Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Palladium-catalyzed oxidative direct arylation polymerization (Oxi-DArP) of an ester-functionalized thiophene

*Nemal S. Gobalasingham, Sangtaik Noh, and Barry C. Thompson**

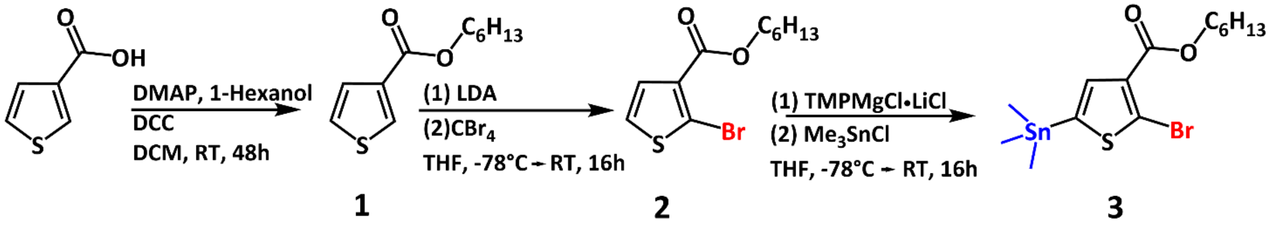
Department of Chemistry and Loker Hydrocarbon Research Institute, University of Southern California, Los Angeles, California 90089-1661, United States

*Email: barrycth@usc.edu

Synthetic Procedures:

The synthesis of 3-hexylthiophene was executed as reported in the literature.[1] The synthesis of 2-bromo-3-hexylthiophene, 2-bromo-5-trimethylstannyl-3-hexylthiophene and the synthesis of P3HT via Stille polycondensation was performed as reported in the literature.[2]

Synthesis of 2-bromo-5-trimethylstannyl-2-hexylesterthiophene.



Scheme S1. Synthesis of 3

3-Hexylesterthiophene (1). To a solution of thiophene-3-carboxylic acid (1.545 g, 12.06 mmol) in 36 mL dichloromethane (DCM) is added DMAP (515.7 mg, 4.22 mmol, 0.35 eq.) and 1-hexanol (2.464g, 24.12 mmol, 2eq.). After about 5-10 min, N,N'-Dicyclohexylcarbodiimide (DCC) (2.737g, 13.27mmol, 1.1eq.) was added. The mixture was allowed to stir at room temperature for 2 days. Precipitated urea is filtered off and the filtrate is subjected to flash column chromatography with hexane:DCM = 1:1. After vacuum distillation, the product is acquired as a colorless liquid (2.21g, 10.4 mmol, 86.4%). ^{1}H NMR (400 MHz, CDCl3: δ8.10 (dd, 1H), 7.53 (dd, 1H), 7.30 (dd, 1H) 4.27 (t, 2H), 1.74 (m, 2H), 1.42 (m, 2H), 1.34 (m, 4H), 0.90 (t, 3H).

2-Bromo-3-hexylesterthiophene (2). Two 3-neck flasks were flame dried, and backfilled with dry N_2. To flask 1, fresh lithium diisopopylamine (LDA) was synthesized by the following steps: Diisopropylamine (DIA) (1.71 mL, 12.203mmol, 1.2 eq.) was added and dissolved in 12 mL THF and the solution was cooled down to -78°C before adding n-butyl lithium (7 mL, 11.19 mmol, 1.1 eq.) dropwise. After 5 min, the mixture was heated to 0°C for 20 min and cooled down backed to -78°C. In flask 2, 3-hexylesterthiophene (2.159 g, 10.17 mmol) is dissolved in 6 mL THF and cooled down to -78 °C. LDA was transferred from flask 1 to flask 2 through cannula transfer and reacted for about 2 hours at -78 °C. Carbon tetrabromide (CBr_4) (3.541 g, 10.68 mmol, 1.05 eq.) dissolved in 5 mL of THF was added rapidly to the reaction mixture. After about an hour, the reaction mixture was heated up to room temperature and stirred overnight. The solvent was evaporated under reduced pressure, the residue was purified by column chromatography with 1:1 hexanes/DCM and vacuum distillation afforded the product as a colorless liquid (1.367g, 4.69 mmol, 46.2%). ^{1}H NMR (400 MHz, CDCl3: δ 7.37 (dd, 1H), 7.22 (d, 1H) 4.28 (t, 2H), 1.75 (m, 2H), 1.44 (m, 2H), 1.34 (m, 4H), 0.90 (t, 3H).

2-bromo-5-trimethyltin-3-hexyesterthiophene (3). To a flame-dried 3-neck flask, 2-bromo-3-hexylesterthiophene (1.367 g, 4.696 mmol) was dissolved in 2.8 mL THF and cooled down to -78°C. 0.61 M solution of 2,2,6,6-tetramethylpiperidinylmagnesium chloride lithium chloride complex (TMPMgCl•LiCl) in THF (9.24 mL, 5.635 mmol, 1.2 eq) was added dropwise under N_2. The mixture was kept at -78°C for 3h before 1.0 M solution of trimethyltin chloride in hexanes (5.635 mL, 5.635 mmol, 1.20 eq) was added slowly. The mixture was allowed to warm up to room temperature and stirred overnight. After extraction with diethyl ether and water, the organic layer was dried over $MgSO_4$. The solvent was evaporated under reduced pressure and the mixture was subjected to column chromatography with 1:1 hexane/DCM and the product was obtained with trace amount of impurity (starting material). The product mixture was put under high vacuum and heated at 60-70°C overnight to remove residual starting material. Purified product was achieved as a yellowish oil (0.783 g, 1.725mmol, 36.7%). ^{1}H NMR (400 MHz, CDCl3: δ 7.41 (s, 1H), 4.28 (t, 2H), 1.76 (m, 2H), 1.45 (m, 2H), 1.34 (m, 4H), 0.90 (t, 3H), 0.39 (s, 9H).

Poly(3-hexylesterthiophene) via Stille polycondensation. Monomer 3 was dissolved in dry DMF to afford a 0.04M solution. This was degassed by purging N_2 for 15 minutes before 0.04 equivalents of $Pd(PPh_3)_4$ was added in one portion. The solution was degassed for 15 additional minutes, then allowed to stir at 95°C for 48h. The reaction mixture was cooled briefly, precipitated into methanol. Purification was achieved through Soxhlet extraction with a sequence of solvents—MeOH, hexanes, chloroform—and the last fraction was concentrated under reduced pressure, reprecipitated into MeOH, vacuum filtered and then dried overnight under high vacuum (~1 mmHg).

Stille P3HET. Yield: 69%. Mn = 11.3 kDA, Đ 2.7. ^{1}H NMR (600 MHz, CDCl3): δ7.86 (m, 1H), 4.30 (t, 2H), 1.75 (m, 2H), 1.44 (br, 6H), 0.89 (t, 3H).

General procedure for the synthesis of polymers (P3HT, P3HET) via DArP: Respective monomers (0.5 or 0.1 mmol) were dissolved in anhydrous DMA to yield a 0.04M solution, with 1mL of solvent withheld. To the reaction mixture, 0.3 equivalents of neodecanoic acid and 1.5 equivalents of K_2CO_3 were added. The solution was degassed with nitrogen flow for 10 minutes. 0.25 mol% of $Pd(OAc)_2$ was dissolved in 1mL of DMA and added to the reaction mixture, which was further degassed for 15 minutes. Then, the reaction was immersed into a pre-heated oil bath at 70°C and stirred under nitrogen atmosphere for 48 hours. Then the reaction mixture was cooled, precipitated into methanol, filtered, and purified via Soxhlet extraction with methanol, hexanes, and lastly chloroform; this final fraction was concentrated *in vacuo* and precipitated into methanol. Upon filtering, the polymers were dried under high vacuum overnight.

General procedure for the synthesis of polymers (P3HT, P3HET) via Oxi-DArP: Respective monomers (0.5 mmol) were dissolved in anhydrous DMA to yield a 0.05M solution. To the reaction mixture, the appropriate ratio of oxidant, additive, or ligand was added and the reaction mixture was degassed for 15 minutes with nitrogen flow. Then the $Pd(OAc)_2$ was added to the reaction mixture, which was further degassed for 10 minutes. Then the reaction was immersed into a pre-heated oil bath at the appropriate temperature and stirred under nitrogen atmosphere for 72 hours. Then the reaction mixture was cooled, precipitated into methanol, filtered, and purified via Soxhlet extraction with methanol, hexanes, and lastly chloroform; this final fraction was concentrated *in vacuo* and precipitated into methanol. Upon filtering, the polymers were dried under high vacuum overnight.

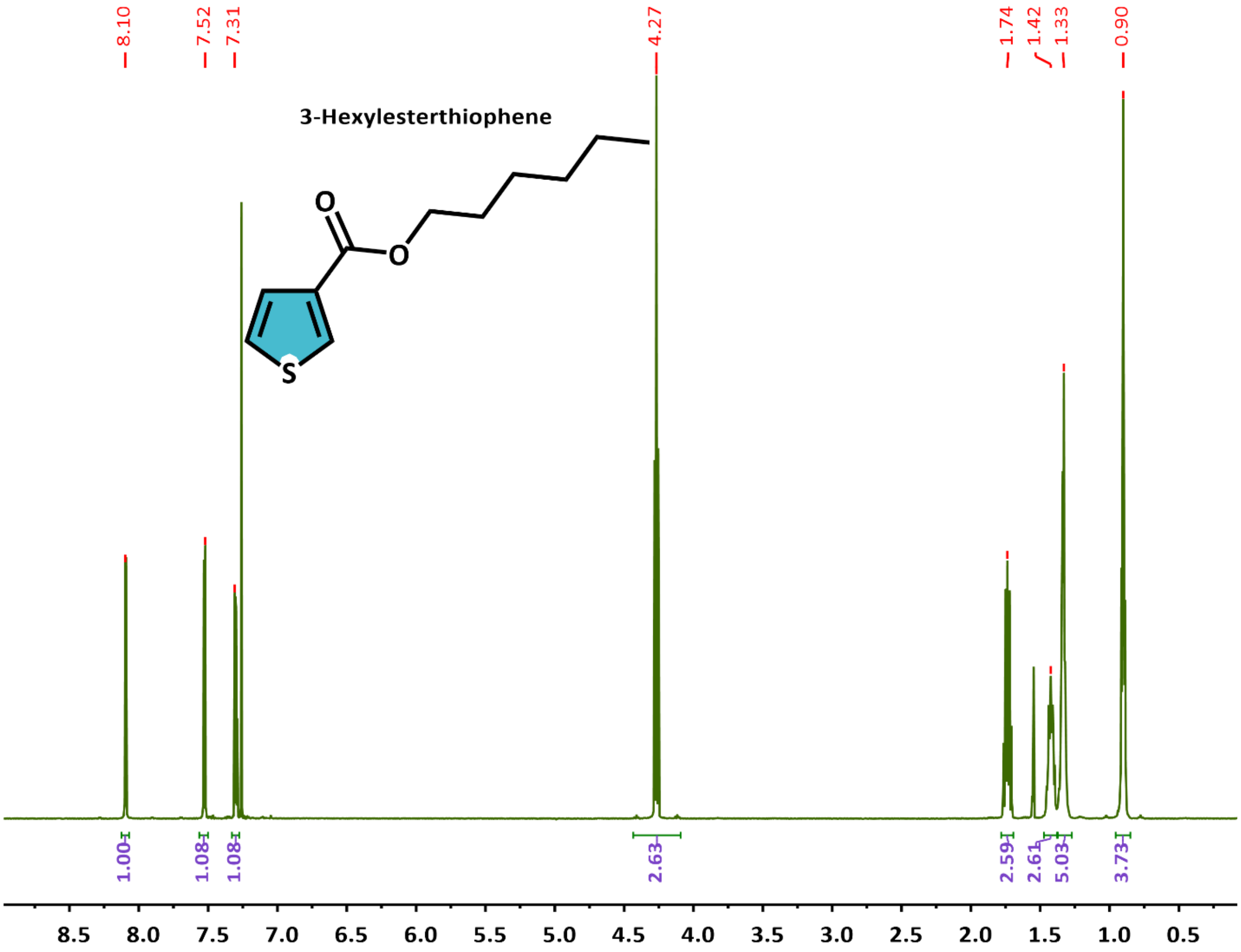


Figure S1. ^{1}H-NMR of **3-hexylesterthiophene** in $CDCl_3$.

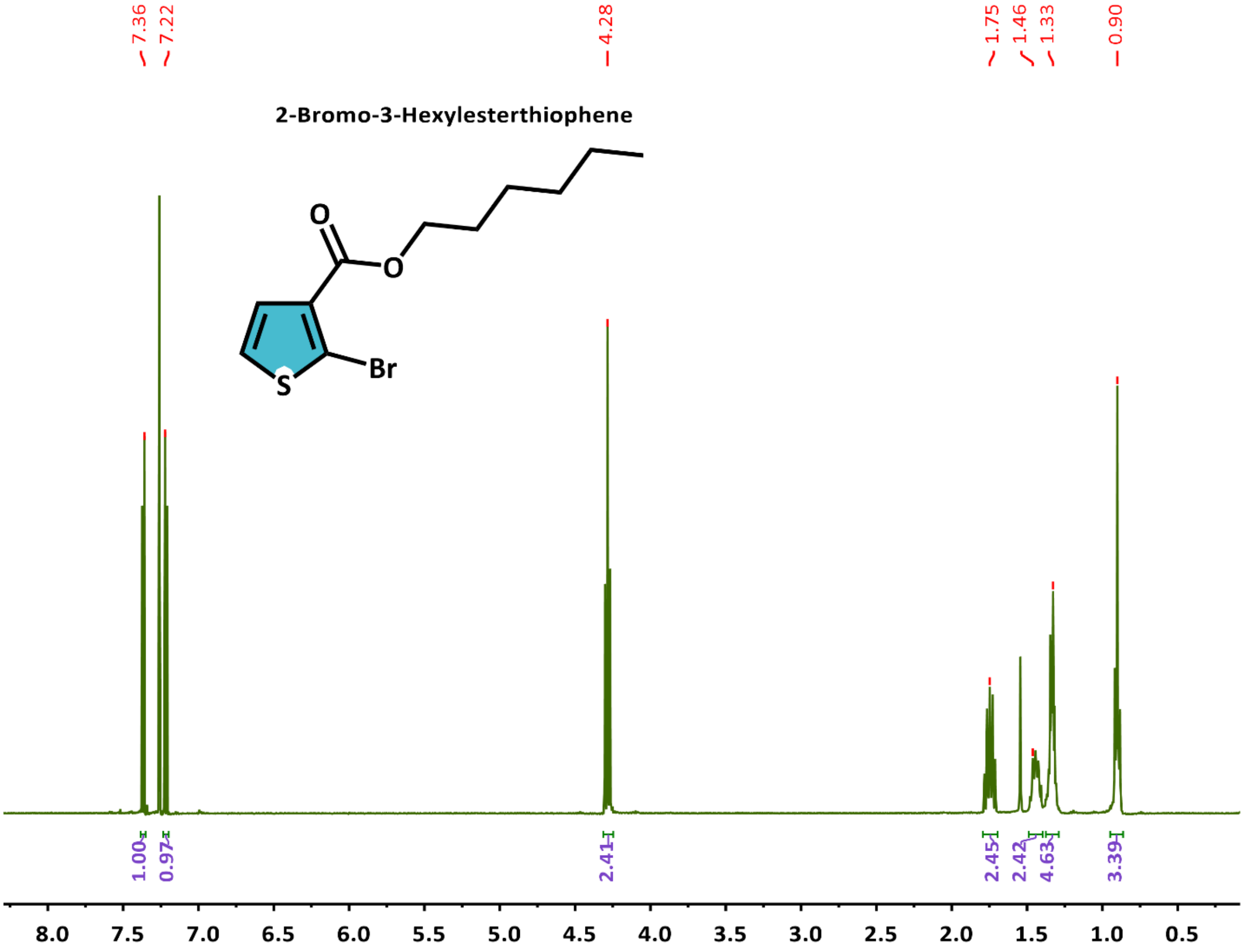


Figure S2. ^{1}H-NMR of **2-bromo-3-hexylesterthiophene** in $CDCl_3$.

