Supplementary Information

AIE/CPL Dual-Functional Poly(aryl isocyanide)s Synthesized by (*S,S*)-Bis(oxazolinylphenyl)amido-Ligated Palladium Phenylethynyl Complexes: High-Security Anti-Counterfeiting and Targeted Cellular Imaging

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Table of contents

EXPERIMENTAL SECTION

Materials.

All manipulations of air and moisture-sensitive compounds were performed under a dry and oxygen-free nitrogen atmosphere by using Schlenk techniques or under a nitrogen atmosphere in an Mbraun glove box. Nitrogen (Beijing AP Beifen Gases Industrial Co., Ltd.) was purified by passing through a Dryclean column (4A molecular sieves, Dalian Replete Science And Technology Co., Ltd.) and a Gasclean column (Dalian Replete Science And Technology Co., Ltd.). The nitrogen in the glovebox was constantly circulated through a copper/molecular sieves catalyst unit. The oxygen and moisture concentrations in the glovebox atmosphere were monitored by an O_2/H_2O Combi-Analyzer (Mbraun) to ensure both were always below 0.1 ppm. Anhydrous THF, hexane and toluene were were purified by a solvent purification system (SPS-800, Mbraun), and dried over fresh Na chips in the glovebox. The isocyanide monomers were synthesized according to the literatures.[1] The deuterated solvents benzene-d6 (99.6 atom% D), chloroform-d1 (99.8 atom% D) and 1,1,2,2,-tetrachloroethane-d2 (99.6 atom% D) were obtained from Cambridge Isotope .

General Methods.

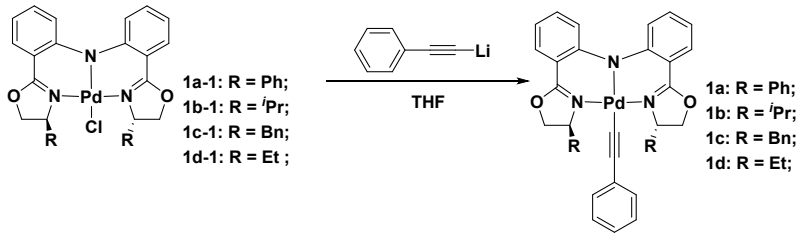
^1H and ^{13}C NMR spectra were recorded on a Bruker Avance (III HD 400 MHz) spectrometer. The molecular weights and the molecular weight distributions of the EPI polymers were determined against polystyrene standard at 25 ^oC by GPC on a Waters HPLC-515 apparatus, $CHCl_3$ was employed as the eluent at a flow rate of 1 mL/min. The molecular weights and the molecular weight distributions of the D-(or L-)IMCI-ITPB copolymers were determined against polystyrene standard at 25 ^oC by GPC on a Waters HLC-8320GPC apparatus, THF was used as the eluent at a flow rate of 1 mL/min. FT-IR spectra were recorded on a Thermo IS5 FT-IR system using KBr pellets at room temperature. The UV-Vis spectra were recorded on a TU-1901 double beam UV-vis spectrophotometer, and the fluorescence spectra were recorded on a HITACHI F-7000 fluorescence spectrophotometer. Quartz cells with 10.0 mm length were used in UV-Vis and fluorescence measurement, and the slit widths were set at 5.0 nm for both excitation and emission during the fluorescence measurement. Circular dichroism spectra were collected on a Jasco J-810 and the quartz cell length is 1.0 mm. The circularly polarized luminescence (CPL) spectra were performed on JASCO CPL-300 spectrometer at room temperature using a 1.0 cm quartz cuvette. Atomic force microscope (AFM) was performed on a Cypher S microscope (Oxford Instruments, Asylum Research). A specimen for AFM imaging was prepared by spin-casting a THF solution of polymer onto a highly oriented pyrolytic graphite (HOPG) or mica substrate at ca. 1,500 rpm. AFM imaging was carried out at room temperature (ca. 20 ℃) in air. NIH3T3 cells were cultured in DMEM medium. Cells were incubated with poly(L-PEGI) aggregates (5.0×10^{-6} mol L^{-1}) for 4 h, washed with PBS, stained with organelle dyes, and observed by CLSM. To conduct a flow cytometry apoptosis assay, incubate cells with poly(L-PEGI) aggregates under designated conditions, and analyze apoptotic cell populations via flow cytometry according to standard protocols.

X-ray Crystallographic Study.

Suitable single crystals of complexes were sealed in a thin−walled glass capillary for determining the single−crystal structure. Data collection was performed at −100 °C on a Bruker SMART diffractometer with graphite−monochromated Mo Kα radiation (λ = 0.71073 Å). The SMART program package was used to determine the unit−cell parameters. The absorption correction was

applied by using SADABS. The structures were solved by direct methods and refined on F2 by full−matrix least−squares techniques with anisotropic thermal parameters for non−hydrogen atoms. Hydrogen atoms were placed at calculated positions and were included in the structure calculation without further refinement of the parameters. All calculations were carried out using the SHELXS−97 program. Molecular structures were generated using ORTEP program. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-2326930 (**1b**) and contain supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Scheme S1. Synthesis of bis(oxazolinylphenyl)amido palladium complexes 1a-d.



Synthesis of [Ph_2-(*S*,*S*)-BOZ)PdC≡CC_6H_5 (1a): Under nitrogen atmosphere, complex **1a-1** (2.4 g, 4 mmol) was dissolved in THF (50 mL), then Li$C{\equiv}CC_6H_5$ (0.5 g, 4.4 mmol) added and the mixture was stirred at room temperature for 2 hours. Finally, the mixture was filtered and concentrated under reduced pressure, the residue was recrystallized from a mixture solvents of toluene and hexane (toluene/hexane = 3/1, v/v) at -30 °C to afford complex **1a** as a dark red solid (1.97 g, 74% yield).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.46 – 7.05 (m, 9H), 6.68 (t, *J* = 7.2 Hz, 1H), 5.91 (dd, *J* = 10.0, 5.0 Hz, 1H), 4.78 (dd, *J* = 9.9, 8.7 Hz, 1H), 4.32 (dd, *J* = 8.5, 5.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.72, 154.16, 142.03, 132.56, 131.22, 130.35, 128.89, 127.96, 127.68, 126.72, 125.37, 122.91, 117.29, 114.21, 102.00, 99.56, 75.55, 69.99.

Synthesis of [^{i}Pr_2-(*S*,*S*)-BOZ)PdC≡CC_6H_5 (1b): The synthetic procedure was the same with that of compound **1a**. (dark red solid, 72% yield).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.34 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.25 – 7.18 (m, 2H), 7.16 – 7.06 (m, 2H), 6.68 – 6.62 (m, 1H), 4.93 – 4.81 (m, 1H), 4.63 (dd, *J* = 9.6, 8.6 Hz, 1H), 4.30 (dd, *J* = 8.5, 5.3 Hz, 1H), 2.14 (dqd, *J* = 15.1, 7.6, 3.0 Hz, 1H), 1.93 – 1.79 (m, 1H), 0.89 (dd, *J* = 9.6, 5.3 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.68, 153.92, 132.34, 131.41, 130.18, 128.09, 127.57, 125.65, 122.96, 117.32, 114.52, 102.38, 97.85, 72.14, 67.62, 29.30, 8.77.

Synthesis of [Bn_2-(*S*,*S*)-BOZ)PdC≡CC_6H_5 (1c): The synthetic procedure was the same with that of compound **1a**. (dark red solid, 73% yield).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.44 (d, *J* = 7.2 Hz, 1H), 7.36 – 7.27 (m, 3H), 7.23 – 7.09 (m, 4H), 6.67 (t, *J* = 7.4 Hz, 1H), 5.34 – 5.19 (m, 1H), 4.53 (t, *J* = 9.1 Hz, 1H), 4.40 (dd, *J* = 8.8, 4.9 Hz, 1H), 3.55 (dd, *J* = 13.5, 3.4 Hz, 1H), 3.04 (dd, *J* = 13.5, 8.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.18, 153.80,

136.36, 132.42, 131.55, 130.17, 129.83, 128.46, 128.04, 126.65, 125.75, 122.97, 117.38, 114.40, 102.71, 100.00, 71.43, 67.55, 41.95.

Synthesis of [Et_2-(*S*,*S*)-BOZ)PdC≡CC_6H_5 (1d): The synthetic procedure was the same with that of compound **1a**. (dark red solid, 79% yield).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 7.9 Hz, 1H), 7.33 (d, *J* = 7.7 Hz, 1H), 7.21 (t, *J* = 7.1 Hz, 2H), 7.11 (dt, *J* = 15.2, 7.6 Hz, 2H), 6.66 (t, *J* = 7.4 Hz, 1H), 4.98 – 4.79 (m, 1H), 4.50 (t, *J* = 9.4 Hz, 1H), 4.38 (dd, *J* = 8.6, 5.1 Hz, 1H), 2.84 – 2.66 (m, 1H), 0.93 (d, *J* = 7.0 Hz, 3H), 0.77 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.42, 153.96, 132.32, 131.30, 130.09, 127.96, 127.40, 125.53, 122.74, 117.18, 114.40, 102.39, 97.50, 70.95, 68.22, 31.69, 18.77, 13.97.

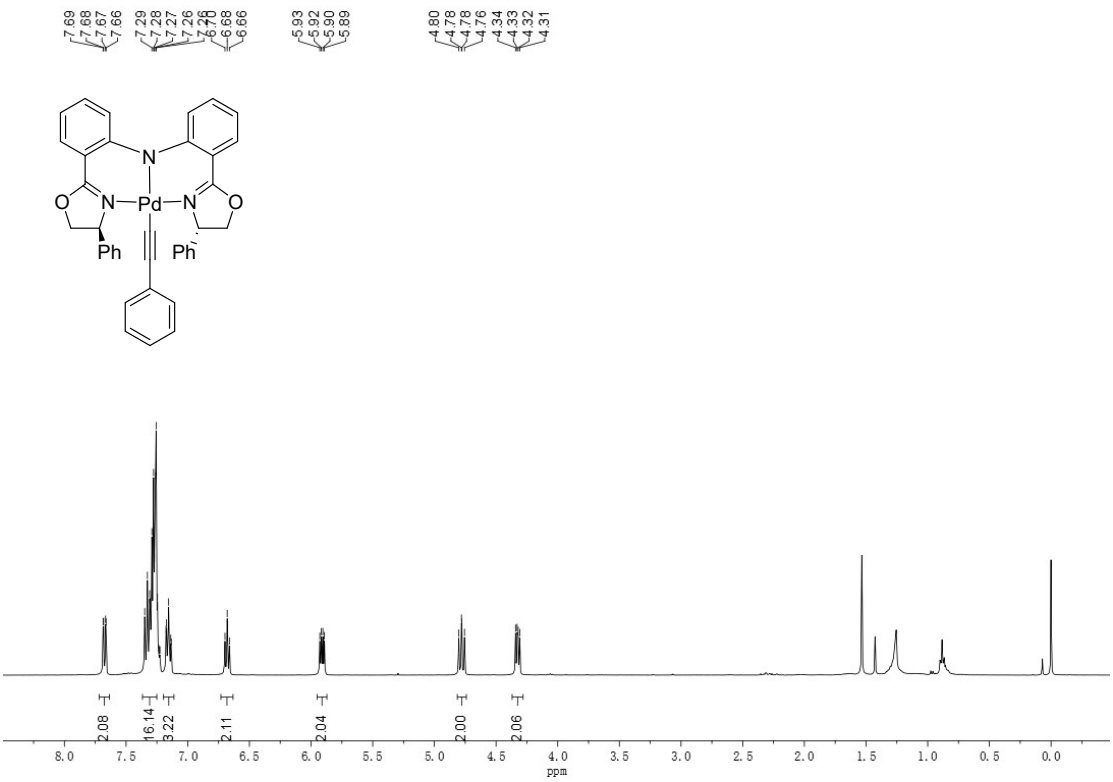


Figure S1. ^{1}H NMR spectrum of [Ph_2-(*S*,*S*)-BOZ)PdC≡CC_6H_5 (**1a)**.

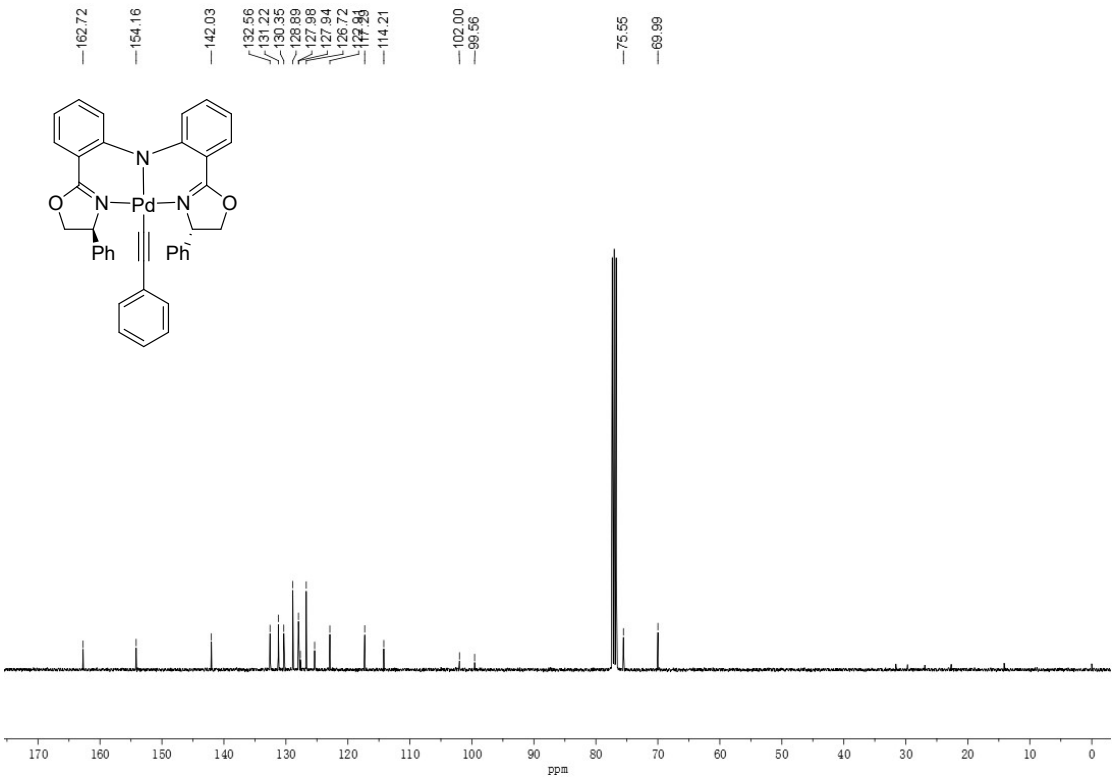


Figure S2. ^{13}C NMR spectrum of [Ph_2-(*S,S*)-BOZ)PdC≡CC_6H_5 (**1a)**.

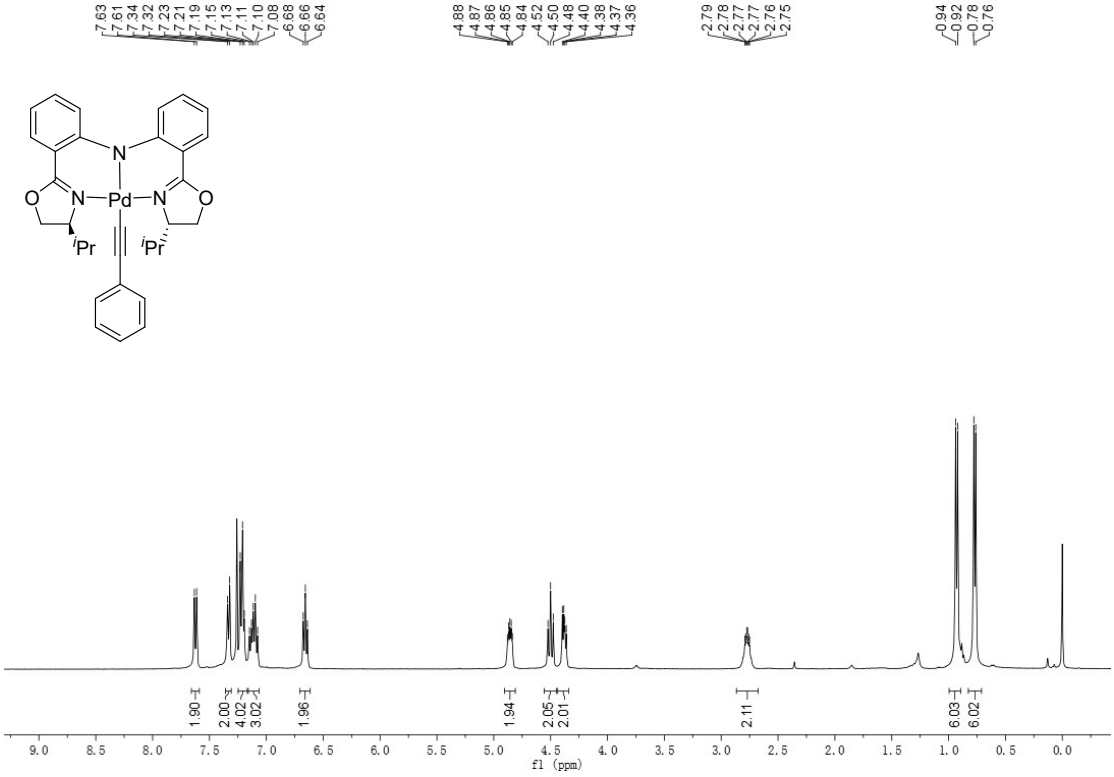


Figure S3. ^{1}H NMR spectrum of [$^{i}Pr_2$-(*S,S*)-BOZ)PdC≡CC_6H_5 (**1b)**.

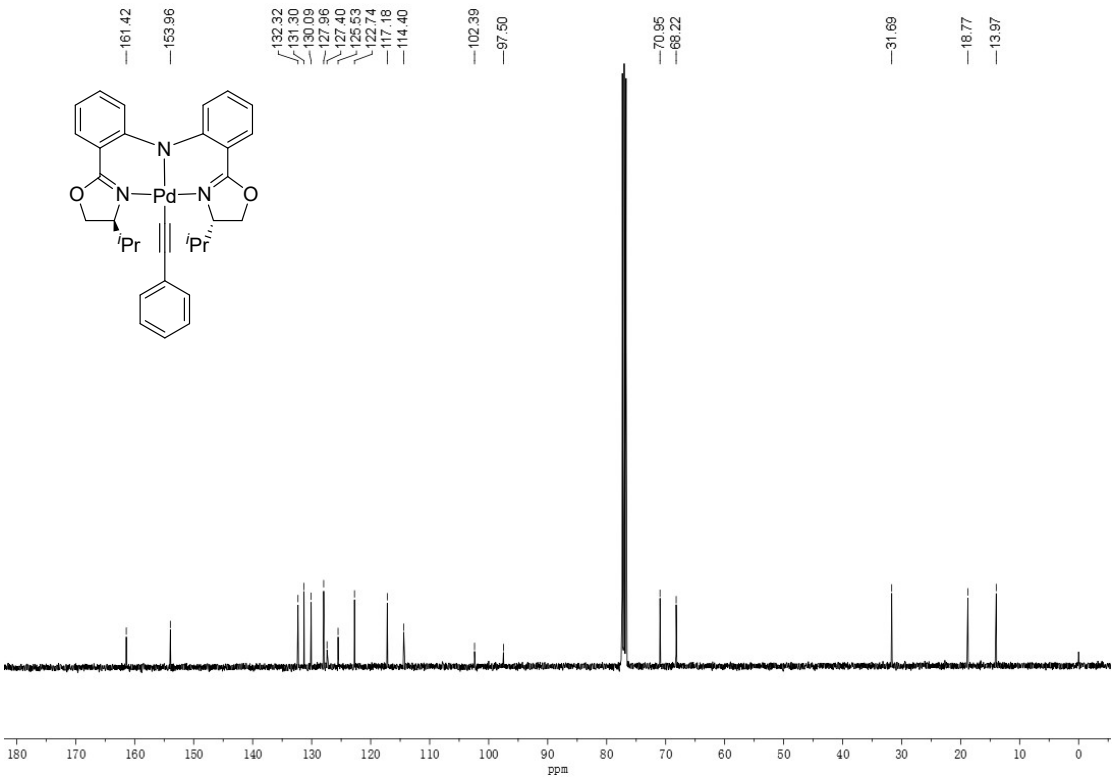


Figure S4. ^{13}C NMR spectrum of [$^{i}Pr_2$-(*S,S*)-BOZ)PdC≡CC_6H_5 (**1b)**.

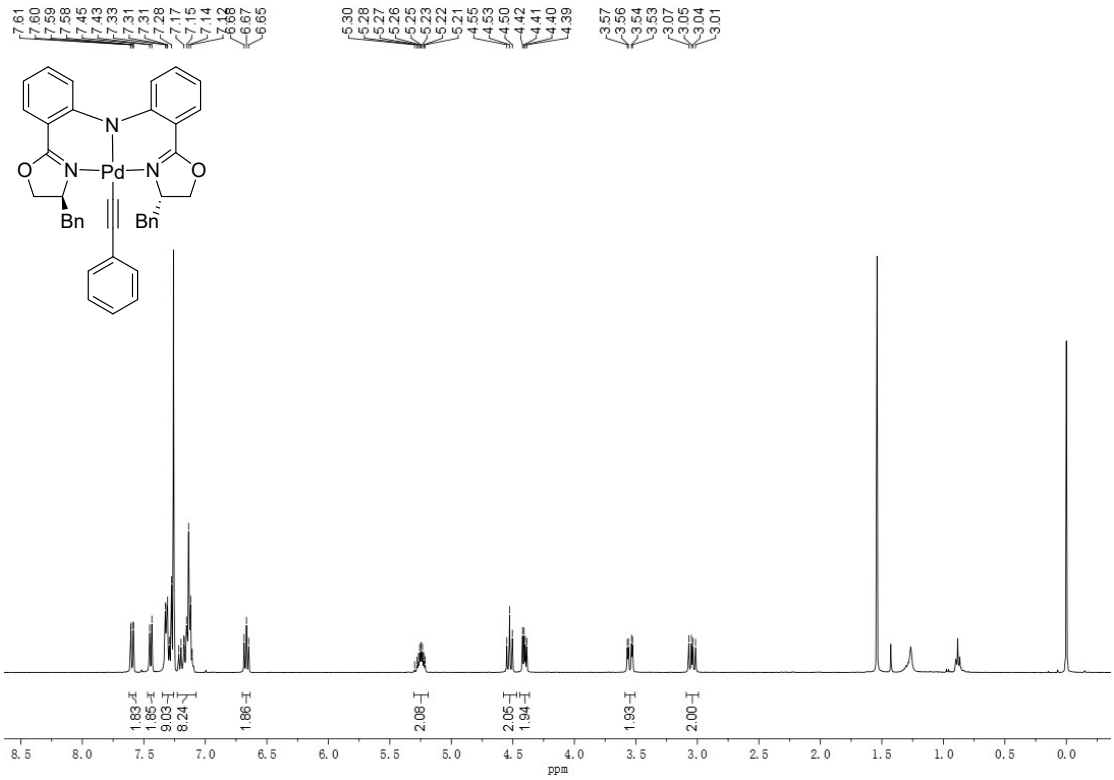


Figure S5. ^{1}H NMR spectrum of [Bn_2-(*S,S*)-BOZ)PdC≡CC_6H_5 (**1c)**.

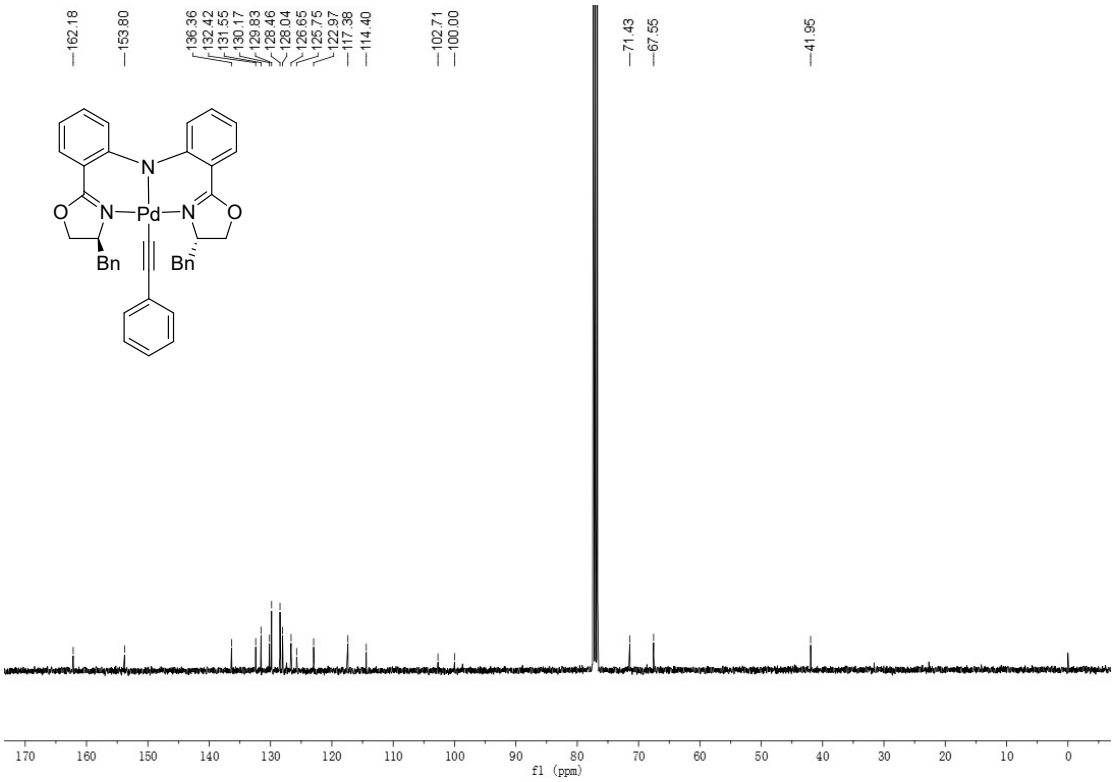


Figure S6. ^{13}C NMR spectrum of [Bn_2-(*S,S*)-BOZ)PdC≡CC_6H_5 (**1c)**.

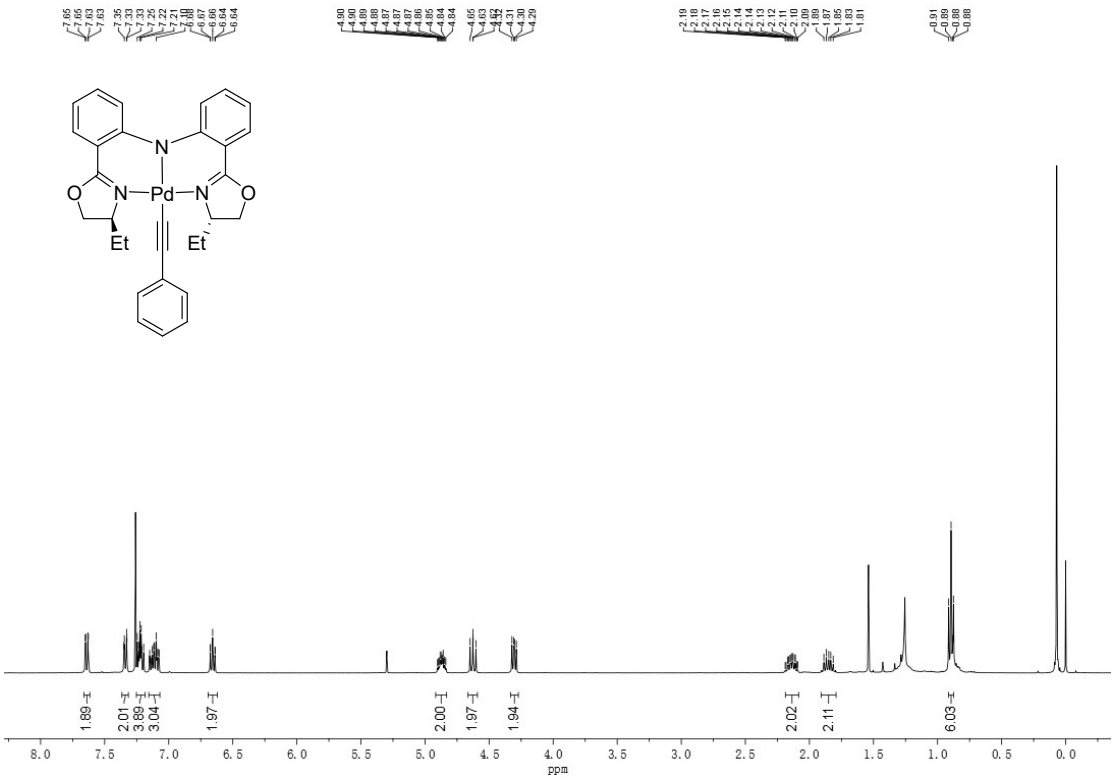


Figure S7. ^{1}H NMR spectrum of [Et_2-(*S,S*)-BOZ)PdC≡CC_6H_5 (**1d)**.

