Supporting Information

Ring-Opening Polymerization of Cyclic Esters by Phenoxy-Thioether Complexes Derived from Biocompatible Metals

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Table of contents

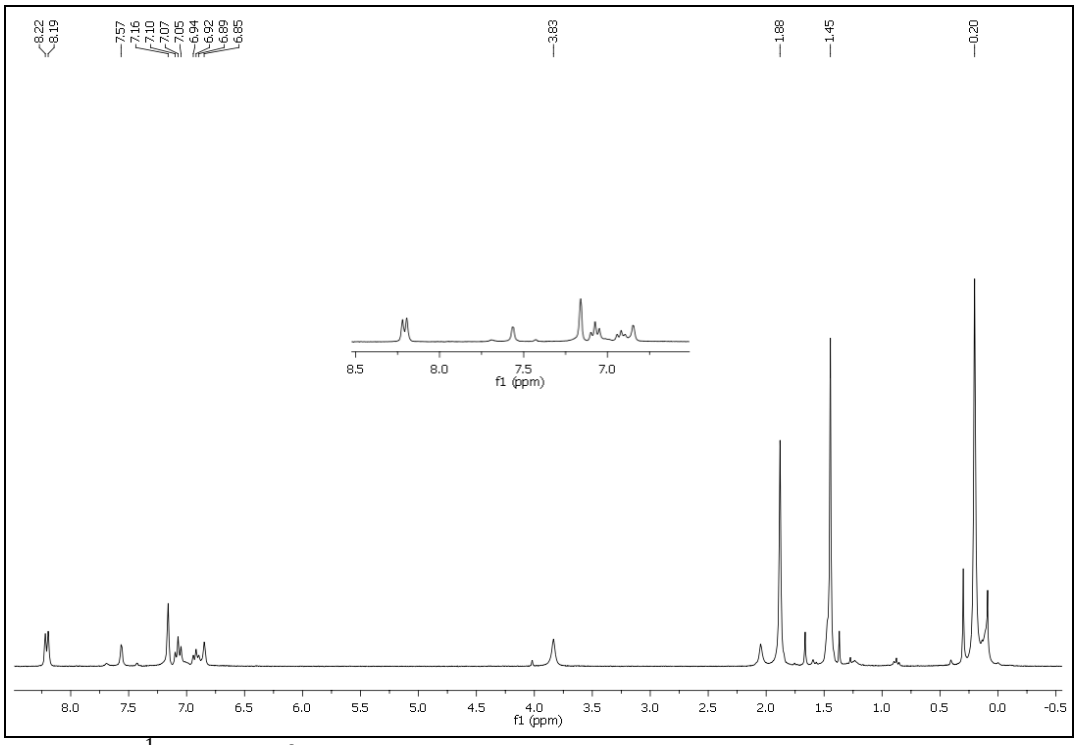

Figure S1. ^{1}H NMR of complex **1** (300 MHz, C_6D_6, 298 K).

