

Electronic Supplementary Information (ESI)

Cationic Half-Sandwich Rare-Earth Metal Alkyl Species Catalyzed Polymerization and Copolymerization of Aryl Isocyanides Possessing Polar, Bulky, or Chiral Substituents

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EXPERIMENTAL SECTION

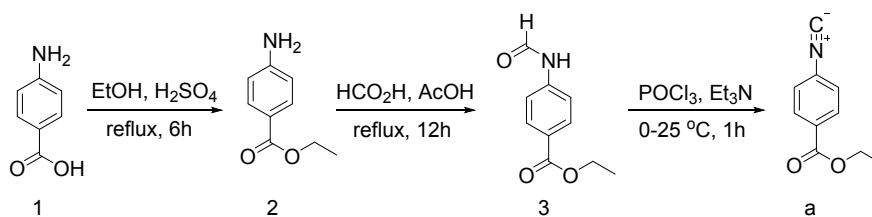
Materials.

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 O₂/H₂O Combi-Analyzer (Mbraun) to ensure both were always below 0.1 ppm. Anhydrous THF, hexane and toluene were purified by a solvent purification system (SPS-800, Mbraun), and dried over fresh Na chips in the glovebox. [Ph₃C][B(C₆F₅)₄], [PhMe₂NH][B(C₆F₅)₄], and B(C₆F₅)₃ were purchased from Tosoh Finechem Corporation and used without purification. LnCl₃ (Ln = Sc, Y, Lu) were purchased from Strem Chemicals, Inc. LiCH₂SiMe₃ (1.0 M solution in pentane) was purchased from Aldrich and used as received. The substituted cyclopentadienyl ligands and the isocyanide monomers were synthesized according to the literatures. 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.

Samples of rare earth metal complexes for NMR spectroscopic measurements were prepared in the glovebox by using J. Young valve NMR tubes. ¹H and ¹³C 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 °C by GPC on a Waters HPLC-515 apparatus, CHCl₃ 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 °C by GPC on a Waters HLC-8320GPC apparatus, THF was used as the eluent at a flow rate of 1 mL/min. The crystallographic data were collected on Rigaku Saturn 724 or Bruker Smart X-ray diffractometer. 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. Optical rotations were measured on a Kruss P8000-T polarimeter using a 0.5 cm cell with a Na 589 nm filter. High resolution mass spectra were collected on an Agilent 6520 Accurate-Mass Q-TOF LC/MS.

Scheme S1. Synthesis of 4-ethoxycarbonyl phenyl isocyanide (EPI)

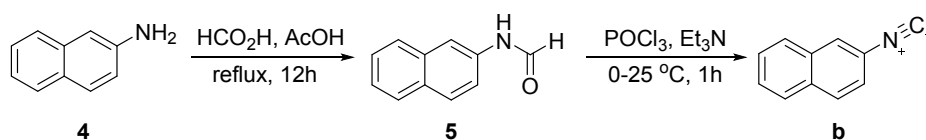


Synthesis of ethyl 4-aminobenzoate (2): To a solution of **1** (3.43 g, 25 mmol) in 100 mL of EtOH was slowly added 13.6 mL of aqueous con. H₂SO₄ (250 mmol) at room temperature. The mixture was refluxed for 6 h, cooled to room temperature, neutralized with a saturated K₂CO₃ aqueous solution and extracted with ethyl acetate (3 × 70 mL), the combined organic phases were washed with brine (2 × 50 mL), dried over Na₂SO₄ 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 (400 MHz, CDCl₃): 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 Na₂CO₃ (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, POCl₃ (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 Na₂CO₃ and stirred at room temperature for 0.5 h, the mixture was extracted with DCM (3 × 50 mL), the combined organic layers were washed with brine, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure, the residue was purified by column chromatography (neutral Al₂O₃, 12:1 hexane to ethyl acetate, v/v) to afford the desired compound **a** as a brown solid (3.13 g, 82% yield). ¹H NMR (400 MHz, CDCl₃): 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); ¹³C NMR (100 MHz, CDCl₃): δ 14.33, 61.66, 126.48, 129.94 (t), 130.88, 131.38, 165.06, 167.10.

Scheme S2. Synthesis of 2-naphthyl Isocyanide (NI)

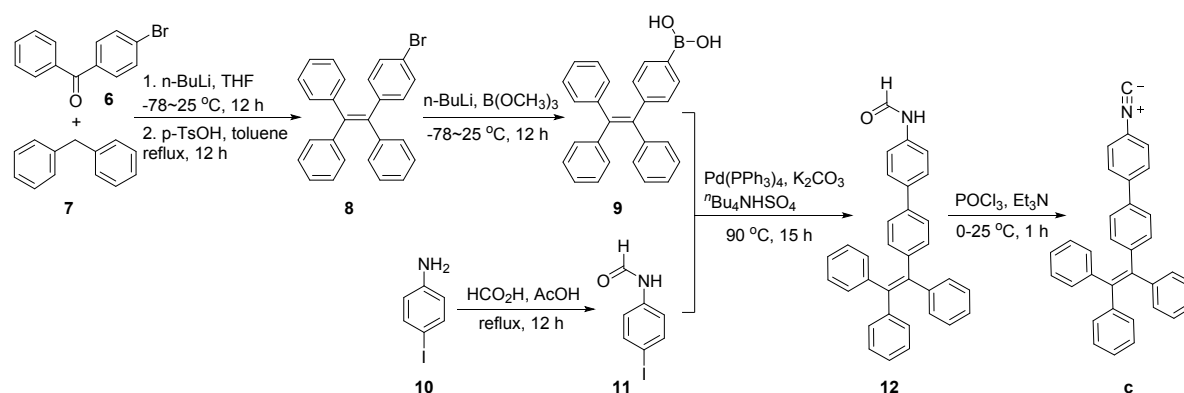


Synthesis of N-(naphthalen-2-yl)formamide (5): compound **4** (5 g, 34.92 mmol) was dissolved in a mixture solvents of formic acid (50 mL) and acetic acid (10 mL), the resulting mixture was refluxed overnight. After the reaction mixture was cooled to room temperature, the solvents were removed by evaporation. The residue was dissolved in CH₂Cl₂ (200 mL) and washed with saturated aqueous Na₂CO₃

(2 × 50 mL), the separated organic phase was dried over anhydrous Na₂SO₄, 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). ¹H NMR (400 MHz, [D₆]DMSO): 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, POCl₃ (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 Na₂CO₃ and stirred at room temperature for 0.5 h, the mixture was extracted with DCM (3 × 70 mL), the combined organic layers were washed with brine, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure, the residue was purified by column chromatography (neutral Al₂O₃, 12:1 hexane to ethyl acetate, v/v) to afford the desired compound **b** as a white solid (3.81 g, 86% yield). ¹H NMR (400 MHz, CDCl₃): 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); ¹³C NMR (100 MHz, CDCl₃): δ 123.34, 123.88 (t), 125.79, 127.61, 127.77, 127.96, 127.99, 129.72, 132.74, 132.86, 164.31 (t).

Scheme S3. Synthesis of 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 warm to room temperature and stirred for 10 h. Then the reaction mixture was quenched with an aqueous solution of ammonium chloride, extracted with CH₂Cl₂ (3 × 100 mL), the combined organic layers were dried over anhydrous Na₂SO₄ 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). ¹H NMR (400 MHz, CDCl₃): δ 6.89 (d, *J* = 8.2 Hz, 2H), 7.08 (m, 15H), 7.22 (d, *J* = 8.2 Hz, 2H).

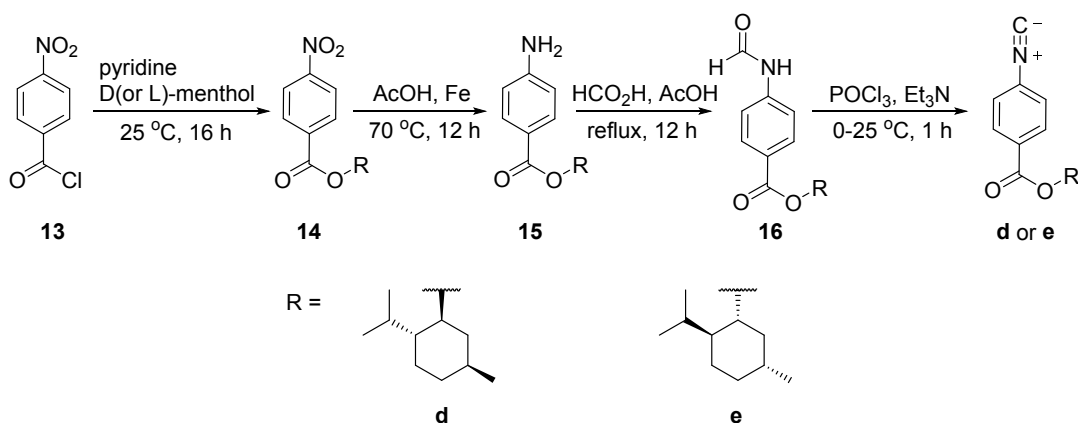
Synthesis of (4-(1,2,2-triphenylvinyl)phenyl)boronic acid (9): Under nitrogen atmosphere, compound **8** (2 g, 4.86 mmol) was dissolved in 20 mL of dry THF, after the solution was cooled to -78 °C, n-BuLi (2.43 mL, 2.4 M in hexane) was added dropwise and the mixture was stirred at -78 °C for 30 min. 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 Na₂SO₄ 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 **5**, 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(PPh₃)₄ (386 mg, 0.33 mmol), K₂CO₃ (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 Na₂SO₄ 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). ¹H NMR (400 MHz, CDCl₃): 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 **b**. (light green solid, 79% yield). ¹H NMR (400 MHz, CDCl₃): 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 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): 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 (d), 144.02, 164.69.

Scheme S4. Synthesis of (1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (D-IMCI) and (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (L-IMCI)



Synthesis of (1*S*,2*R*,5*S*)-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 dichloromethane (30 mL) and washed with 1 N HCl, saturated NaHCO₃ aqueous solution and brine, the separated organic layer was dried over anhydrous Na₂SO₄ 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) ¹H NMR (400 MHz, CDCl₃): 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 (1*S*,2*R*,5*S*)-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) ¹H NMR (400 MHz, CDCl₃): 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 (1*S*,2*R*,5*S*)-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 Na₂CO₃ (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 (1*S*,2*R*,5*S*)-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, POCl₃ (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 Na₂CO₃ and stirred at room temperature for 0.5 h, the mixture was extracted with DCM (3 × 20 mL), the combined organic layers were washed with brine, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure, the residue was purified by column chromatography (neutral Al₂O₃, 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) ¹H NMR (400 MHz, CDCl₃): 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); ¹³C NMR (100 MHz, CDCl₃): 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 (t), 130.90, 131.74, 164.58, 167.05.

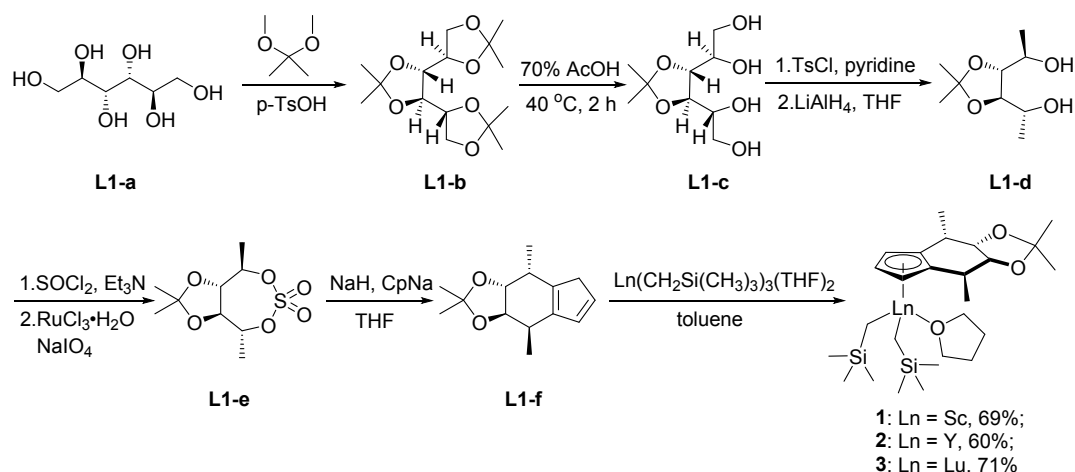
The synthesis of (*1R,2S,5R*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (**e**) was the same with that of (*1S,2R,5S*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (**d**).

Synthesis of (*1R,2S,5R*)-2-isopropyl-5-methylcyclohexyl 4-nitrobenzoate (14e): (yellow solid, 83% yield). ¹H NMR (400 MHz, CDCl₃): 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). ¹H NMR (400 MHz, [D₆]DMSO): 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 (e): (black syrup, 80% yield). ¹H NMR (400 MHz, CDCl₃): 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); ¹³C NMR (100 MHz, CDCl₃): 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 S5. Synthesis of chiral Cp* rare-earth metal dialkyl complexes 1-3



Synthesis of (4*R*,4'*R*,4''*R*,5'*R*)-2,2,2',2'',2''-hexamethyl-4,4':5',4''-ter(1,3-dioxolane) (L₁-b): To a suspension of (2*R*,3*R*,4*S*,5*S*)-hexane-1,2,3,4,5,6-hexaol (1.80 g, 9.88 mmol) in 2,2-dimethoxypropane (20 mL) was added *p*-Toluenesulfonic acid monohydrate (0.12 g, 0.698 mmol), the reaction mixture was stirred at room temperature for 5h, then neutralized with Et₃N (0.13 g, 1.29 mmol), the reaction mixture was concentrated under reduced pressure, the resulting off-white solid was dissolved with dichloromethane (35 mL) and washed with water (2 × 10 mL), the organic layer was separated and dried over anhydrous Na₂SO₄, concentrated and the resulting solid was recrystallized from hexane to afford a white solid (2.60 g, 87% yield). ¹H NMR (400 MHz, CDCl₃): δ 1.34 (s, 6H), 1.37 (s, 6H), 1.41 (s, 6H), 3.95 (m, 4H), 4.06 (dd, *J* = 6.8, 8.0 Hz, 2H), 4.17 (dd, *J* = 5.6, 6.0 Hz, 2H).

Synthesis of (1*R*,1'*R*)-1,1'-((4*R*,5*R*)-2,2-dimethyl-1,3-dioxolane-4,5-diyl)bis(ethane-1,2-diol) (L₁-c): Complex L₁-b (2.6 g, 8.60 mmol) was added into 70% aqueous acetic acid (30 mL), the reaction mixture was stirred at 40 °C for 2h, then concentrated under reduced pressure, the resulting solid was recrystallized from acetone to afford a white solid (1.35 g, 71% yield). ¹H NMR (400 MHz, CDCl₃): δ 1.28 (s, 6H), 3.34-3.38 (m, 1H), 3.45-3.49 (m, 2H), 3.51-3.57 (m, 3H), 3.84-3.88 (m, 2H), 4.45 (t, *J* = 6.0 Hz, 2H), 5.06 (d, *J* = 4.8 Hz, 2H).

Synthesis of (1*R*,1'*R*)-1,1'-((4*R*,5*R*)-2,2-dimethyl-1,3-dioxolane-4,5-diyl)bis(ethan-1-ol) (L₁-d): Under nitrogen atmosphere, a solution of complex L₁-c (1.35 g, 6.07 mmol) in dry pyridine (20 mL) was cooled to -5 °C, then 4-toluene sulfonyl chloride (2.61 g, 13.7 mmol) was added, the reaction mixture was stirred at 0 °C for 4h, 1.5 mL cold water was added and the reaction mixture was concentrated under reduced pressure. The residue was dissolved with dichloromethane (50 mL) and washed with water (3 × 20 mL), the organic layer was separated and dried over anhydrous Na₂SO₄, concentrated and the residue was dissolved in dry THF (30 mL), after the solution was cooled to 0 °C, LiAlH₄ (546 mg, 14.4 mmol) was added in portions, the resulting mixture was stirred at room temperature for 8h. Then 2 mL of water was added dropwise and the mixture was filtered, the filter cake was washed with ethyl acetate (150 mL), the organic phase was dried over anhydrous Na₂SO₄ and concentrated, the residue was purified by column chromatography (silical gel, 3:1 hexane to ethyl acetate, v/v) to afford a white solid (694 mg, 60% yield for two steps). ¹H NMR (400 MHz, CDCl₃): δ 1.29 (d, *J* = 6.0 Hz, 6H), 1.36 (s, 6H), 3.59 (m, 2H), 3.75 (m, 2H), 3.81 (s, 2H).

Synthesis of (3*aS*,4*R*,8*R*,8*aS*)-2,2,4,8-tetramethyltetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxathiepine 6,6-dioxide (L₁-e): Under nitrogen atmosphere, a solution of complex L₁-d (694 mg, 3.64 mmol) and

triethylamine (736 mg, 7.28 mmol) in dry dichloromethane (10 mL) was cooled to 0 °C, then a solution of sulfoxide chloride (520 mg, 4.37 mmol) in dry dichloromethane (3 mL) was added dropwise, the resulting mixture was stirred at 0 °C for 1h. The reaction mixture was quenched with brine (10 mL), the separated aqueous layer was extracted with dichloromethane (3 × 20 mL), the combined organic layers were dried over anhydrous Na₂SO₄, concentrated and the residue was dissolved in a mixture solvents of CCl₄ (8 mL), acetonitrile (8 mL) and water (12 mL), after the mixture was cooled to 0 °C RuCl₃H₂O (11 mg) and NaIO₄ (935 mg, 4.37 mmol) were added, the resulting mixture was stirred at 0 °C for 30 min. Then brine (20 mL) was added, and the separated aqueous layer was extracted with dichloromethane (3 × 20 mL), the combined organic layers were dried over anhydrous Na₂SO₄, concentrated and the residue was purified by column chromatography (silical gel, 9:1 hexane to ethyl acetate, v/v) to afford a white solid (672 mg, 73% yield for two steps). ¹H NMR (400 MHz, CDCl₃): δ 1.42 (s, 6H), 1.58 (d, *J* = 6.8 Hz, 6H), 4.02 (m, 2H), 4.43 (m, 2H).

Synthesis of (3*aR*,4*R*,8*R*,8*aR*)-2,2,4,8-tetramethyl-3*a*,5,8,8*a*-tetrahydro-4*H*-indeno[5,6-*d*][1,3]dioxole (L₁-f): Under nitrogen atmosphere, a suspension of sodium hydride (141 mg, 5.88 mmol) in dry THF (10 mL) was cooled to -78 °C, then a solution of sodium cyclopentadienide (246 mg, 2.80 mmol) in dry THF (5 mL) was added dropwise, the reaction mixture was stirred at -78 °C for 10 min, a solution of complex L₁-e (672 mg, 2.66 mmol) in dry THF (5 mL) was added dropwise, after the addition was completed, the reaction mixture was refluxed at 100 °C for 7h. The reaction mixture was cooled to -78 °C and quenched with water (30 mL), the resulting mixture was extracted with dichloromethane (3 × 30 mL), the combined organic layers were dried over anhydrous Na₂SO₄, concentrated and the residue was purified by column chromatography (silical gel, 5:1 hexane to dichloromethane, v/v) to afford a light yellow solid (176 mg, 30% yield). ¹H NMR (400 MHz, CDCl₃): δ 1.18 (d, *J* = 7.2 Hz, 3H), 1.26 (d, *J* = 7.2 Hz, 3H), 1.56 (d, *J* = 2.4 Hz, 6H), 2.47-2.53 (m, 1H), 2.81-2.97 (m, 3H), 4.12 (m, 2H), 6.29 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 13.52, 14.81, 27.16, 32.55, 33.39, 41.75, 74.84, 74.96, 109.77, 132.72, 133.11, 141.75, 142.20; [α]_D²⁰ = -218 (c = 0.3 g/100 mL, CH₂Cl₂).

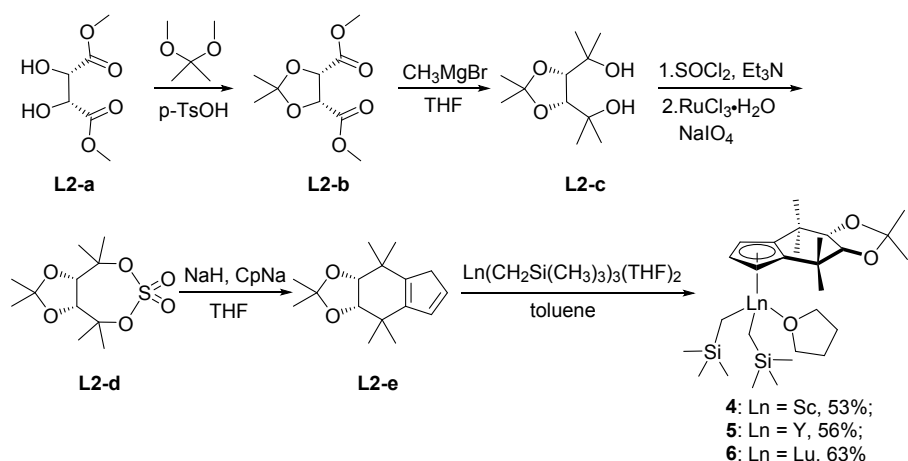
Synthesis of the Sc complex (1): To a solution of Sc(CH₂SiMe₃)₃(THF)₂ (451 mg, 1.0 mmol) in toluene (3 mL) was added a toluene (3 mL) solution of complex L₁-f (220 mg, 1.0 mmol), the mixture was stirred at room temperature for 24h, then removed the solvent under reduced pressure, the residue was recrystallized from a mixture solvents of toluene and hexane (toluene/hexane = 3/1, v/v) at -30 °C to afford complex **1** as a light yellow solid (352 mg, 69% yield). ¹H NMR (400 MHz, C₆D₆): δ -0.35 (s, 1H, CH₂Si(CH₃)₃), -0.14 (s, 3H, CH₂Si(CH₃)₃), 0.28 (s, 18H, CH₂Si(CH₃)₃), 1.11 (br, 4H, THF-β-CH₂), 1.38 (m, 3H, CH₃), 1.48 (m, 6H, CH₃), 1.53 (s, 3H, CH₃), 3.38 (m, 1H, CH(CH₃)), 3.51 (t, *J* = 6.8 Hz, 4H, THF-α-CH₂), 3.65 (m, 1H, CH(CH₃)), 4.15 (m, 1H, CHO-), 4.66 (m, 1H, CHO-), 5.82 (t, *J* = 2.8 Hz, 1H, CpH), 6.04 (t, *J* = 2.8 Hz, 1H, CpH), 6.18 (t, *J* = 2.8 Hz, 1H, CpH); ¹³C NMR (100 MHz, C₆D₆): δ 4.05, 16.28, 17.13, 24.83, 27.45, 27.47, 32.78, 33.21, 72.21, 75.13, 75.45, 108.57, 110.03, 110.33, 112.66, 129.16, 130.58.

Synthesis of the Y complex (2): To a solution of Y(CH₂SiMe₃)₃(THF)₂ (495 mg, 1.0 mmol) in toluene (3 mL) was added a toluene (3 mL) solution of complex L₁-f (220 mg, 1.0 mmol), the mixture was stirred at room temperature for 24h, then removed the solvent 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 **2** as a light yellow solid (332 mg, 60% yield). ¹H NMR (400 MHz, C₆D₆): δ -0.64 (dd, *J* = 2.8, 11.2 Hz, 2H, CH₂Si(CH₃)₃), -0.51 (dd, *J* = 2.8, 11.2 Hz, 2H, CH₂Si(CH₃)₃), 0.29 (s, 18H, CH₂Si(CH₃)₃), 1.23 (br, 4H,

THF- β -CH₂), 1.37 (d, J = 7.2 Hz, 3H, CH₃), 1.44 (d, J = 7.2 Hz, 3H, CH₃), 1.47 (s, 3H, CH₃), 1.53 (s, 3H, CH₃), 3.38 (m, 1H, $\underline{\text{CH}}(\text{CH}_3)$), 3.43 (br, 4H, THF- α -CH₂), 3.61 (m, 1H, $\underline{\text{CH}}(\text{CH}_3)$), 4.16 (dd, J = 6.4, 10.0 Hz, 1H, CHO-), 4.62 (dd, J = 6.4, 10.0 Hz, 1H, CHO-), 5.89 (t, J = 2.8 Hz, 1H, CpH), 6.09 (t, J = 2.8 Hz, 1H, CpH), 6.13 (t, J = 2.8 Hz, 1H, CpH); ¹³C NMR (100 MHz, C₆D₆): δ 4.7, 5.3, 17.3, 25.4, 27.7, 27.8, 27.9, 33.0, 33.3, 75.8, 75.9, 107.2, 108.5, 109.6, 110.3, 113.0, 130.8.

