Supporting Information

Nickel(II)-catalyzed Cross-coupling Polycondensation of Thiophenes via C–S Bond Cleavage

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Experimental Section

General.

All the reactions were carried out under nitrogen atmosphere. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were measured on Varian Gemini 300 as a $CDCl_3$ solution unless noted. The chemical shifts were expressed in ppm with $CHCl_3$ (7.26 ppm for ^{1}H) or $CDCl_3$ (77.0 ppm for ^{13}C) as internal standards. IR spectra were recorded on Bruker Alpha with an ATR attachment (Ge). High resolution mass spectra (HRMS) were measured by JEOL JMS-T100LP AccuTOF LC-Plus (ESI) with a JEOL MS-5414DART attachment. SEC (size exclusion chromatography) analyses were performed with a standard HPLC system equipped with a UV detector using chloroform as an eluent with a Shodex KF-806L or the related column. Molecular weights and molecular weight distributions were estimated on the basis of the calibration curve obtained by 6 standard polystyrenes (M_n = 2630-355000). GC-MS analyses were carried out with SHIMADZU GCMS-QP2010 Plus. For thin layer chromatography (TLC) analyses throughout this work, Merck precoated TLC plates (silica gel 60 F_{254}) were used. TMPMgCl·LiCl was prepared by following the literature procedure[1] and stored in the freezer as 1.0 M THF solution. THF (anhydrous grade) was purchased from Kanto Chemicals Co., Ltd. and stored under nitrogen atmosphere. $NiCl_2$dppe, and $NiCl_2$dppp were prepared according to the literature procedure.[2] $NiCl_2(PPh_3)$IPr was purchased from Tokyo Chemical Industry Co., Ltd. Other materials were purchased and used without further purification.

3-Hexylthiophen-2-yl phenyl sulfide (3): Synthesis of **3** was carried out in a manner shown in the literature[3] with slight modification. To 1.3 M THF solution of ^{i}PrMgCl·LiCl (11.5 mL, 15 mmol) in a 50 mL Schlenk tube equipped with a magnetic stirring bar 2-bromo-3-hexyothiophene (3.0 mL, 15 mmol) was added dropwise under nitrogen atmosphere and stirring was continued at 60 °C for 5 h to furnish the solution of the corresponding Grignard reagent. *N*-Chlorosuccinimide (1.65 g, 16.5 mmol) was added to a solution of benzenethiol (1.53 mL, 15 mmol) in toluene (22 mL) at room temperature. After stirring the mixture for further 20 min, toluene (15 mL) and the formed Grignard solution were added dropwise. After being stirred for another 10 min, the reaction mixture was quenched with H_2O. The aqueous layer was extracted with several portions of diethyl ether. The combined organic layer was dried over anhydrous

Na_2SO_4, and concentrated under reduced pressure. The residue was chromatographed on silica gel using hexane as an eluent to yield 3-hexylthiophen-2-yl phenyl sulfide (**3**) as colorless oil (70% yield). Attempted microanalysis of **3** has not been successful so far due to the difficulties in the separation of unidentified side product. ^{1}H NMR ($CDCl_3$) δ 0.85 (t, *J* = 6.6 Hz, 3H), 1.17-1.36 (m, 6H), 1.46-1.60 (m, 2H), 2.67 (t, *J* = 7.8 Hz, 2H), 7.03 (d, *J* = 5.4 Hz, 1H), 7.05-7.15 (m, 3H), 7.18-7.25 (m, 2H), 7.41 (d, *J* = 5.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ14.0, 22.5, 29.0, 30.4, 31.6, 124.3, 125.5, 126.3, 128.8, 129.1, 129.4, 139.0, 149.9; IR (ATR) 2954, 2925, 2855, 1582, 1477, 1439, 1081, 1024, 835, 736, 688, 667 cm^{-1}; HRMS (DART-ESI+) Calcd for $C_{16}H_{21}S_2$ $[M+H]^+$: 277.1085; found: m/z 277.1085.

2-Phenylsulfinyl-3-hexylthiophene (**4**): To a solution of 3-hexylthiophen-2-yl phenyl sulfide (**3**, 1.52 g, 5.5 mmol) in dichloromethane (20 mL) was added *m*-chloroperoxybenzoic acid (863 mg, 5.0 mmol) at 0 °C. After stirring for 24 h, the reaction mixture was quenched with H_2O. The aqueous layer was extracted with several portions of diethyl ether. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was chromatographed on silica gel using 5:1 hexane:AcOEt as an eluent to afford 2-phenylsulfinyl3-hexylthiophene (**4**) as a colorless oil (63% yield). Attempted microanalysis of **4** has not been successful so far due to the difficulties in purification procedures. ^{1}H NMR ($CDCl_3$) δ 0.90 (t, *J* = 6.9 Hz, 3H), 1.21-1.47 (m, 6H), 1.55-1.77 (m, 2H), 2.93 (t, *J* = 7.7 Hz, 2H), 6.9 (d, *J* = 5.1 Hz, 1H), 7.45-7.55 (m, 4H), 7.65-7.71 (m, 2H); ^{13}C NMR ($CDCl_3$) δ14.0, 22.5, 28.8, 29.0, 30.9, 31.5, 124.6, 128.9, 129.0, 130.8, 131.4, 141.6, 145.1, 148.7; IR (ATR) 2927, 2856, 1522, 1465, 1443, 1398, 1377, 1038, 1046, 1029, 746, 689 cm^{-1}; HRMS (ESI+) Calcd for $C_{16}H_{20}NaOS_2$ $[M+Na]^+$: 315.0853; found: m/z 315.0853.

