

Supporting Information for:

## **Versatile Strategy to Direct Access 4,8-Functionalized Benzo[1,2-b:4,5-b']difurans for Organic Electronics**

Linyi Bian, Jiefeng Hai, Enwei Zhu, Jiangsheng Yu, Yun Liu, Jie Zhou, Guidong Ge, Weihua Tang

### **Table of content**

1. Experimental.....	S2
2. UV-vis absorption spectra of BDF monomers in thin films.....	S9
3. Polymerization results and thermal properties of copolymers.....	S10
4. UV-vis spectra of BDF-based copolymers.....	S11
5. Photovoltaic device fabrication and characterization.....	S11
6. <sup>1</sup> H NMR and <sup>13</sup> C NMR spectra.....	S12

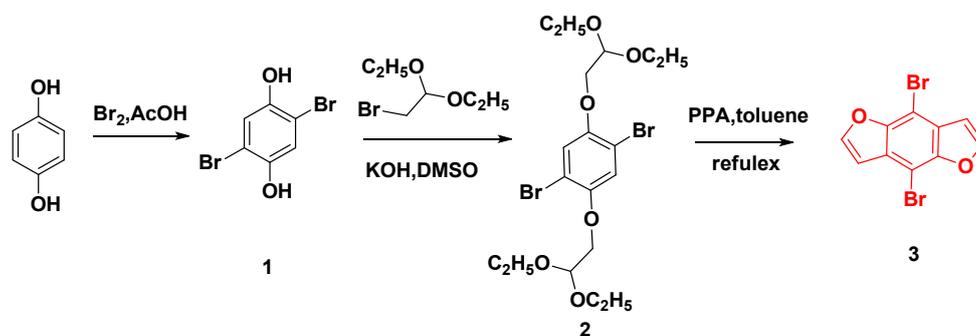
## 1. Experimental

### 1.1. General Details.

All starting materials and reagents were obtained from commercial sources and used without further purification unless otherwise noted. Tetrahydrofuran (THF) and toluene were distilled from sodium prior to use. N, N-Dimethylformamide (DMF) and acetonitrile were dried and distilled from CaH<sub>2</sub>. All reactions were performed under N<sub>2</sub> atmosphere unless otherwise stated.

All compounds were characterized by <sup>1</sup>H NMR and <sup>13</sup>C NMR on a Bruker AVANCE III 500MHz instrument. High-resolution EI mass spectra were recorded using a Finnigan MAT 95 XP spectrometer. Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were obtained on a Bruker Autoflex TOF/TOF instrument using dithranol as the matrix. Number average (*M<sub>n</sub>*) and weight average (*M<sub>w</sub>*) molecular weights were determined by size exclusion chromatography (SEC) using a Waters 717-2410 with polystyrenes as reference standard and THF as an eluent. Thermogravimetric analyses (TGA) were carried out with a TA instrument TGA/SDTA851e with heating rate of 10°C min<sup>-1</sup> under nitrogen gas flow. The temperature of degradation (*T<sub>d</sub>*) corresponds to a 5% weight loss. UV-Visible absorption spectra were taken using a UV-vis instrument Evolution 220. For solid state measurements, polymer solution in chloroform was cast on quartz plates. Cyclic voltammetry measurements were carried out using a CHI Instruments Model CHI 600D electrochemical workstation equipped with a standard three-electrode configuration. The measurements were taken in anhydrous acetonitrile with tetrabutyl ammonium hexafluorophosphate (0.1 M) as the supporting electrolyte under an argon atmosphere at a scan rate of 50 mVs<sup>-1</sup> using ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) as internal standard.

### 1.2. Synthetic procedures



**2,5-Dibromobenzene-1,4-diol (1):** Hydroquinone (10 g, 90.8 mmol) was charged

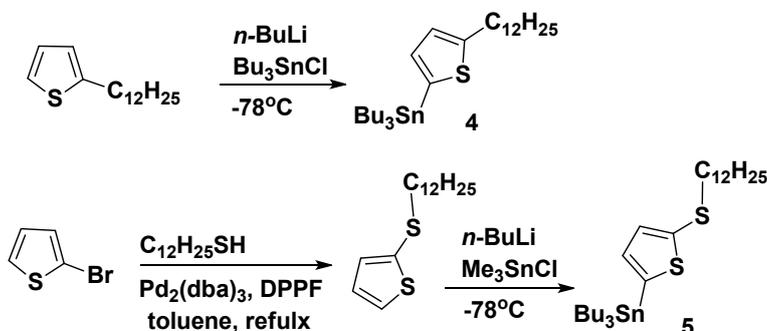
in a round-bottom flask filled with 100 ml of acetic acid, Br<sub>2</sub> (28.9 g, 181.6 mmol) was then added dropwise at 10°C. The solution was kept for stirring for 12 h. A small amount saturated sodium thiosulfate solution was then added to remove the excess Br<sub>2</sub> and the result solution was concentrated under reduced pressure to yield brown solid. The crude product recrystallized from acetic acid to get white solid (20 g, 82%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm): 7.16 (s, 2H), 5.16 (s, 2H).

**1,4-Dibromo-2,5-bis(2,2-diethoxyethoxy)benzene (2):** To a suspension of 2,5-dibromobenzene-1,4-diol **1** (5 g, 18.7 mmol) and KOH (2.6 g, 46.7 mmol) in dimethyl sulfoxide (150 ml) was added 2-bromo-1,1-diethoxyethane (8.1 g, 41 mmol). The mixture was heated at 85°C for 12 h. The resulting mixture was extracted with dichloromethane, and the combined organic layer was dried over Mg<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The residue was purified with flash column chromatography on silica gel eluted with dichloromethane and subsequently recrystallized from ethanol to get white solid (12.1 g, 65%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm): 7.14(s, 2H), 4.83 (t, *J* = 5.2 Hz, 2H), 3.98(d, *J* = 5.2 Hz, 4H), 3.78 (m, 4H), 3.66 (m, 4H), 1.24 (t, *J* = 7.0 Hz, 12H).

**4,8-Dibromobenzo[1,2-b:4,5-b']difuran (3):** 1,4-Dibromo-2,5-bis(2,2-diethoxyethoxy)-benzene (**2**) (10 g, 20 mmol), polyphosphoric acid (PPA, 15 g) and toluene (100 mL) were placed in a round-bottomed flask. The mixture was heated at 100 °C for 5 h. After the mixture was cooled to room temperature, poured onto 2 M NaOH aqueous solution. The resulting mixture was extracted with dichloromethane, washed with water, dried and evaporated under vacuum. The crude product was obtained by column chromatography on silica gel eluted with petroleum ether: dichloromethane (4:1, v/v) and recrystallized from ethanol to get white solid (3.79 g, 60%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm): 7.76 (d, *J* = 2.0 Hz, 2H), 6.98 (d, *J* = 2.0 Hz, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ (ppm): 148.93, 146.59, 127.18, 107.51, 93.92. MALDI-TOF/TOF-MS: *m/z* = 315.88 [M]<sup>+</sup>, calcd for C<sub>10</sub>H<sub>4</sub>Br<sub>2</sub>O<sub>2</sub>: 315.86. Anal. calcd (%) for C<sub>10</sub>H<sub>4</sub>Br<sub>2</sub>O<sub>2</sub>: C, 38.02; H, 1.28; Found: C, 38.05; H, 1.29.

**2-Dodecyl-5-tributyltinthiophene (4):** To a solution of 2-dodecylthiophene (5.0 g, 19.8 mmol) in THF (100 ml) cooled at -78°C was added *n*-BuLi (2.4 M in hexanes, 9.1 ml, 21.8 mmol) drop wise within 20min. After completely added, the reaction was stirred 1h at -78°C and subsequently cooled to -78°C, tributyltin chloride (6.44 g, 19.8 mmol) was added and the reaction mixture was stirred for a future 1h. The mixture

was warmed to room temperature overnight. The reaction was quenched with water and the reaction mixture was extracted with ethyl acetate. The combined organic phases dried over  $\text{MgSO}_4$ , and the solvent removed in vacuo to give the product as a yellow liquid (10 g, 95%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm): 6.98 (d,  $J = 3.5$  Hz, 1H), 6.90 (d,  $J = 3.0$  Hz, 1H), 2.85 (t,  $J = 7.5$  Hz, 2H), 1.74 -0.68 (m, 50H).

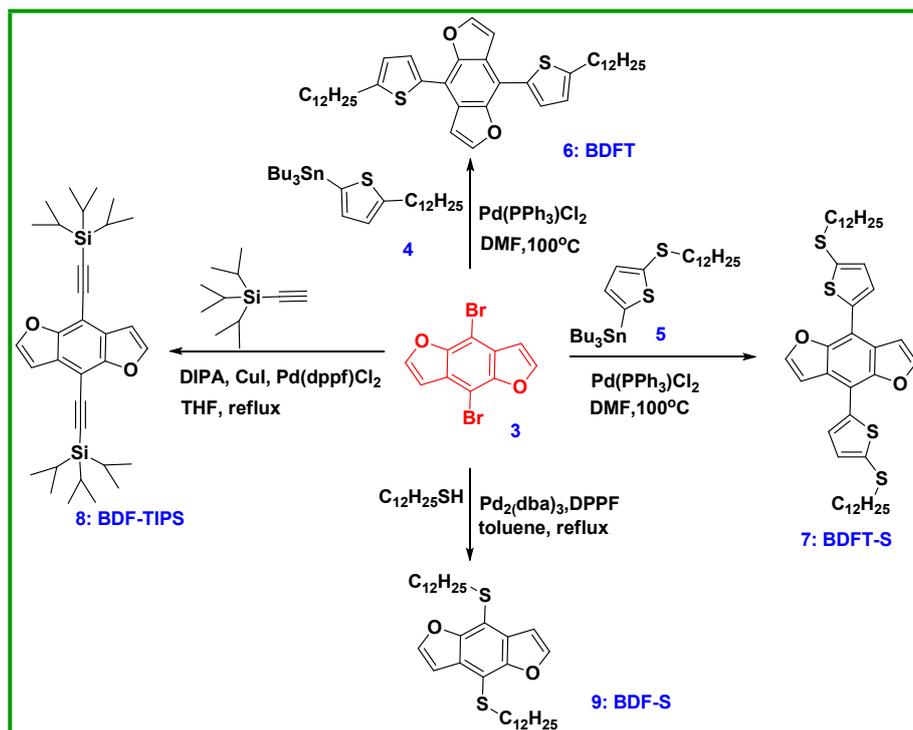


**2-Dodecylthiophene:** To a two-neck round-bottom flask (100 mL), a mixture of 2-dibromothiophene (5 g, 30.6 mmol), 1-dodecanethiol (6.8 g, 33.7 mmol),  $\text{Pd}_2(\text{dba})_3$  (0.56 g, 0.61 mmol), DPPF (0.68 g, 1.22 mmol) were purged with nitrogen, and then dry toluene (50 mL) was added. The mixture was refluxed for 12 h. The resulting mixture was extracted with dichloromethane and the combined organic phases dried over  $\text{MgSO}_4$  and the solvent removed in vacuo to give the crude product. The crude product was purified with flash column chromatography on silica gel eluted with petroleum ether to obtain a yellow liquid (8.0 g, 92%).  $^1\text{H}$  NMR (500MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.34 (dd,  $J = 1.5$  Hz, 5.5 Hz, 1H), 7.12 (dd,  $J = 1.5$  Hz, 3.5 Hz, 1H), 6.98 (m, 1H), 2.80 (t,  $J = 7.0$  Hz, 2H), 1.62 (m, 2H), 1.36-1.26 (m, 18H), 0.90 (t,  $J = 7.0$  Hz, 2H).

