

Highly heteroselective ring-opening polymerization of racemic lactide initiated by divalent ytterbium complexes bearing amino bis(phenolate) ligands

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Supporting information

General Methods. All of the manipulations were performed in a pure argon atmosphere using standard Schlenk techniques or under a nitrogen atmosphere in an glovebox. The solvents were degassed and distilled from sodium benzophenone ketyl prior to use. Ligand H_2L^{OMe} ($L = CH_3OCH_2CH_2N(CH_2-2-OC_6H_2-3-Bu^t-5-Me)_2$)¹, H_2L^{NN} ($L^{NN} = 1,4-bis(2-hydroxy-3-tert-butyl-5-methyl-benzyl)-piperazine$)², $Yb[N(SiMe_3)_2](THF)_2$ ³ and complex **3**⁴ were synthesized according to literature procedures. The phenols and amines were purchased from Aldrich or Alfa Aesar. All liquids were dried over 4 Å molecular sieves for a week and distilled before use, and solid materials were used without purification. Rare earth metal analysis was performed by ethylenediaminetetraacetic acid titration with a xylenol orange indicator and a hexamine buffer.⁵ D,L- Lactide (Aldrich) was recrystallized three times with dry ethyl acetate.

Instruments and Measurements. Organometallic samples for NMR spectroscopic measurements were prepared in a glovebox and then sealed by paraffin film. ¹H, ¹³C NMR spectra were recorded on a Unity Inova-400 (FT, 400 MHz for ¹H; 100 MHz for ¹³C) spectrometer.

Homonuclear decoupled ^1H NMR spectra were recorded on a Unity Inova-400 spectrometer at 20 °C in CDCl_3 . Carbon, hydrogen and nitrogen analyses were performed by direct combustion with a Carlo-ErbaEA-1110 instrument. IR spectra were recorded on a Nicolet-550 Fourier transform IR spectrometer as KBr pellets. Melting points of the complexes were measured in sealed capillaries and are uncorrected. Molar mass (M_n) and molar mass distribution (M_w/M_n) were determined against a polystyrene standard by SEC on a PL 50 apparatus, and THF was used as an eluent at a flow rate of 1.0 mL min^{-1} at 40 °C.

Synthesis of $\text{Yb}[\text{N}(\text{SiMe}_3)_2]_2(\text{TMEDA})$. A solution of $\text{Na}[\text{N}(\text{SiMe}_3)_2]$ (3.67 g, 20 mmol), tetramethylethylenediamine (1.16 g, 10 mmol), and YbI_2 (4.27 g, 10 mmol) in toluene (30 mL) was stirred for 24 h. The solution turned to purple and a purple precipitate formed. Purple crystals were obtained at room temperature in a few days (4.88 g, 80% based on Yb). Elemental analysis and ^1H NMR for $\text{Yb}[\text{N}(\text{SiMe}_3)_2]_2(\text{TMEDA})$ are as follows: Anal. Calcd for $\text{YbC}_{18}\text{H}_{52}\text{N}_4\text{Si}_4$ (610.04): C, 35.04; H, 8.91; N, 9.67; Yb, 28.55. Found: C, 35.44; H, 8.59; N, 9.18; Yb, 28.37. ^1H NMR (400 MHz, C_6D_6 , 25 °C): δ 1.87 (s, 12 H, NCH_3), 1.52 (s, 4 H, $\text{NCH}_2\text{CH}_2\text{N}$), 0.37 (s, 36 H, $\text{Si}(\text{CH}_3)_3$). The ORTEP diagram of $\text{Yb}[\text{N}(\text{SiMe}_3)_2]_2(\text{TMEDA})$ are shown in Figure S1. Selected bond distances (Å) and angles (deg) are listed in Table S1. Details of the intensity data collection and crystal data are given in Tables S2.

CCDC-884172. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

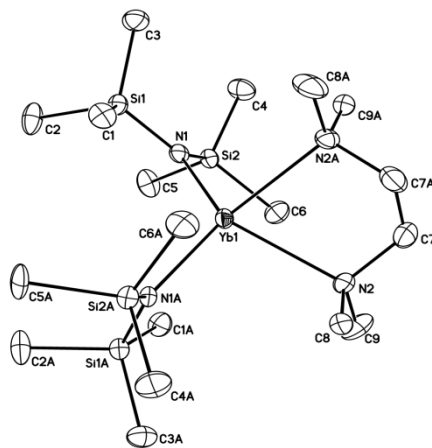


Figure S1. ORTEP diagram of the molecular structures of $\text{Yb}[\text{N}(\text{SiMe}_3)_2]_2(\text{TMEDA})$. Thermal ellipsoids are drawn at 20% probability level. All hydrogens, free solvent molecules are omitted for clarity.

