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Supporting Information

Synthesis and Characterization of Unsymmetrical Zr(IV) Amine Tris(phenolate) Complexes and their Application in ROP of rac-LA

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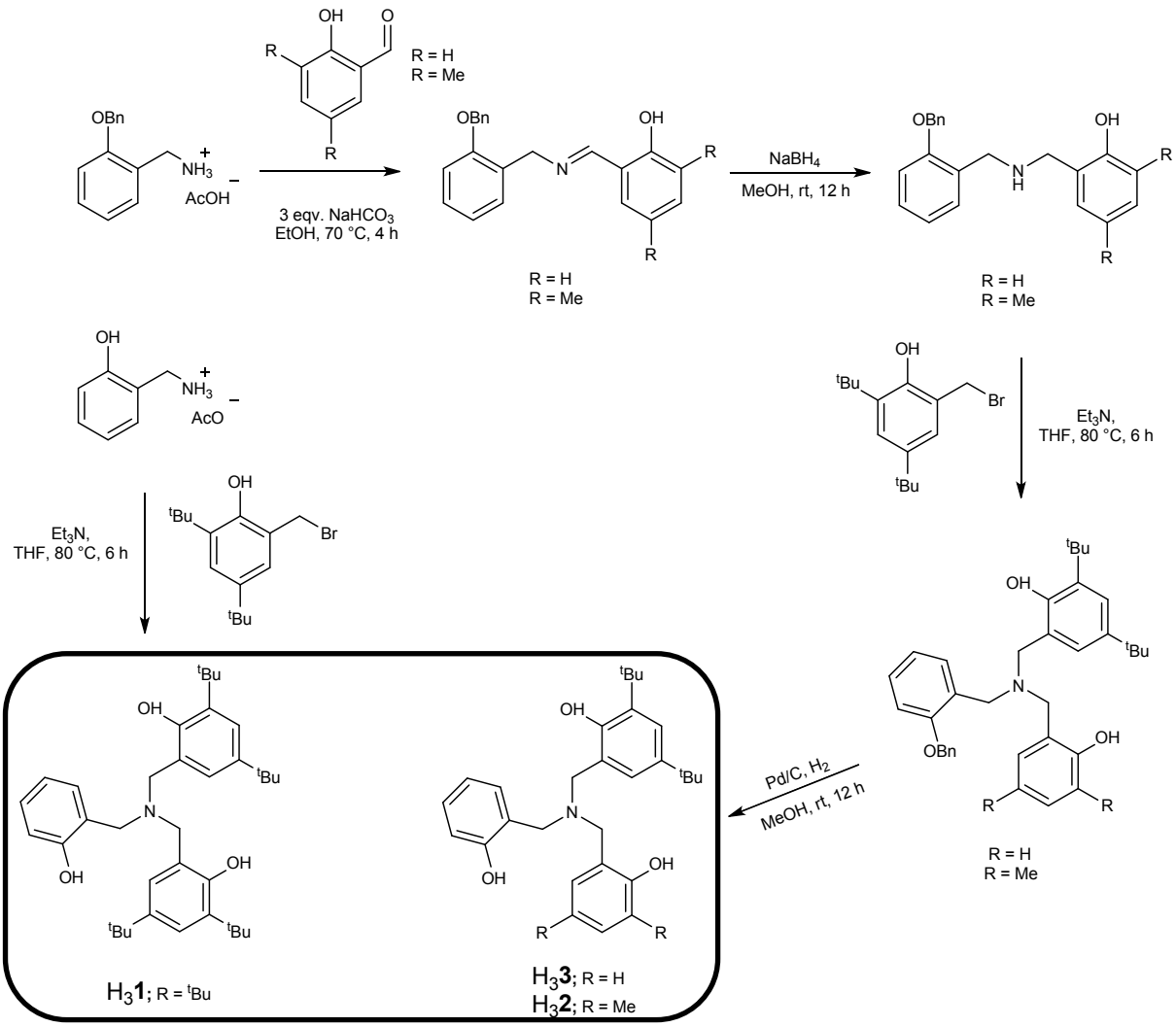
Materials and General Procedures

$Zr(O^iPr)_4{}^iPrOH$ (99.9%, Aldrich) was used without further. *rac*-lactide (Aldrich) was recrystallized from dry toluene and sublimed twice prior to use in polymerisation reactions. All other starting materials were used as received and purchased from Aldrich or Acros.

