Electronic Supplementary Material (ESI) for Polymer Chemistry.

Chain-growth cationic polymerization of 2-halogenated thiophenes promoted by Bronsted acids

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Experimental Section

Characterization methods. ^{1}H and ^{13}C NMR spectra were recorded using Varian Unity 400 MHz spectrometer. IR spectra were measured using Perkin-Elmer 2000 Fourier Transform infrared (FTIR) spectrometer, based on pressed KBr pellets and cast thin film on silicon wafer. UV-vis spectra for the polymer solutions (in THF) were recorded with Hitachi U-3501 spectrophotometer. The molecular weight analysis for the polymers was performed on a gel permeation chromatography (GPC) system equipped with three Waters styragel columns (installed in a 40 ^{o}C oven) and a UV detector (set at the λ_{max} of the analyzed polymers) using THF as the mobile phase (at 1 mL/min). The molecular weight was calibrated against polystyrene standards. The MALDI-TOF MS (matrix-assisted laser desorption and ionization time-of-flight mass spectrometry) spectra for the polymer mixtures were acquired using a Bruker Daltonics, Autoflex III smartbeam LRF200-CID time-of-flight mass spectrometer with a Nd:YAG laser (355 nm) in positive ion and linear mode. Sample solution (0.1wt% in THF) were spotted (0.5 μL) onto a matrix-assisted laser desorption/ionization plate, followed by the addition of 0.5 μL solution of α-cyano-4-hydroxycinnamic acid (CHCA) (prepared in 1:1 co-solvent of H_2O/CH_3CN plus 0.1 wt% of trifluoroacetic acid) as the matrix. Spectra have been first calibrated with Peptide Standard and then with CHCA as an additional internal standard.

Chemicals. 3-Alkylthiothiophenes, 3-alkoxythiophenes, and 3-hexylthiophene are prepared from 3-bromothiophene according to the literature reported procedure. (ref 17a, 24) 2-Bromothiophene, 3-bromothiophene, 3,4-ethylenedioxythiophene were purchased from Aldrich. Alkyl disulfides, *n*-butanol, *n*-hexanol, *n*-butyllithium, *N*-bromosuccinimide (NBS), N-chlorosuccnimide (NCS), hydrazine hydrate, trifluoroacetic acid (MSA), trifluoromethanesulfonic acid (TFMSA), methanesulfonic acid (MSA), boron trifluoride diethyl etherate ($BF_3.Et_2O$), ammonium chloride, sodium hydroxide, chloroform, hexanes, 1,1,2,2-tetrachloroethane (TCE), 1,2-dichlorobenzene, chlorobenzene, chloroform, carbon disulfide, and dichloromethane were purchased from Aldrich, Acros and Alfa-Aesar and they were used as received without further purifications. THF and toluene were dried according to standard procedures before the use.

Typical experiment for the bromination of 3-alkylthiothiophenes

Synthesis of 2-bromo-3-butylthiothiophene (BBTT): 3-Butylthiothiophene (BTT) (2.00 g, 11.61 mmol, 1.00 equiv) was taken in a 50 mL single neck round bottom flask along with chloroform (26.0 mL). The homogeneous solution was added with solid *N*-bromosuccinimide (2.17 g, 12.19 mmol, 1.05 equiv) portionwise for a period of one hour at rt (18 ^{o}C). During the addition of NBS, the colorless solution turned to pale yellow heterogeneous mixture (white solid was precipitated). The reaction mixture was stirred at rt for 3 hours and monitored by TLC. After 3 hours, the reaction mixture was diluted with chloroform (52 mL) and washed successively with 5 wt% NaOH (50 mL) and two times with water (50 mL each time). The separated organic solution was dried over anhydrous magnesium sulfate and concentrated to get a pale yellow liquid, which was distilled at 90-95 ^{o}C under vacuum (0.39 torr). The desired product BBTT was obtained as a colorless liquid (2.47 g, 84.6%). δ_H(400 MHz;

$CDCl_3$; Me_4Si): 7.25 (d, 1 H, *J* 6.00), 6.92 (d, 1 H, *J* 5.60), 2.85 (t, 2 H, *J* 7.40), 1.60-1.53 (m, 2 H), 1.48-1.39 (m, 2 H), 0.91 (t, 3 H, *J* 7.40). δ_C(100 MHz; $CDCl_3$; $CDCl_3$): 133.04, 130.04, 125.82, 113.55, 34.74, 31.56, 21.66, 13.57. υ_{max}/cm^{-1} 3107 (m), 3083 (m), 2859 (s), 2930 (s), 2872 (s), 2859 (s), 1500 (s) 1464 (s), 1437 (m), 1422 (m), 1384 (s), 1337 (s), 1271 (m), 1223 (m), 1154 (s), 1099 (w), 1072 (w), 1052 (w), 990 (s), 916 (w), 880 (s), 811 (m), 747 (w), 706 (s), 658 (m), 607 (s), 459 (m).

Synthesis of 2-bromo-3-hexylthiothiophene (BHTT): The desired product BHTT was obtained as a colorless liquid in 88% yield. δ_H(400 MHz; $CDCl_3$; Me_4Si):7.26 (d, 1H, *J* 5.60), 6.93 (d, 1 H, *J* 6.00), 2.85 (t, 2 H, *J* 7.40), 1.60-1.56 (m, 2 H), 1.42-1.39 (m, 2H), 1.32-1.25 (m, 4 H), 0.88 (t, 3 H, *J* 6.80). δ_C(100 MHz; $CDCl_3$; $CDCl_3$): 133.04, 130.05, 125.84, 113.56, 35.08, 31.30, 29.49, 28.23, 22.49, 14.00. υ_{max}/cm^{-1} 3105 (m), 3084 (m), 2956 (s), 2928 (s), 2870 (s), 2857 (s), 1585 (w), 1498 (m), 1464 (s), 1456 (s), 1436 (w), 1422 (w), 1385 (s), 1337 (m), 1286 (w), 1259 (w), 1210 (w), 1155 (m), 1089 (w), 991 (s), 916 (w), 878 (s), 813 (m), 707 (s), 655 (m), 607 (s), 468 (w).

Synthesis of 2-bromo-3-octylthiothiophene (BOTT): The desired product BOTT was obtained as a colorless liquid in 87% yield. δ_H(400 MHz; $CDCl_3$; Me_4Si): 7.25 (d, 1H, *J* 5.60), 6.92 (d, 1 H, *J* 5.60), m 2.84 (t, 2 H, *J* 7.40), 1.61-1.54 (m, 2 H), 1.41-1.38 (m, 2 H), 1.36-1.26 (m, 8 H), 0.87 (t, 3 H, *J* 6.80). δ_C(100 MHz; $CDCl_3$; $CDCl_3$): 133.08, 130.06, 125.81, 113.56, 35.07, 31.73, 29.51, 29.10, 29.05, 28.53, 22.59, 14.05. υ_{max}/cm^{-1} 3106 (m), 3083 (w), 2955 (s), 2926 (s), 2871 (s), 2855 (s), 1583 (w), 1498 (m), 1464 (s), 1455 (s), 1436 (w), 1421 (w), 1385 (s), 1337 (m), 1307 (w), 1272 (w), 1239 (w), 1201 (w), 1154 (m), 1089 (w), 990 (s), 954 (w), 916 (w), 878 (s), 813 (w), 707 (s), 655 (m), 607 (s), 593 (m), 468 (w).

Synthesis of 2-bromo-3-dodecylthiothiophene (BDDTT): The desired product BDDTT was obtained as a colorless liquid in 85% yield. δ_{H}(400 MHz; $CDCl_3$; Me_4Si): 7.24 (d, 1 H, *J* 5.60), 6.92 (d, 1 H, *J* 5.60), 2.84 (t, 2 H, *J* 7.40), 1.59-1.54 (m, 2 H), 1.39-1.37 (m, 2 H), 1.32-1.25 (m, 16 H), 0.86 (t, 3 H, *J* 6.80). δ_{C}(100 MHz; $CDCl_3$; $CDCl_3$): 133.11, 130.09, 125.81, 113.60, 35.10, 31.89, 29.62, 29.60, 29.54, 29.46, 29.32, 29.12, 28.56, 22.67, 14.10. $\upsilon_{\mathrm{max}}/\mathrm{cm}^{-1}$ 3106 (w), 3087 (w), 2954 (m), 2925 (s), 2871 (m), 2854 (s), 1498 (w), 1464 (m), 1457 (m), 1437 (w), 1422 (w), 1386 (m), 1337 (w), 1300 (w), 1284 (w), 1266 (w), 1223 (w), 1211 (w), 1167 (w), 1155 (w), 1087 (w), 991 (s), 964 (w), 901 (w), 877 (s), 813 (w), 706 (s), 655 (w), 606 (m), 594 (w), 468 (w).

Synthesis of 2-bromo-3-octadecylthiothiophene (BODTT): The desired product BODTT was obtained as a colorless liquid in 83% yield. δ_{H}(400 MHz; $CDCl_3$; Me_4Si): 7.25 (d, 1 H, *J* 6.00), 6.92 (d, 1 H, *J* 5.60), 2.84 (t, 2 H, *J* 7.40), 1.60-1.56 (m, 2H), 1.43-1.36 (m, 2 H), 1.25 (b, 28 H), 0.88 (t, 3 H, *J* 6.80). δ_{C}(100 MHz; $CDCl_3$; $CDCl_3$): 133.08, 130.07, 125.82, 113.58, 35.09, 31.91, 29.69, 29.65, 29.62, 29.56, 29.53, 29.47, 29.35, 29.33, 29.12, 28.56, 22.68, 14.12.

Synthesis of 2-bromo-3-butoxythiophene (BBOT): The desired product BBOT was obtained as a colorless liquid in 83% yield. δ_{H}(400 MHz; $CDCl_3$; Me_4Si): 7.18 (d, 1 H, *J* 6.00), 6.73 (d, 1 H, *J* 6.00), 4.03 (t, 2 H, *J* 6.60), 1.77-1.70 (m, 2 H), 1.54-1.44 (m, 2H), 0.97 (t, 3 H, *J* 7.40). δ_{C}(100 MHz; $CDCl_3$; $CDCl_3$): 154.51, 124.09, 117.46, 91.51, 71.89, 31.50, 19.03, 13.80.

Synthesis of 2-bromo-3-hexyloxythiophene (BHOT): The desired product BHOT was obtained as a colorless liquid in 83% yield. δ_{H}(400 MHz; $CDCl_3$; Me_4Si): 7.18 (d, 1 H, *J* 6.00), 6.73 (d, 1 H, *J* 6.00), 4.03 (t, 2 H, *J* 6.60), 1.78-171 (m, 2 H), 1.58-142 (m, 2 H), 1.34-1.31 (m, 4 H), 0.90 (t, 3 H, *J* 6.80). δ_C(100 MHz; $CDCl_3$; $CDCl_3$): 154.53, 124.09, 117.51, 91.58, 72.23, 31.49, 29.41, 25.46, 22.55, 13.99.

Synthesis of 2-bromo-3-hexoxythiophene (BHOT): NBS (5.94 g, 33.4 mmol) was slowly added to 3-hexyloxy-thiophene (6.16g, 33.4 mmol) in 100 mL DMF. This was stirred overnight in the absence of light. The solution was then poured into 150 mL water and extracted with di ethyl ether (3 x 150 mL). The combined organic layers were then dried, concentrated to 50 mL, filtered through a plug of silica and evaporated to give 7.67 g (87%) of 2-bromo-3-hexyl- oxythiophene as light yellow oil. (Note: this compound is unstable at room temperature for extended periods of time and can be stored at -20 in the dark by making it to 1M solution in Ether). The desired product 2B-HOT was obtained as a colorless liquid in 87% yield. δ_H(600 MHz; $CDCl_3$; Me_4Si): 7.18 (d, 1 H, *J* 6.00), 6.73 (d, 1 H, *J* 6.00), 4.03 (t, 2 H, *J* 6.60), 1.75 (quintet, 2 H, *J* 7.20), 1.48-1.43 (m, 2 H), 1.35-1.32 (m, 4 H), 0.90 (t, 3 H, *J* 6.60). δ_C(150 MHz; $CDCl_3$; $CDCl_3$): 154.54, 124.10, 117.50, 91.55, 72.23, 31.50, 29.43, 25.47, 22.56, 14.01.

Synthesis of 2-bromo-3-hexylthiophene (BHTT): The desired product CHTT was obtained as a colorless liquid in 80% yield. δ_H(600 MHz; $CDCl_3$; Me_4Si): 7.17 (d, 1H, *J* 5.40), 6.79 (d, 1 H, *J* 5.40), 2.56 (t, 2 H, *J* 7.80), 1.56 (quintet, 2 H, *J* 7.50), 1.35-1.29 (m, 6H), 0.88 (t, 3 H, *J* 7.20). δ_C(150 MHz; $CDCl_3$; $CDCl_3$): 141.96 (C), 128.22 (CH), 125.10 (CH), 108.77 (C), 31.61 (CH_2), 29.70 (CH_2), 29.38 (CH_2), 28.88 (CH_2), 22.58 (CH_2), 14.07 (CH_3).

Synthesis of 2-chloro-3-butylthiothiophene (CBTT): 3-Butylthiothiophene (BTT)

(5.00 g, 29.02 mmol, 1.00 equiv) was taken in a 50 mL single neck round bottom flask along with acetonitrile (50.0 mL) and added with acetic acid (0.52 g, 0.50 mL, 8.71 mmol, 0.30 equiv). The homogeneous solution was added with solid *N*-chlorosuccinimide (NCS) (4.07 g, 30.47 mmol, 1.05 equiv) portionwise for a period of 30 min at rt (23 ^{o}C). During the addition of NCS, the colorless solution turned to pale blue heterogeneous mixture (white solid was precipitated). The reaction mixture was stirred at rt for 30 min and monitored by TLC. After 30 min, the reaction mixture was diluted with chloroform (100 mL) and washed successively with 5 wt% NaOH (75 mL) and two times with water (75 mL each time). The separated organic solution was dried over anhydrous magnesium sulfate and concentrated to get a pale brown liquid. The pale brown liquid was purified by column chromatography using hexane as eluent in silica gel to get the desired product CBTT as a colorless liquid (5.74 g, 82%). δ_H(400 MHz; $CDCl_3$; Me_4Si): 7.09 (d, 1 H, *J* 5.60), 6.91 (d, 1 H, *J* 5.60), 2.83 (t, 2 H, *J* 7.40), 1.59-1.52 (m, 2 H), 1.45-1.40 (m, 2 H), 0.90 (t, 3 H, *J* 7.20). δ_C(100 MHz; $CDCl_3$; $CDCl_3$): 129.87 (CH), 129.81 (C), 129.20 (C), 122.60 (CH), 34.60 (CH_2), 31.62 (CH_2), 21.63 (CH_2), 13.56 (CH_3).

Synthesis of 2-chloro-3-octylthiothiophene (COTT): The desired product COTT was obtained as a colorless liquid in 82% yield. δ_H(400 MHz; $CDCl_3$; Me_4Si): 7.09 (d, 1H, *J* 5.80), 6.91 (d, 1 H, *J* 5.8), 2.83 (t, 2 H, *J* 7.40), 1.57 (quintet, 2 H, *J* 7.40), 1.40-1.35 (m, 2 H), 1.31-1.26 (m, 8 H), 0.87 (t, 3 H, *J* 6.80). δ_C(100 MHz; $CDCl_3$; $CDCl_3$): 129.91 (CH), 129.85 (C), 129.24 (C), 122.60 (CH), 34.95 (CH_2), 31.74 (CH_2), 29.59 (CH_2), 29.11 (CH_2), 29.06 (CH_2), 28.51 (CH_2), 22.60 (CH_2), 14.06 (CH_3).

Synthesis of 2-chloro-3-dodecylthiothiophene (CDDTT): The desired product CDDTT was obtained as a colorless liquid in 87% yield. δ_H(600 MHz; $CDCl_3$; Me_4Si):

7.10 (d, 1 H, *J* 6.00), 6.91 (d, 1 H, *J* 6.00), 2.83 (t, 2 H, *J* 7.20), 1.57 (quintet, 2 H, *J* 7.20), 1.39 (quintet, 2 H, *J* 7.20), 1.31~1.25 (m, 16 H), 0.88 (t, 3 H, *J* 6.90). δ_C(150 MHz; $CDCl_3$; $CDCl_3$): 129.92 (CH), 129.85 (C), 129.26 (C), 122.60 (CH), 34.96 (CH_2), 31.89 (CH_2), 29.60 (3*CH_2), 29.55 (CH_2), 29.46 (CH_2), 29.33 (CH_2), 29.11 (CH_2), 28.53 (CH_2), 22.67 (CH_2), 14.11 (CH_3).

Synthesis of 2-Chloro-3-butoxythiophene (CBOT): To a stirred solution of alkoxythiophene (3.8 mmol) in DMF (20 mL) at 0 ºC a solution of N-chlorosuccinimide (0.48 g, 3.6 mmol) in 5 mL of DMF was added dropwise, and the reaction mixture was stirred at room temperature overnight. To the reaction water (20 mL) was added and washed with ethyl acetate (3x20 mL), the organic fraction was dried over anhydrous sulfate magnesium, the solvent removed under reduced pressure and the resulting material purified by chromatography column on silica gel. The desired product 2CBOT was obtained as a colorless liquid in 85% yield. δ_H(600 MHz; $CDCl_3$; Me_4Si): 6.98 (d, 1 H, *J* 6.18), 6.70 (d, 1 H, *J* 6.18), 4.03 (t, 2 H, *J* 6.54), 1.75-1.71 (quintet, *J* 6.60, 2 H), 1.50-1.46 (sextet, *J* 7.48 2H), 0.96 (t, 3 H, *J* 7.44). δ_C(150 MHz; $CDCl_3$; $CDCl_3$): 152.26, 120.58, 117.47, 108.28, 71.89, 31.53, 19.22, 14.09.

Synthesis of 2-Chloro-3-hexoxythiophene (CHOT): To a stirred solution of alkoxythiophene (3.8 mmol) in DMF (20 mL) at 0 ºC a solution of N-chlorosuccinimide (0.48 g, 3.6 mmol) in 5 mL of DMF was added dropwise, and the reaction mixture was stirred at room temperature overnight. To the reaction water (20 mL) was added and washed with ethyl acetate (3x20 mL), the organic fraction was dried over anhydrous sulfate magnesium, the solvent removed under reduced pressure and the resulting material purified by chromatography column on silica gel.

The desired product CHOT was obtained as a colorless liquid in 84% yield. δ_H(600 MHz; $CDCl_3$; Me_4Si): 6.98 (d, 1 H, *J* 6.00), 6.75 (d, 1 H, *J* 6.00), 4.03 (t, 2 H, *J* 6.60), 1.74 (quintet, 2 H, *J* 7.05), 1.45 (quintet, 2 H, *J* 7.20), 1.34-1.31 (m, 4H), 0.90 (t, 3 H, *J* 6.60). δ_C(150 MHz; $CDCl_3$; $CDCl_3$): 152.25 (C), 120.58 (CH), 117.49 (CH), 108.30 (C), 72.21 (CH_2), 31.49 (CH_2), 29.44 (CH_2), 25.44 (CH_2), 22.55 (CH_2), 13.98 (CH_3).

