Supporting Information

Bimetallic aluminum complexes bearing binaphthyl-based iminophenolate ligands as catalysts for the synthesis of polyesters.

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The supplemental file [rac-2] contains the computed Cartesian coordinates of all of the molecules reported in this study

Experimental

General

All manipulations of air- and/or water-sensitive compounds were carried out under a dry nitrogen atmosphere using a Braun Labmaster glove-box or standard Schlenk line techniques. Glassware and vials used in the polymerization were dried in an oven at 120 °C overnight and exposed three times to vacuum–nitrogen cycles.

Reagents and solvents

Benzene, hexane and toluene (Sigma Aldrich) were distilled under nitrogen over sodium benzophenone. The aluminum precursor $AlMe_3$ was purchased from Aldrich and was used as received. Deuterated solvents were dried over molecular sieves. ε-Caprolactone was purchased from Aldrich freshly distilled from CaH_2 under nitrogen and degassed thoroughly by freeze–vacuum–thaw cycles prior to use. *Rac*-lactide and L-lactide were purchased from Aldrich and dried in vacuo over P_2O_5 for 72 h, and afterward stored at −20 °C in a glovebox. All other chemicals were commercially available and used as received unless otherwise stated.

NMR analysis

The NMR spectra were recorded on Bruker Advance 300, 400 and 600 MHz spectrometers at 25 °C, unless otherwise stated. Chemical shifts (δ) are expressed as parts per million and coupling constants (J) in hertz. ^1H NMR spectra are referenced using the residual solvent peak at δ = 7.16 for C_6D_6 and δ = 7.27 for $CDCl_3$. ^{13}C NMR spectra are referenced using the residual solvent peak at δ = 128.06 for C_6D_6 and δ = 77.23 for $CDCl_3$.

Computational details

The DFT calculations were performed with the Gaussian09 set of programs,[(1)] using the BP86 functional of Becke and Perdew.[(2)] The electronic configuration of the molecular systems was described with the standard split-valence basis set with a polarization function of Ahlrichs and co-workers for H, C, O, N, Br and Al (SVP keyword in Gaussian).[(3)] The geometry optimizations were performed without symmetry constraints, and the characterization of the located stationary points was performed by analytical frequency calculations.

CPC analysis

CPC analysis

The molecular weights (Mn and Mw) and the molecular mass distribution (Mw/Mn) of poly-lactide samples were measured by GPC at 30 □C, using THF as solvent, flow rate of eluant 1 mL/min, and narrow polystyrene standards as reference. The measurements were performed on a Waters 1525 binary system equipped with a Waters 2414 RI detector using four Styragel columns (range 1000-1 000 000 Å). Every value was the average of two independent measurements. It was corrected using the factor of 0.58 according to the literature for lactide and 0.56 for caprolactone.

***rac*-Lactide polymerization**

The polymerization was carried out under an inert atmosphere. In a Braun Labmaster glovebox, a magnetically stirred reactor vessel (10 mL) was charged with a solution of *rac*-lactide in toluene. Subsequently, a toluene solution of the metal-complex and ^{i}PrOH (0.1 M) was added. The reaction mixture was stirred at 70 °C. At desired times, small aliquots of the reaction mixture were sampled, dissolved in $CDCl_3$ and analyzed by ^{1}H NMR spectroscopy. At the end of the polymerization, the product was precipitated in MeOH then filtered and dried in a vacuum oven.

ε-Caprolactone polymerization

The polymerization was carried out under an inert atmosphere. In a Braun Labmaster glovebox, a magnetically stirred reactor vessel (10 mL) was charged with a solution of ε-caprolactone in toluene. Subsequently, a toluene solution of the metal-complex and ^{i}PrOH (0.1 M) was added. The reaction mixture was stirred at 70 °C. At desired times, small aliquots of the reaction mixture were sampled, dissolved in $CDCl_3$ and analyzed by ^{1}H NMR spectroscopy. At the end of the polymerization, the product was precipitated in hexane then filtered and dried in a vacuum oven.

Copolymerization of CHO and PA

The polymerization was carried out under an inert atmosphere. In a Braun Labmaster glovebox, a magnetically stirred reactor vessel (10 mL) was charged with a solution of phthalic anhydride in toluene. Subsequently, a toluene solution of the metal complex, PPNCl and cyclohexene oxide was added. The reaction mixture was stirred at 110 °C. At desired times, small aliquots of the reaction mixture were sampled, dissolved in $CDCl_3$ and analyzed by ^{1}H NMR spectroscopy. At the end of the polymerization, the product was dried in a vacuum oven.

Terpolymerization of CHO, PA and LA.

The polymerization was carried out under an inert atmosphere. In a Braun Labmaster glovebox, a magnetically stirred reactor vessel (10 mL) was charged with lactide and a solution of phthalic anhydride in toluene. Subsequently, a toluene solution of the metal complex, PPNCl and cyclohexene oxide and was added. The reaction mixture was stirred at 110 °C. At desired times, small aliquots of the reaction mixture were sampled, dissolved in $CDCl_3$ and analyzed by ^1H NMR spectroscopy. At the end of the polymerization, the product was dried in a vacuum oven.

Synthesis of proligands *rac*- L1 and *rac*-L2.

All proligands were synthetized modifying a procedure previously reported in literature.[1] In a 100 mL two neck round bottom flask equipped with reflux condenser, to a stirred solution containing rac 1 1'-binaphthyl-2 2'-diamine (0.510 g, 1.76 mmol) in ethanol (50 mL), two equivalents (3.54 mmol) of the opportune aldehyde (3,5-di-tert-butyl-2-hydroxybenzaldehyde: 0.825 g, or 3,5-dibromo-2-hydroxybenzaldehyde: 0.991 g) were added. The solution was stirred at reflux for 12 hours. The solid products were isolated by filtration and washed with fresh ethanol. Yields (86% for rac-L1 and 84 % for rac-L2).

***rac*-L1** ^1H NMR (300 MHz, C_6D_6, 298 K): δ 13.23 (s, 2H), 8.31 (s, 2H), 7.88 (d, J = 8.5 Hz, 2H), 7.81 (d, J =8.1 Hz, 2H), 7.52 (d, J = 8.3 Hz, 2H), 7.39 (d, J = 2.1 Hz, 2H),7.24 (d, J = 8.6 Hz, 2H), 7.20 (t, J = 7.8 Hz, 2 H), 7.02 (t, J = 6.9 Hz, 2H), 6.88 (d, J = 2.2 Hz, 2H), 1.40 (s, 18H), 1.23 (s, 18H).

^{13}C NMR (100 MHz, C_6D_6, 298 K): δ 163.2, 158.9, 144.3, 139.9, 136.9, 133.9, 133.0, 130.1, 129.8, 127.3, 127.1, 126.9, 126.0, 118.9, 117.7, 35.2, 34.1, 31.6, 29.5.

