Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information for:

Ring-opening polymerization of ε-caprolactone by lithium piperazinyl-aminephenolate complexes: Synthesis, characterization and kinetic studies

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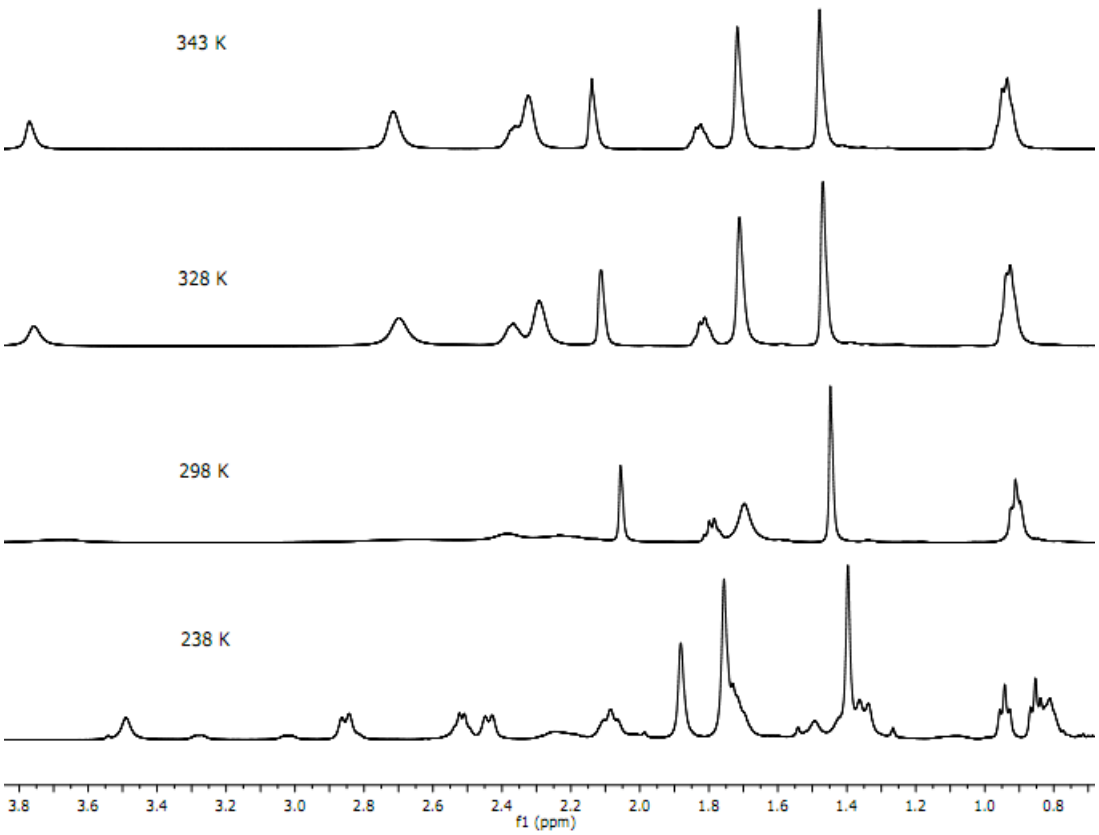

Fig. S1 Variable temperature NMR spectrum of the methylene region of **3** in C_5D_5N.

