Supplementary Information

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

Chatura Goonesinghe, Hootan Roshandel, Carlos Diaz, Hyuk-Joon Jung, Kudzanai Nyamayaro, Maria Ezhova, and Parisa Mehrkhodavandi*^a

Department of Chemistry, University of British Columbia, Vancouver, BC, Canada
mehr@chem.ubc.ca

Table of Contents

A. Experimental procedures ........................................................................................................... 2
B. Characterization of metal complexes and ligands in solution .................................................. 8
C. Characterization of metal complexes in the solid state .......................................................... 50
D. Characterization of complex behavior ..................................................................................... 54
E. References ................................................................................................................................ 67
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 Styrage columns (4.6 × 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$_6^f$]) was generated by reacting dimethylanilinium chloride with sodium BAR$_6^f$ 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. InCl$_3$ was purchased from Strem Chemicals and used without further purification. Isobutylmagnesium chloride (2.0 M in Et$_2$O) and dimethylanilinium chloride ([HNMe$_2$Ph]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. e-caprolactone were dried over CaH$_2$, distilled and stored under molecular sieves. In(Bu)$_3$ was synthesized according to a previously reported procedure.$^2$ Proligands L$_{a-d}$ were synthesized by the modification of a previously reported procedure.$^3$

**Synthesis of proligand L$_{a}$**

(±)- 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, 20.8 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 ethyl acetate and crystallized by slow evaporation at low temperature to yield a pale yellow solid (yield 63%). HRMS [M+H]$^+$, calculated m/z = 551.3096. Found m/z = 551.3100. $^1$H NMR (400 MHz, CDCl$_3$, 25 °C) δ 13.23 (1H, br. s., Ar-OH), 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, $^2$J$_{HH}$ = 14 Hz, -CH$_2$ of thiophenyl), 3.86 (1H, d, $^2$J$_{HH}$ = 14 Hz, -CH$_2$ of thiophenyl), 2.95 (1H, m, -CH- of DACH), 2.63 (1H, m, -CH- of DACH), 1.02 - 1.74 (17H, m, -CH$_2$ of DACH and -CH$_3$ of cumyl), $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) 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 (-CH$_2$ of thiophenyl) 31.1 (-CH$_3$ of cumyl), 30.0 (-CH$_3$ of cumyl), 29.3 (-CH$_3$ of cumyl).

**Synthesis of proligand L$_{b}$**

(±)- 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, 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 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. $^1$H NMR (400 MHz, CDCl$_3$, 25 °C) δ 13.22 (1H, br. s., Ar-OH), 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, $^2$J$_{HH}$ = 15 Hz, -CH$_2$ of furfuryl), 3.69 (1H, d, $^2$J$_{HH}$ = 15 Hz, -CH$_2$ of furfuryl), 2.95 (1H, m, -CH- of DACH), 2.57 (1H, m, -CH- of DACH), 1.06 - 2.12 (17H, m, -CH$_2$ of DACH and -CH$_3$ of cumyl), $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) 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 (-CH$_2$ of furfuryl), 31.1 (-CH$_3$ of cumyl), 29.8 (-CH$_3$ of cumyl), 29.2 (-CH$_3$ of cumyl).

**Synthesis of proligand L$_{c}$**

(±)- 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. $^1$H NMR (400 MHz, CDCl$_3$, 25 °C) δ 8.37 (1H, s, -N=CH-Ar), 7.03 - 7.41 (12H, m, ArH),
Synthesis of complex 1a

