

## *Electronic Supplementary Information*

### **Selenium-substituted polymers for improved photovoltaic performance**

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#### **Table of Contents**

<b>1. Characterization.....</b>	<b>1</b>
<b>2. Synthesis of monomers.....</b>	<b>2</b>
<b>3. TGA analysis.....</b>	<b>5</b>
<b>4. Energy levels of polymers from CV measurement.....</b>	<b>5</b>
<b>5. NMR spectra of intermediates.....</b>	<b>6</b>

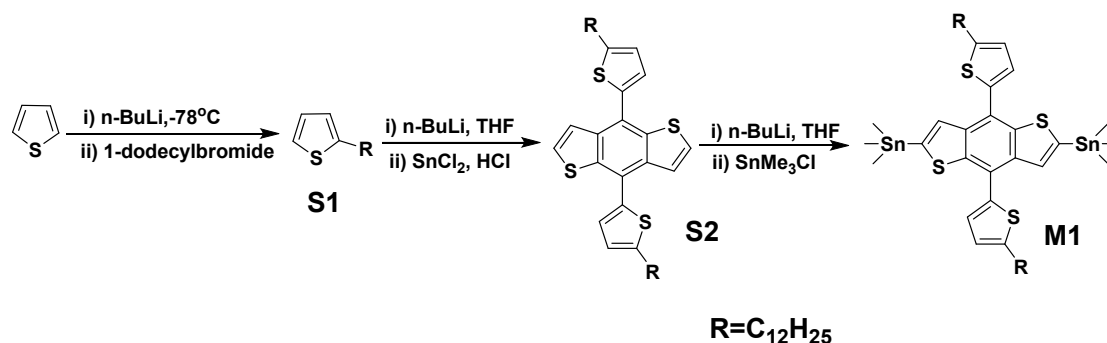
#### **1. Characterization**

$^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVANCE (500 MHz, Bio-Spin Corporation, Europe) spectrometer. The  $M_w$  and PDI of the polymers were determined by GPC on a Waters 717-2410 with polystyrene standards and THF as eluent. TGA was conducted on a TA instrument TGA/SDTA851e under nitrogen at a heating rate of 20 °C /min. Ultraviolet–visible (UV-vis) absorption spectra were recorded using a UV-vis instrument Evolution 220. The electrochemical cyclic voltammetry (CV) measurements were conducted on an electrochemistry workstation (CHI660D, Chenhua Shanghai) under nitrogen in a deoxygenated anhydrous acetonitrile solution of tetrabutylammonium hexafluorophosphate ( $\text{Bu}_4\text{NPF}_6$ , 0.1 M). A standard three-electrode electrochemical cell was employed, where polymer-coated Pt plate, Pt slice and saturated calomel electrode (SCE) were used as working electrode, counter electrode and reference

electrode, respectively. The copolymers were coated on the platinum plate from their dilute solutions in chloroform.

## 2. Synthesis of monomers

The synthetic routes for the 2,6-bis(trimethyltin)-4,8-bis(5-dodecylthiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene (**M1**) were outlined in Scheme S1. The detailed synthetic procedures are described as follows.



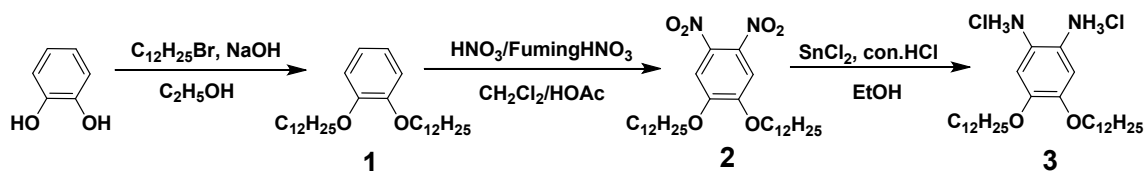
*Scheme S1.* Synthetic routes of the **M1**.

**2-Dodecylthiophene (S1).** Thiophene (6.00 g, 71.31 mmol) was dissolved in 100 mL of anhydrous THF under nitrogen atmosphere. The solution was cooled to -78 °C and 29.7 mL of n-butyllithium (71.31 mmol, 2.4 M) was added dropwise. After being stirred at -78 °C for 1 h, 17.77 g of 1-dodecylbromide (71.31 mmol) was added in one portion and the mixture was stirred at -78 °C for another 1 h, then warmed to RT overnight. The mixture was quenched by 20 mL of cool water and extracted with diethyl ether three times. The organic layer was dried with anhydrous MgSO<sub>4</sub>. After the solvent was removed via rotary evaporation, the residue was purified by vacuum distillation to yield the compound **1** as a colorless oil (17.10 g, 67.73 mmol, 95%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ/ppm): 7.11 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.92 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.78 (dd, *J* = 3.4, 1.1 Hz, 1H), 2.83 (t, *J* = 7.7 Hz, 2H), 1.72-1.64 (m, 2H), 1.36-1.27 (m, 18H), 0.89 (t, *J* = 7.0 Hz, 3H).

**4,8-Bis(5-dodecylthiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene (S2).** Under nitrogen atmosphere, 6.2 mL of n-butyllithium (14.98 mmol, 2.4 M) was added dropwise to the solution of compound **1** (3.44 g, 13.62 mmol) in 50 mL of anhydrous THF at -30 °C. The mixture was then warmed to 50 °C and stirred for 2 h. The system

was cooled in ice-water bath, subsequently, 4,8-dihydrobenzo[1,2-*b*:4,5-*b'*]dithiophen-4,8-dione (1.00 g, 4.54 mmol) was added in one portion, and the mixture was heated at 50 °C for another 2 h. After the mixture was cooled to room temperature, a solution of SnCl<sub>2</sub>·2H<sub>2</sub>O (8.20 g, 36.32 mmol) in 20 mL of aqueous HCl (10%) was added, and the mixture was stirred overnight. The organic layer was washed with water and brine, dried with MgSO<sub>4</sub>, filtered and concentrated via rotary evaporation. Further purification was carried out by column chromatography on silica gel eluting with petroleum ether to obtain pure compound **2** as a yellow solid (2.60 g, 3.76 mmol, 83%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ/ppm): 7.65 (d, *J* = 5.7 Hz, 2H), 7.46 (d, *J* = 5.7 Hz, 2H), 7.30 (d, *J* = 3.5 Hz, 2H), 6.92 (d, *J* = 3.5 Hz, 2H), 2.93 (t, *J* = 7.7 Hz, 4H), 1.83-1.75 (m, 4H), 1.50-1.42 (m, 4H), 1.40-1.27 (m, 32H), 0.89 (t, *J* = 6.9 Hz, 6H).

