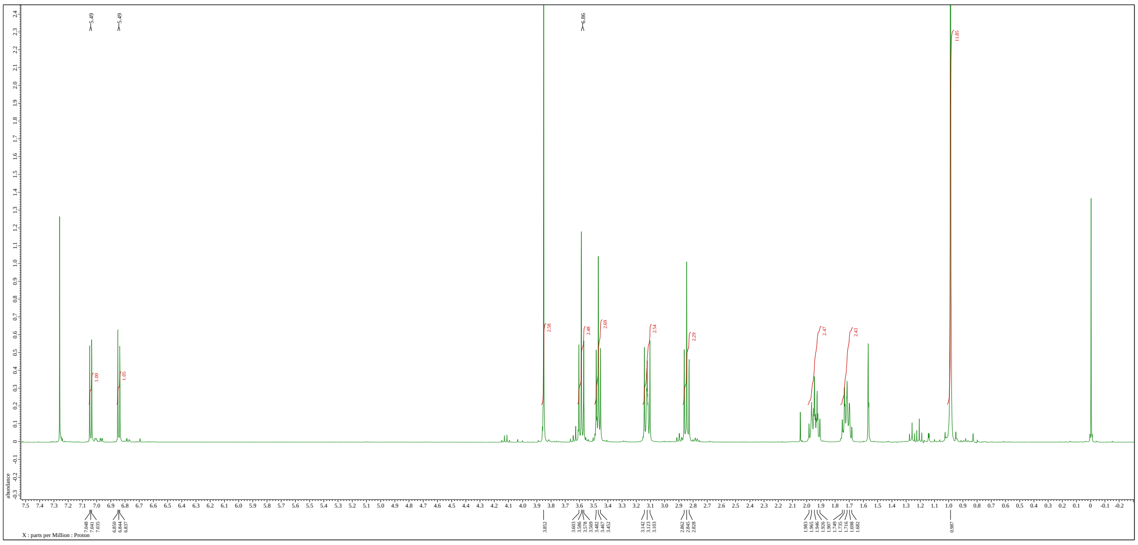


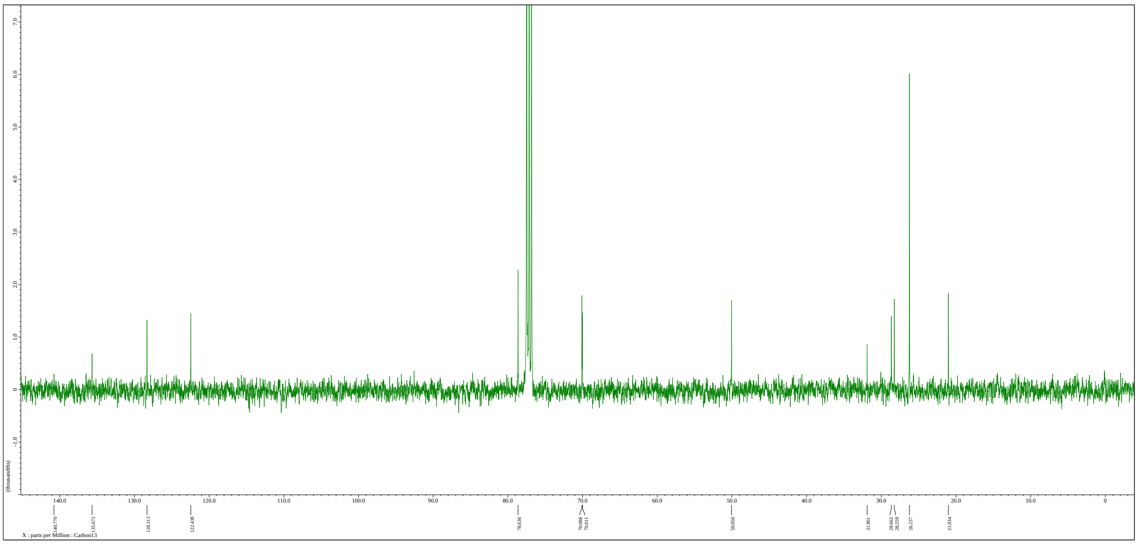
2-Methylpropyl 4-(3-thienylethoxy)-1-butanesulfonate (2d)



