

Electronic Supplementary Information for  
**Gelation-free synthesis of high-molecular-weight hyperbranched aromatic polymers containing silicon by Suzuki-Miyaura polycondensation of tri- or tetra(bromoaryl)silane with arylenediboronate**

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## 1. Materials

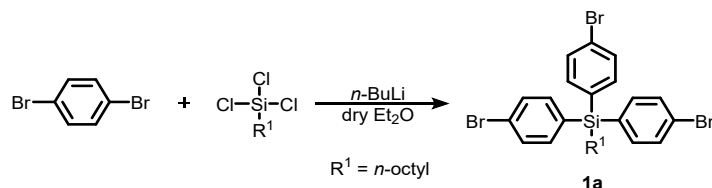
All starting materials were purchased from suppliers (TCI, Aldrich, Wako and Kanto) and used without further purification. Commercially available dehydrated tetrahydrofuran (THF, stabilizer-free, Kanto), dehydrated diethyl ether (Kanto), and distilled water (Wako) was used as received. 2,2'-(2,5-Bis(hexyloxy)-1,4-phenylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**4a**)<sup>1</sup> and 2,2'-(2,5-bis(2-ethylhexyloxy)-1,4-phenylene)diboronic acid (**4a'**)<sup>2</sup> was prepared as described.

## 2. General

<sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained on JEOL ECZ-400R, ECX-400II, and ECA-600 spectrometers. The internal standard for <sup>1</sup>H NMR spectra in CDCl<sub>3</sub> was tetramethylsilane (0.00 ppm), the internal standard for <sup>1</sup>H NMR spectra in CD<sub>2</sub>Cl<sub>2</sub> was CH<sub>2</sub>Cl<sub>2</sub> (5.32 ppm), and the internal standard for <sup>13</sup>C NMR spectra in CDCl<sub>3</sub> was the midpoint of CDCl<sub>3</sub> (77.0 ppm). IR spectra were recorded on a JASCO FT/IR-4600AC. UV-vis absorption spectra were recorded on a Shimadzu UV-1800, and fluorescence spectra were recorded on a Jasco FP-8300 and Jasco FP-8550. All melting points were measured with a Yanagimoto hot stage melting point apparatus without correction. Column chromatography was performed on silica gel (Silicagel 60, 63-200 μm, Merck and Silicagel 60, 63-210 μm, Kanto) with a specified solvent. The *M<sub>n</sub>* and *M<sub>w</sub>/M<sub>n</sub>* values of polymers were measured on Tosoh HLC-8420 gel permeation chromatography unit (eluent, THF 1.00 mL/min; calibration, polystyrene standards; column temperature, 40 °C) with two TSK-gel (G4000HXL) columns, a Shodex GPC-101 (eluent, THF; column temperature, 40 °C) equipped with Shodex UV-41, Shodex RI-71S, and two Shodex KF 804-L columns, and Tosoh HLC-8320 gel permeation chromatography (GPC) unit (eluent, CHCl<sub>3</sub>; calibration, polystyrene standards) with a Shodex LF-804 column and Wyatt Technology DAWN TREOS II multiangle laser light scattering (MALLS, Ga-As laser, λ = 658 nm) detectors. Calibration was carried out using polystyrene standards. MALDI-TOF mass spectra were recorded on a Shimadzu/Biotech AXIMA-Confidence in the reflectron ion mode and linear ion mode by the use of a laser (λ = 337 nm). DCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile) was used as the matrix for the MALDI-TOF mass measurements.

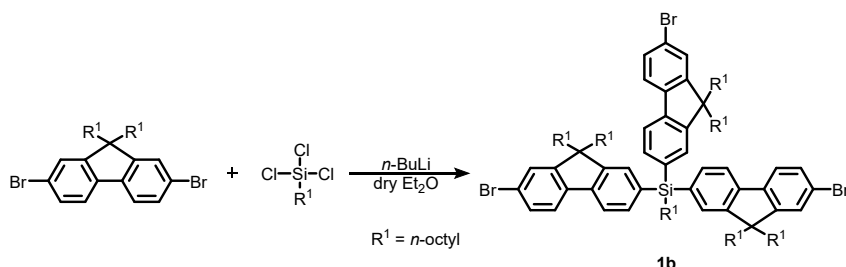
### 3. Synthesis of tribromo monomers **1a**, **b** and tetrabromo monomer **1c**

#### 3-1. Synthesis of **1a**



A round-bottomed flask, equipped with a three-way stopcock, was dried by heating under reduced pressure and then cooled to room temperature under an argon atmosphere. Trichloro-*n*-octylsilane (2.4825 g, 10.0238 mmol) was placed in the flask, and the atmosphere in the flask was replaced with argon. Dry diethyl ether (10 mL) was added to the flask via a syringe under a stream of nitrogen. 1,4-Dibromobenzene (12.0723 g, 50.17 mmol) was placed in a pear-shaped flask, and the atmosphere in the flask was replaced with argon. Dry diethyl ether (16 mL) was added to the flask via a syringe under a stream of nitrogen. 2.70 M *n*-BuLi in hexane (12.0 mL, 32.4 mmol) was added dropwise to the pear-shaped flask at 0 °C under a stream of nitrogen, and the mixture was stirred at 0 °C for 1 h. This solution was added dropwise to the round-bottomed flask, and mixture was stirred at 0 °C for 14 h. 1M Hydrogen chloride was added, and the mixture was extracted with Et<sub>2</sub>O. The organic layer was washed with water, dried over anhydrous MgSO<sub>4</sub>, and concentrated under reduced pressure. The crude product was purified by silica gel chromatography (eluent: hexane) to give 4.8730 g (80%) of **1a** as a colorless liquid. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.51 (d, *J* = 8.4 Hz, 6 H), 7.31 (d, *J* = 8.4 Hz, 6 H), 1.42-1.19 (14 H), 0.86 (t, *J* = 7.2 Hz, 3 H), 7.51 (d, *J* = 8.4 Hz, 6 H), 7.31 (d, *J* = 8.4 Hz, 6 H), 1.42-1.19 (14 H), 0.86 (t, *J* = 7.2 Hz, 3 H); <sup>13</sup>C (150 MHz, CDCl<sub>3</sub>) δ 137.0, 136.9, 133.1, 131.3, 131.2, 124.8, 33.6, 31.8, 29.2, 29.0, 23.7, 22.6, 14.1, 12.8; IR (neat) 2952, 2915, 2857, 2369 cm<sup>-1</sup>.

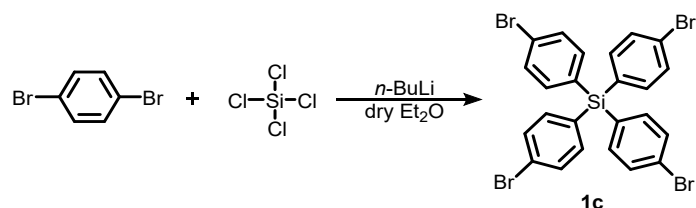
#### 3-2. Synthesis of **1b**



**1b** was synthesized by the same method as **1a** to give 1.8200 g (27%) of **1b** as a white solid (mp 61.5-63.0 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.62-7.60 (m, 6 H), 7.54 (d, *J* = 7.6 Hz, 3 H), 7.47-7.44 (m, 6 H), 7.41 (d, *J* = 8.0 Hz, 3 H), 1.94-1.90 (m, 12 H), 1.51-

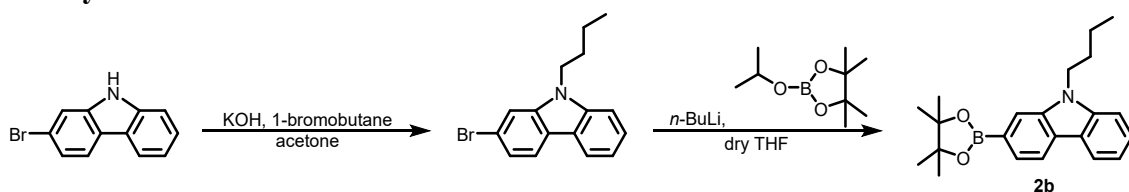
1.34 (m, 6 H), 1.22-1.05 (m, 68 H), 0.83 (t,  $J = 7.4$  Hz, 21 H), 0.68-0.60 (m, 12 H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  153.1, 149.4, 141.2, 140.0, 134.54, 134.50, 130.0, 129.8, 126.2, 121.4, 121.2, 119.2, 55.3, 40.2, 33.9, 31.9, 31.8, 30.1, 29.42, 29.40, 29.34, 29.32, 24.4, 23.9, 22.7, 22.6, 14.2, 14.1; IR (KBr) 2954, 2924, 2853, 1455, 1093, 1065, 1003, 813, 690  $\text{cm}^{-1}$ .

### 3-3. Synthesis of **1c**



A round-bottomed flask, equipped with a three-way stopcock, was dried by heating under reduced pressure and then cooled to room temperature under an argon atmosphere. 1,4-Dibromobenzene (12.7985 g, 54.2 mmol) was placed in the flask, and the atmosphere in the flask was replaced with argon. Dry diethyl ether (150 mL) was added to the flask via a syringe under a stream of nitrogen. 2.70 M  $n\text{-BuLi}$  in hexane (20.0 mL, 54.0 mmol) was added dropwise to the flask at  $-78$   $^\circ\text{C}$  under a stream of nitrogen, and the mixture was stirred at  $-78$   $^\circ\text{C}$  for 15 min and at  $0$   $^\circ\text{C}$  for 1 h. Tetrachlorosilane (2.2239 g, 13.1 mmol) was placed in a pear-shaped flask, and the atmosphere in the pear-shaped flask was replaced with argon. Dry diethyl ether (20 mL) was added to the pear-shaped flask via a syringe under a stream of nitrogen. The solution of tetrachlorosilane in ether was added dropwise to the round-bottomed flask at  $-78$   $^\circ\text{C}$ , and the mixture was stirred at room temperature for 12 h. 1 M hydrochloric acid was added, and  $\text{Et}_2\text{O}$  was removed under reduced pressure. The residue was filtrated, and washed with water and MeOH, and dried over under reduced pressure to give 5.0791 g (60%) of **1c** as a white solid (mp  $237$   $^\circ\text{C}$ ). **1c** was used without further purification.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.54 (d,  $J = 8.4$  Hz, 8 H), 7.34 (d,  $J = 8.4$  Hz, 8 H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  137.6, 131.5, 131.4, 125.4; IR (KBr) 2375, 2346, 1570, 1478, 1066, 1011  $\text{cm}^{-1}$ .

### 3-4. Synthesis of **2b**



#### 3-4-1. Synthesis of 2-bromo-N-n-butylcarbazole

Two-necked flask, equipped with a reflux condenser, on the top of which a three-way stopcock was attached, at one neck and another three-way stopcock at the other, was dried by heating under reduced pressure and then cooled to room temperature under an argon atmosphere. 2-Bromocarbazole (5.1524g, 20.93 mmol) and KOH (3.811 g, 67.92 mmol) were placed in the flask, and the atmosphere in the flask was replaced with argon. Acetone (50 mL) was added to the flask via a syringe under a stream of nitrogen. The mixture was refluxed for 1 h. 1-Bromobutane (4.4 mL, 41.1 mmol) was added slowly to the mixture, and the mixture was refluxed for 1 h. Acetone was removed under reduced pressure, and the residue was dissolved with CH<sub>2</sub>Cl<sub>2</sub>. The solution was washed with 0.7 M hydrogen chloride, water, and brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (eluent: hexane/ethyl acetate = 5/1) to give 2.9217 g (46%) of 2-bromo-*N-n*-butylcarbazole as white solid (mp 44-45 °C). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.03 (d, *J* = 7.8 Hz, 1 H), 7.90 (d, *J* = 7.8 Hz, 1 H), 7.52(s, 1 H), 7.46(t, *J* = 7.5 Hz, 1 H), 7.37 (d, *J* = 8.4 Hz, 1 H), 7.30 (d, *J* = 9.6 Hz, 1 H), 7.22 (t, *J* = 7.8 Hz, 1 H), 4.21 (t, *J* = 7.2 Hz, 2 H), 1.81 (quint, *J* = 7.5 Hz, 2 H), 1.38 (sext, *J* = 7.4 Hz, 2 H), 0.93 (t, *J* = 7.5 Hz, 3 H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 141.20, 125.99, 121.43, 120.30, 119.16, 111.70, 108.86, 42.93, 30.98, 25.72, 20.51, 13.84; IR (KBr) 1159, 1490, 1742, 1450, 1324, 1243, 1213, 7728, 1055, 998, 887, 837, 812, 761, 747, 722, 593, 452 cm<sup>-1</sup>.