Table S1 Selected bond lengths (Å) and angles (°) for $\text{Yb}[\text{N}(\text{SiMe}_3)_2]_2(\text{TMEDA})$

Bond lengths			
Yb(1)-N(1)	2.344(10)	Yb (1)-N(2)	2.607(11)
Yb (1)-N(1A)	2.344(10)	Yb (1)-N(2A)	2.607(11)
Bond angles			
N(1)-Yb(1)-N(1A)	119.6(5)	N(1)-Yb(1)-N(2A)	96.9(3)
N(1)-Yb(1)-N(2)	134.5(4)	N(1A)-Yb(1)-N(2A)	134.5(4)
N(1A)-Yb(1)-N(2)	96.9(3)	N(2)-Yb(1)-N(2A)	70.6(5)

Table S2 Crystallographic data for $\text{Yb}[\text{N}(\text{SiMe}_3)_2]_2(\text{TMEDA})$

Empirical formula	$\text{C}_{18} \text{H}_{52} \text{N}_4 \text{Si}_4 \text{Yb}$	$V (\text{Å}^3)$	3047.6(16)
Formula weight	610.04	Z	4
Temperature (K)	223(2)	$D_{\text{calcd.}} (\text{mg cm}^{-3})$	1.330
Crystal system	Monoclinic	Absorption coefficient (mm^{-1})	3.236
Space group	$C 2/c$	$F(000)$	1256
a (Å)	8.649(3)	θ range (°)	3.04 - 25.50
b (Å)	17.753(5)	Reflections collected / unique	7606 / 2825
c (Å)	20.315(7)	Data/restraints/parameters	[R(int) = 0.1302] 2825 / 0 / 132
α (°)	90	Goodness-of-fit on F^2	0.940
β (°)	102.324(8)	final R [$I > 2\sigma(I)$]	0.0880
γ (°)	90	wR_2 (all data)	0.2110

Synthesis of complex 2: A Schlenk flask was charged with $\text{H}_2\text{L}^{\text{OMe}}$ (1.28 g, 3.00 mmol), toluene (15 mL), and a stirring bar. To this solution was added a toluene (20 mL) solution of $\text{Yb}[\text{N}(\text{SiMe}_3)_2]_2(\text{TMEDA})$ (1.83 g, 3.00 mmol), leading to the formation of a dark red solution. The suspension was stirred at room temperature for 12 h. After concentration, the black-red microcrystals of **2** (1.16 g, 54% based on Yb) were obtained upon crystallization at 5 °C. Mp: 224-226 °C (dec). Elemental analysis, ^1H NMR and ^{13}C NMR for complex **2** are as follows: Anal. Calcd for $\text{YbC}_{33}\text{H}_{55}\text{N}_3\text{O}_3$ (714.84): C, 55.44; H, 7.75; N, 5.88; Yb, 24.21. Found: C, 55.83; H, 7.31; N, 5.74; Yb, 23.93. ^1H NMR (400 MHz, C_6D_6 , 25 °C): δ 6.97-7.39 (m, 4 H, ArH), 4.19-4.22 (d, 2 H, $J_{\text{H-H}} = 12$ Hz, ArCH₂N), 3.04-3.07 (d, 2 H, $J_{\text{H-H}} = 12$ Hz, ArCH₂N), 2.79-2.81 (t, 2 H, $J_{\text{H-H}} = 4$ Hz, MeOCH₂), 2.50-2.52 (t, 2 H, $J_{\text{H-H}} = 4$ Hz, NCH₂), 2.49 (s, 6 H, ArCH₃), 2.43 (s, 3 H, OCH₃), 2.11 (s, 12 H, NCH₃), 1.95 (s, 4 H, NCH₂CH₂N), 1.73 (s, 18 H, C(CH₃)₃). ^{13}C NMR (100 MHz, C_6D_6 , 25 °C): δ 166.42 (arom-CO), 136.02 (arom-CCH₂N), 131.24 (arom-CBu^t), 129.34 (arom-CMe), 124.89 (arom-CH), 118.53 (arom-CH), 73.09 (OCH₂), 64.50 (NCH₂CH₂O), 57.77 (ArCH₂N), 56.38 (NCH₂CH₂N), 47.54 (OCH₃), 46.39 (NCH₃), 35.35 (CMe₃), 30.40 (C(CH₃)₃), 21.52 (ArCH₃). IR (KBr, cm^{-1}): 3442(br), 2945(s), 2848(s), 1621(m), 1458(s), 1231(s), 1155(m), 1058(m), 821(m), 508(m).

