Electronic Supplementary Information

Ring-opening Polymerization of Cyclic Esters with Lithium Amine-bis(phenolate) Complexes

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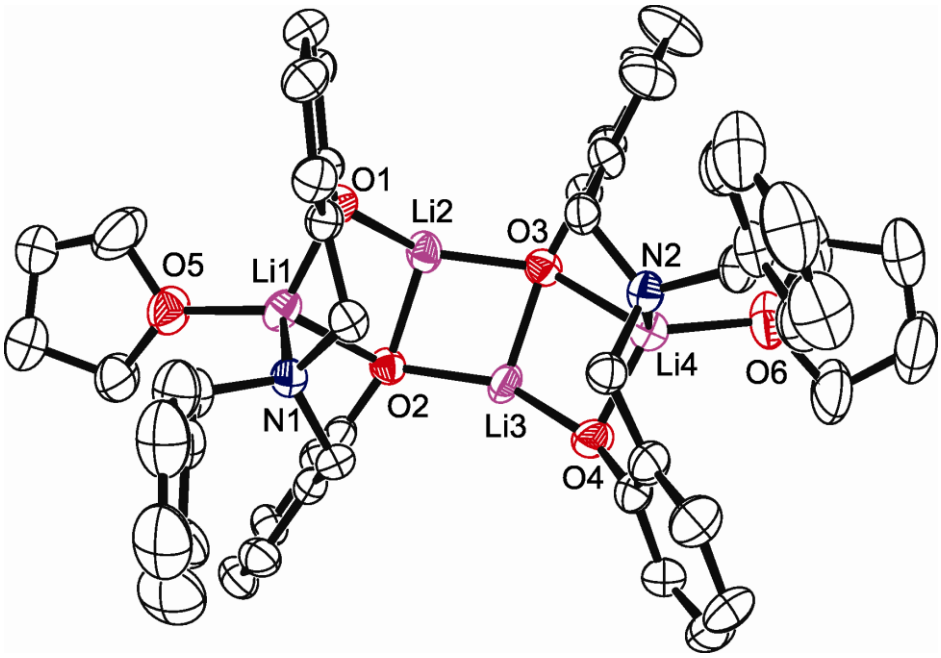

Figure S1: Molecular structure (ORTEP) and partial numbering scheme for compound **5.** Ellipsoids are shown at 50% probability. Hydrogen atoms and *tert*-amyl groups omitted for clarity.

Table S2: Selected bond lengths (Å) and angles (°) for **5**.

Li1-N1	2.037	N1-Li1-O5	112.18
Li1-O1	1.875	O1-Li1-O2	95.79
Li1-O2	2.068	O1-Li1-O5	119.93
Li1-O5	1.927	O2-Li1-O5	126.32
Li2-O1	1.808	O1-Li2-O2	103.34
Li2-O2	1.924	O1-Li2-O3	138.73
Li2-O3	1.894	O2-Li2-O3	100.66
Li3-O2	1.917	O2-Li3-O3	100.03
Li3-O3	1.919	O2-Li3-O4	152.40
Li3-O4	1.783	O3-Li3-O4	101.80
Li4-N2	2.053	N2-Li4-O3	98.90
Li4-O3	2.046	N2-Li4-O4	100.83
Li4-O4	1.878	N2-Li4-O6	107.32
Li4-O6	1.963	O3-Li4-O4	94.08
N1-Li1-O1	102.14	O3-Li4-O6	128.88
N1-Li1-O2	95.66	O4-Li4-O6	121.84