A 20 mL scintillation vial was charged with proligand L₄ (186 mg, 0.345 mmol) in hexane (5 ml). triisobutylindium, In(Ch₂CH(CH₃)₂)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 × 3 mL) and dried under high vacuum for 4 hours. (Yield 94%) Anal. Calcd. For C₄H₅SO₃N₂: 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 (1H, 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, 2JH-H = 7, 15 Hz, -CH₂- of thiophenyl), 3.69 (1H, d, 2JH-H = 7, 15 Hz, -CH₂- of thiophenyl), 2.94 (1H, m, -CH- of DACH), 2.58 (1H, m, -CH- of DACH), 0.95 - 2.29 (2OH, m, -CH₂- of DACH, -CH₃ of cumyl and -CH- of `Bu), 0.84 (6H, d, 2JH-H = 6 Hz, -CH₃ of `Bu), 0.75 (6H, d, 2JH-H = 6 Hz, -CH₃ of `Bu), 0.47 (2H, d, 2JH-H = 7 Hz, -CH₂- of `Bu), 0.24 (2H, d, 3JH-H = 7 Hz, -CH₂- of `Bu), 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 L₄, 0.350 mmol, yield=95%). Anal. Calcd. For C₄H₅SO₃N₂: 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, 2JH-H = 6, 14 Hz, -CH₂- of furfuryl), 3.71 (1H, d, 2JH-H = 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
of's}Bu, 0.74 (6H, m, -CH\(_3\) of's}Bu), 0.50 (2H, m, -CH\(_2\)- of's}Bu), 0.11 (2H, m, -CH\(_2\)- of's}Bu),\(^{13}\)C\(^{1}\)H) NMR (101 MHz, CDCl\(_3\)) \(δ\) 171.7 (N=CH-Ar), 168.8 (Ar C), 152.9 (Ar C), 151 (Ar C), 152.0 (Ar C), 152.0 (Ar C), 142.3 (Furan α), 141.5 (Ar C), 132.2 (Ar C-H), 131.8 (Ar C-H), 128.2 (Ar C-H), 127.8 (Ar C-H), 127.1 (Ar C-H), 124.6 (Ar C-H), 110.8 (Furan β), 107.8 (Furan γ), 70.6 (C-H of DACH), 61.1 (C-H of DACH), 42.5(-CH\(_2\)- of furfuryl) 31.1 (-CH\(_3\) of cumyl), 29.8 (-CH\(_3\) of cumyl), 29.5 (-CH\(_3\) of cumyl), 28.5 (-CH\(_3\) of's}Bu), 28.4(-CH\(_3\) of's}Bu), 28.9 (-CH\(_2\)- of's}Bu), 29.4 (-CH\(_2\)- of's}Bu).

**Synthesis of complex 1c**

Complex 1c was generated using a similar procedure to complex 1a (191 mg of L\(_c\), 0.350 mmol, yield=95%). Anal. Calcd. For C\(_{46}H\(_{40}\)InN\(_2\)O: C 68.83; H 7.83; N 5.43. Found: C 69.87; H 7.61; N 5.70.\(^{1}\)H NMR (400 MHz, CDCl\(_3\), 25 °C) \(δ\) 8.52 (1H, m, Pyr γ), \(\delta\) 8.11 (1H, s, -N=CH-Ar), 7.95 - 7.16 (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\(_2\)- of DACH), 2.63 (1H, m, -CH\(_2\)- of DACH), 0.93 – 2.18 (17H, m, -CH\(_2\)- of DACH, -CH\(_3\) of cumyl and -CH\(_2\)- of's}Bu), 0.88 (6H, m, -CH\(_3\) of's}Bu), 0.60 (6H, m, -CH\(_3\) of's}Bu), 0.52 (2H, m, -CH\(_2\)- of's}Bu), -0.07 (2H, m, -CH\(_2\)- of's}Bu),\(^{13}\)C\(^{1}\)H) NMR (101 MHz, CDCl\(_3\)) \(δ\) 171.3 (N=CH-Ar), 169.3 (Ar C), 158.4 (Ar C), 151 (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's}Bu), 27.9(-CH\(_3\) of's}Bu), 28.2 (-CH\(_2\)- of's}Bu), 28.1 (-CH\(_2\)- of's}Bu).