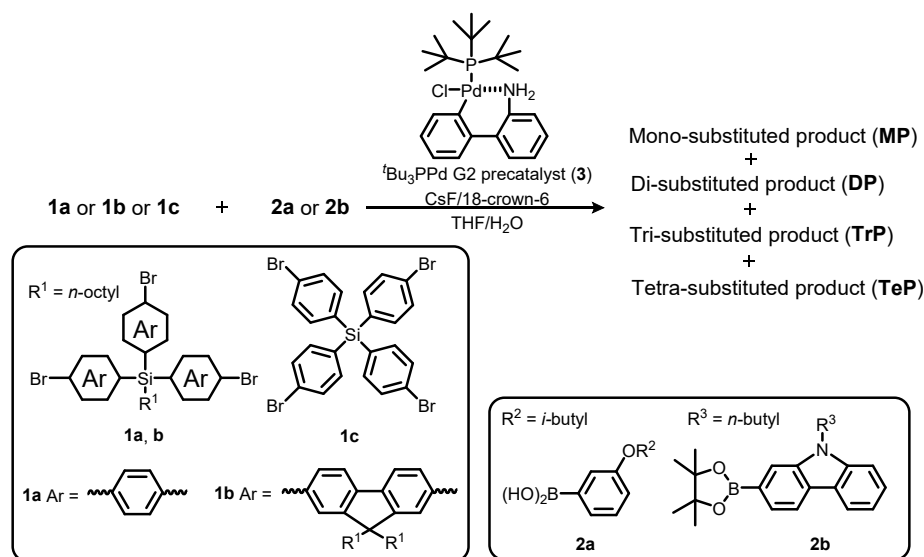
### 3-4-2. Synthesis of 2b

A round-bottomed flask, equipped with a three-way stopcock, was dried by heating under reduced pressure and then cooled to room temperature under an argon atmosphere. 2-Bromo-*N-n*-butylcarbazole (2.5052 g, 8.29 mmol) was placed in the flask, and the atmosphere in the flask was replaced with argon. Dry THF (100 mL) was added to the flask via a syringe under a stream of nitrogen. 2.70 M *n*-BuLi in hexane (4.0 mL, 10.8 mmol) was added dropwise to the flask at -78 °C under a stream of nitrogen, and the mixture was stirred at -78 °C for 1 h. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.0 mL, 15.3 mmol) was added to the flask via a syringe under a stream of nitrogen, and the mixture was stirred at -78 °C for 2 h and at 0 °C for 24 h. Water was added, and the mixture was extracted with Et<sub>2</sub>O. The organic layer was washed with brine, dried over anhydrous MgSO<sub>4</sub>, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (eluent: hexane/CH<sub>2</sub>Cl<sub>2</sub> = 10/1) to give 2.577 g (89%) of **2b** as a pale yellow solid (mp 102-105 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.12-8.09 (m, 2 H), 7.88 (s, 1 H), 7.69 (d, *J* = 7.6 Hz, 1 H), 7.48 (t, *J* = 4.8 Hz, 1 H), 7.41 (d, *J* = 8.4 Hz, 1 H), 7.22 (t, *J* = 6.8 Hz, 1 H), 4.35 (t, *J* = 7.4 Hz, 2 H),

1.87 (quint,  $J = 7.5$  Hz, 2 H), 1.38 (m, 14 H), 0.93 (t,  $J = 9.6$  Hz, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  140.91, 139.88, 126.11, 125.30, 124.92, 122.53, 120.74, 119.57, 118.62, 114.99, 108.80, 83.72, 42.74, 31.21, 24.90, 20.51, 13.89; IR (KBr) 2957, 1560, 1476, 1474, 1364, 1331, 1271, 1248, 1143, 1181, 967, 905, 857, 824, 755, 735, 689  $\text{cm}^{-1}$ .

## 4. Model reactions

### 4-1. General procedure for model reaction of 1 and 2



Tribromide or tetrabromide **1a-c** (0.200 mmol), monoboronic acid (ester) **2a-b** (0.200 mmol), CsF (0.80 mmol), 18-crown-6 (1.60 mmol), and  $^t\text{Bu}_3\text{PPd}$  G2 precatalyst **3** (0.0200 mmol) were placed in a flask, and the atmosphere in the flask was replaced with argon. Dry THF (6.0 mL) and distilled water (0.2 mL) were added to the flask via a syringe. The mixture was degassed with argon and stirred at room temperature for 3 h. 1 M Hydrochloric acid was added, and the mixture was extracted with  $\text{CH}_2\text{CH}_2$ . The organic layer was washed with sat. aq. KCl, dried over anhydrous  $\text{MgSO}_4$ , and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography to give mono-substituted product (MP), di-substituted product (DP), tri-substituted product (TrP), and tetra-substituted product (TeP).

### 4-2. General procedure for the synthesis of MP and DP (for Entries 1-3 in Table 1)

Tribromide **1a-b** (0.099-0.102 mmol), boronic acid (ester) **2a-b** (0.154-0.155 mmol),  $\text{K}_2\text{CO}_3$  (0.37-0.38 mmol), and  $(\text{Ph}_3\text{P})_4\text{Pd}$  (0.0073-0.0083 mmol) were placed in a flask, and the atmosphere in the flask was replaced with argon. Toluene deoxidized by freeze-pump-thaw cycles (5.0 mL) and distilled water (0.2 mL) were added to the flask via a

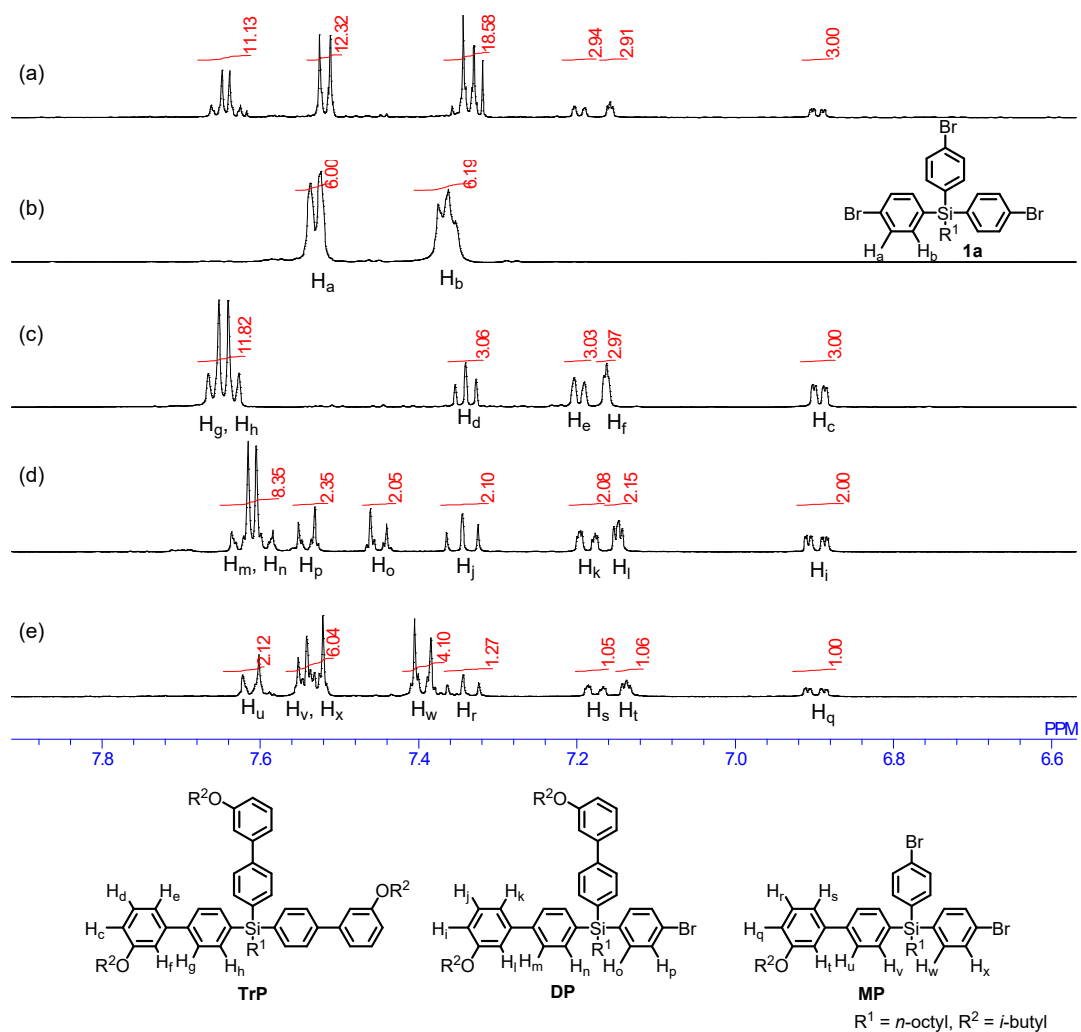
syringe. The mixture was degassed with argon and stirred at 80 °C for 24 h. 1 M Hydrochloric acid was added, and the mixture was extracted with CH<sub>2</sub>CH<sub>2</sub>. The organic layer was washed with sat. aq. NaCl, dried over anhydrous MgSO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: hexane/CH<sub>2</sub>CH<sub>2</sub> = 8/1 to 4/1) to give mono-substituted product (**MP**) and di-substituted product (**DP**).

<b>1</b>	<b>2</b>	Yield of <b>MP</b> (%)	Yield of <b>DP</b> (%)
<b>1a</b>	<b>2a</b>	50	40
<b>1a</b>	<b>2b</b>	45	32
<b>1b</b>	<b>2a</b>	32	38

