Supporting Information

β-Pyridylenolate Zinc Catalysts for the Ring-Opening Homo- and Copolymerization of ε-Caprolactone and Lactides

Jianliang Bai,[†] Xia Xiao,[†] Yue Zhang,[†] Jianbin Chao,[‡] Xia Chen[†]*

[†]School of Chemistry and Chemical Engineering and [‡]Scientific Instrument Center,

Shanxi University, Taiyuan 030006, China

Content

Table S1. Selected bond lengths [Å], angles [°] for **1**, **3**, **4**, **7**, **9** and **11**

1			**3**	**4**	**9**	**7**		**11**	
lengths [Å]									
Zn1-O1	2.0100(12)	Zn1-O1	2.0025(11)	2.0073(12)	1.9994(11)	Zn1-O1^{i}	1.9963(18)	Zn1-O1^{i}	2.0008(12)
Zn1-O2	2.0886(13)	Zn1-O1^{i}	2.0975(12)	2.1082(13)	2.0672(11)	Zn1-O1	2.093(2)	Zn1-O1	2.0693(12)
Zn1-C4	1.962(2)	Zn1-C4	1.9718(17)	1.968(2)	1.9735(17)	Zn1-C14	1.969(3)	Zn1-C16	1.9661(19)
Zn1-N1	2.0561(16)	Zn1-N1	2.0535(15)	2.0561(15)	2.0662(14)	Zn1-N1	2.055(2)	Zn1-N1	2.0739(15)
C3-O1	1.340(2)	C3-O1	1.3340(19)	1.331(2)	1.3439(18)	C8^{i}-O1^{i}	1.339(3)	C2^{i}-O1^{i}	1.343(2)
angles [°]									
C3-O1-Zn1	117.63(11)	C3-O1-Zn1	123.76(11)	124.13(11)	121.05(10)	C8-O1-Zn1^{i}	123.29(15)	C2-O1-Zn1^{i}	120.52(10)
C3-O1-Zn2	126.97(11)	C3-O1-Zn1^{i}	117.14(10)	115.90(11)	126.95(10)	C8-O1-Zn1	119.07(16)	C2-O1-Zn1	126.81(11)
C4-Zn1-O1	125.75(9)	C4-Zn1-O1	134.47(7)	131.82(7)	133.42(6)	C14-Zn1-O1^{i}	131.90(11)	C16-Zn1-O1^{i}	132.99(8)
C4-Zn1-O2	123.09(9)	C4-Zn1-O1^{i}	115.60(6)	115.03(8)	122.72(6)	C14-Zn1-O1	120.39(11)	C16-Zn1-O1	123.05(7)
C4-Zn1-N1	121.24(10)	C4-Zn1-N1	120.98(7)	121.87(8)	119.32(7)	C14-Zn1-N1	121.86(11)	C16-Zn1-N1	118.04(7)
O1-Zn1-N1	90.94(6)	O1-Zn1-N1	91.33(5)	91.64(5)	87.95(5)	O1^{i}-Zn1-N1	89.44(8)	O1^{i}-Zn1-N1	88.27(5)
O2-Zn1-N1	102.88(6)	O1^{i}-Zn1-N1	104.14(5)	106.09(6)	101.60(5)	O1-Zn1-N1	101.90(8)	O1-Zn1-N1	102.60(5)
O1-Zn1-O2	83.52(5)	O1-Zn1-O1^{i}	81.56(5)	82.16(5)	81.92(5)	O1^{i}-Zn1- O1	81.32(8)	O1^{i}-Zn1- O1	82.63(5)
Zn1-O1-Zn2	96.67(5)	Zn1-O1-Zn1^{i}	98.44(5)	97.84(5)	98.08(5)	Zn1-O1^{i}-Zn1^{i}	98.68(8)	Zn1-O1^{i}-Zn1^{i}	97.37(5)

