Electronic Supplementary Information for Dalton Transactions

Supporting Information

Preparation and structures of enantiomeric dinuclear zirconium and hafnium complexes containing two homochiral N atoms, and their catalytic property for polymerization of *rac*-lactide

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Contents:

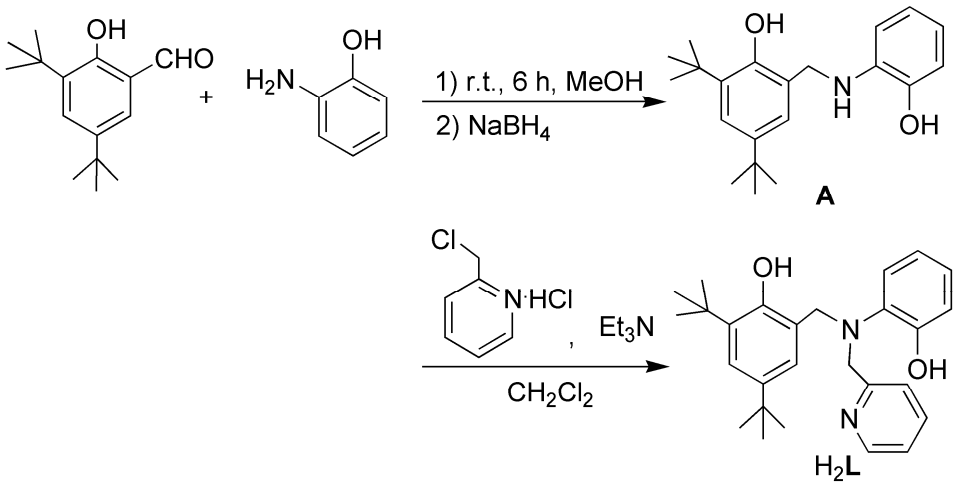
1. Preparation and spectroscopic characterization of H_2L and 1–3

1.1 Preparation and spectroscopic characterization of H_2L

Unsymmetric ligand H_2L was prepared according to a modified procedure of the literature

(Scheme S1). A mixture of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (4.68 g, 0.02 mol) and 2-aminophenol (2.18 g, 0.02 mol) was stirred in CH_3OH (50 mL) for 6 h, and then the solution was cooled to 0 °C before addition of $NaBH_4$ (0.76 g, 0.02 mol) in several portions. After 30 min, the solvent was removed and water (50 mL) was added. The mixture was neutralized with acetic acid. The off-white solid (**A**) was filtered, washed three times with water, and dried in vacuo. Yield: 6.1 g (93%).

To the suspension of 2-(chloromethyl)pyridine hydrochloride (1.4 g, 0.008 mol) in CH_2Cl_2 (20 mL), a solution of **A** (1.64 g, 0.005 mol) in CH_2Cl_2 (20 mL) was added dropwise at 0 °C, followed by dropwise addition of the CH_2Cl_2 solution (10 mL) of Et_3N (2.53 g, 0.025 mol) to the mixture. The stirring was maintained for 72 h at room temperature. The mixture was washed twice with water, and the organic layer was separated and dried with anhydrous $MgSO_4$. After removal of solvent, the residue was recrystallized from acetone/hexane. Ligand H_2L was obtained as an off-white crystalline solid (1.0 g, 48%). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ = 8.55 (d, 1H, Py), 7.39−6.61 (9H, Ph and Py), 4.35 (s, 2H, N-CH_2-Ph), 4.13 (s, 2H, N-CH_2-Py), 1.28 and 1.17 (2s, each for 9H, CH_3 of *tert*-Bu) (Fig. S1).



