

Supporting Information

**Random Copolymerization of ϵ -Caprolactone and Lactides promoted by
Pyrrolyl-pyridylamido Aluminum Complexes**

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Figure S1. ^1H NMR spectrum of complex 1

Figure S2. ^{13}C NMR spectrum of complex 1

Figure S3. ^1H NMR spectrum of complex 2

Figure S4. ^{13}C NMR spectrum of complex 2

Figure S5. Homonuclear decoupled ^{13}C NMR of a PLA sample

Figure S6. ^1H NMR spectra of copolymer samples

Table S1. Copolymerization runs at low monomer conversions.

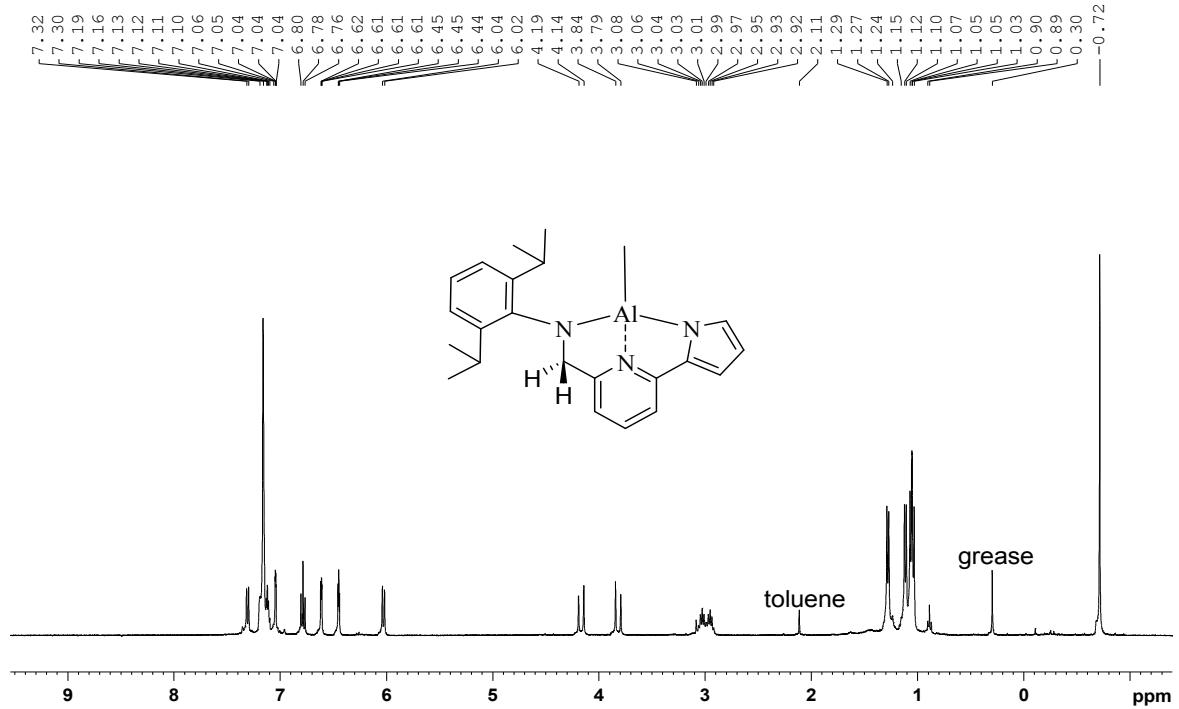


Figure S1. ¹H NMR spectrum of complex 1 (400MHz, C₆D₆, 25°C)

