

# Supporting Information

## Improved Synthesis of Thienothiazole and Its Utility in Developing Polymers for Photovoltaics

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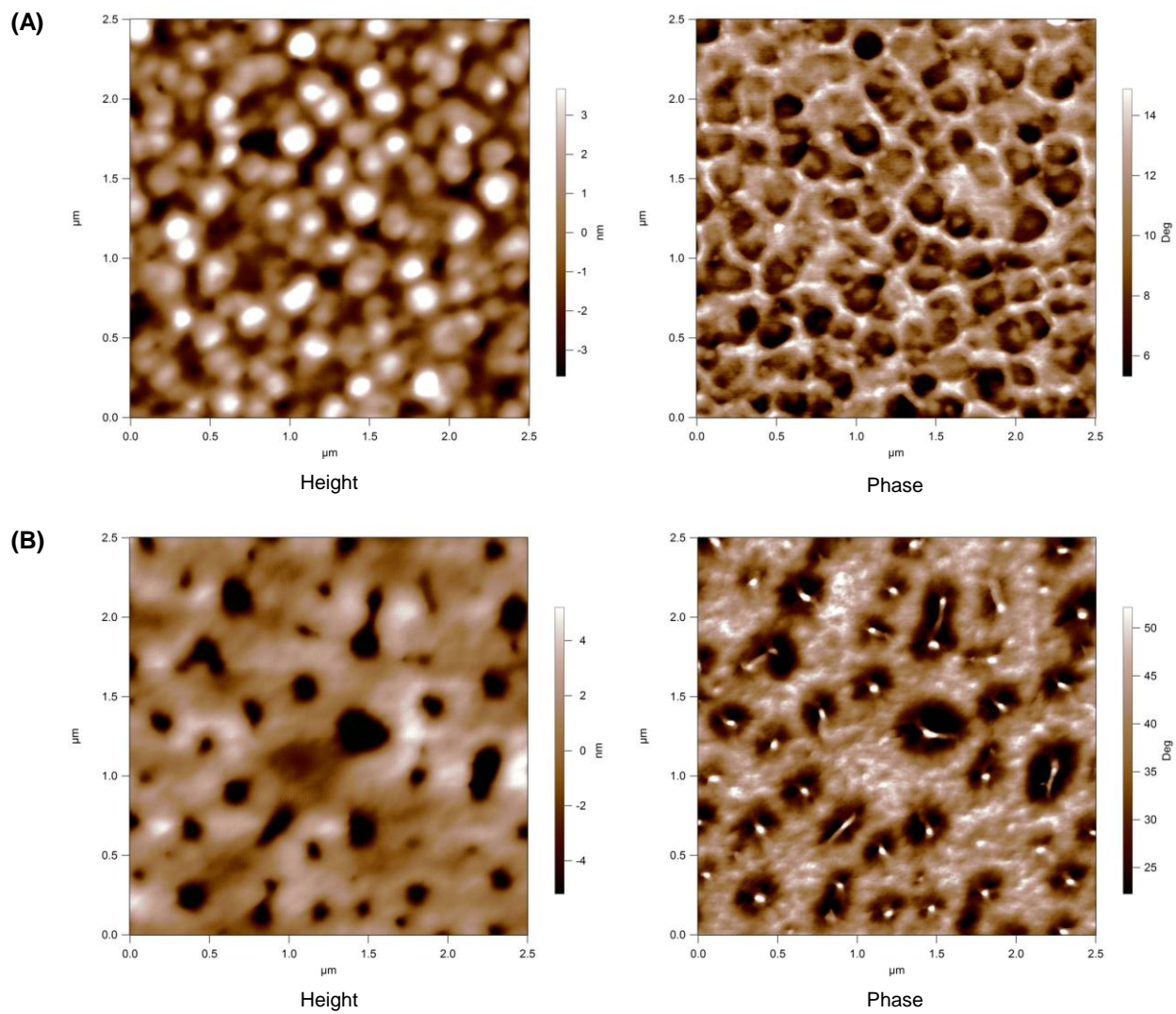
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Hill, North Carolina 27599-3287

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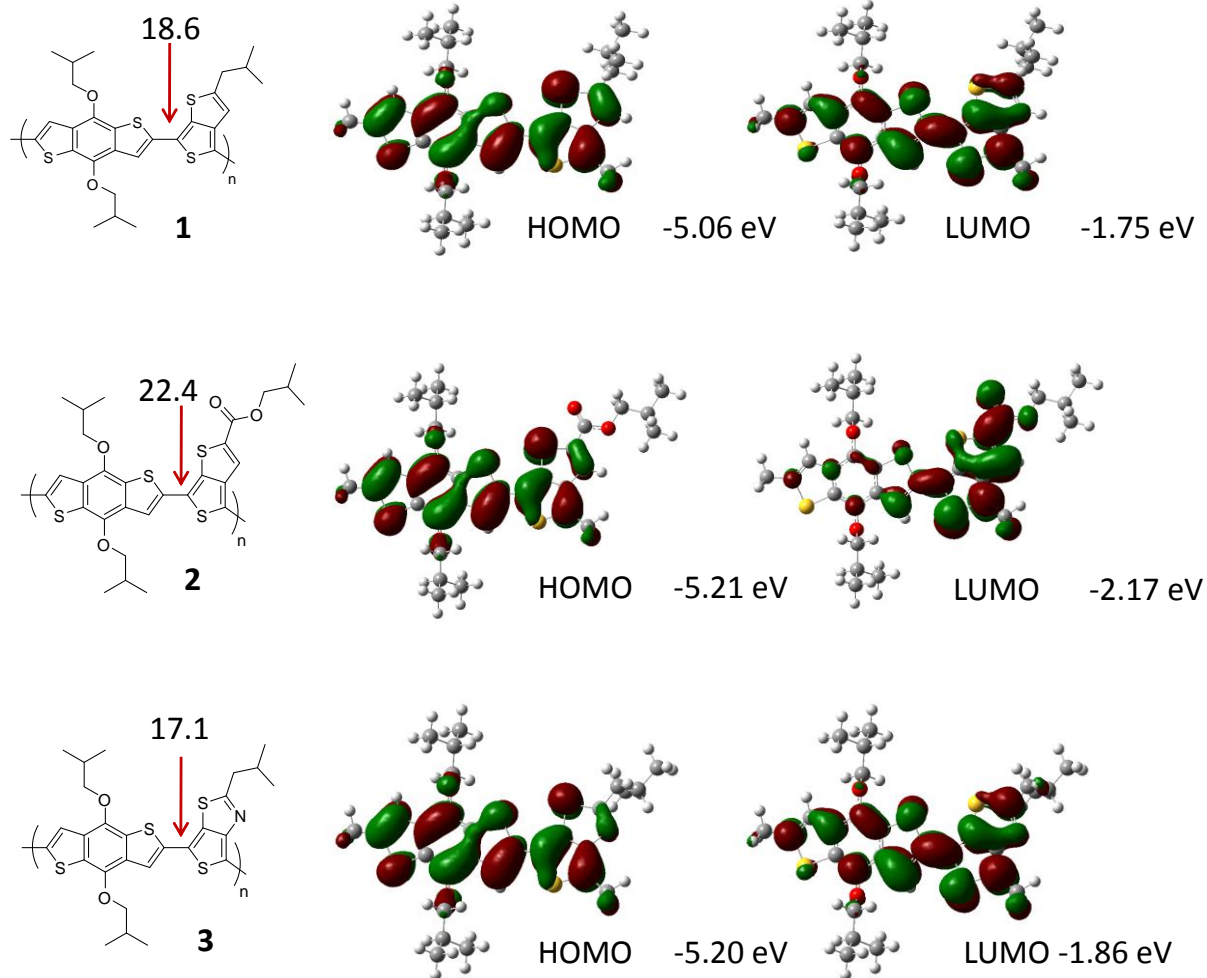
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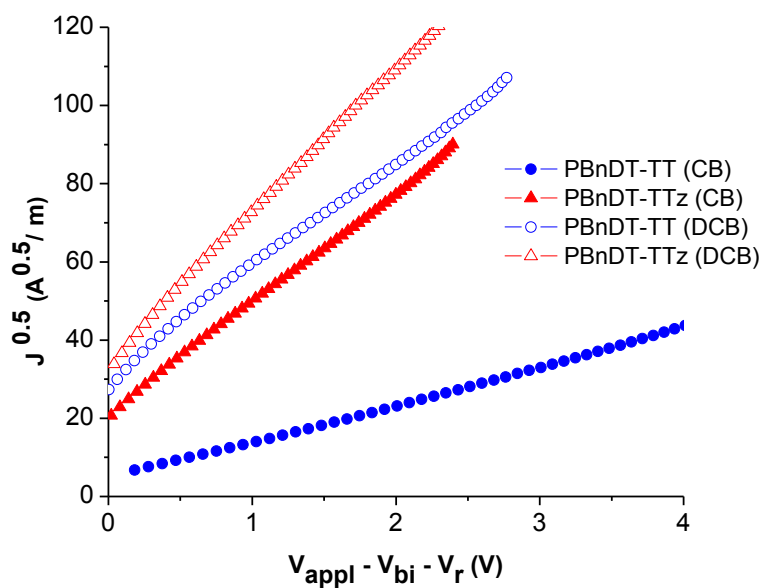
**Figure S0.** AFM images of PBN-DT-TT in (A) chlorobenzene and (B) dichlorobenzene.