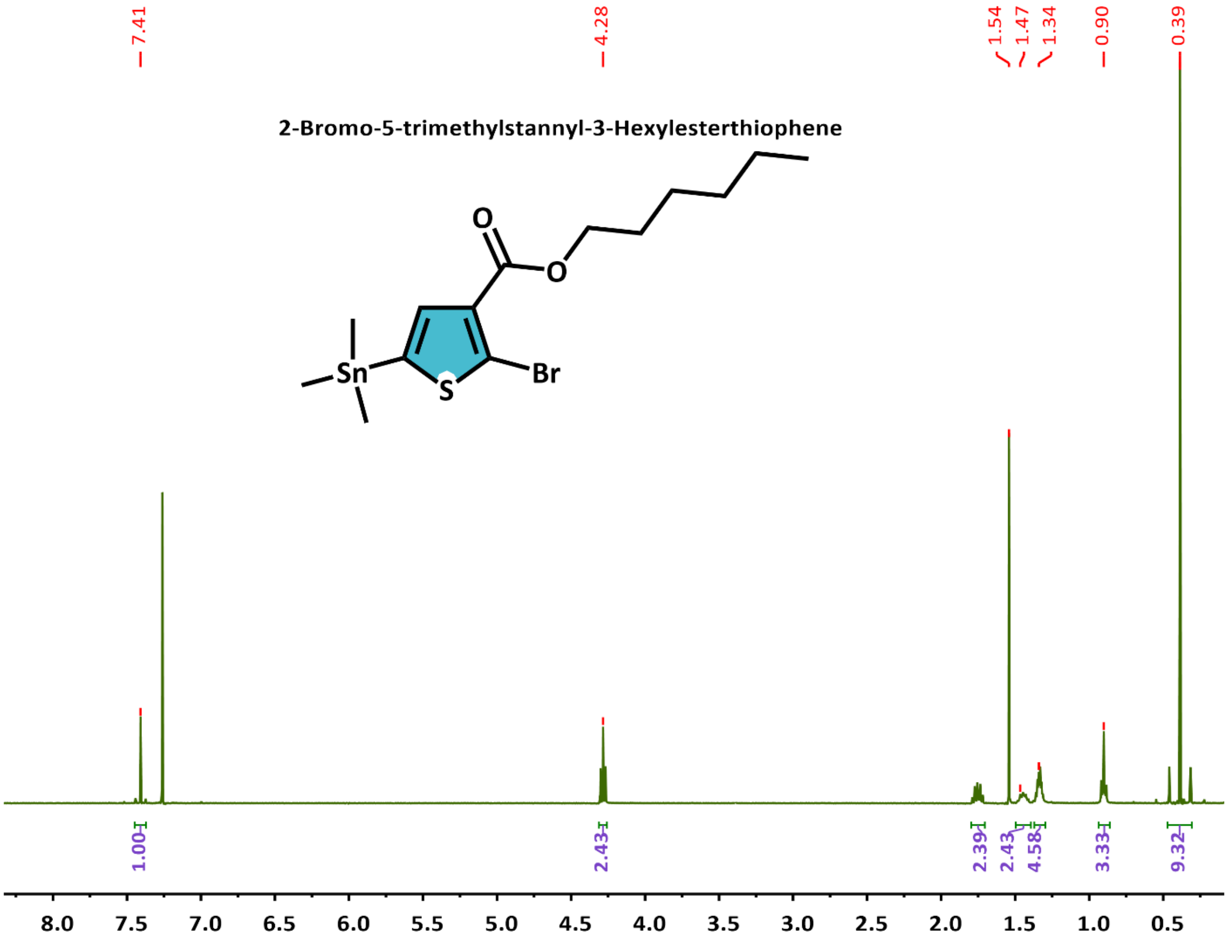


Figure S3. ^{1}H-NMR of **2-bromo-5-trimethylstannyl-3-hexylthiophene** in $CDCl_3$.

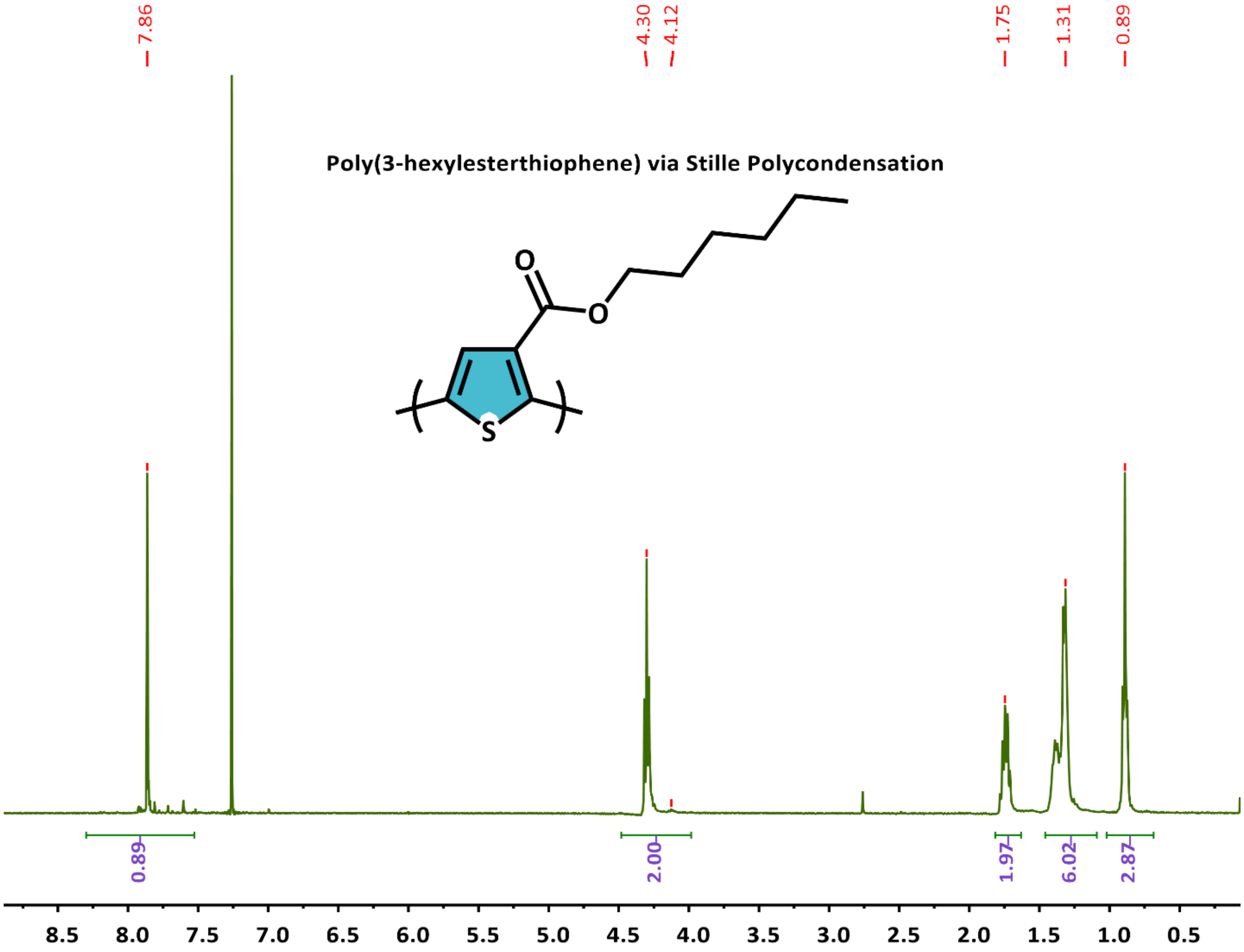


Figure S4. ^{1}H-NMR of **Stille P3HET** in $CDCl_3$.

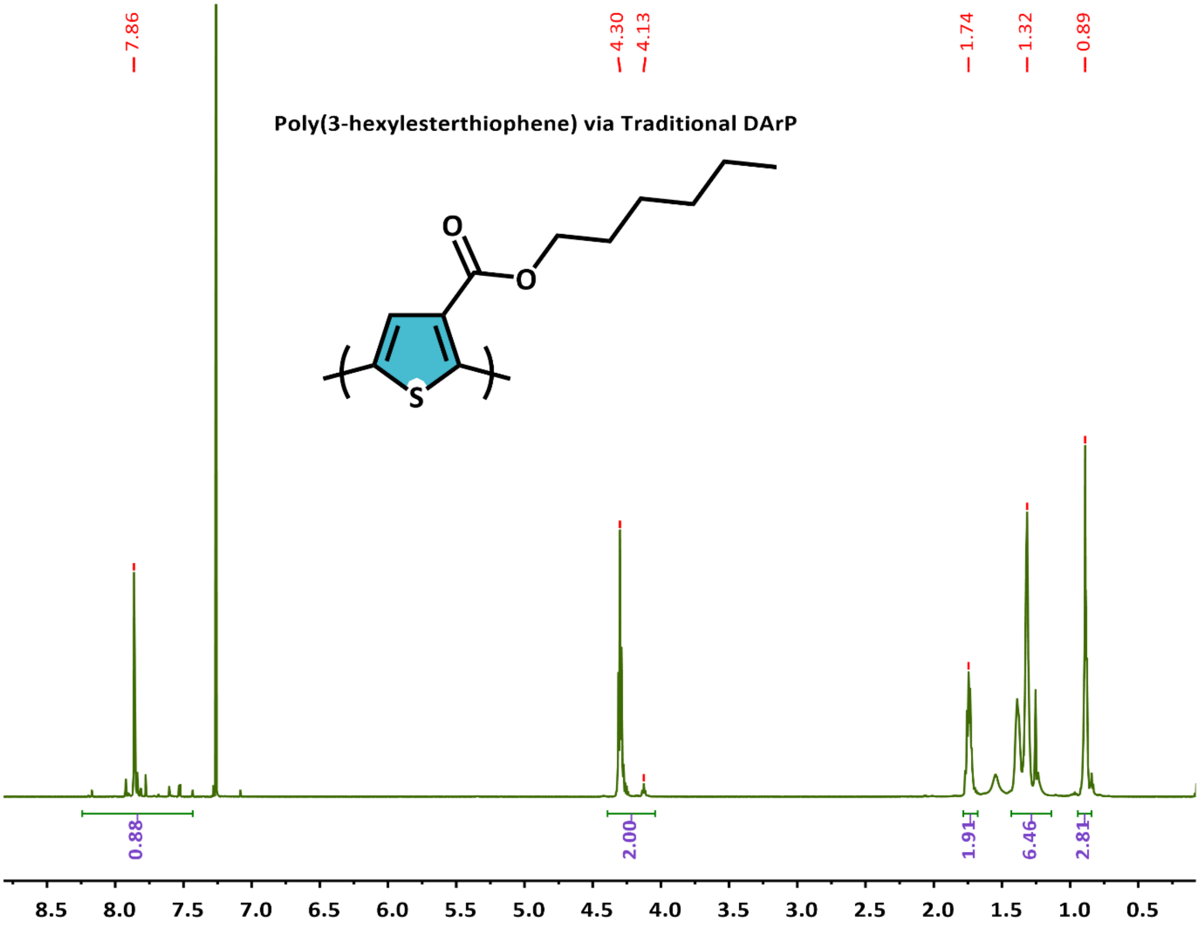


Figure S5. ^{1}H-NMR of **DArP P3HET** in $CDCl_3$.

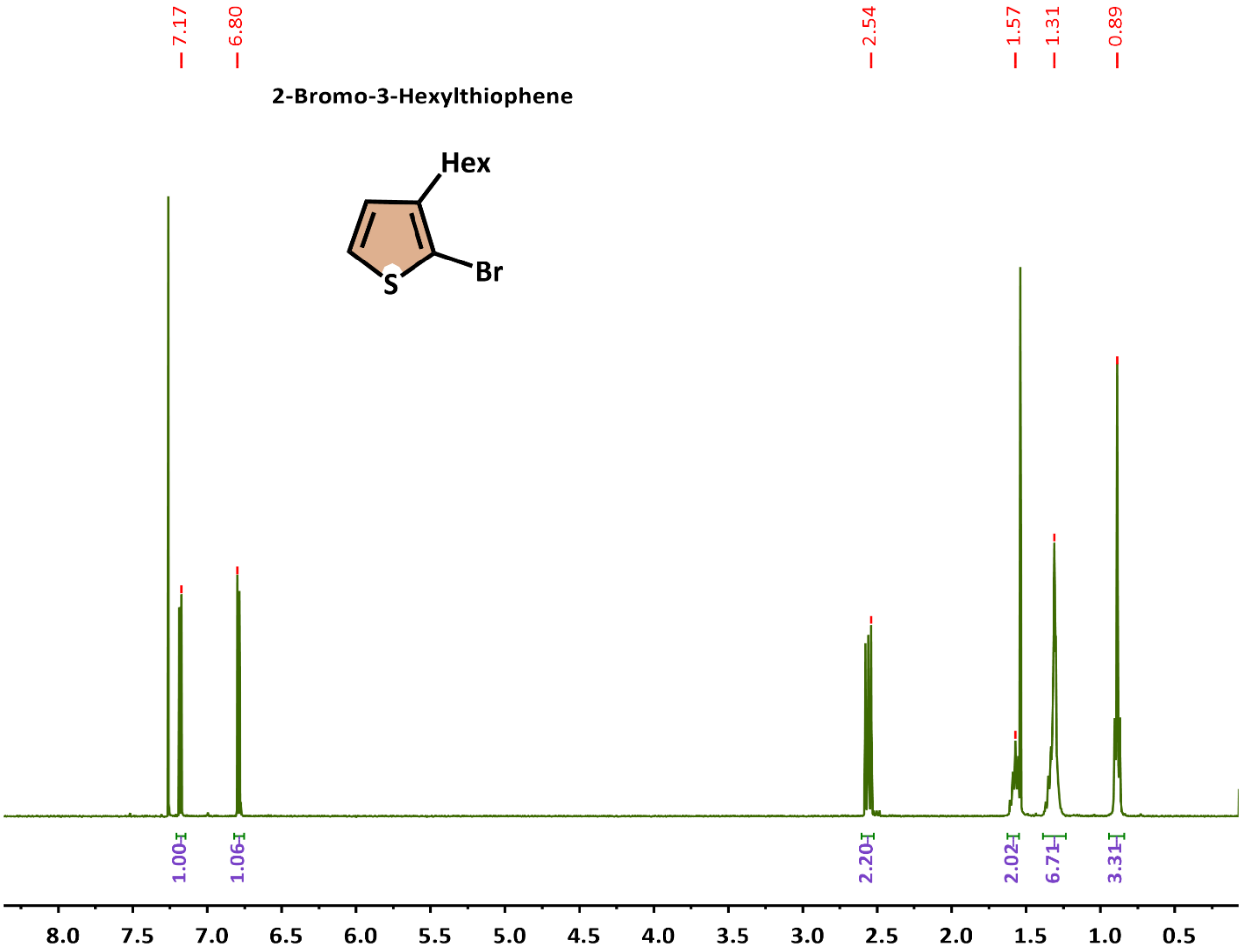


Figure S6. ^{1}H-NMR of **2-bromo-3-hexylthiophene** in $CDCl_3$.

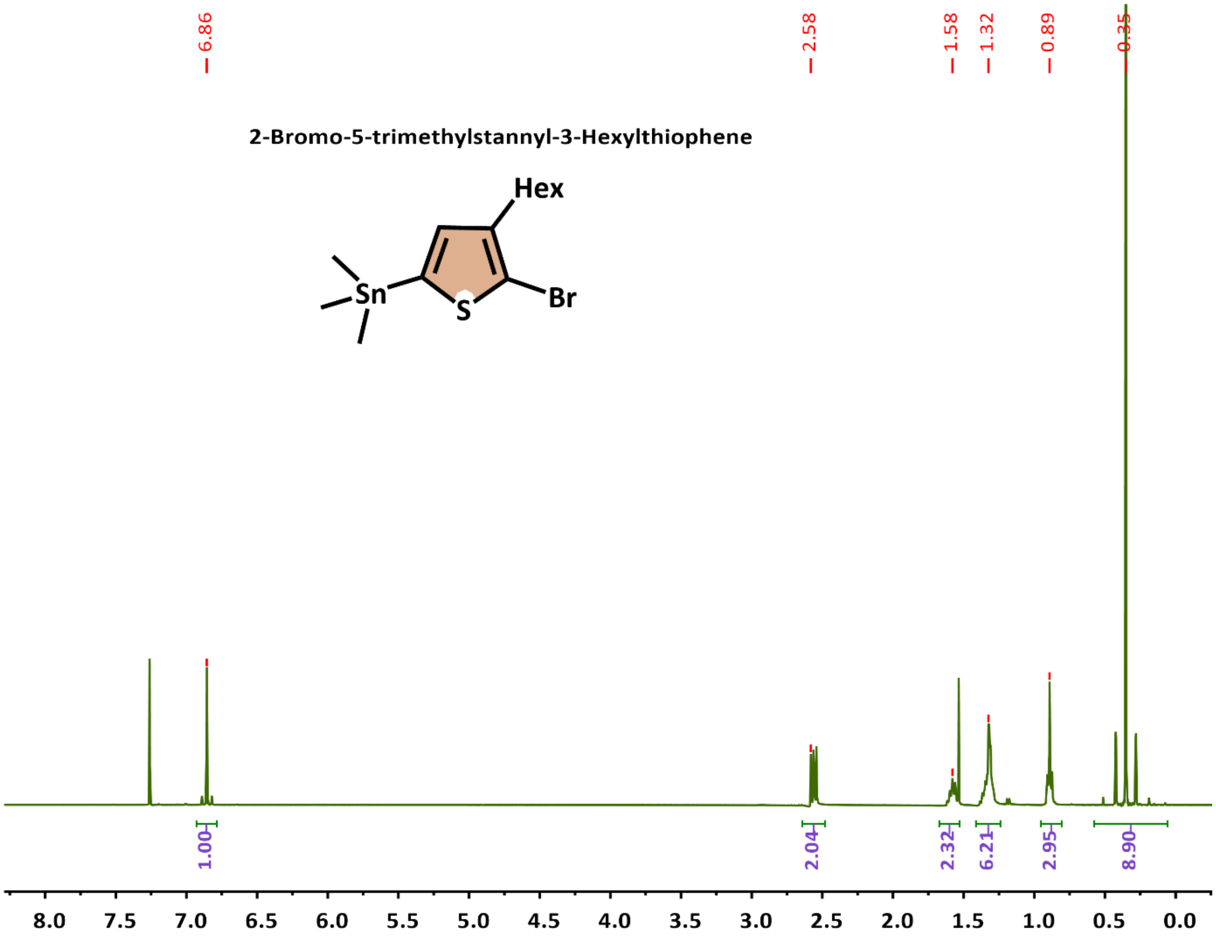


Figure S7. ^{1}H-NMR of **2-bromo-3-trimethylstannyl-3-hexylthiophene** in $CDCl_3$.

