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SUPPORTING INFORMATION

Aluminium Salalens vs. Salans: *"Initiator Design"* for the Polymerisation of *rac*-Lactide

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General Considerations

The preparation and characterisation of all metal complexes was carried out under inert argon atmosphere using standard Schlenk or glovebox techniques. All chemicals used were purchased from Aldrich and used as received except for *rac*-LA which was recrystallised from dry toluene. Imino ligands **A**-**B**H_2 were synthesised and characterised as previously reported.[1] Dry solvents used in handling metal complexes were obtained *via* SPS (solvent purification system). ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker 400 or 500 MHz instrument and referenced to residual solvent peaks. $CDCl_3$ was dried over CaH_2 prior to use with metal complexes. Coupling constants are given in Hertz. CHN microanalysis was performed by Mr. Stephen Boyer of London Metropolitan University. In some cases satisfactory elemental analysis was achieved, however some samples were low on carbon (and the Al-Me samples gave a range of results on the same sample) this is presumably due to the high moisture sensitivity of the samples.

Polymerisations were carried out in a Young's ampoule under inert argon conditions. For a typical solution based polymerisations, *rac*-LA (1.0 g, 0.69 mmol) was dissolved in toluene (10 ml) with required amount of initiator added. When required, a benzyl alcohol co-initiator (typically [I]:[BnOH] 1:1, 7.2 µl) was added. The ampoule was then placed in an oil bath for the set time. After polymerisation, solvent was removed *in vacuo* and a crude ^{1}H NMR recorded. The polymer was then purified by washing with methanol to remove initiator and unreacted monomer. For solvent free polymerisations, a higher initiator ratio was employed (300:1) and the reaction performed at 130 °C. After polymerisation, the product was dissolved in CH_2Cl_2 which was then removed *in vacuo* and a crude ^{1}H NMR recorded. The polymer was then purified in the same fashion as for solution polymerisations.

All purified polymers were characterised by a combination of gel permeation chromatography (GPC) and homonuclear decoupled ^{1}H NMR spectroscopy. GPC was carried out at 1 ml min-1 at 35 °C with a THF eluent and referenced against polystyrene standards (RI). Tacticity was determined via ^{1}H NMR spectroscopy (CDCl3) analysis of the homonuclear decoupled methine region. MALDI ToF mass spectra were determined on a Bruker Autoflex speed instrument using DCTB (trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile) as the matrix and ionized using NaOAc. The DSC analysis was recorded on a TA Instruments DSC Q20. The sample was held at 40 ºC for 1 minute, heated to 250 ºC at 5 ºC/min held at this temperature for 1 minute, cooled to 40 ºC at 5 ºC/min held at this temperature for 1 minute and finally heated to 250 ºC at 5 ºC/min - the T_m values are quoted for the second heating cycle.

All crystallography data were collected on a SuperNova, EOS detector diffractometer using radiation CuKα (λ= 1.54184 Å) or Mo-Kα (λ= 0.71073 Å) or a Nonius kappa diffractometer using Mo-Kα (λ= 0.71073 Å) all recorded at 150(2) K. All structures were solved by direct methods and refined on all F^2 data using the SHELXL-2014 suite of programs. All hydrogen atoms were included in idealised positions and refined using the riding model, all refinement details are given in the .cif file.

Ligand synthesis &characterisation

Synthesis of secondary amine based salans, 1-2H_2. Imino complexes **A-B**H_2 (10 mmol) were dissolved in methanol/THF (25/25ml) and $NaBH_4$ (0.380g, 10 eq) was added portionwise. The solution was then stirred until decolouration after which the reaction was quenched through addition of H_2O (10 ml). The solution was then concentrated *in vacuo* and the white precipitate was washed with H_2O (3x 50ml) and MeOH (50ml).

1H_2: Isolated as a white powder (4.80 g, 8.71 mmol, 87%). ^1H NMR ($CDCl_3$, 400 MHz) δ=11.01 (br s, 2H; ArOH), 7.22 (d, *J* = 2.4 Hz, 1H; ArH), 7.20 (d, *J* = 2.4 Hz, 1H; ArH), 6.85 (d, *J* = 2.4 Hz, 1H; ArH), 6.73 (d, *J* = 2.4 Hz, 1H; ArH), 4.05 (d, *J* = 14.1 Hz, 1H; $ArCH_2$), 3.77 (d, *J* = 13.3 Hz, 1H; $ArCH_2$), 3.59 (br d, *J* = 13.2 Hz, 2H; $ArCH_2$), 2.99 (br s, 1H; CH_2), 2.88 (dd, J = 12.6, 5.4 Hz, 1H; CH_2), 2.78 (br dd, J = 12.6, 3.6 Hz, 1H; CH_2), 2.55 (m, 1H; CH), 2.31 (m, 1H; CH_2), 1.73 (br m, 3H; CH_2), 1.59 (br m, 3H; CH_2), 1.40 (s, 9H; $C(CH_3)_3$), 1.37 (s, 9H; $C(CH_3)_3$), 1.31 (s, 9H; $C(CH_3)_3$), 1.28 (s, 9H; $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ=154.4, 154.2, 140.8, 140.4, 135.84, 135.8, 123.1, 122.9, 122.87, 122.7, 121.6, 121.4. (Ar), 61.7 (CH) 58.9, 53.7, 49.4 (CH_2), 34.8, 34.2, 34.1 ($\mathit{C}(CH_3)_3$), 31.70, 31.67, 29.6, 29.5 ($C(\mathit{C}H_3)_3$) 29.9, 25.0 22.6 (CH_2). Note: CH/CH_2 resonances were weak in ^{13}C NMR, HSQC was used to aid unambiguous identification/assignment. ESI-MS (MeOH): Calcd m/z $[C_{36}H_{58}N_2O_2Na]^+$ = 573.4389, found m/z = 573.4395.

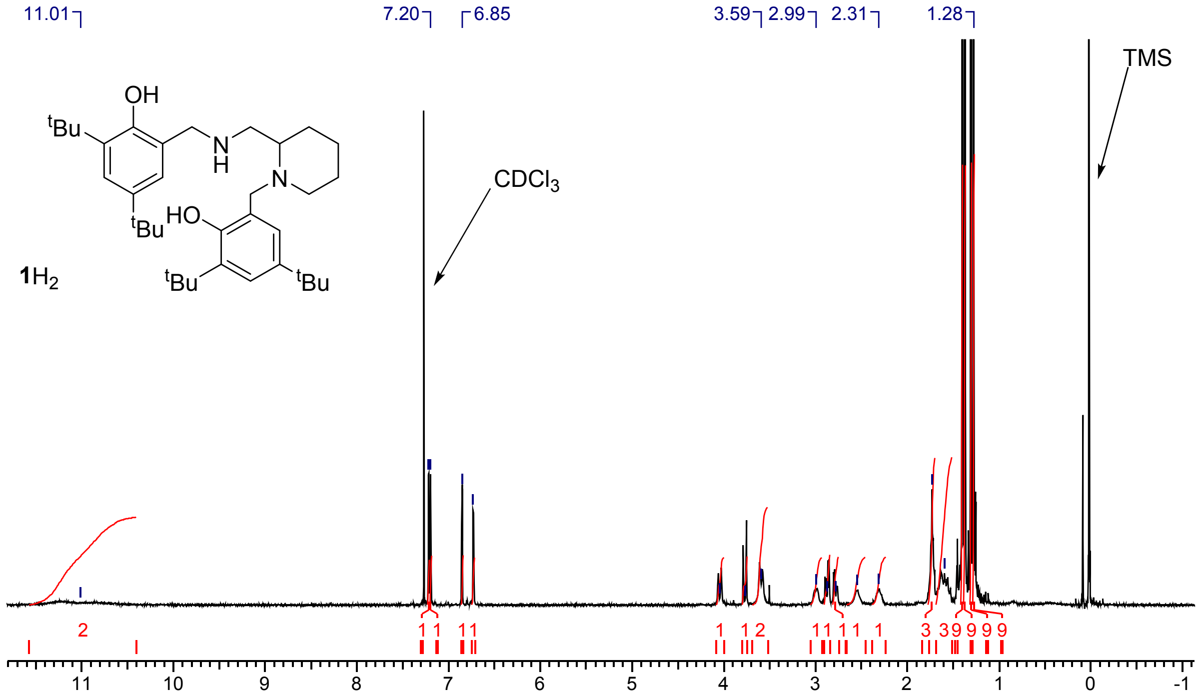

Figure SI1: ^{1}H NMR (CDCl$_3$ 400MHz) spectra of **1**H$_2$.

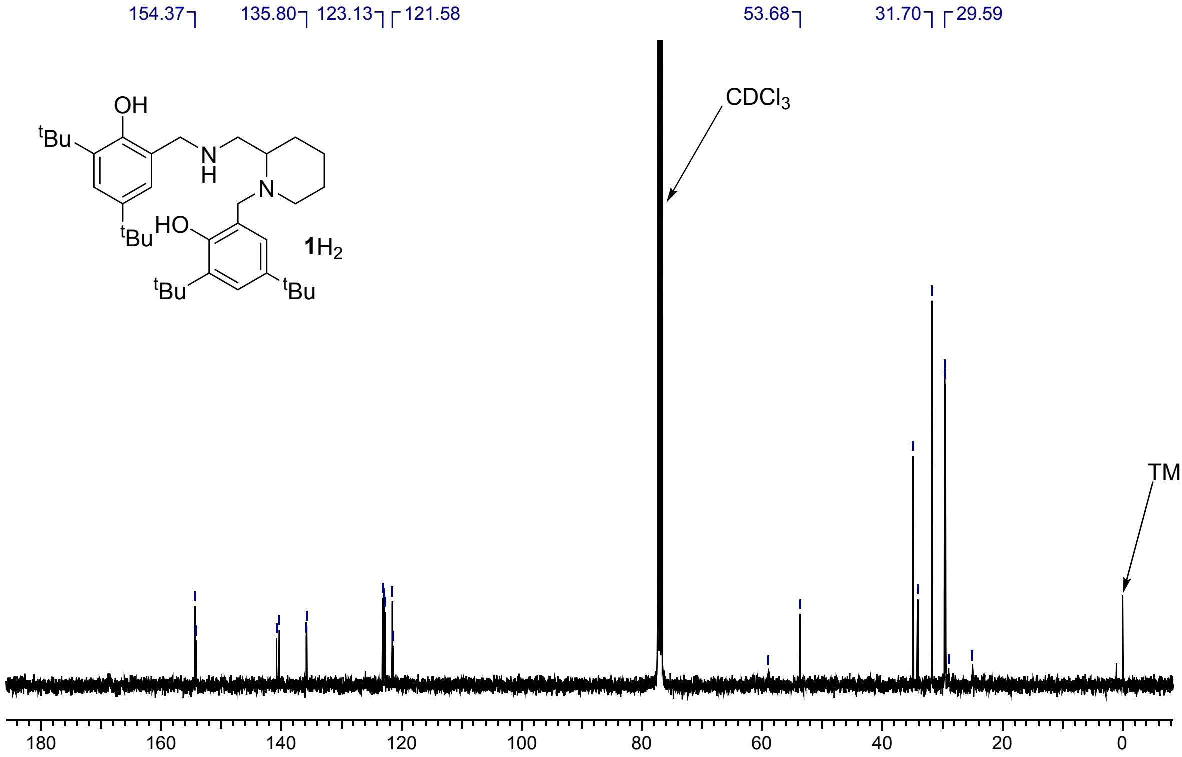

Figure SI2: ^{13}C{^{1}H} NMR (CDCl$_{3,}$ 100MHz) spectra of **1**H$_2$

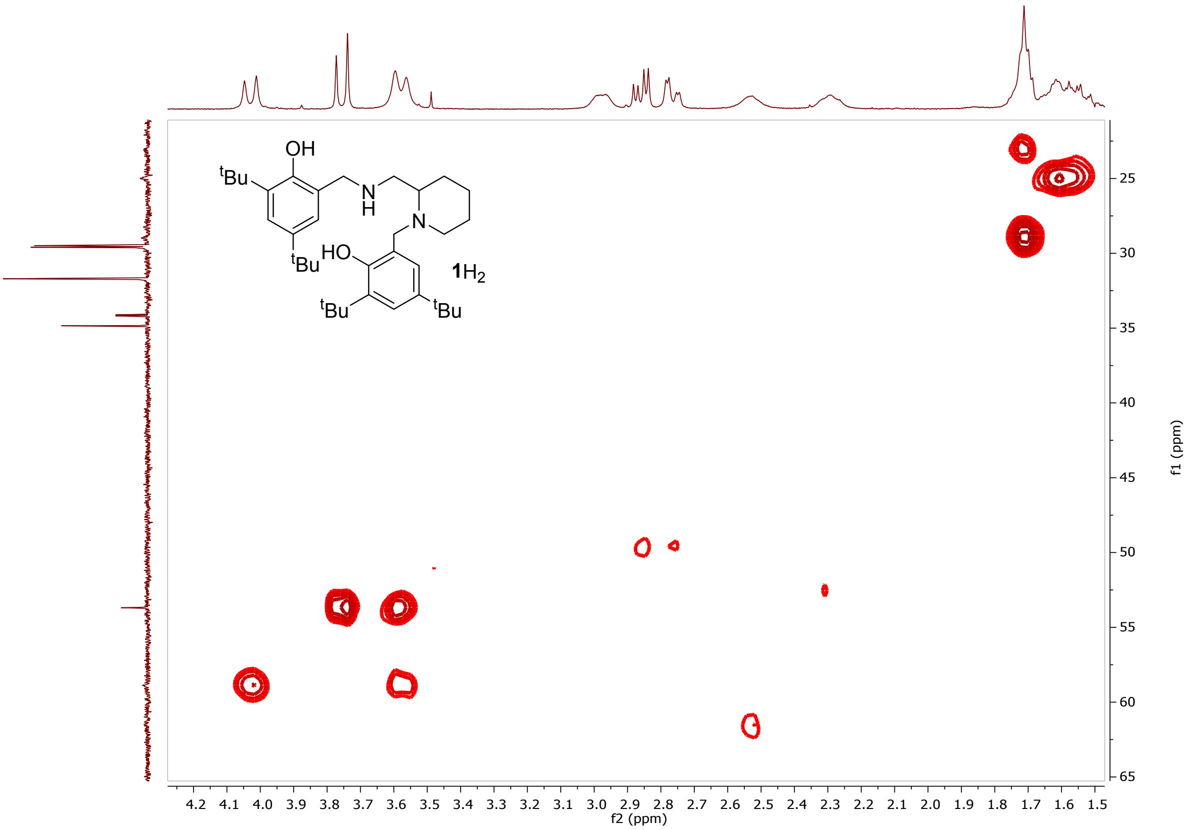

Figure SI3: HSQC NMR ($CDCl_3$) spectra of **1**H_2 showing CH/CH_2 assignments

2H_2: Isolated as a white powder (3.87 g, 8.3 mmol, 83%). ^1H NMR ($CDCl_3$, 400 MHz) δ= 10.91 (s, 2H; ArOH), 7.22 (d, $J = 2.4$ Hz, 1H; ArH), 6.86 (d, $J = 2.4$ Hz, 1H; ArH), 6.84 (s, 1H; ArH), 6.51 (s, 1H; ArH), 4.02 (d, $J = 14.1$ Hz, 1H; $ArCH_2$), 3.68 (d, $J = 13.6$ Hz, 1H; $ArCH_2$), 3.63 (d, $J = 14.1$ Hz, 1H; $ArCH_2$), 3.53 (br d, $J = 13.6$ Hz, 1H; $ArCH_2$), 3.00 (m, 1H; CH_2), 2.83 (m, 2H; CH_2), 2.57 (br s, 1H; CH), 2.34 (m, 1H; CH_2), 2.20 (s, 3H; CH_3), 2.18 (s, 3H; CH_3), 1.72 (m, 3H; CH_2), 1.59 (m, 2H; CH_2), 1.40 (m, 1H; CH_2), 1.37 (s, 9H; $C(CH_3)_3$), 1.31 (s, 9H; $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (CDCl3, 100 MHz) δ=154.1, 153.7, 140.8, 135.9, 130.5, 127.4, 126.4, 124.8, 122.81, 122.80, 121.5, 121.3 (Ar), 61.1 (CH), 58.6, 52.9, 52.5, 49.5 (CH_2), 34.8, 34.2 ($\mathit{C}(CH_3)_3$), 31.7, 29.5 ($C(\mathit{C}H_3)_3$), 28.7, 24.8, 23.0 (CH_2), 20.4, 15.5 (CH_3). ESI-MS (MeOH): Calcd m/z $[C_{30}H_{46}N_2O_2\ Na]^+ = 489.3457$, found m/z = 489.3496.