Synthesis of 2-chloro-3-butoxythiophene (CBOT): The desired product CBOT was obtained as a colorless liquid in 80% yield. δ_H(600 MHz; $CDCl_3$; Me_4Si): 6.98 (d, 1 H, *J* 6.00), 6.75 (d, 1 H, *J* 6.00), 4.03 (t, 2 H, *J* 6.60), 1.73 (quintet, 2 H, *J* 7.05), 1.48 (sextet, 2H, *J* 7.56), 0.96 (t, 3 H, *J* 7.20). δ_C(150 MHz; $CDCl_3$; $CDCl_3$): 152.25(C), 120.58(CH), 117.47(CH), 108.28(C), 71.88(CH_2), 31.52(CH_2), 19.01(CH_2), 13.78(CH_3).

Synthesis of 2-chloro-3-hexylthiophene (CHTT): The desired product CHTT was obtained as a colorless liquid in 83% yield. δ_H(600 MHz; $CDCl_3$; Me_4Si): 7.00 (d, 1H, *J* 5.70), 6.78 (d, 1 H, *J* 5.70), 2.56 (t, 2 H, *J* 7.80), 1.56 (quintet, 2 H, *J* 7.20), 1.34-1.30 (m, 6H), 0.88 (t, 3 H, *J* 7.20). δ_C(150 MHz; $CDCl_3$; $CDCl_3$): 139.17 (C), 127.87(CH), 124.40 (C), 121.94 (CH), 31.60 (CH_2), 29.60 (CH_2), 28.88 (CH_2), 27.91 (CH_2), 22.58 (CH_2), 14.06 (CH_3).

Typical experiment for the polymerization of 2-bromo-3-alkylthiothiophenes

Preparation of poly(3-butylthiothiophene) (PBTT-Br) at rt:

A solution of **BBTT** (0.50 g; 1.99 mmol) in 1.50 mL of toluene was added with trifluoroacetic acid (0.077 mL; 99% pure; *d* 1.48; 0.114 g; 0.995 mmol; 0.50 equiv) in a single neck round bottom flask under nitrogen atmosphere at room temperature (rt; 25 °C). After the addition, the colorless liquid became red-brown liquid, which then, within 5 minutes, turned into a dark blue color solution with the evolution of lot of smoke. The thick mass was stirred for 3 h at rt. Then, the thick blue color mass was diluted in dichloromethane (20 mL), washed successively with 5 wt% aqueous sodium hydroxide solution (20 mL) and two times with water (20 mL each time). The resulting red-brown color solution was concentrated in a rotavapor to get a thick gummy red brown color mass in quantitative yield. The obtained product was confirmed to be poly(3-butythiothiophene) by NMR and IR spectroscopic studies. δ_H(400 MHz; $CDCl_3$; Me_4Si): 7.43 (br m), 7.37 (br m), 7.32 (br m), 7.22 (br m), 7.05 (br m), 7.00 (s), 2.90 (br m, 2 H), 1.63 (br m, 2 H), 1.45 (br m, 2 H), 0.91 (br m, 3 H). υ_{max}/cm^{-1} 3099 (m), 3077 (m), 2956 (s), 2928 (s), 2870 (s), 2859 (s), 1532 (m), 1465 (s), 1436 (m), 1419 (m), 1378 (m), 1346 (m), 1272 (m), 1224 (m), 1156 (w), 1188 (w), 1099 (m), 1072 (w), 980 (m), 914 (w), 878 (m), 832 (m), 815 (m), 745 (w), 713 (m), 628 (m), 475 (m). λ_{max}(THF)/nm 454.

Preparation of poly(3-hexylthiothiophene) (PHTT-Br) at rt:

Procedure and work up were followed as in for PBTT-Br at rt. Thick gummy red brown color mass was obtained in quantitative yield. υ_{max}/cm^{-1} 3099 (w), 3076 (w), 2955 (s), 2926 (s), 2870 (s), 2855 (s), 1529 (w), 1479 (m), 1466 (m), 1457 (m), 1436 (w), 1419 (w),1378 (m), 1344 (w), 1285 (w), 1259 (w), 1208 (w), 1181 (w), 1156 (w), 1083 (w), 980 (w), 915 (w), 879 (m), 831 (m), 818 (m), 723 (m), 715 (m), 668 (w), 630 (m), 472 (w). λ_{max}(THF)/nm 460.

Preparation of poly(3-octylthiothiophene) (POTT-Br) at rt:

Procedure and work up were followed as in for PBTT-Br at rt. Thick gummy red brown color mass was obtained in quantitative yield. υ_{max}/cm^{-1} 3107 (w), 3077 (w), 2955 (s), 2926 (s), 2872 (s), 2854 (s), 1531 (w), 1481 (w), 1464 (m), 1456 (m), 1436 (w), 1417 (w), 1378 (m), 1344 (w), 1299 (w), 1264 (w), 1237 (w), 1200 (w), 1154 (w), 1082 (w), 994 (w), 978 (w), 914 (w), 878 (m), 830 (m), 816 (m), 768 (w), 721 (m), 711 (m), 667 (w), 631 (m), 470 (w). λ_{max}(THF)/nm 464.

Preparation of poly(3-dodecylthiothiophene) (PDDTT-Br) at rt:

Procedure and work up were followed as in for PBTT-Br at rt. Thick gummy red brown color mass was obtained in quantitative yield. δ_H(400 MHz; $CDCl_3$; Me_4Si): 7.42 (br m), 7.37 (br m), 7.32 (br m), 7.20 (br m), 7.04 (br m), 6.99 (s), 2.87 (br m, 2 H), 1.63 (br m, 2 H), 1.40 (br m, 2 H), 1.24 (br m, 16 H), 0.87 (br m, 3 H). υ_{max}/cm^{-1} 3104 (w), 3074 (w), 2954 (s), 2924 (s), 2871 (s), 2852 (s), 1530 (w), 1481 (w), 1466 (s), 1456 (s), 1439 (w), 1419 (w), 1377 (m), 1348 (m), 1300 (w), 1265 (w), 1232 (w), 1156 (w), 1081 (w), 995 (w), 979 (w), 942 (w), 879 (m), 831 (m), 815 (m), 776 (w), 721 (s), 711 (w), 630 (m), 470 (w). λ_{max}(THF)/nm 466.

Preparation of poly(3-octadecylthiothiophene) (PODTT-Br) at rt:

Procedure and work up were followed as in for PBTT-Br at rt. Thick gummy red brown color mass was obtained in quantitative yield. υ_{max}/cm^{-1} . λ_{max}(THF)/nm 456.

Preparation of poly(3-butoxythiophene) (PBOT-Br) at rt:

Procedure and work up were followed as in for PBBT-Br at rt. Dark brown color was obtained in 60% yield as the desired product. δ_H(400 MHz; CDCl$_3$; Me$_4$Si): 6.92 (br m, 1 H), 4.15 (br m, 2 H), 1.86 (br m, 2 H), 1.60 (br m, 2 H), 1.04 (br m, 3 H). υ_{max}/cm^{-1} . λ_{max}(THF)/nm 521.

Preparation of poly(3-hexyloxythiophene) (PHOT-Br) at rt:

Procedure and work up were followed as in for PBTT-Br at rt. Dark brown color was obtained in 55% yield as the desired product. δ_H(400 MHz; CDCl$_3$; Me$_4$Si): 6.94 (br m, 1 H), 4.10 (br m, 2 H), 1.85 (br m, 2 H), 1.69 (br m, 2 H), 1.36 (br m, 4 H), 0.90 (br m, 3 H). λ_{max}(THF)/nm 494.

Typical experiment for the polymerization of 2-bromo-3-alkylthiothiophenes

Preparation of poly(3-butylthiothiophene) (PBTT-Br) from BBTT at 100 °C

A solution of **BBTT** (0.50 g; 1.99 mmol) in 1.50 mL of 1,1,2,2-tetrachloroethane (TCE) was heated to 100 °C and added with trifluoromethanesulfonic acid (0.012 mL; 99% pure; *d* 1.696; 0.021 g; 0.138 mmol; 0.05 equiv) in a single neck round bottom flask under nitrogen atmosphere at room temperature. After the addition, the colorless liquid turned into a dark blue color solution with the evolution of lot of smoke. The thick mass was stirred at 100 °C for 24 h. Then, the thick blue color mass was cooled to rt and diluted with dichloromethane (3 mL) The diluted mass was added with 3 drops of hydrazine hydrate, stirred at rt for 2 h and added slowly into 200 mL of methanol containing 1 mL of hydrazine hydrate. The resulting red-brown color precipitate was stirred at rt for 6 h and filtered, washed with methanol and dried under vacuum. The product was obtained as a brown color solid in 85% yield (0.29 g) and it was confirmed to be poly(3-butythiothiophene) by NMR and IR spectroscopic studies. δ_H(400 MHz; CDCl$_3$; Me$_4$Si): 7.36 (br m), 7.31 (br m), 7.21 (br m), 7.04 (br m), 2.91

(br m, 2 H), 1.62 (br m, 2 H), 1.45 (br m, 2 H), 0.91 (br m, 3 H). λ_{max}(chloroform)/nm 482; λ_{max}(carbon disulfide)/nm 500.

Preparation of poly(3-hexylthiothiophene) (PHTT-Br) at 100 ^oC:

Procedure and work up were followed as in for PBTT-Br at 100 ^oC. Dark brown color solid was obtained as the desired product in 85% yield. δ_H(400 MHz; $CDCl_3$; Me_4Si): 7.37 (br m), 7.31 (br m), 7.21 (br m), 7.04 (br m), 2.87 (br m, 2 H), 1.60 (br m, 2 H), 1.40 (br m, 2 H), 1.25 (br m, 4 H), 0.85 (br m, 3 H). λ_{max}(chloroform)/nm 484; λ_{max}(carbon disulfide)/nm 502.

Preparation of poly(3-octylthiothiophene) (POTT-Br) at 100 ^oC:

Procedure and work up were followed as in for PBTT-Br at 100 ^oC. Dark brown color solid was obtained as the desired product in 85% yield. δ_H(400 MHz; $CDCl_3$; Me_4Si): 7.37 (br m), 7.31 (br m), 7.21 (br m), 7.04 (br m), 2.86 (br m, 2 H), 1.62 (br m, 2 H), 1.41 (br m, 2 H), 1.25 (br m, 8 H), 0.86 (br m, 3 H). λ_{max}(chloroform)/nm 484; λ_{max}(carbon disulfide)/nm 500.

Preparation of poly(3-dodecylthiothiophene) (PDDTT-Br) at 100 ^oC:

Procedure and work up were followed as in for PBTT-Br at 100 ^oC. Dark brown color solid was obtained as the desired product in 85% yield. δ_H(400 MHz; $CDCl_3$; Me_4Si): 7.38 (br m), 7.32 (br m), 7.22 (br m), 7.05 (br m), 2.90 (br m, 2 H), 1.62 (br m, 2 H), 1.42 (br m, 2 H), 1.24 (br m, 16 H), 0.86 (br m, 3 H). λ_{max}(chloroform)/nm 498; λ_{max}(carbon disulfide)/nm 512.

Preparation of poly(3-octadecylthiothiophene) (PODTT-Br) at 100 ^oC:

Procedure and work up were followed as in for PBTT-Br at 100 ^oC. Dark brown color solid was obtained as the desired product in 85% yield. λ_{max}(chloroform)/nm 480; λ_{max}(carbon disulfide)/nm 494.

Preparation of poly(3-hexylthiophene) (PHT-Br) at 100 ^oC:

Procedure and work up were followed as in for PBTT-Br at 100 ^oC. Pale brown color solid was obtained as the desired product in 80% yield. δ_H(400 MHz; $CDCl_3$; Me_4Si): 6.99 (br m, 1 H), 2.78 (br m), 2.55 (br m), 1.65 (br m, 2 H), 1.57 (br m, 2 H), 1.27 (br m, 4 H), 0.87 (br m, 3 H). λ_{max}(chloroform)/nm.

Typical experiment for the polymerization of 2-chloro-3-alkylthiothiophenes

Preparation of poly(3-butylthiothiophene) (PBTT-Cl) from CBTT at 100 ^oC

A solution of CBTT (0.50 g; 2.42 mmol) in 1.50 mL of 1,1,2,2-tetrachloroethane (TCE) was heated to 100 ^{o}C and added with trifluoromethanesulfonic acid (0.011 mL; 99% pure; *d* 1.696; 0.018 g; 0.121 mmol; 0.05 equiv) in a single neck round bottom flask under nitrogen atmosphere. After the addition, the colorless liquid turned into a dark blue color solution with the evolution of lot of smoke. The thick mass was stirred at 100 ^{o}C for 24 h. Then, the thick blue color mass was cooled to rt and diluted with dichloromethane (3 mL) The diluted mass was added with 3 drops of hydrazine hydrate, stirred at rt for 2 h and added slowly into 200 mL of methanol containing 1 mL of hydrazine hydrate. The resulting red-brown color precipitate was stirred at rt for 6 h and filtered, washed with methanol and dried under vacuum. The product was obtained as a brown color solid in 78% yield (0.32 g) and it was confirmed to be poly(3-butythiothiophene) by NMR study. δ_H(400 MHz; $CDCl_3$; Me_4Si): 7.44 (br s), 7.41-7.36 (br m), 7.23-7.21 (br m), 7.06-7.01 (br m), 2.95-2.86 (br m, 2 H), 1.66-1.60 (br m, 2 H), 1.47-1.46 (br m, 2 H), 0.93-0.91 (br m, 3 H). λ_{max}(chloroform)/nm 500.

Preparation of poly(3-octylthiothiophene) (POTT-Cl) at 100 ^{o}C:

Procedure and work up were followed as in for PBTT-Cl at 100 ^{o}C. Dark brown color solid was obtained as the desired product in 78% yield. δ_H(400 MHz; $CDCl_3$; Me_4Si): 7.38 (br m), 7.31 (br m), 7.21 (br m), 7.04 (br m), 2.90 (br m, 2 H), 1.61 (br m, 2 H), 1.41 (br m, 2 H), 1.25 (br m, 8 H), 0.86 (br m, 3 H). λ_{max}(chloroform)/nm 508.

Preparation of poly(3-dodecylthiothiophene) (PDDTT-Cl) at 100 ^{o}C:

Procedure and work up were followed as in for PBTT-Cl at 100 ^{o}C. Dark brown color solid was obtained as the desired product in 80% yield. δ_H(400 MHz; $CDCl_3$; Me_4Si): 7.38 (br m), 7.31 (br m), 7.21 (br m), 7.04 (br m), 2.90 (br m, 2 H), 1.67 (br m, 2 H), 1.41 (br m, 2 H), 1.23 (br m, 16 H), 0.86 (br m, 3 H). λ_{max}(chloroform)/nm 502.

MALDI-TOF MS spectrum results for poly(3-butylthiothiophene)s.

Table S1. Experimental mass and theoretical mass data for the assigned peaks **6-18** and **6'-18'** in the **MALDI-TOF MS** spectrum of **PBTT**.

Peak ID	Possible chemical formula	Calculated mass for [M+1]^a	Measured mass value
6'	$C_{48}H_{62}S_{12}$	1023.157	1023.22
6	$C_{48}H_{61}S_{12}Br$	1101.068	1101.10
7'	$C_{56}H_{72}S_{14}$	1193.180	1193.20
7	$C_{56}H_{71}S_{14}Br$	1271.090	1271.11
8'	$C_{64}H_{82}S_{16}$	1363.202	1363.20
8	$C_{64}H_{81}S_{16}Br$	1441.113	1441.11
9'	$C_{72}H_{92}S_{18}$	1533.224	1533.22
9	$C_{72}H_{91}S_{18}Br$	1611.135	1611.14
10'	$C_{80}H_{102}S_{20}$	1703.247	1703.24
10	$C_{80}H_{101}S_{20}Br$	1781.157	1781.16
11'	$C_{88}H_{112}S_{22}$	1873.269	1873.28
11	$C_{88}H_{111}S_{22}Br$	1951.180	1951.20
12'	$C_{96}H_{122}S_{24}$	2043.292	2043.30
12	$C_{96}H_{121}S_{24}Br$	2121.202	2121.18
13'	$C_{104}H_{132}S_{26}$	2213.314	2213.28
13	$C_{104}H_{131}S_{26}Br$	2291.225	2291.20
14'	$C_{112}H_{142}S_{28}$	2383.336	2383.35
14	$C_{112}H_{141}S_{28}Br$	2461.247	2461.40
15'	$C_{120}H_{152}S_{30}$	2553.359	2553.43

15	$C_{120}H_{151}S_{30}Br$	2631.269	2631.23
16’	$C_{128}H_{162}S_{32}$	2723.381	2723.21
16	$C_{128}H_{161}S_{32}Br$	2801.292	2801.33
17’	$C_{136}H_{172}S_{34}$	2893.404	2893.53
17	$C_{136}H_{171}S_{34}Br$	2971.314	2971.29
18’	$C_{144}H_{182}S_{36}$	3063.426	3063.60
18	$C_{144}H_{181}S_{36}Br$	3141.336	3141.36

[a] Adapted from Bruker mass database for [M+1] (M = exact mass).

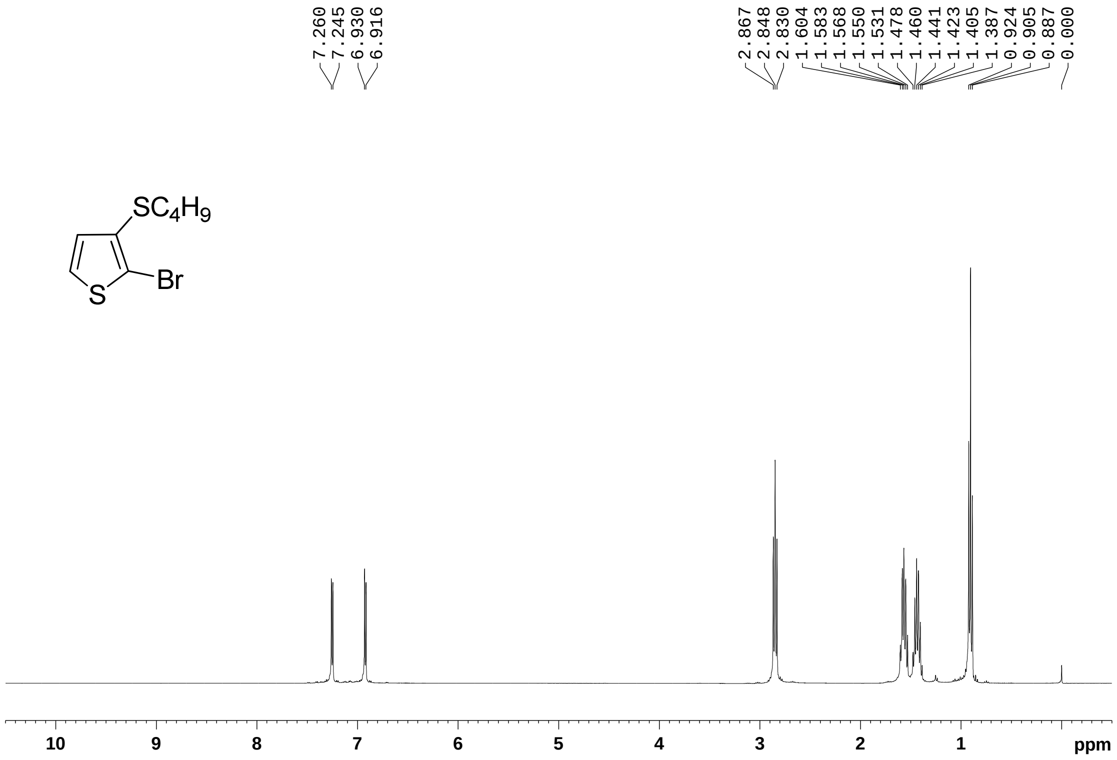

Figure S1. ^{1}H-NMR spectrum of BBTT in $CDCl_3$ (400 MHz).