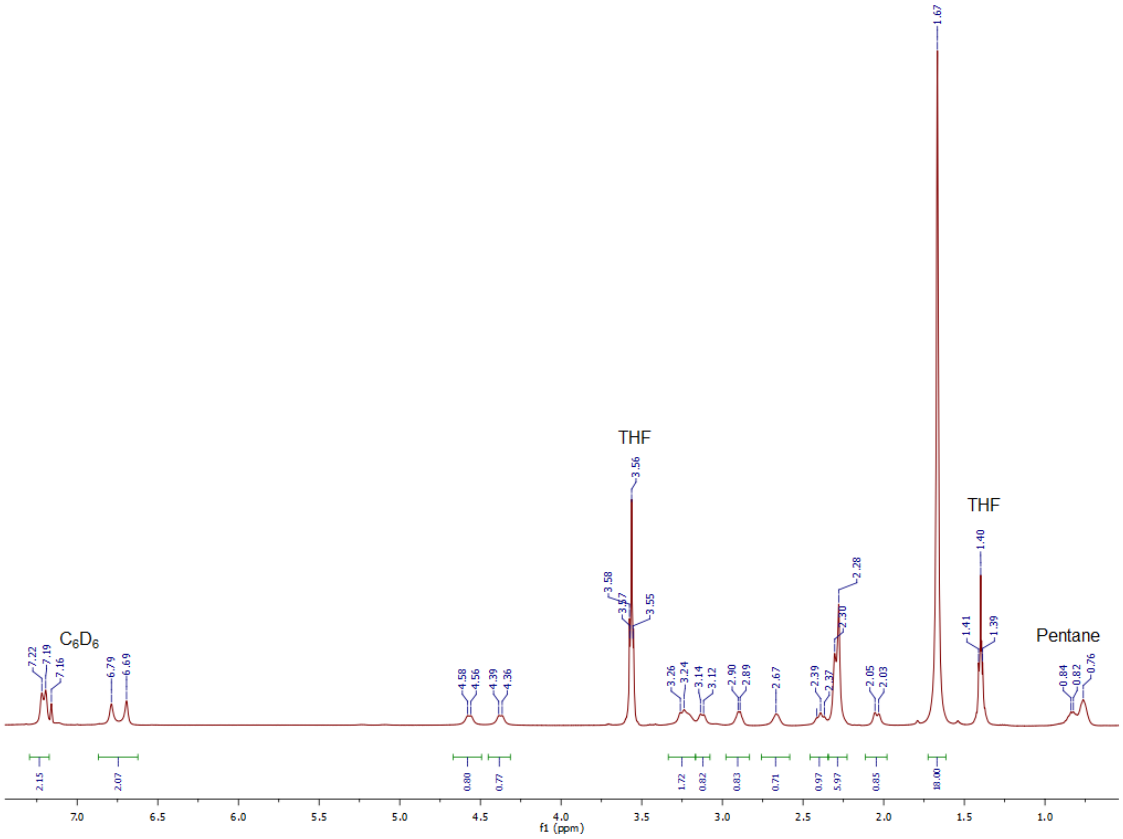

Figure S2. ^{1}H NMR spectrum of **1** in C_6D_6 at 298 K (500 MHz).

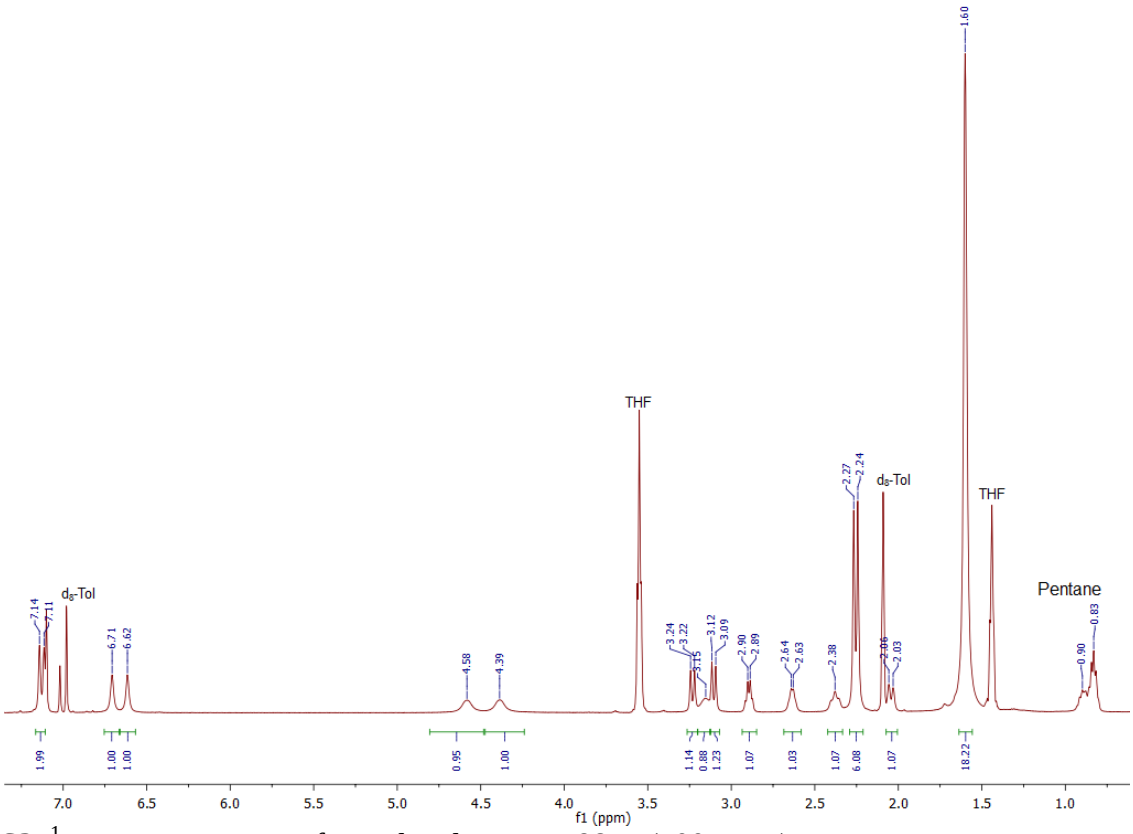

Figure S3. ^{1}H NMR spectrum of **1** in d_8-toluene at 298 K (500 MHz).

