

# Supporting Information

## **Influence of the aryl spacer in 2,5-dialkoxyphenylene and diaryl substituted thieno[3,4-c]pyrrole-4,6-dione copolymers**

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<b>1. General</b> .....	3
<b>2. Monomer Synthesis</b> .....	6
<b>3. Polymer Synthesis</b> .....	10
<b>4. Monomer NMR Spectra</b> .....	13
<b>5. Polymer NMR Spectra</b> .....	20
<b>6. Polymer DSC</b> .....	24
<b>7. Polymer XRD</b> .....	25
<b>8. Polymer CV</b> .....	26
<b>9. Polymer PV Device Characterization</b> .....	26
<b>10. References.</b> .....	29

## 1. General

All reactions were performed under dry N<sub>2</sub> in oven dried glassware, unless otherwise noted. Unless otherwise noted, all reagents were purchased and used as received from commercial sources. Solvents were purchased from VWR and used without purification except for tetrahydrofuran (THF), which was dried over sodium/benzophenone before distillation. Flash chromatography was performed on a Teledyne CombiFlash Rf instrument with RediSep Rf normal phase disposable columns. All NMR were recorded at 25 °C using CDCl<sub>3</sub> on either a Varian Mercury 400 MHz or Varian VNMRS-500 MHz, for small molecules, or a Varian VNMRS-600 MHz, for polymers. All spectra were referenced to CHCl<sub>3</sub> (7.26 ppm), unless otherwise noted. Number average molecular weight (M<sub>n</sub>) and polydispersity (Đ) were determined by size exclusion chromatography (SEC) using a Viscotek GPC Max VE 2001 separation module and a Viscotek Model 2501 UV detector, with 70 °C HPLC grade 1,2-dichlorobenzene (*o*-DCB) as eluent at a flow rate of 0.6 mL/min on one 300 × 7.8 mm TSK-Gel GMHHR-H column (Tosoh Corp). The instrument was calibrated vs. polystyrene standards (1050–3,800,000 g/mol), and data were analysed using OmniSec 4.6.0 software. Polymer samples were dissolved in HPLC grade *o*-dichlorobenzene at a concentration of 0.5 mg ml<sup>-1</sup>, stirred at 65 °C until dissolved, cooled to room temperature, and filtered through a 0.2 μm PTFE filter. Compounds **S5** and **S10** had been previously prepared according to literature methods.<sup>2-5</sup>

Cyclic voltammetry (CV) was performed on Princeton Applied Research VersaStat3 potentiostat under the control of VersaStudio Software. A standard three-electrode cell based on a Pt wire working electrode, a silver wire pseudo reference electrode (calibrated vs Fc/Fc<sup>+</sup> which is taken as 5.1 eV vs vacuum), and a Pt wire counter electrode was purged with nitrogen and maintained under a nitrogen atmosphere during all measurements. Polymer films were made by drop-casting an *o*-DCB solution of polymer (10 mg/mL) and tetrabutylammonium

hexafluorophosphate (TBAPF<sub>6</sub>) (30 mg/mL) directly onto the Pt wire and dried under nitrogen prior to measurement. Acetonitrile was distilled over CaH<sub>2</sub> prior to use, and TBAPF<sub>6</sub> (0.1 M) was used as the supporting electrolyte.

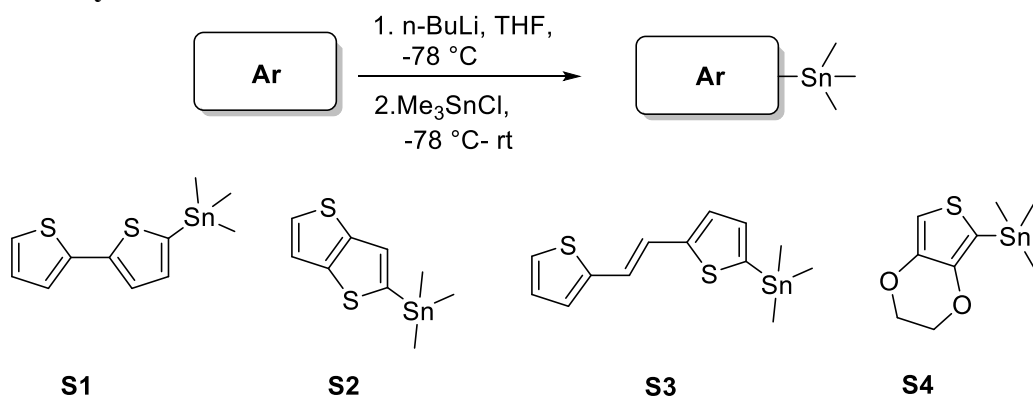
For polymer thin-film measurements, solutions were spin-coated onto pre-cleaned glass slides from *o*-dichlorobenzene (*o*-DCB) solutions at 7 mg/mL. UV–vis absorption spectra were obtained on a Perkin-Elmer Lambda 950 spectrophotometer. Thicknesses of the samples and grazing incidence X-ray diffraction (GIXRD) measurements were obtained using Rigaku diffractometer Ultima IV using a Cu K $\alpha$  radiation source ( $\lambda = 1.54 \text{ \AA}$ ) in the reflectivity and grazing incidence X-ray diffraction mode, respectively. DSC profiles were recorded on a PerkinElmer DSC 8000 under N<sub>2</sub> with a scan rate of 10 °C/min. Sample size was about 3 mg, and polymers were used as obtained after Soxhlet extraction.

**Solar Cell Device Fabrication and Characterization.** All steps of device fabrication and testing were performed at ambient temperatures and humidity in air. ITO-coated glass substrates (10  $\Omega$ /sq, Thin Film Devices Inc.) were sequentially cleaned by sonication in detergent solution, deionized water, tetrachloroethylene, acetone, and isopropyl alcohol, and dried under a nitrogen stream. PEDOT:PSS (Clevios™ PH 1000, filtered with a 0.45  $\mu\text{m}$  poly(vinylidene fluoride) (PVDF) syringe filter—Pall Life Sciences) was spin-coated on the freshly cleaned ITO-coated glass substrates and then annealed at 120 °C for 50 min under vacuum to generate a 40 nm thick film. Separate solutions of the polymers and PC<sub>61</sub>BM were prepared in *o*-DCB. The solutions were stirred for 8 h at 65 °C or 110 °C before they were mixed to afford a 1:1.5 (polymer:PCBM) ratio and stirred for 16 h at 65 °C or 110 °C to form a homogeneous solution prior to spin-coating. The polymer:PC<sub>61</sub>BM active layer was filtered (with a 0.45  $\mu\text{m}$  polytetrafluoroethylene (PTFE) syringe filter—Pall Life Sciences) and spin-coated on top of the PEDOT:PSS layer. Polymer: PC<sub>61</sub>BM

concentrations of the blends were 11 mg/mL respective to the total polymer weight. For consistency across all polymers, every device was kept in a nitrogen box for 25 min after spin-coating and then placed in the vacuum chamber for aluminium deposition. Aluminium was deposited using a Denton Benchtop Turbo IV Coating System. The substrates were pumped down to high vacuum ( $1.5 \times 10^{-6}$  torr) and aluminium (100 nm) was thermally evaporated at 3–6 Å/s onto the active layer through shadow masks to define the active area of the devices as 5.18 mm<sup>2</sup>. Device results shown are the average of at least 8 pixels. The current density–voltage (J–V) characteristics of the photovoltaic devices were measured under ambient conditions using a Keithley 2400 source-measurement unit. An Oriel® Sol3A class AAA S11 solar simulator with a Xenon lamp (450 W) and an AM 1.5G filter was used as the solar simulator. An Oriel PV reference cell system 91150 V was used as the reference cell to calibrate the light intensity of the solar simulator (to 100 mW/cm<sup>2</sup>), achieved by making the  $J_{sc}$  of the reference cell under simulated sunlight as high as it was under the calibration condition. External quantum efficiency (EQE) measurements were performed using a 300 W Xenon arc lamp (Newport Oriel), chopped and filtered monochromatic light (250 Hz, 10 nm FWHM) from a Cornerstone 260 1/4 M double grating monochromator (Newport 74125) together with a light bias lock-in amplifier. A silicon photodiode calibrated at Newport was utilized as the reference cell.

**SCLC Hole Mobility Measurements.** Mobility was measured using a hole-only device configuration of ITO/PEDOT:PSS/Polymer/Al in the space charge limited current regime as described in literature. The device preparation for a hole-only device was the same as that described above for solar cells and thicknesses were determined by GIXRD in the reflectivity mode. The dark current was measured under ambient conditions.

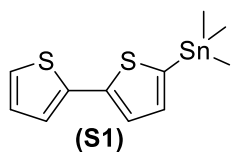
## 2. Monomer Synthesis



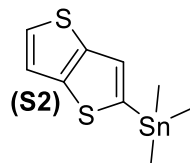
**Scheme S1.** Synthesis of Compounds S1-S4.

### General Procedure for the Synthesis of Compounds S1-S4.

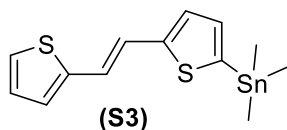
To an oven dried, 3-neck round bottom flask (25 mL) equipped with a stir-bar was added the aromatic compound to be stannylated (3.0 mmol). The flask was N<sub>2</sub>-backfilled 3 times, THF (8 mL) was added and the mixture was cooled to -78 °C. n-BuLi (3.15 mmol, 1.05 equiv) was then added dropwise and the mixture was allowed to stir for 1.5 h at -78 °C. Me<sub>3</sub>SnCl (3.3 mmol, 1.1 equiv) was then added rapidly to the mixture and it was allowed to warm up slowly overnight from -78 °C to room temperature. NH<sub>4</sub>Cl sat. aq. (10 mL) was added to the reaction mixture and it was extracted with Et<sub>2</sub>O (3x25 mL). The combined organics were washed with brine, dried with MgSO<sub>4</sub>, and the solvent stripped. Used without further purification. Referenced to known or similar compounds.<sup>6-10</sup>



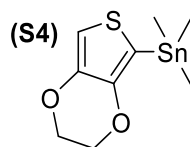
*[2,2'-bithiophen]-5-yltrimethylstannane (S1)* Yield: 95% <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ (ppm) 7.28 (dd, 1H, *J* = 6.0, 4.0 Hz), 7.22-7.16 (m, 2H), 7.08 (dd, 1H, *J* = 4.5, 3.5 Hz), 7.03-7.00 (m, 1H), 0.38 (s, 9 H).



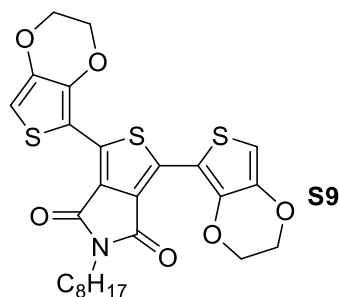
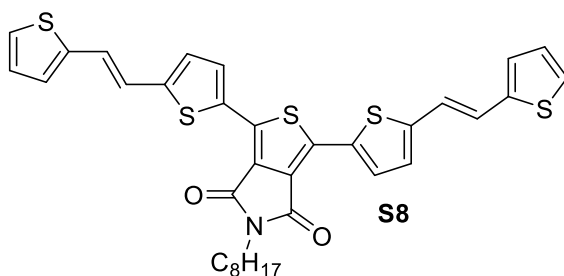
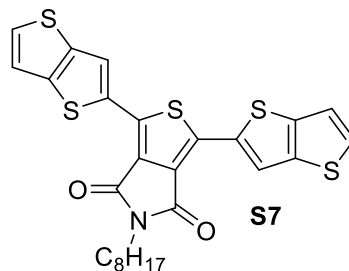
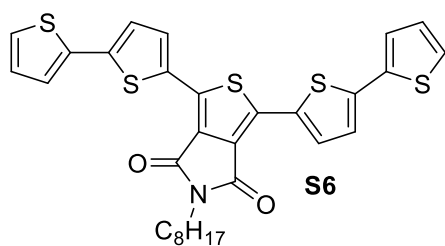
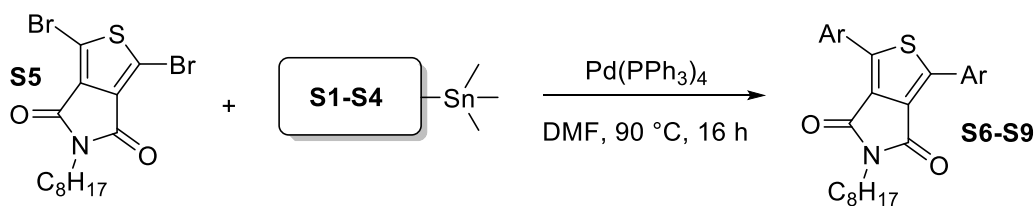
trimethyl(thieno[3,2-b]thiophen-2-yl)stannane (**S2**) Yield: 84% <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ (ppm) 7.35 (d, 1H, *J* = 5.5 Hz), 7.29 (s, 1H), 7.24 (d, 1H, *J* = 5.0 Hz).



