Supporting Information

Bimetallic salen aluminum complexes: cooperation between reactive centers in the ring-opening polymerization of lactide and epoxides.

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Table of contents

Synthesis of the ligand precursor (L1): A solution of 1,3-propanediamine (0.28 gram, 3.78 mmol) in methanol (20 mL) was added to a solution of 3,5-di-tert-butylsalicylaldehyde (1.77 gram, 7.56 mmol) in methanol (20 mL) and the reaction mixture was stirred at room temperature until a yellow solid precipitated. The solid was collected by filtration, washed with cold methanol and dried yielding the ligand precursor quantitatively.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.39 (s, 1H, NCH), 7.38 (d, 1H, *J* = 2.0 Hz, ArH), 7.09 (d, 1H, *J* = 2.0 Hz, ArH), 3.70 (t, 2H, *J* = 6.4 Hz, CH_2), 2.12 (t, 1H, *J* = 6.4 Hz, CH_2), 1.45 (s, 9H, CH_3), 1.30 (s, 9H, CH_3).

^{13}C NMR ($CDCl_3$, 100.67 MHz): δ = 167.2 (CN), 158.8 (CO), 140.8 (C), 137.4 (C), 127.6 (CH), 126.5 (CH), 118.5 (C), 57.4 (NCH_2), 35.7 (CH_2), 34.8 (C), 32.4 (C), 32.2 (CH_3), 30.1 (CH_3).

Synthesis of the ligand precursor (L2): was synthesized quantitatively as on yellow solid in analogy to $Lig^{n=3}H_2$ by reacting 1,5-pentanediamine (0.31 gram, 3.04 mmol) and 3,5-di-tert-butylsalicylaldehyde (1.42 gram, 6.08 mmol).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.34 (s, 1H, NCH), 7.37 (d, 1H, *J* = 2.4 Hz, ArH), 7.08 (d, 1H, *J* = 2.4 Hz, ArH), 3.58 (t, 2H, *J* = 6.8 Hz, CH_2), 1.75 (m, 2H, CH_2), 1.49 (m, 1H, CH_2), 1.44 (s, 9H, CH_3), 1.30 (s, 9H, CH_3).

^{13}C NMR ($CDCl_3$, 100.67 MHz): δ = 165.8 (CN), 158.3 (CO), 139.9 (C), 136.7 (C), 126.7 (CH), 125.8 (CH), 117.9 (C), 59.5 (NCH_2), 35.1 (CH_2), 34.2 (C), 31.6 (CH_3), 30.8 (C), 29.5 (CH_3), 24.9 (CH_2).

Synthesis of the ligand precursor (L3): was synthesized quantitatively as on yellow solid in analogy to $Lig^{n=3}H_2$ by reacting 1,12-dodecanediamine (0.79 gram, 3.95 mmol) and 3,5-di-tert-butylsalicylaldehyde (1.84 gram, 7.90 mmol).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.32 (s, 1H, NCH), 7.36 (d, 1H, *J* = 2.3 Hz, ArH), 7.07 (d, 1H, *J* = 2.3 Hz, ArH), 3.55 (t, 2H, *J* = 6.9 Hz, CH_2), 1.68 (m, 2H, CH_2), 1.44 (s, 9H, CH_3), 1.34 (m, 2H, CH_2), 1.30 (s, 9H, CH_3), 1.27 (m, 6H, CH_2).

^{13}C NMR ($CDCl_3$, 100.67 MHz): δ = 165.5 (CN), 158.4 (CO), 139.9 (C), 136.7 (C), 126.7 (CH), 125.7 (CH), 118.0 (C), 59.6 (NCH_2), 35.1 (CH_2), 34.2 (C), 31.6 (CH_3), 31.0 (C), 29.7 (CH_2), 29.6 (CH_2), 29.5 (CH_3), 29.4 (CH_2), 27.2 (CH_2).