2-Phenylsulfonyl-3-hexylthiophene (1): To a solution of 3-hexylthiophen-2-yl phenyl sulfide (**3**, 3.59 g, 13 mmol) in AcOH (39 mL) was added 30 wt% H_2O_2 in H_2O (3.81 mL g, 3.21 mmol) dropwise at room temperature. After stirring at 60 °C for 5 h, the reaction mixture was washed with water, extracted with Et_2O, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was chromatographed on silica gel using 20:1 hexane:AcOEt as an eluent to afford 2-phenylsulfonyl-3-hexylthiophene (**1**) as a colorless solid (80% yield). Attempted

microanalysis of **1** has not been successful so far due to the difficulties in purification procedures. ^{1}H NMR ($CDCl_3$) δ 1.85 (t, *J* = 6.7 Hz, 3H), 1.14-1.31 (m, 6H), 1.34-1.47 (m, 2H), 2.79 (t, *J* = 7.8 Hz, 2H), 6.93 (d, *J* = 5.0 Hz, 1H), 7.46-7.62 (m, 4H), 7.92-7.99 (m, 2H); ^{13}C NMR ($CDCl_3$) δ14.0, 22.4, 28.5, 29.0, 30.1, 31.5, 127.2, 129.1, 130.7, 131.6, 133.0, 135.8, 142.3, 148.7; IR (ATR) 2955, 2928, 2857, 1523, 1465, 1446, 1398, 1318, 1152, 1112, 1085, 753, 722, 687 cm^{-1}; HRMS (DART-ESI+) Calcd for $C_{16}H_{21}O_2S_2$ $[M+H]^+$: 309.0983; found: m/z 309.0983.

5-Bromo-2-phenylsulfonyl-3-hexylthiophene (6): To a solution of 3-hexylthiophen-2-yl phenyl sulfide (**3**, 830 mg, 3.0 mmol) prepared in a similar manner shown above from 2-bromo-3-hexylthiophene in 10 mL of THF was added *N*-bromosuccinimide (534 mg, 3.0 mmol) at 0 °C. After stirring at 0 °C for 2 h, the mixture was quenched with water and two phases were separated. The organic phase was washed with water and the aqueous phase was extracted with hexane. The combined organic layer was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was chromatographed on silica gel using hexane as an eluent to afford 5-bromo-3-hexylthiophene-2-yl phenylsulfide (ca. 90%). Oxidation with H_2O_2 was performed in a similar manner to the synthesis of **1** to obtain 5-bromo-2-phenylsulfonyl-3-hexylthiophene (**6**) as a colorless solid (59% yield, 3 steps from 2-bromo-3-hexylthiophene). Attempted microanalysis of **6** has not been successful so far due to the difficulties in the separation of unidentified side product. ^{1}H NMR ($CDCl_3$) δ 0.86 (t, *J* = 6.7 Hz, 3H), 1.16-1.28 (m, 6H), 1.31-1.45 (m, 2H), 2.74 (t, *J* = 7.8 Hz, 2H), 6.9 (s, 1H), 7.47-7.64 (m, 3H), 7.86-7.99 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.0, 22.4, 28.5, 28.9, 29.9, 31.4, 120.2, 124.5, 127.3, 129.2, 133.3, 133.6, 141.9, 149.2; IR (ATR) 2954, 2927, 2856, 1526, 1446, 1401, 1359, 1321, 1152, 1089, 755, 723, 686 cm^{-1}; HRMS (DART-ESI+) Calcd for $C_{16}H_{20}{}^{81}BrO_2S_2$ $[M+H]^+$: 389.0067; found: m/z 389.0067.

General procedure for the polymerization of 2-phenylsulfonyl-3-hexylthiophene using Knochel-Hauser Base: To a solution of 1.0 M TMPMgCl·LiCl (0.3 mL, 0.3 mmol) in THF (1 mL) was added 2-phenylsulfonyl-3-hexylthiophene (**1**: 0.3 mmol, 92.5 mg) at room temperature. After stirring at 25 °C for 0.5 h, $NiCl_2$(dppe) (2.4 mg, 0.0045 mmol) was added to the solution. The resulting mixture was allowed to stir at

50 °C for 24 h. Hydrochloric acid (1.0 M, 20 mL) and methanol (50 mL) were added into the reaction mixture. The formed precipitate was filtered and the residue was washed with methanol repeatedly to leave dark purple solid, which was dried under reduced pressure to afford 45 mg of poly(3-hexylthiophene-2,5-diyl) (**2**). (88%) Molecular weight and molecular weight distribution were estimated by SEC analysis (eluent: $CHCl_3$) showing $M_n = 9700$, $M_w/M_n = 1.47$. The regioregularity was estimated by ^{1}H NMR analysis (thienyl-CH_2- signals) at the δ 2.80 (H-T) and δ 2.60 (T-T) signals. (H-T regioregularity = 99%)[4] ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.92 (t, J = 6.6 Hz, 3H), 1.20-1.52 (m, 6H), 1.60-1.80 (m, 2H), 2.81 (t, J = 7.6 Hz, 2H), 6.98 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 22.7, 29.3, 29.5, 30.5, 31.7, 128.6, 130.5, 133.7, 139.9.