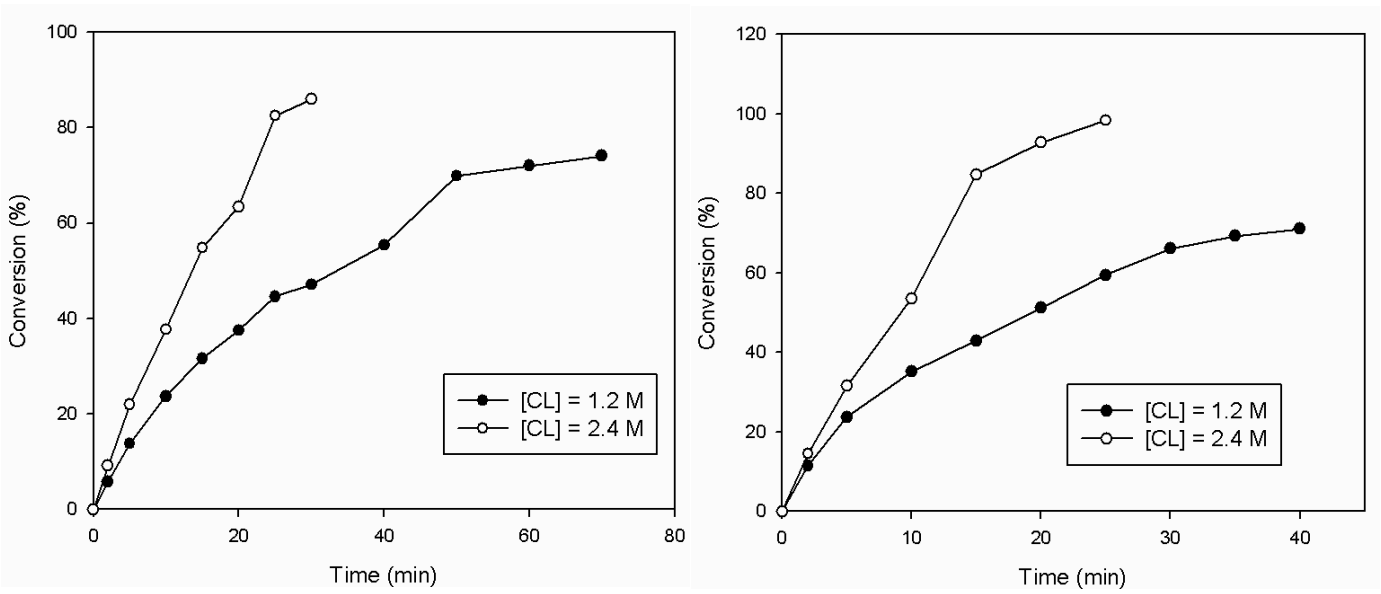

Fig. S2: Effect of monomer concentration on the time of polymer conversion. {Conditions: [**1**] = 17.7 mM in toluene; [CL] = 1.2 (●); [CL] = 2.4 M (○)} at (a) 40 °C and (b) 60 °C

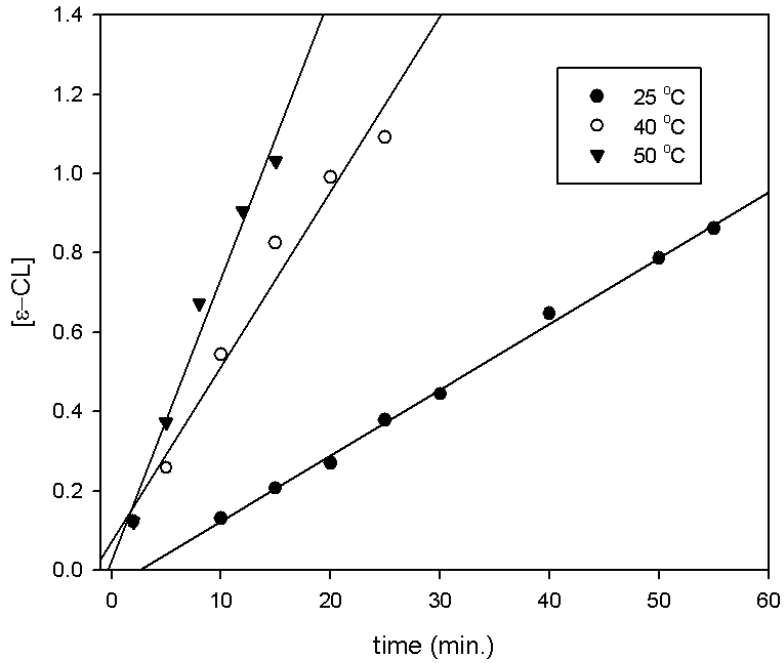

Fig. S3: Semilogarithmic plots of the monomer conversion stated as $\ln[CL]_0/[CL]_t$ versus the reaction time for the polymerization of ε-caprolactone at different temperatures initiated with **3**; $[CL]_0/[\mathbf{3}]_0 = 200$, ($[1]_0 = 17.7$ mM, [CL] = 1.52 M); (●) = 25 °C, (○) = 40 °C, (▼) = 50 °C.

