

Aluminium salalen complexes based on 1,2-diaminocyclohexane and their exploitation for the polymerisation of *rac*-lactide

Stuart L. Hancock, Mary F. Mahon and Matthew D. Jones

Ligand Preparation:

tert-Butyl (2-aminocyclohexyl)carbamate: A solution of di-*tert*-butyl dicarbonate (9.61 g, 44.04 mmol) in CH₂Cl₂ (50 ml) was added dropwise to a cooled (0 °C) solution of *trans*-1,2-diaminocyclohexane (15.08 g, 70.47 mmol) in CH₂Cl₂ (50 ml) over a period of 30 mins while stirring. The solution was allowed to warm to room temperature and stirred overnight. CH₂Cl₂ (50 ml) and water (50 ml) were added to the resulting suspension to dissolve the precipitate and the organic phase was separated then the solvent was removed *in-vacuo*. The residue was dissolved in ethyl ether (50 ml) and water (50 ml) and the solution was acidified to pH 5 with 4M HCl, the mixture was separated and the aqueous layer was washed with ethyl ether (3 × 50 ml). 2M NaOH was added to the aqueous layer until pH 10.5 was reached, at which point the product was extracted with AcOEt (3 × 50 ml). The organic phase was washed with saturated brine (20 ml) and dried with anhydrous MgSO₄. After filtration the solvent was removed *in-vacuo* to yield a pale beige solid (7.17 g, 33.46 mmol, 47 %). ¹H NMR (CDCl₃) δ 1.00 – 1.30 (4H, m, CH₂), 1.38 (2H, s, NH₂), 1.41 (9H, s, ^tBu), 1.65 (2H, m, CH₂), 1.95 (2H, m, CH₂), 2.29 (1H, td, J = 10 Hz, J = 4.0 Hz, CH), 3.08 (1H, br, CH), 4.52 (1H, br, NH).

A. *tert*-Butyl (2-aminocyclohexyl)carbamate (2.00 g, 9.33 mmol) was added to a solution of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (2.18 g, 9.30 mmol) in MeOH (30 ml) / THF (30 ml) and stirred for 1 h. NaBH₄ (2.12 g, 56.03 mmol) was added slowly to the yellow solution and then stirred for 5 h until the solution became colourless. The reaction was quenched with water (10 ml) and the solvent partially removed *in-vacuo*. Water (50 ml) was then used to precipitate a white solid, which was then filtered and washed with water (3 × 50 ml). The resulting solid was dissolved in MeOH (30 ml) and formaldehyde solution (37 % in H₂O, 2.12 ml, 26.74 mmol) was slowly added and allowed to stir for 1 h. The solvent was removed *in-vacuo* and the residue was dissolved in MeOH (30 ml) / THF (30 ml) and cooled (0 °C), then NaBH₄ (2.12 g, 56.03 mmol) was slowly added and the solution was stirred for 2 h. The reaction was quenched with water (10 ml) and the solvent partially removed *in-vacuo*. Water (50 ml) was then used to precipitate a white solid, which was then filtered and washed with water (3 × 50 ml) and dried to yield a white solid (3.40 g, 7.61 mmol, 82 %). ¹H NMR (CDCl₃) δ 1.00 – 1.20 (2H, m, CH₂), 1.28 (9H, s, ^tBu), 1.43 (9H, s, ^tBu), 1.48 (9H, s, ^tBu), 1.60 – 2.10 (6H, m, CH₂), 2.29 (3H, s, CH₃), 2.36 (1H, m, CH), 3.62 (1H, m, CH), 3.75 (1H, m, NH), 3.79 (1H, d, J = 4.5 Hz, CH₂), 4.55 (1H, d, J = 10.0 Hz, CH₂), 6.81 (1H, d, J = 2.5 Hz, ArH), 7.21 (1H, d, J = 2.5 Hz, ArH), 11.10 (1H, br, ArOH). Deprotection of BOC. (2.40 g, 5.37 mmol) was dissolved in methanol (30 ml) and 3M HCl (30 ml) then heated to 60 °C and allowed to stir (16 h). The mixture was neutralised with 3M NaOH and the white precipitate was extracted with AcOEt (4 × 20 ml). The organic phase was washed with saturated brine (20 ml) then dried with MgSO₄, the solid was removed by filtration and the solvent removed *in-vacuo* to yield an oily residue which was used

without further purification (1.80 g, 5.19 mmol, 97 %). ^1H NMR (CDCl_3) δ 1.10 – 1.3 (4H, m, CH_2), 1.28 (9H, s, $t\text{Bu}$), 1.41 (9H, s, $t\text{Bu}$), 1.65 – 2.05 (4H, m, CH_2), 2.25 (3H, s, CH_3), 2.35 (1H, m, CH), 2.79 (1H, m, CH), 3.72 (1H, d, $J = 13.5$ Hz, CH_2), 3.86 (1H, d, $J = 13.5$ Hz, CH_2), 4.12 (1H, q, $J = 7.5$ Hz, NH) 3.50 – 4.00 (3H, br, NH_2 , ArOH), 6.83 (1H, d, $J = 2.5$ Hz, ArH), 7.21 (1H, d, $J = 2.5$ Hz, ArH).

B *tert*-Butyl (2-aminocyclohexyl)carbamate (2.43 g, 11.34 mmol) was added to a solution of 2-hydroxybenzaldehyde (1.39 g, 11.38 mmol) in MeOH (30 ml) / THF (30 ml) and stirred for 1 h. NaBH_4 (1.29 g, 34.10 mmol) was added slowly to the yellow solution and then stirred for 5 h until the solution became colourless. The reaction was quenched with water (10 ml) and the solvent partially removed *in-vacuo*. Water (50 ml) was then used to precipitate a white solid, which was then filtered and washed with water (3×50 ml). The resulting solid was dissolved in MeOH (30 ml) and formaldehyde solution (37 % in H_2O , 2.58 ml, 31.79 mmol) was slowly added and allowed to stir for 1 h. The solvent was removed *in-vacuo* and the residue was dissolved in MeOH (30 ml) / THF (30 ml) and cooled (0°C), then NaBH_4 (2.00 g, 52.87 mmol) was slowly added and the solution was stirred for 2 h. The reaction was quenched with water (10 ml) and the solvent partially removed *in-vacuo*. Water (50 ml) was then used to precipitate a white solid, which was then filtered and washed with water (3×50 ml) and dried to yield a white solid (3.33 g, 9.96 mmol, 81 %). ^1H NMR (CDCl_3) δ 1.00 – 1.30 (4H, m, CH_2), 1.41 (9H, s, $t\text{Bu}$), 1.60 – 2.05 (4H, m, CH_2), 2.21 (3H, s, CH_3), 2.34 (1H, td, $J = 11.0$ Hz, $J = 3.5$ Hz, CH), 3.60 (1H, m, CH), 3.75 (1H, q, $J = 14.0$ Hz, CH_2), 4.40 (1H, br, NH), 6.71 (2H, m, ArH), 6.88 (1H, dd, $J = 7.5$ Hz, $J = 1.5$ Hz, ArH), 7.08 (1H, td, $J = 7.5$ Hz, $J = 1.5$ Hz, ArH), 10.88 (1H, br, ArOH). Deprotection of BOC (3.25g, 9.72 mmol) was dissolved in methanol (30 ml) and 3M HCl (30 ml) then heated to 60°C and allowed to stir (16 h). The mixture was neutralised with 3M NaOH and the white precipitate was extracted with AcOEt (4×30 ml). The organic phase was washed with saturated brine (20 ml) then dried with MgSO_4 , the solid was removed by filtration and the solvent removed *in-vacuo* to yield a white solid (1.85, 7.89 mmol, 81 %). ^1H NMR (CDCl_3) δ 1.10 – 1.35 (4H, m, CH_2), 1.65 – 2.05 (4H, m, CH_2), 2.22 (3H, s, CH_3), 2.34 (1H, td, $J = 10.0$ Hz, $J = 3.5$ Hz, CH), 2.78 (1H, td, $J = 10.0$ Hz, $J = 4.5$ Hz, CH), 3.61 (1H, d, $J = 13.5$ Hz, CH_2), 3.89 (1H, d, $J = 13.5$ Hz, CH_2), 4.39 (3H, br, NH_2 , ArOH), 6.76 (1H, td, $J = 7.5$ Hz, $J = 1.0$ Hz, ArH), 6.82 (1H, dd, $J = 8.0$ Hz, $J = 1.0$ Hz, ArH), 6.97 (1H, dd, $J = 7.5$ Hz, $J = 1.5$ Hz, ArH), 7.15 (1H, td, $J = 7.5$ Hz, $J = 1.5$ Hz, ArH).

