Supporting Information

Diastereoselective Synthesis of Chiral Aminophenolate Magnesium Complexes and Their Application in the Stereoselective Polymerization of *rac*-Lactide and *rac*-β-Butyrolactone

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Contents:

1. Experimental Section

1.1 General considerations

Unless otherwise indicated, all manipulations involving air- and/or water-sensitive substances were carried out under a dry argon atmosphere using either an MBraun glove-box or standard Schlenk techniques. THF, toluene and *n*-hexane were refluxed over sodium benzophenone ketyl prior to use. Benzene-d_6 were properly dried and stored in the glove-box. 2-Propanol were dried over CaH_2 under reflux, collected by vacuum distillation and degassed through three freeze-pump-thaw cycles. $Mg[N(SiMe_3)_2]_2$ were synthesized according to the literature method.[S1] (*R*)-(1-alkylpyrrolidin-2-yl)methanamine were synthesized according to the reported procedures.[S2] *rac*-LA were recrystallized with dry toluene and then sublimed twice under vacuum at 90 °C. Glassware and vials used in the polymerization were dried in an oven at 120°C overnight and exposed to vacuum-argon cycle three times.

NMR spectra were recorded on a Bruker Avance-400 spectrometer. Chemical shifts for ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced internally using the residual solvent resonances and reported relative to tetramethylsilane (TMS). EA analyses were performed using a Carlo Erba EA1106 elemental analyzer. Gel permeation chromatography (GPC) analyses were carried out on a Waters 1515 infinity instrument in THF at 35 °C, at a flow rate of 1 $mL \cdot min^{-1}$, with two PLgel 5 μm Mixed-C columns (7.5 × 300 mm). Calibration standards were commercially available narrowly distributed linear polystyrene samples that cover a broad range of molar masses ($6 \times 10^3 < M_n < 6.6 \times 10^5$ $g \cdot mol^{-1}$). Monomer conversion determination was monitored by integration of monomer *vs.* polymer methine resonances in ^1H NMR spectra. All spectroscopic analyses of polymers and homonuclear decoupled ^1H NMR spectra were performed in $CDCl_3$ on a Bruker Avance 400 MHz spectrometer with acryoprobe.

1.2 Synthesis of chiral aminophenol ligands $L^{2,5\&9}H$.

Synthesis of chiral aminophenol ligands $\mathbf{L^{1,3,4,6\text{-}8\&10}H}$ see our submitted result.[S2]

1.2.1 Synthesis of (*S*)-*N*-alkyl-1-(1-alkylpyrrolidin-2-yl)methanamine

(*S*)-(1-^{n}Butylpyrrolidin-2-yl)methanamine (2.34 g, 0.015 mol) was added to a solution of benzaldehyde (1.75 g, 0.017 mol) in ethanol (20 mL) and the mixture was heated to reflux for 24 h. After cooling to r.t., sodium borohydride (1.33 g, 0.035 mmol) was sequentially added to the above light yellow solution in three times and the mixture was stirred for 3 h at 60 °C. The mixture was poured into water and extracted with methylene dichloride. The organic phase was dried over anhydrous $MgSO_4$. Evaporation of the solvent gave the target product as viscous oil (2.96 g), which was used directly for the next step without further purification. (*S*)-*N*-benzyl-1-(1-^{n}octylpyrrolidin-2-yl) methanamine, and (*S*)-*N*-

methyl-1'-napthyl-1-(1-^{n}octylpyrrolidin-2-yl)methanamine were produced using the same procedure.

1.2.2 Synthesis of $L^{2,5\&9}H$

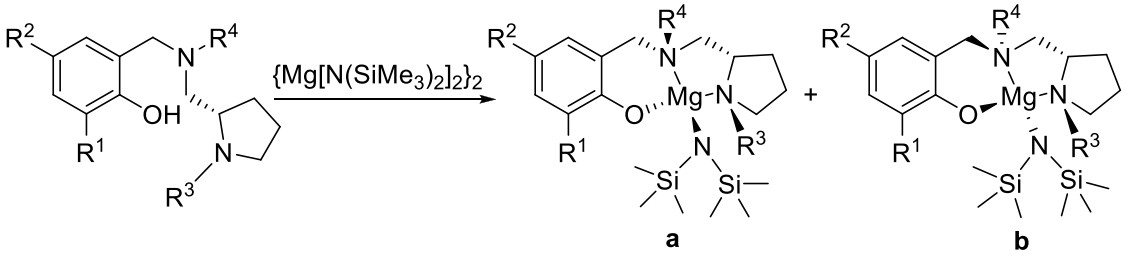
(**$L^{2}H$**). Paraformaldehyde (0.600 g, 20.0 mmol) and 2, 4-dichlorophenol (1.63 g, 10.0 mmol) was added to a solution of (*S*)-*N*-benzyl-1-(1-^{n}octylpyrrolidin-2-yl)methanamine (2.74 g，10.0 mmol) in ethanol (30 mL) at 90 °C during 12 h with magnetic stirring. The mixture was cooled to ambient temperature and concentrated under vacuum to give red oil, which was purified by column chromatography (silica gel 100 Merck, petroleum ether/ethyl acetate = 5 : 1) to provide dark red oil (2.41 g, 50.5%) after removal of all the volatiles. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.23 (m, 6H, Ar*H*), 6.90 (d, ^{4}J = 2.4 Hz, 1H, Ar*H*), 3.90 (d, ^{2}J = 14.1 Hz, 1H, ArCH_2N), 3.72 (d, ^{2}J = 13.0 Hz, 1H, ArCH_2N), 3.61 (d, ^{2}J = 14.1 Hz, 1H, ArCH_2N), 3.47 (d, ^{2}J = 13.0 Hz, 1H, ArCH_2N), 3.14-3.05 (m, 1H, NCH_2- of pyrrolidinyl), 2.67-2.60 (m, 1H, NC*H*- of pyrrolidinyl), 2.60-2.45 (m, 3H, NCH_2- of pyrrolidinyl & NCH_2CH), 2.14-2.03 (m, 2H, NC$H_2(CH_2)_6CH_3$), 2.04-1.92 (m, 1H, -CH_2- of pyrrolidinyl), 1.72-1.61 (m, 2H, -CH_2- of pyrrolidinyl), 1.49-1.34 (m, 3H, -CH_2- of pyrrolidinyl & $NCH_2CH_2(CH_2)_5CH_3$), 1.33-1.18 (m, 10H, $NCH_2CH_2(CH_2)_5CH_3$), 0.89 (t, ^{3}J = 7.3 Hz, 3H, $NCH_2(CH_2)_6CH_3$). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 152.6, 136.2, 123.0, 128.9, 128.8, 128.1, 127.3, 125.0, 123.5, 121.8 (All Ar*C*), 62.9 (Ar*C*H_2N), 59.3 (Ar*C*H_2N), 58.3 (N*C*H- of pyrrolidinyl), 57.9 (N*C*H_2- of pyrrolidinyl), 55.7 (N*C*H_2CH), 54.2 (N*C*$H_2(CH_2)_6CH_3$), 32.0 ($NCH_2CH_2(CH_2)_5CH_3$), 30.2 ($NCH_2(CH_2)_6CH_3$), 29.6 ($NCH_2(CH_2)_6CH_3$), 29.4 (-*C*H_2- of pyrrolidinyl), 28.8 ($NCH_2(CH_2)_6CH_3$), 27.8 ($NCH_2(CH_2)_6CH_3$), 22.8 ($NCH_2(CH_2)_6CH_3$), 22.7 (-*C*H_2- of pyrrolidinyl), 14.3 ($NCH_2(CH_2)_6CH_3$). Anal. Calcd. for $C_{27}H_{38}Cl_2N_2O$: C, 67.91; H, 8.02; N, 5.87. Found: C, 68.02; H, 8.02; N, 5.51%.

(**$L^{5}H$**) The procedure was same as that of **$L^{2}H$**, except that 2-triphenylsilyl-4-methylphenol (3.66 g, 10.0 mmol) and (*S*)-*N*-(methyl-1-napthyl)-1-(1-^{n}butylpyrrolidin-2-yl)methanamine (10.0 mmol) were used to afford **$L^{10}H$** as a white solid (3.19 g，51.0%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.73 (s, 1H, ArO*H*), 7.65 (d, 6H, ^{3}J = 6.6 Hz, Ar*H*), 7.42-7.30 (m, 9H, Ar*H*), 7.23-7.16 (m, 3H, Ar*H*), 7.09 (d, 2H, ^{3}J = 7.3 Hz, Ar*H*), 6.94 (s, 1H, Ar*H*), 6.90 (s, 1H, Ar*H*), 3.91 (d, 1H, ^{2}J = 13.6 Hz, ArCH_2N), 3.64 (d, 1H, ^{2}J = 13.6 Hz, ArCH_2N), 3.62 (d, 1H, ^{2}J = 13.0 Hz, ArCH_2N), 3.43 (d, 1H, ^{2}J = 13.0 Hz, ArCH_2N), 3.02-2.91 (m, 1H, NCH_2- of pyrrolidinyl), 2.58 (m, 1H, NC*H*- of pyrrolidinyl), 2.45 (m, 2H, NC$H_2CH_2CH_2CH_3$ & NCH_2CH), 2.41-2.31 (m, 1H, NCH_2- of pyrrolidinyl), 2.14 (s, 3H, ArCH_3), 2.02-1.91 (m, 2H, NC$H_2CH_2CH_2CH_3$ & NCH_2CH), 1.72-1.58 (m, 1H, -CH_2- of pyrrolidinyl), 1.52-1.39 (m, 2H, -CH_2- of pyrrolidinyl), 1.39-1.28 (m, 2H, -CH_2- of pyrrolidinyl & $NCH_2CH_2CH_2CH_3$), 1.28-1.12 (m, 3H, $NCH_2CH_2CH_2CH_3$), 0.85 (t, 3H, ^{3}J = 7.6 Hz, $NCH_2CH_2CH_2CH_3$). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 160.9, 138.0, 137.5, 136.7, 135.7, 132.7, 130.2, 129.2, 128.5, 127.7, 127.5, 121.8, 120.2(All Ar*C*), 63.1 (Ar*C*H_2N), 59.6 (Ar*C*H_2N), 59.4

(NCH- of pyrrolidinyl), 57.2 (NCH$_2$- of pyrrolidinyl), 55.3 (NCH$_2$CH), 54.3 (NCH$_2$CH$_2$CH$_2$CH$_3$), 30.9 (NCH$_2$CH$_2$CH$_2$CH$_3$), 29.8 (-CH$_2$- of pyrrolidinyl), 22.5 (-CH$_2$- of pyrrolidinyl), 21.0 (ArCH$_3$), 20.8 (NCH$_2$CH$_2$CH$_2$CH$_3$), 14.2 (NCH$_2$CH$_2$CH$_2$CH$_3$). Anal. Calcd. for $C_{42}H_{48}N_2OSi$: C, 80.72; H, 7.74; N, 4.48. Found: C, 80.51; H, 7.62; N, 4.32%.

(**L^{9}H**) The procedure was same as that of **L^{2}H**, except that 2-trityl-4-methylphenol (3.50 g, 10.0 mmol) and (*S*)-*N*-(methyl-1-napthyl)-1-(1-^{n}octylpyrrolidin-2-yl)methanamine (10.0 mmol) were used to afford **L^{9}H** as a white solid (3.12 g, 50%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.26 (s, 1H, ArOH), 7.86 (d, *J* = 8.4 Hz, 1H, ArH), 7.81 (d, *J* = 7.8 Hz, 1H, ArH), 7.73 (d, *J* = 8.2 Hz, 1H, ArH), 7.46–7.36 (m, 2H), 7.32 (dd, *J* = 12.8, 4.7 Hz, 1H, ArH), 7.25–7.22 (m, 6H, ArH), 7.17–7.10 (m, 10H, ArH), 6.95 (d, *J* = 1.6 Hz, 2H, ArH), 6.88 (d, *J* = 1.6 Hz, 2H, ArH), 4.05 (d, *J* = 13.1 Hz, 1H, ArCH$_2$N), 3.81 (d, *J* = 13.1 Hz, 1H, ArCH$_2$N), 3.71(d, *J* = 13.5 Hz, 1H, ArCH$_2$N), 3.62 (d, *J* = 13.5 Hz, 1H, ArCH$_2$N), 2.86–2.73 (m, 1H, NCH- of pyrrolidinyl), 2.56–2.36 (m, 3H, NCH$_2$CH & NCH$_2$- of pyrrolidinyl), 2.18 (s, 3H, ArCH$_3$), 2.15–2.08 (m, 1H, NCH$_2$- of pyrrolidinyl), 1.87–1.68 (m, 2H, NCH$_2$(CH$_2$)$_6$CH$_3$), 1.34–1.14 (m, 12H, NCH$_2$(CH$_2$)$_6$CH$_3$), 1.14–1.07 (m, 2H, -CH$_2$- of pyrrolidinyl), 1.07–1.00 (m, 2H, -CH$_2$- of pyrrolidinyl), 0.89 (t, *J* = 7.0 Hz, 3H, NCH$_2$(CH$_2$)$_6$CH$_3$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 153.9, 146.3, 133.8, 133.7, 133.6, 132.6, 131.3, 131.1, 130.9, 129.6, 128.6, 128.5, 127.9, 127.9, 126.9, 126.3, 126.1, 125.5, 125.3, 125.2, 123.8, 123.2 (All ArC), 63.8(ArCPh$_3$), 63.5(ArCH$_2$N), 60.0(ArCH$_2$N), 55.9(ArCH$_2$N), 55.8(NCH- of pyrrolidinyl), 55.3(NCH$_2$- of pyrrolidinyl), 54.0(ArCH$_2$N), 31.9(CH$_2$CH$_2$(CH$_2$)$_5$CH$_3$), 29.5(-CH$_2$- of pyrrolidinyl), 29.4(-CH$_2$- of pyrrolidinyl), 28.7(CH$_2$CH$_2$(CH$_2$)$_5$CH$_3$), 28.2(CH$_2$CH$_2$(CH$_2$)$_5$CH$_3$), 27.7(CH$_2$CH$_2$(CH$_2$)$_5$CH$_3$), 22.8(CH$_2$CH$_2$(CH$_2$)$_5$CH$_3$), 22.1(CH$_2$CH$_2$(CH$_2$)$_5$CH$_3$), 21.0(CH$_2$CH$_2$(CH$_2$)$_5$CH$_3$), 14.2(CH$_2$CH$_2$(CH$_2$)$_5$CH$_3$). Anal. Calcd. for $C_{51}H_{58}N_2O$: C, 85.67; H, 8.18; N, 3.92; Found: C, 85.17; H, 7.87; N, 3.54 %

1.3 Synthesis of chiral magnesium aminophenolate complexes 1-10



(*S*)-**L^{1}H**: $R^1 = R^2 = Cl$, $R^3 = {}^n$Bu, R^4 = Bn — **Mg1** (**a** : **b** = 1 : 1.8)
(*S*)-**L^{2}H**: $R^1 = R^2 = Cl$, $R^3 = {}^n$Octyl, R^4 = Bn — **Mg2** (**a** : **b** = 1 : 2)
(*S*)-**L^{3}H**: $R^1 = R^2$ = Me, $R^3 = {}^n$Bu, R^4 = Bn — **Mg3** (**a** : **b** = 1 : 1.3)
(*S*)-**L^{4}H**: $R^1 = R^2 = {}^t$Bu, $R^3 = {}^n$Bu, R^4 = Bn — **Mg4** (**a** : **b** = 1 : 1.25)
(*S*)-**L^{5}H**: R^1 = Triphenylsilyl , R^2 = Me, $R^3 = {}^n$Bu, R^4 = Bn — **Mg5**(**a** : **b** = 5.7 : 1)
(*S*)-**L^{6}H**: R^1 = Trityl, R^2 = Me, $R^3 = {}^n$Octyl, R^4 = Bn — **Mg6** (**a** : **b** = 7 : 1)
(*S*)-**L^{7}H**: R^1 = Trityl, R^2 = Me, R^3 = Bn, R^4 = Bn — **Mg7** (**a** : **b** = 2.5 : 1)
(*S*)-**L^{8}H**: R^1 = Trityl, $R^2 = CH_3$, $R^3 = {}^n$Bu, R^4 = naphthalen-1-ylmethyl — **Mg8(Enantiopure)**
(*S*)-**L^{9}H**: R^1 = Trityl, $R^2 = CH_3$, $R^3 = {}^n$Octyl, R^4 = naphthalen-1-ylmethyl — **Mg9(Enantiopure)**
(*S*)-**L^{10}H**: $R^1 = R^2$ = Cumyl, R^3 = Et, R^4 = Bn — **Mg10** (**a** : **b** = 1 : 2)

[**(L^1)MgN($SiMe_3$)$_2$**](**1**). In a glove box, the aminophenol **L^1H** (0.632 g, 1.50 mmol) was dissolved in toluene (3 mL) and was added dropwise to a solution of Mg[N($SiMe_3$)$_2$]$_2$ (0.520 g, 1.50 mmol) in *n*-hexane (3 mL). The reaction mixture was stirred at room temperature overnight, whereas a white precipitate was formed. After filtration, the collected white precipitate was washed with cold *n*-hexane (3 × 2 mL) and dried under vacuum to afford the target complex **1** in 60.6% (0.550 g) as a mixture of two diastereomers in 1 : 2 ratio (isomer **1a** : isomer **1b**). NMR spectroscopic data of **Mg1b**: ^{1}H NMR (400 MHz, C_6D_6): δ 7.35 (d, ^4J = 2.8 Hz, 1H, Ar*H*), 7.11-7.00 (m, 5H, Ar*H*), 6.46 (d, ^4J = 2.8 Hz, 1H, Ar*H*), 3.77 (d, ^2J = 13.6 Hz, 1H, ArCH_2N), 3.51 (d, ^2J = 12.8 Hz, 1H, ArCH_2N), 3.32 (d, ^2J = 13.6 Hz, 1H, ArCH_2N), 2.59 (d, ^2J = 12.8 Hz, 1H, ArCH_2N), 2.48-2.39 (m, 1H, NC*H*- of pyrrolidinyl), 2.37-2.27 (m, 2H, NCH_2CH_2CH_2CH_3), 2.19 (td, ^2J = 11.9, ^3J = 3.9 Hz, 1H, NCH_2- of pyrrolidinyl), 2.01-1.92 (m, 1H, NCH_2- of pyrrolidinyl), 1.89 (dd, ^2J = 13.6, ^3J = 13.6 Hz, 1H, NCH_2CH), 1.47 (dd, ^2J = 13.6, ^3J = 4.4 Hz, 1H, NCH_2CH), 1.43-1.19 (m, 2H, NCH$_2$CH_2CH$_2$CH$_3$), 1.19-0.99 (m, 2H, NCH$_2$CH$_2$CH_2CH$_3$), 0.98-0.92 (m, 1H, -CH_2- of pyrrolidinyl), 0.89 (t, ^3J = 7.2 Hz, 3H, NCH$_2$CH_2CH$_2$CH$_3$), 0.81-0.74 (m, 1H, -CH_2- of pyrrolidinyl), 0.43 (s, 18H, Si(CH_3)$_3$), 0.36-0.24 (m, 2H, -CH_2- of pyrrolidinyl). ^{13}C {^{1}H} NMR (100 MHz, C_6D_6): δ 161.6, 132.9, 132.4, 131.6, 130.7, 129.4, 129.3, 129.0, 125.6, 117.2 (All Ar*C*), 65.5 (Ar*C*H$_2$N), 63.6 (Ar*C*H$_2$N), 59.7 (N*C*H- of pyrrolidinyl), 58.8 (N*C*H$_2$- of pyrrolidinyl), 55.7 (N*C*H$_2$CH), 50.6 (N*C*H$_2$CH$_2$CH$_2$CH$_3$), 31.4 (NCH$_2$*C*H$_2$CH$_2$CH$_3$), 25.9 (-*C*H$_2$- of pyrrolidinyl), 21.1 (-*C*H$_2$- of pyrrolidinyl), 20.9 (NCH$_2$*C*H$_2$CH$_2$CH$_3$), 14.5 (NCH$_2$CH$_2$CH$_2$*C*H$_3$), 7.3 (Si(*C*H$_3$)$_3$). Anal. Calcd. for $C_{29}H_{47}Cl_2MgN_3OSi_2$: C, 57.56; H, 7.83; N, 6.94. Found: C, 57.39; H, 7.55; N, 6.66%.