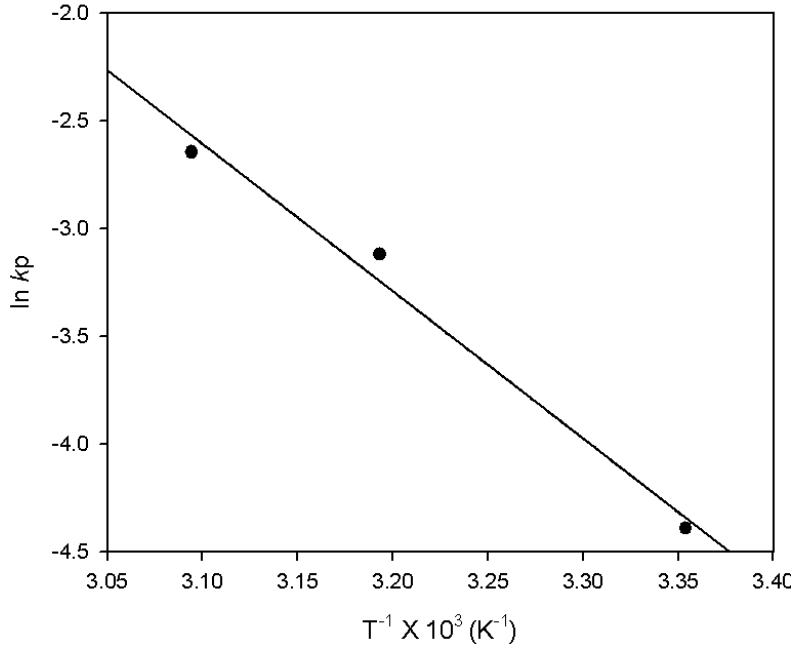

Fig. S4: Arrhenius plots of ln(*k*p) vs. 1/T for the ring-opening polymerization of ε-caprolactone initiated by **3**:[**3**] = 17.7 mM; [CL]/[1] = 200

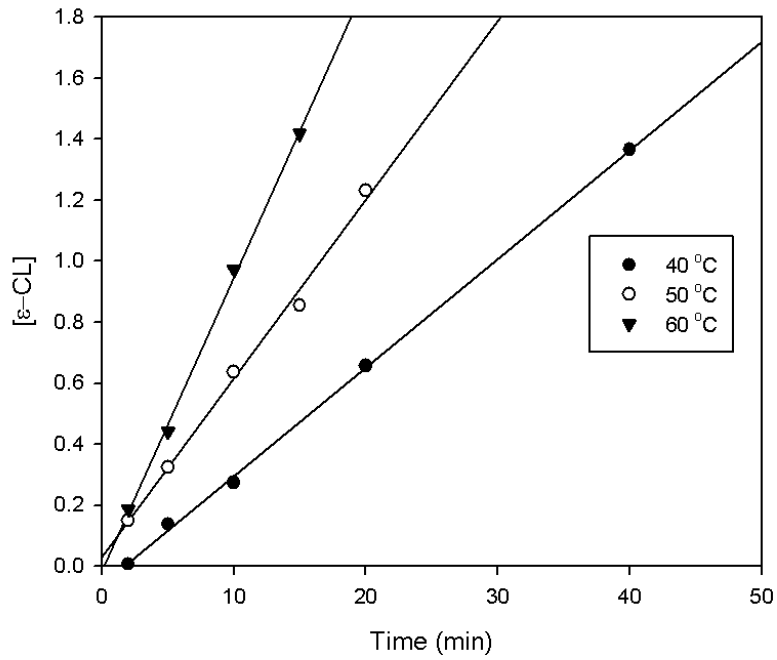

Fig. S5: Semilogarithmic plots of the monomer conversion stated as $\ln[CL]_0/[CL]_t$ versus the reaction time for the polymerization of ε-caprolactone at different temperatures initiated with **3**-BnOH; $[CL]_0/[\mathbf{3}\text{-BnOH}]_0 = 200$, ($[1]_0 = 17.7$ mM, [CL] = 1.52 M); (●) = 40 °C, (○) = 50 °C, (▼) = 60 °C.

