Supporting Information

Ring-Opening Polymerization of Lactide using Chiral Salen Aluminum Complexes as Initiators: High Productivity and Stereoselectivity

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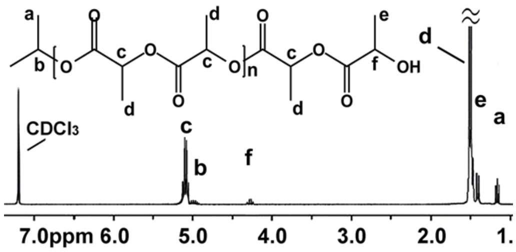

Figure S1. ^{1}H NMR spectrum of poly(L-LA) oligomer catalyzed by the complex **3**, $[LA]_0/[\mathbf{3}]_0$ = 12/1.

Synthesis of pro-ligands

General procedure: An oven dried 250 mL, three-necked flask equipped with a magnetic bar, a reflux condenser, and an addition funnel was in turn charged with (R,R)-1,2-diammonium-cyclohexane mono-(+)-tartrate salt (3.96 g, 15.0 mmol), anhydrous potassium carbonate (4.14 g, 30.0 mmol), and 20 mL of pure water. This mixture was stirred 10 min, and then 80 mL of ethanol was added. The resultant cloudy mixture was heated to reflux for 1.0 h, and salicylaldehyde-modified (30.0 mmol) dissolved in 30 mL ethanol was added slowly. Subsequently, the mixture was refluxed with stirring for 2.5 h and then cooled to ca. 4 °C. Yellow precipitates produced when water was poured into the mixture. The crude product was attained through filtration and then dissolved in CH_2Cl_2 (25 mL) and in turn washed with water (10 mL×2) and brine (15 mL×2). After the solvent was evaporated in vacuo, the pure products were acquired in 86.5–91.4% yields.

Pro-ligand L1: ^{1}H NMR (300 MHz, $CDCl_3$) δ 13.01 (bs, 2H, O*H*), 8.37 (s, 2H, N=C*H*), 7.51 (d, J = 7.8 Hz, 2H, Ph*H*), 7.28 (d, J = 7.5 Hz, 2H, Ph*H*), 6.82 (t, J = 7.6 Hz, 2H, Ph*H*), 3.91–3.72(m, 2H, N-C*H*-), 2.18–2.37 (m, 4H, $(CH_2)_2$), 1.69–1.82 (m, 2H, CH_2), 1.42 (s, 18 H, $C(CH_3)_3$), 1.12–1.31 (m, 4H, $(CH_2)_2$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.14 (2C, N=*C*H), 160.22 (2C, Ph*C*), 144.79 (2C, Ph*C*), 128.90 (2C, Ph*C*), 127.32 (2C, Ph*C*), 123.67 (2C, Ph*C*), 118.85 (2C, Ph*C*), 63.96 (2C, N-*C*H-), 35.68 (2C, $C(CH_3)_3$), 30.10 (2C, $(CH_2)_2$), 29.56 (6C, $C(CH_3)_3$), 25.19 ppm (2C, $(CH_2)_2$). Anal. Calcd for $C_{28}H_{38}N_2O_2$ (%): C, 77.38; H, 8.81; N, 6.45. Found: C, 77.36; H, 8.78; N, 6.43. MS, (EI) m/z: calcd. for $C_{28}H_{38}N_2O_2$ [M]+ 434.29. Found: 434.22.

