Supporting Information

Synthesis of amine-bridged bis(phenolate) rare-earth metal aryloxides and their catalytic performances for the ring-opening polymerization of L-lactic acid *O*-carboxyanhydride and L-lactide

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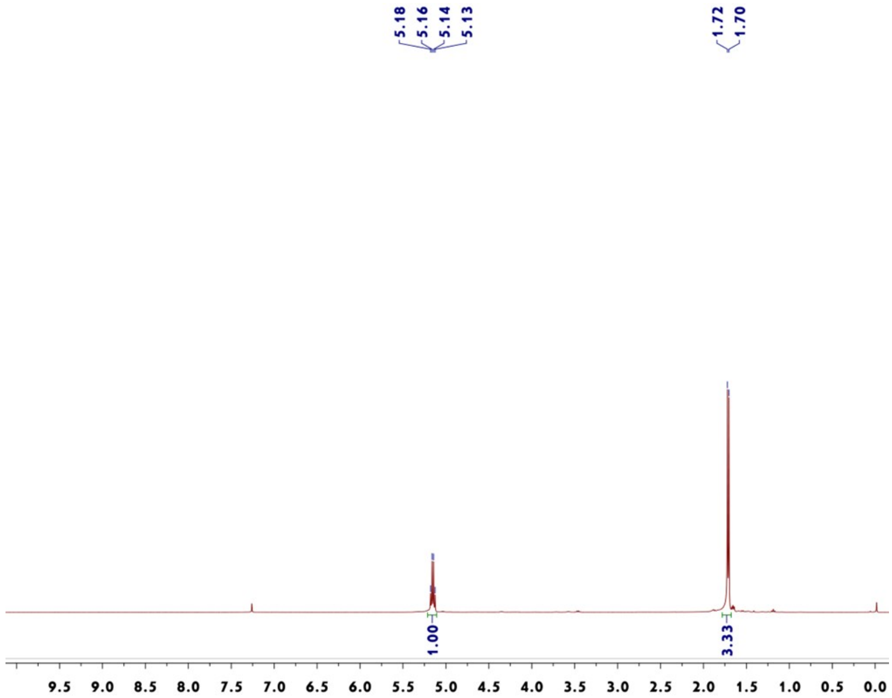


