Supporting information

Preparation of zirconium and hafnium complexes containing chiral N atoms from unsymmetric tertiary amine ligands, and their catalytic properties for polymerization of *rac*-lactide

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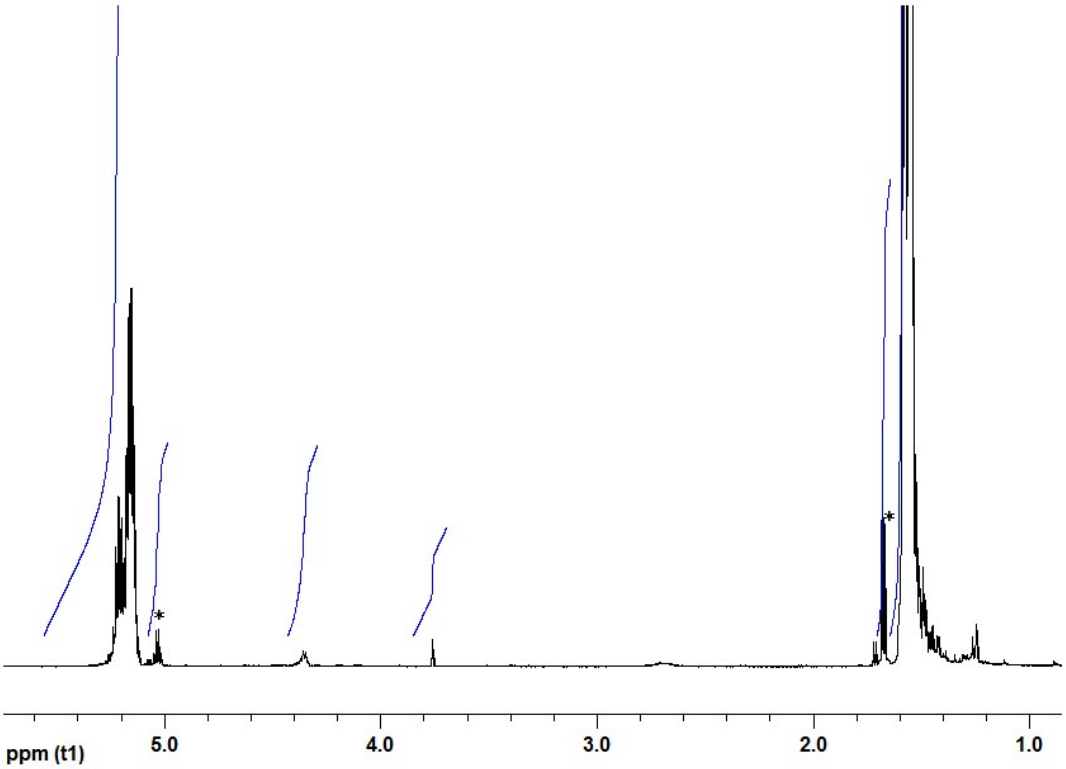

Fig. S1 ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of PLA prepared by the polymerization of *rac*-LA using **3**/methanol (The signals marked with an asterisk are attributed to the monomer).

