Supporting information

Different Mechanisms at Different Temperatures for the Ring-Opening Polymerization of Lactide Catalyzed by Binuclear Magnesium and Zinc Alkoxides

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Table S1. Crystallographic and Structure Refinement Data.

	1	**2**	**3**
Formula	$C_{58}H_{82}Mg_2N_4O_4 \cdot 0.5(C_7H_8) \cdot 1(C_6H_6)$	$C_{58}H_{82}N_4O_4Zn_2 \cdot 0.5(C_7H_8) \cdot 1.5(C_6H_6)$	$C_{54}H_{82}Mg_2N_4O_5 \cdot C_7H_8$
Fw	1072.07	1193.24	1007.99
Temp	293 (2)	293 (2)	293 (2)
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	Pccn	Pccn	$P2_1/n$
a Å	29.2813 (9)	29.0531 (7)	16.7376 (4)
b Å	21.6214 (8)	21.5787 (10)	20.2012 (6)
c Å	20.7411 (6)	20.9114 (6)	7.7913 (4)
α°	90.00	90.00	90.00
β°	90.00	90.00	96.569 (2)
γ°	90.00	90.00	90.00
V $Å^3$	13131.2 (7)	13109.9 (8)	5976.1 (3)
Z	8	8	4
Density(calcd) $g \cdot cm^{-3}$	1.085	1.209	1.120
Absorb.coeff. mm^{-1}	0.084	0.781	0.735
F(000)	4648	5104	2192
Index ranges	-34<h<33 -25<k<25 -23<l<24	-34<h<27 -25<k<24 -15<l<24	-20<h<18 -24<k<24 -21<l<21
Data/restr./param	11519/48/734	11495/50/734	11381/12/677
GOF	1.10	1.045	1.04
$[I > 2\sigma(I)]$	R_1 =0.079 wR_2=0.237	R_1=0.069 wR_2=0.203	R_1=0.061 wR_2=0.176
CCDC number	1045608	1027498	1045550

Table S2. Selected bond lengths [Å] and angles [°].

1			
Mg1—O1	1.943 (2)	Mg2—O3	2.015 (2)
Mg1—O4	1.962 (2)	Mg2—O2	1.938 (2)
Mg1—N2	2.317 (3)	Mg2—O4	1.964 (2)
Mg1—N1	2.135 (3)	Mg2—N4	2.121 (3)
Mg1—O3	2.011 (2)	Mg2—N3	2.380 (3)
O1—Mg1—O3	106.44 (9)	O3—Mg2—N4	109.96 (9)
O1—Mg1—O4	105.31 (10)	O3—Mg2—N3	85.67 (8)
O1—Mg1—N2	160.90 (10)	O2—Mg2—O3	121.09 (9)
O1—Mg1—N1	85.36 (10)	O2—Mg2—O4	101.08 (10)
O3—Mg1—N2	85.04 (9)	O2—Mg2—N4	86.34 (9)
O3—Mg1—N1	136.30 (10)	O2—Mg2—N3	152.04 (10)
O4—Mg1—O3	85.73 (9)	O4—Mg2—O3	85.57 (9)
O4—Mg1—N2	90.47 (9)	O4—Mg2—N4	156.37 (10)
O4—Mg1—N1	132.53 (10)	O4—Mg2—N3	88.01 (9)
N1—Mg1—N2	75.95 (10)	N4—Mg2—N3	75.96 (9)
2			
Zn1—N1	2.042 (3)	Zn2—N3	2.452 (3)
Zn1—N2	2.305 (3)	Zn2—N4	2.030 (3)
Zn1—O1	1.981 (2)	Zn2—O2	1.971 (2)
Zn1—O3	2.047 (2)	Zn2—O3	2.054 (2)
Zn1—O4	1.981 (2)	Zn2—O4	1.970 (2)
N1—Zn1—N2	77.96 (11)	N4—Zn2—N3	76.41 (10)
N1—Zn1—O3	136.66 (10)	N4—Zn2—O3	111.24 (10)
O1—Zn1—N1	88.66 (11)	O2—Zn2—N3	156.01 (9)
O1—Zn1—N2	166.16 (10)	O2—Zn2—N4	90.57 (10)
O1—Zn1—O3	101.51 (9)	O2—Zn2—O3	118.67 (9)
O3—Zn1—N2	86.17 (9)	O3—Zn2—N3	85.07 (9)
O4—Zn1—N1	133.90 (11)	O4—Zn2—N3	84.23 (10)
O4—Zn1—N2	89.12 (10)	O4—Zn2—N4	153.03 (10)
O4—Zn1—O1	102.89 (10)	O4—Zn2—O2	100.25 (10)
O4—Zn1—O3	85.10 (9)	O4—Zn2—O3	85.19 (9)
3			
Mg1—O3	2.058 (2)	Mg2—O3	2.006 (2)
Mg1—O4	2.007 (2)	Mg2—O4	1.944 (2)
Mg1—O1	1.967 (2)	Mg2—O2	1.946 (2)
Mg1—N2	2.365 (2)	Mg2—N4	2.143 (2)
Mg1—N1	2.136 (2)	Mg2—N3	2.426 (2)
Mg1—O5	2.222 (2)		
O3—Mg1—N2	85.79 (6)	N1—Mg1—N2	75.96 (6)
O3—Mg1—N1	101.77 (6)	N1—Mg1—O5	96.73 (6)
O3—Mg1—O5	158.06 (6)	O5—Mg1—N2	87.36 (6)
O4—Mg1—Mg2	40.31 (4)	O3—Mg2—N4	131.44 (6)
O4—Mg1—O3	82.13 (5)	O3—Mg2—N3	81.97 (5)
O4—Mg1—N2	90.81 (6)	O4—Mg2—O3	85.06 (6)
O4—Mg1—N1	165.77 (7)	O4—Mg2—O2	106.73 (6)
O4—Mg1—O5	77.14 (6)	O4—Mg2—N4	135.01 (7)
O1—Mg1—O3	103.35 (6)	O4—Mg2—N3	90.05 (6)
O1—Mg1—O4	106.07 (6)	O2—Mg2—O3	110.49 (6)
O1—Mg1—N2	161.63 (6)	O2—Mg2—N4	86.07 (6)
O1—Mg1—N1	86.50 (6)	O2—Mg2—N3	159.55 (6)
O1—Mg1—O5	89.36 (6)	N4—Mg2—N3	73.68 (6)