C *tert*-Butyl (2-aminocyclohexyl)carbamate (3.00 g, 14.00 mmol) was added to a solution of 3,5-dichloro-2-hydroxybenzaldehyde (2.67 g, 13.98 mmol) in MeOH (30 ml) / THF (30 ml) and stirred for 1 h. NaBH_4 (1.60 g, 42.29 mmol) was added slowly to the yellow solution and then stirred for 16 h until the solution became colourless. The reaction was quenched with water (10 ml) and the solvent partially removed *in-vacuo*. Water (50 ml) was then used to precipitate a white solid, which was then filtered and washed with water (3×50 ml). The resulting solid was dissolved in MeOH (30 ml) and formaldehyde solution (37 % in H_2O , 3.18 ml, 39.18 mmol) was slowly added and allowed to stir for 1 h. The solvent was removed *in-vacuo* and the residue was dissolved in MeOH (30 ml) / THF (30 ml) and cooled (0°C), then NaBH_4 (2.50 g, 66.09 mmol) was slowly added and the solution was stirred for 2 h. The reaction was quenched with water (10 ml) and the solvent partially removed *in-vacuo*. Water (50 ml) was then used to precipitate a white solid, which was then

filtered and washed with water (3 × 50 ml) and dried to yield a white solid (4.30 g, 10.66 mmol, 76 %). ¹H NMR (CDCl₃) δ 1.10 – 1.35 (4H, m, CH₂), 1.48 (9H, s, ^tBu), 1.70 – 2.10 (4H, m, CH₂), 2.27 (3H, s, CH₃), 2.40 (1H, td, J = 11.0 Hz, J = 3.5 Hz, CH), 3.69 (1H, m, CH), 3.71 (1H, d, J = 14.0 Hz, CH₂), 3.87 (1H, d, J = 14.0 Hz, CH₂), 4.48 (1H, d, J = 10.0 Hz, NH), 6.82 (1H, d, J = 2.5 Hz, ArH), 7.22 (1H, d, J = 2.5 Hz, ArH), 9.87 (1H, br, ArOH). Deprotection: (4.20 g, 10.41 mmol) was dissolved in methanol (30 ml) and 3M HCl (30 ml) then heated to 60 °C and allowed to stir (16 h). The mixture was neutralised with 3M NaOH and the white precipitate was extracted with AcOEt (4 × 30 ml). The organic phase was washed with saturated brine (20 ml) then dried with MgSO₄, the solid was removed by filtration and the solvent removed *in-vacuo* to yield a white solid (2.66, 8.77 mmol, 84 %). ¹H NMR (CDCl₃) δ 1.00 – 1.25 (4H, m, CH₂), 1.61 (1H, br, CH₂), 1.71 (1H, br, CH₂), 1.85 (2H, br, CH₂), 2.21 (3H, s, CH₃), 2.25 (1H, br, CH), 2.84 (1H, br, CH), 3.08 (1H, d, J = 12.0 Hz, CH₂), 3.79 (1H, d, J = 12.5 Hz, CH₂), 4.92 (3H, br, NH₂, ArOH), 6.80 (1H, d, J = 2.5 Hz, ArH), 7.14 (1H, d, J = 2.5 Hz, ArH).

1H₂. A (1.00 g, 2.24 mmol) was dissolved in methanol (20 ml) and 3M HCl (20 ml) then heated to 60 °C and allowed to stir (16 h). The mixture was neutralised with 3M NaOH and the white precipitate was extracted with AcOEt (15 ml × 4). The organic phase was washed with saturated brine (10 ml) then dried with MgSO₄, the solid was removed by filtration and the solvent removed *in-vacuo*. The oily residue was dissolved in MeOH (30 ml) and 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (0.52 g, 2.24 mmol) was added. The solution was stirred for 2 h then the solid was filtered and further dried *in-vacuo* to yield a yellow solid (0.50 g, 0.89 mmol, 40 %). ¹H NMR (CDCl₃): δ 1.15 (9H, s, ^tBu), 1.28 (9H, s, ^tBu), 1.32 (9H, s, ^tBu), 1.35 – 1.45 (3H, m, ring-CH₂), 1.51 (9H, s, ^tBu), 1.63 – 2.07 (5H, m, ring-CH₂), 2.26 (3H, s, CH₃), 3.00 (1H, m, ring-CH), 3.33 (1H, m, ring-CH), 3.75 (1H, d, J = 13.0 Hz, CH₂), 3.91 (1H, d, J = 13.0 Hz, CH₂), 6.83(1H, d, J = 2.5 Hz, ArH), 7.06(1H, d, J = 2.5 Hz, ArH), 7.14(1H, d, J = 2.5 Hz, ArH), 7.41(1H, d, J = 2.5 Hz, ArH), 8.40 (1H, s, CH), 10.61 (1H, br, OH), 13.59 (1H, s, OH). ¹³C{¹H} NMR (CDCl₃): δ 24.8 (CH₂), 25.3 (CH₂), 29.5 (CH₃), 29.8 (CH₃), 31.7 (CH₃), 31.9 (CH₃), 34.2 (C), 34.9 (C), 35.2 (CH₂), 35.4 (CH₂), 66.6 (CH), 70.3 (CH), 118.1 (Ar), 121.0 (Ar), 122.5 (ArH), 123.3 (ArH), 125.8 (ArH), 126.9(ArH), 135.4 (Ar), 136.6 (Ar), 139.8 (Ar), 139.8 (Ar), 154.7 (Ar), 158.2 (Ar), 165.8 (CH) Calc. m/z [C₃₇H₅₈N₂O₂ + Na]⁺ 585.4396. Found 585.4398

2H₂. A (1.00 g, 2.89 mmol) was dissolved in MeOH (30 ml) and 2-hydroxybenzaldehyde (0.31 ml, 2.91 mmol) was added. The solution was stirred for 2 h then the solid was filtered and further dried *in-vacuo* to yield a yellow solid (0.98 g, 2.17 mmol, 75 %). ¹H NMR (CDCl₃): δ 1.11 (9H, s, ^tBu), 1.25 (9H, s, ^tBu), 1.31 – 1.53 (3H, m, ring-CH₂), 1.63 – 2.08 (5H, m, ring-CH₂), 2.20 (3H, s, CH₃), 2.97 (1H, m, ring-CH), 3.36 (1H, m, ring-CH), 3.70 (1H, br, CH₂), 3.80 (1H, d, J = 13.0 Hz, CH₂), 6.77 (1H, d, J = 2.0 Hz, ArH), 6.86 (1H, t, J = 7.5 Hz, ArH), 6.99 (1H, d, J = 8.0 Hz, ArH), 7.11 (1H, br, ArH), 7.23 (1H, d, J = 7.5 Hz, ArH), 7.42(1H, t of d, J = 8.0 Hz, , J = 2.0 Hz, ArH), 8.38 (1H, s, CH), 10.62 (1H, br, OH), 13.15 (1H, s, OH). ¹³C{¹H} NMR (CDCl₃): δ 23.1 (CH₂), 24.6 (CH₂), 25.1 (CH₂), 29.3 (CH₃), 31.7 (CH₃), 34.1 (C), 34.6 (C), 34.9 (CH₂), 58.5 (CH₂), 67.2 (CH), 70.1 (CH), 117.0 (ArH), 118.4 (ArH), 119.1 (Ar), 120.7 (Ar), 122.5 (ArH), 123.1 (ArH), 131.3 (ArH), 132.1 (ArH), 135.4 (Ar), 139.8 (Ar), 154.6 (Ar-O), 161.2 (Ar-O), 164.7 (CH). Calc. m/z [C₂₉H₄₂N₂O₂ + Na]⁺ 473.3144. Found 473.3166

3H₂. A (0.80 g, 2.31 mmol) was dissolved in MeOH (30 ml) and 3,5-dichloro-2-hydroxybenzaldehyde (0.44 g, 2.30 mmol) was added. The solution was stirred for 2 h then the solid was filtered and further dried *in-vacuo* to yield a yellow solid (0.77 g, 1.48 mmol, 64 %). ¹H NMR (CDCl₃): δ 1.10 (9H, s, ^tBu), 1.25 (9H, s, ^tBu), 1.28 – 1.50 (3H, m, ring-CH₂), 1.64 – 2.08 (5H, m, ring-CH₂), 2.18 (3H, s, CH₃), 2.94 (1H, m, ring-CH), 3.36 (1H, m, ring-CH), 3.70 (1H, d, J = 13.0 Hz, CH₂), 3.81 (1H, d, J = 13.0 Hz, CH₂), 6.76 (1H, d, J = 2.0 Hz, ArH), 7.10 (1H, br, ArH), 7.14 (1H, d, J = 2.0 Hz, ArH), 7.42 (1H, d, J = 2.5 Hz, ArH), 8.29 (1H, s, CH), 10.50 (1H, br, OH), 14.20 (1H, s, OH). ¹³C{¹H} NMR (CDCl₃): δ 22.5 (CH₂), 24.5 (CH₂), 25.1 (CH₂), 29.3 (CH₃), 31.8 (CH₃), 34.2 (C), 34.6 (C), 34.7 (CH₃), 67.8 (CH), 69.5 (CH), 120.2 (Ar), 120.4 (Ar), 122.7 (Ar), 122.8 (Ar), 122.8 (ArH), 123.2 (ArH), 129.2 (ArH), 132.0 (ArH), 135.5 (Ar), 140.2 (Ar), 154.5 (Ar-O), 156.6 (Ar-O), 163.2 (CH). Calc. m/z [C₂₉H₄₀Cl₂N₂O₂ + H]⁺ 519.2545. Found 519.2564

