Supporting Information

Ultra-Rapid Cerium(III)–NHC Catalysts for High Molar Mass Cyclic Polylactide

Ryan W. F. Kerr,[‡abc] Paul M. D. A. Ewing,[‡ab] Sumesh K. Raman,[c] Andrew D. Smith,[b] Charlotte K. Williams[*c] and Polly L. Arnold[*ad]

[a]*EaStCHEM School of Chemistry, University of Edinburgh, The King's Buildings, Edinburgh, EH9 3FJ, UK.*

[b]*EaStCHEM School of Chemistry, University of St. Andrews, North Haugh, St Andrews, KY16 9ST, UK.*

[c]*University of Oxford, Chemistry Research Laboratory, 12 Mansfield Road, Oxford OX1 3TA, UK.*

[d]*Current address: Department of Chemistry, University of California, Berkeley, Berkeley CA 94720, USA. Chemical Sciences Division, Lawrence Berkeley National Laboratory, One Cyclotron Road, Berkeley 94720, USA.*

E-mails: pla@berkeley.edu; charlotte.williams@chem.ox.ac.uk

General Methods

Materials

All solvents and reagents were purchased and used as obtained from commercial sources (Sigma Aldrich) unless stated otherwise. The synthesis of 3-(3,5-di-*tert*-butyl-2-hydroxyphenol)-1-isopropyl-1*H*-imidazol-3-ium (H_2L^1)[1], **1**[1] and CeN''_3[2] (N'' = $N(SiMe_3)_2$) were performed using literature procedures. All reactions including monomer purification and polymerizations were carried out under inert conditions using standard Schlenk line techniques and a nitrogen-filled glovebox unless otherwise stated. ε-Caprolactone (CL) and β-butyrolactone (β-BL) were dried by stirring over CaH_2 followed by fractional distillation and stored under a nitrogen atmosphere. *rac*-Lactide and L-lactide (LA) were purified by recrystallization from toluene and sublimation in triplicate. Solvents used for polymerizations and the synthesis of catalysts **1**, **2** and **3** were purified using solvent purification system drying columns, degassed by sparging with N_2 and stored over 4 Å molecular sieves under an inert dinitrogen or argon atmosphere.

Methods

NMR Spectroscopy: ^1H, ^{13}C NMR spectra were obtained using Bruker AV 400 MHz and 500 MHz instruments.

Gel Permeation Chromatography: GPC analysis of *rac*-PLA, PCL and P(β-BL) were carried out using a Shimadzu LC-20AD instrument equipped with PSS SDV 5 µm precolumn and two PSS SDV 5 µm linear M columns and Refractive Index (RI) detector. Samples were dissolved in HPLC grade THF, filtered through 0.2 µm PTFE filters (VWR) and run at 1 mL min^{-1} at 30 °C. Monodisperse polystyrene was used for calibration.

GPC analysis of PLLA was carried out using an Agilent PL GPC-50 equipped with two Polymer labs Mixed D columns and Refractive Index (RI) detector. Samples were dissolved in HPLC grade $CHCl_3$, filtered through 0.2 µm PTFE filters (VWR) and run at 1 mL min^{-1} at 40 °C. Monodisperse polystyrene was used for calibration.

Intrinsic volume analysis of PLA was carried out by Polymer RTP, Warwick, using an Agilent Infinity II MDS instrument equipped with differential refractive index (DRI), viscometry (VS), dual angle light scatter (LS) and multiple wavelength UV detectors. The system was equipped with an Agilent PLgel 5 µm and two Agilent PLgel Mixed C columns (300 x 7.5 mm). Samples were dissolved in HPLC grade $CHCl_3$, filtered through a Nylon membrane with 0.22 µm pore size and run at 1 mL min^{-1} at 30 °C.

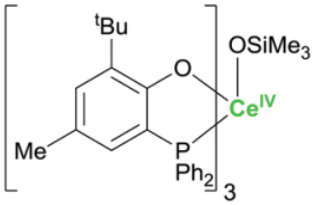
Narrow poly(methyl methacrylate) (2,210,000-550 g mol^{-1}), and polystyrene standards (364,000-162 g mol^{-1}) (Agilent EasiVials) were used for conventional calibration. Universal calibration was created from polystyrene (364,000-370 g mol^{-1}). Molar mass and dispersity (Đ) values of synthesized polymers were determined by conventional and universal calibration using Agilent GPC/SEC software.

Elemental analyses were performed by Elemental Microanalysis Ltd, Hameldown Road, Okehampton Business Park, Exeter Road, Okehampton, Devon, EX20 1UB, UK

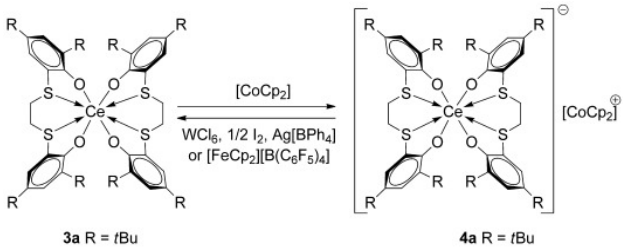
MALDI-ToF mass spectrometry was carried out on a Waters MALDI Micro MX set to positive ion reflectron mode. Samples were dissolved in THF at 10 mg mL^{-1}. Dithranol (10 mg mL^{-1} in THF) or *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (10 mg mL^{-1} in THF) were used as matrix. Potassium trifluoroacetate (KTFA, 10 mg mL^{-1} in THF) or NaI (10 mg ml^{-1} in THF) were used as salts. The components were mixed in the ratio 1:1:1 (polymer:salt:matrix), spotted onto a plate and allowed to dry completely before analysis. For MALDI-ToF MS analysis of intermediates towards the synthesis of complexes **2** and **3**, the samples were spotted from a THF solution at 10 mg mL^{-1}. Red phosphorus was used as a calibration standard.

DSC: A sealed, empty crucible was used as a reference, and the DSC was calibrated using zinc and indium. Samples were heated from 0 °C to 200 °C, at a rate of 10 °C min^{-1} under N_2 flow (80 mL $min^{-1)}$. Samples were subsequently cooled to 0 °C, at a rate of 10 °C min^{-1}, and kept at 0 °C for a further 5 minutes, followed by a heating-cooling procedure from 0 °C to 200 °C, at a rate of 10 °C min^{-1}. Each sample was analyzed over two heating-cooling cycles. Glass transition temperatures (T_g) are reported as the midpoint of the transition taken from the second heating cycle. TGA was measured using a TGA/DSC 1 system (Mettler-Toledo Ltd). Samples were heated from 0 °C to 200 °C, at a rate of 5 °C min^{-1}, under N_2 flow (100 cm^3 min^{-1}).

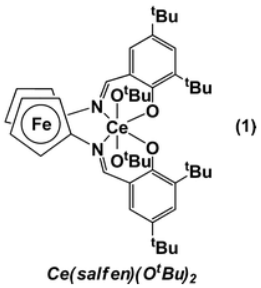
1.0 Synthesis and Characterization of Complexes 2 and 3



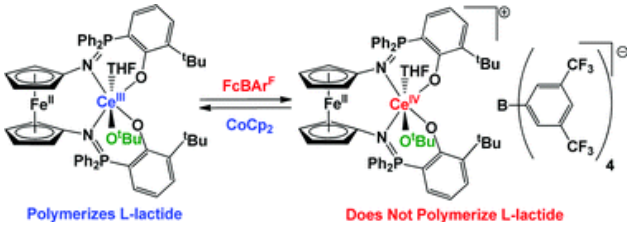
Arnold and Shaver *et al.*
Dalton Trans. 2018
TOF <10 h^{-1}



Okuda *et al.*
ChemCatChem. 2013
TOF <15 h^{-1}



Diaconescu *et al.*
Inorg. Chem., 2009, 4701
TOF <550 h^{-1}

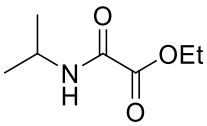


Diaconescu *et al.*
Chem Commun. 2011
TOF <10 h^{-1}

Chart S 1 The cerium ROP catalysts reported to date

1.1 Synthesis of Catalyst 2

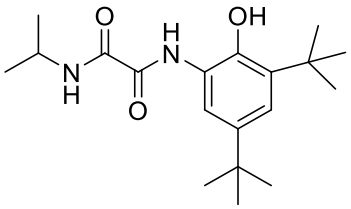
1.1.1 Ethyl 2-(isopropylamino)-2-oxoacetate



The following is a modification of the procedure reported by Grubbs *et al.*[3] To a round bottom flask charged with $^{i}PrNH_2$ (12.2 mL, 149 mmol), NEt_3 (19.8 mL, 142 mmol) and THF (150 mL) cooled to 0 °C was added ethyl chlorooxoacetate (15.2 mL, 136 mmol) dropwise to give a bright yellow solution and a white precipitate. The reaction was warmed to room temperature and stirred overnight. The precipitate was removed by filtration and the filtrate was washed with 2 M HCl (2 × 100 mL). The aqueous layer was extracted with ethyl acetate (3 × 30 mL), the organic layers were combined and washed with brine (2 × 20 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The title compound was obtained as a viscous orange oil without further purification (18.8 g, 118 mmol, 83 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 6.96 (1H, s, N*H*), 4.30 (2H, q, *J* 7.15 CH_2), 4.12–4.00 (1H, m, C*H*(CH_3)$_2$), 1.35 (3H, t, *J* 7.15, CH_3), 1.18 (6H, d, *J* 6.58, CH(*C*H_3)$_2$); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 13.8

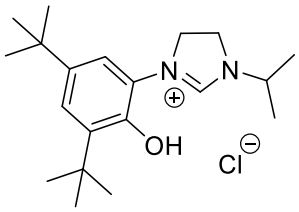
(CH_2CH_3), 22.0 ($CH(CH_3)_2$), 42.1 ($CH(CH_3)_2$), 62.9 (OCH_2CH_3), 155.7 (NC(=O)C), 160.8 (CC(=O)O); HRMS (ESI+) $C_7H_{13}NO_3^+$ $[M]^+$ requires 159.08972, found 159.08900 (–4.5 ppm).

1.1.2 N^1-(3,5-di-*tert*-butyl-2-hydroxyphenyl)-N^2-isopropyloxalamide



The following is a modification of the procedure reported by Grubbs *et al*.[3] To a round bottom flask fitted with a reflux condenser was charged with 2-amino-4,6-di-tertbutylphenol (3.00 g, 13.6 mmol), ethyl 2-(isopropylamino)-2-oxoacetate (2.16 g, 13.6 mmol), NEt_3 (3.80 mL, 27.2 mmol) and toluene (60 mL). The reaction was heated to reflux for 16 h and after cooling to approximately 50 °C, ethyl acetate (100 mL) was added to the warm solution. The reaction mixture was washed with 2M HCl (2 x 50 mL). The aqueous layer was extracted with ethyl acetate (3 x 50 mL). The organic layers were combined and washed with brine (2 x 20 mL), dried over $MgSO_4$ and concentrated under reduced pressure. Recrystallization from a concentrated toluene solution and washing with pentane gave the title compound as a white solid (3.64 g, 10.9 mmol, 80 %). MPt. 140–142 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.48 (1H, s, ArO*H*), 7.97 (1H, s, ArN^1*H*), 7.36 (1H, br. m, CHN^2*H*), 7.27 (1H, d, *J* 2.34, Ar(6)*H*), 6.99 (1H, d, *J* 2.34 Ar(4)*H*), 4.19–4.10 (1H, m, C*H*(CH_3)$_2$), 1.44 (s, 9H, Ar(3)C(C*H*$_3$)$_3$), 1.29 (s, 9H, Ar(5)C(C*H*$_3$)$_3$), 1.26 (6H, d, *J* 6.59, CH(*CH*$_3$)$_2$); ^{13}C NMR {^{1}H} (126 MHz, $CDCl_3$) δ_C: 158.5 (*C*=O), 158.0 (*C*=O), 146.1 (Ar(5)*C*C(CH$_3$)$_3$), 142.9 (Ar(2)*C*C(CH$_3$)$_3$), 140.0 (Ar(3)*C*OH), 124.1 (Ar(1)*C*NH), 123.0 (Ar(4)*C*H), 117.9 (Ar(6)*C*H), 42.6 (*C*(CH$_3$)$_3$), 35.5 (*C*(CH$_3$)$_3$), 34.3 (*CH*(CH$_3$)$_2$), 31.5 (C(*CH*$_3$)$_3$), 29.8 (C(*CH*$_3$)$_3$), 22.3 (CH(*C*H$_3$)$_2$); HRMS (ESI)+ $C_{19}H_{30}N_2O3Na^+$ $[M+Na]^+$ requires 357.21340, found 357.21486 (+4.1 ppm).

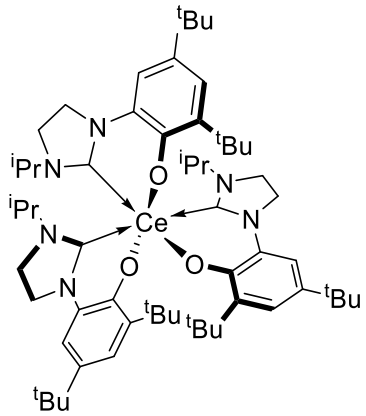
1.1.3 H_2L^2 – 3-(3,5-Di-*tert*-butyl-2-hydroxyphenyl)-1-isopropyl-4,5-dihydro-1*H*-imidazol-3-ium chloride



The following is a modification of the procedure reported by Grubbs *et al.*[3] A round bottom flask charged with N^1-(3,5-di-tert-butyl-2-hydroxyphenyl)-N^2-isopropyloxalamide (7.65 g, 22.9 mmol) was dried under dynamic vacuum at 2.0 x 10^{-2} mbar for 2 h. To the vessel was added BH_3·THF solution (1 M, 229 mL, 229 mmol, 10 equiv.) to give a red/orange solution with some effervesce and was heated to 50 °C for 24 h. The reaction was allowed to cool RT and MeOH (100 mL) was slowly added to quench

the unreacted borane. HCl (7.80 mL, 96.6 mmol, conc.) was added to the reaction and the mixture was stirred at RT for 1 h then the solvent was removed under reduced pressure. The resultant sticky white solid was dissolved in MeOH and the solvent was removed under reduced pressure. This process was carried out three times to remove unreacted BH3. The remaining white solid was dissolved in toluene (30 mL) and to the reaction mixture was added $CH(OMe)_3$ (10.2 mL, 93.2 mmol) and formic acid (1 drop) and heated to 90 °C for 72 h. The solution was allowed to cool to RT. The solvent was removed under reduced pressure. A trituration in diethyl ether gave the title compound as a white powder (5.32 g, 15.1 mmol, 66 %). MPt. 290 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.40 (1H, s, Ar(2)O*H*), 8.61 (1H, s, NC*H*N), 7.30 (1H, d, *J* 2.41, Ar(4)*H*), 6.88 (1H, d, *J* 2.41 Ar(6)*H*), 4.42–4.38 (, NCH_2CH_2N), 4.21–4.16 (2H, m, NCH_2CH_2N), 4.14 (1H, sept., *J* 6.61, $CH(CH_3)_2$), 1.40 (9H, s, 9H, Ar(3)$C(CH_3)_3$), 1.38 (6H, d, *J* 6.63, $CH(CH_3)_2$), 1.25 (9H, s, 9H, Ar(5)$C(CH_3)_3$); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ_C: 20.7 ($CH(CH_3)_2$), 30.0 ($C(CH_3)_3$), 31.5 ($C(CH_3)_3$), 34.5 ($C(CH_3)_3$), 35.7 ($C(CH_3)_3$), 46.3 (NCH_2CH_2N), 50.8 (NCH_2CH_2N), 51.3 ($CH(CH_3)_2$), 119.3 (Ar(6)*CH*), 125.0 (Ar(4)*CH*), 125.7 (Ar(1)*C*), 141.7 (Ar(3)*C*), 143.3 (Ar(5)*C*), 148.7 (Ar(2)*C*), 156.8 (NCHN); EA for $C_{20}H_{33}N_2OCl$: C 68.06 %, H 9.42 %, N 7.94 % calculated, C 67.97, H 9.36 %, N 8.08 % found; MALDI-ToF-MS (ESI)+ $[M\text{-}Cl]^+$ $C_{20}H_{33}N_2O^+$ requires 317.259, found 317.497 (100 %)

1.1.4 Catalyst 2

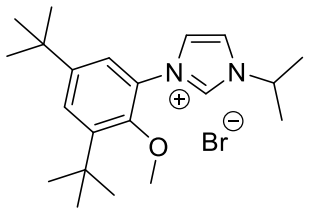


To vial charged with a suspension of H_2L^2 (500 mg, 1.42 mmol), in THF (5 mL) cooled to –20 °C, was added a solution of KN" (282 mg 1.42 mmol) in THF (2 mL). The reaction was stirred for 30 minutes while warming to room temperature to give a white precipitate. The white solid was removed by filtration and added to a stirring solution of $CeN"_3$ (294 mg, 0.473 mmol) in THF (5 mL) and stirred for 12 h. The solvent was removed at reduced pressure and the residue was washed with hexane (3 x 10 mL) and dried under dynamic vacuum. The title compound was obtained by recrystallization of the crude material in hexane (5 mL) at –30 °C overnight as a red solid (400 mg, 0.369 mmol, 78%). Red crystals suitable for X-ray diffraction were obtained from a concentrated hexane solution left at –30 °C overnight. ^{1}H NMR (500 MHz, C_6D_6) δ_H: –23.35 (1H, s, $CH(CH_3)_2$), –22.28 (1H, s, $CH(CH_3)_2$), –10.39

(3H, s, CH(CH_3)$_2$), –10.15 (3H, s, CH(CH_3)$_2$), –8.79 ((1H, s, CH(CH$_3$)$_2$), –5.78 (3H, s, CH(CH_3)$_2$), –5.34 (3H, s, CH(CH_3)$_2$), –3.94 (9H, s, C(CH_3)$_3$), –2.00 (3H, s, CH(*C*H_3)$_2$), –1.42 (9H, s, C(*C*H_3)$_3$), 1.48 ((9H, s, C(CH_3)$_3$), 2.52 (9H, s, C(CH_3)$_3$), 2.74 (3H, s, CH(CH_3)$_2$), 3.18 (9H, s, C(CH_3)$_3$), 3.32 (2H, s, -NCH_2-), 3.76 (2H, s, -NCH_2-), 4.63 (9H, s, C(CH_3)$_3$), 4.83 (2H, s, -NCH_2-), 4.96 (2H, s, -NCH_2-), 5.52 (2H, s, -NCH_2-), 6.54 (2H, s, -NCH_2-), 8.83 (1H, s, CH), 9.37 (1H, s, CH), 10.92 (1H, s, CH), 11.14 (1H, s, CH), 11.22 (1H, s, CH), 11.92 (1H, s, CH); ^{13}C NMR (126 MHz, C_6D_6) δ_C: 200.0, 197.0, 171.1, 156.8, 154.3, 154.0, 152.5, 150.9, 146.8, 145.8, 140.3, 140.0, 139.0, 137.3, 128.0, 127.8, 127.6, 125.3, 124.2, 122.8, 120.8, 119.2, 118.9, 116.8, 61.7, 59.3, 58.4, 57.7, 48.1, 46.1, 44.4, 43.7, 42.7, 41.2, 39.5, 36.4, 36.0, 35.4, 34.2, 33.9, 33.4, 30.2, 26.9, 23.7, 21.0, 15.8, 7.57, 2.27; EA for $C_{60}H_{93}CeO_3N_6$: C 66.33%, H 8.63%, N 7.73% calculated. C 66.10%, H 9.05%, N 7.16% found.