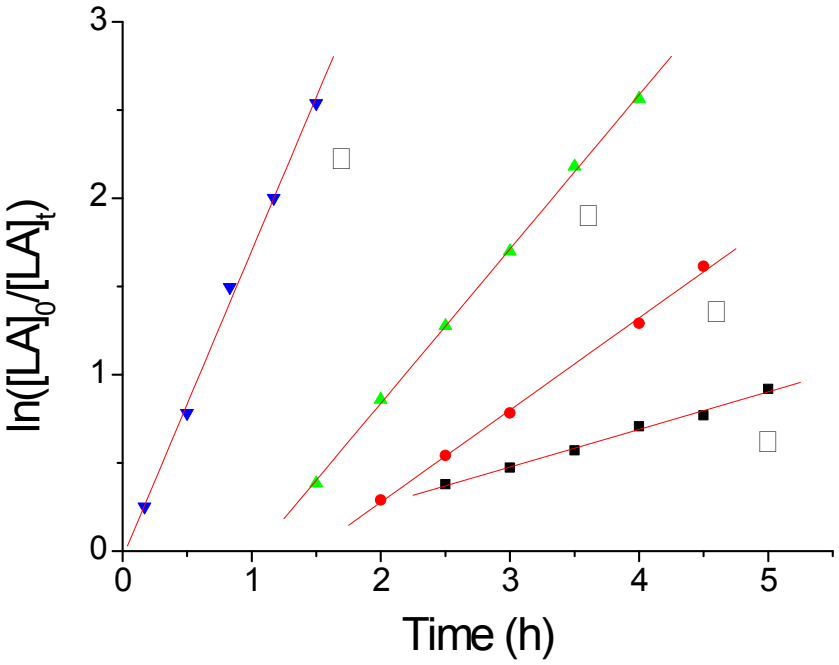

Fig. S2 Kinetics of *rac*-LA polymerization using complexes **3** as a catalyst in toluene at different tempreature with [LA] = 1.0mol/L: Ⅰ, 130℃, k_{app} = 1.74 ± 0.05 (R = 0.998); Ⅱ, 110℃, k_{app} = 0.87 ± 0.01 (R = 0.999); Ⅲ, 90℃, k_{app} = 0.52 ± 0.01 (R = 0.998); Ⅳ, 70℃, k_{app} = 0.21 ± 0.01 (R = 0.996).

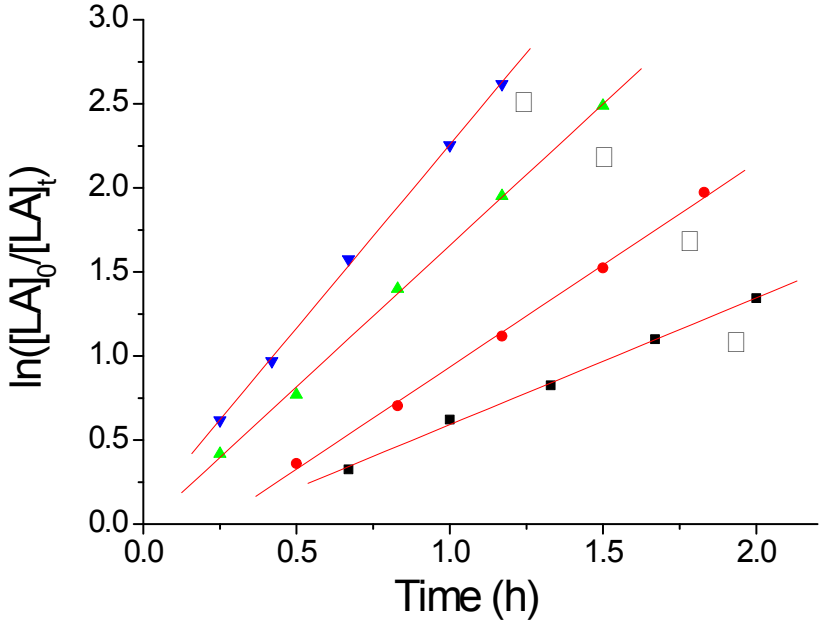

Fig. S3 Kinetics of L-LA polymerization using complexes **3** as a catalyst in toluene at different tempreature with [LA] = 1.0mol/L: Ⅰ, 130℃, k_{app} = 2.19 ± 0.03 (R = 0.999); Ⅱ, 110℃, k_{app} = 1.68 ± 0.03 (R = 0.999); Ⅲ, 90℃, k_{app} = 1.21 ± 0.03 (R = 0.998); Ⅳ, 70℃, k_{app} = 0.75 ± 0.02 (R = 0.998).