[**(L^2)MgN($SiMe_3$)$_2$**](**2**). The procedure was same as that of **[(L^1)MgN($SiMe_3$)$_2$](1)**, except that **L^2H** (0.716 g, 1.50 mmol) and Mg[N($SiMe_3$)$_2$]$_2$ (0.517 g, 1.50 mmol) were used to afford white precipitate target complex **2** in 35% (0.357 g) as a mixture of two diastereomers in 1 : 2 ratio (isomer **2a** : isomer **2b**). NMR spectroscopic data of **Mg2b**: ^{1}H NMR (400 MHz, C_6D_6): ^{1}H NMR (400 MHz, C_6D_6): δ 7.44 (d, ^4J = 2.7 Hz, 1H, Ar*H*), 7.20–7.17 (m, 2H, Ar*H*), 7.13–7.10 (m, 3H, Ar*H*), 6.56 (d, ^4J = 2.7 Hz, 1H, Ar*H*), 3.86 (d, ^2J = 13.5 Hz, 1H, ArCH_2N), 3.61 (d, ^2J = 13.0 Hz, 1H, ArCH_2N), 3.45 (d, ^2J = 13.5 Hz, 1H, ArCH_2N), 2.72 (d, ^2J = 13.0 Hz, 1H, ArCH_2N), 2.60-2.43 (m, 3H, NCH$_2$*CH* & N*CH*$_2$(CH$_2$)$_6$CH$_3$), 2.32 (dd, ^2J = 17.3, ^2J = 5.8 Hz, 1H, NCH_2- of pyrrolidinyl), 2.21–2.11 (m, 1H, NCH_2- of pyrrolidinyl), 2.00 (t, ^2J = ^3J =13.5 Hz, 1H, NCH_2CH), 1.90-1.70 (m, 2H, NCH$_2$CH_2(CH$_2$)$_5$CH$_3$), 1.57 (dd, ^2J = 13.5, ^3J = 4.3 Hz, 1H, NCH_2CH), 1.44–1.17 (m, 10H, NCH$_2$(CH_2)$_6$CH$_3$), 1.15–1.00 (m, 2H, -CH_2- of pyrrolidinyl), 0.96–0.93 (m, 3H), 0.53 (s, 18H, Si(CH_3)$_3$), 0.45–0.40 (m, 2H, -CH_2- of pyrrolidinyl). ^{13}C {^{1}H} NMR (100 MHz, C_6D_6): δ 161.3, 132.6, 132.0, 131.2, 130.4, 129.0, 128.6, 125.2, 124.9, 116.8 (All Ar*C*), 65.1 (Ar*C*H$_2$N), 63.1 (Ar*C*H$_2$N), 59.4 (N*C*H- of pyrrolidinyl), 58.3 (N*C*H$_2$- of pyrrolidinyl), 55.8 (N*C*H$_2$CH), 50.4 (N*C*H$_2$(CH$_2$)$_6$CH$_3$), 32.2 (NCH$_2$*C*H$_2$(CH$_2$)$_5$CH$_3$), 29.8 (NCH$_2$(*C*H$_2$)$_6$CH$_3$), 29.6 (NCH$_2$(*C*H$_2$)$_6$CH$_3$),

29.0 ($NCH_2(CH_2)_6CH_3$), 27.5 (-CH_2- of pyrrolidinyl), 25.5 ($NCH_2(CH_2)_6CH_3$), 23.1 (-CH_2- of pyrrolidinyl), 20.6 ($NCH_2(CH_2)_6CH_3$), 14.4 ($NCH_2(CH_2)_6CH_3$), 7.0 ($Si(CH_3)_3$). Anal. Calcd. for $C_{33}H_{55}Cl_2N_3OSi_2Zn$: C, 59.95; H, 8.38; N, 6.36. Found: C, 59.63; H, 8.32; N, 6.10%.

[**(L^3)MgN($SiMe_3$)$_2$**](**3**). The procedure was same as that of **[(L^3)MgN($SiMe_3$)$_2$](1)**, except that **L^3H** (0.761 g, 2.00 mmol) and $Mg[N(SiMe_3)_2]_2$ (0.690 g, 2.00 mmol) were used to afford the target complex **3** as a colorless crystal in 64% (0.715 g) as a mixture of two diastereomers in 1 : 1.3 ratio (isomer **3a** : isomer **3b**). NMR spectroscopic data for **Mg3b**: ^{1}H NMR (400 MHz, C_6D_6): δ 7.28–7.24 (m, 1H, Ar*H*), 7.19–7.10 (m, 1H, Ar*H*), 7.13–7.09 (m, 1H, Ar*H*), 7.06 (br s, 2H, Ar*H*), 6.87 (d, ^4J = 2.0 Hz, 1H, Ar*H*), 6.54 (d, ^4J = 2.0 Hz, 1H, Ar*H*), 4.02 (d, ^2J = 13.5 Hz, 1H, ArCH_2N), 3.84 (d, ^2J = 12.6 Hz, 1H, ArCH_2N), 3.60 (d, ^2J = 13.5 Hz, 1H, ArCH_2N), 3.07 (d, ^2J = 12.6 Hz, 1H, ArCH_2N), 2.78–2.65 (m, 3H, NCH_2CH & $NCH_2CH_2CH_2CH_3$), 2.50 (s, 3H, Ar-CH_3), 2.45–2.38 (m, 1H, NCH_2- of pyrrolidinyl), 2.27 (s, 3H, Ar-CH_3), 2.20-2.15 (m, 1H, NCH_2- of pyrrolidinyl), 1.90–1.75 (m, 2H, NCH_2CH), 1.40–1.10 (m, 4H, $NCH_2CH_2CH_2CH_3$), 0.97 (t, ^3J = 7.0 Hz, 3H, $NCH_2CH_2CH_2CH_3$), 0.80–0.65 (m, 2H, -CH_2- of pyrrolidinyl), 0.46–0.40 (m, 2H, -CH_2- of pyrrolidinyl). ^{13}C {^{1}H} NMR (100 MHz, C_6D_6): δ 163.5, 133.1, 132.6, 132.2, 131.5, 129.3, 128.8, 128.7, 127.1, 121.3, 121.1 (All Ar*C*), 64.9 (ArCH_2N), 60.0 (ArCH_2N), 58.2 (N*C*H- of pyrrolidinyl), 55.3 (NCH_2- of pyrrolidinyl), 50.5 (NCH_2CH), 48.1 (N$CH_2CH_2CH_2CH_3$), 30.8 ($NCH_2CH_2CH_2CH_3$), 25.7 (-CH_2- of pyrrolidinyl), 20.9 (ArCH_3), 20.8 (-CH_2- of pyrrolidinyl), 20.7 (ArCH_3), 17.7 ($NCH_2CH_2CH_2CH_3$), 14.1 ($NCH_2CH_2CH_2CH_3$), 7.0 ($N(Si(CH_3)_3)_2$). Anal. Calcd. For $C_{31}H_{53}N_3OSi_2Mg$: C, 65.99; H, 9.47; N, 7.45. Found: C, 65.57; H, 9.16; N, 6.86%.

[**(L^4)MgN($SiMe_3$)$_2$**](**4**). In a glove box, the aminophenol **L^4H** (0.697 g, 1.50 mmol) was dissolved in toluene (3 mL) and was cannulated to a solution of $Mg[N(SiMe_3)_2]_2$ (0.517 g, 1.50 mmol) in *n*-hexane (3 mL). The reaction mixture was allowed to be stirred at room temperature overnight. The solvent and volatile components were removed under reduced pressure to afford a white vesicular solid which was then recrystallized with a mixture of *n*-hexane and toluene. The resulting colorless crystals were washed with cold *n*-hexane three times and dried under vacuum to afford the target complex **4** in 58% (0.568 g) as a mixture of two diastereomers in 1 : 1.25 ratio (isomer **4a** : isomer **4b**). NMR spectroscopic data for isomer **4b**: ^{1}H NMR (400 MHz, C_6D_6): δ 7.64 (s, 1H, Ar*H*), 7.34 (d, $^3J_{HH}$ = 7.2 Hz, 2H, Ar*H*), 7.21-7.10 (m, 3H, Ar*H*), 6.80 (s, 1H, Ar*H*), 4.25 (d, $^2J_{HH}$ = 14.0 Hz, 1H, ArCH_2N), 3.94 (d, $^2J_{HH}$ = 14.0 Hz, 1H, ArCH_2N), 3.92 (d, $^2J_{HH}$ = 12.4 Hz, 1H, ArCH_2N)， 3.62-3.50 (m, 1H, NCH_2- of pyrrolidinyl), 3.02-2.84 (m, 1H, NC*H*- of pyrrolidinyl), 2.79 (d, $^2J_{HH}$ = 12.4 Hz, 1H, ArCH_2N), 2.55-2.39 (m, 2H, NC$H_2CH_2CH_2CH_3$), 2.20-2.02 (m, 2H, NCH_2CH & NCH_2- of pyrrolidinyl), 2.00 -1.92 (m, 1H, NCH_2CH), 1.89 (s, 9H, C(CH_3)$_3$), 1.75-1.63 (m, 1H, -CH_2- of pyrrolidinyl), 1.49 (s, 9H, C(CH_3)$_3$), 1.39-1.29 (m, 1H, -CH_2- of pyrrolidinyl), 1.23-1.08 (m, 4H), 1.01-0.92 (m,1H, -CH_2- of pyrrolidinyl), 0.97 (t, $^3J_{HH}$ = 7.2 Hz,

3H), 0.77-0.67 (m, 1H, -CH_2- of pyrrolidinyl), 0.45 (s, 18H, N(Si(CH_3)$_3$)$_2$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 163.8, 138.6, 134.7, 132.6, 132.3, 129.2, 128.9, 126.9, 124.7, 120.7 (All Ar*C*), 61.4 (Ar*C*H_2N), 60.4 (Ar*C*H_2N), 57.2 (N*C*H- of pyrrolidinyl), 57.0 (N*C*H_2- of pyrrolidinyl), 55.6(N*C*H_2CH), 52.4 (N*C*H_2CH_2CH_2CH_3), 36.2 (*C*(CH_3)$_3$), 34.6 (*C*(CH_3)$_3$), 32.7 (C(*C*H_3)$_3$), 30.6 (C(*C*H_3)$_3$), 30.2 (NCH_2*C*H_2CH_2CH_3), 26.2 (-*C*H_2- of pyrrolidinyl), 21.9 (-*C*H_2- of pyrrolidinyl), 21.0 (NCH_2CH_2*C*H_2CH_3), 14.2 (NCH_2CH_2CH_2*C*H_3), 7.0 (N(Si(*C*H_3)$_3$)$_2$). Anal. Calcd. For $C_{37}H_{65}N_3OSi_2Mg\cdot0.25C_6H_{14}$: C, 69.02; H, 10.31; N, 6.27. Found: C, 69.49; H, 9.96; N, 6.25%.

[**(L^5)MgN(SiMe$_3$)$_2$**](**5**). The procedure was same as that of **[(L^4)MgN(SiMe$_3$)$_2$](4)**, except that **L^{5}H** (0.942 g, 1.50 mmol) and Mg[N(SiMe$_3$)$_2$]$_2$ (0.520 g, 1.50 mmol) were used to afford colorless crystals of [**(L^5)MgN(SiMe$_3$)$_2$**](**5**) (0.456 g，37.6%) as a mixture of two diasteromers in 5.7 : 1 (isomer **5a** : isomer **5b**). NMR spectroscopic data of **5a**: ^{1}H NMR (400 MHz, C_6D_6): δ 7.97-7.90 (m, 6H, Ar*H*), 7.37 (d, ^4J = 2.0 Hz, 1H, Ar*H*), 7.30-7.07 (m, 12H, Ar*H*), 6.95-6.89 (m, 2H, Ar*H*), 6.57 (d, ^4J = 2.0 Hz, 1H, Ar*H*), 4.38 (d, ^2J = 12.8 Hz, 1H, ArCH_2N), 4.25 (d, ^2J = 14.0 Hz, 1H, ArCH_2N), 4.15 (d, ^2J = 14.0 Hz, 1H, ArCH_2N), 3.37 (d, ^2J = 12.8 Hz, 1H, ArCH_2N), 3.33-3.18 (m, 1H, NC*H*- of pyrrolidinyl), 2.32-2.13 (m, 2H, NCH_2- of pyrrolidinyl), 2.00 (s, 3H, ArCH_3), 1.97-1.89 (m, 2H, NCH_2CH_2CH_2CH_3), 1.80 (dd, ^2J = 14.0, ^3J = 3.6 Hz, 1H, NCH_2CH), 1.55-1.43 (m, 1H, NCH_2CH), 1.36-1.21 (m, 3H, -CH_2- of pyrrolidinyl & NCH_2CH_2CH_2CH_3), 1.20-1.05 (m, 2H, -CH_2- of pyrrolidinyl), 1.04-0.93 (m, 2H, NCH_2CH_2CH_2CH_3), 0.89 (t, ^3J = 7.0 Hz, 3H, NCH_2CH_2CH_2CH_3), 0.59-0.47 (m, 1H, -CH_2- of pyrrolidinyl), 0.29 (s, 18H, Si(CH_3)$_3$). ^{13}C {^{1}H} NMR (100 MHz, C_6D_6): δ 161.8, 136.4, 138.9, 138.6, 136.6, 133.4, 130.6, 129.7, 129.0, 127.9, 122. 7, 121.2 (All Ar*C*), 63.6 (Ar*C*H_2N), 60.1 (Ar*C*H_2N), 59.8 (N*C*H_2- of pyrrolidinyl), 57.2 (N*C*H- of pyrrolidinyl), 55.6 (N*C*H_2CH), 54.4 (N*C*H_2CH_2CH_2CH_3), 31.6 (-*C*H_2- of pyrrolidinyl), 30.0 (CH_2*C*H_2CH_2CH_3), 23.1(-*C*H_2- of pyrrolidinyl), 21.4 (Ar-*C*H_3), 21.0 (CH_2CH_2*C*H_2CH_3), 14.7 (CH_2CH_2CH_2*C*H_3), 137.4 (Si(*C*H_3)$_3$). Anal. Calcd. for $C_{48}H_{65}N_3OSi_3Mg$: C, 72.37; H, 8.14; N, 4.92. Found: C, 71.93; H, 8.24; N, 5.08%.

