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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**Table S2.** X-ray diffraction experimental details for complexes 1-3 and 6.
**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. H$_2$SO$_4$ (250 mmol) at room temperature. The mixture was refluxed for 6 h, cooled to room temperature, neutralized with a saturated K$_2$CO$_3$ aqueous solution and extracted with ethyl acetate (3 × 70 mL), the combined organic phases were washed with brine (2 × 50 mL), dried over Na$_2$SO$_4$ 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). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 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$_2$CO$_3$ (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$_2$CO$_3$ 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 Na$_2$SO$_4$ and concentrated under reduced pressure, the residue was purified by column chromatography (neutral Al$_2$O$_3$, 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 (400 MHz, CDCl$_3$): $\delta$ 1.40 (t, $J$ = 7.2 Hz, 3H), 4.39 (q, $J$ = 7.2 Hz, 2H), 7.43 (d, $J$ = 8.4 Hz, 2H), 8.08 (dt, $J$ = 2.0, 8.8 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 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 CH$_2$Cl$_2$ (200 mL) and washed with saturated aqueous Na$_2$CO$_3$
(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 (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 7.02-7.13 (m, 18H), 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 (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 dichloromethane (30 mL) and washed with 1 N HCl, saturated NaHCO$_3$ aqueous solution and brine, the separated organic layer was dried over anhydrous Na$_2$SO$_4$ 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 (400 MHz, CDCl$_3$): $\delta$ 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 (400 MHz, CDCl$_3$): $\delta$ 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$_2$CO$_3$ (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
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 x 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, 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 (4R,4'R,4''R,5'R)-2,2,2',2',2'',2''-hexamethyl-4,4':5',4''-ter(1,3-dioxolane) (L1-b): To a suspension of (2R,3R,4S,5S)-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 5 h, 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 (1R,1'R)-1,1'-((4R,5R)-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 2 h, 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 (1R,1'R)-1,1'-((4R,5R)-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 4 h, 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 8 h. 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, 2H), 1.36 (s, 6H), 1.53-1.57 (m, 3H), 1.68-1.72 (m, 2H), 3.75 (s, 2H).

Synthesis of (3aS,4R,8R,8aS)-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 (3aR,4R,8R,8aR)-2,2,4,8-tetramethyl-3a,5,8,8a-tetrahydro-4H-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 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 (352 mg, 69% yield).

**Synthesis of the Sc complex (1):** To a solution of Sc(CH₃SiMe₃)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, CH₃Si(CH₃)₃), -0.14 (s, 3H, CH₂Si(CH₃)₃), 0.28 (s, 18H, CH₂Si(CH₂)₃), 1.11 (br, 4H, THF-β-CH₂), 1.38 (m, 3H, CH₃), 1.48 (m, 6H, CH₂), 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(CH₂)), 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(CH₂)₂), 0.29 (s, 18H, CH₂Si(CH₂)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, CH(CH₃)₂), 3.43 (br, 4H, THF-α-CH₂), 3.61 (m, 1H, CH(CH₃)₂), 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, CH₂Si(CH₃)₃), -0.70 (d, J = 11.6 Hz, 2H, CH₂Si(CH₃)₃), 0.30 (s, 18H, CH₂Si(CH₃)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, CH(CH₃)₂), 3.63 (m, 1H, CH(CH₃)₂), 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 (4R,5S)-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'-(((4R,5S)-2,2-dimethyl-1,3-dioxolane-4,5-diyi)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 NH₄Cl was added slowly, and the mixture was extracted with ethyl acetate (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 (silical gel, 4:1 hexane to ethyl acetate, v/v) to afford a white solid (5.6 g, 95% yield).

**Synthesis of (3aR,8aS)-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 × 100 mL), the combined organic layers were dried over anhydrous Na₂SO₄, and the residue was dissolved in a mixture solvents of toluene and hexane (toluene/hexane = 3/1, v/v) at -30 °C to afford complex 4 (285 mg, 53% yield).

