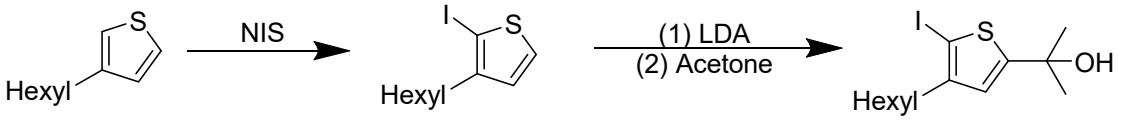
ipso-Arylative polymerization as a route to π-conjugated polymers: Synthesis of poly(3-hexylthiophene)

Feng-Yang Shih†, Sisi Tian†, Nicholas Gallagher†, Dr. Young S. Park‖, Dr. Robert. B. Grubbs,†*

†Department of Chemistry, Stony Brook University, Stony Brook, New York 11794, United States.

‖Department of Chemistry, UNIST, Ulsan 44919, Korea

Supporting Information
Synthetic Procedures



7 (77 %) **2-I** (34 %)

3-Hexyl-2-iodothiophene (7).[1] 3-Hexylthiophene (3.11 g, 18.5 mmol) was dissolved in AcOH (25 ml) and $CHCl_3$ (25 ml) in a flask wrapped with aluminum foil at room temperature, then *N*-iodosuccinimide (4.37 g, 19.4 mmol) was poured into the flask in 5 portions over 30 min. The mixture was allowed to stir overnight at room temperature. The solution was neutralized by cooling the flask in an ice bath and slowly adding aqueous 2M KOH (100 mL). The organic layer was separated in a separatory funnel and the aqueous layer was extracted with dichloromethane (3 x 50 ml), then the first organic fraction and dichloromethane fractions were combined and washed with saturated $NaHCO_3$(aq) (100 ml). The organic layer was dried over with anhydrous Na_2SO_4 and filtered, then the collected solution was concentrated and purified with chromatography (SiO_2, hexanes) to afford 7 as a reddish transparent liquid (4.2 g, 77%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.38 (d, 1H, thienyl 4-H), 6.76 (d, 1H, thienyl 3-H), 2.57 (t, 2H, thiophene-CH_2), 1.57 (m, 2H, thiophene-CH_2-CH_2-), 1.33 (m, 4H, -$(CH_2)_2$-CH_3), 0.91 (t, 3H, -CH_3).

2-(4-Hexyl-5-iodothiophen-2-yl)propan-2-ol (2-I). LDA solution (11.1 ml, 1.5M in THF, 16.7 mmol) was injected into anhydrous THF (20 ml) in a nitrogen-filled glovebox. The flask containing LDA solution was removed from glovebox and cooled to -78 °C in an acetone/liquid nitrogen bath. Compound 7 (4.2 g, 14.4 mmol) was dissolved in anhydrous THF (20 ml) in a flask. The solution of 7 was slowly added to the LDA solution with a syringe pump (40 ml/h) at -78 °C. Then the mixture was stirred for 15 min and a solution of acetone in THF (10 mL, 2.88 M, 28.8 mmol) was slowly injected by syringe at -78 °C. The mixture was stirred for 1 h at -78 °C and then allowed to warm up to room temperature overnight with stirring. The mixture was neutralized by addition of aqueous 1M HCl (20 ml). The organic layer was separated and the aqueous layer was extracted with dichloromethane (3 x 40 ml). The dichloromethane fractions and the first organic layer were combined and dried over anhydrous Na_2SO_4, and then

concentrated under reduced pressure. The crude product was purified by gravity chromatography (SiO_2, hexanes/ethyl acetate 95:5 to 78:15 as a gradient) to give 2-I as a viscous orange liquid (1.7 g, 34%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.60 (s, 1H, thienyl 3-H), 2.47 (t, 2H, thiophene-CH_2-), 1.62 – 1.57 (m, 6H, -COH(CH_3)$_2$), 1.54 (q, J = 7.4 Hz, 2H,-CH_2-CH_2-), 1.37 – 1.30 (m, 6H, -$(CH_2)_3$-CH_3), 0.90 (t, 3H, -CH_3) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.0, 147.1, 123.1, 72.6, 71.8, 32.8, 32.2, 31.9, 30.2, 29.2, 22.9, 14.4; ESI-MS HRMS (positive ion mode) (m/z) $[M+H-H_2O]^+$ calcd. for $C_{13}H_{21}IOS+H-H_2O$, 335.0325; found, 335.0325.

Polymerization of dimethylcarbinol monomer 2. Monomer **2** was equipped with a dimethylcarbinol group on the 5-position instead of a diphenylcarbinol group. Polymerization of monomer 2 was examined with two different catalysts and several ligands in attempts to optimize the polymerization: $Pd(OAc)_2$ was paired with PCy_3, PPh_3, *t*-Bu_3P and $Pd(CNPh)_2Cl_2$ was paired with (*p*-$CF_3Ph)_3P$.[2] As was observed for the polymerization of monomer 1, significantly higher molecular weights for the chloroform fraction were found with PCy_3 as a ligand than with other ligands (Table S1, but fraction yields were exceedingly low (< 3%), indicating that mostly oligomers (M_n < 3 kg/mol) were afforded. As was found for the polymerization of the diphenylcarbinol-functionalized monomer, increasing the polymerization concentration from 0.1 M to 0.5 M led to an increase in the molecular weight and total yield of oligomers, from 55 to 79% (Table S1: entry 1 vs entry 6).

The *ipso*-arylative coupling of triphenylmethanol and bromobenzene has been reported to proceed to higher conversion than that between 2-phenylpropan-2-ol and phenyl bromide with PCy_3 or PPh_3 as the added ligand,[3] which is in agreement with the observed higher reactivity of monomer **1** as compared to monomer **2**. When polymerizations of monomer **2** with PCy_3 were conducted at lower temperatures (80 - 100 °C), polymer/oligomer precipitate was not observed in the first precipitation into methanol. The dimethylcarbinol group of P3HT of hexanes fraction in entry **1** was observed in ^{1}H NMR (peak h in Figure S9). This might be explained by the lower reactivity of dimethylcarbinol as compared to diphenylcarbinol groups in coupling reaction.

