SUPPORTING INFORMATION

Ligands and complexes based on piperidine and their exploitation of the ring opening polymerisation of *rac*-lactide

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General experimental methods

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 and $Ti(O^iPr)_4$ which was vacuum distilled prior to use. Dry solvents used in handling metal complexes were obtained *via* SPS (solvent purification system). ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker 400 or 500 MHz instrument and referenced to residual solvent resonances. $CDCl_3$ was dried over CaH_2 prior to use with metal complexes. C_6D_6 was degassed and stored over molecular sieves. Coupling constants are given in Hertz. For diffusional ordered spectroscopy (DOSY) NMR analysis, the standard Bruker pulse sequence ledgp2s[1] was used, with d1 of 5 seconds, 64k data points and 16 scans per gradient level. Typically the gradient pulse was 1700 μs, with a diffusion time of 0.1 s. Ten gradient strengths were used between 2 and 95 %. Data were processed using DOSY methods.[2] All ligands were characterised by electron-spray ionisation-mass spectrometry (ESI-MS) in positive mode. CHN microanalysis was performed by Mr. Stephen Boyer of London Metropolitan University. All crystallographic data was collected on a SuperNova, EOS detector diffractometer using radiation CuKα (λ = 1.54184 Å) or Mo-Kα (λ = 0.71073 Å) all recorded at 150(2) K. All structures were solved by direct methods and refined on all F2 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. All models were straightforward with the following exceptions: $Zr(\mathbf{5})(O^tBu)_2$ the methyl groups of the O^tBu are disordered over two sites in an approximately 70:30 ratio, as are the methyl groups of on para tBu group in an 80:20 ratio, half a molecule of hexane solvent is also present in the asymmetric unit; $Ti(\mathbf{4})(O^iPr)_2$ the methyl groups of the OiPr are disordered over two sites in a 60:40 ratio; Mg(1)2 contains two molecules of toluene (one is disordered over three positions in a 50:30:20 ratio), one ligand is highly disordered (N2, N4, C12-14, C37-C42) is a 50:50 ratio the other ligand (C19) has minor disorder in a 90:10 ratio; $Zn(\mathbf{1})_2$ crystallised in the centrosymmetric space group and contains one crystallographically unique ligand, this is disordered (N1, C16-C21) in a 60:40 ratio; $Ti(\mathbf{1})(O^iPr)_2$ one isopropoxide (C4-C6) is disordered over two positions in a 70:30 ratio; $Zr(\mathbf{6})(O^tBu)_2$ was twinned (ca. 38%) by a 180° rotation around the 1 0 0 axis; $Zr(\mathbf{1})(O^iPr)_2$ the carbons of both O^iPr groups are disordered over two sites in a 55:45 ratio.

Polymerisations were carried out in a Youngs ampoule under inert argon conditions. For a typical solution based polymerisation, *rac*-lactide (1.0 g, 0.69 mmol) was dissolved in dry toluene (10 ml) with the required amount of initiator ([LA]:[I] = 100:1). When required, a benzyl alcohol co-initiator (typically [I]:[BnOH] = 1:1, 7.2 µl) was added. The ampoule was then placed in a preheated oil bath (80 °C) and stirred for the set time. After polymerisation, solvent was removed *in vacuo* and a crude ^{1}H NMR spectrum 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 or above. After polymerisation, the product was dissolved in CH_2Cl_2 which was then removed *in vacuo* and a crude ^{1}H NMR spectrum 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 using a PLgel 5 µm MIXED-D 300 × 7.5 mm column. The system was referenced against 11 narrow molecular weight standards polystyrene standards with detection *via* refractive index response. A correction factor of 0.58 was applied to measured values.[3] Polymer tacticity was determined *via* ^{1}H NMR spectroscopy ($CDCl_3$) analysis of the homonuclear decoupled methine region utilizing the relationships demonstrated by Coates *et al.*[4] 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 NaTFA. Materials characterisation *(GPC, ESI-MS MALDI-TOF)* facilities were provided through the Chemical Characterisation and Analysis Facility (CCAF) at the University of Bath.

Ligand Synthesis

Monophenol ligands

Imino monophenolate ligands, **1**-**2**H, were prepared according to literature procedures.[5] All ligands were prepared on a 2 mmol scale in a Schlenk tube to allow for subsequent complexation.

2H: Isolated as a yellow oil (94 % conversion, 5:2 imine:cyclic product).
Major product (Imine): ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 13.21 (s, 1H; ArOH), 8.34 (s, 1H; ArCHN) 7.28 (m, 1H; ArH), 7.22 (dd, *J* = 7.7, 1.6 Hz, 1H; ArH), 6.95 (d, *J* = 8.0 Hz, 1H; ArH), 6.86 (td, *J* = 7.5, 1.1 Hz, 1H; ArH), 3.67 (ddd, *J* = 11.9, 4.4, 1.3 Hz, 1H; CH_2), 3.39 (dd, *J* =

11.9, 8.2 Hz, 1H; CH_2), 3.04 (m, 1H; CH_2), 2.83 (m, 1H; CH), 2.61 (m, 1H; CH_2), 1.82 (m, 1H; CH_2), 1.70 (m, 1H; CH_2), 1.57 (m, 1H; CH_2), 1.38 (m, 2H; CH_2), 1.21 (m, 1H; CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ = 166.3 (ArCHN), 161.2, 132.4, 131.4, 118.8, 118.7, 117.0 (Ar), 66.1 (CH_2), 56.8 (CH), 46.9, 30.7, 26.2, 24.6 (CH_2).

Minor product (Cyclic): ^1H NMR ($CDCl_3$, 400 MHz) δ = 7.18 (m, 1H; ArH), 7.05 (dd, J = 7.5, 1.7 Hz, 1H; ArH), 6.81 (dd, J = 8.2, 1.1 Hz, 1H; ArH), 6.86 (td, J = 7.4, 1.3 Hz, 1H; ArH), 4.20 (s, 1H; $ArCHN_2$), 3.18 (dd, J = 9.3, 6.5 Hz, 1H; CH_2), 2.92 (m, 2H; CH_2), 2.40 (m, 1H; CH), 2.05 (td, J = 11.6, 2.9 Hz, 1H; CH_2), 1.93 (m, 1H; CH_2), 1.82 (m, 1H; CH_2), 1.70 (m, 1H; CH_2), 1.57 (m, 1H; CH_2), 1.38 (m, 2H; CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ = 157.6, 130.2, 130.0, 121.8, 119.0, 117.0, (Ar), 83.0 ($ArCHN_2$), 63.6 (CH), 50.5, 48.6, 29.2, 25.0, 23.8 (CH_2).

ESI-MS (MeOH): Calcd m/z $[C_{13}H_{18}N_2ONa]^+$ = 241.1316, found m/z = 241.1302.

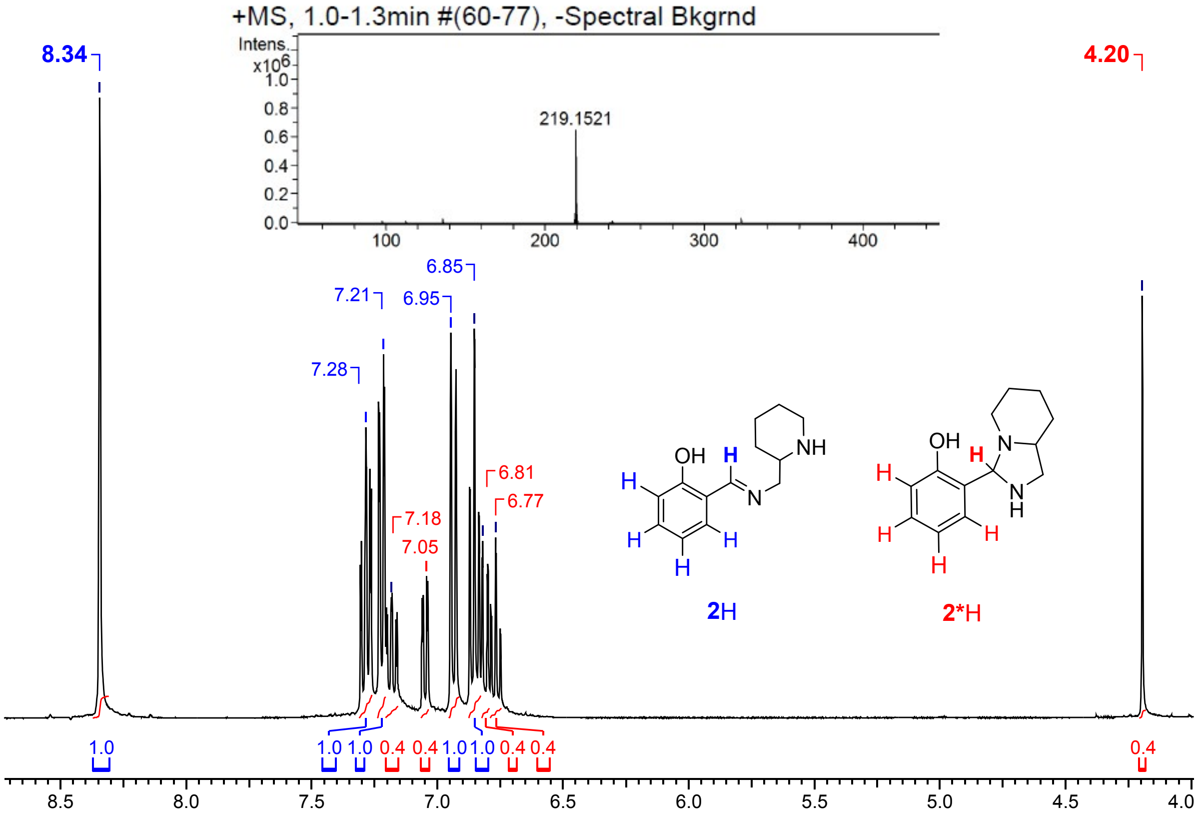


Figure S1: ^1H NMR ($CDCl_3$, 400 MHz) spectrum of **2**H, with assignment of imino and bicyclic structures. Inset: ESI-MS.

Pyridine based ligand, **3**H, was prepared and characterised according to literature methods.[6]

Bisphenol ligands

Salalen and salan, **4**/**5**H_2, were prepared according to previously published protocols.[5, 7] Bicyclic ligand, **6**H, was only isolable in low yield from these methods.[7] Instead, a new pathway was realised for the isolation of **6**H.

6H: 3,5-Di-*tert*-butylsalicylaldehyde (5.78 g, 24.72 mmol)was reacted with 2-AMP (3 ml, 24.72 mmol) in MeOH (100 ml).After 1 hour of stirring, $NaBH_4$ (3 eq, 2.85 g, 75 mmol) was added portionwise. Reaction was continued until decolouration on which H_2O (5 ml) was added to quench the reduction. Solvent was reduced *in vacuo* and the product was washed with H_2O (3 × 50 ml) and MeOH (1 × 25 ml) and dried to an off white powder (8.74 g, 20.3 mmol, 82%). The resultant diamine (6 mmol) was dissolved in hexane (50 ml) and the 3,5-di-*tert*-butylsalicylaldehyde (6 mmol) was added. The reaction mixture was then stirred for 16 hours at reflux. After this period, the product was isolated *via* recrystallisation from the reaction mixture, furnishing a white microcrystalline powder (2.72 g, 4.95 mmol, 83 %). Characterisation for this ligand has been reported previously.[5]

Mg(II)/Zn(II) complexes

Synthesis of imino monophenolate magnesium and zinc complexes, Mg(1)$_2$/Zn(1)$_2$: Mg(^{n}Bu)$_2$ or Zn(Et)$_2$ (1M, 1 ml, 1 mmol) was added to a solution of **1**H (2 mmol) in toluene (10 ml). After complete addition, the solution was stirred for 1 hour before solvent removal. The desired complex was purified *via* washing or recrystallisation from hexane.

Mg(1)$_2$: Isolated as pale yellow crystals (0.42 g, 0.62 mmol, 62%).
^{1}H NMR (C_6D_6, 400 MHz) δ = 8.05 – 7.99 (m, 2H; ArCHN), 7.62 – 7.55 (m, 2H; ArH), 7.11 – 7.05 (m, 2H; ArH), 3.69 – 3.34 (2 × t, J = 13.1 Hz, J = 12.9 Hz, 1H; CH_2), 3.27 – 2.90 (m, 3H; CH_2/CH), 2.86 – 2.62 (m, 2H; CH_2/CH), 2.59 – 2.29 (m, 2H; CH/CH_2), 2.18 – 2.02 (m, 1H; CH_2), 1.88 – 1.72 (m, 1H; CH_2), 1.68 – 1.57 (m, 18H; $C(CH_3)_3$), 1.56 – 1.45 (m, 2H; CH_2), 1.42 – 1.38 (m, 18H; $C(CH_3)_3$), 1.37 – 1.26 (m, 2H; CH_3), 1.18 – 0.94 (m, 4H; CH_2) 0.82 – 0.44 (m, 4H; CH_2), 0.22 (m, 1H; NH). ^{13}C{^{1}H} NMR (C_6D_6, 100 MHz) δ = 169.8, 169.7 (Ar), 169.6, 169.5 (ArCHN), 169.3 (Ar), 169.2, 169.0 (ArCHN), 169.0, 140.8, 140.6, 140.5, 132.4, 132.2, 131.8, 131.7, 129.3, 129.1, 129.0, 128.9, 128.5, 128.32, 128.3, 128.2, 128.0, 127.9, 127.8, 119.90, 119.8 (Ar), 64.2, 64.0, 64.0 (CH_2), 57.8, 57.7, 56.8, 56.4 (CH), 46.7, 46.1, 46.0,

45.4 (CH$_2$), 35.8, 35.73, 35.71, 34.02, 33.99 ($\textit{C}(\mathrm{CH_3})_3$), 32.1, 32.0 ($\mathrm{C}(\textit{C}\mathrm{H_3})_3$), 31.6, 31.4 (CH$_2$), 30.3, 30.3, 30.2, 30.1 ($\mathrm{C}(\textit{C}\mathrm{H_3})_3$), 27.6, 27.5, 27.3, 27.2, 24.3, 24.1, 24.0 (CH$_2$).

Elemental analysis ($C_{42}H_{66}MgN_4O_2$) Calcd in %: C, 73.83; H, 9.74; N, 8.20. Found: C, 73.78; H, 9.77; N, 8.15.

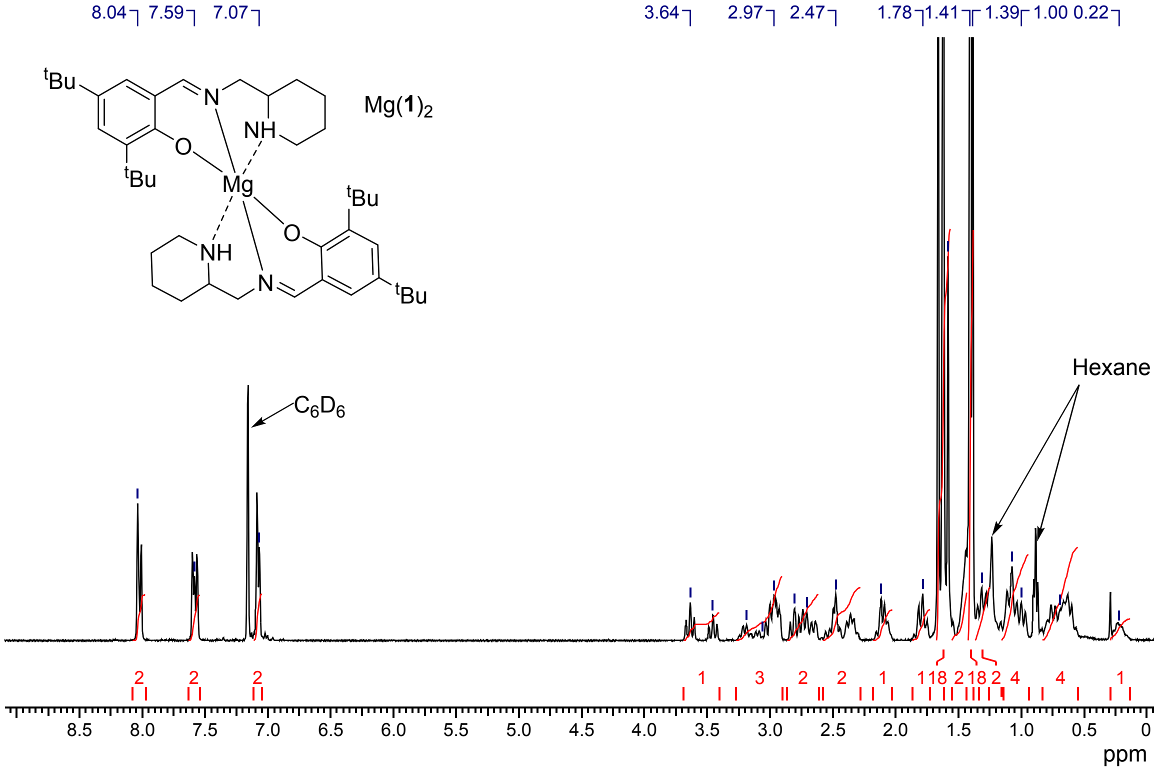


Figure S2: ^{1}H NMR (C_6D_6, 400 MHz) spectrum of Mg(**1**)$_2$.

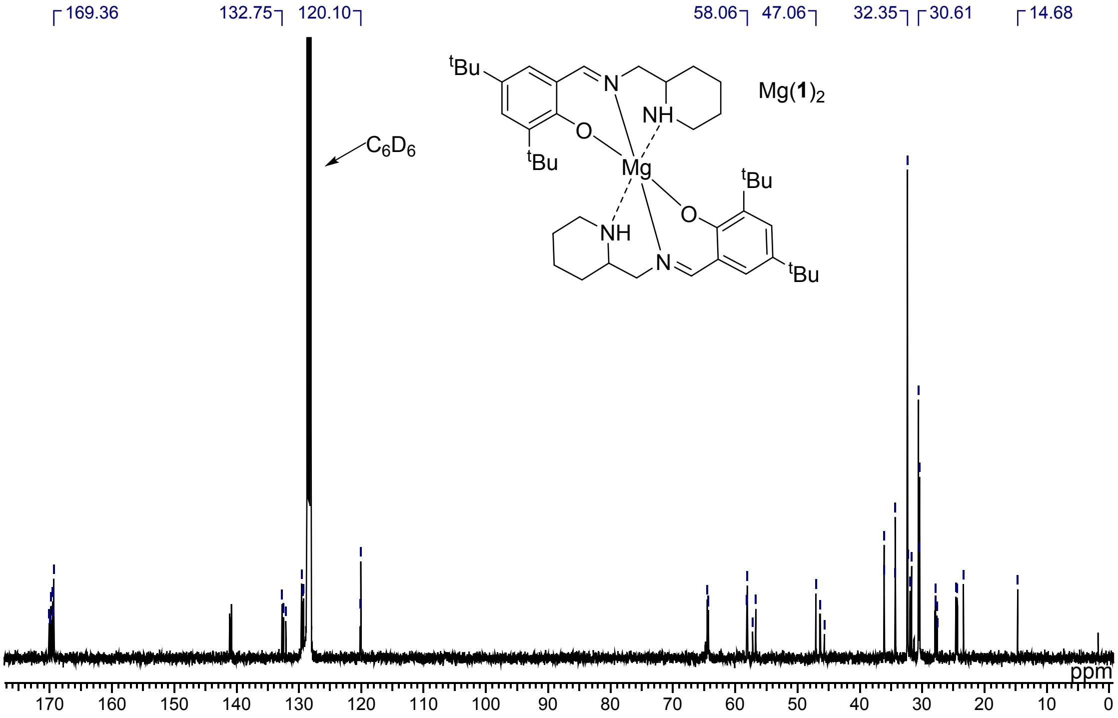


Figure S3: $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz) spectrum of Mg(**1**)$_2$.

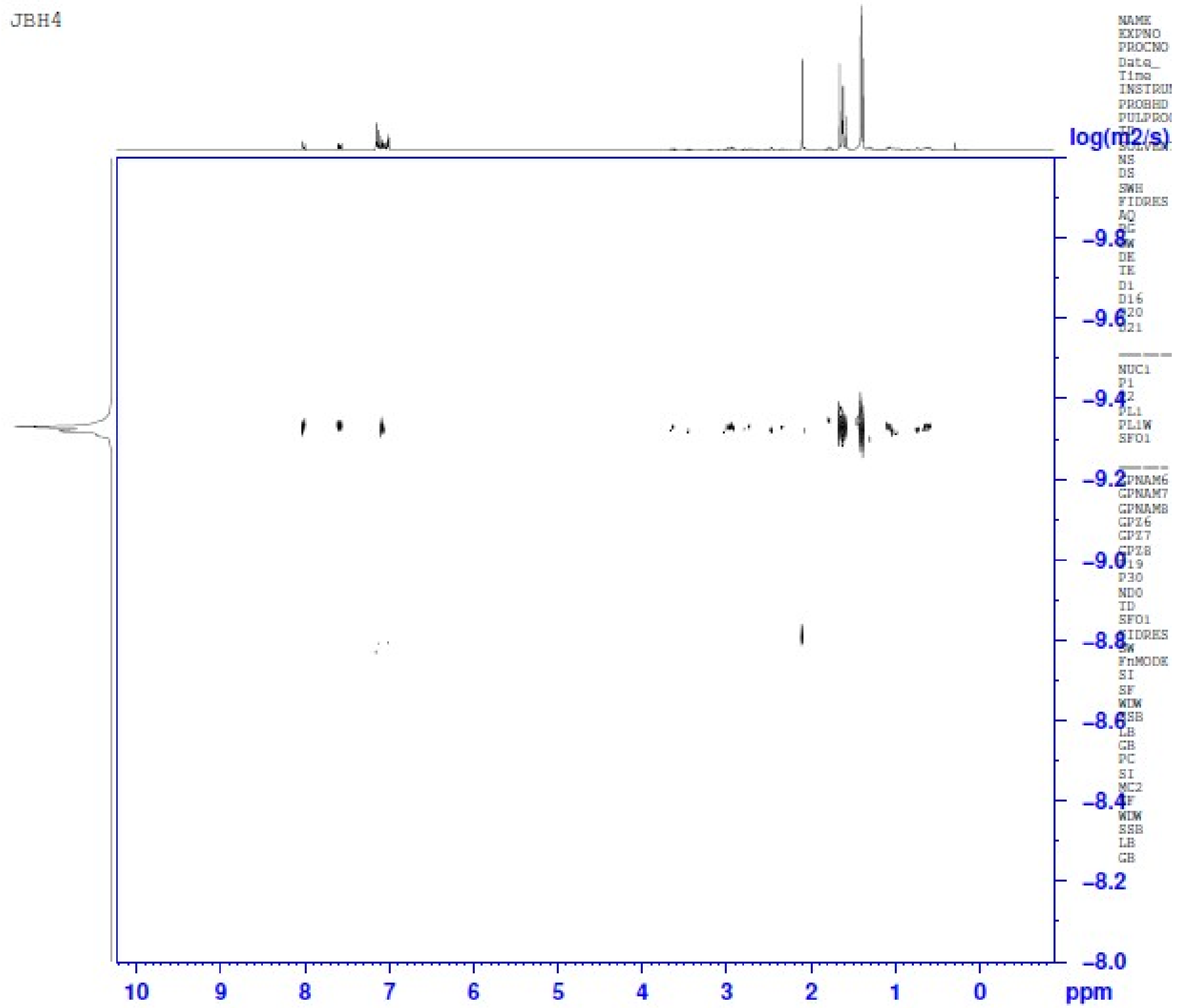


Figure S4: DOSY NMR (C_6D_6, 500 MHz) spectrum of Mg(**1**)$_2$.

Zn(1)$_2$: Isolated as yellow crystals (0.38 g, 0.53 mmol, 53%).

^{1}H NMR (C_6D_6, 400 MHz) δ = 7.98 (m, 2H; ArCHN), 7.62 – 7.52 (m, 2H; ArH), 7.00 (m, 2H; ArH), 3.58 – 3.34 (m, 1H; CH_2), 3.12 – 2.67 (m, 5H; CH_2/CH), 2.55 – 1.74 (m, 4H; CH_2), 1.69 – 1.59 (m, 18H; $C(CH_3)_3$), 1.56 – 1.45 (m, 2H; CH_2), 1.44 – 1.36 (m, 18H; $C(CH_3)_3$), 1.35 – 1.00 (m, 6H; CH_2), 0.93 – 0.56 (m, 4H; CH_2). ^{13}C{^{1}H} NMR (C_6D_6, 100 MHz) δ = 171.1, 170.7, 169.9 (Ar), 169.7, 169.3, 141.5, 141.4 (Ar*C*HN), 141.28, 141.26, 132.7, 132.5, 132.3, 132.2, 129.44, 129.35, 129.3, 129.1, 128.4, 128.35, 128.3, 128.2, 128.1, 118.6, 118.2 (Ar), 64.4, 64.0, 63.8, 63.7 (CH_2), 57.2, 57.1, 56.9, 56.7 (CH), 46.8, 46.2, 46.0, 45.6 (CH_2), 35.9, 35.8, 34.0 ($\mathit{C}(CH_3)_3$), 32.0, 31.9 ($C(\mathit{C}H_3)_3$), 31.7, 31.4, 31.1 (CH_2), 30.2, 30.1, 30.1 ($C(\mathit{C}H_3)_3$), 27.6, 27.5, 27.3, 27.2, 24.4, 24.3, 24.2 (CH_2).

Elemental analysis ($C_{42}H_{66}ZnN_4O_2$) Calcd in %: C, 69.64; H, 9.18; N, 7.73. Found: C, 69.67; H, 9.04; N, 7.66.

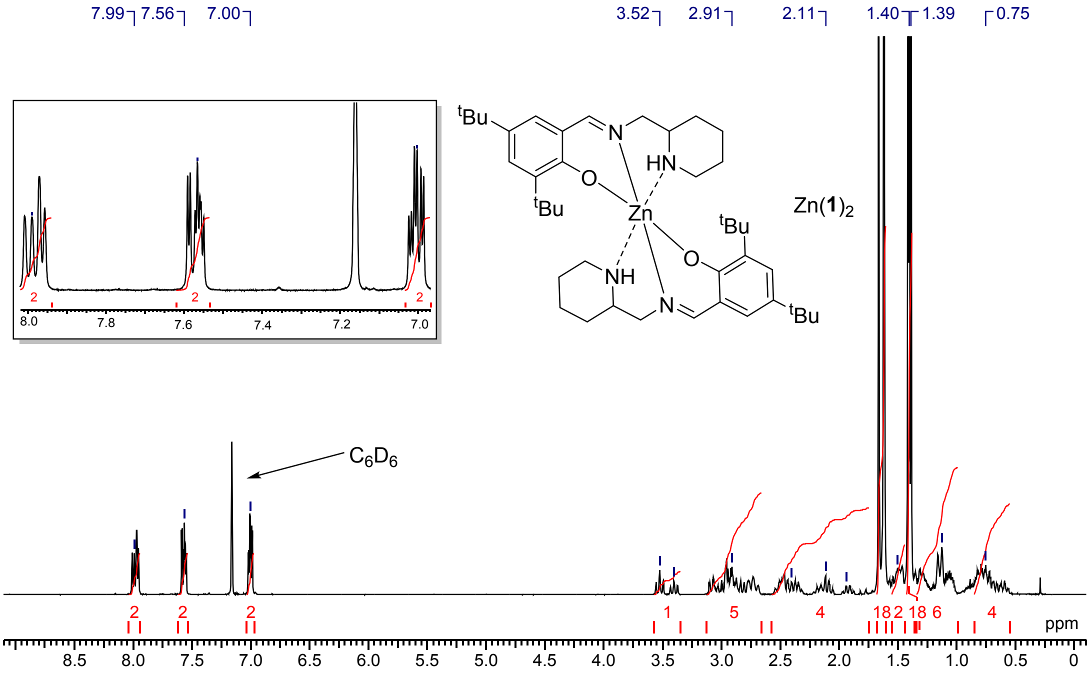


Figure S5: ^{1}H NMR (C_6D_6, 400 MHz) spectrum of Zn(**1**)$_2$. Inset: Imine/aromatic region.

