Supplementary Information

Cationic indium catalysts for ring opening polymerization: Tuning reactivity with hemilabile ligands

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A. Experimental procedures

**General Considerations.** Unless otherwise indicated, all air- and/or water-sensitive reactions were carried out under dry nitrogen using either an MBraun glove box or standard Schlenk line techniques. NMR spectra were recorded on a Bruker Avance 300 MHz, 400 MHz and 600 MHz spectrometers. $^1$H NMR chemical shifts are reported in ppm versus residual protons in deuterated solvents as follows: $\delta$ 7.27 CDCl$_3$, $\delta$ 7.16 C$_6$D$_6$, $\delta$ 7.16 C$_6$D$_5$Br $^{13}$C{$^1$H} NMR chemical shifts are reported in ppm versus residual $^{13}$C in the solvent: $\delta$ 77.2 CDCl$_3$. $^{19}$F{$^1$H} NMR chemical shifts are reported in ppm and externally referenced to neat CFCl$_3$ at 0 ppm. $^{31}$P{$^1$H} NMR chemical shifts are reported in ppm and externally referenced to 85% H$_3$PO$_4$ at 0 ppm.

Diffraction measurements for X-ray crystallography were made on a Bruker X8 APEX II diffraction and a Bruker APEX DUO diffraction with graphite monochromated Mo-K$_\alpha$ radiation. The structures were solved by direct methods and refined by full-matrix least-squares using the SHELXTL crystallographic software of Bruker-AXS. Unless specified, all non-hydrogens were refined with anisotropic displacement parameters, and all hydrogen atoms were constrained to geometrically calculated positions but were not refined.

EA CHN analysis was performed using a Carlo Erba EA1108 elemental analyzer. The elemental composition of unknown samples was determined by using a calibration factor. The calibration factor was determined by analyzing a suitable certified organic standard (OAS) of a known elemental composition.

Polymer molecular weights were determined by triple detection gel permeation chromatography (GPC-LLS) using a Waters liquid chromatograph equipped with a Water 515 HPLC pump, Waters 717 plus autosampler, Waters Styragel columns (4.6 x 300 mm) HR5E, HR4 and HR2, Water 2410 differential refractometer, Wyatt tristar miniDAWN (laser light scattering detector) and a Wyatt ViscoStar viscometer. A flow rate of 0.5 mL min$^{-1}$ was used and samples were dissolved in THF (2 mg mL$^{-1}$). Narrow molecular weight polystyrene standards were used for calibration purposes. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometric analysis of isolated polymers was performed on a Bruker Autoflex MALDI-TOF equipped with a nitrogen laser (337 nm). The accelerating potential of the Bruker instrument was 19.5 kV. The polymer samples were dissolved in tetrahydrofuran (ca. 1 g/mL). The concentration of a cationization agent, sodium trifluoroacetate, in tetrahydrofuran was 1 mM. The matrix used was trans-[3-(4-tert-butylphenyl)2-methyl-2-propenylidene]malononitrile (DCTB) at the concentration of 20 mg/mL. A sample solution was prepared by mixing polymer, matrix, and salt in a volume ratio of 5:5:1, respectively.

**Materials.** Solvents (THF, pentane, toluene, hexane and diethyl ether) were collected from a Solvent Purification System from Innovative Technology, Inc. whose columns were packed with activated alumina. CDCl$_3$ was dried over CaH$_2$, collected by vacuum distillation and degassed through a series of freeze-pump-thaw cycles. Dimethylanilinium Tetrakis(3,5-bis(trifluoromethyl)phenyl)borate ([HNMe$_2$Ph][BAR$_F^8$]) was generated by reacting dimethylanilinium chloride with sodium BAR$_F^8$ in diethyl ether at room temperature for 4 h.$^1$ The solvent was removed under high vacuum, and addition of hexane to the residual precipitated a
white solid. The white solid was isolated by vacuum filtration and dried in vacuo for 4 h. InCl₃ was purchased from Stem Chemicals and used without further purification. Isobutylmagnesium chloride (2.0 M in Et₂O) and dimethylanilinium chloride ([HNMe₂Ph]Cl) were purchased from Aldrich and Alfa Aesar, respectively, and used as received. Rac-lactide was recrystallized 3 times from dry toluene and dried under vacuum. ε-caprolactone were dried over CaH₂, distilled and stored under molecular sieves. In(Bu)₃ was synthesized according to a previously reported procedure.² Proligands Lₐ-d were synthesized by the modification of a previously reported procedure.³

**Synthesis of proligand Lₐ**

(±)- trans-N-(thiophen-2-ylmethyl)cyclohexane-1,2-diamine (4.38 g, 20.8 mmol) was dissolved in 50 ml of acetonitrile (ACN) and 3,5-dicumylsalicylaldehyde (7.45 g, 32.3 mmol) was added while stirring. The solution was heated under reflux for 8 hours, and the solvent was removed under reduced pressure. The residue was dissolved in a minimum amount of ethyl acetate and crystallized by slow evaporation at low temperature to yield a yellow solid (yield 63%). HRMS [M+H]⁺ calculated m/z = 551.3096. Found m/z = 551.3100. ¹H NMR (400 MHz, CDCl₃, 25 °C) δ 13.23 (1H, br. s., Ar-OH), 8.33 (1H, s, -N=CH-Ar), 7.03 - 7.41 (11H, m, ArH), 7.05 (1H, s, ArH), 7.13 (1H, m, Thioph α), 6.89 (1H, m, Thioph β), 6.74 (1H, m, Thioph γ), 3.97 (1H, d, JH,H = 14 Hz, -CH₂ of thiophenyl), 3.86 (1H, d, JH,H = 14 Hz, -CH₂ of thiophenyl), 2.95 (1H, m, -CH- of DACH), 2.63 (1H, m, -CH- of DACH), 1.02 - 1.74 (17H, m, -CH₂ of DACH and -CH₃ of cumyl), ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 165.7 (N=CH-Ar), 157.8 (Ar C), 150.9 (Ar C), 139.8 (Ar C), 129.2 (Ar C-H), 128.2 (Ar C-H), 128.1 (Ar C-H), 126.9 (Ar C-H), 125.0 (Ar C-H), 124.3 (Thioph α), 126.8 (Thioph β), 125.2 (Thioph γ), 74.4 (C-H of DACH), 59.5 (C-H of DACH), 42.8 (-CH₂ of thiophenyl) 31.1 (-CH₃ of cumyl), 30.0 (-CH₃ of cumyl), 29.3 (-CH₃ of cumyl).