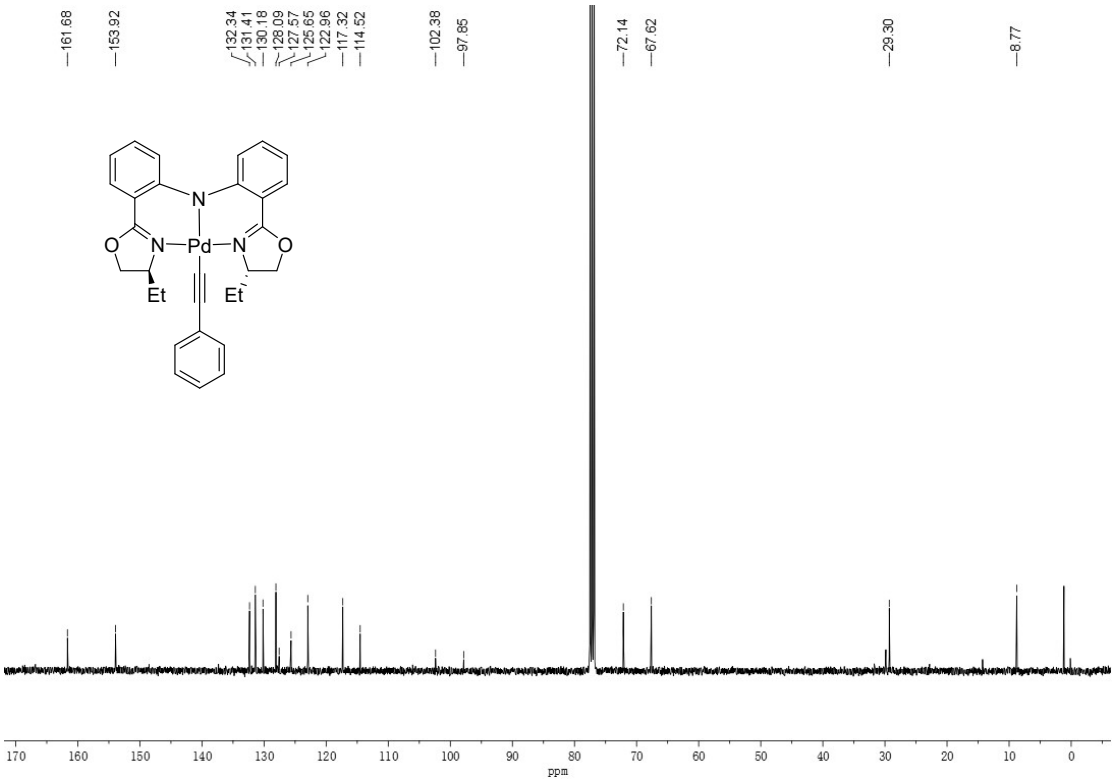
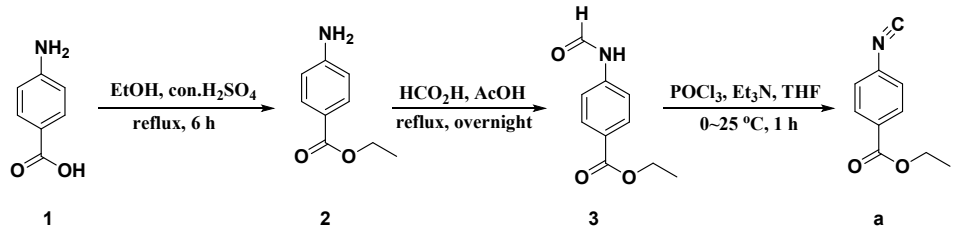


Figure S8. ^{13}C NMR spectrum of [Et_2-(*S,S*)-BOZ)PdC≡CC_6H_5 (**1d).**

Scheme S2. Synthesis of 4-ethoxycarbonyl phenyl isocyanide **(EPI)**



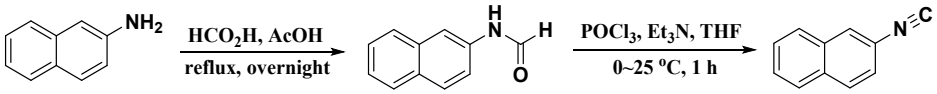
1 2 3 a

Synthesis of ethyl 4-aminobenzoate (2): To a solution of **1** (3.43 g, 25 mmol) in 100 mL of EtOH was slowly added 13.6 mL of aqueous con. H_2SO_4 (250 mmol) at room temperature. The mixture was refluxed for 6 h, cooled to room temperature, neutralized with a saturated K_2CO_3 aqueous solution and extracted with ethyl acetate (3 × 70 mL), the combined organic phases were washed with brine (2 × 50 mL), dried over anhydrous Na_2SO_4 and concentrated in vacuo, the residue was purified by column chromatography (silica gel, 5:1-3:1 hexane to ethyl acetate, v/v) to afford compound **2** as a white solid (3.90 g, 94% yield). ^1H NMR ($CDCl_3$, 400 MHz): δ 1.36 (t, *J* = 7.0 Hz, 3H), 4.06 (br, 2H), 4.31 (q, *J* = 7.2 Hz, 2H), 6.63 (d, *J* = 8.8 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 2H).

Synthesis of ethyl 4-formamidobenzoate (3): compound **2** (3.90 g, 23.6 mmol) was dissolved in a mixture of formic acid (40 mL) and acetic acid (8 mL), the resulting mixture was refluxed overnight. After the reaction mixture was cooled to room temperature, the solvents were removed under reduced pressure, the residue was washed with saturated aqueous Na_2CO_3 (50 mL) and filtered, the filter cake was washed twice with water and dried in vacuum to afford crude compound **3** as a white solid (4.22 g, crude), this compound was used directly for the next step without purification.

Synthesis of 4-ethoxycarbonyl phenyl isocyanide (a): compound **3** (4.22 g, 21.8 mmol) and triethylamine (20 mL, 146 mmol) were dissolved in dry THF (35 mL) under an atmosphere of nitrogen, after the mixture was cooled to 0 °C, $POCl_3$ (3.4 mL, 37.2 mmol) was added dropwise to the mixture, the resulting mixture was slowly warm to room temperature and stirred for 1h, then the reaction mixture was slowly poured into 30 mL saturated aqueous Na_2CO_3 and stirred at room temperature for 0.5 h, the mixture was extracted with CH_2Cl_2 (3 × 50 mL), the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure, the residue was purified by column chromatography (neutral Al_2O_3, 12:1 hexane to ethyl acetate, v/v) to afford the desired compound **a** as a brown solid (3.13 g, 82% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.40 (t, *J* = 7.2 Hz, 3H), 4.39 (q, *J* = 7.2 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 8.08 (dt, *J* = 2.0, 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.33, 61.66, 126.48, 129.94, 130.88, 131.38, 165.06, 167.10.

Scheme S3. Synthesis of 2-naphthyl Isocyanide **(NI)**



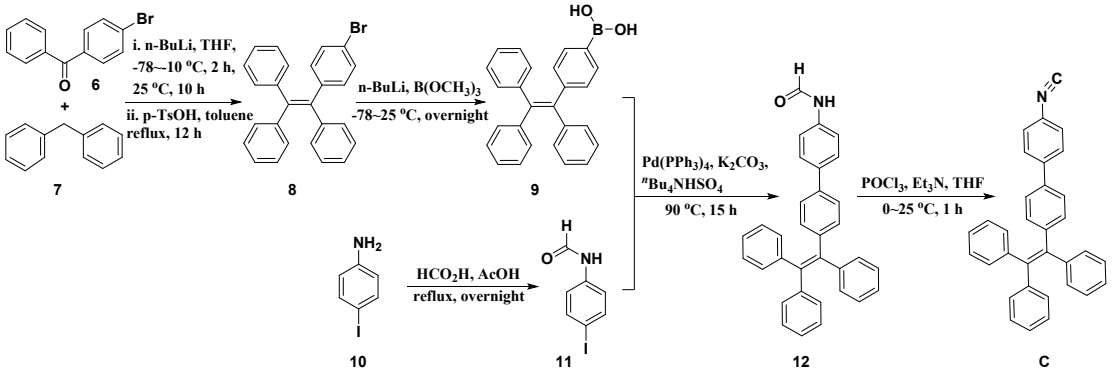
4 5 b

Synthesis of N-(naphthalen-2-yl)formamide (5): compound **4** (5 g, 34.92 mmol) was dissolved in a mixture solvents of formic acid (50 mL) and acetic acid (10 mL), the resulting mixture was refluxed overnight. After the reaction mixture was cooled to room temperature, the solvents were removed by evaporation. The residue was dissolved in CH_2Cl_2 (200 mL) and washed with saturated aqueous Na_2CO_3 (2 × 50 mL), the separated organic phase was dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the residue was purified by column chromatography (silica gel, 3:1-1:1 hexane to ethylacetate, v/v) to afford compound **5** as a white solid (4.95 g, 82.8% yield). ^{1}H NMR (d6-DMSO, 400 MHz): δ 7.41 (dt, *J* = 0.8, 7.2 Hz, 1H), 7.48 (dt, *J* = 0.8, 7.2 Hz, 1H), 7.57 (dd, *J* = 2.0, 8.8 Hz, 0.8H), 7.67 (d, *J* = 1.6 Hz, 0.2H), 7.78 (d, *J* = 8.4 Hz, 0.2H), 7.83 (t, *J* = 6.8 Hz, 1.5H), 7.86 (d, *J* = 5.6 Hz, 0.6H), 7.88 (d, *J* = 5.2 Hz, 0.5H), 8.30 (d, *J* = 1.2 Hz, 0.7H), 8.37 (d, *J* = 1.6 Hz, 0.7H), 8.94 (d, *J* = 11.2 Hz, 0.2H), 10.33 (d, *J* = 11.2 Hz, 0.2H), 10.40 (s, 0.8H).

Synthesis of 2-naphthyl Isocyanide (b): compound **5** (4.95 g, 28.9 mmol) and triethylamine (27.0 mL, 193.6 mmol) were dissolved in dry THF (60 mL) under an atmosphere of nitrogen, after the mixture was cooled to 0 °C, $POCl_3$ (4.5 mL, 49.3 mmol) was added dropwise to the mixture, the resulting mixture was slowly warm to room temperature and stirred for 1h, then the reaction mixture was slowly poured into 50 mL saturated aqueous Na_2CO_3 and stirred at room temperature for 0.5 h, the mixture was extracted with CH_2Cl_2 (3 × 70 mL), the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure, the residue was purified by column chromatography (neutral Al_2O_3, 12:1 hexane to ethyl acetate, v/v) to afford the desired compound **b** as a white solid (3.81 g, 86% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.86 (dd, *J* = 1.8, 8.6 Hz, 1H), 7.11-7.16 (m, 3H), 7.21 (s, 1H), 7.23-7.25 (m, 1H), 7.32-7.37 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 123.34, 123.88, 125.79, 127.61, 127.77, 127.96,

127.99, 129.72, 132.74, 132.86, 164.31.

Scheme S4. 4-isocyano-4'-(1,2,2-triphenylvinyl)-1,1'-biphenyl **(ITPB)**



Synthesis of (2-(4-bromophenyl)ethene-1,1,2-triyl)tribenzene (8): Under nitrogen atmosphere, compound **7** (8.60 g, 51 mmol) was dissolved in 50 mL of dry THF, after the solution was cooled to -78 °C, n-BuLi (35 mL, 1.6 M in hexane) was added dropwise and the resulting mixture was stirred at -10 °C for 2 h, then compound **6** (11.1 g, 42.4 mmol) was added dropwise and the mixture was allowed to warmed to room temperature and stirred for 10 h. Then the reaction mixture was quenched with an aqueous solution of ammonium chloride, extracted with CH_2Cl_2 (3 × 100 mL), the combined organic layers were dried over anhydrous Na_2SO_4 and evaporated to remove the solvent. The residue was dissolved in toluene (100 mL), p-toluene sulfonic acid (1.06 g, 6.20 mmol) was added, the resulting mixture was refluxed for 12 h. after the reaction mixture was cooled to room temperature, the solvent was removed under reduced pressure, the residue was purified by column chromatography (silica gel, 20:1 hexane to ethyl acetate, v/v) to afford the desired compound **8** as a white solid (11.7 g, 68% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.89 (d, J = 8.2 Hz, 2H), 7.08 (m, 15H), 7.22 (d, J = 8.2 Hz, 2H).

Synthesis of (4-(1,2,2-triphenylvinyl)phenyl)boronic acid (9): Under nitrogen atmosphere, compound **8** (2 g, 4.86 mmol) was dissolved in 20 mL of dry THF, after the solution was cooled to -78 °C, n-BuLi (2.43 mL, 2.4 M in hexane) was added dropwise and the mixture was stirred at -78 °C for 30 min. Then a solution of trimethyl borate (0.76 g, 7.29 mmol) in dry THF (10 mL) was added dropwise, the resulting mixture was stirred at -78 °C for 30 min, then allowed to warm to room temperature and stirred overnight. The reaction mixture was quenched with 10% hydrogen chloride aqueous solution, extracted with ethyl acetate (3 × 30 mL), the combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to afford crude compound **9** as white solid (2.40 g, crude), this compound was used directly for the next step without purification.

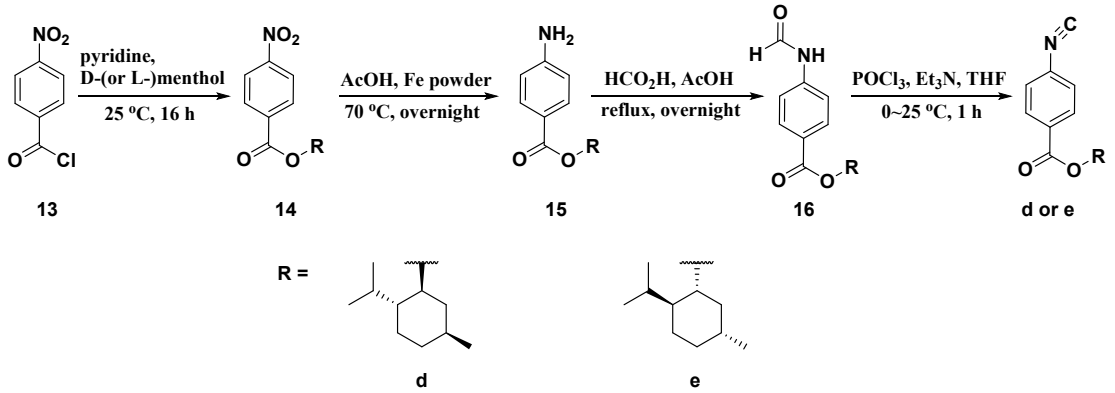
Synthesis of N-(4-iodophenyl)formamide (11): the synthetic procedure was the same with that of compound **3**, and the crude product was directly used for the next step without further purification.

Synthesis of N-(4'-(1,2,2-triphenylvinyl)-[1,1'-biphenyl]-4-yl)formamide (12): Under nitrogen atmosphere, compound **9** (6 g, crude), compound **11** (3.33 g, crude) were dissolved in a mixture

solvents of toluene (100 mL) and water (50 mL), then $Pd(PPh_3)_4$ (386 mg, 0.33 mmol), K_2CO_3 (2.75 g, 19.9 mmol) and tetrabutylammonium hydrogen sulfate (452 mg, 1.33 mmol) were added, the resulting mixture was stirred at 90 °C for 15 h. after the reaction mixture was cooled to room temperature, the organic layer was separated and the aqueous phase was extracted with ethyl acetate (3 × 80 mL), the combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure, the residue was purified by column chromatography (silica gel, 2:1 hexane: ethyl acetate, v/v) to afford the desired compound **12** as a light yellow solid (6.5 g). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.02-7.13 (m, 18H), 7.17 (s, 0.5H), 7.31 (dd, *J* = 2.0, 8.4 Hz, 2H), 7.51-7.58 (m, 3H), 7.64 (d, *J* = 11.6 Hz, 0.6H), 8.39 (d, *J* = 1.6 Hz, 0.5H), 8.71 (d, *J* = 11.6 Hz, 0.4H).

Synthesis of 4-isocyano-4'-(1,2,2-triphenylvinyl)-1,1'-biphenyl (c): the synthetic procedure was the same with that of compound **a**. (light green solid, 79% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.03-7.15 (m, 17H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.56 (dt, J = 1.6, 8.4, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 125.50, 126.36, 126.69, 126.73, 126.76, 126.83, 127.81, 127.84, 127.90, 127.95, 131.43, 131.46, 131.50, 132.15, 137.06, 140.28, 141.75, 141.99, 143.64, 143.69, 144.02, 164.69.

Scheme S5. Synthesis of (*1S,2R,5S*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (**D-IMCI**) and (*1R,2S,5R*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate **(L-IMCI)**



Synthesis of (1S,2R,5S)-2-isopropyl-5-methylcyclohexyl 4-nitrobenzoate (14d): Under nitrogen atmosphere, compound **13** (1.8 g, 9.7 mmol) was dissolved in dry pyridine (20 mL), then D-menthol (1.5 g, 9.7 mmol) was added in one portion and the resulting mixture was stirred at room temperature for 16 h, after removal of pyridine under reduced pressure, the residue was dissolved in CH_2Cl_2 (30 mL) and washed with 1 N HCl, saturated $NaHCO_3$ aqueous solution and brine, the separated organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure, the residue was purified by column chromatography (silica gel, 10 : 1 hexane to ethyl acetate, v/v) to afford the desired compound **14d** as a yellow solid (2.40 g, 81% yield) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.79 (d, *J* = 7.2 Hz, 3H), 0.93 (t, *J* = 6.4 Hz, 6H), 0.88-0.98 (m, 1H), 1.08-1.17 (m, 2H), 1.54-1.62 (m, 2H), 1.74 (d, *J* = 12.4 Hz, 2H), 1.88-1.95 (m, 1H), 2.12 (d, *J* = 11.6 Hz, 1H), 4.97 (dt, *J* = 4.4, 11.2 Hz, 1H), 8.20 (d, *J* = 8.8 Hz, 2H), 8.28 (d, *J* = 8.4 Hz, 2H).

Synthesis of (1S,2R,5S)-2-isopropyl-5-methylcyclohexyl 4-aminobenzoate (15d): Under nitrogen atmosphere, compound **14d** (2.40 g, 7.86 mmol) was dissolved in 30 mL of acetic acid,

then iron powder (4.4 g, 78.6 mmol) was added in one portion, the resulting mixture was stirred at 70 °C overnight. Then the mixture was filtered and the filter cake was washed with ethyl acetate (20 mL), the filtrate was concentrated under reduced pressure, the residue was purified by column chromatography (silica gel, 4 : 1 hexane to ethyl acetate, v/v) to afford the desired compound **15d** as yellow oil (1.61 g, 75% yield) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.78 (d, *J* = 7.2 Hz, 3H), 0.90 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.4 Hz, 3H), 0.85-0.96 (m, 1H), 1.02-1.14 (m, 2H), 1.48-1.54 (m, 2H), 1.69-1.72 (m, 2H), 1.94-1.98 (m, 1H), 2.09-2.12 (m, 1H), 4.04 (s, 2H), 4.87 (dt, *J* = 4.4, 10.8 Hz, 1H), 6.63 (d, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 8.8 Hz, 2H).

Synthesis of (*1S,2R,5S*)-2-isopropyl-5-methylcyclohexyl 4-formamidobenzoate (16d): compound **15d** (1.61 g, 5.85 mmol) was dissolved in a mixture of formic acid (16 mL) and acetic acid (3 mL), the resulting mixture was refluxed overnight. After the reaction mixture was cooled to room temperature, the solvents were removed under reduced pressure, the residue was washed with saturated aqueous Na_2CO_3 (10 mL) and filtered, the filter cake was washed twice with water and dried in vacuum to afford crude compound **16d** as a white solid (1.70 g, crude), this compound was used directly for the next step without purification.

Synthesis of (*1S,2R,5S*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (d): compound **16d** (1.70 g, crude) and triethylamine (5.2 mL, 37.5 mmol) were dissolved in dry THF (15 mL) under an atmosphere of nitrogen, after the mixture was cooled to 0 °C, $POCl_3$ (0.9 mL, 9.5 mmol) was added dropwise to the mixture, the resulting mixture was slowly warm to room temperature and stirred for 1h, then the reaction mixture was slowly poured into 20 mL saturated aqueous Na_2CO_3 and stirred at room temperature for 0.5 h, the mixture was extracted with CH_2Cl_2 (3 × 20 mL), the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure, the residue was purified by column chromatography (neutral Al_2O_3, 12 : 1 hexane to ethyl acetate, v/v) to afford the desired compound **d** as a black syrup (1.35 g, 81% yield for two steps) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.77 (d, *J* = 6.8 Hz, 3H), 0.91 (dd, *J* = 5.6, 6.8 Hz, 6H), 0.86-0.96 (m, 1H), 1.05-1.17 (m, 2H), 1.50-1.59 (m, 2H), 1.70-1.74 (m, 2H), 1.86-1.94 (m, 1H), 2.07-2.12 (m, 1H), 4.93 (dt, *J* = 4.4, 10.8 Hz, 1H), 7.43 (d, *J* = 8.4 Hz, 2H), 8.07 (dt, *J* = 2.0, 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 16.60, 20.82, 22.10, 23.71, 26.66, 31.53, 34.32, 40.98, 47.30, 75.75, 126.48, 129.88, 130.90, 131.74, 164.58, 167.05.

The synthesis of (*1R,2S,5R*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (**e**) was the same with that of (*1S,2R,5S*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (**f**).

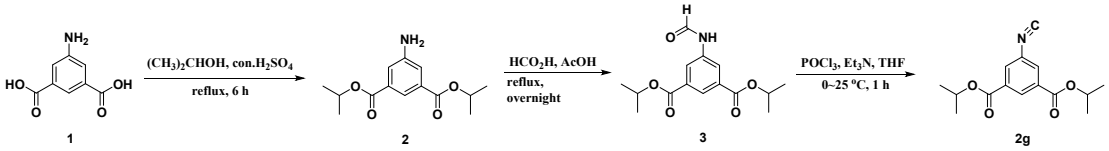
Synthesis of (*1R,2S,5R*)-2-isopropyl-5-methylcyclohexyl 4-nitrobenzoate (14e): (yellow solid, 83% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.79 (d, *J* = 6.8 Hz, 3H), 0.93 (t, *J* = 6.2 Hz, 6H), 0.88-0.98 (m, 1H), 1.08-1.19 (m, 2H), 1.54-1.61 (m, 2H), 1.71-1.78 (m, 2H), 1.85-1.97 (m, 1H), 2.13 (d, *J* = 12.0 Hz, 1H), 4.97 (dt, *J* = 4.4, 10.8 Hz, 1H), 8.20 (d, *J* = 9.2 Hz, 2H), 8.28 (d, *J* = 8.8 Hz, 2H).

Synthesis of (*1R,2S,5R*)-2-isopropyl-5-methylcyclohexyl 4-aminobenzoate (15e): (yellow oil, 72% yield). ^{1}H NMR (DMSO-d6, 400 MHz): δ 0.73 (d, *J* = 6.8 Hz, 3H), 0.87 (t, *J* = 7.4 Hz, 6H), 0.82-0.92 (m, 1H), 0.97-1.09 (m, 2H), 1.43-1.49 (m, 2H), 1.62-1.66 (m, 2H), 1.82-1.89 (m, 1H),

1.92-1.95 (m, 1H), 4.72 (dt, *J* = 4.4, 10.8 Hz, 1H), 5.92 (s, 2H), 6.56 (d, *J* = 8.8 Hz, 2H), 7.62 (d, *J* = 8.8 Hz, 2H).

Synthesis of (*1R,2S,5R*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (d): (black syrup, 80% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.78 (d, *J* = 6.8 Hz, 3H), 0.92 (t, *J* = 6.4 Hz, 6H), 0.87-0.90 (m, 1H), 1.04-1.18 (m, 2H), 1.51-1.60 (m, 2H), 1.70-1.76 (m, 2H), 1.86-1.94 (m, 1H), 2.08-2.13 (m, 1H), 4.93 (dt, *J* = 4.4, 11.2 Hz, 1H), 7.43 (d, *J* = 8.4 Hz, 2H), 8.07 (dt, *J* = 2.0, 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 16.63, 20.86, 22.13, 23.74, 26.69, 31.57, 34.35, 41.01, 47.35, 75.81, 126.52, 129.92, 130.94, 131.78, 164.63, 167.03.

Scheme S6. Synthesis of diisopropyl 5-isocyanoisophthalate **(DIPI)**



Synthesis of diisopropyl 5-aminoisophthalate (2): To a solution of **1** (5.43 g, 30 mmol) in 250 mL of $(CH_3)_2CHOH$ was slowly added 32.64 mL of aqueous con. H_2SO_4 (600 mmol) at room temperature. The mixture was refluxed for 6 h, cooled to room temperature, neutralized with a saturated K_2CO_3 aqueous solution and extracted with ethyl acetate (3 × 80 mL), the combined organic phases were washed with brine (2 × 50 mL), dried over anhydrous Na_2SO_4 and concentrated in vacuo, the residue was purified by column chromatography (silica gel, 5 : 1 – 3 : 1 hexane to ethyl acetate, v/v) to afford compound **2** as a white solid (7.55 g, 95% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.03 (s, 1H), 7.49 (s, 2H), 5.24 (dt, *J* = 12.3, 6.1 Hz, 2H), 3.90 (s, 2H), 1.37 (d, *J* = 6.2 Hz, 12H).

Synthesis of diisopropyl 5-formamidoisophthalate (3): compound **2** (3.13 g, 11.8 mmol) was dissolved in a mixture of formic acid (20 mL) and acetic acid (4 mL), the resulting mixture was refluxed overnight. After the reaction mixture was cooled to room temperature, the solvents were removed under reduced pressure, the residue was washed with saturated aqueous Na_2CO_3 (30 mL) and filtered, the filter cake was washed twice with water and dried in vacuum to afford crude compound **3** as a white solid (2.15 g, crude), this compound was used directly for the next step without purification.

Synthesis of diisopropyl 5-isocyanoisophthalate (2g): t compound **3** (3.13 g, 11.8 mmol) and triethylamine (11 mL, 78.8 mmol) were dissolved in dry THF (30 mL) under an atmosphere of nitrogen, after the mixture was cooled to 0 °C, $POCl_3$ (1.9 mL, 20 mmol) was added dropwise to the mixture, the resulting mixture was slowly warm to room temperature and stirred for 1h, then the reaction mixture was slowly poured into 30 mL saturated aqueous Na_2CO_3 and stirred at room temperature for 0.5 h, the mixture was extracted with CH_2Cl_2 (3 × 50 mL), the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure, the residue was purified by column chromatography (neutral Al_2O_3, 12:1 hexane to ethyl acetate, v/v) to afford the desired compound **2ag** as a brown solid (71% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.60 (s, 1H), 8.11 (s, 2H), 5.22 (dt, *J* = 12.4, 6.2 Hz, 2H), 1.33 (d, *J* = 6.2 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.67, 163.56, 133.01, 131.07, 130.95, 126.95, 69.92, 21.86.

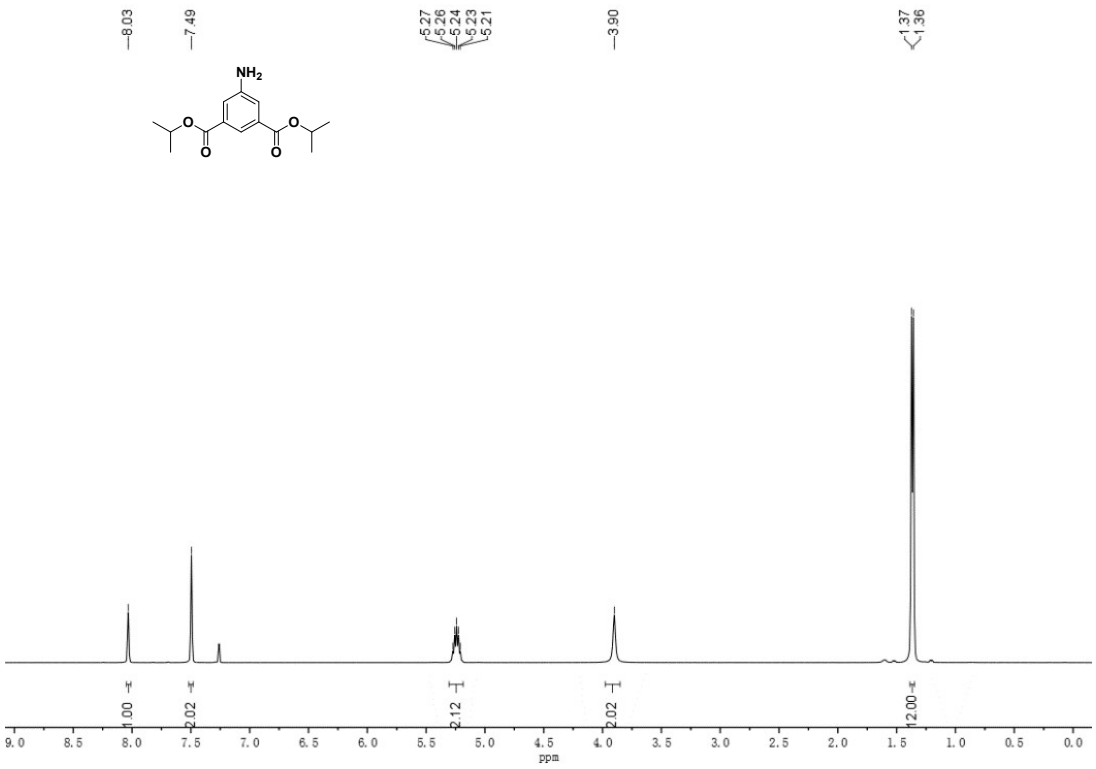


Figure S9. [1]H NMR spectrum of diisopropyl 5-aminoisophthalate (**2**).