**Figure S1.** DFT calculations of the dihedral angles and HOMO/LUMO levels for BnDT co-polymerized with alkyl TT (1), ester TT (2), and alkyl TTz (3).

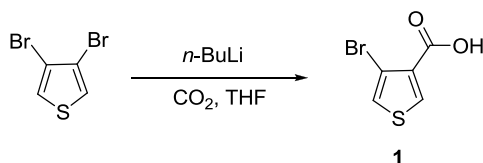
**Table S1.** Mobility data for PBnDT-TTz and PBnDT-TT in CB and DCB.

<i>Polymer</i>	<i>Solvent</i>	<i>Thickness (nm)</i>	<i>Mobility (cm<sup>2</sup>/V.s)</i>
PBnDT-TT	CB	106	$4.52 \times 10^{-5}$
PBnDT-TTz	CB	93	$2.18 \times 10^{-4}$
PBnDT-TT	DCB	100	$2.22 \times 10^{-4}$
PBnDT-TTz	DCB	101	$4.84 \times 10^{-4}$

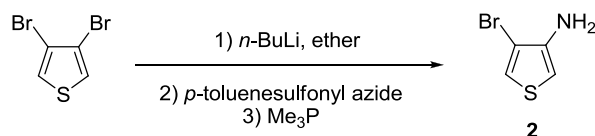


**Figure S2.** Mobility curves for PBnDT-TTz and PBnDT-TT in CB and DCB.

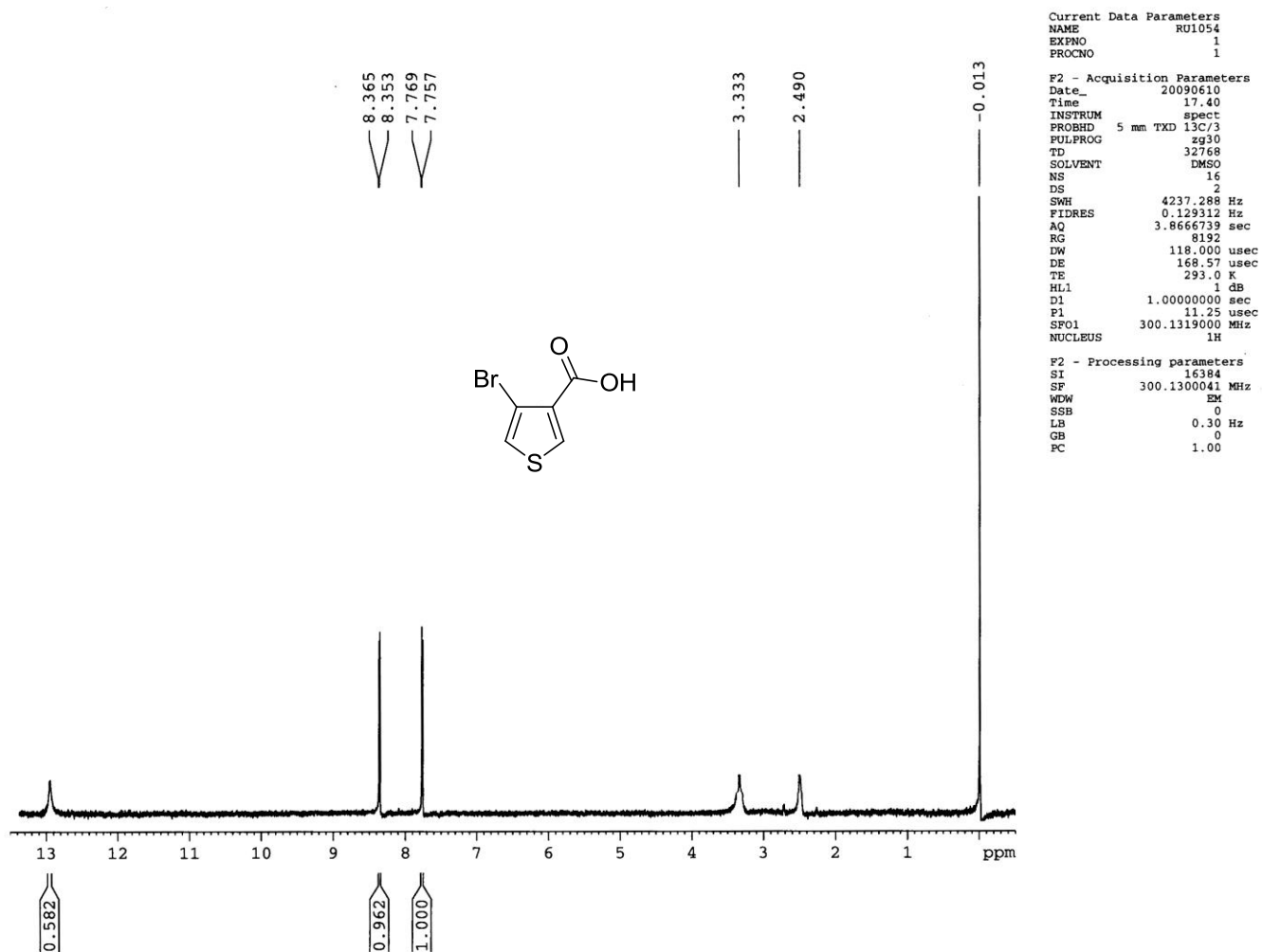
## Experimental Procedures



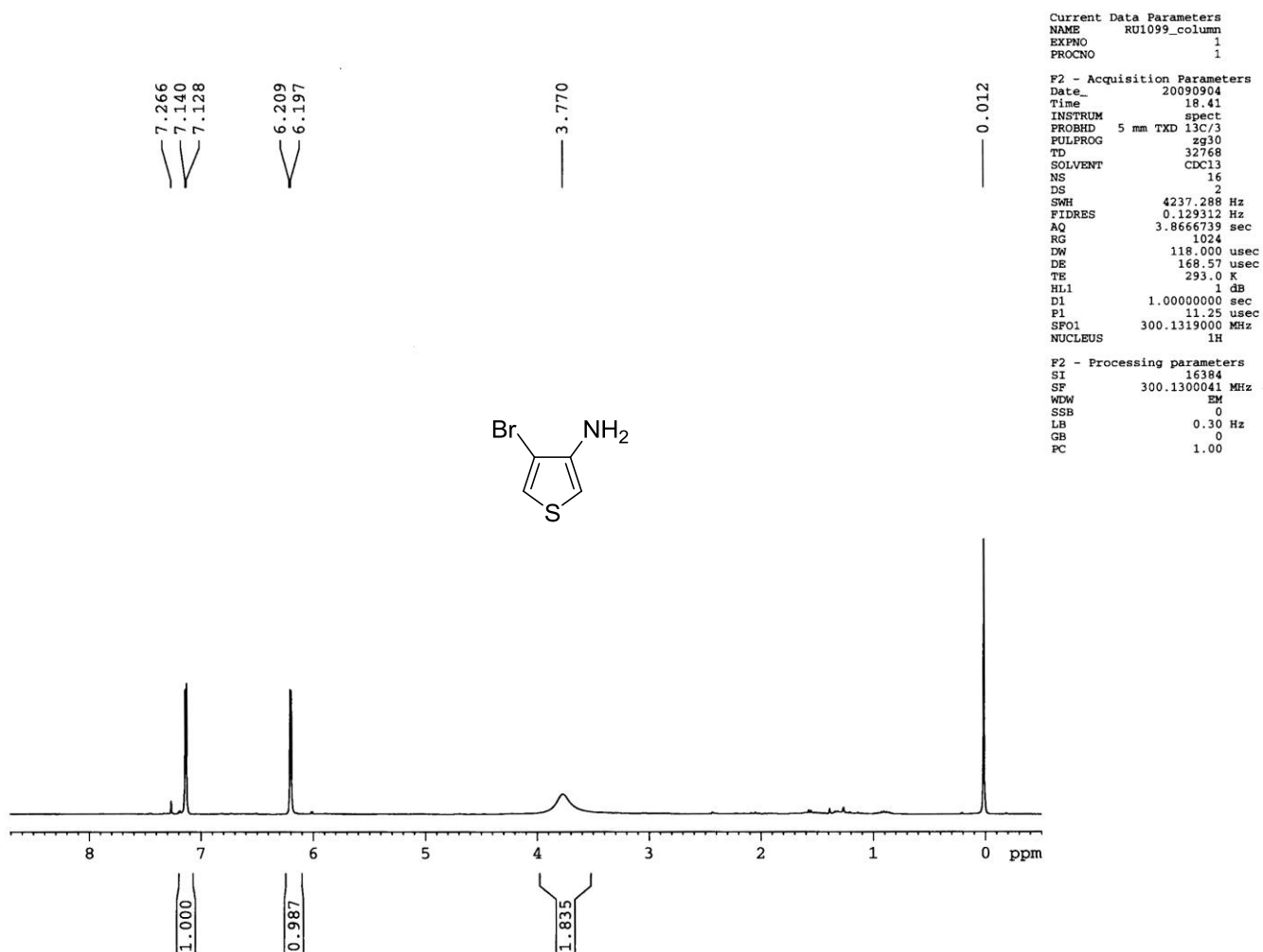
**3-bromothiophene-4-carboxylic acid (1).** To a solution of 3,4-dibromothiophene (13.0 mmol, 3.15 g) stirring in anhydrous hexanes at  $-78\text{ }^\circ\text{C}$ , 2.5M  $n$ -butyllithium in hexanes (13.0 mmol, 5.2 mL) was slowly added. The reaction mixture was stirred for 30 minutes and then 0.6 mL THF was added.  $\text{CO}_2$  (dry ice) was then bubbled into the reaction mixture for 1 hour. Afterward, 10% NaOH solution was added to the reaction mixture. The hexanes layer was extracted 3 times with 10% NaOH solution. The aqueous phases were collected and acidified with 1N HCl until a white precipitate formed. The white solid was collected by filtration with water. Yield: 32%.  $^1\text{H}$  NMR (DMSO- $d_6$ , 300 MHz,  $\delta$ ): 8.36 (d,  $J = 3.6$  Hz, 1H), 7.76 (d,  $J = 3.6$  Hz, 1H).



**3-amino-4-bromothiophene (2).** To a solution of 3,4-dibromothiophene (2.06 mmol, 0.498g) in anhydrous diethyl ether, at  $-78\text{ }^\circ\text{C}$ , 2.5M  $n$ -butyllithium in hexanes (2.22 mmol, 0.89 mL) was slowly added. The reaction mixture was stirred for 30 minutes and then  $p$ -toluenesulfonyl azide (2.22 mmol, 0.438 g) was added. Stirring at  $-78\text{ }^\circ\text{C}$  continued for 3 hours before 1M trimethylphosphine in toluene was added. The reaction was allowed to warm to room temperature and stirred overnight. Afterward, the reaction mixture was extracted with saturated sodium bicarbonate and ethyl acetate. The organic layers were combined and dried over  $\text{MgSO}_4$ . The compound was then purified by column chromatography by eluting with 90/5/5 hexanes/ethyl acetate/triethylamine mixture. Yield: 54% (over two steps).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz,  $\delta$ ): 7.13 (d,  $J = 3.6$  Hz, 1H), 6.20 (d,  $J = 3.6$  Hz, 1H), 3.77 (br, 2H).

