

*Supplementary Information for*

## Thiacycle-fused Benzo[1,2-*b*:4,5-*b'*]dithiophenes (BDTs): Synthesis, Packing, Molecular Orientation and Semiconducting Properties

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## Experimental section

### Materials

The chemical reagents and solvents were directly used as received from commercial companies without further purification except additional notification. **BDT** and compound **3** were prepared based on a literature reported method.<sup>S1</sup>

#### Synthesis of 2,6-bis(allylthio)-benzo[1,2-*b*, 4,5-*b'*]dithiophene (**1**)

In a 3-neck flask, compound **BDT** (500 mg, 2.63 mmol) and THF (200 mL, anhydrous) were added, and the resulted solution was bubbled with N<sub>2</sub> for 30 minutes. The system was cooled down to 0 °C in iced bath, and *n*-BuLi (1.6 M in hexane, 2.0 mL) was added dropwise over 5 minutes. The solution was maintained in iced-bath for further 30 minutes, and S<sub>8</sub> (105 mg, 3.26 mmol) was added in one portion. The solution was kept in iced-bath for 1 hour, after that *n*-BuLi (1.6 M in hexane, 2.0 mL) was added, and 30 minutes later, S<sub>8</sub> (105 mg, 3.26 mmol) was added again. After another 30 minutes, allyl bromide (1 mL, 11.82 mmol) was added, and the temperature of the solution was slowly increased to room temperature and kept overnight. After removing solvent, the crude product was purified by flash column chromatography (silica gel, hexane) to give pale yellow crystal (544mg, 61.9%). Mp, 113.8 °C (760 mmHg); <sup>1</sup>H NMR δ<sub>H</sub> (CDCl<sub>3</sub>, 400 MHz) 8.01 (2H, s, Ar-H), 7.28 (2H, s, Ar-H), 6.01~5.76 (2H, m, CH-H), 5.20~4.98 (4H, m, CH<sub>2</sub>-H), 3.65~3.49 (4H, d, J = 7.1 Hz, CH<sub>2</sub>-H); <sup>13</sup>C NMR δ<sub>C</sub> (CDCl<sub>3</sub>, 100 MHz) 138.92, 137.28, 137.02, 133.13, 127.63, 118.37, 115.63, 40.36; HR-MS (EI<sup>+</sup>) *m/z* [M<sup>+</sup>] found 333.9981, formula C<sub>16</sub>H<sub>14</sub>S<sub>4</sub> [M<sup>+</sup>] calc. 333.9978.

#### Synthesis of benzo[1,2-*f*:4,5-*f'*]bis(2*H*-3,4-dihydrothieno[2,3-*b*]thiopyran) (**α-HTPBDT**)

In a 3-neck flask, tetraline (50 mL) was added and bubbled with N<sub>2</sub> for 30 minutes and heated to reflux. **1** (400 mg, 1.20 mmol) was dissolved in tetraline (20 mL) and added in the flask dropwise over 15 minutes. The solution was kept under reflux for 4 hours, and after that tetraline (40 mL) was removed by N<sub>2</sub> bubbling, and the residue solution was cooled down to room temperature. After filtration, pale brown powder was obtained as crude product (142 mg, 35.5%), which was further purified by sublimation to give an off-white powder (135 mg, 33.8%). Mp, 160 °C

decomposes (760 mmHg);  $^1\text{H}$  NMR  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ , 400 MHz) 7.75 (2H, s, Ar-H), 3.25~3.09 (4H, t,  $J$  = 5.6 Hz,  $\text{CH}_2\text{-H}$ ), 2.94~2.76 (4H, t,  $J$  = 6.4 Hz,  $\text{CH}_2\text{-H}$ ), 2.42~2.19 (4H, m,  $\text{CH}_2\text{-H}$ );  $^{13}\text{C}$  NMR  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ , 100 MHz) 136.91, 134.65, 129.87, 124.03, 111.60, 28.63, 23.07, 22.64; HR-MS ( $\text{EI}^+$ )  $m/z$  [ $\text{M}^+$ ] found 333.9981, formula  $\text{C}_{16}\text{H}_{14}\text{S}_4$  [ $\text{M}^+$ ] calc. 333.9978.

#### Synthesis of 3,7-bis(allylthio)-benzo[1,2-*b*, 4,5-*b'*]dithiophene (**4**)

In a 3-neck flask degassed 3 times with argon (Ar),  $\text{CH}_2\text{Cl}_2$  (30 mL, anhydrous) and  $\text{S}_2\text{Cl}_2$  (1.5 mL, 18.78 mmol) were added successively. Compound **3** (1.09 g, 3.00 mmol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (30 mL, anhydrous) and added to the resulted solution dropwise over 35 minutes, and the system was kept at room temperature for further 4 hours.  $\text{CH}_2\text{Cl}_2$  was removed by  $\text{N}_2$  bubbling, and THF (90 mL, anhydrous) and MeOH (30 mL, anhydrous) were added, followed by addition of allyl bromide (12 mL, 138.90 mmol), and the system was cooled down to 0 °C.  $\text{NaBH}_4$  (2.7g, 71.40 mmol) was added in small portions, and the system was stirred overnight by slowly increasing the temperature to room temperature. The reaction was quenched by pouring solution into iced HCl (0.5 M, 200 mL), which was extracted with  $\text{CH}_2\text{Cl}_2$  (50 mL  $\times$  3). After the evaporation of solvents crude product was given, which was dissolved in THF (30 mL) and  $\text{Bu}_4\text{NF}$  (30 mL) was added. The solution was stirred at room temperature for 3 hours, and then poured into water and extracted with  $\text{CH}_2\text{Cl}_2$  (50 mL  $\times$  3). After evaporating solvents, crude product was obtained, which was further purified by column chromatograph (silica gel,  $\text{CH}_2\text{Cl}_2$ : hexane = 10:1) to give white solid (517 mg, yield 51.5%). Mp, 88.7 °C (760 mmHg);  $^1\text{H}$  NMR  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ , 400 MHz) 8.43 (2H, s, Ar-H), 7.54 (2H, s, Ar-H), 5.96~5.82 (2H, m, CH-H), 5.06~4.90 (4H, m,  $\text{CH}_2\text{-H}$ ), 3.53~3.47 (4H, d,  $J$  = 7.1 Hz,  $\text{CH}_2\text{-H}$ );  $^{13}\text{C}$  NMR  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ , 100 MHz) 137.49, 137.40, 133.71, 129.99, 124.97, 117.93, 116.64, 38.13; HR-MS ( $\text{EI}^+$ )  $m/z$  [ $\text{M}^+$ ] found 333.9973, formula  $\text{C}_{16}\text{H}_{14}\text{S}_4$  [ $\text{M}^+$ ] calc. 333.9978.

#### Synthesis of benzo[1,2-*g*:4,5-*g'*]bis(2*H*-3,4-dihydrothieno[3,2-*b*]thiopyran) ( $\beta$ -HTPBDT)

To a 3-neck flask degassed 3 times with argon (Ar), tetraline (50 mL) was added and heated to reflux. Then **4** (540 mg, 1.62 mmol) was dissolved in tetraline (10 mL) and added dropwise over 15 minutes, and the system was kept under reflux for 12 hours. After that, tetraline was removed by  $\text{N}_2$  bubbling to give a brown solid as crude product (360mg, 66.7%). The crude product was washed by  $\text{Et}_2\text{O}$  (20 mL) and purified by sublimation to give an off-white solid, which was further recrystallized in toluene and washed with  $\text{CHCl}_3$  (3 mL  $\times$  3) to give the pure product (110 mg,

20.4%). Mp, 218 °C decomposes (760 mmHg); <sup>1</sup>H NMR δ<sub>H</sub> (CDCl<sub>3</sub>, 400 MHz) 7.90 (2H, s, Ar-H), 3.21~3.08 (4H, t, J = 5.6 Hz, CH<sub>2</sub>-H), 3.04~2.92 (4H, t, J = 6.3 Hz, CH<sub>2</sub>-H), 2.39~2.26 (4H, m, CH<sub>2</sub>-H); <sup>13</sup>C NMR δ<sub>C</sub> (CDCl<sub>3</sub>, 100 MHz) 135.83, 134.31, 129.26, 118.74, 113.82, 26.32, 25.21, 23.84; HR-MS (EI<sup>+</sup>) *m/z* [M<sup>+</sup>] found 333.9979, formula C<sub>16</sub>H<sub>14</sub>S<sub>4</sub> [M<sup>+</sup>] calc. 333.9978.

