Supporting Information

Rare Earth Silylamido Complexes of Phenoxy-Thioether Ligands: Synthesis and Reactivity in the Ring Opening Polymerization of Cyclic Esters.

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Table S1. PGSE experimental results (r_H) compared to estimated data from DFT optimized structures (r'_H).

Complex	Δ (P30)	D ($\times 10^{-10}$ m^2/s)	D^{TMSS} ($\times 10^{-10}$ m^2/s)	r_H (Å)	V_H (Å^3)	r'_H (Å)
1-a	1780	5.8	12.7	7.16	1537	6.87
1-a-CL	1900	4.5	10.5	7.37	1677	7.07

Table S2. Internal and Free Energies in Gas Phase and Benzene of Minimum Energy Structures Relative to $(\mathbf{L^1})_2$Sc$\{$N(SiH$_3$)$_2\}$ and $(\mathbf{L^1})_2$Y$\{$N(SiH$_3$)$_2\}$(THF).[a]

Structure	ΔE_{gas}	ΔE_{C6H6}	ΔG_{gas}	ΔG_{C6H6}
A	0.0	0.0	0.0	0.0
E	4.2	4.0	3.9	3.8
F	0.0	0.0	0.0	0.0
G	1.4	1.8	-0.3	0.1
H	4.0	3.9	3.2	3.1
I	3.1	2.9	3.4	3.3
J	4.2	4.2	4.1	4.1
K	7.2	6.5	4.4	3.8

[a] Zero Point Energy (ZPE) Corrected Energies in gas phase (ΔE_{gas}) and in benzene (ΔE_{C6H6}) and Free Energies thermodynamically corrected to 298 K in gas phase (ΔE_{gas}) and in benzene (ΔE_{C6H6}) (kcal/mol)
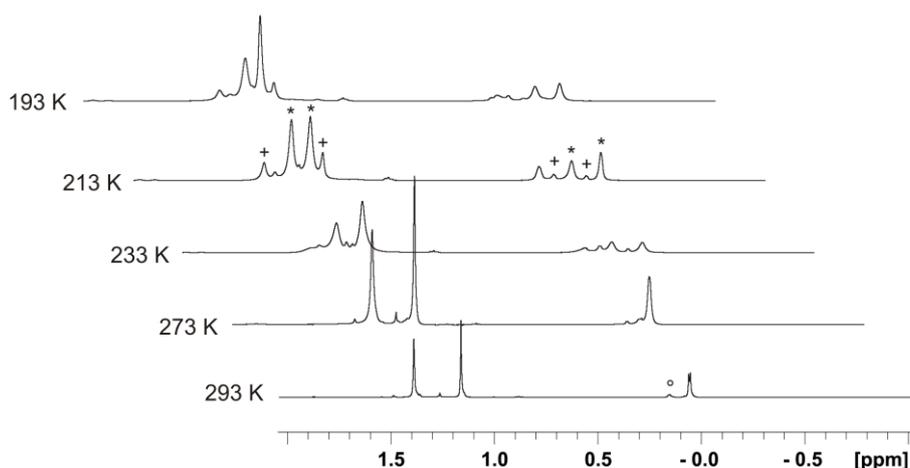
Figure S1. Methyl region of the ^{1}H NMR spectra of complex **1-a** recorded in CD_2Cl_2 at variable temperatures. Signals denoted with (*) and (+) are attributable to the methyl protons of tert-butyl (1.1 – 1.4 ppm) and amido groups (-0.3 – 0.1 ppm) of two different isomers. The complexity of the spectra in this area is also due to the presence of the proton signal of residual hexamethylsilazane (signal denoted with (°) at 293 K).