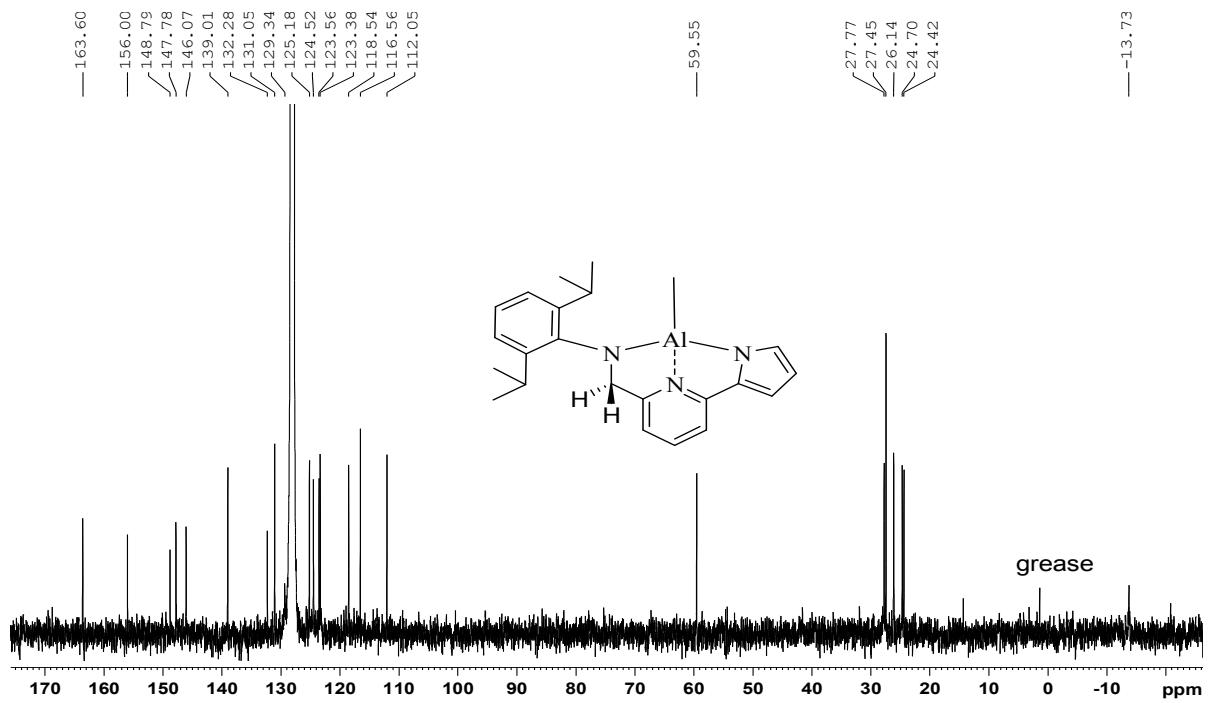


Figure S2. ¹³C NMR spectrum of complex 1 (100.6 MHz, C₆D₆, 25°C)