Synthesis of complex 4: A Schlenk flask was charged with $\text{H}_2\text{L}^{\text{NN}}$ (1.31 g,

3.00 mmol), THF (15 mL), and a stirring bar. To this solution was added a THF (20 mL) solution of $\text{Yb}(\text{N}(\text{SiMe}_3)_2)_2(\text{THF})_2$ (1.91 g, 3.00 mmol), leading to the formation of a red solution. The suspension was stirred at room temperature for 12 h. After concentration, the orange-red microcrystals of **4** (1.97 g, 80% based on Yb) were obtained upon crystallization at 5 °C. Mp: 238-240 °C (dec). Elemental analysis and ^1H NMR for complex **4** are as follows: Anal.Calcd for $\text{YbC}_{40}\text{H}_{64}\text{N}_2\text{O}_5$ (825.97): C, 58.16; H, 7.81; N, 3.39; Yb, 20.95. Found: C, 58.21; H, 7.74; N, 3.30; Yb, 20.86. ^1H NMR (400 MHz, C_6D_6 , 25 °C): δ 7.28 (s, 2 H, ArH), 6.66 (s, 2 H, ArH), 4.03 (br, 2 H, ArCH₂N), 3.62 (s, 12 H, THF-OCH₂), 2.80 (br, 2 H, ArCH₂N), 2.60-2.63 (d, 4 H, $J_{\text{H-H}} = 12$ Hz, NCH₂CH₂N), 2.32 (s, 6 H, ArCH₃), 1.75 (s, 18 H, C(CH₃)₃), 1.43 (s, 12 H, THF-CH₂), 1.26 (s, 4 H, NCH₂CH₂N). IR (KBr, cm^{-1}): 3454(m), 2952(s), 2914(s), 2826(s), 1479(s), 1460(m), 1441(m), 1365(m), 1342(m), 1249(s), 1212(m), 1153(s), 1024(m), 907(w), 866(m), 774(w).

Polymerization of *rac*-Lactide. A typical procedure for polymerization of *rac*-lactide was performed in a 25 mL round flask in a glovebox. To a stirring solution of D,L-lactide (0.55 g, 3.84 mmol) in 3.36 mL of THF was added a THF solution (0.48 mL) of complex **2** (0.0048 mmol, [LA] = 1.00 mol/L). The polymerization took place immediately at room temperature. The system became viscous in a few minutes and kept

stirring for 3 h and then was terminated by 1.0 mL of HCl/CH₃OH (0.05/10 v/v). The viscous solution was quenched by an excess amount of ethanol, filtered, washed with ethanol, and then dried at 40 °C for 24 h in vacuo to give polymer product (0.55 g, 100%). The tacticity of the PLA was calculated according to the methane region homonuclear decoupling ¹H NMR spectrum.⁶

X-Ray crystallographic structure determination. A suitable single crystal of complexes **2** and **4** were sealed in a thin-walled glass capillary. Intensity data were collected with a Rigaku Mercury CCD area detector in ω scan mode using Mo-K α radiation ($\lambda = 0.71075 \text{ \AA}$). The diffracted intensities were corrected for Lorentz/polarization effects and empirical absorption corrections.

The structure was solved by direct methods and refined by full-matrix least-squares procedures based on $|F|^2$. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms in the complex were all generated geometrically (C–H bond lengths fixed at 0.95 Å), assigned appropriate isotropic thermal parameters, and allowed to ride on their parent carbon atoms. All the H atoms were held stationary and included in the structure factor calculation in the final stage of full-matrix least-squares refinement. The structure was solved and refined by using SHELEXL-97 program.⁷ Selected bond distances (Å) and angles (deg) for complex **2** and **4** are listed in Table S3 and S4, respectively. Details of

the intensity data collection and crystal data are given in Table S5. CCDC-884175 (for **2**), -892553 (for **4**) 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.