Scheme S1

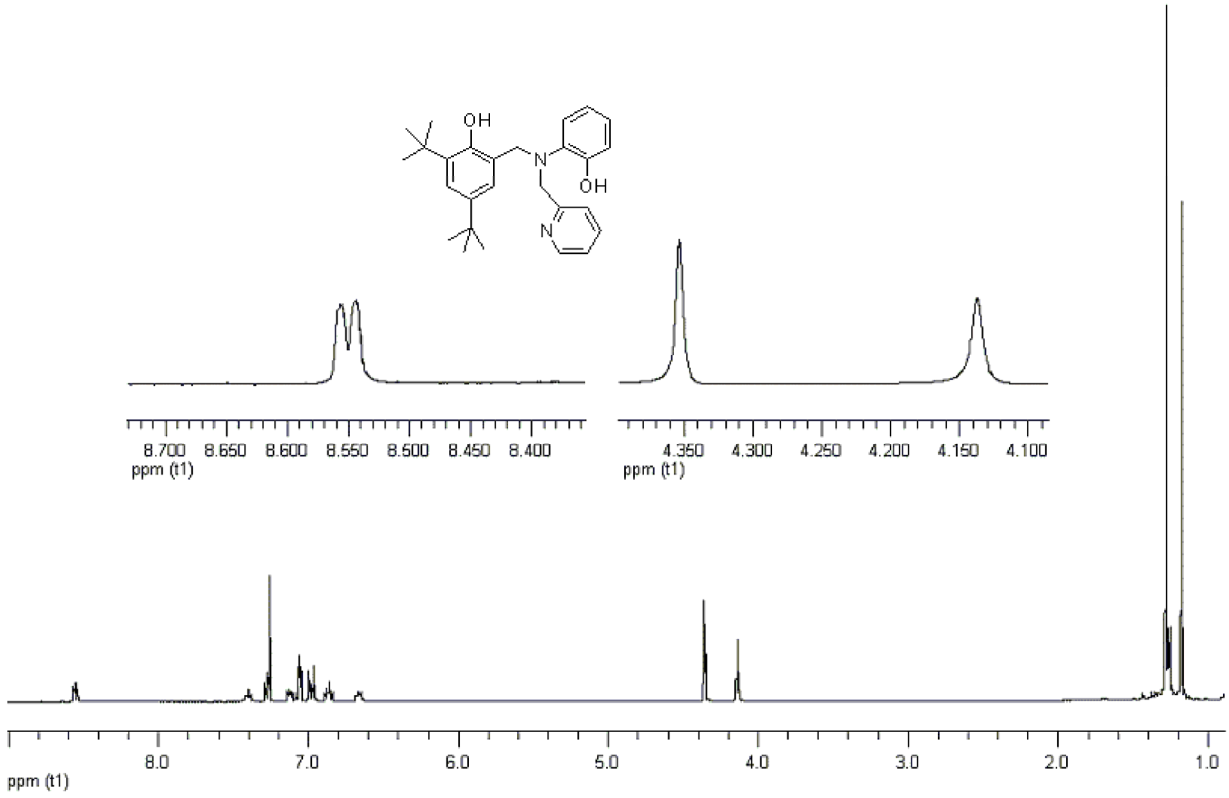


Fig. S1 ^{1}H NMR spectrum of H_2L in $CDCl_3$.

1.2 Spectroscopic characterization of complex L_2Zr (1)

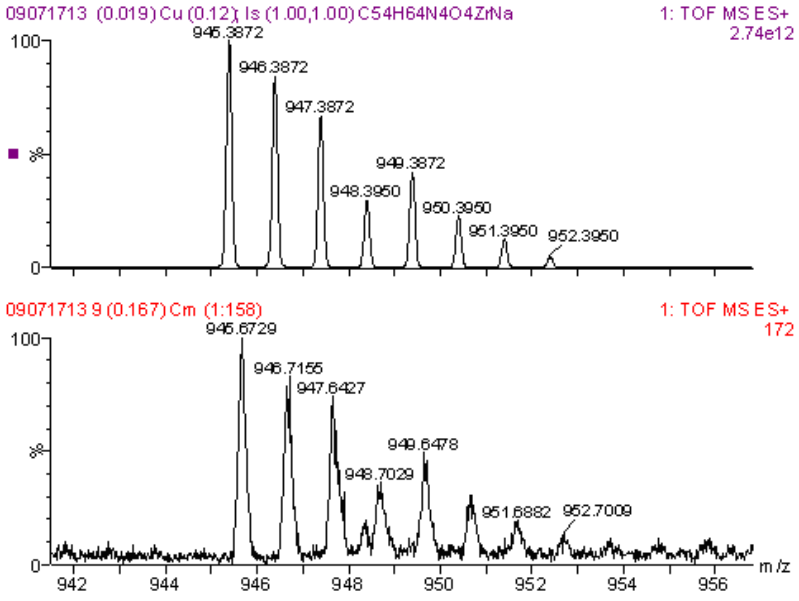


Fig. S2 The calculated (top) and observed (bottom) positive-ion ESI-Q-TOF mass spectra of **1** ($[M + Na]^+$) in CH_2Cl_2/acetone.

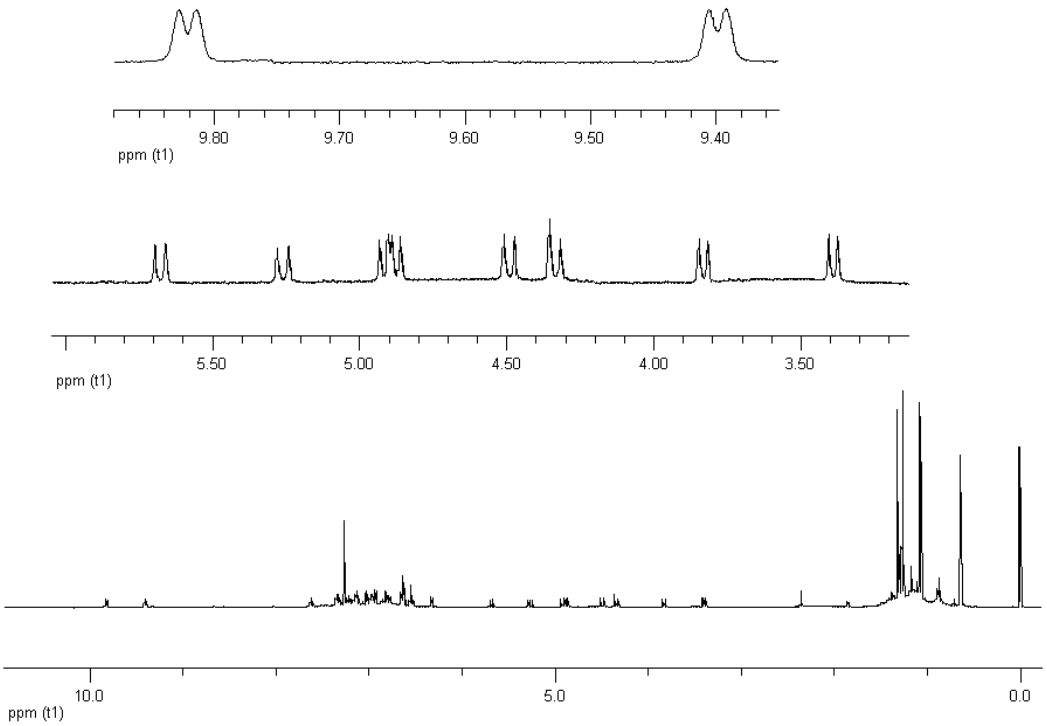


Fig. S3 ^1H NMR spectrum of **1** in $CDCl_3$.