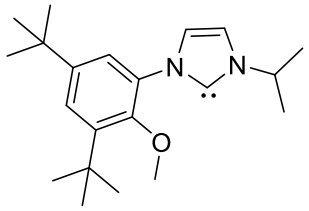
1.2 Synthesis of Catalyst 3

1.2.1 [HL^{1Me}][Br] - 3-(3,5-Di-*tert*-butyl-2-methoxyphenyl)-1-isopropyl-1*H*-imidazol-3-ium



To a round bottom flask charged with H_2L^1 (500 mg, 1.26 mmol), K_2CO_3 (348 mg, 2.52 mmol), KI (10.0 mg, 60 µmol) and acetone (20 mL) was added MeI (100 µL, 1.64 mmol) dropwise. The solution turned from colorless to yellow and was heated to 45 °C for 12 h. The white precipitate was isolated from the suspension by filtration and the filtrate was extracted with CH_2Cl_2 and deionized water. The organic layer was collected and dried over $MgSO_4$, washed with brine (2 × 10 mL) and concentrated under reduced pressure. The title compound was obtained as a white solid (450 mg, 1.10 mmol, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 1.35 (9H, s, C(C*H*$_3$)$_3$), 1.40 (9H, s, C(C*H*$_3$)$_3$), 1.72 (6H, d, *J* 6.60, CH(C*H*$_3$)$_2$), 3.33 (3H, s, OC*H*$_3$), 5.46 (1H, h, *J*, C*H*(CH$_3$)$_2$), 7.50 (1H, d, *J* 2.36, Ar*H*), 7.52 (1H, d, *J* 2.36, Ar*H*), 7.62 (1H, t, *J* 1.9, NC*H*CHN), 7.79 (1H, t, *J* 1.9, NCHC*H*N), 10.29 (1H, m, NC*H*N); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 23.4 (CH(C*H*$_3$)$_2$), 30.8 (C(C*H*$_3$)$_3$), 31.5 (C(C*H*$_3$)$_3$), 35.2 (*C*(CH$_3$)$_3$), 35.8 (*C*(CH$_3$)$_3$), 54.0 (*C*H(CH$_3$)$_2$), 61.2 (OCH$_3$), 120.5 (NCH$_2$CH$_2$N), 121.8 (Ar(6)*CH*), 123.8 (NCH$_2$CH$_2$N), 126.8 (Ar(4)*CH*), 128.1 (Ar(2)*C*), 135.5 (NCHN), 144.6 (Ar(5)*C*), 148.4 (Ar(4)*C*), 150.2 (Ar(2)*C*); HRMS (ESI)+ $C_{21}H_{33}N_2OBr$ [M-Br]$^+$, requires 329.25874, found 329.26009 (+4.1 ppm).

1.2.2 Catalyst 3 - 1-(3,5-di-*tert*-butyl-2-methoxyphenyl)-3-isopropyl-1*H*-imidazol-3-ium-2-ide



The following is a modification of a procedure reported by Arduengo.[4] To a Schlenk charged with a stirring solution of [HL^{1Me}][Br] (129 mg, 0.316 mmol) in THF (5 mL) was added was added NaH (8.32 mg, 0.347 mmol) and stirred for 3 min. A suspension of KO^{t}Bu (1.8 mg, 5 mol %) in THF (2 mL) was added. The reaction was stirred at RT for 4 h. The solid was removed by filtration and the filtrate was concentrated under reduced pressure to give the title compound was obtained as a yellow solid (90 mg, 0.274 mmol, 87%). ^{1}H NMR (500 MHz, C_6D_6) δ_H: 1.34 (9H, s, C(C*H*$_3$)$_3$), 1.41 (6H, d, *J* 6.73, CH(C*H*$_3$)$_2$), 1.61 (9H, s, C(C*H*$_3$)$_3$), 3.31 (3H, s, OC*H*$_3$), 4.61 (1H, h, *J* 6.73 C*H*(CH$_3$)$_2$), 6.65 (1H, d, *J* 1.70, NC*H*CHN),

7.34 (1H, d, *J* 1.70, NCHC*H*N), 7.58 (1H, d, *J* 2.52, Ar(4)*H*), 8.11 (1H, d, *J* 2.52, Ar(6)*H*); ^{13}C NMR {^{1}H} (126 MHz, $CDCl_3$) δ_C: 24.2 (*C*H$(CH_3)_2$), 31.1 (C(*C*H$_3)_3$), 31.6 (C(*C*H$_3)_3$), 34.8 (*C*$(CH_3)_3$), 35.7 (*C*$(CH_3)_3$), 52.5 (*C*H$(CH_3)_2$), 59.4 (O*C*H$_3$), 116.48 (N*C*H$_2$CH$_2$N), 121.2 (NCH$_2$*C*H$_2$N), 122.5 (Ar(6)*C*H), 124.4 (Ar(4)*C*H), 136.6 (Ar(1)*C*), 142.7 (Ar(5)*C*), 146.3 (Ar(3)*C*), 151.3 (Ar(2)*C*); MALDI-ToF-MS (ESI)+ $[M+H]^+$ for $C_{21}H_{33}N_2O$ requires 329.259, found 329.707 (100%), $[M+Na]^+$ $C_{21}H_{32}N_2ONa^+$ requires 351.241 found 351.717 (18%), $[M+K]^+$ $C_{21}H_{32}N_2OK^+$ requires 367.215 found 367.713 (6%)

1.3 NMR spectra for complexes 2 and 3

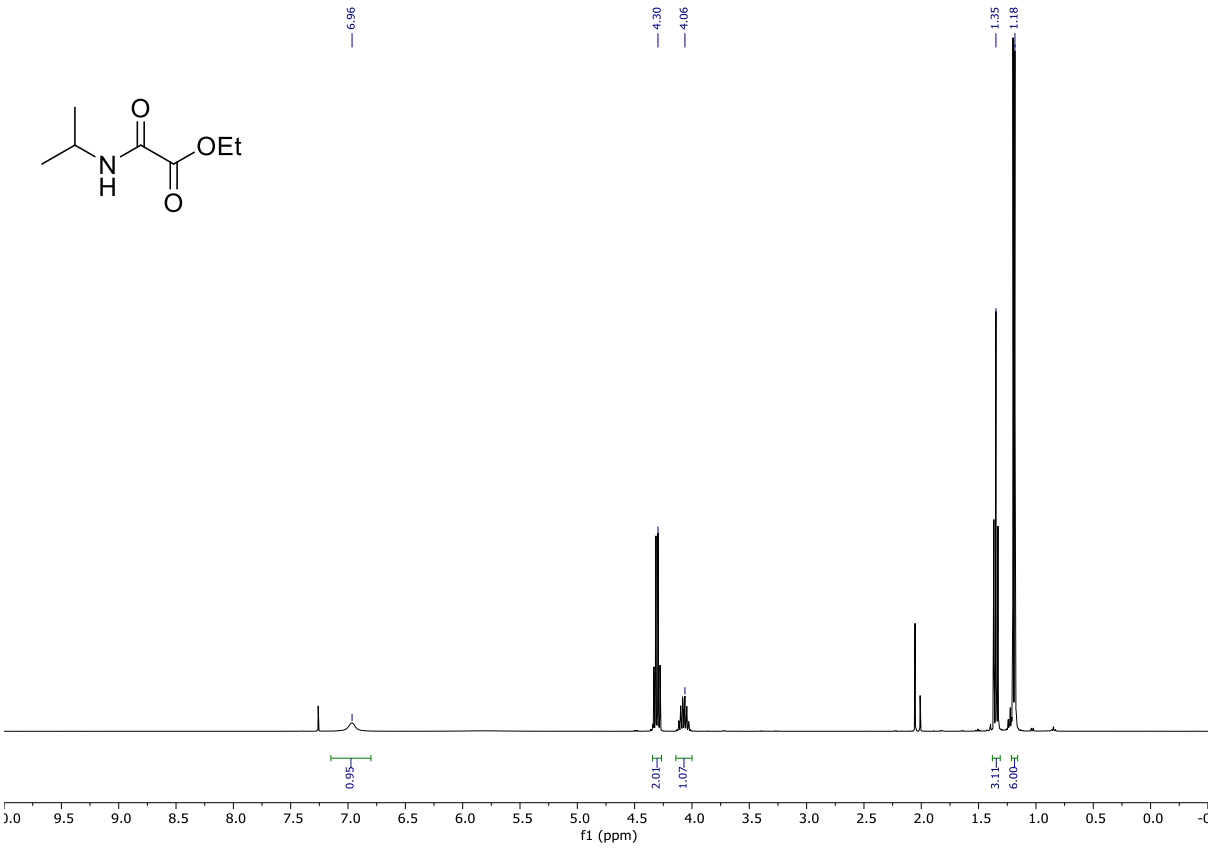


Figure S1: ^{1}H NMR spectrum of ethyl 2-(isopropylamino)-2-oxoacetate (400 MHz, $CDCl_3$)

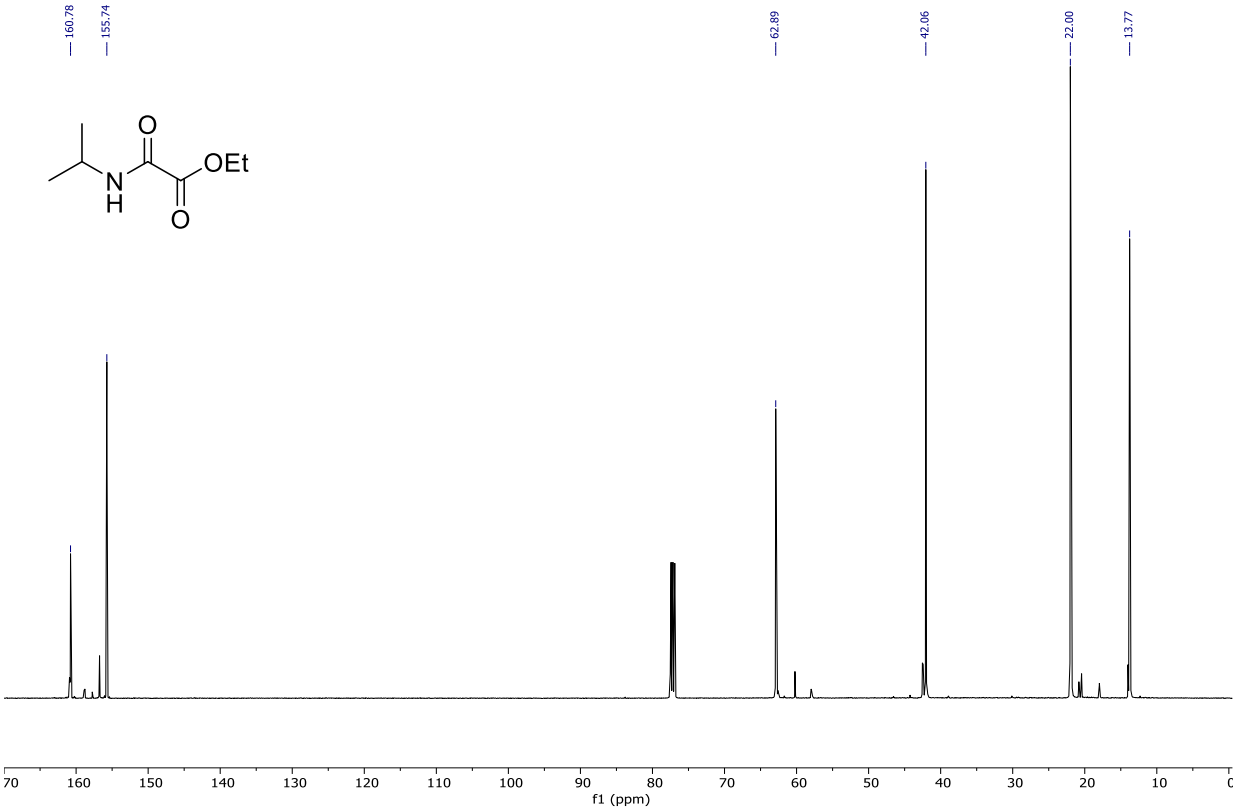


Figure S2: ^{13}C NMR spectrum of ethyl 2-(isopropylamino)-2-oxoacetate (128 MHz, $CDCl_3$)

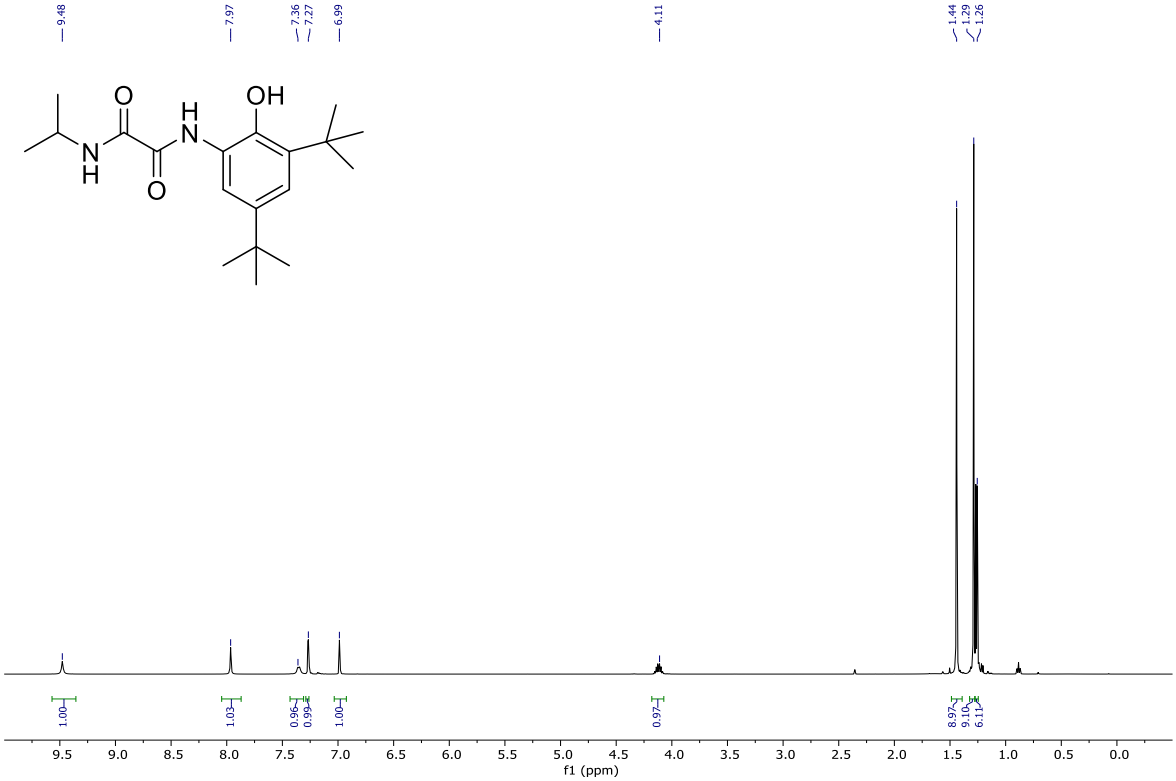


Figure S3: ^{1}H NMR spectrum of N^1-(3,5-di-*tert*-butyl-2-hydroxyphenyl)-N^2-isopropyloxalamide (400 MHz, $CDCl_3$)

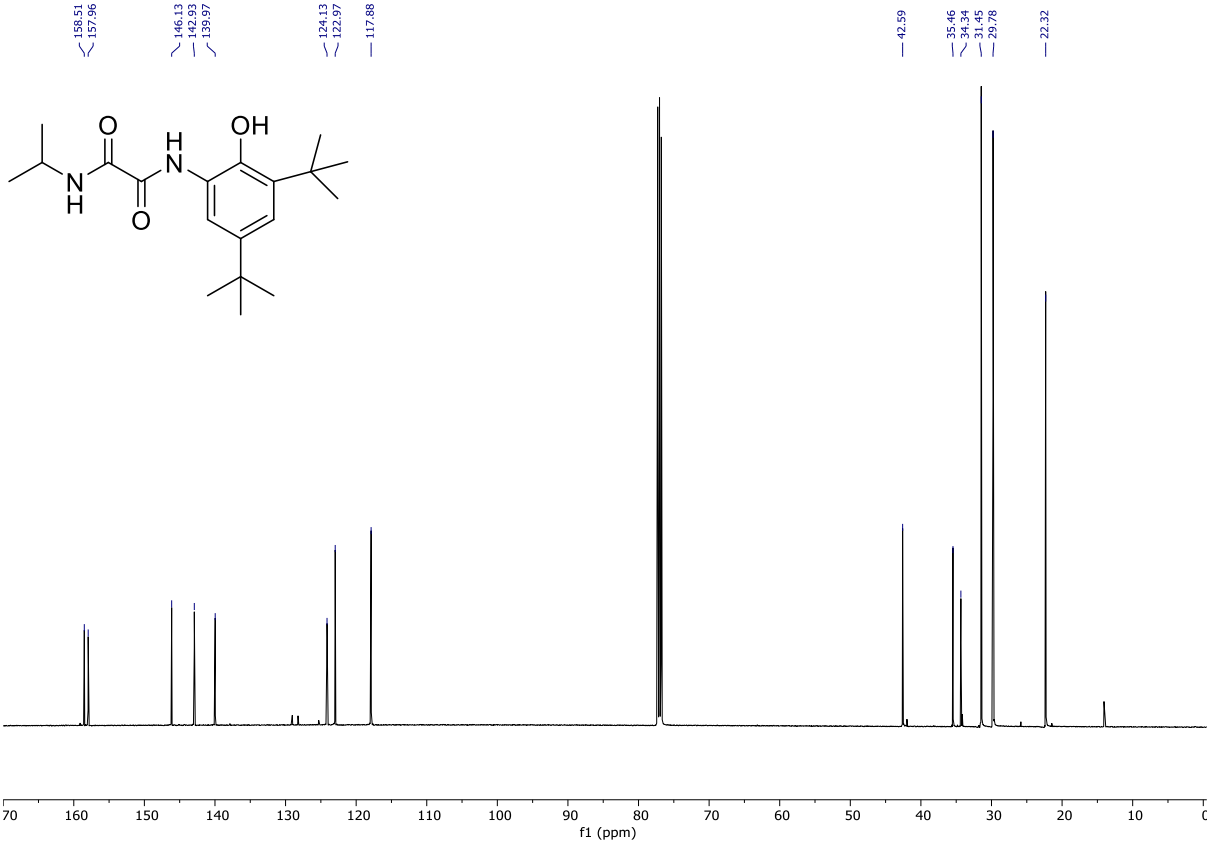


Figure S4: ^{13}C NMR spectrum of N^1-(3,5-di-*tert*-butyl-2-hydroxyphenyl)-N^2-isopropyloxalamide (128 MHz, $CDCl_3$)

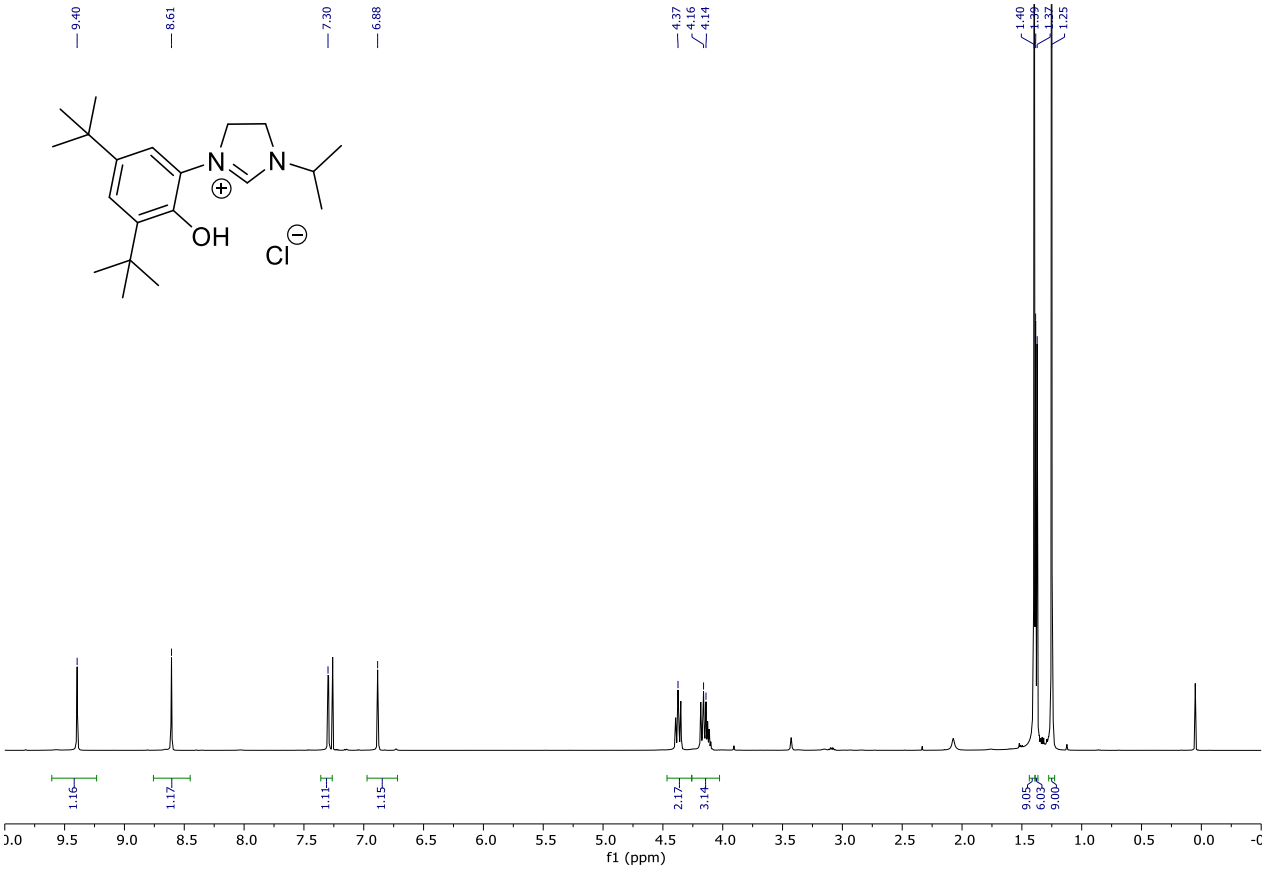


Figure S5: ^{1}H NMR spectrum of H_2L^2 (400 MHz, $CDCl_3$)