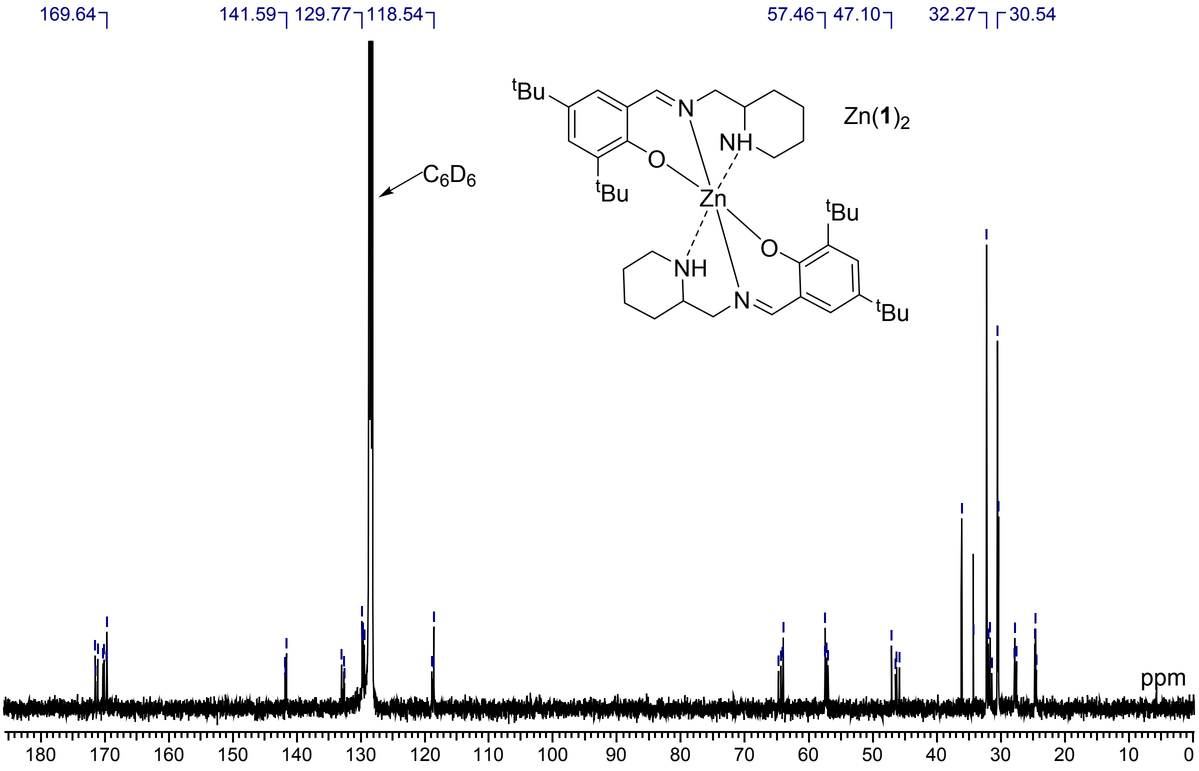


Figure S6: ^{13}C{^{1}H} NMR (C_6D_6, 100 MHz) spectrum of Zn(**1**)$_2$.

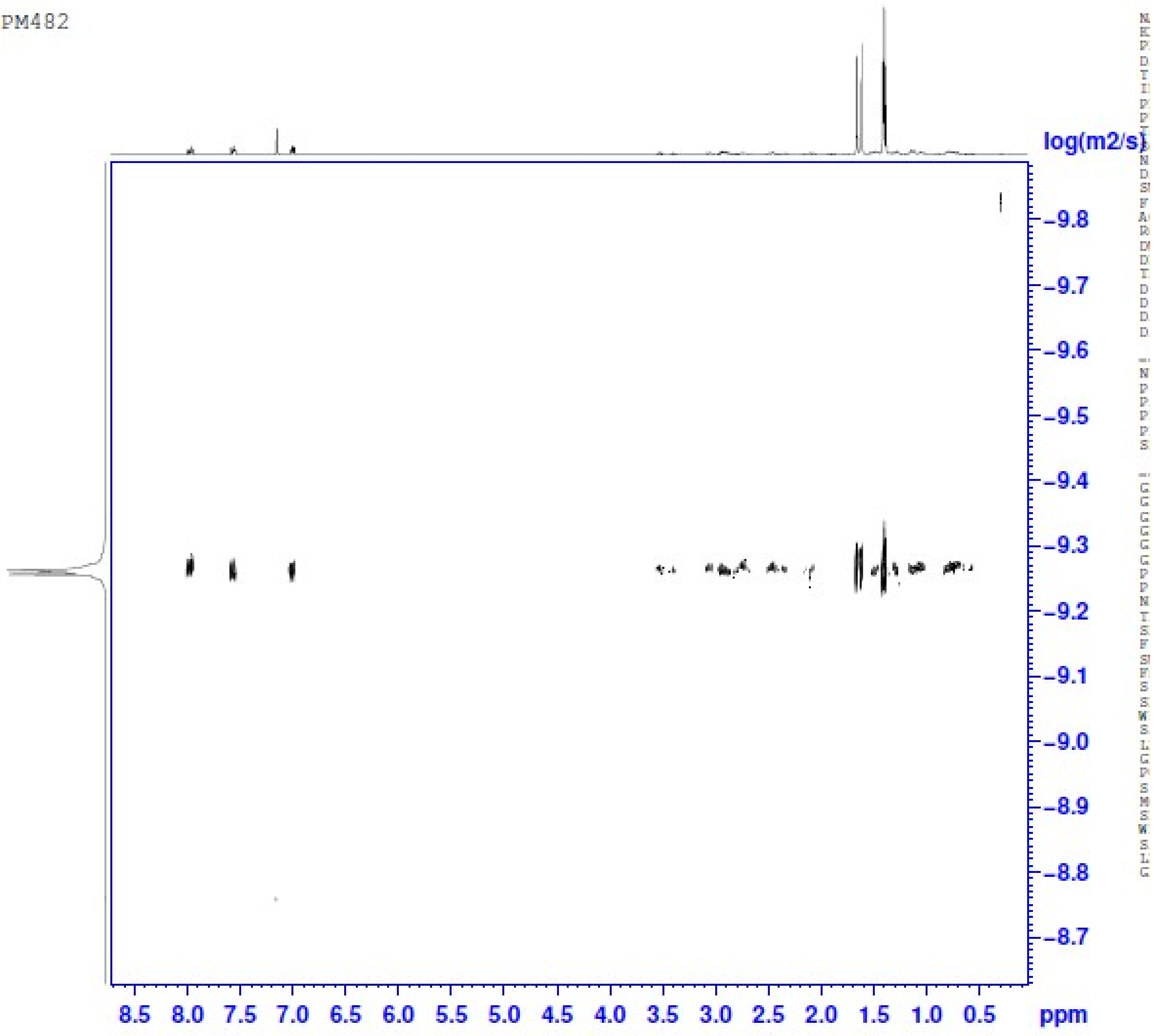


Figure S7: DOSY NMR (C_6D_6, 500 MHz) spectrum of Zn(**1**)$_2$.

Mg(**2**)$_2$: Isolated as pale yellow crystals (0.35 g, 0.76 mmol, 76 %).

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.20 – 8.10 (m, 2H; ArCHN), 7.22 – 7.09 (m, 2H; ArH), 7.09 – 7.00 (m, 2H; ArH), 6.77 – 6.63 (m, 2H; ArH), 6.45 – 6.31 (m, 2H; ArH), 3.81 – 3.50 (m, 2H; CH_2), 3.38 – 3.12 (m, 2H; CH_2), 2.93 – 2.55 (m, 3H; CH_2/CH), 2.54 – 2.37 (m, 1H; CH/CH_2), 2.33–2.19 (m, 1H; CH_2), 1.90 – 1.72 (m, 4H; CH_2), 1.63 – 1.35 (m, 6H; CH_2), 1.33 – 1.00 (m, 4H; CH_2), 0.60 (m, 1H; NH). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ = 170.6 (Ar), 169.2, 168.2, 167.9 (ArCHN), 134.8, 134.6, 133.2, 123.3, 120.7, 111.7, 111.2 (ArH), 64.5, 64.2, 63.0 (CH_2), 58.0, 54.8 (CH), 46.9, 46.2, 45.6 (CH_2), 31.1, 30.8, 27.3, 27.2, 23.9, 23.6 (CH_2). Note: Low solubility in $CDCl_3$ and C_6D_6.

Elemental analysis ($C_{26}H_{34}MgN_4O_2$) Calcd in %: C, 68.05; H, 7.47; N, 12.21. Found: C, 67.97; H, 7.51; N, 12.21.

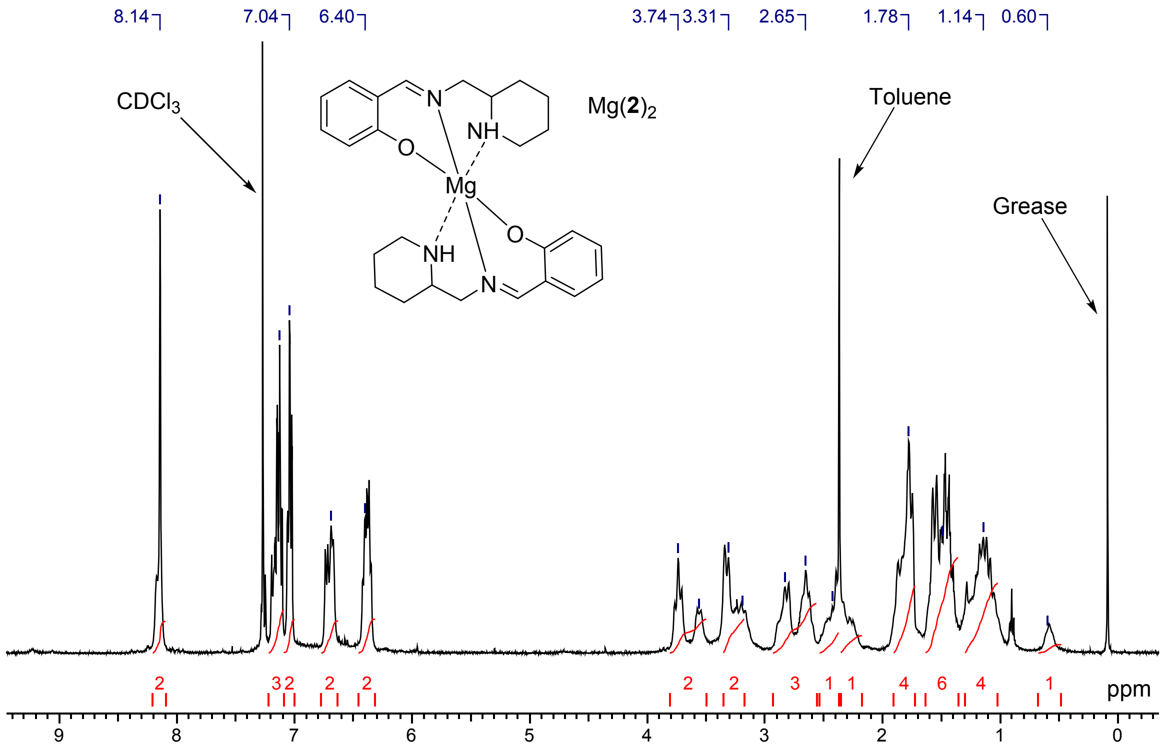


Figure S8: ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of Mg(**2**)$_2$.

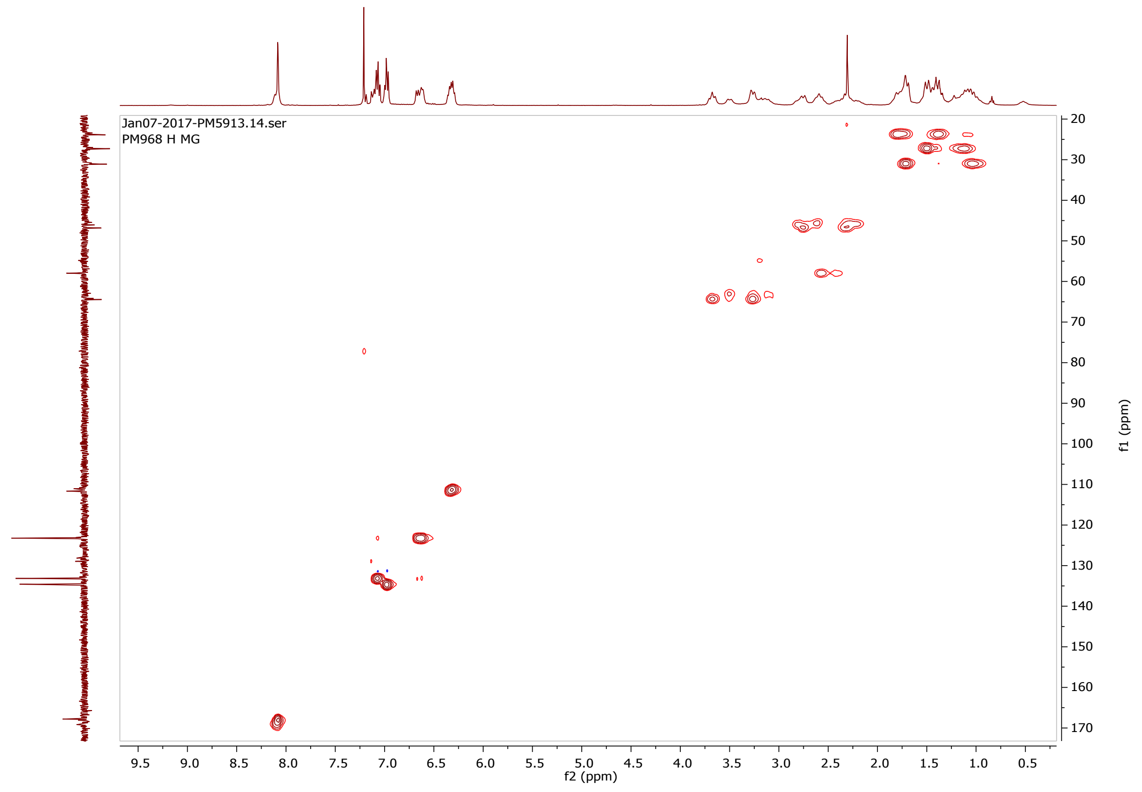


Figure S9: HSQC NMR ($CDCl_3$) spectrum of Mg(**2**)$_2$.

Zn(2)$_2$: Isolated as yellow crystals (0.34 g, 0.68 mmol, 68%).

^{1}H NMR ($CDCl_3$ 400 MHz) δ = 8.19 – 8.10 (m, 2H; ArCHN), 7.16 – 7.09 (m, 2H; ArH), 7.04 – 6.96 (m, 2H; ArH), 6.78 – 6.68 (m, 2H; ArH), 6.43 – 6.34 (m, 2H; ArH), 3.72 – 3.24 (m, 4H; CH_2), 2.88 – 2.50 (m, 3H; CH_2/CH), 2.41 – 2.26 (m, 2H; CH_2), 1.86 – 1.75 (m, 2H; CH_2), 1.75 – 1.64 (m, 2H; CH_2), 1.59 – 1.32 (m, 5H; CH_2), 1.30 – 1.00 (m, 4H; CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ = 172.3, 172.1 (Ar), 169.0, 168.5 (ArCHN), 135.14, 135.05 133.4, 133.3 123.7, 123.6, 119.03, 118.95, 112.0, 111.7 (ArH), 64.4 (CH_2), 57.1 (CH), 46.8, 46.0, 31.1, 30.9, 27.12, 27.07, 23.9, 23.7 (CH_2).

Elemental analysis ($C_{26}H_{34}ZnN_4O_2$) Calcd in %: C, 62.46; H, 6.85; N, 11.21. Found: C, 62.55; H, 6.89; N, 11.11.

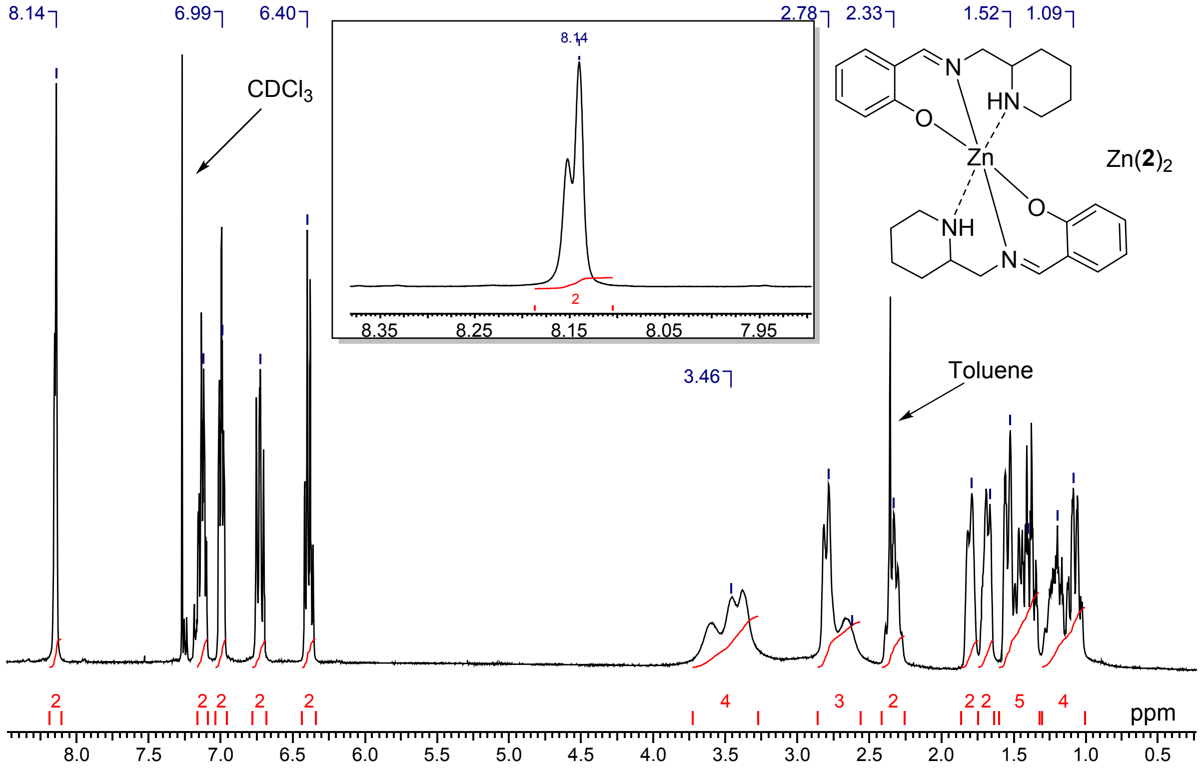


Figure S10: ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of Zn(**2**)$_2$.

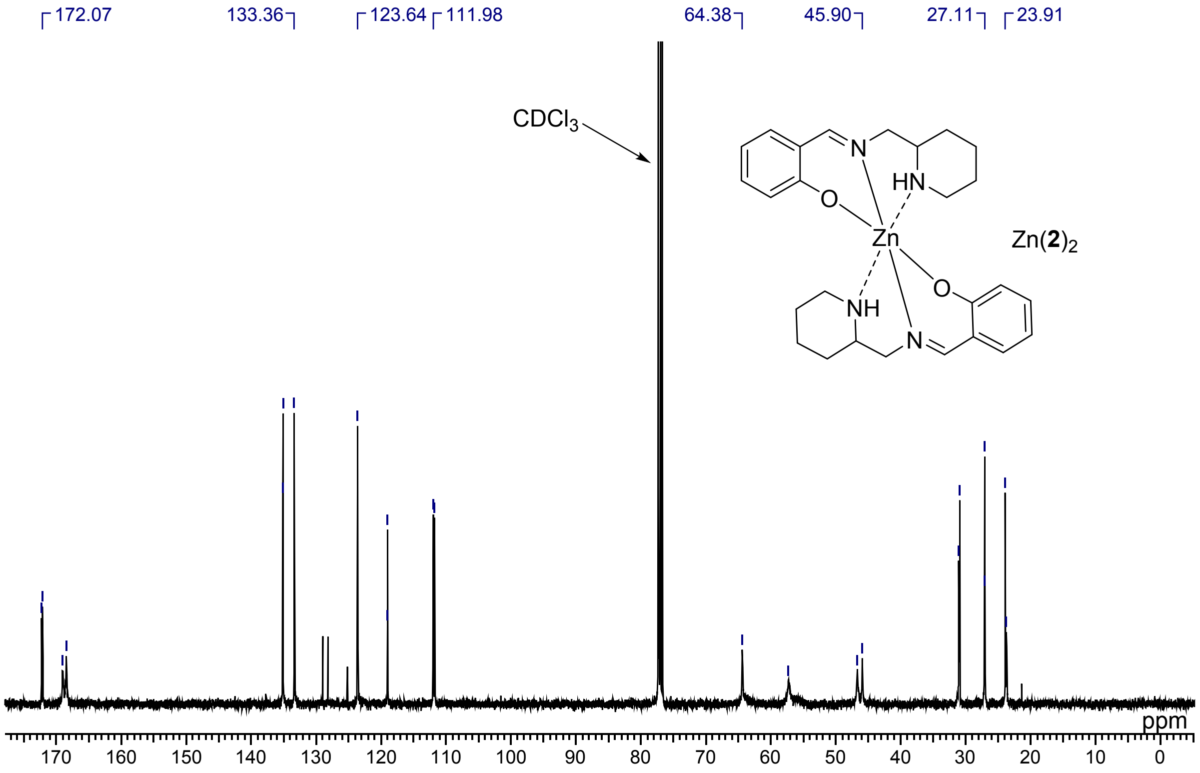


Figure S11: $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) spectrum of Zn(**2**)$_2$.

***Mg(3)$_2$*:** As above using **3**H (0.65 g, 2 mmol). Washed with hexane yielding a yellow powder (0.53 g, 0.79 mmol, 79 %).

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.47 (s, 2H; ArCHN), 7.80 (d, *J* = 4.9 Hz, 2H; ArH), 7.54 (td, *J* = 7.7, 1.5 Hz, 2H; ArH), 7.23 (m, 2H; ArH), 7.16 (m, 2H; ArH), 6.92 (d, *J* = 2.6 Hz, 2H; ArH), 6.88 (t, *J* = 6.5 Hz, 2H; ArH), 5.35 (d, *J* = 19.0 Hz, 2H; $PyrCH_2$), 4.84 (d, *J* = 19.0 Hz, 2H; $PyrCH_2$), 1.26 (s, 9H; $C(CH_3)_3$), 1.11 (s, 9H; $C(CH_3)_3$). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ = 169.7 (ArCHN), 169.0, 158.1, 147.7, 140.5, 137.2, 131.2, 128.4, 127.8, 122.3, 121.4, 119.1 (ArH), 61.5 (CH_2), 35.2, 33.8 ($\mathit{C}(CH_3)_3$), 31.8, 29.4 ($C(\mathit{C}H_3)_3$).

Elemental analysis ($C_{42}H_{54}MgN_4O_2$) Calcd in %: C, 75.16; H, 8.11; N, 8.35. Found: C, 75.05; H, 8.25; N, 8.26.

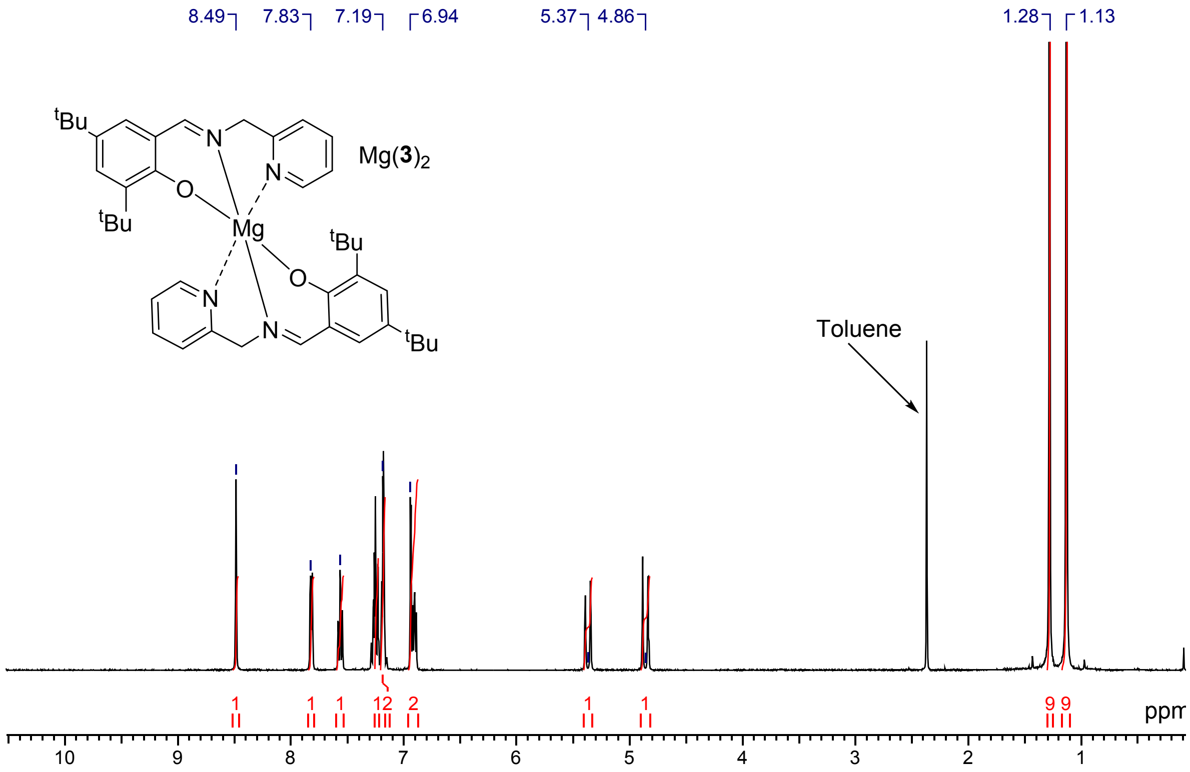


Figure S12: ^{1}H NMR (CDCl$_3$, 400 MHz) spectrum of Mg(**3**)$_2$.

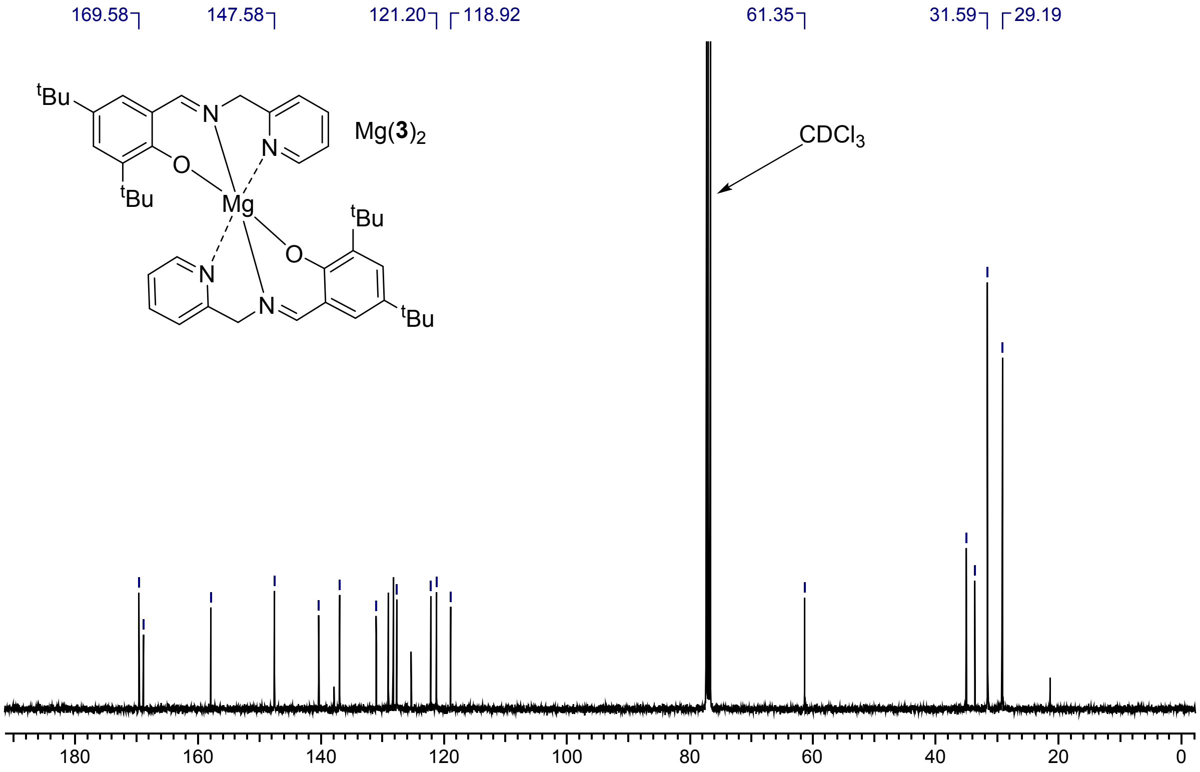


Figure S13: ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz) spectrum of Mg(**3**)$_2$.

