

Electronic Supplementary Information for

Synthesis and Characterization of Neutral and Cationic Aluminum
Complexes Supported by Furfuryl-Containing Aminophenolate
Ligand for Ring-Opening Polymerization of ϵ -Caprolactone

Jiraya Kiriratnikom^a, Sucheewin Chotchatchawankul^b, Setsiri Haesuwannakij^b,

Supavadee Kiatisevi^a and Khamphee Phomphrai^{,b}*

^aDepartment of Chemistry, Faculty of Science, Mahidol University, Rama 6 Road, Bangkok,
10400, Thailand.

^bDepartment of Materials Science and Engineering, School of Molecular Science and
Engineering, Vidyasirimedhi Institute of Science and Technology (VISTEC), Rayong, 21210,
Thailand.

Tel: +(66) 33-014-444; *E-mail: khamphee.p@vistec.ac.th

New Journal of Chemistry 2018

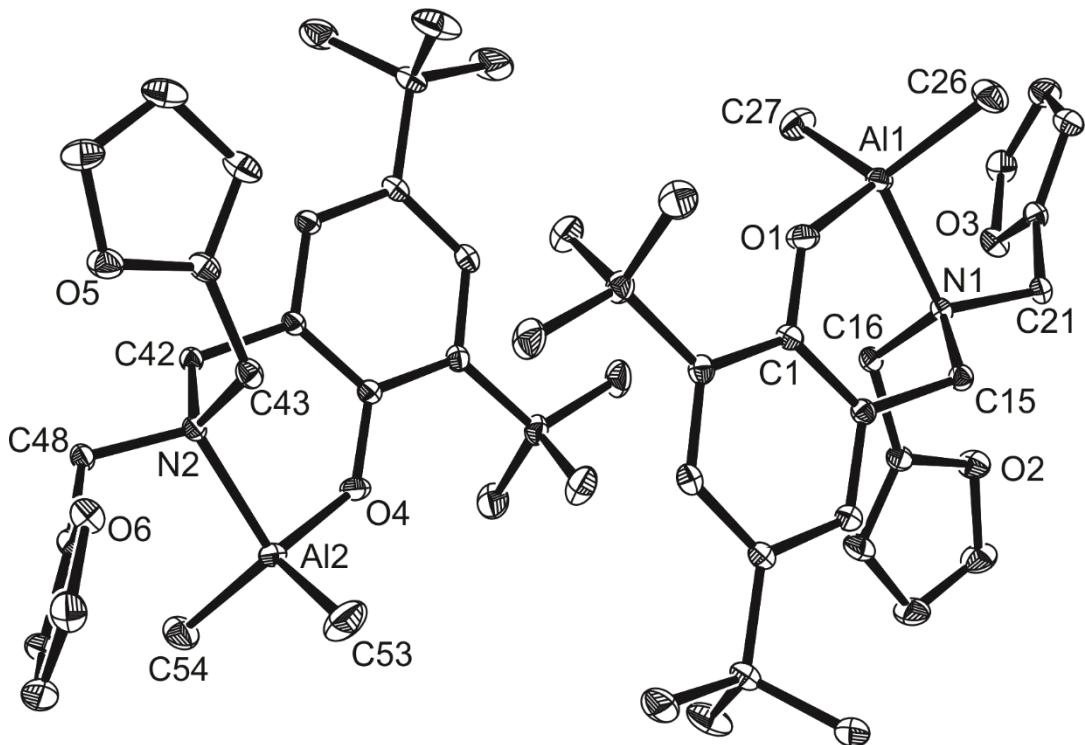


Fig. S1 X-ray crystal structure of LAlMe_2 (**1**) with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