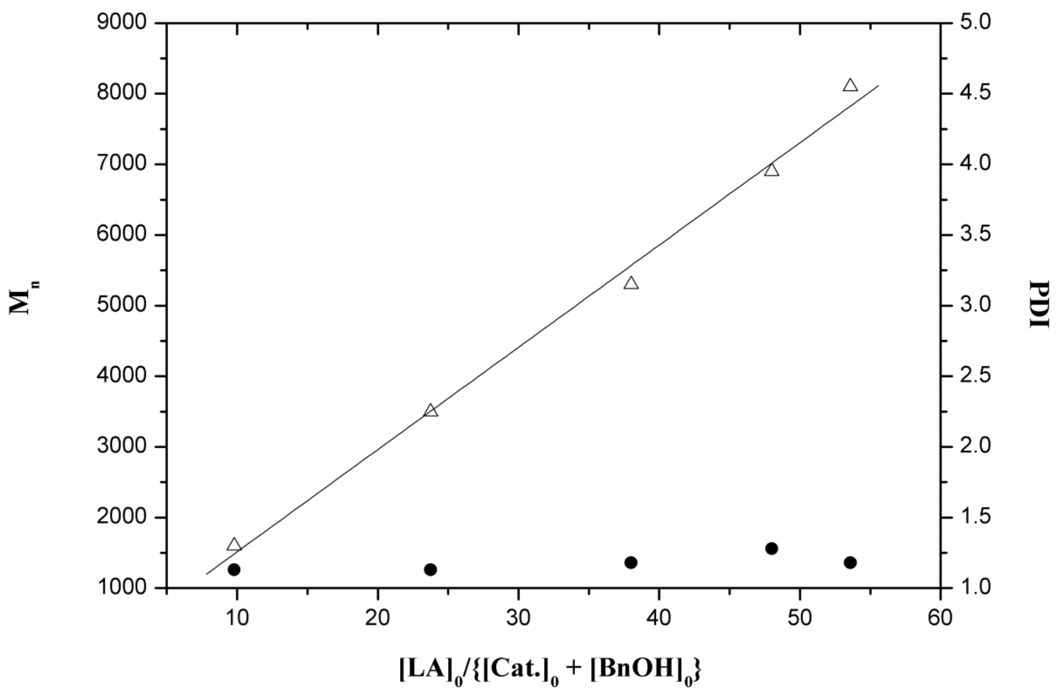

Figure S1. Polymerization of L-LA catalyzed by **1** in toluene at 80 °C. The relationship between M_n (△) (PDI (●)) of the polymer and the initial mole ratio $[LA]_0/\{[cat.]_0 + [BnOH]_0\}$ is shown (Table 1, entries 4-8).

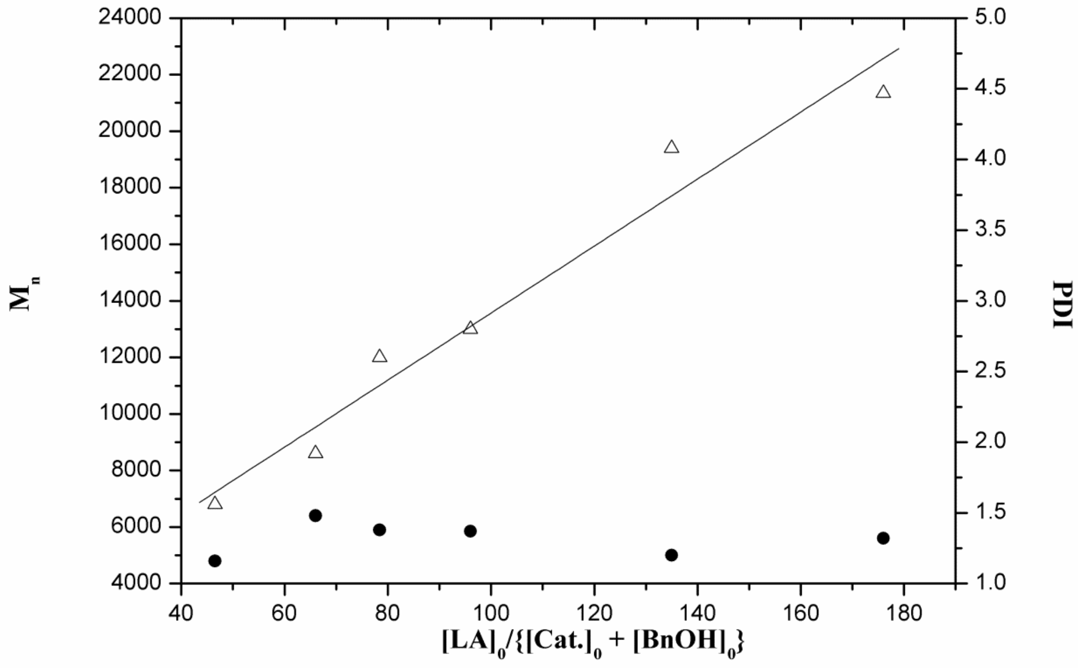

Figure S2. Polymerization of L-LA catalyzed by **1** in melt condition at 130 °C. The relationship between M_n (△) (PDI (●)) of the polymer and the initial mole ratio $[LA]_0/\{[cat.]_0 + [BnOH]_0\}$ is shown (Table 2, entries 2-7).

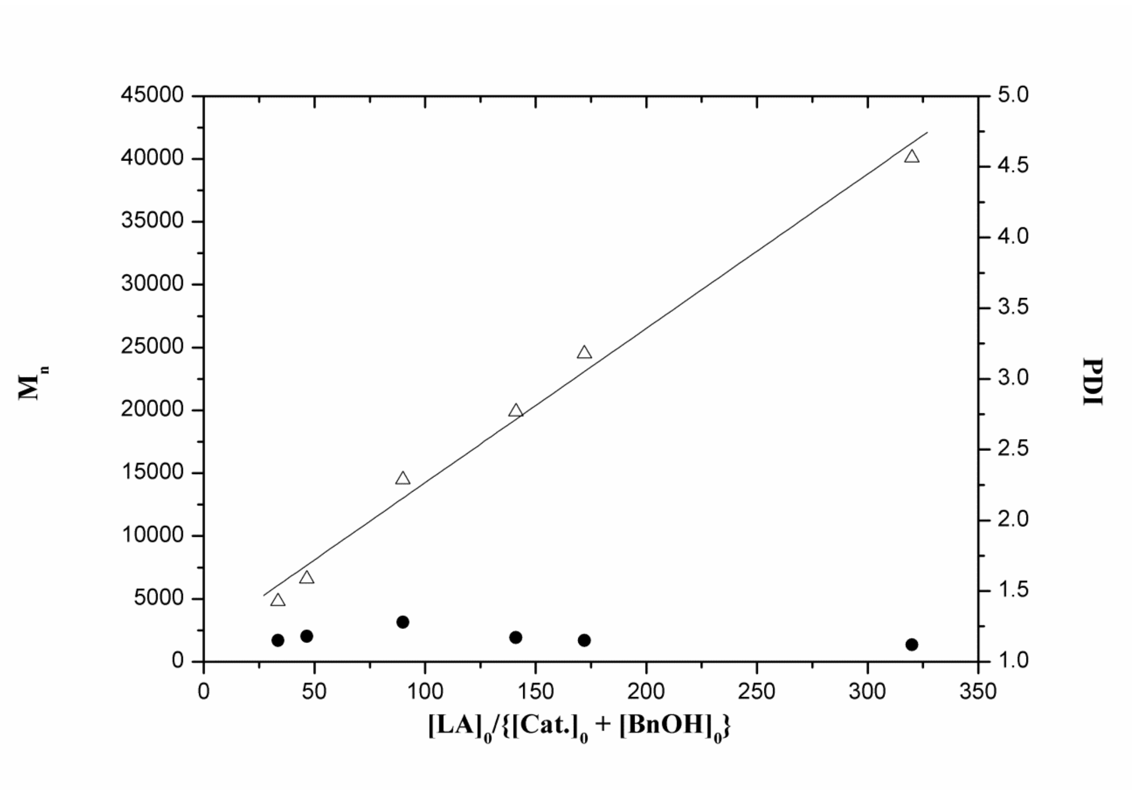

Figure S3. Polymerization of L-LA catalyzed by **2** in melt condition at 130 °C. The relationship between *M*n(△) (PDI (●)) of the polymer and the initial mole ratio $[LA]_0/\{[cat.]_0 + [BnOH]_0\}$ is shown (Table 2, entries 10-15).

