Electronic Supplementary Information (ESI) For

Preparations of Biocompatible, Biodegradable and Sustainable Polylactides Catalysted by Aluminum Complexes Bearing Unsymmetrical Dinaphthalene-imine Derivatives via the Ring-Opening Polymerization of Lactides

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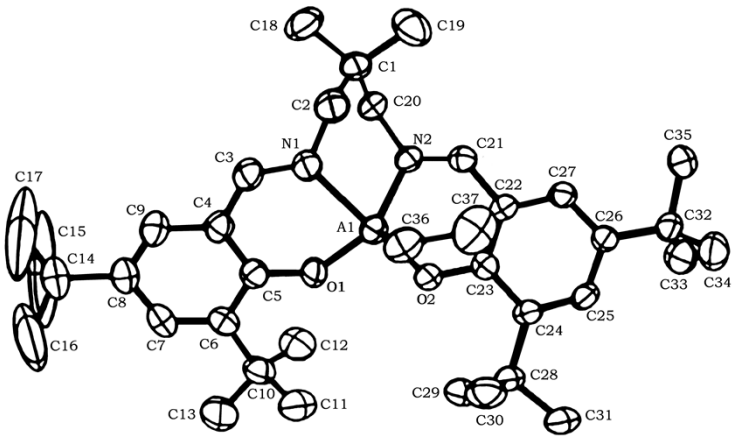

Fig. S1 Crystal structure of compound **2** in reference 14b.

Table S1. Summary of crystallographic data for complexes **(*rac*)-C_1** and **(*rac*)-D_4**.

	(*rac*)-C_1	**(*rac*)-D_4**
Formula	$C_{68}H_{50}AlCl_3N_4O_2$	$C_{71}H_{53}AlCl_4N_4O_3 \cdot 1/2CH_2Cl_2$
F_w	1088.45	1221.42
crystal system	Monoclinic	Monoclinic
space group	P2(1)/n	P2(1)/c
a (Å)	14.265(3)	15.7200(17)
b (Å)	20.847(4)	14.2236(15)
c (Å)	18.412(3)	28.919(3)
α (deg)	90.00	90.00
β (deg)	97.691(4)	96.120(2)
γ (deg)	90.00	90.00
v (Å^3)	5426.1(19)	6429.2(12)
Z	4	4
μ (mm^{-1})	0.237	0.289
$R_{(int)}$	0.1393	0.0839
GOOF	1.005	1.042
R_1 [I>2sigma(I)]	0.0948	0.0904

wR_2[I>2sigma(I)]	0.2932	0.2841

Experimental

General Considerations

All operations refer to air and water-sensitive were employed Schlenk line techniques. Elemental analysis were accomplished by a Varian EL microanalyzer, ^{1}H NMR, ^{13}C NMR and ^{1}H-^{13}C HMQC spectra were performed on Bruker AV 300M or 400M apparatus at 25 °C in $CDCl_3$ for compounds and macromolecules. The momer conversions were confirmed and P_m values were calculated by referencing the reference.[1, 2, 3] Gel permeation chromato-graphy (GPC) measurements were conducted with a Waters 515 GPC with $CHCl_3$ as the eluant (flow rate: 1 mLmin^{-1}, at 35 °C). The molecular weight was adjusted through PS standard. Crystallographic data were gathered and analyzed by referencing the reference[4]. $AlMe_3$, isopropanol, methanol, *rac*-1,1'-dinaphthalene-2,2'-diamine, PTSA, (*S*)-(–)-1,1'-dinaphthalene-2, 2'-diamine, Palladium(II) acetate, *rac*-BINAP, sodium tert butyl alcohol, aryl bromides, salicylaldehyde, 3,5-di-tert-butylsalicylaldehyde and 3,5-dichlorosalicylaldehyde were obtained from Aldrich. and applied without further purification.

Synthesis of compounds (*S*)-L_a, (*S*)-L_b, (*S*)-L_c and (*rac*)-L_a, (*rac*)-L_b, (*rac*)-L_c

Upon stirring a solution of $Pd(OAc)_2$ (0.18 g, 0.50 mmol) and **(*rac*)**-BINAP (0.625 g, 1.00 mmol) in toluene in a Schlenk flask under argon, the aryl bromide (10.00 mmol), **(*S*)**-(–)-1,1'-dinaphthalene-2,2'-diamine or **(*rac*)**-1,1'-dinaphthalene-2,2'-diamine (2.84 g, 10.00 mmol) and sodium tert butyl alcohol (1.44 g, 15.00 mmol) were added. The mixture was stirred at 25 °C for 15 min. The Schlenk flask was heated to 60 °C. After 5–8 h the mixture was cooled to 25 °C, poured into diethyl ether (100 mL), and separated with separating funnel. The solution was dried and distilled dry. The product as colourless solid were attained by flash chromatography on silica gel with petroleum ether/acetic ether (V_1 /V_2 = 12/1) as the eluent, in 62.4–78.1% yield.

Compound (S)-L_a:

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 7.82–7.89 (m, 4H, Ar*H*), 7.70 (d, *J* = 9.0 Hz, 1H, Ar*H*), 7.20–7.32 (m, 5H, Ar*H*), 7.16 (s, 1H, Ar*H*), 7.13–7.08 (m, 1H, Ar*H*), 7.05–7.03 (m, 2H, Ar*H*), 6.95 (t, *J* = 7.3 Hz, 1H, Ar*H*). 5.72–3.40 (bs, 3H, N*H,* NH_2). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): 142.81, 142.76, 140.18, 133.91, 133.72, 129.74, 129.43, 129.20, 129.08, 128.42, 128.16, 128.12, 126.98, 126.84, 124.51, 123.84, 123.32, 122.52, 121.94, 119.78, 118.26, 117.85, 116.81, 112.02 (24C, Ar*C*). Anal. Calcd for $C_{33}H_{24}N_2O$ (%): C, 86.64; H, 5.59; N, 7.77. Found: C, 86.62; H, 5.51; N, 7.73.

***Compound* (S)-L_b**

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.86–7.72 (m, 4H, Ar*H*), 7.29–7.19 (m, 3H, Ar*H*), 7.12–7.09 (m, 3H, Ar*H*), 7.05 (s, 3H, Ar*H*), 6.69 (d, *J* = 8.8 Hz, 1H, Ar*H*), 5.26–4.96 (m, 3H, N*H*, NH_2), 2.07 (bs, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 143.04, 142.46, 137.59, 136.63, 133.97, 133.92, 129.65, 129.48, 128.59, 128.43, 128.22, 128.15, 128.04, 126.84, 126.08, 124.20, 123.78, 122.54, 122.06, 118.31, 114.24, 112.33, 111.93 (Ar*C*), 18.35 (*C*H_3). Anal. Calcd for $C_{27}H_{22}N_2O$ (%): C, 86.56; H, 6.23; N, 7.21. Found: C, 86.59; H, 6.27; N, 7.24.