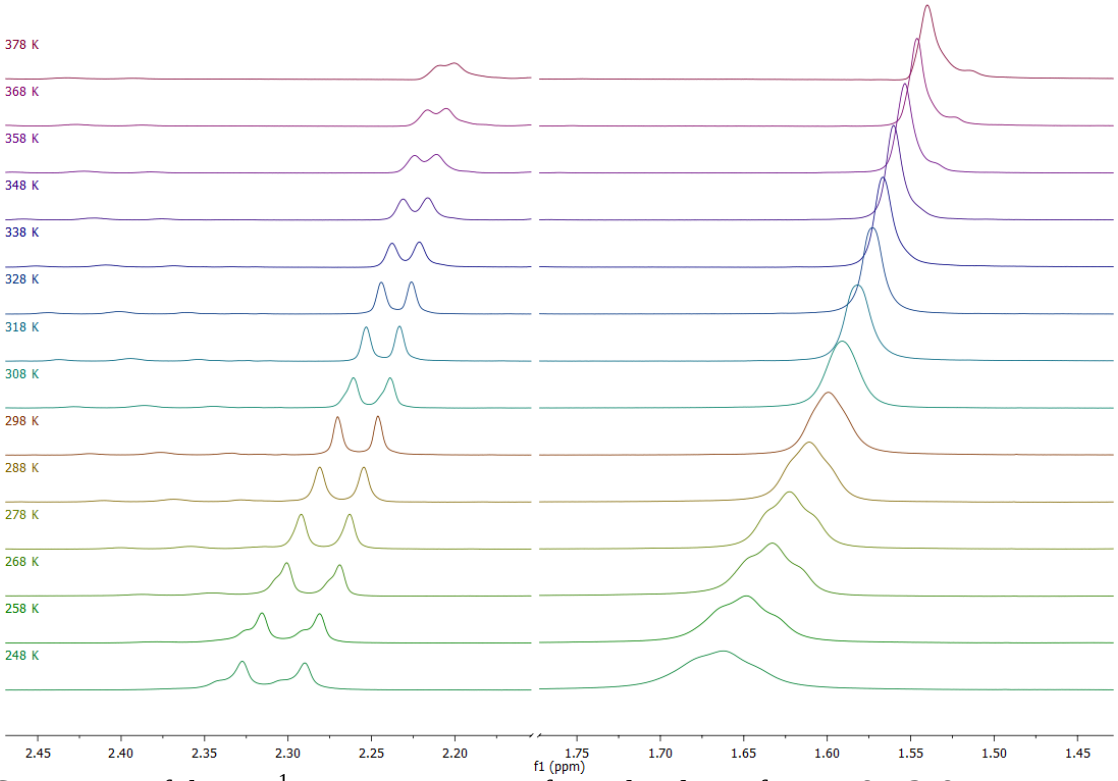

Figure S4. Portion of the VT ^{1}H NMR spectrum of **1** in d_8-toluene from 248 – 378 K, corresponding to methyl and *tert*-butyl peaks (300 MHz).

