Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

High Performance Benzoimidazolyl-Based Aminophenolate Zinc Complexes for Isoselective Polymerization of *rac*-Lactide

Yanmei Gong and Haiyan Ma*

Shanghai Key Laboratory of Functional Materials Chemistry and Laboratory of Organometallic Chemistry, School of Chemistry and Molecular Engineering, East China University of Science and Technology, Shanghai 200237, P. R. China.

Contents:

1. Experimental

1.1 General considerations

All manipulations involving air-sensitive substances were carried out under a dry argon atmosphere using standard Schlenk techniques or an argon-filled glovebox. Toluene, tetrahydrofuran, *n*-hexane and benzene-d_6 were refluxed over sodium/benzophenone prior to use. 2-Propanol was distilled over calcium hydride under argon prior to use. Chloroform-*d* and other reagents were carefully dried and stored in the glovebox. *D*-Lactide, *L*-lactide and *rac*-lactide from Jinan Daigang Biomaterial Co., Ltd. were recrystallized three times with dry toluene and then sublimated three times under vacuum at 100 ℃. $Zn[N(SiMe_3)_2]_2$ was synthesized according to the literature method.[S1] 2-Bromomethyl-4,6-di-*tert*-butylphenol,[S2] 2-bromomethyl-4-methyl-6-(triphenylmethyl)phenol,[S3] 1-alkyl-2-chloromethyl benzimidazoles[S4] were synthesized according to the reported literature procedures. All other chemicals were commercially available and used after appropriate purification. Glassware and vials used in the polymerization were dried in an oven at 120 ℃ overnight and exposed to a vacuum-argon cycle three times.

NMR spectra were recorded on a Bruker AVANCE-400 spectrometer at 25 ℃ (^{1}H, 400 MHz; ^{13}C, 100 MHz) unless otherwise stated. Chemical shifts for ^{1}H and ^{13}C NMR spectra were referenced internally using the residual solvent resonances and reported relative to TMS. Elemental analyses were performed on an EA-1106 instrument. The molecular weights and corresponding polydispersities of the PLAs were measured by gel permeation chromatography (GPC) analyses, using a Waters instrument (M1515 pump, Optilab Rex injector) in THF at 35 ℃, at a flow rate of 1 mL/min. Calibration standards were commercially available narrowly distributed linear polystyrene samples that cover a broad range of molar masses (4×10^3 g/mol < M_n < 4.4×10^5 g/mol).

1.2 Synthesis of proligands L^1H-L^8H

1.2.1 Synthesis of 2-{[N-cyclohexyl-N-(1-benzyl-1H-benzo[d]imidazol-2-yl)methyl] aminomethyl}-4,6-di-tert-butylphenol (L^1H)

1-Benzyl-2-chloromethylbenzoimidazolyl (2.59 g, 10.0 mmol) was dissolved in 25 mL of DMF, and then the solution was slowly added to a mixture of cyclohexylamine (9.92 g, 100 mmol) and K_2CO_3 (1.66 g, 12.0 mmol) within about 2 h. The mixture was poured into water and extracted with ethyl acetate three times, and the

organic phase was dried over anhydrous Na_2SO_4. Evaporation of the solvent gave the target secondary amine, *N*-((1-benzyl-1*H*-benzo[*d*]imidazol-2-yl)methyl)cyclohexanamine, as a yellow solid with a purity of about 80%, which was used directly for the next step. Crude *N*-((1-benzyl-1*H*-benzo[*d*]imidazol-2-yl)methyl)cyclohexanamine (1.79 g, about 5.60 mmol) was dissolved in 30 mL of DMF, and K_2CO_3 (0.93 g, 6.72 mmol) was added. Then, 2-bromomethyl-4,6-di-*tert*-butylphenol (1.68 g, 5.60 mmol) was added slowly in 10 min to the above mixture. The mixture was stirred for 5 h and then poured into water and extracted with ethyl acetate three times. The organic phase was dried over anhydrous Na_2SO_4, and white solids were obtained via recrystallization from dichloromethane and petroleum ether (1.55 g, 51.5%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.35 (s, 1H, O*H*), 7.80 – 7.75 (m, 1H, Ar*H*), 7.26 – 7.20 (m, 4H, Ar*H*), 7.20 – 7.13 (m, 3H, Ar*H*), 6.85 (d, ^4J = 2.3 Hz, 1H, Ar*H*), 6.73 – 6.68 (m, 2H, Ar*H*), 5.24 (s, 2H, ArCH_2), 3.90 (s, 2H, PhCH_2), 3.87 (s, 2H, NCH_2C=N), 2.98 – 2.87 (tt, ^3J = 11.8 Hz, ^3J = 3.1 Hz 1H, NC*H* of cyclohexyl), 1.95 (br d, ^3J = 11.1 Hz, 2H, CH_2 of cyclohexyl), 1.80 (m, 4H, CH_2 of cyclohexyl), 1.63 (m, 1H, CH_2 of cyclohexyl), 1.41 (s, 9H, (CH_3)$_3$), 1.39 – 1.34 (m, 1H, CH_2 of cyclohexyl), 1.27 (s, 9H, (CH_3)$_3$), 1.23 – 1.17 (m, 1H, CH_2 of cyclohexyl), 1.15 – 1.04 (m, 1H, CH_2 of cyclohexyl). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.0, 150.8 (N*C*=N), 142.5, 141.2, 136.3, 135.8, 135.7, 128.9, 127.8, 126.5, 124.3, 123.3, 123.1, 122.2, 121.6, 120.0, 110.2 (all Ar*C*), 58.8 (Ar*C*H$_2$), 54.2 (Ph*C*H$_2$), 47.0 (N*C*H$_2$C=N), 46.8 (N*C*H), 35.0 (*C*(CH$_3$)$_3$), 34.3 (*C*(CH$_3$)$_3$), 31.8 (C(*C*H$_3$)$_3$), 29.8 (C(*C*H$_3$)$_3$), 27.6 (*C*H$_2$ of cyclohexyl), 26.2 (*C*H$_2$ of cyclohexyl), 25.9(*C*H$_2$ of cyclohexyl). Anal. Calcd. for $C_{36}H_{47}N_3O$: C, 80.40; H, 8.81; N, 7.81. Found: C, 80.08; H, 8.59; N, 7.69%.

1.2.2 Synthesis of 2-{[N-cyclohexyl-N-(1-benzyl-1H-benzo[d]imidazol-2-yl)methyl] aminomethyl}-4,6-di-cumylphenol (L^2H)

The procedure was the same as that of **L^1H**, except that 2-bromomethyl-4,6-dicumylphenol (2.10 g, 5.00 mmol), K_2CO_3 (0.83 g, 6.00 mmol) and crude *N*-((1-benzyl-1*H*-benzo[*d*]imidazol-2-yl)methyl)cyclohexylamine (1.60 g, about 5.00 mmol) were used in the second step. White solids were obtained via column chromatography (silica gel 200-300 Merck, petroleum ether/ethyl acetate = 10:1) after removal of all the volatiles (2.16 g, 65.3%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.86 (s, 1H, O*H*), 7.74 (m, 1H, Ar*H*), 7.26–7.10 (m, 17H, Ar*H*), 6.73 (d, ^4J = 2.2 Hz, 1H, Ar*H*), 6.66 (m, 2H, Ar*H*),

4.79 (s, 2H, ArCH_2), 3.79 (s, 2H, PhCH_2), 3.73 (s, 2H, NCH_2C=N), 2.48 (m, 1H, NC*H* of cyclohexyl), 1.69 (m, 1H, CH_2 of cyclohexyl), 1.66 (s, 6H, CH_3), 1.66 (s, 6H, CH_3), 1.54 (m, 3H, CH_2 of cyclohexyl), 1.15 (m, 2H, CH_2 of cyclohexyl), 1.08–0.94 (m, 3H, CH_2 of cyclohexyl), 0.94–0.83 (m, 1H, CH_2 of cyclohexyl). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 153.5, 151.6, 151.4, 150.9 (N*C*=N), 142.4, 140.4, 136.2, 136.1, 135.0, 128.8, 127.9, 127.6, 126.9, 126.3, 126.3, 126.1, 125.6, 125.2, 124.9, 123.0, 122.2, 121.6, 119.9, 110.2 (all Ar*C*), 59.0 (Ar*C*H_2), 54.1 (Ph*C*H_2), 47.4 (NCH_2C=N), 46.6 (N*C*H), 42.6 ((CH$_3$)$_2$*C*Ph), 42.1 ((CH$_3$)$_2$*C*Ph), 31.2 ((*C*H$_3$)$_2$CPh), 29.6 ((*C*H$_3$)$_2$CPh), 27.4 (*C*H$_2$ of cyclohexyl), 26.1 (*C*H$_2$ of cyclohexyl), 26.0 (*C*H$_2$ of cyclohexyl). Anal. Calcd. for $C_{46}H_{51}N_3O$: C, 83.47; H, 7.77; N, 6.35. Found: C, 83.45; H, 7.97; N, 6.01%.

1.2.3 Synthesis of 2-{[N-cyclohexyl-N-(1-benzyl-1H-benzo[d]imidazol-2-yl)methyl] aminomethyl}-4-methyl-6-tritylphenol (L^3H)

The procedure was the same as that of **L^1H**, except that 2-bromomethyl-4-methyl-6-(triphenylmethyl)phenol (3.72 g, 8.40 mmol), crude *N*-((1-benzyl-1*H*-benzo[*d*]imidazol-2-yl)methyl)cyclohexylamine (2.69 g, about 8.40 mmol), and K_2CO_3 (1.39 g, 10.1 mmol) were used in the second step. White solids were obtained via recrystallization from dichloromethane and petroleum ether (4.42 g, 77.2%). ^1H NMR (400 MHz, $CDCl_3$): δ 10.19 (s, 1H, O*H*), 7.74–7.69 (m, 1H, Ar*H*), 7.27–7.11 (m, 21H, Ar*H*), 6.89 (d, ^4J = 1.6 Hz, 1H, Ar*H*), 6.74–6.67 (m, 3H, Ar*H*), 4.84 (s, 2H, ArCH_2), 3.81 (s, 2H, NCH_2Ph), 3.78 (s, 2H, NCH_2C=N), 2.48 (m, 1H, NC*H* of cyclohexyl), 2.12 (s, 3H, ArCH_3), 1.70 (d, ^3J = 11.1 Hz, 3H, CH_2 of cyclohexyl), 1.57 (m, 2H, CH_2 of cyclohexyl), 1.20-1.04 (m, 4H, CH_2 of cyclohexyl), 1.04-0.92 (m, 1H, CH_2 of cyclohexyl). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 154.0, 150.9 (N*C*=N), 146.2, 142.3, 136.0, 133.4, 131.3, 130.6, 128.9, 127.7, 127.0, 126.8, 126.3, 125.3, 123.0, 122.2, 122.1, 119.8, 110.3 (all Ar*C*), 63.3 (Ph$_3$*C*), 58.6 (Ar*C*H_2), 53.9 (Ph*C*H_2), 46.8 (NCH_2C=N), 46.6 (N*C*H), 27.4 (*C*H$_2$ of cyclohexyl), 26.1 (*C*H$_2$ of cyclohexyl), 26.0 (*C*H$_2$ of cyclohexyl), 21.0 (Ar*C*H$_3$). Anal. Calcd. for $C_{48}H_{47}N_3O$: C, 84.54; H, 6.95; N, 6.16. Found: C, 84.41; H, 7.09; N, 6.05%.

1.2.4 Synthesis of 2-{[N-^{n}butyl-N-(1-benzyl-1H-benzo[d]imidazol-2-yl)methyl] aminomethyl}-4-methyl-6-(triphenylmethyl)phenol (L^4H)

The procedure was the same as that of **L^1H**, except that *n*-butylamine (7.31 g, 100 mmol) was used in the first step, and 2-bromomethyl-4-methyl-6-

(triphenylmethyl)phenol (2.84 g, 6.40 mmol), crude *N*-((1-benzyl-1*H*-benzo[*d*]imidazol-2-yl)methyl)butylamine (1.88 g, about 6.40 mmol), and K_2CO_3 (1.06 g, 7.68 mmol) were used in the second step. White solids were obtained via column chromatography (silica gel 200-300 Merck, petroleum ether/ethyl acetate = 10:1) after removal of all the volatiles (2.86 g, 68.1%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.86 (s, 1H, O*H*), 7.77 – 7.73 (m, 1H, Ar*H*), 7.30 – 7.11 (m, 21H, Ar*H*), 6.95 (d, ^4J = 1.7 Hz, 1H, Ar*H*), 6.71 (m, 3H, Ar*H*), 4.87 (s, 2H, ArCH_2), 3.76 (s, 2H, NCH_2Ph), 3.69 (s, 2H, NCH_2C=N), 2.51 – 2.43 (m, 2H, CH_2 of *n*-butyl), 2.16 (s, 3H, ArCH_3), 1.24 – 1.14 (m, 2H, CH_2 of *n*-butyl), 1.06 (m, 2H, CH_2 of *n*-butyl), 0.78 (t, ^3J = 7.2 Hz, 3H, CH_3 of *n*-butyl). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 153.9, 150.4 (N*C*=N), 146.1, 142.4, 136.0, 135.8, 133.7, 131.3, 130.9, 129.1, 128.9, 127.8, 127.1, 127.0, 126.3, 125.4, 123.1, 122.3, 122.3, 120.0, 110.0 (all Ar*C*), 63.3 (Ph_3C), 58.2 (ArCH_2), 53.6 (PhCH_2), 50.1 (NCH_2C=N), 46.8 (NCH_2CH_2), 28.5 (NCH$_2$$CH_2$), 21.0 (Ar$CH_3$), 20.6 ($CH_2CH_3$), 14.0 ($CH_2CH_3$). Anal. Calcd. for $C_{46}H_{45}N_3O$: C, 84.24; H, 6.92; N, 6.41. Found: C, 84.10; H, 6.98; N, 6.31%.

1.2.5 Synthesis of 2-{[N-benzyl-N-(1-benzyl-1H-benzo[d]imidazol-2-yl)methyl] aminomethyl}-4-methyl-6-(triphenylmethyl)phenol (L^5H)

The procedure was the same as that of **L^1H**, except that benzylamine (10.72 g, 100 mmol) was used in the first step, and 2-bromomethyl-4-methyl-6-(triphenylmethyl)phenol (2.70 g, 6.10 mmol), crude *N*-((1-benzyl-1*H*-benzo[d]imidazol-2-yl)methyl)benzylamine (1.99 g, about 6.10 mmol), and K_2CO_3 (1.01 g, 7.32 mmol) were used in the second step. White solids were obtained via recrystallization from dichloromethane and petroleum ether (2.51 g, 59.6%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.86 (s, 1H, O*H*), 7.71 (d, ^3J = 8.0 Hz, 1H, Ar*H*), 7.23 – 7.10 (m, 21H, Ar*H*), 7.05 (t, ^3J = 7.5 Hz, 2H, Ar*H*), 6.92 (s, 1H, Ar*H*), 6.85 (m, 3H, Ar*H*), 6.52 (d, ^3J = 7.5 Hz, 2H, Ar*H*), 4.72 (s, 2H, ArCH_2), 3.93 (s, 2H, NCH_2Ph), 3.62 (s, 2H, CNCH_2Ph), 3.52 (s, 2H, NCH_2C=N), 2.17 (s, 3H, ArCH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 153.6, 150.4 (N*C*=N), 146.2, 142.3, 137.0, 135.6, 133.9, 131.3, 131.1, 130.0, 129.6, 128.8, 128.6, 127.7, 127.6, 127.1, 127.0, 126.2, 125.5, 123.1, 122.3, 122.2, 119.9, 110.1 (all Ar*C*), 63.4 (Ph_3C), 58.4 (ArCH_2), 57.8 (PhCH_2), 49.1 (PhCH_2), 46.7 (NCH_2C=N), 21.0 (ArCH_3). Anal. Calcd. for $C_{49}H_{43}N_3O$: C, 85.31; H, 6.28; N, 6.09. Found: C, 85.30; H, 6.33; N, 6.03%.

1.2.6 Synthesis of 2-{[N-cyclohexyl-N-(1-methyl-1H-benzo[d]imidazol-2-yl)methyl] aminomethyl}-4-methyl-6-(triphenylmethyl)phenol (L^6H)

The procedure was the same as that of **L^1H**, except that 1-methyl-2-chloromethylbenzoimidazole (1.84 g, 10.0 mmol) was used in the first step, and 2-bromomethyl-4-methyl-6-(triphenylmethyl)phenol (2.20 g, 5.00 mmol), crude *N*-((1-methyl-1*H*-benzo[d]imidazol-2-yl)methyl)cyclohexylamine (1.22 g, about 5.00 mmol), and K_2CO_3 (0.83 g, 6.00 mmol) were used in the second step. White solids were obtained via recrystallization from dichloromethane and petroleum ether (2.17 g, 71.6%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.23 (s, 1H, O*H*), 7.70 – 7.65 (m, 1H, Ar*H*), 7.31 – 7.27 (m, 1H, Ar*H*), 7.20 –7.09 (m, 16H, Ar*H*), 6.86 (d, ^4J = 1.6 Hz, 1H, Ar*H*), 6.71 (d, ^4J = 1.5 Hz, 1H, Ar*H*), 3.84 (s, 2H, ArCH_2), 3.80 (s, 2H, NCH_2C=N), 3.18 (s, 3H, NCH_3), 2.44 (m, 1H, NC*H* of cyclohexyl), 2.12 (s, 3H, ArCH_3), 1.78 – 1.73 (m, 4H, CH_2 of cyclohexyl), 1.61 (d, ^3J = 10.2 Hz, 1H, CH_2 of cyclohexyl), 1.29 (m, 2H, CH_2 of cyclohexyl), 1.18 – 1.00 (m, 3H, CH_2 of cyclohexyl). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 153.9, 150.7 (N*C*=N), 146.1, 142.1, 136.4, 133.4, 131.3, 130.6, 128.8, 127.0, 126.8, 125.3, 122.8, 122.1, 121.8, 119.6, 109.5 (all Ar*C*), 63.2 (Ph_3C), 58.8 (Ar*C*H_2), 53.8 (N*C*H_2C=N), 46.6 (N*C*H), 30.0 (N*C*H_3), 27.5 (*C*H_2 of cyclohexyl), 26.1 (*C*H_2 of cyclohexyl), 26.0 (*C*H_2 of cyclohexyl), 21.0 (Ar*C*H_3). Anal. Calcd. for $C_{42}H_{43}N_3O$: C, 83.27; H, 7.15; N, 6.94. Found: C, 82.84; H, 6.97; N, 6.81%.

