

## Supporting Information

### **Controlled synthesis of cyclic helical polyisocyanides and bottlebrush polymers using a cyclic alkyne-Pd(II) catalyst**

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## 1. Measurements

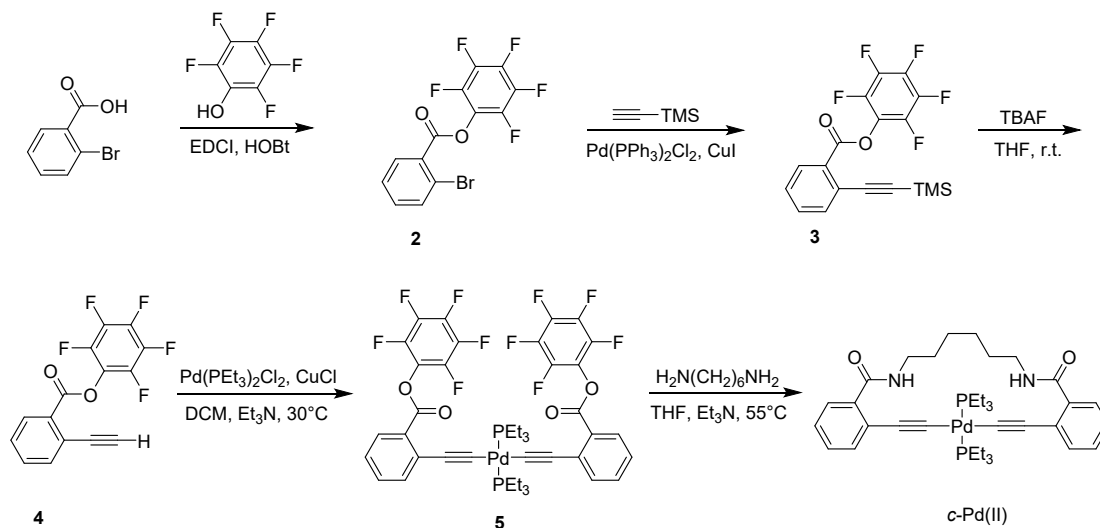
Nuclear magnetic resonance (NMR) spectra were recorded using a Bruker 400 MHz spectrometer. Chemical shifts are expressed in delta ( $\delta$ ) in parts per million (ppm) from tetramethylsilane (TMS) downwards using residual proton solvent as an internal standard. Fourier transform infrared (FT-IR) spectra were recorded at 25 °C on a FT-IR instrument (VERTEX 80V) using KBr pressure plates. Mass spectra were determined using a matrix-assisted laser-resolved time-of-flight mass spectrometer (Autoflex Speed). Size exclusion chromatography (SEC) was performed on a Waters 1515 pump and a Waters 2414 differential refractive index (RI) detector using two linear TSK gel GMHHR-H column series. SEC experiments were performed at 40 °C using a tetrahydrofuran (THF) eluent at a flow rate of 0.8 mL/min; molecular weight ( $M_n$ ) and polydispersity ( $M_w/M_n$ ) data are reported relative to polystyrene standards. Relevant images were taken using a transmission electron microscope 2100 (TEM). Thermogravimetric analysis (TGA) tests were carried out using a TGA 550 (Waters Corporation) in a nitrogen atmosphere, with a heating rate of 10 °C/min, at temperatures ranging from 25 °C to 800 °C. The TGA tests were carried out using the TGA 550. Differential Scanning Calorimetry (DSC) measurements were performed on a Differential Scanning Calorimeter (Q20). The intrinsic viscosity was determined in DMF at 25 °C using an Ubbelohde viscometer.

## 2. Materials

All solvents are from Sinopharm. Co. Ltd. and were purified according to standard procedures before use. All chemicals were purchased from Aladdin, Energy Chemical and Titan Technology Exploration Platform Chemicals Ltd. and were used as received without further purification. No further purification is required unless otherwise stated. Monomer **1** and pentafluorophenol isocyanide monomer were prepared in the same way as reported in the literature with slight modifications.<sup>1,2</sup>

### 3. Experimental procedures

#### Synthesis of cyclic polymers:



**Scheme S1** Synthesis of cyclic catalysts (*c*-Pd(II)).

The *c*-Pd(II) catalyst was first prepared according to Scheme S1.

*Synthesis of 2:*<sup>3</sup> To a solution of 2-bromobenzoic acid (20.00 g, 99.5 mmol) in dichloromethane (250 mL) were added pentafluorophenol (21.98 g, 119.4 mmol), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI, 22.81 g, 119.4 mmol) and 1-hydroxybenzotriazole monohydrate (HOBT, 3.17 g, 14.9 mmol). The mixture was stirred for 12 h at room temperature, then diluted with an appropriate amount of methylene chloride and washed with water saturated with NaHCO<sub>3</sub> and brine sequentially. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness under reduced pressure. The resulting residue was purified by chromatography (petrol ether/ethyl acetate (6:1, v/v)) to give **2** (31.0 g, 85% yield) as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.14–8.08 (m, 1H, ArH), 7.83–7.75 (m, 1H, ArH), 7.52–7.44 (m, 2H, ArH).

*Synthesis of 3:* Compound **2** (5.00 g, 13.6 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.48 g, 0.68 mmol) and CuI (0.13 g, 0.68 mmol) were weighed in a 100 mL double-necked flask. Triethylamine (30 mL) and tetrahydrofuran (30 mL) were added under N<sub>2</sub> atmosphere. After the mixture was stirred for 10 min at room temperature, trimethylsilylacetylene (TMSA, 3.85 mL, 2.68 g, 27.2 mmol) was added and the solution was refluxed at 80

°C for 6 h. The solution was then cooled to room temperature and diluted by ethyl acetate (40 mL), and washed sequentially with water, saturated aqueous NaHCO<sub>3</sub> and brine, sequentially. The organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness. The obtained crude product was subjected to column chromatography (petrol ether/ethyl acetate (10:1, v/v)) to give compound **3** as a brown oil (2.72 g, 52% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.14–8.08 (d, 1H, ArH), 7.74–7.40 (m, 3H, ArH), 0.23–0.20 (s, 9H, Si-CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 162.8, 135.1, 133.3, 131.4, 128.9, 128.4, 124.9, 102.0, 0.3. FT-IR (KBr, 25 °C, cm<sup>-1</sup>): 2947 (ν<sub>C-H</sub>), 2151 (ν<sub>C=C</sub>), 2096 (ν<sub>Si-H</sub>). MS m/z calcd for C<sub>18</sub>H<sub>13</sub>F<sub>5</sub>O<sub>2</sub>Si [M+Na]<sup>+</sup>: 407.05; Found: 407.96.

*Synthesis of 4:* Compound **3** (1.0 g, 2.60 mmol) was weighed in a 100 mL double-necked flask. To this flask, THF (20 mL) and tetrabutylammonium fluoride (TBAF, 0.34 g, 1.30 mmol) were added under the atmosphere of N<sub>2</sub> and the resulting solution was stirred at room temperature for 12 h, then diluted with an appropriate amount of CH<sub>2</sub>Cl<sub>2</sub> and washed with water saturated with NaHCO<sub>3</sub> and brine sequentially. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness under reduced pressure. The obtained crude product was subjected to column chromatography (petrol ether/ethyl acetate (2:1, v/v)) to give compound **4** as a yellow solid (0.32 g, 40% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.21–8.16 (d, 1H, ArH), 7.76–7.69 (d, 1H, ArH), 7.66–7.59 (t, 1H, ArH), 7.56–7.49 (t, 1H, ArH), 3.47–3.44 (s, 1H, CH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 161.6, 135.4, 133.5, 131.4, 128.7, 124.1, 83.9, 81.1. FT-IR (KBr, 25 °C, cm<sup>-1</sup>): 3279 (ν<sub>=C-H</sub>), 2112 (ν<sub>C=C</sub>). MS m/z calcd for C<sub>15</sub>H<sub>5</sub>F<sub>5</sub>O<sub>2</sub> [M+Na]<sup>+</sup>: 335.01; Found: 335.25.

*Synthesis of 5:*<sup>4</sup> Compound **4** (453 mg, 1.45 mmol), Pd(PET<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (300 mg, 0.73 mmol), and CuI (28 mg, 0.29 mmol) were weighed in a 100 mL double-necked flask. To this flask, triethylamine (Et<sub>3</sub>N, 10 mL) and CH<sub>2</sub>Cl<sub>2</sub> (10 mL) were added under N<sub>2</sub> atmosphere. The resulting mixture was heated to 30 °C and stirred for 16 h. Then diluted with an appropriate amount of CH<sub>2</sub>Cl<sub>2</sub> and washed with water saturated with NaHCO<sub>3</sub> and brine sequentially. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness under reduced pressure. The organic phase was subjected to

column chromatography (petrol ether/ethyl acetate (4:1, v/v)) to afford compound **5** as a brown liquid (580 mg, 61% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.23–7.44 (m, 8H, ArH), 1.99–1.87 (m, 12H, P- $\text{CH}_2$ ), 1.20–1.10 (m, 18H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  134.3, 133.0, 131.0, 129.8, 126.7, 125.1, 15.3, 8.2. FT-IR (KBr, 25 °C,  $\text{cm}^{-1}$ ): 2964 ( $\nu_{\text{C-H}}$ ), 2861 ( $\nu_{\text{C-H}}$ ), 2090 ( $\nu_{\text{C}\equiv\text{C}}$ ). MS  $m/z$  calcd for  $\text{C}_{42}\text{H}_{38}\text{F}_{10}\text{O}_4\text{P}_2\text{Pd}$  [ $\text{M}-\text{Cl}$ ]: 928.61; Found: 928.68.