Synthesis of tertiary amine based salan, 3H_2**.** Secondary amine, **1**H_2, (1.2 g, 2.2 mmol) was dissolved in warm methanol (50ml) and an aqueous solution of formaldehyde (37 wt%, 0.41 ml 5 mmol) was added dropwise. After 2 hours of stirring, solvent was removed and the residue redissolved in a methanol/THF mixture. $NaBH_4$ (0.19 g, 5eq) was then added portionwise and the solution was a stirred for a further 3 hours before being quenched with H_2O (15 ml). The solvent was reduced *in vacuo* and the white precipitate was washed with H_2O (3x 50 ml) and MeOH (50 ml). Isolated as a white powder (0.65 g, 1.15 mmol, 53%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ=11.16 (br s, 1H; ArOH), 10.36 (br s, 1H; ArOH), 7.22 (d, *J* = 2.4 Hz, 1H; ArH), 7.20 (d, *J* = 2.4 Hz, 1H; ArH), 6.83 (d, *J* = 1.8 Hz, 2H; ArH), 4.08 (br m, 1H; $ArCH_2$), 3.70 (d, *J* = 13.3 Hz, 1H; $ArCH_2$), 3.58 (br d, *J* = 13.3 Hz, 2H; $ArCH_2$), 2.74 (br m, 4H; CH_2), 2.37 (m, 1H; CH), 2.25 (s, 3H; NCH_3), 1.84 (br s, 1H; CH_2), 1.57 (br m, 2H; CH_2), 1.49 (br m, 1H; CH_2), 1.42 (s, 9H; $C(CH_3)_3$), 1.41 (s, 10H; $C(CH_3)_3/CH_2$), 1.29(s, 9H; $C(CH_3)_3$), 1.28 (s, 10H; $C(CH_3)_3/CH_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ= 154.5, 153.9, 140.7, 140.4, 135.6, 135.4, 123.4, 123.3, 123.0, 122.6, 121.3, 120.9 (Ar), 63.4 58.3 (CH_2), 42.4 (CH_3) 34.8, 34.2, 34.1 ($\mathit{C}(CH_3)_3$), 31.70, 29.6 ($C(\mathit{C}H_3)_3$) 24.3 (CH_2). Note: CH_2 resonances were weak in ^{13}C NMR, HSQC was used to aid unambiguous identification/assignment. ESI-MS (MeOH): Calcd m/z $[C_{37}H_{60}N_2O_2\ Na]^+$ = 587.4552, found m/z = 587.4518.

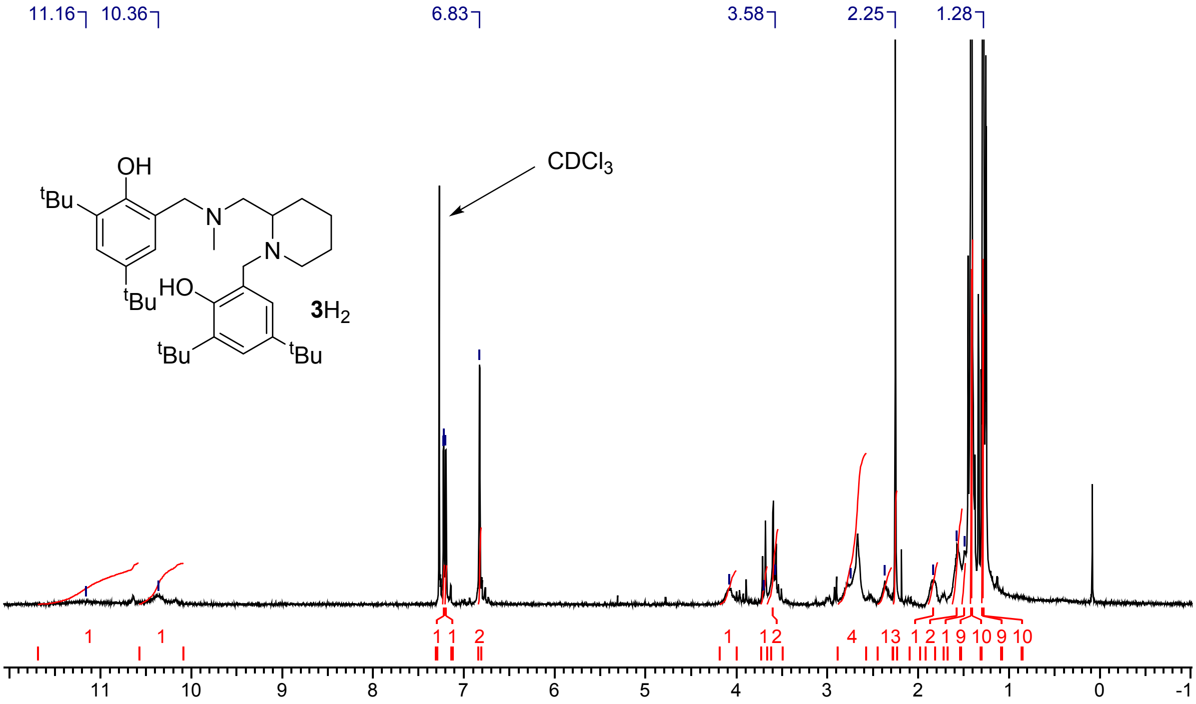

Figure SI4: ^{1}H NMR ($CDCl_3$ 400MHz) spectra of **3**H_2.

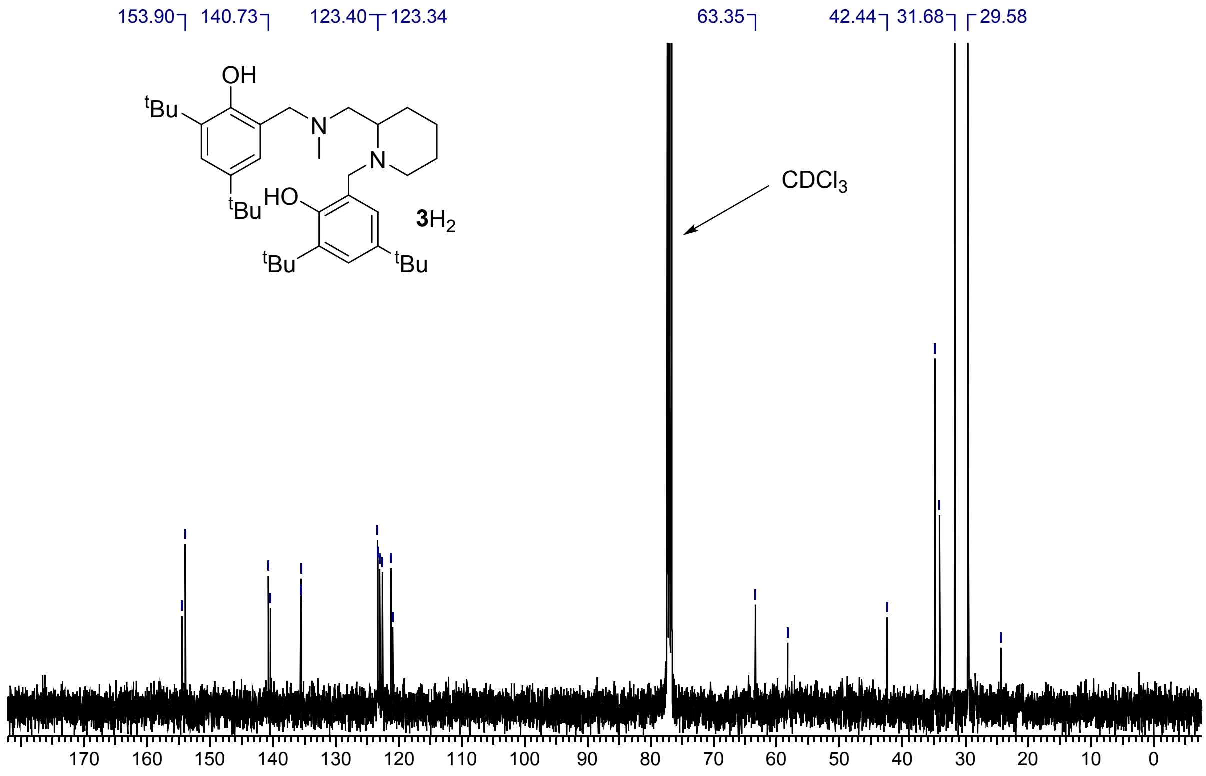

Figure SI5: $^{13}C\{^1H\}$ ($CDCl_3$, 100MHz) spectra of **3**H_2

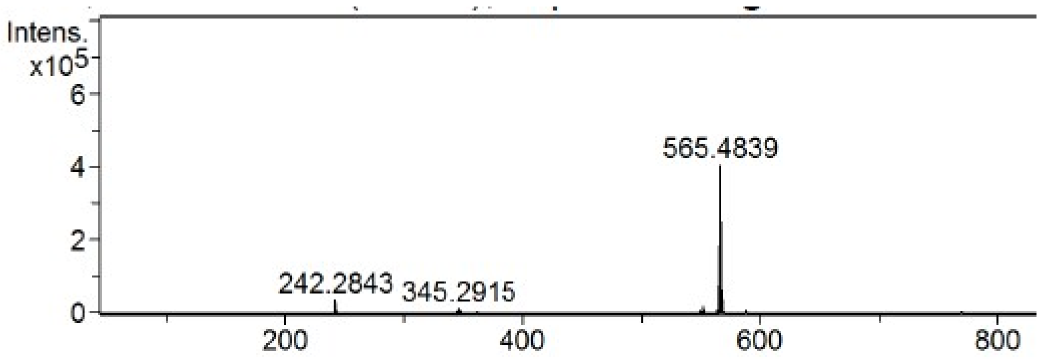

Figure SI6: ESI-TOF spectrum of **3**H_2

Characterisation of bicyclic form (impurity): Small amounts of the cyclised salan impurity was present in **3**H_2 and to a lesser extent **1**H_2. Isolated through washing **A**H_2 or **1**H_2 with hexane. Collected as a white powder. ^1H NMR ($CDCl_3$, 400 MHz) δ = 10.63 (s, 1H; ArOH), 10.17 (br s, 1H; ArOH), 7.25 (d, *J* = 2.5 Hz, 1H; ArH), 7.14 (d, *J*=2.3 Hz, 1H; ArH), 6.80 (d, *J* = 2.4 Hz, 1H; ArH), 6.75 (d, *J* = 2.4 Hz, 1H; ArH), 3.98 (d, *J* = 13.4 Hz, 1H; $ArCH_2$), 3.88 (s, 1H; $ArC\mathit{H}N_2$), 3.52 (d, *J* = 13.4 Hz, 1H; $ArCH_2$), 3.00 (br d, 1H; CH_2), 2.90 (m, 2H; CH_2), 2.53 (m, 1H; CH), 2.10 (dt, *J* = 11.8, 2.8 Hz, 1H; CH_2), 1.87 (m, 2H; CH_2), 1.72 (m, 1H; CH_2), 1.56 (m, 3H; CH_2), 1.44 (s, 9H; $C(CH_3)_3$), 1.33 (s, 9H; $C(CH_3)_3$). 1.25 (s, 9H; $C(CH_3)_3$), 1.24 (s, 9H; $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ =154.2, 154.1, 140.3, 139.9, 136.3, 135.5, 125.4, 124.5, 122.8, 122.8, 120.8, 119.1 (Ar), 89.1 61.8 (CH), 56.2, 55.7, 48.6 (CH_2), 34.9, 34.8, 34.1

(*C*(CH_3)$_3$), 31.7, 29.5, 29.5 (C(*C*H_3)$_3$), 29.1, 24.9, 23.9 (CH_2).ESI-MS (MeOH): Calcd *m/z* $[C_{36}H_{56}N_2O_2Na]^+$ =571.4240 found *m/z* = 571.4225.

