

Supporting Information for

**Stereo-selectivity switchable ROP of *rac*- β -butyrolactone initiated by
salan-ligated rare-earth metal amide complexes: the key role of the substituents
on ligand frameworks**

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1. General procedures.

Moisture and air-sensitive materials were performed under a purified argon atmosphere using standard Schlenk techniques. The solvents were freshly distilled from sodium benzophenone ketyl under argon prior to use. $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3(\mu\text{-Cl})\text{Li}(\text{THF})_3$ ($\text{Ln} = \text{Y}, \text{Yb}$) were prepared by using a literature procedures.¹ Salan ligands $\{\text{H}_2\text{L} = [\text{CH}_2\text{N}(\text{R})\text{CH}_2(\text{C}_6\text{H}_2\text{-2-OH-3,5-}'\text{Bu}_2)]_2$; H_2L^1 , $\text{R} = \text{Ph}$; H_2L^2 , $\text{R} = \text{Cy}$; H_2L^3 , $\text{R} = \text{'Bu}$ \} were synthesized according to the similar procedures reported in the literature.² *rac*- β -Butyrolactone (*rac*-BBL) was freshly distilled from CaH_2 under argon and degassed thoroughly by freeze-pump-thaw cycles prior to use. Carbon, hydrogen, and nitrogen analyses were performed by direct combustion with a Carlo-Erba EA-1110 instrument. ^1H and ^{13}C NMR spectra were recorded with Bruker AV-400 NMR and Bruker AV-600 NMR spectrometer. Molecular weight and molecular weight distribution (PDI) of PHBs were determined by gel permeation chromatography (GPC) on a HLC 8320 apparatus at 40 °C, using THF as solvent, a flow rate of eluent of 0.35 mL/min. X-ray crystallographic data were collected using an Agilent Gemini Atlas or a Bruker D8 QUEST CCD X-ray diffractometer. The diffracted intensities were corrected for Lorentz/polarization effects and empirical absorption corrections. The structures were solved by direct methods and refined by full-matrix least-squares procedures based on $|F|^2$. All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were all generated geometrically, assigned appropriate isotropic thermal parameters, and allowed to ride on their parent carbon atoms. All of the hydrogen atoms were held

stationary and included in the structure factor calculation in the final stage of full matrix least-squares refinement. The structures were solved and refined using SHELXL programs.

2. Synthesis of ligands.

N,N'-Diphenyl-N,N'-bis(2-hydroxy-3,5-di-*tert*-butylbenzyl)ethylenediamine

(H₂L¹). Triethylamine (12.35 mL, 130 mmol), 2,4-di-*tert*-butyl-6-(chloromethyl)phenol (30.58 g, 120 mmol), and N,N'-diphenylethylenediamine (12.74 g, 60 mmol) were dissolved in dichloromethane (250 mL). The solution was stirred at 5 °C for 8 h, then quenched with water. The mixture was extracted by dichloromethane for 3 times and dried over MgSO₄. Evaporation off the solvent gave a solid, which was washed with hexane and recrystallized with dichloromethane (26.09 g, 67%). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 8.82 (s, 2H, OH), 7.31 (d, *J* = 2.4 Hz, 2H, Ar-*H*), 7.16 (m, 4H, Ar-*H*), 6.95 (m, 2H, Ar-*H*), 6.88 (d, *J* = 2.4 Hz, 2H, Ar-*H*), 6.84 (m, 4H, Ar-*H*), 4.26 (s, 4H, ArCH₂), 3.23 (s, 4H, NCH₂), 1.42 (s, 18H, C(CH₃)₃), 1.31 (s, 18H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃, 25 °C): δ 153.6, 149.1, 141.7, 136.2, 129.4, 124.1, 123.7, 122.5, 121.3, 119.3 (Ar-*C*), 58.3 (ArCH₂), 49.0 (NCH₂), 35.03, 34.4 (C(CH₃)₃), 31.9, 29.8 (C(CH₃)₃). Anal. Calcd for C₄₄H₆₀N₂O₂: C, 81.43; H, 9.32; N, 4.32. Found: C, 81.26; H, 9.30; N, 4.32.

N,N'-Dicyclohexyl-N,N'-bis(2-hydroxy-3,5-di-*tert*-butylbenzyl)ethylenediamine

(H₂L²). Paraformaldehyde (3.60 g, 120 mmol) was heated at 135 °C for 10 min, and then a mixture of 2,4-di-*tert*-butylphenol (24.76 g, 120 mmol) and N,N'-dicyclohexylethylenediamine (13.47 g, 60 mmol) in methanol (100 mL) was added. The mixture was stirred and refluxed overnight, followed by cooling to room temperature. The white precipitate was obtained by vacuum suction filtration and washed with methanol (19.83 g, 50%). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 10.92 (br s, 2H, OH), 7.21 (d, *J* = 2.3 Hz, 2H, Ar-*H*), 6.81 (d, *J* = 2.1 Hz, 2H, Ar-*H*), 3.69 (s, 4H, ArCH₂), 2.43(m, 6H, NCH₂ and NCH(CH₂)₅), 1.66-1.52 (m, 10H, CH(CH₂)₅),

1.42 (s, 18H, C(CH₃)₃), 1.27 (s, 18H, C(CH₃)₃), 1.10-0.91 (m, 10H, CH(CH₂)₅). ¹³C NMR (101 MHz, CDCl₃, 25 °C): δ 154.6, 140.8, 135.6, 123.5, 122.8, 122.3 (Ar-C), 61.5 (ArCH₂), 57.3 (NCH(CH₂)₅), 49.8 (NCH₂), 34.9, 34.28 (C(CH₃)₃), 31.9, 29.8 (C(CH₃)₃), 26.0, 25.9 (CH(CH₂)₅). Anal. Calcd for C₄₄H₇₂N₂O₂: C, 79.94; H, 10.98; N, 4.24. Found: C, 80.14; H, 11.02; N, 4.23.

N,N'-Di-*tert*-butyl-N,N'-bis(2-hydroxy-3,5-di-*tert*-butylbenzyl)ethylenediamine

(H₂L³). H₂L³ was synthesized in analogy to H₂L² from N,N'-di-*tert*-butylethylenediamine (10.34 g, 60 mmol). Yield: 18.64 g, 51%. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 10.73 (br s, 2H, OH), 7.19 (d, *J* = 2.4 Hz, 2H, Ar-*H*), 6.81 (d, *J* = 2.3 Hz, 2H, Ar-*H*), 4.16 (br s, 2H, ArCH₂), 3.12 (br s, 2H, ArCH₂), 2.53 (br s, 2H, NCH₂), 2.11 (br s, 2H, NCH₂), 1.44 (s, 18H, C(CH₃)₃), 1.25 (s, 18H, C(CH₃)₃), 0.78 (s, 18H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃, 25 °C): δ 154.6, 140.9, 135.6, 123.9, 123.0, 122.9 (Ar-C), 55.6 (ArCH₂), 55.3 (NC(CH₃)₃), 51.7 (NCH₂), 34.9, 34.3 (C(CH₃)₃), 30.8, 29.8, 26.2 (C(CH₃)₃). Anal. Calcd for C₄₀H₆₈N₂O₂: C, 78.89; H, 11.26; N, 4.60. Found: C, 79.13; H, 11.28; N, 4.60.

3. Synthesis of complexes 1-6.

Synthesis of complex **1**. A solution of $\text{Y}[\text{N}(\text{SiMe}_3)_2]_3(\mu\text{-Cl})\text{Li}(\text{THF})_3$ (11.54 mL, 0.13 M in toluene, 1.5 mmol) was added to a solution of H_2L^1 (0.97 g, 1.5 mmol) in toluene (10 mL). The mixture was stirred at 90 °C for 24 h, and then the solvent was removed under vacuum. The residue was crystallized with a mixture of toluene and *n*-hexane at room temperature to give colourless crystals in several days (0.90 g, 61%). ^1H NMR (400 MHz, CDCl_3 , 25 °C): δ 7.18-7.10 (m, 12H, Ar-*H*), 6.53 (br s, 2H, Ar-*H*), 3.99 (br s, 4H, ArCH₂), 3.47 (s, 4H, NCH₂), 1.45 (s, 18H, C(CH₃)₃), 1.16 (s, 18H, C(CH₃)₃), 0.32 (br s, 9H, N(Si(CH₃)₃)₂), -0.35 (br s, 9H, N(Si(CH₃)₃)₂). ^1H NMR (600 MHz, toluene-*d*₈, 25 °C): δ 7.43 (s, 2H, Ar-*H*), 6.93 (m, 7H, Ar-*H*), 6.77 (s, 2H), 6.55 (m, 3H, Ar-*H*), 3.73 (br s, 4H, ArCH₂), 2.97 (br s, 4H, NCH₂), 1.67 (s, 18H, C(CH₃)₃), 1.28 (s, 18H, C(CH₃)₃), 0.65 (s, 9H, N(Si(CH₃)₃)₂), -0.14 (s, 9H, N(Si(CH₃)₃)₂). ^{13}C NMR (101 MHz, toluene-*d*₈, 25 °C) δ 161.2, 148.1, 138.2, 129.8, 126.8, 126.2, 126.04, 123.9, 123.6 (Ar-C), 66.9 (ArCH₂), 51.3 (NCH₂), 35.9, 34.6, (C(CH₃)₃), 32.5, 30.9 (C(CH₃)₃), 6.0, 5.4 (N(Si(CH₃)₃)₂). Anal. Calcd for $\text{C}_{50}\text{H}_{76}\text{N}_3\text{O}_2\text{Si}_2\text{Y}$: C, 67.01; H, 8.55; N, 4.69. Found: C, 67.05; H, 8.39; N, 4.63.

Synthesis of complex **2**. Complex **2** was synthesized in analogy to complex **1** from $\text{Yb}[\text{N}(\text{SiMe}_3)_2]_3(\mu\text{-Cl})\text{Li}(\text{THF})_3$ (12.50 mL, 1.5 mmol, 0.12 M in toluene). Yellow crystals were obtained in toluene and hexane (0.85 g, 58%). Anal. Calcd for $\text{C}_{50}\text{H}_{76}\text{N}_3\text{O}_2\text{Si}_2\text{Yb}$: C, 61.26; H, 7.81; N, 4.29. Found: C, 61.10; H, 7.65; N, 4.18.