*Synthesis of c-Pd(II)*: Compound **5** (128 mg, 0.13 mmol) and 1,6-hexanediamine (15 mg, 0.13 mmol) were weighed into a 50 mL double-necked flask. The  $\text{Et}_3\text{N}$  (8 mL) and THF (8 mL) were added to this flask under  $\text{N}_2$  atmosphere. The solution was heated to 55 °C and stirred at this temperature for 20 h, then diluted with an appropriate amount of ethyl acetate and washed with water saturated with  $\text{NaHCO}_3$  and brine sequentially. The organic phase was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and evaporated to dryness to obtain the crude product, which was subjected to column chromatography (petrol ether/ethyl acetate (2:1, v/v)) to give *c*-Pd(II) as a brown solid (55 mg, 55% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.54–7.08 (m, 8H, ArH), 3.22–3.11 (m, 4H,  $\text{CH}_2$ ), 1.99–1.87 (m, 12H, P- $\text{CH}_2$ ), 1.29–1.21 (m, 4H,  $\text{CH}_2$ ), 1.20–1.10 (m, 18H,  $\text{CH}_3$ ), 1.08–1.02 (m, 4H,  $\text{CH}_2$ ).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  18.47.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  170.8, 138.2, 132.1, 127.9, 125.9, 124.9, 116.8, 108.0, 42.9, 38.6, 14.3, 13.2, 8.6. FT-IR (KBr, 25 °C,  $\text{cm}^{-1}$ ): 2924 ( $\nu_{\text{C-H}}$ ), 2856 ( $\nu_{\text{C-H}}$ ), 2125 ( $\nu_{\text{C}\equiv\text{C}}$ ). MS  $m/z$  calcd (%) for  $\text{C}_{36}\text{H}_{51}\text{LiN}_2\text{O}_2\text{P}_2\text{Pd}$ : [ $\text{M} + \text{Li}$ ] $^+$ : 719.13; Found: 720.59.

*Synthesis of c-poly-**1**<sub>n</sub>s*: These polymers were prepared according to Scheme 1 in the main text. Taking *c*-poly-**1**<sub>60</sub> as an example, monomer **1** (100 mg, 0.34 mmol) and *c*-Pd(II) (4.0 mg, 0.005 mmol) were dissolved in redistilled THF (1 mL) under an  $\text{N}_2$  atmosphere. The reaction solution was stirred at 55 °C for 12 h, then cooled to room temperature and precipitated into a large volume of cooled methanol. After centrifugation and drying, a yellow solid was obtained (70 mg, 70% yield). SEC:  $M_n = 10.1$  kg/mol,  $M_w/M_n = 1.18$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.71–7.28 (br, 4H, ArH), 4.41–3.52 (br, 2H,  $\text{OCH}_2$ ), 1.41–1.12 (br, 14H,  $\text{CH}_2$ ), 0.97–0.71 (br, 3H,  $\text{CH}_3$ ). FT-IR (KBr, 25 °C,  $\text{cm}^{-1}$ ): 2924 ( $\nu_{\text{C-H}}$ ), 2125 ( $\nu_{\text{C}\equiv\text{C}}$ ), 1706 ( $\nu_{\text{C=O}}$ ), 1692 ( $\nu_{\text{C=N}}$ ).

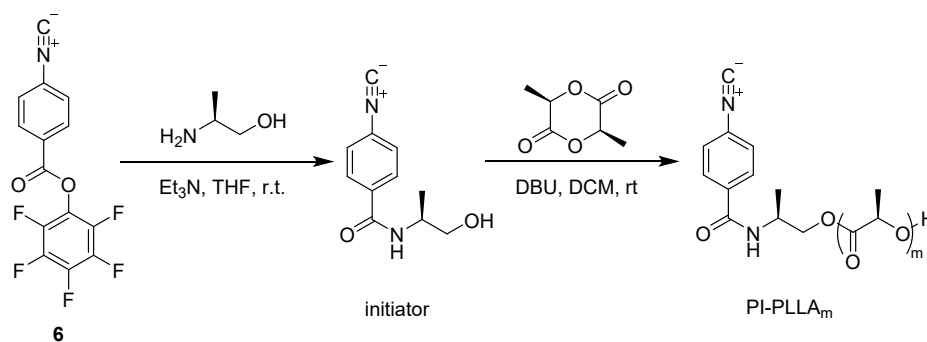
*Kinetic studies*. Monomer **1** (100 mg, 0.34 mmol), catalyst *c*-Pd(II) (6.06 mg, 0.008

mmol) and polystyrene (50 mg) were dissolved in THF (1 mL) under N<sub>2</sub> atmosphere ([**1**]<sub>0</sub> = 0.35 M, [**1**]<sub>0</sub>/[Pd]<sub>0</sub> = 40). The reaction was heated at 55 °C. Aliquots removed from the reaction solution at appropriate time intervals were subjected to SEC determination. The conversion of monomer **1** was calculated from the peak area of unreacted monomer. The conversion of monomer **1** was calculated from the peak area of unreacted monomer **1** relative to the peak area of the internal standard polystyrene based on a linear calibration curve.  $M_n$  and  $M_w/M_n$  were estimated by SEC and reported as equivalents to the polystyrene standard.

*Synthesis of l-poly-1<sub>n</sub>s*: These polymers were prepared according to Scheme 1 in the main text, followed the reported literatures.<sup>5</sup> Taking *l*-poly-**1**<sub>80</sub> as an example. Monomer **1** (100 mg, 0.34 mmol) and alkyne-Pd(II) (2.1 mg, 0.004 mmol) were dissolved in redistilled THF (1 mL) under an N<sub>2</sub> atmosphere. The mixture was stirred at 55 °C for 12 h. The polymerization solution was cooled to room temperature and precipitated into a large volume of cooled methanol. After centrifugation and drying, a yellow solid was obtained (70 mg, 70% yield). SEC:  $M_n = 10.1$  kg/mol,  $M_w/M_n = 1.18$ . <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  7.48–7.24 (br, 4H, ArH), 4.58–3.42 (br, 2H, OCH<sub>2</sub>), 1.75–0.73 (br, 19H, CH<sub>2</sub> and CH<sub>3</sub>). FT-IR (KBr, 25 °C, cm<sup>-1</sup>): 2956 ( $\nu_{C-H}$ ), 2921 ( $\nu_{C-H}$ ), 2847 ( $\nu_{C-H}$ ), 1716 ( $\nu_{C=O}$ ), 1600 ( $\nu_{C=N}$ ).

*Intrinsic viscosity*: The Ubbelohde viscometer was placed in a water bath at a constant temperature of 25 °C, the solvent THF was added and the mean efflux time was recorded  $t_0$ . A solution of cyclic polymer *c*-poly-**1**<sub>80</sub> with an initial mass concentration of 0.002 g/mL was added and then the mass concentration ( $\rho$ ) of the solution was varied and the respective efflux time ( $t$ ) was recorded. Relative viscosity ( $\eta_r = t/t_0$ ); make  $\text{Ln}(\eta_r)/\rho$  plot and extrapolate to  $\rho = 0$  to find intrinsic viscosity ( $\eta$ ). The intrinsic viscosity of linear polymers *l*-poly-**1**<sub>80</sub> was determined in the same way.<sup>6</sup> The intrinsic viscosity of *c*-poly-**1**<sub>80</sub> and *l*-poly-**1**<sub>80</sub> was determined to be 0.78 and 1.08 mL/g, respectively.

## Synthesis of cyclic bottlebrush polymers $c\text{-(PI-PLLA}_m\text{)}_n$



**Scheme S2** Synthesis of initiator and macromonomer PI-PLLA<sub>m</sub>.

*Synthesis of initiator:*<sup>7</sup> Pentafluorophenol isocyanide (**6**, 500 mg, 1.59 mmol) was prepared followed the reported literature, and was added to the solution of *S*-(+)-2-amino-1-propanol (120 mg, 1.59 mmol) in THF (10 mL) and  $\text{Et}_3\text{N}$  (0.08 mL). The mixture was stirred at room temperature for 6 h. Then diluted with an appropriate amount of  $\text{CH}_2\text{Cl}_2$  and washed with water saturated with  $\text{NaHCO}_3$  and brine sequentially. The organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and evaporated to dryness under reduced pressure. The crude product obtained was subjected to column chromatography (petroleum ether/ethyl acetate (2:1, v/v)) to give initiator as a yellow solid (305 mg, 94% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.86–7.79 (d, 2H, ArH), 7.47–7.41 (d, 2H, ArH), 6.38–6.27 (s, 1H, OH), 4.33–4.24 (m, 1H, CH), 3.85–3.62 (d, 2H,  $\text{CH}_2$ ), 1.33–1.29 (d, 3H,  $\text{CH}_3$ ).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  166.5, 166.2, 134.8, 128.4, 126.7, 66.5, 48.2, 17.1. FT-IR (KBr, 25 °C,  $\text{cm}^{-1}$ ): 3332 ( $\nu_{\text{N-H}}$ ), 3063 ( $\nu_{\text{C-H}}$ ), 2961 ( $\nu_{\text{C-H}}$ ), 2134 ( $\nu_{\text{C}\equiv\text{N}}$ ), 1631 ( $\nu_{\text{C=O}}$ ). MS  $m/z$  calcd for  $\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}_2$  [ $\text{M}+\text{H}$ ]<sup>+</sup>: 205.10; Found: 205.15.