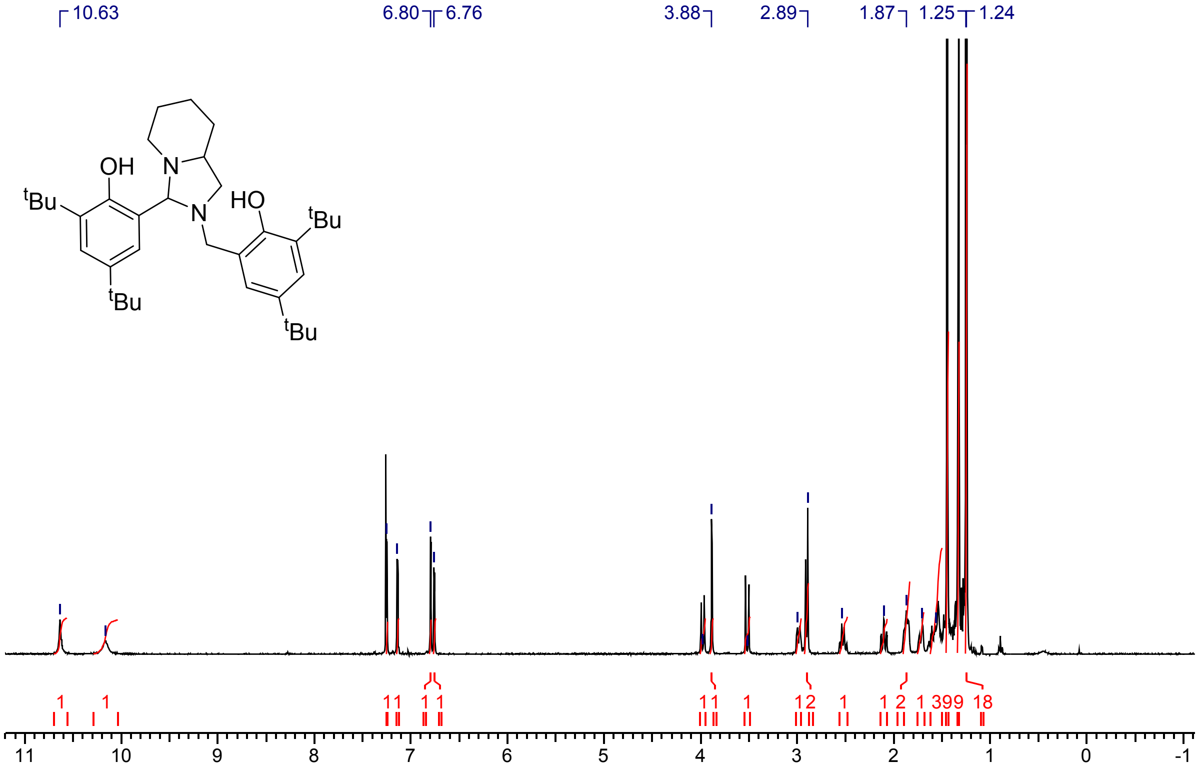

Figure SI7: ^{1}H NMR ($CDCl_3$ 400MHz) spectra of **3**H_2 impurity.

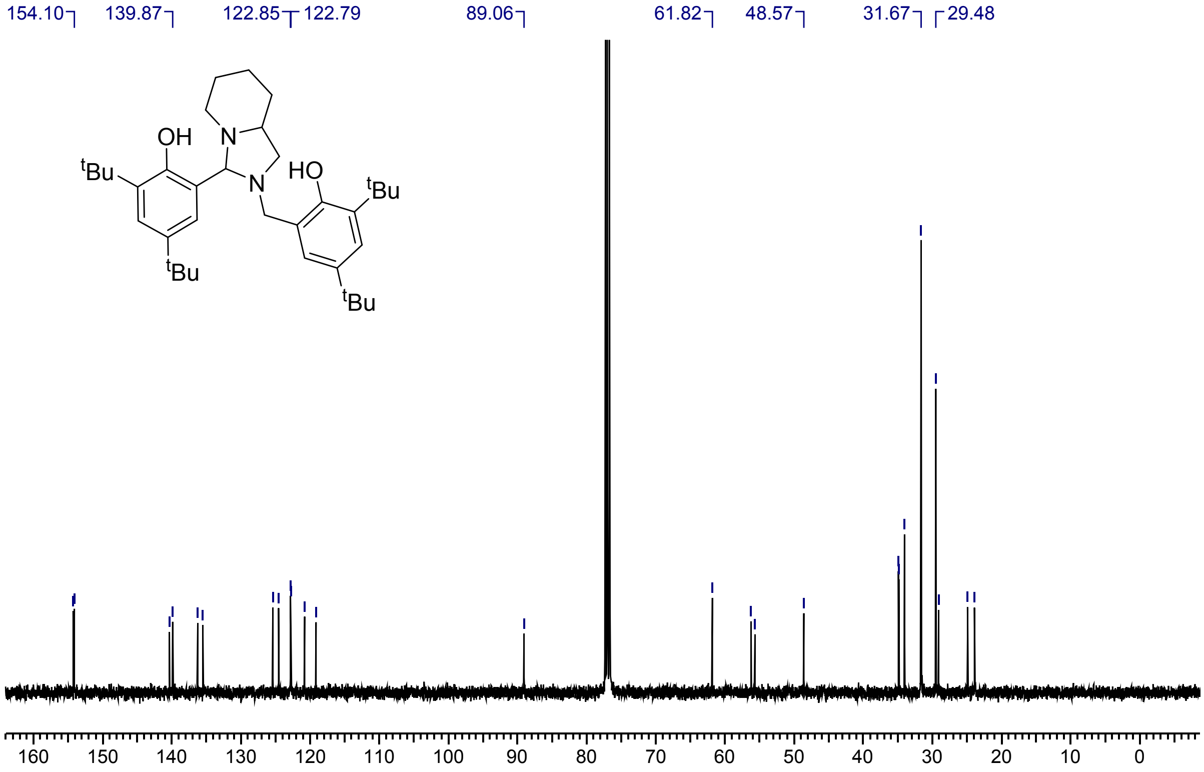

Figure SI8: $^{13}C\{^1H\}$ ($CDCl_{3,}$ 100MHz) spectra of **1/3**H_2 impurity.

SI3. Complex synthesis & Characterisation

Synthesis of aluminium methyl complexes 1/3H_2, (1 mmol) was dissolved in toluene (10ml) and heated to 50°C. $AlMe_3$ (2M, 0.5 ml, 1 mmol) was added dropwise and after complete addition, the solution was heated to 80 °C and stirred for 3 hours. After this time, solvent was removed and the crude product purified.

Al(1)Me: Washed with hexane and isolated as a white powder (0.24 g, 0.41 mmol, 41%). ^{1}H NMR (C_6D_6, 400MHz) δ= 7.68-7.60 (m 2H; ArH), 7.00-6.90 (m 2H; ArH), 3.93-3.66 (m, 2H; CH_2), 3.54-3.26 (m, 1H; CH_2), 3.18-2.76 (m, 2H; CH/CH_2), 2.72-2.03 (m, 3H; CH/CH_2), 1.96-1.80 (m, 18H; ($C(CH_3)_3$), 1.74-1.61 (m, 3H; CH_2), 1.53-1.43 (m, 20H; (CH_2/$C(CH_3)_3$), 1.08-0.93 (m, 1H; CH_2), 0.70-0.41 (m, 2H; CH_2), -0.52- -0.63 (m, 3H; $AlCH_3$). ^{13}C NMR (100 MHz, C_6D_6) δ = 158.7, 158.0, 157.8, 157.0, 139.3, 139.5, 139.0, 138.8, 138.6, 138.4, 138.2, 138.2, 137.8, 137.4, 136.8, 136.6, 129.3, 128.6, 128.3, 124.6, 124.4, 124.3, 124.3, 124.0, 123.8, 123.8, 123.70, 123.6, 123.1, 123.00, 122.9, 122.6, 122.0, 121.5, 121.1, 120.5, 118.2 (Ar), 58.2, 57.9 (CH), 57.2 57.0 (CH_2), 54.4 (CH), 53.6, 51.8, 49.7, 49.0, 48.4, 43.5, 41.3 (CH_2), 36.0, 35.9, 35.9, 35.8, 35.7, 35.6, 34.4, 34.34, 34.33, 34.31, 34.29 ($\mathit{C}(CH_3)_3$), 32.4, 32.3, 32.28, 32.25, 32.2, 30.8, 30.7, 30.6, 30.6, 30.5, 30.3 ($C(\mathit{C}H_3)_3$), 23.9, 20.3, 19.9, 18.9, 18.4, 18.2, 18.0, 17.5 (CH_2), -5.5, 7.6, -11.0 (AlMe).

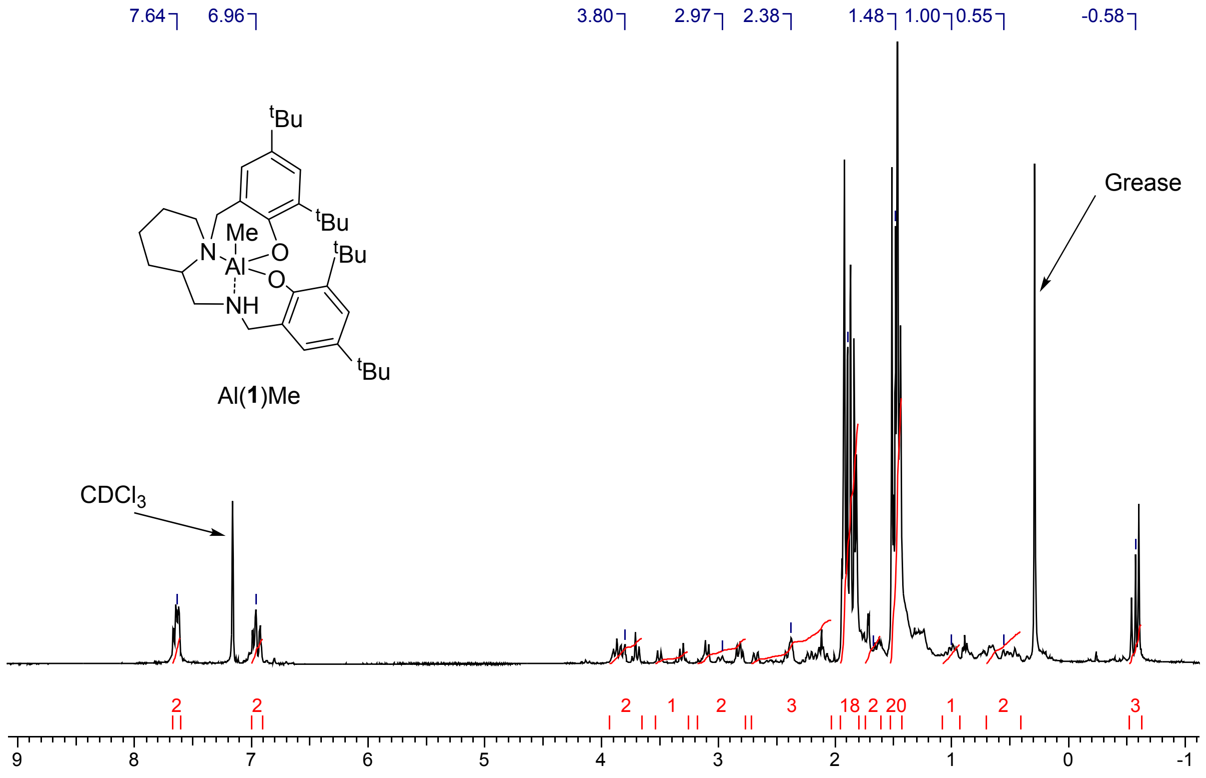

Figure SI9: ^{1}H NMR (C_6D_6, 400MHz) spectra of Al(**1**)Me

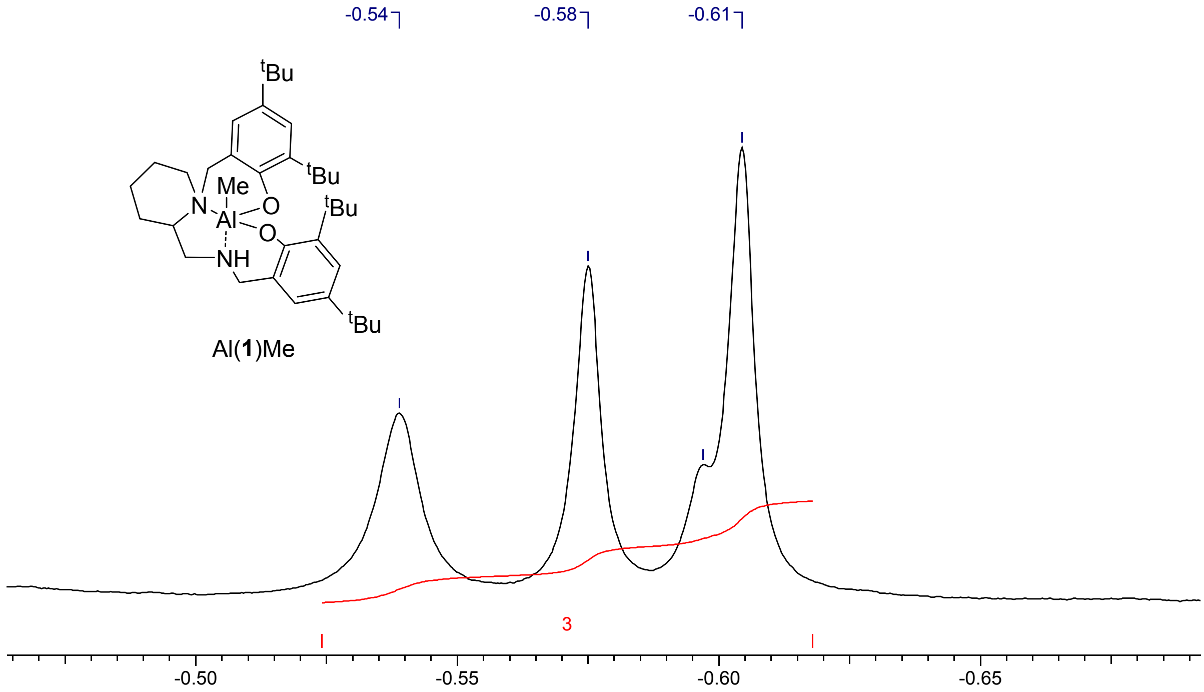

Figure SI10: ^{1}H NMR (C_6D_6,, 400MHz) spectra of Al(**1**)Me showing AlMe region

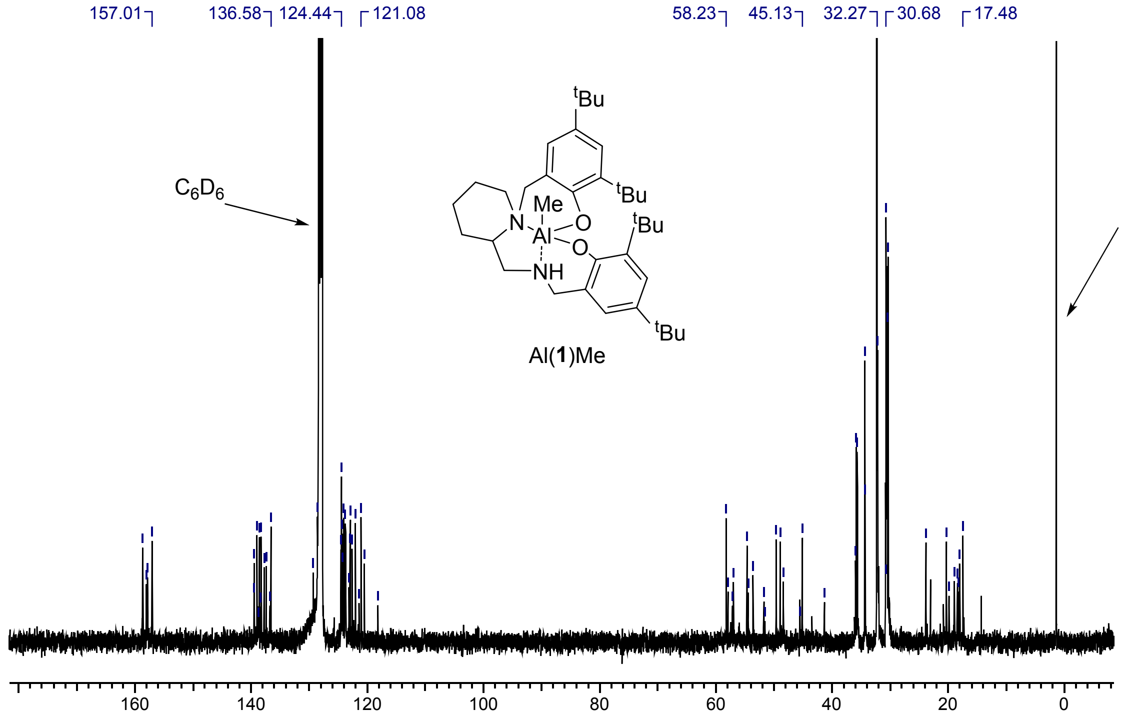

Figure SI11: ^{13}C{^{1}H} NMR (C_6D_6, 100MHz) spectra of Al(**1**)Me.