**Synthesis of (3aR,8aS)-2,2,4,4,8,8-hexamethyl-3a,5,8,8a-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 cooled to 0 °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 × 100 mL), the combined organic layers were dried over anhydrous Na₂SO₄, 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).

**Synthesis of the Sc complex (4):** 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 (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).
Hz, 1H, CpH), 6.36 (t, J = 2.8 Hz, 1H, CpH); \(^{13}C\) NMR (100 MHz, \(CD_2Cl_2\)): \(\delta\) 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 \(Y(CH_2SiMe_3)_2(THF)_2\) (495 mg, 1.0 mmol) in toluene (3 mL) was added a toluene (3 mL) solution of complex \(L_1f\) (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, \(CD_2Cl_2\)): \(\delta\) -0.61 (dd, \(J = 3.2, 11.2\) Hz, 2H, \(CH_2Si(CH_2)3\)), -0.48 (dd, \(J = 3.2, 11.2\) Hz, 2H, \(CH_2Si(CH_2)3\)), 0.28 (s, 18H, \(CH_2Si(CH_2)3\)), 1.25 (br, 8H, THF-\(\beta\)-CH\(_2\)), 1.36 (s, 3H, C(CH\(_2\)2)), 1.48 (s, 3H, C(CH\(_2\)2)), 1.52 (s, 6H, C(CH\(_2\)2)), 1.61 (s, 3H, C(CH\(_2\)2)), 1.63 (s, 3H, C(CH\(_2\)2)), 3.63 (br, 8H, THF-\(\alpha\)-CH\(_2\)), 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, \(CD_2Cl_2\)): \(\delta\) 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 \(Lu(CH_2SiMe_3)_2(THF)_2\) (581 mg, 1.0 mmol) in toluene (3 mL) was added a toluene (3 mL) solution of complex \(L_1f\) (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, \(CD_2Cl_2\)): \(\delta\) -0.78 (d, \(J = 11.2\) Hz, 2H, \(CH_2Si(CH_2)3\)), -0.63 (d, \(J = 11.6\) Hz, 2H, \(CH_2Si(CH_2)3\)), 0.30 (s, 18H, \(CH_2Si(CH_2)3\)), 1.06 (t, \(J = 6.4\) Hz, 4H, THF-\(\beta\)-CH\(_2\)), 1.41 (s, 3H, C(CH\(_2\)2)), 1.49 (s, 3H, C(CH\(_2\)2)), 1.55 (s, 6H, C(CH\(_2\)2)), 1.65 (s, 3H, C(CH\(_2\)2)), 1.68 (s, 3H, C(CH\(_2\)2)), 3.45 (t, \(J = 6.4\) Hz, 4H, THF-\(\alpha\)-CH\(_2\)), 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, \(CD_2Cl_2\)): \(\delta\) 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, 0.2 µmol) in 1,1,2,2-tetrachloroethane (2 mL), then \(\text{[Ph}_3\text{C][B(C}_6\text{F}_3)_4]\) (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 \(\text{[Ph}_3\text{C][B(C}_6\text{F}_3)_4]\) (2.2 mg, 2.3µmol) was added, the resulting mixture was stirred at 25 °C for 5 min, then a solution of \((\text{I}_{2}, \text{R}_{2}, \text{SS})\)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (66 mg, 0.23 mmol) and 4-isocynano-4ʹ-(1,2,2-triphenylvinyl)-1,1ʹ-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:

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

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 \(\beta\)-H of the aryl ring of IMCI units. \(I_{H2}\) is the integration of the peak at 5.82 ppm which assigned to the \(\alpha\)-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 isopropy.