Synthesis of complex **3**. Complex **3** was synthesized in analogy to complex **1** from H_2L^2 (0.99 g, 1.5 mmol). Colourless crystals were obtained in hexane and toluene (1.04 g, 76%). ^1H NMR (400 MHz, toluene- d_8 , 25 °C): δ 7.48 (br s, 2H, Ar-*H*), 6.78 (br, 2H, Ar-*H*), 4.40 (br s, 1H, ArCH₂), 3.99 (br s, 1H, ArCH₂), 3.17-2.67 (m, 8H, ArCH₂ and NCH₂ and NCH(CH₂)₅), 1.88-1.49 (m, 28H, C(CH₃)₃ and NCH(CH₂)₅), 1.39 (s, 18H, C(CH₃)₃), 1.12-0.77 (m, 10H, overlap with the signal of hexane, NCH(CH₂)₅), 0.41 (s, 18H, N(Si(CH₃)₃)₂). ^1H NMR (600 MHz, toluene- d_8 , -10 °C): δ 7.58 (s, 1H, Ar-*H*), 7.47 (s, 1H, Ar-*H*), 7.03 (m, 1H, Ar-*H*), 6.74 (s, 1H, Ar-*H*), 4.40 (d, $J = 12.1$ Hz, 1H, ArCH₂), 3.92 (d, $J = 12.1$ Hz, 1H, ArCH₂), 3.11 (d, $J = 12.1$ Hz, 1H, ArCH₂), 2.93 (d, $J = 12.1$ Hz, 1H, ArCH₂), 2.78 (m, 1H, NCH₂), 2.64 (m, 2H, NCH(CH₂)₅), 2.43 (m, 1H, NCH₂), 2.22 (d, $J = 15.1$ Hz, 1H, NCH₂), 1.95 (d, $J = 15.1$ Hz, 1H, NCH₂), 1.81 (s, 9H, C(CH₃)₃), 1.77-1.67 (m, 6H, CH(CH₂)₅), 1.52 (s, 9H, C(CH₃)₃), 1.43 (s, 9H, C(CH₃)₃), 1.40 (s, 9H, C(CH₃)₃), 1.33-0.67 (m, 14H, CH(CH₂)₅), 0.47 (s, 9H, N(Si(CH₃)₃)₂), 0.44 (s, 9H, N(Si(CH₃)₃)₂). ^{13}C NMR (101 MHz, toluene- d_8 , 25 °C) δ 161.4, 160.3, 138.2, 136.2, 123.9, 123.2, (Ar-C), 60.2, 58.8 (ArCH₂), 57.2, 54.5 (NC(CH₂)₅), 48.0, 44.1 (NCH₂), 35.8, 34.6, (C(CH₃)₃), 32.5, 30.8 (C(CH₃)₃), 27.0, 26.8, 26.7 (NC(CH₂)₅), 6.2, 5.5, (N(Si(CH₃)₃)₂). Anal. Calcd for C₅₀H₈₈N₃O₂Si₂Y: C, 66.11; H, 9.77; N, 4.63. Found: C, 65.79; H, 9.61; N, 4.58.

Synthesis of complex **4**. Complex **4** was synthesized in analogy to complex **2** from H_2L^2 (0.99 g, 1.5 mmol). Yellow crystals were obtained in hexane and toluene (1.01 g, 68%). Anal. Calcd for C₅₀H₈₈N₃O₂Si₂Yb: C, 60.51; H, 8.94; N, 4.23. Found: C, 60.65; H, 8.69; N, 4.23.

Synthesis of complex **5**. Complex **5** was synthesized in analogy to complex **1** from H_2L^3 (0.91 g, 1.5 mmol). Colourless crystals were obtained in hexane and toluene (0.83 g, 65%). ^1H NMR (400 MHz, toluene- d_8 , 25 °C): δ 7.48 (s, 1H, Ar-*H*), 7.37 (s, 1H, Ar-*H*), 7.08 (s, 1H, overlap with residual signal of toluene- d_8 , Ar-*H*), 6.55 (s, 1H, Ar-*H*), 4.50 (d, $J = 10.3$ Hz, 1H, ArCH₂), 3.53 (d, $J = 13.7$ Hz, 1H, ArCH₂), 2.93 (d, $J = 10.4$ Hz, 1H, ArCH₂), 2.71 (m, 2H, ArCH₂ and NCH₂), 2.32 (d, $J = 14.3$ Hz, 1H, NCH₂), 2.15 (m, 1H, overlap with residual signal of toluene- d_8 , NCH₂), 1.98 (m, 1H, NCH₂), 1.73 (s, 9H, C(CH₃)₃), 1.39 (s, 9H, C(CH₃)₃), 1.37 (s, 9H, C(CH₃)₃), 1.27 (s, 9H, C(CH₃)₃), 1.20 (s, 9H, C(CH₃)₃), 0.78 (s, 9H, C(CH₃)₃), 0.53 (s, 9H, N(Si(CH₃)₃)₂), 0.49 (s, 9H, N(Si(CH₃)₃)₂). ^{13}C NMR (400 MHz, toluene- d_8 , 25 °C): δ 162.0, 160.6, 138.9, 137.4, 136.3, 127.4, 126.2, 126.0, 125.1, 123.8, (Ar-*C*), 63.3, 61.1 (ArCH₂), 60.2, 57.7 (NC(CH₃)₃), 53.7, 53.0 (NCH₂), 35.9, 35.8, 34.8, 34.6 (C(CH₃)₃), 32.6, 32.5, 31.3, 30.7, 27.9 (C(CH₃)₃), 6.5, 6.0 (N(Si(CH₃)₃)₂). Anal. Calcd for C₄₆H₈₄N₃O₂Si₂Y: C, 64.52; H, 9.89; N, 4.91. Found: C, 64.31; H, 9.68; N, 4.83.

Synthesis of complex **6**. Complex **6** was synthesized in analogy to complex **2** from H_2L^3 (0.91 g, 1.5 mmol). Yellow crystals were obtained in hexane and toluene (0.94g, 68%). Anal. Calcd for C₄₆H₈₄N₃O₂Si₂Yb: C, 58.75; H, 9.00; N, 4.47. Found: C, 58.94; H, 8.91; N, 4.39.

4. Synthesis of polymers.

All the polymerizations of *rac*-BBL were performed in the glove-box under nitrogen, and a typical polymerization procedure is given (Table 1, run 1). A 20 mL vial equipped with a magnetic stirring bar was charged with a toluene solution of monomer (0.30 mL, 3.69 mmol) and initiator **1** (16.5 mg). The mixture was stirred at 25 °C for 6 h, and quenched with acidic ethanol. The mixture was then poured into excess ethanol to precipitate the polymer, which was dried in a vacuum oven at 50 °C and weighed.

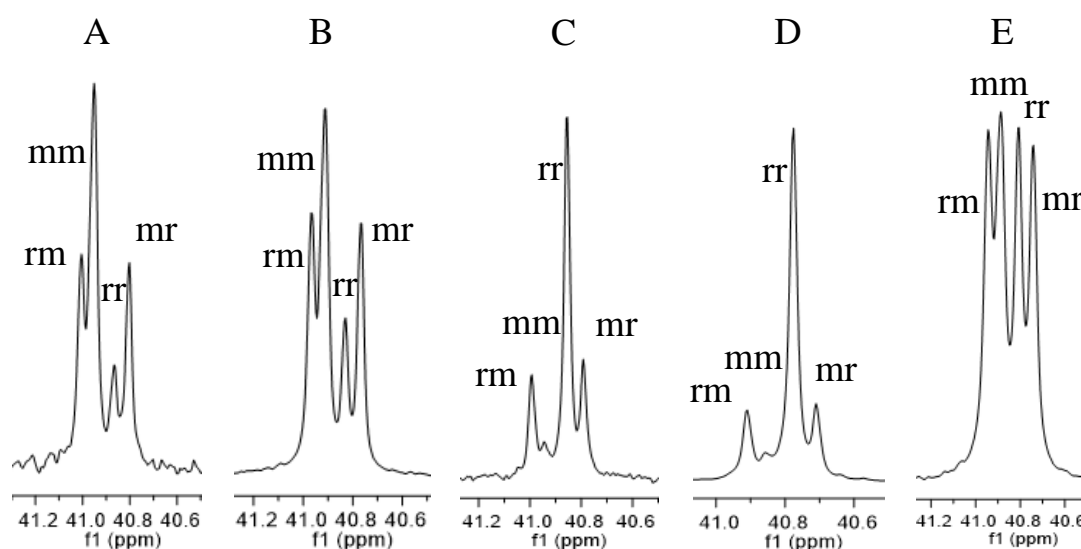


Figure S1. Methylene region of the ^{13}C NMR spectrum (151 MHz, CDCl_3 , 25 °C) of PHBs prepared by ROP of *rac*-BBL. Key: (A) with complex **1** ($P_m = 0.66$); (B) with complex **2** ($P_m = 0.72$); (C) with complex **3** ($P_m = 0.23$); (D) with complex **4** ($P_m = 0.22$). (E) with complex **5** ($P_m = 0.52$).

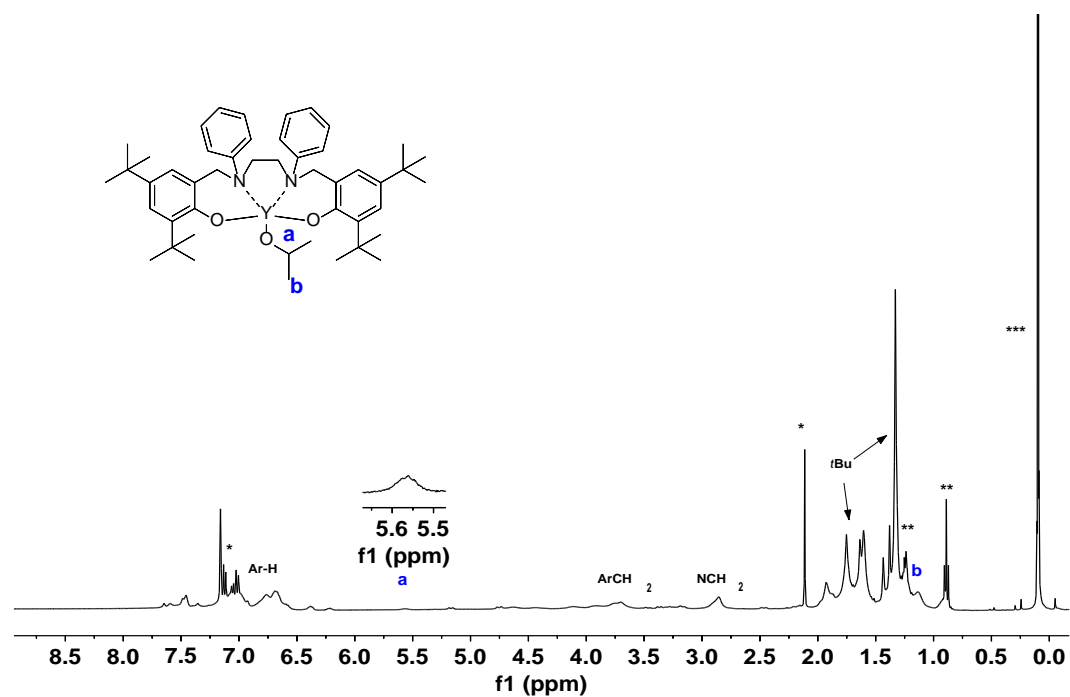


Figure S2. ^1H NMR spectrum (400 MHz, C_6D_6 , 25 $^\circ\text{C}$) of complex **1** + isopropanol ([**1**]:[isopropanol] = 1:1) (*, toluene; **, hexane; ***, free $\text{HN}(\text{SiMe}_3)_2$).