**2-Dodecylthio-5-tributyltinthiophene (5):** Following the similar procedure as for 4, 5 was obtained as an orange liquid (88%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.17 (d,  $J = 3.5$  Hz, 1H), 7.03 (d,  $J = 3.5$  Hz, 1H), 2.80 (t,  $J = 7.5$  Hz, 2H), 1.58 (m, 8H), 1.36-1.26 (m, 24H), 1.11(m, 6H), 0.90 (m, 12H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 141.39, 139.94, 135.54, 133.44, 38.79, 31.92, 29.64, 29.51, 29.44, 29.36, 29.17, 28.91, 28.47, 27.21, 22.69, 14.08, 13.61, 10.78.

**4,8-Bis(5-dodecylthiophen-2-yl)benzofuro[5,6-b]furan (6):** To a 50 mL two-neck round-bottom flask, a mixture of 3 (2 g, 6.3mmol), 4 (3.77 g, 7.0mmol),  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (0.09 g, 0.13 mmol) were purged with nitrogen, and then dry DMF (30ml) was added. The mixture was heated at  $100^\circ\text{C}$  for 12h. After the reaction mixture was cooled to room temperature, the suspension was extracted with

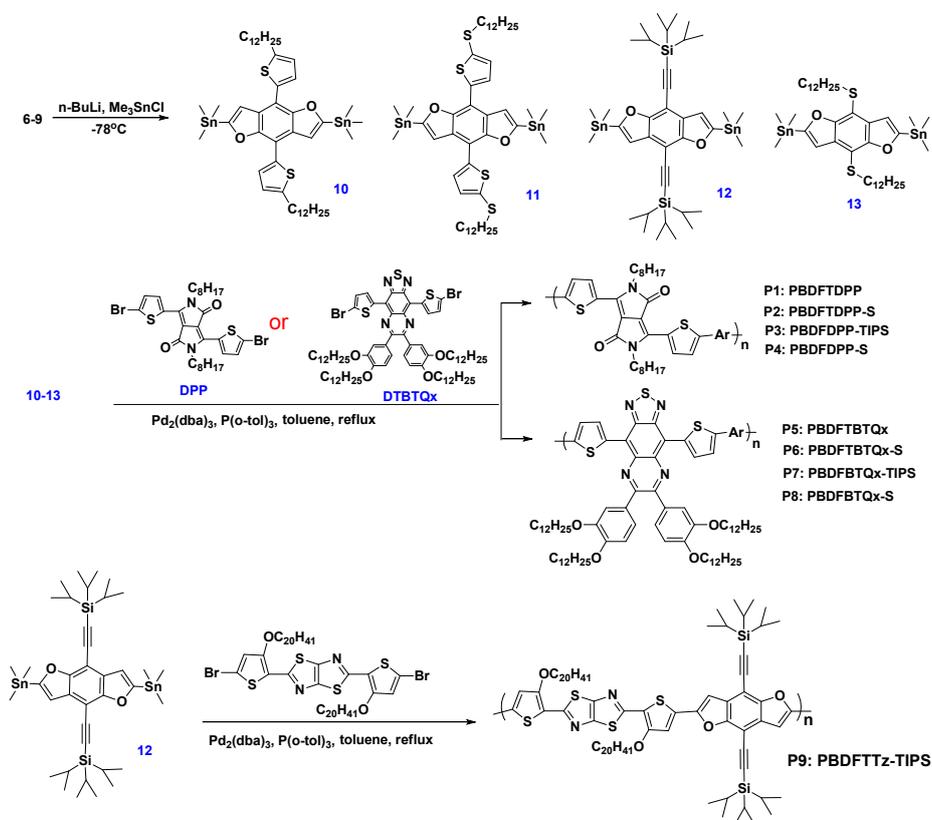
dichloromethane, washed with water, and dried over sodium sulfate. After the solvent was removed, the residue was purified by flash column chromatography with petroleum ether and recrystallized from ethanol to get a bright yellow solid (3.6 g, 87%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.77 (d,  $J = 2.0$  Hz, 2H), 7.66 (d,  $J = 4.0$  Hz, 2H), 7.36 (d,  $J = 2$  Hz, 2H), 6.91 (d,  $J = 4.0$  Hz, 2H), 2.93 (t,  $J = 7.5$  Hz, 4H), 1.77 (m, 4H), 1.43 (m, 4H), 1.35-1.26 (m, 32H), 0.88 (t,  $J = 7.0$  Hz, 6H). MALDI-TOF/TOF-MS:  $m/z = 658.41$   $[\text{M}]^+$ , calcd for  $\text{C}_{42}\text{H}_{58}\text{O}_2\text{S}_2$ : 658.39.



**4,8-Bis(5-(dodecylthio)thiophen-2-yl)benzofuro[5,6-b]furan (7):** Following the similar procedure as for **6**, Stille coupling between **3** (1 g, 3.16mmol) and **5** (4 g, 6.9mmol) afforded the title compound as a bright yellow solid (2.0 g, 87%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.80 (d,  $J = 2.5$  Hz, 2H), 7.72(d,  $J = 3.5$  Hz, 2H), 7.36 (d,  $J = 2.5$  Hz, 2H), 7.23 (d,  $J = 3.5$  Hz, 2H), 2.90 (t,  $J = 7.5$  Hz, 4H), 1.68 (m, 4H), 1.41 (m, 4H), 1.24 (m, 32H), 0.88 (t,  $J = 7.5$  Hz, 6H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 148.35, 145.72, 139.04, 135.53, 133.16, 127.92, 123.08, 109.73, 106.72, 38.69, 31.65, 29.37, 29.26, 29.09, 28.90, 28.23, 22.43, 13.86. MALDI-TOF/TOF-MS:  $m/z = 722.34$   $[\text{M}]^+$ , calcd for  $\text{C}_{42}\text{H}_{58}\text{O}_2\text{S}_4$ : 722.33.

**4,8-Bis((triisopropylsilyl)ethynyl)benzofuro[5,6-b]furan (8):** A two-neck round-bottom flask equipped with a condenser was charged with **3** (1 g, 3.16mmol), (triisopropylsilyl)acetylene (0.69 g, 3.8 mmol), CuI (48 mg, 0.025mmol) and Pd(dppf)Cl<sub>2</sub> (90 mg, 0.013mmol).  $i\text{-Pr}_2\text{Net/THF}$  20ml (1:5, v/v) was added via a

septum. The mixture was stirred for 12 h at 100°C, then after the reaction mixture was cooled to room temperature poured onto aqueous hydrochloric acid (1 ml, 1 M). The resulting mixture was extracted with dichloromethane and dried over sodium sulfate. After the solvent was removed, the residue was purified by flash column chromatography with petroleum ether and recrystallized from ethanol to get white solid(1.41 g, 86%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm): 7.71 (d, *J* = 2.0 Hz, 2H), 6.96 (d, *J* = 2.0 Hz, 2H), 1.20 (m, 42H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ (ppm): 151.79, 146.26, 128.05, 106.78, 100.68, 99.69, 98.92, 18.73, 18.56, 11.30. MALDI-TOF /TOF-MS: *m/z* = 518.31 [M]<sup>+</sup>, calcd for C<sub>32</sub>H<sub>46</sub>O<sub>2</sub>Si<sub>2</sub>: 518.30.



**4,8-Bis(dodecylthio)benzofuro[5,6-b]furan (9):** A mixture of **3** (1 g, 3.16 mmol), 1-dodecanethiol (0.77 g, 3.8 mmol) Pd<sub>2</sub>(dba)<sub>3</sub> (58 mg, 0.063 mmol) and DPPF (0.14 g, 0.25 mmol) in toluene (20 mL) was heated in an oil bath at 110°C for 12h under a N<sub>2</sub> atmosphere. After cooled to room temperature the resulting mixture was extracted with dichloromethane and dried over sodium sulfate. After the solvent was removed, the residue was purified by flash column chromatography with petroleum ether/ethylacetate (20:1, v/v) and recrystallized from ethanol to get yellow solid(1.5 g, 90%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm): 7.71 (d, *J* = 2.0 Hz, 2H), 7.05 (d, *J* = 2.0 Hz, 2H), 3.06 (t, *J* = 7.5 Hz, 4H), 1.53 (m, 4H), 1.38 (m, 4H), 1.27-1.20 (m, 32H), 0.88 (t,

$J = 7.5$  Hz, 6H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 152.08, 145.71, 128.87, 108.98, 106.92, 39.20, 34.77, 31.90, 29.98, 29.61, 29.54, 29.34, 29.23, 29.09, 28.51, 22.68, 14.12. MALDI-TOF/TOF-MS:  $m/z = 558.35$   $[\text{M}]^+$ , calcd for  $\text{C}_{34}\text{H}_{54}\text{O}_2\text{S}_2$ : 558.36.

**(4,8-Bis(5-dodecylthiophen-2-yl)benzofuro[5,6-b]furan-2,6-diyl)bis(trimethylstannane) (10)**: To a solution of **6** (1 g, 1.52 mmol) in 100 ml THF cooled at  $-78^\circ\text{C}$  was added  $n\text{-BuLi}$  (2.4 M in hexanes, 1.6 ml, 3.8 mmol) dropwise within 10 min. After completely added, the reaction was stirred 1 h at  $-78^\circ\text{C}$ . The mixture was warmed to room temperature and stirred for another 1 h, and subsequently cooled to  $-78^\circ\text{C}$ , trimethyltin chloride (1.0 M in THF, 3.8 ml, 3.8 mmol) was added and the reaction mixture was stirred for a further 1 h. The mixture was warmed to room temperature overnight. The reaction was quenched with water and the reaction mixture was extracted with ethyl acetate. The combined organic phases dried over  $\text{MgSO}_4$ , and the solvent removed in vacuo to give the crude product. The target product was obtained by recrystallizing from isopropyl alcohol as a yellow solid (1.07 g, 72%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.71 (d,  $J = 3.5$  Hz, 2H), 7.49 (s, 2H), 6.91 (d,  $J = 3.5$  Hz, 2H), 2.92 (t,  $J = 7.5$  Hz, 4H), 1.78 (m, 4H), 1.44 (m, 4H), 1.37-1.26 (m, 32H), 0.88 (t,  $J = 7.5$  Hz, 6H), 0.46 (s, 18H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 166.10, 152.17, 145.95, 135.06, 127.13, 124.43, 123.36, 117.76, 108.43, 31.92, 31.74, 30.21, 29.66, 29.44, 29.36, 29.24, 22.69, 14.12, -8.96. MALDI-TOF/TOF-MS:  $m/z = 984.51$   $[\text{M}]^+$ , calcd for  $\text{C}_{48}\text{H}_{74}\text{O}_2\text{S}_2\text{Sn}_2$ : 984.32.

