Electronic Supplementary Information

Tandem Kumada-Tamao catalyst-transfer condensation polymerization and Suzuki-Miyaura coupling for the synthesis of end-functionalized poly(3-hexylthiophene)

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Contents

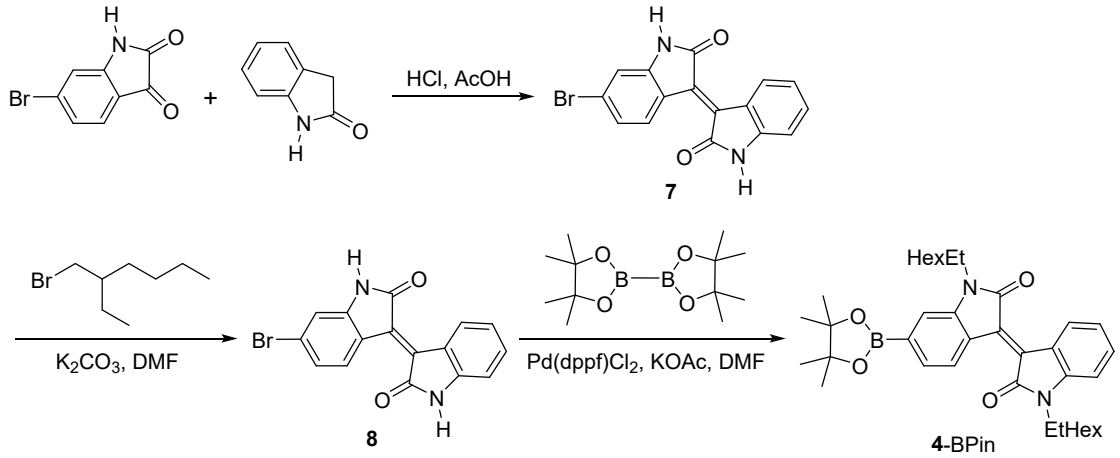
1. Materials

All starting materials were purchased from commercial suppliers (TCI, Aldrich, Wako and Kanto) and used without further purification. Commercially available dehydrated tetrahydrofuran (THF, stabilizer-free, Kanto) and dehydrated DMF (Kanto) were used as a dry solvent.

2. General

^{1}H and ^{13}C NMR spectra were obtained on ECA-600 spectrometer. The internal standard for ^{1}H NMR spectra in $CDCl_3$ was tetramethylsilane (0.00 ppm) and the internal standard for ^{13}C NMR spectra in $CDCl_3$ was the midpoint of $CDCl_3$ (77.0 ppm). IR spectra were recorded on a JASCO FT/IR-410. All melting points were measured with a Yanagimoto hot stage melting point apparatus without correction. Column chromatography was performed on silica gel (Kieselgel 60, 230–400 mesh, Merck) with a specified solvent. The M_n and M_w/M_n values of polymer were measured with a Tosoh HLC-8320 gel permeation chromatography unit (GPC; eluent, chloroform; calibration, polystyrene standards) with two TSK-gel columns (2 × Multipore HZ-M). MALDI-TOF mass spectra were recorded on a Shimadzu/Kratos AXIMA-CFR plus and Shimadzu AXIMA Confidence in the reflectron ion mode by use of a laser (λ = 337 nm). Dithranol (1,8-dihydroxy-9[10H]-anthracenone) and DCTB (trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile) were used as the matrix for the MALDI-TOF mass measurements.

3. Synthesis of 4-BPin



3-1. Synthesis of **7**

Into a schlenk flask was added 6-bromoisatin (2.71 g, 12.0 mmol), indolin-2-one (1.60 g, 12.0 mmol), acetic acid (70 mL), and conc. hydrochloric acid (0.5 mL), and then the mixture was stirred at 100 °C for 1 day. The mixture was filtered and the solid was washed with ethyl acetate, ethanol, and water. The solid was dried under reduced pressure to give 3.07 g of **7** as a dark red solid (75%): mp > 300 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 11.00 (s, 1 H), 10.90 (s, 1 H), 9.17-9.12 (m, 2 H), 7.40-7.37 (m, 1 H), 7.21-7.19 (m, 1 H), 7.13 (d, *J* = 12 Hz, 1 H), 7.01-6.93 (m, 2 H); IR (KBr) 1703, 1613, 1462, 1326, 1254, 1195, 1150, 1117, 1068, 875, 822, 799 cm^{-1}.

3-2. Synthesis of **8**

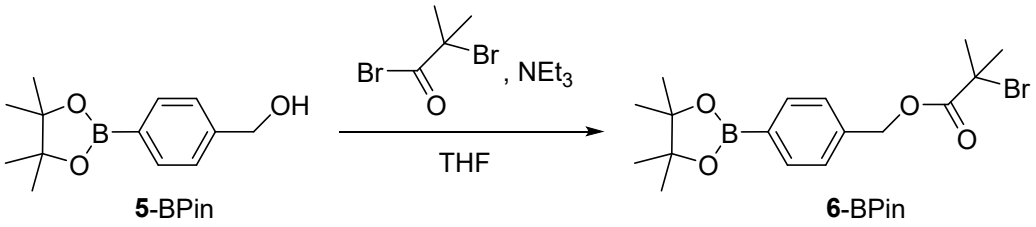
Into a schlenk flask was added **7** (2.73 g, 8.00 mmol) and potassium carbonate (6.63 g, 48.0 mmol), and then the atmosphere in the flask was replaced with argon. Into the solution was added dry DMF (36 mL) via a syringe under a stream of nitrogen, and the atmosphere in the flask was replaced with argon. 3-(Bromomethyl)heptane (4.2 mL, 24 mmol) was added, and the mixture was stirred at 100 °C for 1 day. Water was added, and the mixture was extracted with CH_2Cl_2. The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/CH_2Cl_2 = 2/1) to give 0.92 g of **8** as a red solid (20%): mp > 300 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.14 (d, *J* = 7.6 Hz, 1 H), 9.07 (d, *J* = 8.2 Hz, 1 H), 7.35 (t, *J* = 7.6 Hz, 1 H), 7.16 (dd, *J* = 8.2 and 2.1 Hz, 1 H), 7.03 (t, *J* = 8.2 Hz, 1 H), 6.90 (s, 1 H), 6.77 (d, *J* = 7.6 Hz, 1 H), 3.71-3.59 (m, 4 H), 1.86-1.83 (m, 2 H), 1.42-1.30 (m, 14 H), 0.95-0.87 (m, 12 H); ^{13}C NMR ($CDCl_3$, 151MHz) δ 168.3, 168.1, 146.1, 145.3, 134.0, 132.6, 130.9, 129.8, 126.3, 125.0, 122.3, 121.6, 120.5, 111.4, 108.3, 44.4, 44.3, 37.6, 37.4, 30.7, 30.6, 28.7, 28.6, 24.1, 24.0, 23.1, 14.0, 10.7, 10.6; IR (KBr) 1693, 1597, 1474, 1355, 1193, 1106, 1076, 870, 831, 816, 793 cm^{-1}.

3-3. Synthesis of **4**-BPin

All glass apparatus was dried prior to use. **8** (0.565 g, 1.66 mmol), potassium acetate (0.237 g, 2.41 mmol), [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) ($Pd(dppf)Cl_2$) (0.0351 g, 0.0480 mmol), and 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (0.279 g, 1.10 mmol) were placed in a flask, and the atmosphere in the flask was replaced with argon. Lyophilized DMF (20 mL) were added to the flask via a syringe under a stream of nitrogen, and the mixture was stirred at 95 °C for 1 day. The mixture was filtrated with Celite® 545, and the Celite® 545 was washed with CH_2Cl_2 . The filtrate was concentrated under reduced pressure. The residue was purified by

preparative HPLC (eluent: $CHCl_3$) to give 0.082 g of **4**-Bpin as a dark red viscous oil (13%): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 9.17 (d, *J* = 7.6 Hz, 1 H), 9.12 (d, *J* = 8.2 Hz, 1 H), 7.48 (d, *J* = 8.2 Hz, 1 H),7.34 (t, *J* = 8.2 Hz, 1 H), 7.17 (s, 1 H), 7.03 (t, *J* = 7.6 Hz, 1 H), 6.77 (d, *J* = 8.2 Hz, 1 H), 3.74-3.65 (m, 4 H), 1.91-1.86 (m, 2 H), 1.43-1.25 (m, 28 H), 0.94-0.87 (m, 12 H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 168.2, 145.3, 144.3, 134.3, 133.6, 132.5, 129.8, 128.5, 124.2, 122.1, 121.7, 133.5, 108.1, 84.0, 44.2, 44.1, 37.5, 37.4, 30.7, 30.6, 28.7, 28.6, 24.9, 24.8, 24.1, 23.0, 14.1, 14.0, 10.7; IR (neat) 2223, 1655, 1638, 1509, 1459, 1402, 1122, 854 cm^{-1}.

4. Synthesis of 6-BPin



5-BPin **6**-BPin

5-BPin (0.93 g, 4.0 mmol) was placed in a flask, and the atmosphere in the flask was replaced with argon. Dry THF (20 mL) and triethylamine (0.66 mL, 4.7 mmol) were added to the flask via a syringe under a stream of nitrogen, and the mixture was cooled to 0 °C. Into the solution was added dropwise 2-bromoisobutyryl bromide (0.48 ml, 3.9 mmol), and the mixture was stirred at 0 °C for 1.75 h. The mixture was filtrated with Kiriyama funnel, and the solid on the funnel was washed with THF. The filtrate was concentrated under reduced pressure. The residue was purified by means of distillation (220-230 °C, 0.03 mmHg), and then the product was stored in a cool dark place to give 1.39 g of **6**-BPin as a colorless solid (91%): mp 44.1-45.0 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.82 (d, *J* = 8.2 Hz, 2 H), 7.38 (d, *J* = 7.6 Hz, 2 H), 5.22 (s, 2 H), 1.95 (s, 6 H), 1.34 (s, 12 H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 171.4, 138.4, 135.0, 127.1, 83.9, 67.4, 30.8, 24.8; IR (KBr) 1732, 1616, 1520, 1463, 1362, 1275, 1163, 1091, 964, 859, 820 cm^{-1}.