Prepartion of all metal complexes and subsequent ROP of *rac*-lactide was performed under an inert atmosphere of argon using standard Schlenk or glove-box techniques. All solvents used in the preparation of metal complexes and polymerisations were dry and obtained *via* an SPS (Solvent Purification System).

Experimental - Ligand Synthesis



Scheme S1. Step-wise synthesis of unsymmetrical amine tris(phenolate) ligands

(2-hydroxybenzyl)bis(2-hydroxy-3,5-di-*tert*-butylbenzyl)amine (H_3**1**)

Salicylammonium acetate (2.00 g, 10.9 mmol) and $NaHCO_3$ (3.66 g, 43.6 mmol) were charged to a round-bottom flask and set stirring in THF (50 ml). The reaction mixture was heated to reflux (80 °C) before adding a solution of 2-hydroxy-3,5-di-*tert*-butylbenzyl bromide (6.54 g, 21.8 mmol) in THF (25ml) drop-wise. The reaction mixture was refluxed for approx. one hour before adding triethylamine (3 ml, >21.8 mmol) drop-wise. The reaction was held a reflux for a further five hours before cooling to room temperature. Filtration removed a white solid ($NaHCO_3$ / $Et_3NH^+Br^-$) leaving a yellow solution. Solvent was removed *via* rotary evaporation and further dried under reduced pressure to give a yellow solid. This crude product was redissolved in dichloromethane (~5ml) and subjected to flash chromatography to remove unreacted starting material and triethylamine (3.3 g, 5.9 mmol, 54% yield).

^{1}H NMR ($CDCl_3$) 1.29 (18H, s, ^{t}Bu), 1.40 (18H, s, ^{t}Bu), 3.69 (4H, s, N-CH_2-^{tBu}Ph), 3.70 (2H, s, N-CH_2-^{H}Ph), 6.81-6.89 (2H, m, ^{H}Ar-H), 6.95 (1H, s, ^{tBu}Ar-H), 6.96 (1H, s, ^{tBu}Ar-H), 7.10-7.16 (2H, m, ^{H}Ar-H), 7.22 (1H, s, ^{tBu}Ar-H), 7.22 (1H, s, ^{tBu}Ar-H).

^{13}C{^{1}H} NMR ($CDCl_3$) 28.6 ((H_3*C*)$_3$C), 30.6 ((H_3*C*)$_3$C), 33.2 ((H_3C)$_3$*C*), 33.8 ((H_3C)$_3$*C*), 54.6, 56.3 (N-*C*H_2), 115.4, 119.6 (Ar-*C*H), 121.7, 122.6 (Ar-*C*), 122.7, 124.3, 128.5, 130.5 (Ar-*C*H), 134.9, 140.8 (Ar-*C*), 150.7, 153.8 (Ar-O).

m/z calc. $[C_{37}H_{53}NO_3 + Na]^+$ = 582.3923, found 582.3945.

(2-hydroxybenzyl)(2-hydroxy-3,5-dimethylbenzyl)(2-hydroxy-3,5-di-*tert*-butylbenzyl)amine (H_3**2**)

2-Benzyloxybenzylammonium acetate (2.00 g, 7.23 mmol), sodium bicarbonate (2.46 g, 29.3 mmol) and ethanol (100 ml) were charged to a round-bottom flask and heated to 70 °C under a flow of argon. 3,5-dimethyl-2-hydroxybenzaldehyde (1.10 g, 7.32 mmol) was diluted with ethanol (~20 ml) and added drop-wise to the reaction mixture. The reaction mixture was stirred for four hours before hot filtering to partially remove the sodium bicarbonate. The solvent was removed via rotary evaporation to yield a yellow solid. This crude product was re-dissolved in toluene, heated and hot-filtered to remove the remaining sodium bicarbonate. The solvent was removed via rotary evaporation and further dried under vacuum to yield a yellow solid imine, *N*-(2-benzyloxybenzyl)(2-hydroxy-3,5-dimethylbenzyl)aldimine (0.80g, 2.32 mmol, 32% yield).