Compound (S)-L_c

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.84–7.77 (m, 4H, Ar*H*), 7.51 (d, *J* = 9.0 Hz, 1H, Ar*H*), 7.30–7.16 (m, 3H, Ar*H*), 7.14–7.07 (m, 2H, Ar*H*), 6.99–6.87 (m, 4H, Ar*H*), 5.43 (bs, 1H, N*H*), 3.70 (bs, 2H, NH_2). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 159.88, 157.48, 142.86, 140.95, 138.71, 133.91, 133.67, 129.80, 129.24, 128.17, 127.02, 126.93, 124.39, 123.78, 123.23, 122.79, 122.71, 122.57, 121.94, 118.27, 117.09, 115.94, 115.71, 111.86. Anal. Calcd for $C_{26}H_{19}FN_2$ (%): C, 82.52; H, 5.06; N, 7.40. Found: C, 82.46; H, 5.00; N, 7.32.

The methods described for *chiral* compounds **(*S*)-L_a, (*S*)-L_b, (*S*)-L_c** were used for the synthesis of *racemic* compounds **(*rac*)-L_a, (*rac*)-L_b, (*rac*)-L_c**, the same below.

Synthesis of pro-ligands

Pro-ligand (S)-L_1

A mixture of **(*S*)-L_a** (0.720 g, 2.00 mmol), salicylaldehyde (0.244 g, 2.00 mmol) and a catalytic quantity of PTSA in toluene (50 mL) was refluxed for 7 h. After solvent evaporation at reduced pressure, the crude product was purified by flash chromatography on silica gel with petroleum ether/acetic ether (V_1/V_2 = 16 /1) with 1% NEt_3 as the eluent, affording 0.776 g of the yellow solid of the product in 83.5% isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 12.19 (s, 1H, O*H*), 8.61 (s, 1H, N=C*H*), 8.08 (d, *J* = 8.8 Hz, 1H, Ar*H*), 7.98 (d, *J* = 8.1 Hz, 1H, Ar*H*), 7.91 (d, *J* = 9.0 Hz, 1H, Ar*H*), 7.85 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.68–7.63 (m, 2H, Ar*H*), 7.50 (t, *J* = 7.4 Hz, 1H, Ar*H*), 7.43–7.15 (m, 3H, Ar*H*), 7.08 (t, *J* = 7.8 Hz, 2H, Ar*H*), 6.97–6.77 (m, 6H, Ar*H*), 5.34 (s, 1H, N*H*). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 162.36 (s, 1C, N=*C*H), 160.85, 144.52, 142.84, 139.31, 133.81, 133.44, 132.87, 132.75, 132.14, 130.04, 129.29, 129.11, 129.04, 128.26, 128.16, 127.87, 127.38, 126.53, 126.23, 126.17, 124.52, 123.30, 121.51, 119.20, 118.56, 118.48, 117.68, 117.16 (Ar*C*, 28C). Anal. Calcd for $C_{33}H_{24}N_2O$ (%): C, 85.32; H, 5.21; N, 6.03. Found: C, 85.32; H, 5.21; N, 6.03.

Pro-ligand (S)-L_2

The synthesis of pro-ligand **(*S*)-L_2** was similar with pro-ligand **(*S*)-L_1**, using **(*S*)-L_a** (0.720 g, 2.00 mmol) and 3,5-di-tert-butylsalicylaldehyde (0.268 g, 2.00 mmol). The product was isolated as yellow solid. Yield: 0.878 g, 76.2%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 12.26 (bs, 1H, O*H*), 8.57 (s, 1H, N=C*H*), 8.07 (d, *J* = 8.8 Hz, 1H, Ar*H*), 7.98 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.85 (d, *J* = 9.0 Hz, 1H, Ar*H*), 7.81 (d, *J* = 7.7 Hz, 1H, Ar*H*), 7.72 (dd, *J* = 5.7, 3.3 Hz, 2H, Ar*H*), 7.67–7.62 (m, 2H, Ar*H*), 7.57–7.49 (m, 3H, Ar*H*), 7.48–7.42 (m, 1H, Ar*H*), 7.29 (d, *J* = 2.5 Hz, 1H, Ar*H*), 7.07 (s, 1H, Ar*H*), 7.05 (s, 1H, Ar*H*), 6.92 (d, *J* = 8.6 Hz, 1H, Ar*H*), 6.82 (t, *J* = 7.2 Hz, 1H, Ar*H*), 5.31 (bs, 1H, N*H*) , 1.28 (s, 9H, C(CH_3)$_3$), 1.24 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 167.63 (s, 1C, N=*C*H), 163.04, 158.28, 144.57, 142.90, 139.82, 139.29, 136.72, 134.03, 133.60, 132.58, 132.31, 130.84, 129.90, 128.97, 128.79, 128.27, 128.00, 127.69, 127.29, 126.48, 126.38, 126.25, 125.93, 124.54, 123.08, 121.41, 119.32, 118.40, 118.10, 117.89, 34.87 (1C, *C*(CH$_3$)$_3$), 34.00 (1C, *C*(CH$_3$)$_3$), 31.37 (1C, C(*C*H$_3$)$_3$), 29.14 (1C, C(*C*H$_3$)$_3$). Anal. Calcd for $C_{41}H_{40}N_2O$ (%): C, 85.38; H, 6.99; N, 4.86. Found: C, 85.32; H, 6.93; N, 4.80.

Pro-ligand (S)-L_3

(*S*)-L_a (0.720 g, 2.00 mmol) was dissolved in 10 mL of absolute EtOH, and a solution of 3, 5-dichlorosalicylaldehyde (0.780 g, 2.00 mmol) in 8 mL of absolute EtOH was added. The solution turned red and a powder started to precipitate. After 2 h under stirring, the red solid was removed by filtration, washed twice with EtOH and dried under vacuum. Yield: 0.499 g, 93.6%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 12.89 (bs, 1H, O*H*), 8.39 (s, 1H, N=C*H*), 8.09 (d, *J* = 8.8 Hz, 1H, Ar*H*), 7.99 (d, *J* = 8.2 Hz, 1H, Ar*H*), 7.90 (d, *J* = 9.0 Hz, 1H, Ar*H*), 7.85 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.66 (d, *J* = 9.0 Hz, 1H, Ar*H*), 7.56 (d, *J* = 8.7 Hz, 1H, Ar*H*), 7.37 (d, *J* = 6.0 Hz, 2H, Ar*H*), 7.32–7.27 (m, 2H, Ar*H*), 7.17 (t, *J* = 7.4 Hz, 1H, Ar*H*), 7.09 (t, *J* = 7.8 Hz, 2H, Ar*H*), 6.97 (d, *J* = 2.5 Hz, 1H, Ar*H*), 6.91 (d, *J* = 7.9 Hz, 3H, Ar*H*), 6.84 (t, *J* = 7.3 Hz, 1H, Ar*H*), 5.30 (bs, 1H, N*H*). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 160.98 (s, 1C, N=*C*H), 155.50, 143.83, 142.71, 139.30, 133.78, 133.43, 133.04, 132.39, 130.23, 129.59, 129.41, 129.11, 128.34, 128.27, 127.92, 127.60, 126.69, 126.57, 126.42, 124.40, 123.44, 122.79, 122.50, 121.60, 120.21, 119.80, 118.82, 118.68, 118.25, 117.95. Anal. Calcd for $C_{33}H_{22}Cl_2N_2O$ (%): C, 74.30; H, 4.16; N, 5.25. Found: C, 74.32; H, 4.19; N, 5.28.