**2,6-Bis(trimethyltin)-4,8-bis(5-dodecylthiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene (M1).** Compound **2** (1.00 g, 1.45 mmol) and 50 mL of anhydrous THF were added into a flask under nitrogen atmosphere. The solution was cooled to 0 °C and 1.5 mL of n-butyllithium (3.62 mmol, 2.4 M) was added dropwise. The reaction mixture was then stirred for 2 h at room temperature and cooled to 0 °C. Subsequently, 3.6 mL of trimethyltin chloride (3.62 mmol, 1.0 M in THF) was added in one portion and the mixture was stirred at RT overnight. The mixture was quenched by addition of 20 mL of water and extracted with diethyl ether three times. The combined organic phase was dried with MgSO<sub>4</sub>, filtered and concentrated via rotary evaporation. The residue was recrystallized in isopropanol to obtain compound **M1** as a light yellow solid (1.40 g, 1.38 mmol, 95%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ/ppm): 7.68 (s, 2H), 7.31 (d, *J* = 3.5 Hz, 2H), 6.92 (d, *J* = 3.5 Hz, 2H), 2.93 (t, *J* = 7.7 Hz, 4H), 1.83-1.74 (m, 4H), 1.50-1.41 (m, 4H), 1.39-1.26 (m, 32H), 0.88 (t, *J* = 6.9 Hz, 6H), 0.39 (s, 18H).



**1,2-Bis(dodecyloxy)benzene (1).** To a solution catechol (10 g, 90.82 mmol) in ethanol (100 mL) was added with sodium hydroxide (9.08 g, 227.04 mmol). After stirring at 60 °C for 0.5 h, 1-bromododecane (56.59 g, 227.04 mmol) was added with a syringe. The reaction mixture was then stirred at 60 °C for 40 h. Cooled down to room temperature, the reaction mixture was concentrated and the residue was extracted with dichloromethane and water. The combined organic layer was dried over anhydrous  $\text{MgSO}_4$  and concentrated. The residue was recrystallized using MeOH to afford **1** as a white solid (30.55 g, 75%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ,  $\delta$ /ppm): 6.89 (s, 4H), 3.99 (t,  $J = 6.7$  Hz, 4H), 1.84-1.78 (m, 4H), 1.49-1.44 (m, 4H), 1.36-1.26 (br, 32H), 0.88 (t,  $J = 6.9$  Hz, 6H).

**1,2-Bis(dodecyloxy)-4,5-dinitrobenzene (2).** To compound **1** (10.00 g, 22.38 mmol) solution in  $\text{CH}_2\text{Cl}_2/\text{AcOH}$  (70/70mL) was added with 65% nitric acid (20 mL). After 0.5 h stirring, the reaction mixture was slowly added with fuming nitric acid (50 mL) at 10 °C. After warming to room temperature, the reaction mixture was allowed to stir at rt for 40 h before pouring over an ice-water mixture. Extracted with dichloromethane/water, the combined organic layer was dried over anhydrous  $\text{MgSO}_4$  and concentrated. The title compound **2** was obtained as a yellow solid (10.20 g, 85%) after recrystallization from ethanol.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ,  $\delta$ /ppm) 7.29 (s, 2H), 4.10 (t,  $J = 6.5$  Hz, 4H), 1.89-1.84 (m, 4H), 1.50-1.45 (m, 4H), 1.37-1.26 (br, 32H), 0.88 (t,  $J = 6.9$  Hz, 6H).

**4,5-Bis(dodecyloxy)benzene-1,2-diaminium chloride (3).** To compound **2** (5.00 g,

9.32 mmol) solution in ethanol (100 mL) was added Sn(II)Cl<sub>2</sub>·2H<sub>2</sub>O (17.87 g, 79.18 mmol) in conc. HCl (50 mL) under N<sub>2</sub> atmosphere. The reaction mixture was then refluxed at 80 °C overnight. After cooled to room temperature, the residue was filtered and washed with water and methanol to obtain compound **3** as a white solid (unstable, 4.38 g, 86%).

### 3. TGA analysis

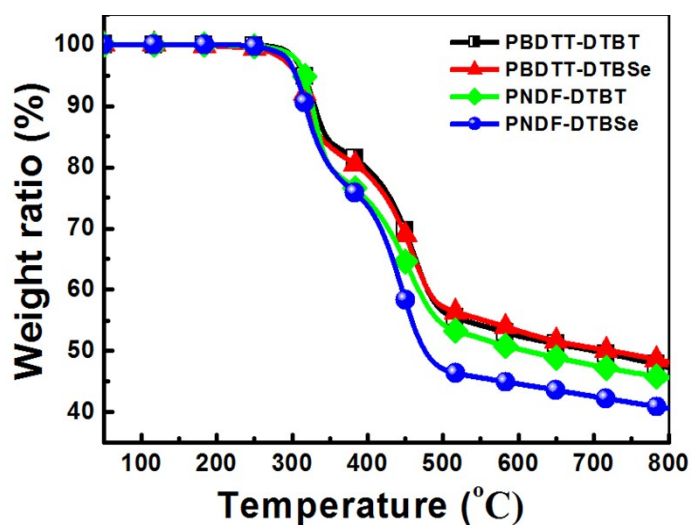


Fig. S1 TGA curves of four D-A copolymers.

