

Supporting Information for:

Remarkable Stereocontrol in the Polymerization of Racemic Lactide using Aluminum Initiators Supported by Tetradentate Aminophenoxide Ligands

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General Experimental

All manipulations were carried out under a nitrogen atmosphere using Schlenk vacuum-line techniques and inert atmosphere glove boxes. Solvents were dried by prolonged reflux over an appropriate drying agent, or via passage over a column containing commercially available Q-5 catalyst (13 % Cu(II) oxide on Al₂O₃) and activated Al₂O₃ (3 mm pellets) under a stream of nitrogen.

NMR spectra were recorded on a Bruker AC250, DRX 400 or AM-500 spectrometer in sealed tubes, and were referenced relative to residual solvent resonances. Elemental analyses were performed at the University of North London.

Synthesis and Characterization of Ligands

(i) *N,N'*-dimethyl-*N,N'*-bis[(2-hydroxyphenyl)methylene]-1,2-diaminoethane

To a stirred room temperature solution of salicylaldehyde (3.63 mL, 34.1 mmol) in methanol (200 mL) was added *N,N'*-dimethyl-1,2-ethylenediamine (3.00 mL, 34.1 mmol). The reaction mixture was stirred at reflux temperature for 30 minutes. After cooling to room temperature, NaBH₄ (5.15 g, 136 mmol) was slowly added. Over the following 15 minutes, the color of the solution changed from yellow to colorless, after which H₂O (250 mL) was added resulting in the precipitation of a white solid. After stirring for an additional 15 minutes to consume any residual NaBH₄, the product was extracted into CH₂Cl₂. The organic layer was collected and dried over Na₂SO₄ and solvent was evaporated to leave a yellow oil which was then redissolved in methanol (200 mL). To this solution was added salicylaldehyde (3.63 mL, 34.1 mmol). The reaction mixture was stirred at reflux temperature for 30 minutes. Reduction using NaBH₄ and extraction into CH₂Cl₂ was then repeated as described above. After removing the solvent, a yellow oil was obtained and this was recrystallised from hot methanol. Colorless crystals formed in 27 % (2.16g) yield.

¹H NMR data (250.13 MHz, CDCl₃, 298 K): δ 10.64 (br s, 2H, OH), 7.17 (td, 2H, ⁴J_{HH} = 1.8, ³J_{HH} = 6.4, ArH), 6.96 (dd, 2H, ⁴J_{HH} = 1.5, ³J_{HH} = 7.4, ArH), 6.84 (dd, 2H, ⁴J_{HH} = 1.0, ³J_{HH} = 8.1, ArH), 6.77 (td, 2H, ⁴J_{HH} = 1.2, ³J_{HH} = 7.4, ArH), 3.70 (s, 4H, ArCH₂), 2.67 (s, 4H, N(CH₂CH₂)N), 2.29 (s, 6H, NCH₃).

¹³C NMR data (100.58 MHz, CDCl₃, 298 K): δ 158.19 (COH), 129.32 (aromatic CH), 128.94 (aromatic CH), 122.02 (aromatic CCH₂N), 119.57 (aromatic CH), 116.62 (aromatic CH), 62.21 (ArCH₂N), 54.48 (N(CH₂CH₂)N), 42.11 (NCH₃).

Elemental analysis for $C_{18}H_{24}N_2O_2$ (F.W. 300.40): C, 71.97; H, 8.05; N, 9.33%. Found C, 72.02; H, 8.08; N, 9.33%.

(ii) N,N'-dimethyl-N,N'-bis[(3,5-dimethyl-2-hydroxyphenyl)methylene]-1,2-diaminoethane

This compound was prepared according to a literature method.^{S1} To a mixture of 2,4-dimethylphenol (6.50 mL, 81.8 mmol) and N,N'-dimethylethylenediamine (2.52 mL, 45.9 mmol) in ethanol (200 mL) was added paraformaldehyde (2.46 g, 81.8 mmol) at reflux temperature (90 °C). Paraformaldehyde gradually dissolved in the solution which became clear after heating for 2 hours. After stirring at 90°C overnight, the reaction was cooled to room temperature, upon which 6.157g colorless crystals formed (42 %).

¹H NMR data (400.13 MHz, $CDCl_3$, 298K): δ 10.60 (br s, 2H, OH), 6.86 (s, 2H, ArH), 6.60 (s, 2H, ArH), 3.63 (s, 4H, ArCH₂), 2.65 (s, 4H, N(CH₂CH₂)N), 2.26 (s, 6H, NCH₃), 2.21 (s, 6H, ArCH₃), 2.19 (s, 6H, ArCH₃).

¹³C NMR data (100.58 MHz, $CDCl_3$, 298 K): δ 153.41 (COH), 130.60 (aromatic CH), 127.60 (aromatic C), 126.59 (aromatic CH), 124.66 (aromatic C), 120.65 (aromatic C), 61.80 (ArCH₂N), 54.15 (N(CH₂CH₂)N), 41.66 (NCH₃), 20.41 (ArCH₃), 15.60 (ArCH₃).

Elemental analysis for $C_{22}H_{32}N_2O_2$ (F.W. 356.50): C, 74.12; H, 9.05; N, 7.86%. Found C, 74.20; H, 9.15; N, 7.91%.

(iii) N,N'-dimethyl-N,N'-bis[(3,5-di-*t*-butyl-2-hydroxyphenyl)methylene]-1,2-diaminoethane

This compound^{S2} was prepared in an analogous manner to that described above for the synthesis of N,N'-dimethyl-N,N'-bis[(3,5-dimethyl-2-hydroxyphenyl)methylene]-1,2-diaminoethane.

¹H NMR data (250.13 MHz, CDCl₃, 298K): δ 10.72 (br s, 2H, OH), 7.20 (d, ⁴J_{HH} = 2.4, 2H, ArH), 6.80 (d, ⁴J_{HH} = 2.4, 2H, ArH), 3.66 (s, 4H, ArCH₂), 2.64 (s, 4H, N(CH₂CH₂)N), 2.26 (s, 6H, NCH₃), 1.40 (s, 18H, ArC(CH₃)₃), 1.28 (s, 18H, ArC(CH₃)₃).

¹³C NMR data (100.58 MHz, CDCl₃, 298 K): δ 154.15 (COH), 140.47 (aromatic C), 135.57 (aromatic C), 123.30 (aromatic CH), 122.94 (aromatic CH), 120.96 (aromatic C), 62.69 (ArCH₂N), 53.72 (N(CH₂CH₂)N), 41.57 (NCH₃), 34.83 (ArC(CH₃)₃), 34.11 (ArC(CH₃)₃), 31.68 (ArC(CH₃)₃), 29.57 (ArC(CH₃)₃).

Elemental analysis for C₃₄H₅₆N₂O₂ (F.W. 524.82): C, 77.81; H, 10.76; N, 5.34%. Found C, 77.81; H, 11.02; N, 5.36%.

