

Supporting Information for:

Unprecedented Reversible Migration of Amide to Schiff Base Ligands Attached to Tin: Latent Single-Site Initiators for Lactide Polymerization.

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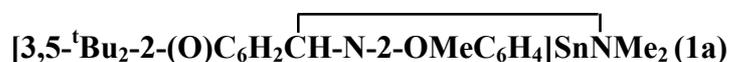
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General Experimental

Air-sensitive reactions were performed using standard Schlenk and vacuum line techniques. Diethyl ether was distilled from Na/benzophenone. Pentane, heptane and toluene were dried by passing through a cylinder filled with commercially available Q-5 catalyst (13 % Cu(II) oxide on Al₂O₃). *rac*-Lactide (Aldrich) was sublimed 3 times prior to use. *n*-BuLi (Fisher Scientific), anhydrous SnCl₂, LiNMe₂, KN(TMS)₂ (Aldrich) were used without further purification. Salicylaldimines were synthesised according to literature procedures.¹ Tin bis(amines) were prepared using the modifications of existing methods.² NMR spectra were recorded on Bruker AC-250 MHz, DRX-400 MHz or AM-500 MHz spectrometers at 293 K. Mass spectra were recorded on either a VG Autospec or a VG Platform II spectrometer. Elemental analyses were performed by the microanalytical services of the Chemistry department of London Metropolitan University and University of London. Gel permeation chromatography (GPC) was performed using Viscotex Trisec software connected to a Knauer differential refractometer. Samples were injected onto two linear 10 micron columns using chloroform as eluent at a flow rate of 1 ml min⁻¹ at room temperature. Molecular weights are quoted relative to polystyrene standards.

Preparation of Tin(II) Complexes



A solution of 3,5-^tBu₂-2-(OH)C₆H₂CH=N-2-OMeC₆H₄ (0.506 g, 1.49 mmol) in diethyl ether (30 mL) was added dropwise to a solution of Sn[NMe₂]₂ (0.309 g, 1.50 mmol) in diethyl ether chilled to -78 °C. The mixture was then stirred for 4 hr at room temperature after which the volatile components were removed under reduced pressure. The crude product was recrystallized by allowing a saturated diethyl ether solution to stand at room temperature for several days to give **1a** as yellow crystals. Yield 0.392 g, 52 %. Found C,

57.66; H, 6.71; N, 5.62. C₂₄H₃₄N₂O₂Sn requires C, 57.51; H, 6.84; N, 5.59. MS (EI): *m/z* 458 [M-NMe₂]⁺. ¹H-NMR (C₆D₆): δ 7.50 (d, 1H, ⁴*J*(HH) 2.5 Hz, 4-C₆H₂), 6.89 (d, 1H, ⁴*J*(HH) 2.7 Hz, 6-C₆H₂), 6.88 (td, 1H, ³*J*(HH) 6.3 Hz, ⁴*J*(HH) 1.4 Hz, 5-C₆H₄), 6.55 (dd, 1H, ³*J*(HH) 6.4 Hz, ⁴*J*(HH) 1.5 Hz, 3-C₆H₄), 6.46 (td, 1H, ³*J*(HH) 6.1 Hz, ⁴*J*(HH) 1.5 Hz, 4-C₆H₄), 6.33 (dd, 1H, ³*J*(HH) 6.6 Hz, ⁴*J*(HH) 1.4 Hz, 6-C₆H₄), 5.55 (s, 1H, HC-N), 3.25 (s, 3H, OCH₃), 2.07 (br, 6H, N(CH₃)₂), 1.67 (s, 9H, 3-C(CH₃)₃), 1.37 (s, 9H, 5-C(CH₃)₃). ¹³C-NMR: δ 155.44 (1-C₆H₂), 150.78 (2-C₆H₄), 141.56 (1-C₆H₄), 138.00 (3-C₆H₂), 137.36 (5-C₆H₂), 126.54 (2-C₆H₂), 125.79 (6-C₆H₂), 124.55 (4-C₆H₂), 122.22 (5-C₆H₄), 114.65 (4-C₆H₄), 113.20 (3-C₆H₄), 109.82 (6-C₆H₄), 89.13 (HC-N), 54.32 (OCH₃), 42.68 (br, 2C resonances, N(CH₃)₂), 35.52 (3-C(CH₃)₃), 34.07 (5-C(CH₃)₂), 32.04 (5-C(CH₃)₃), 29.93 (3-C(CH₃)₃). ¹¹⁹Sn-NMR (C₆D₆): δ -165.96.



[3,5-^tBu₂-2-(O)C₆H₂CH-N-2-SPhC₆H₄]SnNMe₂ (2a**)**

This complex was synthesised using the procedure outlined for **1a** but with 3,5-^tBu₂-2-(OH)C₆H₂CH=N-2-SPhC₆H₄ (2.021 g, 4.84 mmol) and Sn[NMe₂]₂ (1.005 g, 4.86 mmol). The crude product was recrystallized by allowing a saturated diethyl ether solution to stand at room temperature for several days to give **2a** as yellow crystals. Yield 1.381 g, 49 %. Found C, 60.18; H, 6.35; N, 4.71. C₂₉H₃₆N₂OSSn requires C, 60.12; H, 6.25; N, 4.84. MS (CI(NH₃)): *m/z* 536 [M-NMe₂]⁺. ¹H-NMR (C₆D₆): δ 7.54 (d, 1H, ⁴*J*(HH) 2.6 Hz, 4-C₆H₂), 7.31 (dd, 1H, ³*J*(HH) 6.1 Hz, ⁴*J*(HH) 1.6 Hz, 6-C₆H₄), 7.10 (td, 1H, ³*J*(HH) 7.2 Hz, ⁴*J*(HH) 1.7 Hz, 5-C₆H₄), 6.99-6.96 (m, 2H, C₆H₅S), 6.90-6.79 (m, 4H, 4-C₆H₂+C₆H₅S), 6.66 (d, 1H, ³*J*(HH) 7.7 Hz, 3-C₆H₄), 6.36 (td, 1H, ³*J*(HH) 7.5 Hz, ⁴*J*(HH) 1.1 Hz, 4-C₆H₄), 5.38 (s, 1H, HC-N), 1.94 (s, 3H, N(CH₃)₂), 1.80 (s, 3H, N(CH₃)₂), 1.66 (s, 9H, 3-C(CH₃)₃), 1.40 (s, 9H, 5-C(CH₃)₃). ¹³C-NMR: δ 155.92 (2-C₆H₂), 154.86 (1-

$\underline{\text{C}}_6\text{H}_4$), 138.63 (6- $\underline{\text{C}}_6\text{H}_4$), 138.52 (3- $\underline{\text{C}}_6\text{H}_2$), 137.37 (5- $\underline{\text{C}}_6\text{H}_2$), 131.80 (5- $\underline{\text{C}}_6\text{H}_4$), 129.46 (3- $\underline{\text{C}}_6\text{H}_5\text{S}$), 129.46 (5- $\underline{\text{C}}_6\text{H}_5\text{S}$), 126.67 (2- $\underline{\text{C}}_6\text{H}_5\text{S}$), 126.67 (6- $\underline{\text{C}}_6\text{H}_5\text{S}$), 125.99 (4- $\underline{\text{C}}_6\text{H}_5\text{S}$), 125.93 (6- $\underline{\text{C}}_6\text{H}_2$), 124.78 (4- $\underline{\text{C}}_6\text{H}_2$), 115.75 (4- $\underline{\text{C}}_6\text{H}_4$), 114.20 (3- $\underline{\text{C}}_6\text{H}_4$), 88.42 (H $\underline{\text{C}}\text{-N}$), 43.65 (N($\underline{\text{C}}\text{H}_3$)₂), 40.62 (N($\underline{\text{C}}\text{H}_3$)₂), 35.55 (3- $\underline{\text{C}}(\text{CH}_3)$ ₃), 34.11 (5- $\underline{\text{C}}(\text{CH}_3)$ ₂), 32.07 (5- $\underline{\text{C}}(\text{CH}_3)$ ₃), 29.97 (3- $\underline{\text{C}}(\text{CH}_3)$ ₃). ¹¹⁹Sn-NMR (C₆D₆): δ -222.30.