1.2.7 Synthesis of 2-{[N-cyclohexyl-N-(1-methyl-1H-benzo[d]imidazol-2-yl)methyl] aminomethyl}-4-methyl-6-(triphenylmethyl)phenol (L^7H)

The procedure was the same as that of **L^1H**, except that 1-methyl-2-chloromethylbenzoimidazole (2.59 g, 10.0 mmol) and *n*-butylamine (7.31 g, 100 mmol) were used in the first step, and 2-bromomethyl-4-methyl-6-(triphenylmethyl)phenol (2.34 g, 5.30 mmol), crude *N*-((1-methyl-1*H*-benzo[d]imidazol-2-yl)methyl)butylamine (1.15 g, about 5.30 mmol), and K_2CO_3 (0.88 g, 6.36 mmol) were used in the second step. White solids were obtained via column chromatography (silica gel 200-300 Merck, petroleum ether/ethyl acetate = 10:1) after removal of all the volatiles (1.94 g, 63.1%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.84 (s, 1H, O*H*), 7.70 (d, ^3J = 7.0 Hz, 1H, Ar*H*), 7.31 –7.06 (m, 18H, Ar*H*), 6.92 (s, 1H, Ar*H*), 6.75 (s, 1H, Ar*H*), 3.77 (s, 2H, ArCH_2), 3.75 (s, 2H, NCH_2C=N), 3.16 (s, 3H, NCH_3), 2.47 – 2.38 (m, 2H, CH_2 of *n*-butyl), 2.15 (s, 3H, ArCH_3), 1.41 – 1.32 (m, 2H, CH_2 of *n*-butyl), 1.16 – 1.06

(m, 2H, CH_2 of *n*-butyl), 0.81 (t, ^3J = 7.2 Hz, 3H, CH_3 of *n*-butyl). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 153.7, 150.2 (N*C*=N), 146.1, 142.2, 136.1, 133.6, 131.3, 131.0, 129.0, 127.2, 127.1, 125.4, 122.8, 122.2, 122.0, 119.7, 109.4 (all Ar*C*), 63.3 (Ph_3C), 58.5 (ArCH_2), 53.8 (NCH_2C=N), 50.4 (NCH_2CH_2), 30.0 (NCH_3), 28.2 (NCH$_2CH_2$), 21.0 (ArCH_3), 20.6 (CH_2CH_3), 14.0 (CH_2CH_3). Anal. Calcd. for $C_{40}H_{41}N_3O$: C, 82.86; H, 7.13; N, 7.25. Found: C, 82.99; H, 7.52; N, 6.87%.

1.2.8 Synthesis of 2-{[N-benzyl-N-(1-methyl-1H-benzo[d]imidazol-2-yl)methyl] aminomethyl}-4-methyl-6-(triphenylmethyl)phenol (L^8H)

The procedure was the same as that of **L^1H**, except that 1-methyl-2-chloromethylbenzoimidazole (1.84 g, 10.0 mmol) and benzylamine (10.72 g, 100 mmol) were used in the first step, and 2-bromomethyl-4-methyl-6-(triphenylmethyl)phenol (3.41 g, 7.70 mmol), crude *N*-((1-methyl-1*H*-benzo[d]imidazol-2-yl)methyl)benzylamine (1.93 g, about 7.70 mmol), and K_2CO_3 (1.28 g, 9.24 mmol) were used in the second step. White solids were obtained via recrystallization from dichloromethane and petroleum ether (3.16 g, 66.9%). ^1H NMR (400 MHz, $CDCl_3$): δ 10.08 (s, 1H, O*H*), 7.76 – 7.71 (m, 1H, Ar*H*), 7.34 – 7.18 (m, 21H, Ar*H*), 7.01 (dd, ^3J = 7.1, ^4J = 2.1 Hz, 2H, Ar*H*), 6.97 (d, ^4J = 1.6 Hz, 1H, Ar*H*), 6.88 (d, ^4J = 1.6 Hz, 1H, Ar*H*), 3.91 (s, 2H, ArCH_2), 3.75 (s, 2H, PhCH_2), 3.59 (s, 2H, NCH_2C=N), 3.17 (s, 3H, NCH_3), 2.22 (s, 3H, ArCH_3). ^1H NMR (400 MHz, C_6D_6): δ 11.02 (s, 1H, O*H*), 7.67 (d, ^3J = 7.9 Hz, 1H, Ar*H*), 7.72 – 7.66 (m, 6H, Ar*H*), 7.46 (d, ^4J = 1.7 Hz, 1H, ArH), 7.33 – 7.28 (m, 1H, ArH), 7.24 (d, ^4J = 1.9 Hz, 3H, ArH), 7.22 (m, 6H, ArH), 7.21 – 7.18 (m, 3H, ArH), 7.13 (m, 3H, ArH), 6.88 (d, ^4J = 7.9 Hz, 1H, Ar*H*), 6.80 (d, ^4J = 1.6 Hz, 1H, Ar*H*), 3.80 (s, 2H, ArCH_2), 3.63 (s, 2H, PhCH_2), 3.34 (s, 2H, NCH_2C=N), 2.40 (s, 3H, NCH_3), 2.23 (s, 3H, ArCH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 153.5, 150.2 (N*C*=N), 146.2, 142.1, 136.8, 136.1, 133.8, 131.3, 131.1, 130.0, 129.4, 128.6, 127.7, 127.1, 127.0, 125.5, 122.8, 122.2, 121.8, 119.7, 109.4 (all Ar*C*), 63.4 (Ph_3C), 58.4 (ArCH_2), 58.2 (PhCH_2), 49.5 (NCH_2C=N), 29.8 (NCH_3), 21.0 (ArCH_3). Anal. Calcd. for $C_{43}H_{39}N_3O$: C, 84.14; H, 6.40; N, 6.85. Found: C, 84.17; H, 6.34; N, 6.91%.

1.3 Synthesis of zinc complexes 1-8

1.3.1 Synthesis of [L¹ZnN(SiMe₃)₂] (1)

In a glovebox, the aminophenol **L¹H** (538 mg, 1.00 mmol) was dissolved in toluene (5 mL) and was added dropwise to a solution of $Zn[N(SiMe_3)_2]_2$ (384 mg, 1.00 mmol) in toluene (3 mL). The reaction mixture was stirred at room temperature overnight, and all the volatiles were removed under vacuum to afford a white solid which was then recrystallized with a mixture of *n*-hexane and toluene. Colorless crystals of complex **1** were obtained in 56.1% yield (427 mg). ^{1}H NMR (400 MHz, C_6D_6): δ 7.91 (d, ^3J = 8.1 Hz, 1H, Ar*H*), 7.23 (d, ^4J = 2.6 Hz, 1H, Ar*H*), 7.13 (m, 2H × 0.2, toluene), 7.02 (m, 3H × 0.2, toluene), 6.96 (td, ^3J = 7.6 Hz, ^4J = 0.8 Hz, 1H, Ar*H*), 6.94 – 6.90 (m, 3H, Ar*H*), 6.82 (d, ^4J = 2.6 Hz, 1H, Ar*H*), 6.75 (td, ^3J = 7.8 Hz, ^4J = 1.0 Hz, 1H, Ar*H*), 6.48 – 6.41 (m, 3H, Ar*H*), 4.44 (d, ^2J = 16.6 Hz, 1H, ArCH_2), 4.32 (d, ^2J = 16.6 Hz, 1H, ArCH_2), 4.30 (d, ^2J = 11.2 Hz, 1H, NCH_2Ph), 3.64 (d, ^2J = 16.7 Hz, 1H, NCH_2C=N), 3.31 (d, ^2J = 16.7 Hz, 1H, NCH_2C=N), 3.03 (d, ^2J = 11.2 Hz, 1H, NCH_2Ph), 2.90 – 2.75 (m, 2H, CH_2 of cyclohexyl), 2.10 (s, 3H × 0.2, toluene), 1.80 – 1.68 (m, 2H, CH_2 of cyclohexyl), 1.63 – 1.56 (m, 1H, CH_2 of cyclohexyl), 1.54 (s, 9H, (CH_3)$_3$), 1.49 – 1.42 (m, 1H, CH_2 of cyclohexyl), 1.38 (s, 9H, (CH_3)$_3$), 1.33 – 1.17 (m, 2H, CH_2 of cyclohexyl), 1.14 – 1.01 (m, 1H, CH_2 of cyclohexyl), 1.01 – 0.83 (m, 2H, CH_2 of cyclohexyl), 0.60 (s, 18H, N(Si(CH_3)$_2$)$_2$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 165.1, 153.2 (N*C*=N), 138.9, 138.1, 135.3, 134.7, 134.0, 129.5, 126.2, 125.1, 124.5, 124.3, 123.9, 121.2, 119.6, 110.1 (all Ar*C*), 66.9 (Ph_3C), 56.8 (Ar*C*H_2), 49.3 (N*C*H_2Ph), 46.9 (N*C*H_2C=N), 35.6 (N*C*H), 34.1 (*C*(CH$_3$)$_3$), 32.4 (*C*(CH$_3$)$_3$), 30.10 (C(*C*H$_3$)$_3$), 30.05 (C(*C*H$_3$)$_3$), 26.9 (*C*H_2 of cyclohexyl), 26.4 (*C*H_2 of cyclohexyl), 26.0 (*C*H_2 of cyclohexyl), 6.4 (N(Si(*C*H$_3$)$_2$)$_2$). Anal. Calcd. for $C_{42}H_{64}N_4OSi_2Zn$·0.2 C_7H_8: C, 66.75; H, 8.47; N, 7.17. Found: C, 66.38; H, 8.33; N, 7.29%.

1.3.2 Synthesis of [L²ZnN(SiMe₃)₂] (2)

The procedure was the same as that of complex **1**, except that **L²H** (662 mg, 1.00 mmol) and $Zn[N(SiMe_3)_2]_2$ (384 mg, 1.00 mmol) were used to afford complex **2** as colorless crystals (434 mg, 48.9%). ^{1}H NMR (400 MHz, C_6D_6): δ 7.90 (d, ^3J = 8.1 Hz, 1H, Ar*H*), 7.32 (d, ^3J = 7.3 Hz, 2H, Ar*H*), 7.20 – 7.16 (m, 4H, Ar*H*), 7.13 – 7.10 (m, 2H, 1H of Ar*H* & 2H × 0.5 of toluene), 7.07 – 6.99 (m, 6.5H, 5H of Ar*H* & 2H × 0.5 of toluene), 6.92 – 6.86 (m, 4H, Ar*H*), 6.66 – 6.60 (m, 2H, Ar*H*), 6.47 – 6.41 (m, 2H,

Ar*H*), 4.40 (d, ^{2}J = 16.8 Hz, 1H, ArCH_2), 4.16 (d, ^{2}J = 16.8 Hz, 1H, ArCH_2), 4.02 (d, ^{2}J = 11.3 Hz, 1H, NCH_2Ph), 3.44 (d, ^{2}J = 16.6 Hz, 1H, NCH_2C=N), 3.21 (d, ^{2}J = 16.6 Hz, 1H, NCH_2C=N), 2.78 (d, ^{2}J = 11.3 Hz, 1H, NCH_2Ph), 2.72 – 2.60 (m, 2H, CH_2 of cyclohexyl), 2.10 (s, 3H × 0.5, toluene), 1.91 (s, 3H, CH_3), 1.69 (s, 3H, CH_3), 1.66 (s, 3H, CH_3), 1.66 – 1.62 (m, 1H, CH_2 of cyclohexyl), 1.60 – 1.57 (m, 1H, CH_2 of cyclohexyl), 1.56 (s, 3H, CH_3), 1.47 (br d, ^{3}J = 8.9 Hz, 1H, CH_2 of cyclohexyl), 1.37 (br, d, ^{3}J = 11.5 Hz, 1H, CH_2 of cyclohexyl), 1.17 – 1.01 (m, 2H, CH_2 of cyclohexyl), 0.91 – 0.74 (m, 3H, CH_2 of cyclohexyl), 0.47 (s, 18H, N(Si(CH_3)$_2$)$_2$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 165.0, 153.1(N*C*=N), 153.0, 152.4, 138.1, 137.9 (toluene), 135.3, 134.8, 132.9, 129.4, 129.3 (toluene), 128.6 (toluene), 128.2, 127.9, 127.5, 127.3, 127.0, 126.9, 126.1, 125.6 (toluene), 124.9, 124.3, 124.0, 121.8, 119.8, 110.1 (all Ar*C*), 66.7 (Ar*C*H$_2$), 56.5 (N*C*H$_2$Ph), 49.6(N*C*H$_2$C=N), 46.6 (N*C*H), 43.4, 42.2 (Ph*C*(CH$_3$)$_2$), 31.8, 31.7, 31.1, 29.8 (PhC(*C*H$_3$)$_2$), 28.0 (*C*H$_2$ of cyclohexyl), 26.6 (*C*H$_2$ of cyclohexyl), 26.3 (*C*H$_2$ of cyclohexyl), 25.9 (*C*H$_2$ of cyclohexyl), 25.9 (*C*H$_2$ of cyclohexyl), 21.4 (toluene), 6.30 (N(Si(*C*H$_3$)$_2$)$_2$). Anal. Calcd. for $C_{52}H_{68}N_4OSi_2Zn$: C, 70.44; H, 7.73; N, 6.32. Found: C, 70.23; H, 7.67; N, 5.88%.

1.3.3 Synthesis of [L^{3}ZnN(SiMe$_3$)$_2$] (3)

The procedure was the same as that of complex **1**, except that **L^{3}H** (682 mg, 1.00 mmol) and Zn[N(SiMe$_3$)$_2$]$_2$ (384 mg, 1.00 mmol) were used to afford complex **3** as white solids (563 mg, 62.1%). ^{1}H NMR (400 MHz, C_6D_6): δ 7.57 (d, ^{3}J = 8.1 Hz, 1H, Ar*H*), 7.50 (d, ^{3}J = 7.3 Hz, 6H, Ar*H*), 7.33 (d, ^{4}J = 2.2 Hz, 1H, Ar*H*), 7.11 (td, ^{3}J = 7.3 Hz, ^{4}J = 0.8 Hz, 1H, Ar*H*), 6.96 – 6.95 (m, 1H, Ar*H*), 6.94 (t, ^{3}J = 7.8 Hz, 6H, Ar*H*), 6.89-6.85 (m, 3H, Ar*H*), 6.72 (t, ^{3}J = 7.3 Hz, 3H, Ar*H*), 6.67 (d, ^{4}J = 2.2 Hz, 1H, Ar*H*), 6.62 (d, ^{3}J = 8.2 Hz, 1H, Ar*H*), 6.38 – 6.30 (m, 2H, Ar*H*), 4.47 (d, ^{2}J = 11.7 Hz, 1H, ArCH_2), 4.17 (d, ^{2}J = 16.8 Hz, 1H, NCH_2Ph), 3.77 (m, 1H of NCH_2C=N, 1H of ArCH_2), 3.09 (d, ^{2}J = 16.8 Hz, 1H, NCH_2Ph), 3.08 (d, ^{2}J = 11.7 Hz, 1H, NCH_2C=N), 2.87 (d, ^{3}J = 11.7 Hz, 1H, CH_2 of cyclohexyl), 2.43 (t, ^{3}J = 11.4 Hz, 1H, 1*H* of cyclohexyl), 2.19 (s, 3H, ArCH_3), 1.68 (br d, ^{3}J = 12.5 Hz, 1H, CH_2 of cyclohexyl), 1.50 (br, d, ^{3}J = 11.6 Hz, 1H, CH_2 of cyclohexyl), 1.40 – 1.31 (m, 2H, 2*H* of cyclohexyl), 1.25 – 1.17 (m, 1H, CH_2 of cyclohexyl), 1.16 – 1.05 (m, 1H, CH_2 of cyclohexyl), 1.04 – 0.93 (m, 1H, CH_2 of cyclohexyl), 0.91 – 0.82 (m, 1H, CH_2 of cyclohexyl), 0.82 – 0.68 (m, 1H, CH_2 of cyclohexyl), 0.28 (s, 18H, N(Si(CH_3)$_2$)$_2$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 165.2,

154.0 (N*C*=N), 147.9, 138.3, 137.4, 135.2, 134.6, 133.8, 132.0, 131.8, 129.3, 128.6, 127.0, 126.1, 125.2, 124.3, 123.7, 121.6, 121.0, 120.1, 109.6 (all Ar*C*), 64.6 (Ar*C*H_2), 64.3 (Ph_3C), 55.0 (N*C*H_2Ph), 46.0 (N*C*H_2C=N), 44.7 (N*C*H), 29.9 (*C*H_2 of cyclohexyl), 26.7 (*C*H_2 of cyclohexyl), 26.1 (*C*H_2 of cyclohexyl), 25.2 (*C*H_2 of cyclohexyl), 21.1 (Ar*C*H_3), 6.3 (N(Si(*C*H_3)$_2$)$_2$). Anal. Calcd. for $C_{54}H_{64}N_4OSi_2Zn \cdot 0.3\ C_4H_8O$: C, 71.42; H, 7.21; N, 6.04. Found: C, 71.13; H, 7.04; N, 6.06%.