Table S2. Crystallographic Data for Complexes **1-4, 6**

Compound	**1**	**2**	**3**	**4**	**6**
Formula	$C_{26}H_{38}N_2O_2Zn_2$	$C_{30}H_{30}N_2O_2Zn_2$	$C_{32}H_{34}N_2O_2Zn_2$	$C_{32}H_{34}N_2O_2Zn_2$	$C_{32}H_{28}F_6N_2O_2Zn_2$
Formula weight	541.32	581.30	609.35	609.35	717.30
Crystal system	Monoclinic	Triclinic	Orthorhombic	Triclinic	Monoclinic
Space group	$P2_1/n$	P-1	*P*bca	*P*-1	$P2_1/n$
Colour of crystal	colourless	yellow	colourless	colourless	colourless
a(Å)	14.3802(7)	8.6075(5)	14.0974(5)	8.6494(10)	10.0405(6)
b(Å)	13.2221(7)	11.6047(6)	8.6016(3)	9.7141(12)	11.0680(7)
c(Å)	15.0260(8)	13.8778(8)	23.2550(9)	10.1944(13)	13.8622(8)
α(°)	90	93.222(2)	90	109.661(4)	90
β(°)	108.765(2)	96.688(2)	90	104.640(4)	96.454(2)
γ(°)	90	105.4910(10)	90	108.913(3)	90
V(Å^3)	2705.1(2)	1321.24(13)	2819.91(18)	697.30(15)	1530.72(16)
Temperature (K)	200(2)	200(2)	200(2)	200(2)	200(2)
Z	4	2	4	1	2
D (gcm^{-3})	1.329	1.461	1.435	1.451	1.556
μ (mm^{-1})	1.796	1.845	1.732	1.752	1.636
θ range (°)	2.992-28.2755	2.946-28.332	2.890-28.298	3.617-28.356	2.958-28.302
Reflections collected	26054	13059	26571	10052	14700
Number of parameters	297	327	174	174	201
F(000)	1136	600	1264	316	728
Goodness-of-fit onF^2	1.013	1.060	1.048	1.047	1.027
Final *R* indices [$I>2\sigma(I)$]	$R_1 = 0.0304$	$R_1 = 0.0290$	$R_1 = 0.0270$	$R_1 = 0.0278$	$R_1 = 0.0391$
R_1	w$R_2 = 0.0742$	w$R_2 = 0.0708$	w$R_2 = 0.0639$	w$R_2 = 0.0633$	w$R_2 = 0.1000$
wR_2					
R indices (all data)					
R_1	$R_1 = 0.0397$	$R_1 = 0.0370$	$R_1 = 0.0363$	$R_1 = 0.0340$	$R_1 = 0.0485$
wR_2	w$R_2 = 0.0801$	w$R_2 = 0.0744$	w$R_2 = 0.0678$	w$R_2 = 0.0633$	w$R_2 = 0.1050$

Table S3. Crystallographic Data for Complexes **7-11**

Compound	**7**	**8**	**9**	**10**	**11**
Formula	$C_{32}H_{34}N_2O_2Zn_2$	$C_{34}H_{38}N_2O_2Zn_2$	$C_{34}H_{38}N_2O_2Zn_2$	$C_{34}H_{38}N_2O_4Zn_2$	$C_{34}H_{32}F_6N_2O_2Zn_2$
Formula weight	609.35	637.40	637.40	669.40	745.35
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P1$	P-1	C2/c
Colour of crystal	colourless	colourless	colourless	colourless	yellow
a(Å)	8.6781(17)	8.3871(17)	8.3149(5)	8.4891(9)	26.5338(10)
b(Å)	8.5619(17)	18.253(4)	9.3219(6)	9.3386(11)	8.6635(3)
c(Å)	18.781(4)	10.316(2)	10.6244(7)	10.7644(13)	16.4956
α(°)	90	90	82.944(2)	77.632(3)	90
β(°)	90.38	101.63(3)	69.632(2)	73.281(4)	90.5740(10)
γ(°)	90	90	79.457(2)	87.149(3)	90
V(Å^3)	1395.0(5)	1546.9(6)	757.42(8)	798.26(16)	3791.7(2)
Temperature (K)	273(2)	293(2)	200(2)	293(2)	200(2)
Z	2	2	1	1	4
D(gcm^{-3})	1.451	1.368	1.397	1.392	1.306
μ (mm^{-1})	1.751	1.582	1.616	1.541	1.323
θ range (°)	2.169-27.479	2.232-28.383	2.928-28.282	3.276-28.250	3.071-28.298
Reflections collected	9259	10881	7573	7677	17698
Number of parameters	174	184	196	193	210
F(000)	632	664	332	348	1520
Goodness-of-fit onF^2	1.026	1.001	1.062	1.022	1.056
Final R indices [$I>2\sigma(I)$]					
R_1	$R_1 = 0.0374$	$R_1 = 0.0582$	$R_1 = 0.0256$	$R_1 = 0.0539$	$R_1 = 0.0289$
wR_2	w$R_2 = 0.1288$	w$R_2 = 0.2623$	w$R_2 = 0.0652$	w$R_2 = 0.1172$	w$R_2 = 0.1061$
R indices (all data)					
R_1	$R_1 = 0.0436$	$R_1 = 0.0633$	$R_1 = 0.0302$	$R_1 = 0.0975$	$R_1 = 0.0330$
wR_2	w$R_2 = 0.1382$	w$R_2 = 0.2623$	w$R_2 = 0.0676$	w$R_2 = 0.1342$	w$R_2 = 0.1101$

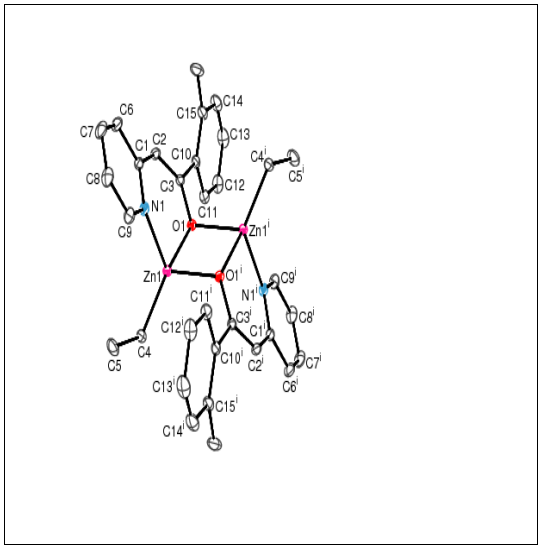

Figure S1. X-ray structure of complex **3** with thermal ellipsoids represented at the 20% probability level. Hydrogen atoms are omitted for clarity.