Fig. S1 ^{1}H NMR spectrum ($CDCl_3$, 25 ^{o}C) of $_{L}$-lacOCA

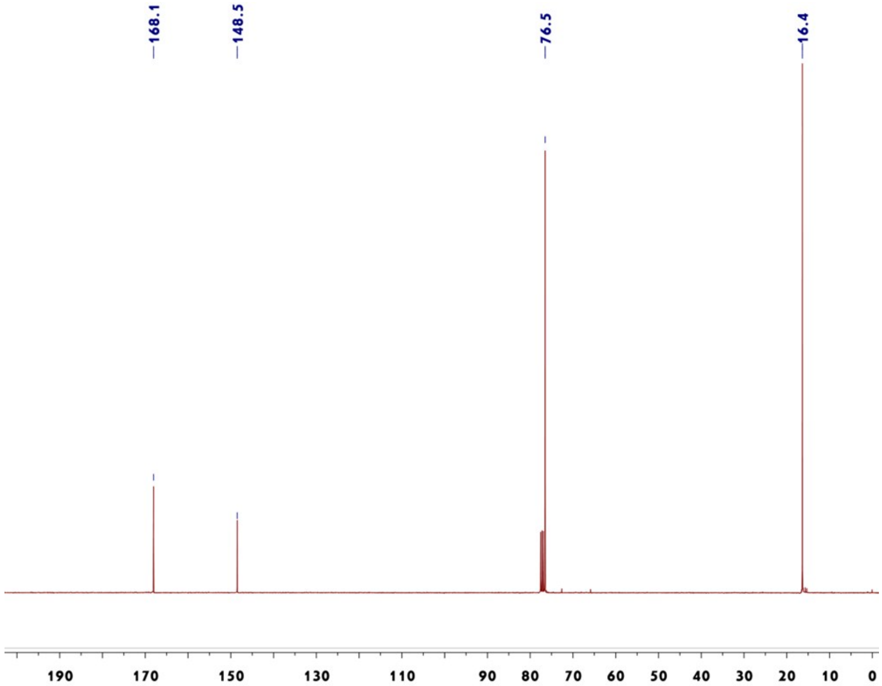


Fig. S2 ^{13}C NMR spectrum ($CDCl_3$, 25 ^{o}C) of $_{L}$-lacOCA

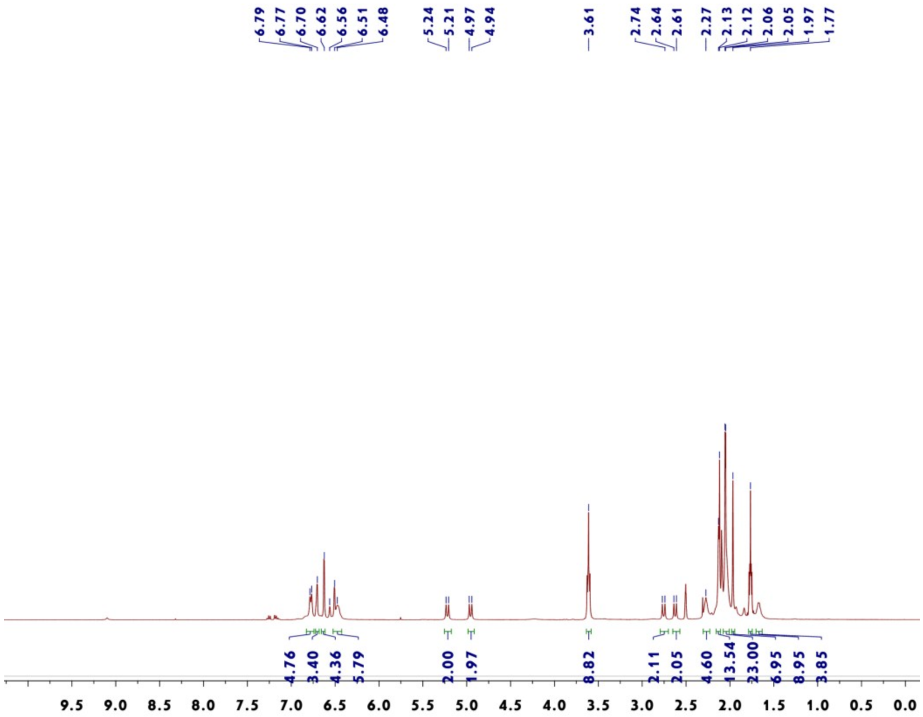


Fig. S3 ^{1}H NMR spectrum (DMSO, 25 ^{o}C) of complex **1**

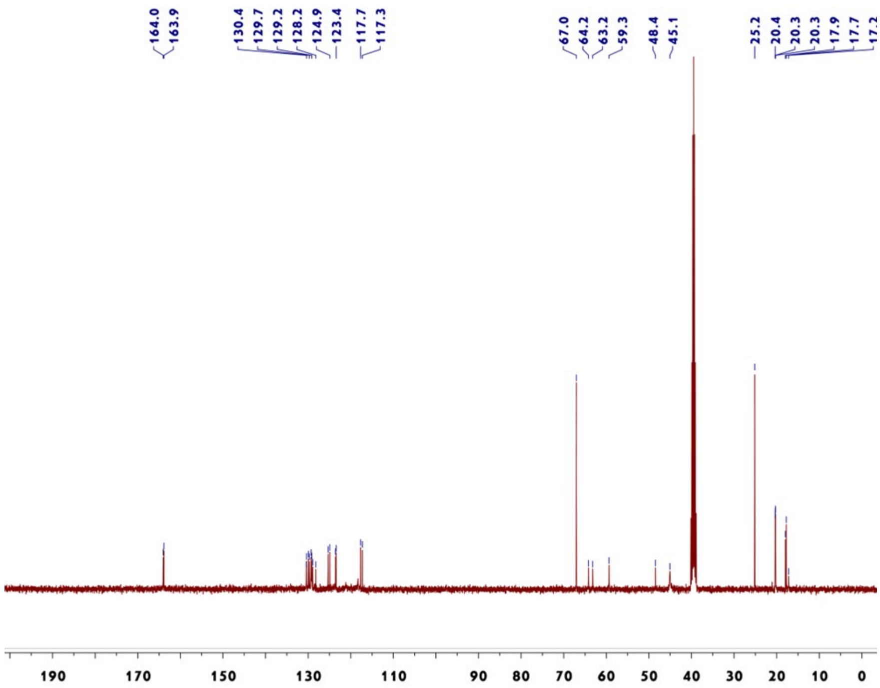