Al(3)Me: Recrystallised from cold toluene/hexane(0.21 g, 0.35 mmol, 35%). ^{1}H NMR (C_6D_6, 400MHz) δ= 7.67-7.60 (m 2H; ArH), 7.02-6.81 (m 2H; ArH), 4.32-391 (m, 1H; CH_2), 3.90-3.64 (m, 1H; CH_2), 3.54-3.11 (m, 1H; CH_2), 2.84-2.45 (m, 3H; CH/CH_2), 2.33-2.09 (m, 2H; CH_2), 1.94-1.85 (m, 12H; $NCH_3/(C(CH_3)_3)$, 1.83-1.70 (m, 9H; $(CH_3)_3)$, 1.49-1.43 (m, 19H; $(CH_2/C(CH_3)_3)$, 1.42-1.23 (m, 3H;

CH_2), 1.15-0.96 (m, 1H; CH_2),0.73-0.50 (m, 2H; CH_2), -0.43- -0.63 (m, 3H; $AlCH_3$). ^{13}C NMR (100 MHz, C_6D_6) δ = 158.5, 158.1, 157.5, 156.9, 139.4, 138.9, 138.6, 138.5, 138.4, 137.6, 137.0, 125.1, 124.8, 124.4, 124.3, 124.1, 124.0, 123.8, 123.8, 121.5, 120.3, 119.9 (Ar), 65.1, 62.2, 61.0, 59.6, 56.8 (CH_2), 56.6 (CH), 49.7 (CH_2), 46.1 (CH_3), 45.7 (CH_2), 44.1 (CH_3), 43.2 (CH_2), 36.1, 36.0, 36.96, 35.88, 34.68, 34.65, 34.6 ($C(CH_3)_3$), 32.7, 32.6, 31.0, 30.9, 30.8, 30.7 ($C(CH_3)_3$), 24.1, 20.6, 18.7, 18.5, 17.7 (CH_2), -10.2, -12.4 (AlMe).

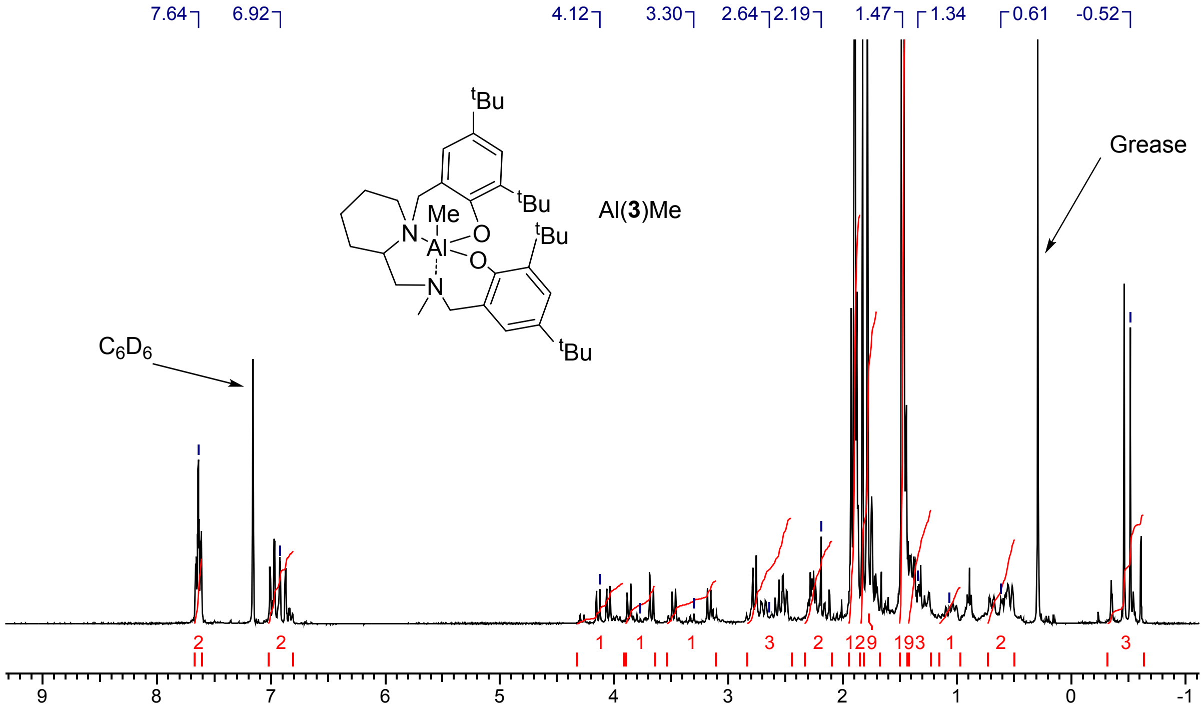

Figure SI12: ^1H NMR (C_6D_6, 400MHz) spectra of Al(**3**)Me

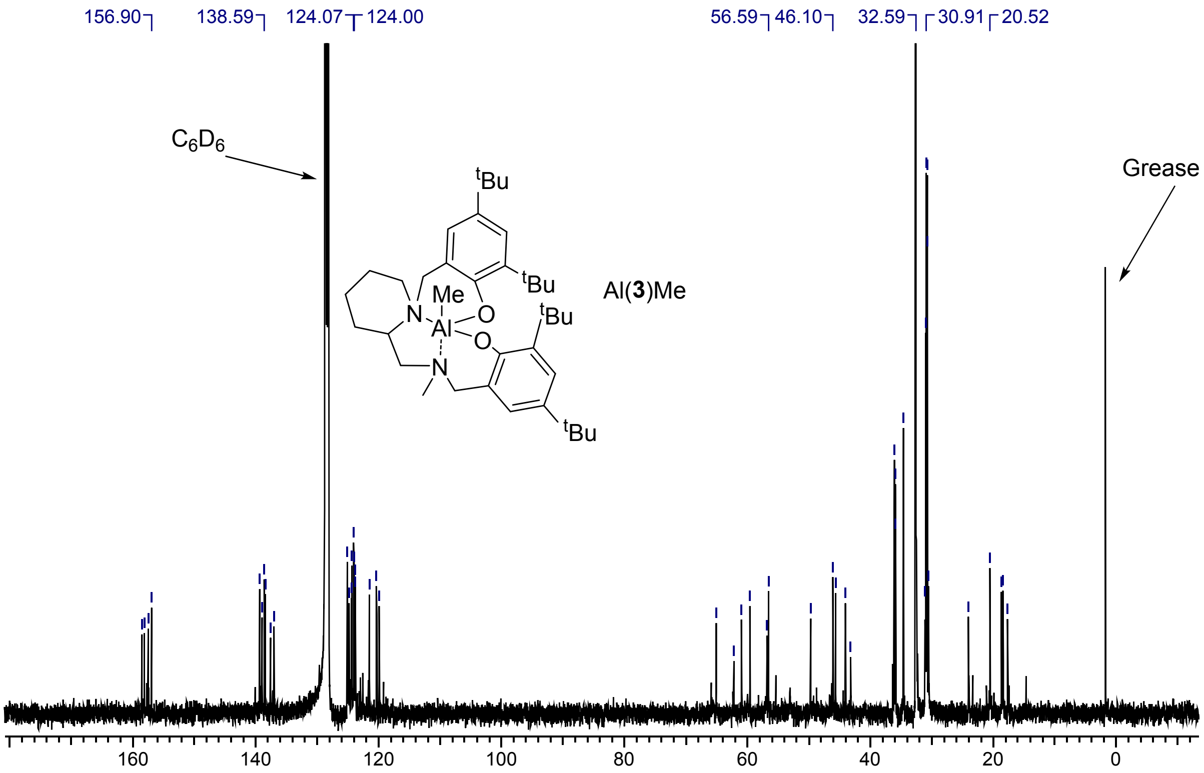

Figure SI13: $^{13}C\{^1H\}$ NMR (C_6D_6, 100MHz) spectra of Al(**3**)Me.

Synthesis of aluminium complexes Al(1-2)O^{i}Pr. Ligand, **1-2**H_2, (1 mmol) was dissolved in toluene (10ml) and heated to 50°C. $AlMe_3$ (2M, 0.5 ml, 1 mmol) was added dropwise and after complete addition, the solution was heated to 80 °C and stirred for 2 hours. The temperature was then reduced to 50°C and ^{i}PrOH (0.15ml, 2eq, 2 mmol) was added dropwise. Temperature was then adjusted to 80 °C for one hour after which the solvent was removed *in vacuo* and the product recrystallised from hexane/toluene mixture.

Al(1)O^{i}Pr: Isolated as clear crystals (0.31 g, 0.49 mmol, 49%). ^{1}H NMR ($CDCl_3$, 400MHz) δ = 7.30 (d, *J*= 2.4 Hz, 1H; ArH), 7.27 (1H; ArH), 6.86 (d, *J*= 2.3 Hz, 1H; ArH), 6.81 (d, *J*= 2.2 Hz, 1H; ArH), 4.61 (dd, *J*= 13.1, 3.1 Hz, 1H; $ArCH_2$), 4.28 (d, *J*= 13.2 Hz, 1H; $ArCH_2$), 4.19 (sept, *J*= 5.9 Hz, 1H; $OCH(CH_3)_2$) 4.10 (d, *J*= 13.2 Hz, 1H; $ArCH_2$), 3.64 (dd, *J*= 13.1, 2.1 Hz, 1H; $ArCH_2$), 3.34 (br d, *J*= 13.8 Hz, 1H; NH), 3.05 (m, 1H; CH), 2.93 (m, 2H; CH_2), 2.59 (dt, *J*= 12.0, 4.3 Hz, 1H; CH_2), 2.46 (br t, *J*= 13.5 Hz, 1H; CH_2), 2.21 (m, 1H; CH_2), 1.59 (m, 1H; CH_2), 1.55 (s, 9H; $C(CH_3)_3$), 1.52 (m, 1H; CH_2), 1.48 (m, 1H; CH_2), 1.42 (s, 9H; $C(CH_3)_3$), 1.32 (m, 19H; $C(CH_3)_3/CH_2$), 1.21 (m, 1H; CH_2), 1.08 (d, *J*= 5.7 Hz, 3H; $OCH(CH_3)_2$), 0.94 (d, *J*= 5.7 Hz, 3H; $OCH(CH_3)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ = 158.1, 156.9, 138.5, 138.1, 137.5, 136.3, 124.1, 123.8, 123.7, 123.2, 120.7, 118.3 (Ar), 62.1 ($OCH(CH_3)_2$), 58.8 (CH), 57.0, 51.2, 44.3, 41.3 (CH_2), 35.3, 35.2, 34.0, 33.9 ($C(CH_3)_3$), 31.9, 31.8, 30.6, 29.9 ($C(CH_3)_3$), 28.4, 27.9 ($OCH(CH_3)_2$), 20.5, 18.8, 18.2 (CH_2). Note: ArH resonance at 7.27

coincides with residual solvent resonance ($CDCl_3$), doublet splitting assumed. CH_3 resonance of isopropoxide coincides with residual solvent resonance (Hexane). Elemental analysis ($C_{39}H_{63}AlN_2O_3$) calcd in %: C, 73.78; H 10.00; N, 4.41. Found: C, 71.20; H 10.50; N, 4.41.

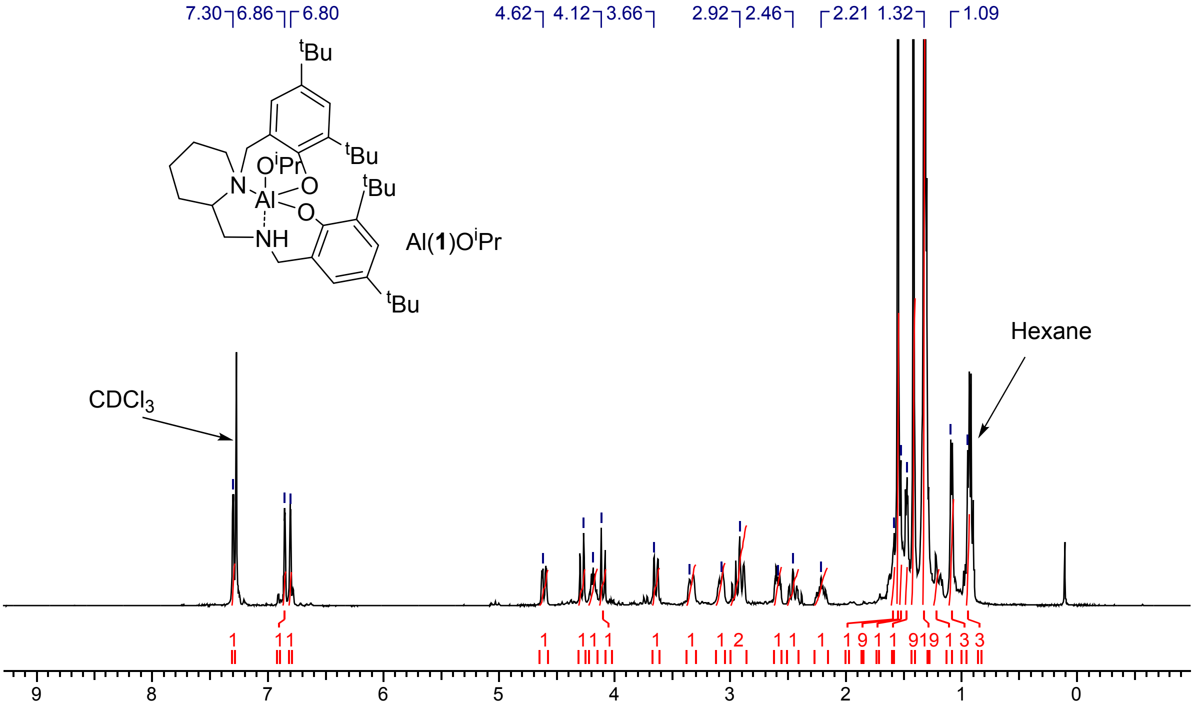

Figure SI14: ^{1}H NMR ($CDCl_3$, 400MHz) spectra of Al(**1**)O^{i}Pr.

