Journal Name

Supporting information

Isoselective Mechanism of Ring-opening Polymerization of *rac*-lactide Catalyzed by Chiral Potassium Binolates

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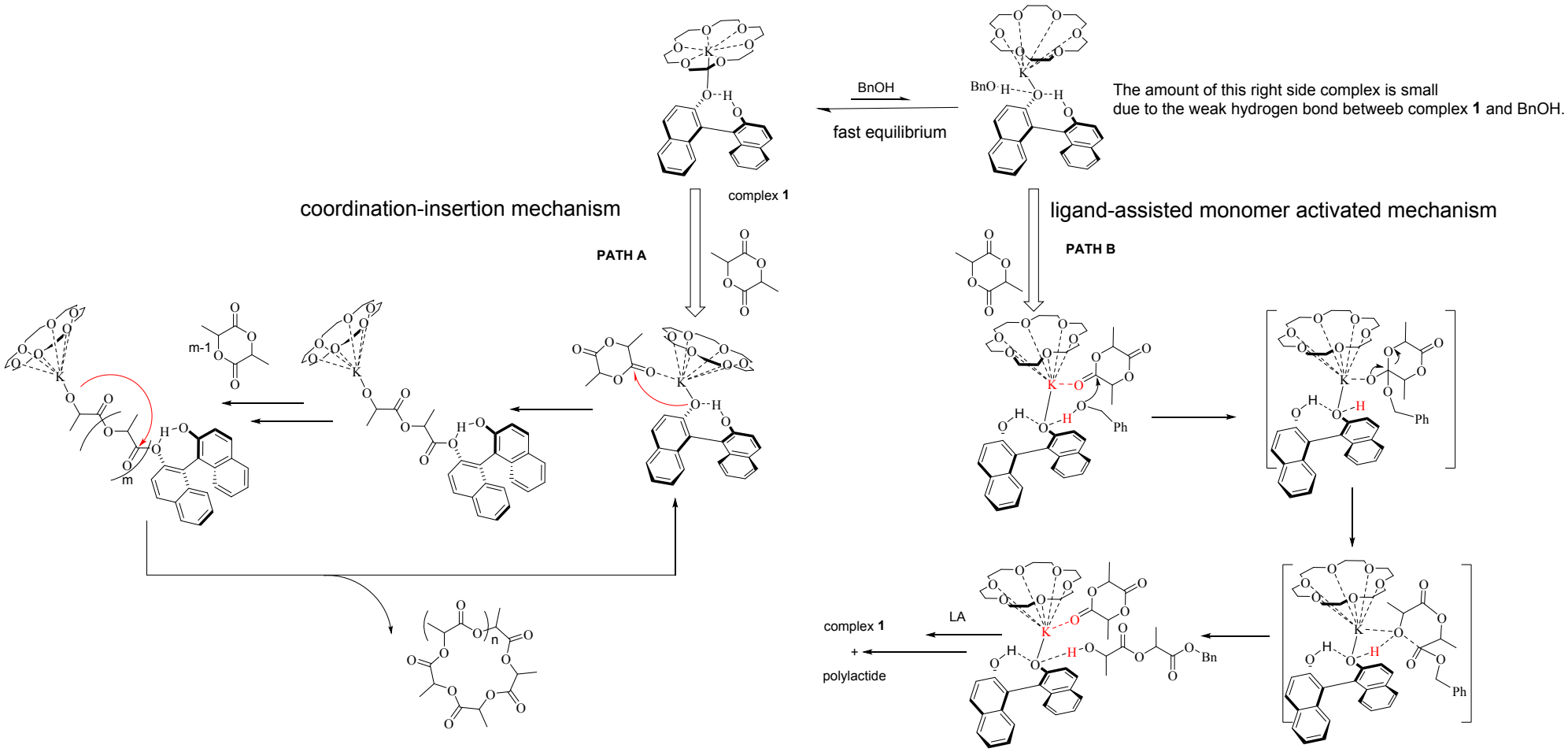
1) Scheme S1
2) NMR data for ligand **2**, complexes **1** and **2** (Figures S1 – S6, Table S1).
3) Polymerization data (Figures S7-S15)
4) Crystallographic data of complexes **1** and **2**



Scheme S1 Two possible mechanisms for the ROP of *rac*-lactide catalyzed by complex **1**.