### 4. Energy levels of polymers from CV measurement

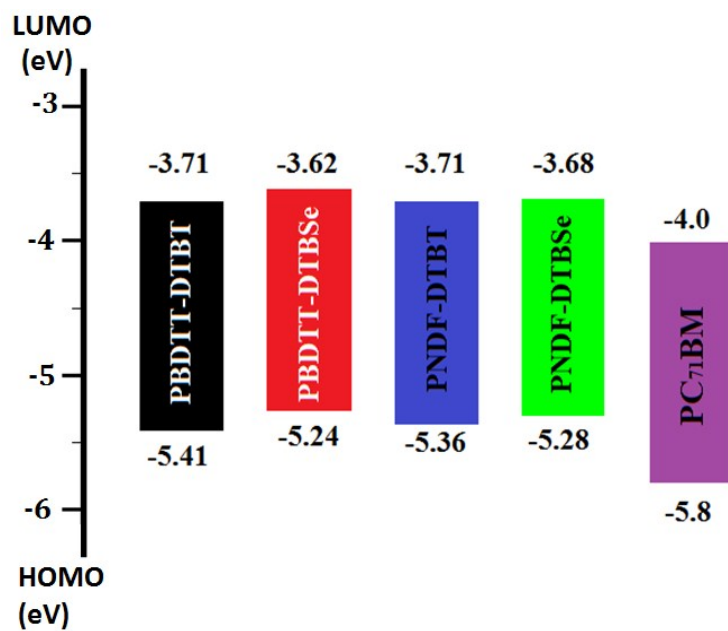


Fig. S2 HOMO and LUMO energy levels of the polymers.

### 5. NMR Spectra of intermediates

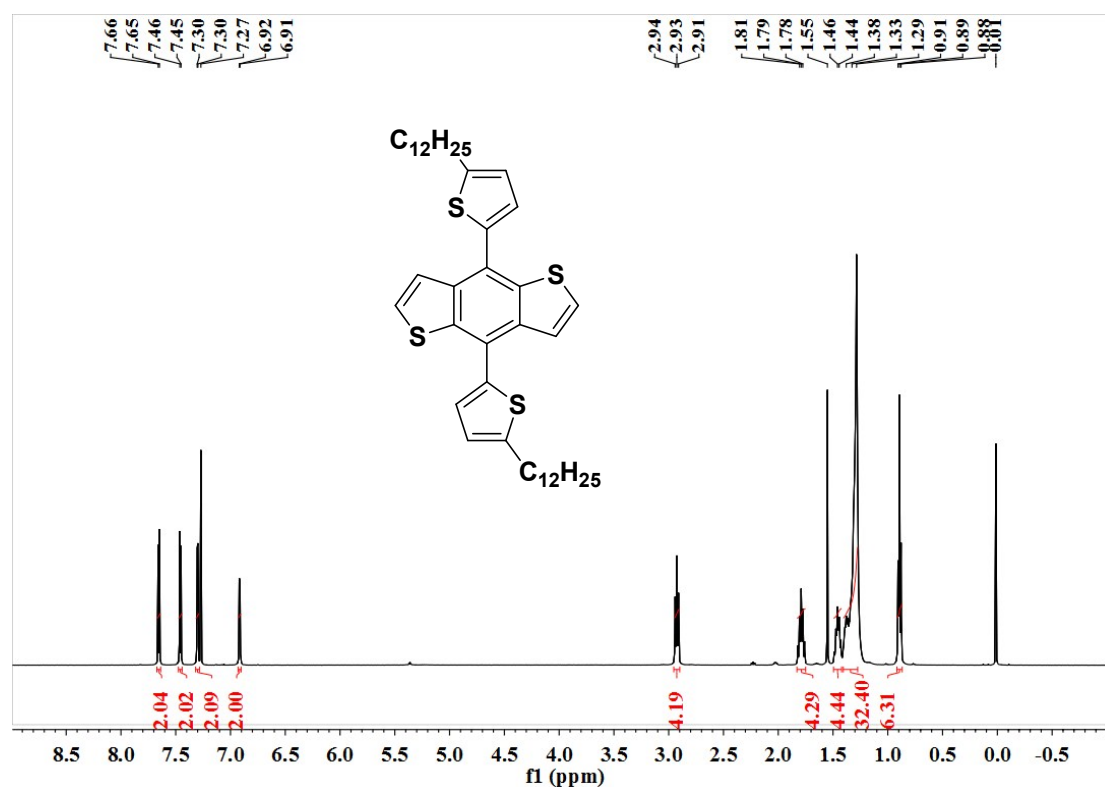


Figure S3. <sup>1</sup>H NMR spectrum of S2.