1.3 ^{1}H NMR and mass spectra of complexes 2 and 3

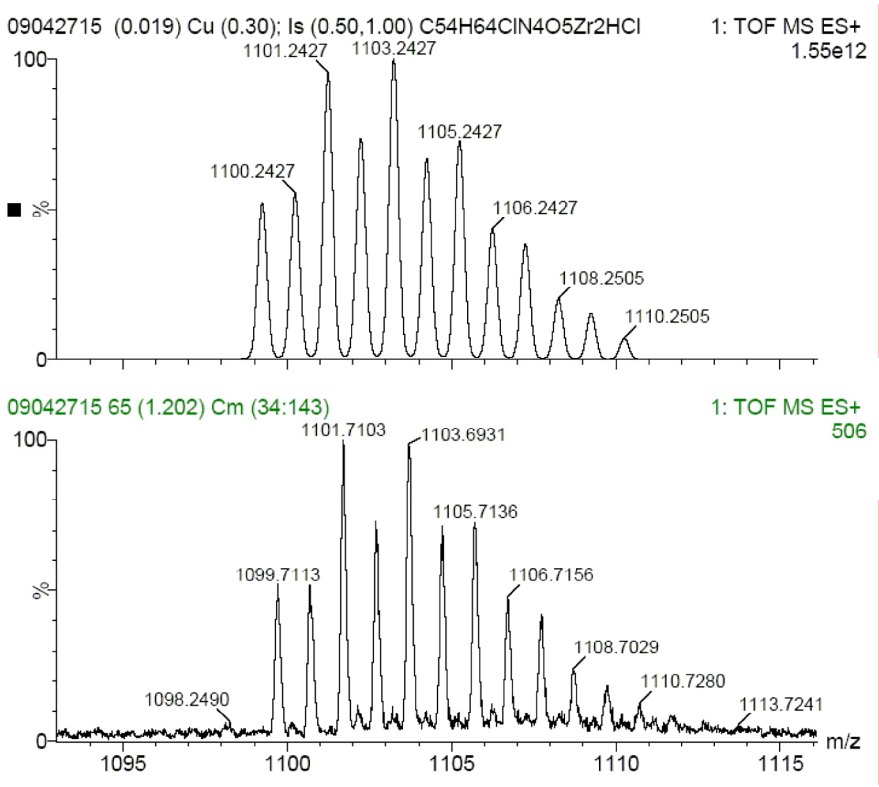


Fig. S4 The calculated (top) and observed (bottom) positive-ion ESI-Q-TOF mass spectra of **2** ($[M–Cl]^{+}$) in CH_2Cl_2/acetone.

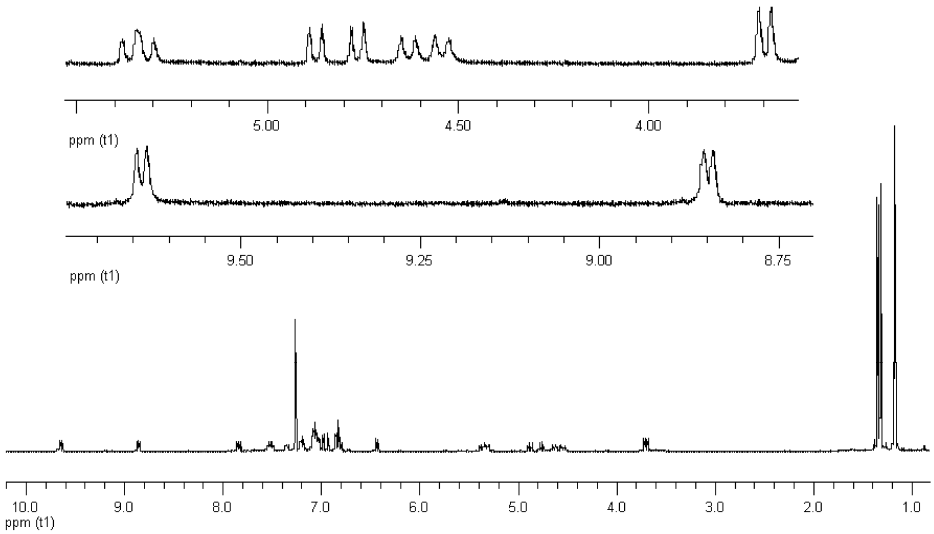


Fig. S5 ^{1}H NMR spectrum of **2** in $CDCl_3$.