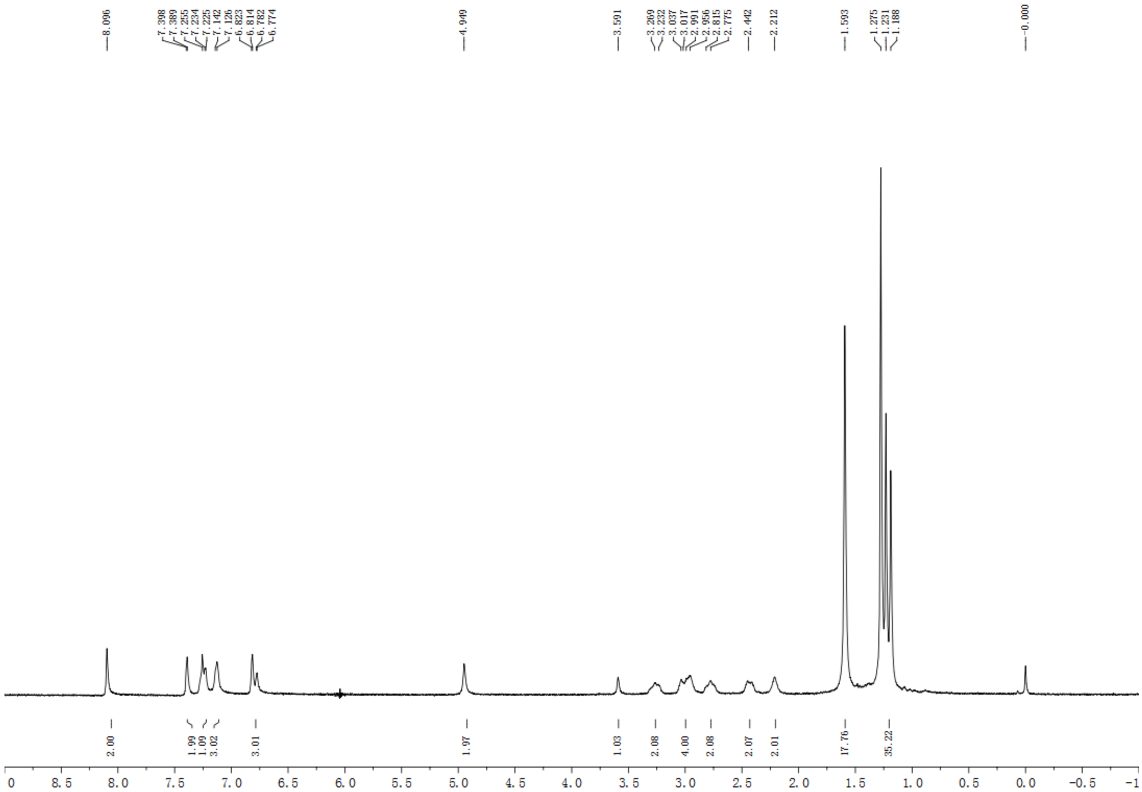

Figure S4. [1]H NMR spectra of the complex **1** after keeping it at 130 °C for one hour.

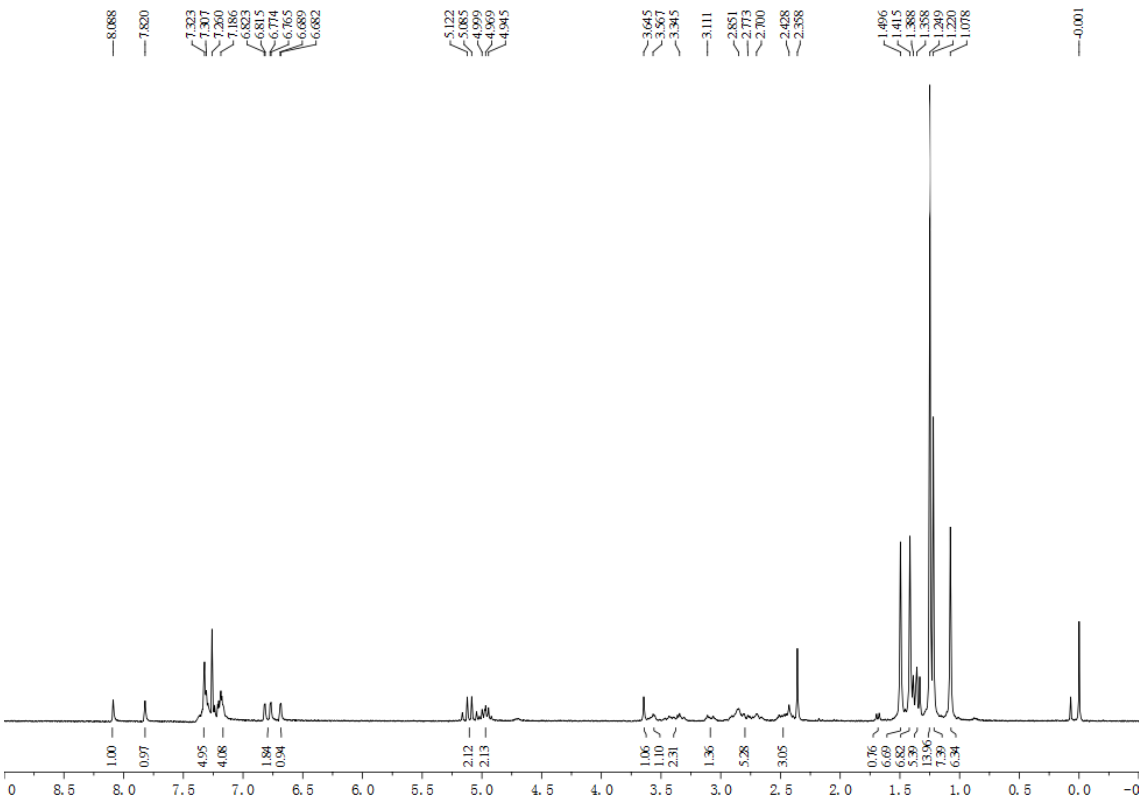

Figure S5. ^{1}H NMR spectra of the complex **1** with one equivalent L-LA in $CDCl_3$ solution.