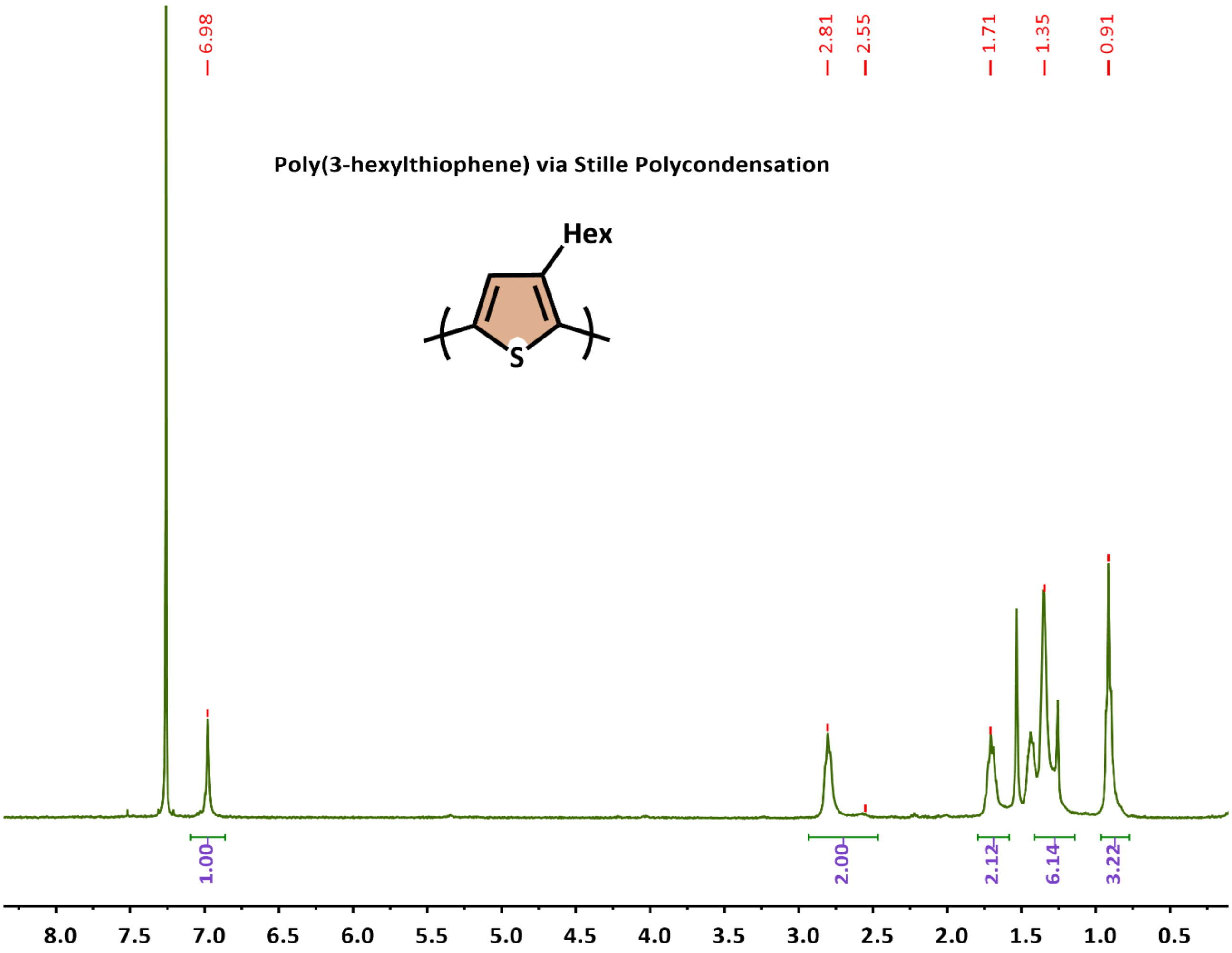


Figure S8. ^{1}H-NMR of **Stille P3HT** in $CDCl_3$.

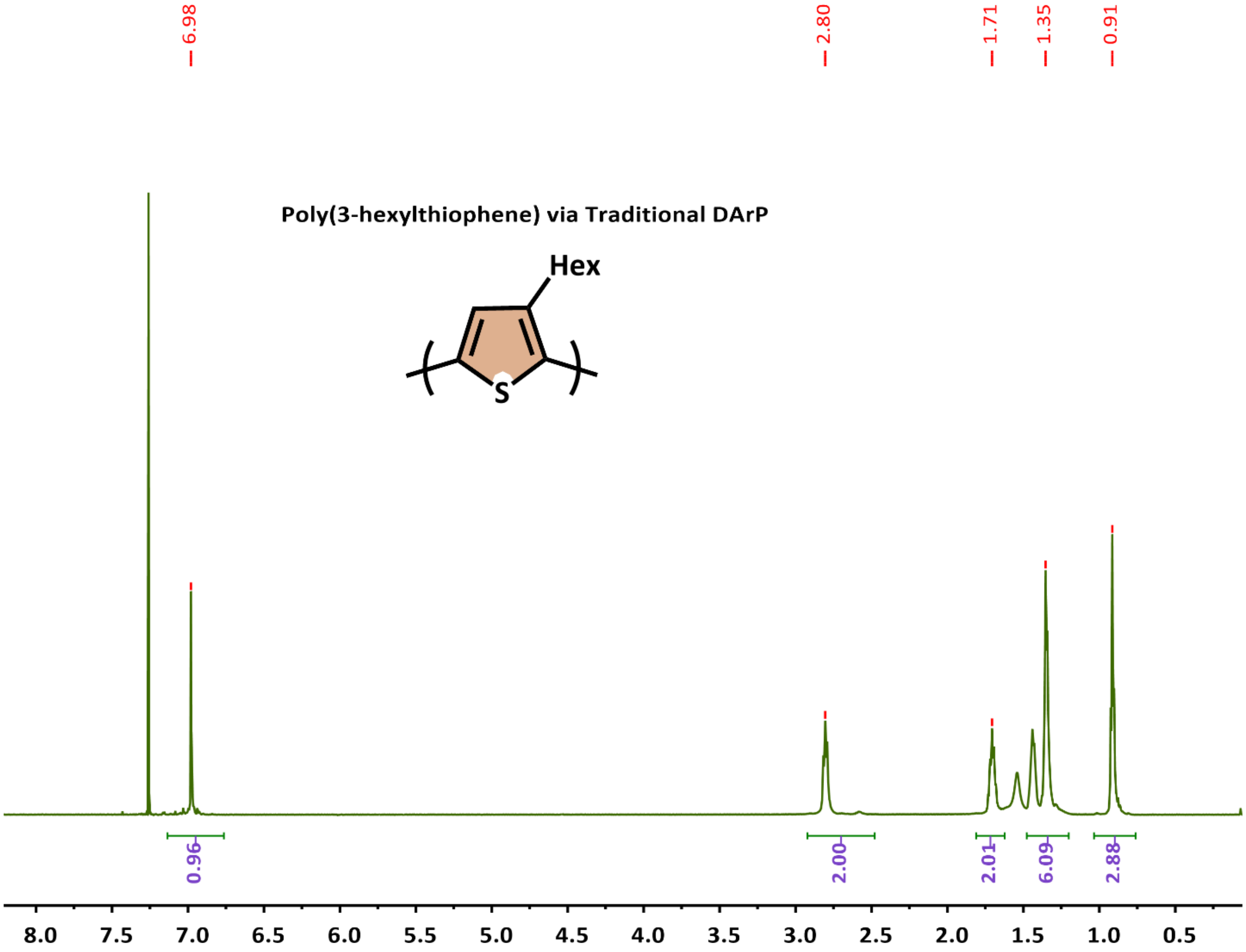


Figure S9. ^{1}H-NMR of **DArP P3HT** in $CDCl_3$.

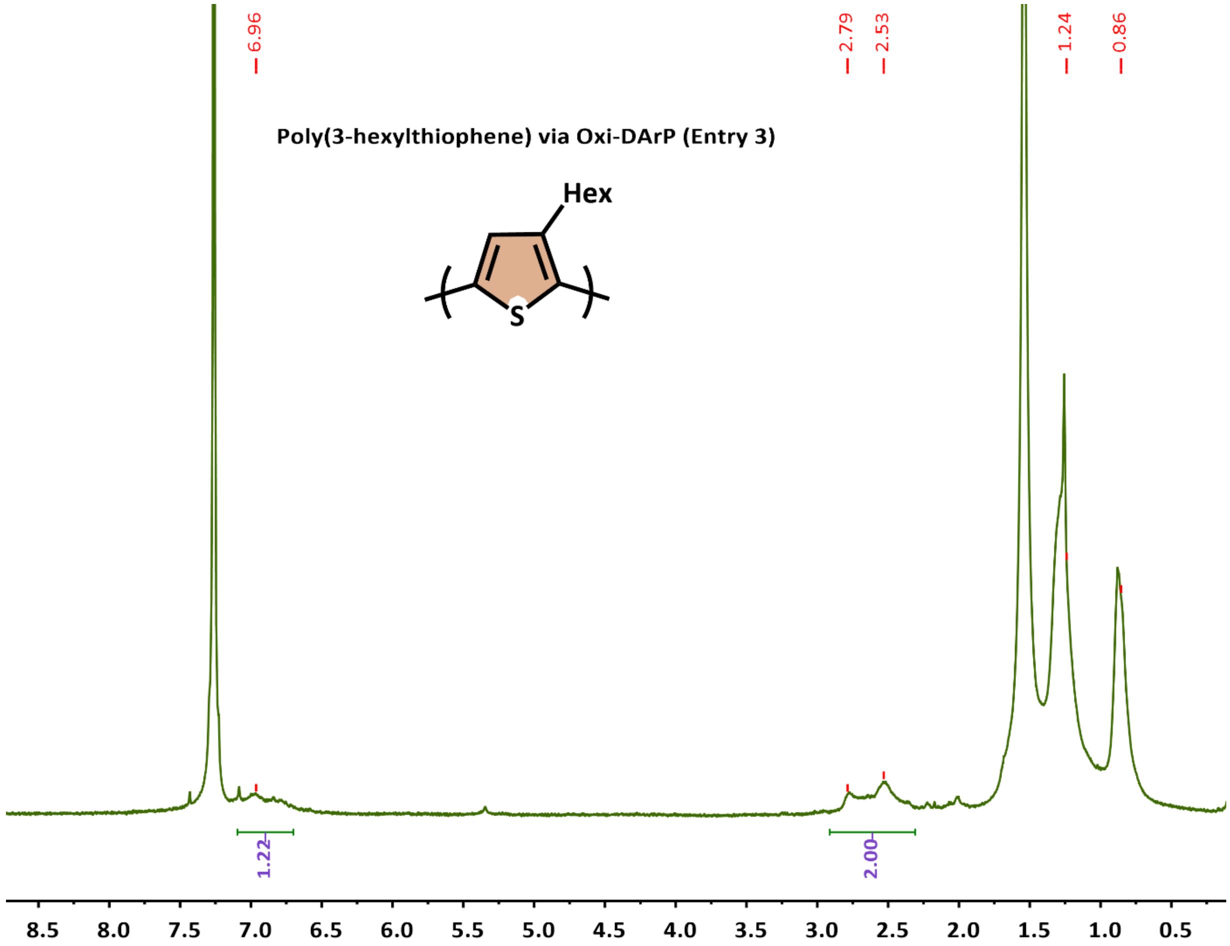


Figure S10. ^{1}H-NMR of **Oxi-DArP P3HT** (Entry 3) in $CDCl_3$.

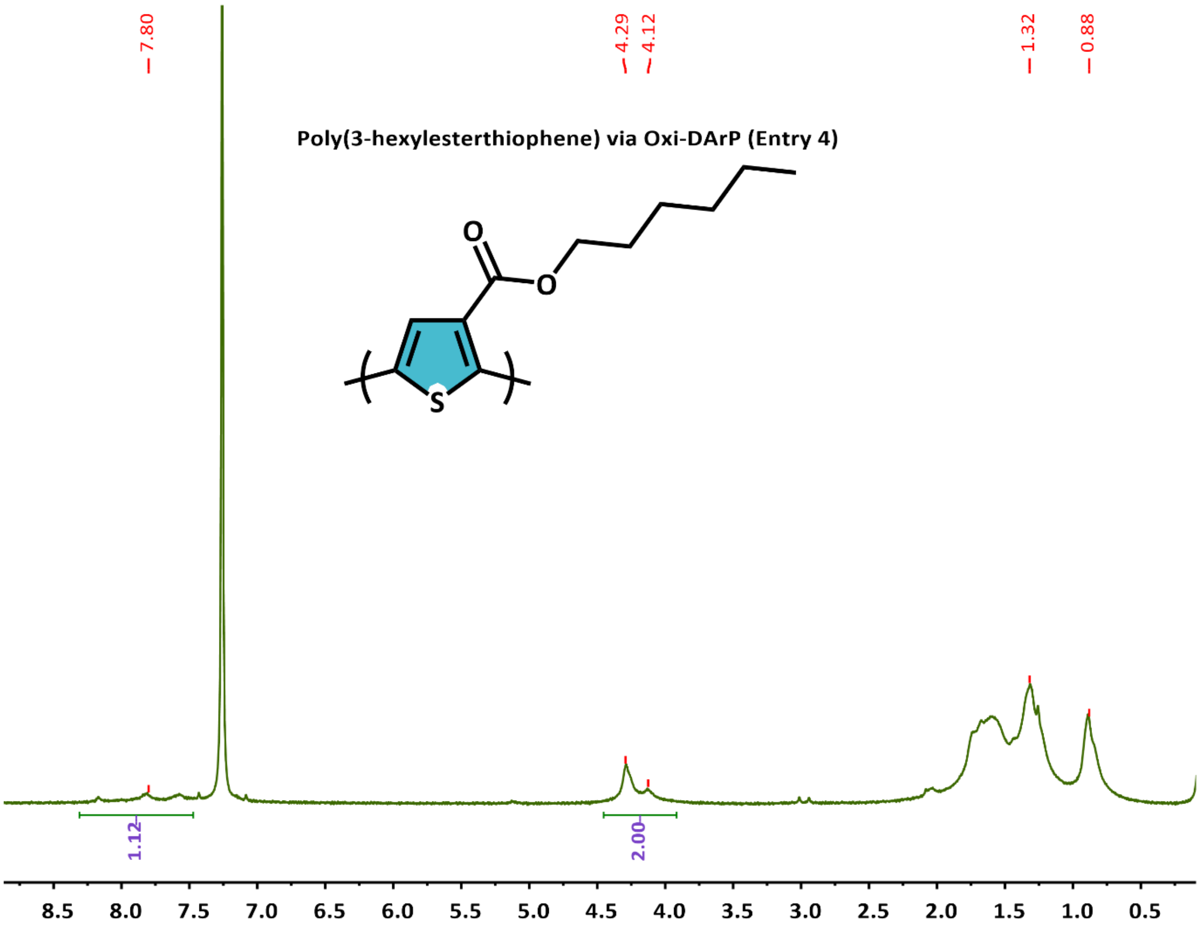


Figure S11. ^{1}H-NMR of **Oxi-DArP P3HET** (Entry 4) in $CDCl_3$.

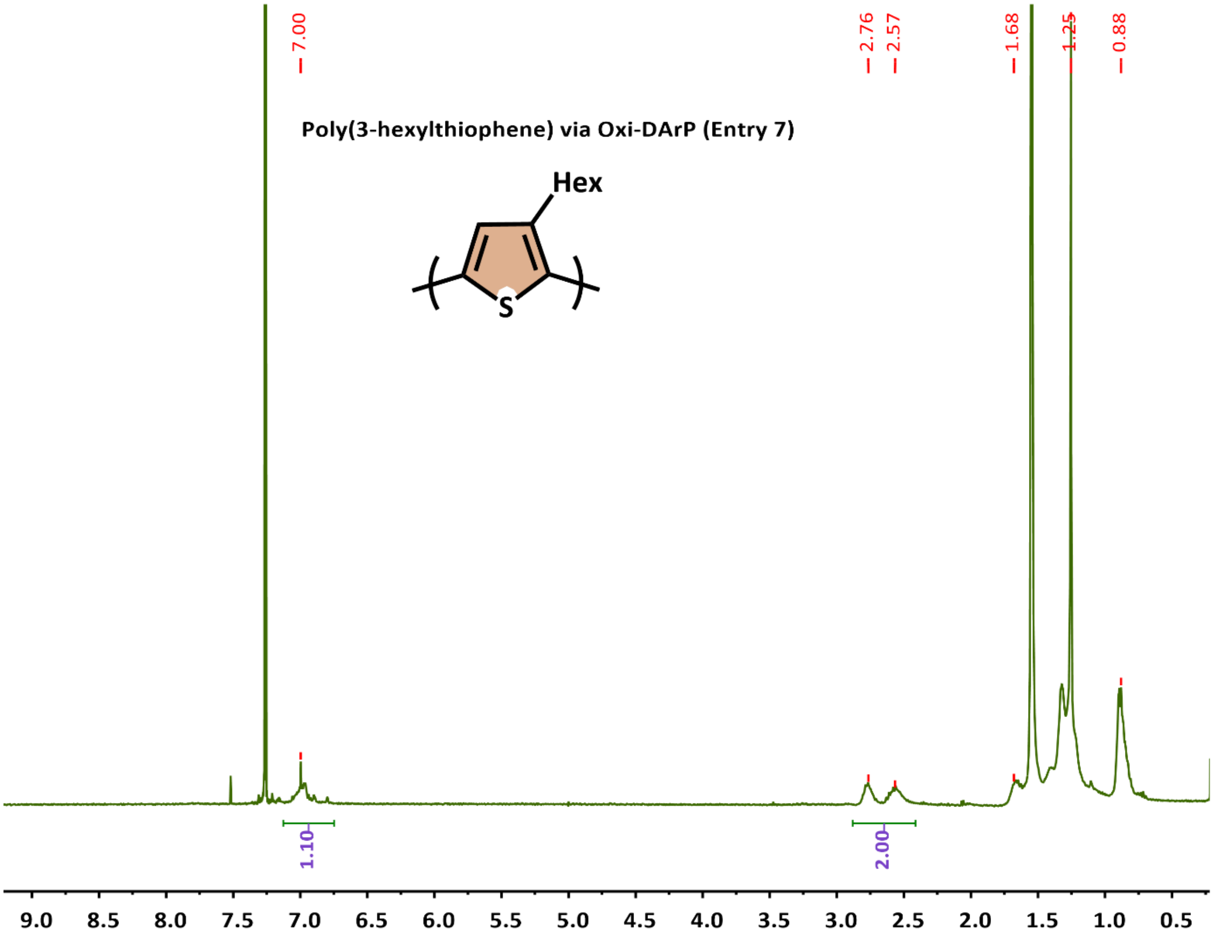


Figure S12. ^{1}H-NMR of **Oxi-DArP P3HT** (Entry 7) in $CDCl_3$.