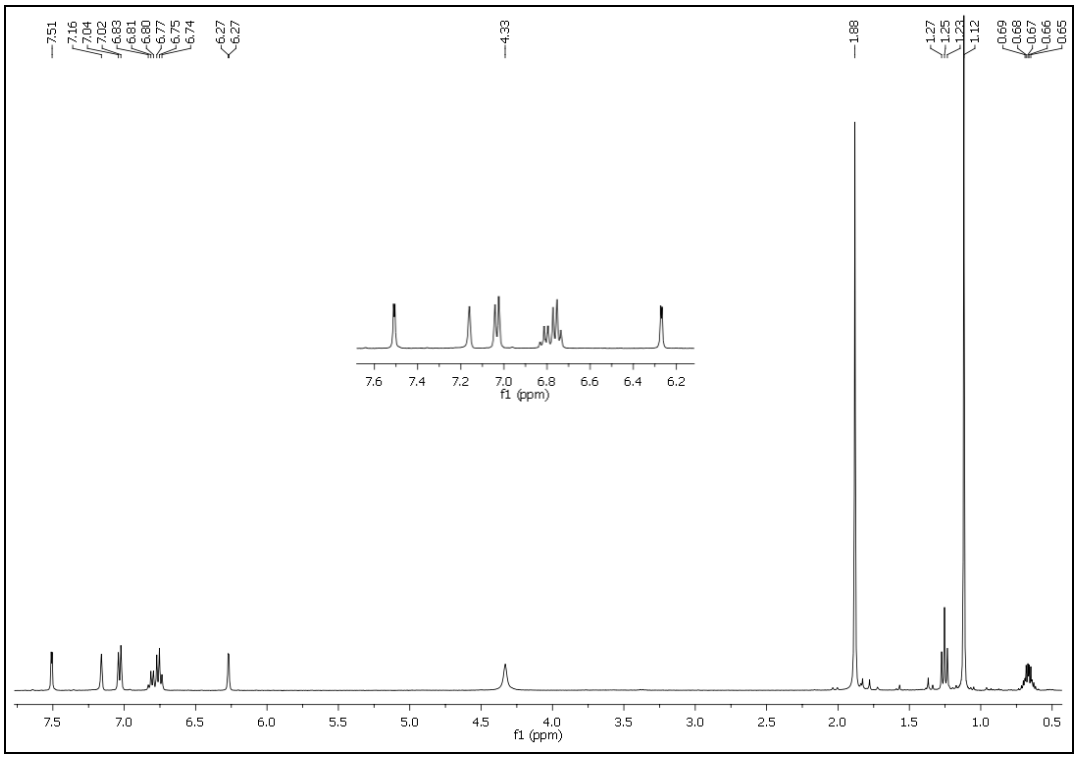

Figure S2. ^{1}H NMR of complex **2** (400 MHz, C_6D_6, 298 K).

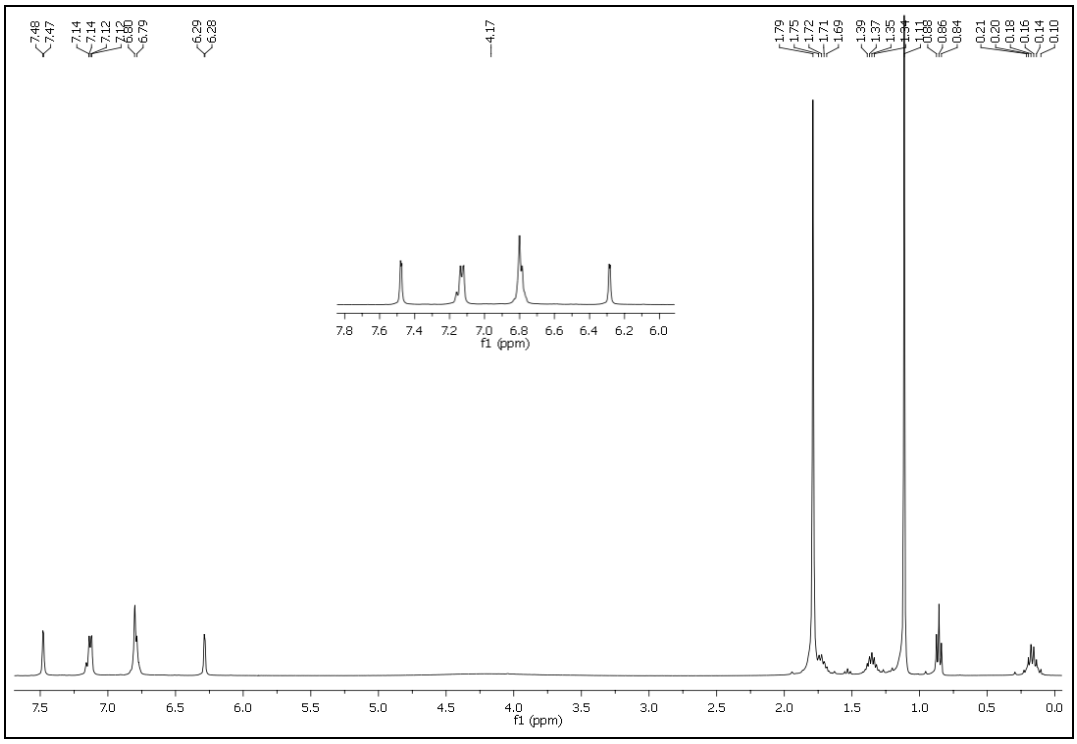

Figure S3. ^{1}H NMR of complex **3** (400 MHz, C_6D_6, 298 K).