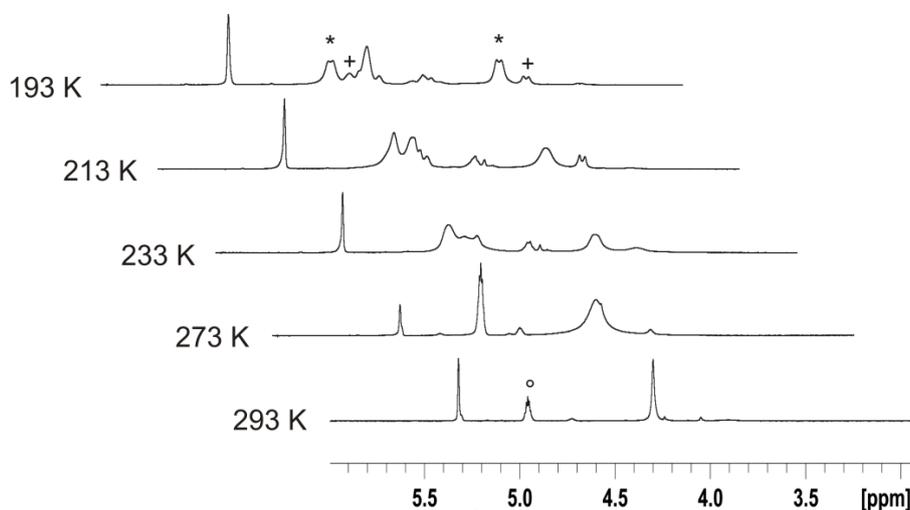
Figure S2. Methylene region of the ^{1}H NMR spectra of complex **1-a** recorded in CD_2Cl_2 at variable temperatures. Signals denoted with (*) and (+) are attributable to the AB patterns of the methylene protons of two different isomers. The complexity of the spectra in this area is also due to the presence of the proton signals of the amido groups (signal denoted with (°) at 293 K).
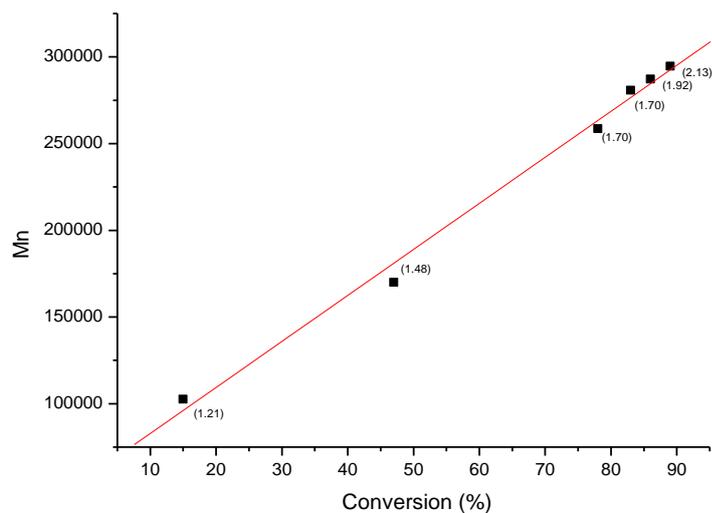
Figure S3. Plot of number-averaged molecular weights, Mn (KDa), and PDI values versus conversion for PCL produced by catalyst **1-b** at 25 °C.