*Synthesis of macromonomer PI-PLLA<sub>m</sub>:* Taking PI-PLLA<sub>60</sub> as an example, initiator (50 mg, 0.25 mmol) and L-lactide (1.08 g, 7.50 mmol) were dissolved in anhydrous  $\text{CH}_2\text{Cl}_2$  (10 mL). After the solid was completely dissolved, 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, 37 mg, 0.25 mmol) was added. The resulting mixture was stirred at room temperature for 12 h. The solution was then precipitated into methanol. The precipitated solid was collected by centrifugation and dried in vacuum at room temperature overnight to give PI-PLLA<sub>60</sub> as a white solid (0.96 g, 85%



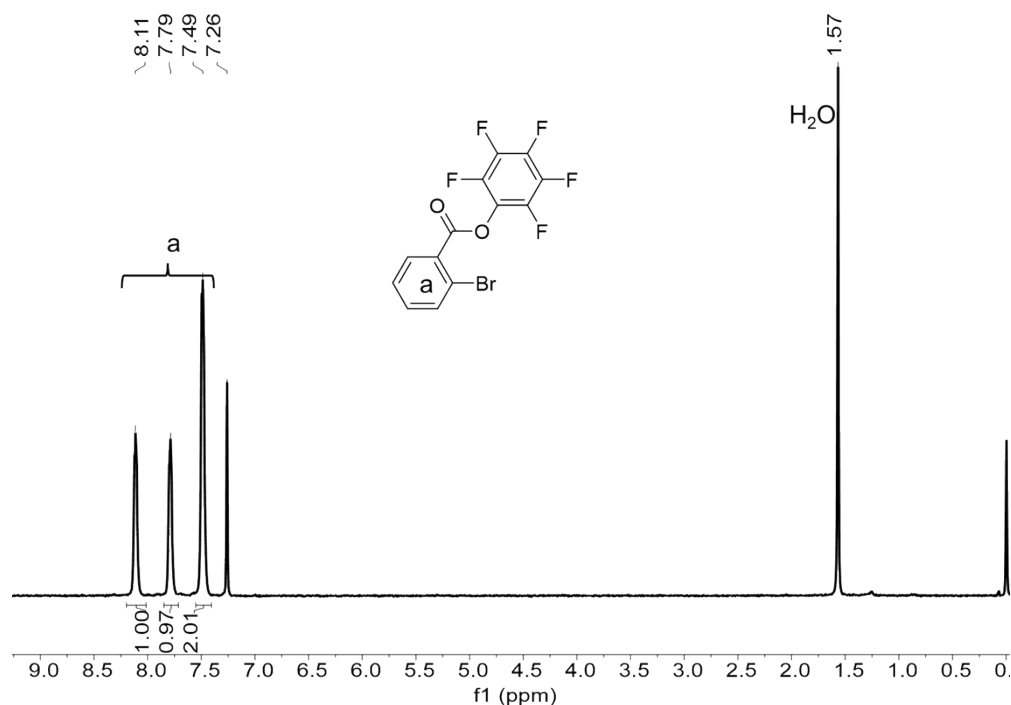
yield). SEC:  $M_n = 5.5$  kg/mol,  $M_w/M_n = 1.21$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.83–7.75 (d, 2H, ArH), 7.47–7.41 (d, 2H, ArH), 5.25–5.02 (br, 70H, CH and  $\text{CH}_2$  of the PLLA chain), 1.59–1.55 (br, 210H,  $\text{CH}_3$  of PLLA main chain). FT-IR (KBr, 25 °C,  $\text{cm}^{-1}$ ): 2993 ( $\nu_{\text{C-H}}$ ), 2955 ( $\nu_{\text{C-H}}$ ), 2125 ( $\nu_{\text{C}\equiv\text{N}}$ ), 1750 ( $\nu_{\text{C=O}}$ ).

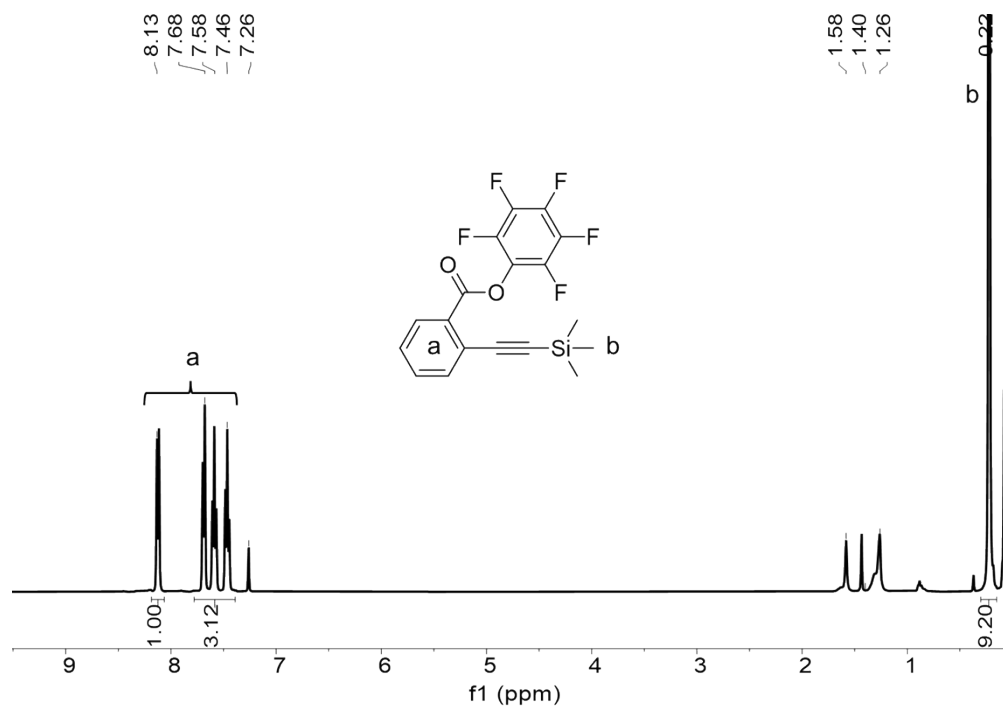
*Synthesis of cyclic bottlebrush polymers c-(PI-PLLA<sub>m</sub>)<sub>n</sub>s*: Taking (PI-PLLA<sub>60</sub>)<sub>50</sub> as an example, PI-PLLA<sub>60</sub> (100 mg, 0.018 mmol) and *c*-Pd(II) (0.22 mg, 0.0003 mmol) were dissolved in redistilled toluene (1 mL) under an  $\text{N}_2$  atmosphere. The reaction solution was stirred at 100 °C for 12 h. The polymerized solution was concentrated and precipitated into a large volume of cooled methanol. After centrifugation and drying, a yellow solid was obtained (62 mg, 62%). SEC:  $M_n = 404.9$  kg/mol,  $M_w/M_n = 1.31$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.83–7.21 (br, 4H, ArH of the terminal phenyl isocyanide), 5.25–5.02 (br, 70H, CH and  $\text{CH}_2$  of the PLLA chain), 1.59–1.55 (br, 210H,  $\text{CH}_3$  of PLLA main chain). FT-IR (KBr, 25 °C,  $\text{cm}^{-1}$ ): 2993 ( $\nu_{\text{C-H}}$ ), 2947 ( $\nu_{\text{C-H}}$ ), 1656 ( $\nu_{\text{C=O}}$ ), 1479 ( $\nu_{\text{C=N}}$ ).

**Table S1.** Characterization Data for linear polymer, (PI-PLLA<sub>m</sub>)<sub>n</sub> and c-(PI-PLLA<sub>m</sub>)<sub>n</sub>s

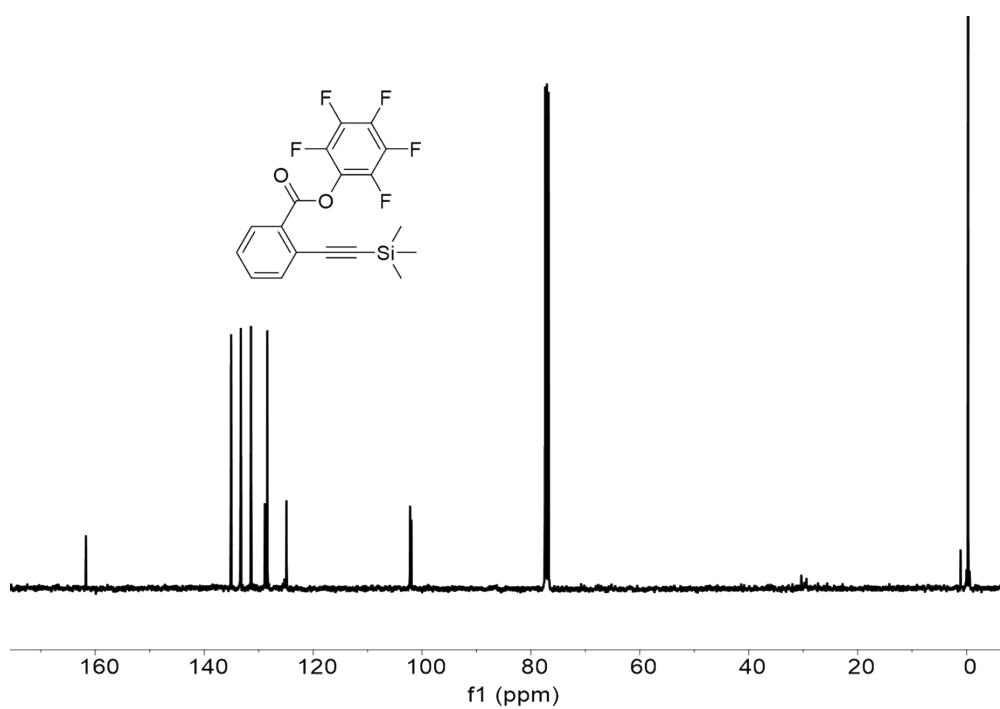
run <sup>a</sup>	Polymer	$M_n^b$ (kg/mol)	$M_w/M_n^b$	Yield <sup>c</sup>
1	<i>l</i> -poly-1 <sub>80</sub>	16.8	1.08	80%
2	(PI-PLLA <sub>20</sub> )	3.0	1.31	83%
3	(PI-PLLA <sub>40</sub> )	4.0	1.34	85%
4	(PI-PLLA <sub>60</sub> )	5.5	1.21	85%
5	(PI-PLLA <sub>80</sub> )	6.1	1.14	81%
6	(PI-PLLA <sub>100</sub> )	8.0	1.24	84%
7	(PI-PLLA <sub>60</sub> ) <sub>50</sub>	404.9	1.31	62%
8	(PI-PLLA <sub>60</sub> ) <sub>100</sub>	468.8	1.34	63%
9	(PI-PLLA <sub>60</sub> ) <sub>150</sub>	688.8	1.24	62%
10	(PI-PLLA <sub>100</sub> ) <sub>100</sub>	904.3	1.28	67%
11	(PI-PLLA <sub>100</sub> ) <sub>150</sub>	1248.2	1.25	65%

<sup>a</sup>The polymers were prepared according to Scheme 1 and Scheme 2. <sup>b</sup>The  $M_n$  and  $M_w/M_n$  values were calculated via SEC using polystyrene standards. <sup>c</sup>Isolated yields.