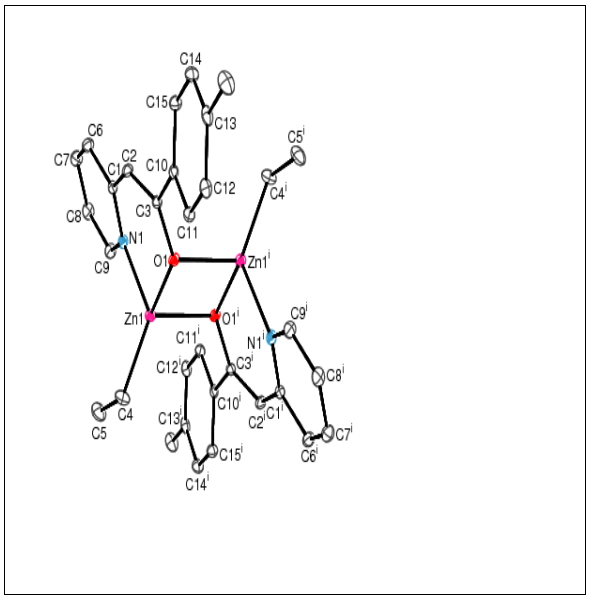

Figure S2. X-ray structure of complex **4** with thermal ellipsoids represented at the 20% probability level. Hydrogen atoms are omitted for clarity.

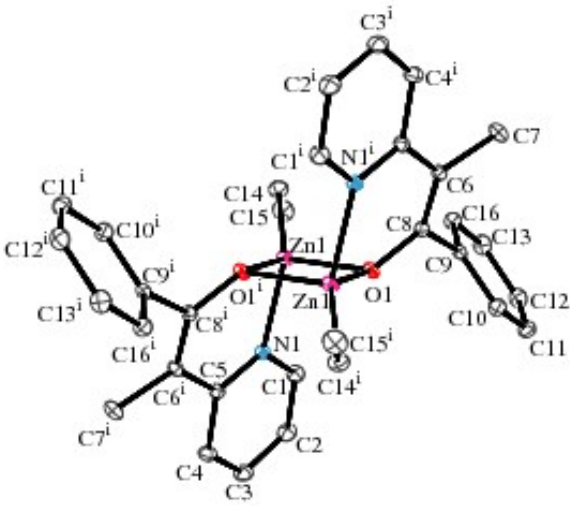

Figure S3. X-ray structure of complex **7** with thermal ellipsoids represented at the 20% probability level. Hydrogen atoms are omitted for clarity.

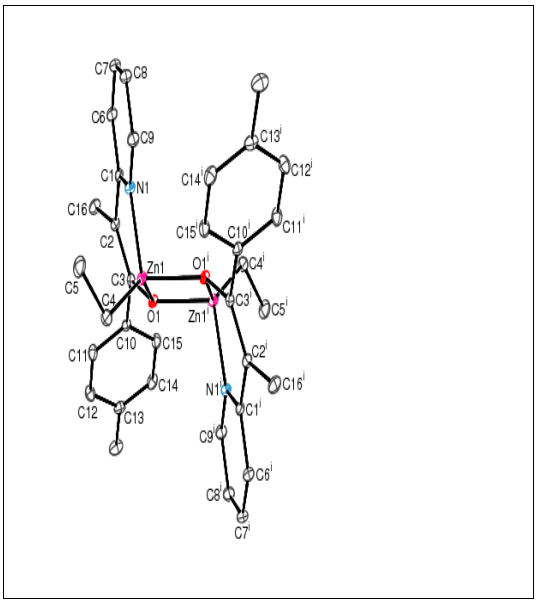

Figure S4. X-ray structure of complex **9** with thermal ellipsoids represented at the 20% probability level. Hydrogen atoms are omitted for clarity.

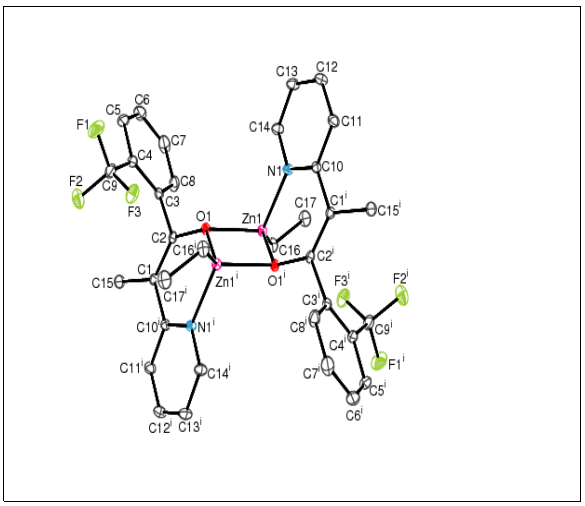

Figure S5. X-ray structure of complex **11** with thermal ellipsoids represented at the 20% probability level. Hydrogen atoms as well as solvent molecules omitted are omitted for clarity.