Pro-ligand L2: ^{1}H NMR (300 MHz, $CDCl_3$) δ 13.75 (bs, 2H, O*H*), 8.57 (s, 2H, N=C*H*), 7.65 (s, 2H, Ph*H*), 7.54 (s, 2H, Ph*H*), 3.80–3.76 (m, 2H, N-C*H*-), 2.52–1.44 (m, 8H, $(CH_2)_4$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.23 (2C, N=*C*H), 162.79 (2C, Ph*C*), 138.35 (2C, Ph*C*), 132.47 (2C, Ph*C*), 128.33 (2C, Ph*C*), 123.60 (2C, Ph*C*), 118.41 (2C, Ph*C*), 69.92 (2C, N-*C*H-), 31.45 (2C, $(CH_2)_2$), 27.50 ppm (2C, $(CH_2)_2$). Anal. Calcd for $C_{20}H_{18}Cl_4N_2O_2$ (%): C, 52.20; H, 3.94; N, 6.09. Found: 52.22; H, 3.90; N, 6.10. MS, (EI) m/z: calcd. for $C_{20}H_{18}Cl_4N_2O_2$ [M]+ 458.02. Found: 458.10.

Pro-ligand L3: ^{1}H NMR (300 MHz, $CDCl_3$) δ 13.32 (bs, 2H, O*H*), 8.33 (s, 2H, N=C*H*), 7.55 (d, J = 6.2 HZ, 2H, Ph*H*), 7.31 (d, J = 6.2 HZ, 2H, Ph*H*), 3.93–3.74 (m, 2H, N-C*H*-), 1.49 (s, 18H, $C(CH_3)_3$), 2.23–1.39 (m, 8H, $(CH_2)_4$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.96 (2C, N=*C*H), 165.79 (2C, Ph*C*), 147.37 (2C, Ph*C*), 131.78 (2C, Ph*C*), 130.89 (2C, Ph*C*), 124.63 (2C, Ph*C*), 121.87 (2C, Ph*C*), 64.32 (2C, N-*C*H-), 36.77 (2C, $C(CH_3)_3$), 30.65 (2C, $(CH_2)_2$), 30.20 (6C, $C(CH_3)_3$), 28.59 ppm (2C, $(CH_2)_2$). Anal. Calcd for $C_{28}H_{36}Cl_2N_2O_2$ (%): C, 66.79; H, 7.21; N, 5.56. Found: C, 66.76; H, 7.19; N, 5.54. MS, (EI) m/z: calcd. for $C_{28}H_{36}Cl_2N_2O_2$ [M]+ 502.22. Found: 502.25.

Complex 3: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.32 (s, 1H, N=C*H*), 8.07 (s, 1H, N=C*H*), 7.36 (d, J = 2.8 Hz, 1H, Ph*H*), 7.33 (d, J = 2.8 Hz, 1H, Ph*H*), 7.12 (d, J = 2.8 Hz, 1H, Ph*H*), 7.09 (d, J = 2.8 Hz, 1H, Ph*H*), 3.94–3.86 (m, 1H, N-C*H*-), 3.65 (sept, J = 6.1 Hz, 1H, OC*H*$(CH_3)_2$), 3.13–3.09 (m, 1H, N-C*H*-), 2.58–2.52 (m, 1H, CH_2), 2.39–2.32 (m, 1H, CH_2), 2.09–2.05 (m, 2H, CH_2), 1.50 (s, 9H, C(CH_3)$_3$), 1.47 (s, 9H, C(CH_3)$_3$), 1.44–1.38 (m, 4H, (CH_2)$_2$), 0.87 (d, J = 6.0 Hz, 3H, OCH(CH_3)$_2$), 0.83 ppm (d, J = 6.0 Hz, 3H, OCH(CH_3)$_2$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.03 (1C, N=*C*H), 164.89 (1C, N=*C*H), 163.42 (1C, Ph*C*), 161.78 (1C, Ph*C*), 144.27 (1C, Ph*C*), 144.01 (1C, Ph*C*), 130.80 (1C, Ph*C*), 130.73 (1C, Ph*C*), 130.48 (1C, Ph*C*), 130.09 (1C, Ph*C*), 121.04 (1C, Ph*C*), 120.60 (1C, Ph*C*), 120.21 (1C, Ph*C*), 119.87 (1C, Ph*C*), 63.41 (1C, N-*C*H-), 62.86 (1C, O*C*H(CH_3)$_2$), 62.62 (1C, N-*C*H-), 35.94 (1C, *C*(CH_3)$_3$), 35.63 (1C, *C*(CH_3)$_3$), 30.04 (1C, *C*H_2), 29.88 (1C, *C*H_2), 29.81 (3C, C(*C*H_3)$_3$), 29.74 (3C, C(*C*H_3)$_3$), 27.84 (1C, *C*H_2), 27.62 (1C, *C*H_2), 27.47 (1C, OCH(*C*H_3)$_2$), 27.22 ppm (1C, OCH(*C*H_3)$_2$). Anal. Calcd for $C_{31}H_{41}AlCl_2N_2O_3$ (%): C, 63.37; H, 7.03; N, 4.77. Found: C, 63.34; H, 7.00; N, 4.75.