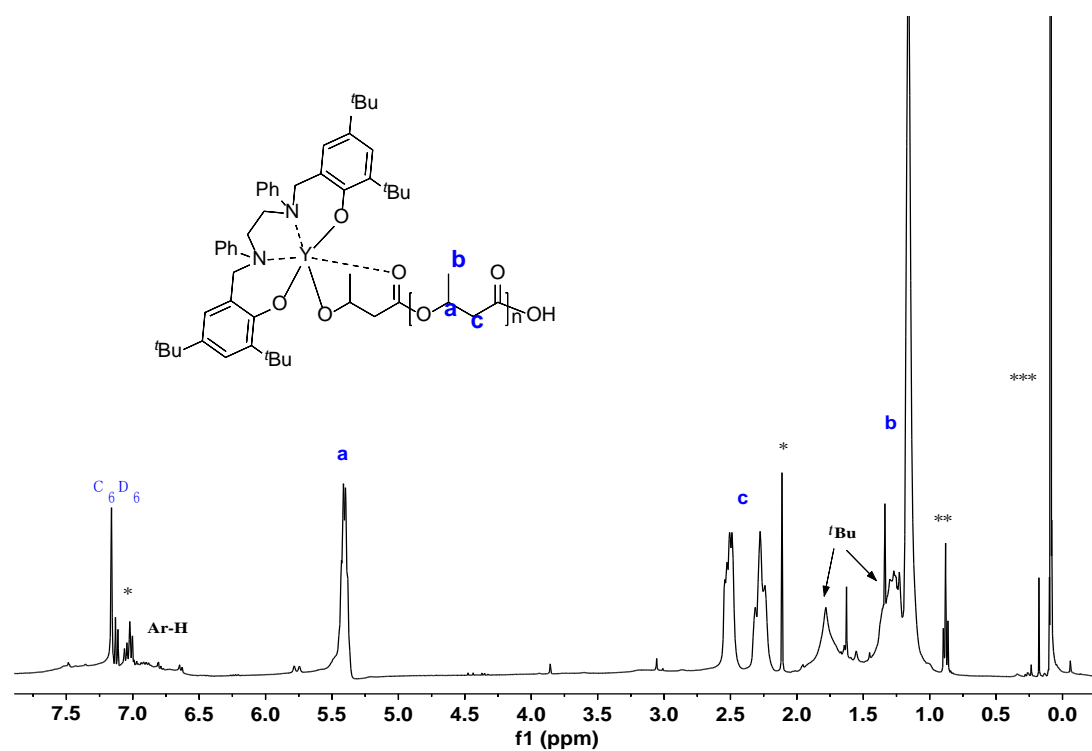


Figure S3. ^1H NMR spectrum (400 MHz, C_6D_6) of oligomer of *rac*-BBL obtained with **1**, [BBL]/[**1**] = 20/1, C_6D_6 , 25 $^\circ\text{C}$ (*, toluene; **, hexane; ***, free $\text{HN}(\text{SiMe}_3)_2$).

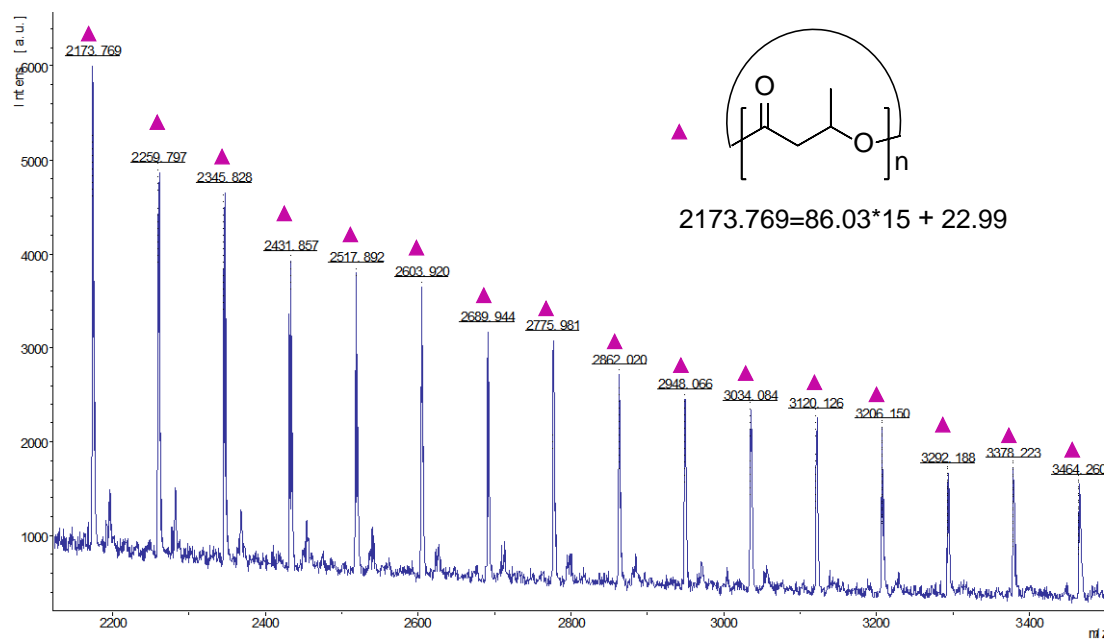


Figure S4. MALDI-TOF mass spectrum of oligomer of *rac*-BBL obtained with **1** [BBL]/[**1**] = 20/1 in toluene, at 25°C. (Doped with Na⁺).

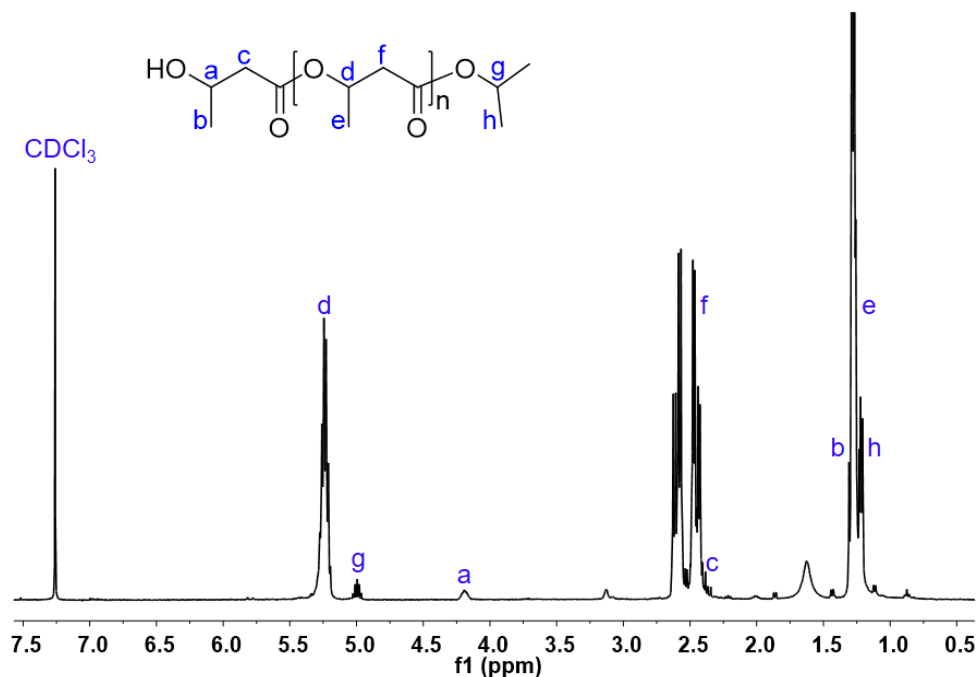


Figure S5. ¹H NMR spectrum (400 MHz, CDCl₃) of oligomer of *rac*-BBL obtained with **1** in the presence of isopropanol after quenching with acidic ethanol. Conditions: [BBL]₀ = 2 M ([BBL]/[**1**]/[isopropanol] = 20/1/1) in toluene, at 25 °C.

Crystal structure for ligands and complexes 1-6.

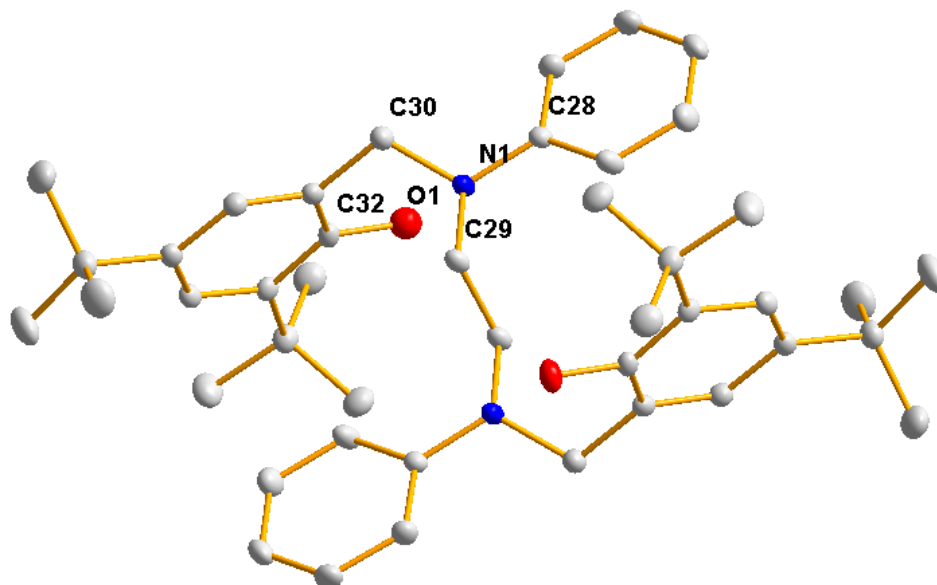


Figure S6. Crystal structure for ligand H_2L^1 . Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (\AA) and bond angles [deg]: N1-C28 1.4220(19), N1-C29 1.467(2), N1-C30 1.484(2), O1-C32 1.3734(19); C28-N1-C29 117.74(13), C28-N1-C30 117.84(12), C29-N1-C30 112.39(13).