Pro-ligand (S)-L_4

The synthesis of pro-ligand **(*S*)-L_4** was similar with pro-ligand **(*S*)-L_3**, using **(*S*)-L_b** (0.777 g, 2.00 mmol) and 3,5-dichlorosalicylaldehyde (0.780 g, 2.00 mmol). The product was isolated as red powder. Yield: 0.975g, 87.0%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 13.24 (s, 1H, O*H*), 8.81 (s, 1H, N=C*H*), 8.35 (d, *J* = 8.8 Hz, 1H, Ar*H*), 8.24 (d, *J* = 7.9 Hz, 1H, Ar*H*), 8.02 (d, *J* = 9.0 Hz, 2H, Ar*H*), 7.91 (d, *J* = 8.8 Hz, 1H, Ar*H*), 7.82–7.73 (m, 3H, Ar*H*), 7.64 (t, *J* = 7.5 Hz, 1H, Ar*H*), 7.47–7.41 (m, 3H, Ar*H*), 7.28 (d, *J* = 2.3 Hz, 2H, Ar*H*), 7.20 (d, *J* = 8.8 Hz, 1H, Ar*H*), 6.93 (d, *J* = 8.9 Hz, 1H, Ar*H*), 5.05 (s, 1H, N*H*), 2.21 (s, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 160.70 (s, 1C, N=*C*H), 155.66, 144.00, 141.62, 137.59,136.52, 136.41, 134.10, 133.38, 133.36,

132.45, 130.24, 129.86, 129.48, 128.57, 128.46, 128.38, 128.32, 127.84, 127.45, 126.75, 126.69, 126.10, 123.51, 122.78, 122.63, 122.07, 120.31, 118.13, 114.27, 112.96, 18.26. Anal. Calcd for $C_{35}H_{26}Cl_2N_2O$ (%): C, 74.87; H, 4.67; N, 4.99. Found: C, 74.82; H, 4.61; N, 4.94.

Pro-ligand (S)-L$_5$

The synthesis of pro-ligand **(*S*)-L$_5$** was similar with pro-ligand **(*S*)-L$_1$**, using **(*S*)-L$_c$** (0.757 g, 2.00 mmol) and salicylaldehyde (0.244 g, 2.00 mmol). The product was isolated as yellow powder. Yield: 0.795g, 82.5%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 12.18 (s, 1H, O*H*), 8.58 (s, 1H, N=C*H*), 8.05 (d, *J* = 8.8 Hz, 1H, Ar*H*), 7.95 (d, *J* = 8.3 Hz, 1H, Ar*H*), 7.87 (d, *J* = 9.0 Hz, 1H, Ar*H*), 7.81 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.62 (d, *J* = 8.8 Hz, 1H, Ar*H*), 7.50–7.46 (m, 2H, Ar*H*), 7.40 (d, *J* = 8.3 Hz, 1H, Ar*H*), 7.35–7.29 (m, 1H, Ar*H*), 7.36–7.29 (m, 1H, Ar*H*), 6.94 (d, *J* = 8.4 Hz, 1H, Ar*H*), 6.90–6.86 (m, 2H, Ar*H*), 6.82–6.73 (m, 4H, Ar*H*), 5.19 (bs, 1H, N*H*). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 161.74 (s, 1C, N=*C*H), 160.84, 159.61, 157.21, 144.55, 139.93, 138.83, 133.84, 133.50, 132.98, 132.82, 132.13, 130.13, 129.25, 129.09, 128.30, 127.80, 127.41, 126.61, 126.25, 124.45, 123.19, 122.00, 121.93, 119.18, 118.68, 118.40, 117.73, 117.20, 115.77, 115.55. Anal. Calcd for $C_{33}H_{23}FN_2O$ (%): C, 82.14; H, 4.80; N, 5.81. Found: C, 82.10; H, 4.72; N, 5.77.

Pro-ligand (S)-L$_6$

The synthesis of pro-ligand **(*S*)-L$_6$** was similar with pro-ligand **(*S*)-L$_3$**, using **(*S*)-L$_c$** (0.757 g, 2.00 mmol) and 3,5-dichlorosalicylaldehyde (0.780 g, 2.00 mmol). The product was isolated as red powder. Yield: 0.943g, 85.8%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.96 (s, 1H, O*H*), 8.38 (s, 1H, N=C*H*), 7.98 (d, *J* = 8.8 Hz, 1H, Ar*H*), 7.88 (d, *J* = 8.1 Hz, 1H, Ar*H*), 7.77 (d, *J* = 9.0 Hz, 1H, Ar*H*), 7.71 (d, *J* = 8.3 Hz, 2H, Ar*H*), 7.64–7.60 (m, 2H, Ar*H*), 7.51 (d, *J* = 8.8 Hz, 1H, Ar*H*), 7.43 (d, *J* = 8.5 Hz, 2H, Ar*H*), 7.19 (d, *J* = 1.9 Hz, 1H, Ar*H*), 6.93 (d, *J* = 2.0 Hz, 1H, Ar*H*), 6.84–6.78 (m, 3H, Ar*H*), 6.71 (t, *J* = 8.5 Hz, 1H, Ar*H*), 5.22 (bs, 1H, N*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.46 (1C, N=C*H*), 160.57, 159.37, 155.35, 143.42, 139.72, 138.50, 133.64, 133.27, 132.93, 132.18, 130.64, 130.05, 128.92, 128.55, 127.31, 126.18, 124.21, 124.03, 123.46, 122.99, 122.66, 121.47, 121.40, 120.06, 118.07, 117.57, 117.47, 116.89, 115.51, 115.29. Anal. Calcd for $C_{33}H_{21}Cl_2FN_2O$ (%): C, 71.88; H, 3.84; N, 5.08. Found: C, 71.79; H, 3.77; N, 5.01.

