

## Support Information

# Synthetic Controlling the Optoelectronic Properties of Dithieno[2,3-*d*:2',3'-*d'*]benzo[1,2-*b*:4,5-*b'*]dithiophene-*alt*- diketopyrrolopyrrole Conjugated Polymers for Efficient Solar Cells

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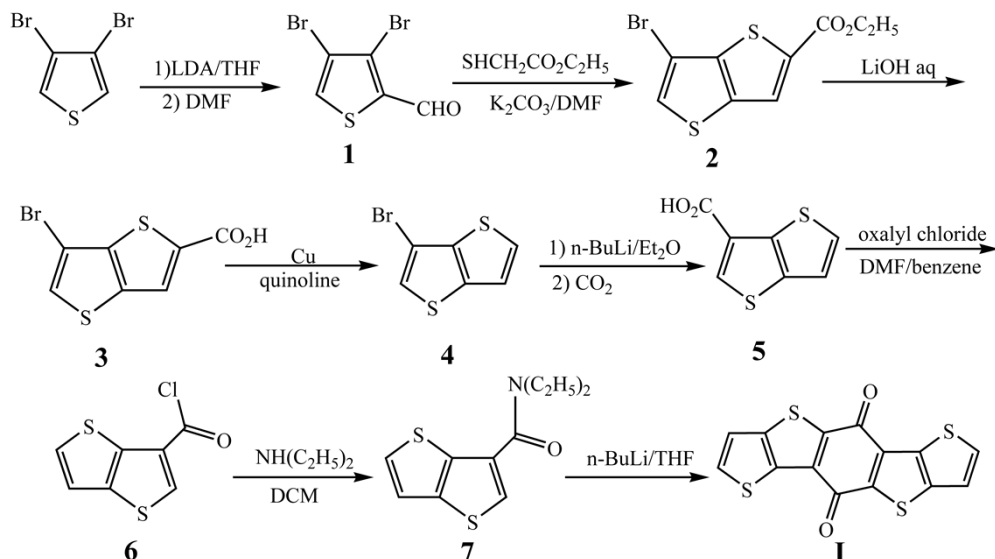
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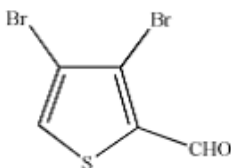
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|--|----|
| 1. Dithieno[2,3- <i>d</i> :2',3'- <i>d'</i> ]benzo[1,2- <i>b</i> :4,5- <i>b'</i> ]dithiophene-5,10-dione ..... | 2  |
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# 1. Dithieno[2,3-*d*:2',3'-*d'*]benzo[1,2-*b*:4,5-*b'*]dithiophene-5,10-dione



Scheme S1. Synthetic route of dithieno[2,3-*d*:2',3'-*d'*]benzo[1,2-*b*:4,5-*b'*]dithiophene-5,10-dione

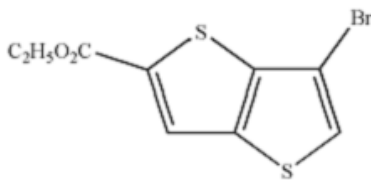
## 3,4-Dibromothiophene-2-carbaldehyde (**1**)<sup>[1]</sup>



3,4-Dibromothiophene (60 g, 248 mmol) was added dropwise to a stirred solution of lithium diisopropylamide (LDA), prepared by addition of  $n\text{-BuLi}$  (2.5 M in hexane; 109 mL, 273.0 mmol, 1.1 eq.) to diisopropylamine (38.87 mL, 27.60 g, 273.0 mmol) in anhydrous THF (500 mL) at 0 °C. The resulting mixture was stirred for a further 1 h at this temperature prior to addition of dry *N,N*-dimethylformamide (DMF) (20.97 mL, 19.93 g, 273.0 mmol, 1.1 eq.). The mixture was stirred further until TLC analysis indicated that all the starting material had been consumed when an excess of 20%

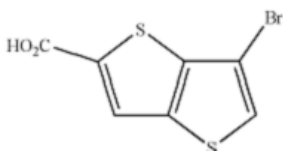
aqueous ammonium chloride was added to it. Extraction of the mixture with ethyl acetate (EA) for several times, and the combined organic phase was washed with brine and distilled water (3×200 mL), dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, concentrated and purified over a silica gel column using petroleum ether (PE) and EA (15:1, v/v) as an eluent, affording **1** as a pale-yellow powder (40.8 g, 61%). M.p. 110–111 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ (ppm): 9.95 (d, 1H), 7.76 (d, 1H).

### Ethyl 6-bromothieno[3,2-*b*]thiophene-2-carboxylate (**2**)



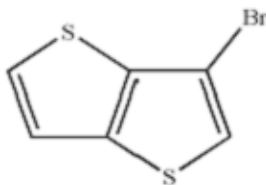
3,4-Dibromothiophene-2-carbaldehyde **1** (40.0 g, 148.1 mmol) was added to a stirred mixture of ethyl 2-sulfanylacetate (18.66 g, 155.3 mmol, 1.05 eq.), potassium carbonate (30.66 g, 222.1 mmol, 1.5eq.) and DMF (400 mL) at ambient temperature and the resulting mixture was stirred about 72 h. The reacting solvent DMF was removed under reduced pressure. Then the residual was poured into water (500 mL) and extracted with EA. The combined organic phase was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and the organic phase was concentrated and purified over a silica gel column using PE-EA (10:1, v/v) as an eluent, affording **2** as white powder (40.95 g, 95%). M.p. 80–81 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ (ppm): 8.01 (d, 1H), 7.46 (d, 1H), 4.38 (q, 2H), 1.40 (t, 3H).

### 6-Bromothieno[3,2-*b*]thiophene-2-carboxylic acid (**3**)



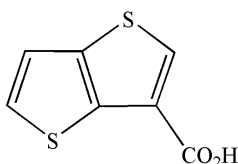
A stirred mixture of the ester **2** (40.0 g, 137.4 mmol), aqueous lithium hydroxide (1.0 mol L<sup>-1</sup>; 300 mL) and THF (300 mL) was heated under reflux for about 3 h (until TLC analysis indicated absence of **2** when the solvent was distilled off under reduced pressure and conc. hydrochloric acid (100 mL) was added to the residue. The precipitate was filtered off, washed with water and dried in a vacuum desiccator to give the acid **3** as grey solid (32.8 g, 91%). M.p. 261–263 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ (ppm): 9.95 (d, 1H), 7.76 (d, 1H).

### **3-Bromothieno[3,2-b]thiophene (4)**



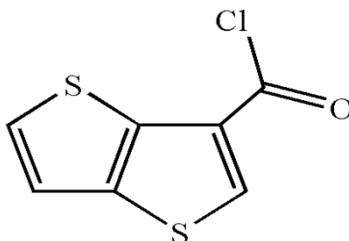
A stirred solution of the acid **3** (30.0 g, 114.0 mmol), copper powder (4.0 g) and quinoline (160 mL) was heated at 260 °C in a sand bath. When TLC analysis confirmed the absence of starting material and the reaction mixture was cooled to ambient temperature. PE (200 mL) was added to the mixture and most of the quinoline was removed by repeated washing of the resulting solution with hydrochloric acid (1.0 mol L<sup>-1</sup>), after which the residue was chromatographed on silica using the PE as an eluent, affording the compound **4** as colorless oil liquid (12.7 g, 51%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ (ppm): 7.44 (dd, 1H), 7.30 (d, 1H), 7.29 (d, 1H).

### **Thieno[3,2-b]thiophene-3-carboxylic acid (5).**



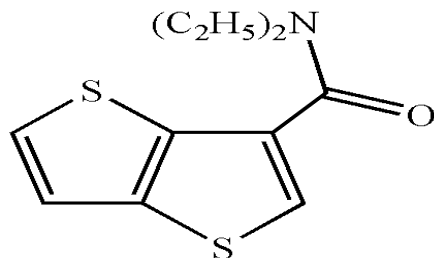
To a solution of 3-bromothieno[3,2-*b*]thiophene (17.0 g, 77.6 mmol) in anhydrous diethyl ether (300 mL) at  $-78\text{ }^{\circ}\text{C}$ , *n*-BuLi (2.5 M in hexane, 46.6 mL) was added dropwise, and the mixture was stirred at the same temperature for 3 h under argon atmosphere. Excess carbon dioxide ( $\text{CO}_2$ ) was slowly bubbled into the reaction system until the 3-bromothieno[3,2-*b*]thiophene was reacted completely (monitored by TLC). After the reaction solution was warmed to ambient temperature, 100 mL distilled water was added. Then the solution was concentrated to 100 mL, and the concentrated hydrochloric acid was added and the pH of mixture solution was adjusted to 3. The precipitate was filtered off, washed successively with water and petroleum ether to give the acid **5** as a yellow solid (13.1 g, 92%). M.p.  $214\text{--}216\text{ }^{\circ}\text{C}$ .  $^1\text{H NMR}$  ( $\text{CD}_3\text{COCD}_3$ , 400 MHz)  $\delta$  (ppm): 8.38 (s, 1H); 7.68 (dd, 1H); 7.48 (d, 1H).

**Thieno[3,2-*b*]thiophene-3-carbonyl chloride. (6)**



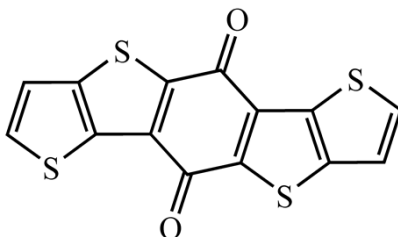
Thieno[3,2-*b*]thiophene-3-carboxylic acid (32.0 g, 173.7 mmol) was dissolved into the solution of benzene (300 mL) and DMF (1 mL). The mixture was cooled down to  $0\text{ }^{\circ}\text{C}$  with an ice-water bath, and then oxalyl chloride (66.22 g, 521.7 mmol, 3 eq.) was added dropwise through a dropping funnel. After the ice-bath was removed and the mixture was heated to reflux for about 3 h until absence of the solid acid, a clear brown solution was obtained. The solvent and oxalyl chloride were removed by rotary evaporation under reduced pressure. 35.4 g brown oil was obtained. It was dissolved into 80 mL of dried dichloromethane (DCM) and used for the next step directly.

***N,N*-Diethylthieno[3,2-*b*]thiophene-3-carboxamide. (7)**



In a 500 mL flask cooled in an ice-water bath, 62.5 mL of diethylamine (38.16 g, 521.7 mmol) was dissolved into 150 mL of dried DCM. The solution of thieno[3,2-*b*]thiophene-3-carbonyl chloride in DCM ( 35.4 g in 80 mL DCM) was slowly added into the flask. After the reaction mixture was stirred at same temperature for 0.5 h, the reactants were stirred at ambient temperature overnight. The solvent DCM and un-reacted diethylamine were removed under reduced pressure. Then the residual was poured into 300 mL distilled water and extracted with ethyl acetate (3×100 mL). The combined organic layer was washed with distilled water (3×50 mL), and dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removing of the solvent, the crude product was purified over a silica gel column using PE and EA solution (V/V; 4:1) as eluent, and compound **7** (32.55 g, yield 80%) was obtained as pale solid. M.p. 47–48 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ (ppm): 7.53 (s, 1H), 7.46 (d, 1H), 7.24 (d, 1H), 3.57 (q, 4H), 1.27 (t, 6H).

**Dithieno[2,3-*d*:2',3'-*d'*]benzo[1,2-*b*:4,5-*b'*]dithiophene-5,10-dione. (I)**



*N,N*-Diethylthieno[3,2-*b*]thiophene-3-carboxamide (17.0 g, 71.0 mmol) was put into a well-dried flask with 150 mL of anhydrous THF under an argon atmosphere at 0 °C, 35.5 mL of *n*-BuLi (2.5 mol/L, 88.7 mmol) was added dropwise into the flask within 15 min. The reactants were stirred at ambient temperature for 1 h, and then quenched by distilled water. The brown precipitate was collected and washed with 200 mL of water, 50 mL of methanol, and 50 mL of hexane successively. After dried in vacuum desiccator, the dione **I** was obtained as a brown powder, and used for the next step without purification (10.5 g,

yield 89%). M.p. >280 °C.

## 2. X-ray crystallographic analysis

Single crystals of 5,10-bis(butyloxy)dithieno[2,3-*d*:2',3'-*d'*]benzo[1,2-*b*:4,5-*b'*]dithiophene (**DTBDT-C4**), 5,10-bis(octyloxy)dithieno[2,3-*d*:2',3'-*d'*] benzo[1,2-*b*:4,5-*b'*]dithiophene (**DTBDT-C8**), 5,10-bis(dodecyloxy)dithieno[2,3-*d*:2',3'-*d'*]benzo[1,2-*b*: 4,5-*b'*]dithiophene (**DTBDT-C12**) and 5,10-bis(trimethylsilylacetyl)dithieno[2,3-*d*: 2',3'-*d'*]benzo[1,2-*b*:4,5-*b'*]dithiophene (**DTBDT-TMS**) suitable for X-ray structural analysis were obtained by recrystallization from the mixture of hexane and chloroform. Single-crystal X-ray diffraction data were collected at 296 K on a BRUKER SMART APEX II CCD diffractometer with graphite monochromated Mo-K $\alpha$  radiation ( $\lambda=0.71073$  Å). The LP factor multi-scan corrections were applied using the SADABS program.<sup>[2]</sup> The structure was solved by direct methods and refined by the full-matrix least-squares method on  $F^2$  using the SHELXTL crystallographic software package.<sup>[3]</sup> All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms were calculated geometrically (C–H = 0.93, 0.96 and 0.97 Å) and refined as a riding model, with  $U_{\text{iso}}(\text{H}) = 1.20 U_{\text{eq}}(\text{C})$ . The crystal data and experimental parameters relevant to the structure determination are listed in **Table S1**.

The molecular structures and packing interaction diagrams of **DTBDT-C4**, **DTBDT-C8**, **DTBDT-C12** and **DTBDT-TMS**, are shown in Fig. S1–S4, respectively. It was noted that all oxygen atoms almost placed in the plane (deviation 0.077 Å, 0.029 Å and 0.018 Å for **DTBDT-C4**, **DTBDT-C8** and **DTBDT-C12**, respectively) defined by dithieno[2,3-*d*:2',3'-*d'*]benzo[1,2-*b*:4,5-*b'*]dithiophene (**DTBDT**) core ring. However, for carbon atoms, there exist different deviations. Deviations of atom C8, C9, C10 and C11

from DTBBDT ring plane were 1.181, 1.005, 0.104 and 0.01 Å in **DTBBDT-C4** molecule, respectively. Deviations of atom C8, C9, C10 and C11 from DTBBDT ring plane were 1.181, 1.005, 0.104 and 0.01 Å in **DTBBDT-C4** molecule, respectively. Deviations of atom C8, C9, C10, C11, C12, C13, C14 and C15 from DTBBDT ring plane were 1.282, 1.213, 1.099, 1.245, 1.249, 1.408, 1.412 and 1.647 Å in **DTBBDT-C8** molecule, respectively. Deviations of atom C8, C9, C10, C11, C12, C13, C14, C15, C16, C17, C18 and C19 from DTBBDT ring plane were 0.069, 0.031, 0.019, 0.040, 0.067, 0.142, 0.162, 0.253, 0.269, 0.350, 0.339 and 0.454 Å in **DTBBDT-C12** molecule, respectively. For compound **DTBBDT-TMS** acetylene bond atoms C8, C9 and silicon atom Si1 placed in the plane defined by DTBBDT core ring.