(*E*)-trimethyl(5-(2-(thiophen-2-yl)vinyl)thiophen-2-yl)stannane (**S3**) Yield: 86% <sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.16 (d, 1H, *J* = 5.0 Hz), 7.13-7.02 (m, 5H), 6.98 (dd, 1H, *J* = 5.0, 4.0 Hz).



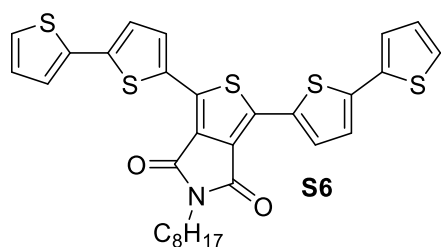
(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)trimethylstannane (**S4**) Yield: 94% <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ (ppm) 6.61 (s, 1H), 4.18 (s, 4H), 0.36 (s, 9H).



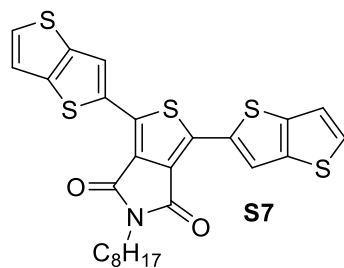
**Scheme S2.** Synthesis of compounds S6-S9.

## General Procedure for the Synthesis of Compounds S6-S9.

To an oven-dried, 3-neck round bottom flask (25 mL) equipped with a condenser and a stir-bar was added **S5** (1 mmol). The apparatus was N<sub>2</sub>-backfilled 3 times, and anhydrous DMF was added (15 mL) and the stannylated aryl compound (**S1-S4**) (2.2 mmol, 2.2 equiv). The mixture was sparged with N<sub>2</sub> for 15 minutes before quickly adding Pd(PPh<sub>3</sub>) (0.06 mmol, 0.06 equiv). The mixture was heated at 90 °C under N<sub>2</sub> for 16 h. The reaction mixture was then poured into a 1:1 solution of MeOH and H<sub>2</sub>O (100 mL), and the solid filtered. For compounds **S5** and **S8**, column chromatography was performed using the appropriate solvent mixture (DCM/hexanes). Compounds **S6** and **S7** were washed successively with MeOH and DCM after filtration and were sufficiently pure for the polymerization step. Referenced to known or similar compounds.<sup>9,11-13</sup>



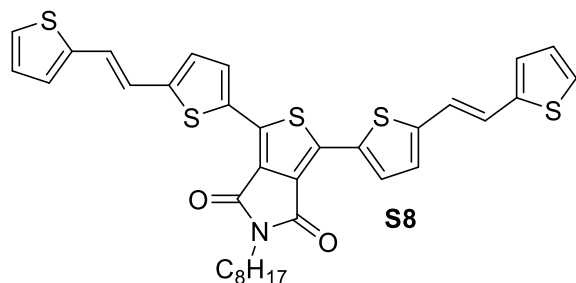
*1,3-di([2,2'-bithiophen]-5-yl)-5-octyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (S6)* Recrystallized from EtOH after column chromatography, affording a fibrous orange solid. Yield: 36% <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ (ppm) 7.88 (d, 2H, *J* = 4.0 Hz), 7.28 (d, 2H, *J* = 5.5 Hz), 7.25 (d, 2H, *J* = 3.5 Hz), 7.13 (d, 2H, *J* = 4.0 Hz), 7.03 (dd, 2H, *J* = 5.5 Hz, 3.5 Hz), 3.64 (t, 2H, *J* = 7.0 Hz), 1.71-1.66 (m, 2H), 1.35-1.26 (m, 10H), 0.88 (t, 3H, *J* = 6.5 Hz). <sup>13</sup>C (CDCl<sub>3</sub>): δ (ppm) 162.5, 140.7, 136.4, 135.8, 130.9, 130.8, 128.3, 128.1, 125.6, 124.8, 124.6, 38.6, 31.8, 29.22, 29.18, 18.5, 27.0, 22.6, 14.1.



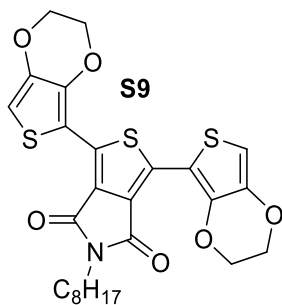
*5-octyl-1,3-bis(thieno[3,2-b]thiophen-2-yl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (S7)* Bright orange solid. Yield: 80% <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ (ppm) 8.36 (s, 2H), 7.48 (d, 2H, *J* = 5.0 Hz), 7.23



(d, 2H,  $J = 5.0$  Hz), 1.71-1.66 (m, 2H), 3.67 (t, 2H,  $J = 7.5$  Hz) 1.35-1.26 (m, 10H), 0.88 (t, 3H,  $J = 6.5$  Hz).  $^{13}\text{C}$  ( $\text{CDCl}_3$ ): 162.6, 141.0, 140.3, 136.9, 133.8, 130.2, 128.8, 122.3, 119.4, 38.7, 31.8, 29.20, 29.17, 28.5, 27.0, 22.6, 14.1.

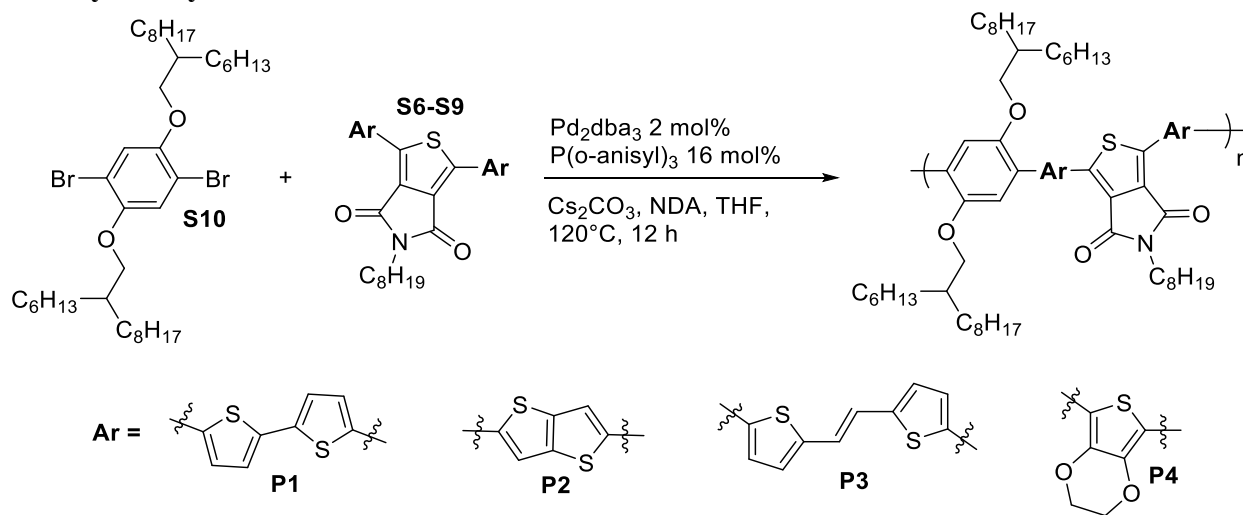


*5-octyl-1,3-bis(5-((E)-2-(thiophen-2-yl)vinyl)thiophen-2-yl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (S8)* Dark red solid. Yield: 93%  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.83 (dd, 2H,  $J = 3.5$ , 0.75 Hz), 7.22 (d, 2H,  $J = 5.0$  Hz), 7.13 (d, 2H, 16.0 Hz), 7.05 (d, 2H,  $J = 3.5$  Hz), 7.00-6.984 (m, 2H), 6.96 (d, 2H,  $J = 3.5$  Hz), 6.94 (d, 2H,  $J = 16.0$  Hz), 3.64 (t, 2H,  $J = 7.5$  Hz), 1.71-1.66 (m, 2H), 1.35-1.26 (m, 10H), 0.88 (t, 3H,  $J = 6.0$  Hz).  $^{13}\text{C}$  ( $\text{CDCl}_3$ ): 162.5, 145.9, 141.9, 136.0, 130.8, 130.6, 128.3, 127.8, 127.2, 127.0, 125.2, 123.5, 120.4, 38.6, 31.8, 29.21, 29.19, 28.5, 27.0, 22.6, 14.1.



*1,3-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-5-octyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (S9)* Recrystallized from EtOH after column chromatography, affording orange crystals. Yield: 66%  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 6.54 (s, 2H) 4.44-4.42 (m, 4H), 4.28-4.27 (m, 4H), 3.63 (t, 2H,  $J = 7.5$  Hz), 1.70-1.64 (m, 2H), 1.32-1.25 (m, 10H), 0.86 (t, 3H,  $J = 6.0$  Hz).  $^{13}\text{C}$  ( $\text{CDCl}_3$ ): 162.9, 140.9, 134.4, 126.5, 109.5, 103.3., 102.9, 65.5, 64.6, 64.2, 38.4, 31.8, 29.2, 28.5, 27.0, 22.6, 14.1.

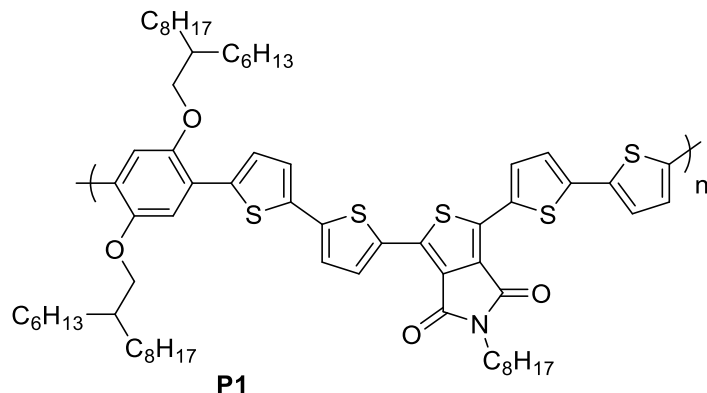
### 3. Polymer Synthesis



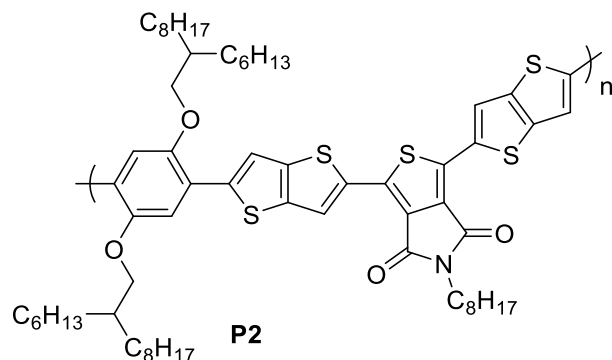
**Scheme S3.** Synthesis of polymers **P1-P4** via direct arylation polymerization.