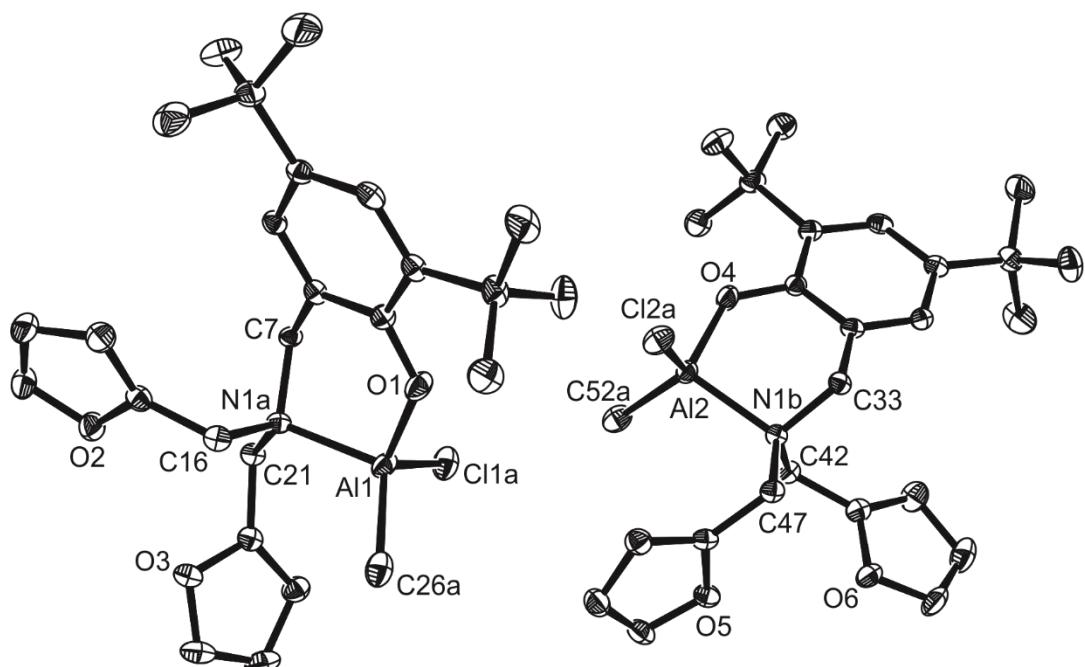


Fig. S2 X-ray crystal structure of LAlMeCl (**2**) with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

Table S1 Selected bond angles (deg) and bond length (Å) for complexes **1** and **2**

| 1 | | 2 | |
|-------------|----------|---------------|----------|
| O1-Al1-C26 | 108.3(1) | O1-Al1-C26a | 116.2(1) |
| O1-Al1-N1 | 96.16(4) | O1-Al1-N1a | 98.29(7) |
| C26-Al1-N1 | 108.2(1) | C26a-Al1-N1a | 112.6(1) |
| O1-Al1-C27 | 112.2(1) | O1-Al1-Cl1a | 107.4(1) |
| C27-Al1-C26 | 120.8(1) | C26a-Al1-Cl1 | 115.4(1) |
| C27-Al1-N1 | 108.4(1) | N1a-Al1-Cl1a | 105.3(1) |
| O4-Al2-C53 | 112.6(1) | O4-Al2-C52a | 110.6(1) |
| O4-Al2-C54 | 107.7(1) | O4-Al2-N1b | 98.01(7) |
| C53-Al2-C54 | 121.0(1) | C52a-Al2-N1b | 109.3(1) |
| O4-Al2- N2 | 96.47(4) | O4-Al2-Cl2a | 107.5(1) |
| C53-Al2-N2 | 107.9(1) | C52a-Al2-Cl2a | 123.5(1) |
| C54-Al2-N2 | 108.3(1) | N1b-Al2-Cl2a | 104.9(1) |
| Al1-O1 | 1.764(1) | Al1-O1 | 1.730(2) |
| Al1-C27 | 1.966(1) | Al1-Cl1a | 2.139(1) |
| Al1-C26 | 1.973(1) | Al1-C26a | 1.961(4) |
| Al1-N1 | 2.045(1) | Al1-N1a | 2.004(2) |
| Al2-O4 | 1.761(1) | Al2-Cl2a | 2.138(1) |
| Al2-C53 | 1.967(2) | Al2-O4 | 1.735(2) |
| Al2-C54 | 1.973(2) | Al2-C52a | 2.021(4) |
| Al2-N2 | 2.041(1) | Al2-N1b | 2.009(2) |