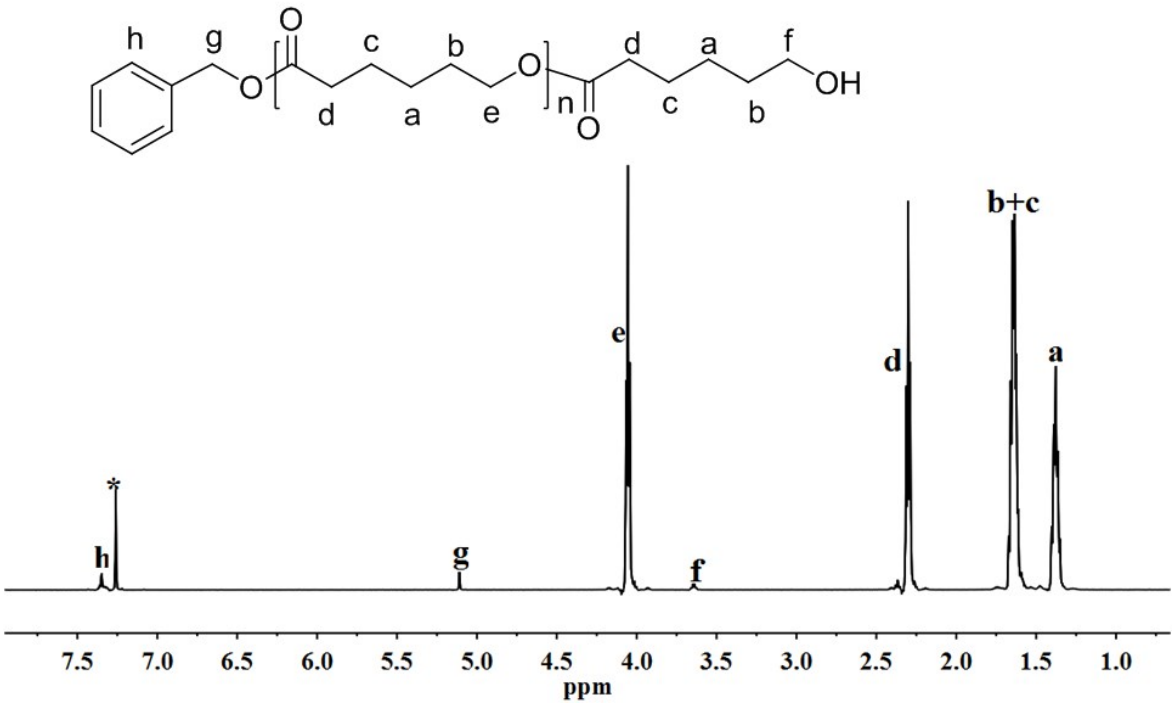

Figure S6. ^{1}H NMR spectrum of PCL-40 initiated by 10/BnOH in the ratio of $[\varepsilon\text{-CL}]_0$: $[Zn]_0$: $[BnOH]_0$ = 40 :1 :1 in toluene at 35 ºC for 20 min ($CDCl_3$, 25 ºC, 600 MHz).

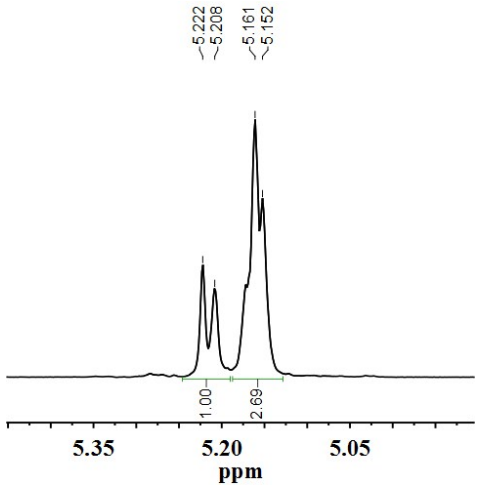

Figure S7. Methine region spectrum of homonuclear decoupled ^{1}H NMR spectrum ($CDCl_3$, 25 ºC, 600 MHz, P_r=0.54, Table 2, entry 1)