**Synthesis of proligand Lₐ**

(±)- trans-N-(furan-2-ylmethyl)cyclohexane-1,2-diamine (6.28 g, 32.3 mmol) was dissolved in 100 ml of acetonitrile (ACN) and 3,5-dicumylsalicylaldehyde (11.6 g, 32.3 mmol) was added while stirring. The solution was heated under reflux for 8 hours, and the solvent was removed under reduced pressure. The residue was dissolved in a minimum amount of hot hexane and crystallized by slow evaporation at low temperature to yield a yellow solid (yield 61%). HRMS [M+H]⁺ calculated m/z = 535.3325. Found m/z = 535.3334. ¹H NMR (400 MHz, CDCl₃, 25 °C) δ 13.22 (1H, br. s., Ar-OH), 8.35 (1H, s, -N=CH-Ar), 7.02 - 7.43 (11H, m, ArH), 7.07 (1H, s, ArH), 7.16 (1H, m, furan α), 6.24 (1H, m, furan β), 5.98 (1H, m, furan γ), 3.73 (1H, d, JH,H = 15 Hz, -CH₂- of furfuryl), 3.69 (1H, d, JH,H = 15 Hz, -CH₂- of furfuryl), 2.95 (1H, m, -CH- of DACH), 2.57 (1H, m, -CH- of DACH), 1.06 - 2.12 (17H, m, -CH₂- of DACH and -CH₃ of cumyl), ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 165.8 (N=CH-Ar), 157.8 (Ar C), 153.8 (Ar C), 150.8 (Ar C), 139.8 (Ar C), 136.2 (Ar C), 142.0 (Ar C-H), 128.2 (Ar C-H), 128.1 (Ar C-H), 126.9 (Ar C-H), 125.2 (Furan β), 110.1 (Furan β), 107.0 (Furan γ), 74.2 (C-H of DACH), 59.3 (C-H of DACH), 43.1 (-CH₂- of furfuryl), 31.1 (-CH₃ of cumyl), 29.8 (-CH₃ of cumyl), 29.2 (-CH₃ of cumyl).

**Synthesis of proligand Lₐ**

(±)- trans-N-(pyridin-2-ylmethyl)cyclohexane-1,2-diamine (7.54 g, 36.8 mmol) was dissolved in 100 ml of acetonitrile (ACN) and 3,5-dicumylsalicylaldehyde (13.2 g, 36.8 mmol) was added while stirring. The solution was heated under reflux for 8 hours, and the solvent was removed under reduced pressure. The residue was dissolved in a minimum amount of hot pentane and crystallized by slow evaporation at low temperature to yield a bright yellow solid (yield 64%). HRMS [M+H]⁺ calculated m/z = 546.3484. Found m/z = 546.3483. ¹H NMR (400 MHz, CDCl₃, 25 °C) δ 8.37 (1H, s, -N=CH-Ar), 7.03 - 7.41 (12H, m, ArH),
7.42 (1H, m, Pyr. α), 7.08 (1H, m, Pyr β), 8.25 (1H, m, Pyr γ), 7.01 (1H, m, Pyr δ), 3.88 (1H, d, \(J_{HH} = 15\) Hz, -CH₂- of pyridyl), 3.82 (1H, d, \(J_{HH} = 15\) Hz, -CH₂- of pyridyl), 3.05 (1H, m, -CH- of DACH), 2.52 (1H, m, -CH- of DACH), 1.09 – 2.14 (20H, m, -CH₂- of DACH and -CH₃ of cumyl), 13C (¹H) NMR (101 MHz, CDCl₃) δ 165.3 (N=CH-Ar), 159.7 (Ar C), 157.6 (Ar C), 150.8 (Ar C), 139.6 (Ar C), 128.9 (Ar C-H), 126.7 (Ar C-H), 125.6 (Ar C-H), 125.1 (Ar C-H), 136.3 (Pyr α), 127.9 (Pyr β), 149.2 (Pyr γ), 122.0 (Pyr δ), 74.4 (C-H of DACH), 59.5 (C-H of DACH), 51.8 (-CH₂- of pyridyl), 30.9 (-CH₃ of cumyl), 30.1 (-CH₃ of cumyl).

**Synthesis of complex 1a**

(±)- trans-N-benzylcyclohexane-1,2-diamine (5.62 g, 27.4 mmol) was dissolved in 100 ml of acetonitrile (ACN) and 3,5-dicumylsalicylaldehyde (9.83 g, 27.4 mmol) was added while stirring. The solution was heated under reflux for 8 hours, and the solvent was removed under reduced pressure. The residue was dissolved in a minimum amount of pentane and crystallized by slow evaporation at low temperature to yield a bright yellow solid (yield 71%). HRMS [M+H]+, calculated m/z = 545.3532. Found m/z = 545.3543.