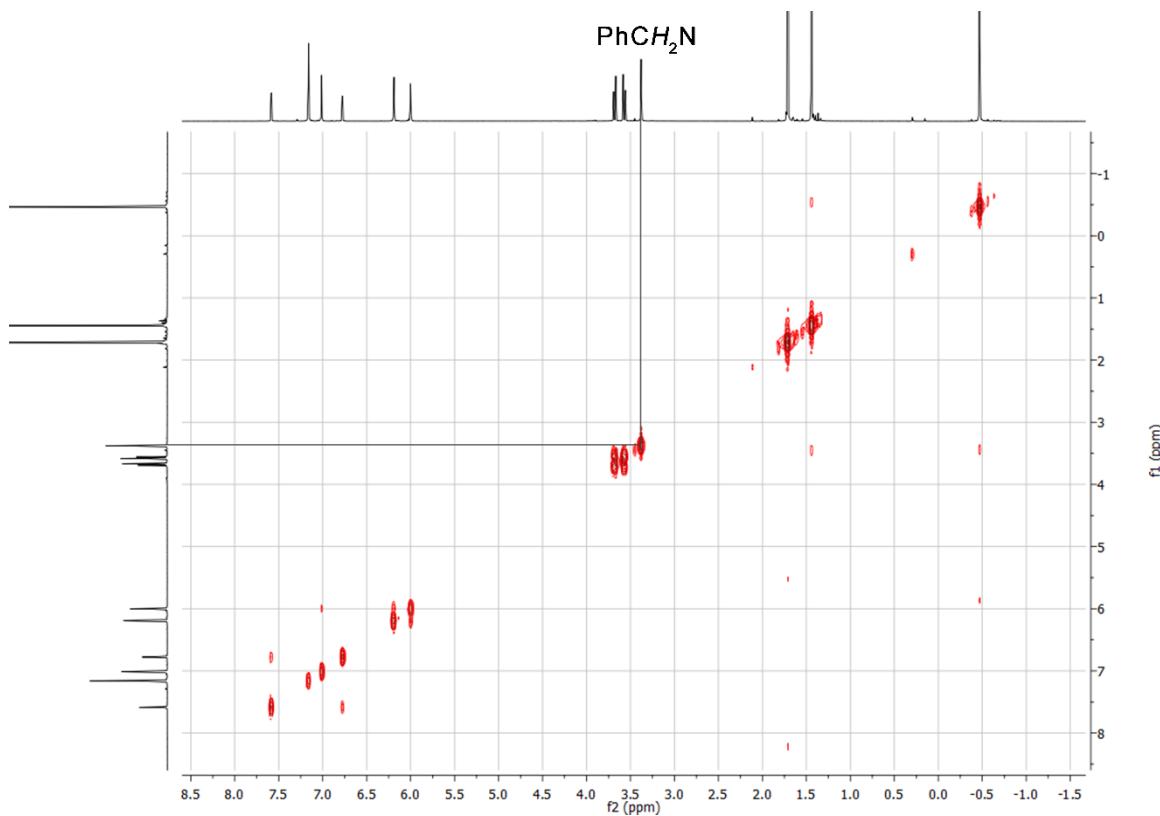


Fig. S3 A 2D COSY NMR of LAlMe₂ (**1**) in C₆D₆ at 30 °C.