**(4,8-Bis(5-(dodecylthio)thiophen-2-yl)benzofuro[5,6-b]furan-2,6-diyl)bis(trimethylstannane) (11)**: Following the same procedure as for the synthesis of **10**, a solution of **7** (1 g, 1.4 mmol) in 100 ml THF was used to afford the target product as a yellow solid (1.1 g, 77%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.77 (d,  $J = 3.5$  Hz, 2H), 7.48 (s, 2H), 7.24 (d,  $J = 3.5$  Hz, 2H), 2.90 (t,  $J = 7.5$  Hz, 4H), 1.72 (m, 4H), 1.44 (m, 4H), 1.29-1.25 (m, 32H), 0.88 (t,  $J = 7.0$  Hz, 6H), 0.49 (s, 18H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 166.95, 152.17, 140.71, 134.87, 133.484, 127.64, 123.41, 117.55, 108.34, 39.04, 31.90, 29.60, 29.33, 29.20, 28.540, 22.67, 14.11, -8.93. MALDI-TOF/TOF-MS:  $m/z = 1048.45$   $[\text{M}]^+$ , calcd for  $\text{C}_{48}\text{H}_{74}\text{O}_2\text{S}_4\text{Sn}_2$ : 1048.26.

**(2,6-Bis(trimethylstannyl)benzofuro[5,6-b]furan-4,8-diyl)bis(ethyne-2,1-diyl)bis(triisopropylsilane) (12)**: Following the same procedure as for the synthesis of **10**, a solution of **8** (1 g, 1.92 mmol) in 100 ml THF was used to afford the title compound (1.12 g, 69%).  $^1\text{H}$  NMR (500 MHz)  $\delta$  (ppm): 7.06 (s, 2H), 1.21 (s, 42H),

0.42 (s, 18H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 167.36, 155.90, 127.63, 117.31, 100.03, 99.65, 97.84, 77.25, 77.00, 76.75, 18.75, 18.56, 11.37, 11.31, -9.15. MALDI-TOF/TOF-MS:  $m/z=844.35$   $[\text{M}]^+$ , calcd for  $\text{C}_{38}\text{H}_{62}\text{O}_2\text{Si}_2\text{Sn}_2$ : 844.23.

**(4,8-Bis(dodecylthio)benzofuro[5,6-b]furan-2,6-diyl)bis(trimethylstannane)**

**(13)**: Following the same procedure as for the synthesis of **10**, a solution of **9** (1 g, 1.8 mmol) in 100 ml THF was used to get the title compound (1.22 g, 80%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.16 (s, 2H), 3.11 (t,  $J = 7.5$  Hz, 4H), 1.55 (m, 4H), 1.38 (m, 4H), 1.29-1.21 (m, 32H). 0.88 (t,  $J = 7.0$  Hz 6H), 0.43 (s 18H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 166.43, 155.38, 128.74, 117.66, 106.74, 34.372, 31.90, 30.00, 29.62, 29.34, 29.15, 28.64, 22.68, 14.12, -9.00. MALDI-TOF/TOF-MS:  $m/z=884.56$   $[\text{M}]^+$ , calcd for  $\text{C}_{40}\text{H}_{70}\text{O}_2\text{S}_2\text{Sn}_2$ : 884.29.

**Synthesis of polymers.** The polymers **P1-P9** were prepared with Stille coupling reactions. Typically, distannyl monomers **10** (or **11**, **12**, **13**) (100 mg, 0.10 mmol) and DPP (or BTQx) (70 mg, 0.10 mmol) were dissolved in 4 ml of dry chlorobenzene. The solution was degassed with argon for 30 min, then  $\text{Pd}_2(\text{dba})_3$  (4.6 mg, 5% mol),  $\text{P}(\text{o-tol})_3$  (6.25 mg, 10% mol) was added into the solution. The solution was stirred at 110 °C for 72 h under argon atmosphere. The end-capping agent 2-(tributylstannyl)thiophene (0.1 equiv) was added. Another capping agent, 2-bromothiophene (0.1 equiv), was added 2h later. The reaction mixture was heated overnight. After cooling to room temperature, the mixture was added into the stirred methanol dropwise. The collected precipitated polymer was extracted with methanol, acetone, hexane and chloroform in a Soxhlet for 24 h sequentially. The chloroform solution was concentrated and purified by flash silica gel chromatography using chloroform as eluent. The product was then concentrated and re-precipitated in MeOH. The polymer was obtained after drying in vacuo.

**P1** (PBDFTDPP): a shiny purple black solid (103 mg, 86%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 9.16 (m, 2H), 7.65 (m, 4H), 7.01 (m, 4H), 4.07 (m, 4H), 3.05 (m, 4H), 1.87-0.87 (br, 72H). Anal. calcd (%) for  $(\text{C}_{72}\text{H}_{94}\text{N}_2\text{O}_4\text{S}_4)_n$ : C, 73.30; H, 8.03; N, 2.37; S, 10.87; Found: C, 74.27; H, 8.09; N, 2.27; S, 10.65.

**P2** (PBDFTDPP-S): a shiny purple black solid (94 mg, 76%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.37 (m, 10H), 3.56 (m, 8H), 2.15-0.80 (m, 76H). Anal. calcd (%) for  $(\text{C}_{72}\text{H}_{94}\text{N}_2\text{O}_4\text{S}_6)_n$ : C, 69.52; H, 7.62; N, 2.25; S, 15.47; Found: C, 68.40; H, 7.88; N, 2.27; S, 15.41.

**P3** (PBDFDPP-TIPS): a red solid (112 mg, 76%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm): 7.64 (m, 3H), 7.46 (m, 3H), 3,78 (m, 4H), 1.58-0.78 (br, 72H). Anal. calcd (%) for (C<sub>62</sub>H<sub>82</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub>Si<sub>2</sub>)<sub>n</sub>: C, 71.63; H, 7.95; N, 2.69; S, 6.17; Found: C, 72.39; H, 7.90; N, 2.81; S, 6.12.

**P4** (PBDFDPP-S): a dark purple solid (170 mg, 82%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm): 7.63 (m, 4H), 7.04 (m, 8H), 4.67 (m, 4H), 1.95-0.87 (br, 80H). Anal. calcd (%) for (C<sub>64</sub>H<sub>90</sub>N<sub>2</sub>O<sub>4</sub>S<sub>4</sub>)<sub>n</sub>: C, 71.20; H, 8.40; N, 2.59; S, 11.88; Found: C, 73.07; H, 8.29; N, 2.52; S, 11.77.

**P5** (PBDFBTQx): a dark purple solid (123 mg, 87%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm): 7.61 (m, 8H), 6.95 (m, 8H), 4.00 (m, 8H), 2.96 (m, 4H), 2.01-0.87 (br, 132H). Anal. calcd (%) for (C<sub>118</sub>H<sub>166</sub>N<sub>4</sub>O<sub>6</sub>S<sub>5</sub>)<sub>n</sub>: C, 74.71; H, 8.82; N, 2.95; S, 8.45; Found: C, 73.89; H, 8.85; N, 2.91; S, 8.43.

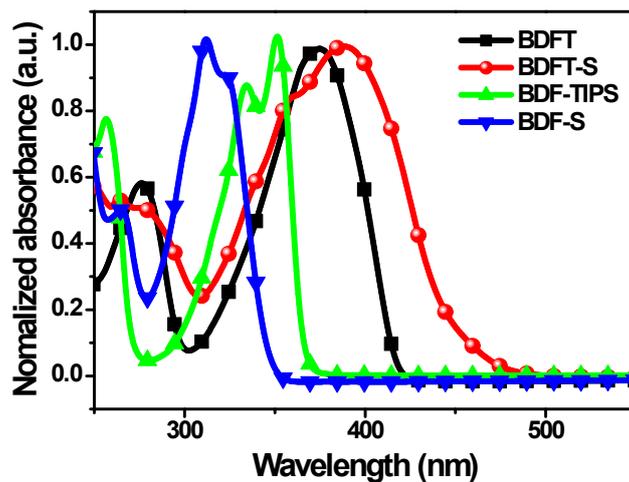
**P6** (PBDFBTQx-S): a shiny purple black solid (145 mg, 74%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm): 7.46 (m, 8H), 6.94 (m, 8H), 2.98(m, 12H), 1.44-0.87 (br, 138H). Anal. calcd (%) for (C<sub>118</sub>H<sub>166</sub>N<sub>4</sub>O<sub>6</sub>S<sub>7</sub>)<sub>n</sub>: C, 72.27; H, 8.53; N, 2.86; S, 11.45; Found: C, 73.41; H, 8.44; N, 2.88; S, 11.42.

**P7** (PBDFBTQx-TIPS): a shiny purple black solid (170 mg, 82%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm): 7.38 (m, 12H), 3.51-0.87 (br, 142H). Anal. calcd (%) for (C<sub>108</sub>H<sub>154</sub>N<sub>4</sub>O<sub>6</sub>S<sub>3</sub>Si<sub>2</sub>)<sub>n</sub>: C, 73.84; H, 8.84; N, 3.19; S, 5.48; Found: C, 74.77; H, 8.73; N, 3.17; S, 5.38.

**P8** (PBDFBTQx-S): a shiny purple black solid (163 mg, 80%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm): 7.33 (m, 4H), 6.85 (m, 8H), 3.03-0.87 (br, 150H). Anal. calcd (%) for (C<sub>110</sub>H<sub>162</sub>N<sub>4</sub>O<sub>6</sub>S<sub>5</sub>)<sub>n</sub>: C, 73.53; H, 9.09; N, 3.12; S, 8.92; Found: C, 73.94; H, 9.01; N, 3.23; S, 8.84.

**P9** (PBDFTTz-TIPS): by adopting the similar procedure, monomer **12** (100 mg, 0.12 mmol) and TTz (124 mg, 0.12 mmol) copolymerized to afford the title polymer as a shiny red solid (115 mg, 74%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm): 8.53 (m, 2H), 7.31 (m, 2H), 4.26 (m, 4H), 1.57-0.88 (br, 120H). Anal. calcd (%) for (C<sub>84</sub>H<sub>128</sub>N<sub>2</sub>O<sub>4</sub>S<sub>4</sub>Si<sub>2</sub>)<sub>n</sub>: C, 71.33; H, 9.12; N, 1.98; S, 9.07; Found: C, 72.24; H, 9.06; N, 1.91; S, 9.18.

## 2. UV-vis absorption spectra of BDF monomers in thin films



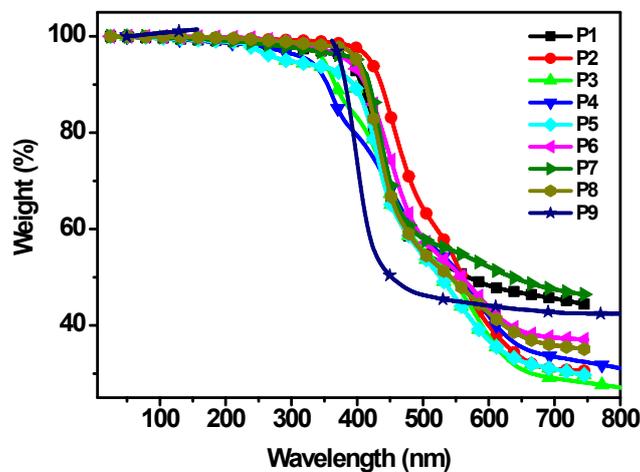
**Figure S1.** Normalized absorption spectra of BDF derivatives in thin films.