4H₂. B (0.60 g, 2.56 mmol) was dissolved in MeOH (30 ml) and 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (0.60 g, 2.56 mmol) was added. The solution was stirred for 2 h then the solid was filtered and further dried *in-vacuo* to yield a yellow solid (0.92 g, 2.04 mmol, 80 %). ¹H NMR (CDCl₃): δ 1.20 – 1.44 (3H, m, ring-CH₂), δ 1.33 (9H, s, ^tBu), 1.49 (9H, s, ^tBu), 1.60 – 2.06 (5H, m, ring-CH₂), 2.30 (3H, s, CH₃), 3.03 (1H, m, ring-CH), 3.36 (1H, td, J = 10.5 Hz, J = 4.5, Hz, ring-CH), 3.92 (2H, m, CH₂), 6.69 – 6.77 (2H, m, ArH), 6.94 (1H, m, ArH), 7.09 (1H, d, J = 2.5 Hz, ArH), 7.13 (1H, m, ArH), 7.41 (1H, d, J = 2.5 Hz, ArH), 8.42 (1H, s, CH), 9.6 – 11.8 (1H, br, OH), 12.1 – 14.2 (1H, br, OH). ¹³C{¹H} NMR (CDCl₃): δ 24.7 (CH₂), 25.3 (CH₂), 25.5 (CH₂), 29.6 (CH₃), 31.7 (CH₃), 34.3 (C), 35.2 (C), 35.6 (CH₃), 35.7 (CH₂), 58.7 (CH₂), 66.1 (CH), 70.1 (CH), 116.5 (ArH), 118.0 (Ar), 119.7 (ArH), 121.9 (Ar), 126.1 (ArH), 127.3 (ArH), 128.8 (ArH), 128.8 (ArH), 136.7 (Ar), 140.1 (Ar), 158.2 (Ar-O), 158.4 (Ar-O), 165.8 (CH). Calc. m/z [C₂₉H₄₂N₂O₂ + Na]⁺ 473.3144. Found 473.3154

5H₂. B (0.60 g, 2.56 mmol) was dissolved in MeOH (30 ml) and 2-hydroxybenzaldehyde (0.31 g, 2.54 mmol) was added. The solution was stirred for 2 h then the solid was filtered and further dried *in-vacuo* to yield a yellow solid (0.70 g, 2.07 mmol, 81 %). ¹H NMR (CDCl₃): δ 1.19 – 1.43 (3H, m, ring-CH₂), 1.48 – 1.63 (1H, m, ring-CH₂), 1.68 (1H, br, ring-CH₂), 1.72 (1H, br, ring-CH₂), 1.80 (1H, m, ring-CH₂), 1.92 (1H, m, ring-CH₂), 2.16 (3H, s, CH₃), 2.88 (1H, m, ring-CH), 3.25 (1H, td, J = 10.5 Hz, J = 4.5, Hz, ring-CH), 3.61 (1H, d, J = 13.5 Hz, CH₂), 3.70 (1H, d, J = 13.5 Hz, CH₂), 6.60 – 6.68 (2H, m, ArH), 6.78 – 6.88 (2H, m, ArH), 6.94 (1H, d, J = 8.0 Hz, ArH), 7.02 (1H, td, J = 7.5 Hz, J = 2.0 Hz, ArH), 7.18 (1H, m, ArH), 7.25 (1H, m, ArH), 8.31 (1H, s, CH), 9.5 – 14.0 (2H, br, OH). ¹³C{¹H} NMR (CDCl₃): δ 23.8 (CH₂), 24.7 (CH₂), 25.1 (CH₂), 35.6 (CH₂), 35.6 (CH₃), 58.1 (CH₂), 66.5 (CH), 70.0 (CH), 116.3 (ArH), 117.2 (ArH), 118.7 (ArH), 118.8 (ArH), 119.0 (Ar), 121.8 (Ar), 128.5 (ArH), 128.6 (ArH), 131.5 (ArH), 132.4 (ArH), 158.3 (Ar-O), 161.2 (Ar-O), 164.7 (CH). Calc. m/z [C₂₁H₂₆N₂O₂ + Na]⁺ 361.1892. Found 361.1895

6H₂. B (0.60 g, 2.56 mmol) was dissolved in MeOH (30 ml) and 3,5-dichloro-2-hydroxybenzaldehyde (0.49 g, 2.57 mmol) was added. The solution was stirred for 2 h then the solid was filtered and further dried *in-vacuo* to yield a yellow solid (0.79 g, 1.91 mmol, 75 %). ¹H NMR (CDCl₃): δ 1.25 – 1.50 (3H, m, ring-CH₂), 1.62 (1H, m, ring-CH₂), 1.70 (2H, br, ring-CH₂), 1.90 (1H, br, ring-CH₂), 2.02 (1H, m, ring-

CH₂), 2.24 (3H, s, CH₃), 2.92 (1H, m, ring-CH), 3.38 (1H, td, J = 10.5 Hz, J = 4.5, Hz, ring-CH), 3.72 (1H, d, J = 13.5 Hz, CH₂), 3.87 (1H, d, J = 13.5 Hz, CH₂), 6.63 – 6.77 (2H, m, ArH), 6.92 (1H, d, J = 7.0 Hz, ArH), 7.1 (1H, td, J = 8.0 Hz, J = 1.5 Hz, ArH), 7.17 (1H, d, J = 2.5 Hz, ArH), 7.41 (1H, d, J = 2.5 Hz, ArH), 8.28 (1H, s, CH), 9.0 – 11.5 (1H, br, OH), 12.5 – 15.0 (1H, br, OH). ¹³C{¹H} NMR (CDCl₃): δ 23.0 (CH₂), 24.5 (CH₂), 25.0 (CH₂), 35.2 (CH₂), 36.3 (CH₃), 57.4 (CH₂), 66.7 (CH), 69.2 (CH), 116.4 (ArH), 118.9 (ArH), 119.9 (Ar), 121.5 (Ar), 122.7 (Ar), 122.8 (Ar), 128.6 (ArH), 128.8 (ArH), 129.3 (ArH), 132.3 (ArH), 156.6 (Ar-O), 158.0 (Ar-O), 163.3 (CH). Calc. m/z [C₂₁H₂₄Cl₂N₂O₂ + Na]⁺ 429.1113. Found 429.1119

7H₂ C (0.75 g, 2.47 mmol) was dissolved in MeOH (30 ml) and 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (0.58 g, 2.48 mmol) was added. The solution was stirred for 2 h then the solid was filtered and further dried *in-vacuo* to yield a yellow solid (1.08 g, 2.08 mmol, 84 %). ¹H NMR (CDCl₃): δ 1.24 – 1.44 (3H, m, ring-CH₂), δ 1.32 (9H, s, ^tBu), 1.48 (9H, s, ^tBu), 1.60 – 2.00 (5H, m, ring-CH₂), 2.28 (3H, s, CH₃), 3.01 (1H, m, ring-CH), 3.36 (1H, td, J = 10.5 Hz, J = 4.5, Hz, ring-CH), 3.85 (1H, d, J = 14.5 Hz, CH₂), 3.95 (1H, d, J = 14.5 Hz, CH₂), 6.83 (1H, d, J = 2.5 Hz, ArH), 7.09 (1H, d, J = 2.5 Hz, ArH), 7.19 (1H, d, J = 2.5 Hz, ArH), 7.42 (1H, d, J = 2.5 Hz, ArH), 8.43 (1H, s, CH), 11.4 – 14.7 (1H, br, OH). ¹³C{¹H} NMR (CDCl₃): δ 24.7 (CH₂), 25.2 (CH₂), 29.6 (CH₃), 31.6 (CH₃), 34.3 (C), 35.2 (C), 35.3 (CH₃), 35.7 (CH₂), 59.5 (CH₂), 66.5 (CH), 70.1 (CH), 117.9 (Ar), 121.5 (Ar), 123.1 (Ar), 124.0 (Ar), 126.1 (ArH), 126.8 (ArH), 127.5 (ArH), 128.6 (ArH), 137.1 (Ar), 140.3 (Ar), 153.3 (Ar-O), 158.1 (Ar-O), 166.1 (CH). Calc. m/z [C₂₉H₄₀Cl₂N₂O₂ + Na]⁺ 541.2365. Found 541.2393

8H₂. C (0.75 g, 2.47 mmol) was dissolved in MeOH (30 ml) and 2-hydroxybenzaldehyde (0.30 g, 2.46 mmol) was added. The solution was stirred for 2 h then the solid was filtered and further dried *in-vacuo* to yield a yellow solid (0.63 g, 1.55 mmol, 63 %). ¹H NMR (CDCl₃): δ 1.23 – 2.05 (8H, m, ring-CH₂), 2.27 (3H, s, CH₃), 2.97 (1H, m, ring-CH), 3.35 (1H, td, J = 10.5 Hz, J = 4.5, Hz, ring-CH), 3.79 (1H, d, J = 14.5 Hz, CH₂), 3.90 (1H, d, J = 14.5 Hz, CH₂), 6.80 (1H, d, J = 2.5 Hz, ArH), 6.91 (1H, td, J = 7.5 Hz, J = 1.0 Hz, ArH), 7.01 (1H, m, ArH), 7.18 (1H, d, J = 2.5 Hz, ArH), 7.26 (1H, dd, J = 7.5 Hz, J = 1.5 Hz, ArH), 7.35 (1H, ddd, J = 8.5 Hz, J = 7.5 Hz, J = 1.5 Hz, ArH), 8.41 (1H, s, CH), 10.5 – 14.0 (2H, br, OH). ¹³C{¹H} NMR (CDCl₃): δ 24.5 (CH₂), 25.1 (CH₂), 25.7 (CH₂), 35.4 (CH₂), 35.7 (CH₃), 58.6 (CH₂), 66.9 (CH), 70.0 (CH), 117.2 (ArH), 118.8 (ArH), 118.8 (Ar), 121.6 (Ar), 123.1 (Ar), 123.9 (Ar), 126.7 (ArH), 128.6 (ArH), 131.6 (ArH), 132.7 (ArH), 153.1 (Ar-O), 161.2 (Ar-O), 165.0 (CH). Calc. m/z [C₂₁H₂₄Cl₂N₂O₂ + Na]⁺ 429.1113. Found 429.1102