Table S1 Polymerization of monomer **2**

			$CHCl_3$ fraction (Polymer)			Hexanes Fraction (oligomers)		
Entry	Pd/Ligand	*T* (°C)	M_n (kg/mol)[c]	*Đ*[c]	yield (%)[d]	M_n (kg/mol)[c]	*Đ*[c]	yield (%)[d]
1[a]	$Pd(OAc)_2/PCy_3$	170	4.6	1.7	Trace	2.8	2.5	55
2[a]	$Pd(OAc)_2/PPh_3$	170	4.4	3.8	2.3	2.7	3.5	57
3[a]	$Pd(OAc)_2$/*t*-PBu_3	170	0.5	5.2	2.3	0.7	2.2	22
4[b]	$Pd(CNPh)_2Cl_2$/ (*p*-$CF_3Ph)_3P$	170	2	1.5	2.3	1.5	1.3	23
5[b]	$Pd(OAc)_2/PCy_3$	140	5.7	1.3	trace	3.8	1.5	41
6[b]	$Pd(OAc)_2/PCy_3$	170	5.3	2.0	trace	2.2	1.6	79
7[f]	$Pd(OAc)_2/PCy_3$	170	6.6	2.5	2.5	2.4	4.4	28
8[b]	$Pd(OAc)_2/PCy_3$	100	N/A[g]	N/A	N/A	N/A	N/A	N/A
9[b]	$Pd(OAc)_2/PCy_3$	80	N/A[g]	N/A	N/A	N/A	N/A	N/A

[a] Monomer **2** (0.1 M), $Pd(OAc)_2$ (2 mM), Ligand (6mM), and Cs_2CO_3 (0.15 M) heated in *o*-xylene for 48 h; [b] Monomer (0.5 M), $Pd(OAc)_2$ (15 mM), PCy_3 (30 mM), and Cs_2CO_3 (0.75 M) heated in *o*-xylene; [c] number-average molecular weight (M_n) and dispersity (*Đ*) of polymers in chloroform fraction were estimated by GPC in THF with polystyrene standards; [d] yield of chloroform fraction based on 100 % conversion; [e] No polymer was collected in Soxhlet extraction with chloroform; [f] **2-I** was used with conditions described in footnote [b]; [g] oligomer/polymer was not observed after precipitation in methanol.

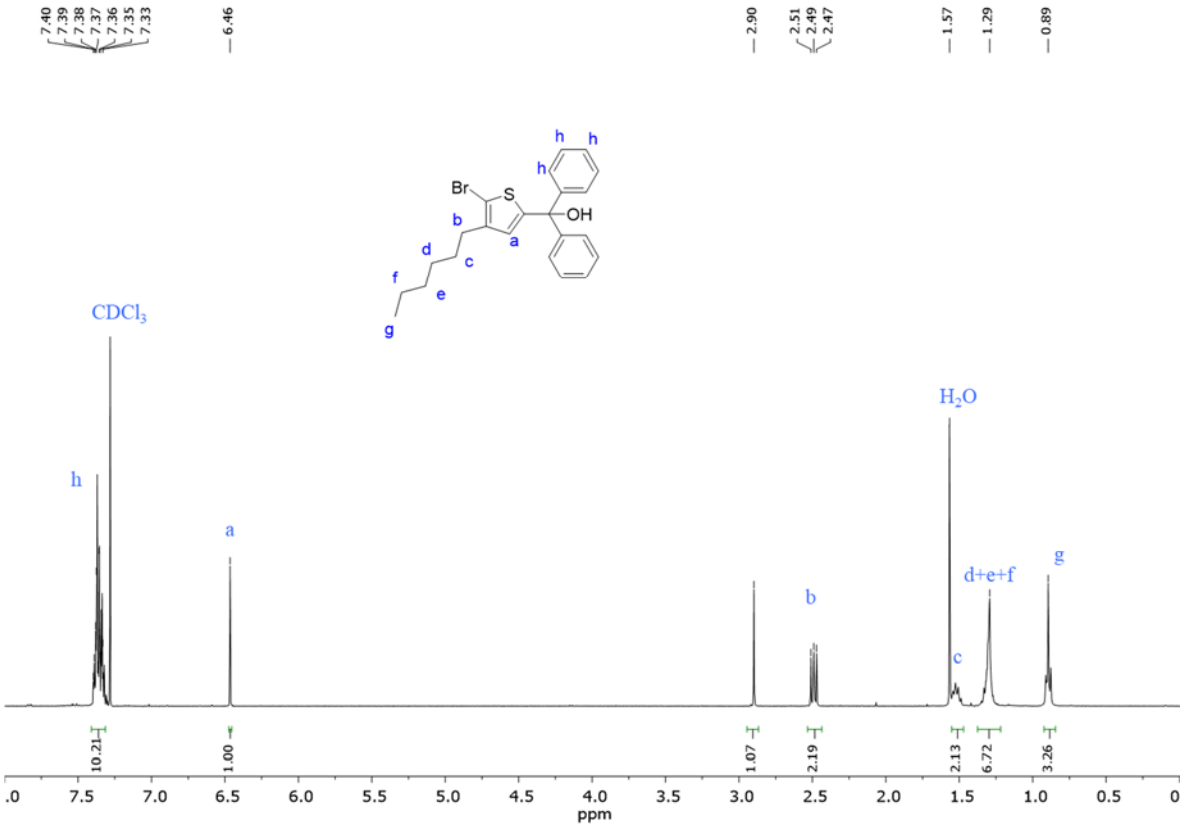


Figure S1 ^{1}H NMR of **1** in $CDCl_3$.