### 3. Polymerization results and thermal properties of copolymers

**Table S1.** Polymerization results and thermal properties of copolymers

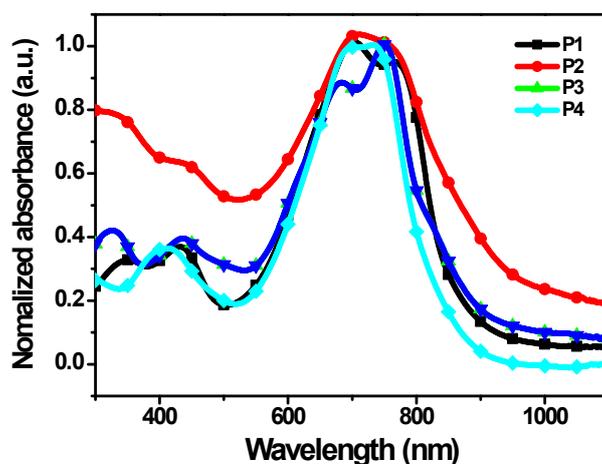
Polymer	Yield (%)	<sup>a</sup> $M_n$ (kDa)	<sup>a</sup> $M_w$ (kDa)	PDI	<sup>b</sup> $T_d$ (°C)
P1	86	9.6	10.4	1.16	376
P2	76	34.4	72.2	2.10	423
P3	87	22.4	31.1	1.39	335
P4	76	25.8	38.2	1.48	339
P5	82	41.7	78.8	1.89	321
P6	82	26.4	61.8	2.34	371
P7	74	9.1	11.4	1.25	370
P8	80	11.7	18.0	1.54	350
P9	74	11.3	14.3	1.27	346

<sup>a</sup> $M_w$ ,  $M_n$ , and PDI of the polymers were measured by GPC using polystyrene standards in THF. <sup>b</sup>The 5% weight-loss temperatures under N<sub>2</sub> and heating from 50 to 800 °C at a rate of 20 °C/min.

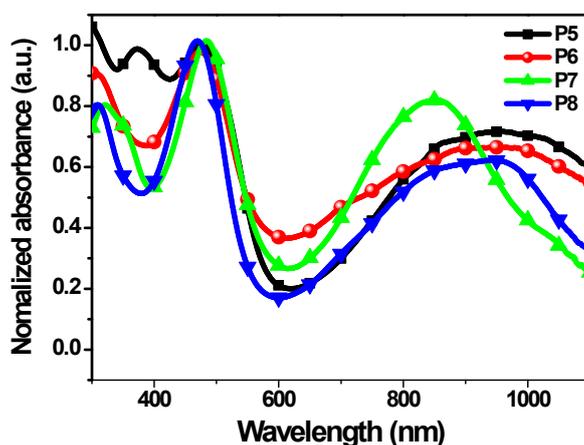


**Figure S2.** TGA plots of the copolymers with a heating rate of 20°C min<sup>-1</sup>.

#### 4. UV-vis and CV of BDF-based copolymers



**Figure S3.** Normalized absorption spectra of DPP-based polymers in thin films.



**Figure S4** Normalized absorption spectra of BTQx-based polymers in thin films.

#### 5. Photovoltaic characterization of BDF polymer

BHJ solar cells were prepared on ITO glass substrates. The substrates were ultrasonicated sequentially in deionized water, acetone, deionized water and isopropanol. Immediately prior to device fabrication, the substrates were treated by oxygen plasma cleaning for 10 min. Firstly, a thin film (45 nm) of poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonate) (PEDOT/PSS, H.C. Starck) was spin-coated and then baked at 150°C for 10 min. Secondly, blend solutions (20 mg/mL) of **P9**:PC<sub>61</sub>BM (1:2, w/w) or **P9**:PC<sub>71</sub>BM (1:2, w/w) in chlorobenzene (CB) containing 5% (v/v) DIO were filtered through a 0.45 μm poly(tetrafluoroethylene) (PTFE) filter, spin-coated onto ITO glass at 1000 rpm (or unless specified) for 60 s. The 1.0 nm LiF layer (0.2A/s) and 100 nm Al (2A/s) layer were then thermally

evaporated on the active layer at a pressure of  $1.0 \times 10^{-6}$  mbar through a shadow mask (active area  $7.25 \text{ mm}^2$ ). Altogether 10 devices with the same configuration were prepared under the same processing conditions, with the average values and variances of device PCEs reported.

The  $J$ - $V$  characteristics of the photovoltaic cells were measured using a Kheithy 2400 (I-V) digital source meter under simulated AM 1.5G solar irradiation at  $100 \text{ mW/cm}^2$  (Newport, Class AAA solar simulator, 94023A-U). The light intensity was calibrated by a certified Oriol Reference Cell (91150V) and verified with a NREL calibrated Hamamatsu S1787-04 diode. The external quantum efficiency (EQE) was performed using a certified IPCE instrument (Zolix Instruments, Inc, SolarCellScan100).

## 6. $^1\text{H}$ -NMR and $^{13}\text{C}$ -NMR Spectra

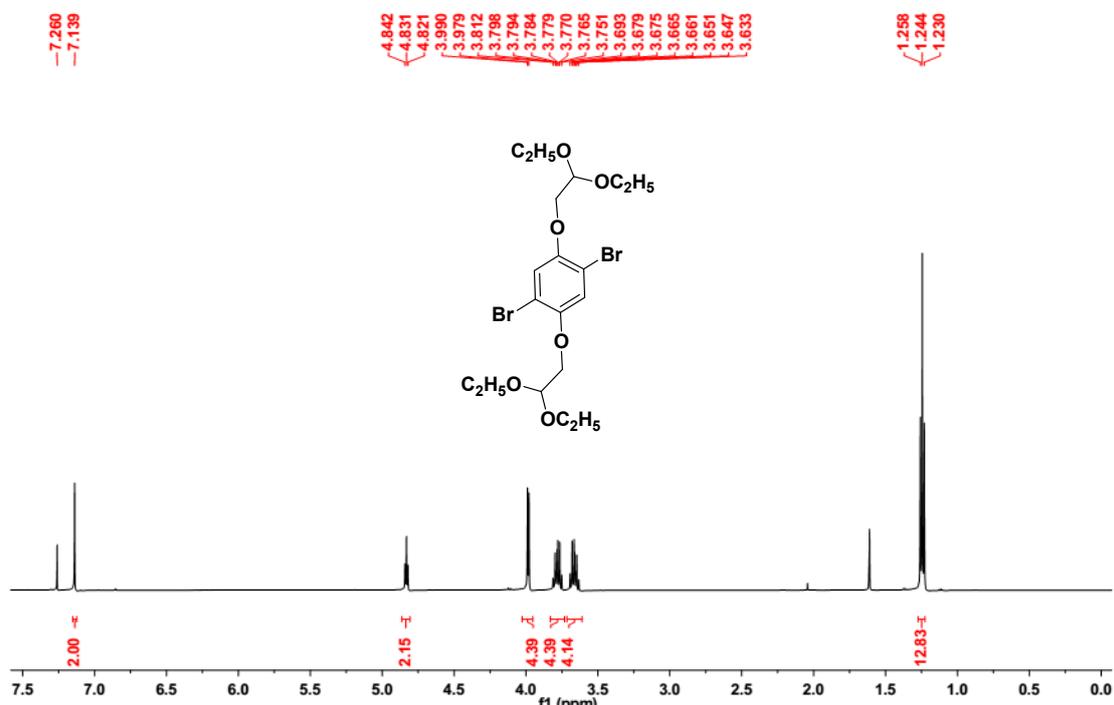


Figure S5.  $^1\text{H}$  NMR spectrum of **2**.

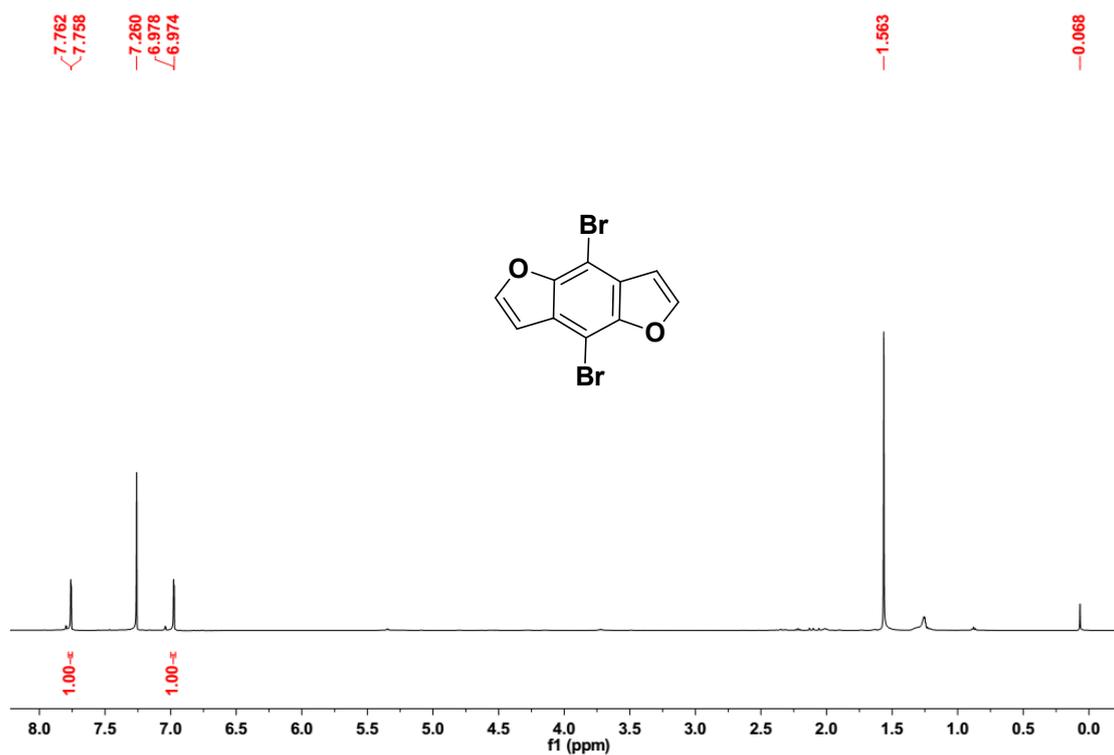


Figure S6.  $^1\text{H}$  NMR spectrum of 3.