Table S3 Selected bond lengths (Å) and angles (°) for complex **2**

Bond lengths		Complex 2	
Yb(1)-N(1)	2.508(4)	Yb (1)-O(1)	2.201(3)
Yb (1)-N(2)	2.570(4)	Yb (1)-O(2)	2.229(3)
Yb (1)-N(3)	2.692(4)	Yb (1)-O(3)	2.483(3)
Bond angles			
N(1)-Yb(1)-N(3)	104.16(12)	O(2)-Yb(1)-O(3)	91.03(12)
N(2)-Yb(1)-N(3)	71.02(12)	O(1)-Yb(1)-N(1)	80.12(11)
O(1)-Yb(1)-N(3)	87.19(11)	O(2)-Yb(1)-N(1)	81.97(12)
O(2)-Yb(1)-N(3)	172.99(12)	O(3)-Yb(1)-N(1)	69.98(12)
O(3)-Yb(1)-N(3)	87.94(12)	O(1)-Yb(1)-N(2)	104.57(12)
N(1)-Yb(1)-N(2)	172.84(12)	O(2)-Yb(1)-N(2)	102.56(12)
O(1)-Yb(1)-O(2)	97.34(12)	O(3)-Yb(1)-N(2)	104.14(13)
O(1)-Yb(1)-O(3)	147.48(12)		

Table S4 Selected bond lengths (Å) and angles (°) for complex **4**

Bond lengths		Complex 3	
Yb(1)-O(1)	2.327(5)	Yb (1)-O(5)	2.484(6)
Yb (1)-O(2)	2.328(5)	Yb (1)-N(1)	2.614(7)
Yb (1)-O(3)	2.493(6)	Yb (1)-N(2)	2.604(6)
Yb (1)-O(4)	2.552(6)		
Bond angles			
O(1)-Yb(1)-O(2)	171.31(19)	O(2)-Yb(1)-N(2)	71.51(19)
O(1)-Yb(1)-O(5)	85.10(19)	O(5)-Yb(1)-N(2)	119.9(2)
O(2)-Yb(1)-O(5)	92.83(19)	O(3)-Yb(1)-N(2)	83.7(2)
O(1)-Yb(1)-O(3)	92.9(2)	O(4)-Yb(1)-N(2)	151.1(2)
O(2)-Yb(1)-O(3)	85.3(2)	O(1)-Yb(1)-N(1)	71.04(19)
O(5)-Yb(1)-O(3)	154.4(2)	O(2)-Yb(1)-N(1)	117.19(19)
O(1)-Yb(1)-O(4)	85.9(2)	O(5)-Yb(1)-N(1)	83.9(2)
O(2)-Yb(1)-O(4)	85.4(2)	O(3)-Yb(1)-N(1)	119.6(2)
O(5)-Yb(1)-O(4)	77.3(2)	O(4)-Yb(1)-N(1)	151.4(2)
O(3)-Yb(1)-O(4)	77.2(2)	N(2)-Yb(1)-N(1)	57.51(19)
O(1)-Yb(1)-N(2)	116.79(19)		

Table S5 Crystallographic data for complexes **2** and **4**

2	3
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Empirical formula	C ₃₃ H ₅₅ N ₃ O ₃ Yb	C ₄₀ H ₆₄ N ₂ O ₅ Yb
Formula weight	714.84	825.97
Temperature (K)	223(2)	223(2)
Crystal system	Monoclinic	Triclinic
Space group	P 21/c	P -1
<i>a</i> (Å)	9.792(3)	12.5079(2)
<i>b</i> (Å)	23.618(6)	14.1307(4)
<i>c</i> (Å)	15.158(5)	14.1381(5)
α (°)	90	67.194(15)
β (°)	105.411(6)	64.666(14)
γ (°)	90	64.700(15)
<i>V</i> (Å ³)	3379.7(17)	1976.8(3)
<i>Z</i>	4	2
<i>D</i> _{calcd.} (mg cm ⁻³)	1.405	1.388
Absorption coefficient (mm ⁻¹)	2.801	2.408
<i>F</i> (000)	1472	856
θ range (°)	2.99 - 25.50	3.22 - 25.50
Reflections	16360 / 6246	16579 / 7288
collected / unique	[R(int) = 0.0393]	[R(int) = 0.0748]
Data/restraints/parameters	6246 / 0 / 375	7288 / 22 / 405
Goodness-of-fit on <i>F</i> ²	1.138	1.149
final <i>R</i> [<i>I</i> > 2 σ (<i>I</i>)]	0.0367	0.0675
<i>wR</i> ₂ (all data)	0.0936	0.1588