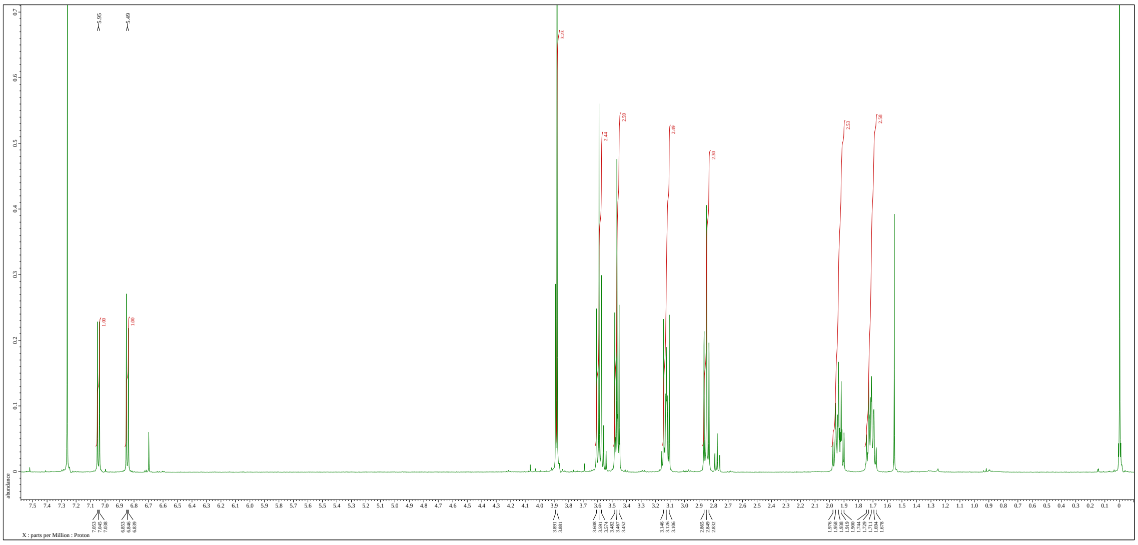


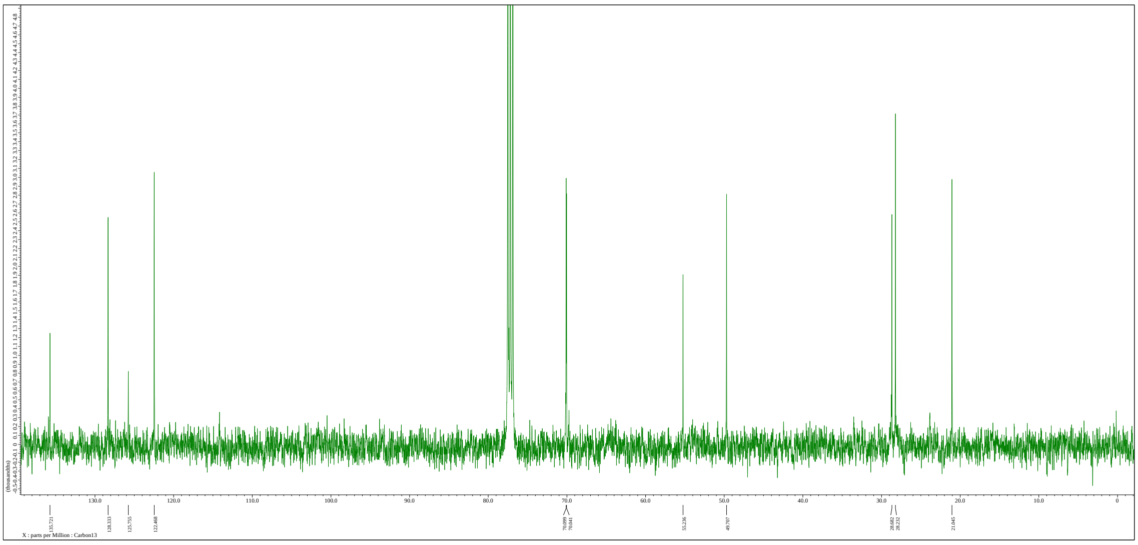
2,2-Dimethylpropyl 4-(3-(2-chlorothienyl)ethoxy)-1-butanesulfonate (3a)



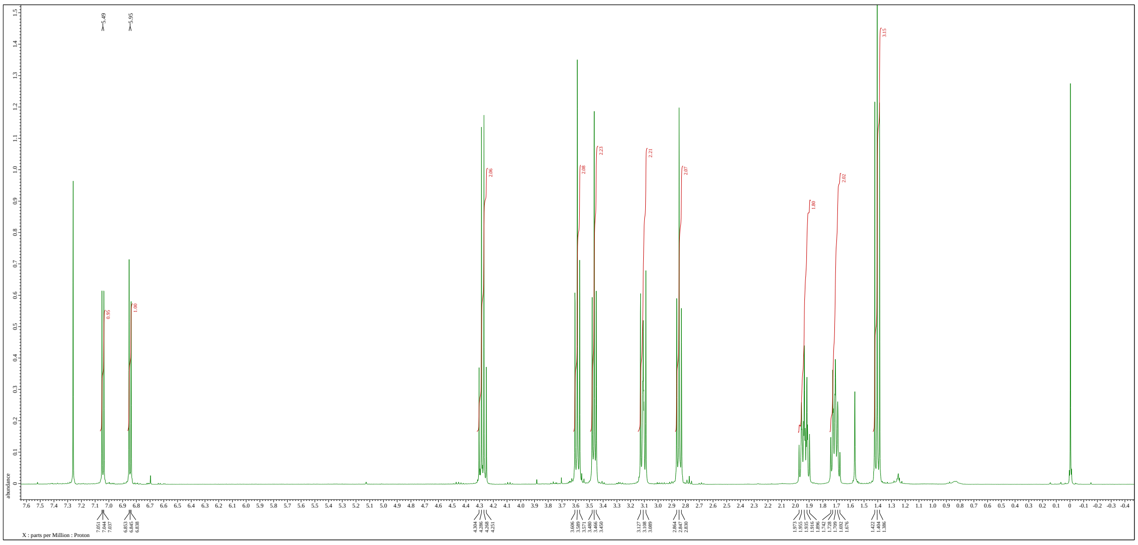


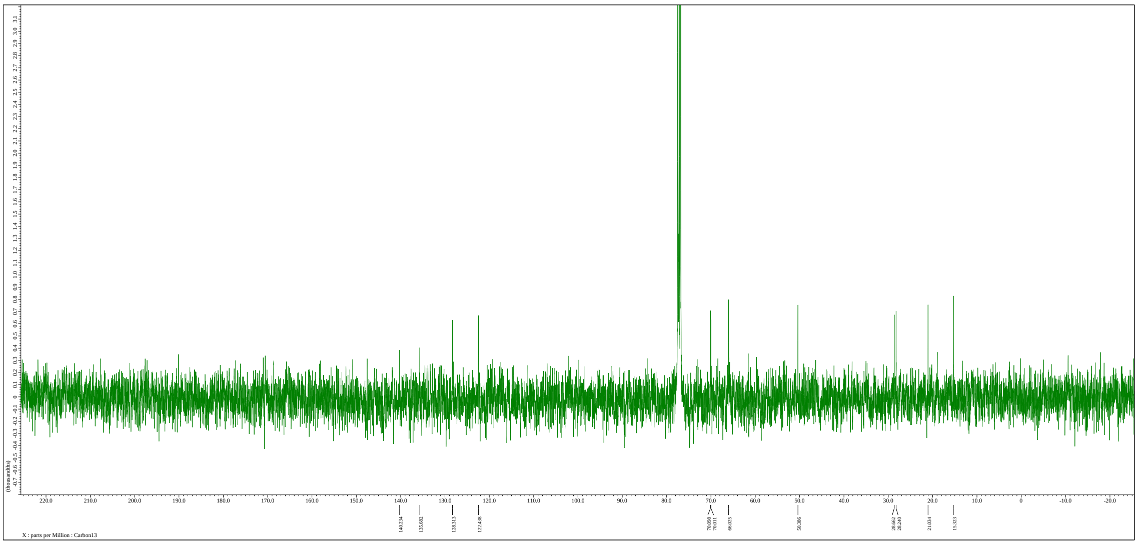
Methyl 4-(3-(2-chlorothienyl)ethoxy)-1-butanesulfonate (3b)





Ethyl 4-(2-chloro-3-thienylethoxy)-1-butanesulfonate (3c)