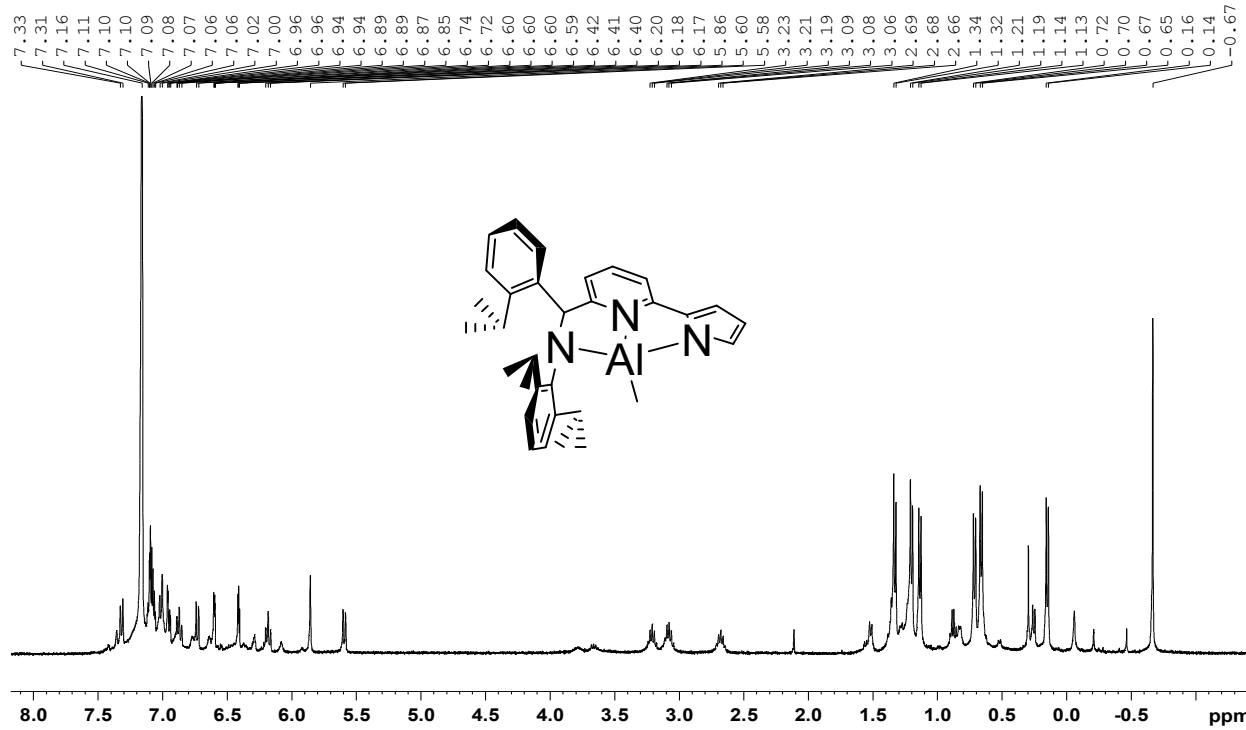


Figure S3. ¹H NMR spectrum of complex **2** (400MHz, C₆D₆, 25°C)

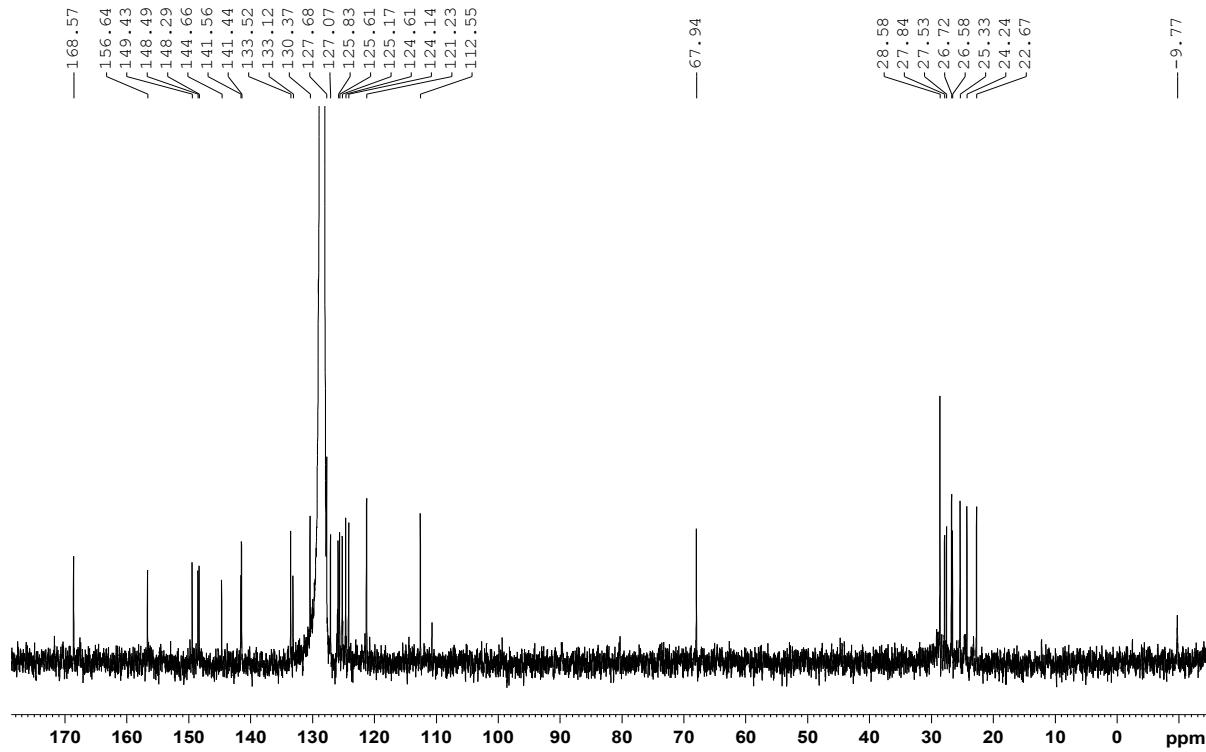


Figure S4. ¹³C NMR spectrum of Complex **2** (100.6 MHz, C₆D₆, 25 °C)