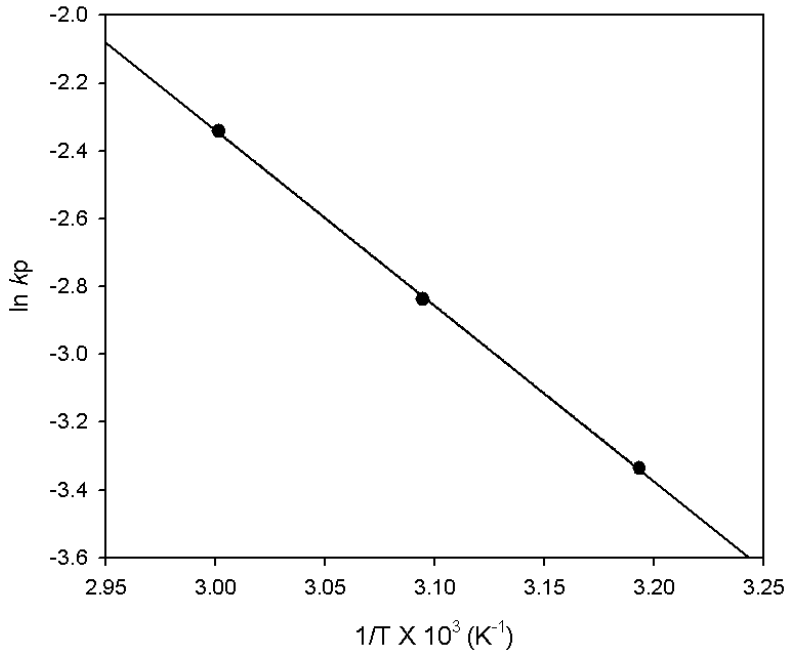

Fig. S6: Arrhenius plots of ln(*k*p) vs. 1/T for the ring-opening polymerization of ε-caprolactone initiated by **3**:[**3**-BnOH] = 17.7 mM; [CL]/[1] = 200

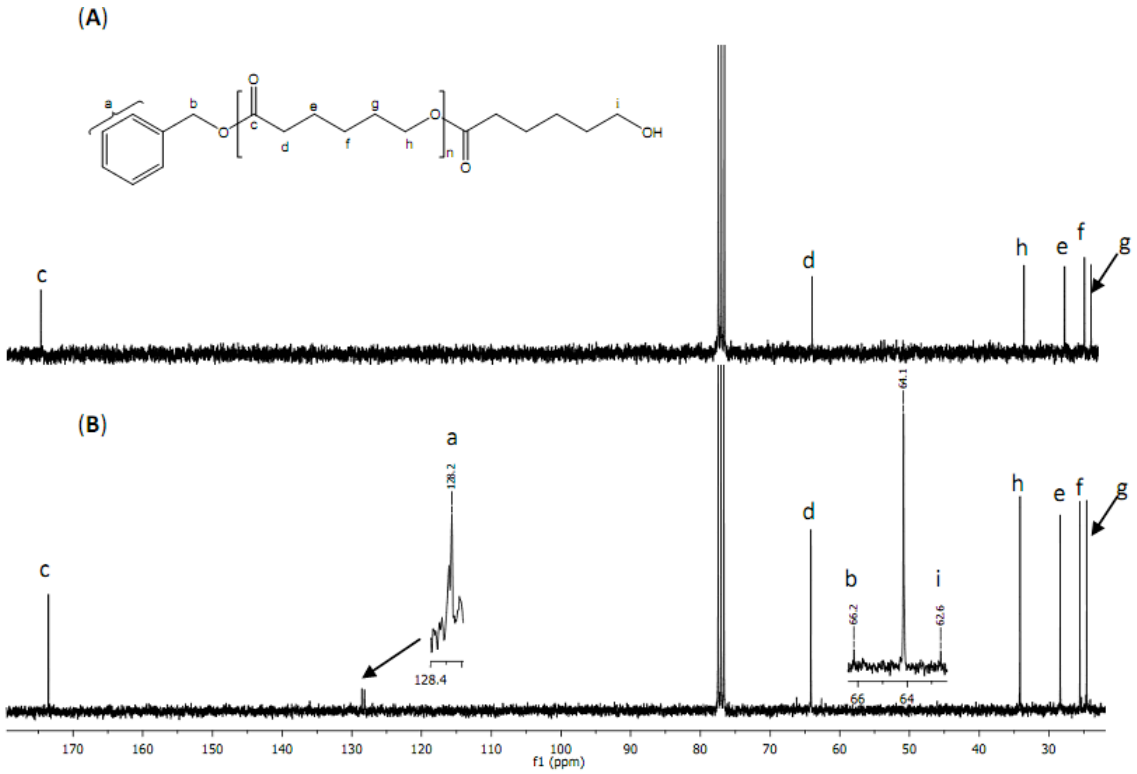

Fig. S7: ^{13}C NMR spectra for PCL initiated by (A) **3** and (B) **2**-BnOH (Table 1, entry 18 and 15).

