

*Electronic Supplementary Information for*

**Commercially available palladium salts as practical and green  
single-component catalysts in coordination polymerization of 1-  
chloro-2-phenylacetylenes in air**

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## Table of Contents

<b>EXPERIMENTAL SECTION</b> .....	1
<b>Materials</b> .....	1
<b>General Methods</b> .....	1
<b>Synthesis of 1-(chloroethynyl)-4-methylbenzene (c)</b> .....	2
<b>Synthesis of (chloroethynyl)benzene (a)</b> .....	2
<b>Synthesis of 1-(chloroethynyl)-3-methylbenzene (b)</b> .....	2
<b>Synthesis of 1-(chloroethynyl)-4-methoxybenzene (d)</b> .....	2
<b>Synthesis of 1-(chloroethynyl)-4-fluorobenzene (e)</b> .....	2
<b>Synthesis of 1-chloro-4-(chloroethynyl)benzene (f)</b> .....	3
<b>Synthesis of ethyl 4-(chloroethynyl)benzoate (i)</b> .....	3
<b>Synthesis of 1-(4-(chloroethynyl)phenyl)ethan-1-one (g)</b> .....	3
<b>Synthesis of methyl 4-(chloroethynyl) benzoate (h)</b> .....	3
<b>Synthesis of 1-(chloroethynyl)-4-nitrobenzene (j)</b> .....	4
<b>Typical procedure for the polymerization of 1-chloro-2-phenylacetylenes</b> .....	4
<b>Figure S1. <sup>1</sup>H NMR spectrum of a in CDCl<sub>3</sub></b> .....	5
<b>Figure S2. <sup>1</sup>H NMR spectrum of b in CDCl<sub>3</sub></b> .....	5
<b>Figure S3. <sup>1</sup>H NMR spectrum of c in CDCl<sub>3</sub></b> .....	6
<b>Figure S4. <sup>1</sup>H NMR spectrum of d in CDCl<sub>3</sub></b> .....	6
<b>Figure S5. <sup>1</sup>H NMR spectrum of e in CDCl<sub>3</sub></b> .....	6
<b>Figure S6. <sup>1</sup>H NMR spectrum of f in CDCl<sub>3</sub></b> .....	7
<b>Figure S7. <sup>1</sup>H NMR spectrum of g in CDCl<sub>3</sub></b> .....	7
<b>Figure S8. <sup>1</sup>H NMR spectrum of h in CDCl<sub>3</sub></b> .....	8
<b>Figure S9. <sup>1</sup>H NMR spectrum of i in CDCl<sub>3</sub></b> .....	8
<b>Figure S10. <sup>1</sup>H NMR spectrum of j in CDCl<sub>3</sub></b> .....	9
<b>Figure S11. <sup>1</sup>H NMR spectrum of Poly(a) in CDCl<sub>3</sub> (Table 1, entry 20)</b> .....	9

<b>Figure S12.</b> <sup>1</sup> H NMR spectrum of Poly( <b>b</b> ) in CDCl <sub>3</sub> (Table 1, entry 21).....	10
<b>Figure S13.</b> <sup>1</sup> H NMR spectrum of Poly( <b>c</b> ) in CDCl <sub>3</sub> (Table 1, entry 2).....	10
<b>Figure S14.</b> <sup>1</sup> H NMR spectrum of Poly( <b>d</b> ) in CDCl <sub>3</sub> (Table 1, entry 22).....	11
<b>Figure S15.</b> <sup>1</sup> H NMR spectrum of Poly( <b>e</b> ) in CDCl <sub>3</sub> (Table 1, entry 23).....	11
<b>Figure S16.</b> <sup>1</sup> H NMR spectrum of Poly( <b>f</b> ) in CDCl <sub>3</sub> (Table 1, entry 24) .....	12
<b>Figure S17.</b> <sup>1</sup> H NMR spectrum of Poly( <b>g</b> ) in CDCl <sub>3</sub> (Table 1, entry 10).....	12
<b>Figure S18.</b> <sup>1</sup> H NMR spectrum of Poly( <b>h</b> ) in CDCl <sub>3</sub> (Table 1, entry 25).....	13
<b>Figure S19.</b> <sup>1</sup> H NMR spectrum of Poly( <b>i</b> ) in CDCl <sub>3</sub> (Table 1, entry 26).....	13
<b>Figure S20.</b> <sup>1</sup> H NMR spectrum of Poly( <b>j</b> ) in CDCl <sub>3</sub> (Table 1, entry 27) .....	14
<b>Figure S21.</b> FT-IR spectra of <b>a</b> and Poly( <b>a</b> ) (Table 1, entry 20) .....	14
<b>Figure S22.</b> FT-IR spectra of <b>b</b> and Poly( <b>b</b> ) (Table 1, entry 21).....	15
<b>Figure S23.</b> FT-IR spectra of <b>c</b> and Poly( <b>c</b> ) (Table 1, entry 2).....	15
<b>Figure S24.</b> FT-IR spectra of <b>d</b> and Poly( <b>d</b> ) (Table 1, entry 22).....	16
<b>Figure S25.</b> FT-IR spectra of <b>e</b> and Poly( <b>e</b> ) (Table 1, entry 23).....	16
<b>Figure S26.</b> FT-IR spectra of <b>f</b> and Poly( <b>f</b> ) (Table 1, entry 24).....	17
<b>Figure S27.</b> FT-IR spectra of <b>g</b> and Poly( <b>g</b> ) (Table 1, entry 10) .....	17
<b>Figure S28.</b> FT-IR spectra of <b>h</b> and Poly( <b>h</b> ) (Table 1, entry 25).....	18
<b>Figure S29.</b> FT-IR spectra of <b>i</b> and Poly( <b>i</b> ) (Table 1, entry 26) .....	18
<b>Figure S30.</b> FT-IR spectra of <b>j</b> and Poly( <b>j</b> ) (Table 1, entry 27).....	19
<b>Figure S31.</b> Raman spectra of poly( <b>j</b> ) (Table 1, entry 27).....	19
<b>Figure S32.</b> PXRD curves of poly( <b>a</b> ) (Table 1, entry 20).....	20
<b>Figure S33.</b> PXRD curves of poly( <b>b</b> ) (Table 1, entry 22) .....	20
<b>Figure S34.</b> PXRD curves of poly( <b>c</b> ) (Table 1, entry 2).....	20
<b>Figure S35.</b> PXRD curves of poly( <b>d</b> ) (Table 1, entry 22) .....	21
<b>Figure S36.</b> PXRD curves of poly( <b>e</b> ) (Table 1, entry 23).....	21
<b>Figure S37.</b> PXRD curves of poly( <b>f</b> ) (Table 1, entry 24) .....	21
<b>Figure S38.</b> PXRD curves of poly( <b>g</b> ) (Table 1, entry 10).....	22
<b>Figure S39.</b> PXRD curves of poly( <b>h</b> ) (Table 1, entry 25) .....	22

<b>Figure S40.</b> PXRD curves of poly( <b>i</b> ) (Table 1, entry 26) .....	22
<b>Figure S41.</b> PXRD curves of poly( <b>j</b> ) (Table 1, entry 27) .....	23
<b>Figure S42.</b> GPC curve of poly( <b>c</b> ) obtained by <b>Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub></b> in Table 1, entry 2 .....	23
<b>Figure S43.</b> GPC curve of poly( <b>c</b> ) obtained by <b>Pd(C<sub>6</sub>H<sub>5</sub>CN)<sub>2</sub>Cl<sub>2</sub></b> in Table 1, entry 3.....	24
<b>Figure S44.</b> GPC curve of poly( <b>g</b> ) obtained by <b>Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub></b> in Table 1, entry 7.....	24
<b>Figure S45.</b> GPC curve of poly( <b>g</b> ) obtained by <b>Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub></b> in Table 1, entry 8.....	25
<b>Figure S46.</b> GPC curve of poly( <b>g</b> ) obtained by <b>Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub></b> in Table 1, entry 9.....	25
<b>Figure S47.</b> GPC curve of poly( <b>g</b> ) obtained by <b>Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub></b> in Table 1, entry 10.....	26
<b>Figure S48.</b> GPC curve of poly( <b>g</b> ) obtained by <b>Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub></b> in Table 1, entry 11.....	26
<b>Figure S49.</b> GPC curve of poly( <b>g</b> ) obtained by <b>Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub></b> in Table 1, entry 12.....	27
<b>Figure S50.</b> GPC curve of poly( <b>g</b> ) obtained by <b>Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub></b> in Table 1, entry 13.....	27
<b>Figure S51.</b> GPC curve of poly( <b>g</b> ) obtained by <b>Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub></b> in Table 1, entry 14.....	28
<b>Figure S52.</b> GPC curve of poly( <b>g</b> ) obtained by <b>Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub></b> in Table 1, entry 15.....	28
<b>Figure S53.</b> GPC curve of poly( <b>c</b> ) obtained by <b>Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub></b> in Table 1, entry 16.....	29
<b>Figure S54.</b> GPC curve of poly( <b>c</b> ) obtained by <b>Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub></b> in Table 1, entry 18.....	29
<b>Figure S55.</b> GPC curve of poly( <b>d</b> ) obtained by <b>Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub></b> in Table 1, entry 22.....	30
<b>Figure S56.</b> GPC curve of poly( <b>h</b> ) obtained by <b>Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub></b> in Table 1, entry 25.....	30
<b>Figure S57.</b> GPC curve of poly( <b>i</b> ) obtained by <b>Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub></b> in Table 1, entry 26.....	31
<b>References</b> .....	31

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## EXPERIMENTAL SECTION

### Materials

Anhydrous toluene and THF were purified by use of a SPS-800 solvent purification system (Mbraun). Chlorobenzene, 1,4-dichlorobenzene, 1,1,2,2-tetrachloroethane were distilled from CaH<sub>2</sub> to get rid of moisture and stored in a brown bottle with 4 Å molecular sieves. Methanol, ethanol, acetonitrile, petroleum ether, dichloromethane, n-hexane, carbon tetrachloride and trichloromethane were purchased from J&K Scientific Ltd. Pd(CH<sub>2</sub>CN)<sub>2</sub>Cl<sub>2</sub>, Pd(CH<sub>2</sub>CN)<sub>2</sub>Cl<sub>2</sub>, Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, Pd/C, Pd(OAc)<sub>2</sub>, PdCl<sub>2</sub>, AgNO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, NEt<sub>3</sub>, CuI, triphenylphosphine, phenylacetylene, 4-ethynyltoluene, 3-ethynyltoluene, 4-chlorophenylacetylene, 4-fluorophenylacetylene, 1-ethynyl-naphthalene, 4-methoxyphenylacetylene, trimethylsilylacetylene, tetrabutylammonium fluoride (TBAF), N-chlorosuccinimide (NCS), 4-methylmorpholine, 2-methyl-1-propylchlorocarbonate, 4-bromobenzoic acid, 4-bromoacetophenone and 1-bromo-4-nitrobenzene were purchased from Energy Chemistry. The deuterated solvents 1,1,2,2-tetrachloroethane-*d*<sub>2</sub> (99.6 atom% D) and chloroform-*d*<sub>1</sub> (99.8 atom% D) were obtained from Cambridge Isotope.

### General Methods.

The <sup>1</sup>H, <sup>13</sup>C NMR spectra of Pd complexes and the <sup>1</sup>H NMR spectra of all the polymers were recorded on an AVANCE 400 spectrometer at room temperature with CDCl<sub>3</sub> as a solvent. The molecular weights and molecular weight distributions (*M*<sub>w</sub>/*M*<sub>n</sub>) of polymers were determined against polystyrene standard at 25 °C by GPC on a Water HLC-8320 GPC apparatus, THF was used as the eluent at a flow rate of 1 mL/min. FT-IR spectra was recorded on a Thermo IS5 FT-IR system using KBr pellets at room temperature. High resolution mass spectra was collected on an Agilent 6520 Accurate-Mass Q-TOF LC/MS. Differential scanning calorimetry (DSC) was performed on a DSC-60. Thermo-gravimetric analysis (TGA) was performed on a TG-DTA 6200 at a scanning rate of 10 °C min<sup>-1</sup> under N<sub>2</sub>.

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### **Synthesis of 1-(chloroethynyl)-4-methylbenzene (c)<sup>1</sup>**

4-Ethynyltoluene (1.31 mL, 10 mmol) and potassium carbonate (2.76 g, 20 mmol) were dissolved in CCl<sub>4</sub> (10 mL) under an atmosphere of nitrogen, TBAF (1 M in THF 5 mL, 5 mmol) was added dropwise to the mixture, the resulting mixture was stirred at 25 °C for 3 h. Finally, the mixture was filtered and concentrated under reduced pressure, the residue was purified by column chromatography (silica gel, PE) to afford the desired compound **a** as a colourless liquid in 85% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.34 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 2.35 (s, 3H).

### **Synthesis of (chloroethynyl)benzene (a)**

The synthetic procedure was the same with that of compound **c**. The residue was purified by column chromatography (silica gel, PE) to afford the desired compound **a** as a yellow liquid in 85% yield. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.42 (m, 2H), 7.32 (dt, *J* = 5.6, 1.9 Hz, 3H).

### **Synthesis of 1-(chloroethynyl)-3-methylbenzene (b)**

The synthetic procedure was the same with that of compound **c**. The residue was purified by column chromatography (silica gel, PE) to afford the desired compound **b** as a colourless liquid in 81% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.27 – 7.22 (m, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.14 (d, *J* = 7.0 Hz, 1H), 2.32 (s, 3H).

### **Synthesis of 1-(chloroethynyl)-4-methoxybenzene (d)**

The synthetic procedure was the same with that of compound **c**. The residue was purified by column chromatography (silica gel, PE) to afford the desired compound **d** as a yellow liquid in 86% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.37 (s, 2H), 6.83 (d, *J* = 8.9 Hz, 2H), 3.81 (s, 3H).

### **Synthesis of 1-(chloroethynyl)-4-fluorobenzene (e)**

The synthetic procedure was the same with that of compound **c**. The residue was purified by column chromatography (silica gel, PE) to afford the desired

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compound **e** as a yellow liquid in 82% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.42 (dd, *J* = 8.9, 5.3 Hz, 2H), 7.00 (t, *J* = 8.7 Hz, 2H).

#### **Synthesis of 1-chloro-4-(chloroethynyl)benzene (f)**

The synthetic procedure was the same with that of compound **c**. The residue was purified by column chromatography (silica gel, PE) to afford the desired compound **f** as a white solid in 90% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.37 (d, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 7.6 Hz, 2H).

#### **Synthesis of ethyl 4-(chloroethynyl)benzoate (i)<sup>2</sup>**

Under nitrogen atmosphere, ethyl 4-bromobenzoate (5.7 g, 25 mmol), PPh<sub>3</sub> (360 mg, 1.25 mmol), Pd (PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (630 mg, 0.9 mmol) and CuI (240 mg, 1.25 mmol) were dissolved in 60 mL of Et<sub>3</sub>N, and ethynyltrimethylsilane (7 mL, 50 mmol) was added dropwise to the mixture, the resulting mixture was stirred at 80 °C for 8 h. Finally, the mixture was filtered and washed with brine, dried using anhydrous magnesium sulfate, concentrated under reduced pressure, the residue was purified by column chromatography (silica gel, PE) to afford the desired compound as a yellow liquid in 83% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.90 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H).

#### **Synthesis of 1-(4-(chloroethynyl)phenyl)ethan-1-one (g)**

The synthetic procedure was the same with that of compound **i**. The residue was purified by column chromatography (silica gel, PE) to afford the desired compound **g** as a colourless liquid in 81% yield. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 7.7 Hz, 2H), 7.51 (d, *J* = 7.7 Hz, 2H), 2.59 (s, 3H).

#### **Synthesis of methyl 4-(chloroethynyl) benzoate (h)**

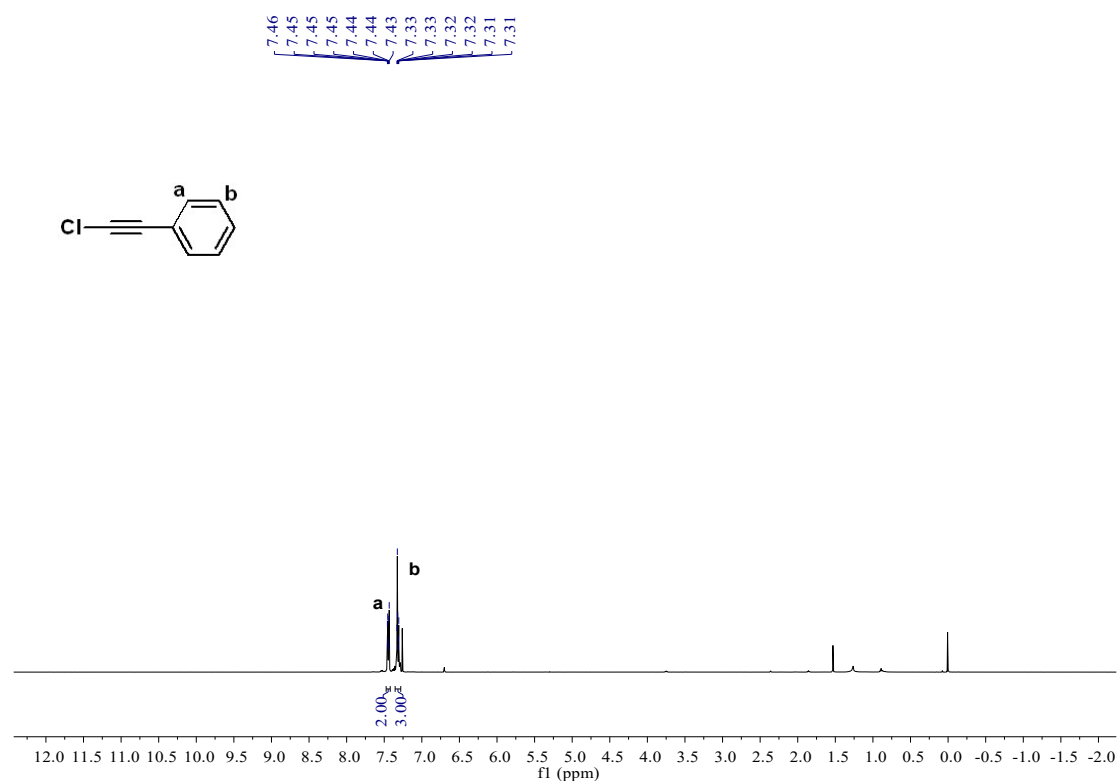
The synthetic procedure was the same with that of compound **i**. The residue was purified by column chromatography (silica gel, PE) to afford the desired compound **h** as a white solid in 88% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.98 (d, *J* = 8.5 Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 2H), 3.92 (s, 3H).

## Synthesis of 1-(chloroethynyl)-4-nitrobenzene (j)

The synthetic procedure was the same with that of compound **i**. The residue was purified by column chromatography (silica gel, PE) to afford the desired compound **j** as a white solid in 91% yield.  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  8.19 (d,  $J = 7.6$  Hz, 2H), 7.59 (d,  $J = 7.6$  Hz, 2H).