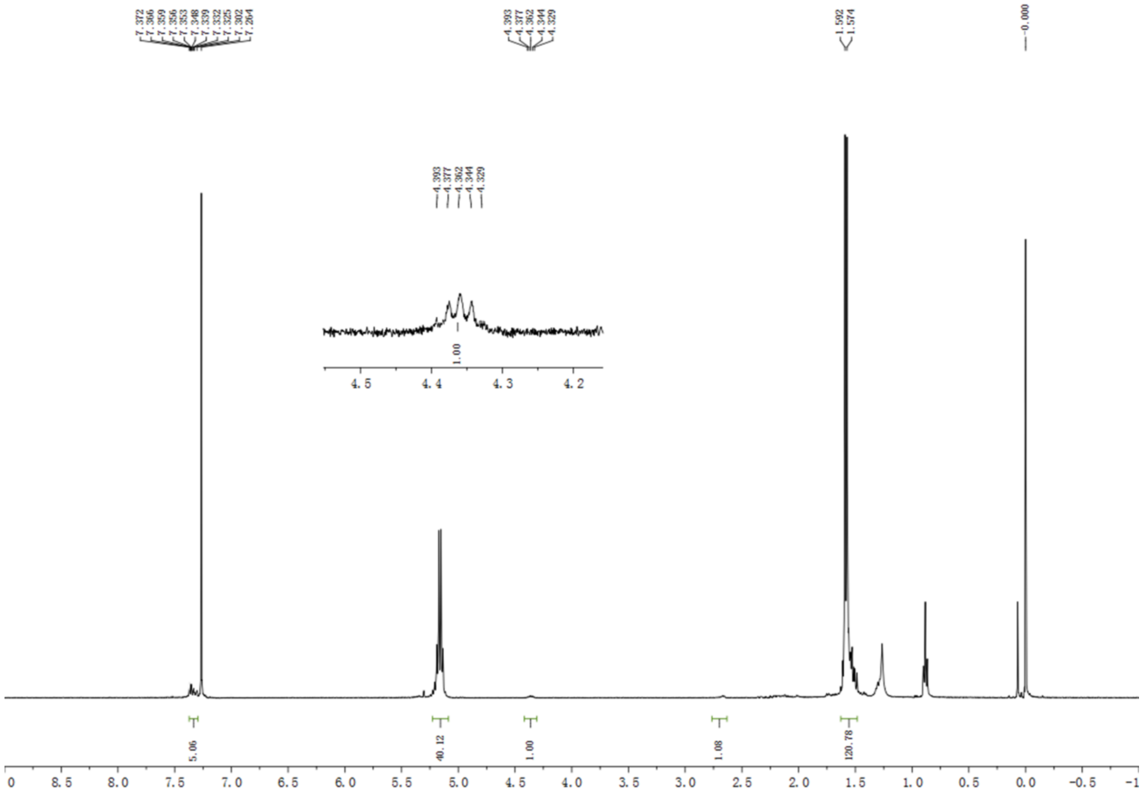

Figure S6. ^{1}H NMR spectra of PLLA-20 (20 indicates $[LA]_0/[\mathbf{1}]_0 = 20$) produced by **1** at 130 °C (Table 2, entry 2).

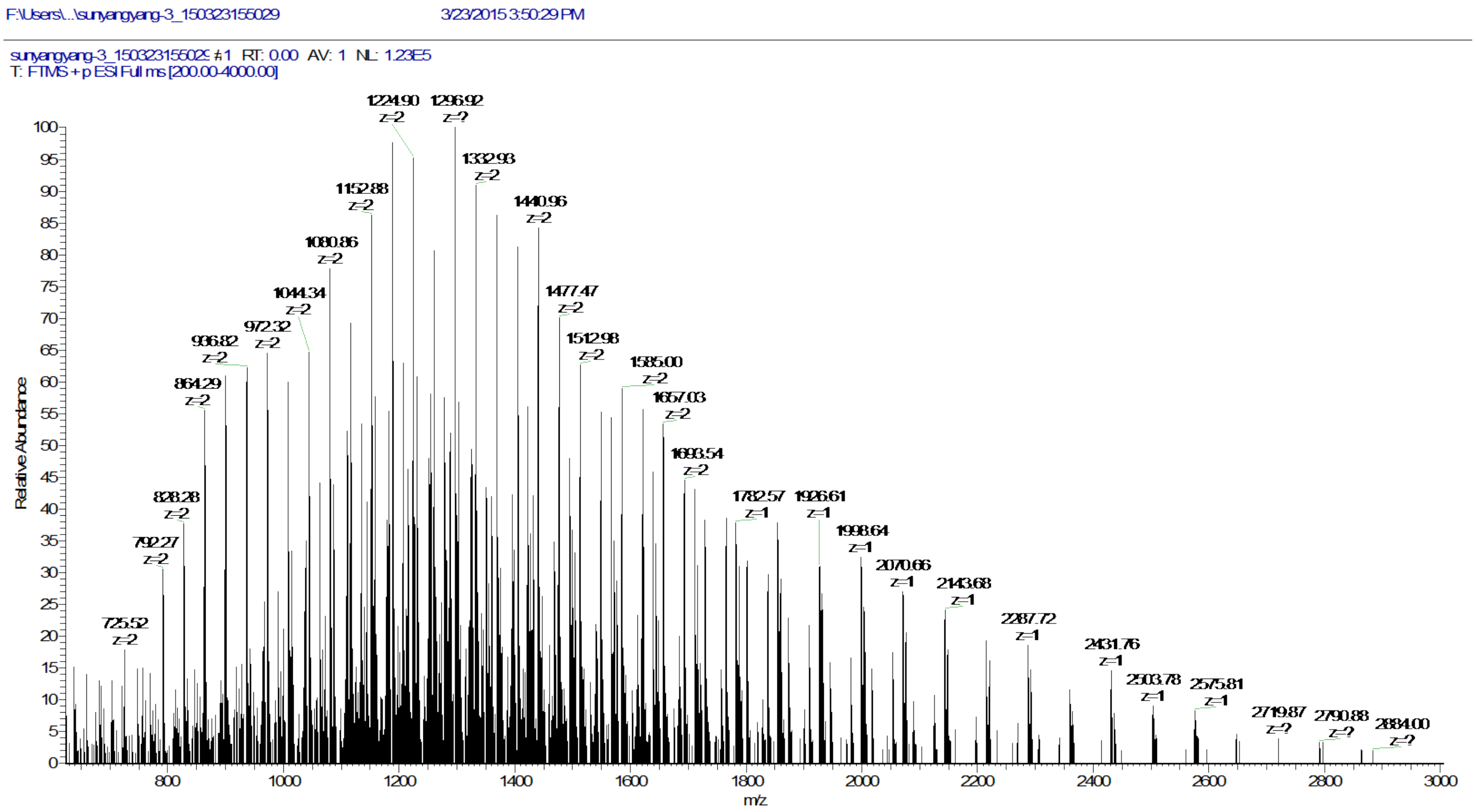

Figure S7. The ESI-MASS mass spectrum of one benzyl ester and a hydroxyl end-capped PLLA-20(20 indicates $[LA]_0/[\mathbf{1}]_0 = 20$) produced by **1** at 130 °C (Table 2, entry 2).