#### General Procedure for the Preparation of Polymers **P1-P4**.

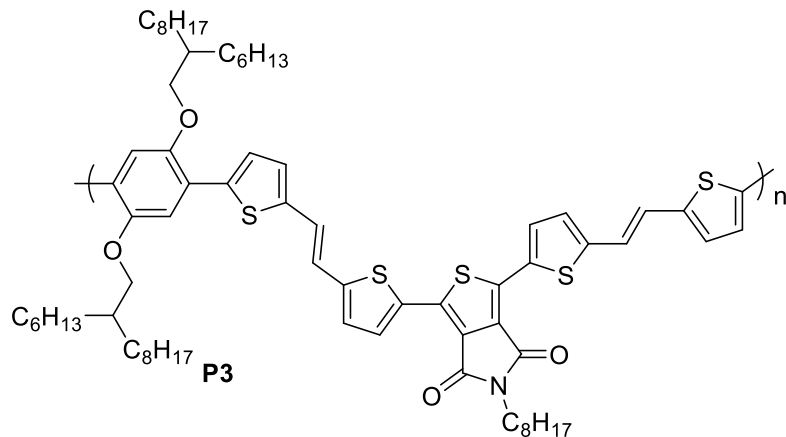
An oven dried 15 mL high pressure vessel was cooled under a stream of  $\text{N}_2$ . Then neodecanoic acid (0.5 mmol), **S10** (0.25 mmol), the acceptor (**S6-S9**) (0.25 mmol),  $\text{P(o-anisyl)}_3$  (16 mol%),  $\text{CsCO}_3$  (3 equiv.), and freshly distilled THF (2.5 mL) were added to the vessel. It was sparged with  $\text{N}_2$  for 15 minutes, then  $\text{Pd}_2\text{dba}_3$  (2 mol%) was added quickly, and the Teflon screwcap with o-ring was fastened tightly. It was then placed in a preheated oil bath at 120 °C for 12 hr. The vessel was then cooled, the contents dissolved in chlorinated solvents ( $\text{CHCl}_3$  or chlorobenzene), and then the polymer was precipitated slowly via pipette to cold MeOH and allowed to stir for several minutes. The solids were then filtered off into a Soxhlet thimble and extracted with MeOH (24 hr.), hexanes (16 hr.), and then  $\text{CHCl}_3$ . The  $\text{CHCl}_3$  fraction was concentrated and the polymer precipitated into cold MeOH, filtered off, and dried under vacuum.



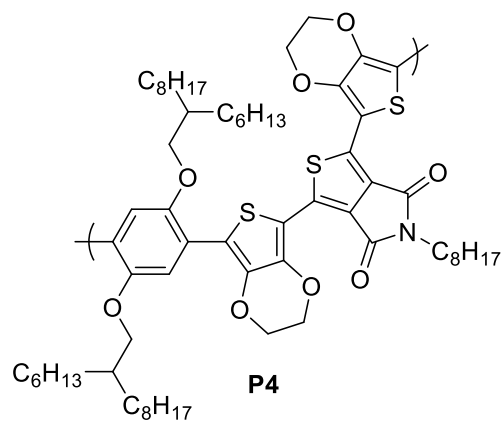
*poly[(2,5-bis[(2-hexyldecyl)oxyphenylene])-alt-(1,3-di[(2,2'-bithiophen]-5-yl)-5-octyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione)] (P1)* Yield: 92%  $M_n$  ( $\bar{M}$ ): 16.5 kDa (2.12)  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.00-7.50 (b, 2H), 7.50-7.30 (b, 2H), 7.20-6.95 (b, 2H) 6.93-6.30 (b, 4H), 4.03-3.92 (b, 4H), 3.75-3.65 (b, 2H), 1.95 (b, 2H), 1.50-1.10 (b, 60H), 0.88 (b, 15H).  $^1\text{H}$  NMR ( $\text{C}_2\text{D}_2\text{Cl}_4$ ) 600 MHz 100 °C:  $\delta$  (ppm) 8.04 (b, 2H), 7.55 (b, 2H), 7.32-7.26 (bm, 6H), 4.11 (b, 4H), 3.75-3.74 (b, 2H), 2.02 (b, 2H), 1.80 (b, 2H), 1.67 (b, 4H), 1.57-1.34 (bm, 54H), 0.93 (b, 15 H).



*poly[(2,5-bis[(2-hexyldecyl)oxyphenylene])-alt-(5-octyl-1,3-bis(thieno[3,2-b]thiophen-2-yl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione)] (P2)* Yield: 69%  $M_n$  ( $\bar{M}$ ): 3.9 kDa (1.69)  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.40-8.10 (b, 2H), 7.90-7.32 (b, 2H), 7.22-6.80 (b, 2H), 4.20-3.90 (b, 4H), 3.75-3.60 (b, 2H), 2.10-1.90 (b, 2H), 1.45-1.10 (b, 60H), 1.10-0.75 (b, 15H).  $^1\text{H}$  NMR ( $\text{C}_2\text{D}_2\text{Cl}_4$ ) 600 MHz 100 °C:  $\delta$  (ppm) 8.41-8.36 (bm, 2H), 7.70-7.55 (b, 2H), 7.32-7.26 (bm, 2H), 4.12 (b, 4H), 3.77-3.74 (b, 2H), 2.05 (b, 2H), 1.81-1.35 (b, 60H), 0.98-0.95 (b, 15H).

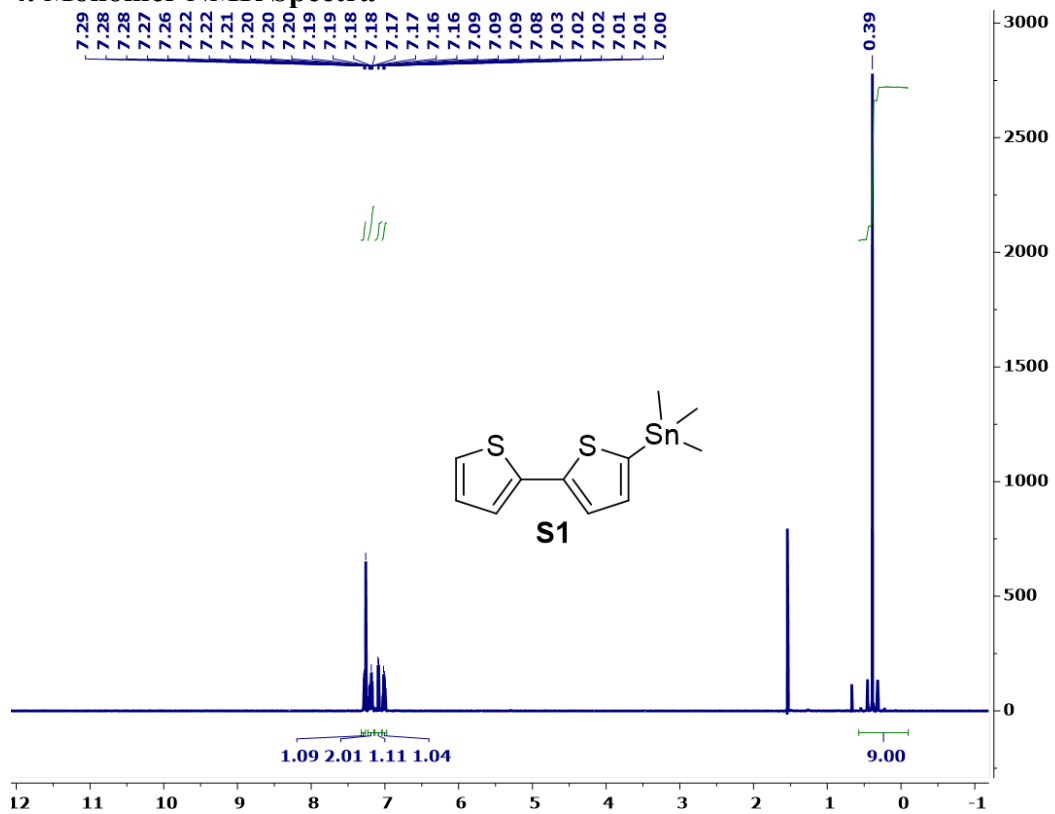


*poly[(2,5-bis[(2-hexyldecyl)oxyphenylene])-alt-(5-octyl-1,3-bis(5-((E)-2-(thiophen-2-yl)vinyl)thiophen-2-yl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione)] (P3)* Yield: 70%  $M_n$  (Đ): 7.47 kDa (2.13)  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.05-7.70 (b, 2H), 7.45-7.35 (b, 2H), 7.75-6.85 (b, 10H), 3.97-3.87 (b, 4H), 3.67-3.62 (b, 2H), 1.95-1.92 (b, 2H), 1.50-1.10 (b, 60H), 1.10-0.75 (b, 15H).  $^1\text{H}$  NMR ( $\text{C}_2\text{D}_2\text{Cl}_4$ ) 600 MHz 100 °C:  $\delta$  (ppm) 7.99-7.97 (bm, 2H), 7.53 (b, 2H), 7.29-7.08 (bm, 10H), 4.08 (b, 4H), 3.76-3.73 (bm, 2H), 2.00 (b, 2H), 1.79 (b, 2H), 1.66 (b, 4H), 1.56-1.40 (bm, 54H), 0.97-0.95 (bm, 15H).

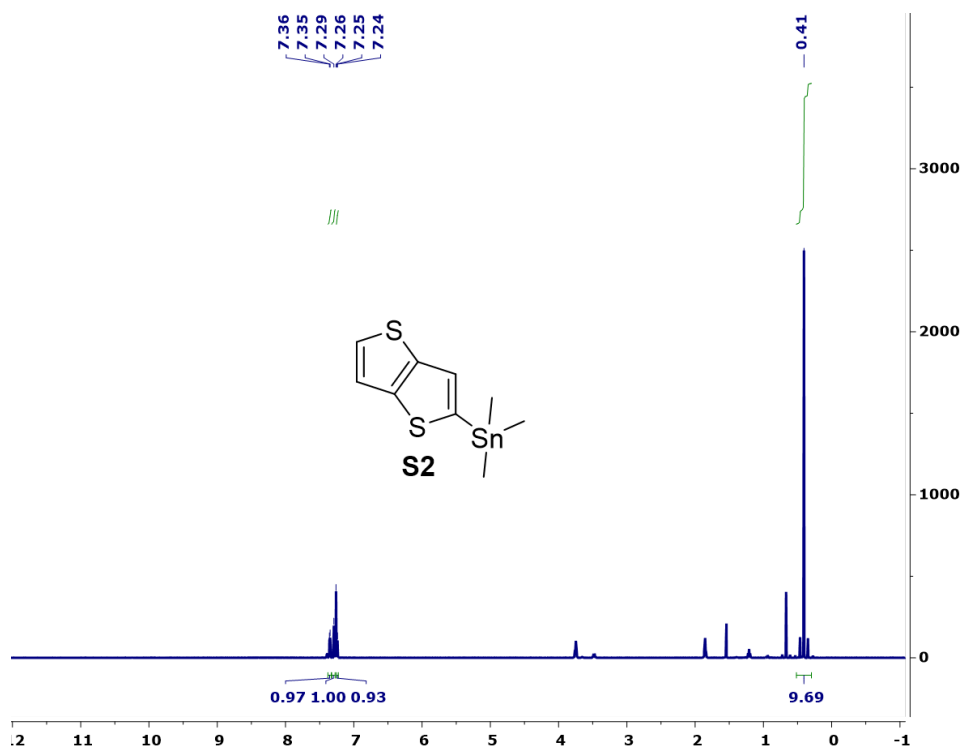


*poly[(2,5-bis[(2-hexyldecyl)oxyphenylene])-alt-(1,3-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-5-octyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione)] (P4)* Yield: 87%  $M_n$  (Đ): 9.03 kDa (1.50)  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.93 (b, 2H), 4.80-3.58 (b, 14H), 2.56 (b, 2H), 1.50-1.11 (b, 60H), 0.91 (b, 12H), 0.88 (b, 3H).  $^1\text{H}$  NMR ( $\text{C}_2\text{D}_2\text{Cl}_4$ ) 600 MHz 100 °C:  $\delta$  (ppm) 7.75 (s, 2H), 4.53-4.45 (bm, 8H), 4.07 (b, 4H), 3.76-3.69 (bm, 2H), 2.15 (b, 2H), 1.89-1.34 (bm, 60H), 0.96-0.91 (bm, 15H).