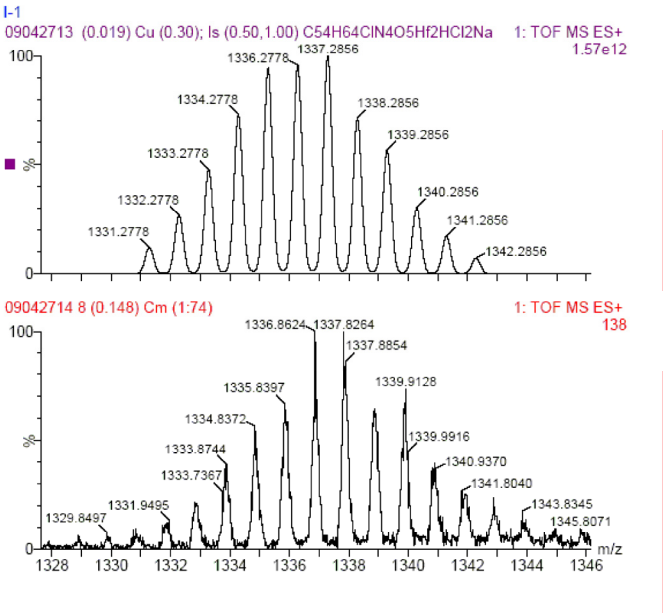


Fig. S6 The calculated (top) and observed (bottom) positive-ion ESI-Q-TOF mass spectra of **3** ($[M+Na]^+$) in CH_2Cl_2/acetone.

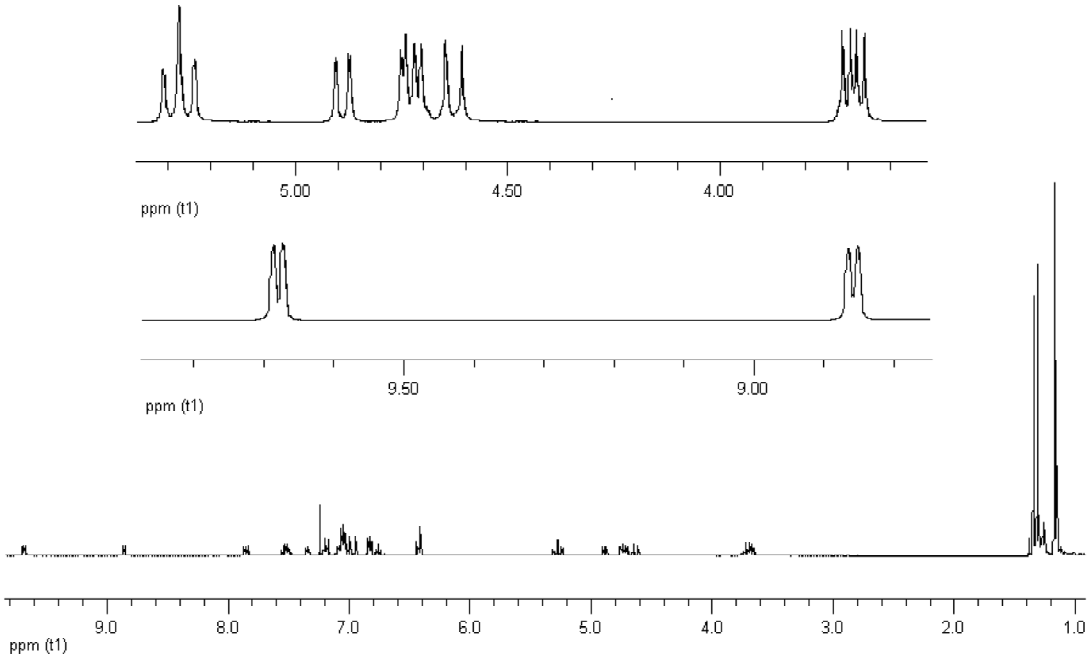


Fig. S7 ^{1}H NMR spectrum of **3** in $CDCl_3$.

1.4 Crystallographic data of H_2L and 1–3

Table S1 Crystallographic data for H_2L and **1**

	H_2L	$L_2Zr{\cdot}0.5C_6H_{14}$
Formula	$C_{27}H_{34}N_2O_2$	$C_{54}H_{64}N_4O_4Zr{\cdot}0.5C_6H_{14}$
Formula weight	418.56	967.40
T/K	298(2)	298(2)
Crystal size/mm	$0.28 \times 0.52 \times 0.88$	$0.16 \times 0.21 \times 0.28$
Crystal system	Orthorhombic	Monoclinic
Space group	*P*bca	*P*2/c
a/Å	10.309(4)	12.6470(15)
b/Å	19.877(7)	20.723(3)
c/Å	23.543(8)	10.6438(14)
β(°)		110.525(7)
V/Å^3	4824(3)	2612.4(6)
Z	8	2
D_{calc}/g cm^{-3}	1.153	1.230
μ/mm^{-1}	0.072	0.259
F_{000}	1808	1026
θ Range/deg	2.05–25.50	2.27–25.00
Reflections collected	30162	11462
Independent reflections	4489	4440
R_{int}	0.0738	0.0340
Final $R_1{}^a$, $wR_2{}^b$ [I > 2σ(I)]	0.0641, 0.1204	0.0469, 0.1264
R_1, wR_2 (all data)	0.1676, 0.1411	0.0612, 0.1352
Goodness-of-fit on F^2	1.009	1.058
Residual electron density/e Å^{-3}	0.216, –0.278	1.045, –0.219