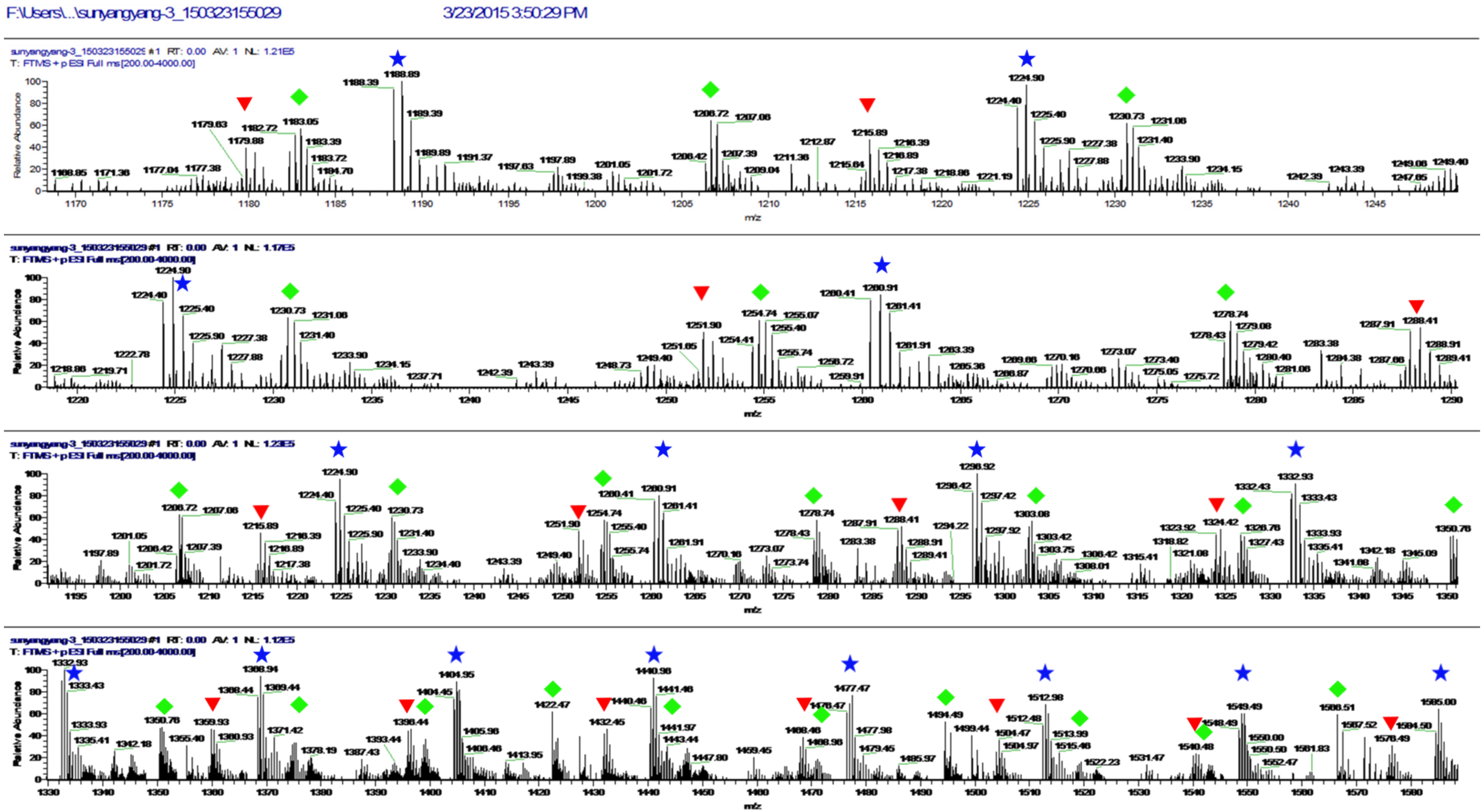

Figure S8. Enlarged ESI-MS spectrum of PLLA-20 (Table 2, entry 2), Peak series labelled "▼"correspond to m($C_3H_4O_2$) + BnOH + NH_4^+ + H^+, Peak series labelled "◆"correspond to m($C_3H_4O_2$) + BnOH + 3 × NH_4^+. Peak series labelled "★" correspond to m($C_3H_4O_2$) + BnOH + H_3O^+ + NH_4^+.

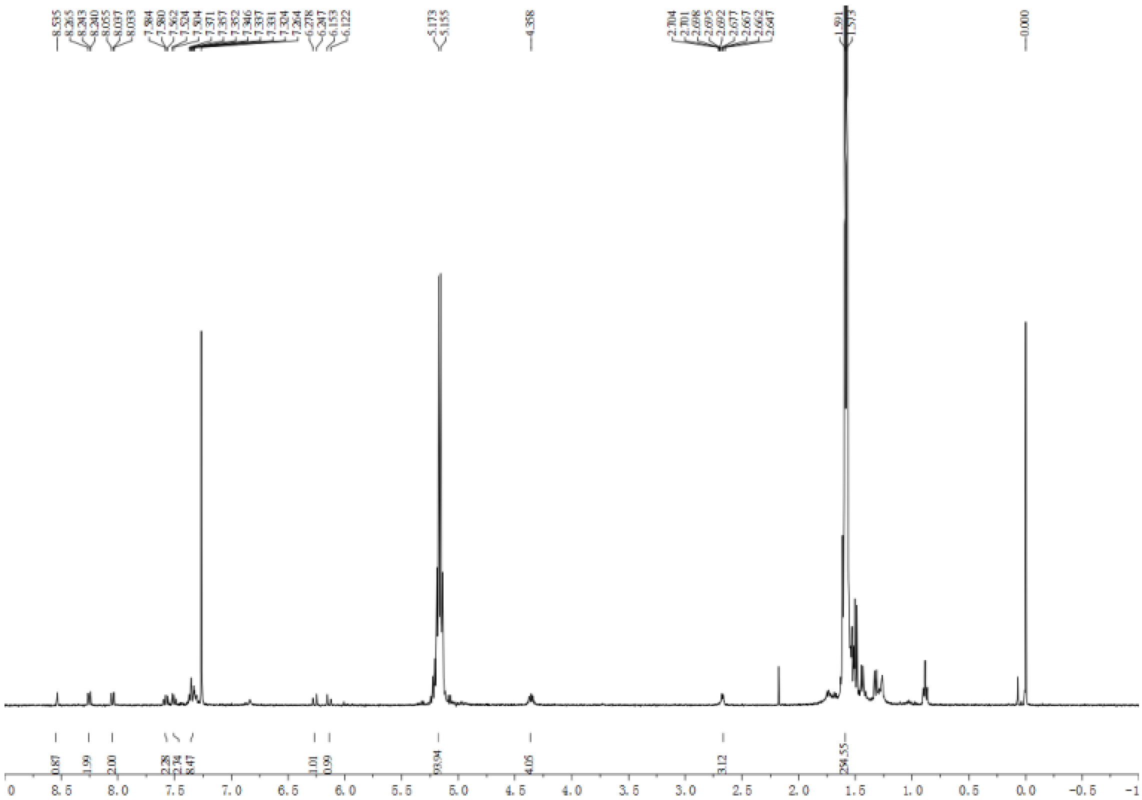

Figure S9. ¹H NMR spectrum of PLLA obtained from polymerization of L-LA catalyed by complex **1** and 9-anthracenemethanol.