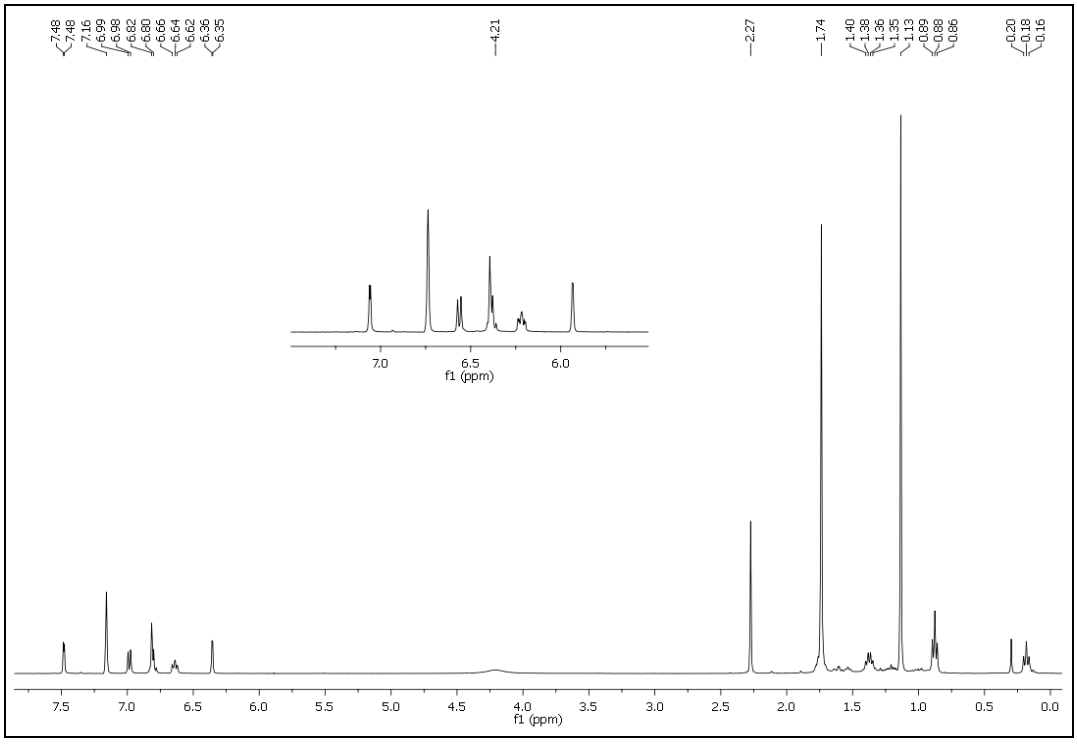

Figure S4. ^{1}H NMR of complex **4** (400 MHz, C_6D_6, 298 K).

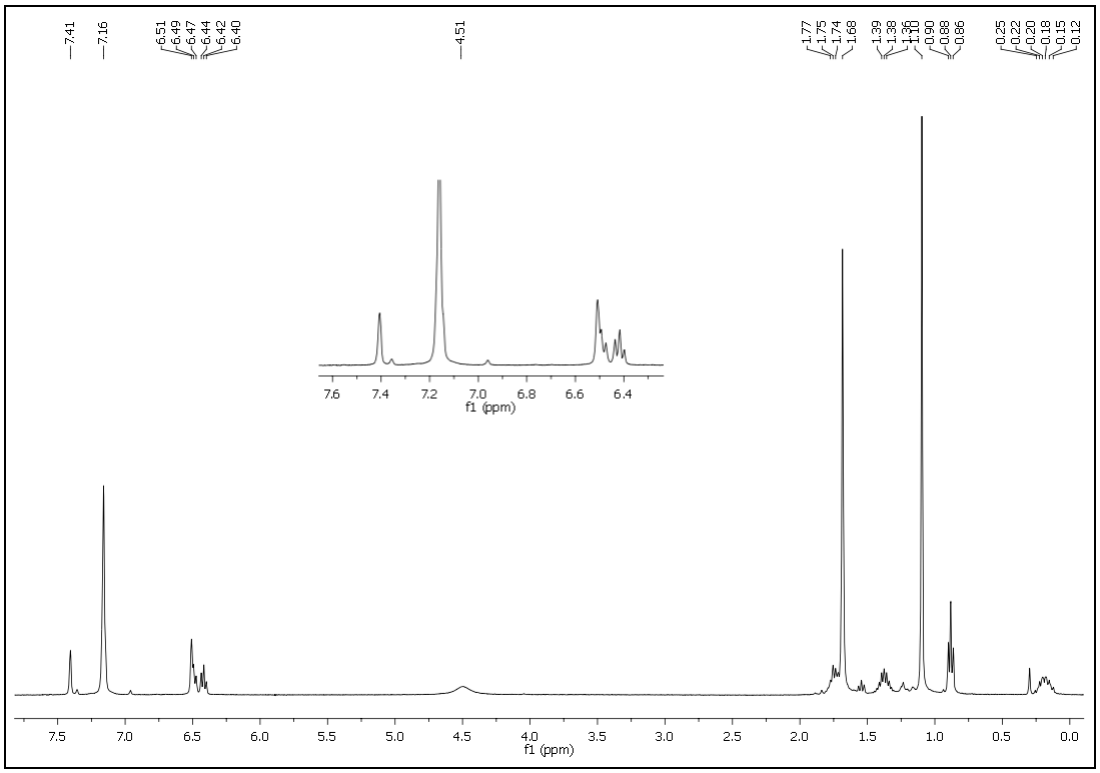

Figure S5. ^{1}H NMR of complex **5** (300 MHz, C_6D_6, 298 K).