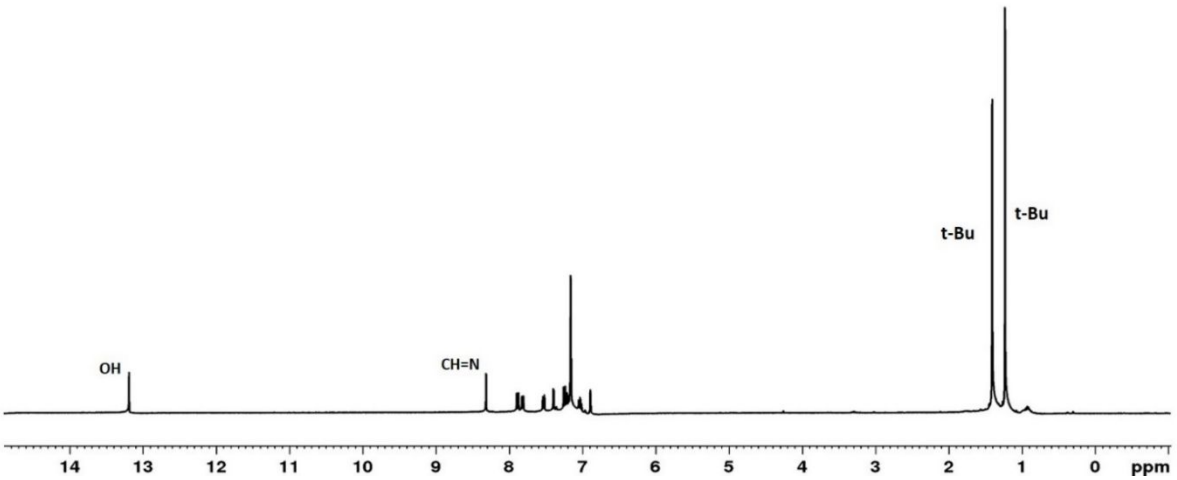


Figure S2. ^1H NMR (300 MHz, C_6D_6, 298 K) of proligand *rac*-L1

***rac*-L2** ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 13.12 (s, 2H), 7.75 (s, 2H), 7.84 (d, J = 8.5 Hz, 2H), 7.73 (d, J =8.1 Hz, 2H), 7.29 (d, J = 8.3 Hz, 2H), 7.24(d, J = 2.1 Hz, 2H),7.23 (d, J = 8.6 Hz, 2H), 7.14 (t, J = 7.8 Hz, 2 H), 6.98 (t, J = 6.9 Hz, 2H), 6.55 (d, J = 2.1 Hz, 2H).

^{13}C NMR (100 MHz, C_6D_6, 298 K): δ 164.2, 157.3, 144.2, 139.5, 137.9, 132.7, 133.0, 130.7, 129.8, 127.3, 127.1, 126.3, 125.0, 118.4, 115.5.

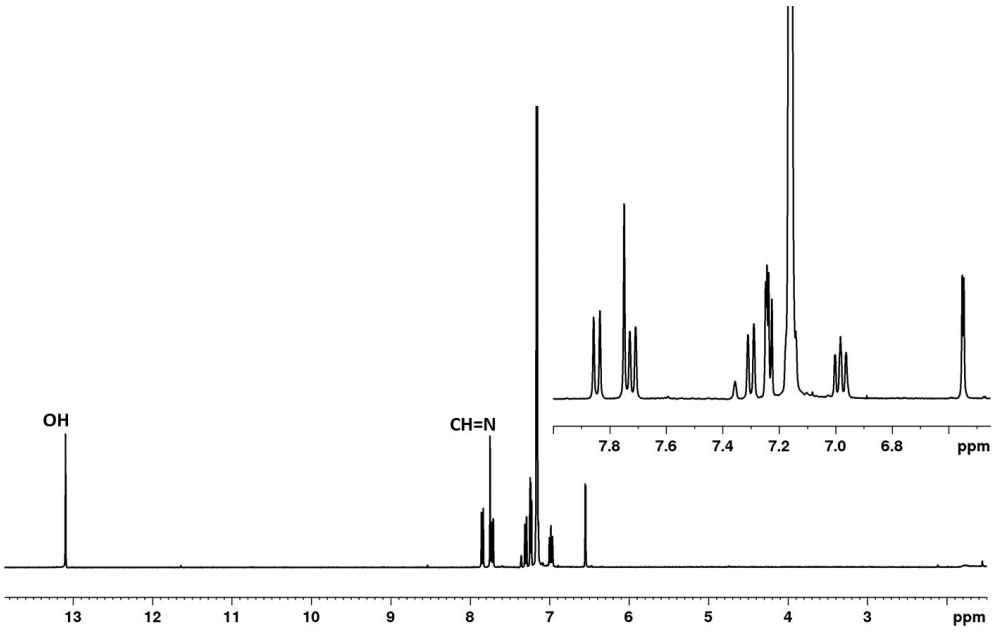


Figure S2. ^{1}H NMR (300 MHz, C_6D_6, 298 K): of proligand *rac*-L2

Synthesis of proligand (R) L1

The synthetic procedure was the same described for the related chiral proligand *rac*-L1, but the chiral diamine was used. (R)-1 1'-binaphthyl-2 2'-diamine (505 mg, 1.76 mmol) in ethanol (50mL), 3,5-di-tert-butyl-2-hydroxybenzaldehyde (833 mg, 3.52 mmol) was added. The solution was stirred at reflux for 12 hours. The solid product was isolated by filtration and washed with fresh ethanol. Yield (89%) $[\alpha]^{D}_{25}$= -432.28.

Synthesis of complexes

Complex *rac*-1. To a stirred solution containing $AlMe_3$ (0.083 g, 1.1 mmol) in benzene (2 mL) was added dropwise a solution of the ligand precursor *rac*-**L1** (0.400 g, 0.56 mmol) in benzene (4 mL). The solution was stirred for 3 h at room temperature. The solvent was removed under vacuum, forming a pale-yellow solid in almost quantitative yield (96%).

^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 7.82 (s, 2H, CH=N), 7.63 (d, J = 2.4 Hz, 2H, ArH), 7.51 (d, J = 8.4 Hz, 2H, ArH), 7.43 (d, J = 8.7 Hz, 2H, ArH), 7.28 (d, J = 8.4 Hz, 2H, ArH), 7.24 (d, J = 8.7 Hz, 2H, ArH), 7.14 (t, J = 7.4 Hz, 2H, ArH), 7.01 (t, J = 7.1 Hz, 2H, ArH), 6.36 (d, J = 2.4 Hz, 2H, ArH), 1.54 (s, 18H, t-Bu), 1.23 (s, 18H, t-Bu), -0.45 (s, 6H, Al–CH_3), -0.75 (s, 6H, Al–CH_3).

^{13}C NMR (100 MHz, C_6D_6, 298 K): δ 173.7, 163.0, 144.7, 140.8, 139.2, 134.9, 133.2, 132.7, 131.0, 130.1, 126.6, 125.4, 124.2, 119.6 (Ar or ArCNH), 35.5 ($C(CH_3)_3$), 34.0 ($C(CH_3)_3$), 31.4 (CH_3), 29.7 (CH_3), -9.1 (Al–CH_3).

Complex *R-1*. To a stirred solution containing $AlMe_3$ (0.044 g, 0.54 mmol) in benzene (2 mL) was added dropwise a solution of the ligand precursor R-L1 (0.193 g, 0.27 mmol) in benzene (4 mL). The solution was stirred for 3 h at room temperature. The solvent was removed under vacuum, forming a pale-yellow solid in almost quantitative yield (94%). The NMR characterization was reported for complex racemic *rac*-1

