Supporting Information

Bimetallic aluminum alkyl complexes as highly active initiators for the polymerization of *ε*-caprolactone

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Experimental Section

General procedures. All of the manipulations were performed under an argon atmosphere using the standard Schlenk techniques and glovebox. $AlMe_3$ and $AlEt_3$ are commercially available. THF, toluene, and hexane were distilled from sodium benzophenone ketyl before use. ε-Caprolactone (ε-CL) was purchased from Arcos， and were dried by CaH_2 for 48 h, and then distilled under reduced pressure. Deuterated solvents (C_6D_6 and d_8-THF) were obtained from CIL, $[ONNO]H_2$ {$H_2[ONNO]$ = 1,4-bis(2-hydroxy-3,5-di-methyl-benzyl)-piperazidine} was prepared according to the published methods.[1] Carbon, hydrogen, and nitrogen analyses were performed by direct combustion with a Carlo-Erba EA-1110 instrument. The IR spectra were recorded with a Nicolet-550 FTIR spectrometer as KBr pellets. NMR (^{1}H, ^{13}C) spectra were recorded on a Unity Varian spectrometer at 25 °C. Molecular weight and molecular weight distribution (PDI) were determined against a polystyrene standard by gel permeation chromatography (GPC) on a PL 50 apparatus, and THF was used as an eluent at a flow rate of 1.0 mL min^{-1} at 40 °C.

Synthesis of complex 1: $AlEt_3$ (1.50 mL, 2 M solution in toluene) was added to a solution of $[ONNO]H_2$ (1.06 g, 3.00 mmol) in 20 mL of THF at 0 °C. The reaction mixture warm slowly to room temperature, and was stirred overnight. The solution was concentrated to about 2 mL under vacuum, and then 15 mL of *n*-hexane was added. The precipitates were removed by centrifugation, and colorless crystalline solid was obtained at room temperature in a few days (0.87 g, 71%). Anal. calcd. for $C_{24}H_{33}AlN_2O_2$: C, 70.56; H, 8.14; N, 6.86. Found: C, 70.31; H, 8.08; N, 6.38%. ^{1}H

NMR (C_6D_6, 300MHz): δ 7.01 (s, 2H, Ar-H), 6.50 (s, 2H, Ar-H), 3.88 (d, *J* = 13.2 Hz, 2H, Ar-CH_2), 2.63, 2.59 (b, s, 2H, Ar-CH_2; 6H, CH_3; 4H, pip-CH), 2.31 (s, 6H, CH_3), 1.59-1.53 (t, 3H, Al-CH_2-CH_3), 1.51-1.44 (m, 2H, pip-CH), 1.11-1.01 (m, 2H, pip-CH), 0.18-0.10 (m, 2H, Al-CH_2). ^{13}C NMR (C_6D_6, 75 MHz): δ 157.40 (Ar-C), 131.70(Ar-CH), 128.86(Ar-CH), 126.93 (Ar-C), 124.41 (Ar-C), 119.29 (Ar-CH), 57.86 (CH_2), 50.10, 46.31 (pip-C), 20.78 (CH_3), 17.38 (CH_3), 10.97 (Al-CH_2-C), -0.15 (Al-C).

Synthesis of complex 2: $AlEt_3$ (4.50 mL, 2 M solution in toluene) was added slowly to a solution of [ONNO]H_2 (1.06 g, 3.00 mmol) in 20 mL of THF at 0 °C. The reaction mixture warm slowly to room temperature, and was stirred overnight. THF was evaporated completely under reduced pressure, and the solid resulted was washed with hexane (10.00 mL) for three times. The powder obtained was dissolved in hot toluene, and colorless crystals were obtained from a concentrate toluene solution (about 15 mL) at -5 °C in several days (1.43 g, 69%). Anal. calcd. for $C_{30}H_{48}Al_2N_2O_2$: C, 68.94; H, 9.26; N, 5.36. Found: C, 69.03; H, 9.52; N, 5.28%. ^1H NMR (C_6D_6, 300 MHz): δ 6.99 (d, *J* = 15.3 Hz, 2H, Ar-H), 6.46 (d, *J* = 15.9 Hz, 2H, Ar-H), 3.19 (b, 4H, Ar-CH_2), 2.51-2.42 (m, 4H, pip-CH; overlap with methyl signal), 2.41 (s, 6H, CH_3), 2.29 (s, 2H, CH_3), 2.18 (s, 4H, CH_3), 2.05-1.90 (m, 4H, pip-CH), 1.39-1.29 (m, 12H, Al-CH_2-CH_3), 0.18-0.03 (m, 8H, Al-CH_2). ^{13}C NMR (C_6D_6, 75 MHz): δ 156.56 (Ar-C), 133.27 (Ar-CH), 128.20 (Ar-CH, overlap with C_6D_6 signal), 127.84 (Ar-C), 126.12 (Ar-C), 118.26 (Ar-CH), 62.27 (CH_2), 50.56, 46.17 (pip-C), 20.64 (CH_3), 16.42 (CH_3), 9.57 (Al-CH_2-C), 1.29 (Al-CH_3).