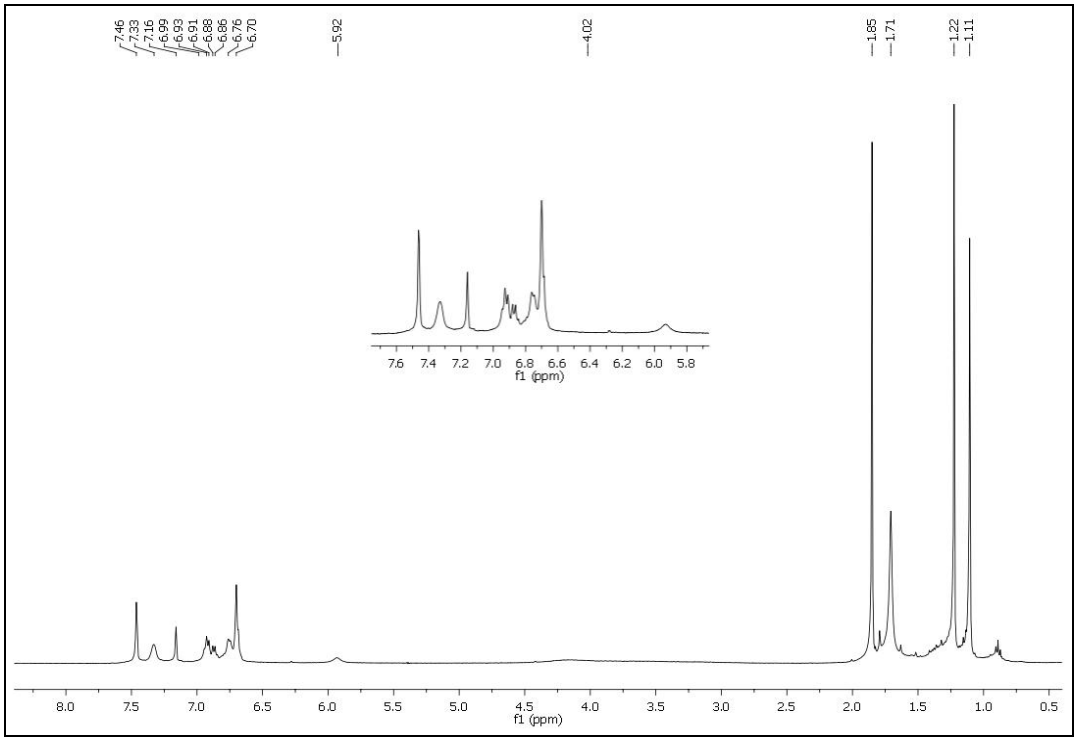

Figure S6. ^{1}H NMR of complex **6** (400 MHz, C_6D_6, 298 K).

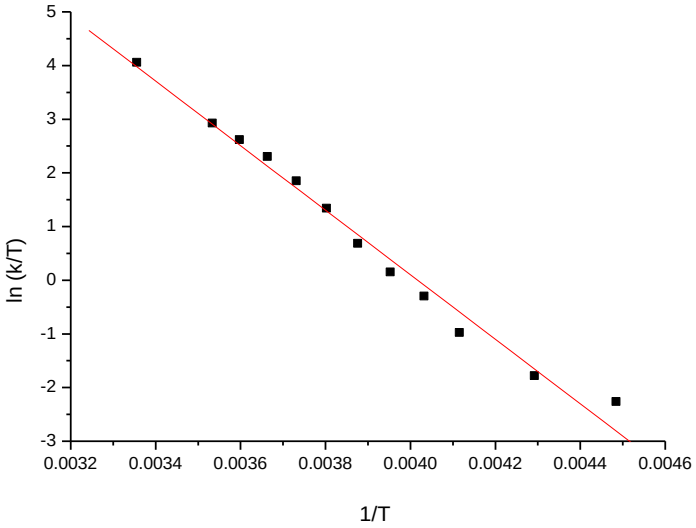

Figure S7 Eyring plot for the temperature-dependent fluxional process for complex **2**.

