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Supplementary Material

Magnesium alkoxide complexes of (benzimidazolylmethyl)amino ligands: Synthesis and applications in ring-opening polymerization reactions of ε-caprolactone and lactides

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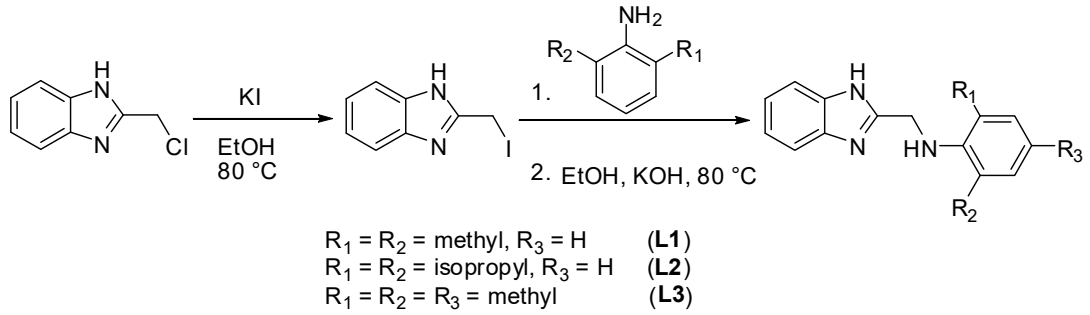
Typical procedure for the synthesis of (benzimidazolylmethyl) amine ligands



Scheme S1 : Synthesis of (benzimidazolylmethyl)amine ligands **L1**–**L3**.

The starting materials, 2-(chloromethyl)benzimidazole (1 mole equivalent), and equimolar quantities of KI and the respective amines were dissolved in ethanol (20 mL) and the resulting mixture was heated to reflux for 6 h at 80 °C. An equimolar amount of KOH was then added to the mixture and further refluxed for 2 h, after which the reaction mixture was cooled to room temperature and poured into ice-cold water to give a precipitate. The resulting precipitate was filtered, washed with water and dried in *vacuo* to give the respective compounds.

N-((1H-benzo[s]imidazol-2-yl)methyl)-2,6-dimethylaniline ***(L1)***

This compound was prepared using 2-(chloromethyl)benzimidazole (0.50 g, 3.00 mmol), 2,6-dimethylaniline (0.36 g, 0.37 mL, 3.00 mmol), KI (0.50 g, 3.00 mmol) and KOH (0.17 g, 3.00 mmol) and was obtained as a pale-yellow solid (0.61 g, 81%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 2.31 (s, 6H, CH_3), 4.45 (s, 2H, CH_2), 6.95 (t, ^{3}J = 7.5 Hz, 1H, Ar), 7.06 (d, ^{3}J = 7.5 Hz, 2H, Ar), 7.29 (m, 2H, Ar), 7.61 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 153.3, 144.8, 130.2, 129.1, 123.3, 122.6, 46.7, 18.3. IR (Nujol): ν = 2927 (w), 1630 (m), 1533 (s), 1428 (s).

ESI-TOF MS: *m/z* calculated for $C_{16}H_{17}N_3$ [M + H^+] 252.33; found 252.15. Anal. Calcd. For $C_{16}H_{17}N_3$: C, 76.46; H, 6.83; N, 16.72. Found: C, 76.40; H, 6.79; N, 16.69.

N-((1H-benzo[d]imidazol-2-yl)methyl)-2,6-diisopropylaniline ***(L2)***

A mixture of 2-(chloromethyl)benzimidazole (0.50 g, 3.00 mmol), 2,6-diisopropylaniline (0.53 g, 0.56 mL, 3.00 mmol), KI (0.50 g, 3.00 mmol) and KOH (0.17 g, 3.00 mmol) a Pale-yellow solid. (0.82 g, 88%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 1.26 (d, ^3J = 5.3 Hz, 12H, CH_3), 3.34 (m, 2H, CH), 4.39 (s, 2H, CH_2), 7.17 (s, 3H, Ar), 7.30 (m, 3H, Ar), 7.49 (t, ^3J = 7.5 Hz, 1H, Ar), 7.78 (t, ^3J = 7.5 Hz, 1H, Ar), 9.73 (1H, NH). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 152.9, 142.9, 141.6, 125.0, 123.9, 49.9, 27.8, 24.2. IR (Nujol): ν = 3354 (w), 2960 (s), 2869 (m), 1630 (m), 1544 (w), 1457 (s), 1432 (s). ESI-TOF MS: *m/z* calculated for $C_{20}H_{25}N_3$ [M + H^+] 308.43; found 308.58 Anal. Calcd. For $C_{20}H_{25}N_3$: C, 78.14; H, 8.20; N, 13.67. Found: C, 78.30; H, 8.29; N, 13.69.