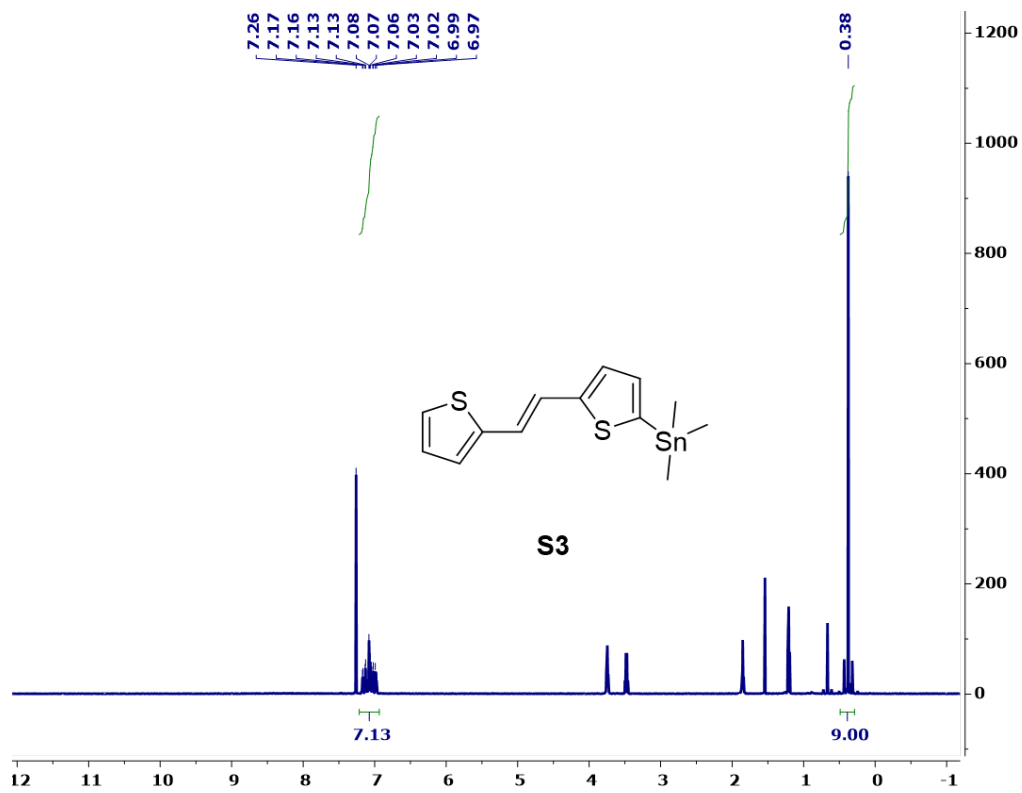
#### 4. Monomer NMR Spectra



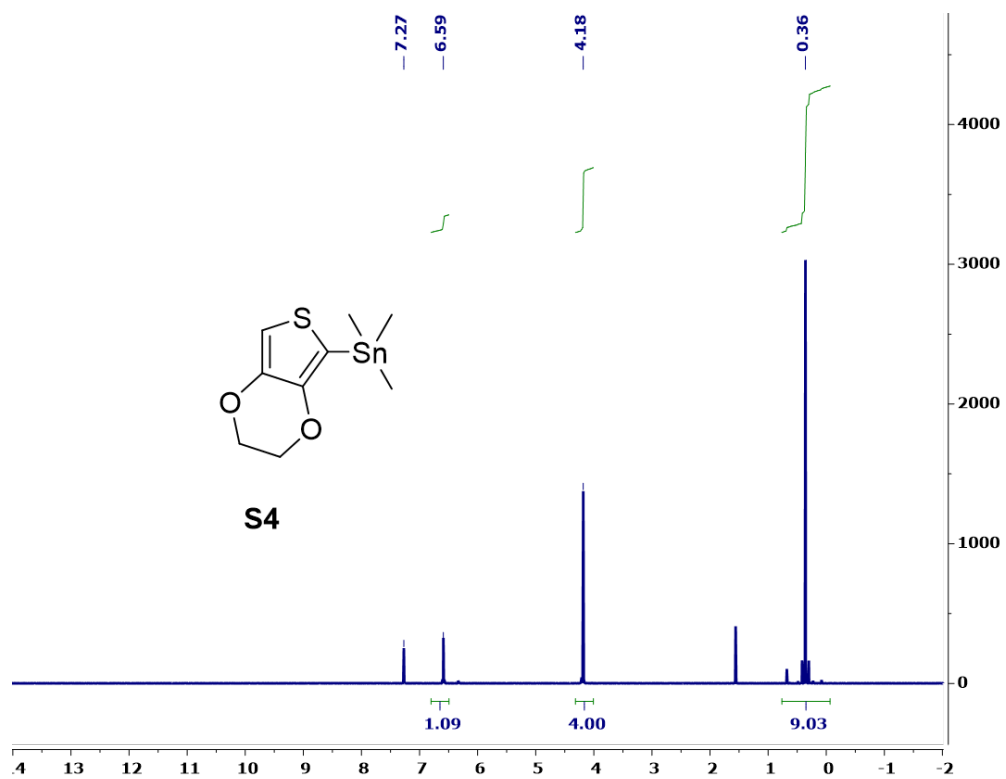
Proton NMR of compound S1 in  $\text{CDCl}_3$ .



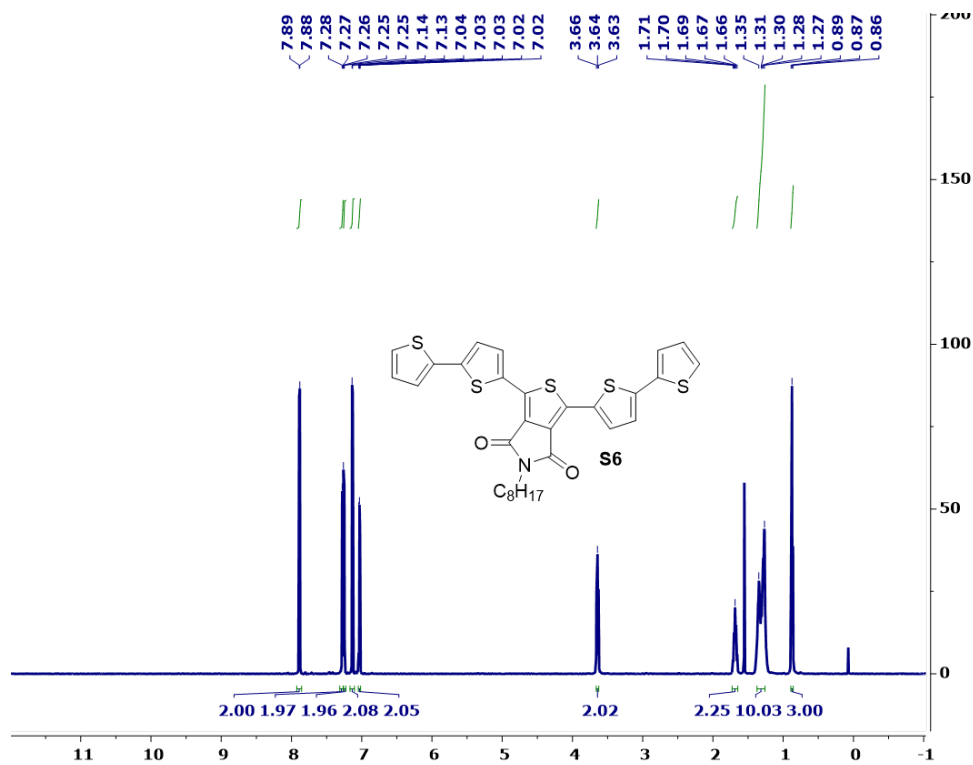
Proton NMR of compound S2 in  $\text{CDCl}_3$ .



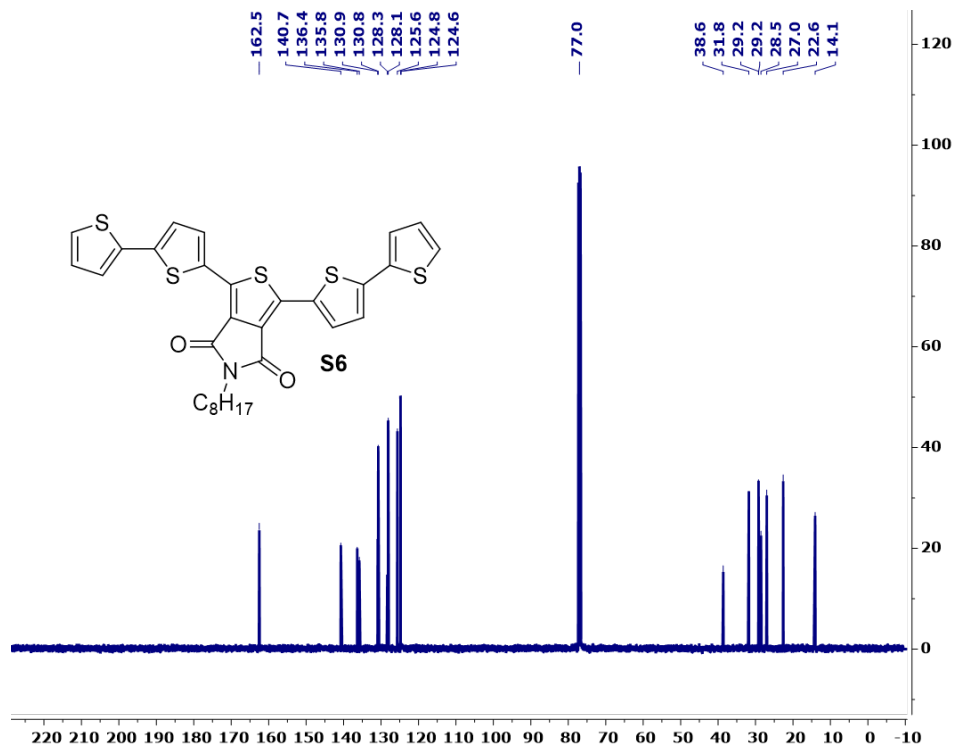
Proton NMR of compound S3 in  $\text{CDCl}_3$ .



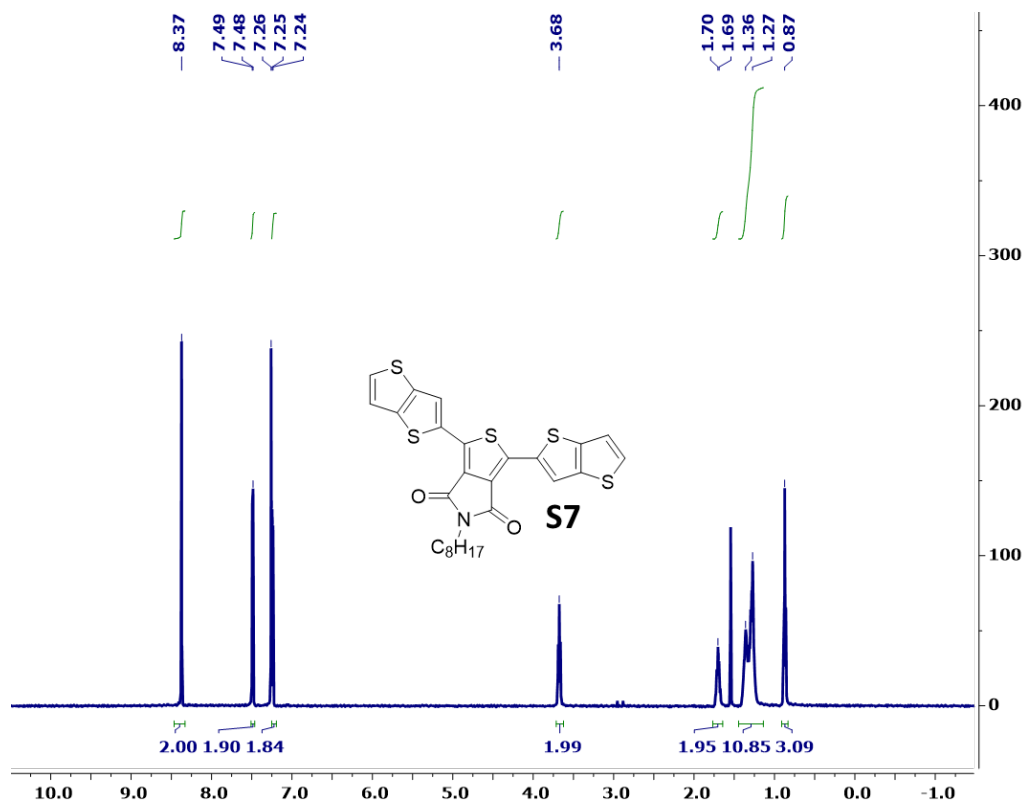
Proton NMR of compound S4 in  $\text{CDCl}_3$ .