Synthesis of the Lu complex (3): To a solution of Lu(CH₂SiMe₃)₃(THF)₂ (581 mg, 1.0 mmol) in toluene (3 mL) was added a toluene (3 mL) solution of complex L₁-f (220 mg, 1.0 mmol), the mixture was stirred at room temperature for 24h, then removed the solvent 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 **3** as a white solid (454 mg, 71% yield). ¹H NMR (400 MHz, C₆D₆): δ -0.82 (d, J = 11.6 Hz, 2H, $\underline{\text{CH}}_2\text{Si}(\text{CH}_3)_3$), -0.70 (d, J = 11.6 Hz, 2H, $\underline{\text{CH}}_2\text{Si}(\text{CH}_3)_3$), 0.30 (s, 18H, CH₂Si($\underline{\text{CH}}_3$)₃), 1.08 (t, J = 6.0 Hz, 4H, THF- β -CH₂), 1.39 (d, J = 6.8 Hz, 3H, CH₃), 1.45 (d, J = 7.2 Hz, 3H, CH₃), 1.48 (s, 3H, CH₃), 1.54 (s, 3H, CH₃), 3.40 (br, 4H, THF- α -CH₂), 3.41 (m, 1H, $\underline{\text{CH}}(\text{CH}_3)$), 3.63 (m, 1H, $\underline{\text{CH}}(\text{CH}_3)$), 4.16 (dd, J = 6.4, 10.4 Hz, 1H, CHO-), 4.65 (dd, J = 6.4, 10.4 Hz, CHO-), 5.82 (t, J = 2.8 Hz, 1H, CpH), 6.05 (t, J = 2.8 Hz, 1H, CpH), 6.09 (t, J = 2.8 Hz, 1H, CpH); ¹³C NMR (100 MHz, C₆D₆): δ 4.51, 16.75, 17.38, 24.86, 27.43, 27.49, 32.50, 33.10, 39.76, 71.42, 75.26, 75.38, 107.52, 108.26, 109.96, 111.98, 128.50, 128.58.

Scheme S6. Synthesis of chiral Cp* rare-earth metal dialkyl complexes 4-6



Synthesis of dimethyl ((4*R*,5*S*)-2,2-dimethyl-1,3-dioxolane-4,5-dicarboxylate (L₂-b): To a solution of complex L₂-a (5.0 g, 28.1 mmol) in dry methanol (3 mL) were added 2,2-dimethoxypropane (7.5 mL, 61.0 mmol) and p-Toluenesulfonic acid monohydrate (45 mg, 0.26 mmol), the resulting mixture was refluxed for 1h, then cyclohexane (10 mL) was added and the mixture was concentrated to remove the solvents under reduced pressure. Then 2,2-dimethoxypropane (2 mL, 16.3 mmol) and cyclohexane (3 mL) were added, the resulting mixture was refluxed for 1h, after the reaction mixture was cooled to room temperature, Et₃N (0.2 mL, 1.38 mmol) was added and the mixture was concentrated under reduced pressure, the residue was distilled under reduced pressure to afford a light yellow oil (5.9 g, 96% yield). ¹H NMR (400 MHz, CDCl₃): δ 1.46 (s, 6H), 3.80 (s, 6H), 4.78 (s, 2H).

Synthesis of 2,2'-((4*R*,5*S*)-2,2-dimethyl-1,3-dioxolane-4,5-diyl)bis(propan-2-ol) (L₂-c): Under nitrogen atmosphere, a solution of MeMgBr (16.1 g, 135 mmol) in dry THF (80 mL) was cooled to 0 °C, then a solution of complex L₂-b (5.9 g, 27.0 mmol) in dry THF (15 mL) was added dropwise, the resulting mixture

was refluxed for 2h, then cooled to room temperature. An aqueous saturated NH_4Cl was added slowly, and the mixture was extracted with ethyl acetate ($3 \times 50 \text{ mL}$), 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 (silical gel, 4:1 hexane to ethyl acetate, v/v) to afford a white solid (5.6 g, 95% yield). ^1H NMR (400 MHz, CDCl_3): δ 1.25 (s, 6H), 1.30 (s, 6H), 1.36 (s, 6H), 3.72 (s, 2H), 3.90 (br, 2H).

Synthesis of (3*aR*,8*aS*)-2,2,4,4,8,8-hexamethyltetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxathi-epine 6,6-dioxide (L₂-d**):** Under nitrogen atmosphere, a solution of complex **L₂-c** (5.6 g, 25.6 mmol) and triethylamine (5.18 g, 51.2 mmol) in dry dichloromethane (100 mL) was cooled to 0 °C, then a solution of sulfoxide chloride (3.66 g, 30.7 mmol) in dry dichloromethane (30 mL) was added dropwise, the resulting mixture was stirred at 0 °C for 1h. The reaction mixture was quenched with brine (150 mL), the separated aqueous layer was extracted with dichloromethane ($3 \times 100 \text{ mL}$), the combined organic layers were dried over anhydrous Na_2SO_4 , concentrated and the residue was dissolved in a mixture solvents of CCl_4 (50 mL), acetonitrile (50 mL) and water (130 mL), after the mixture was cooled to 0 °C $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (128 mg, 0.57 mmol) and NaIO_4 (6.83 g, 31.9 mmol) were added, the resulting mixture was stirred at 0 °C for 30 min. Then brine (100 mL) was added, and the separated aqueous layer was extracted with dichloromethane ($3 \times 150 \text{ mL}$), the combined organic layers were dried over anhydrous Na_2SO_4 , concentrated and the residue was purified by column chromatography (silical gel, 9:1 hexane to ethyl acetate, v/v) to afford a white solid (5.2 g, 73% yield for two steps). ^1H NMR (400 MHz, CDCl_3): δ 1.41 (s, 6H), 1.55 (s, 6H), 1.64 (s, 6H), 4.32 (s, 2H).

Synthesis of (3*aR*,8*aS*)-2,2,4,4,8,8-hexamethyl-3*a*,5,8,8*a*-tetrahydro-4H-indeno[5,6-*d*][1,3]-dioxole (L₂-e**):** Under nitrogen atmosphere, a suspension of sodium hydride (980 mg, 40.8 mmol) in dry THF (60 mL) was cooled to -78 °C, then a solution of sodium cyclopentadienide (1.72 g, 19.5 mmol) in dry THF (50 mL) was added dropwise, the reaction mixture was stirred at -78 °C for 10 min, a solution of complex **L₂-d** (5.2 g, 18.5 mmol) in dry THF (50 mL) was added dropwise, after the addition was completed, the reaction mixture was refluxed at 100 °C for 7h. The reaction mixture was cooled to -78 °C and quenched with water (180 mL), the resulting mixture was extracted with dichloromethane ($3 \times 100 \text{ mL}$), the combined organic layers were dried over anhydrous Na_2SO_4 , concentrated and the residue was purified by column chromatography (silical gel, 5:1 hexane to dichloromethane, v/v) to afford a light yellow solid (1.16 g, 25% yield). ^1H NMR (400 MHz, CDCl_3): δ 1.13 (d, $J = 6.0 \text{ Hz}$, 6H), 1.25 (d, $J = 4.0 \text{ Hz}$, 6H), 1.46 (s, 6H), 2.88 (d, $J = 7.6 \text{ Hz}$, 2H), 3.68 (dd, $J = 5.6, 10 \text{ Hz}$, 2H), 6.32 (dd, $J = 0.4, 5.2 \text{ Hz}$, 1H), 6.40 (dd, $J = 0.4, 5.2 \text{ Hz}$, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 21.60, 22.77, 26.97, 27.26, 27.28, 28.24, 36.18, 37.12, 38.63, 82.02, 82.08, 109.90, 130.70, 132.53, 144.83, 145.21; $[\alpha]_{\text{D}}^{20} = 68.8$ ($c = 0.3 \text{ g}/100 \text{ mL}$, CH_2Cl_2).

Synthesis of the Sc complex (4): To a solution of $\text{Sc}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ (451 mg, 1.0 mmol) in toluene (3 mL) was added a toluene (3 mL) solution of complex **L₁-f** (248 mg, 1.0 mmol), the mixture was stirred at room temperature for 24h, then removed the solvent 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 **4** as a white solid (285 mg, 53% yield). ^1H NMR (400 MHz, C_6D_6): δ -0.37 (d, $J = 11.2 \text{ Hz}$, 1H, $\text{CH}_2\text{Si}(\text{CH}_3)_3$), -0.15 (d, $J = 10.8 \text{ Hz}$, 1H, $\text{CH}_2\text{Si}(\text{CH}_3)_3$), -0.06 (d, $J = 11.2 \text{ Hz}$, 1H, $\text{CH}_2\text{Si}(\text{CH}_3)_3$), 0.00 (d, $J = 10.0 \text{ Hz}$, 1H, $\text{CH}_2\text{Si}(\text{CH}_3)_3$), 0.26 (s, 18H, $\text{CH}_2\text{Si}(\text{CH}_3)_3$), 1.16 (br, 4H, THF- β - CH_2), 1.36 (s, 3H, $\text{C}(\text{CH}_3)_2$), 1.48 (s, 3H, $\text{C}(\text{CH}_3)_2$), 1.53 (s, 6H, $\text{C}(\text{CH}_3)_2$), 1.65 (d, $J = 3.2 \text{ Hz}$, 6H, $\text{C}(\text{CH}_3)_2$), 3.58 (br, 4H, THF- α - CH_2), 3.95 (d, $J = 10.0 \text{ Hz}$, 1H, OCH), 4.54 (d, $J = 10.0 \text{ Hz}$, 1H, OCH), 5.80 (t, $J = 2.8 \text{ Hz}$, 1H, CpH), 5.98 (t, $J = 3.2$

Hz, 1H, CpH), 6.36 (t, J = 2.8 Hz, 1H, CpH); ^{13}C NMR (100 MHz, C_6D_6): δ 3.97, 24.83, 24.96, 26.08, 27.52, 27.58, 28.25, 30.73, 36.86, 37.37, 72.39, 81.48, 83.00, 105.86, 107.82, 110.06, 112.40, 133.74, 136.01.

Synthesis of the Y complex (5): To a solution of $\text{Y}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ (495 mg, 1.0 mmol) in toluene (3 mL) was added a toluene (3 mL) solution of complex **L₁-f** (248 mg, 1.0 mmol), the mixture was stirred at room temperature for 24h, then removed the solvent 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 **5** as a white solid (326 mg, 56% yield). ^1H NMR (400 MHz, C_6D_6): δ -0.61 (dd, J = 3.2, 11.2 Hz, 2H, $\text{CH}_2\text{Si}(\text{CH}_3)_3$), -0.48 (dd, J = 3.2, 11.2 Hz, 2H, $\text{CH}_2\text{Si}(\text{CH}_3)_3$), 0.28 (s, 18H, $\text{CH}_2\text{Si}(\text{CH}_3)_3$), 1.25 (br, 8H, THF- β -CH₂), 1.36 (s, 3H, C(CH₃)₂), 1.48 (s, 3H, C(CH₃)₂), 1.52 (s, 6H, C(CH₃)₂), 1.61 (s, 3H, C(CH₃)₂), 1.63 (s, 3H, C(CH₃)₂), 3.63 (br, 8H, THF- α -CH₂), 3.96 (d, J = 10.0 Hz, 1H, OCH), 4.42 (d, J = 10.0 Hz, 1H, OCH), 5.88 (t, J = 2.4 Hz, 1H, CpH), 6.11 (t, J = 3.2 Hz, 1H, CpH), 6.29 (t, J = 2.4 Hz, 1H, CpH); ^{13}C NMR (100 MHz, C_6D_6): δ 4.37, 24.88, 25.08, 25.70, 27.47, 27.62, 29.13, 30.19, 35.94, 36.38, 36.62, 37.16, 71.10, 81.92, 82.72, 105.11, 105.49, 110.09, 112.82, 132.91, 134.08.

Synthesis of the Lu complex (6): To a solution of $\text{Lu}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ (581 mg, 1.0 mmol) in toluene (3 mL) was added a toluene (3 mL) solution of complex **L₁-f** (248 mg, 1.0 mmol), the mixture was stirred at room temperature for 24h, then removed the solvent 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 **6** as a white solid (421 mg, 63% yield). ^1H NMR (400 MHz, C_6D_6): δ -0.78 (d, J = 11.2 Hz, 2H, $\text{CH}_2\text{Si}(\text{CH}_3)_3$), -0.63 (d, J = 11.6 Hz, 2H, $\text{CH}_2\text{Si}(\text{CH}_3)_3$), 0.30 (s, 18H, $\text{CH}_2\text{Si}(\text{CH}_3)_3$), 1.06 (t, J = 6.4 Hz, 4H, THF- β -CH₂), 1.41 (s, 3H, C(CH₃)₂), 1.49 (s, 3H, C(CH₃)₂), 1.55 (s, 6H, C(CH₃)₂), 1.65 (s, 3H, C(CH₃)₂), 1.68 (s, 3H, C(CH₃)₂), 3.45 (t, J = 6.4 Hz, 4H, THF- α -CH₂), 4.00 (d, J = 9.6 Hz, 1H, OCH), 4.53 (d, J = 9.6 Hz, 1H, OCH), 5.81 (t, J = 2.4 Hz, 1H, CpH), 6.03 (t, J = 2.8 Hz, 1H, CpH), 6.28 (t, J = 2.4 Hz, 1H, CpH); ^{13}C NMR (100 MHz, C_6D_6): δ 4.47, 24.77, 25.15, 25.99, 27.49, 27.60, 28.88, 30.52, 36.62, 37.19, 40.88, 71.93, 81.75, 82.90, 104.66, 105.60, 110.09, 112.08, 132.65, 134.24.

A typical procedure for the polymerization of EPI (Table 2, entry 6): In the glove box, a 50 mL round bottom flask was charged with a solution of compound **1** (5.2 mg, 10.2 μmol) in 1,1,2,2-tetrachloroethane (2 mL), then $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (7.8 mg, 8.46 μmol) was added, the resulting mixture was stirred at 25 °C for 5 min and then added to a solution of 4-ethoxycarbonyl phenyl isocyanide (150 mg, 0.851 mmol) in 1,1,2,2-tetrachloroethane (3 mL). The reaction mixture was stirred at 25 °C for 1 min, then the flask was taken out of the glove box and the reaction mixture was poured into methanol (100 mL) to precipitate the polymer product, the yellow polymer solid was collected by filtration, and dried in vacuo at 40 °C to a constant weight (140 mg, 93% yield). The product obtained is soluble thoroughly in CHCl_3 at 25 °C.

A typical procedure for the copolymerization of D-IMCI with ITPB (Table 3, entry 3): In the glove box, a 50 mL round bottom flask was charged with a solution of compound **1** (1.5 mg, 2.8 μmol) in 1,1,2,2-tetrachloroethane (2 mL), then $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (2.2 mg, 2.3 μmol) was added, the resulting mixture was stirred at 25 °C for 5 min, then a solution of (*1S,2R,5S*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (66 mg, 0.23 mmol) and 4-isocyno-4'-(1,2,2-triphenylvinyl)-1,1'-biphenyl (100 mg, 0.23 mmol) in 1,1,2,2-tetrachloroethane (3 mL) was added, the reaction mixture was stirred at 25 °C for 3 min, then the flask was taken out of the glove box and 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 (158 mg, 95% yield), The product obtained is soluble thoroughly in CHCl₃ and THF at 25 °C.

Calculation of the IMCI contents of the copolymers

The IMCI contents of the copolymers were calculated from the ¹H NMR spectra according to the following formula:

$$\text{Mol IMCI \%} = \{[23(I_{\text{H3}} + I_{\text{H4}})]/[19(I_{\text{H1}} + I_{\text{H2}} + I_{\text{H3}} + I_{\text{H4}})]\} \times 100$$

In which I_{H1} 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. I_{H2} is the integration of the peak at 5.82 ppm which assigned to the α-H of the aryl ring of IMCI units. I_{H3} is the integration of the peak at 4.88 ppm ascribed to the proton of the cyclohexyl carbon connected with the oxygen. I_{H4} 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 isopropyl.

Solvent separation experiments

3 mg of poly(D-IMCI) was added into 1.5 mL of toluene, the mixture was shaken for about 1 min and all of the solid dissolved in toluene completely. 3 mg of poly(ITPB) was added into 1.5 mL of toluene and exhibited poor solubility, after shaken for about 1 hour there was still some solid precipitated in the solution. Then 60 mg of the copolymer product (Table 3, entry 3) was added into 10 mL of toluene, the mixture was shaken for about 5 min and the solid dissolved in toluene completely.

Table S1. Homopolymerization of aryl isocyanide **a** catalyzed by the half-sandwich rare-earth metal dialkyl complex **1**/activator binary systems.^a

Entry	Comp. 1 (μmol)	A ^b (μmol)	[Mon.]/[Com.] ^c	Mon.	Solvent	Temp. (°C)	Time (min.)	Yield (%)	Act. ^d	M _n ^e (10 ⁴)	M _w /M _n ^e
1	1	A	100:1	a	PhCl	25	1	54	574	16.9	3.90
2	1	B	100:1	a	PhCl	25	180	21	1.22	13.0	3.20
3	1	C	100:1	a	PhCl	25	720	8	0.12	-	-

^a Conditions: 10.2 μmol of Ln complex, [Ln]/[activator] = 1.2:1, 5 mL of solvent. ^b Activator: **A** = [Ph₃C][B(C₆F₅)₄], **B** = [PhNHMe₂][B(C₆F₅)₄], **C** = B(C₆F₅)₃. ^c Molar ratio of monomer to complex. ^d Activity: kg of polymer mol_{Ln}⁻¹ h⁻¹. ^e Determined by GPC in CHCl₃ at 25 °C against polystyrene standard.

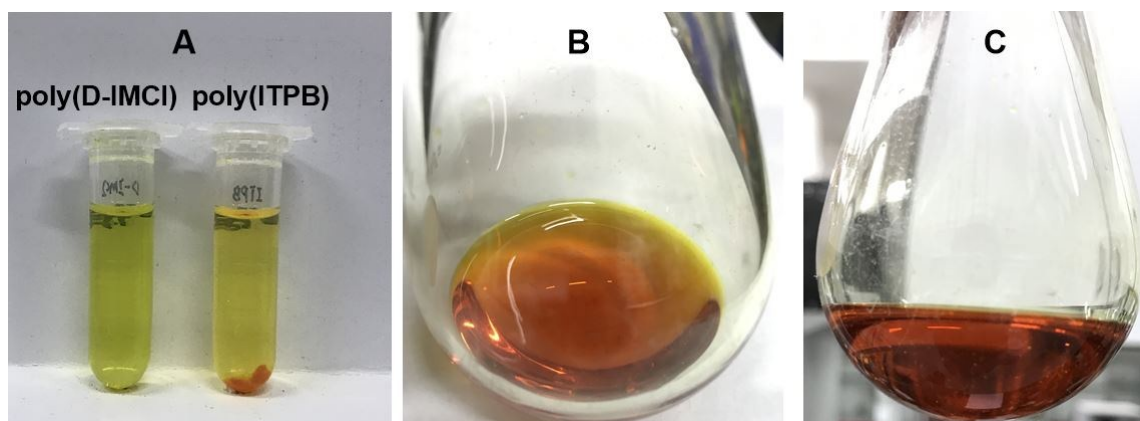


Figure S1. Photos of solubility of poly(D-IMCI) (A, left), poly(ITPB) (A, right) and polymer product (Table 3, entry 3) (B, C) in toluene.

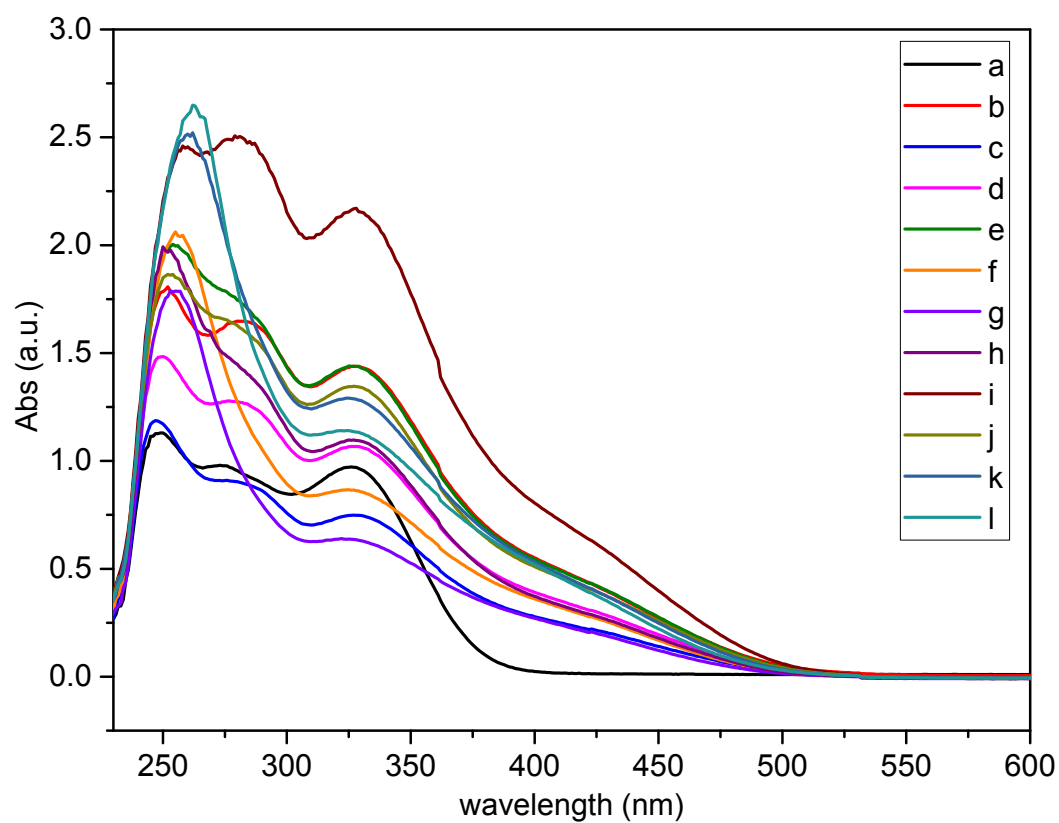


Figure S2. UV-vis absorption spectra of ITPB monomer (a), poly(ITPB) (b), poly(D-IMCI-co-ITPB)s (Table 3, entries 1-5) (c-g) and poly(L-IMCI-co-ITPB)s (Table 3, entries 6-10) (h-l) in THF.

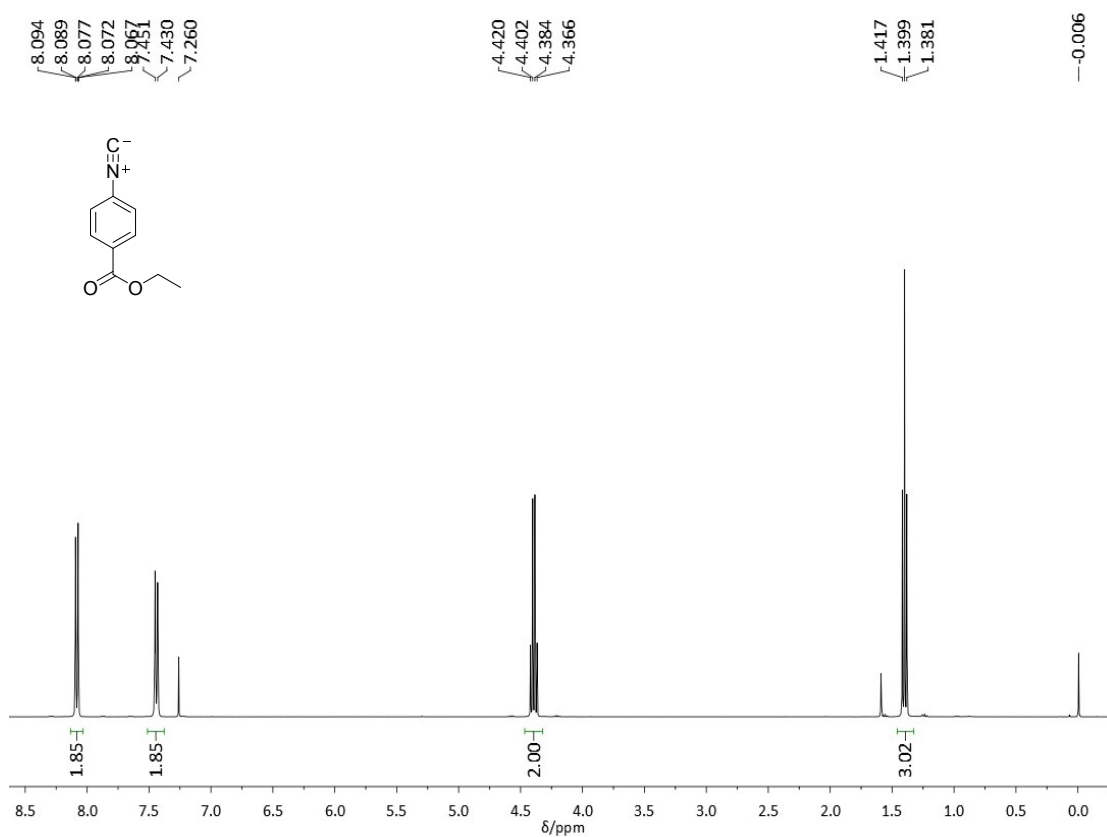


Figure S3. ¹H NMR spectrum of 4-ethoxycarbonyl phenyl isocyanide (**a**).