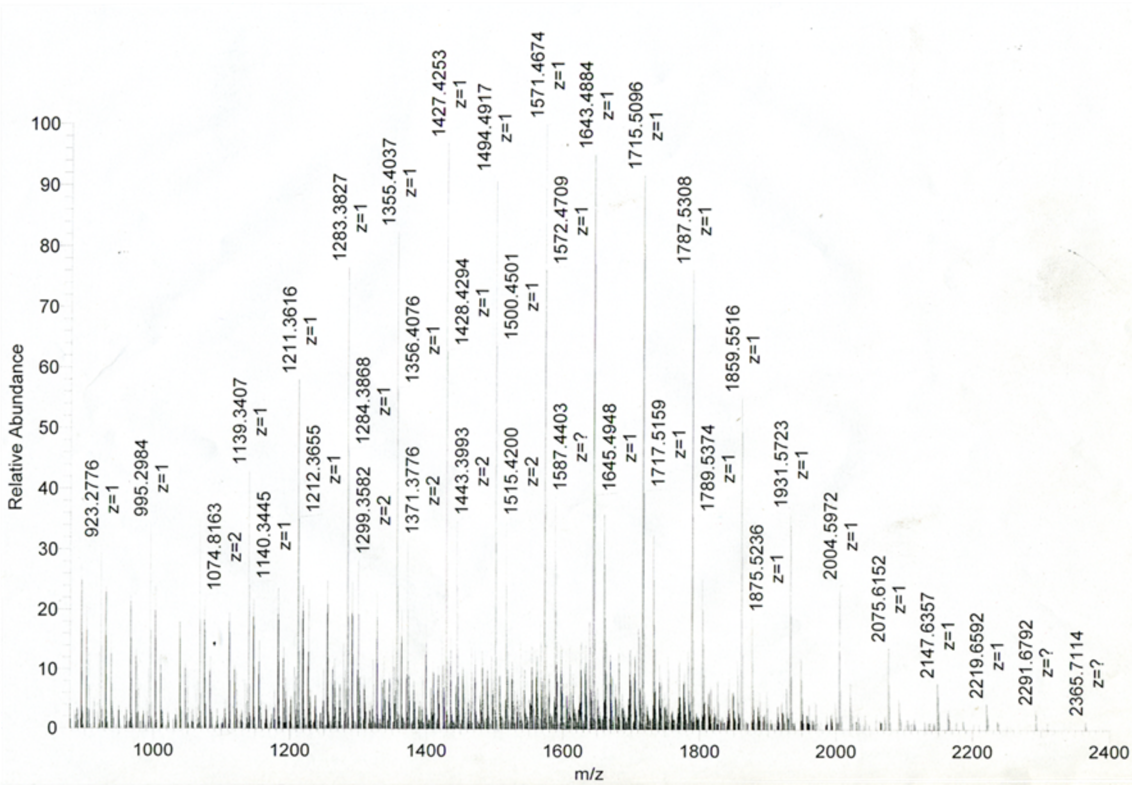

Figure S10. The ESI-MASS mass spectra of one benzyl ester and a hydroxyl end-capped PLLA-10 (10 indicates $[LA]_0/[\mathbf{1}]_0 = 20$) produced by **1** at 80 °C in toluene (Table 1, entry 5).

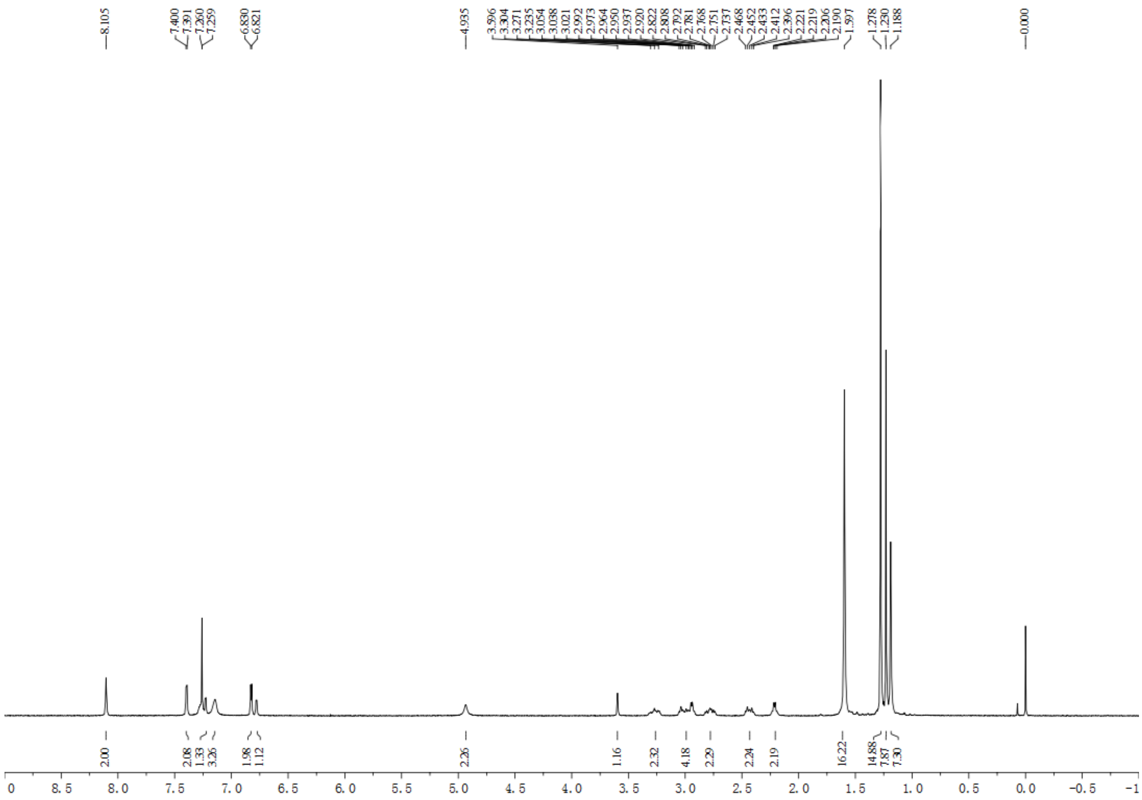

Figure S11. ^{1}H NMR spectra of complex **1**.

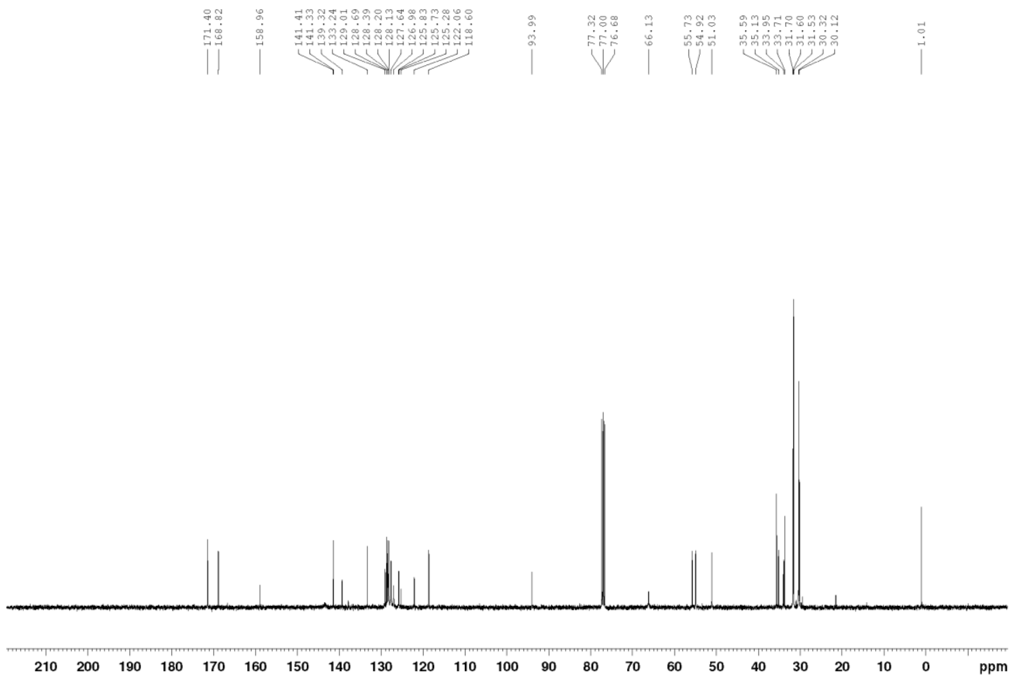

Figure S12. ^{13}C NMR spectra of complex **1**.