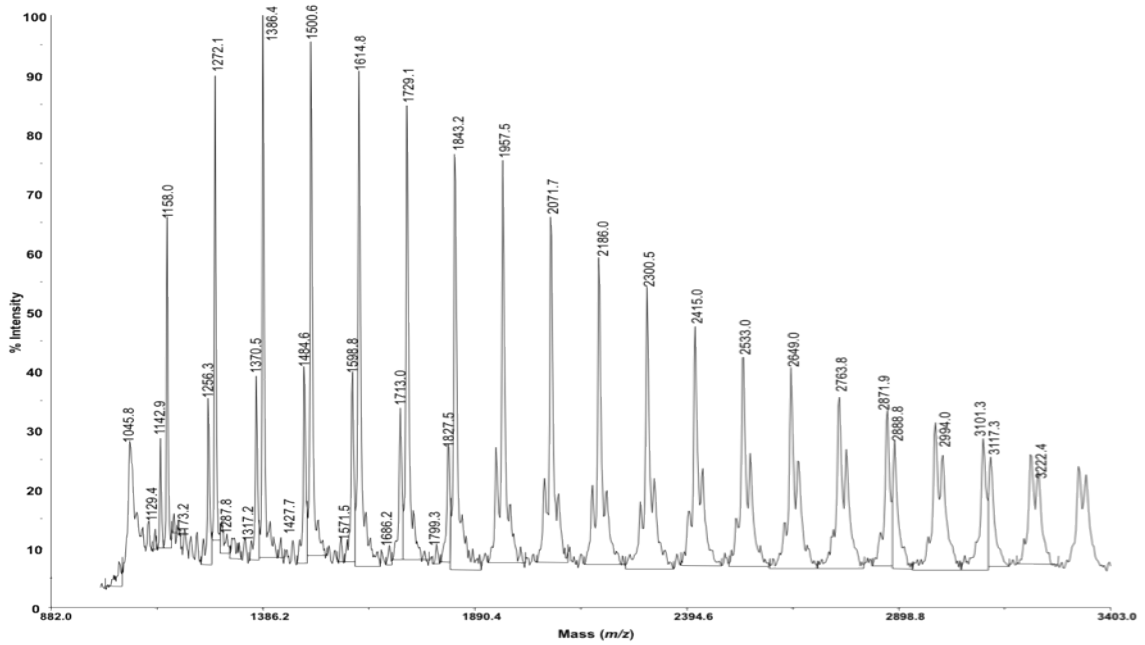

Fig. S8 MALDI-TOF mass spectrum of PCL initiated by **1** in THF at 60 °C, [CL]/[1] = 50 (Table 1, entry 2). The absolute mass values meet the data of 114.14×n for $(CL)_n$, 114.14×n + 17 for H-$(CL)_n$-OH 114.14×n + 17+ 22 for H-$(CL)_n$-OH•Na^+ and 114.14×n + 17+ 22 for H-$(CL)_n$-OH•K^+.

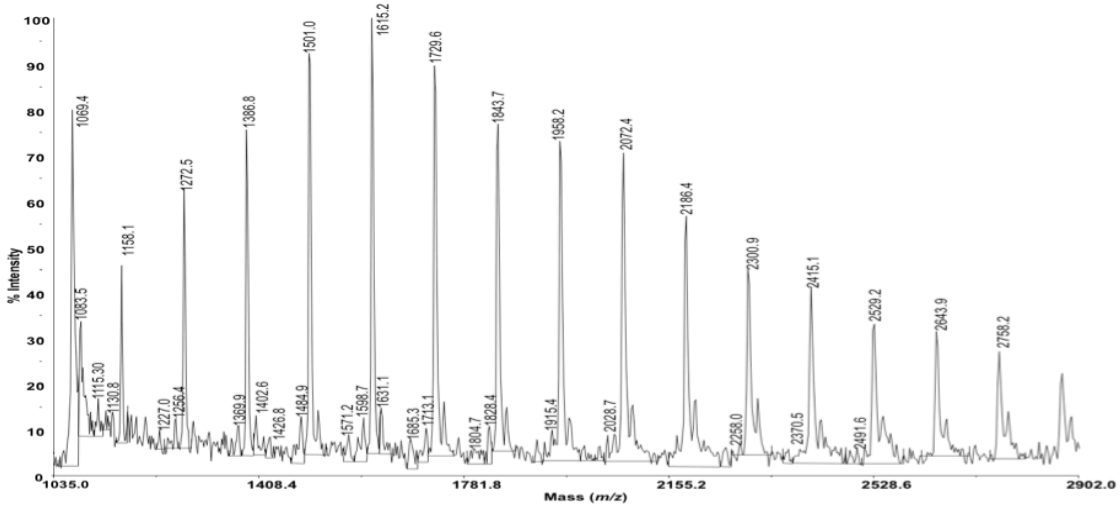

Fig. S9 MALDI-TOF mass spectrum of PCL initiated by **1** in toluene at 25 °C, [CL]/[1] = 50 (Table 1, entry 5). The absolute mass values meet the data of 114.14×n for $(CL)_n$, 114.14×n + 17 for H-$(CL)_n$-OH 114.14×n + 17+ 22 for H-$(CL)_n$-OH•Na^+ and 114.14×n + 17+ 22 for H-$(CL)_n$-OH•K^+