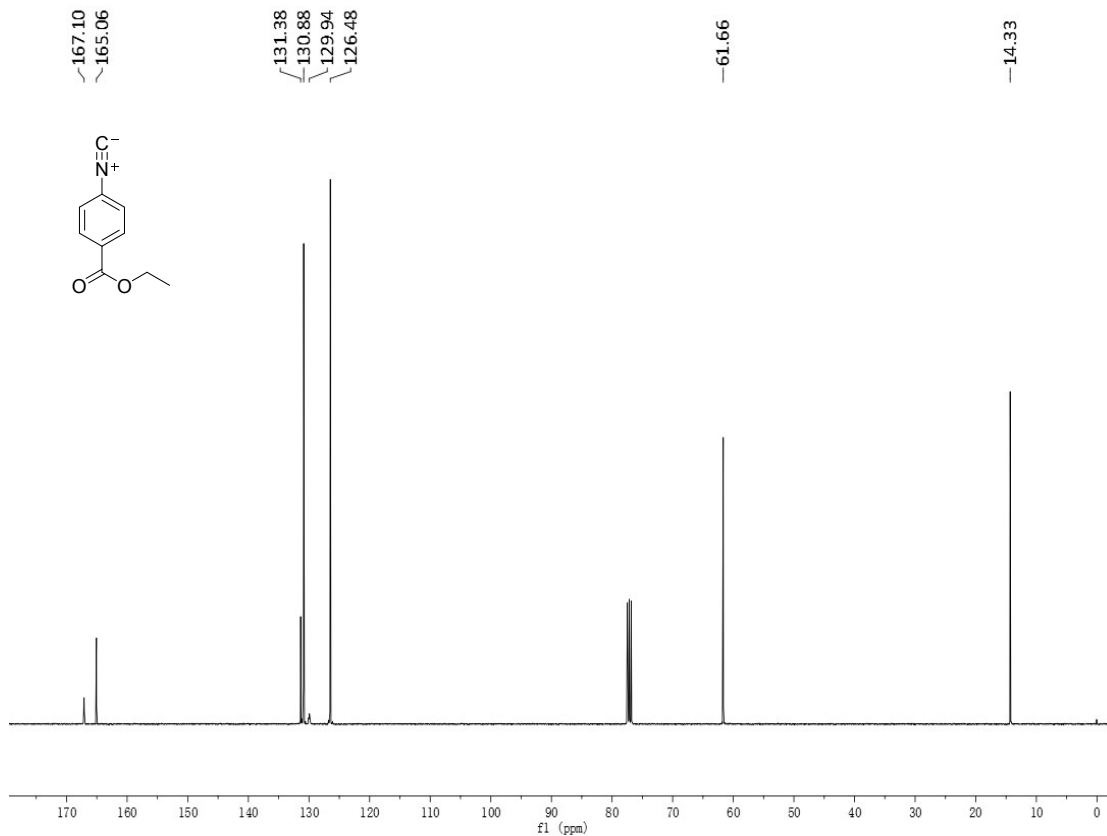


Figure S4. ¹³C NMR spectrum of 4-ethoxycarbonyl phenyl isocyanide (**a**).

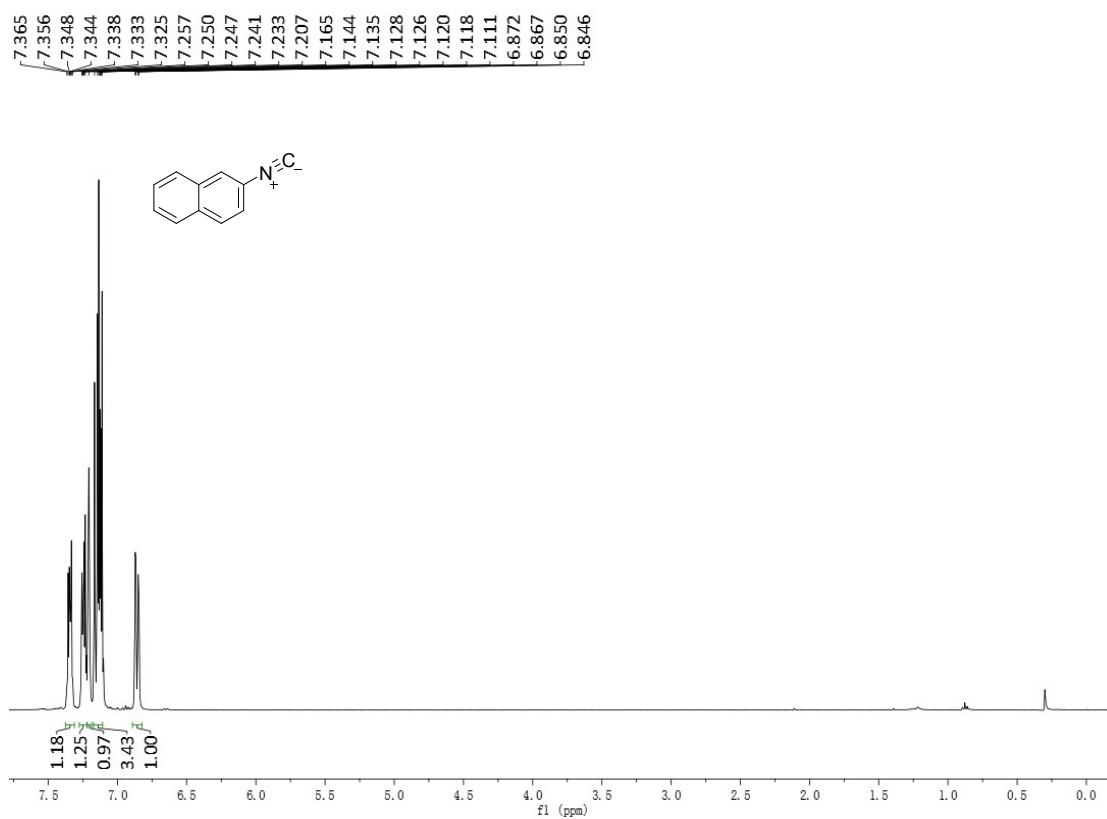


Figure S5. ¹H NMR spectrum of 2-naphthyl isocyanide (**b**).

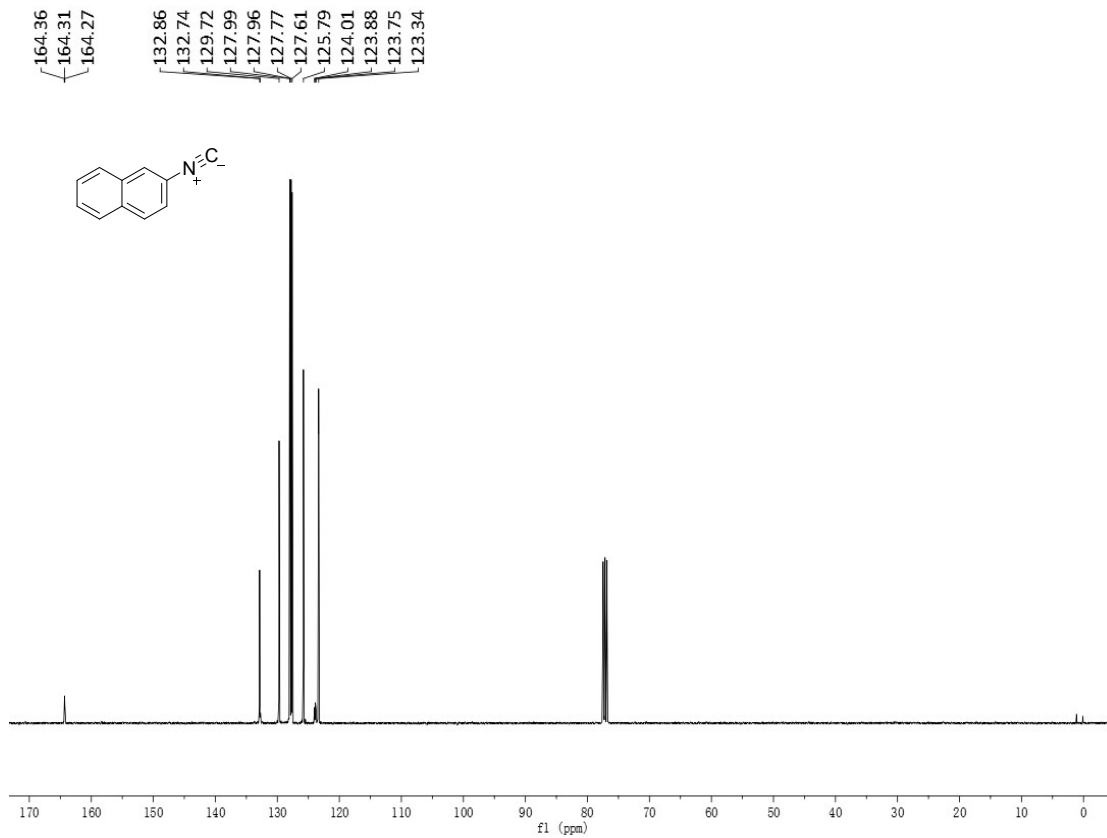


Figure S6. ¹³C NMR spectrum of 2-naphthyl isocyanide (**b**).

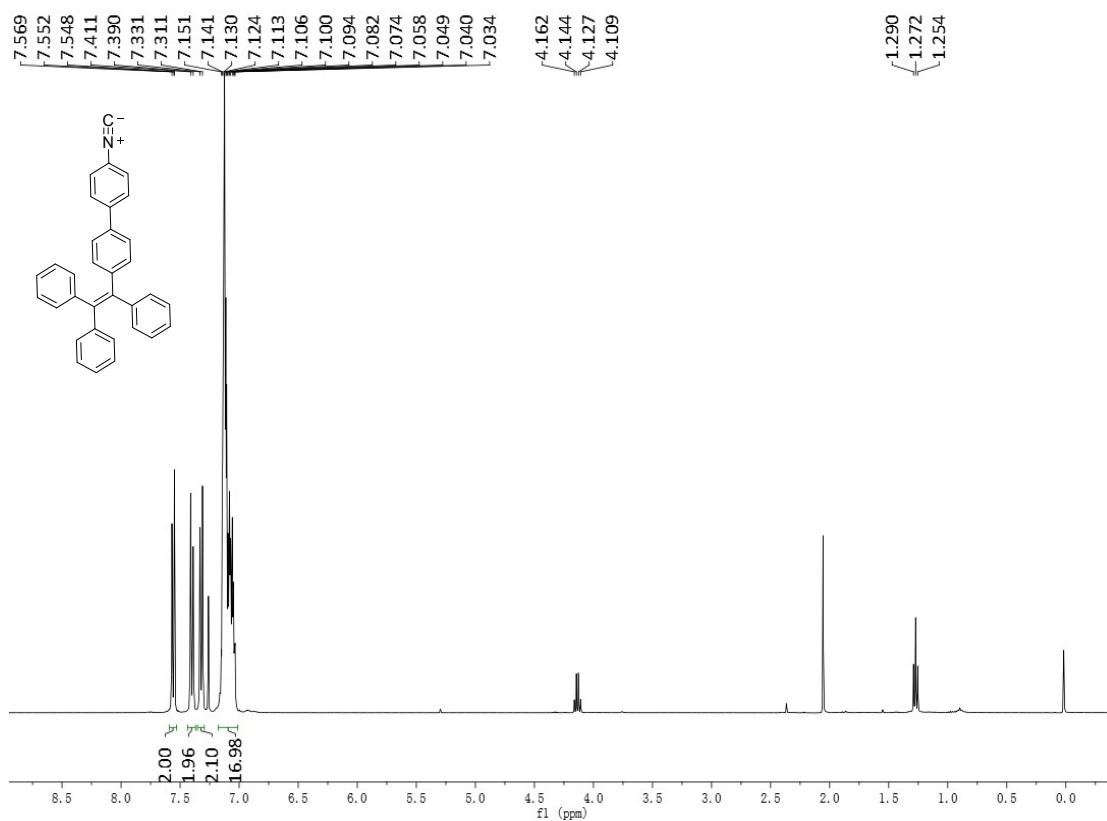


Figure S7. ¹H NMR spectrum of 4-isocyano-4'-(1,2,2-triphenylvinyl)-1,1'-biphenyl (c)

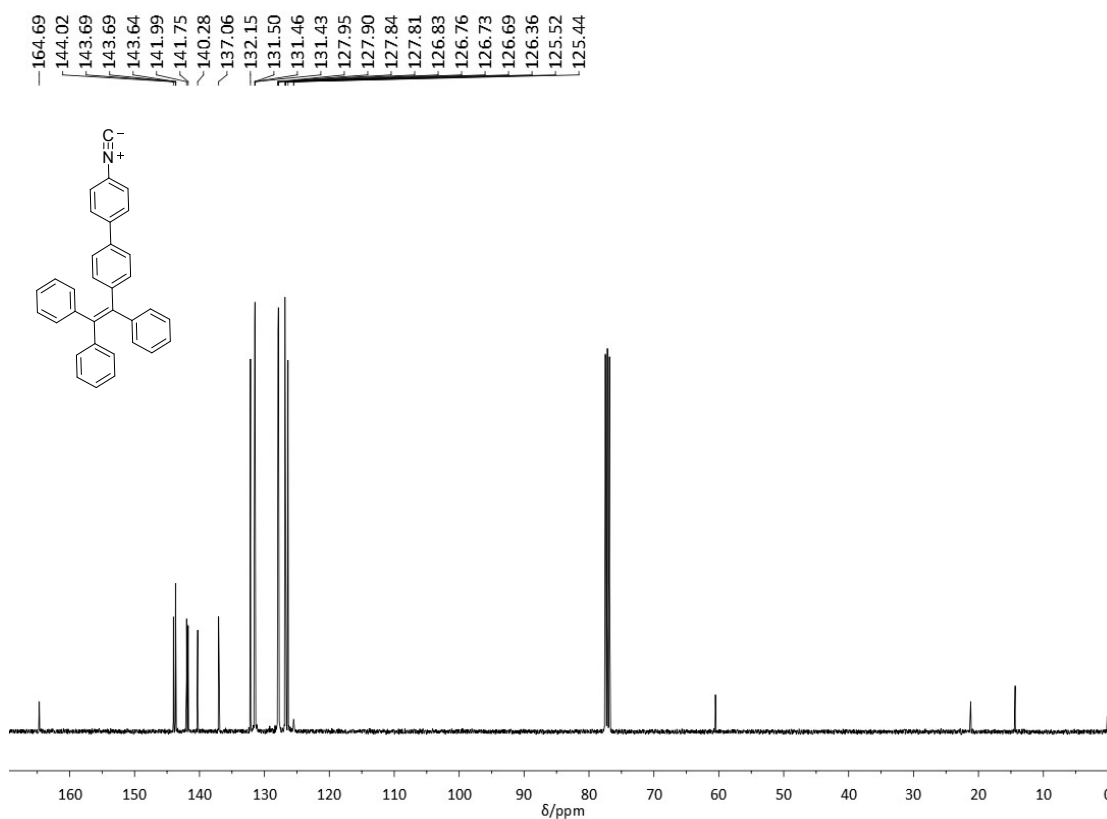


Figure S8. ¹³C NMR spectrum of 4-isocyano-4'-(1,2,2-triphenylvinyl)-1,1'-biphenyl (c).

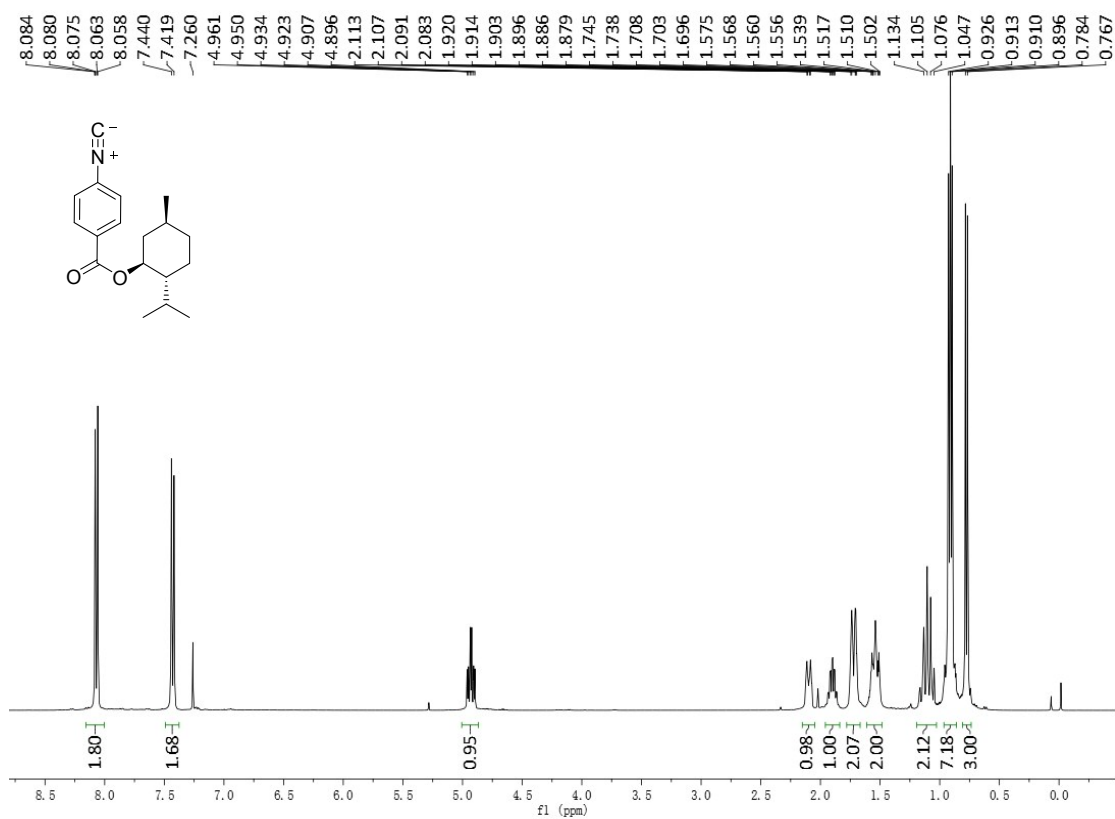


Figure S9. ¹H NMR spectrum of (1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (**d**)

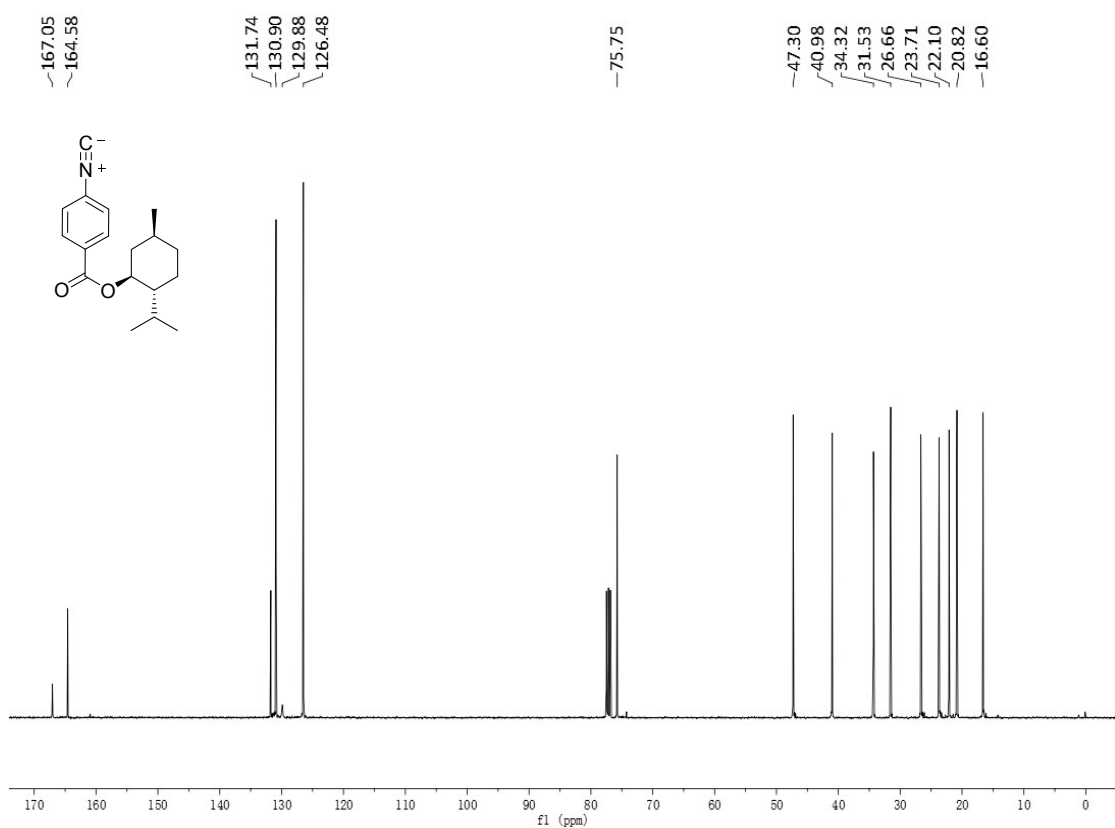


Figure S10. ¹³C NMR spectrum of (1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (**d**).