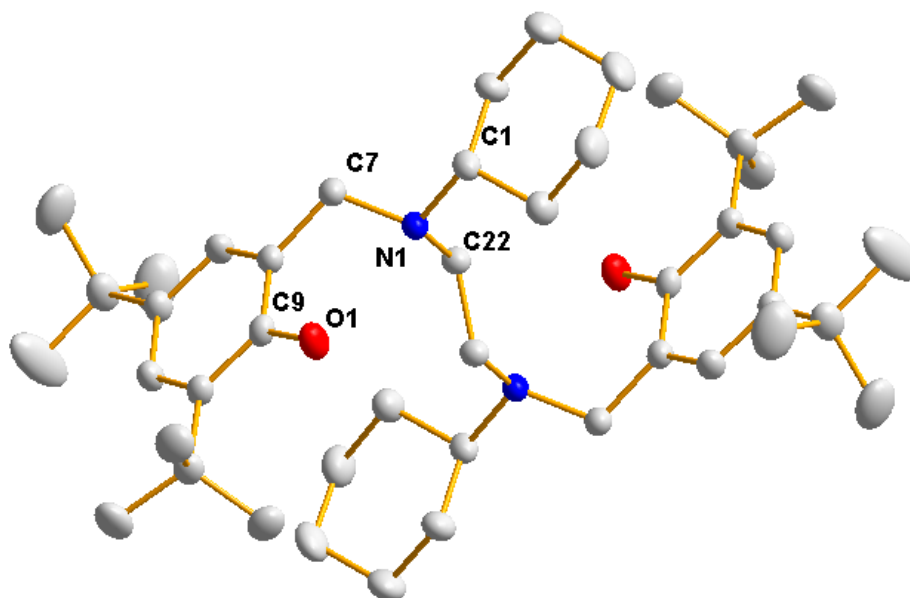


Figure S7. Crystal structure for ligand H_2L^2 . Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (\AA) and bond angles [deg]: N1-C7 1.471(2), N1-C22 1.475(3), N1-C1 1.484(2), O1-C9 1.370(2), C7-N1-C22 111.93(16); C7-N1-C1 112.02(15), C22-N1-C1 114.46(14).

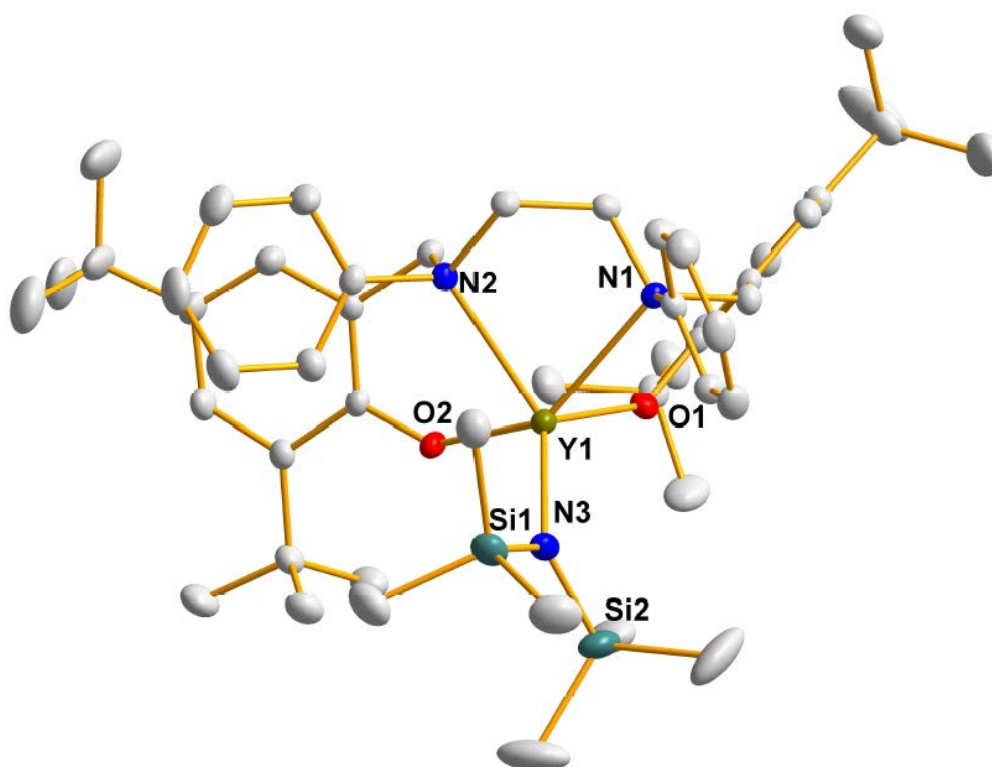


Figure S8. Crystal structure for complex **1**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles [deg]: Y1-O1 2.1123(18), Y1-O2 2.101(2), Y1-N1 2.591(2), Y1-N2 2.548(2), Y1-N3 2.393(3); N1-Y1-N² 72.1(3), N3-Y1-N1 109.3(3), N3-Y1-N2 125.2(3), O1-Y1-N1 145.5(3), O1-Y1-N2 81.3(3), O1-Y1-N3 121.5(3), O1-Y1-O2 92.9(3), O2-Y1-N1 78.0(3), O2-Y1-N2 112.5(3), O2-Y1-N3 121.5(3).

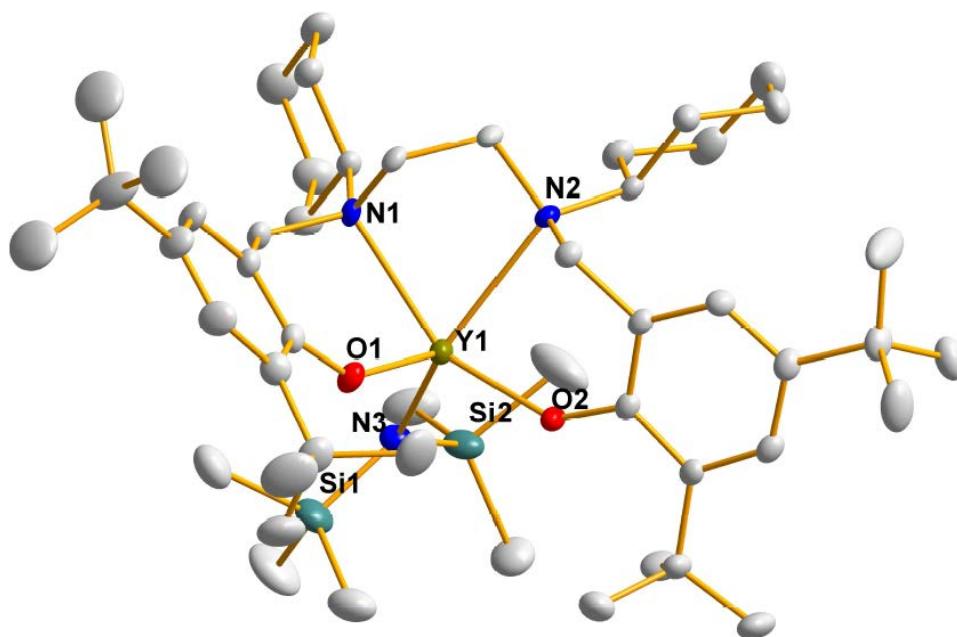


Figure S9. Crystal structure for complex **3**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and bond angles [deg]: Y1-O1 2.097(3), Y1-O2 2.108(3), Y1-N1 2.530(3), Y1-N2 2.683(3), Y1-N3 2.259(4); N1-Y1-N2 70.60(10), N3-Y1-N1 109.90(13), N3-Y1-N2 143.48(12), O1-Y1-N1 77.82(11), O1-Y1-N2 110.81(11), O1-Y1-N3 104.67(13), O1-Y1-O2 99.05(11), O2-Y1-N1 145.83(11), O2-Y1-N2 79.20(10), O2-Y1-N3 103.84(13).

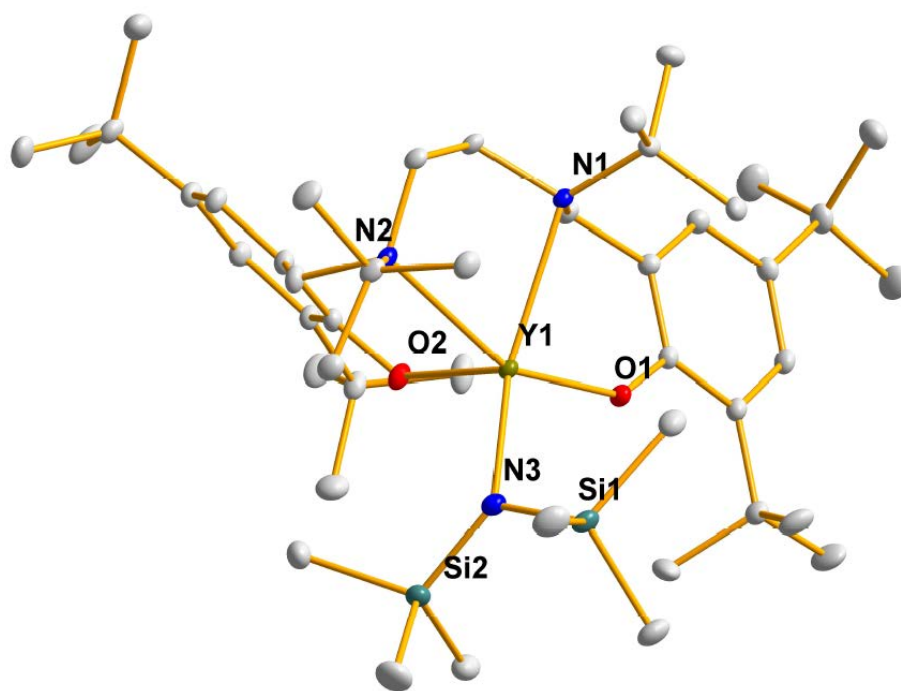


Figure S10. Crystal structure for complex **5**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles [deg]: Y1-O1 2.101(16), Y1-O2 2.088(17), Y1-N1 2.619(2), Y1-N2 2.624(2), Y1-N3 2.252(3); N1-Y1-N2 74.04(6), N3-Y1-N1 158.59(7), N3-Y1-N2 103.32(7), O1-Y1-N1 78.40 (6), O1-Y1-N2 152.03(6), O1-Y1-N3 104.06(7), O1-Y1-O2 97.54(7), O2-Y1-N1 96.76(7), O2-Y1-N2 81.24(6), O2-Y1-N3 103.89(7).