5. General procedure for tandem Kumada-Tamao CTCP of 1 with Pd-PEPPSI-IPr and Suzuki-Miyaura end-functionalization with Ar-Bpin

5-1. $[\mathbf{1}]_0/[\ \mathbf{Pd\text{-}PEPPSI\text{-}IPr}]_0 = 10$

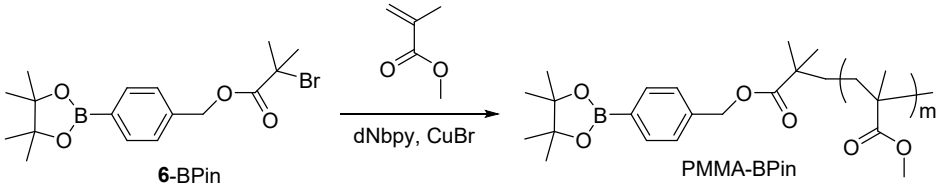
All glass apparatus was dried prior to use. Addition of reagents to a reaction flask and withdrawal of a small aliquot of the reaction mixture for analysis were carried out via a syringe from a three-way stopcock under a stream of nitrogen. A round-bottomed flask

equipped with a three-way stopcock was heated under reduced pressure, and then cooled to room temperature under an argon atmosphere. A solution of 2-bromo-3-hexyl-5-iodothiophene (0.42 mmol) in dry THF (2.5 mL) was added via a syringe and stirred at 0 °C. Isopropylmagnesium chloride (2.1 M solution in THF, 0.42 mmol) was added via a syringe, and the mixture was stirred at room temperature for 2 h. A solution of Pd-PEPPSI-IPr (0.042 mmol) in dry THF (0.7 mL) was added via a syringe, and the mixture was stirred at room temperature for 3 h. Ar-BPin (0.13 mmol) and K_3PO_4 (0.50 mmol) were placed in another flask, and the atmosphere in the flask was replaced with argon. Dry THF (9.2 mL) and distilled water (0.6 mL) were added to the flask via a syringe, and the mixture was degassed with argon. The mixture of Ar-BPin and K_3PO_4 in dry THF and distilled water was added to the above reaction mixture via a cannula, and the reaction mixture was stirred at room temperature for 24 h. The reaction was quenched with 6 M hydrochloric acid, and the mixture was extracted with $CHCl_3$. The organic layers were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to give polymer.

5-2. $[\mathbf{1}]_0/[\text{ Pd-PEPPSI-IPr}]_0 = 42$

All glass apparatus was dried prior to use. Addition of reagents to a reaction flask and withdrawal of a small aliquot of the reaction mixture for analysis were carried out via a syringe from a three-way stopcock under a stream of nitrogen. A round-bottomed flask equipped with a three-way stopcock was heated under reduced pressure, and then cooled to room temperature under an argon atmosphere. A solution of 2-bromo-3-hexyl-5-iodothiophene (0.235g, 0.63 mmol) in dry THF (4.2 mL) was added via a syringe and stirred at 0 °C. Isopropylmagnesium chloride (2.1 M solution in THF, 0.3mL, 0.63 mmol) was added via a syringe, and the mixture was stirred at room temperature for 2 h. A solution of Pd-PEPPSI-IPr (0.0103g, 0.015 mmol) in dry THF (1.5 mL) was added via a syringe, and the mixture was stirred at room temperature for 3 h. 4-(Trifluoromethyl)phenylboronic acid pinacol ester (0.0087g, 0.32 mmol) and K_3PO_4 (0.0265g, 0.125 mmol) were placed in another flask, and the atmosphere in the flask was replaced with argon. Dry THF (3.4 mL) and distilled water (0.05 mL) were added to the flask via a syringe, and the mixture was degassed with argon. The reaction mixture (1.0 mL) was added to the above mixture of 4-(trifluoromethyl)phenylboronic acid pinacol ester and K_3PO_4 in dry THF and distilled water via a syringe, and the reaction mixture was stirred at room temperature for 24 h. The reaction was quenched with 6 M hydrochloric acid, and the mixture was extracted with $CHCl_3$. The organic layers were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to give polymer. 0.0109g of polymer as a dark purple solid (62%).

6. Synthesis of PMMA-BPin



6-BPin PMMA-BPin

Methyl methacrylate (MMA) (3.0 mL, 28 mmol), **6**-BPin (0.0958 g, 0.250 mmol), 4,4′-dinonyl-2,2′-dipyridyl (dNbpy) (0.207 g, 0.507 mmol), and anisole (3.0 mL) were placed in a glass tube. The mixture was deoxygenated by three freeze-pump-thaw cycles, and the flask was backfilled with nitrogen. CuBr (0.0359 g, 0.250 mmol) was then added to the frozen solution. The mixture was deoxygenated by additional three freeze-pump-thaw cycles and stirred at 90 °C for 2.6 h. The polymerization was terminated by placing the flask in an ice bath and exposing the contents to air. The resulting mixture was diluted with THF and passed through a neutral aluminum oxide column to remove the copper catalyst. The mixture was precipitated into methanol, and insoluble polymer was collected and dried in a desiccator to give 0.792 g of PMMA-BPin as a colorless solid (27%, M_n = 7650, M_w/M_n = 1.21, DP based on ^{1}H NMR spectrum = 82).

7. Synthesis of PMMA-*b*-P3HT-*b*-PMMA

All glass apparatus was dried prior to use. Addition of reagents to a reaction flask and withdrawal of a small aliquot of the reaction mixture for analysis were carried out via a syringe from a three-way stopcock under a stream of nitrogen. A round-bottomed flask equipped with a three-way stopcock was heated under reduced pressure, and then cooled to room temperature under an argon atmosphere. A solution of 2-bromo-3-hexyl-5-iodothiophene (0.313 g, 0.84 mmol) in dry THF (5.6 mL) was added via a syringe and stirred at 0 °C. Isopropylmagnesium chloride (2.1 M solution in THF, 0.4 mL, 0.84 mmol) was added via a syringe, and the mixture was stirred at room temperature for 0.5 h. A solution of Pd-PEPPSI-IPr (0.0570g, 0.084 mmol) in dry THF (2.0 mL) was added via a syringe, and the mixture was stirred at room temperature for 2.25 h. PMMA-BPin (0.260 g, 0.0340 mmol) and 2.5 M K_3PO_4 (0.1mL, 0.25 mmol) were placed in another flask, and the atmosphere in the flask was replaced with argon. Dry THF (1.4 mL) was added to the flask via a syringe, and the mixture was degassed with argon. Into the mixture of PMMA-BPin and aq. K_3PO_4 in THF was added the above reaction mixture (1.0 mL, 0.0105 mmol of P3HT), via a syringe, and the reaction mixture was stirred at room temperature for

41.25 h. The reaction was quenched with 6 M hydrochloric acid, and the mixture was extracted with $CHCl_3$. The organic layers were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was dissolved with a small amount of $CHCl_3$ and precipitated into diethyl ether to afford 0.0962 g (49%) of the block copolymer.

8. Supporting Tables

Table S1. Effects of H_2O and 18-crown-6 on Suzuki-Miyaura end-functionalization of P3HT with **2**-BPin[a]

entry	base (equiv. to **2**-BPin)	H_2O/THF (= v/v)	end-groups[b]
1	K_3PO_4/18-crown-6 (4.0/12.0)	0.07	**2**/**2** > **2**/H > H/Br
2	K_3PO_4/18-crown-6 (4.0/12.0)	0.04	**2**/**2** > **2**/H > H/Br
3	K_3PO_4/18-crown-6 (4.0/12.0)	0.02	**2**/**2** > **2**/H > H/Br
4	K_3PO_4/18-crown-6 (4.0/8.0)	0.07	**2**/**2** > **2**/H
5	K_3PO_4/18-crown-6 (4.0/8.0)	0.04	**2**/**2** > **2**/H
6	K_3PO_4/18-crown-6 (4.0/8.0)	0.02	**2**/**2** > **2**/H
7	K_3PO_4 (4.0)	0.07	**2**/**2**
8	K_3PO_4 (4.0)	0.04	**2**/**2**
9	K_3PO_4 (4.0)	0.02	**2**/**2**

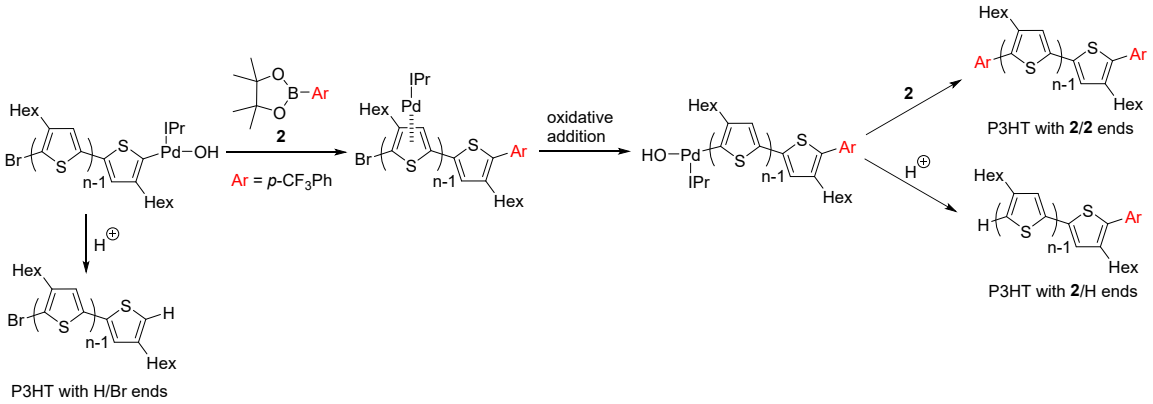
[a] Kumada-Tamao CTCP of **1** with Pd-PEPPSI-IPr ($[\mathbf{1}]_0/[\text{Pd-PEPPSI-IPr}]_0$ = 10) was carried out in THF at rt for 2 h, followed by addition of a solution of 30 mol% of **2**-BPin and K_3PO_4/18-crown-6 in THF ($[\mathbf{2}\text{-BPin}]_0$ = 0.014 mol/L) and H_2O and stirring for 24 h. [b]Determined by MALDI-TOF mass spectrometry.

Table S2. Effects of catalyst on Suzuki-Miyaura end-functionalization of P3HT with **2**-BPin[a]

entry	catalyst	end-groups[b]
1	$Ni(dppp)Cl_2$	H/Br > H/H > **2**/H
2	$Ni(dppe)Cl_2$	H/Br
3	$Ni(depe)Cl_2$	H/Br
4	$Ni(IPr)PPh_3Cl_2$	H/Br > **2**/**2** > **2**/H > H/H

[a]Kumada-Tamao CTCP of **1** with catalyst ($[\mathbf{1}]_0/[\text{catalyst}]_0$ = 10) was carried out in THF at rt for 2 h, followed by addition of a solution of 30 mol% of **2**-BPin and K_3PO_4 (4 equiv to **2**-BPin) in THF ($[\mathbf{2}\text{-BPin}]_0$ = 0.014 mol/L) and H_2O (H_2O/THF = 0.07, v/v) and stirring for 24 h. [b]Determined by MALDI-TOF mass spectrometry.

9. Supporting scheme



Scheme S1. Proposed mechanism for the formation of P3HT with H/Br, **2**/**2**, and **2**/H ends.