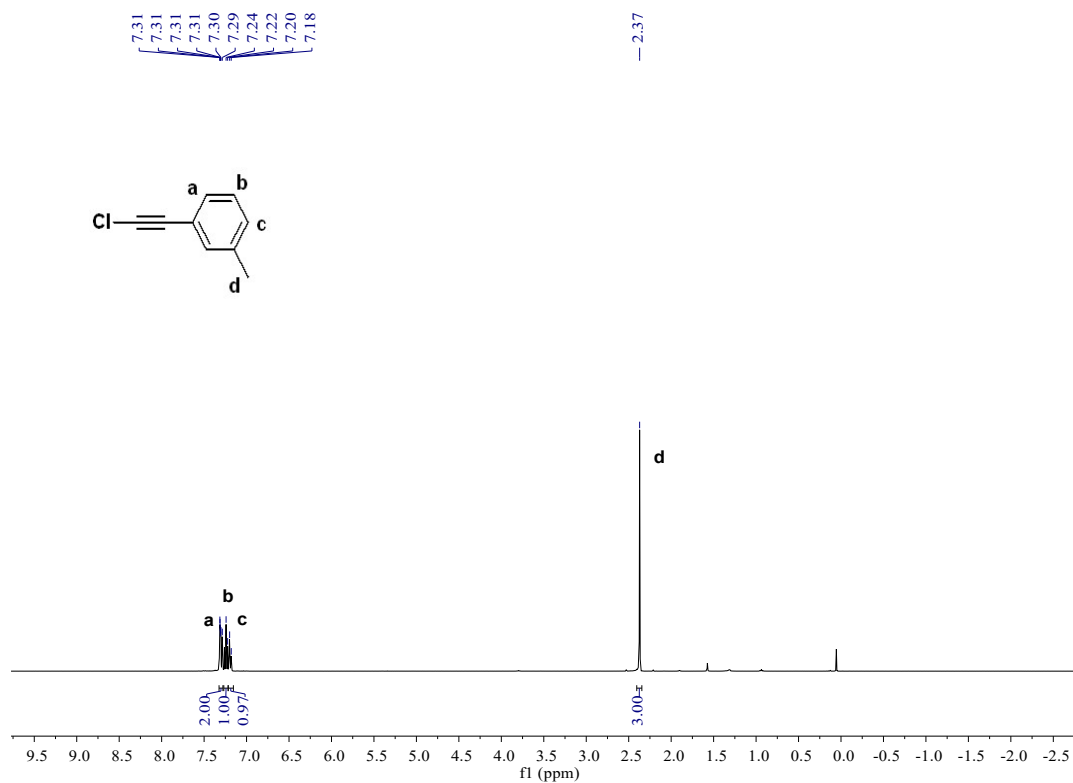
## Typical procedure for the polymerization of 1-chloro-2-phenylacetylenes

Under air atmosphere, a 25 mL round bottom flask was charged with a solution of Pd catalyst (1 equiv., 0.02 mmol) in 1,1,2,2-tetrachloroethane (3 mL) and then added to a solution of monomer (100 equiv., 2 mmol) in 1,1,2,2-tetrachloroethane (3 mL). The reaction mixture was stirred at a preset temperature and time, then the reaction mixture was poured into petroleum ether (100 mL) to precipitate the polymer product, the polymer solid was collected by filtration and washed with petroleum ether three times and dried under vacuum. The PCPAs obtained by the palladium salts showed a main signal around 6.63 ppm and a shoulder peak around 6.96 ppm similar to the *cis*-selective PCPAs obtained by the known Pd catalysts.<sup>3-4</sup>





**Figure S1.**  $^1\text{H}$  NMR spectrum of **a** in  $\text{CDCl}_3$ .



**Figure S2.**  $^1\text{H}$  NMR spectrum of **b** in  $\text{CDCl}_3$ .

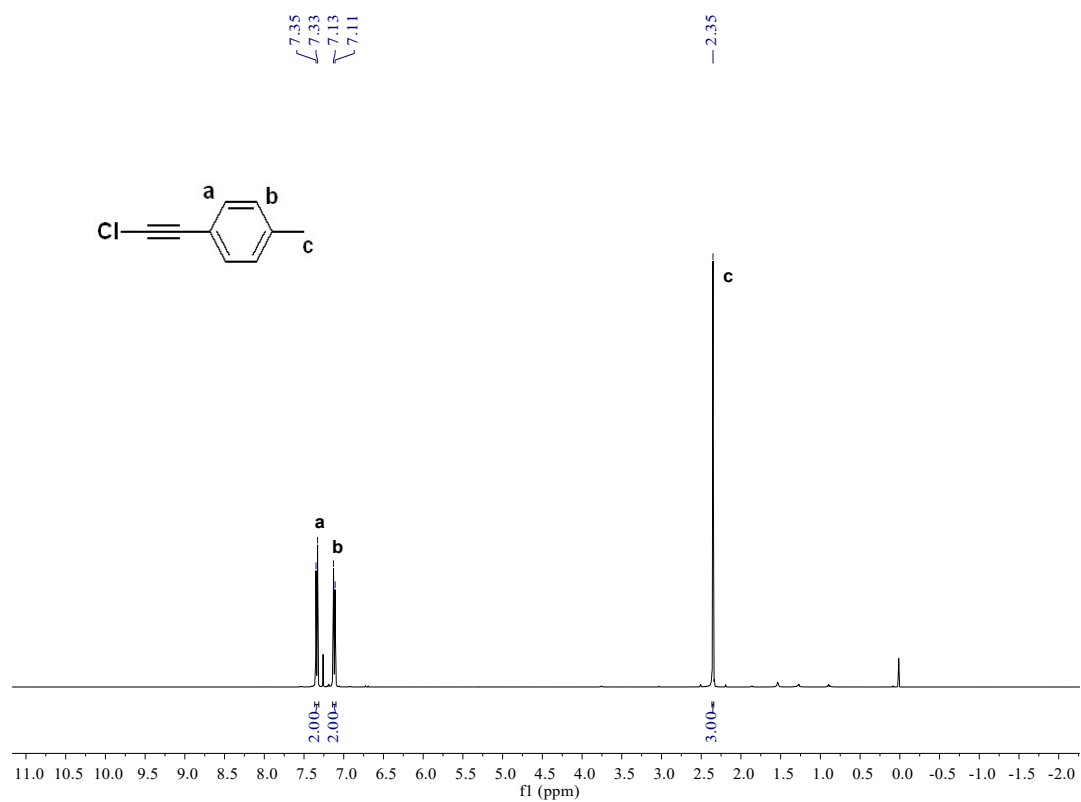


Figure S3.  $^1\text{H}$  NMR spectrum of **c** in  $\text{CDCl}_3$ .

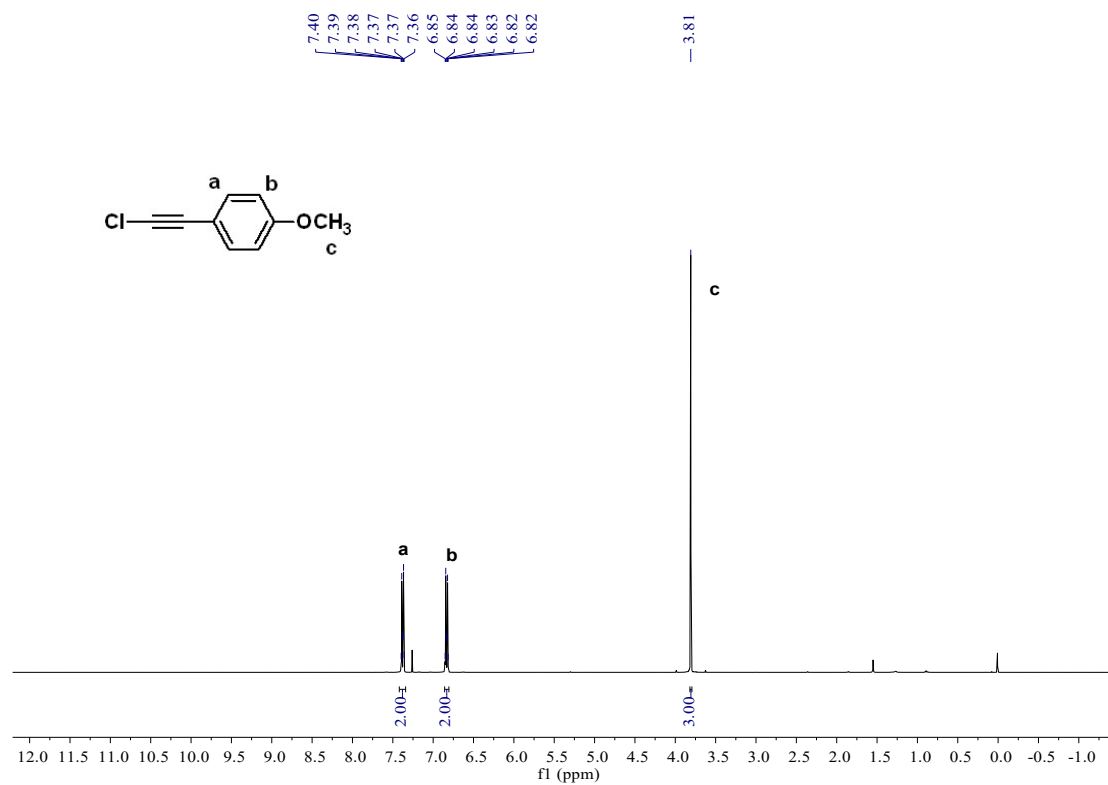


Figure S4.  $^1\text{H}$  NMR spectrum of **d** in  $\text{CDCl}_3$ .

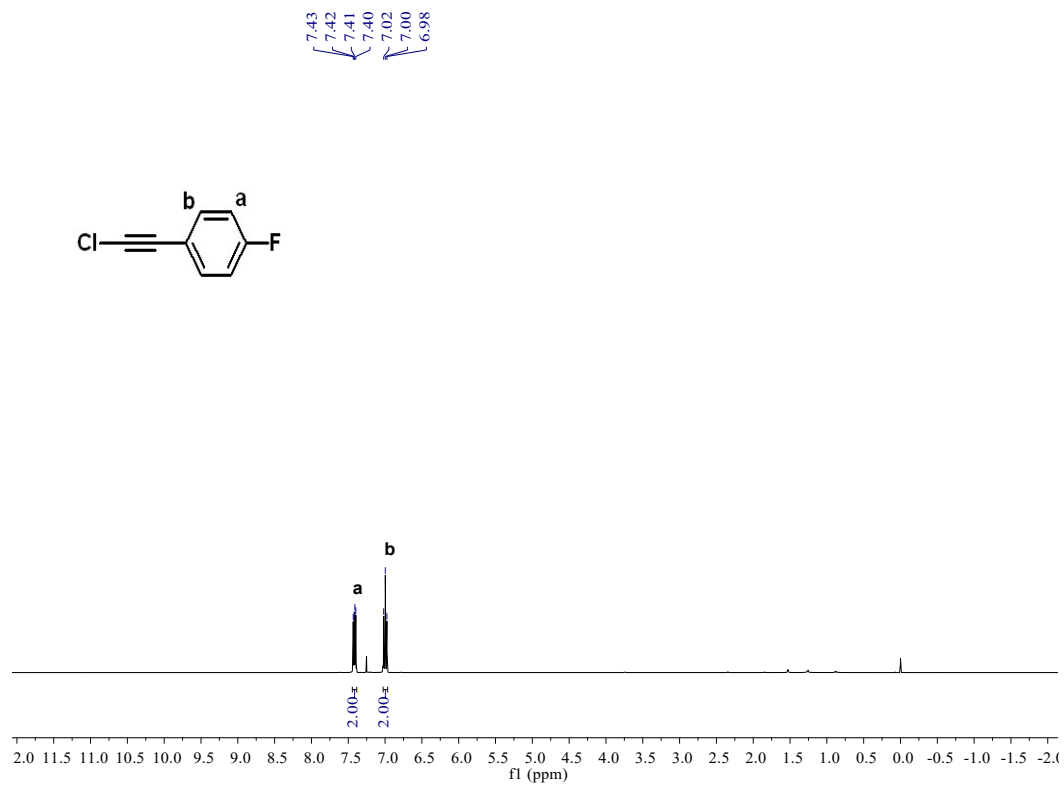
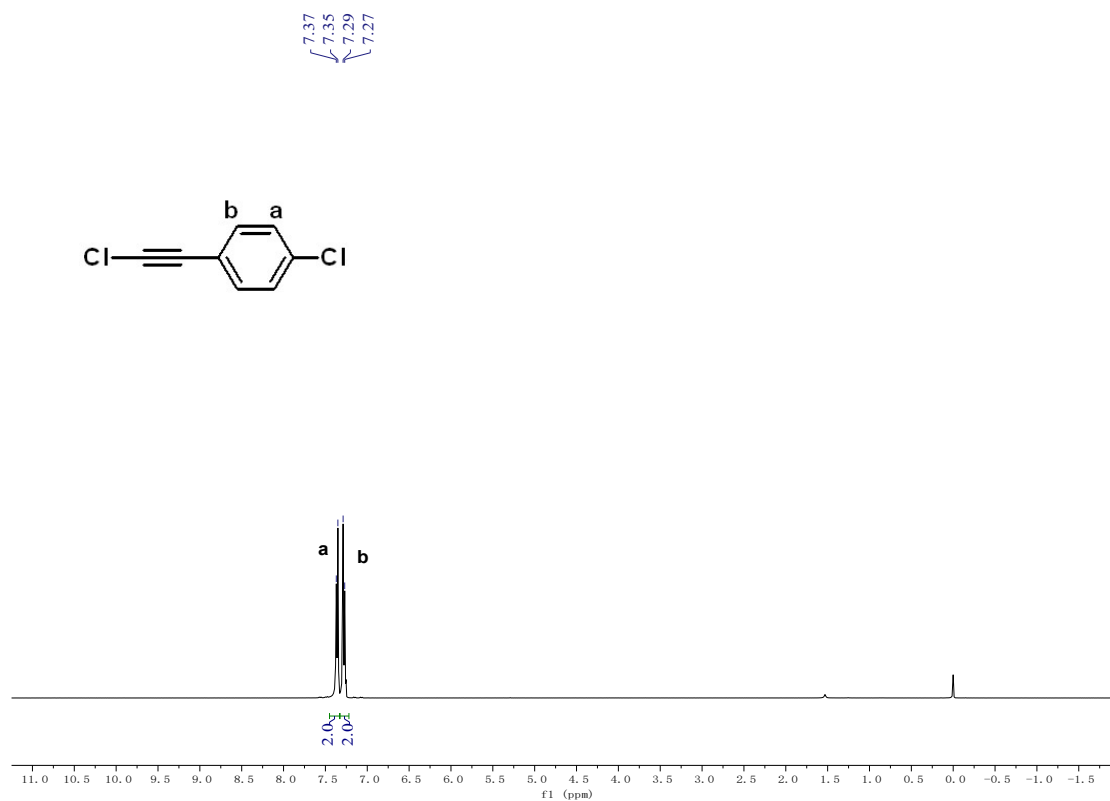
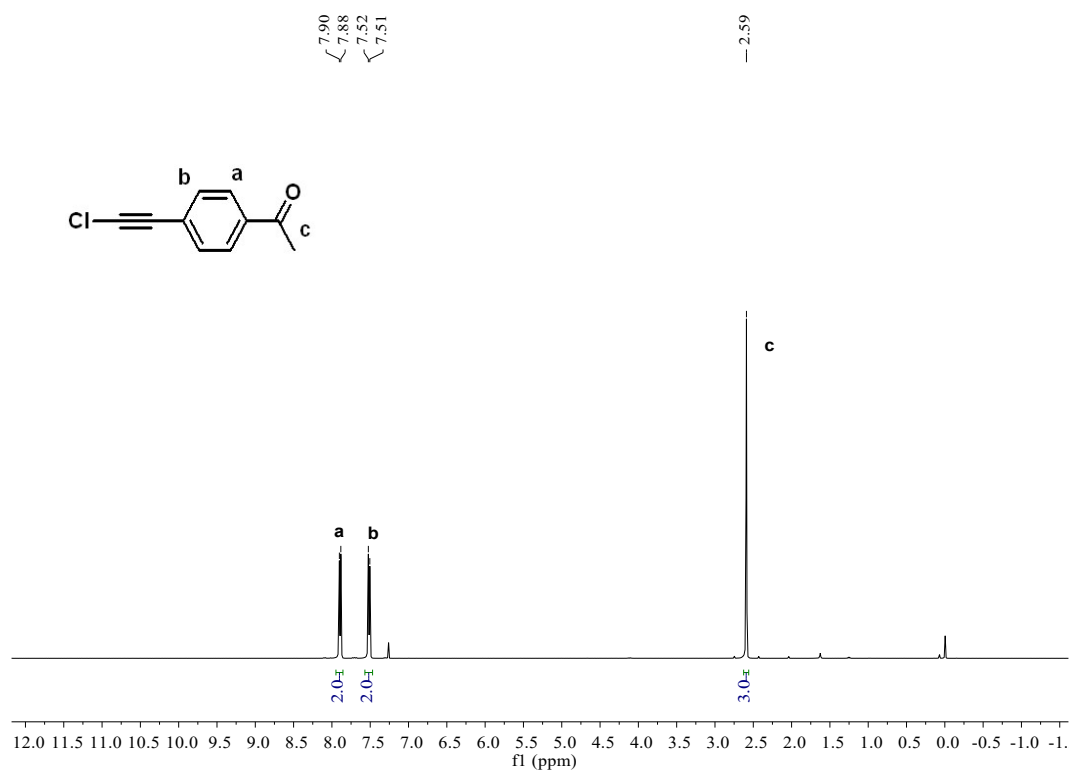


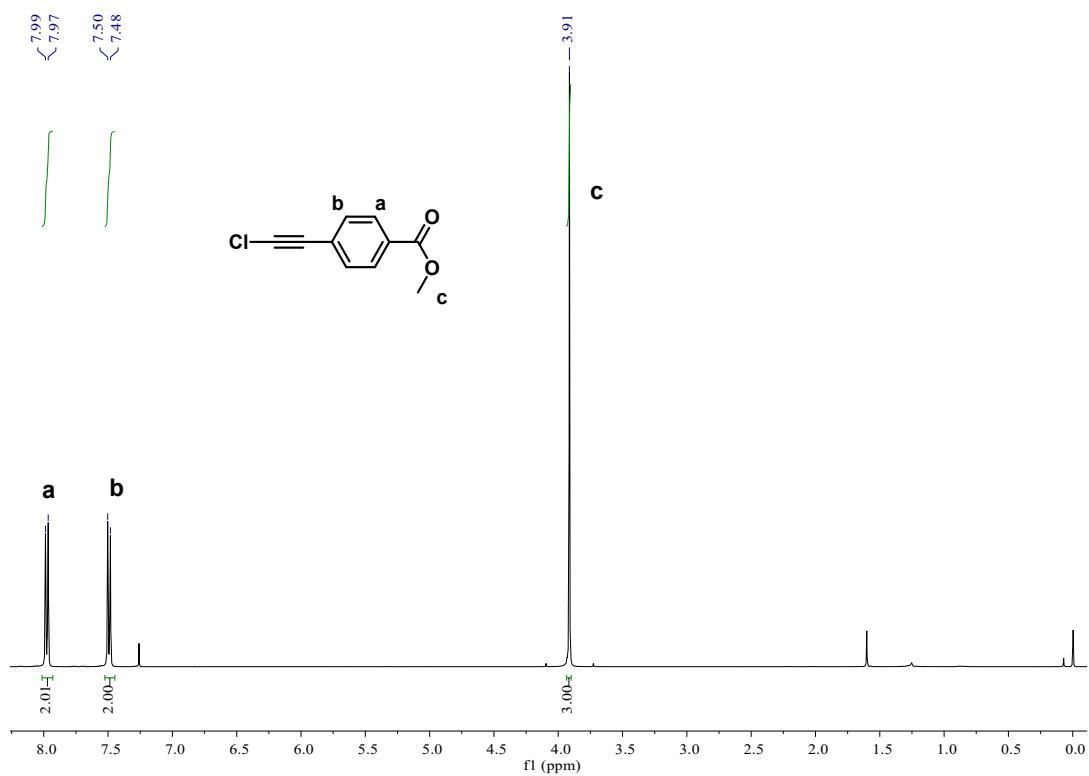
Figure S5.  $^1\text{H}$  NMR spectrum of **e** in  $\text{CDCl}_3$ .