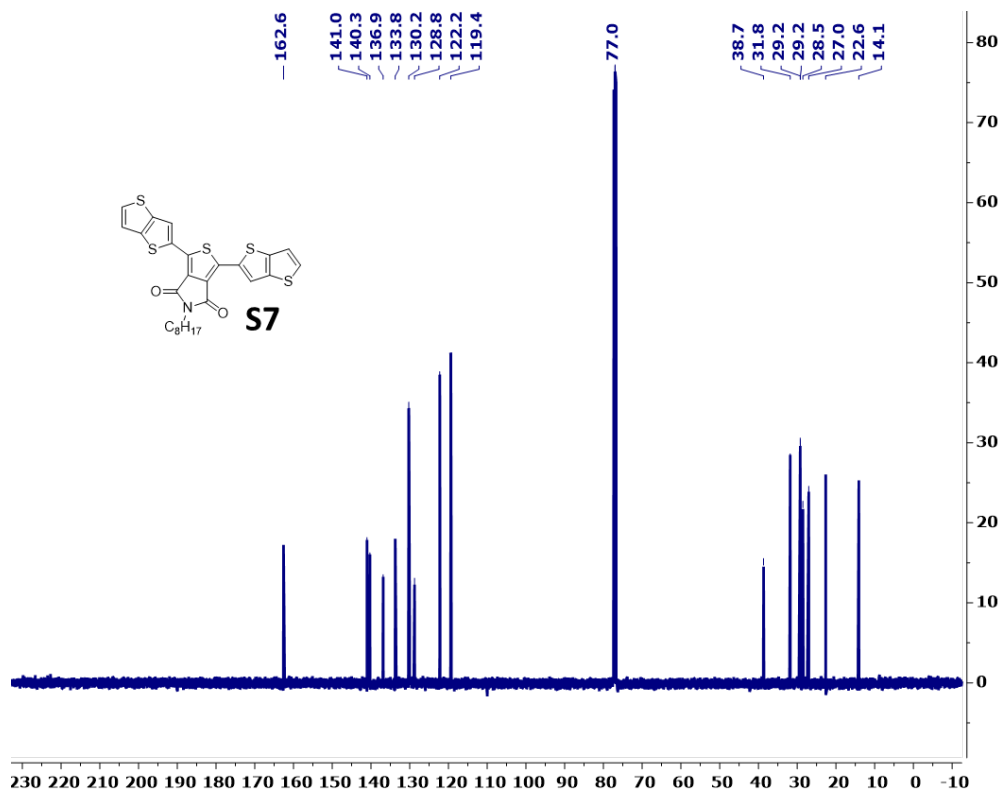
Proton NMR of compound S6 in  $\text{CDCl}_3$ .



$^{13}\text{C}$  NMR of compound S6 in  $\text{CDCl}_3$ .

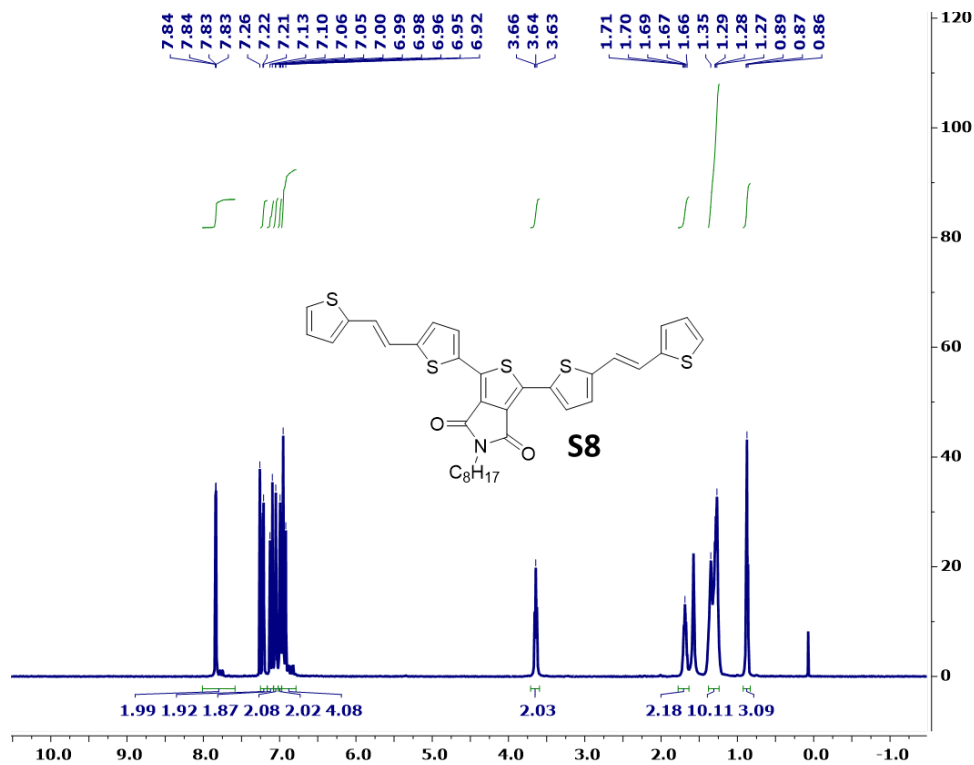


Proton NMR of compound S7 in  $\text{CDCl}_3$ .

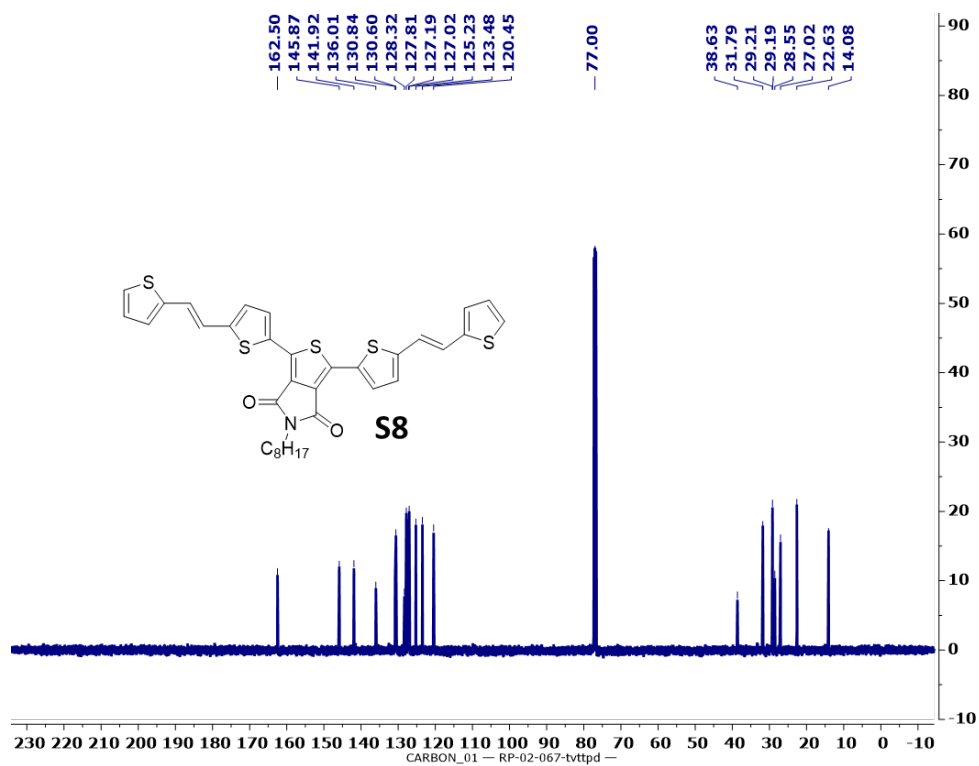


$^{13}\text{C}$  NMR of compound S7 in  $\text{CDCl}_3$ .

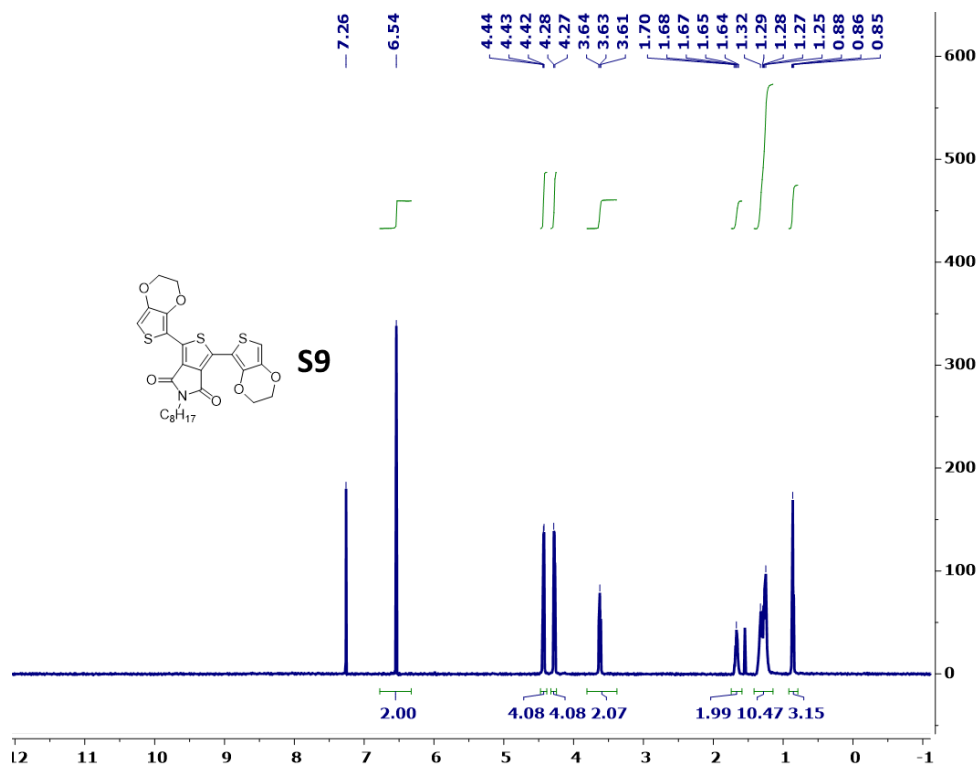




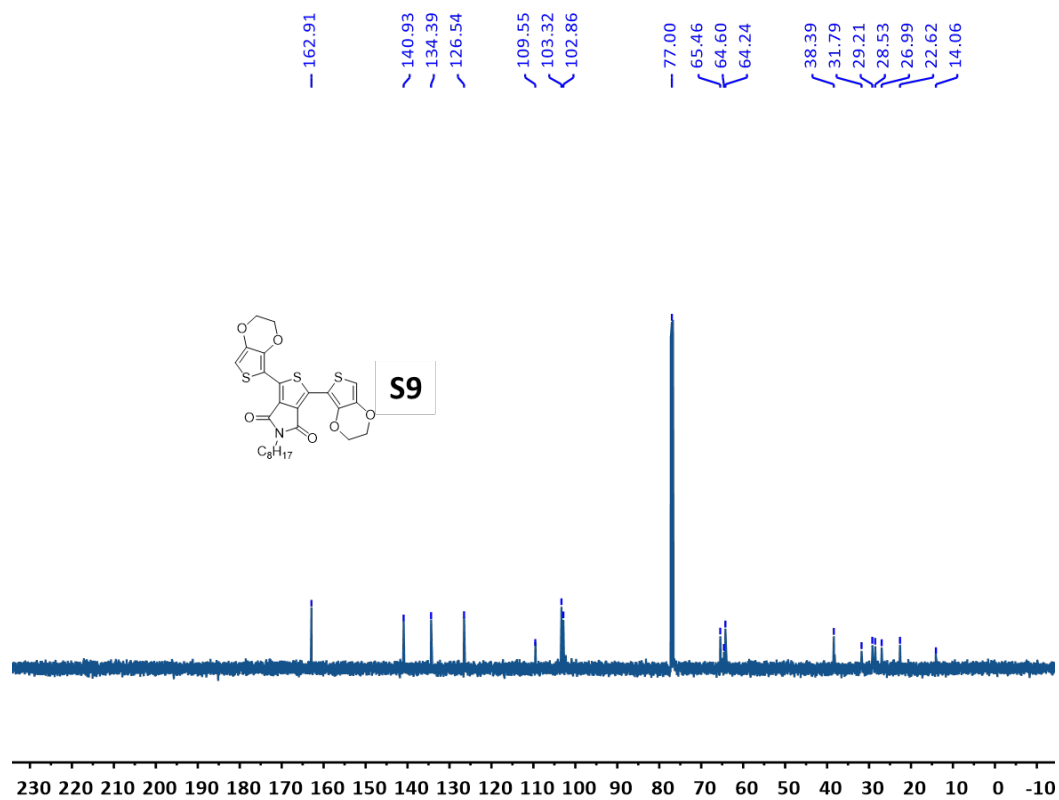
Proton NMR of compound S8 in CDCl<sub>3</sub>.