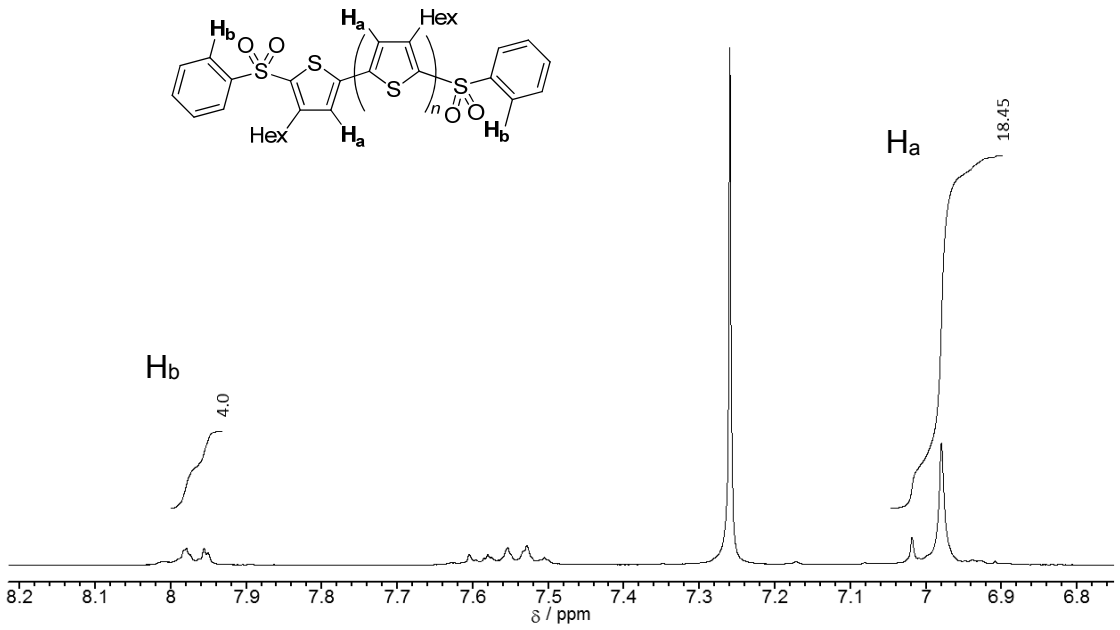


Figure S1. ^{1}H NMR spectrum of P3HT (**2**). The average degree of polymerization (H_a/H_b) was underestimated because of low mobility of polymer proton assigned as H_a.

ESI-MS analysis of reaction mixture: Polymerization of 2-phenylsulfonyl -3-hexylthiophene was performed in a similar manner. The formed precipitate was filtered and the residue was washed with methanol repeatedly. The filtrate was

concentrated under reduced pressure. The residue was analyzed by ESI-MS without further purification. HRMS (ESI-) Calcd for $C_6H_5O_2S$ $[M]^-$: 441.0010; found: m/z 441.0012.

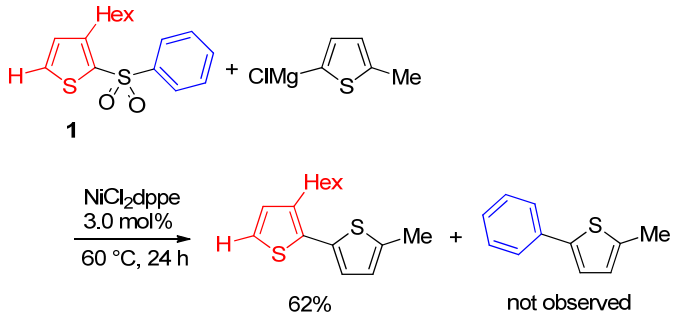
3-Hexyl-5-iode-2-phenylsulfonylthiophene: To a solution of 1.3 M ^{i}PrMgCl·LiCl (0.15 mL, 0.2 mmol) in 1 mL of THF were added diethylamine (2.0 μL, 0.02 mmol), and 2-phenylsulfonyl-3-hexylthiophene (**1**, 61.6 mg, 0.2 mmol) dropwise under an nitrogen atmosphere. After stirring at room temperature for 1 h, I_2 (1.0 mmol) was added portionwise and stirring was continued for further 10 min. The mixture was quenched by $Na_2S_2O_3$ aq. and the resulting solution was poured into the mixture of diethyl ether/water to cause separation into two phases. Aqueous was extracted with diethyl ether twice and the combined organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a crude oil. Conversion of **1**into the corresponding iodide was determined to be 86% by ^{1}H NMR analysis.