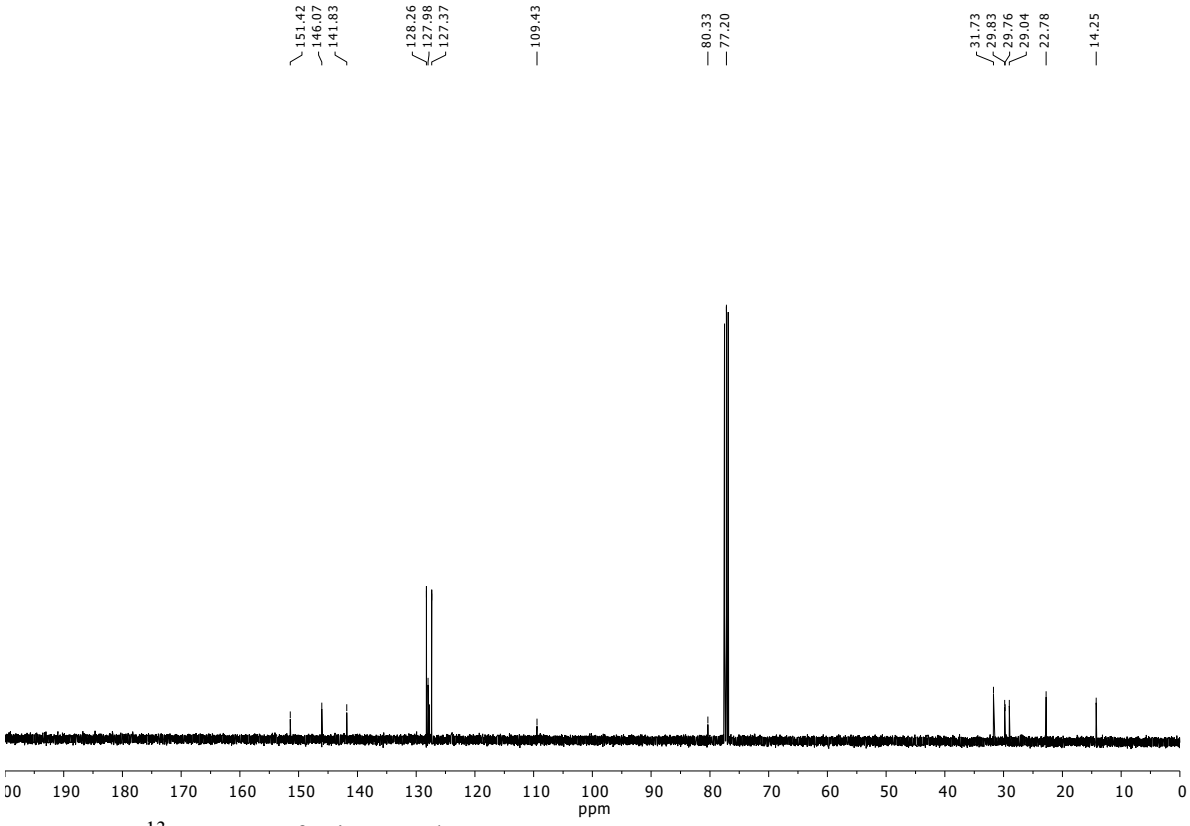


Figure S2 ^{13}C NMR of **1** in $CDCl_3$.

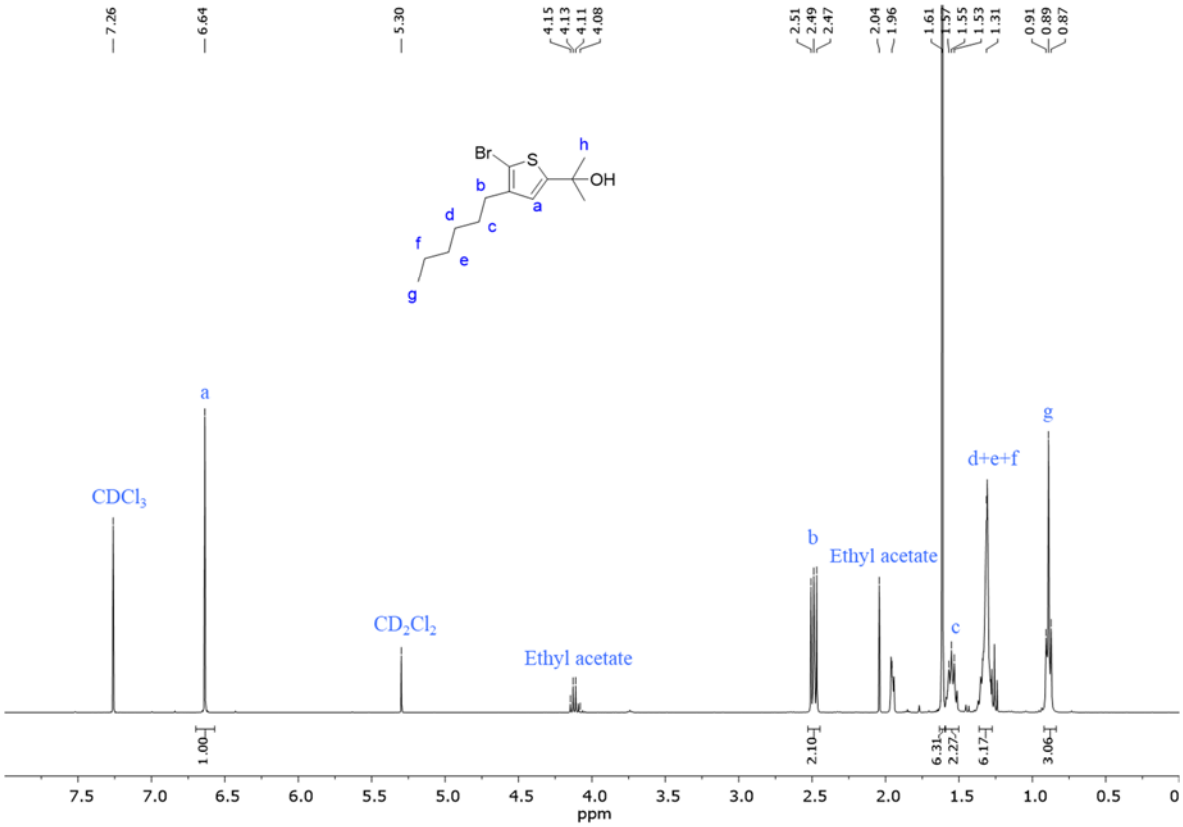


Figure S3 ^{1}H NMR of **2** in $CDCl_3$.

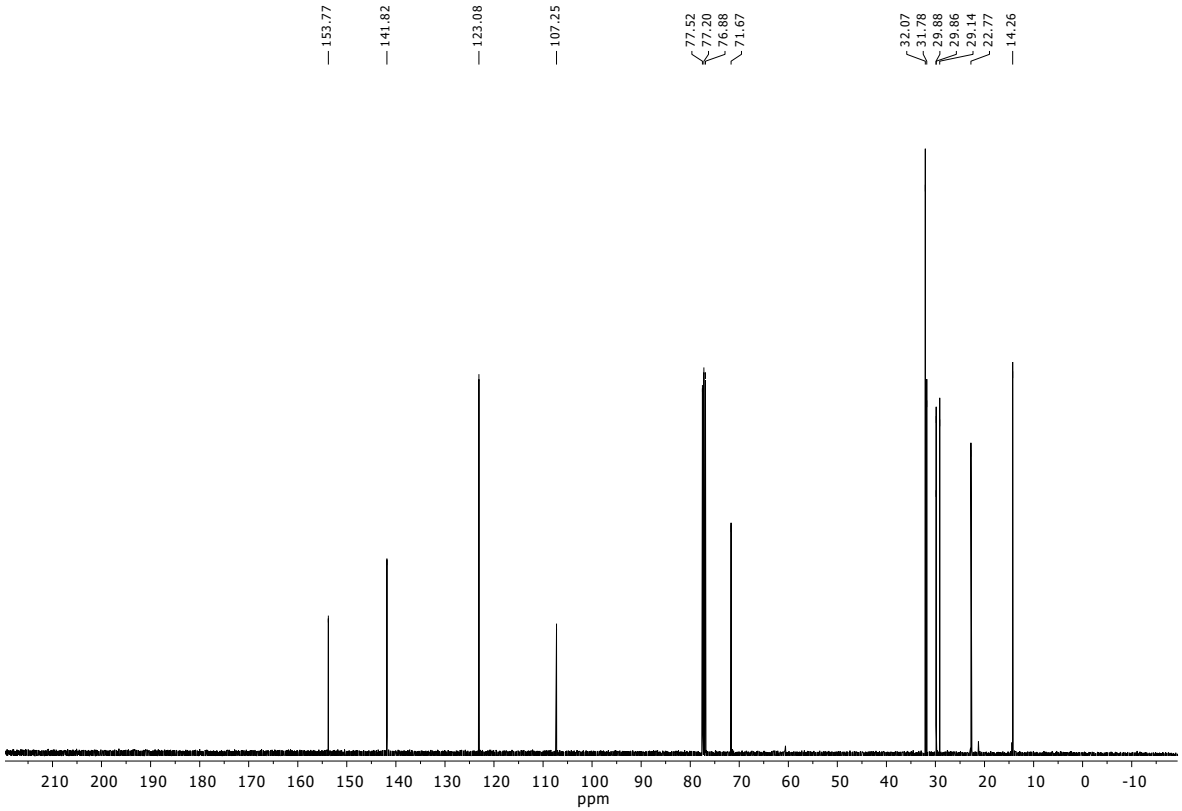


Figure S4 ^{13}C NMR of **2** in $CDCl_3$.