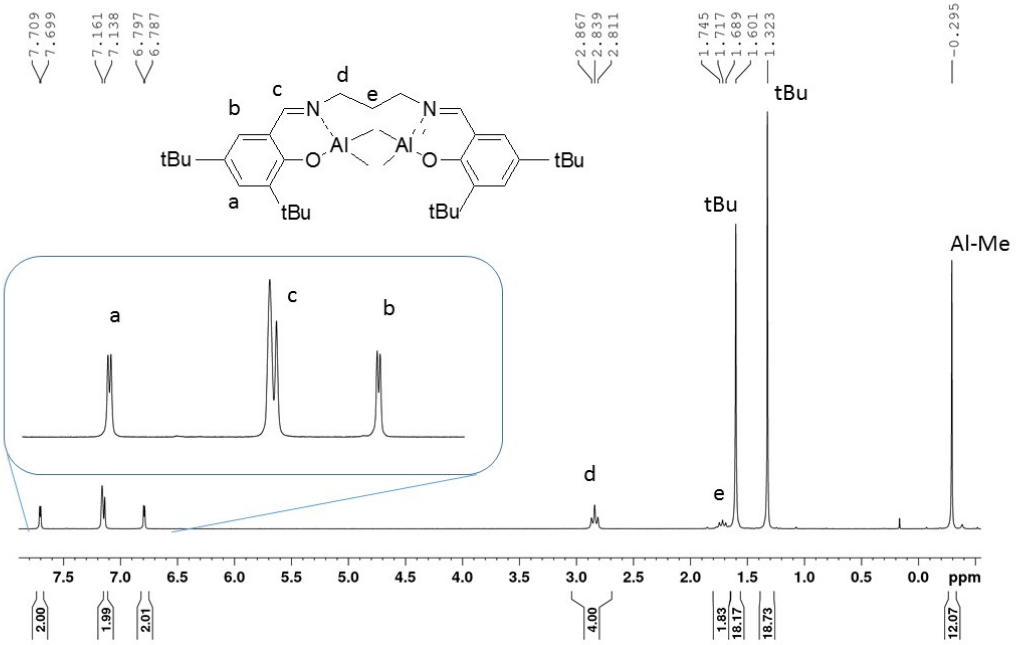

Figure S1.^{1}H NMR of complex **1** (600 MHz, C_6D_6, 298 K).

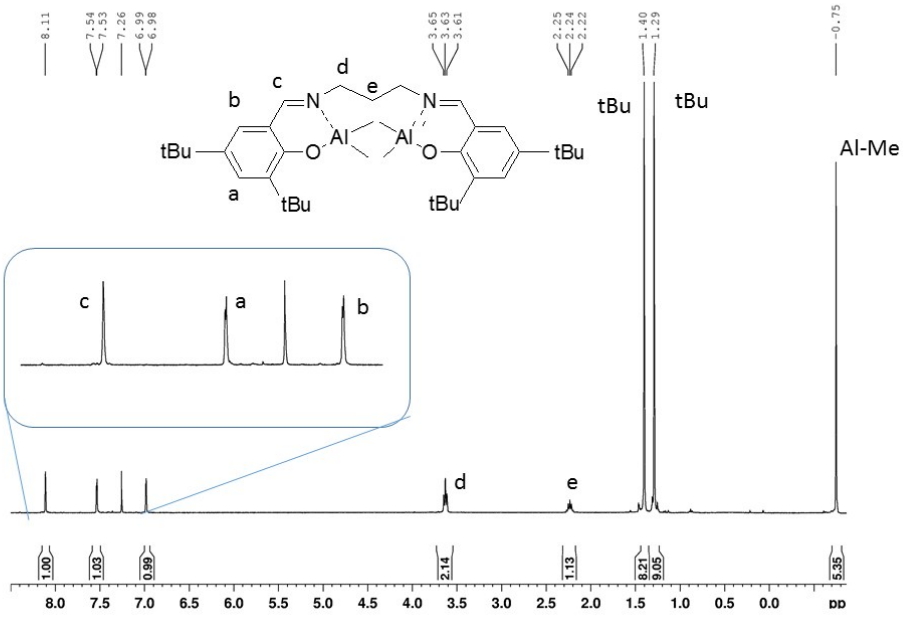

Figure S2.[1]H NMR of complex **1** (400 MHz, $CDCl_3$, 298 K).

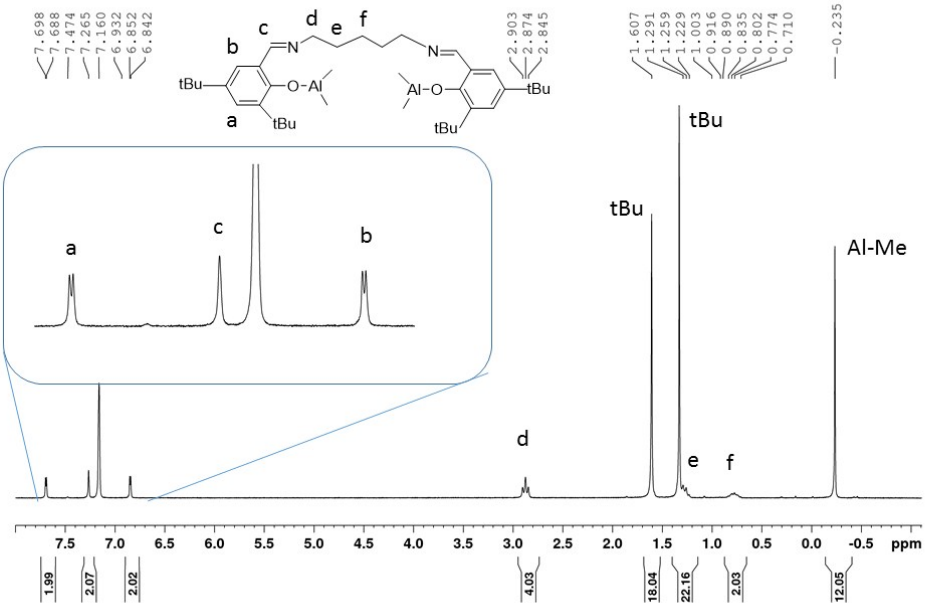

Figure S3.[1]H NMR of complex **2** (250 MHz, C_6D_6, 298 K).