**Synthesis of complex 1b**

A 20 mL scintillation vial was charged with proligand Lₐ (186 mg, 0.345 mmol) in hexane (5 ml). triisobutylindium, In(CH₃)₃ (100 mg, 0.345 mmol) was added to the stirring mixture. The reaction mixture was stirred for 4 h at room temperature. The concentrated in vacuo, the residue was cooled to -30 °C give yellow crystals. The solid was washed with hexane (3 x 3 mL) and dried under high vacuum for 4 hours. (Yield 94%) Anal. Calcd. For C₄₄H₉₀InN₂O₂: C 67.84; H 7.65; N 3.60. Found: C 67.56; H 7.55; N 3.70.¹H NMR (400 MHz, CDCl₃, 25 °C) δ 8.02 (1H, s, -N=CH-Ar), 7.10 - 7.32 (11H, m, ArH), 7.18 (1H, m, Thioph α), 6.93 (1H, m, Thioph β), 6.86 (1H, m, Thioph γ), 6.79 (1H, s, ArH), 3.96 (1H, dd, \(J_{HH} = 7\), 15 Hz, -CH₂- of thiophenyl), 3.69 (1H, d, \(J_{HH} = 7\), 15 Hz, -CH₂- of thiophenyl), 2.94 (1H, m, -CH- of DACH), 2.58 (1H, m, -CH- of DACH), 0.95 – 2.29 (20H, m, -CH₂- of DACH, -CH₃ of cumyl and -CH- of ′Bu), 0.84 (6H, d, \(J_{HH} = 6\) Hz, -CH₃ of ′Bu), 0.75 (6H, d, \(J_{HH} = 6\) Hz, -CH₃ of ′Bu), 0.47 (2H, d, \(J_{HH} = 7\) Hz, -CH₂- of ′Bu), 0.24 (2H, d, \(J_{HH} = 7\) Hz, -CH₂- of ′Bu),¹³C (¹H) NMR (101 MHz, CDCl₃) δ 171.2 (N=CH-Ar), 168.1 (Ar C), 151.8 (Ar C), 151.5 (Ar C), 143.1 (Ar C), 141.3 (Ar C), 132.0 (Ar C-H), 131.7 (Ar C-H), 127.9 (Thioph α), 127.5 (Thioph β), 125.4 (Thioph γ), 72.4 (C-H of DACH), 60.9 (C-H of DACH), 44.6 (-CH₂- of thiophenyl) 31.0 (-CH₃ of cumyl), 29.6 (-CH₃ of cumyl), 28.1 (-CH₃ of ′Bu), 27.9 (-CH₃ of ′Bu), 29.5 (-CH₂- of ′Bu), 29.3 (-CH₂- of ′Bu).

**Synthesis of complex 1b**

Complex 1b was generated using a similar procedure to complex 1a (187 mg of Lₐ, 0.350 mmol, yield 95%). Anal. Calcd. For C₄₄H₉₀InN₂O₂: C 69.27; H 7.81; N 3.67. Found: C 69.10; H 7.69; N 3.64.¹H NMR (400 MHz, CDCl₃, 25 °C) δ 8.06 (1H, s, -N=CH-Ar), 7.02 - 7.36 (11H, m, ArH), 7.34 (1H, m, Furan α), 6.80 (1H, ArH), 6.28 (1H, m, Furan β), 6.14 (1H, m, Furan γ), 3.81 (1H, dd, \(J_{HH} = 6\), 14 Hz, -CH₂- of furfuryl), 3.71 (1H, d, \(J_{HH} = 6\), 14 Hz, -CH₂- of furfuryl), 2.94 (1H, m, -CH- of DACH), 2.58 (1H, m, -CH- of DACH), 0.97 – 2.31 (16H, m, -CH₂- of DACH, -CH₃ of cumyl and -CH- of ′Bu), 0.88 (6H, m, -CH₃
Synthesis of complex 1c

Complex 1c was generated using a similar procedure to complex 1a (191 mg of Lc, 0.350 mmol, yield = 95%). Anal. Calcd. For C_{45}H_{60}InN_2O: C 68.83; H 7.83; N 5.43. Found: C 69.87; H 7.61; N 5.70. 1H NMR (400 MHz, CDCl_3, 25 °C) δ 8.52 (1H, m, Pyr γ), 8.11 (1H, s, -N=CH-Ar), 7.09 - 7.35 (11H, m, ArH), 7.61 (1H, m, Pyr α), 7.16 (1H, m, Pyr δ), 7.03 (1H, m, Pyr β), 6.79 (1H, ArH), 3.84 (2H, m, -CH_2- of pyridyl), 3.01 (1H, m, -CH- of DACH), 2.63 (1H, m, -CH- of DACH), 0.93 - 2.18 (17H, m, -CH_2- of DACH, -CH_3 of cumyl and -CH_2- of 'Bu), 0.88 (6H, m, -CH_3 of 'Bu), 0.60 (6H, m, -CH_2 of 'Bu), 0.52 (2H, m, -CH_2 of 'Bu), 0.07 (2H, m, -CH_2 of 'Bu), 1.13 (1H, d, J_{H,H}=7 Hz, -CH_2 of benzyl), 3.50 (1H, d, J_{H,H}=7 Hz, -CH_2 of benzyl), 2.75 (1H, m, -CH- of DACH), 2.41 (1H, m, -CH- of DACH), 0.77 - 2.13 (17H, m, -CH_2- of DACH, -CH_3 of cumyl and -CH_2 of 'Bu), 0.68 (6H, m, J_{H,H}=7 Hz, -CH_3 of 'Bu), 0.53 (6H, d, J_{H,H}=7 Hz, -CH_3 of 'Bu), 0.32 (2H, d, J_{H,H}=7 Hz, -CH_2 of 'Bu), -0.01 (2H, d, J_{H,H}=7 Hz, -CH_2 of 'Bu), 13C{1H} NMR (101 MHz, CDCl_3) δ 171.3 (N=CH-Ar), 169.3 (Ar C), 158.4 (Ar C), 151.2 (Ar C), 152.0 (Ar C), 142.3 (Pyr γ), 141.3 (Ar C), 136.6 (Pyr α), 131.9 (Ar C-H), 131.4 (Ar C-H), 128.0 (Ar C-H), 127.1 (Ar C-H), 125.4 (Pyr δ), 124.4 (Pyr β), 68.4 (C-H of DACH), 61.5 (C-H of DACH), 49.5 (-CH_2 of pyridyl) 31.0 (-CH_3 of cumyl), 29.9 (-CH_3 of cumyl), 29.0 (-CH_3 of cumyl), 28.3 (-CH_3 of 'Bu), 27.9(-CH_3 of 'Bu), 28.2 (-CH_2 of 'Bu), 28.1 (-CH_2 of 'Bu).

