SUPPORTING INFORMATION

Ring-Opening Homo- and Co-polymerization reaction of ε-Caprolactone and Lactides by Salalen Aluminum Complexes

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NMR characterization of complex 2b.

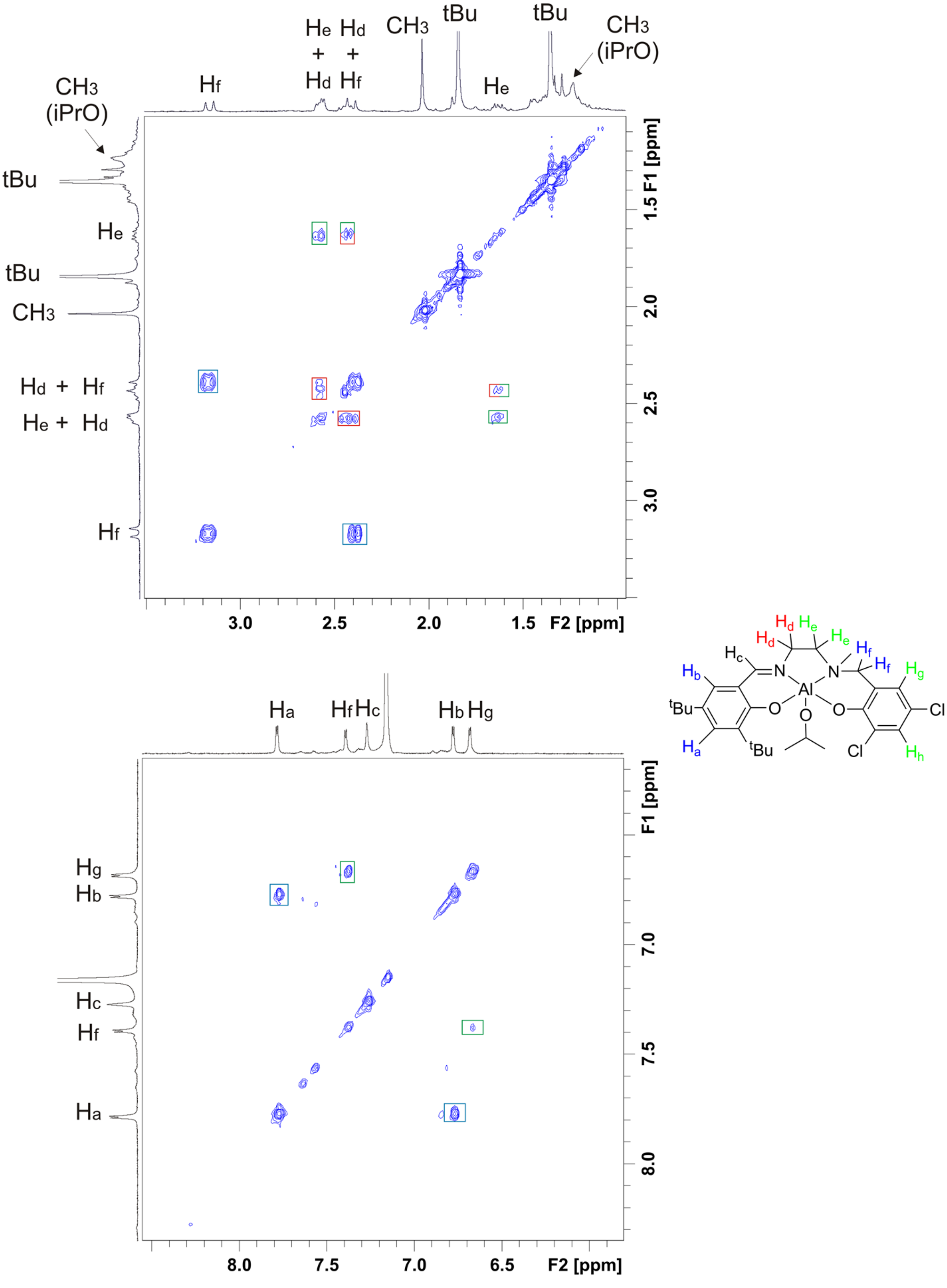

Figure S1. Aliphatic (up) and aromatic (down) area of NMR COSY spectrum of complex **2b** (C_6D_6).

