Electronic Supplementary Information

Zinc complexes supported by claw-type aminophenolate ligands: synthesis, characterization and catalysis in the ring-opening polymerization of *rac*-lactide

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Table S1. ROP of lactides initiated by complex **2a** under various conditions

Run	$[LA]_0/[Zn]_0$ /$[^iPrOH]_0$ [a]	Solv.	T (ºC)	t (h)	Conv. [b] (%)	$M_{n,calcd.}$ [c] (10^{-4})	M_n [d] (10^{-4})	PDI [d]	P_m [e]
1	200:1:0	Tol.	24	3	95	2.74	9.34	1.55	0.65
2	200:1:1	Tol.	24	1	98	2.82	4.74	1.46	0.65
3	200:1:1 [g]	Tol.	24	0.75	91	2.62	4.10	1.47	0.66
4	200:1:1 [h]	Tol.	24	1	97	2.80	4.85	1.39	0.63
5	400:1:0	Tol.	25	8	93	5.36	28.43	1.23	0.65
6	400:1:1	Tol.	25	1.25	97	5.59	8.96	1.34	0.61
7	200:1:0	Tol.	–39	96	12	0.35	--- [f]	--- [f]	--- [f]
8	200:1:1	Tol.	–39	96	84	2.42	5.13	1.35	0.62
9	200:1:1	Tol.	0	12	96	2.77	3.98	1.36	0.63
10	200:1:0	DMC	25	3	68	1.96	12.64	1.34	0.60
11	200:1:1	DMC	25	0.75	95	2.74	3.05	1.23	0.60
12	200:1:1	DMC	0	12	83	2.39	5.83	1.34	0.63
13	200:1:1	DMC	–39	72	86	2.48	1.14	1.26	0.62
14	200:1:1	DMC	60	0.75	83	2.39	17.25	1.20	0.61
15 [i]	200:1:1	Tol.	25	0.75	97	2.80	4.94	1.33	100
16 [i]	200:1:0	Tol.	25	2	96	2.77	--- [f]	--- [f]	--- [f]

[a] $[rac\text{-LA}]_0$ = 1.0 M, $[Zn]_0$ = 0.005 M. [b] Determined by ^{1}H NMR spectroscopy. [c] $M_{n,calcd}$ = $([LA]_0/[Zn]_0) \times 144.13 \times$ conv.%. [d] Determined by GPC. [e] P_m is the probability of forming a new *m*-dyad, determined by homonuclear decoupled ^{1}H NMR spectroscopy. [f] Not detected. [g] Complex **2a** and ^{i}PrOH were mixed together and then monomer was added. [h] BnOH was added instead of ^{i}PrOH. [i] Polymerization of *L*-LA.

Table S2. The crystal data and structure refinement of complex **4b**

	4b
Empirical formula	$C_{57}H_{78}N_2O_4Zn\cdot(0.5\ C_6H_{14})$
Formula weight	963.67
Temp (K)	293(2) K
Crystal size (mm)	0.407 x 0.361 x 0.257
Crystal system	Triclinic
Space group	P-1
a (Å)	14.726(2)
b (Å)	14.998(2)
c (Å)	15.817(2)
α (°)	63.485(3)
β (°)	67.435(3)
γ (°)	75.481(3)
Volume(Å ^{3})	2873.0(7)
Z	2
Density $_{calc}$ (mg/m^3)	1.114
Abs coeff (mm^{-1})	0.471
F(000)	1042
θ range (°)	1.68 to 25.50
Data collected (hkl)	±17, -18 to 17, -18 to 19
Reflns collected/unique	15287 / 10556
R(int)	0.1084
Max. and min. transmn.	1.0000 and 0.3091
Data / restrains / para	10556 / 4 / 622
Final R_1 ,wR_2 [I > 2σ(I)]	0.0720, 0.1511
R_1 , wR_2 (all data)	0.1531, 0.1823
Goodness-of-fit on F^2	0.839
Δρmax, min/e Å^{-3}	0.575 and -0.589