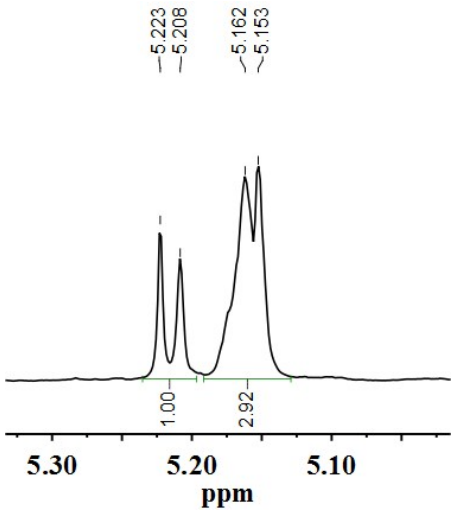

Figure S8. Methine region spectrum of homonuclear decoupled ^{1}H NMR spectrum ($CDCl_3$, 25 ºC, 600 MHz, P_r=0.51, Table 2, entry 2)

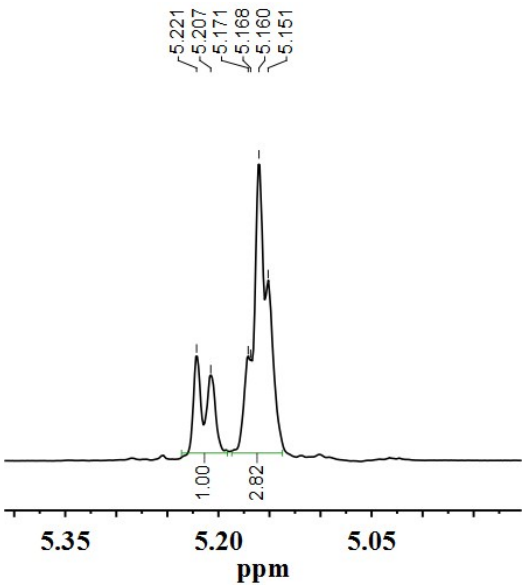

Figure S9. Methine region spectrum of homonuclear decoupled ^{1}H NMR spectrum ($CDCl_3$, 25 ºC, 600 MHz, P_r=0.52, Table 2, entry 6)

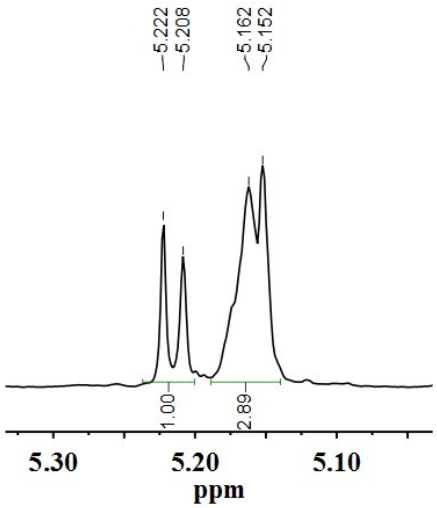

Figure S10. Methine region spectrum of homonuclear decoupled ^{1}H NMR spectrum ($CDCl_3$, 25 ºC, 600 MHz, P_r=0.51, Table 2, entry 10)

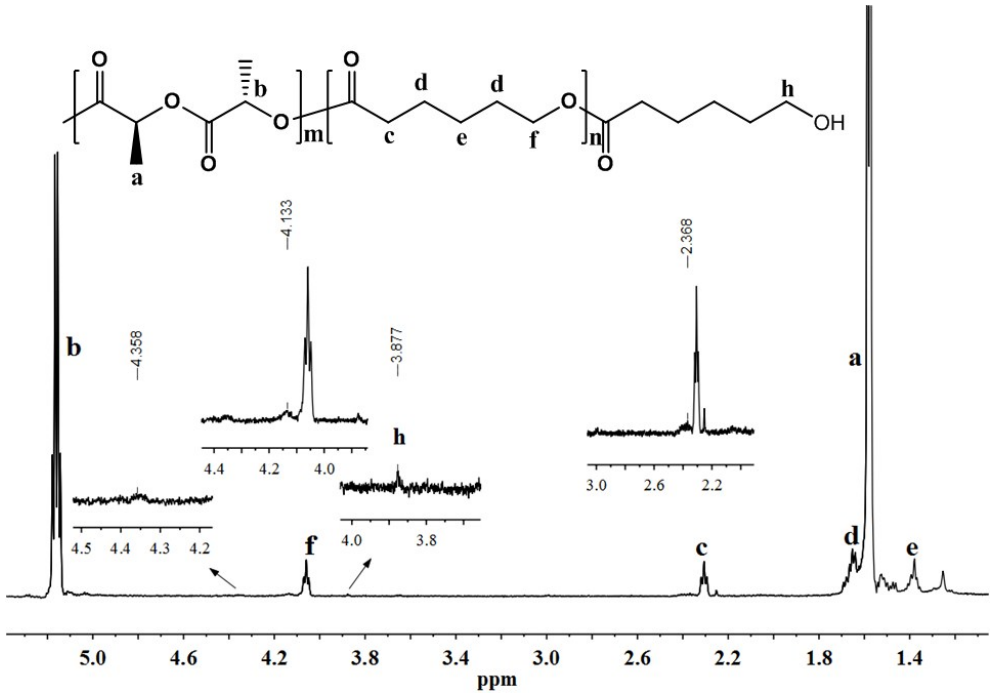

Figure S11. ^{1}H NMR spectrum of PLLA-*b*-PCL copolymer by complex **10** ($CDCl_3$, 25 ºC, 600 MHz)