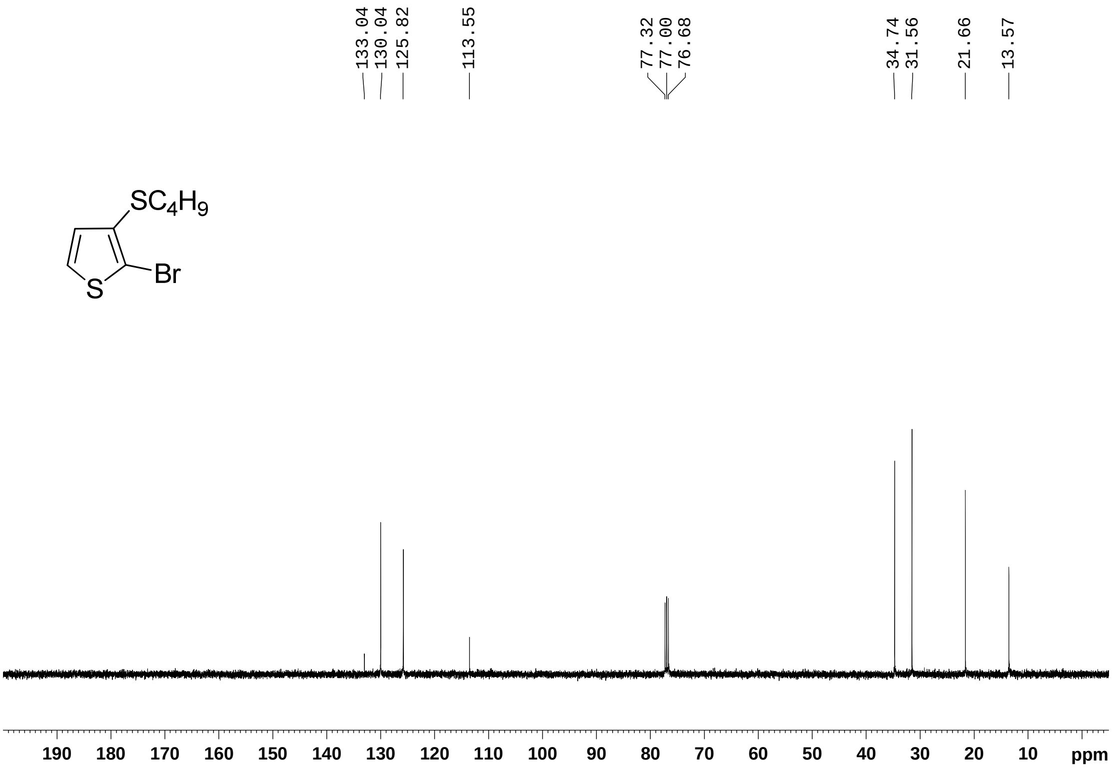

Figure S2. ^{13}C-NMR spectrum of BBTT in $CDCl_3$ (100 MHz).

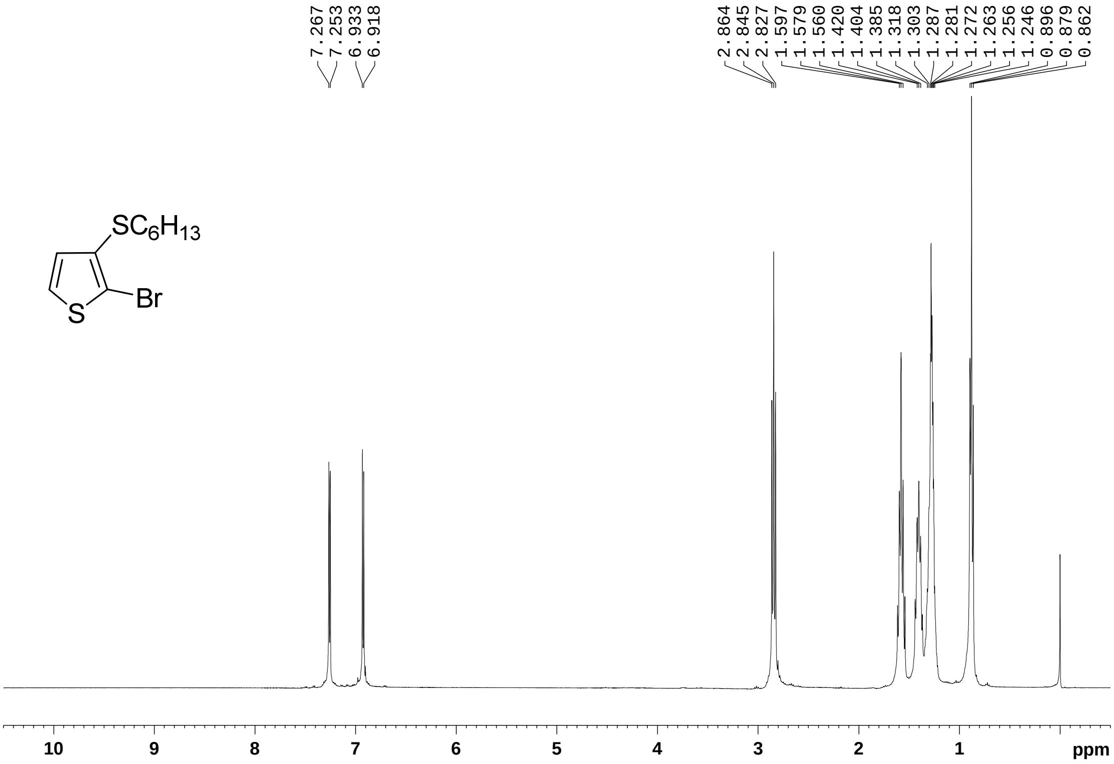

Figure S3. ^{1}H-NMR spectrum of BHTT in $CDCl_3$ (400 MHz).

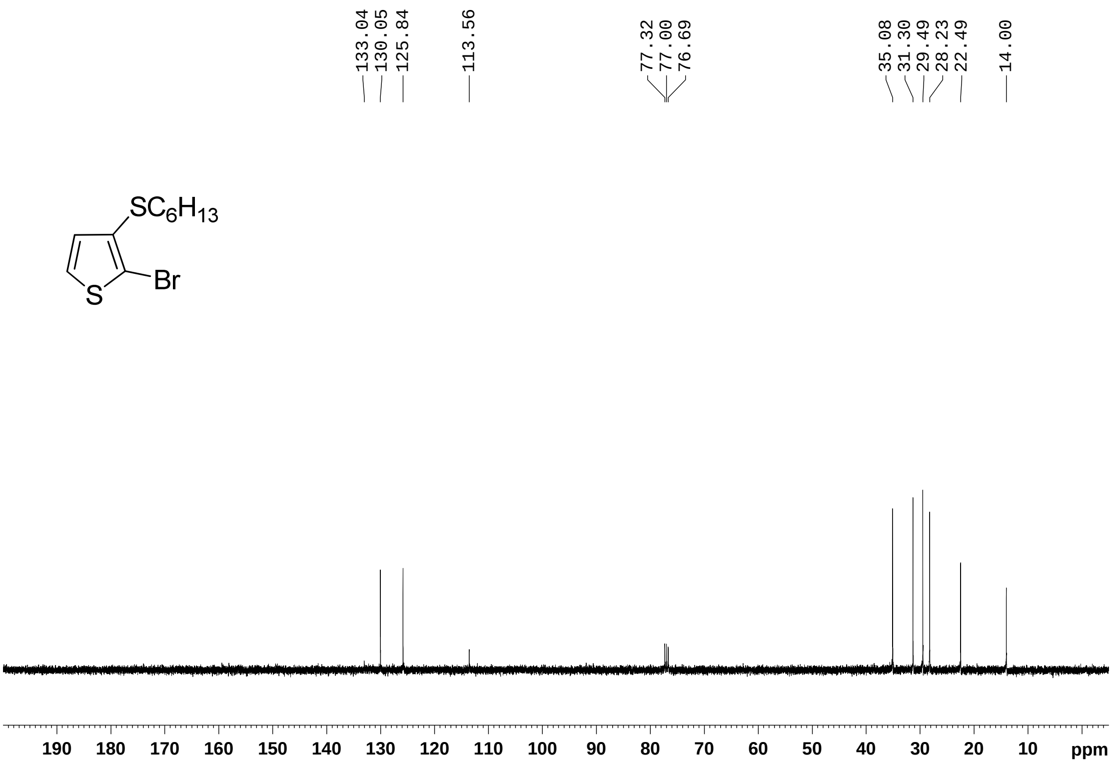

Figure S4. ^{13}C-NMR spectrum of BHTT in $CDCl_3$ (100 MHz).

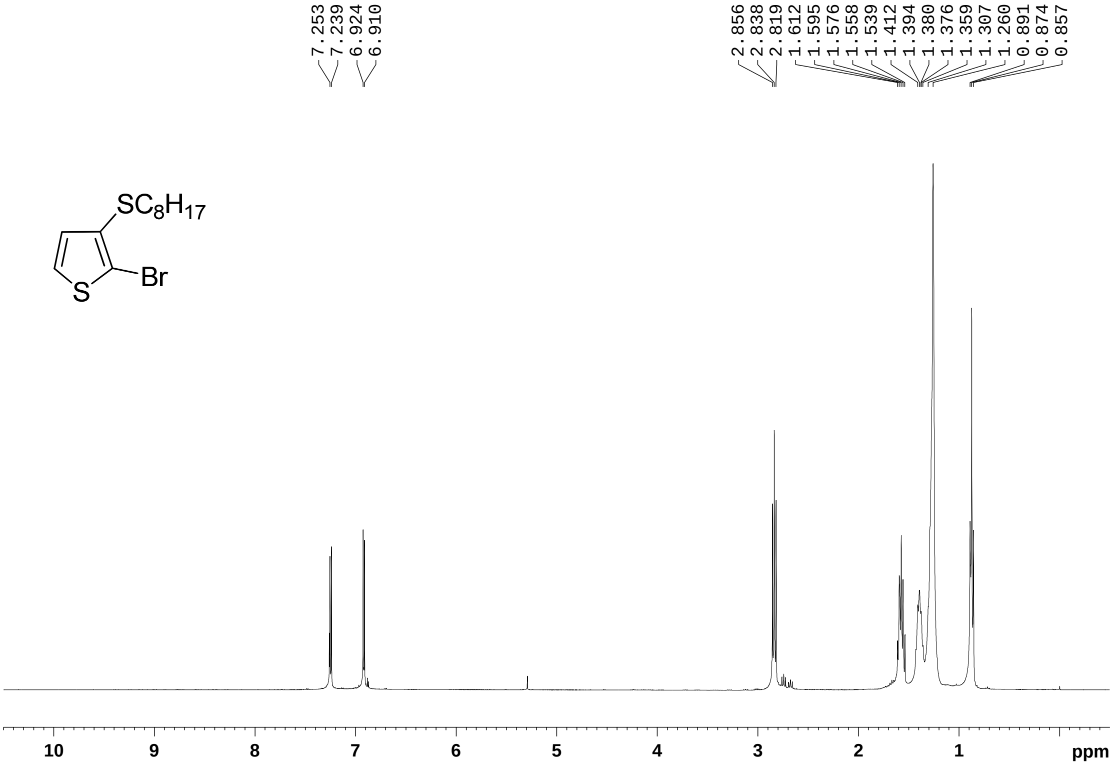

Figure S5. ^{1}H-NMR spectrum of BOTT in $CDCl_3$ (400 MHz).

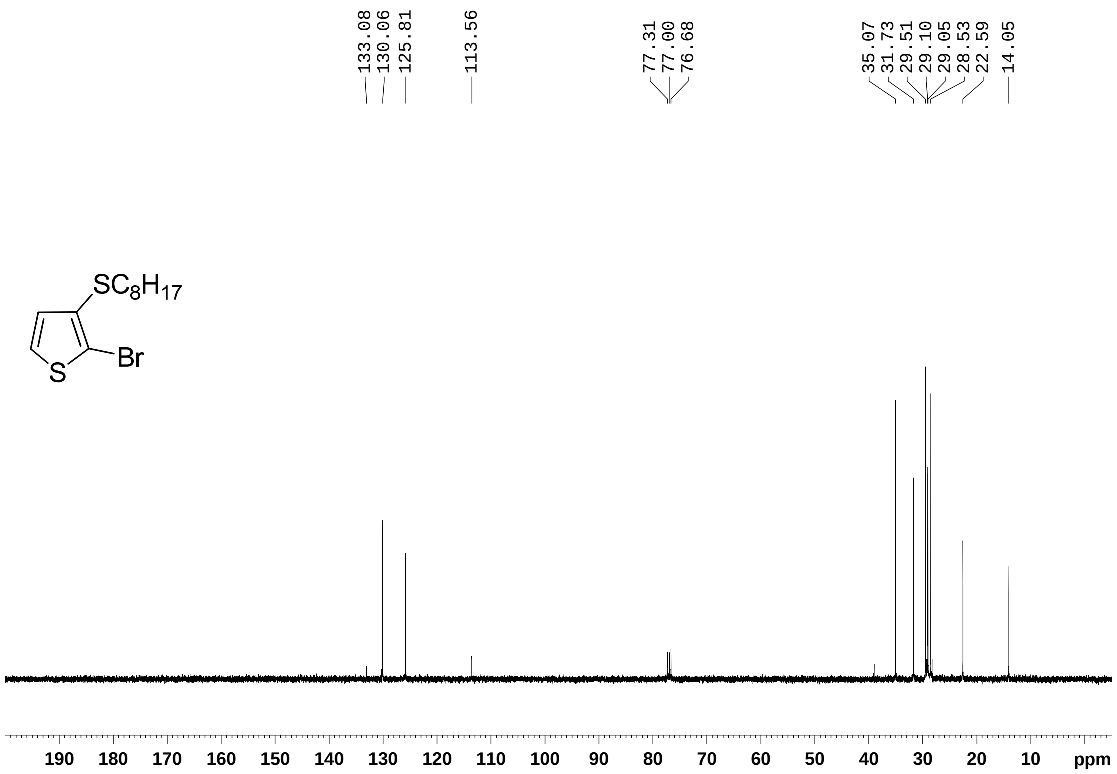

Figure S6. ^{13}C-NMR spectrum of BOTT in $CDCl_3$ (100 MHz).

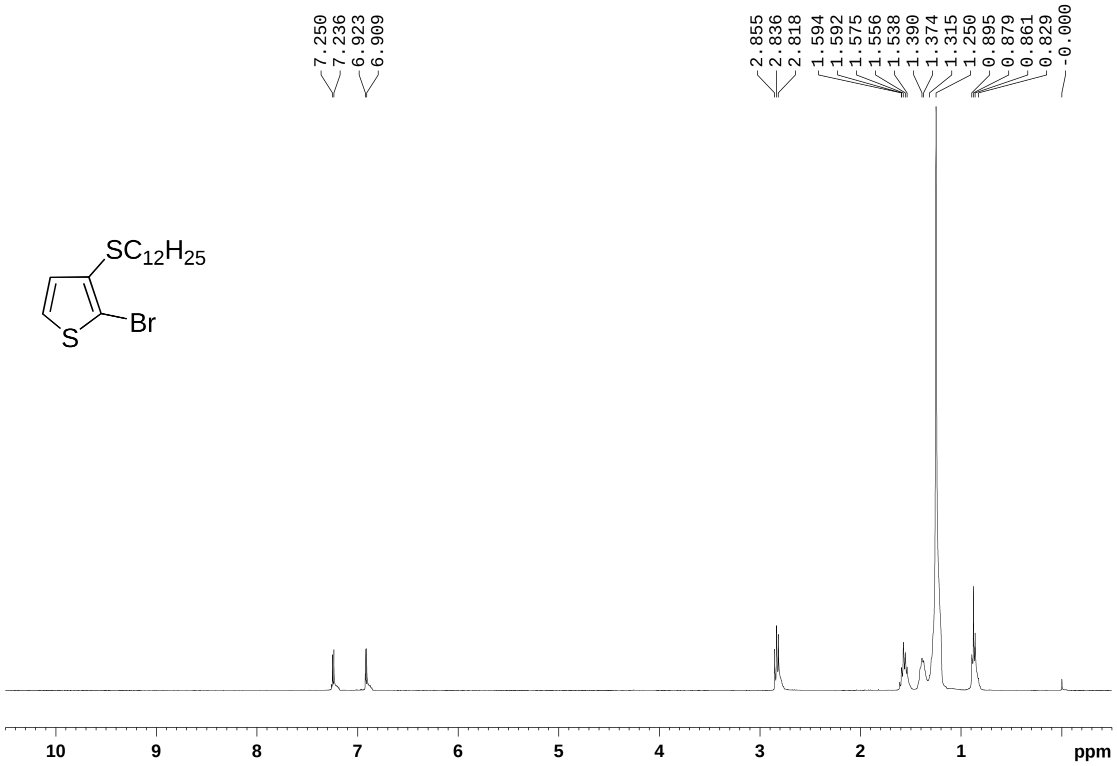

Figure S7. ^{1}H-NMR spectrum of BDDTT in $CDCl_3$ (400 MHz).

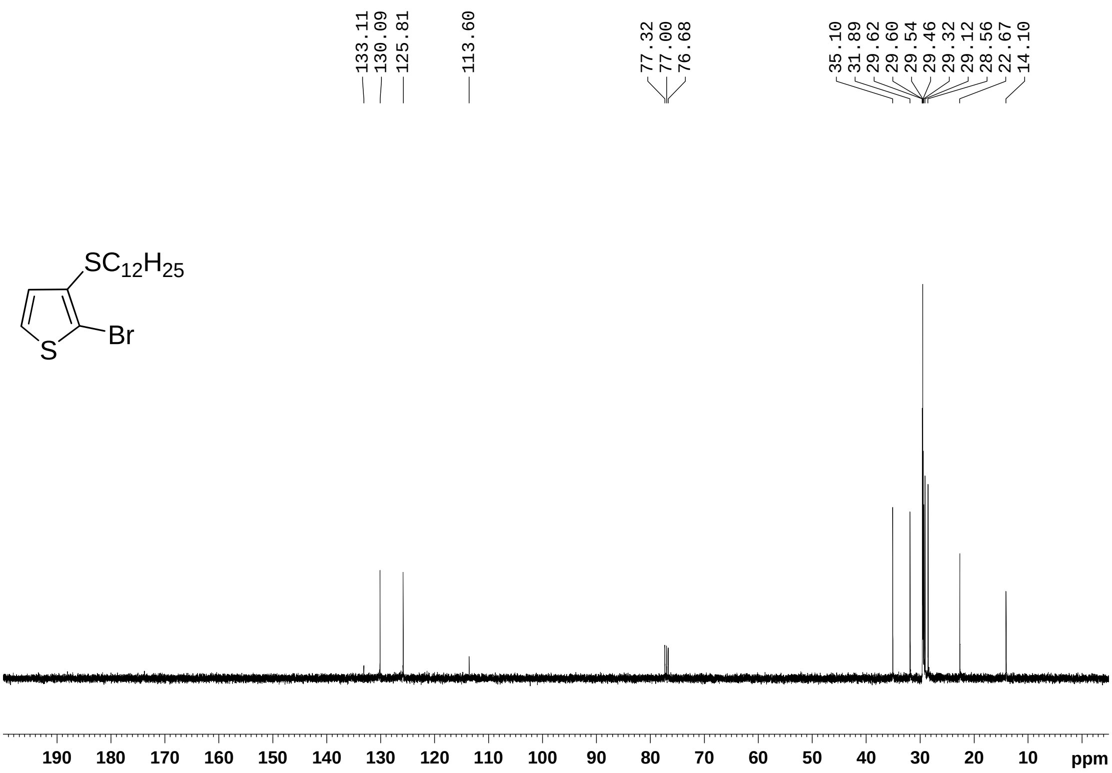

Figure S8. ^{13}C-NMR spectrum of BDDTT in CDCl$_3$ (100 MHz).