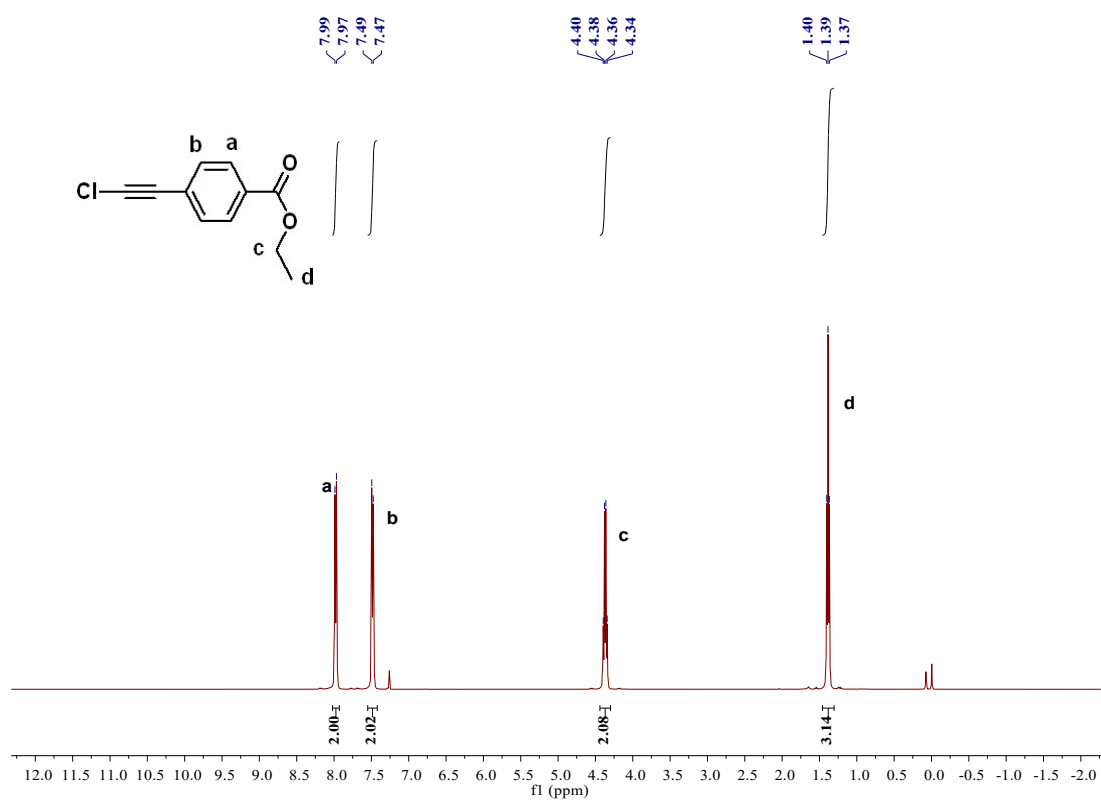
**Figure S6.**  $^1\text{H}$  NMR spectrum of **f** in  $\text{CDCl}_3$ .



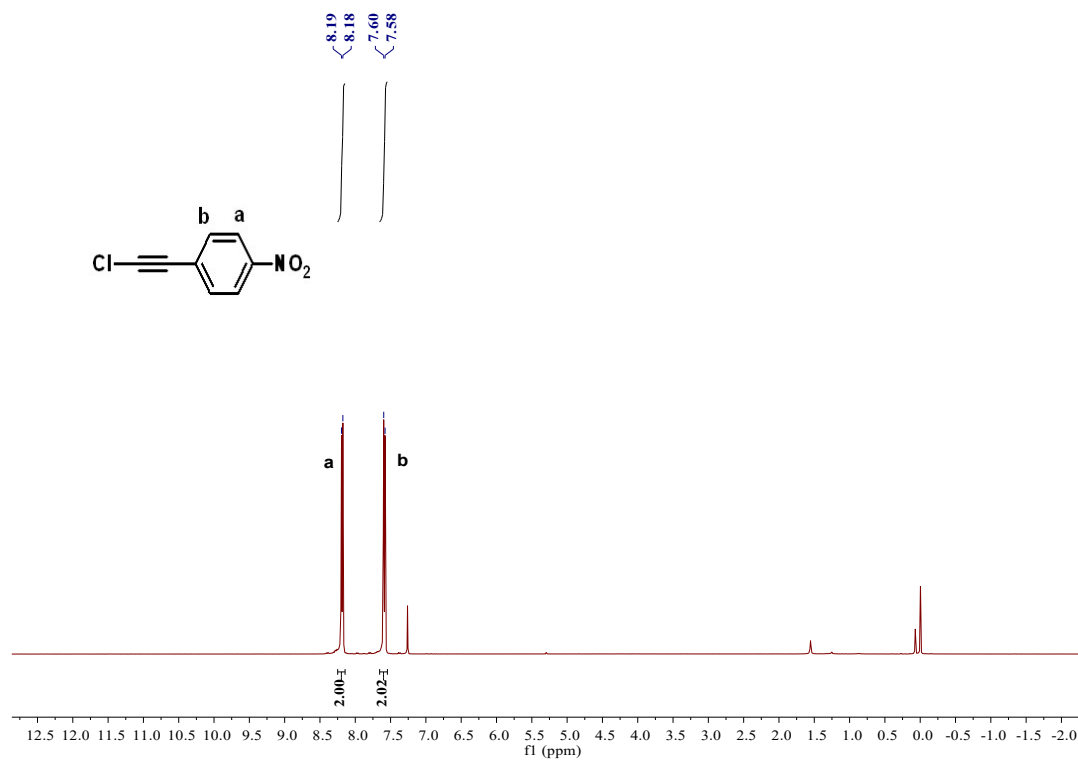
**Figure S7.**  $^1\text{H}$  NMR spectrum of **g** in  $\text{CDCl}_3$ .



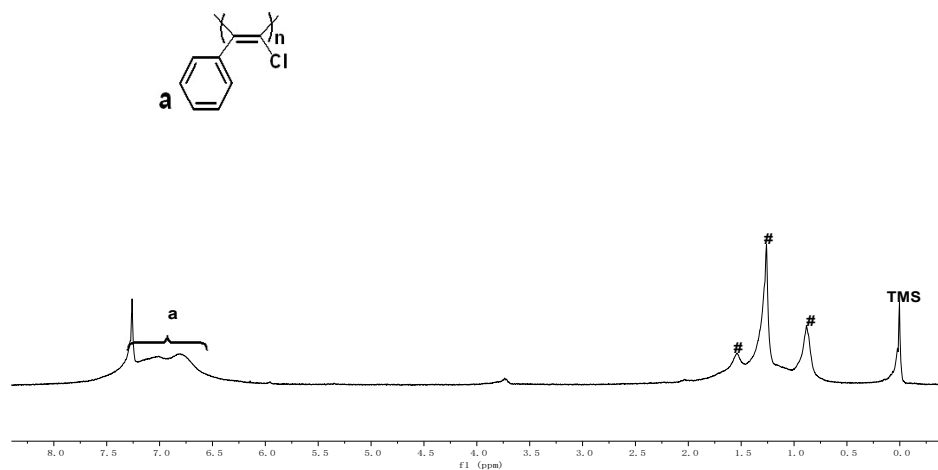
**Figure S8.** <sup>1</sup>H NMR spectrum of **h** in CDCl<sub>3</sub>.



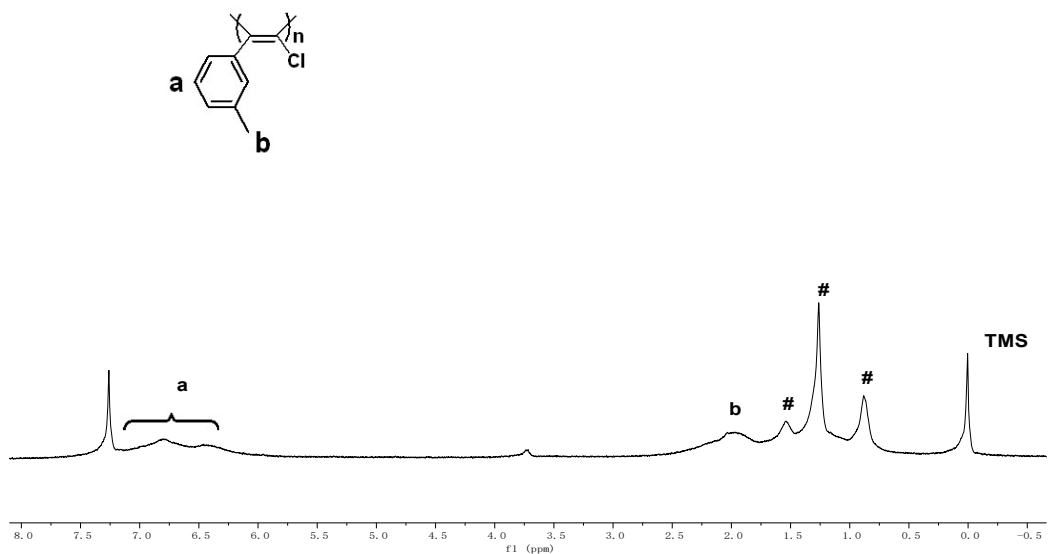
**Figure S9.** <sup>1</sup>H NMR spectrum of **i** in CDCl<sub>3</sub>.



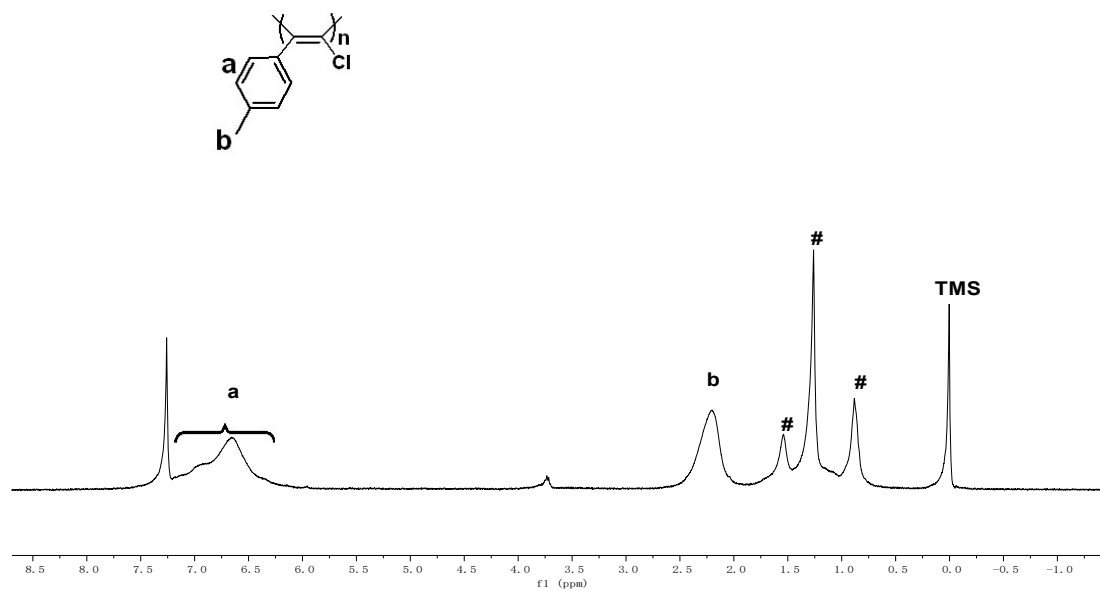
**Figure S10.** <sup>1</sup>H NMR spectrum of **j** in CDCl<sub>3</sub>.



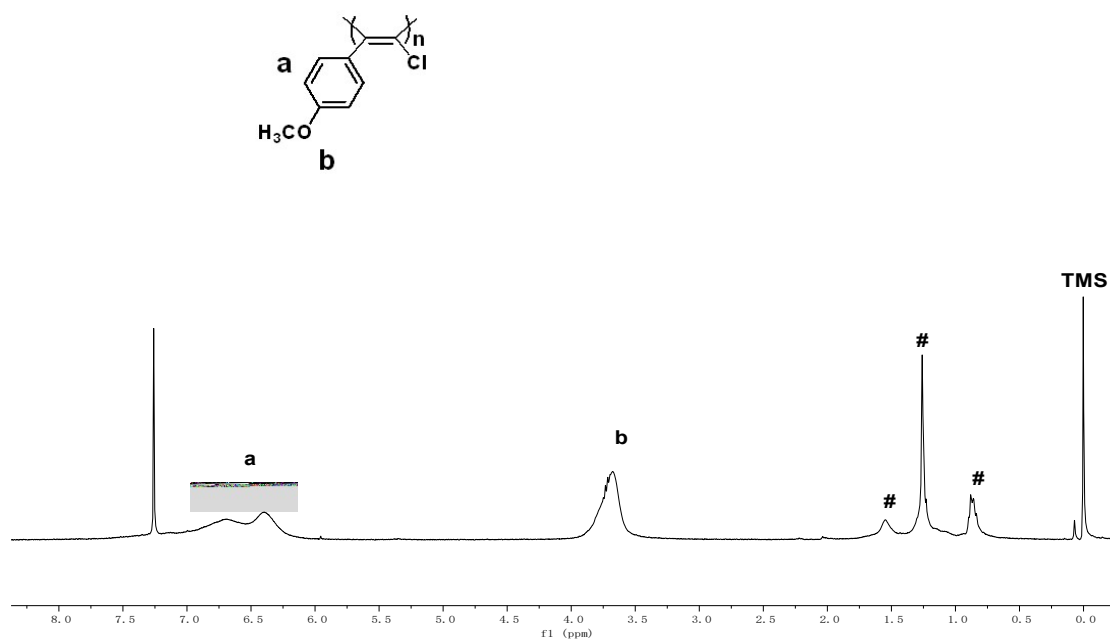
**Figure S11.** <sup>1</sup>H NMR spectrum of Poly(**a**) in CDCl<sub>3</sub> (Table 1, entry 20).



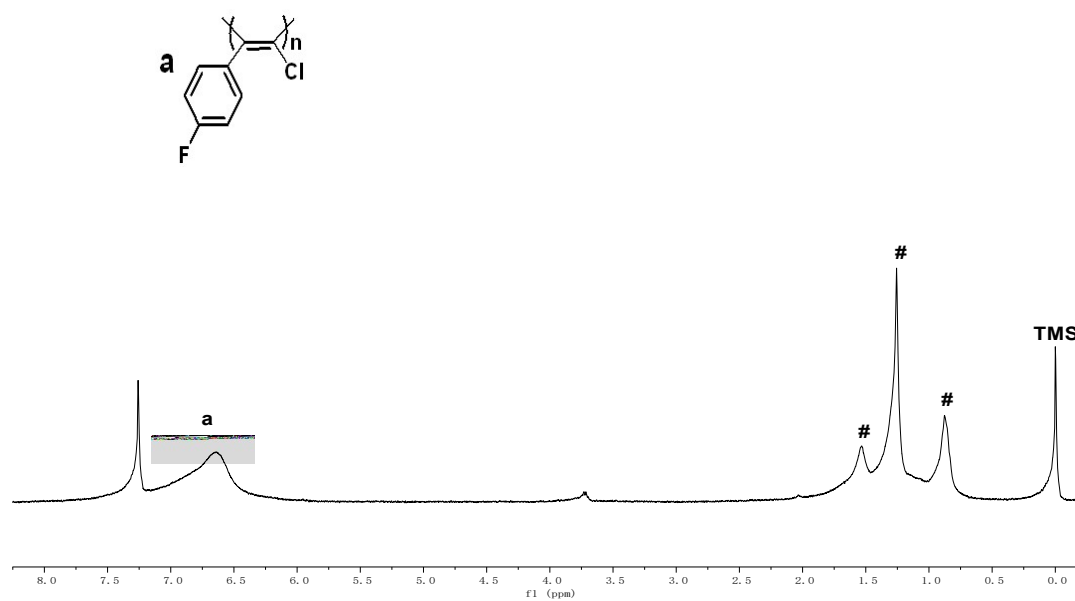
**Figure S12.** <sup>1</sup>H NMR spectrum of Poly(b) in CDCl<sub>3</sub> (Table 1, entry 21).



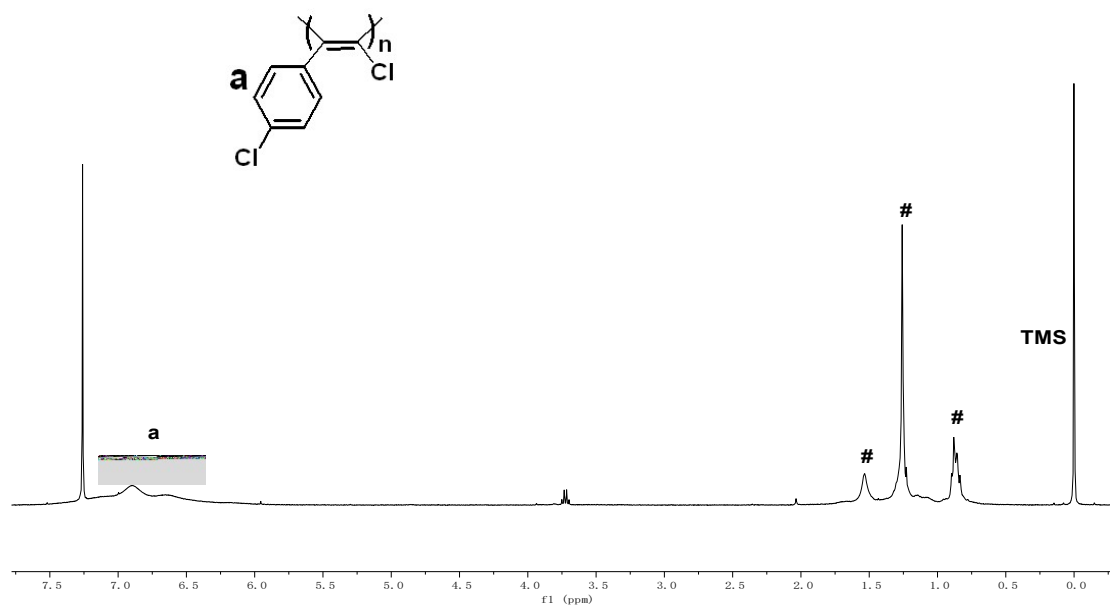
**Figure S13.** <sup>1</sup>H NMR spectrum of Poly(c) in CDCl<sub>3</sub> (Table 1, entry 2).