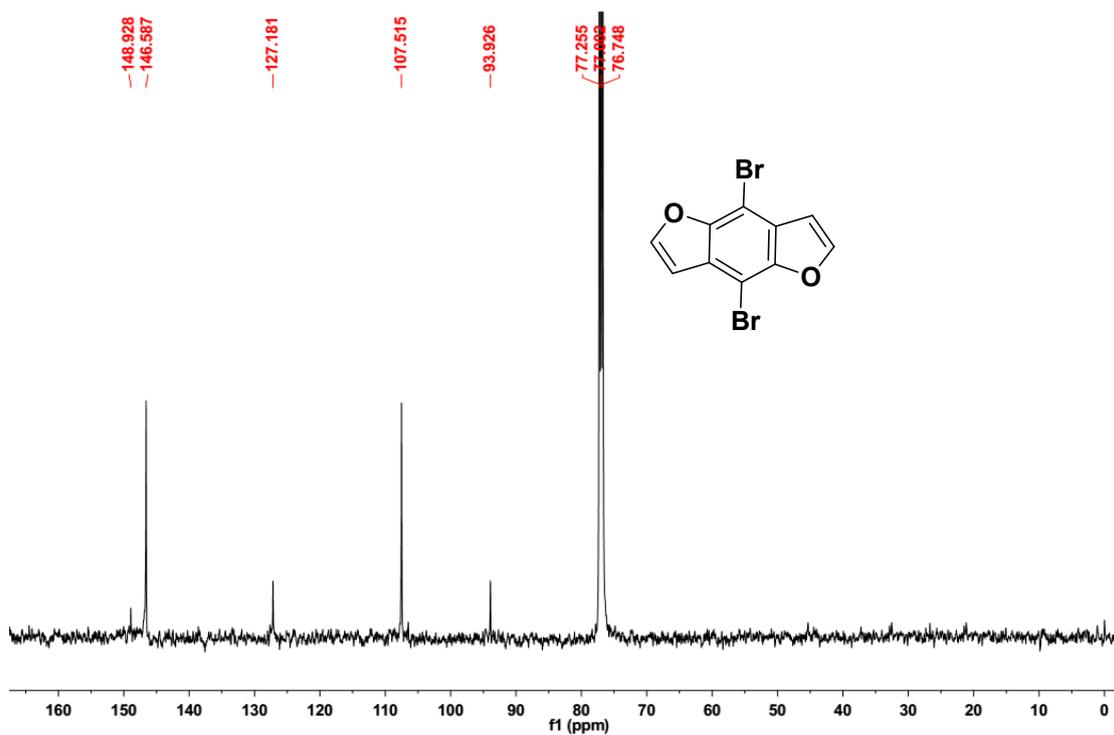


Figure S7.  $^{13}\text{C}$  NMR spectrum of 3.

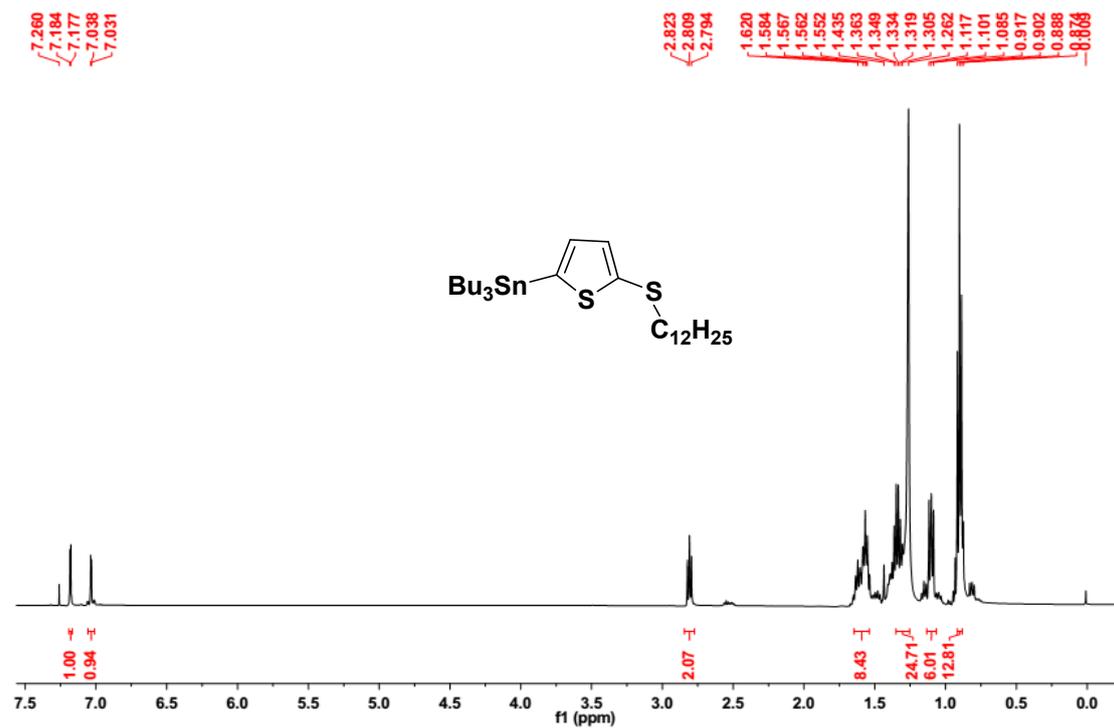


Figure S8.  $^1\text{H}$  NMR spectrum of 5.

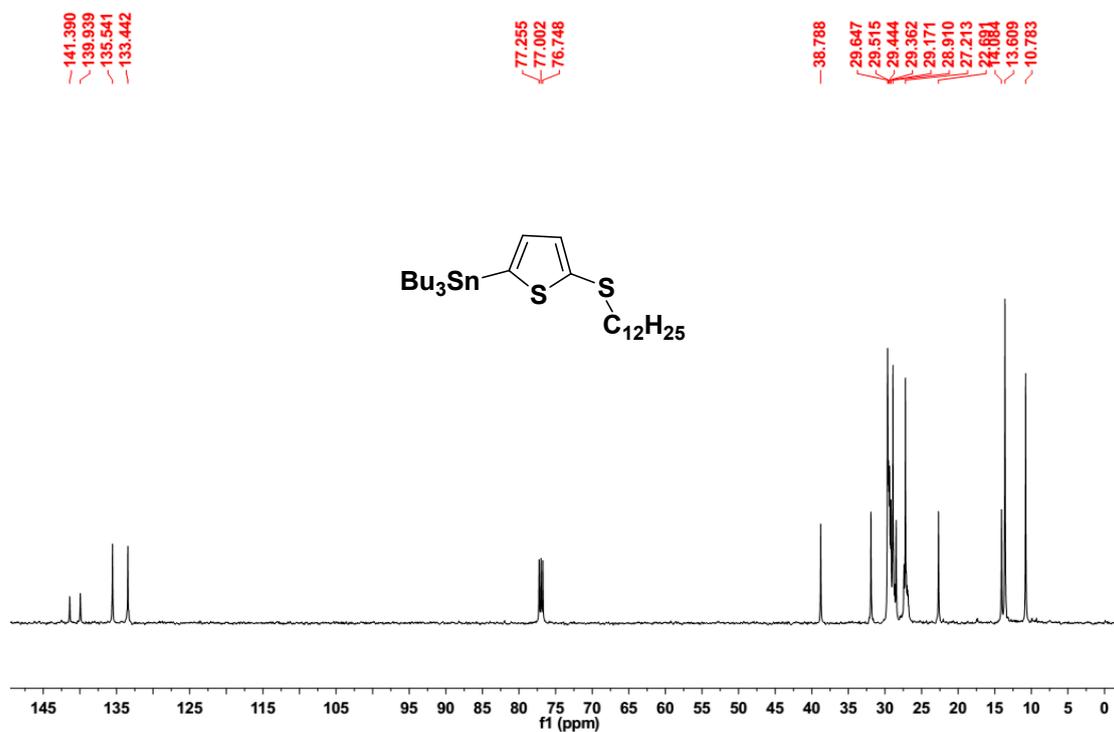


Figure S9.  $^{13}\text{C}$  NMR spectrum of 5.

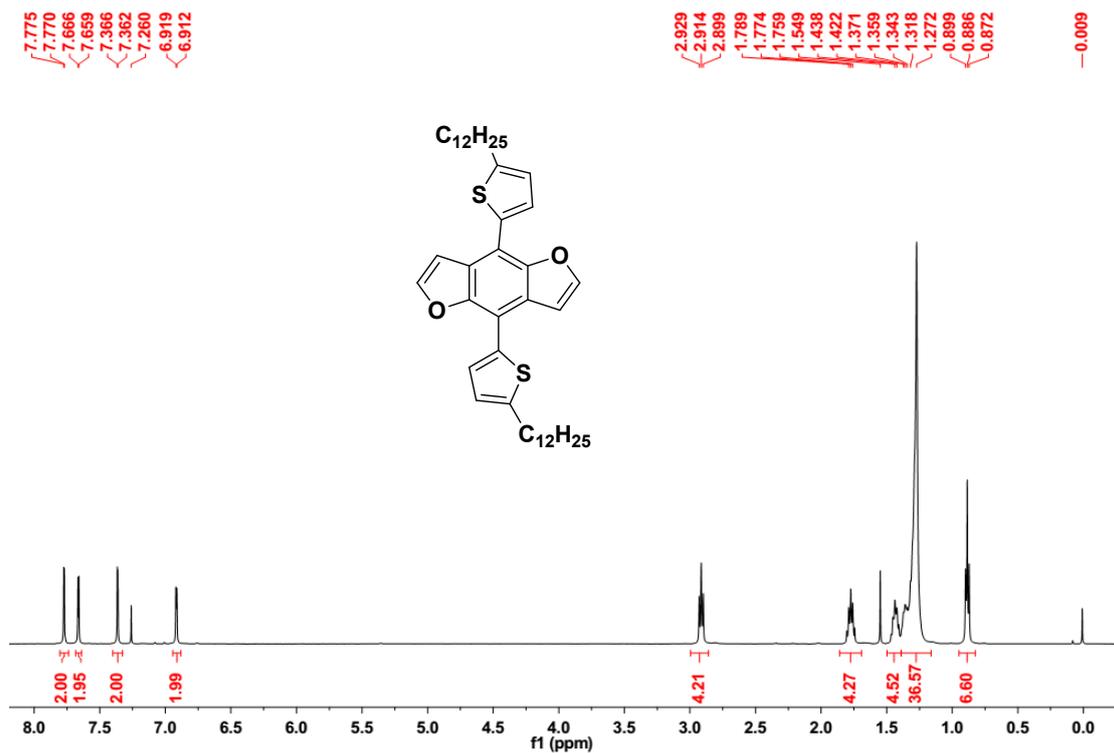


Figure S10.  $^1\text{H}$  NMR spectrum of 6.