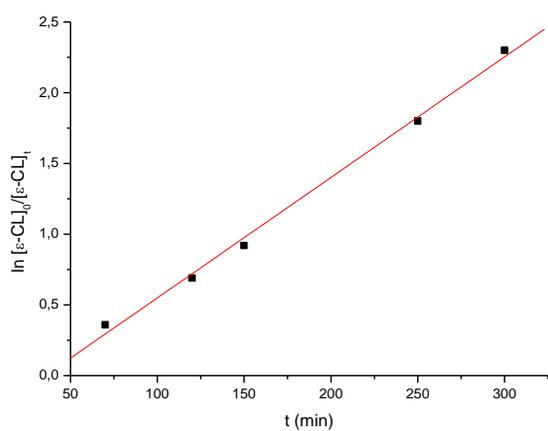
Figure S4. Pseudo-first-order kinetic plots for ROP of ε-caprolattone promoted by **1-a.** Pseudo-first-order rate constant is k_{app} = (8.52 ± 0.32) ×10^{-3} min^{-1} R = 0,99784 ([ε-CL]=3·10^{-3} M; [ε-CL]/[I]= 500; T = 298 K solvent= THF)
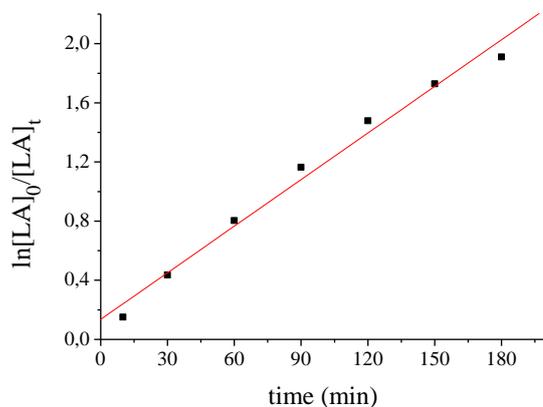
Figure S5. Pseudofirst-order kinetic plot for ROP of L-LA promoted by **1-a**. Pseudofirst-order rate costant is $(1.05 \pm 0.06) \times 10^{-2}$ min^{-1} R= 0.99385 ($[I]_0$ = 8.4 mM, $[L\text{-}LA]_0/[I]_0$ =100 toluene-d$_8$ as solvent; T = 313 K)
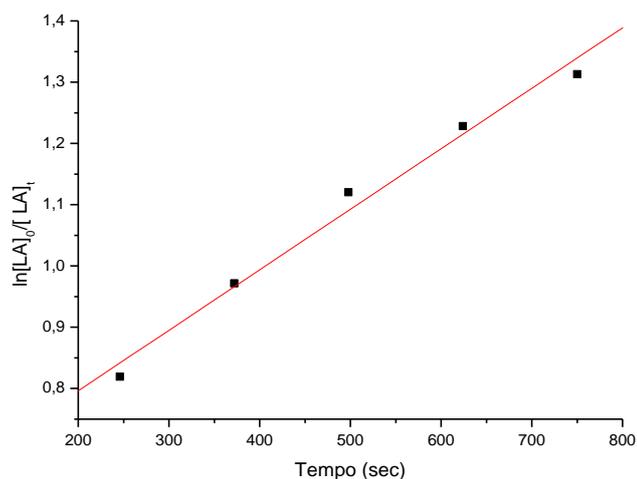