Synthesis of complex 2a

A 20 mL scintillation vial was charged with 1a (200 mg, 0.257 mmol) in C_6H_6 (3 ml). [HNMe_2Ph][BARF_{24}] (253 mg, 0.266 mmol) in C_6H_6 (2 ml) was added to the stirring solution of 1a. The reaction mixture was stirred for 4 h at r.t. The solvent was removed in vacuo to obtain a yellow residue and cold hexane (3 ml) was added to the residue. After stirring for 1 h, the supernatant was decanted off to remove the byproduct NMe_2Ph. This step was repeated at least 3 times until a pale-yellow solid precipitate formed. The product was washed with hexane (2 x 3 ml) and dried under high vacuum for a few hours. (70%) Anal. Calcd. For C_{72}H_{60}BF_{24}InN_2O: C 54.79; H 4.10; N 1.75. Found: C 55.16; H 4.57; N 2.02. 1H NMR (400 MHz, CDCl_3, 25 °C) δ 8.22 (1H, s, -N=CH-Ar), 7.76 (8H, br. s., ortho H of BARF), 7.62 (1H, m, ArH), 7.57 (4H, br. s., para H of BARF), 6.94 - 7.42 (14H, m, ArH), 7.36 (1H, m, Thioph α), 7.05 (1H, m, Thioph β), 6.86 (1H, m, Thioph γ), 4.38 (1H, br. s., J_{H,H}=13 Hz, -CH_2 of thiophenyl), 3.75 (1H, m, -CH_2 of thiophenyl), 3.17 (1H, m, -CH- of DACH), 2.29 (1H, m, -CH- of DACH), 0.83 - 2.04 (16H, m, -CH_2 of DACH, -CH_3 of cumyl and -CH_2 of 'Bu), 0.66 (6H, m, -CH_3 of 'Bu), 0.73 (2H, m, -CH_2 of 'Bu), 13C{1H} NMR (101 MHz, CDCl_3)
δ 169.3 (N=CH-Ar), 163.9 (Ar C), 161.3-162.4 (B-C), 151.7 (Ar C), 150.0 (Ar C), 141.8 (Ar C), 140.2 (Ar C), 138.8 (Ar C), 134.9 (ortho C-H of BArF), 134.4 (ArC=H), 131.7 (ArC-H), 130.9 (ArC-H), 129.6 (Thioph γ), 128.6-129.4 (qq, J_αF = 3, 32 Hz, meta C of BArF), 127.4,125.6,123.8,121.9 (q, J_αF = 273 Hz, -CF3), 128.8 Thioph β), 128.3 (Thioph α), 118.1 (Ar C), 117.6 (para C-H of BArF), 65.5 (C-H of DACH), 62.6 (C-H of DACH), 46.6 (-CH2- of furfuryl) 32.2 (-CH2- of 'Bu), 30.7 (-CH3 of cumyl), 30.8 (-CH3 of cumyl), 28.7 (-CH3 of cumyl), 27.6 (-CH3 of 'Bu), 19F {^1}H NMR (282 MHz, CDC13): δ -61.9.

Synthesis of complex 2b

Complex 2b was generated using a similar procedure to complex 2a (200 mg of 1b, 0.262 mmol, yield=75%). Anal. Calcd. For C72H62BF24InN2O: C 55.35; H 4.15; N 1.77. Found: C 54.86; H 4.18; N 1.89. ^1H NMR (400 MHz, CDCl3, 25 °C) δ 8.19 (1H, s, -N=CH-Ar), 7.71 (8H, br. s., ortho H of BArF), 7.62 (1H, m, ArH), 7.53 (4H, br. s., para H of BArF), 6.90 - 7.36 (12H, m, ArH), 6.21 (1H, m, Furanyl α), 6.14 (1H, m, Furanyl β), 6.13 (1H, m, Furanyl γ), 4.03 (1H, d, J_H-H=15 Hz, -CH2- of furfuryl), 3.80 (1H, m, -CH2- of furfuryl), 3.12 (1H, m, -CH- of DACH), 2.33 (1H, m, -CH- of DACH), 0.85 – 2.29 (19H, m, -CH2- of DACH, -CH3 of cumyl, -CH- of 'Bu and -CH2- of 'Bu), 0.83 (6H, m, -CH3 of 'Bu), 13C {^1}H NMR (101 MHz, CDCl3) δ 170.7 (N=CH-Ar), 165.7 (Ar C), 161.2-162.4 (B-C), 150.0 (Ar C), 146.1 (Furan δ), 144.2 (Furan γ), 141.5 (Ar C), 139.4 (Ar C), 134.9 (ortho C-H of BArF), 134.8 (ArC=H), 132.4 (ArC-H), 128.7-129.4 (qq, J_αF = 3, 32 Hz, meta C of BArF), 127.4,125.6,123.8,121.9 (q, J_αF = 273 Hz, -CF3), 126.2 (Ar C-H), 125.5 (Ar C-H), 122.0 (Ar C), 117.6 (para C-H of BArF), 117.3 (Ar C), 112.3 (Furan β), 110.9 (Furan α), 64.7 (C-H of DACH), 61.6 (C-H of DACH), 42.5 (-CH2- of furfuryl) 31.3 (-CH3 of cumyl), 30.9 (-CH3 of cumyl), 30.8 (-CH2- of DACH), 30.3 (-CH2- of 'Bu), 28.4 (-CH3 of cumyl), 27.9 (-CH2- of DACH), 27.8 (-CH3 of 'Bu), 23.9 (-CH2- of DACH), 23.5 (-CH- of 'Bu), 19F {^1}H NMR (282 MHz, CDC13): δ -62.0.

Synthesis of complex 2c

Complex 2c was generated using a similar procedure to complex 2a (200 mg of 1c, 0.259 mmol, yield=86%). Anal. Calcd. For C73H63BF24InN2O: C 55.72; H 4.18; N 2.64. Found: C 55.60; H 4.28; N 2.82. ^1H NMR (400 MHz, CDCl3, 25 °C) δ 8.20 (1H, s, -N=CH-Ar), 7.76 (9H, br. s., ortho H of BArF and Pyr γ), 7.61 (1H, m, ArH), 7.54 (4H, br. s., para H of BArF), 7.19 - 7.39 (10H, m, ArH), 7.16 (1H, m, Pyr α), 7.10 (1H, m, Pyr δ), 6.95 (2H, m, Pyr β and ArH), 4.02 (2H, m, -CH2- of pyridyl), 3.12 (1H, m, -CH2- of thiophenyl), 3.17 (1H, m, -CH- of DACH), 0.95 – 2.56 (20H, m, -CH2- of DACH, -CH3 of cumyl, -CH3 of 'Bu and -CH2- of 'Bu), 0.87 (6H, m, -CH3 of 'Bu), 13C {^1}H NMR (101 MHz, CDCl3) δ 171.0 (N=CH-Ar), 167.1 (Ar C), 161.8 (B-C), 152.2 (Ar C), 152.1 (Ar C), 150.0 (Pyr β), 149.9 (Ar C), 141.9 (Pyr γ), 135.1 (ortho C-H of BArF), 134.2 (ArC-H), 132.8 (Pyr δ), 128.7-129.4 (qq, J_αF = 3, 32 Hz, meta C of BArF), 127.4,125.6,123.8,121.9 (q, J_αF = 273 Hz, -CF3), 126.2 (Ar C-H), 125.5 (Ar C-H), 124.0 (Pyr α), 117.6 (para C-H of BArF), 64.2 (C-H of DACH), 60.6 (C-H of DACH), 47.3 (-CH2- of pyridyl) 33.8 (-CH3 of cumyl), 30.9 (-CH3 of cumyl), 25.9 (-CH3 of cumyl), 27.8 (-CH3 of 'Bu), 27.3 (-CH2- of 'Bu), 19F {^1}H NMR (282 MHz, CDC13): δ -61.8.