[3,5-^tBu₂-2-(O)C₆H₂CH-N-2-PPh₂C₆H₄]SnNMe₂ (3a)

This complex was synthesised using the procedure outlined for **1a** but with 3,5-^tBu₂-2-(OH)C₆H₂CH=N-2-PPh₂C₆H₄ (1.315 g, 2.66 mmol) and Sn[NMe₂]₂ (0.551 g, 2.66 mmol). The crude product was recrystallized by allowing a saturated toluene solution to stand at room temperature for several days to give **3a** as yellow crystals. Yield 1.204 g, 69 %. Found C, 64.27; H, 6.38; N, 4.33 C₃₅H₄₁N₂OPSn requires C, 64.14; H, 6.31; N, 4.27. MS (EI) *m/z* 612 [M-NMe₂]⁺. ¹H-NMR (C₆D₆): δ 7.60 (d, 1H, ⁴*J*(HH) 2.6 Hz, 4- $\underline{\text{C}}_6\text{H}_2$), 7.47-7.42 (m, 2H, ($\underline{\text{C}}_6\text{H}_5$)₂P), 7.22-7.12 (m, 4H, $\underline{\text{C}}_6\text{H}_4$ + ($\underline{\text{C}}_6\text{H}_5$)₂P), 7.02-7.00 (m, 2H, ($\underline{\text{C}}_6\text{H}_5$)₂P), 6.94 (d, 1H, ⁴*J*(HH) 2.6 Hz, 6- $\underline{\text{C}}_6\text{H}_2$), 6.93-6.86 (m, 4H, $\underline{\text{C}}_6\text{H}_4$ + ($\underline{\text{C}}_6\text{H}_5$)₂P), 6.75 (t, 1H, ³*J*(HH) 7.2 Hz, $\underline{\text{C}}_6\text{H}_4$), 6.41 (tt, 1H, ³*J*(HH) 7.0 Hz, ⁴*J*(HH) 1.1 Hz, $\underline{\text{C}}_6\text{H}_4$), 5.46 (s, 1H, $\underline{\text{H}}\text{C-N}$), 2.08 (s, 3H, N($\underline{\text{C}}\text{H}_3$)₂), 1.93 (s, 3H, N($\underline{\text{C}}\text{H}_3$)₂), 1.74 (s, 9H, 3- $\underline{\text{C}}(\text{CH}_3)$ ₃), 1.41 (s, 9H, 5- $\underline{\text{C}}(\text{CH}_3)$ ₃). ¹³C-NMR: δ 156.58 (1- $\underline{\text{C}}_6\text{H}_2$), 138.53 (3- $\underline{\text{C}}_6\text{H}_2$), 136.80 (5- $\underline{\text{C}}_6\text{H}_2$), 134.51, 134.38, 133.61, 133.46, 131.59, 129.74, 129.30, 129.18, 129.11, 128.73, 128.65 (12 C resonances, 1- $\underline{\text{C}}_6\text{H}_4$, 2- $\underline{\text{C}}_6\text{H}_4$ + ($\underline{\text{C}}_6\text{H}_5$)₂P), 128.26 (3/6- $\underline{\text{C}}_6\text{H}_4$), 127.78 (6/3- $\underline{\text{C}}_6\text{H}_4$), 126.50 (6- $\underline{\text{C}}_6\text{H}_2$), 126.35 (2- $\underline{\text{C}}_6\text{H}_2$), 124.43 (4- $\underline{\text{C}}_6\text{H}_2$), 115.70 (4/5- $\underline{\text{C}}_6\text{H}_4$), 114.83 (5/4- $\underline{\text{C}}_6\text{H}_4$), 87.10 ($\underline{\text{H}}\text{C-N}$), 43.80 (N($\underline{\text{C}}\text{H}_3$)₂), 40.87 (N($\underline{\text{C}}\text{H}_3$)₂), 35.68 (3- $\underline{\text{C}}(\text{CH}_3)$ ₃), 34.09 (5- $\underline{\text{C}}(\text{CH}_3)$ ₂), 32.11 (5- $\underline{\text{C}}(\text{CH}_3)$ ₃), 30.12 (3- $\underline{\text{C}}(\text{CH}_3)$ ₃). ¹¹⁹Sn-NMR (C₆D₆): δ -270.99 (d, ¹*J*(SnP) 1444 Hz).

[3,5-^tBu₂-2-(O)C₆H₂CH=N-2-OMeC₆H₄]SnCl (1b)

2.5 M n-BuLi (1.87 ml, 4.68 mmol) was slowly added into a solution of 3,5-^tBu₂-2-(OH)C₆H₂CH=N-2-OMeC₆H₄ (1.515 g, 4.46 mmol) in toluene (60 ml) cooled to 0 °C. The reaction was stirred at room temperature for 3 hr and then added dropwise to a suspension of SnCl₂ (0.876 g, 4.62 mmol) in toluene (20 ml) chilled to -78 °C. The reaction mixture was allowed to stir for 18 hr whilst warming to room temperature. The yellow solution was filtered and the volatiles removed under reduced pressure. The crude product was recrystallized by cooling a hot heptane solution from 70 °C to room temperature to give **1b** as yellow needles. Yield 1.086 g, 49 %. Found C, 53.54; H, 5.81; N, 2.91. C₂₂H₂₈NO₂SnCl requires C, 53.64; H, 5.74; N, 2.84. MS (EI): *m/z* 493 [M]⁺. ¹H-NMR (C₆D₆): δ 7.84 (d, 1H, ⁴*J*(HH) 2.6 Hz, 4-C₆H₂), 7.61 (s, 1H, HC=N), 6.90 (td, 1H, ³*J*(HH) 6.1 Hz, ⁴*J*(HH) 1.6 Hz, 4-C₆H₄), 6.87 (d, 1H, ⁴*J*(HH) 2.5 Hz, 6-C₆H₂), 6.65 (td, 1H, ³*J*(HH) 6.5 Hz, ⁴*J*(HH) 1.2 Hz, 5-C₆H₄), 6.37 (dd, 1H, ³*J*(HH) 6.3 Hz, ⁴*J*(HH) 1.5 Hz, 3-C₆H₄), 6.31 (dd, 1H, ³*J*(HH) 7.2 Hz, ⁴*J*(HH) 1.1 Hz, 6-C₆H₄), 3.28 (s, 3H, OC H₃), 1.74 (s, 9H, 3-C(CH₃)₃), 1.30 (s, 9H, 5-C(CH₃)₃). ¹³C-NMR: δ 166.81 (H C=N), 163.72 (2-C₆H₂), 151.82 (2-C₆H₄), 142.14 (3-C₆H₂), 138.97 (5-C₆H₂), 137.26 (1-C₆H₄), 132.55 (4-C₆H₂), 130.78 (6-C₆H₂), 128.37 (4-C₆H₄), 122.33 (3-C₆H₄), 122.24 (5-C₆H₄), 120.44 (1-C₆H₂), 111.72 (6-C₆H₄), 54.71 (OC H₃), 35.70 (3-C(CH₃)₃), 34.16 (5-C(CH₃)₂), 31.50 (5-C(CH₃)₃), 30.11 (3-C(CH₃)₃). ¹¹⁹Sn-NMR (C₆D₆): δ -377.20.