1.4.1 Crystallographic data of H_2L

Table S2 Selected bond lengths (Å) and angles (deg) for H_2L

N1–C6	1.430(4)	C18–C24	1.537(4)	C3–C2	1.368(6)
N1–C13	1.473(4)	C24–C26	1.529(4)	C20–C21A	1.479(8)
N1–C7	1.476(4)	C24–C25	1.530(4)	C20–C21B	1.493(11)
O1–C1	1.362(4)	C24–C27	1.538(4)	C20–C23A	1.495(9)
O2–C19	1.374(3)	C6–C5	1.383(4)	C20–C22B	1.518(12)
C19–C14	1.391(4)	C6–C1	1.390(5)	C20–C22A	1.578(7)
C19–C18	1.400(4)	C13–C14	1.507(4)	C20–C23B	1.587(10)
N2–C12	1.334(4)	C14–C15	1.384(4)	C12–C11	1.365(5)
N2–C8	1.337(4)	C16–C15	1.384(4)	C9–C10	1.385(5)
C8–C9	1.373(4)	C16–C17	1.390(4)	C10–C11	1.367(6)
C8–C7	1.499(4)	C16–C20	1.528(4)	C2–C1	1.388(4)
C18–C17	1.393(4)	C3–C4	1.359(6)	C5–C4	1.389(5)
C6–N1–C13	115.3(2)	O2–C19–C14	119.3(3)	C1–C6–N1	117.8(3)
C6–N1–C7	115.0(2)	O2–C19–C18	119.6(3)	N2–C8–C9	122.5(3)
C13–N1–C7	111.7(2)	N1–C7–C8	111.7(3)	N2–C8–C7	115.0(3)
O1–C1–C2	116.8(4)	N1–C13–C14	112.7(3)	C12–N2–C8	117.9(3)
O1–C1–C6	123.0(3)	C5–C6–N1	123.6(3)	N2–C12–C11	123.5(4)

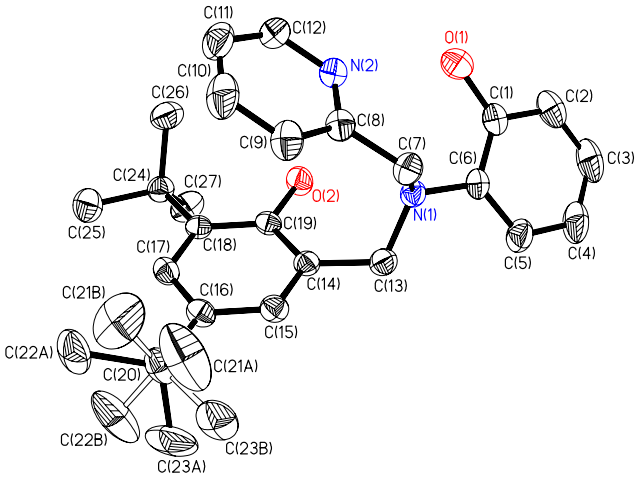


Fig. S8 Molecular structure of H_2L (30% probability ellipsoids). All hydrogen atoms are omitted for clarity.

1.4.2 Crystallographic data of 1

Table S3 Selected bond lengths (Å) and angles (deg) for **1**

Zr1–O2	2.039(2)	Zr1–O1	2.101(2)	Zr1–N2	2.496(3)
Zr1–N1	2.517(2)				
O2–Zr1–O2A	95.44(11)	O1–Zr1–N2A	70.22(8)	O1–Zr1–N1A	130.36(8)
O2–Zr1–O1	143.93(8)	O2–Zr1–N2	89.00(9)	N2–Zr1–N1A	141.30(8)
O2A–Zr1–O1	84.69(8)	O1–Zr1–N2	72.44(9)	O2–Zr1–N1	72.87(8)
O1–Zr1–O1A	115.72(11)	N2–Zr1–N2A	106.02(13)	O1–Zr1–N1	71.34(8)
O2–Zr1–N2A	145.78(8)	O2–Zr1–N1A	83.12(8)	N2–Zr1–N1	65.80(8)
N1–Zr1–N1A	144.13(11)				

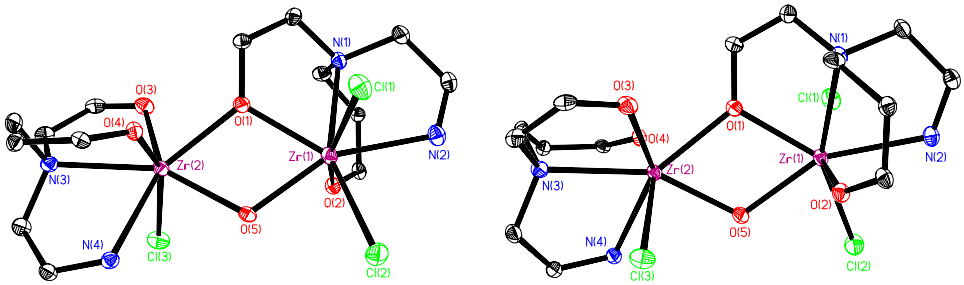
1.4.3 Crystallographic data of N(*R*)N(*R*)-2 and N(*S*)N(*S*)-2