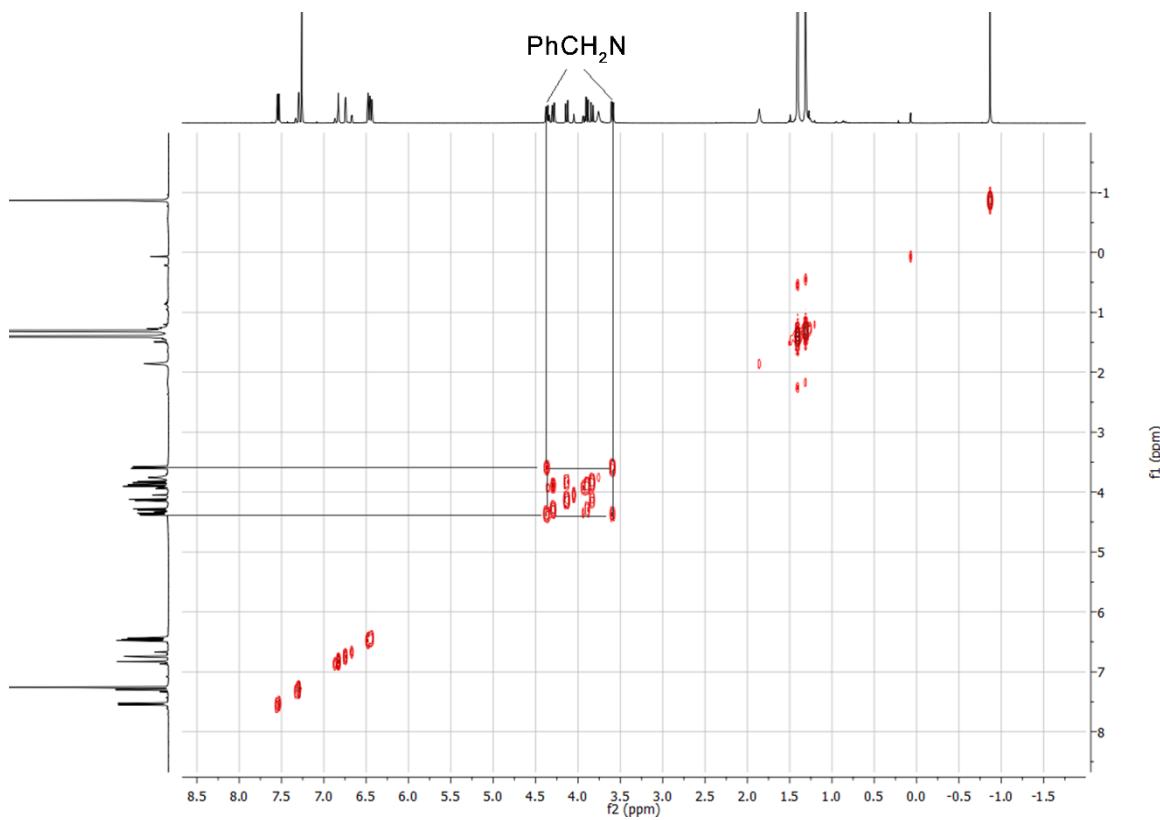


Fig. S4 A 2D COSY NMR of LAlMeCl (**2**) in CDCl₃ at 30 °C.