**Table S1** Details of the crystal structures analyses for **DTBDT**-based derivatives

| Compound No.                               | <b>DTBDT-C4</b>   | <b>DTBDT-C8</b>  | <b>DTBDT-C12</b>   | <b>DTBDT-TMS</b>   |
|--|---|--|--|--|
| CCDC No.                                   | 906863  | 906864   | 906862   | 906865   |
| Empirical formula                          | C <sub>22</sub> H <sub>20</sub> O <sub>2</sub> S <sub>4</sub>   | C <sub>30</sub> H <sub>38</sub> O <sub>2</sub> S <sub>4</sub>    | C <sub>38</sub> H <sub>54</sub> O <sub>2</sub> S <sub>4</sub>  | C <sub>24</sub> H <sub>22</sub> S <sub>4</sub> Si <sub>2</sub> |
| Formula weight (g mol <sup>-1</sup> )      | 444.62  | 558.84   | 671.06   | 494.84   |
| Crystal system                             | Monoclinic  | Monoclinic   | Triclinic  | Monoclinic   |
| Space group                                | <i>P</i> 2 <sub>1</sub> / <i>n</i>                              | <i>P</i> 2 <sub>1</sub> / <i>n</i>                               | <i>P</i> $\bar{1}$   | <i>P</i> 2 <sub>1</sub> / <i>c</i>                             |
| Temperature (K)                            | 296(2)  | 296(2)   | 296(2)   | 296(2)   |
| <i>a</i> (Å)                               | 8.451(6)  | 8.568(10)  | 7.507(4)   | 6.330(4)   |
| <i>b</i> (Å)                               | 9.412(7)  | 17.79(2)   | 9.506(5)   | 21.410(14)   |
| <i>c</i> (Å)                               | 13.83(1)  | 9.479(11)  | 13.155(7)  | 9.618(7)   |
| $\alpha$ (°)                               | 90.00   | 90.00  | 81.790(6)  | 90.00  |
| $\beta$ (°)                                | 106.097(6)  | 99.479(12)   | 76.147(6)  | 103.021(7)   |
| $\gamma$ (°)                               | 90.00   | 90.00  | 89.255(6)  | 90.00  |
| <i>V</i> (Å <sup>3</sup> )                 | 1056.7(13)  | 1425(3)  | 902.0(9)   | 1270.0(15)   |
| <i>Z</i>                                   | 2   | 2  | 1  | 2  |
| $\rho_{\text{calcd}}$ (mg/m <sup>3</sup> ) | 1.397   | 1.302  | 1.235  | 1.294  |
| $\mu$ (mm <sup>-1</sup> )                  | 0.465   | 0.360  | 0.295  | 0.478  |
| $\theta$ range for data collection (°)     | 2.55 to 25.00   | 2.29 to 25.30  | 2.51 to 25.50  | 2.37 to 25.30  |
| Limiting indices                           | -10 ≤ <i>h</i> ≤ 10, -11 ≤ <i>k</i> ≤ 8,<br>-16 ≤ <i>l</i> ≤ 16 | -10 ≤ <i>h</i> ≤ 10, -21 ≤ <i>k</i> ≤ 18,<br>-10 ≤ <i>l</i> ≤ 11 | -9 ≤ <i>h</i> ≤ 9, -11 ≤ <i>k</i> ≤ 11,<br>-13 ≤ <i>l</i> ≤ 15 | -7 ≤ <i>h</i> ≤ 7, -22 ≤ <i>k</i> ≤ 25,<br>-11 ≤ <i>l</i> ≤ 11 |
| <i>F</i> (000)                             | 464   | 596  | 362  | 516  |
| Crystal size (mm <sup>3</sup> )            | 0.22×0.20×0.14  | 0.22×0.20×0.14   | 0.30×0.24×0.15   | 0.30×0.25×0.14   |

|  |                                       |                                       |                                       |                                       |
|--|---------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|
| Reflections collected/unique                         | 5929/1852                             | 6254/3208                             | 6254/3208                             | 8668/2313                             |
| $R_{\text{int}}$                                     | 0.0234                                | 0.0354                                | 0.0382                                | 0.0617                                |
| Refinement method                                    | Full-matrix least<br>squares on $F^2$ | Full-matrix least<br>squares on $F^2$ | Full-matrix least<br>squares on $F^2$ | Full-matrix least<br>squares on $F^2$ |
| Data/restraints/parameters                           | 1852/0/128                            | 2574/0/164                            | 3208/0/200                            | 2313/0/139                            |
| GOF  | 1.051                                 | 1.071                                 | 1.292                                 | 1.197                                 |
| Final R indices [ $I > 2\sigma(I)$ ]                 | $R_1=0.0475$ , $wR_2=0.1268$          | $R_1=0.0391$ , $wR_2=0.0928$          | $R_1=0.0631$ , $wR_2=0.1481$          | $R_1=0.0657$ , $wR_2=0.1178$          |
| R indices (all data)                                 | $R_1=0.0613$ , $wR_2=0.1398$          | $R_1=0.0580$ , $wR_2=0.1083$          | $R_1=0.0934$ , $wR_2=0.1592$          | $R_1=0.1166$ , $wR_2=0.1412$          |
| Max./min. $\Delta\rho$ ( $\text{e}\text{\AA}^{-3}$ ) | 0.689/-0.345                          | 0.265/-0.248                          | 0.475/-0.347                          | 0.289/-0.350                          |

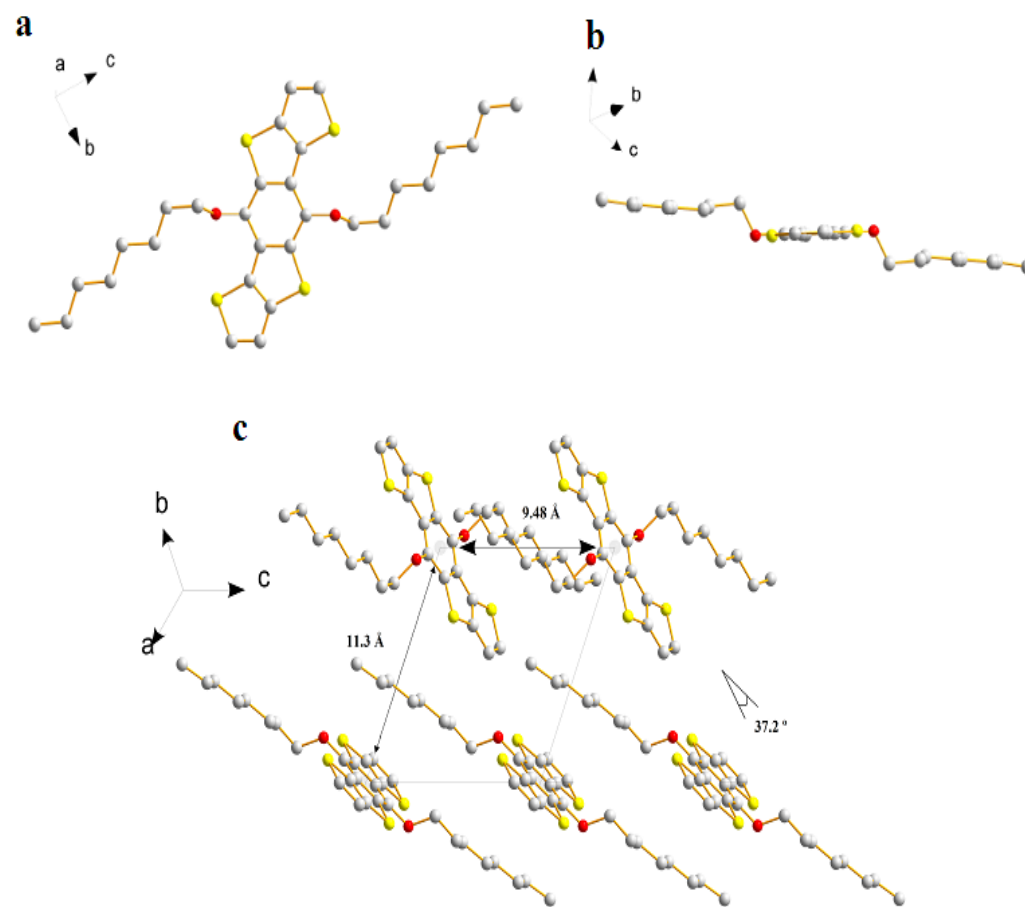


Fig. S1 Molecular structures in top view (a) and side view (b) of **DTBDT-C8**. (c) Packing diagram of **DTBDT-C8**, showing the distances 9.48 Å and 11.3 Å between the centroids of adjacent molecules and the dihedral angle of 37.2°.

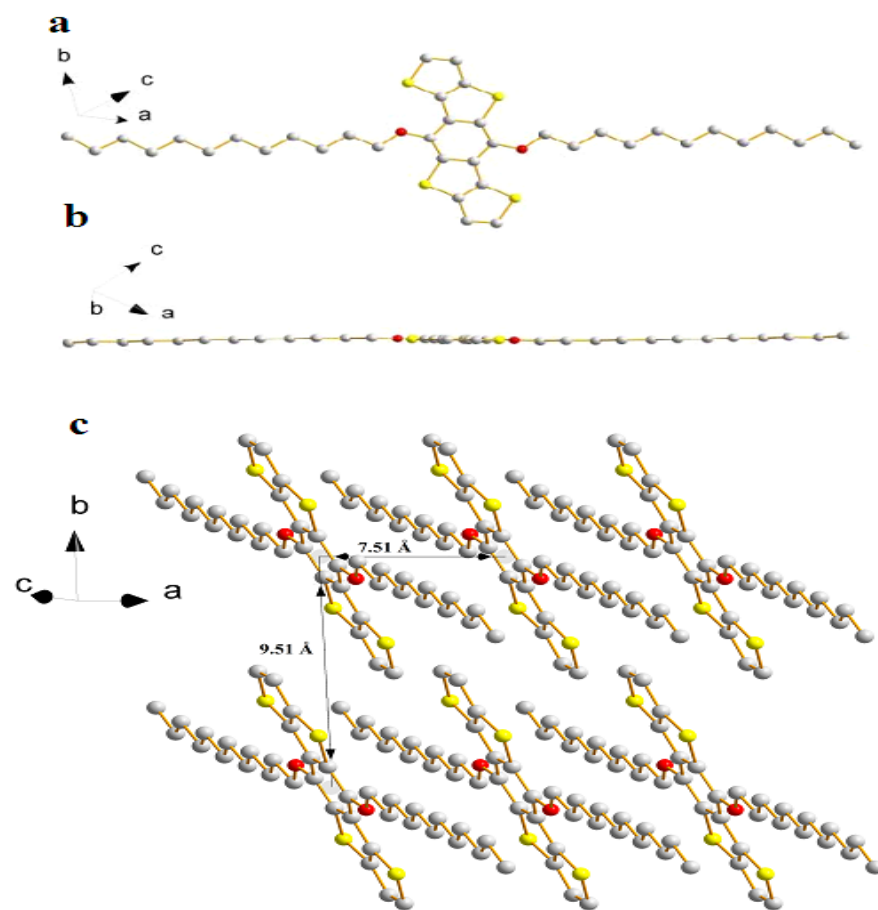


Fig. S2 Molecular structures in top view (a) and side view (b) of DTBBDT-C12. (c) Packing diagram of DTBBDT-C12, showing the distances 7.51 Å and 9.51 Å between the centroids of adjacent molecules and the dihedral angle of 0°.

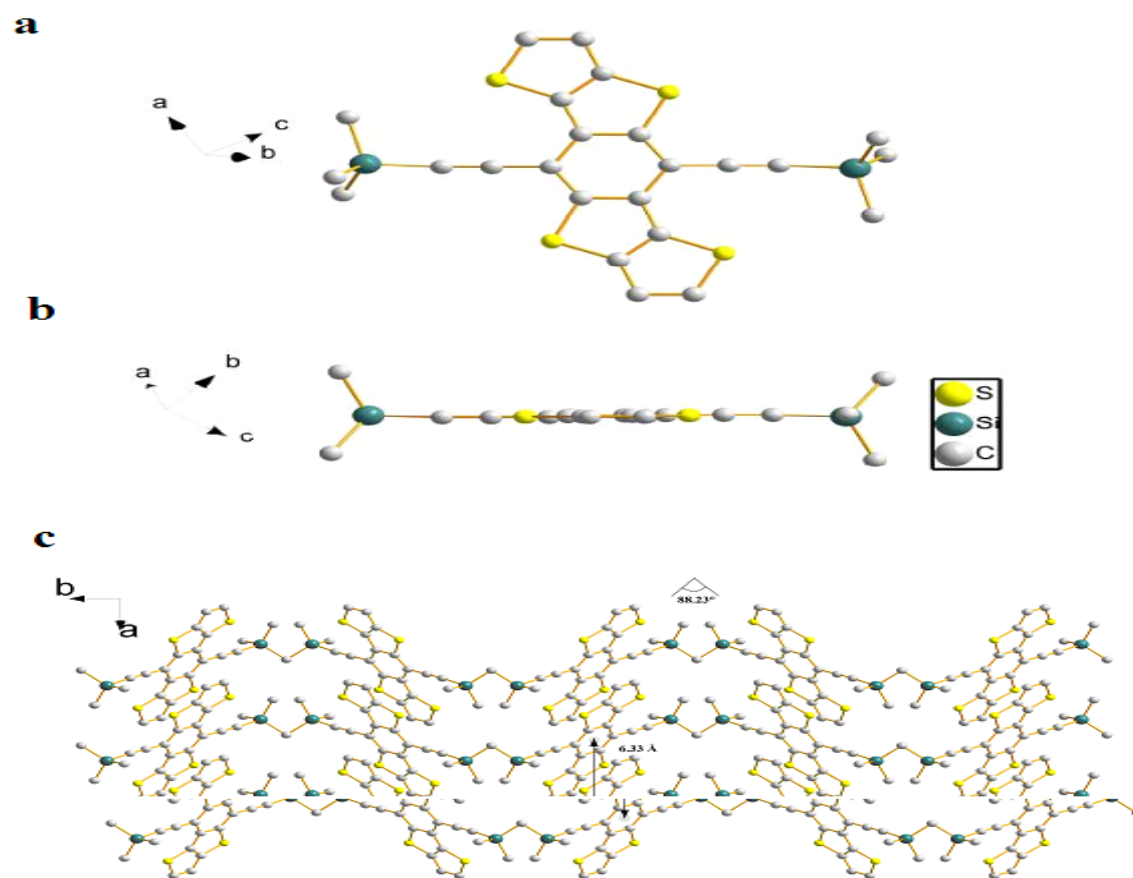


Fig. S3 Molecular structures in top view (a) and side view (b) of **DTBBDT-TMS**. (c) Packing diagram of **DTBBDT-TMS** in crystals with layered herringbone structure, showing the distances 6.33 Å between the centroids of adjacent molecules and the dihedral angle of planes defined two adjacent molecules of 88.25°.

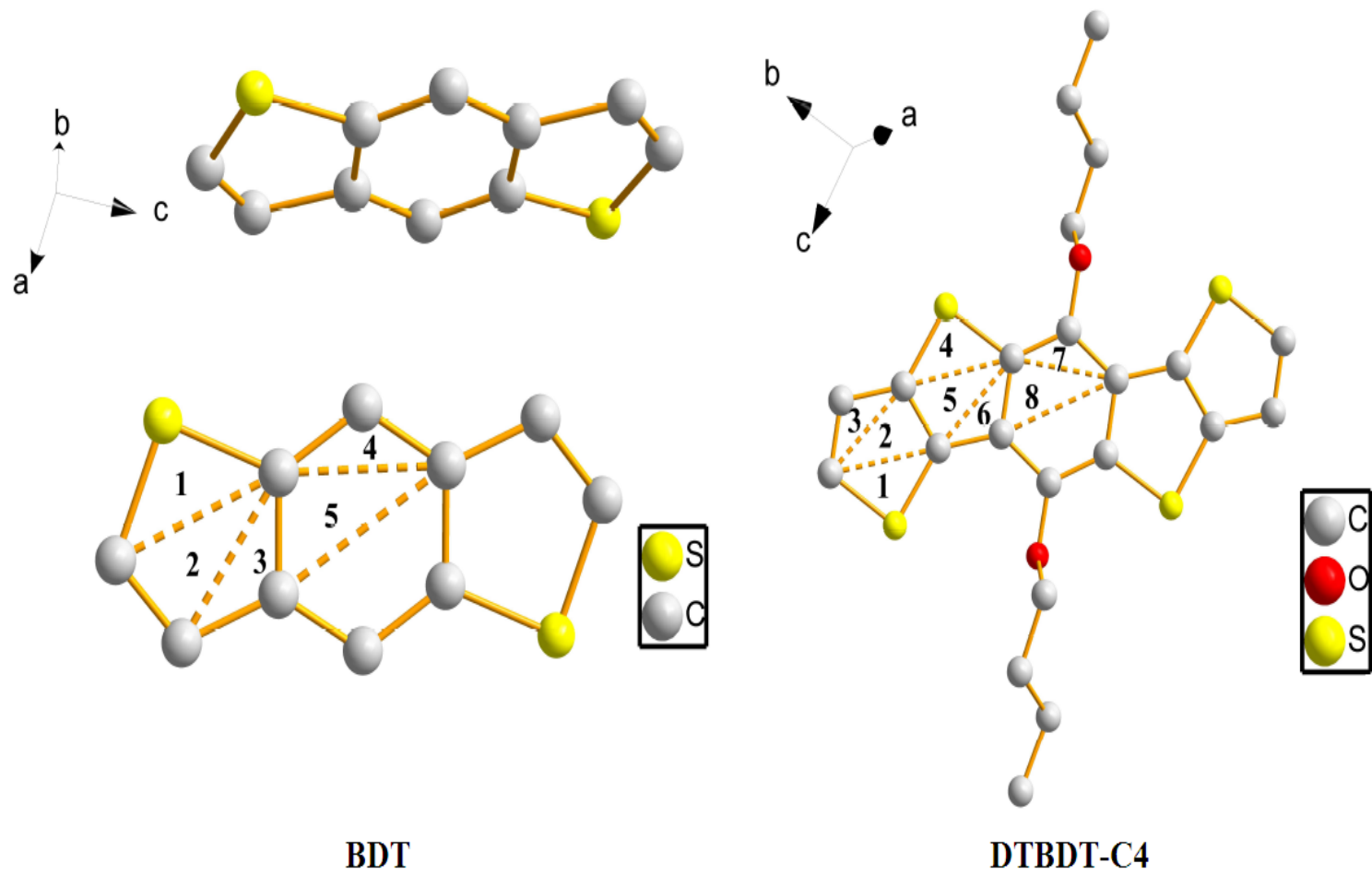


Fig. S4 Diagram showing the area calculation for BDT (left) and DTBBDT-C4 (right)