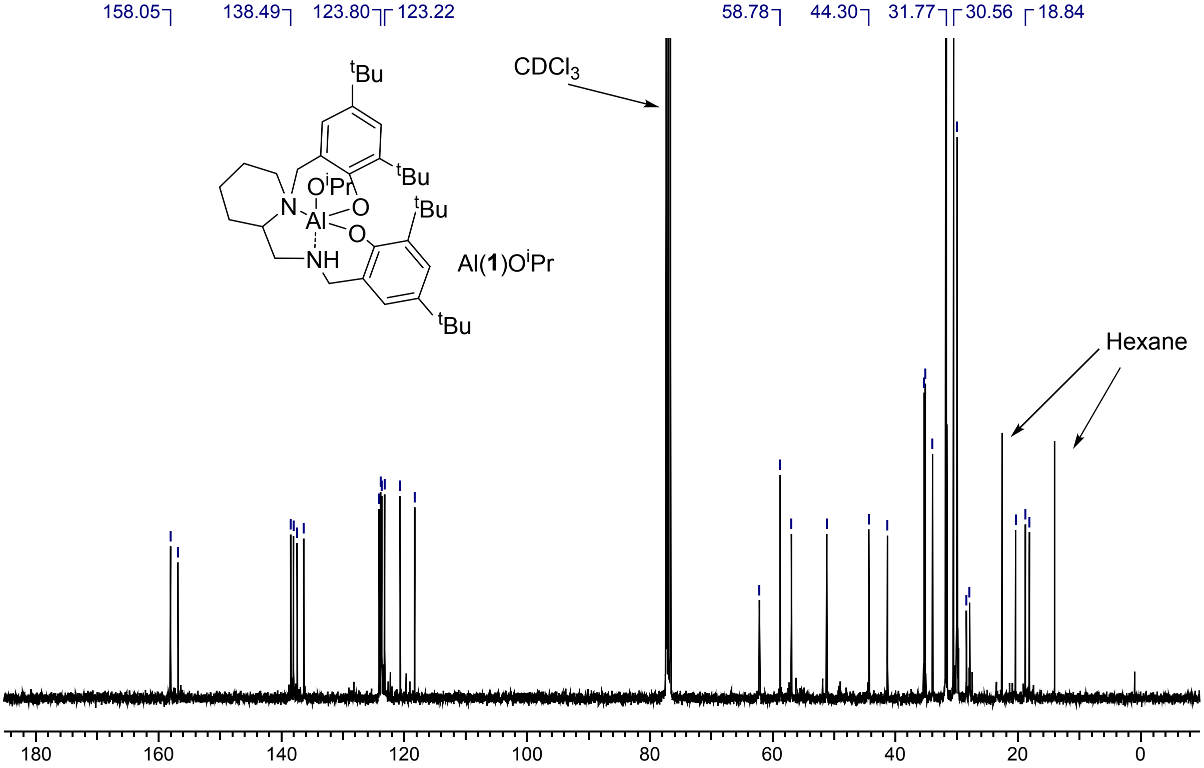

Figure SI15: $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100MHz) spectra of Al(**1**)O^{i}Pr.

Al(2)O^{i}Pr: Isolated as clear crystals (0.31 g, 0.61 mmol, 61%). ^{1}H NMR ($CDCl_3$, 400MHz) δ =7.29 (d, *J*= 2.4 Hz, 1H; ArH), 6.85 (s, 1H; ArH), 6.83 (d, *J*= 2.3 Hz, 1H; ArH), 6.64 (s, 1H; ArH), 4.47 (dd, *J*= 12.9, 3.1 Hz, 1H; $ArCH_2$),), 4.24 (sept, *J*= 5.9 Hz, 1H; $OC\mathit{H}(CH_3)_2$) 4.18 (d, *J*= 12.8 Hz, 1H; $ArCH_2$), 4.05 (d, *J*= 12.8 Hz, 1H; $ArCH_2$), 3.54 (dd, *J*= 13.9, 2.4 Hz, 1H; $ArCH_2$), 3.45 (m, 1H; NH), 3.09 (m, 1H; CH), 2.83 (q, *J*= 12.8 Hz 1H; CH_2), 2.68 (br d, *J*= 14.7 Hz, 1H; CH_2), 2.61 (dt, *J*= 12.4, 5.0 Hz, 1H; CH_2), 2.20 (s, 3H; CH_3), 2.16 (m, 2H; CH_2), 2.07 (s, 3H; CH_3), 1.58 (m, 1H; CH_2), 1.55 (s, 9H; $C(CH_3)_3$), 1.50 (m, 1H; CH_2), 1.40 (m, 1H; CH_2), 1.30 (s, 9H; $C(CH_3)_3$), 1.25 (m, 1H; CH_2), 1.10 (m, 4H; $CH_2/OCH(C\mathit{H}_3)_2$), 0.97 (d, *J*= 5.1 Hz, 3H; $OCH(C\mathit{H}_3)_2$). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ= 158.1, 156.2, 137.3, 136.3, 131.3, 128.5, 127.1, 125.2, 124.0, 123.3, 120.2, 118.5 (Ar), 62.4 ($O\mathit{C}H(CH_3)_2$), 57.8 (CH), 56.0, 50.4, 44.2, 39.3 (CH_2), 35.1, 34.0, ($\mathit{C}(CH_3)_3$), 31.9, 29.8 ($C(\mathit{C}H_3)_3$), 28.4, 27.9 ($OCH(\mathit{C}H_3)_2$), 20.4 (CH_3), 20.0, 18.5, 17.7 (CH_2), 17.2 (CH_3). Elemental analysis ($C_{33}H_{51}AlN_2O_3$) calcd in %: C, 71.97; H 9.33; N, 5.09. Found: C, 69.78; H 9.12; N, 4.93.

Synthesis of aluminium complexes Al(A)OBn. Ligand, AH_2, (0.548g, 1 mmol) was dissolved in toluene (10ml) and heated to 50°C. $AlMe_3$ (2M, 0.5 ml, 1 mmol) was added dropwise and after complete addition, the solution was heated to 80 °C and stirred for 2 hours. The temperature was then reduced to 50°C and BnOH (0.10ml, 1eq, 1 mmol) was added dropwise. Temperature was then adjusted to 80 °C for one hour after which the solvent was removed *in vacuo* and the product recrystallised from hexane/toluene mixture. Isolated as yellow crystals (%) ^{1}H NMR ($CDCl_3$, 400MHz) δ = 8.36 (s, 1H; ArCHN),7.59 (d, *J* = 2.5 Hz 1H; ArH), 7.29 (d, *J* = 2.5 Hz, 1H; ArH), 7.23 (m, 4H; ArH), 7.12 (m, 1H; ArH), 6.92 (d, *J* = 2.5 Hz, 1H; ArH), 6.93 (d, *J* = 2.5 Hz, 1H; ArH), 4.92 (d, *J* = 13.6 Hz, 1H; $ArCH_2$), 4.79 (d, *J* = 13.6 Hz, 1H; $ArCH_2$), 3.92 (d, *J* = 12.2 Hz, 1H; $ArCH_2$), 3.82 (t, *J* = 13.4 Hz, 1H; CH_2), 3.72 (d, *J* = 12.2 Hz, 1H; $ArCH_2$), 3.48 (m, 2H; CH/CH_2), 3.26 (dt, *J* = 13.8, 2.6 Hz, 1H; CH_2), 2.77 (br d, *J* = 14.5 Hz, 1H; CH_2), 1.91 (m, 1H; CH_2), 1.80 (m, 1H; CH_2), 1.71 (m, 1H; CH_2), 1.57 (s, 9H $C(CH_3)_3$), 1.51 (s, 9H $C(CH_3)_3$), 1.48 (m, 1H; CH_2), 1.34 (s, 9H $C(CH_3)_3$), 1.32 (s, 9H $C(CH_3)_3$), 1.23 (m, 1H; CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 173.7 (ArCHN) 165.8, 156.7, 146.6, 140.8, 138.2, 137.7, 137.3, 132.1, 127.5, 127.3, 127.1, 126.3, 125.4, 123.5, 123.4, 120.8, 117.5 (Ar), 65.4 (CH_2), 57.9 (CH), 56.4, 48.9, 44.7 (CH_2), 35.4, 35.2, 34.0, 33.9 ($\mathit{C}(CH_3)_3$), 31.8, 31.3, 30.1, 29.8 ($C(\mathit{C}H_3)_3$), 23.5, 20.8, 17.5 (CH_2). Elemental analysis ($C_{43}H_{61}AlN_2O_3$) calcd in %: C, 75.85; H 9.03; N, 4.11. Found: C, 75.44; H 9.04; N, 4.12.

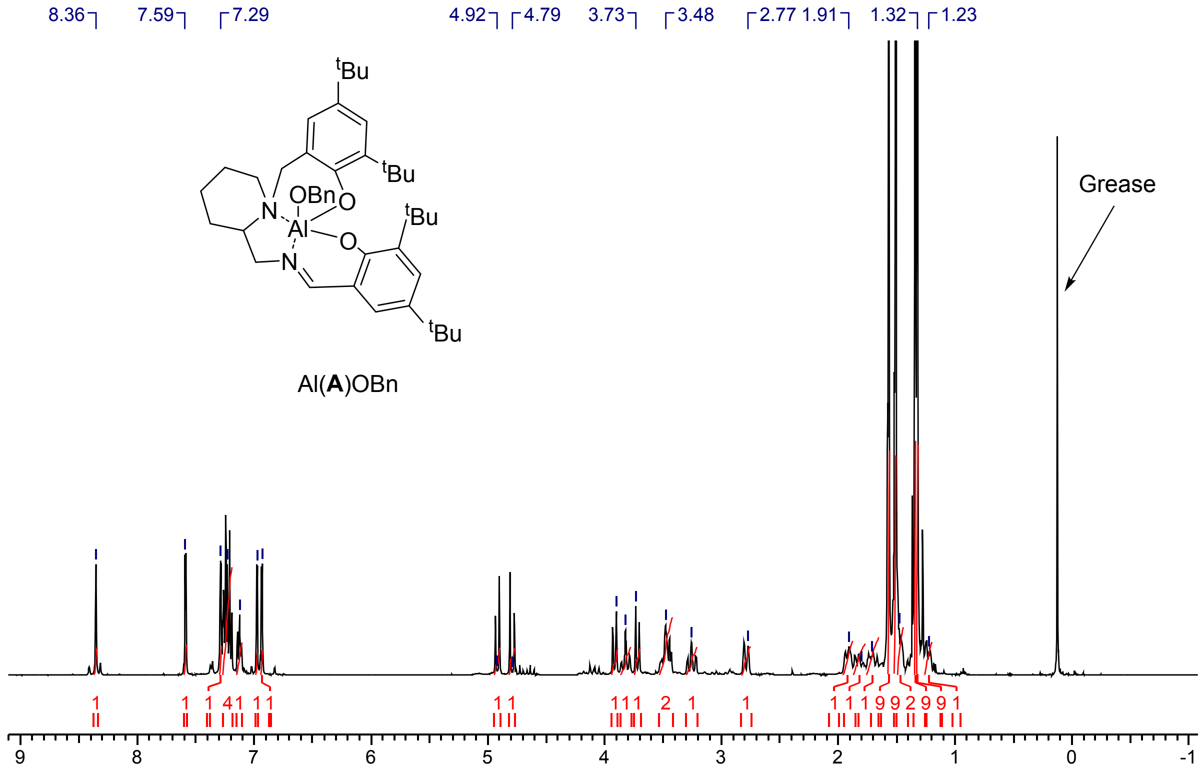

Figure SI16: ^{1}H NMR ($CDCl_3$, 400MHz) spectra of Al(**A**)OBn.

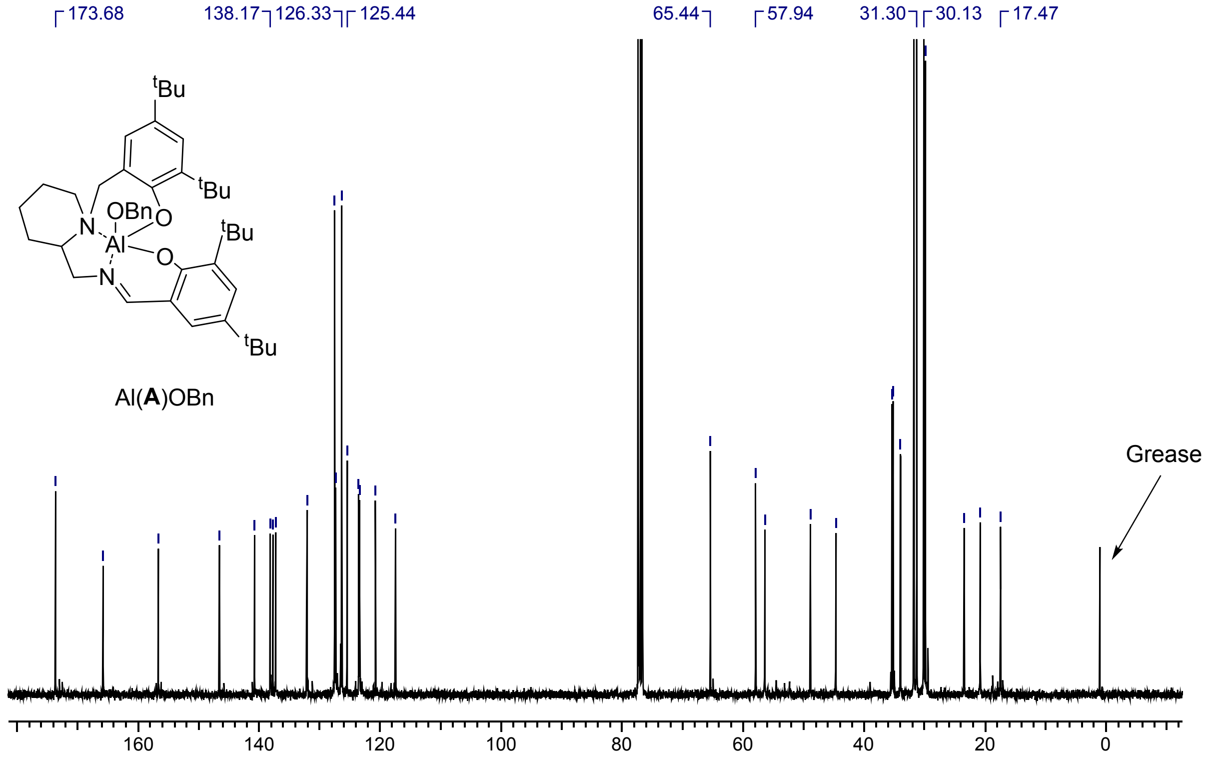

Figure SI17: $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100MHz) spectra of Al(**A**)OBn