^{1}H NMR (d_6-DMSO) 2.11 (3H, s, CH_3), 2.20 (3H, s, CH_3), 4.78 (2H, s, Ph-CH_2-N), 5.14 (2H, s, Ph-CH_2-O), 6.89-7.13 (4H, m, Ar-H), 7.25-7.38 (5H, m, Ar-H), 7.42-7.47 (2H, m, Ar-H).

^{13}C{^{1}H} NMR (d_6-DMSO) 15.2 (H_3*C*-Ph), 19.9 (H_3*C*-Ph), 57.5 (Ph-*C*H_2-N), 69.2 (Ph-*C*H_2-O), 112.1, 117.5 (Ar-H), 120.7, 124.6, 126.4 (Ar-C), 126.5, 127.6, 127.8, 128.4, 128.8, 129.2, 129.3 (Ar-H), 134.0, 137.1 (Ar-C), 156.1, 156.7 (Ar-O), 166.9 (Ph-*C*=N).

m/z calc. $[C_{23}H_{23}NO_2 + Na]^+$ = 368.1626, found 368.1625.

N-(2-benzyloxybenzyl)(2-hydroxy-3,5-dimethylbenzyl)aldimine (0.80 g, 2.32 mmol) was dissolved in methanol before the addition of sodium borohydride (1.5 eqv.) and allowed to stir at room temperature for 12 hours / overnight. The solvent was removed via rotary evaporation and purified as above to yield the corresponding amine. This amine (0.52 g, 1.52 mmol) was dissolved in THF (80 ml) and heated to reflux (80 °C). 3,5-di-*tert*-butyl-2-hydroxybenzyl bromide (0.45 g, 1.52 mmol) was dissolved in THF (~20 ml) before being added drop-wise to the reaction mixture. The reaction mixture was refluxed for approx. one hour before adding triethylamine (0.18 ml, 1.65 mmol) .The reaction was held at reflux for a further 5 hours before cooling to room temperature. Filtration removed a white solid ($Et_3NH^+Br^-$) leaving a yellow solution. Solvent was removed *via* rotary evaporation and further dried under reduced pressure to give a yellow solid. This crude product was redissolved in dichloromethane (~5 ml) and subjected to flash chromatography to remove unreacted starting material and triethylamine. Removal of solvent under vacuum yielded an off white solid monobenzyloxy-protected amine tris(phenolate) which was subsequently dissolved in methanol and deprotected by stirring under H_2 with Pd/C. Filtration, removal of solvent *via* rotary evaporation and further drying under vacuum yielded a while solid product (0.3 g, 0.63 mmol, 41 % yield).

^{1}H NMR ($CDCl_3$) 1.27 (9H, s, ^{t}Bu), 1.39 (9H, s, ^{t}Bu), 2.19 (3H, s, Me), 2.20 (3H, s, Me), 1.97 (2H, s, CH_2-N), 3.70 (2H, s, CH_2-N), 3.71 (2H, s, CH_2-N), 6.75 (1H, s, Ar-H) 8.82-6.87 (3H, m, Ar-H), 6.92 (1H, d (J = 2.3 Hz), ^{tBu}Ar-H), 7.08-7.18 (2H, m, Ar-H), 7.20 (1H, d (J = 2.3 Hz), ^{tBu}Ar-H).