Representative Analytical Data of Products

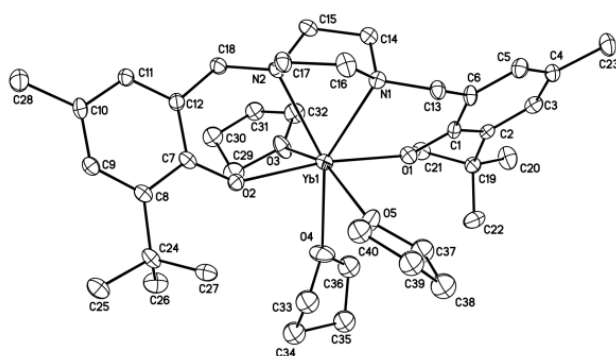


Figure S2. ORTEP diagram of the molecular structures of complex **4**. Thermal ellipsoids are drawn at 20% probability level. All hydrogens, free solvent molecules are omitted for clarity.

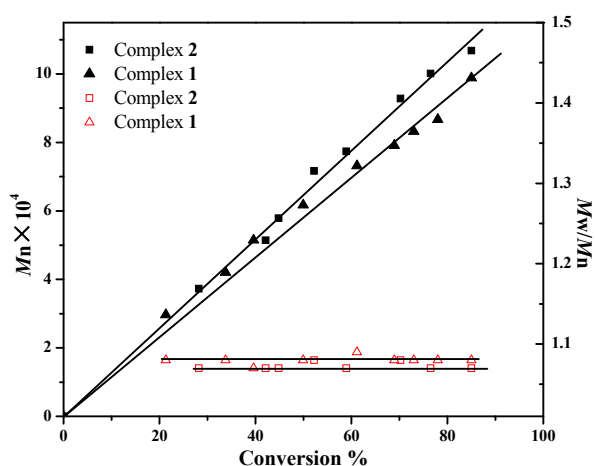


Figure S3. Plots of conversion vs M_n and M_w/M_n for the polymerization of *rac*-lactide initiated by **1** and **2**. Condition: $[M]/[I] = 800$, solvent = THF, $[M] = 1.0$ M, $T = 20$ °C.

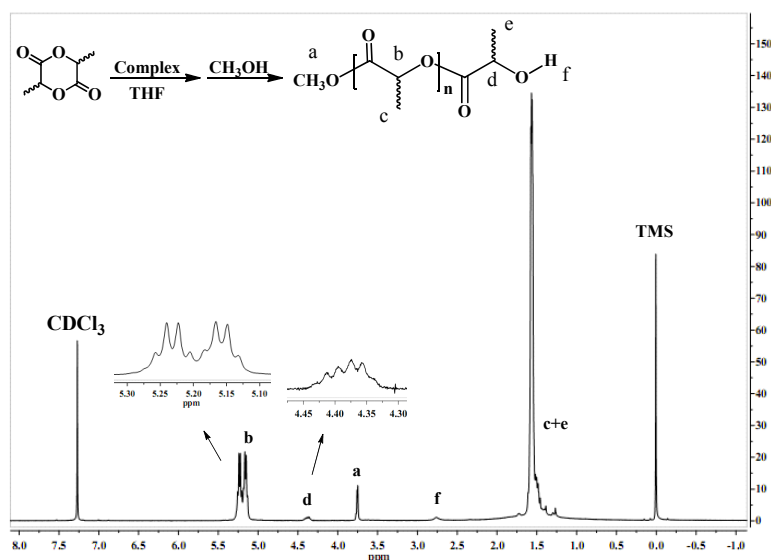


Figure S4. ^1H NMR spectrum of the oligomer of *rac*-lactide initiated by complex **1**, **2**, **3** or **4** after quenching with CH_3OH . Conditions: $[\text{LA}]_0/[\text{Yb}]_0 = 15$, CDCl_3 , THF, 25°C .