1.3.4 Synthesis of [L⁴ZnN(SiMe₃)₂] (4)

The procedure was the same as that of complex **1**, except that **L⁴H** (656 mg, 1.00 mmol) and Zn[N(SiMe$_3$)$_2$]$_2$ (384 mg, 1.00 mmol) were used to afford complex **4** as white solids (453 mg, 51.4%). ^{1}H NMR (400 MHz, C_6D_6): δ 7.54 (d, ^3J = 8.2 Hz, 1H, Ar*H*), 7.51 (d, ^3J = 7.5 Hz, 6H, Ar*H*), 7.35 (d, ^4J = 2.0 Hz, 1H, Ar*H*), 7.14 – 6.97 (m, 2H, Ar*H*; 5H × 0.5, toluene), 6.97 – 6.90 (t, ^3J = 7.8 Hz, 6H, Ar*H*), 6.89 – 6.85 (m, 3H, Ar*H*), 6.72 (t, ^3J = 7.3 Hz, 3H, Ar*H*), 6.66 (d, ^4J = 2.0 Hz, 1H, Ar*H*), 6.60 (d, ^3J = 8.2 Hz, 1H, Ar*H*), 6.37 – 6.32 (m, 2H, Ar*H*), 4.54 (d, ^2J = 11.9 Hz, 1H, ArCH_2), 4.08 (d, ^2J = 16.9 Hz, 1H, NCH_2Ph), 3.80 (d, ^2J = 17.1 Hz, 1H, NCH_2C=N), 3.75 (d, ^2J = 16.9 Hz, 1H, NCH_2Ph), 2.92 (d, ^2J = 11.9 Hz, 1H, ArCH_2), 2.75 (td, ^2J = 12.0 Hz, ^3J = 4.0 Hz, 1H, CH_2 of *n*-butyl), 2.69 (d, ^2J = 17.1 Hz, 1H, NCH_2C=N), 2.30 – 2.22 (m, 1H, CH_2 of *n*-butyl), 2.20 (s, 3H, ArCH_3), 2.10 (s, 3H × 0.5, toluene), 1.91 – 1.78 (m, 1H, CH_2 of *n*-butyl), 1.27 – 1.14 (m, 1H, CH_2 of *n*-butyl), 1.13 – 1.01 (m, 1H, CH_2 of *n*-butyl), 0.98 – 0.86 (m, 1H, CH_2 of *n*-butyl), 0.82 (t, ^3J = 7.1 Hz, 3H, CH_3 of *n*-butyl), 0.26 (s, 18H, N(Si(CH_3)$_2$)$_2$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 165.0, 153.5 (N*C*=N), 147.8, 138.3, 137.7, 135.3, 134.5, 133.7, 131.8, 129.3, 127.0, 125.9, 125.2, 124.3, 123.7, 109.6 (all Ar*C*), 64.2 (Ph_3C), 60.1 (Ar*C*H_2), 59.5 (N*C*H_2Ph), 47.7 (N*C*H_2C=N), 45.9 (N*C*H_2CH_2), 31.9 (*n*-hexane), 26.1 (NCH_2*C*H_2), 23.1 (*n*-hexane), 21.1 (Ar*C*H_3), 21.0 (*C*H_2CH_3), 14.4 (*n*-hexane),14.0 (*C*H_2CH_3), 6.4 (N(Si(*C*H_3)$_2$)$_2$). Anal. Calcd. for $C_{52}H_{62}N_4OSi_2Zn \cdot 0.5\ C_7H_8$: C, 71.93; H, 7.18; N, 6.05. Found: C, 71.87; H, 6.91; N, 6.14%.

1.3.5 Synthesis of [L⁵ZnN(SiMe₃)₂] (5)

The procedure was the same as that of complex **1**, except that **L⁵H** (690 mg, 1.00 mmol) and Zn[N(SiMe$_3$)$_2$]$_2$ (384 mg, 1.00 mmol) were used to afford complex **5** as white solids (586 mg, 64.1%). ^{1}H NMR (400 MHz, C_6D_6): δ 7.59 – 7.50 (m, 7H, Ar*H*), 7.31 (d, ^4J = 2.0 Hz, 1H, Ar*H*), 7.14 – 7.03 (m, 6H, Ar*H* & toluene), 7.03 – 6.94 (m,

12H, Ar*H*), 6.92 – 6.88 (m, 3H, Ar*H*), 6.83 (t, ^{3}J = 7.3 Hz, 3H, Ar*H*), 6.57 (d, ^{3}J = 8.2 Hz, 1H, Ar*H*), 6.42 (d, ^{3}J = 7.1 Hz, 2H, Ar*H*), 6.38 (s, 1H, Ar*H*), 6.36 (d, ^{4}J = 1.8 Hz, 2H, Ar*H*), 4.50 (d, ^{2}J = 11.9 Hz, 1H, ArCH_2), 4.39 (d, ^{2}J = 14.4 Hz, 1H, NCH_2Ph), 4.09 (d, ^{2}J = 17.1 Hz, 1H, CNCH_2Ph), 3.79 (d, ^{2}J = 14.4 Hz, 1H, NCH_2Ph), 3.60 (d, ^{2}J = 17.5 Hz, 1H, NCH_2C=N), 3.49 (d, ^{2}J = 17.2 Hz, 1H, CNCH_2Ph), 3.43 (d, ^{2}J = 17.5 Hz, 1H, NCH_2C=N), 3.32 (d, ^{2}J = 11.9 Hz, 1H, NCH_2Ph), 2.10 (s, 3H × 1.2, toluene), 2.06 (s, 3H, ArCH_3), 0.29 (s, 18H, N(Si(CH_3)$_2$)$_2$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 165.8, 153.6 (N*C*=N), 147.8, 138.1, 137.9 (toluene) 137.5, 135.7, 134.8, 133.9, 132.1, 131.9, 131.8, 129.5, 129.3 (toluene), 128.9, 128.6, 128.6 (toluene) 127.1, 126.0, 125.7 (toluene), 125.3, 124.5, 123.7, 121.2, 121.1, 120.2, 109.5 (all Ar*C*), 64.3 (Ph$_3$*C*), 60.6 (Ar*C*H$_2$), 59.7 (Ph*C*H$_2$), 45.7 (Ph*C*H$_2$), 43.7 (N*C*H$_2$C=N), 21.4 (Ar*C*H$_3$), 21.1 (toluene), 6.5 (N(Si(*C*H$_3$)$_2$)$_2$). Anal. Calcd. for $C_{55}H_{60}N_4OSi_2Zn \cdot 1.2\ C_7H_8$: C, 74.28; H, 6.84; N, 5.46. Found: C, 73.74; H, 6.68; N, 5.21%.

1.3.6 Synthesis of [L^{6}ZnN(SiMe$_3$)$_2$] (6)

The procedure was the same as that of complex **1**, except that **L^{6}H** (830 mg, 1.00 mmol) and Zn[N(SiMe$_3$)$_2$]$_2$ (384 mg, 1.00 mmol) were used to afford complex **6** as colorless crystals (500 mg, 60.2%). ^{1}H NMR (400 MHz, C_6D_6): δ 7.54 – 7.46 (m, 7H, Ar*H*), 7.27 (d, ^{4}J = 2.2 Hz, 1H, Ar*H*), 7.10 (td, ^{3}J = 7.7 Hz, ^{4}J = 0.8 Hz, 1H, Ar*H*), 6.97 (m, 7H, Ar*H*), 6.76 (t, ^{3}J = 7.3 Hz, 3H, Ar*H*), 6.66 (d, ^{4}J = 2.2 Hz, 1H, Ar*H*), 6.50 (d, ^{3}J = 8.1 Hz, 1H, Ar*H*), 4.45 (d, ^{2}J = 11.7 Hz, 1H, ArCH_2), 3.59 (d, ^{2}J = 17.1 Hz, 1H, NCH_2C=N), 3.58 – 3.53 (m, 4H × 0.5, THF), 3.11 (d, ^{2}J = 11.7 Hz, 1H, ArCH_2), 3.07 (d, ^{2}J = 17.1 Hz, 1H, NCH_2C=N), 2.75 (br, d, ^{2}J = 11.4 Hz, 1H, CH_2 of cyclohexyl), 2.69 – 2.59 (m, 1H, CH_2 of cyclohexyl), 2.16 (s, 3H, NCH_3), 2.06 (s, 3H, ArCH_3), 1.85 (br, d, ^{2}J = 10.7 Hz, 1H, CH_2 of cyclohexyl), 1.70 (m, 2H, CH_2 of cyclohexyl), 1.46 (d, ^{2}J = 12.0 Hz, 1H, CH_2 of cyclohexyl), 1.43 – 1.38 (m, 2H × 0.5, THF), 1.27 – 1.10 (m, 3H, CH_2 of cyclohexyl), 1.09 – 0.91 (m, 2H, CH_2 of cyclohexyl), 0.29 (s, 18H, N(Si(CH_3)$_2$)$_2$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 165.5, 153.6 (N*C*=N), 148.0, 138.2, 137.0, 135.3, 133.7, 131.8, 131.4, 127.0, 125.1, 123.7, 123.6, 121.6, 120.7, 119.9, 109.3 (all Ar*C*), 67.8 (THF), 64.9 (Ar*C*H$_2$), 64.3 (Ph$_3$*C*), 55.8 (N*C*H$_2$C=N), 44.7 (N*C*H), 32.0 (hexane), 29.6 (N*C*H$_3$), 28.0 (*C*H$_2$ of cyclohexyl), 26.5 (*C*H$_2$ of cyclohexyl), 26.14 (*C*H$_2$ of cyclohexyl), 26.06 (*C*H$_2$ of cyclohexyl), 25.7 (THF), 23.1 (hexane), 21.1 (Ar*C*H$_3$), 14.4 (hexane), 6.4 (N(Si(*C*H$_3$)$_2$)$_2$). The great solvent signal strength is

attributed to the poor solubility of the complex. Anal. Calcd. for $C_{48}H_{60}N_4OSi_2Zn{\cdot}0.5\ C_4H_8O$: C, 69.30; H, 7.44; N, 6.46. Found: C, 69.13; H, 7.80; N, 6.11%.

1.3.7 Synthesis of [L^{7}ZnN(SiMe$_3$)$_2$] (7)

The procedure was the same as that of complex **1**, except that **L^{7}H** (580 mg, 1.00 mmol) and Zn[N(SiMe$_3$)$_2$]$_2$ (384 mg, 1.00 mmol) were used to afford complex **7** as white solids (456 mg, 56.7%). ^{1}H NMR (400 MHz, C_6D_6): δ 7.52 (d, ^3J = 8.1 Hz, 1H, Ar*H*), 7.48 (d, ^3J = 7.3 Hz, 6H, Ar*H*), 7.32 (d, ^4J = 2.2 Hz, 1H, Ar*H*), 7.10 (t, ^3J = 7.3 Hz, 1H, ArH), 7.01 (t, ^3J = 7.3 Hz, 1H, Ar*H*), 6.93 (t, ^3J = 7.8 Hz, 6H, Ar*H*), 6.75 (d, ^4J = 2.2 Hz, 1H, Ar*H*), 6.72 (t, ^3J = 7.3 Hz, 3H, Ar*H*), 6.55 (d, ^3J = 8.1 Hz, 1H, Ar*H*), 4.61 (d, ^2J = 12.0 Hz, 1H, ArC*H*$_2$), 3.71 (d, ^2J = 17.0 Hz, 1H, NC*H*$_2$C=N), 3.57 (m, 4H × 0.8, THF), 2.96 (d, ^2J = 12.0 Hz, 1H, ArC*H*$_2$), 2.87 – 2.77 (m, 1H, 1*H* of *n*-butyl), 2.59 (d, ^2J = 17.0 Hz, 1H, NC*H*$_2$C=N), 2.39 – 2.25 (m, 2H, C*H*$_2$ of *n*-butyl), 2.22 (s, 3H, NC*H*$_3$), 2.02 (s, 3H, ArC*H*$_3$), 1.55 – 1.45 (m, 1H, C*H*$_2$ of *n*-butyl), 1.41 (m, 4H × 0.8, THF), 1.29 – 1.16 (m, 1H, C*H*$_2$ of *n*-butyl), 1.16 – 1.02 (m, 1H, C*H*$_2$ of *n*-butyl), 0.92 (t, ^3J = 7.3 Hz, 3H, C*H*$_3$ of *n*-butyl), 0.26 (s, 18H, N(Si(C*H*$_3$)$_2$)$_2$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 165.1, 153.1 (N*C*=N), 147.8, 138.3, 137.7, 135.5, 133.7, 131.8, 131.7, 127.0, 125.1, 123.9, 123.6, 121.4, 120.7, 120.0, 109.4 (all Ar*C*), 67.8 (THF), 64.3 (Ph$_3$*C*), 60.4 (Ar*C*H$_2$), 60.1 (N*C*H$_2$C=N), 47.9 (N*C*H$_2$CH$_2$), 28.1 (N*C*H$_3$), 26.8 (*C*H$_2$CH$_3$), 25.7 (THF), 21.1 (Ar*C*H$_3$), 14.1 (CH$_2$*C*H$_3$), 6.4 (N(Si(*C*H$_3$)$_2$)$_2$). Anal. Calcd. for $C_{46}H_{58}N_4OSi_2Zn{\cdot}0.8\ C_4H_8O$: C, 68.54; H, 7.53; N, 6.50. Found: C, 68.28; H, 7.62; N, 6.46%.

1.3.8 Synthesis of [L^{8}ZnN(SiMe$_3$)$_2$] (8)

The procedure was the same as that of complex **1**, except that **L^{8}H** (614 mg, 1.00 mmol) and Zn[N(SiMe$_3$)$_2$]$_2$ (384 mg, 1.00 mmol) were used to afford complex **8** as white solids (444 mg, 52.9%). ^{1}H NMR (400 MHz, C_6D_6): δ 7.55 – 7.48 (m, 7H, Ar*H*), 7.27 (d, ^4J = 2.1 Hz, 1H, Ar*H*), 7.14 – 7.08 (m, 4H, ArH), 7.06 – 7.00 (m, 1H, Ar*H*), 6.98 (t, ^3J = 7.8 Hz, 6H, Ar*H*), 6.87 (dd, ^3J = 7.1, ^4J = 2.2 Hz, 2H, Ar*H*), 6.79 (t, ^3J = 7.3 Hz, 3H, Ar*H*), 6.54 (d, ^3J = 8.0 Hz, 1H, Ar*H*), 6.42 (d, ^4J = 2.1 Hz, 1H, Ar*H*), 4.55 (d, ^2J = 11.8 Hz, 1H, ArC*H*$_2$), 4.39 (d, ^2J = 14.5 Hz, 1H, PhC*H*$_2$), 3.95 (d, ^2J = 14.5 Hz, 1H, PhC*H*$_2$), 3.56 (m, 4H × 0.7, THF), 3.43 – 3.36 (m, 2H, 1H of ArC*H*$_2$, 1H of NC*H*$_2$C=N), 3.31 (d, ^2J = 17.1 Hz, 1H, NC*H*$_2$C=N), 2.05 (s, 3H, NC*H*$_3$), 1.99 (s, 3H,

ArCH_3), 1.43 – 1.38 (m, 4H × 0.7, THF), 0.31 (s, 18H, N(Si(CH_3)$_2$)$_2$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 165.7, 153.0 (N*C*=N), 147.9, 138.3, 137.4, 135.5, 133.7, 132.1, 132.0, 131.8, 131.7, 129.0, 128.9, 127.0, 125.2, 123.9, 123.7, 121.0, 120.6, 120.1, 109.5 (all ArC), 64.3 (Ph$_3$*C*) , 60.5 (Ar*C*H$_2$), 59.8 (N*C*H$_2$Ph), 43.7 (N*C*H$_2$C=N), 28.0 (N*C*H$_3$), 20.9 (Ar*C*H$_3$), 6.6 (N(Si(*C*H$_3$)$_2$)$_2$). Anal. Calcd. for $C_{49}H_{56}N_4OSi_2Zn$·0.7 C_4H_8O: C, 69.98; H, 6.98; N, 6.30. Found: C, 69.36; H, 6.57; N, 6.39%.

1.4 X-Ray Crystallography

The X-ray diffraction measurements of single crystals of complexes **2** and **6** were performed on a Bruker SMART APEX II diffractometer with graphite-monochromated Mo-Kα radiation (λ= 0.71073 Å). The structures were solved by using the SHELXTL program. Refinement was performed on F^2 anisotropically for all non-hydrogen atoms by the full-matrix least-squares method.[S5] The hydrogen atoms were placed at calculated positions and were included in the structure calculations without further refinement of the parameters. The cell refinement, data collection, and reduction were done by Bruker SAINT.[S6] Molecular structures were generated using ORTEP program.[S7] For further crystal data collection and details of measurements, see Table S1. CCDC numbers 1919496 (for **2**), 1919497 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

1.5 General Polymerization Procedure

In a glovebox, a catalyst solution (0.05 mmoL) from a stock solution in toluene or THF was injected sequentially into a series of 10 mL of Schlenk tubes loaded with *rac*-LA (0.144 g, 1.00 mmol) and a suitable amount (0.5 mL) of the same dry solvent. The mixture was stirred at 25 ℃ and quenched at specific time intervals by adding an excess amount of normal light petroleum ether. After being dissolved with dichloromethane, a small amount of an aliquot of the bulk solution was withdrawn and dried under reduced pressure for monomer conversion determination via ^{1}H NMR spectroscopy. The bulk solution was slightly concentrated and the polymer was precipitated from dichloromethane via the addition of excess methanol. The collected polymer sample was further dried *in vacuo* to constant weight for GPC and ^{1}H and homonuclear-decoupled ^{1}H NMR analyses. In the cases where 2-propanol was used, the catalyst was

dissolved in toluene or THF and treated with the respective amount of 2-propanol, otherwise, the procedures were the same.