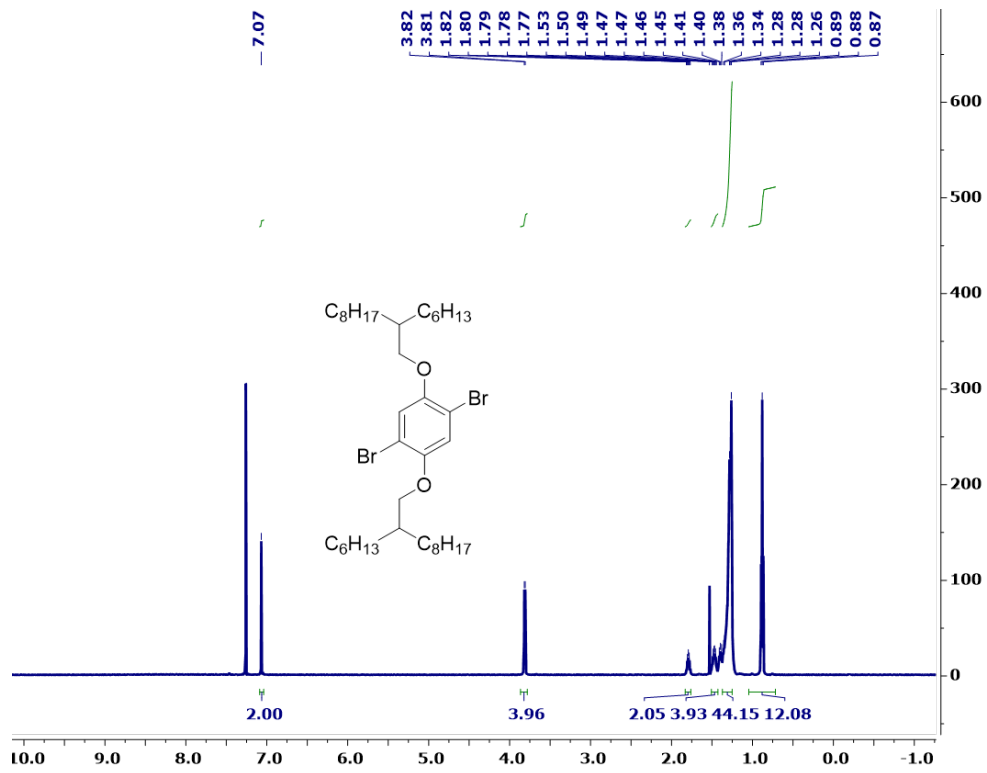
<sup>13</sup>C NMR of compound S8 in CDCl<sub>3</sub>.



Proton NMR of compound S9 in  $\text{CDCl}_3$ .

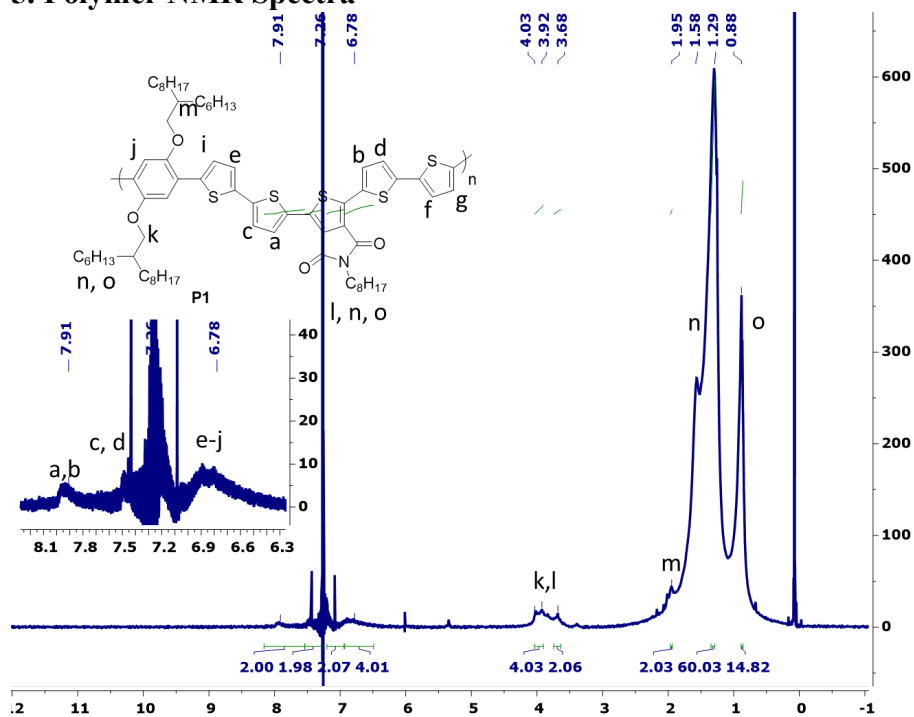


$^{13}\text{C}$  NMR of compound S9 in  $\text{CDCl}_3$ .

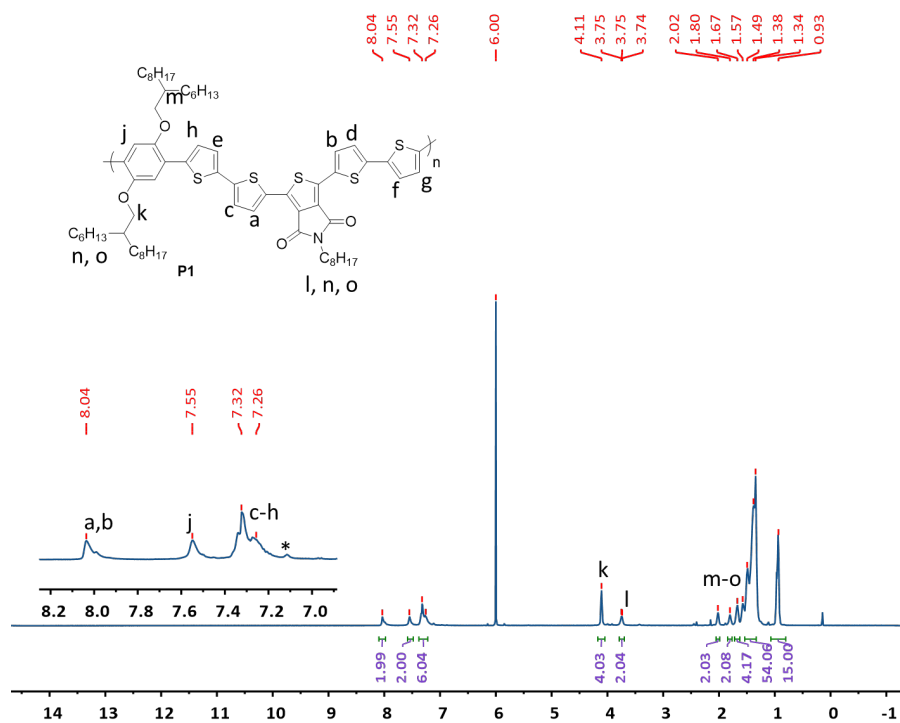


Proton NMR of compound S10.

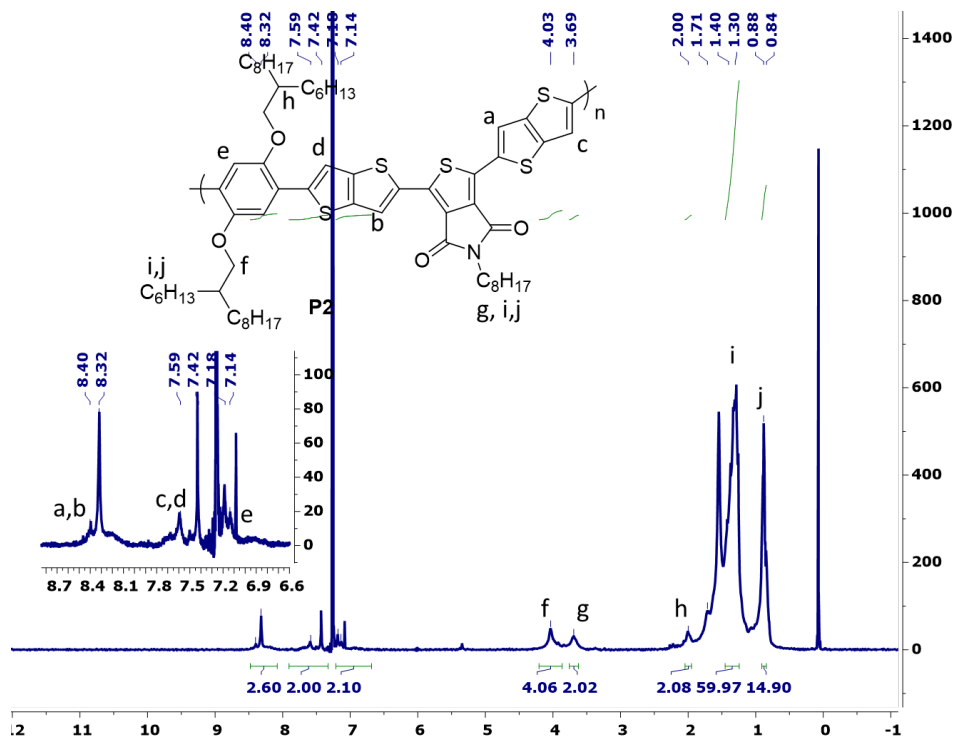
## 5. Polymer NMR Spectra



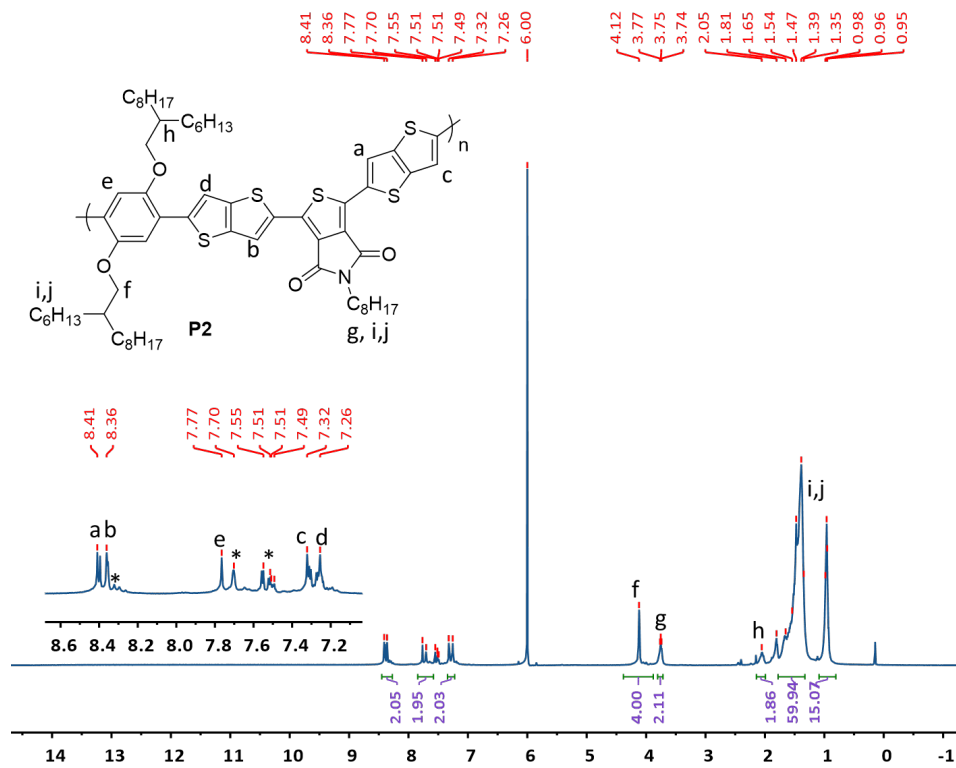
Proton NMR of polymer P1 in  $\text{CDCl}_3$  25 °C.