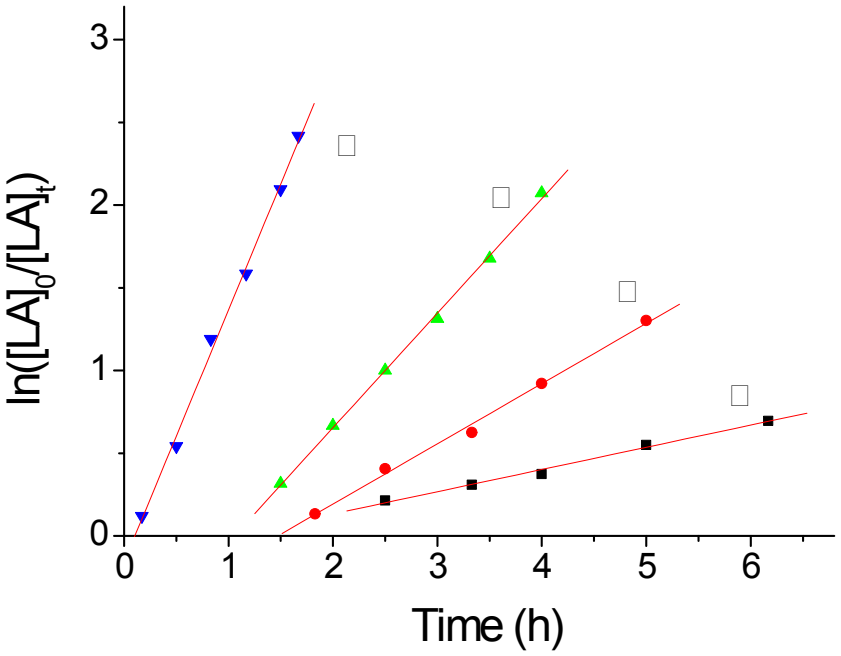

Fig. S4 Kinetics of *rac*-LA polymerization using complexes **2** as a catalyst in toluene at different tempreature with [LA] = 1.0mol/L: Ⅰ, 130℃, k_{app} = 1.52 ± 0.04 (R = 0.998); Ⅱ, 110℃, k_{app} = 0.69 ± 0.01 (R = 0.999); Ⅲ, 90℃, k_{app} = 0.36 ± 0.01 (R = 0.997); Ⅳ, 70℃, k_{app} = 0.13 ± 0.006 (R = 0.996).

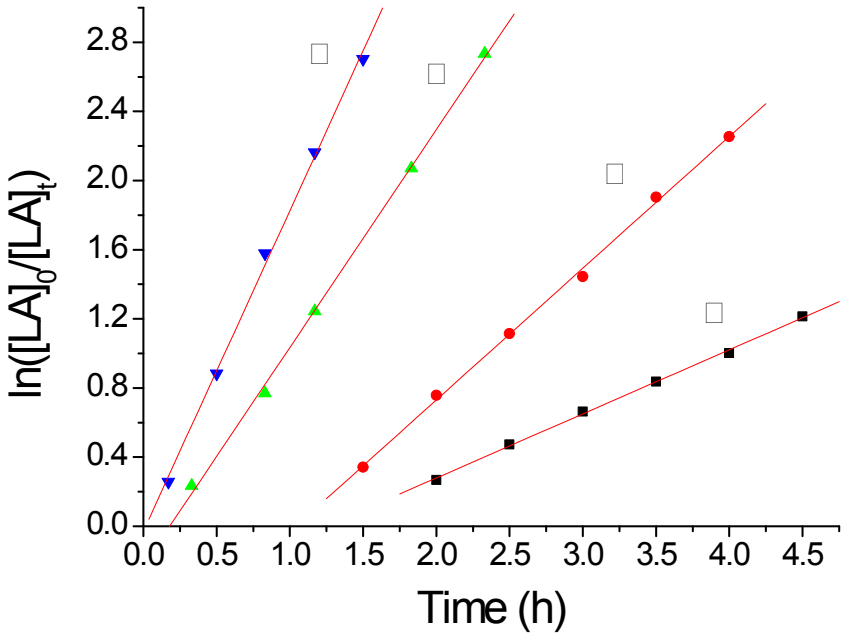

Fig. S5 Kinetics of L-LA polymerization using complexes **2** as a catalyst in toluene at different tempreature with [LA] = 1.0mol/L: Ⅰ, 130℃, k_{app} = 1.85 ± 0.05 (R = 0.998); Ⅱ, 110℃, k_{app} = 1.26 ± 0.02 (R = 0.999); Ⅲ, 90℃, k_{app} = 0.76 ± 0.01 (R = 0.999); Ⅳ, 70℃, k_{app} = 0.37 ± 0.01 (R = 0.999).