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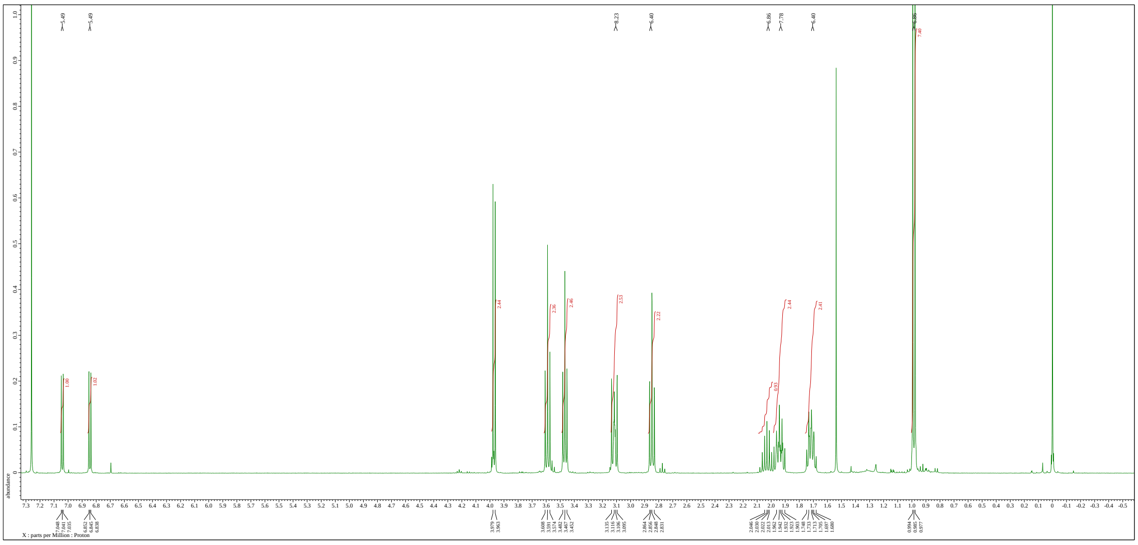
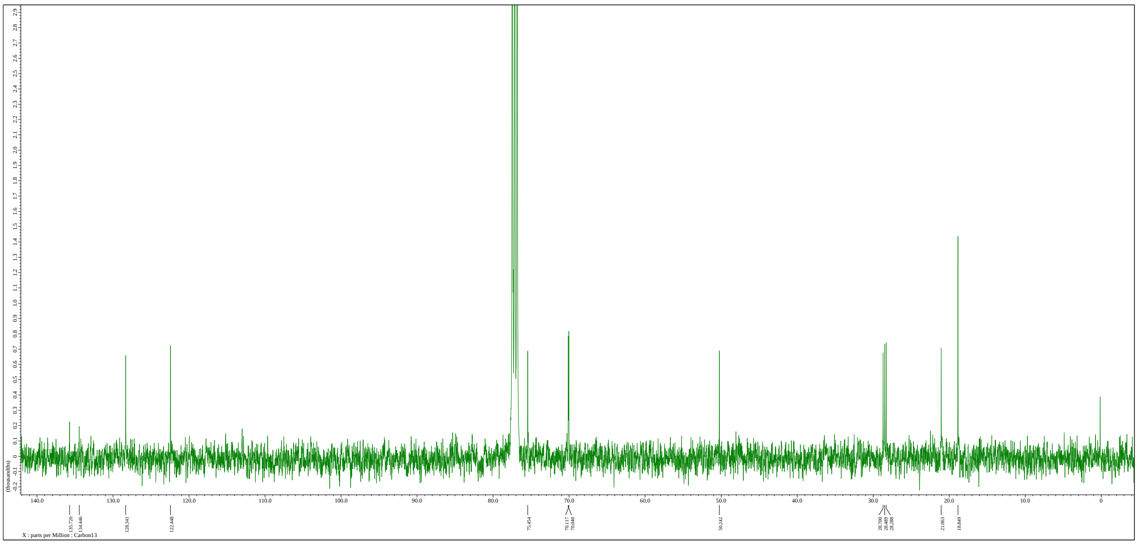
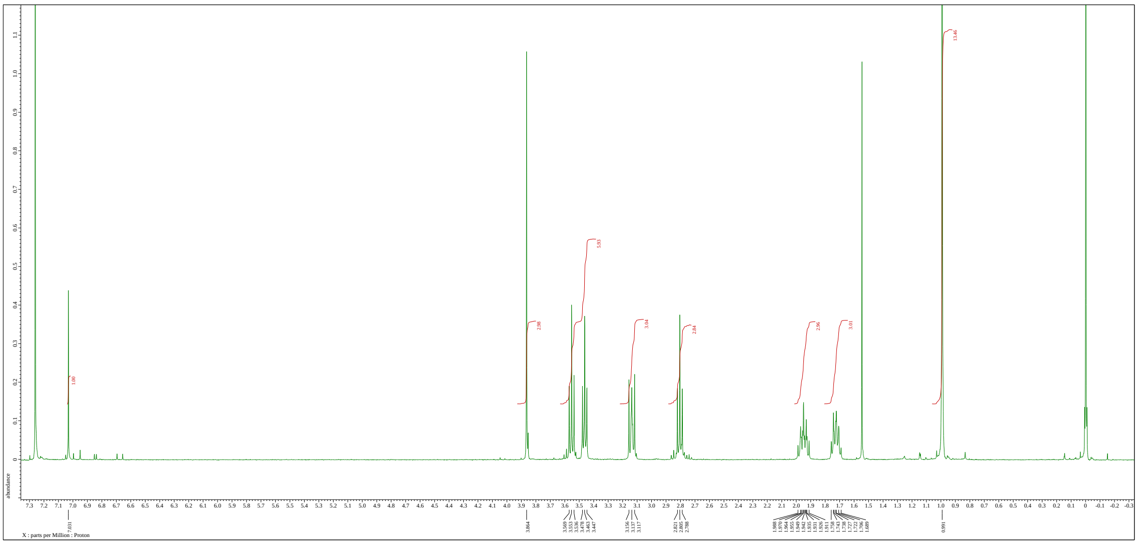
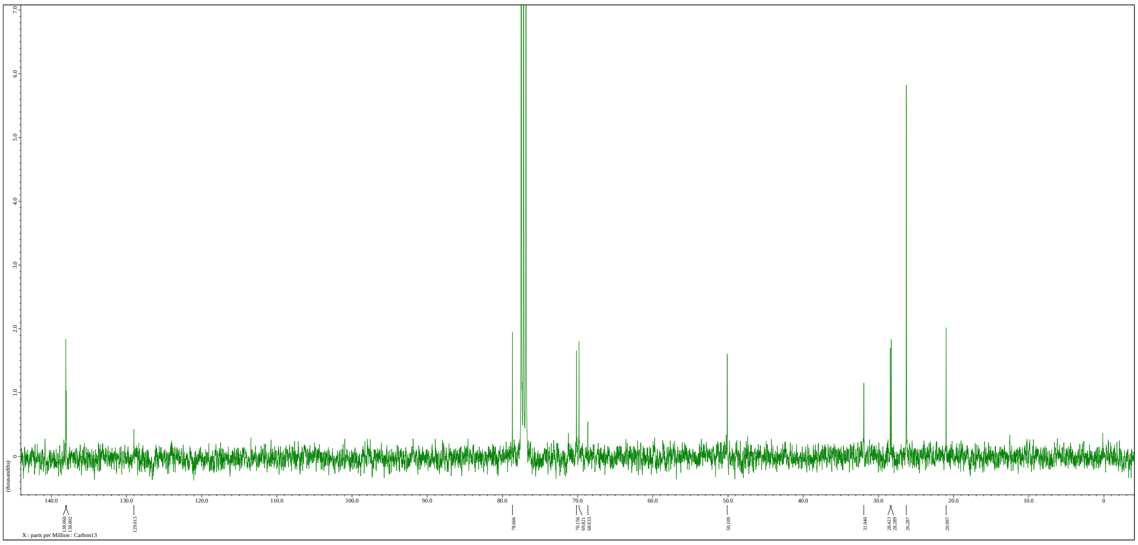