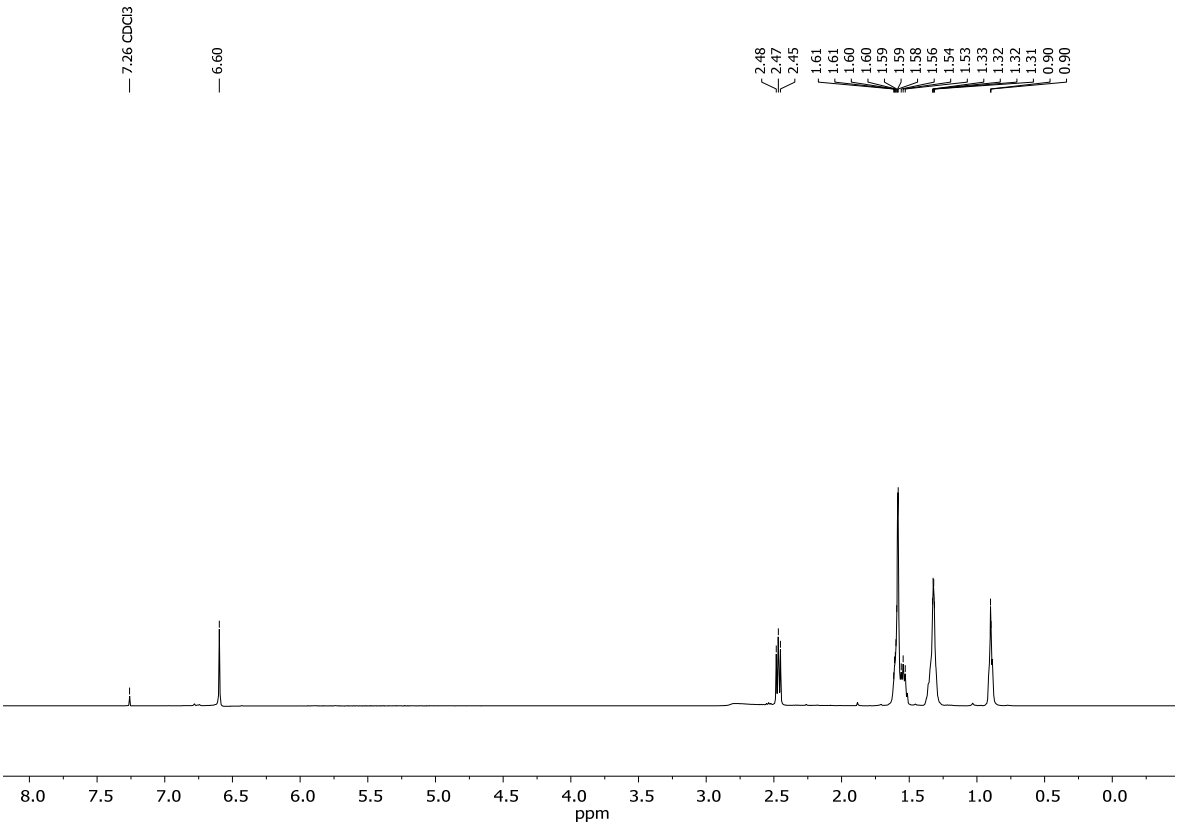


Figure S5 ^{1}H NMR of **2-I** in $CDCl_3$.

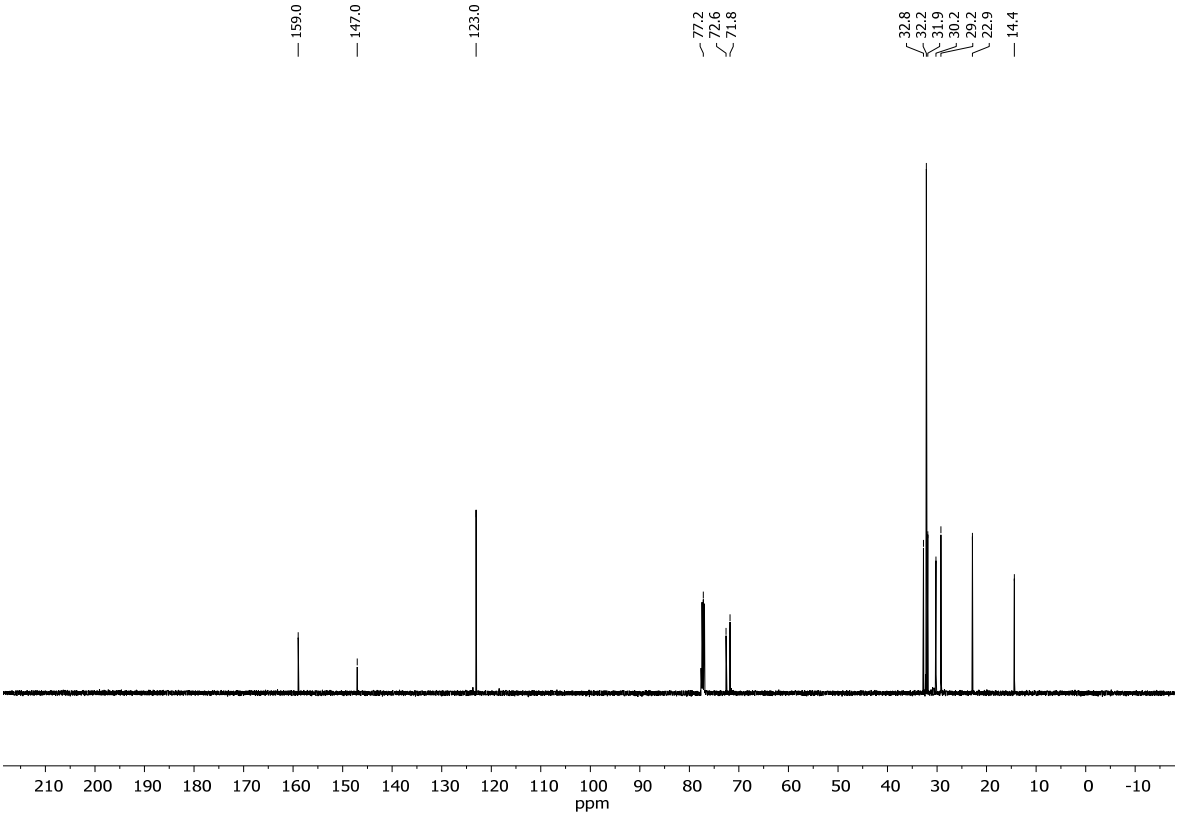


Figure S6 ^{13}C NMR of **2-I** in $CDCl_3$.