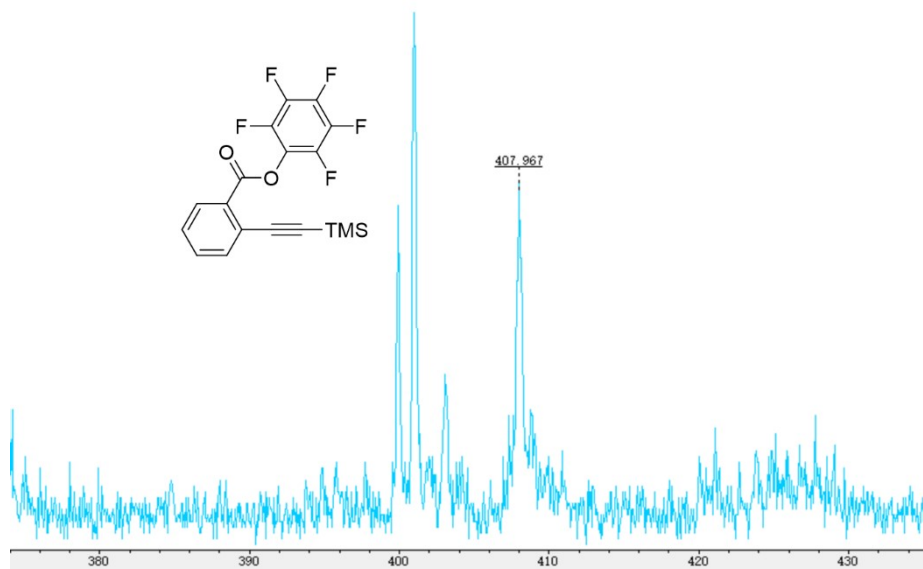
**Fig. S1** <sup>1</sup>H NMR spectrum of the compound 2 measured in CDCl<sub>3</sub> at room temperature.



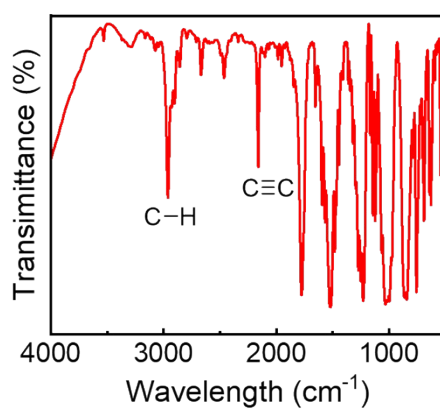
**Fig. S2** <sup>1</sup>H NMR spectrum of the compound **3** measured in CDCl<sub>3</sub> at room temperature.



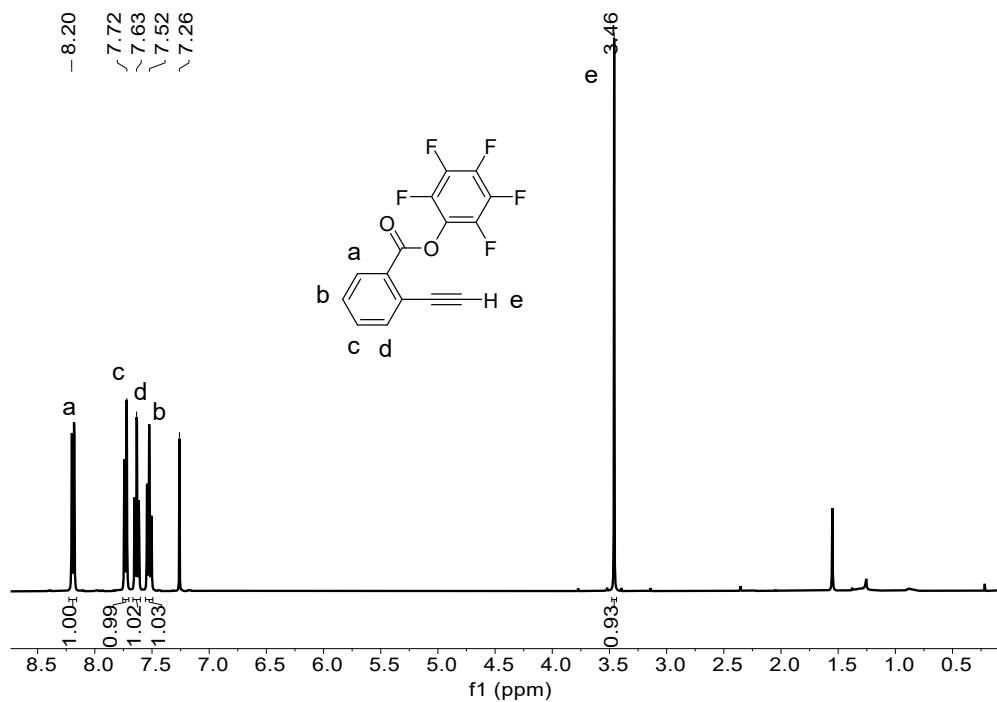
**Fig. S3** <sup>13</sup>C NMR spectrum of the compound **3** measured in CDCl<sub>3</sub> at room temperature.



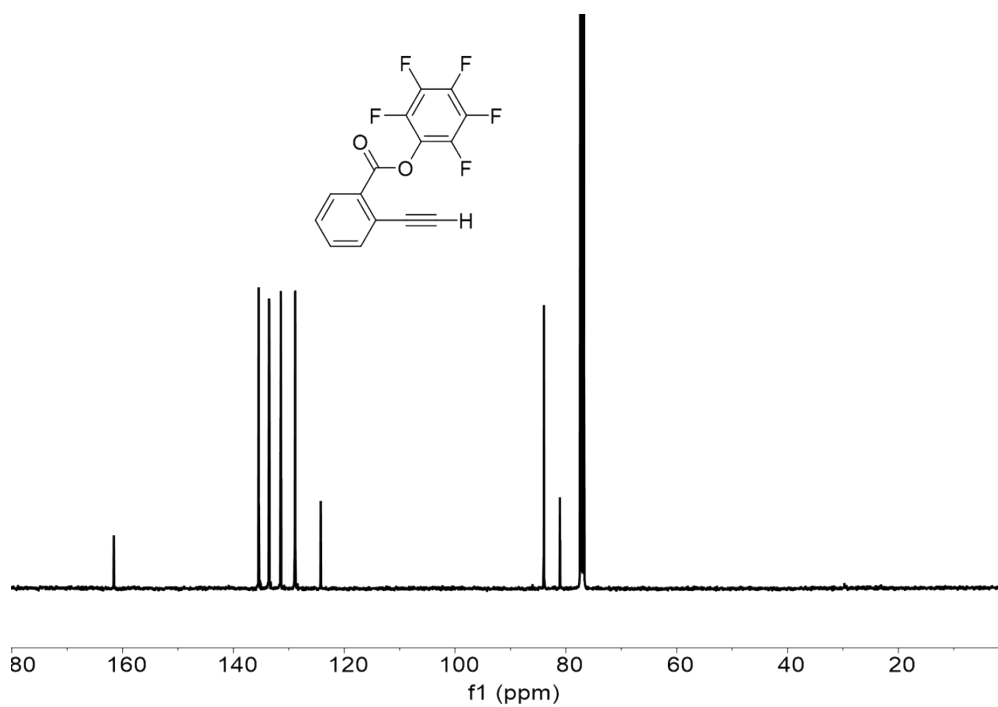
**Fig. S4** Mass spectrometry of the compound **3**.



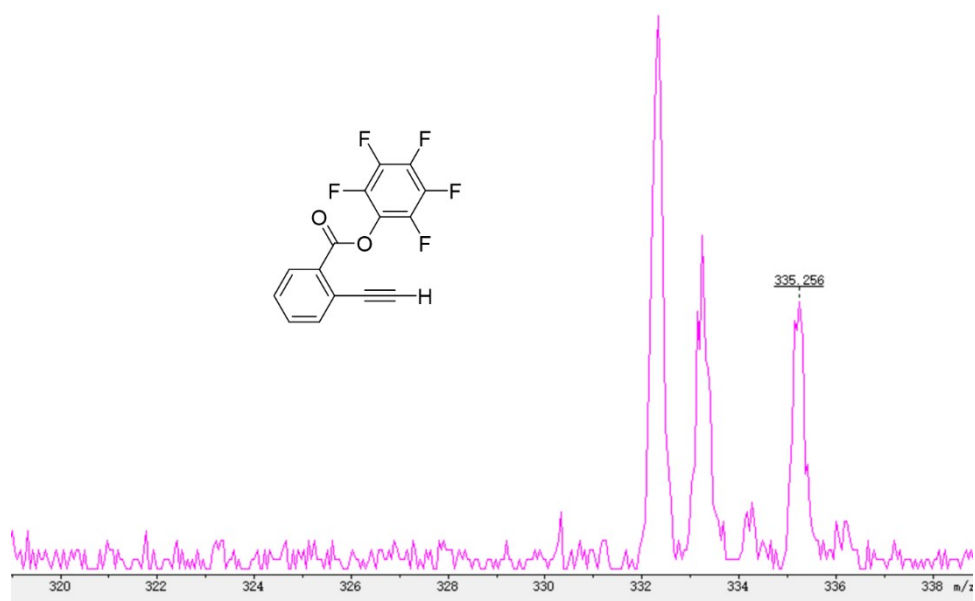
**Fig. S5** FT-IR spectrum of the compound **3** measured at room temperature using KBr pellets.