Synthesis of complexes

Complex (S)-A$_1$

A mixture of **(*S*)-L$_1$** (0.465 g, 1.00 mmol) and $AlMe_3$ (1.00 M in toluene, 1.00 mL, 1.00 mmol) in 15 mL toluene was stirred for 6 h at 50 °C under an argon atmosphere. And concentrated to 2 mL to give a yellow powder, from which the mother liquor was decanted, and the product was washed with about 0.5 mL of hexane and dried in vacuum. The product was isolated as yellow solid. Yield: 0.497 g, 95.6%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 8.09 (d, *J* = 8.4 Hz, 1H, Ar*H*), 8.05 (s, 1H, N=C*H*), 8.00 (d, *J* = 8.1 Hz, 1H, Ar*H*), 7.93 (s, 1H, Ar*H*), 7.77–7.70 (m, 3H, Ar*H*), 7.58–7.50 (m, 1H, Ar*H*), 7.47 (d, *J* = 9.0 Hz, 1H, Ar*H*), 7.37–7.29 (m, 4H, Ar*H*), 7.04–6.87 (m, 3H, Ar*H*), 6.74 (d, *J* = 8.3 Hz, 1H, Ar*H*), 6.54–6.48 (m, 1H, Ar*H*), 6.38–6.22 (m, 2H, Ar*H*), 5.27 (s, 1H, N*H*), –0.85 (s, 3H, AlCH_3), –0.88 (s, 3H, AlCH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 172.12, 169.89 (1C, N=*C*H), 140.41, 137.68, 135.44, 135.00, 130.19, 129.92, 129.34, 128.87, 128.54, 128.31, 127.91, 127.54, 127.15, 126.90, 126.64, 125.88, 124.79, 124.49, 123.55, 122.88, 122.59, 121.61, 120.67, 119.67, 118.07, 117.94, 117.40, 117.11, 115.20, -8.86 (1C, Al*C*H$_3$), -9.59 (1C, Al*C*H$_3$). Anal. Calcd for $C_{35}H_{29}AlN_2O$ (%): C, 80.75; H, 5.61; N, 5.38. Found: C, 80.72; H, 5.50; N, 5.33.

Complex (S)-A$_2$

Complex **(S)-A$_2$** as yellow solid was acquired by a similar way for **(*S*)-A$_1$** with **(*S*)-L$_2$** (0.576 g, 1.00 mmol) and $AlMe_3$ (1.00 mmol). Yield: 0.525 g, 91.2%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 8.06 (d, *J* = 8.8 Hz, 1H, Ar*H*), 7.98 (s, 1H, N=C*H*), 7.80–7.72 (m, 2H), 6.80–7.99 (m, 16H, Ar*H*), 7.67 (d, *J* = 9.1 Hz, 1H, Ar*H*), 7.57–7.47 (m, 2H, Ar*H*), 7.42 (s, 1H, Ar*H*), 7.40–7.33 (m, 4H, Ar*H*), 7.06–7.00 (m, 1H, Ar*H*), 6.98–6.85 (m, 4H, Ar*H*), 5.90 (d, *J* = 2.3 Hz, 1H,Ar*H*), 5.23 (s, 1H, N*H*), 1.34 (s, 9H, C(CH_3)$_3$), 1.10 (s, 9H, C(CH_3)$_3$), –0.83 (s, 3H, AlCH_3), –0.97 (s, 3H, AlCH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 172.85, 162.03 (s, 1C, N=*C*H), 143.95, 141.29, 140.35, 139.93, 138.39, 135.22, 133.67, 132.71, 132.47, 130.77, 129.91, 129.64, 129.16, 128.85, 128.72, 128.35, 128.21, 127.60, 127.41, 126.53, 125.46, 124.28, 123.08, 122.84, 122.67, 121.27, 118.10, 116.67, 114.78, 35.45, (1C, *C*(CH$_3$)$_3$), 33.88 (1C, *C*(CH$_3$)$_3$), 30.47 (1C, C(*C*H$_3$)$_3$), 29.16 (1C, C(*C*H$_3$)$_3$), -8.53 (1C, Al*C*H$_3$), -10.05 (1C, Al*C*H$_3$). Anal. Calcd for $C_{43}H_{45}AlN_2O$ (%): C, 81.61; H, 7.17; N, 4.43. Found: C, 81.70; H, 7.18; N, 4.49.

Complex (S)-A_3

Complex **(S)-A_3** as orange solid was acquired by a similar way for **(*S*)-A_1** with **(*S*)-L_3** (0.533 g, 1.00 mmol) and $AlMe_3$ (1.00 mmol). Yield: 0.534 g, 90.7%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 8.11 (d, *J* = 8.8 Hz, 1H, Ar*H*), 8.02 (d, *J* = 8.8 Hz, 1H, Ar*H*), 8.00 (s, 1H, N=C*H*), 7.96–7.90 (m, 1H, Ar*H*), 7.79 (t, *J* = 7.6 Hz, 3H, Ar*H*), 7.69 (d, *J* = 8.7 Hz, 1H, Ar*H*), 7.58 (t, *J* = 7.4 Hz, 1H, Ar*H*), 7.52 (d, *J* = 9.1 Hz, 1H, Ar*H*), 7.46–7.38 (m, 1H, Ar*H*), 7.01 (d, *J* = 7.7 Hz, 1H, Ar*H*), 6.90 (t, *J* = 7.7 Hz, 3H, Ar*H*), 6.81–6.75 (m, 1H, Ar*H*), 6.68–6.55 (m, 1H, Ar*H*), 6.17 (d, *J* = 2.6 Hz, 1H, Ar*H*), 5.24 (s, 1H, N*H*), –0.87 (s, 3H, AlCH_3), –0.96 (s, 3H, AlCH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 170.96, 169.57, 158.51 (s, 1C, N=*C*H), 141.28, 140.22, 136.34, 134.51, 133.53, 131.85, 130.50, 130.37, 130.18, 129.03, 128.61, 128.35, 127.97, 127.68, 127.21, 126.68, 126.14, 125.29, 124.44, 124.17, 123.84, 122.87, 122.25, 121.04, 119.92, 119.54, 117.34, 109.55, –9.26 (1C, Al*C*H_3), –9.60 (1C, Al*C*H_3). Anal. Calcd for $C_{37}H_{33}AlN_2O$ (%): C, 81.00; H, 6.06; N, 5.11. Found: C, 81.07; H, 6.12; N, 5.15.