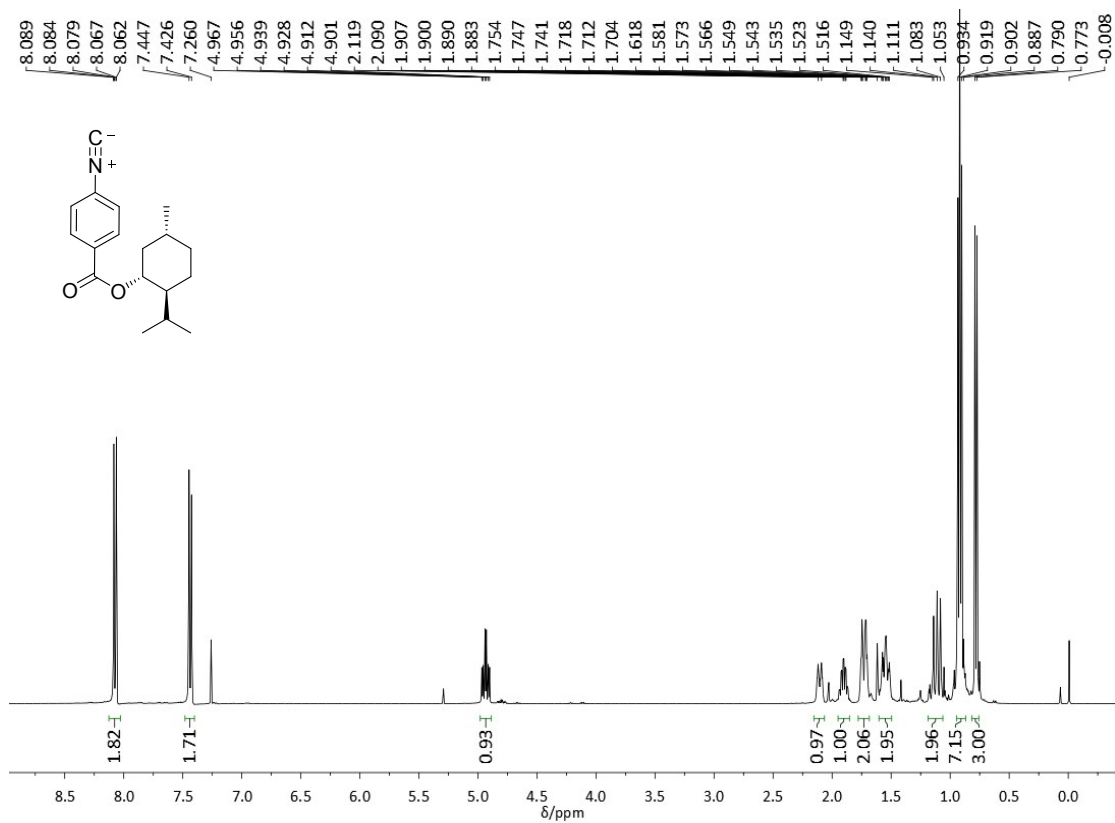


Figure S11. ¹H NMR spectrum of (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (e)

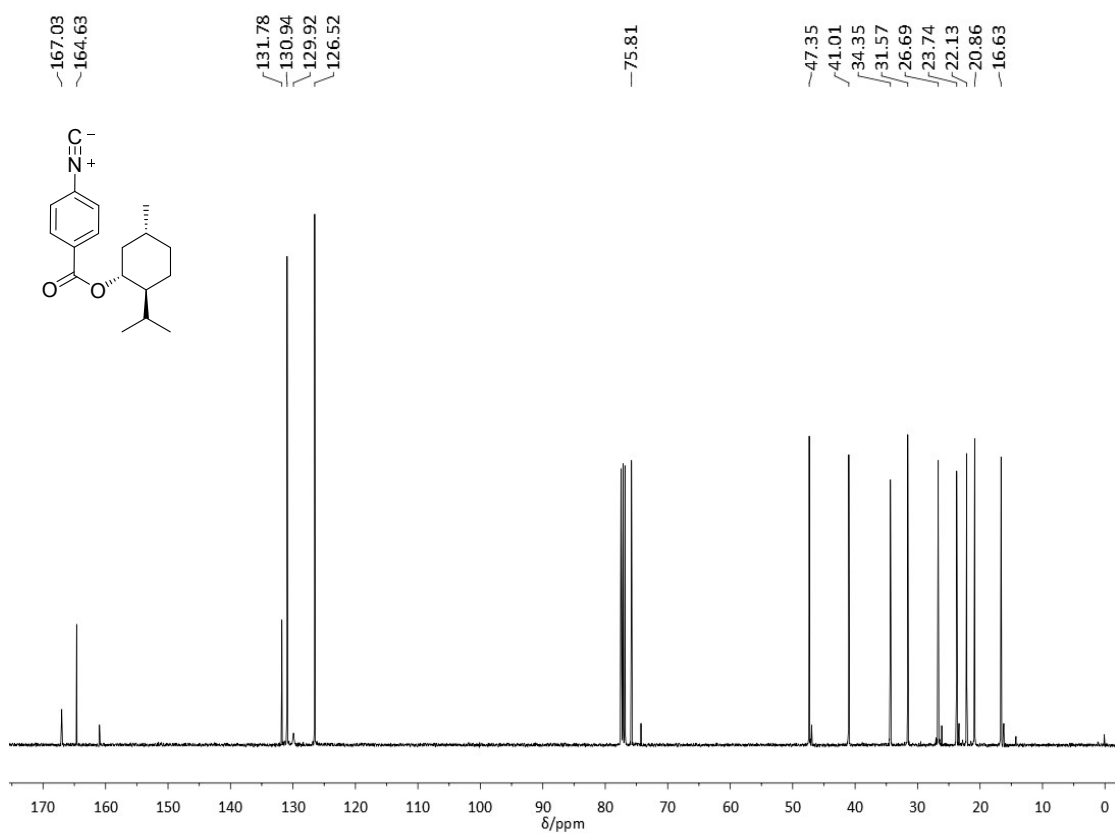


Figure S12. ¹³C NMR spectrum of (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (e).

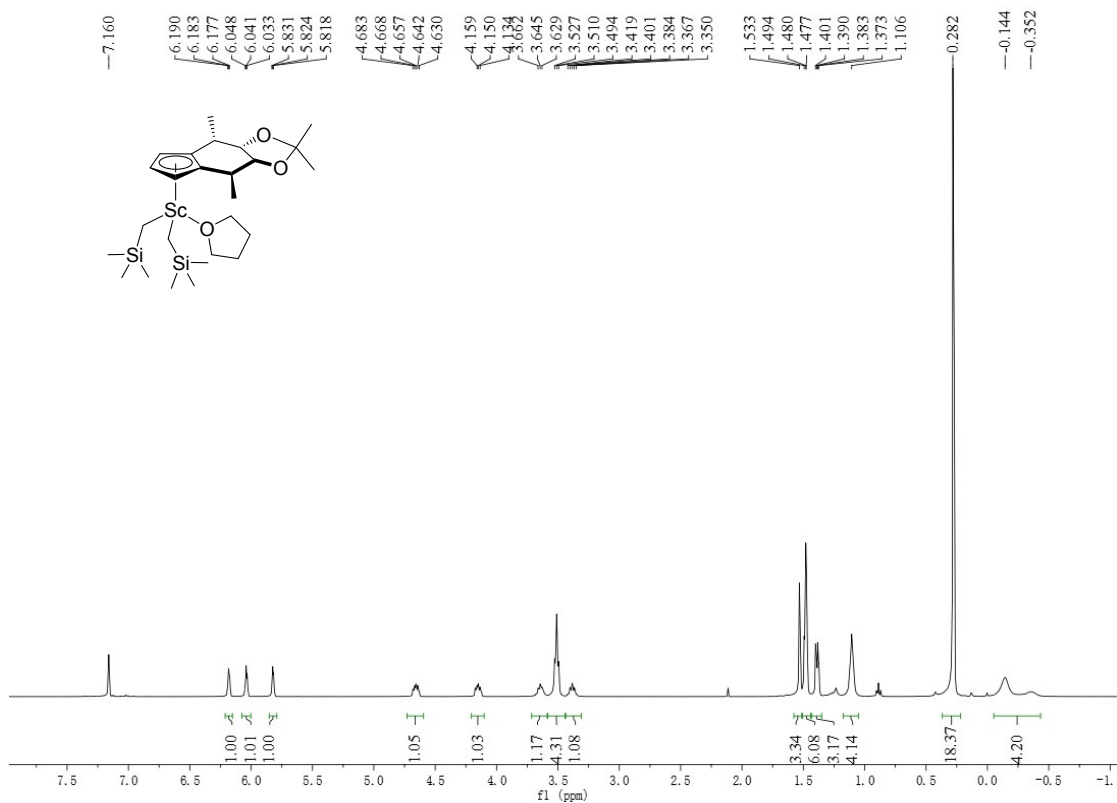


Figure S13. ¹H NMR spectrum of Scandium complex 1.

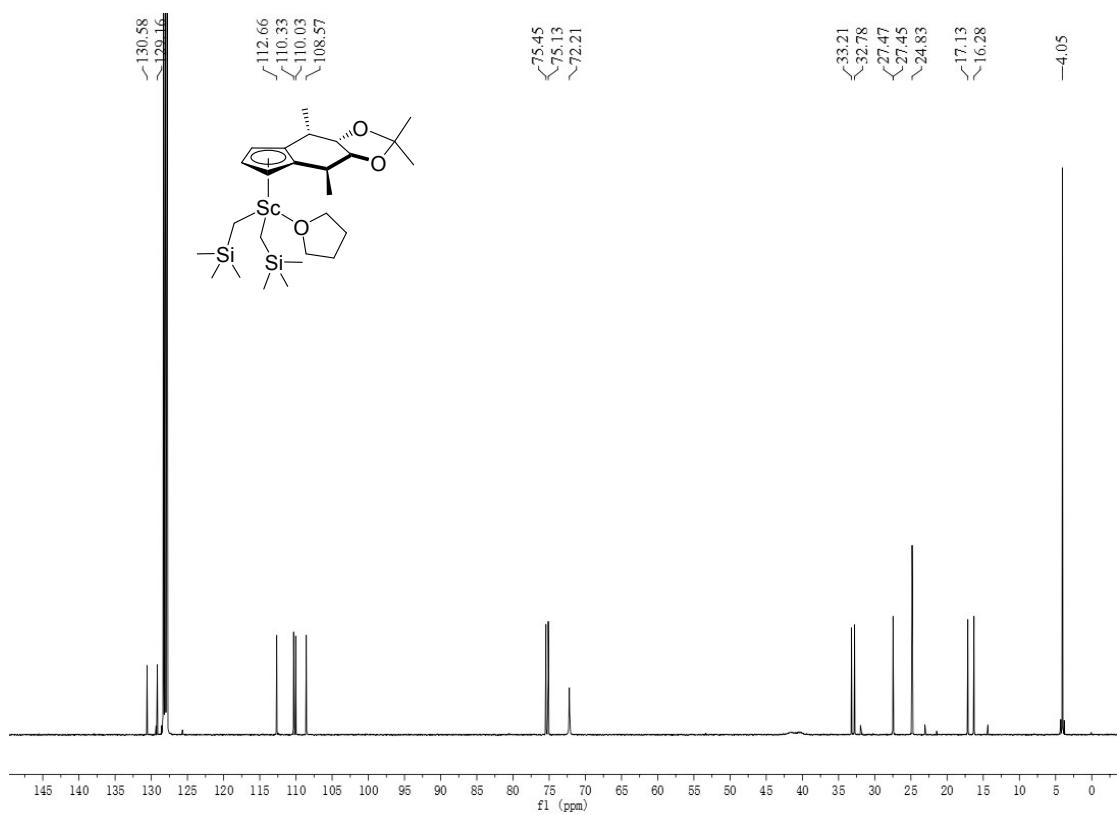


Figure S14. ¹³C NMR spectrum of Scandium complex 1.

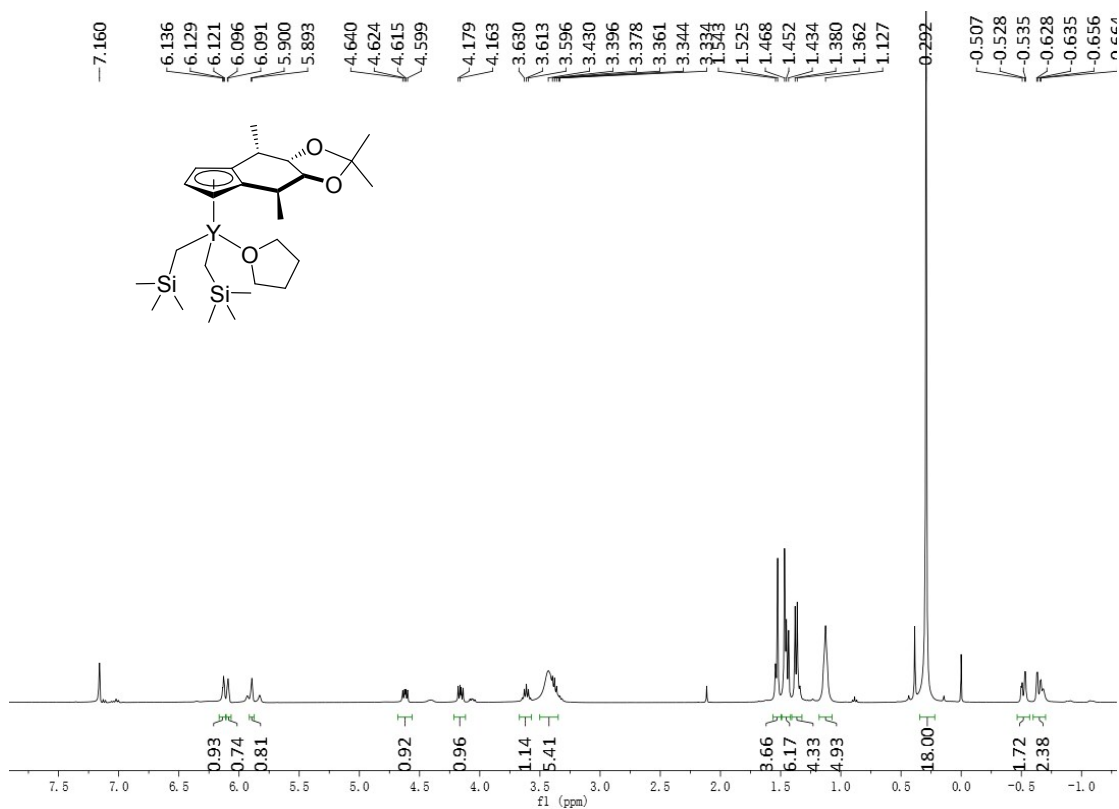


Figure S15. ¹H NMR spectrum of Yttrium complex **2**.

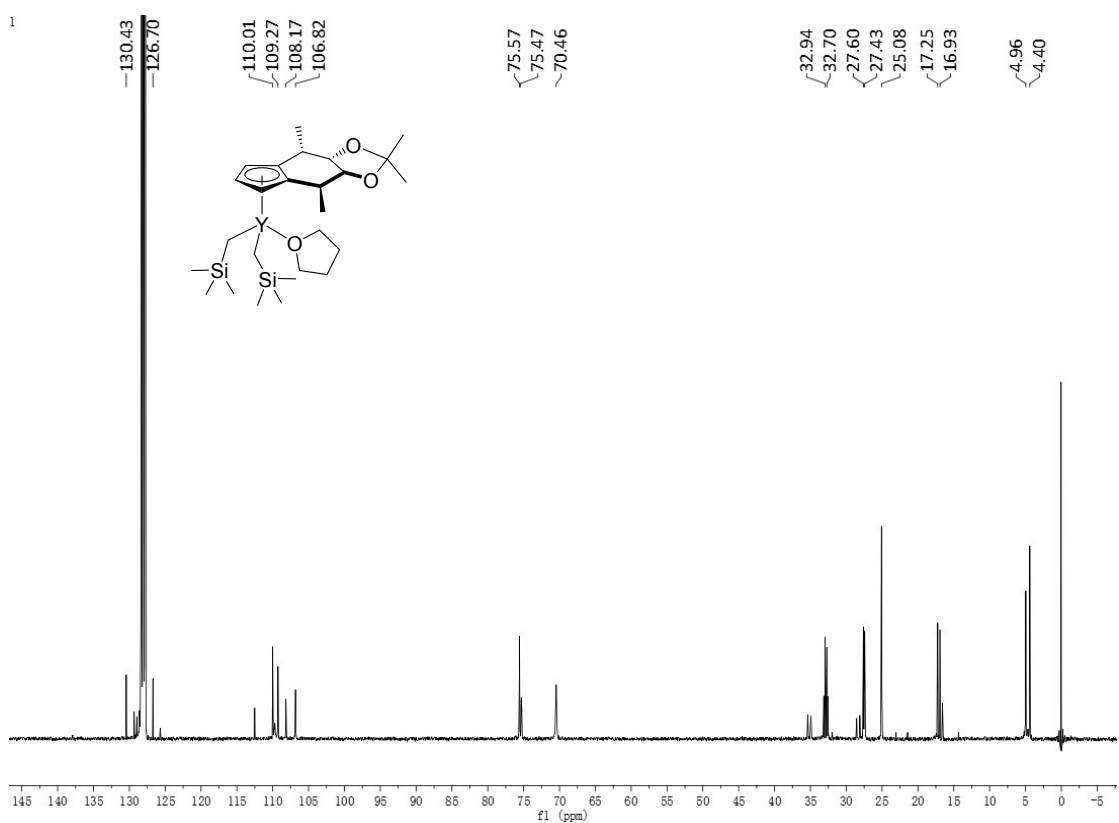


Figure S16. ¹³C NMR spectrum of Yttrium complex **2**.

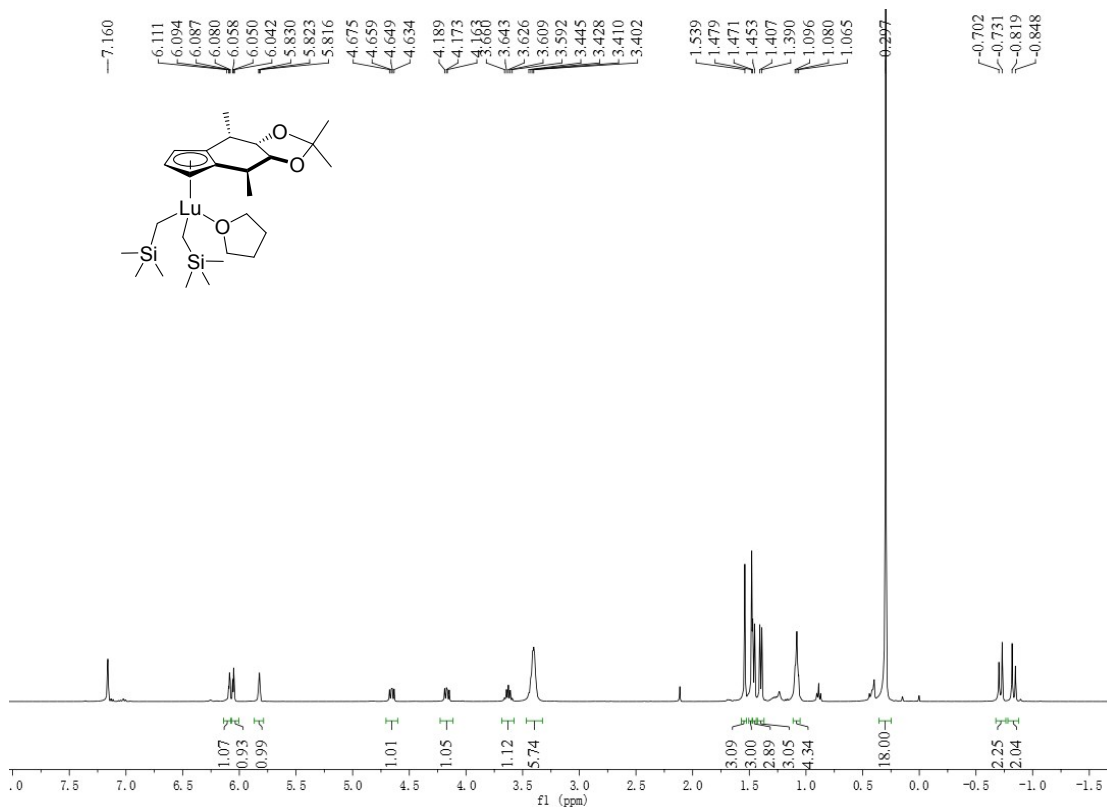


Figure S17. ¹H NMR spectrum of Lutetium complex **3**.

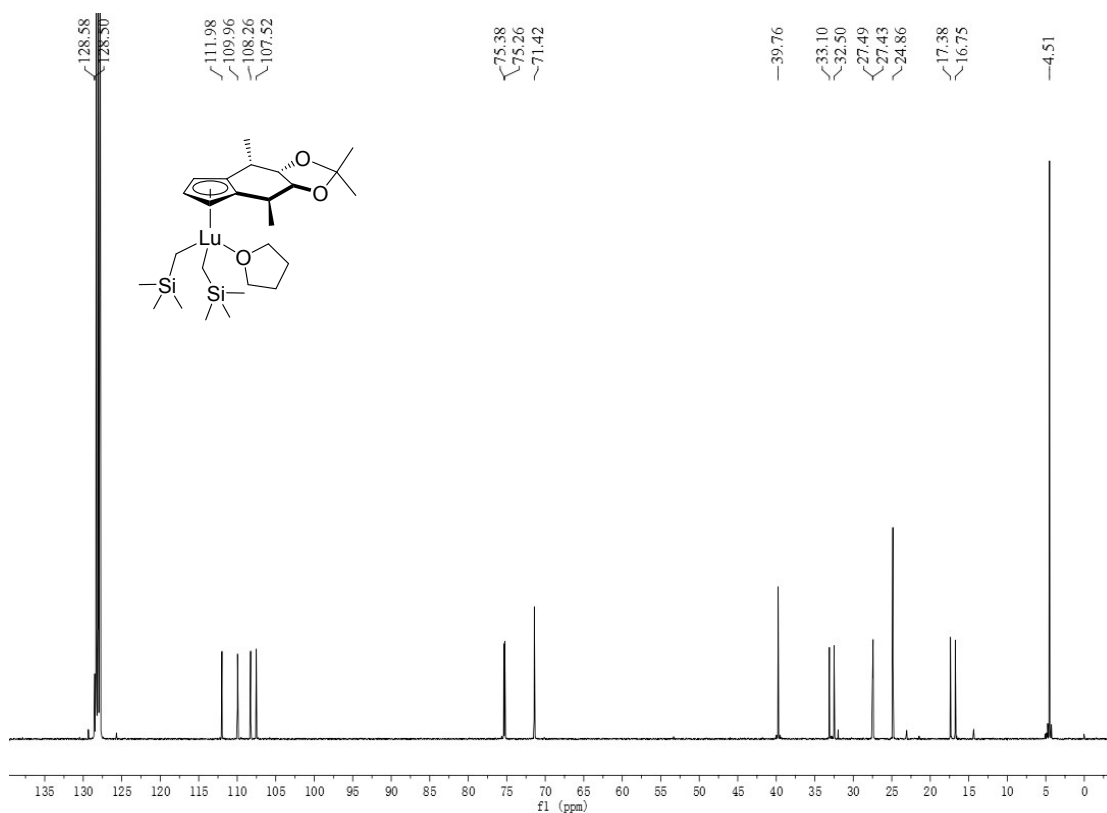


Figure S18. ¹³C NMR spectrum of Lutetium complex **3**.

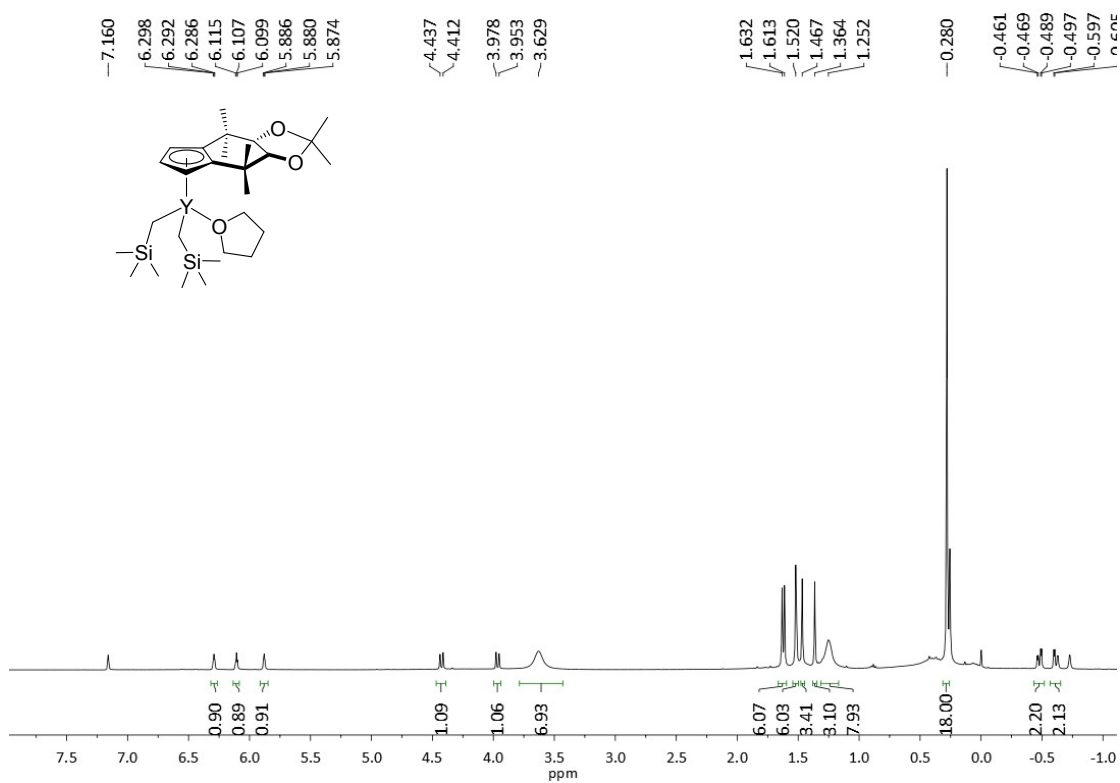


Figure S21. ¹H NMR spectrum of Yttrium complex **5**.