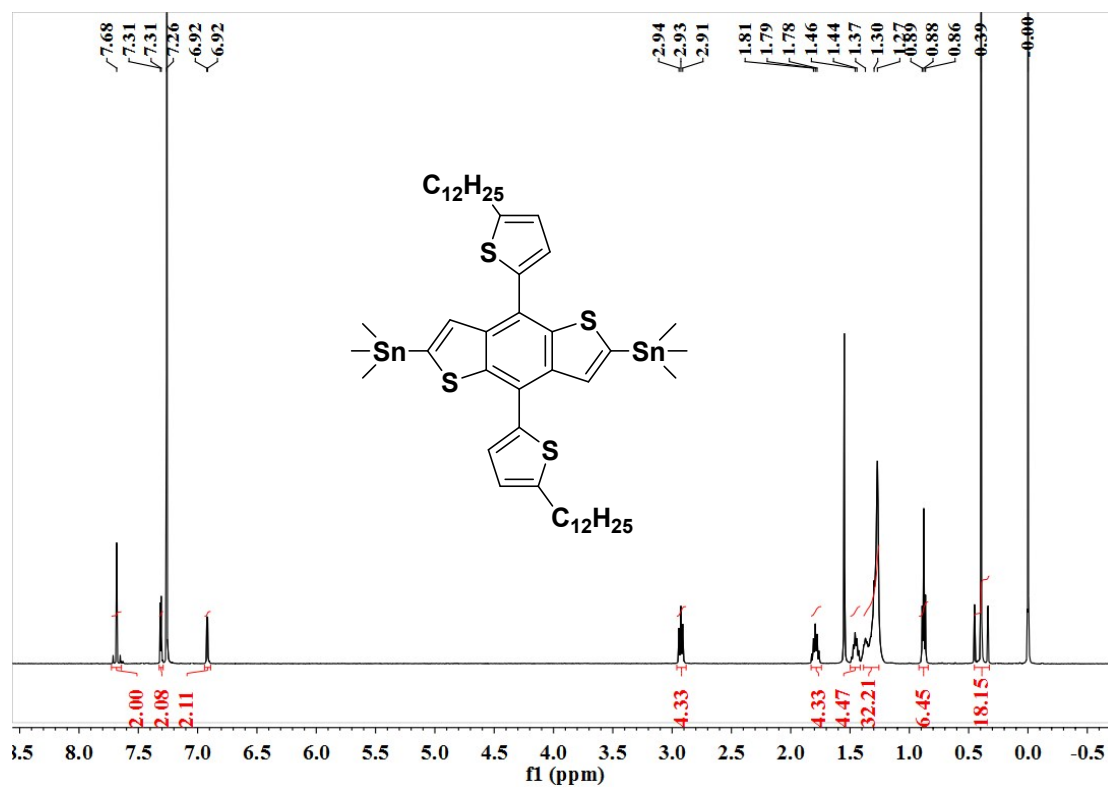


Figure S4.  $^1\text{H}$  NMR spectrum of M1.

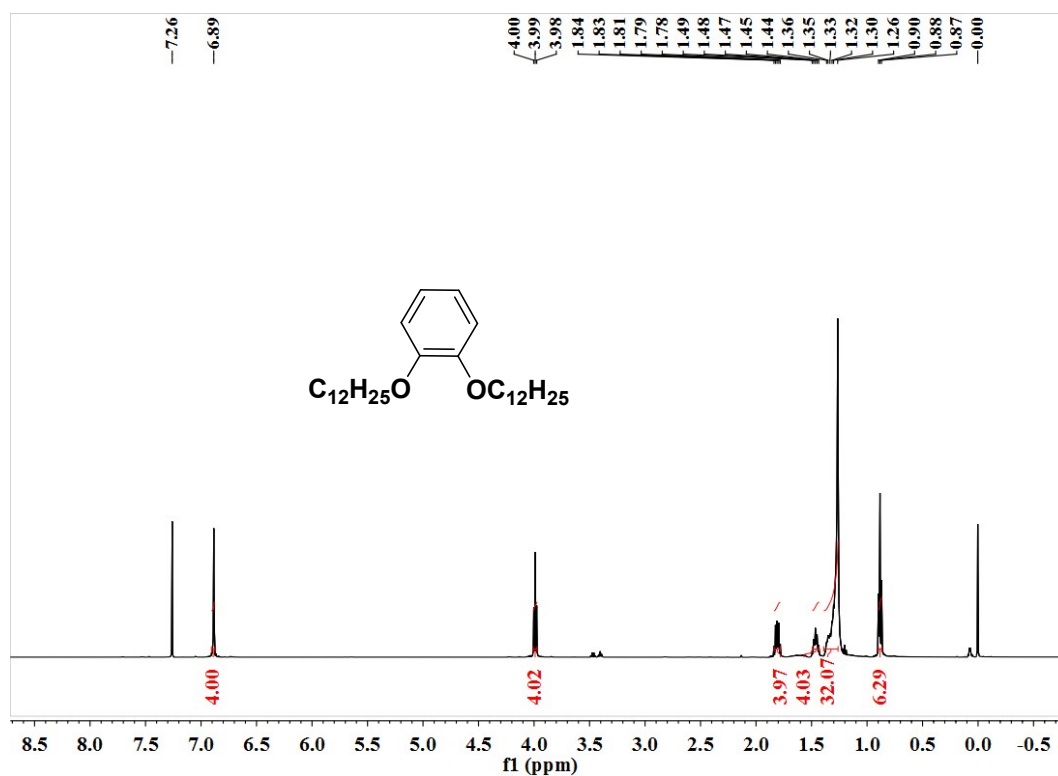


Figure S5.  $^1\text{H}$  NMR spectrum of 1.