9H₂. C (0.75 g, 2.47 mmol) was dissolved in MeOH (30 ml) and 3,5-dichloro-2-hydroxybenzaldehyde (0.46 g, 2.46 mmol) was added. The solution was stirred for 2 h then the solid was filtered and further dried *in-vacuo* to yield a yellow solid (0.94 g, 1.97 mmol, 80 %). ¹H NMR (CDCl₃): δ 1.23 – 2.06 (8H, m, ring-CH₂), 2.25 (3H, s, CH₃), 2.91 (1H, m, ring-CH), 3.37 (1H, td, J = 10.5 Hz, 4.5 Hz, ring CH), 3.73 (1H, d, J = 14.5 Hz, CH₂), 3.86 (1H, d, J = 14.5 Hz, CH₂), 6.80 (1H, d, J = 2.5 Hz, ArH), 7.18 (1H, m, ArH), 7.42 (1H, d, J = 2.5 Hz, ArH), 8.30 (1H, s, CH), 11.0 – 14.5 (1H, br, OH). ¹³C{¹H} NMR (CDCl₃): δ 24.0 (CH₂), 24.4 (CH₂), 25.0 (CH₂), 35.1 (CH₂), 36.1 (CH₃), 57.8 (CH₂), 67.0 (CH), 69.4 (CH), 119.8 (Ar), 121.8 (Ar), 122.8 (Ar), 123.0 (Ar), 123.3 (Ar), 123.6 (Ar), 126.6 (ArH), 128.8 (ArH), 129.3

(ArH), 132.4 (ArH), 152.9 (Ar-O), 156.3 (Ar-O), 163.5 (CH). Calc. m/z $[\text{C}_{21}\text{H}_{22}\text{Cl}_4\text{N}_2\text{O}_2 + \text{Na}]^+$ 497.0333. Found 497.0350

Chiral version *R,R*-1H₂

tert-butyl (1*R*,2*R*)-2-aminocyclohexyl)carbamate (0.375 g, 1.75 mmol) was added to a solution of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (0.41 g, 1.75 mmol) in MeOH (15 ml) / THF (15 ml) and stirred for 1 h. NaBH₄ (0.30 g, 9.99 mmol) was added slowly to the yellow solution and then stirred for 5 h until the solution became colourless. The reaction was quenched with water (10 ml) and the solvent partially removed *in-vacuo*. Water (30 ml) was then used to precipitate a white solid, which was then filtered and washed with water (3 × 30 ml). The resulting solid was dissolved in MeOH (30 ml) and formaldehyde solution (37 % in H₂O, 0.40 ml, 4.93 mmol) was slowly added and allowed to stir for 1 h. The solvent was removed *in-vacuo* and the residue was dissolved in MeOH (15 ml) / THF (15 ml) and cooled (0 °C), then NaBH₄ (0.30 g, 9.99 mmol) was slowly added and the solution was stirred for 16 h. The reaction was quenched with water (10 ml) and the solvent partially removed *in-vacuo*. Water (30 ml) was then used to precipitate a white solid, which was then filtered and washed with water (3 × 30 ml) and dried to yield a white solid. The white solid was dissolved in methanol (20 ml) and 3M HCl (20 ml) then heated to 60 °C and allowed to stir (16 h). The mixture was neutralised with 3M NaOH and the white precipitate was extracted with AcOEt (10 ml × 4). The organic phase was washed with saturated brine (10 ml) then dried with MgSO₄, the solid was removed by filtration and the solvent removed *in-vacuo*. The residue was dissolved in MeOH (20 ml) and 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (0.41 g, 1.75 mmol) was added. The solution was stirred for 16 h then the solid was filtered and further dried *in-vacuo* to yield a pale yellow solid (0.49 g, 0.87 mmol, 50 %). ¹H NMR (CDCl₃): δ 1.12 (9H, s, ^tBu), 1.25 (9H, s, ^tBu), 1.29 (9H, s, ^tBu), 1.35 – 1.45 (3H, m, ring-CH₂), 1.48 (9H, s, ^tBu), 1.63 – 2.07 (5H, m, ring-CH₂), 2.23 (3H, s, CH₃), 2.98 (1H, m, ring-CH), 3.31 (1H, m, ring-CH), 3.72 (1H, d, J = 12.0 Hz, CH₂), 3.88 (1H, d, J = 12.0 Hz, CH₂), 6.80 (1H, d, J = 2.5 Hz, ArH), 7.03 (1H, d, J = 2.5 Hz, ArH), 7.11 (1H, d, J = 2.5 Hz, ArH), 7.38 (1H, d, J = 2.5 Hz, ArH), 8.38 (1H, s, CH), 10.61 (1H, br, OH), 13.58 (1H, s, OH). ¹³C{¹H} NMR (CDCl₃): δ 24.8 (CH₂), 25.3 (CH₂), 29.5 (CH₃), 29.7 (CH₃), 31.6 (CH₃), 31.9 (CH₃), 34.2 (C), 34.8 (C), 35.2 (CH₂), 35.5 (CH₂), 66.7 (CH), 70.4 (CH), 118.2 (Ar), 121.0 (Ar), 122.6 (ArH), 123.4 (ArH), 125.9 (ArH), 126.9 (ArH), 135.5 (Ar), 136.6 (Ar), 139.9 (Ar), 154.8 (Ar), 158.2 (Ar), 165.8 (CH). Calc. m/z $[\text{C}_{37}\text{H}_{57}\text{N}_2\text{O}_2]^-$ 561.4410. Found 561.4415

Al(1)Me. 1H₂ (0.45 g, 0.80 mmol) was dissolved in toluene (30 ml) then 2M AlMe₃ in heptane (0.40 ml, 0.80 mmol) was slowly added and stirred (16 h). The solvent was removed *in-vacuo* and the crude mixture was recrystallised from hexane to yield yellow crystals (0.29 g, 0.48 mmol, 60 %). ¹H NMR (d₈-Tol) (233 K): δ -0.35 (3H, s, Al-Me), 0.50 (2H, m, ring-CH₂), 0.63 (2H, br, ring-CH₂), 1.05 – 1.30 (4H, m, ring-CH₂), 1.40 (9H, s, ^tBu), 1.49 (9H, s, ^tBu), 1.60 (3H, s, CH₃), 1.82 (9H, s, ^tBu), 1.86 (9H, s, ^tBu), 2.35 (2H, m, ring-CH), 2.78 (1H, d, J = 13.0 Hz, CH₂), 3.98 (1H, d, J = 13.0 Hz, CH₂), 6.84 (1H, s, ArH), 6.98 (1H, s, ArH), 7.52 (1H, s, ArH), 7.58 (1H, s, ArH), 7.76 (1H, s, CH). ¹³C{¹H} NMR (d₈-Tol): δ -9.7 (CH₃), 21.5 (CH₂), 24.1 (CH₂), 24.8 (CH₂), 30.0 (CH₃), 30.1 (CH₃), 31.5 (CH₃), 32.1 (CH₃), 33.1 (CH₂), 34.1 (C), 34.3 (C), 35.6 (C), 35.7 (C), 36.3 (CH₃), 58.5 (CH₂), 60.2 (CH), 60.3 (CH), 118.1 (Ar), 120.9 (Ar), 123.6 (ArH), 123.7 (ArH), 127.5 (ArH), 131.7 (ArH), 136.7

(Ar), 138.1 (Ar), 138.4 (Ar), 141.7 (Ar), 157.1 (Ar-O), 166.0 (Ar-O), 171.4 (N=CH). Calc.(%) for $C_{38}H_{59}AlN_2O_2$; C 75.71, H 9.86, N 4.65. Found (%); C 68.27, H 9.15, N 4.71. Despite significant efforts and elemental analysis of the single crystals satisfactory elemental analysis could not be obtained for complexes containing ligand **1H₂**, the NMRs are clean and the single crystal data supports the complex.