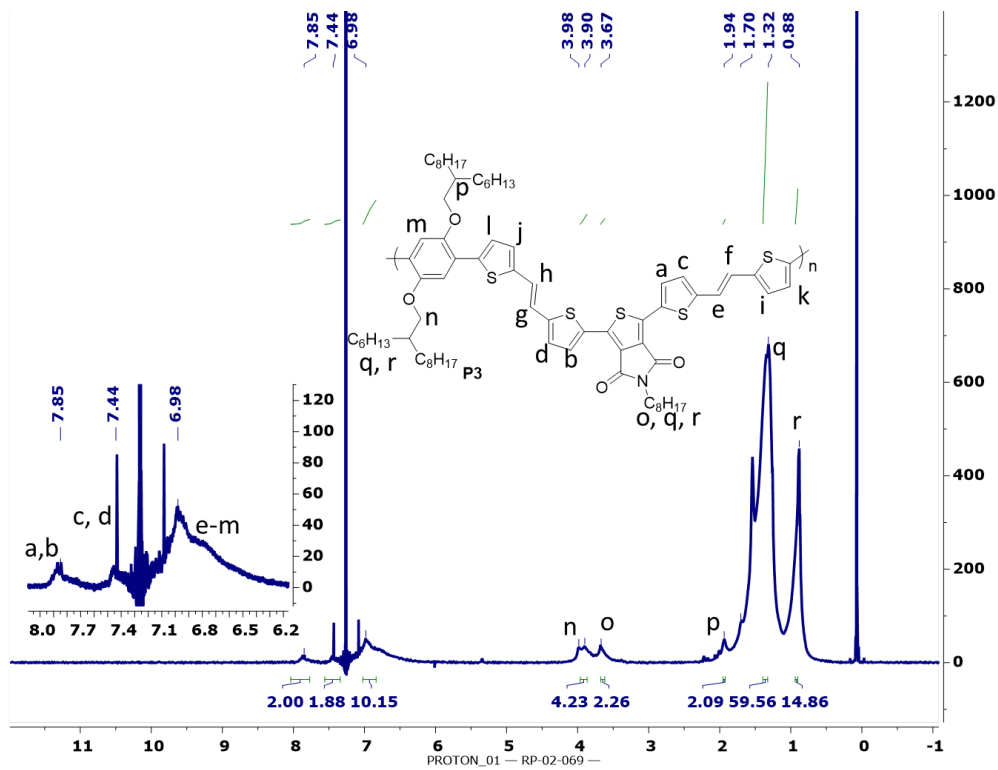
Proton NMR of polymer P1 in  $\text{C}_2\text{D}_2\text{Cl}_4$  at 100 °C. End-groups denoted with \*.



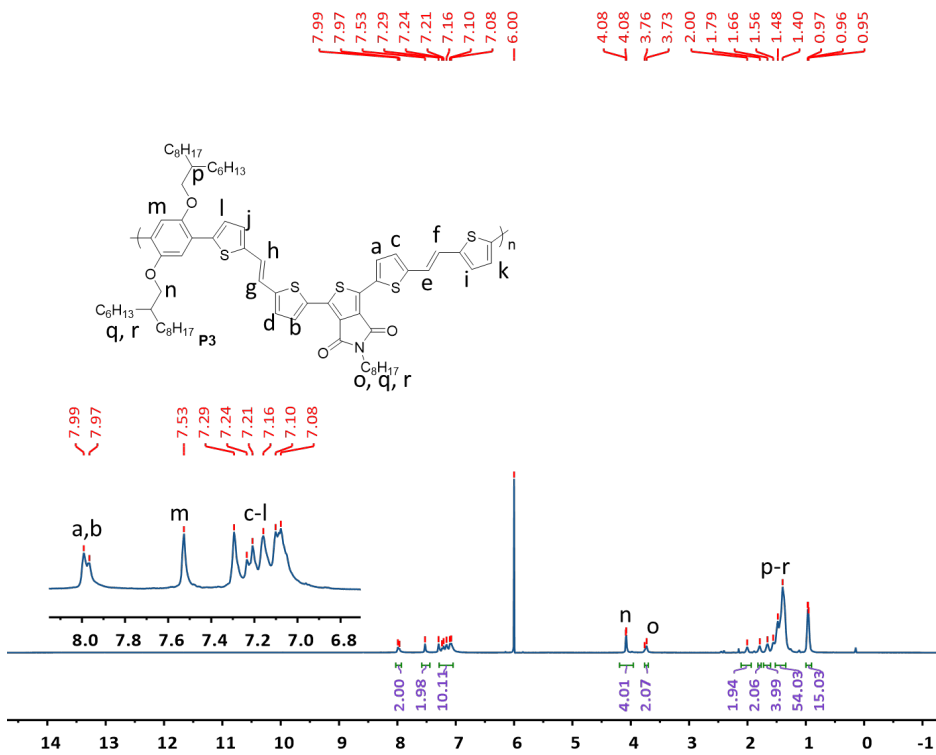
Proton NMR of polymer P2 in  $\text{CDCl}_3$  25 °C.



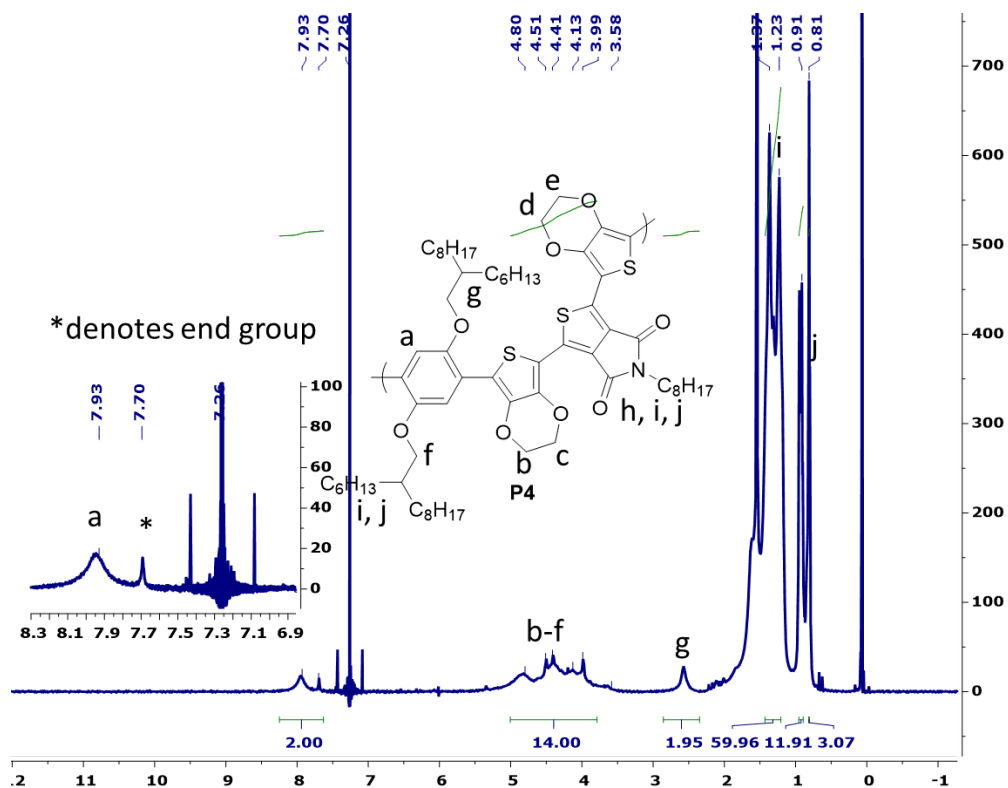
Proton NMR of polymer P2 in  $\text{C}_2\text{D}_2\text{Cl}_4$  at 100 °C.



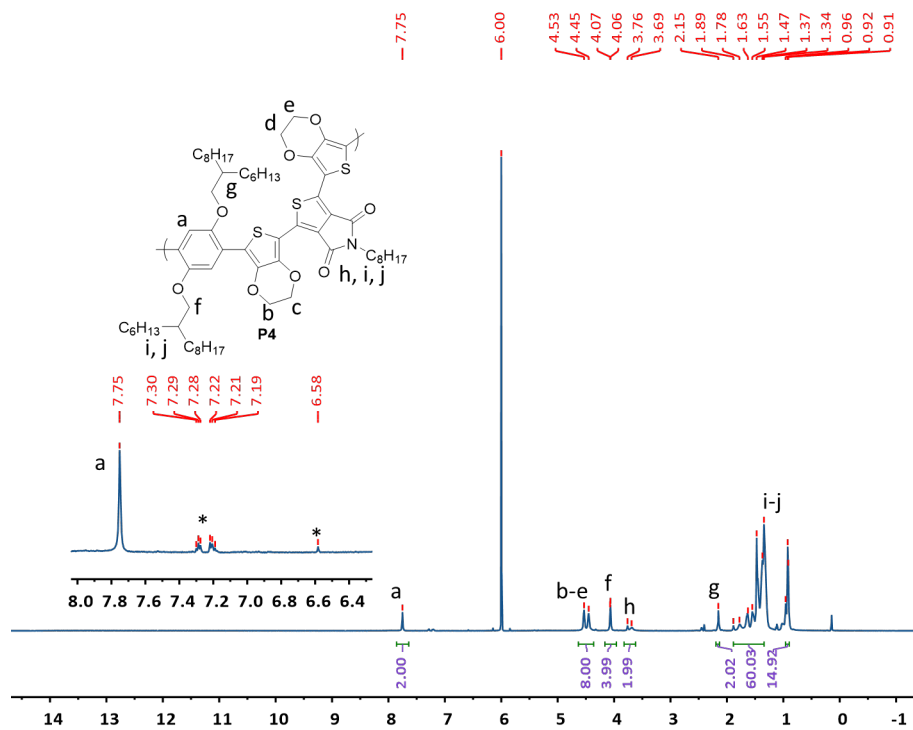
Proton NMR of polymer P3 in  $\text{CDCl}_3$  25 °C.



Proton NMR of polymer P3 in  $\text{C}_2\text{D}_2\text{Cl}_4$  at 100 °C.