[3,5-^tBu₂-2-(O)C₆H₂CH=N-2-SPhC₆H₄]SnCl (2b)

This complex was synthesised using the procedure outlined for **1b** but with 2.5 M n-BuLi (1.52 ml, 3.78 mmol), 3,5-^tBu₂-2-(OH)C₆H₂CH=N-2-SPhC₆H₄ (1.502 g, 3.60 mmol), and

SnCl₂ (0.689 g, 3.63 mmol). The crude product was recrystallized by cooling a hot heptane solution from 70 °C to room temperature to give **2b** as yellow needles. Yield 1.319 g, 64 %. Found C, 57.19; H, 5.47; N, 2.42. C₂₇H₃₀NOSSnCl requires C, 56.82; H, 5.30; N, 2.45. MS (EI): *m/z* 571 [M]⁺. ¹H-NMR (C₆D₆): δ 7.81 (d, 1H, ⁴*J*(HH) 2.6 Hz, 4-C₆H₂), 7.44 (s, 1H, HC=N), 7.13-6.73 (several m, 9H, C₆H₄+C₆H₅S), 6.75 (d, 1H, ⁴*J*(HH) 2.3 Hz, 6-C₆H₂), 1.68 (s, 9H, 3-C(CH₃)₃), 1.30 (s, 9H, 5-C(CH₃)₃). ¹³C-NMR: δ 169.15 (HC=N), 162.14 (2-C₆H₂), 147.98, 134.52, 132.90, 131.60, 130.05, 129.66, 129.51, 127.93, 125.31 (9c resonances, C₆H₄+C₆H₅S), 142.08 (5-C₆H₂), 139.14 (3-C₆H₂), 132.93 (4-C₆H₄), 130.77 (6-C₆H₂), 120.08 (1-C₆H₂), 35.64 (3-C(CH₃)₃), 34.13 (5-C(CH₃)₂), 31.45 (5-C(CH₃)₃), 30.00 (3-C(CH₃)₃). ¹¹⁹Sn-NMR (C₆D₆): δ -353.71.

[3,5-^tBu₂-2-(O)C₆H₂CH=N-2-PPh₂C₆H₄]SnCl (**3b**)

This complex was synthesised using the procedure outlined for **1b** but with 2.5 M n-BuLi (0.88 ml, 2.191 mmol), 3,5-^tBu₂-2-(OH)C₆H₂CH=N-2-PPh₂C₆H₄ (1.030 g, 2.09 mmol), and SnCl₂ (0.390 g, 2.059 mmol). The product was recrystallized by layering a toluene solution with pentane at room temperature for several days to give **3b** as yellow crystals. Yield 1.022 g, 76 %. Found C, 61.04; H, 5.58; N, 2.02. C₃₃H₃₅NOPSnCl requires C, 61.28; H, 5.45; N, 2.17. MS (CI(NH₃)): *m/z* 647 [M]⁺. ¹H-NMR (C₆D₆): δ 7.79 (d, 1H, ⁴*J*(HH) 2.6 Hz, 4-C₆H₂), 7.60 (s, 1H, HC=N), 7.28 (m, 4H, (C₆H₅)₂P), 7.08 (m, 1H, 3/6-C₆H₄), 6.96 (m, 1H, 4/5-C₆H₂), 6.95-6.89 (m, 6H, (C₆H₅)₂P), 6.85 (td, 1H, ³*J*(HH) 6.3 Hz, ⁴*J*(HH) 0.9 Hz, 4/5-C₆H₄), 6.77 (br, 1H, 3/6-C₆H₄), 6.61 (d, 1H, ⁴*J*(HH) 2.6 Hz, 6-C₆H₂), 1.71 (s, 9H, 3-C(CH₃)₃), 1.23 (s, 9H, 5-C(CH₃)₃). ¹³C-NMR: δ 169.16 (HC=N), 162.97 (2-C₆H₂), 154.42 (1-C₆H₄), 159.20, 134.41, 134.24, 131.08, 129.63, 129.02, 128.94, 124.58 (8C resonances, (C₆H₅)₂P), 142.10 (3-C₆H₂), 138.69 (5-C₆H₂), 133.80 (3/6-C₆H₄),

132.70 (4- $\underline{\text{C}}_6\text{H}_2$), 131.57 (4/5- $\underline{\text{C}}_6\text{H}_2$), 130.33 (6- $\underline{\text{C}}_6\text{H}_2$), 127.78 (5/4- $\underline{\text{C}}_6\text{H}_4$), 124.60 (3/6- $\underline{\text{C}}_6\text{H}_4$), 120.46 (1- $\underline{\text{C}}_6\text{H}_2$), 35.69 (3- $\underline{\text{C}}(\text{CH}_3)_3$), 34.06 (5- $\underline{\text{C}}(\text{CH}_3)_2$), 31.41 (5- $\text{C}(\underline{\text{C}}\text{H}_3)_3$), 30.09 (3- $\text{C}(\underline{\text{C}}\text{H}_3)_3$).

[3,5-^tBu₂-2-(O)C₆H₂CH=N-2-OMeC₆H₄]SnOCMePh₂ (1c)

A solution of Ph₂MeCOH (0.200 g, 1.01 mmol) in toluene (30 ml) was added dropwise into a solution of **1a** (0.501 g, 1.00 mmol) in toluene (30 ml) chilled to -78 °C. The reaction was stirred at room temperature for 4 hr and volatiles were removed under reduced pressure. The crude product was recrystallized by allowing a saturated heptane solution to stand at -30 °C for several days to give **1c** as yellow crystals. Yield 0.319 g, 49 %. Found C, 65.92; H, 6.17; N, 2.06. C₃₆H₄₁NO₃Sn requires C, 66.07; H, 6.32; N, 2.14. MS (EI): *m/z* 655 [M]⁺. ¹H-NMR (C₆D₆): δ 7.84 (d, 1H, ⁴*J*(HH) 2.6 Hz, 4- $\underline{\text{C}}_6\text{H}_2$), 7.75 (s, 1H, $\underline{\text{H}}\text{C}=\text{N}$), 7.43-7.37 (m, 4H, OMe($\underline{\text{C}}_6\text{H}_5$)₂), 7.12-6.98 (m, 4H, OMe($\underline{\text{C}}_6\text{H}_5$)₂), 6.96 (d, 1H, ⁴*J*(HH) 2.6 Hz, 6- $\underline{\text{C}}_6\text{H}_2$), 6.92 (td, 1H, ³*J*(HH) 7.0 Hz, ⁴*J*(HH) 1.5 Hz, 4- $\underline{\text{C}}_6\text{H}_4$), 6.67 (td, 1H, ³*J*(HH) 6.6 Hz, ⁴*J*(HH) 1.0 Hz, 5- $\underline{\text{C}}_6\text{H}_4$), 6.52 (dd, 1H, ³*J*(HH) 6.3 Hz, ⁴*J*(HH) 1.5 Hz, 3- $\underline{\text{C}}_6\text{H}_4$), 6.33 (dd, 1H, ³*J*(HH) 6.5 Hz, ⁴*J*(HH) 0.7 Hz, 6- $\underline{\text{C}}_6\text{H}_4$), 3.00 (s, 3H, O $\underline{\text{C}}\text{H}_3$), 1.97 (s, 3H, OC($\underline{\text{C}}\text{H}_3$)Ph₂), 1.70 (s, 9H, 3- $\text{C}(\underline{\text{C}}\text{H}_3)_3$), 1.39 (s, 9H, 5- $\text{C}(\underline{\text{C}}\text{H}_3)_3$). ¹³C-NMR: δ 166.44 ($\underline{\text{H}}\text{C}=\text{N}$), 164.06 (2- $\underline{\text{C}}_6\text{H}_2$), 154.92 (1- OMe($\underline{\text{C}}_6\text{H}_5$)₂), 153.95, 126.98, 126.88, 125.93, 125.81 (5 C resonances, OMe($\underline{\text{C}}_6\text{H}_5$)₂), 152.10 (2- $\underline{\text{C}}_6\text{H}_4$), 141.84 (3- $\underline{\text{C}}_6\text{H}_2$), 138.06 (5- $\underline{\text{C}}_6\text{H}_2$), 137.81 (1- $\underline{\text{C}}_6\text{H}_4$), 131.73 (4- $\underline{\text{C}}_6\text{H}_2$), 130.27 (6- $\underline{\text{C}}_6\text{H}_2$), 128.24 (4- $\underline{\text{C}}_6\text{H}_4$), 123.35 (3- $\underline{\text{C}}_6\text{H}_4$), 121.87 (5- $\underline{\text{C}}_6\text{H}_4$), 120.85 (1- $\underline{\text{C}}_6\text{H}_2$), 111.30 (6- $\underline{\text{C}}_6\text{H}_4$), 77.22 (OC($\underline{\text{C}}\text{H}_3$)Ph₂), 54.42 (O $\underline{\text{C}}\text{H}_3$), 35.71 (3- $\underline{\text{C}}(\text{CH}_3)_3$), 34.40 (5- $\underline{\text{C}}(\text{CH}_3)_2$), 34.18 (OC($\underline{\text{C}}\text{H}_3$)Ph₂), 31.64 (5- $\text{C}(\underline{\text{C}}\text{H}_3)_3$), 30.03 (3- $\text{C}(\underline{\text{C}}\text{H}_3)_3$). ¹¹⁹ Sn-NMR (C₆D₆): δ -378.53.