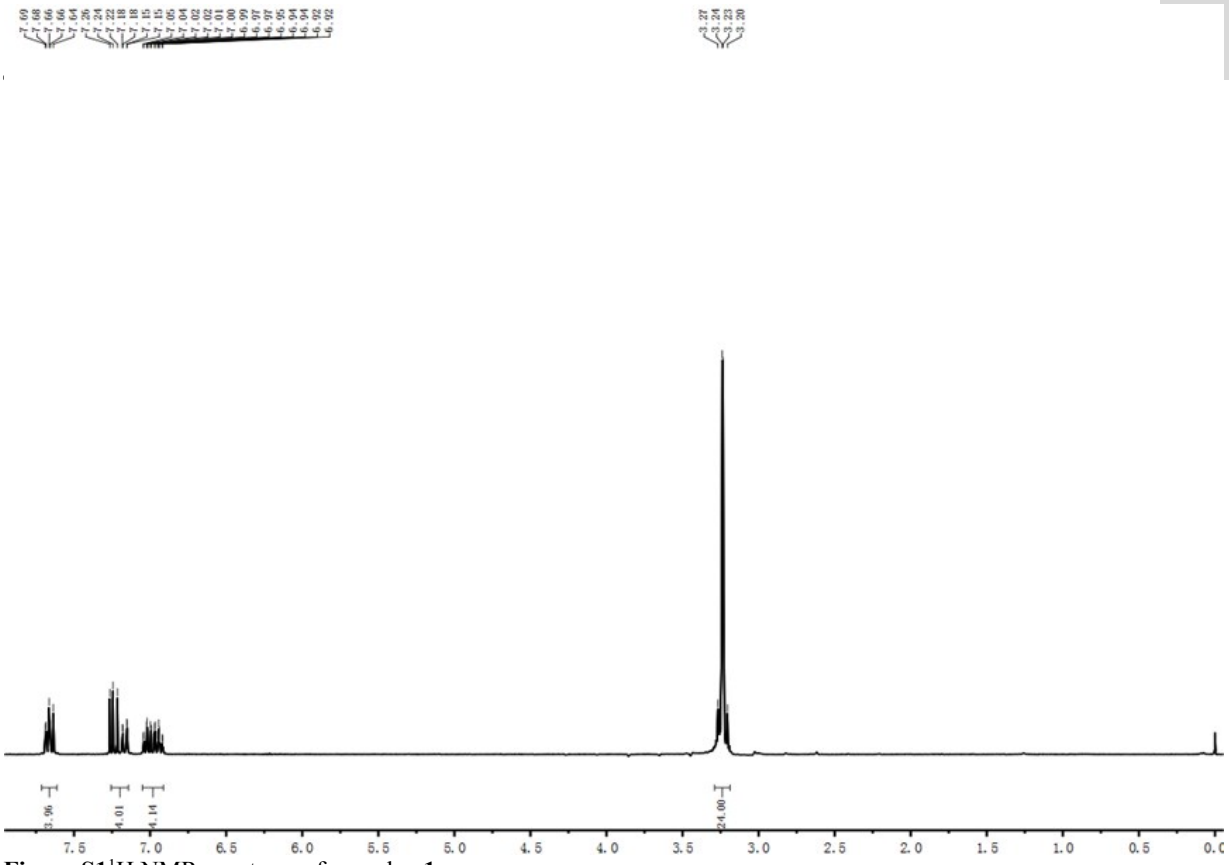


Figure S1[1]H NMR spectrum of complex **1**

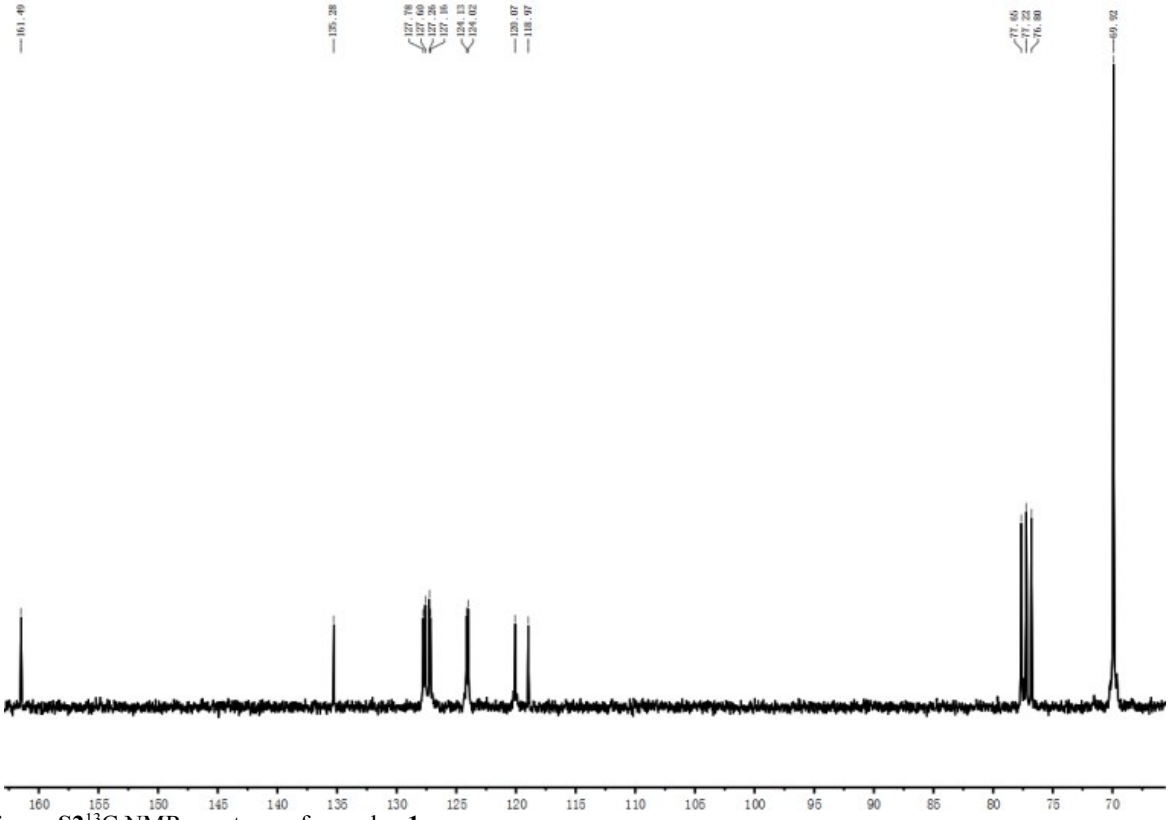


Figure S2[13]C NMR spectrum of complex **1**