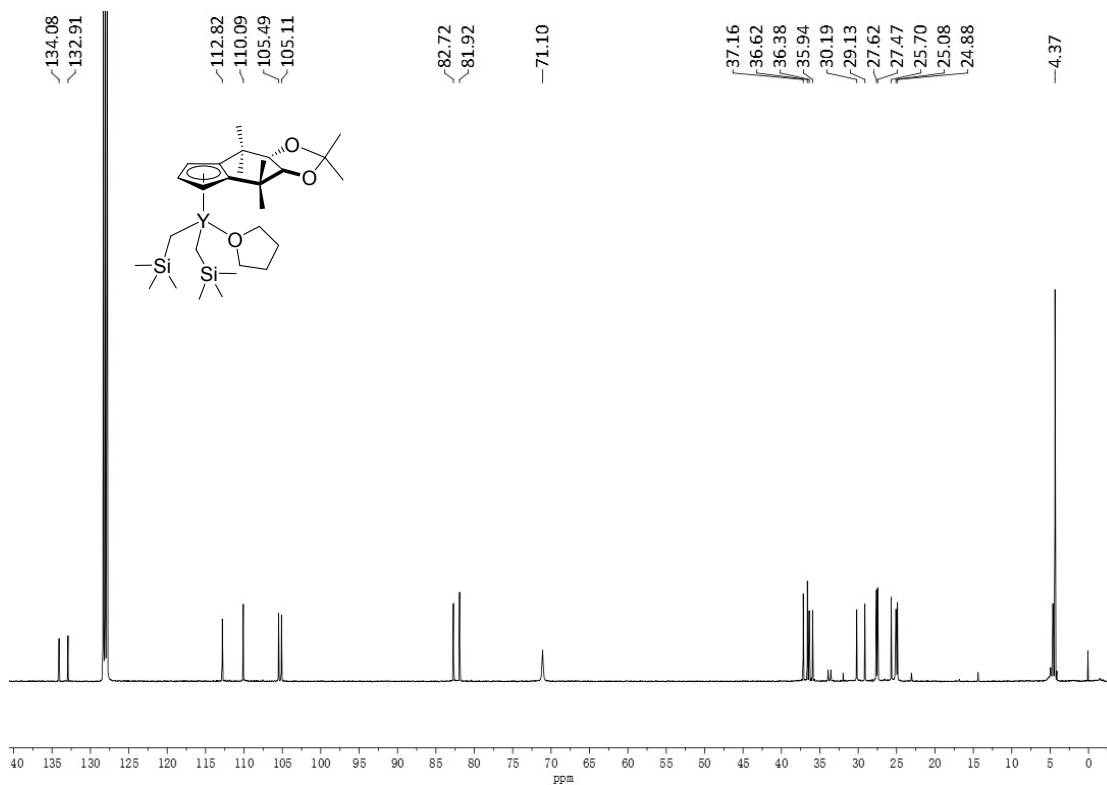


Figure S22. ¹³C NMR spectrum of Yttrium complex **5**.

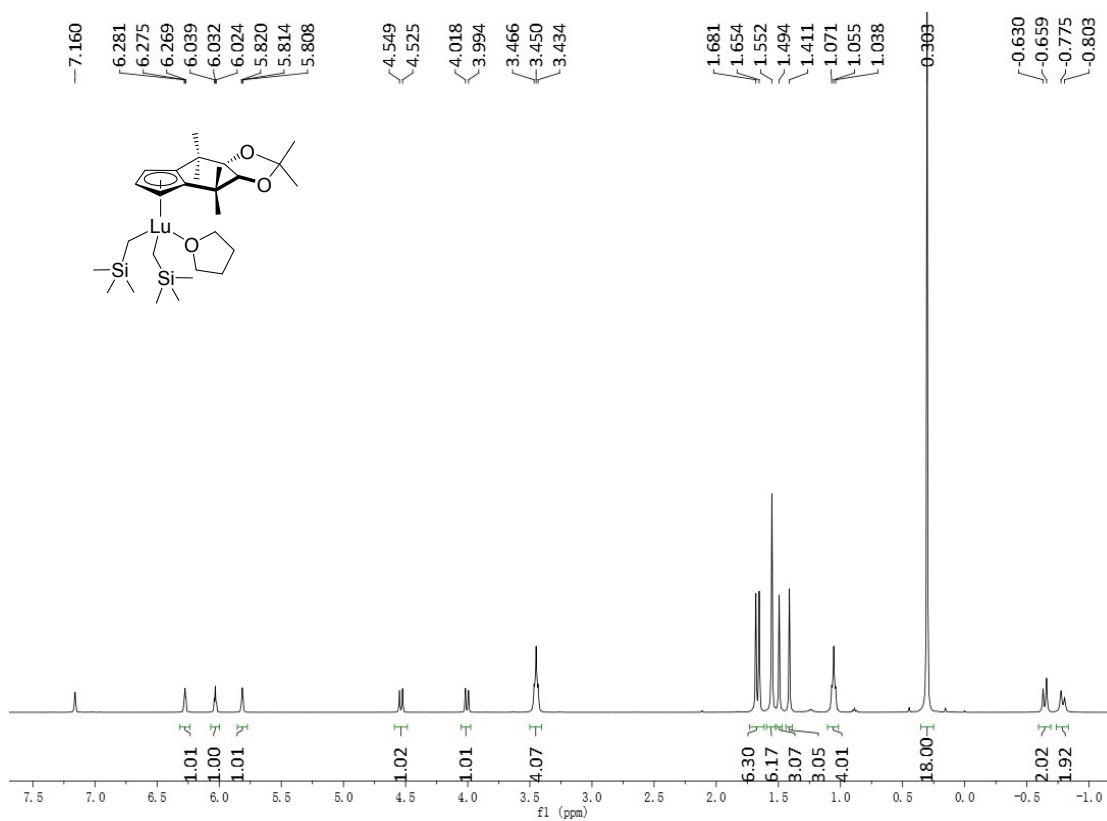


Figure S23. ¹H NMR spectrum of Lutetium complex 6.

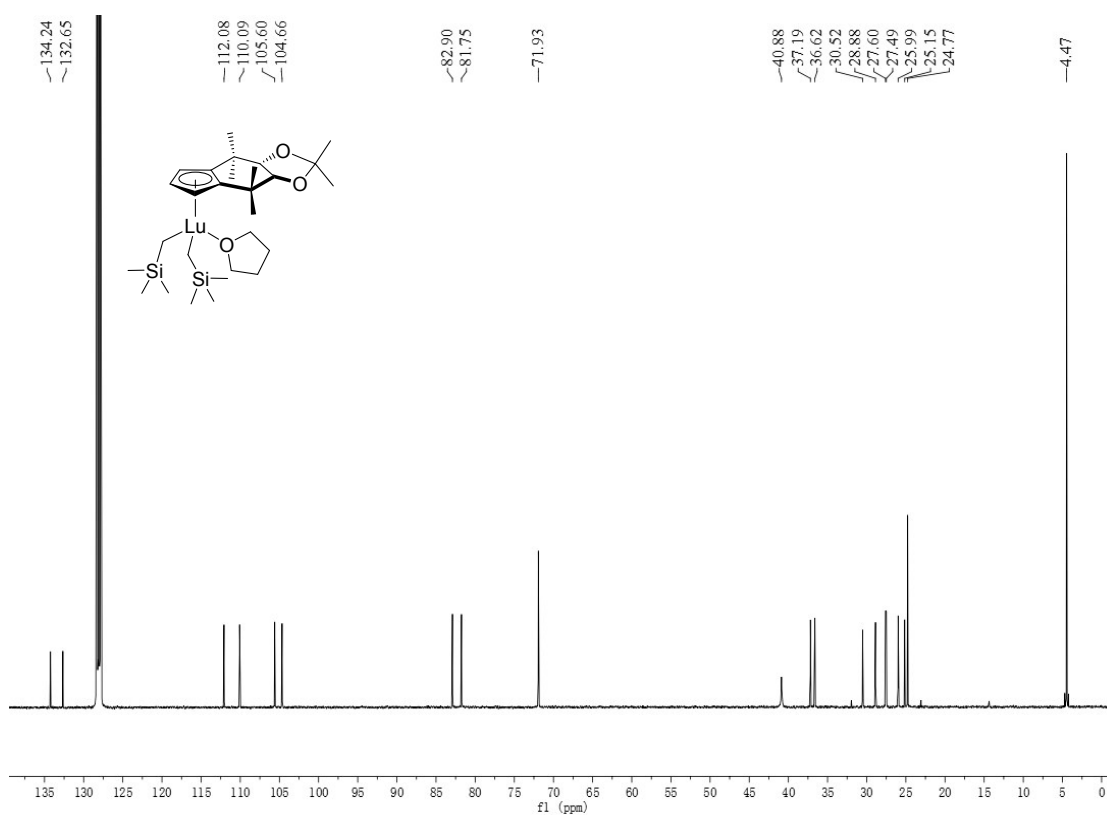


Figure S24. ¹³C NMR spectrum of Lutetium complex 6.

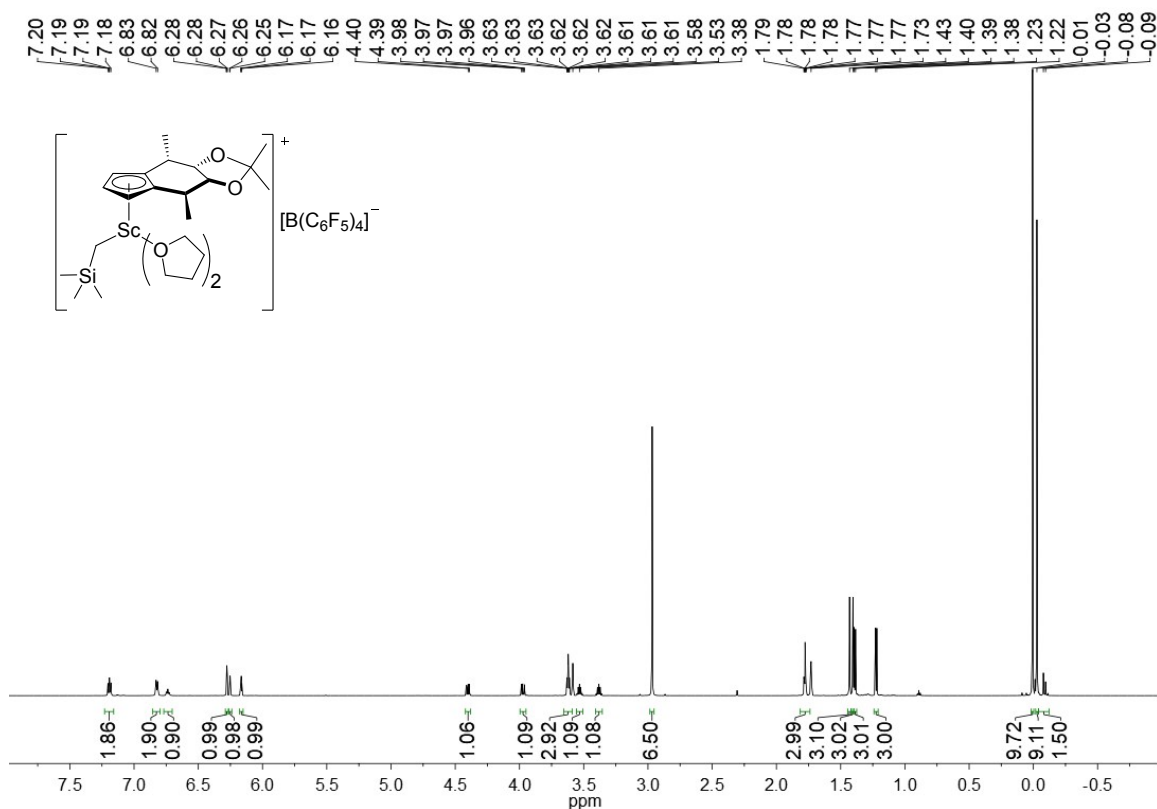


Figure S25. ^1H NMR spectrum of cationic Scandium species generated *in-situ* from complex **1** in THF-d₈ at 25 °C.

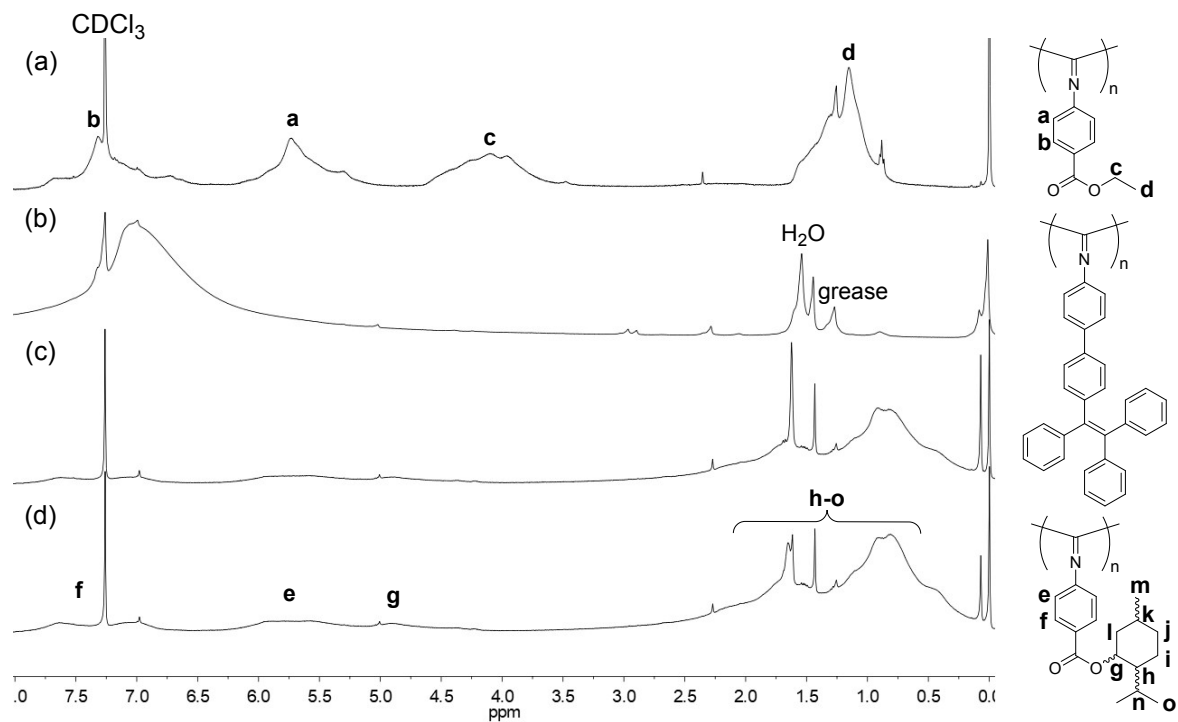


Figure S26. ^1H NMR spectra of poly(EPI) (a), poly(ITPB) (b), poly(D-IMCI) (c), poly(L-IMCI) (d) in CHCl₃ at 25 °C.

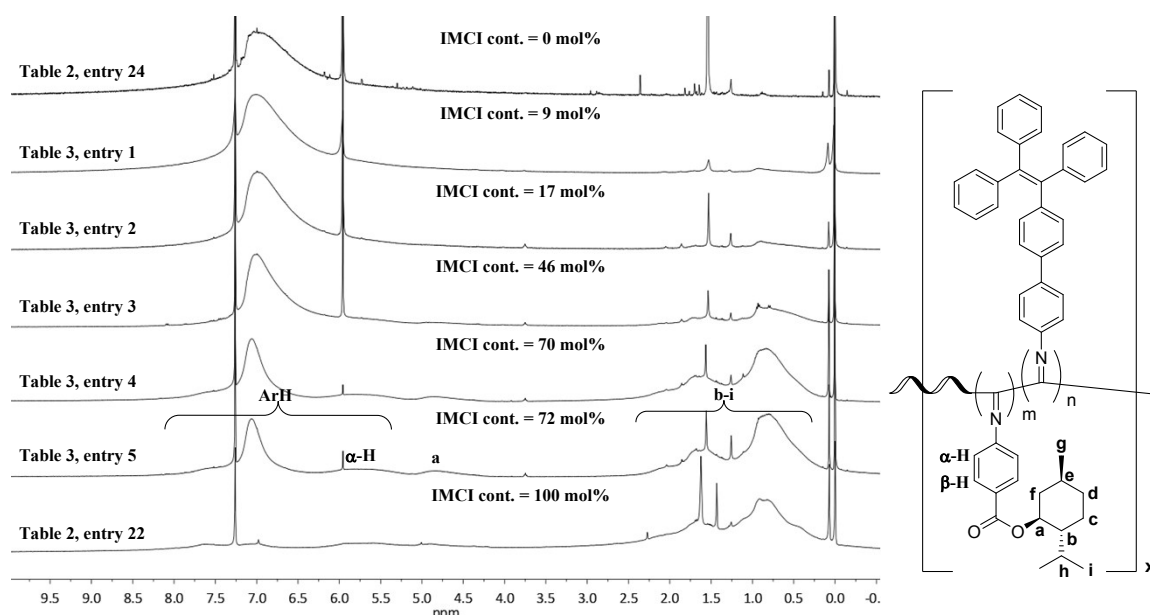


Figure S27. ^1H NMR spectra of poly(ITPB), poly(D-IMCI-co-ITPB)s and poly(D-IMCI) (Table 2, entries 22, 24 and Table 3, entries 1-5).

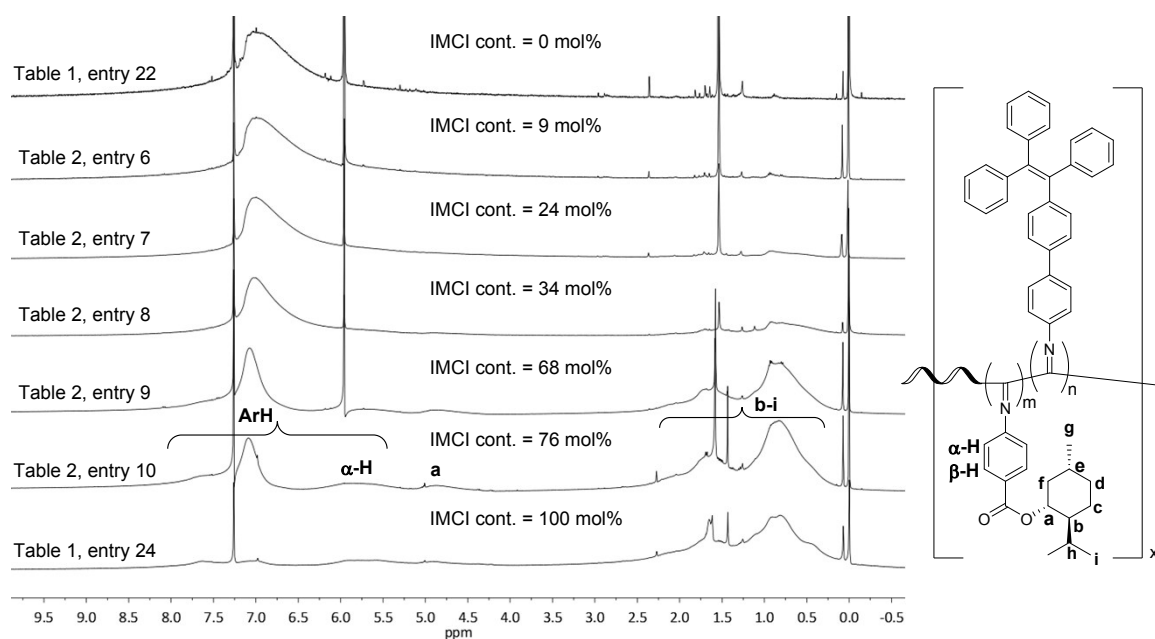


Figure S28. ^1H NMR spectra of poly(ITPB), poly(L-IMCI-co-ITPB)s and poly(L-IMCI) (Table 2, entries 22, 24 and Table 3, entries 6-10).

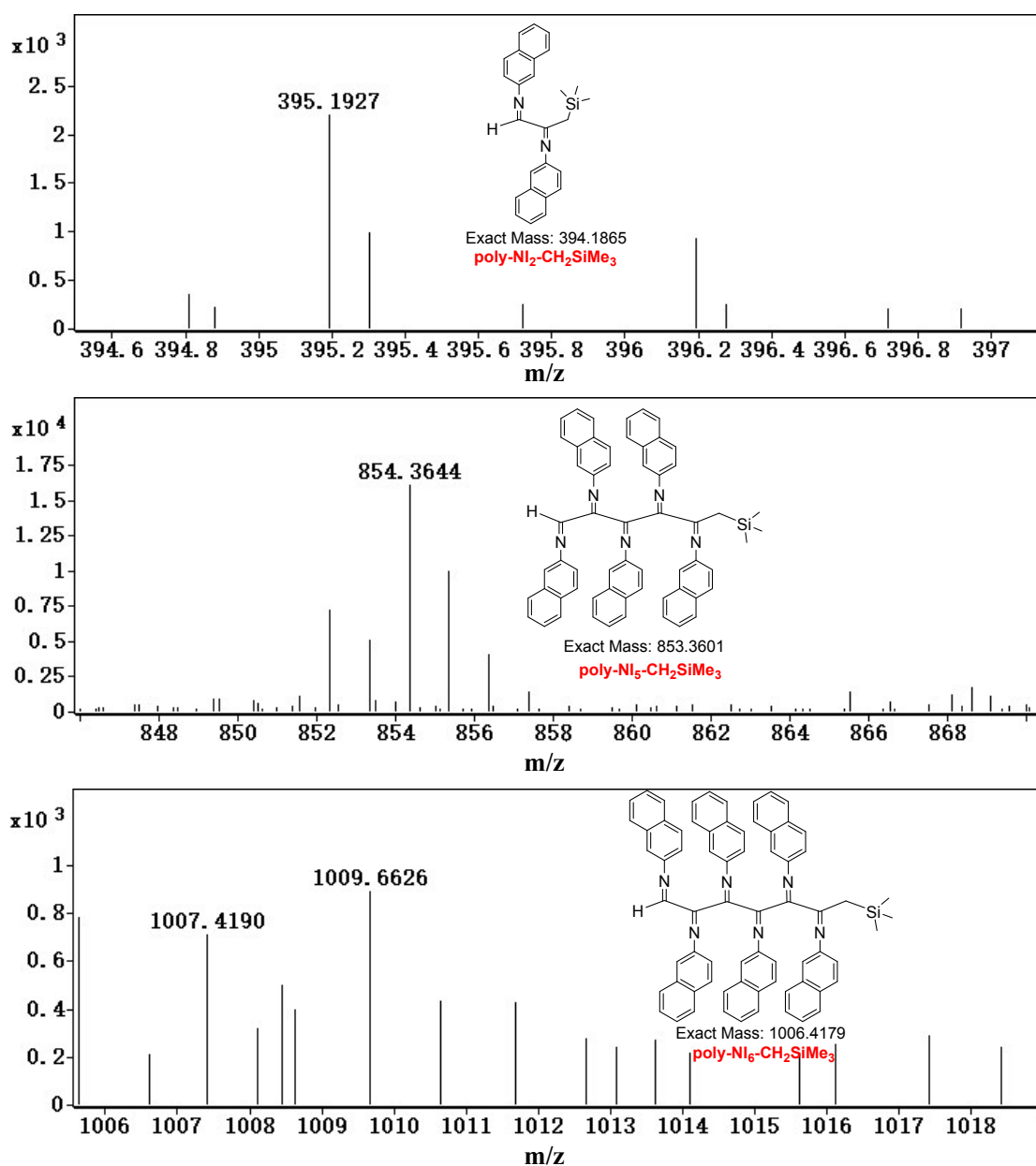


Figure S29. High resolution ESI-MS spectra of NiI oligomer obtained by complex 1/ $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ binary system.

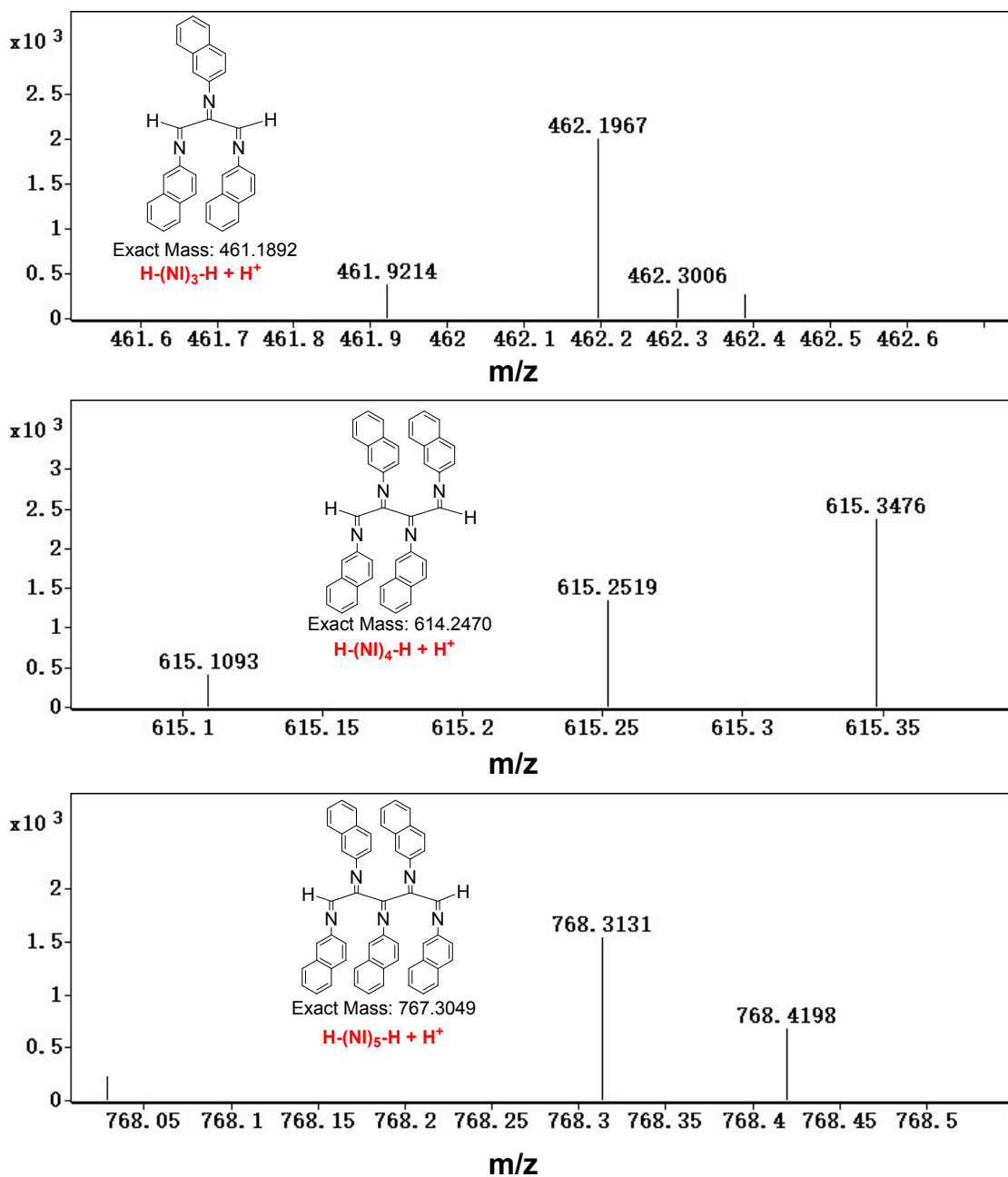


Figure S30. High resolution ESI-MS spectra of Ni oligomer obtained by complex 1/[Ph₃C][B(C₆F₅)₄] binary system.