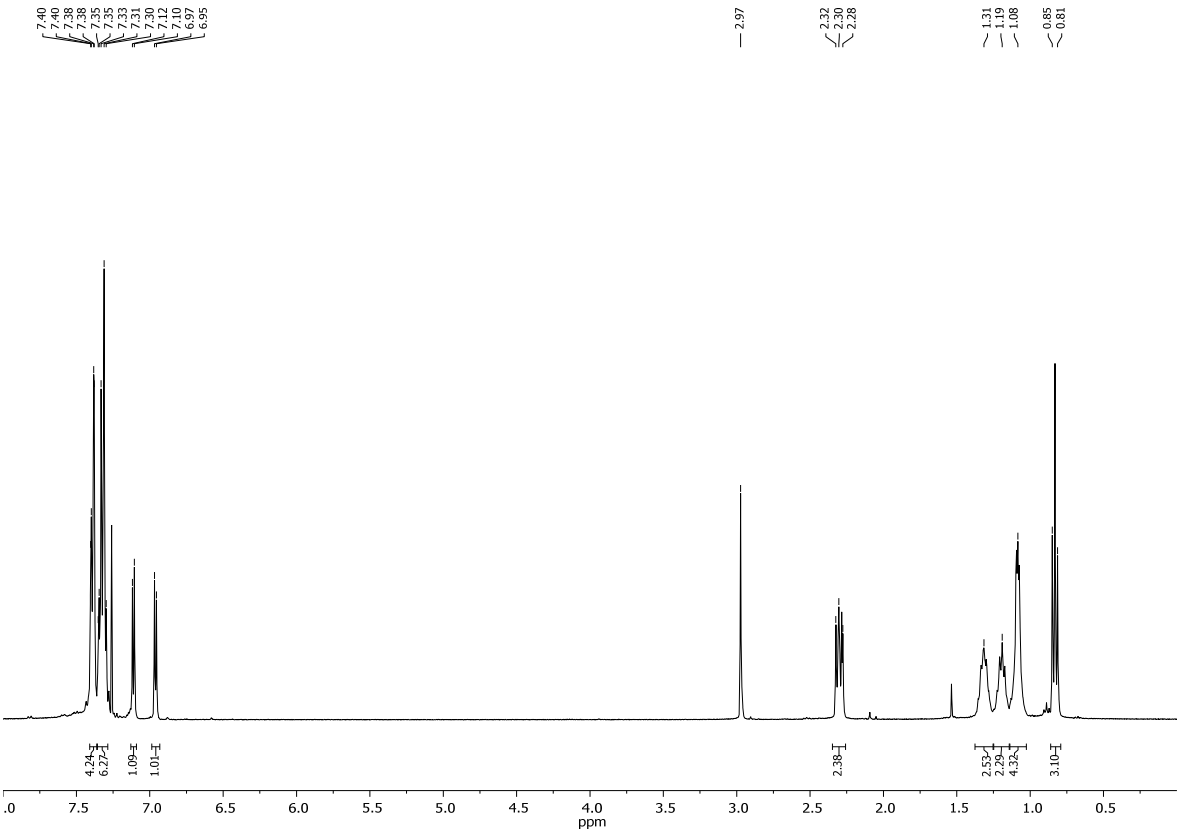


Figure S7 ^{1}H NMR of model diphenylcarbinol **4** in $CDCl_3$.

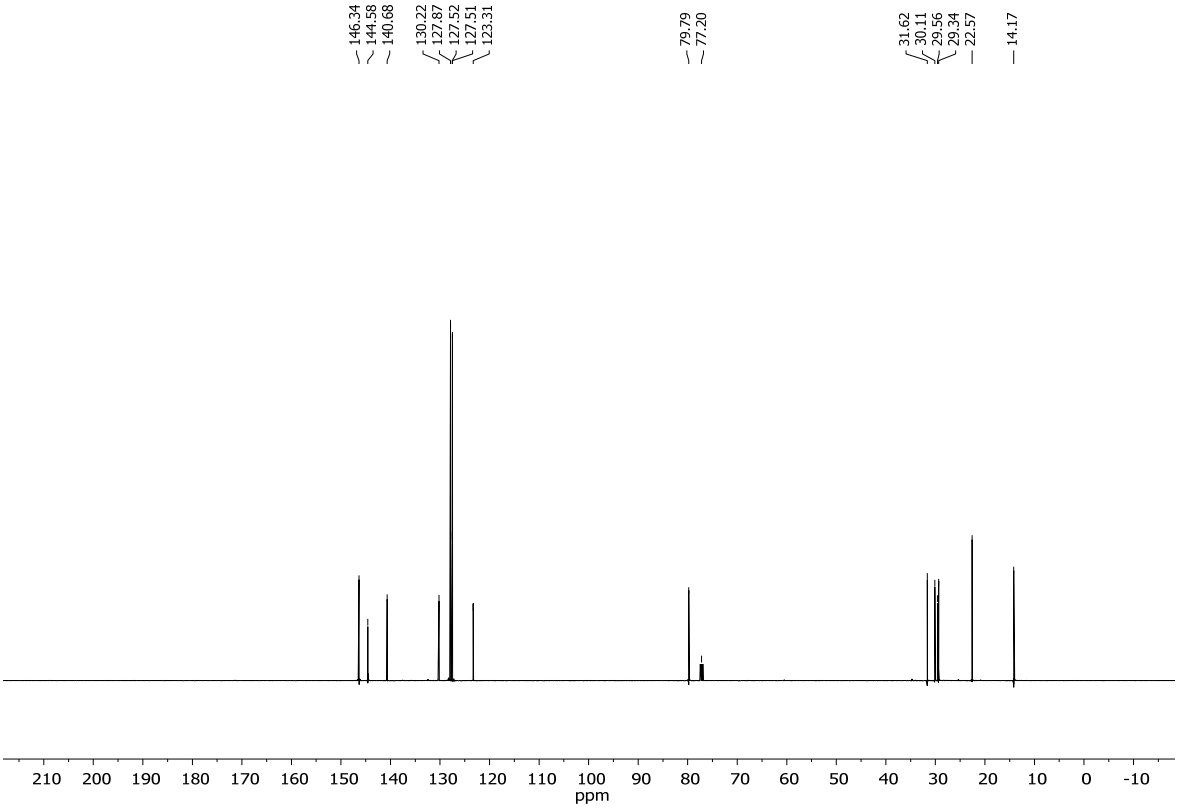


Figure S8^{13}C NMR of model diphenylcarbinol **4** in $CDCl_3$.