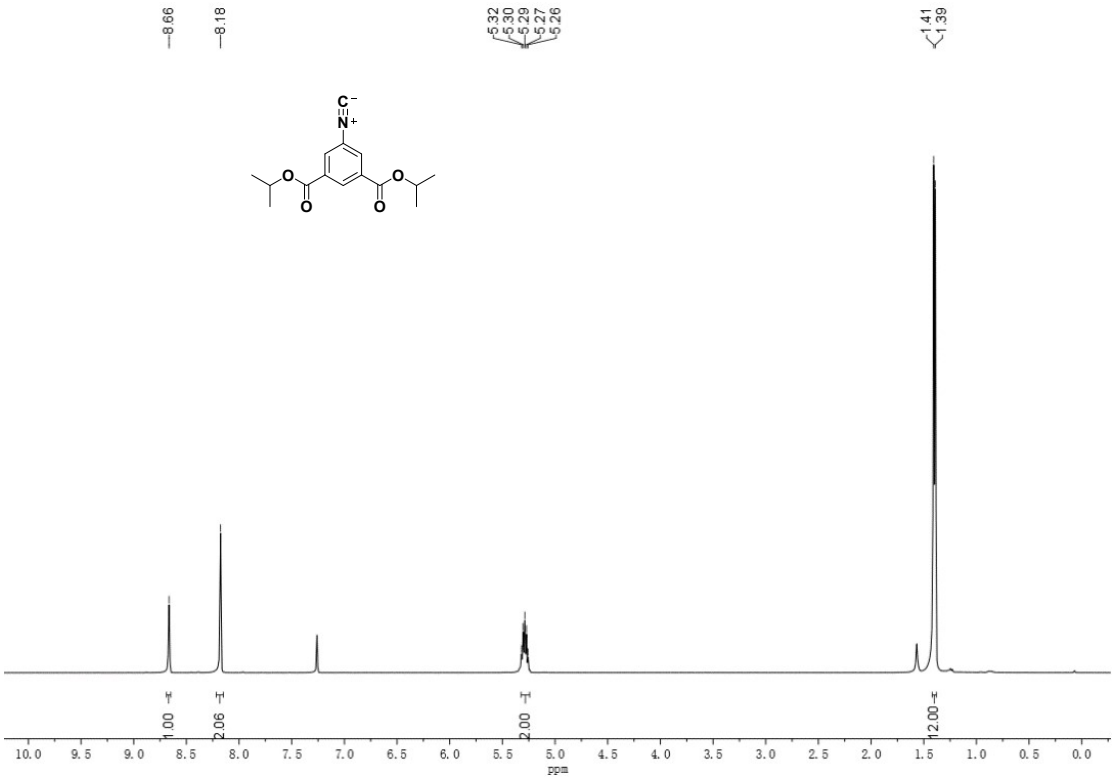


Figure S10. [1]H NMR spectrum of diisopropyl 5-isocyanoisophthalate (**2g**).

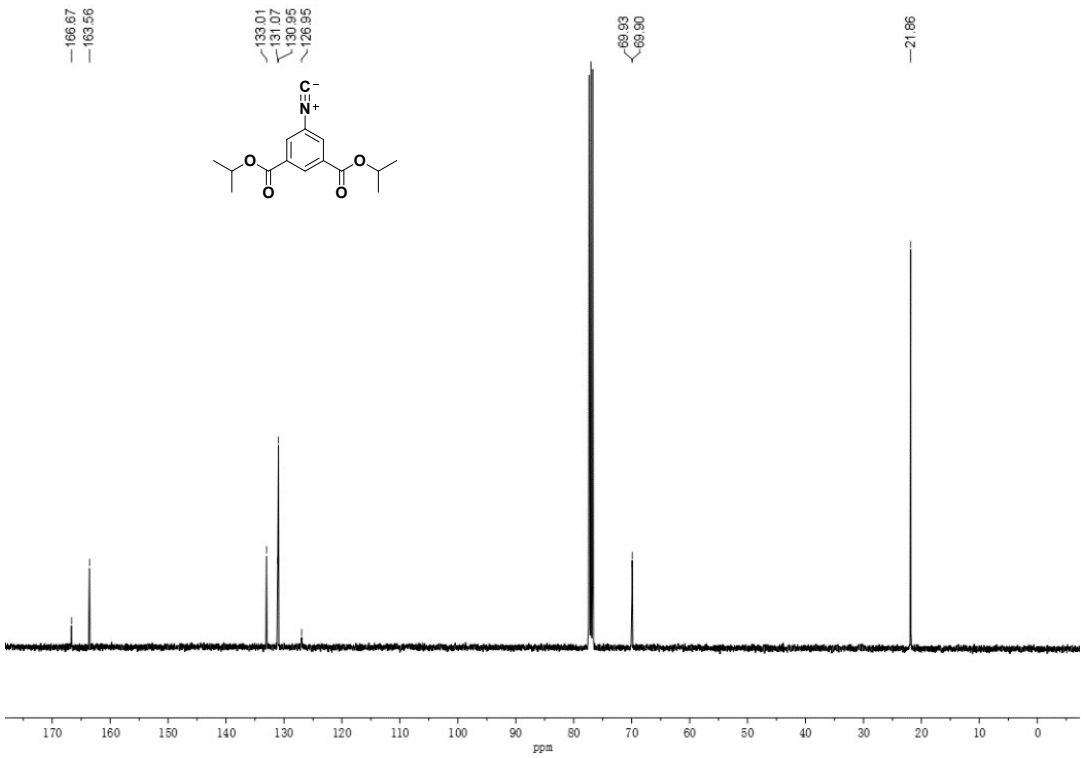
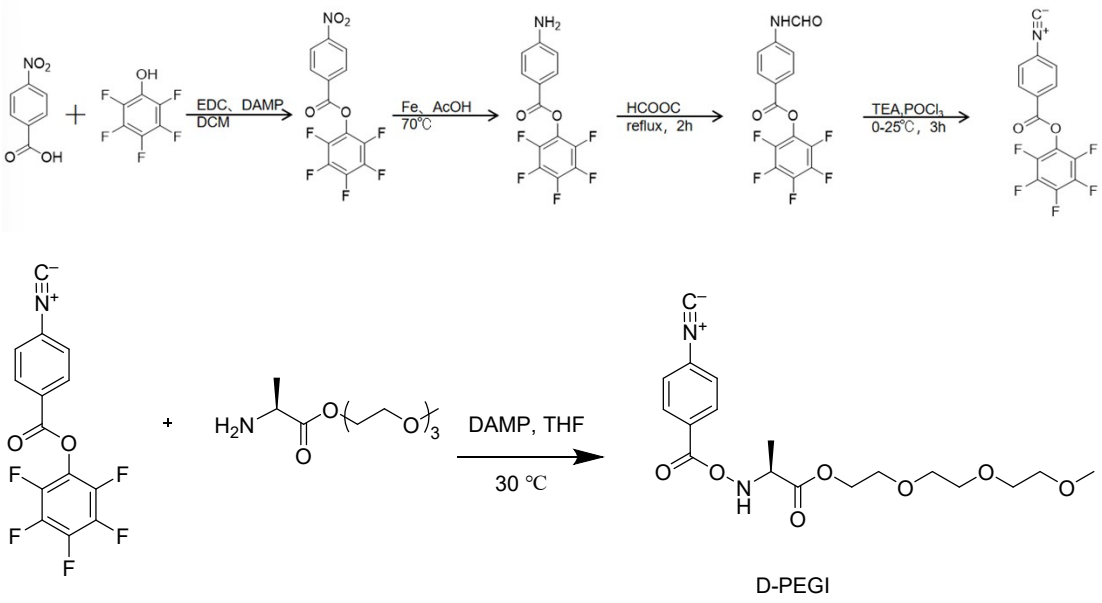
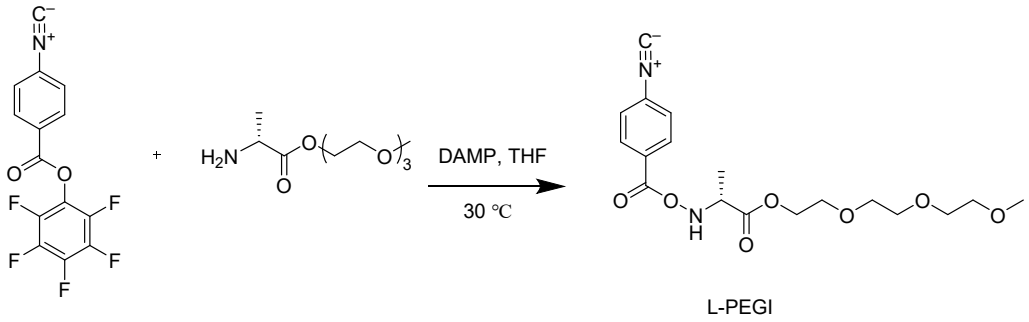


Figure S11. ^{13}C NMR spectrum of diisopropyl 5-isocyanoisophthalate (**2g**).

Scheme S7. Synthesis of 4-((*2R*)-2-alanine-3-(2-methoxyethyl) carbonyl phenyl isocyanide(**D-OEGI**) and 4-((*2S*)-2-alanine-3-(2-methoxyethyl) carbonyl phenyl isocyanide **(L-OEGI)**





L-PEGI

Synthesis of 4-((*2R*)-2-alanine-3-(2-methoxyethyl) carbonyl phenyl isocyanide(D/L-OEGI) (2h/2i): Weigh 0.3 g of the previous reaction product with a small spoon, add 1.00 g of pre-prepared PFI, then incorporate 1.00 g of EDC•HCI. Dissolve the mixture in 25 mL of DMF measured with a graduated cylinder. Set the reaction temperature to 50° C and run the reaction for 12 hours. After completion, gradually add saturated Na_2CO_3 aqueous solution to the flask to achieve alkaline pH. Perform DCM extraction first, followed by washing with saturated saline solution. Dry the residue with anhydrous sodium sulfate and filter. Remove the solvent by rotary evaporation. The remaining compound is isolated via column chromatography to yield D-PEGI (yield 84%). ^{1}H NMR(400 MHz,CDCl3)：δ 7.87(d, J=8.3 Hz, 2H),7.45(d, J=8.3 Hz, 2H),7.00(d, J=7.4 Hz, 1H), 4.83(q, J=7.2 Hz, 1H),4.34 (s, 2H),4.12 (q, J=7.1 Hz, 1H),3.75-3.71 (m,2H),3.64 (d, J=5.8 Hz, 6H), 3.58-3.52(m, 2H),3.36 (s, 3H), 2.04 (s, 1H),1.54 (d, J=7.1 Hz, 3H）.

A typical procedure for the polymerization of 2a (EPI) by neutral chiral (*S,S*)-bis(oxazoline) palladium complexes 1a/PPh_3 (Table 1, entry 1):

Under air atmosphere, a 25 mL round bottom flask was charged with a solution of complexe **1a** (5.3 mg, 8 μmol) in toluene (1 mL), then PPh_3 (52.5 mg, 0.2 μmol) was added, the resulting mixture was stirred at room temperature for 1 min, then added to a solution of **2a** (70 mg, 0.4 mmol) in toluene (2 mL). The reaction mixture was stirred at 90 °C for 2 hours, then the reaction mixture was poured into petroleum ether (10 mL) to precipitate the polymer product, the gray polymer solid was collected by filtration, and dried in vacuo at 40 °C to a constant weight (70 mg, 100% yield), The product obtained is soluble thoroughly in $CHCl_3$ at 25 °C.

A typical procedure for the polymerization of 2a (EPI) by neutral chiral (*S,S*)-bis(oxazoline) palladium complexes 1a (Table 1, entry 5):

Under air atmosphere, a 25 mL round bottom flask was charged with a solution of complexe **1a** (5.3 mg, 8 μmol) in toluene (1 mL), then added to a solution of **2a** (70 mg, 0.4 mmol) in toluene (1 mL). The reaction mixture was stirred at 110 °C for 24 hours, then the reaction mixture was poured into petroleum ether (10 mL) to precipitate the polymer product, the gray polymer solid was collected by filtration, and dried in vacuo at 40 °C to a constant weight (40 mg, 57% yield), The product obtained is soluble thoroughly in $CHCl_3$ at 25 °C.

A typical procedure for the copolymerization of (*1S,2R,5S*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (D-IMCI) with 4-isocyano-4'-(1,2,2-triphenylvinyl)-1,1'-biphenyl (ITPB) (Table 3, entry 3):

Under air atmosphere, a 50 mL round bottom flask was charged with a solution of complexe **1b**

(2.62 mg, 4.6 μmol) in toluene (2 mL), then PPh_3 (30 mg, 120 μmol) was added, the resulting mixture was stirred at 25 °C for 3 min, then a solution of (*1S,2R,5S*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (66 mg, 0.23 mmol) and 4-isocyano-4'-(1,2,2-triphenylvinyl)-1,1'-biphenyl (100 mg, 0.23 mmol) in toluene (3 mL) was added, the reaction mixture was stirred at 90 °C for 3 min, then the reaction mixture was poured into methanol (100 mL) to precipitate the copolymer product, the orange copolymer solid was collected by filtration, and dried in vacuo at 40 °C to a constant weight (143 mg, 86% yield), The product obtained is soluble thoroughly in $CHCl_3$ and THF at 25 °C.

A typical procedure for the copolymerization of (*1S,2R,5S*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (D-IMCI) with isopropyl 3-isocyanobenzoate (IPI) (Table 4, entry 3):
Under air atmosphere, a 50 mL round bottom flask was charged with a solution of complexe **1b** (2.6 mg, 4.6 μmol) in toluene (2 mL), then PPh_3 (30 mg, 120 μmol) was added, the resulting mixture was stirred at 25 °C for 3 min, then a solution of (*1S,2R,5S*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (66 mg, 0.23 mmol) and isopropyl 3-isocyanobenzoate (44 mg, 0.23 mmol) in toluene (3 mL) was added, the reaction mixture was stirred at 25 °C for 3 min, then the reaction mixture was poured into methanol (100 mL) to precipitate the copolymer product, the orange copolymer solid was collected by filtration, and dried in vacuo at 40 °C to a constant weight (76 mg, 69% yield), The product obtained is soluble thoroughly in $CHCl_3$ and THF at 25 °C.

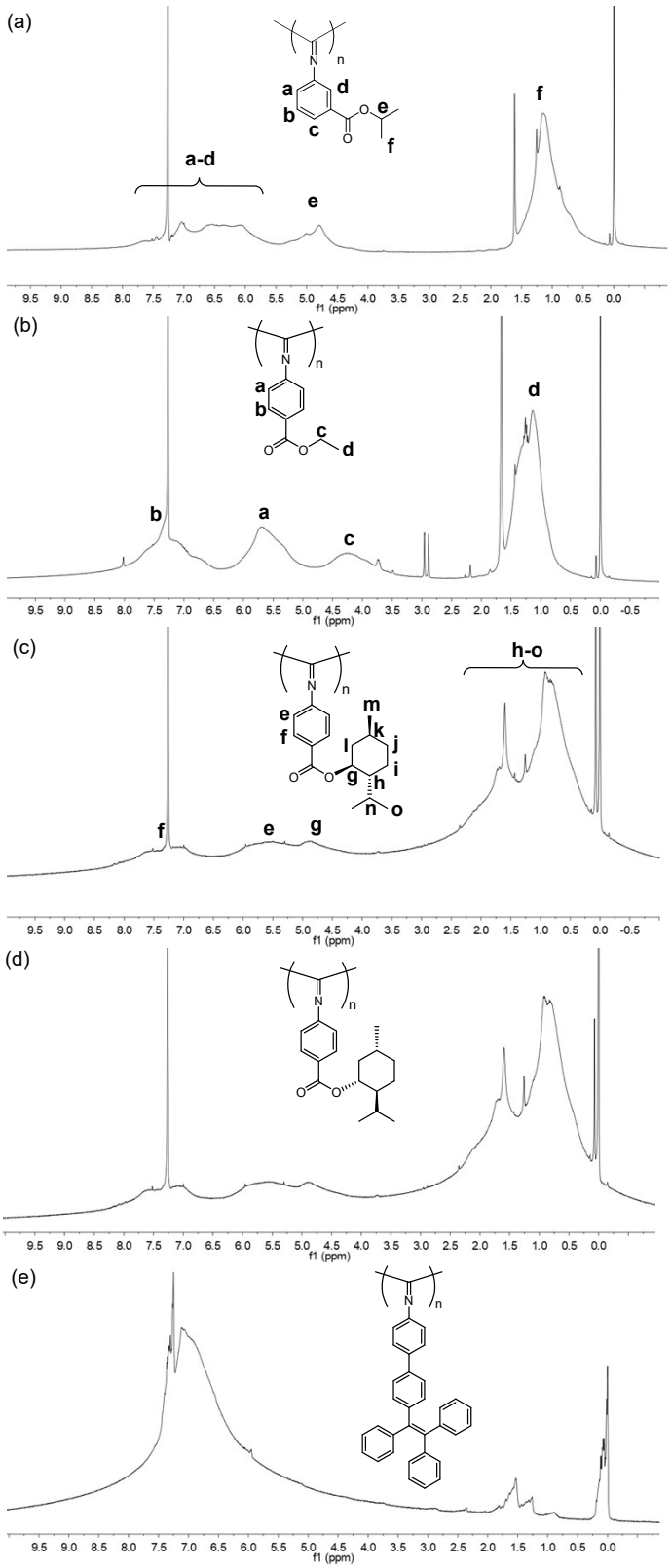


Figure S12. ^{1}H NMR spectrum of polymers (a) poly(IPI) (Table 2, entry 23), (b) poly(EPI) (Table 2, entry 13), (c) poly(D-IMCI) (Table 2, entry 21), (d) poly(L-IMCI) (Table 2, entry 22), (e) poly(ITPB) (Table 1, entry 18) in $CDCl_3$ at 25 ^{o}C.

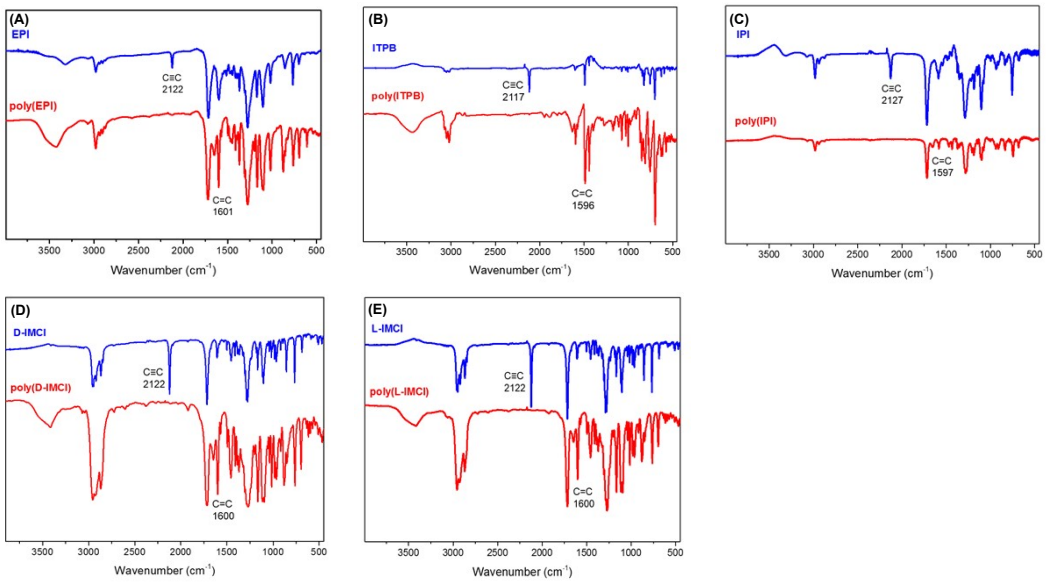
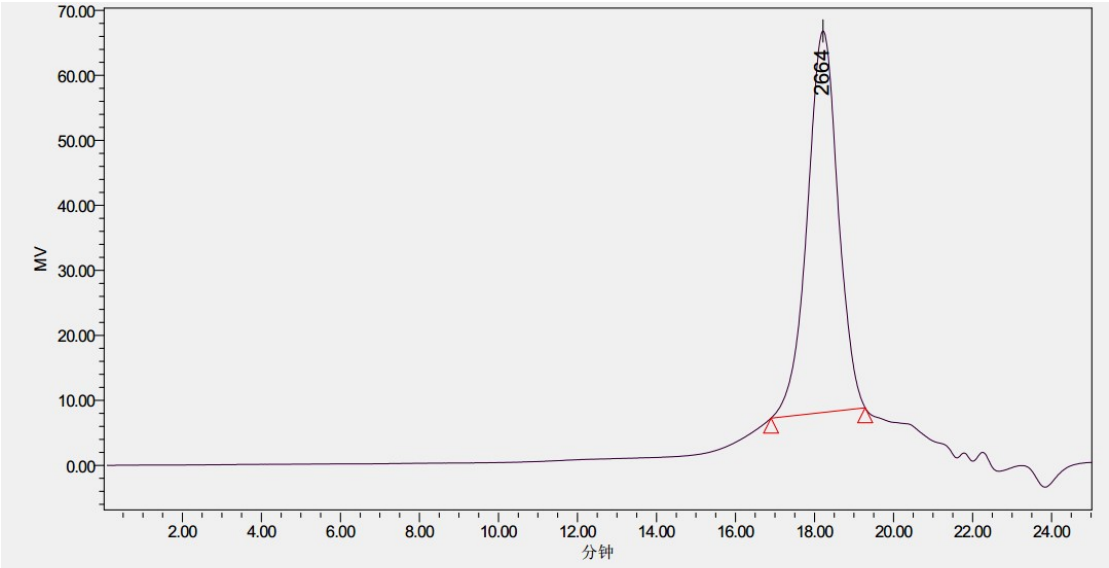


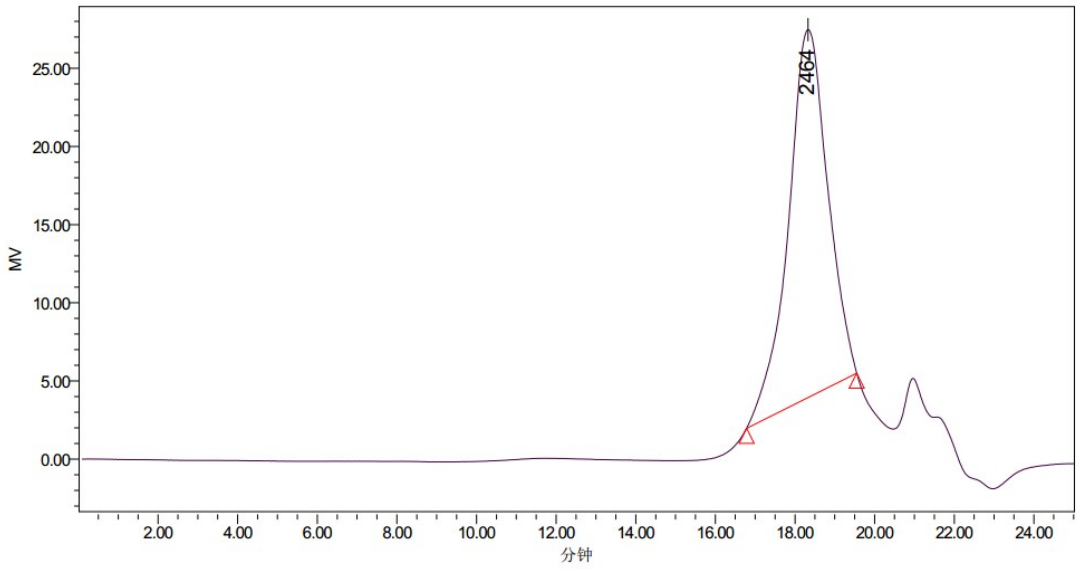
Figure S13. FT-IR spectra of polymers (A) EPI and poly(EPI), (B) ITPB and poly(ITPB), (C) poly(IPI), (D) poly(D-IMCI) and (E) poly(L-IMCI).



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		18.216	18.216	18.216	2586	2758	2664	2940	3133	1.066209	1.136316

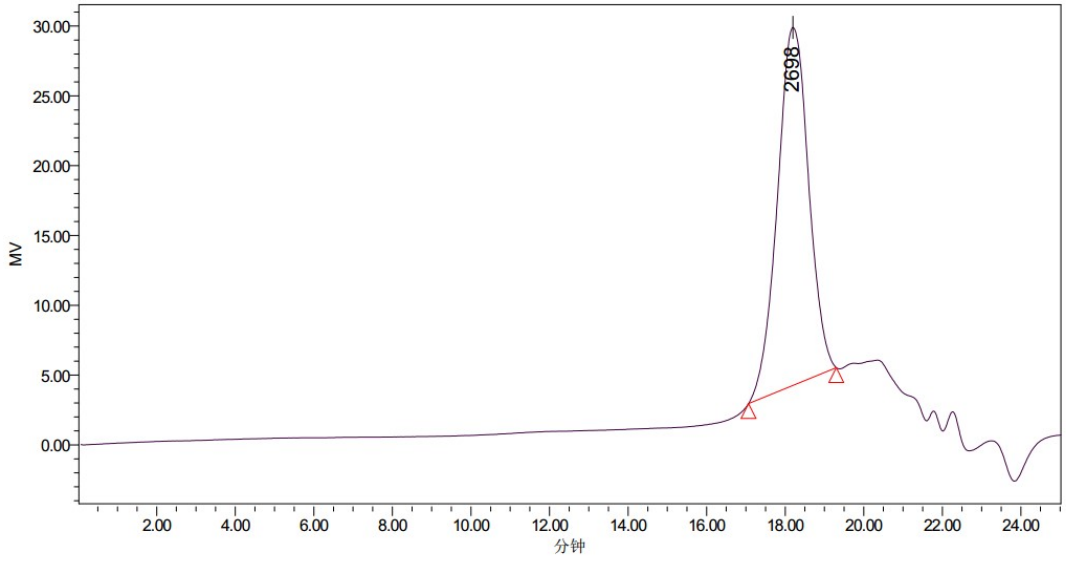
Figure S14. GPC curve of polyEPI obtained by complex **1a** in Table 1, entry 1.



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		18.330	18.330	18.330	2325	2595	2464	2895	3220	1.115553	1.240964

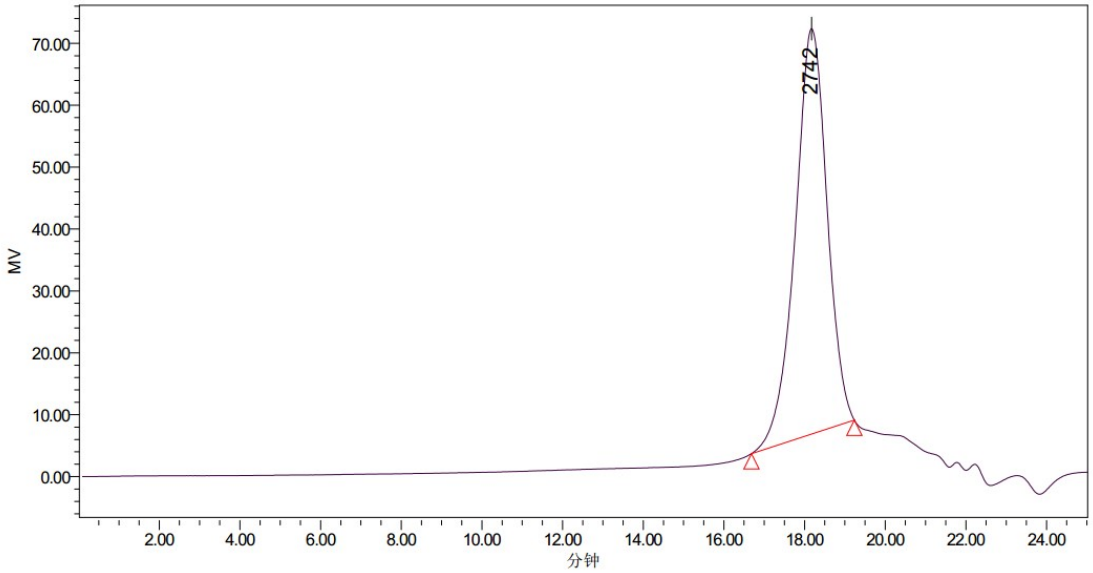
Figure S15. GPC curve of polyEPI obtained by complex **1b** in Table 1, entry 2.