**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

<table>
<thead>
<tr>
<th>Entry</th>
<th>Comp. (μmol)</th>
<th>Activator (μmol)</th>
<th>[Mon.]/[Com.]</th>
<th>Mon.</th>
<th>Solvent</th>
<th>Temp. (°C)</th>
<th>Time (min.)</th>
<th>Yield (%)</th>
<th>Act. (kg mol⁻¹ h⁻¹)</th>
<th>M₅/z (10⁴)</th>
<th>M₅/M₀ (°)</th>
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<td>a</td>
<td>PhCl</td>
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<td>1</td>
<td>54</td>
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<td>16.9</td>
<td>3.90</td>
<td></td>
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<tr>
<td>2</td>
<td>B</td>
<td>100:1</td>
<td>a</td>
<td>PhCl</td>
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<td>180</td>
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<td>1.22</td>
<td>13.0</td>
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</tr>
<tr>
<td>3</td>
<td>C</td>
<td>100:1</td>
<td>a</td>
<td>PhCl</td>
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<td>720</td>
<td>8</td>
<td>0.12</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
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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⁻¹ h⁻¹. e Determined by GPC in CHCl₃ at 25 °C against polystyrene standard.
**Figure S1.** Photos of solubility of poly(D-IMCl) (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-IMCl-co-ITPB)s (Table 3, entries 1-5) (c-g) and poly(L-IMCl-co-ITPB)s (Table 3, entries 6-10) (h-l) in THF.
Figure S3. $^1$H NMR spectrum of 4-ethoxycarbonyl phenyl isocyanide (a).

Figure S4. $^{13}$C NMR spectrum of 4-ethoxycarbonyl phenyl isocyanide (a).
Figure S5. $^1$H NMR spectrum of 2-naphthyl isocyanide (b).

Figure S6. $^{13}$C NMR spectrum of 2-naphthyl isocyanide (b).
Figure S7. $^1$H NMR spectrum of 4-isocyano-4'-{(1,2,2-triphenylvinyl)}-1,1'-biphenyl (c).

Figure S8. $^{13}$C NMR spectrum of 4-isocyano-4'-{(1,2,2-triphenylvinyl)}-1,1'-biphenyl (c).
Figure S9. $^1$H NMR spectrum of $(1S,2R,5S)$-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (d).

Figure S10. $^{13}$C NMR spectrum of $(1S,2R,5S)$-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (d).
Figure S11. $^1$H NMR spectrum of ($IR,2S,5R$)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (e).

Figure S12. $^{13}$C NMR spectrum of ($IR,2S,5R$)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (e).
Figure S13. $^1$H NMR spectrum of Scandium complex 1.

Figure S14. $^{13}$C NMR spectrum of Scandium complex 1.
Figure S15. $^1$H NMR spectrum of Yttrium complex 2.

Figure S16. $^{13}$C NMR spectrum of Yttrium complex 2.
Figure S17. $^1$H NMR spectrum of Lutetium complex 3.

Figure S18. $^{13}$C NMR spectrum of Lutetium complex 3.
Figure S19. $^1$H NMR spectrum of Scandium complex 4.

Figure S20. $^{13}$C NMR spectrum of Scandium complex 4.
Figure S21. $^1$H NMR spectrum of Yttrium complex 5.

Figure S22. $^{13}$C NMR spectrum of Yttrium complex 5.
Figure S23. $^1$H NMR spectrum of Lutetium complex 6.

Figure S24. $^{13}$C NMR spectrum of Lutetium complex 6.
Figure S25. $^1$H NMR spectrum of cationic Scandium species generated in-situ from complex 1 in THF-d8 at 25 °C.

Figure S26. $^1$H NMR spectra of poly(EPI) (a), poly(ITPB) (b), poly(D-IMCI) (c), poly(L-IMCI) (d) in CHCl$_3$ at 25 °C.
Figure S27. $^1$H 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. $^1$H 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 NI oligomer obtained by complex 1/[Ph3C][B(C6F5)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).
Figure S33. GPC curve of poly(EPI) obtained by cationic species generated from complex 1 in Table 2, entry 1.

Figure S34. GPC curve of poly(EPI) obtained by cationic species generated from complex 1 in Table 2, entry 2.
Figure S35. GPC curve of poly(EPI) obtained by cationic species generated from complex 1 in Table 2, entry 3.