#### Synthesis of 2,6-bis(2-chloroethylthio)-3,7-bis(methylthio)-benzo[1,2-*b*, 4,5-*b'*]dithiophene (**6**)

In a 3-neck flask, **β-MT-BDT** (290 mg, 1.03 mmol) was added. The flask was degassed with Ar 3 times, then THF (60 mL, anhydrous) was added, and the system was cooled down to 0 °C. *n*-BuLi (1.6 M, 1.3 mL) was added dropwise, and the system was stirred at 0 °C for 30 minutes. S<sub>8</sub> (66 mg, 2.06 mmol) was added in one portion, and the system was kept at room temperature for 1 hour. After that, the system was cooled down to 0 °C again, *n*-BuLi (1.6 M, 2 mL) was added, and the temperature was kept at 0 °C for another 30 minutes. S<sub>8</sub> (99 mg, 3.10 mmol) was added in one portion, and the system was stirred at room temperature for another 1 hour. Then the system was cooled down to 0 °C, 1-bromo-2-chloroethane (1.7 mL, 20.40 mmol) was added slowly, and the temperature was slowly increased to room temperature and kept at room temperature overnight. The reaction was quenched by water, and the crude product could be obtained by evaporating solvents, which was further purified by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>: hexane = 1:1) to give pure product (226 mg, 46.5%). Mp, 171.1 °C (760 mmHg); <sup>1</sup>H NMR δ<sub>H</sub> (CDCl<sub>3</sub>, 400 MHz) 8.28 (2H, s, Ar-H), 3.80~3.70 (4H, t, J = 7.6 Hz, CH<sub>2</sub>-H), 3.45~3.34 (4H, t, J = 7.6 Hz, CH<sub>2</sub>-H), 2.41 (6H, s, SCH<sub>3</sub>-H); <sup>13</sup>C NMR δ<sub>C</sub> (CDCl<sub>3</sub>, 100 MHz) 141.52, 138.49, 137.09, 128.59, 115.97, 42.37, 37.81, 18.67; HR-MS (EI<sup>+</sup>) *m/z* [M<sup>+</sup>] found 469.8950, formula C<sub>16</sub>H<sub>14</sub>S<sub>4</sub> [M<sup>+</sup>] calc. 469.8953.

#### Synthesis of benzo[1,2-*g*:4,5-*g'*]bis(thieno[2,3-*b*][1,4]dithiin) (**BEDT-BDT**)

In a single-neck flask, compound **6** (237 mg, 0.50 mmol) was added, and the system was degassed 3 times with Ar. DMF (30 mL, anhydrous) and NaI (1 g, 6.67 mmol) was added successively. The system was refluxed overnight. After that, it was cooled down to room temperature, and water was added. Precipitate was collected by filtration as crude product, which was further purified by recrystallization from CHCl<sub>3</sub> and sublimation to give pure product (164 mg, 70.4%). Mp, 255 °C decomposes (760 mmHg); <sup>1</sup>H NMR δ<sub>H</sub> (CDCl<sub>3</sub>, 400 MHz) 7.79 (2H, s, Ar-H), 3.45 (8H, s, CH<sub>2</sub>-H); <sup>13</sup>C NMR δ<sub>C</sub> (CDCl<sub>3</sub>, 100 MHz) 135.75, 133.76, 116.17, 112.15, 28.83, 26.74; HR-MS (EI<sup>+</sup>) *m/z* [M<sup>+</sup>] found 369.9105, formula C<sub>16</sub>H<sub>14</sub>S<sub>4</sub> [M<sup>+</sup>] calc. 369.9107.

Synthesis of 2,6-bis(1-chloromethylthio)-3,7-bis(methylthio)-benzo[1,2-*b*, 4,5-*b'*]dithiophene (**7**)

Compound **7** was synthesized following the procedure in the synthesis of compound **6**, with  **$\beta$ -MT-BDT** (442 mg, 1.56 mmol), *n*-BuLi (1.6M, 2 mL, 1<sup>st</sup> addition & 1.6 M, 3 mL, 2<sup>nd</sup> addition), S<sub>8</sub> (99 mg, 3.10 mmol, 1<sup>st</sup> addition & 149 mg, 4.66 mmol, 2<sup>nd</sup> addition), bromochloromethane (2.2 mL, 32.81 mmol) in THF (70 mL, anhydrous). The crude solution was quenched by water, and organic solvent was evaporated to give the crude product, which was washed by ether to give the target product (368 mg, 53.2%). Mp, 180.2 °C (760 mmHg); <sup>1</sup>H NMR  $\delta_{\text{H}}$  (CDCl<sub>3</sub>, 400 MHz) 8.38 (2H, s, Ar-H), 5.08 (4H, s, CH<sub>2</sub>-H), 2.42 (6H, s, SCH<sub>3</sub>-H); <sup>13</sup>C NMR  $\delta_{\text{C}}$  (CDCl<sub>3</sub>, 100 MHz) 139.86, 138.49, 137.93, 130.38, 116.71 50.66, 19.23; HR-MS (EI<sup>+</sup>) *m/z* [M<sup>+</sup>] found 441.8635, formula C<sub>16</sub>H<sub>14</sub>S<sub>4</sub> [M<sup>+</sup>] calc. 441.8640.

Synthesis of benzo[1,2-*f*:4,5-*f'*]bis(2*H*-thieno[2,3-*d*][1,3]dithiole) (**BMDT-BDT**)

**BMDT-BDT** was synthesized following the same procedure for the synthesis of **BEDT-BDT**, with compound **7** (405 mg, 0.91 mmol), NaI (1.5 g, 10.01 mmol) in DMF (50 mL, anhydrous), to yield target product (246 mg, 78.7%). Mp, 242 °C decomposes (760 mmHg); <sup>1</sup>H NMR  $\delta_{\text{H}}$  (1,1,2,2-C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 400 MHz) 7.70 (2H, s, Ar-H), 5.11 (4H, s, CH<sub>2</sub>-H); <sup>13</sup>C NMR can not be obtained because of its low solubility; HR-MS (EI<sup>+</sup>) *m/z* [M<sup>+</sup>] found 341.8790, formula C<sub>16</sub>H<sub>14</sub>S<sub>4</sub> [M<sup>+</sup>] calc. 341.8794.

## Methods & Instruments

Nuclear magnetic resonance (NMR) spectra were obtained through a JEOL Lambda 400 spectrometer operating at 400 MHz for <sup>1</sup>H or 100 MHz for <sup>13</sup>C with TMS as internal reference. HR-MS was carried out in Materials Characterization Support Unit, RIKEN Advanced Technology Support Division. Melting points were uncorrected. UV-vis spectra were recorded on a Shimadzu UV-3600 spectrometer. Cyclic voltammograms (CVs) were recorded on a ALS Electrochemical Analyzer Model 612D in benzonitrile with tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>, 0.1 M) as supporting electrolyte at a scanning rate of 100 mV/s. Pt was used as working and counter electrodes, and Ag/AgCl was used as reference electrode. Ferrocene/ferrocenium redox couple (Fc<sup>+</sup>/Fc) was used as external reference. Differential scanning calorimetry (DSC) was carried out on a Seiko Instruments EXSTAR6000 (SII Nanotechnology,

Inc.) at a cooling and heating rate of 10 °C min<sup>-1</sup>. The decomposition temperatures of the compounds determined from DSC diagrams were derived from the peak temperatures at the corresponding decomposition peaks. Single-crystal chromatography was carried on a Rigaku Rapid-IP (MoK $\alpha$  radiation,  $\lambda = 0.71069$  Å, graphite monochromator,  $T = -180$  °C,  $2\theta_{\max} = 55.0^\circ$ ). The structure was solved by direct methods. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in the calculations but not refined. All calculations were performed using the crystallographic software package CrystalStructures4.2.<sup>S2</sup> Theoretical calculations were carried out by DFT method at the B3LYP/6-31G(d) level using Gaussian 09 program package.<sup>S3</sup> Thin film X-Ray Diffractions (XRD) patterns were obtained with a Rigaku RINT-2200 diffractometer with a Cu K $\alpha$  source ( $\lambda = 1.541$  Å) in air. Dynamic force-mode atomic force microscopic images were obtained with Nanocute scanning probe microscope system (SII Nanotechnology, Inc.) by using a canti-lever, SI-DF20 (Seiko Instruments Inc.) OFETs were fabricated on heavily doped n<sup>+</sup>-Si (100) wafer with a 200 nm thermally grown SiO<sub>2</sub> ( $C_i = 17.3$  nF cm<sup>-2</sup>). The substrate surface was treated with octadecyltrichlorosilane (ODTS) for  **$\alpha$ -HTPBDT**,  **$\beta$ -HTPBDT** & **BEDT-BDT**, and hexamethyldisilazane (HMDS) for **BMDT-BDT**, respectively. Thin films of the compounds was vacuum-deposited on the Si/SiO<sub>2</sub> substrates maintained at rate of 1 Å s<sup>-1</sup> under pressure of  $\sim 10^{-3}$  Pa. On the top of the organic thin film, gold (80 nm) as drain and source electrodes were deposited through a shadow mask with channel length (L) and width (W) as 50  $\mu$ m and 1500  $\mu$ m, respectively. Characteristics of the OFETs were measured at room temperature under ambient conditions with a Keithley 4200 semiconducting parameter analyzer. Field-effect mobility ( $\mu$ ) was calculated in the saturation regime using the following equation,  $I_D = C_i \mu (W/2L)(V_G - V_{th})^2$ , where  $C_i$  is the capacitance of the SiO<sub>2</sub> insulator, and  $V_G$  and  $V_{th}$  are the gate and threshold voltages, respectively.