Fig. S4 ^{13}C NMR spectrum (DMSO, 25 ^{o}C) of complex **1**

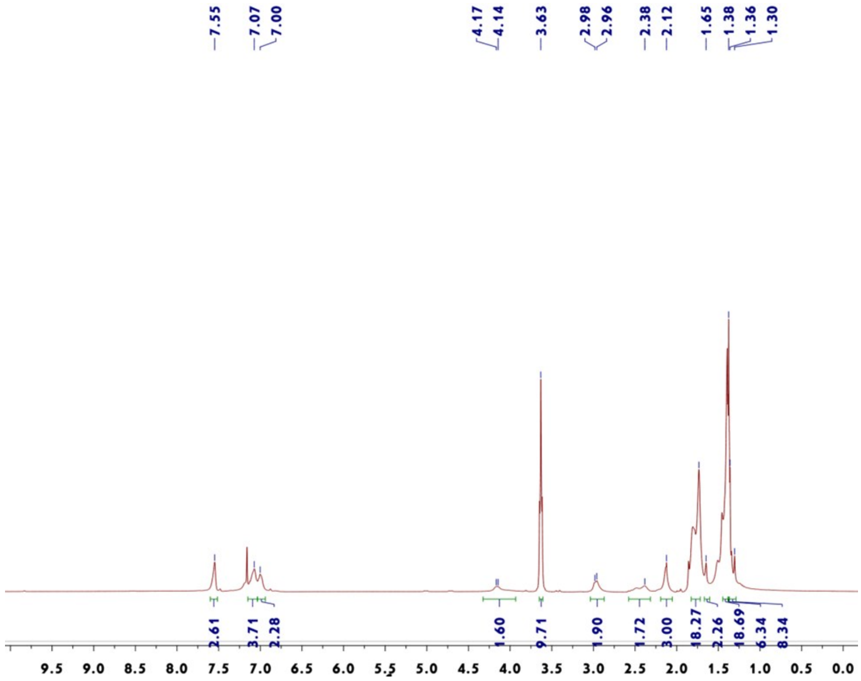
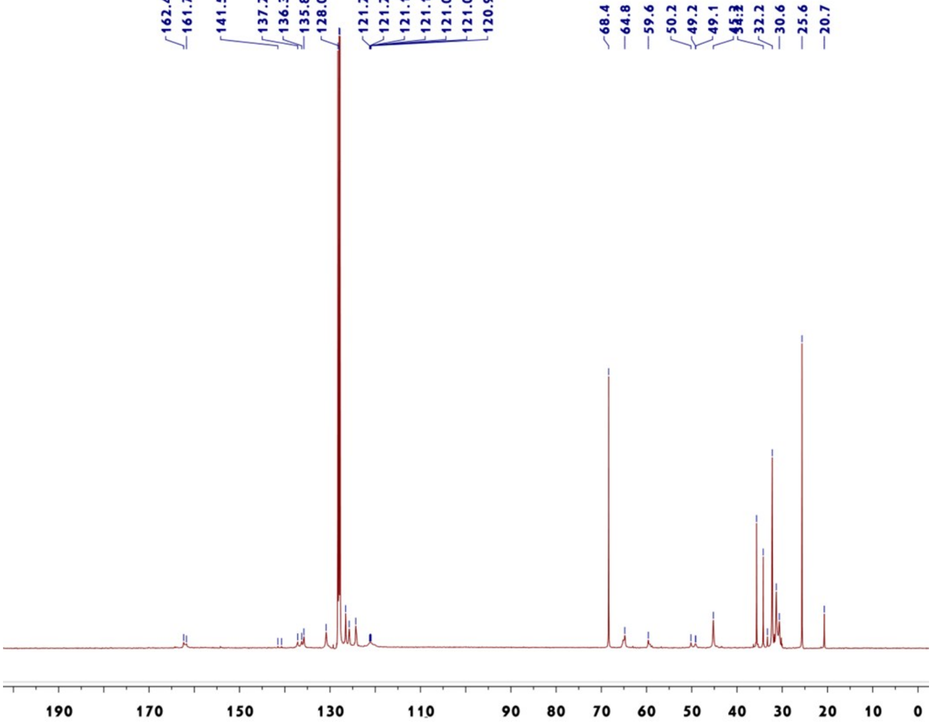


Fig. S5 ^{1}H NMR spectrum (C_6D_6, 25 ^{o}C) of complex **2**



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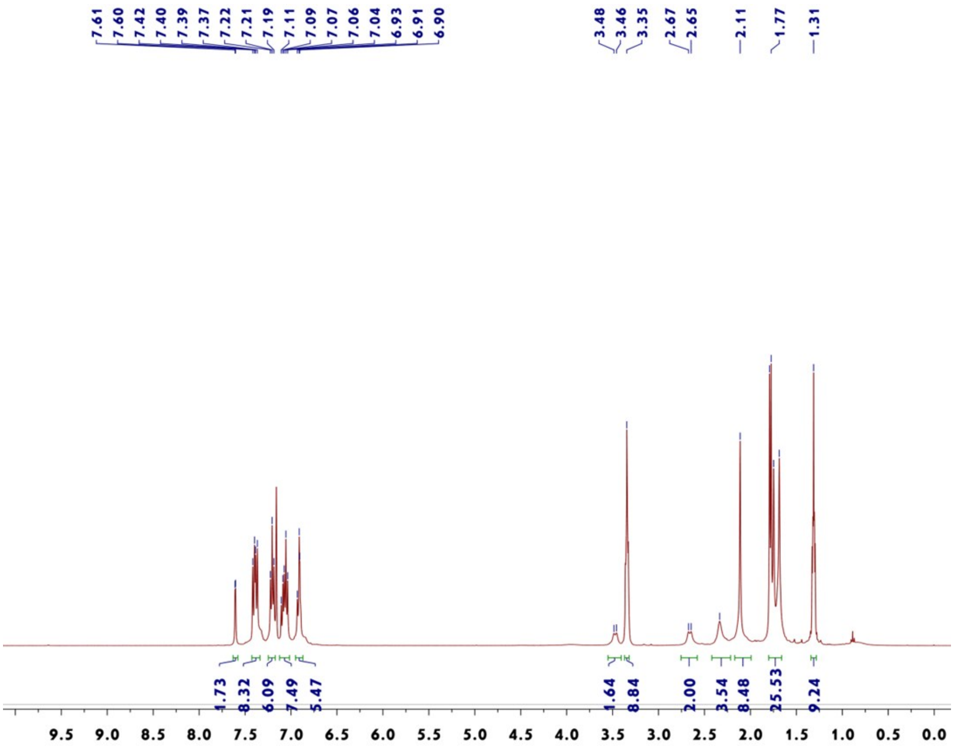