Al(*R,R*-**1**)Me. *R,R*-**1H₂** (0.225 g, 0.80 mmol) was dissolved in toluene (30 ml) then 2M AlMe₃ in heptane (0.20 ml, 0.40 mmol) was slowly added and stirred (16 h). The solvent was removed *in-vacuo* and the crude mixture was recrystallised from hexane to yield yellow crystals (0.08 g, 0.13 mmol, 33 %). The following analysis shows a diastereomeric compound in an approximate 1:1 ratio. ¹H NMR (d₈-Tol): δ -0.48 (3H, s, Al-Me), -0.41 (3H, s, Al-Me), 0.50 - 0.85 (8H, m, ring-CH₂), 1.15 - 1.35 (8H, m, ring-CH₂), 1.35 (9H, s, ^tBu), 1.37 (9H, s, ^tBu), 1.41 (9H, s, ^tBu), 1.45 (9H, s, ^tBu), 1.69 (9H, s, ^tBu), 1.74 (9H, s, ^tBu), 1.76 (3H, s, CH₃), 1.77 (9H, s, ^tBu), 1.78 (9H, s, ^tBu), 1.85 (3H, s, CH₃), 2.35 - 2.50 (2H, m, ring-CH), 2.59 (1H, m, ring-CH), 2.80 (1H, d, J = 12.0 Hz, CH₂), 2.83 (1H, m, ring-CH), 2.94 (1H, d, J = 13.0 Hz, CH₂), 2.71 (1H, d, J = 12.0 Hz, CH₂), 4.08 (1H, d, J = 13.0 Hz, CH₂), 6.81 (1H, d, J = 2.5 Hz, ArH), 6.92 (1H, d, J = 2.5 Hz, ArH), 6.96 (2H, t, J = 2.5 Hz, ArH), 7.49 (1H, d, J = 2.5 Hz, ArH), 7.54 (1H, d, J = 2.5 Hz, ArH), 7.71 (1H, d, J = 2.5 Hz, ArH), 7.73 (1H, d, J = 2.5 Hz, ArH), 7.74 (1H, d, J = 1.0 Hz, ArH), 7.77 (1H, d, J = 1.0 Hz, ArH). ¹³C{¹H} NMR (d₈-Tol): δ 21.2 (CH₂), 21.6 (CH₂), 23.1 (CH₂), 24.2 (CH₂), 24.8 (CH₂), 25.0 (CH₂), 30.0 (CH₃), 30.2 (CH₃), 30.4 (CH₃), 30.5 (CH₃), 31.5 (CH₃), 31.6 (CH₃), 32.0 (CH₂), 32.1 (CH₃), 32.2 (CH₃), 32.6 (CH₂), 33.1 (C), 34.1 (C), 34.3 (C), 34.3 (C), 35.6 (C), 35.7 (C), 35.8 (C), 35.8 (C), 36.3 (CH₃), 41.1 (CH₃), 52.3 (CH₂), 58.6 (CH₂), 60.3 (CH), 61.2 (CH), 66.4 (CH), 118.1 (Ar), 120.9 (Ar), 122.2 (Ar), 123.7 (ArH), 123.7 (ArH), 123.8 (ArH), 123.9 (ArH), 127.5 (ArH), 127.8 (ArH), 131.7 (ArH), 132.0 (ArH), 136.7 (Ar), 136.8 (Ar), 138.0 (Ar), 138.2 (Ar), 138.4 (Ar), 141.4 (Ar), 141.8 (Ar), 157.1 (Ar-O), 157.4 (Ar-O), 166.1 (Ar-O), 166.5 (Ar-O), 171.4 (N=CH), 171.7 (N=CH). Calc.(%) for $C_{38}H_{59}AlN_2O_2$; C 75.71, H 9.86, N 4.65. Found (%); C 65.18, H 9.46, N 4.35. see comment for Al(**1**)Me

Al(**1**)OBn. **1H₂** (0.45 g, 0.80 mmol) was dissolved in toluene (30 ml) then 2M AlMe₃ in heptane (0.40 ml, 0.80 mmol) was slowly added and stirred (16 h). The solvent was removed *in-vacuo* and the crude mixture was briefly washed with hexane to remove any traces of AlMe₃. The residue was dissolved in toluene (30 ml) then benzyl alcohol (0.092 ml, 0.89 mmol) was slowly added and the reaction was stirred (16 h). The solvent was removed *in-vacuo* and the crude mixture was recrystallised from hexane to yield a yellow solid (0.06 g, 0.09 mmol, 11 %). The following analysis shows a diastereomeric compound in an approximate 1:1 ratio. ¹H NMR (d₈-Tol) : δ 0.45 - 0.9 (8H, m, ring-CH₂), 1.10 - 1.55 (8H, m, ring-CH₂), 1.35 (9H, s, ^tBu), 1.37 (9H, s, ^tBu), 1.39 (9H, s, ^tBu), 1.44 (9H, s, ^tBu), 1.62 (9H, s, ^tBu), 1.73 (9H, s, ^tBu), 1.74 (9H, s, ^tBu), 1.78 (9H, s, ^tBu), 2.18 (3H, s, CH₃), 2.23 (3H, s, CH₃), 2.30 (1H, td, J = 11.5 Hz, J = 3.0 Hz, ring-CH), 2.60 - 2.80 (3H, m, ring-CH), 2.83 (1H, d, J = 12.0 Hz, CH₂), 3.00 (1H, d, J = 13.0 Hz, CH₂), 3.71 (1H, d, J = 12.0 Hz, CH₂), 4.50 (1H, d, J = 13.0 Hz, CH₂), 5.20 (4H, br, CH₂), 6.80 (1H, d, J = 2.5 Hz, ArH), 6.93 (1H, d, J = 2.5 Hz, ArH), 6.96 (1H, s, ArH), 7.00 (1H, d, J = 2.5 Hz, ArH), 7.04 (2H, br, ArH), 7.15 - 7.40 (8H, br, ArH), 7.47 (1H, d, J = 2.5 Hz, ArH), 7.54 (1H, d, J = 2.5 Hz, ArH), 7.71 (1H, s, N=CH), 7.74 (1H, d, J = 2.5 Hz, ArH), 7.78 (1H, d, J = 2.5 Hz, ArH), 7.80 (1H, s, N=CH). ¹³C{¹H} NMR (d₈-Tol): δ 24.1 (CH₂), 24.8 (CH₂), 30.0 (CH₃), 30.4 (CH₃), 30.5 (CH₃), 30.7 (CH₃), 31.5 (CH₃), 31.5

(CH₃), 32.0 (CH₂), 32.1 (CH₃), 32.2 (CH₃), 32.2 (CH₂), 34.1 (C), 34.2 (C), 34.3 (C), 34.3 (C), 35.5 (C), 35.7 (C), 35.8 (C), 35.9 (C), 37.6 (CH₃), 41.7 (CH₃), 52.1 (CH₂), 59.2 (CH₂), 60.2 (CH), 60.2 (CH), 60.7 (CH), 66.2 (CH), 118.4 (Ar), 121.2 (Ar), 122.1 (Ar), 123.6 (ArH), 123.7 (ArH), 123.8 (ArH), 123.9 (ArH), 126.8 (ArH), 127.8 (ArH), 128.0 (ArH), 128.2 (ArH), 132.1 (ArH), 132.3 (ArH), 137.3 (Ar), 137.3(Ar), 138.5 (Ar), 141.4 (Ar), 141.5 (Ar), 156.9 (Ar-O), 157.3 (Ar-O), 166.4 (Ar-O), 171.2 (N=CH), 171.5 (N=CH). see comment for Al(1)Me.

Al(2)Me. 2H₂ (0.45 g, 1.00 mmol) was dissolved in toluene (30 ml) then 2M AlMe₃ in heptane (0.50 ml, 1.00 mmol) was slowly added and stirred (16 h). The solvent was removed *in-vacuo* and the crude mixture was recrystallised from toluene to yield yellow crystals (0.10 g, 0.20 mmol, 20 %). ¹H NMR (d₈-Tol): δ -0.36 (3H, s, Al-Me), 0.70 - 1.00 (4H, br, ring-CH₂), 1.30 - 1.60 (4H, m, ring-CH₂), 1.45 (9H, s, ^tBu), 1.75 (9H, s, ^tBu), 1.86 (3H, s, CH₃), 2.45 - 2.65 (2H, m, ring-CH), 2.72 (1H, d, J = 12.0 Hz, CH₂), 3.49 (1H, d, J = 12.0 Hz, CH₂), 6.53 (1H, ddd, J = 8.0 Hz, J = 6.5 Hz, J = 1.5 Hz, ArH), 6.90 (1H, d, J = 1.5 Hz, ArH), 6.93 (1H, d, J = 2.0 Hz, ArH), 7.14 (1H, d, J = 1.5 Hz, ArH), 7.18 (1H, dd, J = 6.5 Hz, J = 2.0 Hz, ArH), 7.52 (1H, d, J = 2.5 Hz, ArH), 7.69 (1H, s, CH). ¹³C{¹H} NMR (d₈-Tol): δ -10.2 (CH₃), 29.7 (CH₂), 29.8 (CH₂), 34.8 (CH₃), 37.1 (CH₃), 38.0 (C), 39.1 (C), 40.3 (CH₂), 45.5 (CH₃), 57.2 (CH₂), 66.7 (CH), 70.9 (CH), 120.1 (ArH), 123.4 (Ar), 126.4 (Ar), 127.8 (ArH), 128.3 (ArH), 128.6 (ArH), 138.7 (ArH), 142.1 (ArH), 142.7 (Ar), 143.3 (Ar), 162.1 (Ar-O), 173.9 (Ar-O), 176.3 (N=CH). Calc.(%) for C₃₀H₄₃AlN₂O₂; C 73.44, H 8.83, N 5.71. Found (%); C 73.57, H 8.83, N 5.80.