Table S2. Data of area ( $\text{\AA}^2$ ) calculation for BDT and DTBDT-C4

| BDT              |                         | DTBDT derivatives  |                         |          |           |           |
|------------------|-------------------------|--------------------|-------------------------|----------|-----------|-----------|
| Section No.      | Area ( $\text{\AA}^2$ ) | Section No.        | Area ( $\text{\AA}^2$ ) |          |           |           |
|                  |                         |                    | DTBDT-C4                | DTBDT-C8 | DTBDT-C12 | DTBDT-TMS |
| S1               | 1.503                   | S1                 | 1.477                   | 1.486    | 1.475     | 2.951     |
| S2               | 1.569                   | S2                 | 1.539                   | 1.538    | 1.533     | 3.048     |
| S3               | 0.968                   | S3                 | 0.892                   | 0.887    | 0.895     | 1.771     |
| S4               | 0.860                   | S4                 | 1.527                   | 1.528    | 1.531     | 3.060     |
| S5               | 1.696                   | S5                 | 1.577                   | 1.636    | 1.586     | 3.140     |
|                  |                         | S6                 | 0.951                   | 0.894    | 0.941     | 1.871     |
|                  |                         | S7                 | 0.846                   | 0.855    | 0.867     | 1.752     |
|                  |                         | S8                 | 1.684                   | 1.695    | 1.674     | 3.397     |
| $S_{\text{BDT}}$ | 13.191                  | $S_{\text{DTBDT}}$ | 20.989                  | 21.036   | 21.004    | 20.990    |

Note:  $S_{\text{BDT}} = 2 \times (S1 + S2 + S3 + S4 + S5)$ ,  $S_{\text{DTBDT}} = 2 \times (S1 + S2 + S3 + S4 + S5 + S6 + S7 + S8)$

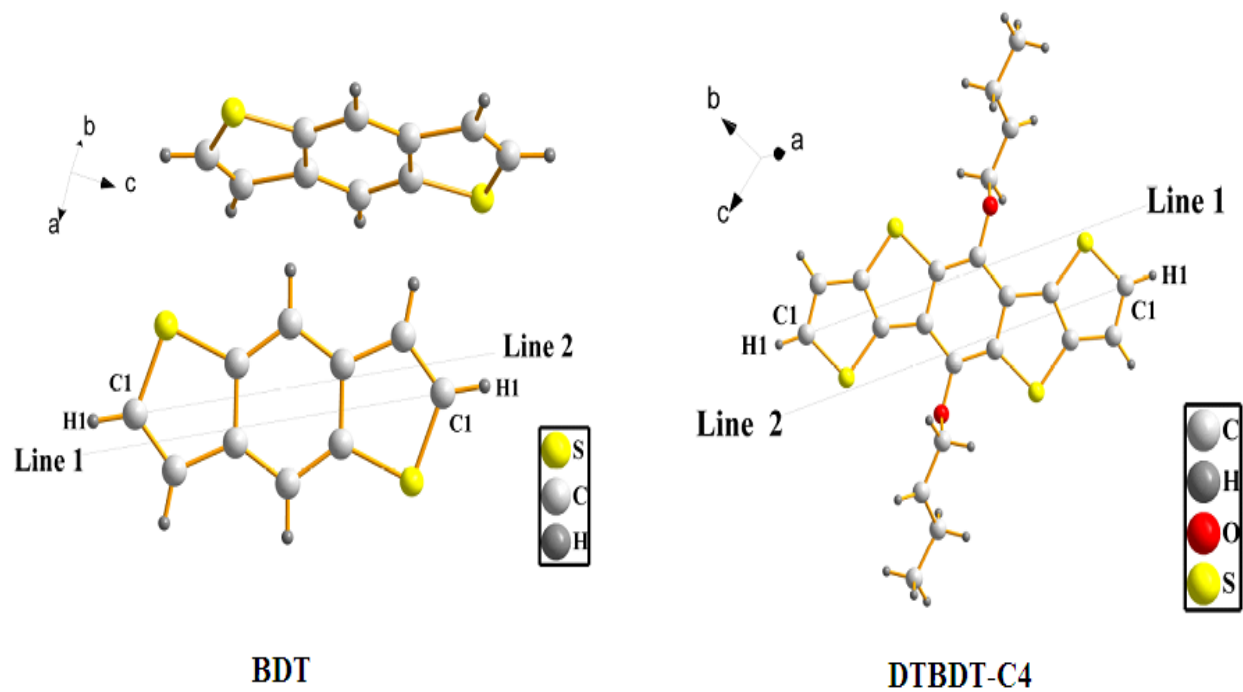


Fig.S5 Diagram showing the lines through  $\alpha$  position (C1 and H1) of peripheral thiophene for BDT and DTBBDT-C4, respectively, exhibiting line 1 and line 2 are parallel each other.



### 3. Characterization of the DTBDT derivatives and conjugated polymers based on DTBDTS

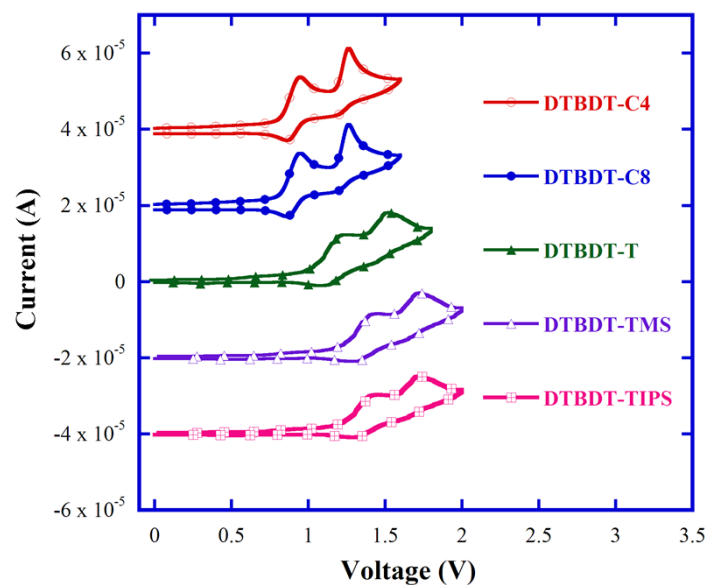


Fig. S6 Electrochemical properties of DTBDT derivatives

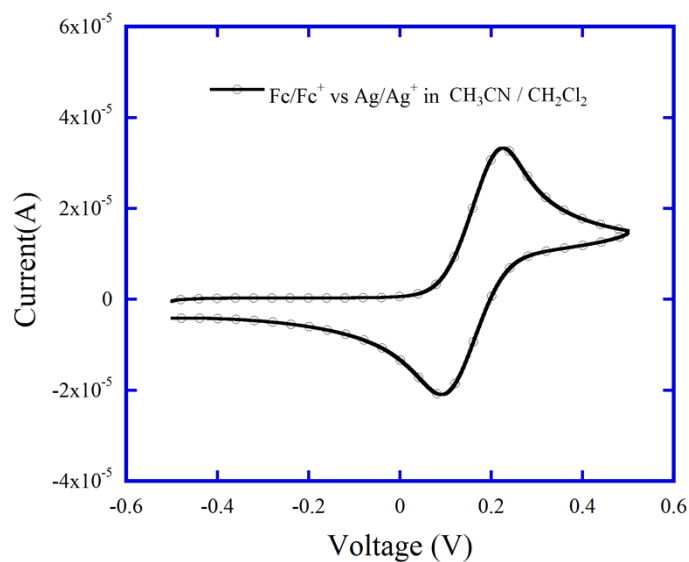


Fig. S7 Electrochemical curve of Fc/Fc<sup>+</sup> in 0.1 M tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) with acetonitrile (CH<sub>3</sub>CN) and dichloromethane (V:V, 1:1) as solvent

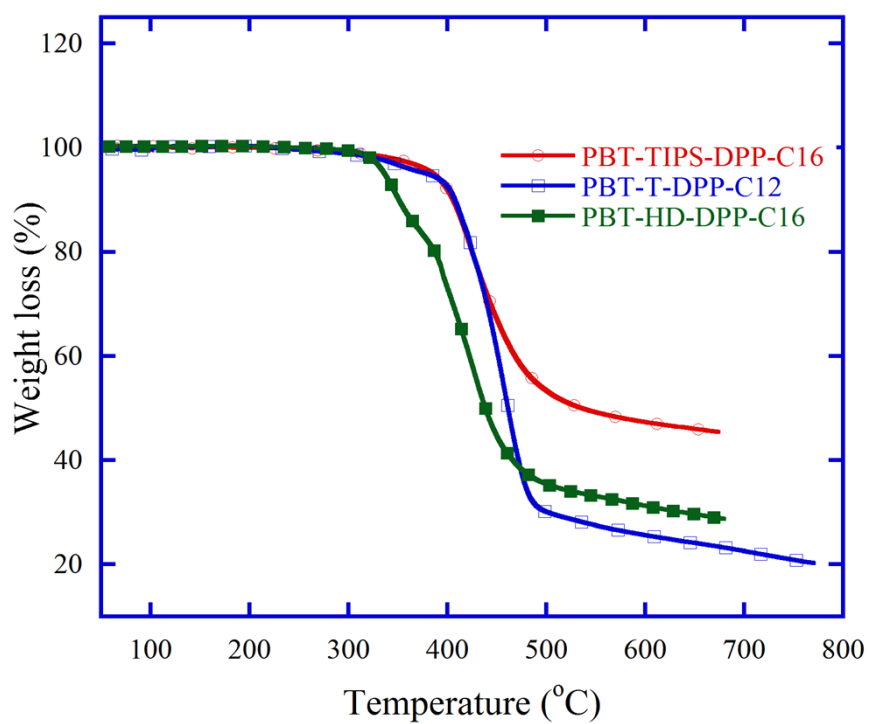


Fig. S8 TG curves of DTBBDT derivatives

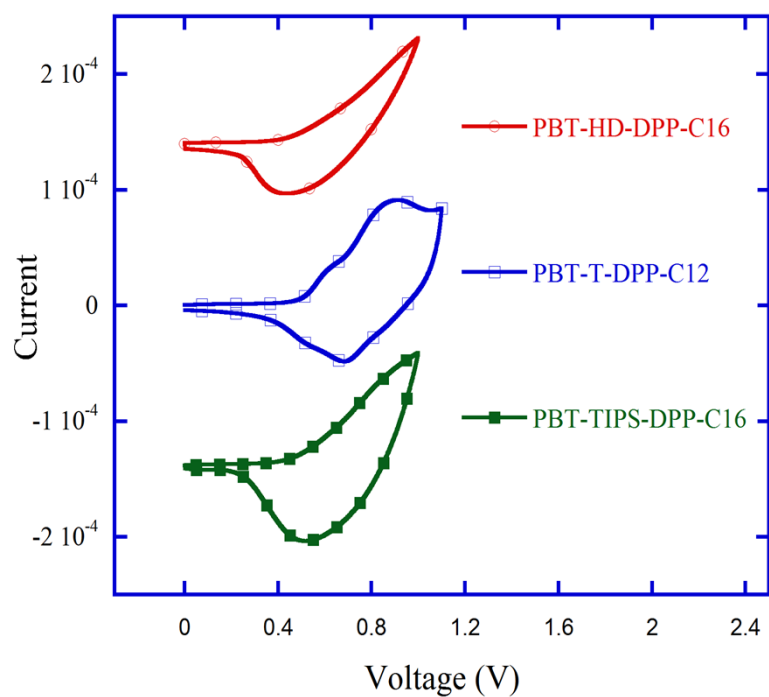


Fig. S9 Electrochemical properties of DTBBDTs-based conjugated polymers

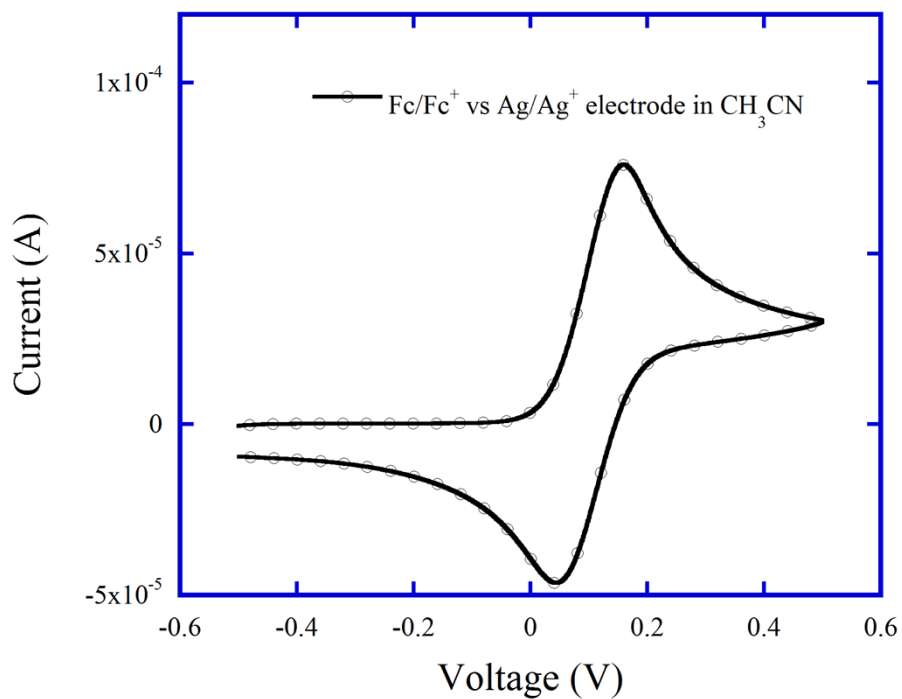


Fig. S10 Electrochemical curve of Fc/Fc<sup>+</sup> in 0.1 M tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) with acetonitrile (CH<sub>3</sub>CN) as solvent

Table S3. Hole mobilities of DTBDTs-based conjugated polymers and PC<sub>71</sub>BM blend measured by SCLC model

| Active layer                                   | Thickness (nm) | Hole mobility (cm <sup>-2</sup> V <sup>-1</sup> ·s <sup>-1</sup> ) |
|--|----------------|--|
| PBT-HD-DPP-C16/PC <sub>71</sub> BM (W:W,1:1.5) | 95             | 8.5×10 <sup>-6</sup>   |
| PBT-HD-DPP-C16/PC <sub>71</sub> BM (W:W,1:1.5) | 115            | 1.78×10 <sup>-4</sup>  |
| PBT-HD-DPP-C16/PC <sub>71</sub> BM (W:W,1:1.5) | 115            | 1.33×10 <sup>-4</sup>  |

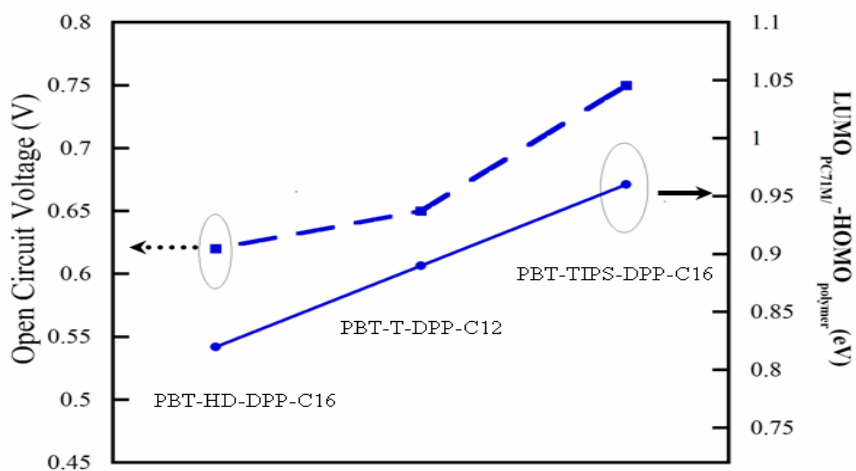


Fig. S11 Open circuit voltage and the differences between of the LUMO energy level of PC<sub>71</sub>BM and the DTBDTs-based polymers

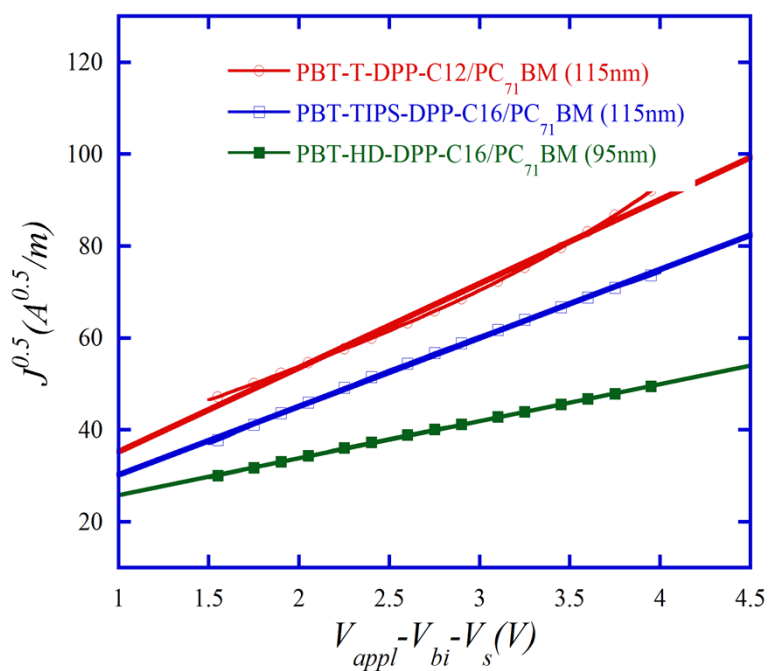


Fig. S12 I-V characteristics of the SCLC measurement of DTBDTs-based conjugated polymers and PC<sub>71</sub>BM blend