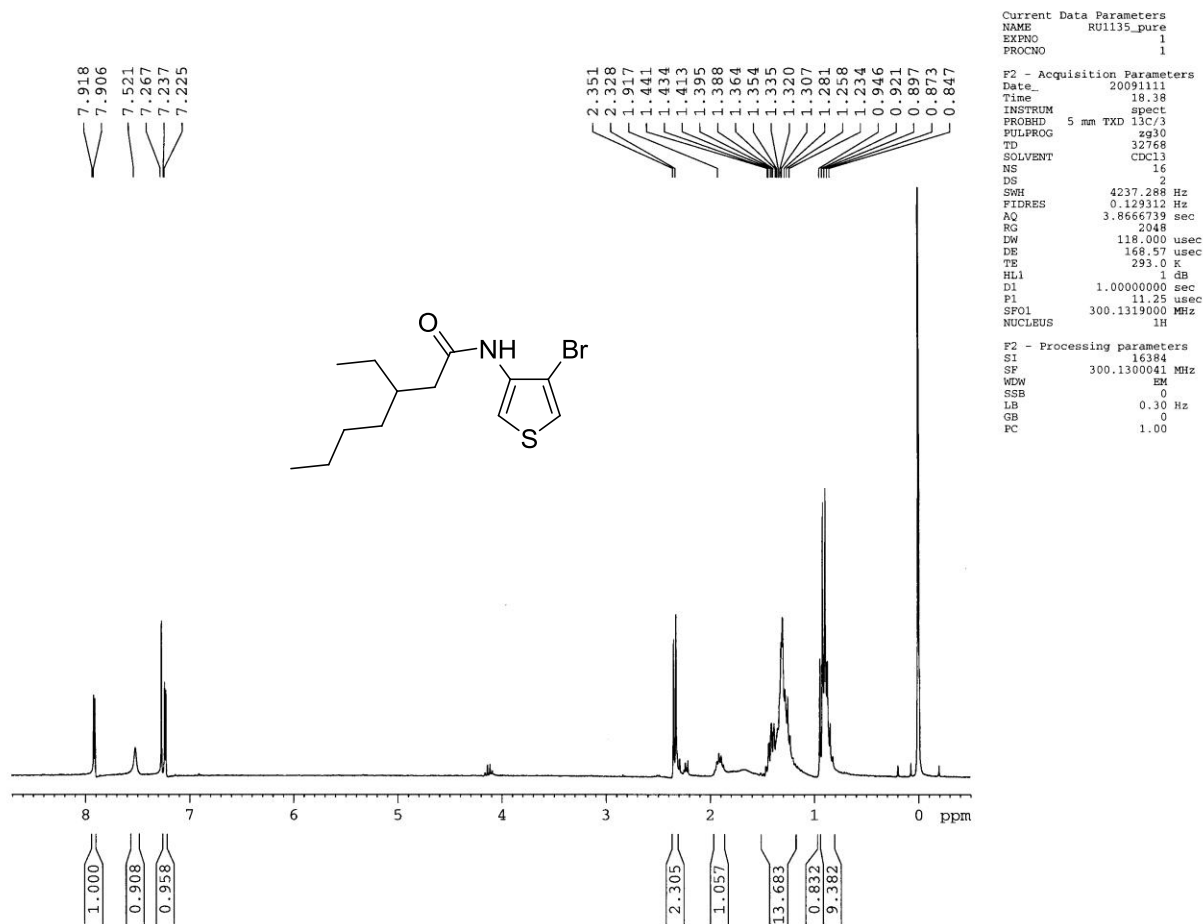


**Figure S3.**  $^1\text{H}$  NMR spectrum of 3-bromothiophene-4-carboxylic acid (compound 1).

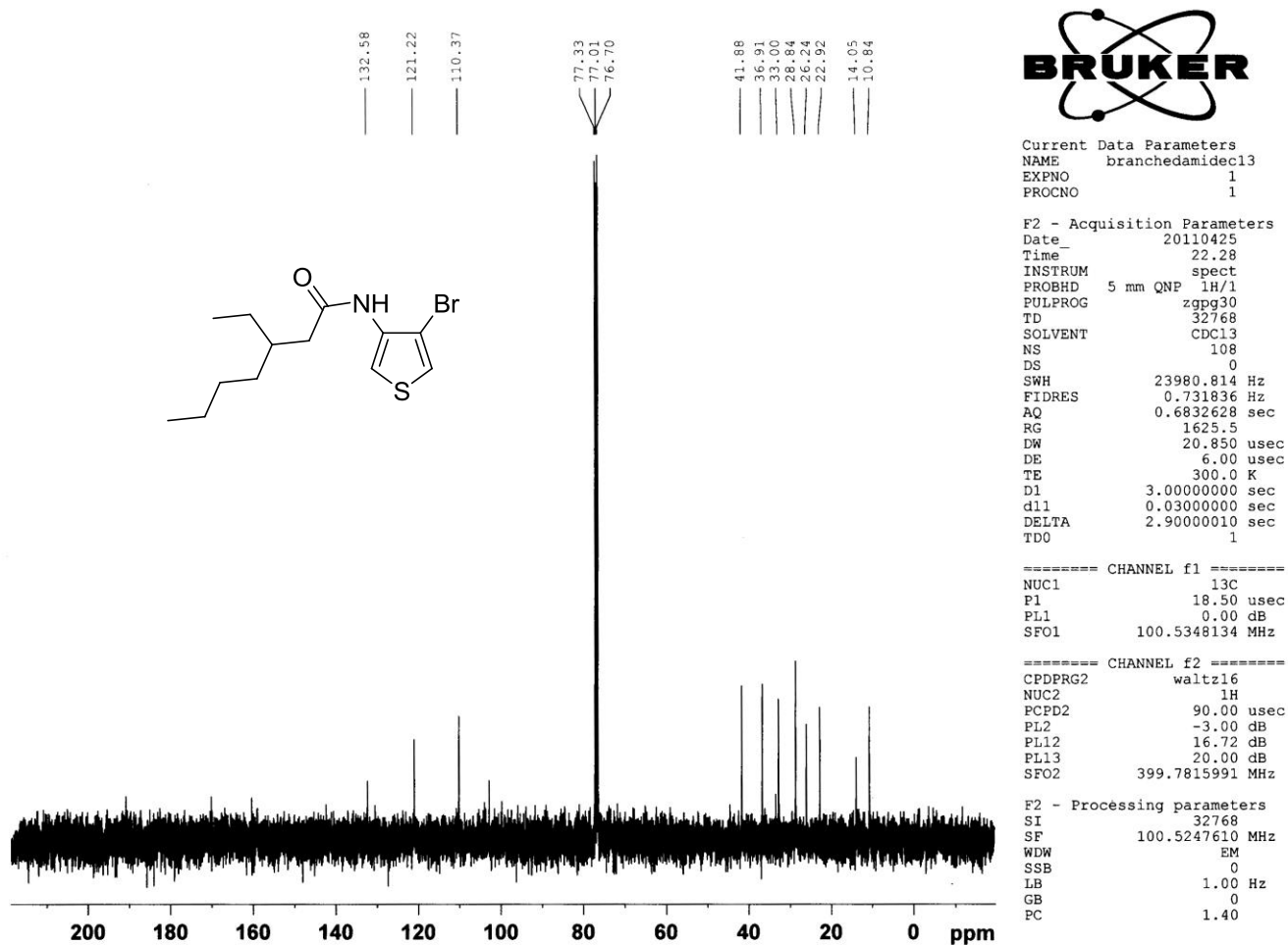


**Figure S4.**  $^1\text{H}$  NMR spectrum of 