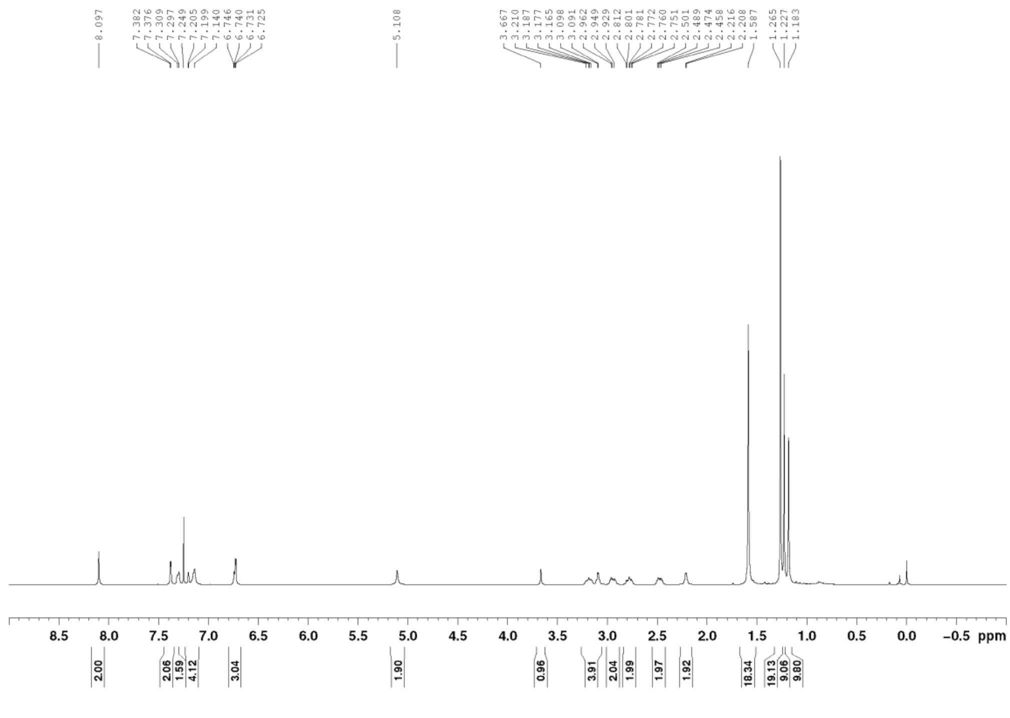

Figure S13. ^{1}H NMR spectra of complex **2**.

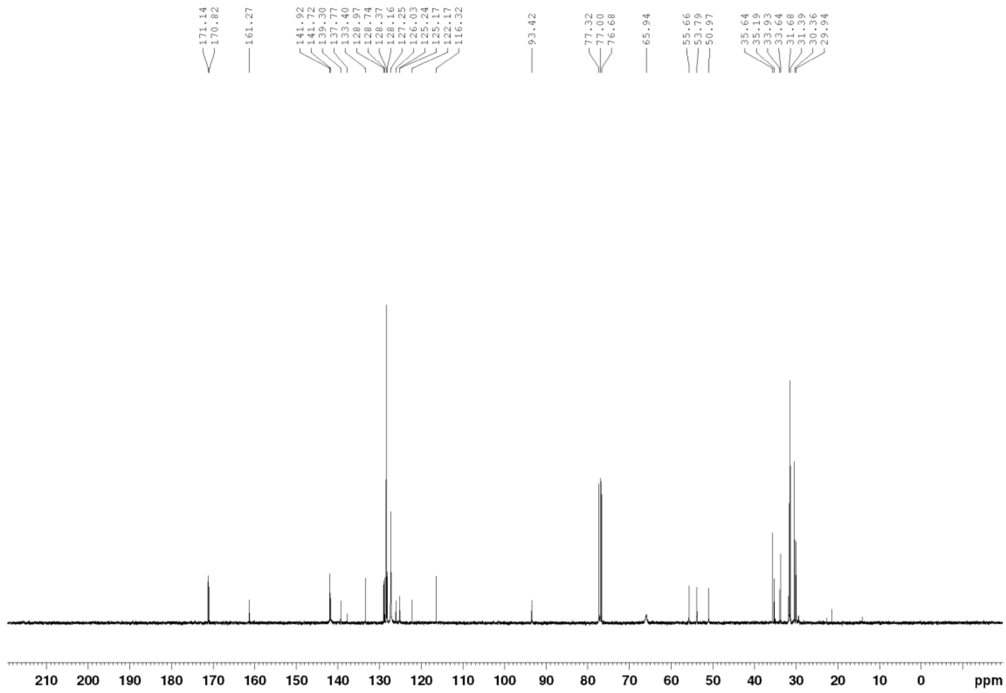

Figure S14. ^{13}C NMR spectra of complex **2**.