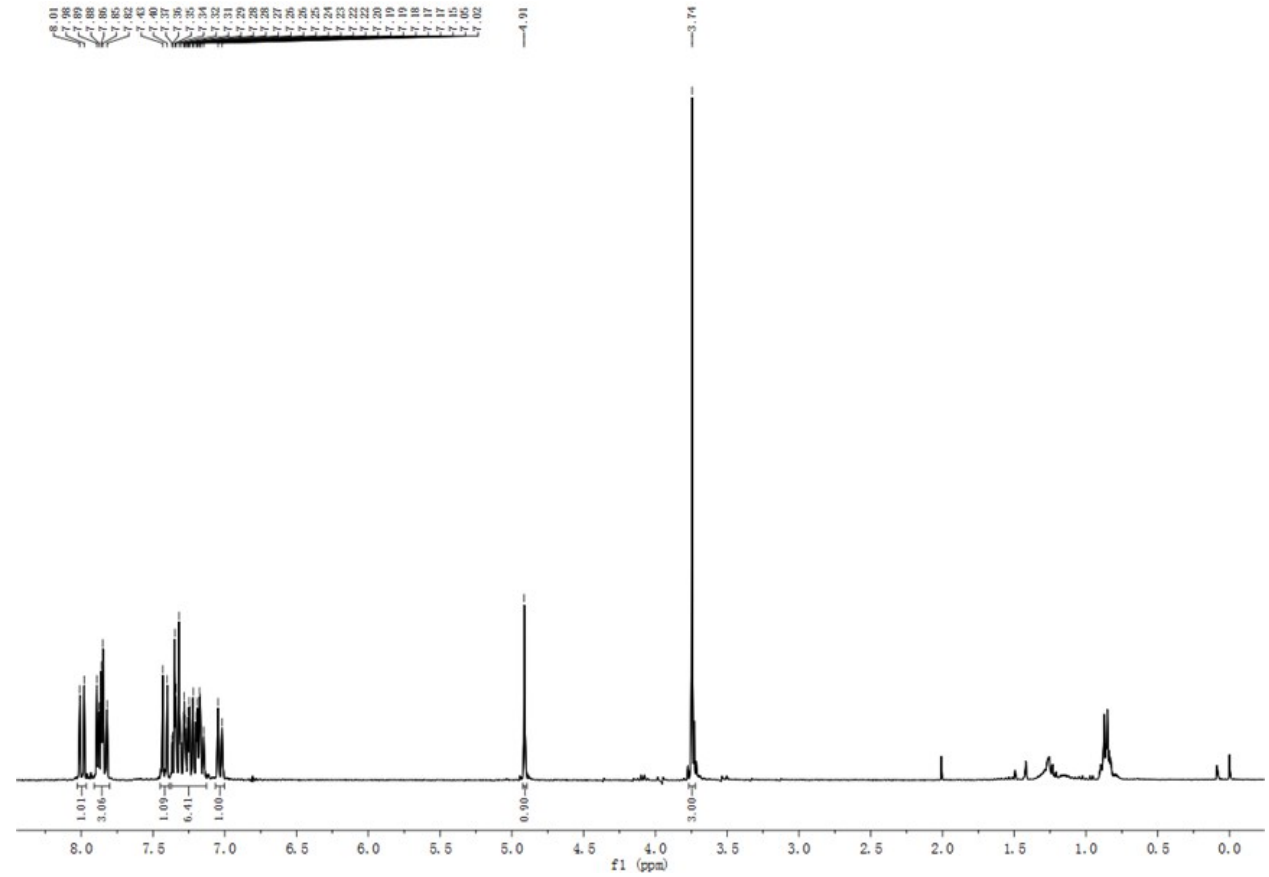


Figure S3 ^{1}H NMR spectrum of **HL**

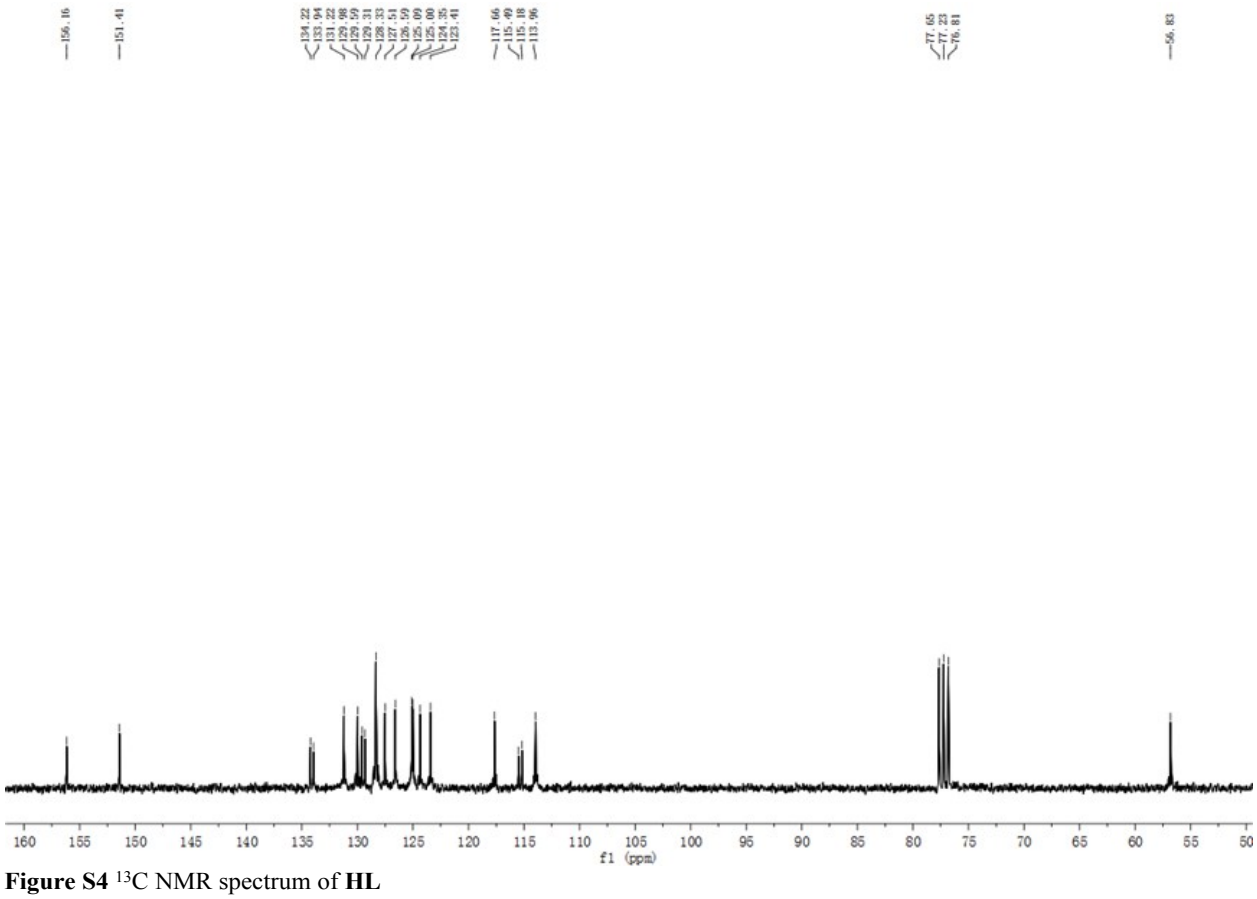


Figure S4 ^{13}C NMR spectrum of **HL**

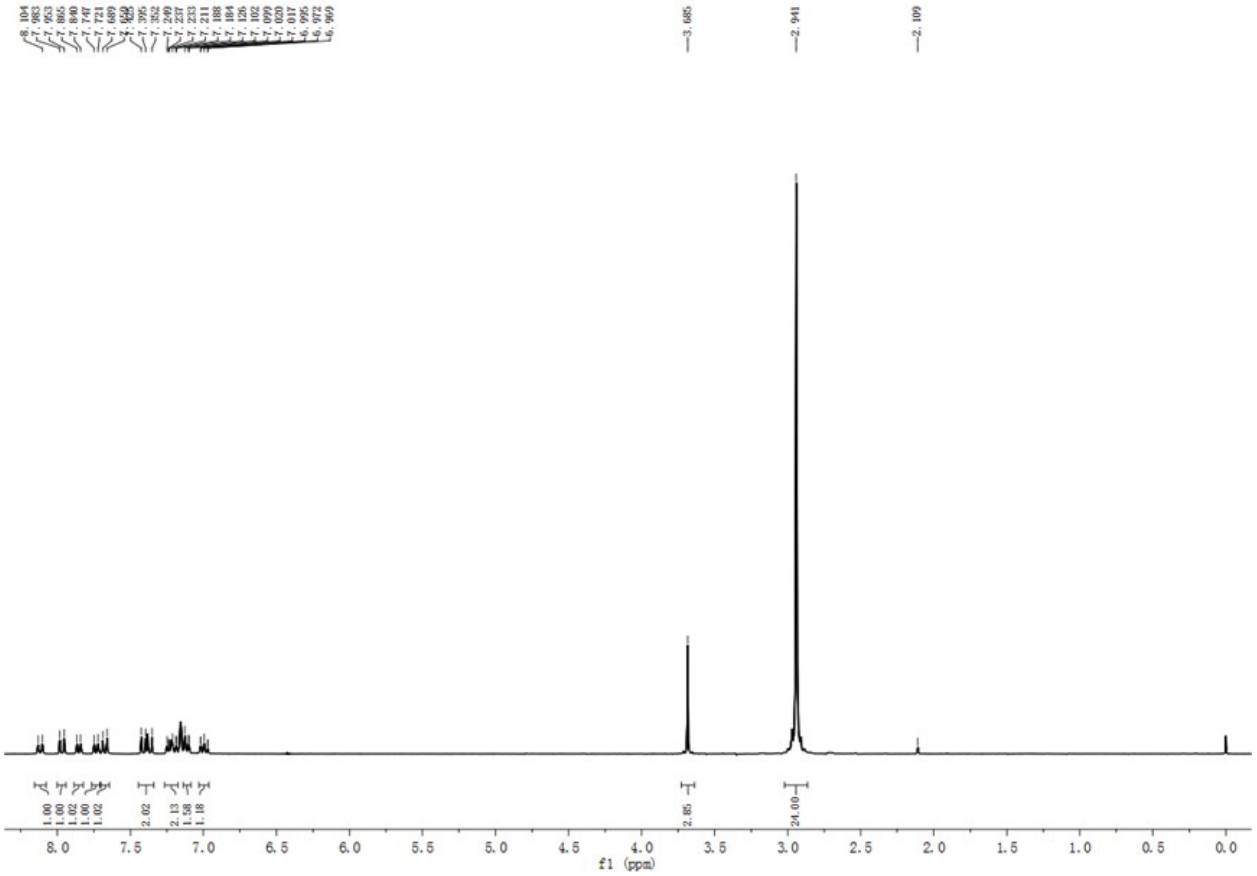