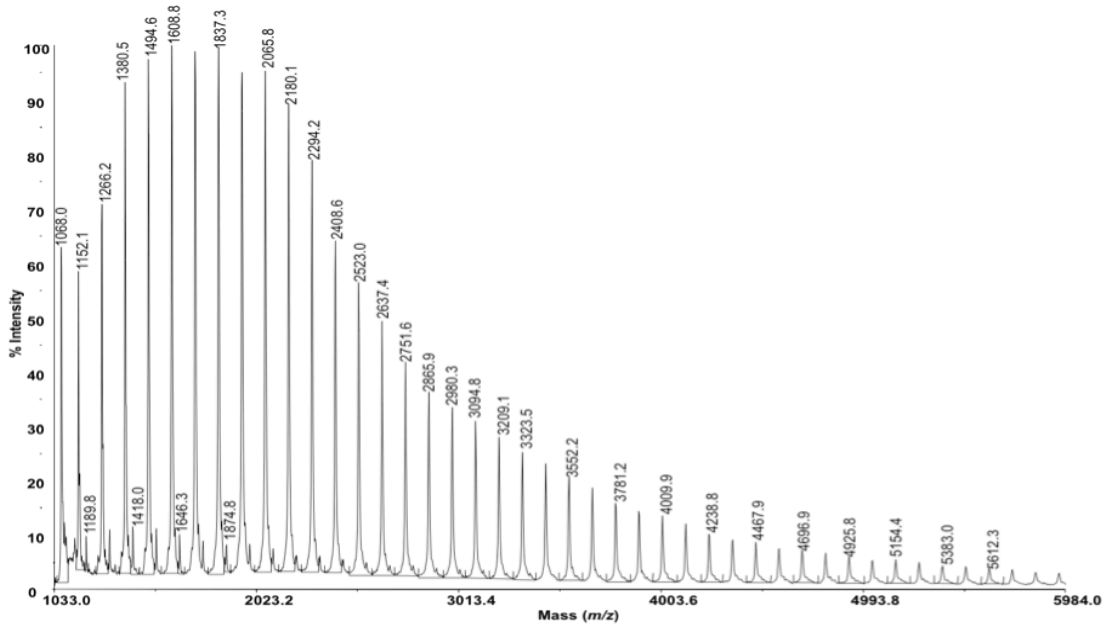

Fig. S10 MALDI-TOF mass spectrum of PCL initiated by **1**-BnOH in toluene at 25 °C, [CL]/[**1**-BnOH] = 50 (Table 1, entry 9). The absolute mass values meet the data of 114.14×n + 108 for BnO-$(CL)_n$-H, 114.14×n + 108 +17 for BnO-$(CL)_n$-OH and 114.14×n + 108 + 17 + 22 for BnO-$(CL)_n$-OH•K^+.