Table S3. The selected bond lengths (Å) and angles (°) of complex **4b**

4b			
Zn-O(2)	1.863(3)	O(4)-C(57)	1.432(6)
Zn-O(1)	1.939(3)	N(1)-C(2)	1.479(5)
Zn-N(1)	2.097(4)	N(1)-C(3)	1.493(5)
Zn-N(2)	2.109(4)	N(1)-C(20)	1.515(5)
O(1)-C(22)	1.322(5)	N(2)-C(16)	1.437(7)
O(2)-C(45)	1.400(5)	N(2)-C(18)	1.480(7)
O(3)-C(5)	1.392(5)	N(2)-C(1)	1.493(6)
O(3)-C(15)	1.431(6)	C(1)-C(2)	1.501(7)
O(4)-C(47)	1.401(5)		
O(2)-Zn-O(1)	111.16(14)	C(2)-N(1)-Zn	106.6(3)
O(2)-Zn-N(1)	134.74(15)	C(3)-N(1)-Zn	120.3(3)
O(1)-Zn-N(1)	97.43(13)	C(20)-N(1)-Zn	105.8(2)
O(2)-Zn-N(2)	113.55(16)	C(16)-N(2)-C(18)	114.1(5)
O(1)-Zn-N(2)	110.65(16)	C(16)-N(2)-C(1)	108.9(5)
N(1)-Zn-N(2)	86.11(16)	C(18)-N(2)-C(1)	108.9(5)
C(22)-O(1)-Zn	124.8(3)	C(16)-N(2)-Zn	110.0(4)
C(45)-O(2)-Zn	116.8(3)	C(18)-N(2)-Zn	113.6(4)
C(5)-O(3)-C(15)	113.8(4)	C(1)-N(2)-Zn	100.4(3)
C(47)-O(4)-C(57)	113.8(4)	N(2)-C(1)-C(2)	112.3(5)
C(2)-N(1)-C(3)	109.4(3)	N(2)-C(1)-H(1A)	109.1
C(2)-N(1)-C(20)	109.8(3)	N(1)-C(2)-C(1)	113.5(4)
C(3)-N(1)-C(20)	104.6(3)	N(1)-C(3)-C(4)	114.6(4)