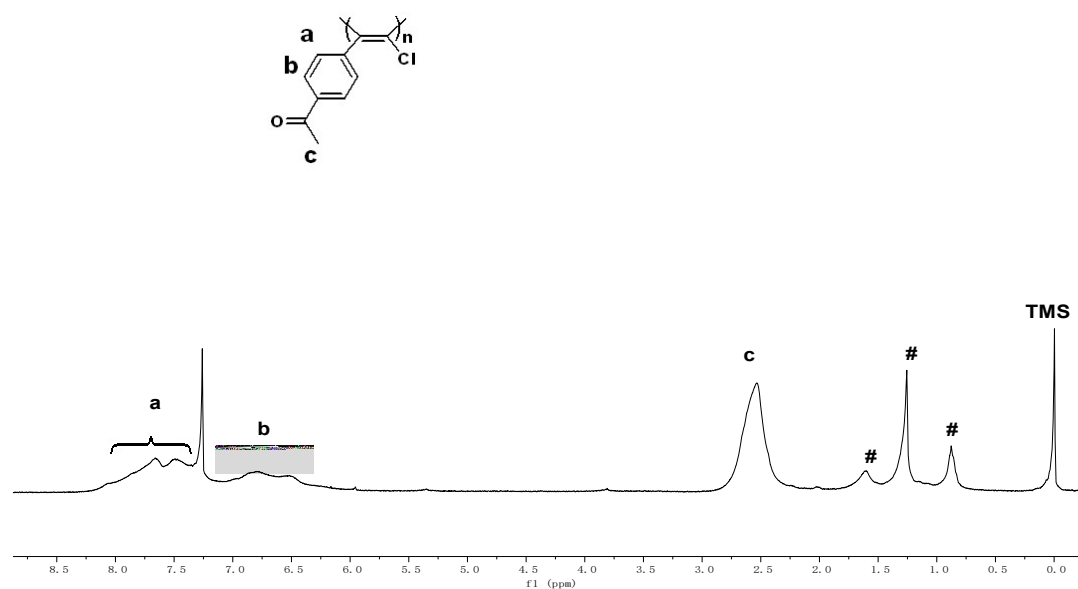
**Figure S14.**  $^1\text{H}$  NMR spectrum of Poly(**d**) in  $\text{CDCl}_3$  (Table 1, entry 22).



**Figure S15.**  $^1\text{H}$  NMR spectrum of Poly(**e**) in  $\text{CDCl}_3$  (Table 1, entry 23).

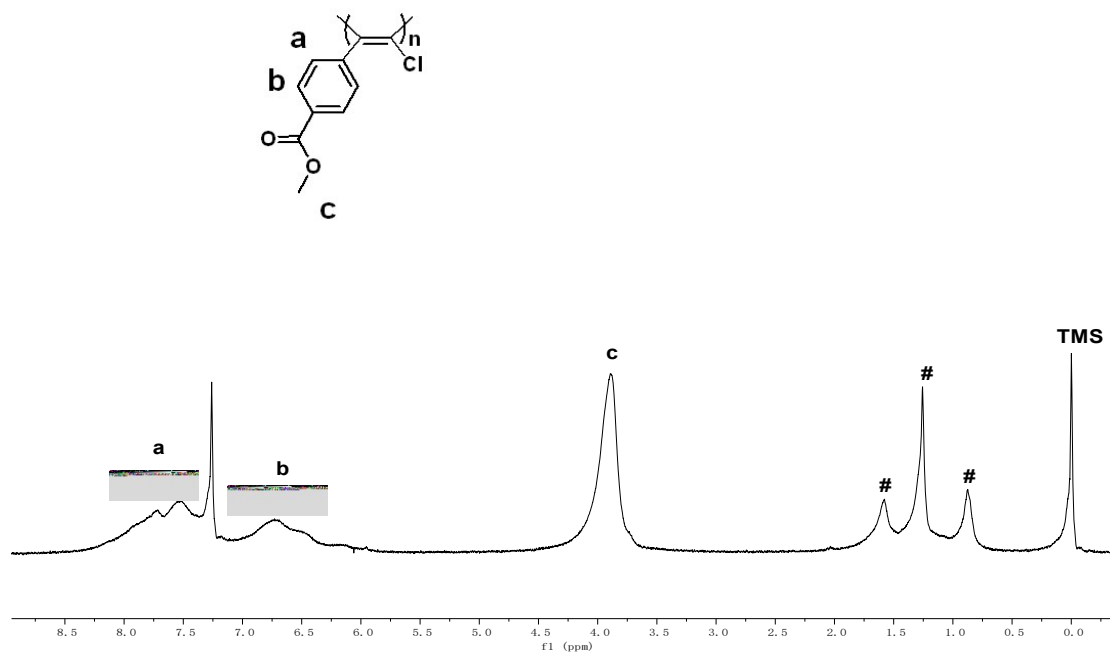


**Figure S16.** <sup>1</sup>H NMR spectrum of Poly(f) in CDCl<sub>3</sub> (Table 1, entry 24).

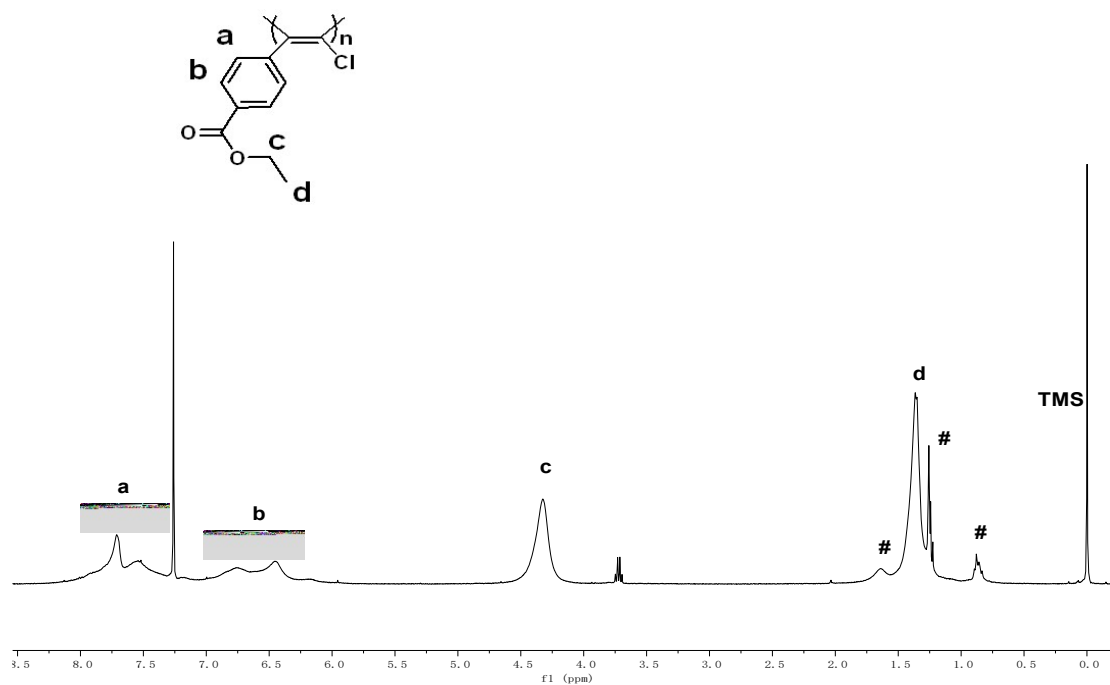


**Figure S17.** <sup>1</sup>H NMR spectrum of Poly(g) in CDCl<sub>3</sub> (Table 1, entry 10).

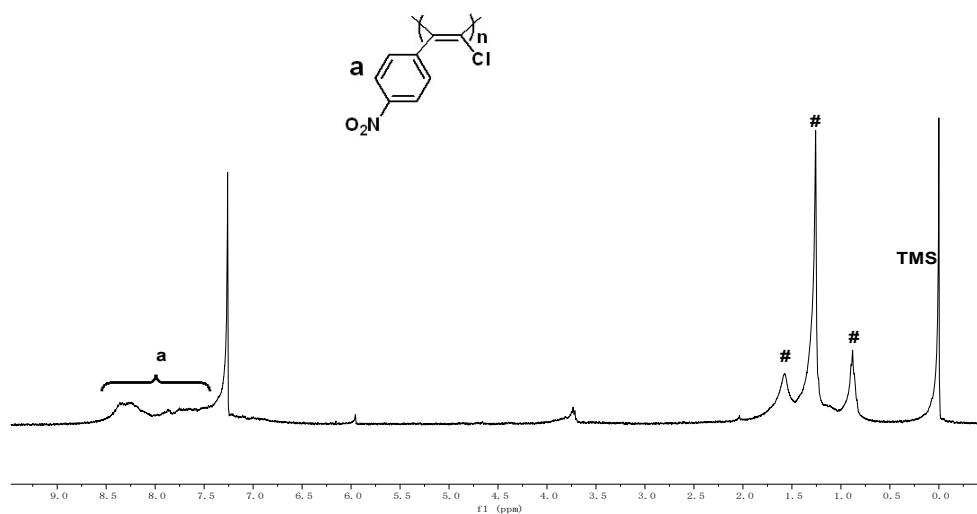




**Figure S18.**  $^1\text{H}$  NMR spectrum of Poly(**h**) in  $\text{CDCl}_3$  (Table 1, entry 25).

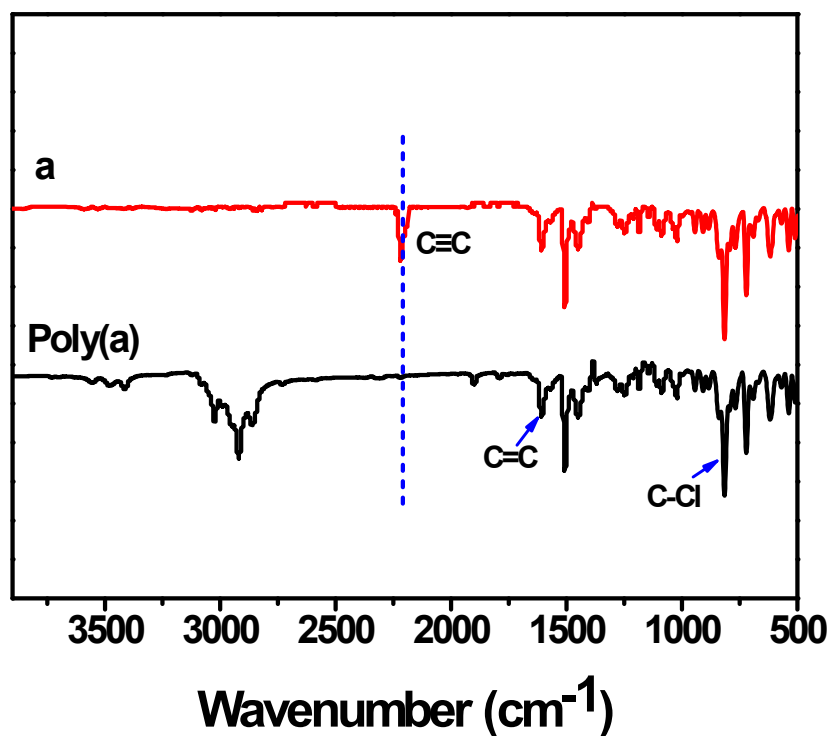


**Figure S19.**  $^1\text{H}$  NMR spectrum of Poly(**i**) in  $\text{CDCl}_3$  (Table 1, entry 26).



**Figure S20.**  $^1\text{H}$  NMR spectrum of Poly(j) in  $\text{CDCl}_3$  (Table 1, entry 27).

The FT-IR analysis identified the formation of the PCPAs in view of the disappeared peak around  $2221\text{ cm}^{-1}$  assigned to the  $\text{C}\equiv\text{C}$  stretching band of monomers and the generated peak around  $1608\text{ cm}^{-1}$  attributed to the  $\text{C}=\text{C}$  stretching bands of PCPAs. Moreover, a strong signal at  $830\text{ cm}^{-1}$  belonging to the  $\text{C}-\text{Cl}$  stretching absorption bands also demonstrated the retention of Cl atom in the polymers.



**Figure S21.** FT-IR spectra of a and Poly(a) (Table 1, entry 20).

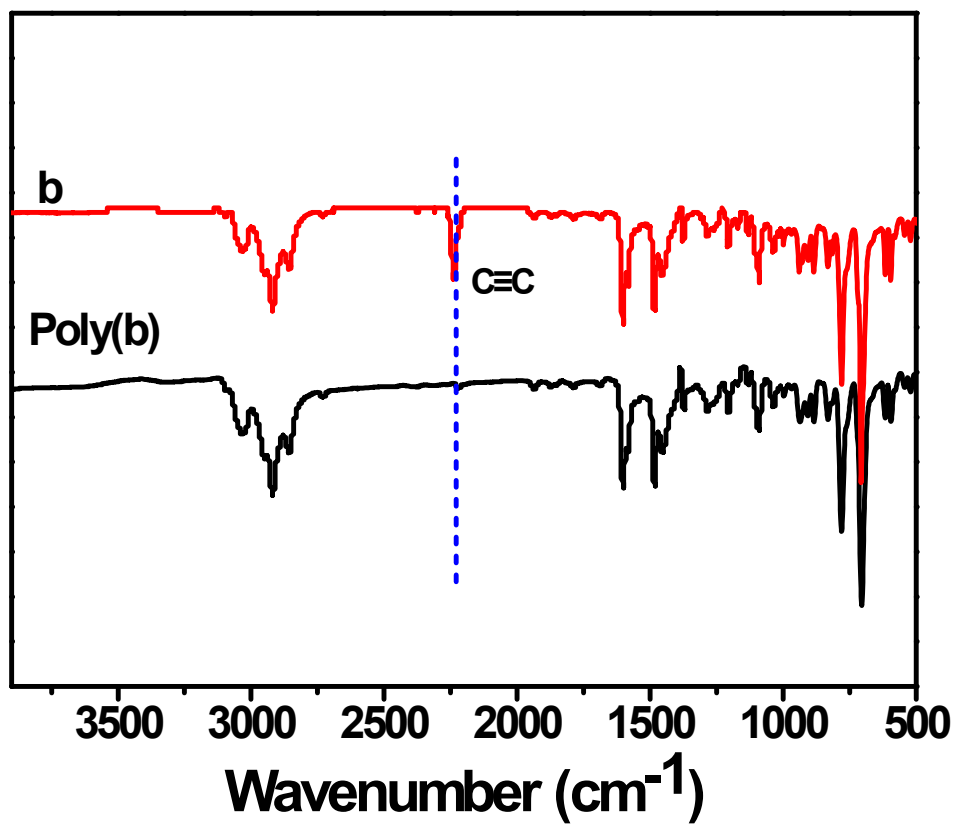


Figure S22. FT-IR spectra of **b** and Poly(**b**) (Table 1, entry 21).

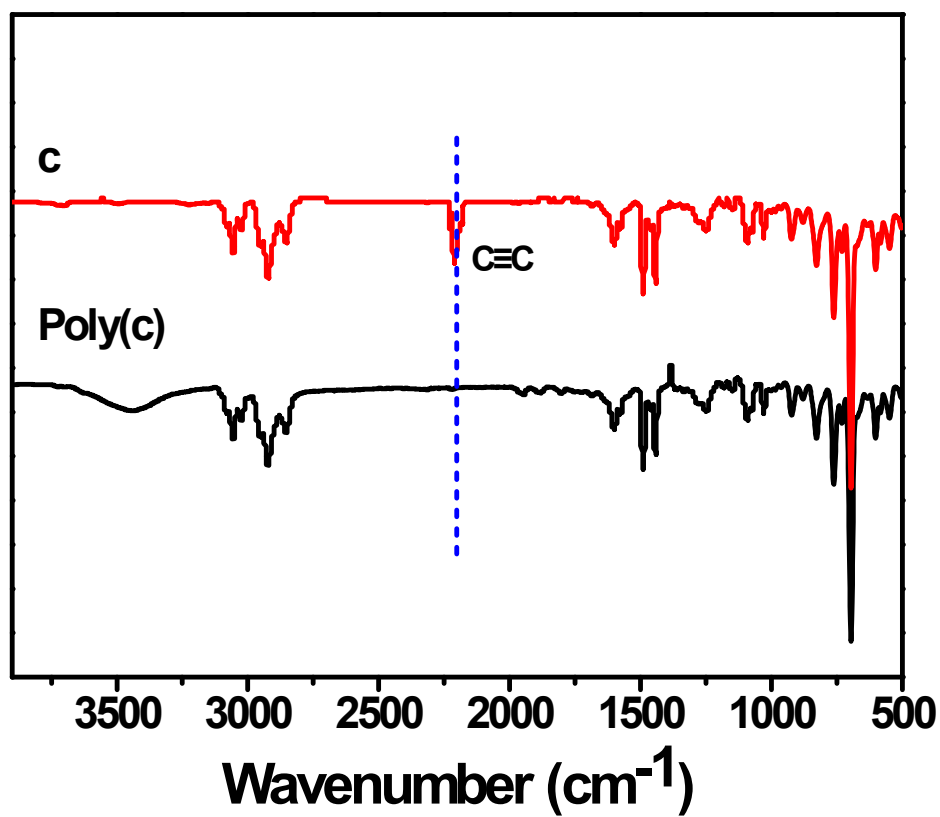


Figure S23. FT-IR spectra of **c** and Poly(**c**) (Table 1, entry 2).