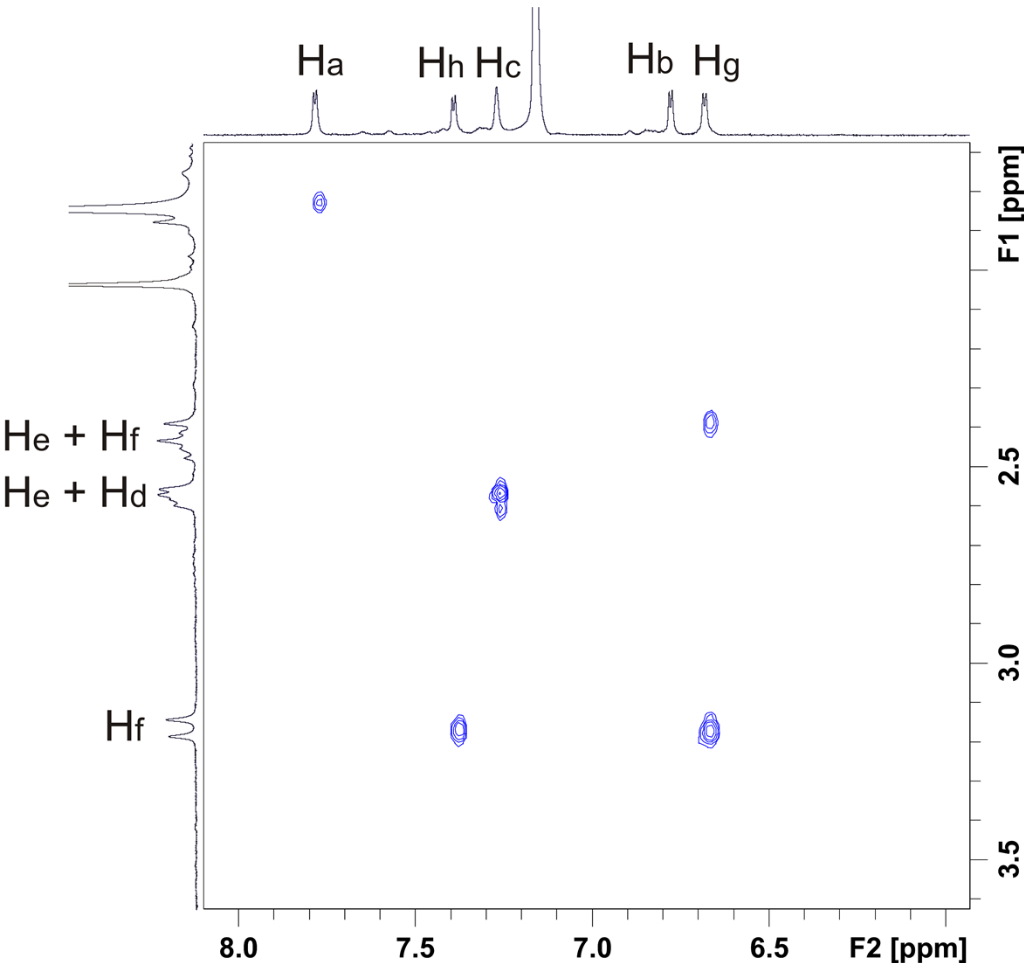

Figure S2. Aliphatic/aromatic cross peaks of NMR COSY spectrum of complex **2b** (C_6D_6).