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		18.198	18.198	18.198	2593	2758	2698	2928	3100	1.061521	1.123933

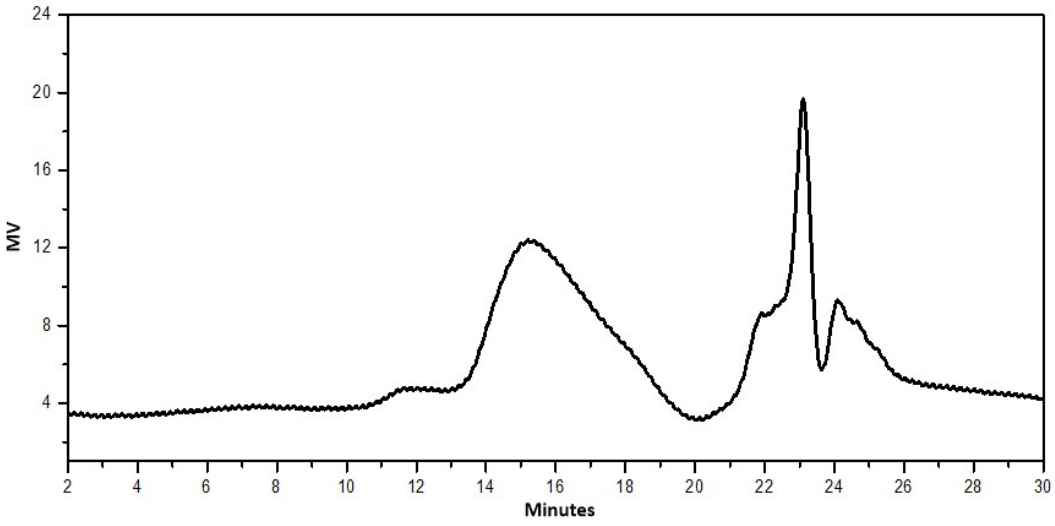
Figure S16. GPC curve of polyEPI obtained by complex **1c** in Table 1, entry 3.



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		18.174	18.174	18.174	2676	2861	2742	3062	3282	1.070471	1.147159

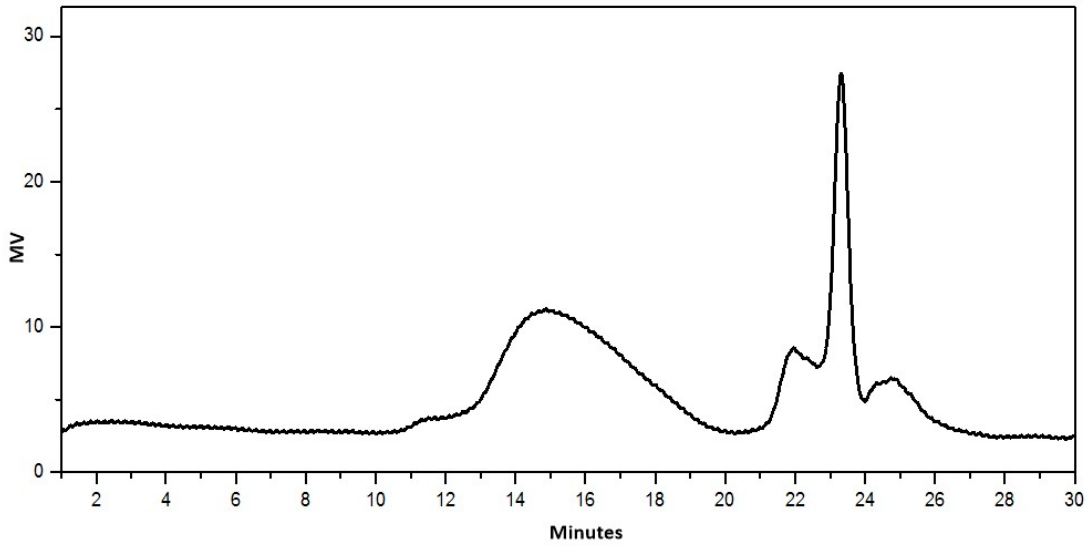
Figure S17. GPC curve of polyEPI obtained by complex **1d** in Table 1, entry 4.



Broad Unknown Relative Peak Table

	Distributionn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		151136	581647	587830	1304603	3.84850	2.24294

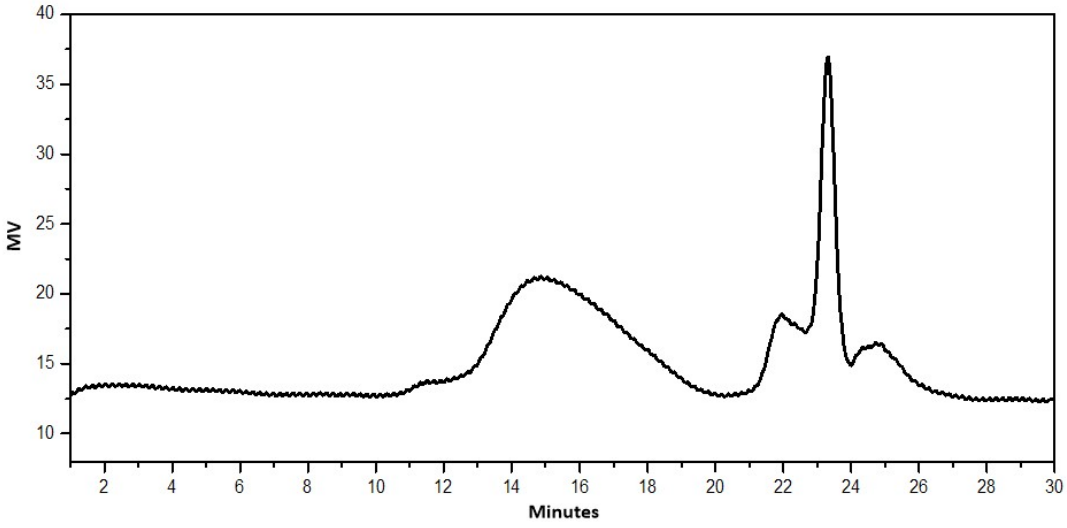
Figure S18. GPC curve of polyEPI obtained by complex **1a**/PPh_3 in Table 1, entry 5.



Broad Unknown Relative Peak Table

	Distributionn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		138275	523896	530124	1158983	3.78879	2.18625

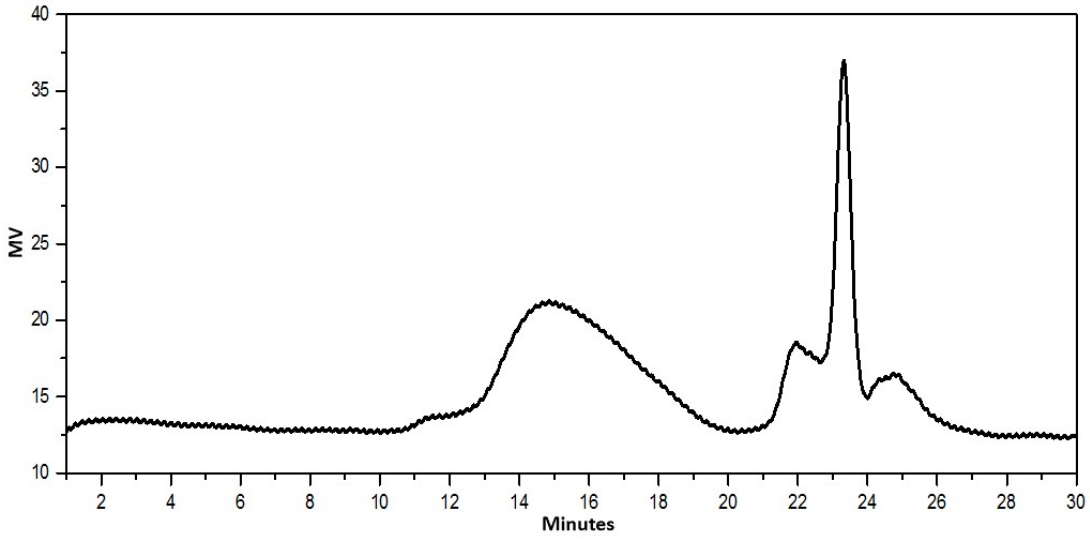
Figure S19. GPC curve of polyEPI obtained by complex **1d**/PPh_3 in Table 1, entry 6.



Broad Unknown Relative Peak Table

	Distributionn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		118118	333671	409251	599850	2.82489	1.79772

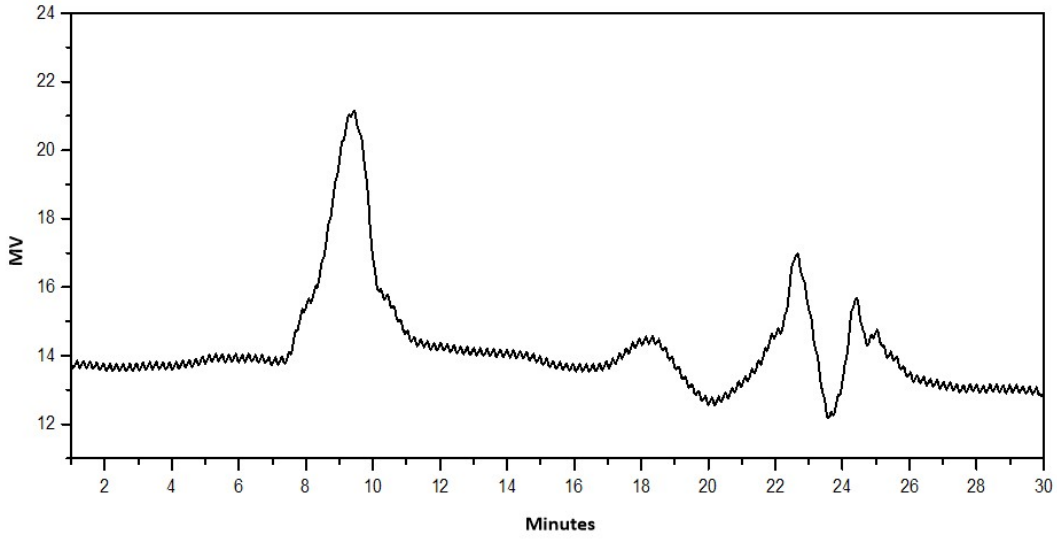
Figure S20. GPC curve of polyEPI obtained by complex **1c**/PPh_3 in Table 1, entry 7.



Broad Unknown Relative Peak Table

	Distributionn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		224634	988557	985229	2519057	4.40075	2.54822

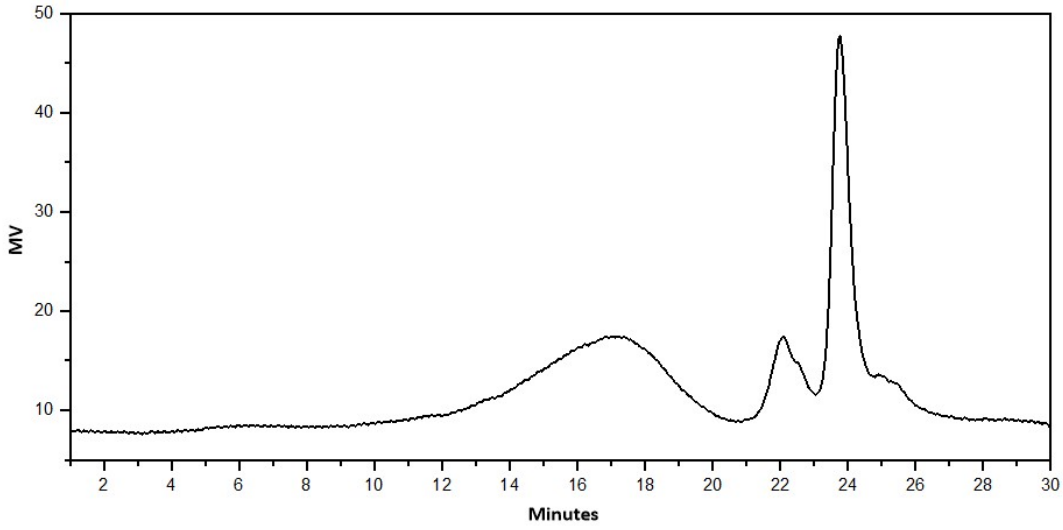
Figure S21. GPC curve of polyEPI obtained by complex **1b**/PPh_3 in Table 1, entry 8.



Broad Unknown Relative Peak Table

	Distributionn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		22986	36099	32549	49321	1.57048	1.51528

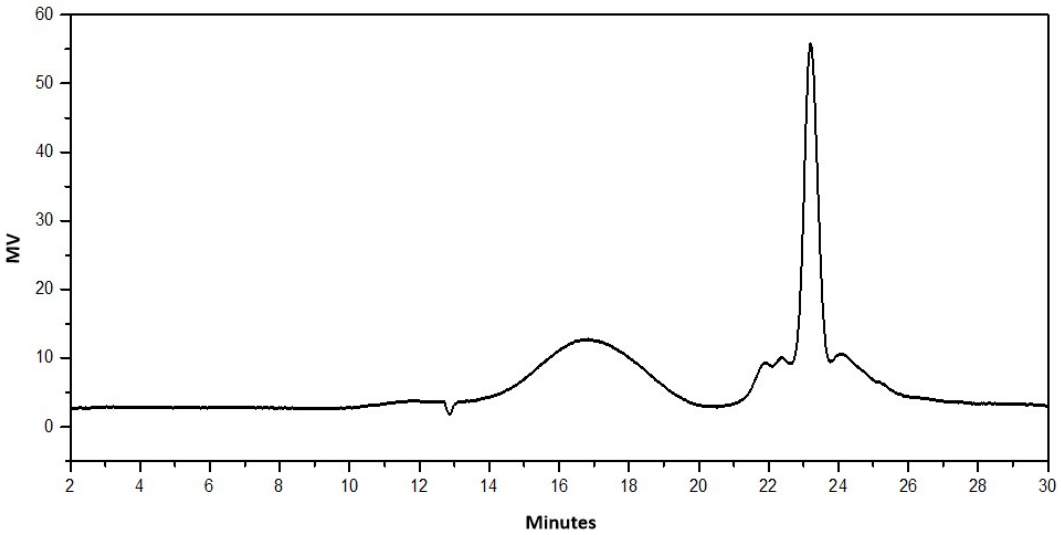
Figure S22. GPC curve of polyEPI obtained by complex **1d**/PPh_3 in Table 1, entry 9.



Broad Unknown Relative Peak Table

	Distributionn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		84902	245269	83605	606883	2.88884	7.25893

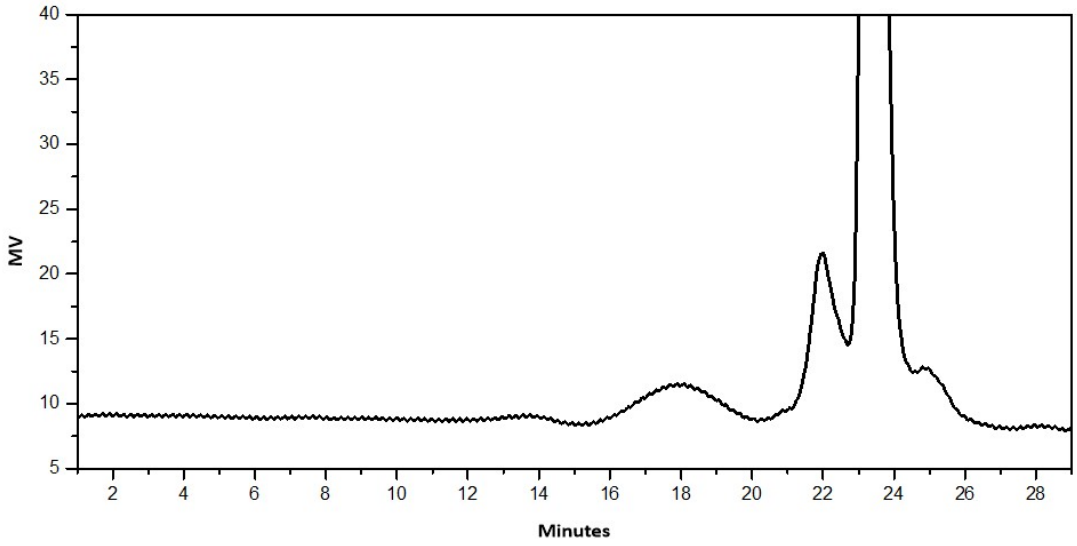
Figure S23. GPC curve of polyEPI obtained by complex **1d**/PPh_3 in Table 1, entry 10.



Broad Unknown Relative Peak Table

	Distributionn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		81353	221894	160057	502773	2.72754	3.14121

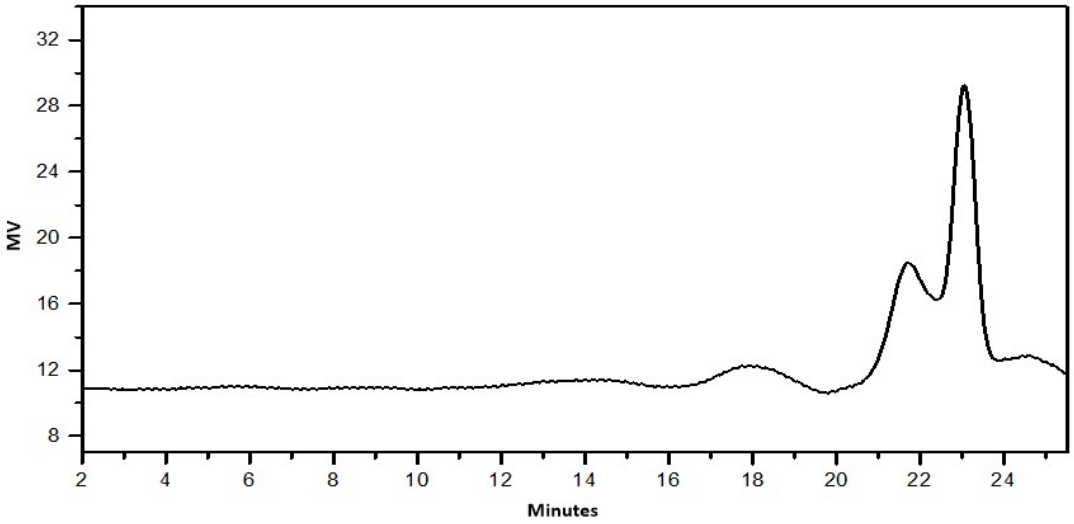
Figure S24. GPC curve of polyEPI obtained by complex **1d**/PPh_3 in Table 1, entry 13.



Broad Unknown Relative Peak Table

	Distributionn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		35111	64946	49062	104182	1.84973	2.12347

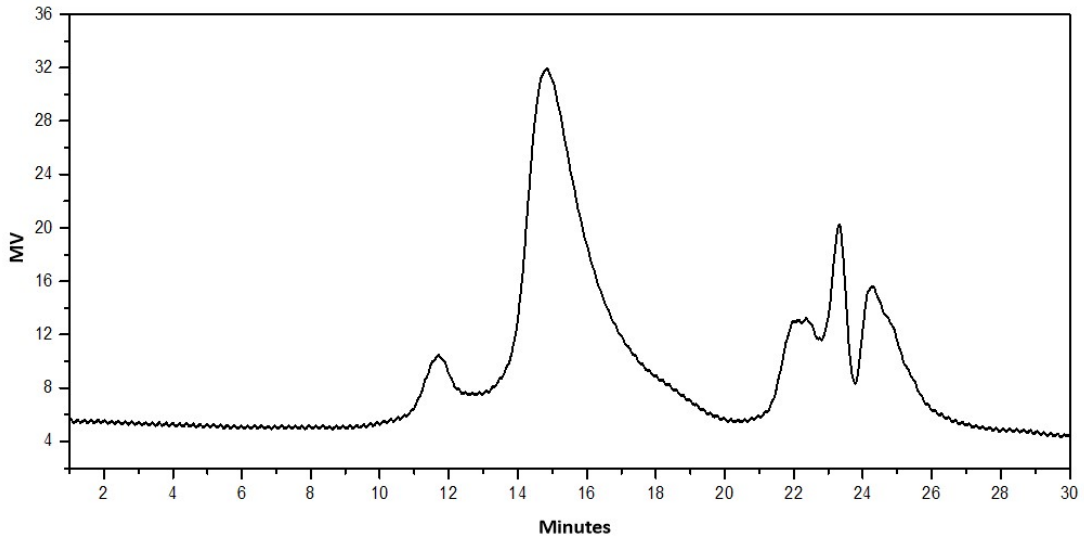
Figure S25. GPC curve of polyEPI obtained by complex **1d**/PPh_3 in Table 1, entry 14.



Broad Unknown Relative Peak Table

	Distributionn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		32411	52132	51839	74132	1.60846	1.43004

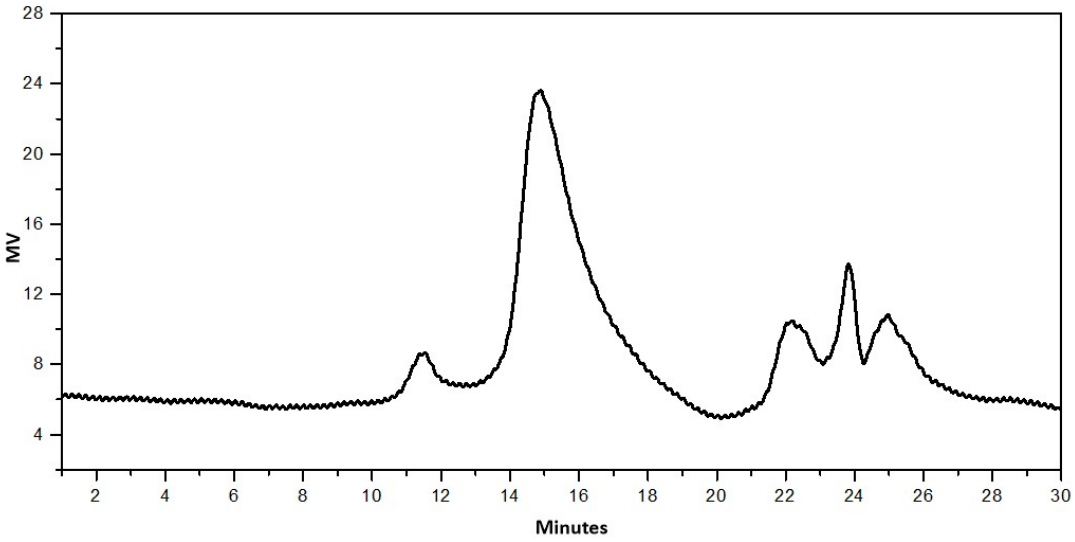
Figure S26. GPC curve of polyEPI obtained by complex **1d**/PPh_3 in Table 1, entry 15.



Broad Unknown Relative Peak Table

	Distributionn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		333969	769612	979985	1191032	2.30444	1.21535

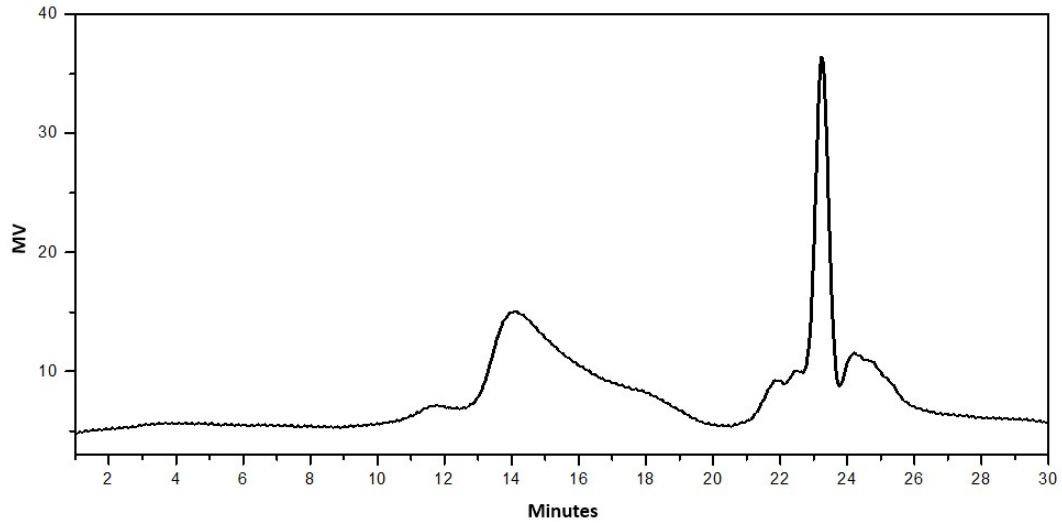
Figure S27. GPC curve of polyEPI obtained by complex **1d**/PPh_3 in Table 1, entry 17.



Broad Unknown Relative Peak Table

	Distributionn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		417451	745004	952132	1069770	1.78465	1.12355

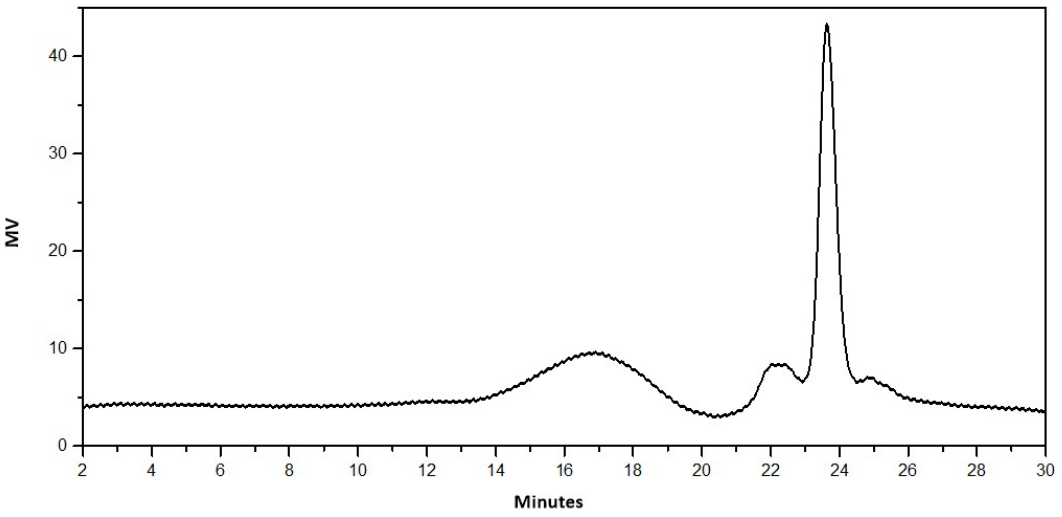
Figure S28. GPC curve of polyEPI obtained by complex **1d**/PPh_3 in Table 1, entry 18.



Broad Unknown Relative Peak Table

	Distributionn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		474808	1523665	2160805	2700017	3.20901	1.24954

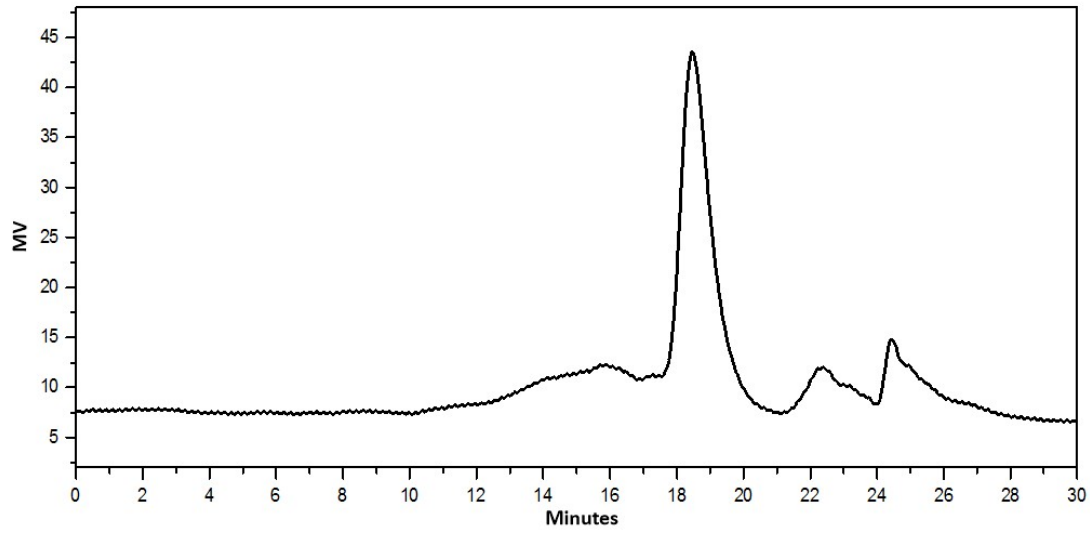
Figure S29. GPC curve of polyEPI obtained by complex **1d**/PPh_3 in Table 1, entry 19.