# Figures

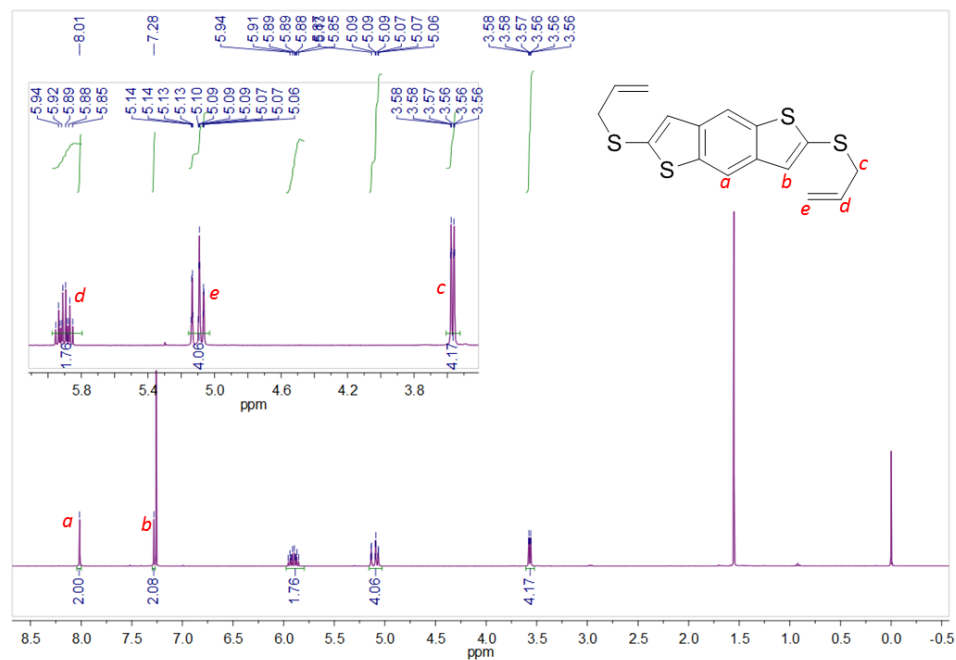


Figure S1.  $^1\text{H}$  NMR spectra of **1**.

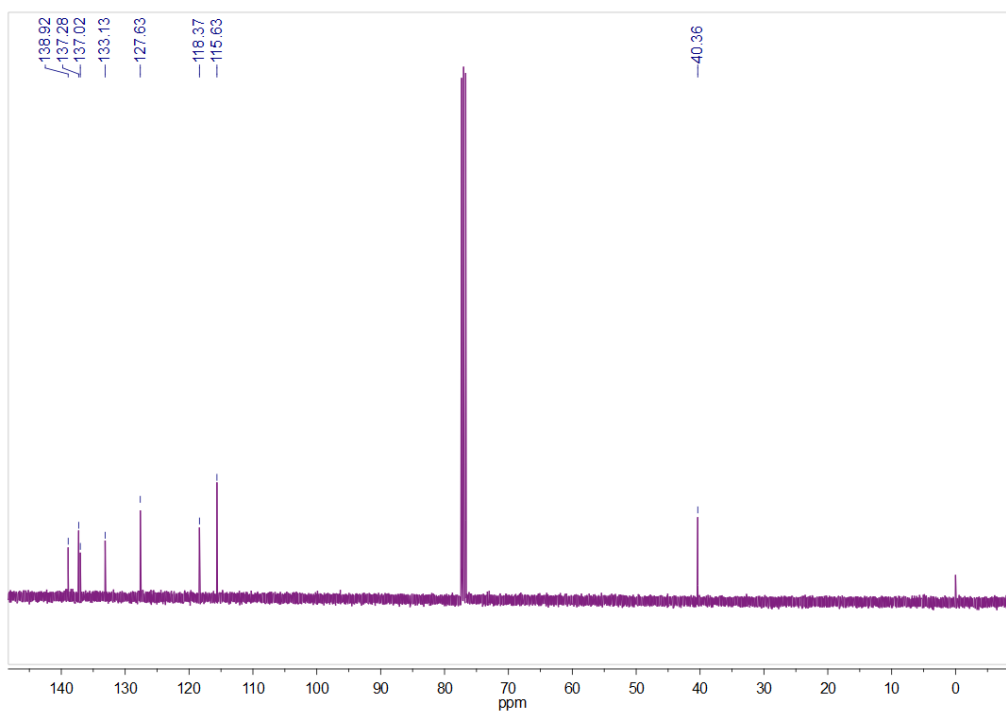


Figure S2.  $^{13}\text{C}$  NMR spectra of **1**.

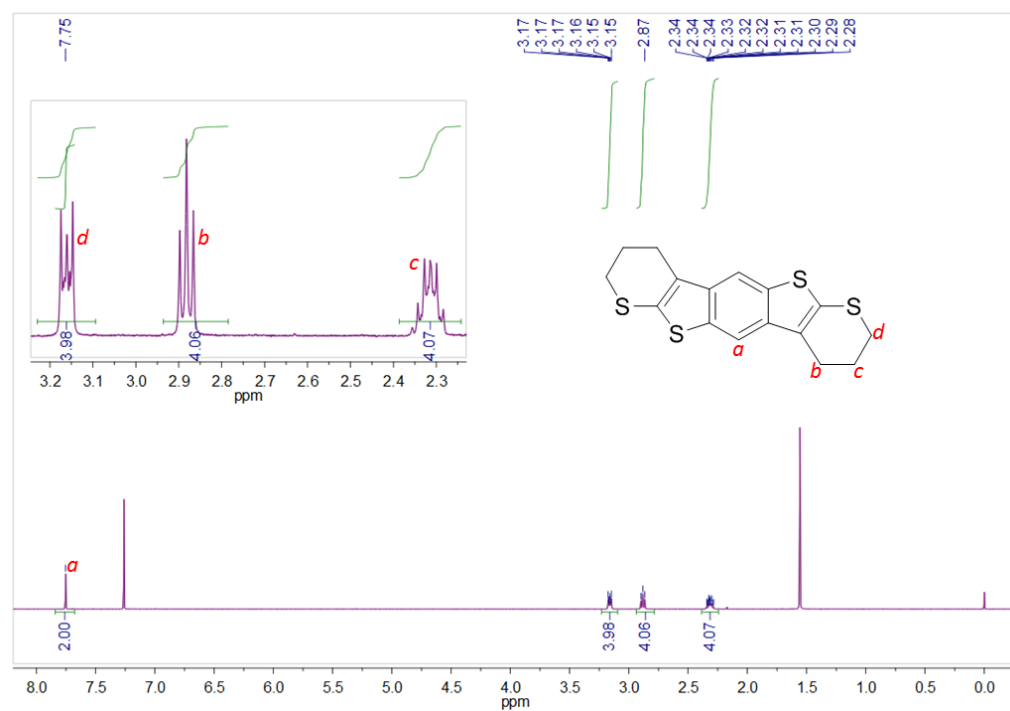


Figure S3. <sup>1</sup>H NMR spectra of  $\alpha$ -HTPBDT.