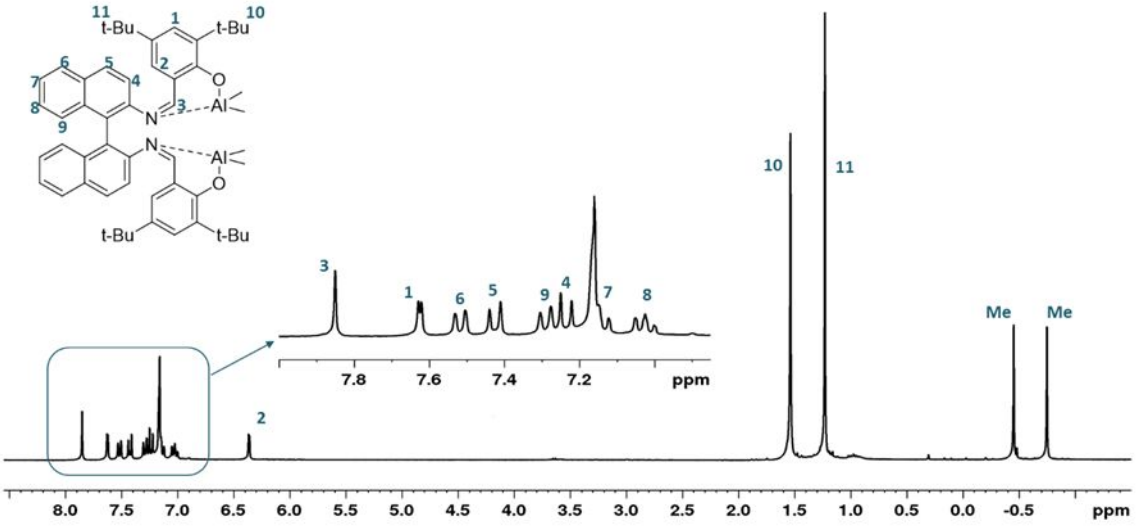
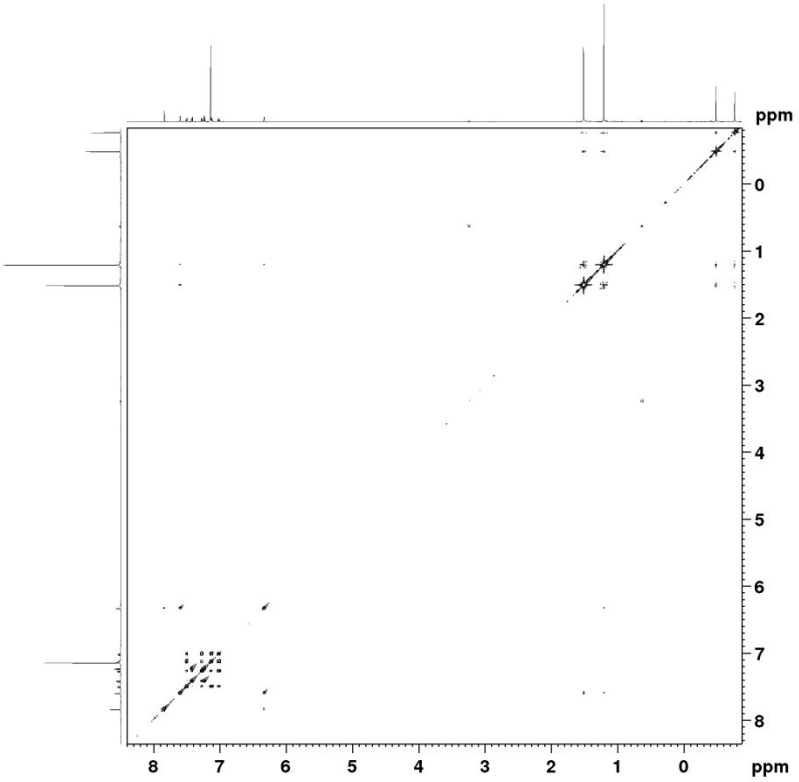


Figure S3. ^{1}H NMR (400 MHz, C_6D_6, 298 K) of complex *rac*-**1**



FigureS4 ^{1}H-^{1}H COSY NMR (400 MHz, C_6D_6, 298 K) del complex *rac*-**1**.

Complex *rac*-2. To a stirred solution containing $AlMe_3$ (0.050 g, 0.62 mmol) in benzene (2 mL) was added dropwise a solution of the ligand precursor *rac*-**L1** (0.250 g, 0.31 mmol) in benzene (4 mL). The solution was stirred for 3 h at room temperature. The solvent was removed under vacuum, forming a pale-yellow solid in almost quantitative yield (97%).

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 7.56 (d, J = 2.3 Hz, 2H), 7.51 (d, J = 8.8 Hz, 2H), 7.43 (d, J = 8.8 Hz, 2H), 7.23 (s, 2H), 7.10 (t, J = 7.0 Hz, 2H), 7.09 (d, J = 8.6 Hz, 2H) 6.90 (t, J = 7.1 Hz, 2H), 6.89(d, J = 8.6 Hz, 2H), 6.58 (d, J = 2.3 Hz, 2H,) -0.67 (s, 6H), -1.25 (s, 6H).

^{13}C NMR (75 MHz, C_6D_6, 298 K): δ 143.0, 142.7, 136.2, 134.3, 132.7, 131.4, 128.4, 128.3, 128.2, 128., 127.2, 127.1, 124.8, 123.3, 120.6, 120.6, 117.6, 108.9.