4. Selected polymer characterisation

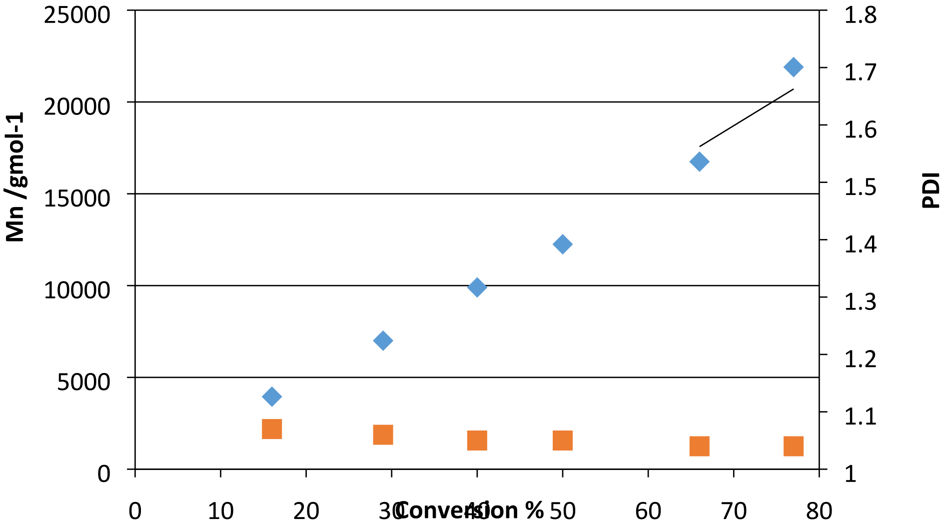

Figure SI18: M_n and M_w/M_n against conversion for the solution polymerisation of *rac*-LA with Al(**1**)O^{i}Pr (80°C, toluene, [LA]:[Al(**1**)O^{i}Pr]=100:1).

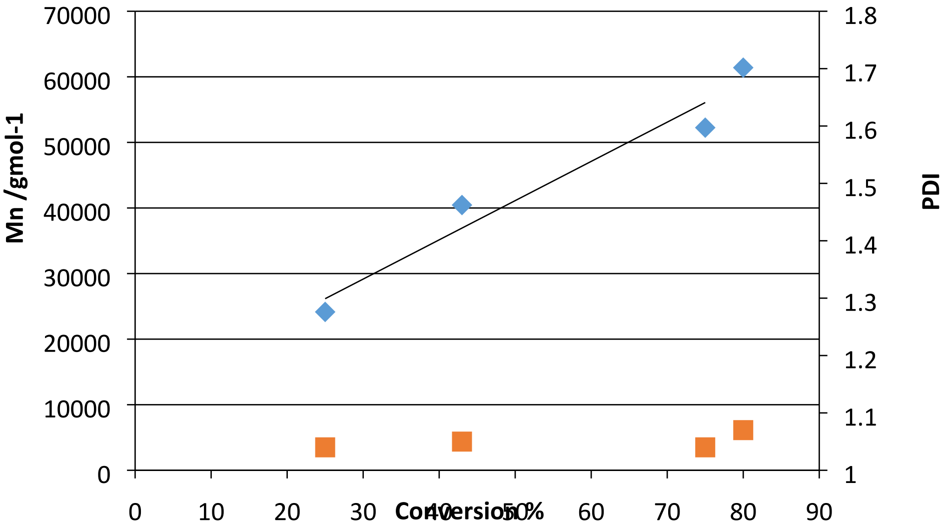

Figure SI19: M_n and M_w/M_n against conversion for the solvent free polymerisation of *rac*-LA with Al(**1**)O^{i}Pr (130°C, [LA]:[Al(**1**)O^{i}Pr]=300:1).

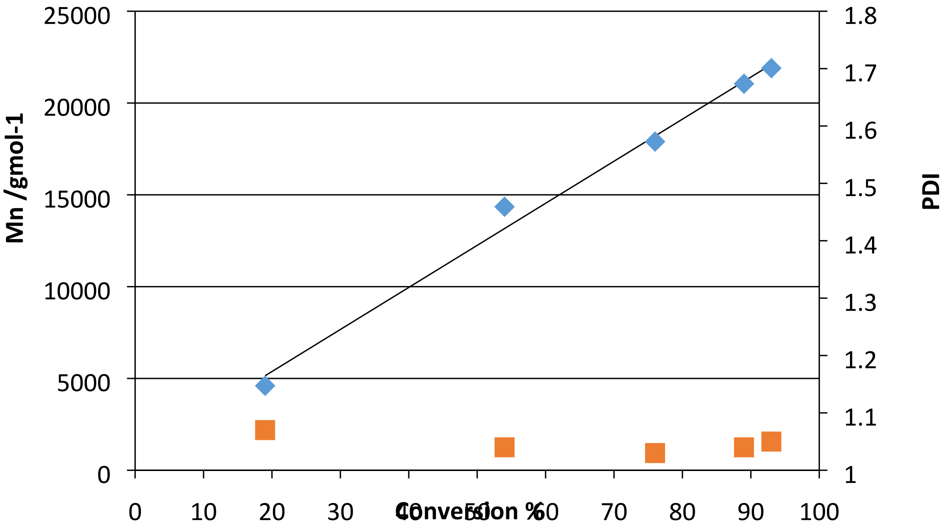

Figure SI20: M_n and M_w/M_n against conversion for the solution polymerisation of *rac*-LA with Al(**2**)O^{i}Pr (80°C, toluene, [LA]:[Al(**2**)O^{i}Pr]=100:1).

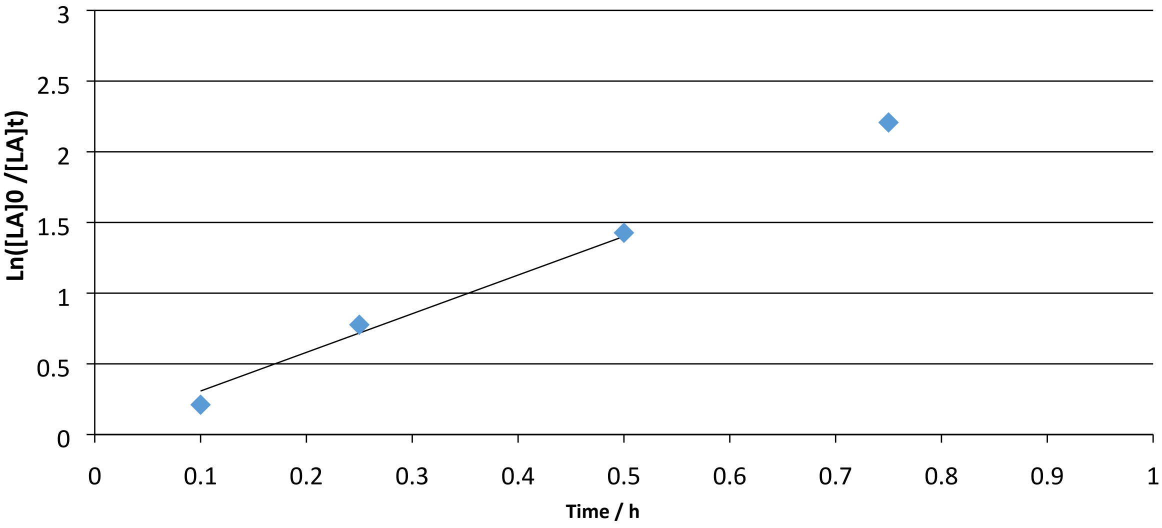

Figure SI21: Semi-logarithmic plot for the solution polymerisation of Al(**2**)O^{i}Pr. (Toluene, 80°C, [LA]:[Al(**2**)O^{i}Pr] = 100:1).

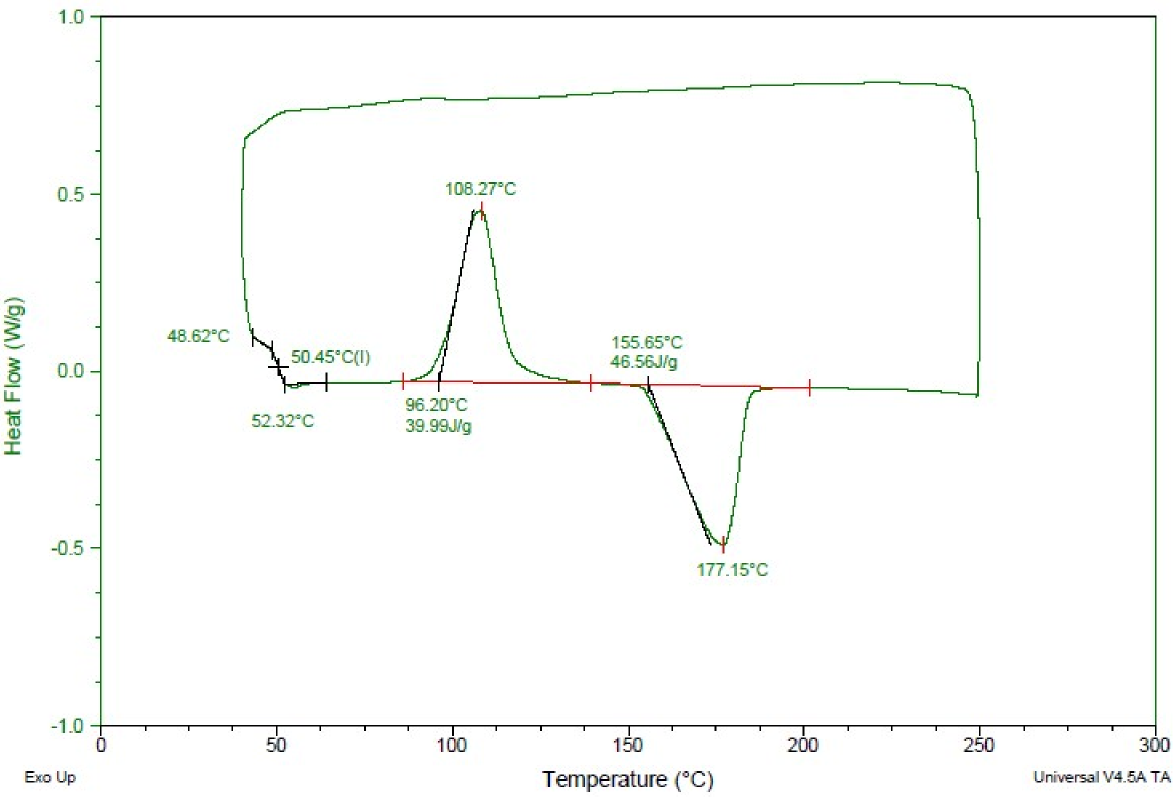

Figure SI22: DSC trace of PLA from Al(**1**)O^{i}Pr (table 2, entry 6; CH_2Cl_2, 25°C).

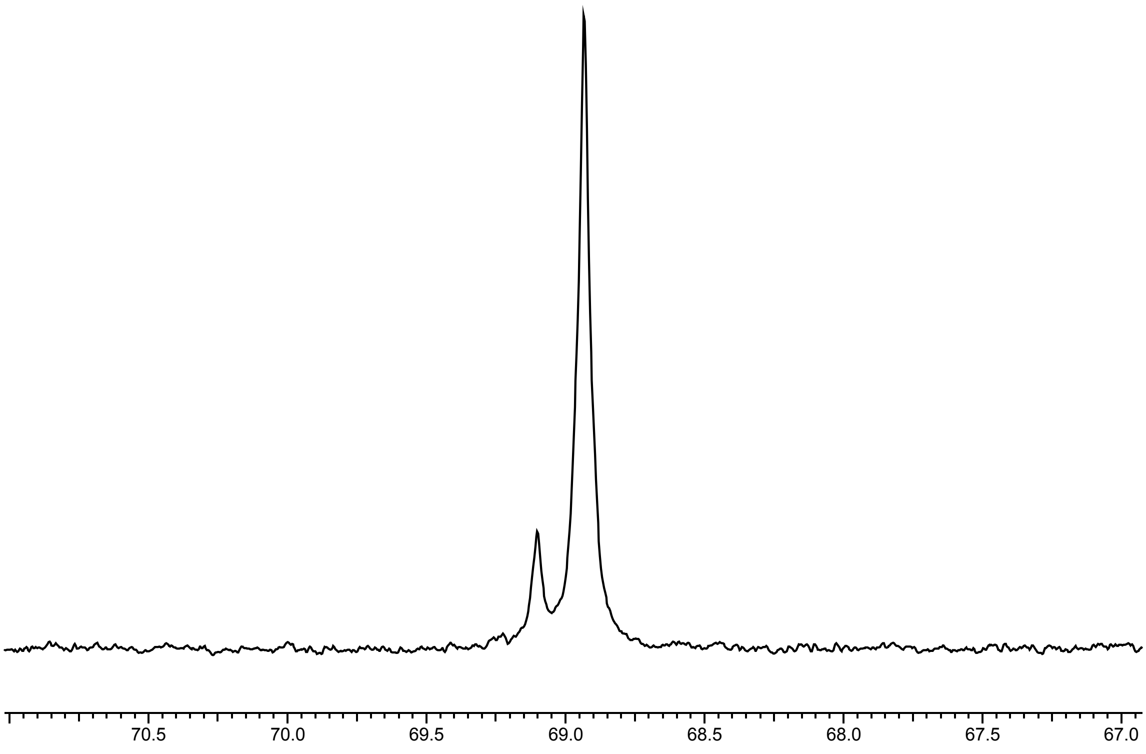

Figure SI23: $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100MHz) spectra of methine region for PLA from Al(**1**)O^{i}Pr (table 3, entry 1, solvent free 130 °C).