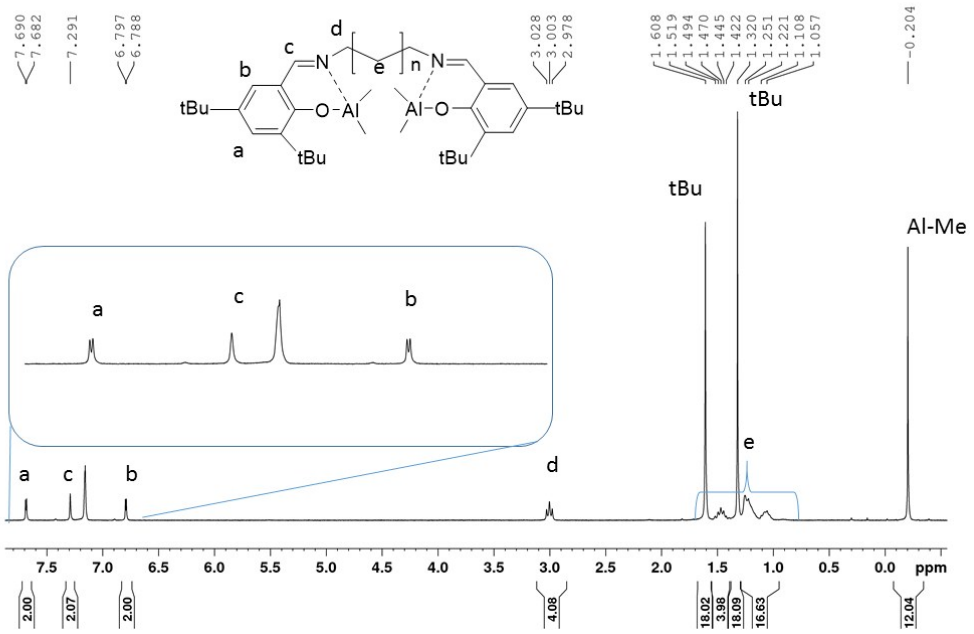

Figure S4.[1]H NMR of complex **3** (300 MHz, C_6D_6, 298 K).

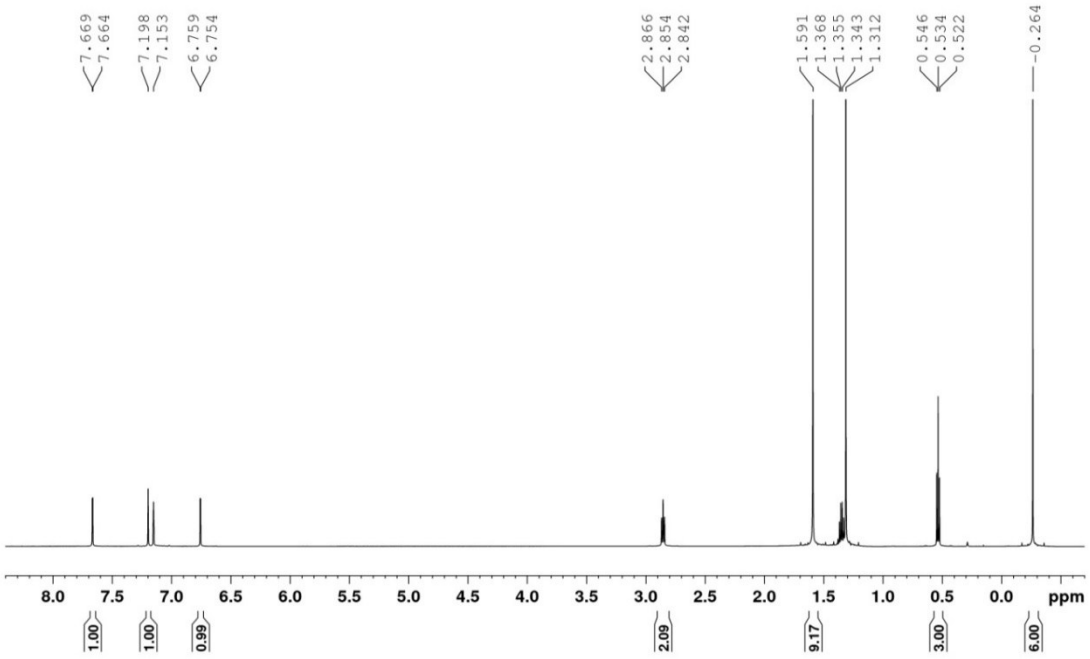

Figure S5. [1]H NMR spectrum of complex **4** (400 MHz, C_6D_6, 298 K).