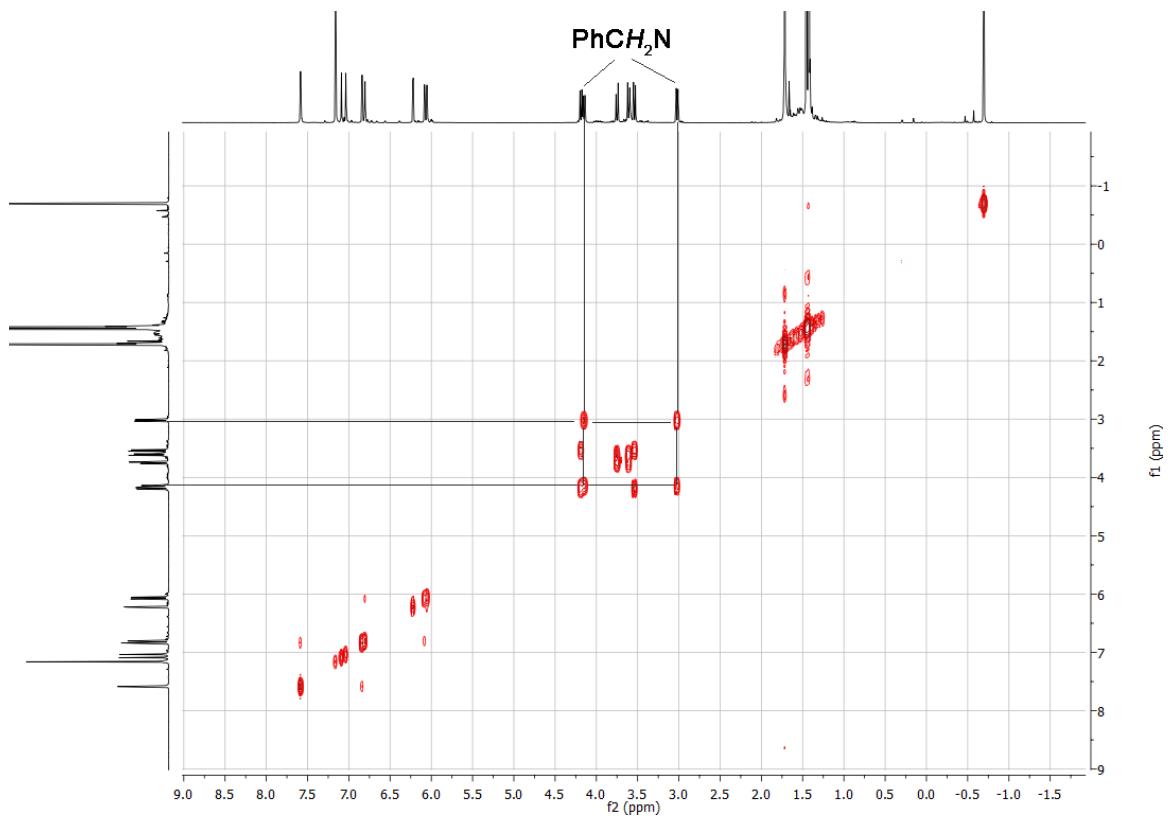


Fig. S5 A 2D COSY NMR of LAlMeO'Bu (**3**) in C_6D_6 at 30 °C.

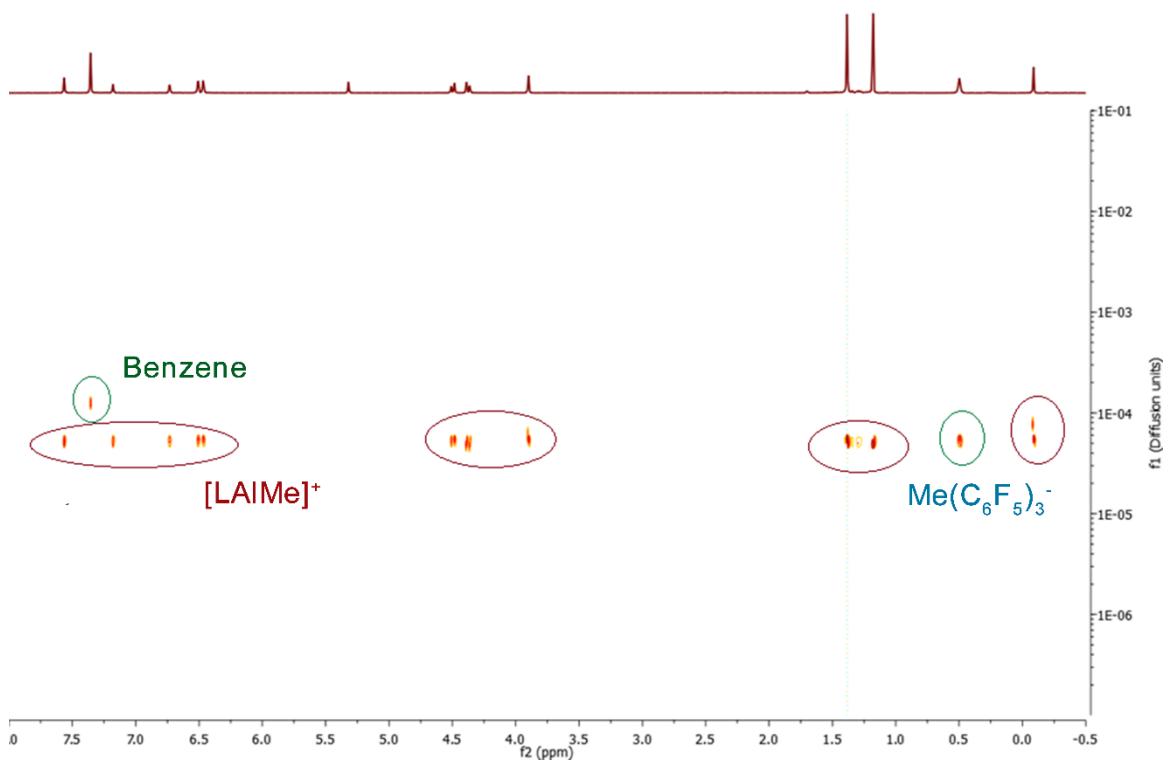


Fig. S6 A diffusion-ordered spectroscopy (DOSY) NMR of $[\text{LAlMe}][\text{MeB}(\text{C}_6\text{F}_5)_3]$ (**4**) in CD_2Cl_2 at 30°C using benzene and $[\text{MeB}(\text{C}_6\text{F}_5)_3]$ as internal standard.