(iv) N,N'-dimethyl-N,N'-bis[(3,5-dichloro-2-hydroxyphenyl)methylene]-1,2-diaminoethane

This compound was prepared in an analogous manner to that described above for the synthesis of N,N'-dimethyl-N,N'-bis[(3,5-dimethyl-2-hydroxyphenyl)methylene]-1,2-diaminoethane in 74 % yield.

¹H NMR data (250.13 MHz, CDCl₃, 298K): δ 7.27 (d, ⁴J_{HH} = 2.4, 2H, ArH), 6.86 (d, ⁴J_{HH} = 2.4, 2H, ArH), 3.69 (s, 4H, ArCH₂), 2.70 (s, 4H, N(CH₂CH₂)N), 2.31 (s, 6H, NCH₃).

¹³C NMR data (100.58 MHz, CDCl₃, 298 K): δ 152.42 (COH), 128.94 (aromatic CH), 126.70 (aromatic CH), 123.64 (aromatic C), 123.44 (aromatic C), 121.66 (aromatic C), 61.12 (ArCH₂N), 54.01 (N(CH₂CH₂)N), 41.78 (NCH₃).

Elemental analysis for C₁₈H₂₀N₂O₂Cl₄ (F.W. 438.18): C, 49.34; H, 4.60; N, 6.39%. Found C, 49.25; H, 4.70; N, 6.47%.

(v) N,N'-dibenzyl-N,N'-bis[(2-hydroxyphenyl)methylene]-1,2-diaminoethane

This compound was prepared in an analogous manner to that described above for the synthesis of N,N'-dimethyl-N,N'-bis[(2-hydroxyphenyl)methylene]-1,2-diaminoethane from the stepwise reaction of N,N'-dibenzyl-1,2-ethylenediamine with 1.0 equivalent of salicylaldehyde, NaBH₄ reduction, addition of a further equivalent of salicylaldehyde, and a second reduction with NaBH₄, in an overall yield of 38%.

¹H NMR data (250.13 MHz, CDCl₃, 298K): δ 10.51 (br s, 2H, OH), 7.33-7.15 (m, 12H, ArH), 6.92 (dd, 2H, ³J_{HH} = 7.4, ⁴J_{HH} = 1.4, ArH), 6.82 (dd, 2H, ³J_{HH} = 8.6, ⁴J_{HH} = 1.0,

ArH), 6.77 (td, $^3J_{\text{HH}} = 7.4$, $^4J_{\text{HH}} = 1.0$, 2H, ArH), 3.67 (s, 4H, NCH₂C₆H₄OH), 3.52 (s, 4H, NCH₂C₆H₅), 2.70 (s, 4H, N(CH₂CH₂)N).

^{13}C NMR data (100.58 MHz, CDCl₃, 298 K): δ 157.46 (COH), 136.15 (C₆H₅ C_{ipso}), 129.49 (C₆H₅ C_{meta}), 128.94 (aromatic CH), 128.76 (aromatic CH), 128.65 (C₆H₅ C_{ortho}), 127.78 (aromatic CH), 121.60 (aromatic CCH₂N), 119.36 (aromatic CH), 116.17 (aromatic CH), 58.39 (CH₂C₆H₅), 58.08 (CH₂C₆H₄OH), 49.80 (N(CH₂CH₂)N).

Elemental analysis for C₃₆H₃₂N₂O₂ (F.W. 452.59): C, 79.61; H, 7.13; N, 6.19%. Found C, 79.64; H, 7.06; N, 5.99%.

(vi) *N,N'*-dibenzyl-*N,N'*-bis[(3,5-dimethyl-2-hydroxyphenyl)methylene]-1,2-diaminoethane

This bis(aminophenol) was prepared in an analogous manner to that described above for *N,N'*-dimethyl-*N,N'*-bis[(3,5-dimethyl-2-hydroxyphenyl)methylene]-1,2-diaminoethane, starting from *N,N'*-dibenzyl-1,2-ethylenediamine in 31 % yield.

^1H NMR data (400.13 MHz, CDCl₃, 298 K): δ 10.40 (br s, 2H, OH), 7.33-7.12 (m, 10H, ArH), 6.86 (s, 2H, ArH), 6.59 (s, 2H, ArH), 3.63 (s, 4H, NCH₂C₆H₄OH), 3.53 (s, 4H, NCH₂C₆H₅), 2.68 (s, 4H, N(CH₂CH₂)N), 2.22 (s, 6H, ArCH₃), 2.19 (s, 6H, ArCH₃).

^{13}C NMR data (100.58 MHz, CDCl₃, 298 K): δ 153.12 (COH), 136.41 (C₆H₅ C_{ipso}), 130.71 (aromatic CH), 129.44 (C₆H₅ C_{meta}), 128.60 (C₆H₅ C_{ortho}), 127.81 (aromatic C), 127.65 (aromatic CH), 126.85 (aromatic CH), 124.62 (aromatic C), 120.63 (aromatic C), 58.43 (CH₂C₆H₅), 58.29 (CH₂C₆H₄OH), 49.82 (N(CH₂CH₂)N), 20.44 (ArCH₃), 15.69 (ArCH₃).

Elemental analysis for C₃₄H₄₀N₂O₂ (F.W. 508.69): C, 80.28; H, 7.93; N, 5.51%. Found C, 80.43; H, 8.04; N, 5.39%.

(vii) N,N'-dibenzyl-N,N'-bis[(3,5-di-*t*-butyl-2-hydroxyphenyl)methylene]-1,2-diaminoethane

This compound was prepared as described above for N,N'-dibenzyl-N,N'-bis[(3,5-dimethyl-2-hydroxyphenyl)methylene]-1,2-diaminoethane in 25 % yield.

¹H NMR data (250.13 MHz, CDCl₃, 298 K): δ 10.56 (s, 2H, OH), 7.31-7.24 (m, 6H, ArH), 7.20 (d, ⁴J_{HH} = 2.4, 2H, ArH), 7.16-7.13 (m, 4H, ArH), 6.80 (d, ⁴J_{HH} = 2.3, 2H, ArH), 3.66 (s, 4H, NCH₂C₆H₄OH), 3.50 (s, 4H, NCH₂C₆H₅), 2.68 (s, 4H, N(CH₂CH₂)N), 1.42 (s, 18H, ArC(CH₃)₃), 1.27 (s, 18H, ArC(CH₃)₃).

¹³C NMR data (100.58 MHz, CDCl₃, 298 K): δ 153.81 (COH), 140.68 (C₆H₅ C_{ipso}), 136.60 (aromatic C), 135.66 (aromatic C), 129.56 (C₆H₅ C_{meta}), 128.48 (C₆H₅ C_{ortho}), 127.51 (aromatic CH), 123.65 (aromatic CH), 123.00 (aromatic CH), 121.03 (aromatic C), 59.15 (CH₂C₆H₄OH), 58.05 (CH₂C₆H₅), 50.00 (N(CH₂CH₂)N), 34.83 (ArC(CH₃)₃), 34.11 (ArC(CH₃)₃), 31.66 (ArC(CH₃)₃), 29.55 (ArC(CH₃)₃).