#### 4-3. Synthesis of **MP**, **DP**, and **TrP** (for Entries 4 in Table 1)

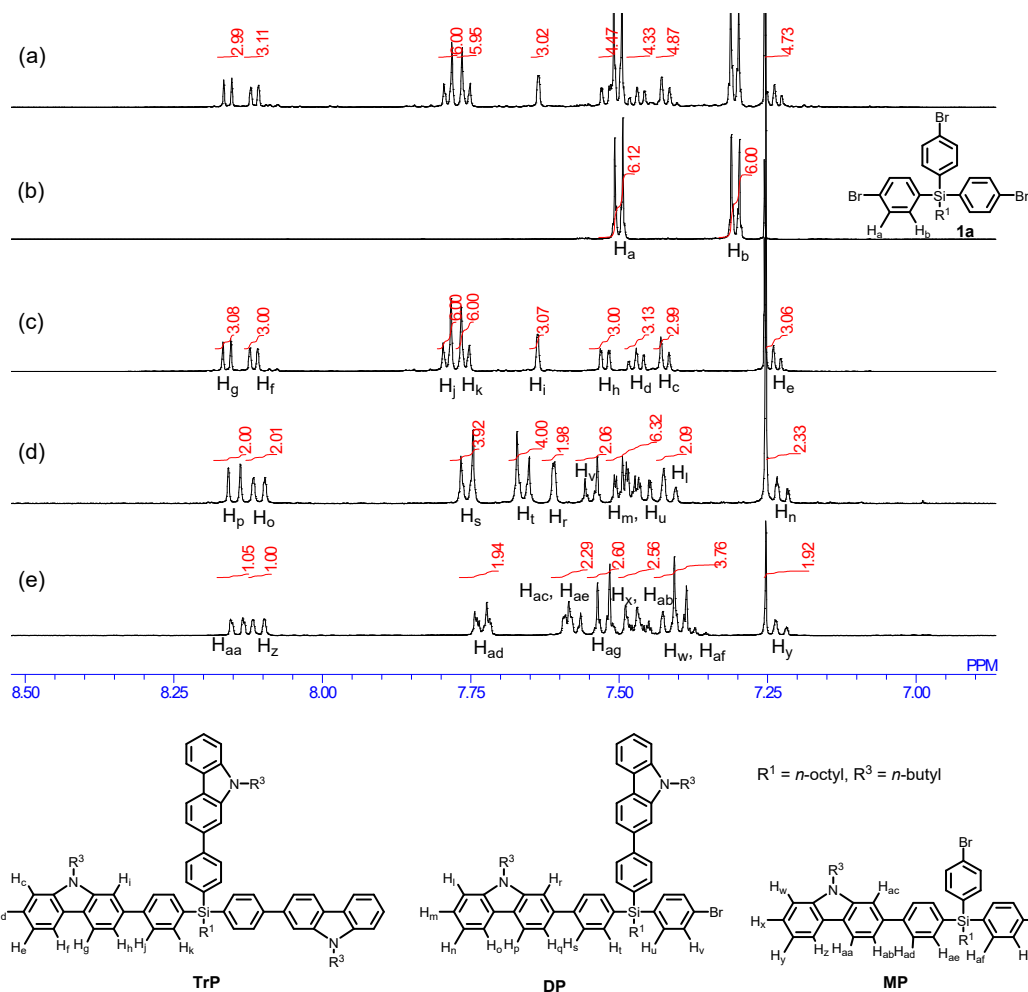
Tribromide **1c** (0.100 mmol), boronic acid **2a** (0.200 mmol), K<sub>2</sub>CO<sub>3</sub> (0.47 mmol), and (Ph<sub>3</sub>P)<sub>4</sub>Pd (0.0073 mmol) were placed in a flask, and the atmosphere in the flask was replaced with argon. Toluene deoxidized by freeze-pump-thaw cycles (5.0 mL) and distilled water (0.2 mL) were added to the flask via a syringe. The mixture was degassed with argon and stirred at 80 °C for 24 h. 1 M Hydrochloric acid was added, and the mixture was extracted with CH<sub>2</sub>CH<sub>2</sub>. The organic layer was washed with sat. aq. NaCl, dried over anhydrous MgSO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: hexane/CH<sub>2</sub>CH<sub>2</sub> = 6/1 to 4/1) to give mono-substituted product (**MP**, 41%), di-substituted product (**DP**, 22%), and tri-substituted product (**TrP**, 30%).

#### 4-4. $^1\text{H}$ NMR spectra

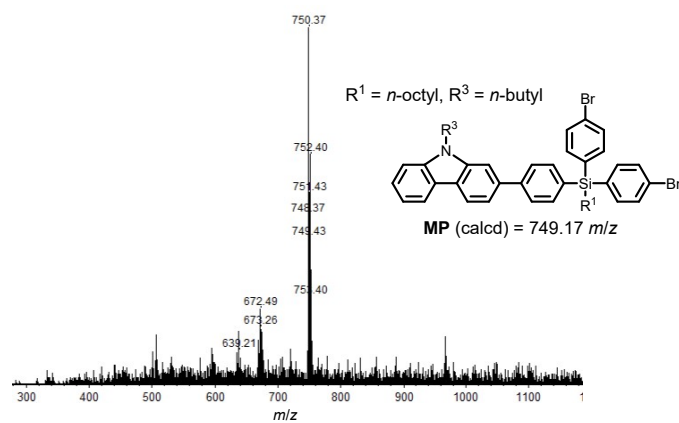


**Fig. S1.**  $^1\text{H}$  NMR spectra ( $\text{CD}_2\text{Cl}_2$ , 22  $^\circ\text{C}$ ) of (a) crude product obtained by the model reaction of equimolar **1a** and **2a**, (b) **1a**, (c) **TrP**, (d) **DP**, and (e) **MP**.

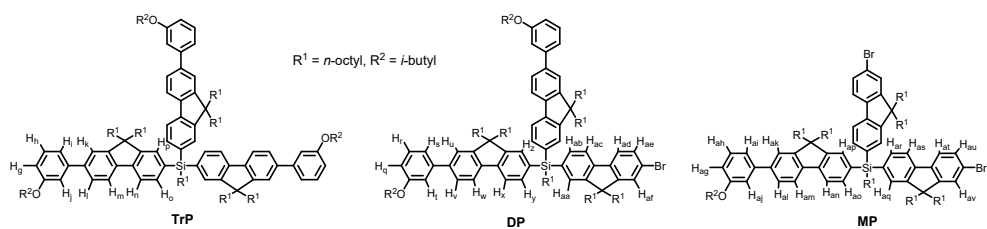
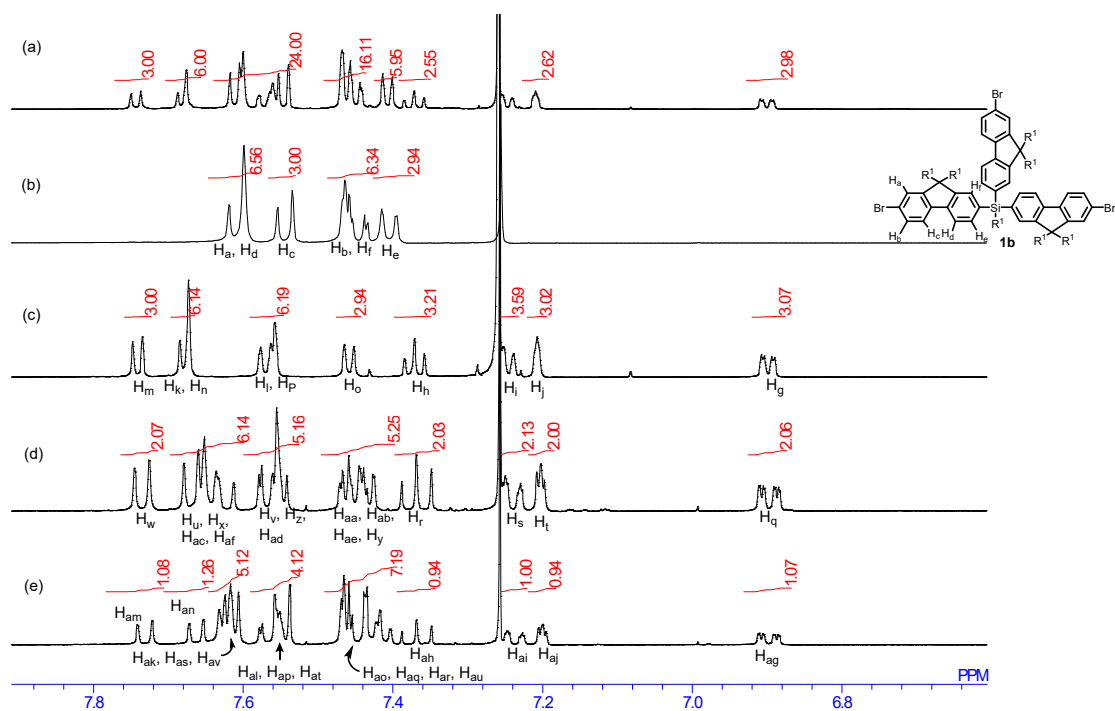




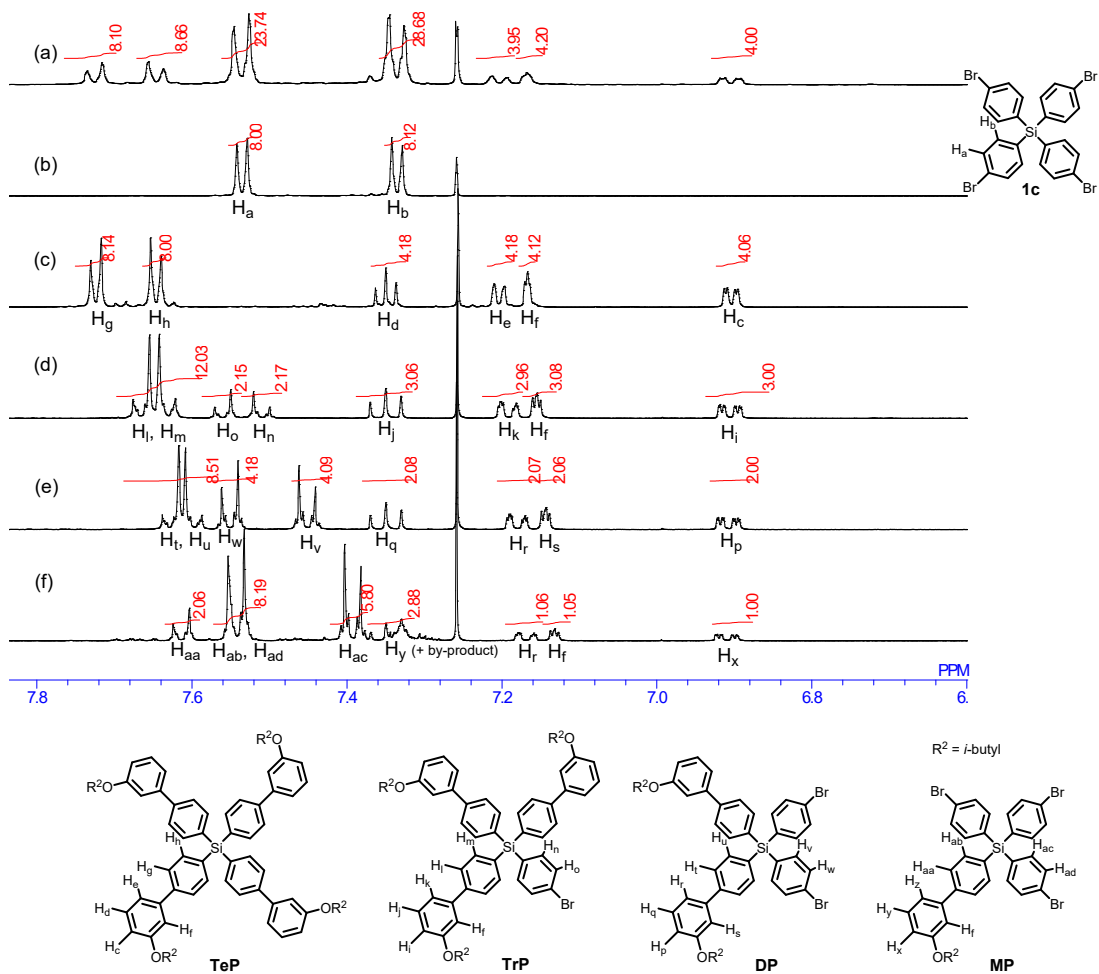
**Fig. S2-1.** <sup>1</sup>H NMR spectra (CDCl<sub>3</sub>, 20 °C) of (a) crude product obtained by the model reaction of equimolar **1a** and **2b**, (b) **1a**, (c) **TrP**, (d) **DP**, and (e) **MP**, which was confirmed by MALDI-TOF mass spectrum (Figure S2-2).