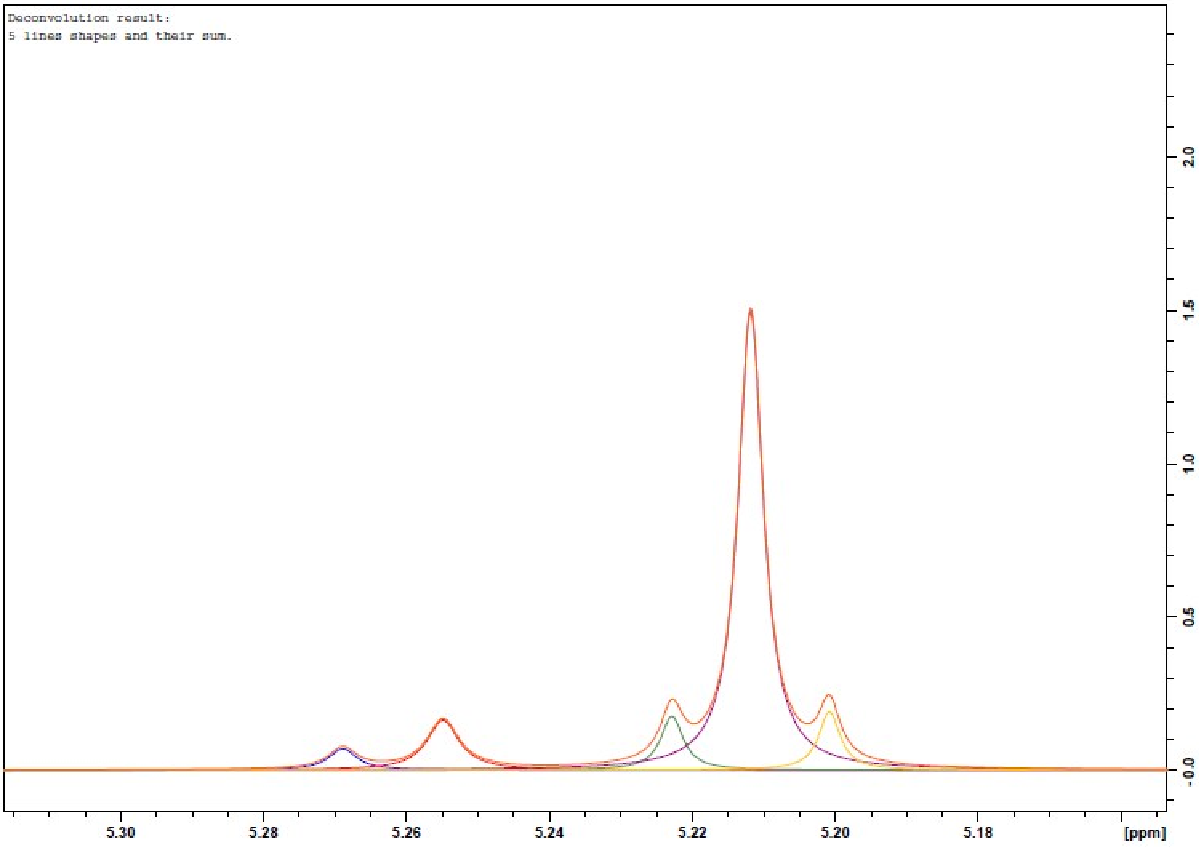

Figure SI24: ^{1}H NMR ($CDCl_3$, 400MHz) decoupled and deconvoluted spectrum of PLA synthesised from solvent free polymerisation with Al(**1**)O^{i}Pr (table 3, entry 2).

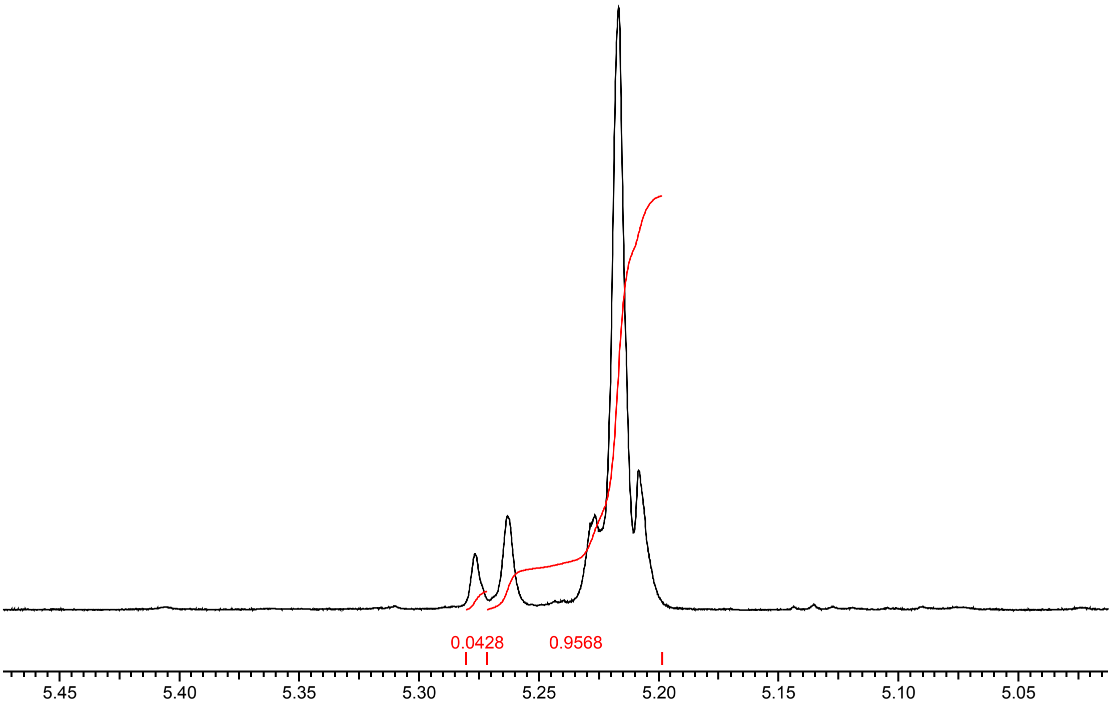

Figure SI25: ^{1}H NMR ($CDCl_3$, 400MHz) decoupled spectrum of PLA synthesised from solution polymerisation with Al(**1**)O^{i}Pr (table 2, entry 4).

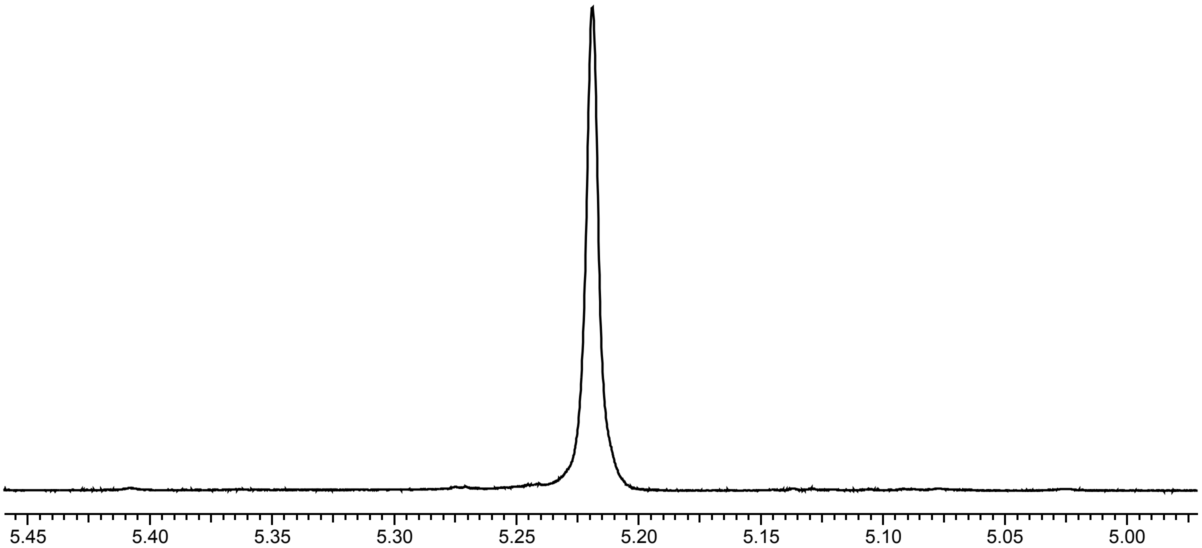

Figure SI26: ^1H NMR ($CDCl_3$, 400MHz) decoupled spectrum of PLLA synthesised from solution polymerisation with Al(**1**)O^{i}Pr (table 2, entry 5).

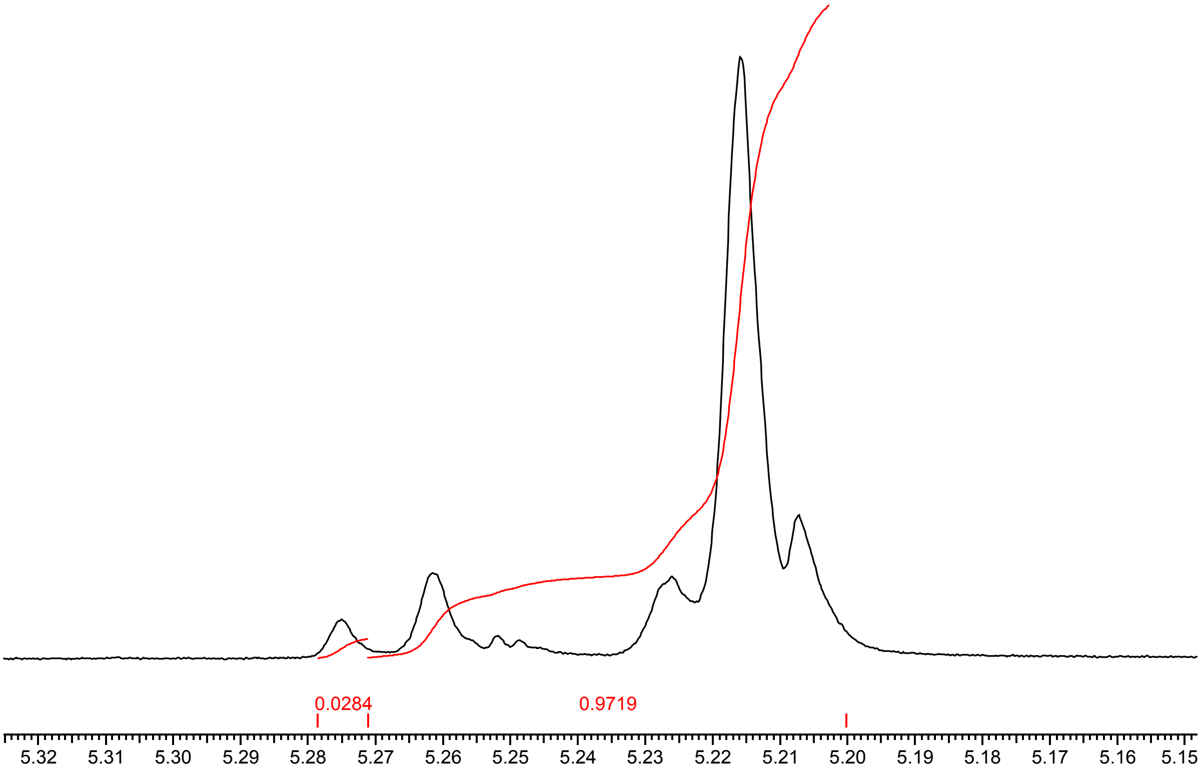

Figure SI27: ^1H NMR ($CDCl_3$, 400MHz) decoupled spectrum of PLA synthesised from the solvent free polymerisation with Al(**1**)O^{i}Pr (table 3, entry 1).

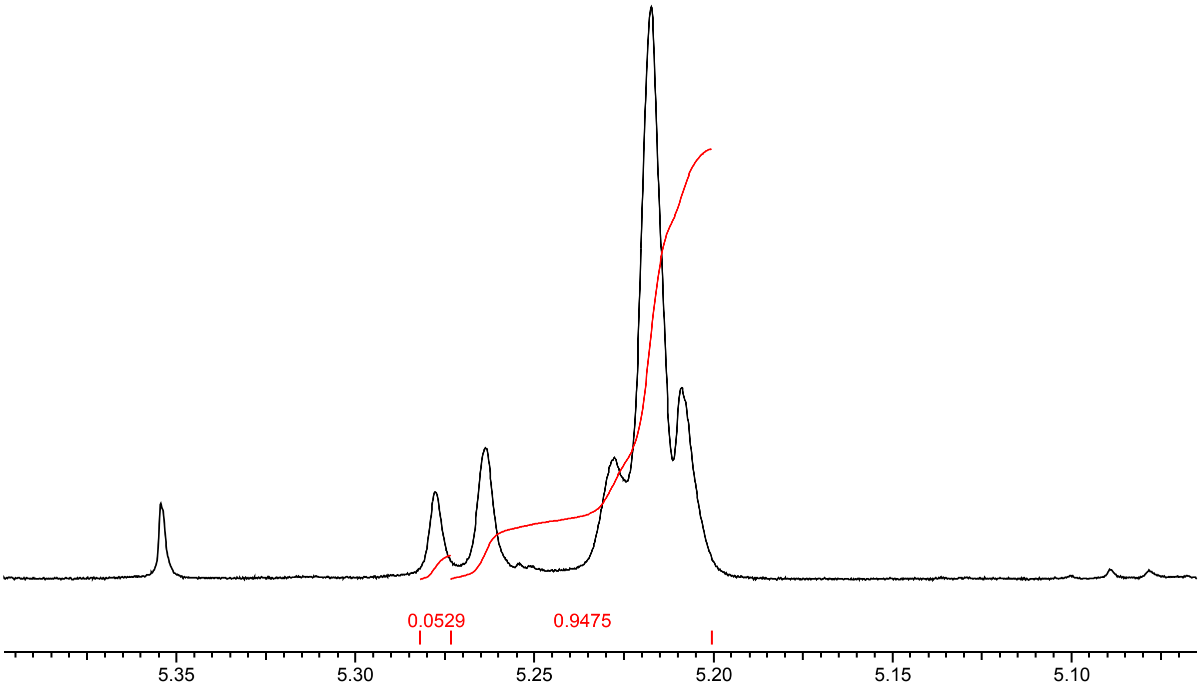

Figure SI28: ^{1}H NMR ($CDCl_3$, 400MHz) decoupled spectrum of PLA synthesised from the solvent free polymerisation with Al(**2**)O^{i}Pr (table 3, entry 8).

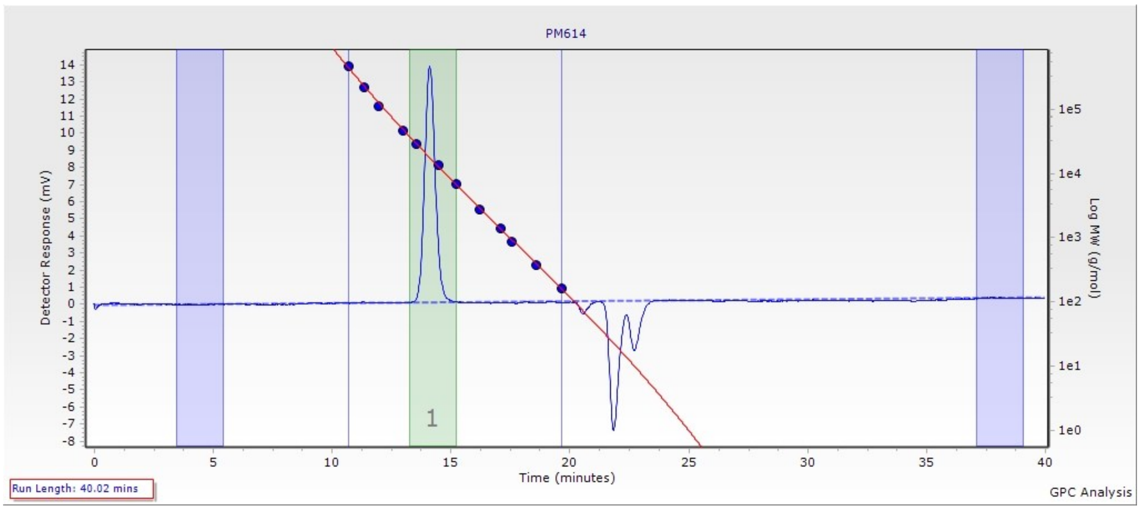

Figure SI29: GPC trace of PLA prepared by solution polymerisation with Al(**1**)O^{i}Pr (table 2, entry 4).