Synthesis of complex 3: $AlMe_3$ (9.0 mL, 1 M solution in heptane) was added slowly to a solution of $[ONNO]H_2$ (1.06 g, 3.00 mmol) in 20 mL of THF at 0 °C. The reaction mixture warm slowly to room temperature, and was stirred overnight. THF was evaporated to about 1 mL under vacuum, and then 15 mL of toluene was added. The precipitate was removed by centrifugation. Colorless crystals were obtained at room temperature in several days (1.19 g, 85%). Anal. calcd. for $C_{26}H_{40}Al_2N_2O_2$: C, 66.93; H, 8.64; N, 6.00. Found: C, 66.58; H, 8.53; N, 5.99%. ^1H NMR (C_6D_6+THF-d_8, 300 MHz): δ 6.92 (s, 2H, Ar-H), 6.49 (s, 2H, Ar-H), 3.42 (br, 4H, Ar-CH_2), 2.44 (br, 8H, pip-CH), 2.28 (s, 6H, Me), 2.17 (s, 6H, Me), -0.60 (s, 12H, Al-CH_3). ^{13}C NMR (C_6D_6+ THF-d_8, 75 MHz): δ 156.15 (Ar-C), 132.82 (Ar-CH), 128.02 (Ar-CH), 127.93 (Ar-C), 125.88 (Ar-C), 118.55 (Ar-CH), 66.97 (THF-d8), 59.67 (CH_2), 48.37 (pip-C)，24.76 (THF-d_8), 20.47 (CH_3), 16.47 (CH_3), -9.13 (Al-CH_3).

Typical polymerization procedures: The procedures for the polymerization of ε-CL initiated by complexes **2** and **3** were similar, and a typical polymerization procedure is given below. A 50 mL Schlenk flask, equipped with a magnetic stirring bar, was charged with the desired amount of initiator and BnOH in a toluene solution. The solution was stirred for 2 min in glovebox at room temperature, and then desired amount of toluene along and desired amount of ε-CL were added to the solution, respectively. The reaction mixture was quickly placed into an oil bath pre-heated at 60 °C, and the solution was stirred for the prescribed time, during which time an increase in viscosity was observed. The reaction mixture was quenched by the addition of 1M HCl-ethanol solution, and then poured into methanol to precipitate the polymer, which was dried under vacuum and weighted.

Preparation of oligomers for end-group analysis. With a monomer-to-initiator ratio of 10, the oligomers were prepared in toluene at 60 °C, terminated with 10% HCl-H_2O and precipitated with hexane from THF several times. The oligomers were then dried under vacuum to constant weight.

NMR experiments. Under argon atmosphere, **2** (10 mg, 0.019 mmol) was placed in an NMR tube, and 0.4 mL of C_6D_6 was added. ε-CL (0.021 mL, 0.19 mmol) was then introduced. The reaction mixture was quickly placed into an oil bath pre-heated at 60 °C, followed by NMR analysis after 1.5 h and 8.5 h.

X-Ray crystallography. Suitable single crystals of complexes **1–3** were sealed in a thin-walled glass capillary for determining the single-crystal structure. Intensity data were collected with a Rigaku Mercury CCD area detector in ω scan mode using Mo Kα radiation (λ = 0.71070 Å). The diffracted intensities were corrected for Lorentz polarization effects and empirical absorption corrections.

The structures were solved by direct methods and refined by full-matrix least-squares procedures based on $|F|^2$. All of the non-hydrogen atoms were refined anisotropically. All of the hydrogen atoms were held stationary and included in the structure factor calculation in the final stage of full-matrix least-squares refinement. The structures were solved and refined using *SHELEXL-97* programs.

Structure of complex 1. The boat conformation of the piperazidine ring in complex **1**, different from that in the dinuclear complexes **2** and **3**, might be contributed to the formation of the mononuclear aluminum alkyl complex. The aluminum metal center is five-coordinated by two oxygen atoms, two nitrogen atoms from the bis(phenolate) ligands, and one carbon atom from the ethyl group. The coordination geometry at the central metal can be best described as a distorted square based pyramidal geometry if the η^4-coordinated piperazidine-based ligand (N_2O_2) is considered to occupy the base of the pyramid and the ethyl group occupies the axial position, which is different from those observed in complexes **2** and **3**. The Al–O bond distances are 1.760(16) and 1.791(17) Å, respectively, and the Al–C bond distance is 1.980(2) Å, which are comparable with the corresponding values in complexes **2** and **3**. The bond lengths of Al–N1 and Al–N2 are 2.082(19) and 2.185(2) Å, respectively, giving the average 2.133(5) Å, which is slightly larger than the corresponding bond lengths in the dinuclear complexes **2** and **3**, reflecting the increased steric congestion because of the formation of the mononuclear structure.