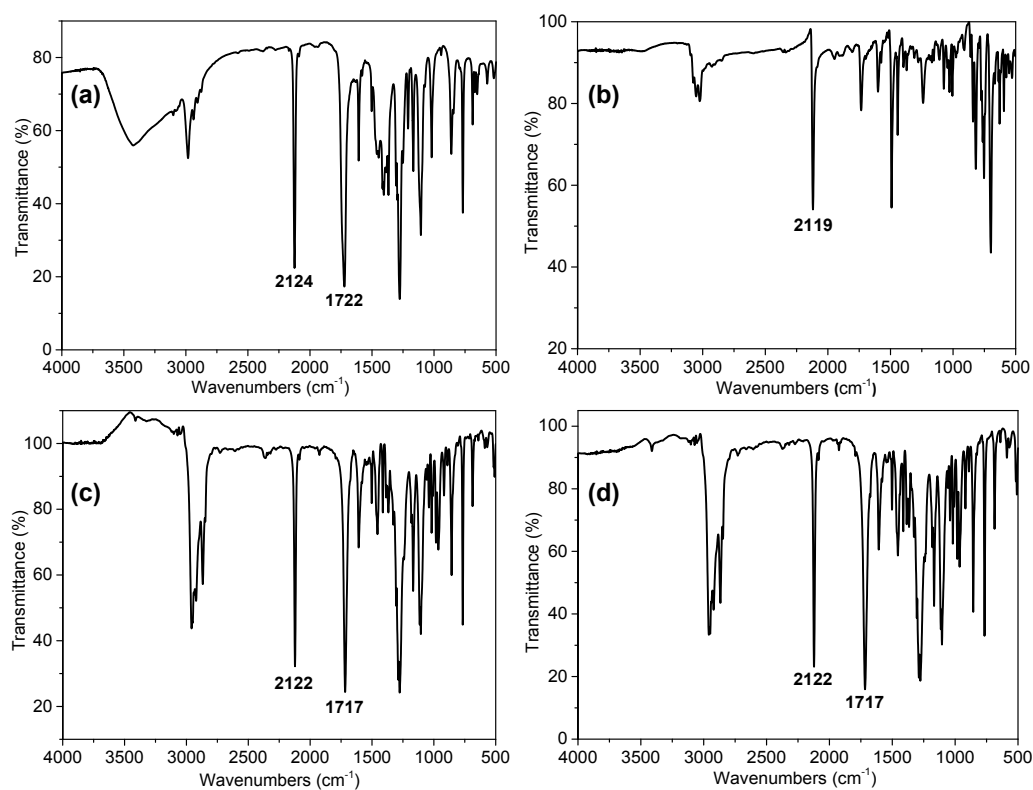


Figure S31. FT-IR spectra of aryl isocyanide monomers EPI (a), ITPB (b), D-IMCI (c) and L-IMCI (d).

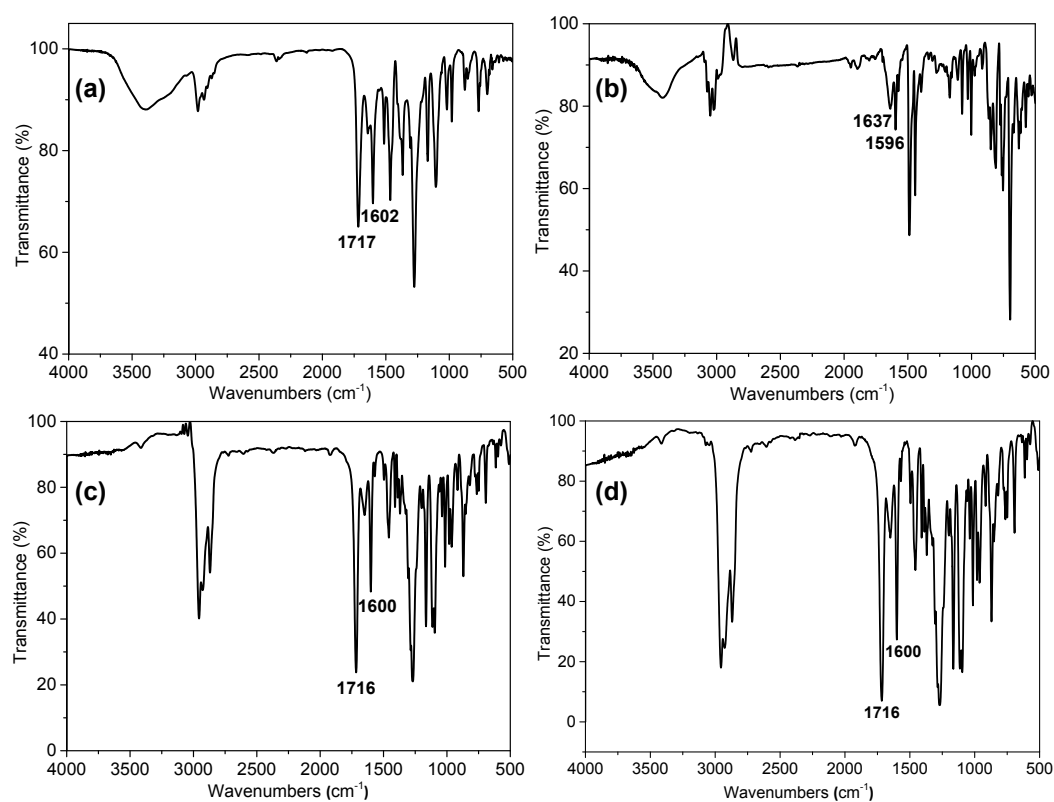
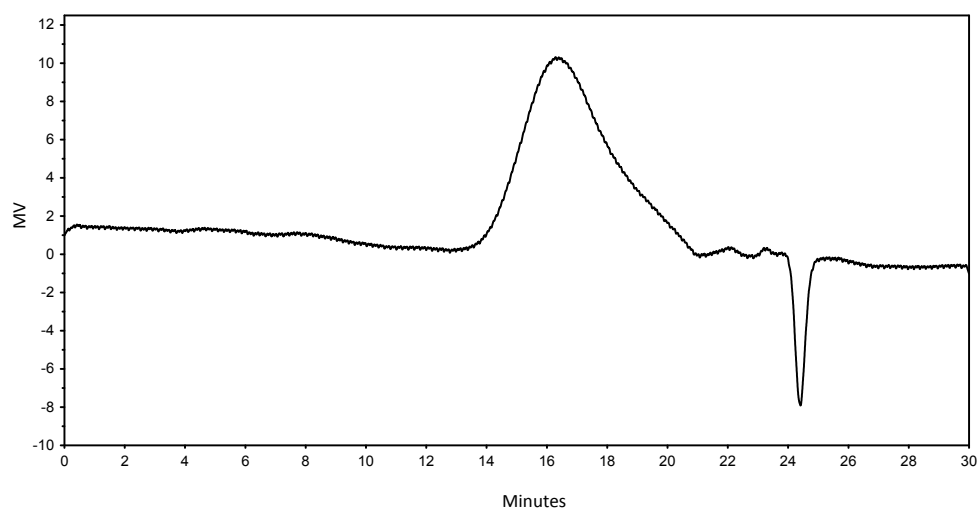


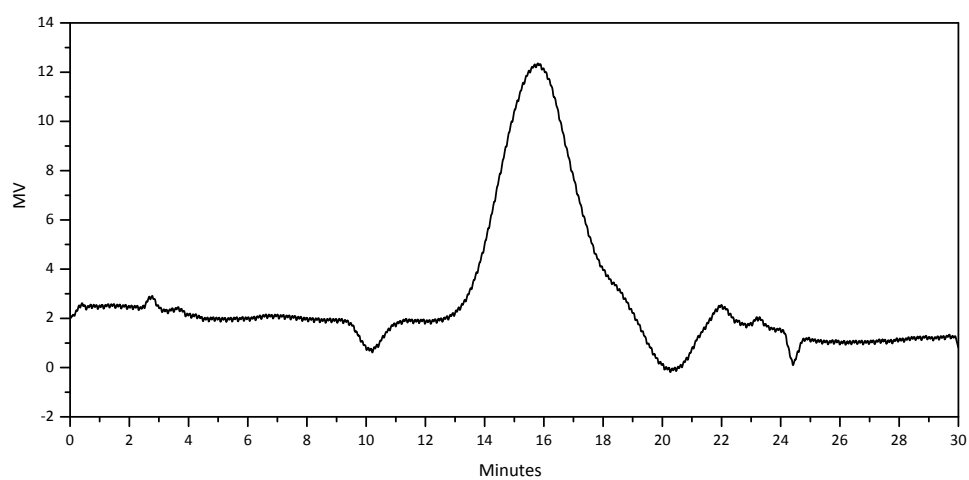
Figure S32. FT-IR spectra of poly(EPI) (a), poly(ITPB) (b), poly(D-IMCI) (c) and poly(L-IMCI) (d).



Broad Unknown Relative Peak Table

	Distributionn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		46479	266277	677685	208066	5.72897	0.78139

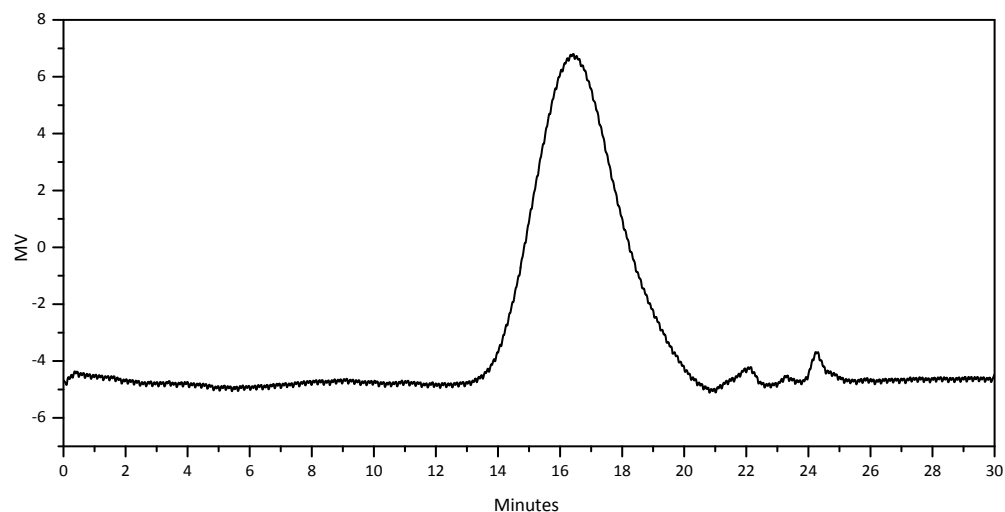
Figure S33. GPC curve of poly(EPI) obtained by cationic species generated from complex **1** in Table 2, entry 1.



Broad Unknown Relative Peak Table

	Distributionn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		169016	659669	355419	1962950	3.90300	2.97566

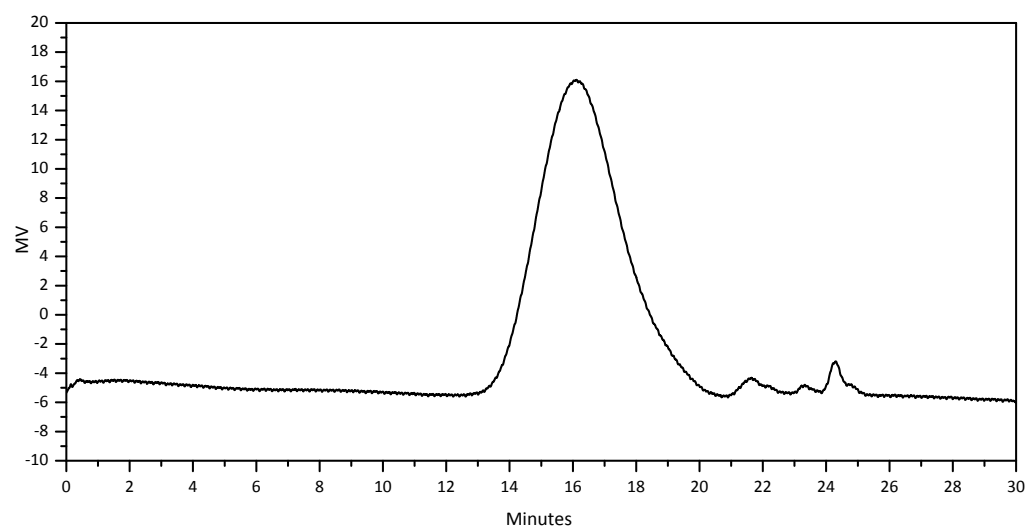
Figure S34. GPC curve of poly(EPI) obtained by cationic species generated from complex **1** in Table 2, entry 2.



Broad Unknown Relative Peak Table

	Distributionn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		79762	328206	212751	923194	4.11482	2.81285

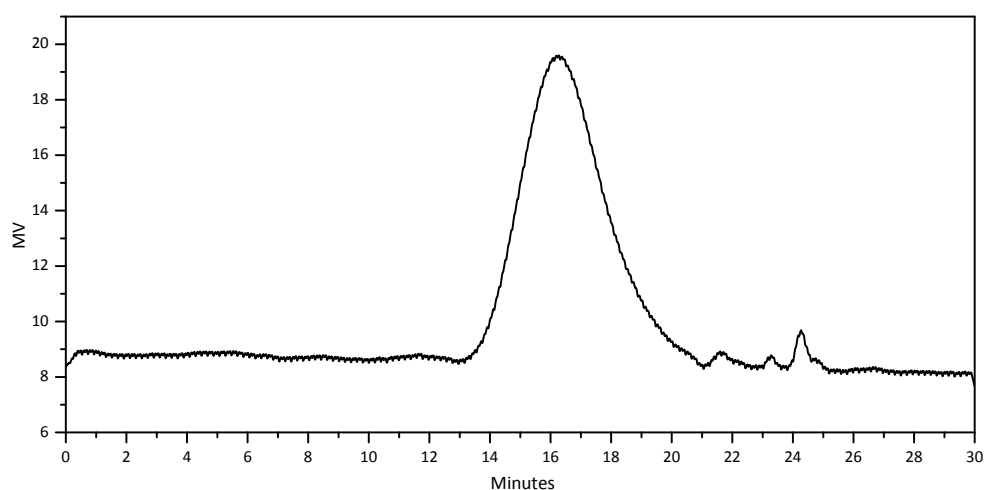
Figure S35. GPC curve of poly(EPI) obtained by cationic species generated from complex **1** in Table 2, entry 3.



Broad Unknown Relative Peak Table

	Distributionn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		96170	419448	281780	1154800	4.36153	2.75314

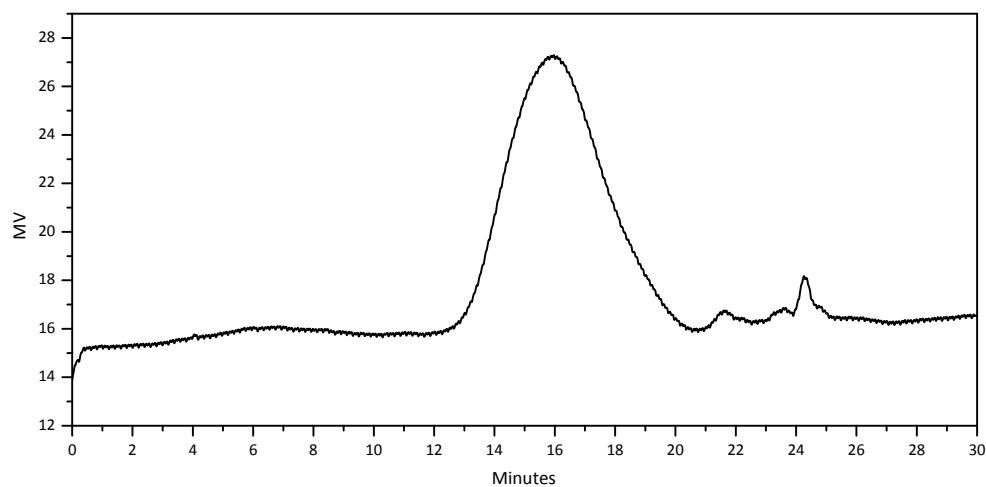
Figure S36. GPC curve of poly(EPI) obtained by cationic species generated from complex **1** in Table 2, entry 4.



Broad Unknown Relative Peak Table

	Distributiononn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		70268	363107	220568	1031530	5.16746	2.84084

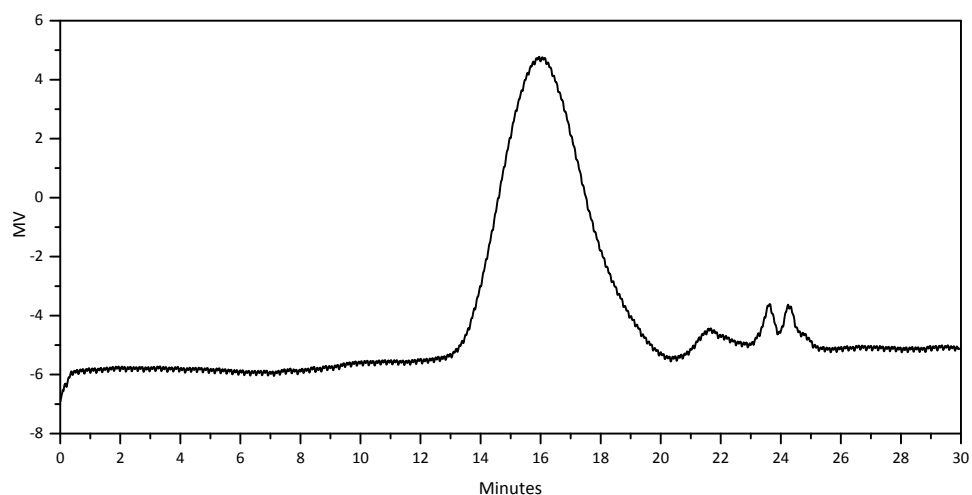
Figure S37. GPC curve of poly(EPI) obtained by cationic species generated from complex **1** in Table 2, entry 5.



Broad Unknown Relative Peak Table

	Distributiononn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		121911	616338	327742	1938269	5.05564	3.14482

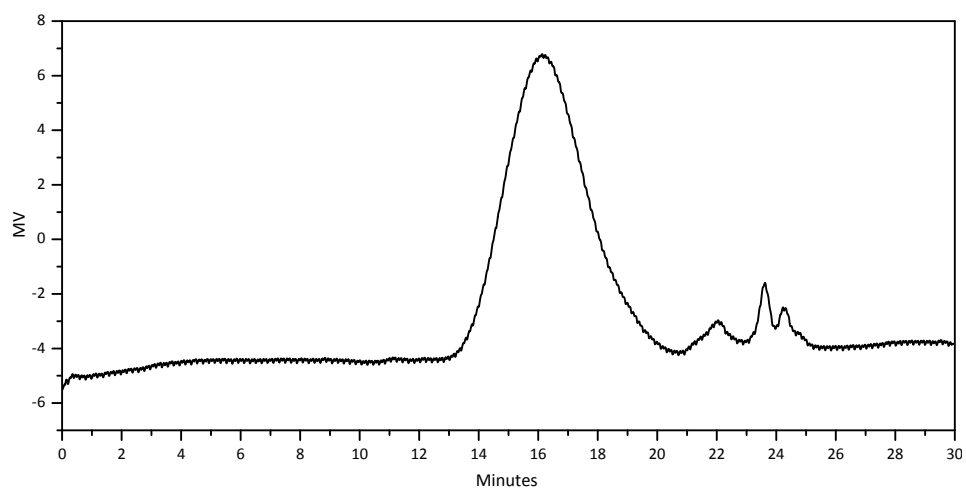
Figure S38. GPC curve of poly(EPI) obtained by cationic species generated from complex **1** in Table 2, entry 6.



Broad Unknown Relative Peak Table

	Distributionn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		116324	513707	328767	1492676	4.41617	2.90569

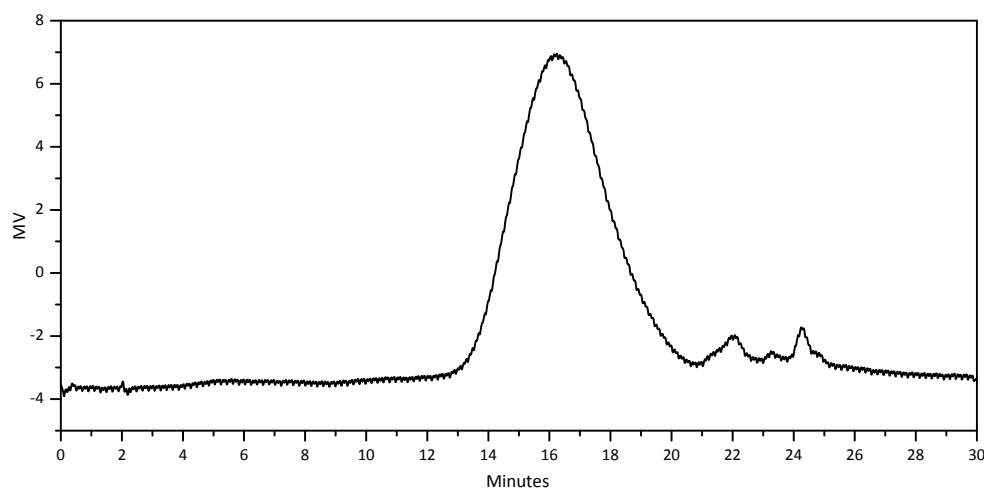
Figure S39. GPC curve of poly(EPI) obtained by cationic species generated from complex **2** in Table 2, entry 9.



Broad Unknown Relative Peak Table

	Distributionn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		107458	410373	240394	1074822	3.81891	2.61913

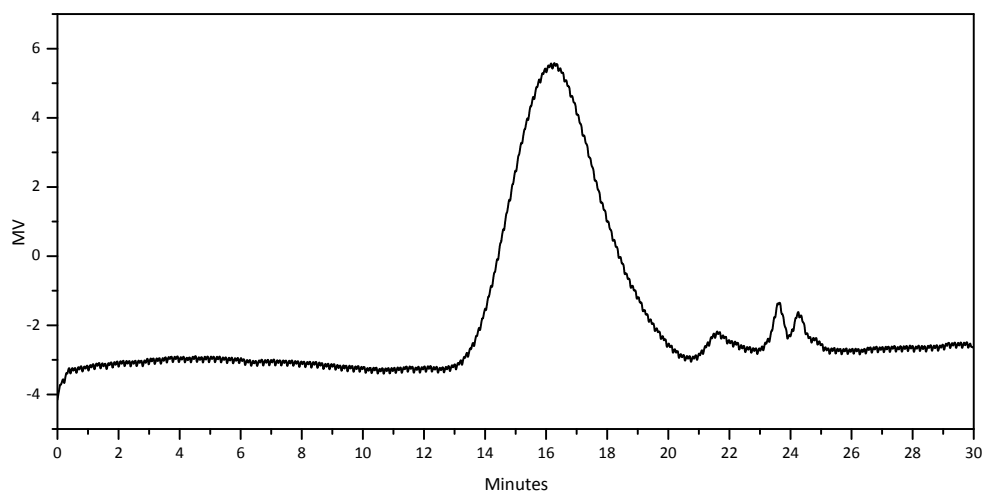
Figure S40. GPC curve of poly(EPI) obtained by cationic species generated from complex **3** in Table 2, entry 10.