A = 24.152 (0.918)
B = -6012.531 (236.540)
R = -0.989 SD = 0.2555
$\Delta H^{\#}$ = 11.95 ± 0.47 kcal mol^{-1}
$\Delta S^{\#}$= 0.78 ± 1.82 cal mol^{-1} K^{-1}
$\Delta G^{\#}$ = 11.72 ± 0.07 kcal mol^{-1}

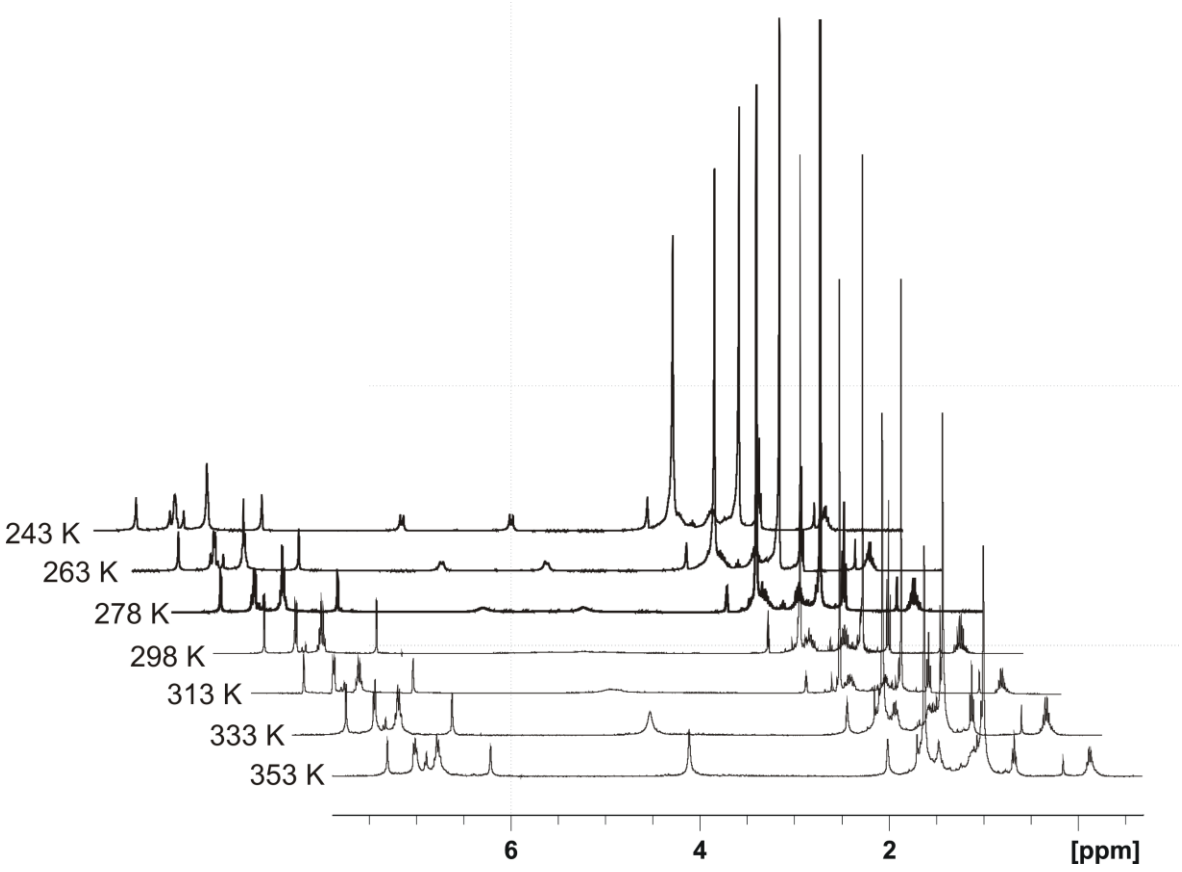

Figure S8. Variable-temperature ^{1}H NMR spectra of **3** in toluene-d_8.

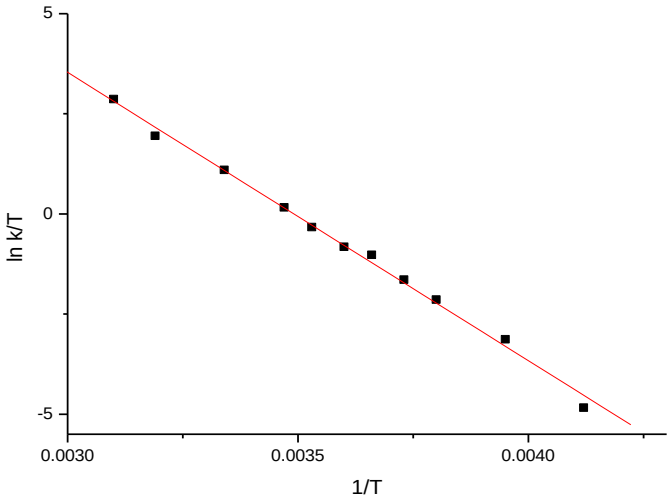

Figure S9. Eyring plot for the temperature-dependent fluxional process for complex **3**.