Broad Unknown Relative Peak Table

	Distributionn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		87232	250638	142692	618658	2.87323	4.33561

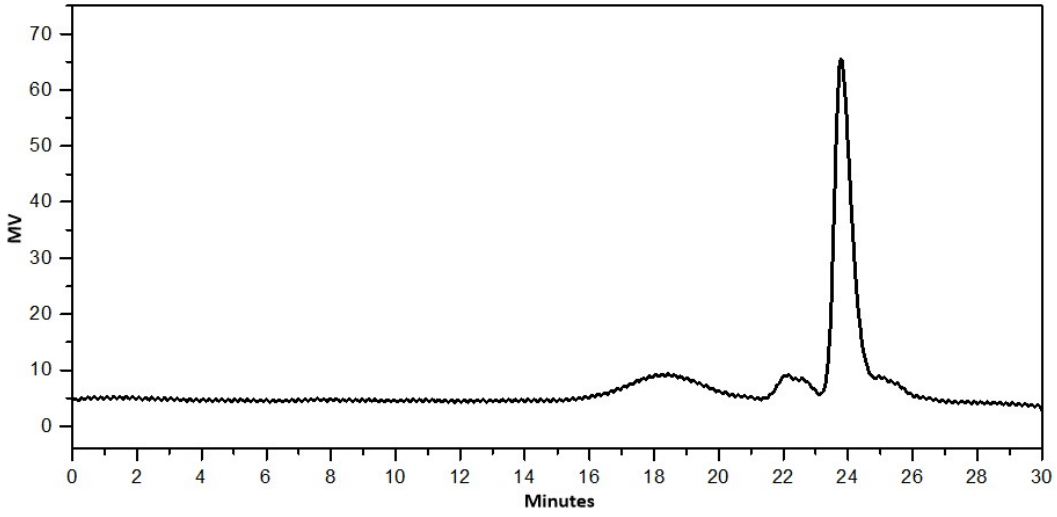
Figure S30. GPC curve of polyEPI obtained by complex **1d**/PPh_3 in Table 1, entry 20.



Broad Unknown Relative Peak Table

	Distributionn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		17801	27636	30598	34781	1.55249	1.13671

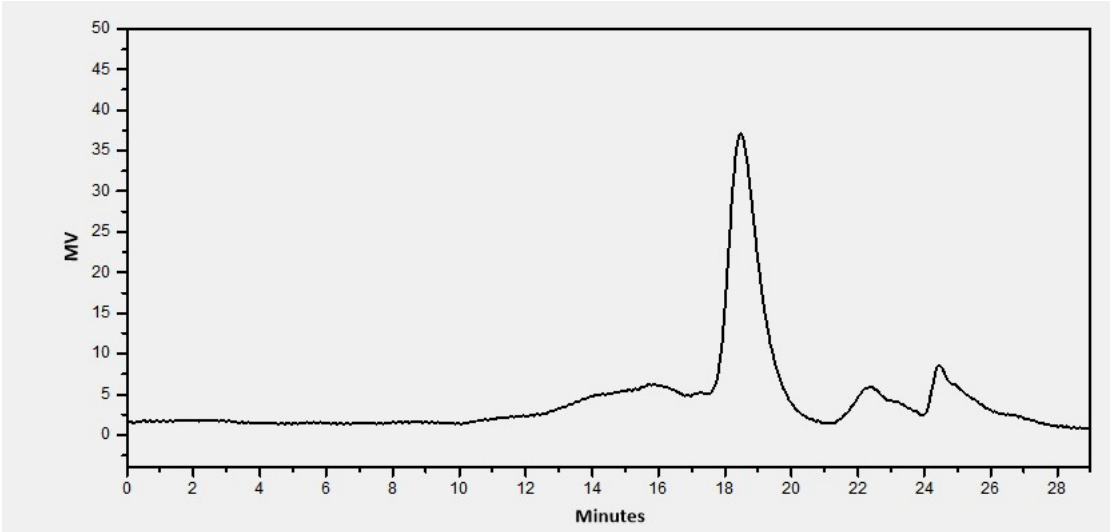
Figure S31. GPC curve of polyEPI obtained by complex **1d**/PEt_3 in Table 1, entry 22.



Broad Unknown Relative Peak Table

	Distributionn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		24969	53516	32039	102551	2.14329	3.20081

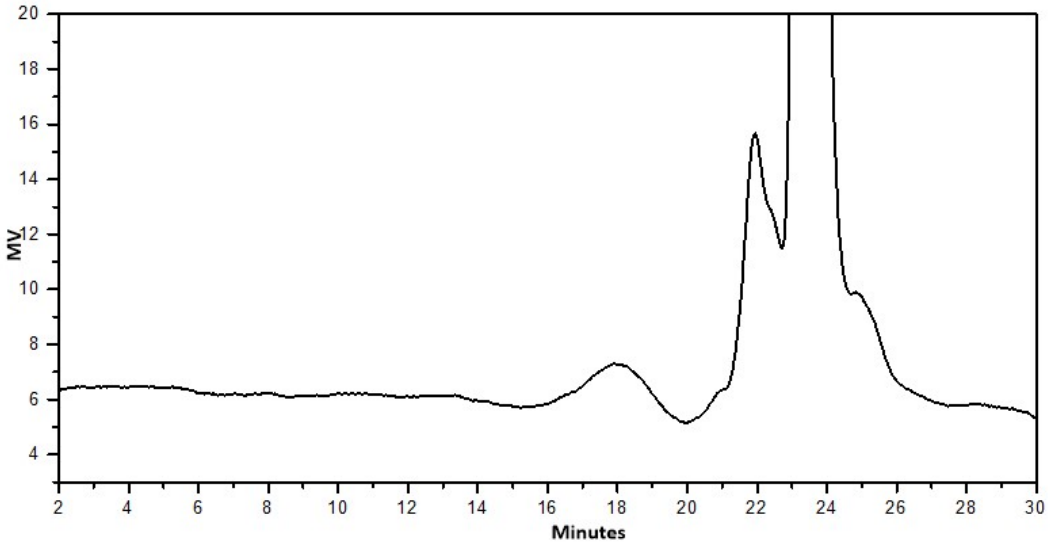
Figure S32. GPC curve of polyEPI obtained by complex **1d**/P(*n*-Bu)$_3$ in Table 1, entry 23.



Broad Unknown Relative Peak Table

	Distributionn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		18331	21628	25044	34364	1.17985	1.37214

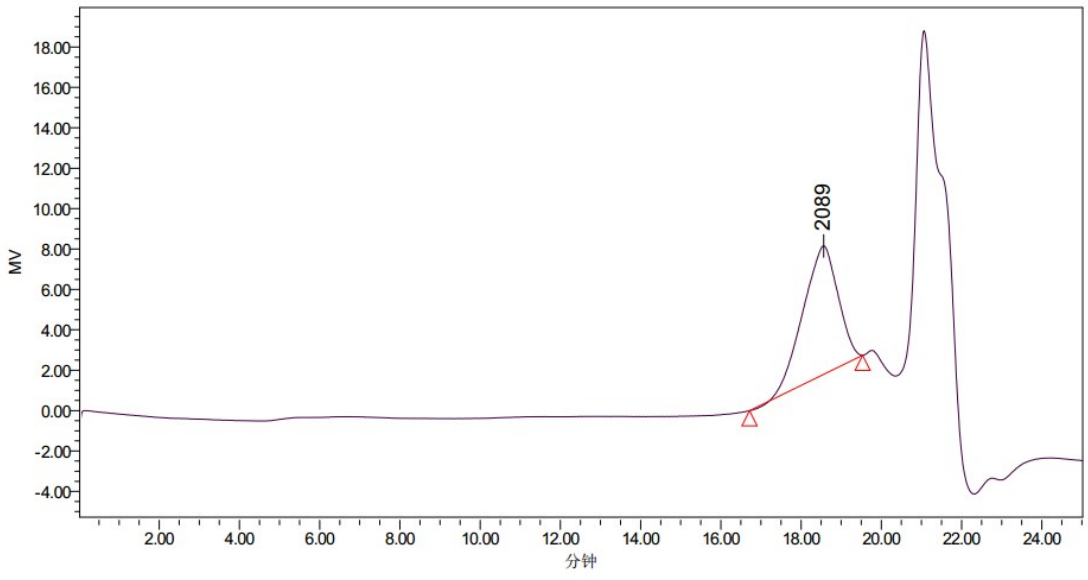
Figure S33. GPC curve of polyEPI obtained by complex **1d**/P(*n*-Oct)$_3$ in Table 1, entry 24.



Broad Unknown Relative Peak Table

	Distributionn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		35172	53389	49075	74327	1.51794	1.51455

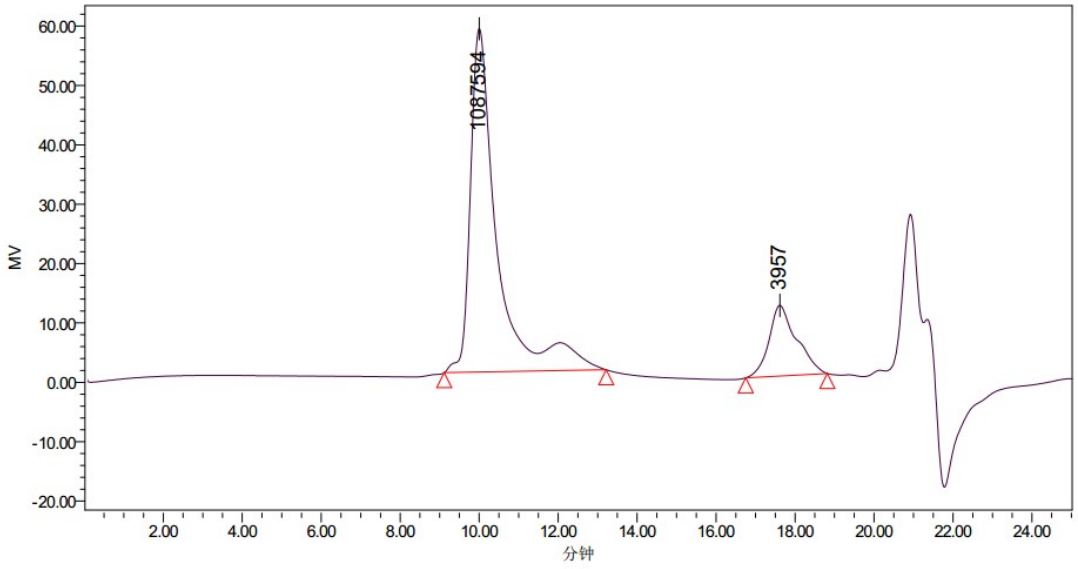
Figure S34. GPC curve of polyEPI obtained by complex **1d**/P(C_6H_{11})$_3$ in Table 1, entry 25.



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		18.563	18.563	18.563	2154	2337	2089	2535	2741	1.084663	1.172779

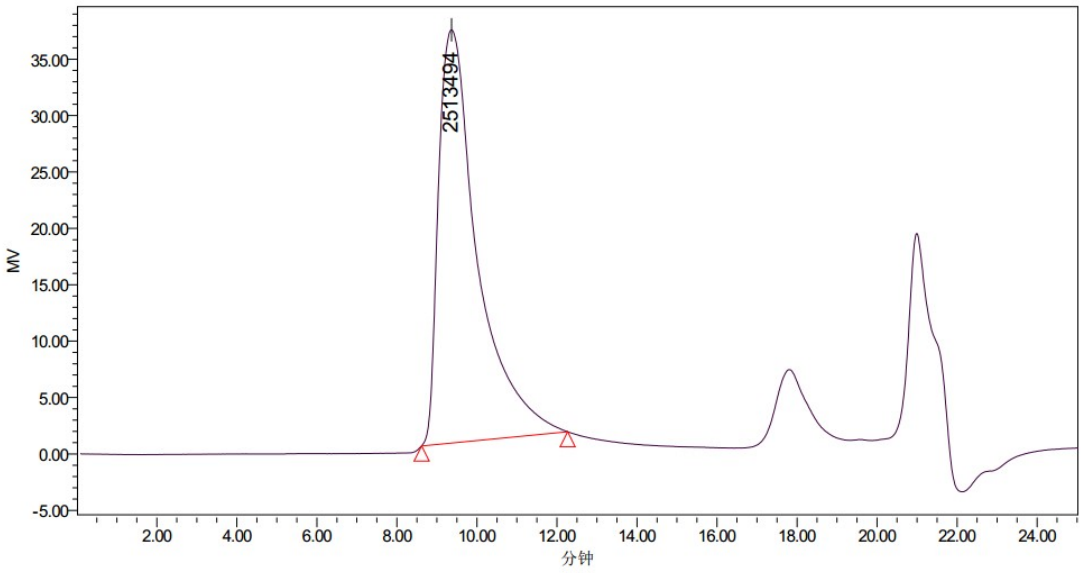
Figure S35. GPC curve of polyNI obtained by complex **1d**/PPh_3 in Table 1, entry 26.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		10.003	10.003	10.003	504967	886382	1087594	111459	1286415	1.257469
2		17.614	17.614	17.614	3527	3719	3957	3902	4074	1.049230

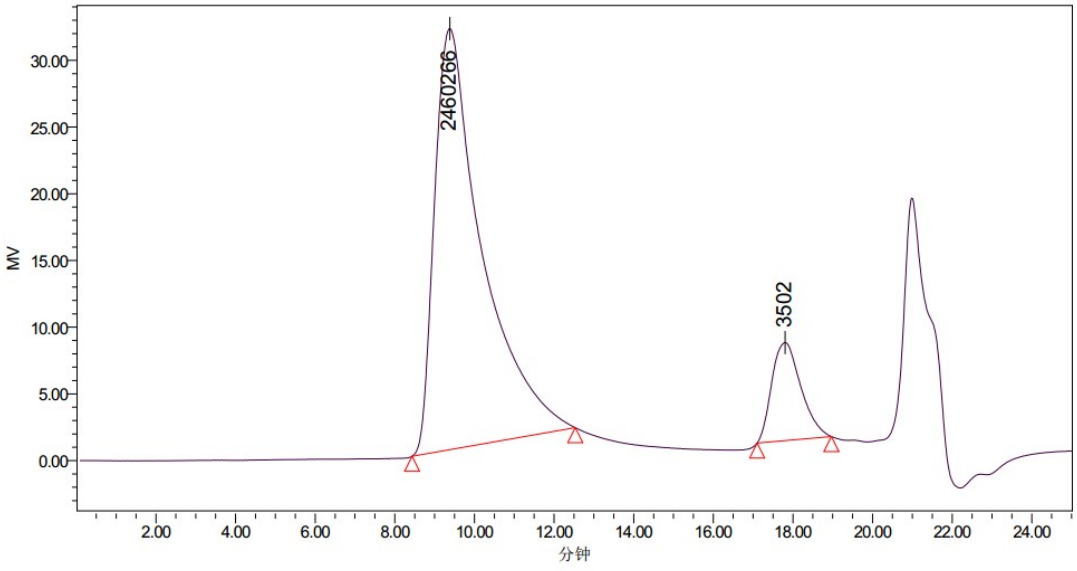
Figure S36. GPC curve of polyITPB obtained by complex **1d**/PPh_3 in Table 1, entry 27.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		9.366	9.366	9.366	1164795	2035664	2513494	2738514	3261706	1.345268

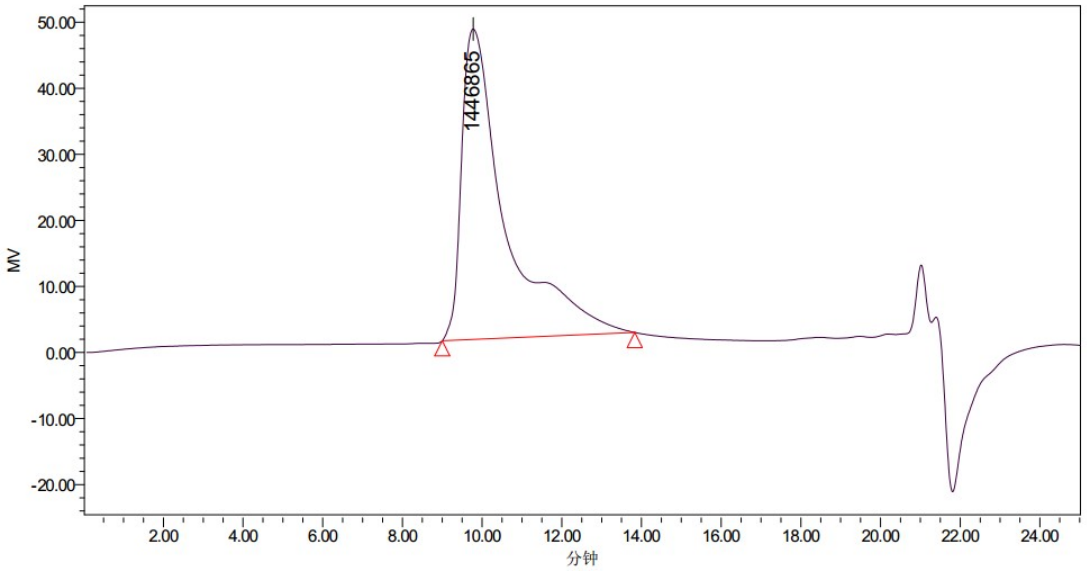
Figure S37. GPC curve of poly(D-IMCI) obtained by complex **1d**/PPh_3 in Table 1, entry 28.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		9.381	9.381	9.381	929102	1960435	2460266	2961678	3763994	1.510725
2		17.805	17.805	17.805	3244	3405	3502	3554	3690	1.043686

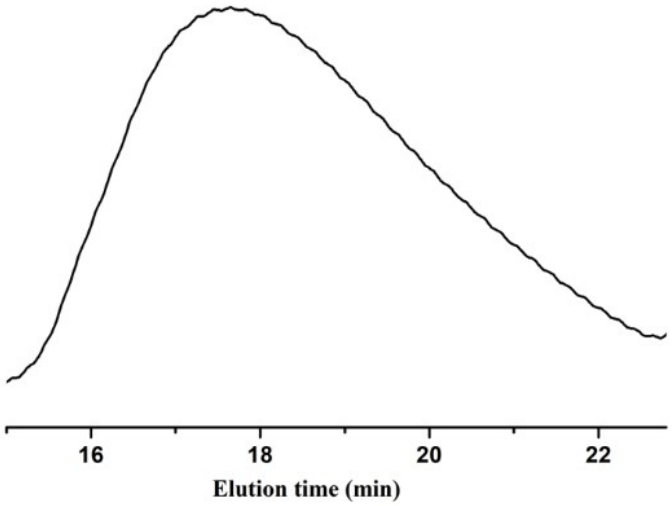
Figure S38. GPC curve of poly(L-IMCI) obtained by complex **1d**/PPh_3 in Table 1, entry 29.



GPC Results

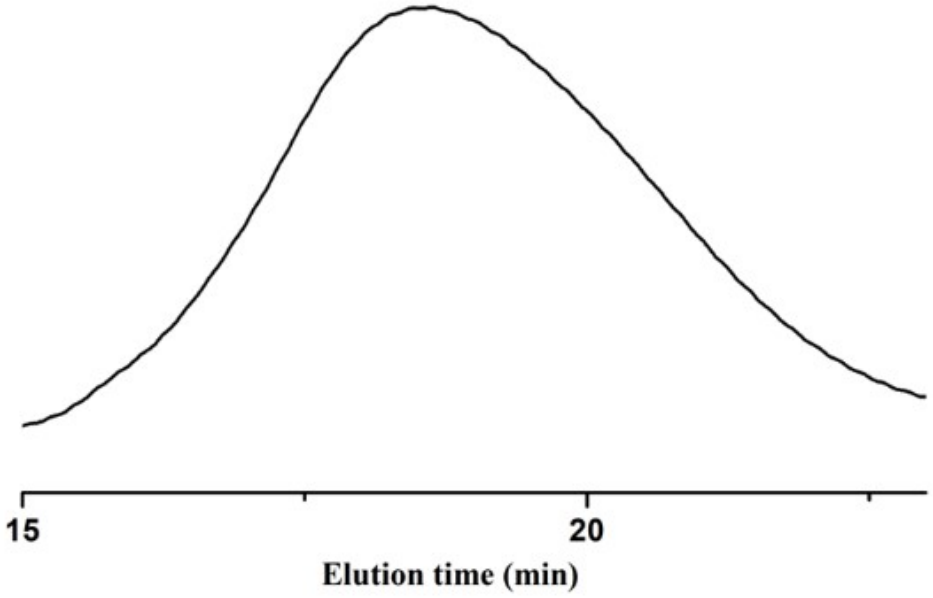
	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		9.777	9.777	9.777	428411	1012349	1446865	1460213	1754591	1.442400

Figure S39. GPC curve of polyIPI obtained by complex **1d**/PPh_3 in Table 1, entry 30.



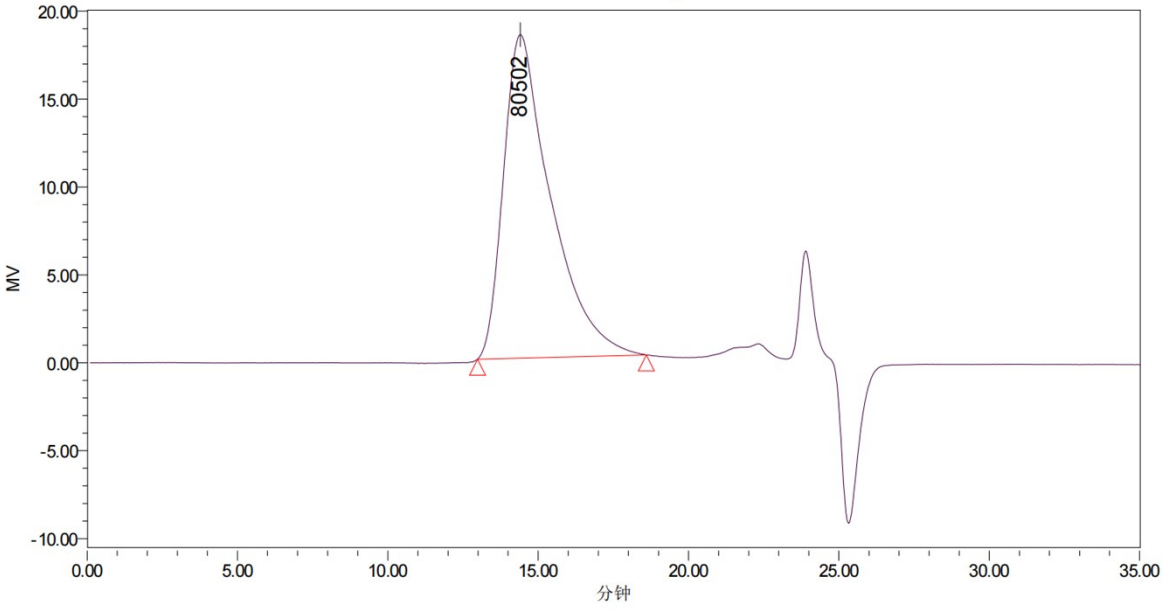
Peak No	M_n (Da)	M_w (Da)	PDI
1	14242	29580	2.077

Figure S40. GPC curve of poly(D-OEGI) obtained by complex **1d**/PPh_3 in Table 1, entry 32.



Peak No	M_n (Da)	M_w (Da)	PDI
1	10982	20634	1.879

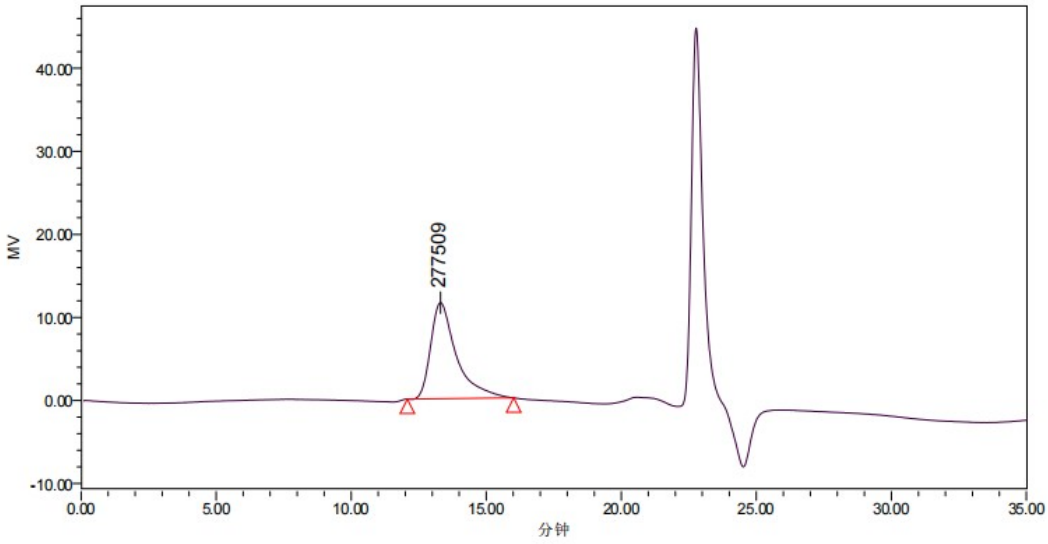
Figure S41. GPC curve of poly(L-OEGI) obtained by complex **1d**/PPh_3 in Table 1, entry 33.