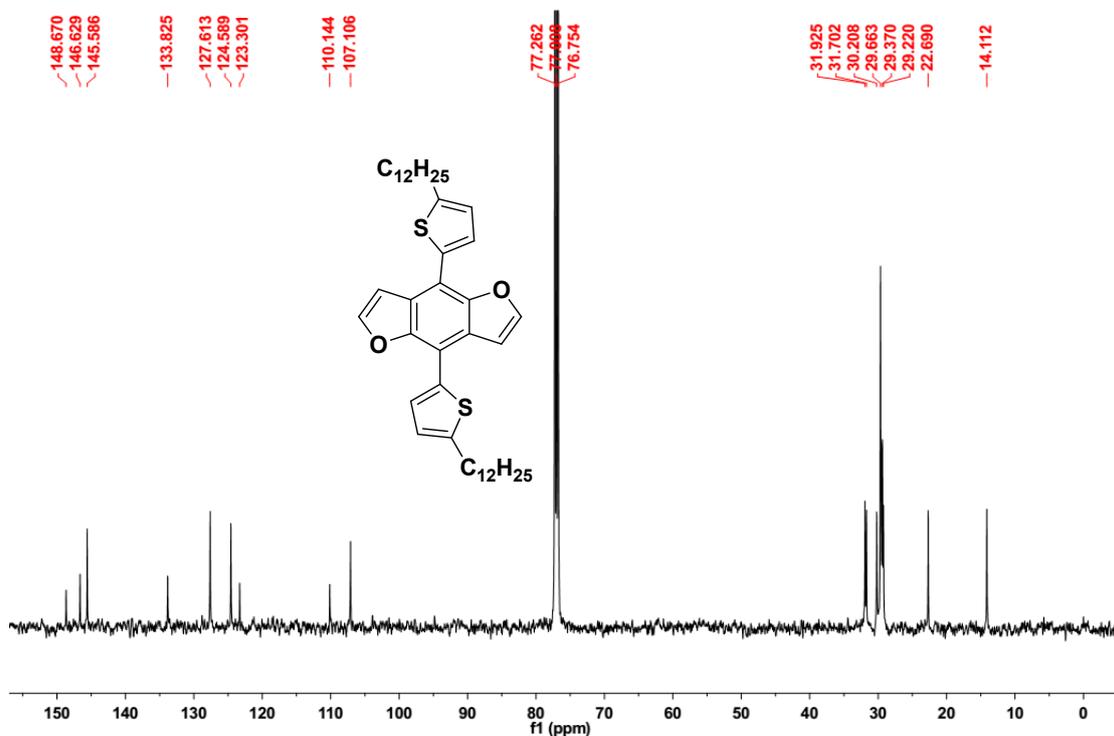


Figure S11.  $^{13}\text{C}$  NMR spectrum of 6.

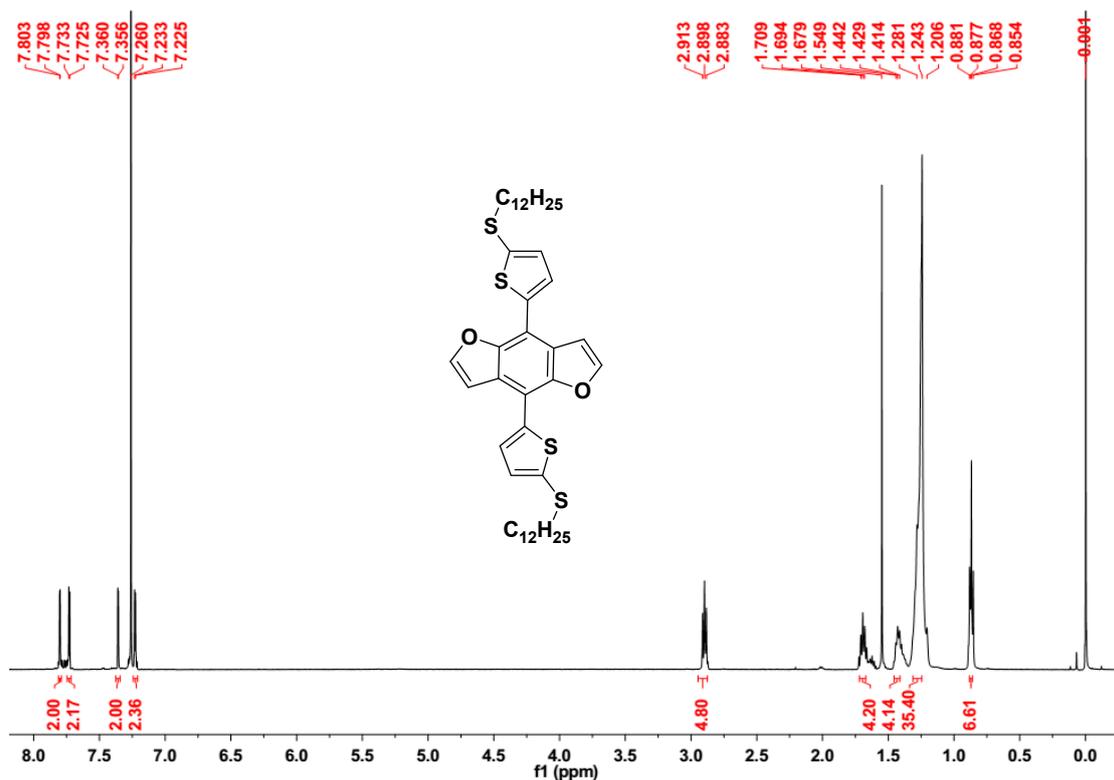


Figure S12. <sup>1</sup>H NMR spectrum of 7.

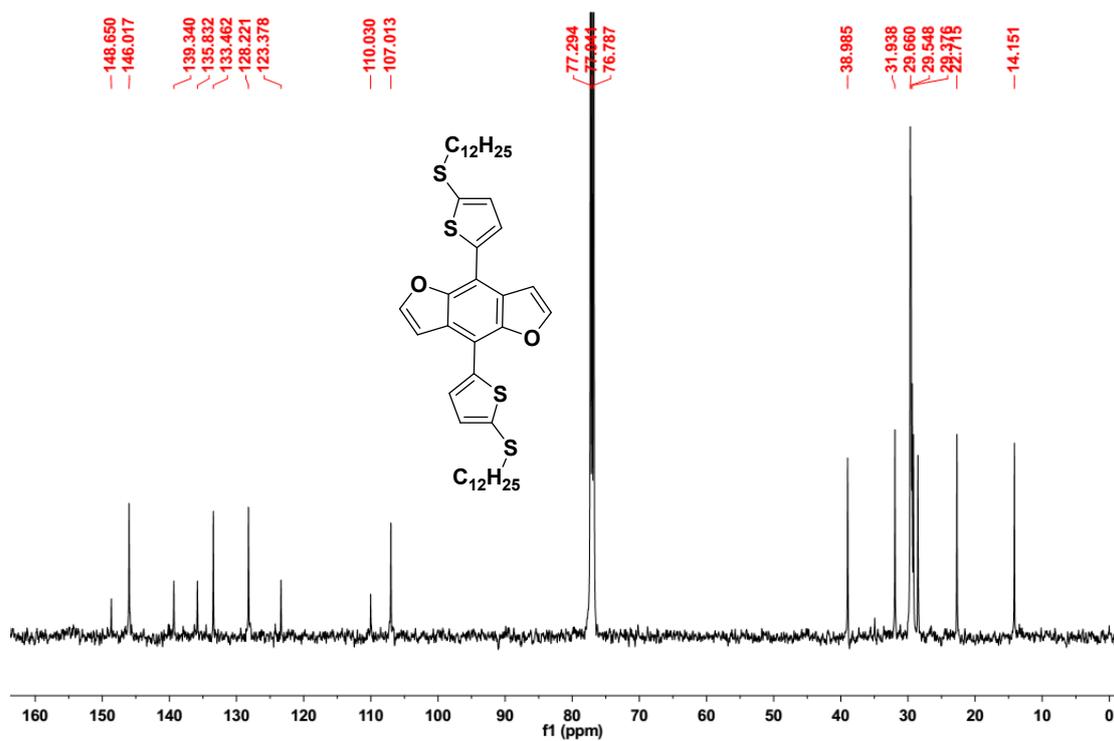


Figure S17. <sup>13</sup>C NMR spectrum of 7.

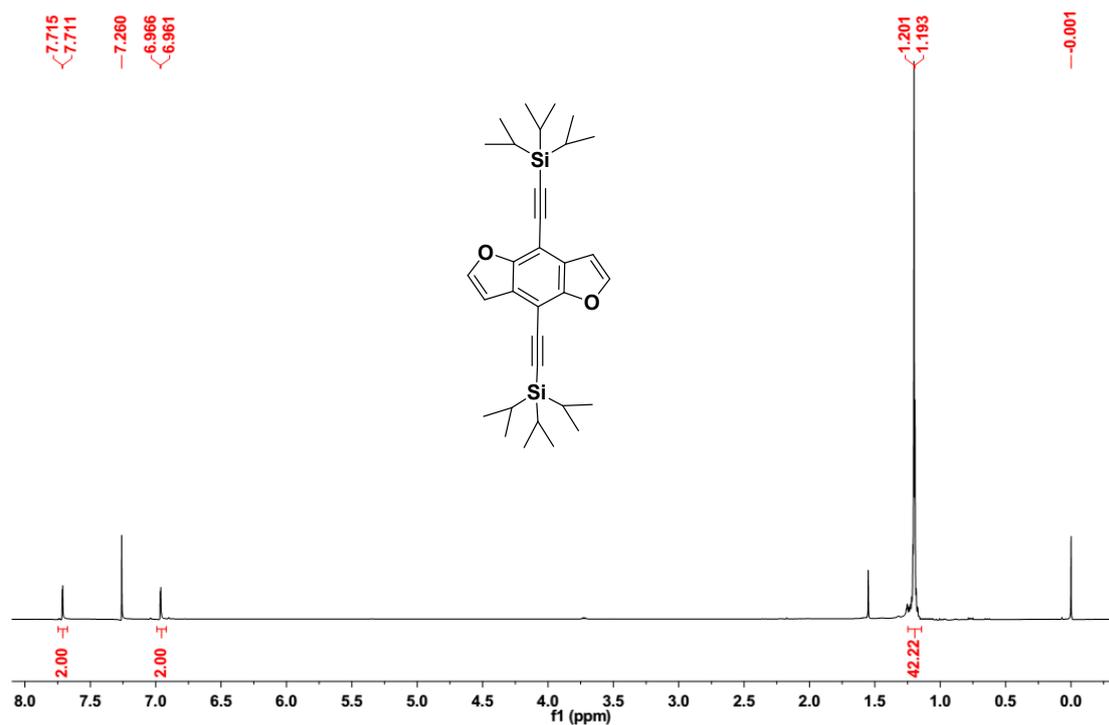


Figure S18.  $^1\text{H}$  NMR spectrum of **8**.

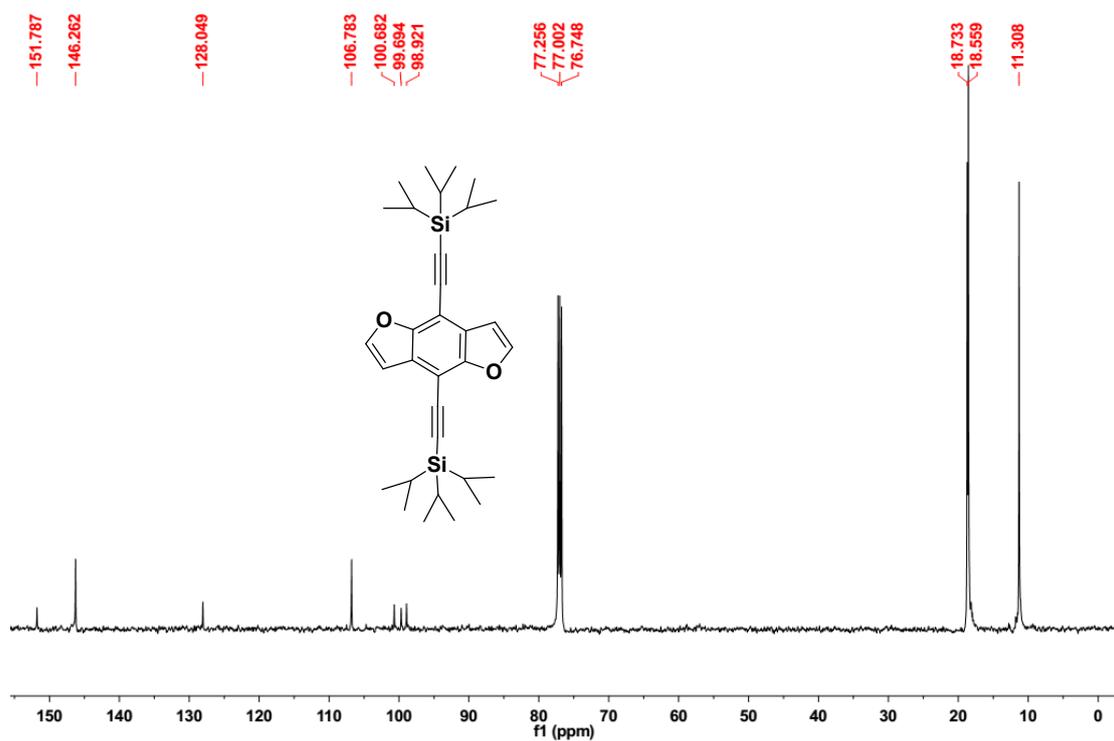


Figure S19.  $^{13}\text{C}$  NMR spectrum of **8**.