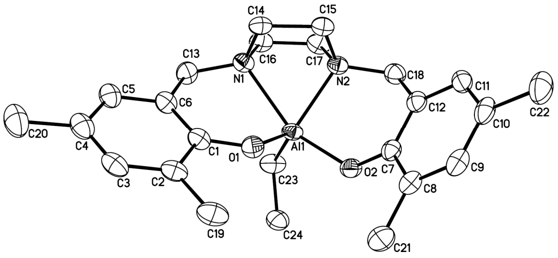

Fig. S1 ORTEP diagram of complex **3**. Thermal ellipsoids are draw at the 20% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Al1–O1 1.760(16), Al1–O2 1.791(17), Al1–C23 1.980(2), Al1–N2 2.082(19), Al1–N1 2.185(2).

Reference

(1) Tshuva, E. Y.; Goldberg, I.; Kol, M. *Organometallics* **2001**, *20*, 3017.

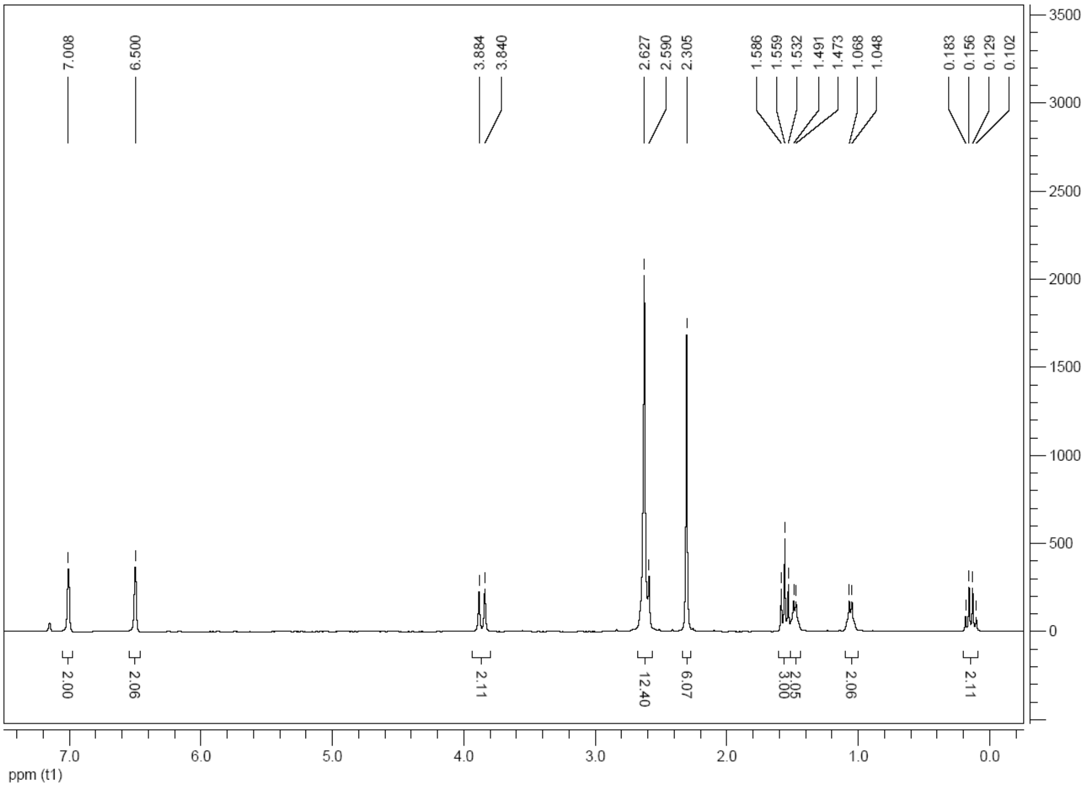

Figure **S2**. ^{1}H NMR spectrum of complex **1**

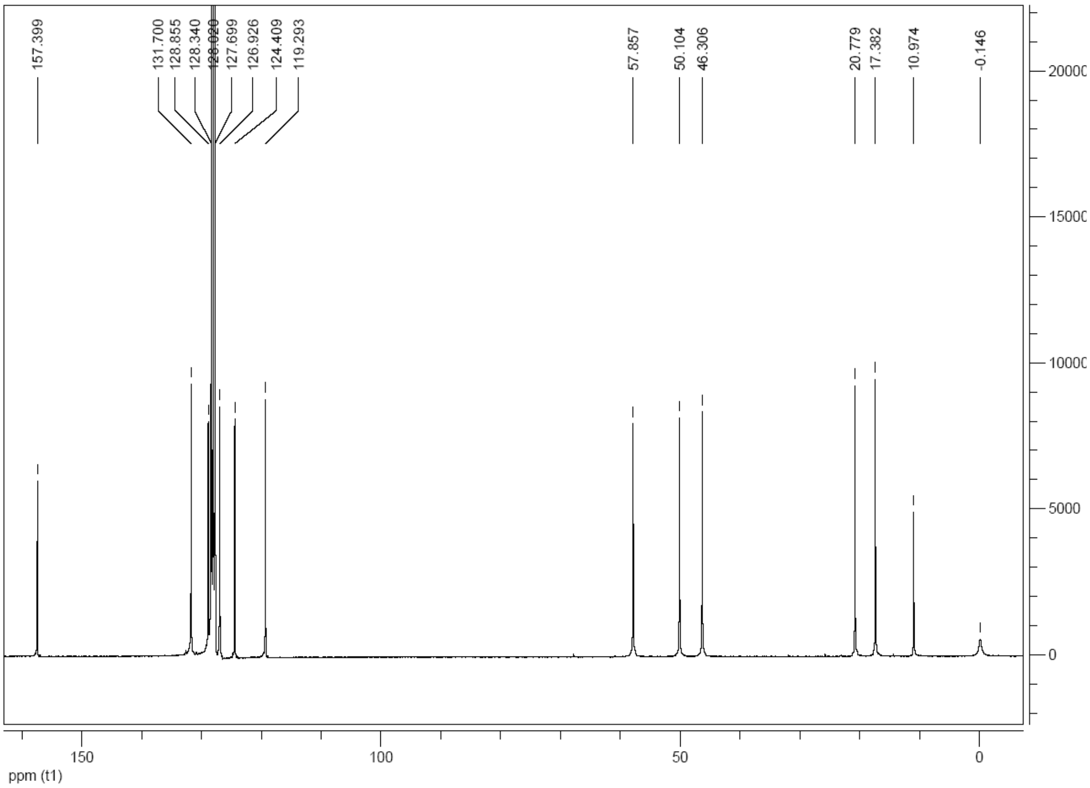