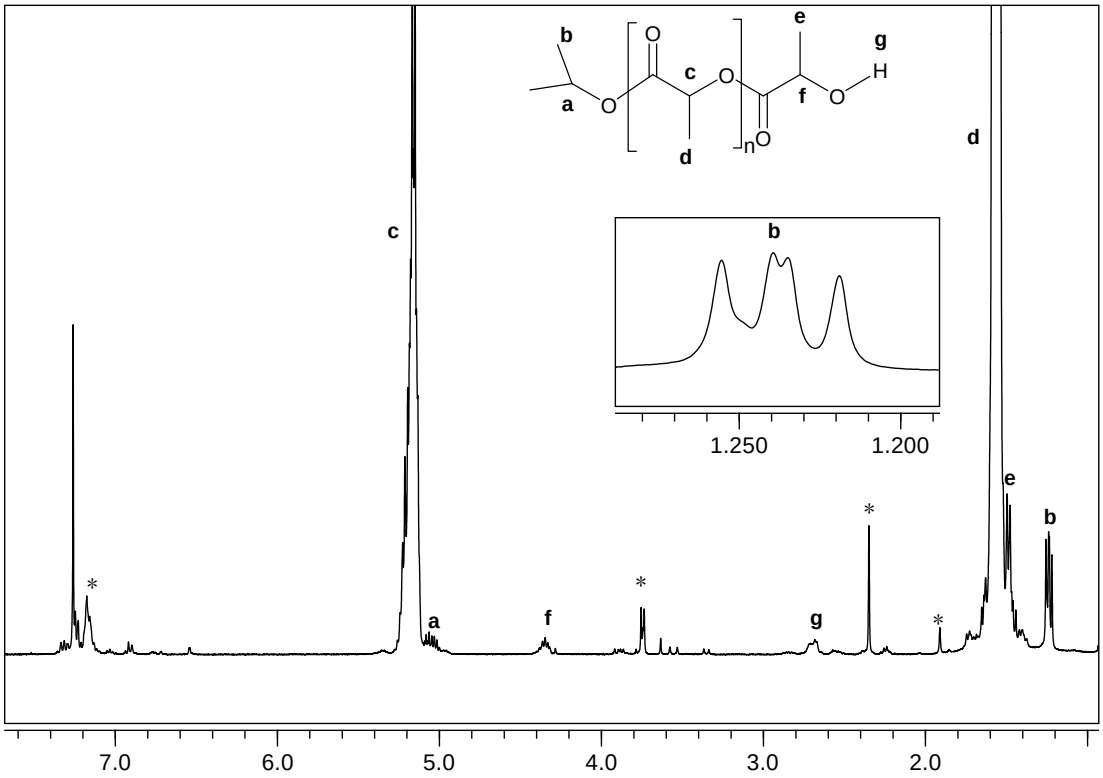


Fig. S1. ^{1}H NMR spectrum of oligomer of *rac*-LA initiated by **2a**/ ^{i}PrOH ($CDCl_3$, 400 MHz; $[rac\text{-LA}]_0$:$[Zn]_0$:$[^{i}PrOH]_0$ = 10:1:1; *, proton peaks of ligand).