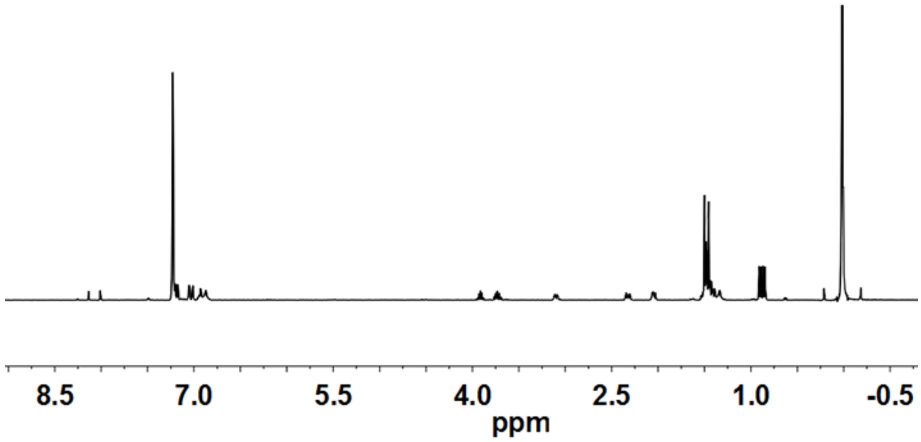

Figure S2. ^{1}H spectrum for Al complex **1**.

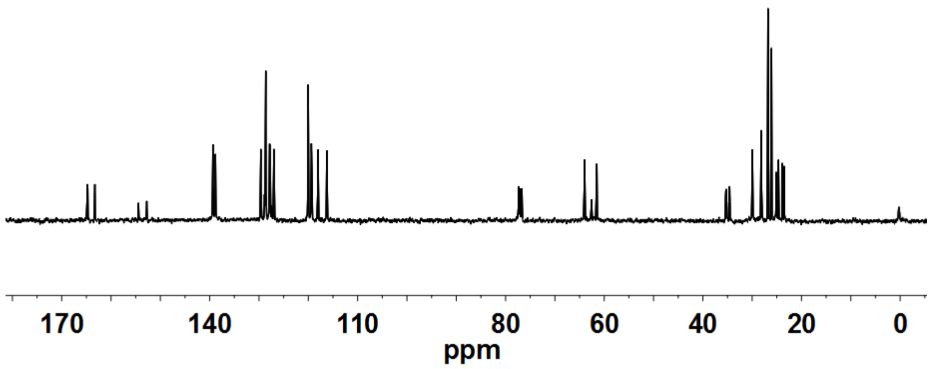

Figure S3. ^{13}C spectrum for Al complex **1**.