#### 4. <sup>1</sup>H NMR spectra of the Monomers

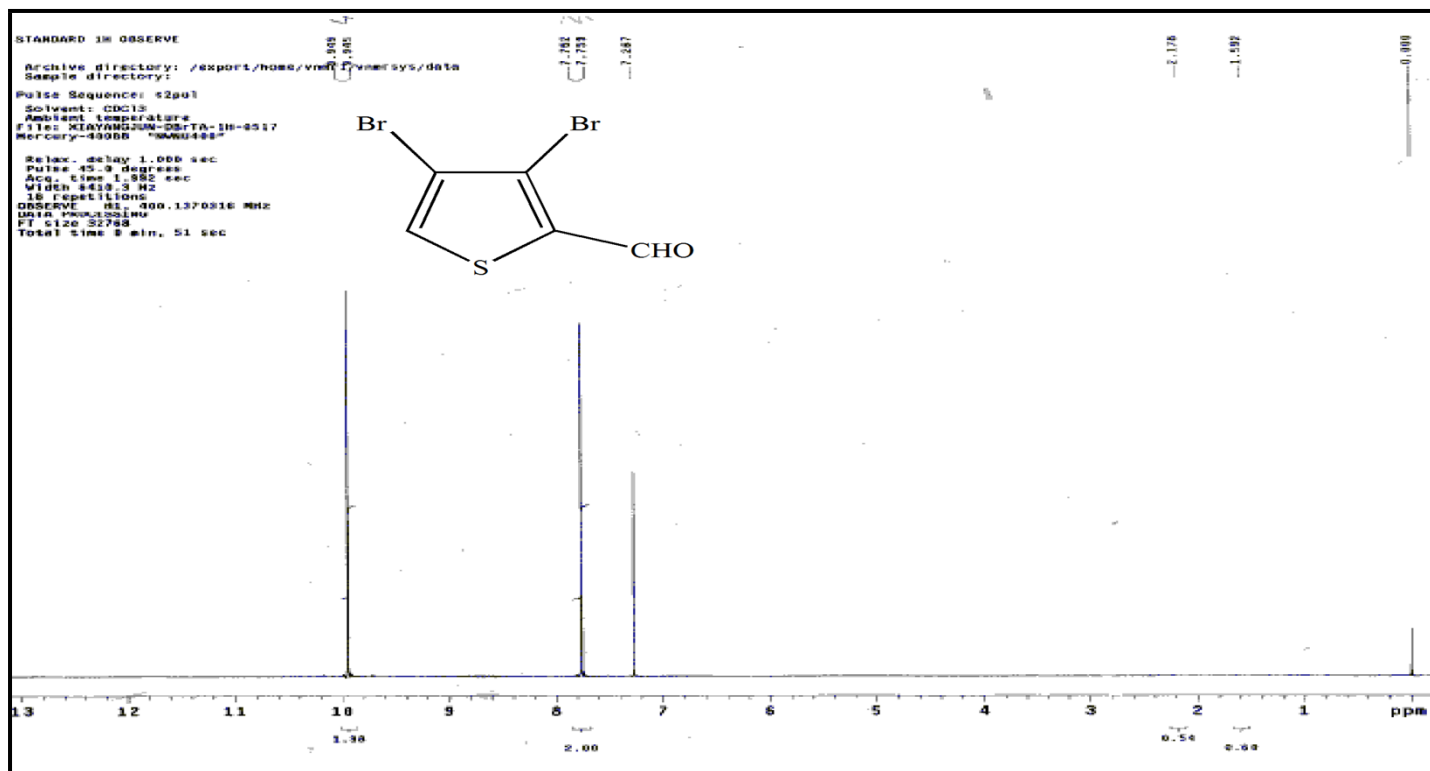


Fig. S13 <sup>1</sup>H NMR spectrum of 3,4-dibromothiophene-2-carbaldehyde in CDCl<sub>3</sub>

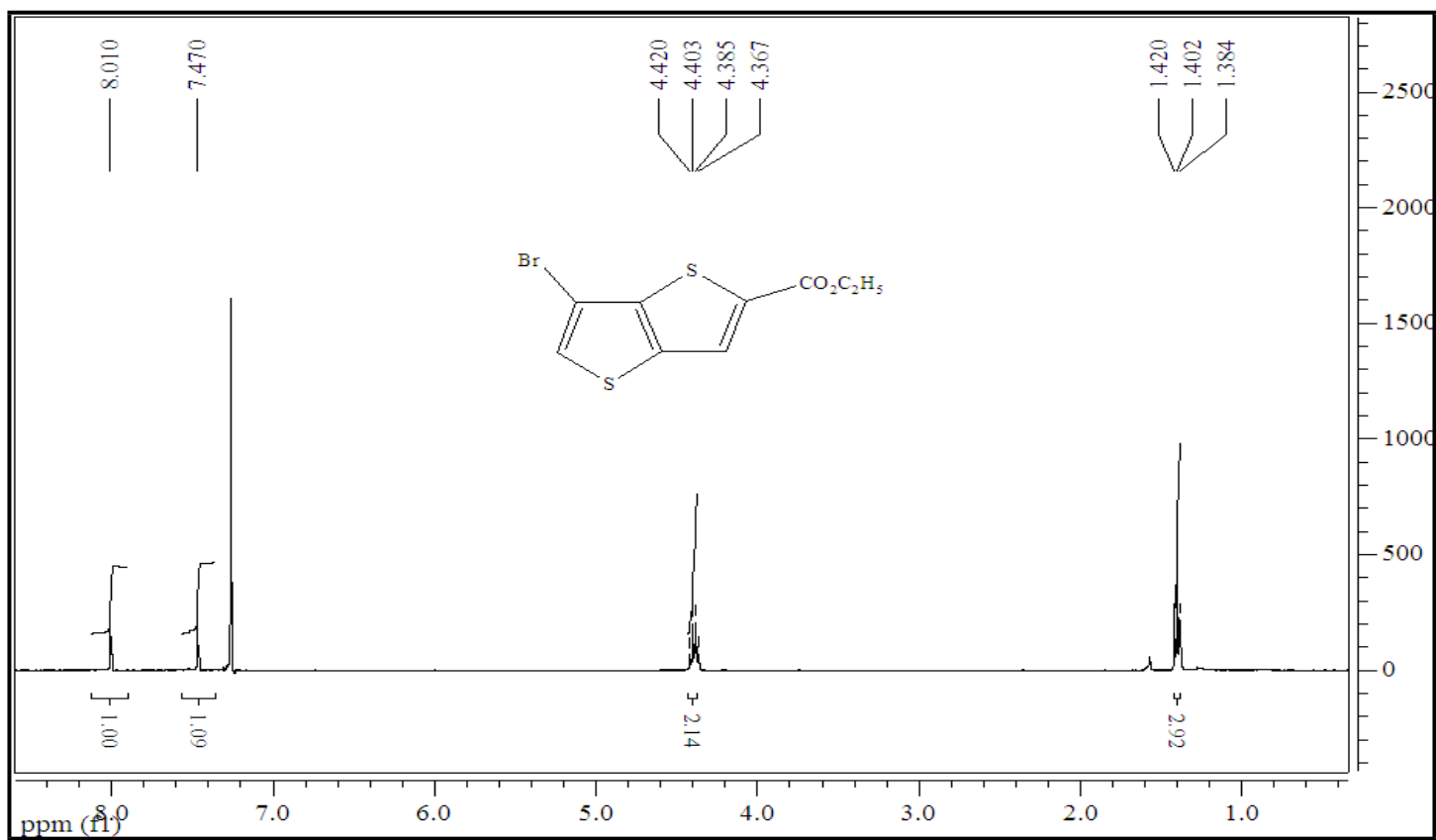


Fig. S14. <sup>1</sup>H NMR spectrum of ethyl 6-bromothieno[3,2-*b*]thiophene-2-carboxylic acid in CDCl<sub>3</sub>

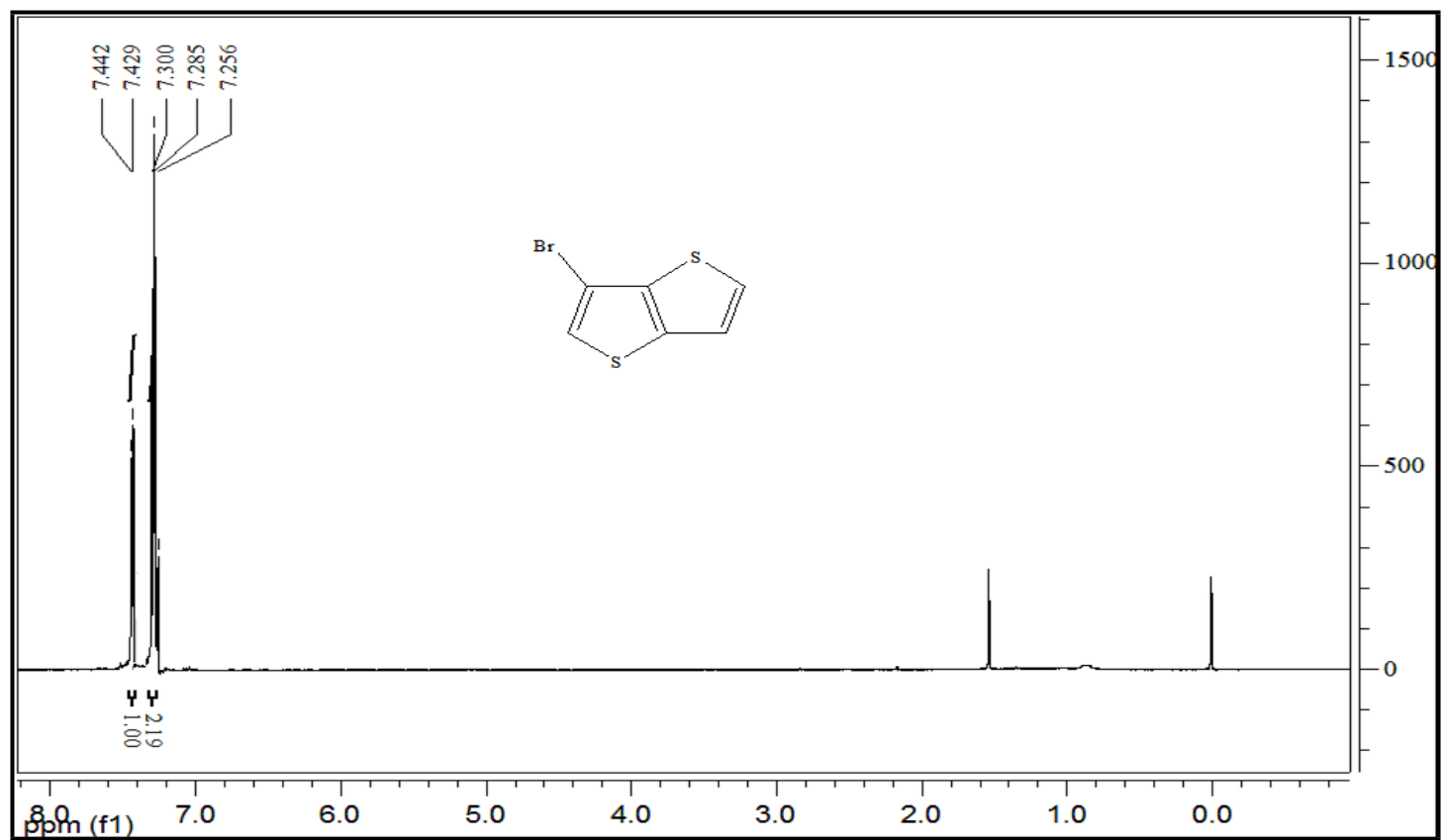


Fig. S15. <sup>1</sup>H NMR spectrum of 3-bromothieno[3,2-*b*]thiophene in CDCl<sub>3</sub>

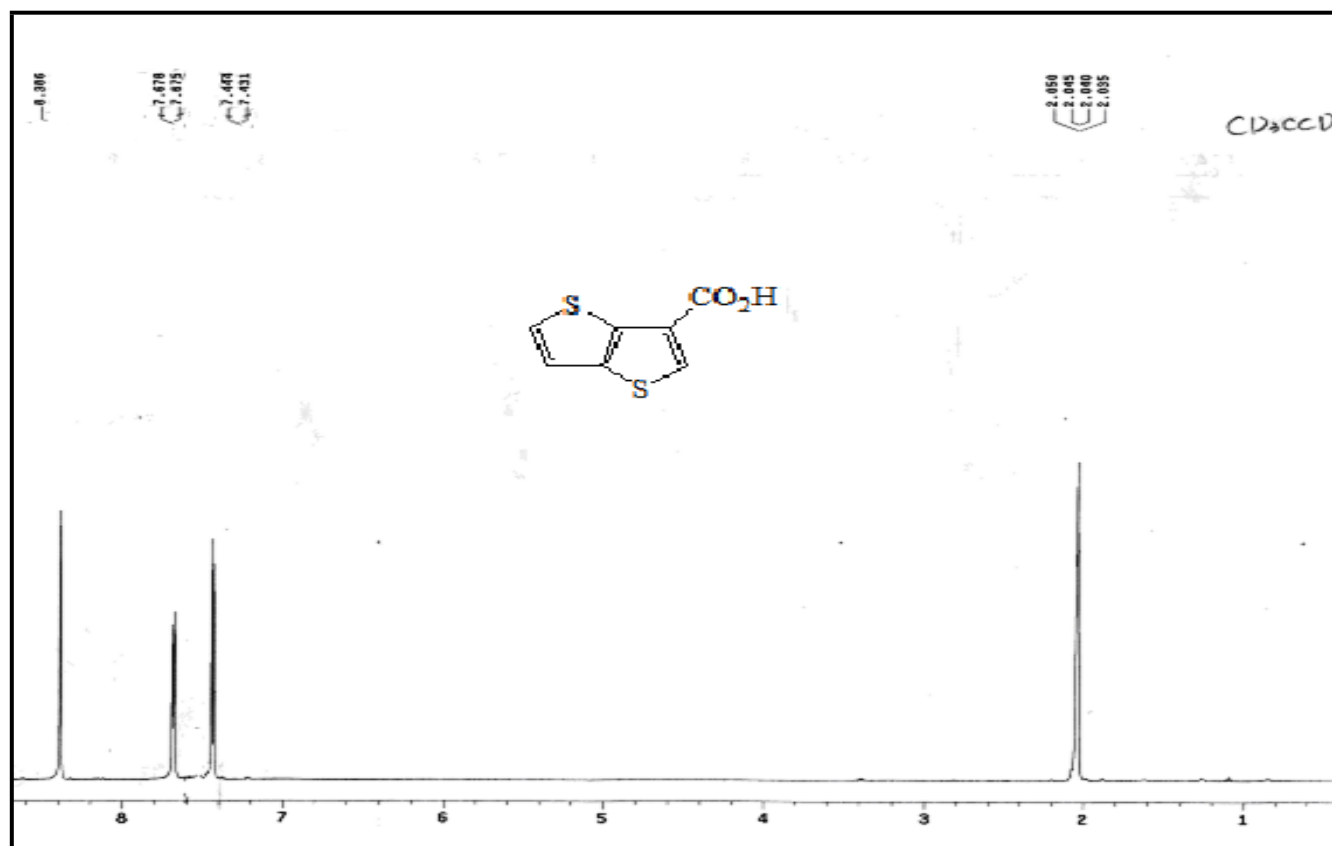


Fig. S16.  $^1\text{H}$  NMR spectrum of thieno[3,2-*b*]thiophene-3-carboxylic acid in  $(\text{CD}_3)_2\text{CO}$