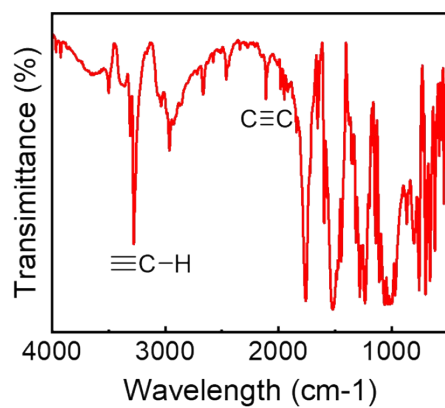
**Fig. S6** <sup>1</sup>H NMR spectrum of the compound **4** measured in CDCl<sub>3</sub> at room temperature.



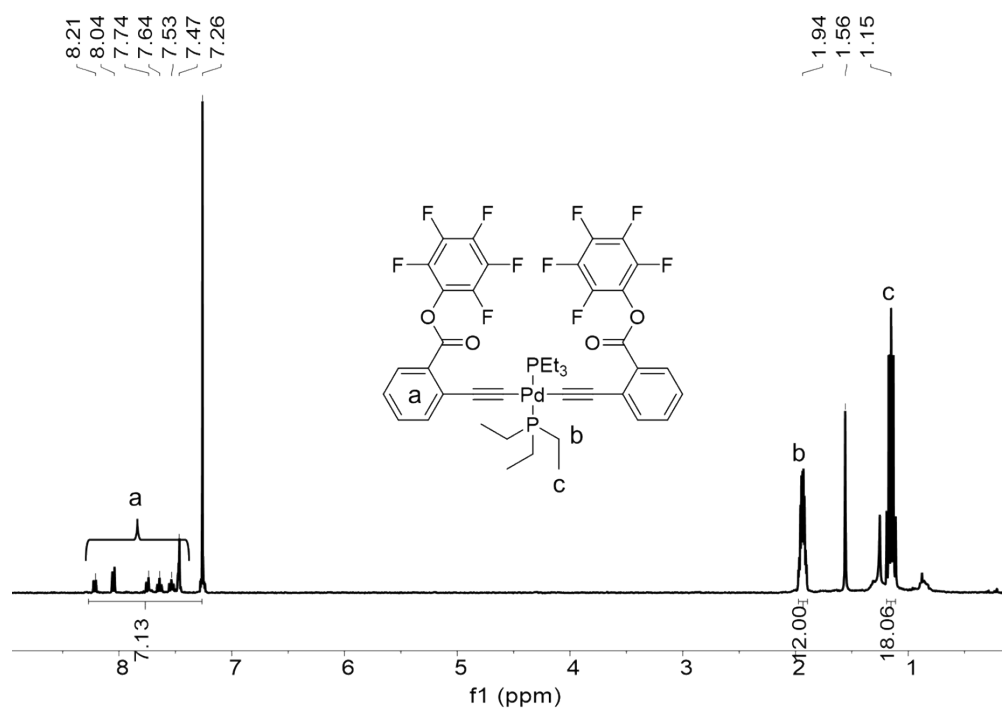
**Fig. S7** <sup>13</sup>C NMR spectrum of the compound **4** measured in CDCl<sub>3</sub> at room temperature.



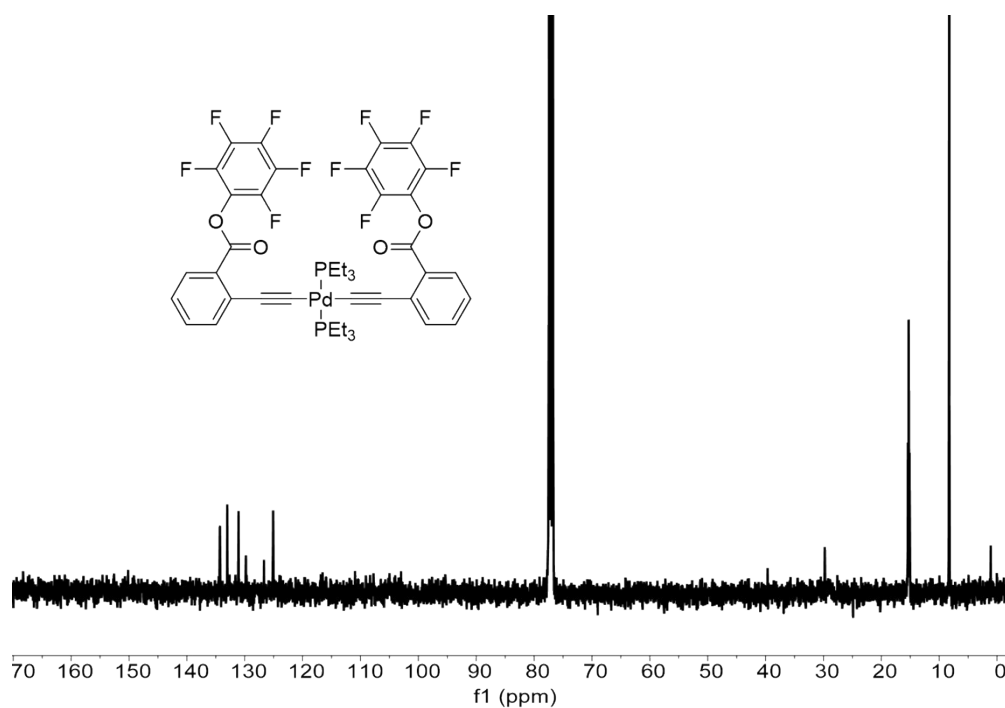
**Fig. S8** Mass spectrometry of the compound 4.



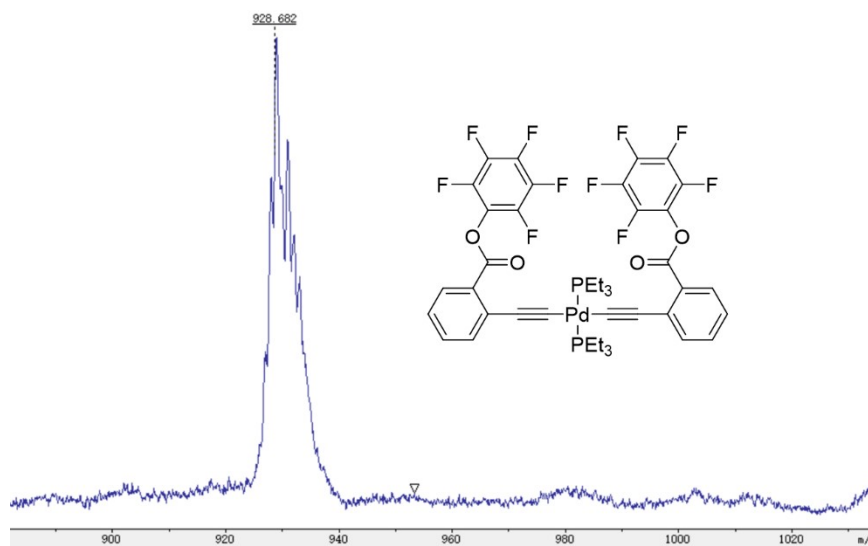
**Fig. S9** FT-IR spectrum of the compound 4 measured at room temperature using KBr pellets.



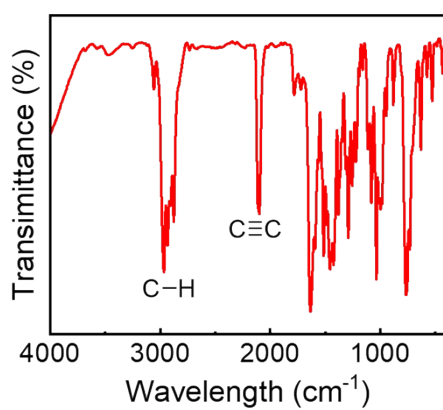
**Fig. S10** <sup>1</sup>H NMR spectrum of the compound **5** measured in CDCl<sub>3</sub> at room temperature.