N-((1H-benzo[d]imidazol-2-yl)methyl)-2,4,6-trimethylaniline ***(L3)***

2-(chloromethyl)benzimidazole (0.50 g, 3.00 mmol), 2,4,6-trimethylaniline (0.41 g, 0.43 mL, 3.00 mmol), KI (0.50 g, 3.00 mmol) and KOH (0.17 g, 3.00 mmol) Pale-yellow solid. (0.72 g, 90%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 2.27 (s, 6H, CH_3), 4.40 (s, 2H, CH_2), 6.88 (s, 2H, Ar), 7.29 (m, 3H, Ar), 7.44 (b, 1H, Ar), 7.76 (1H, Ar), 9.83 (s, 1H, NH). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 153.4, 143.4, 132.8, 130.5, 129.7, 122.9, 122.3, 119.4, 110.7, 46.9, 20.6, 18.1. IR (Nujol): ν = 2908 (m), 1630 (s), 1481 (s), 1420 (s). ESI-TOF MS: *m/z* calculated for $C_{17}H_{19}N_3$ [M + H^+] 266.35; found 266.25. Anal. Calcd. For $C_{17}H_{19}N_3$: C, 76.95; H, 7.22; N, 15.84. Found: C, 76.70; H, 7.29; N, 15.69.

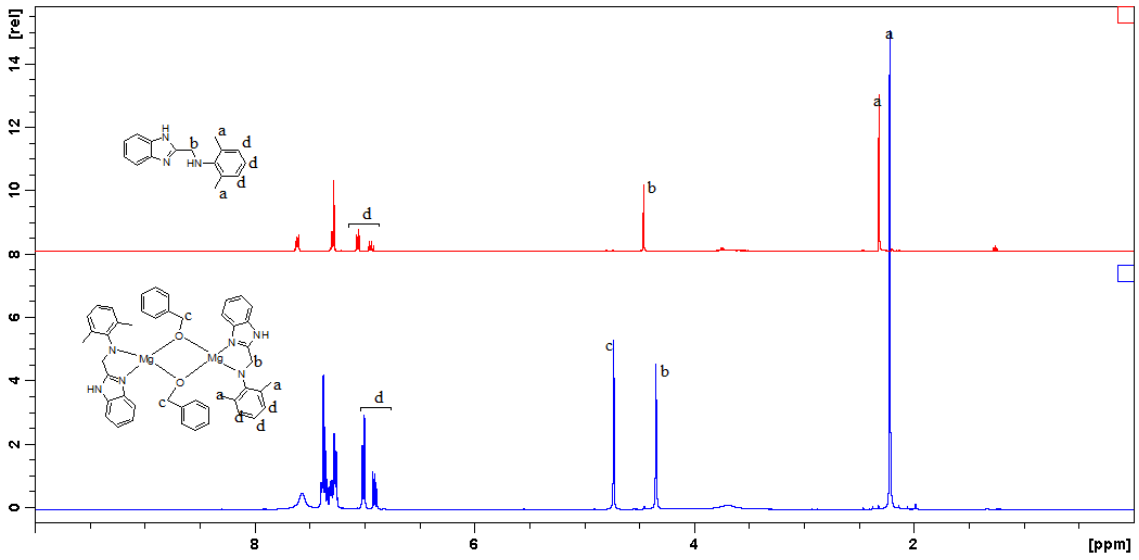


Fig. S1: ^{1}H NMR spectra of ligand **L1** (top) and complex **1** (bottom) showing the appearance of resonance of methylene hydrogen of the bridging benzyl alkoxides at 4.73 ppm indicative of complex formation.