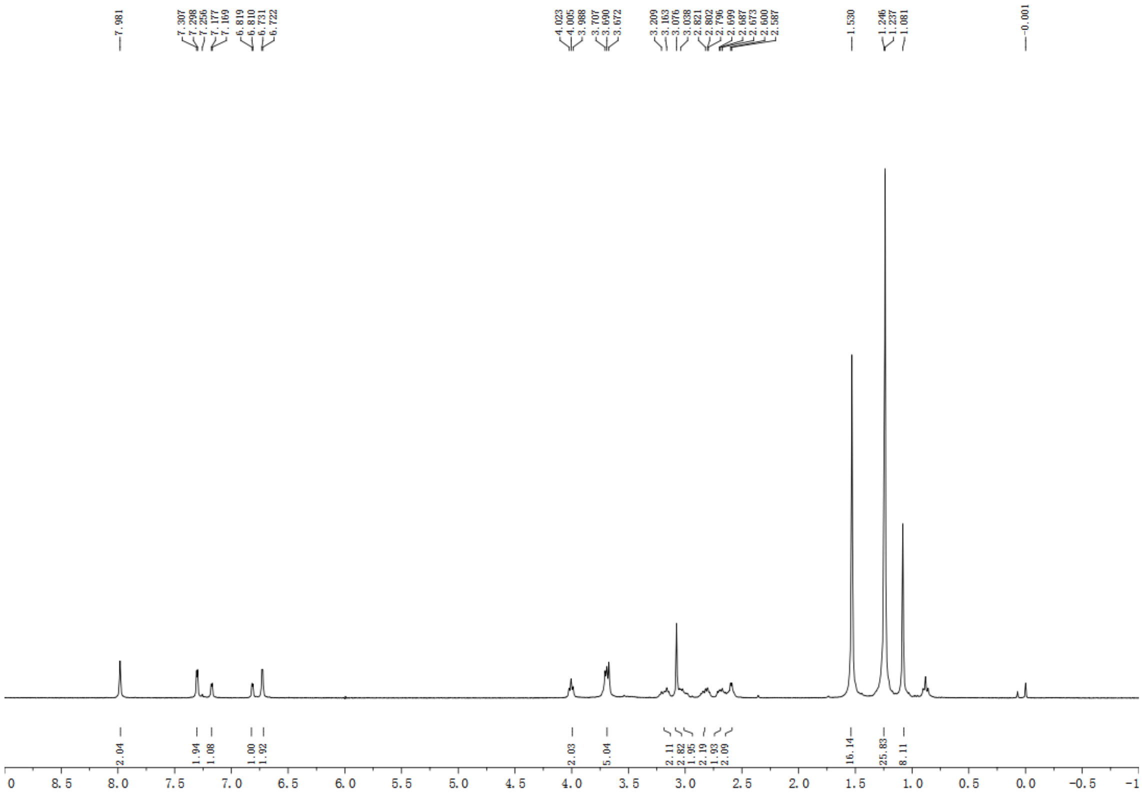

Figure S15. ^{1}H NMR spectra of complex **3**.

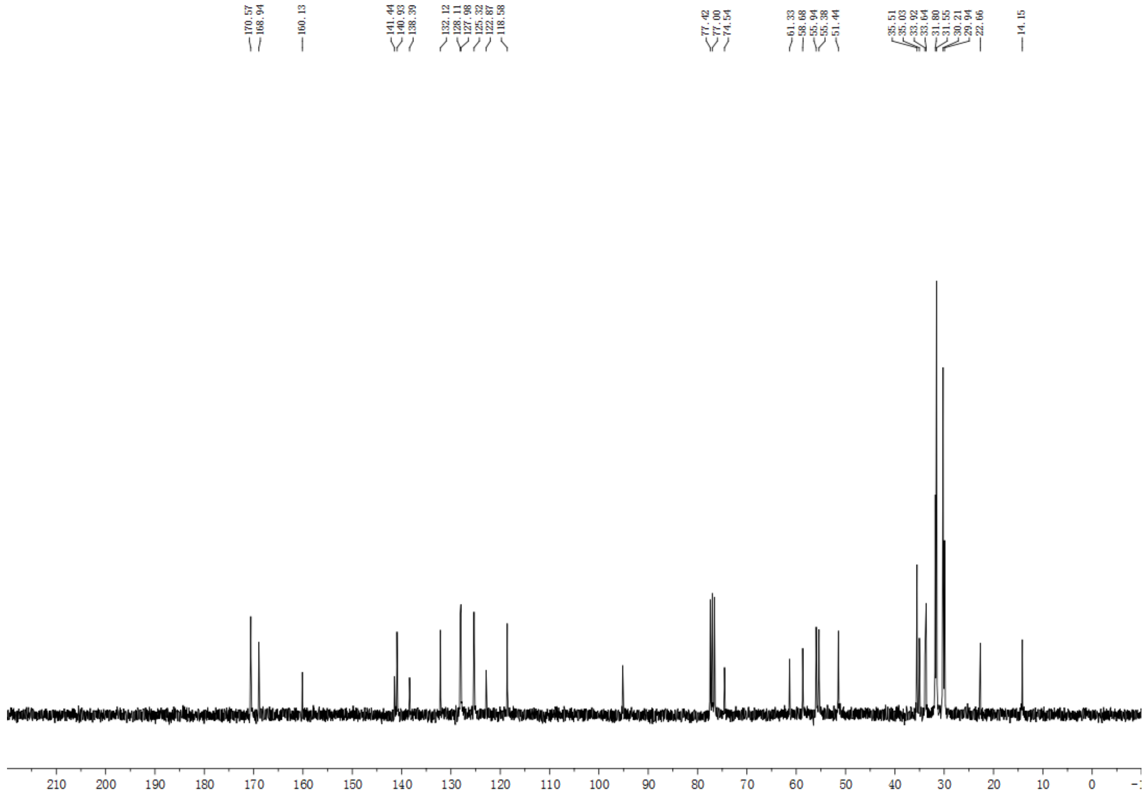

Figure S16. ^{13}C NMR spectra of complex **3**.

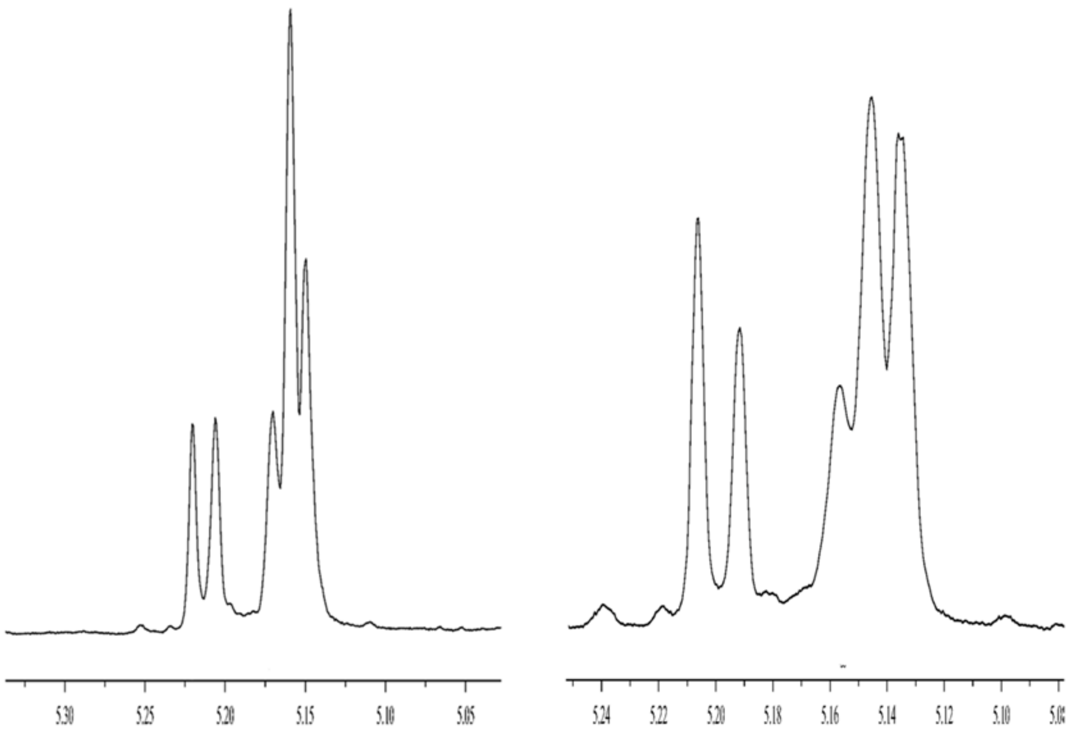

Figure S17. Homonuclear decoupled ^{1}H NMR spectra of the PLA produced by complex **1** (Table 3, entry 1 (left) and entry 3 (right)).