**Fig. S11** <sup>13</sup>C NMR spectrum of the compound **5** measured in CDCl<sub>3</sub> at room temperature.

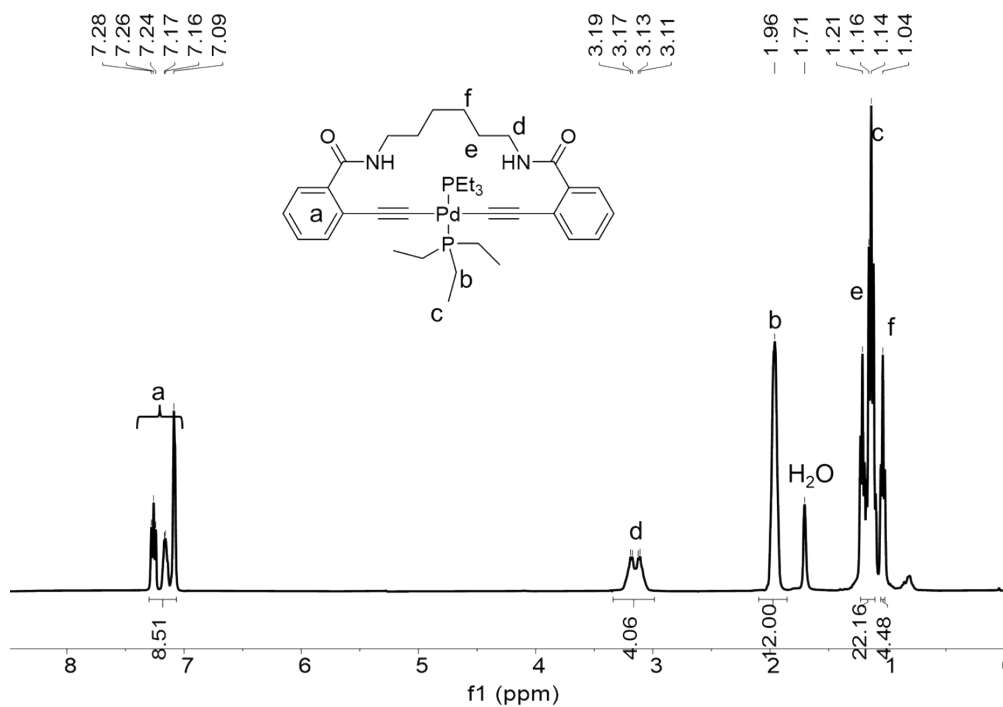


**Fig. S12** Mass spectrometry of the compound **5**.

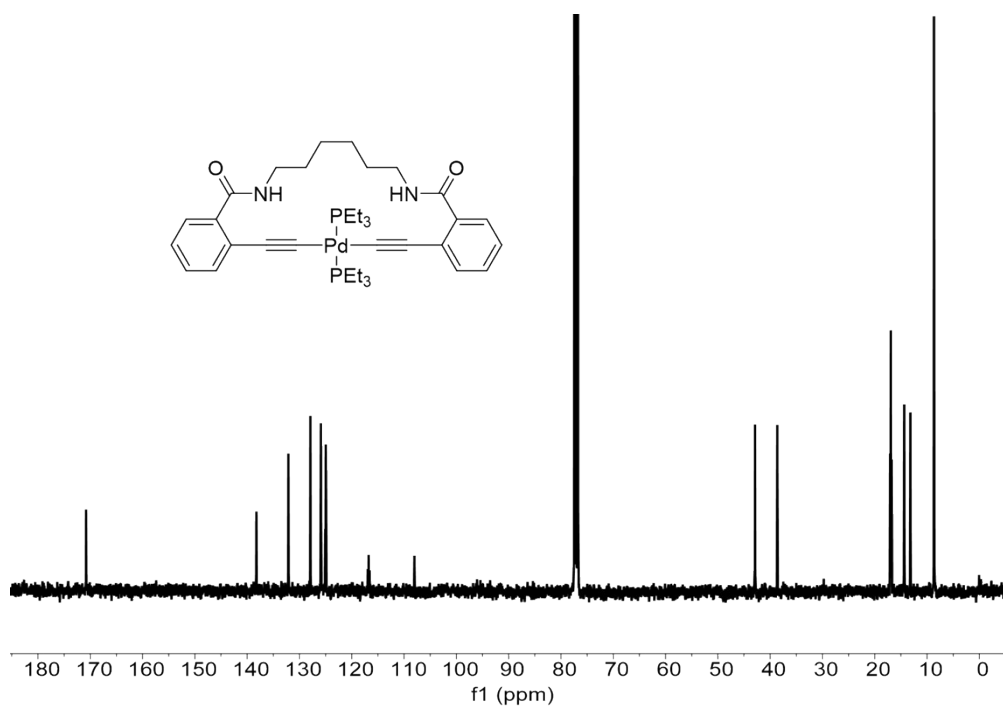


**Fig. S13** FT-IR spectrum of the compound **5** measured at room temperature using KBr pellets.

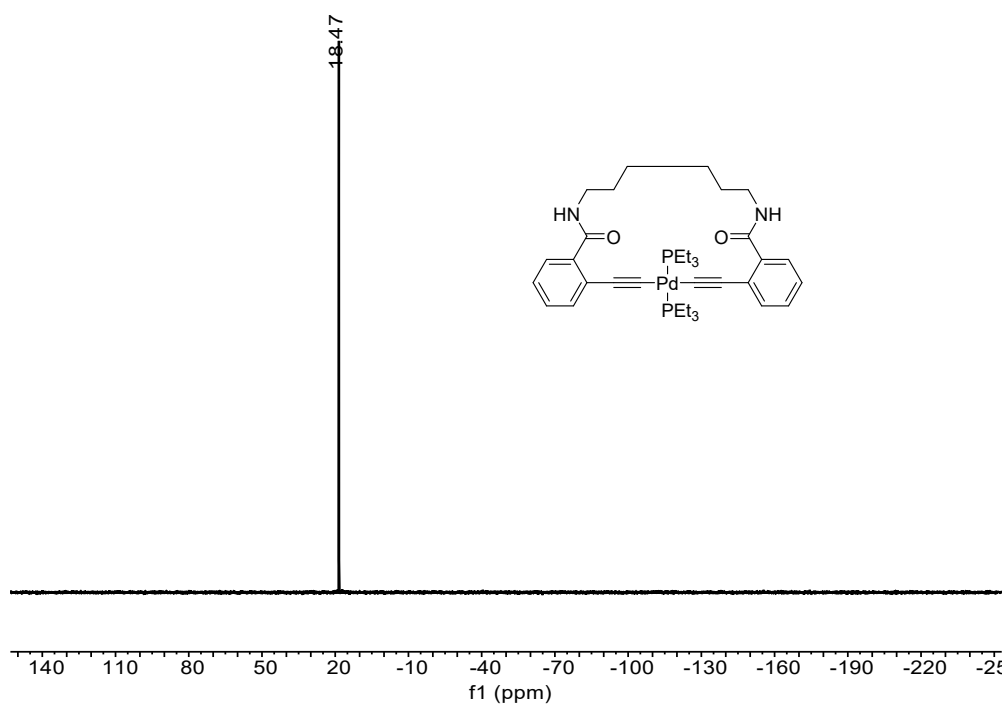




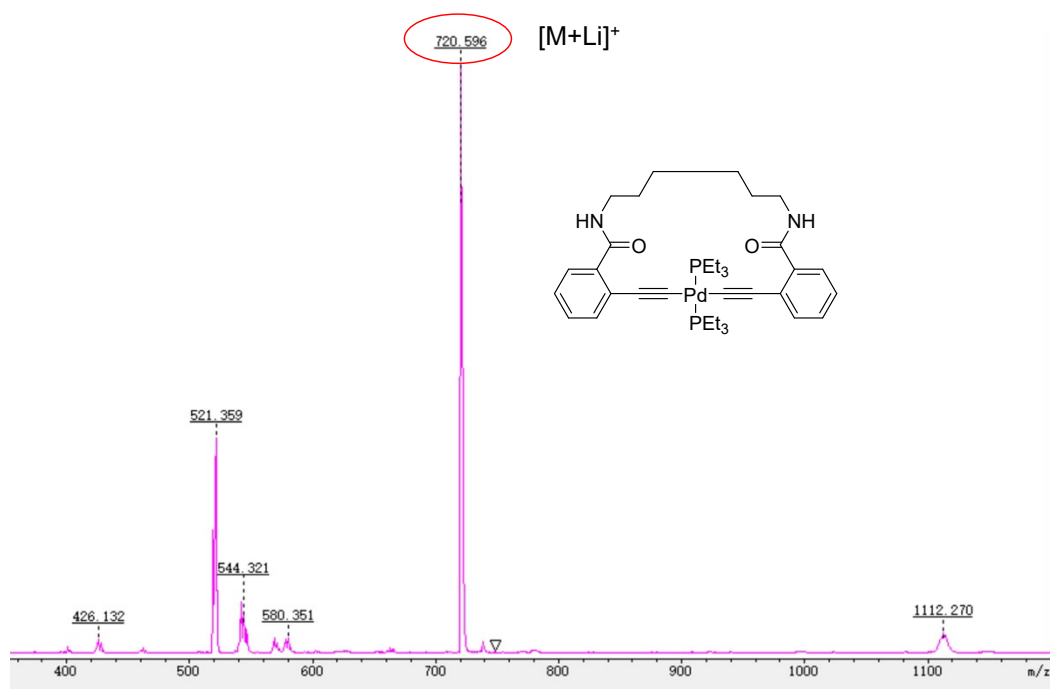
**Fig. S14** <sup>1</sup>H NMR spectrum of the *c*-Pd(II) measured in CDCl<sub>3</sub> at room temperature.



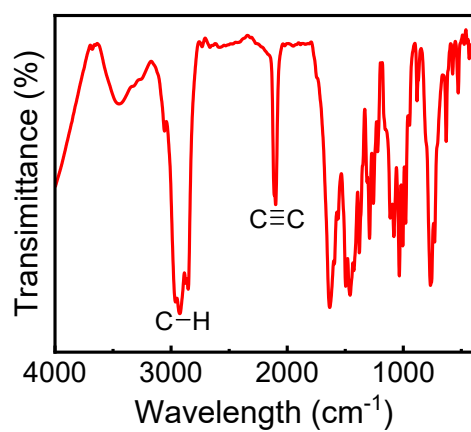
**Fig. S15** <sup>13</sup>C NMR spectrum of the *c*-Pd(II) measured in CDCl<sub>3</sub> at room temperature.



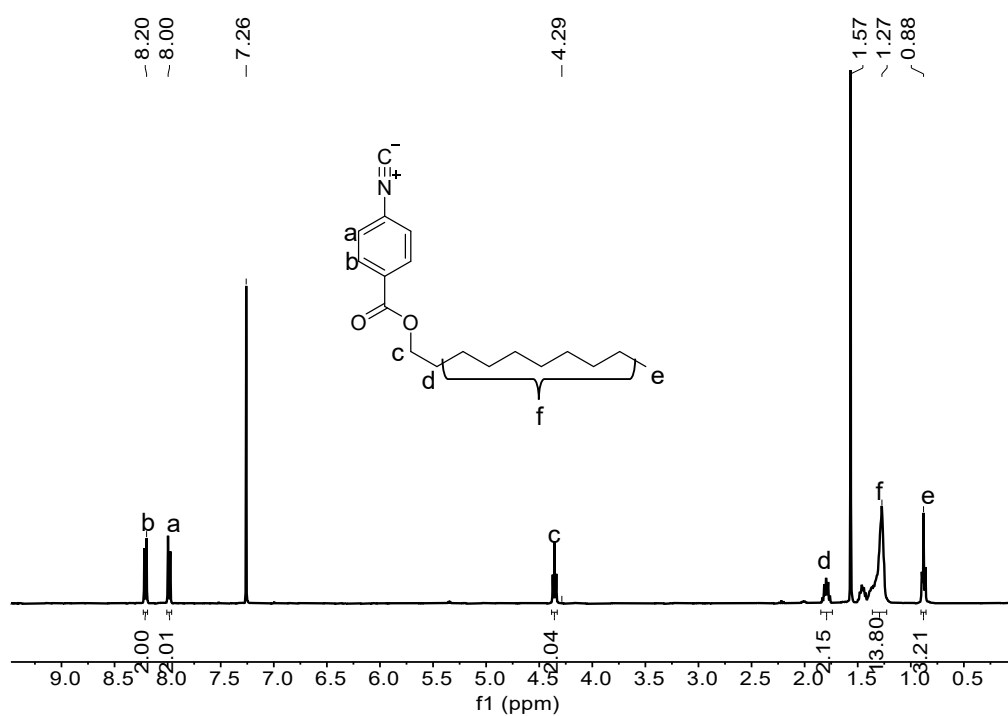
**Fig. S16**  $^{31}\text{P}$  NMR spectrum of the *c*-Pd(II) measured in  $\text{CDCl}_3$  at room temperature.