Table S2 Diffusion coefficient (D), estimated molecular mass (m) and molecular weight of monomeric (FW) and dimeric species (FW2)

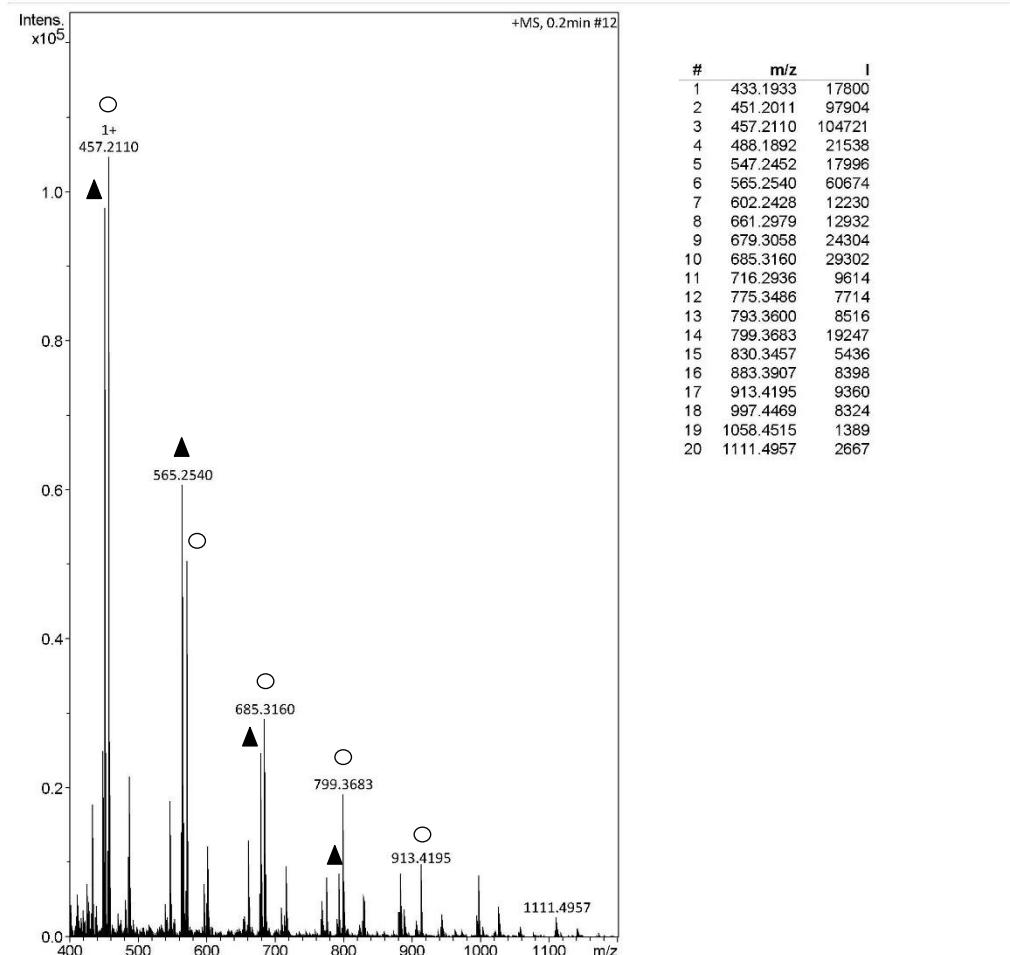
| Complex | $D (\times 10^{-9} \text{ m}^2 \text{ s}^{-1})$ | $D_{\text{benzene}} (\times 10^{-9} \text{ m}^2 \text{ s}^{-1})$ | m ^a (Da) | FW (Da) | FW2 (Da) |
|--------------------|---|--|------------------------|------------|-------------|
| $[\text{LAlMe}]^+$ | 1.269 | 2.886 | 578 | 436 | 872 |