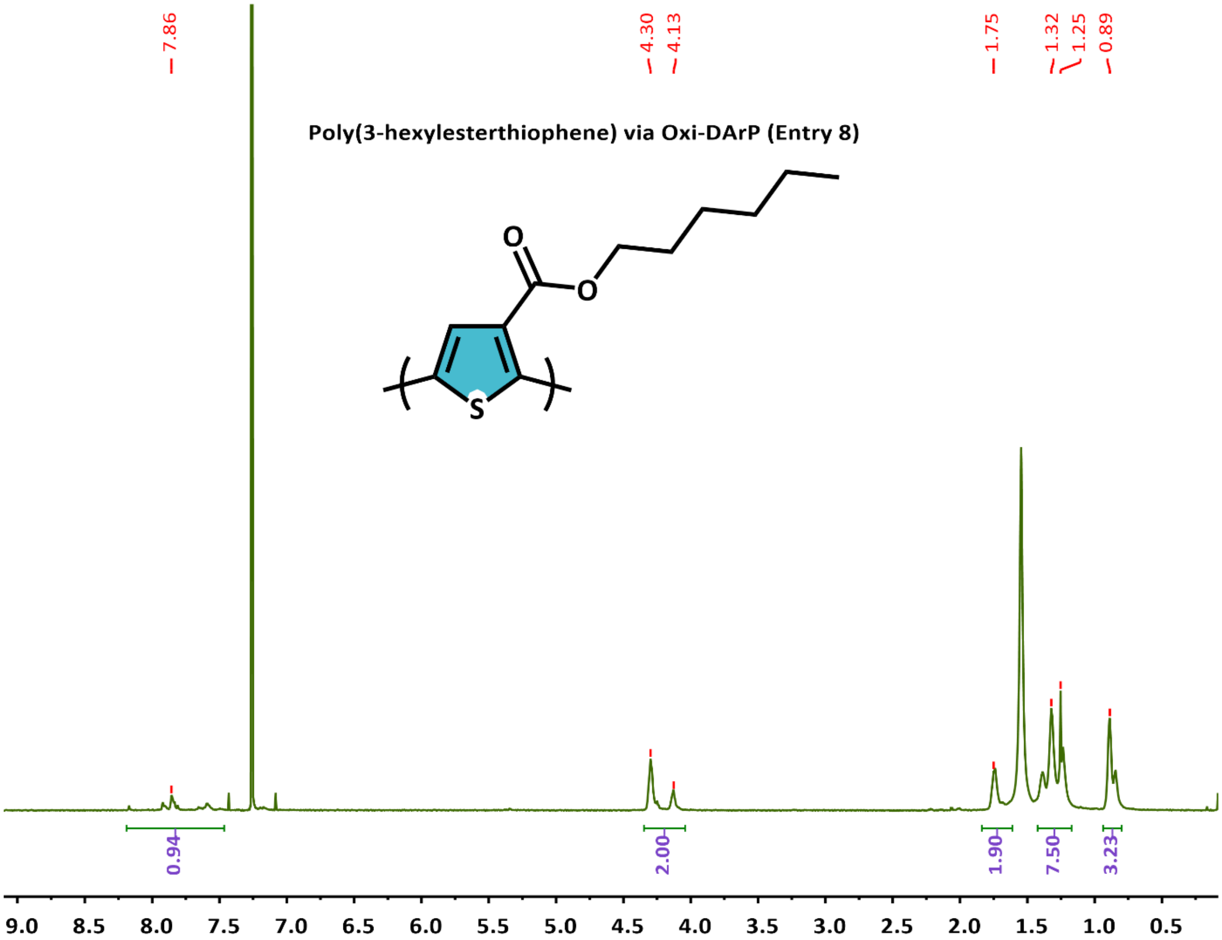


Figure S13. ^{1}H-NMR of **Oxi-DArP P3HET** (Entry 8) in $CDCl_3$.

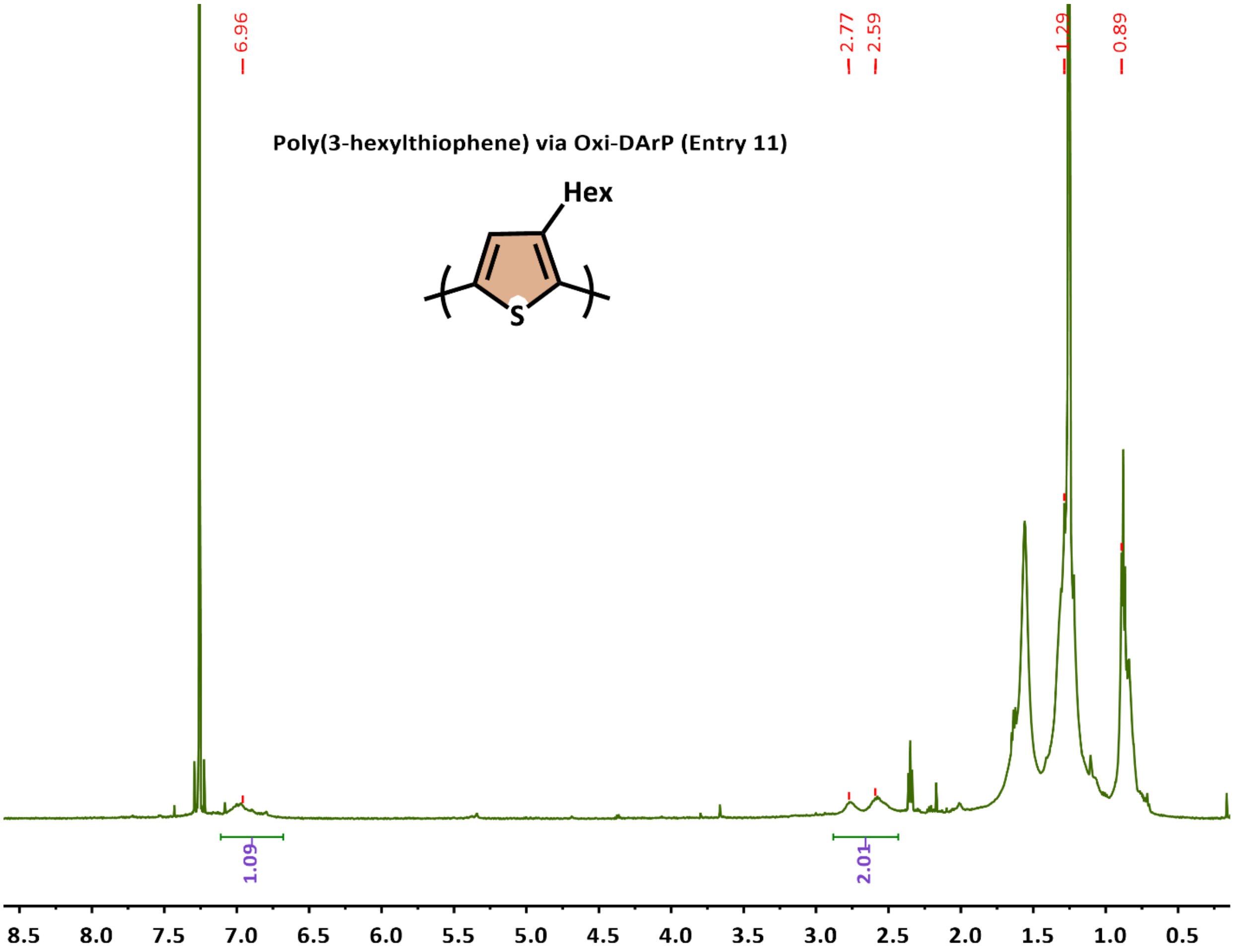


Figure S14. ^{1}H-NMR of **Oxi-DArP P3HT** (Entry 11) in $CDCl_3$.

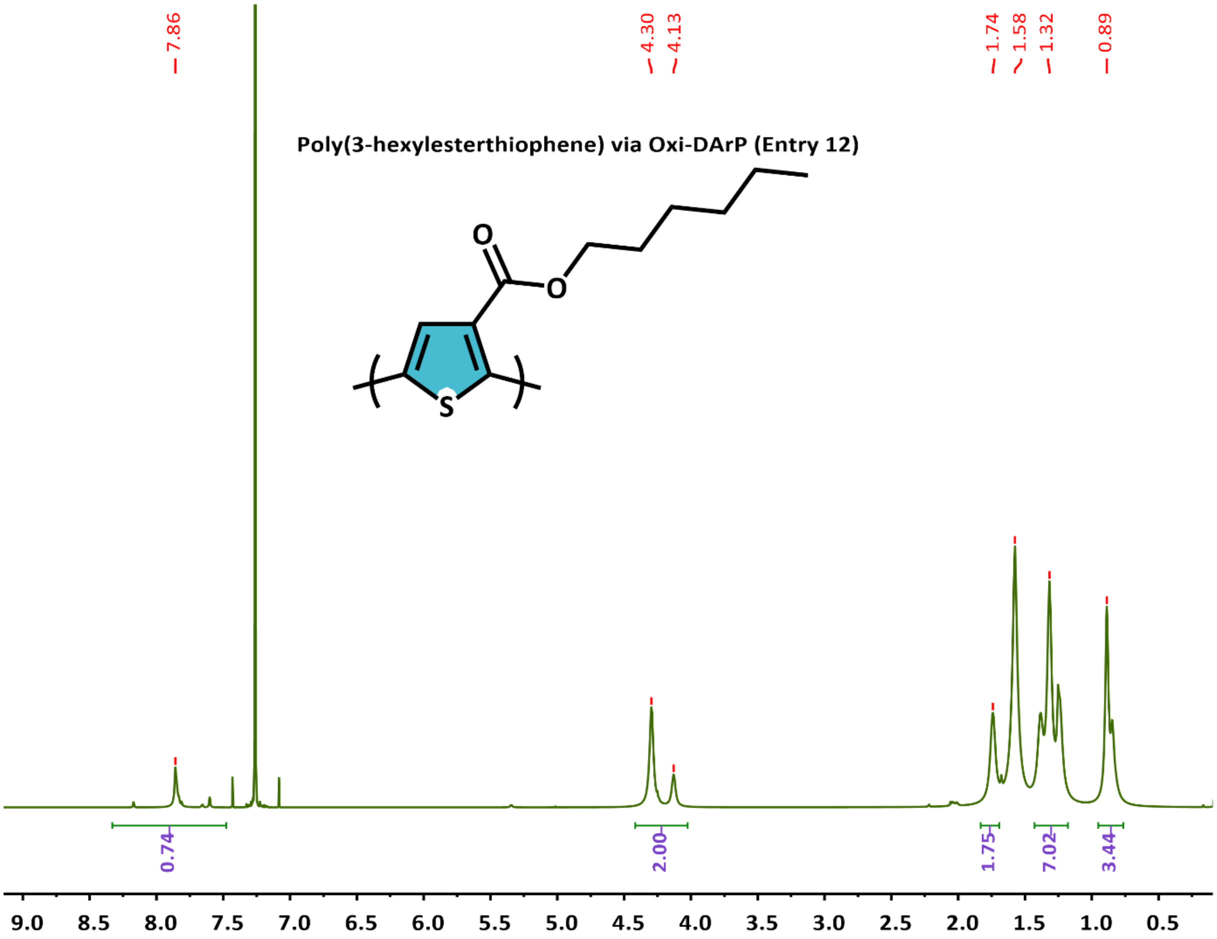


Figure S15. ^{1}H-NMR of **Oxi-DArP P3HET** (Entry 12) in $CDCl_3$.

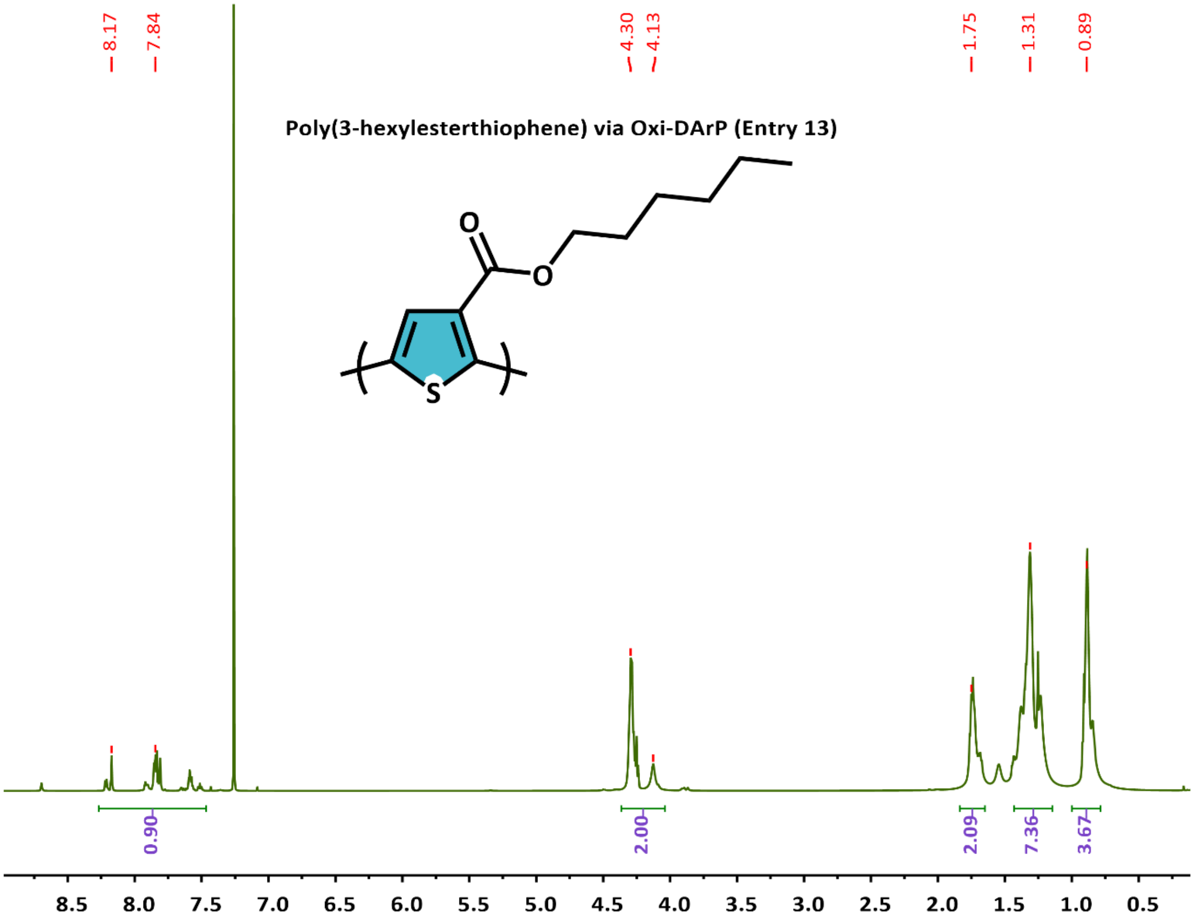


Figure S16. ^{1}H-NMR of **Oxi-DArP P3HXT** (Entry 13) in $CDCl_3$.