Table S4 Selected bond lengths (Å) and angles (deg) for N(*R*)N(*R*)-**2**

Zr1–O2	1.996(3)	Zr1–Cl1	2.4527(11)	Zr2–O1	2.218(3)
Zr1–O5	2.159(3)	Zr1–Cl2	2.5156(11)	Zr2–N4	2.375(3)
Zr1–O1	2.172(3)	Zr2–O4	2.004(3)	Zr2–N3	2.441(3)
Zr1–N2	2.422(3)	Zr2–O3	2.023(2)	Zr2–Cl3	2.5086(11)
Zr1–N1	2.444(3)	Zr2–O5	2.133(2)	Zr2···Zr1	3.6238(6)
O4–Zr2–O3	107.34(11)	N3–Zr2–Cl3	84.42(8)	O1–Zr1–Cl1	85.52(7)
O4–Zr2–O5	100.84(10)	O4–Zr2–Zr1	97.33(7)	N2–Zr1–Cl1	81.04(8)
O3–Zr2–O5	130.21(10)	O3–Zr2–Zr1	102.50(8)	N1–Zr1–Cl1	83.16(8)
O4–Zr2–O1	83.56(10)	O5–Zr2–Zr1	32.61(7)	O2–Zr1–Cl2	98.12(8)
O3–Zr2–O1	77.26(10)	O1–Zr2–Zr1	33.96(6)	O5–Zr1–Cl2	76.83(7)
O5–Zr2–O1	65.97(9)	N4–Zr2–Zr1	116.53(8)	O1–Zr1–Cl2	136.50(7)
O4–Zr2–N4	79.54(11)	N3–Zr2–Zr1	173.31(7)	N2–Zr1–Cl2	83.45(9)
O3–Zr2–N4	139.38(11)	Cl3–Zr2–Zr1	99.36(3)	N1–Zr1–Cl2	152.60(8)
O5–Zr2–N4	85.09(10)	O2–Zr1–O5	88.58(10)	Cl1–Zr1–Cl2	88.61(4)
O1–Zr2–N4	142.92(10)	O2–Zr1–O1	103.11(10)	O2–Zr1–Zr2	92.00(8)
O4–Zr2–N3	80.93(10)	O5–Zr1–O1	66.35(9)	O5–Zr1–Zr2	32.18(6)
O3–Zr2–N3	72.07(11)	O2–Zr1–N2	79.10(11)	O1–Zr1–Zr2	34.77(7)
O5–Zr2–N3	154.02(10)	O5–Zr1–N2	155.02(11)	N2–Zr1–Zr2	166.55(8)
O1–Zr2–N3	139.4(1)	O1–Zr1–N2	137.49(11)	N1–Zr1–Zr2	99.40(8)
N4–Zr2–N3	69.63(11)	O2–Zr1–N1	81.37(10)	Cl1–Zr1–Zr2	105.76(3)
O4–Zr2–Cl3	155.18(8)	O5–Zr1–N1	130.36(10)	Cl2–Zr1–Zr2	107.99(3)
O3–Zr2–Cl3	86.81(8)	O1–Zr1–N1	68.97(10)	Zr2–O5–Zr1	115.20(11)
O5–Zr2–Cl3	83.95(7)	N2–Zr1–N1	69.49(11)	Zr1–O1–Zr2	111.27(10)
O1–Zr2–Cl3	120.06(7)	O2–Zr1–Cl1	158.12(8)		
N4–Zr2–Cl3	76.61(8)	O5–Zr1–Cl1	113.26(7)		

Table S5 Selected bond lengths (Å) and angles (deg) for N(*S*)N(*S*)-**2**

Zr1–O2	1.997(2)	Zr1–Cl1	2.4540(8)	Zr2–O1	2.2142(18)
Zr1–O5	2.1569(19)	Zr1–Cl2	2.5155(8)	Zr2–N4	2.377(2)
Zr1–O1	2.170(2)	Zr2–O4	2.001(2)	Zr2–N3	2.448(2)
Zr1–N2	2.418(2)	Zr2–O3	2.0232(19)	Zr2–Cl3	2.5104(9)
Zr1–N1	2.446(2)	Zr2–O5	2.1325(19)	Zr2···Zr1	3.6236(4)
O4–Zr2–O3	107.44(9)	N3–Zr2–Cl3	84.45(6)	O1–Zr1–Cl1	85.64(6)
O4–Zr2–O5	101.10(8)	O4–Zr2–Zr1	97.51(6)	N2–Zr1–Cl1	81.12(7)
O3–Zr2–O5	130.14(8)	O3–Zr2–Zr1	102.62(6)	N1–Zr1–Cl1	83.11(6)
O4–Zr2–O1	83.82(8)	O5–Zr2–Zr1	32.56(5)	O2–Zr1–Cl2	98.19(6)
O3–Zr2–O1	77.45(7)	O1–Zr2–Zr1	33.88(5)	O5–Zr1–Cl2	76.96(5)
O5–Zr2–O1	65.87(7)	N4–Zr2–Zr1	116.46(6)	O1–Zr1–Cl2	136.58(5)
O4–Zr2–N4	79.47(8)	N3–Zr2–Zr1	173.39(6)	N2–Zr1–Cl2	83.31(6)
O3–Zr2–N4	139.28(8)	Cl3–Zr2–Zr1	99.36(2)	N1–Zr1–Cl2	152.47(6)
O5–Zr2–N4	85.10(8)	O2–Zr1–O5	88.58(8)	Cl1–Zr1–Cl2	88.56(3)
O1–Zr2–N4	142.87(8)	O2–Zr1–O1	102.94(8)	O2–Zr1–Zr2	92.03(6)
O4–Zr2–N3	80.68(8)	O5–Zr1–O1	66.23(7)	O5–Zr1–Zr2	32.15(5)
O3–Zr2–N3	72.08(8)	O2–Zr1–N2	79.06(8)	O1–Zr1–Zr2	34.66(5)
O5–Zr2–N3	153.99(8)	O5–Zr1–N2	154.97(8)	N2–Zr1–Zr2	166.60(6)
O1–Zr2–N3	139.55(8)	O1–Zr1–N2	137.62(8)	N1–Zr1–Zr2	99.46(6)
N4–Zr2–N3	69.59(8)	O2–Zr1–N1	81.37(8)	Cl1–Zr1–Zr2	105.68(2)
O4–Zr2–Cl3	155.05(6)	O5–Zr1–N1	130.37(8)	Cl2–Zr1–Zr2	108.06(2)
O3–Zr2–Cl3	86.63(7)	O1–Zr1–N1	69.03(8)	Zr2–O5–Zr1	115.29(9)
O5–Zr2–Cl3	83.87(6)	N2–Zr1–N1	69.51(8)	Zr1–O1–Zr2	111.47(8)
O1–Zr2–Cl3	119.95(6)	O2–Zr1–Cl1	158.13(6)		
N4–Zr2–Cl3	76.60(6)	O5–Zr1–Cl1	113.25(6)		