**Fig. S2-2.** MALDI-TOF mass spectrum of MP and byproduct.



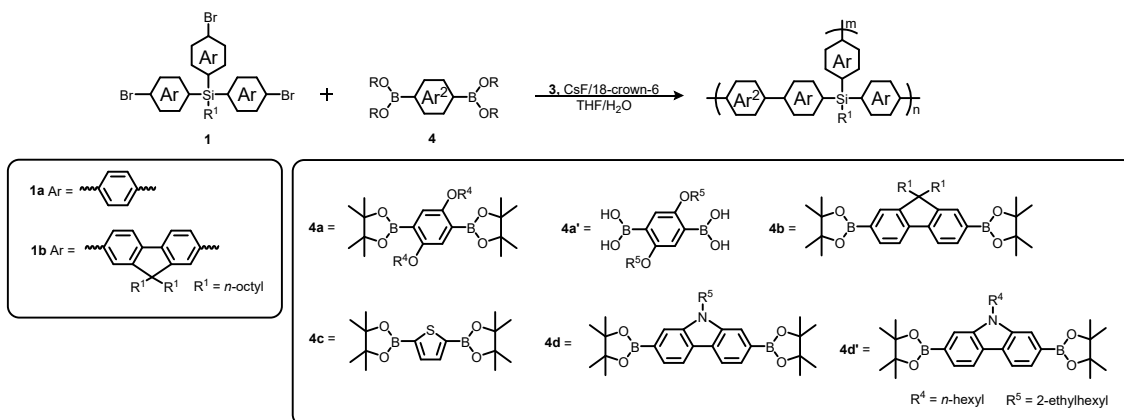
**Fig. S3.**  $^1\text{H}$  NMR spectra ( $\text{CDCl}_3$ ,  $21\text{ }^\circ\text{C}$ ) of (a) crude product, (b) **1b** obtained by the model reaction of equimolar **1b** and **2a**, (c) **TrP**, (d) **DP**, and (e) **MP**.



**Fig. S4.** <sup>1</sup>H NMR spectra (CDCl<sub>3</sub>, 23 °C) of (a) crude product obtained by the model reaction of equimolar **1c** and **2a**, (b) **1c**, (c) **TeP**, (d) **TrP**, (e) **DP**, and (f) **MP**.

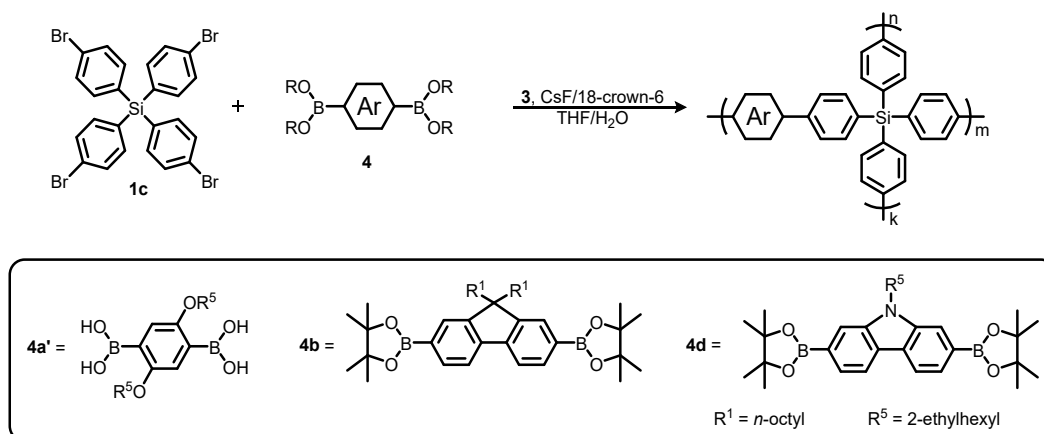
## 5. Polymerization

### 5-1. General procedure for A<sub>2</sub> + B<sub>3</sub> polymerization of 1a-b with 4.



All glass apparatuses were dried prior to use. Addition of reagents into a reaction flask was carried out via a syringe from a three-way stopcock under a stream of nitrogen. **1a-b** (0.050 mmol), **4** (0.040-0.050 mmol), CsF (0.20 mmol), 18-crown-6 (0.40 mmol), and **3** (0.0025 mmol) were placed in the flask, and the atmosphere in the flask was replaced with argon. Dry THF (6.0 mL) and distilled water (0.2 mL) were added to the flask via a syringe. The mixture was degassed with argon and stirred at room temperature or 40 °C for 0.5-24 h. 1 M Hydrochloric acid was added, and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was washed with sat. aq. KCl, dried over anhydrous MgSO<sub>4</sub>, and concentrated under reduced pressure. The crude product was purified by precipitation into MeOH or hexane/acetone to give the polymer.

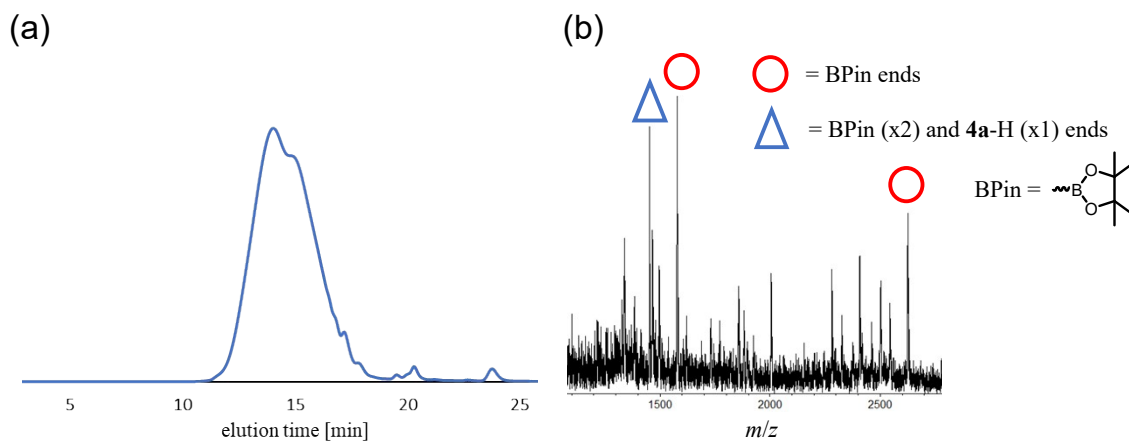
### 5-2. General procedure for A<sub>2</sub> + B<sub>4</sub> polymerization of 1c and 4.



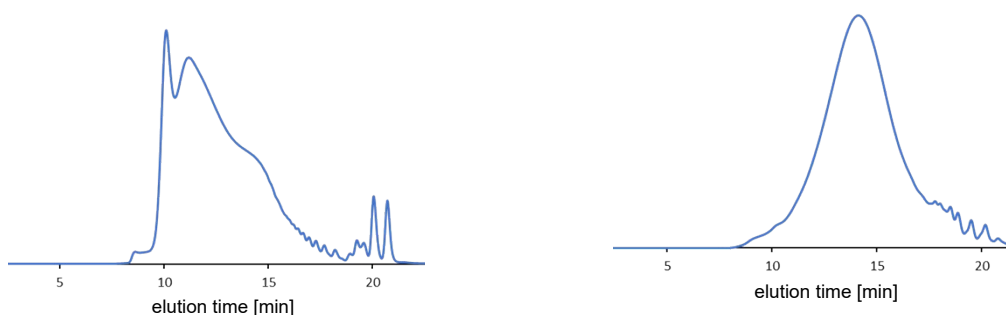
All glass apparatuses were dried prior to use. Addition of reagents into a reaction flask was carried out via a syringe from a three-way stopcock under a stream of nitrogen. **1c**

(0.031-0.033 mmol), **4** (0.050 mmol), CsF (0.20 mmol), and 18-crown-6 (0.40 mmol) and **3** (0.0025 mmol) were placed in the flask, and the atmosphere in the flask was replaced with argon. Dry THF (6.0 mL) and distilled water (0.2 mL) were added to the flask via a syringe. The mixture was degassed with argon and stirred at room temperature for 3-24 h. 1 M Hydrochloric acid was added, and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was washed with sat. aq. KCl, dried over anhydrous MgSO<sub>4</sub>, and concentrated under reduced pressure. The crude product was purified by precipitation into MeOH to give the polymer.

### 5-3. GPC profiles and MALDI TOF mass spectra

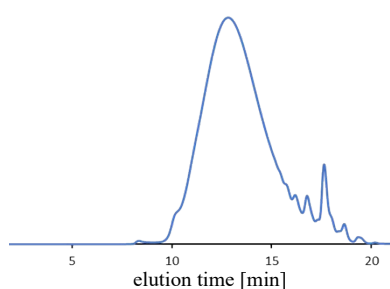


**Fig. S5.** (a) GPC profile and (b) MALDI-TOF MS of the polymer obtained by the polymerization of **1a** and **4a** at room temperature for 3 h (Table 2, Entry 1).

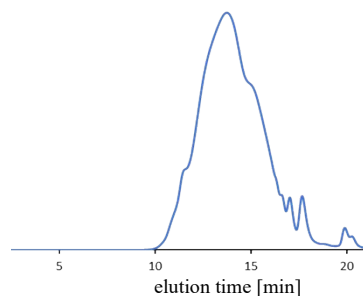


**Fig. S6.** GPC profile of the polymer obtained by the polymerization of **1a** and **4b** at 40 °C for 3 h. MALDI-TOF MS peaks were not observed (Entry 4).

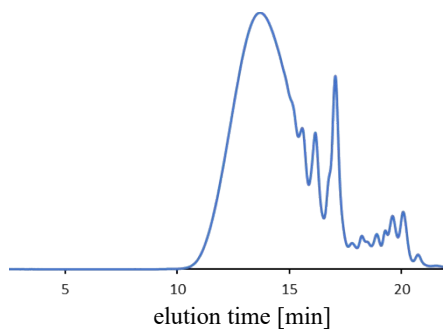
**Fig. S7.** GPC profile of the polymer obtained by the polymerization of **1a** and **4c** at room temperature for 3 h. MALDI-TOF MS peaks were not observed (Entry 5).



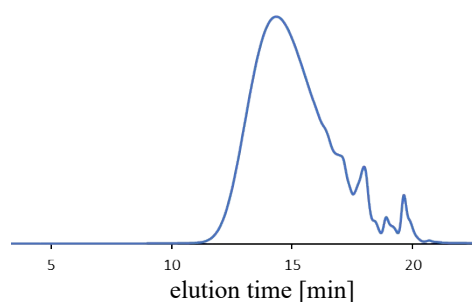
**Fig. S8.** GPC profile of the polymer obtained by the polymerization of **1a** and **4d** at room temperature for 24 h. MALDI-TOF MS peaks were not observed (Entry 7).



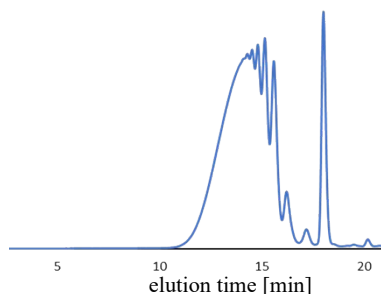
**Fig. S9.** GPC profile of the polymer obtained by the polymerization of **1c** and **4a'** at room temperature for 3 h. MALDI-TOF MS peaks were not observed (Entry 8).



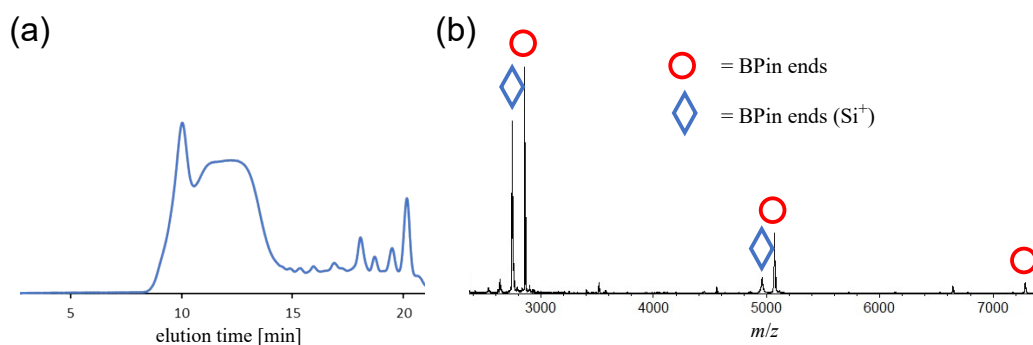
**Fig. S10.** GPC profile of the polymer obtained by the polymerization of **1c** and **4b** at room temperature for 24 h. MALDI-TOF MS peaks were not observed (Entry 9).