Elemental analysis for C₄₆H₆₄N₂O₂ (F.W. 677.01): C, 81.61; H, 9.53, N, 4.14%. Found C, 81.63; H, 9.47; N, 3.99%.

(iix) N,N'-dibenzyl-N,N'-bis[(3,5-dichloro-2-hydroxyphenyl)methylene]-1,2-diaminoethane

This compound was prepared as described above for N,N'-dibenzyl-N,N'-bis[(3,5-dimethyl-2-hydroxyphenyl)methylene]-1,2-diaminoethane in 17 % yield.

¹H NMR data (250 MHz, CDCl₃, 298 K): δ 11.46 (br s, 2H, OH), 7.36-7.25 (m, 8H, ArH), 7.17-7.11 (m, 4H, ArH), 6.80 (d, ⁴J_{HH} = 2.5, 2H, ArH), 3.64 (s, 4H, NCH₂C₆H₄OH), 3.54 (s, 4H, NCH₂C₆H₅), 2.63 (s, 4H, N(CH₂CH₂)N).

¹³C NMR data (100.58 MHz, CDCl₃, 298 K): δ 152.13 (COH), 135.18 (C₆H₅ C_{ipso}), 129.38 (C₆H₅ C_{meta}), 128.97 (aromatic CH), 128.91 (C₆H₅ C_{ortho}), 128.24 (aromatic CH), 126.82 (aromatic CH), 123.82 (aromatic C), 123.60 (aromatic C), 121.54 (aromatic C), 58.94 (CH₂C₆H₄OH), 57.94 (CH₂C₆H₅), 50.02 (N(CH₂CH₂)N).

Elemental analysis for C₃₀H₂₈Cl₄N₂O₂ (F.W. 590.37): C, 61.03; H, 4.78; N, 4.75%. Found C, 60.94; H, 4.62; N, 4.67%.

Synthesis and Characterization of Aluminum alkyl complexes 1 - 8

(i) Complex 1

To a stirred solution of N,N'-dimethyl-N,N'-bis[(2-hydroxyphenyl)methylene]-1,2-diaminoethane (1.200 g, 4.00 mmol) in toluene (20 mL) was added AlMe₃ (2.00 mL of a 2.0 M solution in toluene, 4.00 mmol). The reaction mixture was stirred at 110 °C overnight. The solvent was evaporated to dryness to leave a white solid which was then recrystallized from hot toluene. White crystals formed in 77 % yield (1.050 g).

¹H NMR data (400.13 MHz, C₆D₆, 298 K): δ 7.23-7.19 (m, 4H, ArH), 6.83 (m, 4H, ArH), 3.76 (br d, 2H, ³J_{HH} = 12.3, ArCH₂), 2.53 (br d, 2H, ³J_{HH} = 11.7, ArCH₂), 1.90 (br s, 2H, N(CH₂CH₂)N), 1.68 (s, 6H, NCH₃), 1.61 (br s, 2H, N(CH₂CH₂)N), -0.53 (s, 3H, AlCH₃).

¹³C NMR data (100.58 MHz, C₆D₆, 298 K): δ 160.90 (COH), 130.54 (aromatic CH), 128.89 (aromatic CH), 121.77 (aromatic CCH₂N), 120.52 (aromatic CH), 116.59 (aromatic CH), 61.28 (ArCH₂N), 54.30 (N(CH₂CH₂)N), 43.57 (NCH₃), -10.84 (AlCH₃).

Elemental analysis for C₁₉H₂₃N₂AlO₂ (F.W. 340.40): C, 67.04; H, 7.40; N, 8.23%. Found C, 67.09; H, 7.50; N, 8.15%.

(ii) Complex 2

Complex 2 was prepared according to the procedure outlined for 1 using N,N'-dimethyl-N,N'-bis[(3,5-dimethyl-2-hydroxyphenyl)methylene]-1,2-diaminoethane in 85 % yield.

¹H NMR data (400.13 MHz, C₆D₆, 298 K): δ 7.08 (s, 2H, ArH), 6.62 (s, 2H, ArH), 3.82 (br s, 2H, ArCH₂), 2.62 (br s, 2H, ArCH₂), 2.59 (s, 6H, ArCH₃), 2.36 (s, 6H, ArCH₃),

2.06 (br s, 2H, N(CH₂CH₂)N), 1.77 (s, 6H, N(CH₃)₂), 1.63 (br s, 2H, N(CH₂CH₂)N), -0.52 (s, 3H, AlCH₃).

¹³C NMR data (100.58 MHz, C₆D₆, 298 K): δ 156.69 (COH), 132.01 (aromatic CH), 128.05 (aromatic CH), 127.71 (aromatic C), 126.77 (aromatic C), 120.79 (aromatic CCH₂N), 61.77 (ArCH₂N), 54.40 (N(CH₂CH₂)N), 43.48 (NCH₃), 20.77 (ArCH₃), 16.68 (ArCH₃), -12.00 (AlCH₃).

Elemental analysis for C₂₃H₃₃N₂AlO₂ (F.W. 396.50): C, 69.67; H, 8.39; N, 7.07%. Found C, 69.83; H, 8.31; N, 6.93%.

(iii) Complex 3

Complex **3** was prepared according to the procedure outlined for **1** using N,N'-dimethyl-N,N'-bis[(3,5-di-*t*-butyl-2-hydroxyphenyl)methylene]-1,2-diaminoethane in 60 % yield.

¹H NMR data (250.13 MHz, C₆D₆, 298 K): δ 7.64 (d, ⁴J_{HH} = 2.1, 2H, ArH), 6.90 (d, ⁴J_{HH} = 2.1, 2H, ArH), 3.93 (d, ²J_{HH} = 12.3, 2H, ArCH₂), 2.47 (d, ²J_{HH} = 12.3, 2H, ArCH₂), 1.85 (s, 18H, C(CH₃)₃), 1.84 (br s, 2H, N(CH₂CH₂)N), 1.67 (s, 6H, NCH₃), 1.46 (s, 18H, C(CH₃)₃), 1.45 (br s, 2H, N(CH₂CH₂)N), -0.60 (s, 3H, AlCH₃).

¹³C NMR data (100.58 MHz, C₆D₆, 298 K): δ 156.95 (COH), 138.53 (aromatic C), 137.79 (aromatic C), 124.34 (aromatic CH), 123.66 (aromatic CH), 121.35 (aromatic CCH₂N), 62.16 (ArCH₂N), 54.62 (N(CH₂CH₂)N), 43.4 (NCH₃), 35.6 (ArC(CH₃)₃), 34.3 (ArC(CH₃)₃), 32.2 (ArC(CH₃)₃), 30.1 (ArC(CH₃)₃), -10.8 (AlCH₃).