Figure **S3**. ^{13}C NMR spectrum of complex **1**

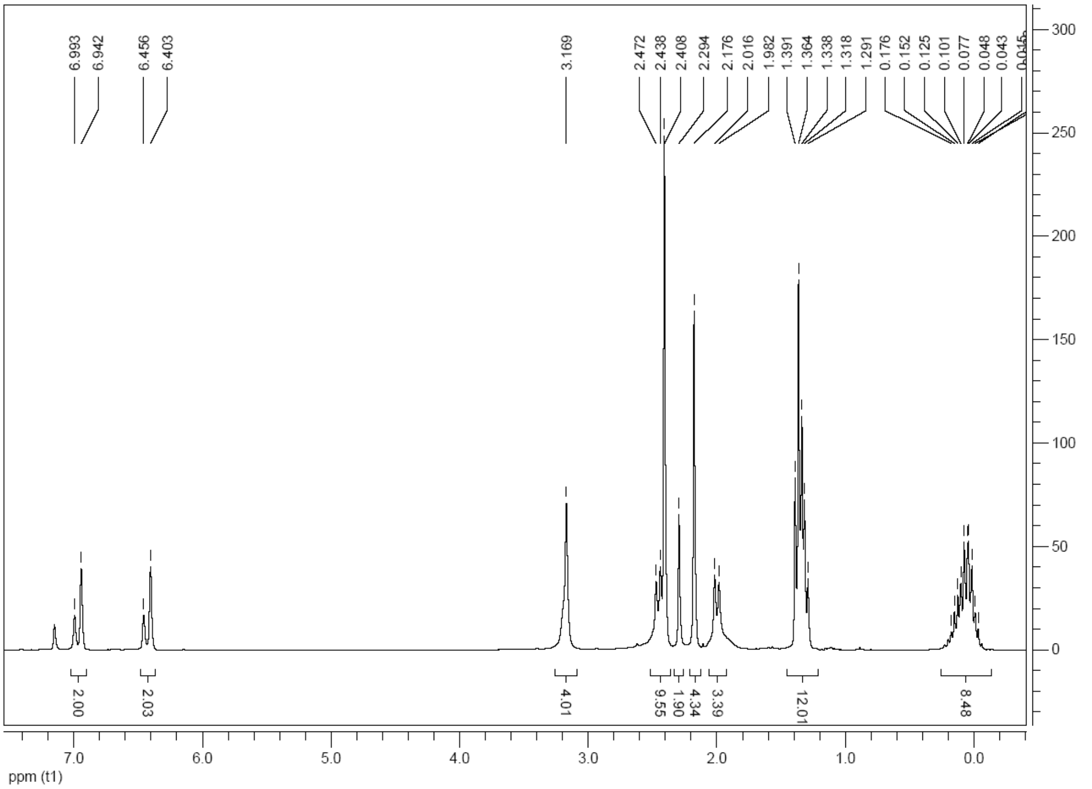

Figure **S4**. ^{1}H NMR spectrum of complex **2**

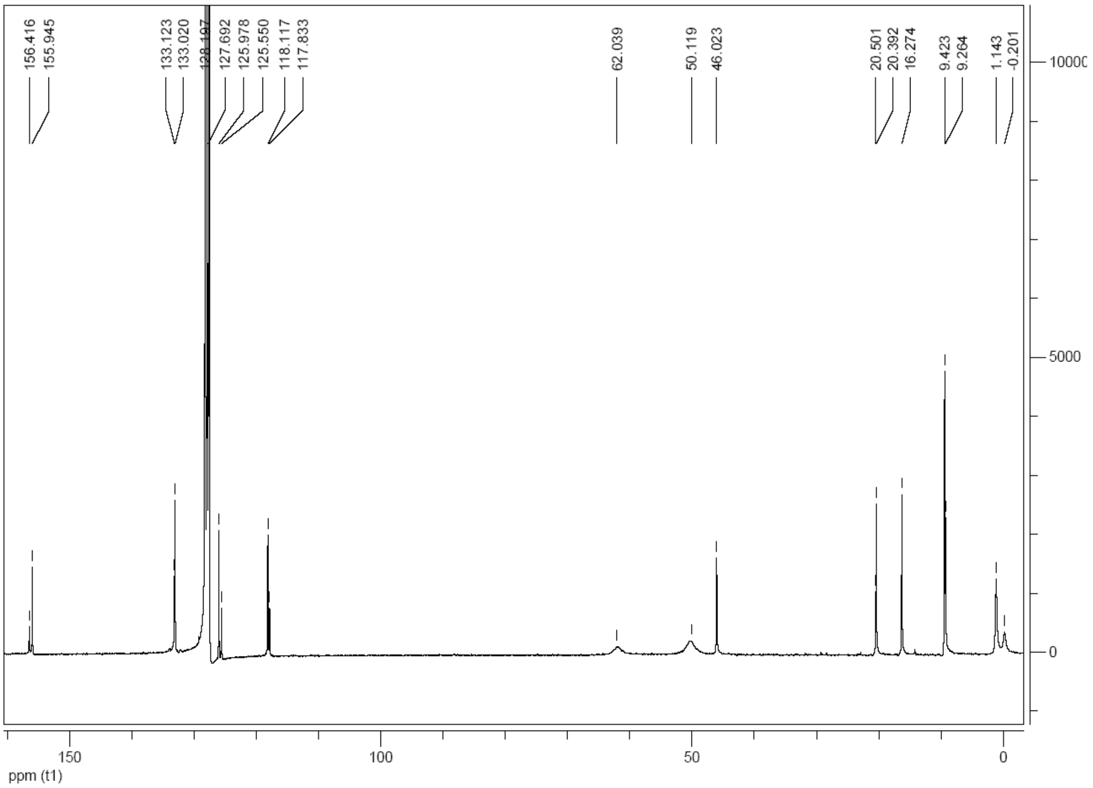

Figure **S5**. ^{13}C NMR spectrum of complex **2**