Synthesis of imino monophenolate titanium complex, Ti(1)$_2$(O^{i}Pr)$_2$: Ti(O^{i}Pr)$_4$ (0.30 ml, 1 mmol) was added dropwise to ligand, **1**H (2 mmol) in toluene (10ml). After 1 hour, solvent was removed *in vacuo* and complex recrystallised from hexane to yield yellow crystals (0.18 g, 0.218 mmol, 22%). Multiple species in solution.

Treated as one species: ^{1}H NMR (CDCl$_3$, 400 MHz), δ = 8.09 – 8.00 (m, 2H; ArCHN), 7.50 – 7.42 (m, 2H; ArH), 7.10 – 7.04 (m, 2H; ArH), 4.82 – 4.53 (m, 2H; OC*H*(CH$_3$)$_2$), 4.06 – 3.89 (m, 1H; CH$_2$), 3.73 – 3.15 (m, 2H; CH$_2$), 3.10 – 2.83 (m, 5H; CH/CH$_2$), 2.57 – 2.17 (m, 3H; CH/CH$_2$), 1.72 – 1.59 (m, 1H; CH$_2$), 1.56 – 1.52 (m, 19H; CH$_2$/C(CH$_3$)$_3$), 1.47 – 1.37 (m, 4H; CH$_2$), 1.32 – 1.28 (m, 19H; CH$_2$/C(CH$_3$)$_3$), 1.24 – 1.10 (m, 4H; CH$_2$), 1.06 – 0.93 (m, 12H; C(CH$_3$)$_2$) 0.85 – 0.70 (m, 2H; NH). ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz) δ = 168.2, 168.0, 167.7, 167.0 (ArCHN), 161.7, 138.69, 138.67, 138.60, 138.58, 137.6, 137.5, 137.45, 129.5, 129.3, 129.3, 129.1, 128.3, 128.3, 128.1, 121.9, 121.5 (Ar), 78.1, 78.0, 77.83, 77.80 (O*C*H(CH$_3$)$_2$), 69.2, 68.7, 68.5 (CH$_2$), 55.1, 54.8, 54.7, 54.7 (CH), 47.0, 47.0, 46.9, 46.8 (CH$_2$), 35.4, 35.37, 34.22, 34.2 (*C*(CH$_3$)$_3$), 31.6, 30.5, 30.4, 30.2, 30.1, 30.4, 30.2, 30.1 (C(*C*H$_3$)$_3$), 26.2, 26.1 (CH$_2$), 26.05, 25.99, 25.90, 25.86, 25.8 (HC(*C*H$_3$)$_2$), 24.62, 24.5, 24.4 (CH$_2$). Note: ^{1}H assignment aided by HSQC

Elemental analysis (C$_{48}$H$_{80}$TiN$_4$O$_4$) calcd in %: C, 69.88; H 9.77; N, 6.79. Found: C, 68.15; H 10.35; N, 6.76.

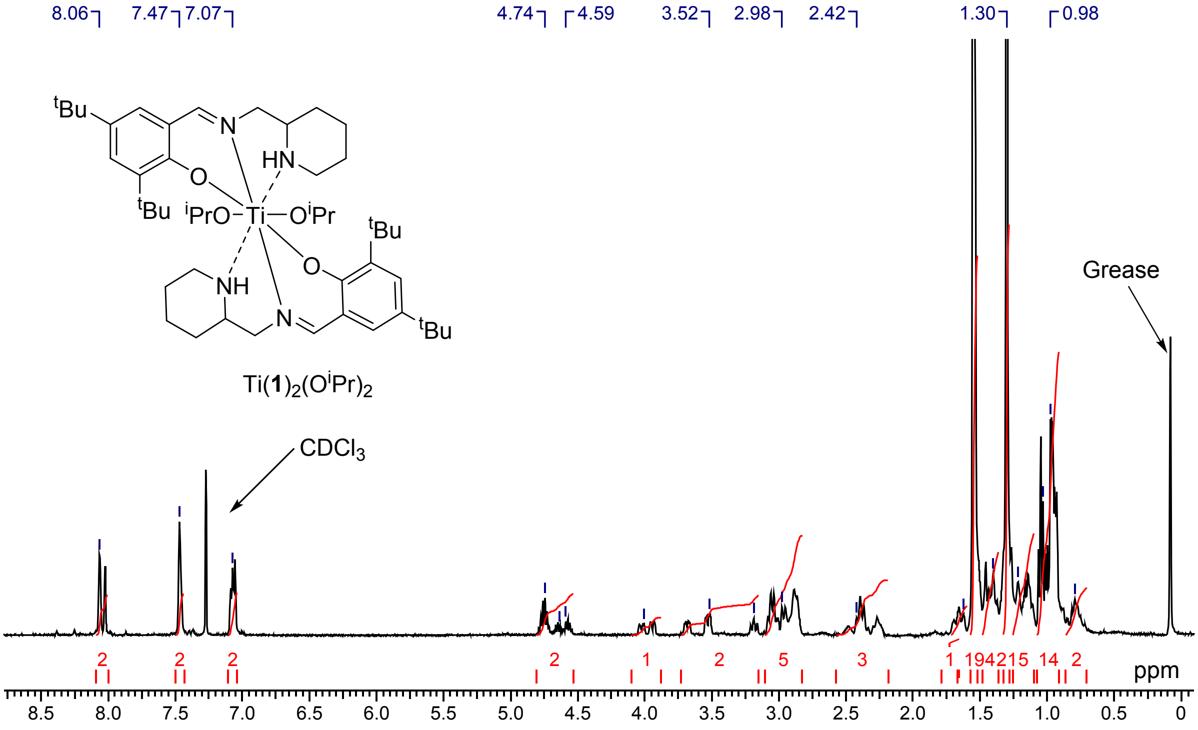


Figure S14: ^{1}H NMR (CDCl$_3$, 400 MHz) spectrum of Ti(**1**)$_2$(O^{i}Pr)$_2$.

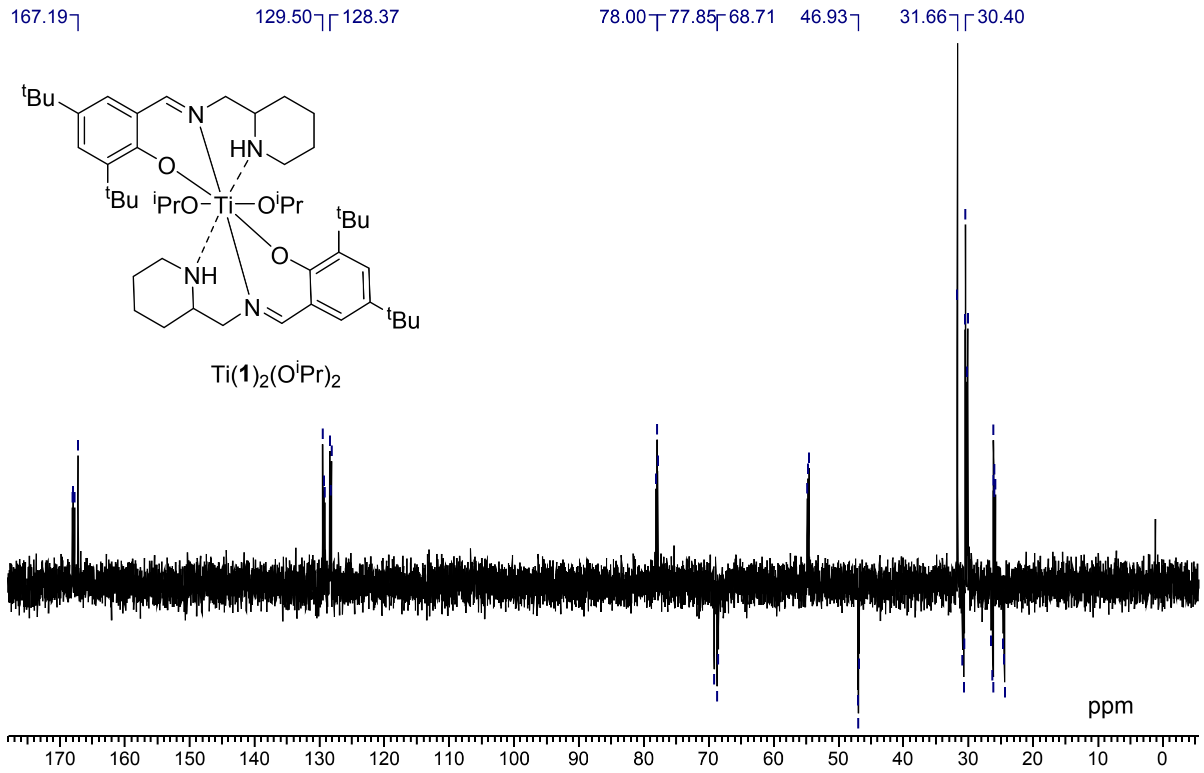


Figure S15: $^{13}C\{^{1}H\}$DEPT135 NMR ($CDCl_3$, 100 MHz) spectrum of Ti(**1**)$_2$(O^{i}Pr)$_2$.

Synthesis of imino monophenolate titanium complex, Ti(3*)(O^{i}Pr)$_2$: Ti(O^{i}Pr)$_4$ (0.30 ml, 1 mmol) was added dropwise to ligand, **3**H (0.649 g, 2 mmol) in toluene (10ml). The colour of the solution was observed to darken on addition. Complexation was stirred overnight before solvent was removed *in vacuo* and complex recrystallised from hexane to yield orange crystals (0.13 g). These crystals afforded two species in solution *via* ^{1}H NMR spectroscopy.

The remaining solution was reduced further to yield a second crop of crystals (0.342 g, 0.42 mmol, 42 %).

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.61 (dq, J = 4.8, 0.9 Hz, 1H; ArH), 8.48 (dq, J = 4.9, 0.9 Hz, 1H; ArH), 8.03 (s, 1H; ArCHN), 7.80 (br d, J = 7.4 Hz, 2H; ArH), 7.68 (td, J = 7.9, 1.9 Hz, 1H; ArH), 7.56 (td, J = 7.7, 1.8 Hz, 1H; ArH), 7.43 (d, J = 2.5 Hz, 1H; ArH), 7.23 (br dd, J = 7.5, 4.8 Hz, 1H; ArH), 7.18 (m, 2H; ArH), 6.94 (br d, J = 7.8 Hz, 1H; ArH), 6.92 (d, J = 2.6 Hz, 1H; ArH), 6.73 (d, J = 2.5 Hz, 1H; ArH), 5.75 (dt, J = 9.7, 3.1 Hz, 1H; NH), 5.00 (sept, J = 6.0 Hz, 1H; $OCH(CH_3)_2$), 4.81 (s, 1H; CH), 4.55 (sept, J = 6.0 Hz, 1H; $OCH(CH_3)_2$), 4.44 (d, J = 3.0 Hz, 1H; CH), 4.36 (dd, J = 14.9, 3.51 Hz, 1H; CH_2), 4.36 (dd, J = 14.9, 9.7 Hz, 1H; CH_2), 1.55 (s, 9H; $C(CH_3)_3$), 1.28 (d, J = 6.0 Hz, 3H; $OCH(CH_3)_2$), 1.27 (m, 9H; $C(CH_3)_3$), 1.25 (m, 18H; $C(CH_3)_3$), 1.18 (d, J = 6.2 Hz, 3H; $OCH(CH_3)_2$), 1.00 (d, J = 6.2 Hz, 3H; $OCH(CH_3)_2$), 0.86 (d, J = 6.2 Hz, 3H; $OCH(CH_3)_2$). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ =

166.3 (ArCHN), 160.3, 159.2, 157.4, 155.8, 148.6, 147.8, 137.7, 136.5, 136.0, 135.8, 135.6, 135.1, 128.7, 127.5, 124.1, 123.0, 122.6, 122.4, 122.2, 121.7, 121.5, 120.0 (Ar), 80.7, 75.8, 75.0, 64.6 (CH), 52.5 ($\mathrm{CH_2}$), 34.5, 34.2, 33.3, 33.2 ($C(\mathrm{CH_3})_3$), 31.1, 30.6, 28.8 28.8 ($\mathrm{C}(C\mathrm{H_3})_3$), 25.8, 25.7, 25.53, 25.45 ($\mathrm{HC}(C\mathrm{H_3})_2$). Note: One $\mathrm{CH(C}H_3)_2$ resonance overlaps with hexane resonance (~1.28 ppm). ESI-MS: Attempts to observe the isopropoxide complex by mass spectrometry where unsuccessful, instead, only [Ti(**3***)OMe]$^+$ was observed: (MeOH): Calcd *m/z* $[\mathrm{C_{43}H_{57}N_4O_3Ti}]^+$ = 725.3910, found *m/z* = 725.4007. Despite repeated attempts the elemental analysis was always lower in carbon, this may well be related to the increased air/moisture sensitivity.

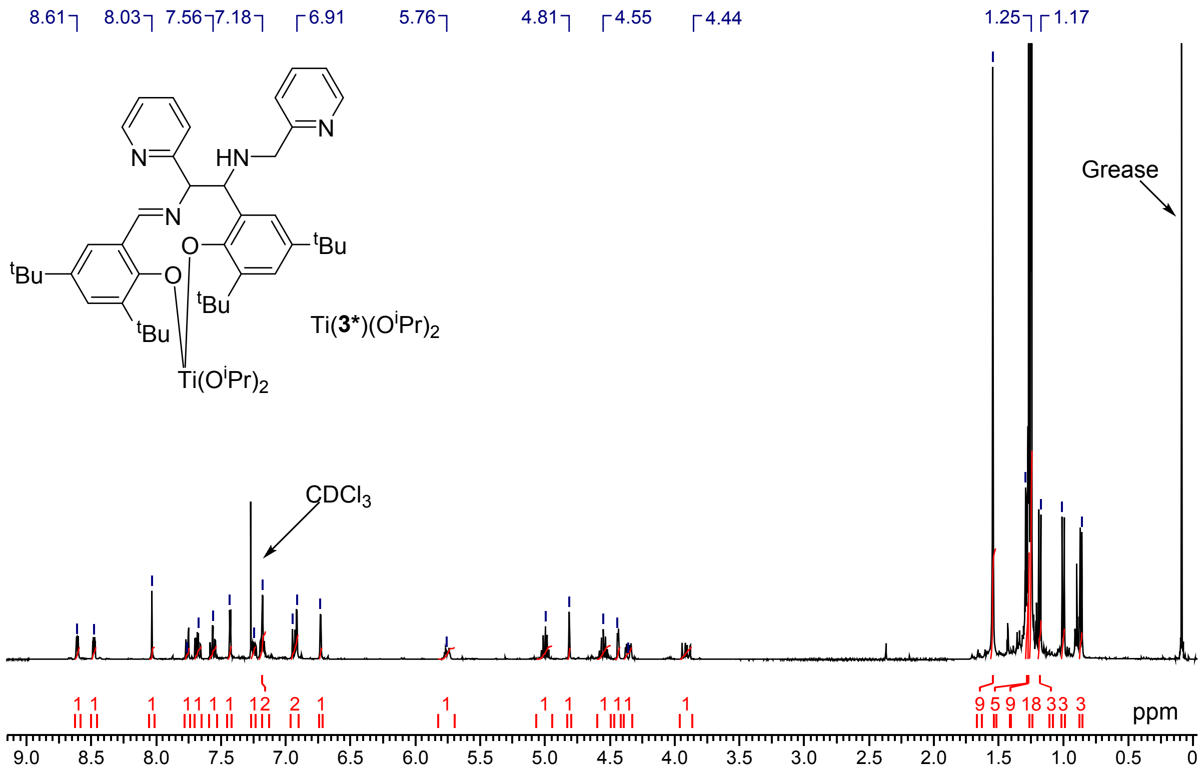


Figure S16: ^{1}H NMR ($\mathrm{CDCl_3}$, 400 MHz) spectrum of Ti(**3***)(O^{i}Pr)$_2$.

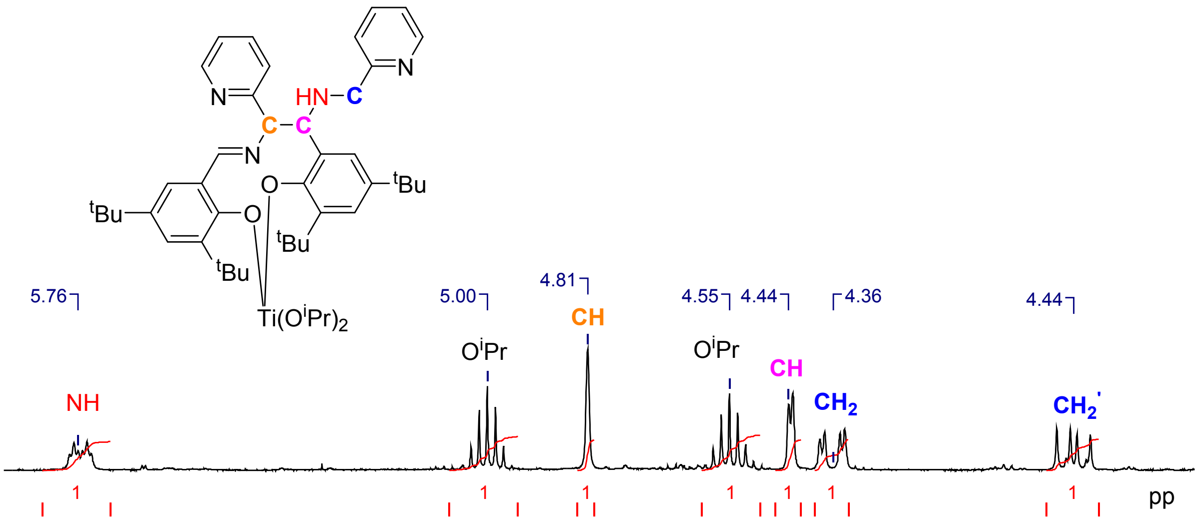


Figure S17: ^{1}H NMR (CDCl$_3$, 400 MHz) spectrum of Ti(**3***)(O^{i}Pr)$_2$ showing methine/methylene resonance assignment.

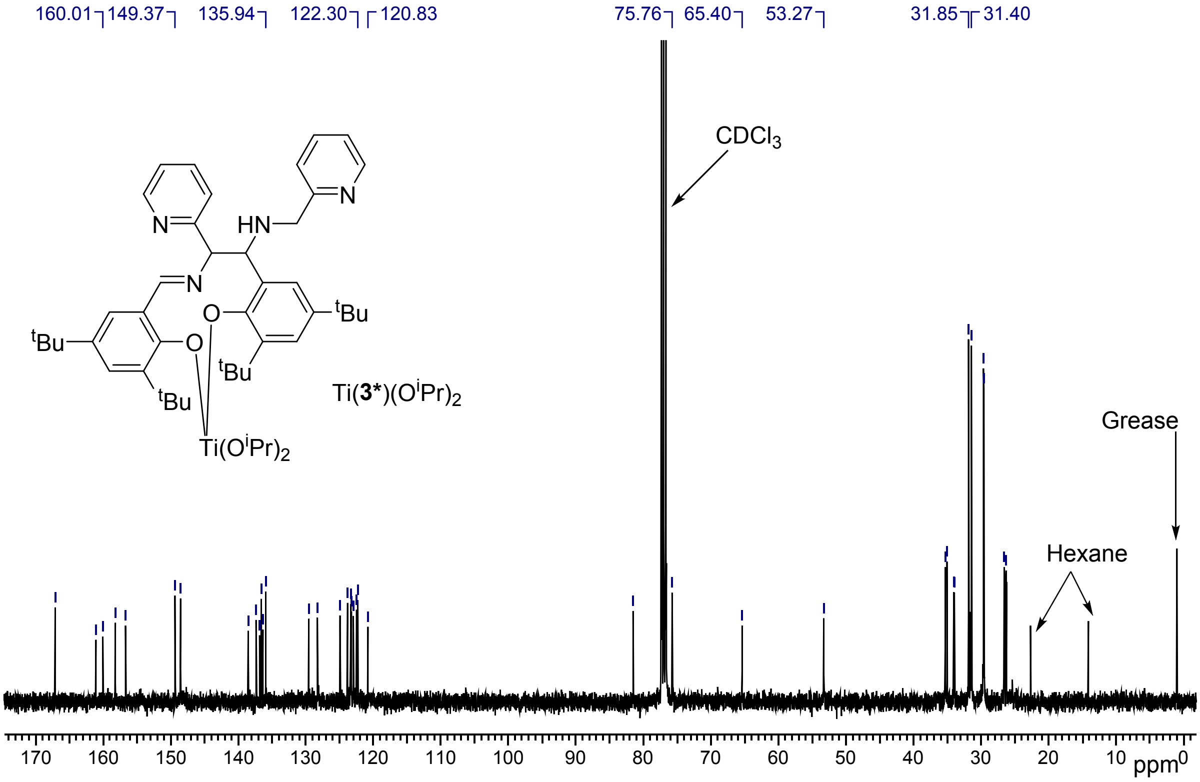


Figure S18: ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz) spectrum of Ti(**3***)(O^{i}Pr)$_2$.

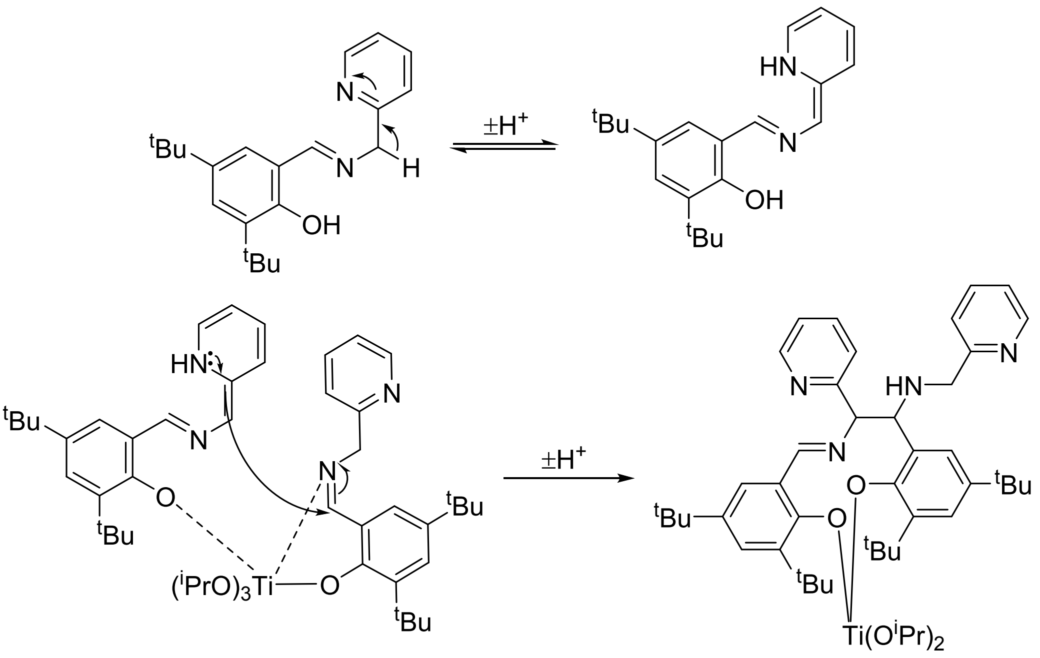


Figure S19: Potential mechanism for formation of **3***H_2.

Synthesis of salalen/salan titanium complexes, Ti(4-5)(O^{i}Pr)$_2$: Ti(O^{i}Pr)$_4$ (0.30 ml, 1 mmol) was added dropwise to ligand, **4-5**H_2 (1 mmol) in CH_2Cl_2 (10ml). After 1 hour, solvent was removed *in vacuo* and the complexes recrystallised from hexane

Ti(4)(O^{i}Pr)$_2$: Isolated as yellow crystals (0.15 g, 0.22 mmol, 22 %) Two species in a ratio of 5:1.

Major series: ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.94 (d, *J* = 1.5 Hz, 1H; ArCHN), 7.48 (d, *J* = 2.6 Hz, 1H; ArH), 7.16 (d, *J* = 2.5 Hz, 1H; ArH), 6.98 (d, *J* = 2.5 Hz, 1H; ArH), 6.91 (d, *J* = 2.1 Hz, 1H; ArH), 5.15 (sept, *J* = 6.1 Hz, 1H; $OCH(CH_3)_2$), 4.59 (m, 2H; $OCH(CH_3)_2/CH_2$), 4.51 (t, *J* = 13.9 Hz, 1H; CH_2), 4.15 (m, 2H; CH_2), 3.21 (br d, *J* = 14.8 Hz, 1H; CH_2), 3.08 (m, 2H; CH/CH_2), 2.09 (m, 1H; CH_2), 1.74 (m, 2H; CH_2), 1.57 (m, 2H; CH_2),1.51 (s, 9H; $C(CH_3)_3$), 1.37 (m, 1H; CH_2), 1.32 (s, 9H; $C(CH_3)_3$), 1.29 (s, 9H; $C(CH_3)_3$), 1.24 (d, *J* = 6.0 Hz, 3H; $OCH(CH_3)_2$), 1.22 (d, *J* = 6.2 Hz, 3H; $OCH(CH_3)_2$), 1.12 (d, *J* = 6.2 Hz, 3H; $OCH(CH_3)_2$), 1.09 (d, *J* = 6.2 Hz, 3H; $OCH(CH_3)_2$), 1.03 (s, 9H; $(C(CH_3)_3)$. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ = 161.1 (ArCHN), 160.1, 158.4, 137.8, 136.1, 136.0, 134.7, 128.0, 126.6, 123.0, 122.1, 121.04, 121.02 (Ar), 76.2, 73.9, ($OCH(CH_3)_2$), 60.4 (CH), 57.4, 53.6, 50.5 (CH_2), 34.3, 33.6, 33.0 ($C(CH_3)_3$), 30.8, 30.4, 28.9, 28.5 ($C(CH_3)_3$), 25.54, 25.51, 25.4, 25.2 ($OCH(CH_3)_2$), 20.0, 18.7, 18.4 (CH_2).