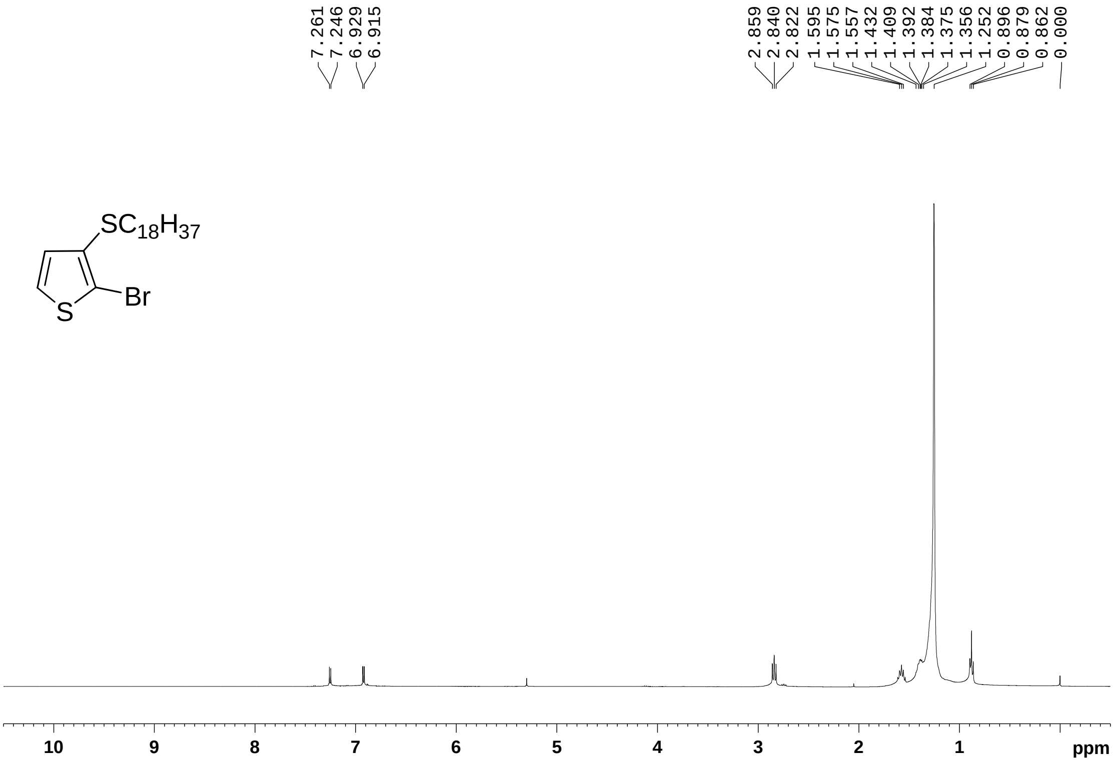

Figure S9. ^{1}H-NMR spectrum of BODTT in CDCl$_3$ (400 MHz).

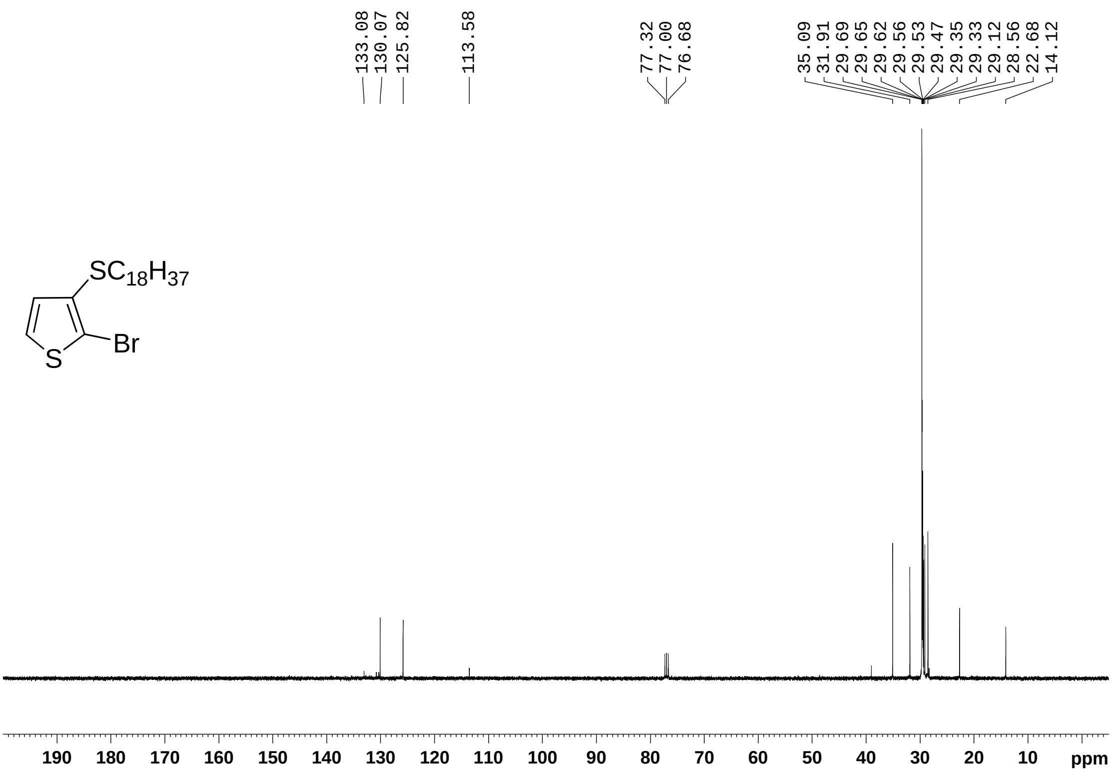

Figure S10. ^{13}C-NMR spectrum of BODTT in CDCl$_3$ (100 MHz).

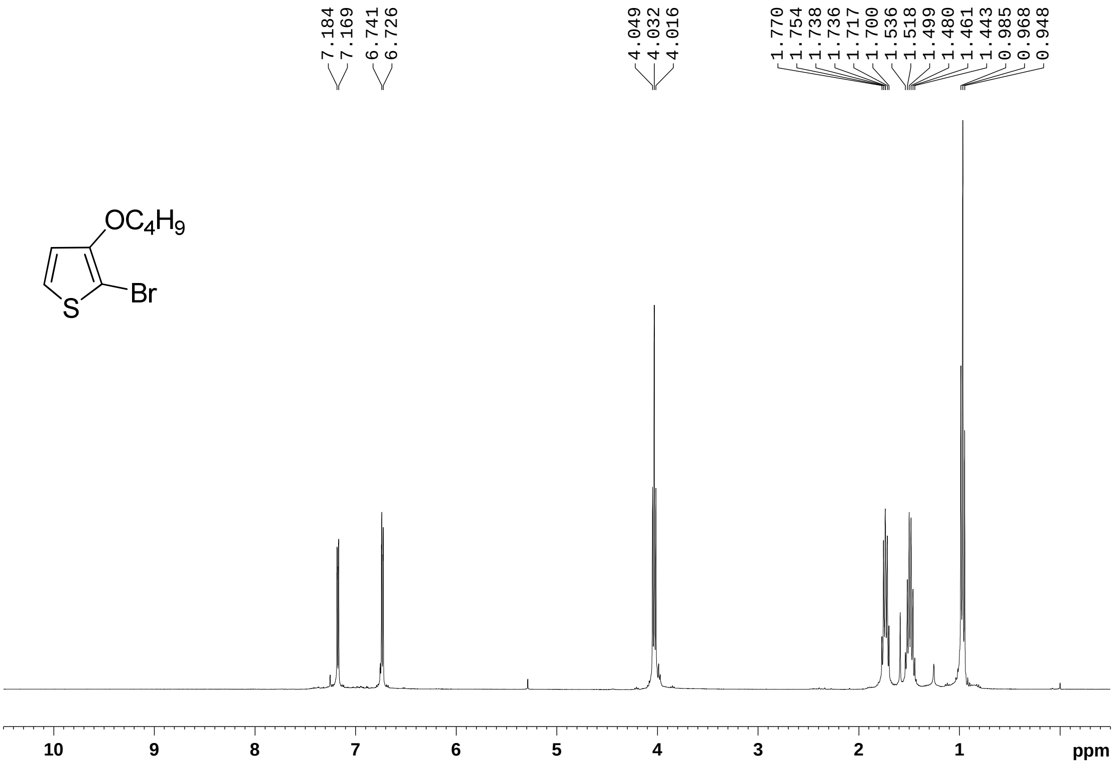

Figure S11. ^{1}H-NMR spectrum of BBOT in CDCl$_3$ (400 MHz).

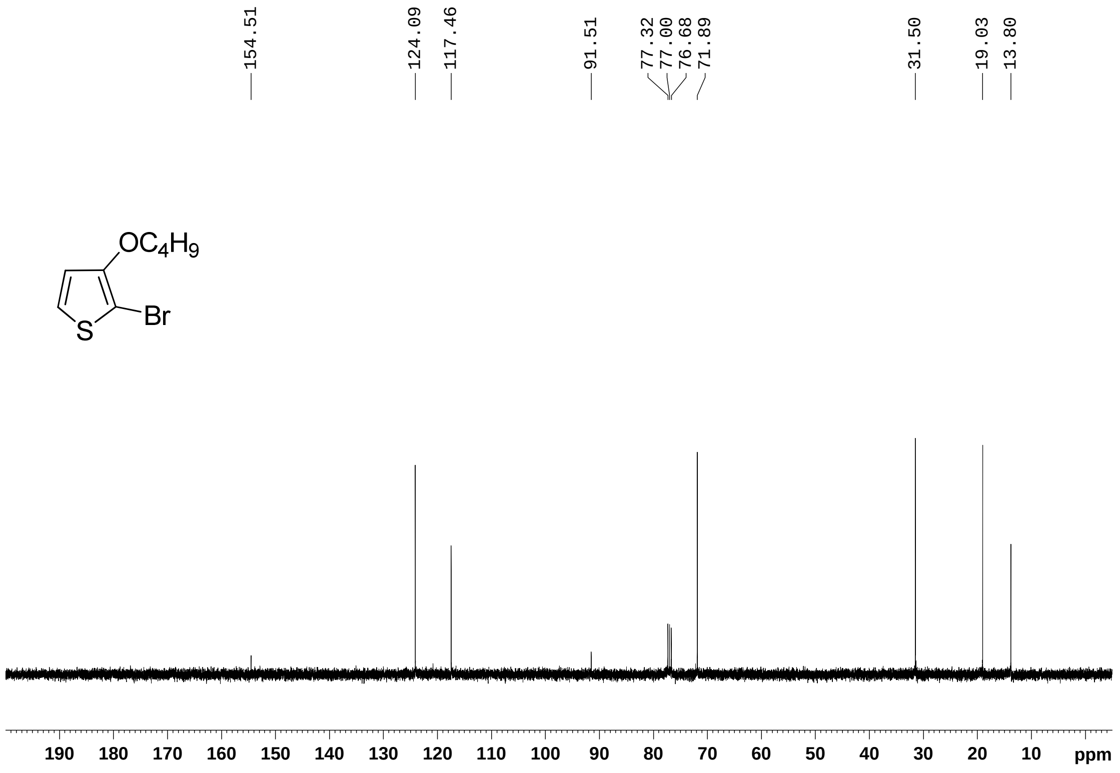

Figure S12. ^{13}C-NMR spectrum of BBOT in $CDCl_3$ (100 MHz).

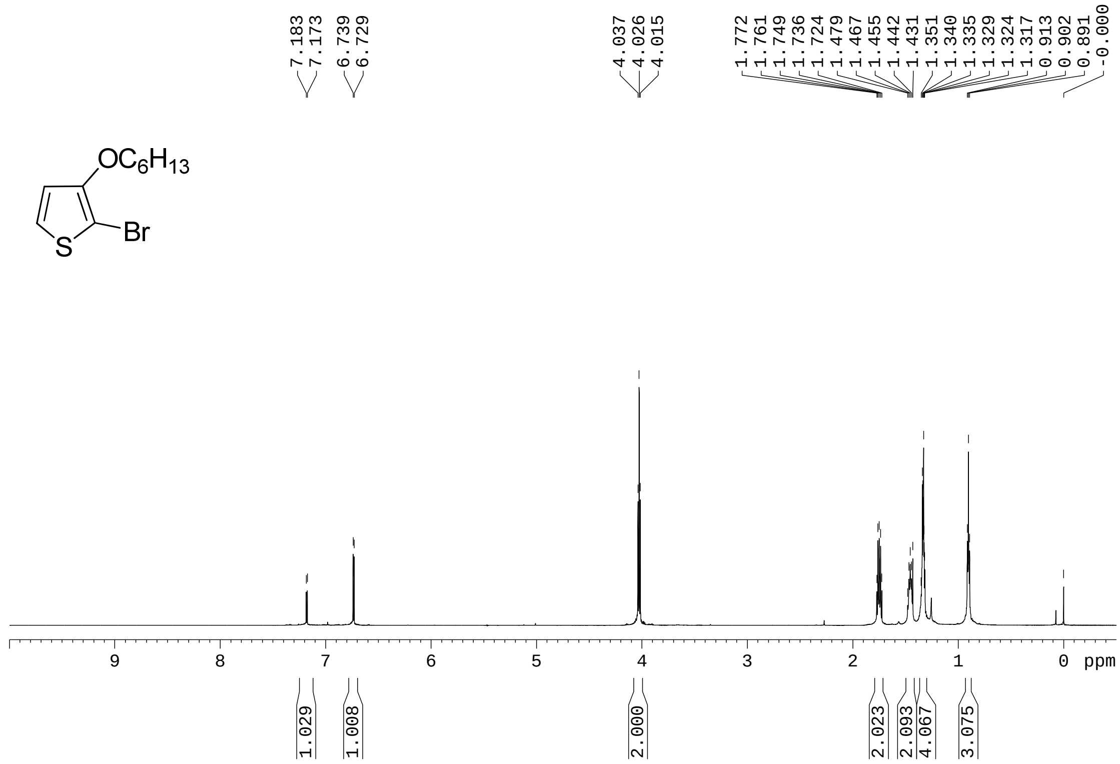

Figure S13. ^{1}H-NMR spectrum of BHOT in $CDCl_3$ (600 MHz).

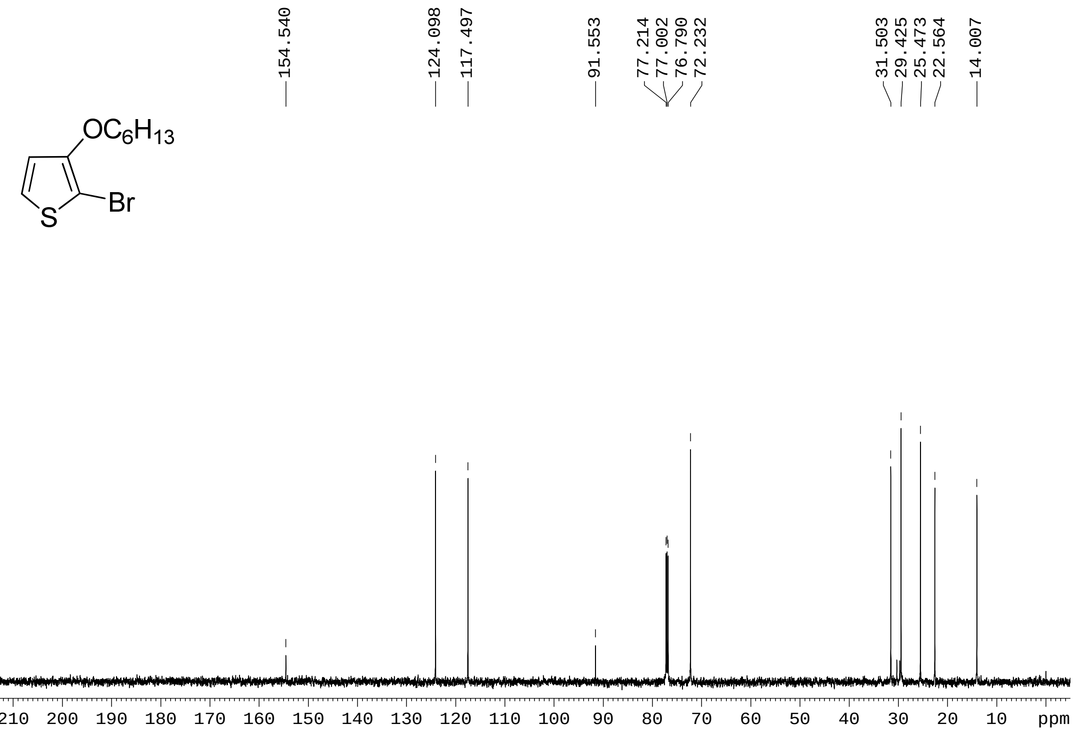

Figure S14. ^{13}C-NMR spectrum of BHOT in CDCl$_3$ (150 MHz).

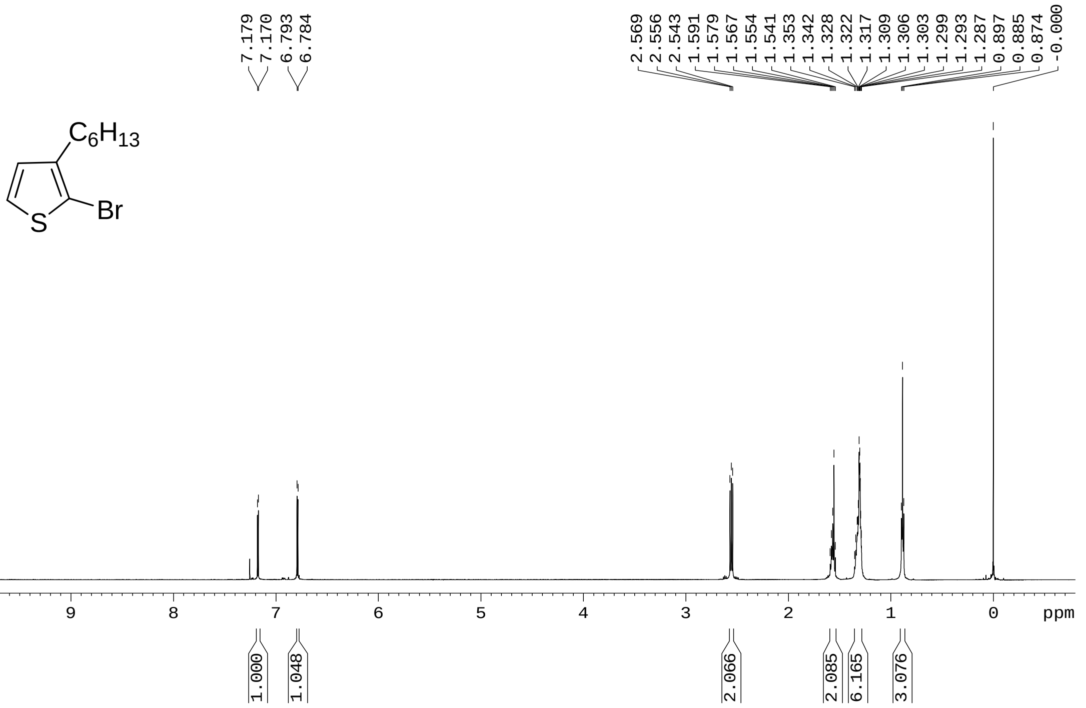

Figure S15. ^{1}H-NMR spectrum of BHT in CDCl$_3$ (600 MHz).