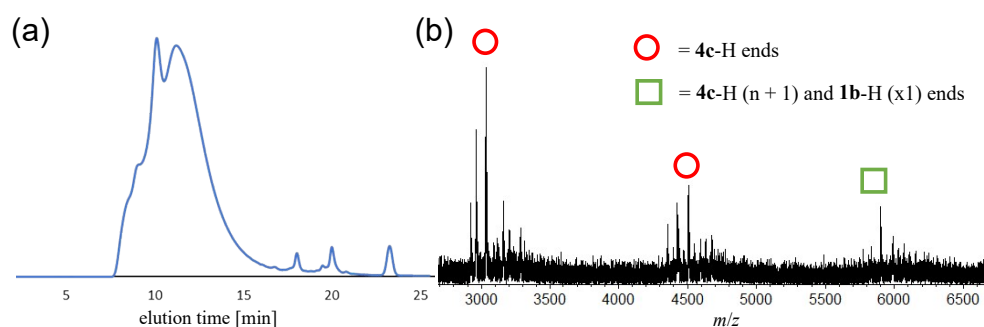
**Fig. S11.** GPC profile of the polymer obtained by the polymerization of **1c** and **4d** at room temperature for 24 h. MALDI-TOF MS peaks were not observed (Entry 10).



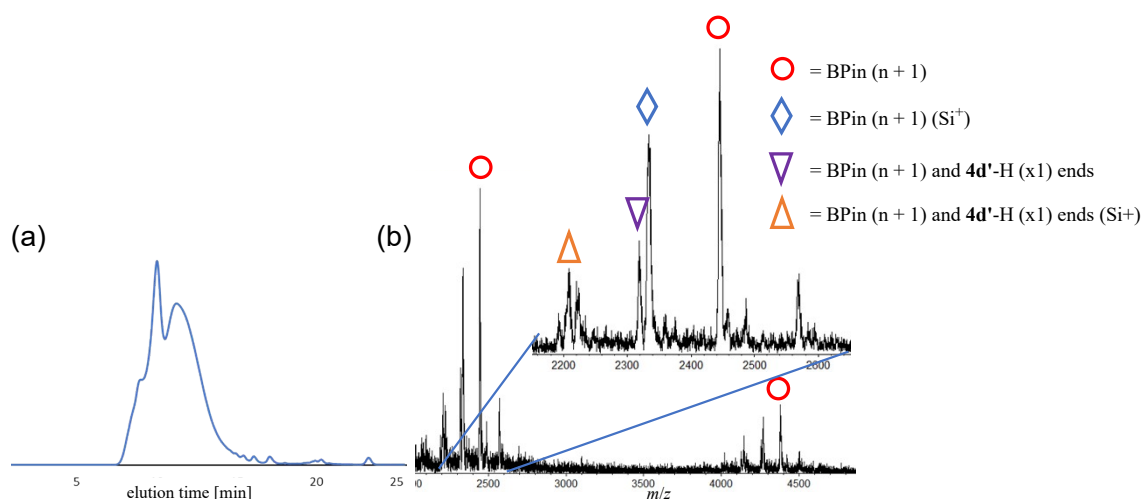
**Fig. S12.** GPC profile of the polymer obtained by the polymerization of **1b** and **4a** at room temperature for 5 h. MALDI-TOF MS was not measured (Entry 11).



**Fig. S13.** (a) GPC profile and (b) MALDI TOF MS of the polymer obtained by the polymerization of **1b** and **4b** at room temperature for 5 h (Entry 12).

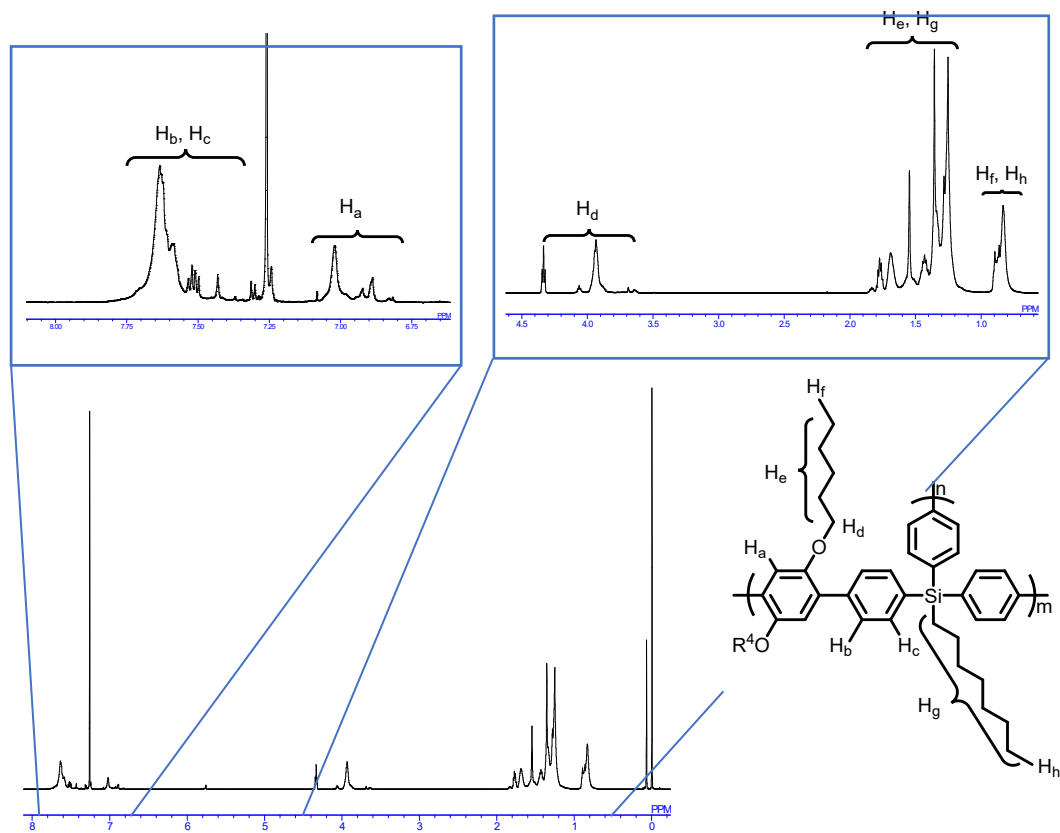


**Fig. S14.** (a) GPC profile and (b) MALDI TOF MS of the polymer obtained by the polymerization of **1b** and **4c** at room temperature for 4 h (Entry 13).



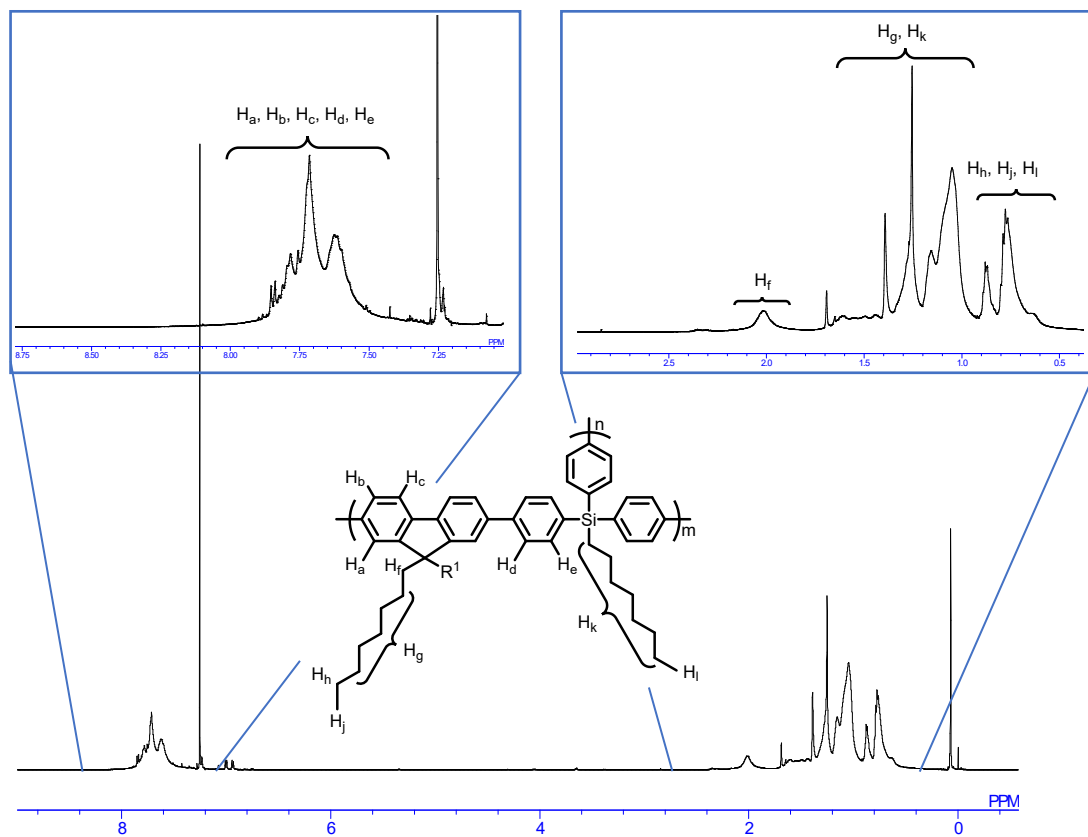
**Fig. S15.** (a) GPC profile and (b) MALDI TOF MS of the polymer obtained by the polymerization of **1b** and **4d'** at room temperature for 5 h (Entry 14).

#### 5-4. $^1\text{H}$ NMR spectra

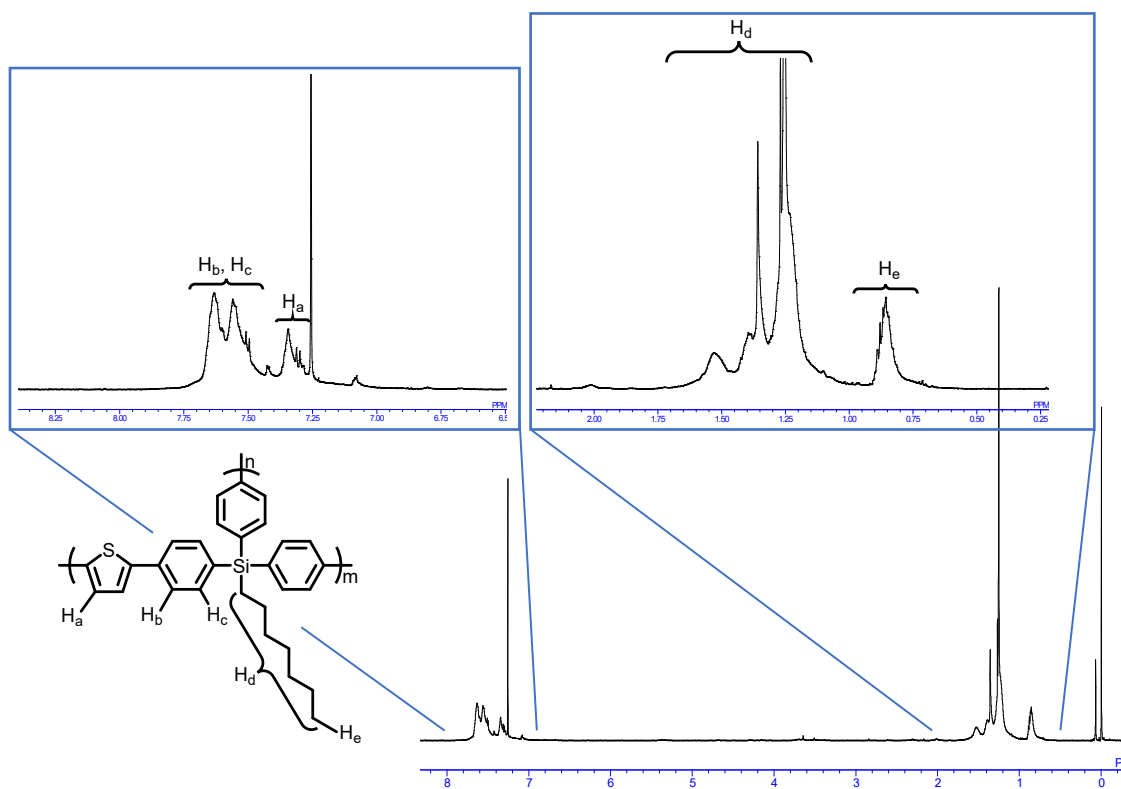


**Fig. S16.**  $^1\text{H}$  NMR spectrum of the polymer obtained by the polymerization of **1a** and **4a** at room temperature for 3 h (Table 2, Entry 1).