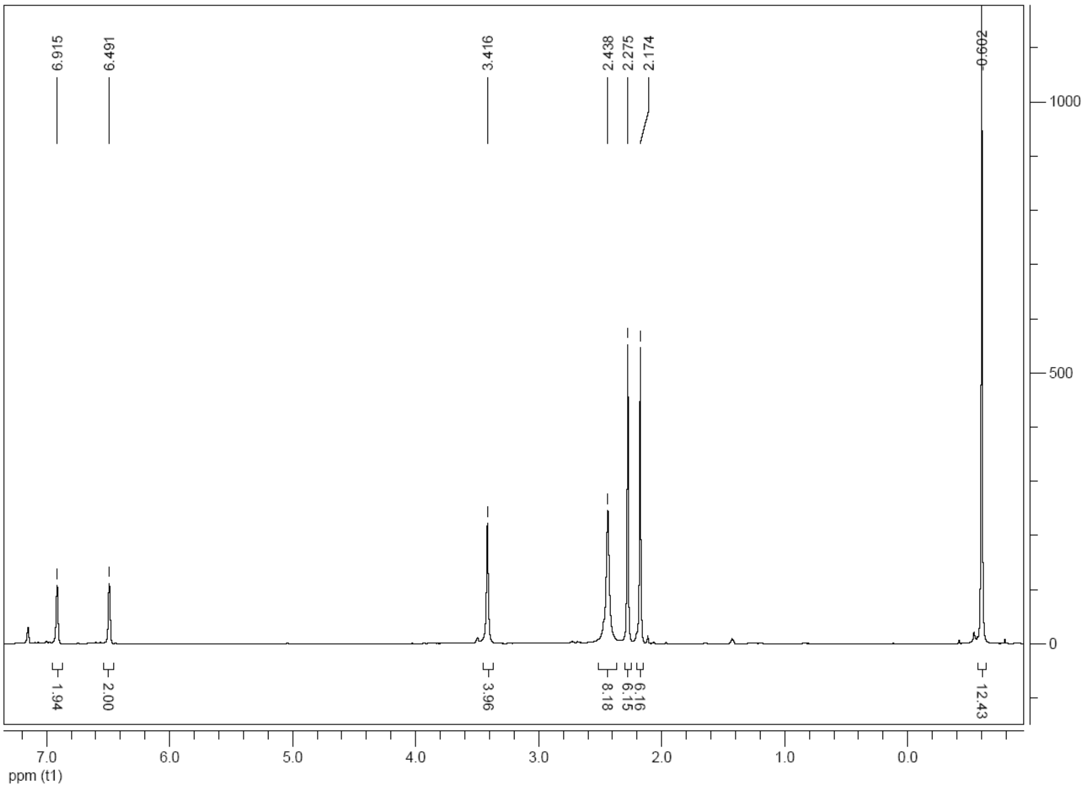

Figure **S6**. ^{1}H NMR spectrum of complex **3**

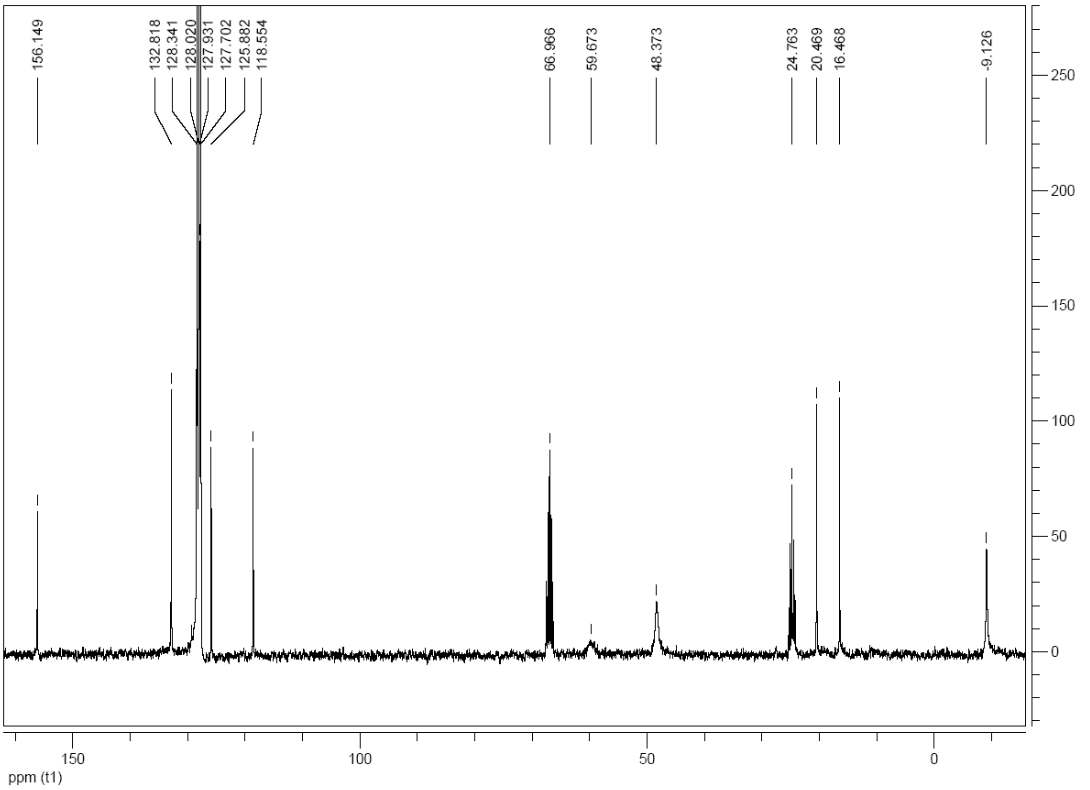

Figure **S7**. ^{13}C NMR spectrum of complex **3**

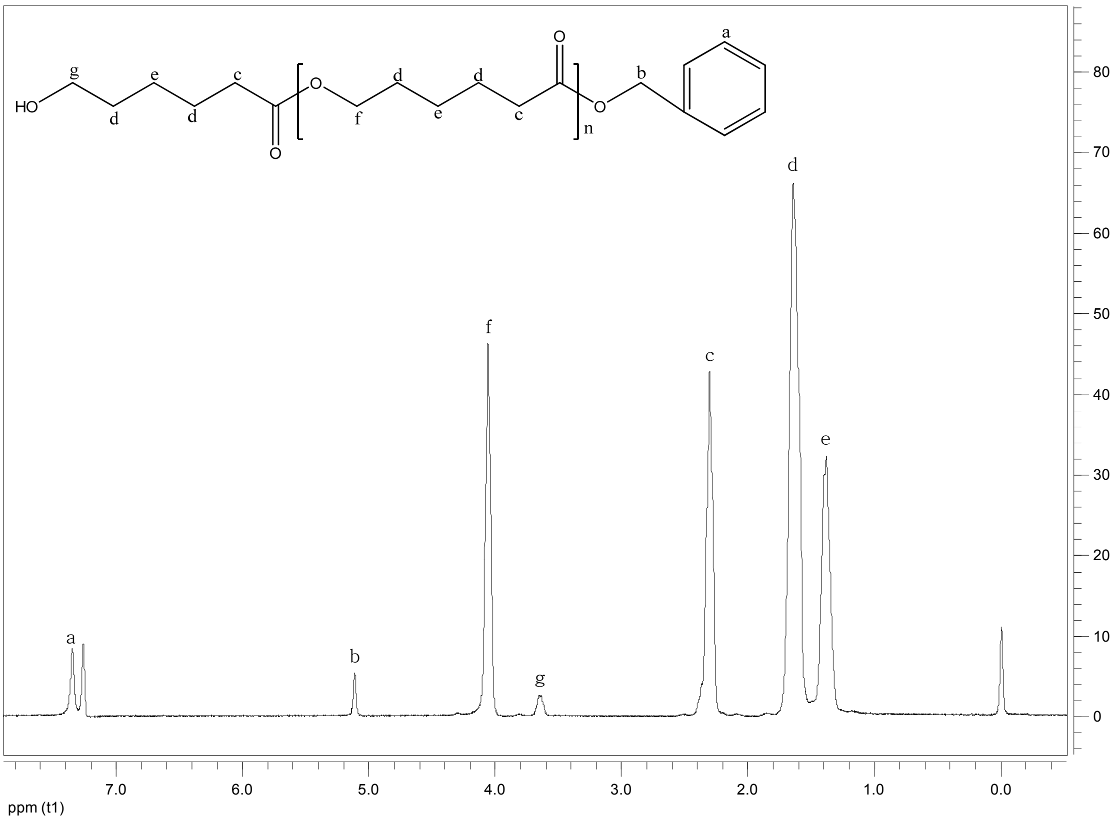