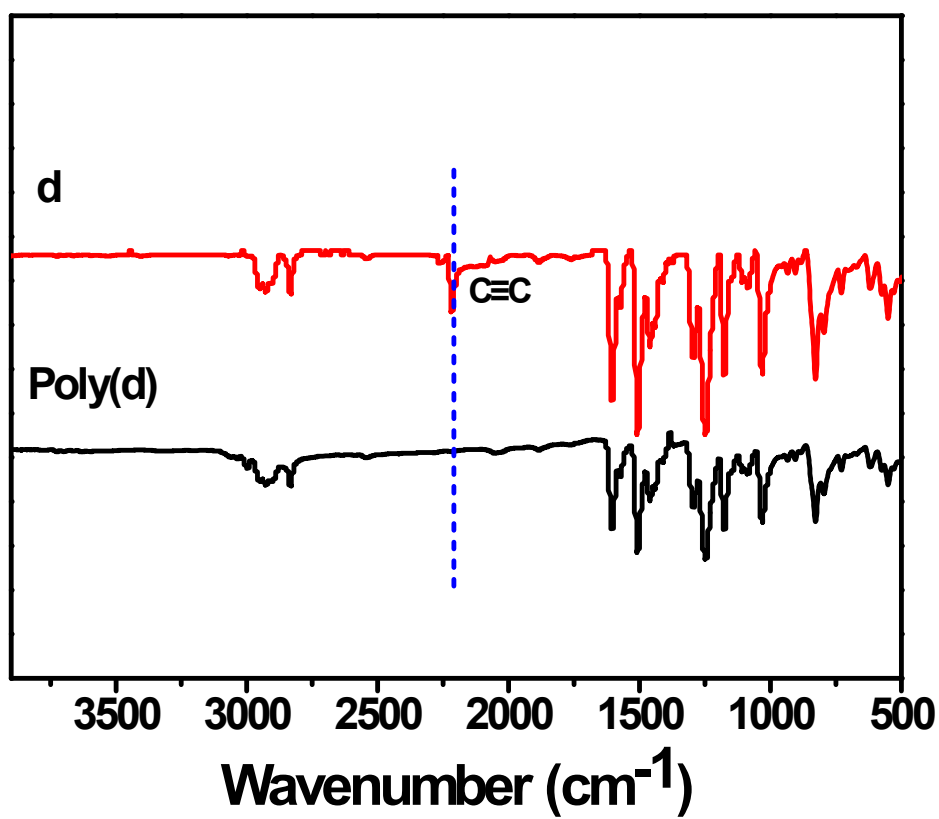


Figure S24. FT-IR spectra of **d** and Poly(**d**) (Table 1, entry 22).

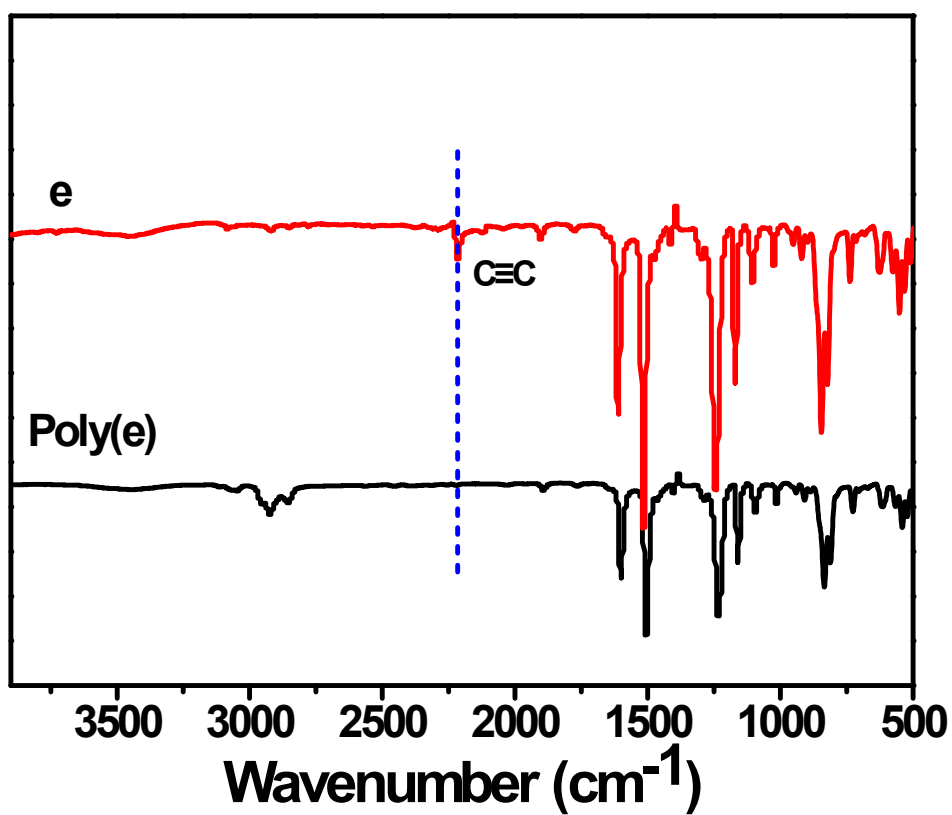


Figure S25. FT-IR spectra of **e** and Poly(**e**) (Table 1, entry 23).

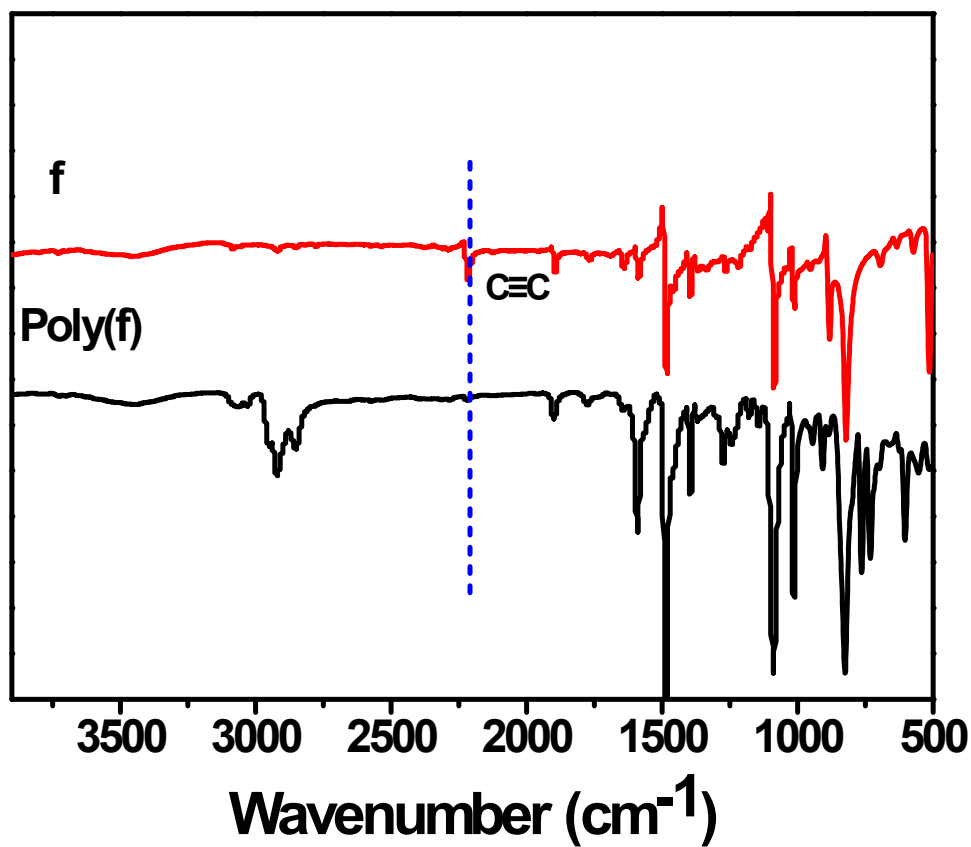


Figure S26. FT-IR spectra of **f** and Poly(**f**) (Table 1, entry 24).

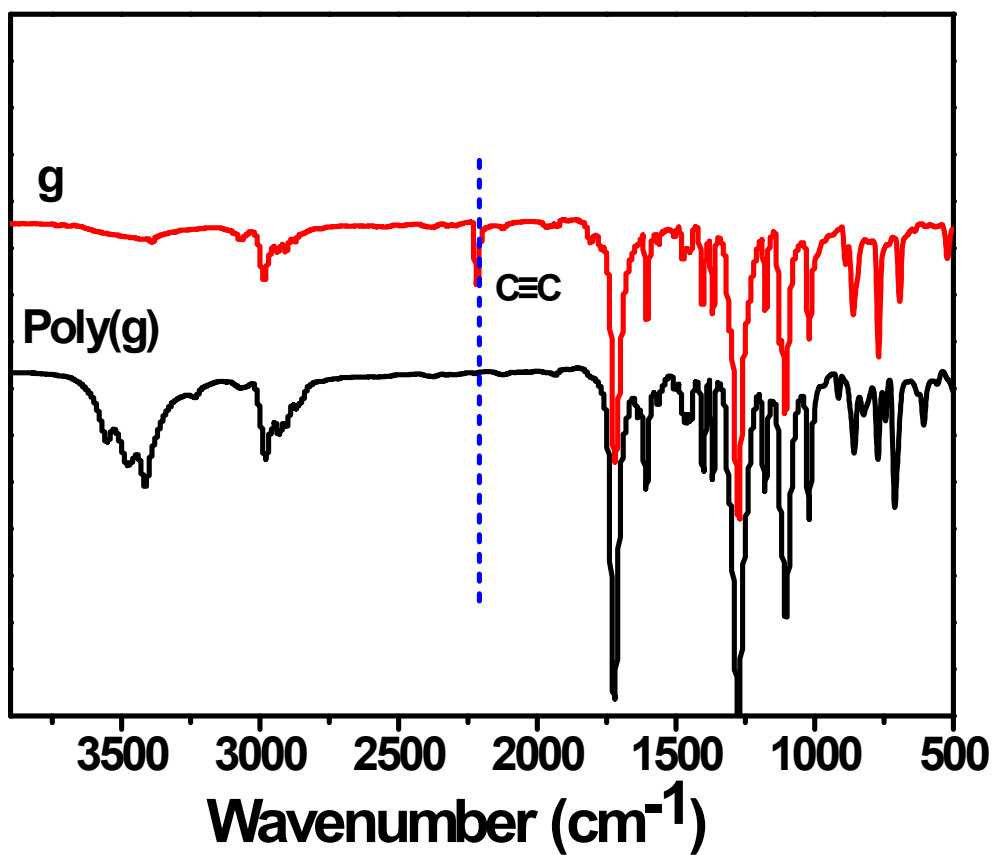


Figure S27. FT-IR spectra of **g** and Poly(**g**) (Table 1, entry 10).

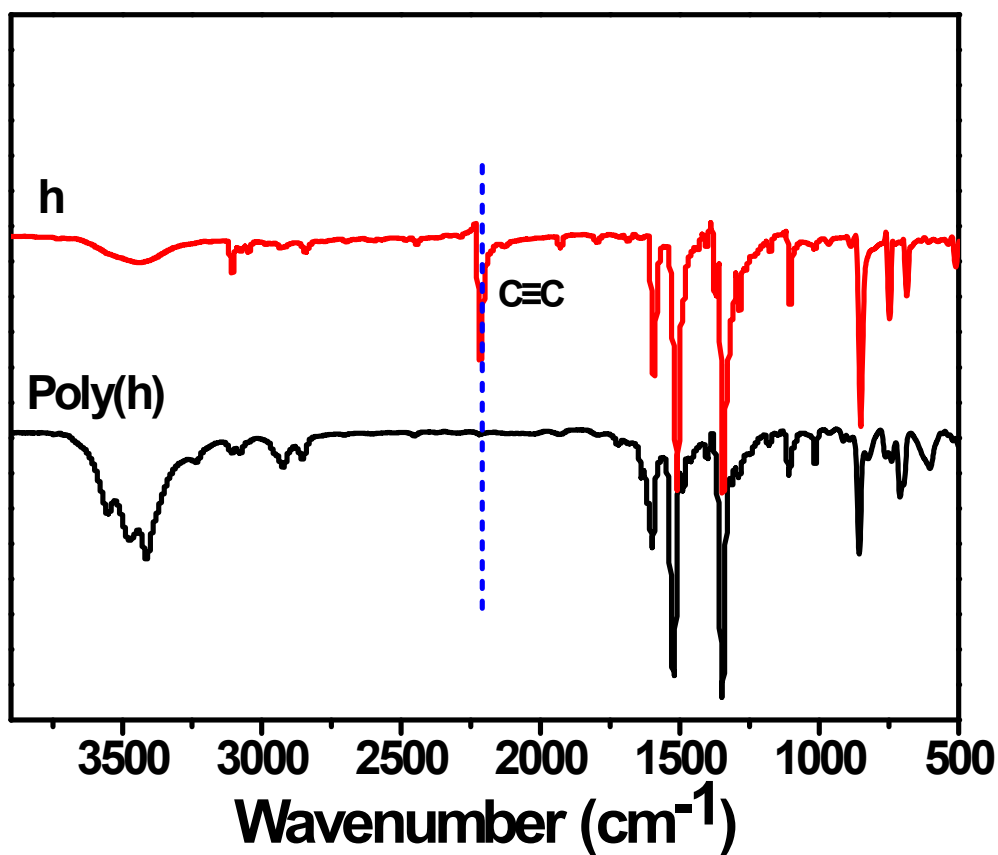


Figure S28. FT-IR spectra of **h** and Poly(**h**) (Table 1, entry 25).

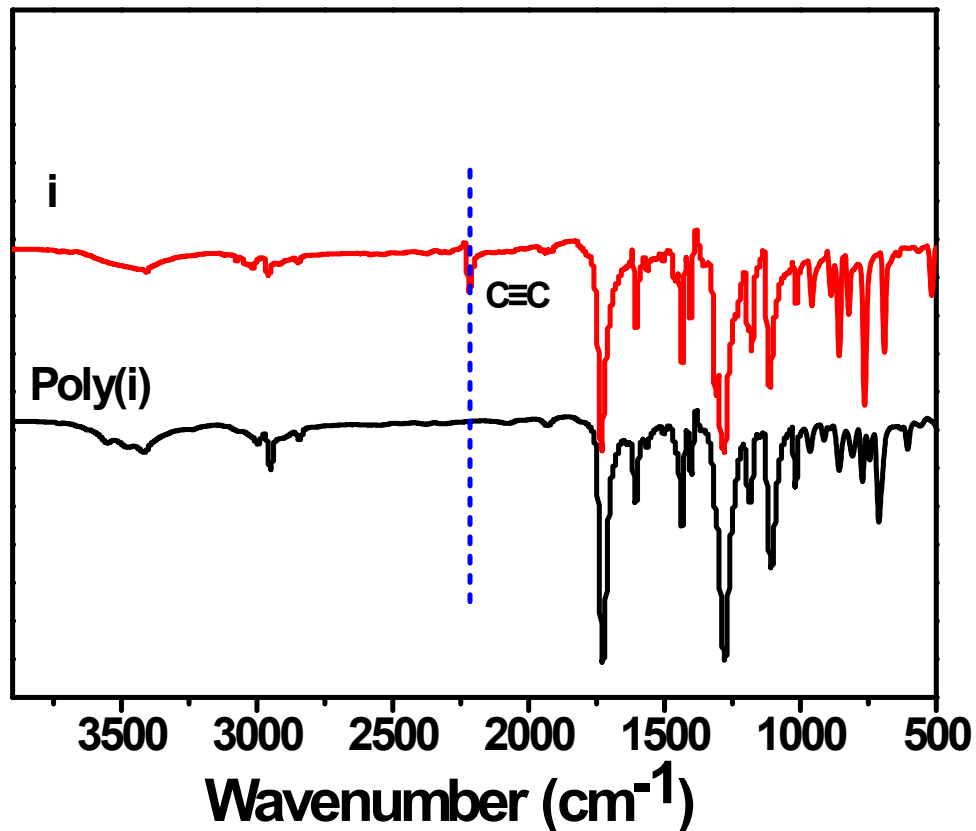


Figure S29. FT-IR spectra of **i** and Poly(**i**) (Table 1, entry 26).

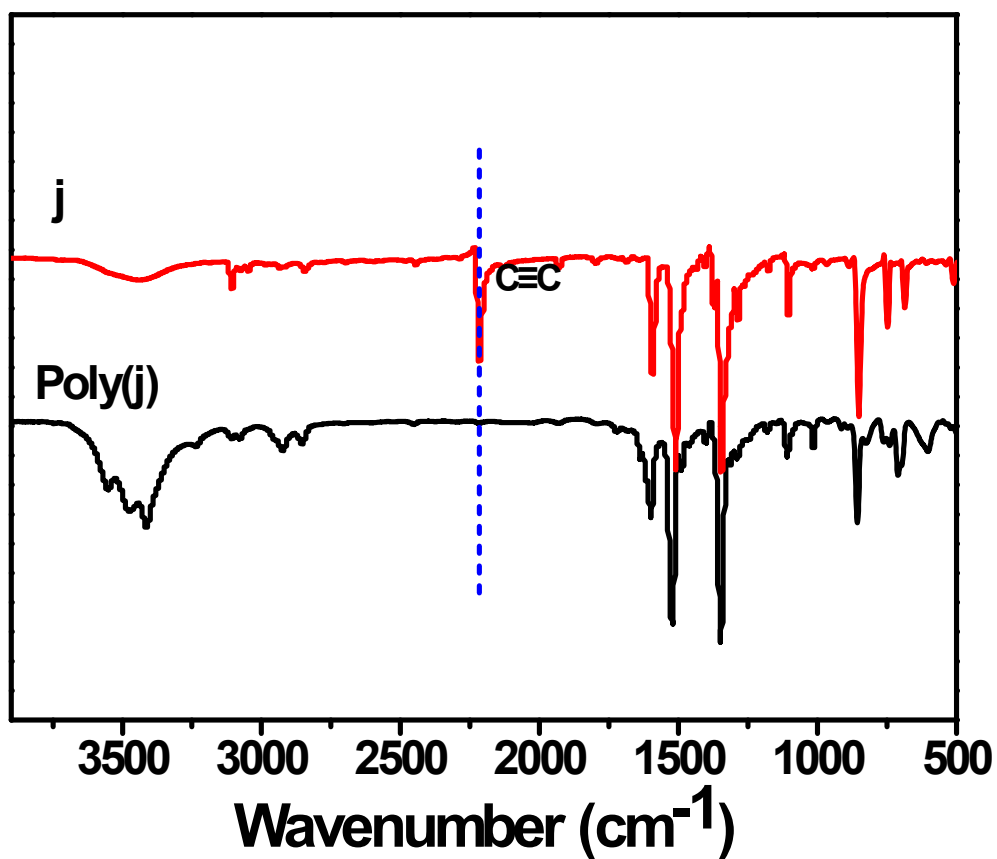


Figure S30. FT-IR spectra of **j** and Poly(**j**) (Table 1, entry 27).