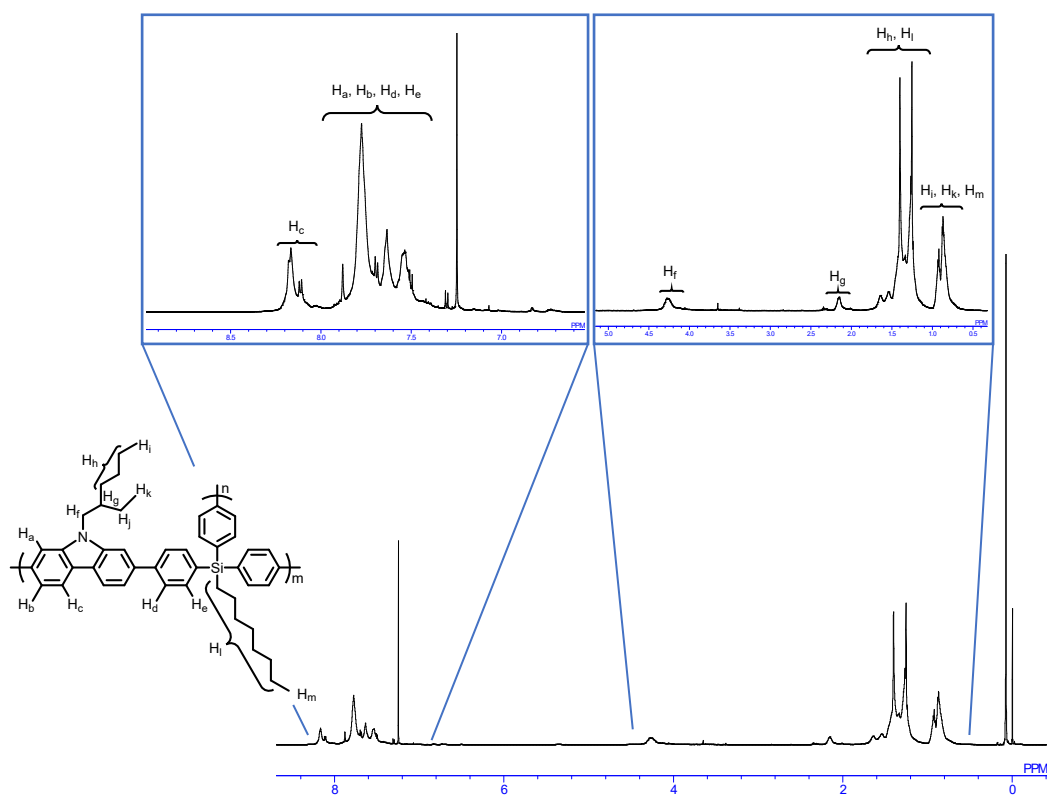




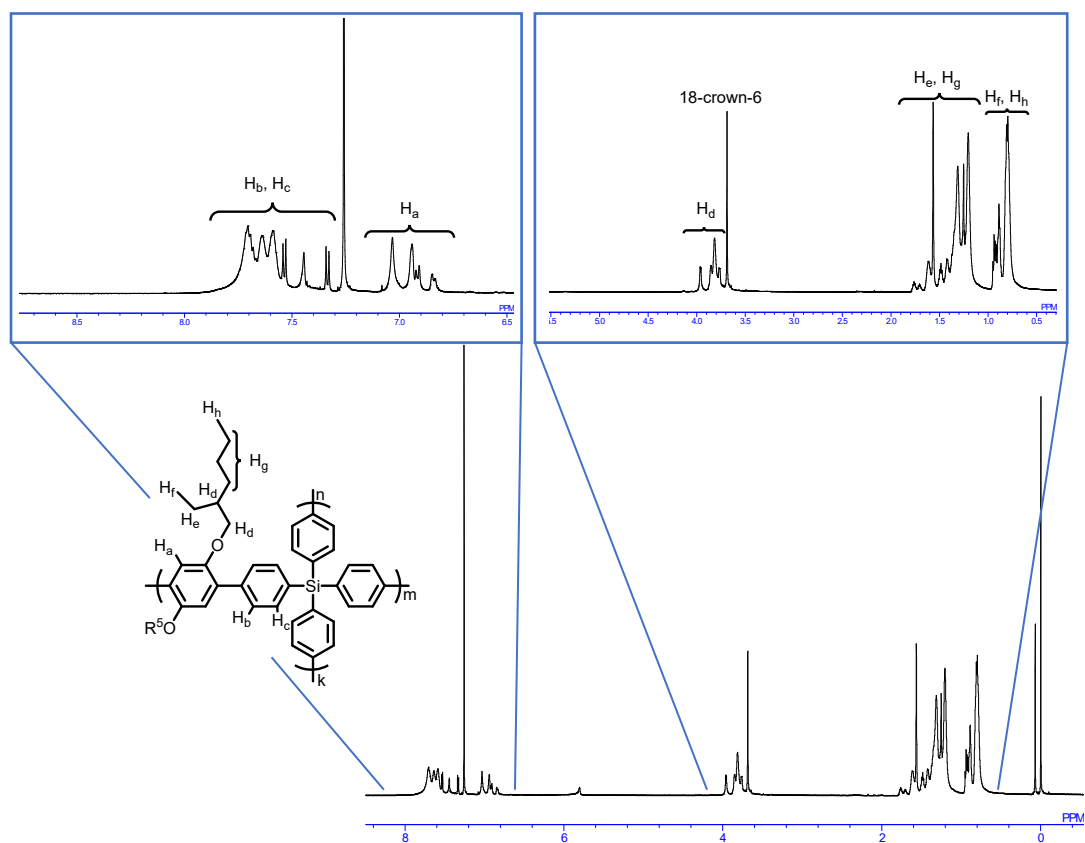
**Fig. S17.** <sup>1</sup>H NMR spectrum of the polymer obtained by polymerization of **1a** and **4b** at 40 °C for 3 h (Entry 4).



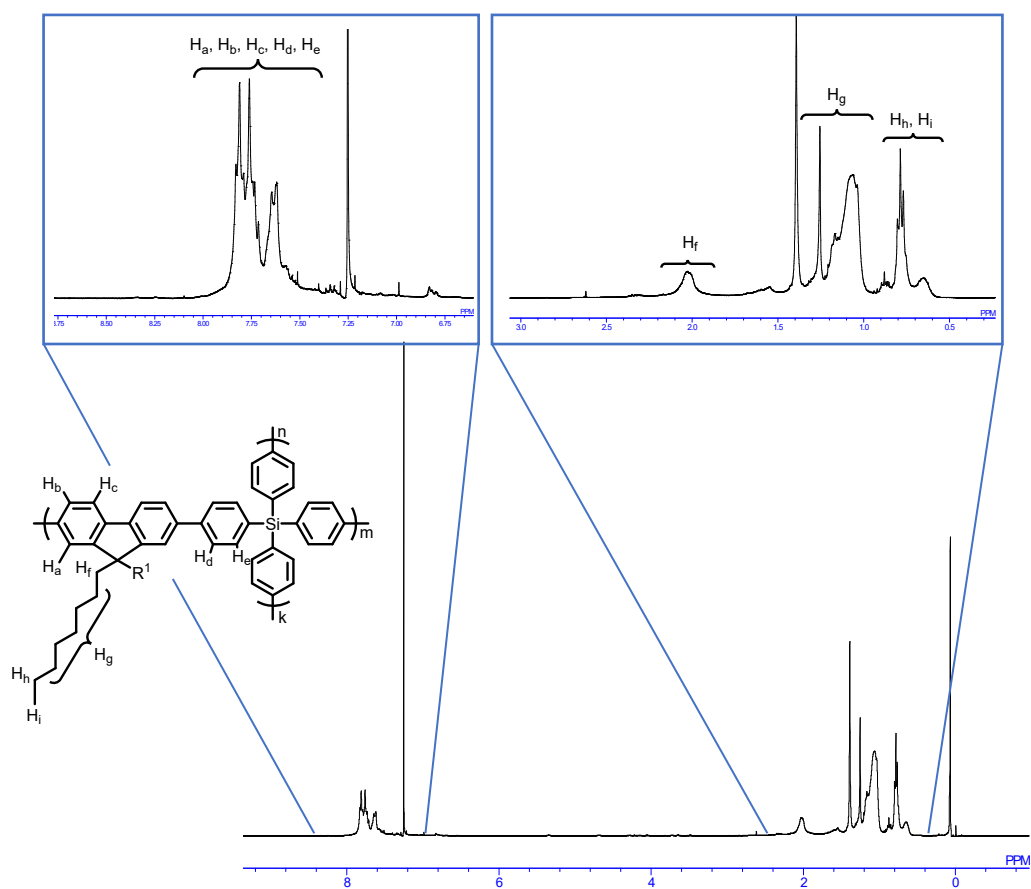
**Fig. S18.** <sup>1</sup>H NMR spectrum of the polymer obtained by the polymerization of **1a** and **4c** at room temperature for 0.5 h (Entry 5).



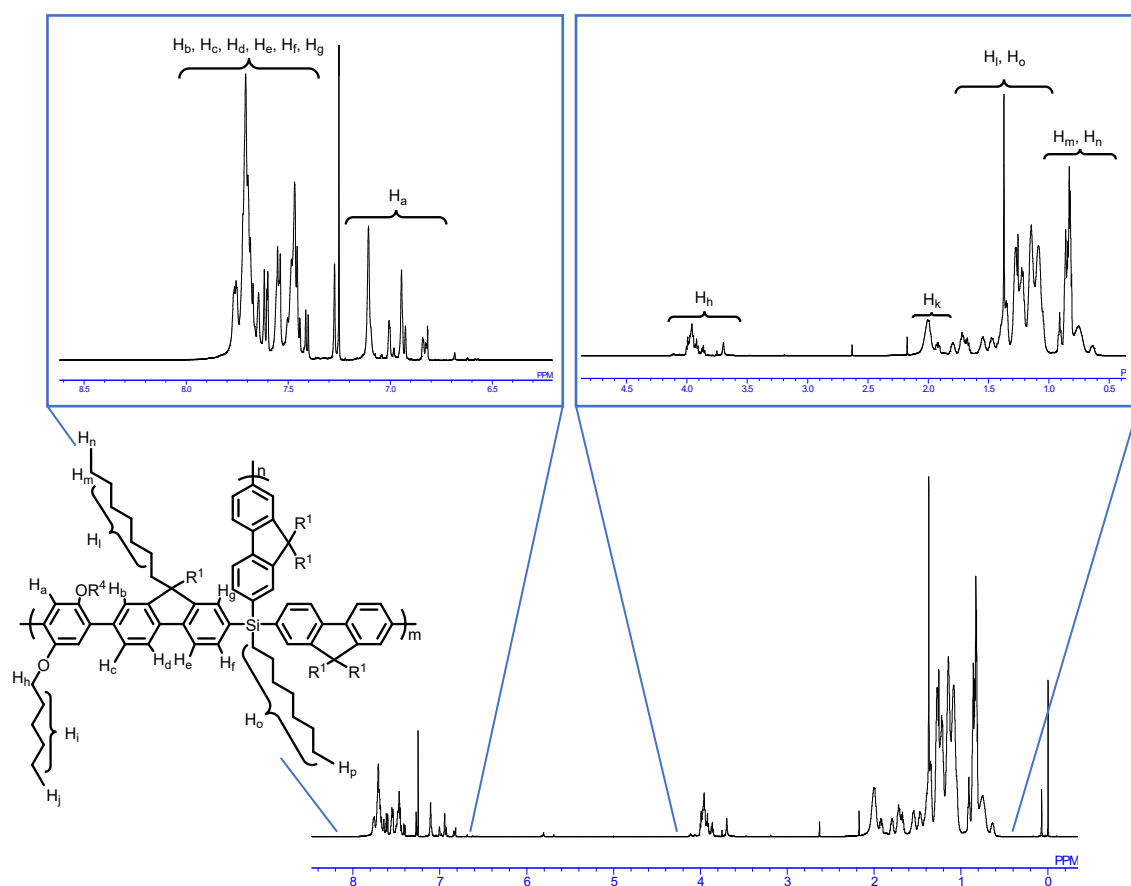
**Fig. S19.**  $^1\text{H}$  NMR spectrum of the polymer obtained by the polymerization of **1a** and **4d** at room temperature for 24 h (Entry 7).