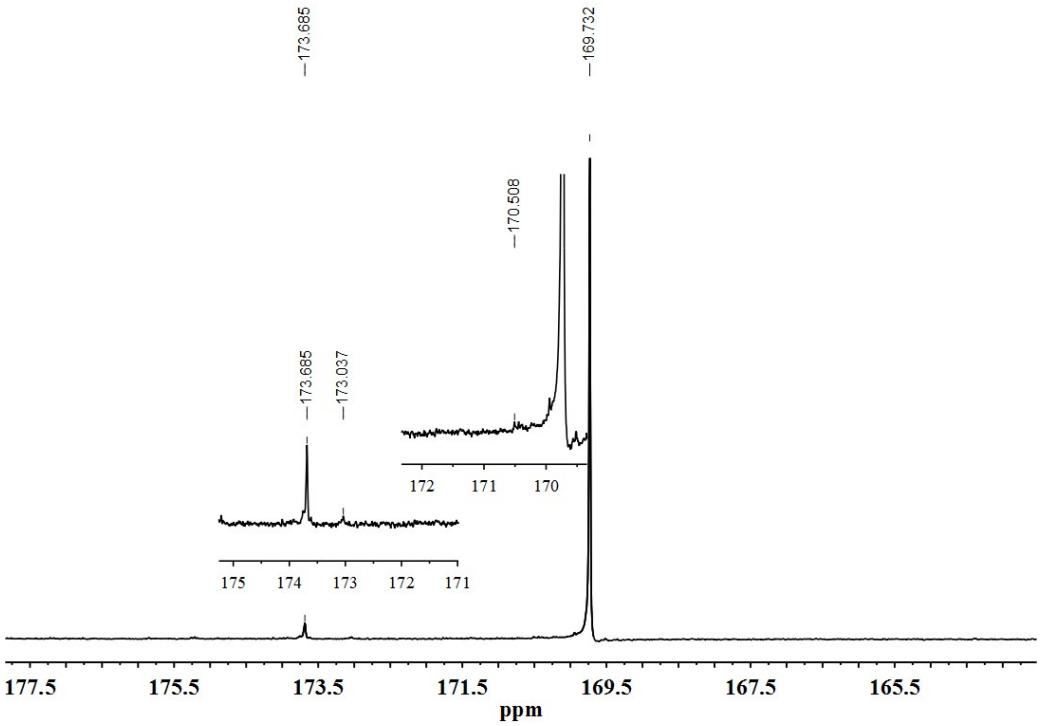

Figure S12. ^{13}C HNR spectrum of PCL-*b*-PLLA copolymer by complex **10** ($CDCl_3$, 25 ºC, 150 MHz)

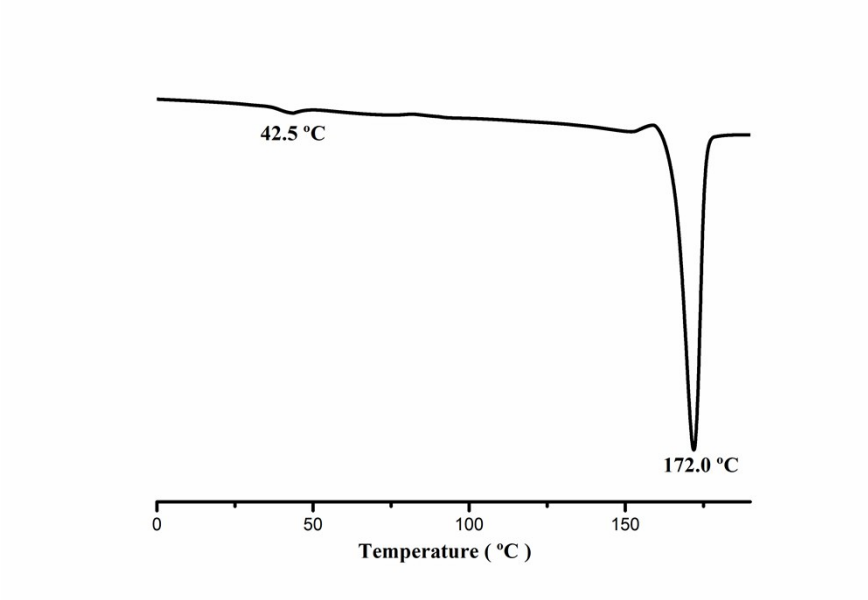

Figure S13. DSC analysis of PLLA-*b*-PCL copolymer prepared by complex **10**.