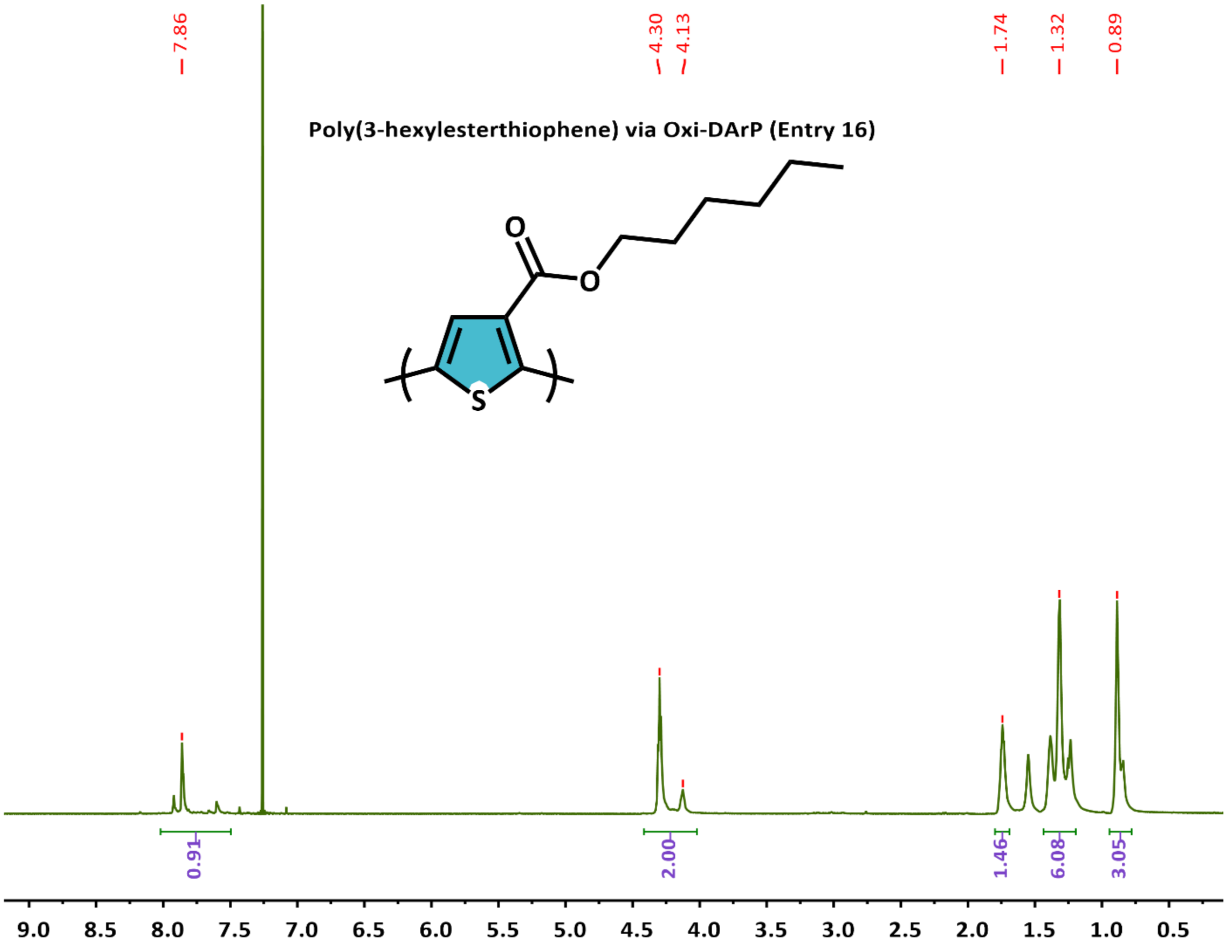


Figure S17. ^{1}H-NMR of **Oxi-DArP P3HET** (Entry 16) in $CDCl_3$.

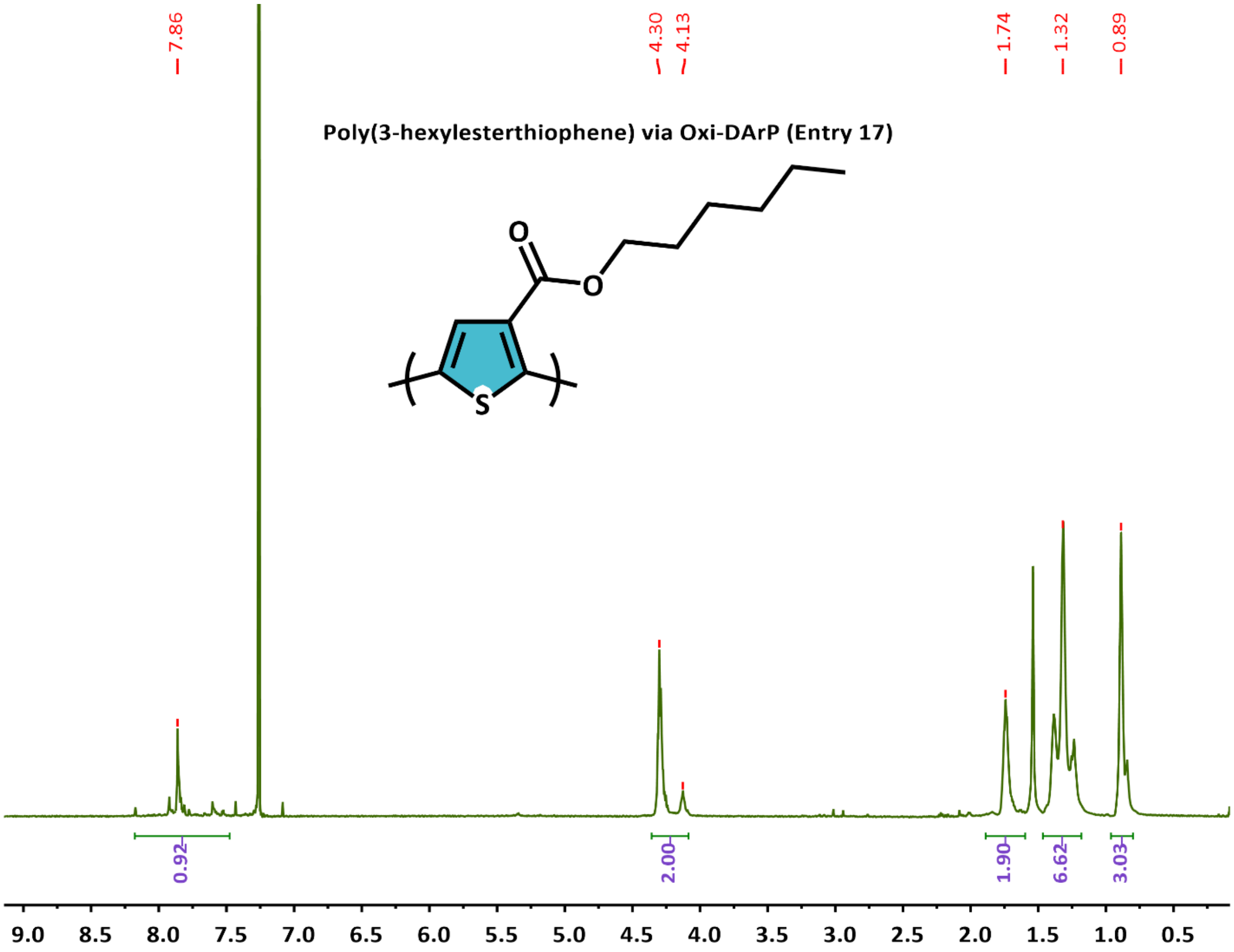


Figure S18. ^{1}H-NMR of **Oxi-DArP P3HET** (Entry 17) in $CDCl_3$.

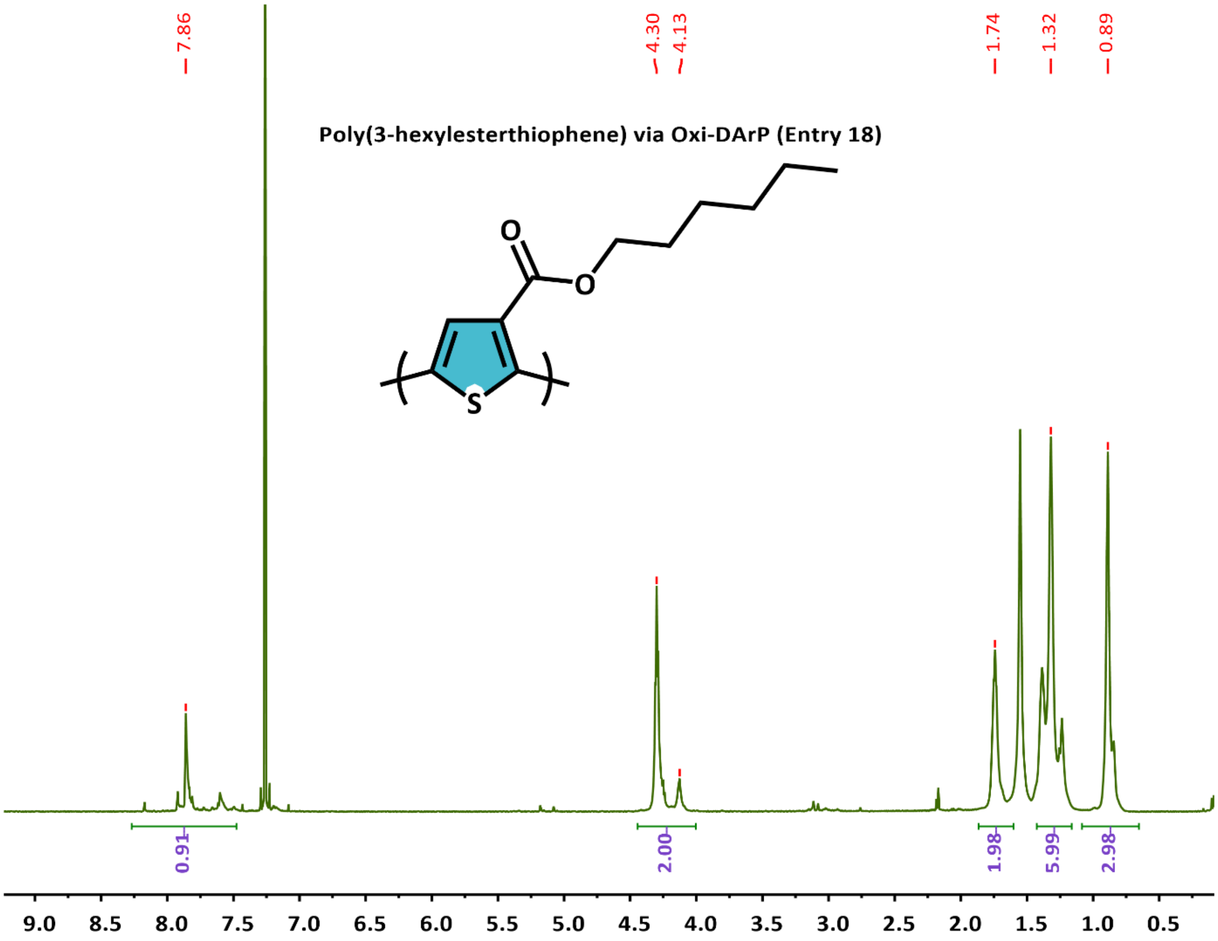


Figure S19. ^{1}H-NMR of **Oxi-DArP P3HET** (Entry 18) in $CDCl_3$.

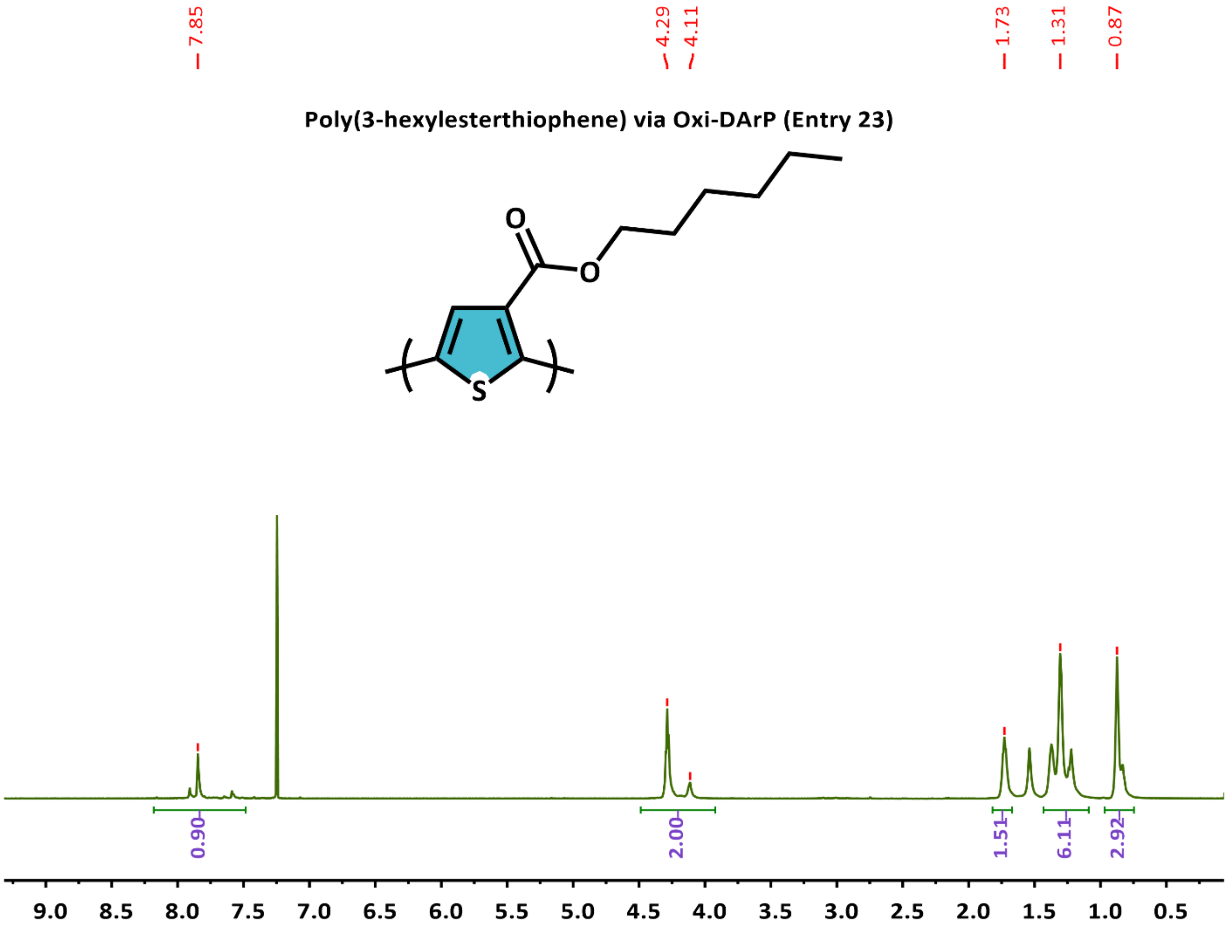


Figure S20. ^{1}H-NMR of **Oxi-DArP P3HET** (Entry 23) in $CDCl_3$.

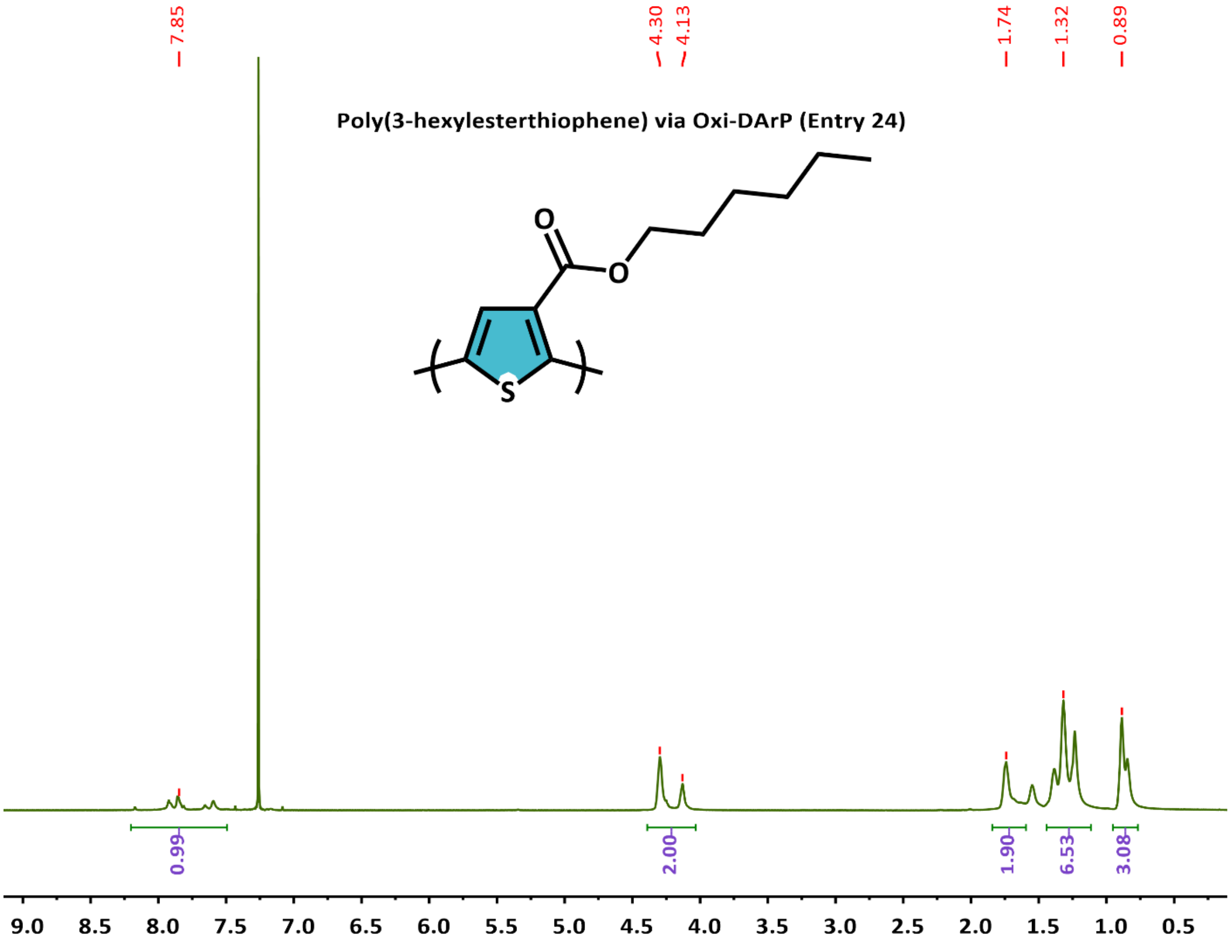


Figure S21. ^{1}H-NMR of **Oxi-DArP P3HET** (Entry 24) in $CDCl_3$.