[**(L^6)MgN(SiMe$_3$)$_2$**](**6**). The procedure was same as that of **[(L^4)MgN(SiMe$_3$)$_2$](4)**, except that **L^{6}H** (0.997 g, 1.50 mmol) and Mg[N(SiMe$_3$)$_2$]$_2$ (0.520 g, 1.50 mmol) were used to afford colorless crystals of [**(L^6)MgN(SiMe$_3$)$_2$**](**6**) (0.856 g, 66.6%) as a mixture of two diasteromers in 7 : 1 (isomer **6a** : isomer **6b**). NMR spectroscopic data of **6a**: ^{1}H NMR (400 MHz, C_6D_6): δ 7.72-7.43 (m, 6H, Ar*H*), 7.28 (d, ^4J = 2.0 Hz, 1H, Ar*H*), 7.15-7.07 (m, 8H, Ar*H*), 7.04-6.90 (m, 6H, Ar*H*), 6.53 (d, ^4J = 2.0 Hz, 1H, Ar*H*), 4.38 (d, ^2J = 12.8 Hz, 1H, ArCH_2N), 4.23 (d, ^2J = 14.0 Hz, 1H, ArCH_2N), 4.16 (d, ^2J = 14.0 Hz, 1H, ArCH_2N), 3.44 (d, ^2J = 12.8 Hz, 1H, ArCH_2N), 3.36-3.20 (m, 1H, NC*H*- of pyrrolidinyl), 2.07 (s, 3H, ArCH_3), 2.04-1.93 (m, 3H, NCH_2- of pyrrolidinyl & NCH_2CH), 1.75 (dd, ^2J = 14.0, ^3J = 3.6 Hz, 1H, NCH_2CH), 1.64-1.54 (m, 2H, NCH_2(CH_2)$_5$CH_2CH_3), 1.47-1.36 (m, 2H, -CH_2- of pyrrolidinyl), 1.38-1.21 (m, 10H,

$NCH_2(CH_2)_5CH_2CH_3$), 1.17-1.02 (m, 2H, $N(CH_2)_6CH_2CH_3$), 0.90 (t, ^3J = 6.9 Hz, 1H, $N(CH_2)_7CH_3$), 0.87-0.72 (m, 1H, -CH_2- of pyrrolidinyl), 0.52-0.39 (m, 1H, -CH_2- of pyrrolidinyl), 0.32 (s, 18H, $Si(CH_3)_3$). ^{13}C {^1H} NMR (100 MHz, C_6D_6): δ 163.2, 136.4, 134.4, 132.5, 131.8, 130.8, 129.2, 127.7, 125.6, 121.7, 120.9 (All Ar*C*), 64.6 (Ar*C*Ph_3), 60.4 (Ar*C*H_2N), 59.4 (Ar*C*H_2N), 56.7 (N*C*H- of pyrrolidinyl), 55.8 (N*C*H_2- of pyrrolidinyl), 52.0 (N*C*H_2CH), 49.4 ($NCH_2(CH_2)_6CH_3$), 32.5 ($NCH_2(CH_2)_6CH_3$), 30.3 (-*C*H_2- of pyrrolidinyl), 30.2 ($NCH_2(CH_2)_6CH_3$), 28.7 ($NCH_2(CH_2)_6CH_3$), 28.3 ($NCH_2(CH_2)_6CH_3$), 25.3 (-*C*H_2- of pyrrolidinyl), 23.4 ($NCH_2(CH_2)_6CH_3$), 21.9 (Ar*C*H_3), 21.2 ($NCH_2(CH_2)_6CH_3$), 14.7 ($N(CH_2)_7CH_3$), 7.4 ($Si(CH_3)_3$). Anal. Calcd. for $C_{53}H_{73}N_2OSi_2Mg$: C, 75.01; H, 8.67; N, 4.95; Found: C, 75.17; H, 8.60; N, 4.84%.

[**(L^7)MgN($SiMe_3$)$_2$**](**7**). The procedure was same as that of **[(L^4)MgN($SiMe_3$)$_2$](4)**, except that **L^7H** (0.964 g, 1.50 mmol) and $Mg[N(SiMe_3)_2]_2$ (0.520 g, 1.50 mmol) were used to afford colorless crystals of [**(L^7)MgN($SiMe_3$)$_2$**](**7**) (0.511 g, 41.2%) as an diastereomer mixture product **7a** : **7b =** 2.5 : 1. ^1H NMR (400 MHz, C_6D_6): δ 7.58 (d, ^3J = 7.2 Hz, 6H, Ar*H*), 7.27 (d, ^4J = 2.0 Hz, 1H, Ar*H*), 7.16-7.10 (m, 9H, Ar*H*), 7.04-6.94 (m, 10H, Ar*H*), 6.56 (d, ^4J = 2.0 Hz, 1H, Ar*H*), 4.41 (d, ^2J = 13.2 Hz, 1H, ArCH_2N), 3.98 (d, ^2J = 14.0 Hz, 1H, ArCH_2N), 3.68 (d, ^2J = 12.8 Hz, 1H, ArCH_2N), 3.51 (d, ^2J = 14.0 Hz, 1H, ArCH_2N), 3.46 (d, ^2J = 13.2 Hz, 1H, ArCH_2N), 3.27-3.15 (m, 1H, NCH_2- of pyrrolidinyl), 2.84 (d, *J* = 12.8 Hz, 1H, ArCH_2N), 2.09 (s, 1H, ArCH_3), 1.98 (t, ^2J = ^3J = 13.6 Hz, 1H, NCH_2CH), 1.84-1.74 (m, 1H, NCH_2- of pyrrolidinyl), 1.69-1.58 (m, 1H, NC*H*- of pyrrolidinyl), 1.51 (dd, ^2J = 14.0, ^3J = 4.0 Hz, 1H, NCH_2CH), 1.24-0.98 (m, 3H, -CH_2- of pyrrolidinyl), 0.86-0.70 (m, 1H, -CH_2- of pyrrolidinyl), 0.39 (s, 18H, $Si(CH_3)_3$). ^{13}C {^1H} NMR (100 MHz, C_6D_6): δ 162.9, 136.7, 135.8, 134.3 132.3, 132.2, 131.7, 131.5, 130.8, 129.6, 129.5, 129.3, 129.1, 127.9, 127.7, 125.6, 121.8, 120.9 (All Ar*C*), 64.6 (Ar*C*Ph_3), 59.9 (Ar*C*H_2N), 59.3 (Ar*C*H_2N), 58.8 (Ar*C*H_2N), 55.4 (N*C*H- of pyrrolidinyl), 51.5 (N*C*H_2- of pyrrolidinyl), 48.4 (N*C*H_2CH), 25.3 (-*C*H_2- of pyrrolidinyl), 21.9 (-*C*H_2- of pyrrolidinyl), 21.2 (Ar*C*H_3), 7.6 ($Si(CH_3)_3$). Anal. Calcd. for $C_{52}H_{63}N_3OSi_2Mg$: C, 75.56; H, 7.68; N, 5.08. Found: C, 75.21; H, 7.82; N, 4.97%.

[**(L^8)MgN($SiMe_3$)$_2$**](**8**). The procedure was same as that of **[(L^4)MgN($SiMe_3$)$_2$](4)**, except that **L^8H** (0.988 g, 1.50 mmol) and $Mg[N(SiMe_3)_2]_2$ (0.520 g, 1.50 mmol) were used to afford colorless crystals of [**(L^8)MgN($SiMe_3$)$_2$**](**8**) (0.685 g, 41%) as an enantiopure product **8**. ^1H NMR (400 MHz, C_6D_6): δ 8.39 (d, ^3J = 8.7 Hz, 1H, Ar*H*), 7.74–7.49 (m, 10H, Ar*H*), 7.43–7.38 (m, 1H, ArH), 7.26–7.19 (m, 5H, Ar*H*), 7.12–6.94 (m, 6H, Ar*H*), 6.16 (d, ^4J = 2.1 Hz, 1H, Ar*H*), 5.07 (d, ^2J = 14.6 Hz, 1H, ArCH_2N), 4.65 (d, ^2J = 12.7 Hz, 1H, ArCH_2N), 4.43 (d, ^2J = 14.7 Hz, 1H, ArCH_2N), 3.32 (d, ^2J = 12.8 Hz, 1H, ArCH_2N), 3.40–3.29 (m, 1H, NC*H*- of pyrrolidinyl), 2.09–1.93 (m, 4H, NCH_2- of pyrrolidinyl & NCH_2CH), 1.89 (s, 3H, ArCH_3), 1.50–1.10 (m, 8H, NCH_2CH_2CH_2CH_3 & -CH_2- of pyrrolidinyl), 0.96 (t, ^3J = 7.1 Hz, 3H, $NCH_2CH_2CH_2CH_3$), 0.80–0.72 (m, 1H, -CH_2- of pyrrolidinyl), 0.51 (m, 1H, -CH_2- of pyrrolidinyl), 0.37 (s, 18H, $Si(CH_3)_3$). ^{13}C {^1H} NMR (100

MHz, C_6D_6): δ 162.8, 135.6, 134.8, 134.6, 134.1, 131.6, 131.3, 130.1, 129.5, 127.5, 127.4, 127.3, 126.4, 125.2, 124.8, 124.1, 121.7, 120.5(All Ar*C*), 64.2 (Ar*C*Ph_3), 61.1 (Ar*C*H_2N), 60.0 (Ar*C*H_2N), 56.1 (N*C*H- of pyrrolidinyl), 51.0 (N*C*H_2- of pyrrolidinyl), 50.7 (N*C*H_2CH), 48.1 (N*C*$H_2CH_2CH_2CH_3$), 30.3 (NCH_2*C*$H_2CH_2CH_3$), 24.9 (-*C*H_2- of pyrrolidinyl), 21.2(Ar-*C*H_3), 21.0 (-*C*H_2- of pyrrolidinyl), 20.6 (NCH_2CH_2*C*H_2CH_3), 14.1 ($NCH_2CH_2CH_2$*C*H_3), 7.1 (Si(*C*H_3)$_3$). Anal. Calcd. for $C_{53}H_{67}N_3OSi_2Mg$: C, 74.55; H, 8.01; N, 4.99; Found: C, 74.01; H, 8.17; N, 4.56%.

[**(L^9)MgN(SiMe$_3$)$_2$**](**9**). The procedure was same as that of **[(L^4)MgN(SiMe$_3$)$_2$](4)**, except that **L^{9}H** (0.715 g, 1.00 mmol) and Mg[N(SiMe$_3$)$_2$]$_2$ (0.345 g, 1.00 mmol) were used to afford colorless crystals of [**(L^9)MgN(SiMe$_3$)$_2$**](**9**) (0.449 g, 50%) as an enantiopure product **9**. ^{1}H NMR (400 MHz, C_6D_6): δ 8.40 (d, ^2J = 8.6 Hz, 1H), 7.70–7.53 (m, 10H, Ar*H*), 7.45–7.39 (m, 1H, Ar*H*), 7.29–7.20 (m, 5H, Ar*H*), 7.13–6.98 (m, 6H, Ar*H*), 6.17 (d, ^2J = 2.1 Hz, 1H, Ar*H*), 5.08 (d, ^2J = 14.6 Hz, 1H, ArC*H*$_2$N), 4.65 (d, ^2J = 12.6 Hz, 1H, ArC*H*$_2$N), 4.47 (d, ^2J = 14.7 Hz, 1H, ArC*H*$_2$N), 3.45–3.36 (m, 1H, NC*H*- of pyrrolidinyl), 3.33 (d, ^2J = 12.7 Hz, 1H, ArC*H*$_2$N), 2.06–1.97 (m, 4H, NC*H*$_2$- of pyrrolidinyl & NC*H*$_2$CH), 1.90 (s, 3H, ArC*H*$_3$), 1.65–1.10 (m, 16H, -C*H*$_2$- of pyrrolidinyl, N(C*H*$_2$)$_7$CH$_3$), 0.91 (t, ^3J = 6.7 Hz, 3H, N(CH$_2$)$_7$C*H*$_3$), 0.82–0.73 (m, 1H, -C*H*$_2$- of pyrrolidinyl), 0.55–0.46 (m, 1H, -C*H*$_2$- of pyrrolidinyl), 0.38 (s, 18H, Si(C*H*$_3$)$_3$). ^{13}C {^{1}H} NMR (100 MHz, C_6D_6): δ 162.9, 135.5, 134.8, 134.6, 134.1, 131.6, 131.3, 130.1, 129.5, 129.3, 128.5, 127.5, 127.4, 126.4, 125.2, 124.8, 124.1(All Ar*C*), 64.2 (Ar*C*Ph_3), 61.2 (Ar*C*H_2N), 60.0 (Ar*C*H_2N), 56.2 (N*C*H- of pyrrolidinyl), 51.1 (N*C*H_2- of pyrrolidinyl), 50.6 (N*C*H_2CH), 48.1 (N*C*$H_2CH_2(CH_2)_5CH_3$), 32.2 (NCH_2*C*$H_2(CH_2)_5CH_3$), 29.9 (-*C*H_2- of pyrrolidinyl), 29.9 (NCH_2CH_2(*C*H_2)$_5$CH$_3$), 28.4 (NCH_2CH_2(*C*H_2)$_5$CH$_3$), 27.9 (NCH_2CH_2(*C*H_2)$_5$CH$_3$), 25.0 (NCH_2CH_2(*C*H_2)$_5$CH$_3$), 23.0 (Ar-*C*H_3), 21.1 (-*C*H_2- of pyrrolidinyl), 20.7 (NCH_2CH_2(*C*H_2)$_5$CH$_3$), 14.3 (N(CH$_2$)$_6$*C*H_3), 7.2 (Si(*C*H_3)$_3$). Anal. Calcd. for $C_{57}H_{75}N_3OSi_2Mg$: C, 76.18; H, 8.41; N, 4.68; Found: C, 75.69; H, 7.98; N, 4.45 %.

[**(L^{10})MgN(SiMe$_3$)$_2$**](**10**). The procedure was same as that of **[(L^4)MgN(SiMe$_3$)$_2$](4)**, except that **L^{10}H** (0.439 g，1.00 mmol) and Mg[N(SiMe$_3$)$_2$]$_2$ (0.345 g, 1.00 mmol) were used to afford colorless crystals of [**(L^{10})MgN(SiMe$_3$)$_2$**](**10**) (0.818 g, 71%) as an diastereomer mixture product **10a** : **10b =** 2 : 1. ^{1}H NMR (400 MHz, C_6D_6): δ 7.72 (d, ^4J = 2.4 Hz, 1H, Ar*H*), 7.56 (d, ^3J = 7.2 Hz, 2H, Ar*H*), 7.47 (d, ^3J = 8.0 Hz, 3H, Ar*H*), 7.25 (t, ^3J = 7.6 Hz, 2H, Ar*H*), 7.15-7.06 (m, 6H, Ar*H*), 7.02 (t, ^3J = 6.8 Hz, 2H, Ar*H*), 6.83 (d, ^4J = 2.4 Hz, 1H, Ar*H*), 4.18 (d, ^2J = 13.6 Hz, 1H, ArC*H*$_2$N), 3.90 (d, ^2J = 13.6 Hz, 1H, ArC*H*$_2$N), 3.65 (d, ^2J = 12.8 Hz, 1H, ArC*H*$_2$N), 3.47-3.36 (m, 1H, NC*H*$_2$- of pyrrolidinyl), 2.73-2.61 (m, 1H, NC*H*- of pyrrolidinyl), 2.51 (d, ^2J = 12.8 Hz, 1H, ArC*H*$_2$N), 2.39-2.31 (m, 1H, NC*H*$_2$CH$_3$), 2.29 (s, 3H, C(C*H*$_3$)$_2$Ph), 2.08-1.91 (m, 2H, NC*H*$_2$CH), 1.88 (s, 3H, C(C*H*$_3$)$_2$Ph), 1.81 (s, 6H, C(C*H*$_3$)$_2$Ph), 1.74-1.56 (m, 2H, NC*H*$_2$- of pyrrolidinyl & NC*H*$_2$CH$_3$), 1.21-1.09 (m, 2H, -C*H*$_2$- of pyrrolidinyl), 0.90-0.80 (m, 1H, -C*H*$_2$- of pyrrolidinyl), 0.59 (t, ^3J = 7.2 Hz, 3H, NCH$_2$C*H*$_3$), 0.56-0.49 (m, 1H, -C*H*$_2$- of pyrrolidinyl), 0.33 (s, 18H, Si(C*H*$_3$)$_3$). ^{13}C {^{1}H}

NMR (100 MHz, C_6D_6): δ 163.3, 153.3, 153.0, 137.9, 132.5, 132.4, 132.0, 130.0, 129.1, 128.9, 128..5, 127.8, 127.5, 127.1, 126.3, 125.9, 124.9, 121.3 (All Ar*C*), 59.5 (Ar*C*H_2N), 56.4 (Ar*C*H_2N), 55.8 (N*C*H- of pyrrolidinyl), 55.4 (N*C*H_2- of pyrrolidinyl), 54.5 (N*C*H_2CH), 51.0 (N*C*$H_2$$CH_3$), 43.7 (*C*$(CH_3)_2$Ph), 43.1 (*C*$(CH_3)_2$Ph), 34.2 (C(*C*$H_3)_2$Ph), 32.2 (C(*C*$H_3)_2$Ph), 31.9 (C(*C*$H_3)_2$Ph), 27.7 (C(*C*$H_3)_2$Ph), 26.2 (-*C*$H_2$- of pyrrolidinyl), 21.9 (-*C*H_2- of pyrrolidinyl), 13.5 (NCH$_2$*C*H_3), 6.9 (Si(*C*$H_3)_3$). Anal. Calcd. For $C_{45}H_{65}N_3OSi_2Mg$: C, 72.60; H, 8.80; N, 5.64. Found: C, 72.18; H, 8.69; N, 5.38%.

1.3 X-Ray diffraction measurements

Single crystals of complexes **3**, **4**, **5** and **10** were obtained from a mixture of toluene/*n*-hexane or benzene/*n*-hexane solution by slow evaporation at room or low temperature. The X-ray diffraction measurements were performed on a Bruker SMART APEX II diffractometer with graphite-monochromated Mo-Kα (λ= 0.71073 Å) radiation. Complex 3 was collected at 130 K and the others were collected at 140 K using the *ω*-scan techniques. All the structures were solved by direct methods and refined using Fourier techniques. An absorption correction based on SADABS was applied.[S3] All non-hydrogen atoms were refined by full-matrix least-squares on F^2 using the SHELXTL program package.[S4] Hydrogen atoms were located and refined by the geometry method. The cell refinement, data collection, and reduction were done by Bruker SAINT.[S5] The structure solution and refinement were performed by SHELXS-97[S6] and SHELXL-97[S7] respectively. For further crystal data and details of measurements see Tables S1 and S2. Molecular structures were generated using ORTEP program.[S8] CCDC numbers 1450912 (**3**), 1450913 (**4**), 1450915 (**5**) and 1450914 (**10**) contain the supplementary crystallographic data for this paper.