2. NMR spectra of zinc complexes 1-8

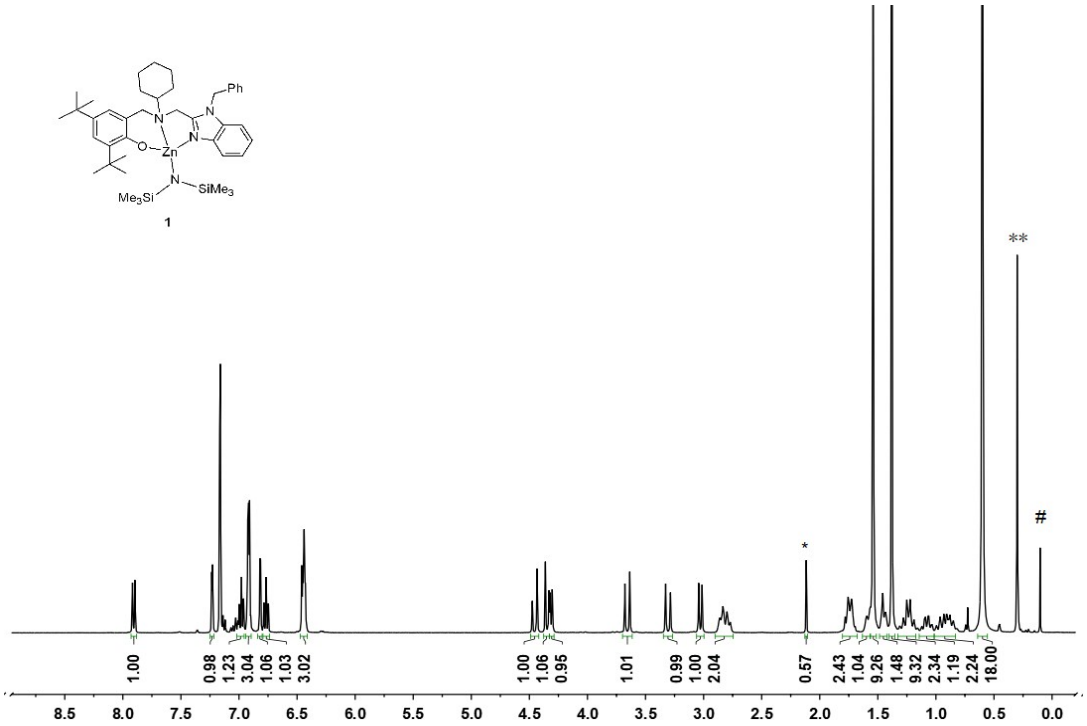


Figure S1. ^{1}H NMR spectrum of complex **1** (400 MHz, C_6D_6, 25 °C; *: signals of residual toluene; **: impurity in C_6D_6; #: free $HN[Si(CH_3)_2]_2$).

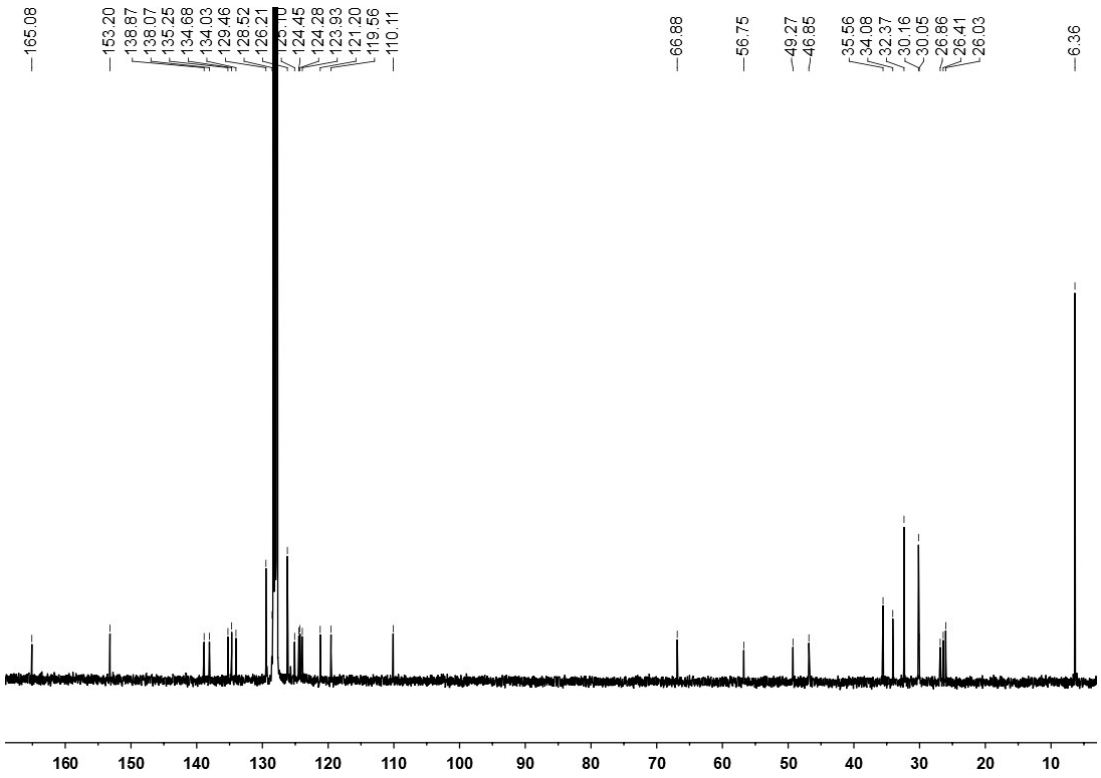


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of complex **1** (100 MHz, C_6D_6, 25 °C).

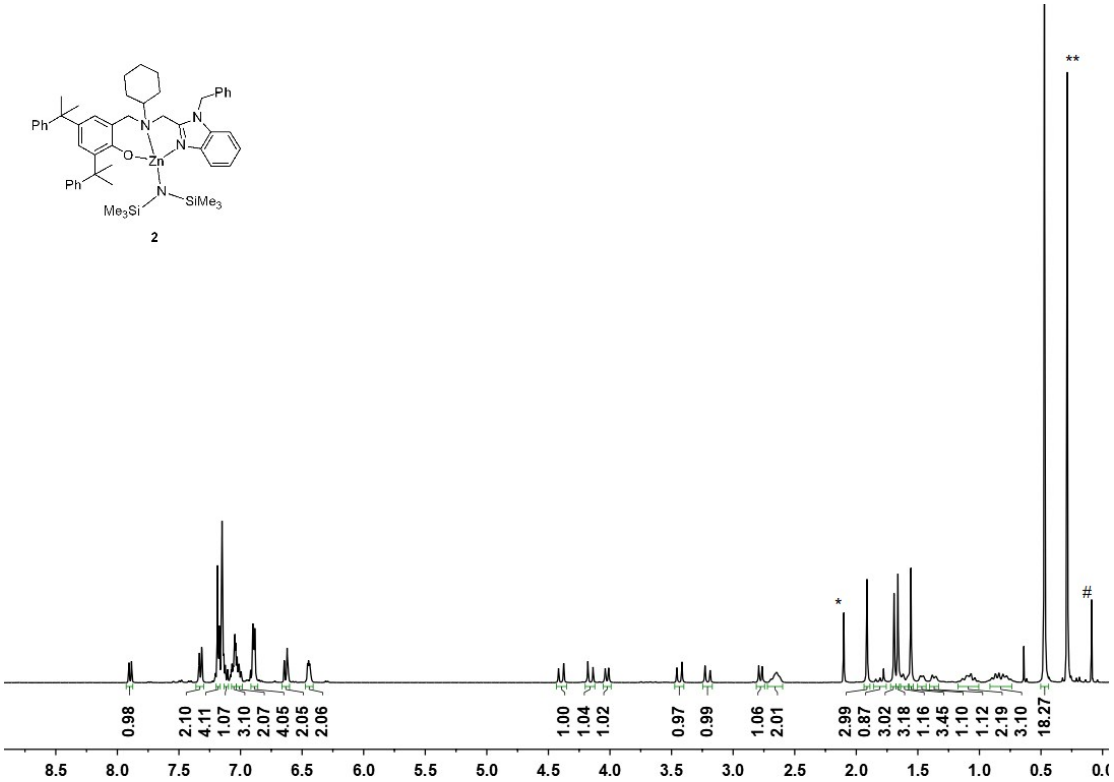


Figure S3. ^{1}H NMR spectrum of complex **2** (400 MHz, C_6D_6, 25 °C; *: signals of residual toluene; **: impurity in C_6D_6; #: free $HN[Si(CH_3)_2]_2$).

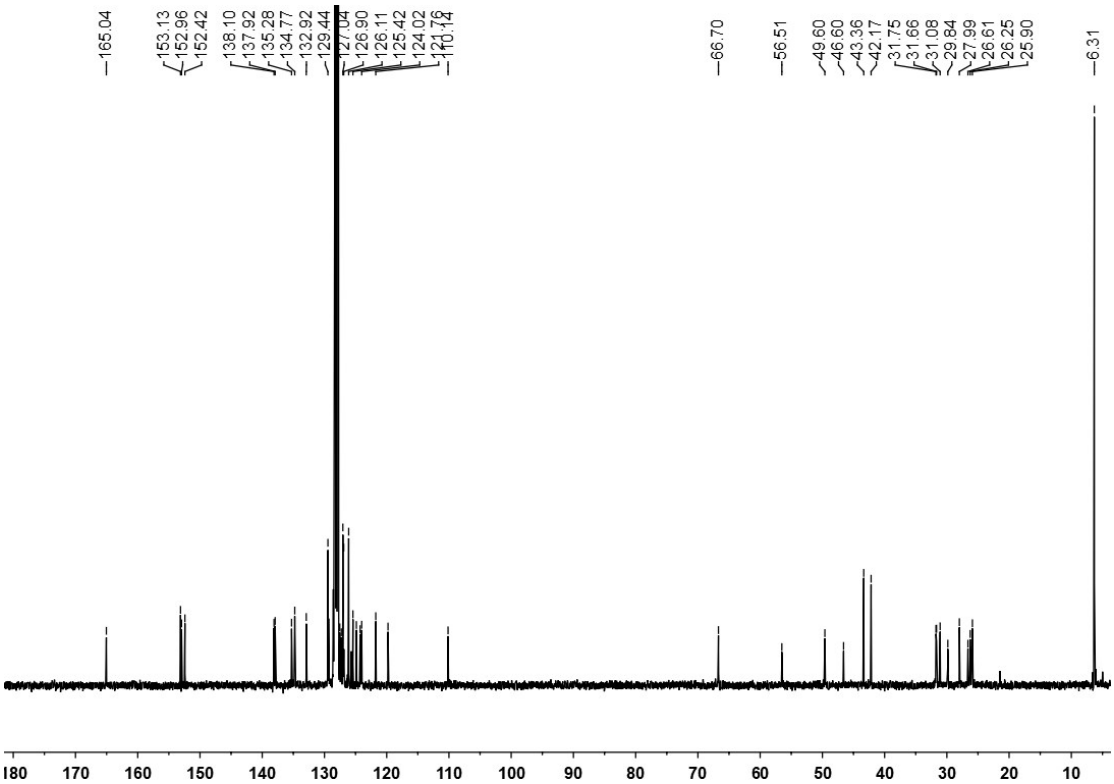


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of complex **2** (100 MHz, C_6D_6, 25 °C).

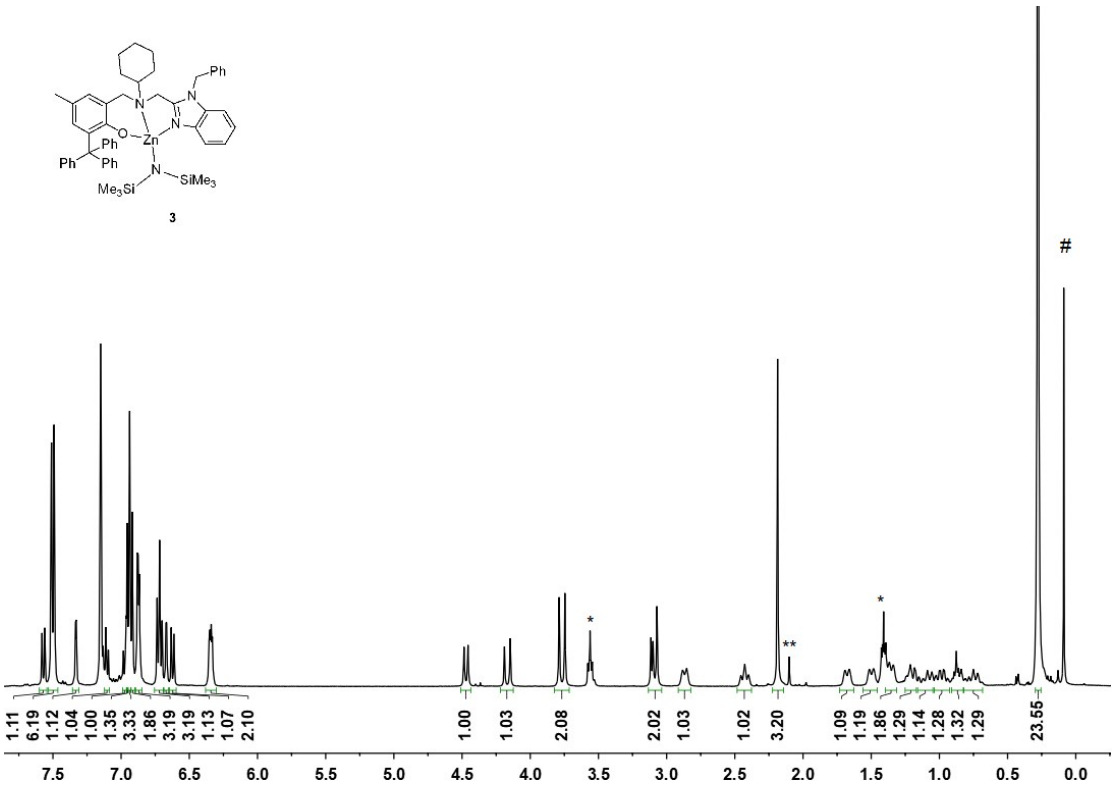


Figure S5. ^{1}H NMR spectrum of complex **3** (400 MHz, C_6D_6, 25 °C; *: signals of residual tetrahydrofuran; **: signals of residual toluene; #: free $HN[Si(CH_3)_2]_2$).

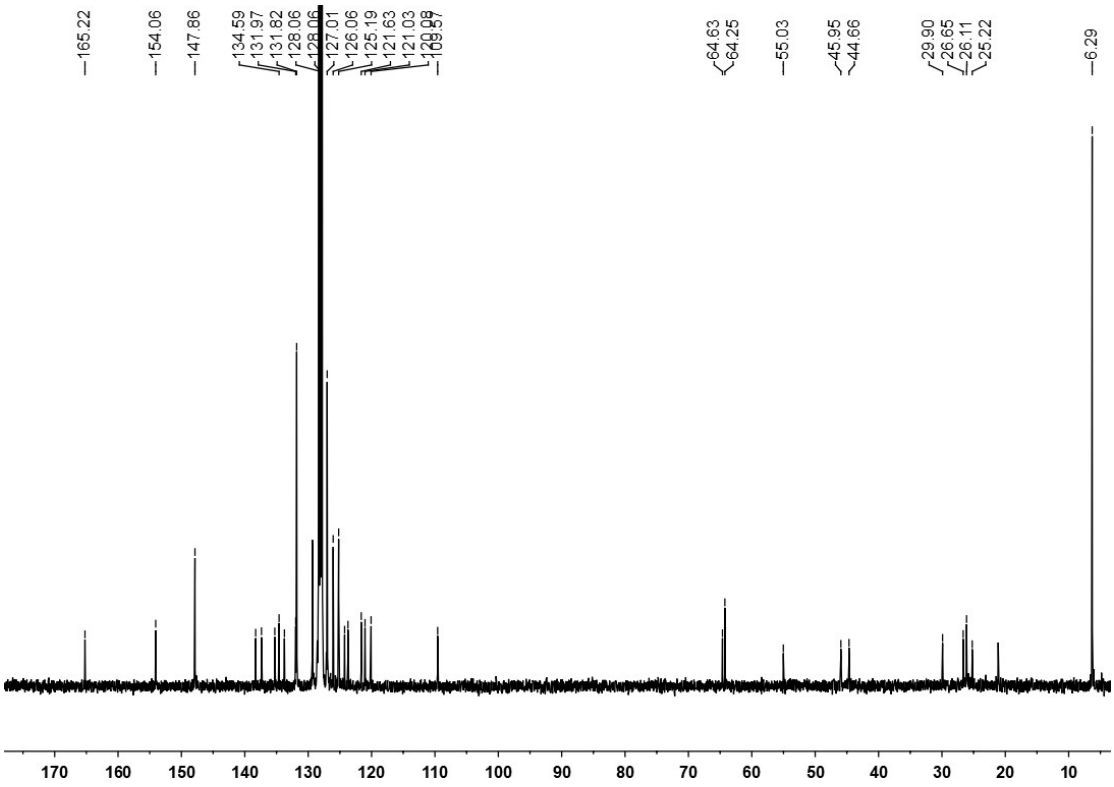


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of complex **3** (100 MHz, C_6D_6, 25 °C).

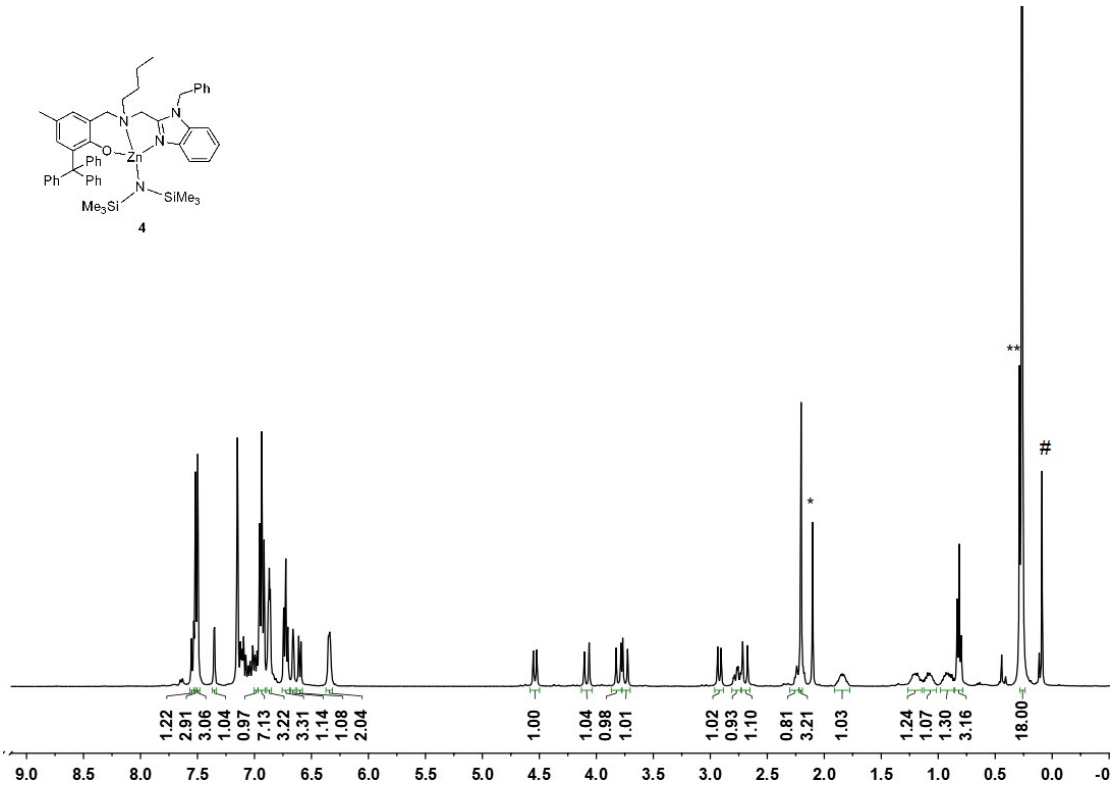


Figure S7. ^{1}H NMR spectrum of complex **4** (400 MHz, C_6D_6, 25 °C; *: signals of residual toluene; **, impurity in C_6D_6; #: free $HN[Si(CH_3)_2]_2$).