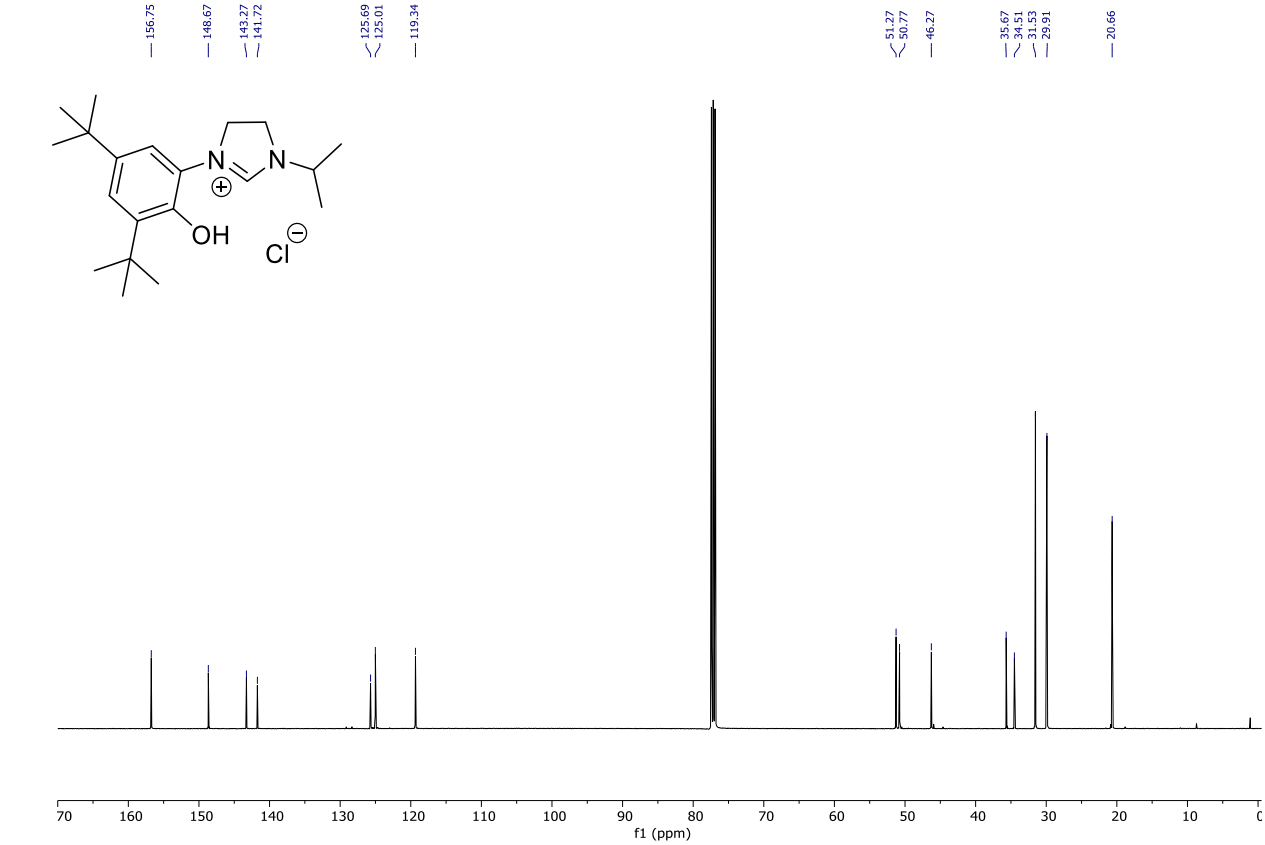


Figure S6: ^{13}C NMR spectrum of H_2L^2 (128 MHz, $CDCl_3$)

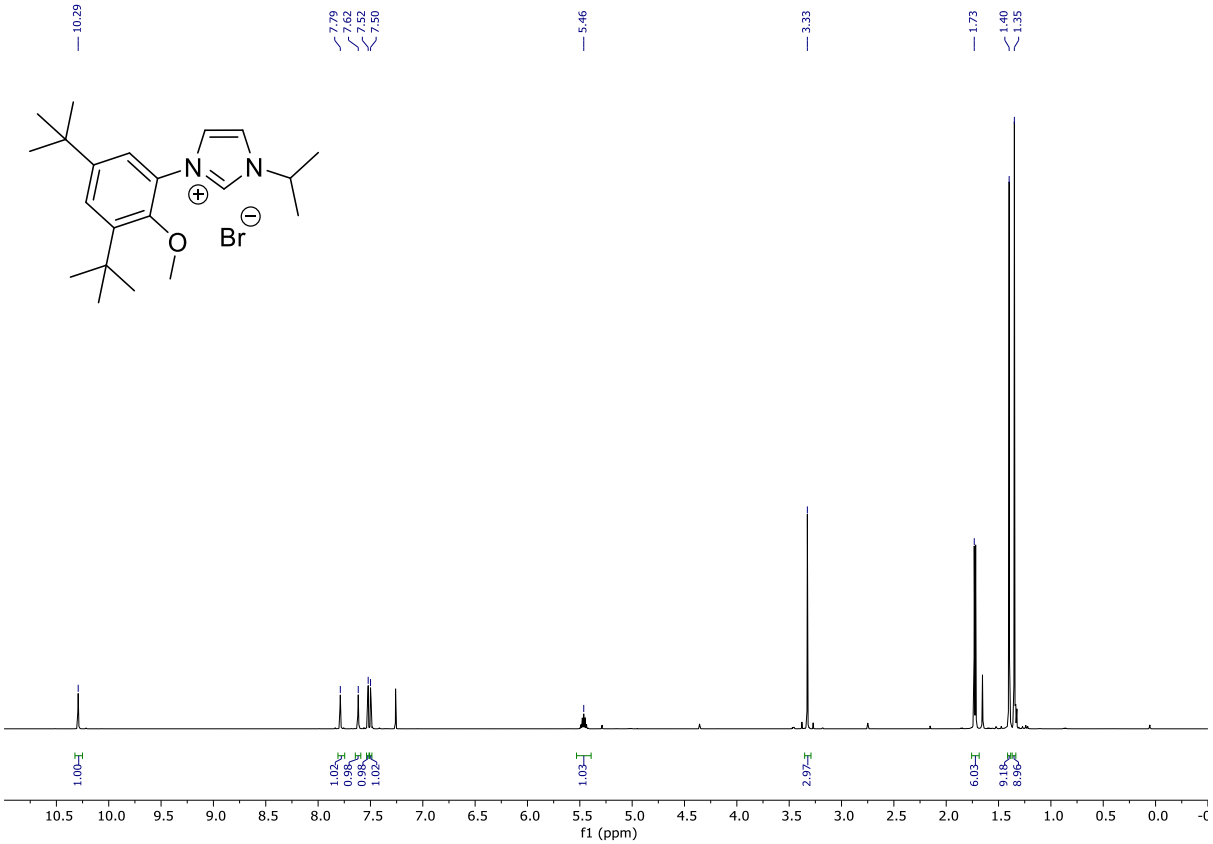


Figure S7: ^{1}H NMR spectrum of $[H_2L^{1Me}][Br]$ (400 MHz, $CDCl_3$)

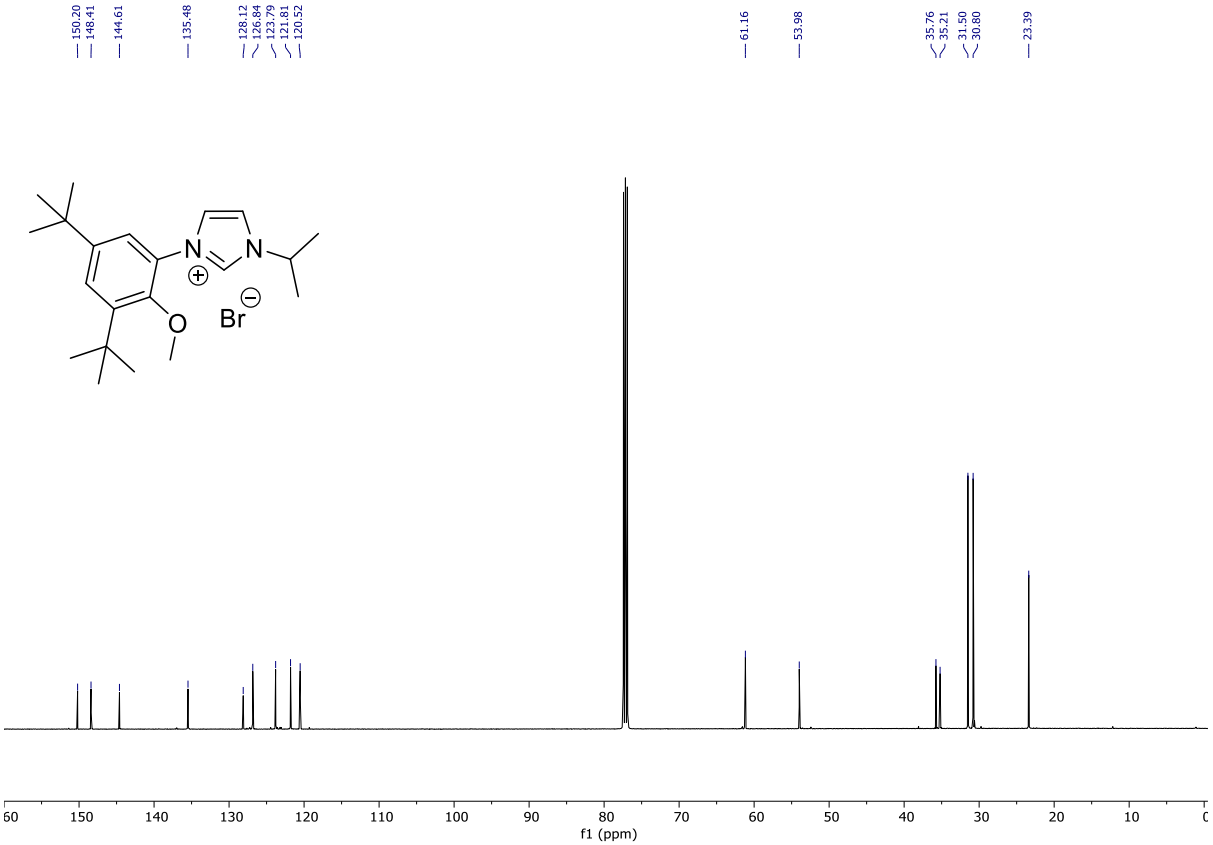


Figure S8: ^{13}C spectrum NMR of $[H_2L^{1Me}][Br]$ (128 MHz, $CDCl_3$)

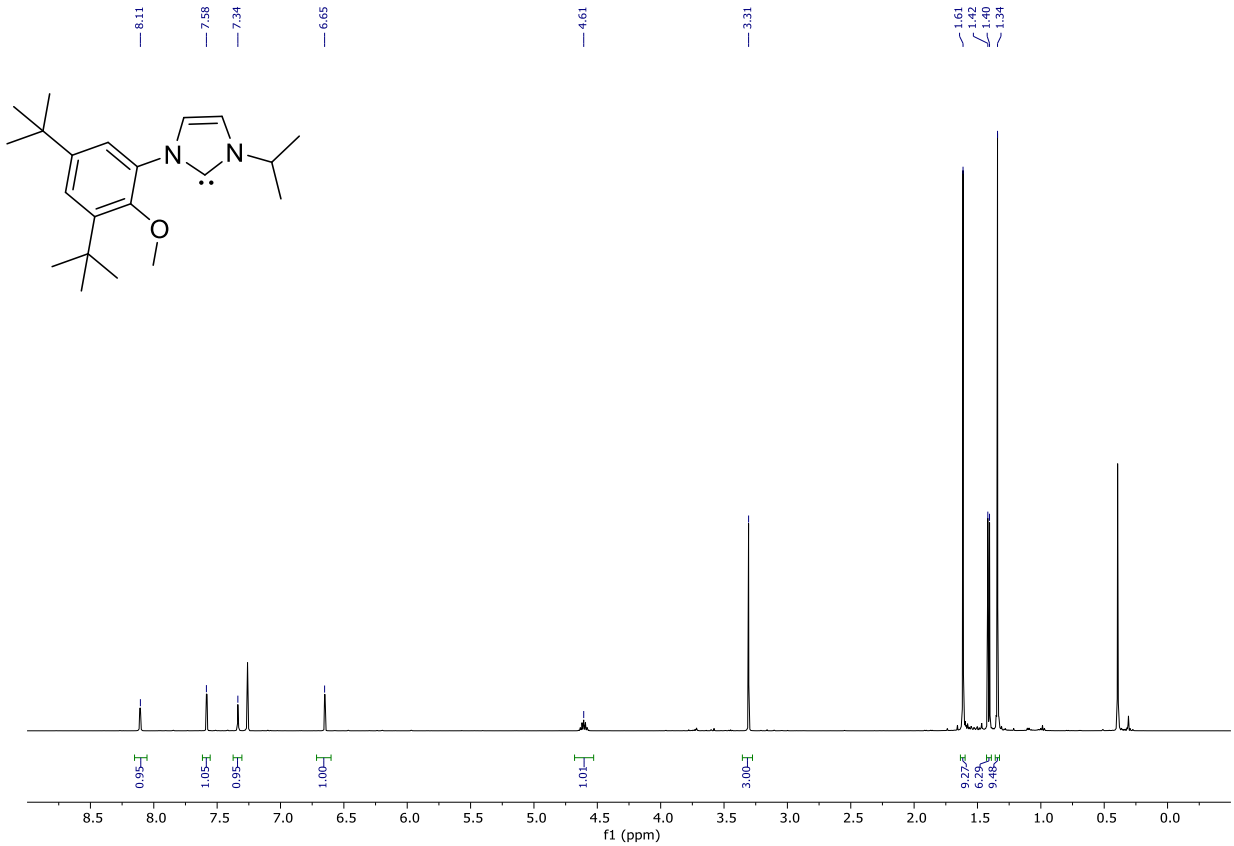


Figure S9: ^{1}H NMR spectrum of **3** (400 MHz, C_6D_6)

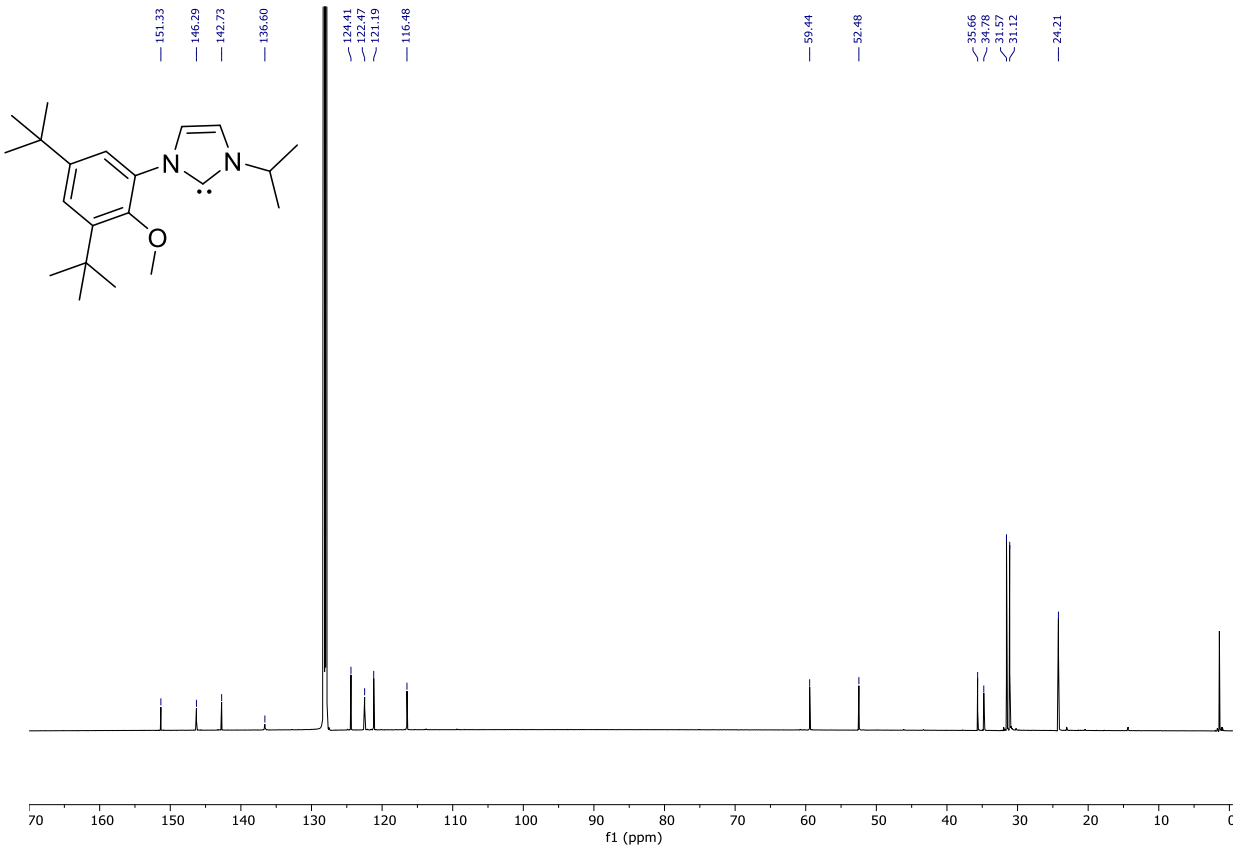


Figure S10: ^{13}C NMR spectrum of **3** (128 MHz, C_6D_6)

2.0 Ring opening polymerization of *rac*-lactide

General method

In a glove box, *rac*-LA (*rac*-lactide) (144 mg, 1 mmol) was dissolved in THF (≤1 mL). A stock solution of **1** or **2** in THF [0.01 M] was diluted as required to 1 mL in THF and injected into the rapidly stirring solution (1400 RPM, total 2 mL THF) and run at the specified temperature and time. The reaction was quenched with the addition of hexane (10 mL) and immediately removed from the glovebox *via* pre-cycled vacuum ports and exposed to air to completely quench any residual cerium catalyst. The polymer was obtained as a colorless solid by triplicate precipitation of the crude material in DCM/MeOH or DCM/^{i}PrOH with spectroscopic data in accordance with the literature.[5] Samples were analyzed by ^{1}H NMR spectroscopy, homonuclear-decoupled ^{1}H NMR spectroscopy ($CDCl_3$)[5] and by GPC in THF; Example ^{1}H NMR spectrum (400 MHz, $CDCl_3$) δ_H: PLA 1.49–1.65 (3H, m, CH*CH$_3$*), 5.10–5.28 (1H, m, *CH*CH$_3$).