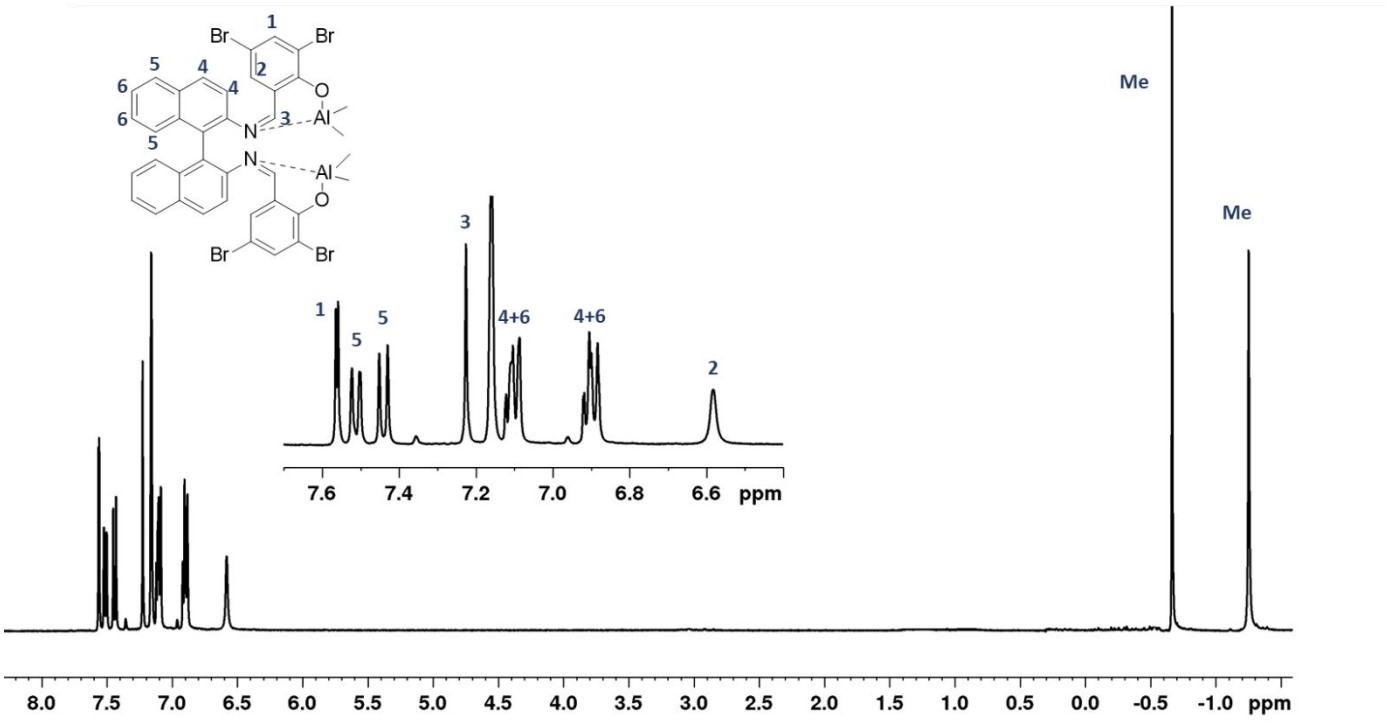


Figure S5. ^{1}H NMR (400 MHz, C_6D_6, 298 K) of complex ***rac*-1**

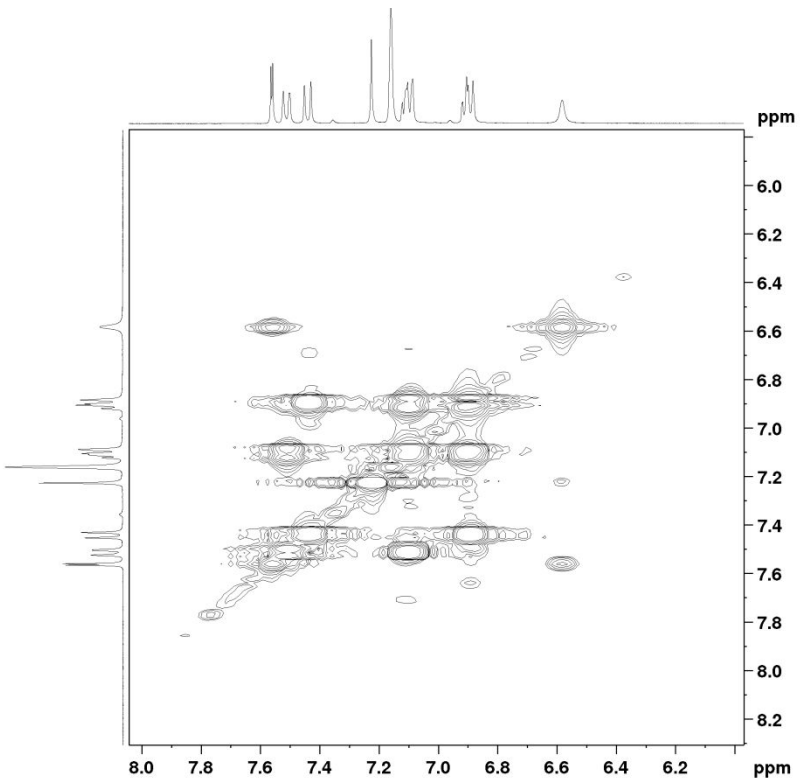


Figure S6: ^{1}H-^{1}H COSY NMR (400 MHz, C_6D_6, 298 K) spectrum of complex ***rac*-2**.

Preparation of the isopropoxide derivative

A solution of complex ***rac*-1** was prepared in deuterated benzene. Subsequently four equivalents of ^{i}PrOH were added. After 1 hour at room temperature, no alcoholysis of complex **1** was observed. The exhaustive alcoholysis of all the methyl groups was achieved only at 70 °C after 24 hours. This is agreement with observations reported in the literature, indicating the formation of the alkoxide active species requires an activation energy.5 The ^{1}H NMR spectrum of the isopropoxide derivative showed (Figures S5 and S6) doubled signals in comparison to the related alkyl complex, such as two resonances for the inequivalent imine protons and four signals for the aromatic protons of the phenoxy moieties for the coordinated ligand. In addition, four singlets for the tert buthyl groups (at 1.83, 1.81, 1.16 and 1.03 ppm) were observed in the aliphatic region. These evidences suggested the loss of the initial symmetry observed for the related alkyl complex *rac* 1.

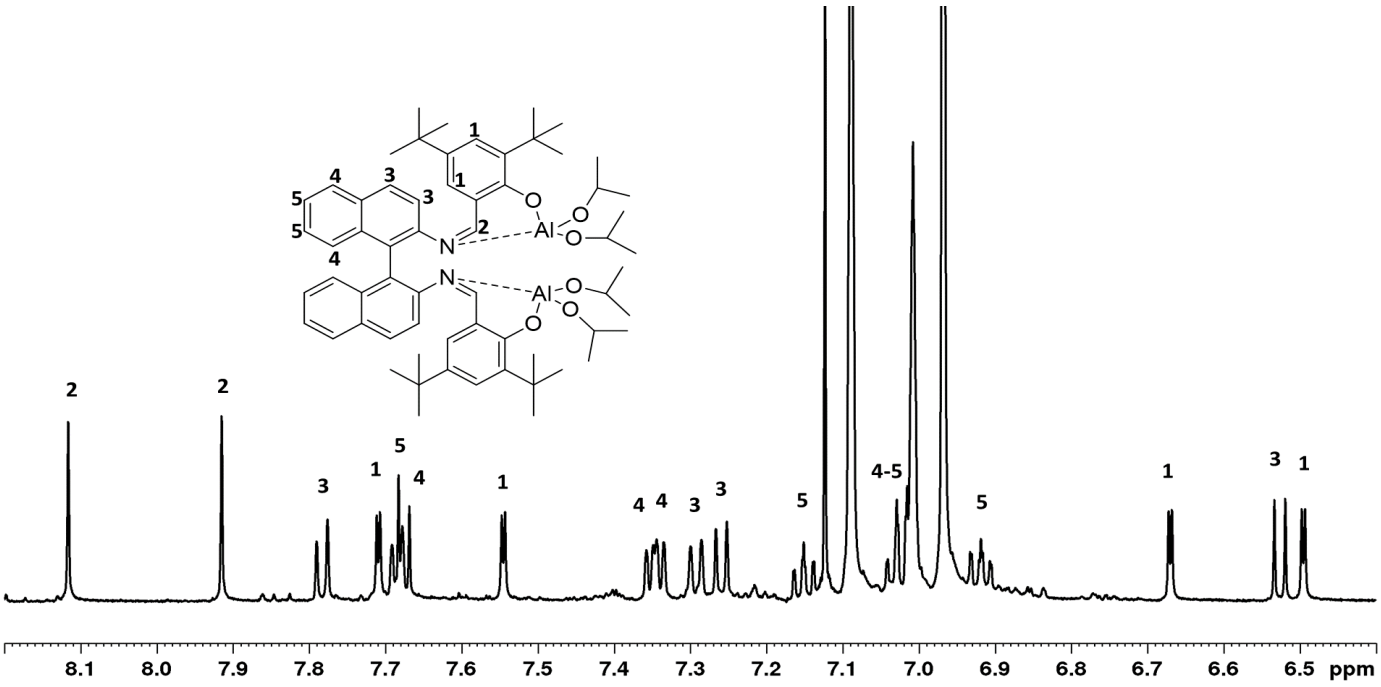


Figure S7. ^{1}H NMR (400 MHz, C_6D_6, 298 K) of isopropoxide derivative of complex rac-1. Aromatic region.

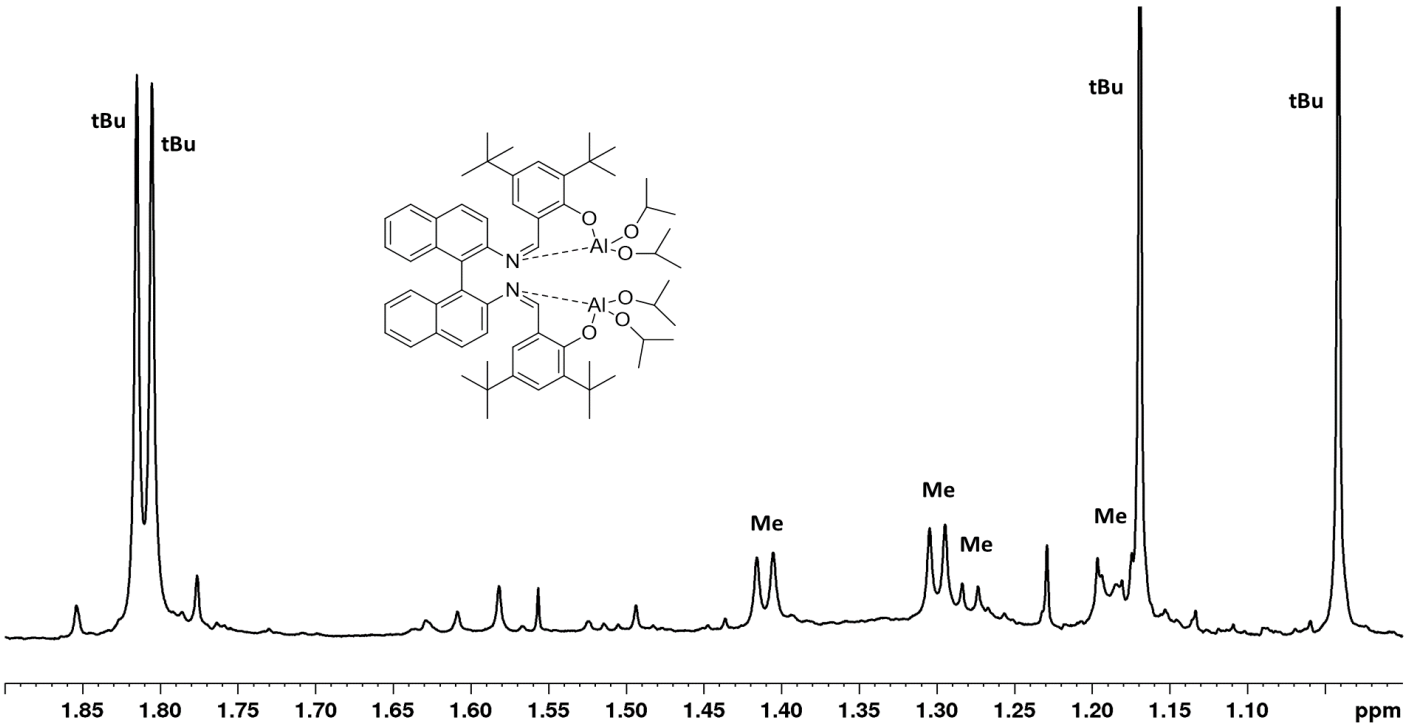


Figure S8. ^{1}H NMR (400 MHz, C_6D_6, 298 K) of isopropoxide derivative of complex rac-1. Aliphatic region.