N(*R*)N(*R*)-**2** N(*S*)N(*S*)-**2**

Fig. S9 Framework structures of N(*R*)N(*R*)-**2** and N(*S*)N(*S*)-**2** (30% probability ellipsoids). Parts of the phenyl and pyridyl rings are omitted for clarity.

1.4.4 Crystallographic data of N(*R*)N(*R*)-3 and N(*S*)N(*S*)-3

Two enantiomers were identified for complex **3**, that is, N(*S*)N(*S*)-**3** and N(*R*)N(*R*)-**3** (Table S6 and S7)

Table S6 Selected bond lengths (Å) and angles (deg) for N(*R*)N(*R*)-**3**

Hf1–O2	1.999(6)	Hf1–Cl1	2.437(3)	Hf2–O1	2.211(5)
Hf1–O5	2.117(6)	Hf1–Cl2	2.487(2)	Hf2–N4	2.375(6)
Hf1–O1	2.158(6)	Hf2–O4	1.968(6)	Hf2–N3	2.382(7)
Hf1–N2	2.385(8)	Hf2–O3	2.018(6)	Hf2–Cl3	2.482(2)
Hf1–N1	2.434(7)	Hf2–O5	2.119(5)	Hf2···Hf1	3.5960(6)
O4–Hf2–O3	106.0(2)	N3–Hf2–Cl3	84.34(17)	O1–Hf1–Cl1	85.55(17)
O4–Hf2–O5	100.3(2)	O4–Hf2–Hf1	97.26(16)	N2–Hf1–Cl1	83.1(2)
O3–Hf2–O5	130.1(2)	O3–Hf2–Hf1	102.25(19)	N1–Hf1–Cl1	82.4(2)
O4–Hf2–O1	82.9(2)	O5–Hf2–Hf1	31.89(15)	O2–Hf1–Cl2	98.77(17)
O3–Hf2–O1	76.7(2)	O1–Hf2–Hf1	34.14(15)	O5–Hf1–Cl2	77.53(17)
O5–Hf2–O1	65.3(2)	N4–Hf2–Hf1	115.48(18)	O1–Hf1–Cl2	137.10(15)
O4–Hf2–N4	80.8(2)	N3–Hf2–Hf1	174.45(17)	N2–Hf1–Cl2	83.1(2)
O3–Hf2–N4	140.7(3)	Cl3–Hf2–Hf1	97.89(6)	N1–Hf1–Cl2	151.8(2)
O5–Hf2–N4	84.5(2)	O2–Hf1–O5	87.0(2)	Cl1–Hf1–Cl2	88.41(11)
O1–Hf2–N4	142.3(2)	O2–Hf1–O1	101.4(2)	O2–Hf1–Hf2	89.36(17)
O4–Hf2–N3	82.2(2)	O5–Hf1–O1	66.2(2)	O5–Hf1–Hf2	31.92(15)
O3–Hf2–N3	72.7(3)	O2–Hf1–N2	79.0(3)	O1–Hf1–Hf2	35.08(14)
O5–Hf2–N3	153.7(2)	O5–Hf1–N2	154.0(3)	N2–Hf1–Hf2	164.75(19)
O1–Hf2–N3	140.5(2)	O1–Hf1–N2	137.8(3)	N1–Hf1–Hf2	99.55(19)
N4–Hf2–N3	69.9(2)	O2–Hf1–N1	82.5(2)	Cl1–Hf1–Hf2	106.36(7)
O4–Hf2–Cl3	157.26(16)	O5–Hf1–N1	130.5(2)	Cl2–Hf1–Hf2	108.61(6)
O3–Hf2–Cl3	87.21(19)	O1–Hf1–N1	68.8(2)	Hf1–O5–Hf2	116.2(3)
O5–Hf2–Cl3	84.08(17)	N2–Hf1–N1	69.4(3)	Hf1–O1–Hf2	110.8(2)
O1–Hf2–Cl3	118.64(16)	O2–Hf1–Cl1	159.75(18)		
N4–Hf2–Cl3	77.42(19)	O5–Hf1–Cl1	113.15(17)		