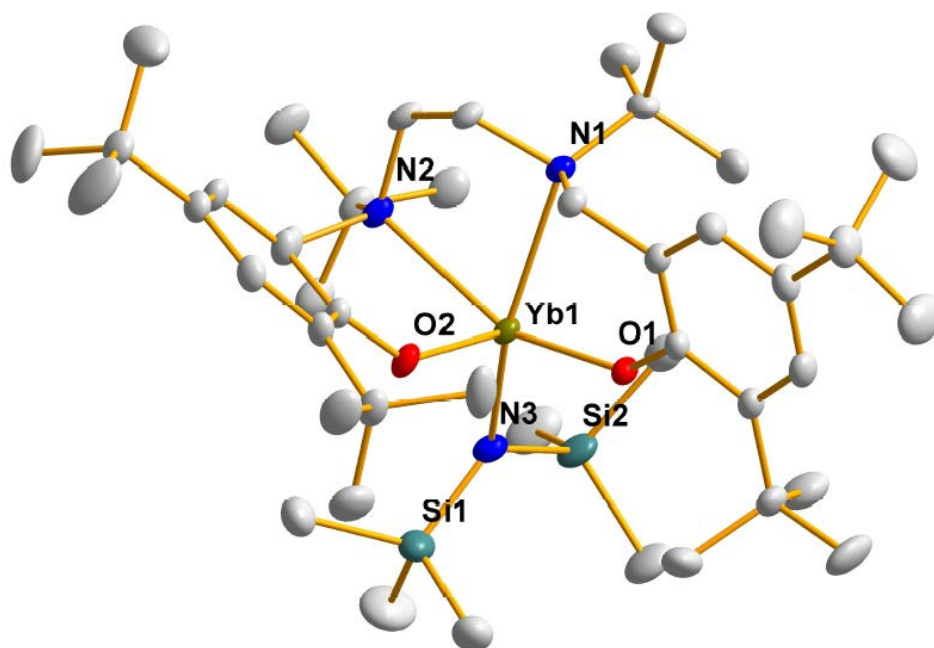


Figure S11. Crystal structure for complex **6**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (\AA) and bond angles [deg]: Yb1-O1 2.070(3), Yb1-O2 2.061(3), Yb1-N1 2.586(3), Yb1-N2 2.583(3), Yb1-N3 2.211(3); N1-Yb1-N2 74.80(11), N3-Yb1-N1 158.35(12), N3-Yb1-N2 102.74(12), O1-Yb1-N1 79.05(10), O1-Yb1-N2 153.55(11), O1-Yb1-N3 103.03(12), O1-Yb1-O2 97.38(11), O2-Yb1-N1 97.30(11), O2-Yb1-N2 82.18(10), O2-Yb1-N3 103.72(12).

5 X-ray crystallographic data for ligands H₂L¹, H₂L² and complexes 1-6.

Table S1. Crystallographic data for ligands H₂L¹ and H₂L².

Compound	H ₂ L ¹	H ₂ L ²
Empirical formula	C ₄₄ H ₆₀ N ₂ O ₂	C ₄₄ H ₇₂ N ₂ O ₂
Formula weight	648.94	661.03
Temperature/K	296(2)	293(2)
Crystal system	Monoclinic	Triclinic
Space group	I2/c	P $\bar{1}$
a/Å	13.5259(12)	9.6188(6)
b/Å	9.7850(9)	9.9837(7)
c/Å	29.268(3)	12.2473(9)
α /°		101.903(6)
β /°	95.506(5)	98.362(6)
γ /°		113.312(6)
Volume/Å ³	3855.8(6)	1022.59(13)
Z	4	1
$\rho_{\text{calc}}/\text{cm}^3$	1.118	1.073
μ/mm^{-1}	0.067	0.485
F(000)	1416	366
Crystal size/mm ³	0.35 × 0.20 × 0.12	0.35 × 0.30 × 0.30
Radiation	MoK α (λ = 0.71073)	CuK α (λ = 1.54184)
2 θ range for data collection/°	4.392 to 54.98	7.624 to 146.918
Index ranges	-17 ≤ h ≤ 17, -12 ≤ k ≤ 12, -37 ≤ l ≤ 37	-7 ≤ h ≤ 11, -12 ≤ k ≤ 11, -13 ≤ l ≤ 15
Reflections collected	71170	6688
Independent reflections	4378 [R _{int} = 0.0971, R _{sigma} = 0.0525]	3974 [R _{int} = 0.0284, R _{sigma} = 0.0385]
Data/restraints/parameters	4378/0/223	3974/0/224
Goodness-of-fit on F ²	1.120	1.029
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0580, wR ₂ = 0.1514	R ₁ = 0.0698, wR ₂ = 0.2009
Final R indexes [all data]	R ₁ = 0.0984, wR ₂ = 0.1694	R ₁ = 0.0867, wR ₂ = 0.2220
Largest diff. peak/hole / e Å ⁻³	0.19/-0.23	0.41/-0.28

Table S2. Crystallographic data for complexes **1–3**.

Compound	1	2	2(3).3C₇H₈
Empirical formula	C ₅₀ H ₇₆ N ₃ O ₂ Si ₂ Y	C ₅₀ H ₇₆ N ₃ O ₂ Si ₂ Yb	C ₁₂₁ H ₂₀₀ N ₆ O ₄ Si ₄ Y ₂
Formula weight	896.22	980.35	2093.05
Temperature/K	293(2)	293(2)	223(2)
Crystal system	Monoclinic	monoclinic	monoclinic
Space group	P2 ₁ /c	P2 ₁ /c	P2/c
a/Å	15.3478(4)	15.2120(12)	23.3487(9)
b/Å	16.3591(5)	16.174(2)	12.1983(5)
c/Å	20.5634(6)	20.7742(15)	21.8684(9)
β/°	94.045(3)	95.218(6)	92.992(4)
Volume/Å ³	5150.1(3)	5090.0(8)	6219.9(4)
Z	4	4	2
ρ _{calc} /cm ³	1.156	1.279	1.118
μ/mm ⁻¹	1.217	1.923	1.016
F(000)	1920	2044	2268
Crystal size/mm ³	0.75 × 0.5 × 0.4	0.75 × 0.55 × 0.3	0.75 × 0.45 × 0.3
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	5.876 to 60.618	5.71 to 50	6 to 52.74
Index ranges	-21 ≤ h ≤ 21, -22 ≤ k ≤ 22, -28 ≤ l ≤ 27	-17 ≤ h ≤ 18, -19 ≤ k ≤ 19, -24 ≤ l ≤ 24	-29 ≤ h ≤ 29, -15 ≤ k ≤ 15, -26 ≤ l ≤ 27
Reflections collected	41842	30215	44381
Independent reflections	13814 [R _{int} = 0.0805, R _{sigma} = 0.1445]	8875 [R _{int} = 0.1537, R _{sigma} = 0.1295]	12704 [R _{int} = 0.0850, R _{sigma} = 0.0970]
Data/restraints/parameters	13814/6/541	8875/19/541	12704/8/585
Goodness-of-fit on F ²	1.003	1.017	1.016
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0652, wR ₂ = 0.0972	R ₁ = 0.0665, wR ₂ = 0.1315	R ₁ = 0.0719, wR ₂ = 0.1757
Final R indexes [all data]	R ₁ = 0.1408, wR ₂ = 0.1201	R ₁ = 0.1249, wR ₂ = 0.1943	R ₁ = 0.1221, wR ₂ = 0.2003
Largest diff. peak/hole / e Å ⁻³	0.64/-0.59	2.17/-2.13	1.08/-0.98

Table S3. Crystallographic data for complexes **4–6**.

Compound	2(4).1C ₇ H ₈	5	2(6).1C ₇ H ₈
Empirical formula	C ₁₀₇ H ₁₈₂ N ₆ O ₄ Si ₄ Yb ₂	C ₄₆ H ₈₄ N ₃ O ₂ Si ₂ Y	C ₉₉ H ₁₇₆ N ₆ O ₄ Si ₄ Yb ₂
Formula weight	2075.02	856.25	1972.89
Temperature/K	120(2)	120(2)	296(2)
Crystal system	monoclinic	triclinic	triclinic
Space group	P2/c	P $\bar{1}$	P $\bar{1}$
a/Å	21.5295(6)	10.8751(10)	10.9326(19)
b/Å	12.1512(4)	12.0478(12)	12.067(2)
c/Å	23.1374(7)	20.872(2)	21.041(4)
α /°		105.371(3)	105.472(6)
β /°	93.7523(9)	96.234(3)	96.265(6)
γ /°		94.373(3)	94.586(6)
Volume/Å ³	6040.0(3)	2605.5(4)	2642.0(8)
Z	2	2	1
ρ_{calc} /cm ³	1.141	1.091	1.240
μ /mm ⁻¹	1.624	1.199	1.852
F(000)	2188	464	1040
Crystal size/mm ³	0.55 × 0.40 × 0.35	0.45 × 0.40 × 0.30	0.60 × 0.40 × 0.20
Radiation	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)
2 θ range for data collection/°	4.868 to 68.282	4.538 to 60.064	4.518 to 52.744
Index ranges	-33 ≤ h ≤ 34, -17 ≤ k ≤ 17, -31 ≤ l ≤ 31	-15 ≤ h ≤ 15, -16 ≤ k ≤ 16, -29 ≤ l ≤ 29	-13 ≤ h ≤ 13, -15 ≤ k ≤ 15, -26 ≤ l ≤ 26
Reflections collected	153045	77201	234317
Independent reflections	20116 [R _{int} = 0.0440, R _{sigma} = 0.0264]	14862 [R _{int} = 0.0818, R _{sigma} = 0.0720]	10716 [R _{int} = 0.1062, R _{sigma} = 0.0307]
Data/restraints/parameters	20116/226/602	14862/0/511	10716/1/522
Goodness-of-fit on F ²	1.129	0.723	1.095
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0308, wR ₂ = 0.0717	R ₁ = 0.0482, wR ₂ = 0.1241	R ₁ = 0.0400, wR ₂ = 0.0847
Final R indexes [all data]	R ₁ = 0.0404, wR ₂ = 0.0752	R ₁ = 0.0709, wR ₂ = 0.1408	R ₁ = 0.0452, wR ₂ = 0.0874
Largest diff. peak/hole / e Å ⁻³	1.25/-1.34	0.47/-0.78	1.43/-1.56

6 ^1H NMR, ^{13}C NMR spectra for ligands and complexes 1, 3, and 5.