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		14.406	14.406	14.406	44073	73121	80502	107826	145147	1.474623	1.985017

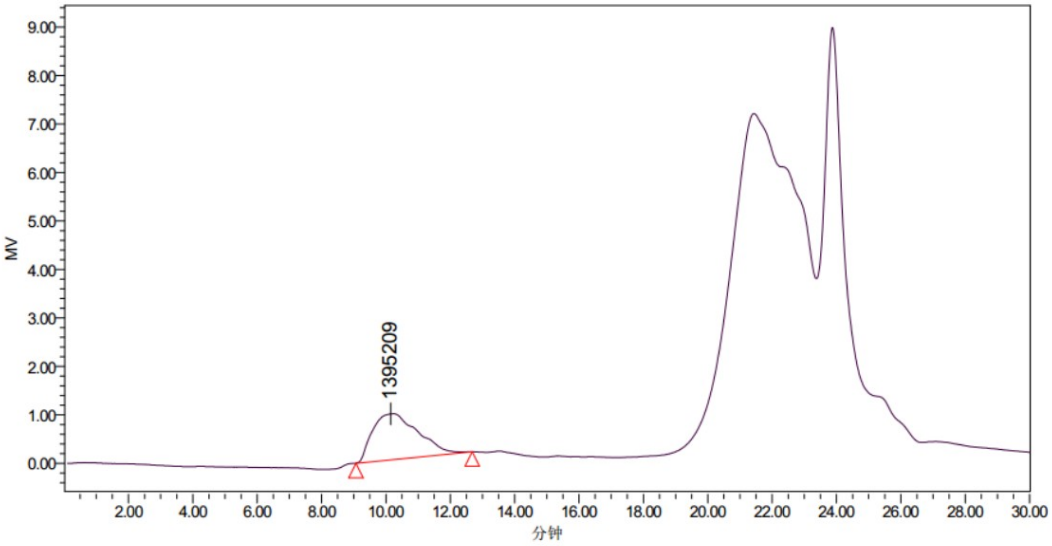
Figure S42. GPC curve of polyEPI obtained by complex **1d** in Table 1, entry 34.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		13.309	13.309	13.309	164756	255436	277509	345858	434839	1.353991

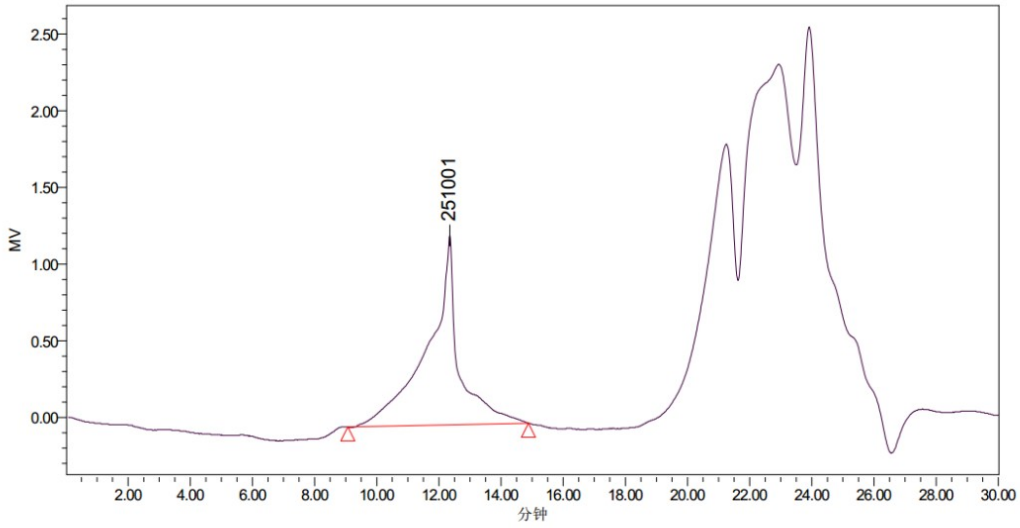
Figure S43. GPC curve of polyEPI obtained by complex **1d** in Table 1, entry 35.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		10.150	10.150	10.150	990355	1329904	1395209	1679673	1986588	1.263004

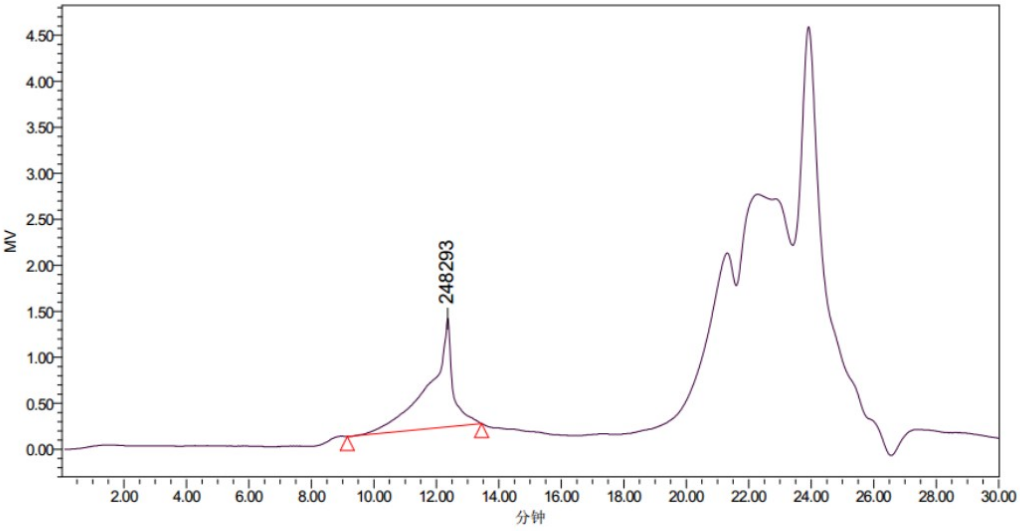
Figure S44. GPC curve of polyITPB obtained by complex **1d** in Table 1, entry 36.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		12.348	12.348	12.348	275891	415496	251001	689322	1109467	1.659033

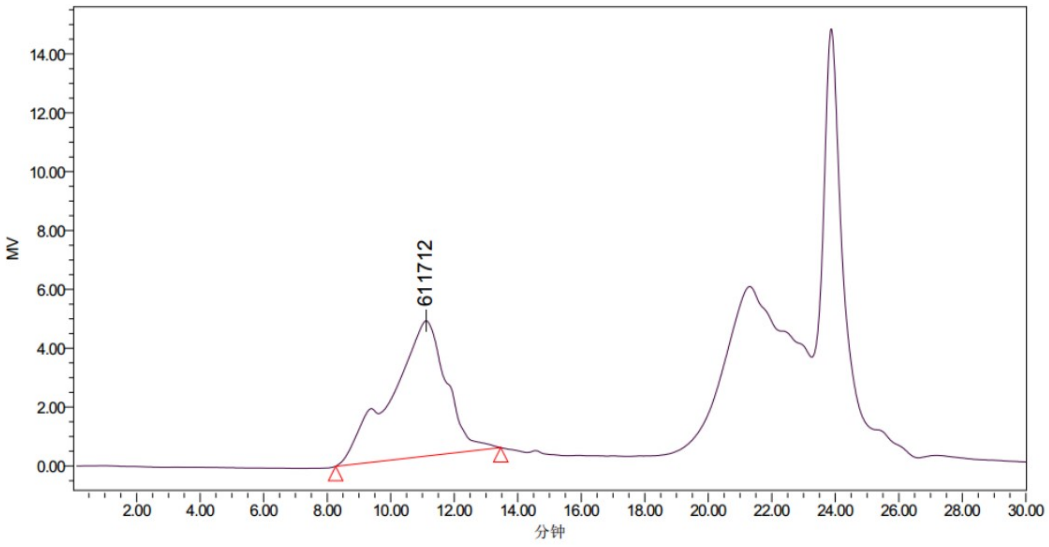
Figure S45. GPC curve of polyITPB obtained by complex **1d** in Table 1, entry 37.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		12.364	12.364	12.364	320598	410462	248293	587190	873230	1.430559

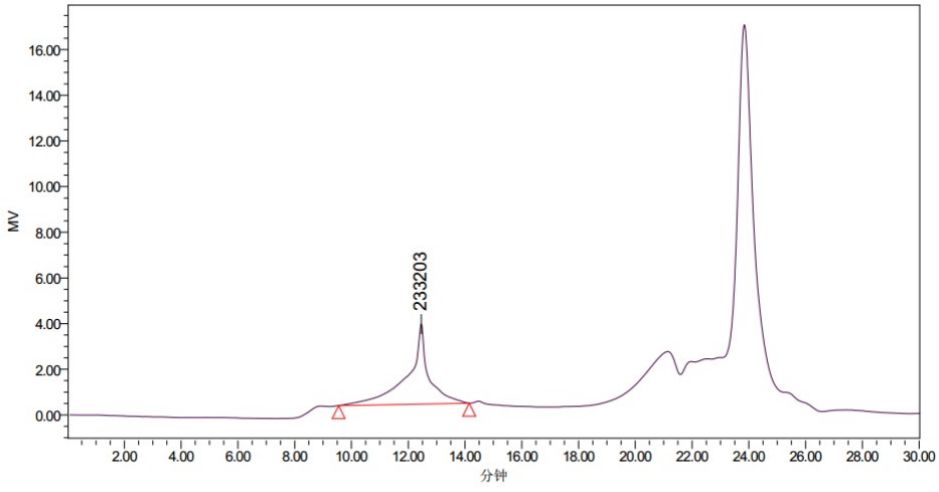
Figure S46. GPC curve of polyITPB obtained by complex **1d** in Table 1, entry 38.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		11.117	11.117	11.117	665868	1231175	611712	2452921	3885247	1.992340

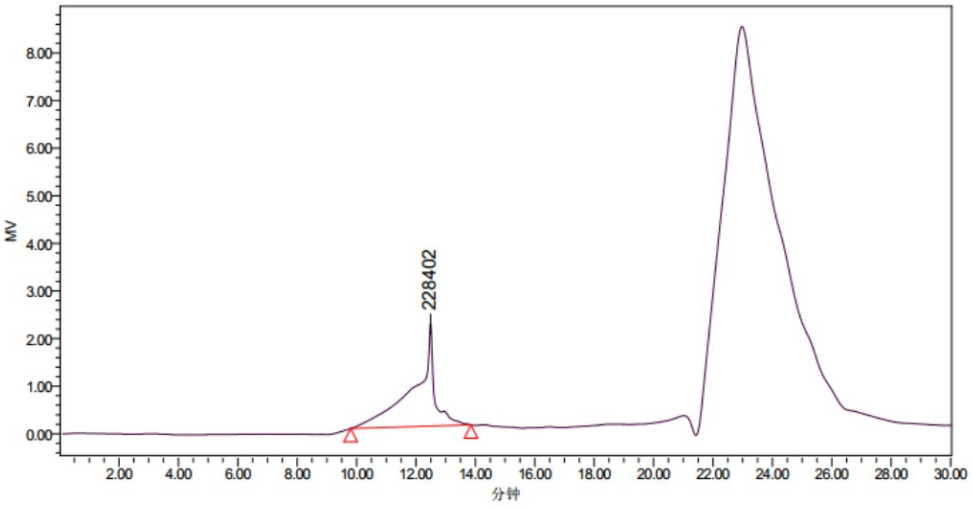
Figure S47. GPC curve of polyIPI obtained by complex **1d** in Table 1, entry 39.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		12.460	12.460	12.460	259395	342802	233203	527950	859586	1.540102

Figure S48. GPC curve of polyIPI obtained by complex **1d** in Table 1, entry 40.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		12.492	12.492	12.492	300989	390595	228402	546712	762632	1.399691

Figure S49. GPC curve of polyIPI obtained by complex **1d** in Table 1, entry 41.

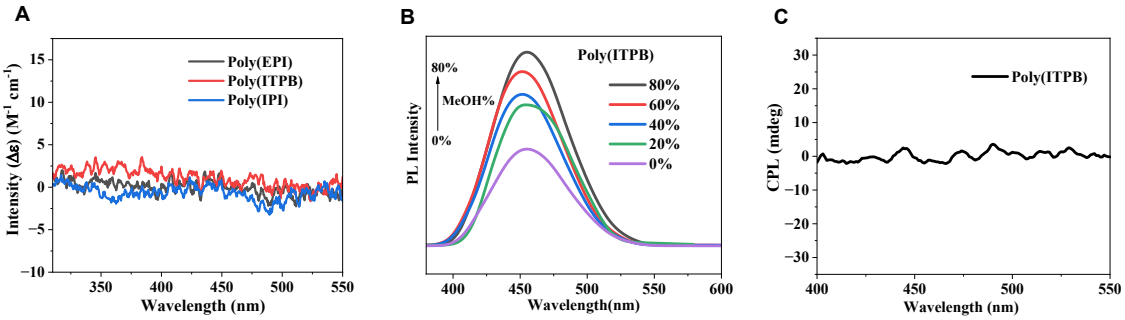


Figure S50. (A) CD spectra of poly(EPI), poly(ITPB), and poly(IPI) obtained by complex **1d** in THF (c = 0.2 mg mL^{-1}) at 25 °C. (B) PL spectra of poly(ITPB) obtained by complex **1d** in the different concentration ratios of MeOH/THF (c = 0.5 mg mL^{-1}, under 365 nm UV irradiation). (C) CPL spectra of poly(ITPB) obtained by complex **1d** in THF (c = 0.2 mg mL^{-1}).

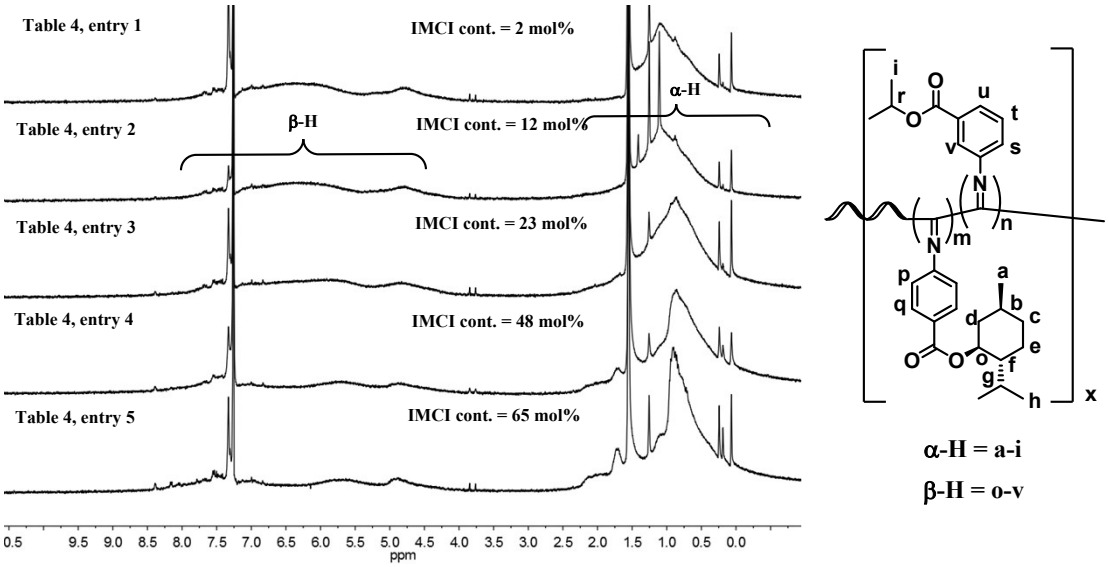


Figure S51. [1]H NMR spectra of poly(D-IMCI-*co*-IPI)s (Table 2, entries 1-5).

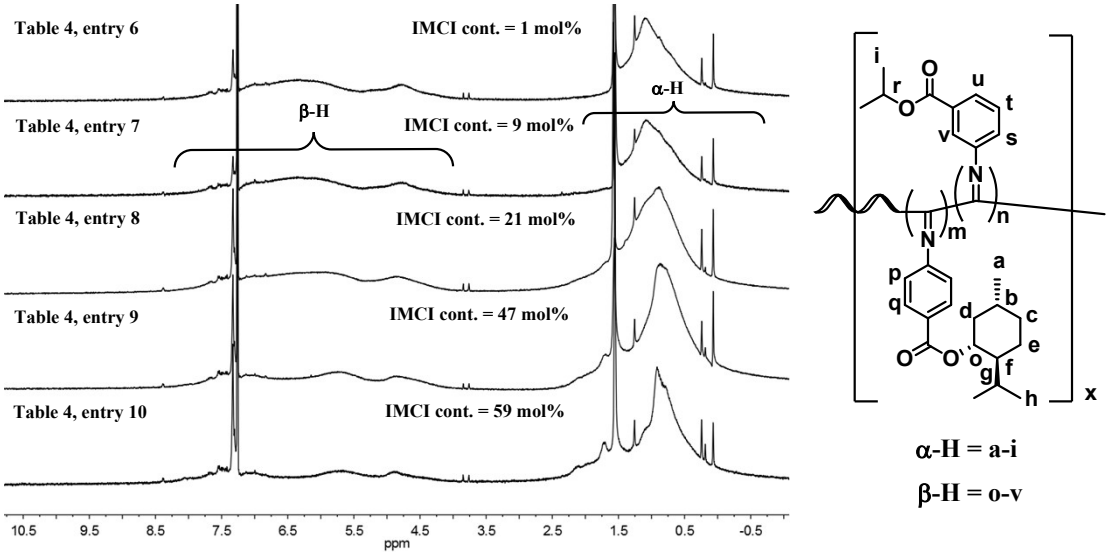


Figure S52. [1]H NMR spectra of poly(L-IMCI-*co*-IPI)s (Table 2, entries 6-10).

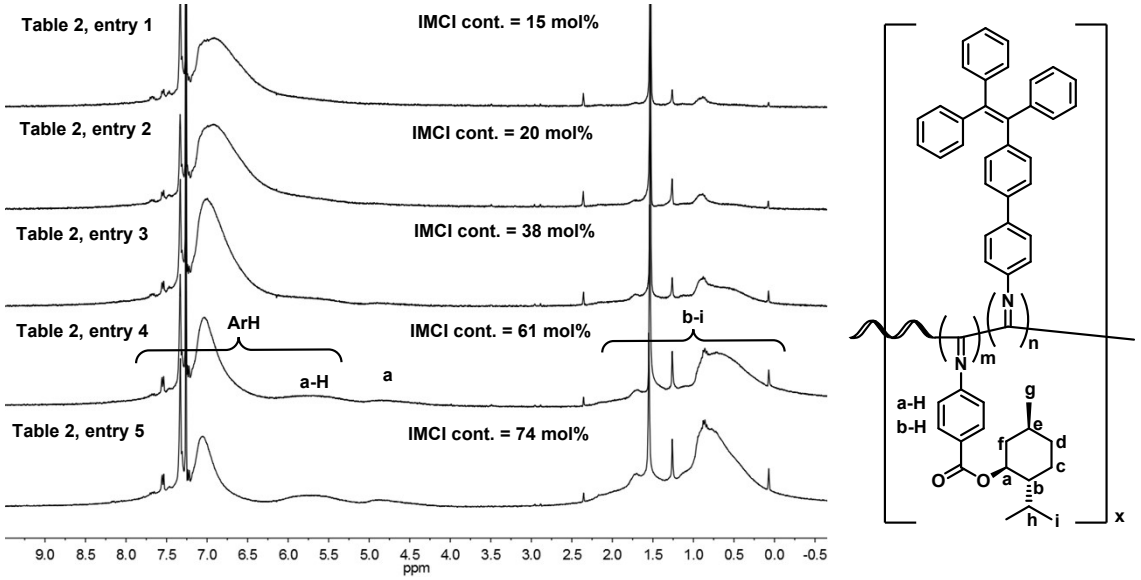


Figure S53. [1]H NMR spectra of poly(D-IMCI-*co*-ITPB)s (Table 2, entries 11-15).

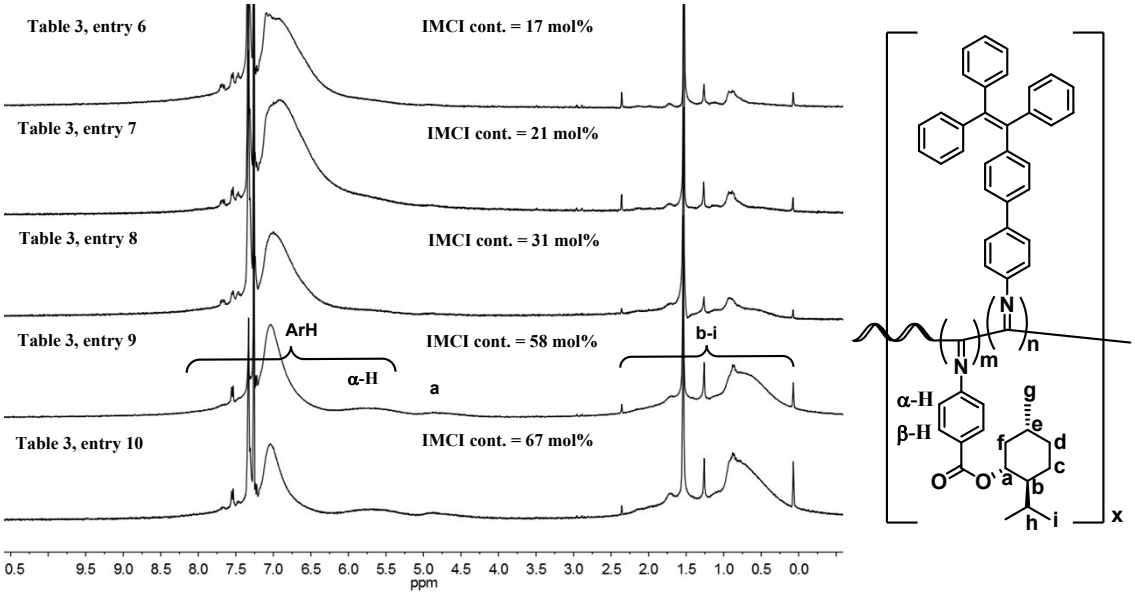
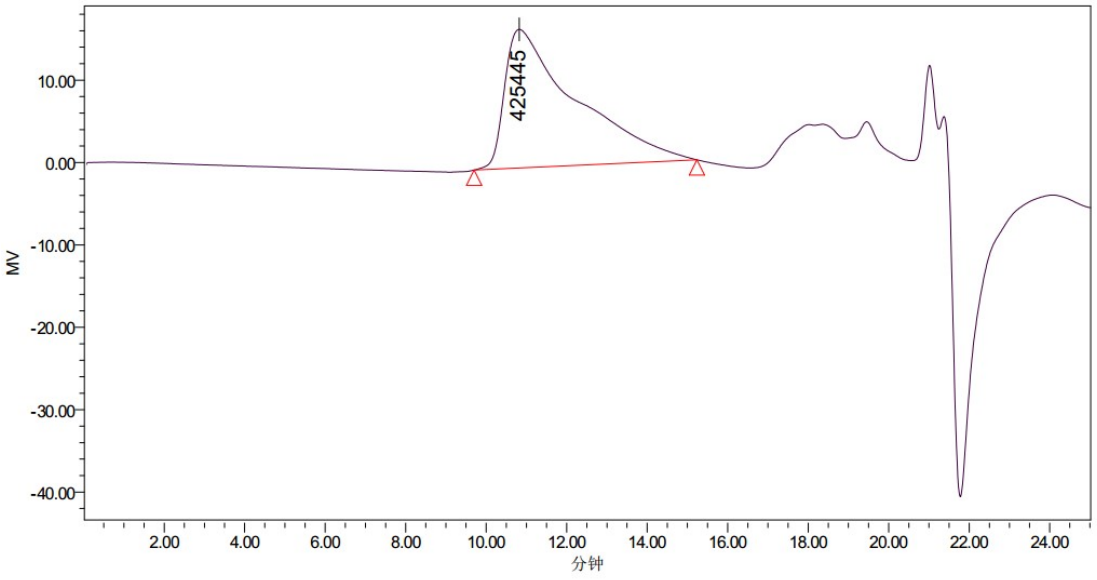


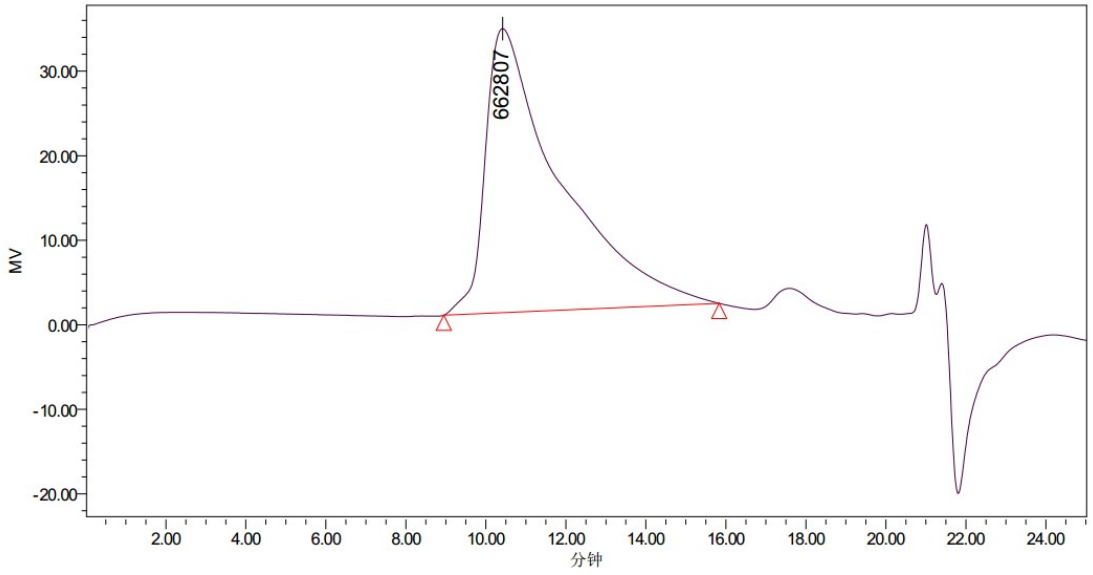
Figure S54. [1]H NMR spectra of poly(L-IMCI-*co*-ITPB)s (Table 2, entries 16-20).



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		10.822	10.822	10.822	120049	260412	425445	409791	523903	1.573627

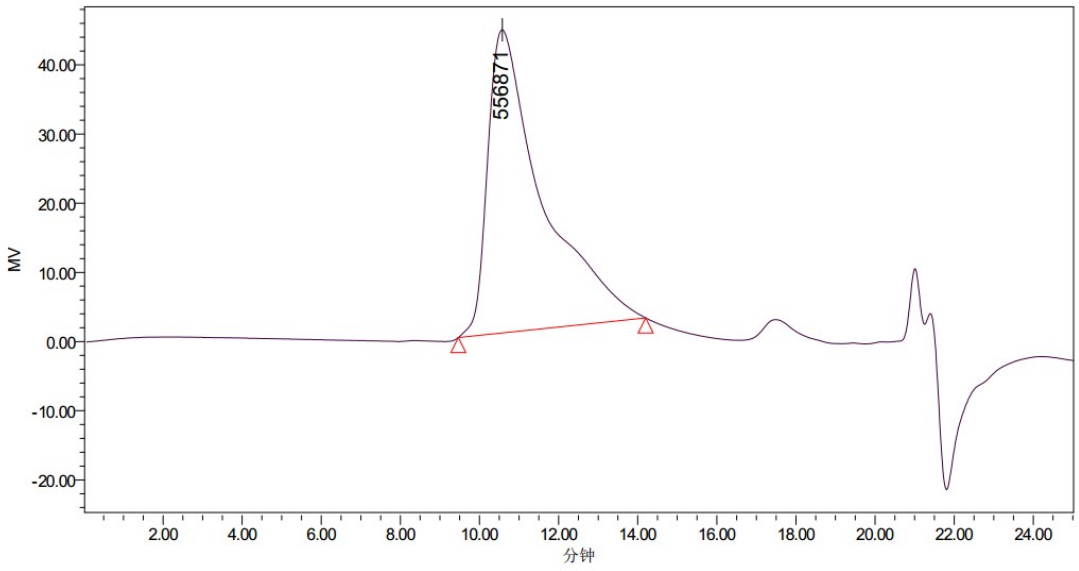
Figure S55. GPC curve of poly(D-IMCI-*co*-IPI) obtained by complex **1d**/PPh_3 in Table 2, entry 1.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		10.419	10.419	10.419	140858	435217	662807	828133	1283166	1.902805

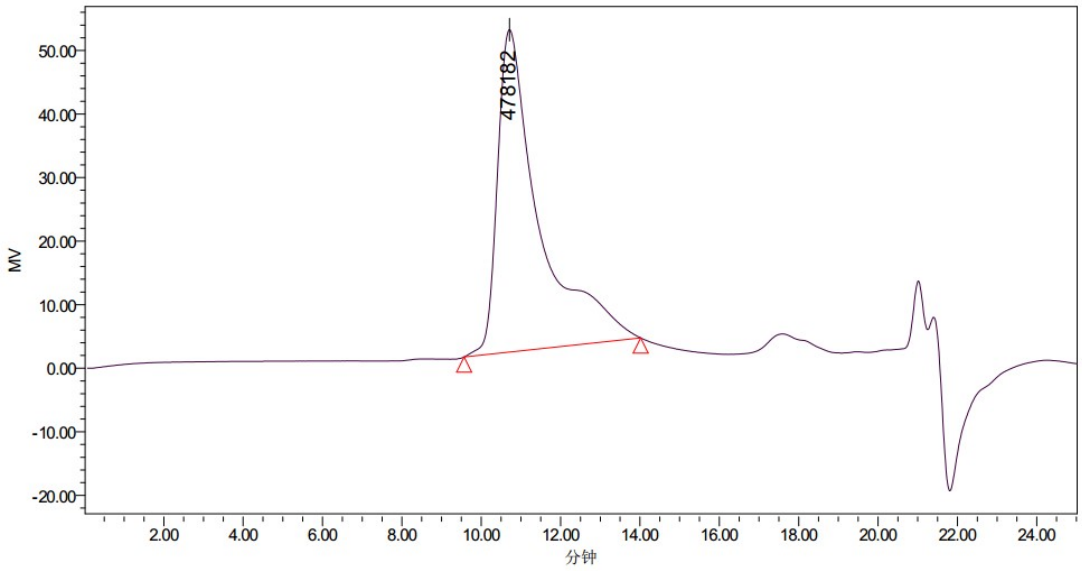
Figure S56. GPC curve of poly(D-IMCI-*co*-IPI) obtained by complex **1d**/PPh_3 in Table 1, entry 2.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		10.574	10.574	10.574	209043	400463	556871	585588	737831	1.462278