General procedure for the polymerization of 2-phenylsulfonyl-3-hexylthiophene using diethylamine and a Grignard reagent: To a solution of 1.3 M ^{i}PrMgCl·LiCl (0.23 mL, 0.3 mmol) in 1 mL of THF were added 2-phenylsulfonyl-3-hexylthiophene (**1**: 0.3 mmol, 92.5 mg) and diethylamine (0.03 mmol 3.0 μL) dropwise at room temperature and the resulting mixture was stirred for 1 h. $NiCl_2$(dppe) (2.4 mg, 0.0045 mmol) was successively added and stirring was continued at 50 °C for 24 h. Hydrochloric acid (1.0 M, 20 mL) and methanol (50 mL) were added to form a precipitate. The mixture was filtered and the residue was washed with methanol repeatedly to leave dark purple solid, which was dried under reduced pressure to afford 25 mg of poly(3-hexylthiophen-2,5-diyl) (**2**). (50% yield). M_n = 11900, M_w/M_n= 1.27.

Polymerization of 5-bromo-2-phenylsulfonyl-3-hexylthiophene using ^{i}PrMgCl·LiCl: To a solution of 1.3 M ^{i}PrMgCl·LiCl (0.23 mL, 0.3 mmol) in 1 mL of THF were added 5-bromo-2-phenylsulfonyl-3-hexylthiophene (**6**: 0.3 mmol, 116 mg) at room temperature and the resulting mixture was stirred for 0.5 h. $NiCl_2$(dppe) (2.4 mg, 0.0045 mmol) was successively added and stirring was continued at 50 °C for 24 h. Hydrochloric acid (1.0 M, 20 mL) and methanol (50 mL) were added to form a precipitate. The mixture was filtered and the residue was washed with methanol

repeatedly to leave dark purple solid, which was dried under reduced pressure to afford 27 mg of poly(3-hexylthiophen-2,5-diyl) (**2**). (54% yield). M_n = 4600, M_w/M_n= 1.42.

Cross-coupling reaction of 2-phenylsulfonyl-3-hexylthiophene with thienyl Grignard reagent: To a solution of 1.0 M TMPMgCl·LiCl (0.6 mL, 0.6 mmol) in 1 mL of THF was added 2-methylthiophene (58 μL, 0.6 mmol) at room temperature and the resulting mixture was stirred at 60 °C for 1 h. $NiCl_2$(dppe) (4.8 mg, 0.009 mmol) and 2-phenylsulfonyl-3-hexylthiophene (**1**: 0.3 mmol, 92.5 mg) were successively added and stirring was continued at 60 °C for 24 h. The mixture was quenched with water and the solution was poured into the mixture of diethyl ether/water. Two phases were separated. Aqueous was extracted with diethyl ether twice and the combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to leave a crude oil, which was subjected to ^{1}H NMR analysis. The conversion into 2-(5'-methylthiophene-2'-yl)-3-hexylthiophene was determined to be 62% by ^{1}H NMR analysis, whereas 2-phenyl-3-hexylthiophene was not observed at all by GC-MS analysis.



Desulfonylation of poly(3-hexylthiophen-2,5-diyl): To a solution of poly(3-hexylthiophen-2,5-diyl) bearing a $PhSO_2$ group at the end (16 mg) in THF (2 mL) were added ^{t}BuMgCl (0.3 mL, 0.3 mmol) and $NiCl_2$dppe (2.6 mg, 0.005 mmol). The resulting mixture was stirred at 60 °C for 16 h. Hydrochloric acid (1.0 M, 20 mL) and methanol (50 mL) were added to form a precipitate. The mixture was filtered and the residue was washed with methanol repeatedly to leave dark purple solid, which was dried under reduced pressure to afford 7 mg of polythiophene **5**. M_n = 9200, M_w/M_n= 1.68.

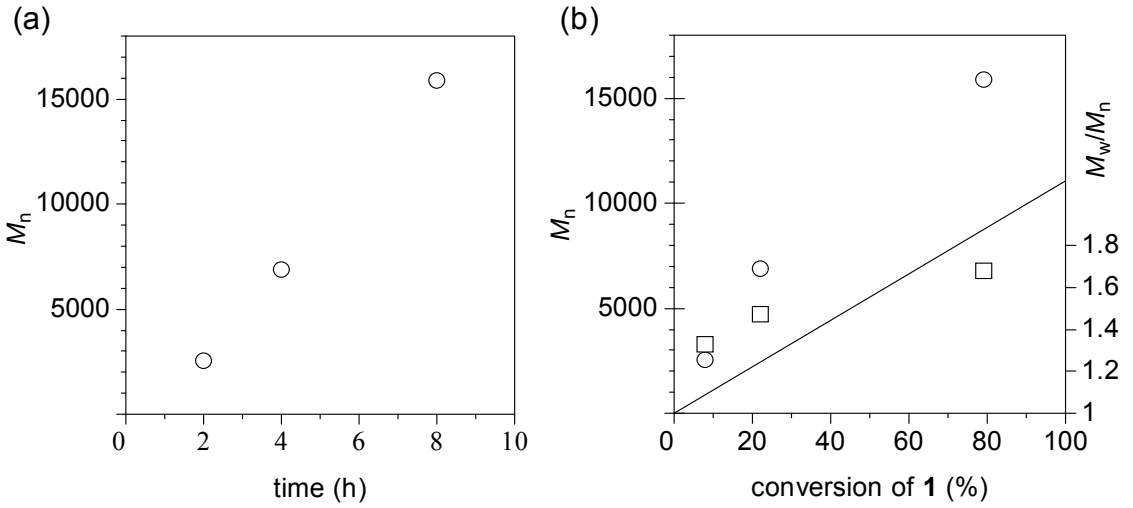


Figure S2. (a) The relationship of reaction period toward M_n; (b) The relationship of monomer conversion vs. M_n, obtained with 1.5 mol% of $NiCl_2$dppe; The solid line indicates theoretical relationship of [conversion]/[catalyst] toward M_n; ○ and □ shows M_n and M_w/M_n, respectively.