Figure S5 ^{1}H NMR spectrum of complex **2**

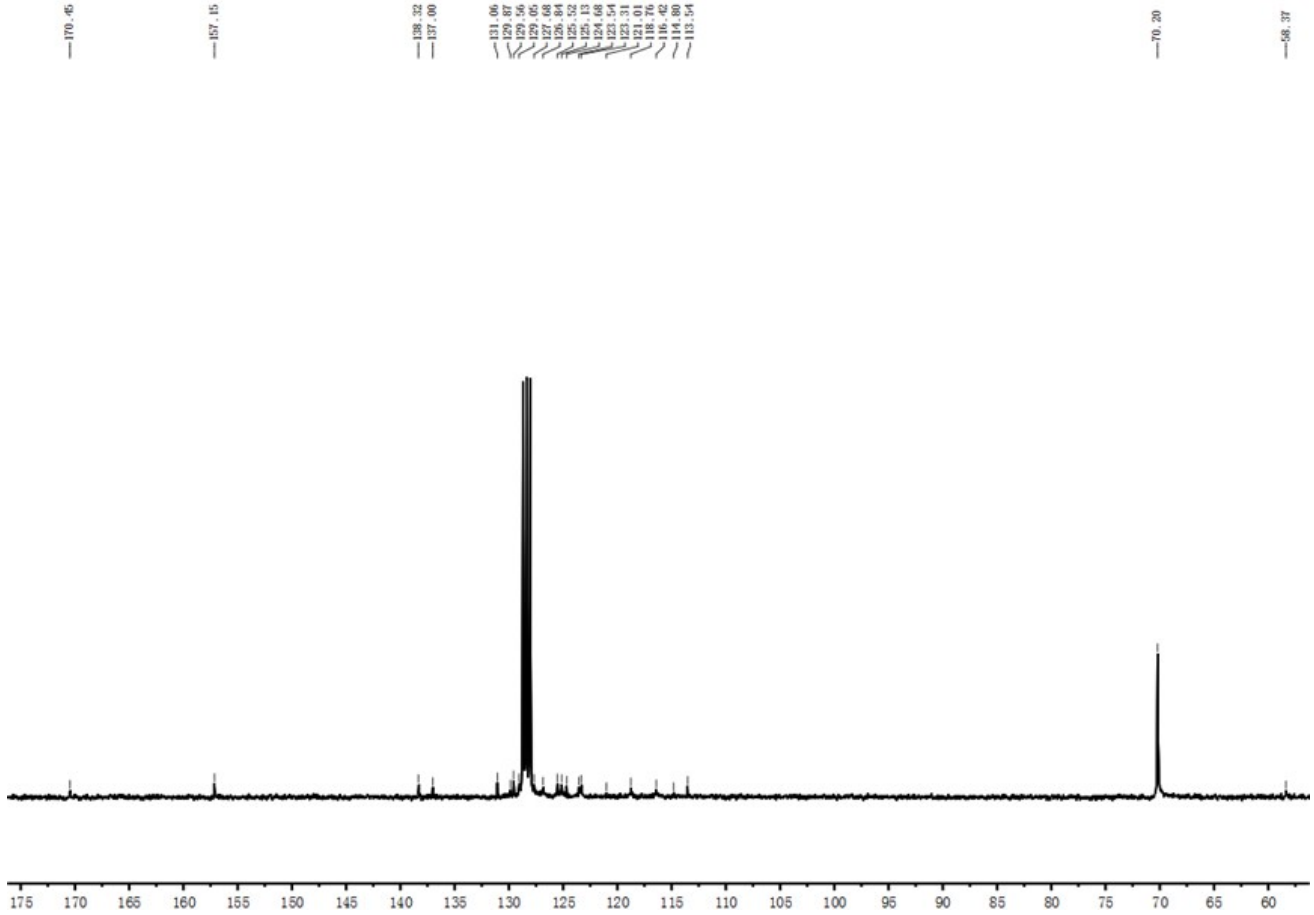


Figure S6 ^{13}C NMR spectrum of complex **2**

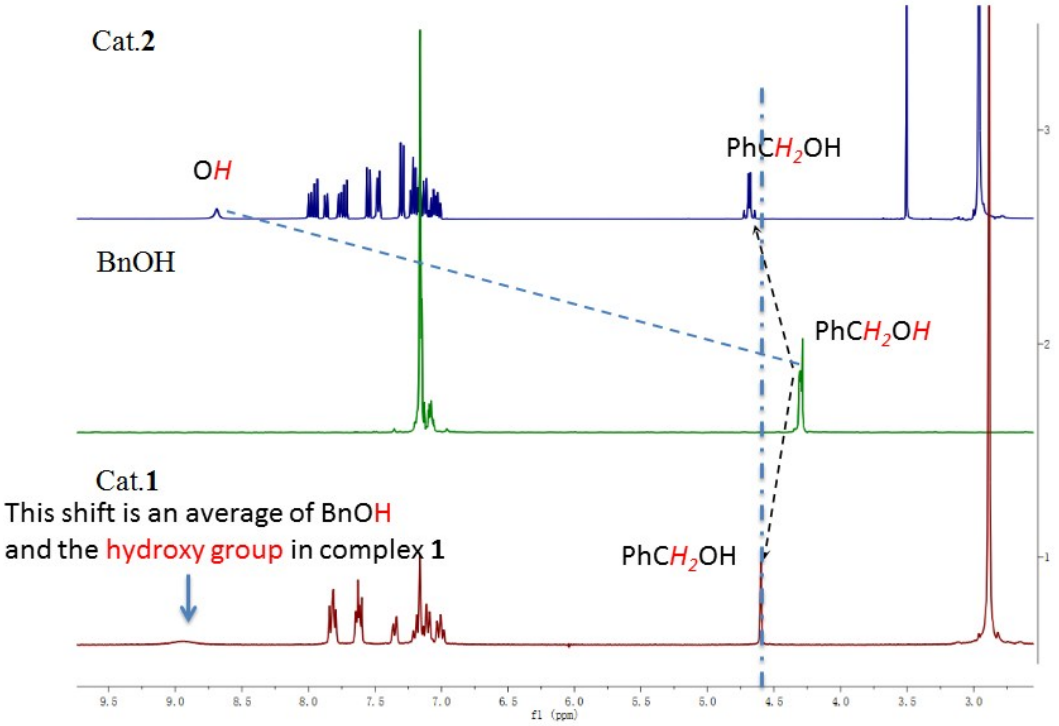