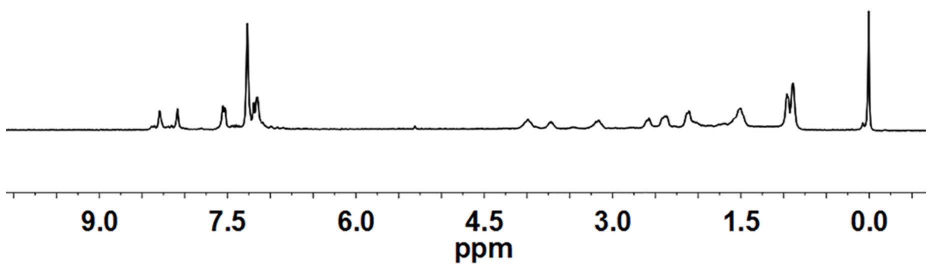

Figure S4. ^{1}H spectrum for Al complex **2**.

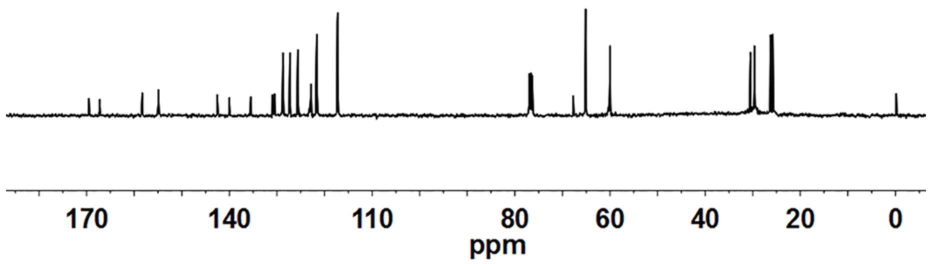

Figure S5. ^{13}C spectrum for Al complex **2**.

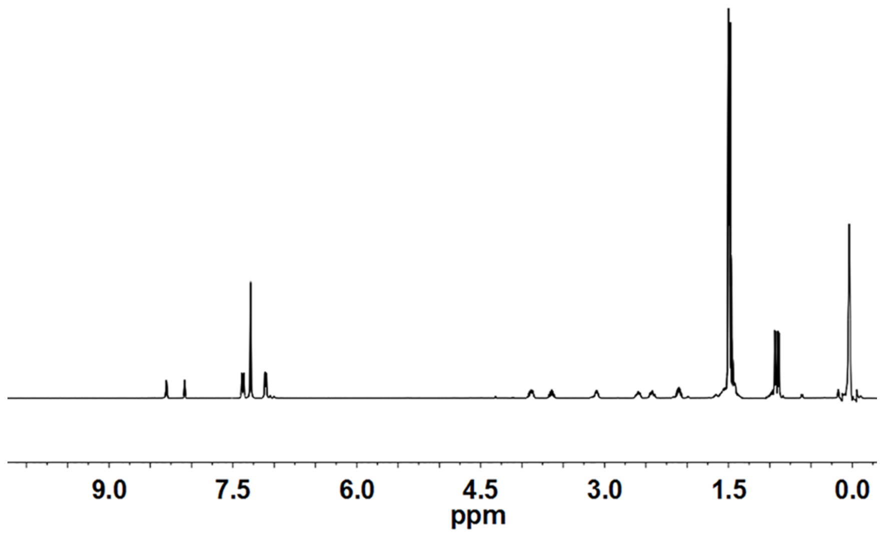

Figure S6. ^{1}H spectrum for Al complex **3**.

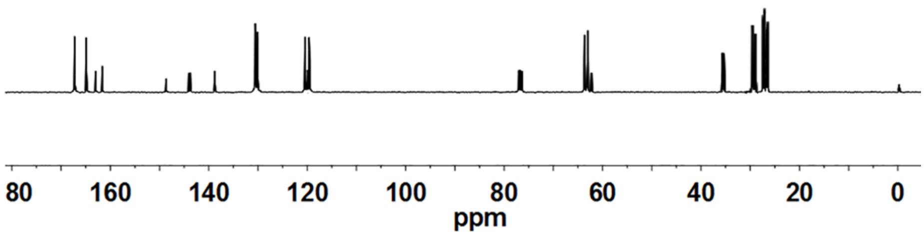

Figure S7. ^{13}C spectrum for Al complex **3**.