**Synthesis of complex 1d**

Complex 1d was generated using a similar procedure to complex 1a (191 mg of L\(_d\), 0.350 mmol, yield=96%). Anal. Calcd. For C\(_{46}H\(_{40}\)InN\(_2\)O: C 71.48; H 7.97; N 3.63. Found: C 71.74; H 7.99; N 3.57.\(^{1}\)H NMR (400 MHz, CDCl\(_3\), 25 °C) \(δ\) 7.85 (1H, s, -N=CH-Ar), 6.80 - 7.20 (11H, m, ArH), 6.61 (1H, m, ArH), 3.61 (1H, dd, \(\delta\)\(_{J_{HH}}\)=7, 13 Hz -CH\(_2\)- of benzyl), 3.50 (1H, dd, \(\delta\)\(_{J_{HH}}\)=7, 13 Hz -CH\(_2\)- of benzyl), 2.75 (1H, m, -CH\(_2\)- of DACH), 2.41 (1H, m, -CH\(_2\)- of DACH), 0.77 – 2.13 (17H, m, -CH\(_2\)- of DACH, -CH\(_3\) of cumyl and -CH\(_2\)- of's}Bu), 0.68 (6H, d, \(\delta\)\(_{J_{HH}}\)=7 Hz, -CH\(_3\) of's}Bu), 0.63 (6H, d, \(\delta\)\(_{J_{HH}}\)=7 Hz, -CH\(_3\) of's}Bu), 0.32 (2H, d, \(\delta\)\(_{J_{HH}}\)=7 Hz, -CH\(_2\)- of's}Bu), -0.01 (2H, d, \(\delta\)\(_{J_{HH}}\)=7 Hz, -CH\(_2\)- of's}Bu),\(^{13}\)C\(^{1}\)H) NMR (101 MHz, CDCl\(_3\)) \(δ\) 171.0 (N=CH-Ar), 168.2 (Ar C), 151.7 (Ar C), 151.5 (Ar C), 141.2 (Ar C), 139.8 (Ar C), 132.0 (Ar C-H), 131.5 (Ar C-H), 128.7 (Ar C-H), 127.9 (Ar C-H), 124.4 (Ar C-H), 71.7 (C-H of DACH), 61.1 (C-H of DACH), 50.1 (-CH\(_2\)- of benzyl) 30.9(-CH\(_3\) of cumyl), 29.4 (-CH\(_3\) of cumyl), 29.5 (-CH\(_3\) of cumyl), 27.8 (-CH\(_3\) of's}Bu), 28.1 (-CH\(_3\) of's}Bu), 29.4 (-CH\(_2\)- of's}Bu), 29.4 (-CH\(_2\)- of's}Bu).