3-amino-4-bromothiophene (compound 2).

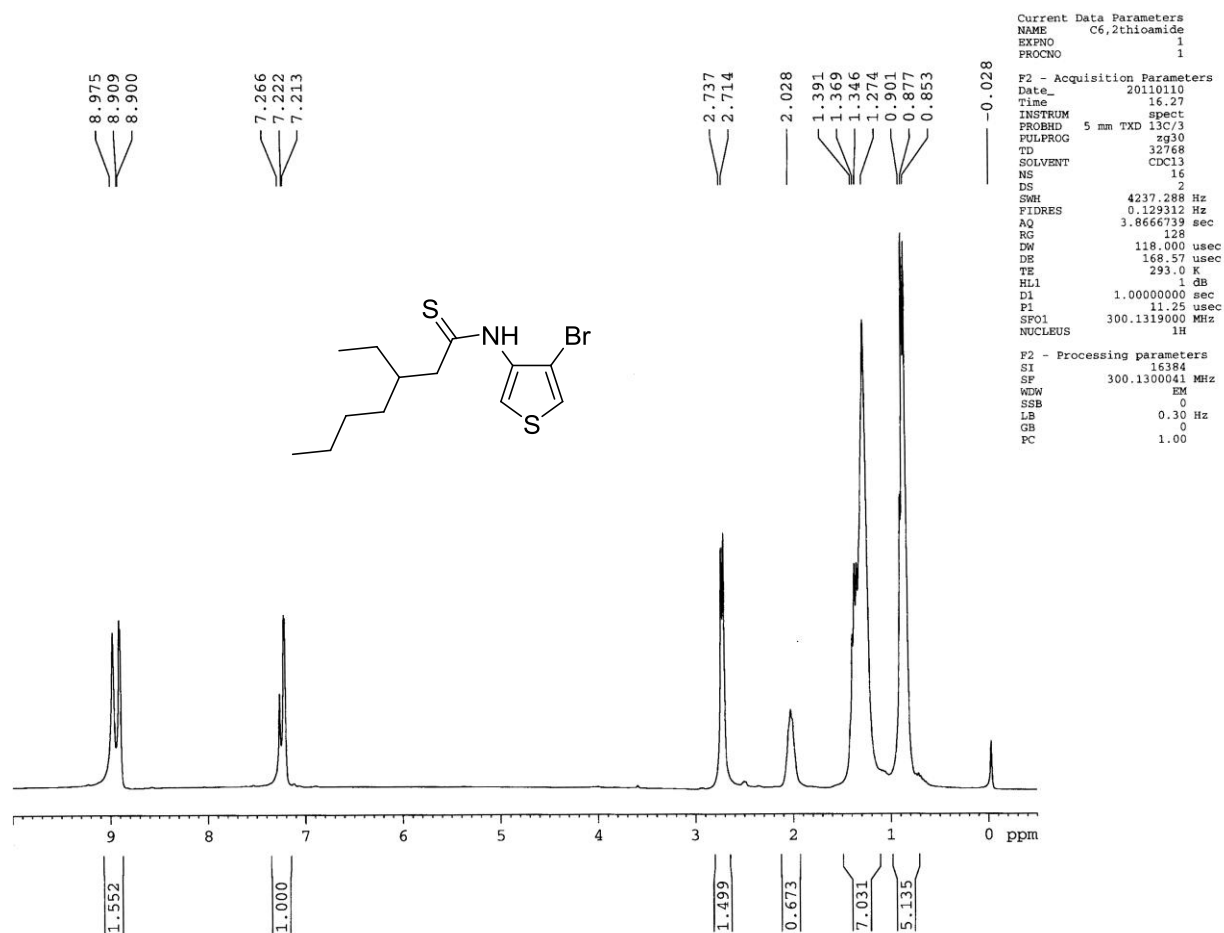




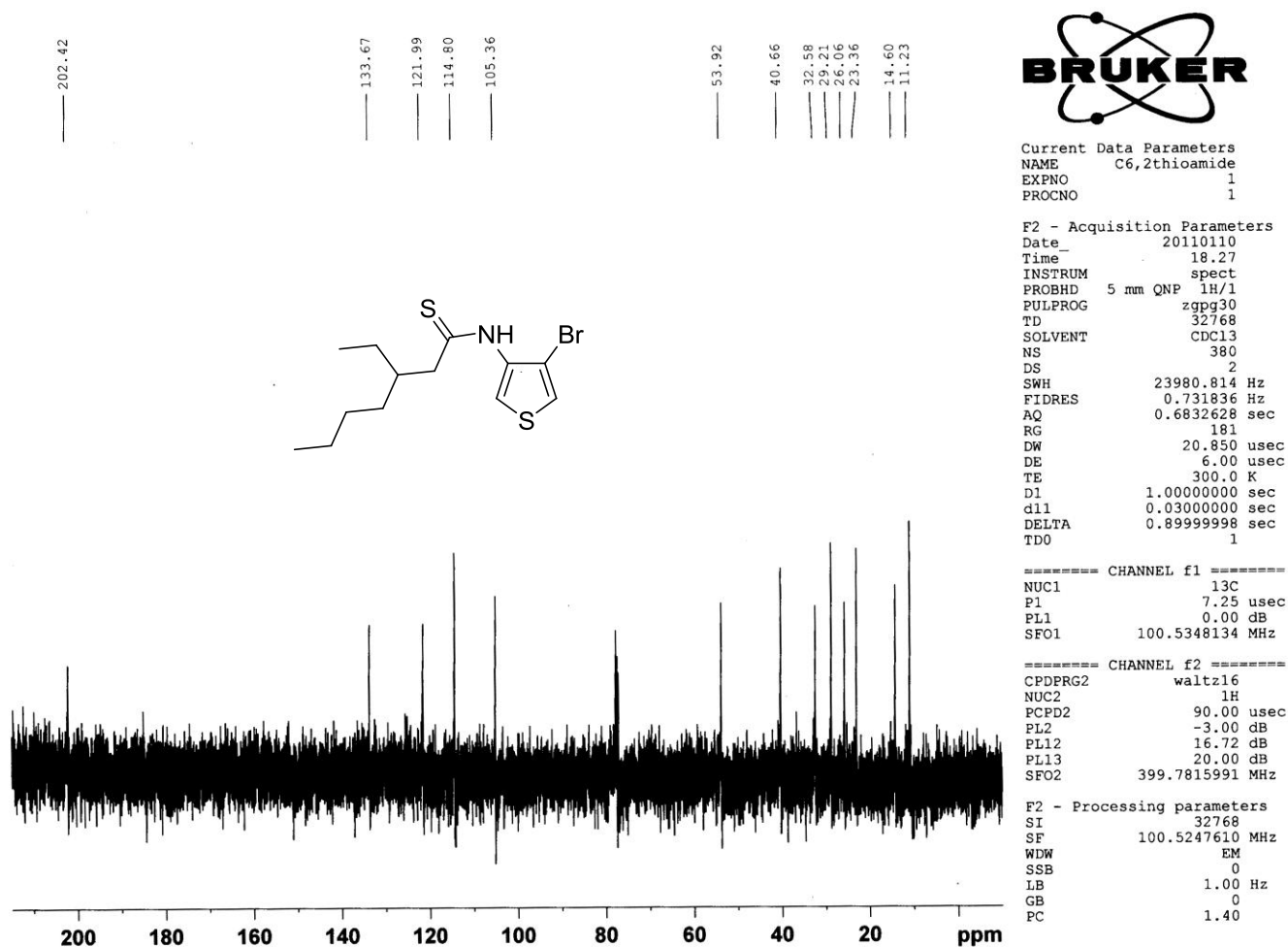
**Figure S5.** <sup>1</sup>H NMR spectrum of *N*-(4-bromothiophenyl)-3-ethylheptanamide (compound 3).