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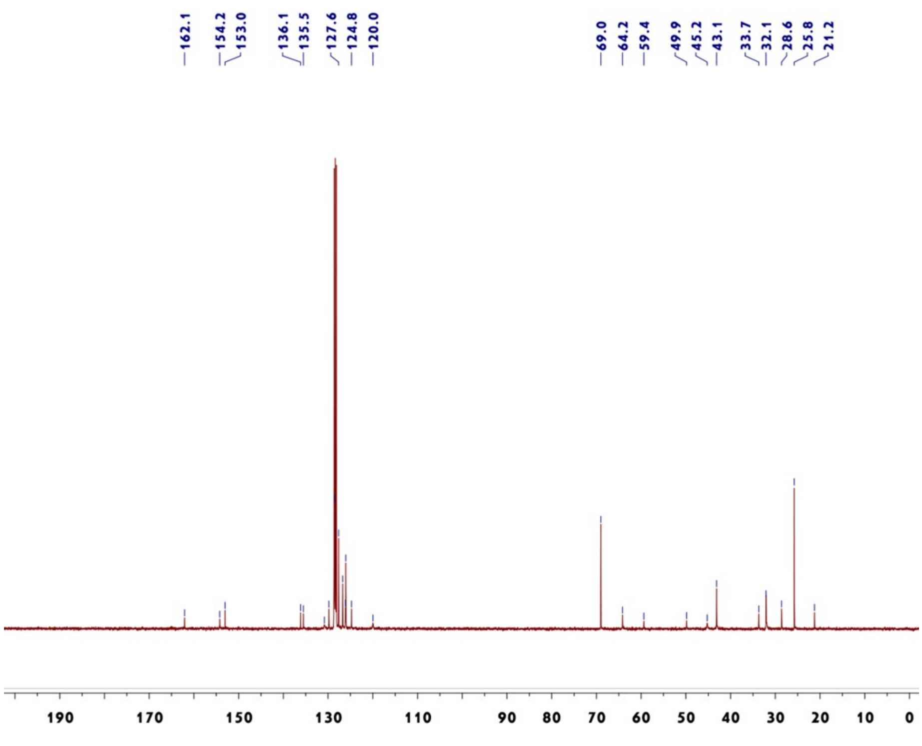