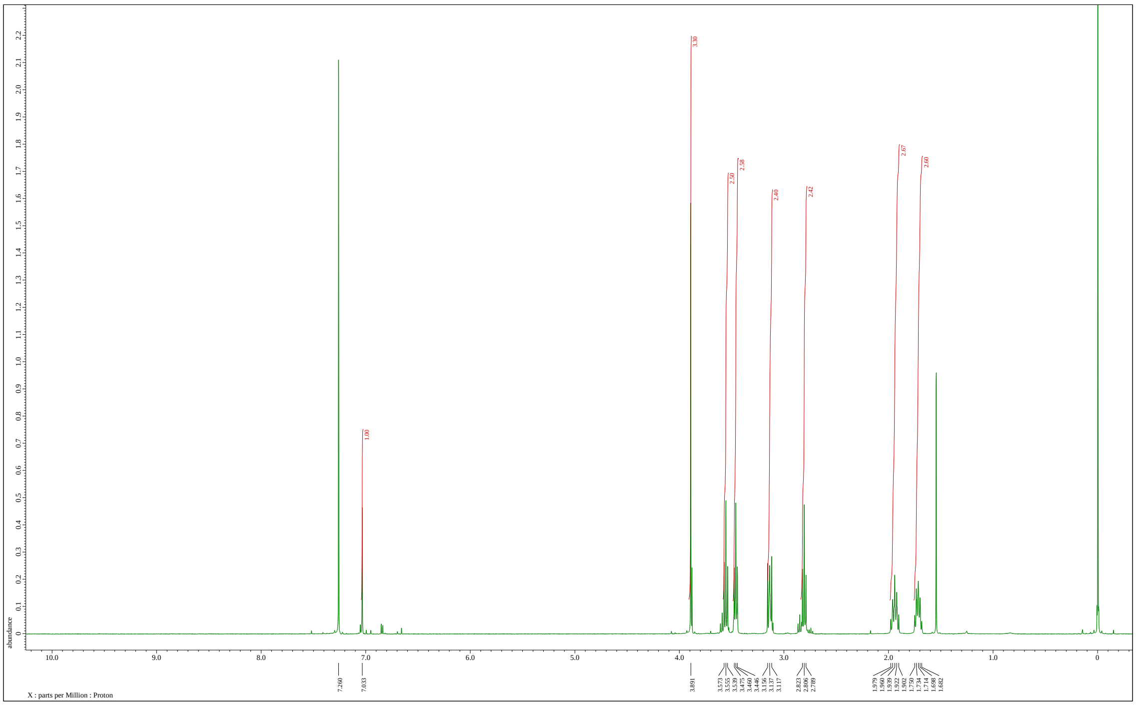


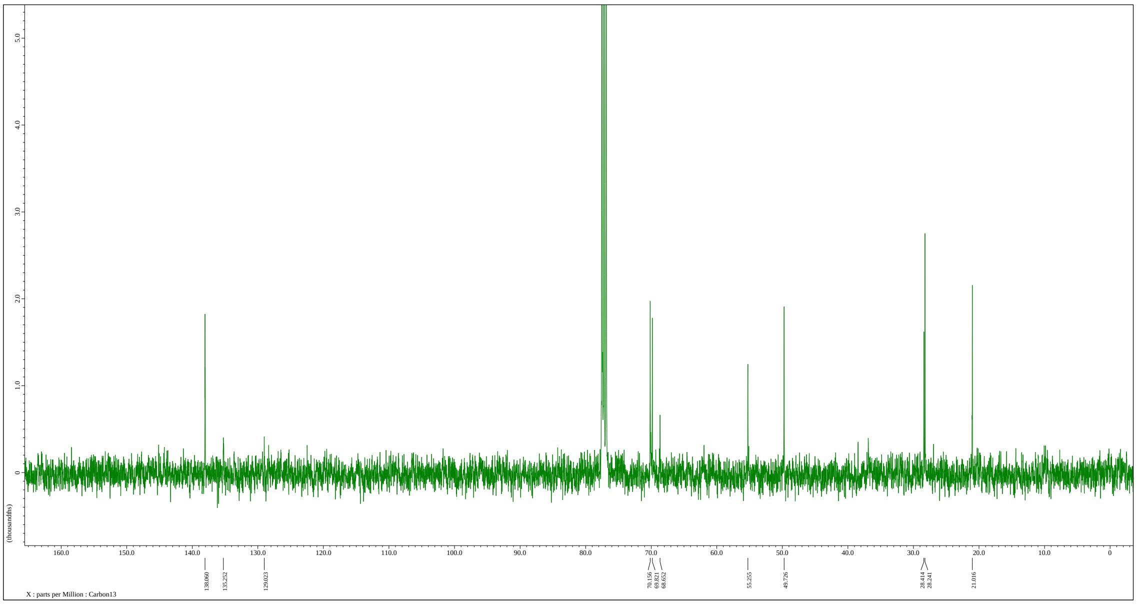
2,2-Dimethylpropyl 4-(2-chloro-5-iodo-3-thienylethoxy)-1-butanesulfonatethiophene (4a)