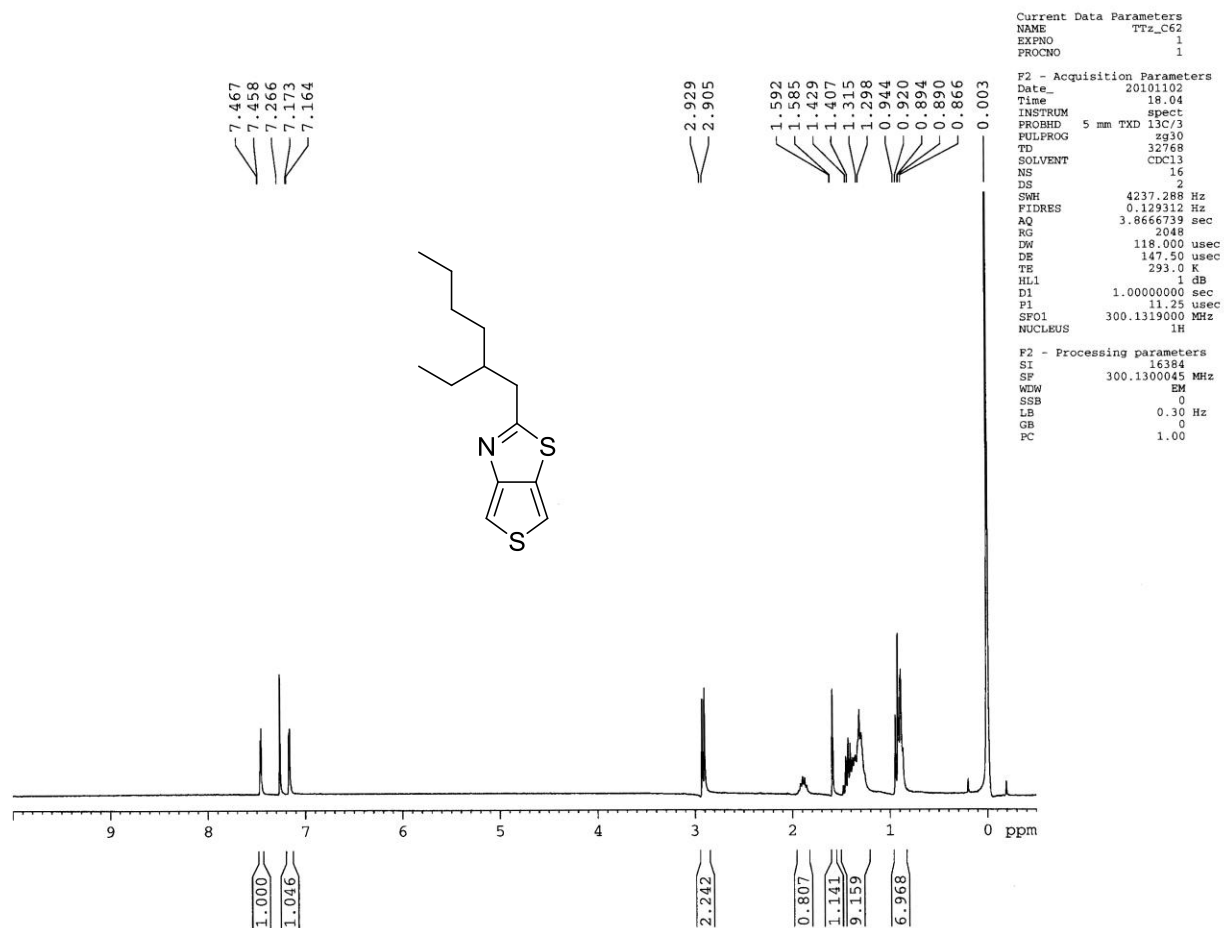
**Figure S6.** <sup>13</sup>C NMR spectrum of *N*-(4-bromothiophenyl)-3-ethylheptanamide (compound 3).



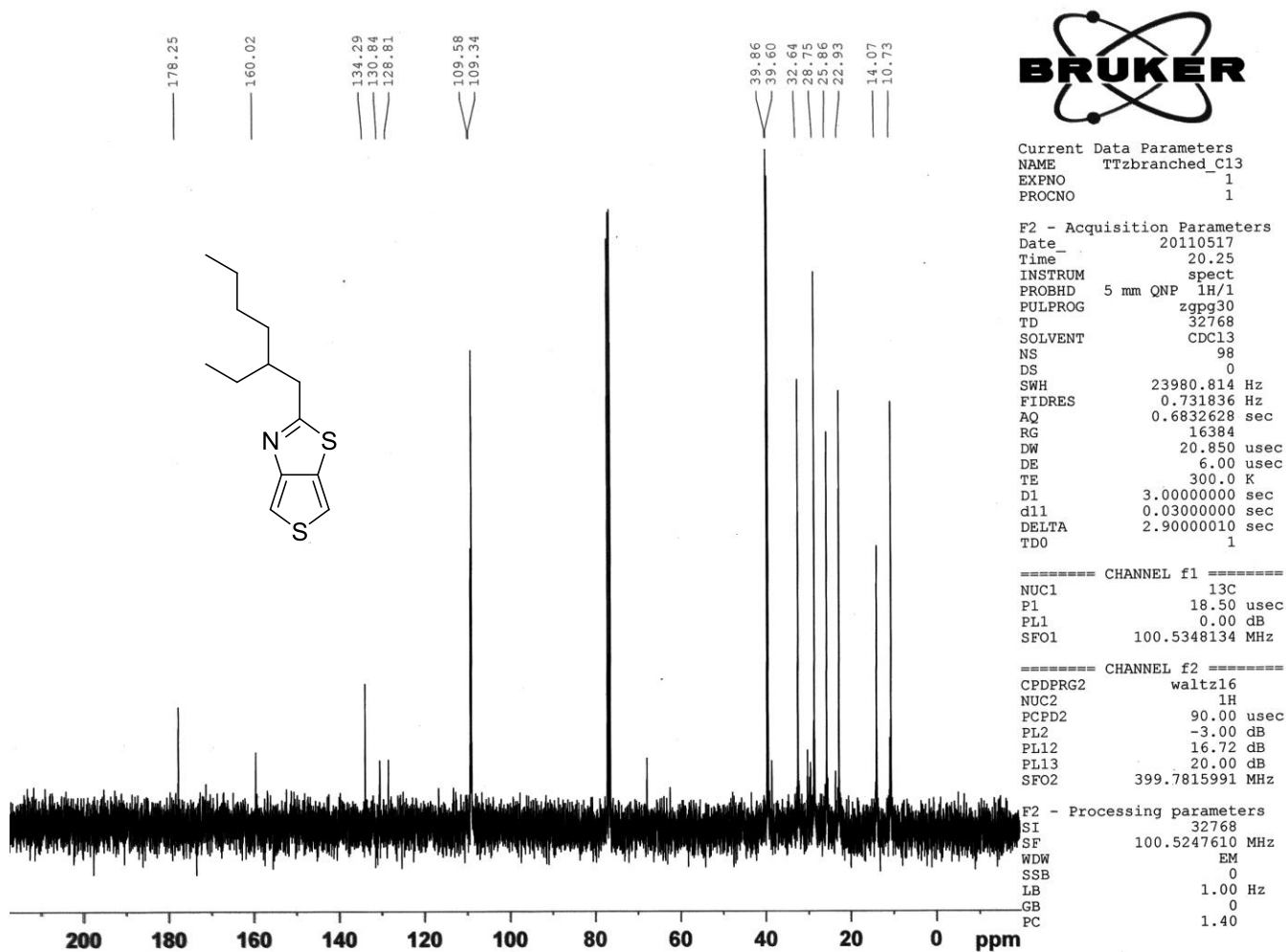
**Figure S7.**  $^1\text{H}$  NMR spectrum of *N*-(4-bromothiophenyl)-3-ethylheptanethioamide (compound 4).