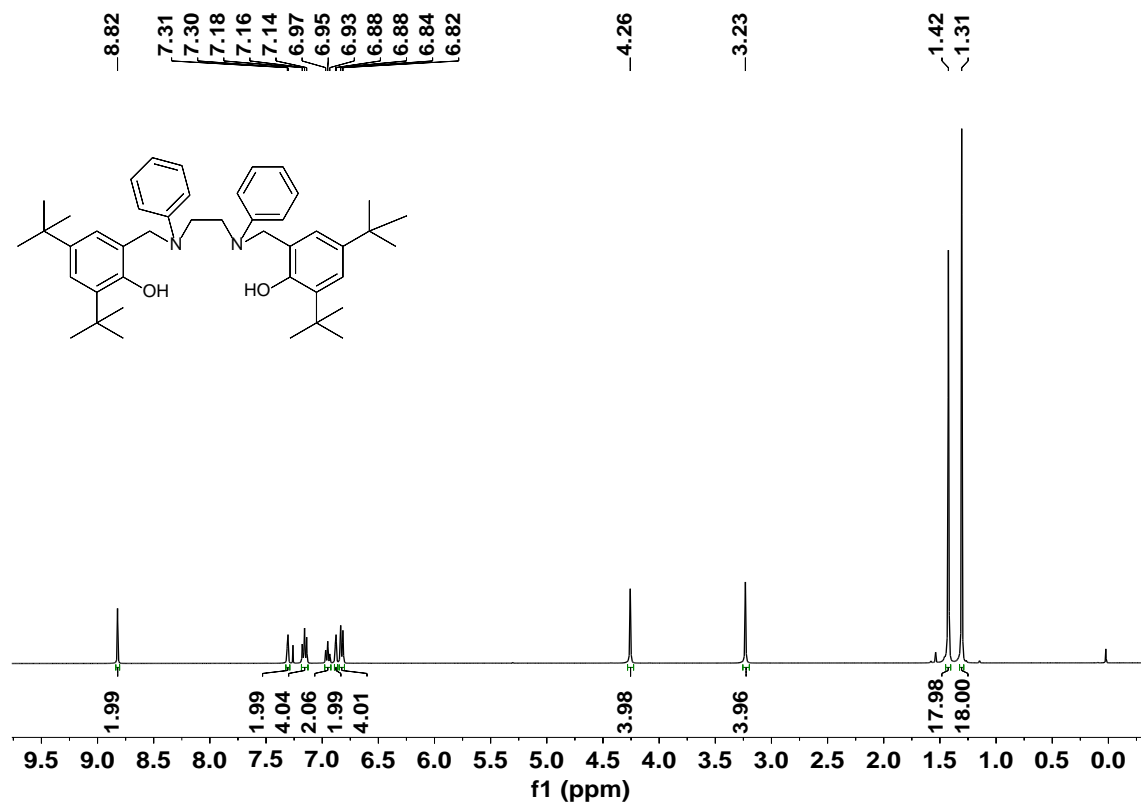


Figure S12. ^1H NMR spectrum (400 MHz, CDCl_3 , 25 $^\circ\text{C}$) of H_2L^1 .

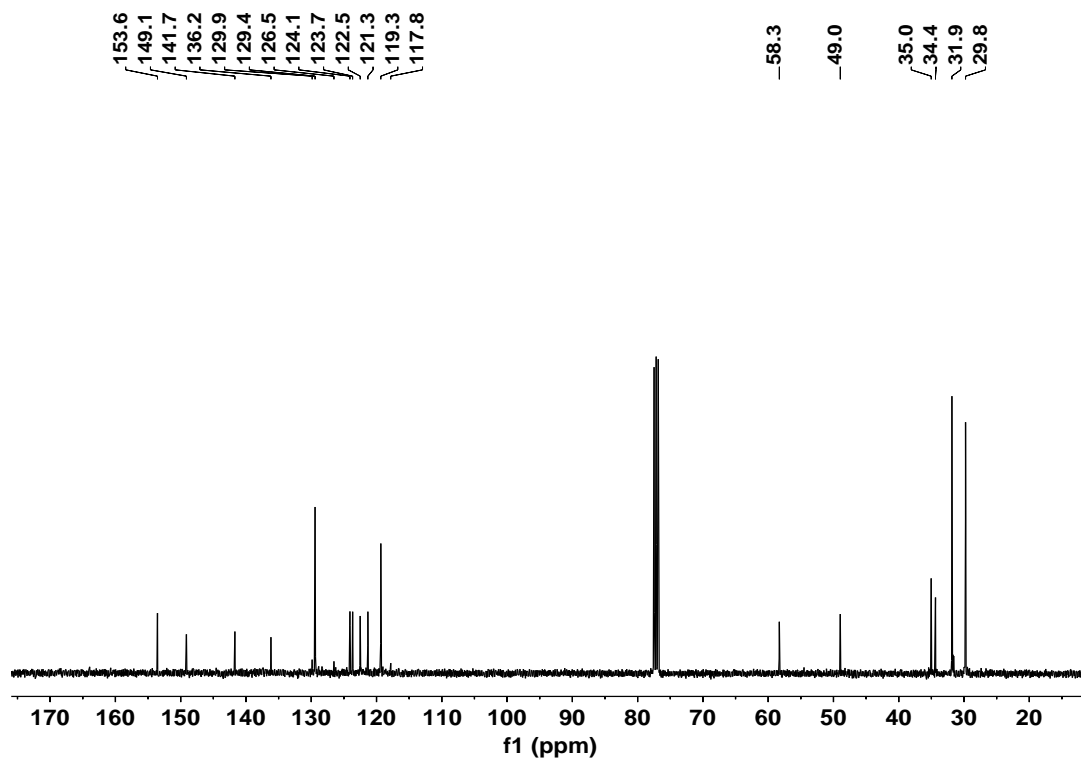


Figure S13. ^{13}C NMR spectrum (101 MHz, CDCl_3 , 25 $^\circ\text{C}$) of H_2L^1 .

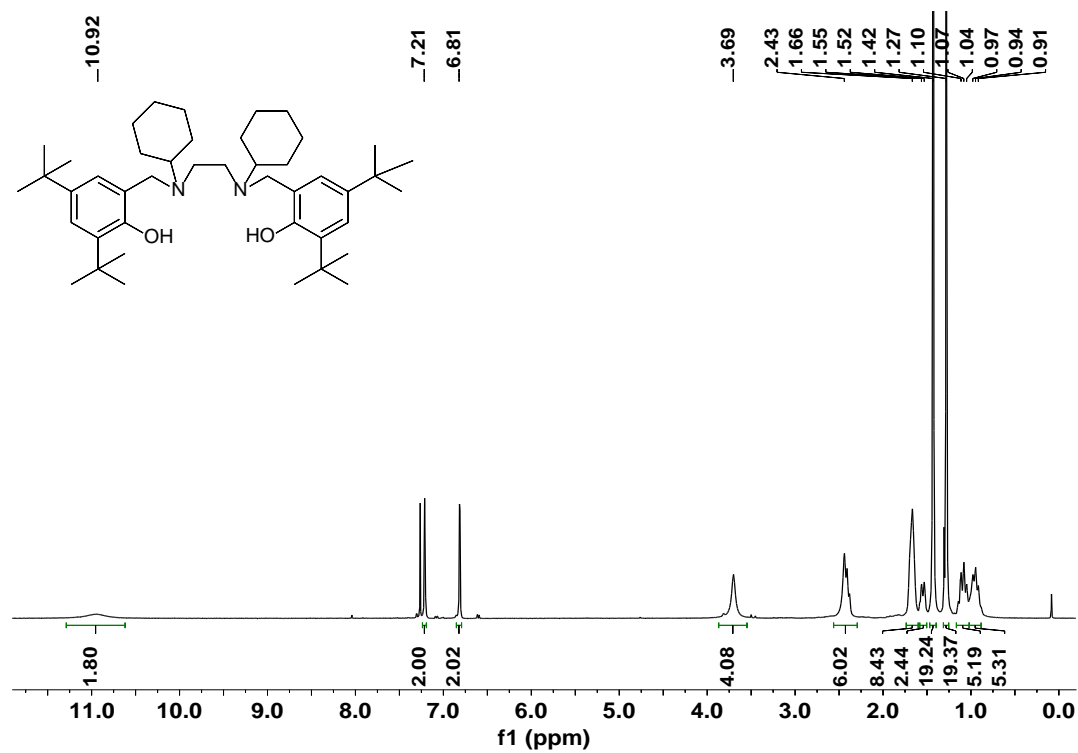


Figure S14. 1H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of H_2L^2 .

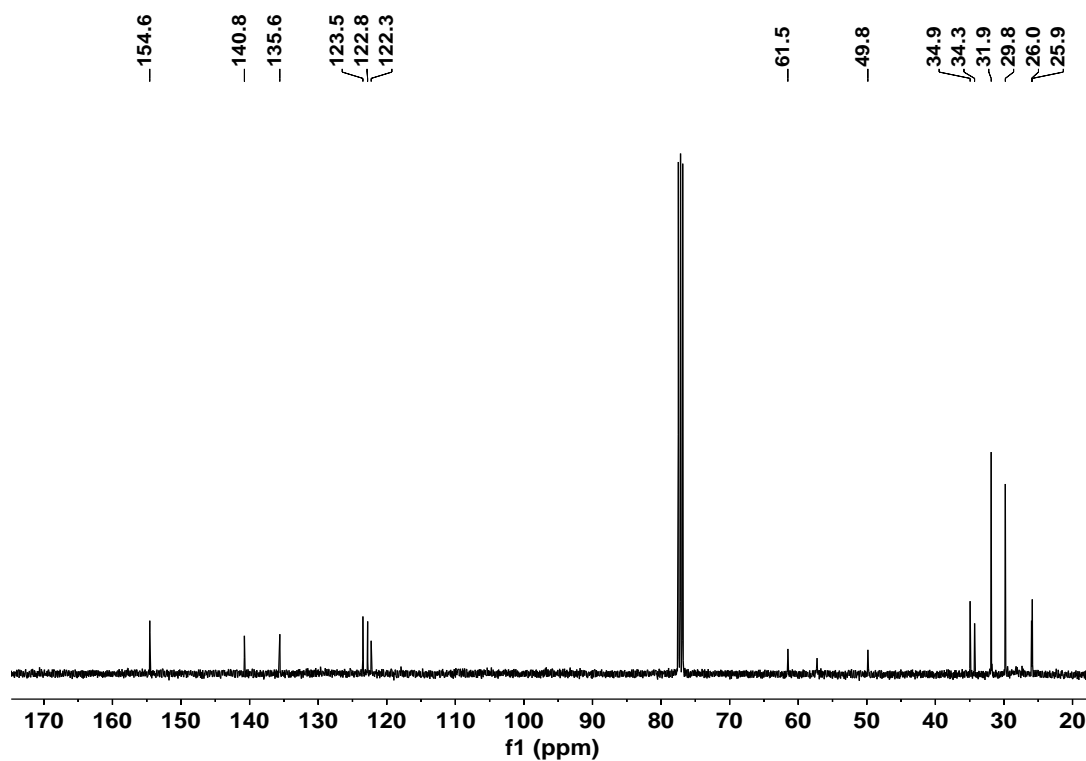


Figure S15. ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 25 °C) of H_2L^2 .