A = 25.14025 (0.59292)
B = -7201.26068 (164.60229)
R = -0.99766 SD = 0.16126
$\Delta H^{\ddagger}$= 13.49 ± 0.07 kcal mol^{-1}
$\Delta S^{\ddagger}$= 2.74 ± 1.18 cal mol^{-1} K^{-1}cal/mol K
$\Delta G^{\ddagger}$= 14.31 ± 0.33 kcal mol^{-1}

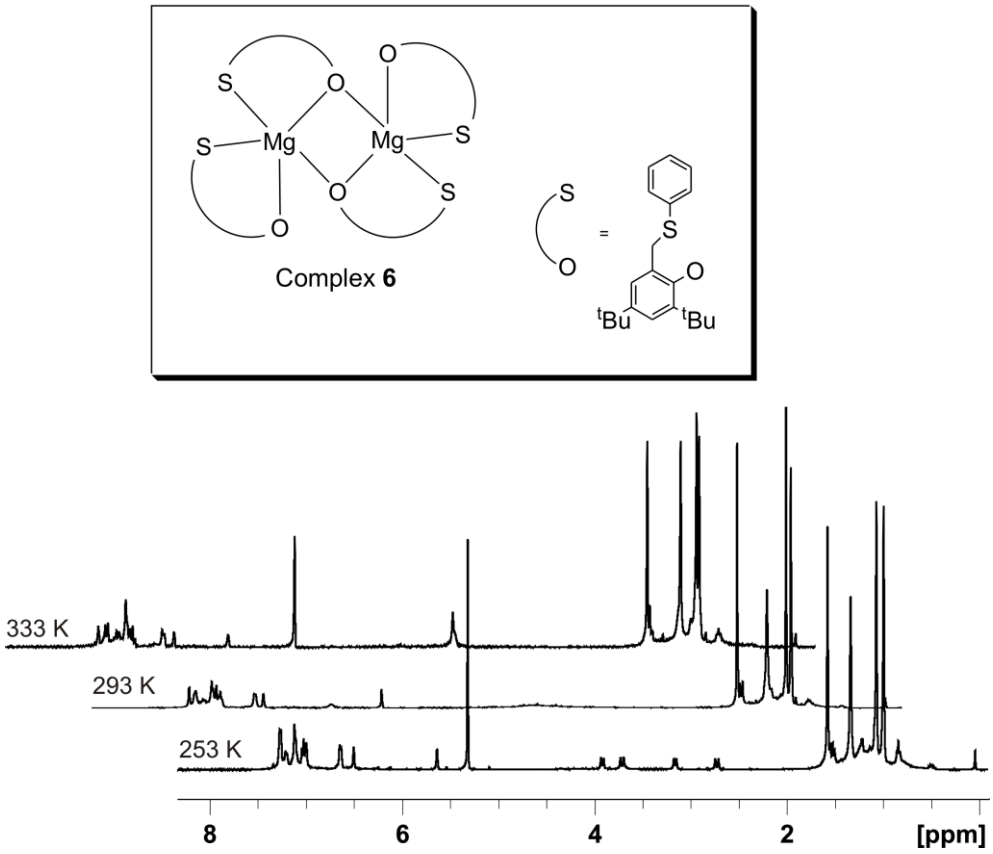

Figure S10. Variable-temperature ^{1}H NMR spectra of homoleptic complex **6** in CD_2Cl_2.