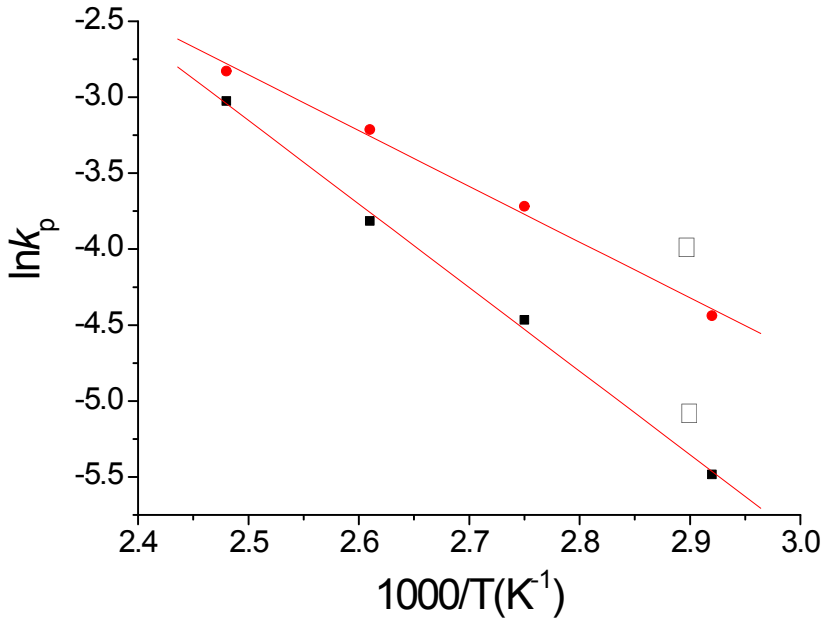

Fig. S6 Arrhenius plot of ln k_p versus $1/T$ for the polymerization of L- and *rac*-LA at different temperatures by using **2**/methanol (I, L-LA; II, *rac*-LA).

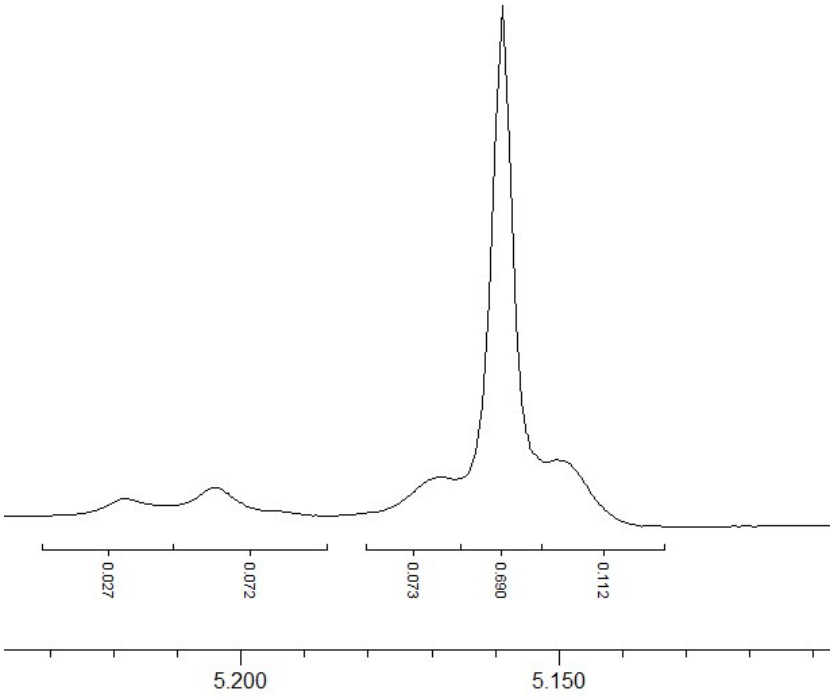

Fig. S7 Methine region of homonuclear decoupled ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of isolated PLA prepared from *rac*-LA using complex **3** as a catalyst (P_m = 0.79, run 6, Table 1).