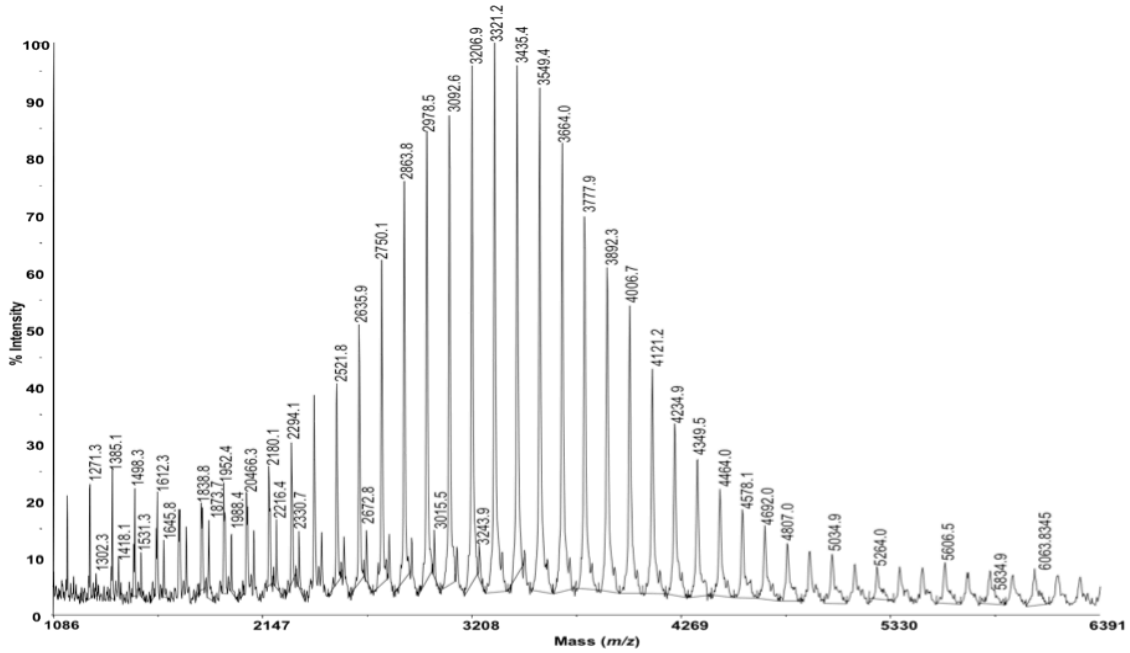

Fig. S11 MALDI-TOF mass spectrum of PCL initiated by **1**-BnOH in toluene at 60 °C, [CL]/[**1**-BnOH] = 200 (Table 1, entry 12).

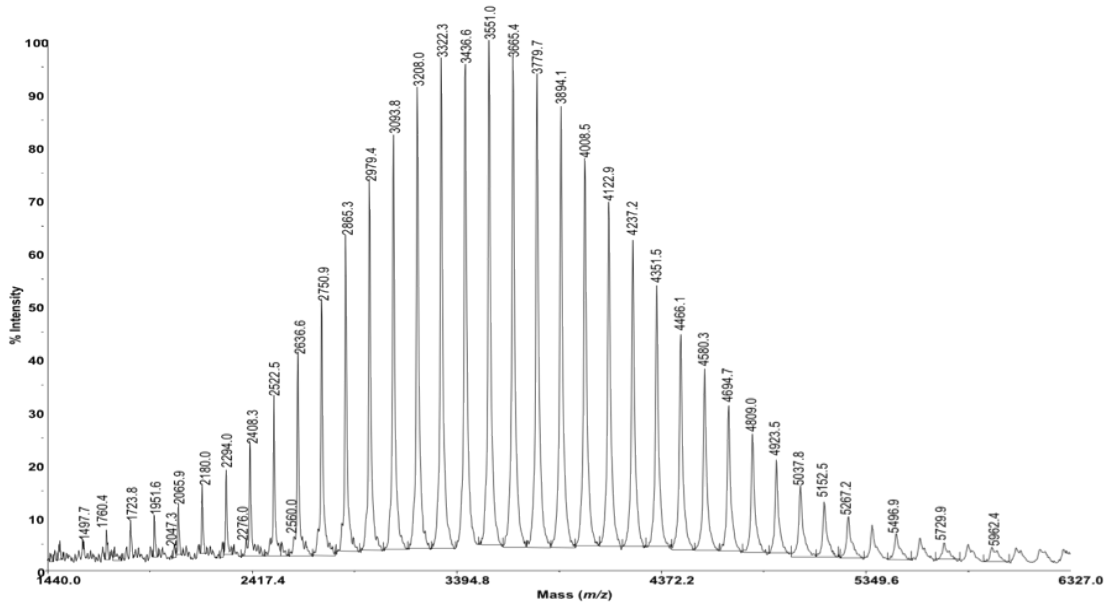

Fig. S12 MALDI-TOF mass spectrum of PCL initiated by **3**-BnOH in toluene at 25 °C, [CL]/[**3**-BnOH] = 200 (Table 1, entry 24). The absolute mass values meet the data of 114.14×n + 108 for BnO-$(CL)_n$-H, 114.14×n + 108 +17 for BnO-$(CL)_n$-OH and 114.14×n + 108 + 17 + 22 for BnO-$(CL)_n$-OH•K^+.