Compounds **2c** and **3c** were synthesised in NMR tubes from the reaction of an appropriate tin dimethylamide complex and Ph₂MeCOH and the product was characterised by ¹H-NMR only.

[3,5-^tBu₂-2-(O)C₆H₂CH=N-2-SPhC₆H₄]SnOCMePh₂ (2c**)**

¹H-NMR (C₆D₆): δ 7.81 (d, 1H, ⁴J(HH) 2.6 Hz, 4-C₆H₂), 7.54 (s, 1H, HC=N), 7.13-6.85 (several m, 19H, C₆H₄+C₆H₅S+OCMe(C₆H₅)₂+6-C₆H₂), 1.92 (s, 3H, OC(C H₃)Ph₂), 1.68 (s, 9H, 3-C(CH₃)₃), 1.30 (s, 9H, 5-C(CH₃)₃).

[3,5-^tBu₂-2-(O)C₆H₂CH=N-2-PPh₂C₆H₄]SnOCMePh₂ (3c**)**

¹H-NMR (C₆D₆): δ 7.75 (d, 1H, ⁴J(HH) 2.5 Hz, 4-C₆H₂), 7.57 (s, 1H, HC=N), 7.47, 7.21-6.87 (several m, 24H, C₆H₄+(C₆H₅)₂P+OCMe(C₆H₅)₂), 6.58 (d, 1H, ⁴J(HH) 2.5 Hz, 6-C₆H₂), 1.97 (s, 3H, OC(CH₃)Ph₂), 1.67 (s, 9H, 3-C(CH₃)₃), 1.35 (s, 9H, 5-C(CH₃)₃).

[3,5-^tBu₂-2-(O)C₆H₂CH-N-2-OMeC₆H₄]SnNEt₂ (1a'**)**

A solution of LiNEt₂ (0.234 g, 2.95 mmol) in diethyl ether (30 ml) was added dropwise in to a suspension of SnCl₂ (0.280 g, 1.48 mmol) in diethyl ether (20 ml) chilled to -78 °C. The mixture was stirred for 1 hr at room temperature. This solution was then cooled to -78 °C and was added dropwise with a solution of 3,5-^tBu₂-2-(OH)C₆H₂CH=N-2-OMeC₆H₄ (0.501 g, 1.48 mmol) in diethyl ether (30 mL). The mixture was stirred for another 2 hr at room temperature after which the volatile components were removed under reduced pressure. The crude product was recrystallized by allowing a saturated diethyl ether solution to stand at 5 °C for 18 hr to give **1a'** as yellow crystals. Yield 0.217 g, 52 %. ¹H-NMR (C₆D₆): δ 7.49 (d, 1H, ⁴J(HH) 1.5 Hz, 4-C₆H₂), 6.91 (d, 1H, ⁴J(HH) 1.5

Hz, 6-C₆H₂), 6.89 (td, 1H, ³J(HH) 7.5 Hz, ⁴J(HH) 1.1 Hz, 5-C₆H₄), 6.53 (dd, 1H, ³J(HH) 6.8 Hz, ⁴J(HH) 1.1 Hz, 3-C₆H₄), 6.47 (td, 1H, ³J(HH) 6.8 Hz, ⁴J(HH) 1.2 Hz, 4-C₆H₄), 6.35 (d, 1H, ³J(HH) 6.8 Hz, 6-C₆H₄), 5.79 (s, 1H, HC-N), 3.26 (s, 3H, OC H₃), 3.15 (br, 1H, N(CH₂CH₃)₂), 2.81 (br, 1H, N(CH₂CH₃)₂), 2.57 (br, 2H, N(CH₂CH₃)₂), 1.67 (s, 9H, 3-C(CH₃)₃), 1.38 (s, 9H, 5-C(CH₃)₃), 0.72 (br, 3H, N(CH₂CH₃)₂), 0.53 (br, 3H, N(CH₂CH₃)₂). ¹³C-NMR: δ missing (1-C₆H₂), 155.99 (2-C₆H₂), 150.79 (2-C₆H₄), 141.50 (1-C₆H₄), 138.09 (5-C₆H₂), 137.22 (3-C₆H₂), 126.04 (6-C₆H₂), 124.28 (4-C₆H₂), 122.23 (5-C₆H₄), 114.43 (4-C₆H₄), 112.90 (3-C₆H₄), 109.77 (6-C₆H₄), 85.06 (H C-N), 54.28 (OCH₃), 43.27 (N(CH₂CH₃)₂), 40.25 (N(CH₂CH₃)₂), 35.53 (3-C(CH₃)₃), 34.07 (5-C(CH₃)₂), 32.03 (5-C(CH₃)₃), 29.95 (3-C(CH₃)₃), 10.97 (N(CH₂CH₃)₂), 8.37 (N(CH₂CH₃)₂). ¹¹⁹Sn-NMR (C₆D₆): δ -171.99.

[3,5-^tBu₂-2-(O)C₆H₂CH=N-2-OMeC₆H₄]SnNⁱPr₂

This complex was synthesised using the procedure outlined for **1a'** but with LiNⁱPr₂ (0.514 g, 4.80 mmol), SnCl₂ (0.455 g, 2.40 mmol) and 3,5-^tBu₂-2-(OH)C₆H₂CH=N-2-OMeC₆H₄ (0.810 g, 2.386 mmol). ¹H-NMR (C₆D₆): δ 7.69 (d, 1H, ⁴J(HH) 2.6 Hz, 4/6-C₆H₂), 7.57 (s, 1H, HC=N), 6.94 (td, 1H, ³J(HH) 7.5 Hz, ⁴J(HH) 1.7 Hz, 4/5-C₆H₄), 6.79 (d, 1H, ⁴J(HH) 2.7 Hz, 4/6-C₆H₂), 6.70 (td, 1H, ³J(HH) 7.7 Hz, ⁴J(HH) 1.2 Hz, 4/5-C₆H₄), 6.60 (dd, 1H, ³J(HH) 7.7 Hz, ⁴J(HH) 1.8 Hz, 3/6-C₆H₄), 6.40 (dd, 1H, ³J(HH) 8.2 Hz, ⁴J(HH) 1.1 Hz, 3/6-C₆H₄), 3.91 (sept, 2H, ³J(HH) 6.6 Hz, N(CH(CH₃)₂)), 3.27 (s, 3H, OCH₃), 1.68 (s, 9H, 3-C(CH₃)₃), 1.42 (d, 6H, ³J(HH) 6.5 Hz, N(CH(CH₃)₂)), 1.32 (s, 9H, 5-C(CH₃)₃), 0.97 (d, 6H, ³J(HH) 6.6 Hz, N(CH(CH₃)₂)).