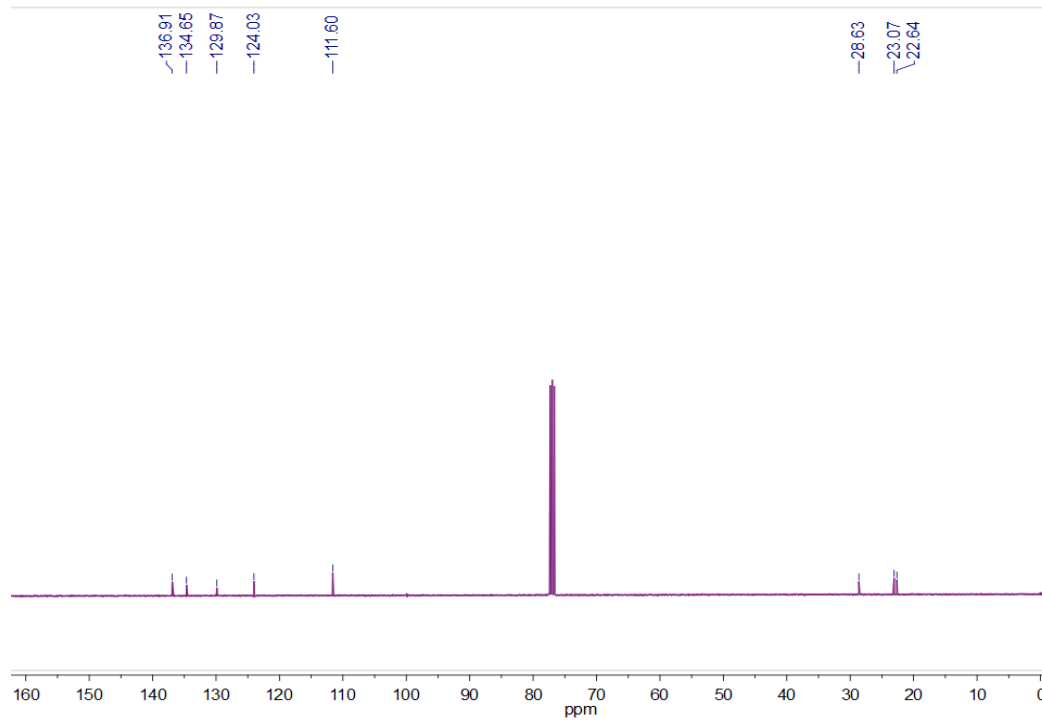


Figure S4. <sup>13</sup>C NMR spectra of  $\alpha$ -HTPBDT.



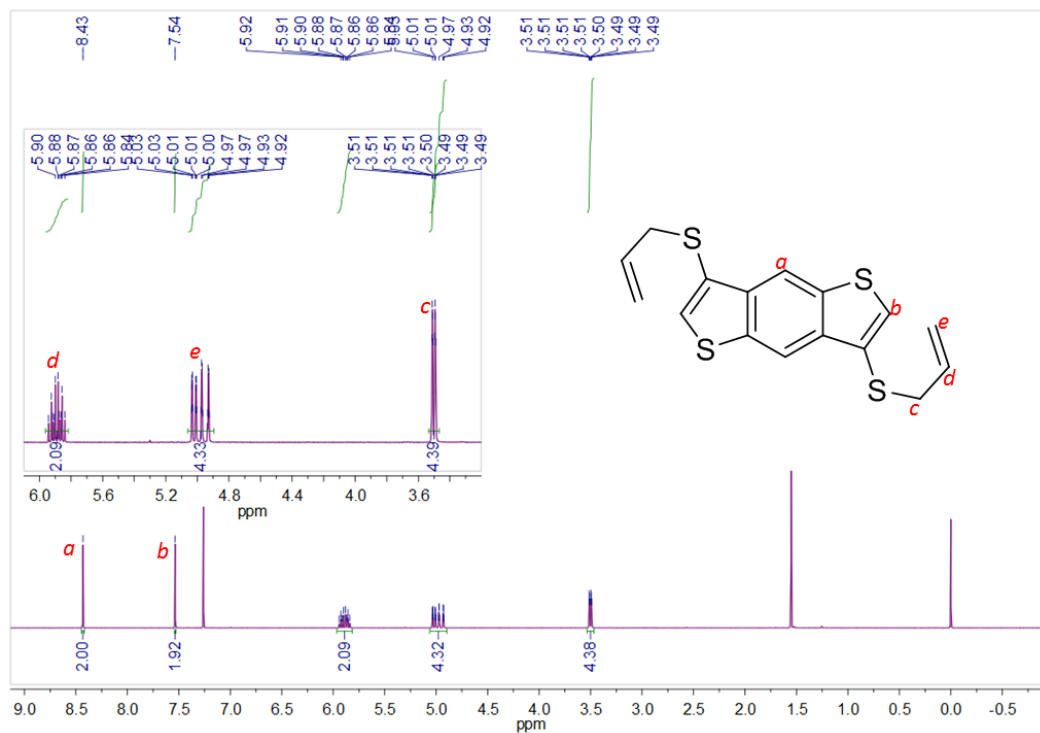


Figure S5. <sup>1</sup>H NMR spectra of **4**.

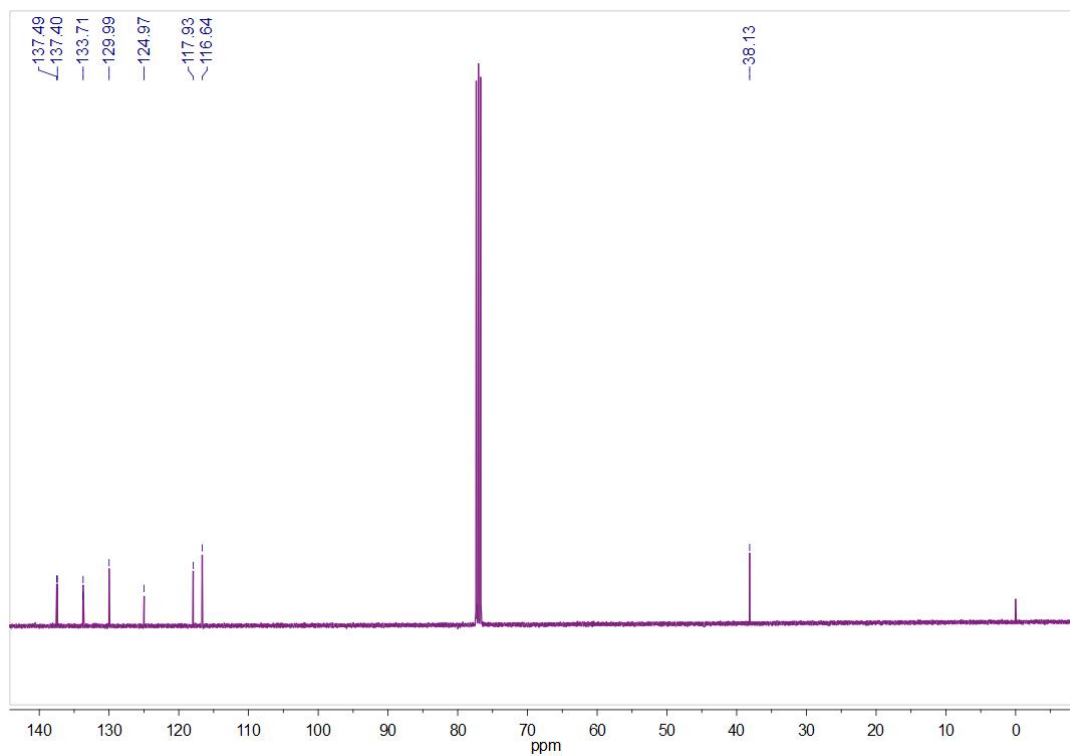


Figure S6. <sup>13</sup>C NMR spectra of **4**.