Synthesis of complex 2d

Complex 2d was generated using a similar procedure to complex 2a but was obtained in a mixture of decomposition products and could not be purified. Synthesis of 2d in THF at -30 °C resulted in less decomposition products. However, 2d could not be isolated. Anal. Calcd. For C74H64BF24InN2O: C 56.70; H 4.20; N 1.70. Found: C 55.10; H 4.50; N 1.71. ^1H NMR (400 MHz, CDCl3, 25 °C) δ 8.36 (1H, s, -N=CH-Ar), 7.70 (8H, br. s., ortho H of BArF), 7.52 (4H, br. s., para H of BArF), 7.07 - 7.45 (14H, m, ArH), 4.17 (1H, m, -CH2- of benzyl), 3.98 (1H, m, -CH2- of benzyl), 3.76 (-CH2- of THF), 3.50 (1H, m, -CH- of...
DACH), 3.14 (1H, m, -CH- of DACH), -0.22 – 2.31 (24H, m, -CH₂- of DACH, -CH₃ of cumyl, -CH- of iBu, -CH₂- of iBu and -CH₃ of iBu).

**Representative polymerization of epoxides using cationic complexes (2a)**

A 7 mL scintillation vial was charged with a solution of complex 2a (19.0 mg, 0.012 mmol) in 0.3 ml of C₆D₆. Epichlorohydrin (0.30 mL, 3.8 mmol) was added directly to the vial by a syringe. The mixture was stirred at 25 °C for 24 h. The resulting solution was concentrated under vacuum for 3 h and then cold methanol was added to it (0 °C, 15 mL). The polymer precipitated from solution and was isolated by decantation or centrifugation. The isolated polymer was dried under high vacuum for at least 3 h prior to analysis.

**Representative polymerization of ε-CL using cationic complexes (2b)**

A 20 ml scintillation vial was charged with a solution of complex 2b (20.0 mg, 0.013 mmol) in 0.5 ml of toluene. A solution of ε-CL (0.5 ml, 4.5 mmol) in 0.5 ml of toluene was added to the vial. The mixture was stirred at 100 °C for 24 h. The resulting solution was concentrated under vacuum for 3 h and then cold methanol was slowly added to the vial (0 °C, 15 mL). The polymer precipitated from the solution and was isolated by decantation of the supernatant. The isolated polymer was dried under high vacuum for at least 3 h prior to analysis.

**Representative polymerization of rac-LA using cationic complexes (2c)**

A 20 ml scintillation vial was charged with a solution of complex 2c (10.1 mg, 0.006 mmol) in 1 ml of toluene. Rac-LA (230 mg, 1.6 mmol) was directly added to the vial. The mixture was stirred at 100 °C for 24 h. The resulting solution was concentrated under vacuum for 3 h and then cold methanol was slowly added to the vial (0 °C, 15 mL). The polymer precipitated from the solution and was isolated by decantation of the supernatant. The isolated polymer was dried under high vacuum for at least 3 h prior to analysis.

**Table S1** Summary of cationic complex synthesis, storage and shelf life.

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<thead>
<tr>
<th>Complex</th>
<th>2a</th>
<th>2b</th>
<th>2c</th>
<th>2d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pendant group donor strength (D₅)⁴</td>
<td>11</td>
<td>10</td>
<td>33</td>
<td>38</td>
</tr>
<tr>
<td>Synthesis temperature</td>
<td>Ambient temperature</td>
<td>Ambient temperature</td>
<td>Ambient temperature</td>
<td>-30 °C</td>
</tr>
<tr>
<td>Synthesis solvents</td>
<td>THF, DCM, C₆D₆</td>
<td>THF, DCM, C₆D₆</td>
<td>THF, DCM, C₆D₆</td>
<td>THF</td>
</tr>
<tr>
<td>Shelf life*</td>
<td>~48 h at r.t.</td>
<td>Stable up to 10 weeks at r.t.</td>
<td>Stable up to 10 weeks at r.t.</td>
<td>~20 mins at r.t.</td>
</tr>
<tr>
<td></td>
<td>~2 weeks at -30 °C</td>
<td>Up to 10 days exposed to moist air</td>
<td>Up to 10 days exposed to moist air</td>
<td>~1 day at -30 °C</td>
</tr>
</tbody>
</table>

*Stored under dry N₂ unless otherwise stated.
B. Characterization of metal complexes and ligands in solution

Figure S1 $^1$H NMR spectrum (400 MHz, CDCl$_3$, 25 °C) of L$_a$.

Figure S2 $^{13}$C$\{^1$H$\}$ NMR spectrum (101 MHz, CDCl$_3$, 25 °C) of L$_a$. 
Figure S3 2D $^1$H-$^1$H COSY NMR spectrum (400 MHz, CDCl$_3$, 25 °C) of La.
Figure S4 $^1$H-$^{13}$C Heteronuclear Single Quantum Coherence (HSQC) NMR spectrum (CDCl$_3$, 25 °C) of $L_a$. 
Figure S5 $^1$H NMR spectrum (400 MHz, CDCl$_3$, 25 °C) of L$_b$.

Figure S6 $^{13}$C{$^1$H} NMR spectrum (101 MHz, CDCl$_3$, 25 °C) of L$_b$. 
Figure S7 $^1$H-$^1$H COSY NMR spectrum (400 MHz, CDCl$_3$, 25 °C) of L$_b$. 
Figure S8 $^1$H-$^{13}$C Heteronuclear Single Quantum Coherence (HSQC) NMR spectrum (CDCl$_3$, 25 °C) of L$_b$. 
Figure S9 $^1$H NMR spectrum (400 MHz, CDCl$_3$, 25 °C) of L$_c$.