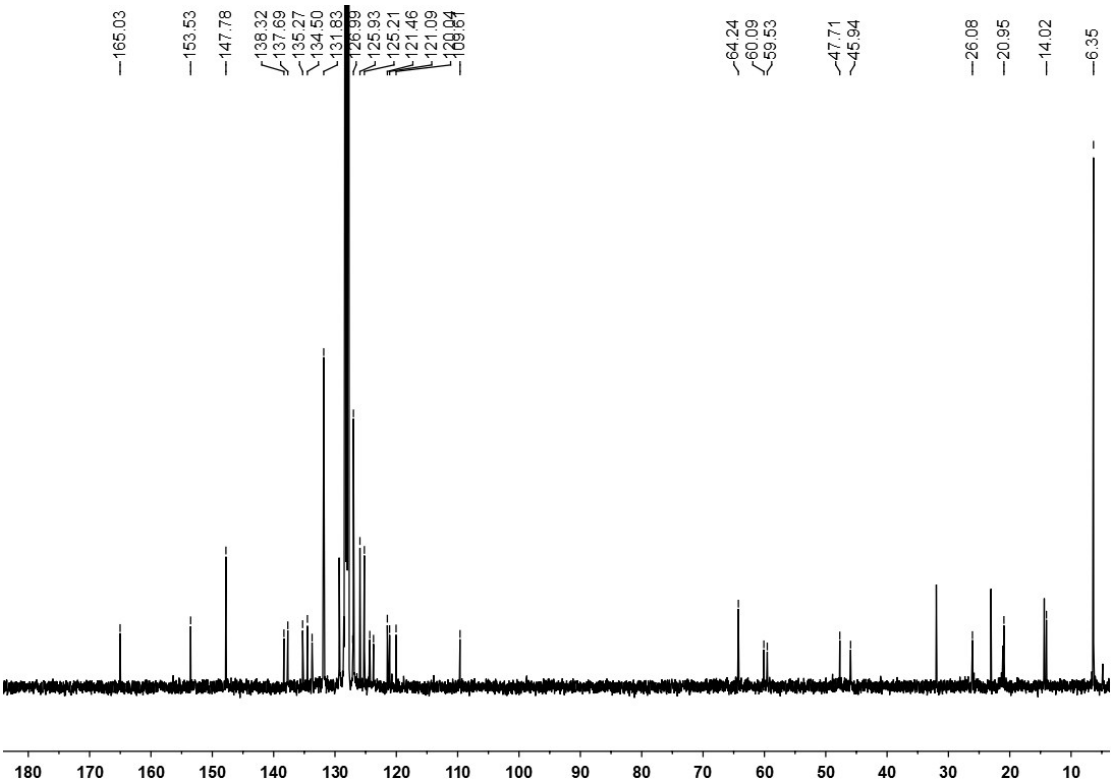


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of complex **4** (100 MHz, C_6D_6, 25 °C).

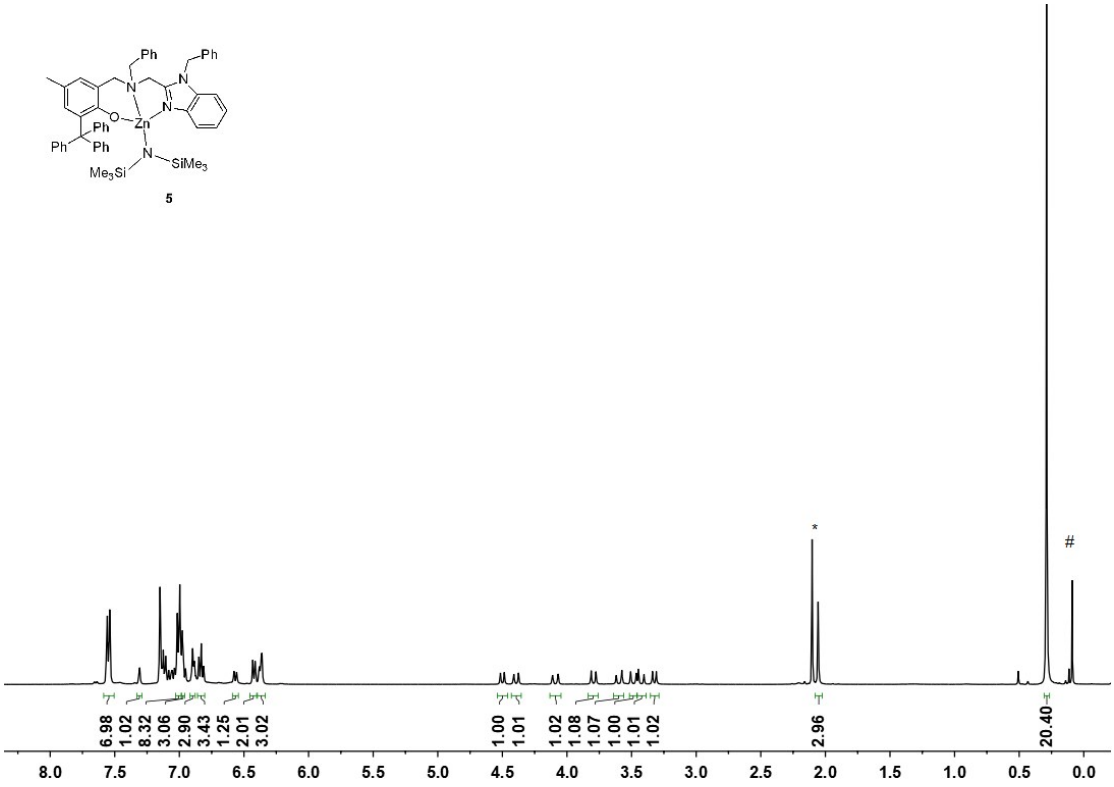


Figure S9. ^{1}H NMR spectrum of complex **5** (400 MHz, C_6D_6, 25 °C; *: signals of residual toluene; #: free $HN[Si(CH_3)_2]_2$).

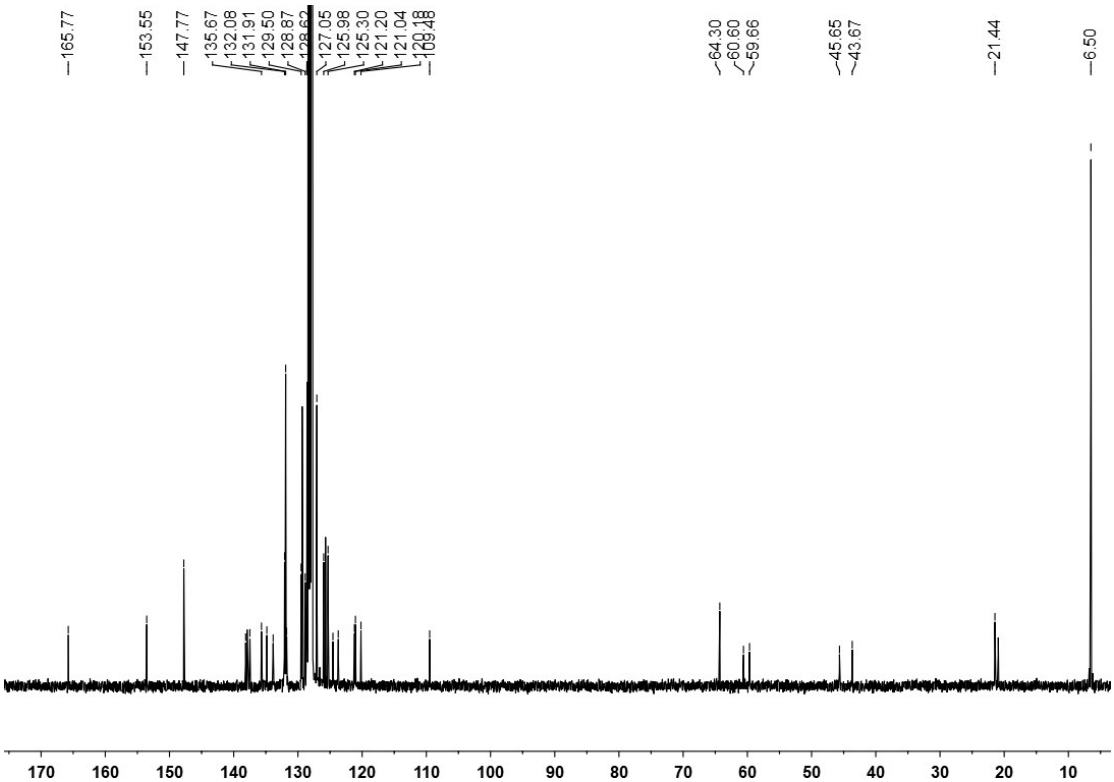


Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of complex **5** (100 MHz, C_6D_6, 25 °C).

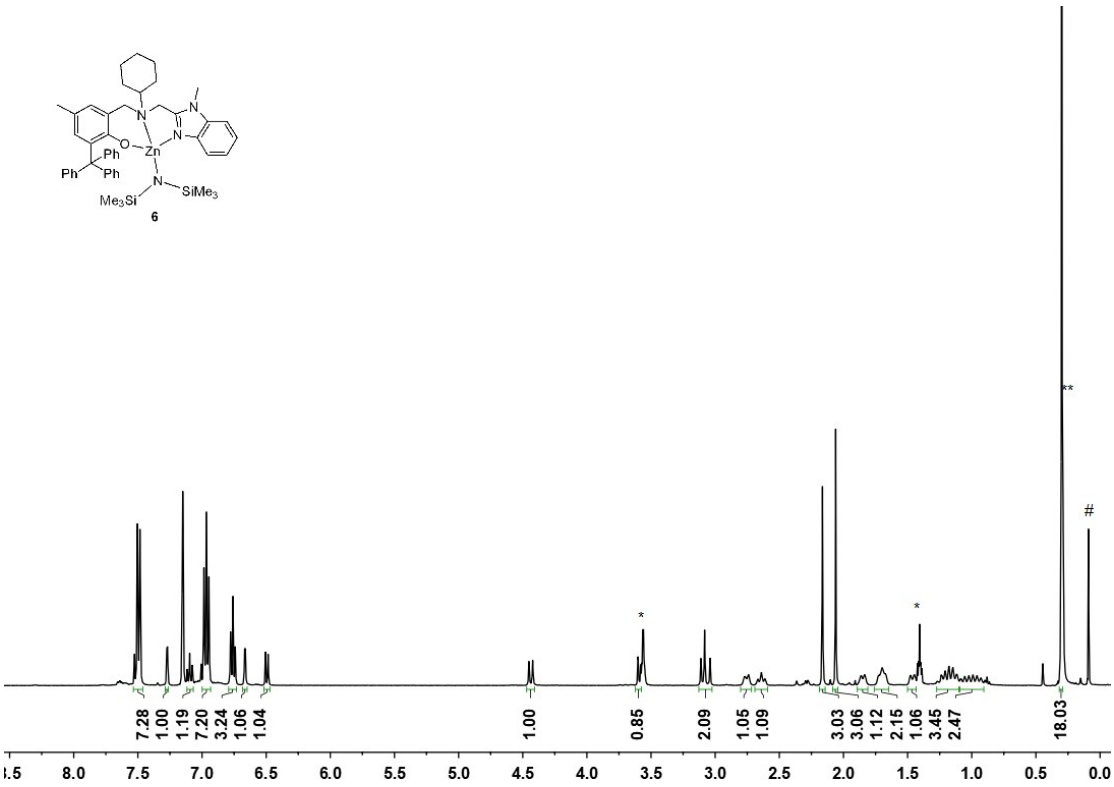


Figure S11. ^{1}H NMR spectrum of complex **6** (400 MHz, C_6D_6, 25 °C; *: signals of residual tetrahydrofuran; **: impurity in C_6D_6; #: free $HN[Si(CH_3)_2]_2$).

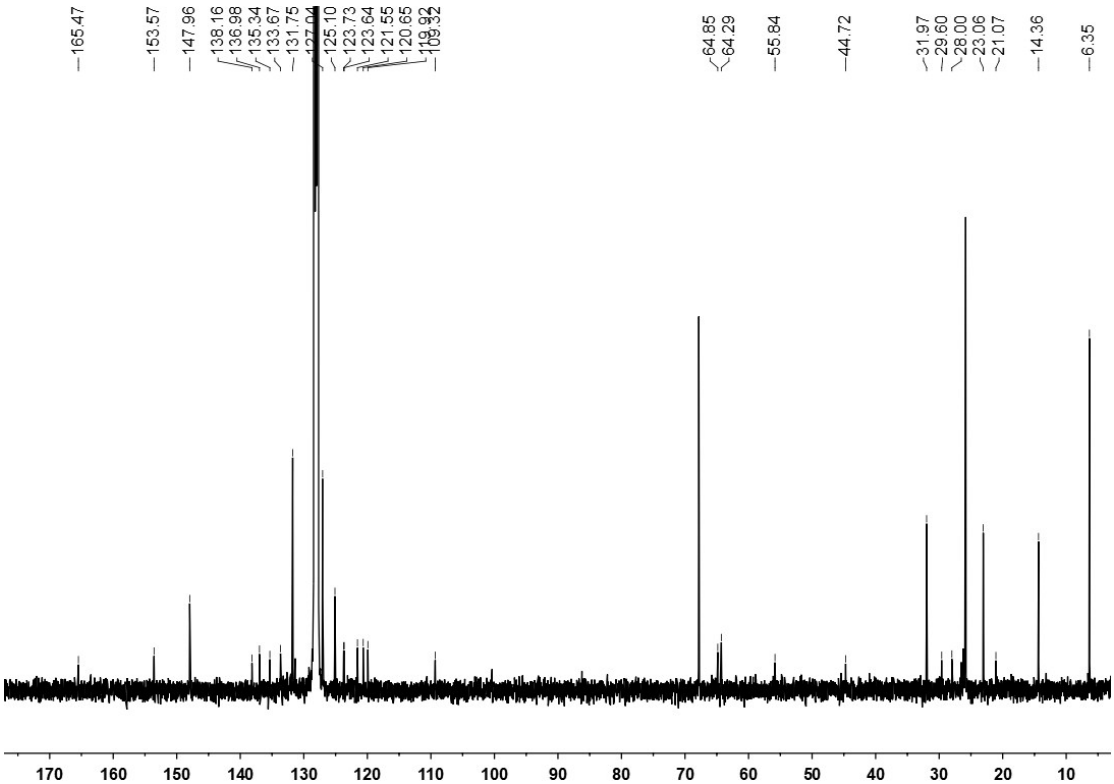


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of complex **6** (100 MHz, C_6D_6, 25 °C).

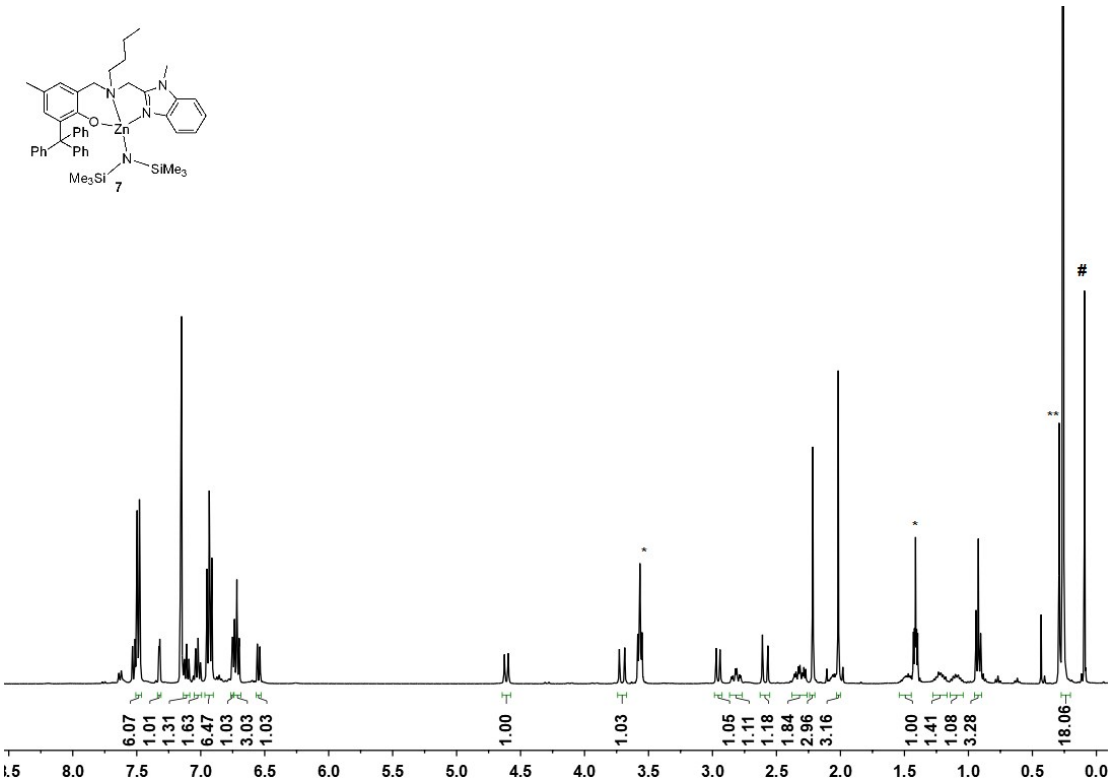


Figure S13. ^{1}H NMR spectrum of complex **7** (400 MHz, C_6D_6, 25 °C; *: signals of residual tetrahydrofuran; **: impurity in C_6D_6; #: free $HN[Si(CH_3)_2]_2$).