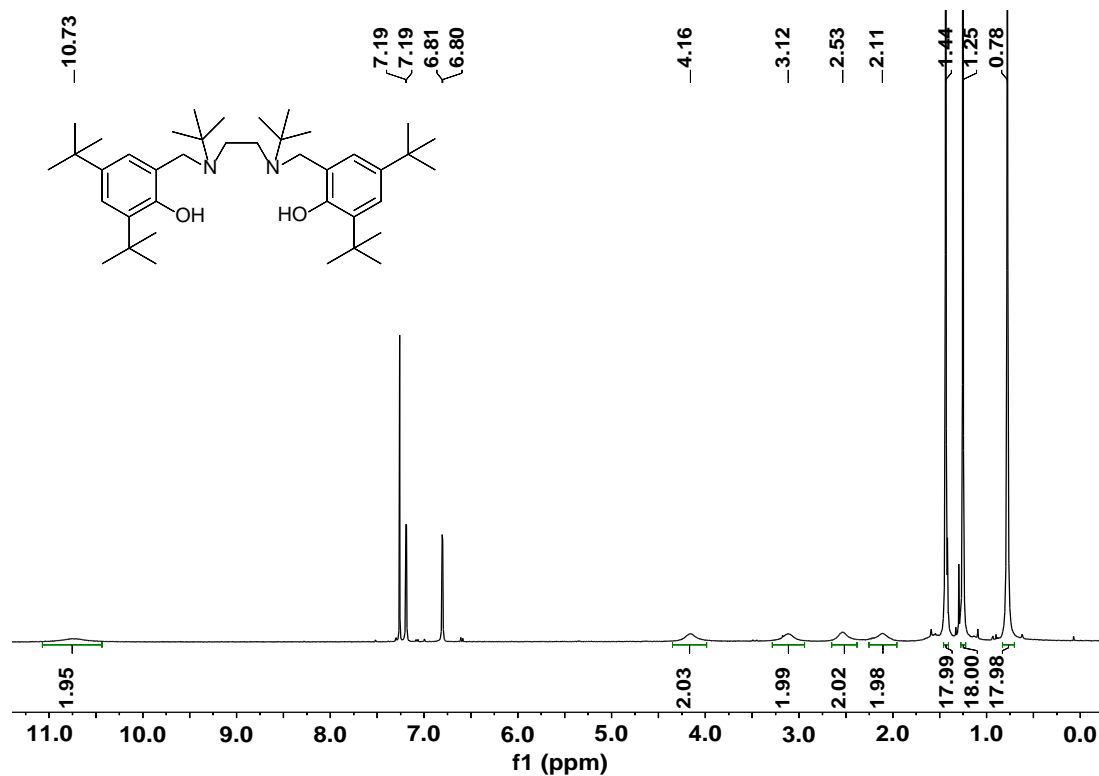


Figure S16. 1H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of H_2L^3 .

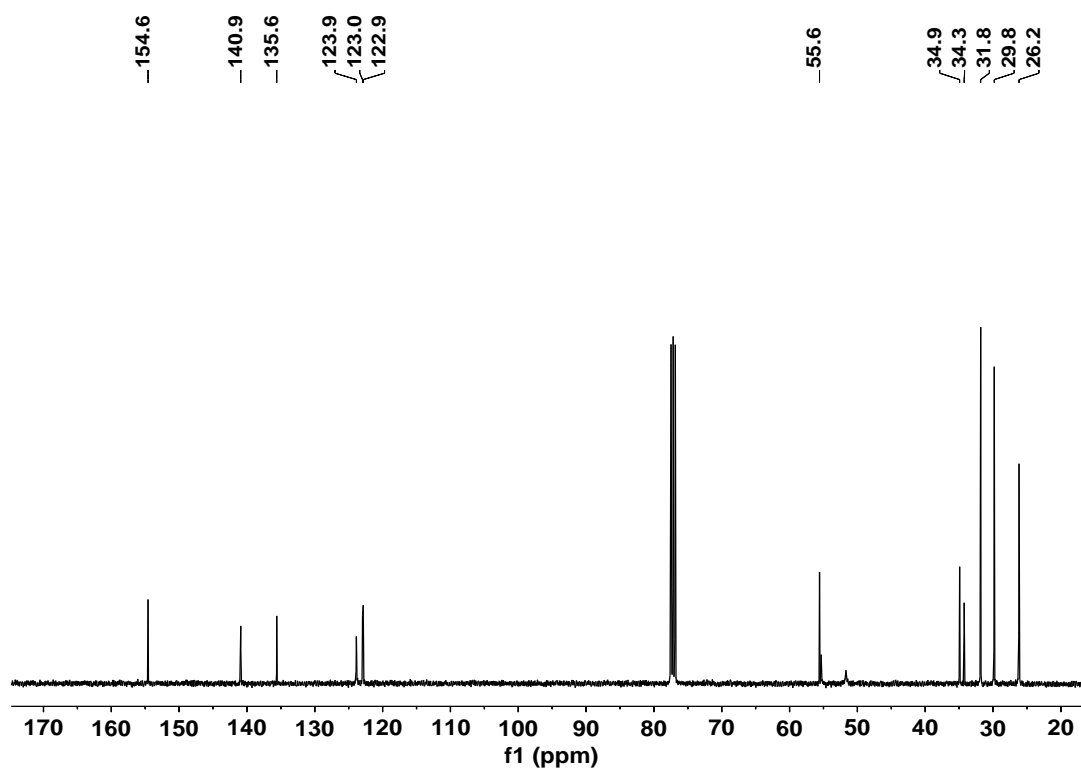


Figure S17. ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 25 °C) of H_2L^3 .

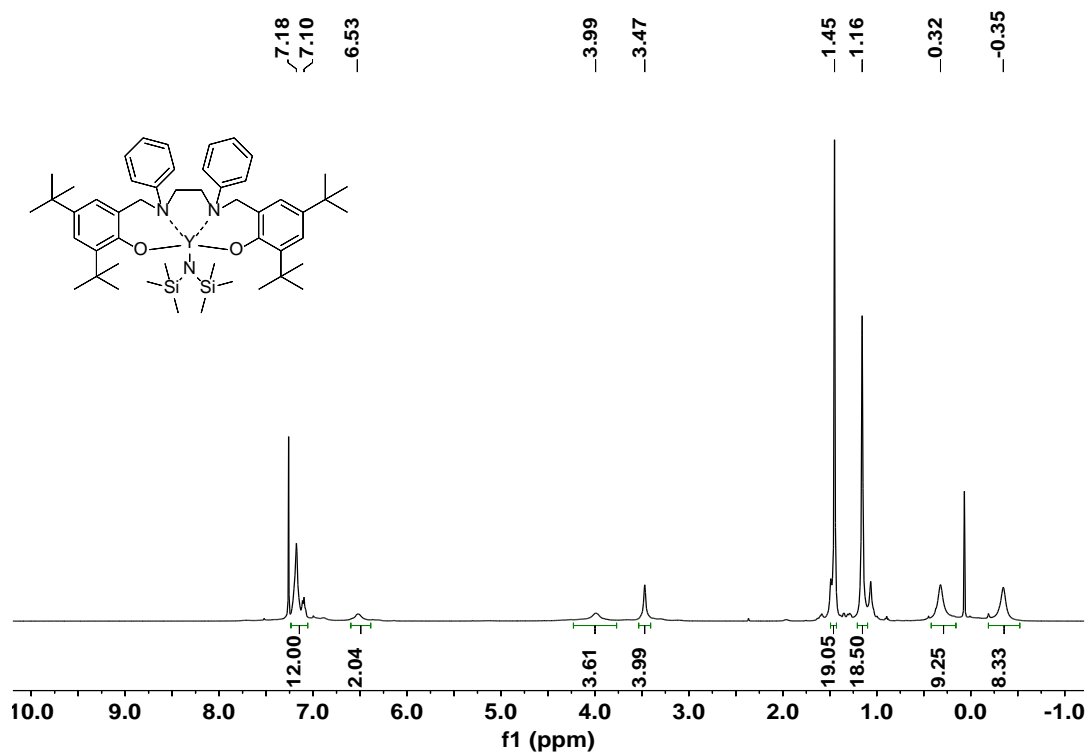


Figure S18. ^1H NMR spectrum (400 MHz, CDCl_3 , 25 $^\circ\text{C}$) of complex 1.

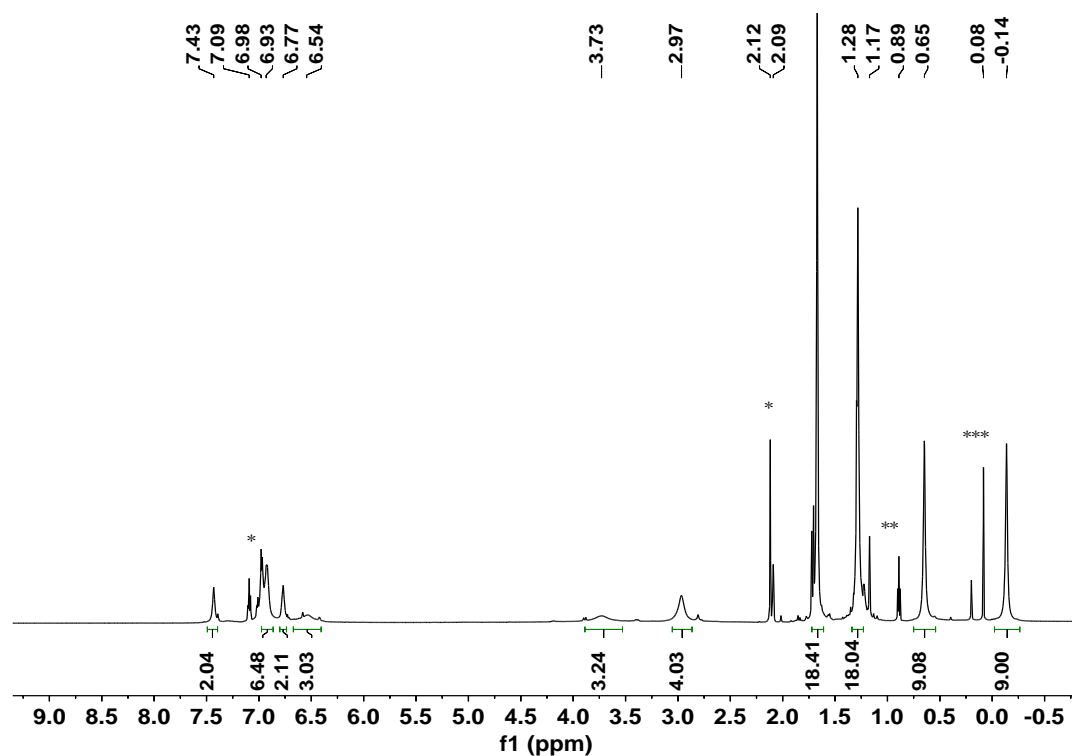


Figure S19. ^1H NMR spectrum (600 MHz, toluene- d_8 , 25 $^\circ\text{C}$) of complex 1. (*, toluene and toluene- d_8 ; **, hexane; ***, free $\text{HN}(\text{SiMe}_3)_2$).