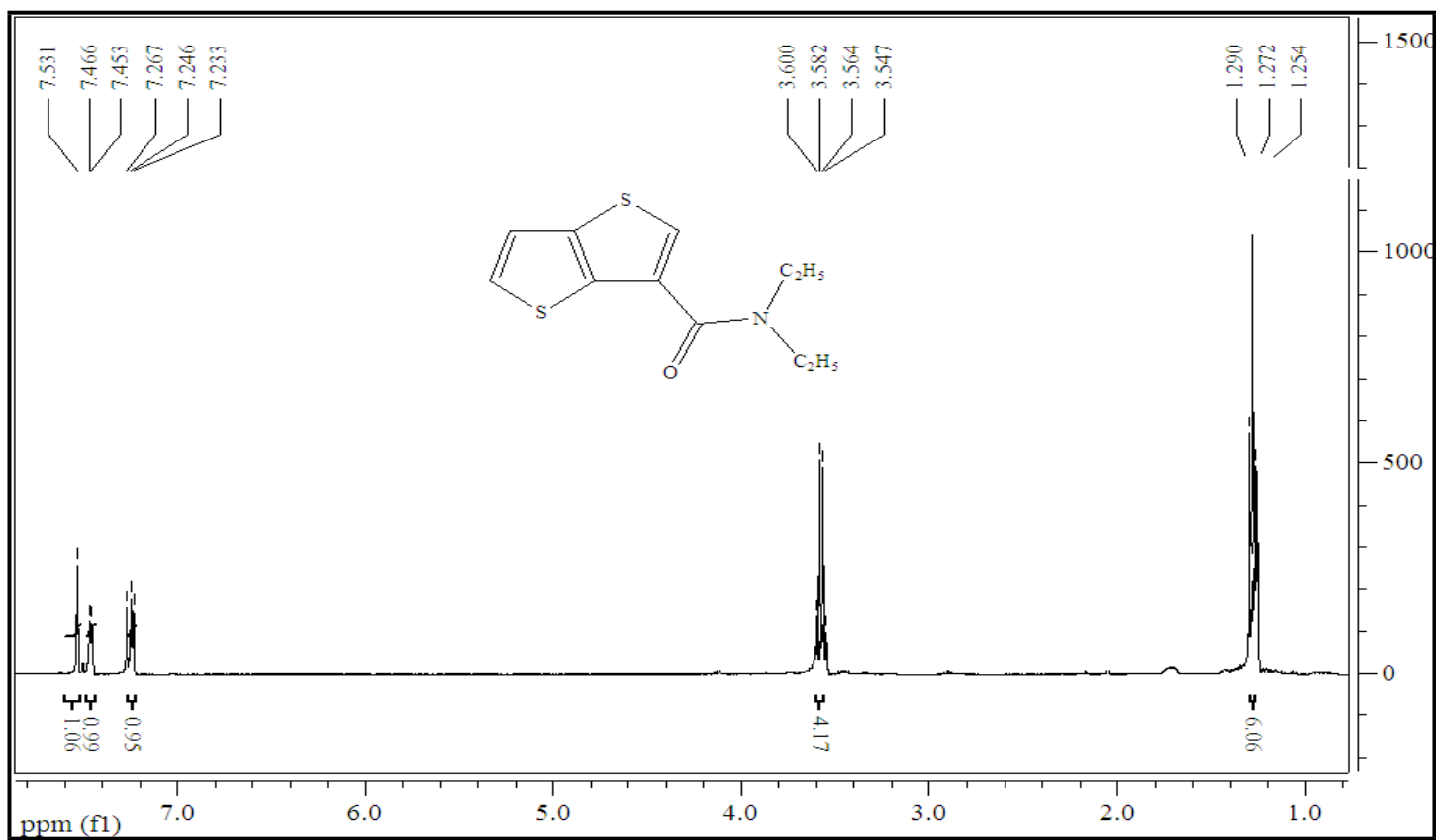


Fig. S17. <sup>1</sup>H NMR spectrum of *N,N*-diethylthieno[3,2-*b*]thiophene-3-carboxamide in CDCl<sub>3</sub>

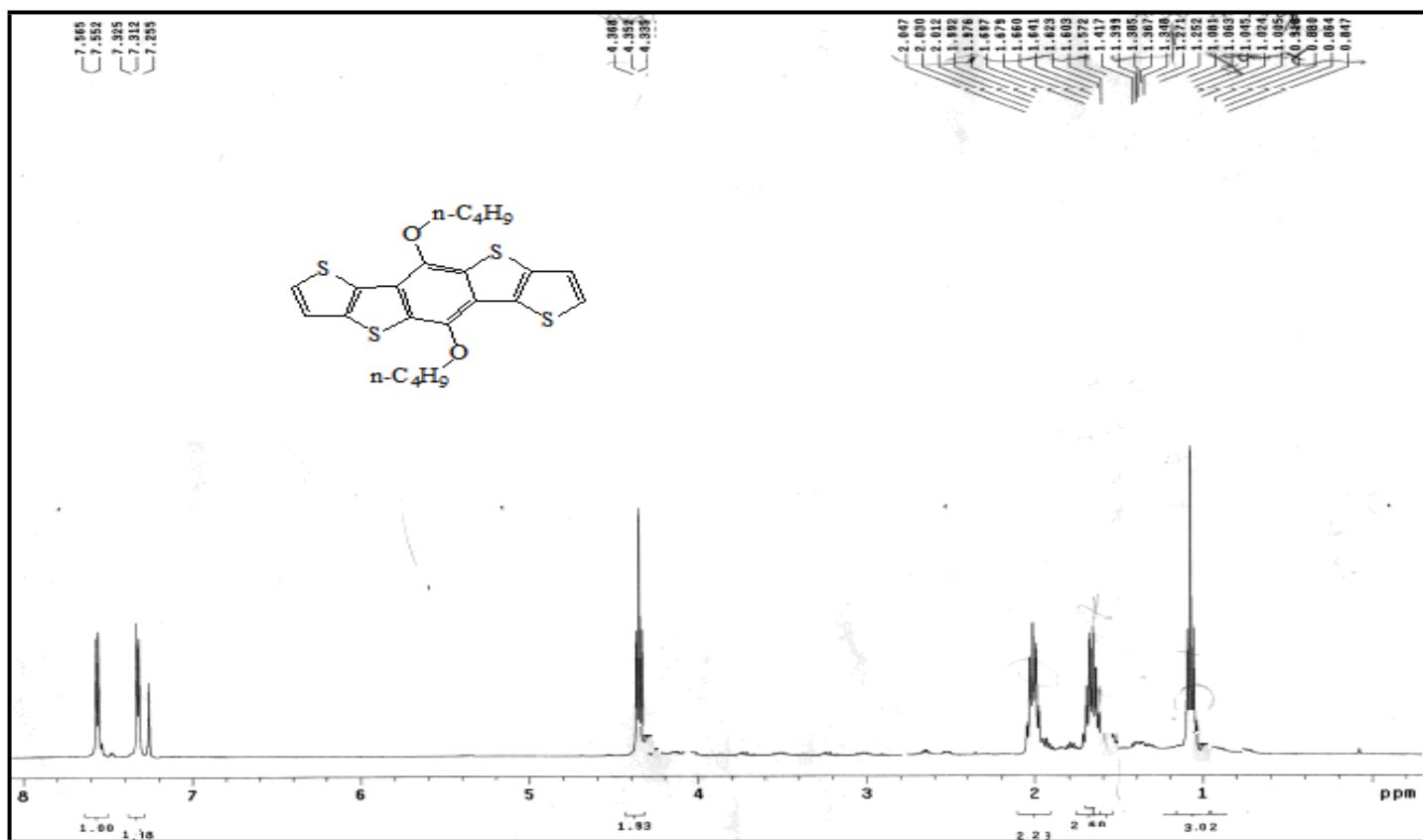


Fig. S18.  $^1\text{H}$  NMR spectrum of 5,10-bis(butyloxy)dithieno[2,3-*d'*:2',3'-*d''*]benzo[1,2-*b*:4,5-*b'*]dithiophene in  $\text{CDCl}_3$

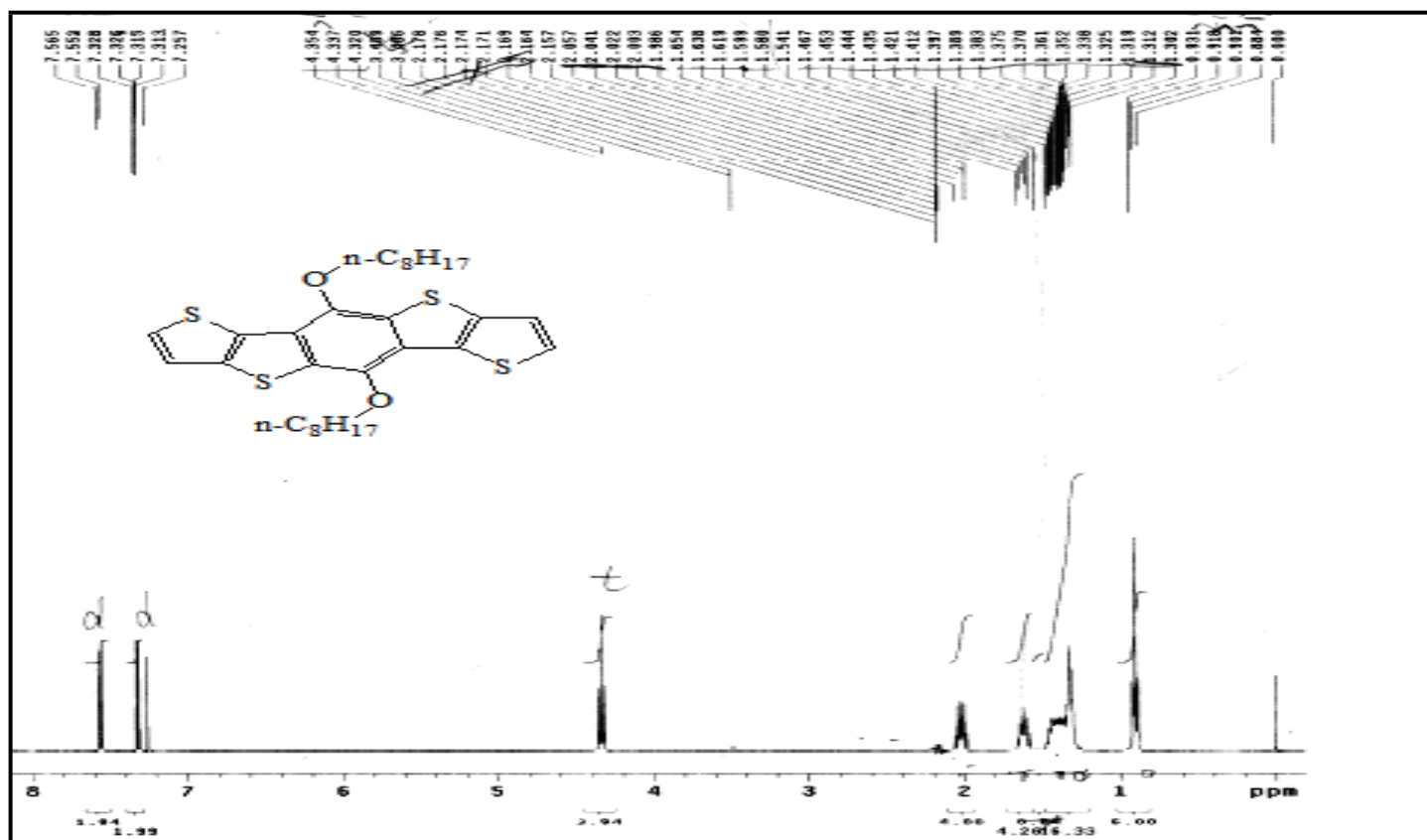


Fig. S19 <sup>1</sup>H NMR spectrum of 5,10-bis(octyloxy)dithieno[2,3-d':2',3'-d']benzo[1,2-b:4,5-b']dithiophene in CDCl<sub>3</sub>

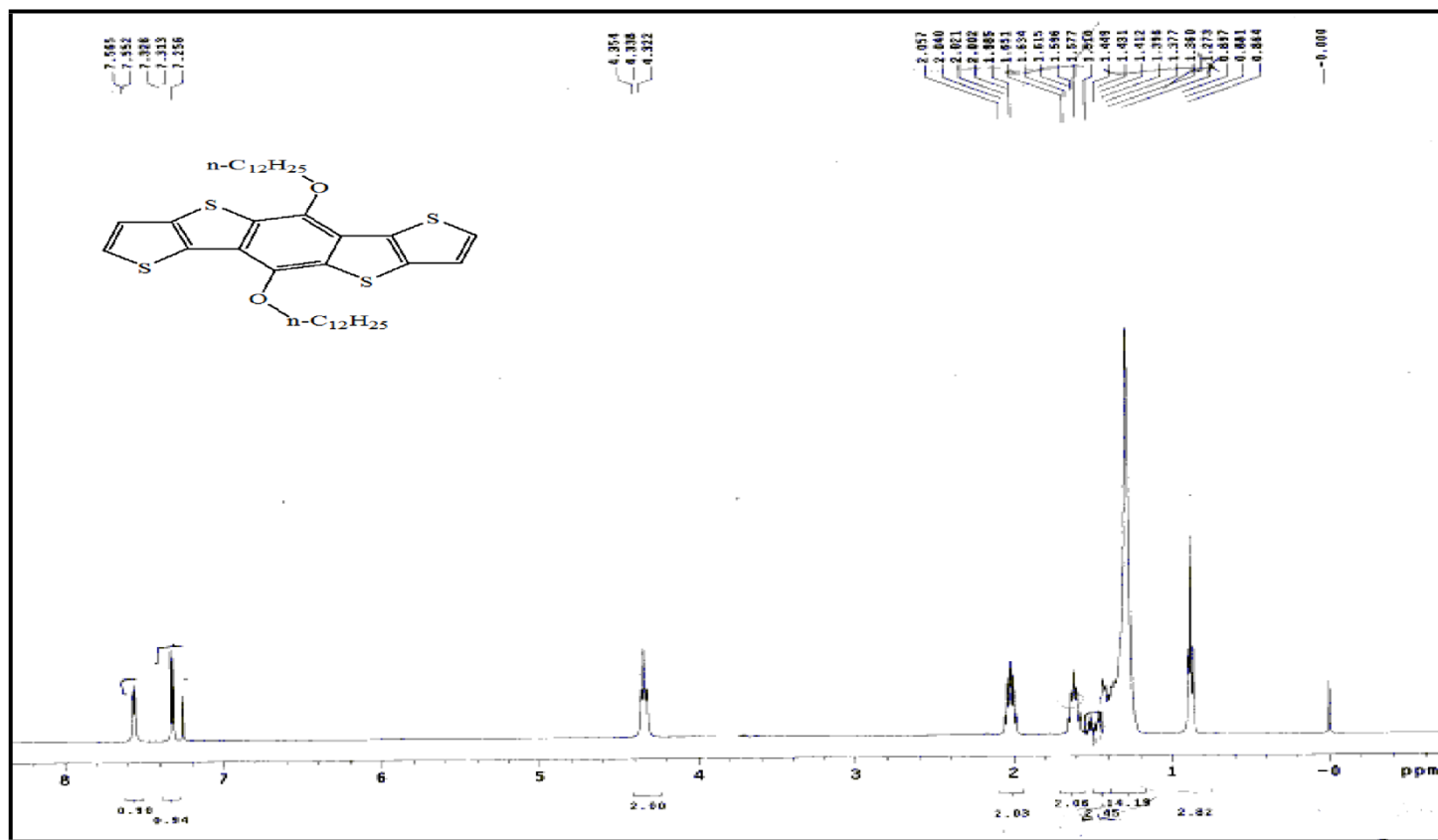


Fig. S20. <sup>1</sup>H NMR spectrum of 5,10-bis(dodecyloxy)dithieno[2,3-*d'*:2',3'-*d'*]benzo[1,2-*b*:4,5-*b'*]dithiophene in CDCl<sub>3</sub>