Figure S7 The compared ^{1}H NMR spectrum of BnOH and Cat.**2**/Cat.**1**:BnOH = 1: 1.

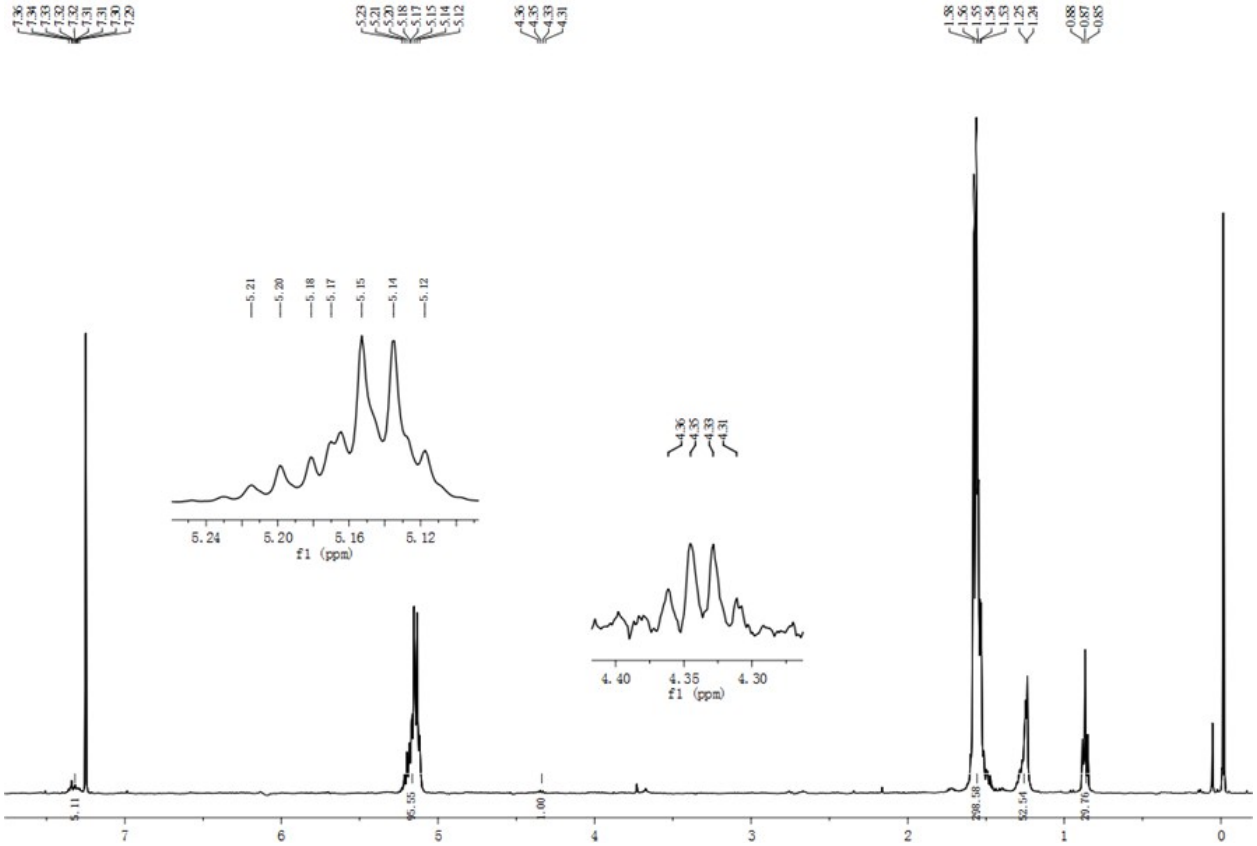
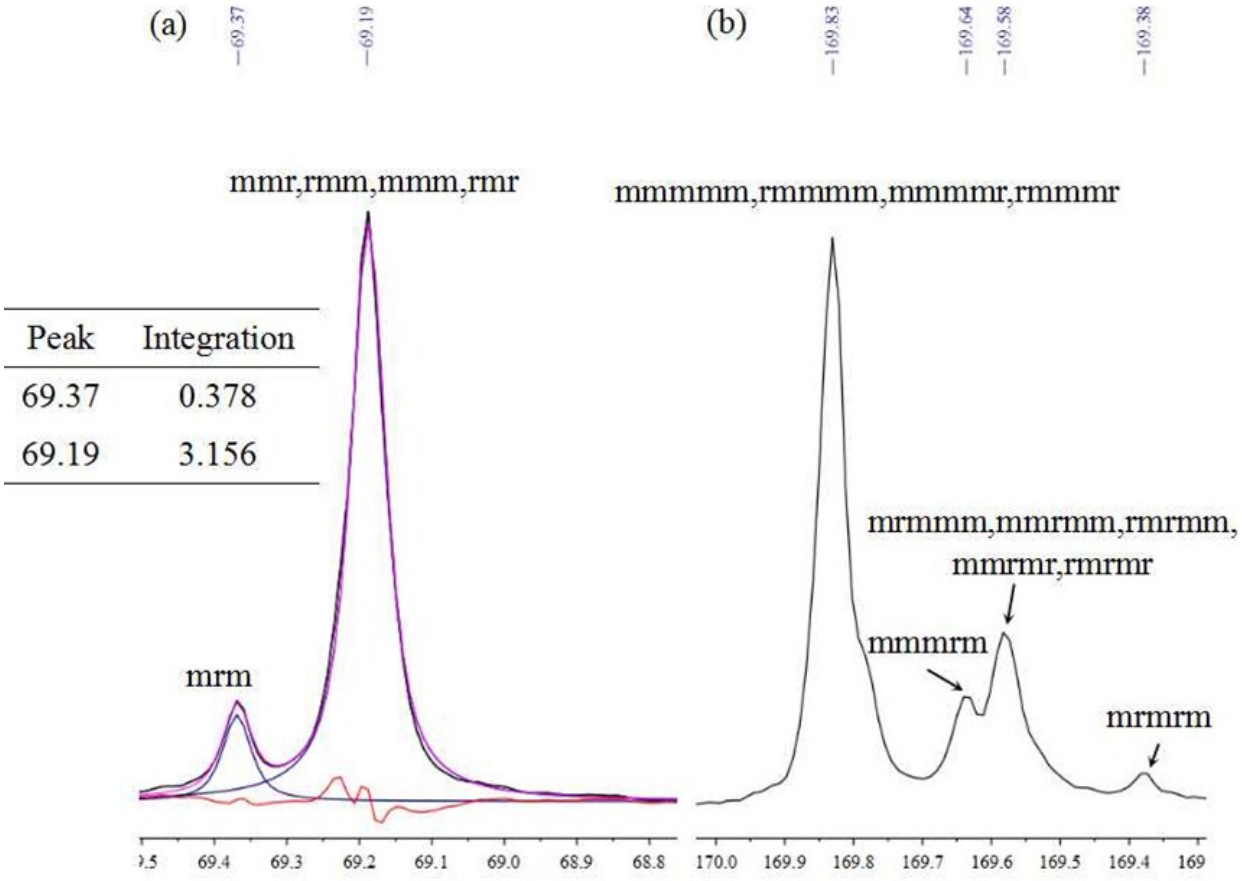