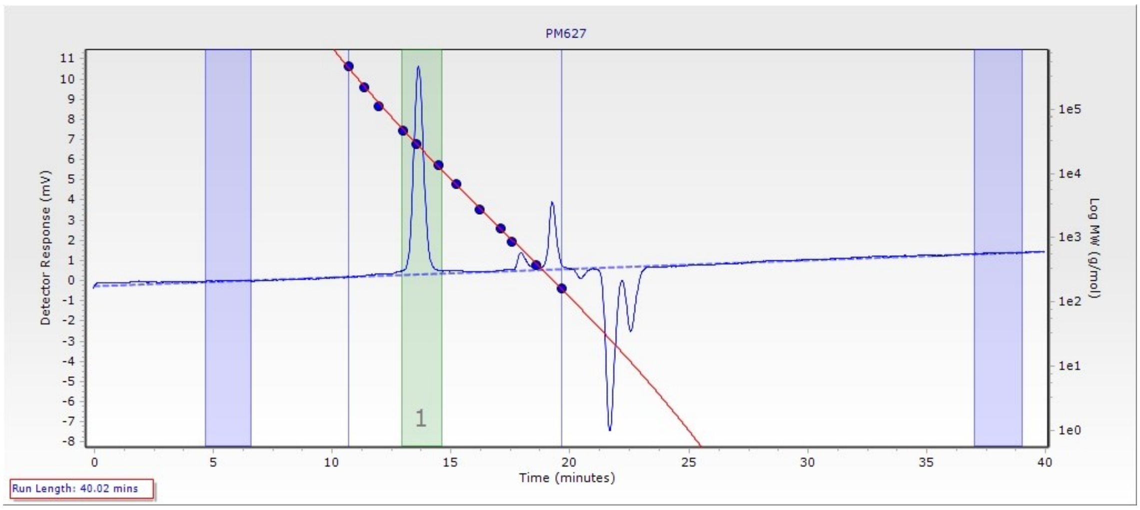

Figure SI30: GPC trace of PLLA prepared by solution polymerisation with Al(**1**)O^{i}Pr (table 2, entry 5).

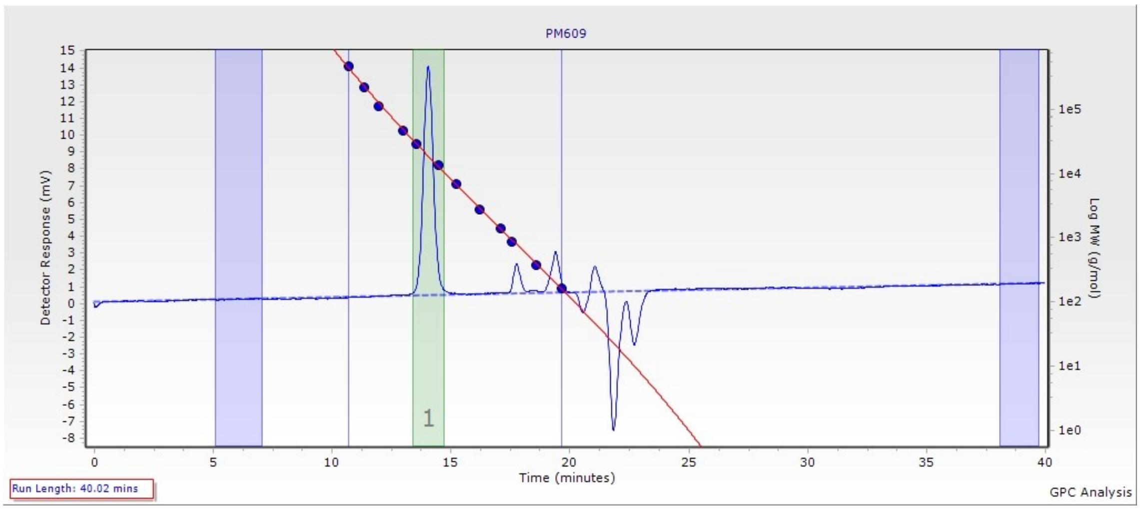

Figure SI31: GPC trace of PLA prepared by solution polymerisation with Al(**2**)O^{i}Pr (table 2, entry 7).

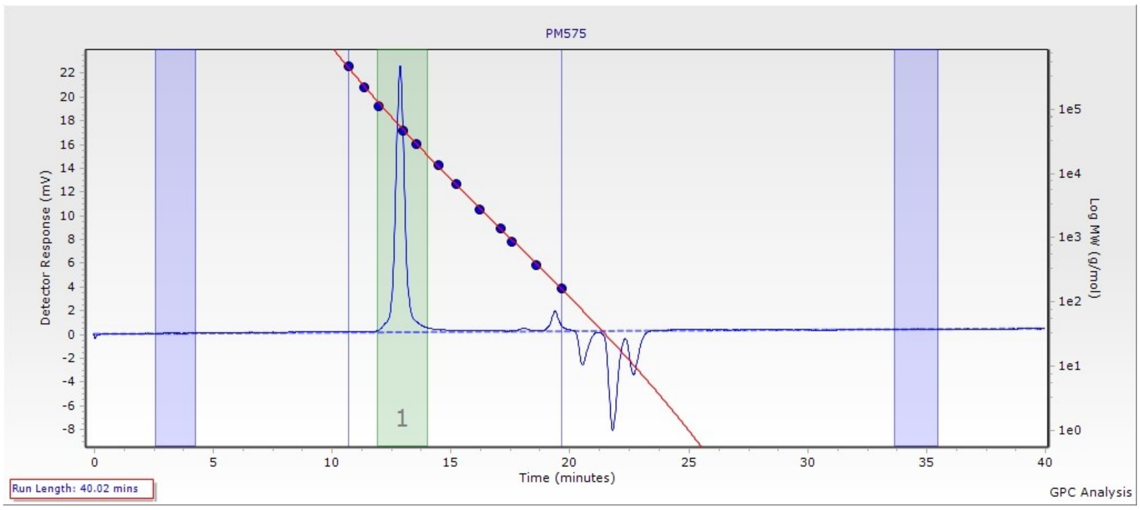

Figure SI32: GPC trace of PLA prepared by solvent free polymerisation with Al(**1**)O^{i}Pr (table 3, entry 1).

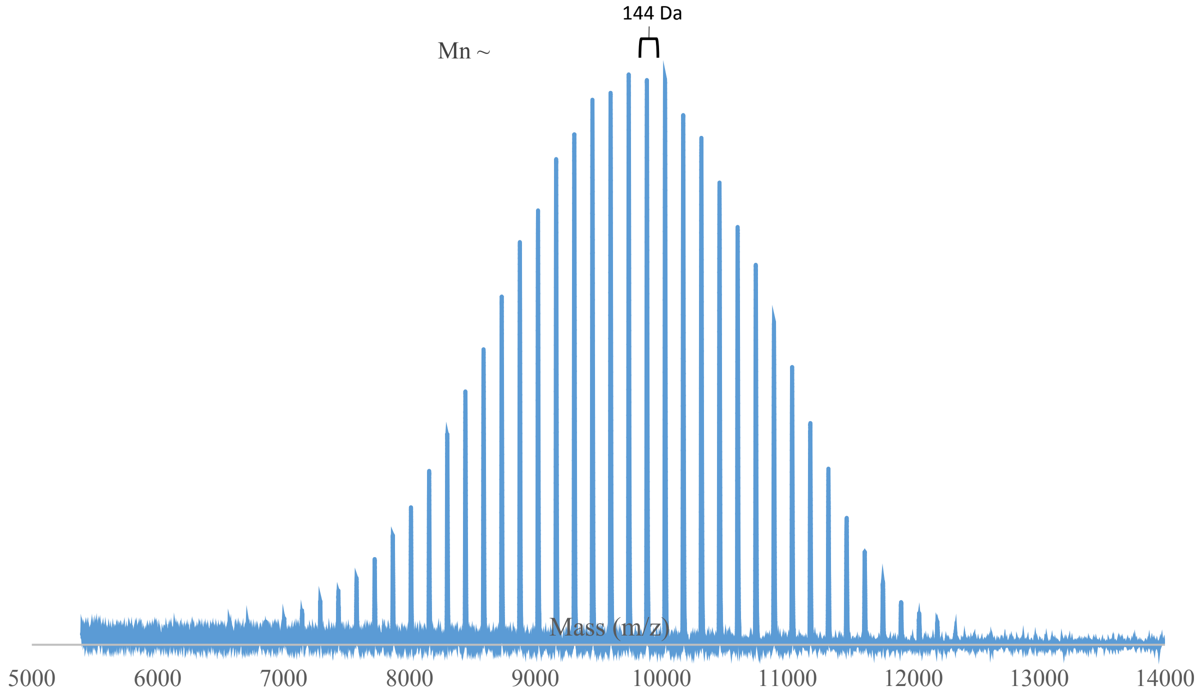

Figure SI33: MALDI spectrum of PLA prepared by solution polymerisation with Al(**1**)O^{i}Pr (table 3, entry 4).

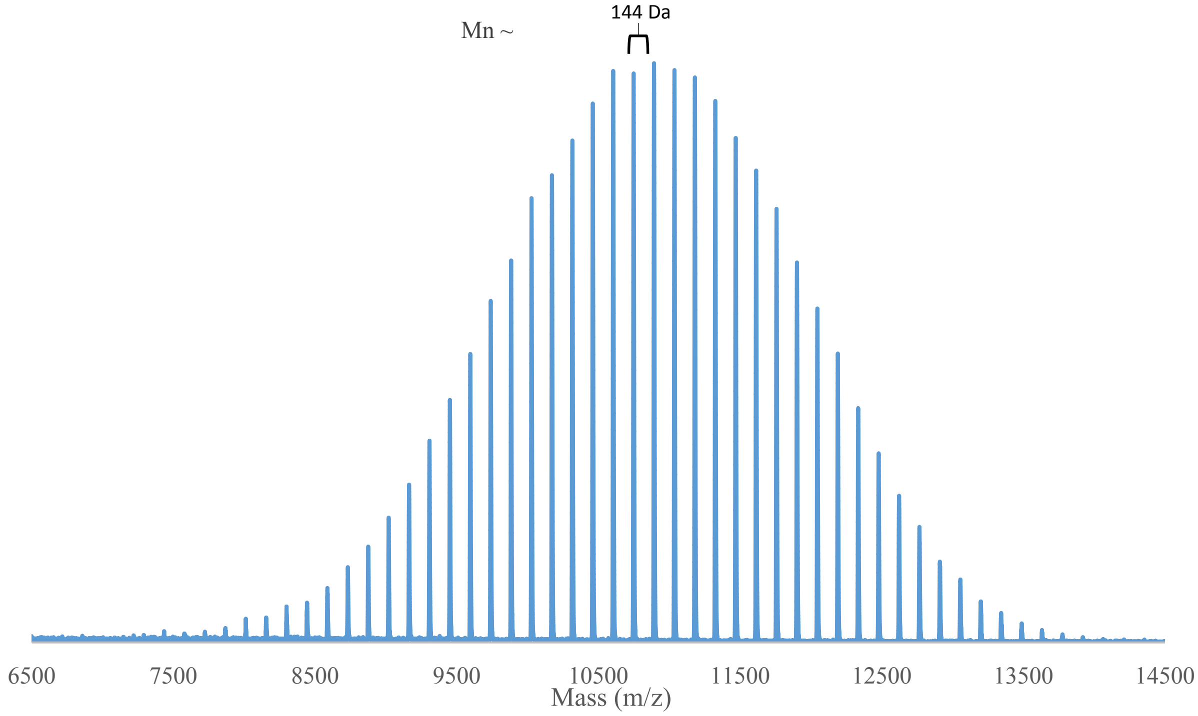

Figure SI34: MALDI spectrum of PLA prepared by solution polymerisation with Al(**2**)O^{i}Pr (table 2, entry 7).

Table SI1: Crystallographic parameters

Compound reference	Al(**1**)(O^{i}Pr)	Al(**2**)(O^{i}Pr)	Al(**3**)Me	Al(**4**)(OBn)
Chemical formula	$4(C_{39}H_{63}AlN_2O_3)\bullet C_{11}H_{26}$	$C_{33}H_{51}AlN_2O_3$	$C_{38}H_{61}AlN_2O_2$	$C_{43}H_{61}AlN_2O_3$
Formula Mass	2697.88	550.73	604.86	680.91
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
a/Å	29.9091(5)	12.1388(3)	13.8779(12)	10.9794(3)
b/Å	11.0908(2)	19.0837(2)	13.00200(10)	14.2923(4)
c/Å	25.9834(4)	14.1406(2)	20.8532(16)	15.1168(5)
α/°	90	90	90	115.692(3)
β/°	108.075(2)	102.663(2)	98.2288(8)	100.605(3)
γ/°	90	90	90	102.864(2)
Unit cell volume/Å^3	8193.8(3)	3196.04(10)	3724.0(4)	1974.85(11)
Temperature/K	150(2)	150(2)	150(2)	150(2)
Space group	$I2/a$	$P2_1/c$	$P2_1/c$	*P***Error!**
No. of formula units per unit cell, Z	2	4	4	2
No. of reflections measured	24017	49741	26907	22254
No. of independent reflections	8123	6364	7072	7902
R_{int}	0.0186	0.0266	0.0231	0.0206
Final R_1 values ($I > 2\sigma(I)$)	0.0368	0.0336	0.0392	0.0395
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0989	0.0865	0.1036	0.1024
Final R_1 values (all data)	0.0399	0.0367	0.0431	0.0427
Final $wR(F^2)$ values (all data)	0.1017	0.0886	0.1070	0.1051

References

1. P. McKeown, M. G. Davidson, J. P. Lowe, M. F. Mahon, L. H. Thomas, T. J. Woodman and M. D. Jones, *Dalton Trans.*, 2016, **45**, 5374-5387.