Elemental analysis for C₃₅H₅₇N₂O₂Al (F.W. 564.83): C, 74.43; H, 10.17; N, 4.96%. Found C, 74.41; H, 10.26; N, 4.90%.

(iv) Complex 4

Complex **4** was prepared according to the procedure outlined for **1** using N,N'-dimethyl-N,N'-bis[(3,5-dichloro-2-hydroxyphenyl)methylene]-1,2-diaminoethane in 60 % yield.

^1H NMR data (250.13 MHz, CD_2Cl_2 , 298 K): δ 7.29 (br s, 2H, ArH), 6.87 (d, $^4J_{\text{HH}} = 2.3$, 2H, ArH), 4.12 (d, $^2J_{\text{HH}} = 12.8$, 2H, ArCH₂), 3.35 (d, $^2J_{\text{HH}} = 12.8$, 2H, ArCH₂), 3.00 – 2.77 (m, 4H, N(CH₂CH₂)N), 2.34 (s, 6H, NCH₃), -0.78 (s, 3H, AlCH₃).

^{13}C NMR data (100.58 MHz, CD_2Cl_2 , 298 K): δ 154.47 (COH), 129.74 (aromatic CH), 127.41 (aromatic CH), 124.69 (aromatic C), 123.90 (aromatic C), 120.61 (aromatic C), 61.01 (ArCH₂N), 54.74 (N(CH₂CH₂)N), 44.80 (NCH₃), -11.4 (AlCH₃).

Elemental analysis for $\text{C}_{19}\text{H}_{21}\text{N}_2\text{O}_2\text{Cl}_4\text{Al}$ (F.W. 478.18): C, 47.72; H, 4.43; N, 5.86%. Found C, 47.82; H, 4.57; N, 5.88%.

(v) Complex 5

Complex **5** was prepared according to the procedure outlined for **1** using N,N'-dibenzyl-N,N'-bis[(2-hydroxyphenyl)methylene]-1,2-diaminoethane in 72 % yield.

^1H NMR data (400.13 MHz, CD_2Cl_2 , 298 K): δ 7.37 (br s, 6H, ArH), 7.26-7.17 (m, 6H, ArH), 6.94 (dd, $^4J_{\text{HH}} = 1.6$, $^3J_{\text{HH}} = 7.4$, 2H, ArH), 6.82 (br d, $^3J_{\text{HH}} = 8.2$, 2H, ArH), 6.72 (td, $^4J_{\text{HH}} = 1.2$, $^3J_{\text{HH}} = 7.3$, 2H, ArH), 4.1 – 3.4 (br m, 4H, NCH₂C₆H₄OH) 3.88 (s, 4H, NCH₂C₆H₅), 3.1 (br s, 2H, N(CH₂CH₂)N), 2.7 (br s, 2H, N(CH₂CH₂)N), -0.60 (s, 3H, AlCH₃).

^{13}C NMR data (100.58 MHz, CD_2Cl_2 , 298 K): δ 160.55 (COH), 132.42 (C₆H₅ C_{meta}), 131.28 (C₆H₅ C_{ipso}), 130.00 (aromatic CH), 129.69 (aromatic CH), 129.31 (aromatic C),

129.11 (aromatic CH), 128.88 (C_6H_5 C_{ortho}), 120.30 (aromatic CH), 117.11 (aromatic CH), 58.48 ($CH_2C_6H_4OH$), 55.79 ($CH_2C_6H_5$), 48.64 ($N(CH_2CH_2)N$), -10.00 ($AlCH_3$).

Elemental analysis for $C_{31}H_{33}N_2AlO_2$ (F.W. 492.59): C, 75.59; H, 6.75; N, 5.69%. Found C, 75.33; N, 6.67; N, 5.51%.

(vi) Complex 6

Complex 6 was prepared according to the procedure outlined for 1 using N,N'-dibenzyl-N,N'-bis[(3,5-dimethyl-2-hydroxyphenyl)methylene]-1,2-diaminoethane in 90 % yield.

1H NMR data (400.13 MHz, C_6D_6 , 298 K): δ 7.15-6.96 (m, 12H, ArH), 6.55 (s, 2H, ArH), 3.8 - 3.2 (br m, 4H, $NCH_2C_6H_4OH$) 3.65 (s, 4H, $NCH_2C_6H_5$), 2.6 – 1.9 (br m, 4H, $N(CH_2CH_2)N$), 2.52 (s, 6H, ArCH₃), 2.21 (s, 6H, ArCH₃), -0.15 (s, 3H, $AlCH_3$).

^{13}C NMR data (100.58 MHz, C_6D_6 , 298 K): δ 156.92 (COH), 132.32 (aromatic C), 131.84 (aromatic C), 128.92 (aromatic C), 127.27 (aromatic C), 125.65 (aromatic C), 124.88 (aromatic C), 121.80 (aromatic C), 120.28 (aromatic C), 57.63 ($CH_2C_6H_4OH$), 55.05 ($CH_2C_6H_5$), 47.46 ($N(CH_2CH_2)N$), 20.82 (ArCH₃), 16.85 (ArCH₃); $AlCH_3$ resonance not observed.

Elemental analysis for $C_{35}H_{41}N_2O_2Al$ (F.W. 548.69): C, 76.61; H, 7.53; N, 5.11%. Found C, 76.84; H, 7.68; N, 4.97%.

(vii) Complex 7

Complex 7 was prepared according to the procedure outlined for 1 using N,N'-dibenzyl-N,N'-bis[(3,5-di-t-butyl-2-hydroxyphenyl)methylene]-1,2-diaminoethane in 62 % yield.

^1H NMR spectroscopic analysis revealed that **7** exists as a complex mixture of isomers at room temperature.

Elemental analysis for $\text{C}_{47}\text{H}_{65}\text{N}_2\text{AlO}_2$ (F.W. 717.01): C, 78.73; H, 9.14; N, 3.91%. Found C, 78.56; H, 9.38; N, 3.65%.

(iix) Complex 8.

Complex **8** was prepared according to the procedure outlined for **1** using N,N'-dibenzyl-N,N'-bis[(3,5-dichloro-2-hydroxyphenyl)methylene]-1,2-diaminoethane in 66 % yield.