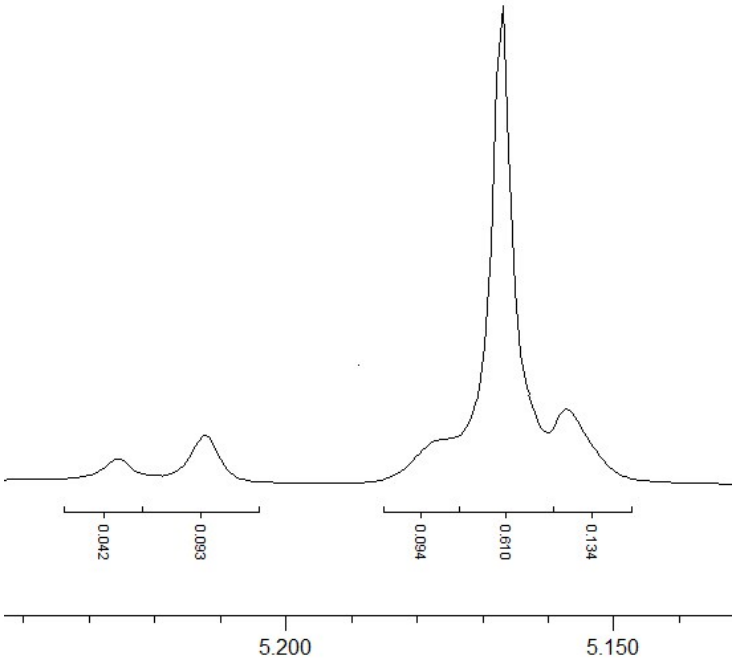

Fig. S8 Methine region of homonuclear decoupled ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of isolated PLA prepared from *rac*-LA using complex **3** as a catalyst (P_m = 072, run 7, Table 1).

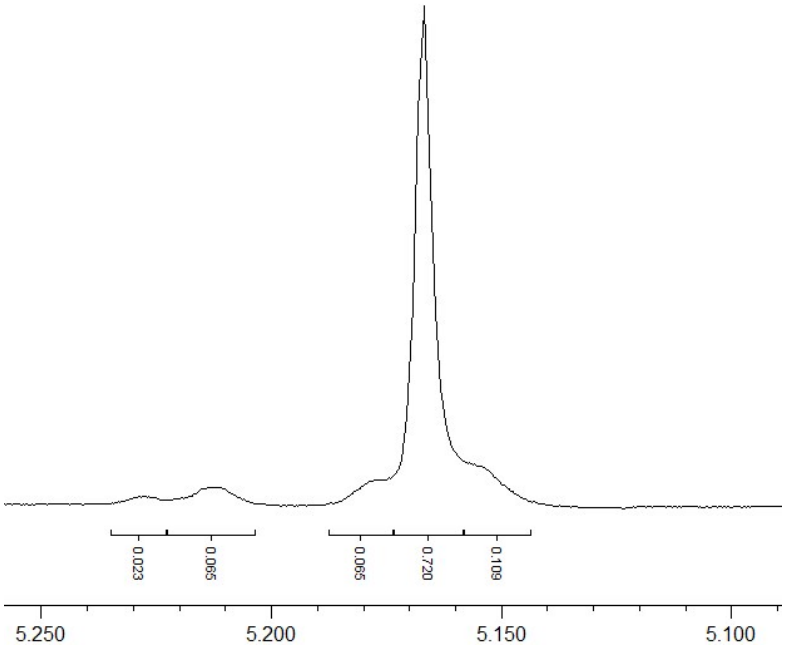

Fig. S9 Methine region of homonuclear decoupled ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of isolated PLA prepared from *rac*-LA using complex **3** as a catalyst (P_m = 0.81, run 8, Table 1).