Figure S6. Pseudofirst-order kinetic plot for ROP of L-LA promoted by **1-b**. Pseudofirst-order rate costant is k_{app}: 9.87 $\pm$ 0.6) $\times 10^{-4}$ s^{-1} R = 0.99267 ($[I]_0$=8,4 mM; $[LA]_0/[I]_0$: =100; toluene-d$_8$ as solvent; T = 313 K)
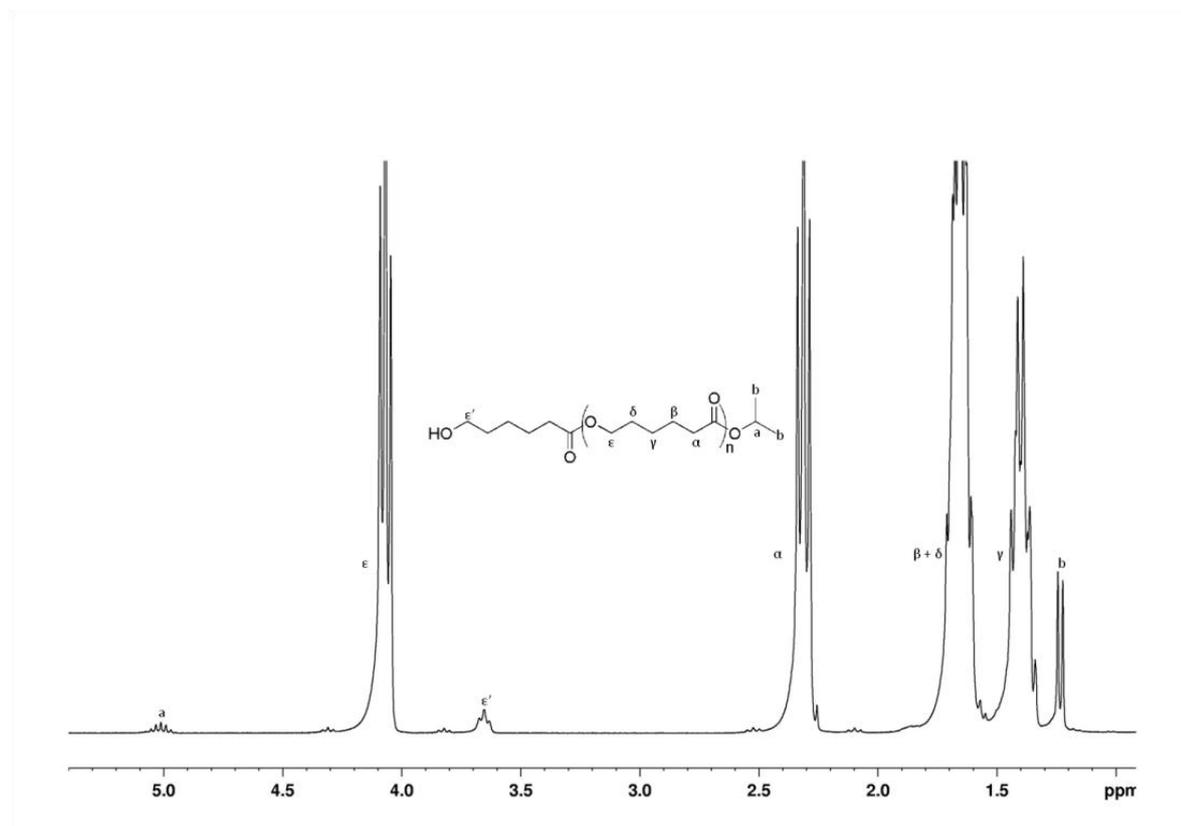
Figure S7. ^{1}H NMR spectrum (400 MHz, CDCl$_3$, 298 K) of oligomers of ε-CL obtained using **1-b**/2-propanol 1:10 as initiator after quenching with wet n-hexane (run 8, Table 2)
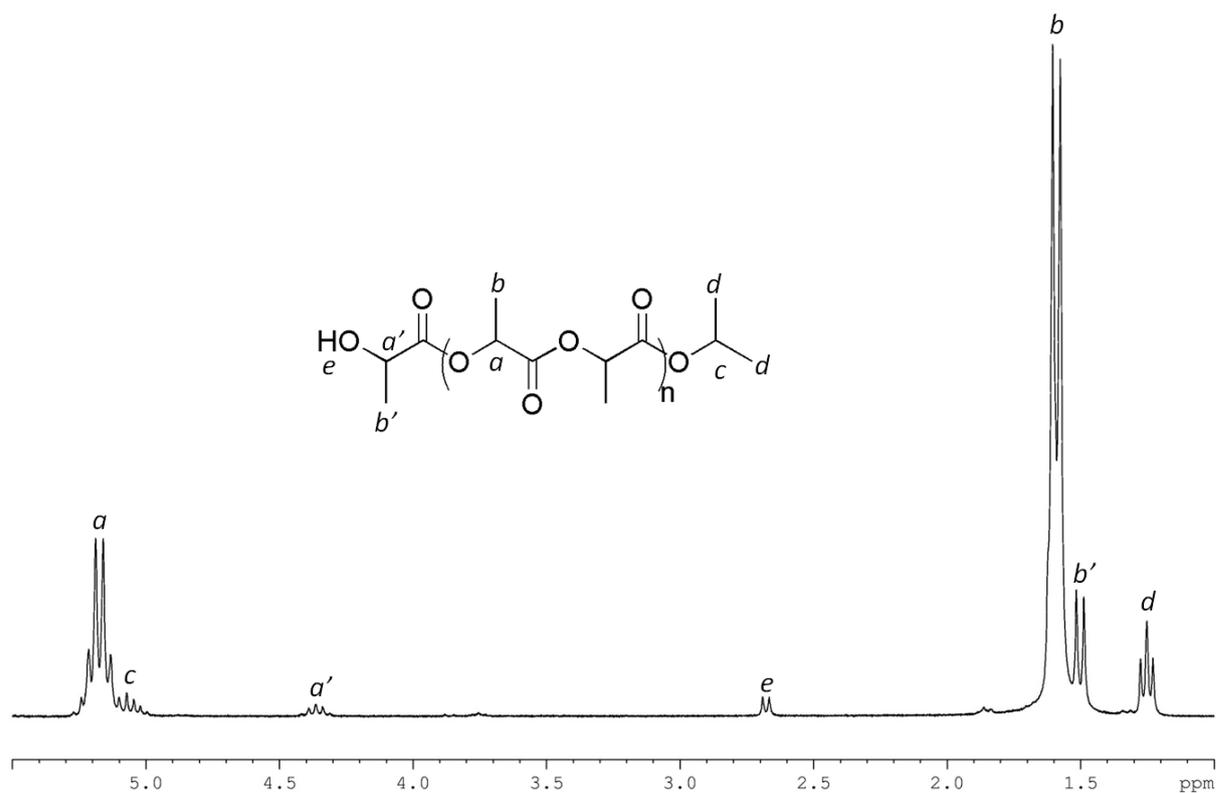
Figure S8. ^{1}H NMR spectrum (400 MHz, CDCl$_3$, 298 K) of oligomers of L-lactide obtained using **1-b**/2-propanol = 1:10 as initiator