1.4 Ring-opening polymerization of *rac*-lactide

Typical polymerization procedure. In a glove box, an initiator solution (0.5 mL, 10 mmol/mL) from a stock solution in toluene or THF was injected sequentially to a series of 10 mL vials loaded with *rac*-lactide (0.144 g, 1.00 mmol) and suitable amounts (0.5 mL) of the same dry solvent. The mixture was stirred at room temperature and quenched at the 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 a vacuum oven at 60 °C for 16 h to constant weight for gel permeation chromatography (GPC), ^{1}H and homonuclear decoupled ^{1}H NMR analyses. In the cases where 2-propanol was used, the monomer solution was treated first with the solution of 2-propanol for 5 min, and then the solution of initiator was injected to the

mixture. Otherwise the procedures were the same.

1.5 Ring-opening polymerization of *rac-β*-butyrolactone

In a glove box, an initiator solution (1.0 mL, 0.01 mmol/mL) in toluene was injected sequentially to a series of 10 mL vials loaded with rac-BBL (0.172 g, 2.0 mmol/mL). The mixture was stirred at room temperature and quenched at the specific time intervals by adding an excess amount of normal light petroleum ether. The reaction liquid was dissolved with dichloromethane, and then concentrated slightly. The polymer was precipitated from dichloromethane via the addition of excess methanol. The collected polymer sample was further dried in a vacuum oven at 60 °C for 16 h to constant weight. Monomer conversion rate is the ratio of the weight of the polymer and the monomer used. The collected polymer would be used for gel permeation chromatography (GPC) and ^{13}C NMR analyses.

2. X-Ray Diffraction Studies

Tables S1. Crystallographic data and structure refinement for complexes **3a/b**, **4a/b**, **5a**, **10b**

	3a/b	**4a/b**	**5a**	**10b**
Empirical formula	$C_{62}H_{106}Mg_2N_6O_2Si_4$	$C_{80}H_{136}MgN_6O_2Si_4$	$C_{48}H_{65}MgN_3OSi_3 \cdot C_7H_8$	$C_{45}H_{65}MgN_3OSi_2$
Formula weight	564.25	1374.93	744.49	1296.15
Temp (K)	130(2)	140(2)	140(2)	140(2)
Crystal size (mm)	0.25 × 0.22 × 0.18	0.30 × 0.10 × 0.02	0.20 × 0.15 × 0.10	0.357 × 0.311 × 0.269
Crystal system	Monoclinic	Monoclinic	Triclinic	Orthorhombic
Space group			P 1	P 21 21 21
a (Å)	14.6459(18)	10.578(3)	8.7667(15)	10.0092(4)
b (Å)	13.6541(18)	17.438(5)	11.5603(19)	22.1908(9)
c (Å)	18.104(2)	23.315(7)	12.315(2)	23.6773(9)
α (°)	90	90	64.610(3)	90
β (°)	111.227(2)°	100.208(5))	78.219(3)	90
γ (°)	90	90	88.125(3)	90
Volume(Å^3)	3374.8(7)	4233(2)	1101.7(3)	5259.0(4)
Z	4	2	1	4
Density $_{calc}$ (mg/m^3)	1.111	1.079	1.122	1.138
Abs coeff (mm^{-1})	0.150	0.130	0.130	1.242
F(000)	1232	1508	404	1944
θ range (°)	1.207 to 25.996	0.89 to 26.00	1.954 to 30.688	3.734 to 70.010
Data collected (*hkl*)	-18 to 15, -14 to 16, ±22	–13 to 12, ±21, ±28	±12, –16 to 15, ±17	–10 to 11, –26 to 24, –28 to 26
Reflns collected/unique	24894 / 11868	29633 / 16449	10913 / 9075	49130 / 9521
R(int)	0.0647	0.0887	0.0258	0.1762
Max. and min. transmn	0.7461 and 0.6748	0.9974 and 0.9620	0.7461 and 0.6483	0.7461 and 0.4989
Data / restrains / para	11868 / 73 / 703	16449 / 35 / 873	9075 / 117 / 468	9521 / 0 / 578
Goodness-of-fit on F^2	1.008	0.992	1.028	0.977
Final R_1, wR_2 [I > 2σ(I)]	0.0673, 0.1493	0.0702, 0.1424	0.0580, 0.1528	0.0626, 0.1359
R_1 , wR_2 (all data)	0.1247, 0.1796	0.1257, 0.1670	0.0714, 0.1728	0.1072, 0.1605
$\Delta\rho_{max, min}$/e Å^{-3}	1.063 and -0.357	1.177 and –0.613	1.024 and –0.851	0.389 and –0.394

3. ^{1}H NMR and ^{13}C NMR Spectra of Complexes 1-10

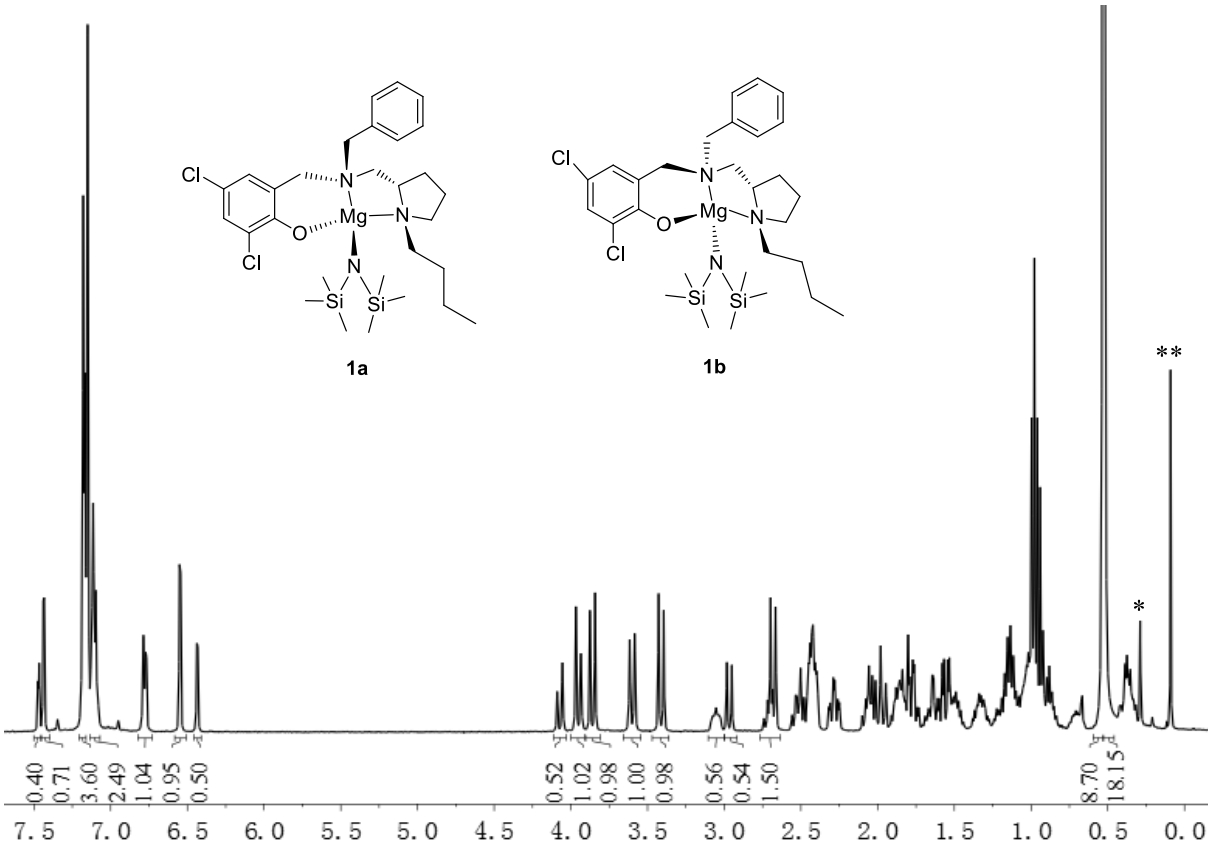


Figure S1. ^{1}H NMR spectrum (C_6D_6, 400 MHz, 20 °C) of [(*S*)-L^{1}]MgN(SiMe$_3$)$_2$ (**1**) (*:impurity in C_6D_6; **: free HN[Si(C*H*$_3$)$_2$]$_2$).

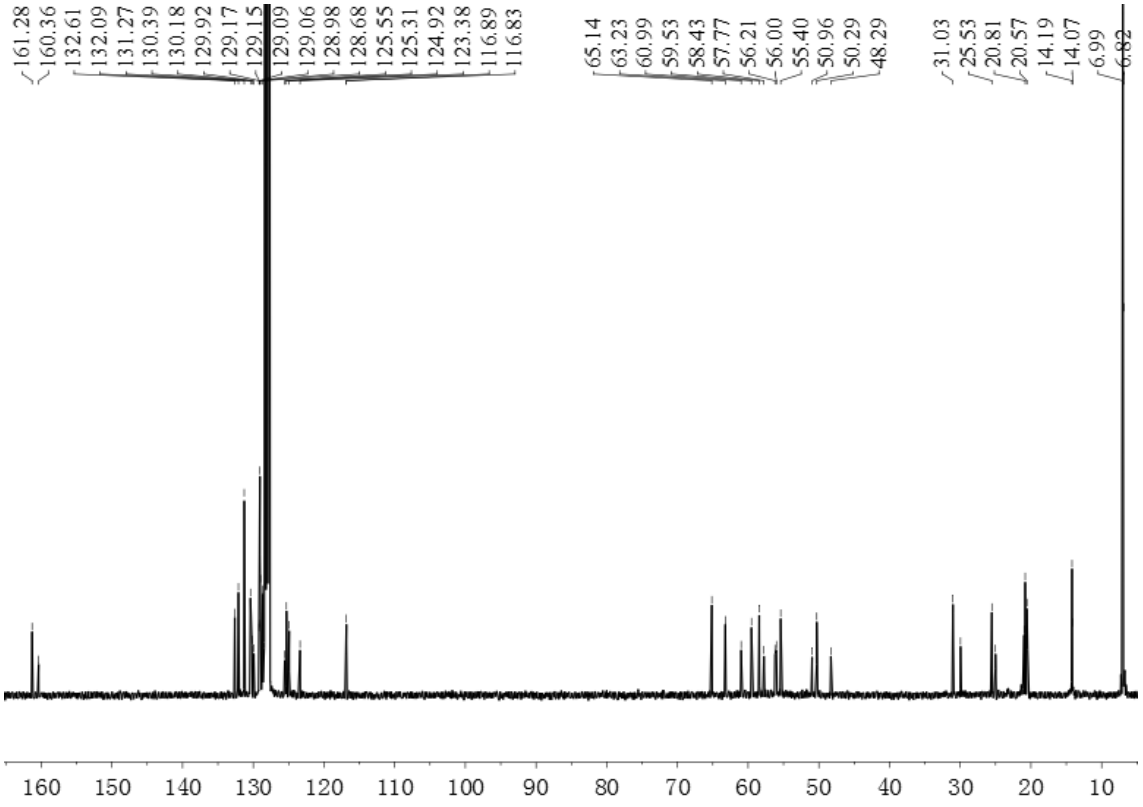


Figure S2. ^{13}C{^{1}H} NMR spectrum (C_6D_6, 400 MHz, 20 °C) of [(*S*)-L^{1}]MgN(SiMe$_3$)$_2$ (**1**).

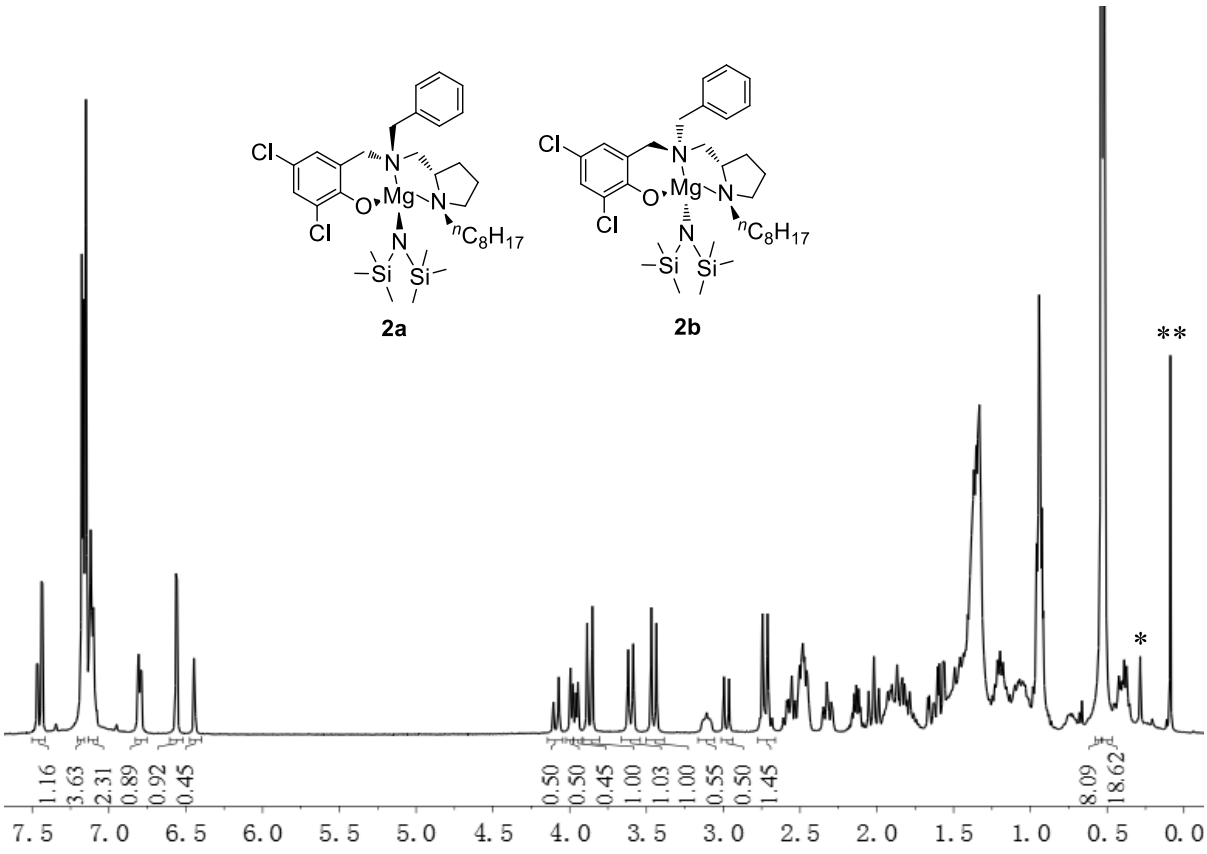


Figure S3. ^{1}H NMR spectrum (C_6D_6, 400 MHz, 20 °C) of [(*S*)-L^2]MgN(SiMe$_3$)$_2$ (**2**) (*:impurity in C_6D_6; **: free HN[Si(C*H*$_3$)$_2$]$_2$).

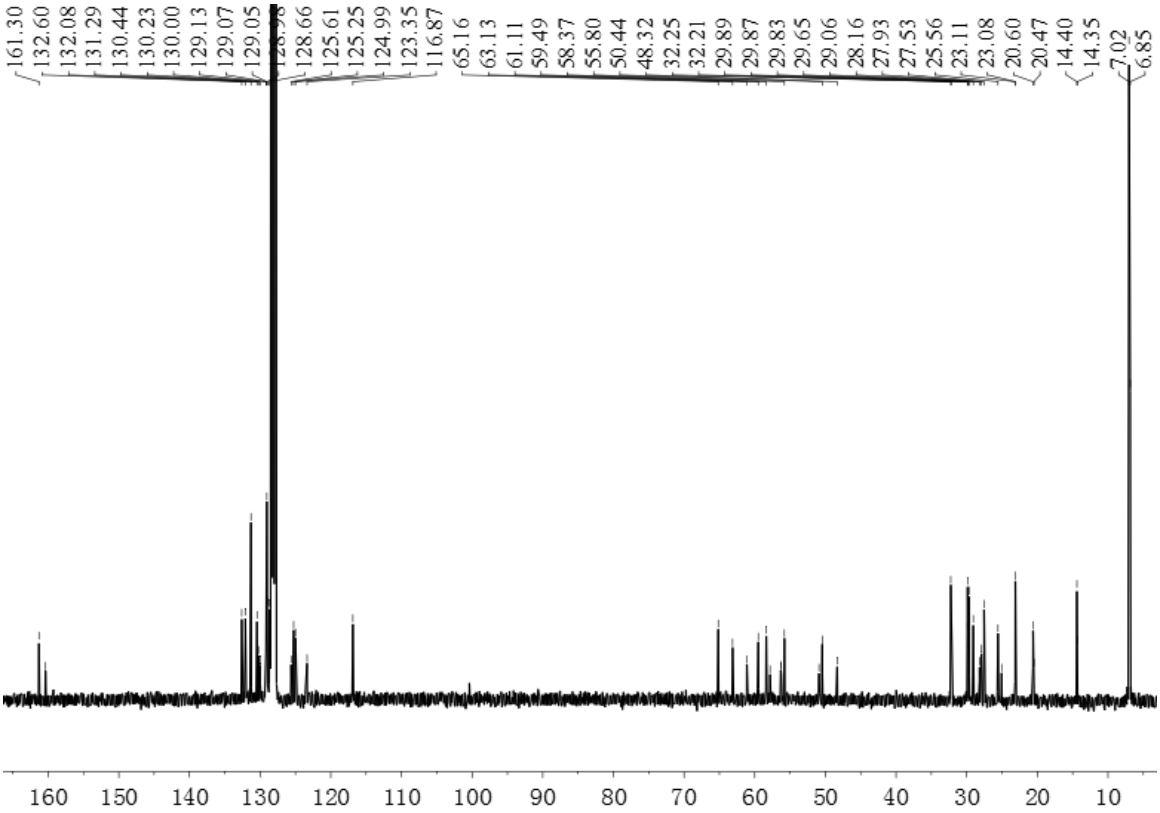


Figure S4. ^{13}C{^{1}H} NMR spectrum (C_6D_6, 400 MHz, 20 °C) of [(*S*)-L^2]MgN(SiMe$_3$)$_2$ (**2**).