10. MALDI-TOF mass spectra

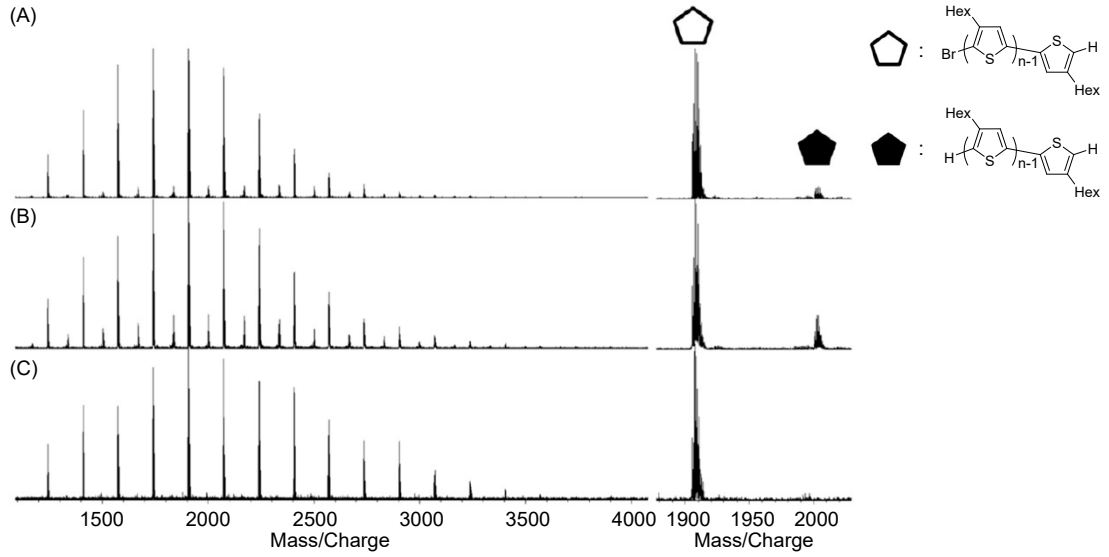


Fig S1. MALDI-TOF mass spectra of P3HT obtained by (A) Kumada-Tamao CTCP of **1** with 10 mol% of Ni(dppp)Cl_2 at room temperature and Suzuki-Miyaura end-functionalization of P3HT with **2**-BPin in the presence of CsF/18-crown-6 in H_2O/THF (= 0.07, v/v) at room temperature for (B) 3 h and (C) 24 h (Table 1, entry 1).

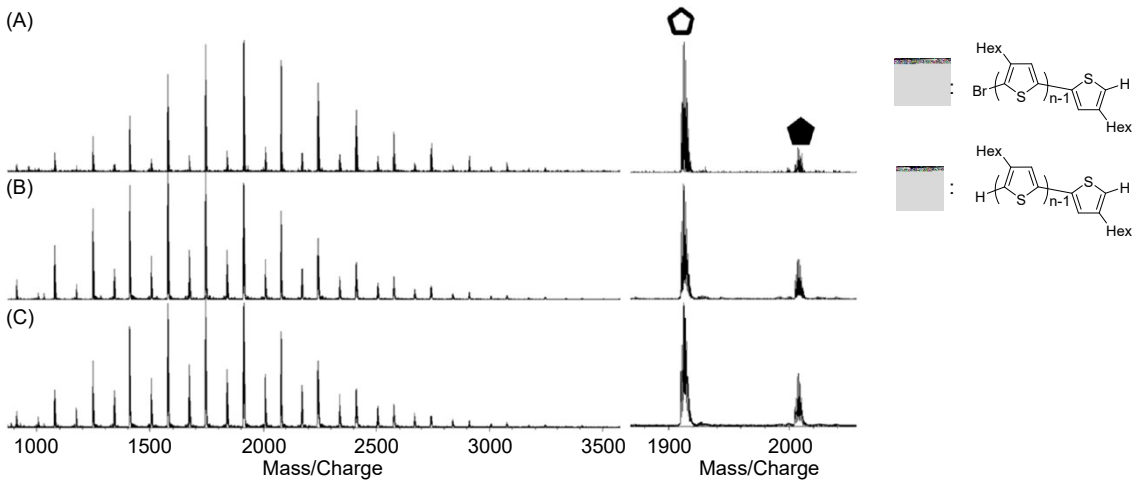


Fig S2. MALDI-TOF mass spectra of P3HT obtained by (A) Kumada-Tamao CTCP of **1** with 10 mol% of Ni(dppp)Cl_2 at room temperature and Suzuki-Miyaura end-functionalization of P3HT with **2**-BPin in the presence of KOH/18-crown-6 in H_2O/THF (= 0.07, v/v) at room temperature for (B) 3 h and (C) 24 h (Table 1, entry 2).

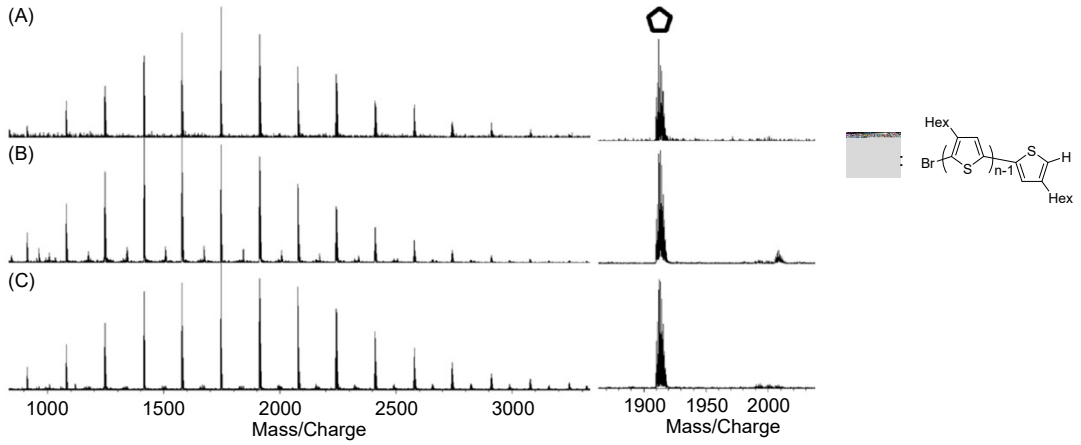


Fig S3. MALDI-TOF mass spectra of P3HT obtained by (A) Kumada-Tamao CTCP of **1** with 10 mol% of Ni(dppp)Cl_2 at room temperature and Suzuki-Miyaura end-functionalization of P3HT with **2**-BPin in the presence of K_3PO_4/18-crown-6 in H_2O/THF (= 0.07, v/v) at room temperature for (B) 3 h and (C) 24 h (Table 1, entry 3).

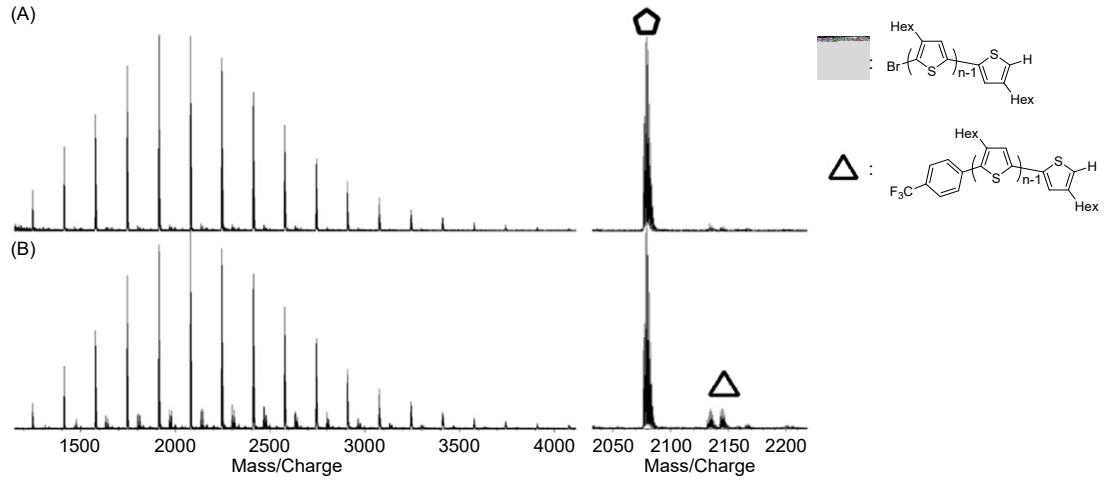


Fig S4. MALDI-TOF mass spectra of P3HT obtained by (A) Kumada-Tamao CTCP of **1** with 10 mol% of Pd-PEPPSI-IPrNi(dppp)Cl_2 at room temperature and (B) Suzuki-Miyaura end-functionalization of P3HT with **2**-BPin in the presence of CsF/18-crown-6 in H_2O/THF (= 0.07, v/v) at room temperature for 24 h (Table 1, entry 4).

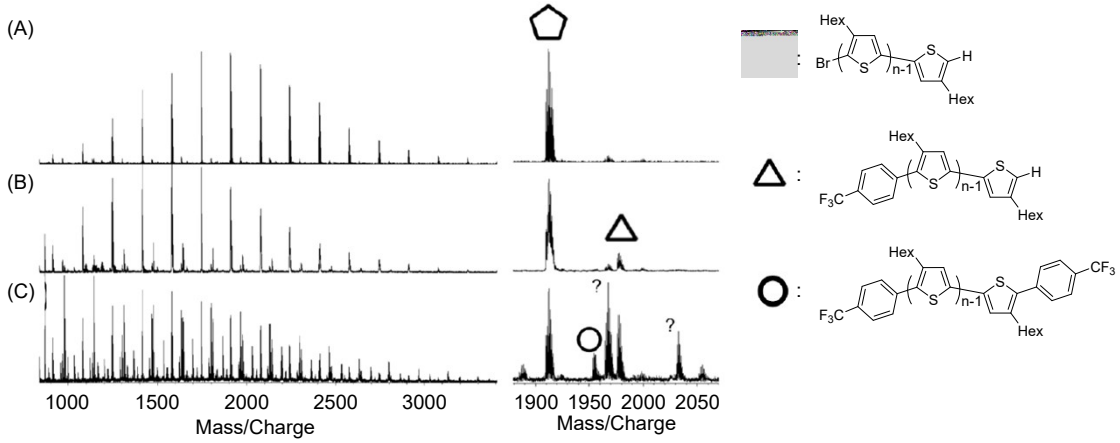


Fig S5. MALDI-TOF mass spectra of P3HT obtained by (A) Kumada-Tamao CTCP of **1** with 10 mol% of Pd-PEPPSI-IPr at room temperature and Suzuki-Miyaura end-functionalization of P3HT with **2**-BPin in the presence of KOH/18-crown-6 in H_2O/THF (= 0.07, v/v) at room temperature for (B) 3 h and (C) 24 h (Table 1, entry 5).