[3,5-^tBu₂-2-(O)C₆H₂CH=N-2-OMeC₆H₄]SnN(SiMe₃)₂

This complex was synthesised using the procedure outlined for **1a** but with 3,5-^tBu₂-2-(OH)C₆H₂CH=N-2-OMeC₆H₄ (1.052 g, 3.10 mmol) and Sn[N(SiMe₃)₂]₂ (1.362 g, 3.10 mmol). The crude product was recrystallized by allowing a saturated diethyl ether solution to stand at room temperature overnight to give the product as red-orange crystals. Yield 1.265 g, 68 %. Found C, 55.57; H, 7.63; N, 2.22. C₂₈H₄₆NO₂Si₂Sn requires C, 55.72; H, 7.68; N, 2.32. MS (+ve CI): *m/z* 485 [M-N(SiMe₃)₂+H]⁺, 475 [M-N(SiMe₃)₂+NH]₄⁺. ¹H-NMR (C₆D₆): δ 7.70 (d, 1H, ⁴*J*(HH) 2.4 Hz, 4-C₆H₂), 7.48 (s, 1H, HC=N), 6.94 (m, 1H, 3/4/5/6-C₆H₄), 6.78 (d, 1H, ⁴*J*(HH) 2.4 Hz, 6-C₆H₂), 6.70 (d, 1H, ³*J*(HH) 4.0 Hz, 3/4/5/6-C₆H₄), 6.70 (d, 1H, ³*J*(HH) 4.0 Hz, 3/4/5/6-C₆H₄), 6.42 (d, 1H, ³*J*(HH) 8.4 Hz, 3/4/5/6-C₆H₄), 3.32 (s, 3H, OCH₃), 1.66 (s, 9H, 3-C(CH₃)₃), 1.30 (s, 9H, 5-C(CH₃)₃), 0.31 (s, 18H, N(Si(CH₃)₃)₂). ¹³C-NMR: δ 167.58 (HC=N), 163.79 (1-C₆H₂), 152.74 (2-C₆H₄), 142.75 (3-C₆H₂), 138.05 (5-C₆H₂), 137.92 (2-C₆H₂), 131.85 (4-C₆H₂), 130.22 (6-C₆H₂), 128.03, 123.57, 121.90, 111.53 (3/4/5/6-C₆H₄), 120.48 (1-C₆H₄), 55.03 (OCH₃), 35.50 (3-C(CH₃)₃), 34.06 (5-C(CH₃)₂), 31.47 (5-C(CH₃)₃), 30.15 (3-C(CH₃)₃), 6.04 (N(Si(CH₃)₃)₂). ¹¹⁹Sn-NMR (C₆D₆): δ -149.91.

General Polymerization Procedure.

To an ampoule charged with *rac*-lactide (0.4036 g, 2.80 mmol) and the tin complex (0.0028 mmol), was added toluene (10 ml). The reaction was stirred at 60 °C and samples were taken at pre-selected reaction times. The reaction was quenched with 1 drop of methanol and the conversion was determined by ¹H-NMR spectroscopy. After the solvent was removed under reduced pressure the residue was dissolved in a small amount of chloroform and the polymer then precipitated by addition of excess cold acidic methanol. After drying *in vacuo* for 18 hr, the molecular weight and PDI were determined by gel permeation chromatography.

References

1. Cameron, P. A.; Gibson, V. C.; Redshaw, C.; Segal, J. A.; White, A. J. P.; Williams, D.J. *Dalton Trans.*, **2002**, 415–422.
2. Foley, P.; Zeldin, M. *Inorg. Chem.*, **1975**, *14*, 2264.

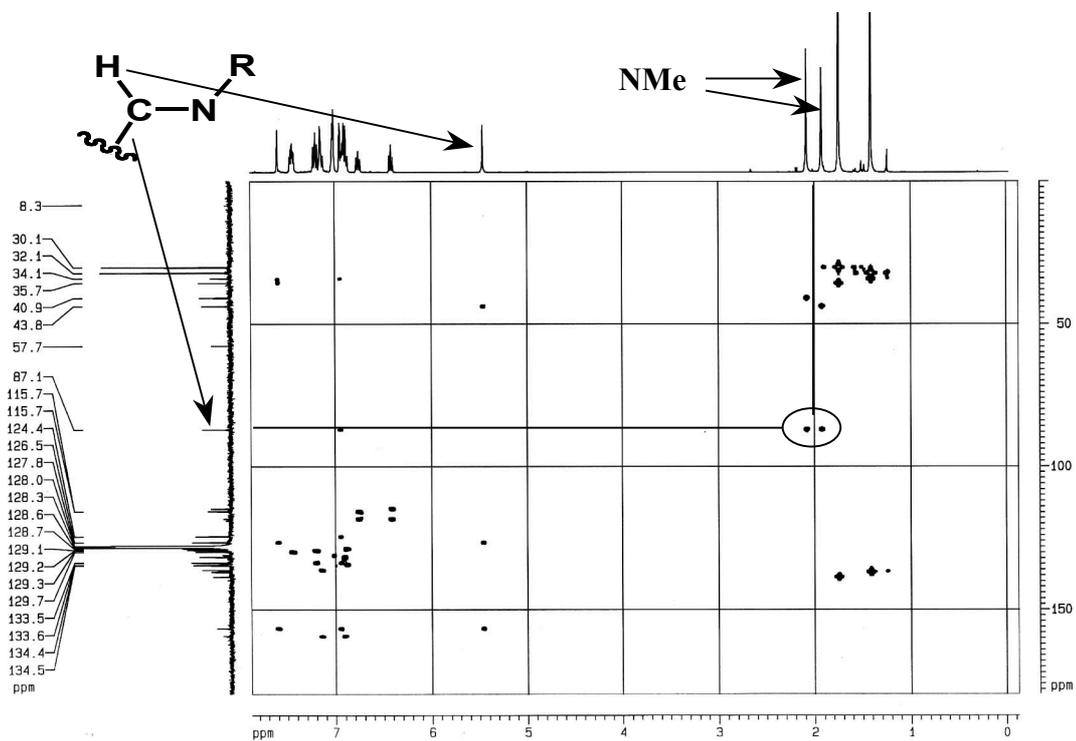


Fig. S1. 2D-HMBC NMR spectrum of **3a** (400 MHz, 298 K, C_6D_6) showing the coupling between the NMe_2 protons and the saturated carbon centre (formerly the imino- C_α).