Figure S8 ^{1}H NMR spectrum of PLA50 prepared by catalyst **2** ($[LA]_0/[Cat.]_0/[BnOH]_0$ = 50:1:1, Table 2, entry 5).



Peak	Integration
69.37	0.378
69.19	3.156

Figure S9 ^{13}C NMR (100MHz) spectrum of PLA obtained from ROP of *rac*-lactide using catalyst **2**($[LA]_0/[Cat.]_0/[BnOH]_0$ = 100:1:1, Table 2, entry 6) showing the tetrads in the methine region (a) and the hexads in the carbonyl region (b). The P_m value determined from ^{13}C NMR for this sample is 0.79, comparable to the result from the determination by homonuclear decouple ^{1}H NMR (P_m =0.78). The probablity of formation of a meso linkage (P_m) of PLA can be derived from the methine region of ^{13}C NMR spectrum as follows (Bernoullian statistics).[1]

$$(1- P_m)/2=[mrm]/([mrm]+[mmm]+[mmr]+[rmm]+[rmr])$$

[mmm]	$P_m(P_m+1)/2$
[mmr]	$P_m(P_m-1)/2$
[rmm]	$P_m (1- P_m)/2$
[rmrm]	$(1- P_m)^2/2$
[mrm]	$(1-P_m)/2$

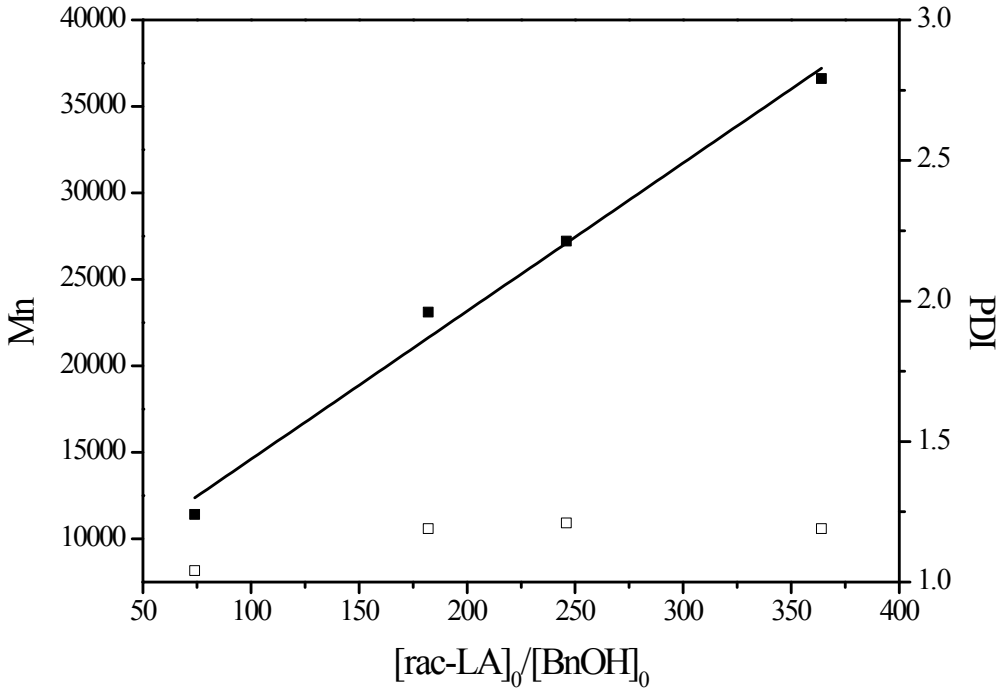


Figure S10 Polymerization of *rac*-LA catalyzed by **1** in toluene at room temperature. The relationships between M_n(■), D (□) of the polymer and the initial mole ratios $[LA]_0/[BnOH]_0$ (Table 1, entries 3-6) is shown.