^1H NMR data (400.13 MHz, C_6D_6 , 298 K): δ 7.37 (d, $^4J_{\text{HH}} = 2.6$, 2H, ArH), 7.06-7.02 (m, 6H, ArH), 6.86-6.83 (m, 4H, ArH), 6.56 (d, $^4J_{\text{HH}} = 2.6$, 2H, ArH), 5.0 – 3.0 (br m, 4H, $\text{NCH}_2\text{C}_6\text{H}_4\text{OH}$), 3.24 (br s, 4H, $\text{NCH}_2\text{C}_6\text{H}_5$), 2.5 – 1.5 (br m, $\text{N}(\text{CH}_2\text{CH}_2)\text{N}$), -0.25 (s, 3H, AlCH_3). ^{13}C NMR data (100.58 MHz, C_6D_6 , 298 K): δ 154.95 (COH), 132.23 (C_6H_5 C_{meta}), 130.99 (C_6H_5 C_{ipso}), 129.89 (aromatic CH), 129.11 (aromatic CH), 128.71 (C_6H_5 C_{ortho}), 127.14 (aromatic CH), 126.37 (aromatic C), 123.04 (aromatic C), 120.79 (aromatic C), 57.12 ($\text{CH}_2\text{C}_6\text{H}_4\text{OH}$), 56.51 ($\text{CH}_2\text{C}_6\text{H}_5$), 46.75 ($\text{N}(\text{CH}_2\text{CH}_2)\text{N}$), -8.19 (AlCH_3).

Elemental analysis for $\text{C}_{31}\text{H}_{29}\text{N}_2\text{O}_2\text{Cl}_4\text{Al}$ (F.W. 630.37): C, 59.07; H, 4.64; N, 4.44%. Found C, 58.82; H, 4.76; N, 4.38%.

X-ray Crystallography

Crystal data for 2: $C_{23}H_{33}AlN_2O_2$, $M = 396.49$, orthorhombic, $Pbca$ (no. 61), $a = 7.7325(10)$, $b = 15.6579(13)$, $c = 35.803(2)$ Å, $V = 4334.8(7)$ Å³, $Z = 8$, $D_c = 1.215$ g cm⁻³, $\mu(\text{Cu-K}\alpha) = 0.971$ mm⁻¹, $T = 183$ K, colorless needles; 3203 independent measured reflections, F^2 refinement, $R_1 = 0.045$, $wR_2 = 0.114$, 2697 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$], $2\theta_{\text{max}} = 120^\circ$, 259 parameters.

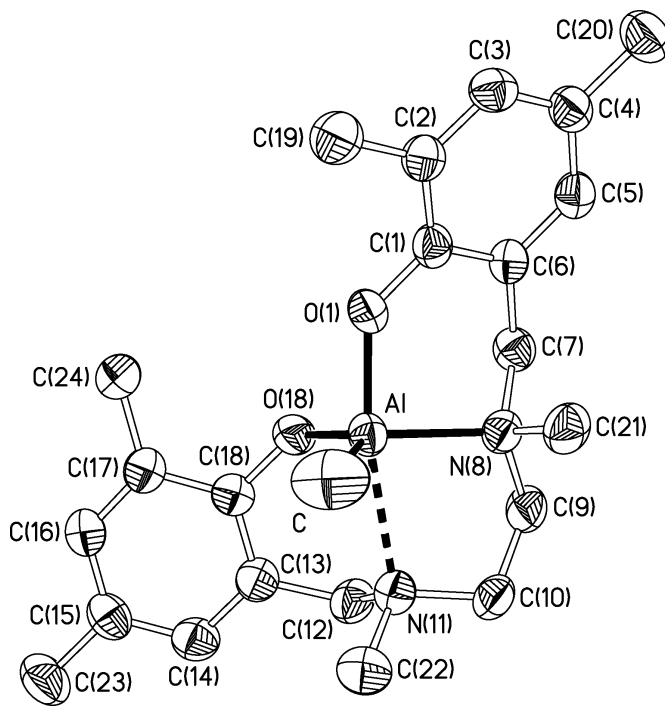


Fig S1. The molecular structure of **2** (70% probability ellipsoids).

Polymerization Data

General Polymerization Procedure

In a drybox, *rac*-lactide (720 mg, 5.0 mmol) and benzyl alcohol (5.17 μ L, 0.05 mmol) were placed in a polymerization ampoule. To this ampoule was added a solution of catalyst (0.05 mmol) in toluene (6.00 mL) ([monomer]:[Al] = 100:1). The reaction was stirred at the desired reaction time at 70 °C. Then a small sample was removed for characterization. Once the conversion exceeded 90 %, the reaction was quenched with methanol (2-3 drops). The polymer was precipitated from excess methanol.

Molecular weight of the polymers were determined by gel permeation chromatography (gpc) performed in CHCl_3 at 1.0 ml min⁻¹ using a Polymer Laboratories LC1220 HPLC pump and a Spark Midas autosampler connected to two 5 μ m columns (PLgel Mixed C 300 x 7.5 mm, Polymer Laboratories) and a Shodex RI-101 differential refractometer. The columns were calibrated with polystyrene standards (Easical™, Polymer Laboratories) ranging in molecular weight from 2.9×10^3 to 3.2×10^6 a.m.u. and chromatograms were analysed using Cirrus software (Polymer Laboratories).

General Procedure for Kinetic Studies

The polymerizations were carried out at 70 °C in a drybox. The molar ratio of monomer to initiator was fixed at 50:1. At appropriate time intervals, 0.5 mL aliquots were removed and quenched with methanol. The solvent was removed *in vacuo* and the percent conversion determined by ¹H NMR in CDCl_3 .