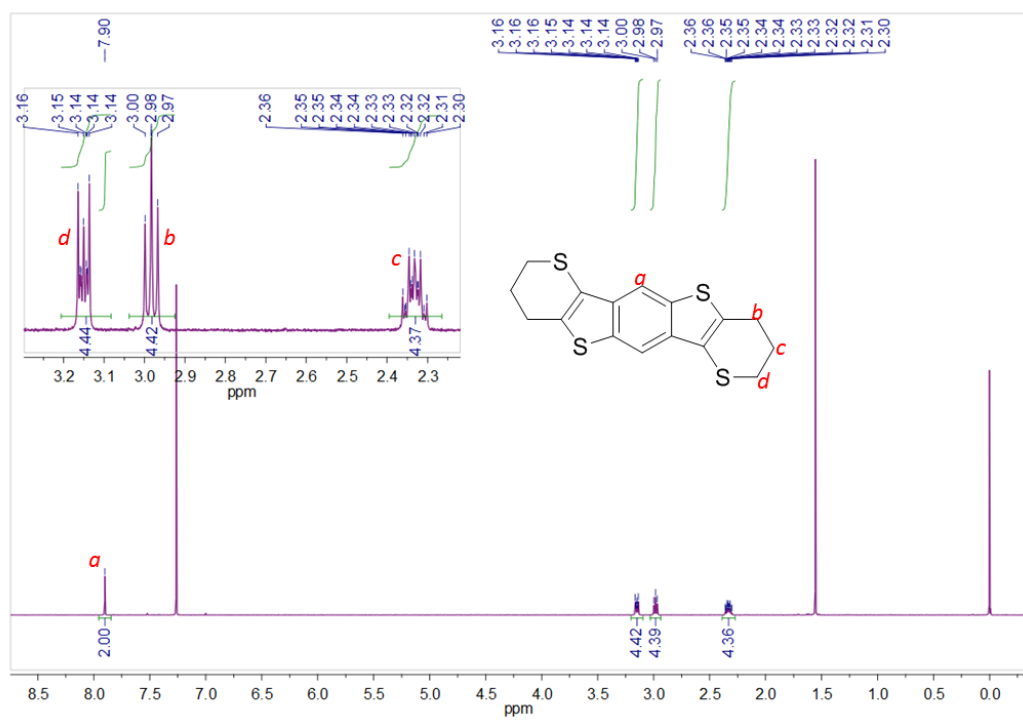


Figure S7.  $^1\text{H}$  NMR spectra of  $\beta$ -HTPBDT.

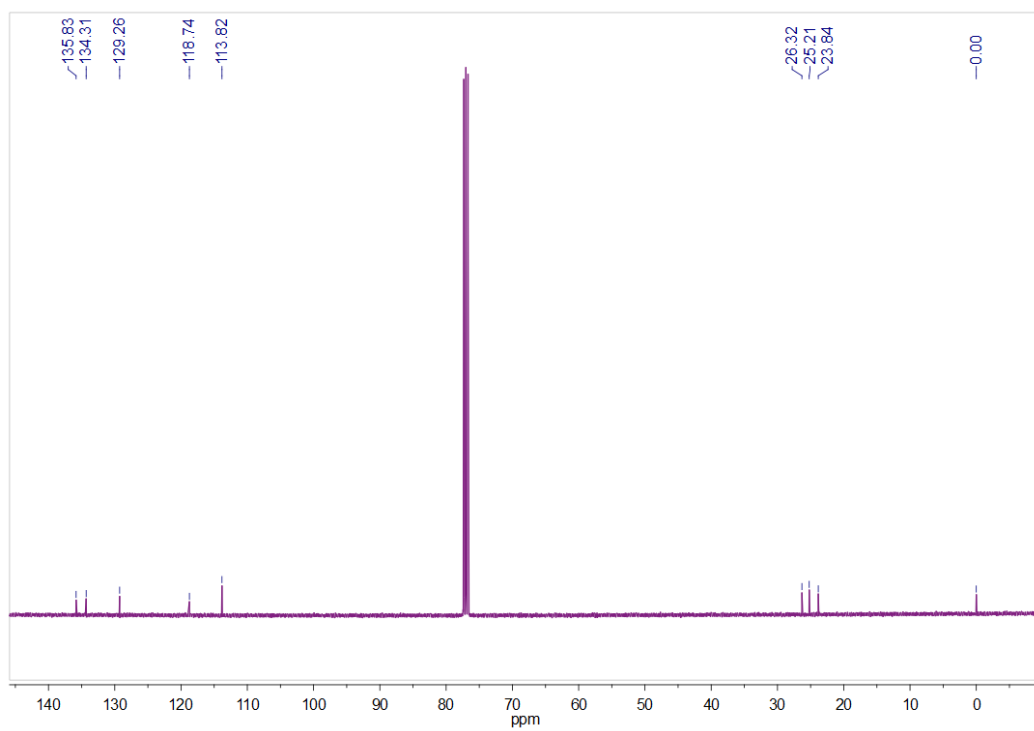


Figure S8.  $^{13}\text{C}$  NMR spectra of  $\beta$ -HTPBDT.

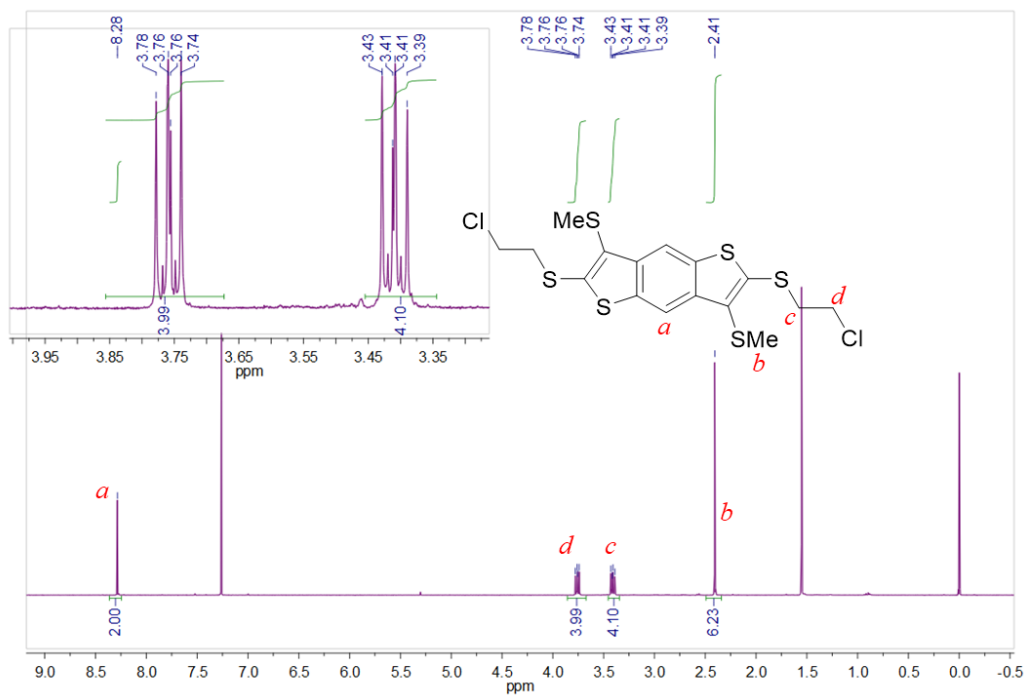


Figure S9. <sup>1</sup>H NMR spectra of **6**.

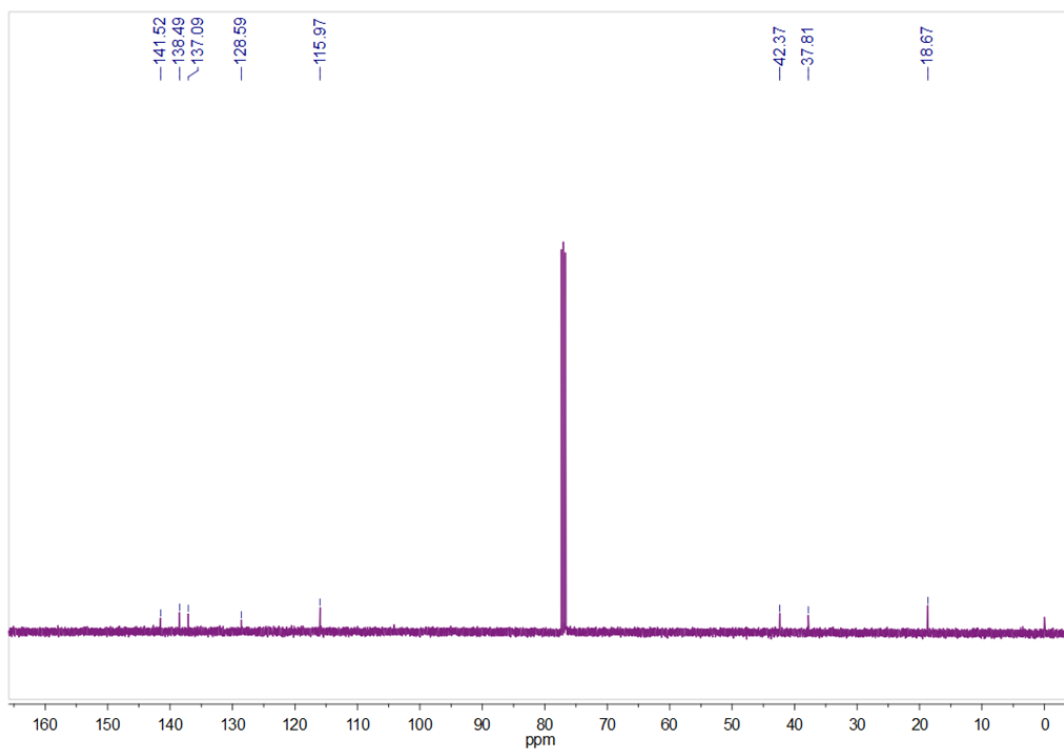


Figure S10. <sup>13</sup>C NMR spectra of **6**.