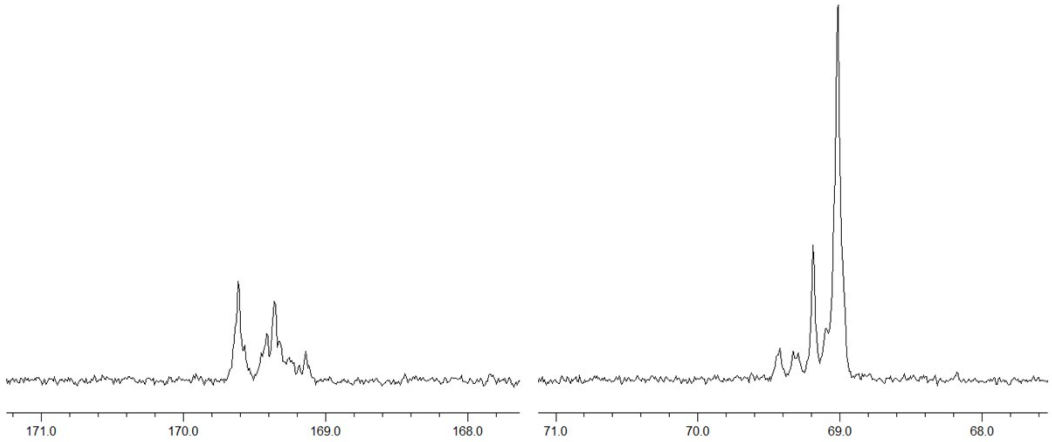

Fig. S10 ^{13}C spectrum (150 MHz, $CDCl_3$) of PLA prepared by the polymerization of *rac*-LA using **3**/methanol.

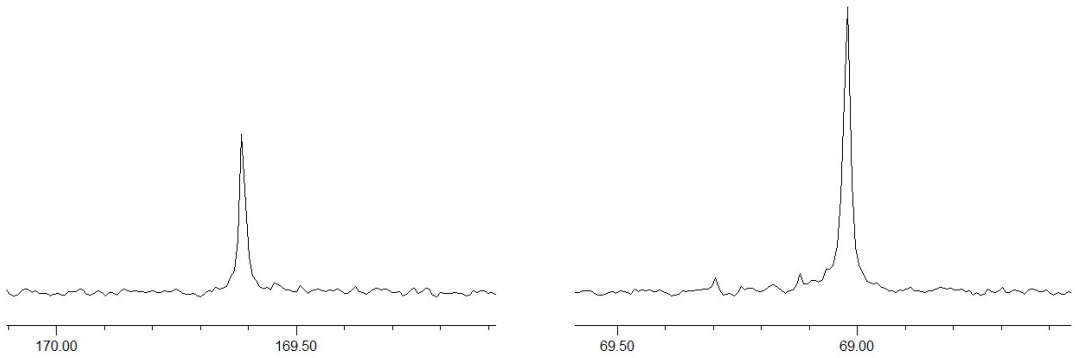

Fig. S11 ^{13}C spectrum (150 MHz, $CDCl_3$) of PLLA prepared by the polymerization of L-LA using **3**/methanol.

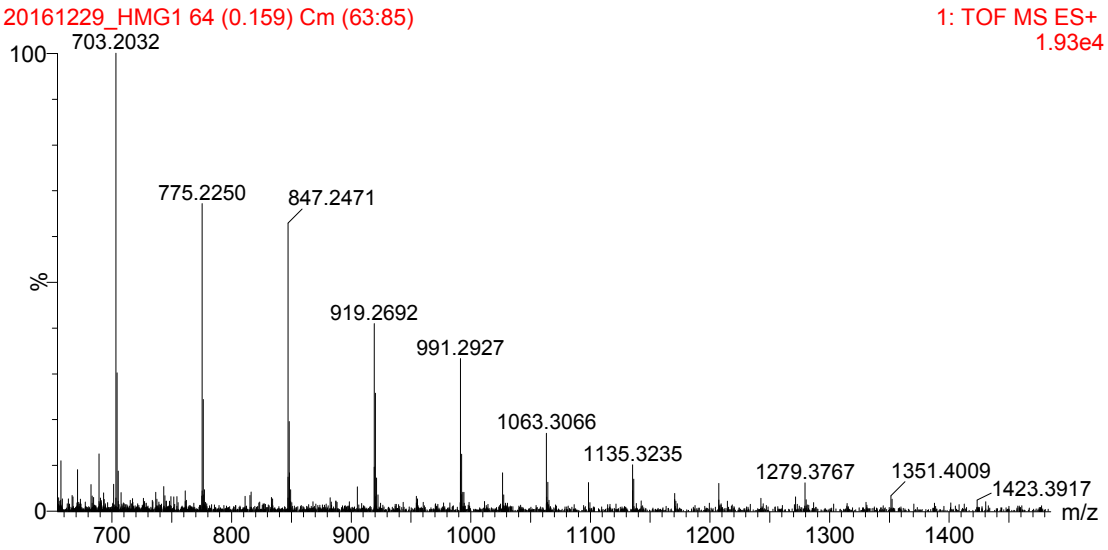

Fig. S12 A mass spectrum of the oligomer by **3** in toluene at 130 °C ([LA]/[cat]/[MeOH] = 20/1/1).