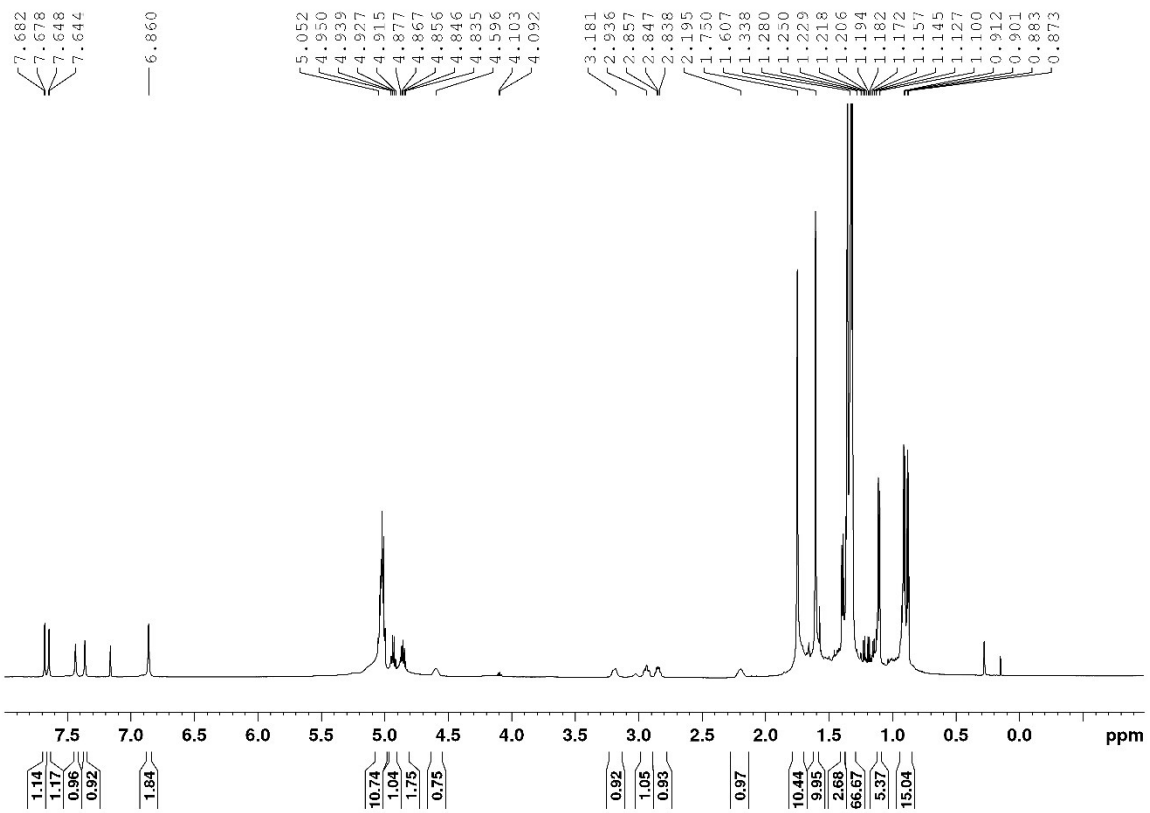

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Figure S6. ^{1}H NMR spectrum of the propagating species after the addition of 5 equivalents of LA (600 MHz, C_6D_6, 298 K).