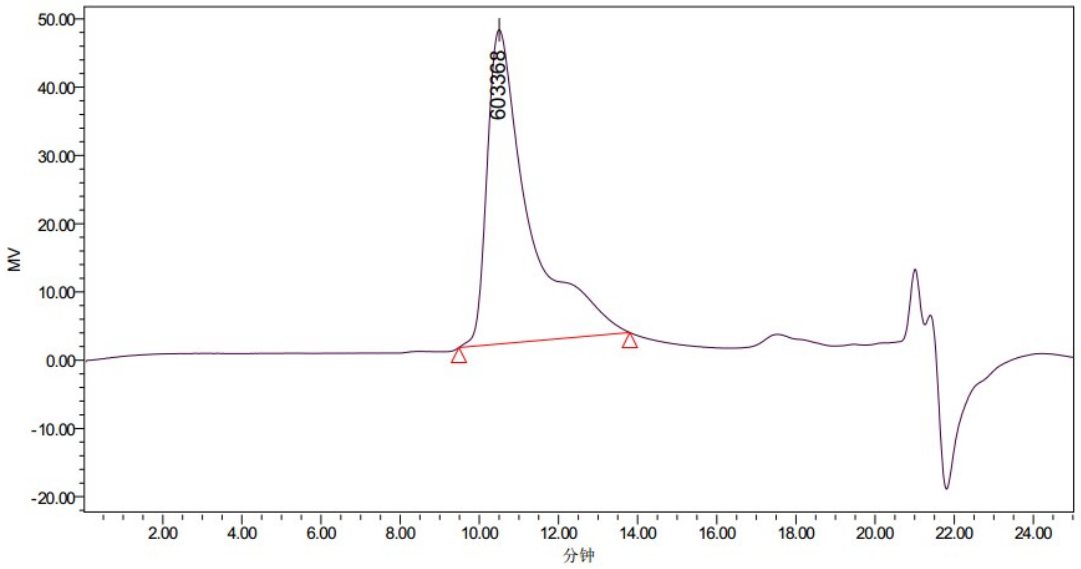
Figure S57. GPC curve of poly(D-IMCI-*co*-IPI) obtained by complex **1d**/PPh_3 in Table 2, entry 3.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		10.713	10.713	10.713	214622	362539	478182	484633	584799	1.336777

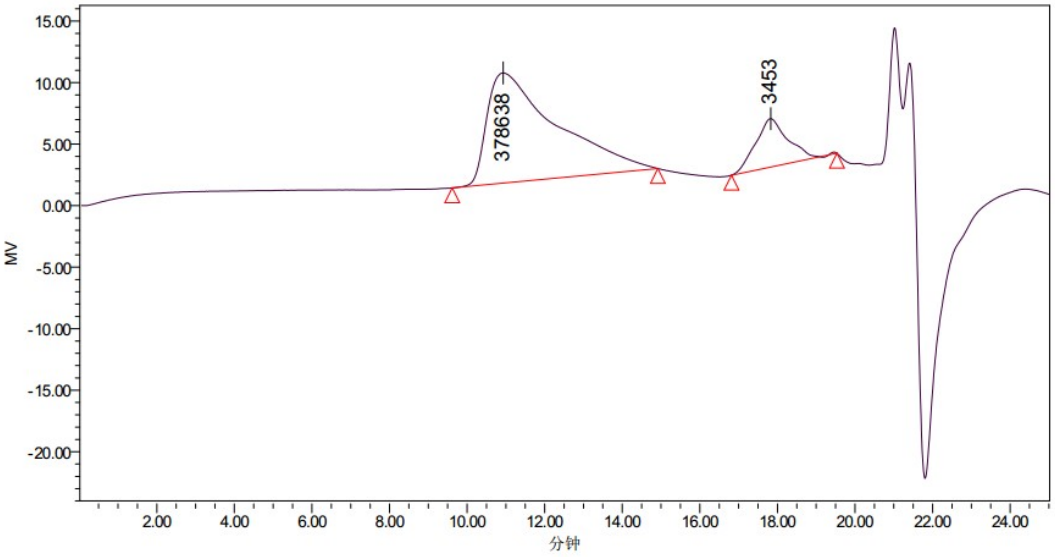
Figure S58. GPC curve of poly(D-IMCI-*co*-IPI) obtained by complex **1d**/PPh_3 in Table 2, entry 4.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		10.502	10.502	10.502	260557	453520	603368	610560	730097	1.346269

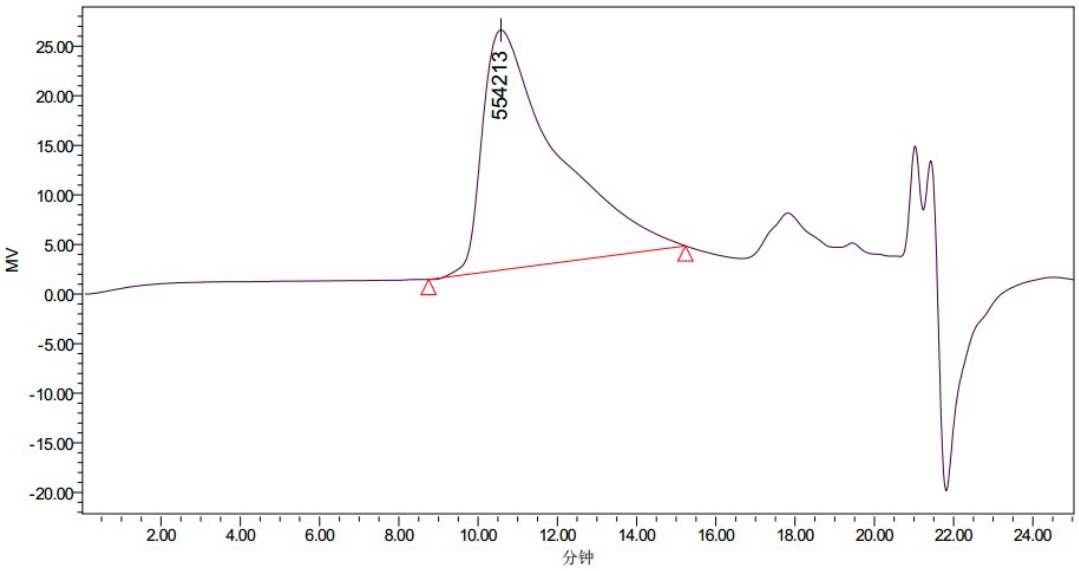
Figure S59. GPC curve of poly(D-IMCI-*co*-IPI) obtained by complex **1d**/PPh_3 in Table 2, entry 5.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		10.934	10.934	10.934	124539	250498	378638	384290	487161	1.534100
2		17.827	17.827	17.827	3182	3422	3453	3652	3868	1.067284

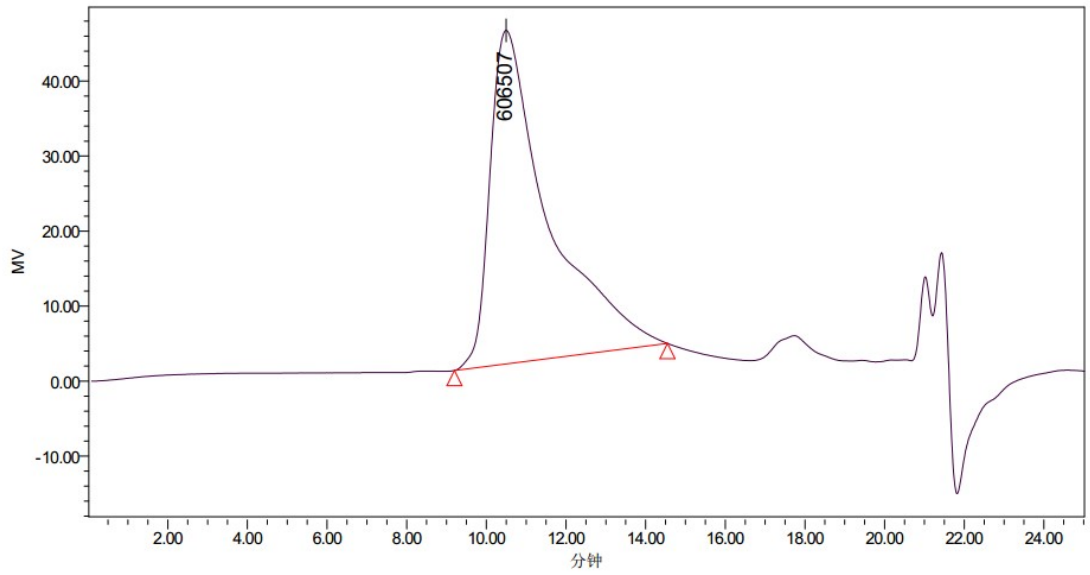
Figure S60. GPC curve of poly(L-IMCI-*co*-IPI) obtained by complex **1d**/PPh_3 in Table 2, entry 6.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		10.578	10.578	10.578	144126	378543	554213	665936	950800	1.759205

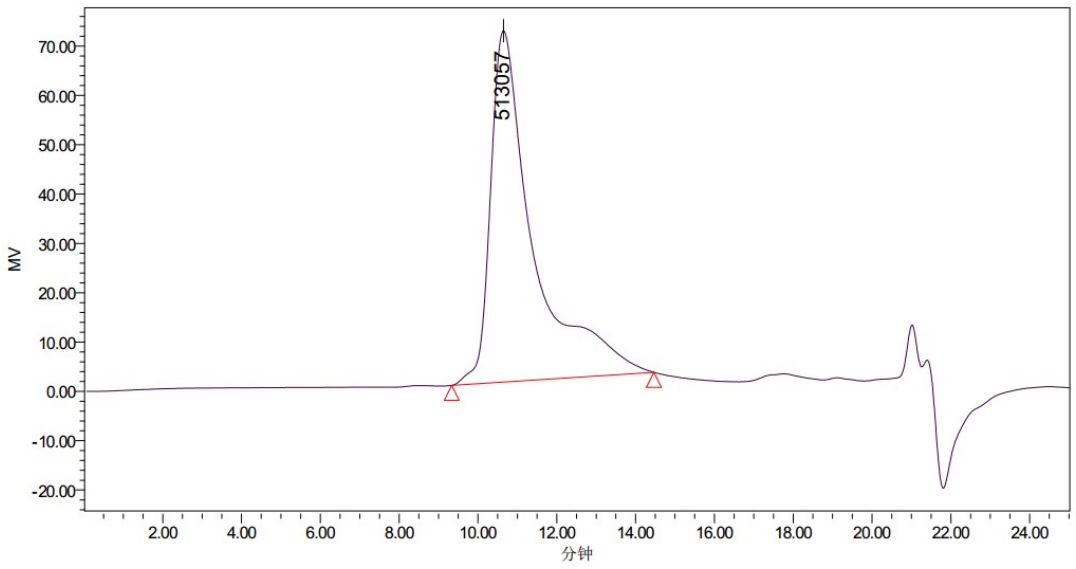
Figure S61. GPC curve of poly(L-IMCI-*co*-IPI) obtained by complex **1d**/PPh_3 in Table 2, entry 7.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		10.498	10.498	10.498	204525	445851	606507	691424	910296	1.550793

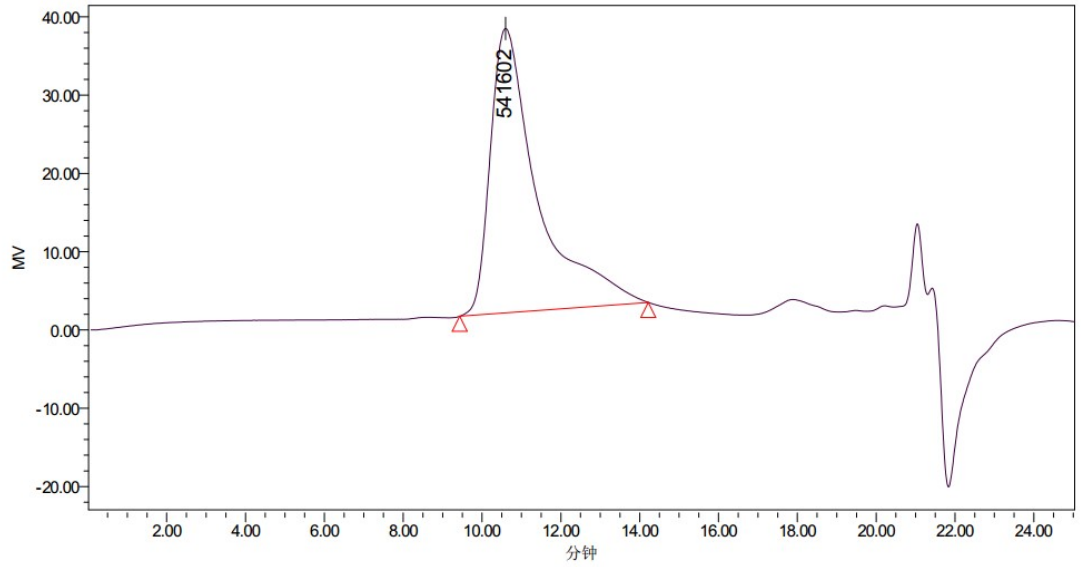
Figure S62. GPC curve of poly(L-IMCI-*co*-IPI) obtained by complex **1d**/PPh_3 in Table 2, entry 8.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		10.648	10.648	10.648	212776	400536	513057	561282	717331	1.401328

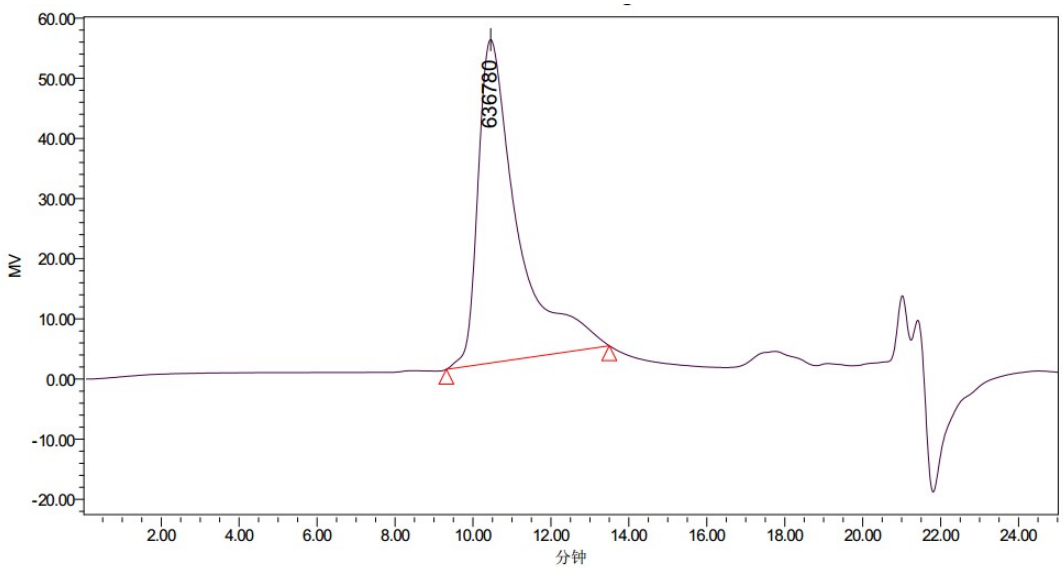
Figure S63. GPC curve of poly(L-IMCI-*co*-IPI) obtained by complex **1d**/PPh_3 in Table 2, entry 9.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		10.599	10.599	10.599	234784	435710	541602	607172	747618	1.393522

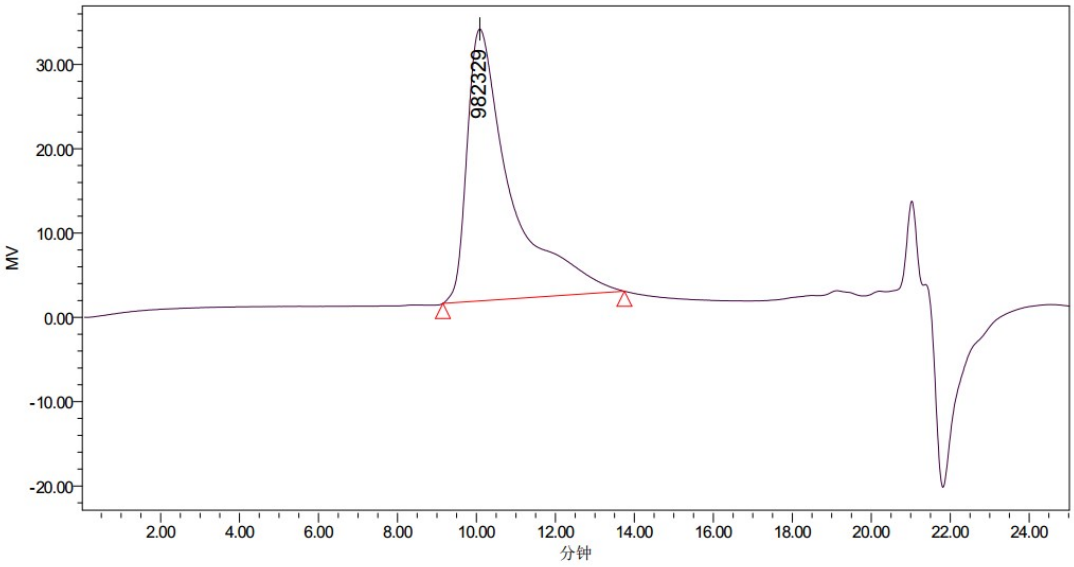
Figure S64. GPC curve of poly(L-IMCI-*co*-IPI) obtained by complex **1d**/PPh_3 in Table 2, entry 10.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		10.455	10.455	10.455	311972	515652	636780	684591	835896	1.327621

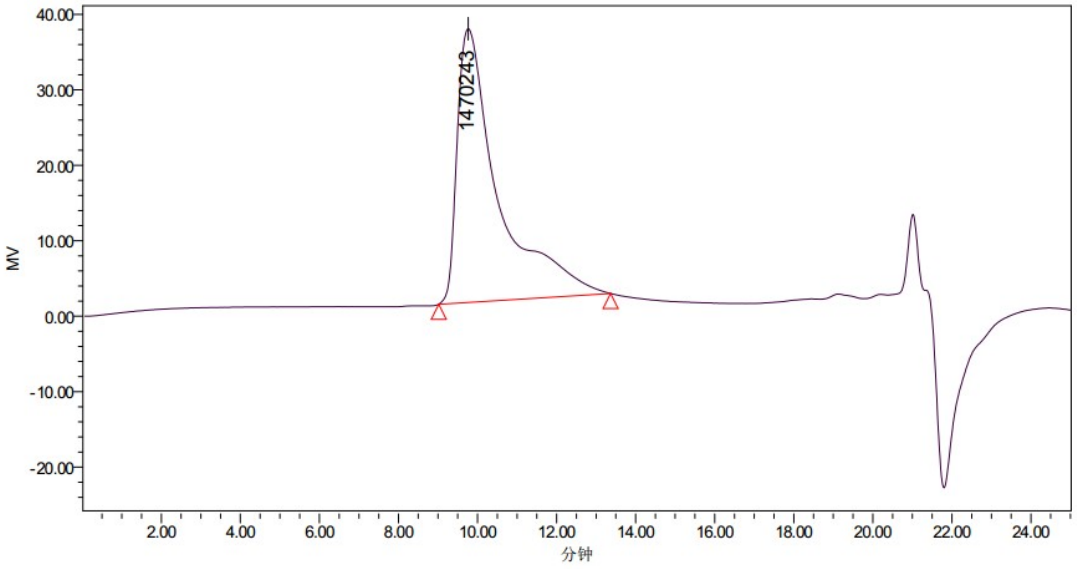
Figure S65. GPC curve of poly(D-IMCI-*co*-ITPB) obtained by complex **1d**/PPh_3 in Table 2, entry 11.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		10.086	10.086	10.086	363298	734519	982329	1036749	1261378	1.411467

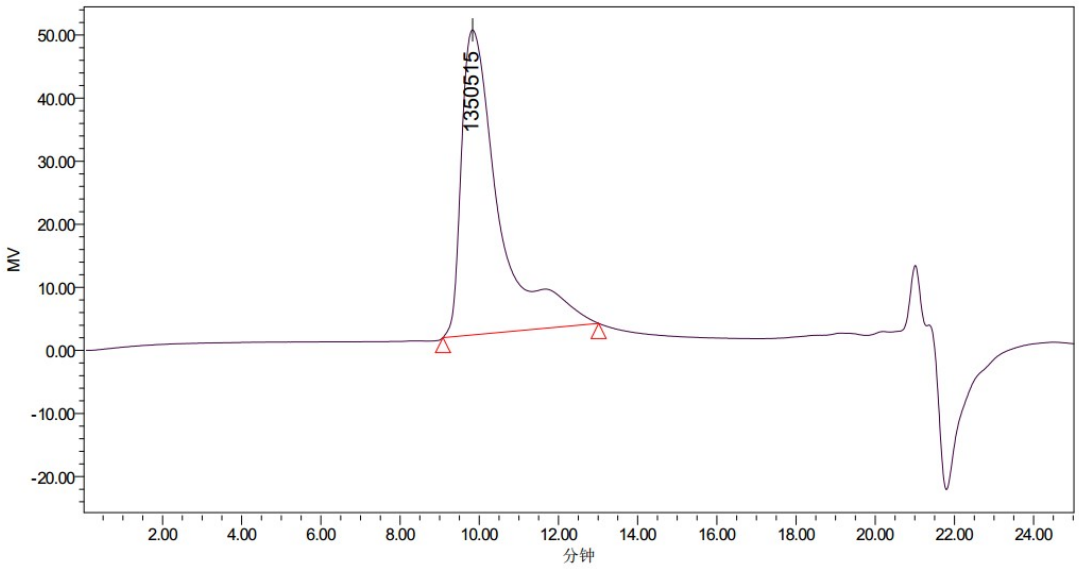
Figure S66. GPC curve of poly(D-IMCI-*co*-ITPB) obtained by complex **1d**/PPh_3 in Table 2, entry 12.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		9.765	9.765	9.765	488116	1035773	1470243	1451386	1717214	1.401259

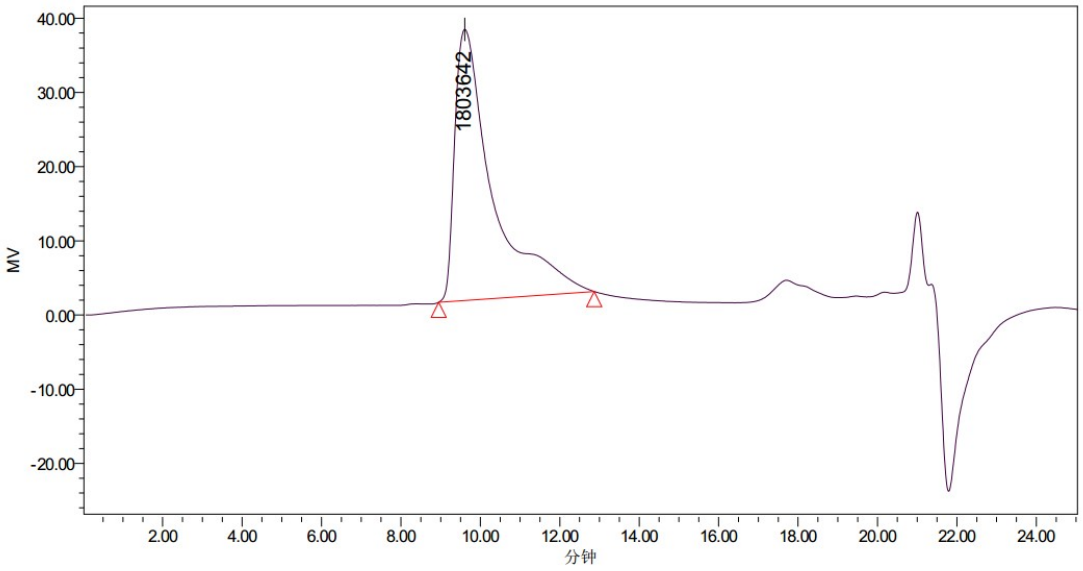
Figure S67. GPC curve of poly(D-IMCI-*co*-ITPB) obtained by complex **1d**/PPh_3 in Table 2, entry 13.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		9.831	9.831	9.831	549355	1024653	1350515	1361918	1591212	1.329150

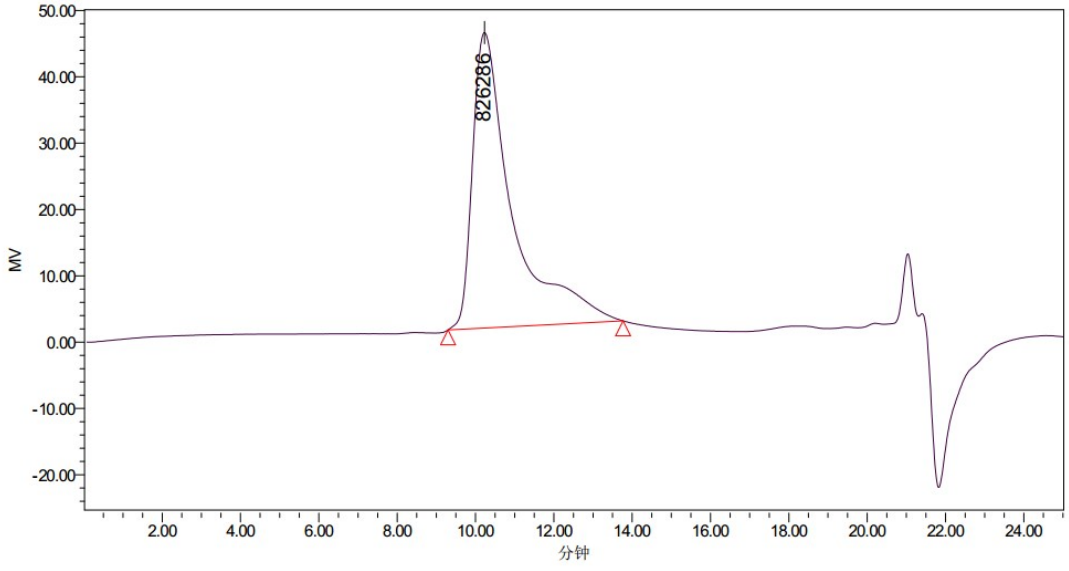
Figure S68. GPC curve of poly(D-IMCI-*co*-ITPB) obtained by complex **1d**/PPh_3 in Table 2, entry 14.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		9.609	9.609	9.609	641112	1275996	1803642	1737491	2024964	1.361674

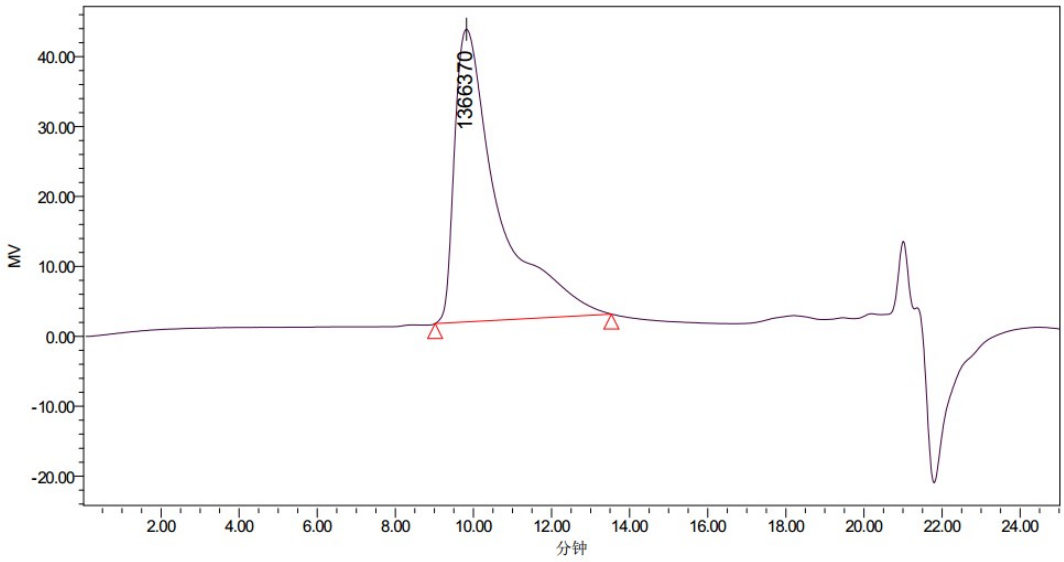
Figure S69. GPC curve of poly(D-IMCI-*co*-ITPB) obtained by complex **1d**/PPh_3 in Table 2, entry 15.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		10.230	10.230	10.230	336591	631895	826286	853609	1013582	1.350872