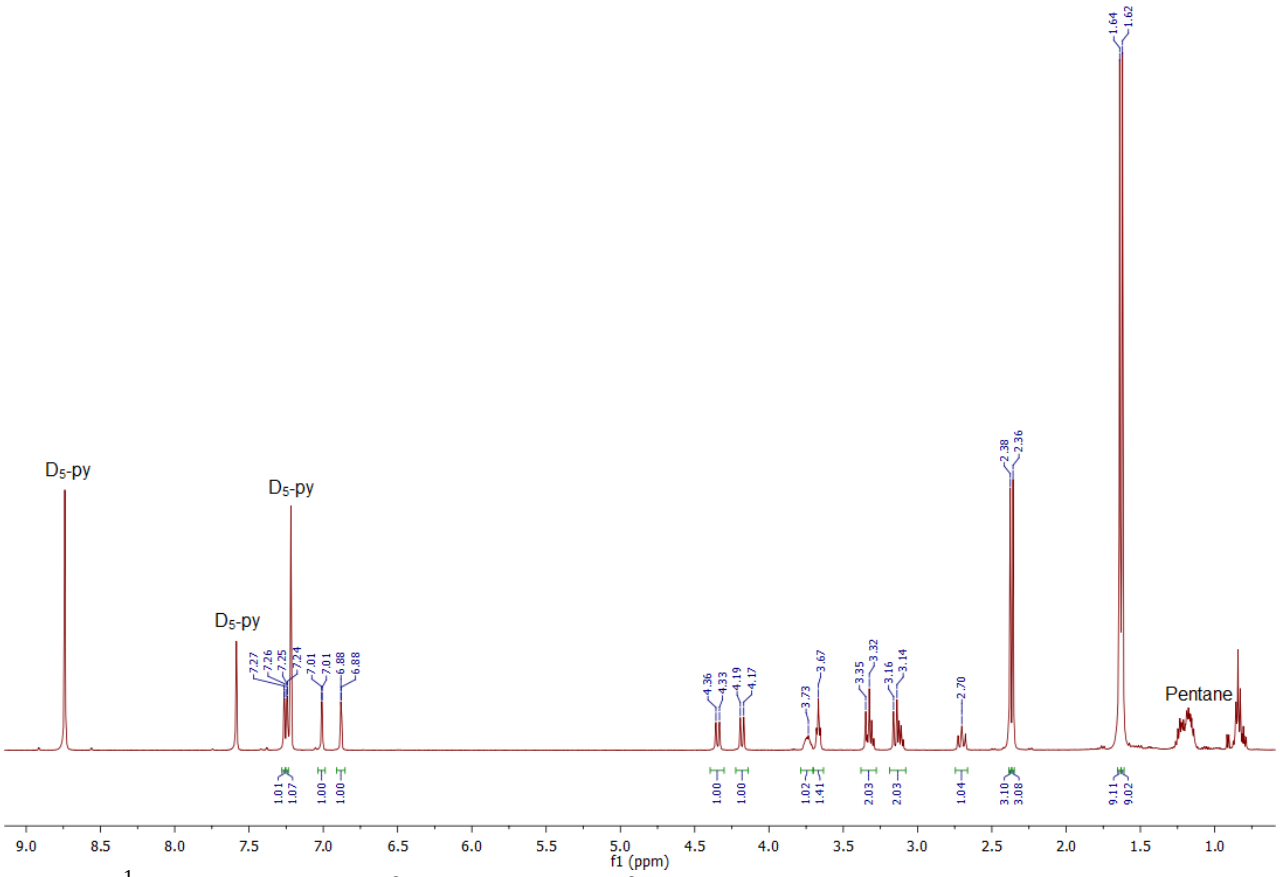

Figure S5. ^{1}H NMR spectrum of **1** in d_5-pyridine, forming **3**, at 298 K (500 MHz).

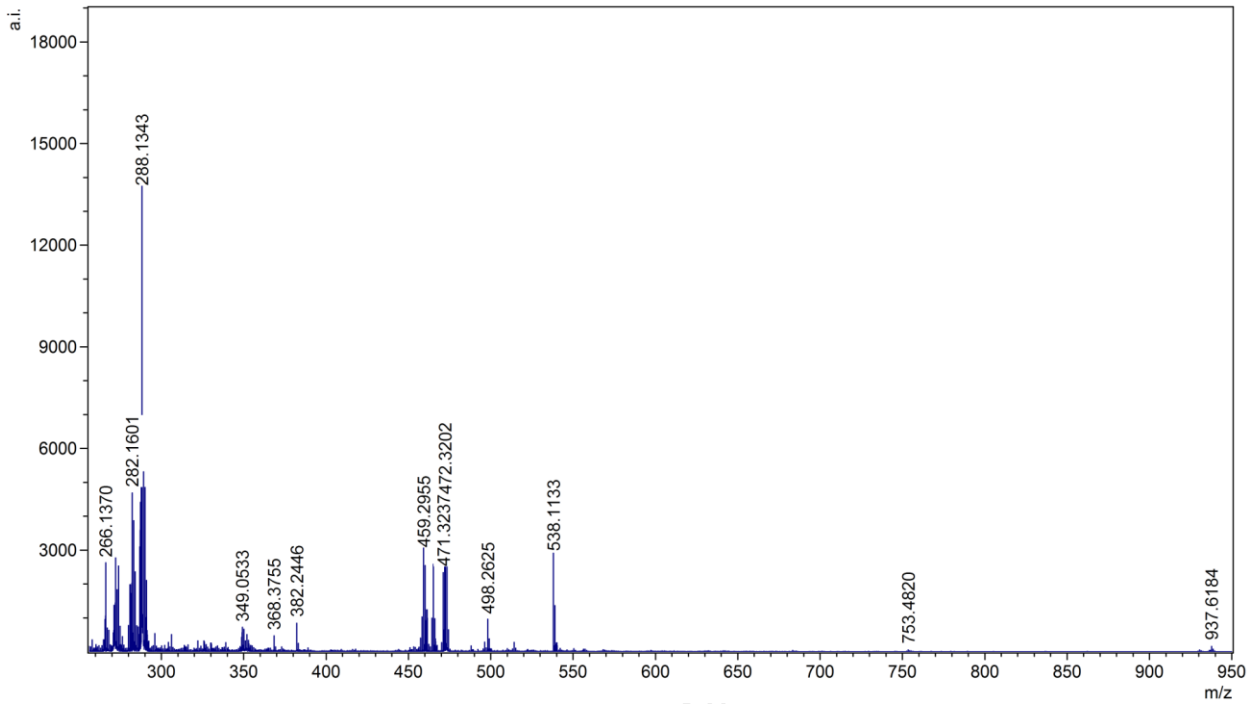

Figure S6. MALDI-TOF mass spectrum of $\{Li_2[O_2NO]^{BuMe}\}_2$ (**1**).