Calculation of reaction exotherm: THF (1.778 g, 0.0247 mol, c_m = 124 J mol^{-1} K^{-1}), Lactide (1 mmol, $\Delta H_{polymerization}$ = -22.9 kJ mol^{-1}).

$$\Delta T = \frac{Q}{C} = \frac{22.9\ J\ mol^{-1}}{0.0247\ x\ 124\ J\ mol^{-1}\ K^{-1}} = \mathbf{+7.48\ K}$$

Additional experiments

a) Larger scale, glove box polymerization - 5000:1 [LA]:[Catalyst]

In a glove box, *rac*-LA (*rac*-lactide) (576 mg, 4 mmol) was dissolved in THF (4 mL). A stock solution of **1** in THF [0.8 µmol in 4mL] was injected into the rapidly stirring solution (1400 RPM, total 8 mL THF) and run for 60 secs at room temperature. The reaction was quenched with the addition of hexane (30mL) and immediately removed from the glovebox *via* N_2-filled vacuum ports and exposed to air to completely quench any residual cerium catalyst. ^{1}H NMR analysis of the crude revealed identical rates to the smaller scale reaction.

b) Schlenk Line polymerization – 5000:1 [LA]:[Catalyst]

In a Schlenk flask capped with a subaseal, *rac*-LA (*rac*-lactide) (144 mg, 1 mmol) was dissolved in THF (1 mL). The contents of a separate Schleck containing a solution of catalyst **1** in THF [0.2 µmol in 1 mL] was injected into the rapidly stirring solution (1400 RPM, total 2 mL THF) and run for 60 secs at room temperature. The reaction was quenched at the allotted time with “wet” hexane and exposed to air to ensure complete quenching; polymerization results were the same as the glovebox technique.

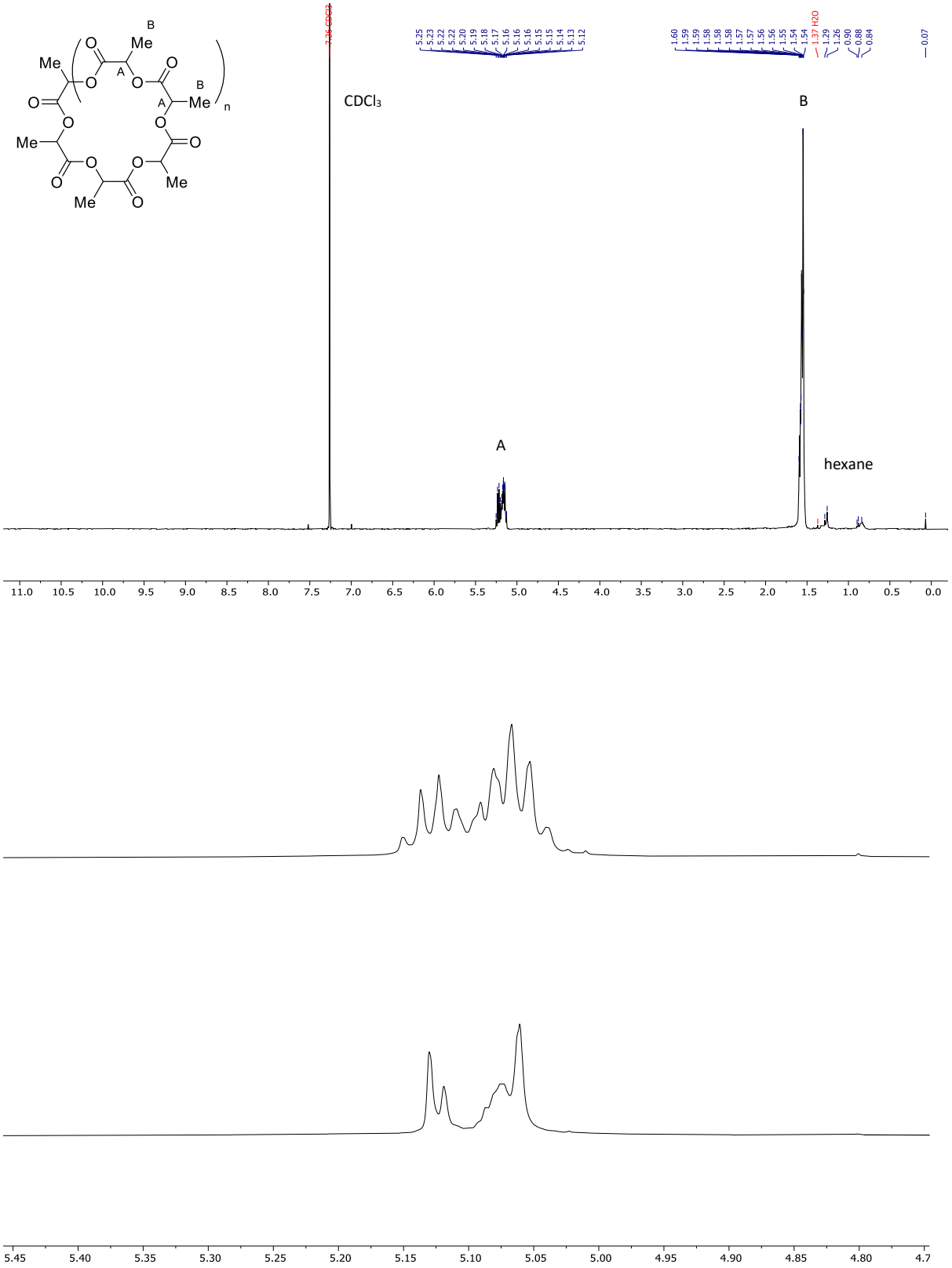


Figure S11: ^{1}H NMR spectrum of PLA produced from the reaction of 300:1 *rac*-LA and catalyst **1** in THF (top) and the same sample with and without ^{1}H{^{1}H} at the CH position (middle and bottom).The sample was worked up from MeOH/DCM, triturated with $CDCl_3$ and vacuum dried. No end-groups from ligand or MeOH are observed but residual hexane can be seen and is labelled in the top spectrum.

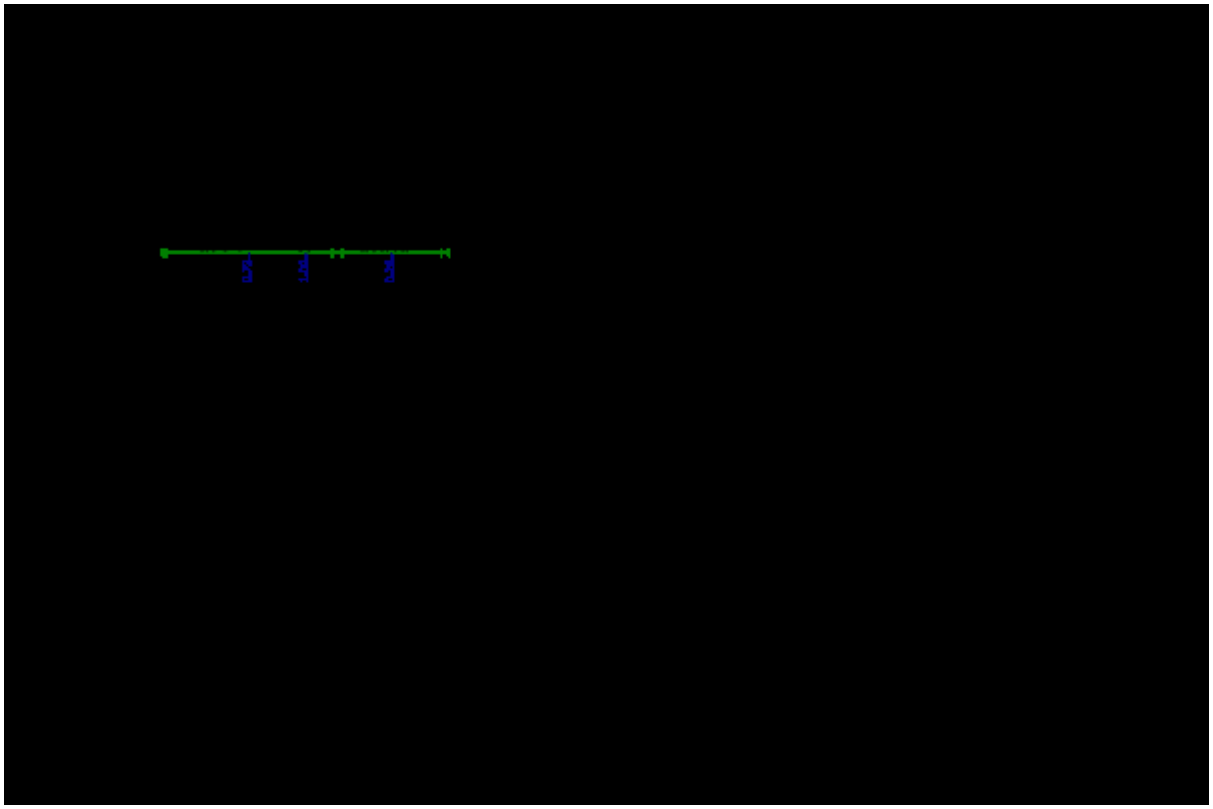


Figure S12: ^{1}H NMR spectrum of the crude reaction mixture of 5000:1 *rac*-LA and catalyst **2**; inset shows the methine region used to calculate conversion.

2.1 GPC traces for entries 1-8 in Table 1 of manuscript

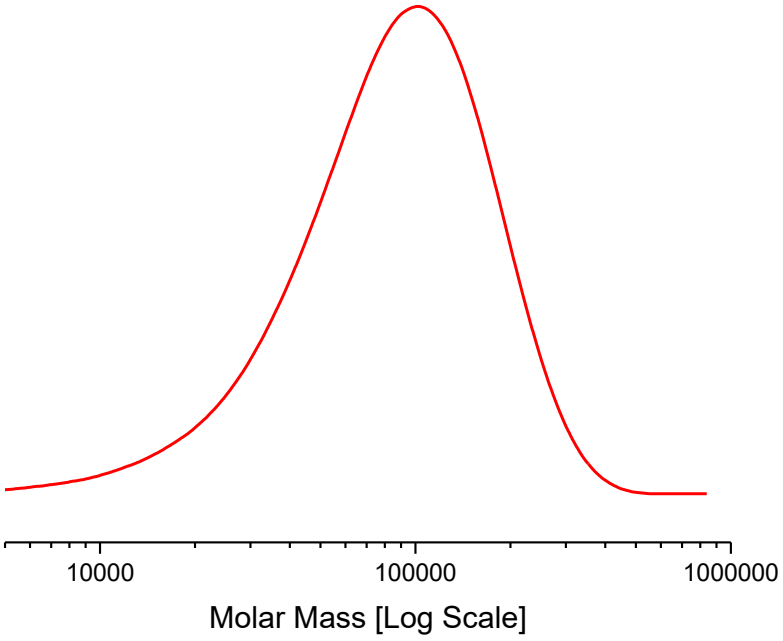


Figure S13: GPC trace of PLA produced from the reaction of 300:1 *rac* -LA and catalyst **1** in THF. M_n = 61 kg mol^{-1}, Đ = 1.67, time = 15 secs, conversion = 100%.

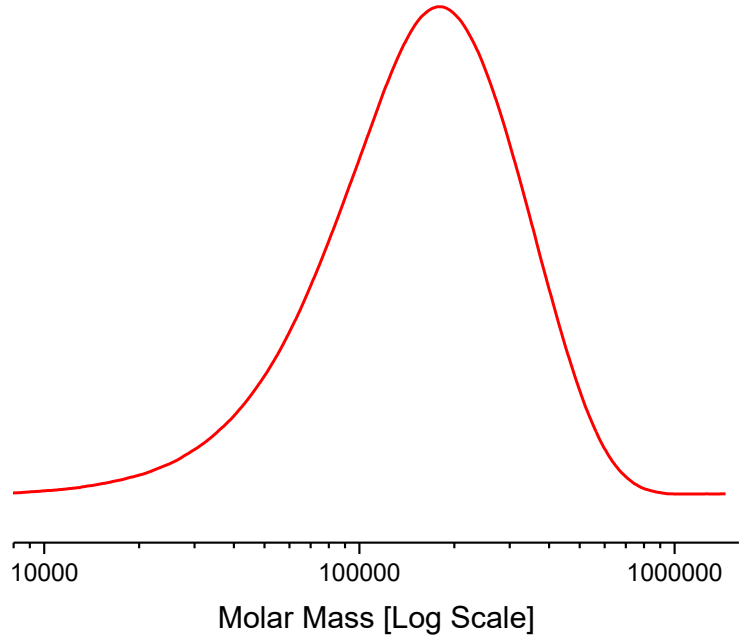


Figure S14: GPC trace of PLA produced from the reaction of 1200:1 *rac*-LA and catalyst **1** in THF**.** M_n = 114 kg mol^{-1}, Đ = 1.65, time = 30 secs, conversion = 81%.

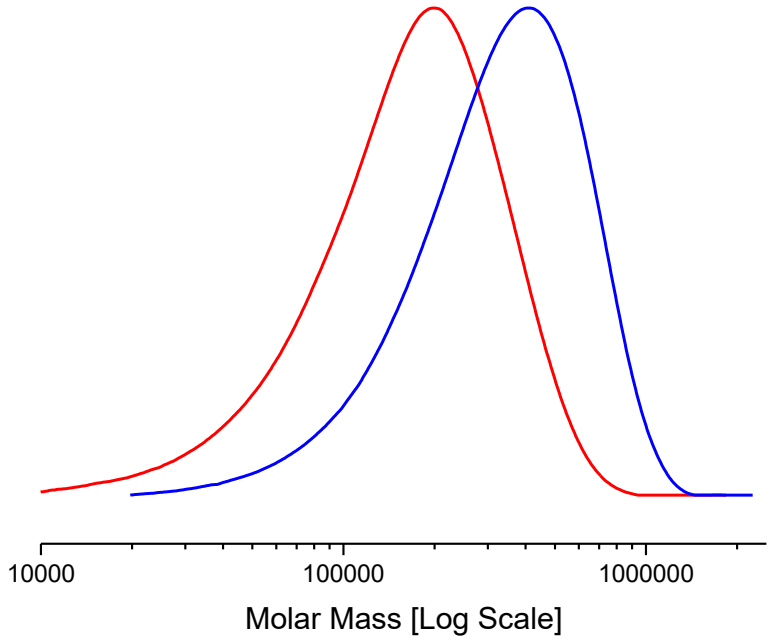


Figure S15: GPC trace of PLA produced from the reaction of 5000:1 *rac*-LA and catalyst **1** in THF**.**

Red: M_n = 119 kg mol^{-1}, Đ = 1.68, time = 30 secs, conversion = 31%

Blue: M_n = 250 kg mol^{-1}, Đ = 1.53, time = 60 secs, conversion = 90%

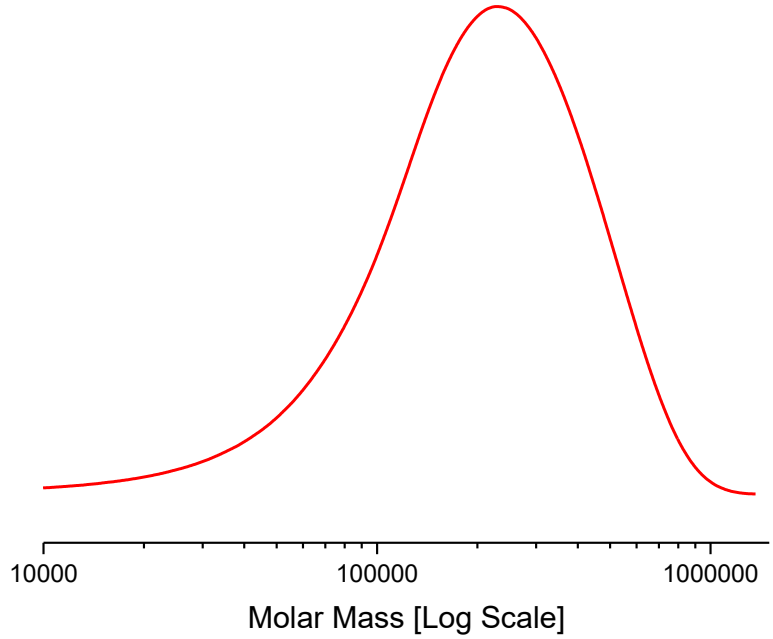


Figure S16: GPC trace of PLA produced from the reaction of 1200:1 *rac*-LA and catalyst **2** in THF. M_n = 135 kg mol^{-1}, Đ = 1.85, time = 5 secs, conversion = 96%.

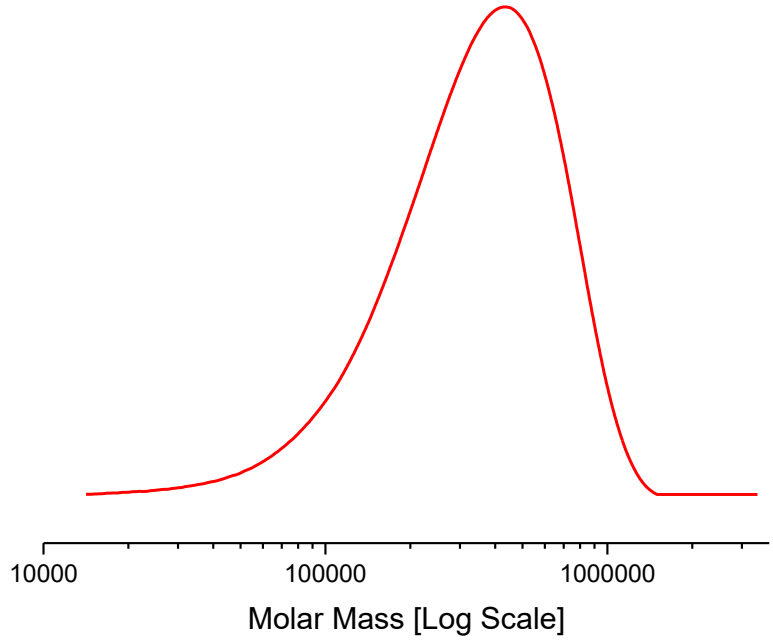


Figure S17: GPC trace of PLA produced from the reaction of 5000:1 *rac*-LA and catalyst **2** in THF. M_n = 253 kg mol^{-1}, Đ = 1.59, time = 15 secs, conversion = 72%.

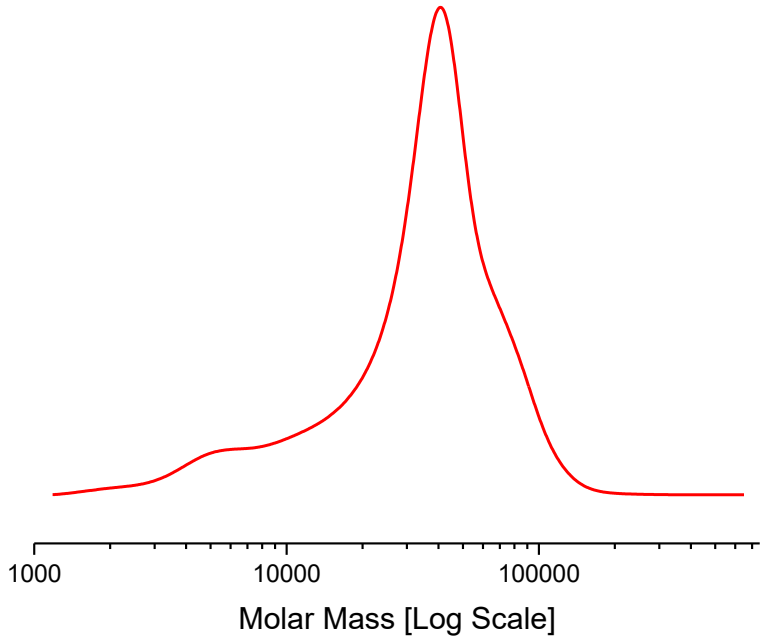


Figure S18: GPC trace of PLA produced from the reaction of 300:1 *rac*-LA and catalyst **3** in THF**.** M_n = 22 kg mol^{-1}, Đ = 1.89, time = 15 secs, conversion = 90%.

3.0 Ring opening polymerization with *rac*-LA and ^{i}PrOH

In a glove box, LA (144 mg, 1 mmol) was dissolved in THF (≤1 mL), the required amount of ^{i}PrOH was injected from a stock solution of ^{i}PrOH in THF [0.1 mM] to make a 1 mL THF solution. A stock solution of **1** or **2** in THF [0.01 M] was diluted as required to 1 mL in THF and injected into the reaction (total 2 mL THF) and run at the temperature and time specified in table S1, with stirring at 1400 RPM. The reaction was quenched by the addition of hexane (2 mL) and exposure to air. The polymer was obtained as a colorless solid by triplicate precipitation of the crude material in DCM/MeOH; spectroscopic data of the resulting material are in accordance with the literature.[5] Samples were analyzed by ^{1}H NMR spectroscopy and by GPC in THF; Example ^{1}H NMR chemical shifts (400 MHz, $CDCl_3$) δ_H: PLA 1.49–1.65 (3H, m, CHC*H*$_3$), 5.10 – 5.28 (1H, m, *CH*CH_3).