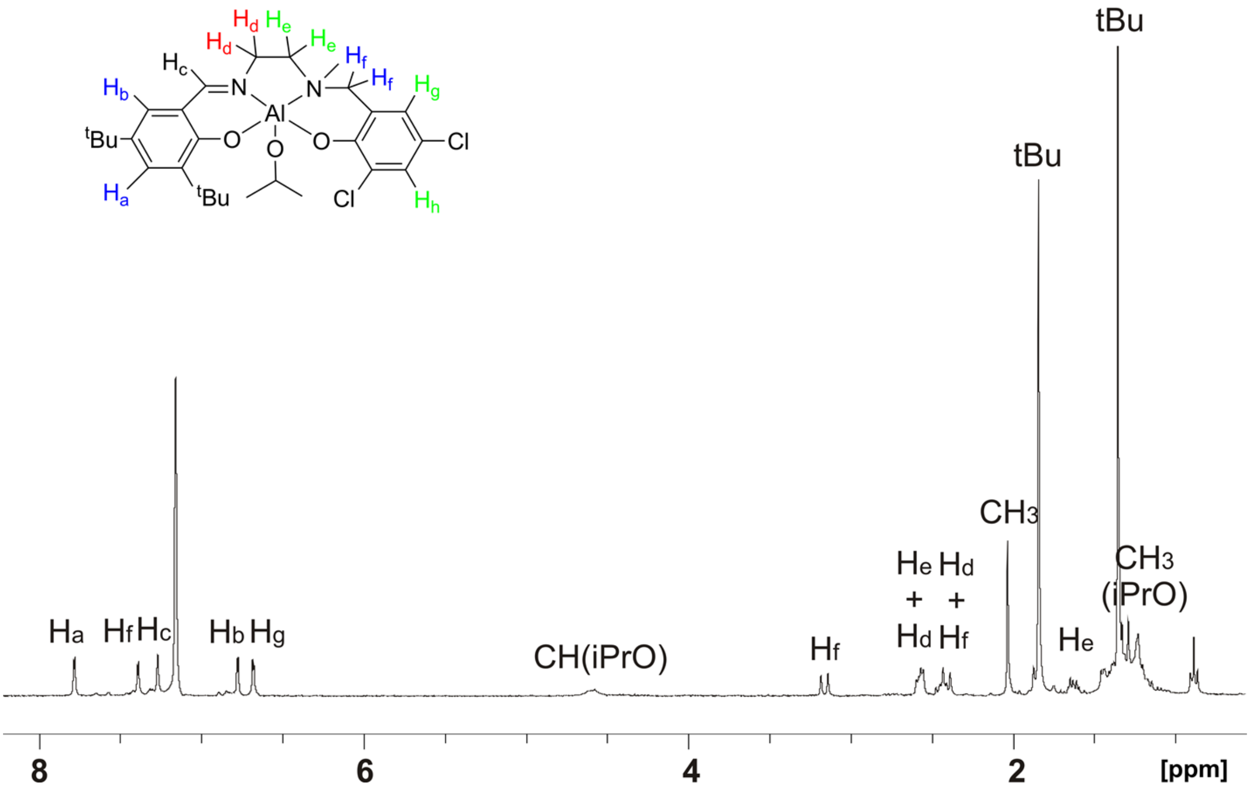

Figure S3. ^{1}H NMR spectrum of complex **2b** (C_6D_6).

Table S1. Tetrad probabilities based on Bernoullian Statistic (Th) and experimental values (Exp) as obtained by NMR analysis (entry 2, Table 1). $P_m = 0.72$

Tetrad	Formula	Th	Exp
[*mmm*]	$P_m^2+P_rP_m/2$	0.621	0.621
[*mmr*]	$P_rP_m/2$	0.101	0.099
[*rmm*]	$P_rP_m/2$	0.101	0.101
[*rmr*]	$P_r^2/2$	0.039	0.049
[*mrm*]	$(P_r^2+P_rP_m)/2$	0.140	0.130

Table S2. Tetrad probabilities based on Enantiomorphic Site Control Statistic (Th) and experimental values (Exp) as obtained by NMR analysis (entry 2, Table 1). $\alpha = 0.81$

Tetrad	Formula	Th	Exp
[*mmm*]	$[\alpha^2+(1-\alpha)^2+\alpha^3+(1-\alpha)^3]/2$	0.621	0.621
[*mmr*]	$[\alpha^2(1-\alpha)+\alpha(1-\alpha)^2]/2$	0.077	0.099
[*rmm*]	$[\alpha^2(1-\alpha)+\alpha(1-\alpha)^2]/2$	0.077	0.101
[*rmr*]	$[\alpha^2(1-\alpha)+\alpha(1-\alpha)^2]/2$	0.077	0.049
[*mrm*]	$[\alpha(1-\alpha)+\alpha(1-\alpha)]/2$	0.154	0.130