Complex (S)-A_4

Complex **(S)-A_4** as orange solid was acquired by a similar way for **(*S*)-A_3** with **(*S*)-L_5** (0.560 g, 1.00 mmol) and $AlMe_3$ (1.00 mmol). Yield: 0.532 g, 86.2%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 8.05 (d, *J* = 8.8 Hz, 1H, Ar*H*), 7.94 (d, *J* = 8.2 Hz, 1H, Ar*H*), 7.91 (s, 1H, N=C*H*), 7.80 (d, *J* = 8.8 Hz, 1H, Ar*H*), 7.70 (d, *J* = 7.2 Hz, 1H, Ar*H*), 7.57 (d, *J* = 9.0 Hz, 1H, Ar*H*), 7.53–7.48 (m, 1H, Ar*H*), 7.30 (d, *J* = 3.5 Hz, 2H, Ar*H*), 7.27–7.14 (m, 3H, Ar*H*), 6.95 (s, 2H, Ar*H*), 6.92 (d, *J* = 8.0 Hz, 1H, Ar*H*), 6.55 (d, *J* = 9.0 Hz, 1H, Ar*H*), 5.87 (d, *J* = 2.6 Hz, 1H, Ar*H*), 5.18 (s, 1H, N*H*), 1.80 (s, 6H, CH_3), –0.70 (s, 3H, AlCH_3), –0.93 (s, 3H, AlCH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 170.04 (s, 1C, N=*C*H), 158.38, 142.96, 141.72, 136.90, 136.24, 135.59, 133.62, 133.24, 131.37, 130.54, 130.39, 129.02, 128.54, 128.21, 128.06, 127.81, 127.56, 127.25, 127.16, 126.71, 126.58, 125.73, 125.29, 123.14, 122.60, 121.85, 120.91, 119.65, 114.18, 109.59, 18.07, -7.51, -10.21. Anal. Calcd for $C_{37}H_{31}AlCl_2N_2O$ (%): C, 71.96; H, 5.06; N, 4.54. Found: C, 72.01; H, 5.10; N, 4.61.

Complex (S)-A_5

Complex **(S)-A_5** as yellow solid was acquired by a similar way for **(*S*)-A_1** with **(*S*)-L_5** (0.482g, 1.00 mmol) and $AlMe_3$ (1.00 mmol) except for the reaction temperature was set at 25 °C. Yield: 0.456 g, 84.7%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 8.7 Hz, 1H, Ar*H*), 8.02 (d, *J* = 8.8 Hz, 1H, Ar*H*), 7.99 (s, 1H, N=C*H*), 7.77 (t, *J* = 8.0 Hz, 2H, Ar*H*), 7.69 (d, *J* = 9.0 Hz, 1H, Ar*H*), 7.55 (t, *J* = 8.0 Hz, 2H, Ar*H*), 7.39–7.25 (m, 4H, Ar*H*), 6.99–6.85 (m, 4H, Ar*H*), 6.76 (d, *J* = 8.4 Hz, 1H, Ar*H*), 6.50 (t, *J* = 7.4 Hz, 1H, Ar*H*), 6.21 (d, *J* = 7.8 Hz, 1H, Ar*H*), 5.13 (s, 1H, N*H*), –0.79 (s, 3H, AlCH_3), –0.93 (s, 3H, AlCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.95 (Ar*C*), 164.64 (Ar*C*), 160.40 (s, 1C, N=*C*H), 158.45, 143.62, 140.79, 137.75, 135.11, 134.81, 133.70, 132.97, 130.88, 130.22, 130.02, 128.83, 128.53, 127.85, 126.88, 126.71, 124.20, 123.84, 123.76, 123.35, 122.44, 121.58, 118.71, 117.45, 116.41, 116.09, 115.87, 114.04, –8.55 (1C, Al*C*H_3), –9.87 (1C, Al*C*H_3). Anal. Calcd for $C_{35}H_{28}AlFN_2O$ (%): C, 78.05; H, 5.24; N, 5.20. Found: C, 78.00; H, 5.17; N, 5.14.

Complex (S)-A_6

Complex **(S)-A_6** as orange solid was acquired by a similar way for **(*S*)-A_5** with **(*S*)-L_6** (0.550g, 1.00 mmol) and $AlMe_3$ (1.00 mmol). Yield: 0.567 g, 93.6%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, *J* = 8.8 Hz, 1H, Ar*H*), 8.03 (d, *J* = 8.1 Hz, 1H, Ar*H*), 7.95 (s, 1H, N=C*H*), 7.80 (d, *J* = 7.6 Hz, 1H, Ar*H*), 7.74 (d, *J* = 8.8 Hz, 2H, Ar*H*), 7.59 (t, *J* = 7.3 Hz, 1H, Ar*H*), 7.45–7.38 (m, 1H, Ar*H*), 7.37–7.25 (m, 3H, Ar*H*), 6.94 (t, *J* = 8.3 Hz, 3H, Ar*H*), 6.89–6.82 (m, 2H, Ar*H*), 6.08 (d, *J* = 2.0 Hz, 1H, Ar*H*), 5.09 (s, 1H, N*H*), –0.83 (s, 3H, AlCH_3), –0.91 (s, 3H, AlCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.76, 160.43, 158.39 (1C, N=C*H*), 158.12, 143.25, 140.76, 137.14, 136.42, 135.00, 133.60, 133.18, 131.59, 130.43, 130.32, 128.62, 128.50, 128.12, 127.89, 127.25, 126.78, 125.71, 124.05, 123.61, 123.51, 123.43, 122.05, 121.09, 119.59, 116.45, 116.06, 113.84, –8.75 (1C, Al*C*H_3), –9.85, (1C, Al*C*H_3). Anal. Calcd for $C_{35}H_{26}AlCl_2FN_2O$ (%): C, 69.20; H, 4.31; N, 4.61. Found: C, 69.25; H, 4.37; N, 4.70.

Complex (S)-B_1

A mixture of **(*S*)-L_1** (0.465 g, 1.00 mmol) and $AlMe_3$ (1.00 mmol) in 15 mL toluene was stirred for 30 h at 90 °C under an argon atmosphere. And concentrated to 2 mL to give a yellow powder, from which the mother liquor was decanted, and the product as yellow solid was acquired by washing with about 0.5 mL of hexane and dried in vacuum. Yield: 0.464 g, 92.1%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (s, 1H, N=C*H*), 8.05 (d, *J* = 8.5 Hz, 1H, Ar*H*), 7.95 (d, *J* = 8.5 Hz, 2H, Ar*H*), 7.75–7.71 (m, 3H, Ar*H*), 7.54–7.52 (m, 2H, Ar*H*), 7.44–7.39 (m, 1H, Ar*H*), 7.33 (s, 2H, Ar*H*), 7.24 (t, *J* = 8.3 Hz, 2H, Ar*H*), 7.05 (t, *J* = 8.2 Hz, 1H, Ar*H*), 6.95 (d, *J* = 8.5 Hz, 1H, Ar*H*), 6.81–6.70 (m, 4H, Ar*H*), –0.76 (s, 3H, AlCH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.91 (1C, N=*C*H), 167.73, 164.70, 157.85, 155.49, 148.82, 147.84, 141.11, 138.04, 134.96, 134.38, 133.62, 132.88, 132.42, 130.86, 130.32, 129.96, 129.78, 128.80, 128.68, 127.89, 126.36, 125.94, 125.85, 123.51, 122.26, 122.07, 120.13, 118.40, 115.34, 115.12, –12.63 (1C, Al*C*H$_3$). Anal. Calcd for $C_{35}H_{29}AlN_2O$ (%): C, 80.94; H, 4.99; N, 5.55. Found: C, 80.88; H, 4.90; N, 5.47.