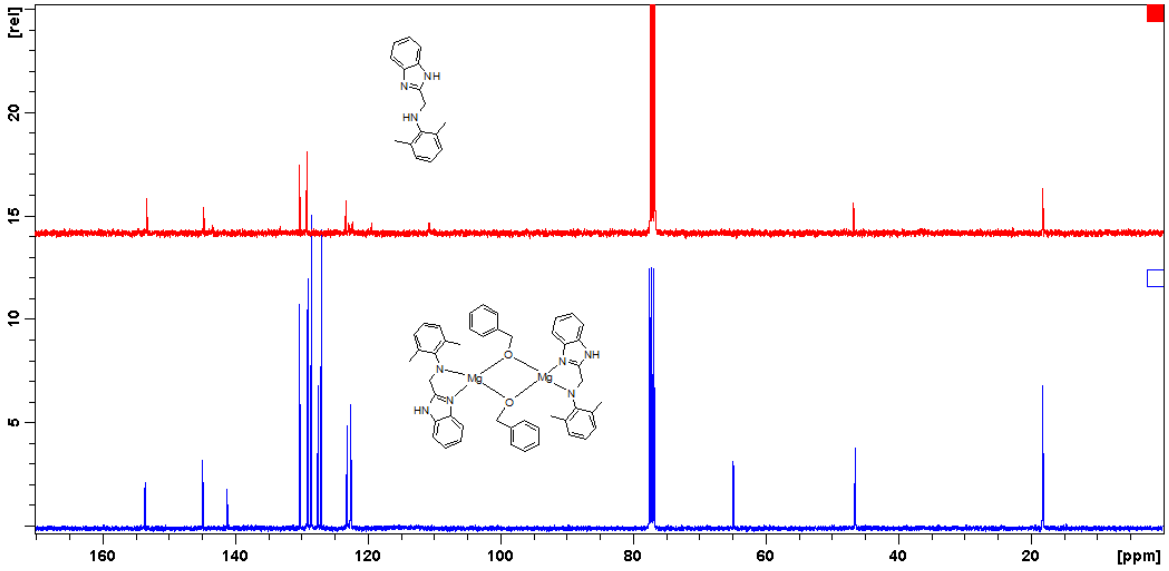


Fig. S2: ^{13}C NMR spectrum of ligand **L1** (top) and complex **1** (bottom) showing the appearance of resonance peak at 64.88 ppm for the methylene linkage carbon of $–OCH_2C_6H_5$ derivative indicating formation of complex.