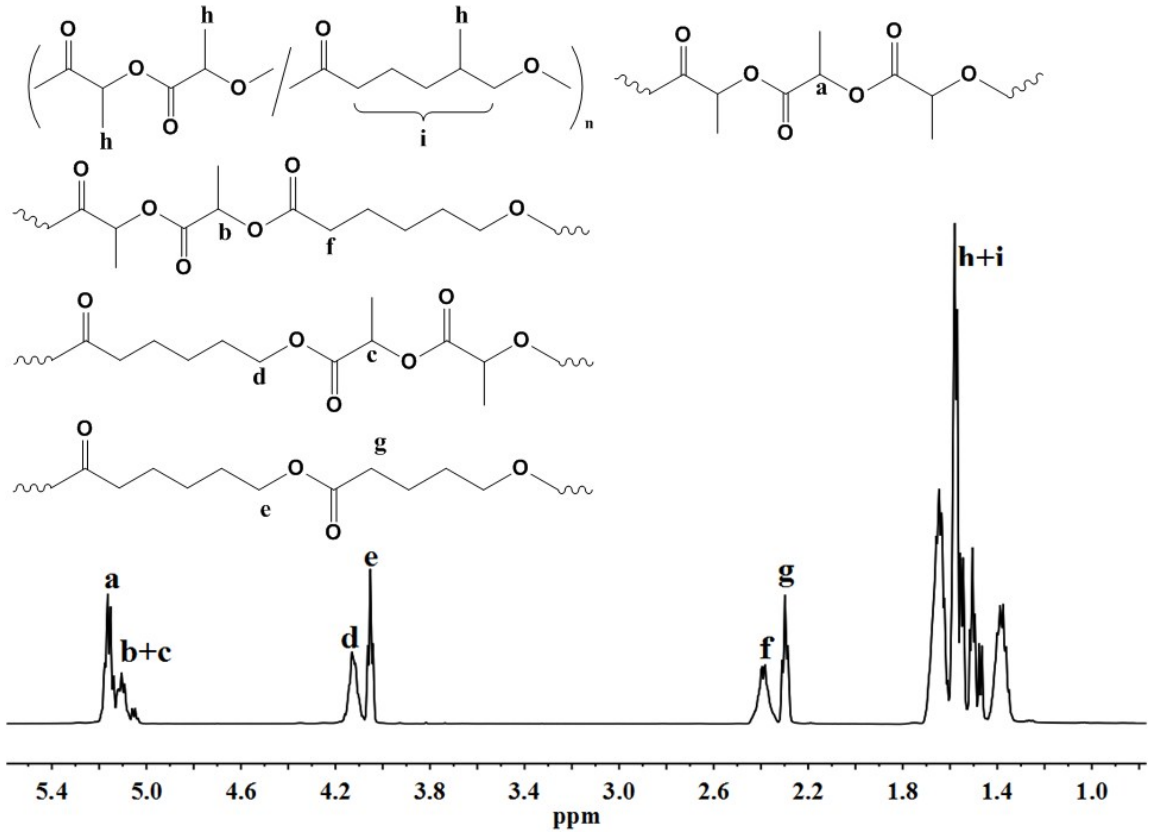

Figure S14. ^{1}H NMR spectrum of PCL-*ran*-PLLA prepared by complex 10 ($CDCl_3$, 25 °C, 600MHz).