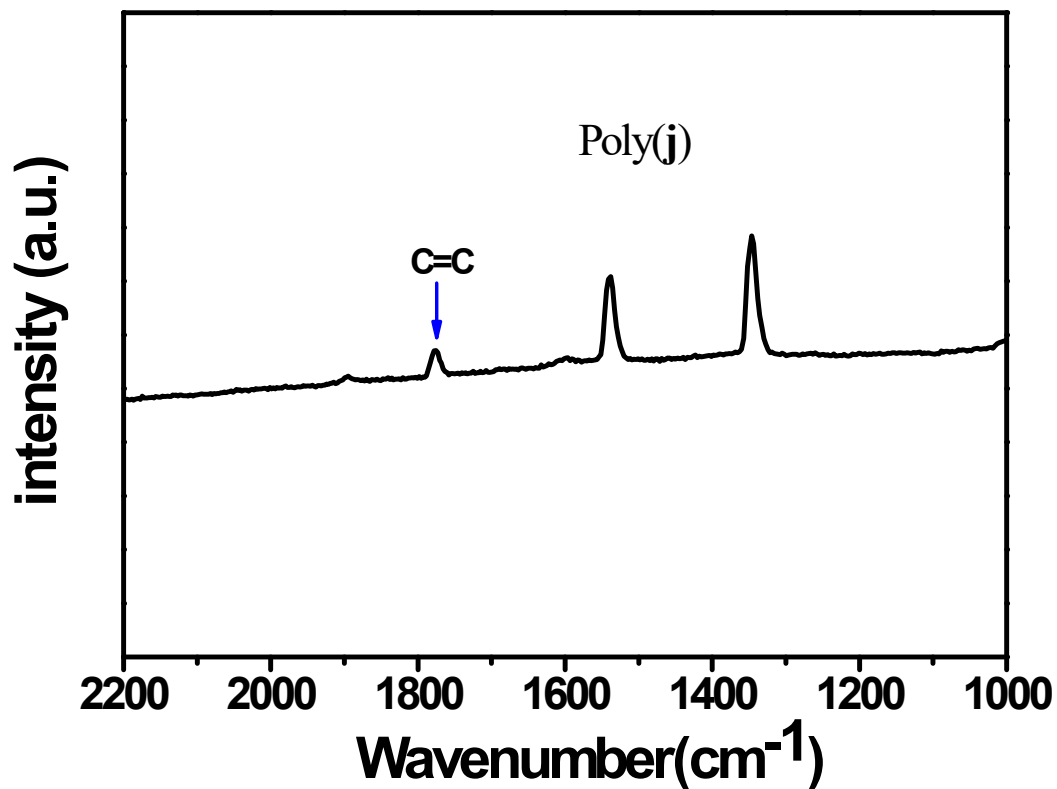


Figure S31. Raman spectra of poly(**j**) (Table 1, entry 27).

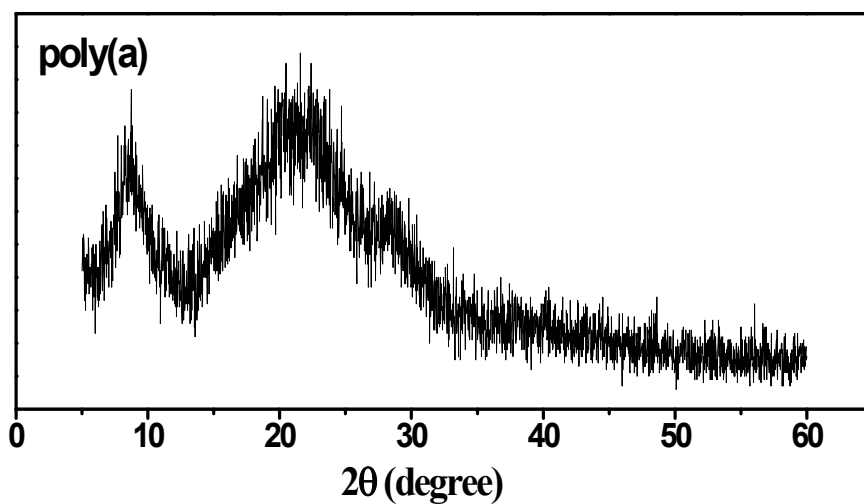


Figure S32. PXRD curves of poly(a) (Table 1, entry 20).

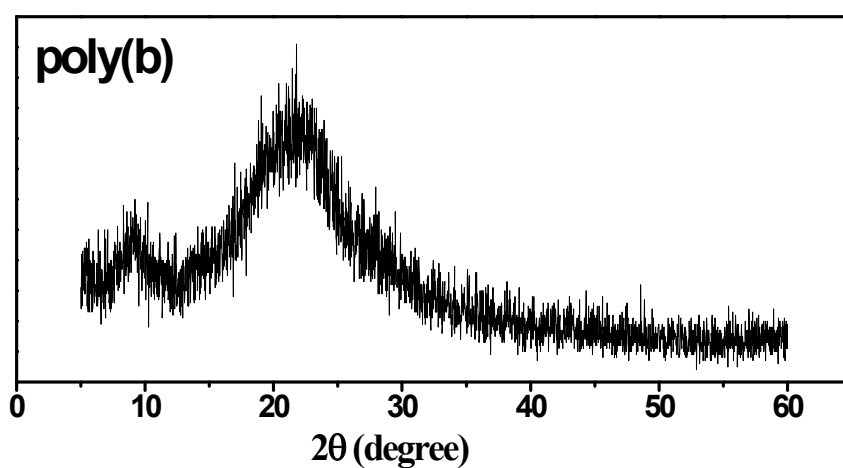


Figure S33. PXRD curves of poly(b) (Table 1, entry 22).

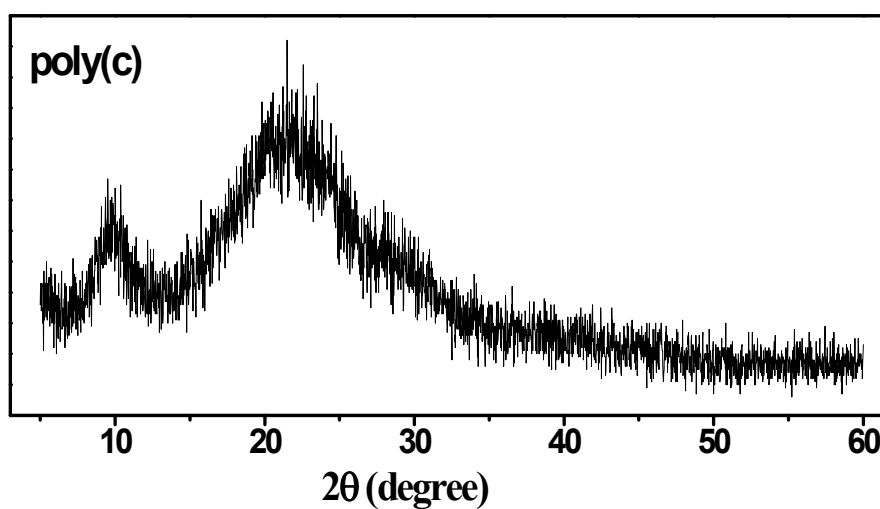


Figure S34. PXRD curves of poly(c) (Table 1, entry 2).



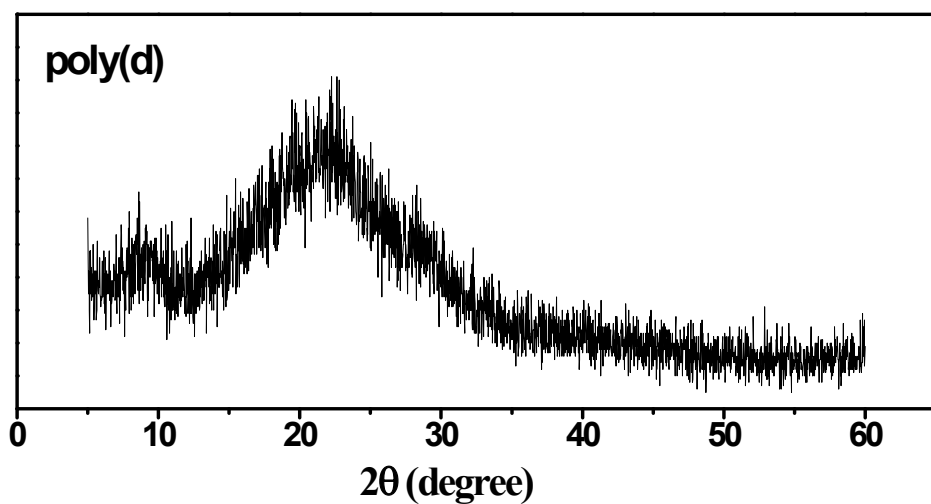


Figure S35. PXRD curves of poly(d) (Table 1, entry 22).

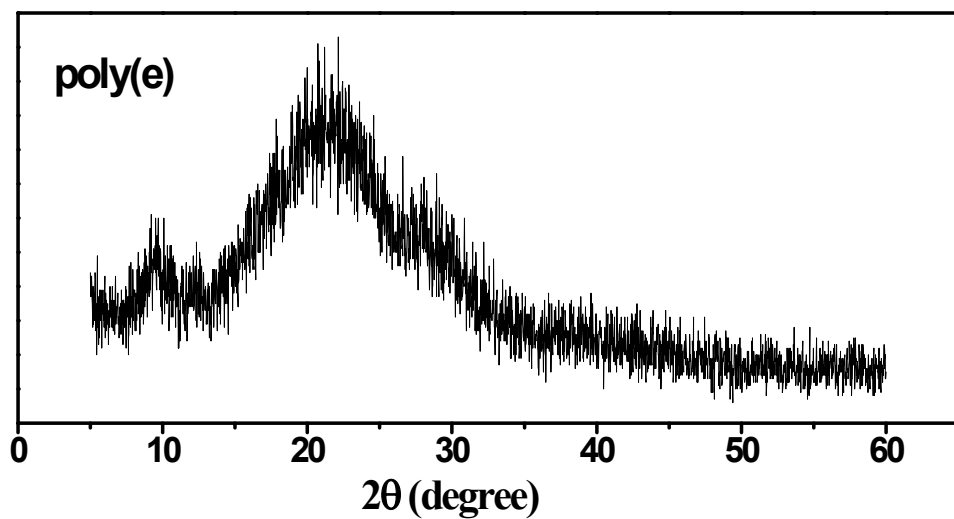


Figure S36. PXRD curves of poly(e) (Table 1, entry 23).

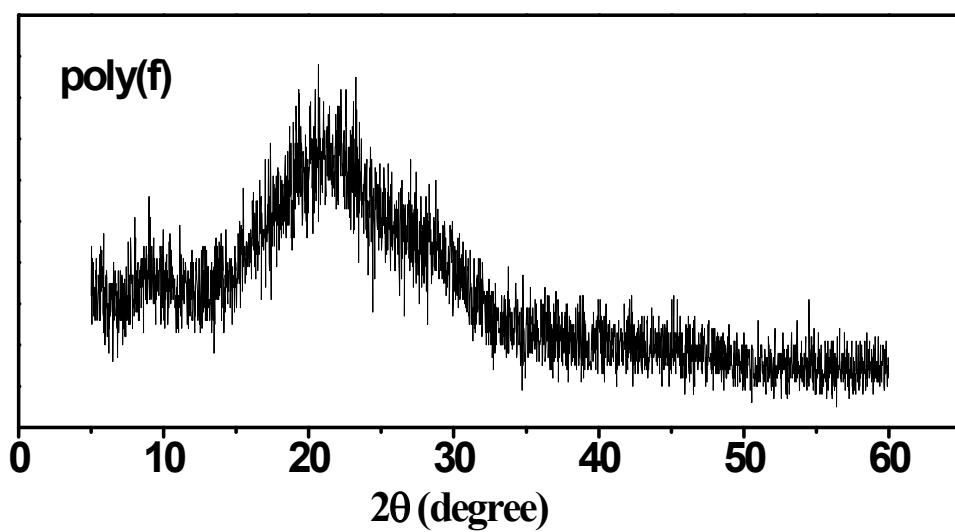


Figure S37. PXRD curves of poly(f) (Table 1, entry 24).

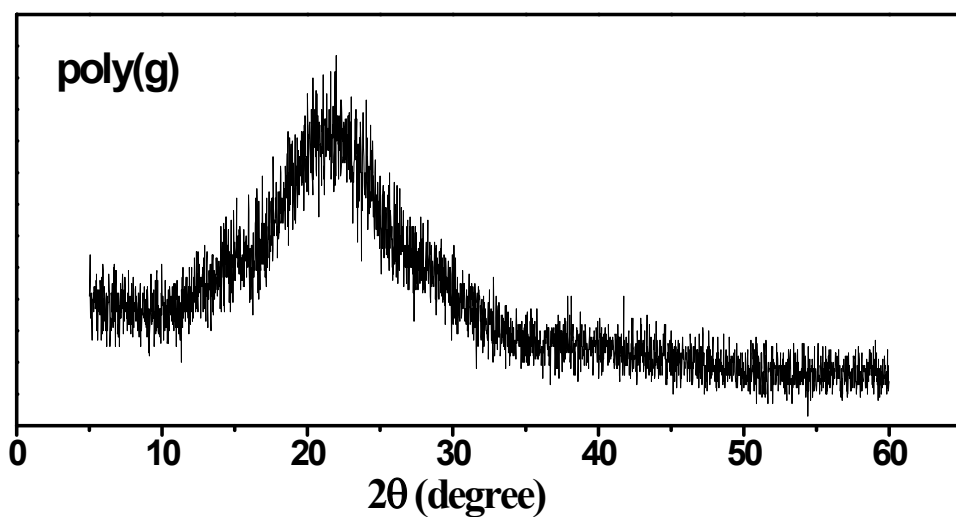


Figure S38. PXRD curves of poly(g) (Table 1, entry 10).

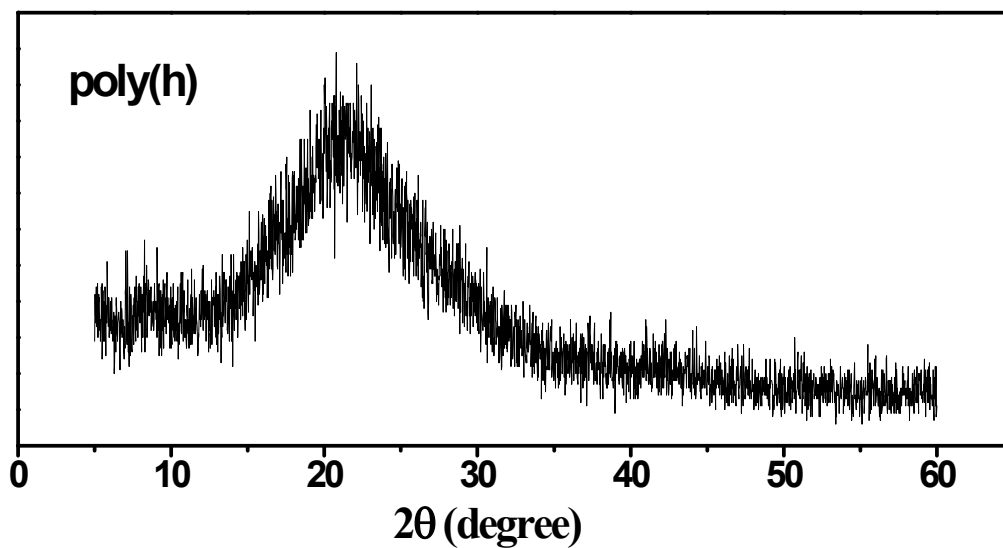


Figure S39. PXRD curves of poly(h) (Table 1, entry 25).

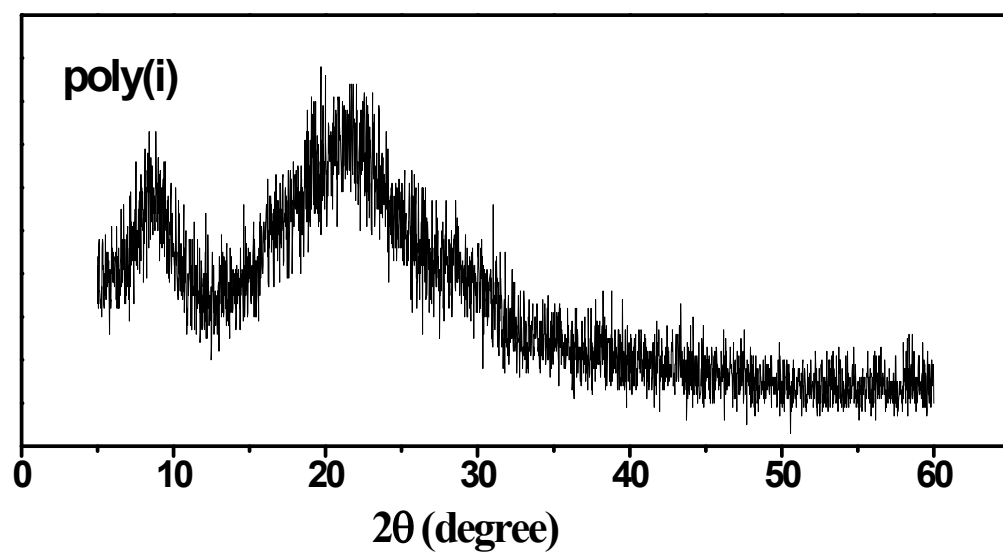


Figure S40. PXRD curves of poly(i) (Table 1, entry 26).