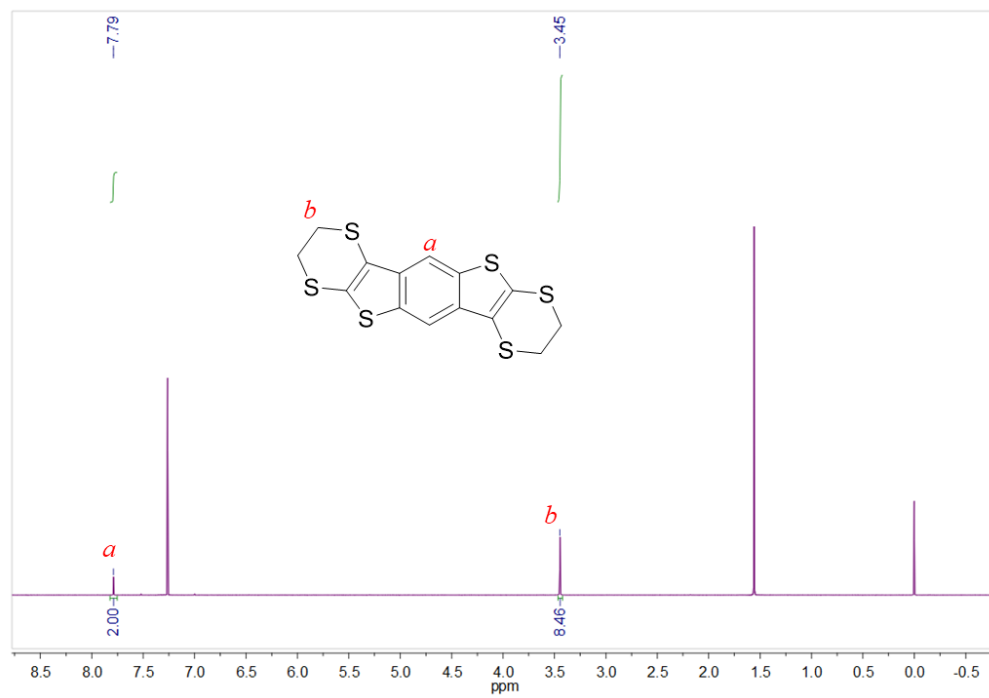


Figure S11.  $^1\text{H}$  NMR spectra of **BEDT-BDT**.

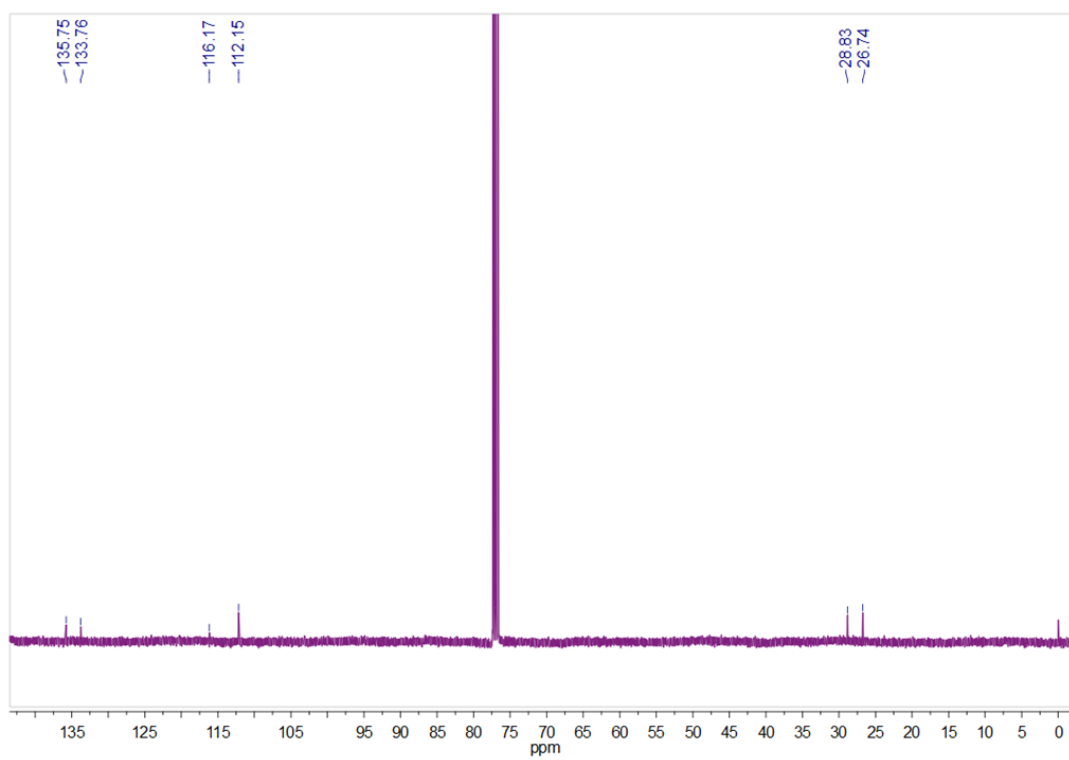


Figure S12.  $^{13}\text{C}$  NMR spectra of **BEDT-BDT**.

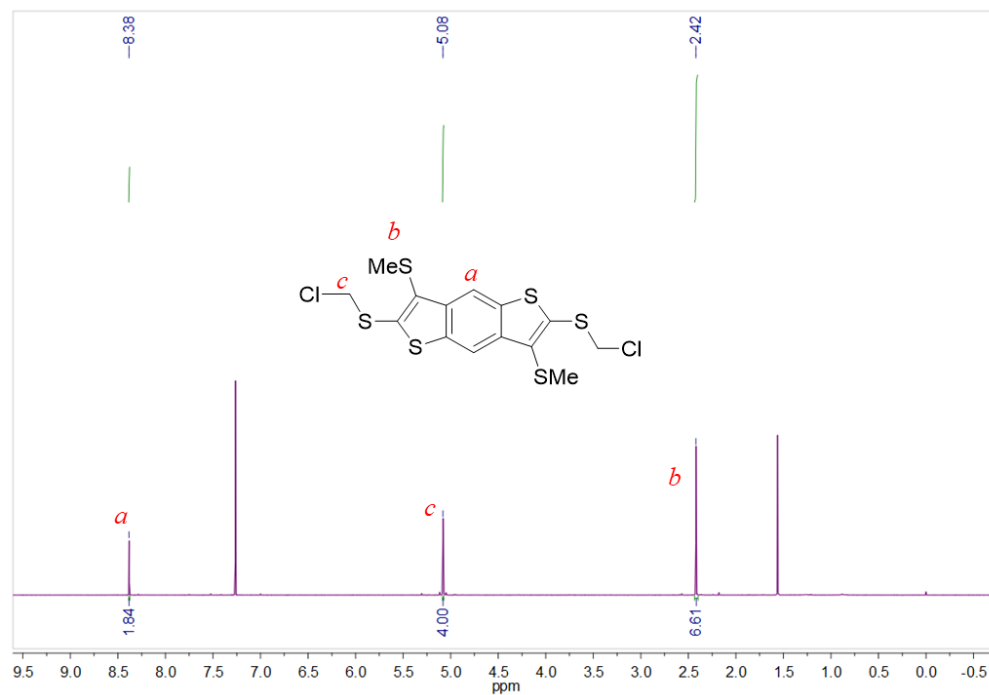


Figure S13. <sup>1</sup>H NMR spectra of **7**.