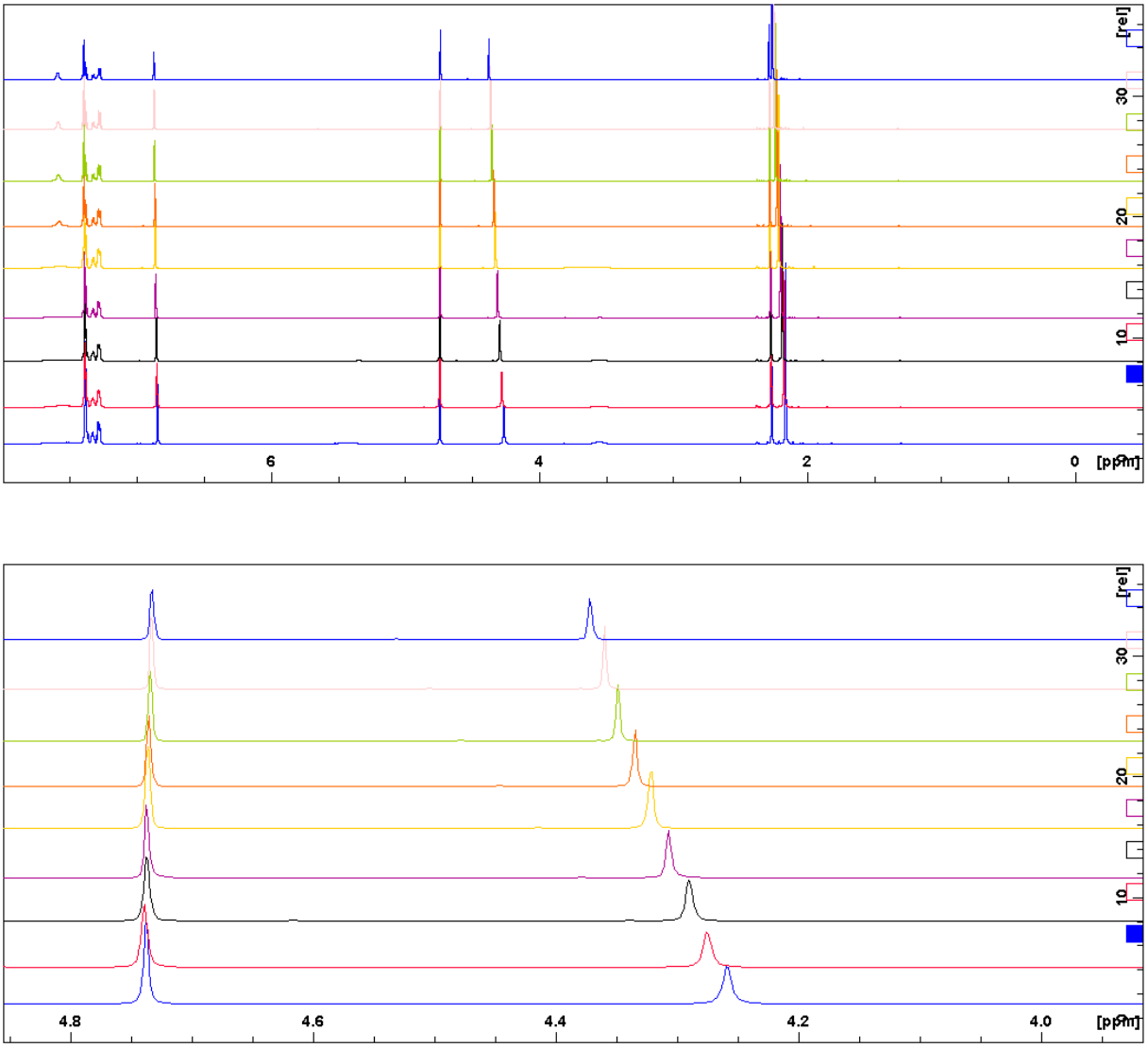


Fig. S3: Variable temperature of complex 1 from -40 ºC to 40 ºC, showing no changes to the CH_2 linker protons.

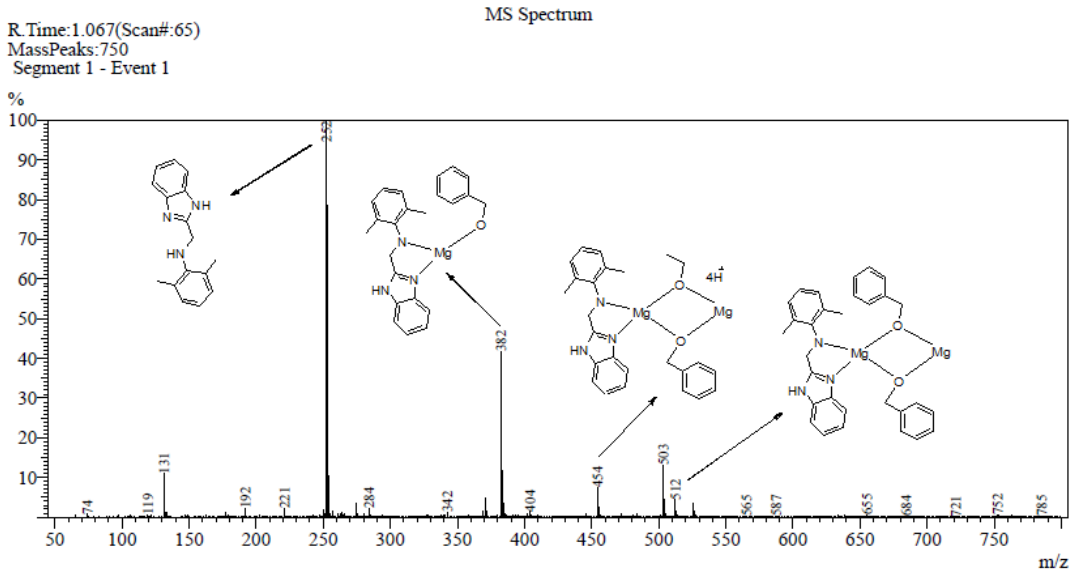


Fig. S4: Mass spectra showing complex **1** showing its fragmentation pattern to give a base peak at 252 amu corresponding to **L1** unit.