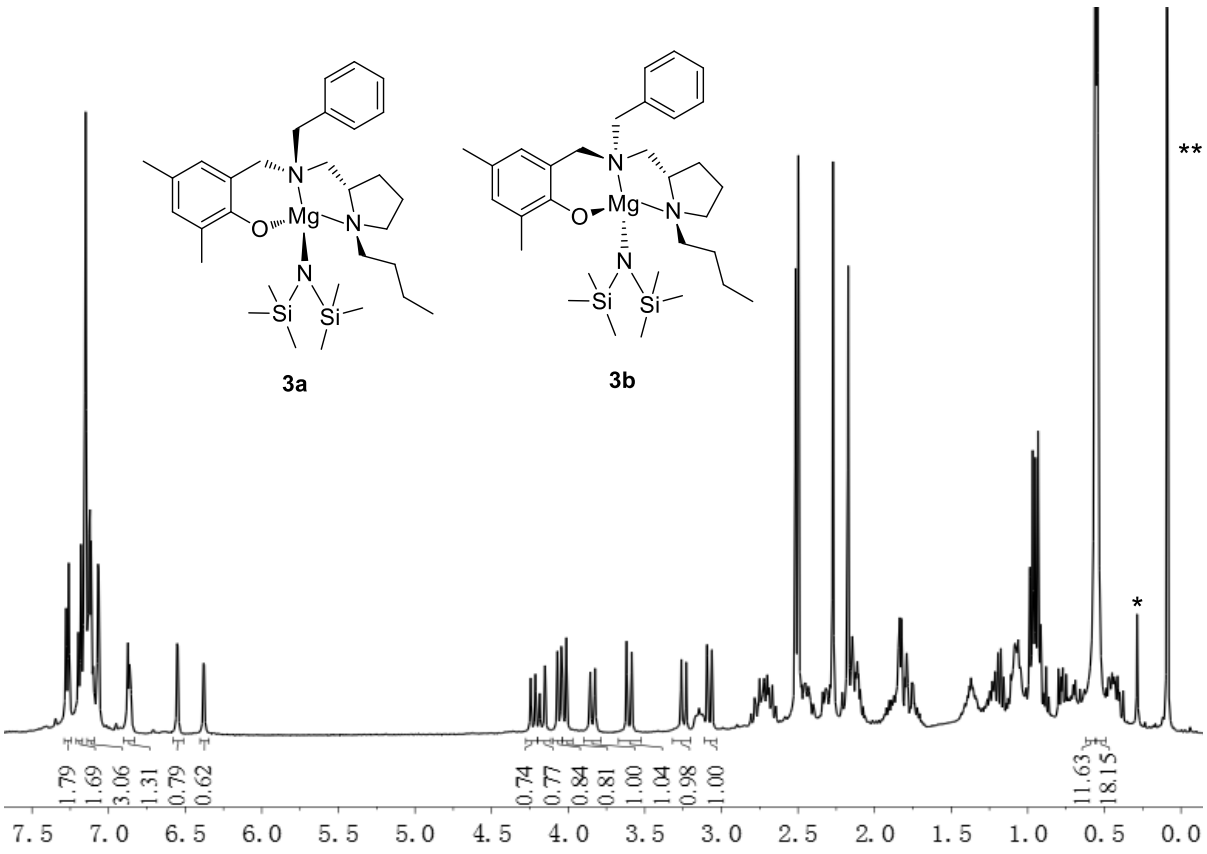


Figure S5. ^{1}H NMR spectrum (C_6D_6, 400 MHz, 20 °C) of [(*S*)-L^3]MgN($SiMe_3$)$_2$ (**3**). (*:impurity in C_6D_6; **: free HN[Si(CH_3)$_2$]$_2$).

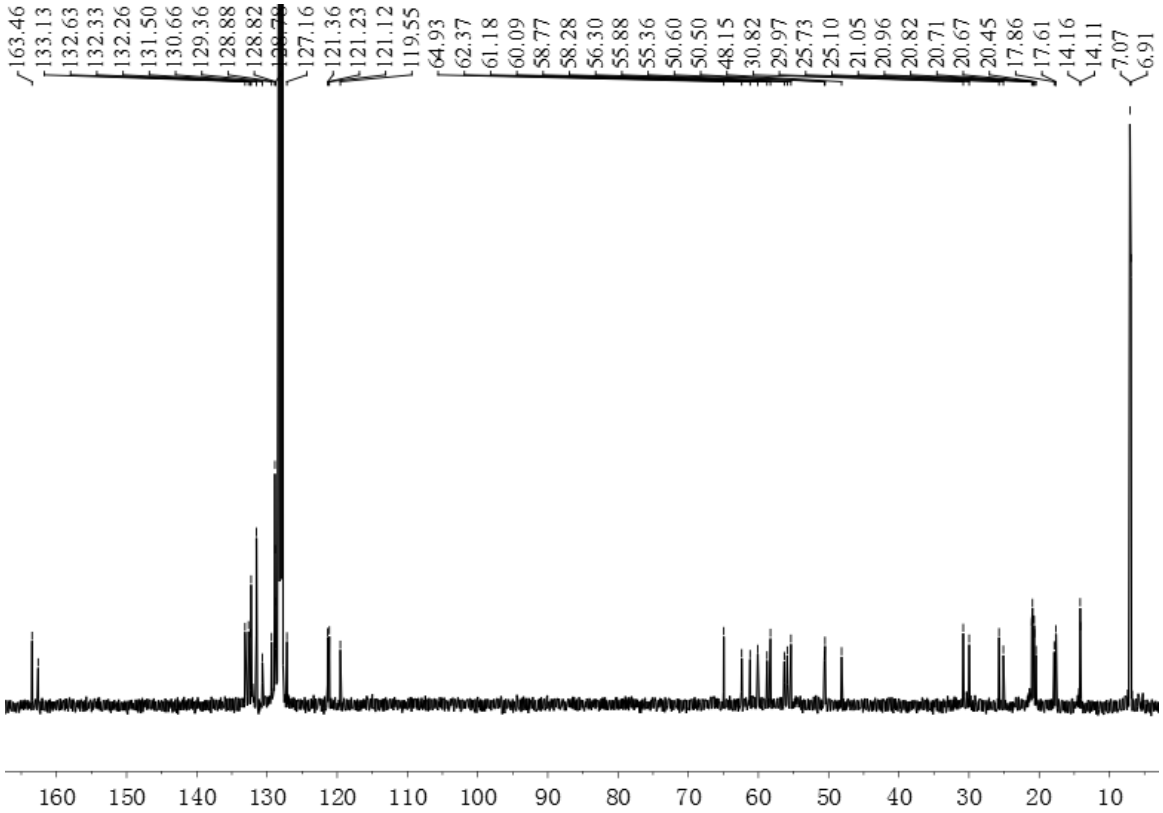


Figure S6. ^{13}C{^{1}H} NMR spectrum (C_6D_6, 400 MHz, 20 °C) of [(*S*)-L^3]MgN($SiMe_3$)$_2$ (**3**).

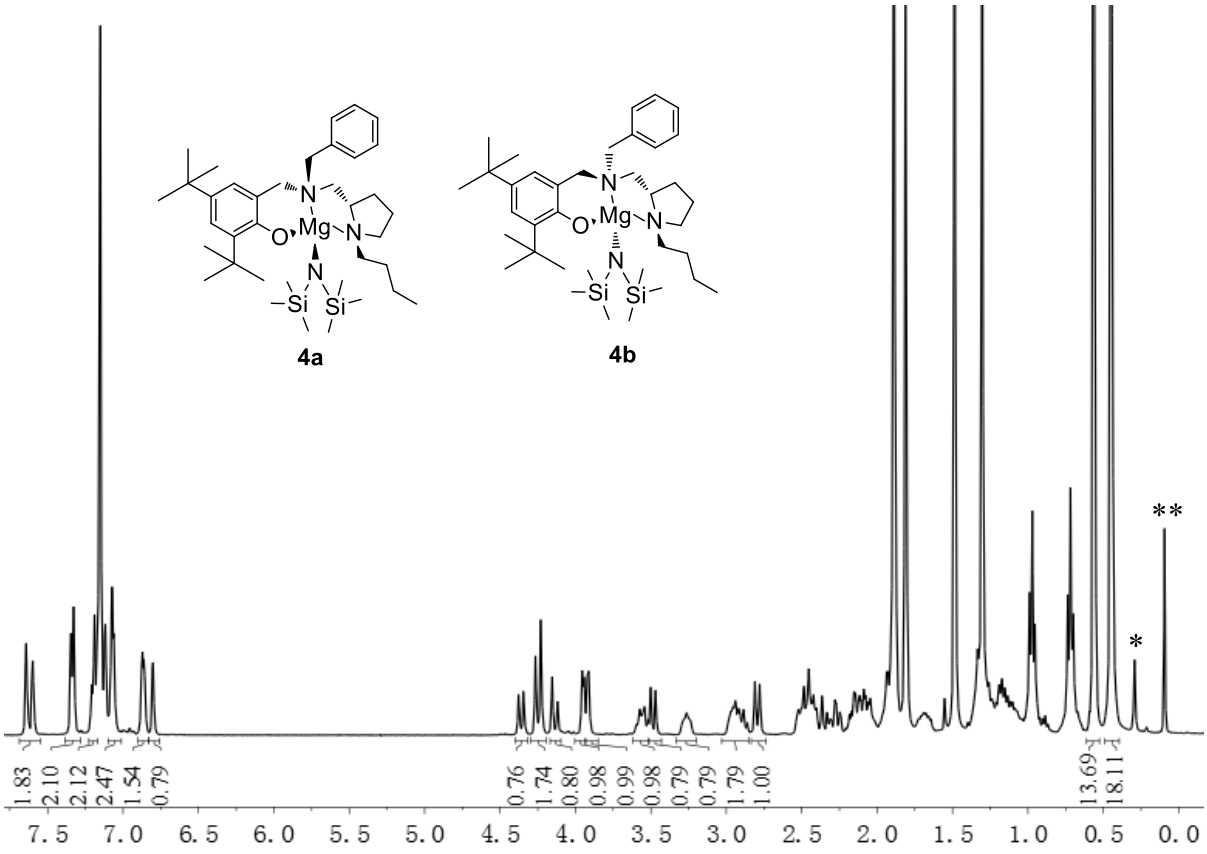


Figure S7. ^{1}H NMR spectrum (C_6D_6, 400 MHz, 20 °C) of [(*S*)-L^{4}]MgN(SiMe$_3$)$_2$ (**4**). (*:impurity in C_6D_6; **: free HN[Si(C*H*$_3$)$_2$]$_2$).

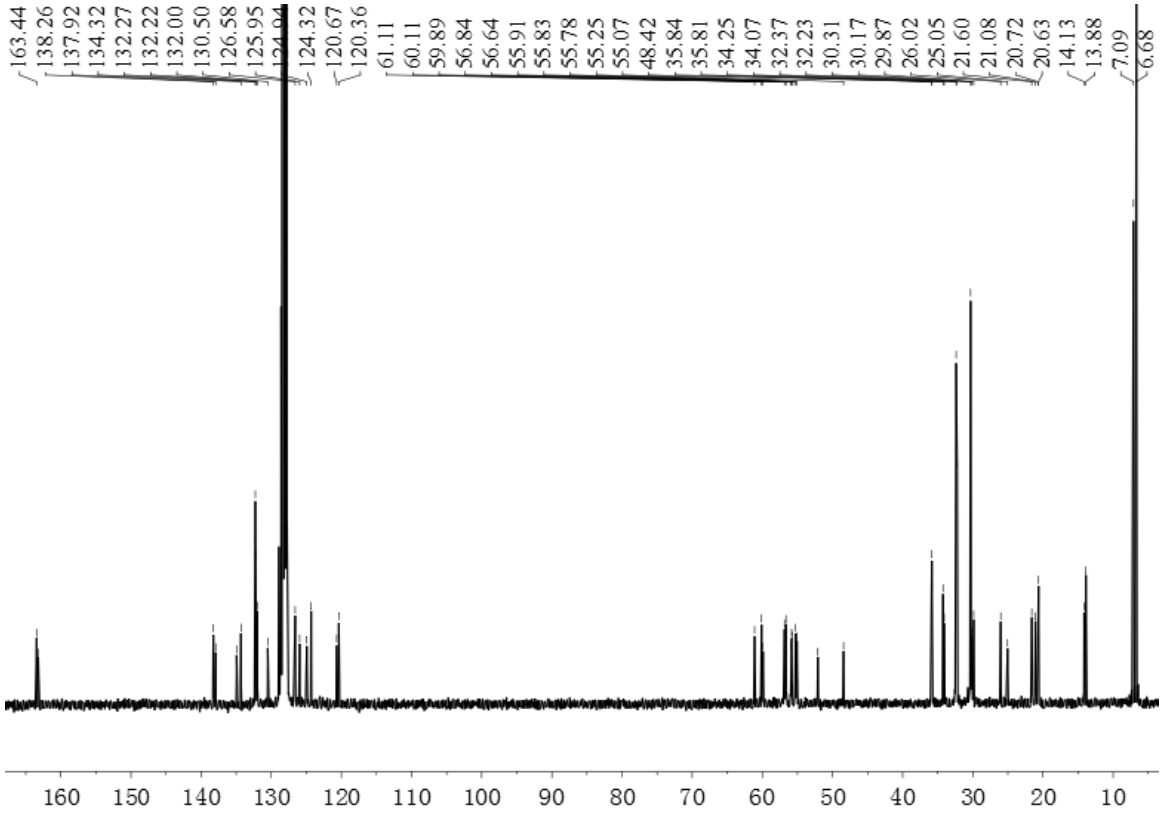


Figure S8. ^{13}C{^{1}H} NMR spectrum (C_6D_6, 400 MHz, 20 °C) of [(*S*)-L^{4}]MgN(SiMe$_3$)$_2$ (**4**).

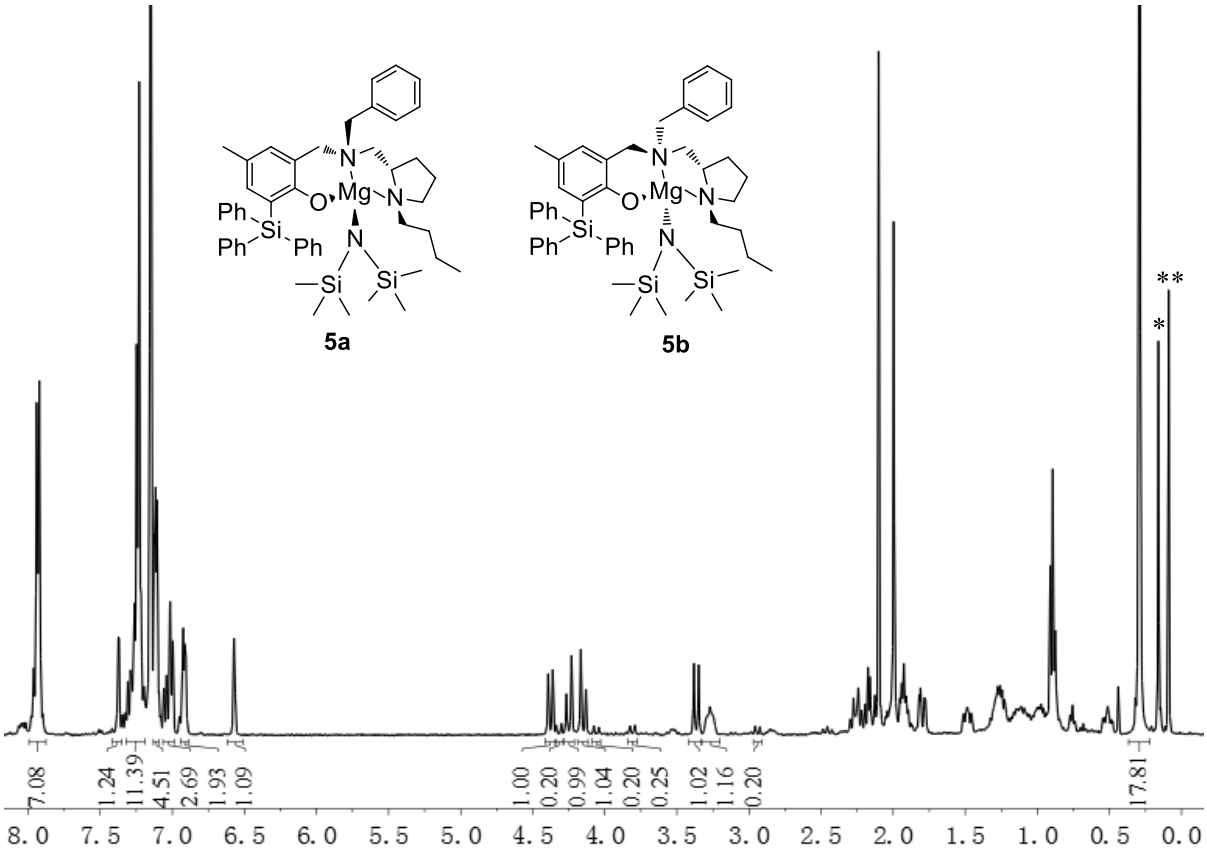


Figure S9. ^{1}H NMR spectrum (C_6D_6, 400 MHz, 20 °C) of [(*S*)-L^{5}]MgN(SiMe$_3$)$_2$ (**5**). (*:impurity in C_6D_6; **: free HN[Si(C*H*$_3$)$_2$]$_2$).