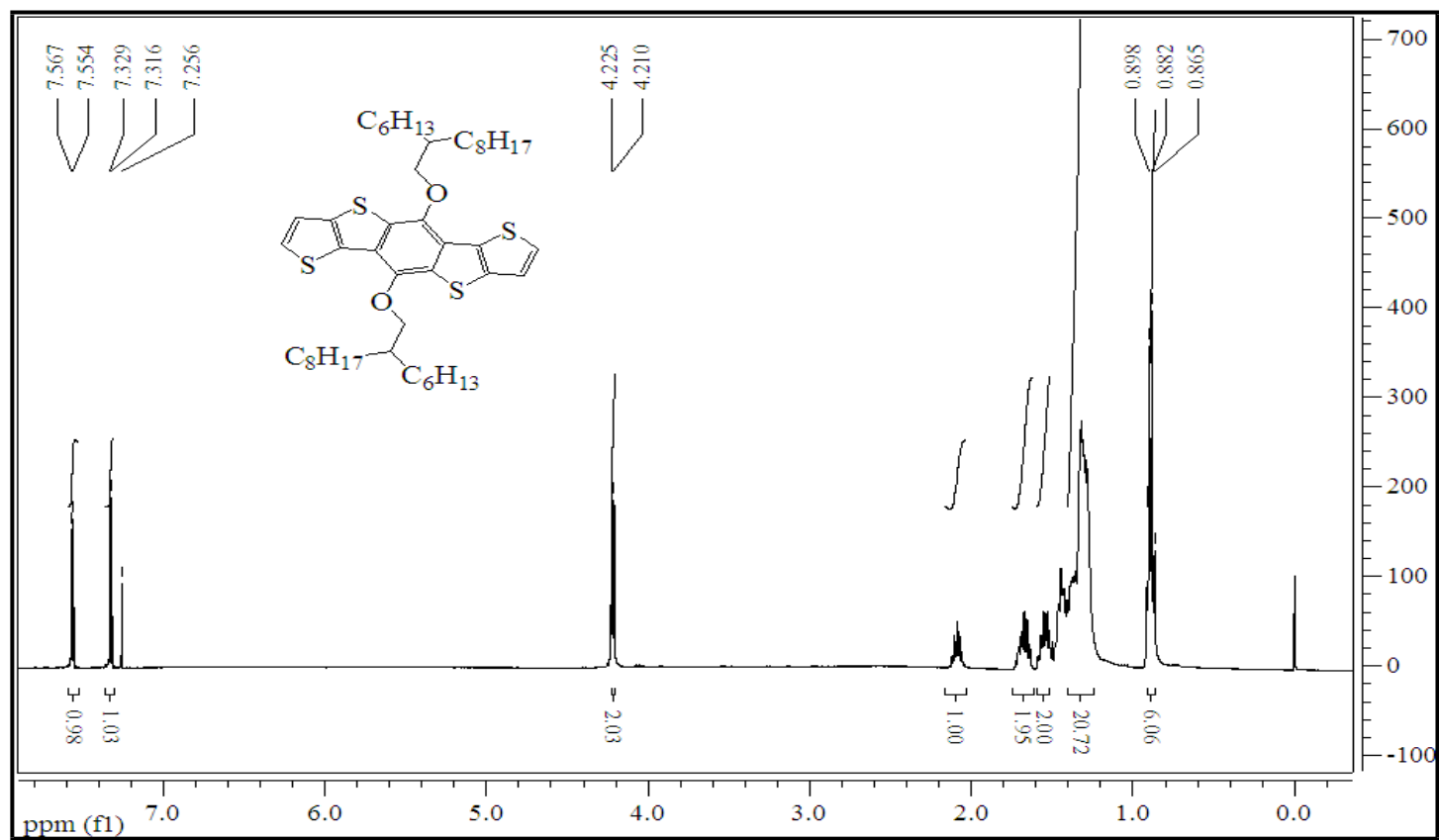


Fig. S21. <sup>1</sup>H NMR spectrum of 5,10-bis(2-hexyldecyloxy)dithieno[2,3-*d'*:2',3'-*d'*]benzo[1,2-*b*:4,5-*b'*]dithiophene in CDCl<sub>3</sub>

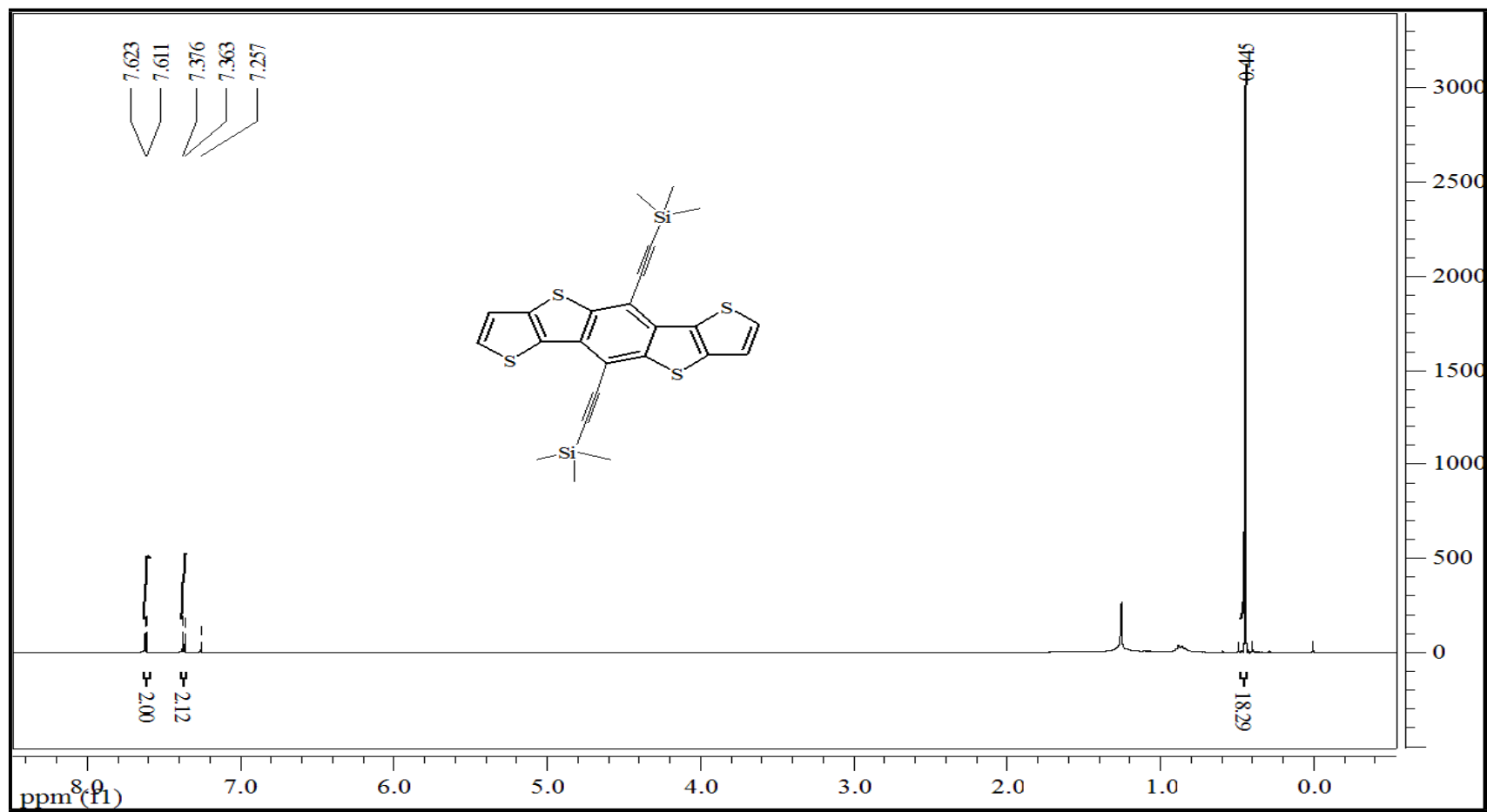


Fig. S22. <sup>1</sup>H NMR spectrum of 5,10-di(2-trimethylsilyl)ethynyl)dithieno[2,3-*d'*:3'-*d''*]benzo[1,2-*b*:4,5-*b'*]dithiophene in CDCl<sub>3</sub>

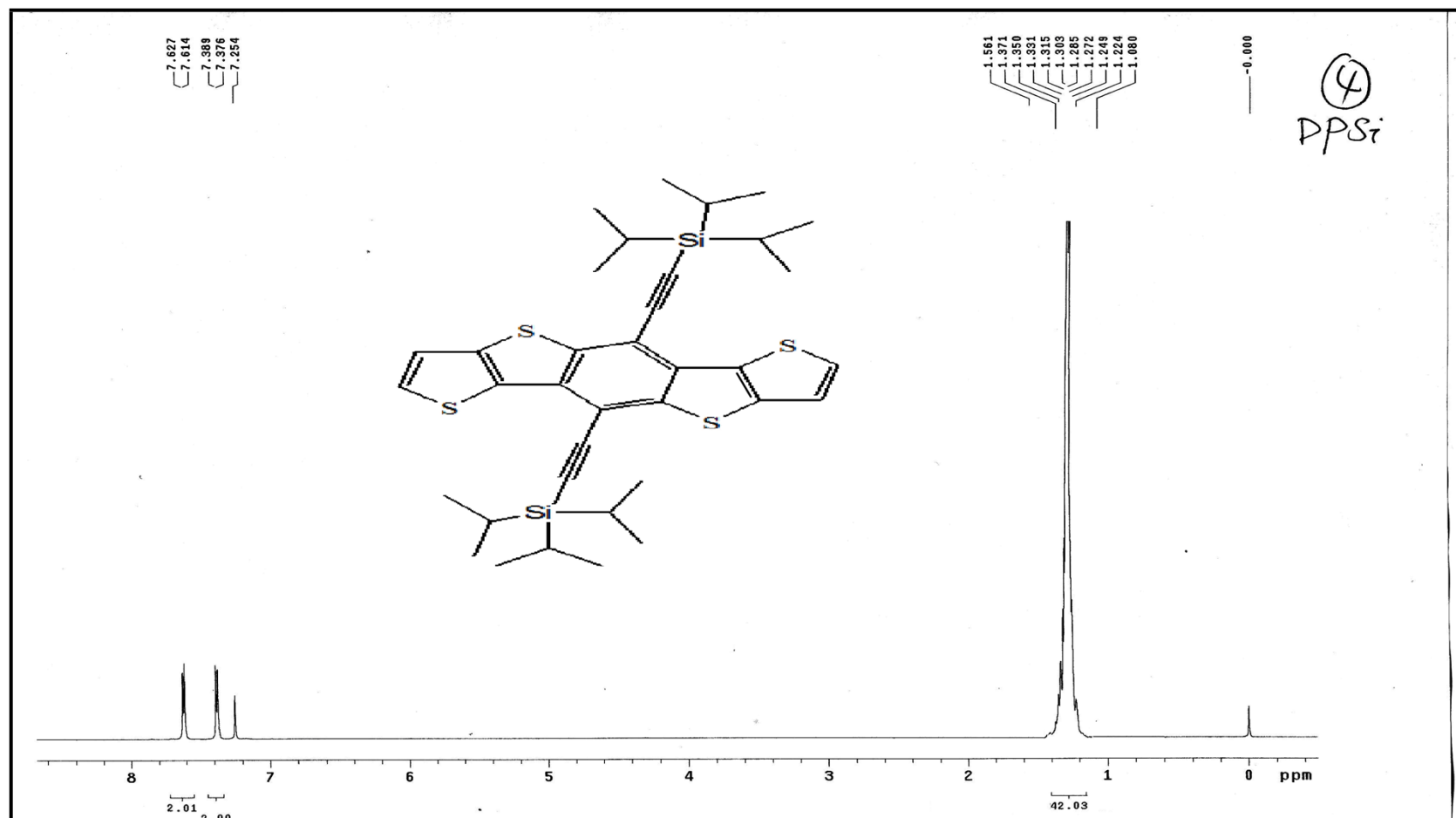


Fig. S23. <sup>1</sup>H NMR spectrum of 5,10-bis(tri-*iso*-propylsilyethynyl)dithieno[2,3-*d*:2',3'-*d'*]benzo[1,2-*b*:4,5-*b'*]dithiophene in CDCl<sub>3</sub>

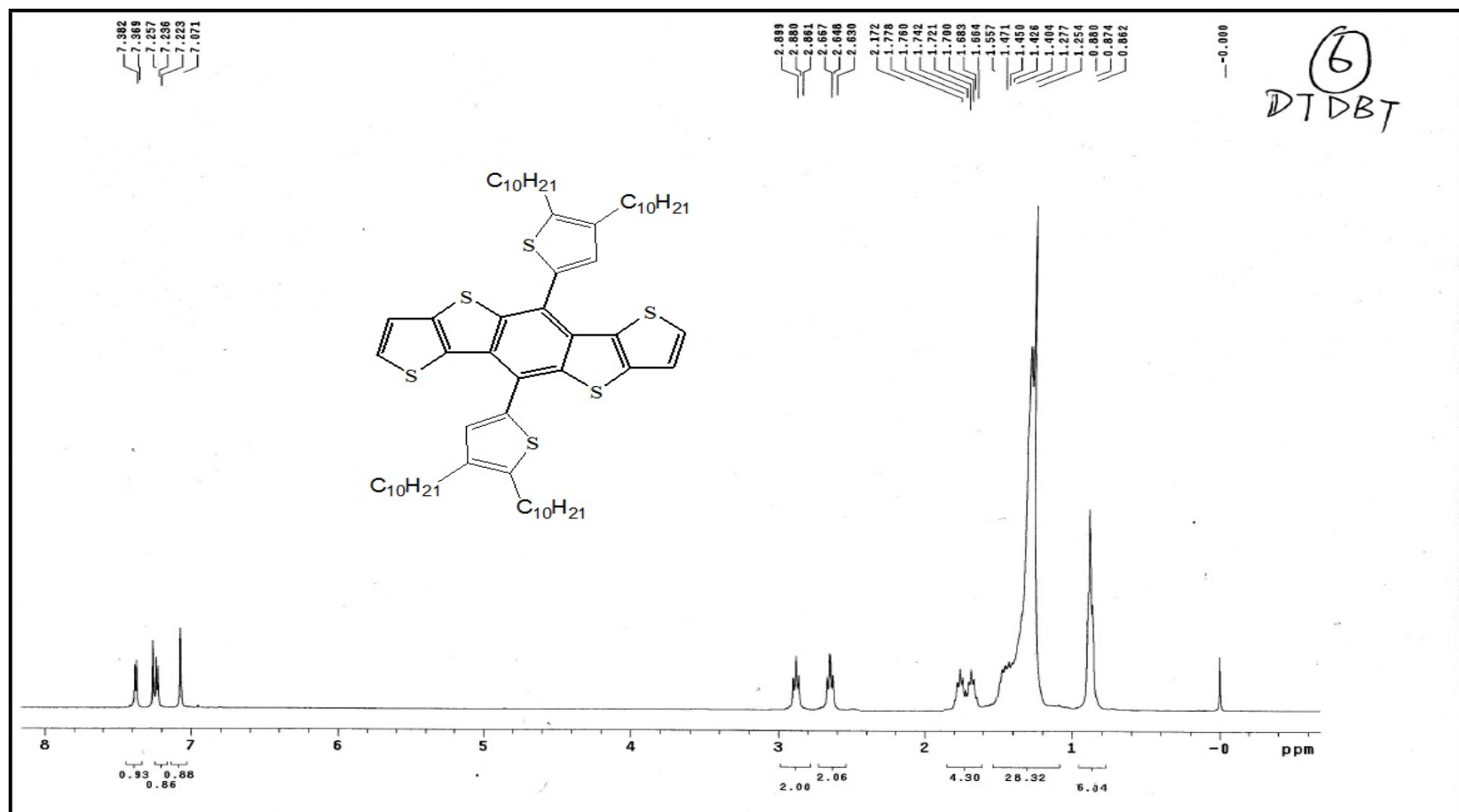


Fig. S24. <sup>1</sup>H NMR spectrum of 5,10-bis(4,5-didecylthien-2-yl)dithieno[2,3-d':2',3'-d'']benzo[1,2-b:4,5-b']dithiophene in CDCl<sub>3</sub>



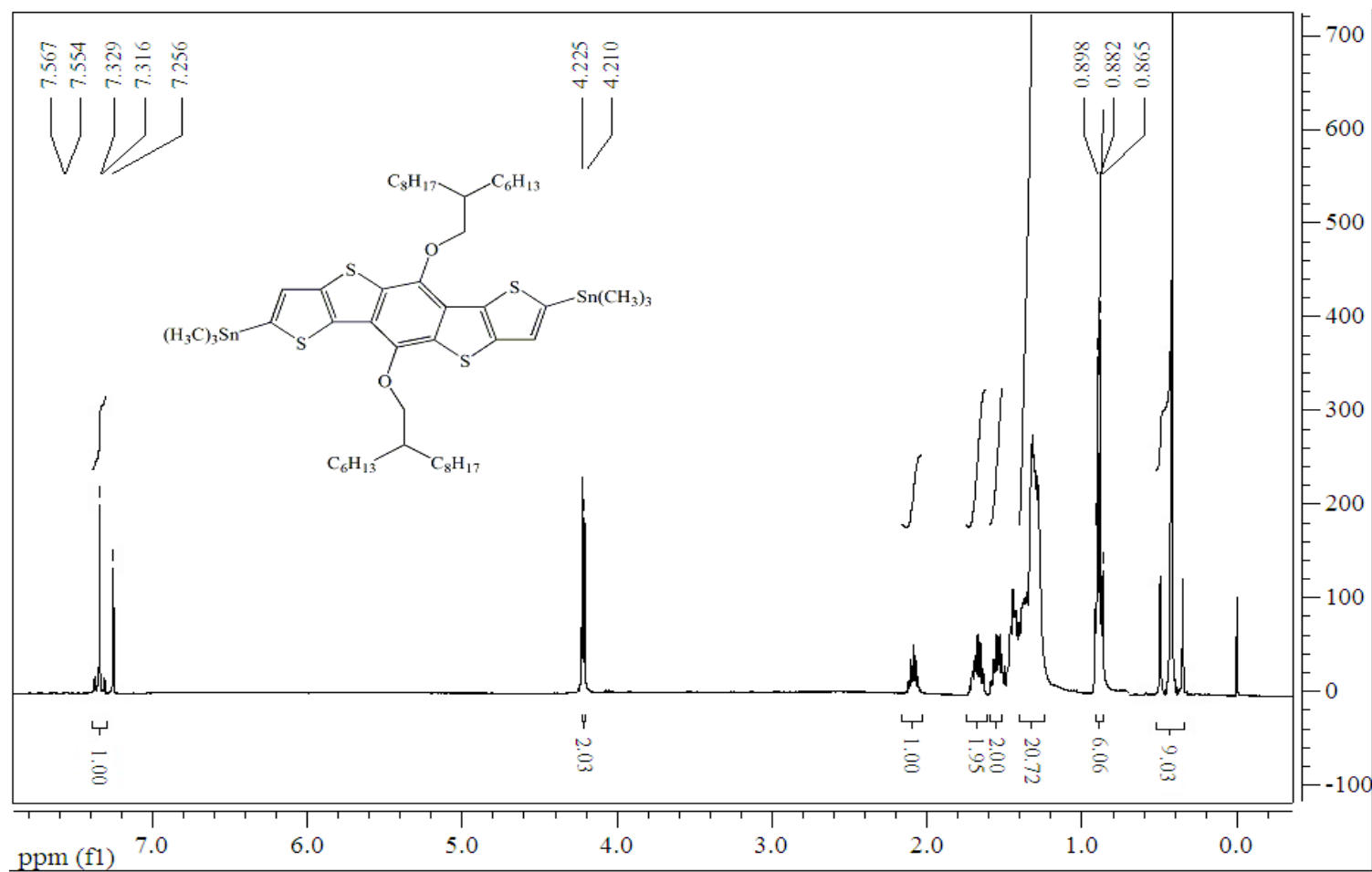


Fig. S25. <sup>1</sup>H NMR spectrum of 2,7-di(trimethylstannyl)-5,10-di(2-hexyldecyloxy)dithieno[2,3-*d*:2',3'-*d'*]benzo[1,2-*b*:4,5-*b'*]dithiophene in CDCl<sub>3</sub>