Minor series: ^{1}H NMR (CDCl$_3$, 400 MHz), $\delta = 7.91$ (s, 1H; ArCHN), 7.43 (d, $J = 2.6$ Hz, 1H; ArH), 7.16 (d, $J = 2.5$ Hz, 1H; ArH), 6.97 (m, 1H; ArH), 6.93 (d, $J = 2.5$ Hz, 1H; ArH), 5.30 (sept, $J = 6.2$ Hz, 1H; OCH(CH$_3$)$_2$), 4.33 (sept, $J = 6.0$ Hz, 1H; OCH(CH$_3$)$_2$), 4.27 (d, $J = 12.9$ Hz, 1H; ArCH$_2$), 3.98 (m, 2H; CH$_2$), 3.52 (m, 3H; CH/CH$_2$), 2.99 (m, 1H; CH$_2$), 2.29 (m, 1H; CH$_2$), 2.09 (m, 1H; CH$_2$), 1.98 (m, 1H; CH$_2$), 1.60 (m, 1H; CH$_2$), 1.59 (m, 1H; CH$_2$) 1.54 (s, 9H; C(CH$_3$)$_3$), 1.48 (m, 1H; CH$_2$), 1.31 (d, $J = 6.2$ Hz, 3H; OCH(CH_3)$_2$), 1.30 (s, 9H; C(CH$_3$)$_3$), 1.28 (s, 9H; C(CH$_3$)$_3$), 1.16 (s, 9H; (C(CH$_3$)$_3$), 1.09 (d, $J = 6.2$ Hz, 3H; OCH (CH_3)$_2$), 1.00 (d, $J = 6.0$ Hz, 3H; OCH(CH_3)$_2$), 0.90 (d, $J = 6.0$ Hz, 3H; OCH(CH_3)$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz) $\delta = 162.3$ (ArCHN), 161.5, 159.7, 137.7, 136.5, 135.6, 135.0, 127.9, 126.7, 123.0, 122.5, 122.3, 120.7 (Ar), 75.7, 73.6 (OCH(CH$_3$)$_2$), 62.9 (CH), 62.7 56.9, 51.2 (CH$_2$), 34.3, 33.7, 33.0, 32.9 (C(CH$_3$)$_3$), 30.9, 30.4, 28.7, 28.6 (C(CH$_3$)$_3$), 25.3, 25.02, 25.01, 24.9 (OCH(CH$_3$)$_2$), 23.5, 19.5, 17.6 (CH$_2$). Note: (CH$_3$)$_2$$C$H resonance overlapped with residual solvent resonance in ^{13}C{^{13}H} spectrum.

Elemental analysis (C$_{42}$H$_{68}$N$_2$O$_4$Ti$_1$) Calcd in %: C, 70.76; H, 9.62; N, 3.93. Found: C, 70.62; H, 9.71; N, 3.92.

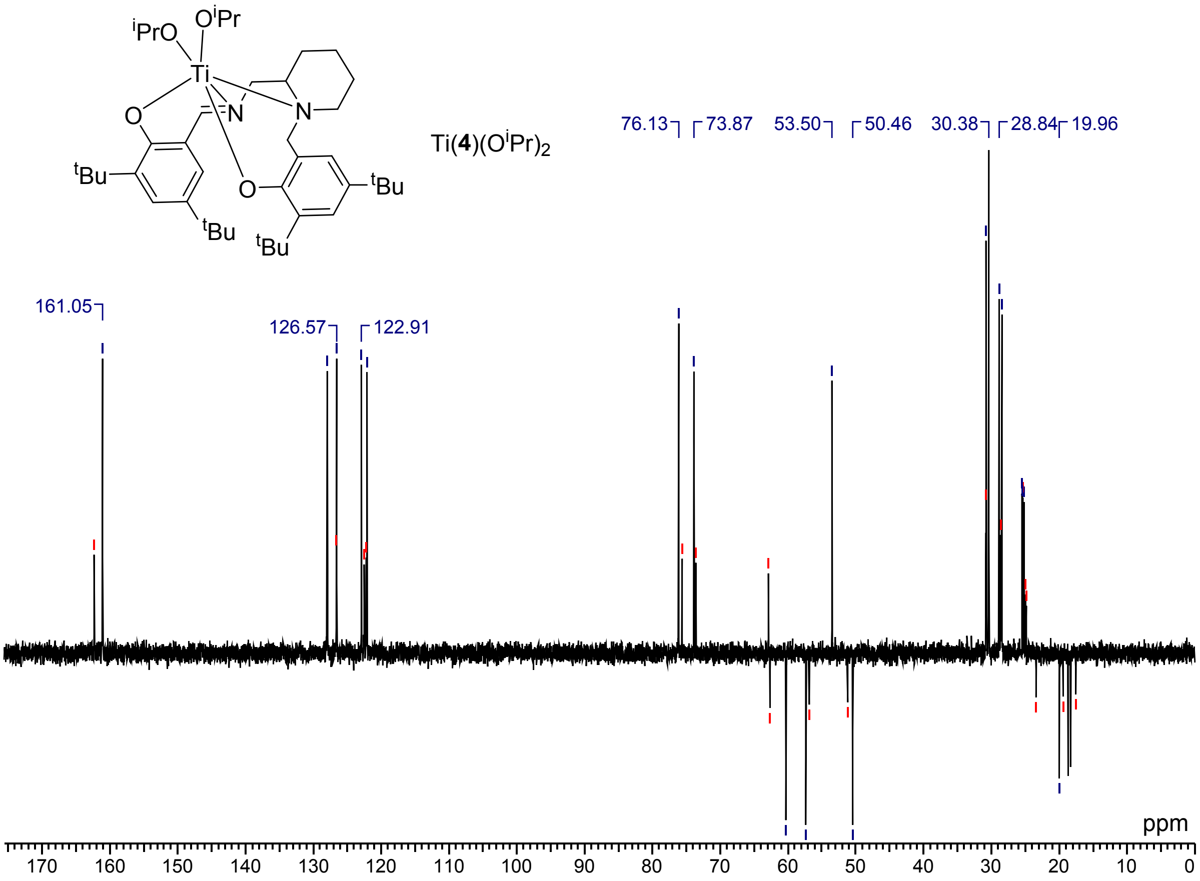


Figure S20: ^{13}C{^{1}H}DEPT135 NMR (CDCl$_3$, 100 MHz) spectrum of Ti(**4**)(O^{i}Pr)$_2$. Resonances indicated in red are minor series which is suggested to be diastereomeric form.

Ti(5)(O^{i}Pr$_2$): Isolated as yellow crystals (0.35 g, 0.49 mmol, 49 %) ~5% impurity, presumed diastereomer.

^{1}H NMR (CDCl$_3$, 400 MHz), δ = 7.25 (s, 1H; ArH), 7.21 (s, 1H; ArH), 6.91 (s, 1H; ArH), 6.77 (s, 1H; ArH), 4.81 (sept, *J* = 6.0 Hz, 1H; OC*H*(CH$_3$)$_2$), 4.70 (m, 2H; OC*H*(CH$_3$)$_2$/CH$_2$), 4.38 (d, *J* = 13.1 Hz, 1H; ArCH$_2$), 3.96 (d, *J* = 13.2 Hz, 1H; ArCH$_2$), 3.69 (m, 2H; CH$_2$), 3.30 (q, *J* = 12.7 Hz, 1H; CH$_2$), 3.01 (d, *J* = 14.7 Hz, 1H; CH$_2$), 2.93 (br d, *J* = 13.3 Hz, 1H; CH), 2.65 (br d, *J* = 12.3 Hz, 1H; NH), 2.30 (br d, *J* = 11.9 Hz, 1H; CH$_2$), 1.90 (q, *J* = 13.7 Hz, 1H; CH$_2$), 1.69 (m, 1H; CH$_2$), 1.53 (s. 9H; (C(CH$_3$)$_3$), 1.50 (m, 1H; CH$_2$), 1.33 (s. 9H; (C(CH$_3$)$_3$), 1.31 (br s. 11H; CH$_2$/(C(CH$_3$)$_3$), 1.24 (d, *J* = 6.0 Hz, 3H; OCH(C*H*$_3$)$_2$), 1.19 (d, *J* = 6.2 Hz, 3H; OCH(C*H*$_3$)$_2$), 1.15 (m, 1H; CH$_2$) 1.13 (d, *J* = 6.2 Hz, 3H; OCH(C*H*$_3$)$_2$), 0.95 (d, *J* = 6.0 Hz, 3H;OCH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz) δ = 159.3, 158.9, 138.5, 138.1, 136.0, 135.8, 124.5, 123.6, 123.5, 123.0, 122.5, 121.6 (Ar), 77.3, 77.0 (O*C*H(CH$_3$)$_2$), 56.8, 54.0 (CH$_2$), 53.2 (CH), 49.6, 49.0 (CH$_2$), 35.4, 35.3, 34.3, 34.2 (*C*(CH$_3$)$_3$), 32.0, 32.0, 31.8, 30.5, 29.8 (C(*C*H$_3$)$_3$), 26.8, 26.8, 26.6, 26.3 (OCH(*C*H$_3$)$_2$), 21.0, 19.7, 19.0 (CH$_2$). Note: O*C*H(CH$_3$)$_2$ resonance overlapped with residual solvent resonance in ^{13}C{^{13}H} spectrum.

Elemental analysis (C$_{42}$H$_{70}$N$_2$O$_4$Ti$_1$) Calcd in %: C, 70.56; H, 9.87; N, 3.92. Found: C, 70.45; H, 9.94; N, 3.92.

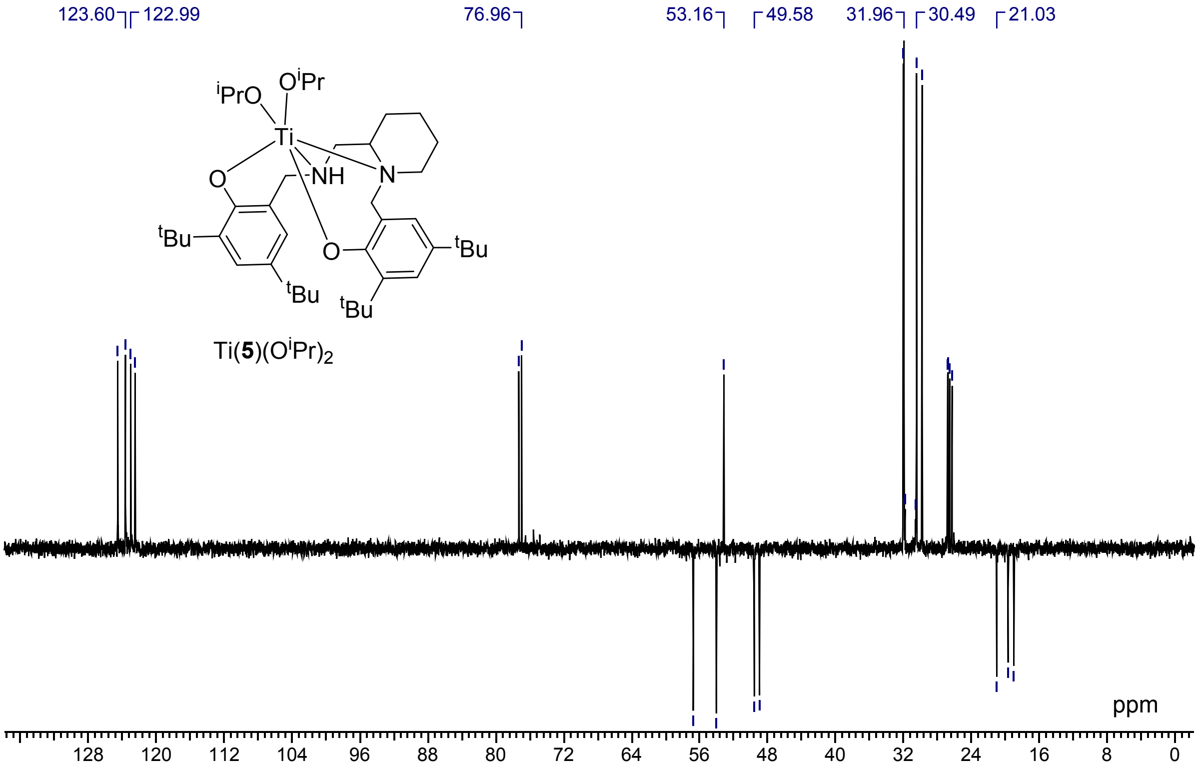


Figure S21: ^{13}C{^{1}H}DEPT135 NMR (CDCl$_3$, 100 MHz) spectrum of Ti(**5**)(O^{i}Pr)$_2$.

Synthesis of bicyclic bisphenolate titanium complex, Ti(6)(O^{i}Pr)$_2$: Ti(O^{i}Pr)$_4$ (0.30 ml, 1 mmol) was added dropwise to ligand, **6**H$_2$ (1 mmol) in CH_2Cl_2 (10ml). After 1 hour, solvent was removed *in vacuo* and the complexes recrystallised from hexane.

Ti(6)(O^{i}Pr)$_2$: Isolated as a pale yellow powder (0.20 g, 0.281 mmol, 28 %)

^{1}H NMR ($CDCl_3$, 400 MHz), $\delta = 7.26$ (d, $J = 2.4$ Hz, 1H; ArH), 7.20 (d, $J = 2.5$ Hz, 2H; ArH), 6.88 (d, $J = 2.4$ Hz, 1H; ArH), 5.08 (m, 2H; OCH(CH$_3$)$_2$), 4.74 (s, 1H; ArCHN$_2$), 3.48 (m, 1H; CH$_2$), 3.36 (m, 2H; CH$_2$), 3.28 (d, $J = 12.7$ Hz, 1H; ArCH$_2$), 3.08 (d, $J = 12.7$ Hz, 1H; ArCH$_2$), 2.35 (m, 2H; CH/CH), 1.86 (m, 5H; CH$_2$), 1.47 (s, 9H; C(CH$_3$)$_3$), 1.44 (m, 16H; CH(CH_3)$_2$/CH$_2$/C(CH$_3$)$_3$), 1.35 (s, 9H; C(CH$_3$)$_3$). 1.26 (m, 12H; OCH(CH_3)$_2$/C(CH$_3$)$_3$). 1.19 (d, $J = 6.2$ Hz, 3H; OCH(CH_3)$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) $\delta = 160.2$, 158.2, 139.9, 139.9, 134.2, 134.1, 124.3, 124.0, 122.6, 121.8, 121.6, 119.6. (Ar), 81.9 (ArCHN$_2$), 78.6, 77.2 (OCH(CH$_3$)$_2$), 64.2 (CH), 56.0, 54.2, 51.0 (CH$_2$), 33.94, 33.90, 34.4, 33.2 (C(CH$_3$)$_3$), 30.8, 30.7, 28.6, 28.5 (C(CH$_3$)$_3$), 28.2 (CH$_2$), 25.7, 25.6, 25.5, 25.4 (OCH(CH$_3$)$_2$), 23.9, 23.5 (CH$_2$). Elemental analysis ($C_{42}H_{68}N_2O_4Ti_1$) Calcd in %: C, 70.76; H, 9.62; N, 3.93. Found: C, 67.84; H, 9.85; N, 3.87. Despite repeated attempts the elemental analysis was always lower in carbon, this may well be related to the increased air/moisture sensitivity of the 5 coordinated complex.

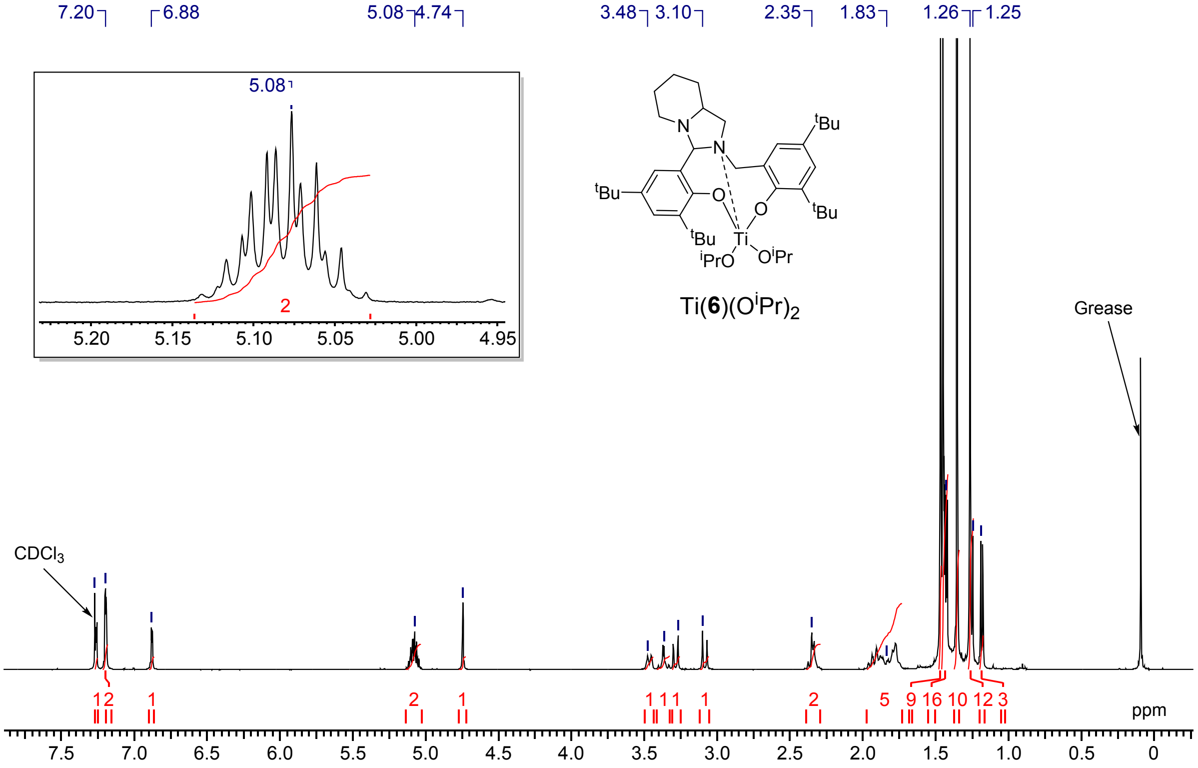


Figure S22: ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of Ti(**6**) (O^{i}Pr)$_2$. Inset: Asymmetrical O^{i}Pr methine resonance.

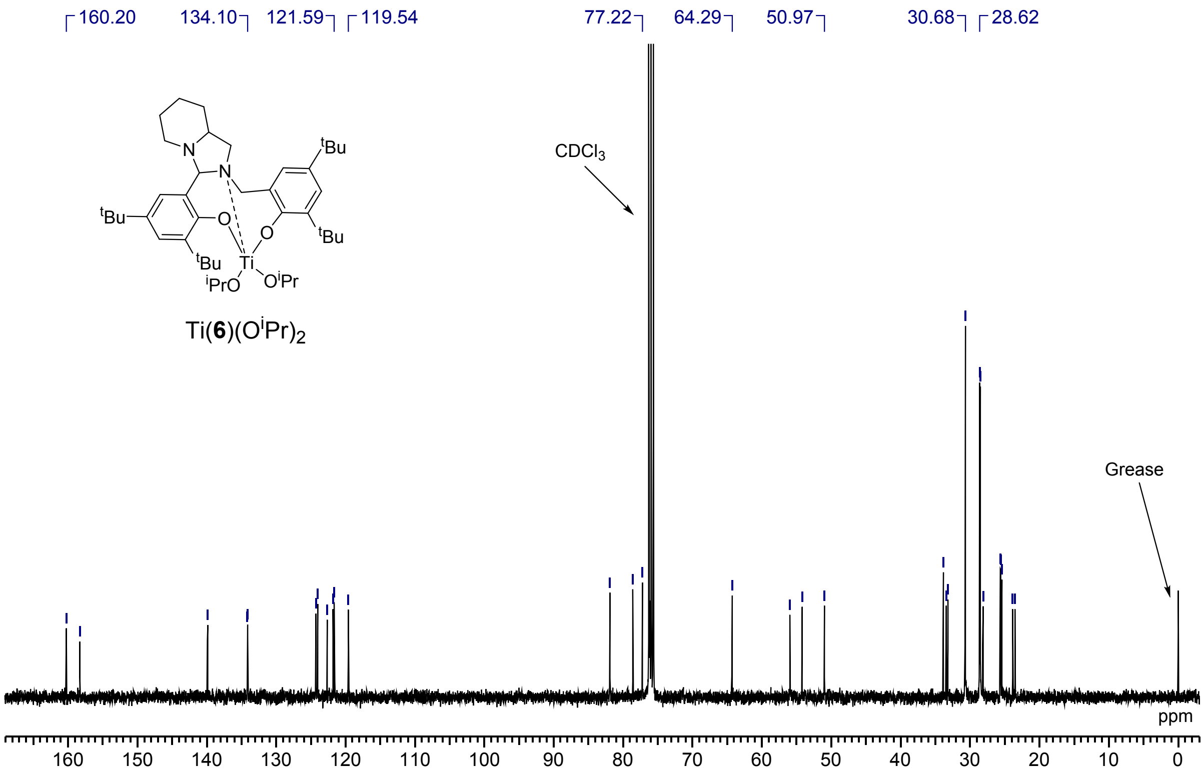


Figure S23: $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) spectrum of Ti(**6**)(O^{i}Pr)$_2$.

Synthesis of imino monophenolate zirconium complex, Zr(1)(O^{i}Pr)$_2$: A solution of $Zr(O^iPr)_4 \cdot HO^iPr$ (0.387 g, 1 mmol, 10 ml CH_2Cl_2) was added dropwise to ligand, **1**H$_2$ (0.504 g, 2 mmol) in CH_2Cl_2 (10ml). After 1 hour, solvent was removed *in vacuo* and complex recrystallised from hexane to yield pale yellow crystals (0.24 g, 0.27 mmol, 27%). Multiple species in solution.

Treated as one species: ^{1}H NMR ($CDCl_3$, 400 MHz), δ = 8.13 – 8.01 (m, 2H; ArCHN), 7.49 (s, 2H; ArH), 7.12 – 7.03 (m, 2H; ArH), 4.39 – 4.21 (m, 2H; OC*H*(CH_3)$_2$), 3.71 – 3.55 (m, 2H; CH_2), 3.19 – 2.79 (m, 6H; CH/CH_2), 2.55 – 2.14 (m, 3H; CH/CH_2), 1.71 – 1.61 (m, 2H; CH_2), 1.58 – 1.48 (m, 19H; CH_2/C(CH_3)$_3$), 1.47 – 1.33 (m, 4H; CH_2), 1.32 – 1.28 (m, 20H; CH_2/C(CH_3)$_3$), 1.24 – 1.18 (m, 2H; CH_2), 1.17 – 1.11 (m, 6H; OCH(CH_3)$_2$), 1.08 – 0.97 (m, 6H; OCH(CH_3)$_2$) 0.96 – 0.81 (m, 2H; NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ = 170.1, 169.9 (ArCHN), 169.3, 160.7, 160.4, 138.9, 138.8, 138.4, 129.9, 129.8, 128.9, 128.9, 121.9, 121.7, 121.5, 121.3 (Ar), 71.5, 71.4 (O*C*H(CH_3)$_2$), 69.0 (CH_2), 54.5, 54.32 (CH), 46.8, 46.6 (CH_2), 35.5, 34.2 (*C*(CH_3)$_3$), 31.62, 31.60, 30.2, 30.1, 30.0, 29.9 (C(*C*H_3)$_3$), 27.4, 27.3, 27.1 (OCH(*C*H_3)$_3$), 26.1, 24.3, 24.3 (CH_2).

Elemental analysis ($C_{48}H_{80}ZrN_4O_4$) calcd in %: C, 66.39; H 9.29; N, 6.45. Found: C, 66.28; H 9.16; N, 6.46.

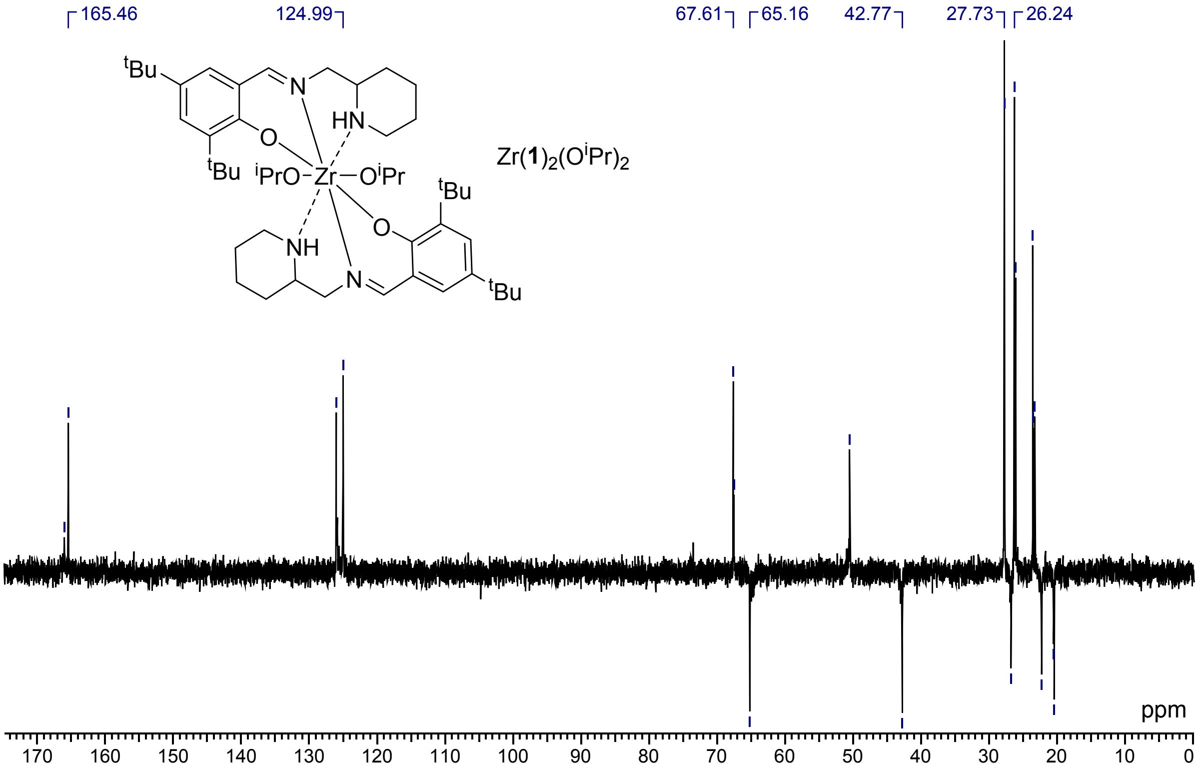


Figure S24: $^{13}C\{^{1}H\}$DEPT135 NMR ($CDCl_3$, 100 MHz) spectrum of $Zr(\mathbf{1})_2(O^{i}Pr)_2$.

Synthesis of imino monophenolate zirconium complex, $Zr(3)(O^{i}Pr)_2$: A solution of $Zr(O^{i}Pr)_4{\cdot}HO^{i}Pr$ (0.387 g, 1 mmol, 10 mlm CH_2Cl_2) was added dropwise to ligand, $\mathbf{3}H_2$ (0.504 g, 2 mmol) in CH_2Cl_2 (10ml). After 1 hour, solvent was removed *in vacuo* and complex precipitated from hexane/toluene to yield a pale yellow powder (0.52 g, 0.61 mmol, 61%).

Treated as one species*:* ^{1}H NMR ($CDCl_3$, 273 K, 400 MHz), δ = 8.38 (d, *J* = 3.4 Hz, 2H; ArCHN), 7.90 (s, 2H; ArH), 7.41 (s, 2H; ArH), 7.32 (t, *J* = 7.3 Hz, 2H; ArH), 7.04 (m, 4H; ArH), 6.84 (s, 2H; ArH), 4.79 (d, *J* = 14.4 Hz, 2H; CH_2), 4.61 (d, *J* = 14.4 Hz, 2H; CH_2), 4.25 (sept, *J* = 5.8 Hz, 2H; $OC\mathit{H}(CH_3)_2$), 1.42 (s, 18H; $C(CH_3)_3$), 1.28 (s, 18H; $C(CH_3)_3$), 1.06 (d, *J* = 5.8 Hz, 6H; $OCH(C\mathit{H}_3)_2$), 1.02 (d, *J* = 5.8 Hz, 6H; $OCH(C\mathit{H}_3)_2$). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ = 171.9 (ArCHN), 160.4, 158.1, 148.7, 138.6, 136.0, 129.5, 128.9, 123.1, 121.7 (Ar), 71.09 ($O\mathit{C}H(CH_3)_2$), 63.9 (CH_2), 35.20, 34.00 ($\mathit{C}(CH_3)_3$), 31.5, 29.7 ($C(\mathit{C}H_3)_3$), 27.0 ($OCH(\mathit{C}H_3)_3$). Despite repeated attempts the elemental analysis was always lower in carbon, this may well be related to the increased air/moisture sensitivity.