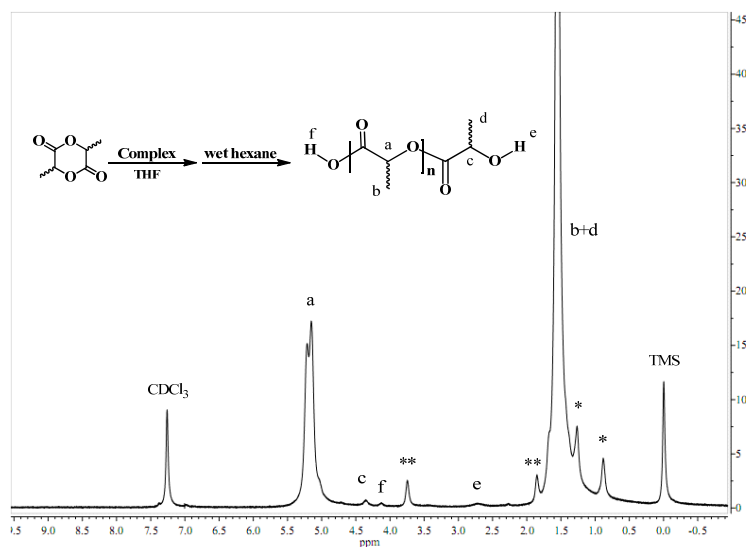


Figure S5. ^1H NMR spectrum of the oligomer of *rac*-lactide initiated by complex **1**, **2**, **3** or **4** after quenching with wet *n*-hexane (*, free hexane signals; **, free THF signals). Conditions: $[\text{LA}]_0/[\text{Yb}]_0 = 15$, CDCl_3 , THF, 25°C .

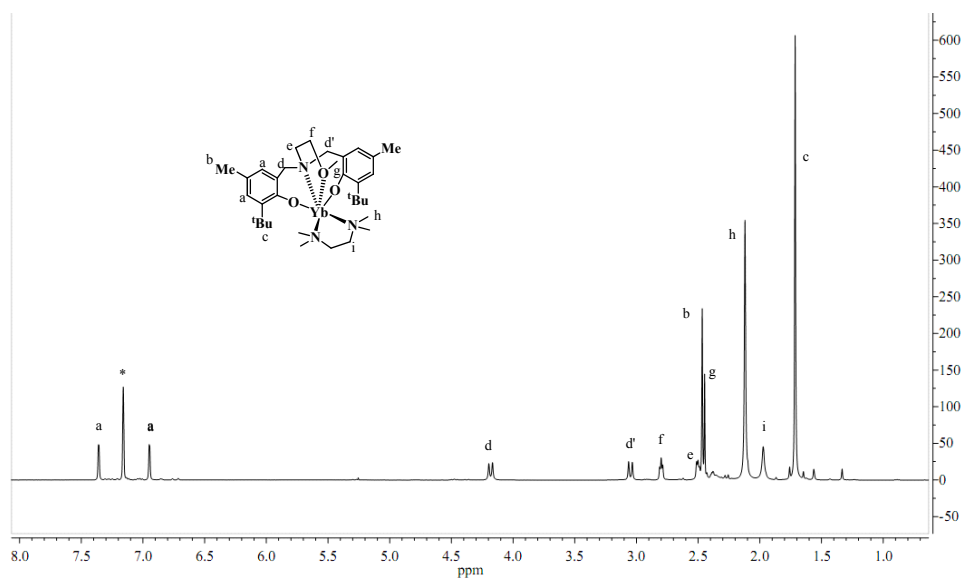


Figure S6. ^1H NMR spectrum of complex **2**.