Fig. S8 ^{13}C NMR spectrum (C_6D_6, 25 °C) of complex **3**

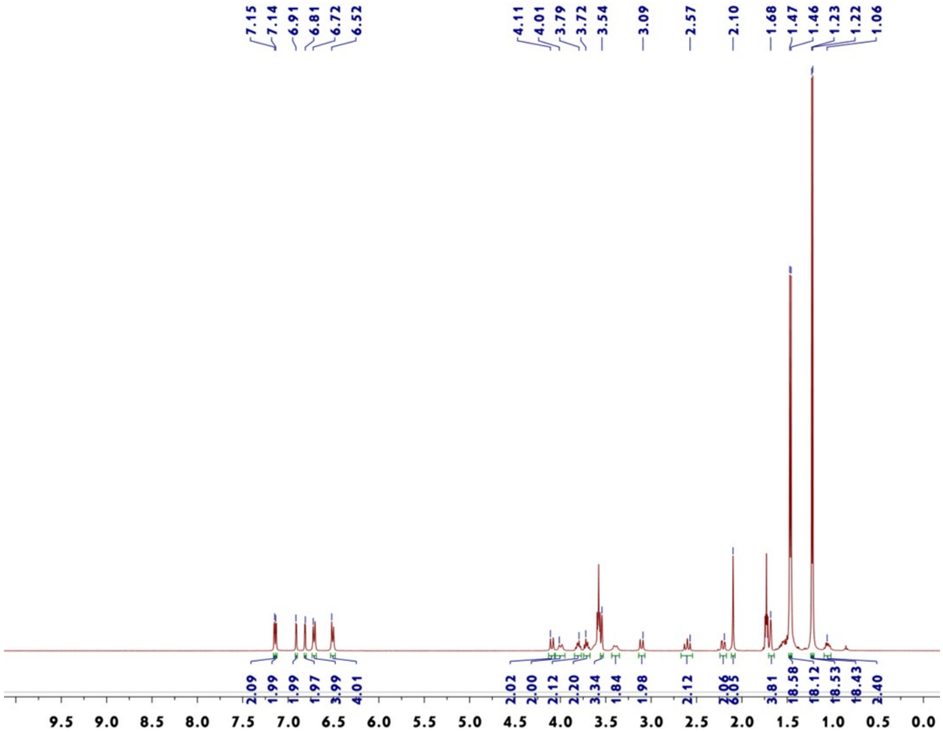

Fig. S9 ^{1}H NMR spectrum (d_8-THF, 25 ^{o}C) of complex **5**

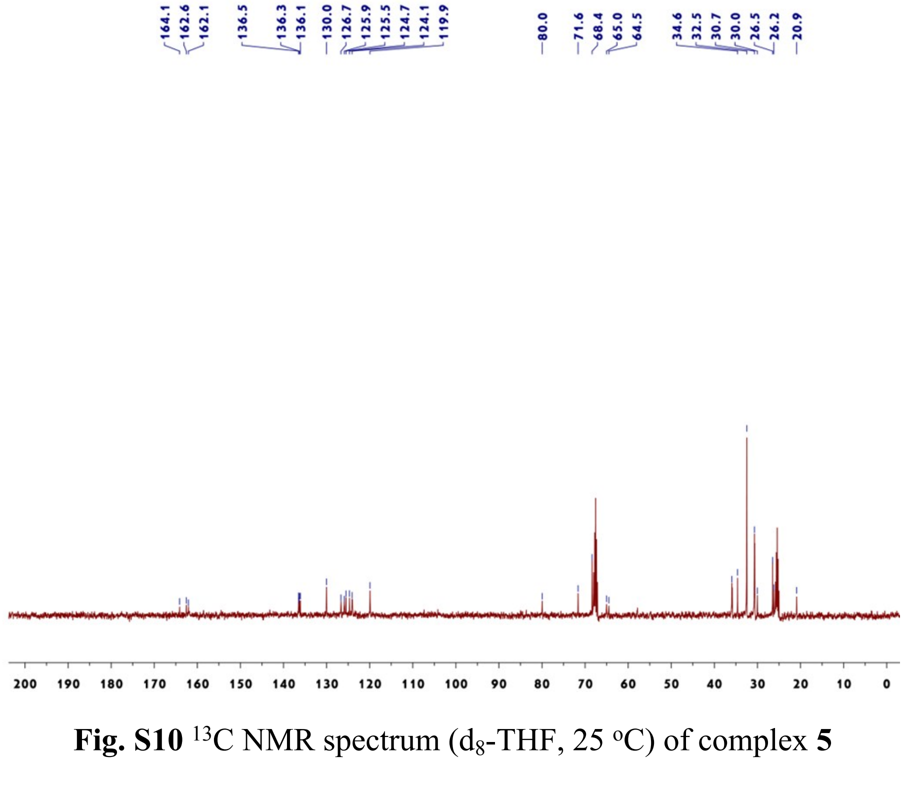

Fig. S10 ^{13}C NMR spectrum (d_8-THF, 25 ^{o}C) of complex **5**

Table S1. Crystallographic data for complexes **1**, **2**, **3** and **5**

Compound	**1**	**2**	**3**	**5**·3**THF**
Formula	$C_{74}H_{106}La_2N_4O_{10}$	$C_{49}H_{77}N_2O_5La$	$C_{69}H_{85}LaN_2O_5$	$C_{180}H_{264}N_4O_{19}Y_4$
fw	1489.45	913.03	1161.29	3143.58
T/K	293(2)	100(2)	293(2)	223(2)
Crystal system	triclinic	orthorhombic	monoclinic	triclinic
Crystal size/mm	0.60 x 0.40 x 0.20	0.35 × 0.30 × 0.20	0.75 x 0.6 x 0.4	0.80 x 0.70 x 0.30
Space group	P-1	Pnma	P 1	P-1
a/Å	12.4210(6)	21.8235(10)	15.1660(3)	15.5796(11)
b/Å	12.9473(5)	20.4867(8)	33.8032(8)	18.2982(14)
c/Å	13.3644(7)	10.6023(5)	24.5524(6)	18.7574(18)
α/deg	114.347(4)	90	90	75.610(15)
β/deg	109.435(5)	90	101.496(2)	70.403(14)
γ/deg	95.310(4)	90	90	66.585(13)
V/Å^3	1779.31(16)	4740.2(4)	12334.6(5)	4581.5(9)
Z	1	4	8	1
D_{calcd}/g cm^{-3}	1.390	1.279	1.251	1.139
μ/mm^{-1}	1.243	0.946	0.743	1.312
F(000)	772	1928	4880	1680
θ_{max}/deg	26.37	27.51	26.37	26.37
Collected	17526	42156	74083	40070
Unique reflns	7289	5581	25165	18548
Obsd reflns [I >2.0$\sigma(I)$]	6495	4642	19002	11014
No. of variables	371	295	1471	951
GOF	1.052	1.072	1.060	1.071
R	0.0368	0.0266	0.0447	0.0804
w*R*	0.0875	0.0553	0.0936	0.2251
R_{int}	0.0316	0.0508	0.0414	0.0675
Largest diff. peak, hole/e Å^{-3}	1.573,-1.712	0.875, -0.399	0.962,-0.755	1.480，-1.358

Table S2. Selected bond lengths (Å) and bond angles (deg) for complexes **1-3 and 5.**

Bond lengths	**1**	**Bond lengths**	**2**
Ln1-O1	2.465(2)	Ln1-O1	2.285(13)
Ln1-O1A	2.435(2)	Ln1-O1A	2.285(13)
Ln1-O2	2.313(2)	Ln1-O2	2.284(2)
Ln1-O3	2.289(3)	Ln1-O3	2.608(2)
Ln1-O4	2.682(3)	Ln1-O4	2.646(2)
Ln1-N1	2.848(3)	Ln1-N1	2.754(2)
Ln1-N2	2.730(3)	Ln1-N2	2.755(3)
Bond angles		**Bond angles**	
O2-Ln1-N1	71.20(8)	O1-Ln1-O2	106.74(4)
N2-Ln1-N1	63.97(9)	O2-Ln1-O1A	106.74(3)
O1A-Ln1-N1	106.15(8)	O1-Ln1-O1A	145.52(7)
O3-Ln1-N1	131.12(9)	O2-Ln1-N1	140.88(8)
O3-Ln1-O1	86.79(9)	O1-Ln1-N1	74.48(4)
O3-Ln1-O2	138.69(10)	O2-Ln1-N2	76.84(8)
O3-Ln1-O1A	105.72(9)	O1-Ln1-N2	89.85(4)
O2-Ln1-O1A	97.01(8)	N1-Ln1-N2	64.04(7)
O1A-Ln1-O1	67.67(8)		