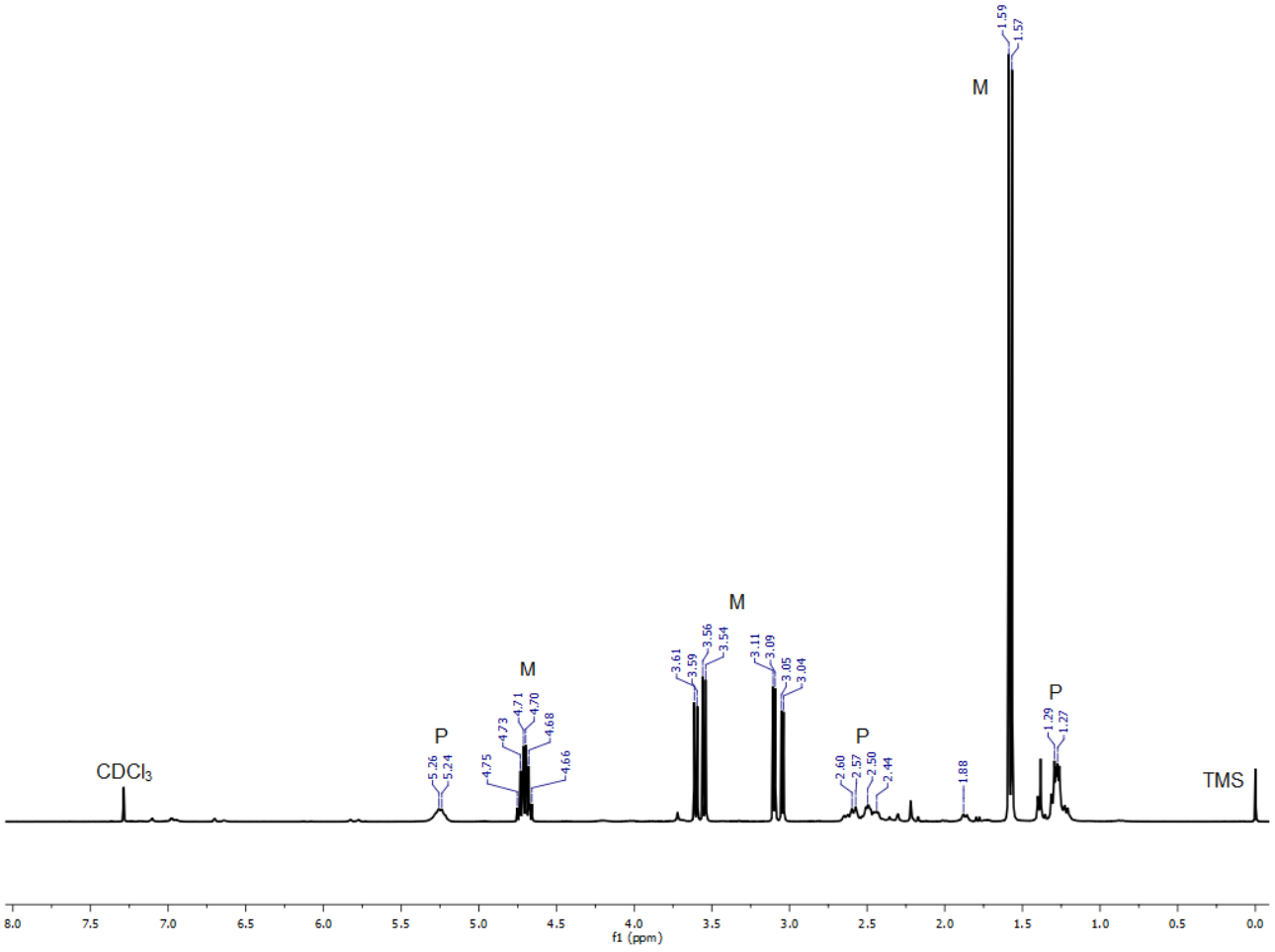

Figure S7. ^{1}H NMR spectrum for an attempted ROP reaction of β–BL, where M = monomer and P = polymer (in $CDCl_3$).