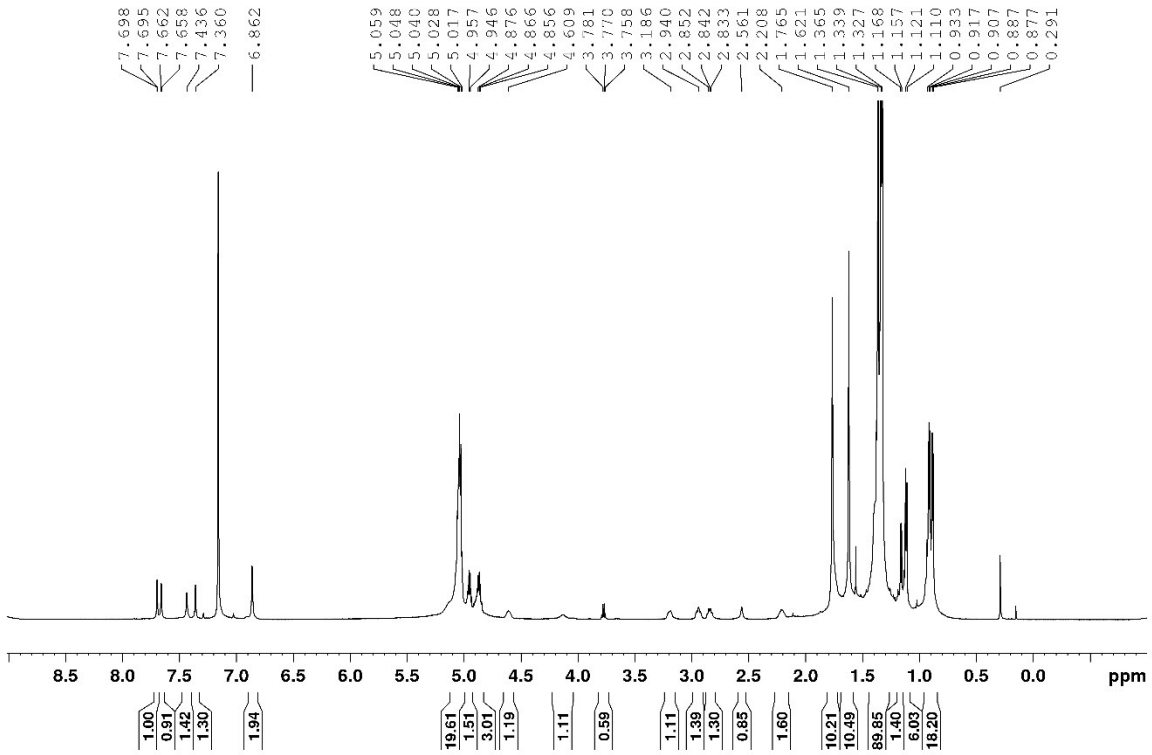

Figure S7. ^{1}H NMR spectrum of the propagating species after the addition of 10 equivalents of LA (600 MHz, C_6D_6, 298 K).

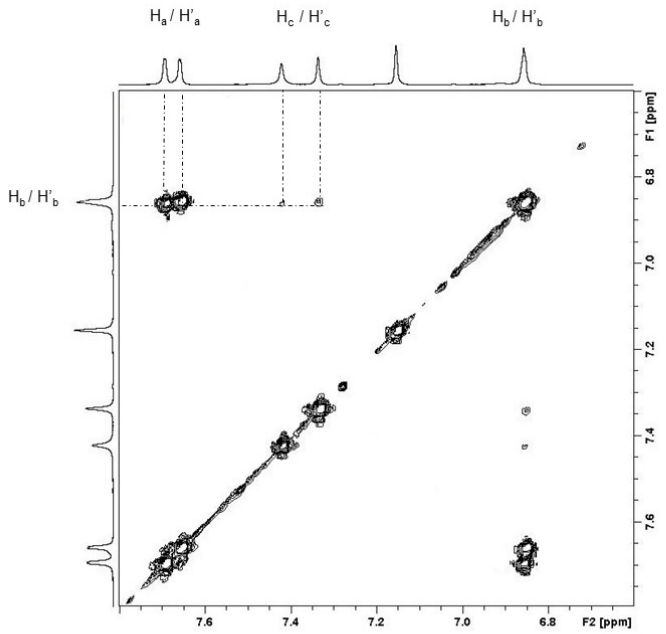

Figure S8. ^{1}H-^{1}H COSY of the propagating species formed by complex **1** (600 MHz, C_6D_6, 298 K).

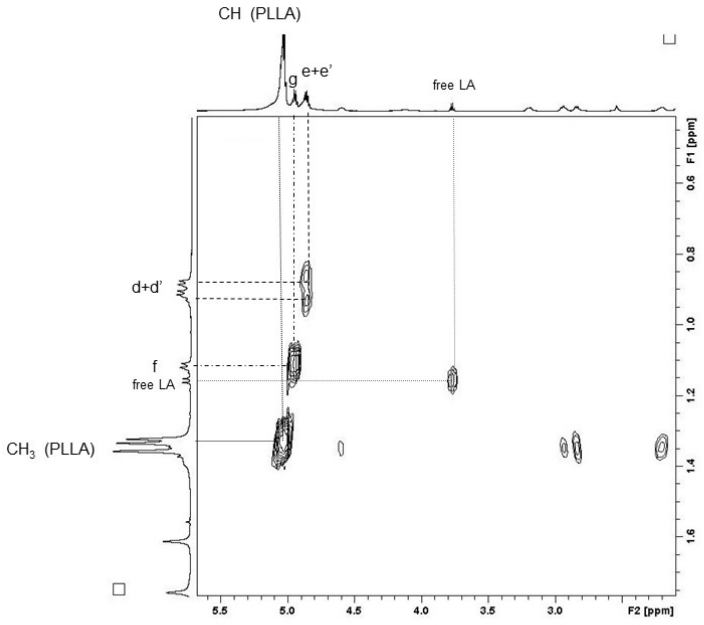

Figure S9. ^{1}H-^{1}H COSY of the propagating species formed by complex **1** (600 MHz, C_6D_6, 298 K).

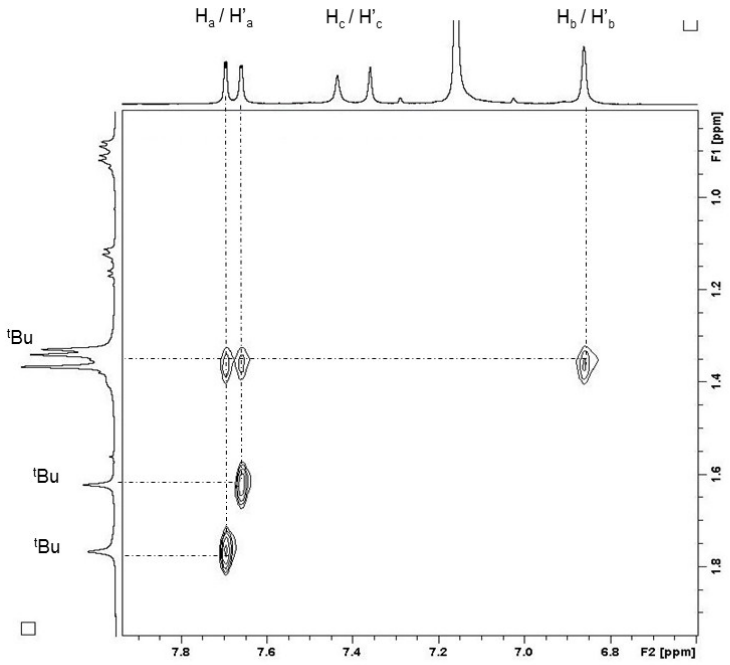

Figure S10. ^{1}H-^{1}H NOESY of the propagating species (600 MHz, C_6D_6, 298 K).