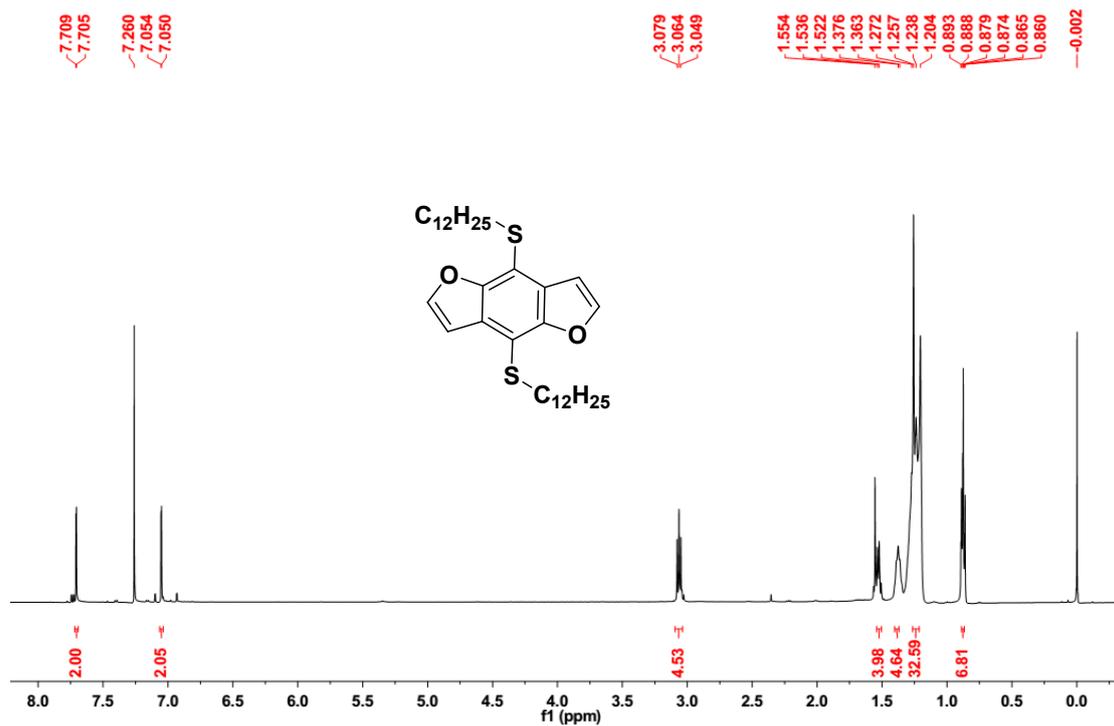


Figure S20.  $^{13}\text{C}$  NMR spectrum of 9.

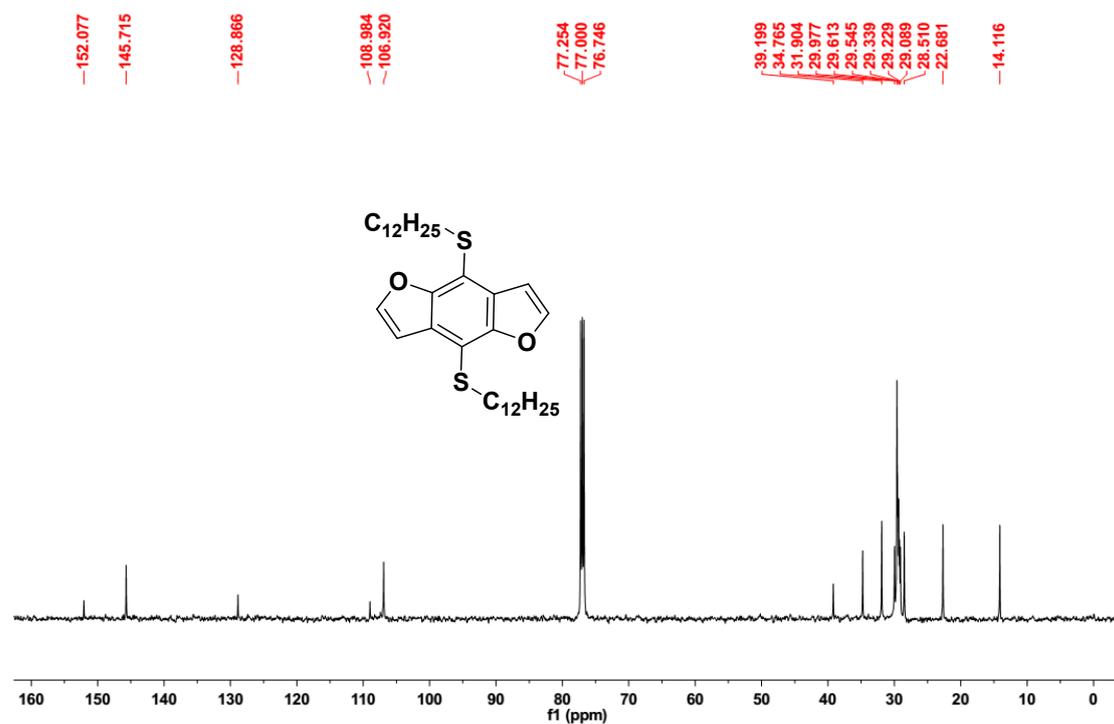


Figure S21.  $^{13}\text{C}$  NMR spectrum of 9.

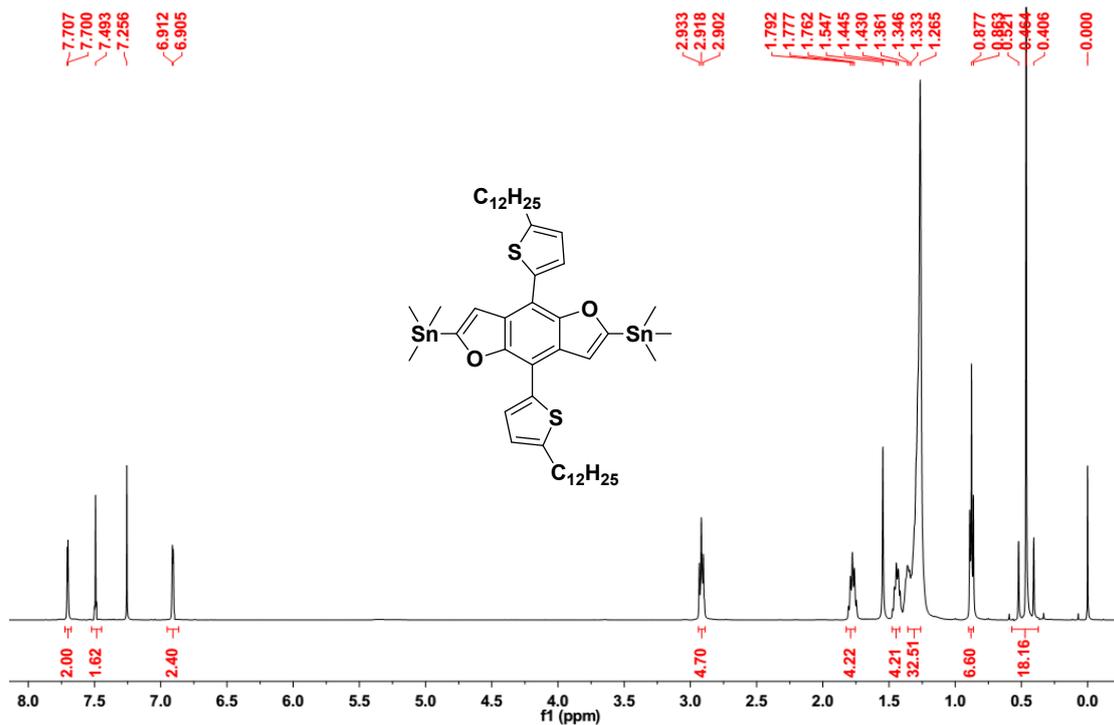


Figure S22.  $^1\text{H}$  NMR spectrum of 10.

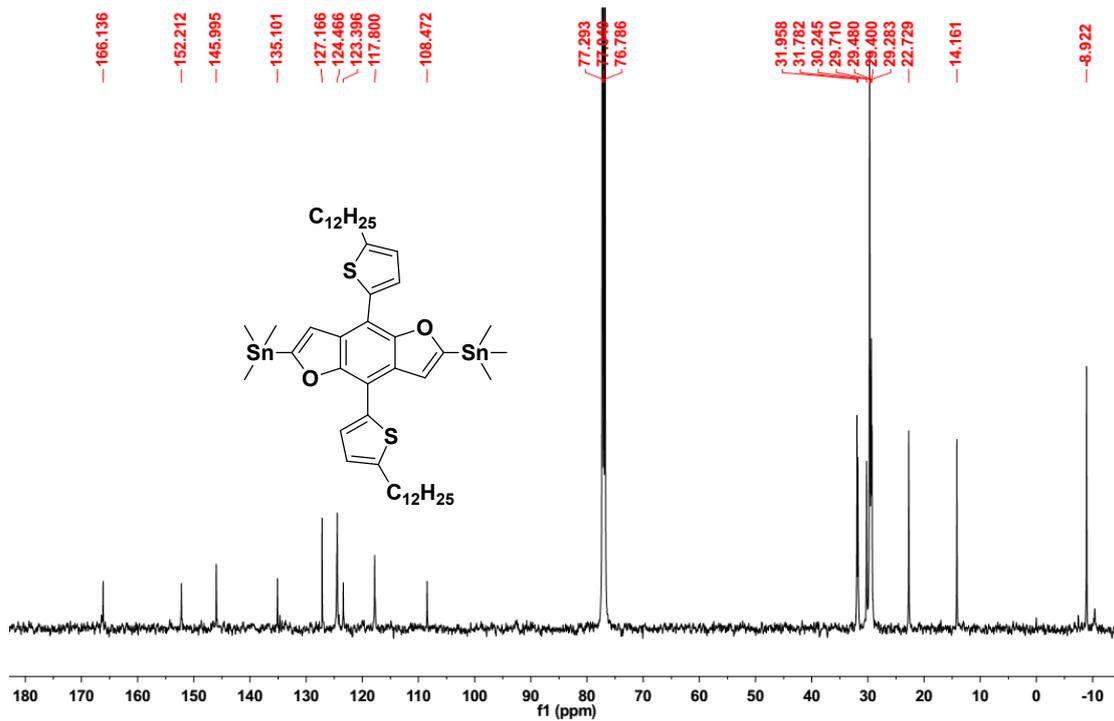


Figure S23.  $^{13}\text{C}$  NMR spectrum of 10.