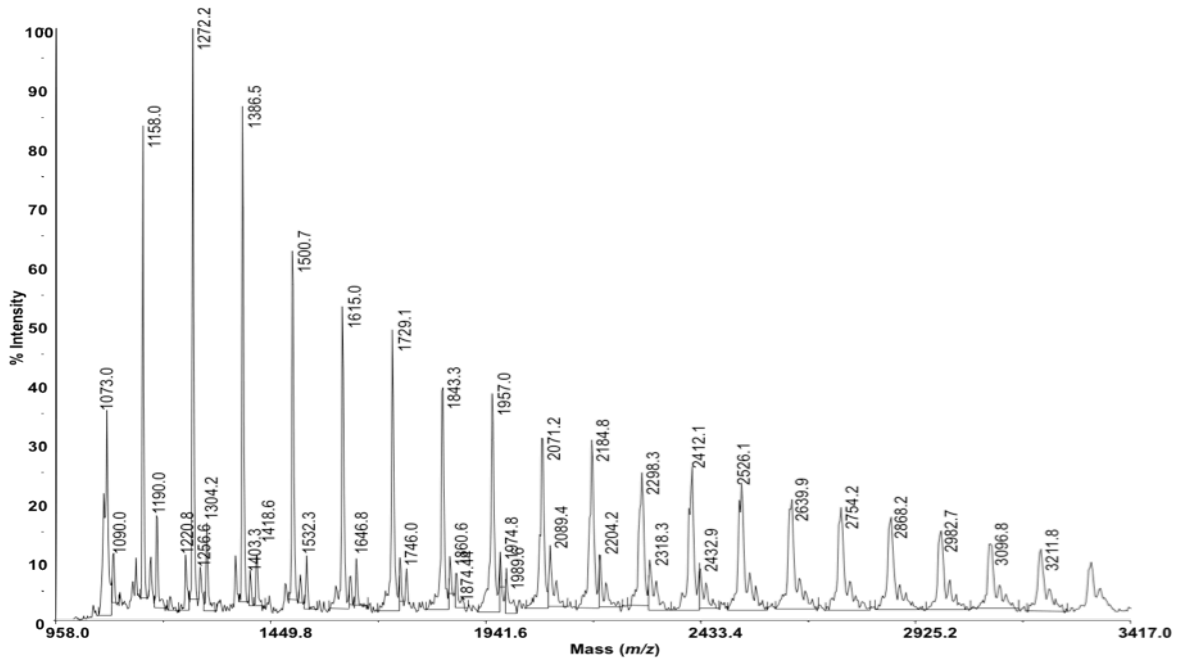

Fig. S13 MALDI-TOF mass spectrum of PCL initiated by **3**-BnOH in toluene at 40 °C, [CL]/[**3**-BnOH] = 200 (Table 1, entry 20).

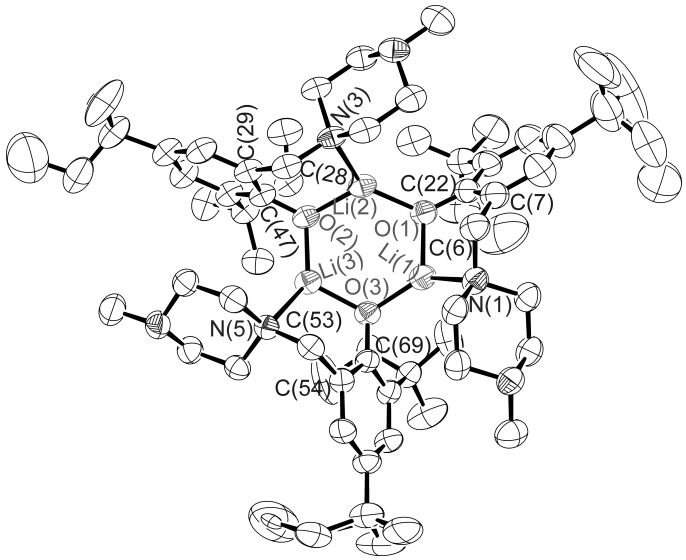

Fig. S14 Molecular structure of **3**. (50% thermal ellipsoids; H atoms excluded for clarity). Selected bond lengths (Å) and bond angles (°): O(1)-Li(1), 1.839(5); O(1)-Li(2), 1.862(5); O(2)-Li(2), 1.839(5); O(2)-Li(3), 1.845(5); O(3)-Li(1), 1.837(5); O(3)-Li(3), 1.857(5); N(1)-Li(1), 2.133(5); N(3)-Li(2), 2.138(5); N(5)-Li(3), 2.150(6); Li(1)-O(1)-Li(2), 112.1(2); Li(2)-O(2)-Li(3), 115.5(2); Li(1)-O(3)-Li(3), 110.4(2); O(3)-Li(1)-O(1), 121.9(2); O(2)-Li(2)-O(1), 119.5(3); O(2)-Li(3)-O(3), 120.1(3); O(3)-Li(1)-N(1), 132.3(3); O(1)-Li(1)-N(1), 99.7(2); O(2)-Li(2)-N(3), 101.0(2).