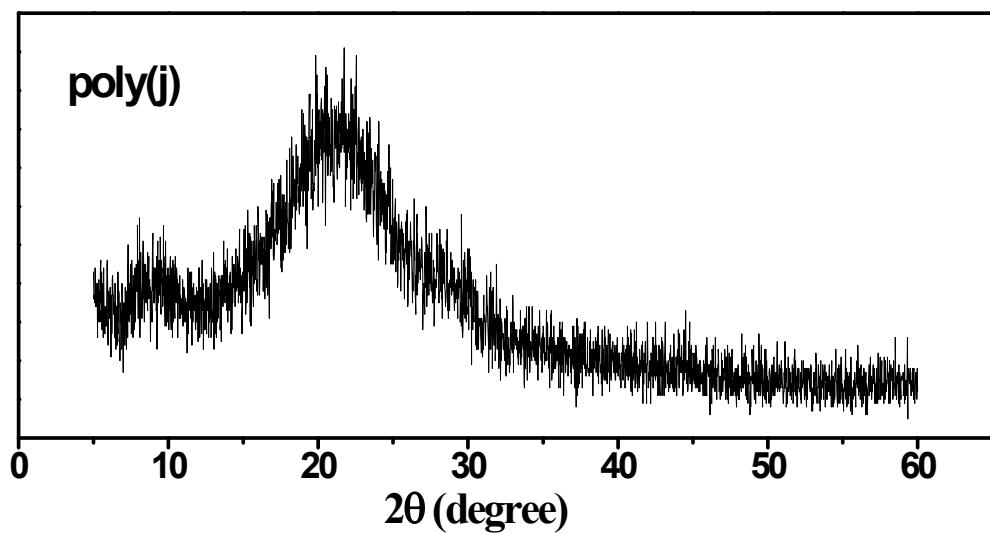
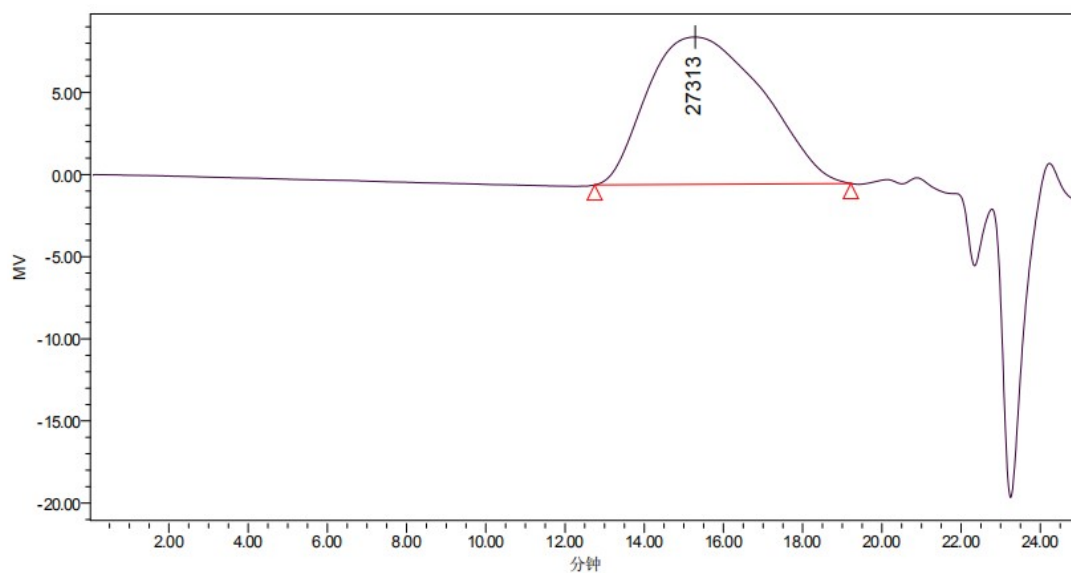


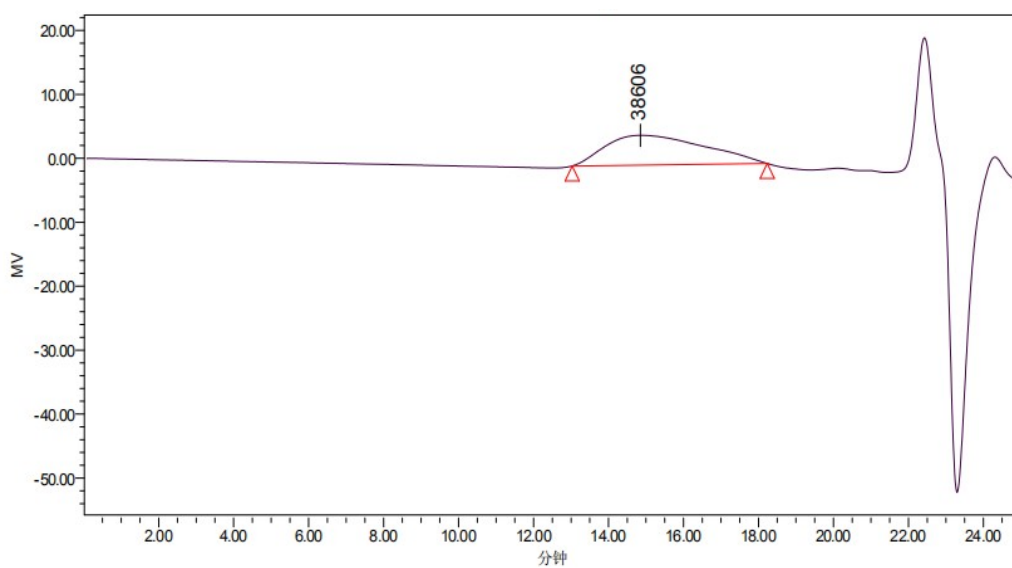
Figure S41. PXRD curves of poly(j) (Table 1, entry 27).



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		15.287	15.287	15.287	15399	33656	27313	69964	117831	2.078795	3.501020

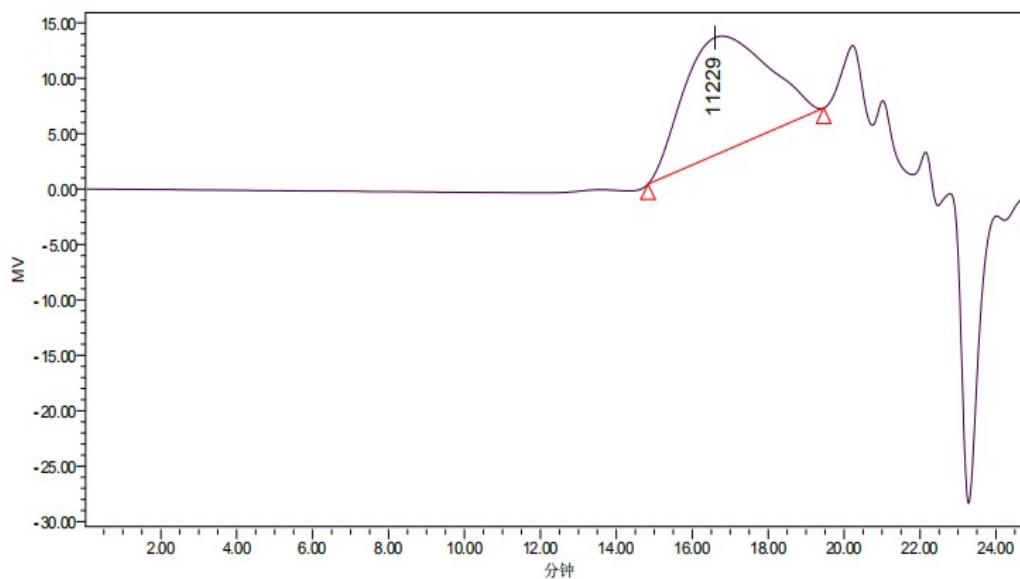
Figure S42. GPC curve of poly(c) obtained by  $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$  in Table 1, entry 2.



GPC Results

Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1	14.850	14.850	14.850	19407	38992	38606	71505	106250	1.833836	2.724929

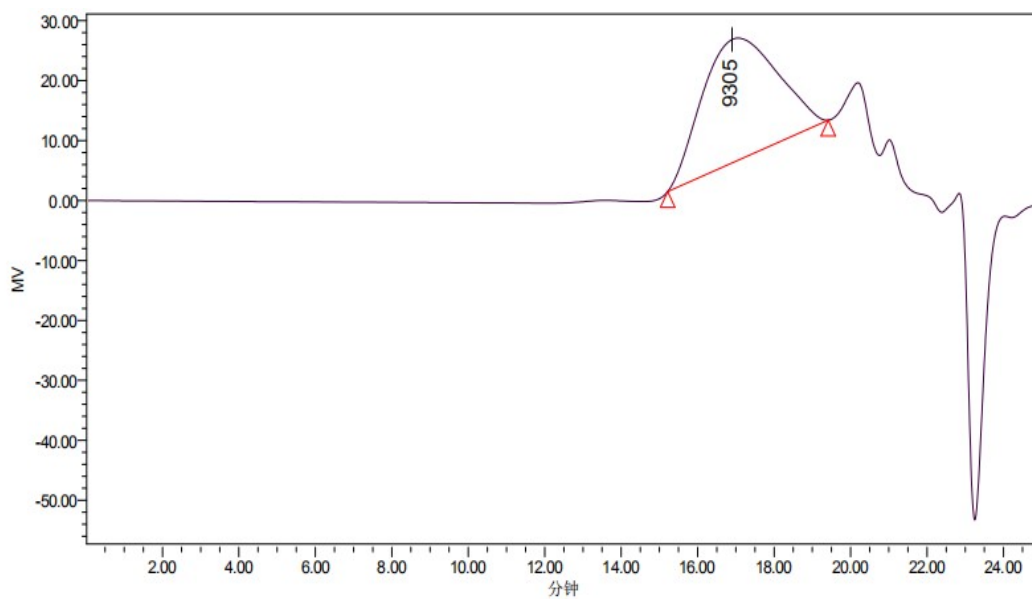
Figure S43. GPC curve of poly(c) obtained by  $\text{Pd}(\text{C}_6\text{H}_5\text{CN})_2\text{Cl}_2$  in Table 1, entry 3.



GPC Results

Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1	16.600	16.600	16.600	7451	10747	11229	14327	17638	1.333108	1.641184

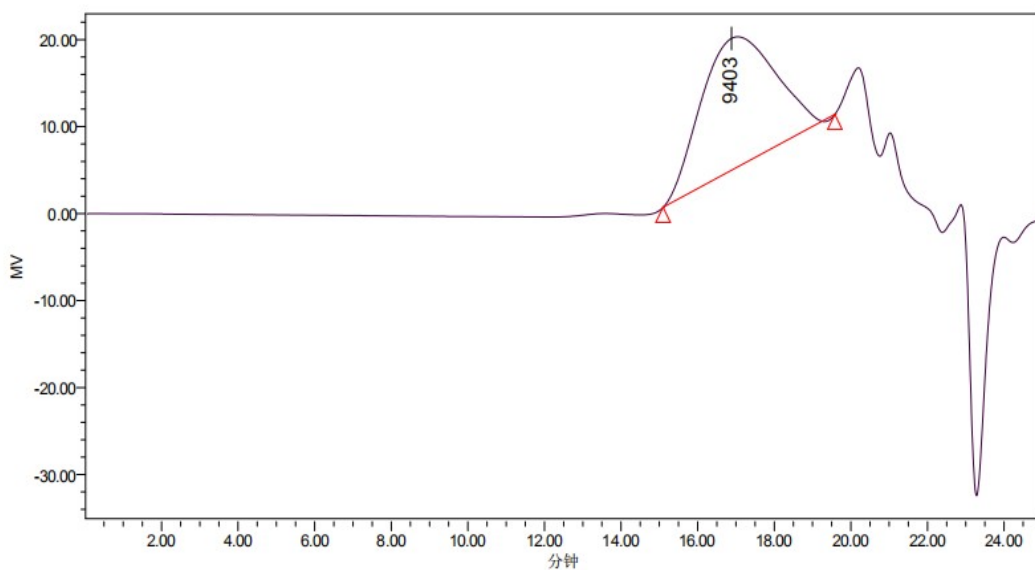
Figure S44. GPC curve of poly(g) obtained by  $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$  in Table 1, entry 7.



GPC Results

Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1	16.900	16.900	16.900	6786	9089	9305	11506	13743	1.265928	1.511952

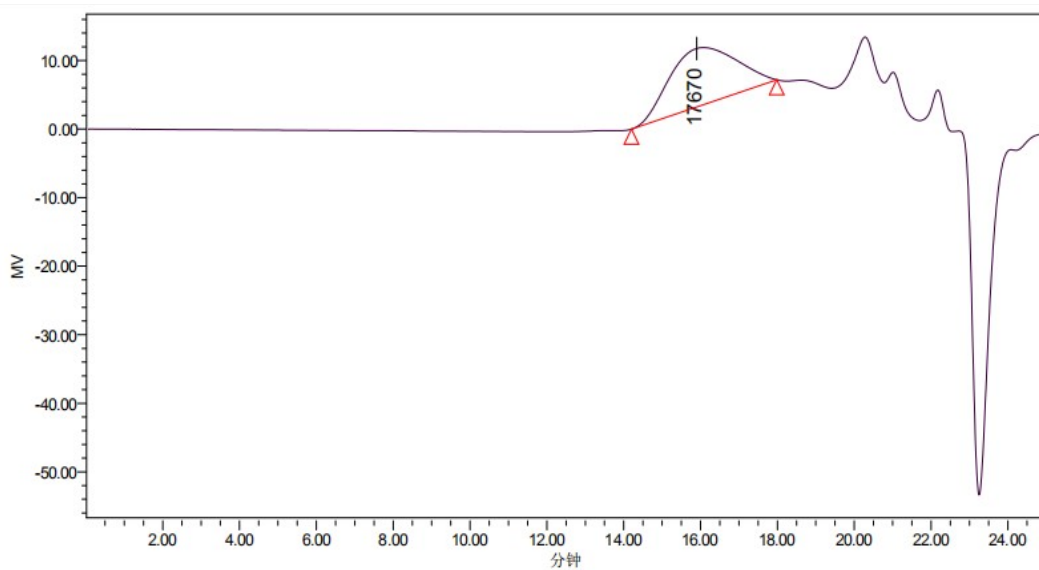
Figure S45. GPC curve of poly(g) obtained by  $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$  in Table 1, entry 8.



GPC Results

Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1	16.883	16.883	16.883	7124	9424	9403	11898	14263	1.262517	1.513410

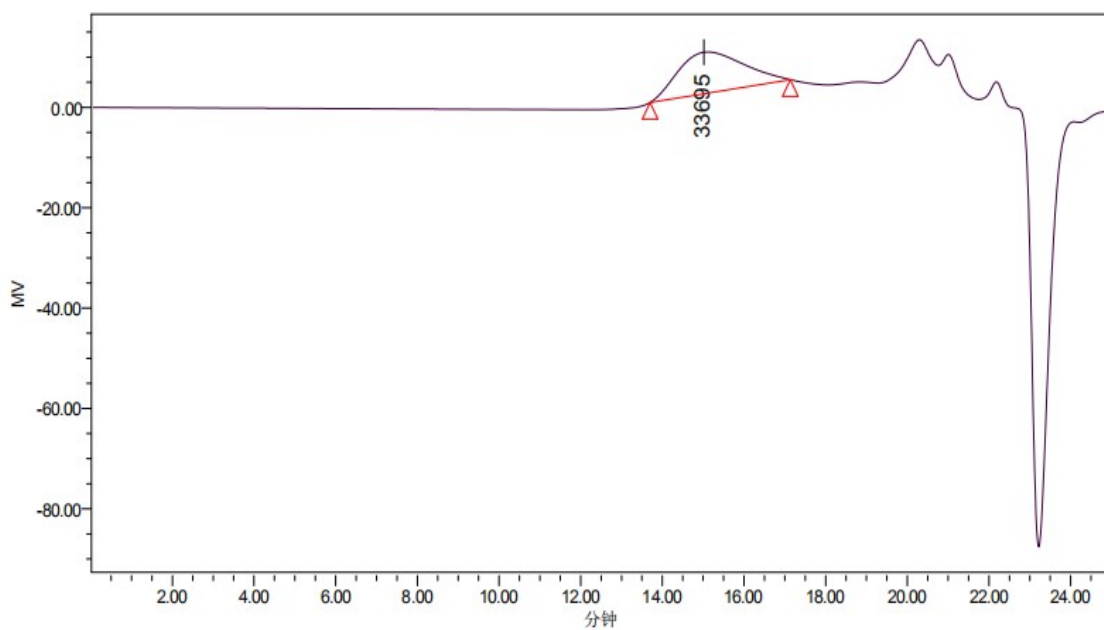
Figure S46. GPC curve of poly(g) obtained by  $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$  in Table 1, entry 9.



GPC Results

Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1	15.900	15.900	15.900	14227	18008	17670	22461	27092	1.247235	1.504424

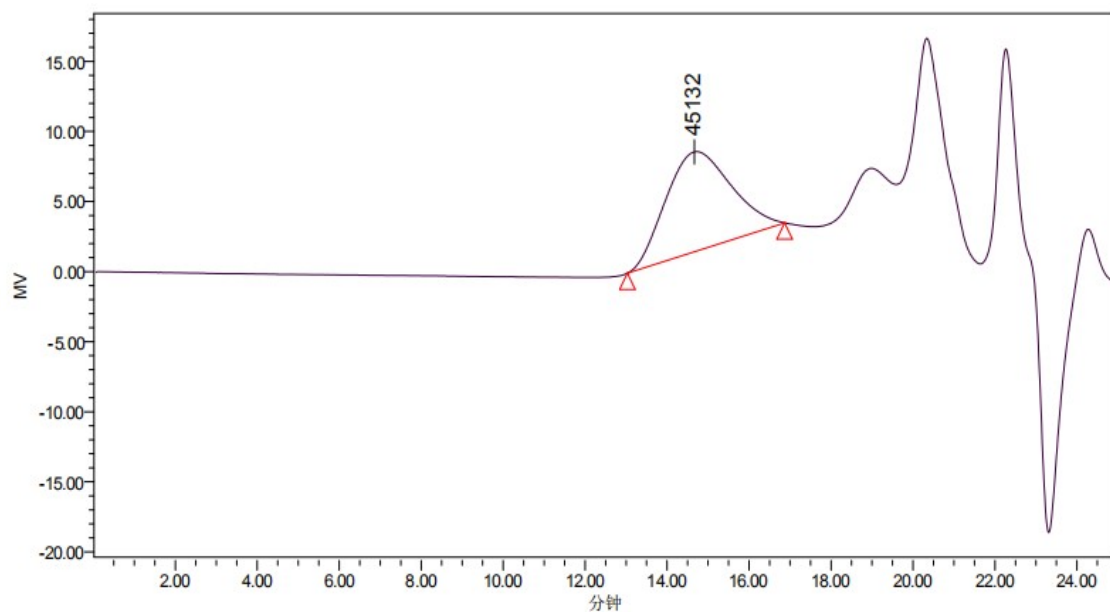
Figure S47. GPC curve of poly(g) obtained by  $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$  in Table 1, entry 10.



GPC Results

Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1	15.017	15.017	15.017	25527	33545	33695	43192	53102	1.287575	1.583005

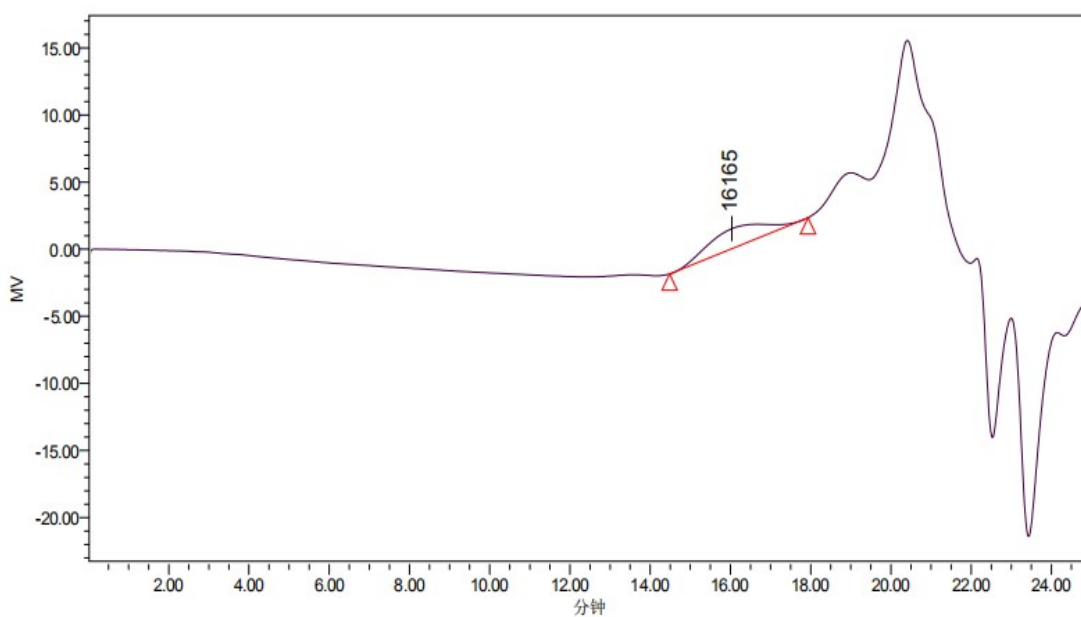
Figure S48. GPC curve of poly(g) obtained by  $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$  in Table 1, entry 11.