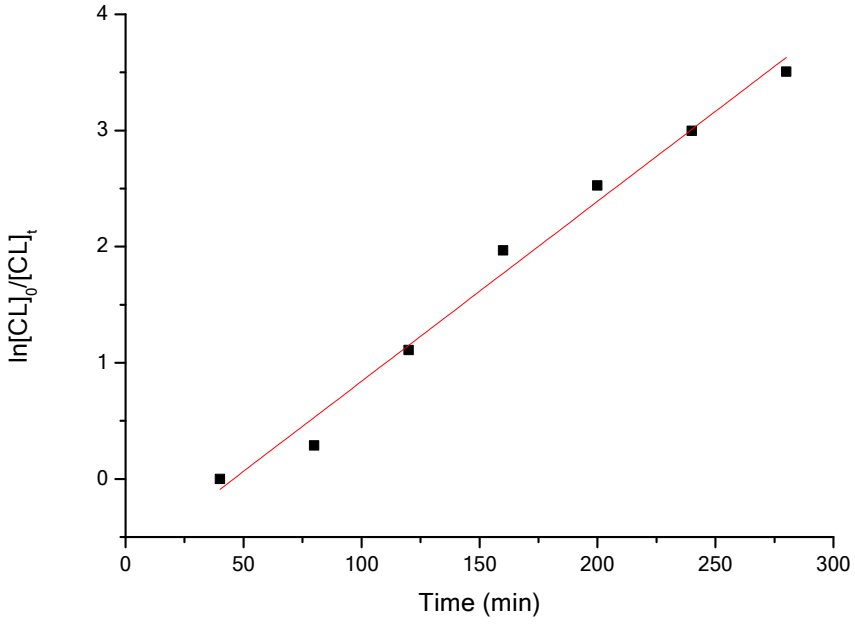


Figure S9. Kinetic plot for ROP of ε-CL by *rac*-**1** depicting a reaction order of unity with respect to monomer concentration after the initial induction period. K_{app}=0.0155 min^{-1}(R^2 = 0.985) Reaction conditions: [cat] = 0.01M; [ε-CL]/[cat] = 100; T=298 K; toluene-d8 as solvent.

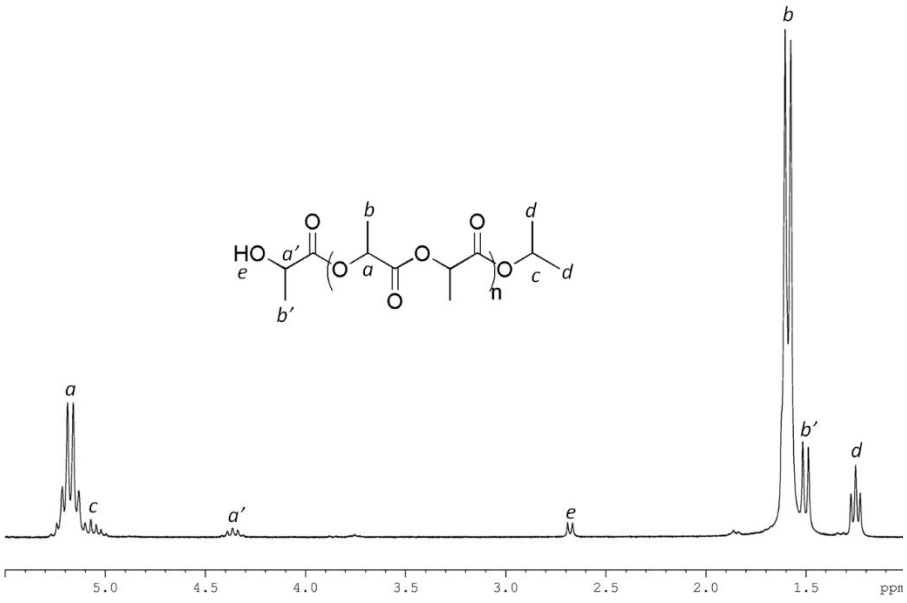
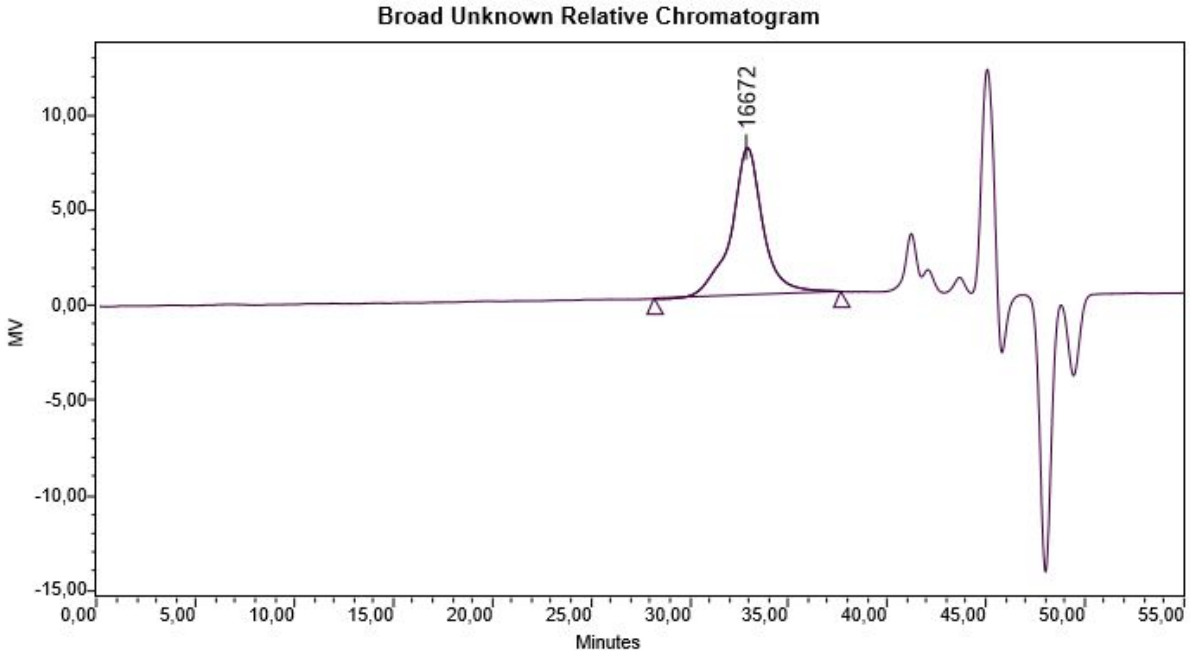


Figure S10. ^{1}H NMR (100 MHz, $CDCl_3$, 298 K) of polymer obtained in run 4 of Table 1



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		15653	17673	16672	19806	22298	1,129056	1,120696	1,261710