Table S3. Tetrad probabilities based on Bernoullian Statistic (Th) and experimental values (Exp) as obtained by NMR analysis (entry 3, Table 1). $P_m = 0.69$

Tetrad	**Formula**	**Th**	**Exp**
[*mmm*]	$P_m^2+P_rP_m/2$	0.583	0.583
[*mmr*]	$P_rP_m/2$	0.107	0.112
[*rmm*]	$P_rP_m/2$	0.107	0.131
[*rmr*]	$P_r^2/2$	0.048	0.060
[*mrm*]	$(P_r^2+P_rP_m)/2$	0.155	0.114

Table S4. Ring-Opening Polymerization of L-lactide promoted by **2b** and *S*-**4b**.

Monomer	**Time**	**Conv**	$M_n(_{th})$[c] (Kg/mol)	$M_n(_{GPC})$[b] (Kg/mol)	**PDI**
L-LA	25h	70%	20.2	21.4	1.05

[a] Conditions: initiator: **2b**: 10 µmol + *S*-**4b**: 10 µmol; toluene: 4 mL; lactide: 4 mmol; temperature: 80 °C.

[b] Experimental M_n values were determined by GPC analysis in THF using polystyrene standards and corrected by the factor 0.58.

[c] 144.13 x $[LA]_0/[I]_0$ x conv LA.

Meso-Lactide

Table S5. Tetrad probabilities based on Bernoullian Statistic (Th) and experimental values (Exp) as obtained by ^{13}C NMR analysis (entry 6, Table 1). $P_m = 0.79$

Tetrad	**Formula**	**Th**	**Exp**
[*rmr*]	$(P_m^2+P_rP_m)/2$	0.395	0.382
[*rrr*]	$P_r^2+P_rP_m/2$	0.127	0.136
[*rrm*]	$P_rP_m/2$	0.083	0.078
[*mrr*]	$P_rP_m/2$	0.083	0.090
[*mrm*]	$P_m^2/2$	0.314	0.314

Table S6. Tetrad probabilities based on Enantiomorphic Site Control Statistics (Th) and experimental values (Exp) as obtained by ^{13}C NMR analysis (entry 6, Table 1). $\alpha = 0.76$

Tetrad	Formula	Th	Exp
[*rmr*]	$[\alpha(1-\alpha)+\alpha(1-\alpha)]/2$	0.182	0.382
[*rrr*]	$[\alpha^2+(1-\alpha)^2+\alpha^3+(1-\alpha)^3]/2$	0.544	0.136
[*rrm*]	$[\alpha^2(1-\alpha)+\alpha(1-\alpha)^2]/2$	0.078	0.078
[*mrr*]	$[\alpha^2(1-\alpha)+\alpha(1-\alpha)^2]/2$	0.078	0.090
[*mrm*]	$[\alpha^2(1-\alpha)+\alpha(1-\alpha)^2]/2$	0.078	0.314

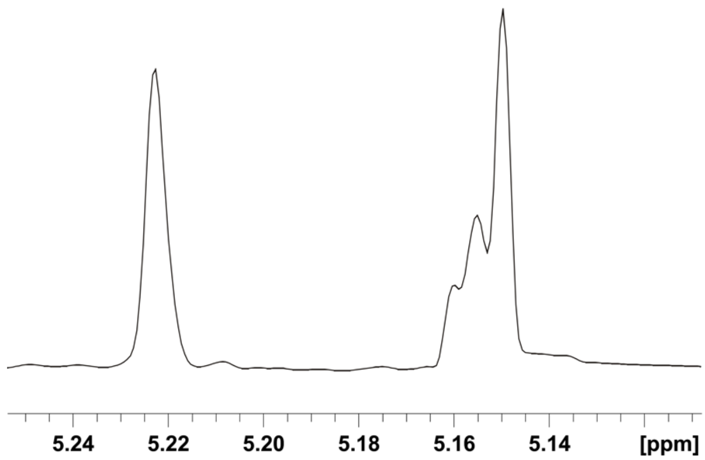

Figure S4. Homonuclear decoupled ^1H NMR of the PLA sample obtained by complex **2b** and *meso*-LA in toluene at 80 °C

Determination of Reactivity Ratios: The reactivity ratios were calculated using the nonlinear least squares (NLLS) method, carrying out the copolymerizations at low conversion with different ratios of the monomers.