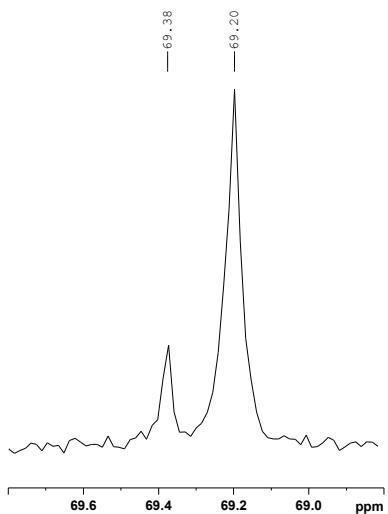


Figure S5. Methine region of the homonuclear decoupled ^{13}C NMR of the PLA sample obtained by complex **2**/benzyl alcohol in toluene at 70°C (run 8 in Table 2).

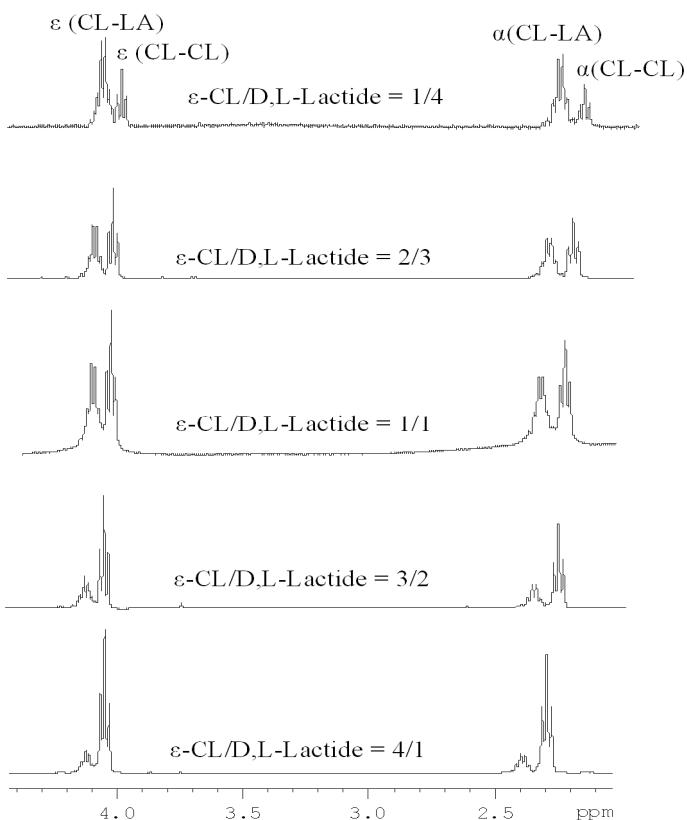


Figure S6. ^1H NMR spectra (CDCl_3 , 25°C) showing the ϵ - and α -methylene ranges of the copolymers obtained at different ϵ -CL/D,L-LA ratios (runs 1-5, table 3).

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 S1. Copolymerization runs at low monomer conversions.

[LA] ₀ (f1)	[CL] ₀ (f2)	LAconv.,%	CL conv.,%	LA in the copolymer (F1)	CL in the copolymer (F2)
0.06	0.94	8.72	10.53	0.0465	0.9535
0.3	0.7	8.40	9.97	0.2654	0.7346
0.5	0.5	7.57	9.22	0.4461	0.5540
0.7	0.3	9.40	7.67	0.7685	0.2315
0.85	0.15	10.2	7.62	0.8832	0.1168