**GPC Results**

Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1	14.667	14.667	14.667	35199	50062	45132	70781	94972	1.413881	1.897101

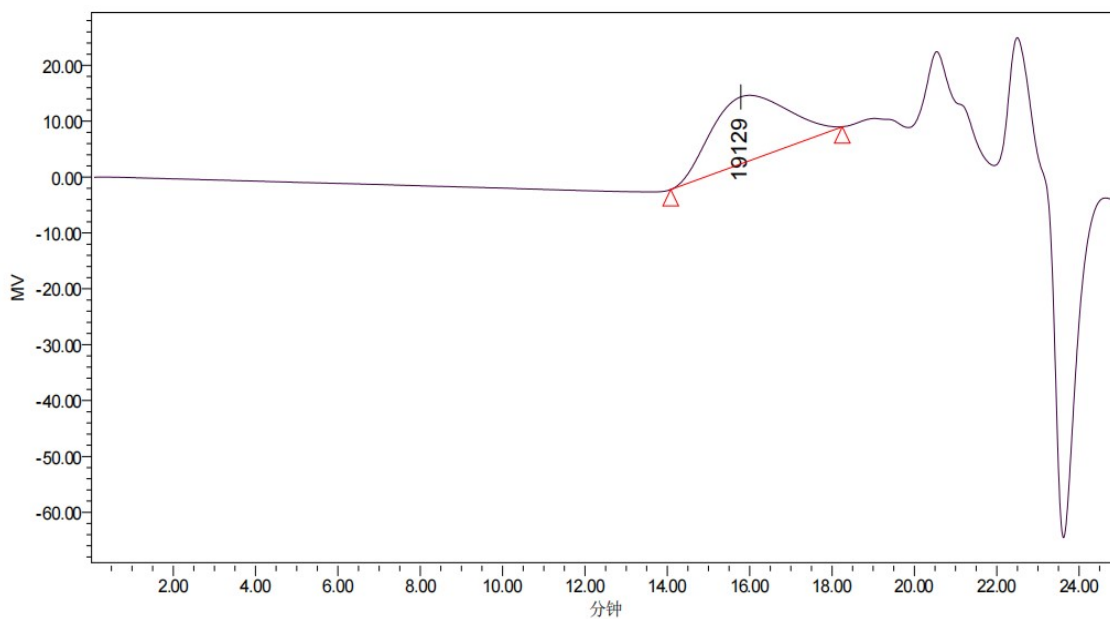
**Figure S49.** GPC curve of poly(g) obtained by  $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$  in Table 1, entry 12.



**GPC Results**

Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1	16.033	16.033	16.033	14481	16807	16165	19429	22140	1.156004	1.317321

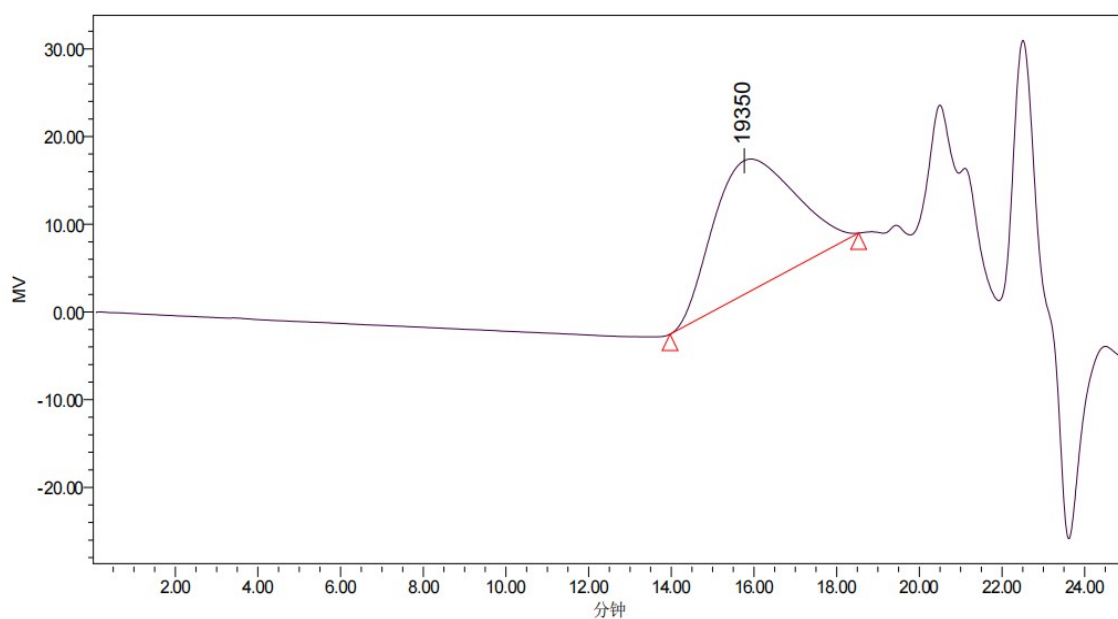
**Figure S50.** GPC curve of poly(g) obtained by  $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$  in Table 1, entry 13.



**GPC Results**

Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1	15.783	15.783	15.783	14454	19151	19129	24736	30542	1.291657	1.594848

**Figure S51.** GPC curve of poly(**g**) obtained by  $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$  in Table 1, entry 14.

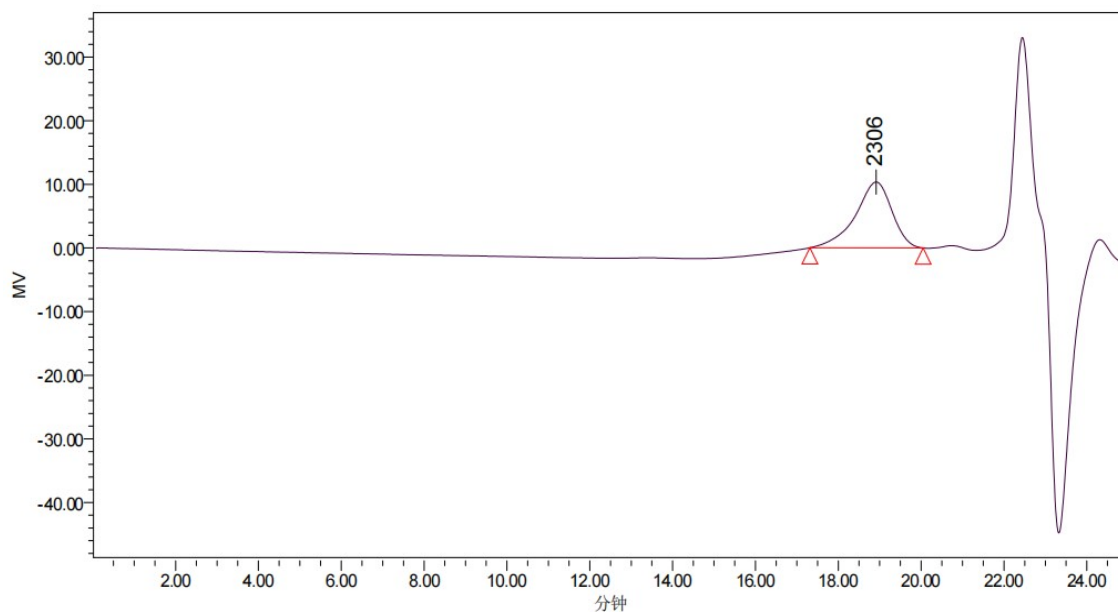


**GPC Results**

Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1	15.767	15.767	15.767	13786	19149	19350	25566	32202	1.335129	1.681653

**Figure S52.** GPC curve of poly(**g**) obtained by  $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$  in Table 1, entry 15.

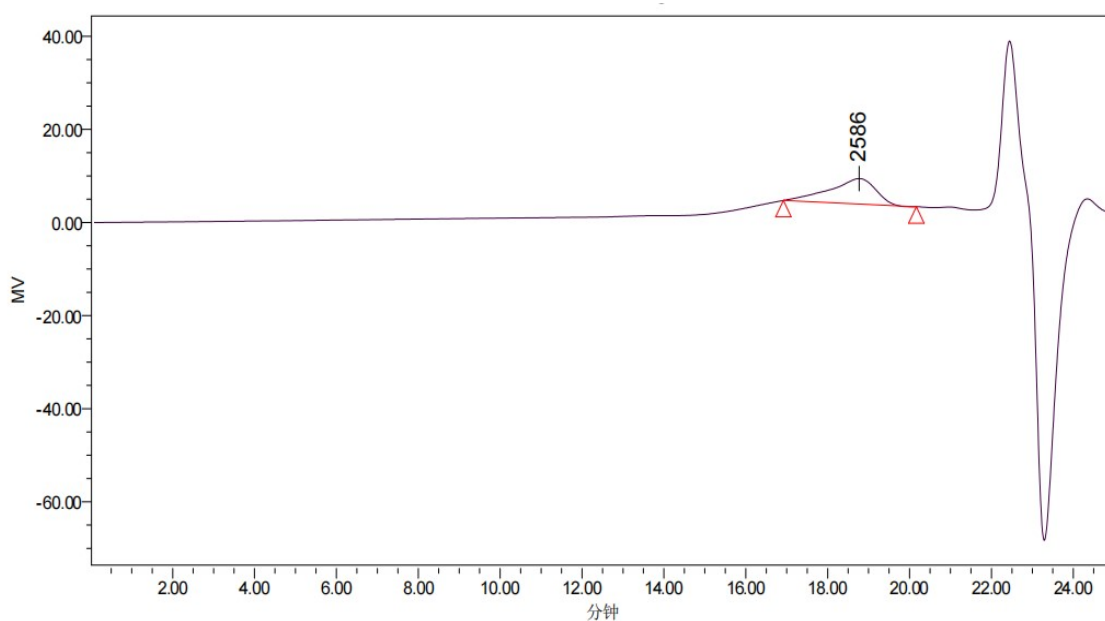




GPC Results

Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1	18.914	18.914	18.914	2316	2622	2306	2982	3387	1.137001	1.291757

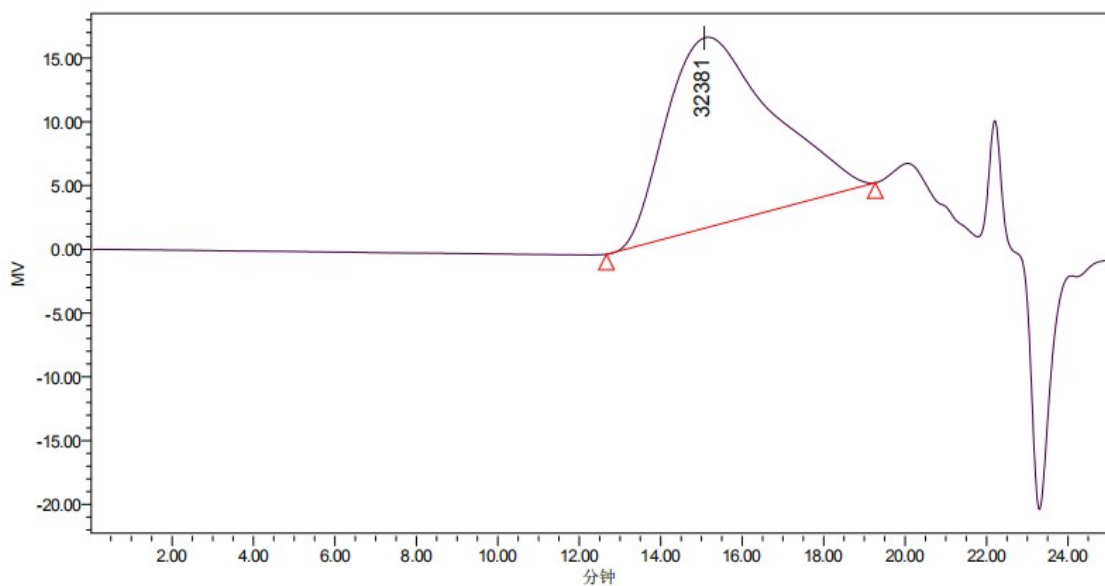
Figure S53. GPC curve of poly(c) obtained by  $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$  in Table 1, entry 16.



GPC Results

Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1	18.773	18.773	18.773	2850	3371	2586	4014	4714	1.190819	1.398418

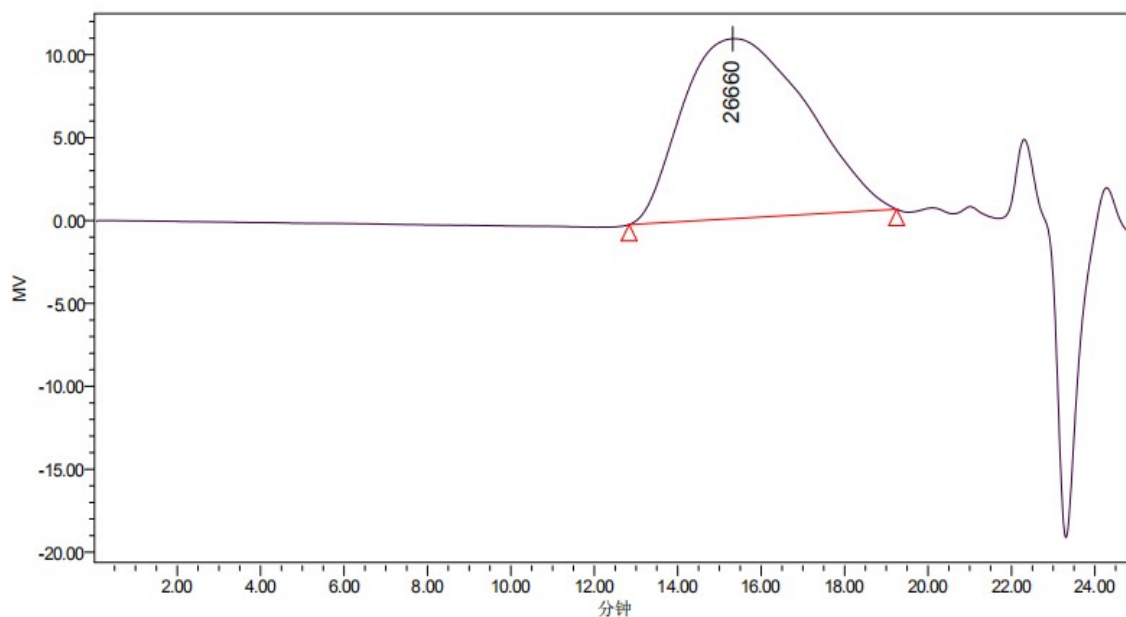
Figure S54. GPC curve of poly(c) obtained by  $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$  in Table 1, entry 18.



**GPC Results**

Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1	15.067	15.067	15.067	15518	33296	32381	61984	96132	1.861614	2.887205

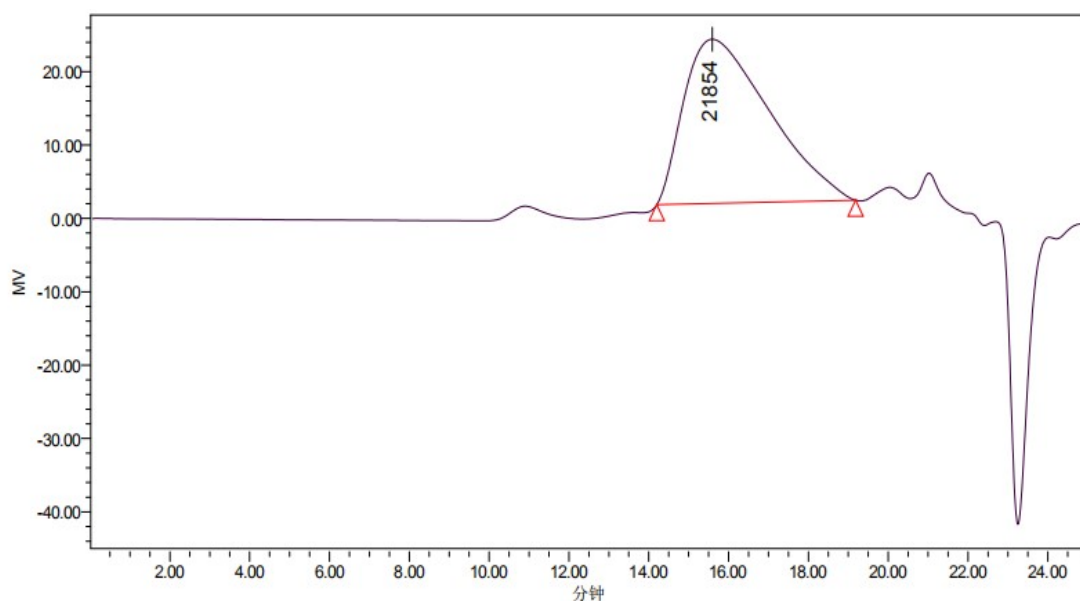
**Figure S55.** GPC curve of poly(**d**) obtained by  $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$  in Table 1, entry 22.



**GPC Results**

Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1	15.319	15.319	15.319	14259	32029	26660	66019	108839	2.061201	3.398119

**Figure S56.** GPC curve of poly(**h**) obtained by  $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$  in Table 1, entry 25.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		15.592	15.592	15.592	12105	18711	21854	25754	32037	1.376444	1.712264

**Figure S57.** GPC curve of poly(i) obtained by  $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$  in Table 1, entry 26.

## References

- 1 X. L. Wu, Z. Yang, X. W. Yan, P. F. Zhang, L. Wang, G. Guo, Y. P. Dong and X. F. Li, *Polym. Chem.*, 2018, **9**, 4856–4865.
- 2 Z. J. Zhao, S. M. Chen, J. W. Y. Lam, C. K. W. Jim, C. Y. K. Chan, Z. M. Wang, P. Lu, C. M. Deng, H. S. Kwok, Y. G. Ma and B. Z. Tang, *J. Phys. Chem. C.*, 2010, **114**, 7963–7972.
- 3 J. R. Castanon, N. Sano, M. Shiotsuki and F. Sanda, *ACS Macro Lett.*, 2014, **3**, 51–54.
- 4 J. R. Castanon, Y. Murayama, N. Sano and F. Sanda, *Chem. Lett.*, 2015, **44**, 1200–1201.