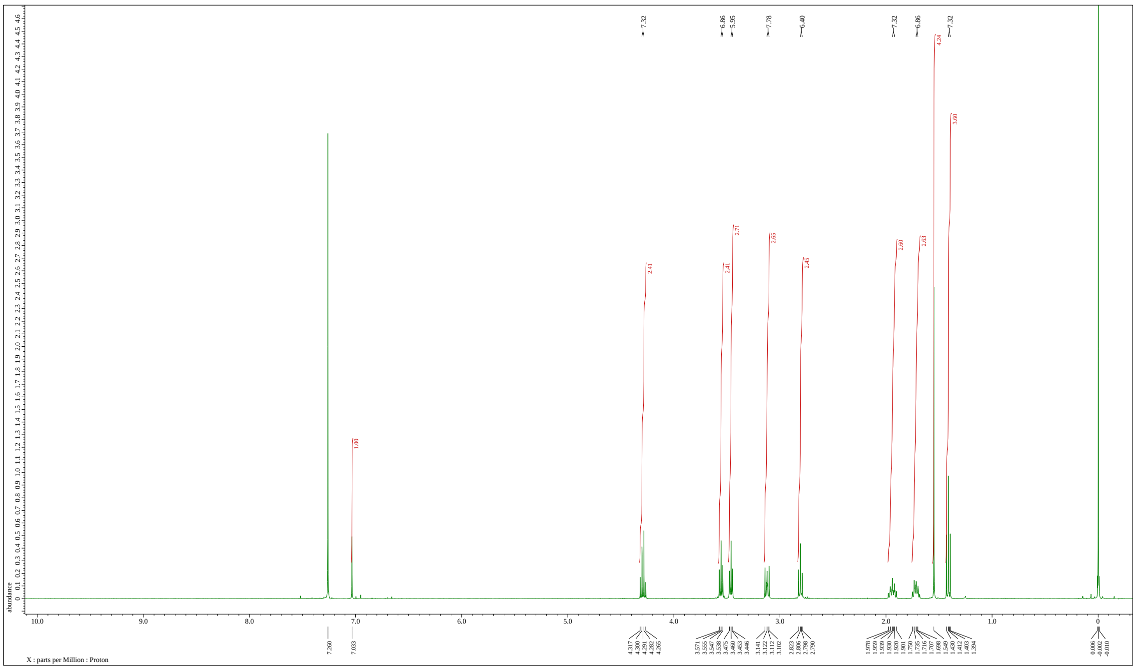


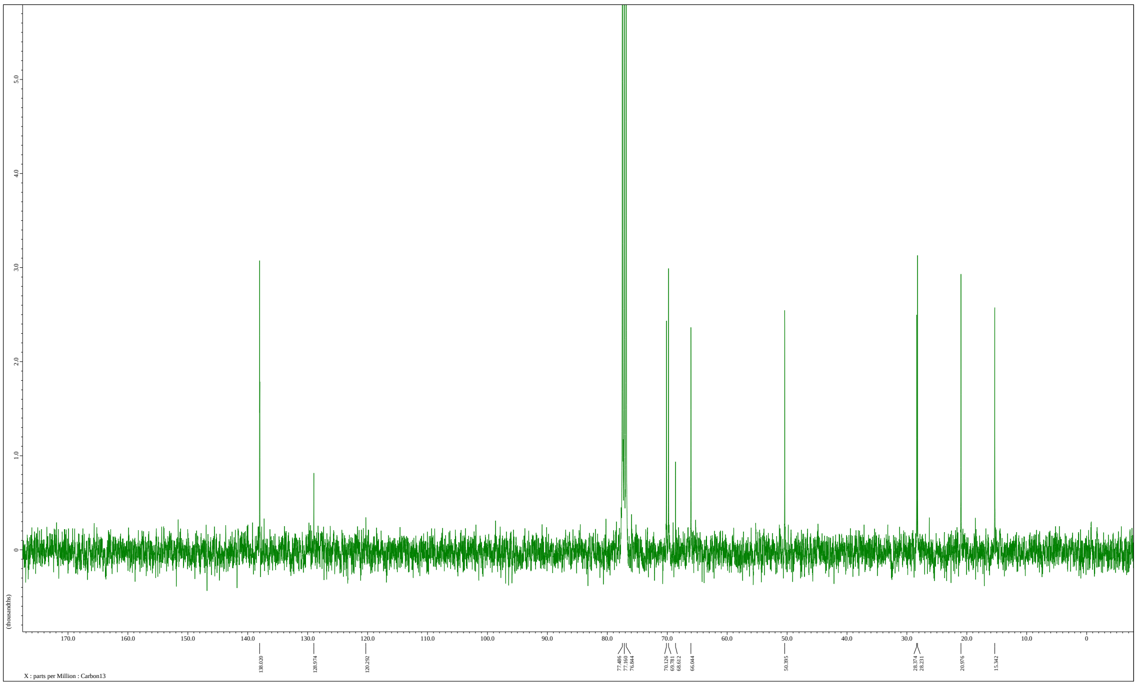
Methyl 4-(2-chloro-5-iodo-3-thienylethoxy)-1-butanesulfonate (4b)