Table S1: Polymerizations of *rac*-LA with catalyst 1 and ^{i}PrOH co-initiator in THF

Entry	[LA]:[1]:[iPrOH][a]	Time (mins)	Conv. [b] (%)	M_n[c,d] (GPC) [kg mol^{-1}]	M_n[b,e] (theo) [kg mol^{-1}]	Đ[c]
1	50/1/0	0.5	98	15	7.1	1.98
2	50/1/3	5	90	3.3	1.1	1.38
3	5000/1/1	30	66	82	118	1.40
4	5000/1/3	60	85	73	102	1.49
5	5000/1/9	120	86	30	52	1.34

[a]Reaction conditions: [LA] = 0.5 M, THF, 25 °C. [b]Determined by the integration of normalised resonances for the methine resonances of lactide (5.02 ppm) and PLA (5.15 ppm) in the ^{1}H NMR spectra of crude reaction products. [c]Determined by GPC, using THF as the eluent, and calibrated using narrow MW polystyrene standards [d]Entries 2-5 were multiplied by a correction factor of 0.58[6] [e]Theoretical M_n for entry 1 is calculated from the monomer conversion data and assume one initiation per catalyst; Theoretical M_n for entries 2-5 are calculated from the monomer conversion data divided by the sum of ligands and co-initiator.

3.1 GPC traces for PLA in table S1 entries 1-5

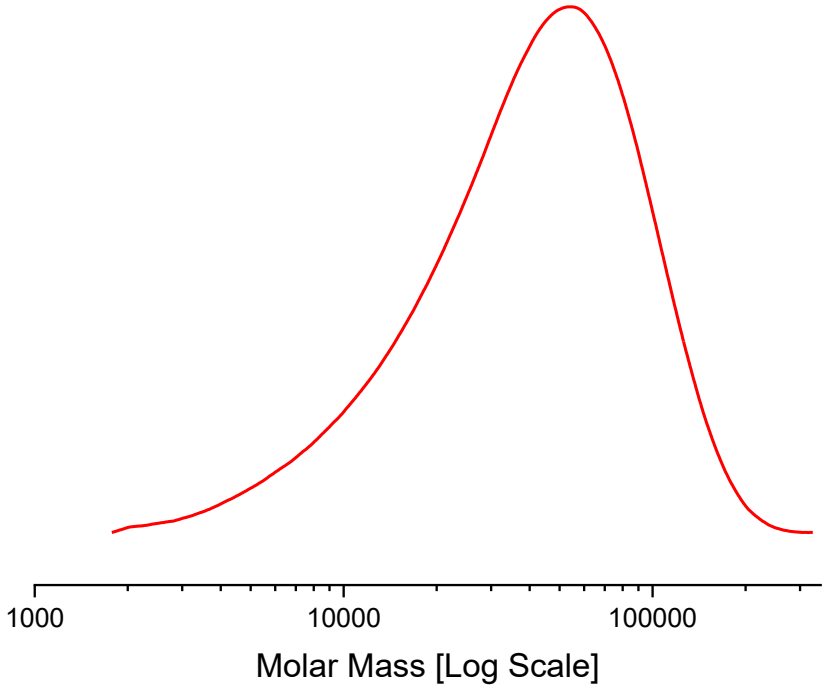


Figure S19: GPC trace of PLA produced from the reaction of 50:1 *rac* -LA and catalyst **1** in THF. M_n = 26 kg mol^{-1}, Đ = 1.98, time = 30 secs, conversion = 98%.

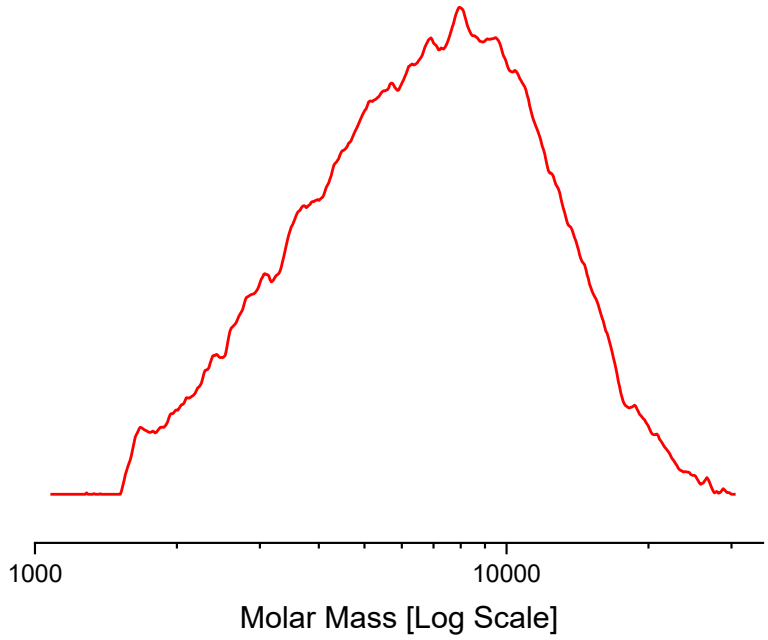


Figure S20: GPC trace of PLA produced from the reaction of 50:1:3 *rac*–LA, catalyst **1** and ^{i}PrOH in THF. M_n = 5.6 kg mol^{-1}, Đ = 1.38, time = 5 mins, conversion = 90%.

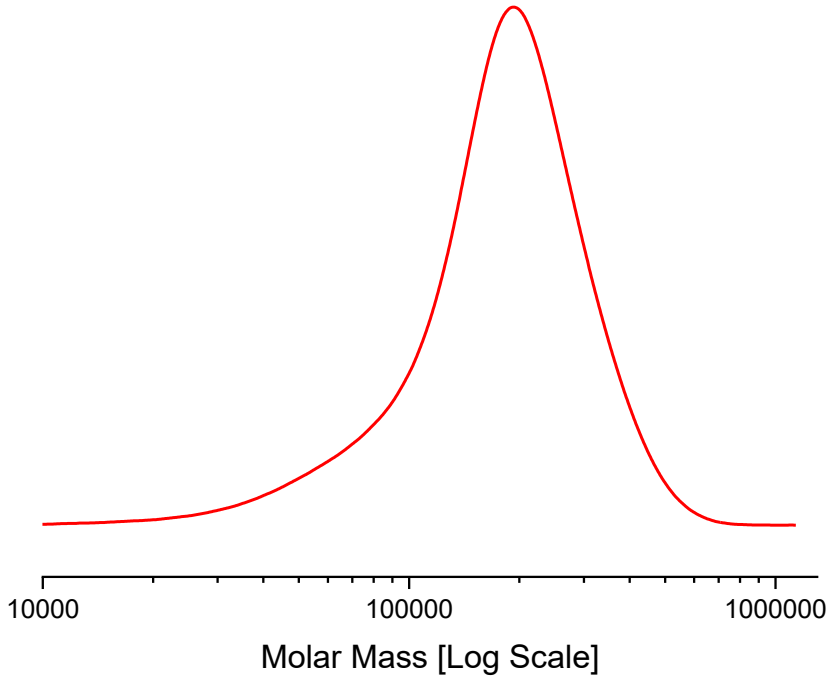


Figure S21: GPC trace of PLA produced from the reaction of 5000:1:1 *rac* -LA, catalyst **1** and ^{i}PrOH in THF. M_n = 142 kg mol^{-1}, Đ = 1.40, time = 30 mins, conversion = 66%.

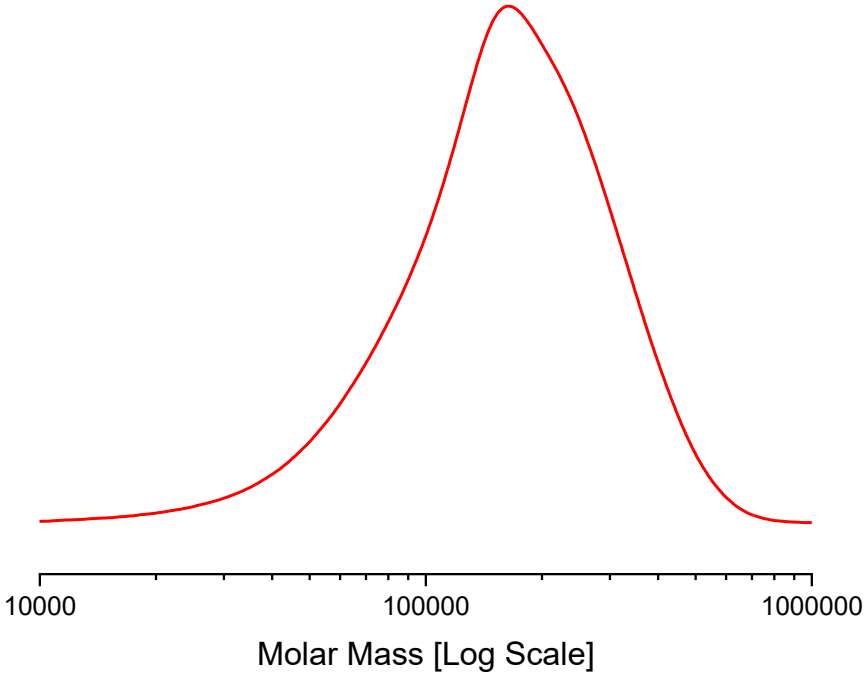


Figure S22: GPC trace of PLA produced from the reaction of 5000:1:3 *rac* -LA, catalyst **1** and ^{i}PrOH in THF**.** M_n = 126 kg mol^{-1}, Đ = 1.49, time = 60 mins, conversion = 85%.

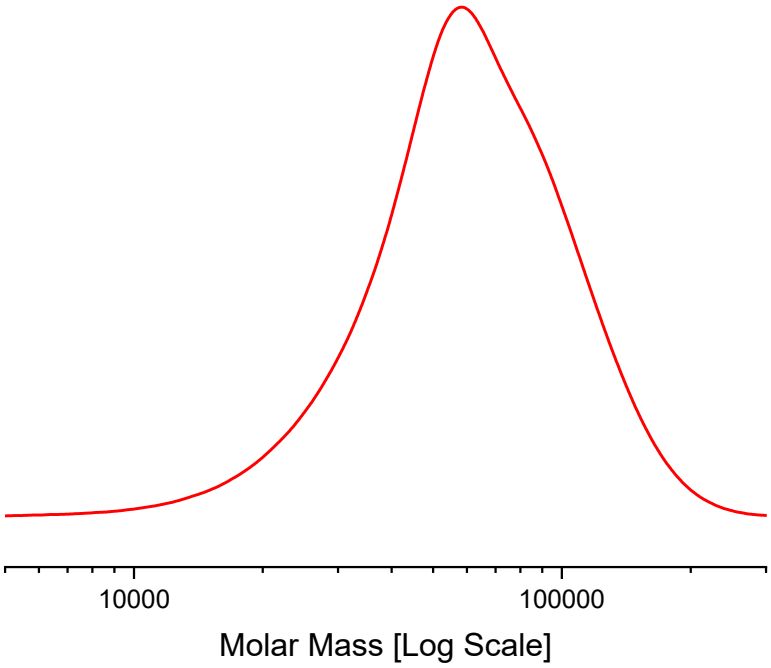


Figure S23: GPC trace of PLA produced from the reaction of 5000:1:9 *rac* -LA, catalyst **1** and ^{i}PrOH in THF**.** M_n = 51 kg mol^{-1}, Đ = 1.34, time = 120 mins, conversion = 86%.

4.0 Polymer topology determination

4.1 End-group analysis of low molar mass PLA

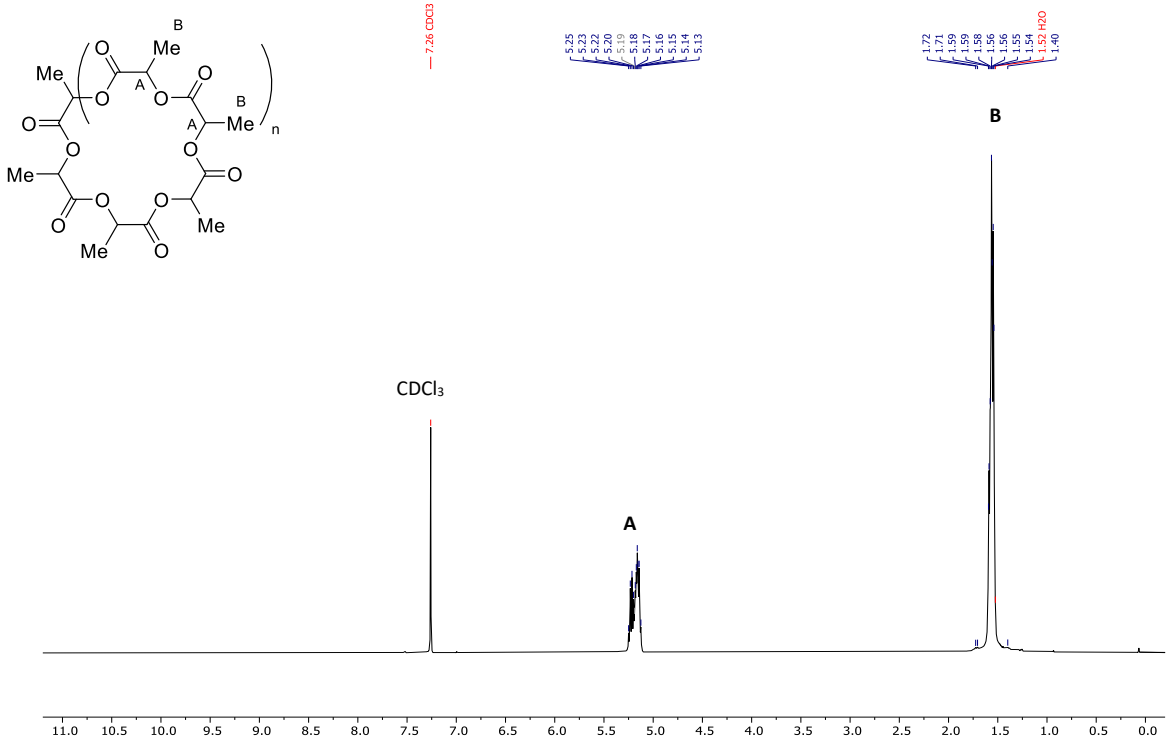


Figure S24: ^{1}H NMR spectrum of PLA produced from the reaction of 50:1 *rac*-LA and catalyst **1** in THF after work-up in MeOH/DCM. No end-groups from ligand or MeOH are observed.

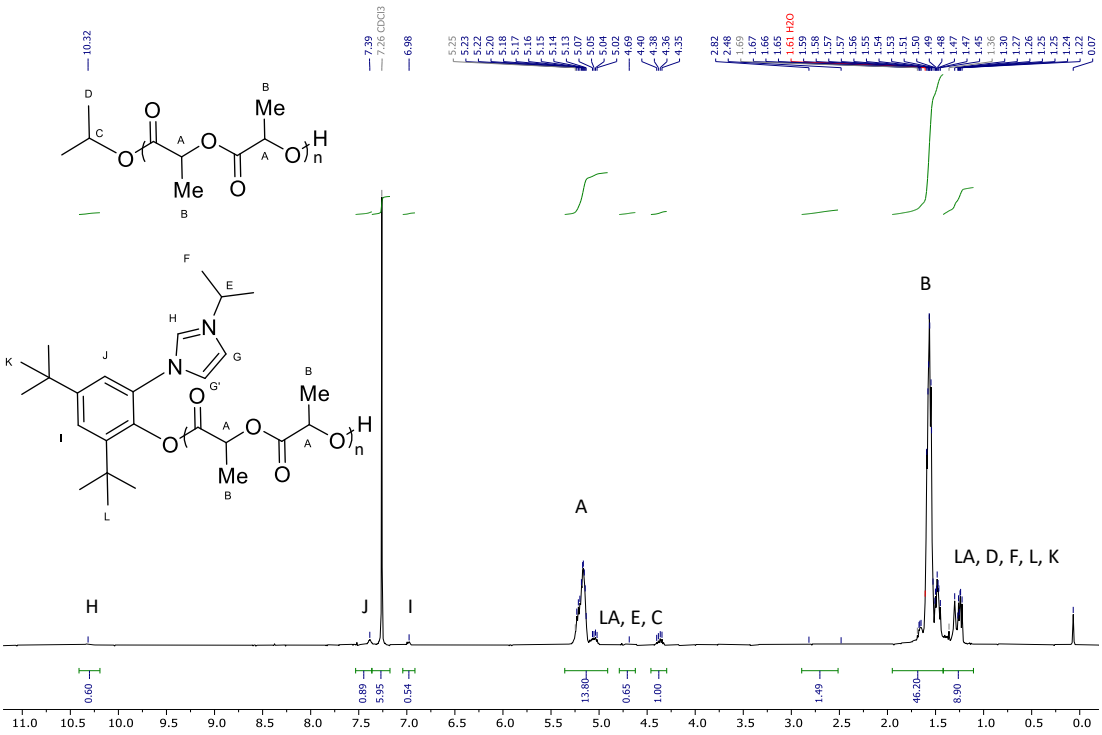
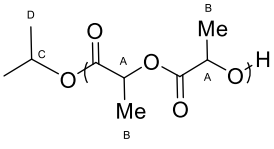


Figure S25: ^{1}H NMR spectrum of PLA produced from the reaction of 50:1:3 *rac* –LA, catalyst **1** and ^{i}PrOH in THF after triplicate precipitation in MeOH/DCM. End groups from ligand and ^{i}PrOH are observed.



4.2 Intrinsic viscosity data for PLLA

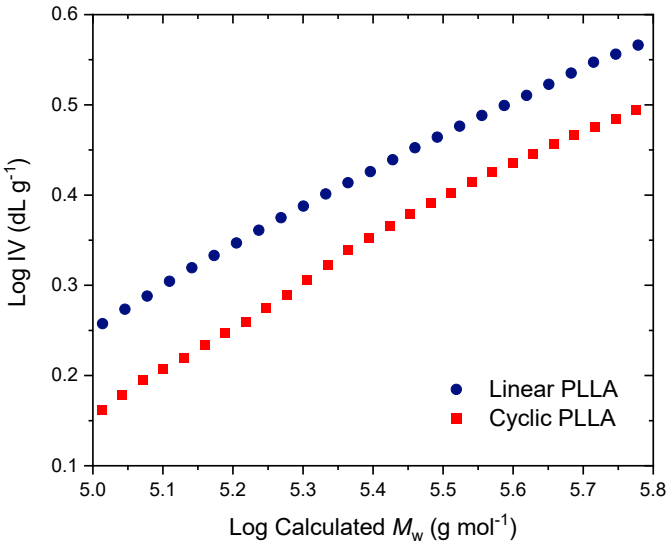


Figure S26: Plot of logarithm of molecular weight versus retention time of cyclic PLLA (red squares) from 5000:1 LA:**1** and linear PLLA (blue circles) from 5000:1:1 LA:**1**:^{i}PrOH.

4.3 MALDI-ToF analysis of cyclic PLA

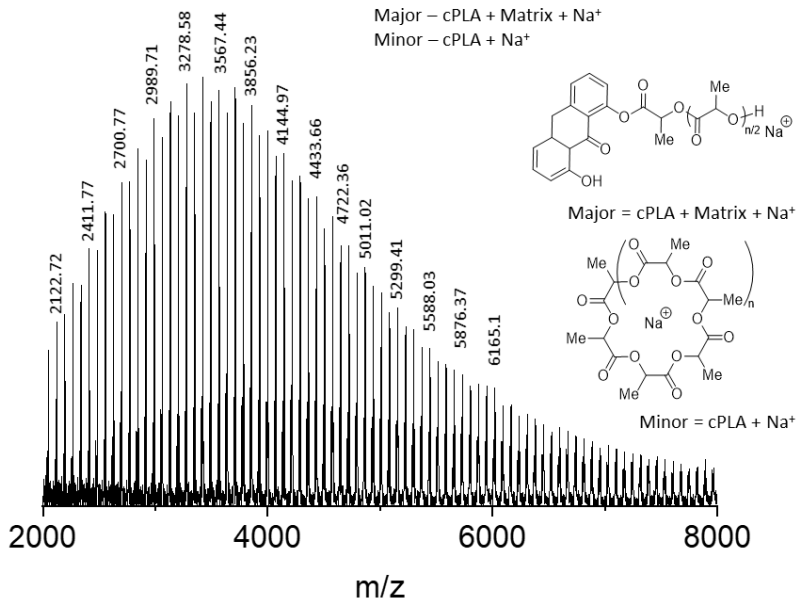


Figure S27: MALDI-ToF spectrum of PLA produced from the reaction of 50:1 *rac*-LA and catalyst **1** in THF. 2 series are observed: Minor = cPLA + Na^+, Major = cPLA + Dithranol + Na^+. The presence of the matrix dithranol "end-group" indicates the polymer must be cyclic before ring-opening under ionization. No end-groups from ligand or MeOH are observed. Different concentrations of matrix and salt gave identical results for this polymer.