Al(2)OBn. 2H₂ (0.36 g, 0.80 mmol) was dissolved in toluene (30 ml) then 2M AlMe₃ in heptane (0.40 ml, 0.80 mmol) was slowly added and stirred (16 h). The solvent was removed *in-vacuo*, then the residue was dissolved in toluene (30 ml). Benzyl alcohol (0.083 ml, 0.80 mmol) was slowly added to the reaction and allowed to stir (16 h). The solvent was removed *in-vacuo* and the crude mixture was recrystallised from hexane to yield a yellow solid (0.06 g, 0.09 mmol, 11 %). ¹H NMR (d₈-Tol) (233 K): δ 0.40 - 0.65 (4H, m, ring-CH₂), 1.05 - 1.30 (4H, m, ring-CH₂), 1.46 (9H, s, ^tBu), 1.74 (9H, s, ^tBu), 2.21 (3H, s, CH₃), 2.29 (2H, br, ring-CH), 2.88 (1H, d, J = 13.5 Hz, CH₂), 4.56 (1H, d, J = 13.5 Hz, CH₂), 5.31 (1H, d, J = 14.0 Hz, CH₂), 5.57 (1H, d, J = 14.0 Hz, CH₂), 6.56 (1H, t, J = 7.5 Hz, ArH), 6.82 (1H, s, ArH), 6.87 (1H, d, J = 7.5 Hz, ArH), 7.04 (1H, s, ArH), 7.20 (1H, s, ArH), 7.23 (1H, s, ArH), 7.29 (2H, t, J = 7.5 Hz, ArH), 7.41 (1H, s, ArH), 7.56 (1H, s, ArH), 7.60 (1H, s, ArH), 7.62 (1H, s, CH). ¹³C{¹H} NMR (d₈-Tol): δ 25.0 (CH₂), 25.6 (CH₂), 30.9 (CH₃), 32.7 (C), 33.2 (CH₃), 36.4 (C), 38.6 (CH₃), 60.3 (CH₂), 60.7 (CH), 60.9 (CH), 67.5 (CH₂), 116.9 (ArH), 118.9 (Ar), 121.3 (Ar), 122.0 (Ar), 123.1 (ArH), 124.0 (ArH), 126.0 (ArH), 126.2 (ArH), 127.3 (ArH), 128.4 (ArH), 129.7 (ArH), 134.2 (ArH), 137.5 (ArH), 138.7 (Ar), 138.8 (Ar), 143.3 (Ar), 157.2 (Ar-O), 168.1 (Ar-O), 170.6 (N=CH). Calc.(%) for C₃₆H₄₇AlN₂O₃; C 74.20, H 8.13, N 4.81. Found (%); C 72.31, H 7.86, N 4.47.

Al(3)Me. 3H₂ (0.41 g, 0.79 mmol) was dissolved in toluene (30 ml) then 2M AlMe₃ in heptane (0.40 ml, 0.80 mmol) was slowly added and stirred (16 h). The solvent was removed *in-vacuo* and the crude mixture was recrystallised from a toluene / hexane mix to yield a yellow solid (0.34 g, 0.61 mmol, 77 %). ¹H NMR (d₈-Tol) (233 K): δ -0.41 (3H, s, Al-Me), 0.70 - 0.95 (4H, br, ring-CH₂), 1.30 - 1.50 (4H, m, ring-CH₂), 1.43 (9H, s, ^tBu), 1.73 (9H, s, ^tBu), 1.81 (3H, s, CH₃), 2.50 (1H, m, ring-CH),

2.70 (1H, br ring, CH), 2.71 (1H, d, J = 12.0 Hz, CH₂), 3.44 (1H, d, J = 12.0 Hz, CH₂), 6.65 (1H, d, J = 2.5 Hz, ArH), 6.92 (1H, d, J = 2.5 Hz, ArH), 7.34 (1H, s, ArH), 7.35 (1H, s, CH), 7.52 (1H, d, J = 2.5 Hz, ArH). ¹³C{¹H} NMR (d₈-Tol): δ -10.3 (CH₃), 24.7 (CH₂), 24.9 (CH₂), 30.0 (CH₃), 32.2 (CH₃), 33.0 (C), 34.3 (C), 35.5 (CH₂), 40.8 (CH₃), 52.3 (CH₂), 62.2 (CH), 60.9 (CH), 66.0 (CH₂), 116.5 (ArH), 117.9 (Ar), 120.7 (ArH), 122.2 (Ar), 127.4 (ArH), 128.8 (ArH), 130.0 (ArH), 131.9 (ArH), 136.8 (Ar), 141.6 (Ar), 161.5 (Ar-O), 166.4 (Ar-O), 172.1 (N=CH). Calc.(%) for C₃₀H₄₁AlCl₂N₂O₂; C 64.40, H 7.39, N 5.01. Found (%); C 64.39, H 7.46, N 5.18.

Al(3)OBn. 2H₂ (0.42 g, 0.81 mmol) was dissolved in toluene (30 ml) then 2M AlMe₃ in heptane (0.40 ml, 0.80 mmol) was slowly added and stirred (16 h). The solvent was removed *in-vacuo* and the crude mixture was briefly washed with hexane to remove any traces of AlMe₃. The residue was dissolved in toluene (30 ml) then benzyl alcohol (0.091 ml, 0.88 mmol) was slowly added and the reaction was stirred (16 h). The solvent was removed *in-vacuo* and the crude mixture was recrystallised from hexane to yield a yellow solid (0.22 g, 0.34 mmol, 42 %). ¹H NMR (d₈-Tol) (K): δ 0.65 – 0.85 (4H, br, ring-CH₂), 1.30 – 1.55 (4H, m, ring-CH₂), 1.42 (9H, s, ^tBu), 1.74 (9H, s, ^tBu), 2.23 (3H, s, CH₃), 2.74 (2H, br, CH₂), 2.77 (1H, br, CH), 3.51 (1H, d, J = 12.0 Hz, CH), 5.14 (2H, br, CH₂), 6.64 (1H, d, J = 2.0 Hz, ArH), 6.93 (1H, s, ArH), 7.03 (1H, s, ArH), 7.12 (1H, s, ArH), 7.13 (1H, s, CH), 7.30 (1H, s, ArH), 7.33 (1H, s, ArH), 7.35 (1H, s, ArH), 7.53 (1H, d, J = 2.5 Hz, ArH). ¹³C{¹H} NMR (d₈-Tol): δ 24.6 (CH₂), 24.7 (CH₂), 30.0 (CH₃), 31.8 (CH₂), 32.2 (C), 34.3 (C), 35.5 (CH₂), 41.6 (CH₃), 52.3 (CH₂), 61.0 (CH), 65.9 (CH₂), 66.2 (CH), 118.8 (Ar), 119.1 (Ar), 121.1 (Ar), 123.4 (ArH), 124.0 (ArH), 126.0 (ArH), 127.1 (ArH), 128.0 (ArH), 130.9 (ArH), 135.8 (ArH), 138.7 (Ar), 138.9 (Ar), 156.8 (Ar-O), 162.0 (Ar-O), 169.7 (N=CH). Calc.(%) for C₃₆H₄₅AlCl₂N₂O₃; C 66.35, H 6.96, N 4.30. Found (%); C 66.20, H 7.08, N 4.28

Al(4)Me. 4H₂ (0.36 g, 0.80 mmol) was dissolved in toluene (30 ml) then 2M AlMe₃ in heptane (0.40 ml, 0.80 mmol) was slowly added and stirred (16 h). The solvent was removed *in-vacuo* and the crude mixture was recrystallised from a toluene / hexane mix to yield a yellow solid (0.18 g, 0.37 mmol, 46 %). ¹H NMR (d₈-Tol) (233 K): δ -0.35 (3H, s, Al-Me), 0.70 – 0.90 (4H, br, ring-CH₂), 1.35 – 1.55 (4H, m, ring-CH₂), 1.40 (9H, s, ^tBu), 1.79 (9H, s, ^tBu), 1.86 (3H, s, CH₃), 2.55 (1H, m, ring CH), 2.66 (1H, d, J = 12.0 Hz, CH₂), 3.49 (1H, d, J = 12.0 Hz, CH₂), 6.73 (1H, t, J = 7.0 Hz, ArH), 6.86 (1H, d, J = 7.0 Hz, ArH), 6.94 (1H, d, J = 2.5 Hz, ArH), 7.05 (1H, d, J = 8.0 Hz, ArH), 7.19 (1H, t, J = 7.5 Hz, ArH), 7.72 (1H, s, ArH), 7.73 (1H, s, CH). ¹³C{¹H} NMR (d₈-Tol): δ -9.7 (CH₃), 24.9 (CH₂), 25.0 (CH₂), 29.7 (CH₃), 31.6 (CH₃), 33.4 (C), 34.2 (C), 35.7 (CH₂), 40.8 (CH₃), 51.7 (CH₂), 61.5 (CH), 66.3 (CH), 118.9 (Ar), 119.0 (Ar), 121.3 (Ar), 123.5 (ArH), 124.0 (ArH), 128.1 (Ar), 130.9 (ArH), 135.9 (ArH), 138.4 (Ar), 138.9 (Ar), 156.9 (Ar-O), 162.0 (Ar-O), 170.4 (N=CH). Calc.(%) for C₃₀H₄₃AlN₂O₂; C 73.44, H 8.83, N 5.71. Found (%); C 73.37, H 8.90, N 5.82.