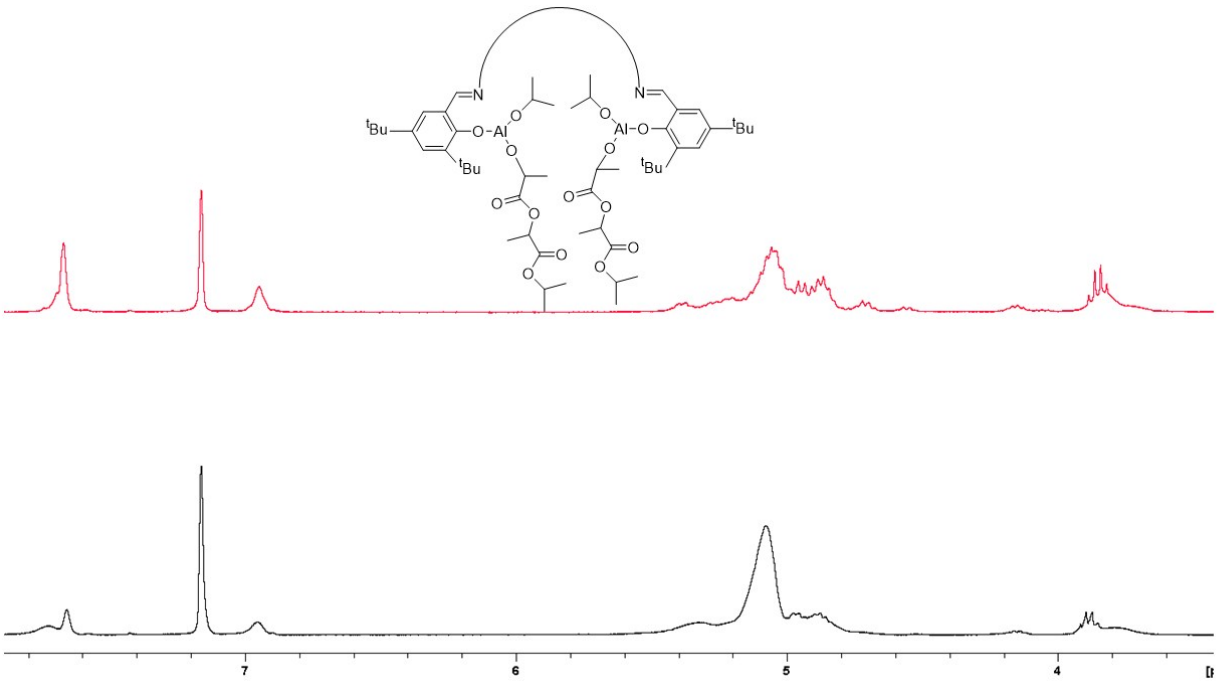

Figure S11. ^{1}H NMR spectra of the propagating species formed by complexes **2** (black) and **3** (red) after the addition of 4 equivalents of ^{i}PrOH and 10 equivalents of LA (300 MHz, C_6D_6, 298 K).