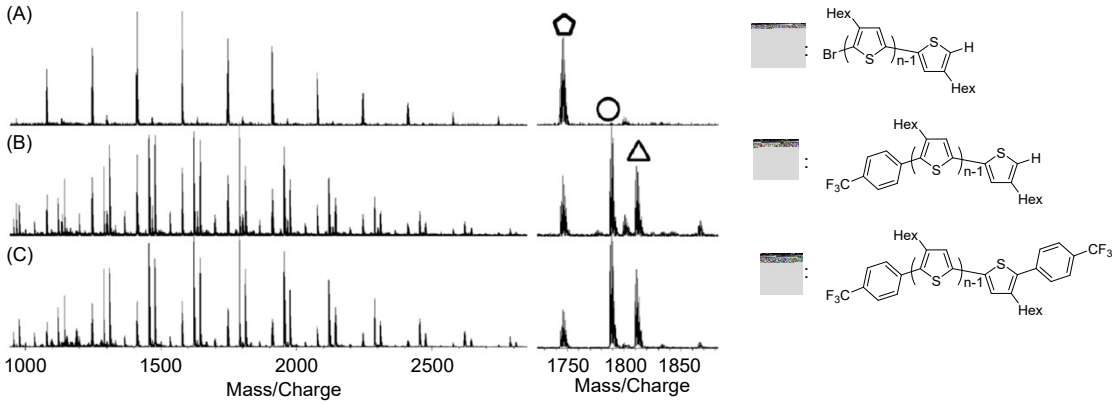


Fig S6. MALDI-TOF mass spectra of P3HT obtained by (A) Kumada-Tamao CTCP of **1** with 10 mol% of Pd-PEPPSI-IPr at room temperature and Suzuki-Miyaura end-functionalization of P3HT with **2**-BPin in the presence of K_3PO_4/18-crown-6 (4/12 equiv to **2**-BPin) in H_2O/THF (= 0.07, v/v) at room temperature for (B) 3 h and (C) 24 h (Table 1, entry 6).

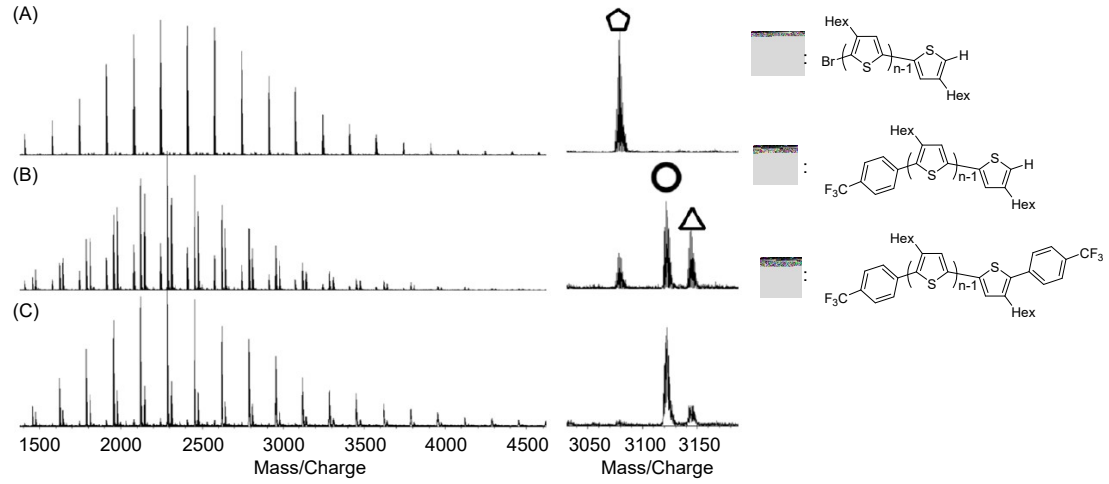


Fig S7. MALDI-TOF mass spectra of P3HT obtained by (A) Kumada-Tamao CTCP of **1** with 10 mol% of Pd-PEPPSI-IPr at room temperature and Suzuki-Miyaura end-functionalization of P3HT with **2**-BPin in the presence of K_3PO_4/18-crown-6 (4/8 equiv to **2**-BPin) in H_2O/THF (= 0.07, v/v) at room temperature for (B) 3 h and (C) 24 h (Table 1, entry 7, Table S1, entry 1).

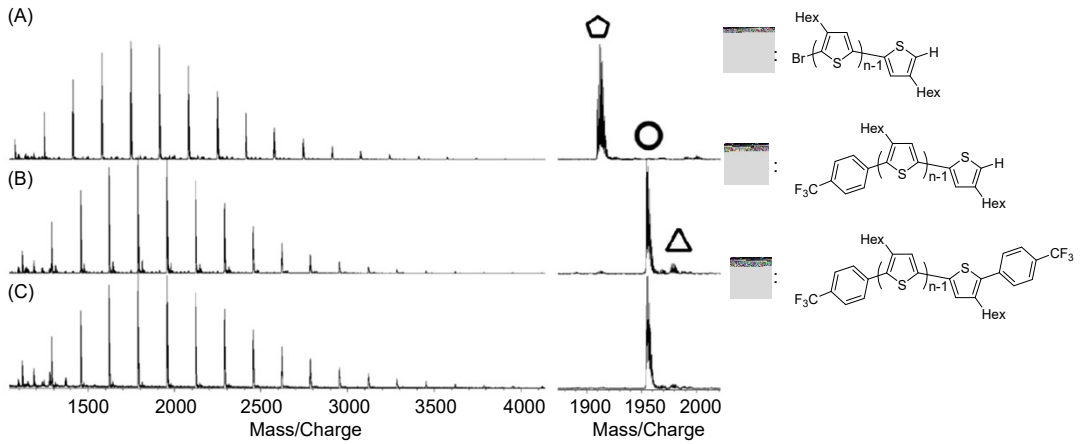


Fig S8. MALDI-TOF mass spectra of P3HT obtained by (A) Kumada-Tamao CTCP of **1** with 10 mol% of Pd-PEPPSI-IPr at room temperature and Suzuki-Miyaura end-functionalization of P3HT with **2**-BPin in the presence of K_3PO_4 (4 equiv to **2**-BPin) in H_2O/THF (= 0.07, v/v) at room temperature for (B) 3 h and (C) 24 h (Table 1, entry 8, Table S1, entry 7).

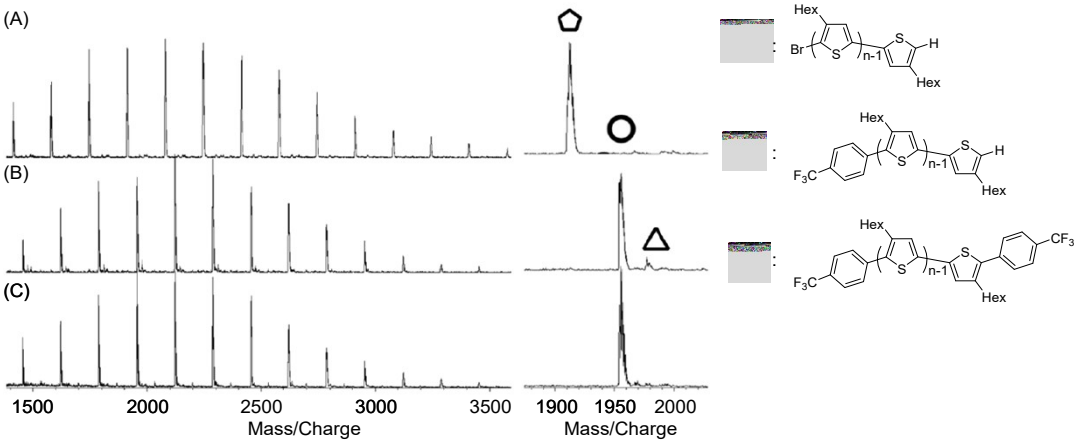


Fig S9. MALDI-TOF mass spectra of P3HT obtained by (A) Kumada-Tamao CTCP of **1** with 10 mol% of Pd-PEPPSI-IPr at room temperature and Suzuki-Miyaura end-functionalization of P3HT with **2**-BPin in the presence of K_3PO_4 (4 equiv to **2**-BPin) in H_2O/THF (= 0.04, v/v) at room temperature for (B) 3 h and (C) 24 h (Table 1, entry 9, Table S1, entry 8).

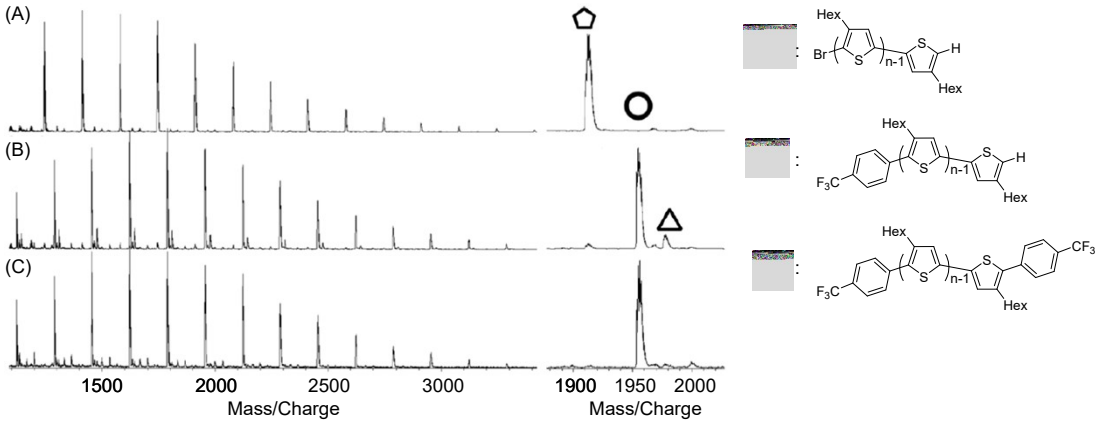


Fig S10. MALDI-TOF mass spectra of P3HT obtained by (A) Kumada-Tamao CTCP of **1** with 10 mol% of Pd-PEPPSI-IPr at room temperature and Suzuki-Miyaura end-functionalization of P3HT with **2**-BPin in the presence of K_3PO_4 (4 equiv to **2**-BPin) in H_2O/THF (= 0.02, v/v) at room temperature for (B) 3 h and (C) 24 h (Table 1, entry 10, Table S1, entry 9).