Al(4)OBn. 4H₂ (0.36 g, 0.80 mmol) was dissolved in toluene (30 ml) then 2M AlMe₃ in heptane (0.40 ml, 0.80 mmol) was slowly added and stirred (16 h). The solvent was removed *in-vacuo* and the crude mixture was briefly washed with hexane to remove any traces of AlMe₃. The residue was dissolved in toluene (30 ml) then benzyl alcohol (0.083 ml, 0.80 mmol) was slowly added and the reaction was stirred (16 h). The solvent was removed *in-vacuo* and the crude mixture was recrystallised

from a toluene / hexane mix to yield a yellow solid (0.23 g, 0.39 mmol, 49 %). ^1H NMR (d_8 -Tol) (233 K): δ 0.40 – 0.80 (4H, m, ring- CH_2), 1.15 – 1.55 (4H, m, ring- CH_2), 1.48 (9H, s, ^tBu), 1.88 (9H, s, ^tBu), 2.24 (3H, s, CH_3), 2.25 (1H, br, ring CH), 2.59 (1H, d, $J = 12.0$ Hz, CH_2), 2.77 (1H, t, $J = 11.0$ Hz, ring CH), 3.39 (1H, d, $J = 12.0$ Hz, CH_2), 5.34 (1H, d, $J = 13.0$ Hz, CH_2), 5.44 (1H, d, $J = 13.0$ Hz, CH_2), 6.86 (1H, t, $J = 7.0$ Hz, ArH), 6.93 (1H, d, $J = 7.5$ Hz, ArH), 7.15 – 7.30 (5H, m, ArH), 7.48 (2H, d, $J = 7.5$ Hz, ArH), 7.60 (1H, s, ArH), 7.85 (1H, s, ArH). $^{13}\text{C}\{^1\text{H}\}$ NMR (d_8 -Tol): δ 24.9 (CH_2), 25.0 (CH_2), 30.0 (CH_3), 31.6 (CH_3), 32.4 (C), 34.2 (C), 35.8 (CH_2), 41.4 (CH_3), 51.5 (CH_2), 60.7 (CH), 66.1 (CH), 66.2 (CH_2), 116.9 (ArH), 118.2 (Ar), 120.6 (ArH), 122.1 (Ar), 125.9 (ArH), 127.3 (ArH), 128.0 (ArH), 128.7 (ArH), 130.0 (ArH), 132.1 (ArH), 137.3 (Ar), 141.8 (Ar), 161.3 (Ar-O), 166.6 (Ar-O), 171.8 (N=CH). Calc.(%) for $\text{C}_{36}\text{H}_{47}\text{AlN}_2\text{O}_3$; C 74.20, H 8.13, N 4.81. Found (%); C 74.29, H 8.11, N 4.72.

Al(5)Me – too insoluble for analysis

Al(5)OBn. **5H₂** (0.34 g, 1.00 mmol) was dissolved in toluene (30 ml) then 2M AlMe_3 in heptane (0.50 ml, 1.00 mmol) was slowly added and stirred (16 h). The solvent was removed *in-vacuo* and the crude mixture was briefly washed with hexane to remove any traces of AlMe_3 . The residue was dissolved in toluene (30 ml) then benzyl alcohol (0.11 ml, 1.06 mmol) was slowly added and the reaction was stirred (16 h). The solvent was removed *in-vacuo* and the crude mixture was recrystallised from a toluene / hexane mix to yield a yellow solid (0.27 g, 0.57 mmol, 57 %). The following analysis shows a diastereomeric compound in an approximate 1:1 ratio. ^1H NMR (d_8 -Tol) : δ 0.45 – 0.90 (8H, m, ring- CH_2), 1.15 – 1.55 (8H, m, ring- CH_2), 2.16 (3H, s, CH_3), 2.22 (3H, s, CH_3), 2.39 (1H, td, $J = 12.0$ Hz, $J = 2.5$ Hz, ring CH), 2.52 (1H, t, $J = 11.0$ Hz, ring CH), 2.64 (1H, br, ring CH), 2.67 (1H, d, $J = 12.0$ Hz, CH_2), 2.74 (1H, t, $J = 11.0$ Hz, CH_2), 2.99 (1H, d, $J = 13.5$ Hz, CH), 3.50 (1H, d, $J = 12.5$ Hz, CH), 4.51 (1H, d, $J = 12.5$ Hz, CH), 5.09 (4H, br, CH_2), 6.54 (2H, t, $J = 6.5$ Hz, ArH), 6.70 (2H, m, ArH), 6.76 (1H, d, $J = 7.5$ Hz, ArH), 6.86 (2H, t, $J = 8.0$ Hz, ArH), 6.92 (1H, d, $J = 7.5$ Hz, ArH), 7.03 – 7.09 (5H, m, ArH), 7.16 (8H, m, ArH), 7.38 (4H, br, ArH), 7.56 (1H, s, ArH), 7.67 (1H, s, ArH). $^{13}\text{C}\{^1\text{H}\}$ NMR (d_8 -Tol): δ 21.3 (CH_2), 23.9 (CH_2), 24.6 (CH_2), 24.7 (CH_2), 24.8 (CH_2), 31.0 (CH_2), 32.0 (CH_2), 37.4 (CH_3), 41.6 (CH_3), 51.6 (CH_2), 58.3 (CH_3), 59.7 (CH), 59.8 (CH), 60.5 (CH), 66.1 (CH), 66.2 (CH_2), 115.7 (ArH), 115.7 (ArH), 117.0 (ArH), 117.2 (ArH), 118.6 (Ar), 118.7 (Ar), 120.4 (ArH), 120.5 (ArH), 121.1 (Ar), 122.2 (Ar), 122.6 (ArH), 122.8 (ArH), 125.9 (ArH), 127.1 (ArH), 128.1 (ArH), 130.1 (ArH), 130.2 (ArH), 133.9 (ArH), 134.0 (ArH), 137.1 (ArH), 137.2 (ArH), 160.9 (Ar-O), 161.3 (Ar-O), 168.4 (Ar-O), 168.8 (Ar-O), 170.8 (N=CH), 171.1 (N=CH). Calc.(%) for $\text{C}_{28}\text{H}_{31}\text{AlN}_2\text{O}_3$; C 71.47, H 6.64, N 5.95. Found (%); C 71.38, H 6.65, N 6.02.

Al(6)Me – too insoluble for analysis

Al(6)OBn. **6H₂** (0.41 g, 1.00 mmol) was dissolved in toluene (30 ml) then 2M AlMe_3 in heptane (0.50 ml, 1.00 mmol) was slowly added and stirred (16 h). The solvent was removed *in-vacuo* and the crude mixture was briefly washed with hexane to remove any traces of AlMe_3 . The residue was dissolved in toluene (30 ml) then benzyl alcohol (0.11 ml, 1.06 mmol) was slowly added and the reaction was stirred (16 h). The solvent was removed *in-vacuo* and the crude mixture was recrystallised from a toluene / hexane mix to yield a yellow solid (0.20 g, 0.37 mmol, 37 %). The

following analysis shows a diastereomeric compound in an approximate 1:1 ratio. ^1H NMR (d_8 -Tol) : δ 0.30 – 0.80 (8H, m, ring- CH_2), 1.30 – 1.50 (8H, m, ring- CH_2), 1.66 (1H, m, CH_2), 2.12 (3H, s, CH_3), 2.16 (3H, s, CH_3), 2.36 (1H, m, ring CH), 2.57 (1H, m, ring CH), 2.65 (1H, d, $J = 12.5$ Hz, CH_2), 2.72 (1H, d, $J = 12.5$ Hz, CH_2), 2.79 (1H, m, ring CH), 2.96 (1H, d, $J = 13.5$ Hz, CH_2), 3.51 (1H, d, $J = 12.5$ Hz, CH_2), 4.45 (1H, d, $J = 13.5$ Hz, CH_2), 5.13 (4H, br, CH_2), 6.50 – 6.85 (7H, m, ArH), 7.03 (2H, m, ArH), 7.14 (5H, m, ArH), 7.25 – 7.40 (7H, m, ArH), 7.51 (1H, s, $\text{N}=\text{CH}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (d_8 -Tol): δ 21.3 (CH_2), 23.8 (CH_2), 24.5 (CH_2), 24.7 (CH_2), 24.8 (CH_2), 30.9 (CH_2), 32.0 (CH_2), 37.5 (CH_3), 41.7 (CH_3), 51.6 (CH_2), 58.3 (CH_3), 59.5 (CH), 60.2 (CH), 60.9 (CH), 65.9 (CH_2), 66.1 (CH), 117.3 (ArH), 117.5 (ArH), 118.9 (Ar), 119.0 (Ar), 119.2 (Ar), 119.3 (Ar), 120.4 (ArH), 120.6 (ArH), 120.8 (Ar), 121.9 (Ar), 126.2 (ArH), 127.0 (ArH), 128.1 (ArH), 130.2 (ArH), 130.3 (ArH), 131.0 (ArH), 131.1 (ArH), 135.7 (ArH), 135.82 (ArH), 160.5 (Ar-O), 160.8 (Ar-O), 161.3 (Ar-O), 161.8 (Ar-O), 169.7 ($\text{N}=\text{CH}$), 170.3 ($\text{N}=\text{CH}$). Calc.(%) for $\text{C}_{28}\text{H}_{29}\text{AlCl}_2\text{N}_2\text{O}_3$; C 62.34, H 5.42, N 5.19. Found (%); C 62.28, H 5.46, N 5.07.