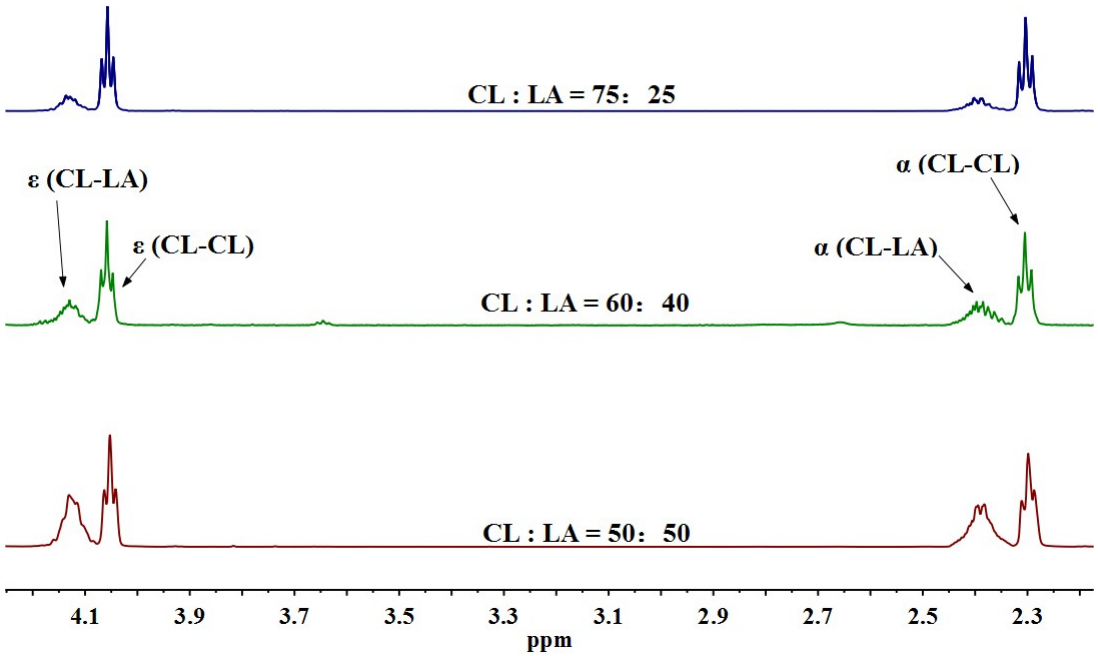

Figure S15. Spectra composition at different molar ratios in the initial feed (Table 5, $CDCl_3$, 25 ºC, 600 MHz).

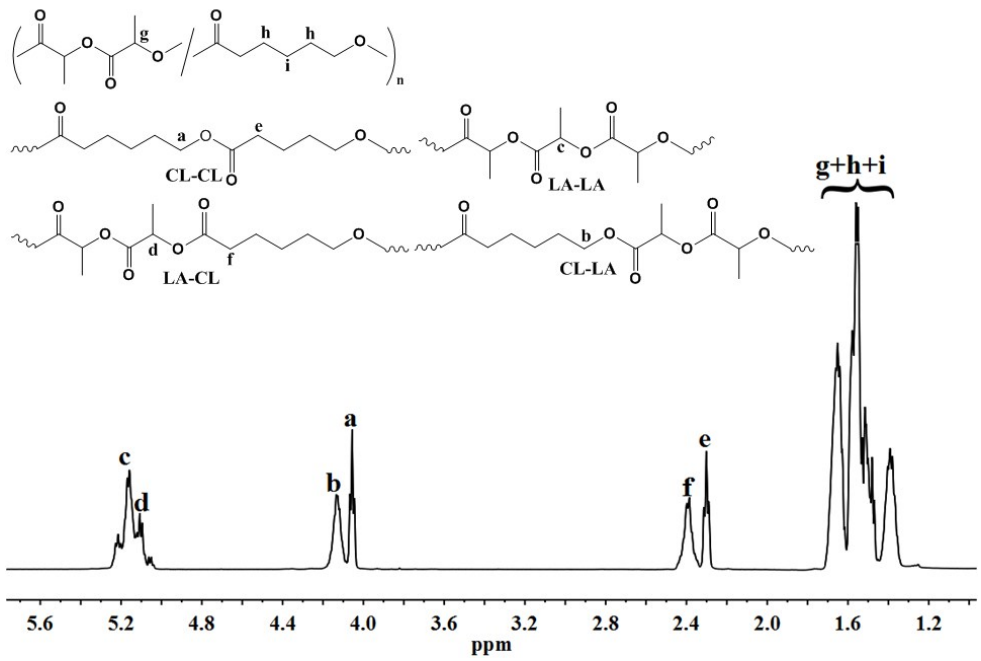

Figure S16. ^{1}H NMR spectrum of PCL-*ran*-PDLLA by complex **10** ($CDCl_3$, 25 ºC, 600MHz).

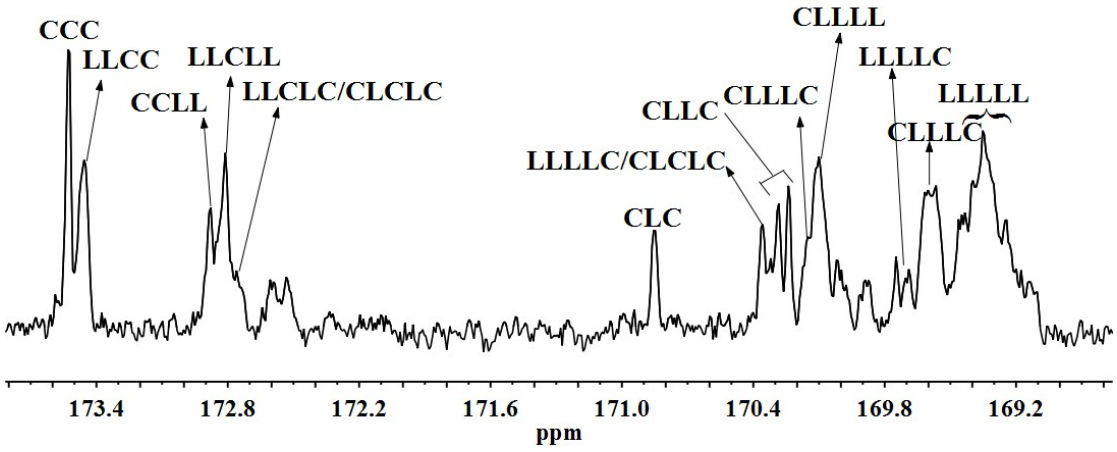

Figure S17. ^{13}C NMR spectrum of the PCL-*ran*-PDLA by complex **10** ($CDCl_3$, 25 ºC, 150 MHz).