Figure S11. GPC trace of polymer obtained in run 4 of Table 1

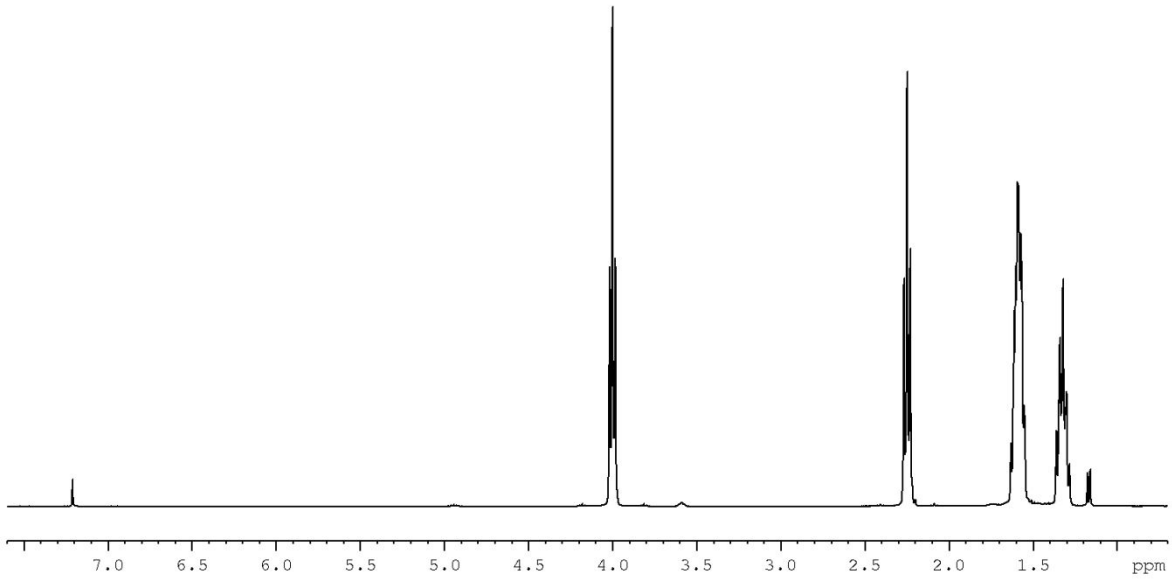
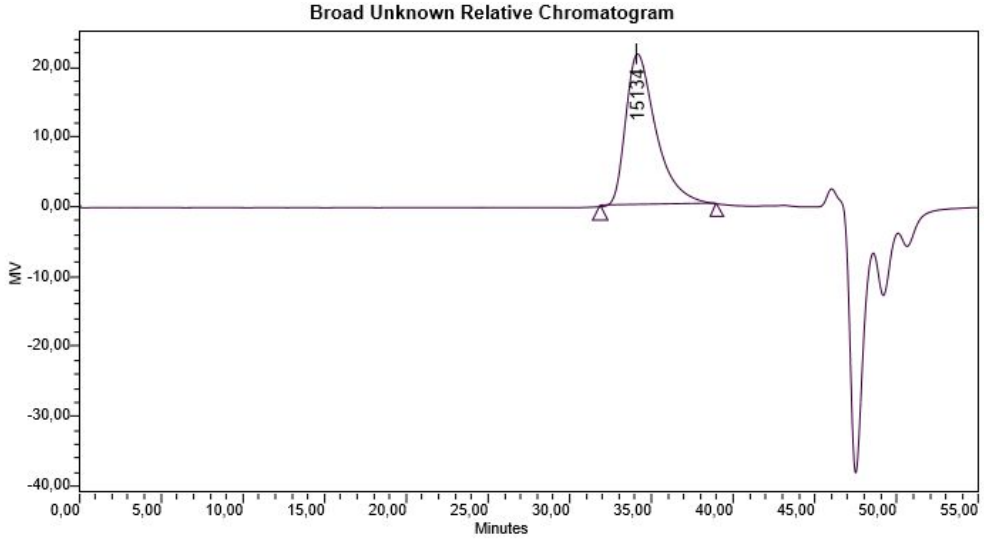


Figure S12. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of polymer obtained in run 2 of Table 2



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		12320	13859	15134	15126	16200	1,124905	1,091424	1,168941

Figure S13. GPC trace of polymer obtained in run 2 of Table2

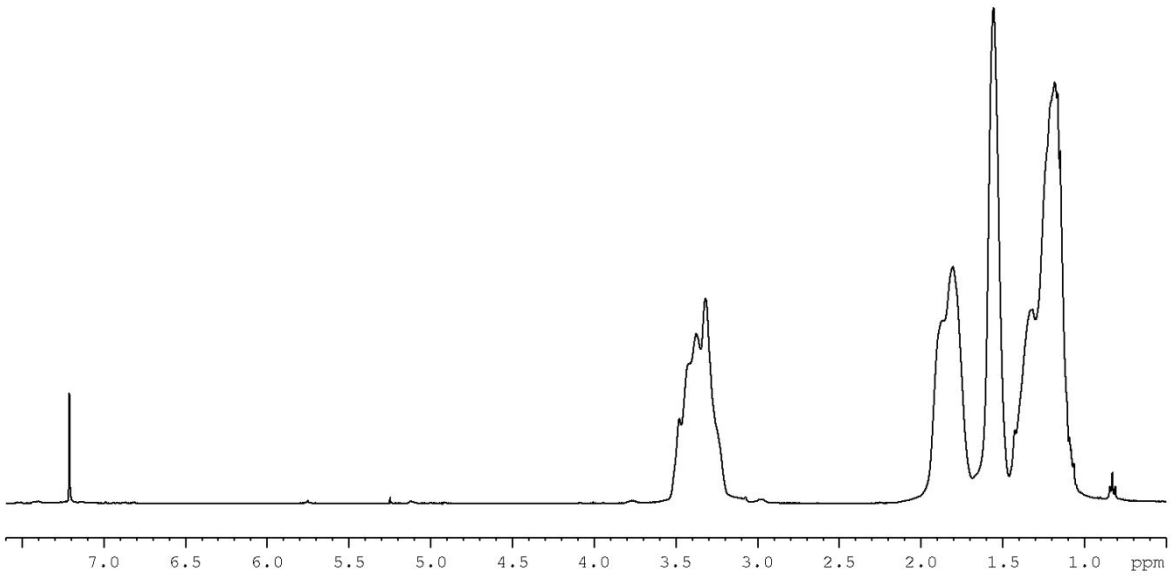
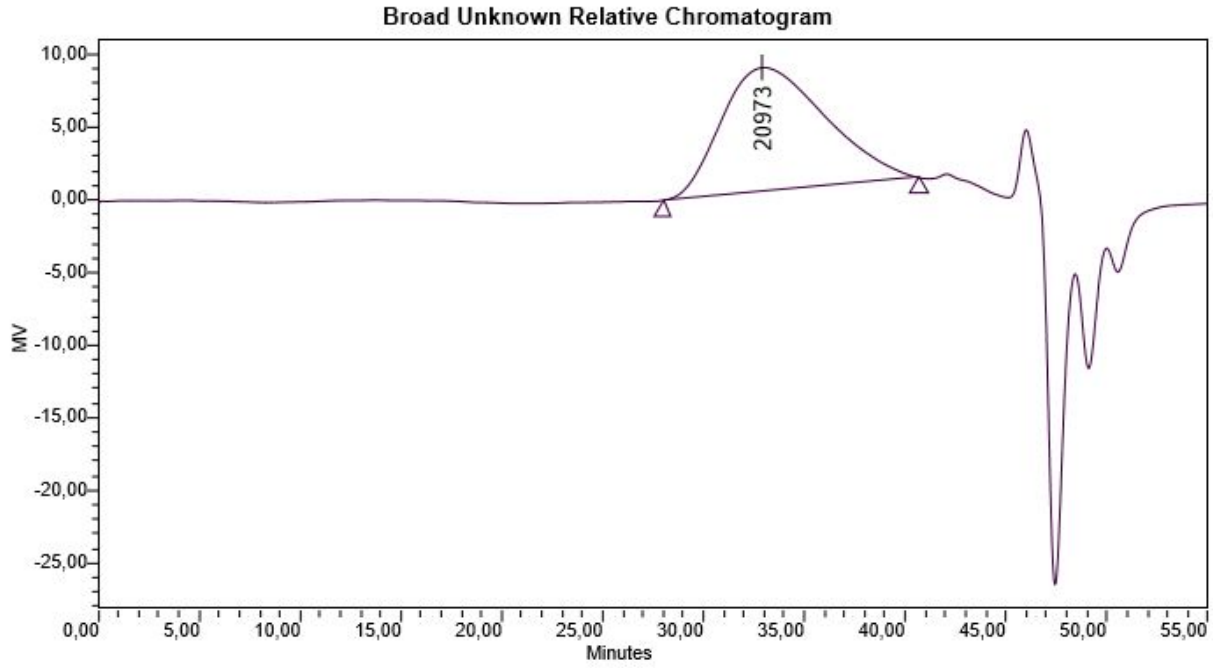