Figure **S8**. ^{1}H NMR spectrum of PCL-10 initiated by complex **2**/BnOH in the $CDCl_3$

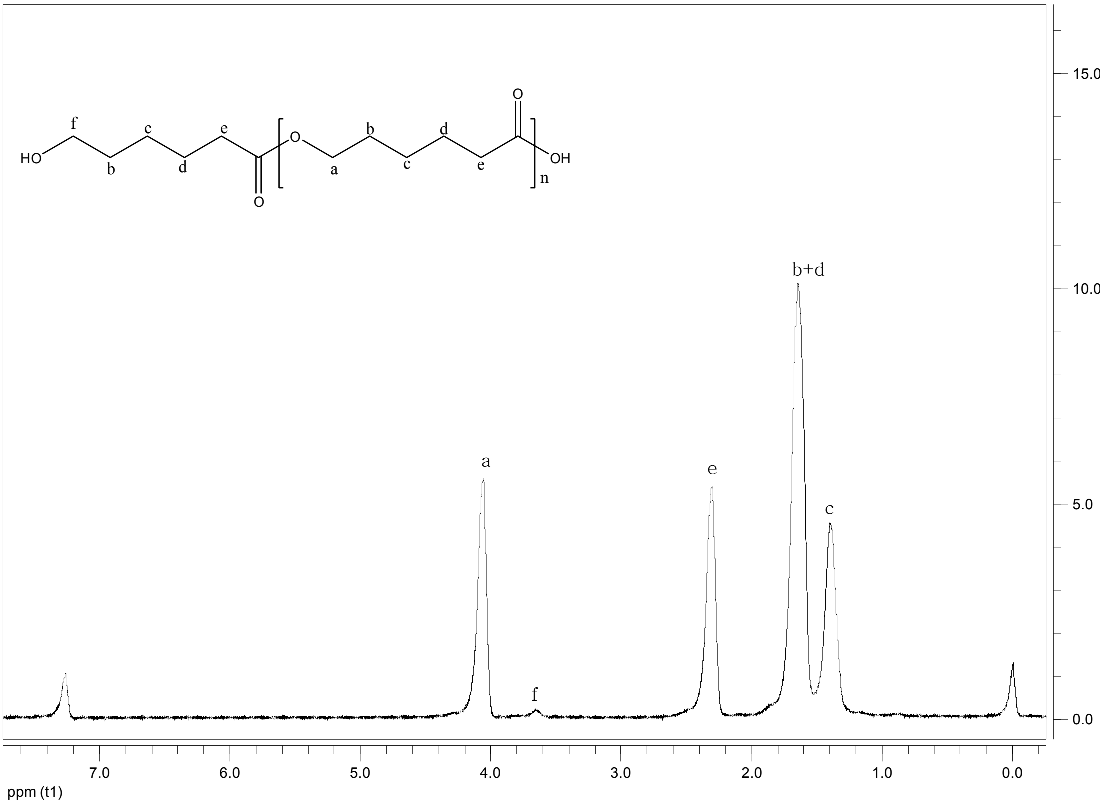

Figure **S9**. ^{1}H NMR spectrum of PCL-10 initiated by complex **2** in the $CDCl_3$