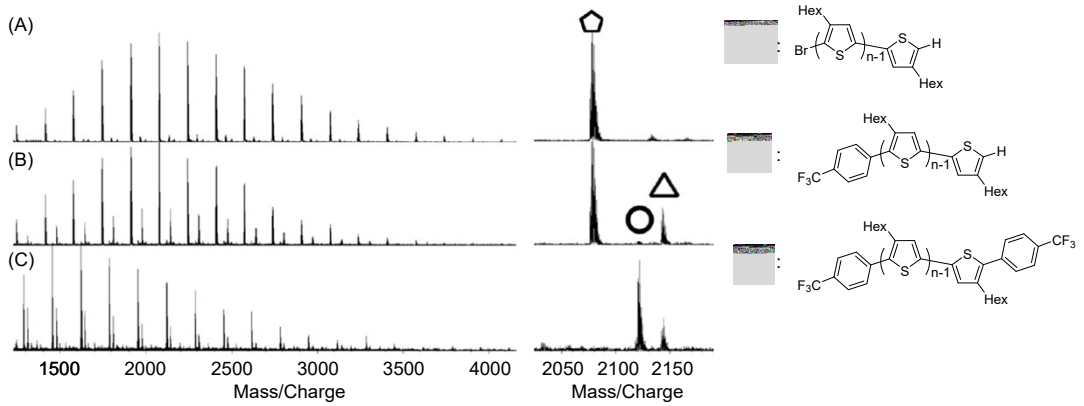


Fig S11. MALDI-TOF mass spectra of P3HT obtained by (A) Kumada-Tamao CTCP of **1** with 10 mol% of Pd-PEPPSI-IPr at room temperature and Suzuki-Miyaura end-functionalization of P3HT with **2**-BPin in the presence of K_3PO_4/18-crown-6 (4/12 equiv to **2**-BPin) in H_2O/THF (= 0.04, v/v) at room temperature for (B) 3 h and (C) 24 h (Table S1, entry 2).

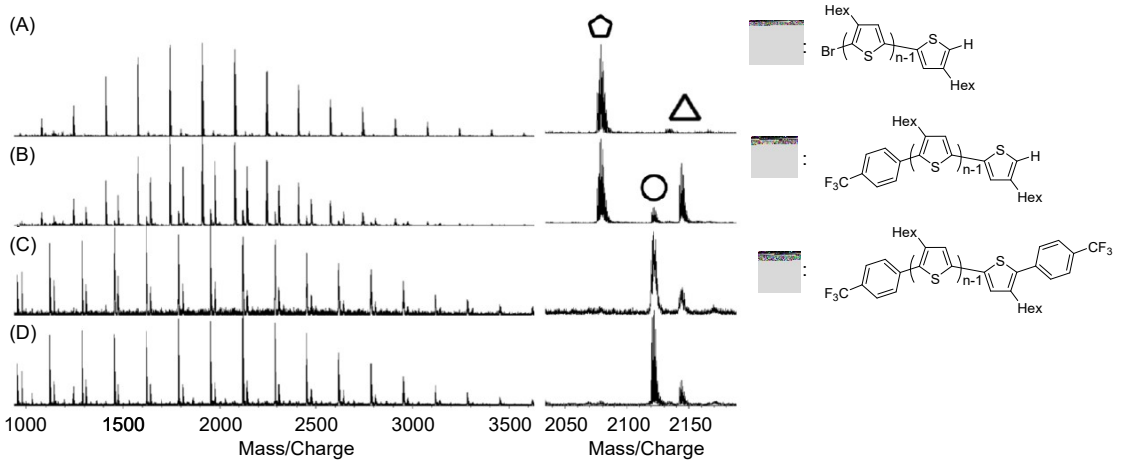


Fig S12. MALDI-TOF mass spectra of P3HT obtained by (A) Kumada-Tamao CTCP of **1** with 10 mol% of Pd-PEPPSI-IPr at room temperature and Suzuki-Miyaura end-functionalization of P3HT with **2**-BPin in the presence of K_3PO_4/18-crown-6 (4/12 equiv to **2**-BPin) in H_2O/THF (= 0.02, v/v) at room temperature for (B) 3 h, (C) 24 h (Table S1, entry 3), and (D) 40 h.

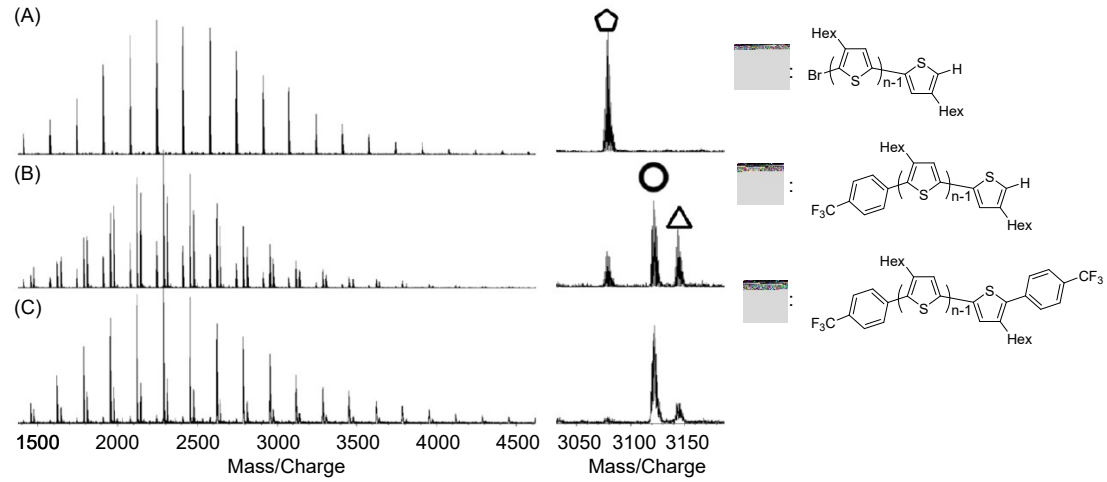


Fig S13. MALDI-TOF mass spectra of P3HT obtained by (A) Kumada-Tamao CTCP of **1** with 10 mol% of Pd-PEPPSI-IPr at room temperature and Suzuki-Miyaura end-functionalization of P3HT with **2**-BPin in the presence of K_3PO_4/18-crown-6 (4/8 equiv to **2**-BPin) in H_2O/THF (= 0.07, v/v) at room temperature for (B) 3 h and (C) 24 h (Table S1, entry 4).

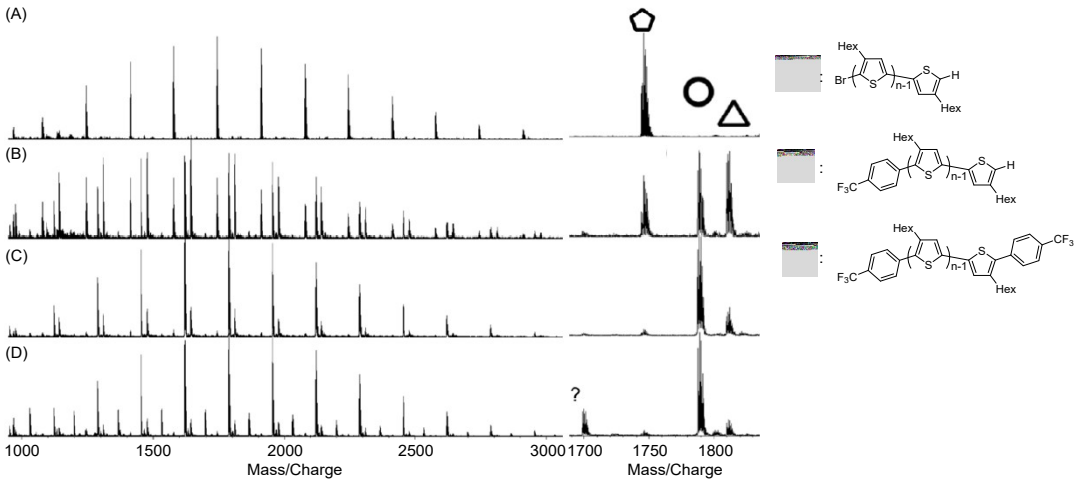


Fig S14. MALDI-TOF mass spectra of P3HT obtained by (A) Kumada-Tamao CTCP of **1** with 10 mol% of Pd-PEPPSI-IPr at room temperature and Suzuki-Miyaura end-functionalization of P3HT with **2**-BPin in the presence of K_3PO_4/18-crown-6 (4/8 equiv to **2**-BPin) in H_2O/THF (= 0.04, v/v) at room temperature for (B) 3 h, (C) 24 h (Table S1, entry 5), and (D) 118 h.

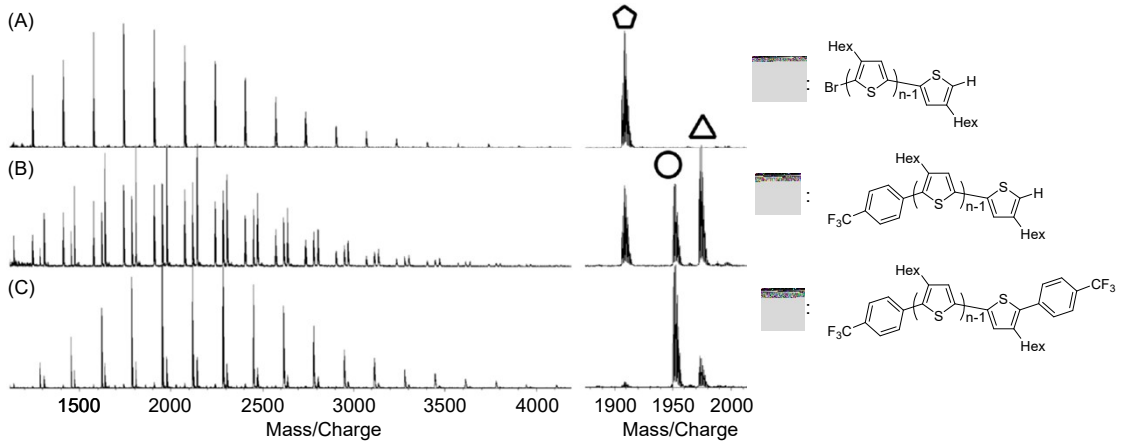


Fig S15. MALDI-TOF mass spectra of P3HT obtained by (A) Kumada-Tamao CTCP of **1** with 10 mol% of Pd-PEPPSI-IPr at room temperature and Suzuki-Miyaura end-functionalization of P3HT with **2**-BPin in the presence of K_3PO_4/18-crown-6 (4/8 equiv to **2**-BPin) in H_2O/THF (= 0.02, v/v) at room temperature for (B) 3 h and (C) 24 h (Table S1, entry 6).

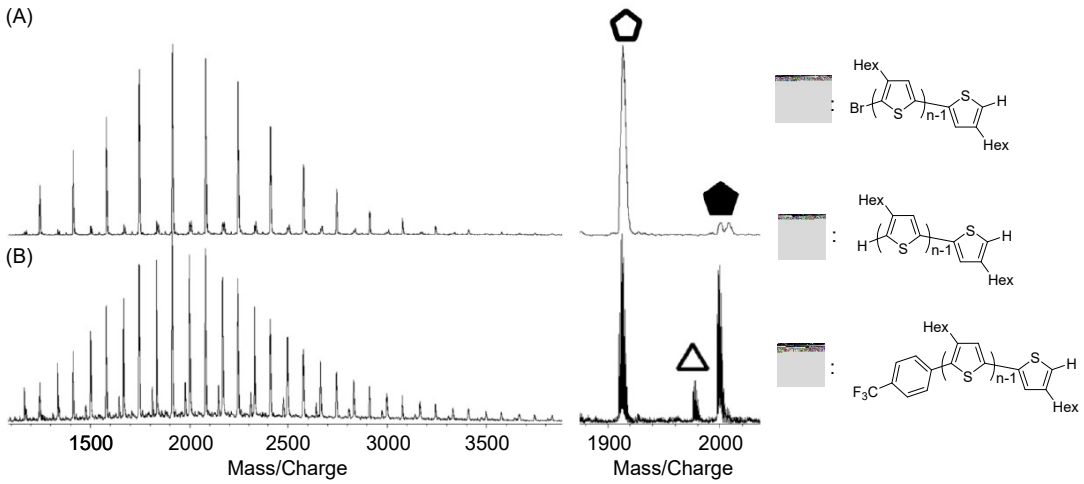


Fig S16. MALDI-TOF mass spectra of P3HT obtained by (A) Kumada-Tamao CTCP of **1** with 10 mol% of Ni(dppp)Cl_2 at room temperature and (B) Suzuki-Miyaura end-functionalization of P3HT with **2**-BPin in the presence of K_3PO_4 (4 equiv to **2**-BPin) in H_2O/THF (= 0.07, v/v) at room temperature for 24 h (Table S2, entry 1).