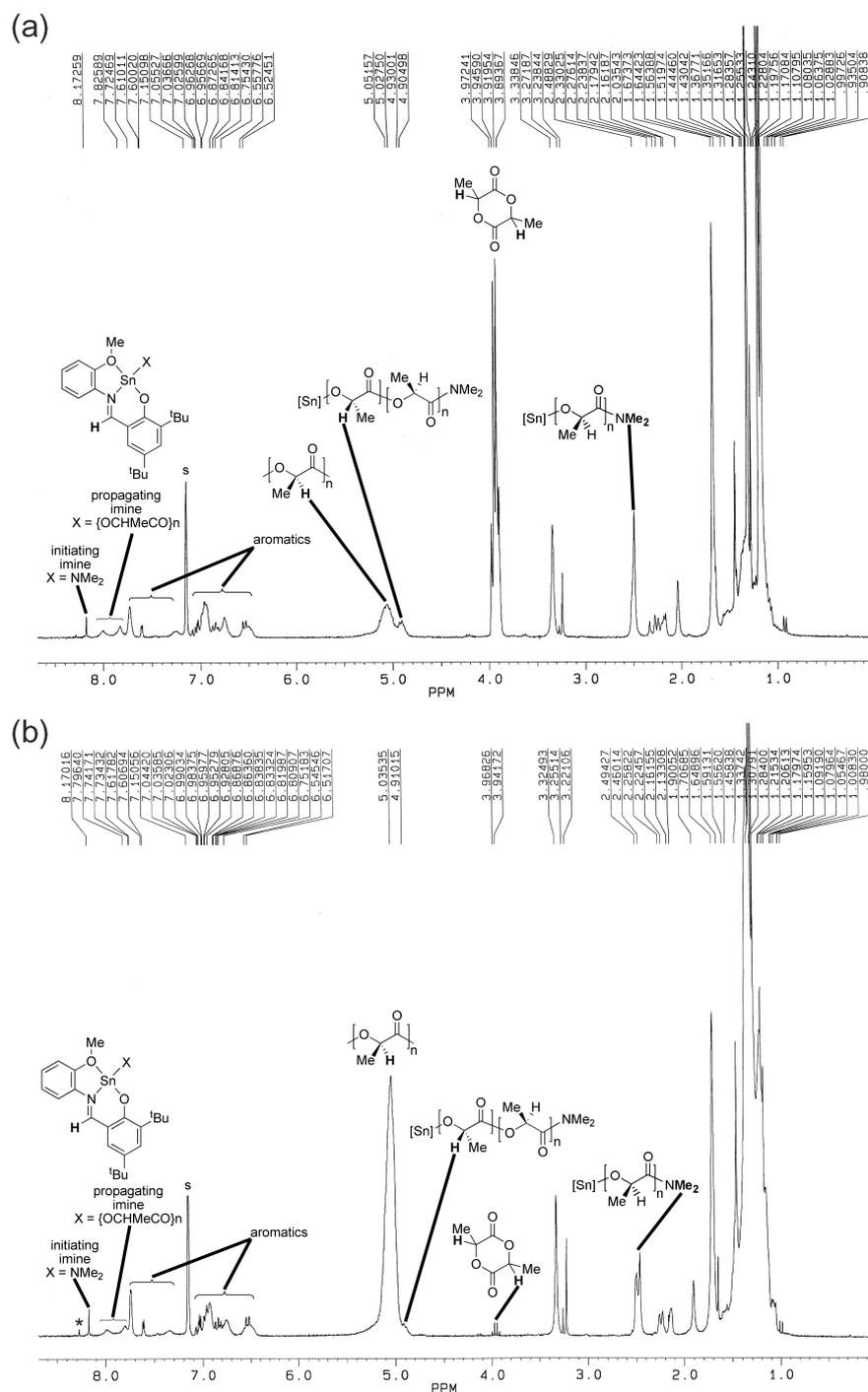


Fig. S2. ^1H NMR spectra (250MHz, 298 K, C_6D_6) of the reaction between **1a** and 10 equivalents *rac*-lactide after (a) 15 mins and (b) 40 hr at room temperature showing the regeneration of imine resonances (s = solvent, * = free ligand).

Fig. S3. $^1\text{H} / ^{13}\text{C}$ HETCOR spectrum (400MHz, 298K, C_6D_6) of the reaction between **1a** and *rac*-LA (10 eq.) showing correlation of the regenerated imine resonances (* = free ligand).

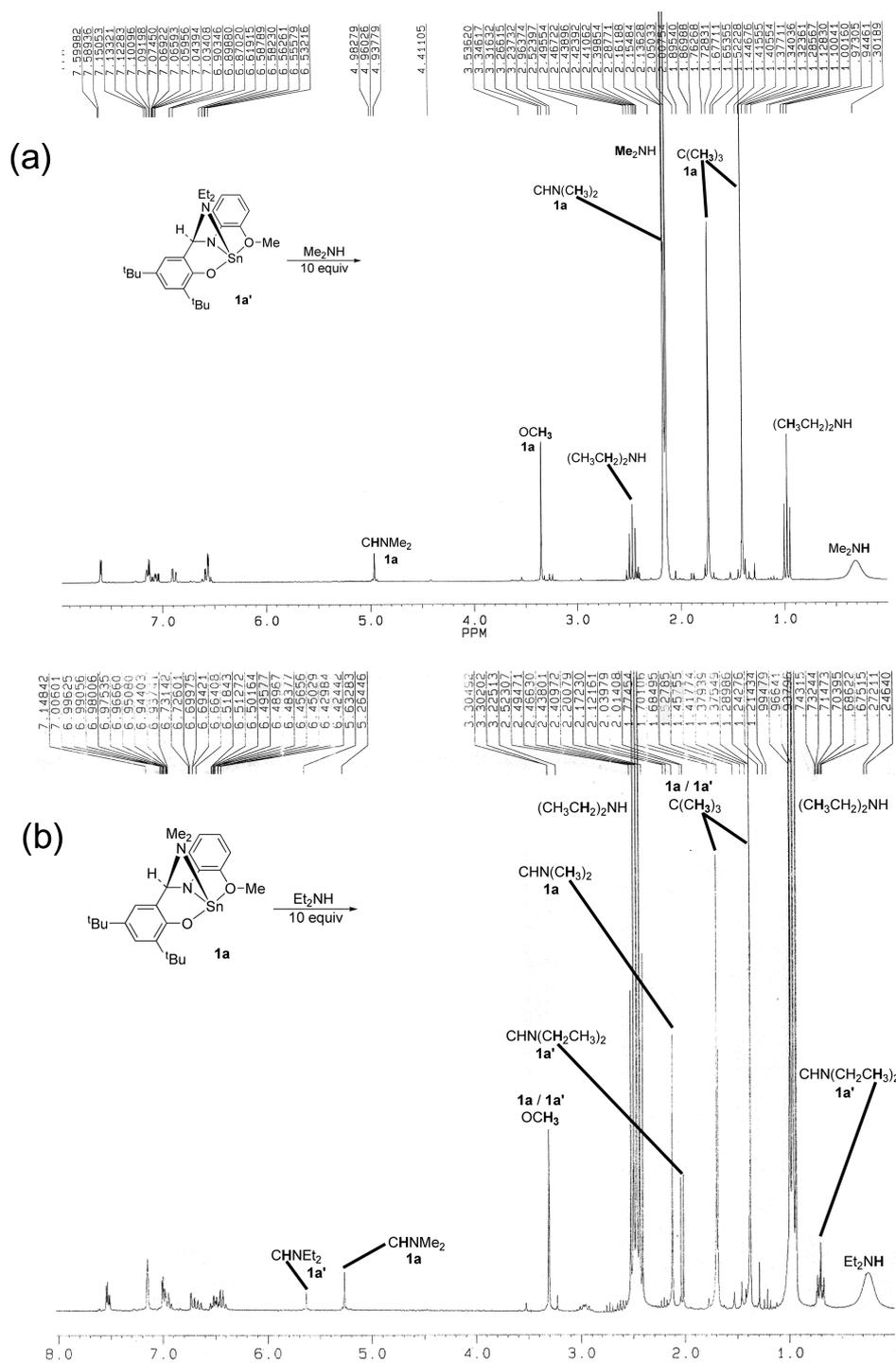


Fig. S4. ^1H NMR spectra (250MHz, 298K, C_6D_6) of the reactions between (a) **1a'** and 10 equivalents Me_2NH and (b) **1a** and 10 equivalents of Et_2NH .

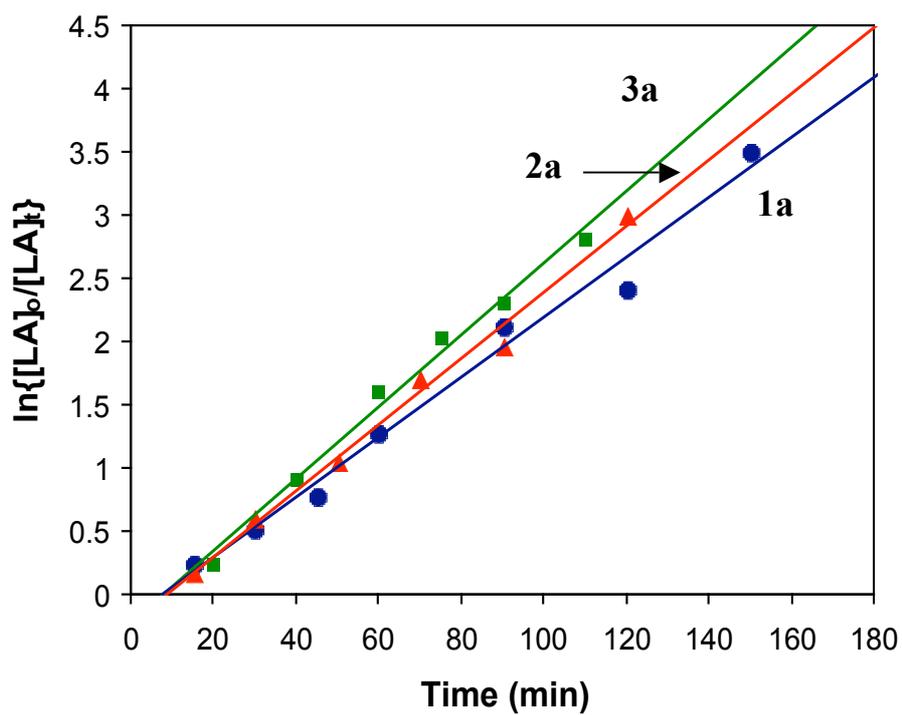


Fig. S5. Plots of $\ln\{[LA]_0/[LA]_t\}$ as a function of time for polymerization of *rac*-LA initiated by **1a-3a** ($[LA]/[Sn]=100$, $[LA]=0.28$ M/L, toluene, 60°C).