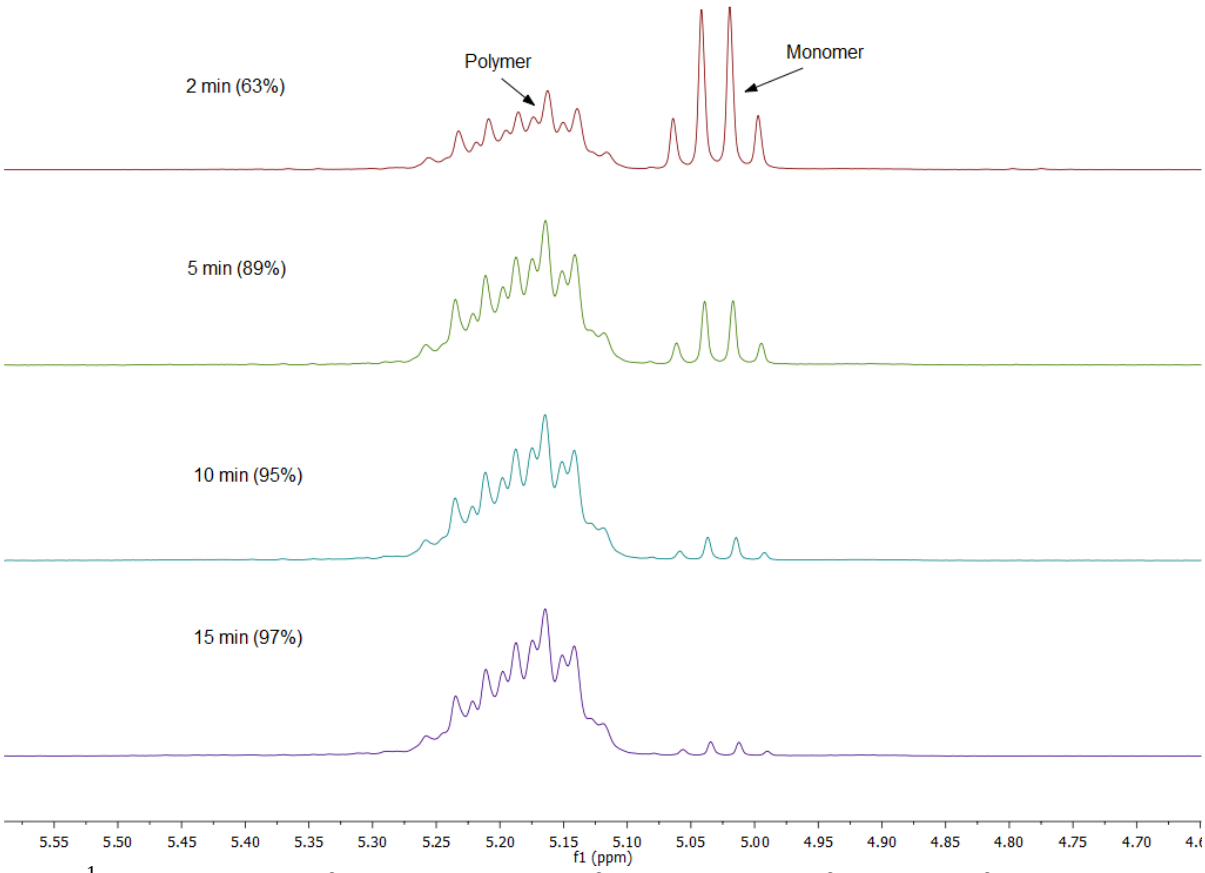

Figure S8. ^{1}H NMR spectra of the methine region for aliquots taken from ROP of LA initiated by complex **1** at 60 °C (300 MHz, $CDCl_3$).