**Synthesis of complex 2a**

A 20 mL scintillation vial was charged with 1a (200 mg, 0.257 mmol) in C\(_6\)H\(_6\) (3 ml). [HNMe\(_2\)Ph][BAr\(_{24}\)] (253 mg, 0.266 mmol) in C\(_6\)H\(_6\) (2 ml) was added to the stirring solution of 1a. The reaction mixture was stirred for 4 h at rt. 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\(_2\)Ph. 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\(_{92}\)BF\(_24\)InN\(_2\)OS: C 54.79; H 4.10; N 1.75. Found: C 55.16; H 4.57; N 2.02.\(^{1}\)H NMR (400 MHz, CDCl\(_3\), 25 °C) \(δ\) 8.22 (1H, s, -N=CH-Ar), 7.76 (8H, br. s., ortho H of BA\(_F^2\)), 7.62 (1H, m, ArH), 7.57 (4H, br. s., para H of BA\(_F^2\)), 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, d, \(\delta\)\(_{J_{HH}}\)=13 Hz, -CH\(_2\)- of thiophenyl), 3.75 (1H, m, -CH\(_2\)- of thiophenyl), 3.17 (1H, m, -CH\(_3\)- of DACH), 2.29 (1H, m, -CH\(_3\)- of DACH), 0.83 – 2.04 (16H, m, -CH\(_2\)- of DACH, -CH\(_3\) of cumyl and -CH\(_2\)- of's}Bu), 0.66 (6H, m, -CH\(_3\) of's}Bu), 0.73 (2H, m, -CH\(_2\)- of's}Bu),\(^{13}\)C\(^{1}\)H) 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 (Ar-C-H), 131.7 (Ar-C-H), 130.9 (Ar-C-H), 129.6 (Thioph γ), 128.6-129.4 (qq, J_C-F = 3, 32 Hz, meta C of BArF), 127.4,125.6,123.8,121.9 (q, J_C-F = 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 furyl) 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 {1H} NMR (282 MHz, CDCl3): 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 C_{72}H_{62}BF_{24}InN_{22}O_{7}: 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, Furan α), 6.14 (1H, m, Furan β), 6.13 (1H, m, Furan γ), 4.03 (1H, d, J_{H-H}=15 Hz, -CH2- of furyl), 3.80 (1H, m, -CH2- of furyl), 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{1H} 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 (Ar-C-H), 124.2 (Ar-C-H), 128.7-129.4 (qq, J_{C-F} = 3, 32 Hz, meta C of BArF), 127.4,125.6,123.8,121.9 (q, J_{C-F} = 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 furyl) 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 {1H} NMR (282 MHz, CDCl3): 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 C_{75}H_{63}BF_{24}InN_{25}O_{7}: 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, -CH- of 'Bu and -CH2- of 'Bu), 0.87 (6H, m, -CH3 of 'Bu), 13C{1H} 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 (Ar-C-H), 132.8 (Pyr δ), 128.7-129.4 (qq, J_{C-F} = 3, 32 Hz, meta C of BArF), 127.4,125.6,123.8,121.9 (q, J_{C-F} = 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 {1H} NMR (282 MHz, CDCl3): 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 C_{30}H_{26}BF_{12}InN_{22}O_{7}: 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 ‘Bu, -CH2- of ‘Bu and -CH3 of ‘Bu).

**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.

| Complex | 2a | 2b | 2c | 2d |
|---------|----|----|----|----|
| Pendant group donor strength (D₄)⁴ | 11 | 10 | 33 | 38 |
| Synthesis temperature | Ambient temperature | Ambient temperature | Ambient temperature | -30 °C |
| Synthesis solvents | THF, DCM, C₆D₆ | THF, DCM, C₆D₆ | THF, DCM, C₆D₆ | THF |
| Shelf life* | ~48 h at r.t. | Stable up to 10 weeks at r.t. | Stable up to 10 weeks at r.t. | ~20 mins at r.t. |
| | ~2 weeks at -30 °C | Up to 10 days exposed to moist air | | ~ 1 day at -30 °C |

*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 $\text{L}_a$.

**Figure S2** $^{13}$C-$^1$H NMR spectrum (101 MHz, CDCl$_3$, 25 °C) of $\text{L}_a$. 

S8
Figure S3 2D $^1$H-$^1$H COSY NMR spectrum (400 MHz, CDCl$_3$, 25 °C) of L$_a$. 
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 ¹H-¹³C Heteronuclear Single Quantum Coherence (HSQC) NMR spectrum (CDCl₃, 25 °C) of L₉.
Figure S9 $^1$H NMR spectrum (400 MHz, CDCl$_3$, 25 °C) of $\text{L}_c$.

Figure S10 $^{13}$C{$^1$H} NMR spectrum (101 MHz, CDCl$_3$, 25 °C) of $\text{L}_c$. 
Figure S11 $^1$H-$^1$H COSY NMR spectrum (400 MHz, CDCl$_3$, 25 °C) of L$_e$. 
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 \(^1\text{H}-^{13}\text{C}\) 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 $^1$H-$^1$H COSY NMR spectrum (400 MHz, CDCl$_3$, 25 °C) of 1a.
Figure S20 ¹H-¹³C Heteronuclear Single Quantum Coherence (HSQC) NMR spectrum (CDCl₃, 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 $^1$H-$^1$H COSY NMR spectrum (400 MHz, CDCl$_3$, 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, CDCl$_3$, 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, CDCl₃, 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 °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 °C) of 2a.
Figure S40  Nuclear Overhauser Effect spectroscopy (NOESY) NMR spectrum (400 MHz, CDCl₃, 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 ¹H-¹H COSY NMR spectrum (400 MHz, CDCl₃, 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 2e.
Figure S53 $^1$H-$^{13}$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.