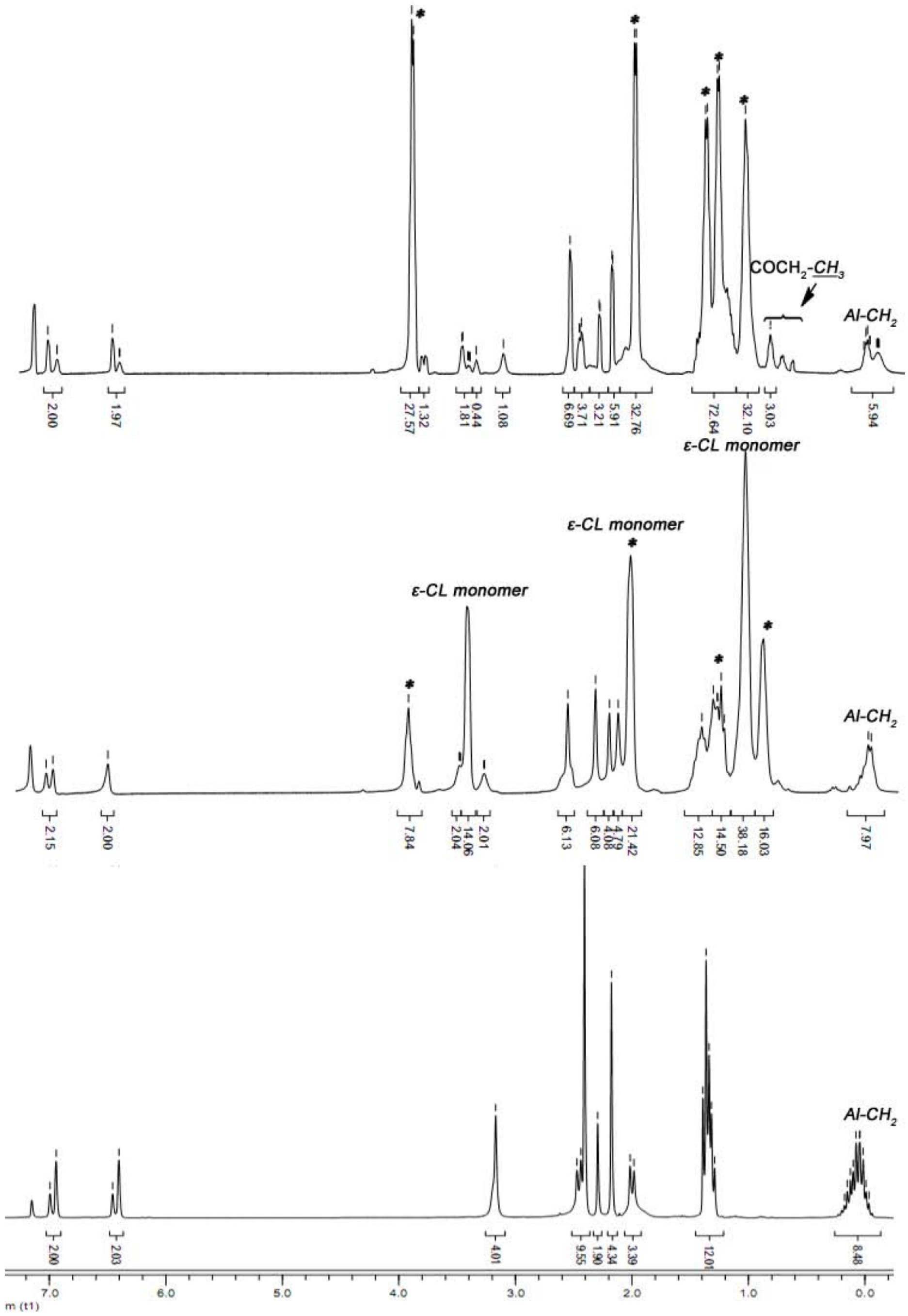

Figure **S10**. ^{1}H NMR spectra in C_6D_6 for **2** (bottom), reaction of **2** + 10 ε-CL after 1.5 h (middle), and reaction of **2** + 10 ε-CL after 8.5 h (top).