Table S7. Copolymerization runs at low monomer conversions.

Time	$[LA]_0$(f1)	$[CL]_0$(f2)	LA conv.,%	CL conv.,%	LA in the copolymer (F1)	CL in the copolymer (F2)
10’	0.1	0.9	11	33	0.01	0.99
30’	0.3	0.7	6	20	0.12	0.88
1h 30’	0.5	0.5	7	12	0.34	0.66
1h 30’	0.7	0.3	7	13	0.58	0.42
1h 30’	0.9	0.1	5	9	0.84	0.16

$r_{CL} = 2.95$ $r_{LA} = 0.85$

Thermal analysis of the L-LA/ε-CL copolymers.

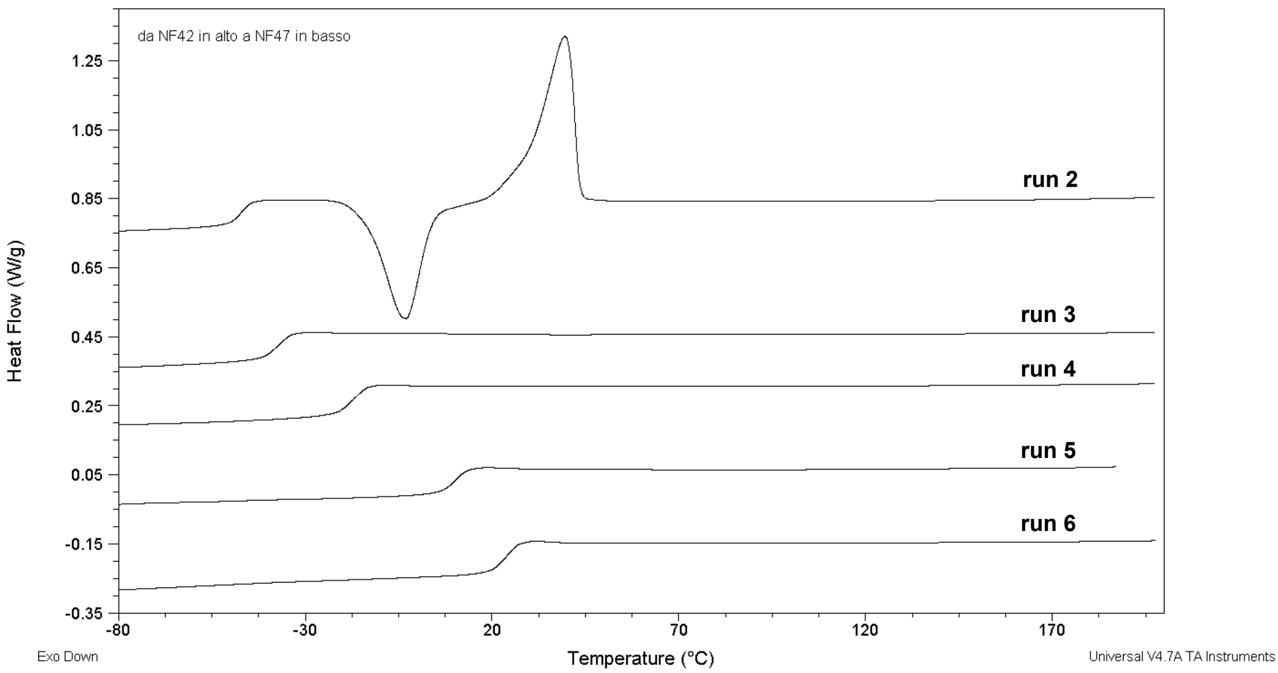

Figure S5. DSC (second heating run) of random L-LA/ε-CL copolymers reported in Table 2 of the paper.