References

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(3) Cheng, J.-H.; Ramesch, C.; Kao, H.-L.; Wang, Y.-J.; Chan, C.-C.; Lee, C.-F. *J. Org. Chem.* **2012**, *77*, 10369.

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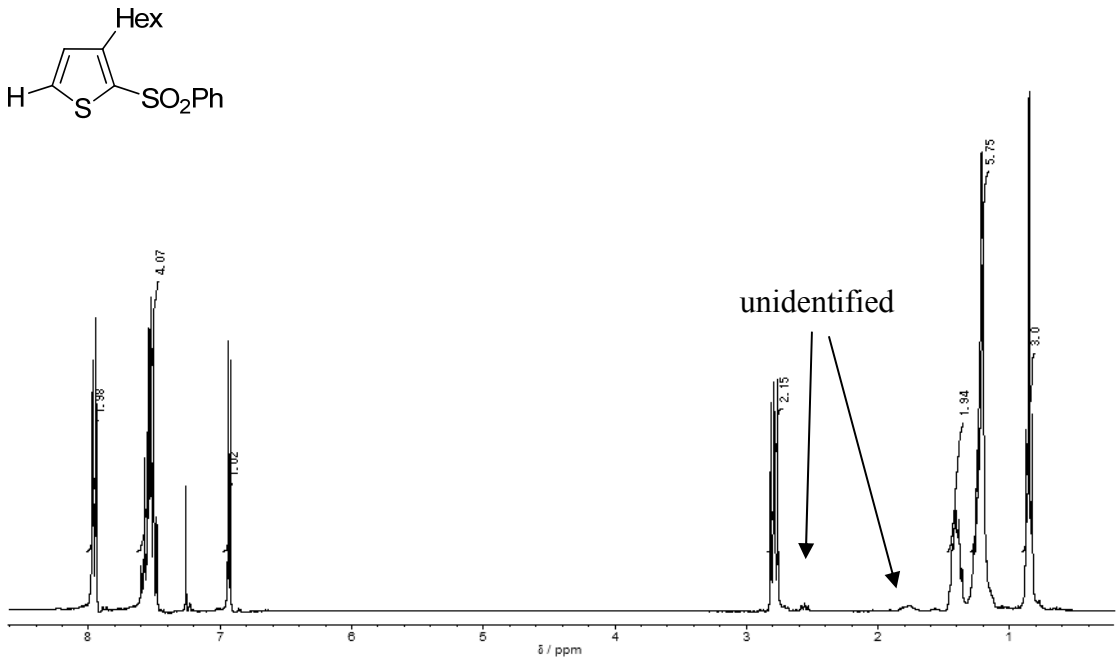
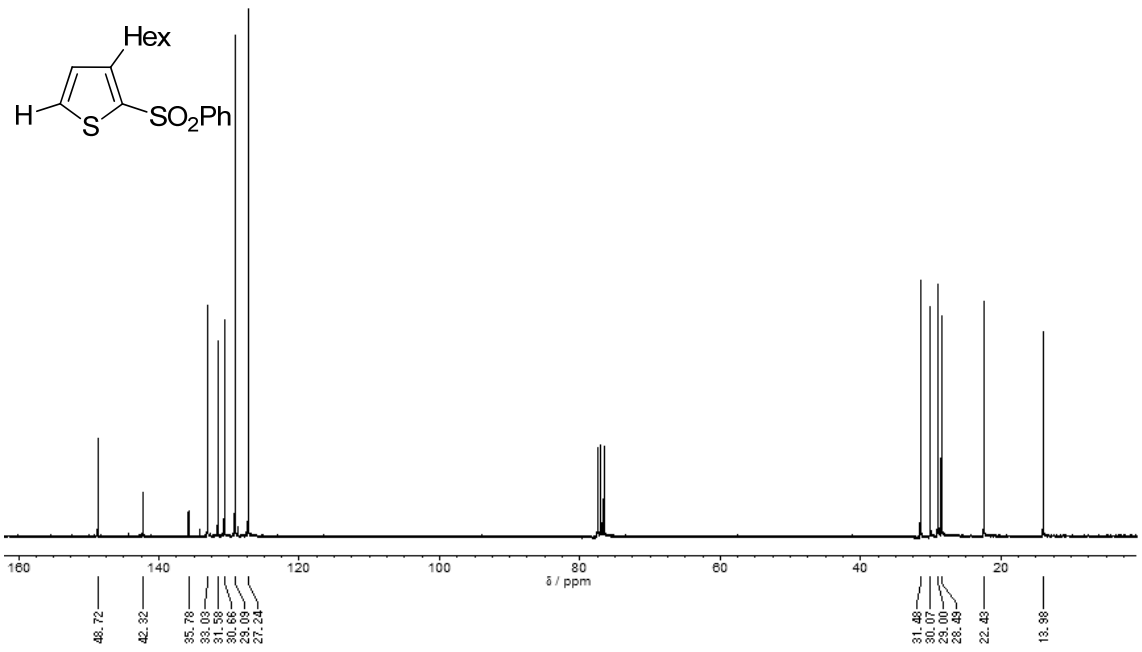
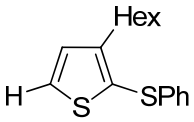
^{1}H NMR spectrum of 2-phenylsulfonyl-3-hexylthiophene (**1**)