Figure S14. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of PCHO obtained in run 5 of Table 2



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		11305	20860	20973	32177	43258	1,845185	1,542545	2,073773

Figure S15. GPC trace of a PCHO of run 6 of Table 2

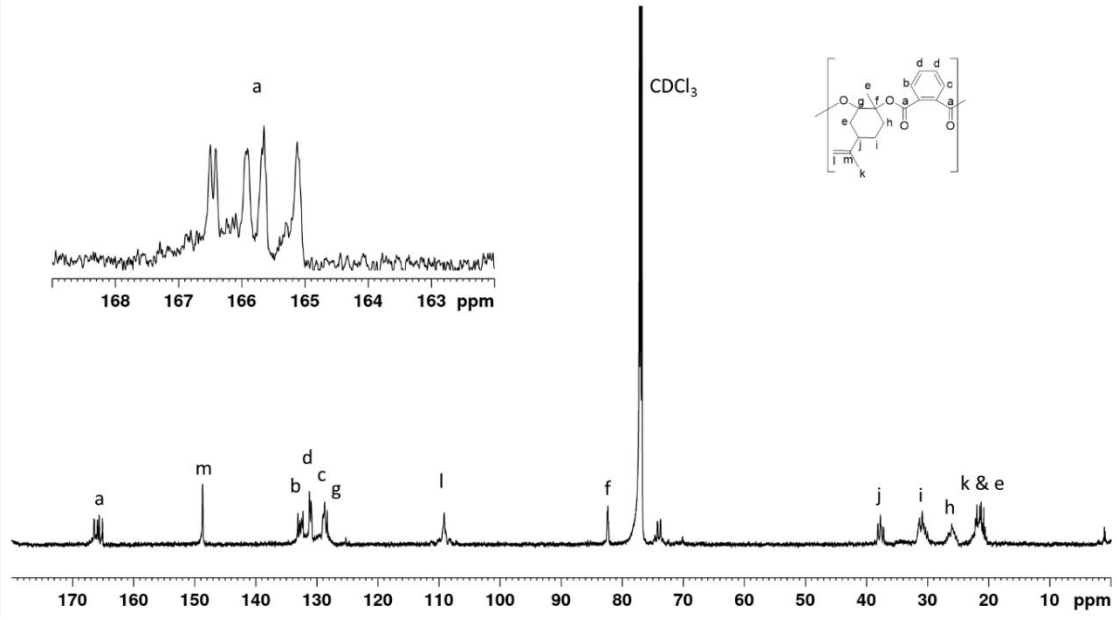
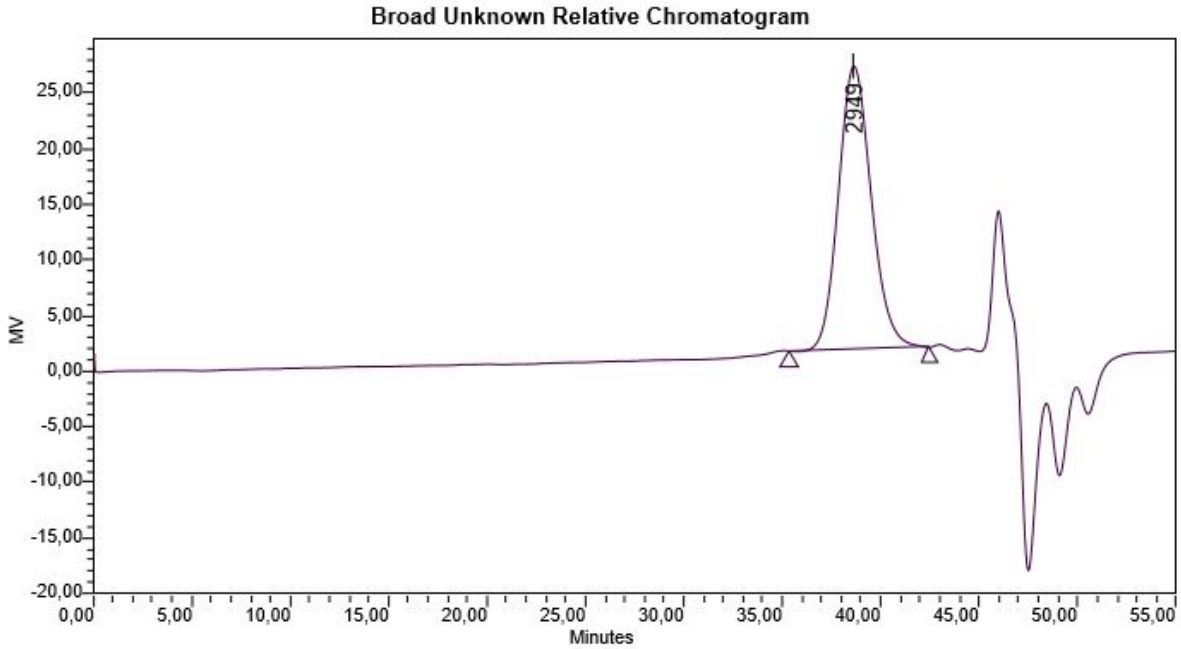


Figure S16. ^{1}H NMR (100 MHz, $CDCl_3$, 298 K) of polymer obtained in run 4 of Table 4



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		2642	2927	2949	3193	3446	1,108174	1,090752	1,177327

Figure S17. GPC trace of a sample of run 4 of Table 3

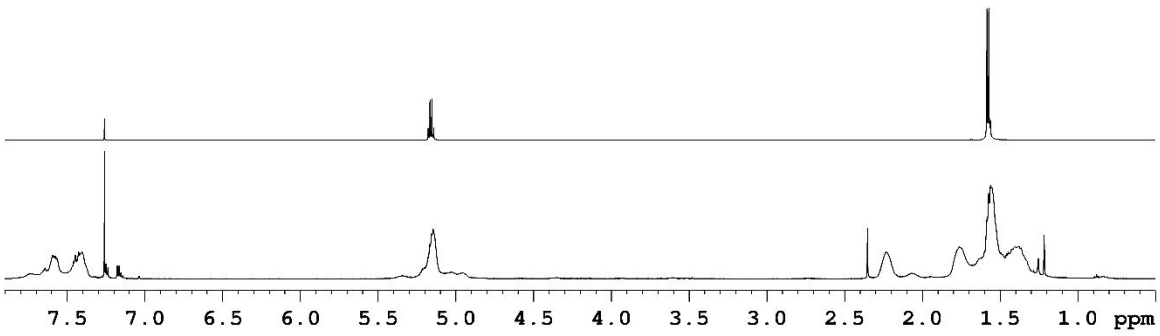


Figure S18. ^{1}H NMR spectra of the copolymer poly[(cyclohexene phthalate)-block-(lactide)] obtained in run 6 of Table 3 (down) and a PLA sample (up).