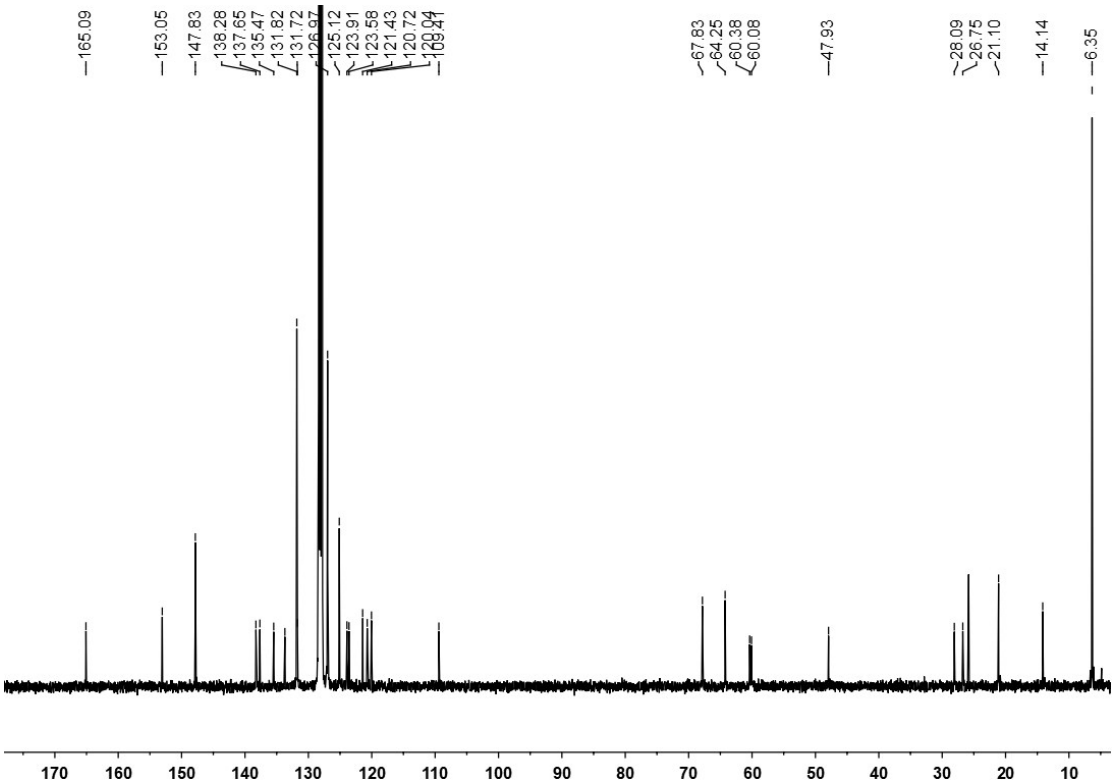


Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum of complex **7** (100 MHz, C_6D_6, 25 °C).

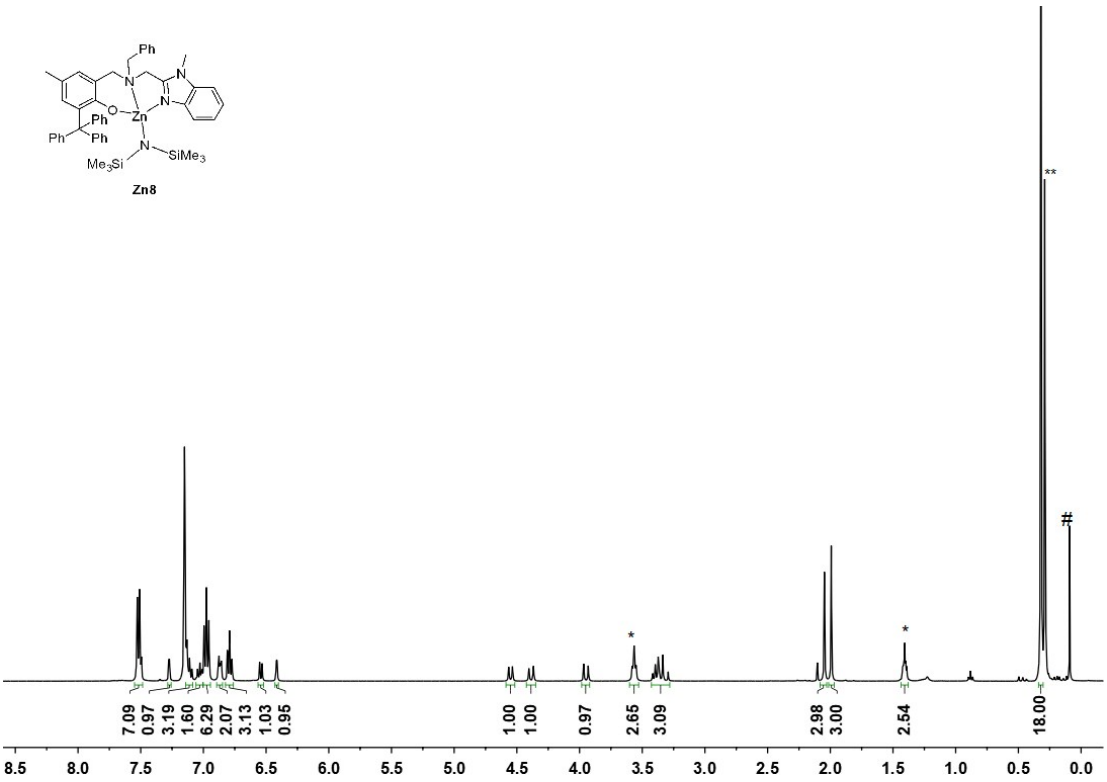


Figure S15. ^{1}H NMR spectrum of complex **8** (400 MHz, C_6D_6, 25 °C; *: signals of residual tetrahydrofuran; **: impurity in C_6D_6; #: free $HN[Si(CH_3)_2]_2$).

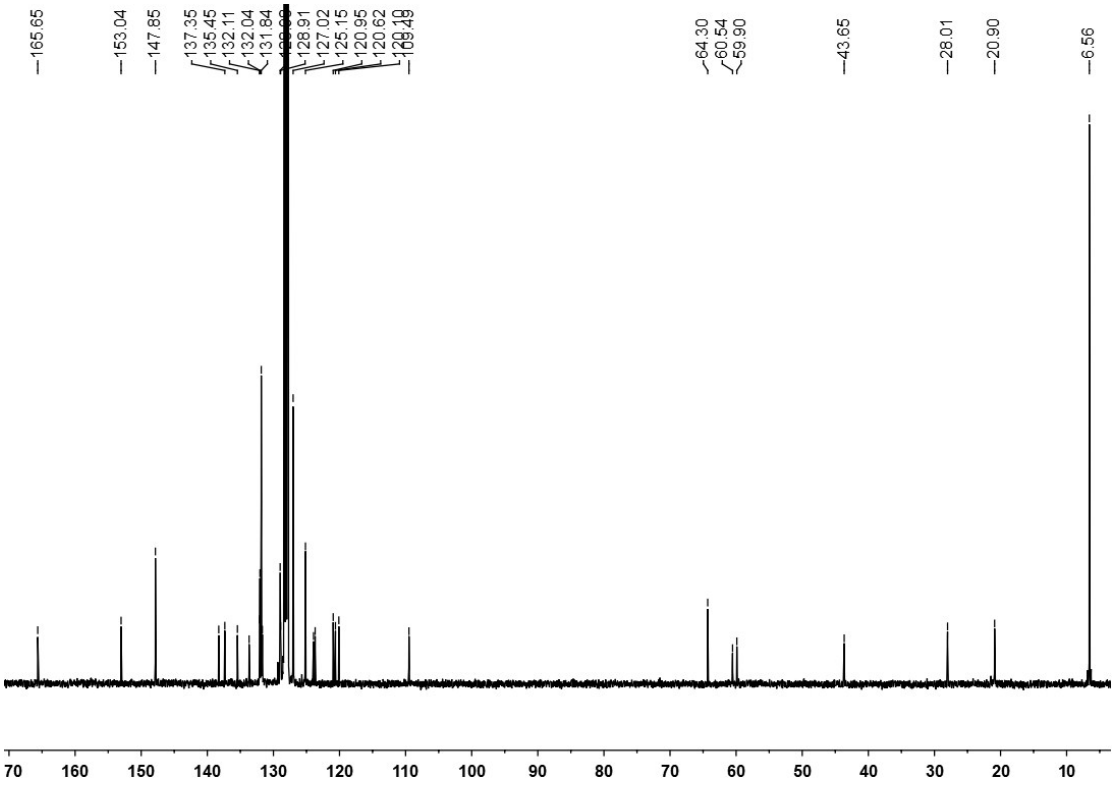


Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum of complex **8** (100 MHz, C_6D_6, 25 °C)

3. Crystallographic data

Table S1. Crystallographic data for complexes **2** and **6**

	2	**6**
Empirical formula	$C_{52}H_{68}N_4OSi_2Zn$	$C_{48}H_{60}N_4OSi_2Zn$
Formula weight	886.65	830.55
Temp (K)	190	169.99
Crystal size (mm^3)	0.20 × 0.18 × 0.12	0.15 × 0.12 × 0.08
Crystal system	Triclinic	Monoclinic
Space group	P-1	P21/c
a (Å)	15.3692(6)	10.78250(10)
b (Å)	18.4170(8)	41.7789(6)
c (Å)	19.6974(8)	11.4854(2)
α (°)	86.9530(10)	90
β (°)	89.9900(10)	114.1380(10)
γ (°)	86.4220(10)	90
Volume ($Å^3$)	5556.7(4)	4721.56(12)
Z	4	4
$Density_{calcd}$ (Mg/m^3)	1.060	1.168
Abs coeff (mm^{-1})	0.521	0.940
F (000)	1896	1768.0
θ range (°)	2.297 to 25.999	8.212 to 109.798
Data collected (*hkl*)	–18 to 18, –22 to 22, –24 to 24	–13 to 13, –50 to 47, –14 to 13
Reflections collected/unique	110512	36826
R (int)	0.0586	0.0441
Max. and min. transmn	0.7456, 0.5821	0.7508, 0.6258
Data/restraints/parameters	21771/0/1102	8922/108/567
Goodness-of-fit on F^2	1.013	1.024
Final R_1, wR_2 [I > 2σ(I)]	0.0417	0.0608, 0.1395
R_1, wR_2 (all data)	0.1080	0.0772, 0.1519
$\Delta\rho_{max,\ min}$(e $Å^{-3}$)	0.649, –0.385	0.69, –0.73

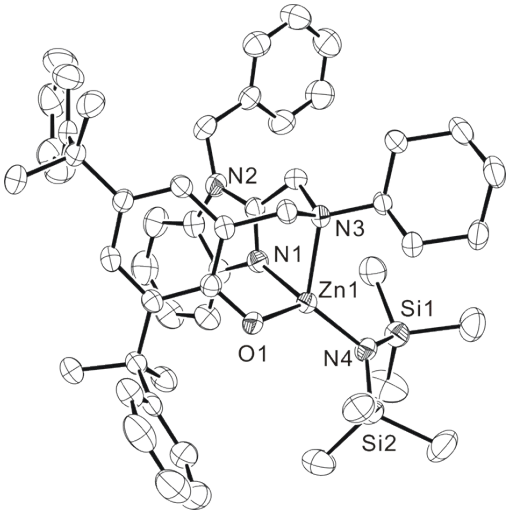


Figure 17. The molecular structures of **2**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) for **2**: Zn1−N4 1.9127(16), Zn1−O1 1.9423(13), Zn1−N1 2.0669(17), Zn1−N3 2.2106(16); N4−Zn1−O1 122.63(7), N4−Zn1−N1 123.85(7), O1−Zn1−N1 101.75(6), N4−Zn1−N3 122.66(7), O1−Zn1−N3 94.38(6), N1−Zn1−N3 81.55(6).

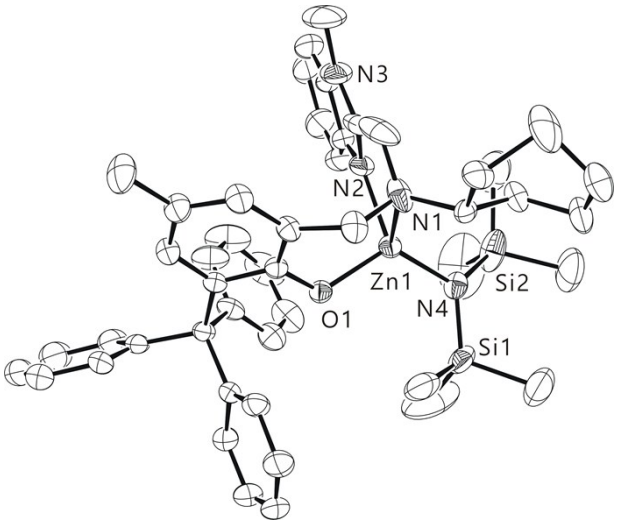


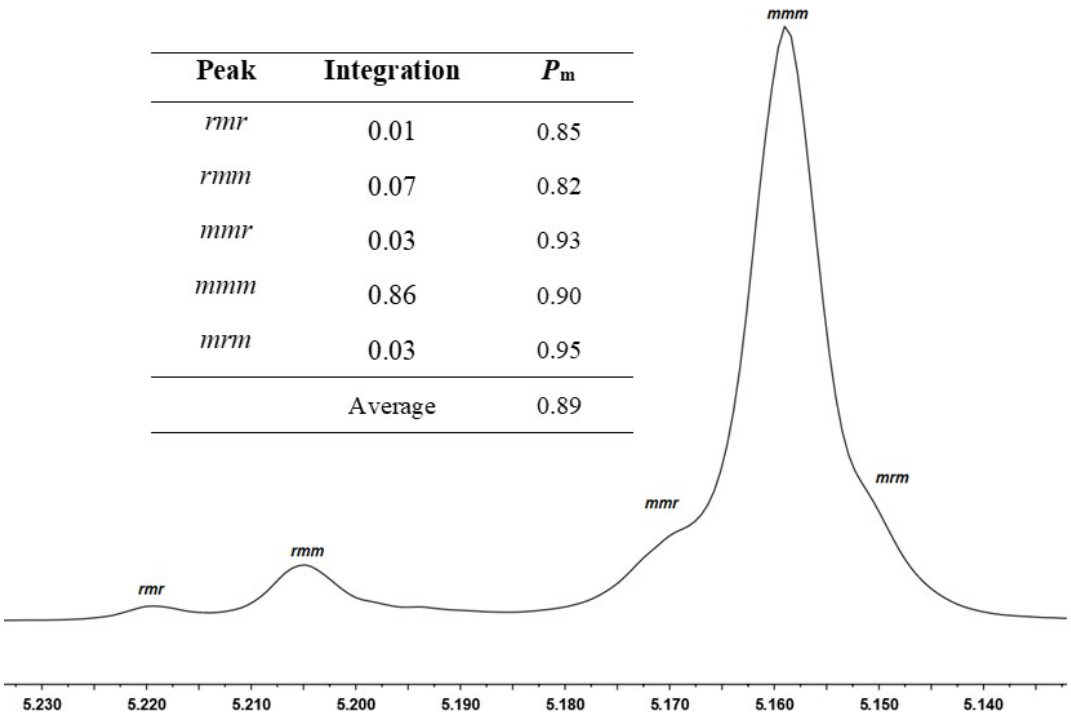
Figure 18. The molecular structures of **6**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) for **6**: Zn1−O1 1.9281(19), Zn1−N1 2.267(2), Zn1−N2 2.051(3), Zn1−N4 1.925(2); O1−Zn1−N1 94.88(9), O1−Zn1−N2 107.54(9), N2−Zn1−N1 80.60(11), N4−Zn1−O1 120.12(10), N4−Zn1−N1 120.96(10), N4−Zn1−N2 123.28(11).

4. Ring-opening polymerization of *rac*-lactide

Table S2. ROPs of *rac*-LA initiated by zinc complexes **1**–**8** in THF[a]

Cat.	Feed ratio	Time (min)	Conv.[b] (%)	$M_{n,calcd}$[c] ($\times 10^4$)	M_n[d] ($\times 10^4$)	M_w/M_n[d]	P_m[e]
1	200:1:0	27	87	2.50	7.08	1.53	0.67
	200:1:1	12	89	2.51	1.85	1.19	0.66
2	200:1:0	40	90	2.59	12.42	1.60	0.76
	200:1:1	13	88	2.54	3.10	1.23	0.75
3	200:1:0	45	90	2.60	4.30	1.28	0.87
	200:1:1	15	90	2.60	3.26	1.11	0.86
4	200:1:0	18	96	2.65	7.99	1.63	0.86
	200:1:1	12	95	2.74	3.03	1.34	0.86
5	200:1:0	14	91	2.62	2.91	1.51	0.85
	200:1:1	9	82	2.37	1.80	1.13	0.86
6	200:1:0	41	70	2.02	11.96	1.38	0.87
	200:1:1	20	86	2.48	3.51	1.19	0.86
7	200:1:0	18	92	2.65	12.84	1.28	0.88
	200:1:1	12	93	2.69	3.27	1.16	0.88
8	200:1:0	15	93	2.68	5.66	1.34	0.86
	200:1:1	11	88	2.54	2.70	1.16	0.86

[a] $[rac\text{-LA}]_0$ = 1.0 M, feed ratio = $[rac\text{-LA}]_0$:$[Zn]_0$:$[^i PrOH]_0$, THF, 25 ℃. [b] Determined by ^1H NMR spectroscopy. [c] $M_{n,calcd} = ([rac\text{-LA}]_0/[Zn]_0) \times 144.13 \times$ Conv.%; with the presence of ^{i}PrOH, $M_{n,calcd} = ([rac\text{-LA}]_0/[^i PrOH]_0) \times 144.13 \times$ Conv.% + 60. [d] Determined by GPC. [e] P_m is the probability of forming a new *m*-dyad, determined by homonuclear decoupled ^1H NMR spectroscopy.