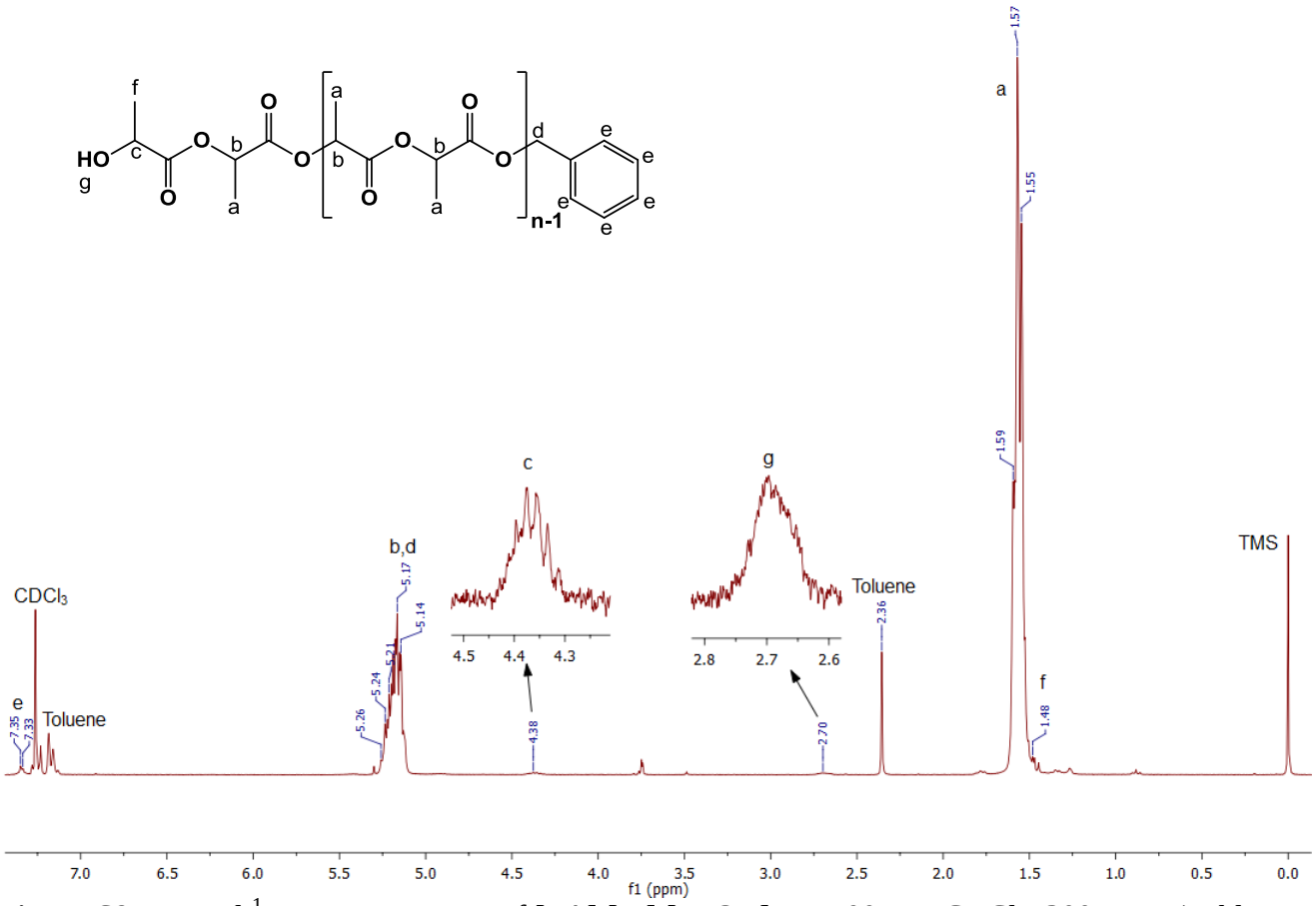

Figure S9. Typical ^{1}H NMR spectrum of [LA]:[Li]:[BnOH] = 1:100:1 in $CDCl_3$, 300 MHz (Table 5, entry 9).