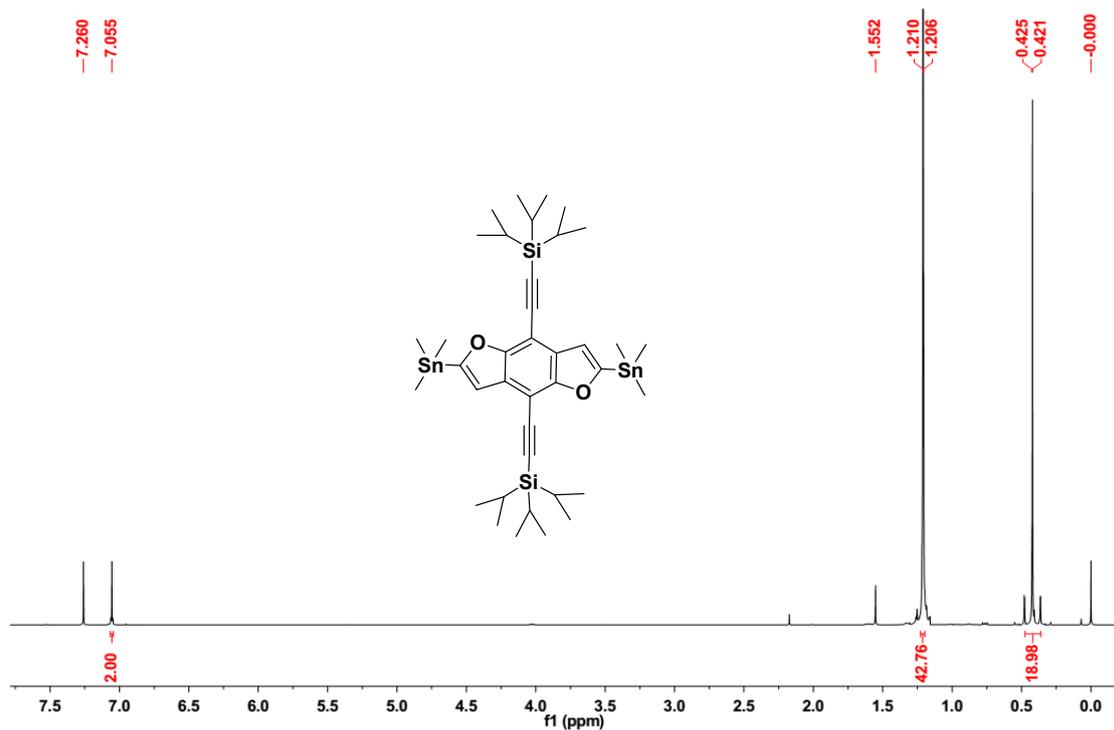


Figure S26.  $^1\text{H}$  NMR spectrum of 12.

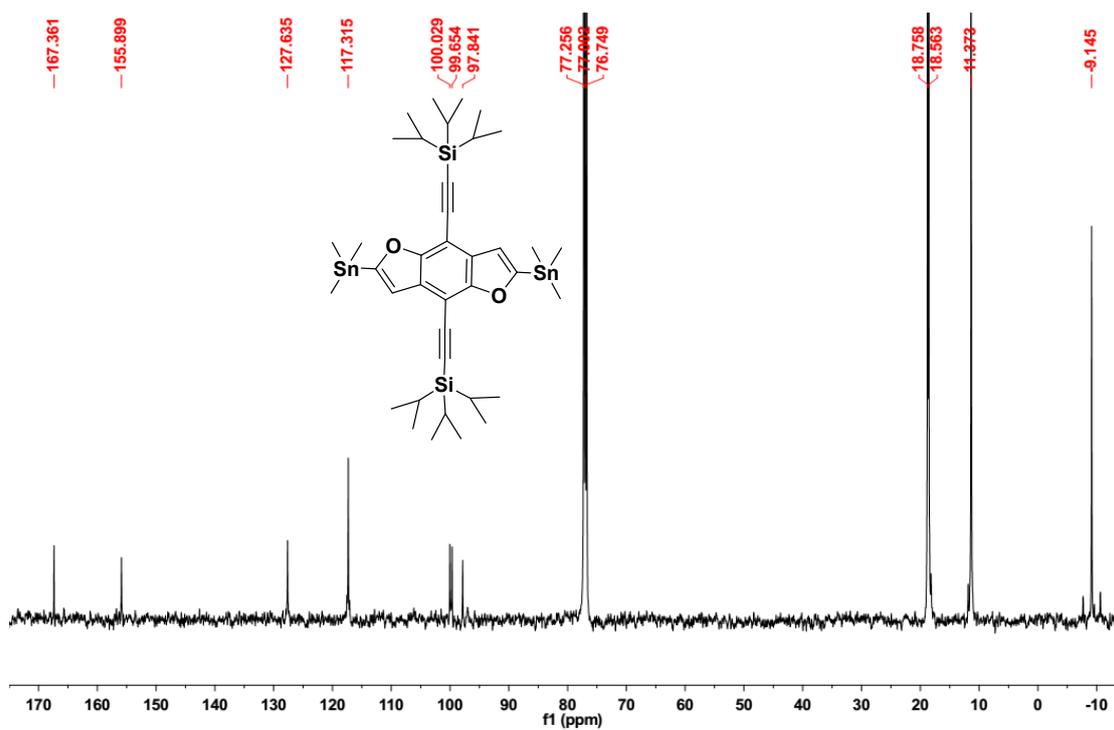


Figure S27.  $^{13}\text{C}$  NMR spectrum of 12.

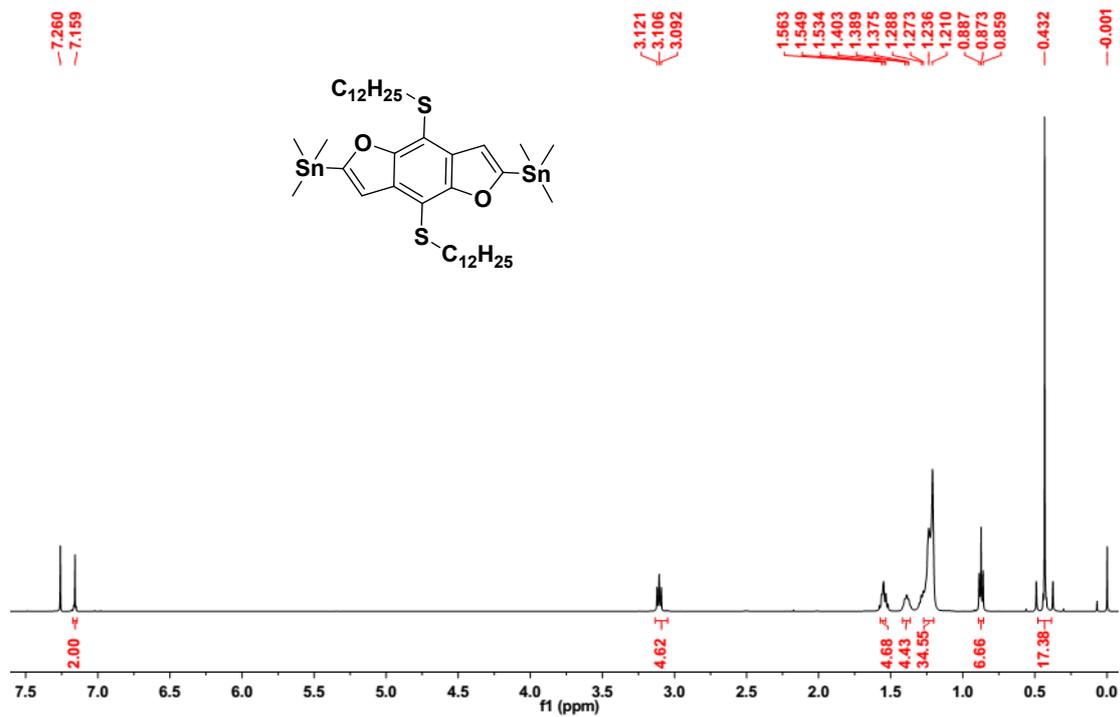


Figure S28. <sup>1</sup>H NMR spectrum of 13.

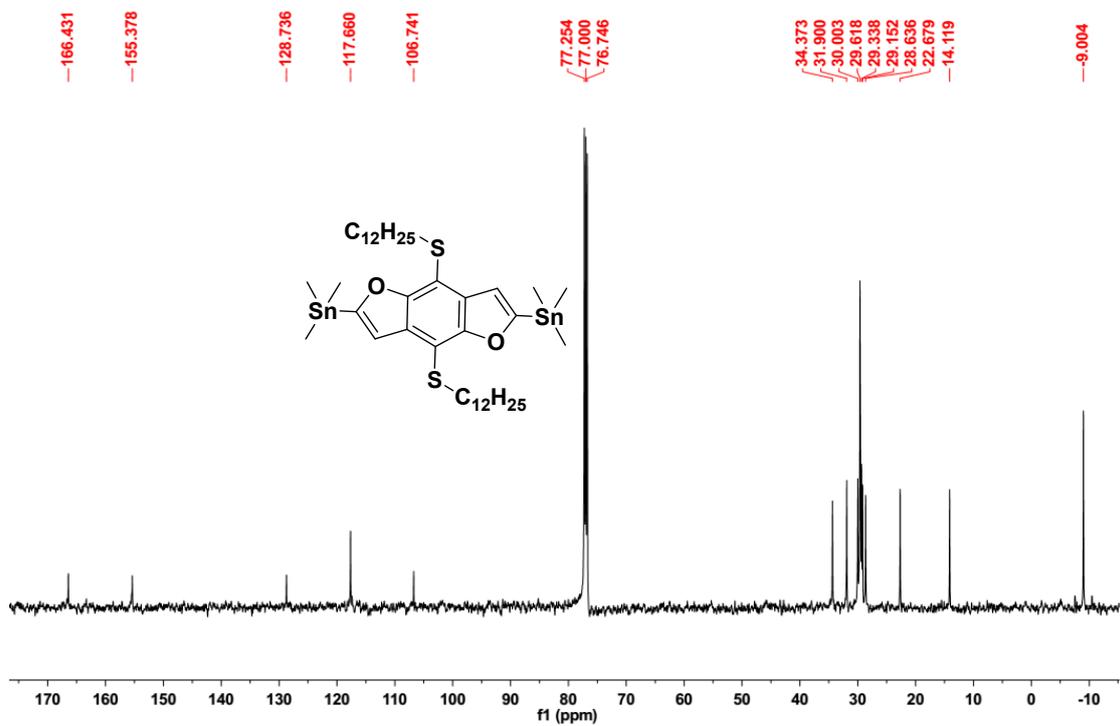


Figure S29. <sup>13</sup>C NMR spectrum of 13.