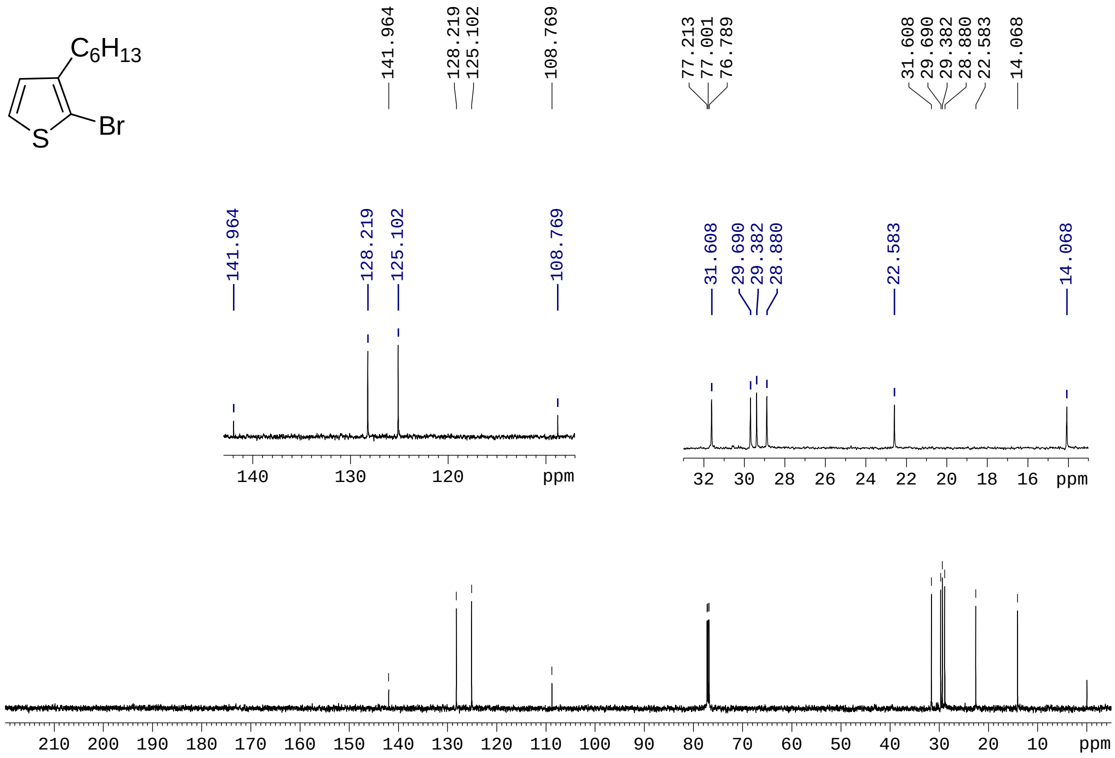

Figure S16. ^{13}C-NMR spectrum of BHT in CDCl$_3$ (150 MHz).

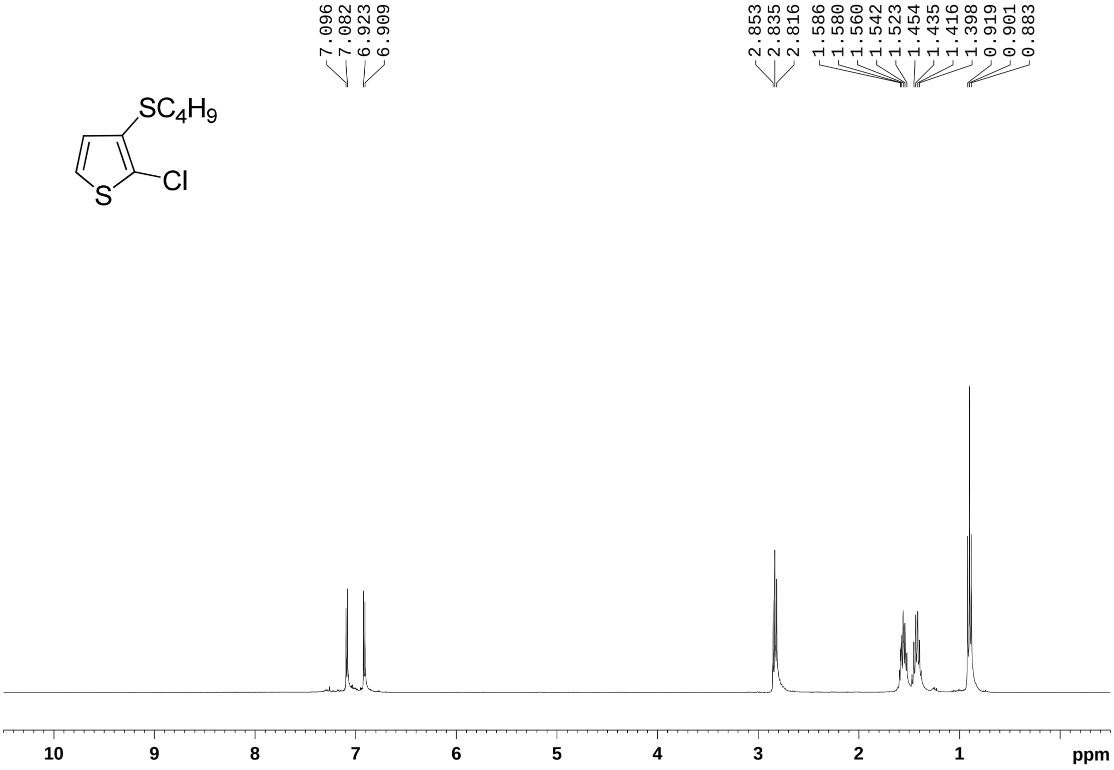

Figure S17. ^{1}H-NMR spectrum of CBTT in CDCl$_3$ (400 MHz).

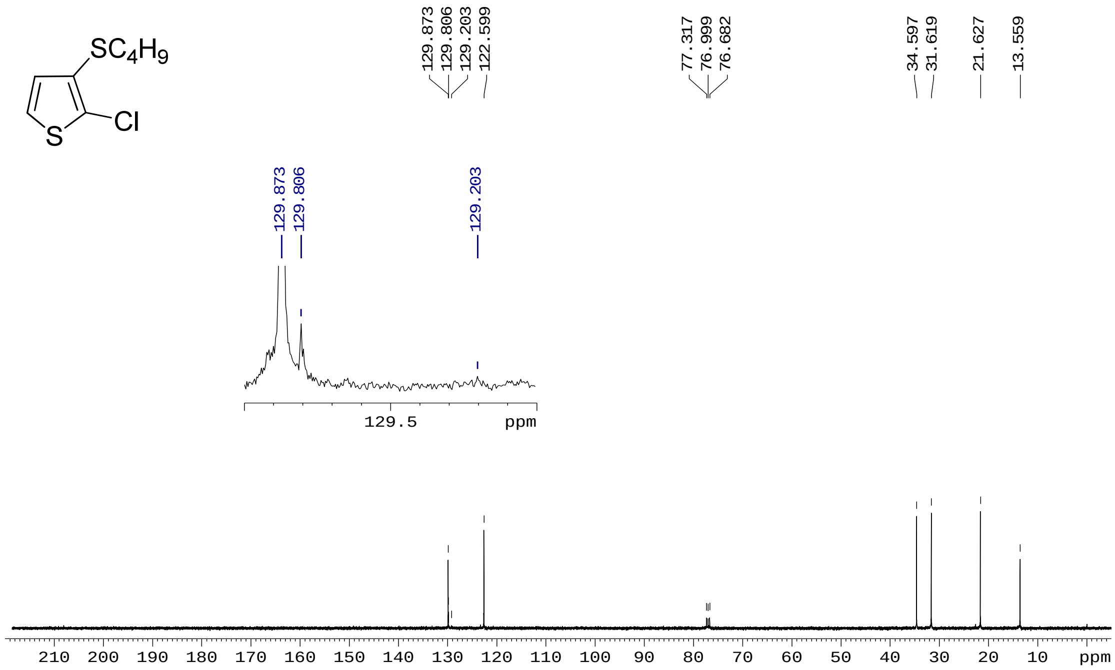

Figure S18. ^{13}C-NMR spectrum of CBTT in $CDCl_3$ (100 MHz).

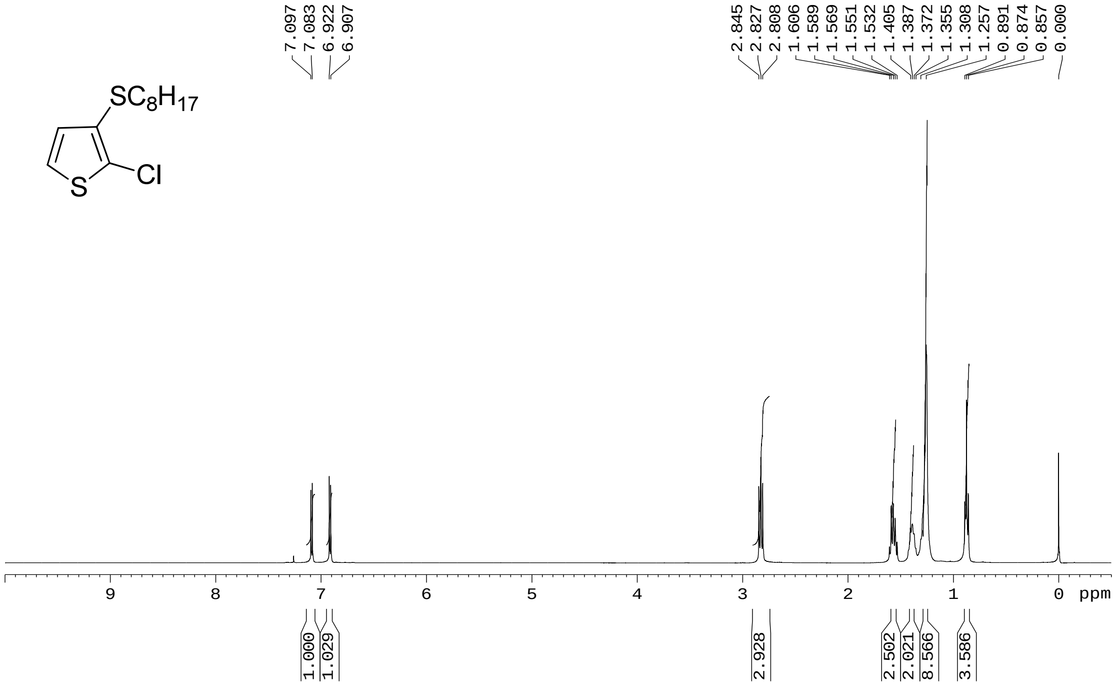

Figure S19. ^{1}H-NMR spectrum of COTT in $CDCl_3$ (400 MHz).

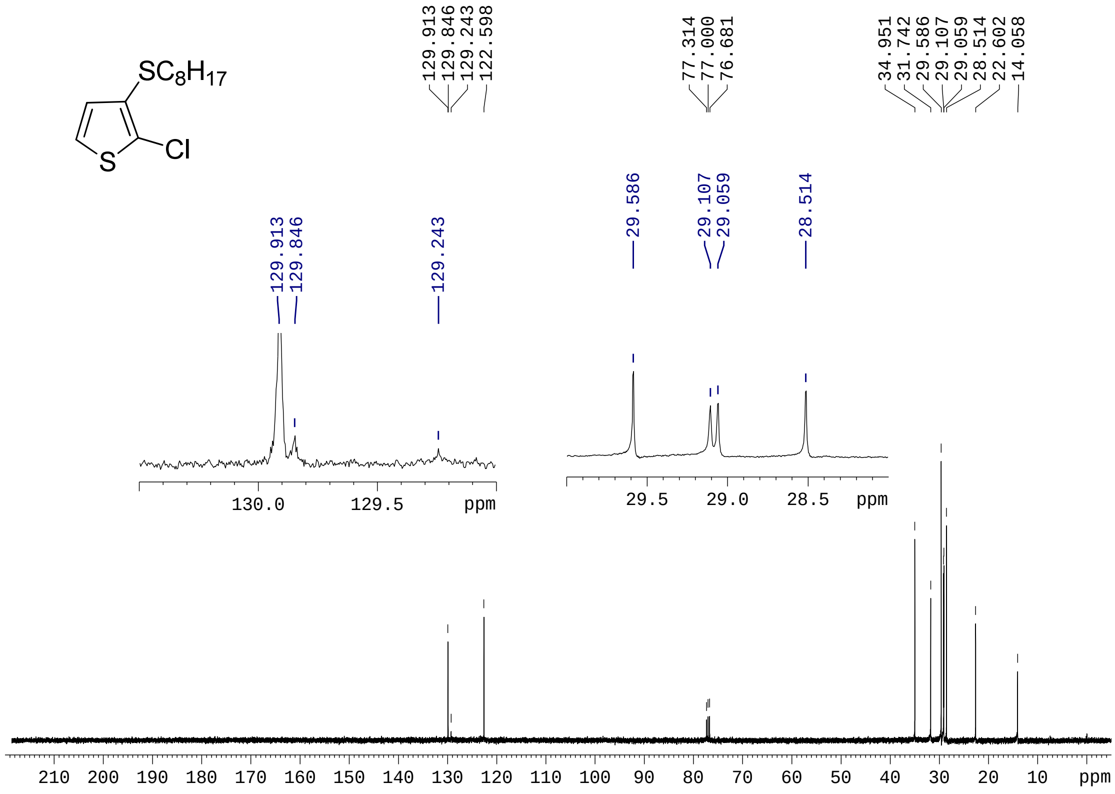

Figure S20. ^{13}C-NMR spectrum of COTT in $CDCl_3$ (100 MHz).

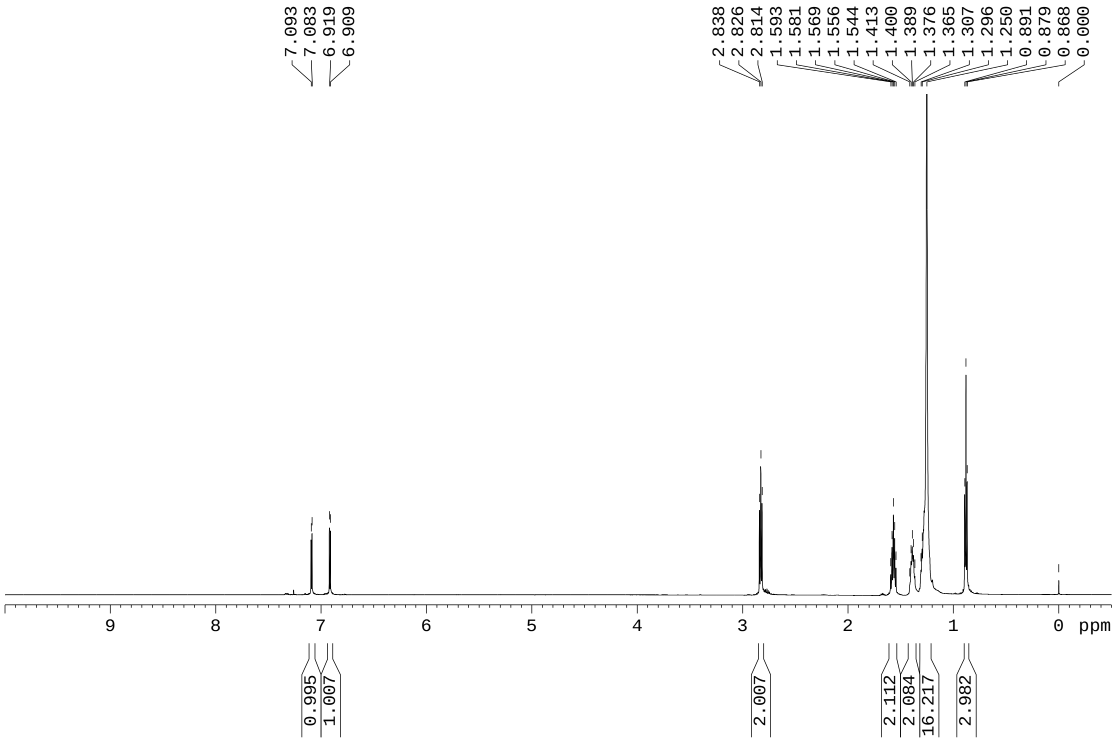

Figure S21. ^{1}H-NMR spectrum of CDDTT in $CDCl_3$ (600 MHz).

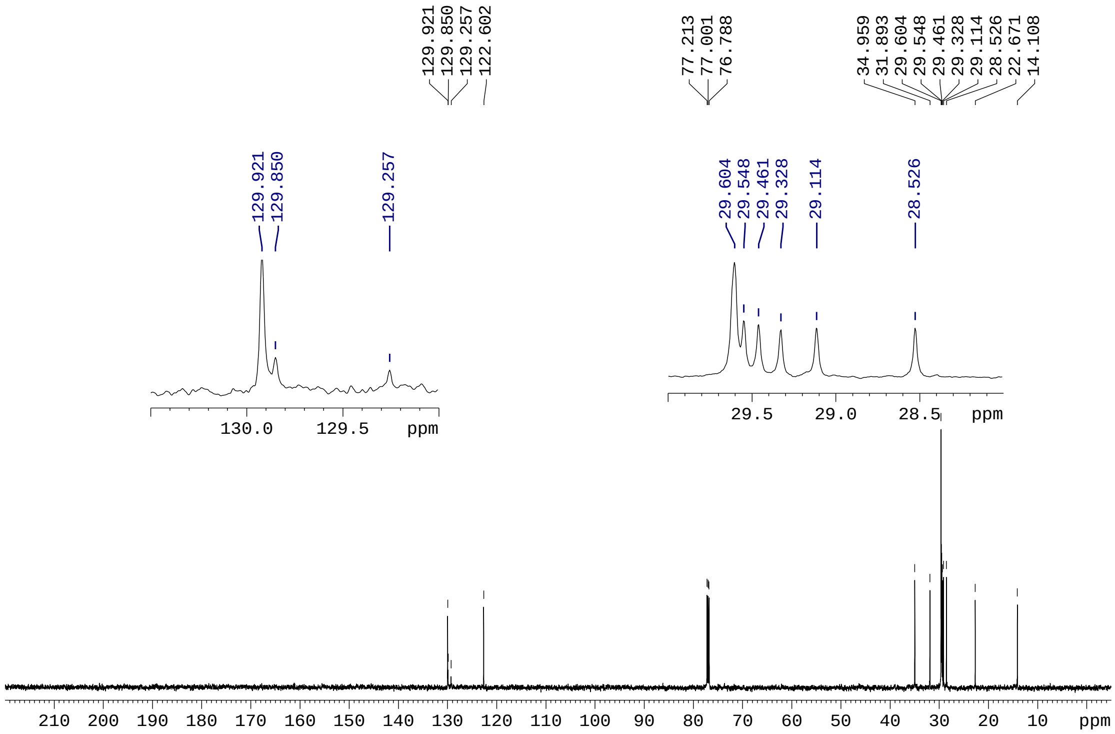

Figure S22. ^{13}C-NMR spectrum of CDDTT in $CDCl_3$ (150 MHz).