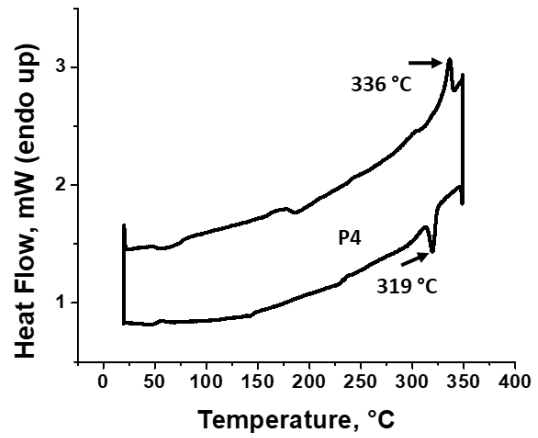
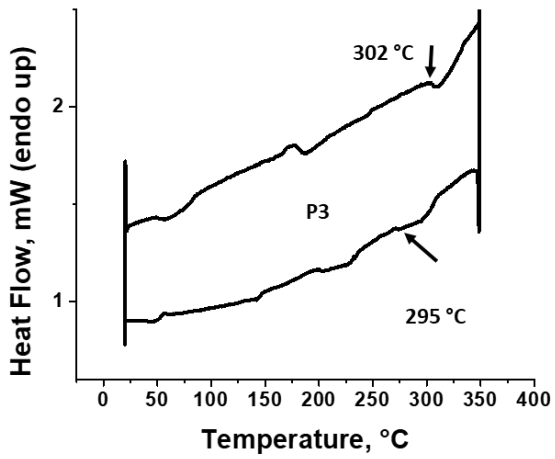
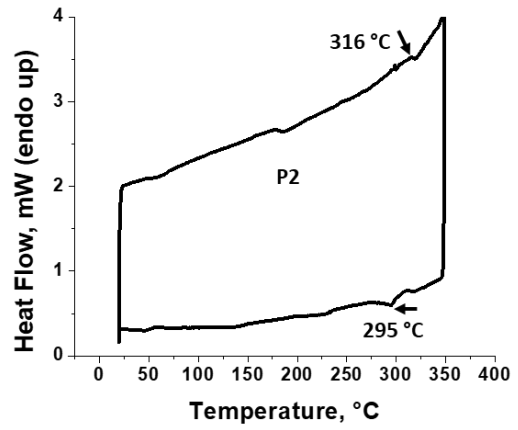
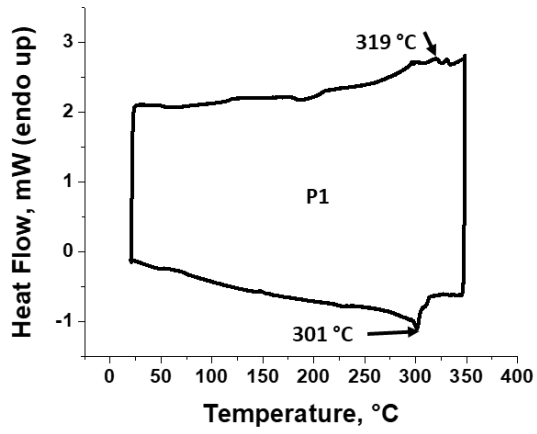


Proton NMR of polymer P4 in CDCl<sub>3</sub> 25 °C.



Proton NMR of polymer P4 in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> at 100 °C. End-groups denoted with \*.

## 6. Polymer DSC





## 7. Polymer XRD

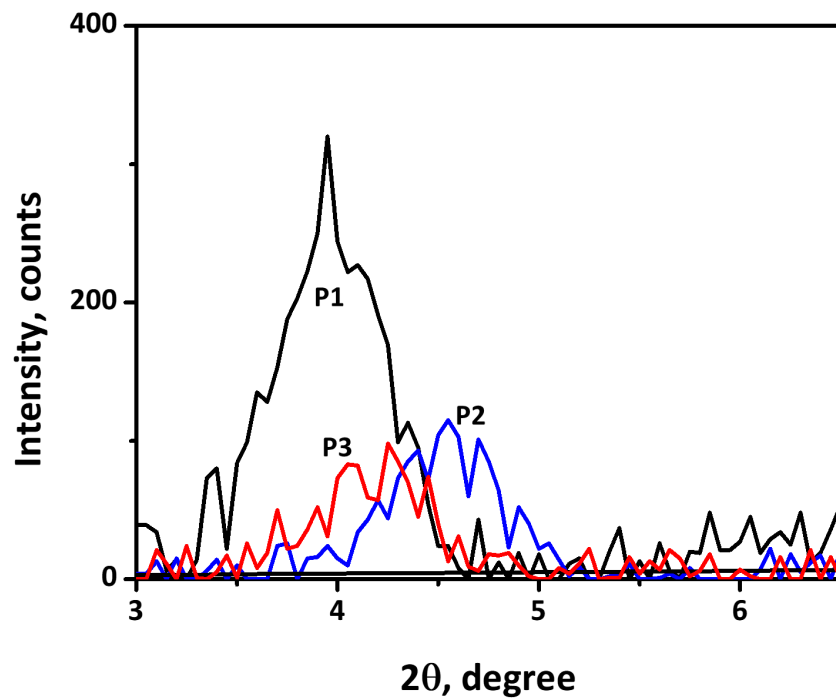
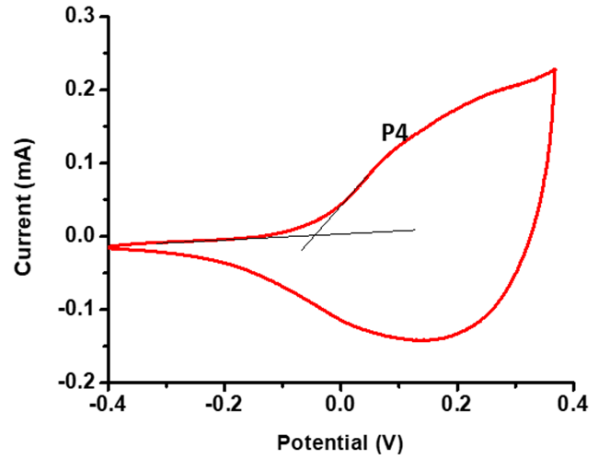
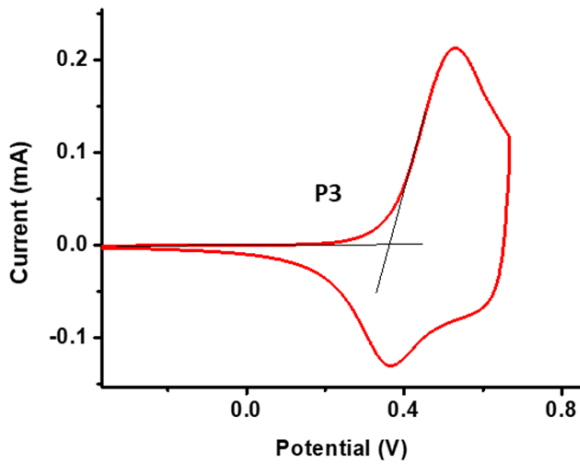
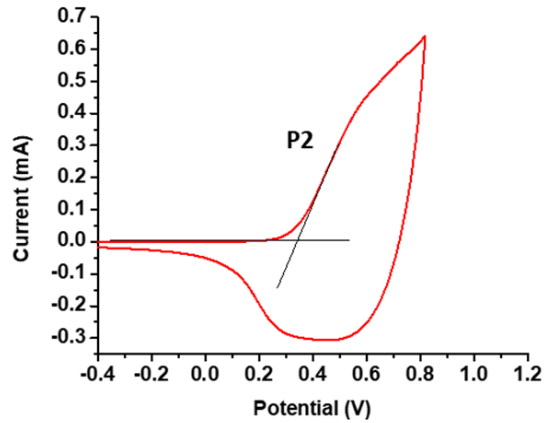
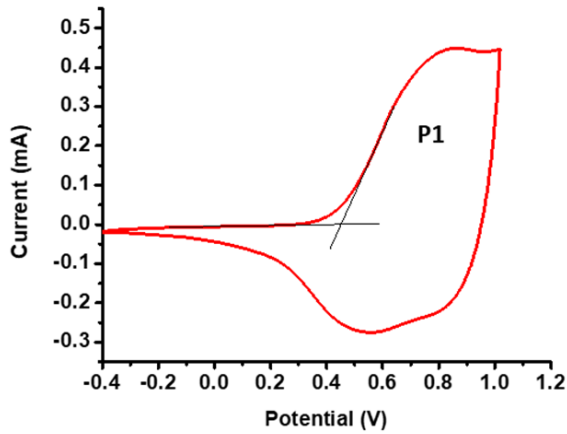


Table S1. Peak listings for polymers P1-P4.

Polymer	2θ	d <sub>100</sub> (Å)	FWHM	Height
P1	3.950	22.3530	0.430	303
P2	4.547	19.4161	0.434	104
P3	4.258	20.7334	0.373	86
P4	-	-	-	-

## 8. Polymer CV



## 9. Polymer PV Device Characterization

As emphasized by Shrotriya et al.,<sup>14</sup> there can be a spectral error in the measured short-circuit current due to differences in the spectra irradiance of the light source and the reference spectrum or differences in the spectral responses of the reference detector and test cell. This error can be conveyed by a spectra mismatch correction factor ( $M$ )<sup>15</sup> which is defined as:

$$M = \frac{\int_{\lambda_1}^{\lambda_2} E_{Ref}(\lambda) S_R(\lambda) d\lambda \int_{\lambda_1}^{\lambda_2} E_S(\lambda) S_T(\lambda) d\lambda}{\int_{\lambda_1}^{\lambda_2} E_{Ref}(\lambda) S_T(\lambda) d\lambda \int_{\lambda_1}^{\lambda_2} E_S(\lambda) S_R(\lambda) d\lambda} \quad (2),$$

where  $E_{Ref}(\lambda)$  is the reference spectral irradiance;  $E_S(\lambda)$  is the source spectral irradiance;  $S_R(\lambda)$  is the spectral responsivity; and  $S_T(\lambda)$  is the spectral responsivity of the test cell, each as a function of wavelength ( $\lambda$ ). Spectral responsivities  $S(\lambda)$  for the tested devices were calculated based on the external quantum efficiency (EQE) values, according to equation 3:

$$S(\lambda) = \frac{q\lambda}{hc} EQE(\lambda) \quad (3),$$

where the constant term  $q/hc$  equals  $8.0655 \times 10^5$  for wavelength in units of meters and  $S(\lambda)$  in units of  $\text{AW}^{-1}$ . Based on the spectral responsivities  $S(\lambda)$  obtained using equation 3, integrated short-circuit current densities ( $J_{sc,EQE}$ ) can be obtained:

$$J_{sc,EQE} = \int_{\lambda_1}^{\lambda_2} E_{Ref}(\lambda) S_T(\lambda) d\lambda \quad (4).$$

In order to mismatch-correct the efficiencies of the BHJ solar cells, short-circuit current densities ( $J_{sc}$ ) were divided by the  $M$ , as defined in equation 5. The raw data ( $J_{sc}$ ), spectral-mismatch factor ( $M$ ) and the spectral mismatch-corrected short-circuit current densities ( $J_{sc,corr}$ ) are summarized in **Table S1**.

$$J_{sc,corr} = \frac{J_{sc}}{M} \quad (5).$$

**Table S2.** Raw short-circuit current densities ( $J_{SC}$ ), spectral mismatch factor (M), spectral mismatch-corrected short-circuit current densities ( $J_{SC,Corr}$ ), and integrated short-circuit current densities ( $J_{SC,EQE}$ ) for all polymers (**P1-P4**) as referenced in Table 2.

Entry	$J_{SC,Raw}$ (mA cm <sup>-2</sup> )	M	$J_{SC,Corr}$ (mA cm <sup>-2</sup> )	$J_{SC,EQE}$ (mA cm <sup>-2</sup> )	Error (%)
P1	10.2175	0.96958	10.53806803	10.1657	3.66
P2	3.335	0.97354	3.425642501	3.3280	0.21
P3	8.5457	0.9208	9.280749659	8.19305	4.30
P4	2.0725	0.8438	2.456150747	2.41139	1.86

**Table S3.** Average values and standard deviations for photovoltaic device data for polymers **P1-P4**.

Entry	$J_{sc}$ (mA cm <sup>-2</sup> )	$V_{oc}$ , V	$FF$	$\eta$ , %
P1	10.53807±0.62	0.735875±0.003	0.61285±0.008	4.75247±0.22
P2	7.59096±0.24	0.699±0.033	0.487825±0.010	2.58844±0.21
P3	9.28075 ±0. 0.54	0.60037 ± 0.003	0.51833 ± 0.017	2.88814 ±0.19
P4	2.456151±0.12	0.489375±0.008	0.4068±0.017	0.488965±0.037

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