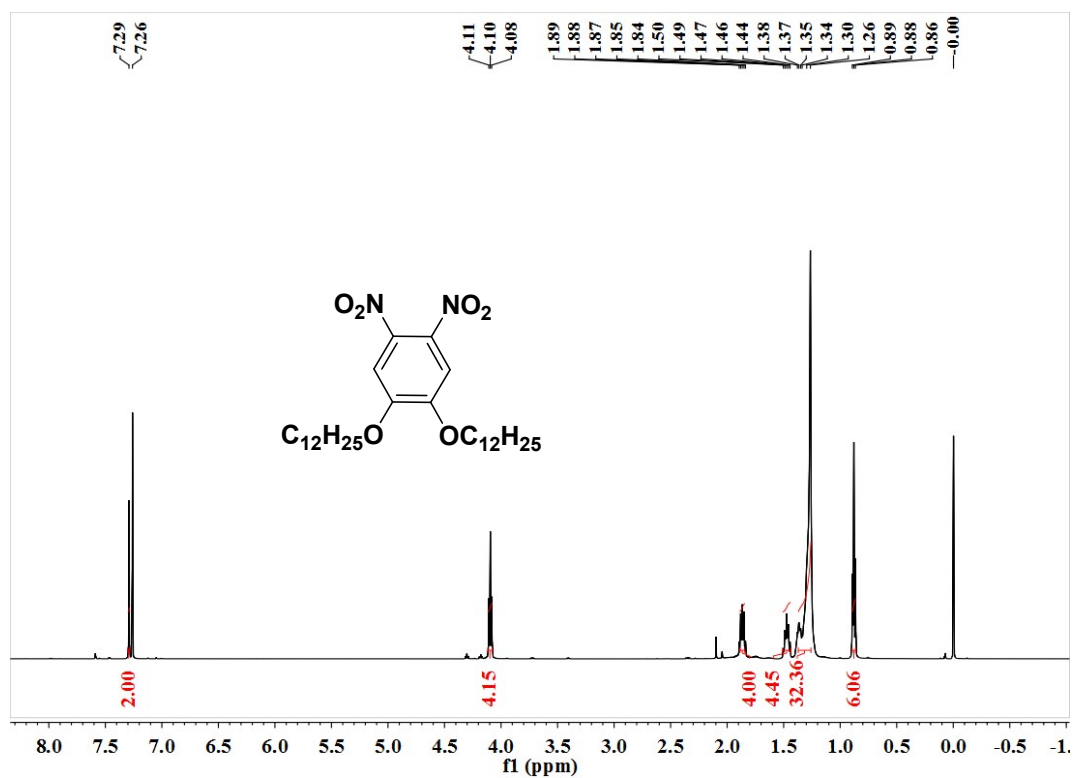


Figure S6.  $^1\text{H}$  NMR spectrum of 2.

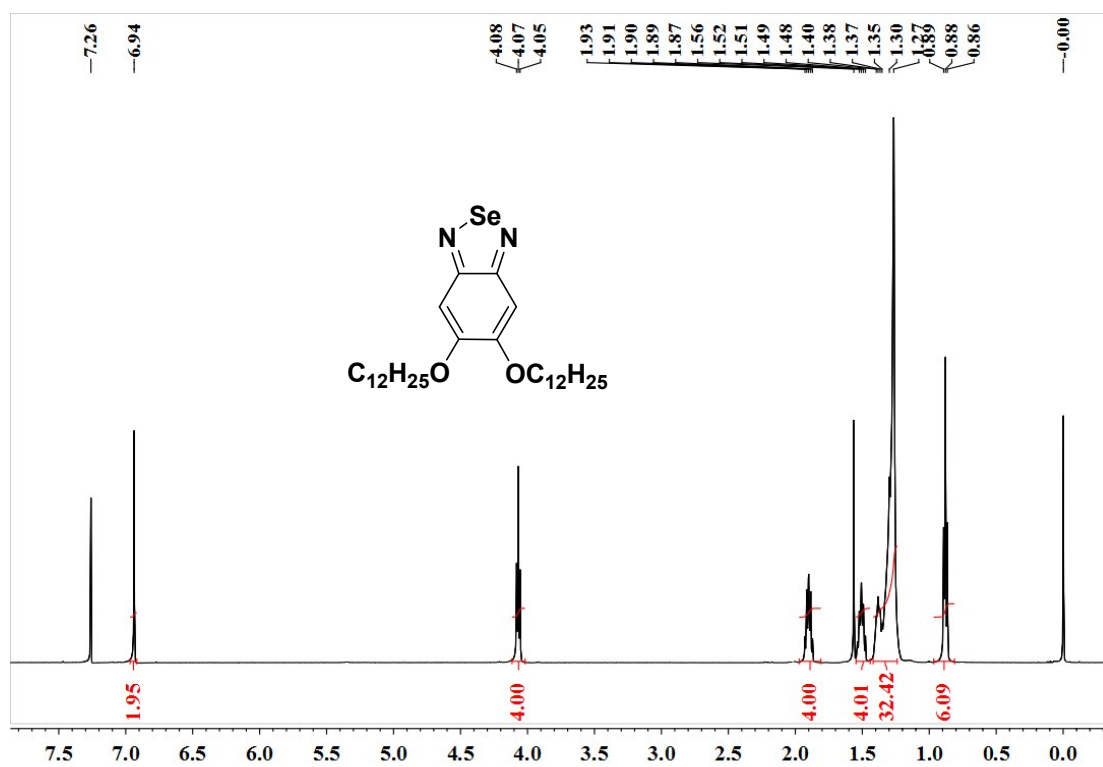


Figure S7.  $^1\text{H}$  NMR spectrum of 4.



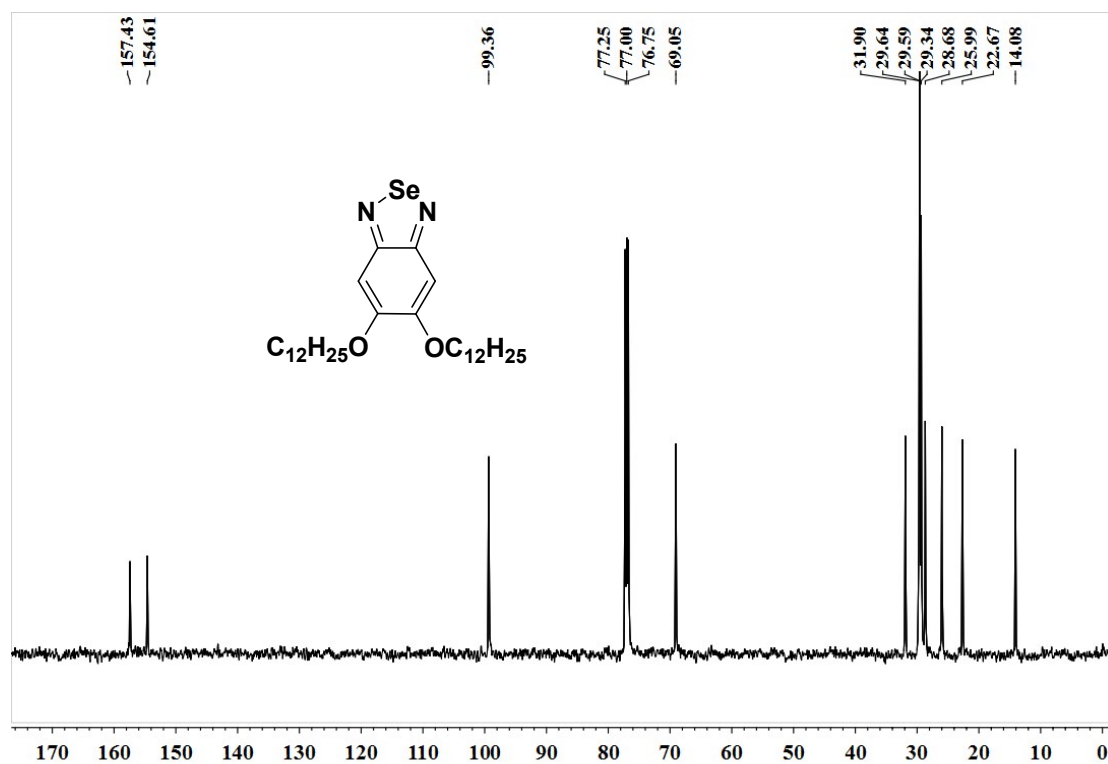


Figure S8.  $^{13}\text{C}$  NMR spectrum of 4.