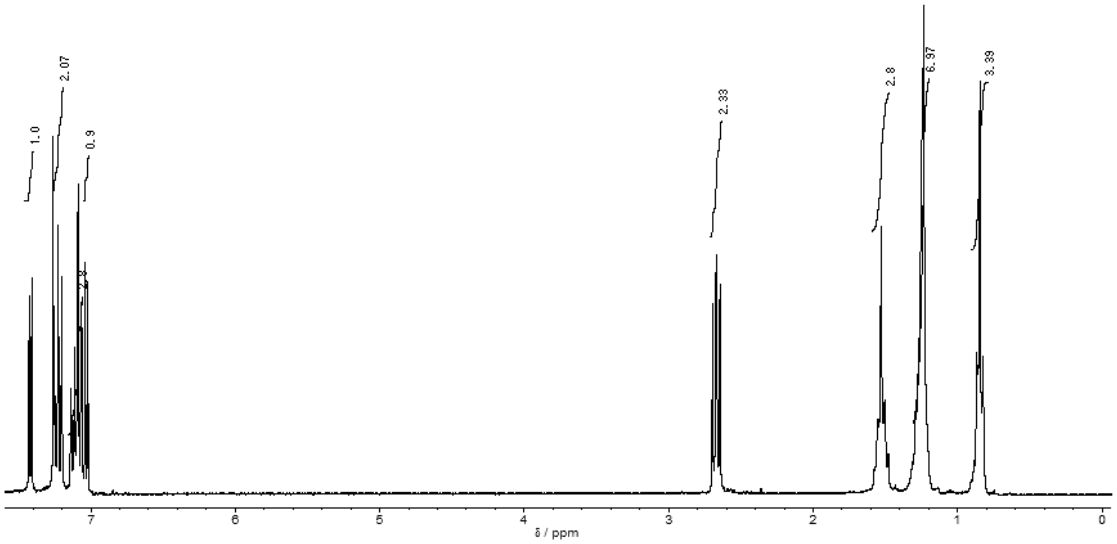


^{13}C NMR spectrum of 2-phenylsulfonyl-3-hexylthiophene (**1**)

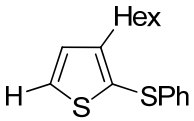


^{1}H NMR spectrum of 3-hexylthiophene-2-yl phenyl sulfide (**3**)