Broad Unknown Relative Peak Table

	Distributiononn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		69132	471516	240371	1803361	6.82052	3.82460

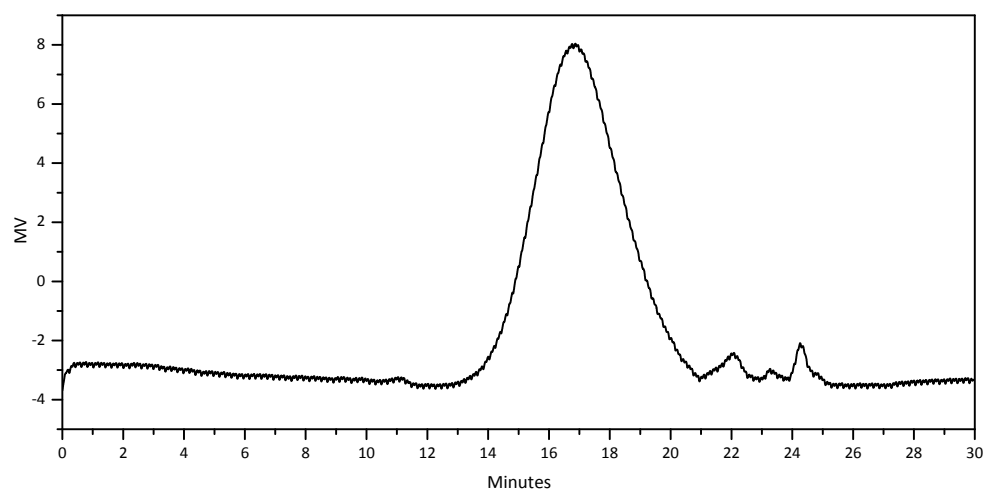
Figure S41. GPC curve of poly(EPI) obtained by cationic species generated from complex **4** in Table 2, entry 11.



Broad Unknown Relative Peak Table

	Distributiononn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		79778	412964	235974	1250549	5.17641	3.02823

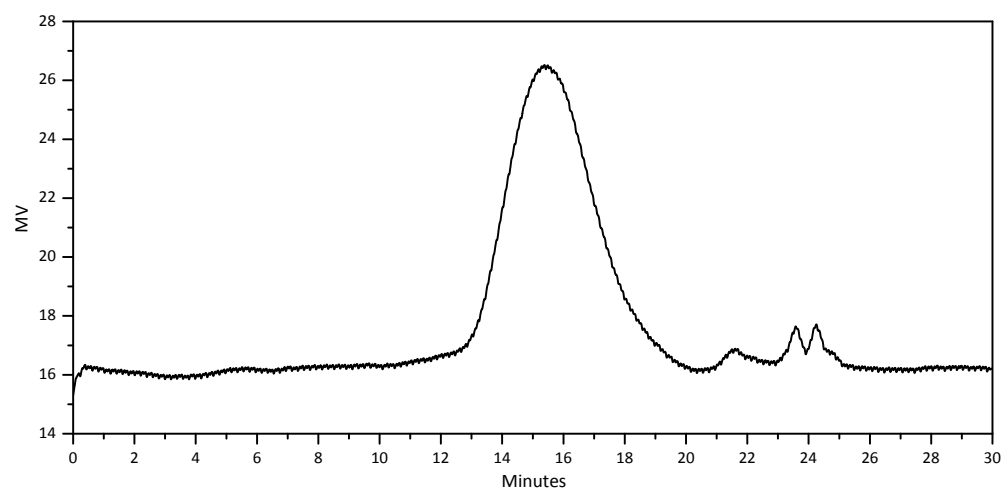
Figure S42. GPC curve of poly(EPI) obtained by cationic species generated from complex **5** in Table 2, entry 12.



Broad Unknown Relative Peak Table

	Distributionn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		52281	254628	144647	964149	4.87037	3.78650

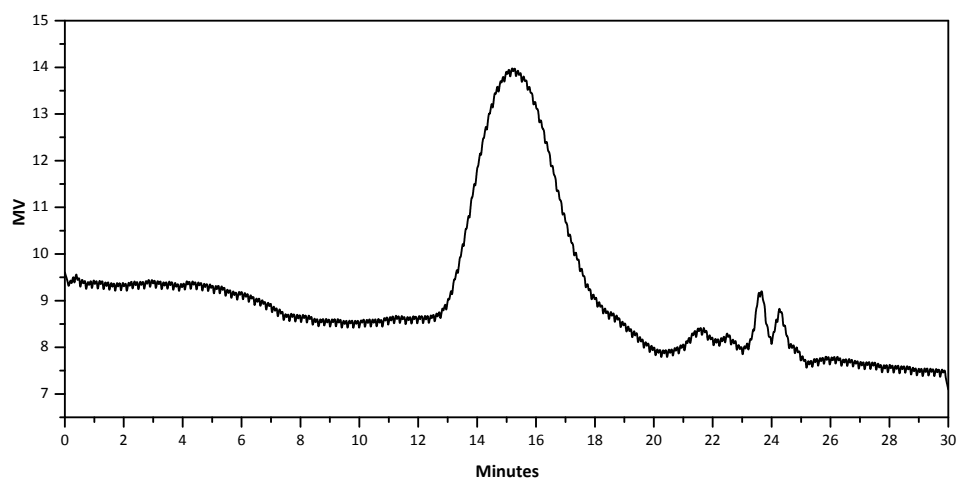
Figure S43. GPC curve of poly(EPI) obtained by cationic species generated from complex **6** in Table 2, entry 13.



Broad Unknown Relative Peak Table

	Distributionn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		199223	875215	571035	2776701	4.39314	3.17259

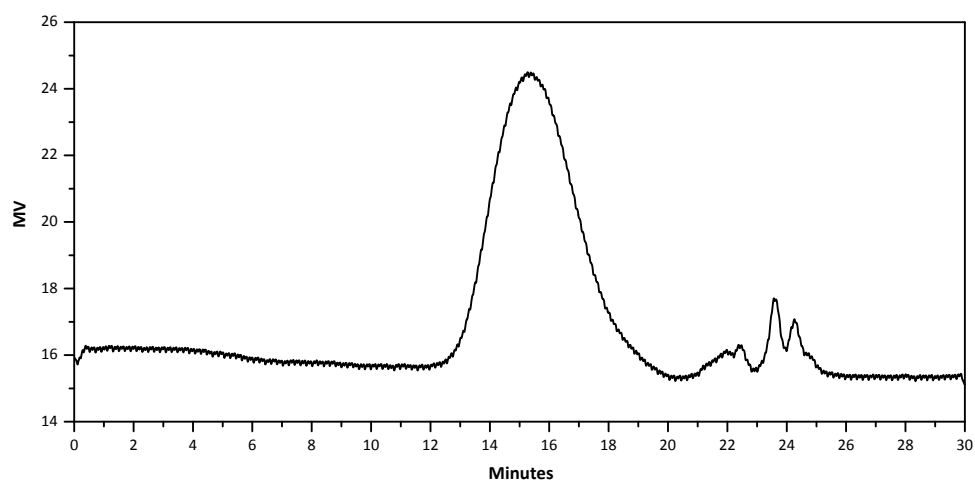
Figure S44. GPC curve of poly(EPI) obtained by cationic species generated from complex **4** in Table 2, entry 14.



Broad Unknown Relative Peak Table

	Distributionnn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		208704	977719	631833	2786802	4.68472	2.85031

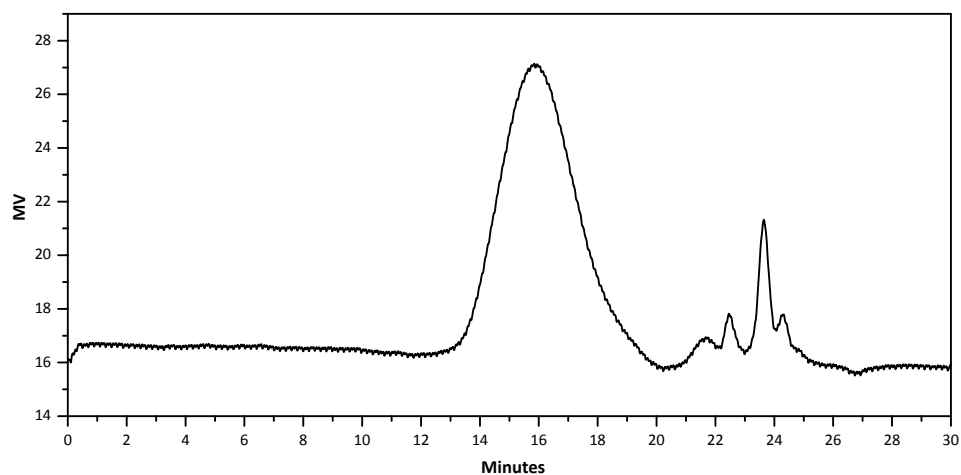
Figure S45. GPC curve of poly(EPI) obtained by cationic species generated from complex **4** in Table 2, entry 15.



Broad Unknown Relative Peak Table

	Distributionnn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		214597	935917	627736	2847507	4.36128	3.04248

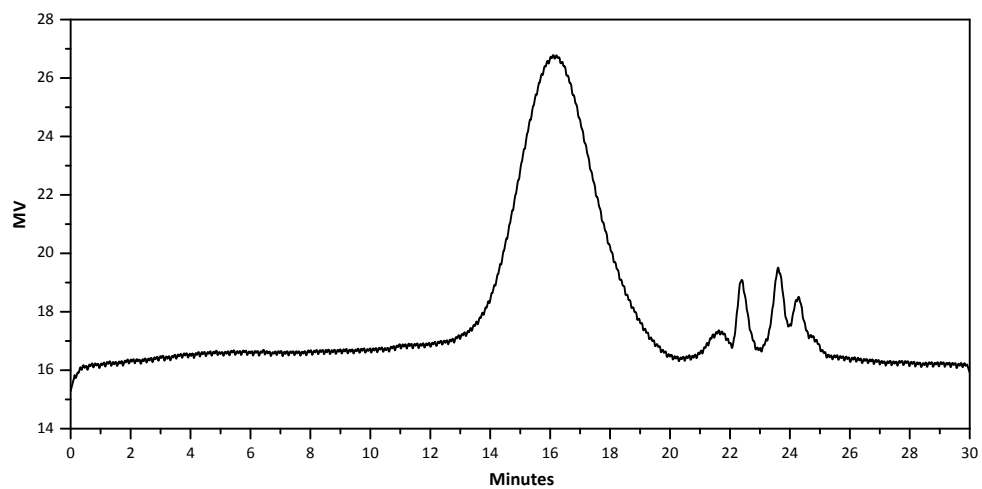
Figure S46. GPC curve of poly(EPI) obtained by cationic species generated from complex **4** in Table 2, entry 16.



Broad Unknown Relative Peak Table

	Distributionnn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		146356	533029	311251	1424117	3.64200	2.67174

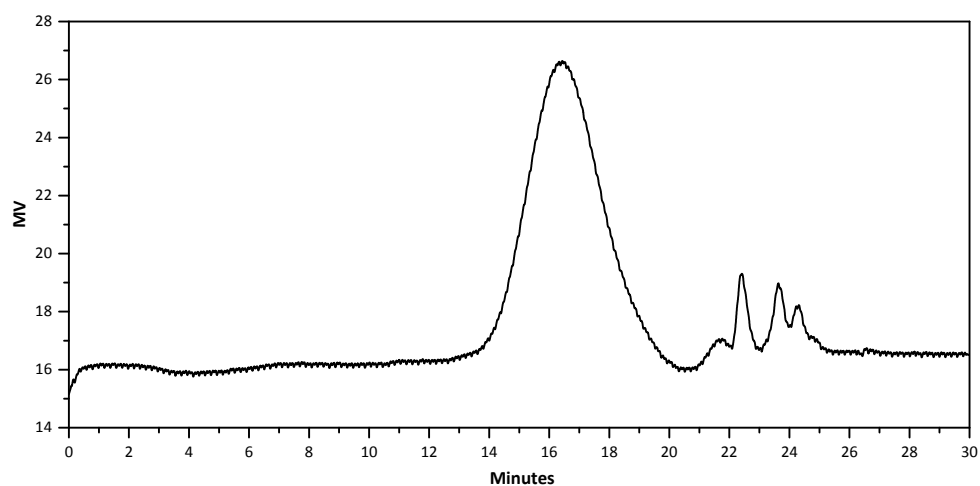
Figure S47. GPC curve of poly(EPI) obtained by cationic species generated from complex **4** in Table 2, entry 17.



Broad Unknown Relative Peak Table

	Distributionnn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		136785	467461	247944	1536530	3.41749	3.28697

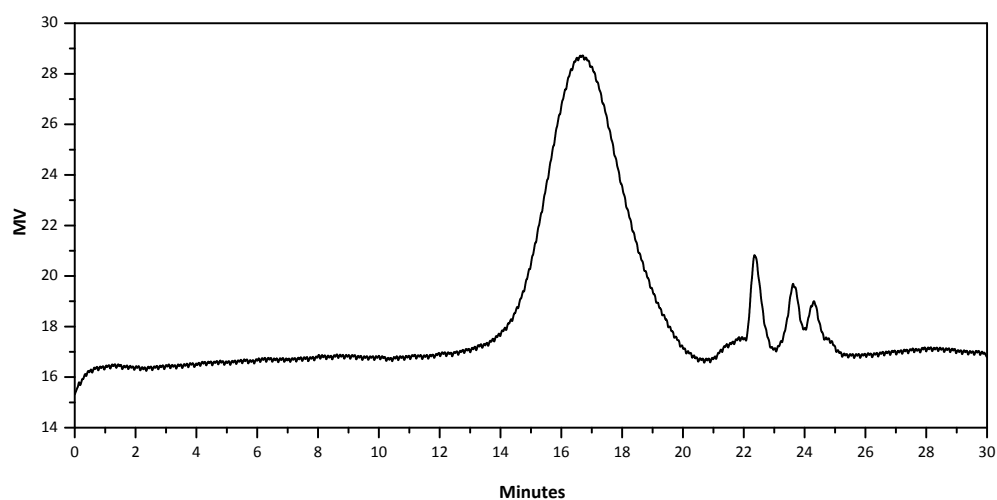
Figure S48. GPC curve of poly(EPI) obtained by cationic species generated from complex **4** in Table 2, entry 18.



Broad Unknown Relative Peak Table

	Distributiononn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		102852	350891	196523	1167821	3.41161	3.32816

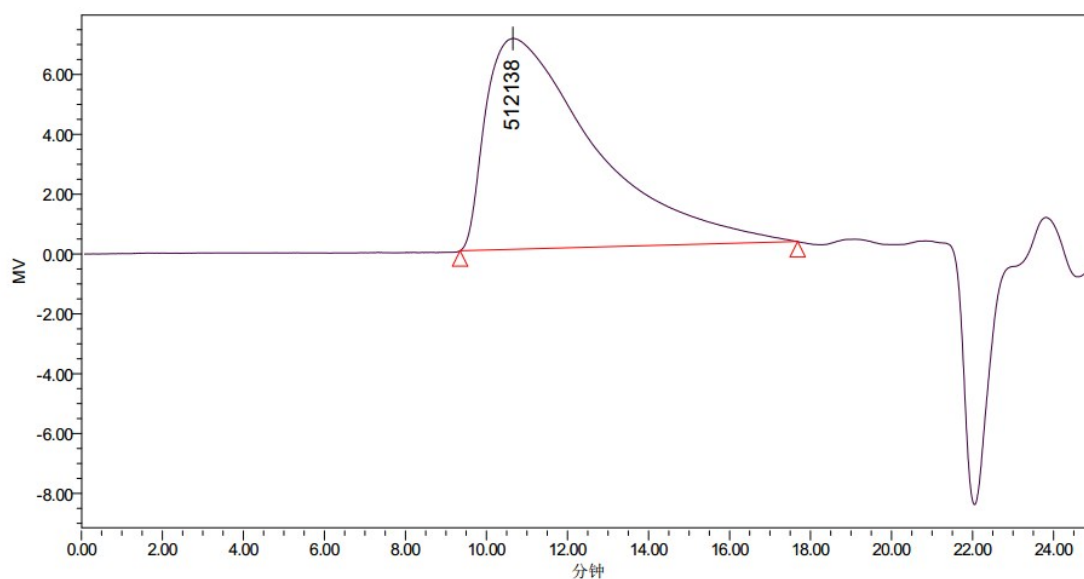
Figure S49. GPC curve of poly(EPI) obtained by cationic species generated from complex **4** in Table 2, entry 19.



Broad Unknown Relative Peak Table

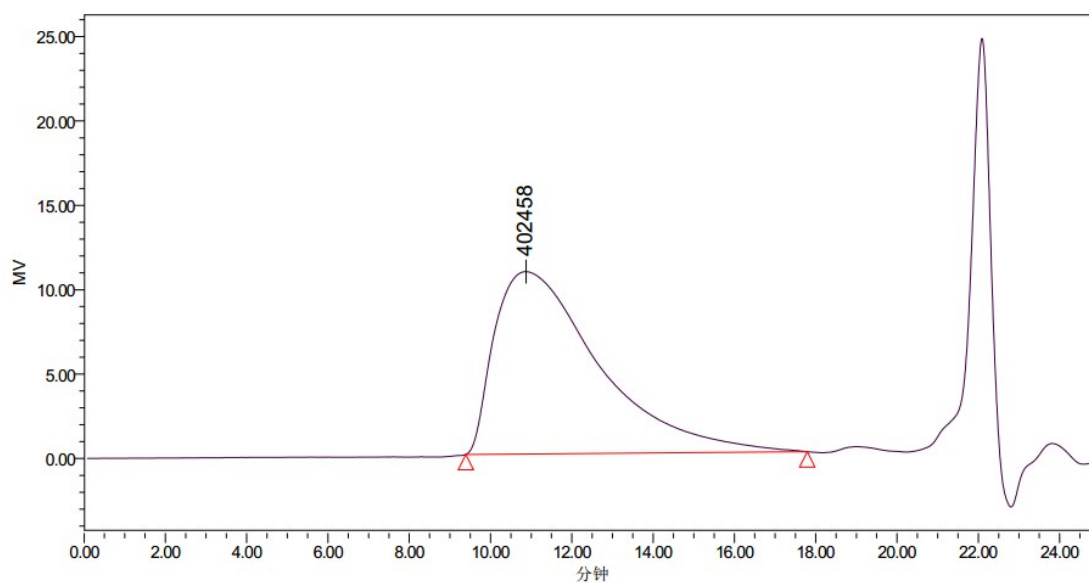
	Distributiononn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		80949	261523	164500	737604	3.23071	2.82042

Figure S50. GPC curve of poly(EPI) obtained by cationic species generated from complex **4** in Table 2, entry 20.



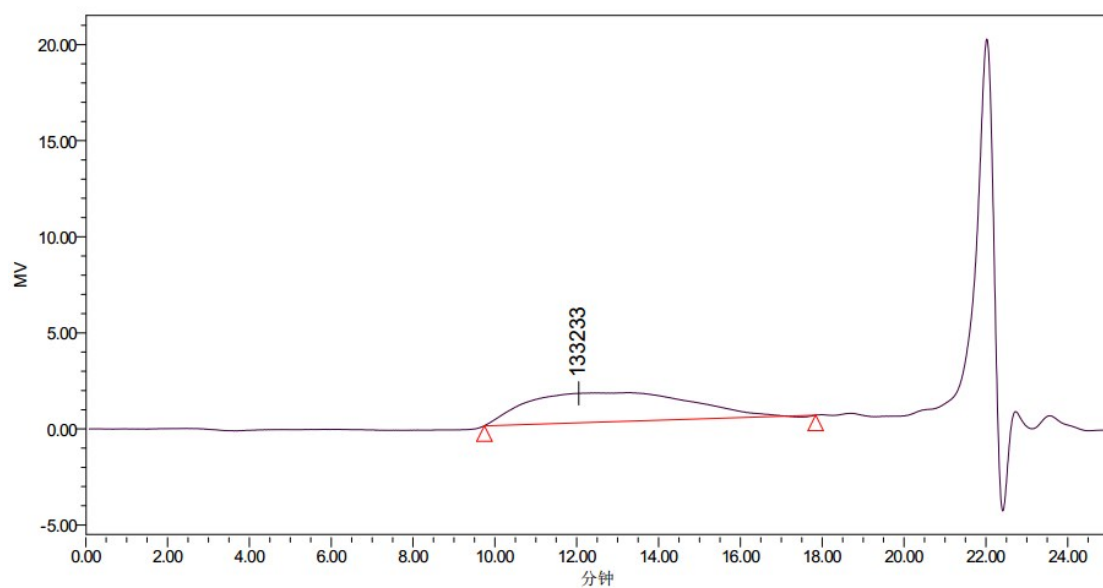
GPC Results										
	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		10.650	10.650	10.650	75512	346257	512138	721389	1007307	2.083391

Figure S51. GPC curve of poly(D-IMCI) obtained by cationic species generated from complex **1** in Table 2, entry 23.



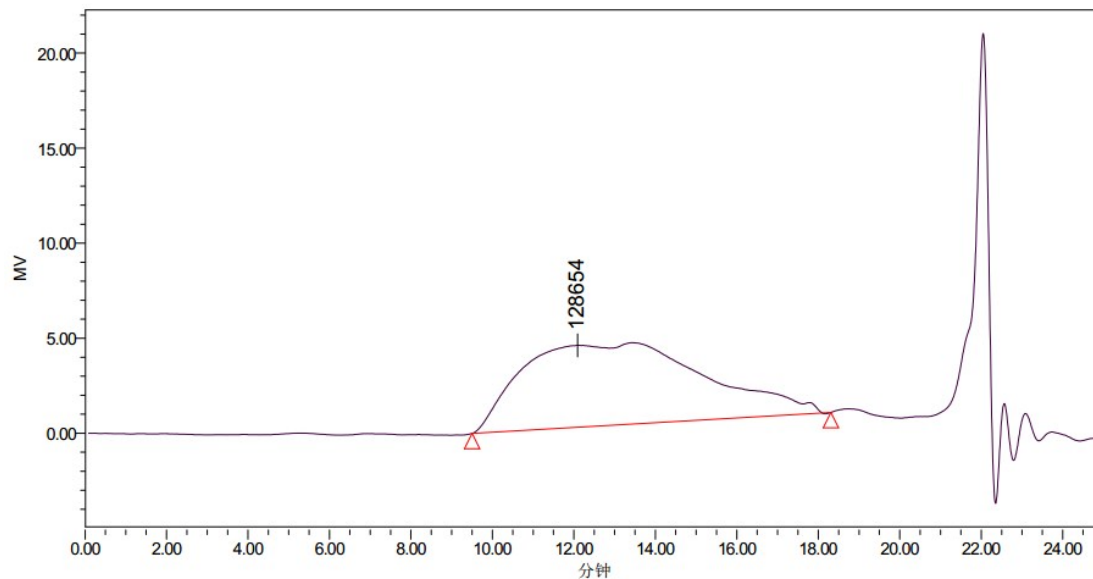
GPC Results										
	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		10.875	10.875	10.875	86647	331205	402458	663523	937248	2.003358

Figure S52. GPC curve of poly(L-IMCI) obtained by cationic species generated from complex **1** in Table 2, entry 24.