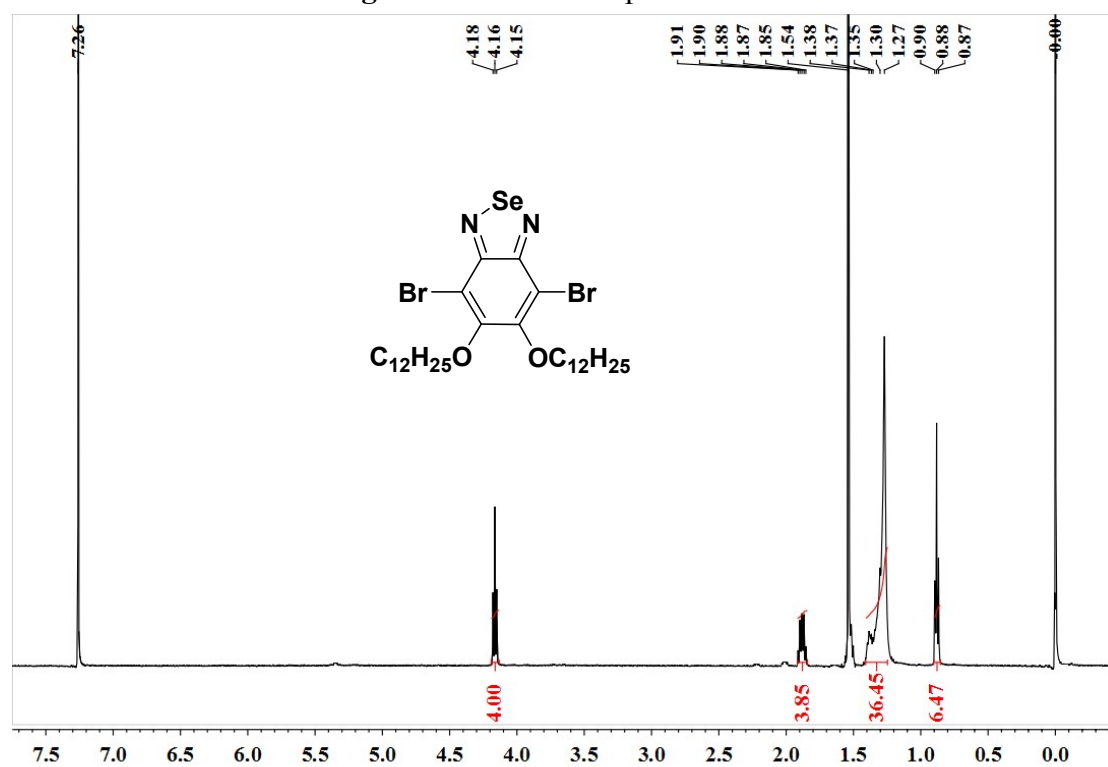


Figure S9.  $^1\text{H}$  NMR spectrum of 5.

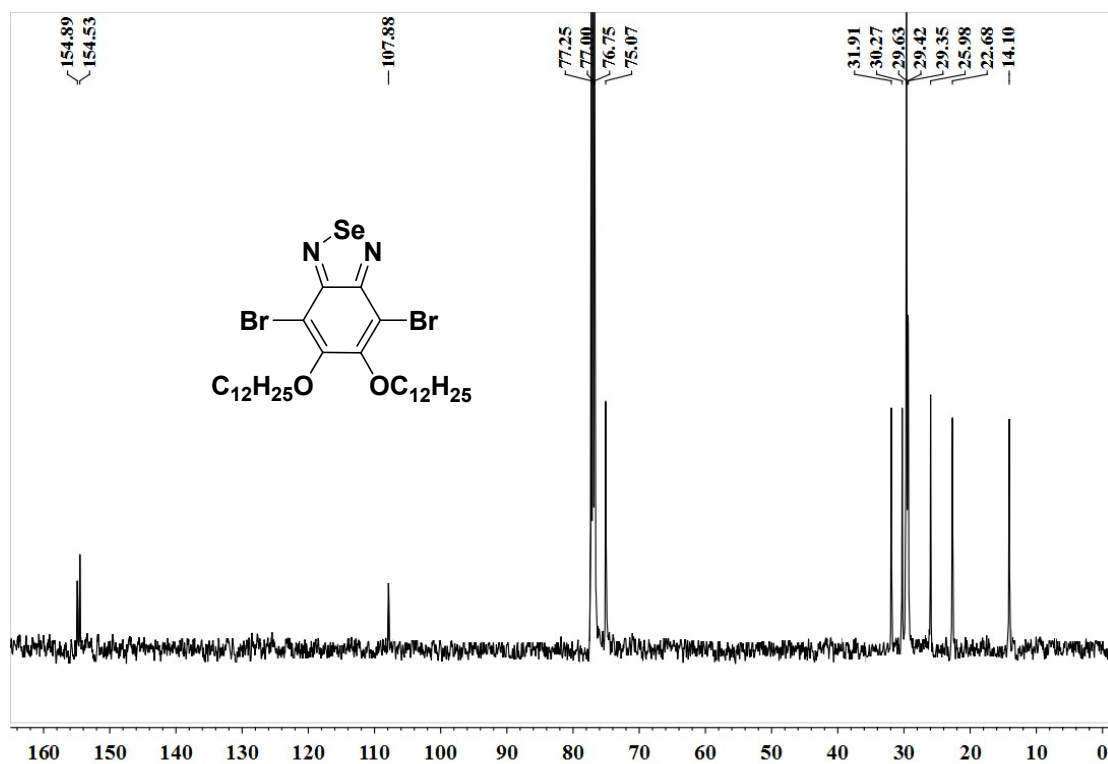


Figure S10.  $^{13}\text{C}$  NMR spectrum of 5.