Bond lengths	**3**	**Bond lengths**	**5**
Ln1-O1	2.301(2)	Ln1-O1	2.136(4)
Ln1-O2	2.269(2)	Ln1-O2	2.128(4)
Ln1-O3	2.270(3)	Ln1-O3	2.339(4)
Ln1-O4	2.679(3)	Ln1-O3A	2.263(4)
Ln1-O5	2.619(3)	Ln1-O4	2.365(4)
Ln1-N1	2.783(2)	Ln1-N1	2.542(5)
Ln1-N2	2.809(3)		
Bond angles		**Bond angles**	
O2-Ln1-N1	74.26(7)	O2-Ln1-N1	76.66(15)
N1-Ln1-N2	63.46(8)	O3-Ln1-N1	127.13(14)
O3-Ln1-N1	139.95(9)	O3A-Ln1-N1	163.70(15)
O4-Ln1-N1	77.43(8)	O4-Ln1-N1	67.47(14)
O1-Ln1-O3	111.44(10)	O2-Ln1-O3	100.19(14)
O1-Ln1-O4	84.00(8)	O2-Ln1-O3A	104.36(14)
O3-Ln1-O4	141.24(9)	O3-Ln1-O3A	69.02(15)
O4-Ln1-O5	68.92(9)	O4-Ln1-O3A	119.38(14)

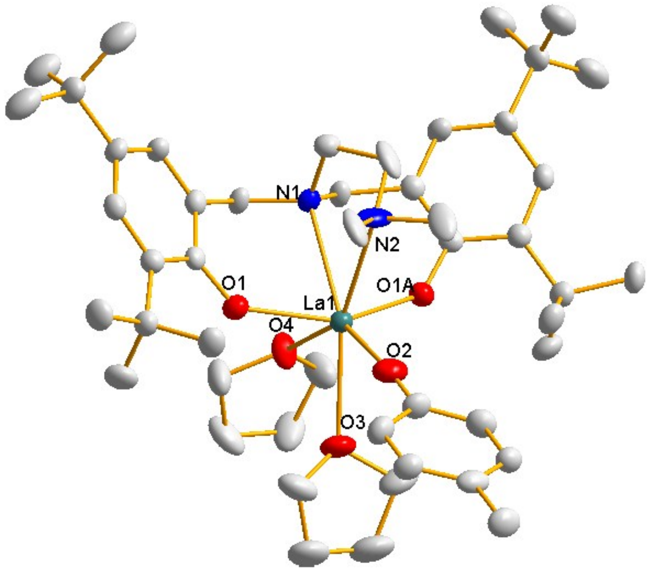

Fig. S11 Solid state structure of complex **2** showing an atom numbering scheme. Thermal ellipsoids are drawn at 30% probability level, and hydrogen atoms are omitted for clarity.

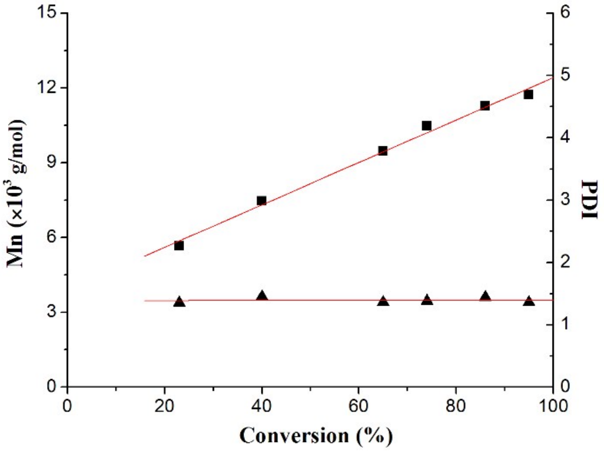

Fig. S12 Plot of PLA Mn(■) and polydispersity (▲) as a function of $_L$-lacOCA conversion initiated by complex **5**, $[OCA]_0/[I]_0$= 200:1, T = 30 ^{o}C.