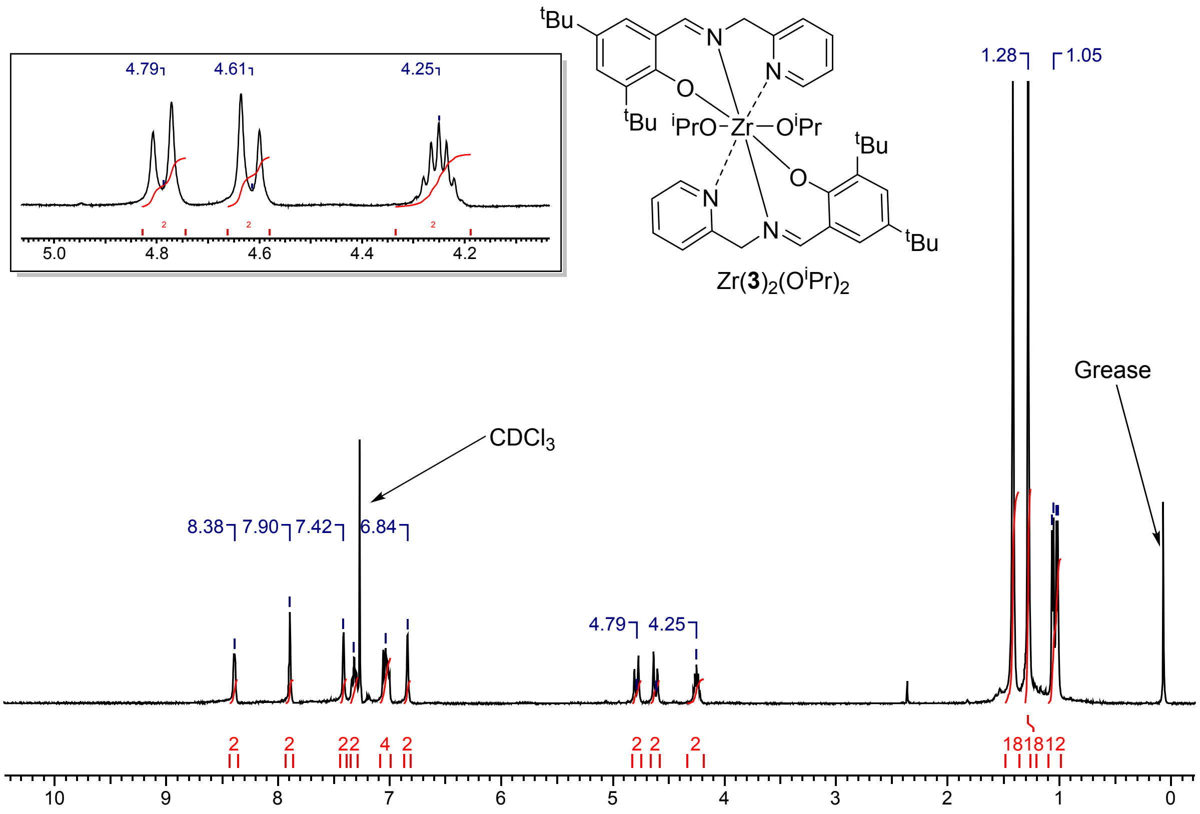


Figure S25: ^{1}H NMR (CDCl$_3$, 273 K, 400 MHz) spectrum of Zr(**3**)(O^{i}Pr)$_2$. Inset: Diastereotopic -CH$_2$- and O^{i}Pr resonances.

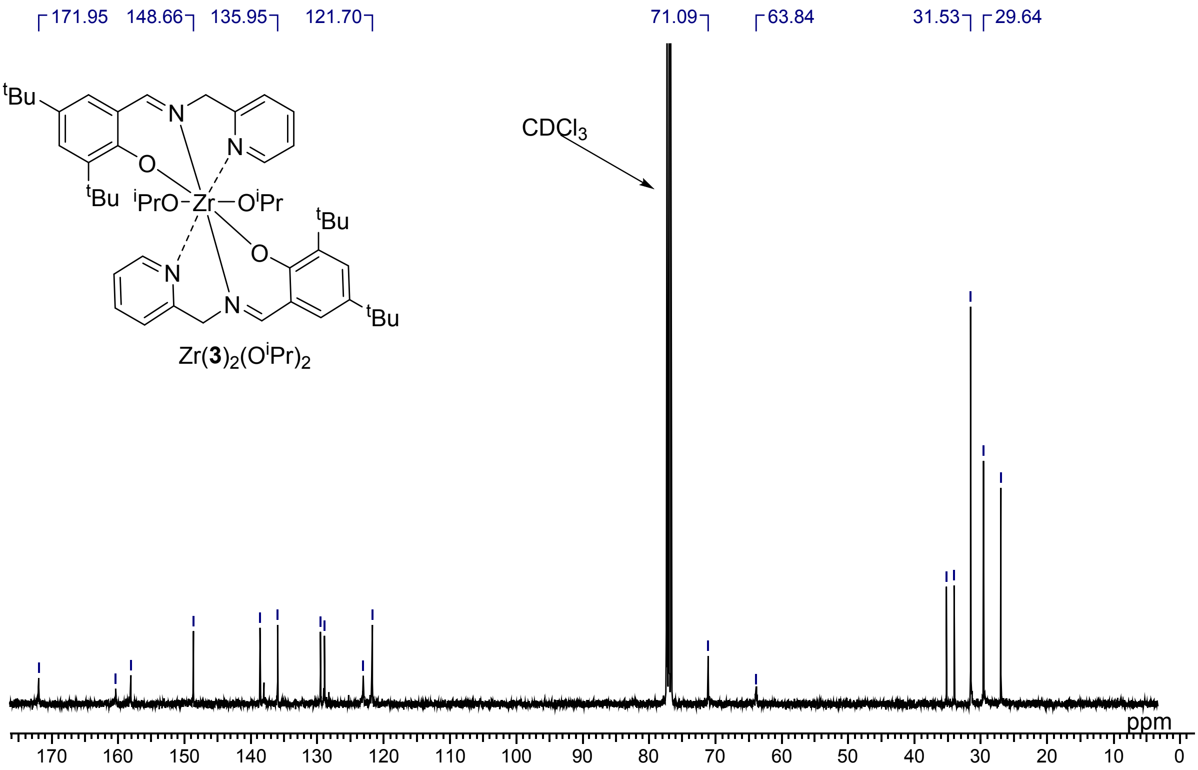


Figure S26: ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz) spectrum of Zr(**3**)$_2$(O^{i}Pr)$_2$.

Synthesis of salalen/salan zirconium complexes, Zr(4-5)(O^{t}Bu)$_2$: $Zr(O^tBu)_4$ (0.34 ml, 1 mmol) was added dropwise to ligand, **26/31**H_2 (1 mmol) in CH_2Cl_2 (10ml). The solution was stirred at room temperature for 16 hours before solvent removal and recrystallisation from hexane

Zr(4)(O^{t}Bu)$_2$: Isolated as colourless crystals (0.64 g, 0.81 mmol, 81%) Two species in a ratio of 5:1.

Major series: ^{1}H NMR ($CDCl_3$, 400 MHz), δ = 7.89 (d, *J* = 1.6 Hz, 1H; ArCHN), 7.48 (d, *J* = 2.5 Hz, 1H; ArH), 7.15 (d, *J* = 2.6 Hz, 1H; ArH), 6.92 (d, *J* = 2.5 Hz, 1H; ArH), 6.90 (d, *J* = 2.4 Hz, 1H; ArH), 4.63 (td, *J* = 13.1, 1.6 Hz, 1H; CH_2), 4.39 (d, *J* = 12.9 Hz, 1H; $ArCH_2$), 4.34 (m, 1H; CH_2), 4.07 (d, *J* = 13.2 Hz, 1H; $ArCH_2$), 3.05 (m, 2H; CH_2), 2.94 (m, 1H; CH), 2.09 (m, 1H; CH_2), 1.73 (m, 2H; CH_2), 1.58 (m, 2H; CH_2), 1.55 (s, 9H; $C(CH_3)_3$), 1.32 (m, 1H; CH_2), 1.30 (s, 9H; $C(CH_3)_3$), 1.29 (s, 9H; $C(CH_3)_3$), 1.28 (s, 9H; $C(CH_3)_3$), 1.20 (s, 9H; ($C(CH_3)_3$), 1.07 (s, 9H; ($C(CH_3)_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ = 164.6 (ArCHN), 160.0, 159.5, 138.5, 136.5, 136.4, 129.3, 128.3, 124.2, 123.6, 122.0, 121.5 (Ar), 74.9, 74.5 ($\mathrm{O}\mathit{C}(\mathrm{CH_3})_3$), 61.7, 57.4 ($CH_2$), 54.2 (CH), 50.3 ($CH_2$), 35.5, 34.9, 34.2, 34.1 ($\mathit{C}(\mathrm{CH_3})_3$), 33.2, 33.1, 33.08, 32.9, 32.1, 31.7, 30.0, 29.4 ($\mathrm{C}(\mathit{C}\mathrm{H_3})_3$), 21.5, 19.6, 19.2 ($CH_2$).

Minor series: ^{1}H NMR ($CDCl_3$, 400 MHz), δ = 7.84 (s, 1H; ArCHN), 7.43 (d, *J* = 2.6 Hz, 1H; ArH), 7.15 (d, *J* = 2.5 Hz, 1H; ArH), 6.96 (d, *J* = 2.6 Hz, 1H; ArH), 6.92 (m, 1H; ArH), 4.30 (m, 1H; $ArCH_2$), 4.00 (m, 2H; CH_2), 3.87 (m, 1H; CH), 3.50 (t d, *J* = 13.9, 2.0 Hz, 1H; CH_2), 3.39 (br dd, *J* = 13.4, 3.6 Hz, 1H; CH_2), 2.95 (m, 1H; CH_2), 2.32 (m, 1H; CH_2), 2.09 (m, 1H; CH_2), 1.96 (m, 1H; CH_2), 1.64 (m, 1H; CH_2), 1.59 (m, 1H; CH_2), 1.54 (s, 9H; $C(CH_3)_3$), 1.44 (m, 1H; CH_2), 1.33 (s, 9H; ($C(CH_3)_3$), 1.30 (s, 9H; ($C(CH_3)_3$), 1.28 (s, 9H; ($C(CH_3)_3$), 1.15 (s, 9H; ($C(CH_3)_3$), 1.08 (s, 9H; ($C(CH_3)_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ = 166.0 (ArCHN), 161.4, 159.8, 138.4, 138.1, 136.9, 136.7, 129.2, 128.5, 124.0, 123.7, 123.5, 122.2 (Ar), 75.2, 74.6 ($\mathrm{O}\mathit{C}(\mathrm{CH_3})_3$), 63.6 ($CH_2$), 63.4 (CH), 56.2, 52.7 (CH_2), 35.5, 34.9, 34.2, 34.1 ($\mathit{C}(\mathrm{CH_3})_3$), 33.10, 33.08, 32.1, 31.7, 29.9, 29.7 ($\mathrm{C}(\mathit{C}\mathrm{H_3})_3$), 24.7, 20.6, 18.1 ($CH_2$).

Elemental analysis ($C_{44}H_{72}N_2O_4Zr_1$) Calcd in %: C, 67.38; H, 9.25; N, 3.57. Found: C, 67.21; H, 9.31; N, 3.50.

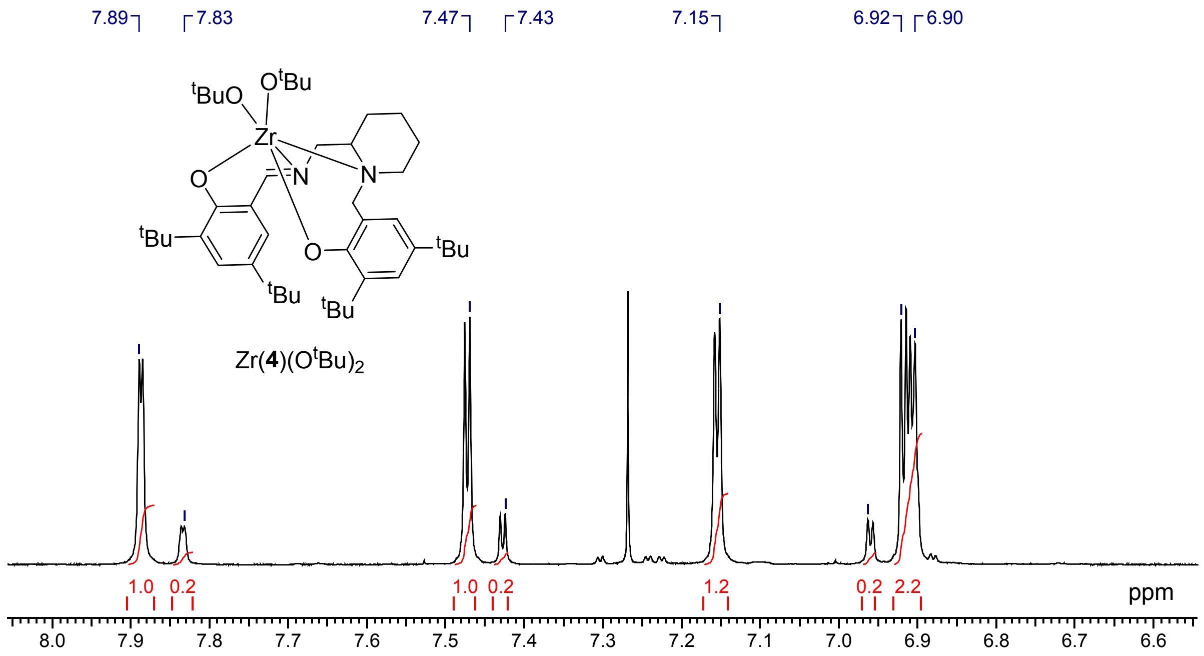


Figure S27: ^{1}H NMR (CDCl$_3$, 400 MHz) spectrum of Zr(**4**)(O^{t}Bu)$_2$ showing imino/aromatic region.

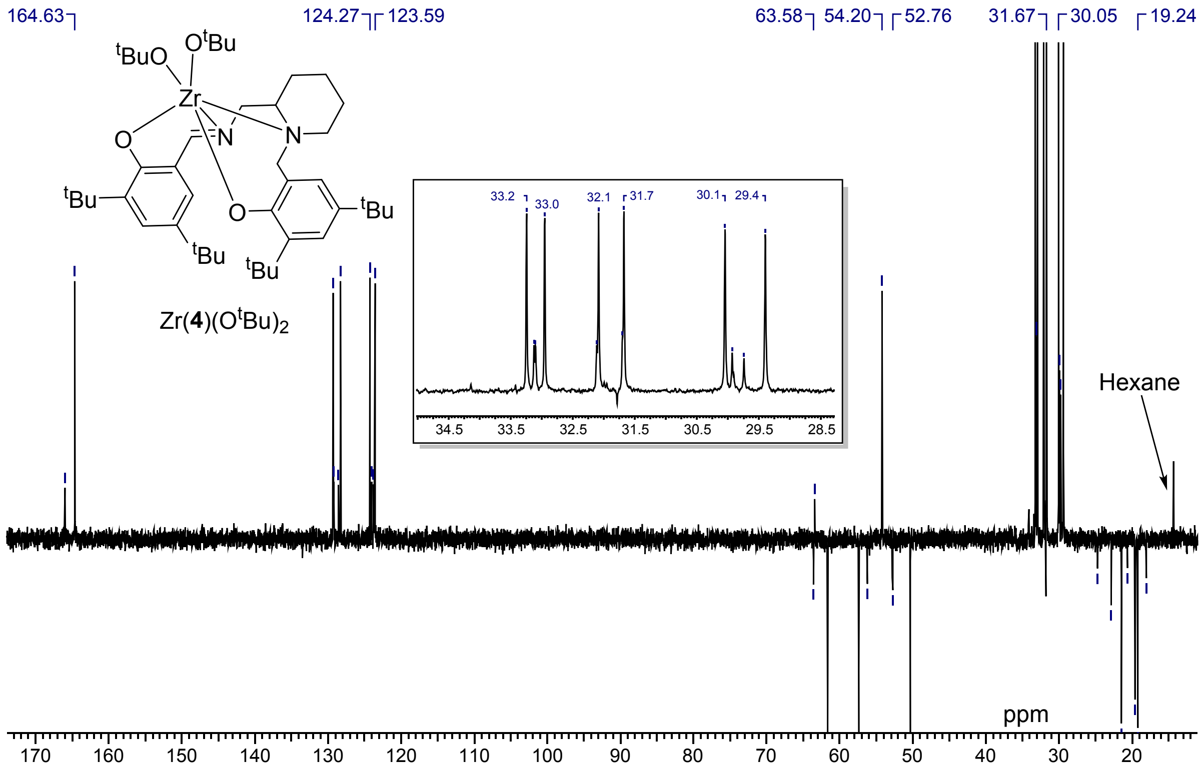


Figure S28: ^{13}C{^{1}H}DEPT135 NMR (CDCl$_3$, 100 MHz) spectrum of Zr(**4**)(O^{t}Bu)$_2$. Inset: ^{t}Bu methyl resonances.

Zr(5)(O^{t}Bu)$_2$: Isolated a colourless crystals (0.11 g, 0.140 mmol, 14 %).

^{1}H NMR (CDCl$_3$, 400 MHz), δ = 7.26 (s, 1H; ArH), 7.21 (s, 1H; ArH), 6.92 (s, 1H; ArH), 6.75 (s, 1H; ArH), 4.80 (d, J = 13.6 Hz, 1H; ArCH$_2$), 4.56 (d, J = 12.9 Hz, 1H; ArCH$_2$), 3.91 (d, J = 12.9 Hz, 1H; ArCH$_2$), 3.64 (d, J = 13.3 Hz, 1H; ArCH$_2$), 3.46 (t, J = 13.8 Hz, 1H; CH$_2$), 3.24 (q, J = 12.9 Hz, 1H; CH$_2$), 3.03 (d, J = 13.9 Hz, 1H; CH$_2$), 2.83 (br d, J = 11.2 Hz, 1H; CH), 2.29 (t, J = 11.2 Hz, 2H; CH$_2$/NH), 1.93 (q, J = 13.7 Hz, 1H; CH$_2$), 1.65 (m, 1H; CH$_2$), 1.53 (s, 9H; C(CH$_3$)$_3$), 1.52 (s. 9H; C(CH$_3$)$_3$), 1.46 (m, 1H; CH$_2$), 1.32 (s. 18H; C(CH$_3$)$_3$), 1.30 (s. 9H; C(CH$_3$)$_3$), 1.27 (m, 2H; CH$_2$), 1.22 (s. 9H; C(CH$_3$)$_3$), 1.08 (m, 1H; CH$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz) δ = 158.4, 157.7, 138.0, 137.9, 136.7, 136.3, 124.7, 124.2, 123.4, 123.4, 123.1, 121.5 (Ar), 75.9, 75.5 (O*C*(CH$_3$)$_3$), 56.1, 53.9 (CH$_2$), 52.6 (CH), 48.2, 47.2 (CH$_2$), 35.4, 35.3, 34.3, 34.2 (*C*(CH$_3$)$_3$), 33.4, 33.3, 32.1 32.0, 30.3, 29.8 (C(*C*H$_3$)$_3$), 21.0, 19.3, 18.4 (CH$_2$). Elemental analysis (C$_{44}$H$_{74}$N$_2$O$_4$Zr$_1$) Calcd in %: C, 67.21; H, 9.49; N, 3.56. Found: C, 66.93; H, 9.42; N, 3.47.

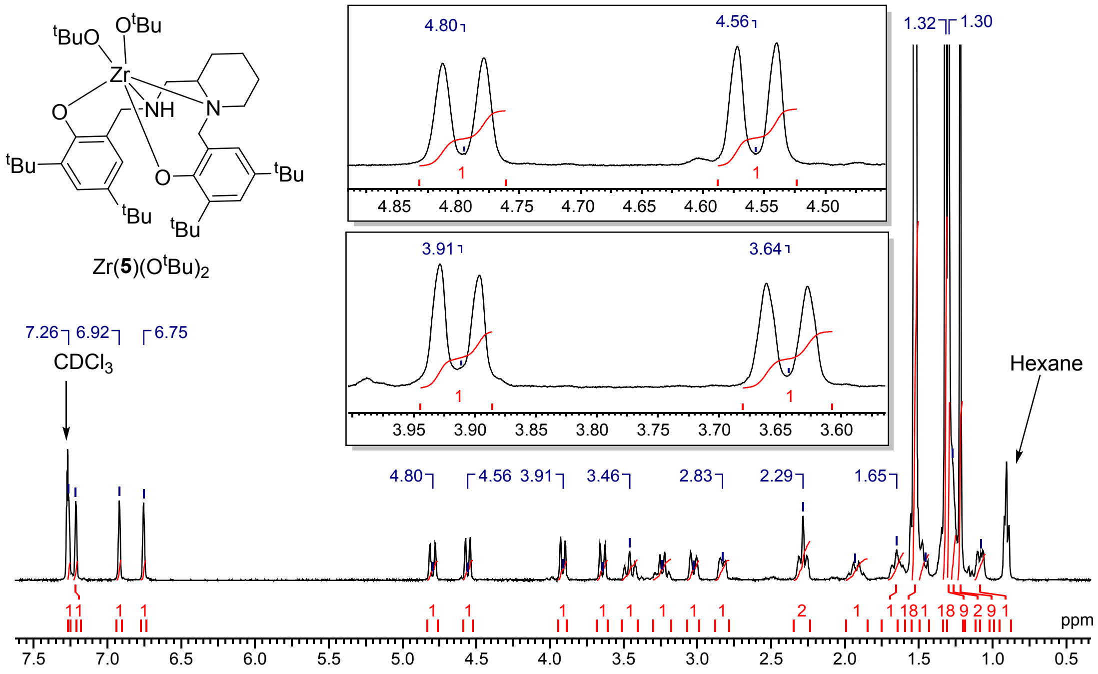


Figure S29: ^{1}H NMR (CDCl$_3$, 400 MHz) spectrum of Zr(**5**)(O^{t}Bu)$_2$. Inset: Diasteretopic -CH$_2$- resonances.

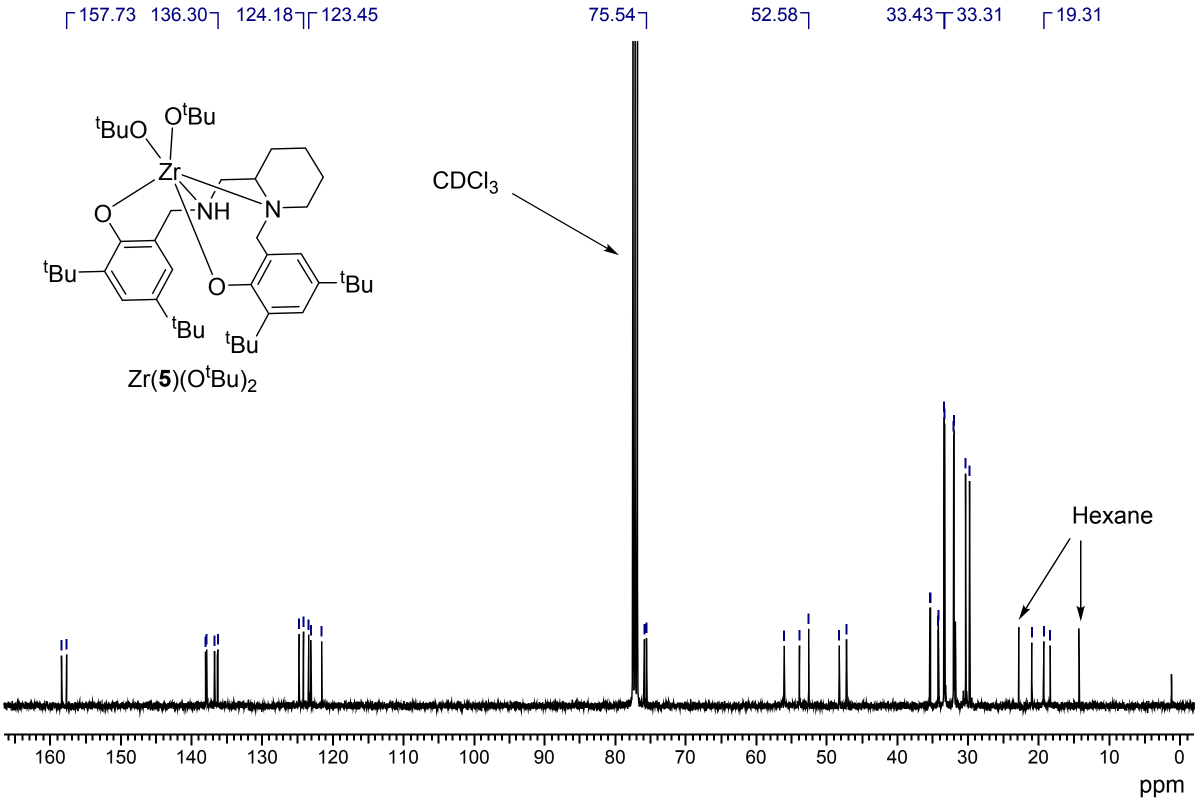


Figure S30: $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) spectrum of Zr(**5**)(O^tBu)$_2$.

Synthesis of bicyclic bisphenolate zirconium complexes, Zr(6)(O^tBu)$_2$: Zr(O^tBu)$_4$ (0.34 ml, 1 mmol) was added dropwise to ligand, **6**H_2 (1 mmol) in CH_2Cl_2 (10ml). The solution was stirred at room temperature for 16 hours before solvent removal and recrystallisation from hexane.

Zr(6)(O^tBu)$_2$: Isolated as colourless crystals (0.24 g, 0.306 mmol, 31 %).

^{1}H NMR ($CDCl_3$, 400 MHz), δ = 7.30 (d, J = 2.5 Hz, 1H; ArH), 7.24 (d, J = 2.5 Hz, 1H; ArH), 7.22 (d, J = 2.3 Hz, 1H; ArH), 6.87 (d, J = 2.4 Hz, 1H; ArH), 4.58 (s, 1H; $ArCHN_2$), 3.45 (m, 1H; CH_2), 3.25 (m, 2H; CH_2/$ArCH_2$), 3.12 (d, J = 12.0 Hz, 1H; $ArCH_2$), 2.45 (m, 2H; CH/CH_2), 1.86 (m, 5H; CH_2), 1.48 (2 x s, 19H; CH_2/$C(CH_3)_3$), 1.44 (s, 10H; CH_2/$C(CH_3)_3$), 1.36 (s, 9H; $C(CH_3)_3$). 1.34 (s, 9H; $C(CH_3)_3$). 1.27 (s, 9H; $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ = 159.1, 157.5, 140.4, 140.3, 136.3, 136.2, 125.8, 124.9, 123.4, 123.3, 122.8, 121.5 (Ar), 82.8 ($ArCHN_2$), 76.7 ($OC(CH_3)_3$), 64.8 (CH), 55.6, 55.5, 52.2 (CH_2), 35.2, 34.6, 34.4 ($\mathit{C}(CH_3)_3$), 33.12, 30.10, 32.0, 31.9, 29.9 ($C(\mathit{C}H_3)_3$), 29.2, 25.0, 24.7 (CH_2).

Elemental analysis ($C_{44}H_{72}N_2O_4Zr_1$) Calcd in %: C, 67.37; H, 9.25; N, 3.57. Found: C, 67.45; H, 9.26; N, 3.63.