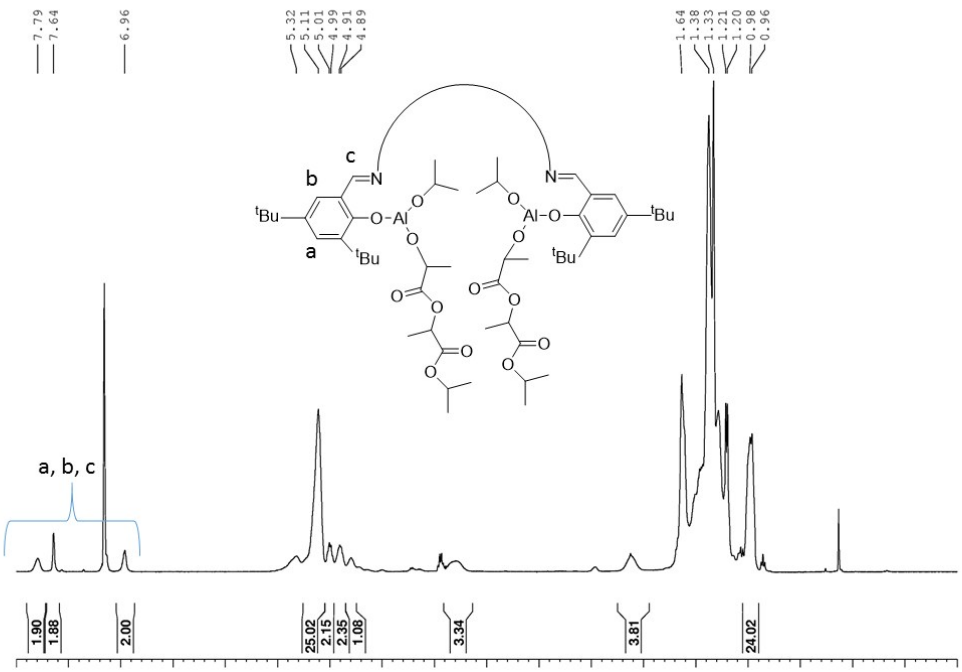

Figure S12. ^{1}H NMR spectrum of the propagating species formed by complex **2** at 70 °C (300 MHz, C_6D_6, 343 K).

Table S1. Tetrad probabilities based on Bernoullian Statistic (Th) for a P_m of 0.82 and experimental values (Exp) as obtained by NMR analysis of PLA sample obtained by 1.

Tetrad	**Formula**	**Exp**	**Th**
[*mmm*]	$P_m^2+P_rP_m/2$	0.75	0.75
[*mmr*]	$P_rP_m/2$	0.08	0.07
[*rmm*]	$P_rP_m/2$	0.07	0.07
[*rmr*]	$P_r^2/2$	0.02	0.02
[*mrm*]	$(P_r^2+P_rP_m)/2$	0.08	0.09

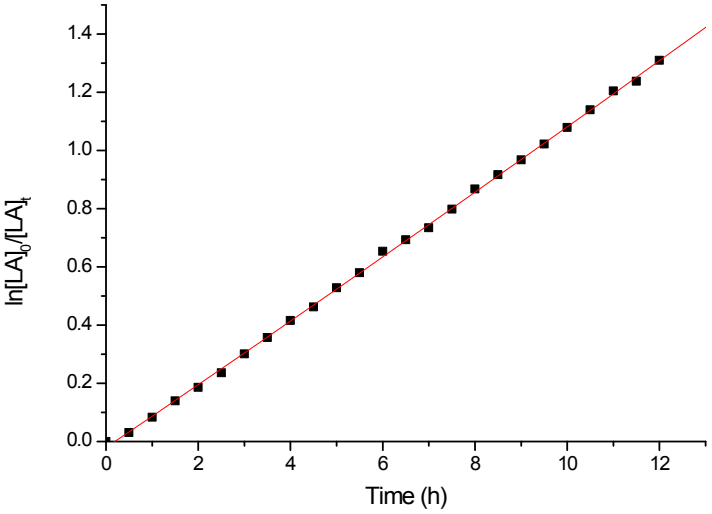

Figure S13 . Kinetic plot for ROP of *rac*-LA promoted by **3**. The concentrations were determined by ^{1}H NMR spectroscopy, $[LA]_0$ is the initial concentration of *rac*-LA and $[LA]_t$ the concentration at time *t*. The pseudofirst-order rate constant k_{app}=*0.111* h^{-1} R = 0.9975. Reaction conditions: [**3**]= 0.01M; [LA]/[**3**] = 100; T=373 K; toluene-d_8 as solvent.

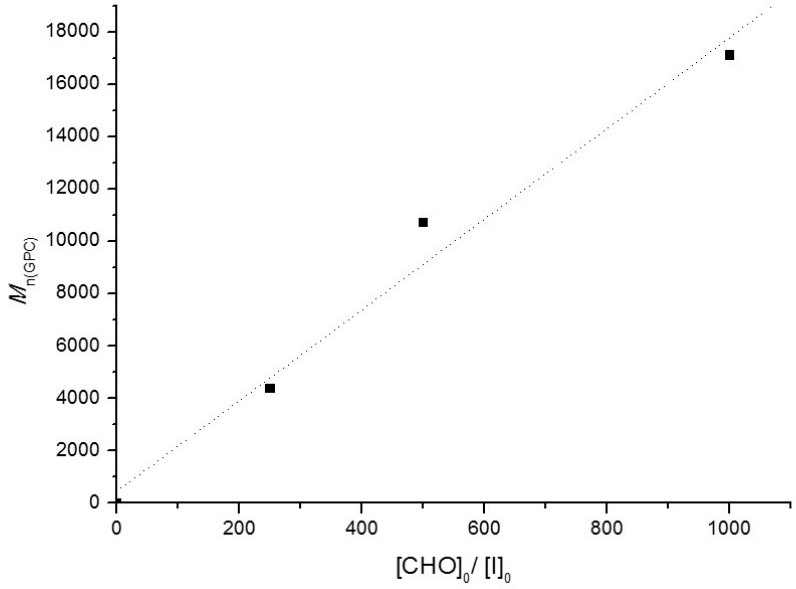

Figure S14. Linear relationship between M_n and the initial mole ratio $[CHO]_0/[I]_0$