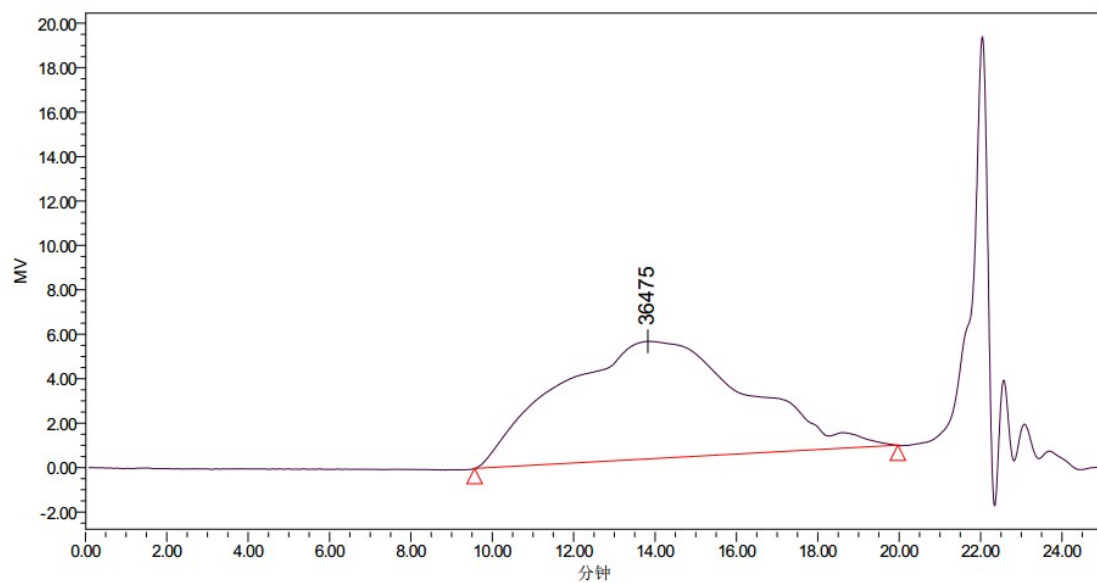
GPC Results										
	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		12.050	12.050	12.050	43780	157629	133233	419752	661966	2.662921

Figure S53. GPC curve of poly(ITPB) obtained by cationic species generated from complex **1** in Table 2, entry 22.



GPC Results										
	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		12.092	12.092	12.092	29048	155603	128654	488892	803357	3.141924

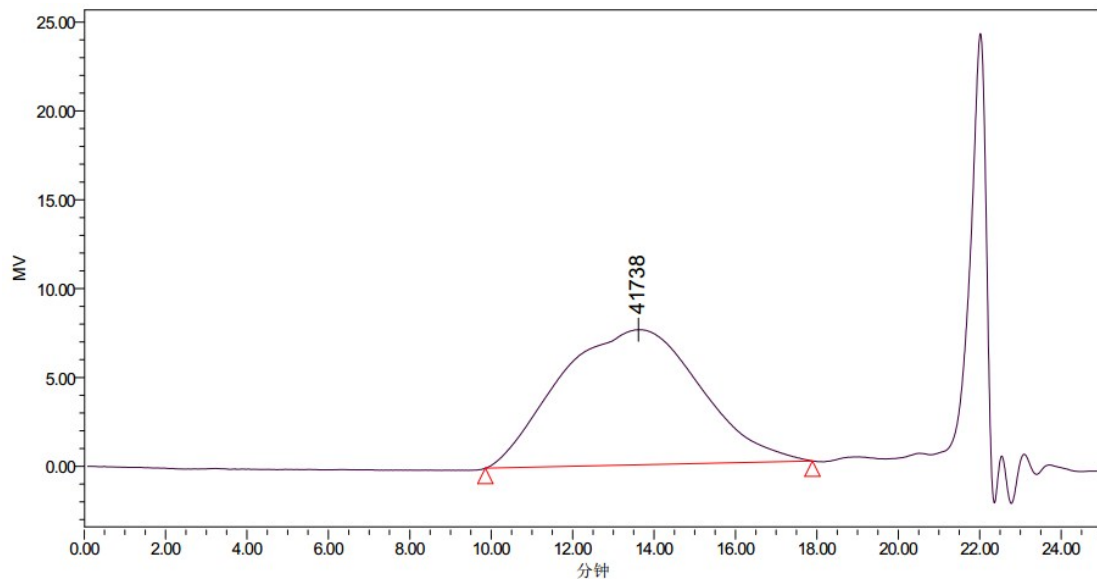
Figure S54. GPC curve of poly(D-IMCI-co-ITPB) obtained by cationic species generated from complex **1** in Table 3, entry 1.



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		13.825	13.825	13.825	15075	97771	36475	394595	708469	4.035921	7.246221

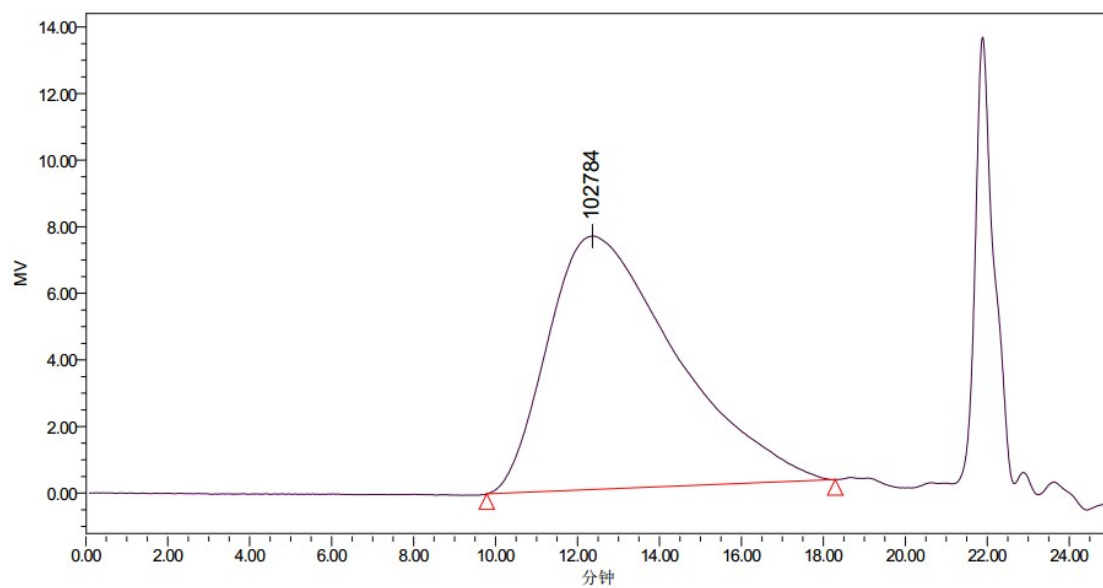
Figure S55. GPC curve of poly(D-IMCI-*co*-ITPB) obtained by cationic species generated from complex **1** in Table 3, entry 2.



GPC Results

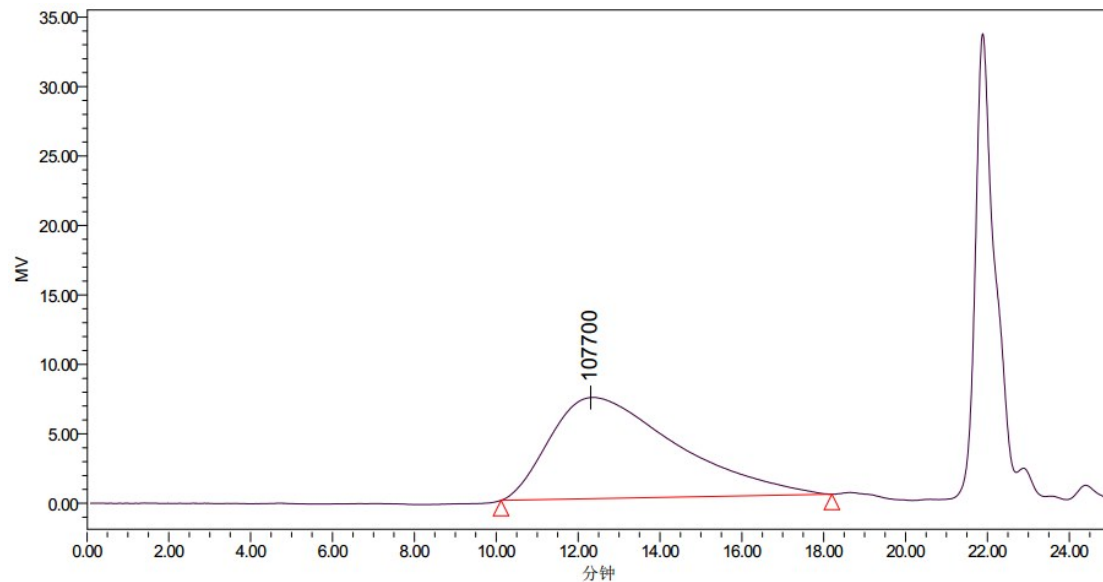
	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		13.617	13.617	13.617	32345	91892	41738	248529	452275	2.704592	4.921830

Figure S56. GPC curve of poly(D-IMCI-*co*-ITPB) obtained by cationic species generated from complex **1** in Table 3, entry 3.



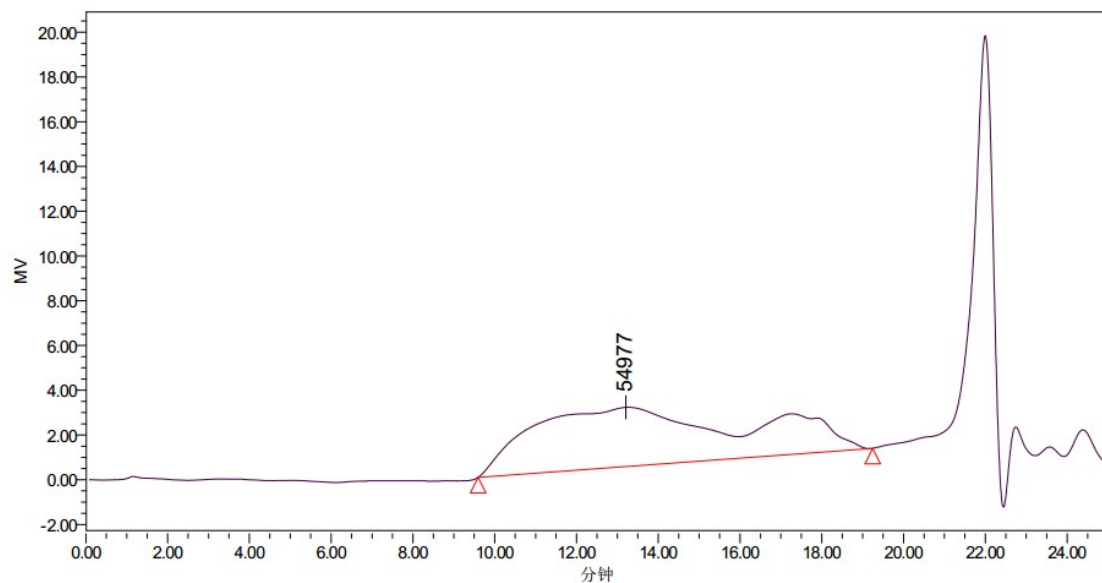
GPC Results										
	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		12.367	12.367	12.367	35782	106977	102784	243626	414967	2.277381

Figure S57. GPC curve of poly(D-IMCI-*co*-ITPB) obtained by cationic species generated from complex **1** in Table 3, entry 4.



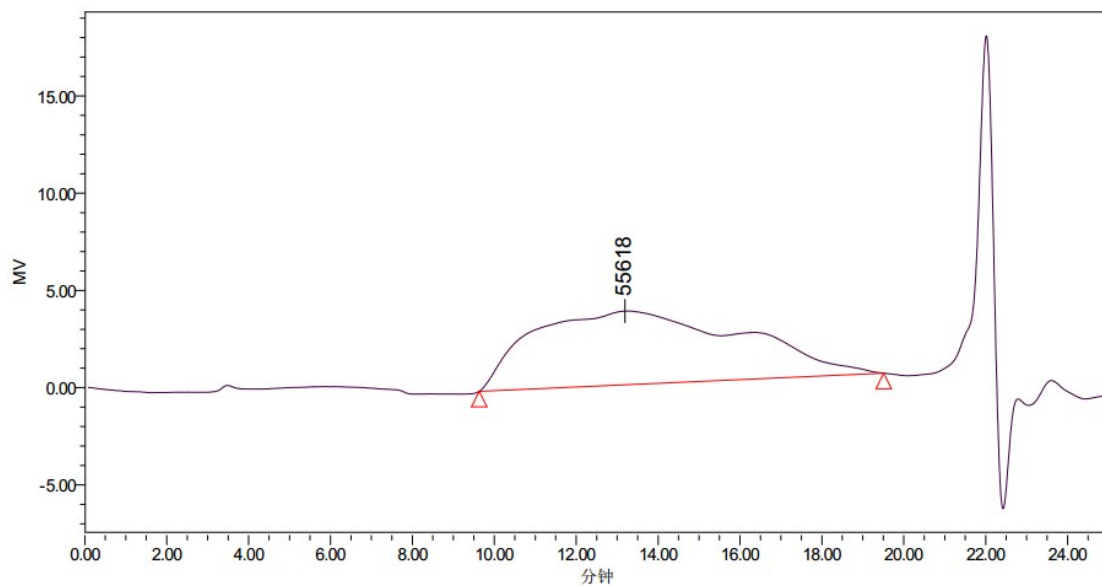
GPC Results										
	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		12.308	12.308	12.308	35044	101180	107700	213848	336401	2.113530

Figure S58. GPC curve of poly(D-IMCI-*co*-ITPB) obtained by cationic species generated from complex **1** in Table 3, entry 5.



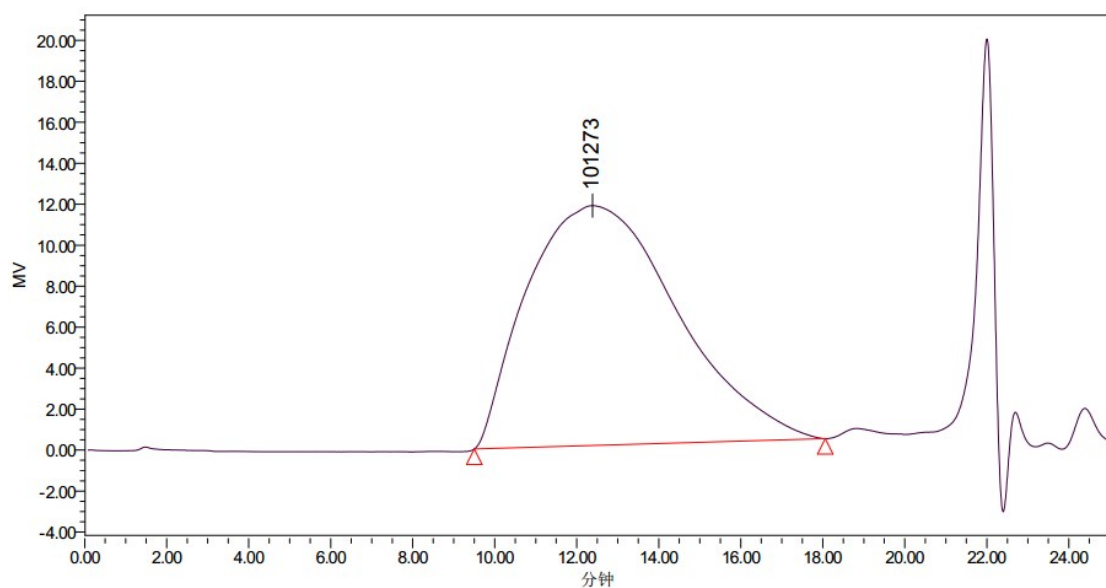
GPC Results											
	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		13.208	13.208	13.208	14280	133062	54977	484794	786000	3.643381	5.907034

Figure S59. GPC curve of poly(L-IMCI-co-ITPB) obtained by cationic species generated from complex **1** in Table 3, entry 6.



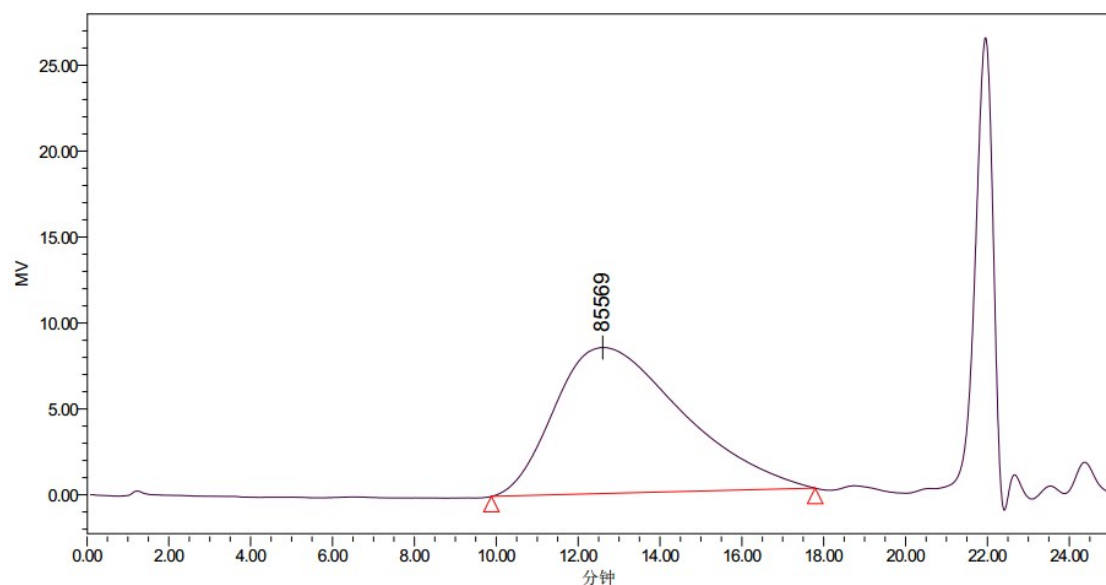
GPC Results											
	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		13.192	13.192	13.192	17350	129183	55618	459582	739952	3.557611	5.727952

Figure S60. GPC curve of poly(L-IMCI-co-ITPB) obtained by cationic species generated from complex **1** in Table 3, entry 7.



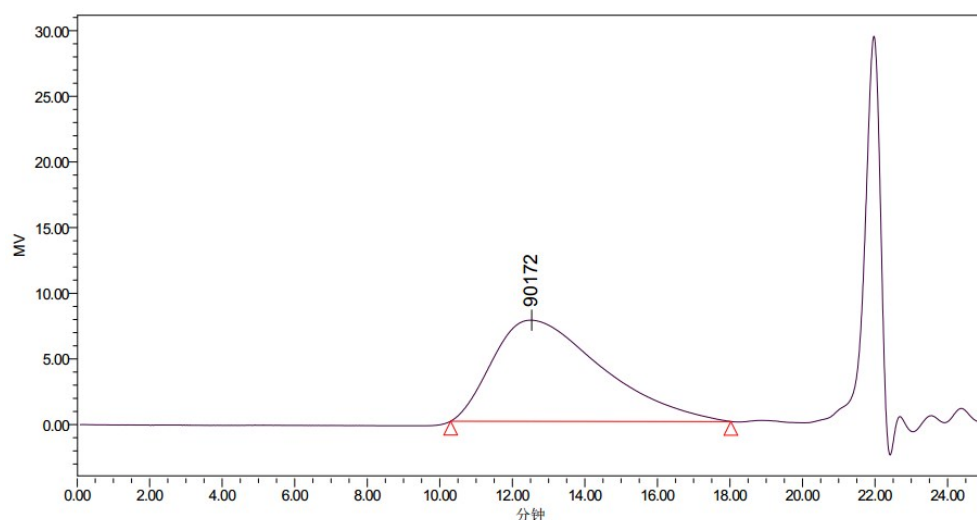
GPC Results										
	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		12.385	12.385	12.385	42752	166248	101273	465558	778076	2.800381

Figure S61. GPC curve of poly(L-IMCI-co-ITPB) obtained by cationic species generated from complex **1** in Table 3, entry 8.



GPC Results											
	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		12.601	12.601	12.601	35762	96881	85569	220376	384028	2.274711	3.963911

Figure S62. GPC curve of poly(L-IMCI-co-ITPB) obtained by cationic species generated from complex **1** in Table 3, entry 9.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		12.533	12.533	12.533	35216	91283	90172	183252	282764	2.007528	3.097679

Figure S63. GPC curve of poly(L-IMCI-*co*-ITPB) obtained by cationic species generated from complex **1** in Table 3, entry 10.

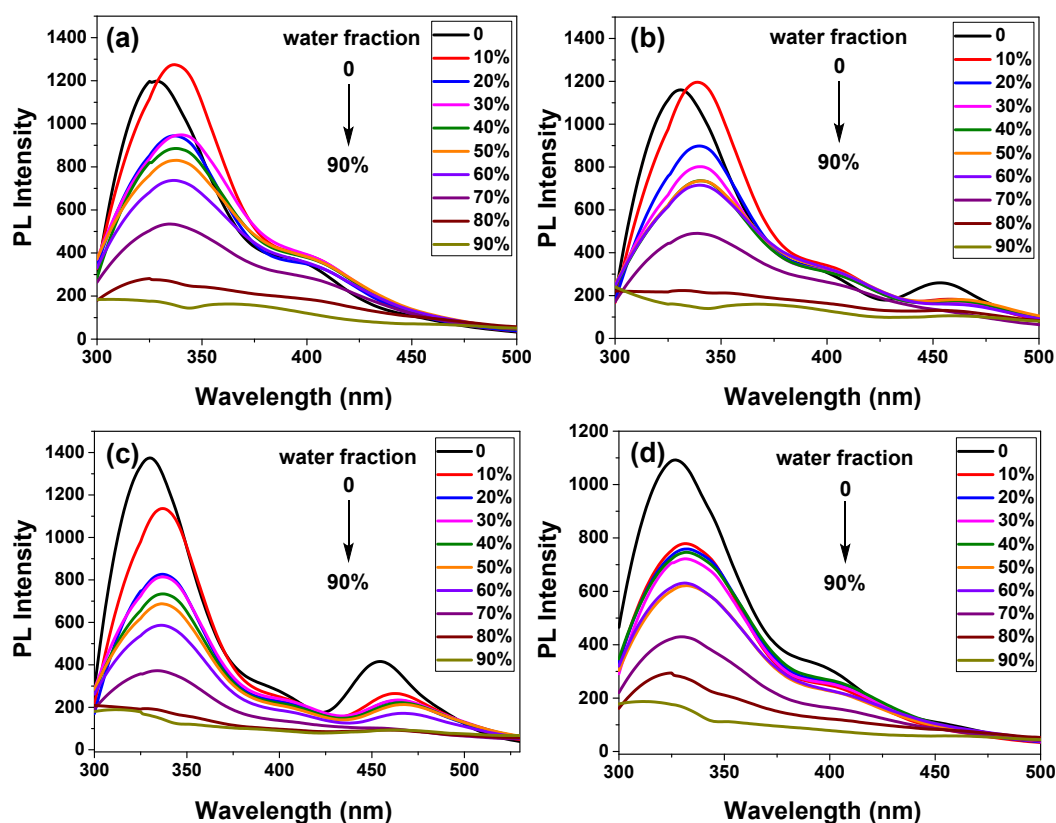


Figure S64. Plots of fluorescence intensity vs water fraction in THF/water mixture (0.01 mg/mL). (a) poly(D-IMCI-*co*-ITPB) (Table 3, entry 2), (b) poly(D-IMCI-*co*-ITPB) (Table 3, entry 3), (c) poly(D-IMCI-*co*-ITPB) (Table 3, entry 5), (d) poly(L-IMCI-*co*-ITPB) (Table 3, entry 6) (conditions: EX wavelength: 290 nm, EX slit: 5 nm, EM slit: 5 nm, 700 V).

Table S2. X-ray diffraction experimental details for complexes **1-3** and **6**.

	1	2	3	6
Empirical formula	C ₂₆ H ₄₉ O ₃ Si ₂ Sc	C ₂₆ H ₄₉ O ₃ Si ₂ Y	C ₂₆ H ₄₉ O ₃ Si ₂ Lu	C ₂₈ H ₅₃ O ₃ Si ₂ Lu
Formula weight	510.79	554.74	640.80	668.85
Temperature (K)	153.15	173.15	153.15	173.15
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	P2 ₁	P2 ₁	P2 ₁	P2 ₁ /n
a (Å)	8.2245(16)	8.2000(16)	8.2286(16)	13.3321(6)
b (Å)	17.776(4)	18.000(4)	17.857(4)	15.5971(7)
c (Å)	10.845(2)	10.900(2)	10.889(2)	16.0371(7)
α (°)	90	90	90	90
β (°)	109.79(3)	109.60(3)	109.76(3)	104.6700(10)
γ (°)	90	90	90	90
Volume (Å ³)	1491.8(6)	1515.6(5)	1505.8(6)	3226.1(2)
Z	2	2	2	4
Calc. ρ (g/cm ³)	1.137	1.216	1.413	1.377
μ(mm ⁻¹)	0.350	2.025	3.380	3.158
Crystal size (mm ³)	0.26 × 0.24 × 0.23	0.45 × 0.43 × 0.42	0.27 × 0.26 × 0.24	0.45 × 0.43 × 0.42
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection (°)	5.264 to 55.002	4.52 to 50.02	5.26 to 54.978	5.224 to 55.112
Goodness-of-fit on F ²	1.050	0.893	1.062	1.130
R1, wR2 [I>=2σ (I)]	0.0484, 0.1156	0.0279, 0.0587	0.0389, 0.0913	0.0233, 0.0606
Flack parameter	0.02(2)	-0.030(6)	0.019(9)	-