Kinetic analysis

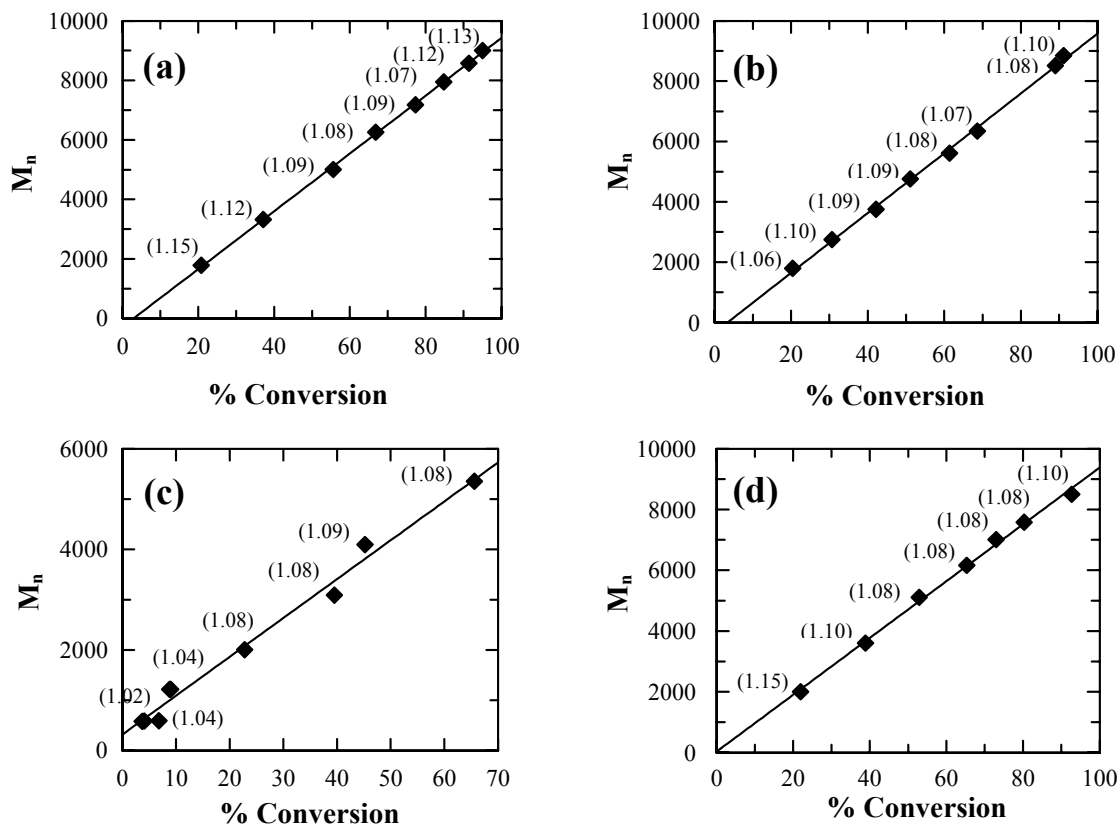


Figure S2. Plot of PLA M_n as a function of conversion using *rac*-lactide and (a) complex **1** / PhCH₂OH; (b) complex **2** / PhCH₂OH; (c) complex **3** / PhCH₂OH; (d) complex **4** / PhCH₂OH; toluene, 70°C, [LA]/[Al] = 50. Polydispersities are shown in brackets.

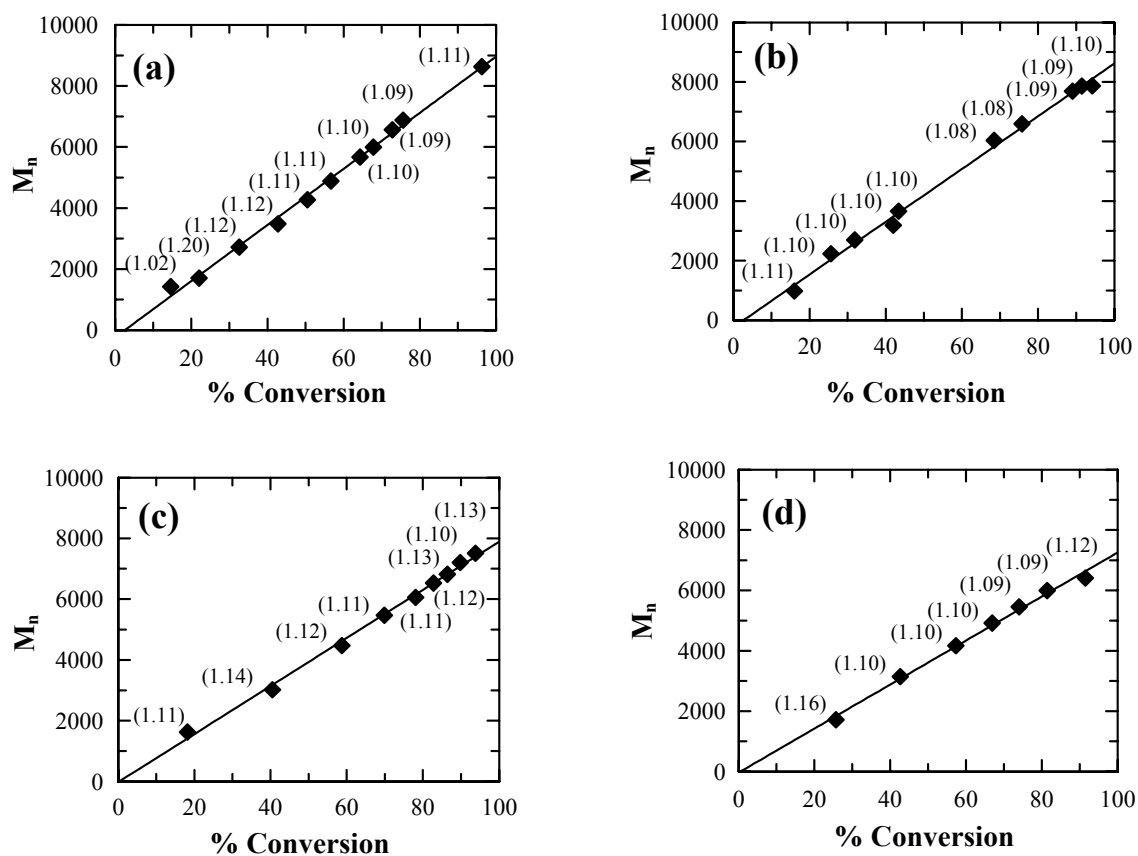


Figure S3. Plot of PLA M_n as a function of conversion using *rac*-lactide and (a) complex **5** / PhCH₂OH; (b) complex **6** / PhCH₂OH; (c) complex **7** / PhCH₂OH; (d) complex **8** / PhCH₂OH; toluene, 70°C, [LA]/[Al] = 50. Polydispersities are shown in brackets.