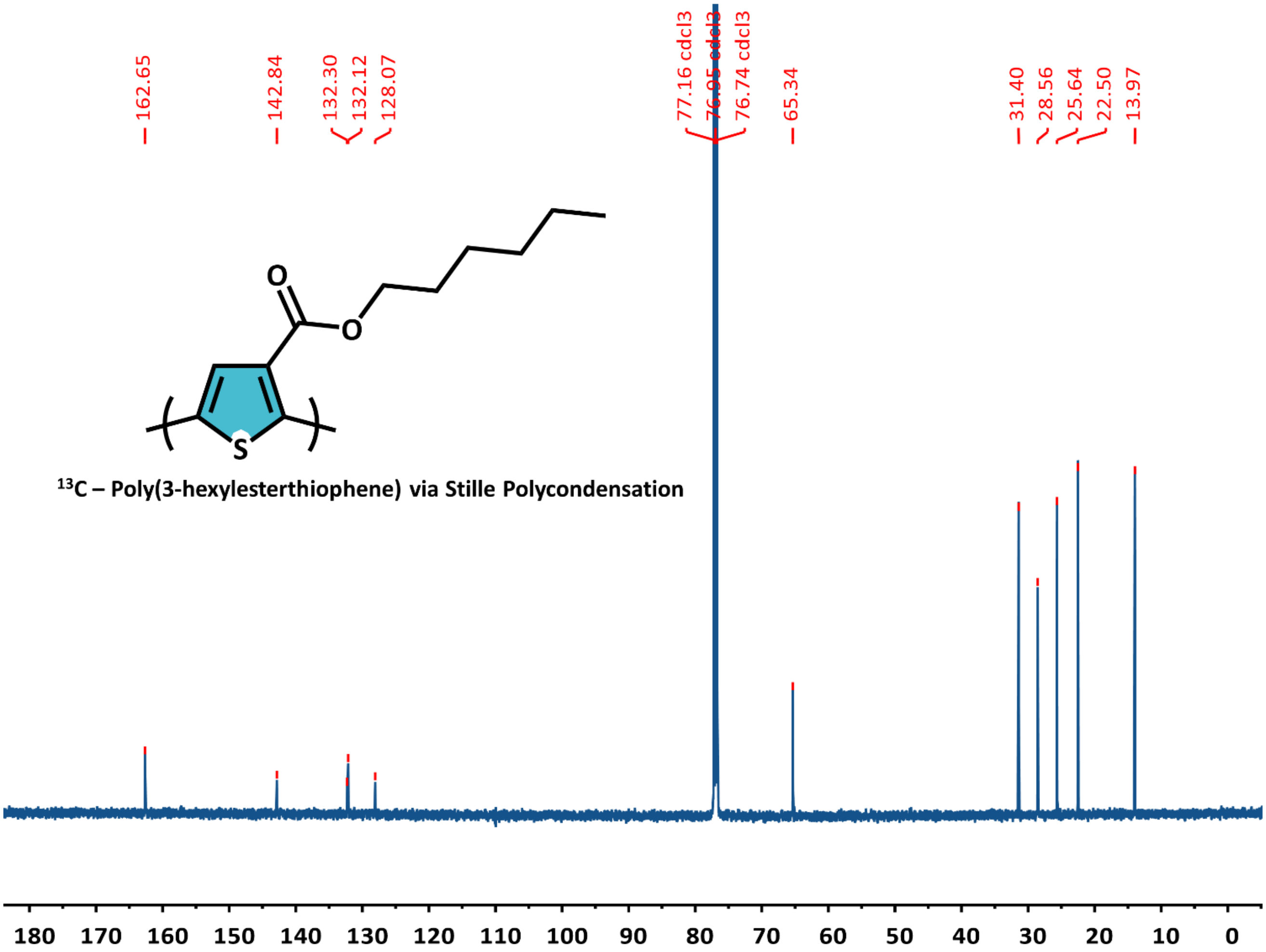


Figure S22. ^{13}C-NMR of **Stille P3HET** in $CDCl_3$.

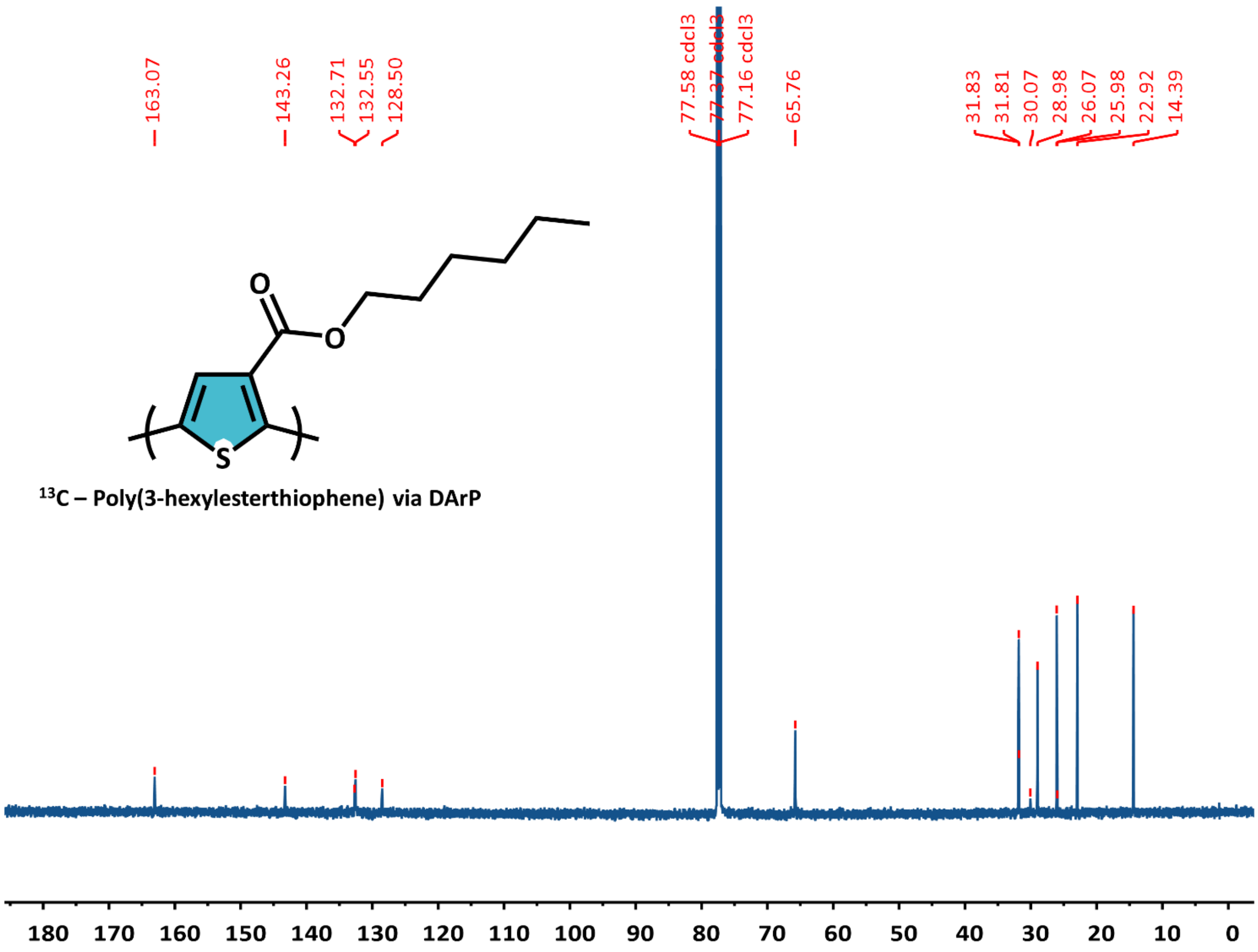


Figure S23. ^{13}C-NMR of **DArP P3HET** in $CDCl_3$.

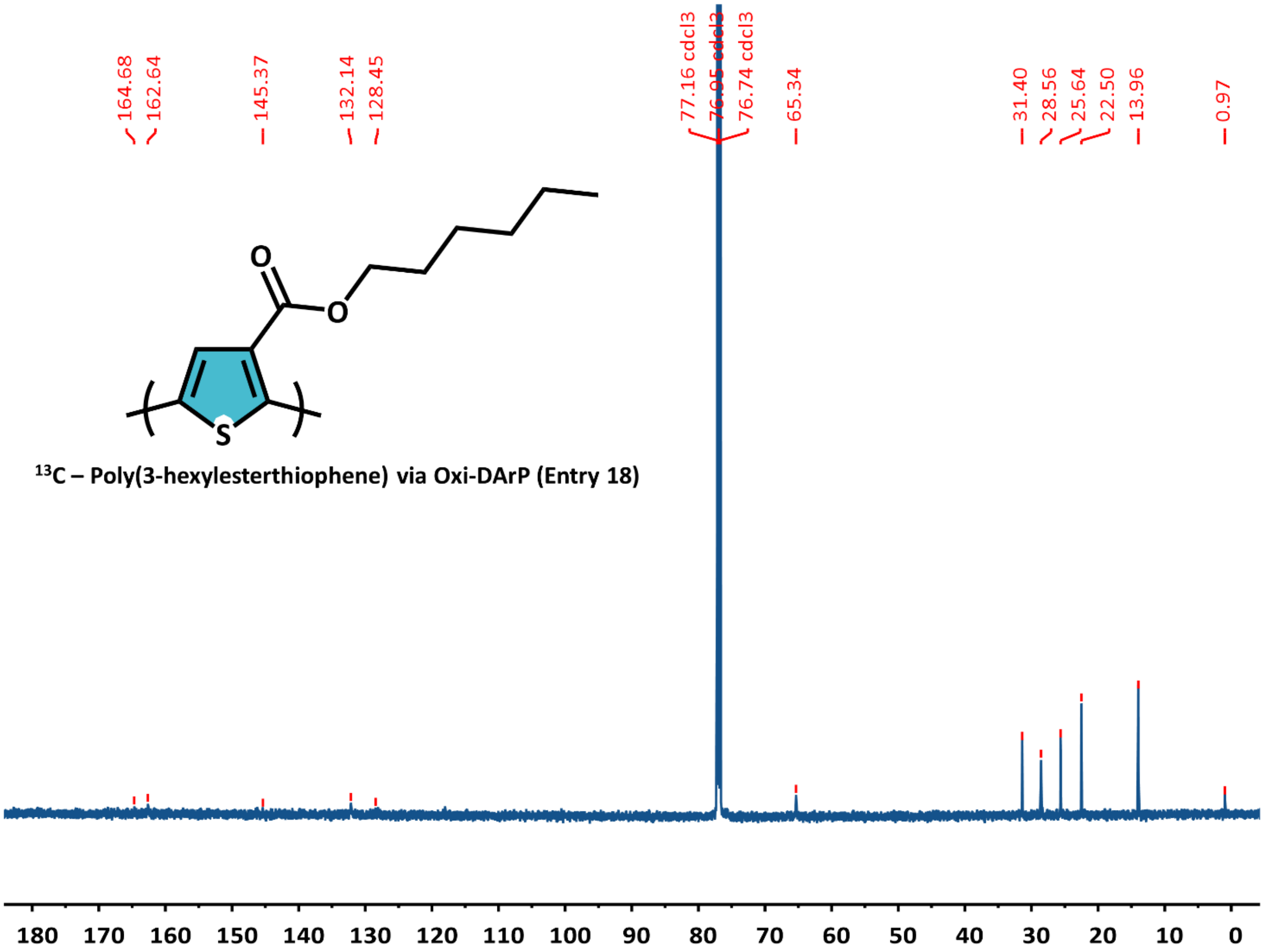


Figure S24. ^{13}C-NMR of **Oxi-DArP P3HET (Entry 16)** in $CDCl_3$.

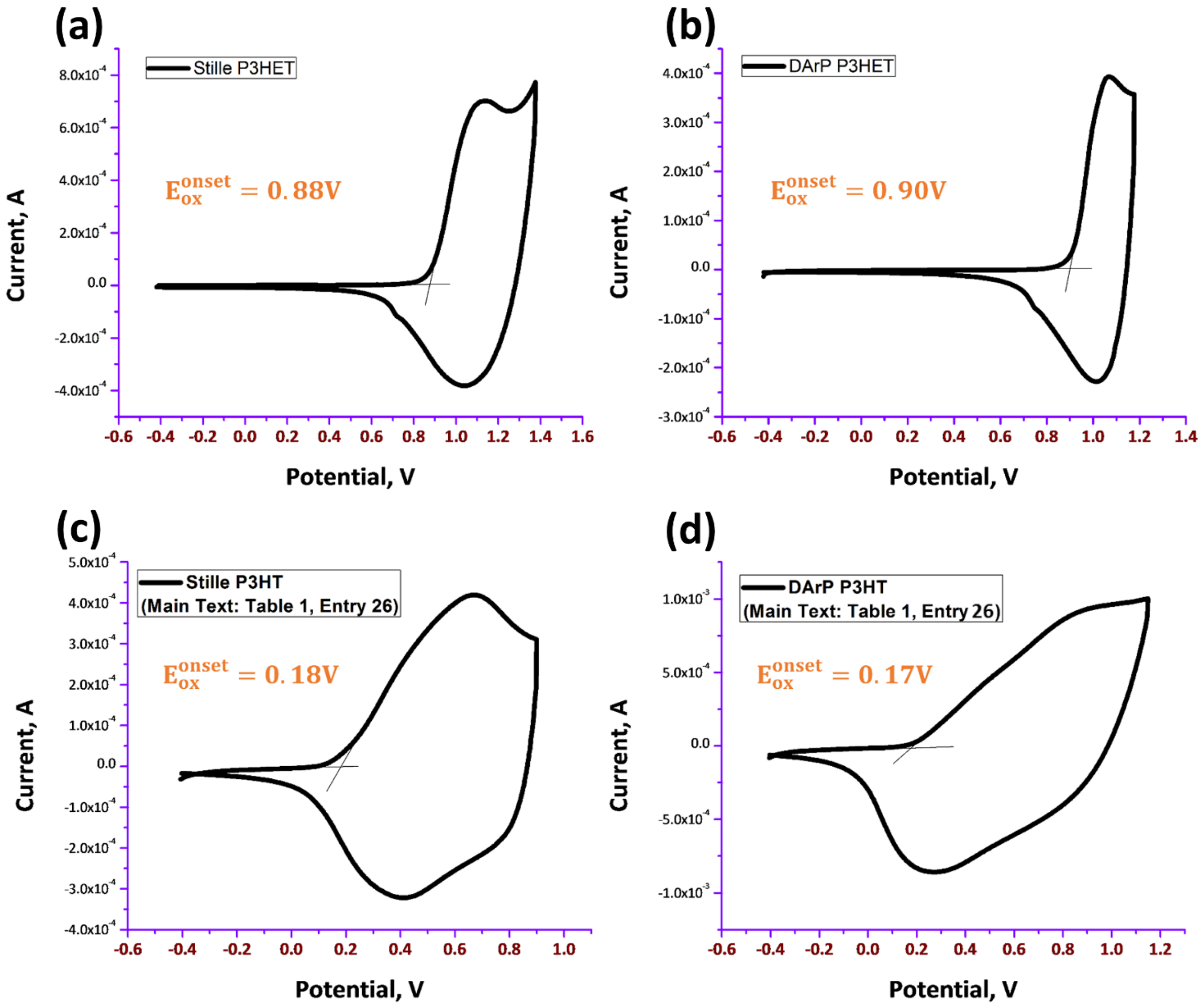


Figure S25. CV Traces for the electrochemical oxidation of **Stille P3HET** (a), **DArP P3HET** (b), **Stille P3HT** (c), and **DArP P3HT** (d).