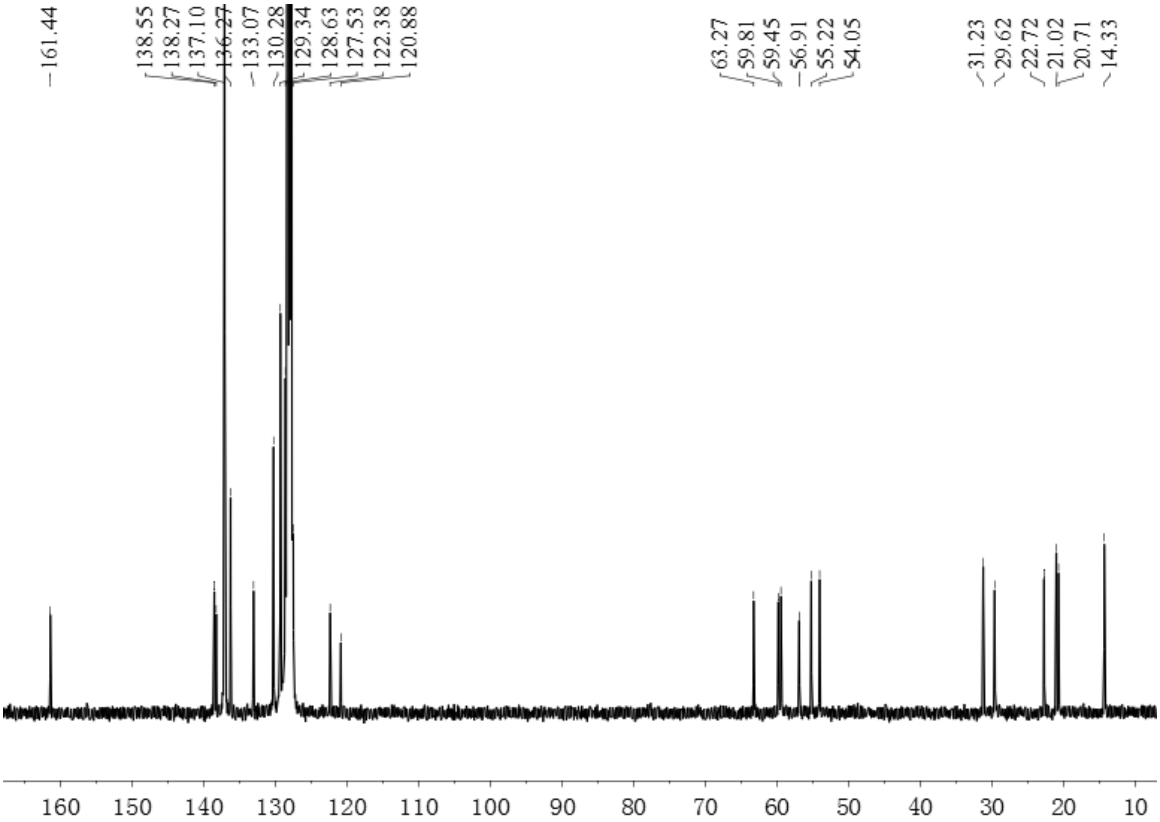


Figure S10. ^{13}C{^{1}H} NMR spectrum (C_6D_6, 400 MHz, 20 °C) of [(*S*)-L^{5}]MgN(SiMe$_3$)$_2$ (**5**).

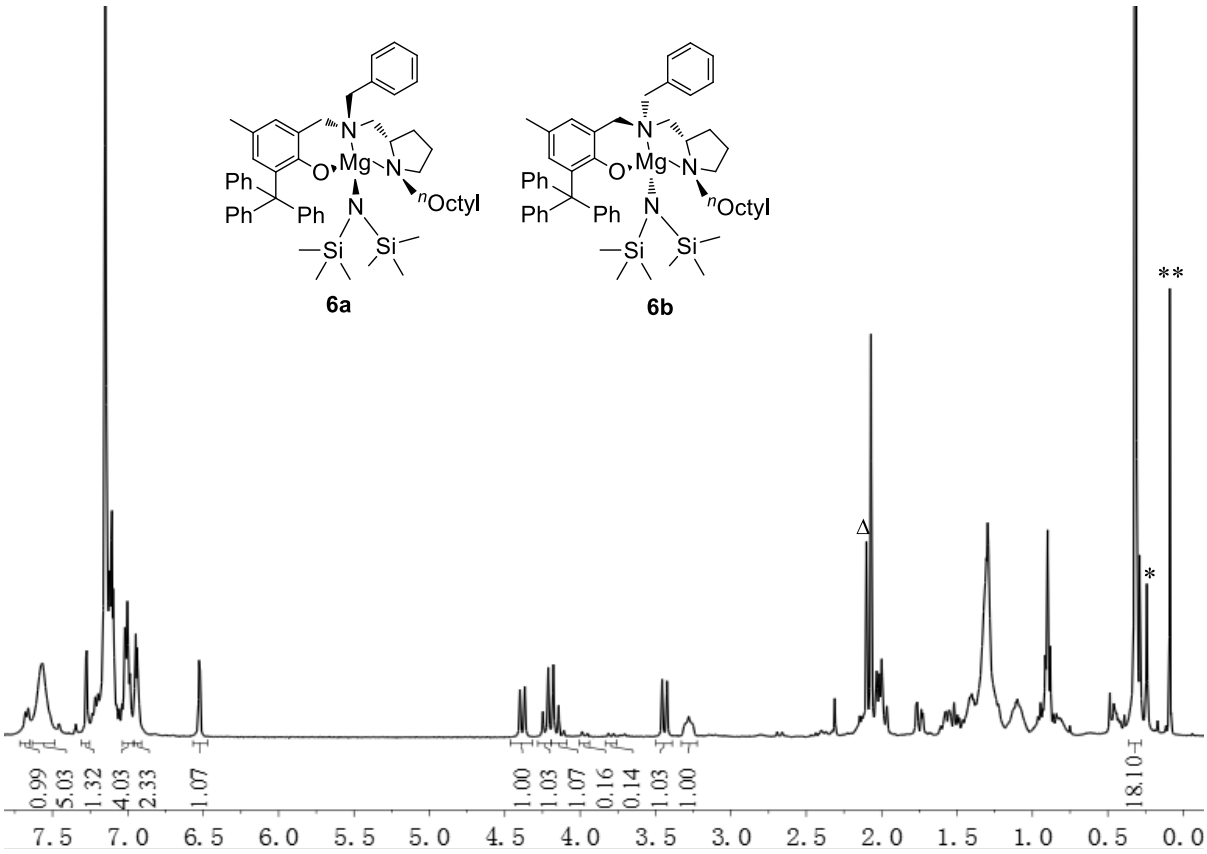


Figure S11. ^{1}H NMR spectrum (C_6D_6, 400 MHz, 20 °C) of [(*S*)-L^{6}]MgN(SiMe$_3$)$_2$ (**6**). (Δ :methyl signal of residual toluene; *:impurity in C_6D_6; **: free HN[Si(C*H*$_3$)$_2$]$_2$).

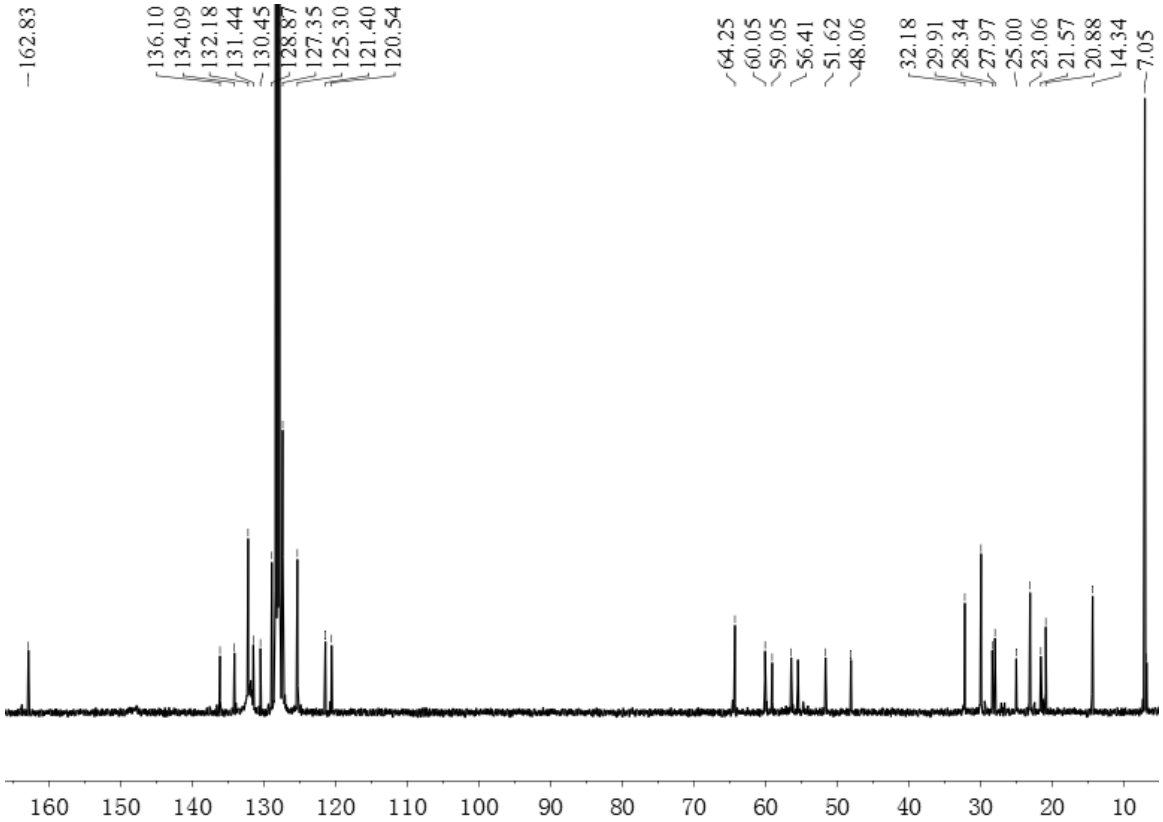


Figure S12. ^{13}C{^{1}H} NMR spectrum (C_6D_6, 400 MHz, 20 °C) of [(*S*)-L^{6}]MgN(SiMe$_3$)$_2$ (**6**).

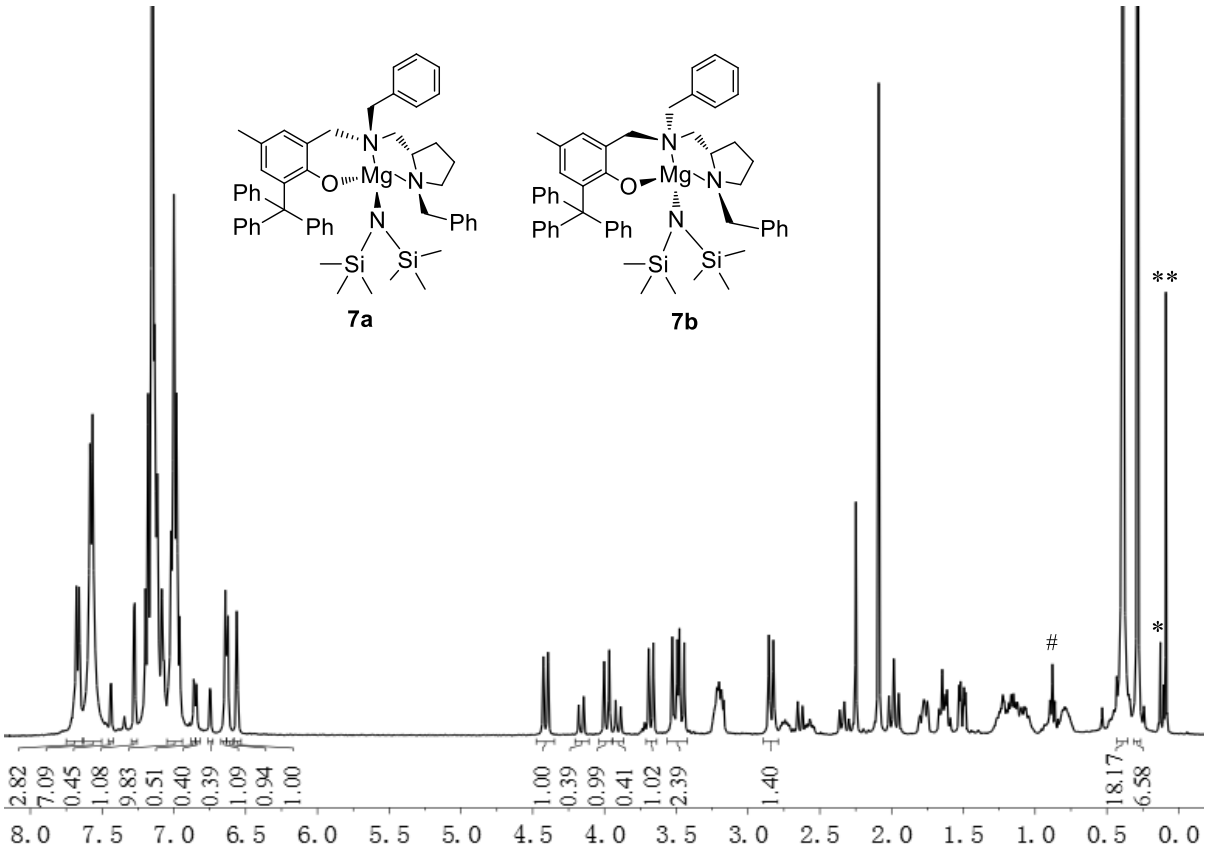


Figure S13. ^{1}H NMR spectrum (C_6D_6, 400 MHz, 20 °C) of [(*S*)-L^{7}]MgN(SiMe$_3$)$_2$ (**7**). (# :methyl signal of *n*-hexane; *:impurity in C_6D_6; **: free HN[Si(C*H*$_3$)$_2$]$_2$).

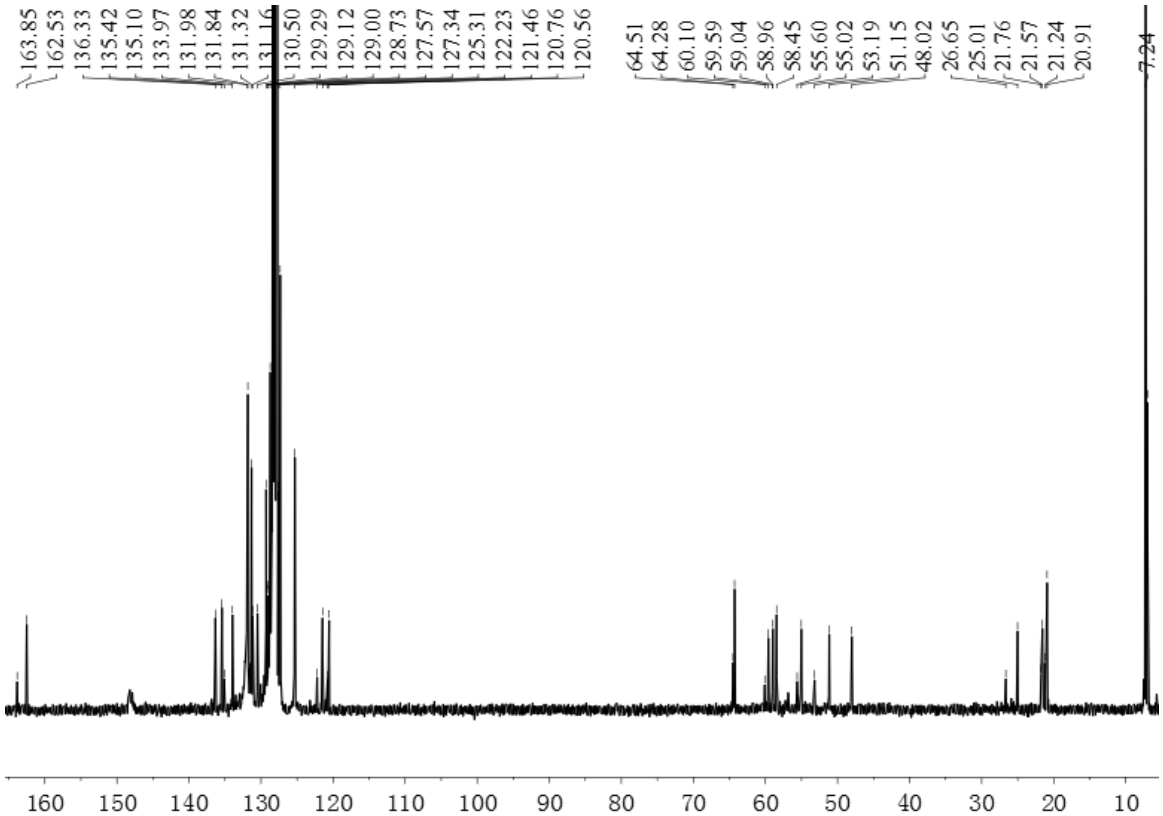


Figure S14. ^{13}C{^{1}H} NMR spectrum (C_6D_6, 400 MHz, 20 °C) of [(*S*)-L^{7}]MgN(SiMe$_3$)$_2$ (**7**).