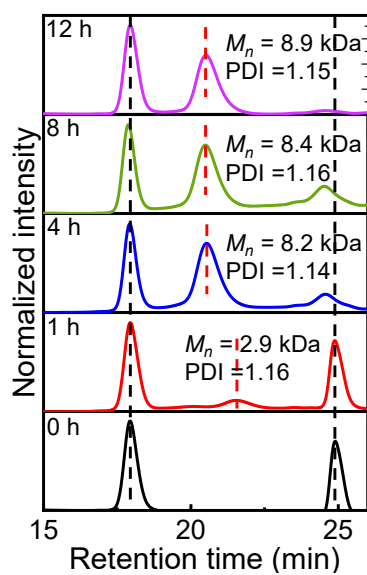
**Fig. S17** Mass spectrometry of the *c*-Pd(II).



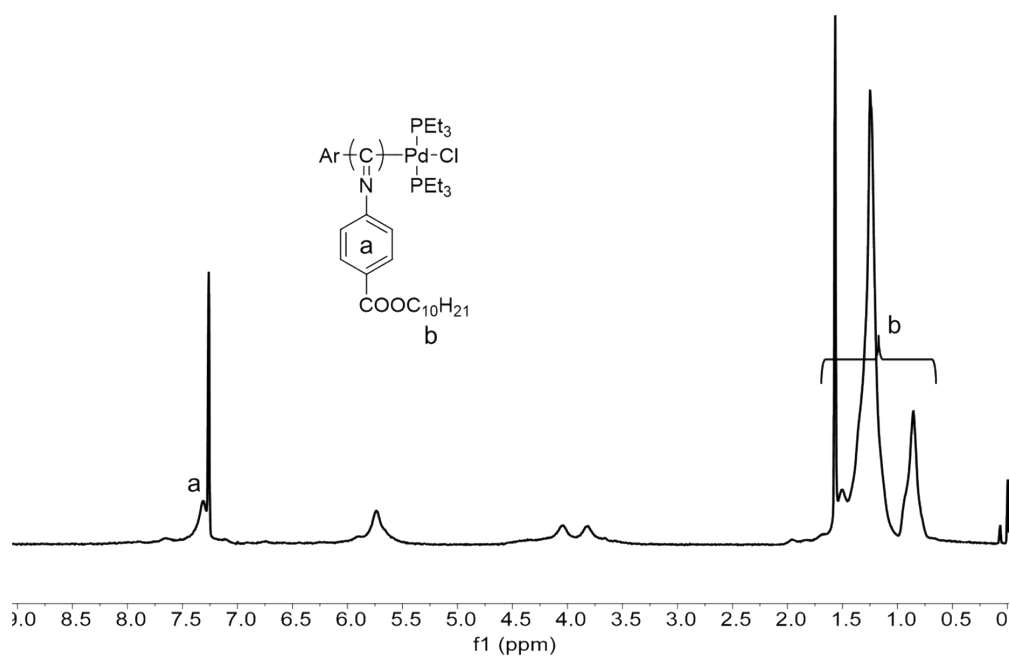
**Fig. S18** FT-IR spectrum of *c*-Pd(II) measured at room temperature using KBr pellets.



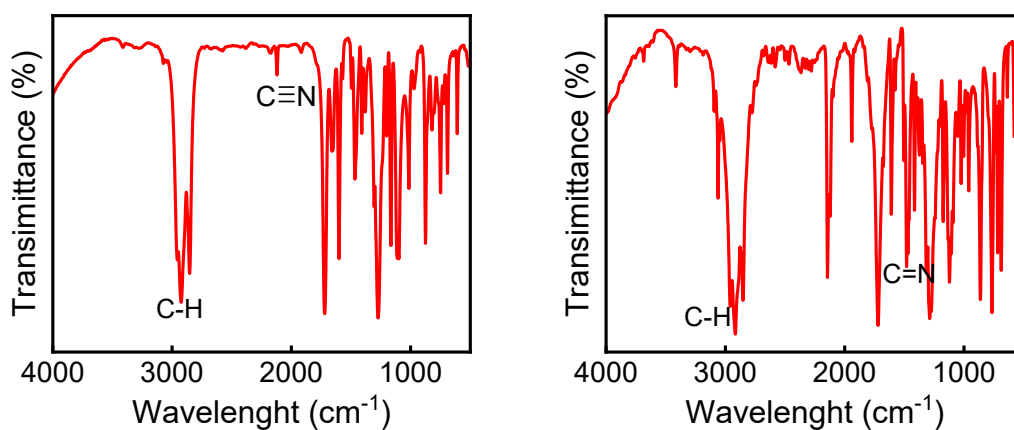
**Fig. S19** <sup>1</sup>H NMR spectrum of the monomer **1** measured in CDCl<sub>3</sub> at room temperature.



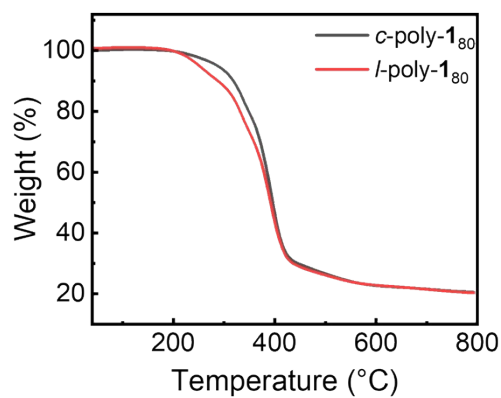
**Fig. S20** Time-dependent SEC for the polymerization of monomer **1** initiated by *c*-Pd(II) using polystyrene ( $M_n = 190$  kg/mol,  $M_w/M_n = 1.13$ ) as the internal standard in THF at 55 °C.



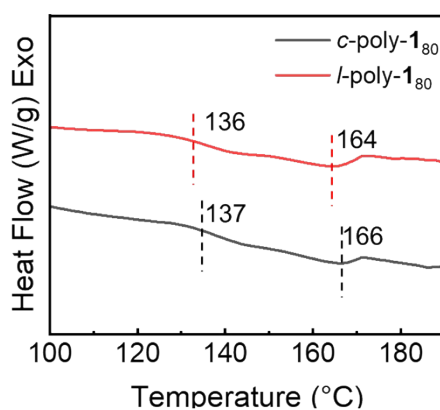
**Fig. S21**  $^1\text{H}$  NMR spectrum of the *l*-poly-**1**<sub>60</sub> measured in  $\text{CDCl}_3$  at room temperature.



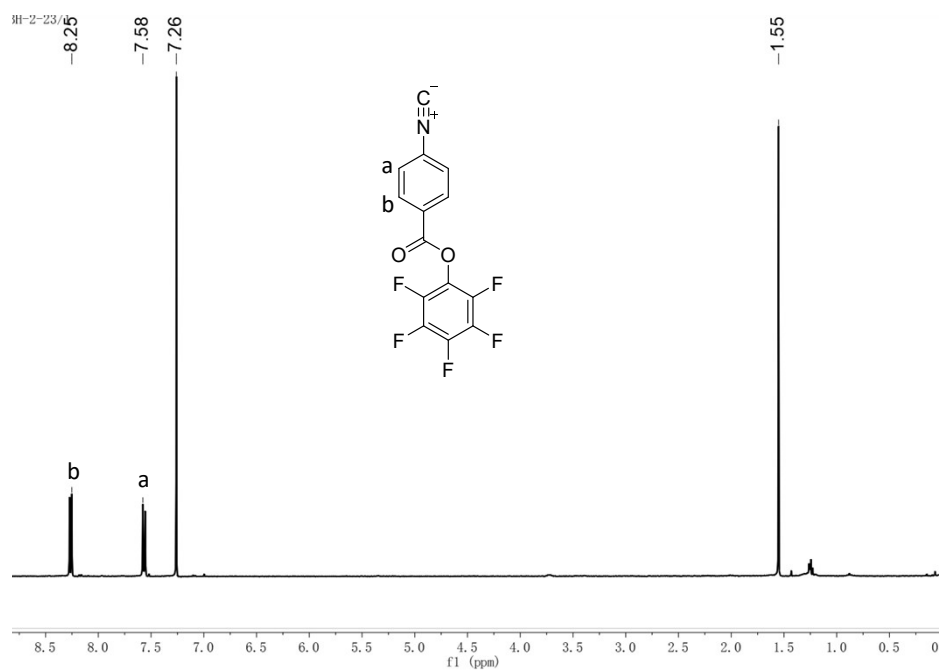
**Fig. S22** FT-IR spectrum of the monomer **1** and *c*-poly-**1**<sub>60</sub>.