Figure S10 $^{13}$C{$^1$H} NMR spectrum (101 MHz, CDCl$_3$, 25 °C) of L$_c$. 
Figure S11 $^1$H-$^1$H COSY NMR spectrum (400 MHz, CDCl$_3$, 25 °C) of L$_c$. 
Figure S12 $^1$H-$^{13}$C Heteronuclear Single Quantum Coherence (HSQC) NMR spectrum (CDCl$_3$, 25 °C) of L$_e$
Figure S13 $^1$H NMR spectrum (400 MHz, CDCl$_3$, 25 °C) of L$_d$.

Figure S14 $^{13}$C{$^1$H} NMR spectrum (101 MHz, CDCl$_3$, 25 °C) of L$_d$. 
Figure S15 2D $^1$H-$^1$H COSY NMR spectrum (400 MHz, CDCl$_3$, 25 °C) of L$_d$. 
Figure S16 $^1$H-$^{13}$C Heteronuclear Single Quantum Coherence (HSQC) NMR spectrum (CDCl$_3$, 25 °C) of $L_d$
Figure S17 $^1$H NMR spectrum (400 MHz, CDCl$_3$, 25 °C) of 1a

Figure S18 $^{13}$C {$^1$H} NMR spectrum (101 MHz, CDCl$_3$, 25 °C) of 1a
Figure S19  \( ^1\text{H}-^1\text{H} \) COSY NMR spectrum (400 MHz, CDCl\(_3\), 25 °C) of 1a.
Figure S20 $^1$H-$^{13}$C Heteronuclear Single Quantum Coherence (HSQC) NMR spectrum (CDCl$_3$, 25 °C) of 1a.
Figure S21 Nuclear Overhauser Effect spectroscopy (NOESY) NMR spectrum (400 MHz, CDCl$_3$, 25 °C) of 1a
Figure S22 $^1$H NMR spectrum (400 MHz, CDCl$_3$, 25 °C) of 1b.

Figure S23 $^{13}$C{$^1$H} NMR spectrum (101 MHz, CDCl$_3$, 25 °C) of 1b
Figure S24 ¹H-¹H COSY NMR spectrum (400 MHz, CDCl₃, 25 °C) of 1b
Figure S25 $^1$H-$^{13}$C Heteronuclear Single Quantum Coherence (HSQC) NMR spectrum (CDCl$_3$, 25 °C) of 1b.
Figure S26 Nuclear Overhauser Effect spectroscopy (NOESY) NMR spectrum (400 MHz, CDCl₃, 25 °C) of 1b.
Figure S27 $^1$H NMR spectrum (400 MHz, CDCl$_3$, 25 °C) of 1c.

Figure S28 $^{13}$C{$^1$H} NMR spectrum (101 MHz, CDCl$_3$, 25 °C) of 1c
Figure S29: $^1$H-$^1$H COSY NMR spectrum (400 MHz, CDCl$_3$, 25 °C) of 1c
Figure S30  $^1$H-$^{13}$C Heteronuclear Single Quantum Coherence (HSQC) NMR spectrum (CDCl$_3$, 25 °C) of 1c.
Figure S31  Nuclear Overhauser Effect spectroscopy (NOESY) NMR spectrum (400 MHz, CDCl$_3$, 25 °C) of 1c.
Figure S32 $^1$H NMR spectrum (400 MHz, CDCl$_3$, 25 °C) of 1d.

Figure S33 $^{13}$C{$^1$H} NMR spectrum (101 MHz, CDCl$_3$, 25 °C) of 1d
Figure S34 $^1$H-$^1$H COSY NMR spectrum (400 MHz, CDCl$_3$, 25 °C) of 1d.
Figure S35 $^1$H-$^{13}$C Heteronuclear Single Quantum Coherence (HSQC) NMR spectrum (CDCl$_3$, 25 $^\circ$C) of 1d.
Figure S36 $^1$H NMR spectrum (300 MHz, CDCl$_3$, 25 °C) of 2a. (Residual diethyl ether q, 3.48 and t, 1.22 ppm)

Figure S37 $^{13}$C{$^1$H} NMR spectrum (151 MHz, CDCl$_3$, 25 °C) of 2a
Figure S38 $^1$H-$^1$H COSY NMR spectrum (400 MHz, CDCl$_3$, 25 °C) of 2a.
Figure S39 $^1$H-$^{13}$C Heteronuclear Single Quantum Coherence (HSQC) NMR spectrum (CDCl$_3$, 25 $^\circ$C) of 2a.
Figure S40  Nuclear Overhauser Effect spectroscopy (NOESY) NMR spectrum (400 MHz, CDCl$_3$, 25 °C) of 2a.
Figure S41  $^1$H-$^{13}$C Heteronuclear Multiple Bond Correlation (HMBC) NMR spectrum (CDCl$_3$, 25 °C) of 2b.

Figure S42  $^{19}$F{$^1$H} NMR spectrum (282 MHz, CDCl$_3$, 25 °C) of 2a
Figure S43 $^1$H NMR spectrum (300 MHz, CDCl$_3$, 25 °C) of 2b.

Figure S44 $^{13}$C{$^1$H} NMR spectrum (151 MHz, CDCl$_3$, 25 °C) of 2b
Figure S45 $^1$H-$^1$H COSY NMR spectrum (400 MHz, CDCl$_3$, 25 °C) of 2b.
Figure S46 $^1$H-$^{13}$C Heteronuclear Single Quantum Coherence (HSQC) NMR spectrum (CDCl$_3$, 25 °C) of 2b.
Figure S47 Nuclear Overhauser Effect spectroscopy (NOESY) NMR spectrum (400 MHz, CDCl₃, 25 °C) of 2b.
Figure S48 $^1$H-$^{13}$C Heteronuclear Multiple Bond Correlation (HMBC) NMR spectrum (CDCl$_3$, 25 °C) of 2b.