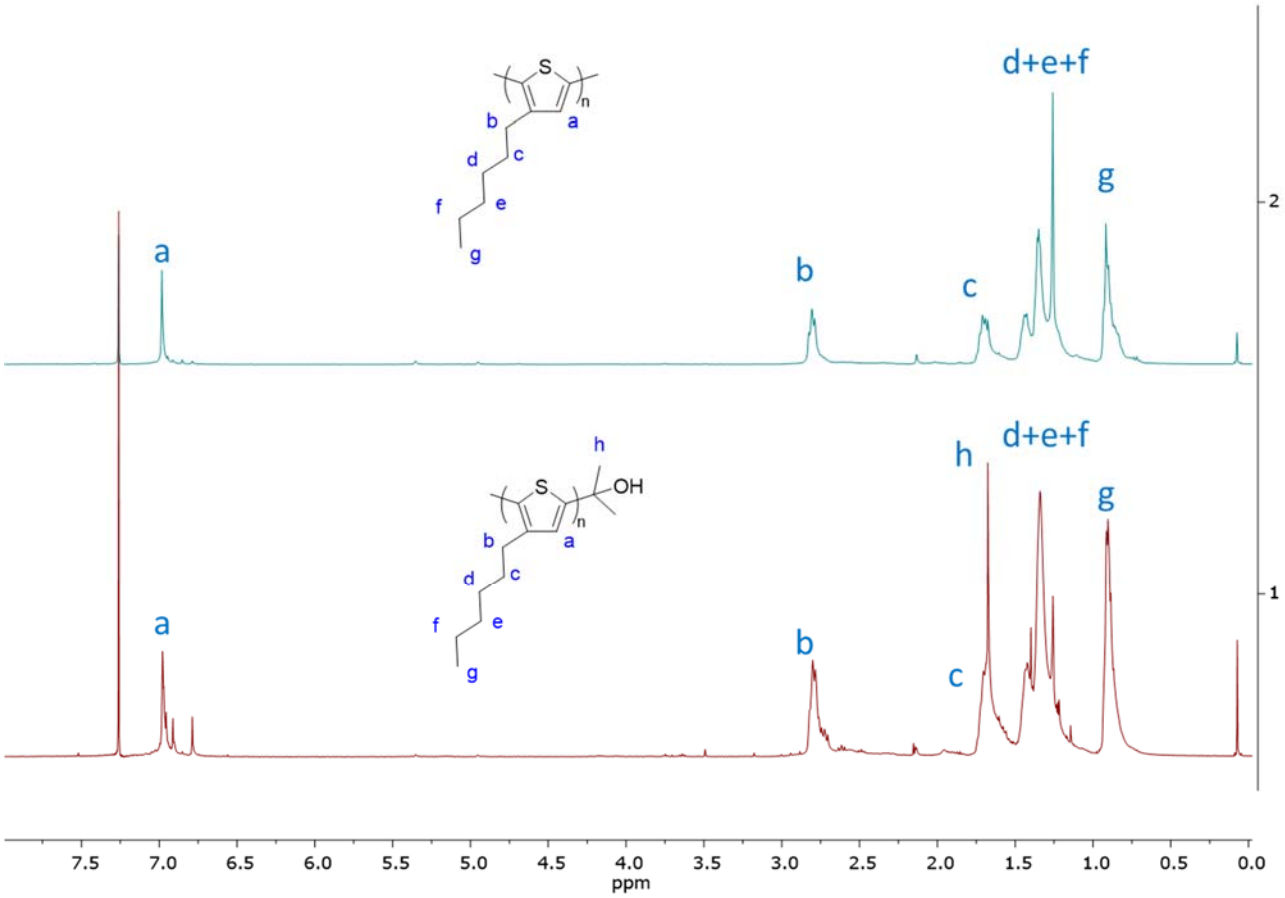


Figure S9. ^{1}H NMR spectra of chloroform-soluble (top) and hexanes-soluble (bottom) fractions of P3HT prepared from monomer **2** (Table S1, entry 1).

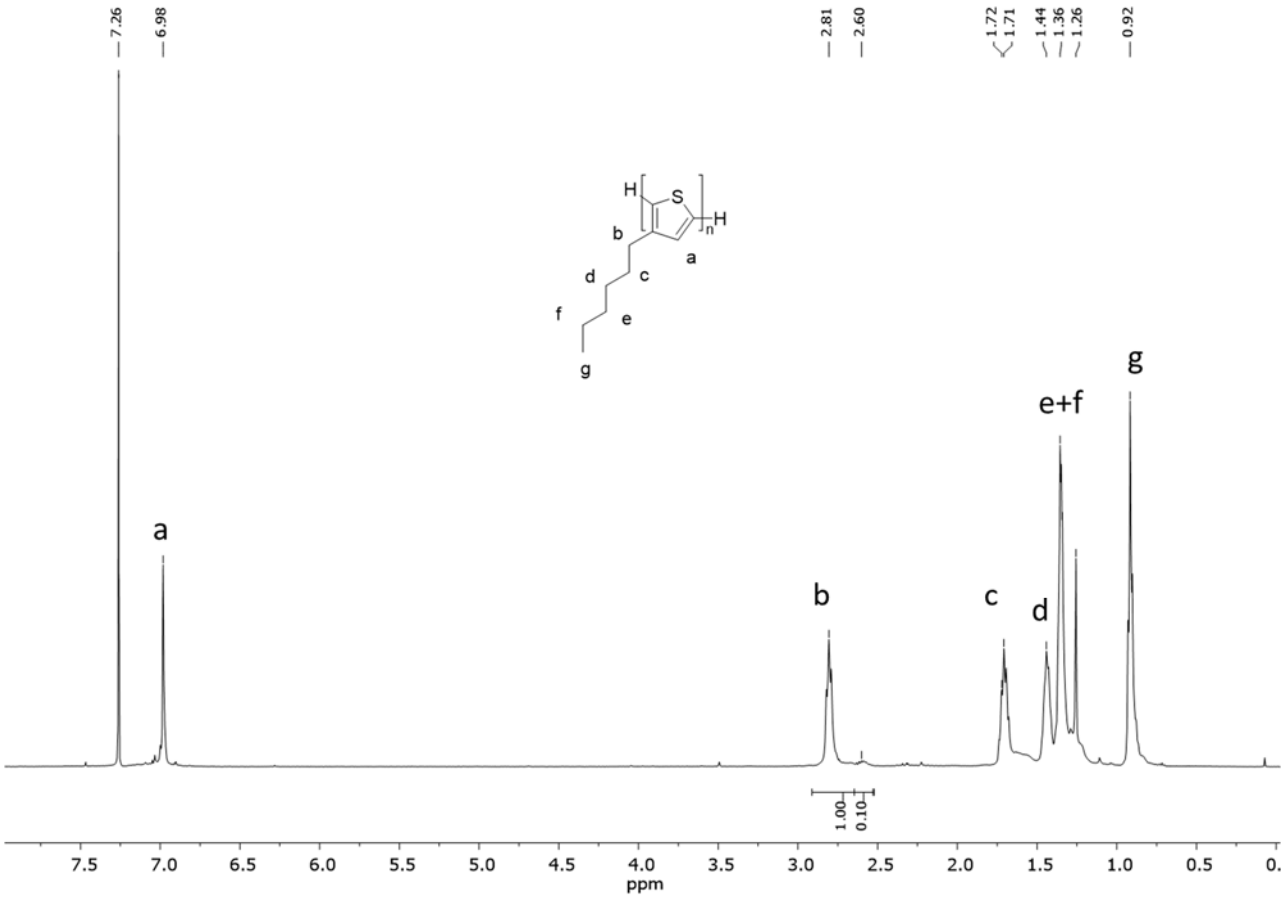


Figure S10 ^{1}H NMR of P3HT prepared by polymerization of monomer **1** (0.5 M) at 140 °C for 48 h (Table 2: entry 8).