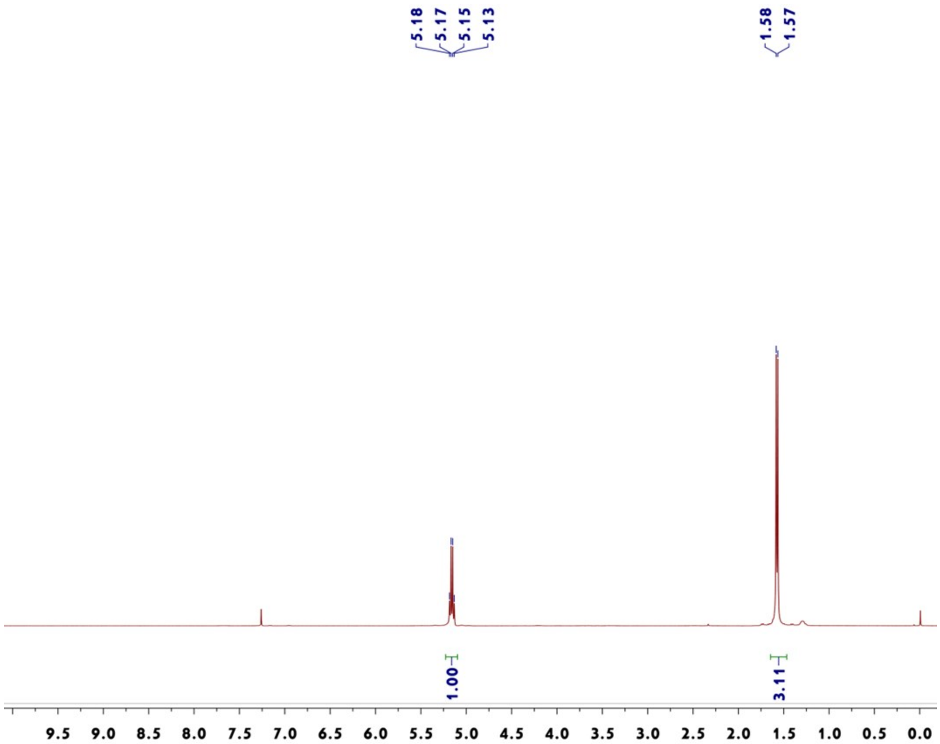

Fig. S13 ^{1}H NMR (normal) spectrum of PLLA obtained from $_L$-lacOCA by complex **5**.