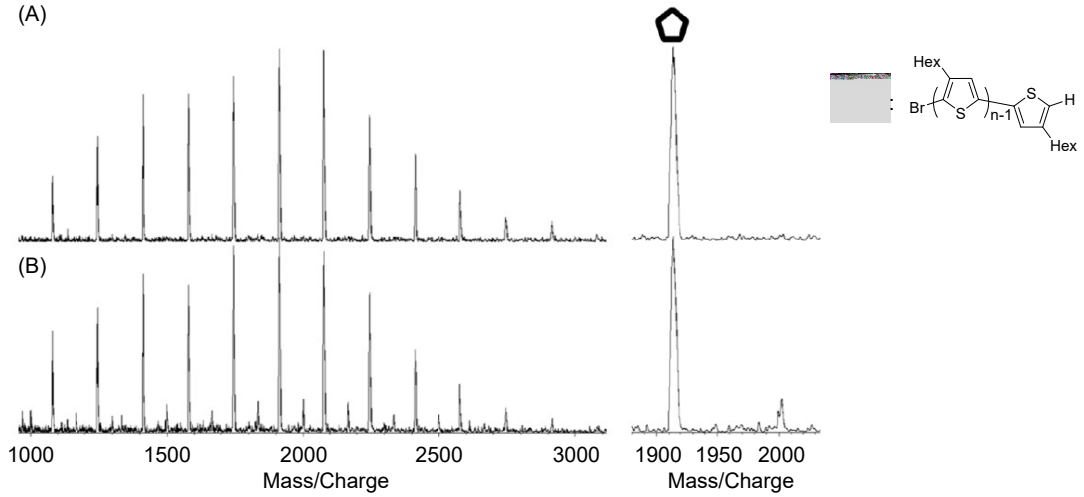


Fig S17. MALDI-TOF mass spectra of P3HT obtained by (A) Kumada-Tamao CTCP of **1** with 10 mol% of Ni(dppe)Cl_2 at room temperature and (B) Suzuki-Miyaura end-functionalization of P3HT with **2**-BPin in the presence of K_3PO_4 (4 equiv to **2**-BPin) in H_2O/THF (= 0.07, v/v) at room temperature for 24 h (Table S2, entry 2).

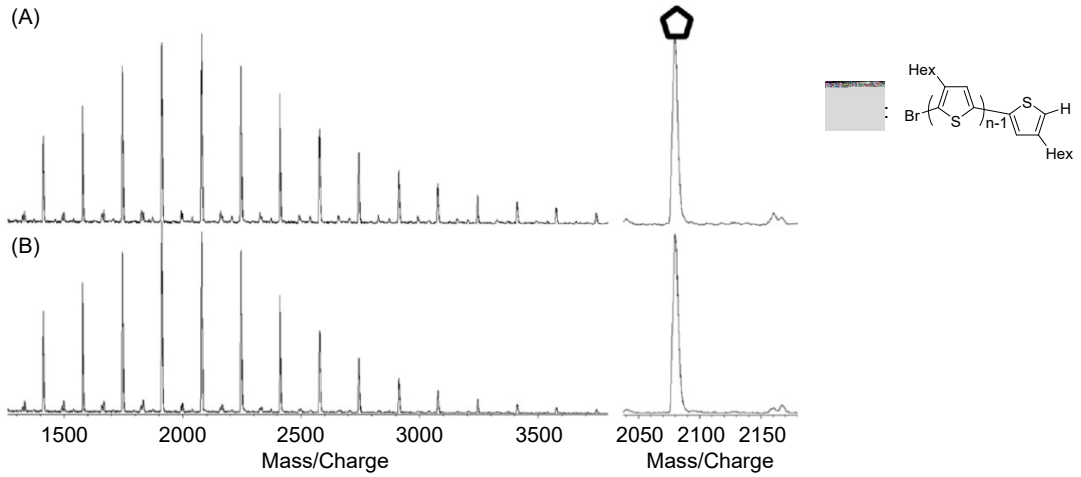


Fig S18. MALDI-TOF mass spectra of P3HT obtained by (A) Kumada-Tamao CTCP of **1** with 10 mol% of Ni(depe)Cl_2 at room temperature and (B) Suzuki-Miyaura end-functionalization of P3HT with **2**-BPin in the presence of K_3PO_4 (4 equiv to **2**-BPin) in H_2O/THF (= 0.07, v/v) at room temperature for 24 h (Table S2, entry 3).

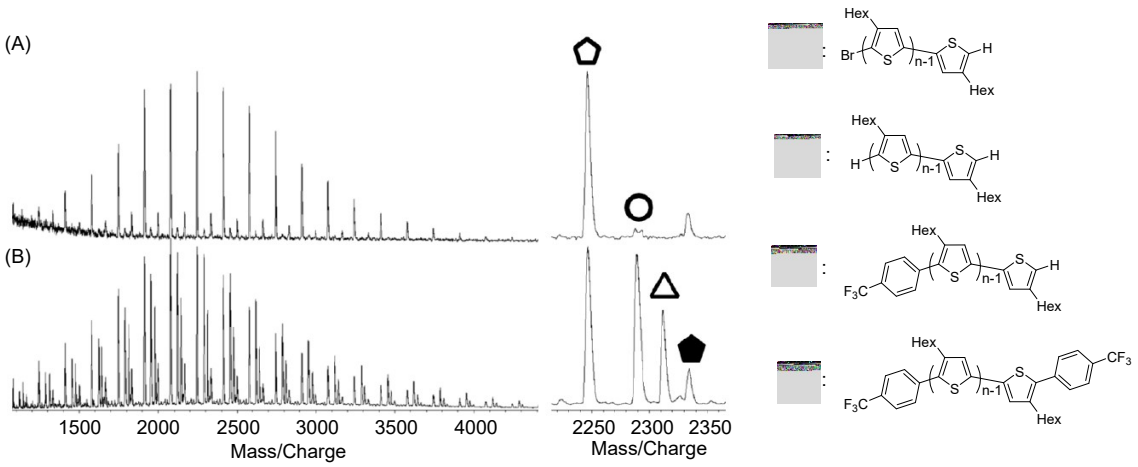


Fig S19. MALDI-TOF mass spectra of P3HT obtained by (A) Kumada-Tamao CTCP of **1** with 10 mol% of Ni(IPr)PPh_3Cl_2 at room temperature and (B) Suzuki-Miyaura end-functionalization of P3HT with **2**-BPin in the presence of K_3PO_4 (4 equiv to **2**-BPin) in H_2O/THF (= 0.07, v/v) at room temperature for 24 h (Table S2, entry 4).

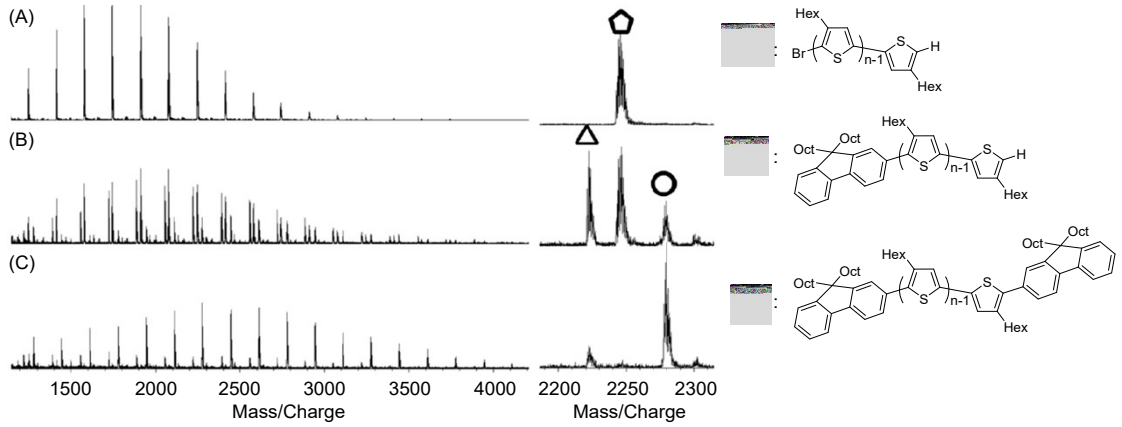


Fig S20. MALDI-TOF mass spectra of P3HT obtained by (A) Kumada-Tamao CTCP of **1** with 10 mol% of Pd-PEPPSI-IPr at room temperature and Suzuki-Miyaura end-functionalization of P3HT with **3**-BPin in the presence of K_3PO_4 in H_2O/THF (= 0.02, v/v) at room temperature for (B) 7 h and (C) 3 days.

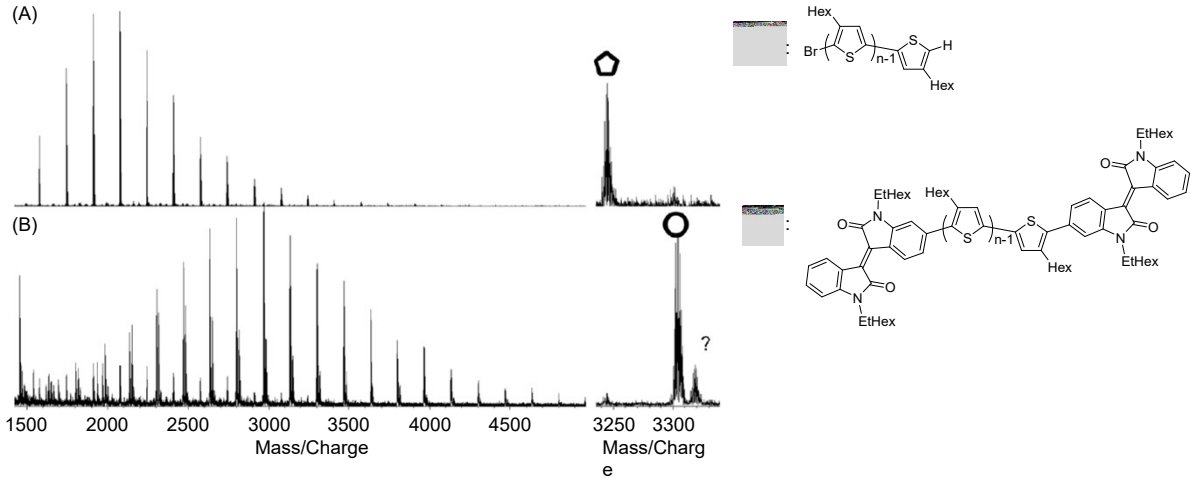


Fig S21. MALDI-TOF mass spectra of P3HT obtained by (A) Kumada-Tamao CTCP of **1** with 10 mol% of Pd-PEPPSI-IPr at room temperature and (B) Suzuki-Miyaura end-functionalization of P3HT with **4**-BPin in the presence of K_3PO_4 in H_2O/THF (= 0.02, v/v) at room temperature for 24 h.