Figure S49 $^{19}$F{$^1$H} NMR spectrum (282 MHz, CDCl$_3$, 25 °C) of 2b
Figure S50 $^1$H NMR spectrum (300 MHz, CDCl$_3$, 25 °C) of 2c

Figure S51 $^{13}$C{${^1}$H} NMR spectrum (151 MHz, CDCl$_3$, 25 °C) of 2c
Figure S52 $^1$H-$^1$H COSY NMR spectrum (400 MHz, CDCl$_3$, 25 °C) of 2c.
Figure S53 $^1$H-$^1$C Heteronuclear Single Quantum Coherence (HSQC) NMR spectrum (CDCl$_3$, 25 °C) of 2c.
Figure S54  Nuclear Overhauser Effect spectroscopy (NOESY) NMR spectrum (400 MHz, CDCl₃, 25 °C) of 2c.
Figure S55 $^{19}$F{$^1$H} NMR spectrum (282 MHz, CDCl$_3$, 25 °C) of 2c

Figure S56 $^1$H NMR spectrum (300 MHz, CDCl$_3$, 25 °C) of 2d
C. Characterization of metal complexes in the solid state

| Bond distances | In1-N1    | 2.510(3) | In1-C32   | 2.165(4) |
|               | In1-N2    | 2.293(3) | In1-C36   | 2.169(4) |
|               | In1-O1    | 2.205(3) |

| Bond Angles    | O1-In1-C32A | 98.0(1)  | O1-In1-N1 | 147.4(1) |
|               | O1-In1-C36  | 95.0(1)  | N1-In1-C32 | 99.4(1)  |
|               | C32-In1-C36 | 135.0(2) | N1-In1-C36 | 91.9(1)  |
|               | N1-In1-N2   | 69.6(1)  |

**Figure S57** Molecular structure of complex 1a. (depicted with thermal ellipsoids at 50% probability and H atoms, as well as solvent molecules omitted for clarity).
Selected bond distance (Å) and angles (°) for complex 1b.

<table>
<thead>
<tr>
<th>Bond distances</th>
<th>In1-N1</th>
<th>2.548(1)</th>
<th>In1-C32</th>
<th>2.178(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In1-N2</td>
<td>2.269(2)</td>
<td></td>
<td>In1-C36</td>
<td>2.187(3)</td>
</tr>
<tr>
<td>In1-O1</td>
<td>2.203(1)</td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond Angles</th>
<th>O1-In1-C32A</th>
<th>94.00(7)</th>
<th>O1-In1-N1</th>
<th>148.60(6)</th>
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</thead>
<tbody>
<tr>
<td>O1-In1-C36</td>
<td>101.95(8)</td>
<td></td>
<td>N1-In1-C32</td>
<td>90.98(8)</td>
</tr>
<tr>
<td>C32-In1-C36</td>
<td>129.61(9)</td>
<td></td>
<td>N1-In1-C36</td>
<td>98.52(8)</td>
</tr>
<tr>
<td>N1-In1-N2</td>
<td>70.31(6)</td>
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</table>

**Figure S58** Molecular structure of complex 1b. (depicted with thermal ellipsoids at 50% probability and H atoms, minor disorders as well as solvent molecules omitted for clarity).
Selected bond distance (Å) and angles (°) for complex 1c.

<table>
<thead>
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<th>Bond distances</th>
<th>Bond distances</th>
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</thead>
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<tr>
<td>In1-N1</td>
<td>2.510(2)</td>
<td>In1-C32</td>
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<tr>
<td>In1-N2</td>
<td>2.286(1)</td>
<td>In1-C36</td>
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<tr>
<td>In1-O1</td>
<td>2.209(2)</td>
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</tr>
<tr>
<td>Bond Angles</td>
<td>Bond Angles</td>
<td>Bond Angles</td>
</tr>
<tr>
<td>O1-In1-C32A</td>
<td>94.72(7)</td>
<td>O1-In1-N1</td>
</tr>
<tr>
<td>O1-In-C36</td>
<td>97.68(7)</td>
<td>N1-In1-C32</td>
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<tr>
<td>C32-In1-C36</td>
<td>135.39(8)</td>
<td>N1-In1-C36</td>
</tr>
<tr>
<td>N1-In1-N2</td>
<td>69.95(6)</td>
<td></td>
</tr>
</tbody>
</table>

**Figure S59** Molecular structure of complex 1c. (depicted with thermal ellipsoids at 50% probability and H atoms, as well as solvent molecules omitted for clarity).
**Selected bond distance (Å) and angles (°) for complex 1d.**

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<tr>
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<th>In1-C32</th>
<th>2.170(1)</th>
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<tr>
<td>In1-N2</td>
<td>2.286(1)</td>
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<td>In1-C36</td>
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<td>In1-O1</td>
<td>2.206(1)</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond Angles</th>
<th>O1-In1-C32A</th>
<th>97.49(5)</th>
<th>O1-In1-N1</th>
<th>148.14(4)</th>
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</thead>
<tbody>
<tr>
<td>O1-In1-C36</td>
<td>94.38(5)</td>
<td>N1-In1-C32</td>
<td>98.34(5)</td>
<td></td>
</tr>
<tr>
<td>C32-In1-C36</td>
<td>136.55(6)</td>
<td>N1-In1-C36</td>
<td>92.87(5)</td>
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<tr>
<td>N1-In1-N2</td>
<td>69.81(4)</td>
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</table>

**Figure S60** Molecular structure of complex 1d. (depicted with thermal ellipsoids at 50% probability and H atoms, as well as solvent molecules omitted for clarity).
D. Characterization of complex behavior

Figure S61  $^{31}$P-$^1$H NMR spectra (162 MHz, C$_6$D$_6$, 25 °C) of 1a, 1b, 1c and 1d after the addition of 0.8 equivalents of OPEt$_3$. The free triethylphosphine oxide shift is determined by the addition of a capillary inside the NMR tube containing a solution of triethylphosphine oxide in C$_6$D$_6$. 
Figure S62 $^1$H NMR spectra of 2c before (time = 0 days) and after (time = 10 days) exposure to air for 10 days continuously. No significant changes were observed.
Figure S63 Variable temperature (VT) $^1$H NMR spectra (400 MHz, C$_6$D$_5$Br, 25 to 125 °C) of 1a. Shifts observed were reversible. C$_6$D$_5$Br is taken as a reference.
Figure S64 Variable temperature (VT) $^1$H NMR spectra (400 MHz, C$_6$D$_5$Br, 25 to 85 °C) of 1b. Shifts observed were reversible. C$_6$D$_5$Br is taken as a reference.
Figure S65 Variable temperature (VT) $^1$H NMR spectra (400 MHz, C$_6$D$_5$Br, 25 to 85 °C) of 1c. Shifts observed were reversible. C$_6$D$_5$Br is taken as a reference.
Figure S66 Variable temperature (VT) $^1$H NMR spectra (400 MHz, C$_6$D$_5$Br, 30 to 105 °C) of 2a. Shifts observed were irreversible. C$_6$D$_5$Br is taken as a reference.
Figure S67 Variable temperature (VT) $^1$H NMR spectra (400 MHz, CD$_5$Br, 25 to 125 °C) of 2b free ligand L2. Shifts observed were reversible. CD$_5$Br is taken as a reference.
Figure S68 Variable temperature (VT) $^1$H NMR spectra (400 MHz, C$_6$D$_5$Br, 30 to 120 °C) of 2c. Shifts observed were reversible. C$_6$D$_5$Br is taken as a reference.
Selected bond distance (Å) and angles (°) for complex 2b.2THF.