after quenching with wet *n*-hexane. Conditions: [L-LA]$_0$/[**1-b**]$_0$ = 20, Toluene 2 mL, T=25 °C.

$$A_n = 1.01 + 2n(72.06) + 59.09 + 22.99 \quad a_n = 1.01 + (2n+1)(72.06) + 59.09 + 22.99$$

$$B_n = 1.01 + 2n(72.06) + 17.01 + 1.01 \quad b_n = 1.01 + (2n+1)(72.06) + 17.01 + 1.01$$
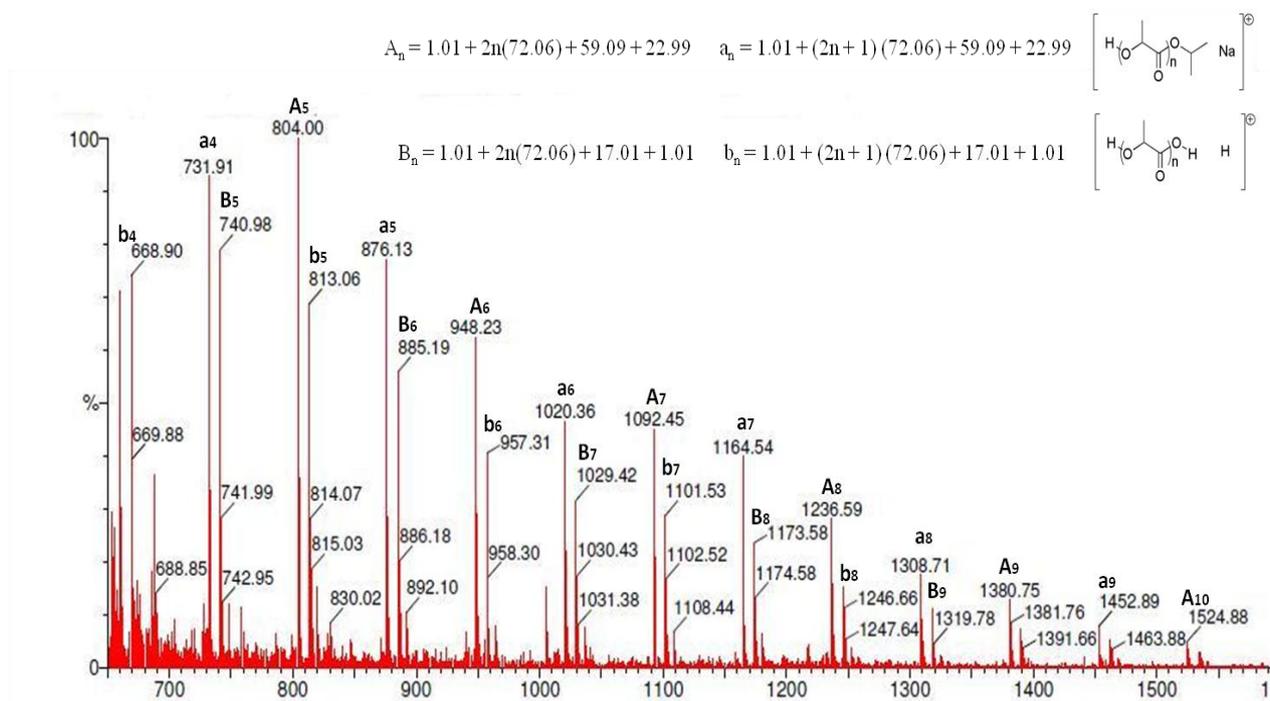
Figure S9. ESI-MS spectrum of oligomers of L-lactide using **1-b** as initiator. Capital letters have been used to denote the oligomers with complete monomer units with isopropoxide and hydroxide end groups (A_n and B_n respectively). Lowercase letters denoted oligomers with odd half monomer units.