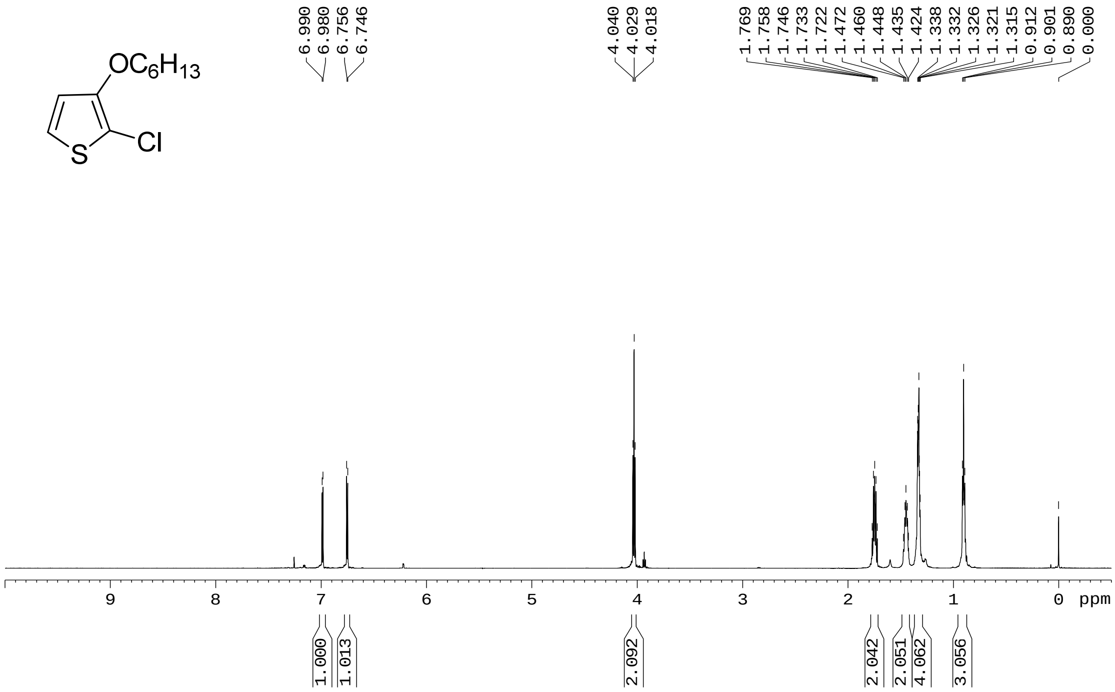

Figure S23. ^{1}H-NMR spectrum of CHOT in $CDCl_3$ (600 MHz).

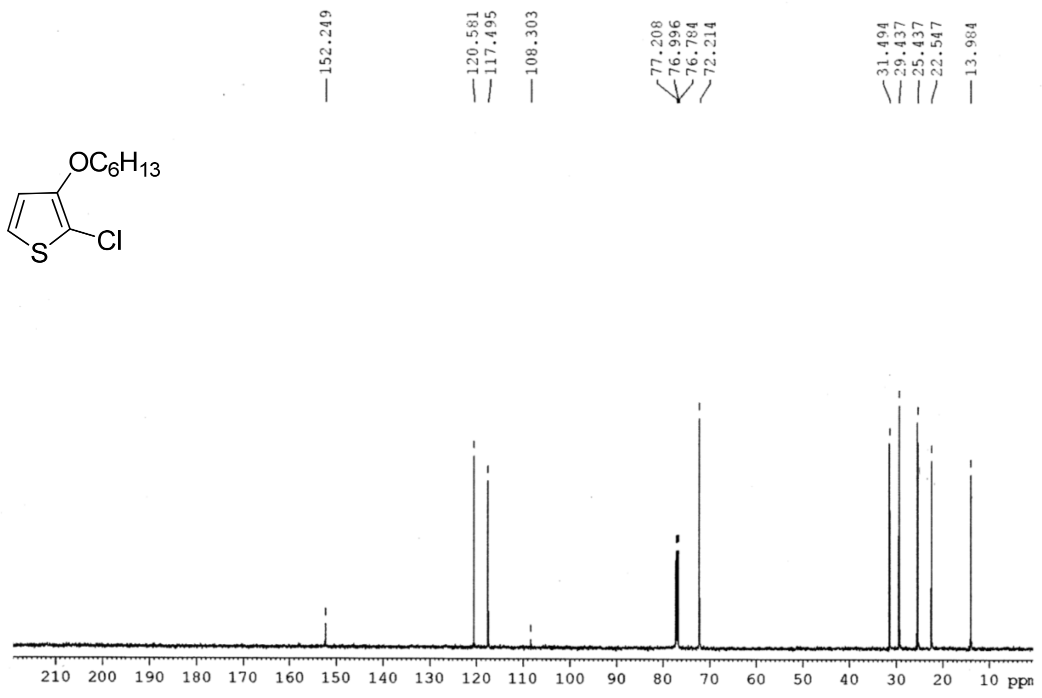

Figure S24. ^{13}C-NMR spectrum of CHOT in $CDCl_3$ (150 MHz).

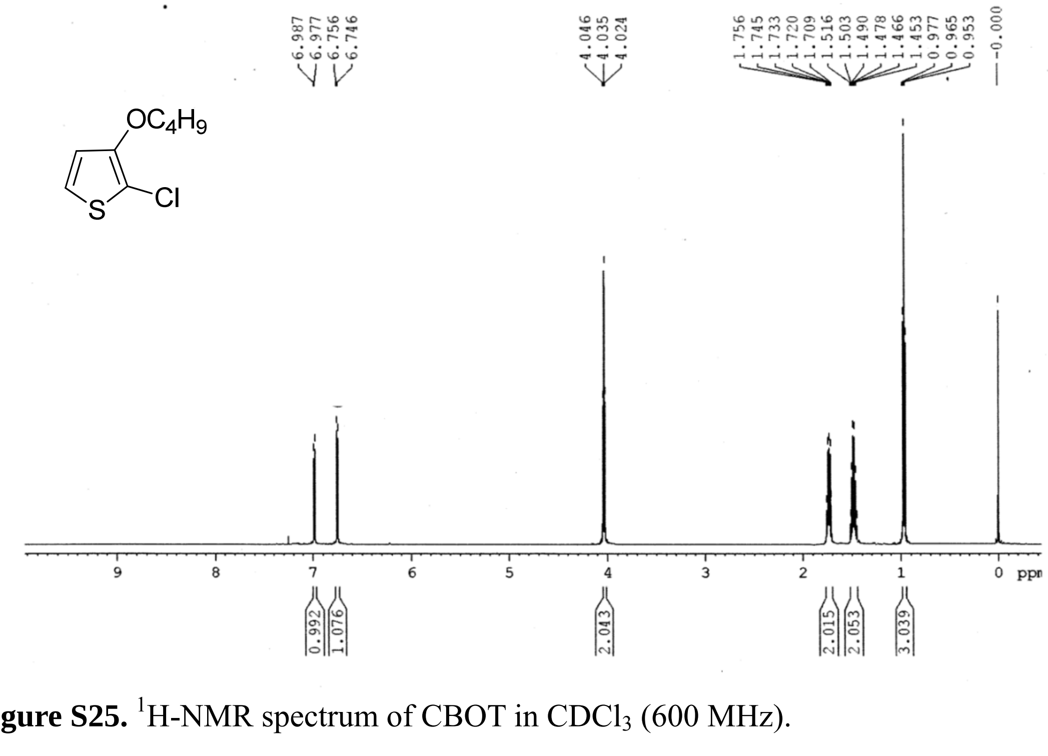

Figure S25. ^{1}H-NMR spectrum of CBOT in $CDCl_3$ (600 MHz).

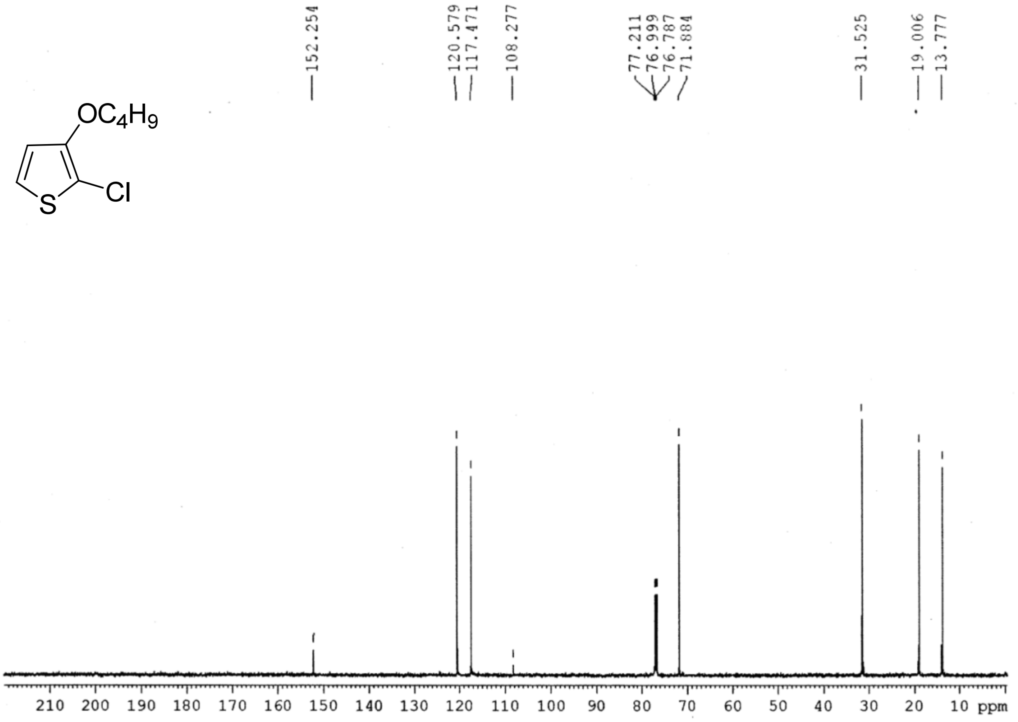

Figure S26. ^{13}C-NMR spectrum of CBOT in CDCl$_3$ (150 MHz).

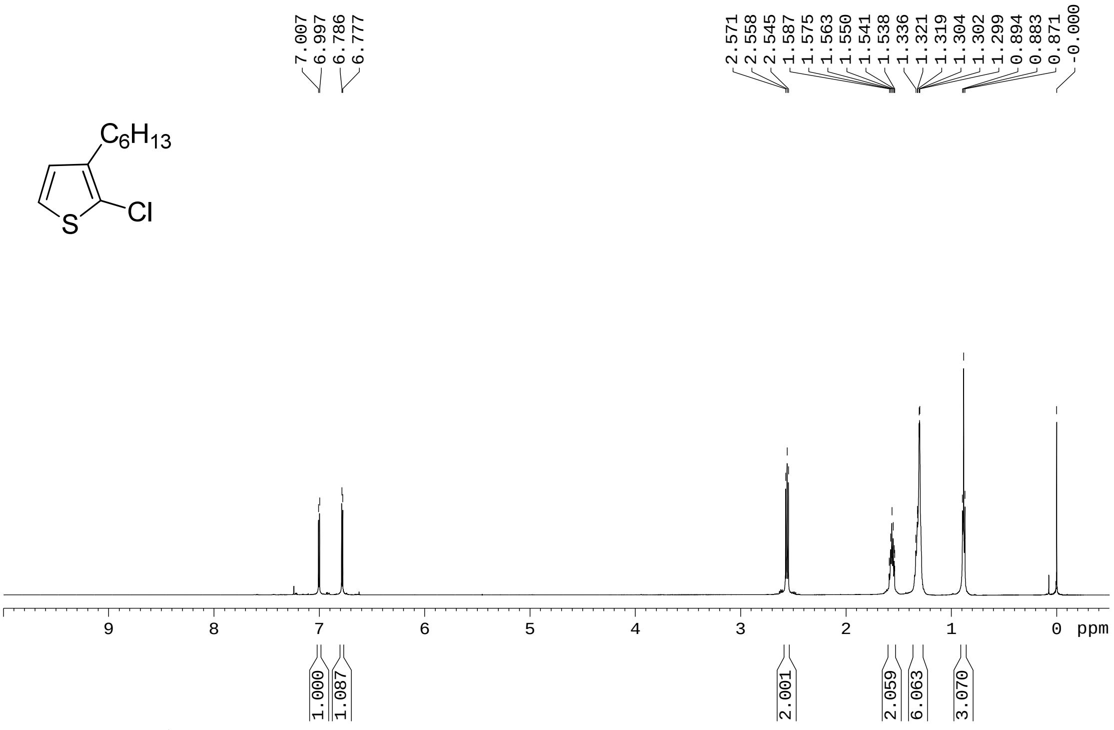

Figure S27. ^{1}H-NMR spectrum of CHT in CDCl$_3$ (600 MHz).

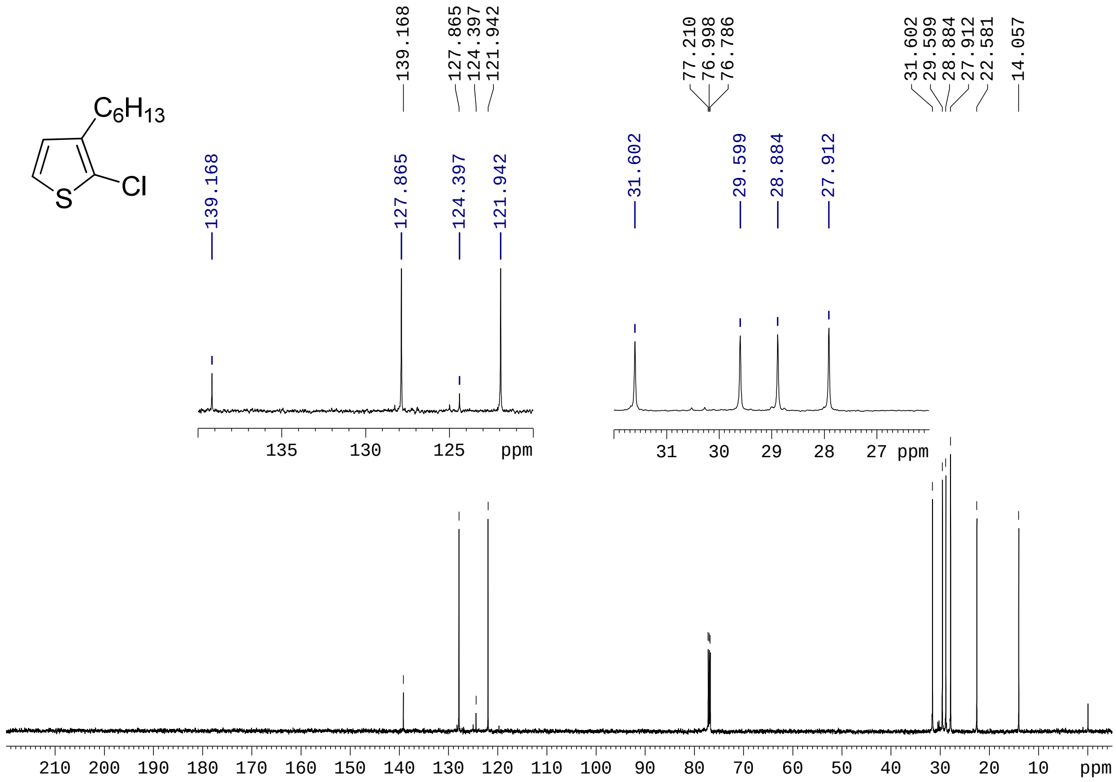

Figure S28. ^{13}C-NMR spectrum of CHT in $CDCl_3$ (150 MHz).

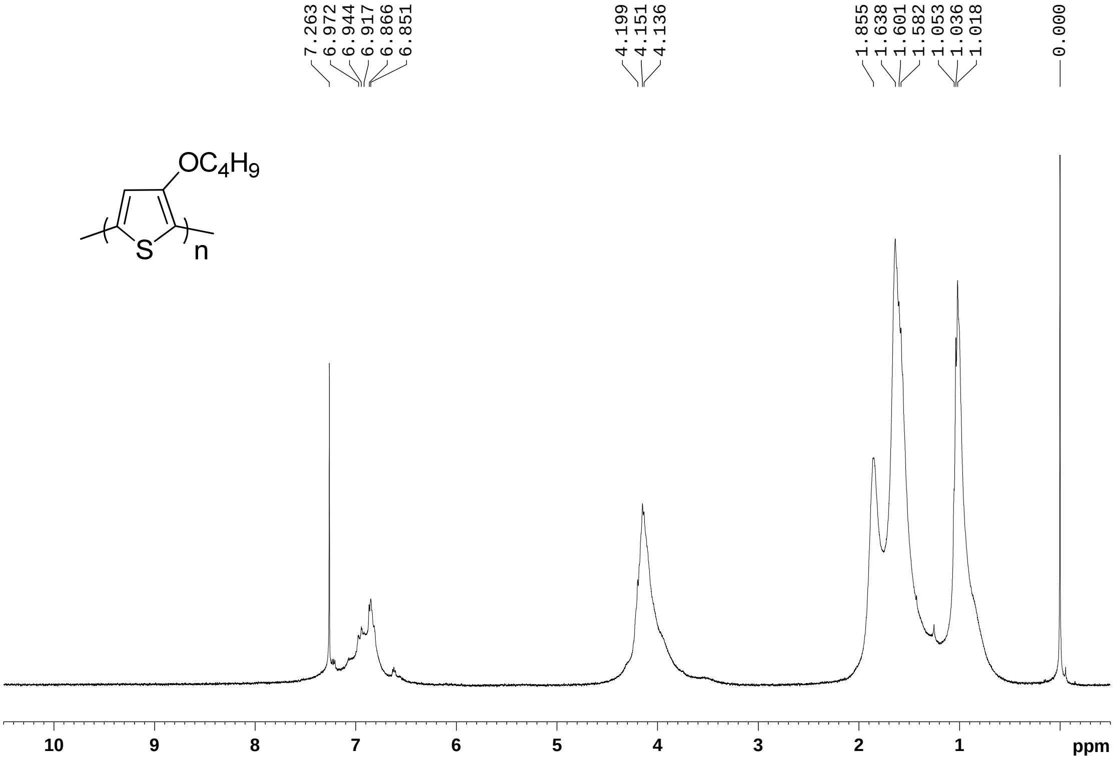

Figure S29. ^{1}H-NMR spectrum of PBOT-Br (rt sample) in $CDCl_3$ (400 MHz).