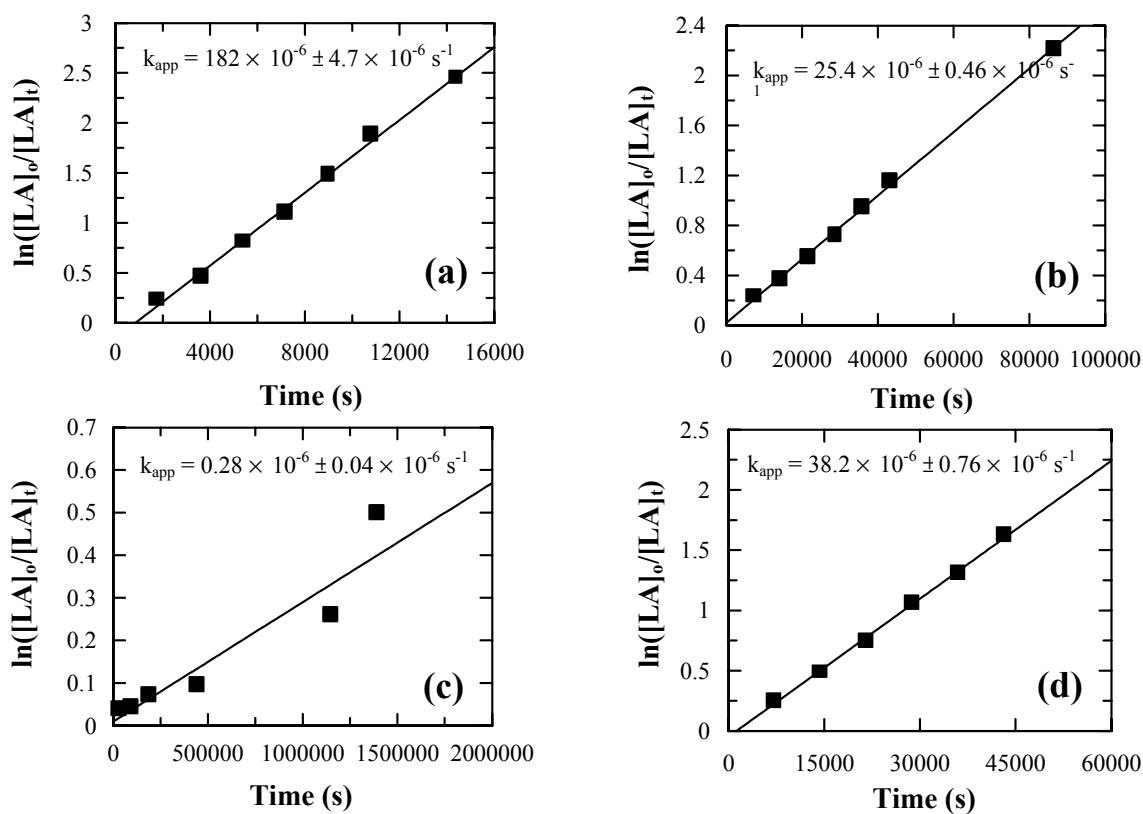


Figure S4. Semilogarithmic plots of *rac*-lactide conversion with time using (a) complex 1 / PhCH₂OH; (b) complex 2 / PhCH₂OH; (c) complex 3 / PhCH₂OH; (d) complex 4 / PhCH₂OH; toluene, 70°C, [LA]/[Al] = 50.

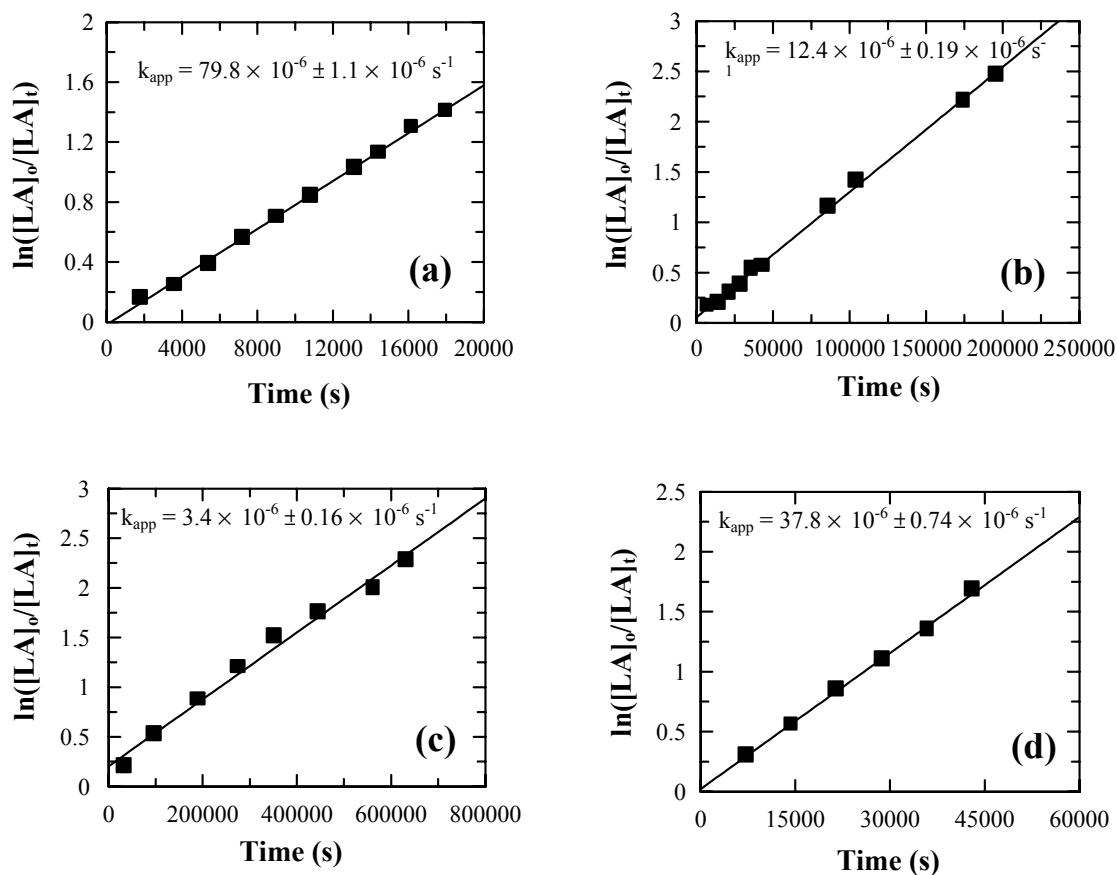


Figure S5. Semilogarithmic plots of *rac*-lactide conversion with time using (a) complex **5** / PhCH₂OH; (b) complex **6** / PhCH₂OH; (c) complex **7** / PhCH₂OH; (d) complex **8** / PhCH₂OH; toluene, 70°C, [LA]/[Al] = 50.

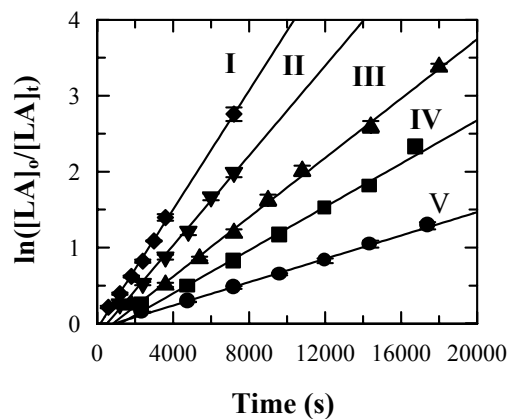


Figure S6. Semilogarithmic plots of *rac*-lactide conversion with time in toluene at 70 °C with complex **1** / PhCH₂OH as the initiator; ([LA]₀ = 0.42 M: **I**, [Al] = 16.67 mM, [LA]/[Al] = 25; **II**, [Al] = 12.50 mM, [LA]/[Al] = 34; **III**, [Al] = 8.33 mM, [LA]/[Al] = 50; **IV**, [Al] = 6.10 mM, [LA]/[Al] = 69; **V**, [Al] = 4.16 mM, [LA]/[Al] 101).