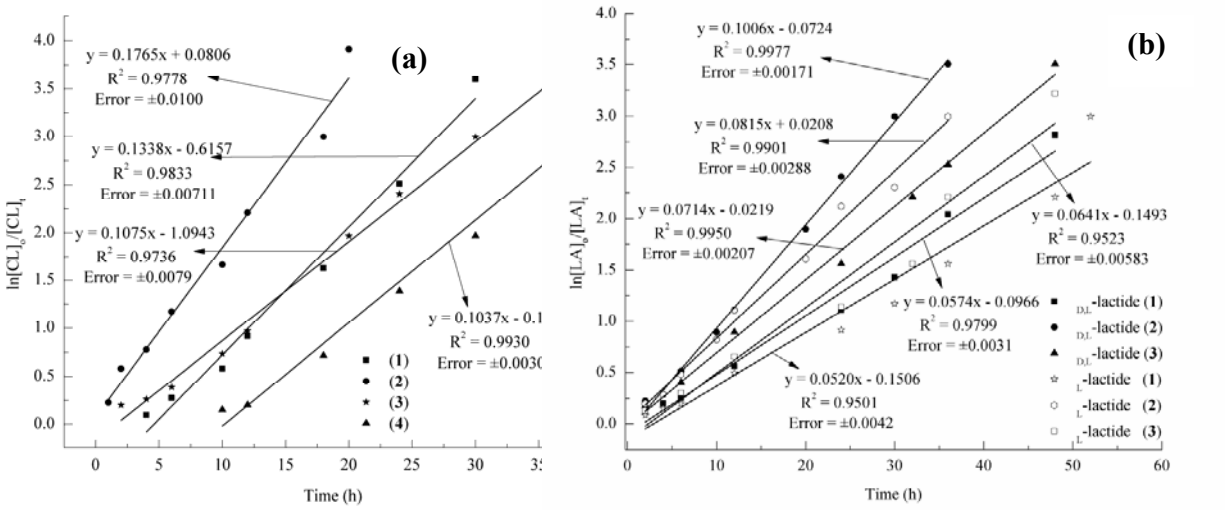


Fig. S5: (a) First order kinetic plots of $\ln[CL]_o/[CL]_t$ *vs.* time for complexes **1**–**4** in the ROP of ε-CL in toluene at 110 °C, $[CL]_o/[I] = 200$. (b) First order kinetic plots of $\ln[LA]_o/[LA]_t$ *vs.* time for complexes **1**–**3** in the ROP of D,L-LA and L-LA to PLAs in toluene at 110 °C, $[LA]_o/[I] = 200$.

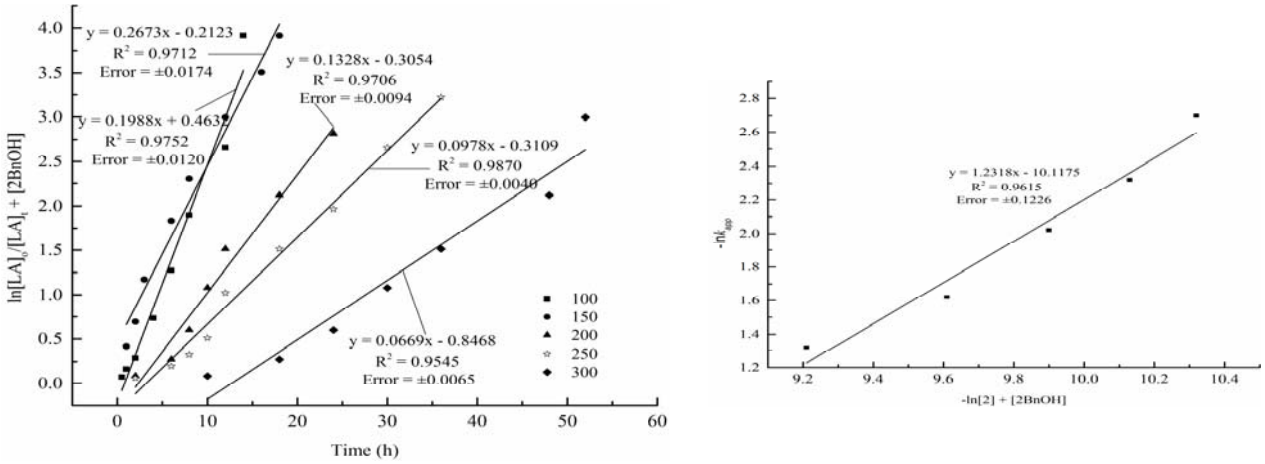


Fig. S6: (a) First order kinetic plots of $\ln[LA]_o/[LA]_t$ *vs*. time for complex **2** in the ROP of L-LA in toluene at 110 °C at different $[LA]_o/[I]$ ratios in the presence of 2 equiv BnOH. (b) Plot of $\ln k_{app}$ *vs*. ln[**2**] for the determination of order of reactions in the ROP of L-LA in the presence of BnOH.