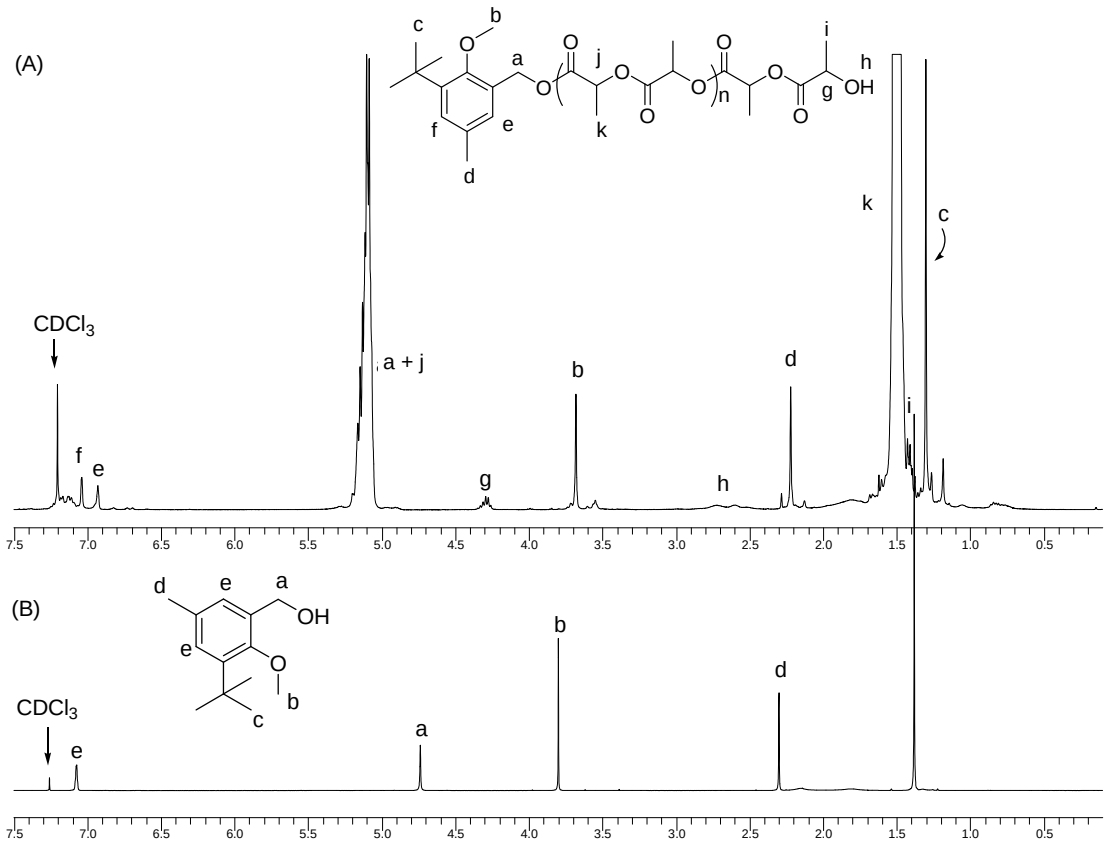


Fig. S2. ^{1}H NMR spectra of **(A)** oligomer of *rac*-LA initiated by **4b** and **(B)** 3-*tert*-butyl-2-methoxy-5-methylbenzyl alcohol ($CDCl_3$, 400 MHz; $[rac\text{-LA}]_0$:$[\mathbf{4b}]_0$ = 10:1).