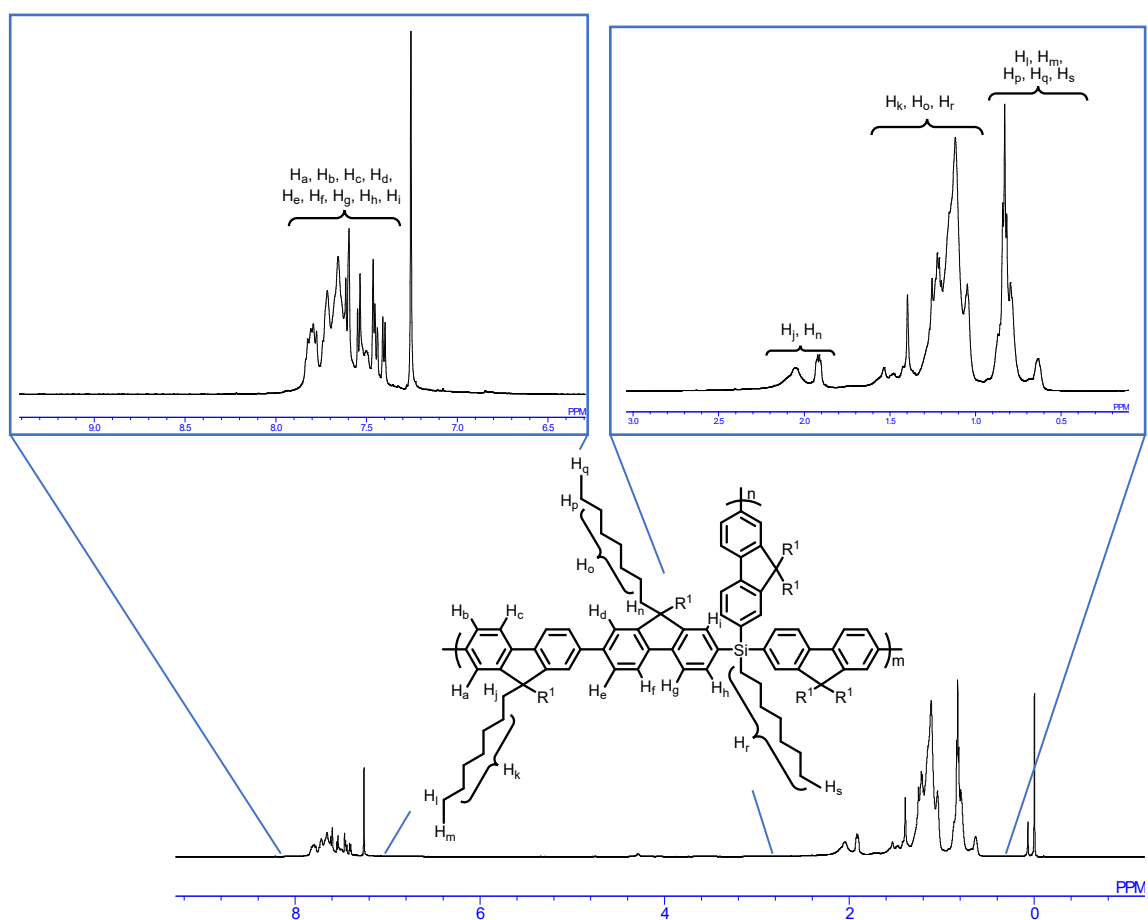
**Fig. S20.**  $^1\text{H}$  NMR spectrum of the polymer obtained by the polymerization of **1c** and **4a'** at room temperature for 3 h (Entry 8).



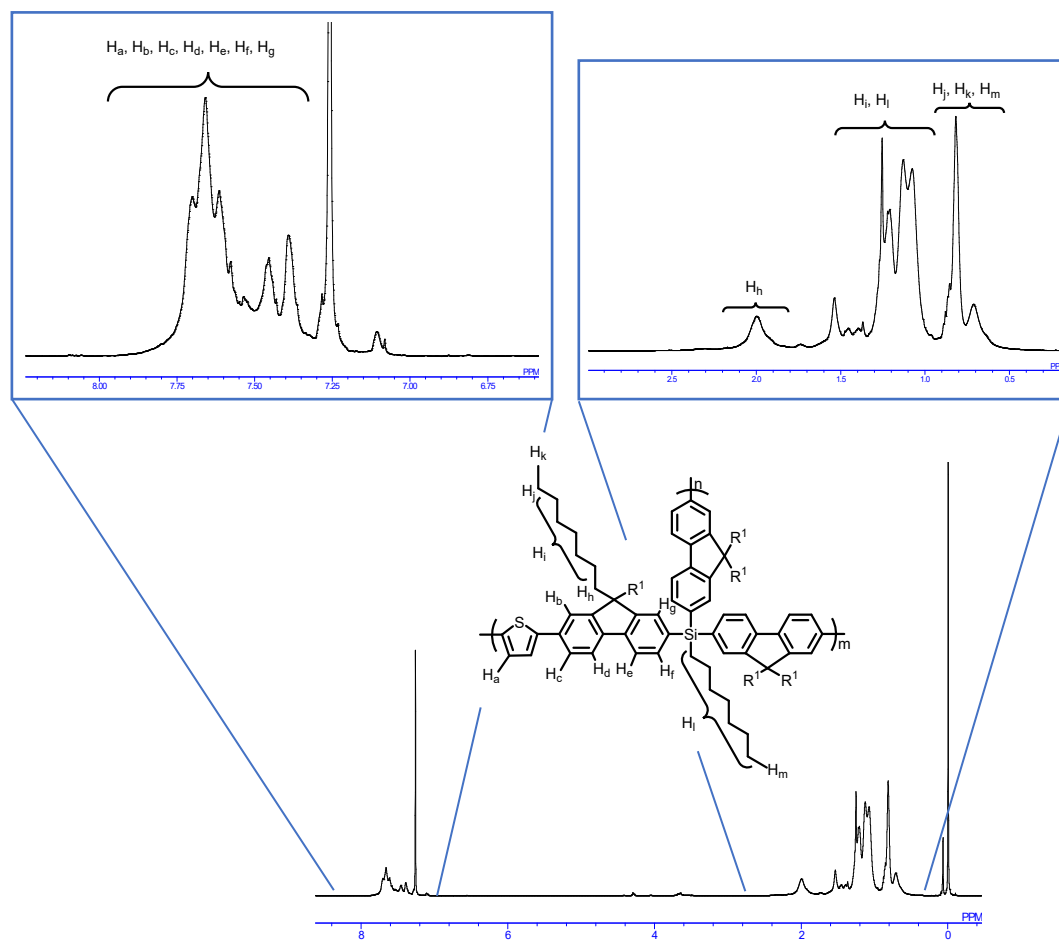
**Fig. S21.** <sup>1</sup>H NMR spectrum of the polymer obtained by the polymerization of **1c** and **4b** at room temperature for 24 h (Entry 9).



**Fig. S22.**  $^1\text{H}$  NMR spectrum of the polymer obtained by the polymerization of **1b** and **4a** at room temperature for 5 h (Entry 11).

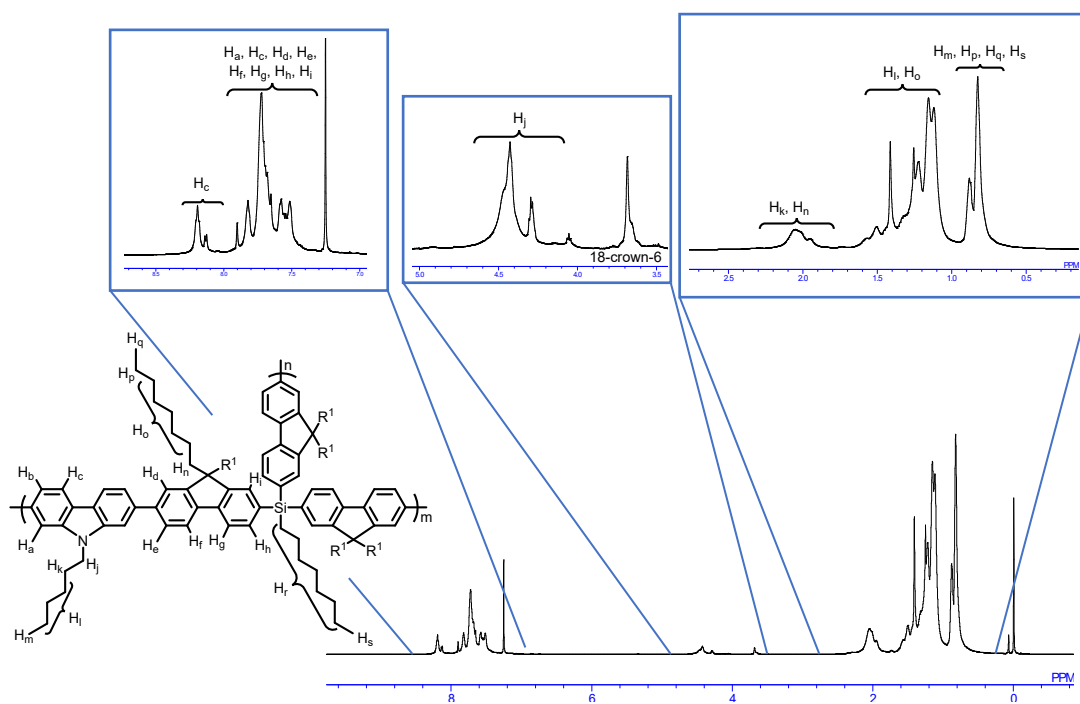


**Fig. S23.**  $^1\text{H}$  NMR spectrum of the polymer obtained by the polymerization of **1b** and **4b** at room temperature for 5 h (Entry 12).