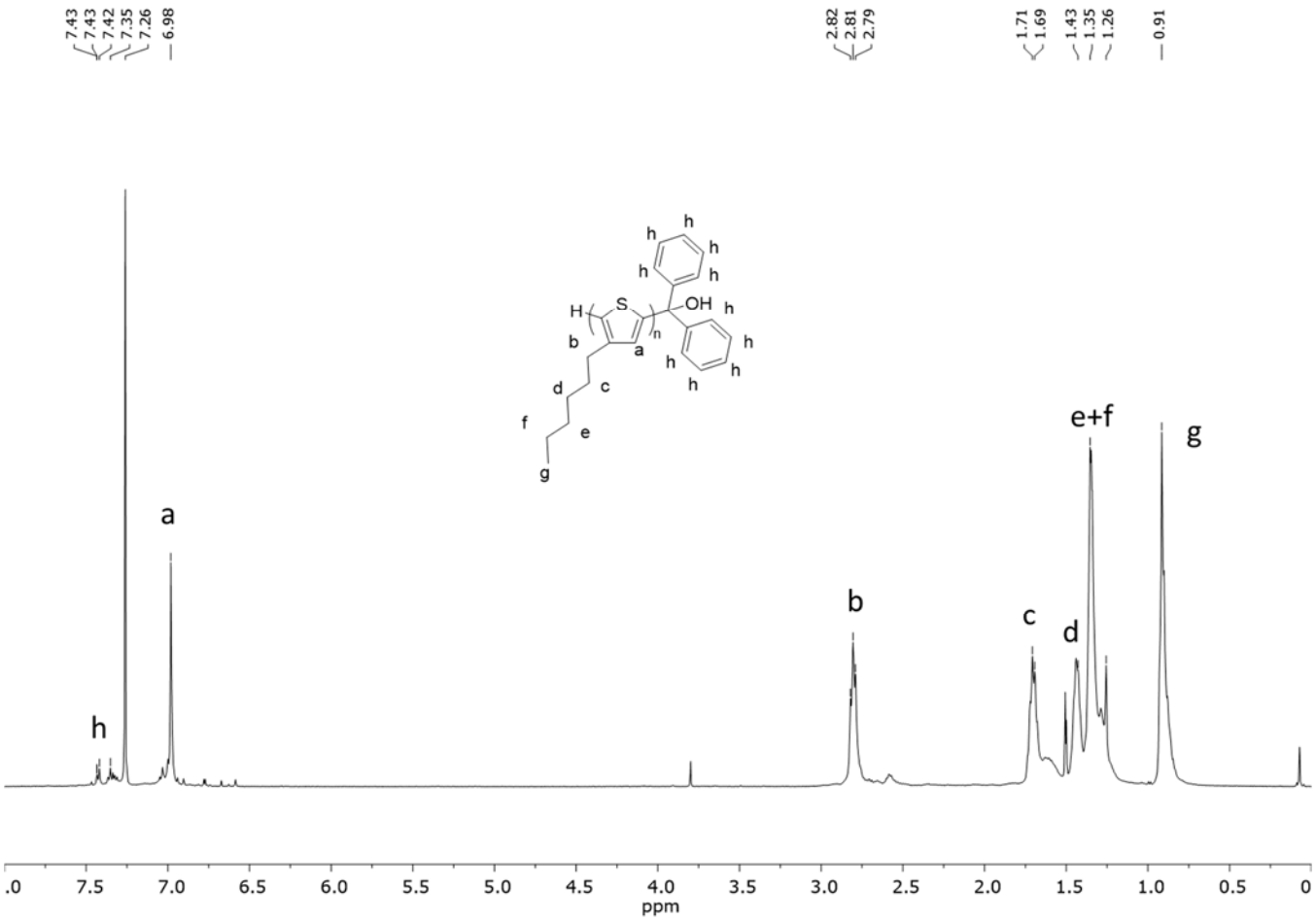


Figure S11. ^{1}H NMR of P3HT prepared by polymerization of monomer **1** (0.1 M) at 100 °C for 48 h (Table 2: entry 5).