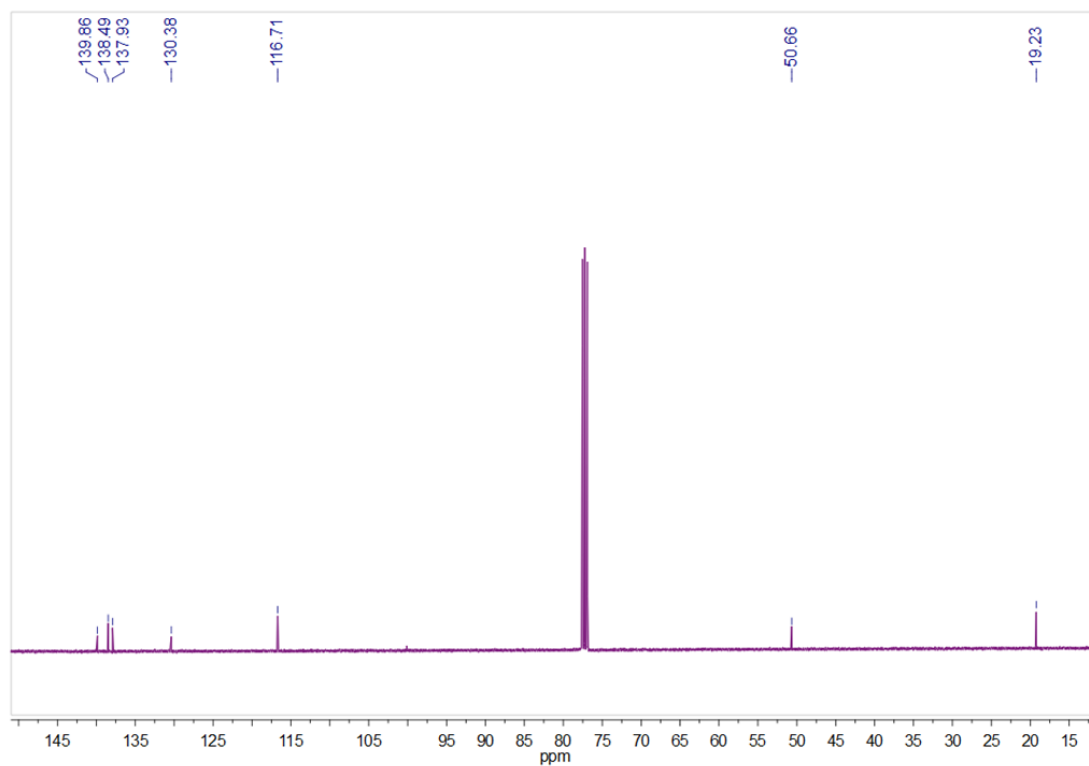


Figure S14. <sup>13</sup>C NMR spectra of **7**.



Figure S15. <sup>1</sup>H NMR spectra of **BMDT-BDT**.

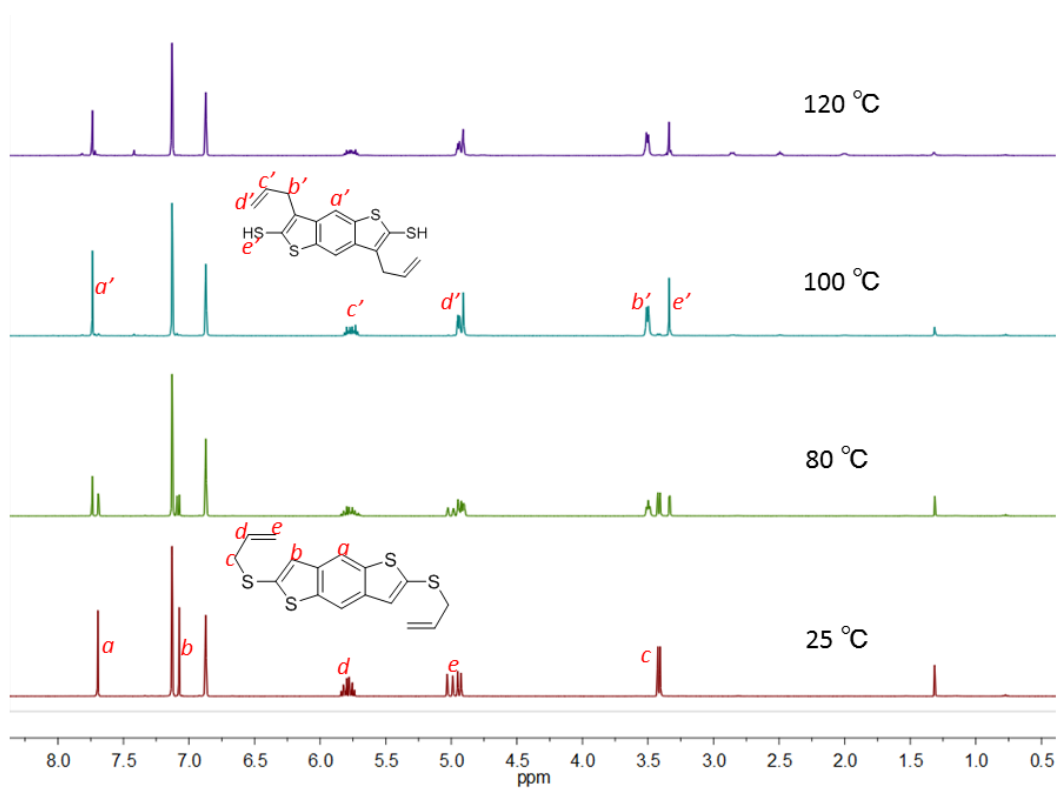


Figure S16. [3,3]-sigmatropic rearrangement of **1** in *o*-DCB-*d*<sub>4</sub>.

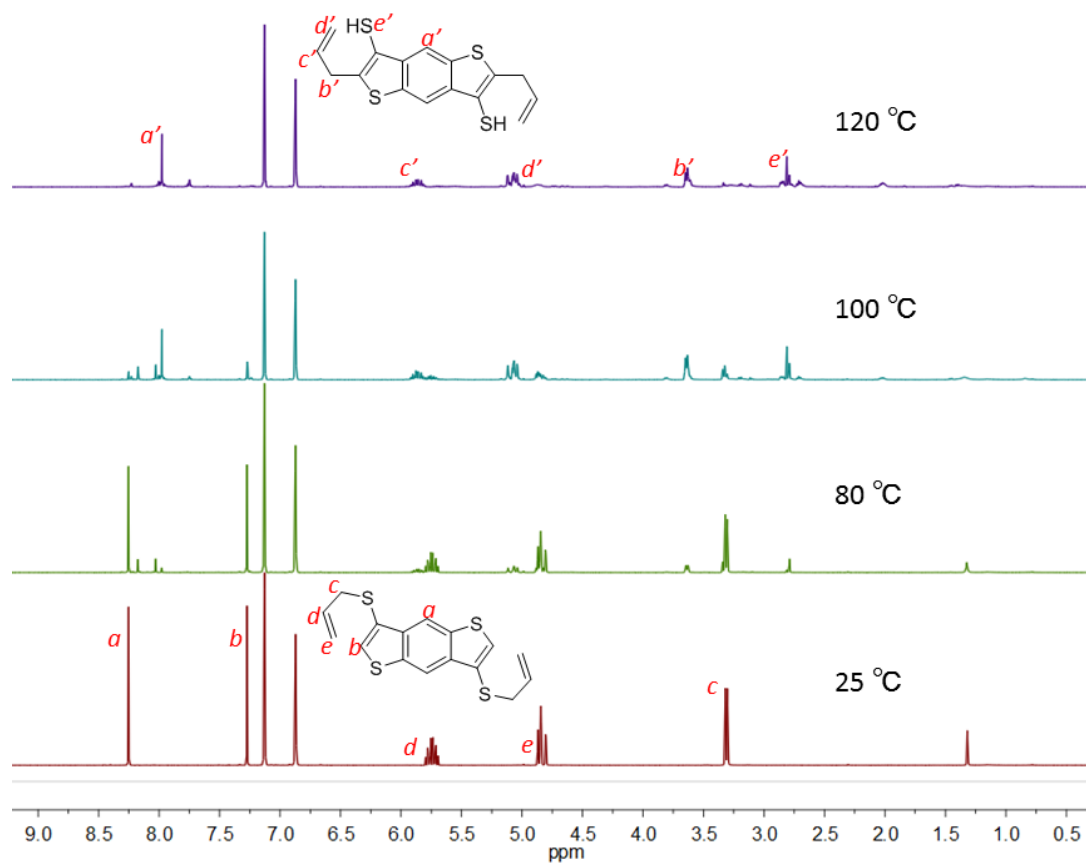


Figure S17. [3,3]-sigmatropic rearrangement of **4** in *o*-DCB- $d_4$ .