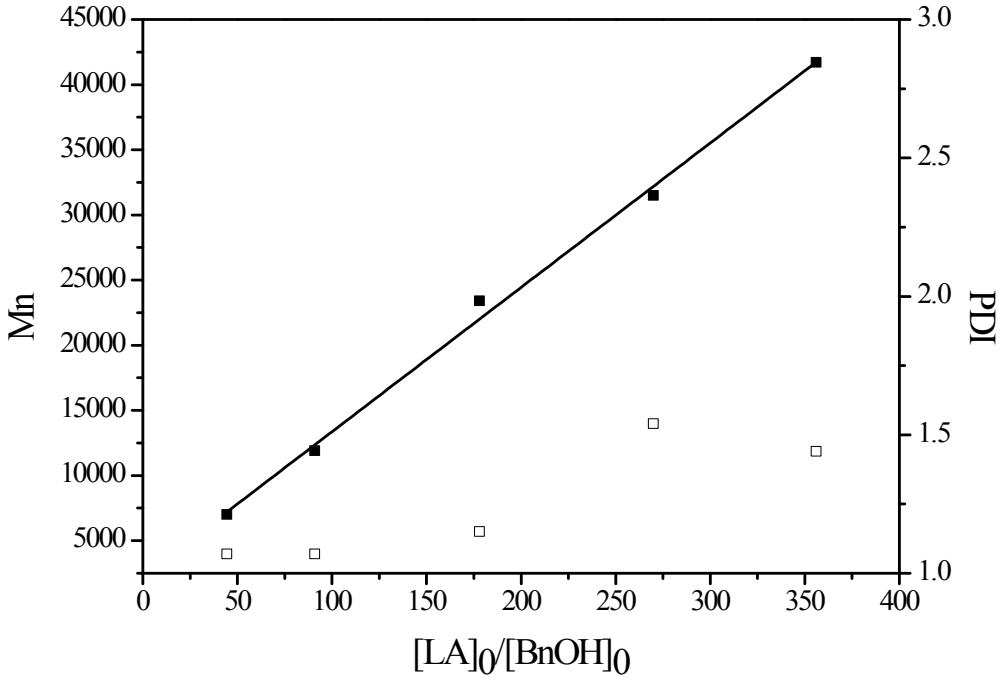


Figure S11 Polymerization of rac-LA catalyzed by **2** in toluene at room temperature. The relationships between M_n(■), D (□) of the polymer and the initial mole ratios $[LA]_0/[BnOH]_0$ (Table 2, entries 5-9) is shown.

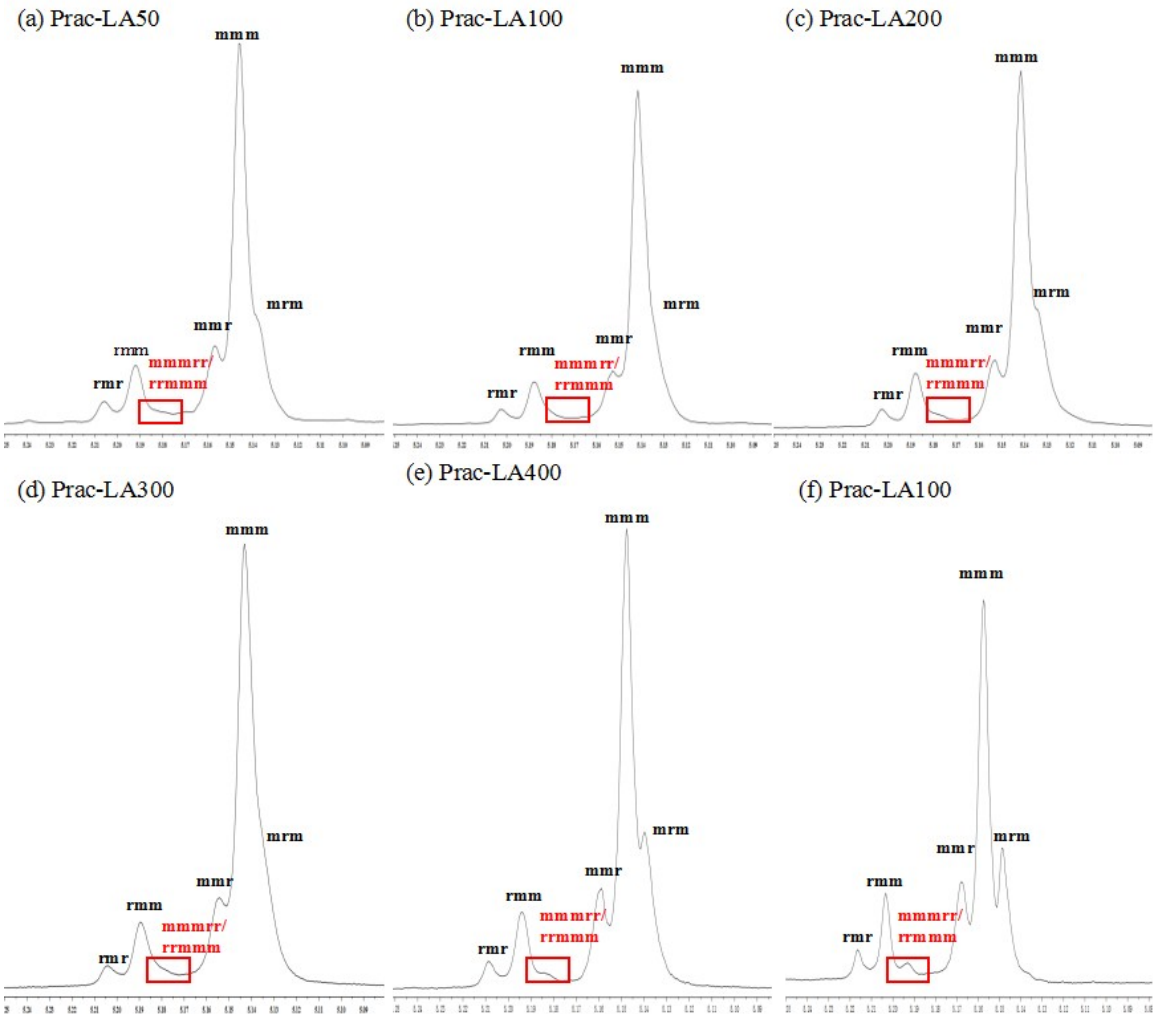


Figure S12 (a)-(e) is the deconvolution of the homonuclear-decoupled ^{1}H NMR spectrums of PLA (entry 5-9, Table 2). (f) is the deconvolution of the homonuclear-decoupled 1H NMR spectrums of PLA (entry 1, Table 2).