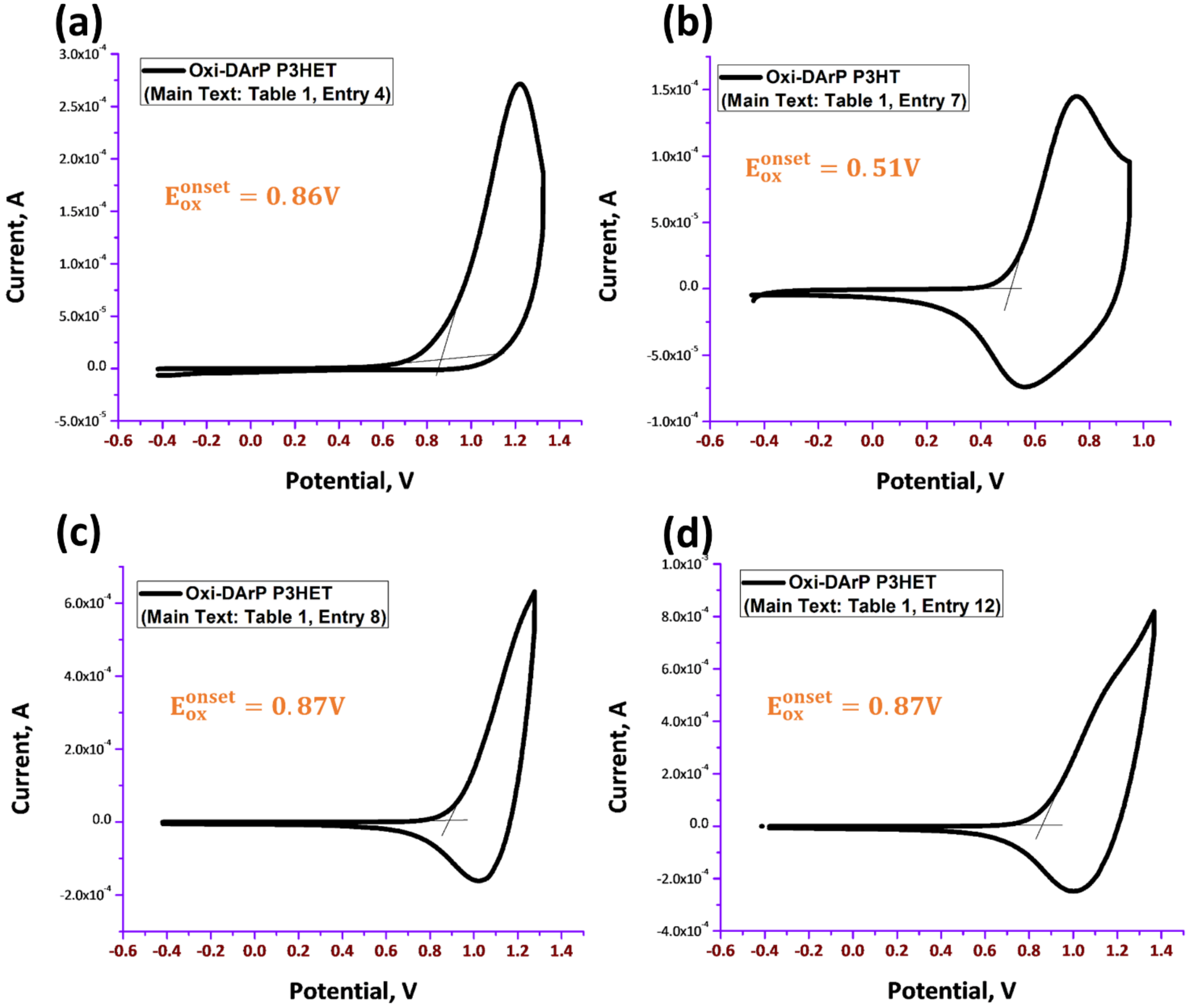


Figure S26. CV Traces for the electrochemical oxidation of **Entry 4** (a), **Entry 7** (b), **Entry 8** (c), **and Entry 12** (d).

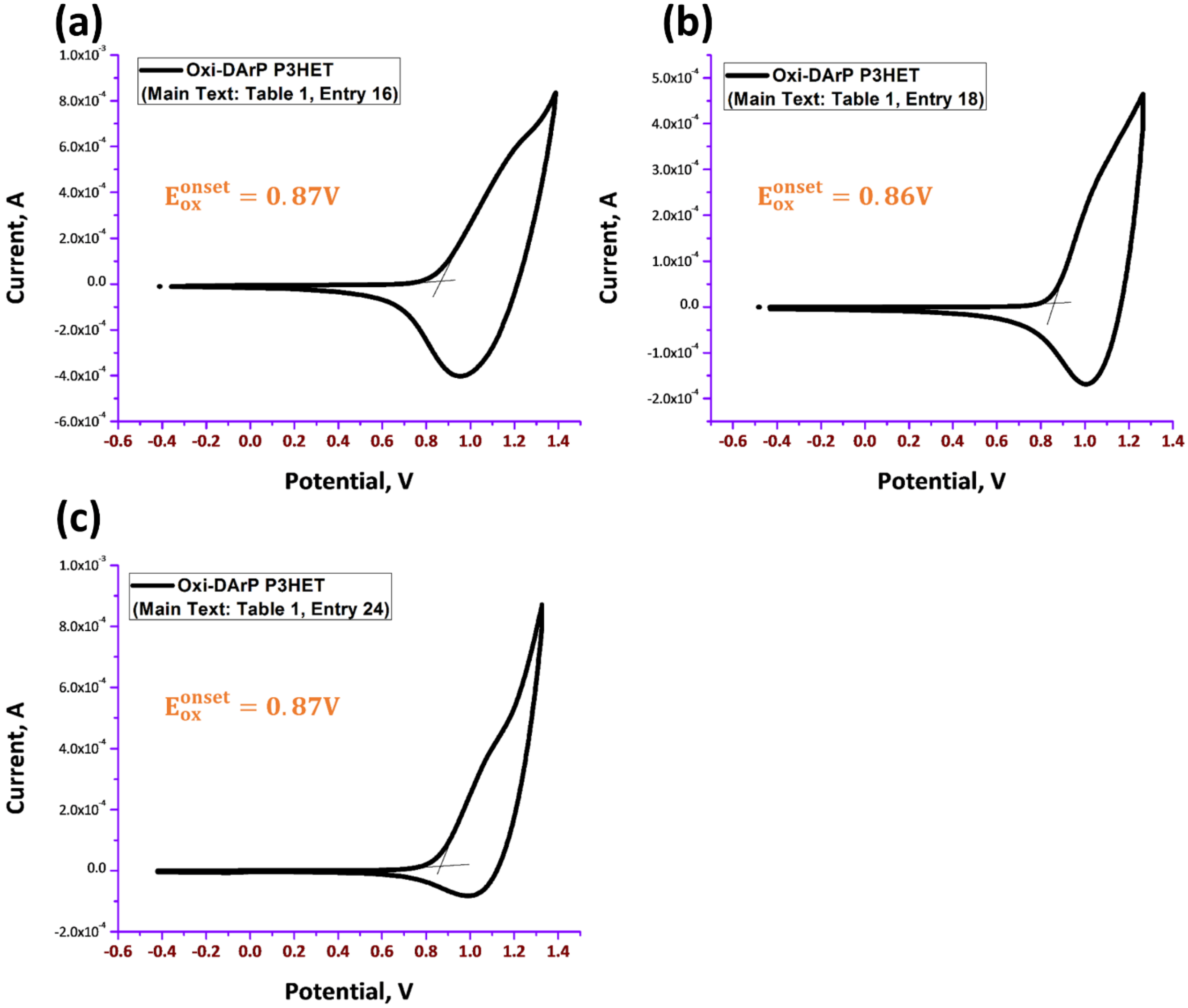


Figure S27. CV Traces for the electrochemical oxidation of **Entry 16** (a), **Entry 18** (b), **Entry 24** (c).

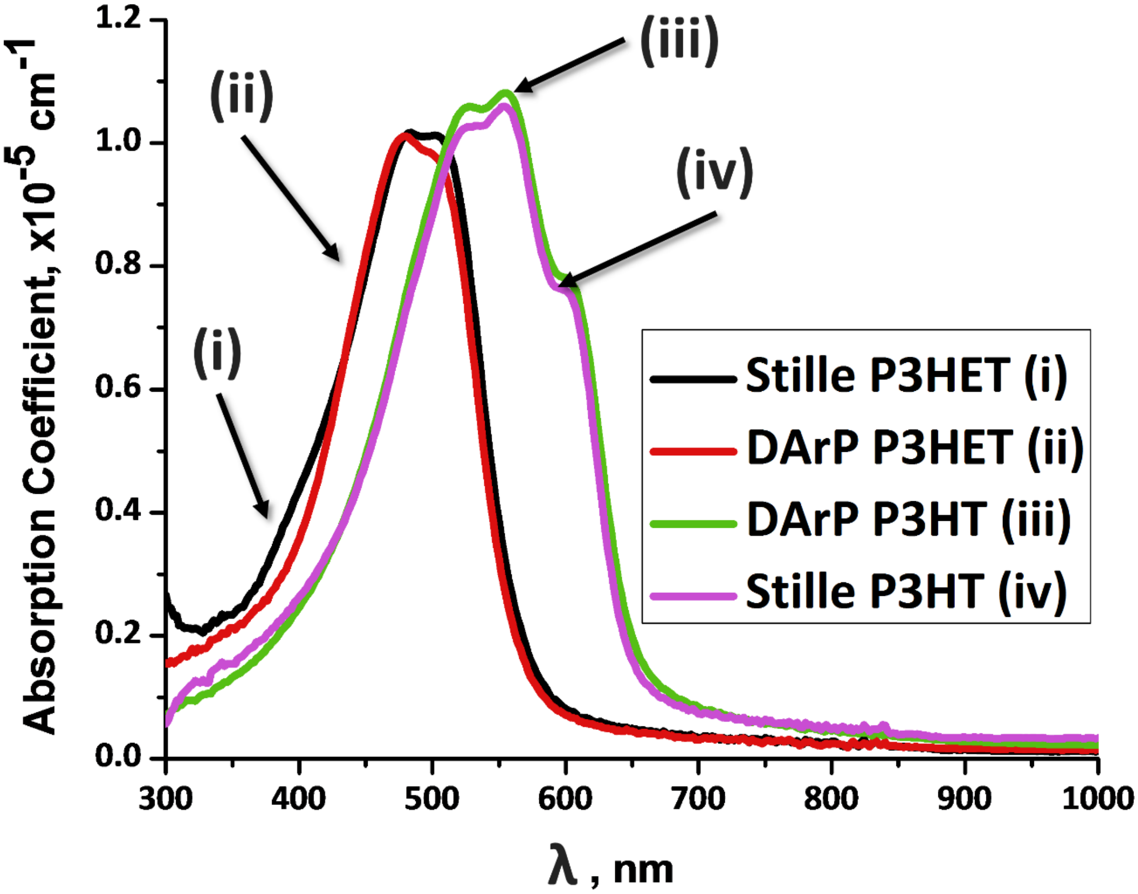


Figure S28. UV-Vis Spectra for **Stille P3HET** (i), **DArP P3HET** (ii), **DArP P3HT** (iii), and **Stille P3HT** (iv).

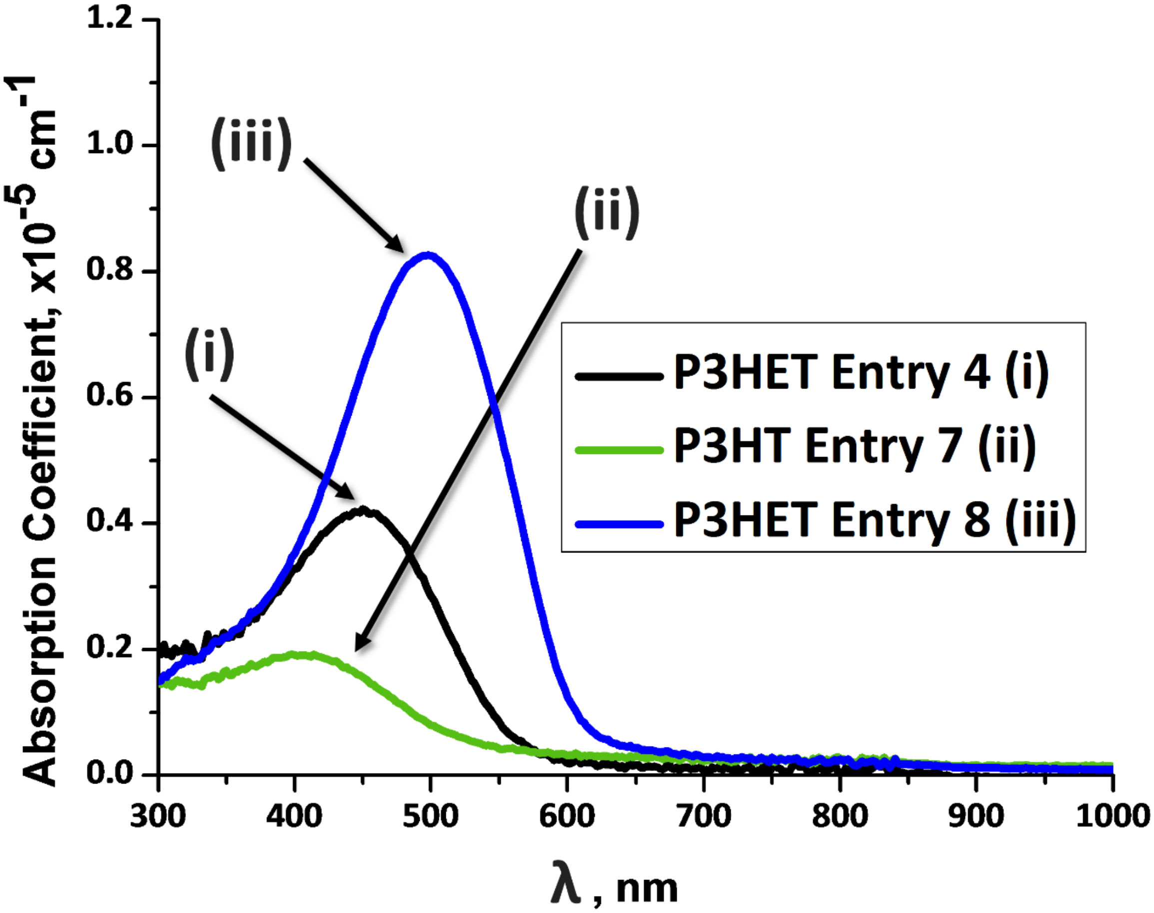


Figure S29. UV-Vis Spectra for **Oxi-DArP P3HET Entry 4** (i), **Oxi-DArP P3HT Entry 7** (ii), and **Oxi-DArP P3HET Entry 8** (iii).

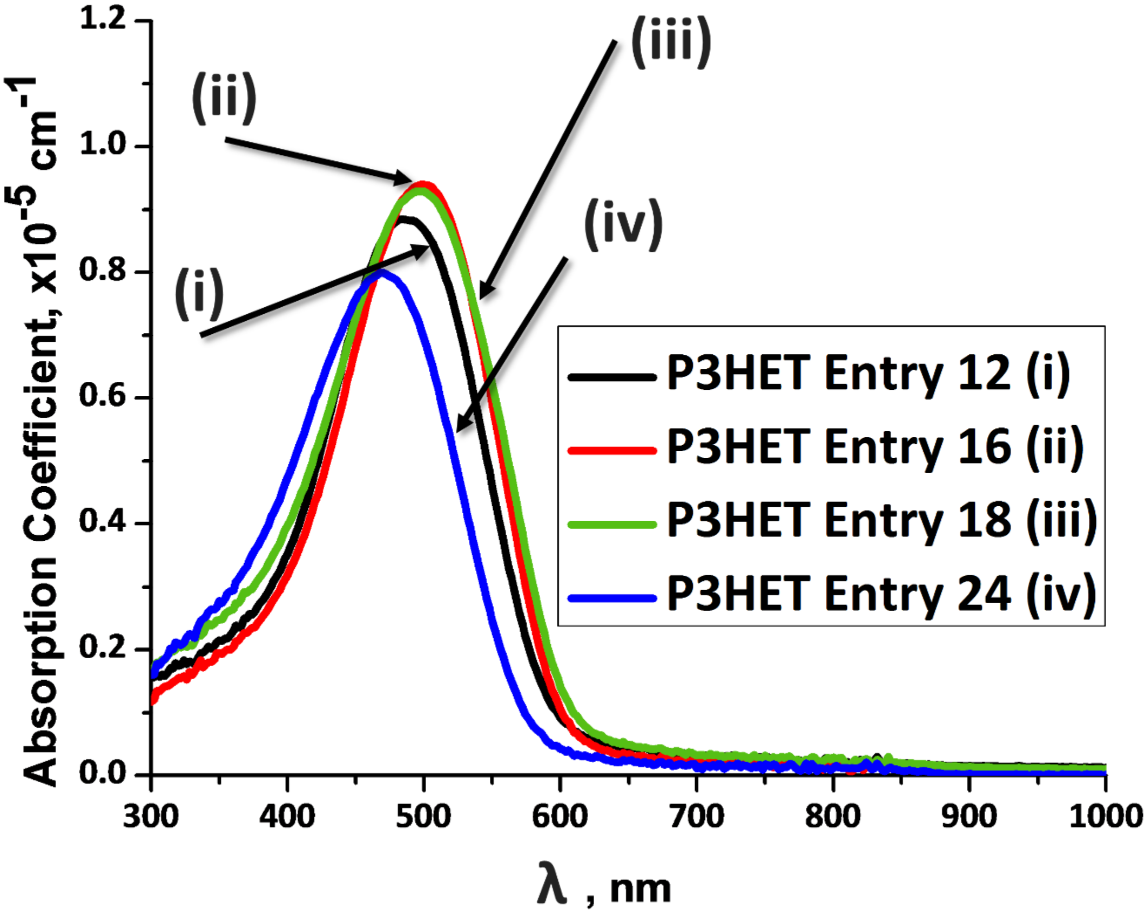


Figure S30. UV-Vis Spectra for **Oxi-DArP P3HET Entry 12** (i), **Oxi-DArP P3HET Entry 16** (ii), **Oxi-DArP P3HET Entry 18** (iii), and **Oxi-DArP P3HET Entry 24** (iv).