^aEstimated molecular mass using benzene as internal reference species

| Analysis Info | | Acquisition Date 3/22/2017 5:43:06 PM | |
|---------------|--|---------------------------------------|-----------------------|
| Analysis Name | D:\Data\VISTEC Data QTOF\KPLab\Jiraya\60-03-2201_10-1CL-AlMe2t-Bu+BCF+BnOH 15 min CH2Cl2.d | | |
| Method | APCI_DirectProbe.m | Operator | VISTEC_Scientist |
| Sample Name | 60-03-2201_10-1CL-AlMe2t-Bu+BCF+BnOH 15 min CH2Cl | Instrument | compact 8255754.20068 |
| Comment | | | |

Acquisition Parameter

| | | | | | |
|-------------|------------|----------------------|----------|------------------|-----------|
| Source Type | APCI | Ion Polarity | Positive | Set Nebulizer | 2.0 Bar |
| Focus | Not active | Set Capillary | 4000 V | Set Dry Heater | 220 °C |
| Scan Begin | 100 m/z | Set End Plate Offset | -500 V | Set Dry Gas | 5.0 l/min |
| Scan End | 4000 m/z | Set Charging Voltage | 2000 V | Set Divert Valve | Source |
| | | Set Corona | 4000 nA | Set APCI Heater | 450 °C |



60-03-2201_10-1CL-AlMe2t-Bu+BCF+BnOH 15 min CH2Cl2.d
Bruker Compass DataAnalysis 4.3 printed: 8/16/2017 10:10:18 AM by: VISTEC Page 1 of 1

Fig. S7 ESI mass spectra of PCL synthesized from ε-CL: **5**: BnOH = 10:1:1 at room temperature where ○ = [CL]_n + H⁺ and ▲ = BnO[CL]_nH + H⁺.

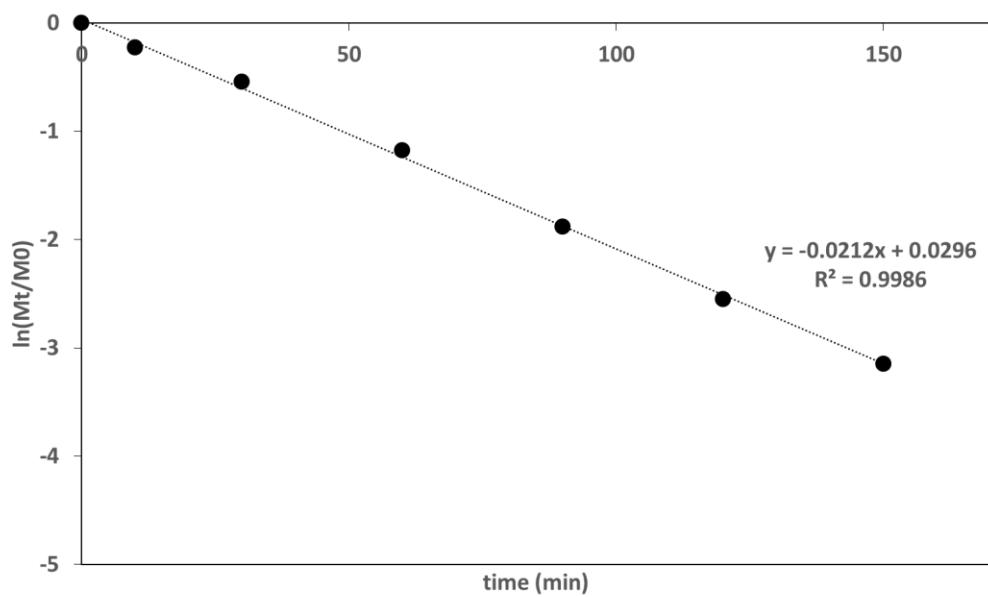


Fig. S8 Plot of $\ln([CL]/[CL]_0)$ vs time for the polymerization of 100 equiv of ε -CL using complex **5**/benzyl alcohol at room temperature.