Table 1 Polymerization data for *rac*-lactide polymerizations initiated by **1a-3a**^a.

| Initiators | Time (min) | Conversion ^b (%) | M_n^c | PDI ^c | k_{app} (min ⁻¹) |
|------------|------------|-----------------------------|---------|------------------|--------------------------------|
| 1a | 15 | 22 | 4 500 | 1.09 | 0.0236 |
| | 45 | 58 | 12 800 | 1.09 | |
| | 60 | 71 | 14 900 | 1.12 | |
| | 120 | 91 | 18 600 | 1.29 | |
| 2a | 15 | 17 | 5 010 | 1.09 | 0.0263 |
| | 50 | 64 | 14 500 | 1.15 | |
| | 70 | 81 | 16 000 | 1.20 | |
| | 120 | 95 | 19 100 | 1.27 | |
| 3a | 20 | 22 | 7 200 | 1.06 | 0.0284 |
| | 40 | 60 | 11 100 | 1.18 | |
| | 60 | 80 | 15 700 | 1.19 | |
| | 110 | 94 | 20 400 | 1.25 | |

^a Polymerisations carried out at 60 °C in toluene; [LA]:[Sn] = 100:1; [LA] = 0.28 M. ^b Determined by ¹H-NMR, integration of methine resonances of LA and PLA (CDCl₃, 250 MHz). ^c Determined by gel permeation chromatography, calibrated with PS standards in CHCl₃.

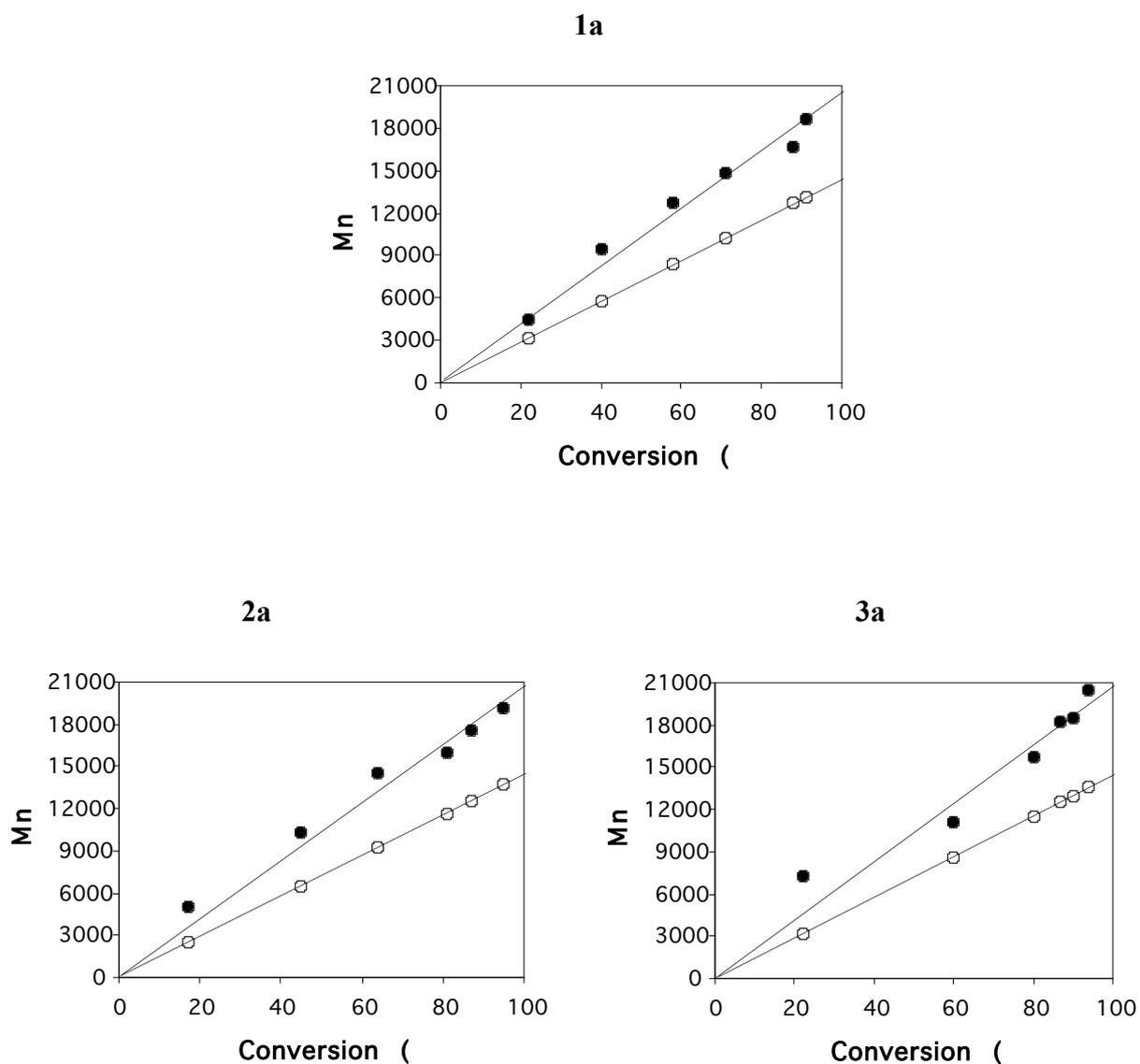


Fig. S6 Plots of PLA M_n as a function of conversion for polymerization of *rac*-LA initiated by **1a-3a** ($[LA]/[Sn]=100$, $[LA]=0.28$ M/L, toluene, 60 °C; \blacksquare = calculated M_n , \circ = observed M_n as measured using gel permeation chromatography).

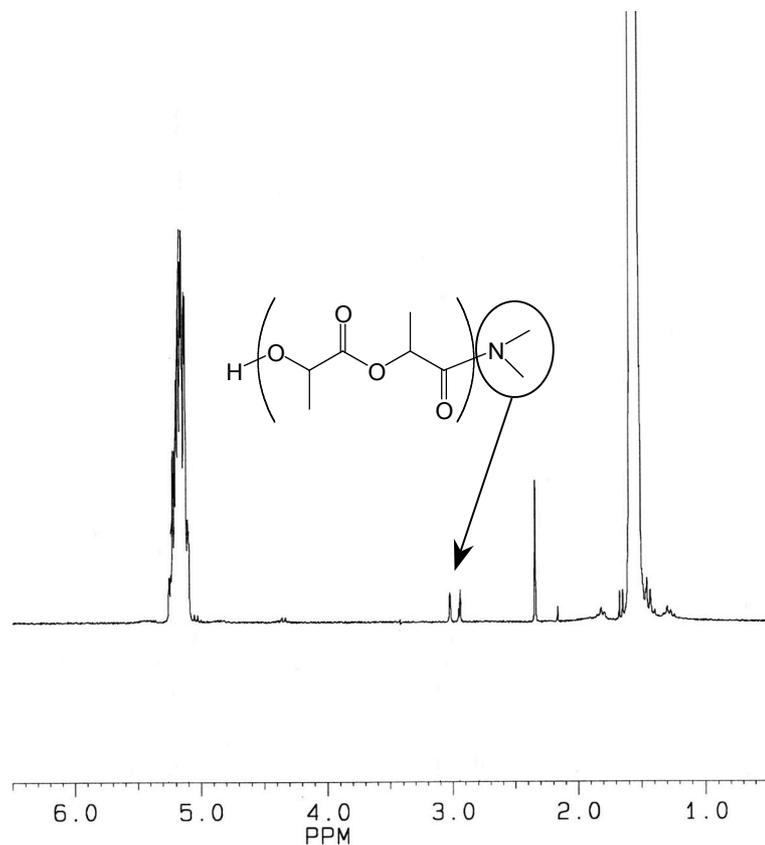


Fig. S7. ¹H-NMR spectrum (250 MHz, 298 K, CDCl₃) of PLA prepared from polymerization of *rac*-LA initiated by **3a** at 94 % conversion showing resonances for the amide chain termini ([LA]/[Sn]=100, [LA]=0.28 M/L, toluene, 60 °C).