Figure S36. GPC curve of poly(EPI) obtained by cationic species generated from complex 1 in Table 2, entry 4.
**Figure S37.** GPC curve of poly(EPI) obtained by cationic species generated from complex 1 in Table 2, entry 5.

**Figure S38.** GPC curve of poly(EPI) obtained by cationic species generated from complex 1 in Table 2, entry 6.
Figure S39. GPC curve of poly(EPI) obtained by cationic species generated from complex 2 in Table 2, entry 9.

Figure S40. GPC curve of poly(EPI) obtained by cationic species generated from complex 3 in Table 2, entry 10.
Figure S41. GPC curve of poly(EPI) obtained by cationic species generated from complex 4 in Table 2, entry 11.

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**

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<th>Mz  (Daltons)</th>
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<th>Mz/Mw</th>
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**Broad Unknown Relative Peak Table**

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

**Figure S44.** GPC curve of poly(EPI) obtained by cationic species generated from complex 4 in Table 2, entry 14.
**Figure S45.** GPC curve of poly(EPI) obtained by cationic species generated from complex 4 in Table 2, entry 15.

**Figure S46.** GPC curve of poly(EPI) obtained by cationic species generated from complex 4 in Table 2, entry 16.
Figure S47. GPC curve of poly(EPI) obtained by cationic species generated from complex 4 in Table 2, entry 17.

Figure S48. GPC curve of poly(EPI) obtained by cationic species generated from complex 4 in Table 2, entry 18.
**Figure S49.** GPC curve of poly(EPI) obtained by cationic species generated from complex 4 in Table 2, entry 19.

**Figure S50.** GPC curve of poly(EPI) obtained by cationic species generated from complex 4 in Table 2, entry 20.
Figure S51. GPC curve of poly(D-IMCI) obtained by cationic species generated from complex 1 in Table 2, entry 23.

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

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

Figure S54. GPC curve of poly(D-IMCI-co-ITPB) obtained by cationic species generated from complex 1 in Table 3, entry 1.
Figure S55. GPC curve of poly(D-IMCI-co-ITPB) obtained by cationic species generated from complex 1 in Table 3, entry 2.

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

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

**Figure S58.** GPC curve of poly(D-IMCI-co-ITPB) obtained by cationic species generated from complex 1 in Table 3, entry 5.
Figure S59. GPC curve of poly(L-IMCI-co-ITPB) obtained by cationic species generated from complex 1 in Table 3, entry 6.

Figure S60. GPC curve of poly(L-IMCI-co-ITPB) obtained by cationic species generated from complex 1 in Table 3, entry 7.
Figure S61. GPC curve of poly(L-IMCl-co-ITPB) obtained by cationic species generated from complex 1 in Table 3, entry 8.

<table>
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<th>Dist Name</th>
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Figure S62. GPC curve of poly(L-IMCl-co-ITPB) obtained by cationic species generated from complex 1 in Table 3, entry 9.

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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.

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<td>C&lt;sub&gt;26&lt;/sub&gt;&lt;br&gt;H&lt;sub&gt;49&lt;/sub&gt;&lt;br&gt;O&lt;sub&gt;3&lt;/sub&gt;&lt;br&gt;Si&lt;sub&gt;2&lt;/sub&gt;&lt;br&gt;Sc</td>
<td>C&lt;sub&gt;26&lt;/sub&gt;&lt;br&gt;H&lt;sub&gt;49&lt;/sub&gt;&lt;br&gt;O&lt;sub&gt;3&lt;/sub&gt;&lt;br&gt;Si&lt;sub&gt;2&lt;/sub&gt;&lt;br&gt;Y</td>
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<td>C&lt;sub&gt;28&lt;/sub&gt;&lt;br&gt;H&lt;sub&gt;53&lt;/sub&gt;&lt;br&gt;O&lt;sub&gt;3&lt;/sub&gt;&lt;br&gt;Si&lt;sub&gt;2&lt;/sub&gt;&lt;br)Lu</td>
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<td>c (Å)</td>
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<td>MoKα (λ = 0.71073)</td>
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