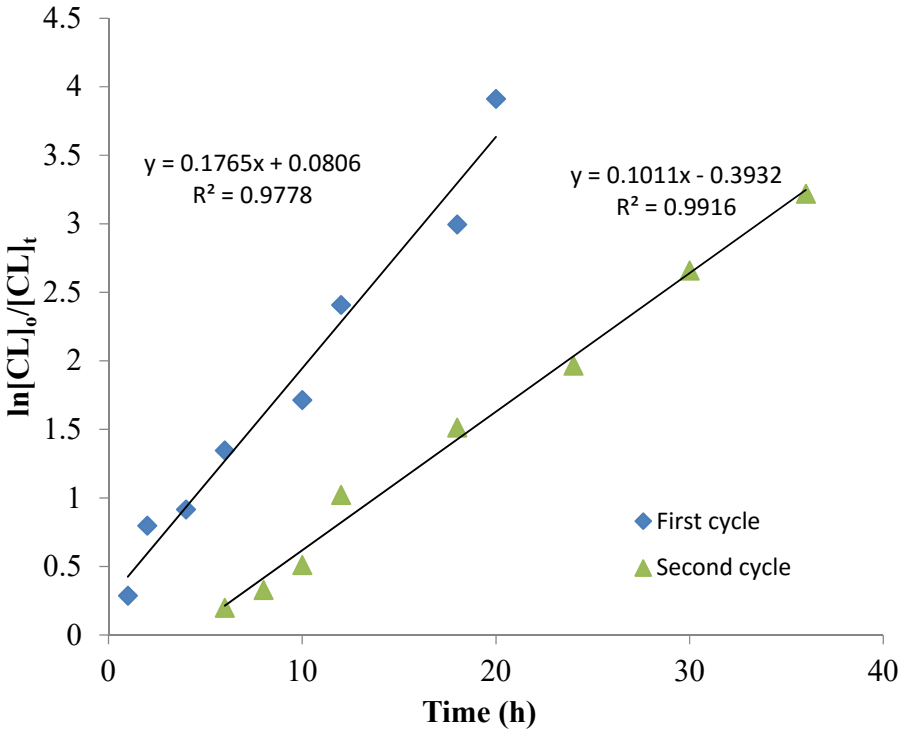


Fig. S7: Stability studies showing the catalytic activities of catalyst **2** in the ROP of ε-CL in the first and second cycle. The k_{obs} of 0.101 h- was observed in the second cycle compared to k_{obs} of 0.177 h- reported in the first cycle, representing about 40% drop in activity.

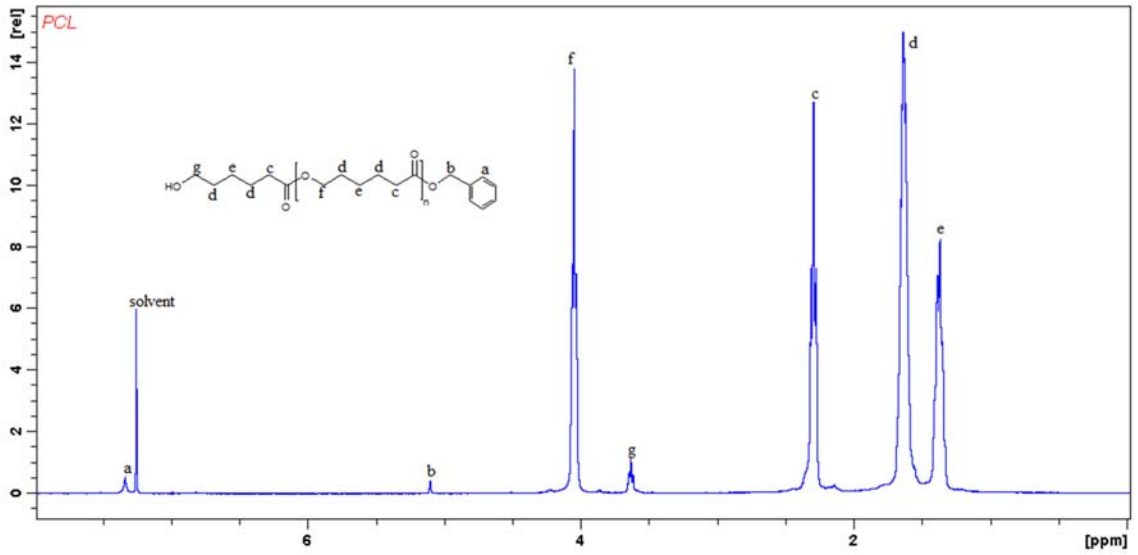


Fig. S8: ^{1}H NMR spectrum of PCL in $CDCl_3$ obtained using complex **2**, revealing the presence of phenyl ring protons (7.37 ppm) and CH_2 (5.12 ppm) signal of $–OCH_2C_6H_5$ group. Reaction condition:$[CL]_o$:$[I]_o$ = 200:1 in toluene at 110 °C, 12 h.