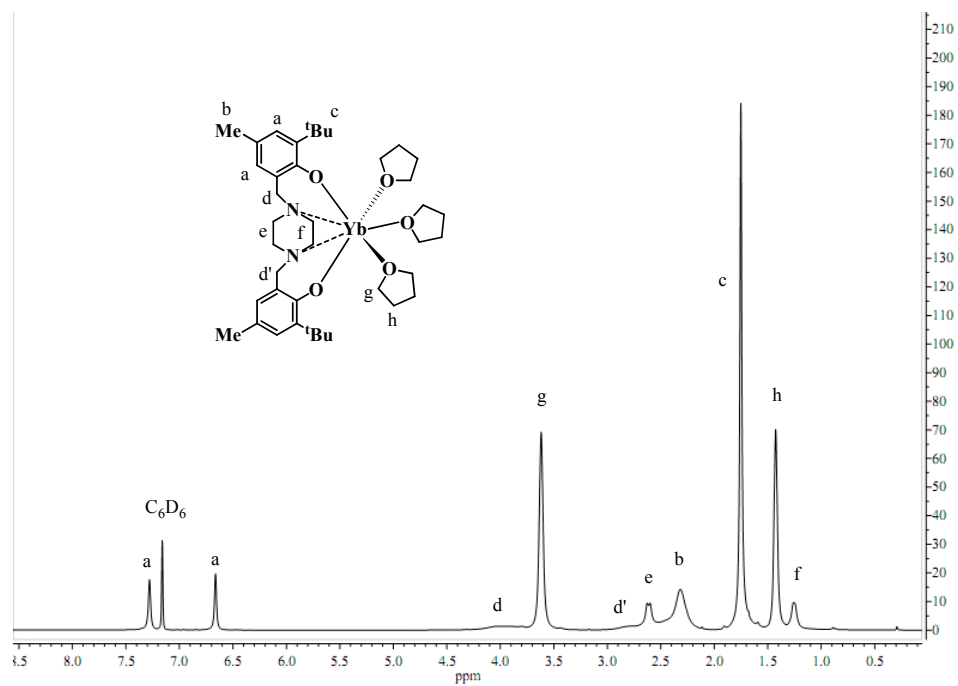


Figure S7. ^1H NMR spectrum of complex **4**.

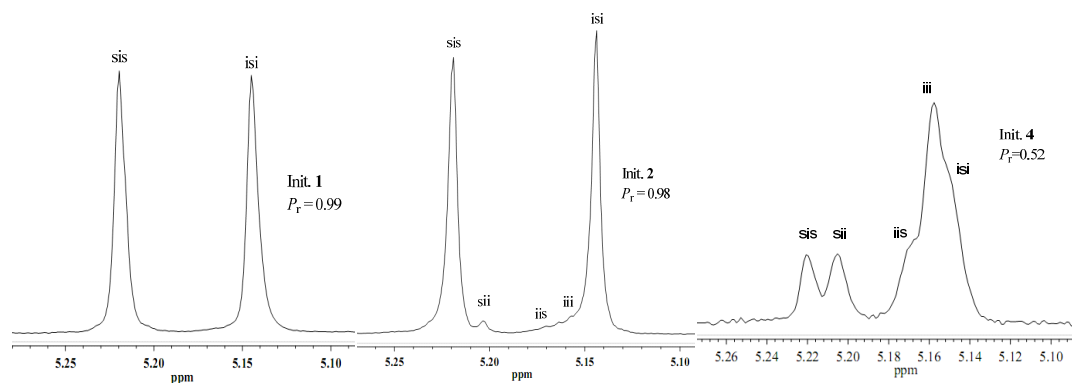


Figure S8. Representative homonuclear decoupled ^1H NMR spectra of the methane region of PLAs (Table 1, entries 3, 7 and 16) at 25 °C (400 MHz, CDCl_3).

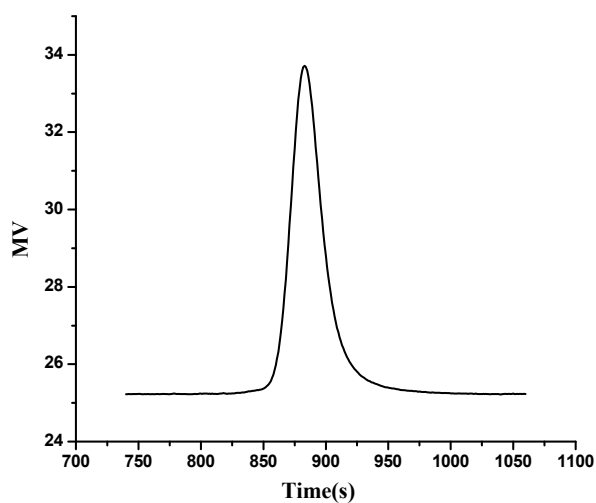


Figure S9. SEC curve of a selected sample (Table 1, entry 2)

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