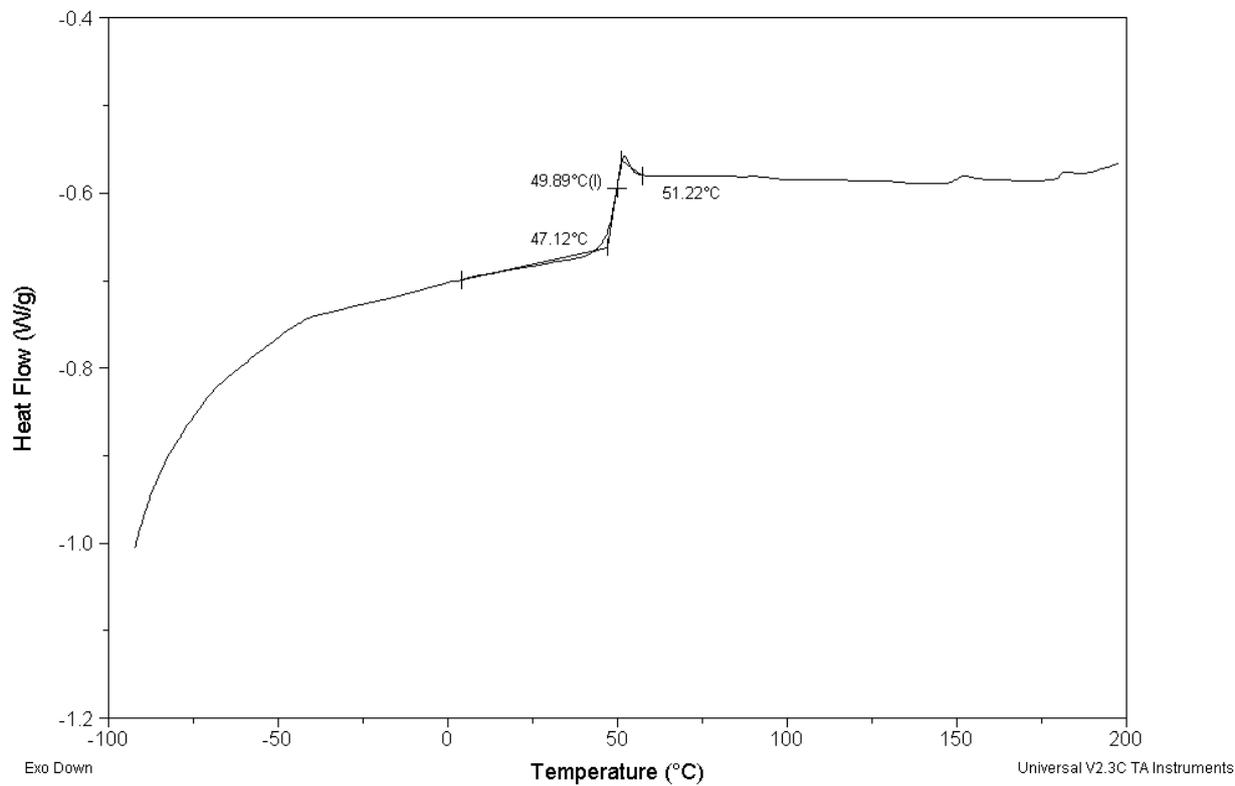
Figure S10. Thermal analysis of heterotactic PLA obtained in run 16 of Table 3.