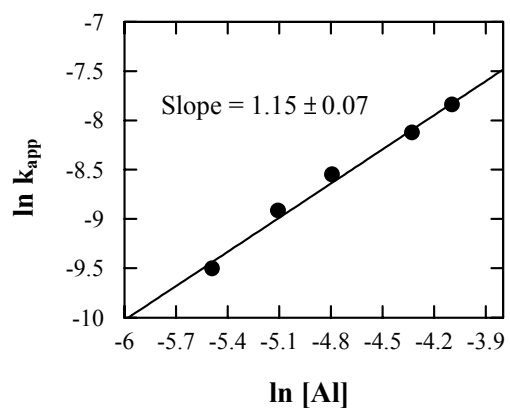


Figure S7. Plot of $\ln k_{app}$ versus $\ln [Al]$ for the polymerization of *rac*-lactide with complex **1** / PhCH₂OH as the initiator (toluene, 70 °C, [LA]₀ = 0.42 M).

Fig. S8

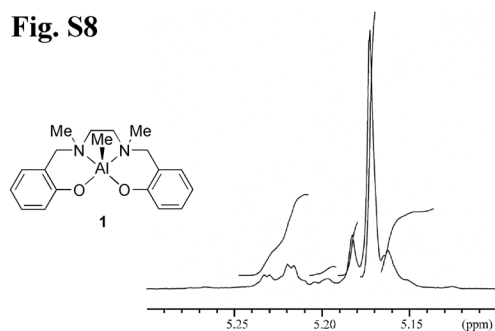


Fig. S9

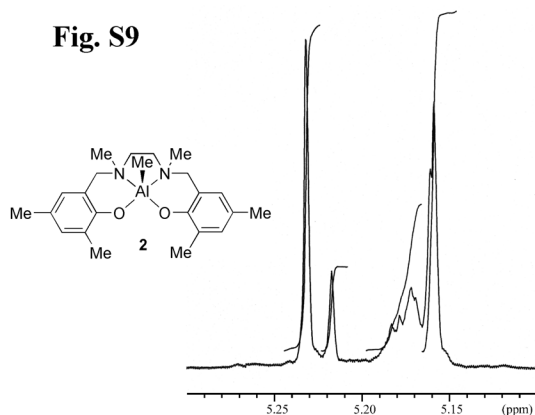


Fig. S10

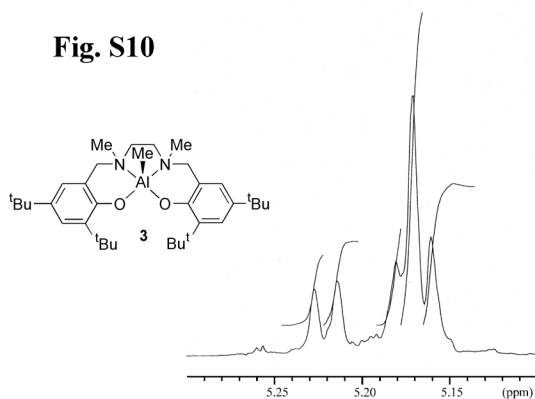


Fig. S11

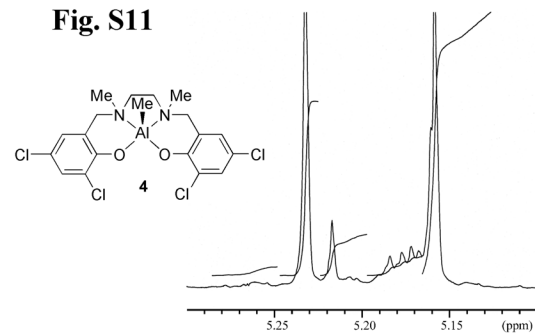


Figure S8 - S11. Homonuclear decoupled ^1H NMR spectra (CDCl_3 , 500MHz, δ 5.30-5.10) for PLA prepared using complexes **1** - **4** / PhCH_2OH

Fig. S12

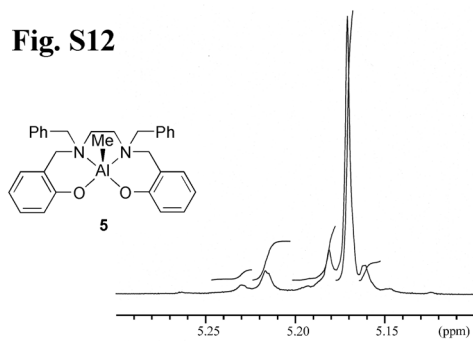


Fig. S13

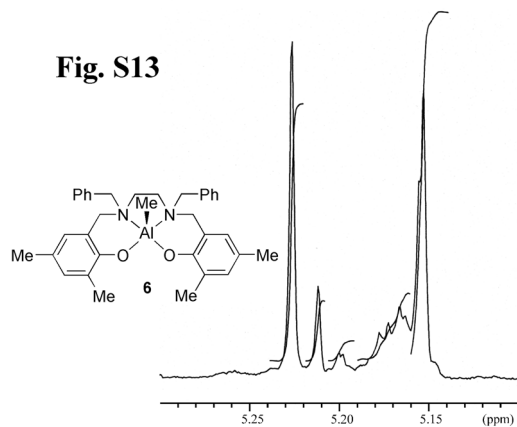


Fig. S14

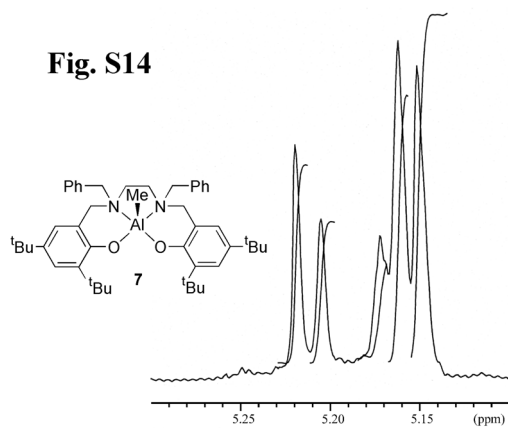


Fig. S15

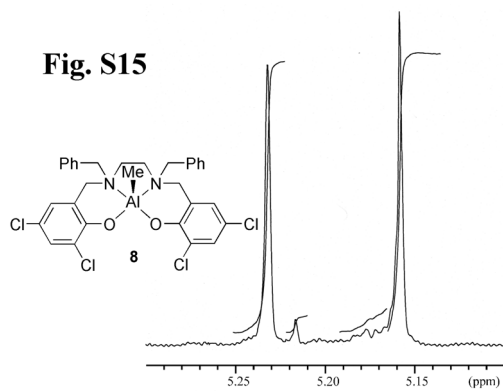


Figure S12 - S15. Homonuclear decoupled ^1H NMR spectra (CDCl_3 , 500MHz, δ 5.30-5.10) for PLA prepared using complexes **5** - **8** / PhCH_2OH

References

- S1. Tshuva, E.Y.; Gendeziuk, N.; Kol, M. *Tet. Lett.* **2001**, 42, 6405.
- S2. Tshuva, E.Y.; Goldberg, I.; Kol, M. *J. Am. Chem. Soc.* **2000**, 122, 10706.