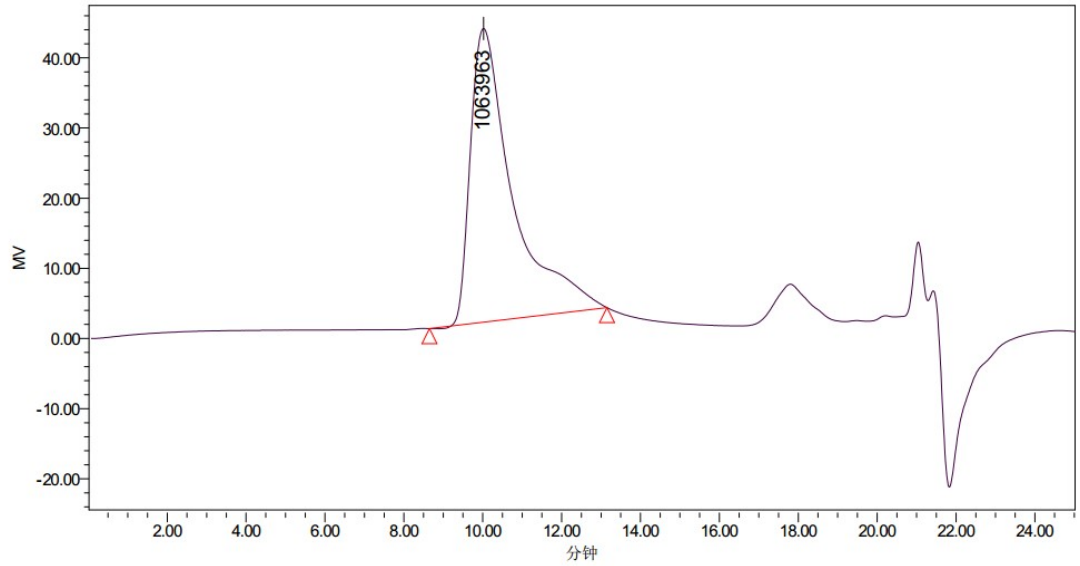
Figure S70. GPC curve of poly(L-IMCI-*co*-ITPB) obtained by complex **1d**/PPh_3 in Table 2, entry 16.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		9.822	9.822	9.822	452290	969937	1366370	1380426	1653577	1.423212

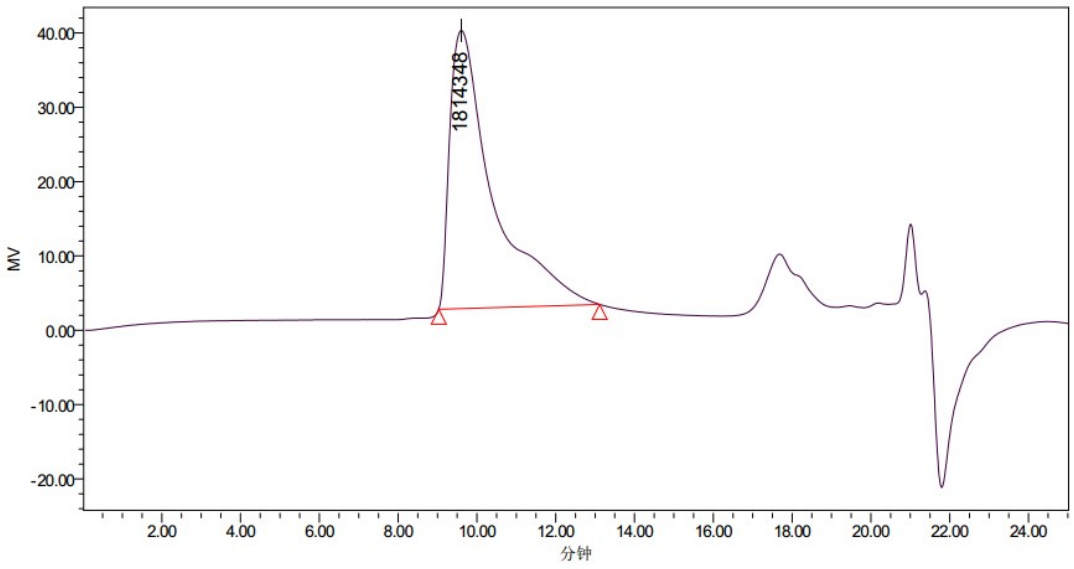
Figure S71. GPC curve of poly(L-IMCI-*co*-ITPB) obtained by complex **1d**/PPh_3 in Table 2, entry 17.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		10.021	10.021	10.021	454775	827711	1063963	1128287	1346932	1.363141

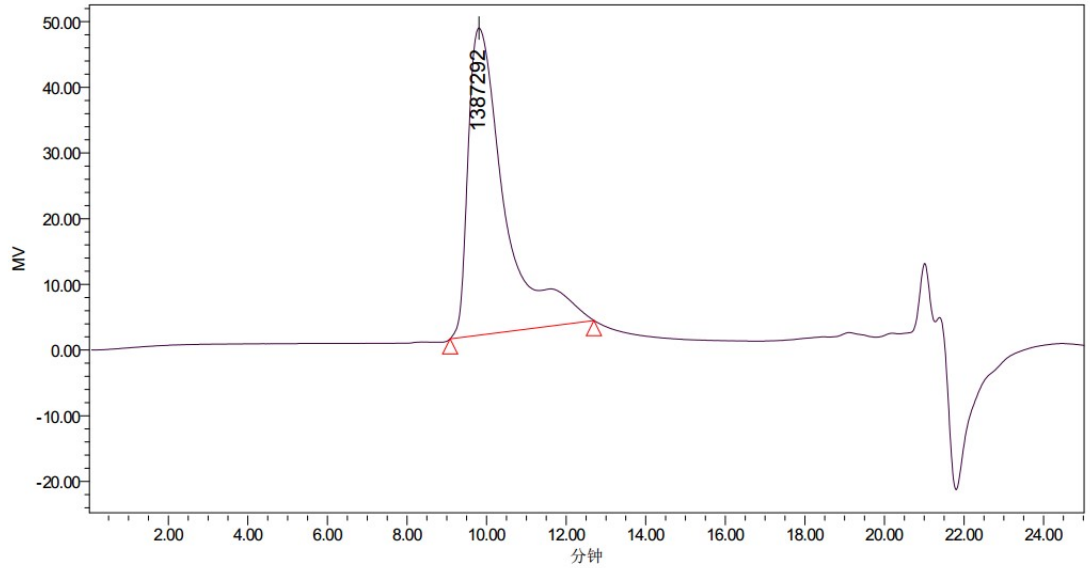
Figure S72. GPC curve of poly(L-IMCI-*co*-ITPB) obtained by complex **1d**/PPh_3 in Table 2, entry 18.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		9.605	9.605	9.605	591268	1266349	1814348	1794665	2124891	1.417196

Figure S73. GPC curve of poly(L-IMCI-*co*-ITPB) obtained by complex **1d**/PPh_3 in Table 2, entry 19.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		9.810	9.810	9.810	610498	1061323	1387292	1385558	1610306	1.305500

Figure S74. GPC curve of poly(L-IMCI-*co*-ITPB) obtained by complex **1d**/PPh_3 in Table 2, entry 20.

Calculation of the IMCI contents of the copolymers

The IMCI contents of poly(D-IMCI-*co*-ITPB)s and poly(L-IMCI-*co*-ITPB)s were calculated from the ^{1}H NMR spectra according to the following formula:

Mol IMCI % = {[23(IH3 + IH4)]/[19(IH1 + IH2 + IH3 + IH4)]} × 100

In which IH1 is the integration of the peak at 7.08 ppm which assigned to the aryl protons of ITPB units and the β-H of the aryl ring of IMCI units. IH2 is the integration of the peak at 5.82 ppm which assigned to the α-H of the aryl ring of IMCI units. IH3 is the integration of the peak at 4.88 ppm ascribed to the proton of the cyclohexyl carbon connected with the oxygen. IH4 is the integration of the peaks between 0.3 to 2.5 ppm which assigned to the rest protons of the cyclohexyl group as well as the substituted methyl and the isopropy.

The IMCI contents of poly(D-IMCI-*co*-IPI)s and poly(L-IMCI-*co*-IPI)s were calculated from the ^{1}H NMR spectra according to the following formula:

Mol IMCI % = {[5 × IH4 - 6(IH1 + IH2 + IH3)]/[12(IH1 + IH2 + IH3)]} × 100

In which IH1 is the integration of the peak at 7.08 ppm which assigned to the aryl protons of IPI units and the H of the aryl ring of IMCI units. IH2 is the integration of the peak at 5.82 ppm which assigned to the H of the aryl ring of IMCI units. IH3 is the integration of the peak at 4.88 ppm ascribed to the proton of the cyclohexyl carbon connected with the oxygen and the proton of the isopropyl carbon connected with the oxygen. IH4 is the integration of the peaks between 0.3 to 2.5 ppm which assigned to the rest protons of the cyclohexyl group as well as the substituted methyl and the isopropy and the rest protons of the isopropyl.

Calculation of the reactivity ratio:

Formula: Fineman-Ross plot:

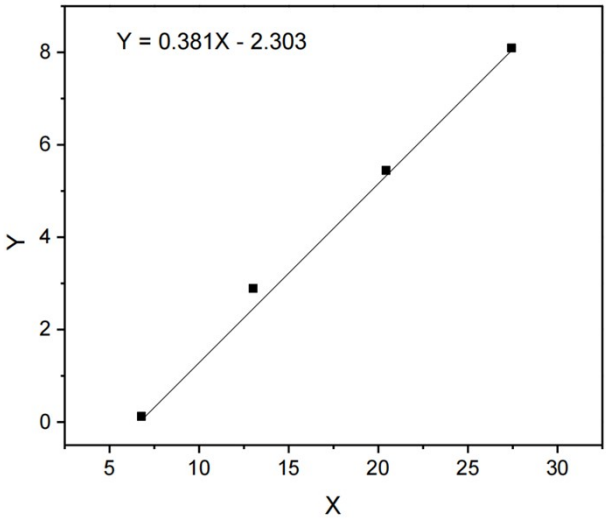
$$\frac{F}{f} * (f-1) = r_1 * \frac{F^2}{f} - r_2$$

F: IPI/D-IMCI feed ratio in the reaction

f: IPI/D-IMCI content in the copolymers

Copolymerization of IPI with D-IMCI

IPI (mmol)	D-IMCI (mmol)	IPI cont. (%)	D-IMCI cont. (%)	F	f	X	Y
0.368	0.138	51	49	2.667	1.174	6.072	0.396
0.736	0.138	69	31	5.333	2.030	13.995	2.704
1.104	0.138	76	24	8.000	2.846	22.432	5.183
1.472	0.138	81	19	10.667	4.556	24.942	8.320



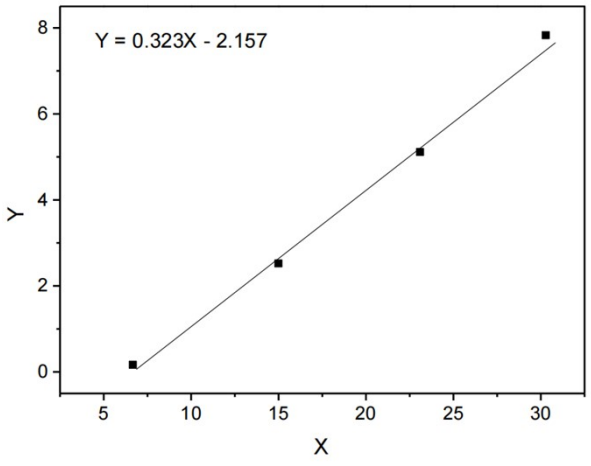
$$Y = 0.381 * X - 2.303$$

$$r_{IPI} = 0.381 \quad r_{D\text{-}IMCI} = 2.303$$

Figure S75. Experimental data of competitive aggregation rate between chiral isonitrile D-IMCI and non-chiral isonitrile IPI.

Copolymerization of ITPB with D-IMCI

IPTB (mmol)	D-IMCI (mmol)	IPTB cont. (%)	D-IMCI cont. (%)	F	f	X	Y
0.368	0.138	52	48	2.667	1.067	6.668	0.167
0.736	0.138	66	34	5.333	1.898	14.987	2.523
1.104	0.138	74	26	8.000	2.772	23.089	5.114
1.472	0.138	79	21	10.667	3.758	30.278	7.829



$$Y = 0.323 * X - 2.157$$

$$r_{DMPDIB} = 0.323 \quad r_{L\text{-}IMCI} = 2.157$$

Figure S76. Experimental data of competitive aggregation rate between chiral isonitrile D-IMCI and non-chiral isonitrile IPTB.

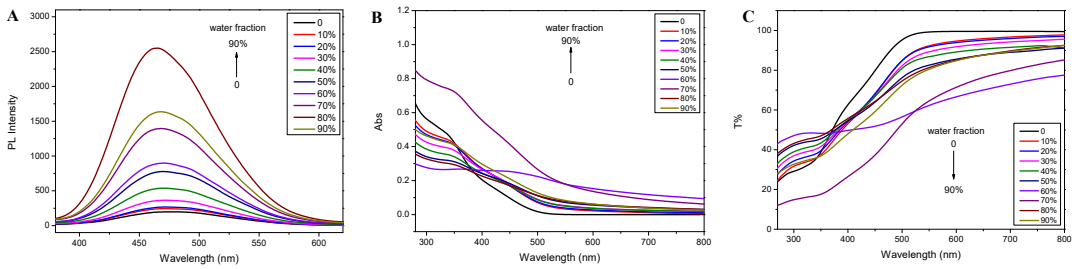


Figure S77. AIE nature characterization of ITPB monomer in THF/MeOH mixture. (A) Plots of fluorescence intensity vs water fraction in THF/MeOH mixture (0.01 mol of ITPB unit/mL, EX wavelength: 321 nm, EX slit: 5 nm, EM slit: 5 nm, 700 V). (B) The UV absorption spectra with the water fraction in THF/MeOH mixture ranging from 0 to 90%. (C) The UV/Vis transmittance spectra with the water fraction in THF/MeOH mixture ranging from 0 to 90%.

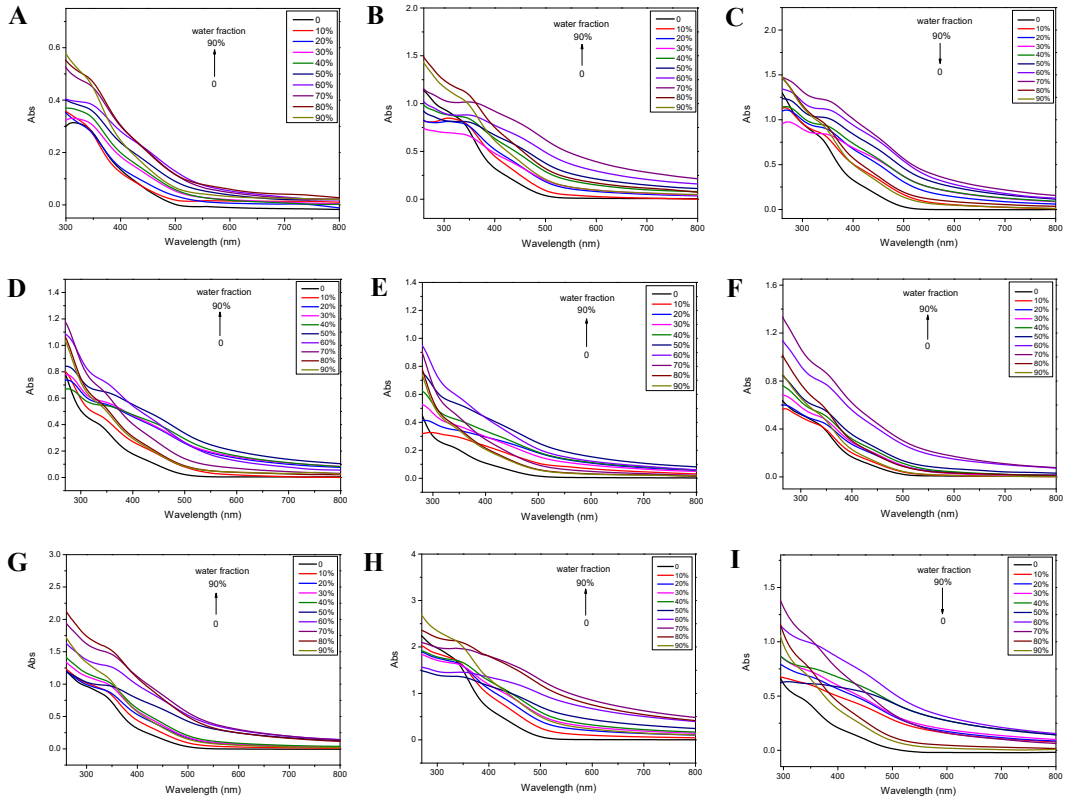


Figure S78. AIE nature characterization of (A) poly(D-IMCI-*co*-ITPB) (Table 2, entry 11), (B) poly(D-IMCI-*co*-ITPB) (Table 2, entry 12), (C) poly(D-IMCI-*co*-ITPB) (Table 2, entry 13), (D) poly(D-IMCI-*co*-ITPB) (Table 2, entry 14), (E) poly(D-IMCI-*co*-ITPB) (Table 2, entry 15), (F) poly(L-IMCI-*co*-ITPB) (Table 2, entry 16), (G) poly(L-IMCI-*co*-ITPB) (Table 2, entry 18), (H) poly(L-IMCI-*co*-ITPB) (Table 2, entry 19), (I) poly(L-IMCI-*co*-ITPB) (Table 2, entry 20) in THF/MeOH mixture. The UV absorption spectra with the water fraction in THF/MeOH mixture ranging from 0 to 90%.

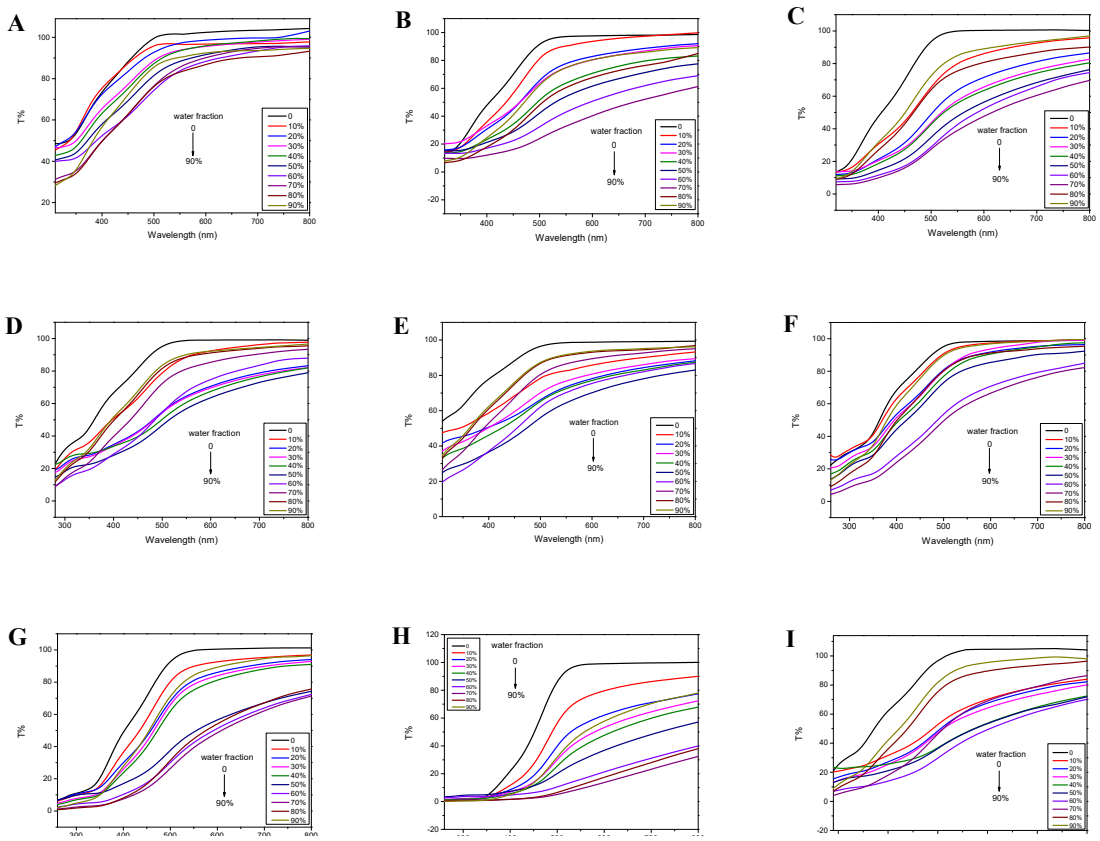


Figure S79. AIE nature characterization of (A) poly(D-IMCI-*co*-ITPB) (Table 2, entry 11), (B) poly(D-IMCI-*co*-ITPB) (Table 2, entry 12), (C) poly(D-IMCI-*co*-ITPB) (Table 2, entry 13), (D) poly(D-IMCI-*co*-ITPB) (Table 2, entry 14), (E) poly(D-IMCI-*co*-ITPB) (Table 2, entry 15), (F) poly(L-IMCI-*co*-ITPB) (Table 2, entry 16), (G) poly(L-IMCI-*co*-ITPB) (Table 2, entry 18), (H) poly(L-IMCI-*co*-ITPB) (Table 3, entry 19), (I) poly(L-IMCI-*co*-ITPB) (Table 3, entry 20) in THF/MeOH mixture. The UV/Vis transmittance spectra with the MeOH fraction in THF/MeOHmixture ranging from 0 to 90%.

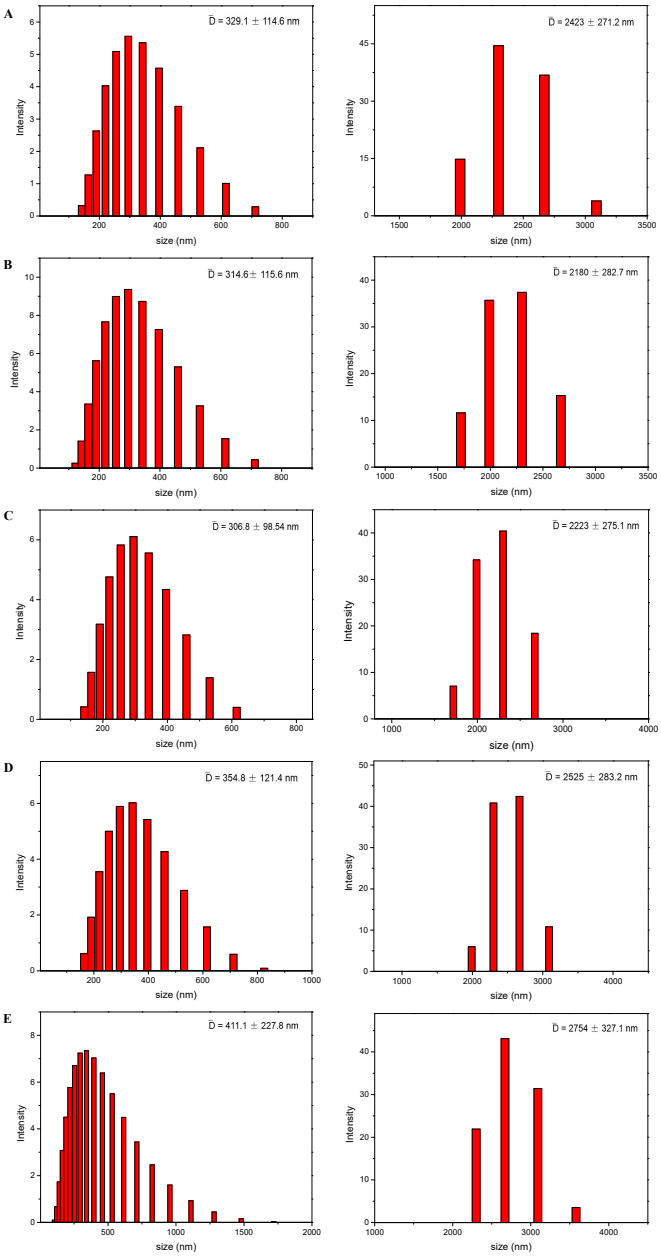


Figure S80. AIE nature characterization of poly(D-IMCI-*co*-ITPB)s in THF/MeOH mixture. (A) Dynamic light scattering measurement of poly(D-IMCI-*co*-ITPB) (Table 1, entry 11) at 0% MeOH fraction in THF-MeOH mixture (left side) and at 60% MeOH fraction in THF-MeOH mixture (right side). (B) Dynamic light scattering measurement of poly(D-IMCI-*co*-ITPB) (Table 1, entry 12) at 0% MeOH fraction in THF-MeOH mixture (left side) and at 60% MeOH fraction in THF-MeOH mixture (right side). (C) Dynamic light scattering measurement of poly(D-IMCI-*co*-ITPB) (Table 1, entry 13) at 0% MeOH fraction in THF-MeOH mixture (left side) and at 50% MeOH fraction in THF-MeOH mixture (right side). (D) Dynamic light scattering measurement of poly(D-IMCI-*co*-ITPB) (Table 1, entry 14) at 0% MeOH fraction in THF-MeOH mixture (left side) and at 60% MeOH fraction in THF-MeOH mixture (right side). (E) Dynamic light scattering measurement of poly(D-IMCI-*co*-ITPB) (Table 1, entry 15) at 0% MeOH fraction in THF-MeOH mixture (left side) and at 60% MeOH fraction in THF-MeOH mixture (right side).

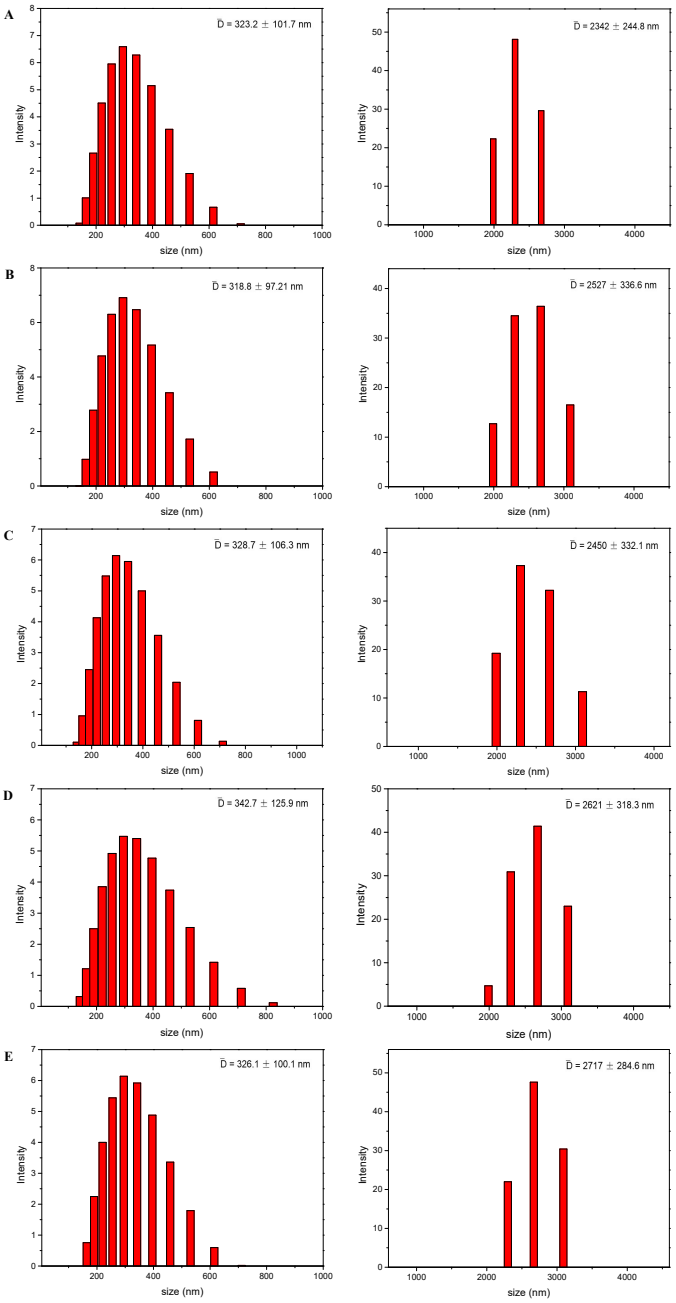


Figure S81. AIE nature characterization of poly(L-IMCI-*co*-ITPB)s in THF/MeOH mixture. (A) Dynamic light scattering measurement of poly(L-IMCI-*co*-ITPB) (Table 2, entry 16) at 0% MeOH fraction in THF-MeOH mixture (left side) and at 60% MeOH fraction in THF-MeOH mixture (right side). (B) Dynamic light scattering measurement of poly(L-IMCI-*co*-ITPB) (Table 2, entry 17) at 0% MeOH fraction in THF-MeOH mixture (left side) and at 60% MeOH fraction in THF-MeOH mixture (right side). (C) Dynamic light scattering measurement of poly(L-IMCI-*co*-ITPB) (Table 2, entry 18) at 0% MeOH fraction in THF-MeOH mixture (left side) and at 60% MeOH fraction in THF-MeOH mixture (right side). (D) Dynamic light scattering measurement of poly(L-IMCI-*co*-ITPB) (Table 2, entry 19) at 0% MeOH fraction in THF-MeOH mixture (left side) and at 60% MeOH fraction in THF-MeOH mixture (right side). (E) Dynamic light scattering measurement of poly(L-IMCI-*co*-ITPB) (Table 2, entry 20) at 0% MeOH fraction in THF-MeOH mixture (left side) and at 60% MeOH fraction in THF-MeOH mixture (right side).

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