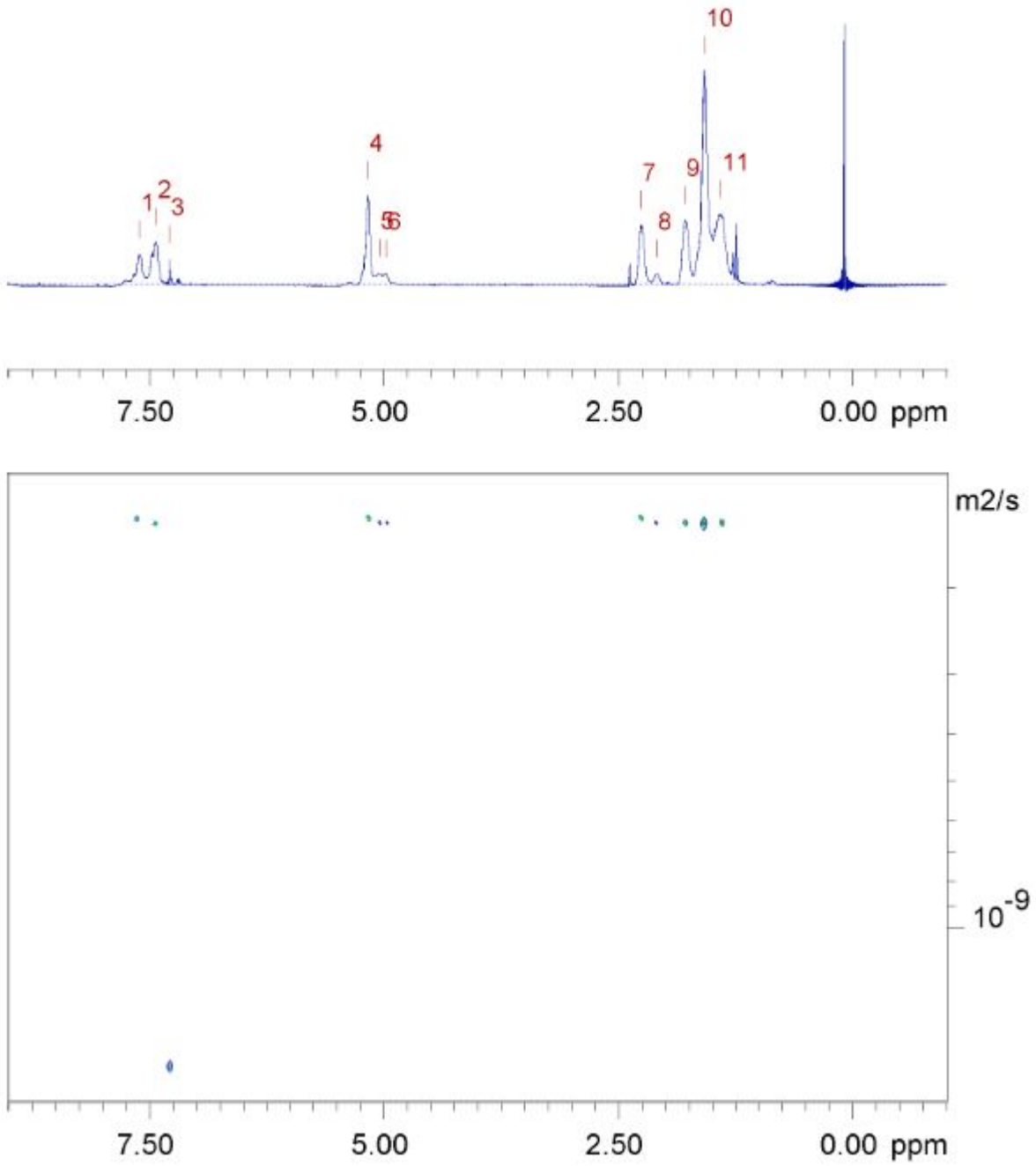
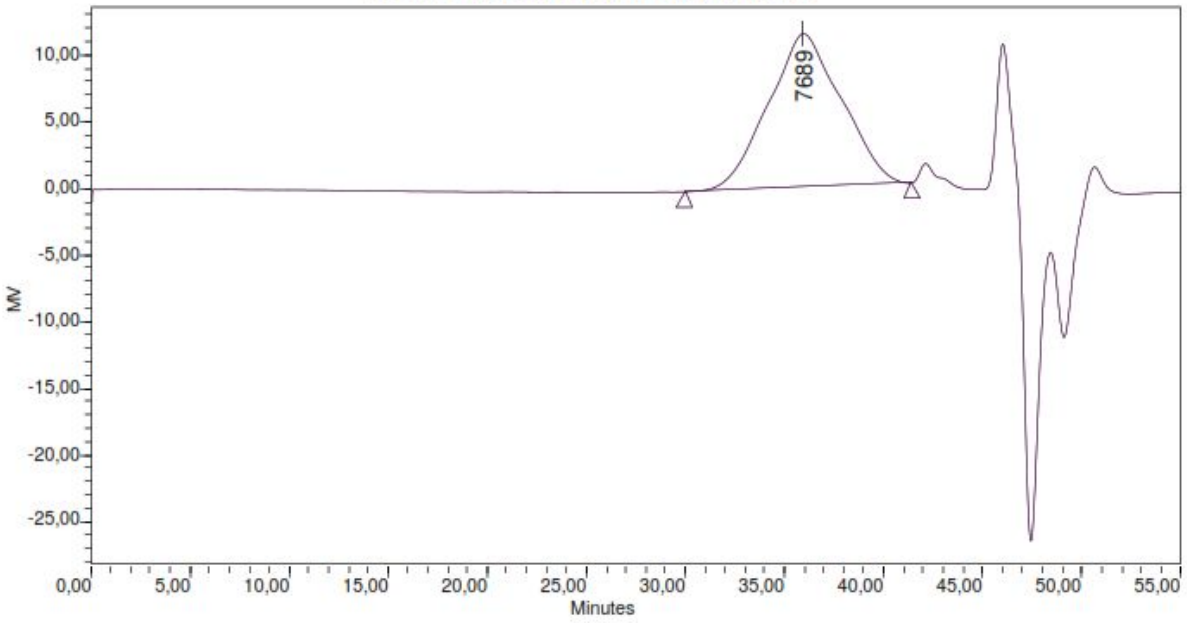


Figure S19. ^{2}D DOSY NMR (600 MHz, $CDCl_3$, RT) of poly[(cyclohexene phthalate)-block-(lactide)]

SAMPLE INFORMATION

Sample Name:	FS_M_85	Acquired By:	System
Sample Type:	Broad Unknown	Date Acquired:	03/04/2019 10.14.43
Vial:	22	Acq. Method:	MG_F1A_RI35C_UV254_M19
Injection #:	1	Date Processed:	04/04/2019 11.40.12
Injection Volume:	100,00 ul	Channel Name:	410
Run Time:	55,00 Minutes	Channel Desc.:	RI Detector
Column Type:		Sample Set Name:	2019_Aprile2

Broad Unknown Relative Chromatogram



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		6067	8722	7689	12022	15711	1,437494	1,378316	1,801275

Figure S20. GPC trace of polymer obtained in run 6 of Table 3

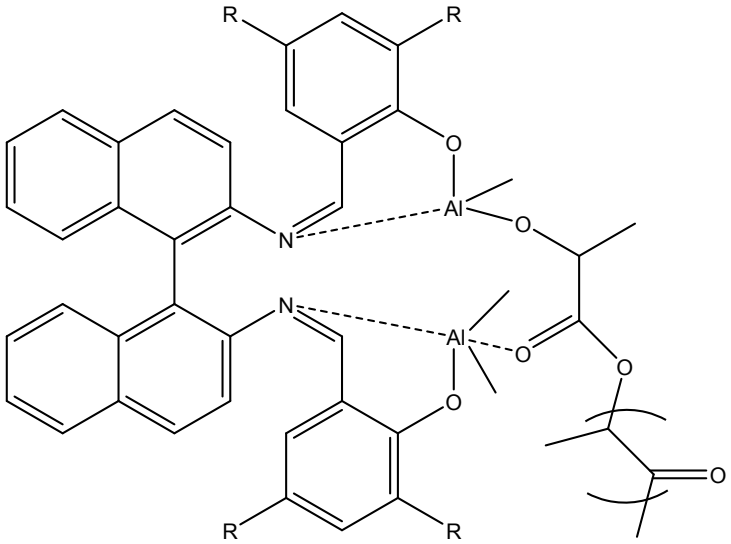


Figure S21. Structure for the hypothetical O-lactate chelated species

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