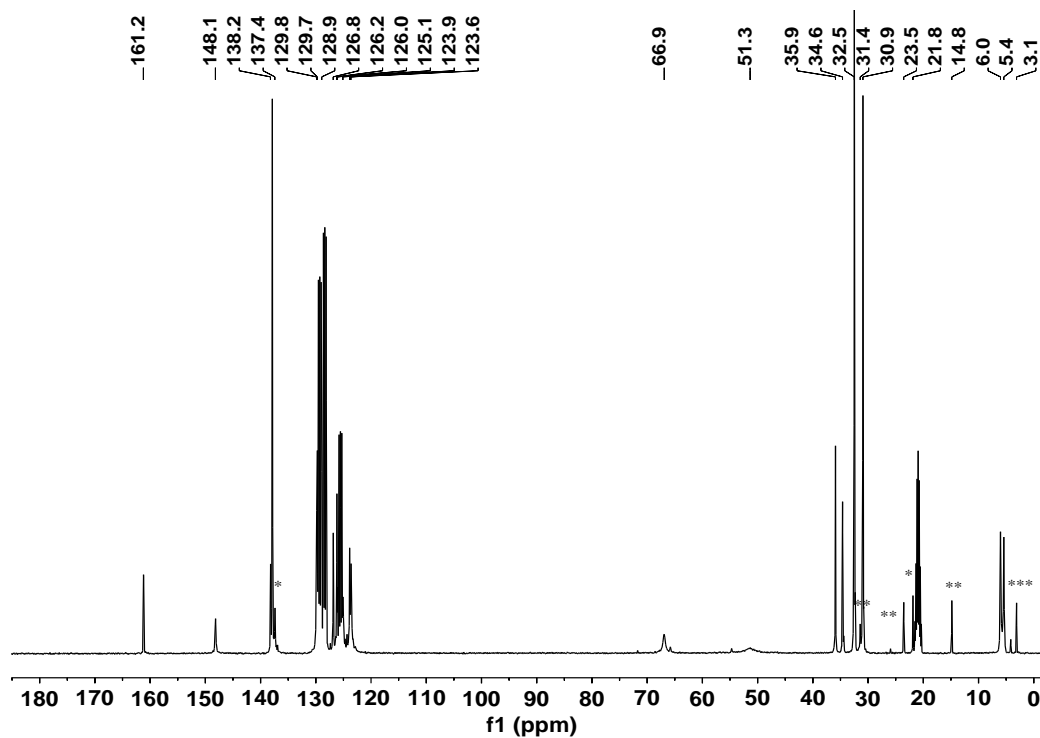


Figure S20. ^{13}C NMR spectrum (101 MHz, toluene- d_8 , 25 $^\circ\text{C}$) of complex **1**. (* toluene; **, hexane; ***, free $\text{HN}(\text{SiMe}_3)_2$).

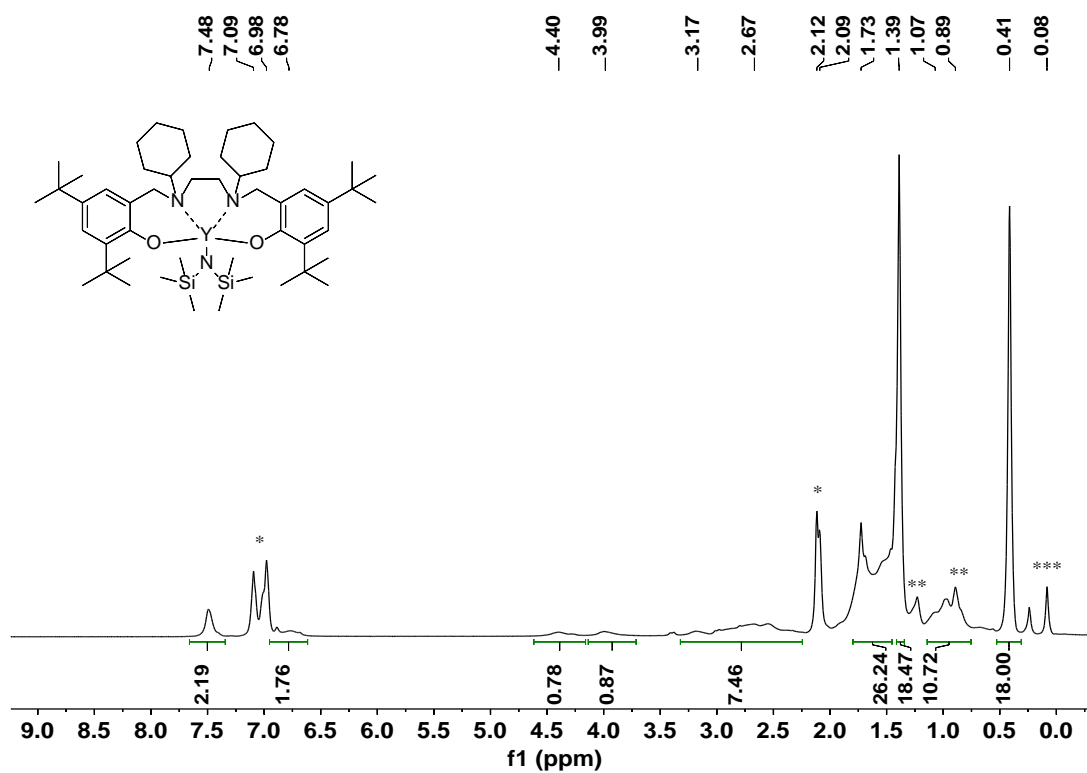


Figure S21. ^1H NMR spectrum (400 MHz, toluene- d_8 , 25 $^\circ\text{C}$) of complex **3** (*, toluene and toluene- d_8 ; **, hexane; ***, free $\text{HN}(\text{SiMe}_3)_2$).

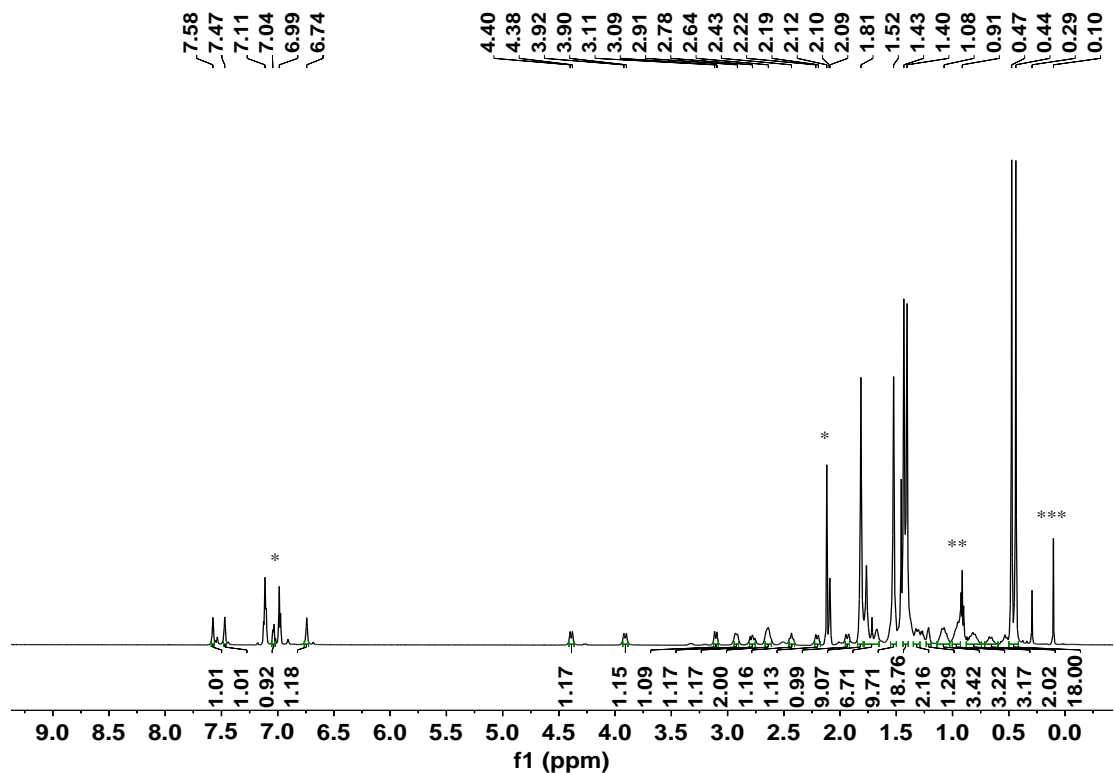


Figure S22. ^1H NMR spectrum (600 MHz, toluene- d_8 , $-10\text{ }^\circ\text{C}$) of complex **3** (*, toluene and toluene- d_8 ; **, hexane; ***, free $\text{HN}(\text{SiMe}_3)_2$).

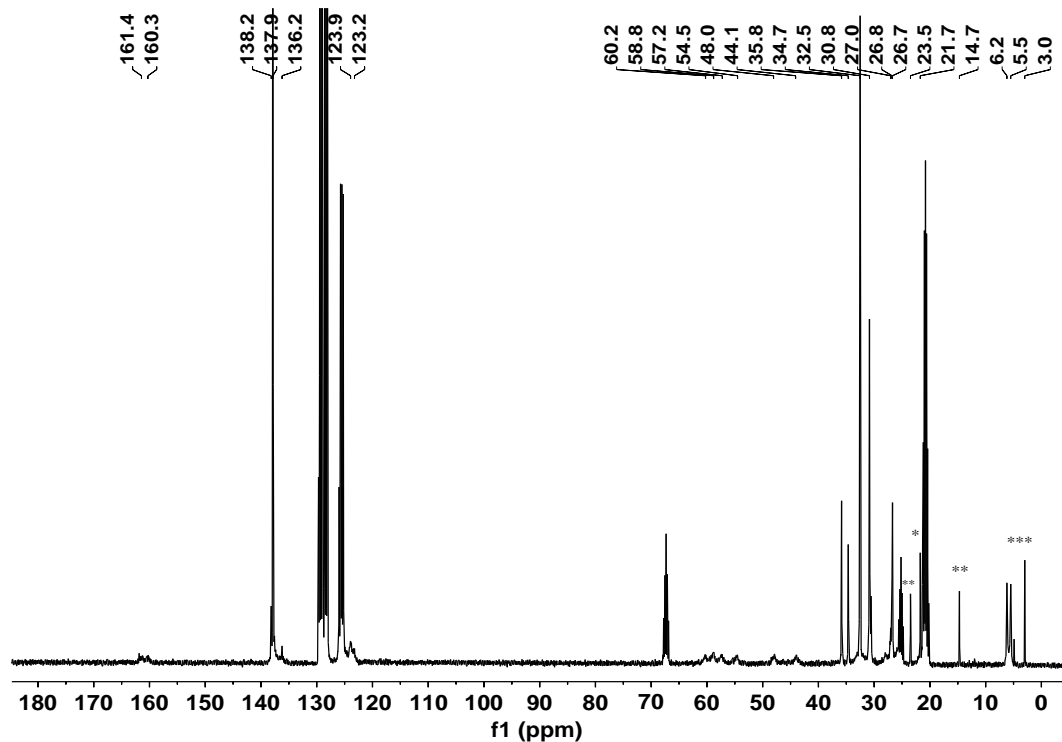


Figure S23. ^{13}C NMR spectrum (101 MHz, toluene- d_8 , $25\text{ }^\circ\text{C}$) of complex **3** (*, toluene; **, hexane; ***, free $\text{HN}(\text{SiMe}_3)_2$).

5 References.

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