Complex (S)-B_2

Complex **(*S*)-B_2** as yellow solid was acquired by a similar way for **(*S*)-B_1** with **(*S*)-L_2** (0.576 g, 1.00 mmol) and $AlMe_3$ (1.00 mmol). Yield: 0.515 g, 83.5%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.27 (s, 1H, N=C*H*), 8.01 (d, *J* = 8.5 Hz, 1H, Ar*H*), 7.91 (d, *J* = 8.2 Hz, 1H, Ar*H*), 7.72 (dd, *J* = 8.4, 3.4 Hz, 2H, Ar*H*), 7.54 (d, *J* = 2.2 Hz, 1H, Ar*H*), 7.46–7.44 (m, 1H, Ar*H*), 7.37 (d, *J* = 8.7 Hz, 2H, Ar*H*), 7.27–7.19 (m, 1H, Ar*H*), 7.09 (t, *J* = 7.8 Hz, 2H, Ar*H*), 7.06–7.01 (m, 1H, Ar*H*), 6.97 (d, *J* = 2.2 Hz, 1H, Ar*H*), 6.86 (d, *J* = 7.9 Hz, 2H, Ar*H*), 6.70 (t, *J* = 7.9 Hz, 2H, Ar*H*), 1.44 (s, 9H, C(CH_3)$_3$), 1.22 (s, 9H, C(CH_3)$_3$), –0.79 (s, 3H, AlCH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.29 (s, 1C, N=*C*H), 162.14, 153.04, 147.83, 141.30, 140.99, 139.71, 134.46, 133.76, 133.15, 132.79, 130.89, 130.79, 130.44, 129.92, 129.65, 128.98, 128.85, 128.79, 128.20, 127.82, 127.39, 127.13, 126.18, 126.03, 125.67, 123.72, 121.01, 120.34, 118.45, 118.11, 35.34 (1C, *C*(CH$_3$)$_3$), 34.02 (1C, *C*(CH$_3$)$_3$), 31.51 (1C, C(*C*H$_3$)$_3$), 29.35 (1C, C(*C*H$_3$)$_3$), –12.36 (1C, Al*C*H$_3$). Anal. Calcd for $C_{42}H_{41}AlN_2O$ (%): C, 81.79; H, 6.70; N, 4.54. Found: C, 81.70; H, 6.62; N, 4.43.

Complex (S)-B_3

Complex **(S)-B_3** as orange solid was acquired by a similar way for **(*S*)-B_1** with **(*S*)-L_3** (0.533 g, 1.00 mmol) and $AlMe_3$ (1.00 mmol). Yield: 0.514 g, 89.6%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 8.20 (s, 1H, N=C*H*), 8.05 (d, *J* = 8.5 Hz, 2H, Ar*H*), 7.94 (d, *J* = 8.1 Hz, 2H, Ar*H*), 7.75 (d, *J* = 8.6 Hz, 2H, Ar*H*), 7.52–7.44 (m, 5H, Ar*H*), 7.28–7.25 (m, 2H, Ar*H*), 6.82 (d, *J* = 8.1 Hz, 2H, Ar*H*), 6.73–6.68 (m, 1H, Ar*H*), 6.56 (d, *J* = 7.7 Hz, 1H, Ar*H*), –0.74 (s, 3H, AlCH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 171.87 (s, 1C, N=*C*H), 169.86, 159.20, 142.11, 141.45, 135.76, 135.10, 134.19, 133.66, 131.12, 130.79, 130.33, 129.00, 128.68, 128.40, 127.89, 127.55, 127.10, 126.55, 126.00, 125.83, 124.77, 124.20, 123.98, 123.13, 122.78, 121.78, 120.99, 119.81, 117.79, 112.30, –12.71 (1C, Al*C*H$_3$). Anal. Calcd for $C_{37}H_{33}AlN_2O$ (%): C, 71.21; H, 4.04; N, 4.89. Found: C, 71.28; H, 4.10; N, 5.00.

Complex (S)-B_4

Complex **(S)-B_4** as orange solid was acquired by a similar method for **(*S*)-B_1** with **(*S*)-L_4** (0.561 g, 1.00 mmol) and $AlMe_3$ (1.00 mmol). Yield: 0.516 g, 85.2%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 8.09 (s, 1H, N=C*H*), 8.00 (d, *J* = 8.8 Hz, 1H, Ar*H*), 7.92 (d, *J* = 8.2 Hz, 1H, Ar*H*), 7.81 (d, *J* = 8.8 Hz, 1H, Ar*H*), 7.57–7.49 (m, 5H, Ar*H*), 7.33–7.30 (m, 2H, Ar*H*), 6.89 (d, *J* = 8.8 Hz, 2H, Ar*H*), 6.78–6.73 (m, 1H, Ar*H*), 6.61 (d, *J* = 7.7 Hz, 1H, Ar*H*), 1.92 (s, 6H, CH_3), –0.75 (s, 3H, AlCH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 175.52 (s, 1C, N=*C*H), 171.36, 164.78, 143.42, 142.93, 141.70, 137.59, 137.04, 135.62, 134.70, 133.76, 133.03, 130.24, 130.17, 129.12, 128.48, 128.40, 128.23, 127.77, 127.55, 127.04, 126.87, 126.44, 125.46, 125.32, 122.32, 121.51, 119.80, 117.89, 116.17, 114.13, –12.52 (1C, Al*C*H$_3$). Anal. Calcd for $C_{36}H_{27}AlCl_2N_2O$ (%): C, 71.88; H, 4.52; N, 4.66; Found: C, 71.81; H, 4.48; N, 4.47.