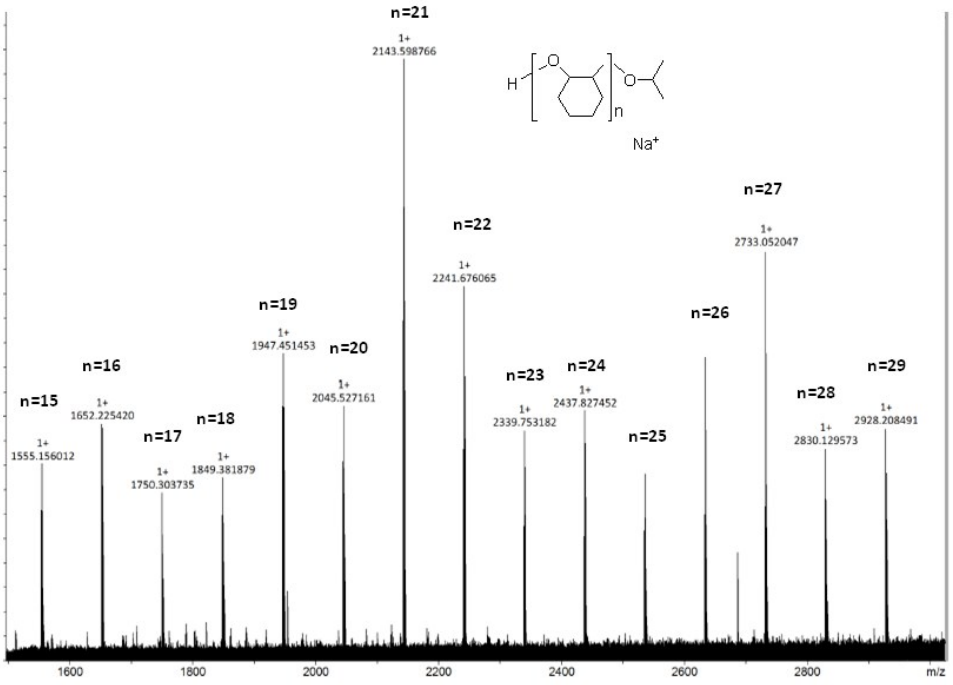

Figure S15. MALDI-TOF spectrum of oligomers of PCHO obtained in run 6 of Table 2

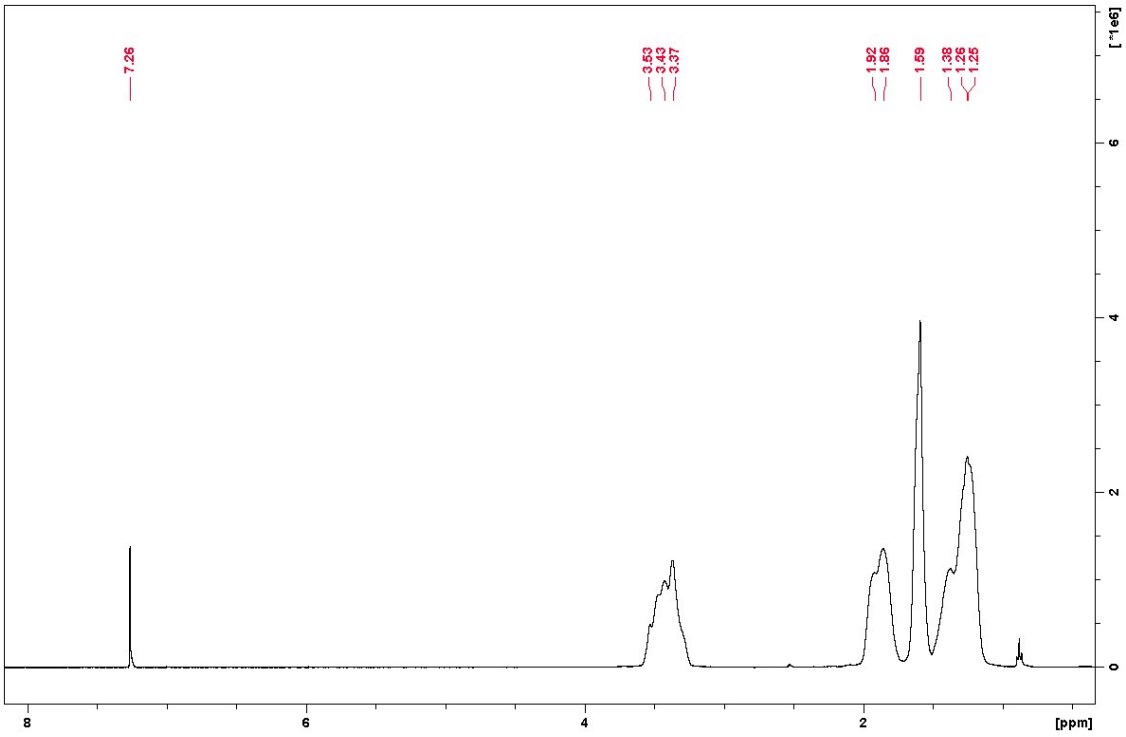

Figure S16. ^{1}H NMR (400 MHz, C_6D_6, 298 K) of PCHO obtained in run 6 of Table 2