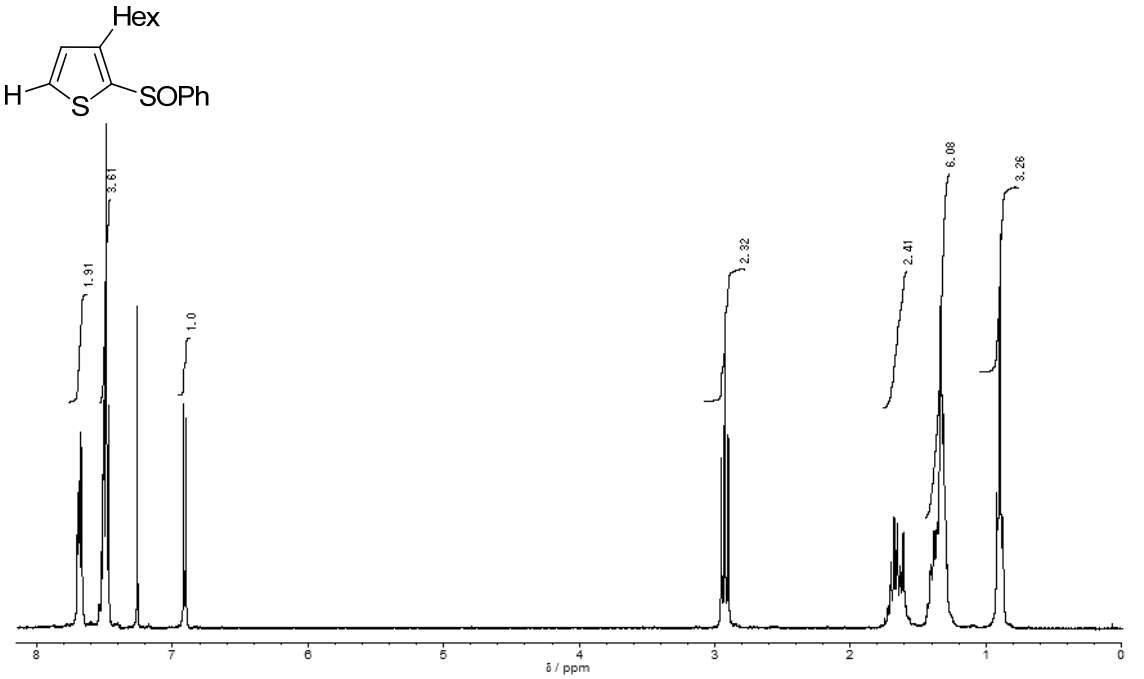




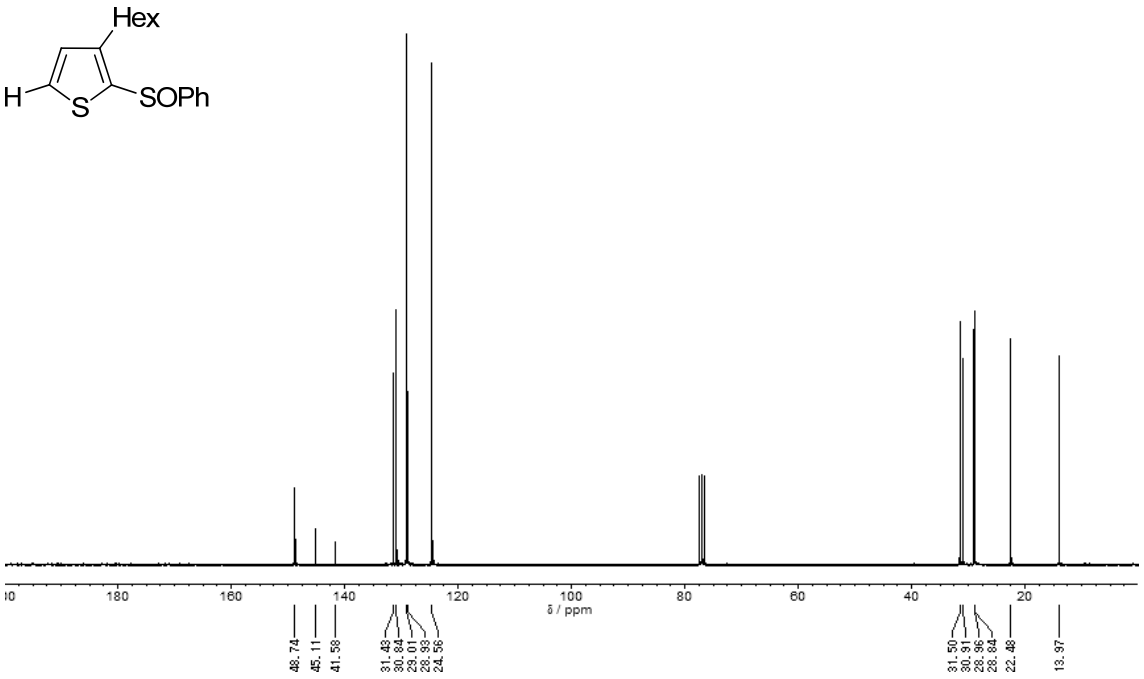
^{13}C NMR spectrum of 3-hexylthiophene-2-yl phenyl sulfide (**3**)



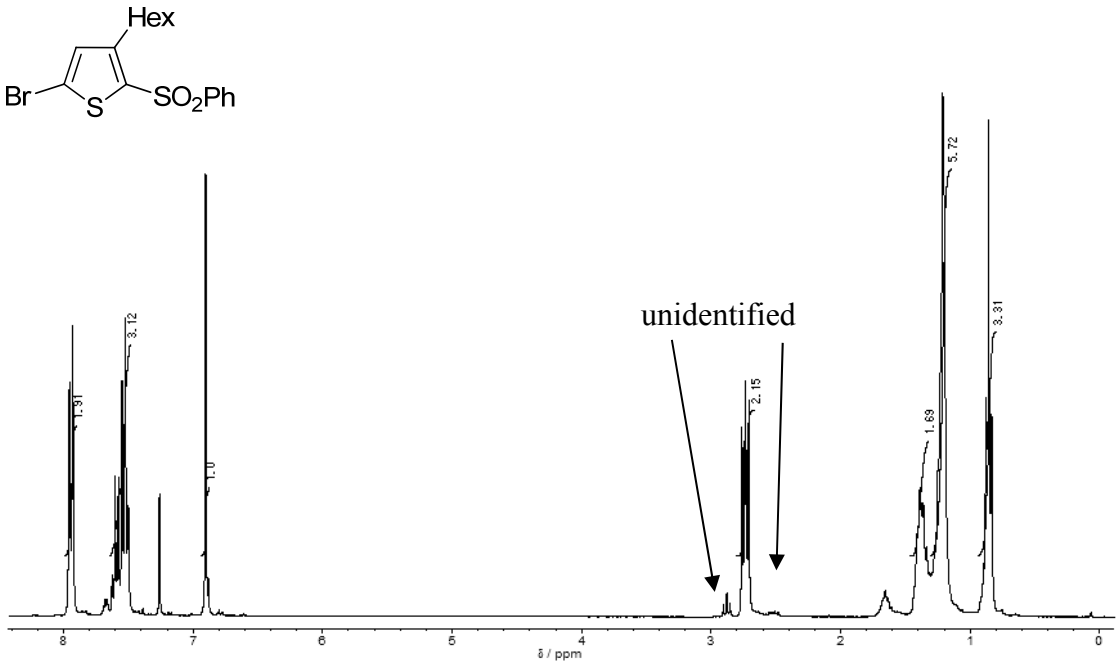
^{1}H NMR spectrum of 2-phenylsulfinyl-3-hexylthiophene (**4**)