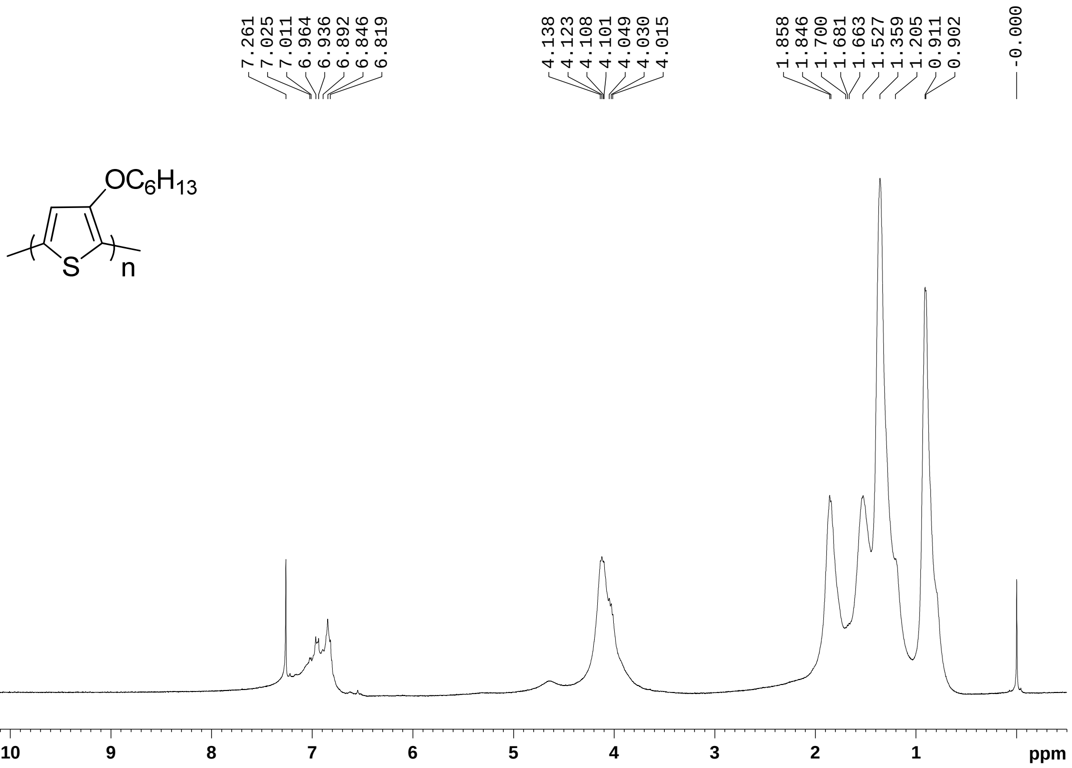

Figure S30. ^{1}H-NMR spectrum of PHOT-Br (rt sample) in CDCl$_3$ (400 MHz).

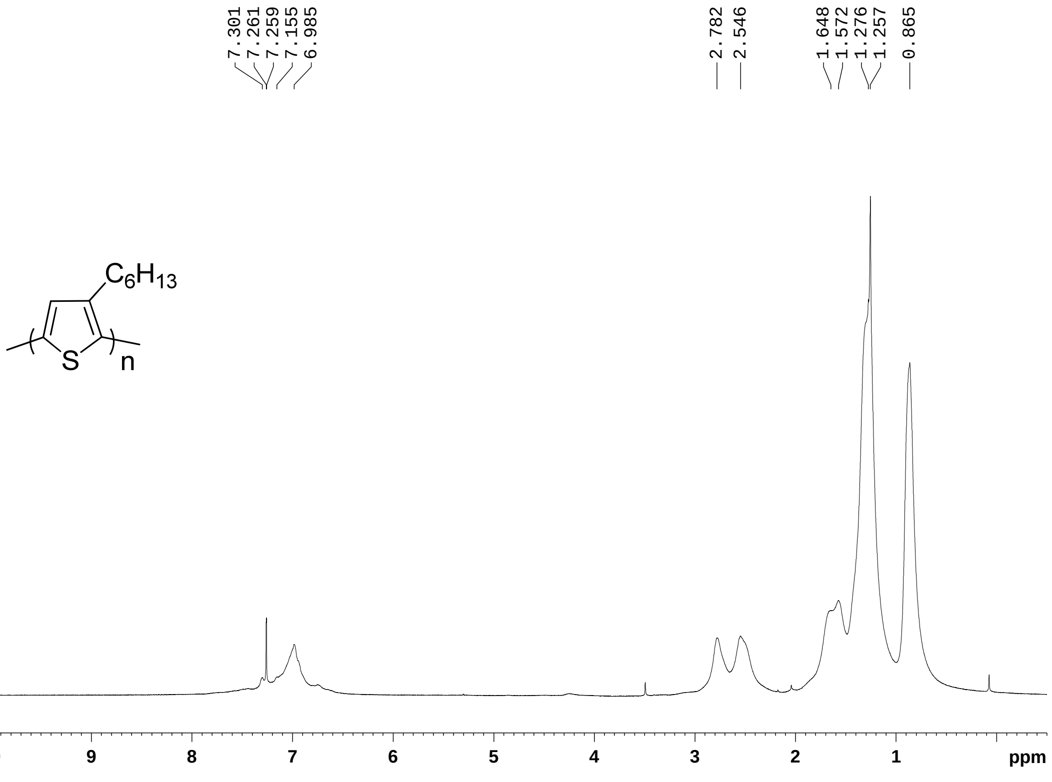

Figure S31. ^{1}H-NMR spectrum of PHT-Br (100 °C sample) in CDCl$_3$ (400 MHz).

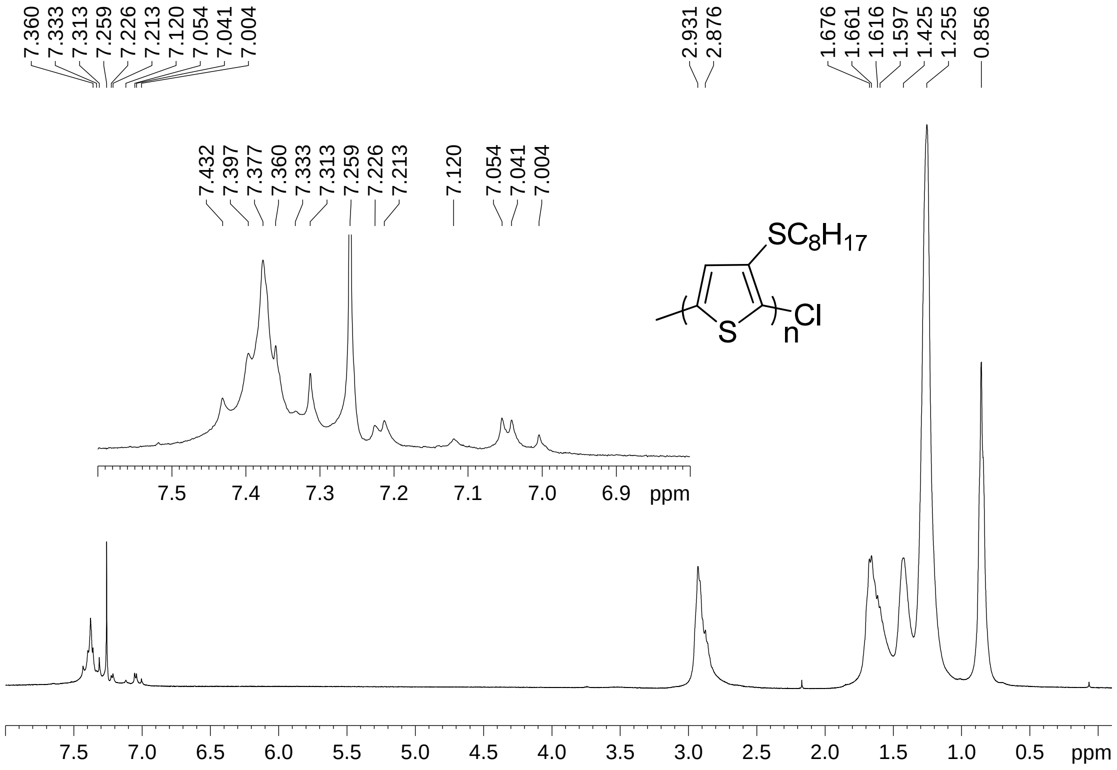

Figure S32. ^{1}H-NMR spectrum of POTT-Cl (100 °C sample) in $CDCl_3$ (400 MHz).

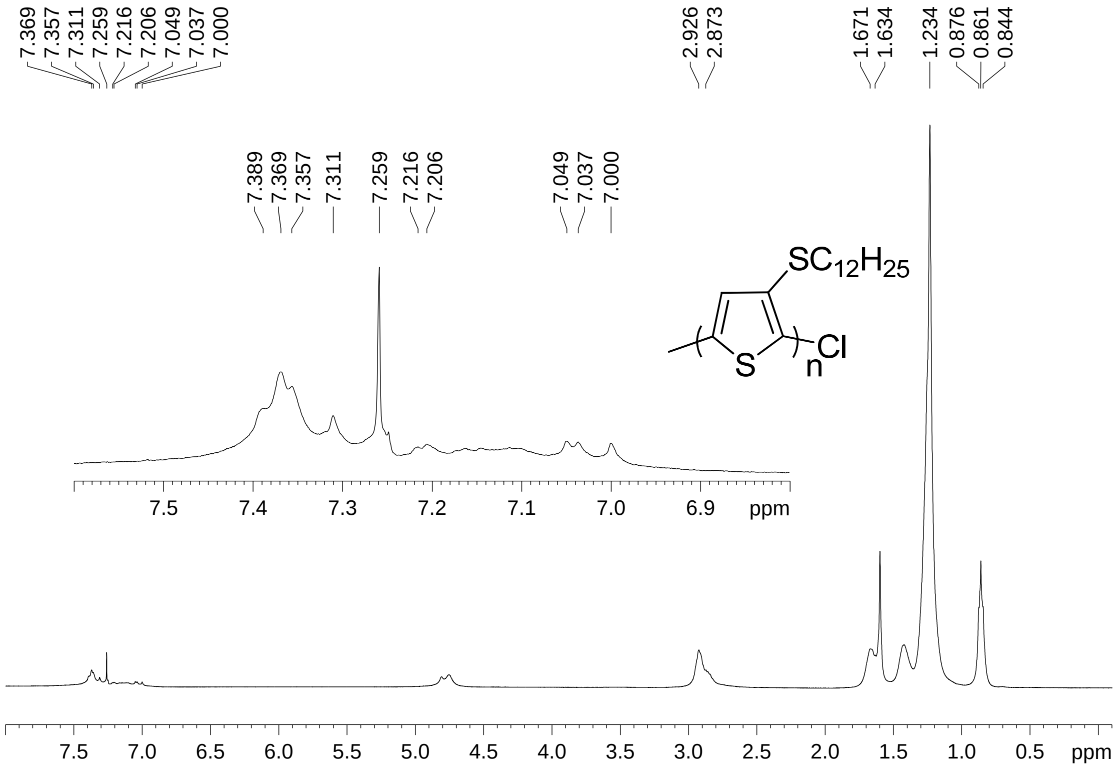

Figure S33. ^{1}H-NMR spectrum of PDDTT-Cl (100 °C sample) in $CDCl_3$ (400 MHz).

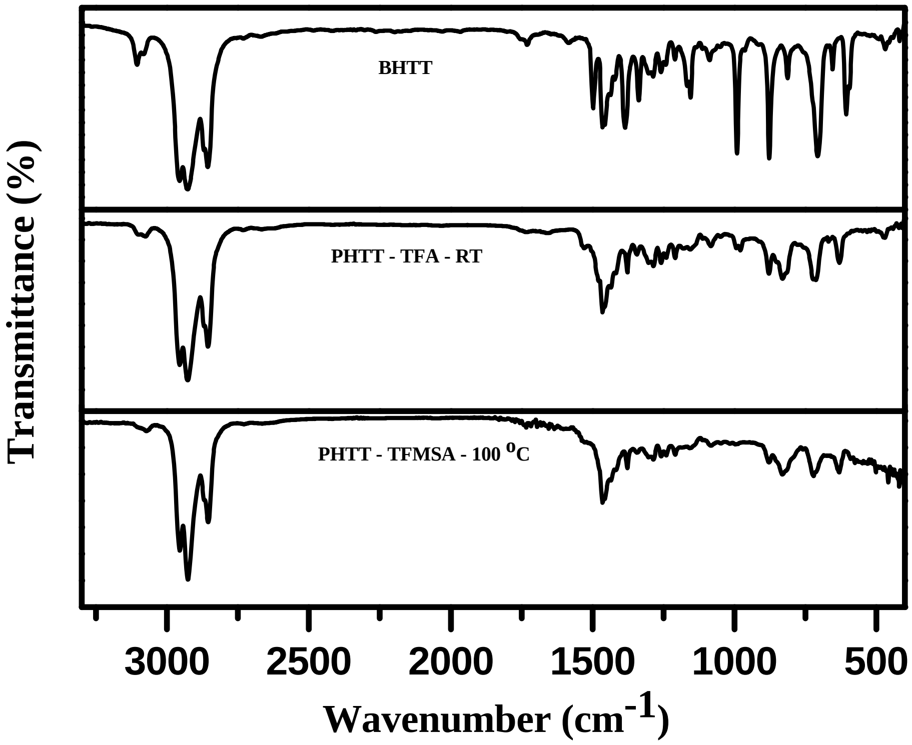

Figure S34. FT-IR spectra of PHTT-Br along with BHTT for the drop casted samples on silicon wafer.

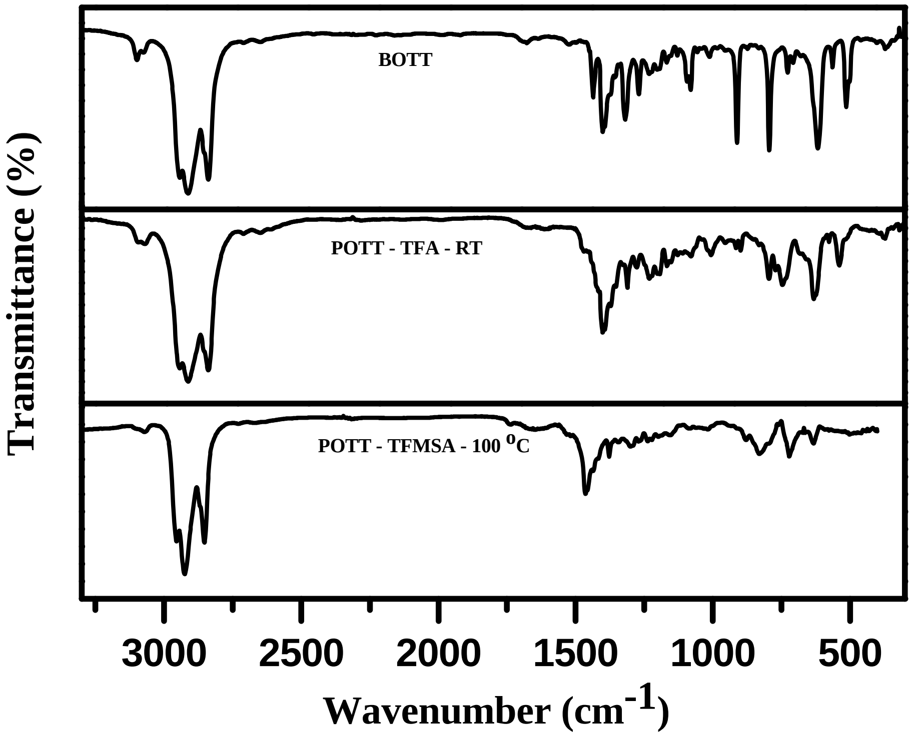

Figure S35. FT-IR spectra of POTT-Br along with BOTT for the drop casted samples on silicon wafer.

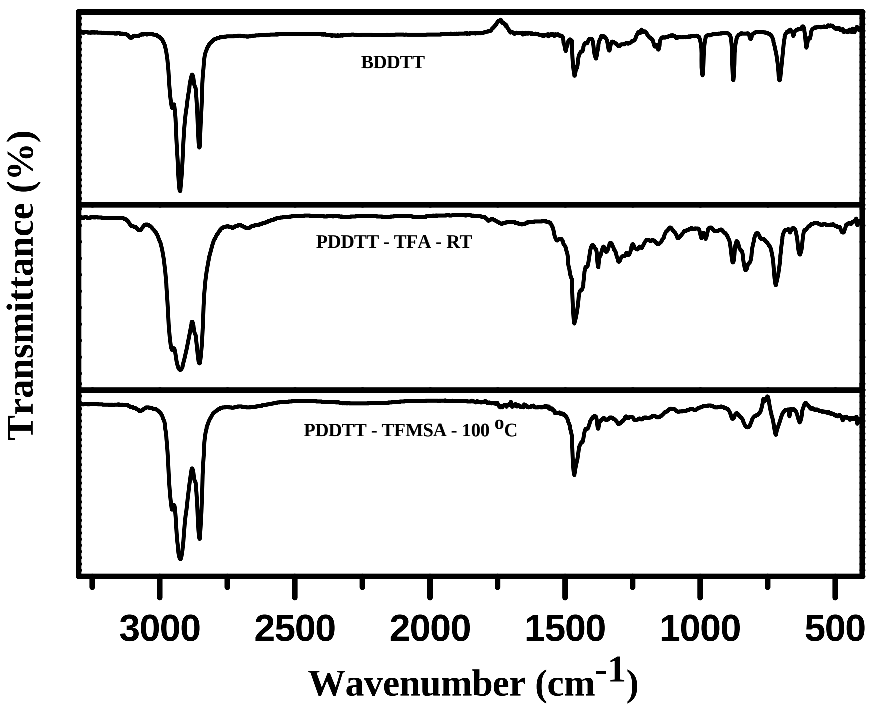

Figure S36. FT-IR spectra of PDDTT-Br along with BDDTT for the drop casted samples on silicon wafer.

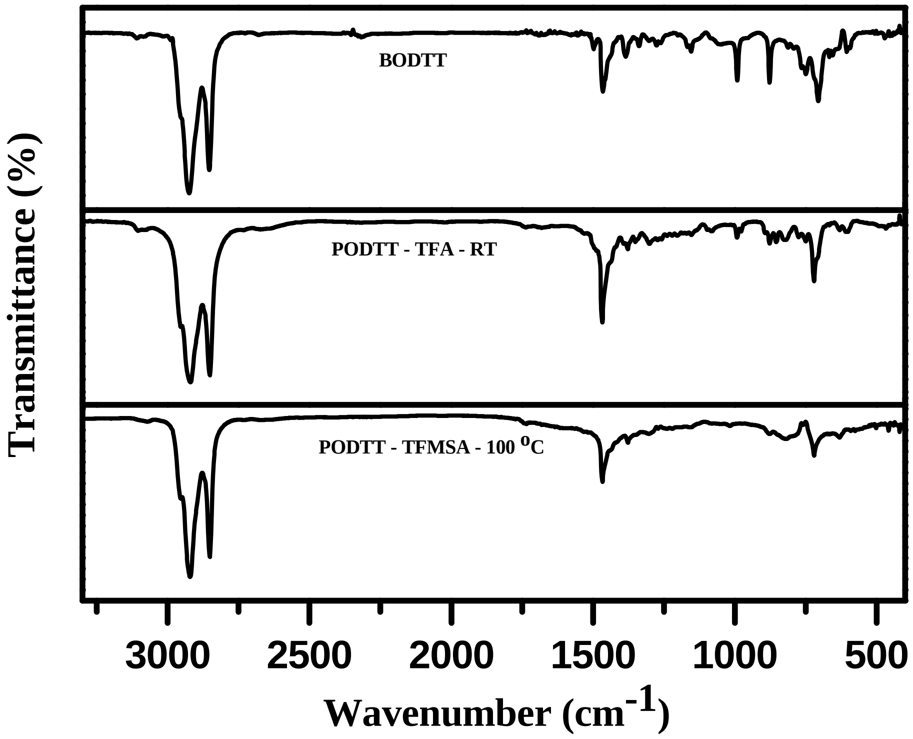

Figure S37. FT-IR spectra of PODTT-Br along with BODTT for the drop casted samples on silicon wafer.