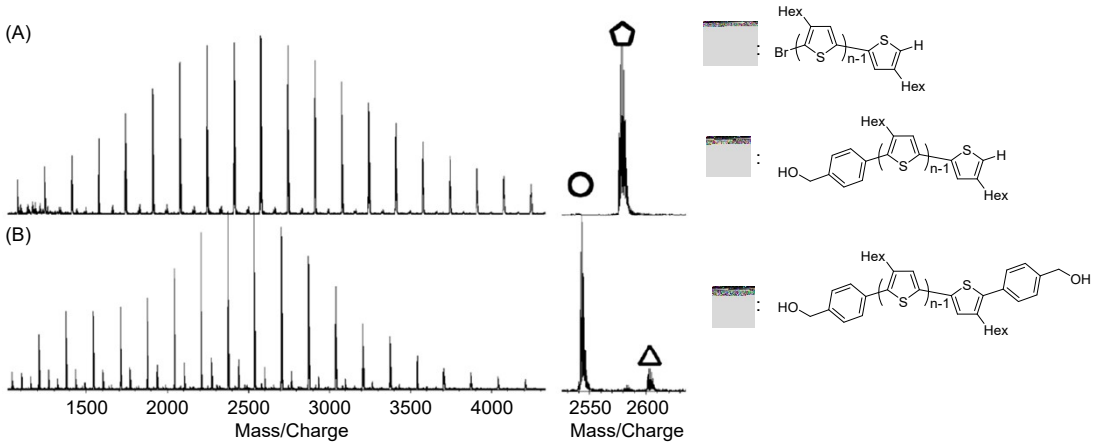


Fig S22. MALDI-TOF mass spectra of P3HT obtained by (A) Kumada-Tamao CTCP of **1** with 10 mol% of Pd-PEPPSI-IPr at room temperature and (B) Suzuki-Miyaura end-functionalization of P3HT with **5**-BPin in the presence of K_3PO_4 in H_2O/THF (= 0.02, v/v) at room temperature for 24 h.

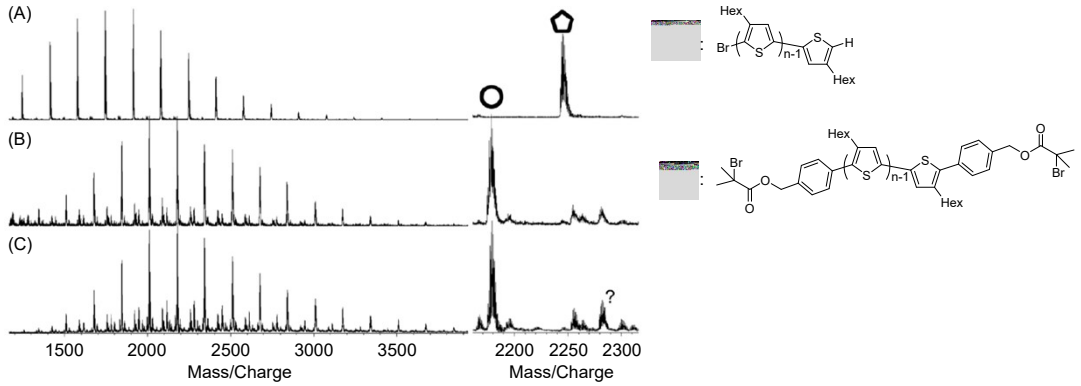


Fig S23. MALDI-TOF mass spectra of P3HT obtained by (A) Kumada-Tamao CTCP of **1** with 10 mol% of Pd-PEPPSI-IPr at room temperature and Suzuki-Miyaura end-functionalization of P3HT with **6**-BPin in the presence of K_3PO_4 in H_2O/THF (= 0.02, v/v) at room temperature for (B) 7 h and (C) 3 days.

11. ^{1}H NMR spectra

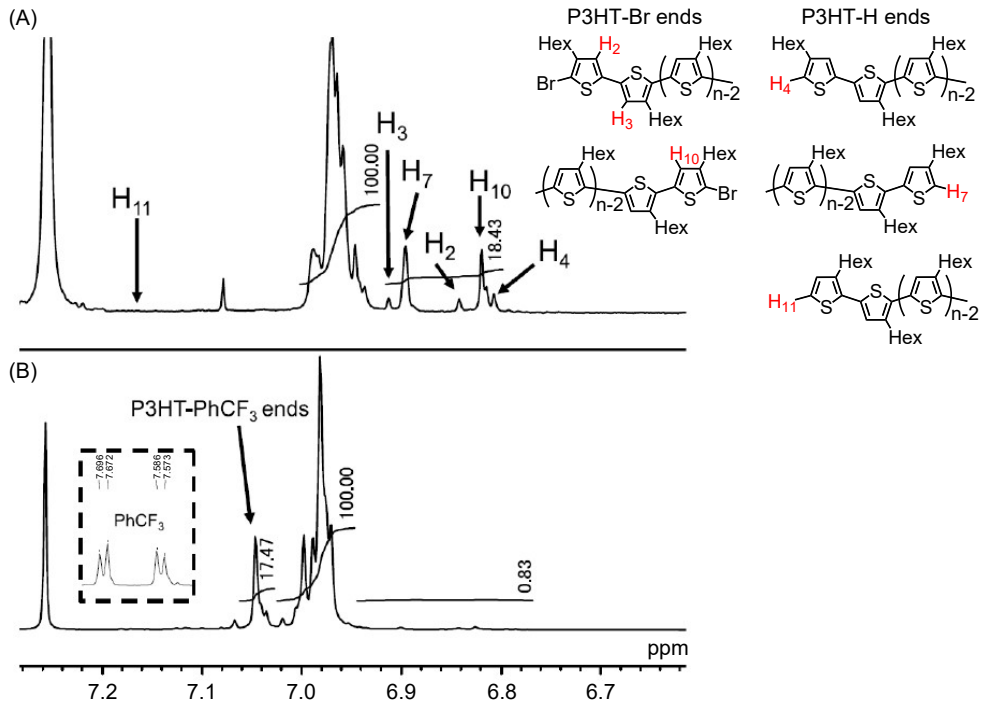


Fig S24. ^{1}H NMR spectra of P3HT obtained by (A) CTCP of **1** with 10 mol% of Pd-PEPPSI-IPr at room temperature and (B) successive Suzuki-Miyaura end-functionalization with **2**-BPin in the presence of K_3PO_4 (4.0 equivalents to **2**-BPin) in THF/H_2O at room temperature for 24 h.

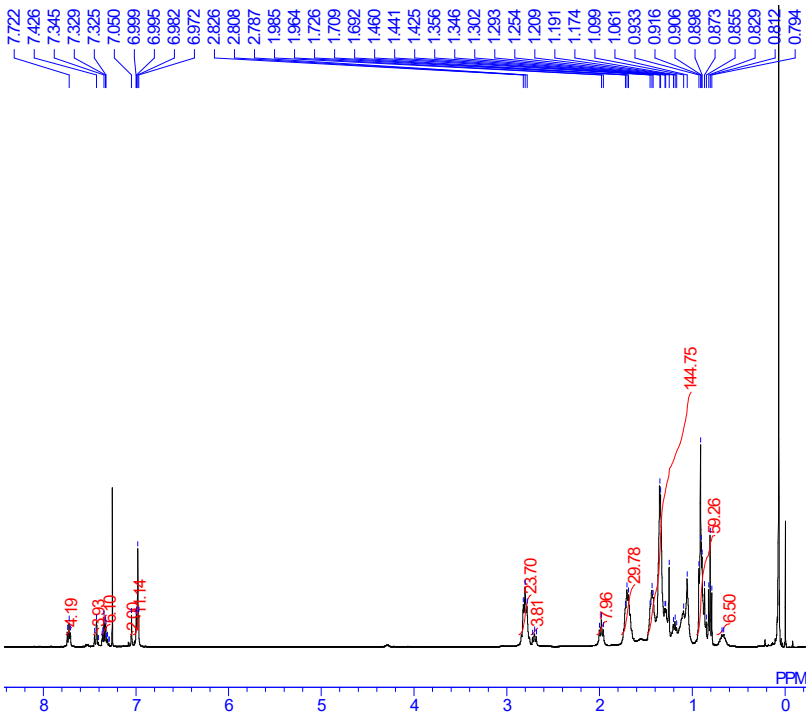


Fig S25. ^{1}H NMR spectrum of P3HT obtained by Suzuki-Miyaura end-functionalization with **3**-BPin in in $CDCl_3$ at 25 °C.

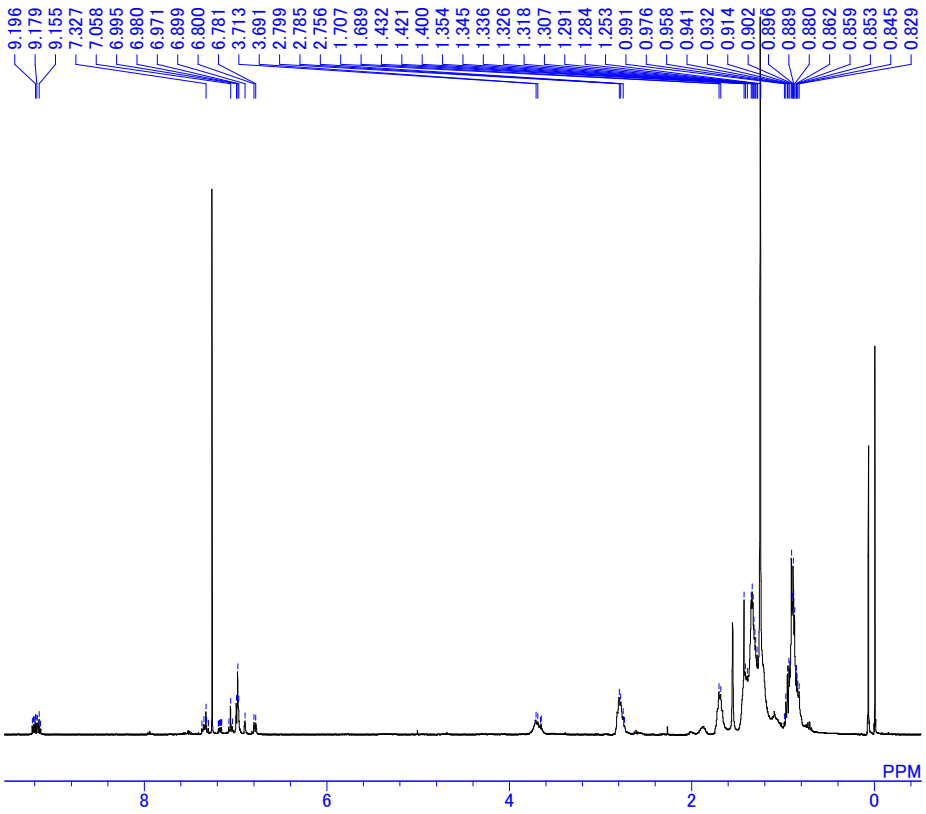


Fig S26. ^{1}H NMR spectrum of P3HT obtained by Suzuki-Miyaura end-functionalization with **4**-BPin in in $CDCl_3$ at 25 °C.