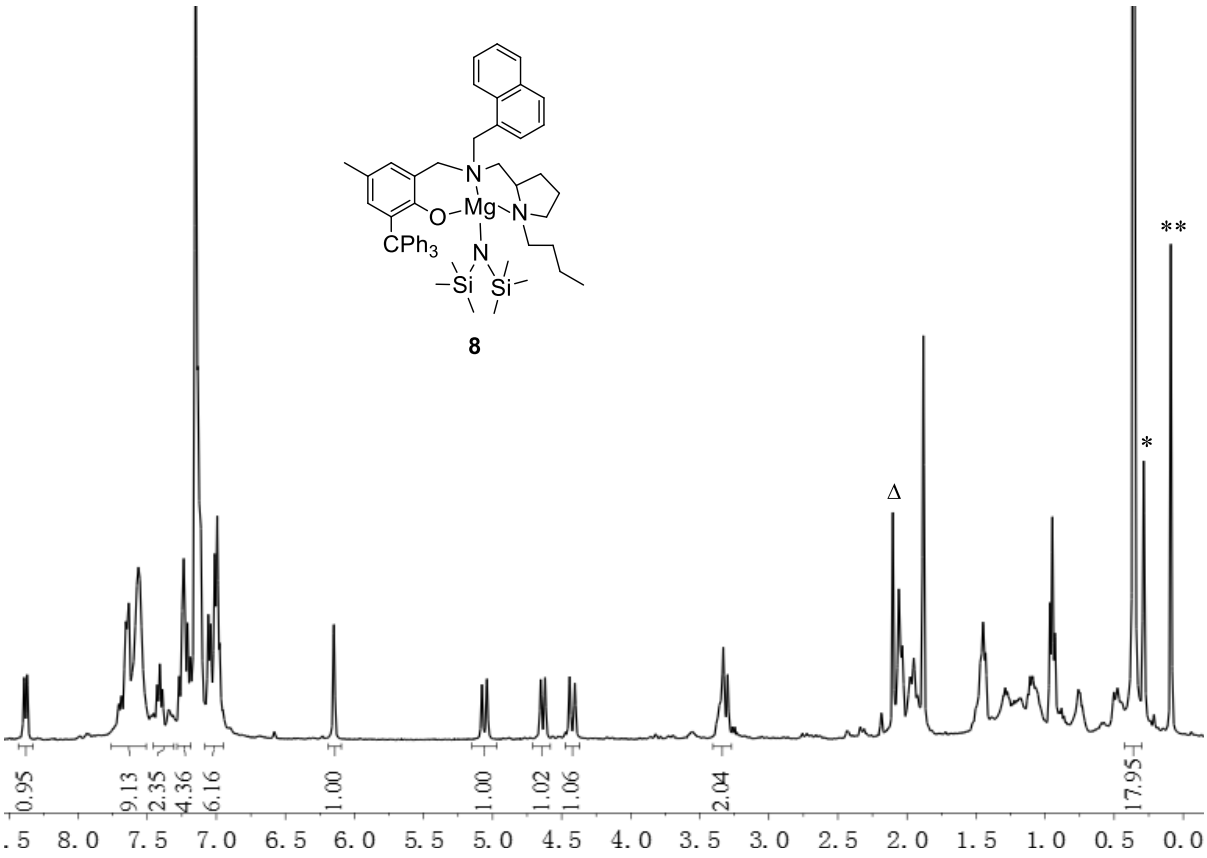


Figure S15. ^{1}H NMR spectrum (C_6D_6, 400 MHz, 20 °C) of [(*S*)-L^{8}]MgN(SiMe$_3$)$_2$ (**8**). (Δ :methyl signal of residual toluene; *:impurity in C_6D_6; **: free HN[Si(C*H*$_3$)$_2$]$_2$).

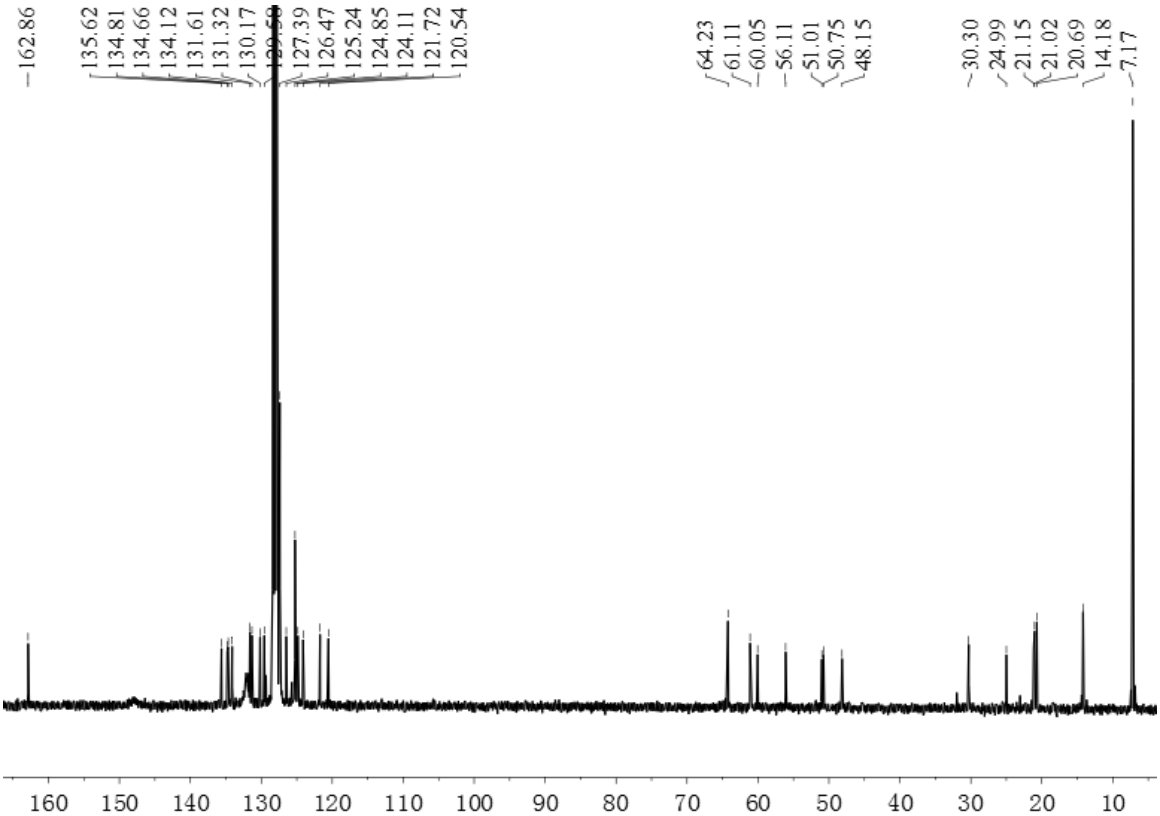


Figure S16. ^{13}C{^{1}H} NMR spectrum (C_6D_6, 400 MHz, 20 °C) of [(*S*)-L^{8}]MgN(SiMe$_3$)$_2$ (**8**).

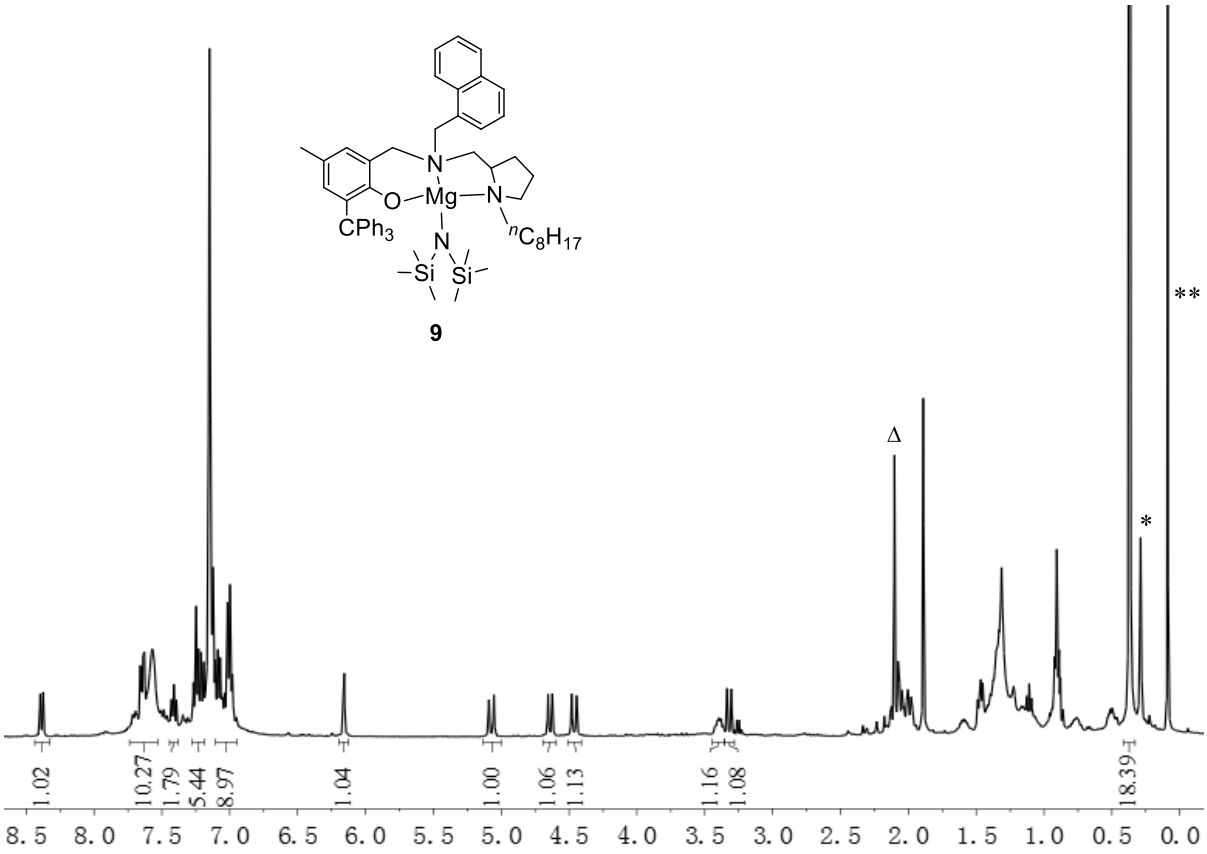


Figure S17. ^{1}H NMR spectrum (C_6D_6, 400 MHz, 20 °C) of [(*S*)-L^{9}]MgN(SiMe$_3$)$_2$ (**9**). (Δ :methyl signal of residual toluene; *:impurity in C_6D_6; **: free HN[Si(C*H*$_3$)$_2$]$_2$).

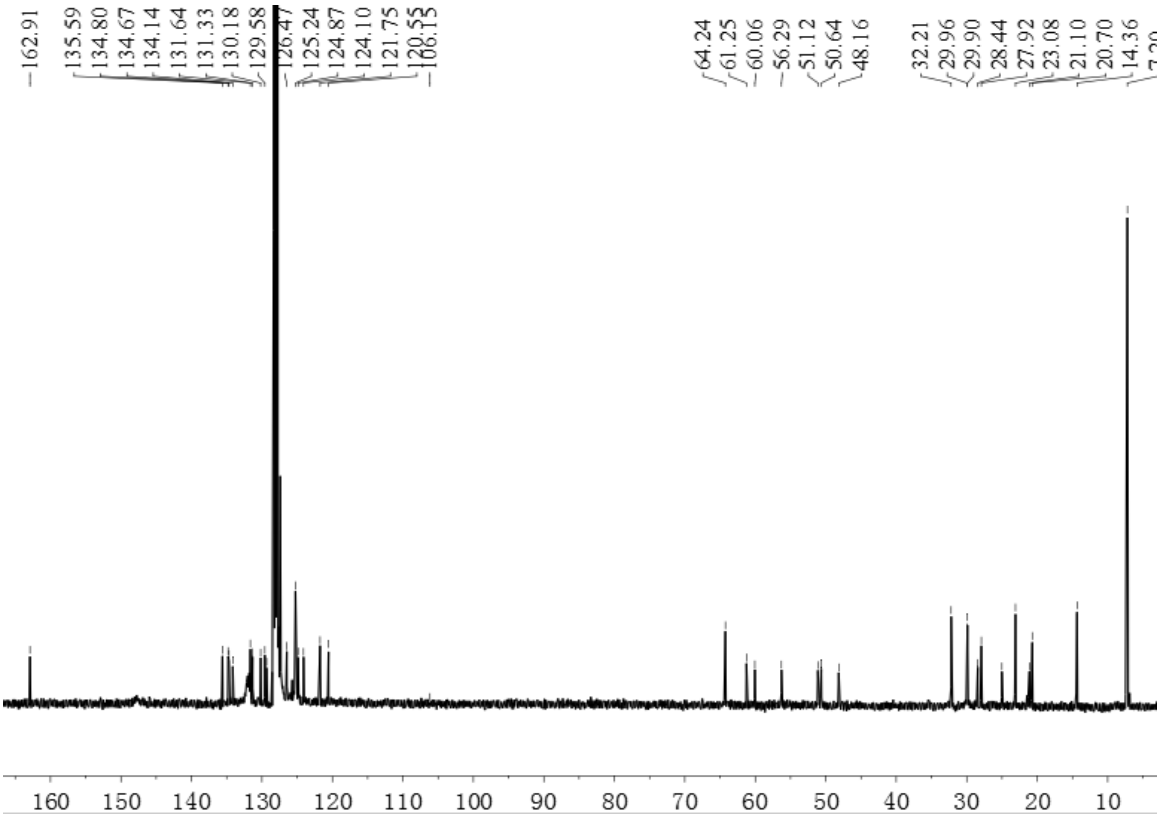


Figure S18. ^{13}C{^{1}H} NMR spectrum (C_6D_6, 400 MHz, 20 °C) of [(*S*)-L^{9}]MgN(SiMe$_3$)$_2$ (**9**).

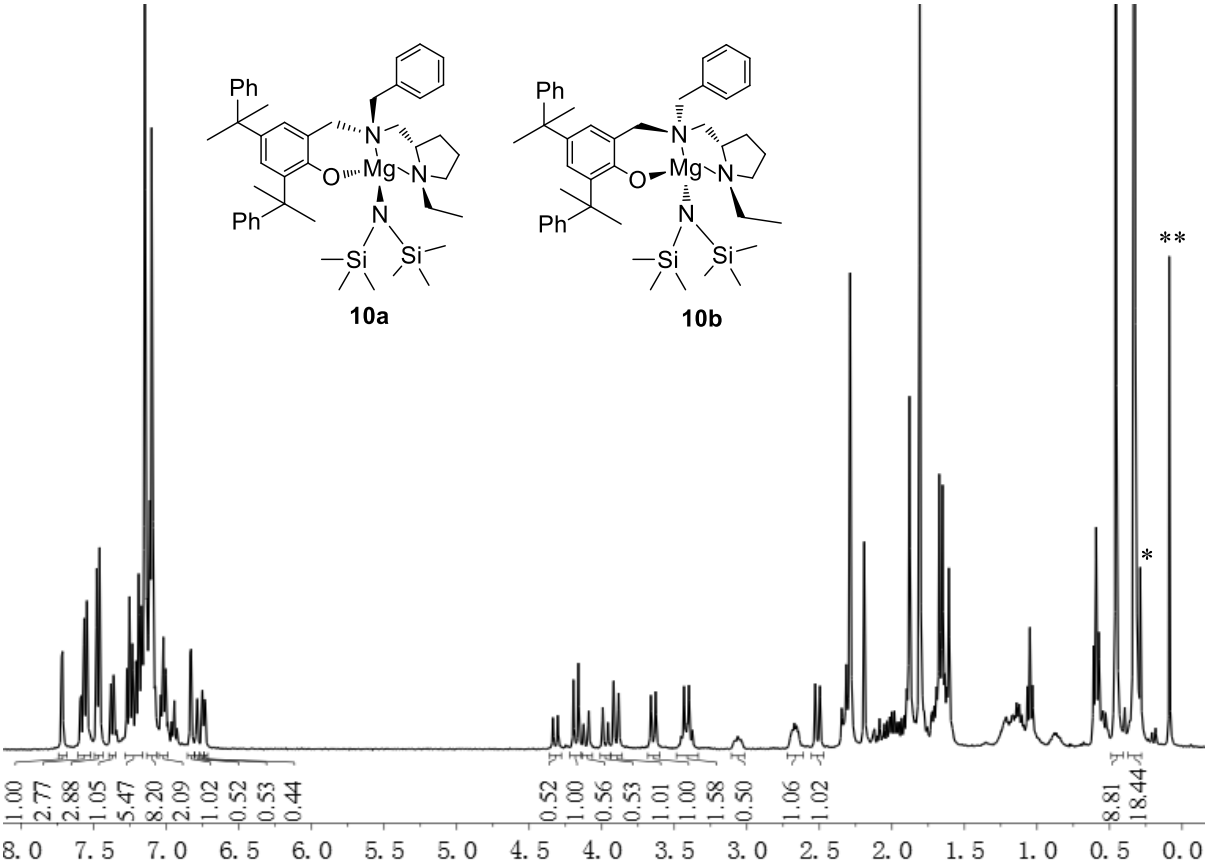


Figure S19. ^{1}H NMR spectrum (C_6D_6, 400 MHz, 20 °C) of [(*S*)-L^{10}]MgN(SiMe$_3$)$_2$ (**10**). (*:impurity in C_6D_6; **: free HN[Si(C*H*$_3$)$_2$]$_2$).