Complex (S)-B_5

Complex **(*S*)-B_5** as yellow solid was acquired by a similar way for **(*S*)-B_1** with **(*S*)-L_5** (0.482 g, 1.00 mmol) and $AlMe_3$ (1.00 mmol) except for the reaction temperature was set at 45 °C. Yield: 0.472 g, 90.3%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (s, 1H, N=C*H*), 8.03 (d, *J* = 8.5 Hz,

1H, Ar*H*),7.86 (d, *J* = 8.2 Hz, 1H, Ar*H*), 7.80 (d, *J* = 8.4Hz, 1H, Ar*H*), 7.70 (d, *J* = 8.3 Hz, 1H, Ar*H*), 7.62 (d, *J* = 8.2 Hz, 1H, Ar*H*), 7.51 (d, *J* = 8.5 Hz, 1H, Ar*H*), 7.45–7.43 (m, 1H, Ar*H*), 7.38 (d, *J* = 8.6 Hz, 1H, Ar*H*), 7.33–7.20 (m, 2H, Ar*H*), 7.15–7.10 (m, 2H, Ar*H*), 6.97(d, *J* = 8.4 Hz, 1H, Ar*H*), 6.72 (d, *J* = 8.4 Hz, 1H, Ar*H*), 6.53 (d, *J* = 9.0 Hz, 1H, Ar*H*), 6.45 (t, *J* = 8.4 Hz, 1H, Ar*H*), 6.27 (t, *J* = 8.5 Hz, 1H, Ar*H*), 6.08 (d, *J* = 8.0 Hz, 1H, Ar*H*), –0.76 (s, 3H, AlCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.45 (s, 1C, N=*C*H), 164.27, 144.49, 142.87, 141.37, 137.93, 137.00, 135.42, 134.63, 133.55, 132.69, 130.39, 130.28, 129.10, 128.45, 128.32, 128.10, 127.90, 127.68, 127.11, 126.91, 126.59, 125.73, 125.29, 122.40, 121.72, 120.00, 119.12, 117.96, 115.22, 112.43, –12.80 (1C, Al*C*H_3). Anal. Calcd for $C_{34}H_{24}AlFN_2O$ (%): C, 78.15; H, 4.63; N, 5.36. Found: C, 78.11; H, 4.59; N, 5.32.

Complex (S)-B$_6$

Complex **(S)-B$_6$** as orange solid was acquired by a similar way for **(*S*)-B$_5$** with **(*S*)-L$_6$** (0.533 g, 1.00 mmol) and $AlMe_3$ (1.00 mmol). Yield: 0.538 g, 91.0%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (s, 1H, N=C*H*), 8.06 (d, *J* = 8.5 Hz, 1H, Ar*H*), 7.95 (d, *J* = 8.2 Hz, 1H, Ar*H*), 7.73 (d, *J* = 8.5 Hz, 2H, Ar*H*), 7.54–7.47 (m, 2H, Ar*H*), 7.38 (d, *J* = 8.8 Hz, 1H, Ar*H*), 7.33 (d, *J* = 8.6 Hz, 2H, Ar*H*), 7.29–7.22 (m, 1H, Ar*H*), 7.08–7.01 (m, 1H, Ar*H*), 6.96 (d, *J* = 2.1 Hz, 1H, Ar*H*), 6.82–6.72 (m, 3H, Ar*H*), 6.67 (d, *J* = 8.5 Hz, 1H, Ar*H*), –0.74 (s, 1H, AlCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.79 (1C, N=C*H*), 165.82, 165.10, 158.06, 155.70, 148.45, 147.48, 140.61, 134.24, 133.54, 133.06, 131.84, 130.89, 130.74, 130.26, 129.99, 128.80, 128.60, 127.97, 127.51, 127.25, 126.68, 126.08, 125.82, 124.89, 124.04, 122.19, 119.65, 119.32, 115.49, 115.27, –12.75 (1C, Al*C*H_3). Anal. Calcd for $C_{34}H_{22}AlCl_2FN_2O$ (%): C, 69.05; H, 3.75; N, 4.74. Found: C, 69.11; H, 3.82; N, 4.78.

Complex (S)-C$_1$

A mixture of **(*S*)-L$_1$** (0.93 g, 2.00 mmol) and $AlMe_3$ (1.00 mmol) in 25 mL toluene was stirred for 8 h at 70 °C under an argon atmosphere. And concentrated to 3 mL to give a yellow solid, from which the mother liquor was decanted, and the product as yellow solid was acquired by washing with about 0.5 mL of hexane and dried in vacuum. Yield: 0.876 g, 90.4%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (s, 1H, N=C*H*), 7.97 (d, *J*= 8.8 Hz, 1H, Ar*H*), 7.69 (d, *J* = 8.8 Hz, 1H, Ar*H*), 7.61 (t, *J* = 8.3 Hz, 1H, Ar*H*), 7.49 (d, *J*= 7.6 Hz, 1H, Ar*H*), 7.30 (t, *J*= 7.7 Hz, 2H, Ar*H*), 7.18 (t, *J* = 7.5 Hz, 1H, Ar*H*), 7.03–7.01 (m, 2H, Ar*H*), 6.95–6.85 (m, 5H, Ar*H*), 6.79 (d, *J* = 8.4 Hz, 2H, Ar*H*), 6.50 (d, *J* = 9.0 Hz, 1H, Ar*H*), 6.10 (t, *J* = 7.3 Hz, 1H, Ar*H*), 6.00 (d, *J*= 7.7 Hz, 1H, Ar*H*), 5.22 (s, 1H, N*H*), –0.26 (s, 3H, AlCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.22 (1C, N=*C*H), 169.54, 167.39, 162.44, 159.21, 151.38, 150.14, 146.19, 141.84, 137.23, 136.01, 135.48, 134.27, 133.53, 132.96, 132.02, 130.89, 130.10, 129.70, 129.00, 128.11, 127.89, 126.92, 126.04, 125.23, 124.87, 123.59, 122.46, 119.80, 118.03, 116.09, –8.92 (1C, Al*C*H_3). Anal. Calcd for $C_{67}H_{49}AlN_4O_2$ (%): C, 83.04; H, 5.10; N, 5.78. Found: C, 83.11; H, 5.16; N, 5.82.

Complex (rac)-C$_1$

The process described for **(*S*)-C$_1$** was used for the synthesis of **(*rac*)-C$_1$** from pro-ligand **(*rac*)-L$_1$**. Crystals of **(*rac*)-C$_1$** suitable for X-ray structural determination was grown in dichloromethane/ hexane mixed solution. CCDC: 951766.