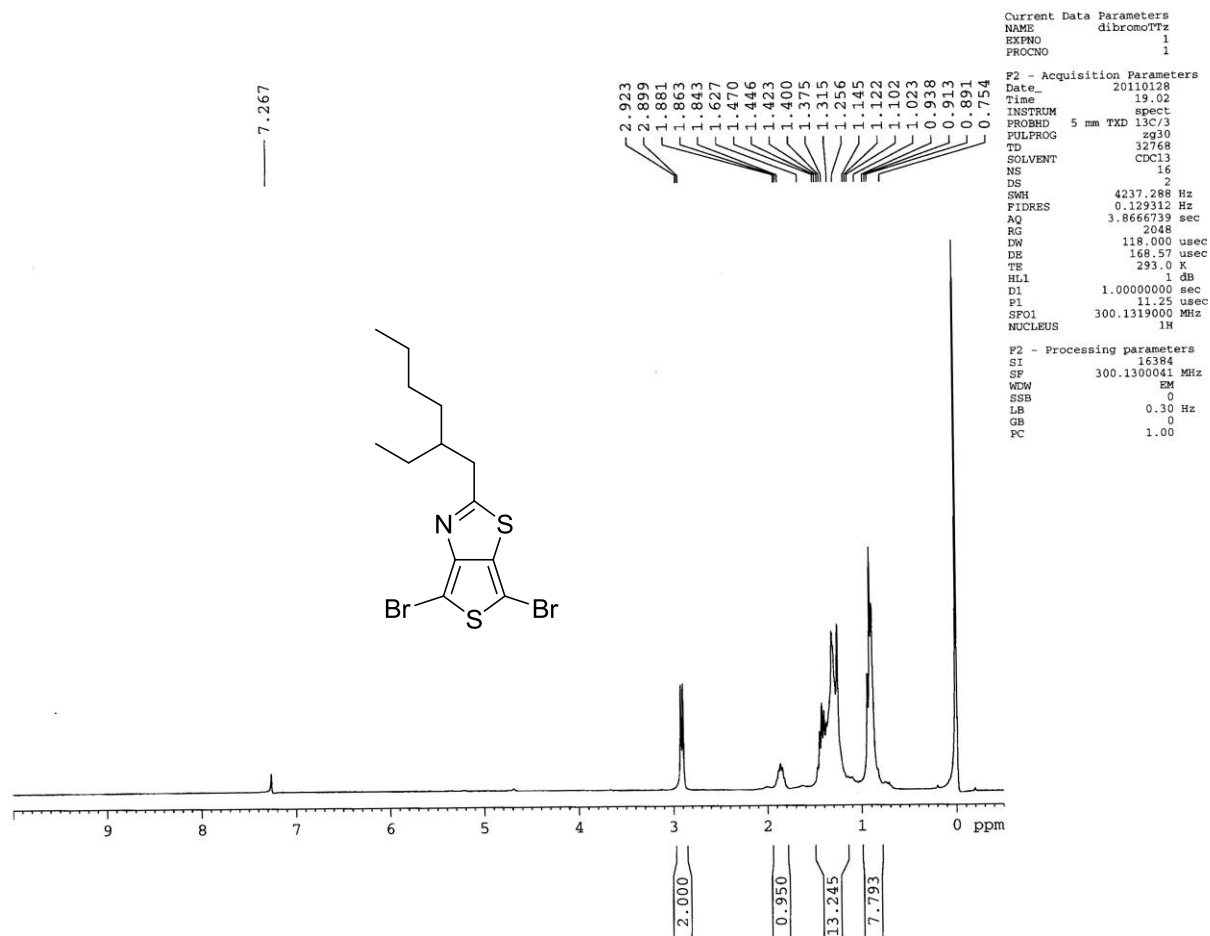
**Figure S8.**  $^{13}\text{C}$  NMR spectrum of *N*-(4-bromothiophenyl)-3-ethylheptanethioamide (compound 4).



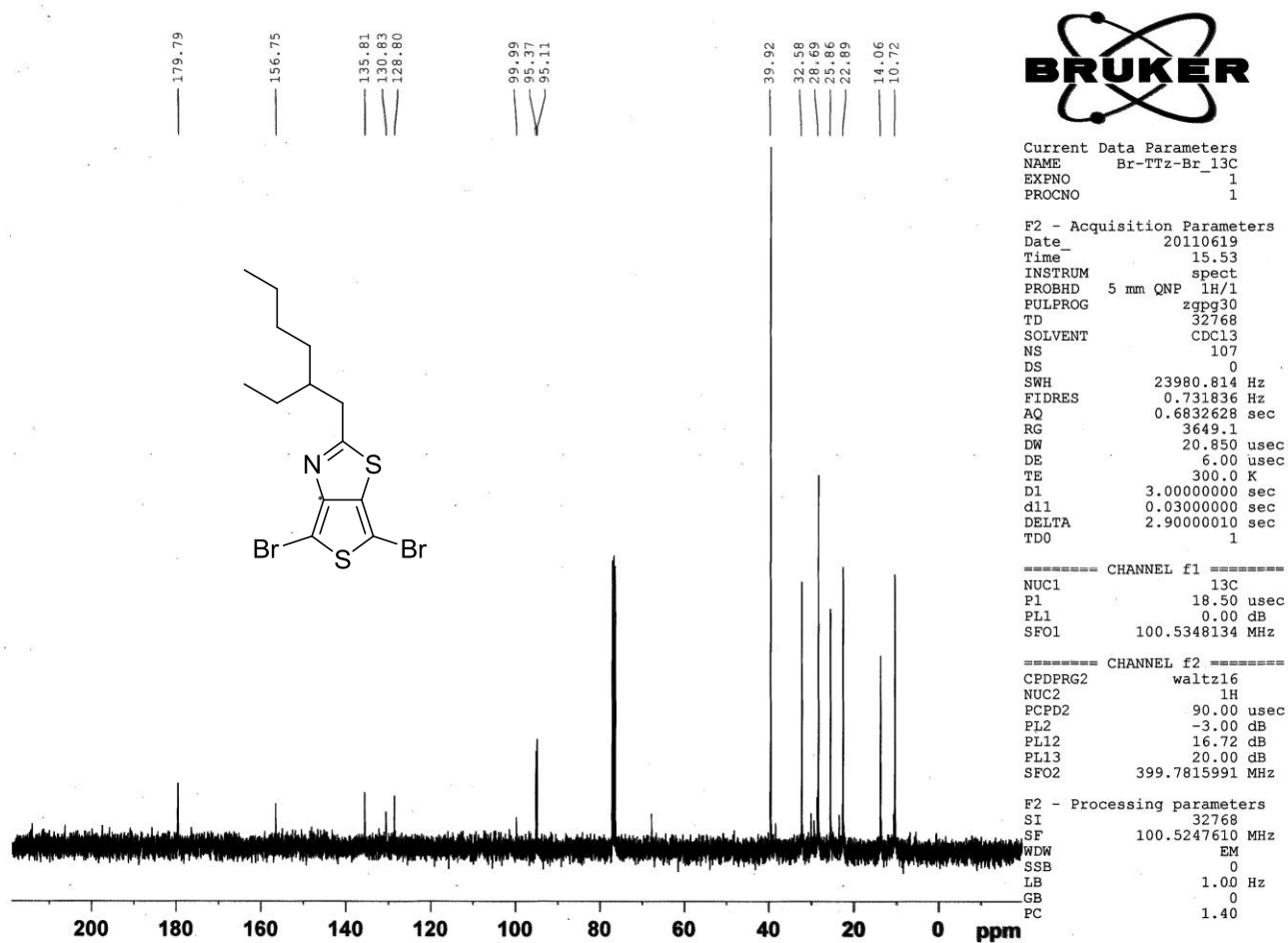
**Figure S9.**  $^1\text{H}$  NMR spectrum of 2-(2-ethylhexyl)thieno[3,4-*d*]thiazole (compound TTz).