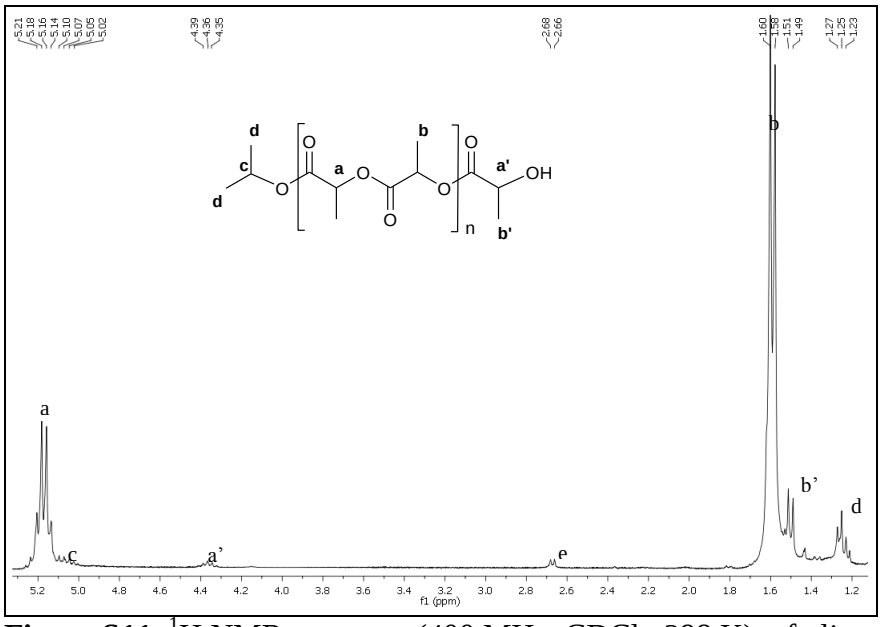

Figure S11. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of oligomers of L-lactide obtained using **3**/iPrOH = 1. Reaction conditions: $[L\text{-}LA]_0/[\mathbf{3}]_0 = 20$, T= 25°C, t=5h.

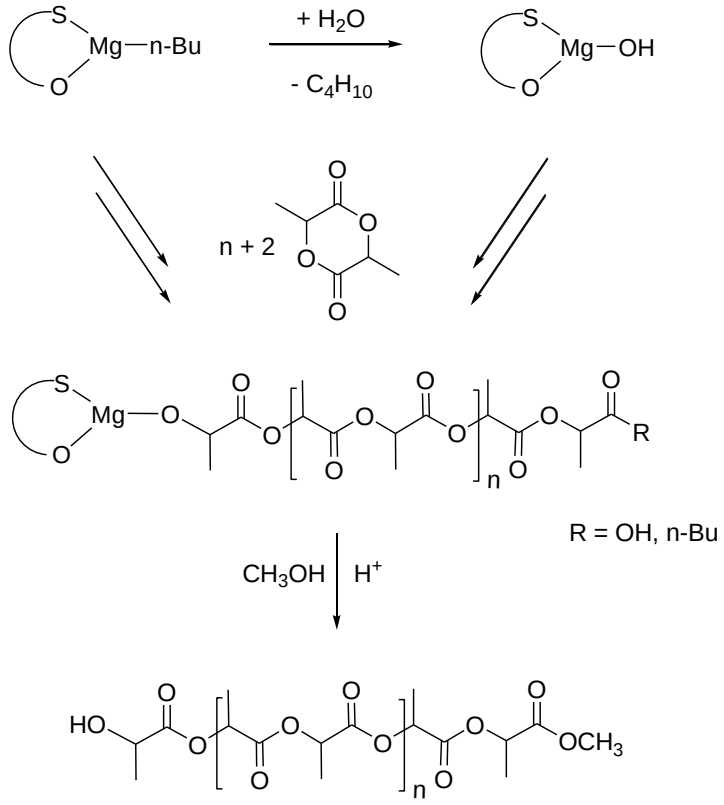

Figure S12. Plausible mechanism for the polymerization of L-LA by **3** in the absence of alcohol.