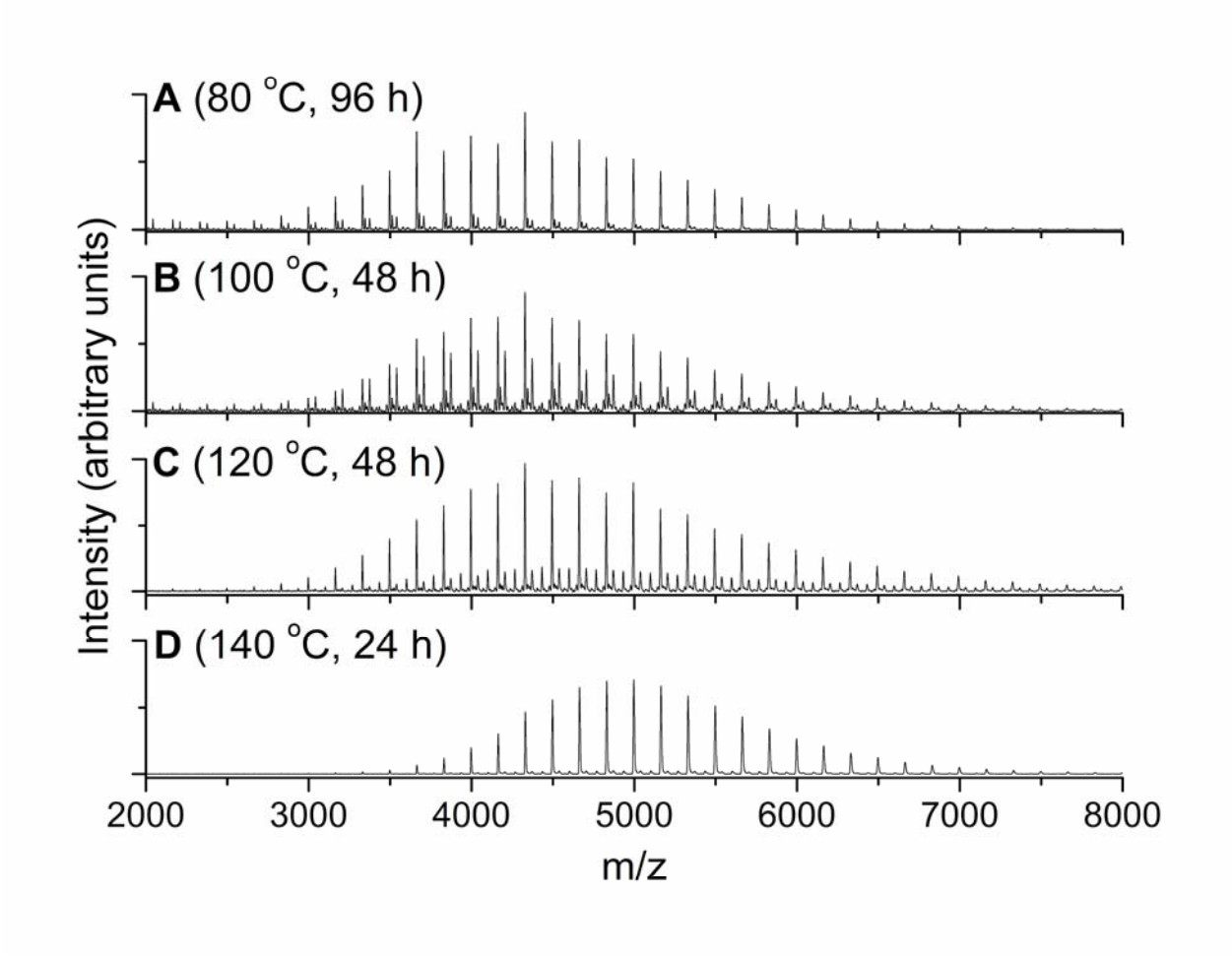


Figure S12. MALDI-TOF mass spectrograms of P3HT resulting from *ipso*-arylative polymerization of monomer **1** at A) 80 °C for 4 days (Table 2, entry 6), B) 100 °C for 2 days (Table 2, entry 5), C) 120 °C for 2 days (Table 2, entry 4), D) 140 °C for 1 day (Table 2, entry 2). Major peaks (M_{major}) at each temperature correspond to series with either H-/-H or H-/-$C(Ph)_2^+$ endgroups (Fig. 3). The end-groups that give rise to the most abundant minor series of peaks at lower temperatures (M_{major}+44) have not yet been identified. They do not match to expected masses for the expected Br-/-$C(Ph)_2OH$ or Br-/$C(Ph)_2OH$ endgroups or any other expected species. It is plausible that this series results from either enchainment of monomer through *ortho*-arylation, which would result in additional carbinol groups on each chain, or direct arylation of *ortho*-xylene, but further study will be necessary to identify these species. The second most abundant minor series (M_{major}+16) is likely to arise from either H-/-CPh_2OH or $Ph_2(HO)C$-/-CPh_2^+ end-groups.

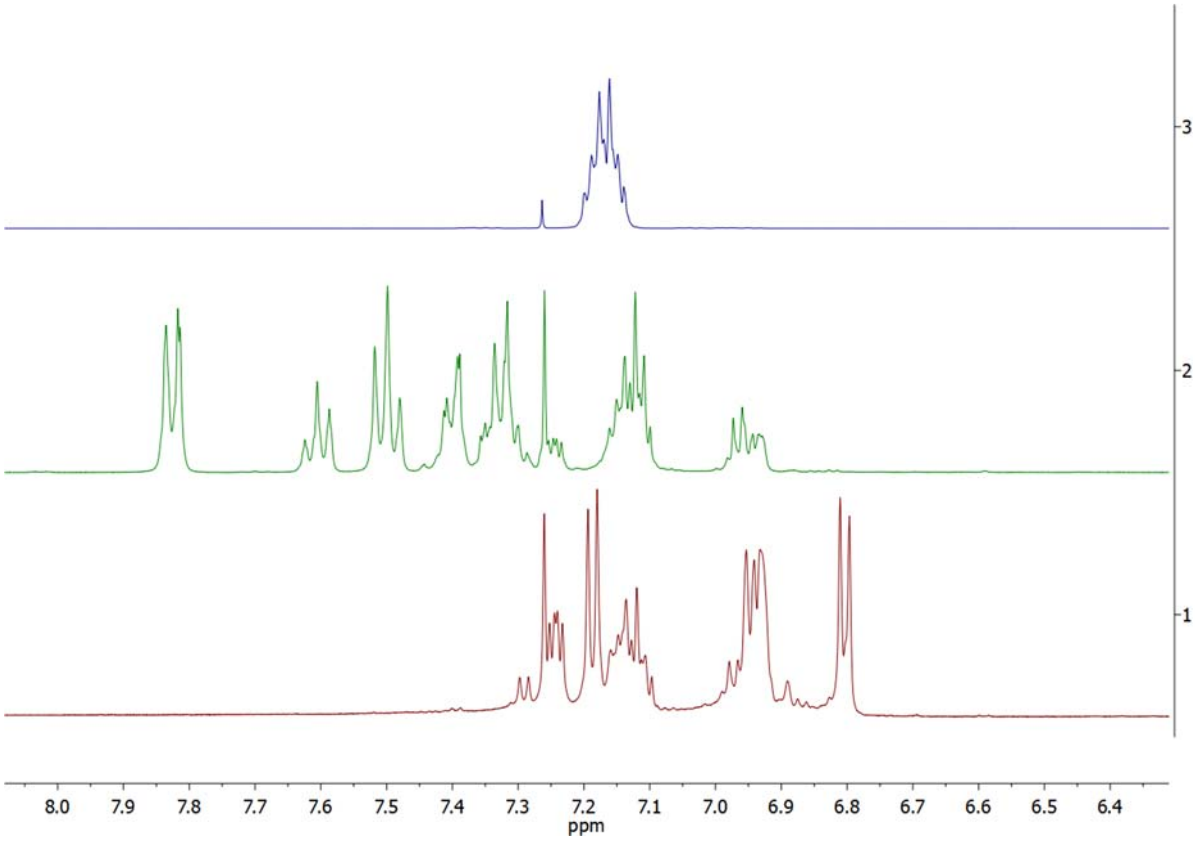


Figure S13. Comparison of ^{1}H NMR of *o*-xylene, reaction **B**, and reaction **C** (from top to bottom).

References

1. R. Tkachov, V. Senkovskyy, H. Komber and A. Kiriy, *Macromolecules*, 2011, **44**, 2006-2015, doi: 10.1021/ma102724y.
2. M. Iwasaki, Y. Araki, S. Iino and Y. Nishihara, *J. Org. Chem.*, 2015, **80**, 9247-9263, doi: 10.1021/acs.joc.5b01693.
3. Yoshito Terao, Hiroyuki Wakui, Tetsuya Satoh, Masahiro Miura and M. Nomura, *J. Am. Chem. Soc.*, 2001, **123**, 10407-10408, doi: 10.1021/ja016914i.