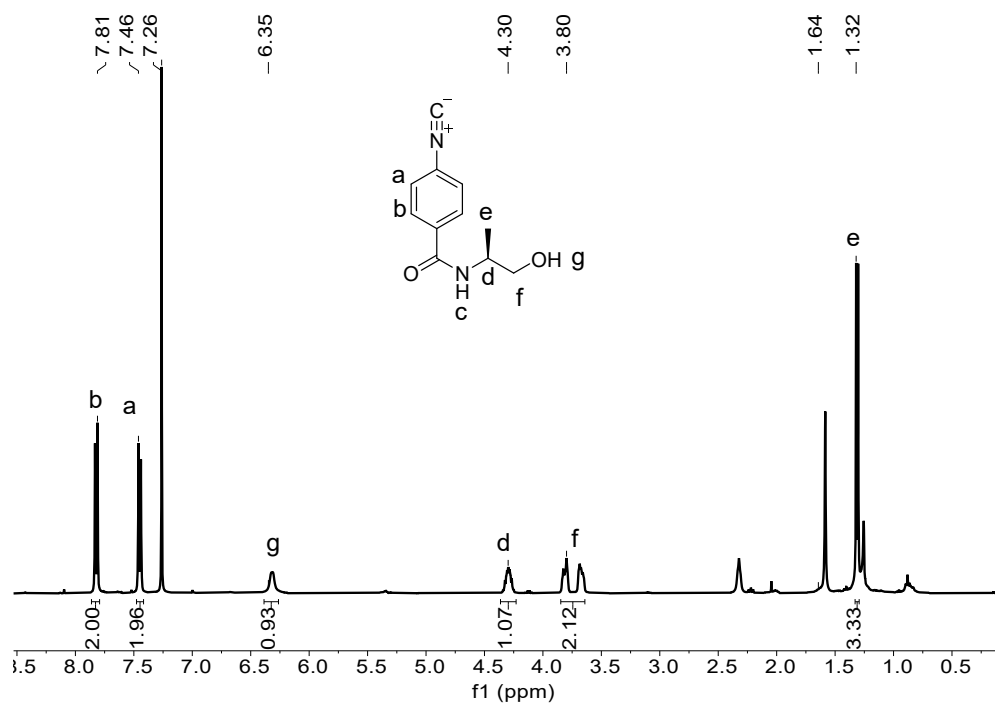
**Fig. S23** TGA of *c*-poly-**1**<sub>80</sub> and *l*-poly-**1**<sub>80</sub>.



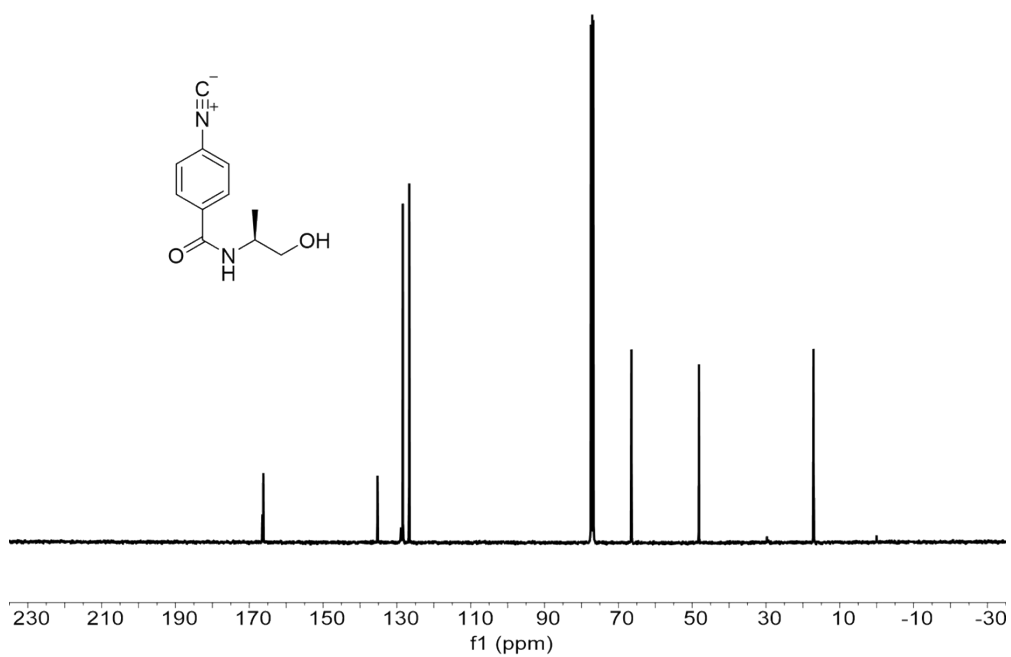
**Fig. S24** DSC of *c*-poly-**1**<sub>80</sub> and *l*-poly-**1**<sub>80</sub>.



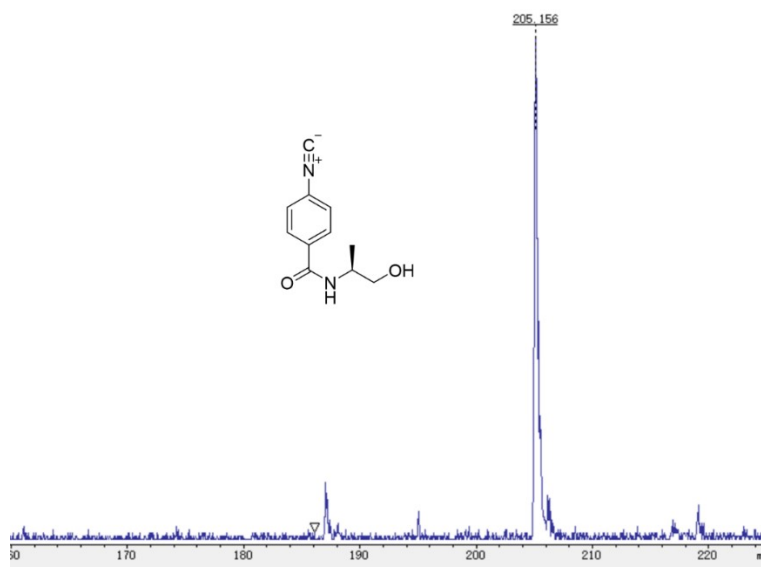
**Fig. S25**  $^1\text{H}$  NMR spectrum of the pentafluorophenol isocyanide measured in  $\text{CDCl}_3$  at room temperature.



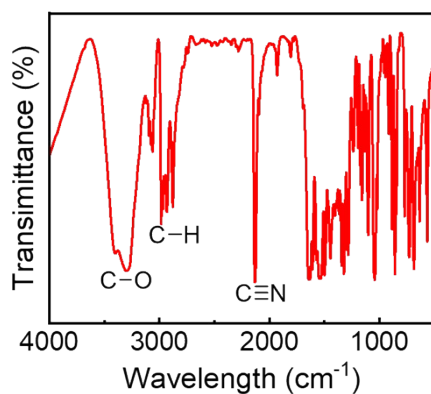
**Fig. S26**  $^1\text{H}$  NMR spectrum of the initiator measured in  $\text{CDCl}_3$  at room temperature.



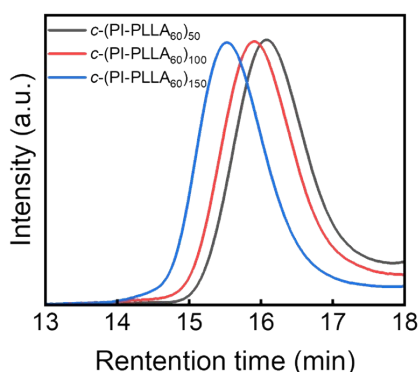
**Fig. S27**  $^{13}\text{C}$  NMR spectrum of the initiator measured in  $\text{CDCl}_3$  at room temperature.



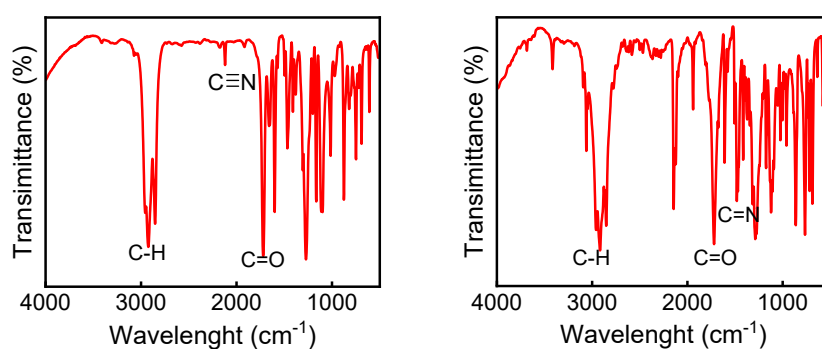
**Fig. S28** Mass spectrometry of the initiator for ring-opening polymerization.



**Fig. S29** FT-IR spectrum of the initiator measured at room temperature using KBr pellets.

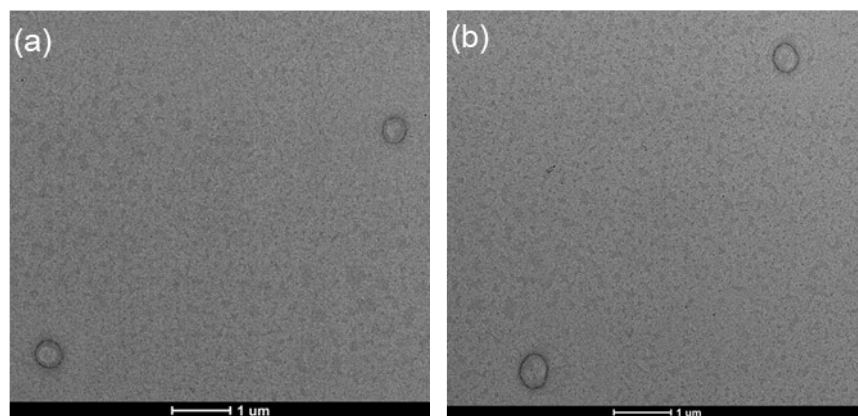


**Fig. S30** SEC for  $c\text{-(PI-PLLA}_{60}\text{)}_n$  prepared in different ratios of PI-PLLA<sub>60</sub> to catalyst. SEC condition: eluent = THF, temperature = 40 °C.



**Fig. S31** FT-IR spectrum of the PI-PLLA<sub>60</sub> and  $c\text{-(PI-PLLA}_{60}\text{)}_{50}$  measured at room temperature using KBr pellets.





**Fig. S32** (a) TEM images of  $c\text{-(PI-PLLA}_{100})_{100}$  and (b)  $c\text{-(PI-PLLA}_{100})_{150}$ .

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