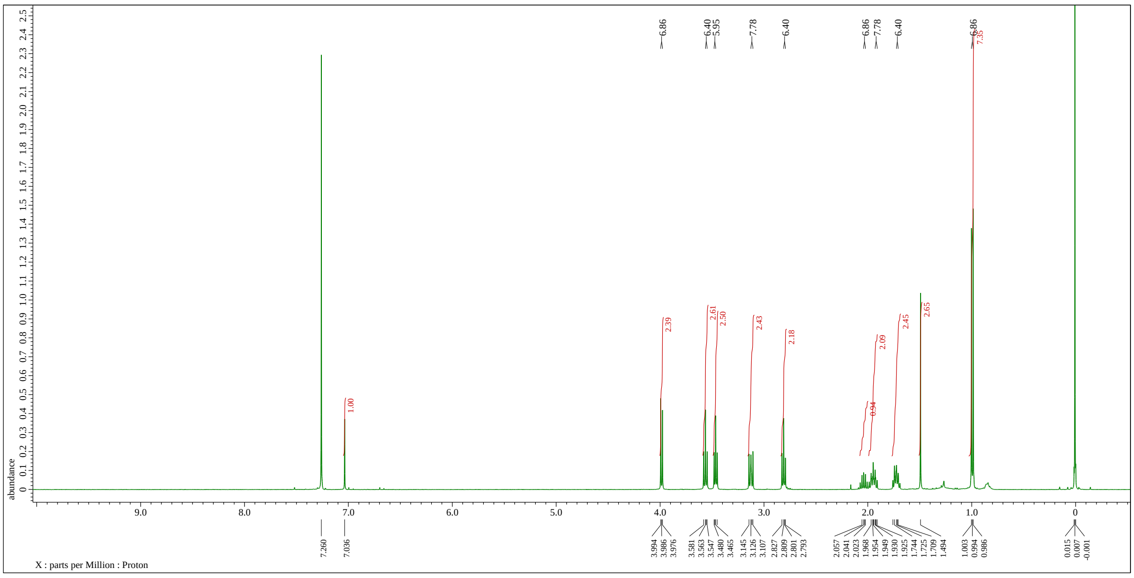


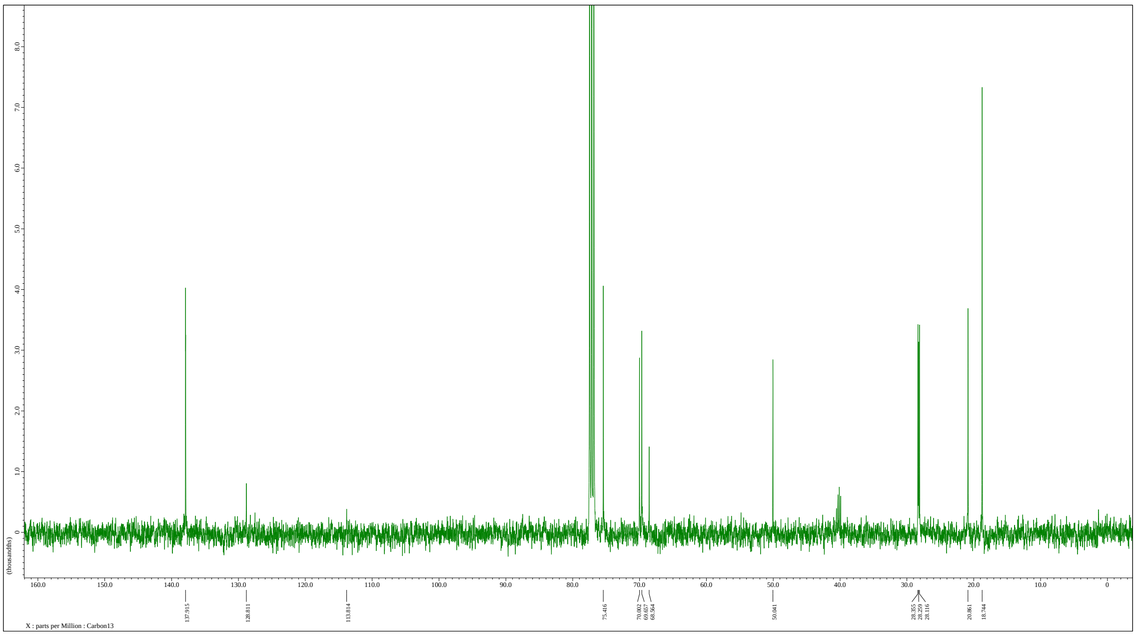
Ethyl 4-(2-chloro-5-iodo-3-thienylethoxy)-1-butanesulfonate (4c)



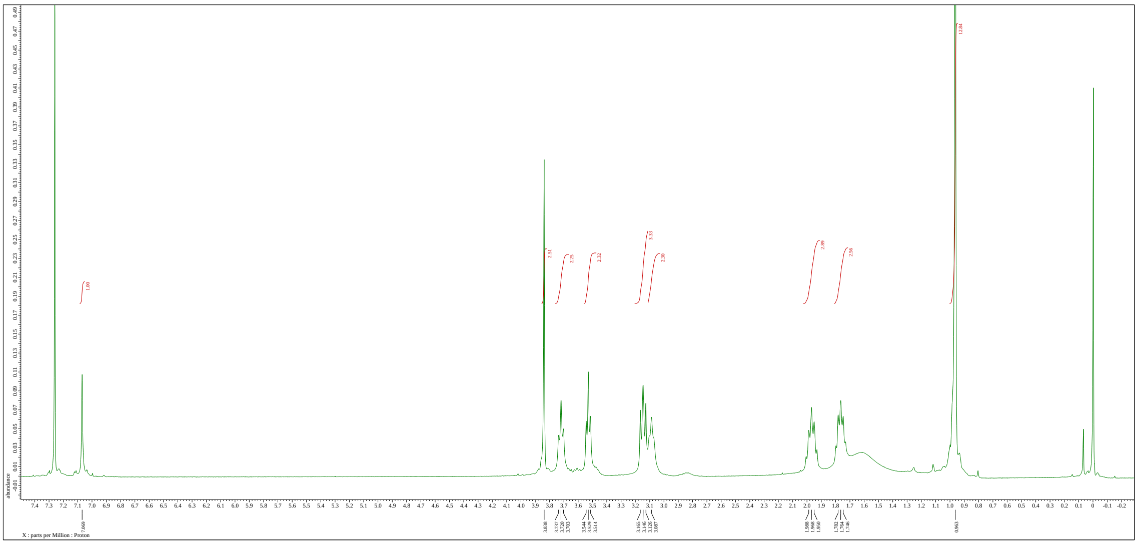


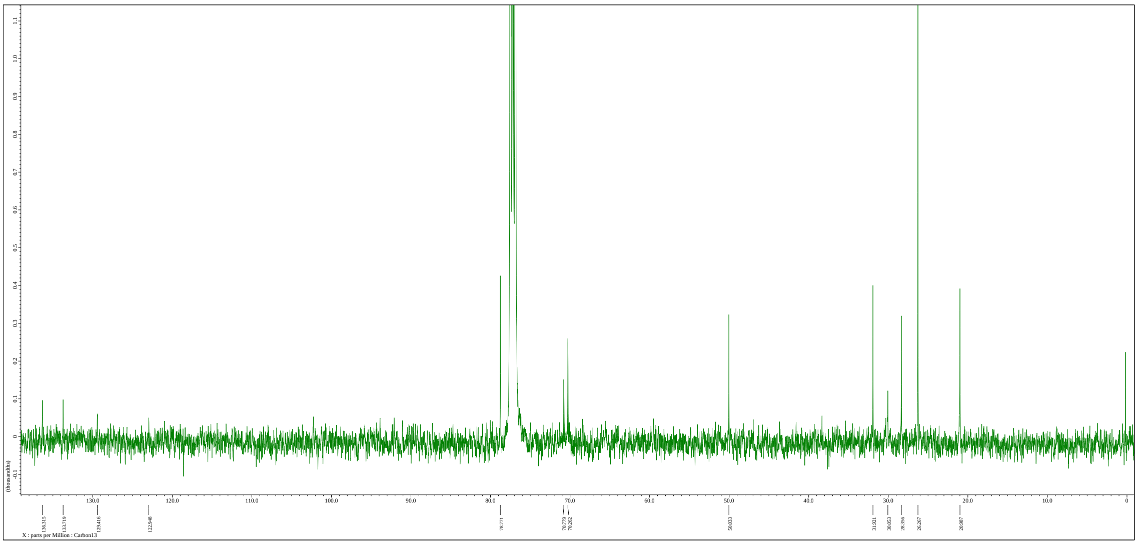
2-Methylpropyl 4-(2-chloro-5-iodo-3-thienylethoxy)-1-butanesulfonate (4d)