Peak	Integration	P_m
rmr	0.01	0.85
rmm	0.07	0.82
mmr	0.03	0.93
mmm	0.86	0.90
mrm	0.03	0.95
	Average	0.89

Figure S19. Methine region of the homonuclear decoupled ^{1}H NMR spectrum of PLA produced by complex **3** in toluene at 25 ℃ (Table 1, [*rac*-LA]$_0$:[Zn]$_0$:[^{i}PrOH]$_0$ = 200:1:0, $CDCl_3$, 400 MHz).

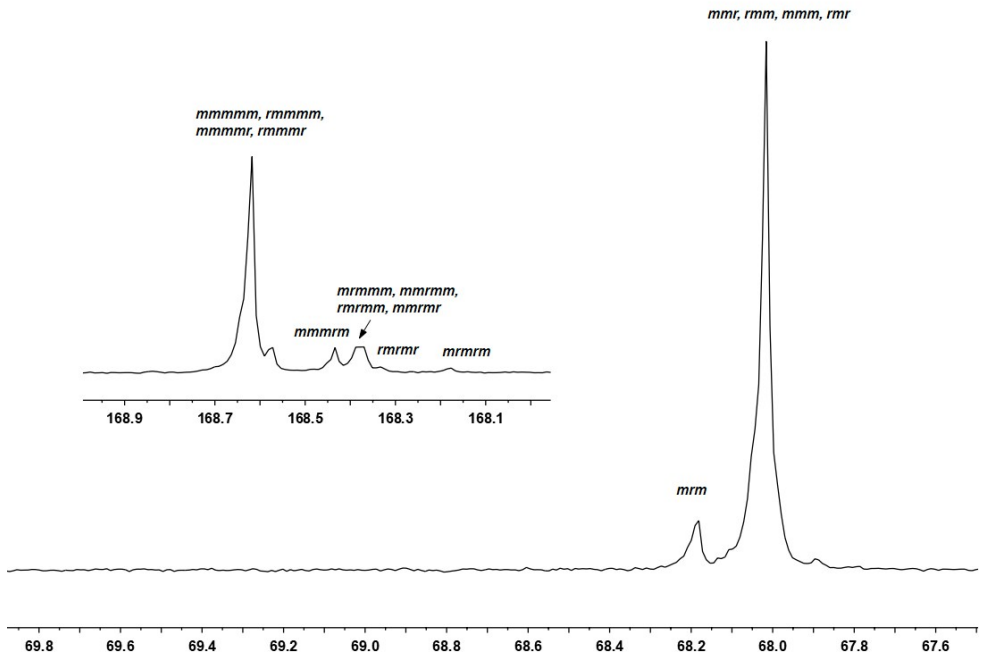


Figure S20. The carbonyl and methine regions of ^{13}C NMR spectrum of PLA produced by complex **3** in toluene at 25 ℃ (Table 1, [*rac*-LA]$_0$:[Zn]$_0$:[^{i}PrOH]$_0$ = 200:1:0, $CDCl_3$, 150 MHz).

Peak	Integration	P_m
rmr	0.01	0.83
rmm	0.08	0.82
mmr	0.03	0.94
mmm	0.85	0.89
mrm	0.03	0.93
	Average	0.88

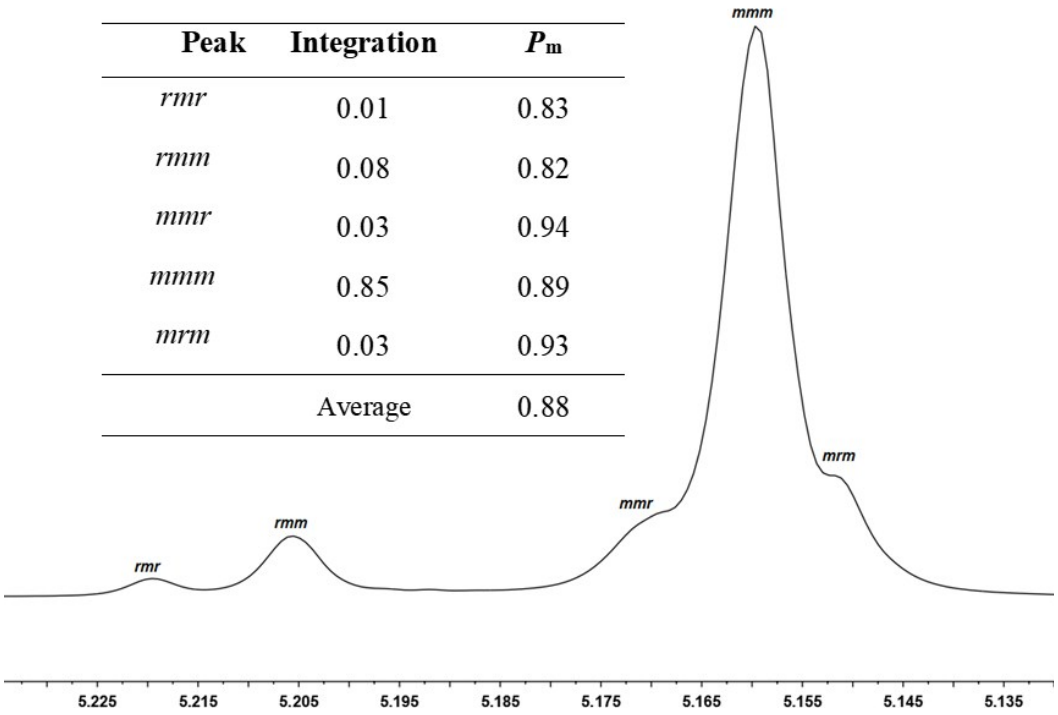


Figure S21. Methine region of the homonuclear decoupled ^{1}H NMR spectrum of PLA produced by complex **4** in toluene at 25 ℃ (Table 1, [*rac*-LA]$_0$:[Zn]$_0$:[^{i}PrOH]$_0$ = 200:1:0, $CDCl_3$, 400 MHz).

Peak	Integration	P_m
rmr	0.01	0.85
rmm	0.07	0.82
mmr	0.03	0.93
mmm	0.86	0.90
mrm	0.03	0.95
	Average	0.89

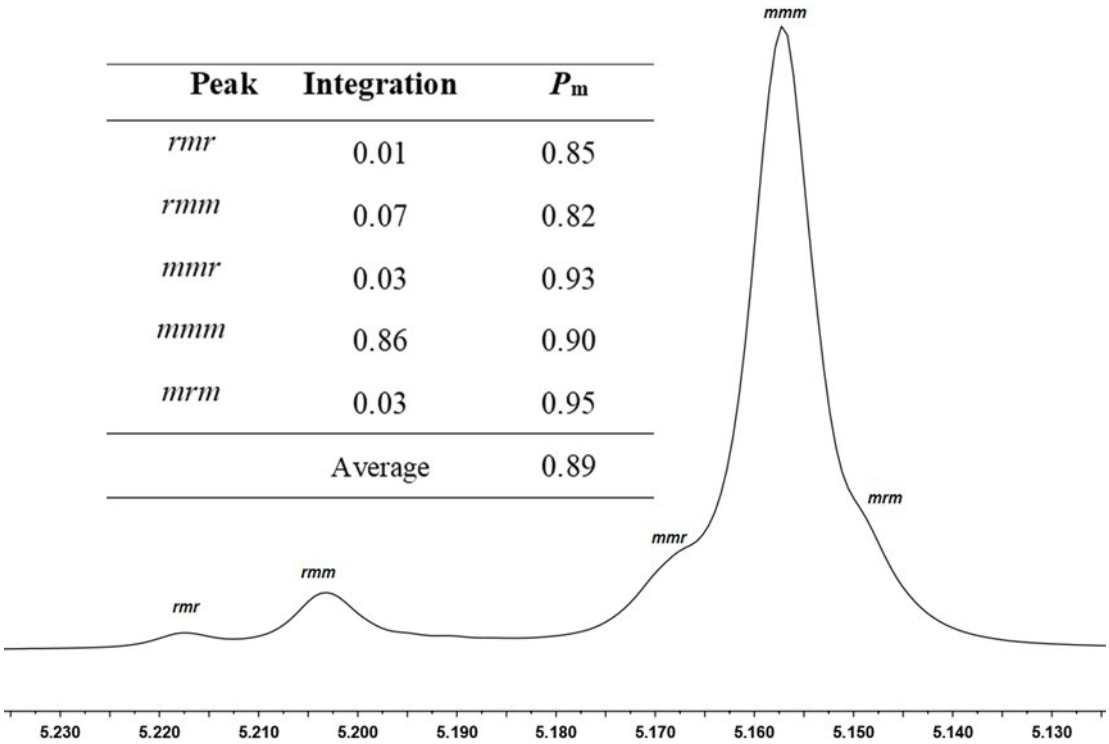


Figure S22. Methine region of the homonuclear decoupled ^{1}H NMR spectrum of PLA produced by complex **6** in toluene at 25 ℃ (Table 1, [*rac*-LA]$_0$:[Zn]$_0$:[^{i}PrOH]$_0$ = 200:1:0, $CDCl_3$, 400 MHz).

Peak	Integration	P_m
rmr	0.01	0.84
rmm	0.07	0.84
mmr	0.04	0.92
mmm	0.85	0.90
mrm	0.03	0.93
	Average	0.89

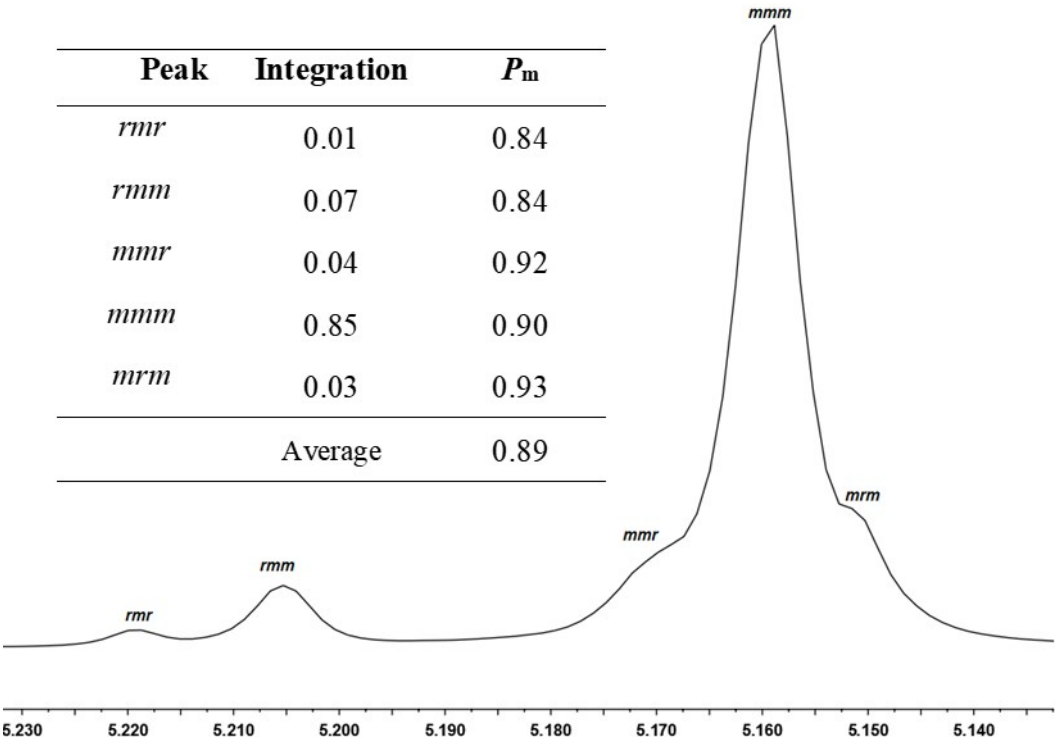


Figure S23. Methine region of the homonuclear decoupled ^{1}H NMR spectrum of PLA produced by complex **7** in toluene at 25 ℃ (Table 1, [*rac*-LA]$_0$:[Zn]$_0$:[^{i}PrOH]$_0$ = 200:1:0, $CDCl_3$, 400 MHz).

Peak	Integration	P_m
rmr	0.02	0.83
rmm	0.06	0.87
mmr	0.02	0.95
mmm	0.89	0.92
mrm	0.02	0.97
	Average	0.91

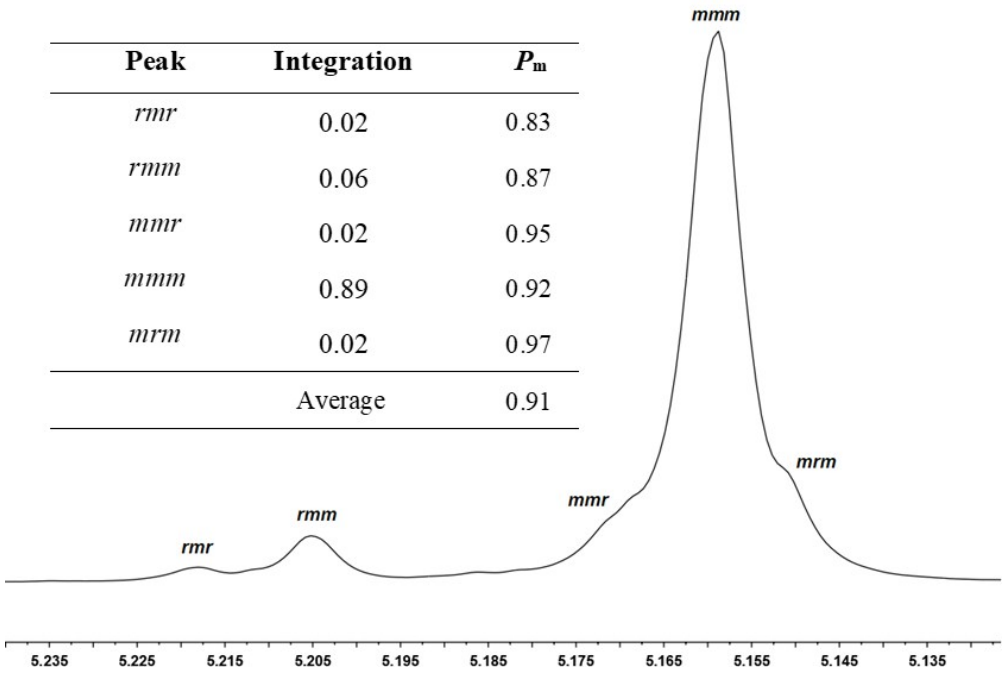


Figure S24. Methine region of the homonuclear decoupled ^{1}H NMR spectrum of PLA produced by complex **7** in toluene at –20 °C (Table 1, $CDCl_3$, 400 MHz).

Peak	Integration	P_m
rmr	0.01	0.88
rmm	0.06	0.86
mmr	0.02	0.96
mmm	0.91	0.94
mrm	0.01	0.99
	Average	0.93

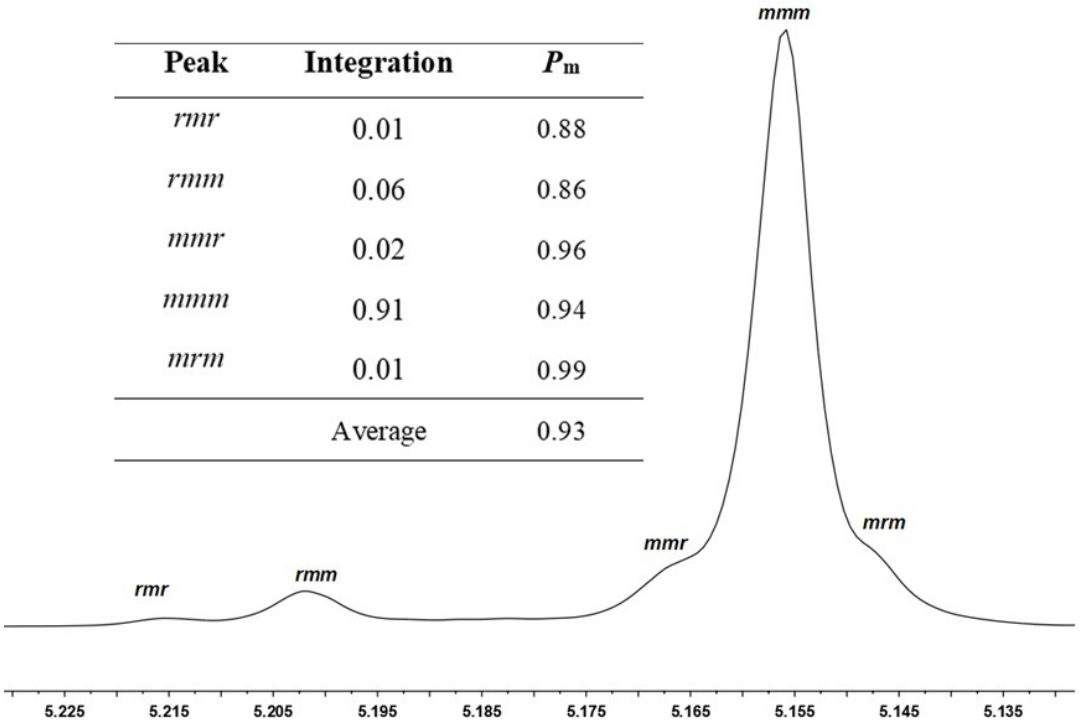


Figure S25. Methine region of the homonuclear decoupled ^{1}H NMR spectrum of PLA produced by complex **7** in toluene at –40 °C (Table 1, $CDCl_3$, 400 MHz).