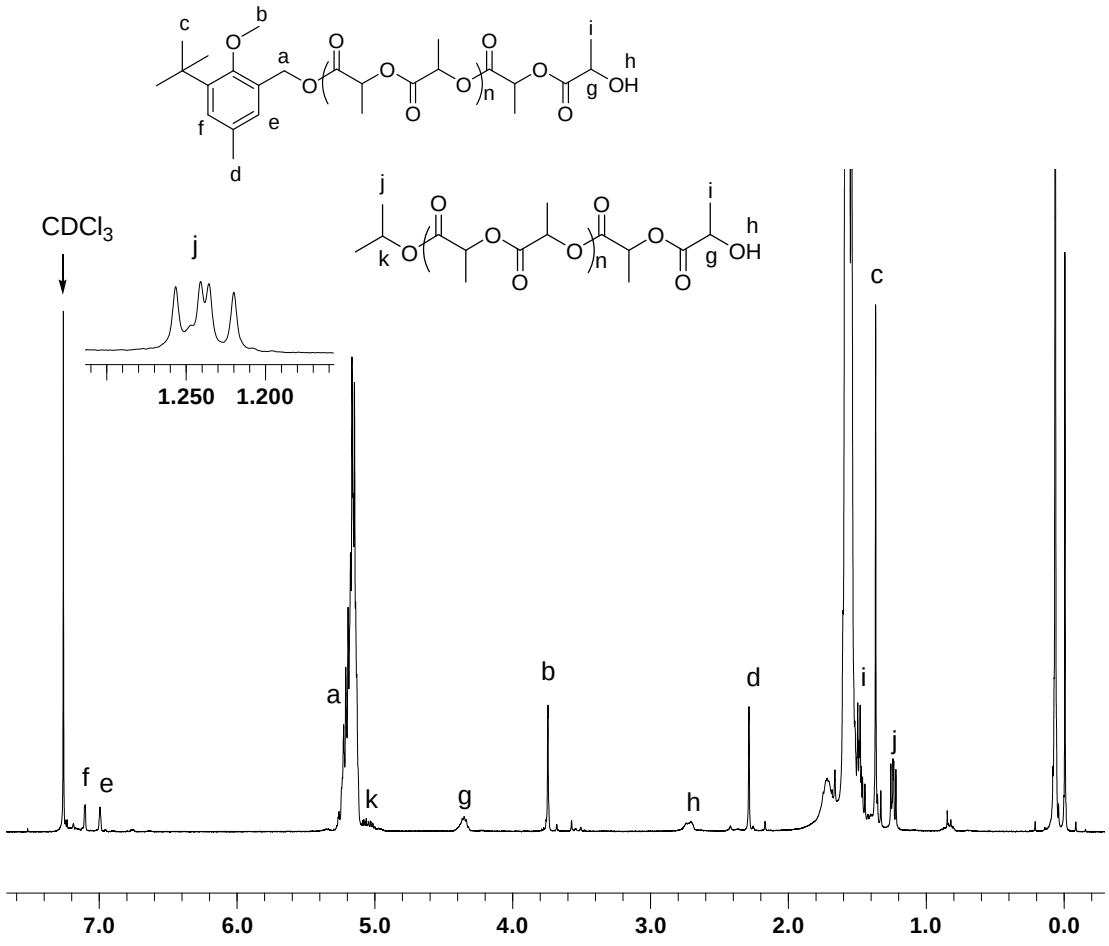
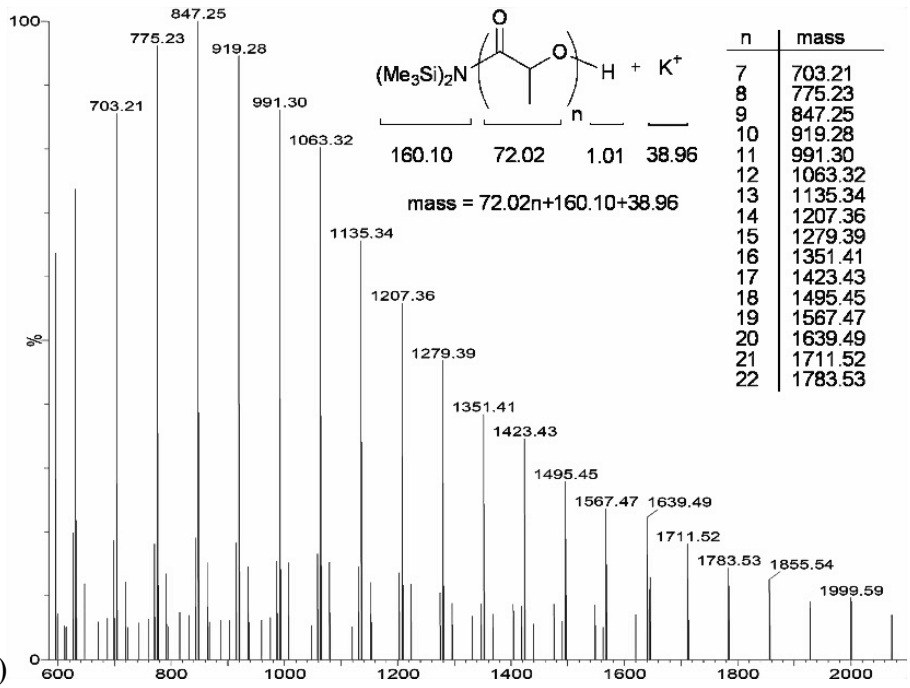