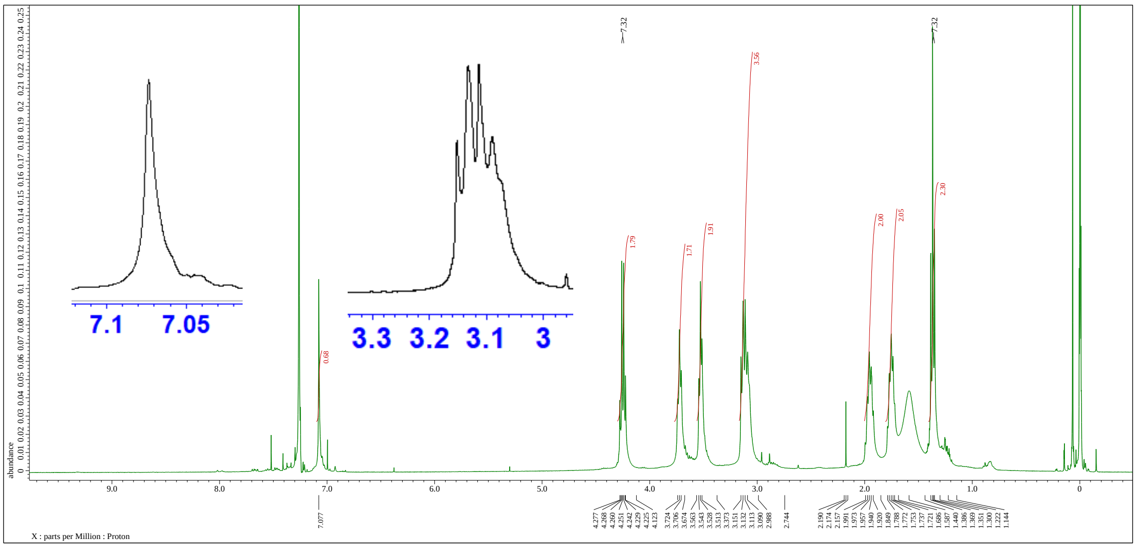


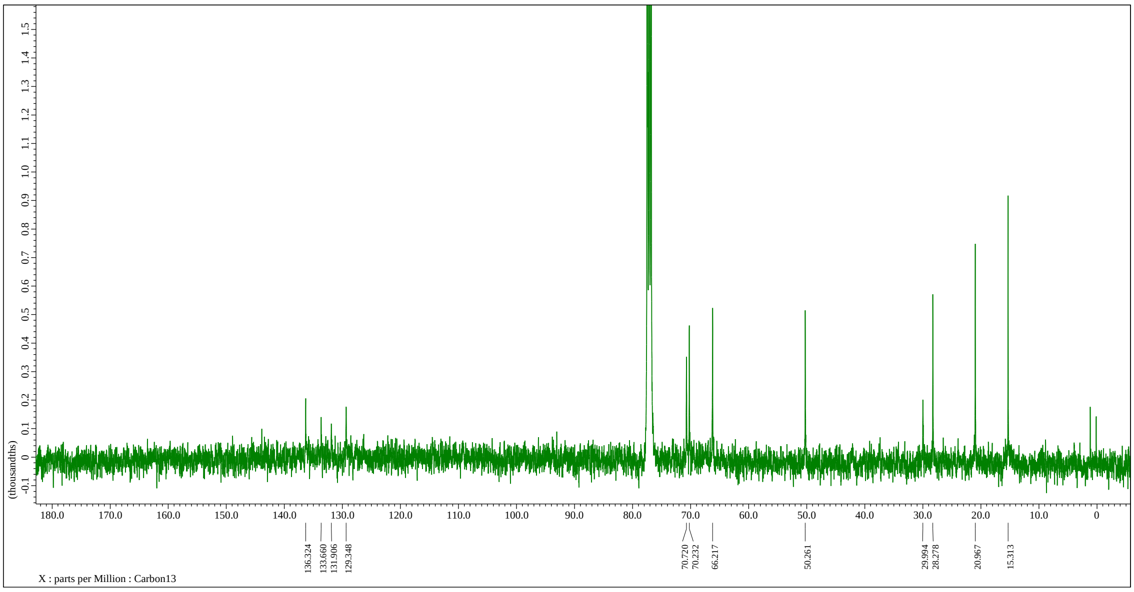
Polythioophene derived from 4a



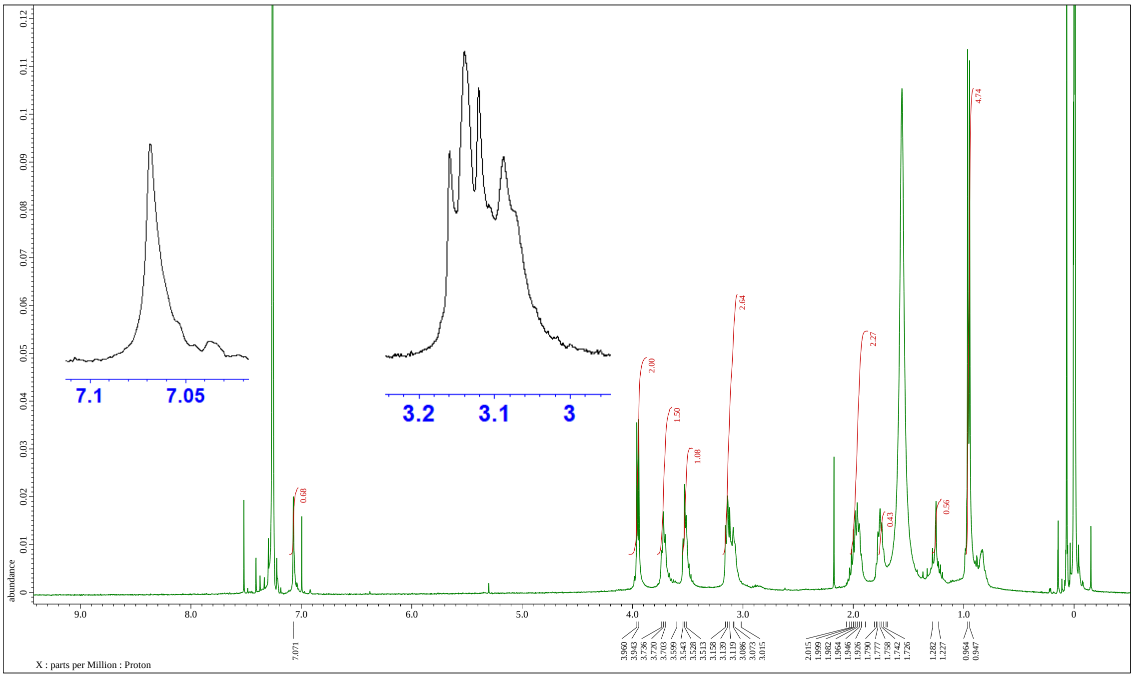


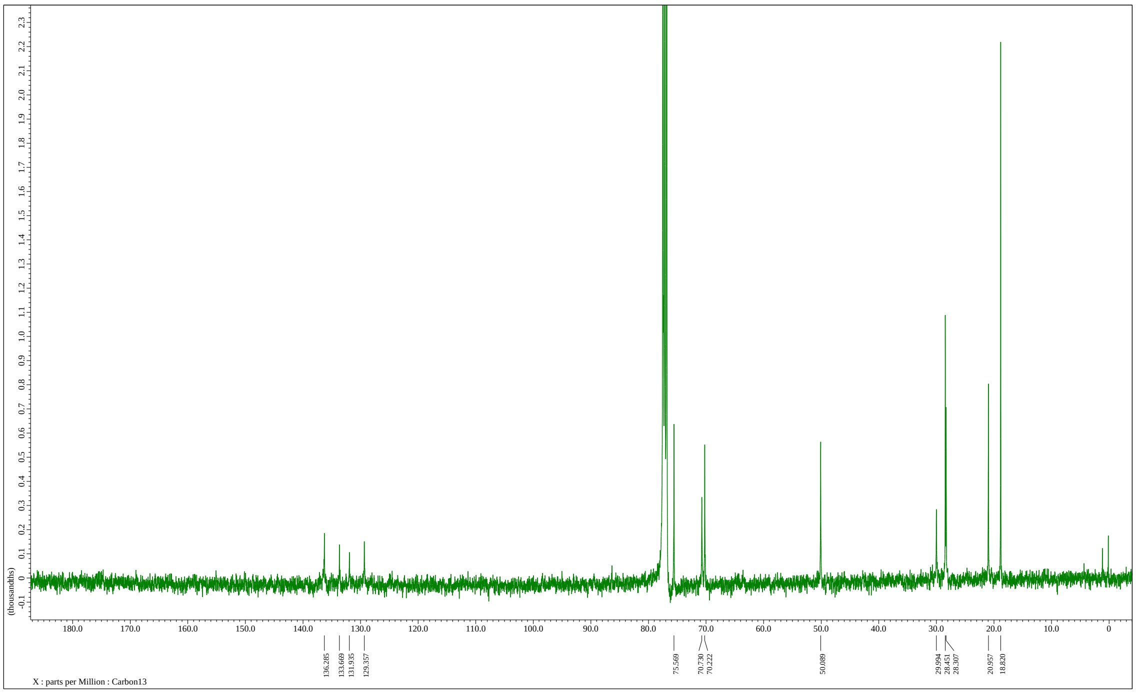