Peak	Integration	P_m
rmr	0.02	0.80
rmm	0.08	0.78
mmr	0.06	0.86
mmm	0.78	0.85
mrm	0.05	0.89
	Average	0.84

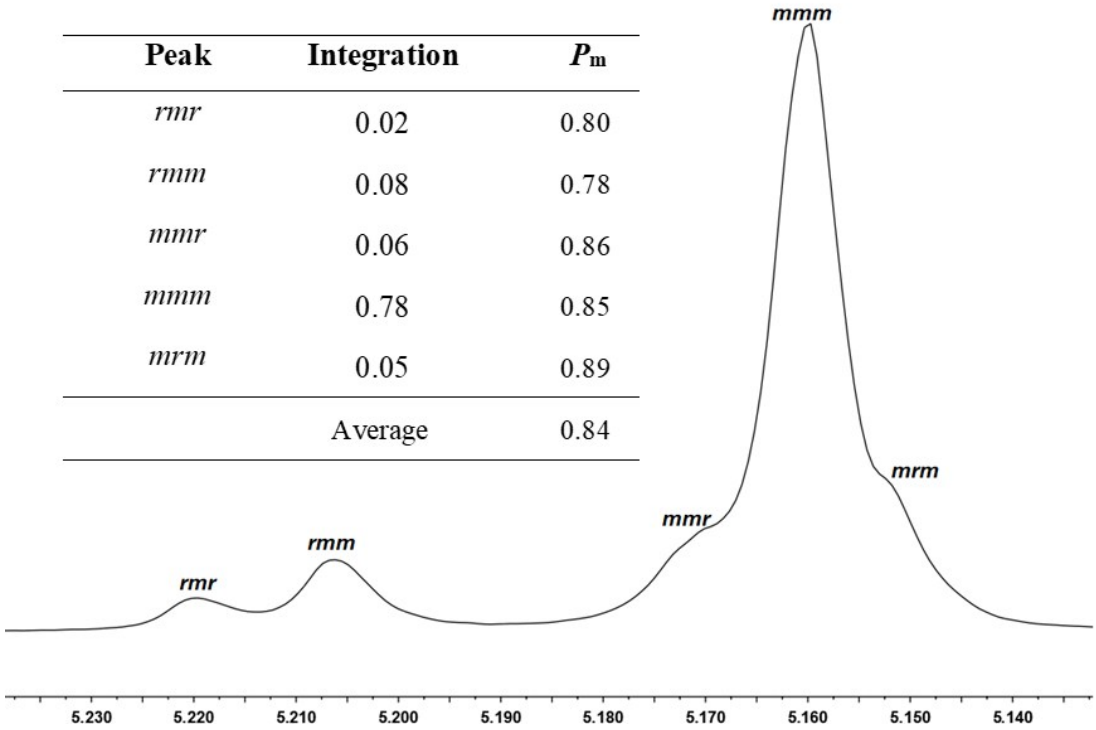


Figure S26. Methine region of homonuclear decoupled ^{1}H NMR spectrum of PLA produced by complex **8**/^{i}PrOH in toluene at 25 ℃ (Table 1, [*rac*-LA]$_0$:[Zn]$_0$:[^{i}PrOH]$_0$ = 200:1:1, $CDCl_3$, 400 MHz).

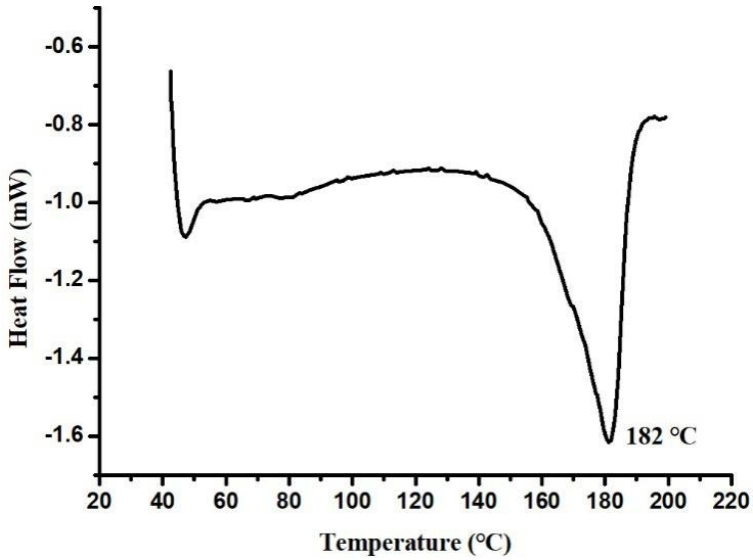


Figure S27. Heat flow *vs*. temperature curve of PLA produced by complex **7** in toluene at –20 °C (Table 1, P_m = 0.91).

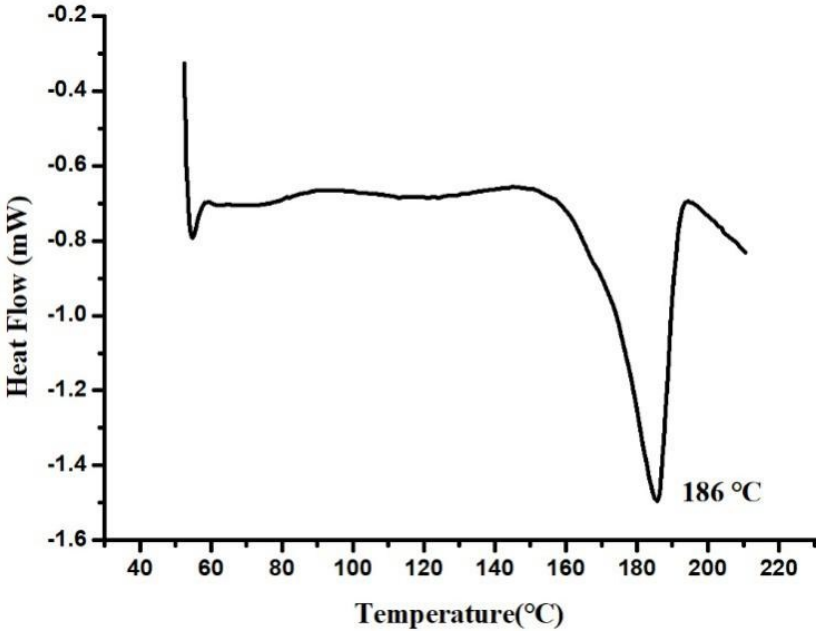


Figure S28. Heat flow *vs*. temperature curve of PLA produced by complex **7** in toluene at –40 °C (Table 1, P_m = 0.93).

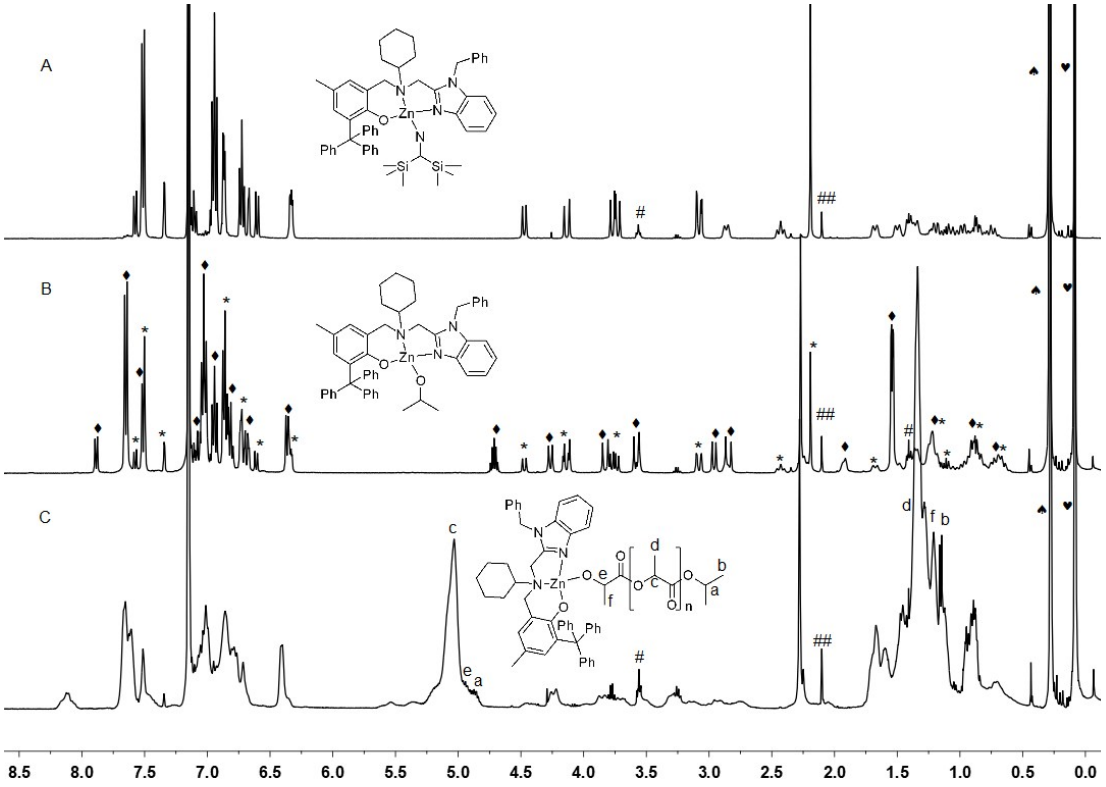


Figure S29. ^{1}H NMR spectrum of A) complex **3**, B) the reaction mixture of complex **3** and ^{i}PrOH (ca. 1:1) and C) the active *rac*-lactide oligomer obtained by complex **3**/^{i}PrOH with 5 equiv. of *rac*-LA (C_6D_6, 400 MHz; ♦, target complex "**L**^{3}ZnO^{i}Pr"; *, the residual complex **3** due to the unsatisfied weighing accuracy of 2-propanol; #, the residual tetrahydrofuran; ##, the residual toluene; ♠, impurity in C_6D_6; ♥, free $HN(SiMe_3)_2$).

The genereation of isopropoxide derivative "**L**^{3}ZnO^{i}Pr" could be confirmed by the facts that: 1) the formation of free ligand **L**^{3}**H** due to the decomposition of the complex **3** is not observed (characterized singlets attributed three methylene units as well as hydroxyl proton are not observed); 2) the disappearance of the Zn–$N(SiMe_3)_2$ signal at δ = 0.30 ppm and the appearance of a new signal at δ = 0.09 ppm attributed to $HN(SiMe_3)_2$ is clear; 3) a new set of resonances attributable to the aminophenolate ligand appears, which is in 1:1 molar ratio with the new signals at around 4.75–4.66 ppm and 1.54 ppm assignable to an isopropoxy group bound to a metal center.

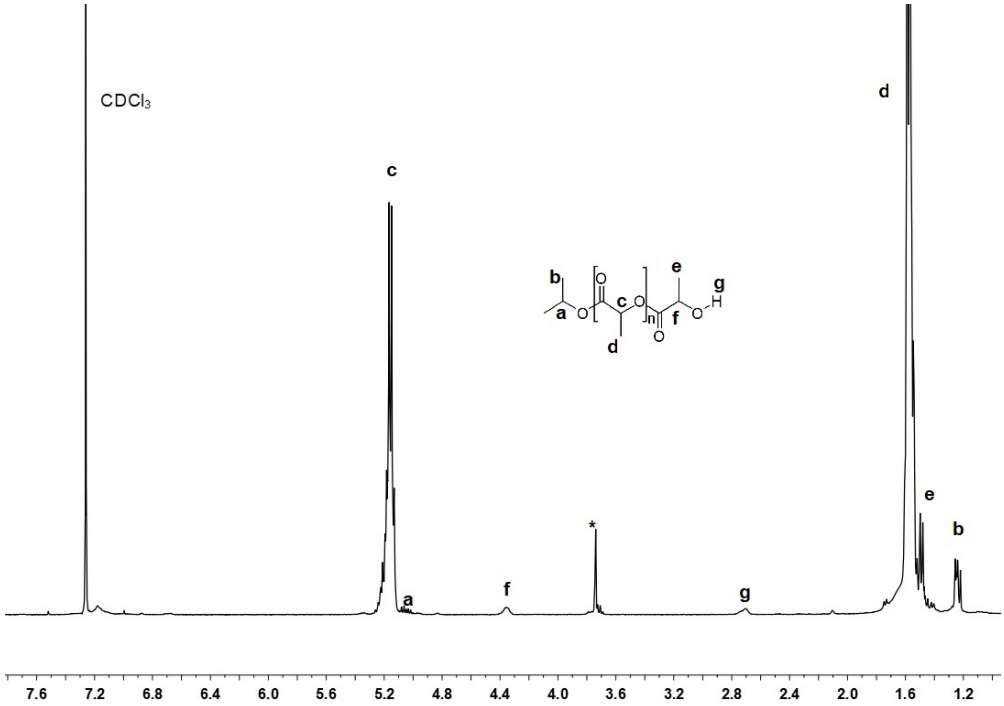


Figure S30. ^{1}H NMR spectrum of PLA oligomer obtained by complex **3**/^{i}PrOH with 5 equiv. of *rac*-LA (25 °C, $CDCl_3$, 400 MHz, *: methyl signal of residual methanol).

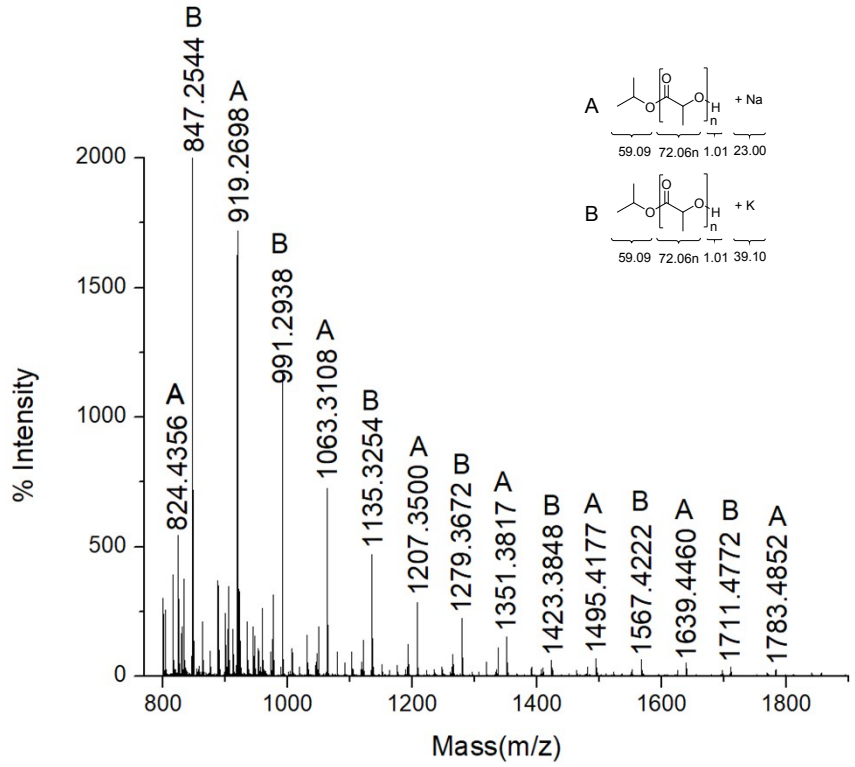


Figure S31. MALDI-TOF mass spectrum of PLA oligomer obtained by complex **3**/^{i}PrOH with 5 equiv. of *rac*-LA.

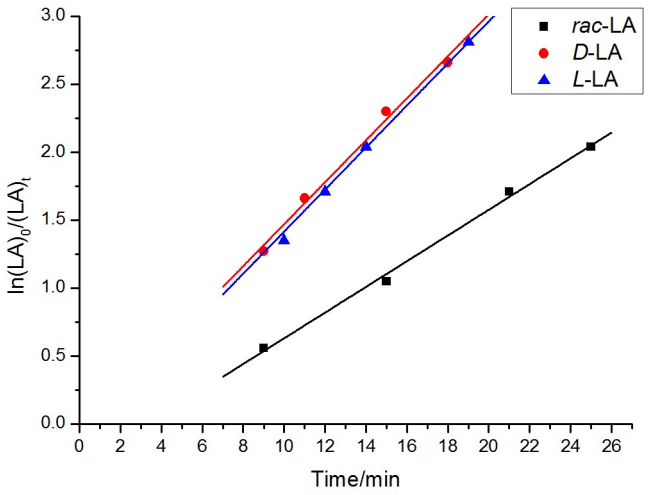


Figure S32. Semilogrithmic plots of lactide conversion versus time of *D*-LA、*L*-LA and *rac*-LA polymerization mediated by complex **8**: *D*-LA (red circles, k_{app}= (1.54 ± 0.09)×10^{-1} min^{-1}, R^2 = 0.996); *L*-LA (blue triangles, k_{app}= (1.55 ± 0.02)×10^{-1} min^{-1}, R^2 = 0.999); *rac*-LA (black squares, k_{app}= (0.95 ± 0.04)×10^{-1} min^{-1}, R^2 = 0.998). Conditions: 25 ℃, $[LA]_0/[Zn]_0/[^iPrOH]_0$ = 200:1:0, $[LA]_0$ = 0.5 M, toluene as solvent.

References

S1. Bürger, H.; Sawodny, W.; Wannagat, U. *J. Organomet. Chem.*, 1965, **3**, 113−120.

S2. Appiah, W.; DeGreeff, A.; Razidlo, G.; Spessard, A.; Pink, M.; Young, V.; Hofmeister, G. *Inorg. Chem.*, 2002, **41**, 3656−3667.

S3. (a) Cohen, A.; Kopilov, J.; Goldberg, I.; Kol, M. *Organometallics*, 2009, **28**, 1391 − 1405; (b) Larrow, J. F.; Jacobsen, E. N.; Gao, Y.; Hong; Y.; Nie, X.; Zepp, C. M. *J. Org. Chem*., 1994, **59**, 1939–1942.

S4. Rao, S. S.; Reddy, C. V. R.; Dubey, P. K. *Asian J. Chem*., 2015, **27**, 98−100.

S5. G. M. Sheldrick, SHELXTL 5.10 for windows NT, Structure Determination Software Programs, Bruker Analytical X-ray Systems, Inc., Madison, WI, **1997**.

S6. SAINT, Version 6.02, Bruker AXS Inc., Madison, WI, **1999**.

S7. L. J. Farrugia, *J. Appl. Crystallogr.* 1997, **30**, 565. ORTEP-III for Windows-Version 2.0, University of Glasgow, **2008**.