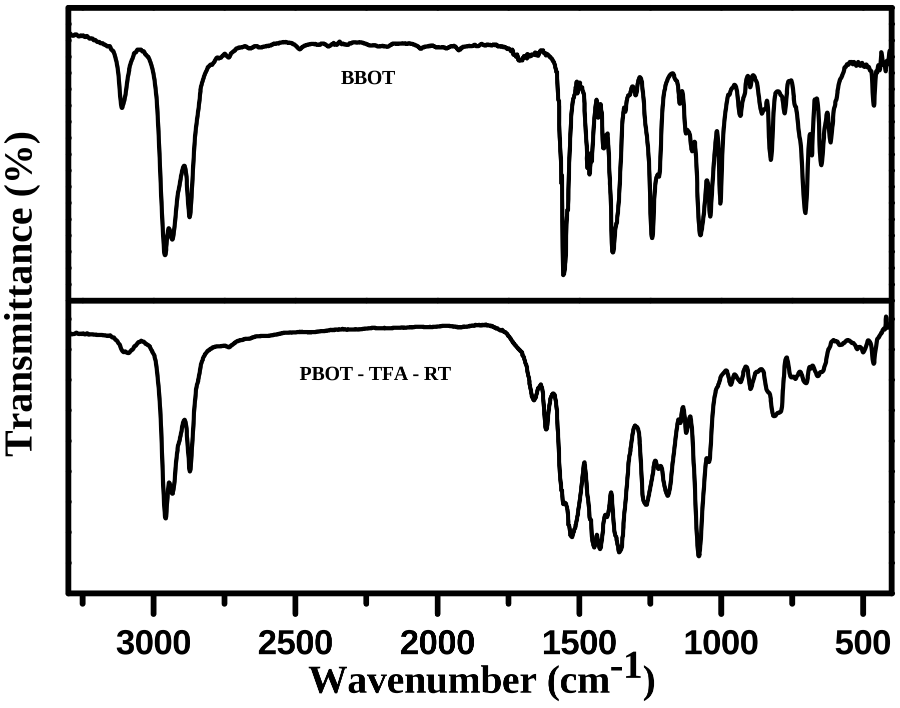

Figure S38. FT-IR spectra of PBOT-Br along with BBOT for the drop casted samples on silicon wafer.

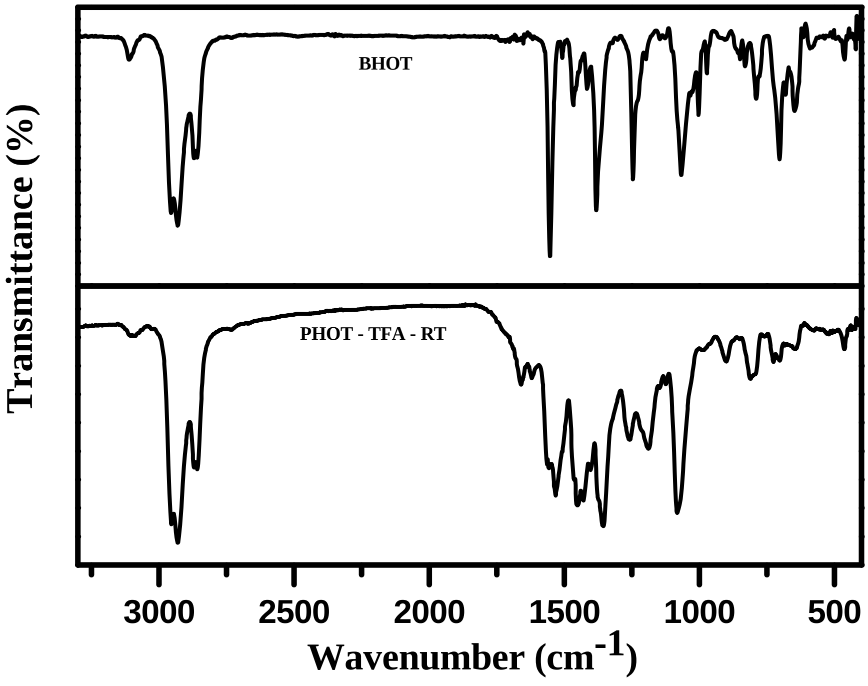

Figure S39. FT-IR spectra of PHOT-Br along with BHOT for the drop casted samples on silicon wafer.

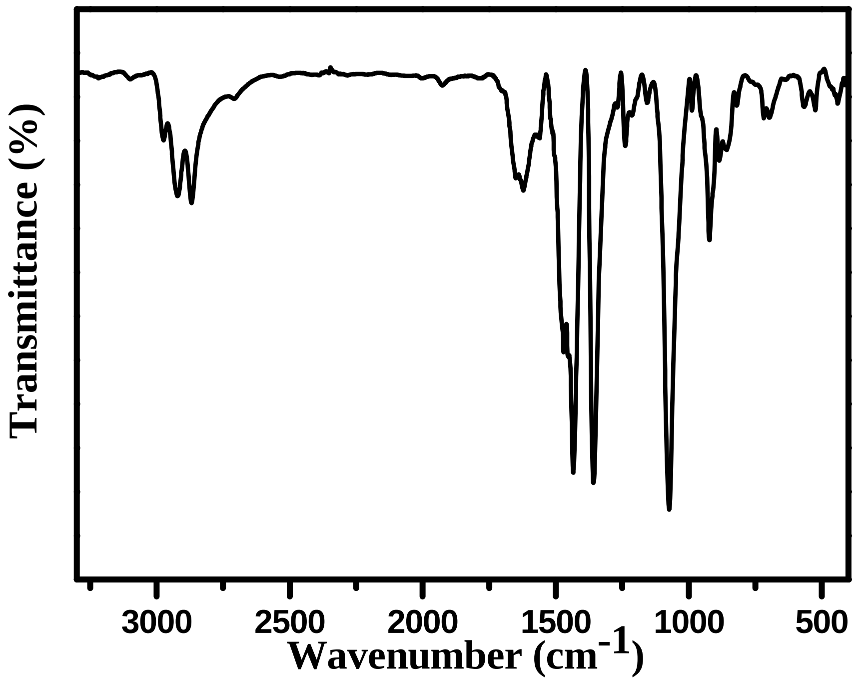

Figure S40. FT-IR spectra of PEDOT-Br in KBr pellet.

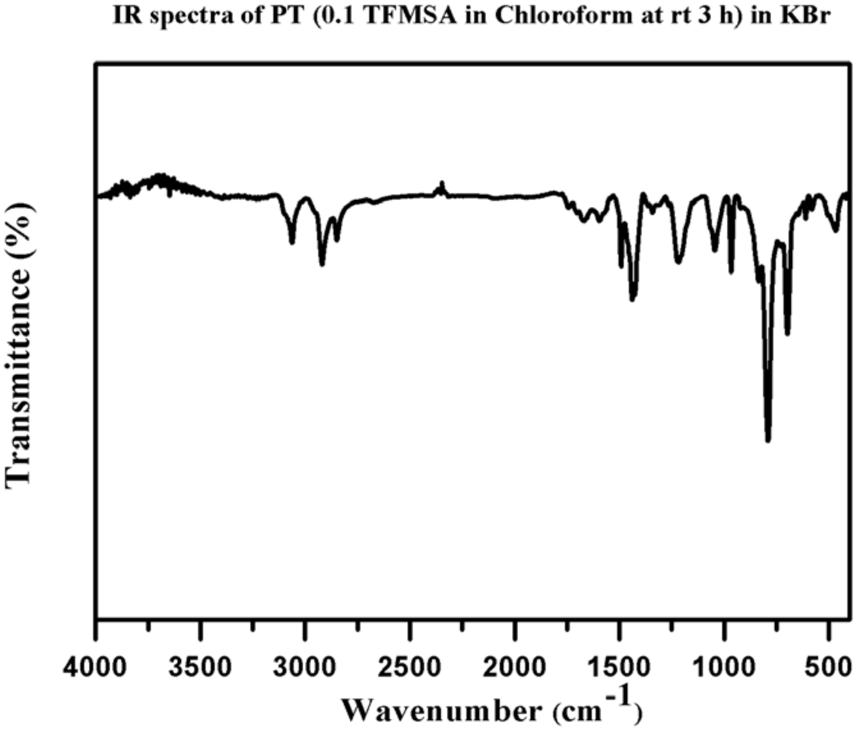

Figure S41. FT-IR spectra of PT-Br (0.1 equiv TFMSA, rt, 3 h) in KBr pellet.

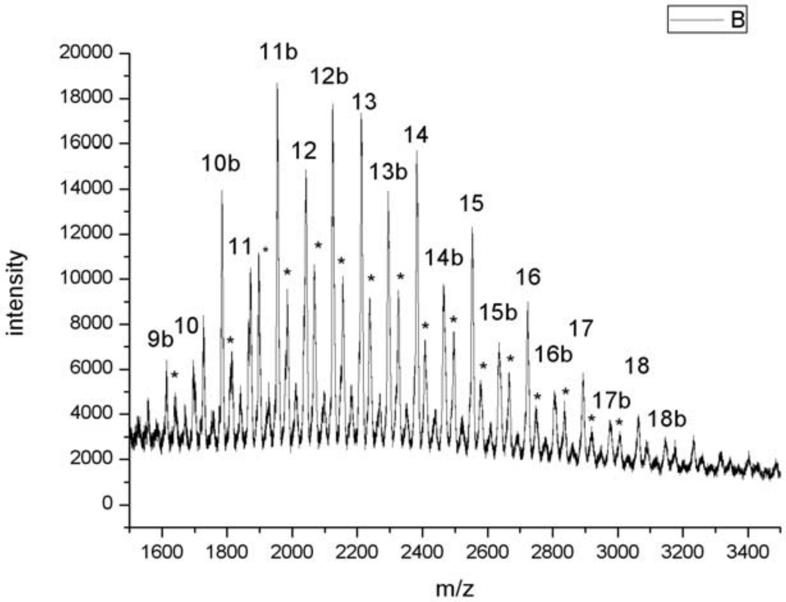

Figure S42. MALDI spectrum for the PBTT-Br prepared with TFMSA (0.05 equiv) at 100 °C for 24 h. The numbers 9-18 standard for the number of repeat units of the respective polymer, and 9b-18b standard for the polymer chains having a Br end group. The peaks labeled with asterisk are the TFA-doped polymer chains.

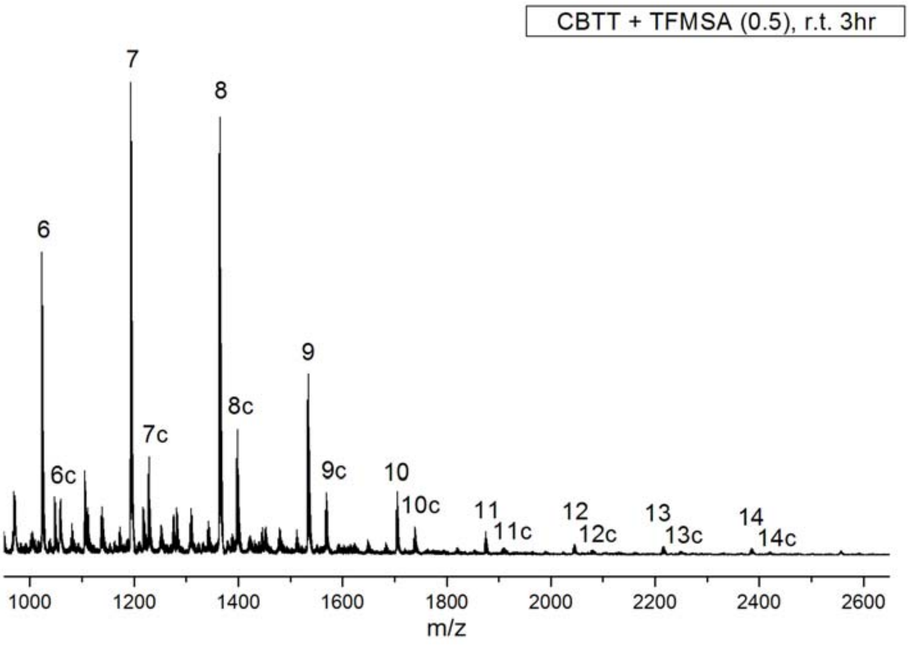

Figure S43. MALDI spectrum for the PBTT-Cl prepared with TFMSA (0.5 equiv) at rt for 3 h. The numbers 6-14 standard for the number of repeat units of the respective polymer, and 6c-14c standard for the polymer chains having a Cl end group.

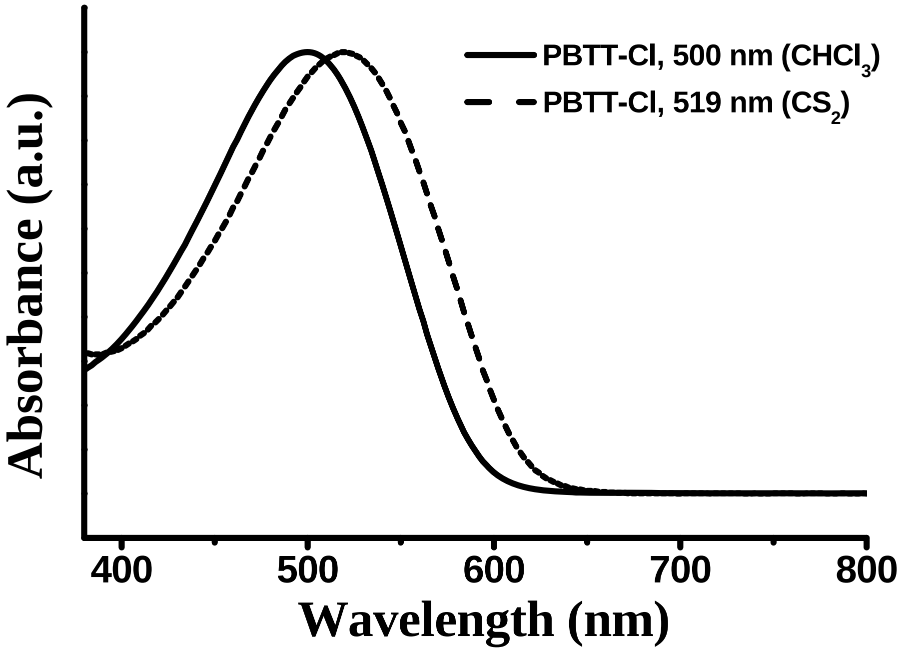

Figure S44. The UV-vis spectra of PBTT-Cl measured in $CHCl_3$ and CS_2 solutions.

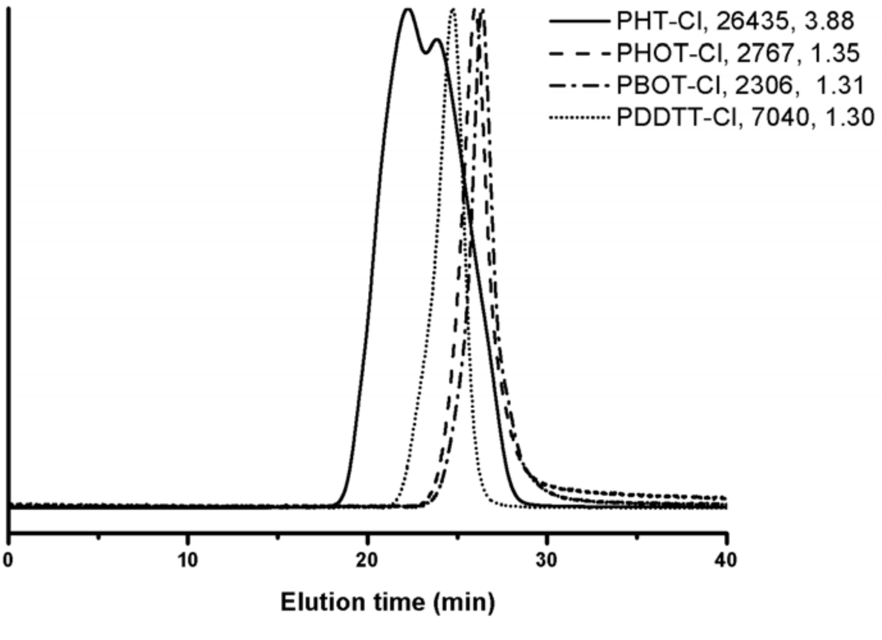

Figure S45. GPC traces for the polythiophenes prepared from the various 2-chloro thiophenes.

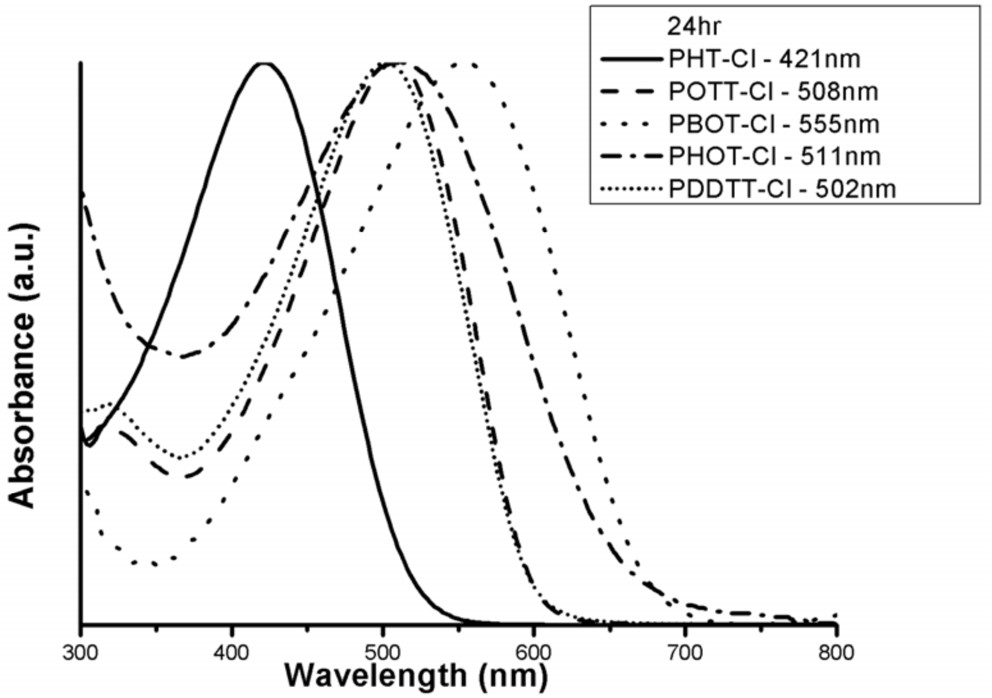

Figure S46. UV-vis spectra for the polythiophenes prepared from the various 2-chloro thiophenes.