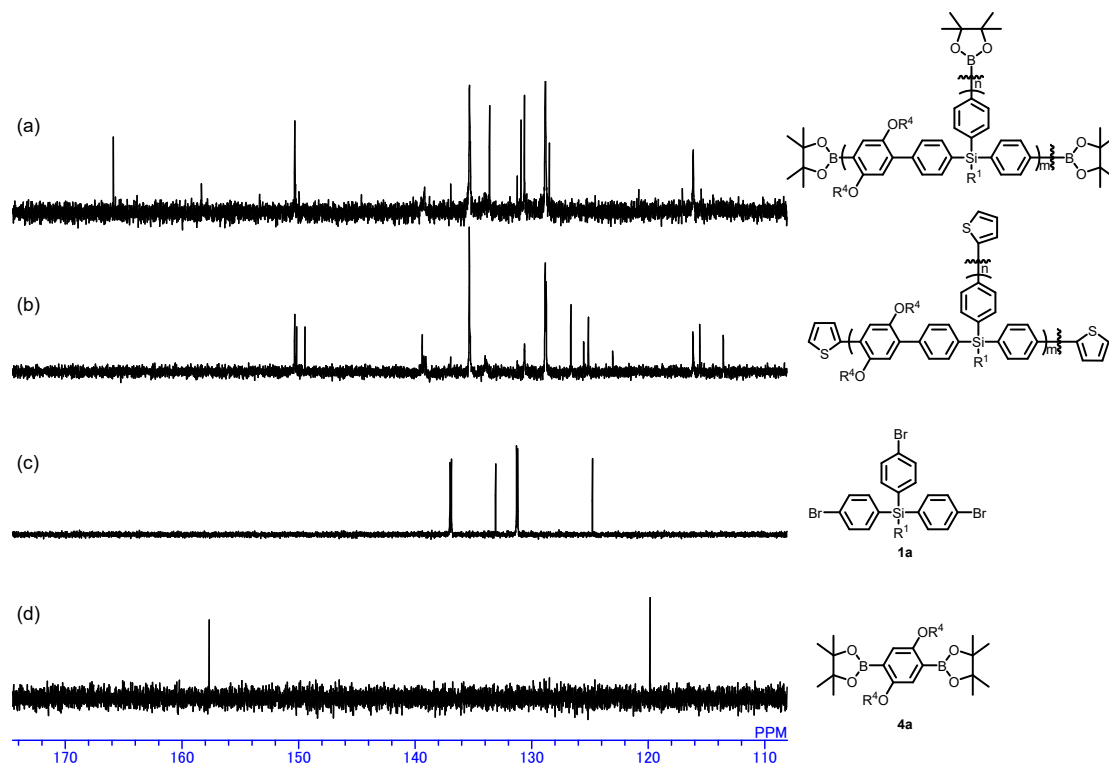
**Fig. S24.**  $^1\text{H}$  NMR spectrum of the polymer obtained by the polymerization of **1b** and **4c** at room temperature for 4 h (Entry 13).



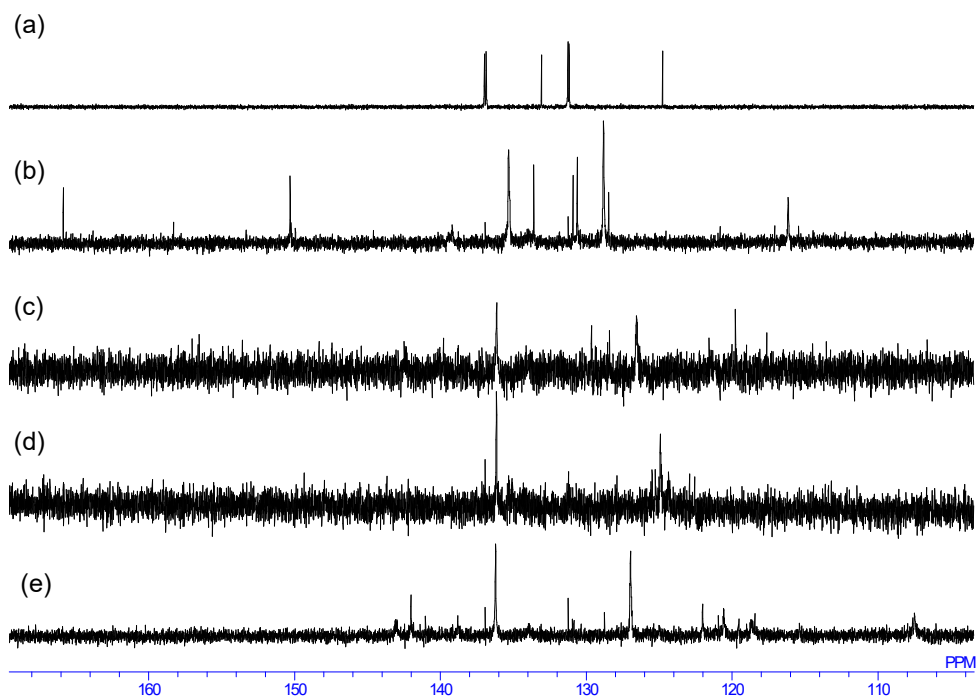


**Fig. S25.**  $^1\text{H}$  NMR spectrum of the polymer obtained by the polymerization of **1b** and **4d'** at room temperature for 5 h (Entry 14).

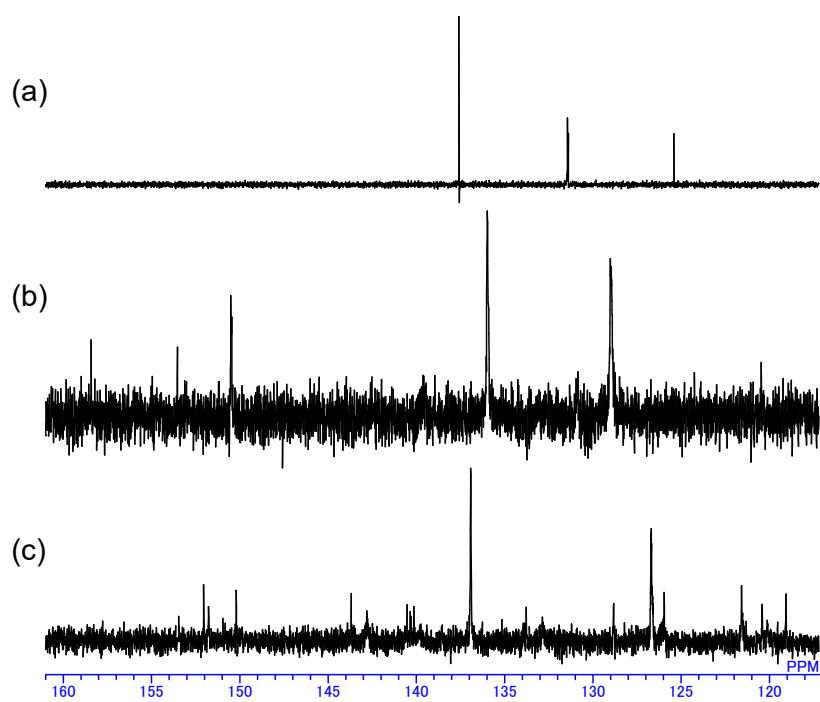
## 5-5. $^{13}\text{C}$ NMR spectra



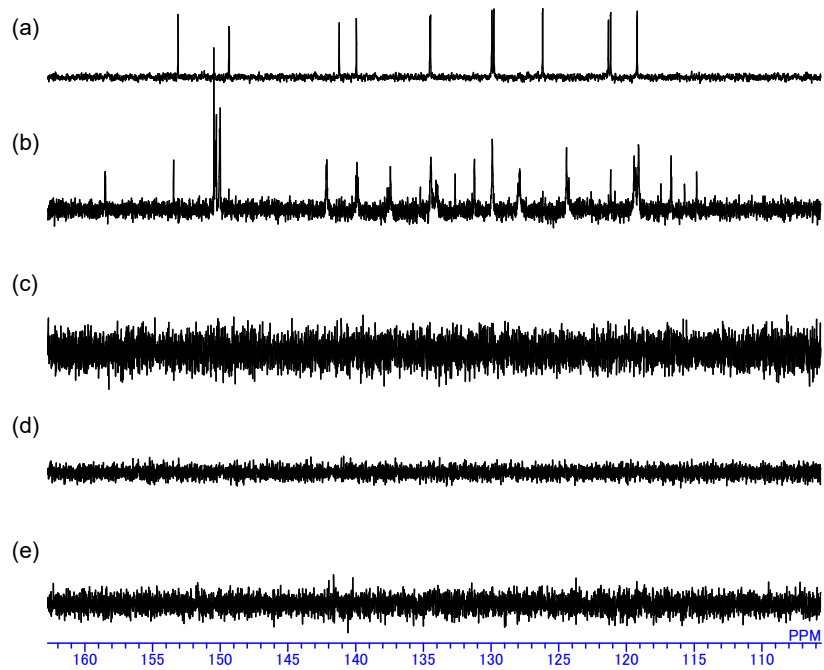
**Fig. S26.**  $^{13}\text{C}$  NMR spectra of (a) Entry 1, (b) end-capping with 2-bromothiophene, (c) **1a**, and (d) **4a**.



**Fig. S27.** <sup>13</sup>C NMR of (a) **1a**, (b) Entry 1, (c) Entry 4, (d) Entry 5, and (e) Entry 7.

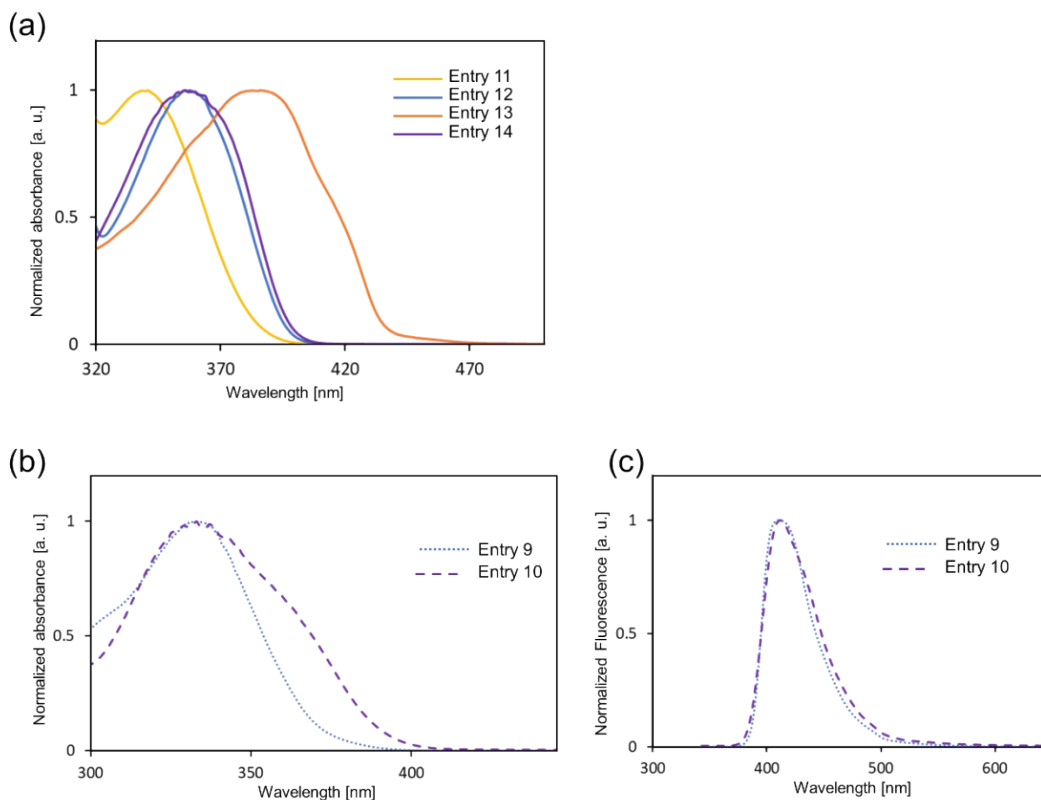


**Fig. S28.**  $^{13}\text{C}$  NMR of (a) **1c**, (b) Entry 8, and (c) Entry 9.



**Fig. S29.**  $^{13}\text{C}$  NMR of (a) **1b**, (b) Entry 11, (c) Entry 12, (d) Entry 13, and (e) Entry 14.

## 5-6. UV-vis absorption and fluorescence spectra



**Fig. S30.** (a) and (b) UV-vis absorption spectra of Table 2, Entries 9, 10, 11, 12, 13, and 14 in chloroform solution. (c) Fluorescence spectra of Table 2, Entries 9 and 10 in chloroform solution.

## 6. References

1. H. Sugita, M. Nojima, Y. Ohta and T. Yokozawa, *Polym. Chem.*, 2019, **10**, 1182-1185.
2. M. Nojima, K. Kosaka, M. Kato, Y. Ohta and T. Yokozawa, *Macromol. Rapid Commun.*, 2016, **37**, 79-85.
3. H. Yu, C. Shen, M. Tian, J. Qu and Z. Wang, *Macromolecules*, 2012, **45**, 5140-5150.