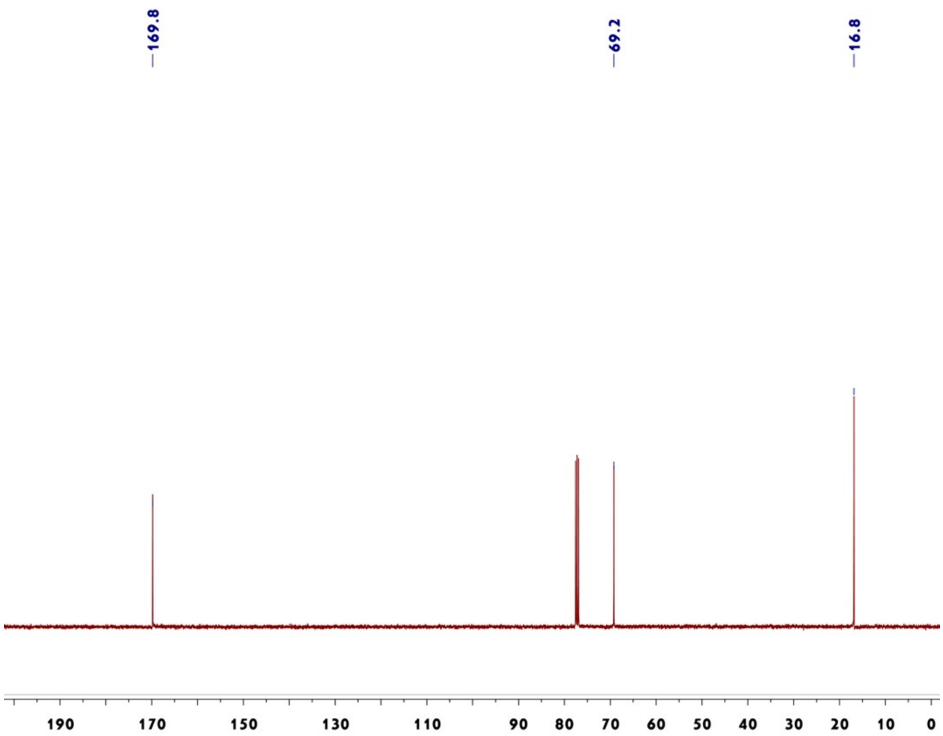

Fig. S14 ^{13}C NMR spectrum of PLLA obtained from $_{L}$-lacOCA

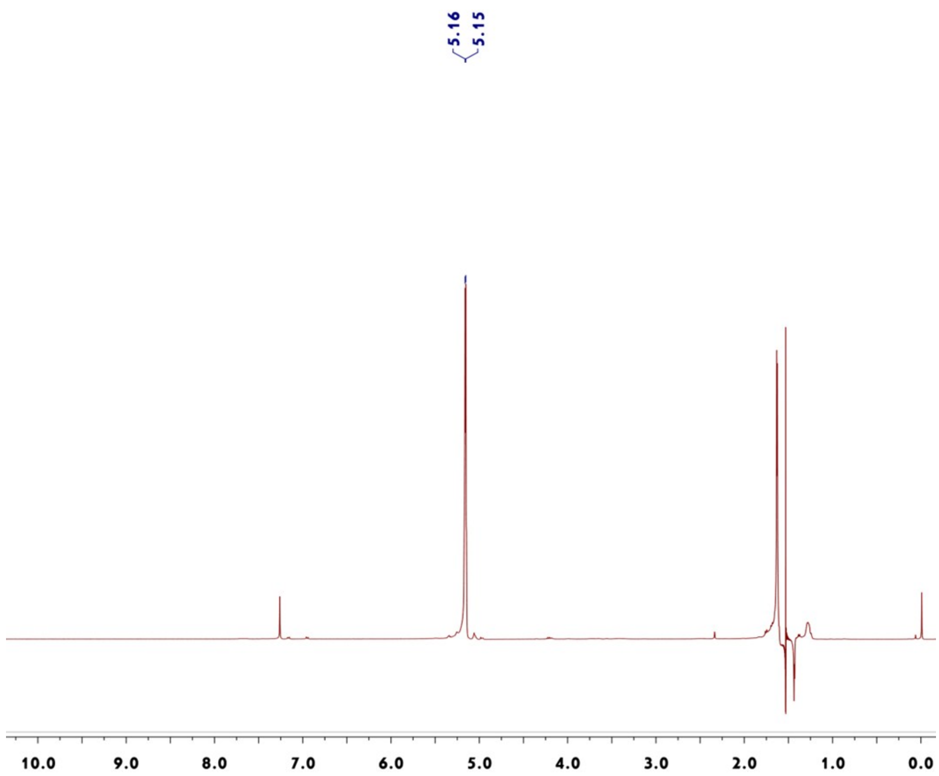

Fig. S15 ^{1}H NMR (homodecoupled) spectrum of PLLA obtained from $_{L}$-lacOCA

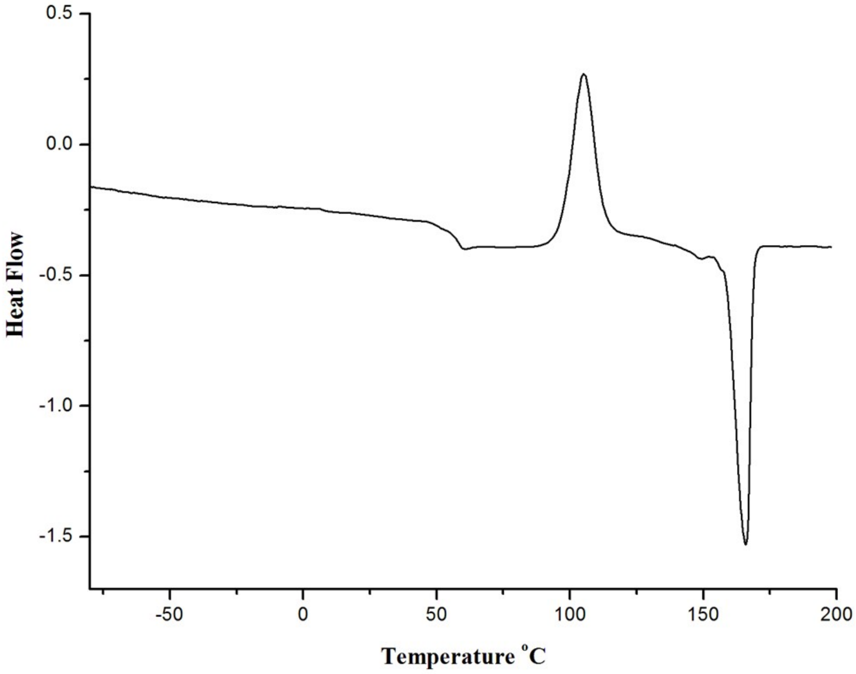

Fig. S16 DSC thermogram of poly(lactic acid)

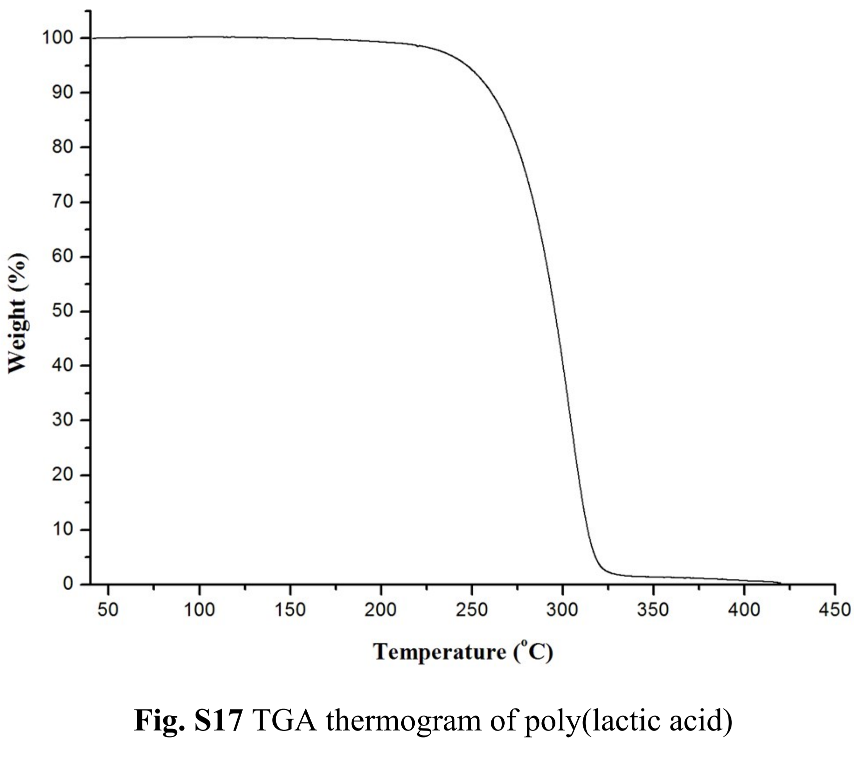

Fig. S17 TGA thermogram of poly(lactic acid)