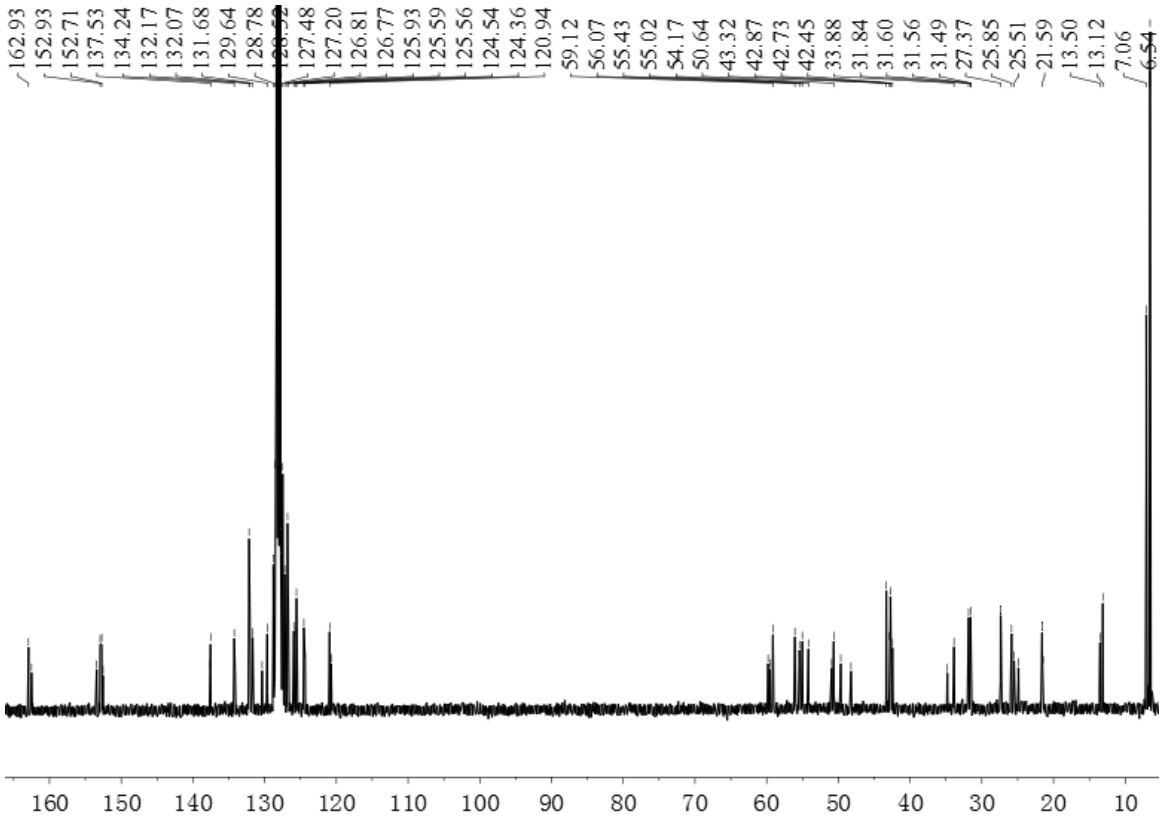


Figure S20. ^{13}C{^{1}H} NMR spectrum (C_6D_6, 400 MHz, 20 °C) of [(*S*)-L^{10}]MgN(SiMe$_3$)$_2$ (**10**).

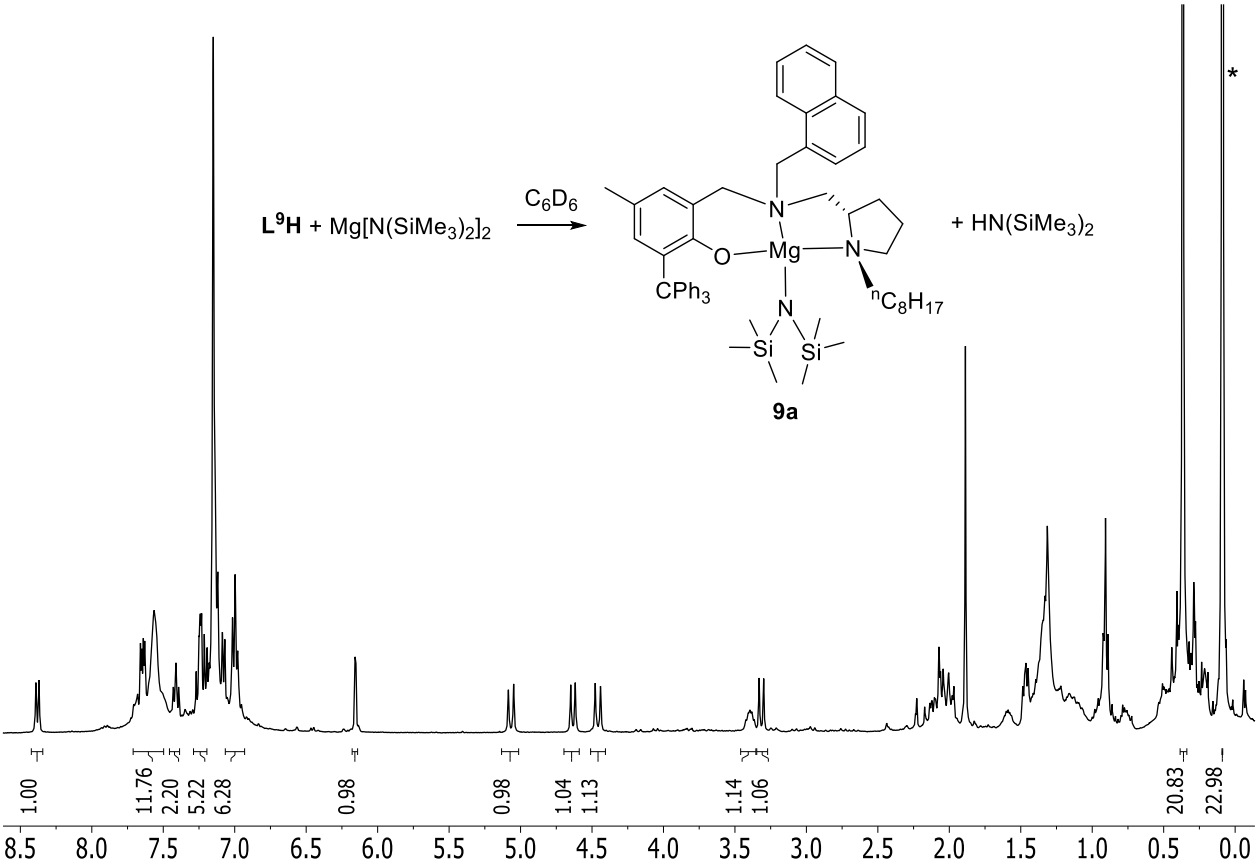


Figure S21. ^{1}H NMR spectrum of the in situ NMR scale reaction of proligand **L^{9}H** with $Mg[N(SiMe_3)_2]_2$ (C_6D_6; 400 MHz, 20 °C; *, $HN(SiMe_3)_2$).

4. Polymerization of *rac*-LA catalyzed by magnesium complexes 1-10

Table S2. Polymerization of *rac*-LA catalyzed by magnesium complexes **1**-**10** in THF [a]

Run	Cat.	Feed Ratio	Solvent	Time (min)	Conv. [b] (%)	M_c [c] ($\times 10^4$ g·mol^{-1})	M_n [d] ($\times 10^4$ g·mol^{-1})	PDI [d]	P_m [e]
1	**1**	200:1:0	THF	5 h	15	n.d	n.d	n.d	0.50
2	**1**	200:1:1	THF	5 h	21	n.d	n.d	n.d	0.51
3	**2**	200:1:0	THF	72 h	62	1.78	2.09	1.32	0.50
4	**2**	200:1:1	THF	96 h	84	2.41	2.54	1.30	0.52
5	**3**	200:1:0	THF	2	92	2.65	2.98	1.36	0.44
6	**3**	200:1:1	THF	2	94	2.70	2.83	1.34	0.47
7	**4**	200:1:0	THF	4	96	2.76	2.79	1.45	0.38
8	**4**	200:1:1	THF	3	93	2.68	1.86	1.42	0.38
9	**5**	200:1:0	THF	15	92	2.65	5.14	1.57	0.27
10	**5**	200:1:1	THF	10	90	2.59	2.97	1.26	0.31
11	**6**	200:1:0	THF	15	93	2.68	3.89	1.72	0.26
12	**6**	200:1:1	THF	10	89	2.56	2.22	1.29	0.32
13	**7**	200:1:0	THF	18	90	2.59	1.61	1.36	0.36
14	**7**	200:1:1	THF	15	98	2.82	1.72	1.32	0.40
15	**8**	200:1:0	THF	2 h	94	2.70	3.36	1.32	0.51
16	**8**	200:1:1	THF	15	94	2.70	2.95	1.30	0.50
17	**9**	200:1:0	THF	2 h	90	2.56	2.91	1.35	0.46
18	**9**	200:1:1	THF	50	93	2.67	2.89	1.37	0.47
19	**10**	200:1:0	THF	10	93	2.68	4.25	1.40	0.36
20	**10**	200:1:1	THF	5	98	2.82	3.57	1.19	0.43

[a] At 25 ± 1 °C, in tetrahydrofuran, [*rac*-LA]$_0$ = 1.0 M; [b] Determined by ^{1}H NMR spectroscopy; [c] $M_{n,Calcd}$ = ([LA]$_0$/[^{i}PrOH]$_0$) × 144.13 × conv.% + 60 or ([LA]$_0$/[Mg]$_0$) × 144.13 × conv.% + 161; [d] Determined by GPC; [e] P_r is the probability of forming a new *r*-dyad, determined by homonuclear decoupled ^{1}H NMR spectroscopy.

5. Microstructure Analysis of Poly(*rac*-lactide)s

	ppm	Height	Width(Hz)	Area
1	5.2229	2778.25	1.4	24463.158
2	5.2070	462.85	1.9	5566.849
3	5.1710	276.62	3.8	6743.377
4	5.1600	499.81	2.5	7873.669
5	5.1490	2085.48	2.4	31783.468

Peak	Integration	P_m
rmr	0.32	0.20
rmm	0.07	0.18
mmr	0.09	0.22
mmm	0.10	0.18
mrm	0.42	0.17
	Average	0.19

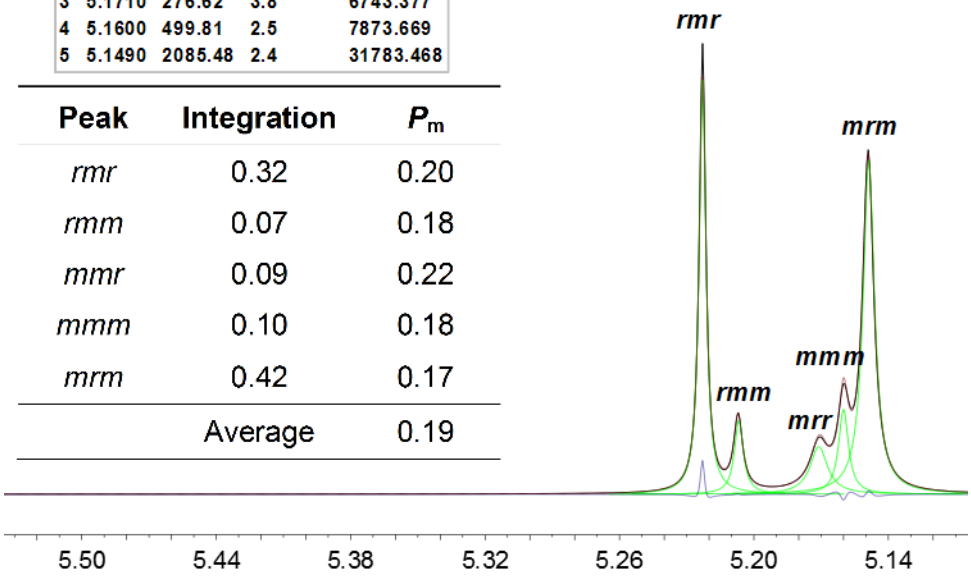


Figure S22. De-convoluted homonuclear decoupled ^{1}H NMR spectra of PLAs obtained from *rac*-lactide by using **6** as initiator in toluene at -38 °C ($CDCl_3$, 400 MHz, P_r = 0.81).

	ppm	Width(Hz)	Height	Area
1	5.1613	3.3	2377.65	49910.751
2	5.1468	3.7	3291.17	64325.474
3	5.112	3.2	3027.05	61257.677
4	5.1004	3.5	14726.48	331854.206
5	5.0905	3.1	4067.73	81929.142

Peak	Integration	P_m
rmr	0.08	0.59
rmm	0.10	0.67
mrr	0.10	0.70
mmm	0.56	0.67
mrm	0.13	0.72
	Average	0.67

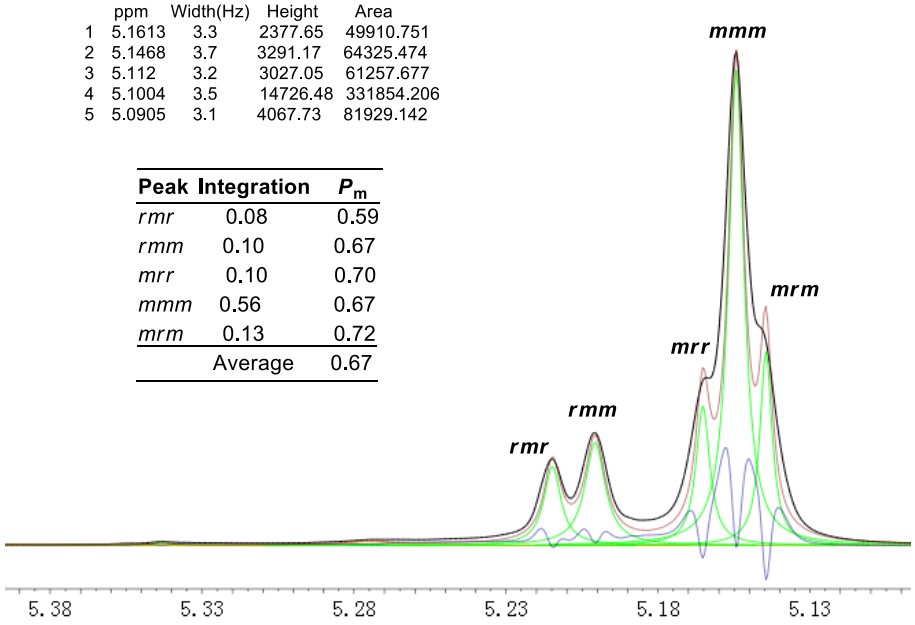


Figure S23. De-convoluted homonuclear decoupled ^{1}H NMR spectra of PLAs obtained from *rac*-lactide by using **3** as initiator in toluene at 25 °C ($CDCl_3$, 400 MHz, P_m = 0.67).

6. Microstructure Analysis of Poly(*rac*-*β*-butyrolactone)s

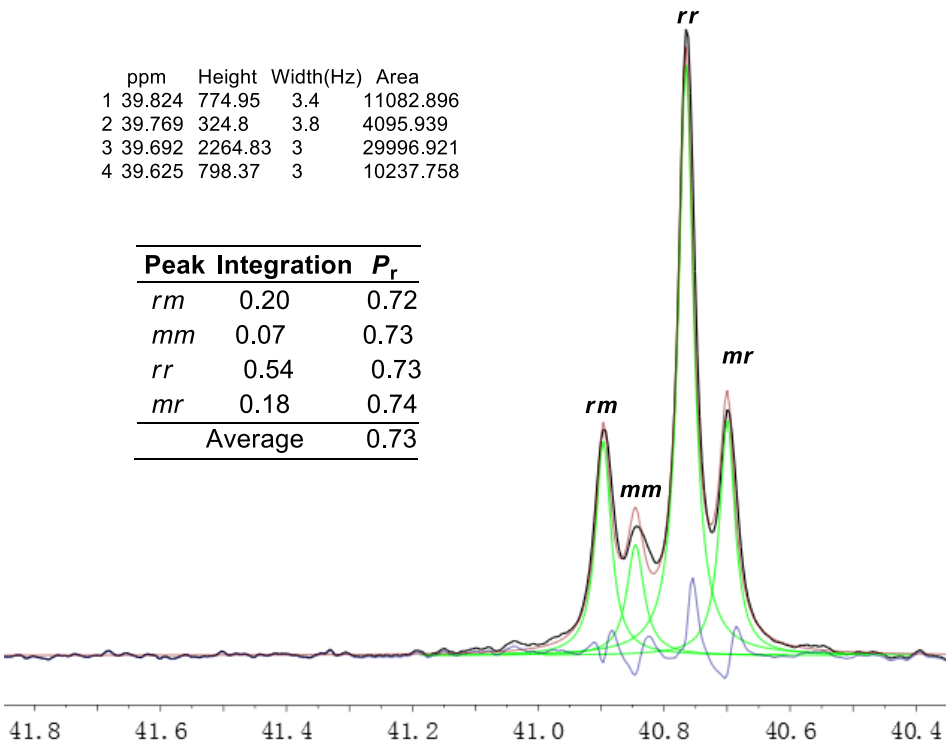


Figure S24. The methylene region of ^{13}C {^{1}H} NMR spectrum($CDCl_3$, 400 MHz, 25°C) of PHB prepared by ROP of *rac*-*β*-butytolactone with **7** as initiator in toluene (P_r = 0.73). P_r = 2(rr)/[2(rr)+rm+mr], rm = mr = P_r(1- P_r), mm = (1- P_r)^2, rr = P_r ^{2}.

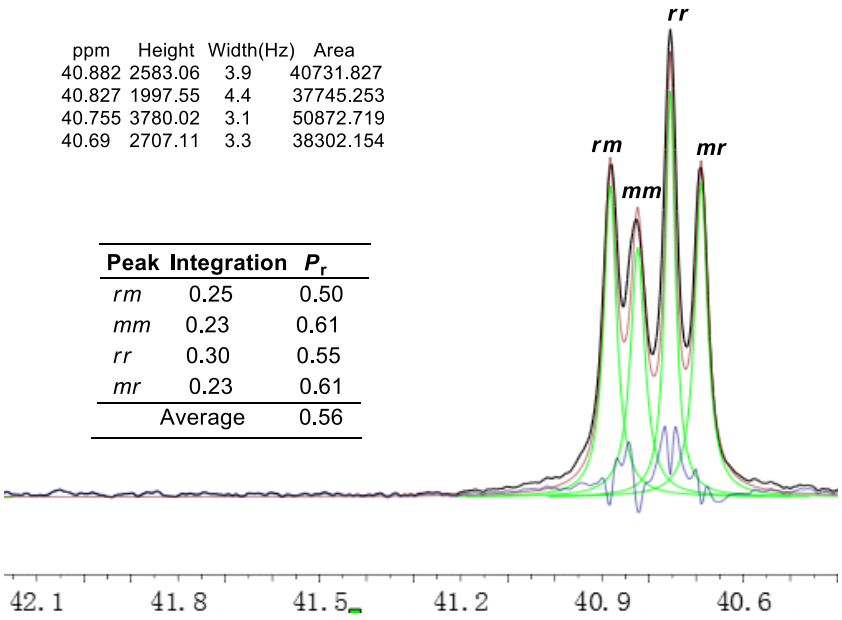


Figure S25. The methylene region of ^{13}C {^{1}H} NMR spectrum($CDCl_3$, 400 MHz, 25°C) of PHB prepared by ROP of *rac*-*β*-butytolactone with **3** as initiator in toluene (P_r = 0.56).

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