**Figure S10.**  $^{13}\text{C}$  NMR spectrum of 2-(2-ethylhexyl)thieno[3,4-*d*]thiazole (compound TTz).



**Figure S11.** <sup>1</sup>H NMR spectrum of 4,6-dibromo-2-(2-ethylhexyl)thieno[3,4-*d*]thiazole (compound 5).



**Figure S12.** <sup>13</sup>C NMR spectrum of 4,6-dibromo-2-(2-ethylhexyl)thieno[3,4-*d*]thiazole (compound 5).



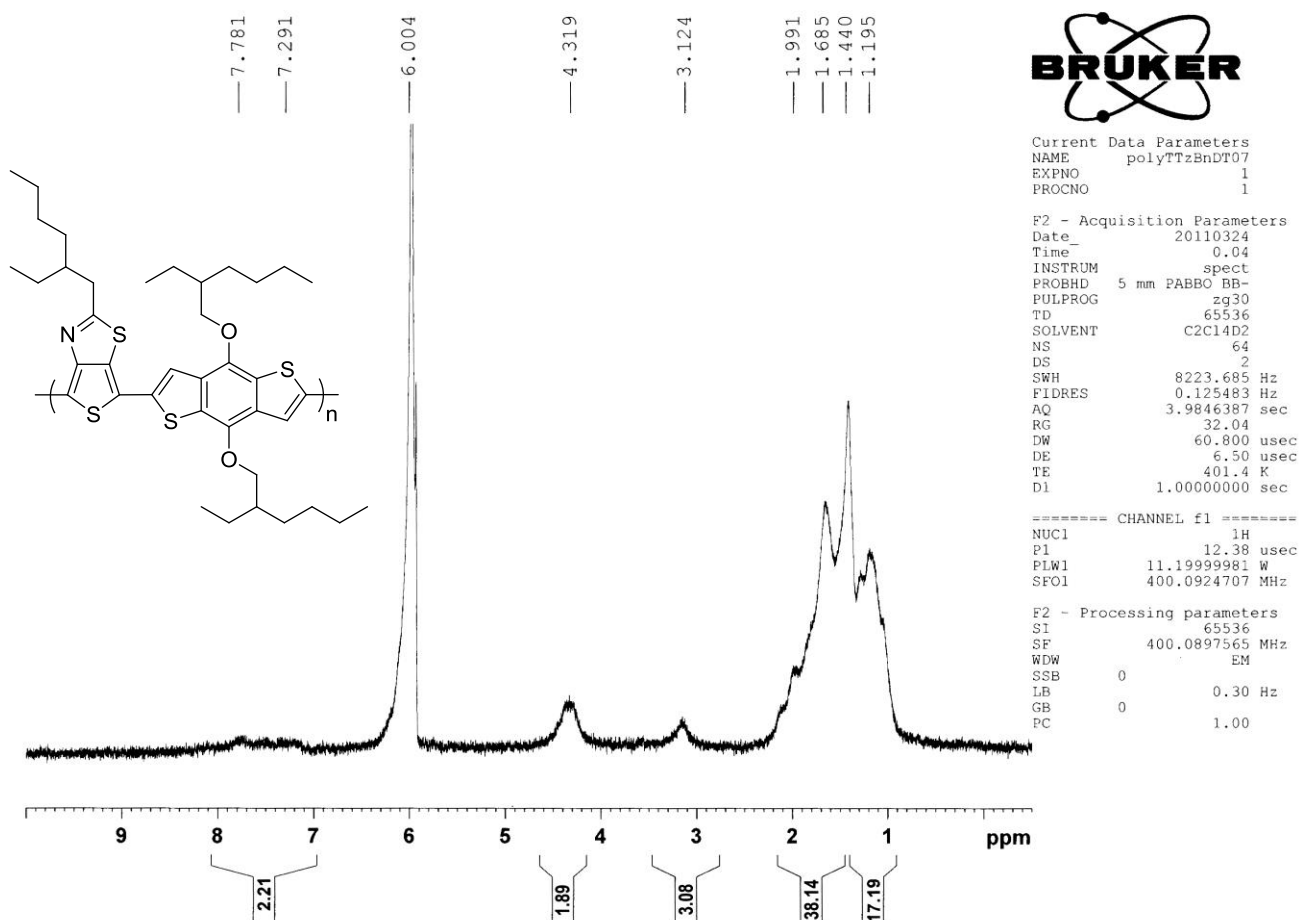


Figure S13.  $^1\text{H}$  NMR spectrum of PBnDT-TTz.

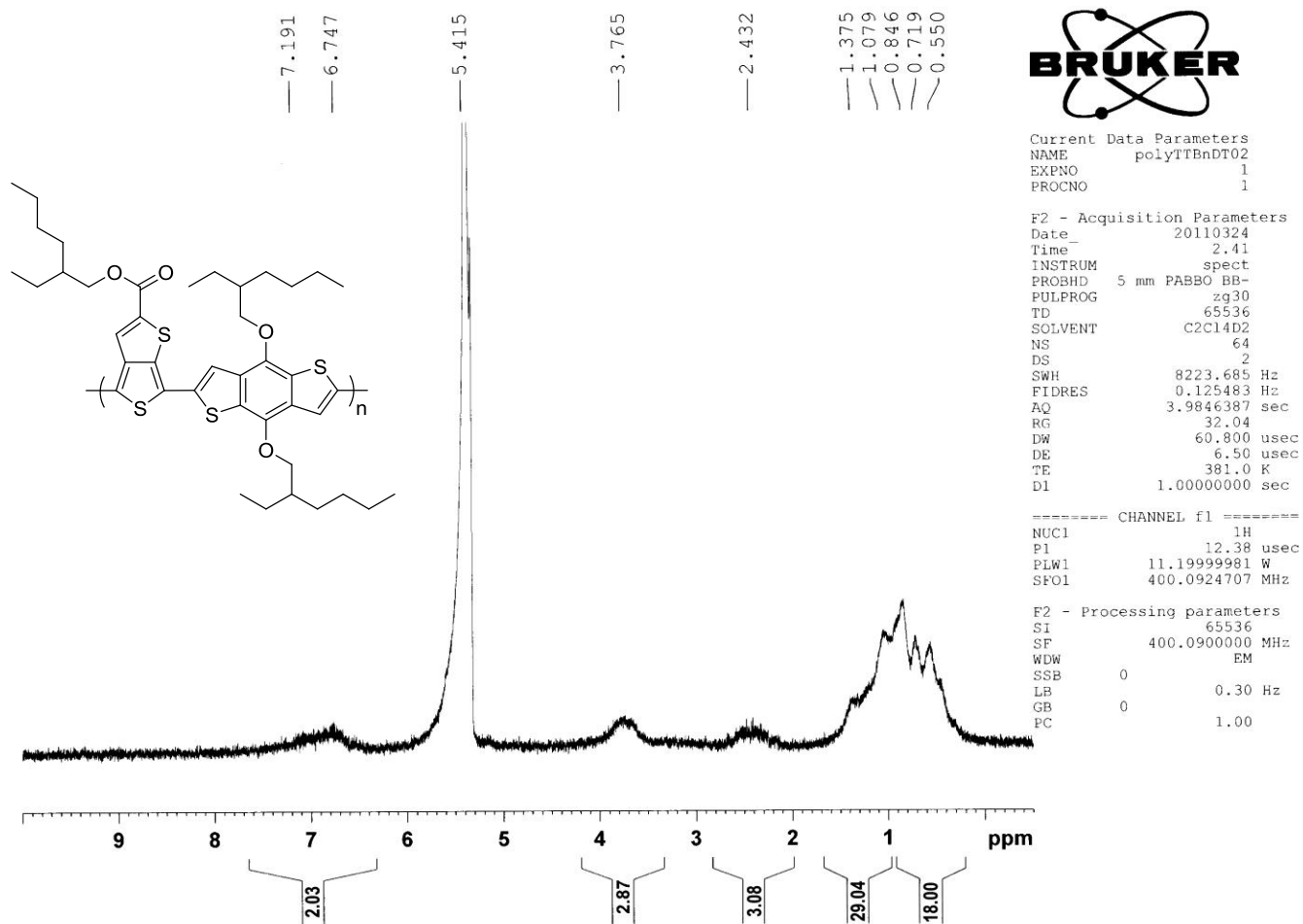


Figure S14.  $^1\text{H}$  NMR spectrum of PBnDT-TT.