<table>
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<tr>
<th>Bond distance</th>
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<th>In1-O3</th>
<th>2.392(4)</th>
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<tbody>
<tr>
<td></td>
<td>In1-N2</td>
<td>2.179(5)</td>
<td>In1-O4</td>
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<tr>
<td></td>
<td>In1-O1</td>
<td>2.127(3)</td>
<td>In1-C32</td>
<td>2.128(7)</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond Angles</th>
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<th>112.9(2)</th>
<th>O1-In1-N1</th>
<th>156.3(1)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>O3-In1-O4</td>
<td>166.3(1)</td>
<td>N1-In1-C32</td>
<td>90.4(2)</td>
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<td></td>
<td>N1-In1-N2</td>
<td>72.9(2)</td>
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</tbody>
</table>

**Figure S69** Molecular structures of complex 2b.2THF (depicted with thermal ellipsoids at 50% probability and H atoms, minor disorders as well as solvent molecules omitted for clarity)
Table S2 Selective crystal data for 1b, 1d, 1a, 1c and 2b.2THF.

<table>
<thead>
<tr>
<th></th>
<th>1b</th>
<th>1d</th>
<th>1a</th>
<th>1c</th>
<th>2b.2THF</th>
</tr>
</thead>
<tbody>
<tr>
<td>empirical formula</td>
<td>C_{44}H_{59}InN_{2}O_{2}</td>
<td>C_{46}H_{61}InN_{2}O</td>
<td>C_{44}H_{59}InN_{2}OS</td>
<td>C_{45}H_{60}InN_{3}O</td>
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<td>Fw</td>
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<tr>
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<td>100</td>
<td>296.15</td>
<td>100</td>
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<td>a (Å)</td>
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<td>18.3672(15)</td>
<td>18.3804(16)</td>
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<tr>
<td>c (Å)</td>
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<td>17.9736(14)</td>
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<td>monoclinic</td>
<td>triclinic</td>
</tr>
<tr>
<td>space group</td>
<td>P 2₁/c</td>
<td>P 2₁/n</td>
<td>P 2₁/c</td>
<td>P 2₁/c</td>
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</tr>
<tr>
<td>d_{calc} (g/cm³)</td>
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<td>1.244</td>
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<td>1.457</td>
</tr>
<tr>
<td>μ (Mo Kα) (cm⁻¹)</td>
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<tr>
<td>2θ_{max} (deg)</td>
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<td>61.2</td>
<td>55.8</td>
<td>61.0</td>
<td>54.6</td>
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<td>absor corr (T_{min}, T_{max})</td>
<td>0.7005, 0.7461</td>
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<td>0.982, 0.997</td>
<td>0.6730, 0.7461</td>
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</tr>
<tr>
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<td>65464</td>
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<td>18759</td>
</tr>
<tr>
<td>no. of indep reflns (R_{int})</td>
<td>12154 (0.0394)</td>
<td>12665 (0.0445)</td>
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<td>12417 (0.0461)</td>
<td>18759 (0.1605)</td>
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<tr>
<td>residuals (refined on F²): R₁; wR₂</td>
<td>0.0523, 0.0887</td>
<td>0.0354, 0.0634</td>
<td>0.0773, 0.1436</td>
<td>0.0465, 0.0808</td>
<td>0.0983, 2141</td>
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<td>GOF</td>
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<td>1.032</td>
<td>1.067</td>
<td>1.094</td>
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<tr>
<td>no. obsrvns [I &gt; 2σ(I)]</td>
<td>9858</td>
<td>9908</td>
<td>9510</td>
<td>9643</td>
<td>9841</td>
</tr>
<tr>
<td>residuals (refined on F²): R₁'; wR₂'</td>
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<td>0.0273, 0.0600</td>
<td>0.0550, 0.1339</td>
<td>0.0373, 0.0772</td>
<td>0.0794, 2047</td>
</tr>
</tbody>
</table>

\[aR_1 = \Sigma \frac{||F_o|| - |F_c||}{\Sigma |F_o||}, \quad wR_2 = \left[ \Sigma \left( w(F_c^2 - F_o^2)^2 \right) \right]^{1/2} \]
Figure S70 DOSY-NMR of the mixture of THF and 2a (400MHz, diffusion time ($\Delta$) = 0.85 s, gradient length ($\delta$) = 400 µs, C$_6$D$_6$, 25 °C).

Figure S71 DOSY-NMR of the mixture of THF and 2b (400MHz, $\Delta$ = 1.2 s, $\delta$ = 400 µs, C$_6$D$_6$, 25 °C).
Figure S72 DOSY-NMR of the mixture of THF and 2c (400 MHz, $\Delta = 0.55$ s, $\delta = 400$ µs, C$_6$D$_6$, 25 °C).

Figure S73 $^1$H NMR of spectra of 2b in the presence of THF, pyridine, triethylphosphine oxide and epichlorohydrin (400 MHz in C$_6$D$_6$ at 25 °C).
Figure S74 MALDI-TOF spectrum of PLA isolated from polymerization of 250 equivalents of rac-LA with 2c in toluene at 100 °C for 24 hours

Figure S75 \( ^{1}H\{^{1}H\} \) NMR spectrum (600 MHz, CDCl\(_3\), 25 °C) of PLA as the product of the polymerization of 250 equivalents of rac-LA 2c in toluene at 100 °C for 24 hours. The methine protons of the polymer are decoupled. (P\(_m\) = 0.46)
E. References