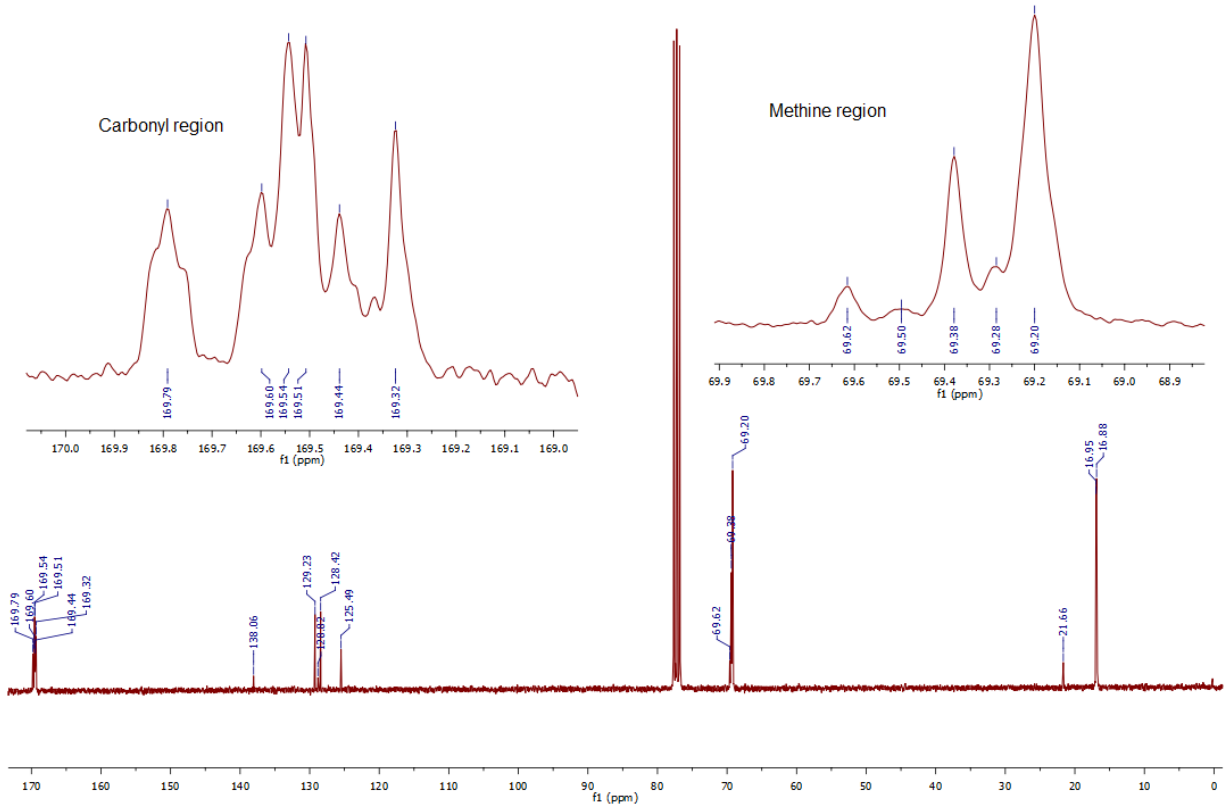

Figure S10. Typical ^{13}C NMR spectrum of PLA in $CDCl_3$, 300 MHz (Table 5, entry 2).

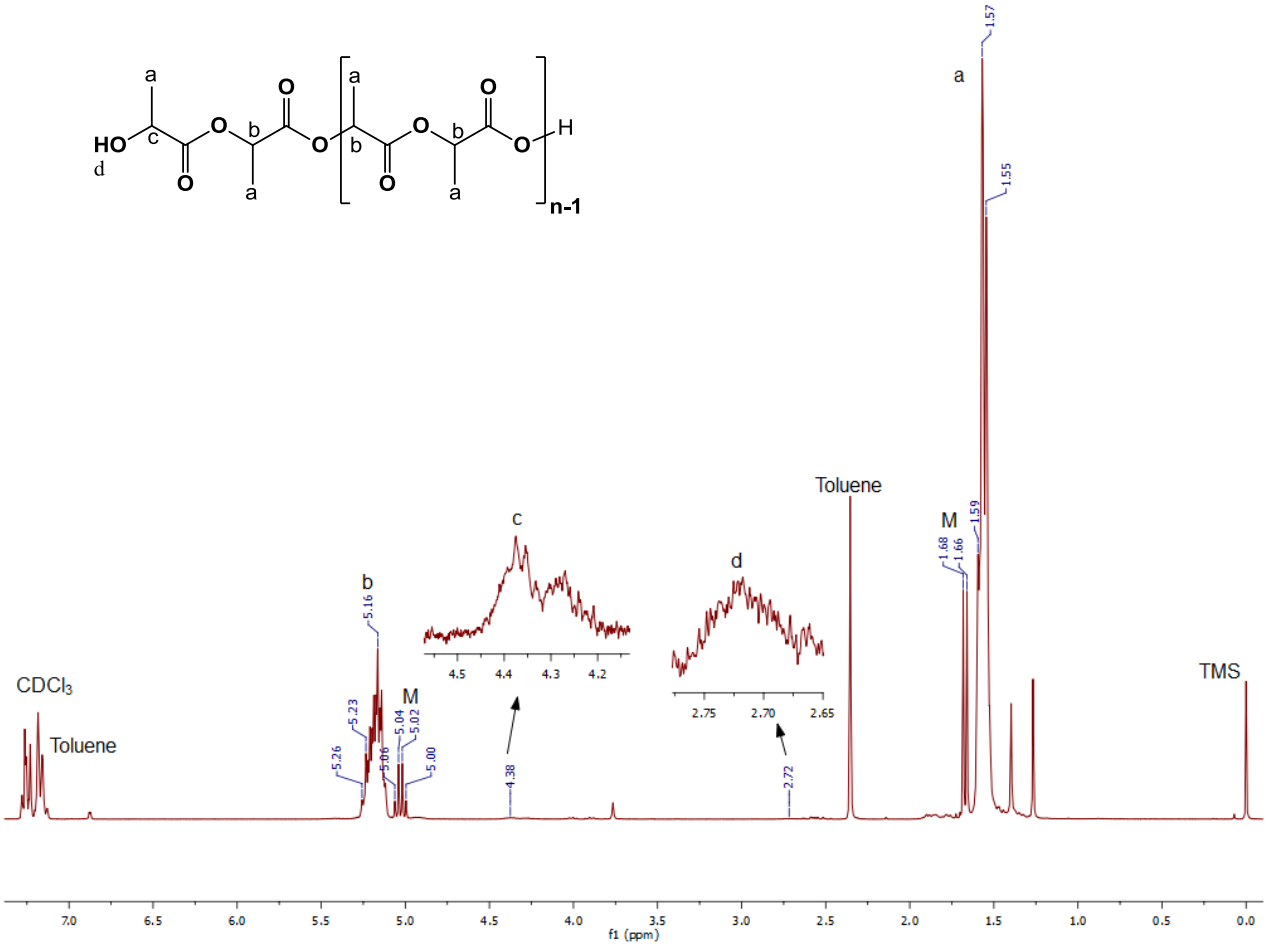

Figure S11. Typical ^{1}H NMR spectrum of [LA]:[Li]:[BnOH] = 1:50:0 in $CDCl_3$, 300 MHz (Table 5, entry 8) where M = monomer.