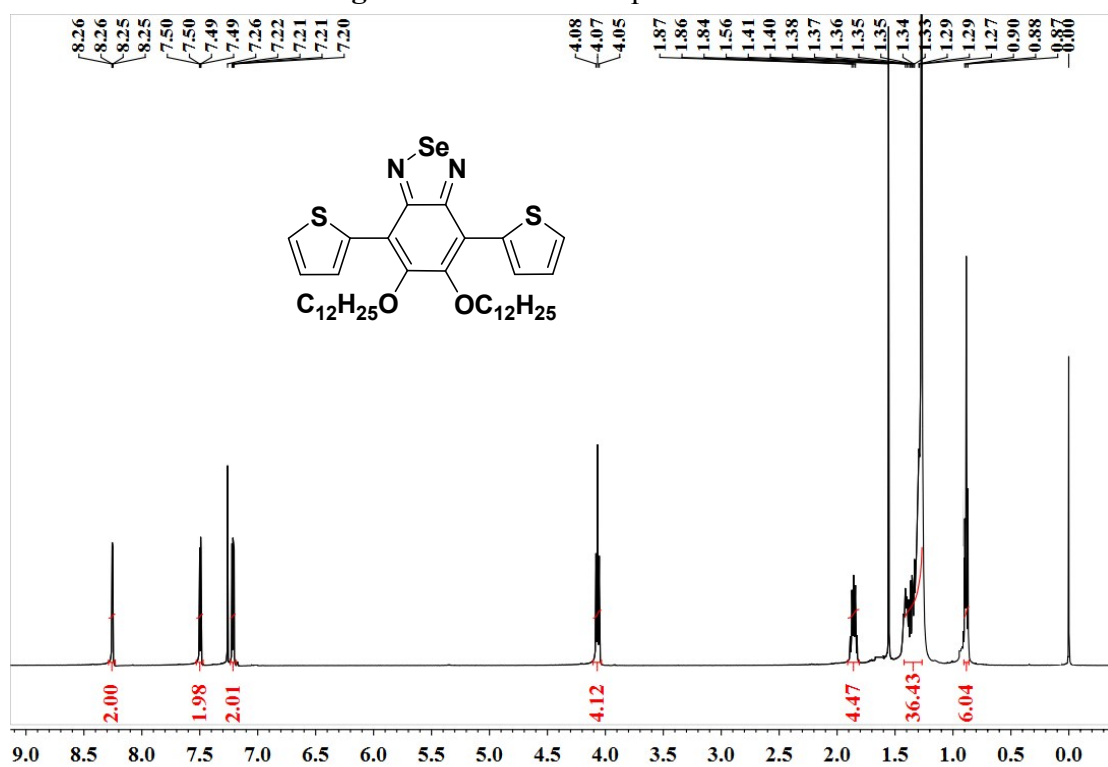


Figure S11.  $^1\text{H}$  NMR spectrum of 6.

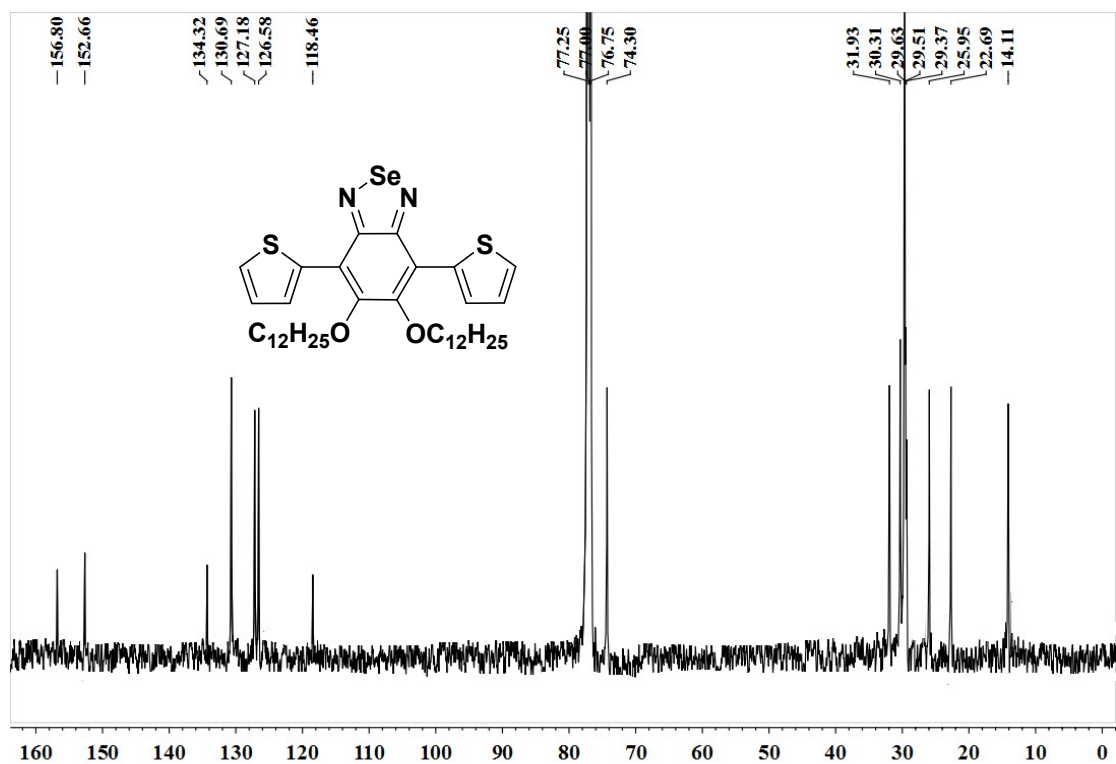


Figure S12.  $^{13}\text{C}$  NMR spectrum of 6.