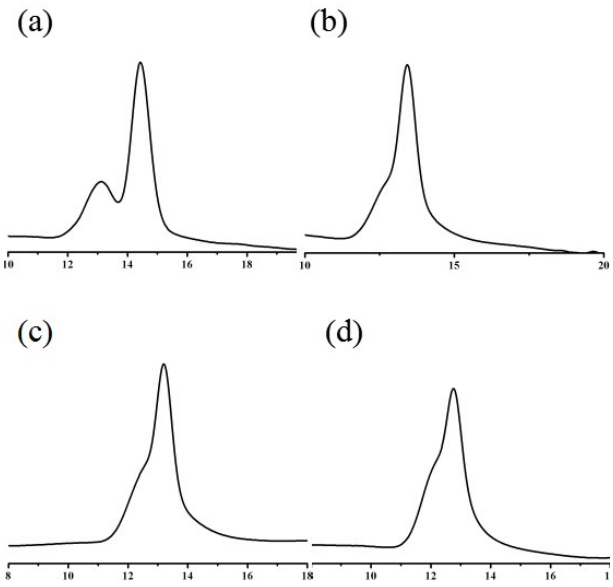


Figure S13 The gel permeation chromatogram of the polymer catalyzed by **1.**

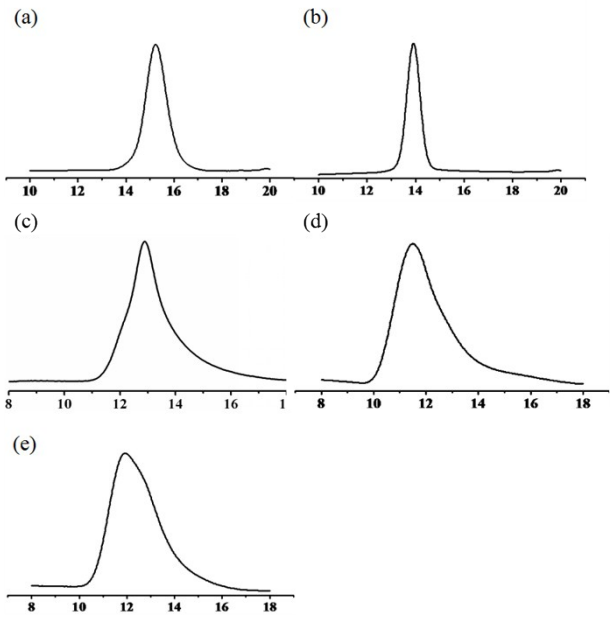


Figure S14 The gel permeation chromatogram of the polymer catalyzed by **2.**

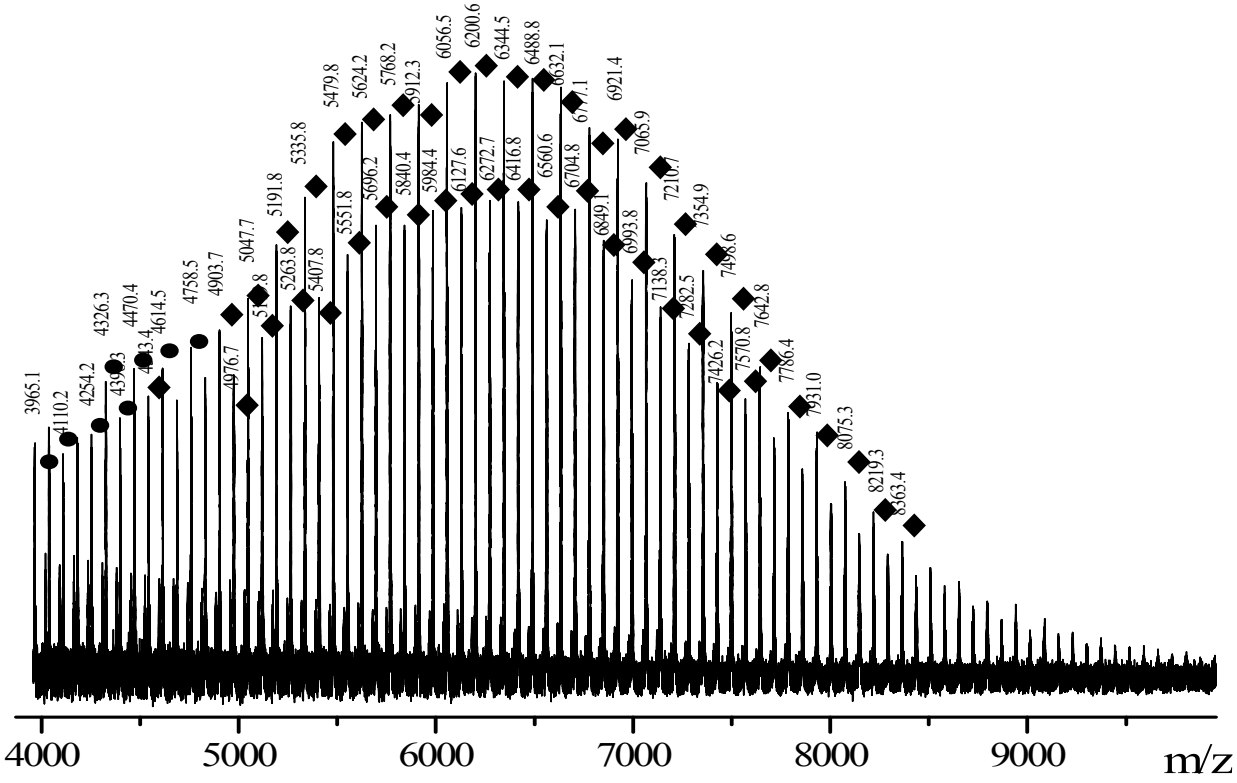


Figure S15 The MALDI-TOF spectrum of PLA50 prepared by catalyst **2** ($[LA]_0/[Cat.]_0/[BnOH]_0$ = 50:1:1, Table 2, entry 5). Mass (♦)= 72m + 108($PhCH_2OH$) + 18 (H_2O) + 23 (Na^+); Mass (•)= 72m + 108($PhCH_2OH$) + 39(K^+).

Table S1 Crystallographic data of complexes **1** and **2**

Compound	**1**	**2**
Formula	$C_{32}H_{37}KO_8$	$C_{66}H_{78}K_2O_{16}$
Fw	588.72	1205.48
Temp	173.00(10)	296(2)
Crystal system	Monoclinic	triclinic
Space group	$I_{2/a}$	P_1
*a*Å	8.1133(4)	10.9339(11)
*b*Å	18.7948(10)	11.3695(12)
*c*Å	19.0856(10)	14.208(2)
α°	90.00	107.602(2)
β°	98.877(5)	96.818(2)
γ□°	90.00	109.876(2)
V Å^3	2875.4(3)	1534.1(3)
Z	4	1
Density(calcd) g·cm^{-3}	1.360	1.305
Absorb.coeff. mm^{-1}	0.237	0.223
F(000)	1248	640
θ range	4.1–28.3°	3.5–26.8°
Index ranges	-10<*h*<10 -18<*k*<25 -24<*l*<23	-13<*h*<13 -13<*k*<13 -11<*l*<17
Data/restr./param	4980/45/373	7016/3/759
GOF	1.048	1.035
[I> 2σ(I)]	R_1 =0.0491 wR_2=0.1171	R_1=0.0492 wR_2=0.1447