Fig. S3. ^{1}H NMR spectrum of oligomer of *rac*-LA initiated by **4b**/ ^{i}PrOH ($CDCl_3$, 400 MHz; $[rac\text{-LA}]_0$:$[Zn]_0$:$[^{i}PrOH]_0$ = 30:1:1;).

(A)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%
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800
1000
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919.28
703.21
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1135.34
1207.36
1279.39
1351.41
1423.43
1495.45
1567.47
1639.49
1711.52
1783.53
1855.54
1999.59
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O
O
H
+
K+
n
160.10
72.02
1.01
38.96
mass = 72.02n+160.10+38.96
n | mass
7 | 703.21
8 | 775.23
9 | 847.25
10 | 919.28
11 | 991.30
12 | 1063.32
13 | 1135.34
14 | 1207.36
15 | 1279.39
16 | 1351.41
17 | 1423.43
18 | 1495.45
19 | 1567.47
20 | 1639.49
21 | 1711.52
22 | 1783.53

(B)

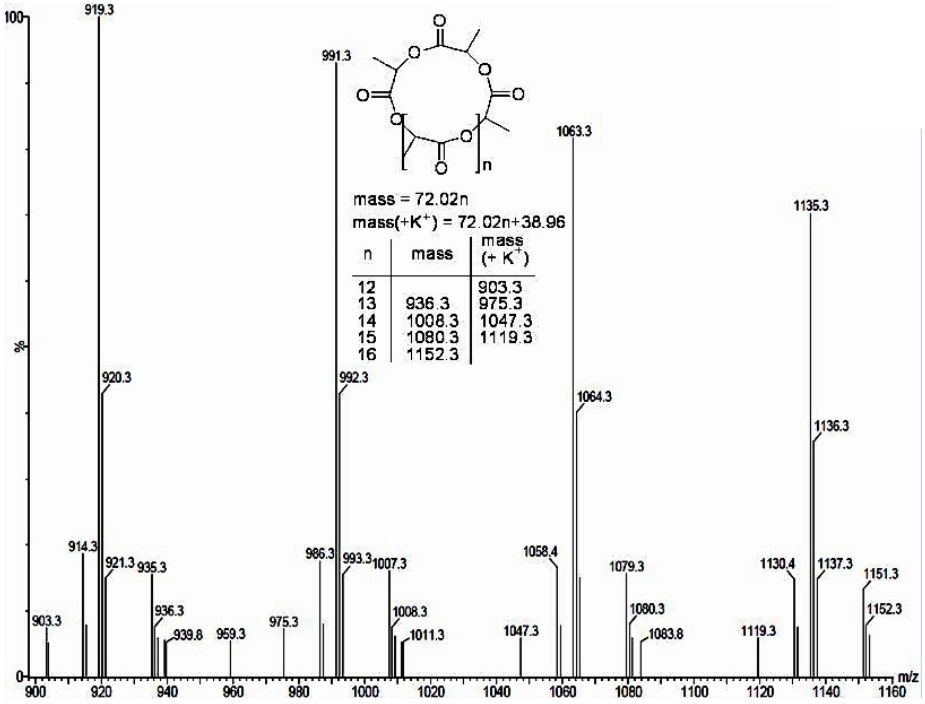

Fig. S4. ESI-TOF spectra of oligomer of *rac*-LA initiated by complex **2a** ([*rac*-LA]$_0$:[**2a**]$_0$ = 10:1, in toluene): **(A)** the whole range; **(B)** Partial enlargement.

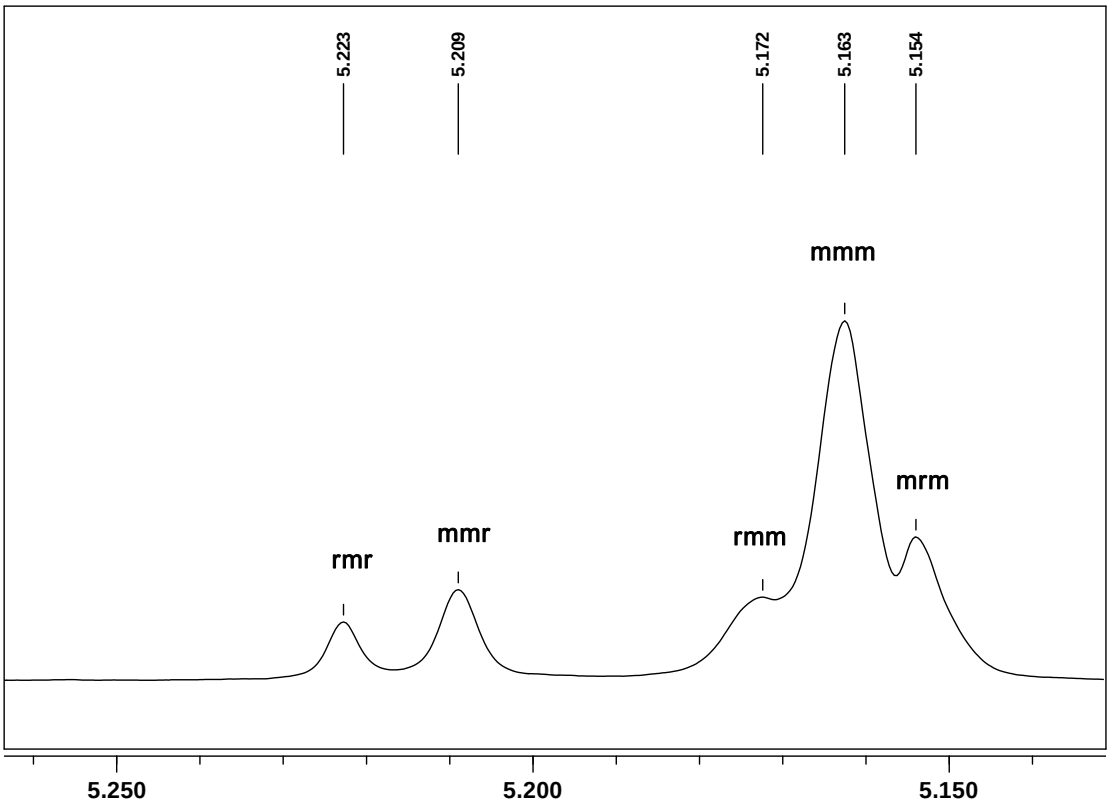

Fig. S5. The methine region of homonuclear decoupled ^{1}H NMR spectrum of poly(*rac*-LA) prepared with **1a** in the presence of ^{i}PrOH in toluene.