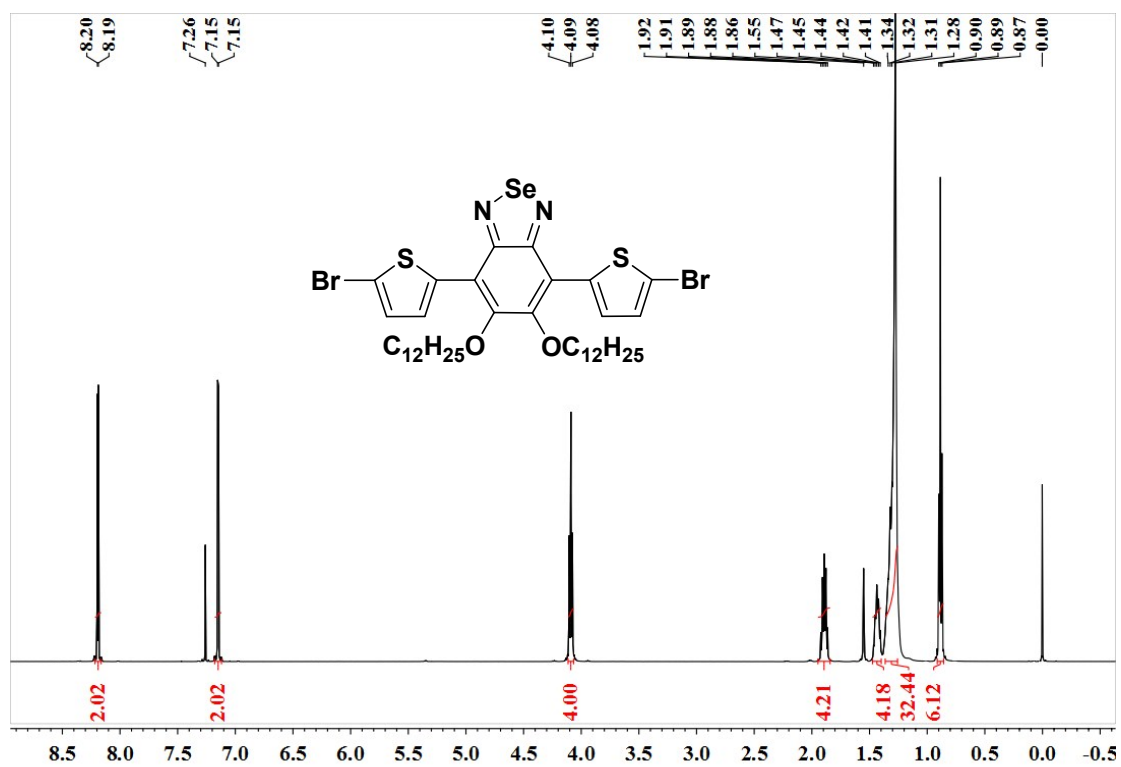


Figure S13.  $^1\text{H}$  NMR spectrum of M4.

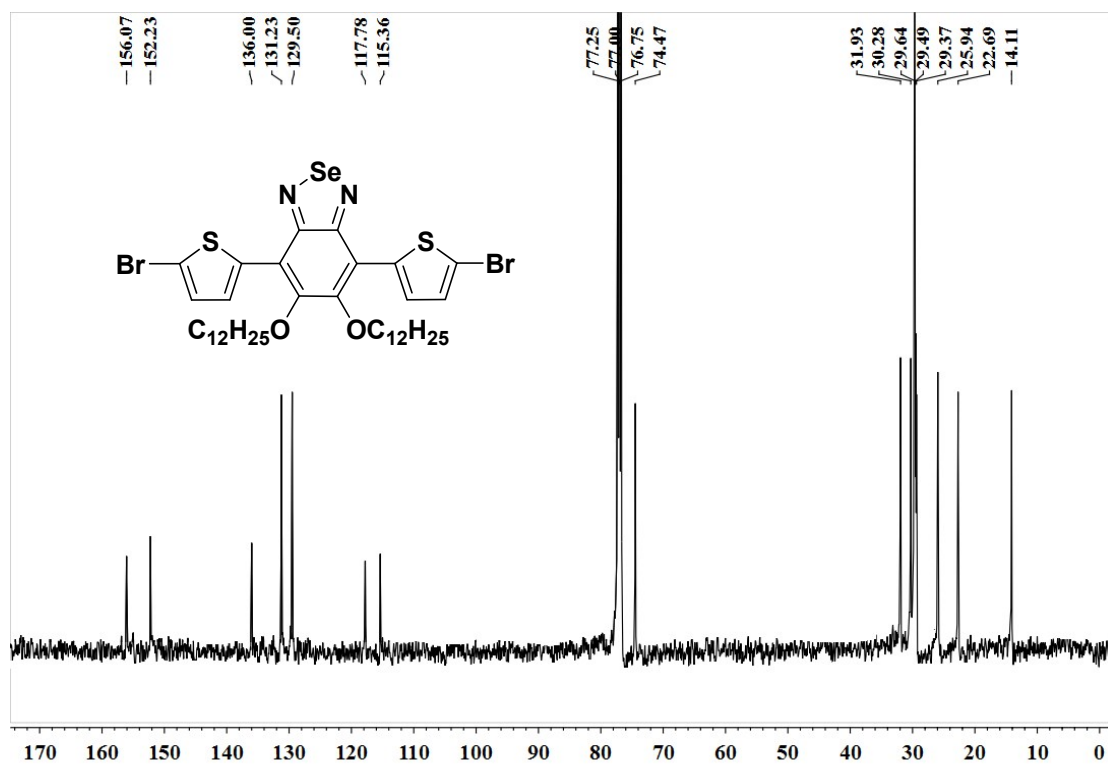


Figure S14.  $^{13}\text{C}$  NMR spectrum of M4.