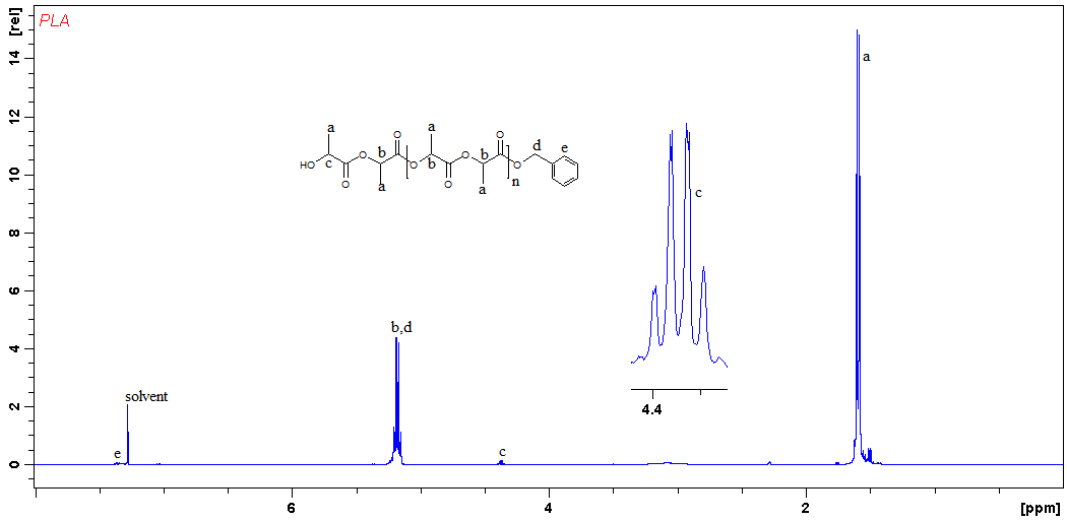


Fig. S9: ^{1}H NMR spectrum of poly(L-LA) in $CDCl_3$ obtained using complex **2**, showing signals that the polymer chain is capped with one benzyl ester and one hydroxyl end. Reaction condition:$[LA]_o$:$[\mathbf{2}]_o$ = 200:1 in toluene at 110 °C, 20 h.