Fig. S8. MALDI-TOF mass spectrum of PLA prepared from polymerization of *rac*-LA initiated by **3a** at 95% conversion ($[LA]/[Sn]=20$, $[LA]=0.28$ M/L, toluene, 60 °C; spectrum recorded in reflection mode using 2,5-dihydroxybenzoic acid (DHBA) as the matrix). The presence of methoxy-end capped signals (labelled B) arise from transesterification following termination of the polymerization by the addition of methanol.

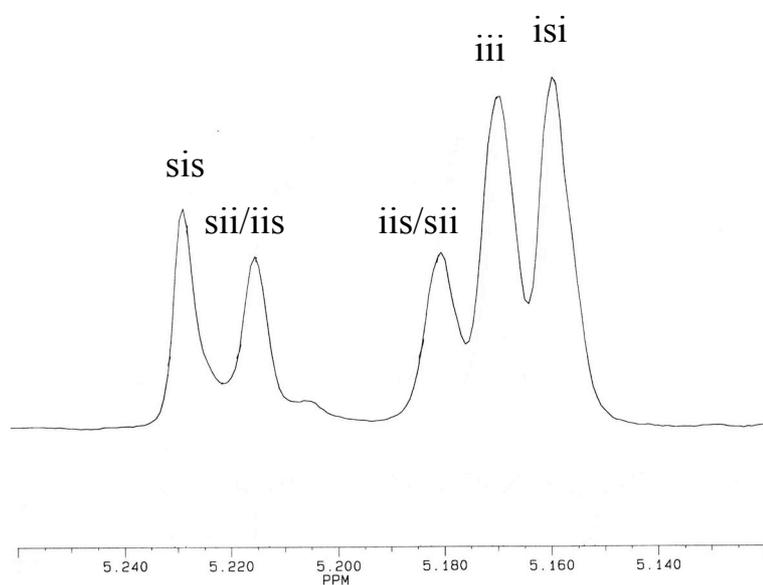


Fig. S9. Homonuclear decoupled ^1H -NMR spectrum (500 MHz, 298 K, CDCl_3) of the methine region of PLA prepared from polymerization of *rac*-LA initiated by **3a** at 94% conversion ($[\text{LA}]/[\text{Sn}]=100$, $[\text{LA}]=0.28$ M/L, toluene, 60 °C).

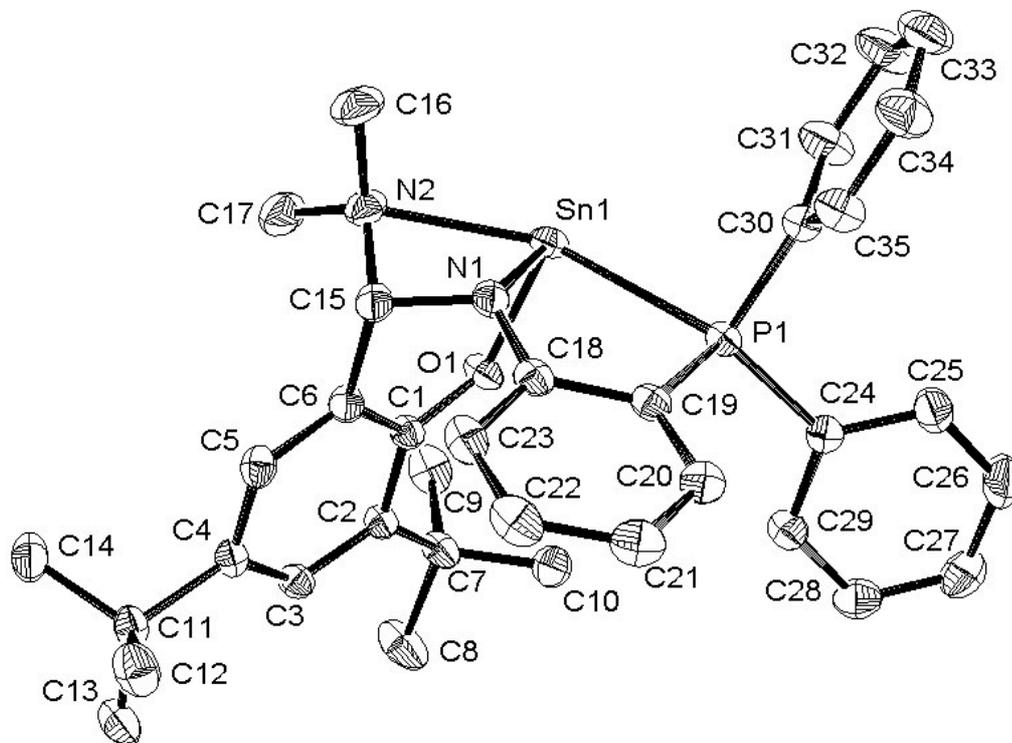


Fig. S10. Molecular structure of **3a** (70% probability ellipsoids). Hydrogen atoms omitted for clarity.

Crystal data and structure refinement for **3a**.

| | | |
|-----------------------------|-------------------------------------|----------------------------|
| Identification code | vg12 | |
| Chemical formula | $C_{35}H_{41}N_2OPSn$ | |
| Formula weight | 655.36 | |
| Temperature | 150(2) K | |
| Radiation, wavelength | MoK α , 0.71073 \AA | |
| Crystal system, space group | triclinic, $P\bar{1}$ | |
| Unit cell parameters | $a = 10.1598(3) \text{\AA}$ | $\alpha = 75.595(2)^\circ$ |
| | $b = 11.7014(4) \text{\AA}$ | $\beta = 78.587(2)^\circ$ |
| | $c = 15.3667(5) \text{\AA}$ | $\gamma = 67.167(2)^\circ$ |
| Cell volume | $1620.22(9) \text{\AA}^3$ | |
| Z | 2 | |
| Calculated density | 1.343 g/cm^3 | |

| | |
|-------------------------------------|--|
| Absorption coefficient μ | 0.867 mm ⁻¹ |
| F(000) | 676 |
| Crystal colour and size | Colourless, 0.50 × 0.35 × 0.22 mm ³ |
| Reflections for cell refinement | 12153 (θ range 2.19 to 28.95°) |
| Data collection method | Bruker SMART 1000 CCD diffractometer ω rotation with narrow frames |
| θ range for data collection | 1.92 to 28.95° |
| Index ranges | h -13 to 13, k -15 to 15, l -19 to 20 |
| Completeness to $\theta = 26.00$ _ | 99.1 % |
| Intensity decay | 0% |
| Reflections collected | 14462 |
| Independent reflections | 7502 ($R_{\text{int}} = 0.0088$) |
| Reflections with $F^2 > 2\sigma$ | 7104 |
| Absorption correction | semi-empirical from equivalents |
| Min. and max. transmission | 0.671 and 0.832 |
| Structure solution | direct methods |
| Refinement method | Full-matrix least-squares on F^2 |
| Weighting parameters a, b | 0.0233, 0.7493 |
| Data / restraints / parameters | 7502 / 0 / 369 |
| Final R indices [$F^2 > 2\sigma$] | R1 = 0.0190, wR2 = 0.0484 |
| R indices (all data) | R1 = 0.0206, wR2 = 0.0493 |
| Goodness-of-fit on F^2 | 1.044 |
| Largest and mean shift/su | 0.001 and 0.000 |
| Largest diff. peak and hole | 0.472 and -0.402 e _u ⁻³ |