| Bond distances | Bond Angles |
|----------------|-------------|
| In1-N1 2.548(1) | O1-In1-C32A 94.00(7) |
| In1-N2 2.269(2) | O1-In1-C36 101.95(8) |
| In1-O1 2.203(1) | C32-In1-C36 129.61(9) |
| In1-C32 2.178(2) | N1-In1-C32 90.98(8) |
| In1-C36 2.187(3) | N1-In1-C36 98.52(8) |
| N1-In1-N2 70.31(6) | O2A |

**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.

| Bond distances | Bond distance  | Bond distances | Bond distance  |
|----------------|----------------|----------------|----------------|
| In1-N1         | 2.510(2)       | In1-C32        | 2.174(2)       |
| In1-N2         | 2.286(1)       | In1-C36        | 2.170(2)       |
| In1-O1         | 2.209(2)       |                |                |
| O1-In1-C32A    | 94.72(7)       | O1-In1-N1      | 148.01(6)      |
| O1-In-C36      | 97.68(7)       | N1-In1-C32     | 92.82(7)       |
| C32-In1-C36    | 135.39(8)      | N1-In1-C36     | 98.55(7)       |
| N1-In1-N2      | 69.95(6)       |                |                |

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).
| Bond distances | Bond Angles          | Selected bond distance (Å) and angles (°) for complex 1d. |
|----------------|----------------------|----------------------------------------------------------|
| In1-N1         | 2.516(2)            | In1-C32                                                |
| In1-N2         | 2.286(1)            | In1-C36                                                |
| In1-O1         | 2.206(1)            | In1-C36                                                |
|                | O1-In1-C32A         | 97.49(5)                                               |
|                | O1-In-C36           | 94.38(5)                                               |
|                | C32-In1-C36         | 136.55(6)                                              |
|                | N1-In1-N2           | 69.81(4)                                               |

**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, C$_6$D$_5$Br, 25 to 125 °C) of 2b free ligand L2. Shifts observed were reversible. C$_6$D$_5$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.

| Bond distances     | In1-N1   | 2.468(5) | In1-O3 | 2.392(4) |
|-------------------|---------|---------|--------|----------|
|                   | In1-N2   | 2.179(5) | In1-O4 | 2.354(4) |
|                   | In1-O1   | 2.127(3) | In1-C32| 2.128(7) |
| Bond Angles        | O1-In1-C32| 112.9(2) | O1-In1-N1| 156.3(1) |
|                   | O3-In1-O4| 166.3(1) | N1-In1-C32| 90.4(2)  |
|                   | N1-In1-N2| 72.9(2)  |        |          |