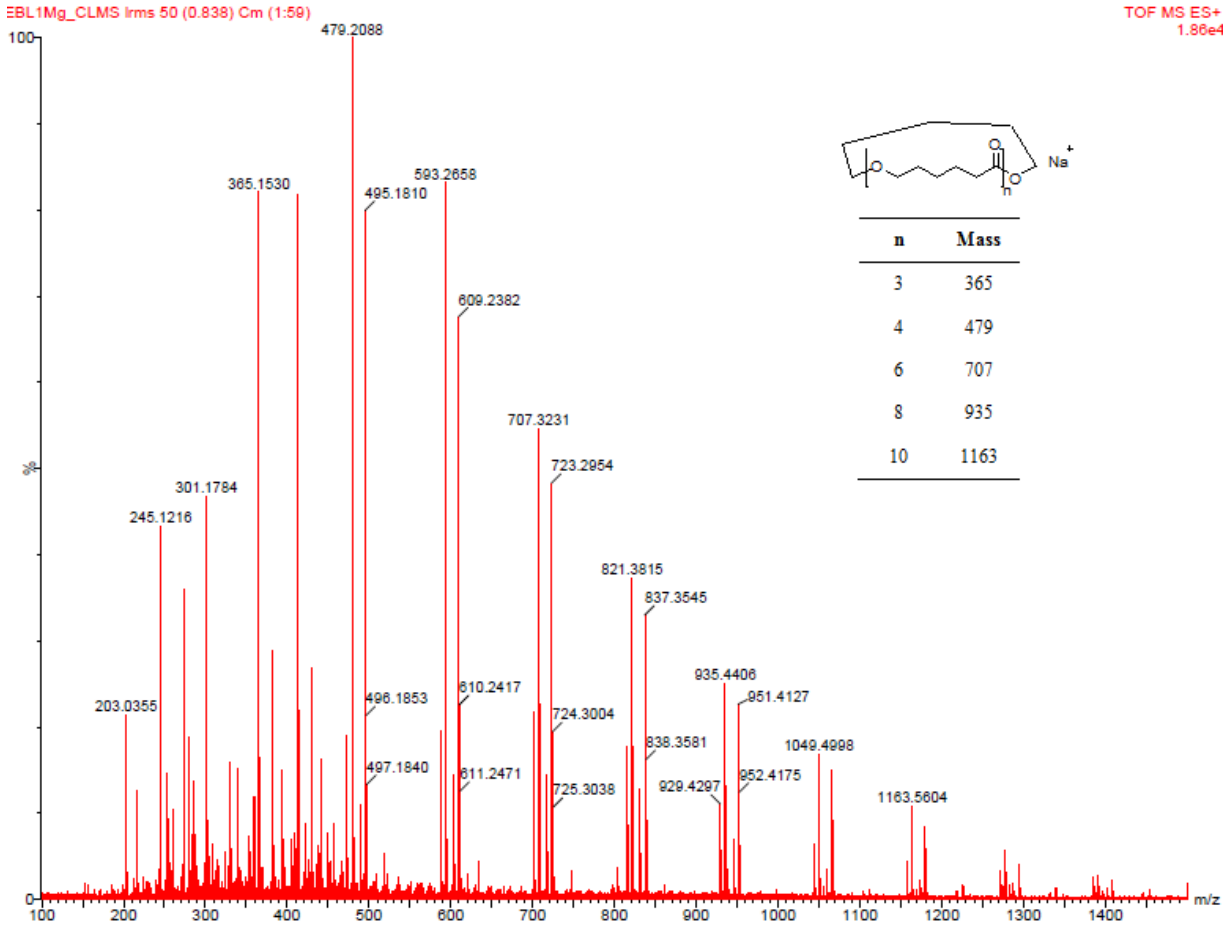


Fig. S10: ESI-MS spectrum of cyclic oligomer obtained by using catalyst **2**. Reaction condition:$[CL]_o$:$[\mathbf{2}]_o$ = 200:1 in toluene at 110 °C, 12 h.

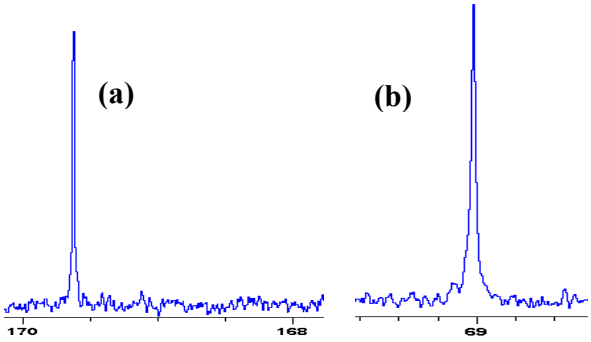


Fig. S11: (a) ^{13}C NMR spectra carbonyl region and (b) ^{13}C NMR methine region of poly(L-LA) supporting isotactic microstructure of PLA prepared from L-LA using complex **2**. Reaction condition:$[LA]_o$:$[\mathbf{2}]_o$ = 200:1 in toluene at 110 °C

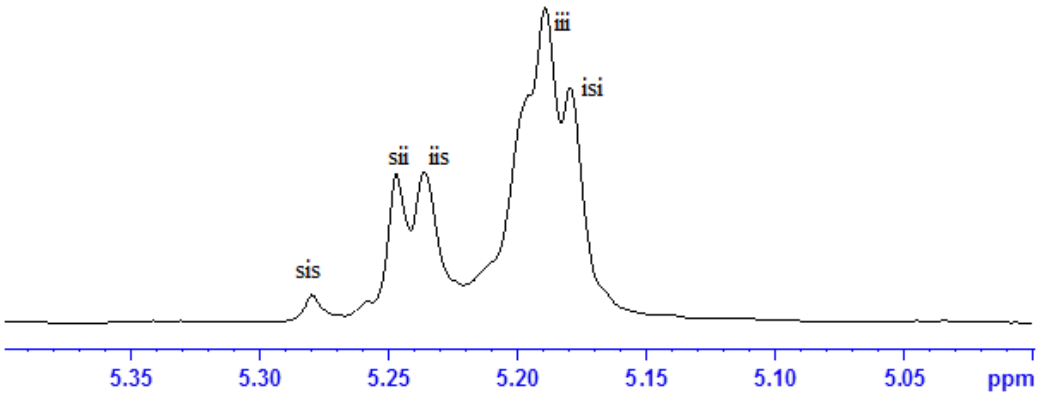


Fig. S12: ^{1}H homonuclear decoupled NMR of the methine region of poly(D,L-LA) obtained from complex **2** showing the formation of atactic microstructure.