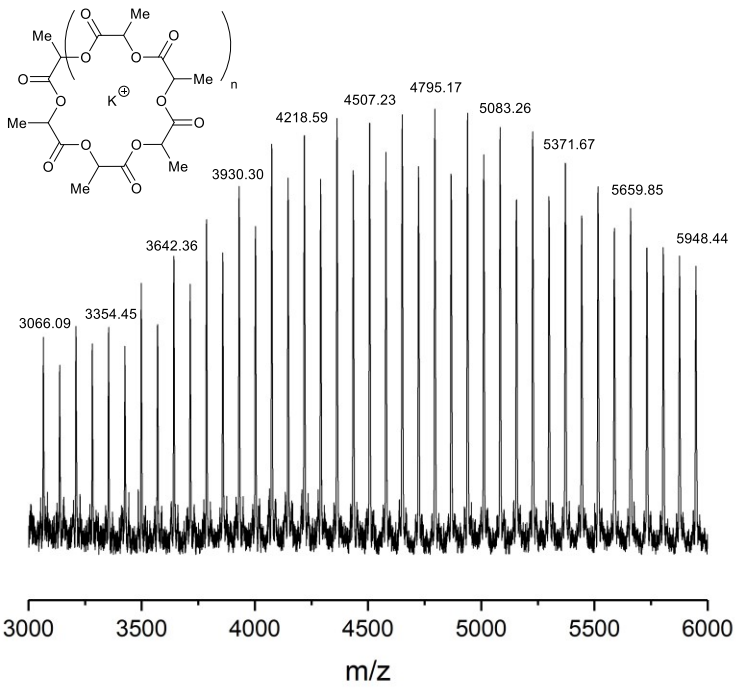


Figure S28: MALDI-ToF spectrum of PLA produced from the reaction of 300:1 *rac*-LA and catalyst **1** in THF**.** 1 series is observed: cPLA + K^+. No end-groups from ligand or MeOH are observed.

5.0 Ring opening polymerization of other lactones

5.1 L-LA ring-opening polymerization

In a glove box, LA (144 mg, 1 mmol) was dissolved in THF (≤1 mL) and for studies involving ^{i}PrOH co-initiator, the required amount was injected from a stock solution of ^{i}PrOH in THF [0.1 mM] to make a 1 mL THF solution. A stock solution of **1** or **2** in THF [0.01 M] was diluted as required to 1 mL in THF and injected into the reaction (total 2 mL THF) and run at 25 °C and time specified in the table with stirring at 1400 RPM. The reaction was quenched with the addition of hexane (2 mL) and exposure to air. The polymer was obtained as a colorless solid by triplicate precipitation of the crude material in DCM/MeOH with spectroscopic data in accordance with the literature.[5] Samples were analyzed by ^{1}H NMR spectroscopy, homonuclear-decoupled ^{1}H NMR spectroscopy in $CDCl_3$[5] and by SEC in $CHCl_3$; Example ^{1}H NMR spectrum (400 MHz, $CDCl_3$) δ_H: PLA 1.49–1.65 (3H, m, CHC*H*$_3$), 5.10 – 5.28 (1H, m, C*H*CH$_3$).

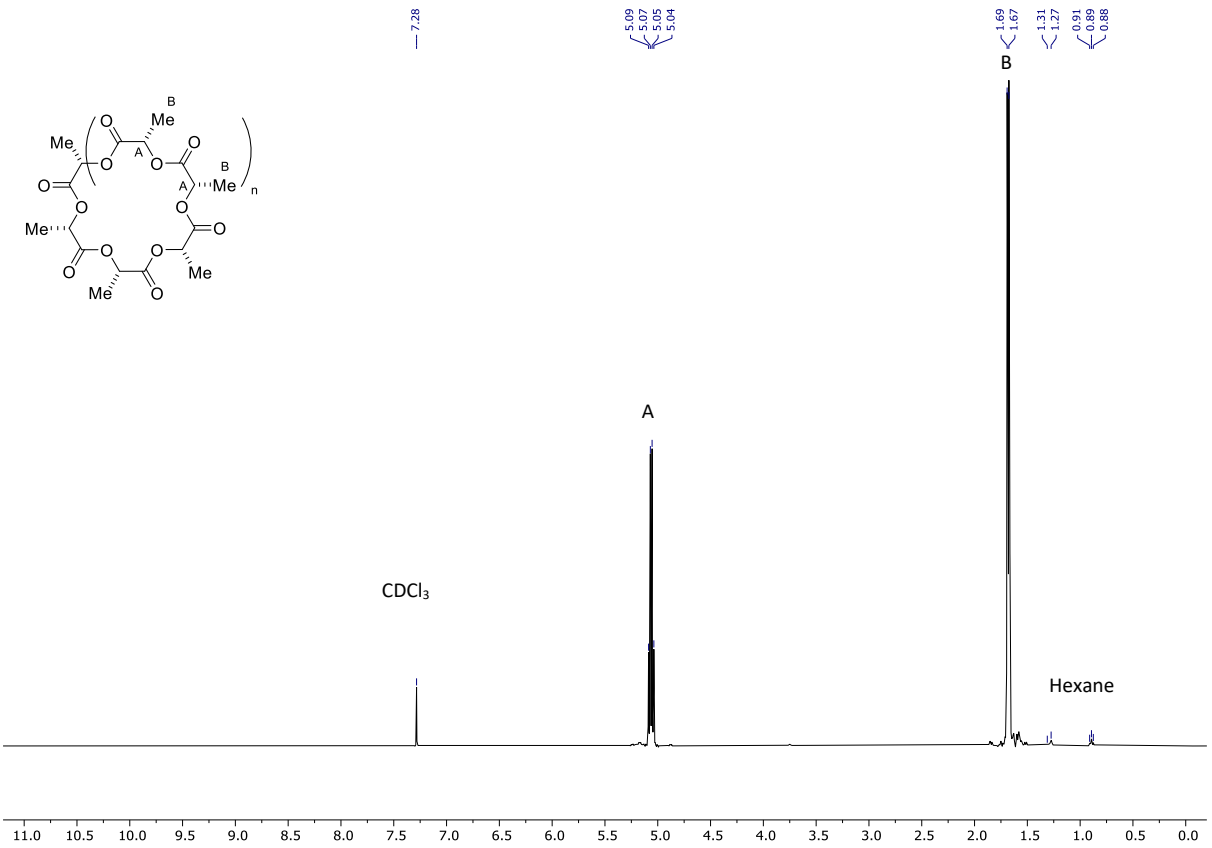


Figure S29: Example ^{1}H NMR spectrum of cPLLA produced from the reaction of 300:1: L-LA: **1**. No end-groups from ligand or MeOH are observed. The sample was purified by trituration with $CHCl_3$ and vacuum drying; residual hexane is labelled.

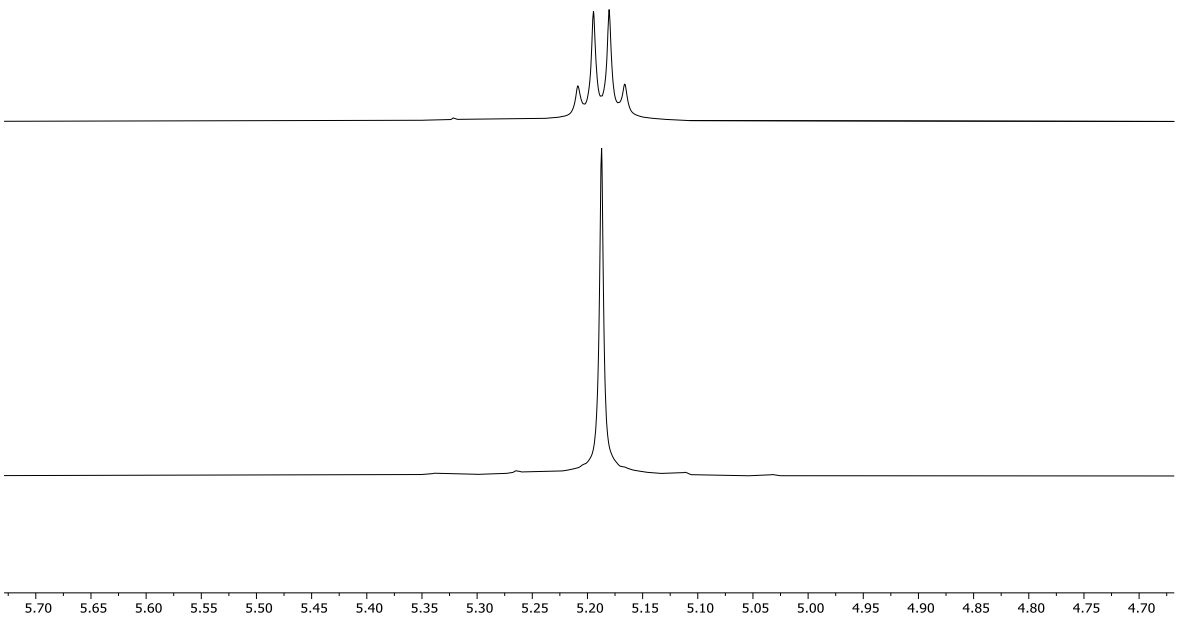


Figure S30: Example ^{1}H NMR spectrum of PLLA produced from the reaction of 300:1: L-LA and catalyst **1** (upper) and spectrum with $^{1}H\{^{1}H\}$ decoupling of the methine CH (lower)

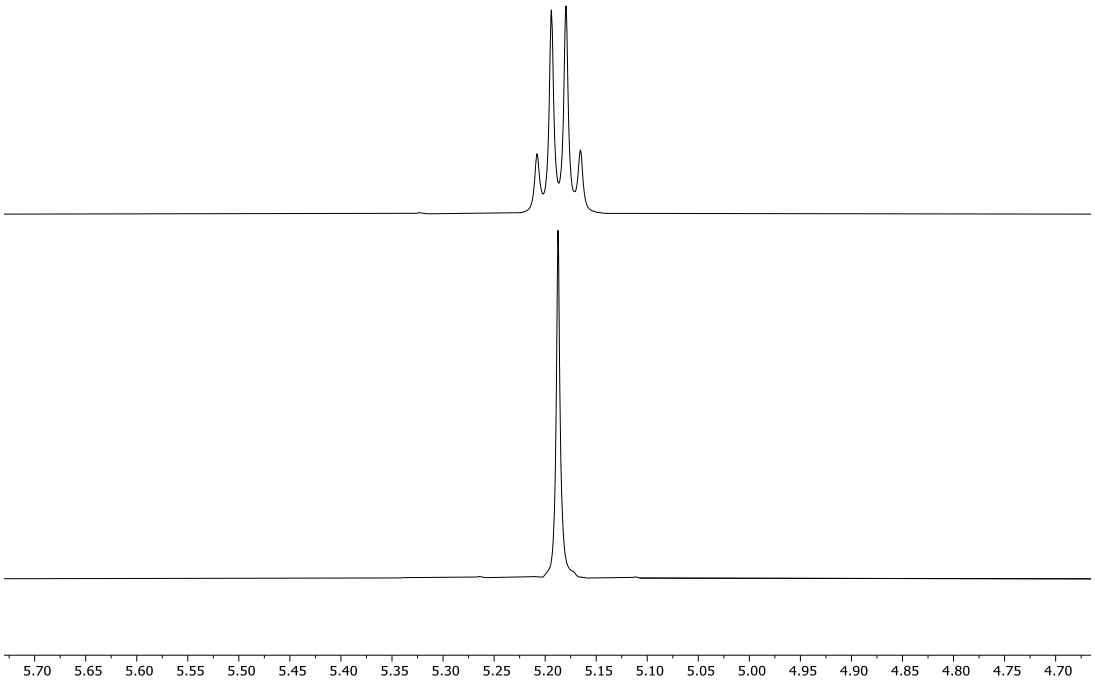


Figure 31: Example ^{1}H NMR spectrum of PLLA produced from the reaction of 300:1: L-LA and catalyst **2** (upper) and spectrum with $^{1}H\{^{1}H\}$ decoupling of the methine CH (lower)

5.2 ε-Caprolactone ring-opening polymerization

In a glove box, CL (114 mg, 1 mmol) was dissolved in THF to make 1 mL solution. A stock solution of **1** in THF [0.01 M] was diluted as required to 1 mL in THF and injected into the reaction (total 2 mL THF) and run at the specified temperature and time with stirring at 1400 RPM. The reaction was quenched by the addition of hexane (2 mL) and exposure to air. The polymer was obtained as a colorless solid by triplicate precipitation of the crude material in DCM/iPrOH with spectroscopic data in accordance with the literature.[7] Samples were analyzed by ^{1}H NMR spectroscopy in $CDCl_3$ and by SEC in THF; Example ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: PCL δ 3.93 (2H, t, *J* 6.7, OCH_2), 2.18 (2H, t, *J* 7.5, $CH_2CH_2C{=}O$), 1.60–1.45 (4H, m, 2x CH_2), 1.30–1.18 (2H, m, CH_2).

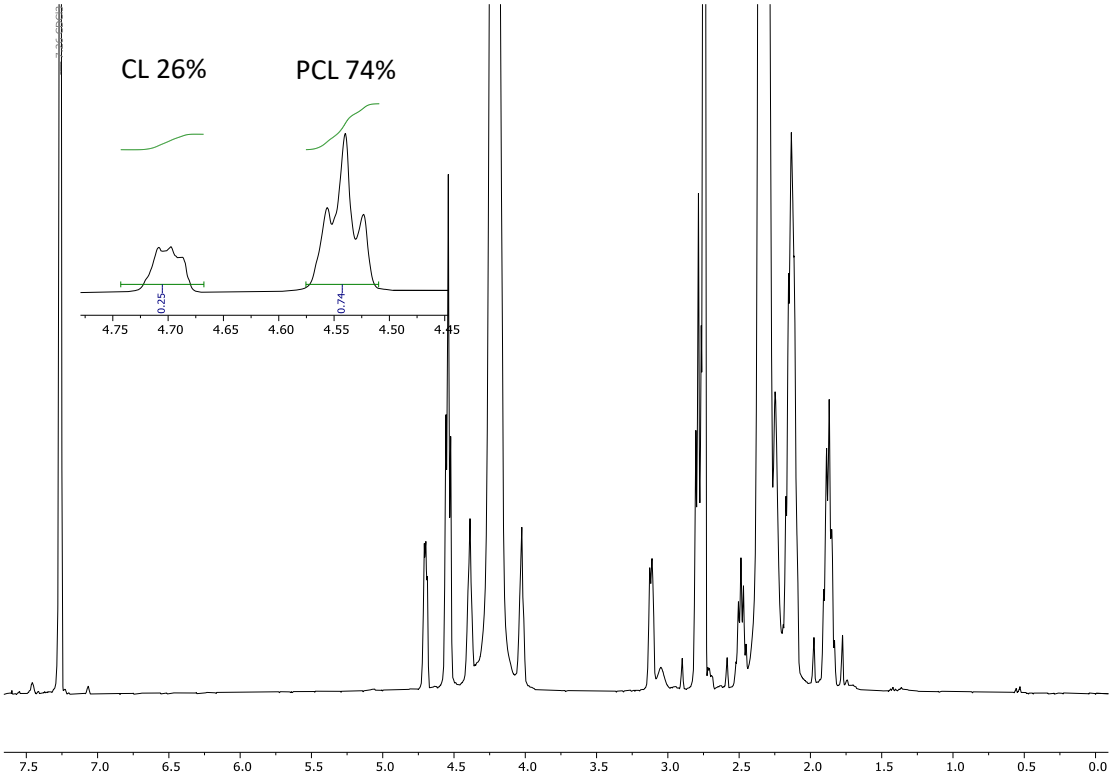


Figure S32: Example crude ^{1}H NMR spectrum in $CDCl_3$ from the reaction of 300:1 CL and catalyst **1**, methine region used to calculate conversion enlarged.

5.3 *rac*-β-Butyrolactone ring-opening polymerization

In a glove box, *rac*-β-butyrolactone (172 µL, 2 mmol) was dissolved in THF or PhMe (≤1 mL) and for studies involving ^{i}PrOH co-initiator, the required amount was injected from a stock solution of ^{i}PrOH in THF or PhMe [1 mM] to make a total 1 mL solution. Secondly, a stock solution of **1** in THF or toluene [0.01 M] was diluted to the required concentration and 1 mL injected into the reaction (total 2 mL) and run at the temperature and time specified in the table with vigorous stirring at 1400 RPM. The

reaction was quenched with the addition of hexane (2 mL) and exposure to air. Poly(hydroxybutyrate) was obtained as a colorless oil by triplicate precipitation of the crude material in DCM/iPrOH with spectroscopic data in accordance with the literature.[8] The reaction was followed by aliquoting and quenching the reaction mixture in hexane at different times. Samples were analyzed by ^{1}H NMR spectroscopy, homonuclear-decoupled ^{1}H NMR spectroscopy in $CDCl_3$ and by SEC in THF; Example ^{1}H NMR spectrum (400 MHz, $CDCl_3$) δ_H: 1.49–1.65 (3H, m, CH*CH$_3$*), 5.10 – 5.28 (1H, m, *CH*CH$_3$).

Table S2: Selected ring-opening polymerizations of β-BL with catalyst 1 and ^{i}PrOH co-initiator

Entry	[β-BL]:[**1**]:[iPrOH]	Solv.	Time	Conv.^{b} (%)	M_n^{c} (GPC) [kg mol^{-1}]	M_n^{b} (theo) [kg mol^{-1}]	Đ^c	TOF (h^{-1})
1	100/1/0	THF	17 h	26	2.38	1.46	1.51	1.5
2	100/1/0	PhMe	17 h	26	1.87	1.46	2.51	1.5
4	100/1/1	THF	3 h	48	5.32	4.13	1.55	16
5	100/1/1	PhMe	1 min	7	2.99	0.603	1.34	420
6	100/1/1	PhMe	10 min	53	5.05	4.56	1.33	318
7	100/1/1	PhMe	20 min	73	6.44	6.28	1.38	219

^{a}Reaction conditions: [β-BL] = 2.0 M, 25 °C. ^{b}Determined by the integration of normalized resonances for the methine resonances of β-BL (4.72 ppm) and P(β-BL) (5.60 ppm) in the ^{1}H NMR spectra of crude reaction mixtures. ^{c}Determined by GPC, using THF as the eluent and calibrated using narrow MW polystyrene standards without correction.