Al(7)Me. 7H_2 (0.41 g, 0.79 mmol) was dissolved in toluene (30 ml) then 2M AlMe_3 in heptane (0.40 ml, 0.80 mmol) was slowly added and stirred (16 h). The solvent was removed *in-vacuo* and the crude mixture was recrystallised from a toluene / hexane mix to yield a yellow solid (0.32 g, 0.57 mmol, 72 %). ^1H NMR (d_8 -Tol) : δ - 0.43 (3H, s, Al-Me), 0.60 – 1.00 (4H, m, ring- CH_2), 1.20 – 1.60 (4H, br, ring- CH_2), 1.37 (9H, s, ^tBu), 1.63 (3H, s, CH_3), 1.78 (9H, s, ^tBu), 2.42 (2H, m, CH_2), 2.61 (1H, m, ring CH), 3.26 (1H, d, $J = 11.5$ Hz, CH), 6.65 (1H, s, ArH), 6.94 (1H, s, ArH), 7.34 (1H, s, ArH), 7.72 (1H, s, ArH), 7.73 (1H, s, CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (d_8 -Tol): δ -9.4 (CH_3), 24.8 (CH_2), 24.9 (CH_2), 29.9 (CH_3), 31.5 (CH_3), 32.2 (C), 34.2 (C), 35.7 (CH_2), 40.7 (CH_3), 51.0 (CH_2), 61.3 (CH), 66.3 (CH), 117.8 (Ar), 120.2 (Ar), 124.7 (Ar), 125.4 (Ar), 127.1 (ArH), 127.4 (ArH), 129.8 (ArH), 127.5 (ArH), 132.3 (ArH), 137.3 (Ar), 141.9 (Ar), 155.7 (Ar-O), 166.2 (Ar-O), 172.3 ($\text{N}=\text{CH}$). Calc.(%) for $\text{C}_{30}\text{H}_{41}\text{AlCl}_2\text{N}_2\text{O}_2$; C 64.40, H 7.39, N 5.01. Found (%); C 64.47, H 7.51, N 5.13.

Al(7)OBn. 7H_2 (0.42 g, 0.81 mmol) was dissolved in toluene (30 ml) then 2M AlMe_3 in heptane (0.40 ml, 0.80 mmol) was slowly added and stirred (16 h). The solvent was removed *in-vacuo* and the crude mixture was briefly washed with hexane to remove any traces of AlMe_3 . The residue was dissolved in toluene (30 ml) then benzyl alcohol (0.083 ml, 0.80 mmol) was slowly added and the reaction was stirred (16 h). The solvent was removed *in-vacuo* and the crude mixture was recrystallised from a toluene / hexane mix to yield a yellow solid (0.34 g, 0.52 mmol, 65 %). ^1H NMR (D_8 -Tol) : δ 0.65 – 0.95 (4H, m, ring- CH_2), 1.30 – 1.55 (4H, br, ring- CH_2), 1.37 (9H, s, ^tBu), 1.75 (9H, s, ^tBu), 2.00 (3H, s, CH_3), 2.41 (1H, d, $J = 12.5$ Hz, CH), 2.58 (1H, m, ring CH), 2.74 (1H, m, ring CH), 3.23 (1H, d, $J = 12.5$ Hz, CH_2), 5.16 (2H, br, CH_2), 6.64 (1H, d, $J = 2.5$ Hz, ArH), 6.97 (1H, s, ArH), 7.06 (1H, d, $J = 7.0$ Hz, ArH), 7.19 (2H, t, $J = 7.5$ Hz, ArH), 7.34 (1H, d, $J = 2.5$ Hz, ArH), 7.41 (2H, $J = 7.5$ Hz, ArH), 7.75 (1H, m, ArH), 7.77 (1H, m, CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (d_8 -Tol): δ 24.8 (CH_2), 24.9 (CH_2), 30.2 (CH_3), 31.5 (CH_3), 32.3 (C), 34.2 (C), 37.8 (CH_2), 41.4 (CH_3), 60.5 (CH), 65.5 (CH_2), 66.2 (CH), 118.1 (Ar), 120.8 (Ar), 124.6 (Ar), 125.6 (Ar), 126.1 (ArH), 127.0 (ArH), 127.4 (ArH), 127.5 (ArH), 128.1 (ArH), 129.3 (ArH), 129.8 (ArH), 132.5 (ArH), 137.8 (Ar), 142.1 (Ar), 146.7 (Ar), 155.5 (Ar-O), 166.4 (Ar-O), 172.1 ($\text{N}=\text{CH}$). Calc.(%) for $\text{C}_{36}\text{H}_{45}\text{AlCl}_2\text{N}_2\text{O}_3$; C 66.35, H 6.96, N 4.30. Found (%); C 66.45, H 7.02, N 4.40.

Al(8)Me – too insoluble for analysis

Al(8)OBn. **8**H₂ (0.33 g, 0.81 mmol) was dissolved in toluene (30 ml) then 2M AlMe₃ in heptane (0.40 ml, 0.80 mmol) was slowly added and stirred (16 h). The solvent was removed *in-vacuo* and the crude mixture was briefly washed with hexane to remove any traces of AlMe₃. The residue was dissolved in toluene (30 ml) then benzyl alcohol (0.091 ml, 0.88 mmol) was slowly added and the reaction was stirred (16 h). The solvent was removed *in-vacuo* and the crude mixture was recrystallised twice from a toluene / hexane mix to yield a yellow solid (0.19 g, 0.35 mmol, 43 %). Analysis shows impurities were present in this sample despite extensive efforts to isolate a pure product. The following analysis shows a diastereomeric compound in an approximate 1:1 ratio. ¹H NMR (d₈-Tol) : δ 0.30 – 0.90 (8H, m, ring-CH₂), 1.10 – 1.65 (8H, m, ring-CH₂), 2.07 (3H, s, CH₃), 1.95 – 2.15 (3H, m, CH₃), 2.30 – 2.70 (4H, m, CH), 2.73 (1H, d, J = 13.5 Hz, CH₂), 3.10 – 4.10 (2H, m, CH₂), 4.24 (1H, d, J = 13.5 Hz, CH₂), 4.90 - 5.30 (4H, br, CH₂), 6.45 – 6.75 (4H, m, ArH), 6.80 – 6.90 (2H, m, ArH), 7.05 (1H, s, ArH), 7.07 (1H, s, ArH), 7.10 – 7.23 (6H, m, ArH), 7.29 (2H, m, ArH), 7.35 (2H, s, ArH), 7.38 (2H, s, ArH), 7.48 (1H, br, ArH), 7.54 (1H, s, N=CH), 7.55 – 7.90 (2H, m, ArH, N=CH). ¹³C{¹H} NMR (d₈-Tol): δ 21.2 (CH₂), 23.7 (CH₂), 24.4 (CH₂), 24.6 (CH₂), 24.7 (CH₂), 30.7 (CH₂), 31.8 (CH₂), 37.4 (CH₃), 41.5 (CH₃), 50.8 (CH₂), 57.4 (CH₂), 59.6 (CH), 60.2 (CH), 60.3 (CH), 66.1 (CH₂), 66.1 (CH), 116.0 (ArH), 118.4 (Ar), 118.5 (Ar), 120.8 (Ar), 120.9 (Ar), 122.7 (ArH), 122.7 (ArH), 123.5 (Ar), 124.2 (Ar), 24.6 (Ar), 126.2 (ArH), 126.9 (ArH), 127.1 (ArH), 127.1 (ArH), 128.1 (ArH), 129.8 (ArH), 129.9 (ArH), 133.8 (ArH), 133.9 (ArH), 137.4 (ArH), 137.6 (ArH), 155.3 (Ar-O), 155.5 (Ar-O), 168.3 (Ar-O), 168.8 (Ar-O), 170.9 (N=CH), 171.1 (N=CH). Calc.(%) for C₂₈H₂₉AlCl₂N₂O₃; C 62.34, H 5.42, N 5.19. Found (%); C 57.91, H 5.78, N 4.39.

Al(9)Me – too insoluble for analysis

Al(9)OBn. **9**H₂ (0.38 g, 0.80 mmol) was dissolved in toluene (30 ml) then 2M AlMe₃ in heptane (0.40 ml, 0.80 mmol) was slowly added and stirred (16 h). The solvent was removed *in-vacuo* and the crude mixture was briefly washed with hexane to remove any traces of AlMe₃. The residue was dissolved in toluene (30 ml) then benzyl alcohol (0.091 ml, 0.88 mmol) was slowly added and the reaction was stirred (16 h). The solvent was removed *in-vacuo* and the crude mixture was recrystallised from a toluene / hexane mix to yield a yellow solid (0.16 g, 0.26 mmol, 33 %). The following analysis shows a diastereomeric compound in an approximate 3:1 ratio (the major diastereomers is characterised). ¹H NMR (d₈-Tol) : δ 0.25 – 0.40 (2H, m, ring-CH₂), 0.50 – 0.75 (2H, m, ring-CH₂), 1.17 (2H, m, ring-CH₂), 1.32 (1H, m, ring-CH₂), 1.44 (1H, m, ring-CH₂), 2.09 (3H, s, CH₃), 2.45 (1H, m, ring CH), 2.68 (1H, m, ring CH), 3.22 (1H, d, J = 12.5 Hz, CH₂), 4.18 (1H, d, J = 12.5 Hz, CH₂), 5.11 (2H, br, CH₂), 6.56 (2H, m, ArH), 7.05 (1H, d, J = 7.5 Hz, ArH), 7.17 (2H, t, J = 7.5 Hz, ArH), 7.25 (1H, s, ArH), 7.29 (2H, m, ArH), 7.37 (1H, s, ArH), 7.39 (1H, s, CH). Solubility does not allow a ¹³C{¹H} NMR to be obtained. Calc.(%) for C₂₈H₂₇AlCl₄N₂O₃; C 55.28, H 4.47, N 4.61. Found (%); C 55.17, H 4.54, N 4.64.