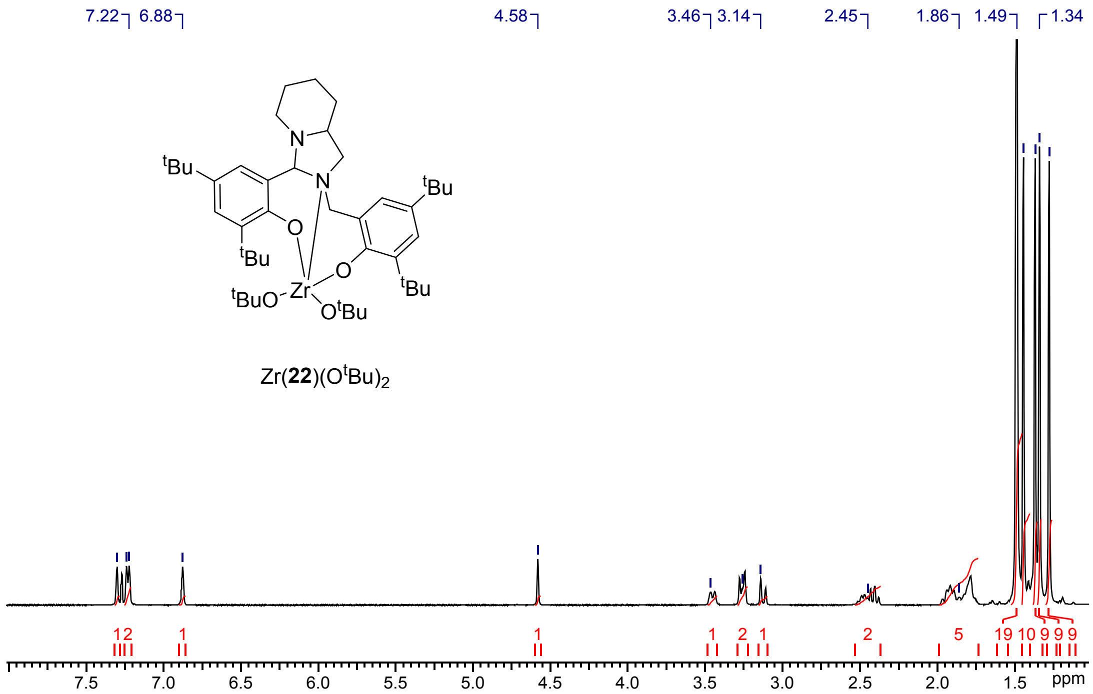


Figure S31: ^{1}H NMR (CDCl$_3$, 400 MHz) spectrum of Zr(**6**)(O^{t}Bu)$_2$.

Suggested stereoisomers present in solution

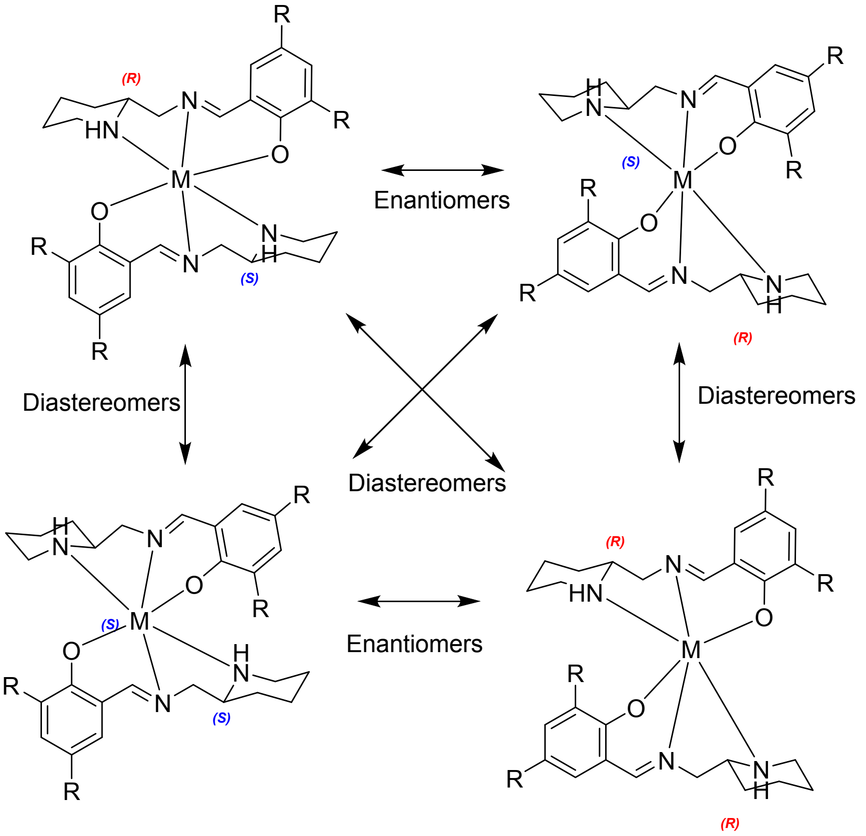
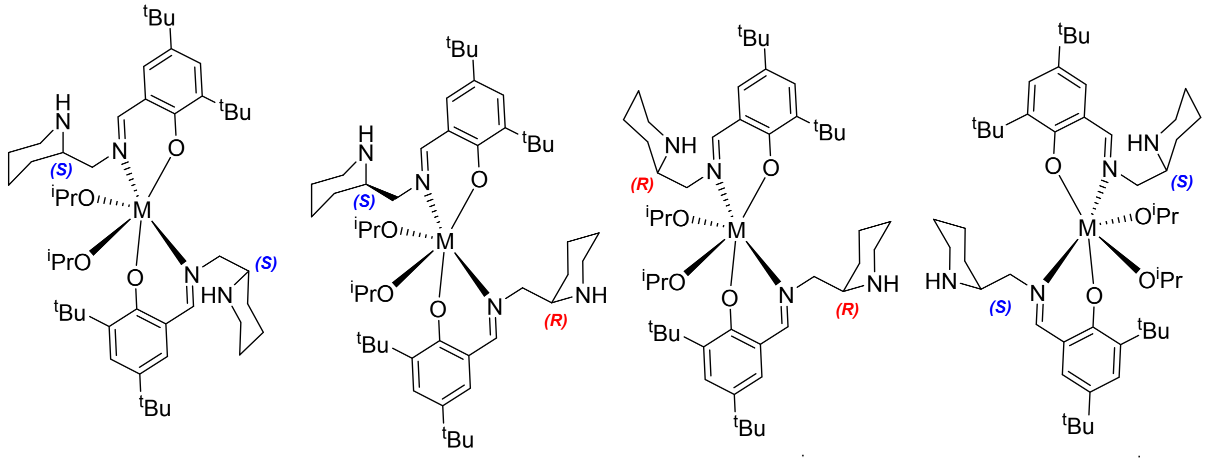


Figure S32: Stereoisomers observed in the solid-state and solution for M(**1-2**)$_2$ {M = Mg(II) or Zn(II)}.



Δ-M(*SS*-**1**)$_2$(O^{i}Pr)$_2$
Λ-M(*RR*-**1**)$_2$(O^{i}Pr)$_2$

Crystal Structure

Δ-M(*SR*-**1**)$_2$(O^{i}Pr)$_2$
Λ-M(*RS*-**1**)$_2$(O^{i}Pr)$_2$

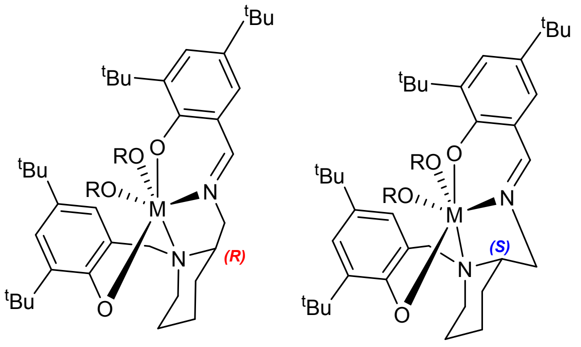
Δ-M(*RR*-**1**)$_2$(O^{i}Pr)$_2$
Λ-M(*SS*-**1**)$_2$(O^{i}Pr)$_2$

Λ-M(*SS*-**1**)$_2$(O^{i}Pr)$_2$
Δ-M(*RR*-**1**)$_2$(O^{i}Pr)$_2$

Potential Solution Diastereomers

M = Ti(IV) or Zr(IV)

Figure S33: Solid-state stereoisomer and anticipated solution diastereomers for M(**1**)$_2$(O^{i}Pr)$_2$ {M = Ti(IV) or Zr(IV)}.



Λ-M(*R*-**4**)(OR)$_2$
Δ-M(*S*-**4**)(OR)$_2$

Crystal Structure

Δ-M(*S*-**4**)(OR)$_2$
Λ-M(*R*-**4**)(OR)$_2$

Potential Solution
Diastereomer

M = Ti(IV) or Zr(IV)
R = ^{i}Pr or ^{t}Bu

Figure S34: Solid-state stereoisomer and anticipated solution diastereomer for M(**4**)(OR)$_2$ {M = Ti(IV) or Zr(IV), R = O^{i}Pr or ^{t}Bu}.

Select polymerisation characterisation data

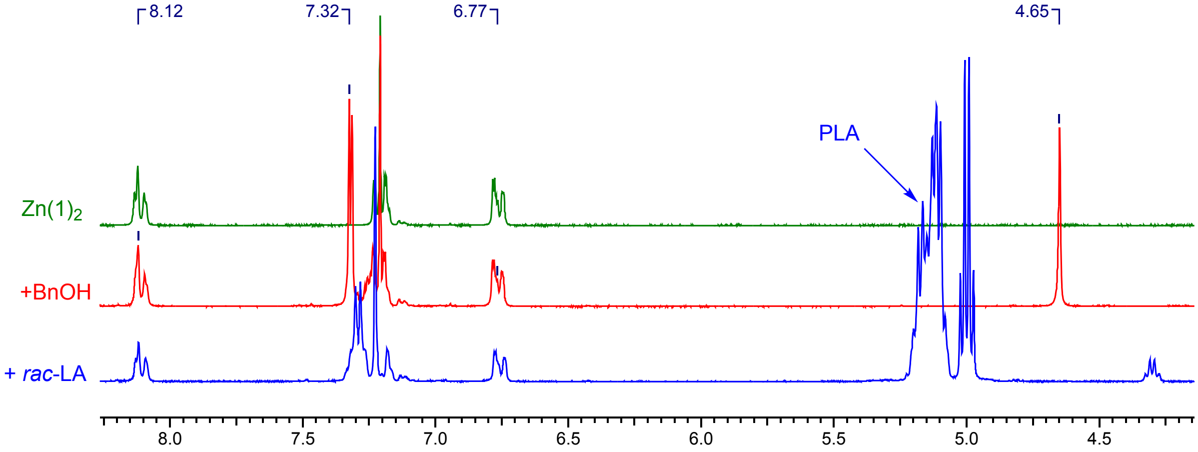


Figure S35: ^{1}H NMR (CDCl$_3$, 298 K, 400 MHz) of a) Zn(**1**)$_2$, b) addition of benzyl alcohol and c) addition of *rac*-LA and formation of polymer.

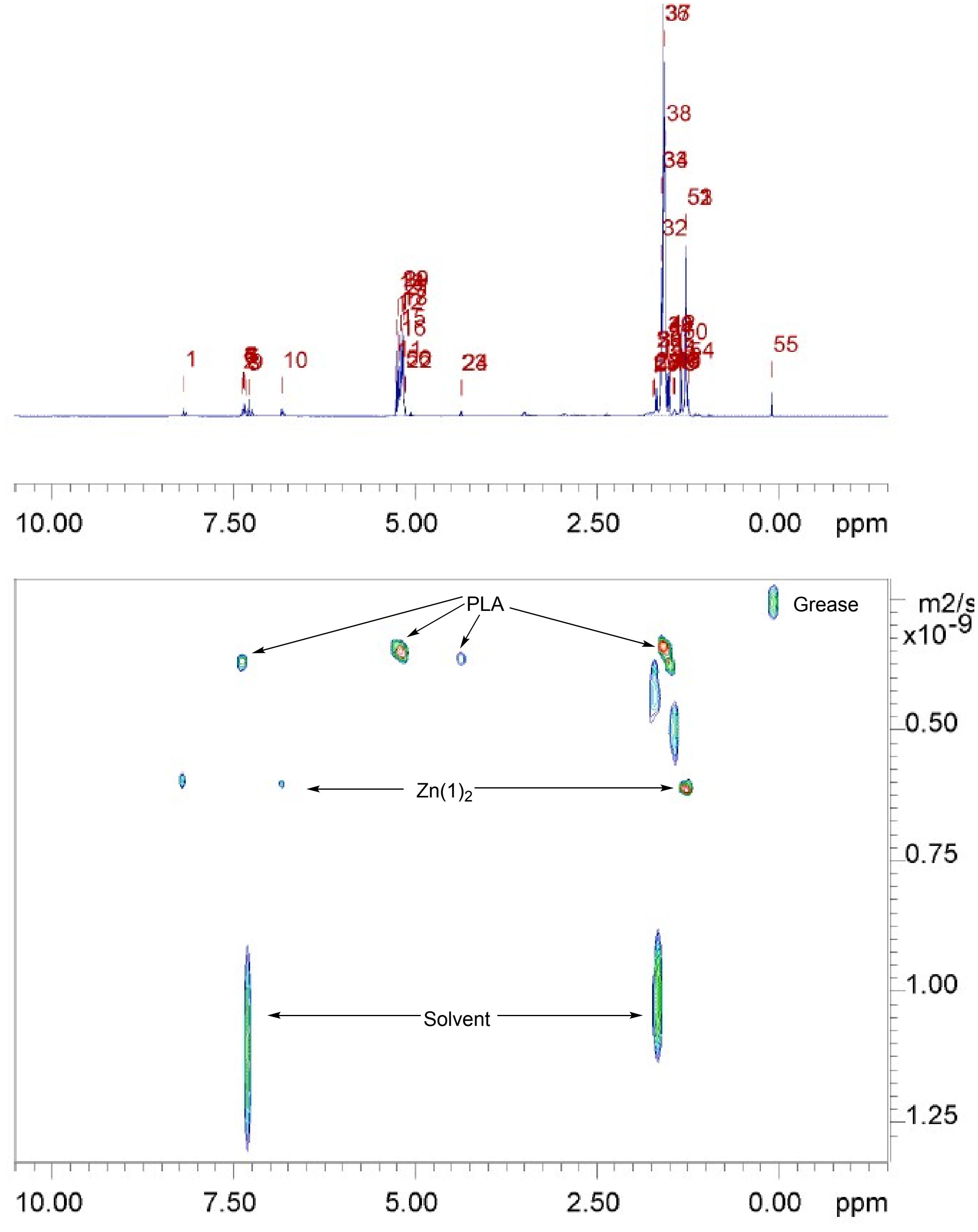


Figure S36: DOSY NMR spectrum of Zn(**1**)$_2$ and PLA showing no explicit binding of polymer to complex.

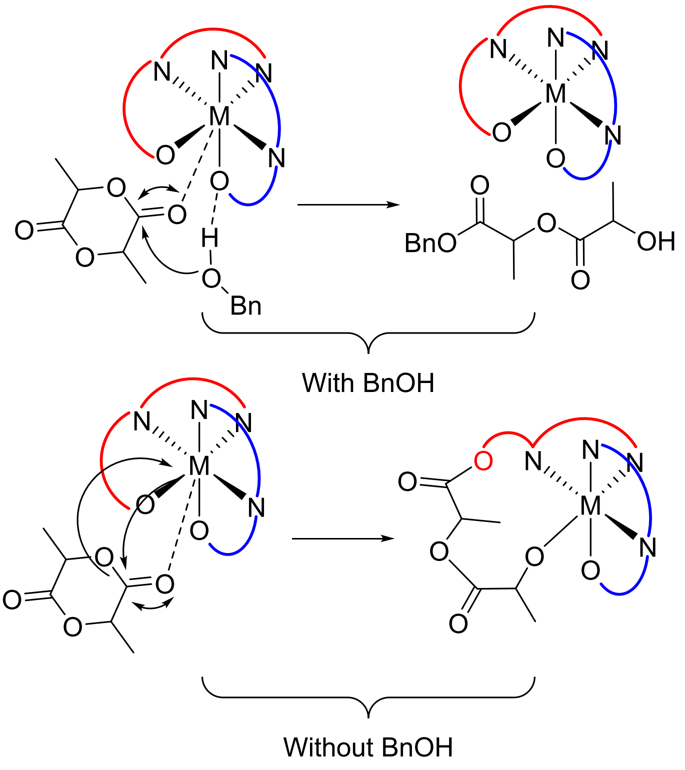


Figure S37: Anticipated initiation mechanisms for M(**1-3**)$_2$, where M = Mg(II) or Zn(II).

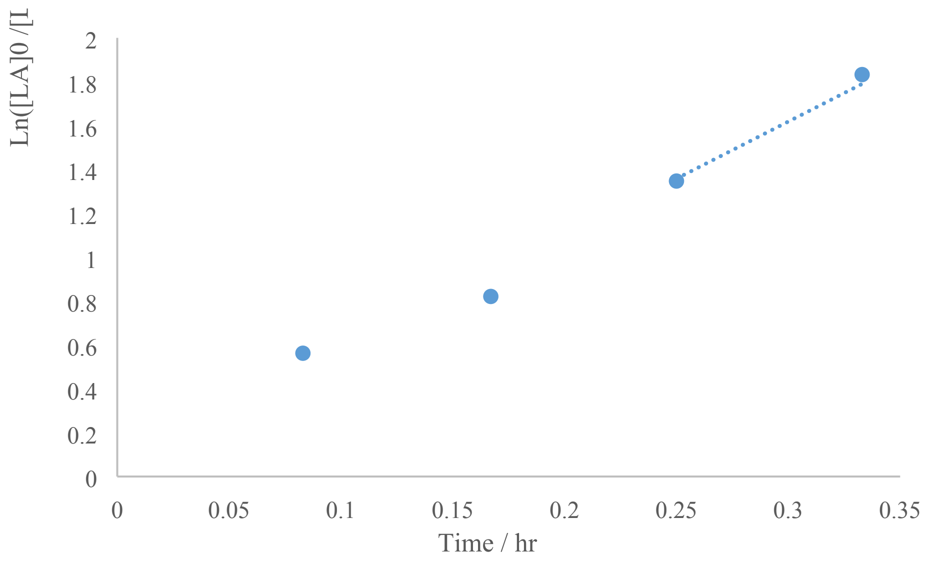


Figure S38: Semi-logarithmic plot for the solution polymerisation of Zn(**2**)$_2$. Conditions: Toluene, 80°C, [LA]:[Zn(**2**)$_2$]:[BnOH] = 100:1:1

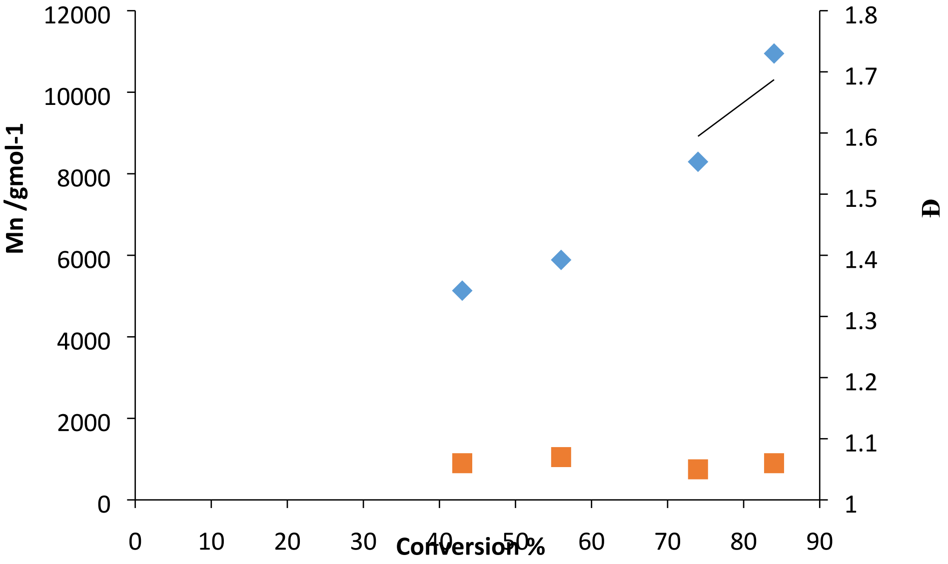


Figure S39: M_n and *Đ* against conversion for the solution polymerisation of *rac*-LA with Zn(**2**)$_2$ (80°C, toluene, [LA]:[Zn(**2**)$_2$]:[BnOH]=100:1:1).

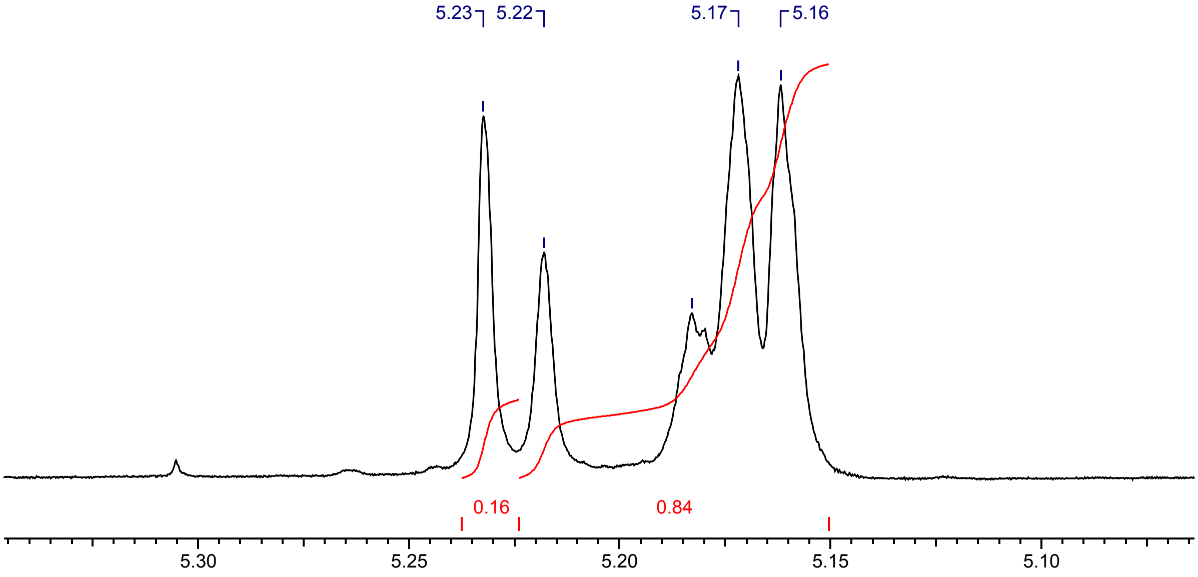


Figure S40: ^{1}H NMR ($CDCl_3$, 400MHz) homonuclear decoupled spectrum of PLA synthesised from solution polymerisation with Zn(**1**)$_2$ (100:1:1, toluene, 80 °C) (Table 2, Entry 4).

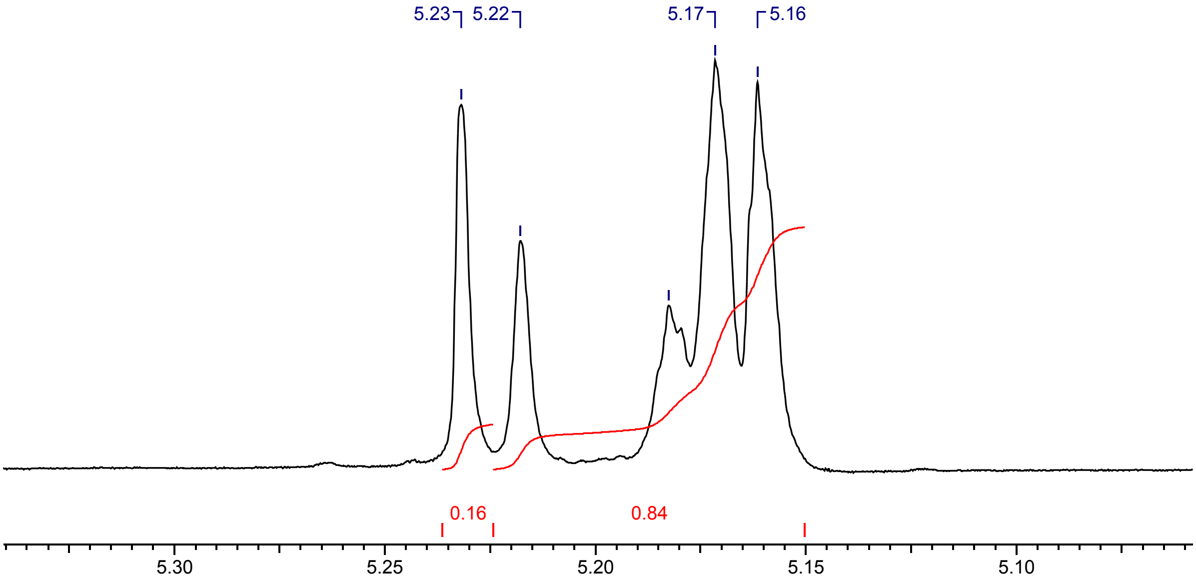


Figure S41: ^{1}H NMR ($CDCl_3$, 400MHz) homonuclear decoupled spectrum of PLA synthesised from solution polymerisation with Zn(**1**)$_2$ (1000:1:10, toluene, 80 °C) (Table 2, Entry 5).

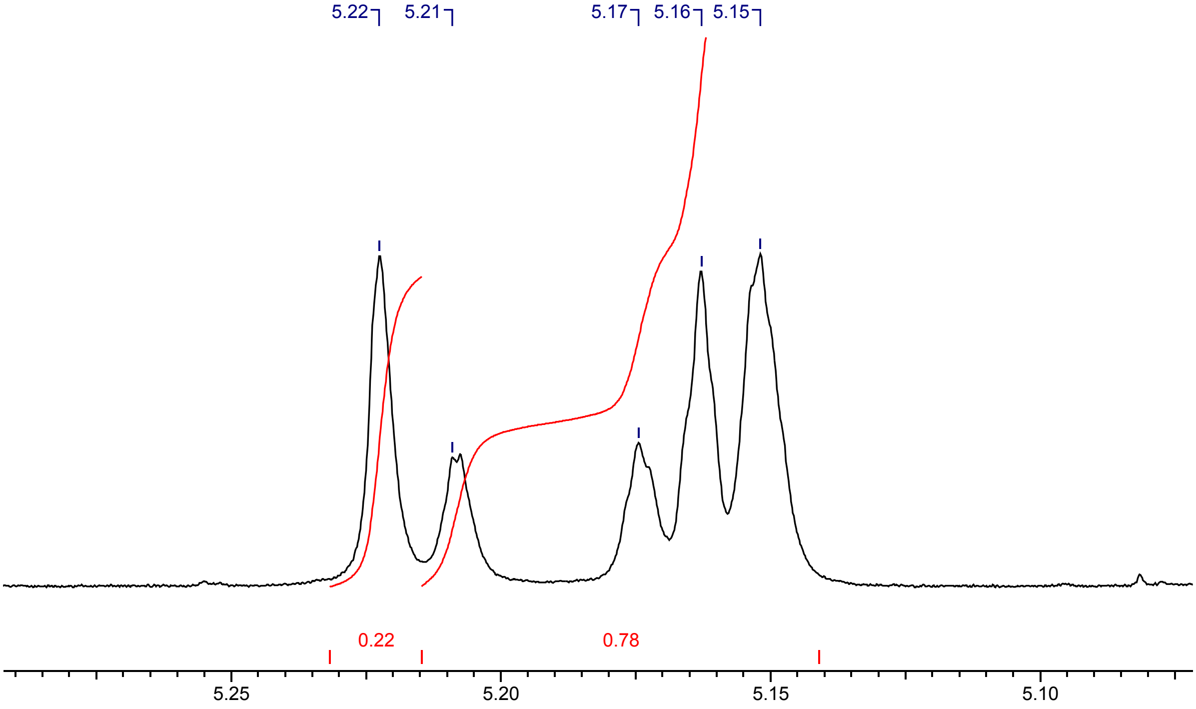


Figure S42: ^{1}H NMR ($CDCl_3$, 400MHz) homonuclear decoupled spectrum of PLA synthesised from melt polymerisation with Zn(**1**)$_2$ (300:1:1, solvent-free 130 °C) (Table 2, Entry 18).