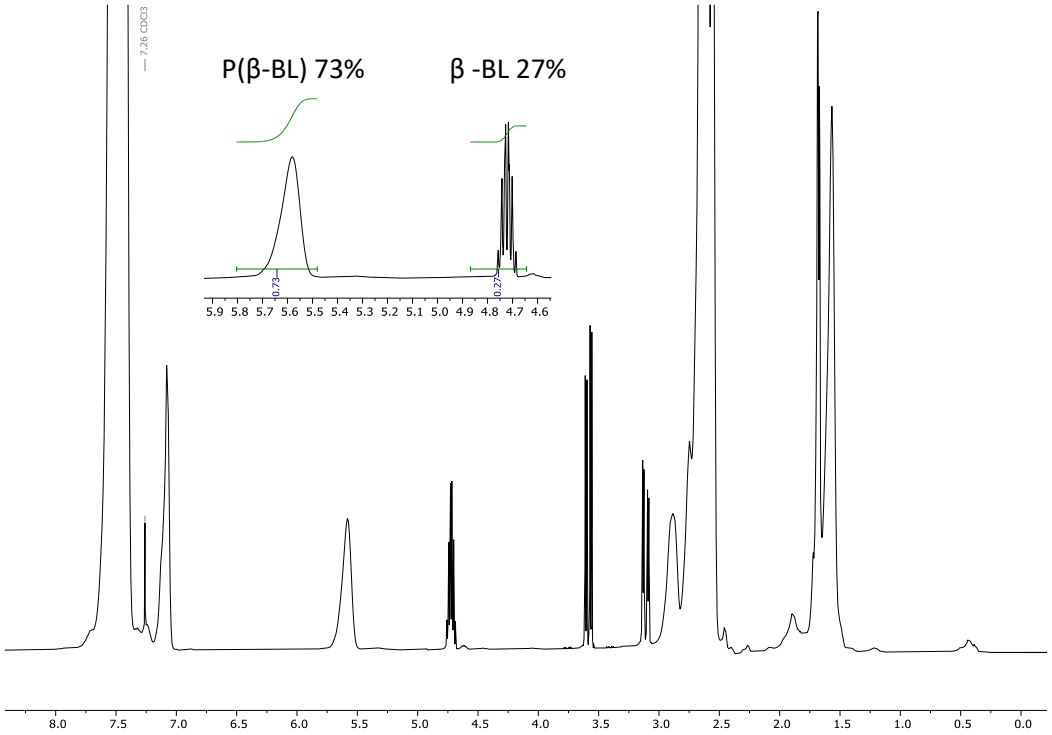


Figure S33: Example crude ^{1}H NMR spectrum in $CDCl_3$ from the reaction of 100:1:1 β-BL, ^{i}PrOH and catalyst **1** in PhMe**,** methine region used to calculate conversion enlarged.

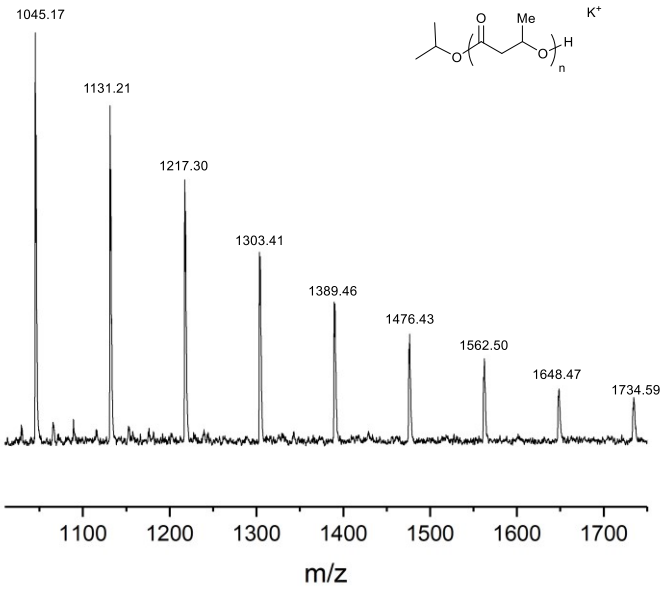


Figure S34: MALDI-ToF spectrum of poly(β-BL) produced from the reaction of 100:1:1 β-BL, ^{i}PrOH and catalyst **1** in PhMe**.**

5.4 GPC traces for the ring opening polymerization of other lactones in Table 2 in manuscript

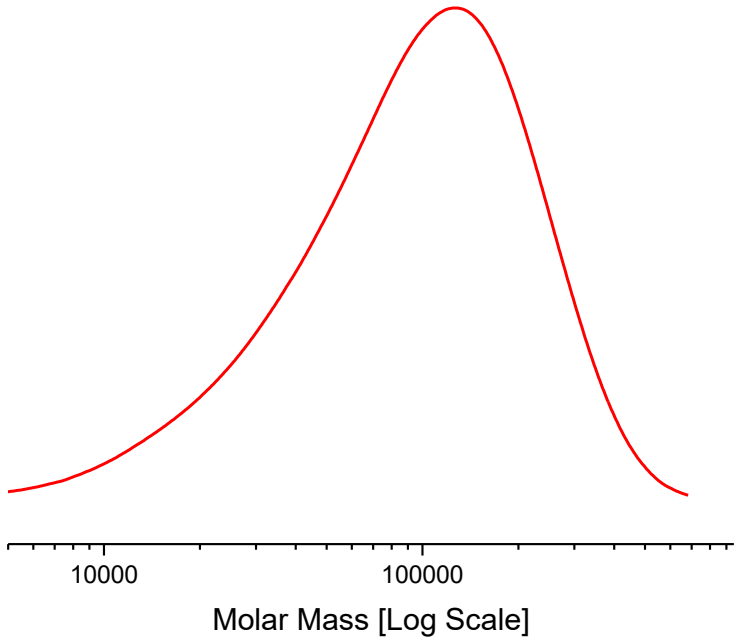


Figure S35: GPC trace of PLLA produced from the reaction of 300:1 L-LA and catalyst **1** in THF**.** M_n = 81 kg mol^{-1}, Đ = 2.01, time = 15 secs, conversion = 92%

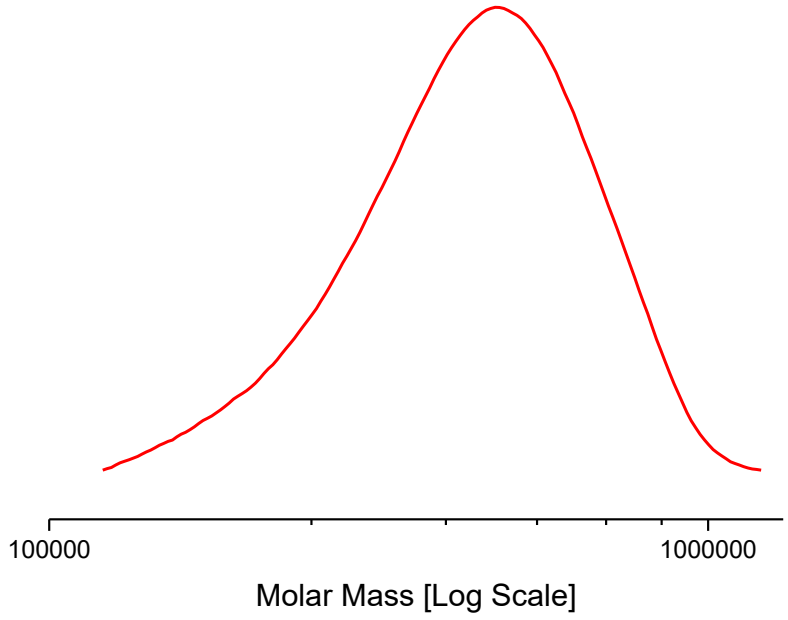


Figure S36: GPC trace of PLLA produced from the reaction of 5000:1 L-LA and catalyst **1** in THF. M_n = 401 kg mol^{-1}, Đ = 1.17, time = 60 secs, conversion = 62%

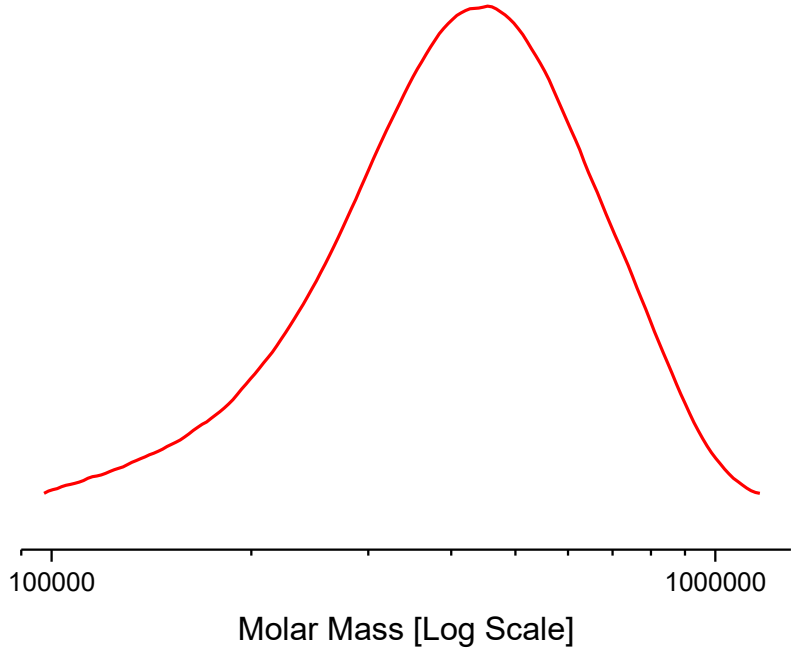


Figure S37: GPC trace of PLLA produced from the reaction of 5000:1 L-LA and catalyst **2** in THF. M_n = 373 kg mol^{-1}, Đ = 1.20, time = 30 secs, conversion = 76%

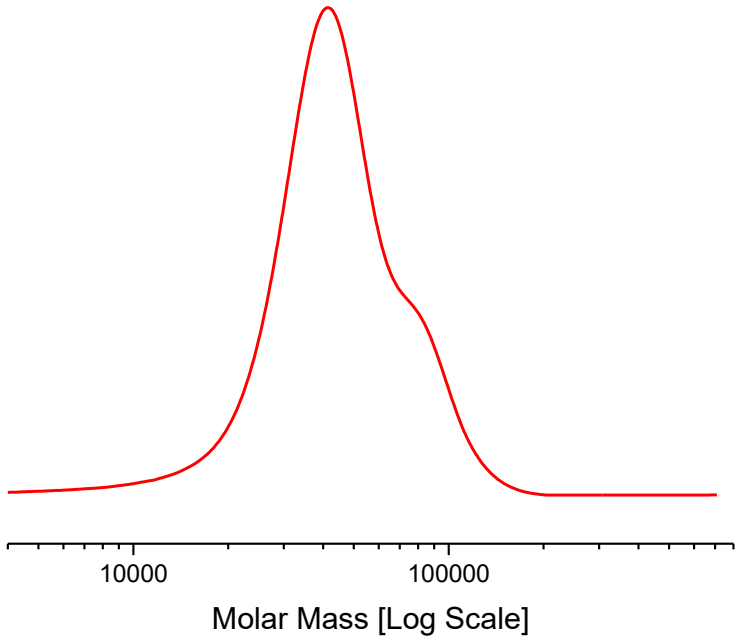


Figure S38: GPC trace of PCL produced from the reaction of 300:1 ε-CL and catalyst **1** in THF. M_n = 39 kg mol^{-1}, Đ = 1.31, time = 3 mins, conversion = 26%

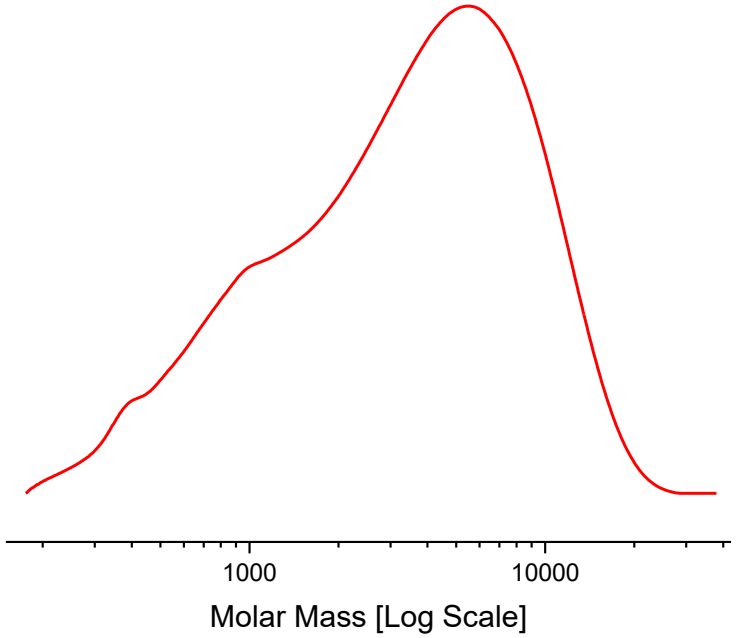


Figure S39: GPC trace of P(β-BL) produced from the reaction of 100:1 β-BL and catalyst **1** in PhMe. M_n = 1.9 kg mol^{-1}, Đ = 2.51, time = 17 h, conversion = 26%

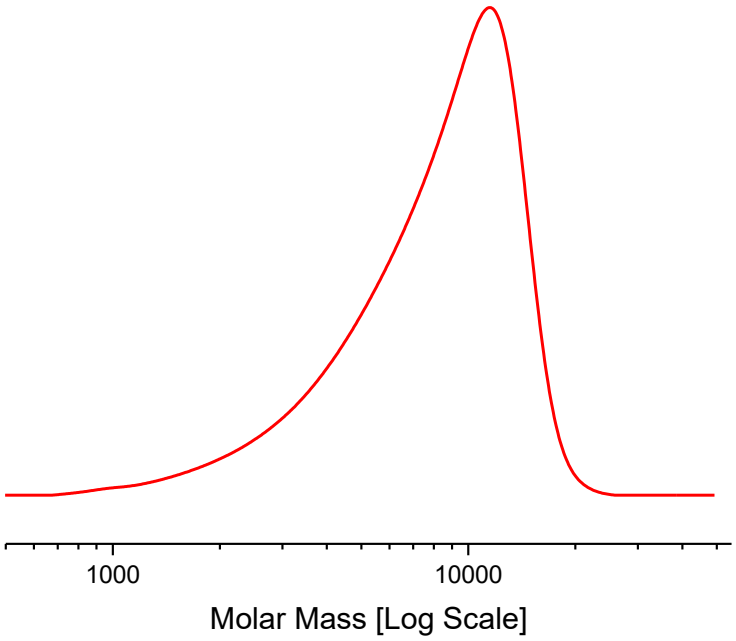


Figure S40: GPC trace of P(β-BL) produced from the reaction of 100:1:1 β-BL, ^{i}PrOH and catalyst **1** in PhMe. M_n = 6.4 kg mol^{-1}, Đ = 1.38, time = 20 min, conversion = 73%.

6.0 DSC analysis of high molecular weight PLA and PLLA

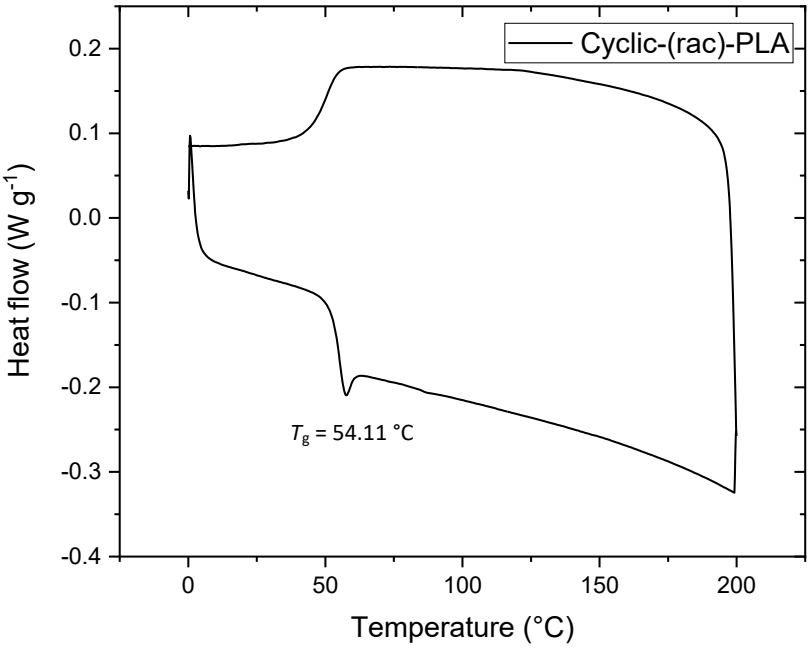


Figure S41: DSC trace of cPLA produced from the reaction of 5000:1 *rac*-LA and catalyst **1** in THF.

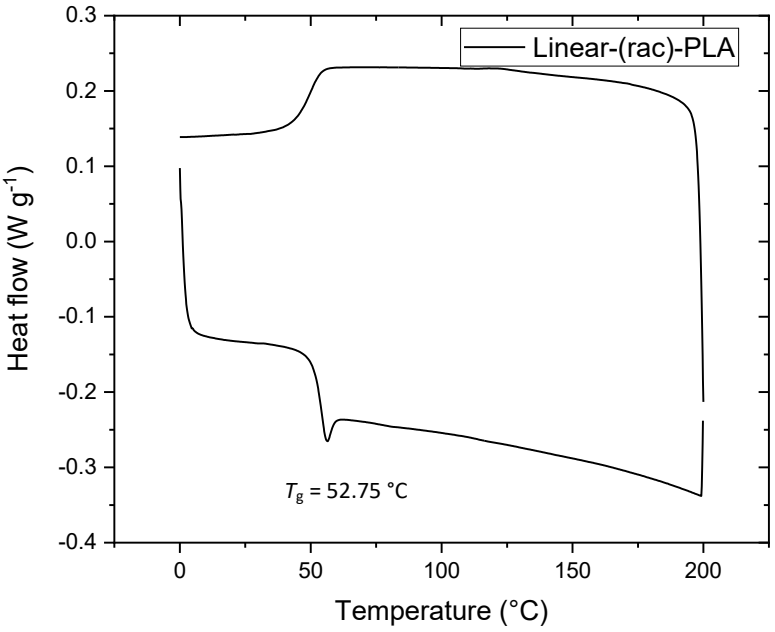


Figure S42: DSC trace of PLA produced from the reaction of 5000:1:1 *rac*-LA, catalyst **1** and ^{i}PrOH in THF**.**

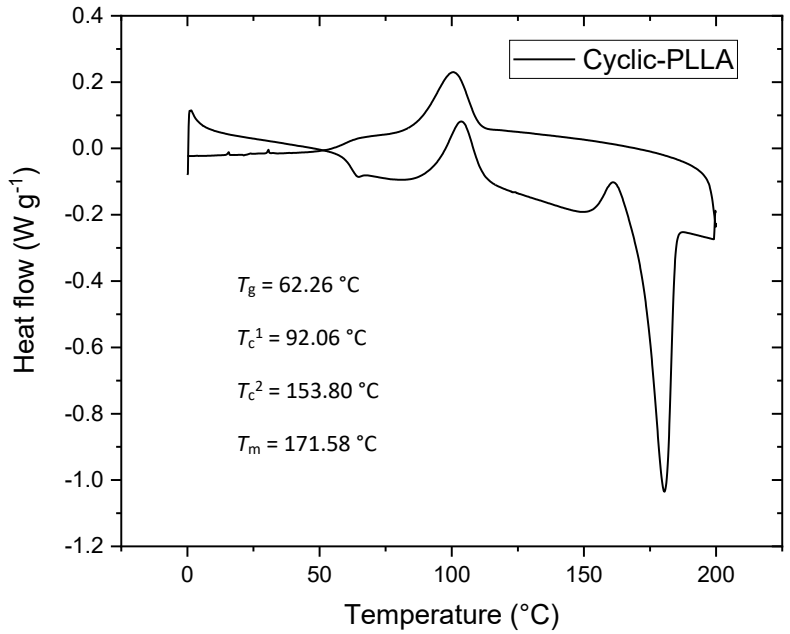


Figure S43: DSC trace of cPLLA produced from the reaction of 5000:1 l-LA and catalyst **1** in THF.

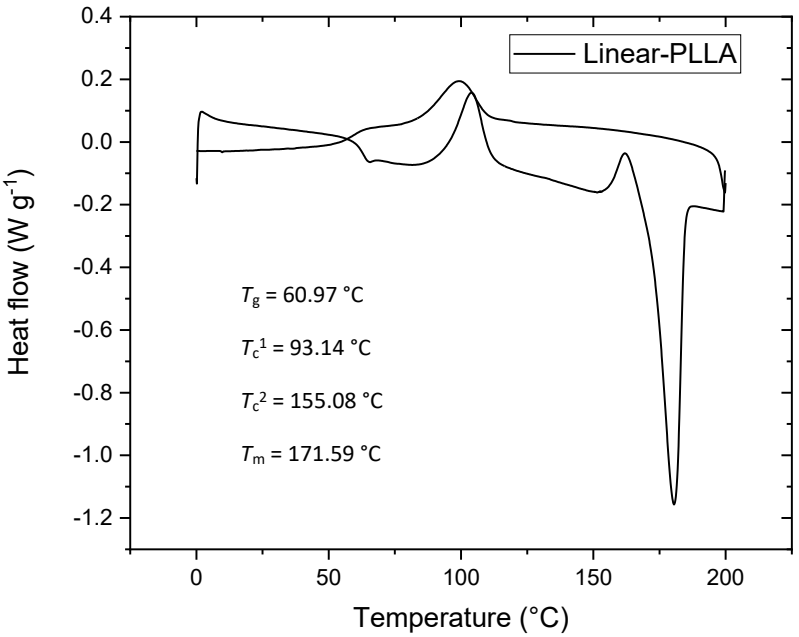


Figure S44: DSC trace of PLLA produced from the reaction of 5000:1:1 l-LA, catalyst **1** and ^{i}PrOH in THF.