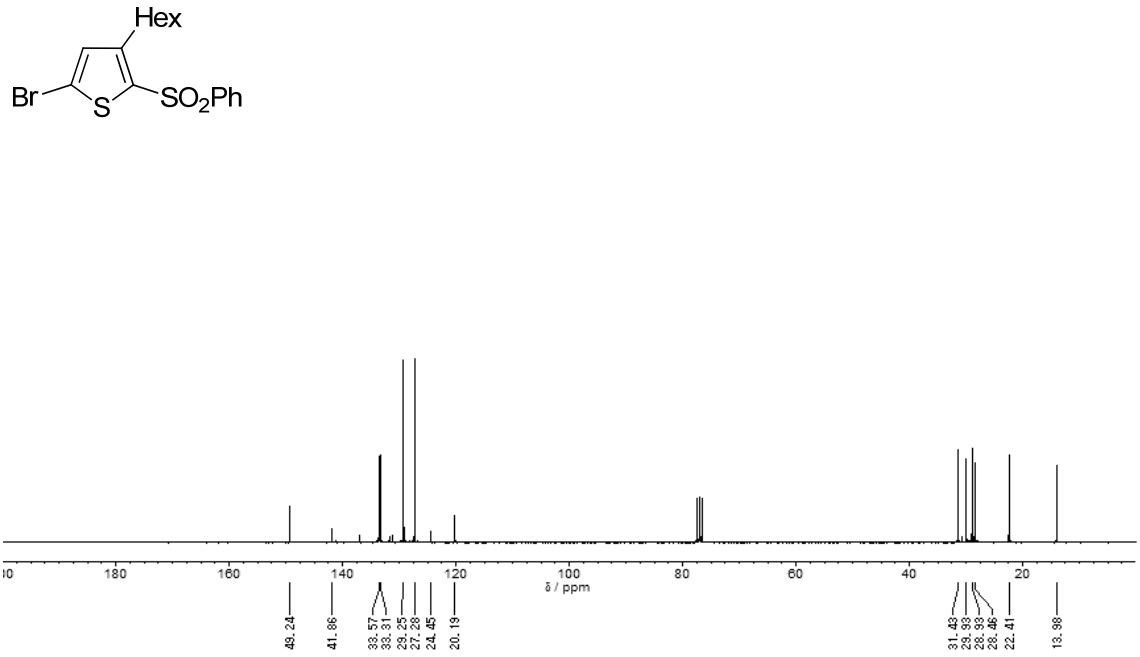
^{13}C NMR spectrum of 2-phenylsulfinyl-3-hexylthiophene (**4**)



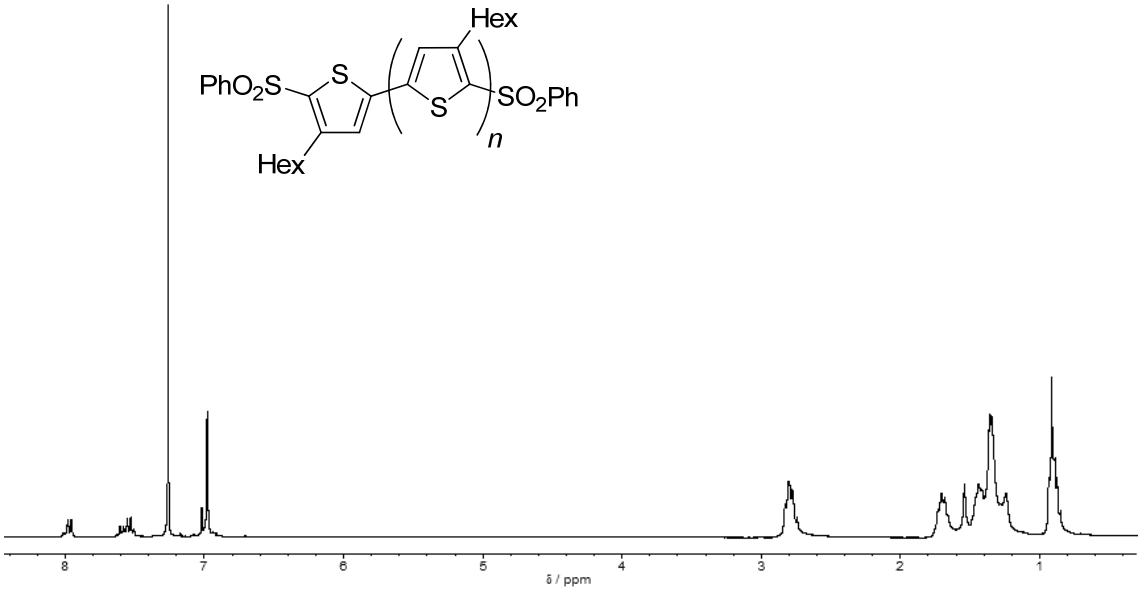
^{1}H NMR spectrum of 5-bromo-2-phenylsulfonyl-3-hexylthiophene (**6**)



^{13}C NMR spectrum of 5-bromo-2-phenylsulfonyl-3-hexylthiophene (**6**)



^{1}H NMR spectrum of poly(3-hexylthiophene) (**2**)



^{1}H NMR spectrum of desulfonylated poly(3-hexylthiophene) (**5**)