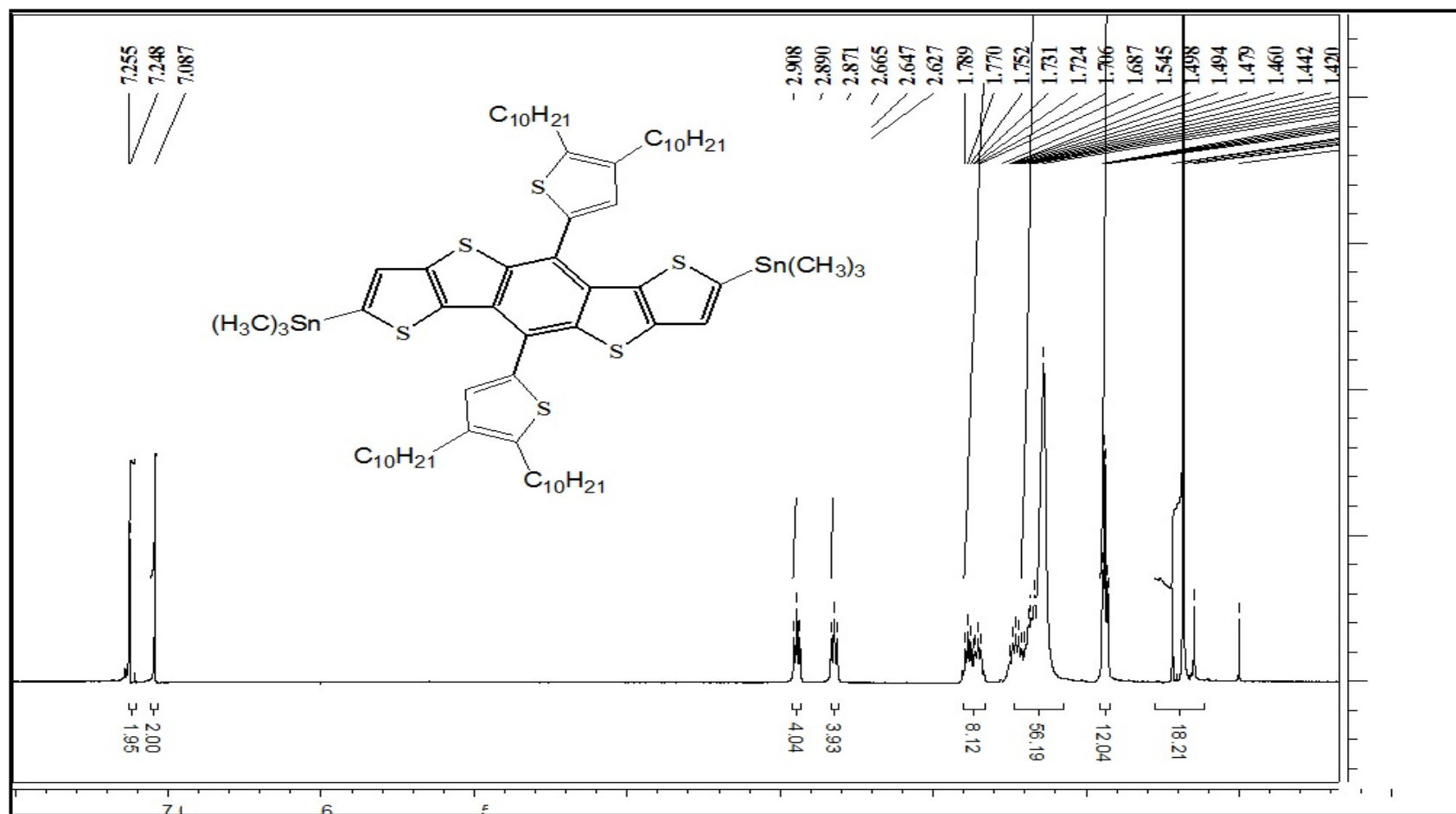


Fig. S26.  $^1\text{H}$  NMR spectrum of 2,7-di(trimethylstannyl)-5,10-bis(4,5-didecylthien-2-yl)dithieno[2,3-*d'*:2',3'-*d'*]benzo[1,2-*b*:4,5-*b'*]dithiophene in  $\text{CDCl}_3$

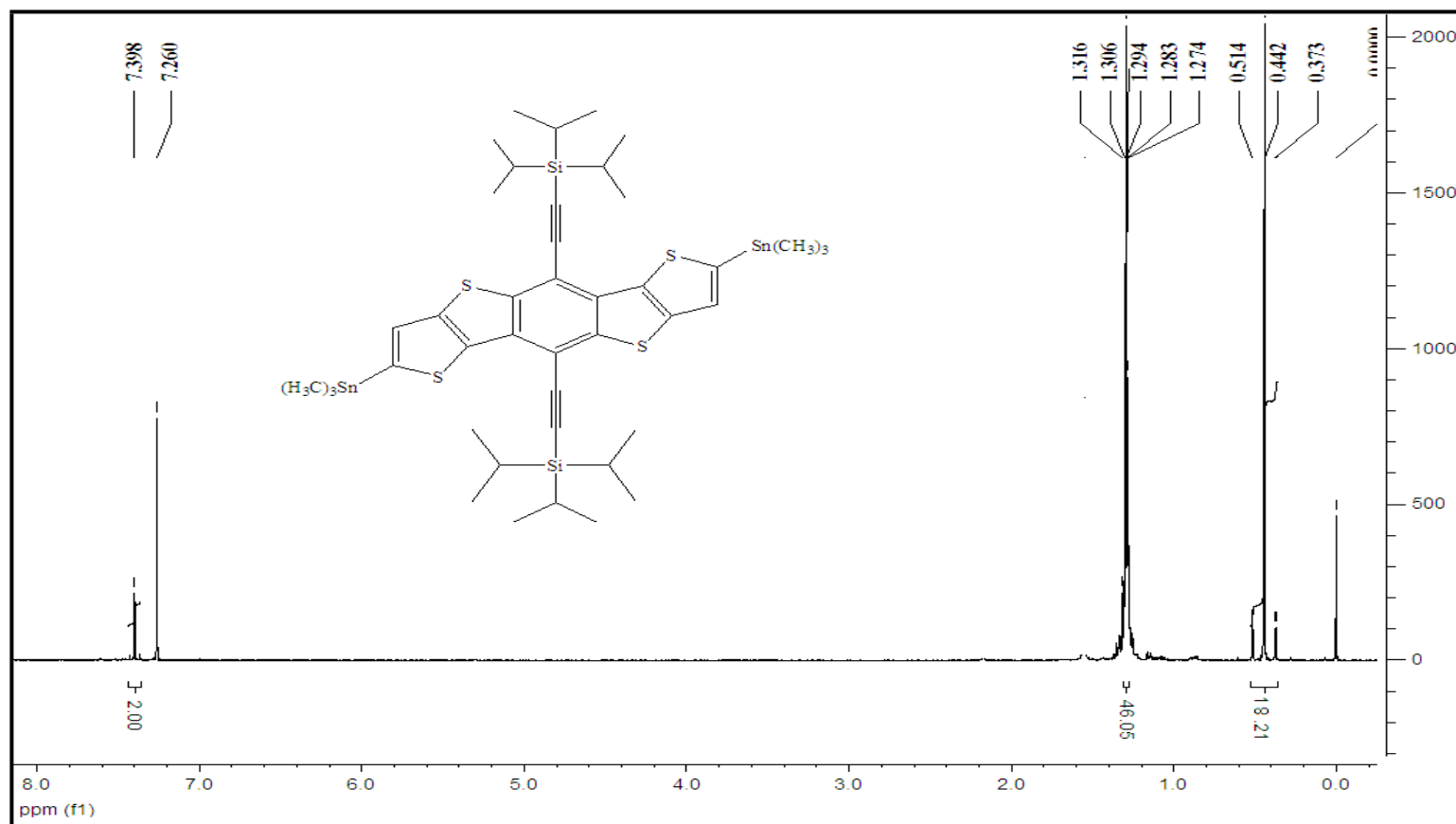


Fig. S27 <sup>1</sup>H NMR spectrum of 2,7-di(trimethylstannyl)-5,10-bis(2-tri-*iso*-propylsilyethynyl)dithieno[2,3-*d*:2',3'-*d'*]-benzo[1,2-*b*:4,5-*b'*]dithiophene in CDCl<sub>3</sub>

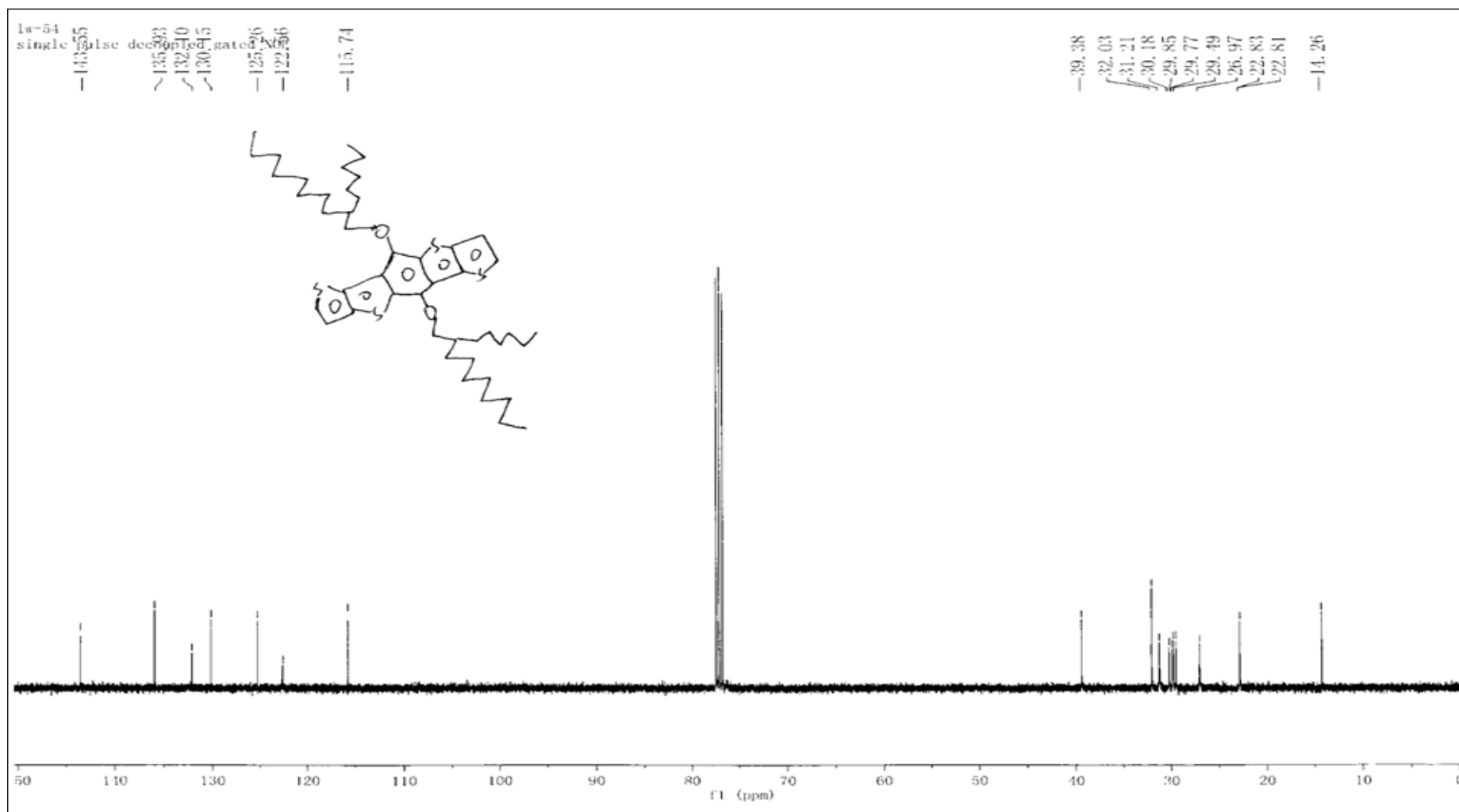


Fig. S28  $^{13}\text{C}$  NMR of 5,10-Di(2-hexyldecyloxy)dithieno[2,3-d':2',3'-d']benzo[1,2-b:4,5-b']dithiophene (IIId).

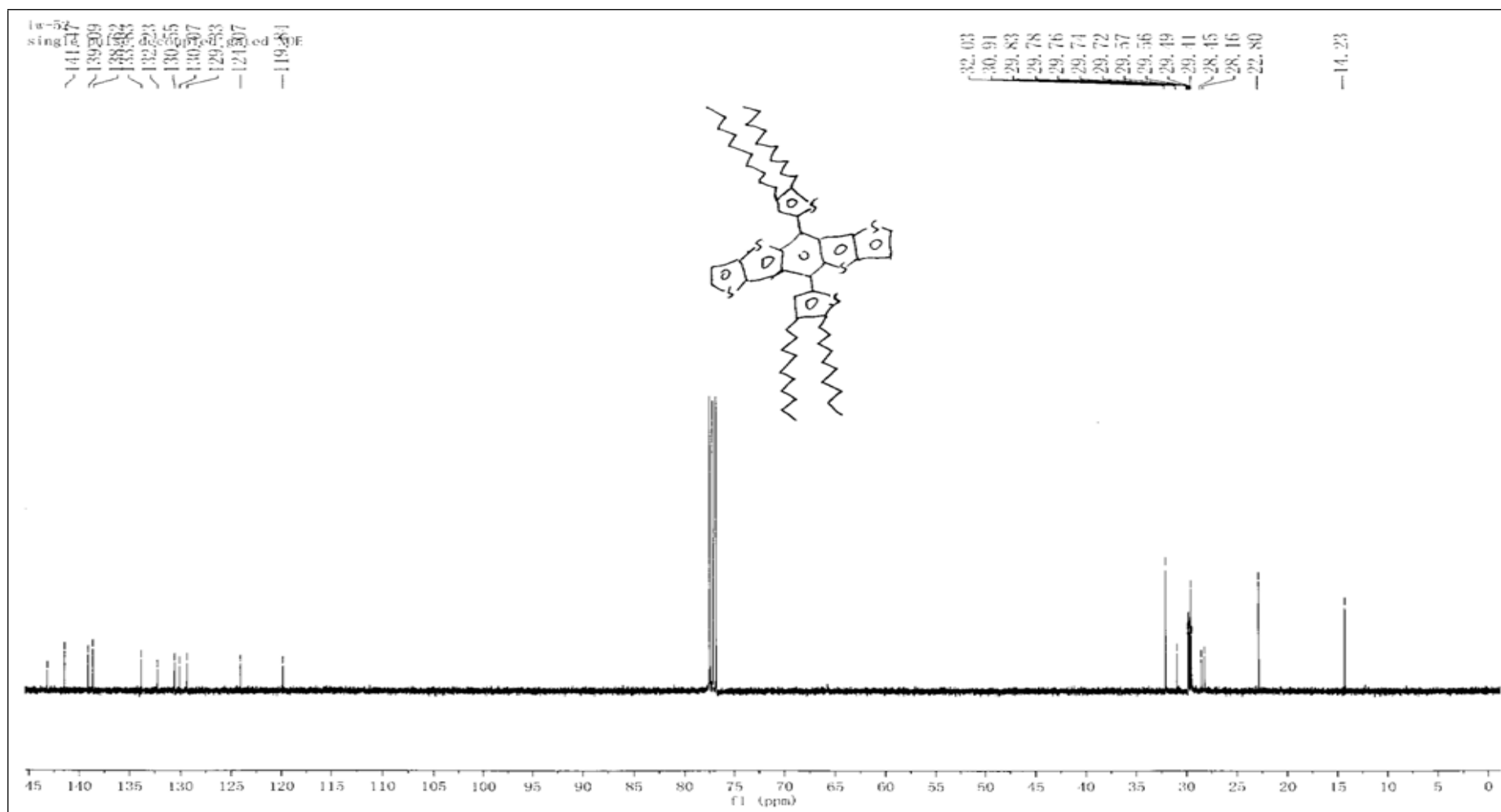


Fig. S29  $^{13}\text{C}$  NMR of 5,10-Bis(4,5-didecylthieno-2-yl)dithieno[2,3-*d'*:2',3'-*d'*] benzo[1,2-*b*:4,5-*b'*]dithiophene (DTBDT-T)