Table S7 Selected bond lengths (Å) and angles (deg) for N(*S*)N(*S*)-**3**

Hf1–O2	1.999(4)	Hf1–Cl1	2.4437(17)	Hf2–O1	2.206(3)
Hf1–O5	2.131(3)	Hf1–Cl2	2.4878(16)	Hf2–N4	2.361(4)
Hf1–O1	2.162(4)	Hf2–O4	1.990(4)	Hf2–N3	2.412(4)
Hf1–N2	2.400(5)	Hf2–O3	2.027(3)	Hf2–Cl3	2.4878(15)
Hf1–N1	2.424(4)	Hf2–O5	2.114(3)	Hf2···Hf1	3.5998(3)
O4–Hf2–O3	106.12(17)	N3–Hf2–Cl3	84.35(12)	O1–Hf1–Cl1	85.95(11)
O4–Hf2–O5	100.36(14)	O4–Hf2–Hf1	97.41(8)	N2–Hf1–Cl1	83.35(14)
O3–Hf2–O5	130.42(16)	O3–Hf2–Hf1	102.37(11)	N1–Hf1–Cl1	82.59(12)
O4–Hf2–O1	83.19(13)	O5–Hf2–Hf1	32.16(9)	O2–Hf1–Cl2	98.58(11)
O3–Hf2–O1	76.83(13)	O1–Hf2–Hf1	34.11(10)	O5–Hf1–Cl2	77.55(10)
O5–Hf2–O1	65.52(13)	N4–Hf2–Hf1	115.89(10)	O1–Hf1–Cl2	137.09(10)
O4–Hf2–N4	79.96(15)	N3–Hf2–Hf1	174.49(10)	N2–Hf1–Cl2	82.86(13)
O3–Hf2–N4	140.33(13)	Cl3–Hf2–Hf1	97.85(4)	N1–Hf1–Cl2	151.90(11)
O5–Hf2–N4	84.71(14)	O2–Hf1–O5	87.26(14)	Cl1–Hf1–Cl2	88.39(7)
O1–Hf2–N4	142.33(13)	O2–Hf1–O1	101.42(14)	O2–Hf1–Hf2	89.62(9)
O4–Hf2–N3	82.03(14)	O5–Hf1–O1	66.02(12)	O5–Hf1–Hf2	31.86(9)
O3–Hf2–N3	72.63(15)	O2–Hf1–N2	78.38(16)	O1–Hf1–Hf2	34.91(8)
O5–Hf2–N3	153.35(13)	O5–Hf1–N2	153.66(17)	N2–Hf1–Hf2	164.68(11)
O1–Hf2–N3	140.61(14)	O1–Hf1–N2	138.24(15)	N1–Hf1–Hf2	99.49(11)
N4–Hf2–N3	69.47(14)	O2–Hf1–N1	82.25(16)	Cl1–Hf1–Hf2	106.57(4)
O4–Hf2–Cl3	157.14(9)	O5–Hf1–N1	130.41(14)	Cl2–Hf1–Hf2	108.60(4)
O3–Hf2–Cl3	87.05(13)	O1–Hf1–N1	68.91(14)	Hf2–O5–Hf1	115.98(16)
O5–Hf2–Cl3	83.97(11)	N2–Hf1–N1	69.72(17)	Hf1–O1–Hf2	110.98(15)
O1–Hf2–Cl3	118.52(11)	O2–Hf1–Cl1	159.41(10)		
N4–Hf2–Cl3	78.10(13)	O5–Hf1–Cl1	113.22(11)		

2. Studies on polymerization of lactide using racemic initiators 2 and 3

2.1 Typical procedure for polymerization of *rac*-LA

The stereoselectivities of the PLA are determined by the homonuclear decoupled ^{1}H NMR spectra of the methine region of the products (Fig. S10).

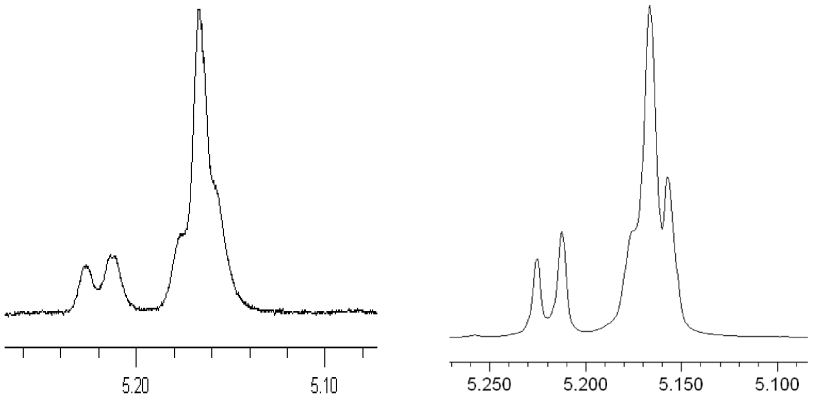


Fig. S10 Methine region of homonuclear decoupled ^{1}H NMR spectra of isotactic-rich PLA made from *rac*-LA initiated by *rac*-**2** ($CDCl_3$, 400 MHz, left) and *rac*-**3** ($CDCl_3$, 600 MHz, right).

2.2 Polymerization of L-LA and microstructure analysis of PLLA

Polymerization of L-LA was made by the same procedure as that for *rac*-LA. The tacticity of the polymers prepared with the racemic initiator **2** was determined by inspection of the homonuclear decoupled ^{1}H NMR spectrum of the methine region. (Fig. S11).

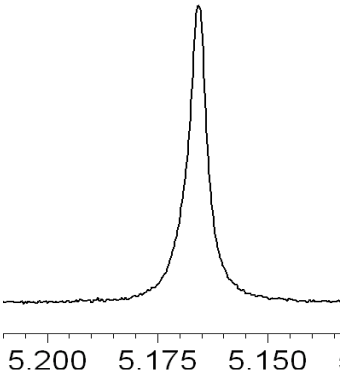


Fig. S11 Homonuclear decoupled ^{1}H NMR spectrum of the methine region of PLLA prepared from L-LA with the racemic initiator **2** at 130 °C (400 MHz, $CDCl_3$).