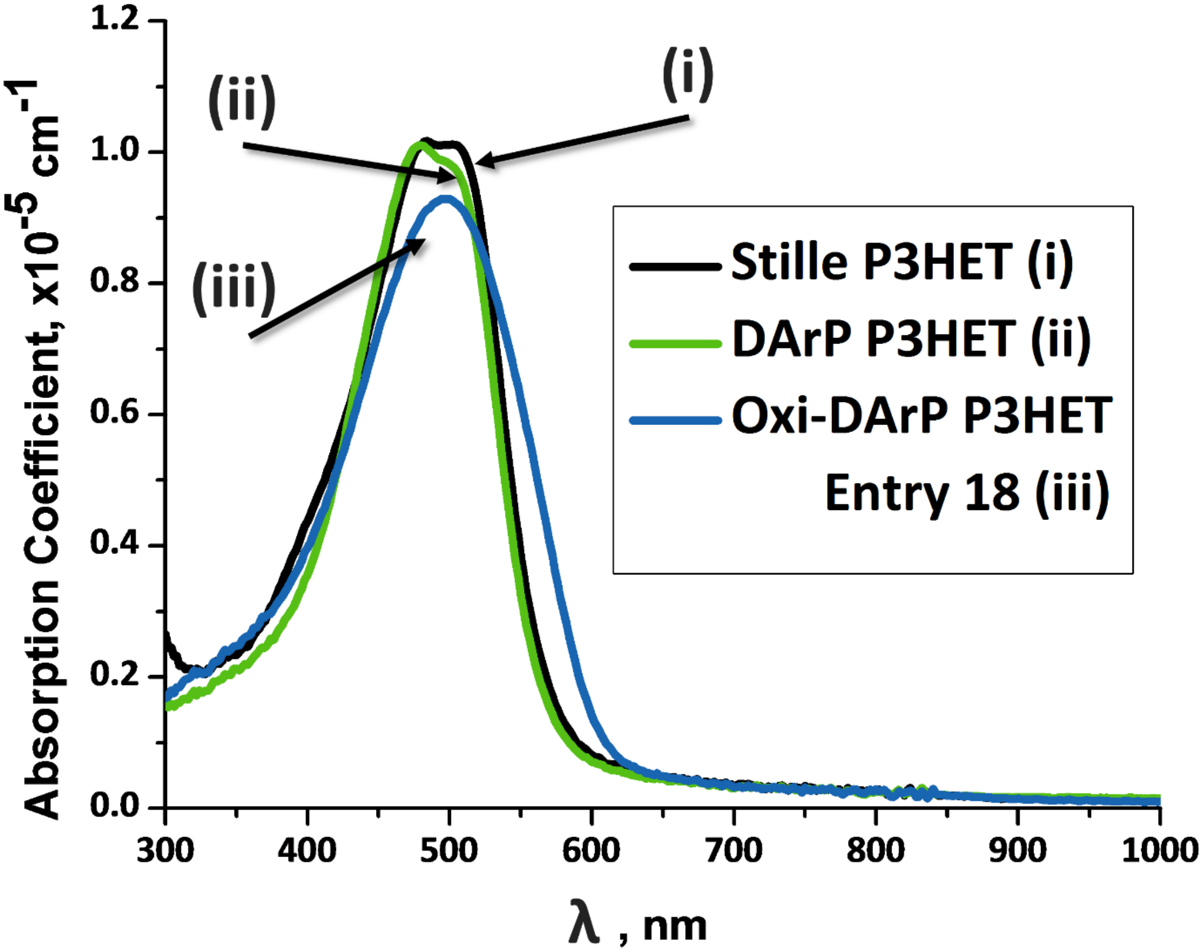


Figure S31. Comparison of the UV-Vis Spectra for **Stille P3HET** (i), **DArP P3HET** (ii), and **Oxi-DArP P3HET Entry 18** (iii).

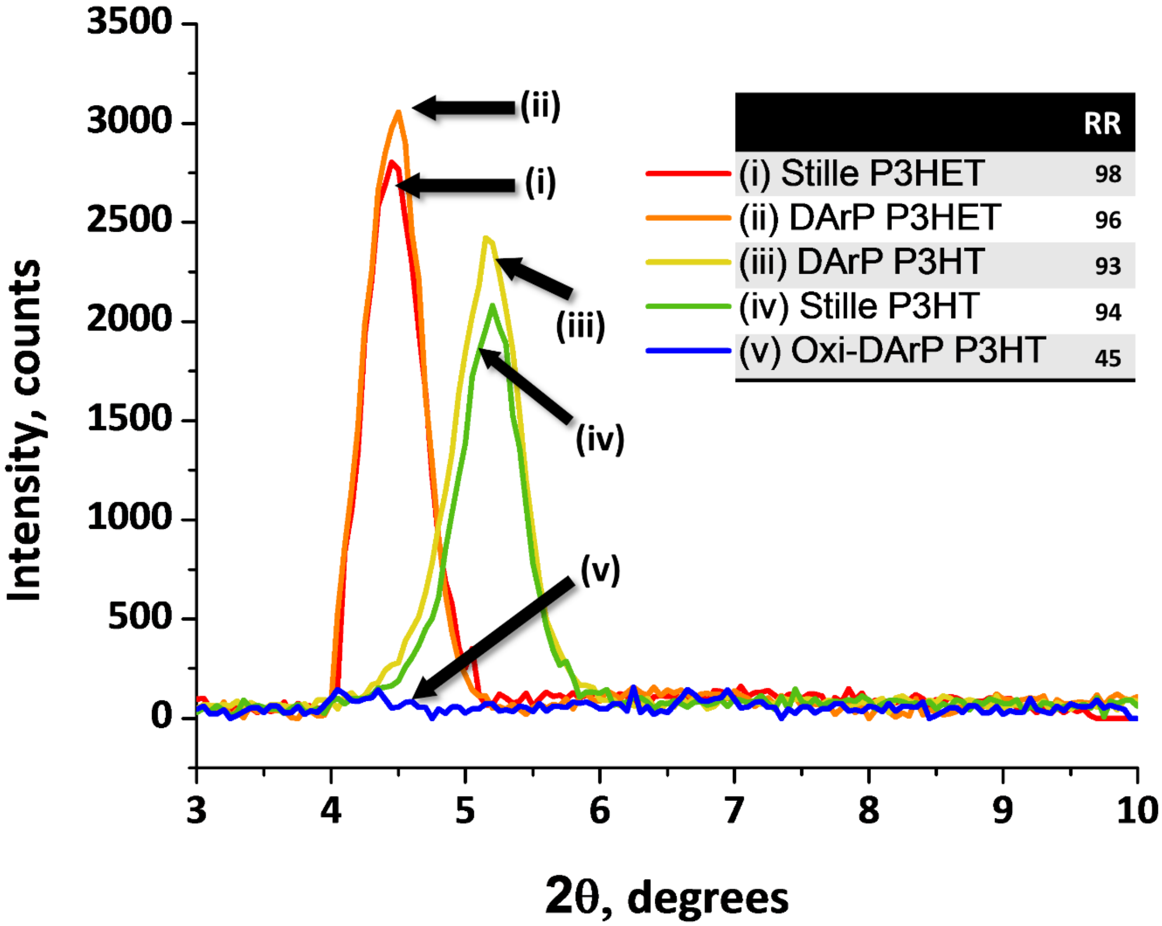


Figure S32. GIXRD Spectra for **Stille P3HET** (i), **DArP P3HET** (ii), **DArP P3HT** (iii), **Stille P3HT** (iv), and **Oxi-DArP P3HT Entry 7** (v). The regioregularity of the corresponding polymers is provided as well.

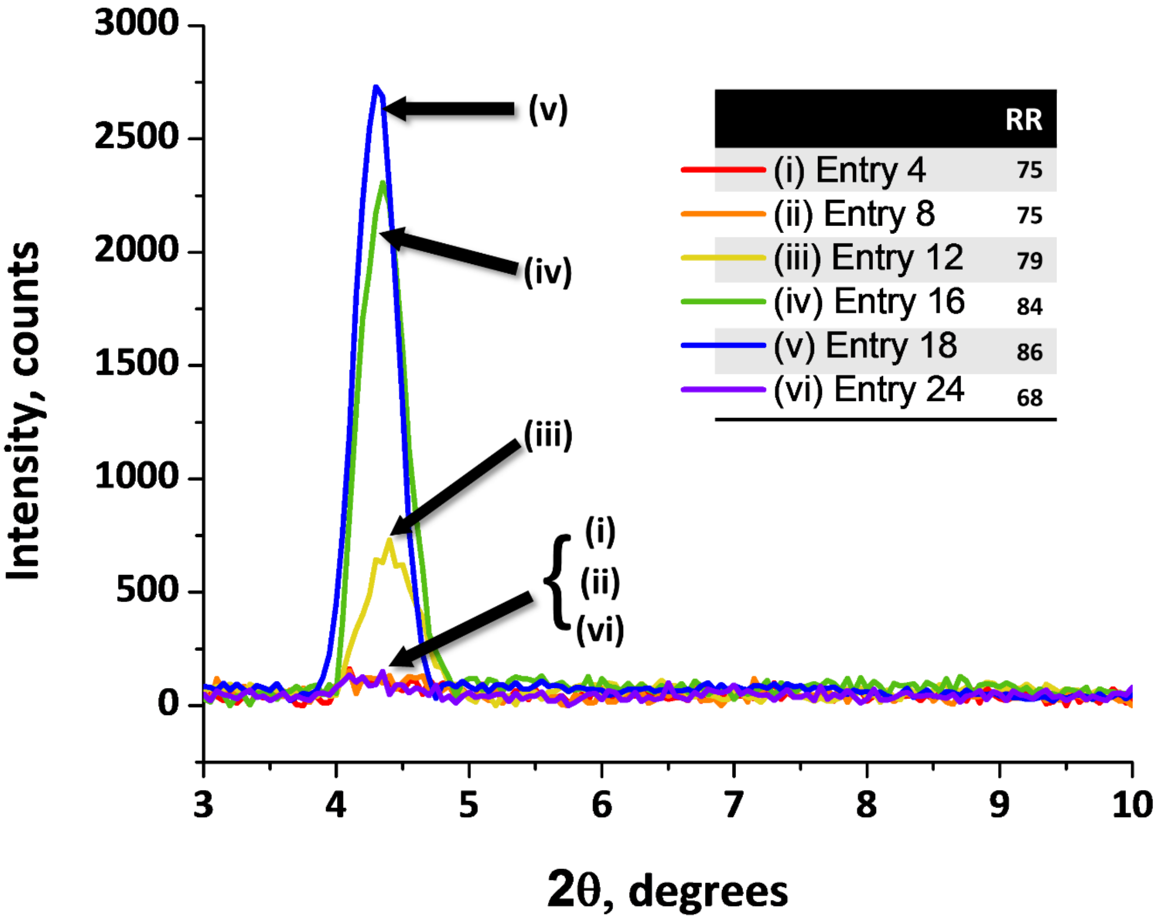


Figure S33. GIXRD Spectra for **Oxi-DArP P3HET Entry 4** (i), **Oxi-DArP P3HET Entry 8** (ii), **Oxi-DArP P3HET Entry 12** (iii), and **Oxi-DArP P3HET Entry 16** (iv), **Oxi-DArP P3HET Entry 18** (v), **Oxi-DArP P3HET Entry 24** (vi). The regioregularity of the corresponding polymers is provided as well.

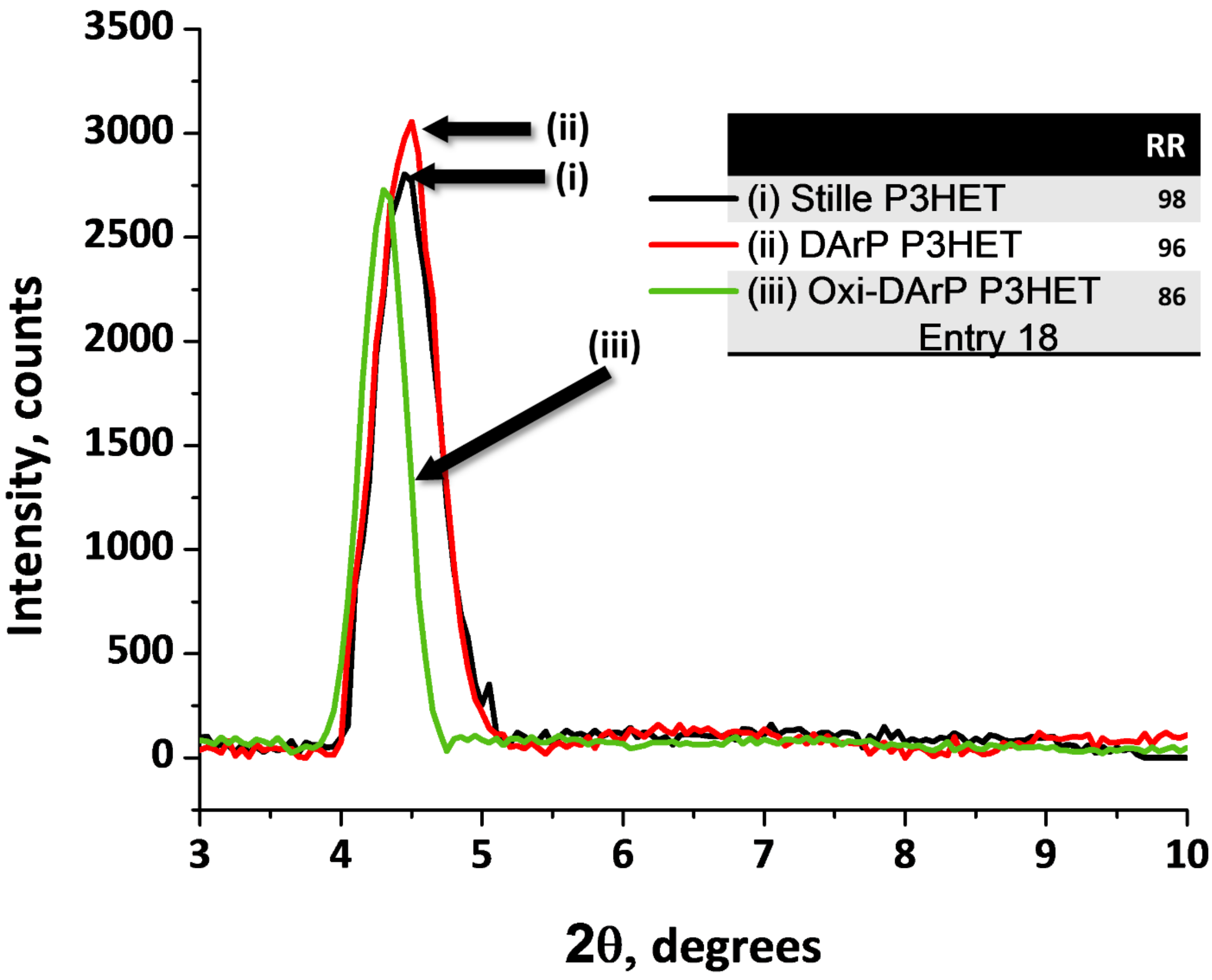


Figure S34. Comparison of GIXRD Spectra for **Stille P3HET** (i), **DArP P3HET** (ii), and optimized **Oxi-DArP P3HET Entry 18** (iii). The regioregularity of the corresponding polymers is provided as well.

Mobility Measurements:

Mobility was measured using a hole-only device configuration of ITO/PEDOT:PSS/Polymer/Al in the space charge limited current regime. The devices preparations for a hole-only device were the same as described below for solar cells. The dark current was measured under ambient conditions. At sufficient potential the mobilities of charges in the device can be determined by fitting the dark current to the model of SCL current and described by equation 1:

$$J_{SCLC} = \frac{9}{8}\varepsilon_R\varepsilon_0\mu\frac{V^2}{L^3} \qquad (1),$$

where J_{SCLC} is the current density, ε_0 is the permittivity of space, ε_R is the dielectric constant of the polymer (assumed to be 3), μ is the zero-field mobility of the majority charge carriers, V is the effective voltage across the device ($V = V_{applied} - V_{bi} - V_r$), and L is the polymer layer thickness. The series and contact resistance of the hole-only device (16 – 20 Ω) was measured using a blank (ITO/PEDOT/Al) configuration and the voltage drop due to this resistance (V_r) was subtracted from the applied voltage. The built-in voltage (V_{bi}), which is based on the relative work function difference of the two electrodes, was also subtracted from the applied voltage. The built-in voltage can be determined from the transition between the ohmic region and the SCL region and is found to be about 1 V. Polymer film thicknesses were measured using GIXRD in the reflectivity mode.

Crystallite Size:

Crystallite size was estimated using Scherrer's equation 1:[3]

$$\boldsymbol{\tau = \frac{K\lambda}{\beta cos\theta}} \qquad (1)$$

where τ is the mean size of the ordered (crystalline) domains, K is a dimensionless shape factor (K = 0.9), λ is X-ray wavelength, β is the line broadening at half the maximum intensity (FWHM) in radians and θ is the Bragg's angle.

Table S1. Polymers (Entry as Designated in Table 1 of the Main Text), $\lambda_{max,abs}$ (nm), absorption coefficient (cm^{-1}), RR (%) as determined by peak ratios in ^{1}H-NMR, 2θ from GIXRD, interchain distances (d) (Å), GIXRD intensities (a.u.), peak widths at half maximum (FWHM), and crystallite size of neat polymers in thin films spin coated from *o*-DCB.

Polymer/Entry	**$\lambda_{max,abs}$ (nm)**	**Absorption Coefficient (cm^{-1})**	**RR (%)**	**2θ (deg)**	**d (Å)**	**Intensity (a.u.)**	**FWHM (deg)**	**Crystallite Size (nm)**
Stille P3HET	485	101816	98	4.45	19.8	2793	0.537	14.8
DArP P3HET	479	101800	96	4.50	19.6	3052	0.510	15.5
Stille P3HT	553	106015	94	5.20	17.0	2070	0.588	13.5
DArP P3HT	555	108895	93	5.15	17.1	2431	0.628	12.6
Entry 7 (P3HT)	409	19630	45	--	--	--	--	--
Entry 4 (P3HET)	450	42034	75	--	--	--	--	--
Entry 8 (P3HET)	498	82612	75	--	--	--	--	--
Entry 12 (P3HET)	487	88856	79	4.41	20.0	718	0.488	16.2
Entry 16 (P3HET)	500	94370	84	4.35	20.3	2314	0.414	19.2
Entry 18 (P3HET)	498	93225	86	4.30	20.5	2730	0.409	19.4
Entry 24 (P3HET)	468	79838	68	--	--	--	--	--

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