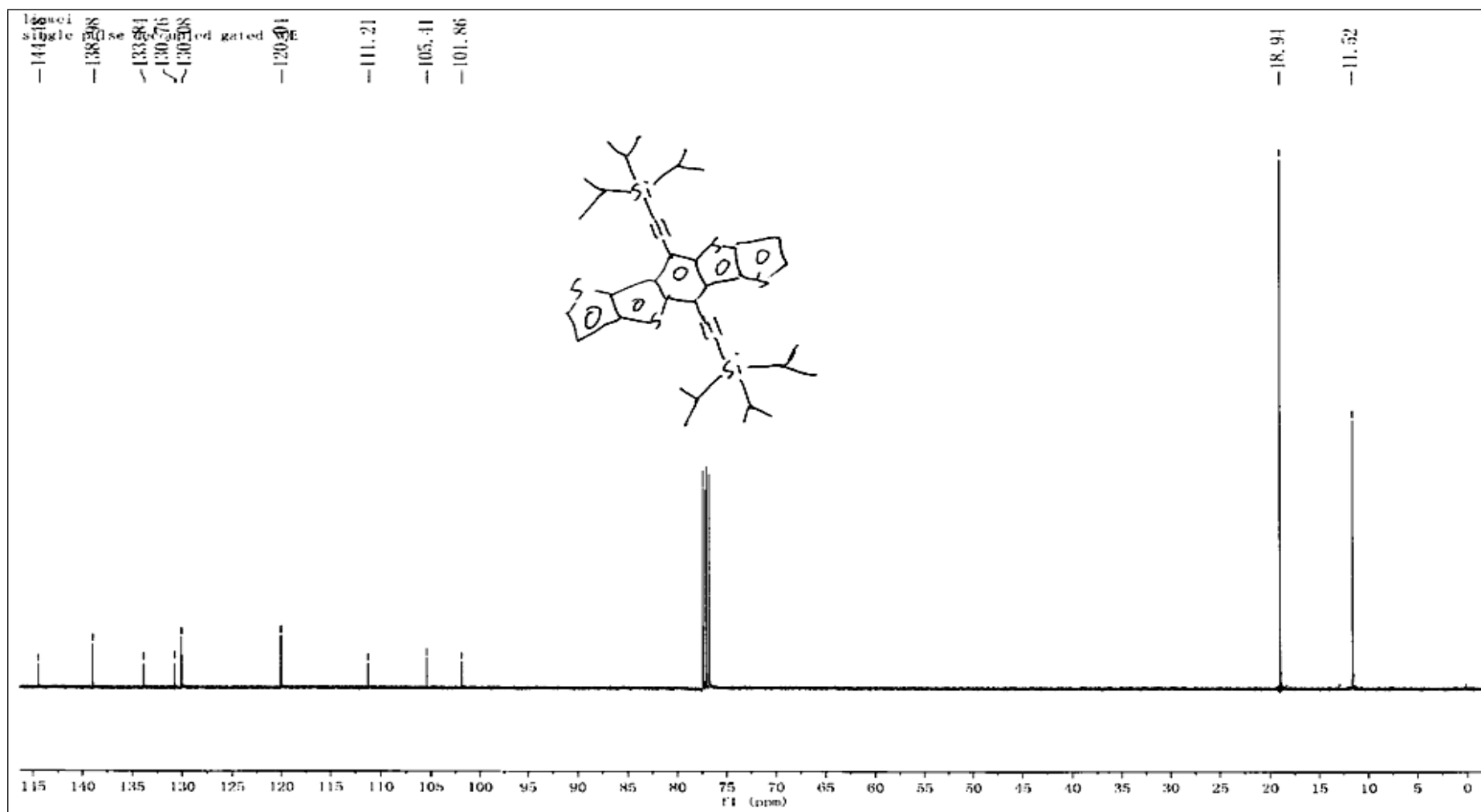


Fig. S30 <sup>13</sup>C NMR of 5,10-Bis(2-tri-*iso*-propylsilyl)ethynyl)dithieno[2,3-*d*:2',3'-*d'*] benzo[1,2-*b*:4,5-*b'*]dithiophene (DTBDT-TIPS).

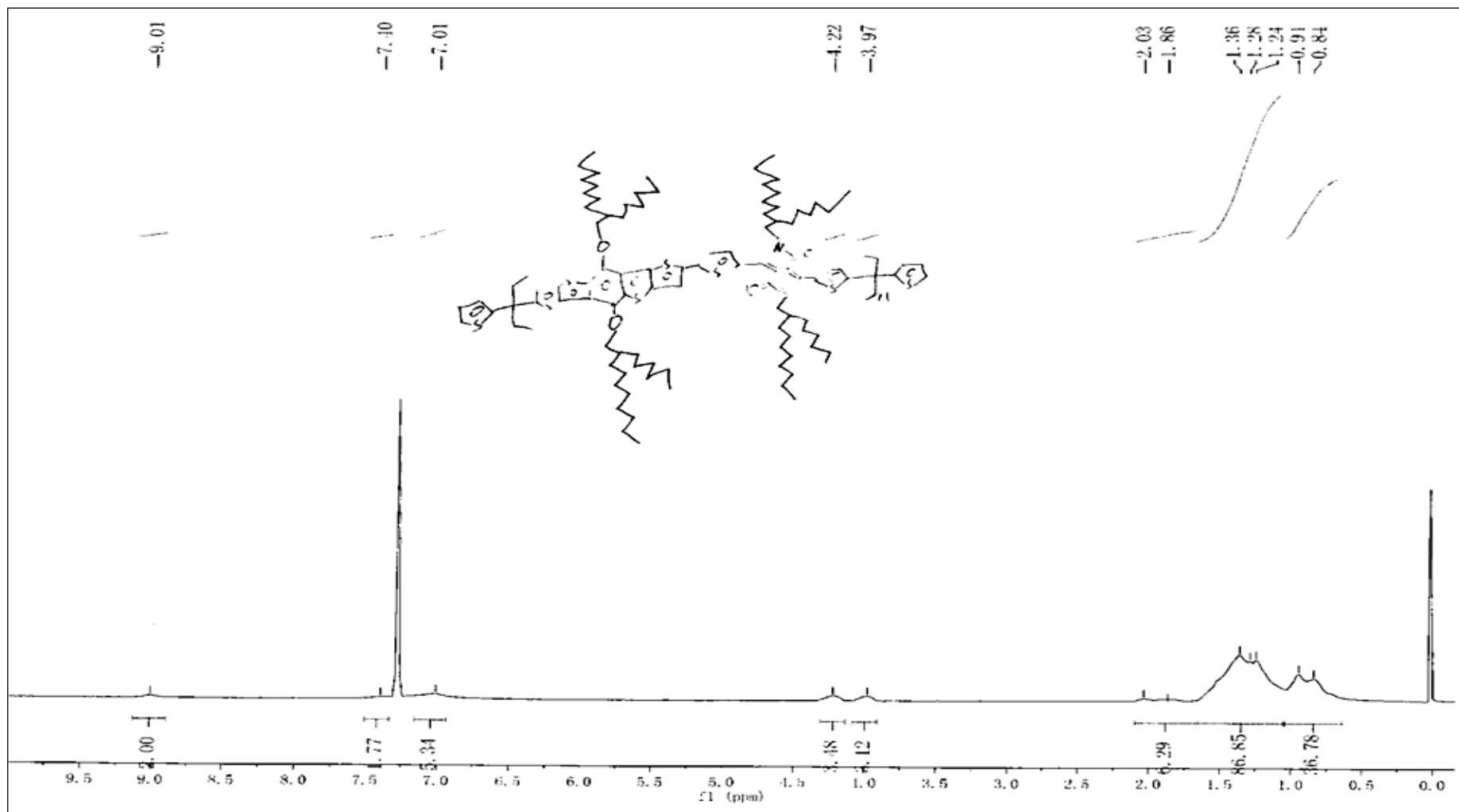


Fig. S31 <sup>1</sup>H-NMR spectra of PBT-HD-DPP-C16

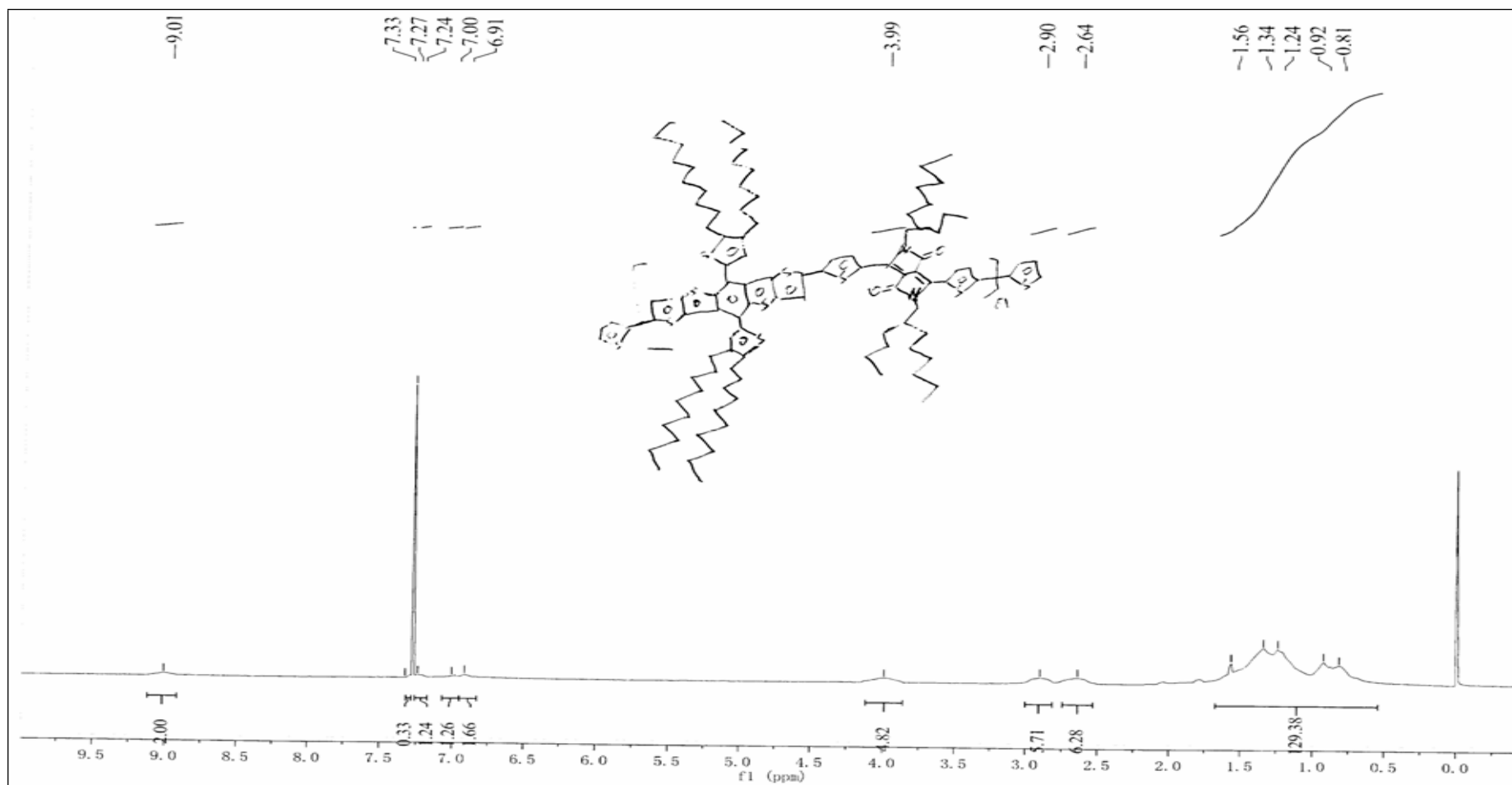


Fig. S32 <sup>1</sup>H-NMR spectra of PBT-T-DPP-C12



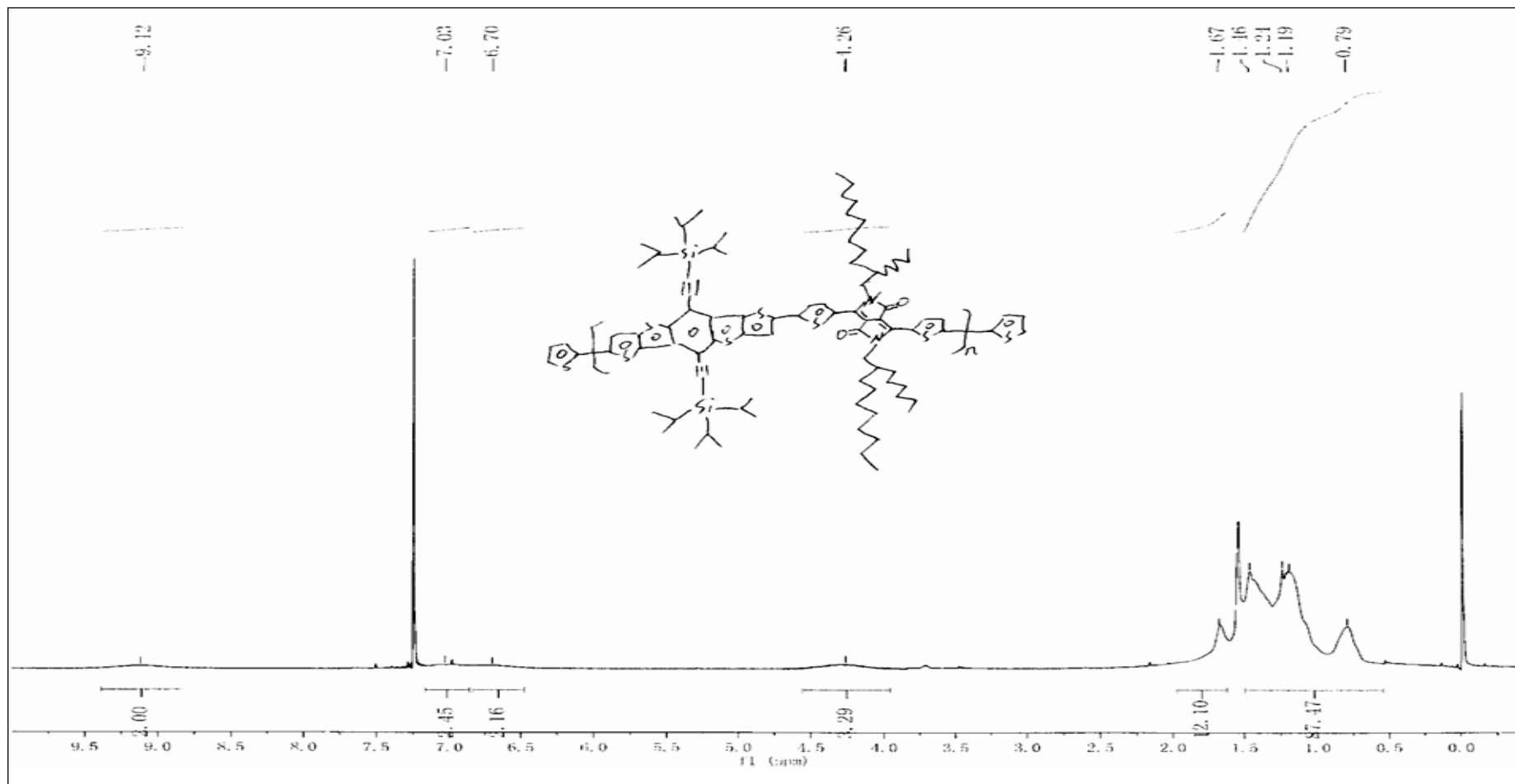


Fig. S33 <sup>1</sup>H-NMR spectra of PBT-TIPS-DPP-C16

## 5. Reference

- [1] L.S. Fuller, B. Iddon, and K. A. Smith, *J. Chem. Soc., Perkin Trans. 1*, 1997, 3465–3470
- [2] Sheldrick, G.M. SADABS. Program for Empirical Absorption Correction of Area Detector, University of Göttingen, Germany. **1996**.
- [3] Sheldrick, G. M. SHELXL97, Program for the Refinement of Crystal Structure, University of Göttingen, Germany, **1997**.