**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)
|                  | 1b      | 1d      | 1a      | 1c      | 2b.2THF                      |
|------------------|---------|---------|---------|---------|------------------------------|
| empirical formula| C₄₄H₅₉InN₂O₂ | C₄₆H₆₁InN₂O | C₄₄H₅₉InN₂OS | C₄₅H₆₀InN₃O | C₈₈H₉₂BF₂₄InN₂O₆           |
| Fw               | 762.75  | 772.78  | 778.81  | 773.78  | 1855.26                      |
| T (K)            | 296.15  | 273(2)  | 100     | 296.15  | 100                          |
| a (Å)            | 17.5732(15) | 18.4020(6)  | 18.3672(15) | 18.3804(16) | 12.616(3)                   |
| b (Å)            | 13.8493(11) | 13.9008(5)  | 14.0583(12) | 13.9887(12) | 13.343(3)                   |
| c (Å)            | 18.4226(15) | 18.4542(7)  | 17.9736(14) | 18.328(2)  | 26.255(5)                   |
| α (deg)          | 90      | 90      | 90      | 90      | 80.163(3)                    |
| β (deg)          | 117.891(2) | 119.051(2)  | 118.8140(10) | 119.839(2) | 76.369(3)                   |
| γ (deg)          | 90      | 90      | 90      | 90      | 85.869(3)                    |
| volume (Å³)      | 3962.81 | 4126.72 | 4066.39 | 4087.71 | 4229.90                      |
| Z                | 4       | 4       | 4       | 4       | 2                            |
| cryst syst       | monoclinic | monoclinic | monoclinic | monoclinic | triclinic                   |
| space group      | P 2₁/c  | P 2₁/n  | P 2₁/c  | P 2₁/c  | P -1                         |
| dcalc (g/cm³)    | 1.278   | 1.244   | 1.272   | 1.257   | 1.457                        |
| μ (Mo Kα) (cm⁻¹) | 6.34    | 6.08    | 6.67    | 6.14    | 3.87                         |
| 2θmax (deg)      | 61.3    | 61.2    | 55.8    | 61.0    | 54.6                         |
| absor corr (Tmin, Tmax) | 0.7005, 0.7461 | 0.909, 0.986 | 0.982, 0.997 | 0.6730, 0.7461 | 0.9887, 0.9977 |
| total no. of reflns | 63957  | 65464   | 9204    | 56696   | 18759                        |
| no. of indep reflns (Rint) | 12154 (0.0394) | 12665 (0.0445) | 9204 (0.0890) | 12417 (0.0461) | 18759(0.1605) |
| residuals (refined on F²): R₁; wR₂ | 0.0523, 0887 | 0.0354, 0634 | 0.0773, 0.1436 | 0.0465, 0.0808 | 0.0983, 2141 |
| GOF              | 1.023   | 1.032   | 1.067   | 1.094   | 1.036                        |
| no. obsrvns [I > 2σ(I)] | 9858   | 9908   | 9510    | 9643    | 9841                         |
| residuals (refined on F²): R₁; wR₂ | 0.0524, 0802 | 0.0273, 0.0600 | 0.0550, 0.1339 | 0.0373, 0.0772 | 0.0794, 2047 |

\[ R₁ = \Sigma \| F_o \| - | F_c | / \Sigma | F_o | ^2 \]
\[ wR₂ = \sqrt{ \Sigma ( w (F_o - F_c)^2 ) / \Sigma w(F_o)^2 } \]

*S63*
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 (400MHz, $\Delta = 0.55$ s, $\delta = 400$ $\mu$s, 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.

2402.5 = [rac-LA_{144}]_{16} + Bu_{57} + Na^{+}_{23} + OH^{-}_{17}
2545.8 = [rac-LA_{144}]_{17} + Bu_{57} + Na^{+}_{23} + OH^{-}_{17}
2690.1 = [rac-LA_{144}]_{18} + Bu_{57} + Na^{+}_{23} + OH^{-}_{17}

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

1. Jung, H. J.; Chang, C.; Yu, I.; Aluthge, D. C.; Ebrahimi, T.; Mehrkhodavandi, P., Coupling of Epoxides and Lactones by Cationic Indium Catalysts To Form Functionalized Spiro-Orthoesters. *ChemCatChem* 2018, **10** (15), 3219-3222.
2. Beachley, O. T.; Rusinko, R. N., Preparation and properties of [(trimethylsilyl)methyl]indium(iii) compounds. *Inorg. Chem.* 1979, **18** (7), 1966-1968.
3. Murphy, A.; Pace, A.; Stack, T. D. P., Ligand and pH influence on manganese-mediated peracetic acid epoxidation of terminal olefins. *Org. Lett.* 2004, **6** (18), 3119-3122.
4. Sandstrom, M.; Persson, I.; Persson, P., A study of solvent electron-pair donor ability and lewis basicity scales. *Acta. Chem. Scand.* 1990, **44** (7), 653-675.