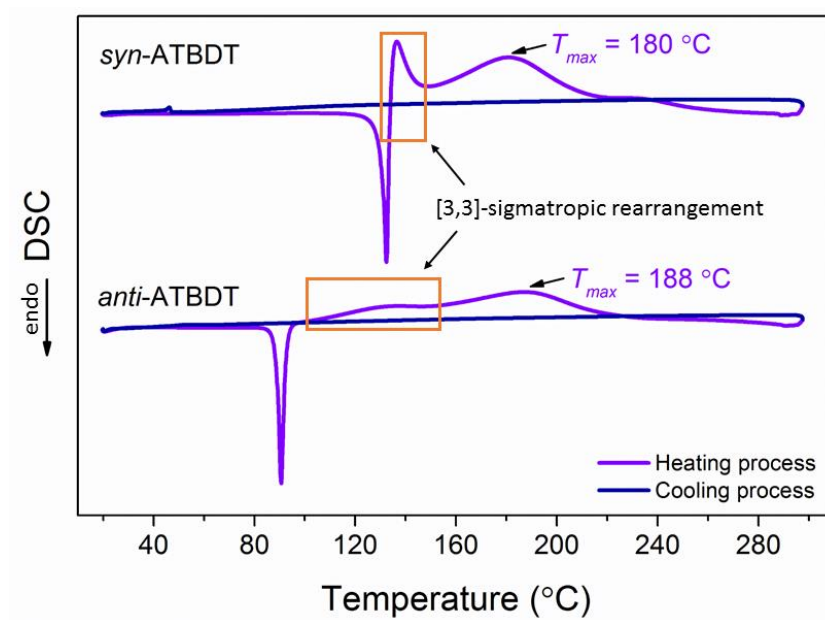


Figure S18. DSC diagrams of **1** & **4**.

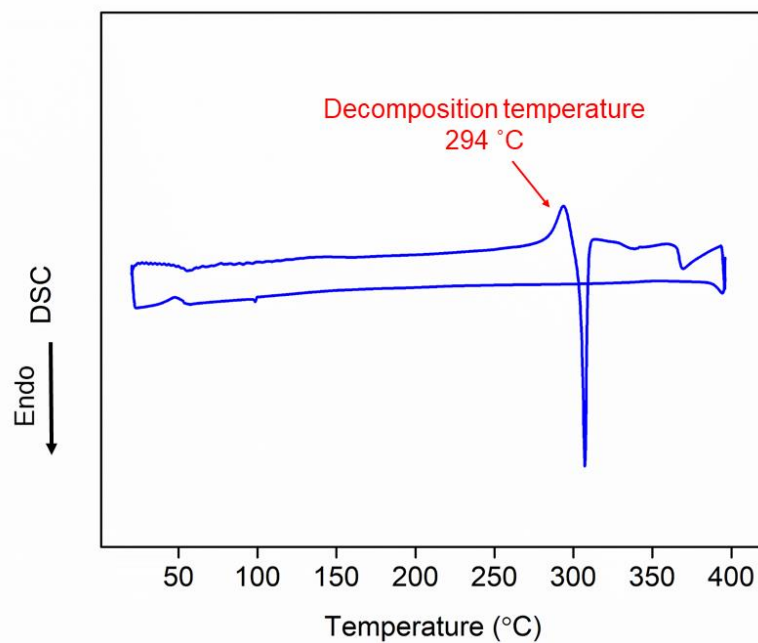


Figure S19. DSC diagrams of  $\alpha$ -HTPBDT.

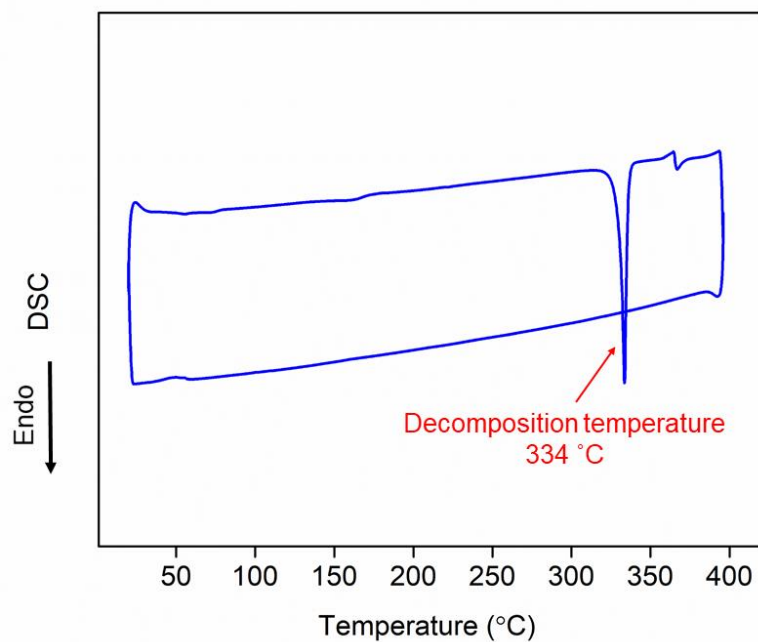


Figure S20. DSC diagrams of  $\beta$ -HTPBDT.



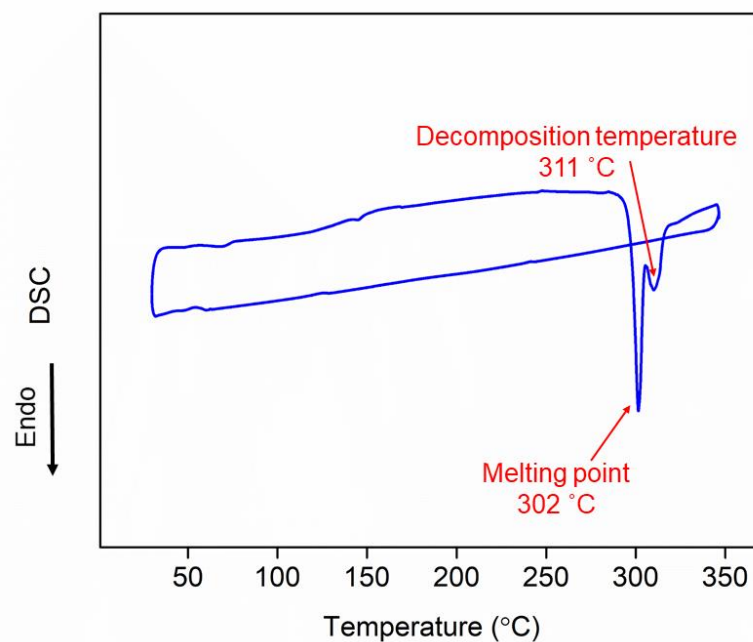


Figure S21. DSC diagrams of **BEDT-BDT**.

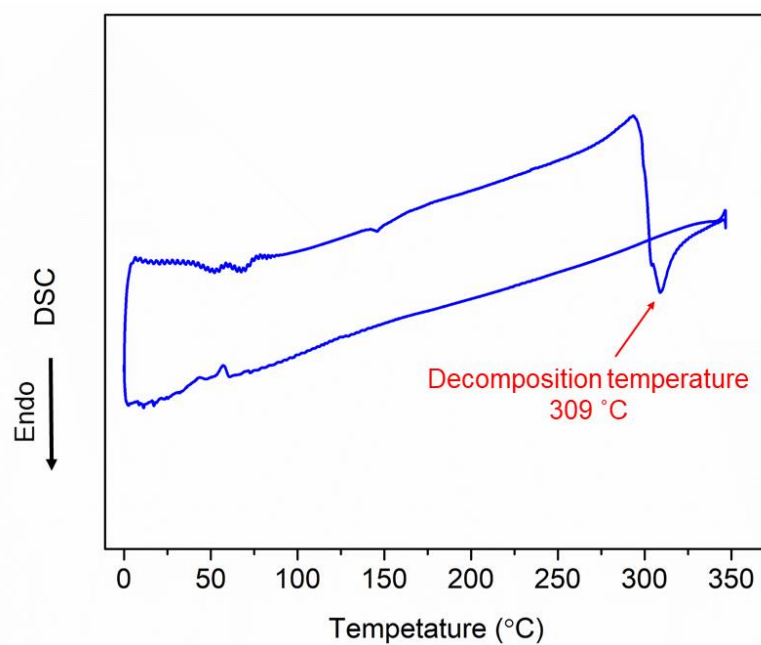


Figure S22. DSC diagrams of **BMDT-BDT**.

## References

S1. Takimiya, K.; Konda, Y.; Ebata, H.; Niihara, N.; Otsubo, T., Facile Synthesis, Structure, and Properties of Benzo[1,2-b:4,5-b']dichalcogenophenes. *J. Org. Chem.*, 2005, **70**, 10569-10571.

S2. Rigaku Cooperation crystal structure analysis package,  
<https://www.rigaku.com/ja/products/protein/cs>.

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