Polythioophene derived from 4c



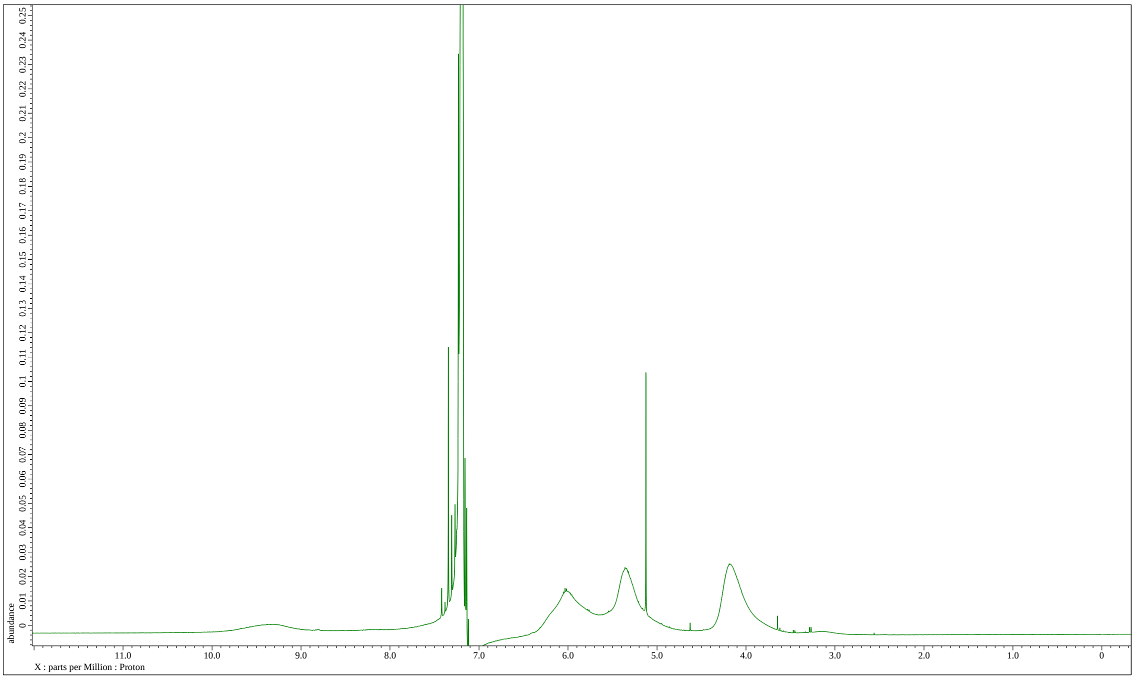


Polythioophene derived from 4d





Poly(3-(5-oxa-1-sodiumsulfonato-heptan-7-yl)thiophen-2,5-diyl) (9)



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