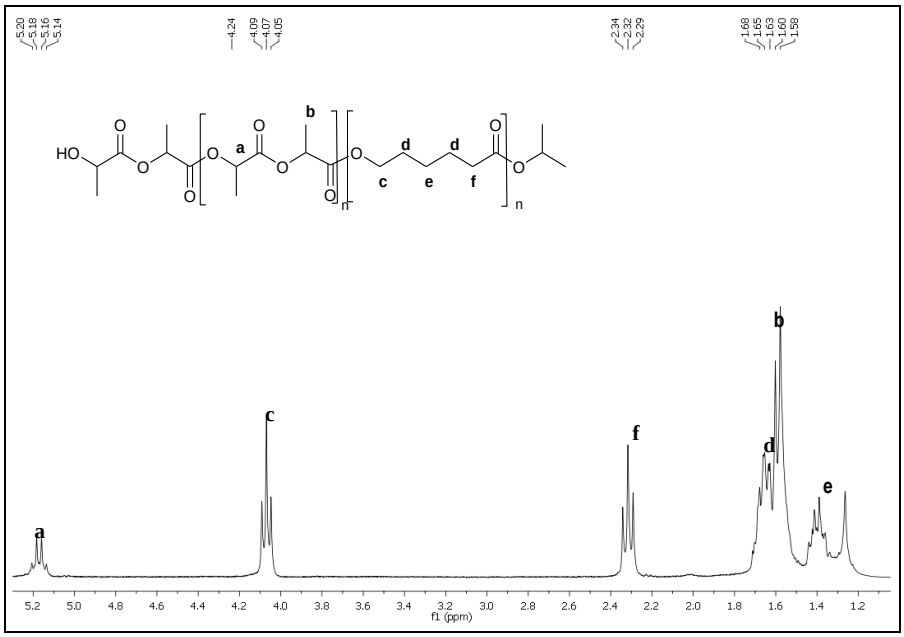

Figure S13. ^{1}H NMR spectrum of the CL-LA block copolymer

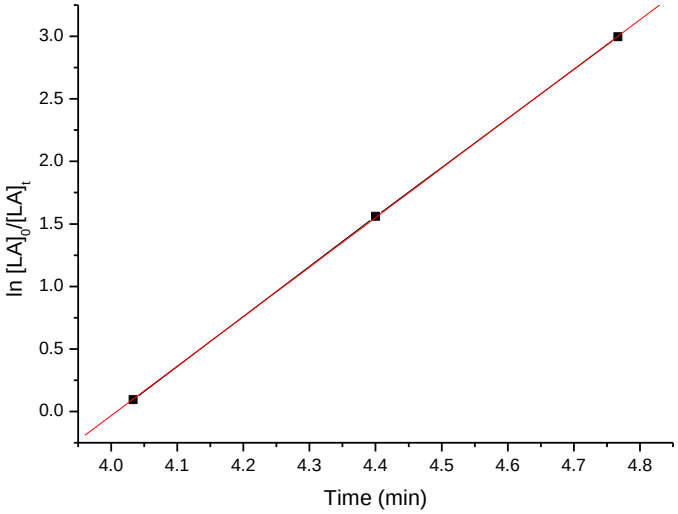

Figure S14. Enlargement of the linear part of graphic in Figure 6 in the MS. Pseudofirst-order rate costant is k_{app}= 3.96 ± 0.02 min^{-1} (R = 0.9998) ([**3**] = 9.1 mM; [LA]/[**3**]/[iPrOH] = 100:1:1; toluene-d_8 as solvent; T = 343 K)

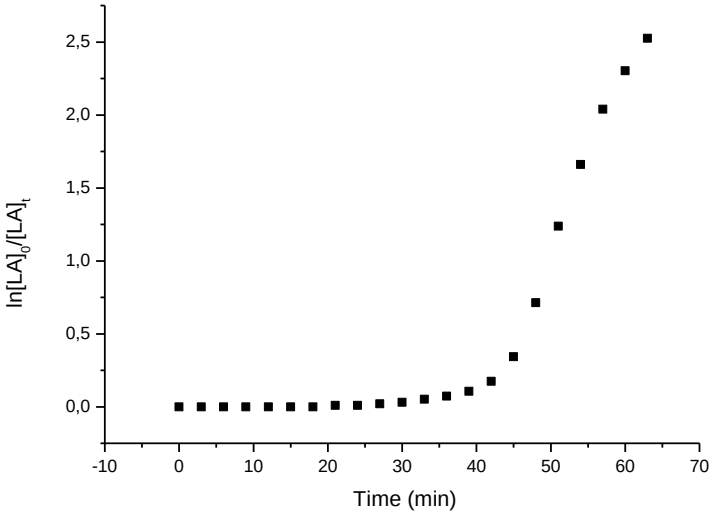

Figure S15. Semilogarithmic plot of LA conversion with time in toluene-d_8 at 323 K using **3** as initiator ([**3**] = 9.1 mM; [LA]/[**3**]/[iPrOH] = 50:1:1)

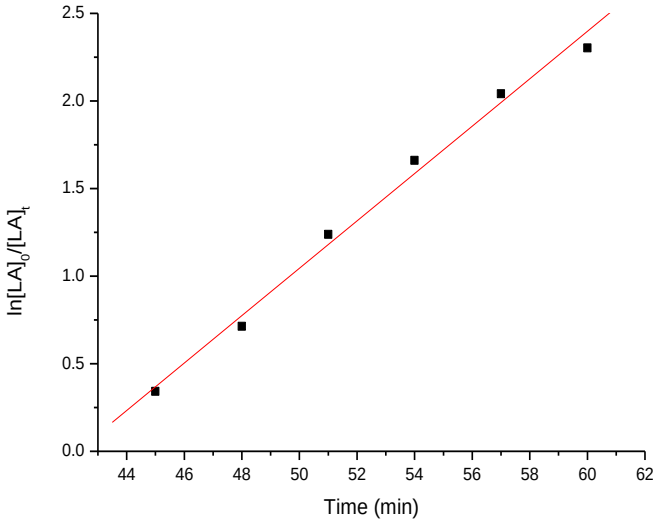

Figure S16. Enlargement of the linear part of graphic in Figure S14. Pseudofirst-order rate costant is k_{app} = 1.35 ± 0.06 × 10^{-1} min^{-1} (R = 0.996) ([**3**]=9.1 mM; [LA]/[**3**]/[iPrOH] = 50:1:1; toluene-d_8 as solvent; T = 323 K)