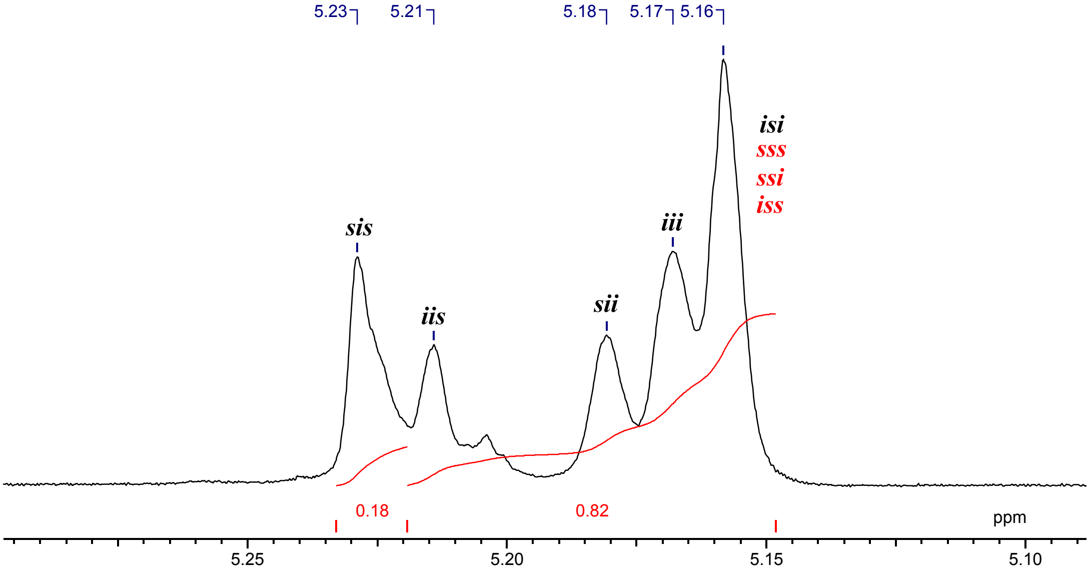


Figure S43: ^{1}H NMR ($CDCl_3$, 400MHz) homonuclear decoupled spectrum of PLA synthesised from solution polymerisation with Zr(**6**)(O^{t}Bu)$_2$ (toluene, 80 °C) (Table 4, Entry 7).

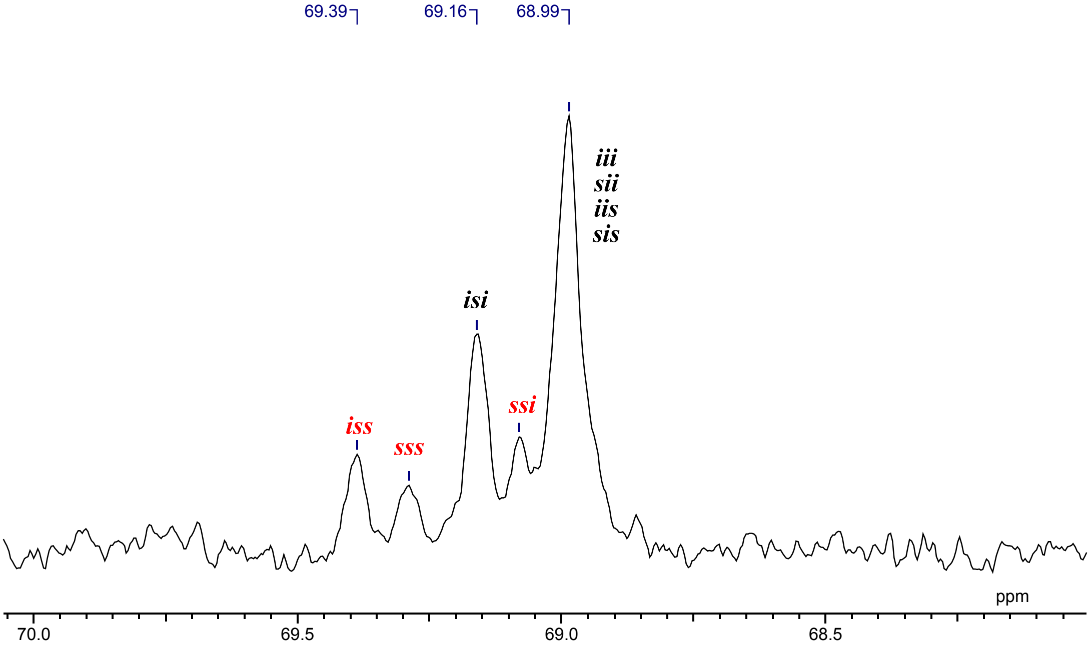


Figure S44: $^{13}C\{^{1}H\}$ NMR spectrum of PLA synthesised from solution polymerisation with Zr(**6**)(O^{t}Bu)$_2$ (toluene, 80 °C) (Table 4, Entry 7).

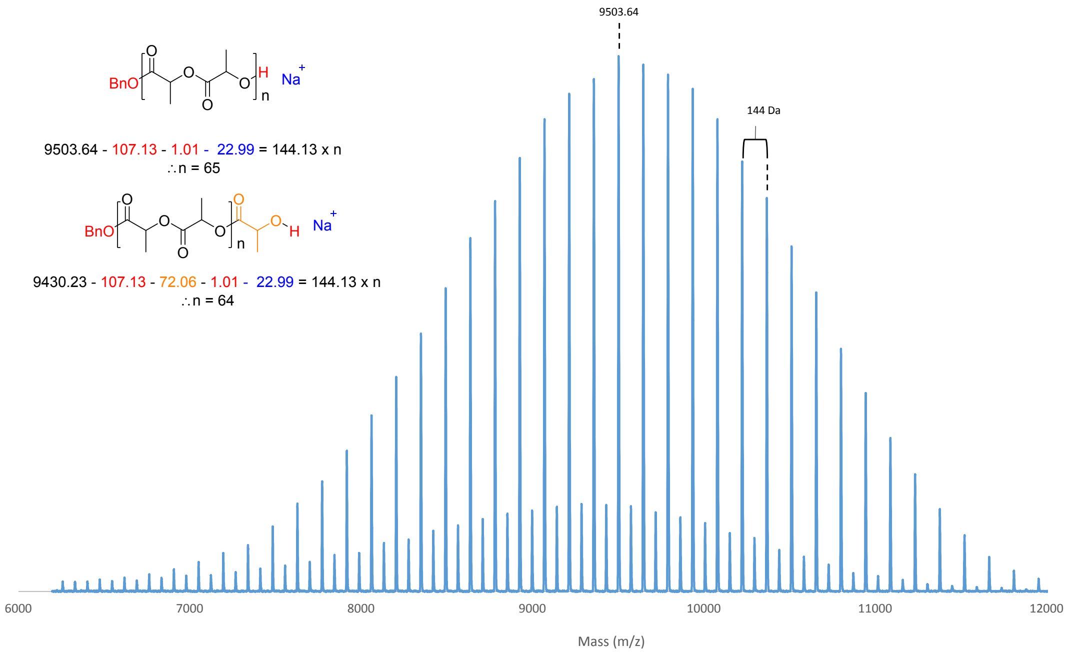


Figure S45: MALDI-ToF of PLA from solution polymerisation with Mg(**1**)$_2$ (80 °C, 100:1:1) (Table 2, Entry 7).

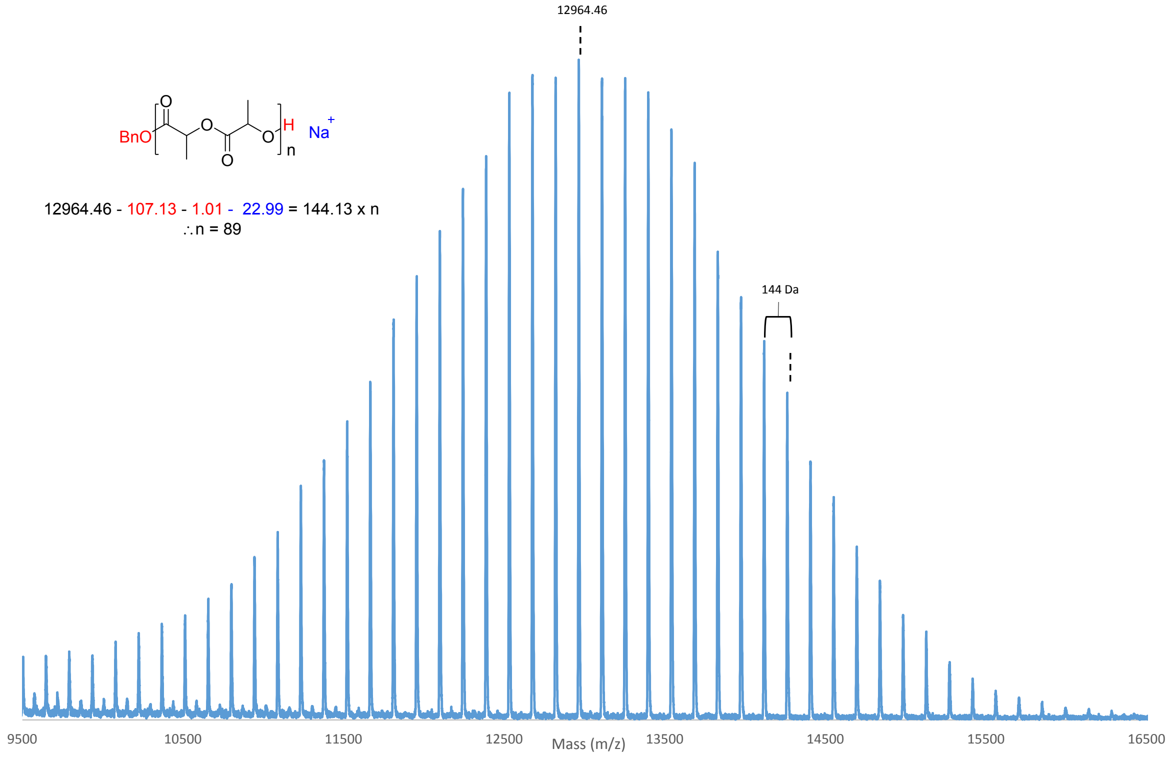


Figure S46: MALDI-ToF of PLA from solution polymerisation with Zn(**1**)$_2$ (80 °C, 1000:1:10) (Table 2, Entry 5).

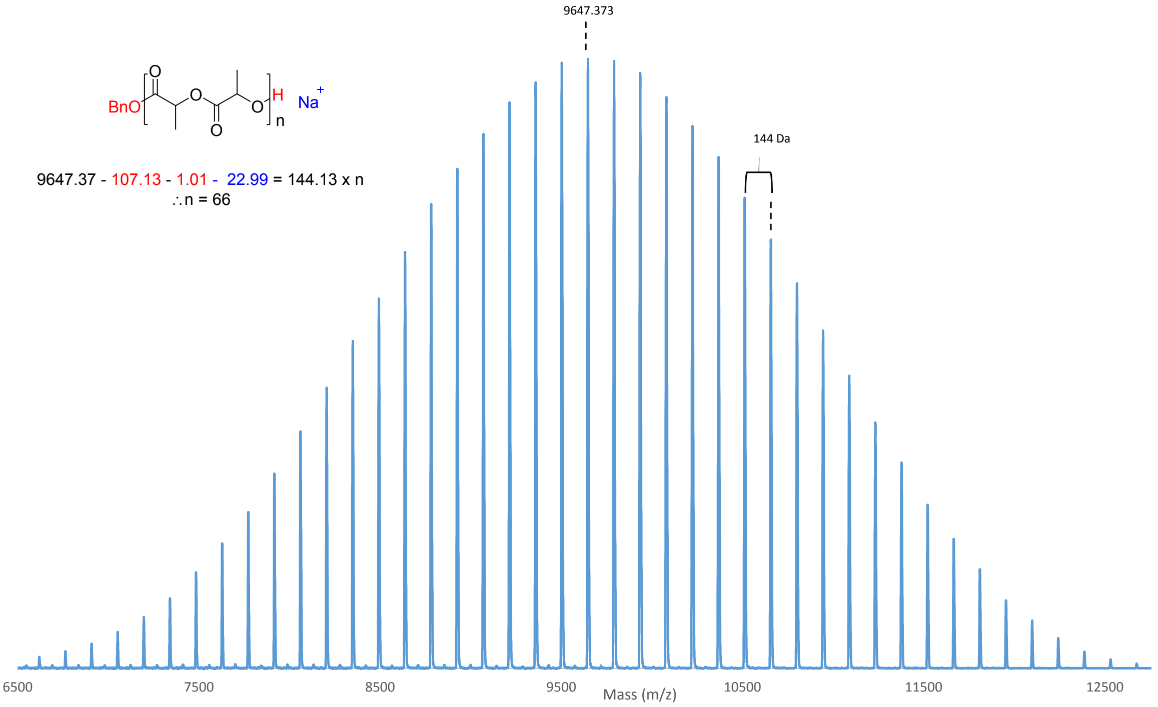


Figure S47: MALDI-ToF of PLA from solution polymerisation with Zn(**2**)$_2$ (80 °C, 100:1:1) (Table 2, Entry 6).

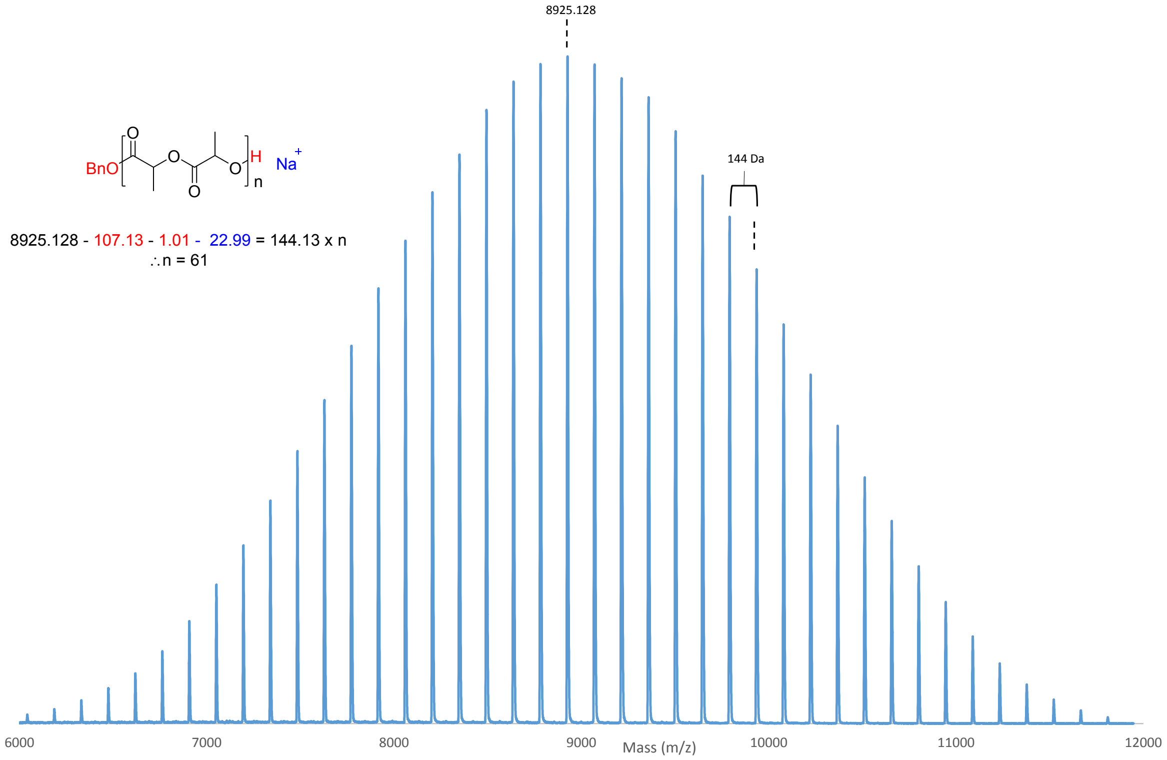


Figure S48: MALDI-ToF of PLA from solution polymerisation with Zn(**2**)$_2$ (80 °C, 1000:1:10) (Table 2, Entry 7).

Table S1: Summary of MALDI-ToF analysis of PLA from Mg(**1-3**)$_2$ and Zn(**1**)$_2$.

Initiator	Series	M_p /Da	End groups	n
Mg(1)$_2$^{a}	1_{Main}	9503.64	BnO-, H-, Na$^+$	65
	2_{Trans}	9430.23	BnO-, H-, Na$^+$	64.5
Mg(2)$_2$^{a}	1_{Main}	2459.97	-	17
	2_{Trans}	2243.689	-	15.5
Mg(3)$_2$^{a}	1_{Main}	11521.78	BnO-, H-, Na$^+$	79
	2_{Trans}	11017.88	BnO-, H-, Na$^+$	75.5
	3_{Cyclic}	3901.15	-	27
Zn(1)$_2$^{a}	1_{Main}	11947.61	BnO-, H-, Na$^+$	82
Zn(1)$_2$^{b}	1_{Main}	12964.46	BnO-, H-, Na$^+$	89
Zn(2)$_2$^{a}	1_{Main}	9647.37	BnO-, H-, Na$^+$	66
Zn(2)$_2$^{b}	1_{Main}	8925.13	BnO-, H-, Na$^+$	61

Conditions: ^{a}[LA]:[I]:[BnOH] = 100:1:1, 80°C, toluene.
^{b}[LA]:[I]:[BnOH] = 1000:1:10, 80°C, toluene.

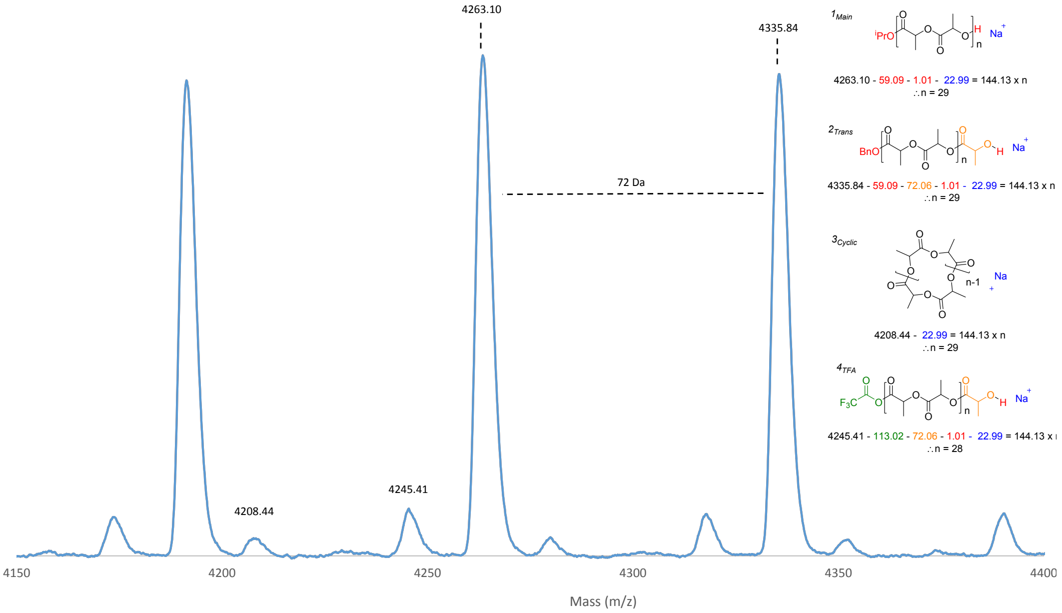


Figure S49: MALDI-ToF of PLA from solution polymerisation with Zr(**1**)$_2$(O^{i}Pr)$_2$ (Table 4, Entry 1).

Table S2: Summary of MALDI-ToF analysis of PLA from Zr(IV) alkoxide complexes.

Initiator	**Series**	**M_p /Da**	**End groups**	**n**
Zr(1)$_2$(O^{i}Pr)$_2$[a]	1_{Main}	4263.10	^{i}PrO-, H-, Na$^+$	29
	2_{Trans}	4335.84	^{i}PrO-, H-, Na$^+$	29.5
	3_{Cyclic}	4208.44	Na$^+$	29
	4_{TFA}	4245.41	TFA-, H-, Na$^+$	28.5
Zr(1)$_2$(O^{i}Pr)$_2$[b]	1_{Main}	8734.81	^{i}PrO-, H-, Na$^+$	60
	2_{Trans}	8806.94	^{i}PrO-, H-, Na	60.5
	3_{TFA}	8789.37	TFA-, H-, Na$^+$	60.5
	4_{Cyclic}	8673.88	Na$^+$	60
Zr(3)$_2$(O^{i}Pr)$_2$[a]	1_{Main}	5703.041	^{i}PrO-, H-, Na$^+$	39
	2_{Trans}	5342.725	^{i}PrO-, H-, Na$^+$	36.5
Zr(4)(O^{t}Bu)$_2$[c]	1_{Main}	8056.14	BnO-, H-, Na$^+$	50
	2_{Trans}	8125.16	BnO-, H-, Na$^+$	49.5
	3_{tBu}	5575.50	^{t}BuO-, H-, Na$^+$	38
Zr(6)(O^{t}Bu)$_2$[a]	1_{Main}	8556.58	MeO-, H-, Na$^+$	59
	2_{Trans}	8629.44	MeO-, H-, Na$^+$	59.5
	3_{Cyclic}	8530.53	Na$^+$	59

Conditions: [a] [LA]:[I] = 100:1, 80 °C, toluene.
[b] [LA]:[I] = 300:1, 130 °C, solvent-free.
[c] [LA]:[I]:[BnOH] = 100:1:1, 80 °C, toluene.

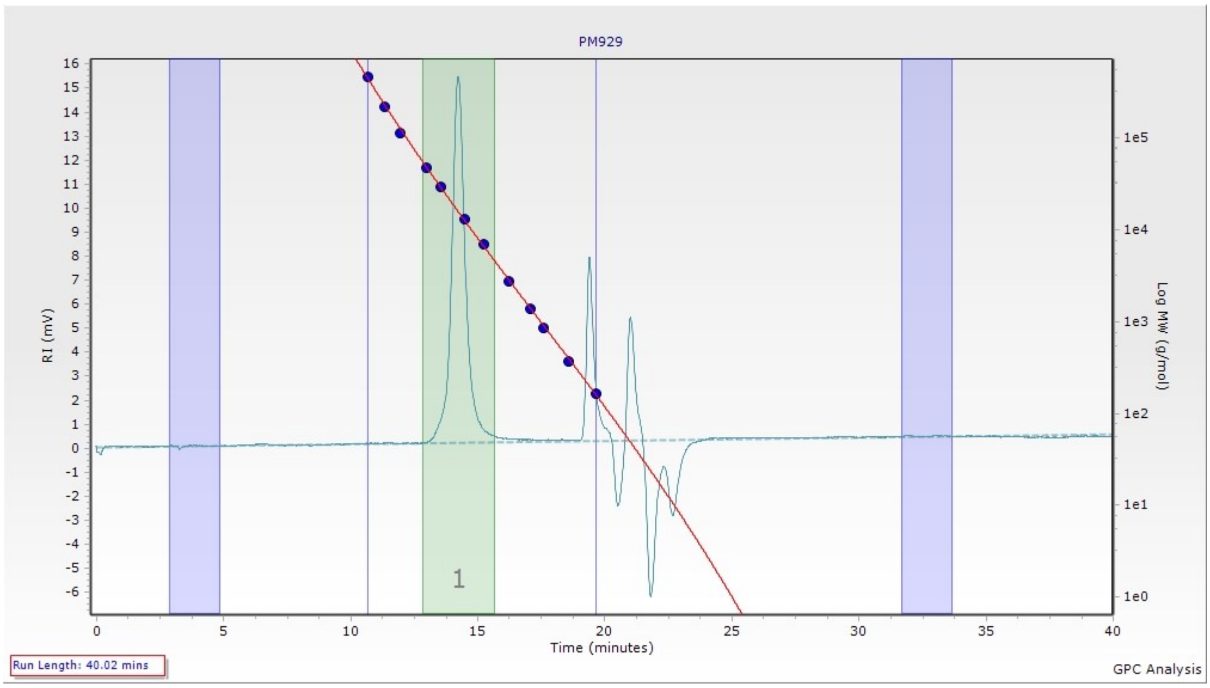


Figure S50: GPC trace of PLA prepared by solution polymerisation with Mg(**1**)$_2$ (100:1:1, 1 hour) (Table 2, Entry 1)

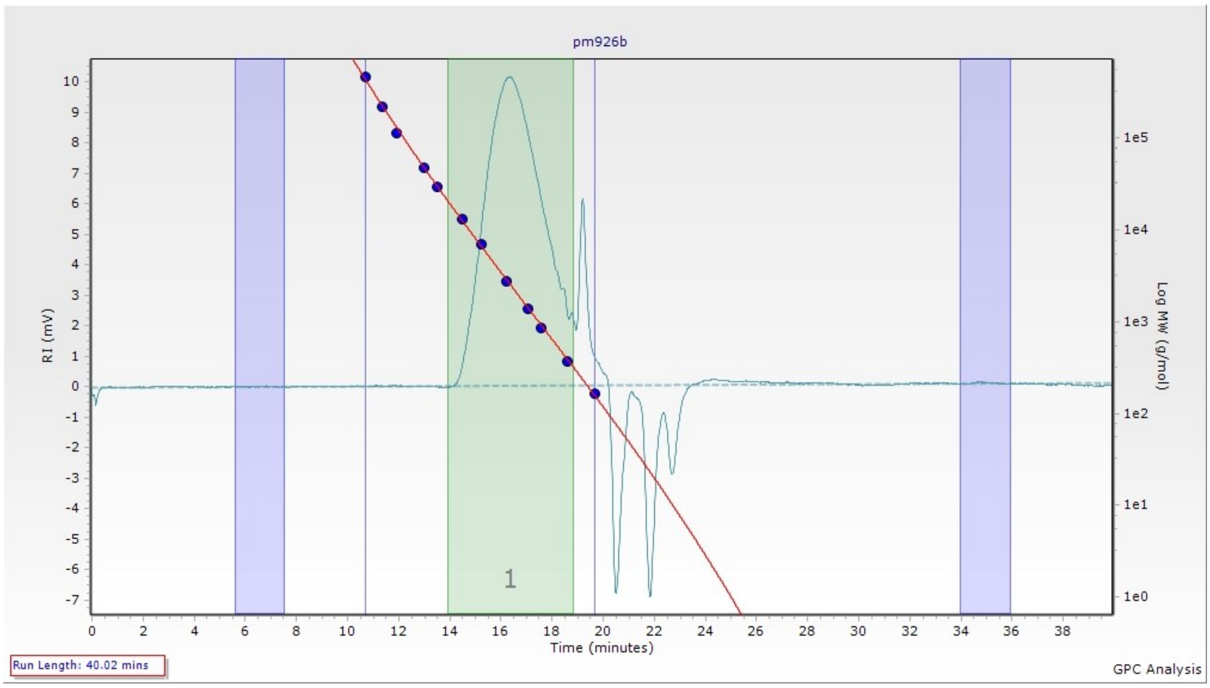


Figure S51: GPC trace of PLA prepared by solution polymerisation with Mg(**1**)$_2$ after methanol treatment (M_n = 1450, Đ = 1.95)

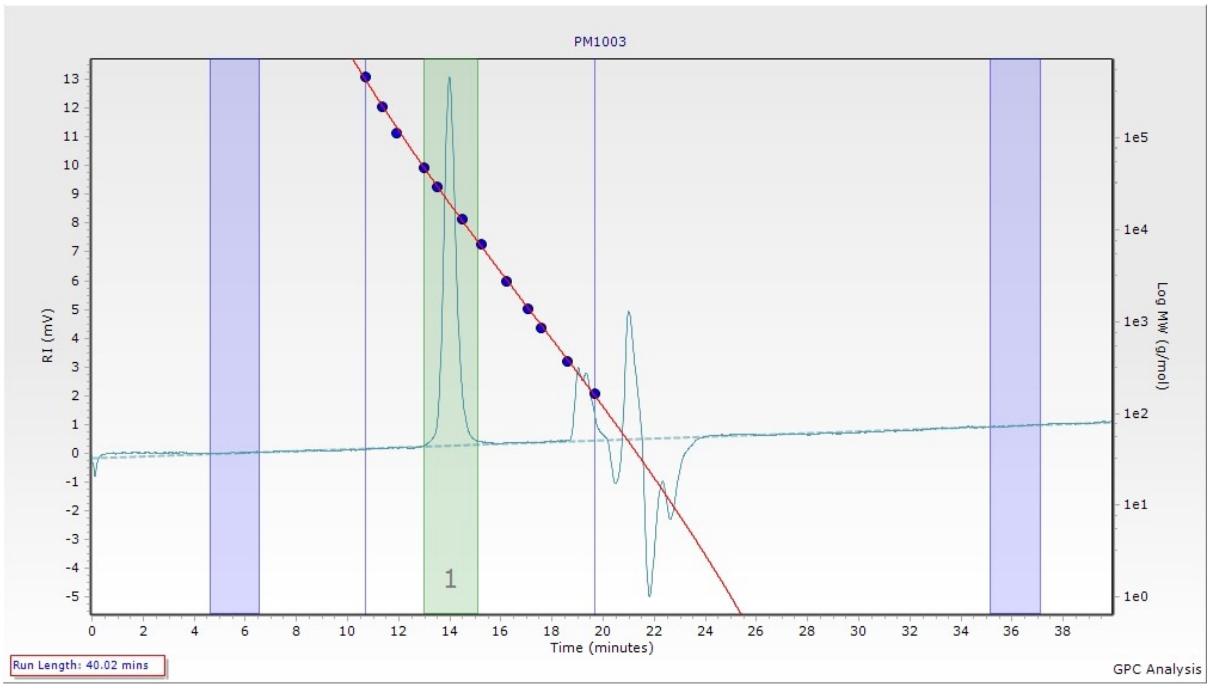


Figure S52: GPC trace of PLA prepared by solution polymerisation with Zn(**1**)$_2$ (100:1:1, 5 mins) (Table 2, Entry 3).