Complex (S)-C$_4$

Complex **(*S*)-C$_4$** as orange solid was acquired by a similar way for **(*S*)-C$_1$** with **(*S*)-L$_4$** (1.122 g, 2.00 mmol) and $AlMe_3$ (1.00 mmol). Yield: 0.981 g, 84.6%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (s, 1H, N=C*H*), 8.08 (d, *J* = 8.8 Hz, 1H, Ar*H*), 7.97 (s, 1H, Ar*H*), 7.86 (d, *J* = 9.1 Hz, 1H, Ar*H*), 7.81 (d, *J* = 8.2 Hz, 1H, Ar*H*), 7.66 (d, *J* = 8.1 Hz, 1H, Ar*H*), 7.59 (d, *J* = 7.9 Hz, 1H, Ar*H*), 7.50–7.41 (m, 2H, Ar*H*), 7.15 (d, *J*= 8.2 Hz, 1H, Ar*H*), 6.92 (t, *J*= 8.1 Hz, 1H, Ar*H*), 6.66 (d, *J* = 7.2 Hz, 1H, Ar*H*), 6.51 (d, *J* = 9.0 Hz, 1H, Ar*H*), 6.32 (d, *J* = 8.8 Hz, 1H, Ar*H*), 5.79 (s, 1H, Ar*H*), 5.67–5.64 (m, 2H, Ar*H*), 5.28 (s, 1H, N*H*), 1.86 (s, 6H, CH_3), –0.29 (s, 3H, AlCH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.96 (N=*C*H), 157.12, 146.86, 142.35, 139.04, 137.18, 136.93, 133.74, 133.07, 130.51, 130.03, 129.58, 128.49, 128.21, 127.94, 127.81, 127.56, 127.23, 126.90, 126.67, 126.62, 126.29, 125.97, 124.74, 124.39, 123.22, 121.69, 121.13, 120.07, 114.56, 109.75, 18.45 (*C*H_3), –8.98 (Al*C*H_3). Anal. Calcd for $C_{71}H_{53}AlCl_4N_4O_2$ (%): C, 73.32; H, 4.59; N, 4.82. Found: C, 73.39; H, 4.63; N, 4.87.

Complex (S)-C_6

Complex **(*S*)-C_6** as orange solid was acquired by a similar way for **(*S*)-C_1** wtih **(*S*)-L_6** (1.066 g, 2.00 mmol) and $AlMe_3$ (1.00 mmol). Yield: 0.993 g, 87.1%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (s, 1H, N=C*H*), 8.08 (d, *J* = 8.4 Hz, 1H, Ar*H*), 7.96 (d, *J* = 8.4 Hz, 1H, Ar*H*), 7.84 (d, *J* = 8.6 Hz, 1H, Ar*H*), 7.77 (d, *J* = 8.7 Hz, 1H, Ar*H*), 7.63 (t, *J* = 8.4 Hz, 1H, Ar*H*), 7.54 (t, *J* = 8.6 Hz, 1H, Ar*H*), 7.48 (d, *J*= 8.4 Hz, 1H, Ar*H*), 7.40 (s, 1H, Ar*H*), 7.35–7.19 (m, 2H, Ar*H*), 7.11 (d, *J* = 8.4 Hz, 2H, Ar*H*), 6.92 (d, *J* = 8.4 Hz, 1H, Ar*H*), 6.79 (d, *J* = 8.8 Hz, 1H, Ar*H*), 6.59 (d, *J* = 8.6 Hz, 1H, Ar*H*), 6.41 (d, *J* = 8.5 Hz, 1H, Ar*H*), 5.55 (s, 1H, N*H*), –0.22 (s, 3H, AlCH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 178.33 (N=*C*H), 169.01, 158.55, 152.38, 148.19, 146.84, 142.98, 139.00, 137.08, 136.88, 134.64, 133.02, 132.85, 131.51, 130.11, 129.77, 128.63, 128.22, 128.05, 127.87, 127.43, 126.98, 126.60, 125.95, 125.55, 124.23, 123.08, 121.73, 121.33, 120.71, 114.59, –8.84 (Al*C*H_3). Anal. Calcd for $C_{67}H_{43}AlCl_4F_2N_4O_2$ (%): C, 70.41; H, 3.79; N, 4.90. Found: C, 70.37; H, 3.70; N, 4.81.

Complex (rac)-D_4

A mixture of **(*rac*)-**C_4 (1.16 g, 1.00 mmol) and methanol (1.00 mmol) in 15 mL toluene was stirred for ca. 10 minuts at 70 °C in nitrogen. And concentrated to 2 mL to attain orange solid, from which the mother liquor was decanted. Yield: 1.062 g, 90.3%. Crystals of **(*rac*)-**D_4 suitable for X-ray structural determination was grown in dichloromethane/hexane mixed solution. CCDC: 908772. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (s, 1H, N=C*H*), 8.04 (d, *J* = 8.6 Hz, 1H, Ar*H*), 7.92 (s, 1H, Ar*H*), 7.86 (d, *J* = 8.4 Hz, 1H, Ar*H*), 7.77–7.59 (m, *2*H, Ar*H*), 7.54 (d, *J* = 8.2 Hz, 1H, Ar*H*), 7.50–7.41 (m, 2H, Ar*H*), 7.12 (d, *J*= 8.4 Hz, 1H, Ar*H*), 6.88–6.61 (m, 2H, Ar*H*), 6.47 (d, *J* = 8.8 Hz, 1H, Ar*H*), 6.28 (d, *J* = 8.6 Hz, 1H, Ar*H*), 5.71–5.60 (m, 4H, Ar*H*), 5.26 (s, 1H, N*H*), 2.65 (s, 3H, AlOCH_3), 1.81 (s, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.56 (N=*C*H), 157.00, 146.71, 142.29, 138.75, 137.02, 136.56, 133.58, 132.85, 130.42, 130.20, 129.33, 128.17, 128.02, 127.66, 127.47, 127.32, 127.10, 126.59, 126.47, 126.32, 126.11, 125.80, 124.65, 124.21, 123.00, 121.65, 120.89, 120.55, 113.98, 107.02, 42.8 (AlO*C*H_3), 18.01 (*C*H_3). Anal. Calcd for $C_{71}H_{53}AlCl_4N_4O_3$ (%): C, 72.33; H, 4.53; N, 4.75. Found: C, 72.40; H, 4.61; N, 4.82.

General procedure for lactide polymerization

In a representational polymerization reaction, aluminum complex (0.3 mmol) and isopropanol (0.3 mmol) in 60 mL toluene were loaded in a flame-dried ampoule containing a magnetic bar. The ampoule was immersed in an oil bath at 70 °C. The solution was stirred for about 10 minutes, when the catalyst was activated completely by isopropanol, subsequently adjust the temperature in the required value, and the required quantity of lactides was added. After a certain reaction time, the polymer was isolated by precipitating with cold methanol. The solid was collected and dried under vacuum at 35°C for 36 hours.

Fig. S2 Maldi Tof spectrum of selected PLA samples (for end group analysis)

Analysis of the oligomers by Maldi Tof exhibited PLA of the formula H(OCHMeCO)$_{2n}$O^{i}Pr·Na.

Fig. S3 Representative GPC traces (black: Table 2, entry 8, M_{nGPC} = 1.00 × 10^4, PDI = 1.07; red: Table 2, entry 10, M_{nGPC} = 2.08 × 10^4, PDI = 1.15)

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