7.0 Mechanistic Proposal

Mechanistic considerations for the formation of cyclic polymer

As discussed in the manuscript, we hypothesize that the polymerization proceeds by lactide co-ordination at Ce(III) which reduces the barrier to nucleophilic attack and ring-opening by the coordinated NHC ligand (Scheme 1). Mechanistic studies conducted by Waymouth show initiation to be the rate determining step in NHC catalyzed zROP of lactide.[9] Here, similarly, the zwitterionic intermediate is the active propagating species, and now the anionic chain-end is stabilized by Ce(III)-coordination, and chain growth occurs by a series of lactide coordination, anionic chain-end nucleophilic attack and ring-opening steps.

Figure S45 summarizes our suggestions that at lower loadings of monomer (eg 300:1) it is more likely that there is only a single propagating chain at each Ce(III) center, while at higher loadings of monomer (1200:1 and 5000:1), it is more likely that up to 3 propagating species exist at each Ce(III) center (i.e. one at each phenoxy-NHC ligand).

Finally, chain termination and extrusion of the macrocycle occurs through an elimination of the macrocyclic product and reformation of the Ce-NHC bonds.

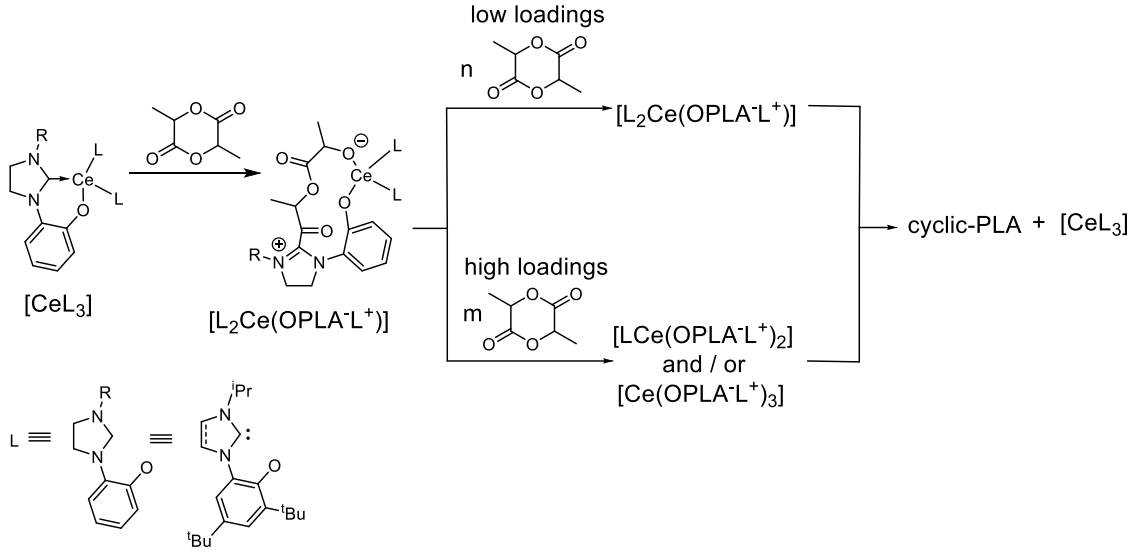
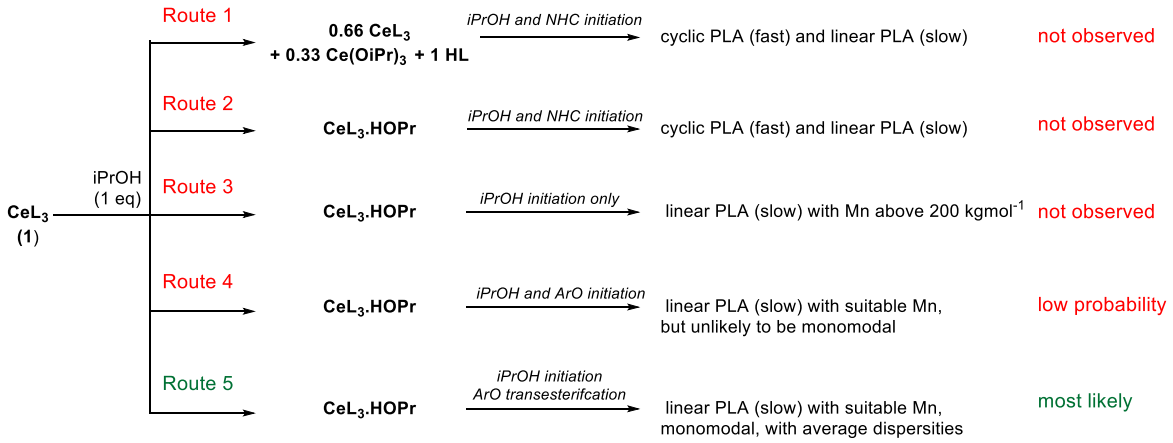


Figure S45: Proposed mechanistic pathways at high and low concentrations of **1** and **2.**

Mechanistic considerations for the formation of linear polymer:

The catalysts presented in this paper were primarily targeted towards highly efficient formation of cyclic polyester. When alcohol is added the resulting PLA is linear, but the precise mechanism(s) likely depend upon both uncoordinated NHC ligand moieties and interactions between Ce(III) and the alcohol. Five pathways producing linear PLA from catalyst+alcohol systems are feasible and shown in Chart S2, upper.



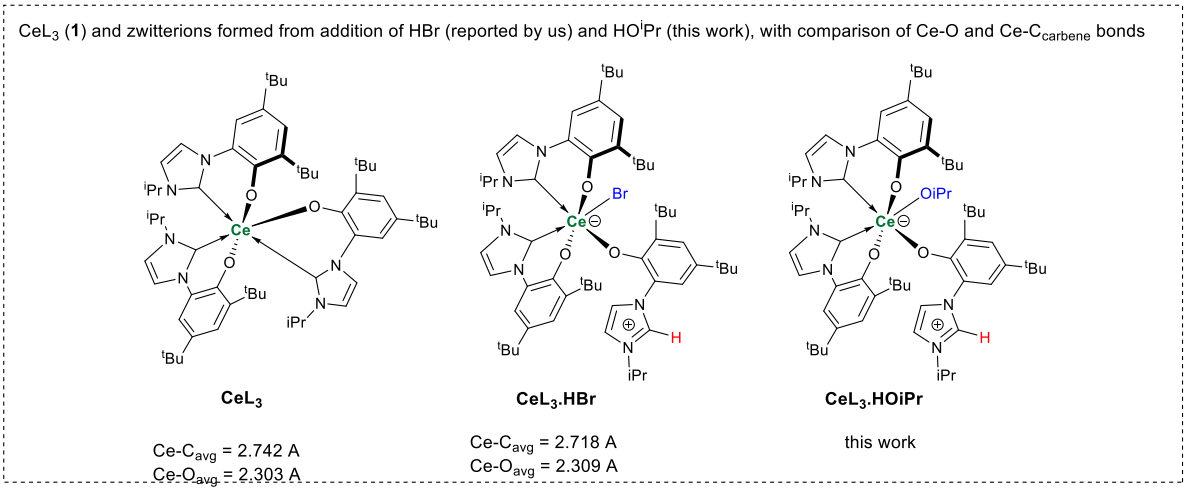


Chart S 2 mechanistic options for the formation of linear PLA by mixtures of CeL_3 (**1**) and isopropanol

1) Route 1: Forms 0.33 equiv. "$Ce(OiPr)_3$" and free HL. However, 0.66 equiv. CeL_3 must remain in solution from the reaction stoichiometry. This route is ruled out due to the very significant drop in activity upon addition of even 1 equiv. of alcohol (the rate decrease would not be consistent with 0.66 equiv. of CeL_3 being present).

2) Route 2: Forms an alcohol adduct. In this case, it would be expected that catalysis occurs by both NHC-initiated (ZROP type) and activated monomer pathways. Once again, the significant decrease in rates upon addition of even 1 equiv. of alcohol are inconsistent with this notion.

3) Route 3: Forms the same alcohol adduct but if only the alcohol initiates linear chains and the NHC components become spectators (deactivated). This route seems less likely as the molecular weight values obtained should be much higher than are observed, e.g., consider the loading LA:Ce:ROH of 5000:1:1 (Table S1, entry 3).

4) Route 4: An adduct is formed and both the alcohol and the aryloxide groups (on the ligand) initiate polymerizations. This route would produce PLA with molecular weight values more closely aligned with experimental values and there is precedent for similar Ln-aryloxide polymerization initiators (e.g., $Sm(II)OAr_2$ and Ln(III)(salen)OAr; Wakatsuki et al Macromolecules, 1999, 8245 and Shen et al Organometallics, 2015, 2907). The molecular weight value for the 50:1:3 (LA:Ce:ROH) sample appears consistent with this type of initiation but it is unexpected that monomodal molecular weight distributions are observed since there would be multiple different initiators (which usually leads to multi-modality and/or very broad distributions).

5) Route 5: An adduct is formed in which the alcohol (iso-propanol) is the only initiator and the ligand aryloxide moieties act as chain transfer reagents. This mechanism is substantiated by the monomodal molecular weight distributions which imply efficient initiation. Further support for this notion comes from the experimental finding that the Ce-$C_{carbene}$ bond length in a similar adduct, [CeL_3.HBr] (2.718 Å) is significantly shorter than in the catalyst [CeL_3] (2.742 Å), Chart S2, lower. This suggests that the formation of the putative alcohol adduct should result in stronger and less reactive Ce-NHC groups, and such an effect might favour initiation by the iPrOH moiety. Route 5 seems consistent with both the experimental molecular weight values, the molecular weight distribution and with the finding that only linear PLA forms.

Route 5 fits all the experimental findings and thus is the working hypothesis to rationalise the formation of linear PLA when alcohol is added. In this mechanism, an alcohol adduct forms which changes the bond-length of the key Ce-NHC moieties, forcing them to become spectator ligands rather than initiators of cyclic PLA. The PLA molecular weight values depend upon both the amount of added alcohol and the number of phenolate groups (1 per ligand) which function as co-initiators/chain transfer agents. Using this rationale allows for a re-determination of the theoretical M_n values in Table S1 (entries 2-5) and provides a much better fit with the experimental Mn data.

8.0 Single crystallographic X-ray analysis of complex 2

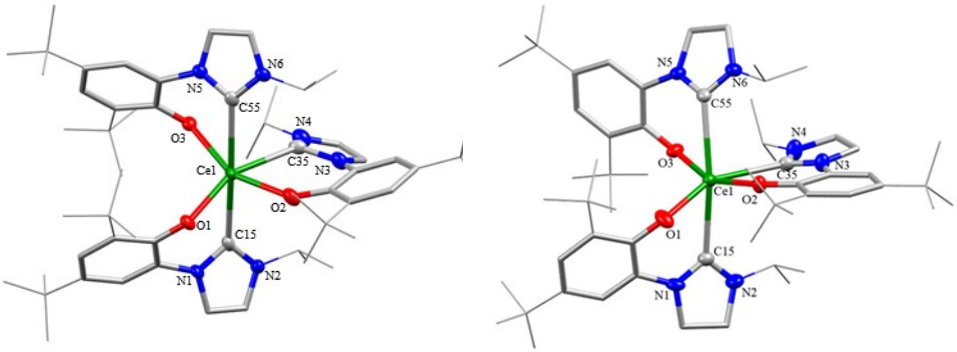
Experimental details

The *tert*-butyl substituents C(10)-C(12), C(50)-C(52) and C(30)-C(32) were rotationally disordered over two positions. As a result, they were split into two parts and refined with an occupancy ratio of 0.33:0.67, 0.49:0.51 and 0.23:0.77 respectively. The C-C bond lengths were restrained to be the similar to one another using the SADI command. Anisotropic refinement of the methyl carbon atoms C(10)-C(12) and C(50)-C(52) were unstable; these atoms were refined using the ISOR command. The methyl carbon atoms C(30)-C(32) were refined anisotropically with the thermal parameters of the carbon atoms restrained through the use of the SIMU command. One of the isopropyl substituents C(19)-C(20) was positionally disordered over two positions, so was split and refined in a 0.23:0.77 ratio. The C-C bond lengths were restrained using the SADI command, and methyl carbon atoms refined using the ISOR command. Finally, the lattice hexanes molecules are disordered over two positions but were left as is because attempts to model the disorder resulted in unstable refinement.

Analysis

Single crystal X-ray analysis of **2** confirms that the C_1 symmetry observed in solution NMR spectroscopic studies, is retained in the solid state, with a distorted octahedral geometry defined by the average bidentate ligand C-Ce-C bond angles of 162.86(10)° and 89.70(9)°; 10.07° smaller and 1.29° larger than the equivalent angles in the previously reported complex **1**, suggesting a more distorted octahedral geometry in complex **2**.

The average Ce–$C_{carbene}$ bond length is 2.777(3) Å, which is approximately 0.035 Å larger than in **1**, which can be attributed to a weaker interaction in complex **2**. The average Ce–O bond length is 2.259(2) Å, which is 0.208 Å shorter than complex **1**.



1 **2**

Figure S46: Molecular structures of **1**[1] and **2** with Ce, O and $C_{carbene}$ shown at 50% ellipsoid probability, framework and peripheral carbon atoms drawn capped stick and wireframe respectively, and H and lattice solvent omitted for clarity.

Table S3: Selected distances (Å) and angles (°) for**1** and **2:**

1	**Bond length/angle (Å/°)**	**2**	**Bond length/angle (Å/°)**
Ce1 - C55	2.747(6)	Ce1 - C55	2.800(3)
Ce1 - C35	2.694(6)	Ce1 - C35	2.769(3)
Ce1 - C15	2.785(7)	Ce1 - C15	2.762(3)
Average Ce – NHC bond length	**2.742**	**Average Ce – NHC bond length**	**2.777**
Ce1 - O3	2.349(4)	Ce1 - O3	2.282(2)
Ce1 - O2	2.277(4)	Ce1 - O2	2.242(2)
Ce1 - O1	2.283(5)	Ce1 - O1	2.253(2)
Average Ce – aryloxide bond length	**2.467**	**Average Ce – aryloxide bond length**	**2.259**
C55 - Ce1 - C15	172.93(18)	C55 - Ce1 - C15	162.86(10)
C55 - Ce1 - C35	88.28(18)	C55 - Ce1 - C35	84.09(10)
C35 - Ce1 - C15	88.53(18)	C35 - Ce1 - C15	95.31(10)
O2 - Ce1 - O3	154.05(15)	O2 - Ce1 - O3	154.71(9)
O1 - Ce1 - O3	107.42(15)	O1 - Ce1 - O3	107.02(9)
O1 - Ce1 - O2	97.45(16)	O1 - Ce1 - O2	95.80(9)
C55 - Ce1 - O3	68.68(16)	C55 - Ce1 - O3	67.09(9)
C35 - Ce1 - O2	69.09(18)	C35 - Ce1 - O2	66.54(9)
C15 - Ce1 - O1	69.66(17)	C15 - Ce1 - O1	67.87(9)

Table S4 Experimental details [10-12]

Crystal data	
Local code	p19066
Chemical formula	$C_{60}H_{93}CeN_6O_3 \cdot C_3H_7$
Mr	1129.60
Crystal system, space group	Triclinic, P1
Temperature (K)	190
a, b, c (Å)	13.1056 (4), 13.6683 (4), 18.4321 (5)
α, β, γ (°)	77.706 (3), 76.664 (2), 83.959 (2)
V (Å3)	3133.58 (16)
Z	2
Radiation type	Mo Kα
μ (mm−1)	0.77
Crystal size (mm)	0.31 × 0.07 × 0.07
Data collection	
Diffractometer	Xcalibur, Eos
Absorption correction	Analytical CrysAlis PRO 1.171.40.54a (Rigaku Oxford Diffraction, 2019) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
Tmin, Tmax	0.758, 0.931
No. of measured, independent and observed [I > 2σ(I)] reflections	67146, 12786, 10783
Rint	0.074
(sin θ/λ)max (Å−1)	0.625
Refinement	
R[F2 > 2σ(F2)], wR(F2), S	0.048, 0.107, 1.05
No. of reflections	12786
No. of parameters	717
No. of restraints	99
H-atom treatment	H-atom parameters constrained
Δρmax, Δρmin (e Å−3)	0.87, −0.58

Computer programs: CrysAlis PRO 1.171.40.54a (Rigaku OD, 2019), SHELXT (Sheldrick, 2015), SHELXL (Sheldrick, 2015), Olex2 (Dolomanov et al., 2009).

9.0 References

(1) Arnold, P. L.; Kerr, R. W. F.; Weetman, C.; Docherty, S. R.; Rieb, J.; Cruickshank, F. L.; Wang, K.; Jandl, C.; McMullon, M. W.; Pöthig, A.; Kühn, F. E.; Smith, A. D., Selective and catalytic carbon dioxide and heteroallene activation mediated by cerium N-heterocyclic carbene complexes. *Chem. Sci.* **2018**, *9* (42), 8035-8045.

(2) Bradley, D. C.; Ghotra, J. S.; Hart, F. A., Low co-ordination numbers in lanthanide and actinide compounds. Part I. The preparation and characterization of tris{bis(trimethylsilyl)-amido}lanthanides. *J. Chem. Soc. Dalton. Trans.* **1973,** (10), 1021-1023.

(3) Waltman, A. W.; Grubbs, R. H., A New Class of Chelating N-Heterocyclic Carbene Ligands and Their Complexes with Palladium. *Organometallics* **2004,** *23* (13), 3105-3107.

(4) Arduengo, A. J.; Dias, H. V. R.; Harlow, R. L.; Kline, M., Electronic stabilization of nucleophilic carbenes. *J. Am. Chem. Soc.* **1992,** *114* (14), 5530-5534.

(5) Zell, M. T.; Padden, B. E.; Paterick, A. J.; Thakur, K. A. M.; Kean, R. T.; Hillmyer, M. A.; Munson, E. J., Unambiguous Determination of the ^{13}C and ^{1}H NMR Stereosequence Assignments of Polylactide Using High-Resolution Solution NMR Spectroscopy. *Macromolecules* **2002,** *35* (20), 7700-7707.

(6) Kowalski, A.; Duda, A.; Penczek, S., Polymerization of L,L-Lactide Initiated by Aluminum Isopropoxide Trimer or Tetramer, *Macromolecules* **1998**, *31* (7), 2114-2122

(7) Kamber, N. E.; Jeong, W.; Gonzalez, S.; Hedrick, J. L.; Waymouth, R. M., N-Heterocyclic Carbenes for the Organocatalytic Ring-Opening Polymerization of ε-Caprolactone. *Macromolecules* **2009,** *42* (5), 1634-1639.

(8) Jan, S.; Roblot, C.; Courtois, J.; Courtois, B.; Barbotin, J. N.; Séguin, J. P., ^{1}H NMR spectroscopic determination of poly 3-hydroxybutyrate extracted from microbial biomass. *Enzyme Microb. Technol.* **1996,** *18* (3), 195-201.

(9) Wonhee, J.; Shin, E, J.; Culkin, D. A.; Hedrick, J. L.; Waymouth, R. M.; Zwitterionic Polymerization: A Kinetic Strategy for the Controlled Synthesis of Cyclic Polylactide. *J. Am. Chem.*, **2009**, *131* (13), 4884-4891.

(10) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H., OLEX2: a complete structure solution, refinement and analysis program. *J. App. Cryst.* **2009,** *42* (2), 339-341.

(11) Sheldrick, G., SHELXT - Integrated space-group and crystal-structure determination. *Acta Cryst. A* **2015,** *71* (1), 3-8.

(12) Sheldrick, G., Crystal structure refinement with SHELXL. *Acta Cryst. C* **2015,** *71* (1), 3-8.