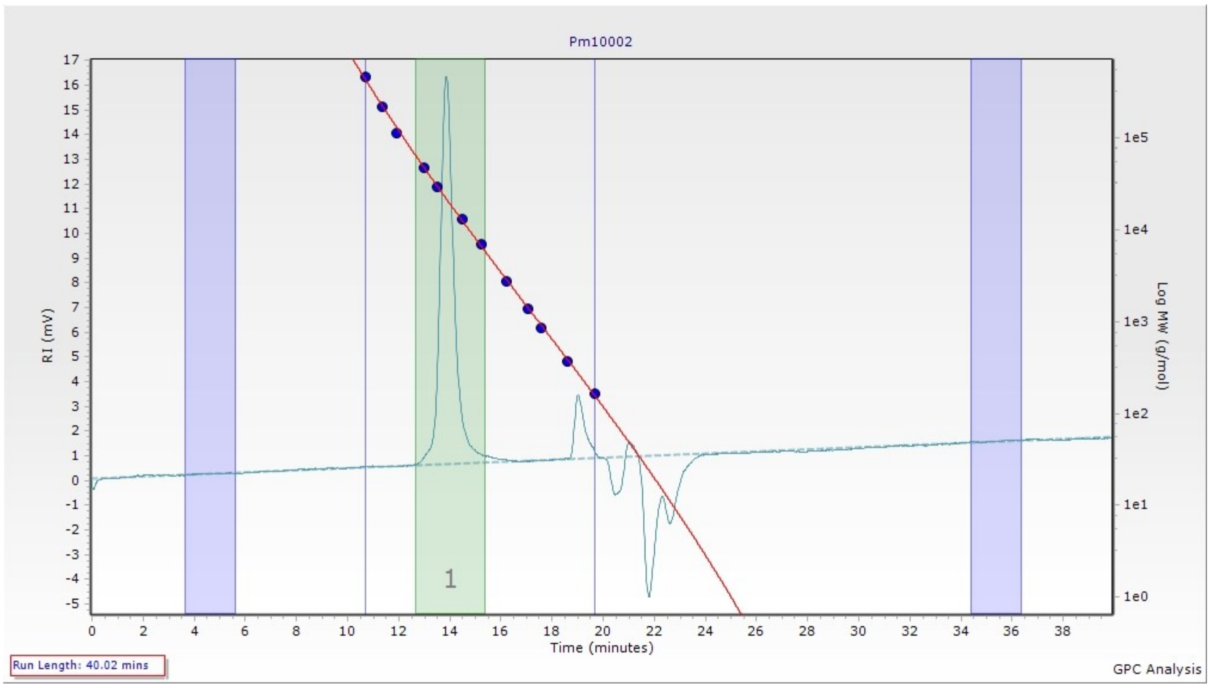


Figure S53: GPC trace of PLA prepared by solution polymerisation with Zn(**1**)$_2$ (1000:1:10, 30 mins) (Table 2, Entry 4).

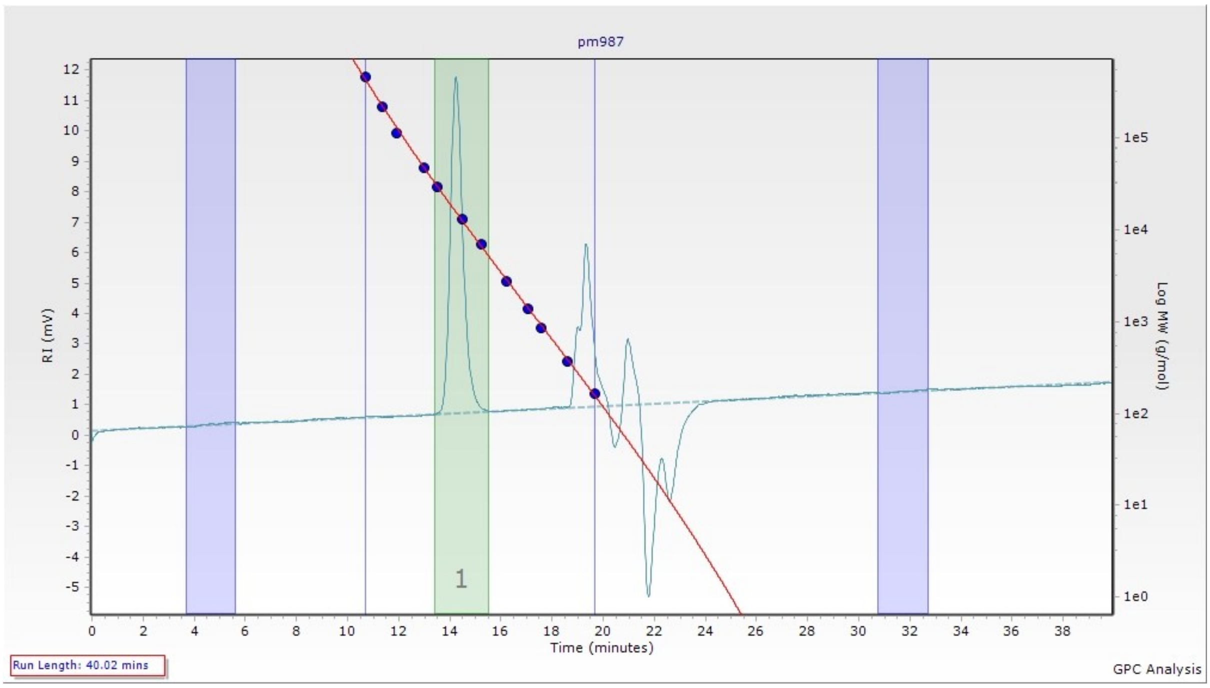


Figure S54: GPC trace of PLA prepared by solution polymerisation with Zn(**2**)$_2$ (100:1:1, 15 mins) (Table 2, Entry 5).

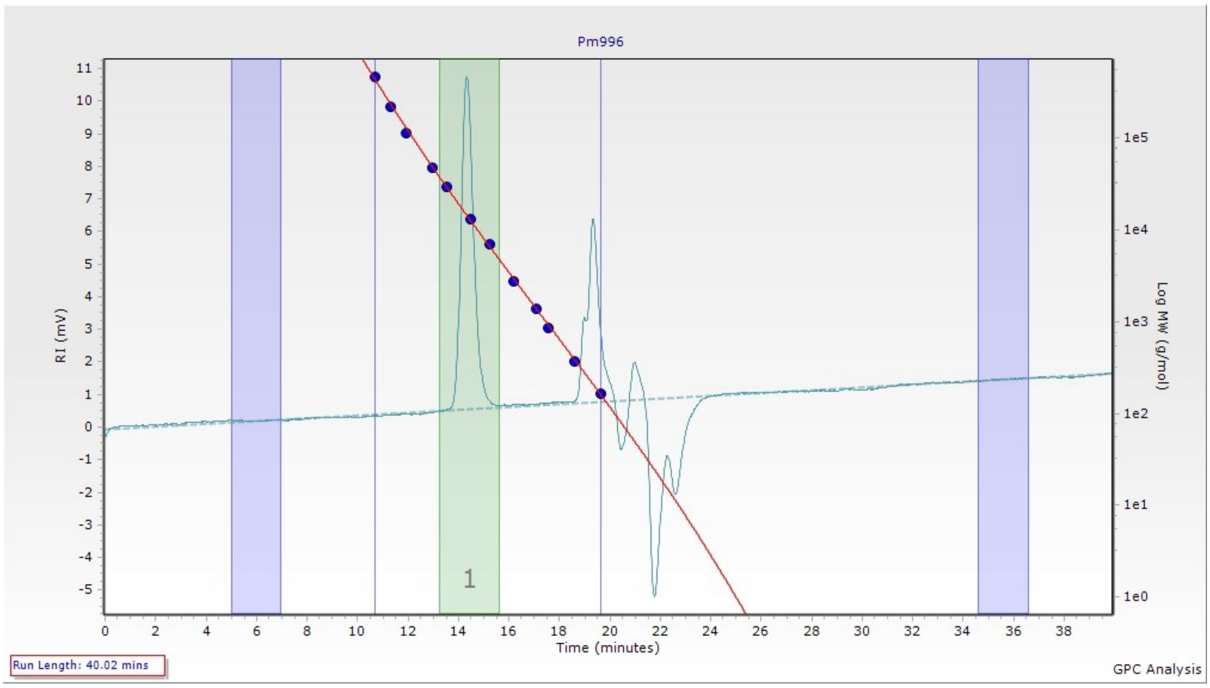


Figure S55: GPC trace of PLA prepared by solution polymerisation with Zn(**2**)$_2$ (1000:1:10, 30 mins) (Table 2, Entry 6).

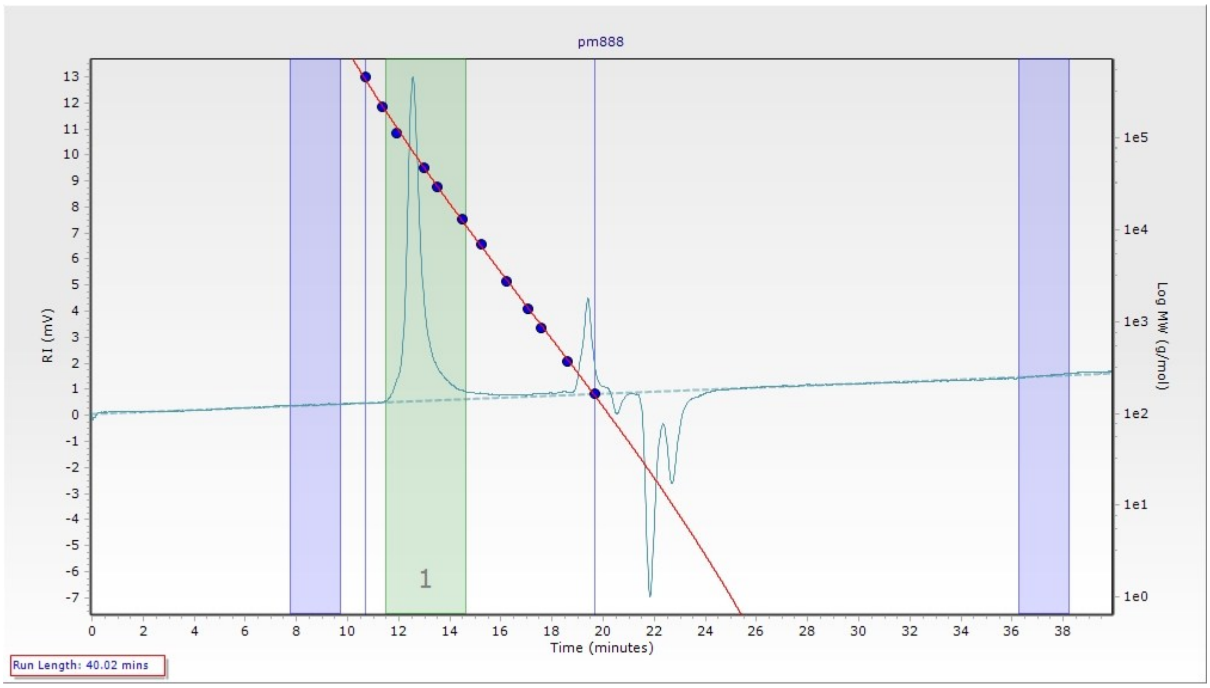


Figure S56: GPC trace of PLA prepared by melt polymerisation with Zn(**1**)$_2$ (300:1, 6 mins) (Table 2, Entry 15).

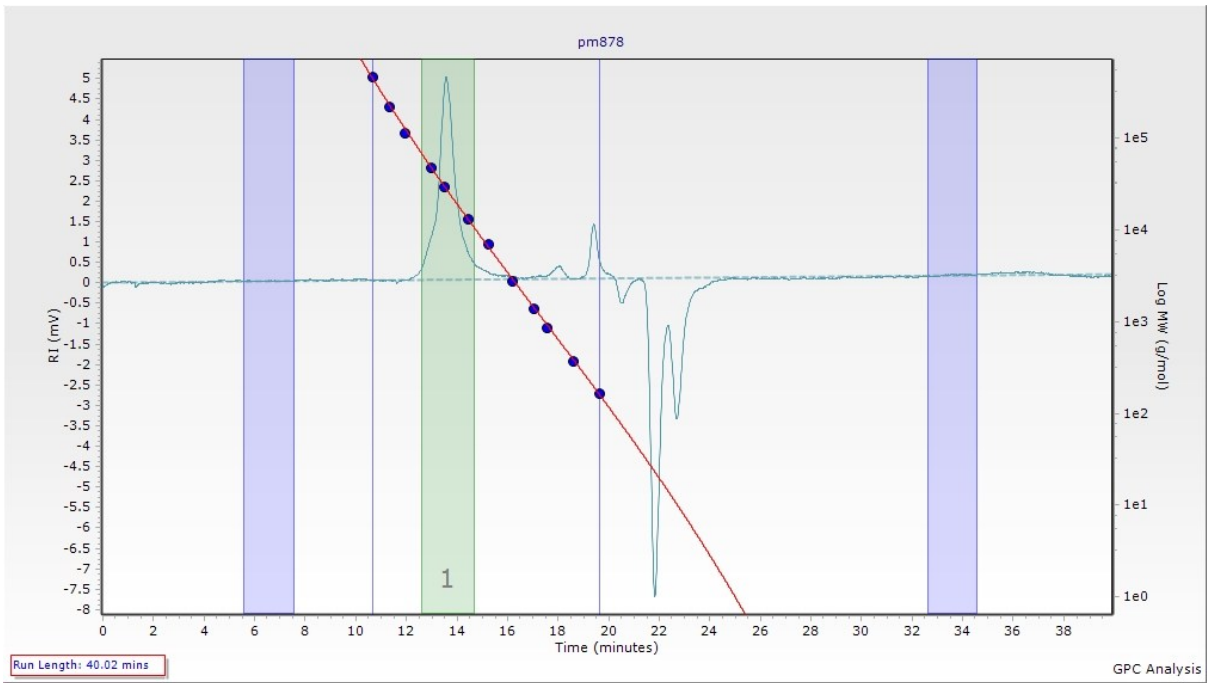


Figure S57: GPC trace of PLA prepared by melt polymerisation with Ti(**5**)(O^{i}Pr)$_2$ (Table 3, Entry 4).

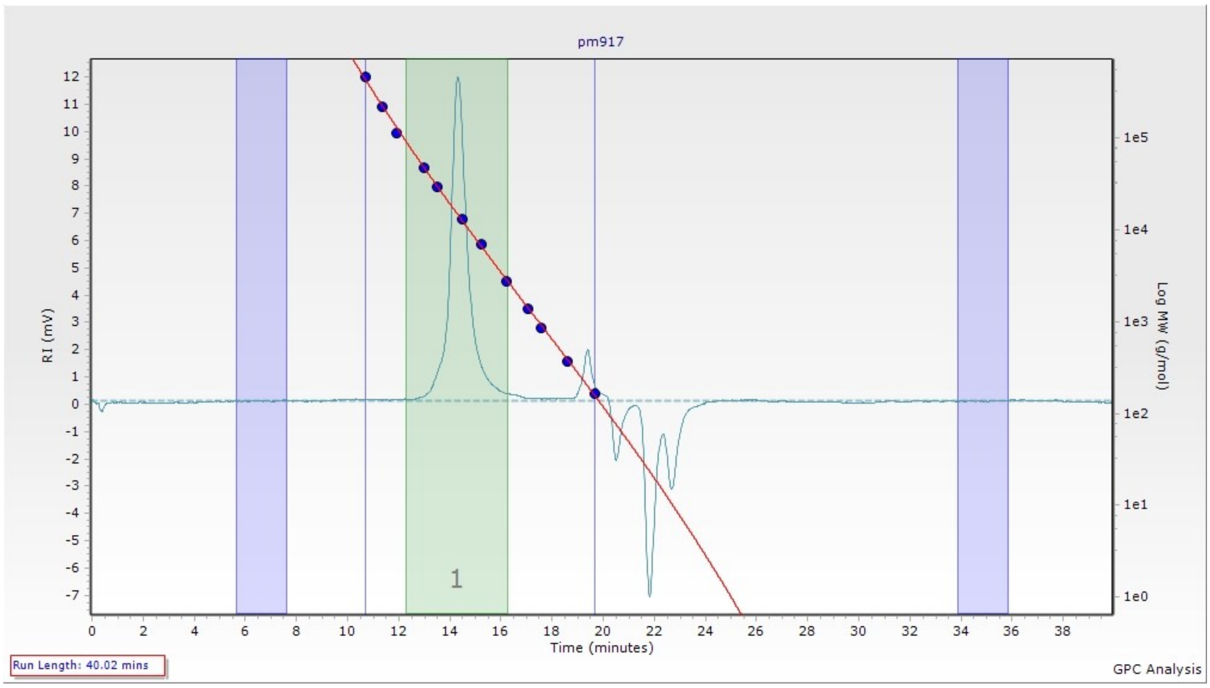


Figure S58: GPC trace of PLA prepared by melt polymerisation with Zr(**1**)$_1$(O^{i}Pr)$_2$ (Table 4, Entry 2).

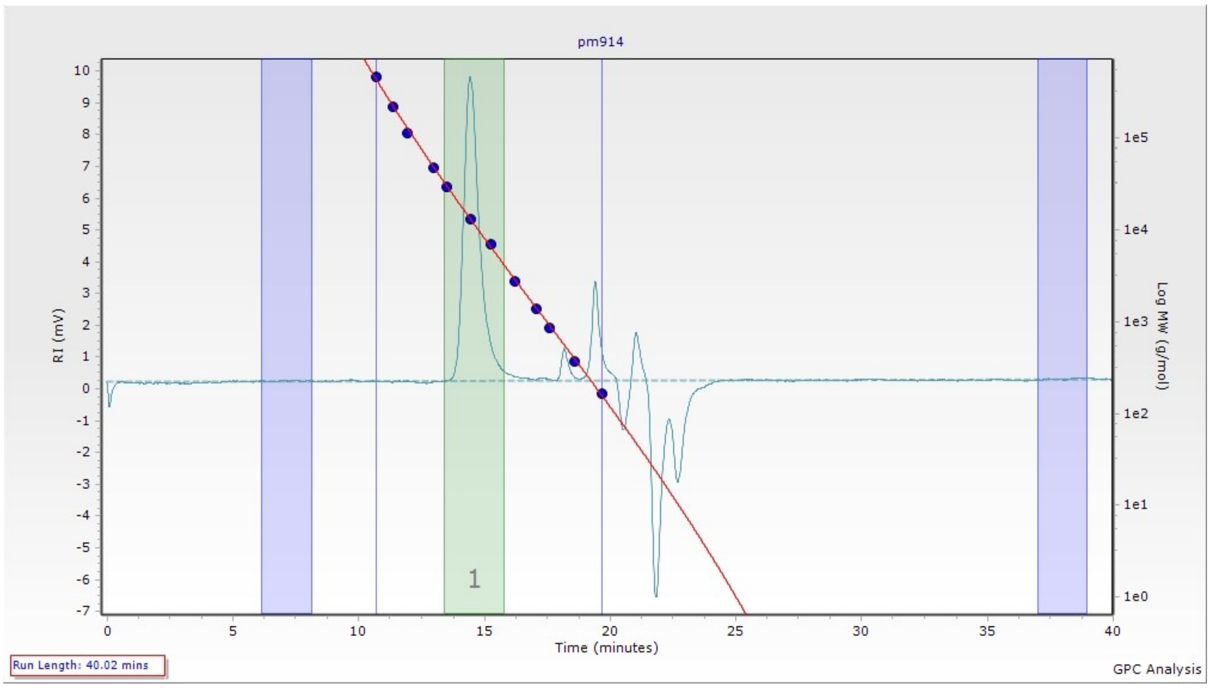


Figure S59: GPC trace of PLA prepared by solution polymerisation with Zr(**6**)(O^{t}Bu)$_2$ (Table 4, Entry 7).

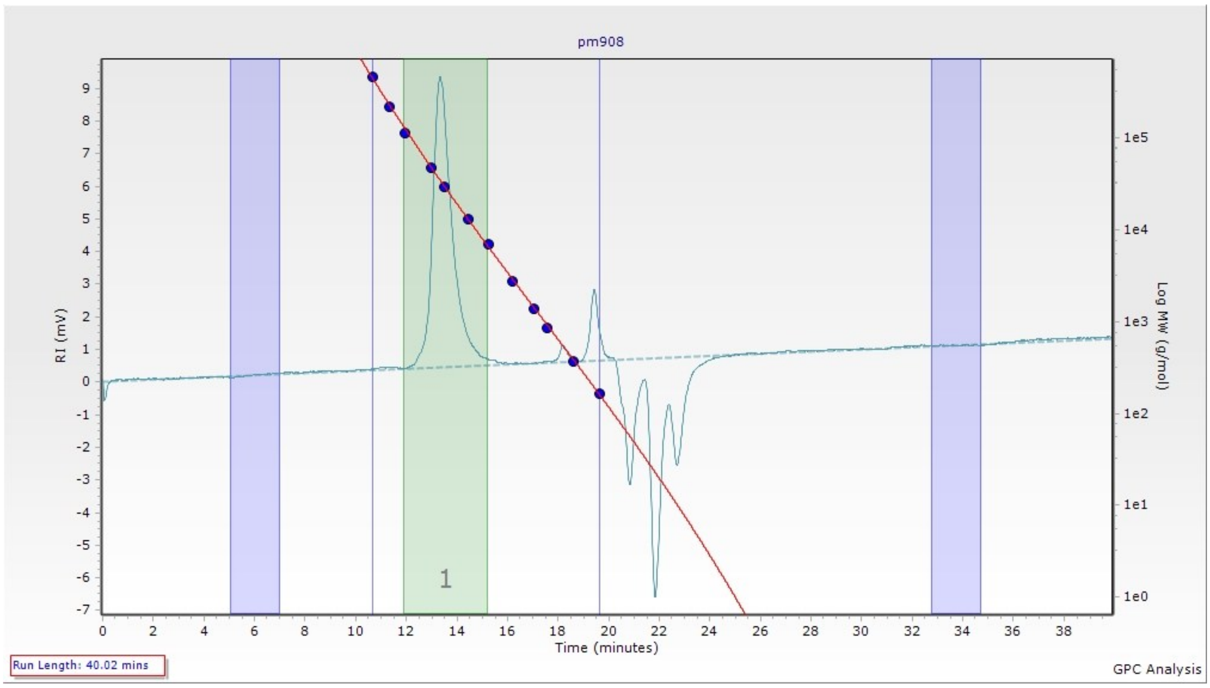


Figure S60: GPC trace of PLA prepared by melt polymerisation with Zr(**6**)(O^{t}Bu)$_2$ (Table 4, Entry 8).

Table S3: Full crystallographic data

Compound reference	Zr(**5**)(O^{t}Bu)$_2$	Ti(**4**)(O^{i}Pr)$_2$	Mg(**1**)$_2$	Zn(**1**)$_2$	Ti(**5**)(O^{i}Pr)$_2$	Ti(**1**)$_2$(O^{i}Pr)$_2$	Zr(**6**)(O^{t}Bu)$_2$	Zr(**1**)(O^{i}Pr)$_2$	Ti(**3***)(O^{i}Pr)$_2$
Chemical formula	$C_{44}H_{72}N_2O_4Zr{\bullet}0.5(C_6H_{14})$	$C_{42}H_{68}N_2O_4Ti$	$C_{42}H_{66}MgN_4O_2{\bullet}2(C_7H_8)$	$C_{21}H_{33}N_2O_1Zn_{0.5}$	$C_{42}H_{70}N_2O_4Ti$	$C_{48}H_{80}N_4O_4Ti$	$C_{88}H_{144}N_4O_8Zr_2$	$C_{48}H_{80}N_4O_4Zr$	$C_{48}H_{68}N_4O_4Ti$
Formula Mass	827.34	712.88	867.56	362.18	714.90	825.06	1568.50	868.38	812.96
Crystal system	Monoclinic	Monoclinic	Monoclinic	Tetragonal	Triclinic	Triclinic	Triclinic	Triclinic	Monoclinic
a/Å	24.0620(6)	23.0224(3)	10.6847(9)	24.0450(2)	11.6663(4)	9.7501(3)	11.3200(4)	9.7777(2)	10.4459(5)
b/Å	15.1035(3)	14.30120(10)	26.0458(7)	24.0450(2)	13.5176(5)	14.1972(4)	11.4648(5)	14.3460(3)	30.1019(4)
c/Å	30.6787(8)	28.4630(4)	19.3381(11)	14.5399(2)	14.0421(4)	19.0565(7)	18.7325(7)	19.2145(6)	14.9279(3)
α/°	90	90	90	90	100.146(3)	76.731(3)	78.072(3)	76.662(2)	90
β/°	117.531(3)	113.744(2)	100.316(7)	90	92.922(2)	80.759(3)	72.528(3)	81.066(2)	103.009(3)
γ/°	90	90	90	90	107.314(3)	71.707(3)	76.808(3)	71.741(2)	90
Unit cell volume/Å^3	9886.7(5)	8578.1(2)	5294.6(6)	8406.42(18)	2068.41(13)	2426.49(15)	2232.65(16)	2480.42(11)	4573.5(3)
Temperature/K	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
Space group	$C2/c$	$I2/a$	$P2_1/n$	*I*Error!*2d*	*P*Error!	*P*Error!	*P*Error!	*P*Error!	$P2_1/n$
No. of formula units per unit cell, Z	8	8	4	16	2	2	1	2	4
No. of reflections measured	41135	34998	42079	28432	25143	21882	16035	31337	63922
No. of independent reflections	12003	8360	10345	4148	8285	9545	16035	9948	9133
R_{int}	0.0283	0.0351	0.0252	0.0298	0.0381	0.0213	-	0.0325	0.0300
Final R_1 values ($I > 2\sigma(I)$)	0.0391	0.0412	0.0685	0.0259	0.0395	0.0398	0.0357	0.0292	0.0400
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0913	0.1099	0.1784	0.0657	0.1062	0.1068	0.0974	0.0734	0.1064
Final R_1 values (all data)	0.0552	0.0458	0.0742	0.0283	0.0437	0.0429	0.0408	0.0326	0.0412
Final $wR(F^2)$ values (all data)	0.1015	0.1137	0.1828	0.0670	0.1093	0.1091	0.0987	0.0752	0.1073

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