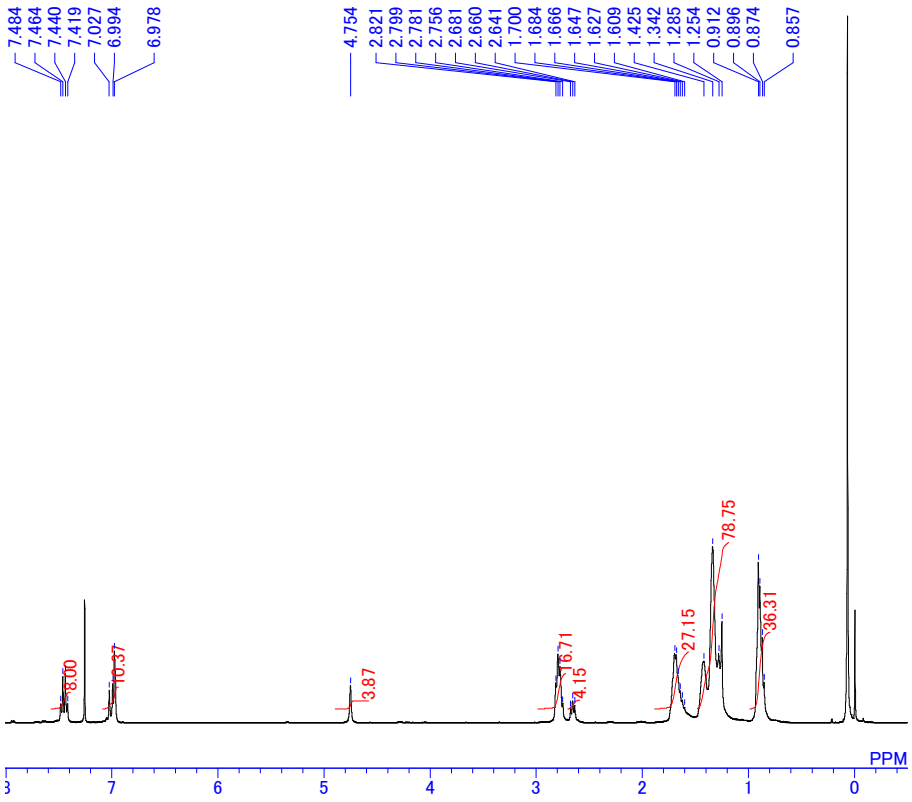


Fig S27. ^{1}H NMR spectrum of P3HT obtained by Suzuki-Miyaura end-functionalization with **5**-BPin in in $CDCl_3$ at 25 °C.

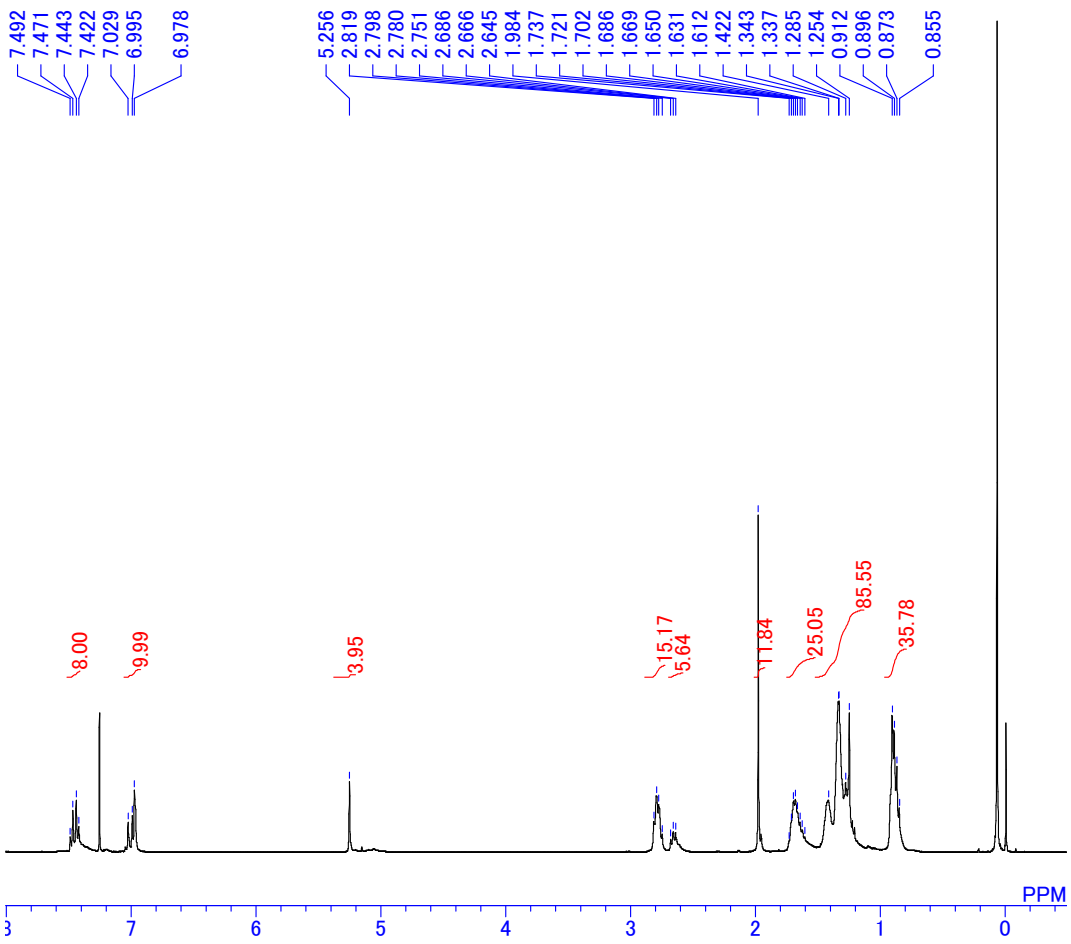


Fig S28. ^{1}H NMR spectra of P3HT obtained by Suzuki-Miyaura end-functionalization with **6**-BPin in in $CDCl_3$ at 25 °C.

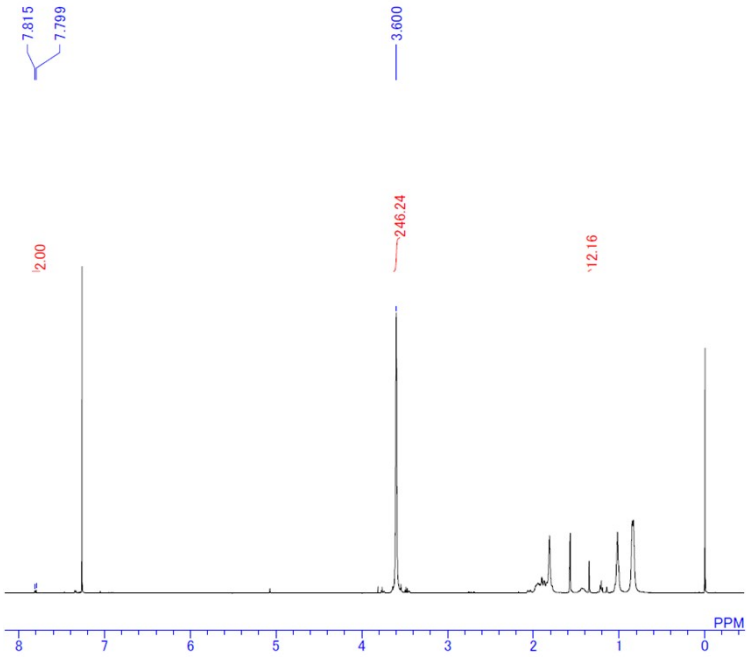


Fig S29. ^{1}H NMR spectrum of PMMA-BPin in $CDCl_3$ at 25 °C.

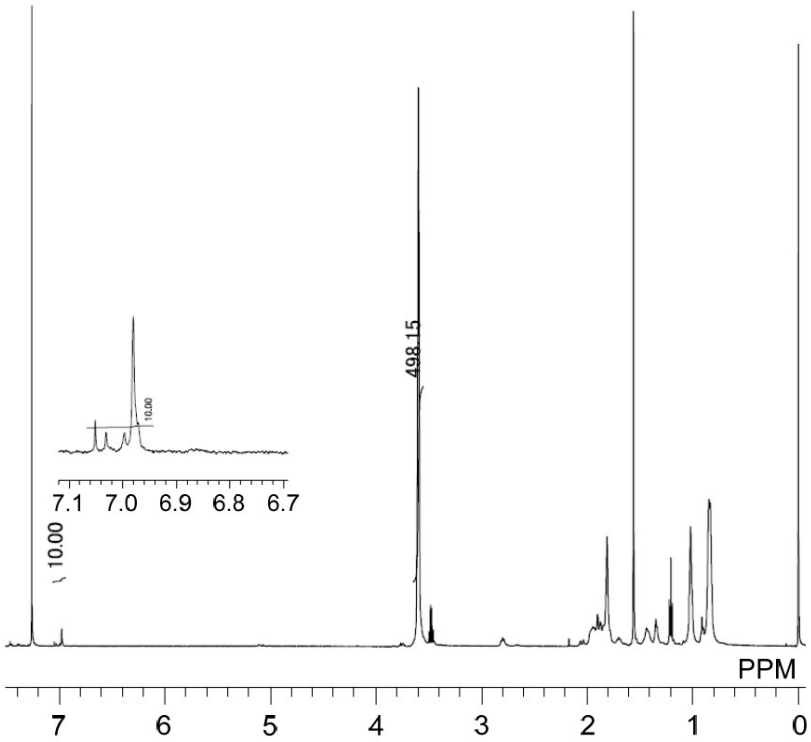


Fig S30. ^{1}H NMR spectrum of the purified PMMA-*b*-P3HT-*b*-PMMA in $CDCl_3$ at 25 °C.