^{13}C{^{1}H} NMR ($CDCl_3$) 14.8, 19.3 (*C*H_3), 28.7, 30.6 ($(H_3C)_3$C), 33.1, 33.8 $(H_3C)_3$*C*), 55.0, 55.1, 56.4 (*C*H_2N), 155.3, 119.4, 120.7, 120.8, 122.6, 123.3, 124.1, 124.5, 128.0, 128.2, 128.4, 130.2, 130.3, 134.9, 140.6 (Ar-*C*), 149.9, 150.9, 154.0 (Ar-O).

m/z calc. $[C_{31}H_{41}NO_3 + H]^+$ = 476.3165, found 476.3159.

Bis(2-hydroxybenzyl)(2-hydroxy-3,5-di-*tert*-butylbenzyl)amine (H_3**3**)

2-Benzyloxybenzylammonium acetate (2.90 g, 10.6 mmol), sodium bicarbonate (3.57 g, 42.4 mmol) and ethanol (150 ml) were charged to a round-bottom flask and heated to 70 °C under a flow of argon. Salicyaldehyde (1.29 g, 10.6 mmol) was diluted with ethanol (~20 ml) and added drop-wise to the reaction mixture. The reaction mixture was stirred for four hours before hot filtering to partially remove the sodium bicarbonate. The solvent was removed via rotary evaporation to yield a yellow

solid. This crude product was re-dissolved in toluene, heated and hot-filtered to remove the remaining sodium bicarbonate. The solvent was removed via rotary evaporation and further dried under vacuum to yield a yellow solid imine *N*-(2-benzyloxybenzyl)(2-hydroxybenzyl)aldimine (1.80 g, 5.64 mmol, 53% yield) .

^{1}H NMR (d_6-DMSO) 4.22 (2H, s, N-CH_2-Ph), 4.94 (2H, s, O-CH_2-Ph), 6.41-6.54 (3H, m, Ar-H), 6.75-6.79 (1H, m, Ar-H), 6.88-6.95 (2H, m, Ar-H), 7.08-7.21 (2H, m, Ar-H), 7.30-7.36 (5H, m, Ar-H), 8.18 (1H, s, Ph-CH=N).

^{13}C NMR (d_6-DMSO) 59.5 (Ph-*C*H_2-N), 69.6 (O-*C*H_2-Ph), 112.1, 113.8, 118.2, 120.5 (Ar-*C*H), 122.7, 124.5 (Ar-*C*), 128.0, 128.2, 128.7, 129.9, 130.9, 134.5, 136.2 (Ar-*C*H), 137.2 (Ar-*C*), 157.1 (Ar-OBn), 170.4 (Ar-O), 171.9 (Ph-*C*=N).

m/z calc. $[C_{21}H_{19}NO_2 + Na]^+$ = 340.1313, found 340.1310.

N-(2-benzyloxybenzyl)(2-hydroxybenzyl)aldimine (1.80 g, 5.64 mmol) was dissolved in methanol before the addition of sodium borohydride (1.5 eqv.) and allowed to stir at room temperature for 12 hours / overnight. The solvent was removed via rotary evaporation and purified as above to yield the corresponding amine. This amine (1.64 g, 5.13 mmol) was dissolved in THF (150 ml) and heated to reflux (80 °C). 3,5-di-*tert*-butyl-2-hydroxybenzyl bromide (1.54 g, 5.13 mmol) was dissolved in THF (~20 ml) before being added drop-wise to the reaction mixture. The reaction mixture was refluxed for approx. one hour before adding triethylamine (0.8 ml, 5.64 mmol) .The reaction was held a reflux for a further 5 hours before cooling to room temperature. Filtration removed a white solid ($Et_3NH^+Br^-$) leaving a yellow solution. Solvent was removed *via* rotary evaporation and further dried under reduced pressure to give a yellow solid. The crude product was dissolved in methanol (50 ml) before the addition of Pd/C and exposure to an atmosphere of H_2. After stirring for 18 hours, the reaction was filtered through celite and the solvent removed via rotary evaporation. Further drying under vacuum yielded a yellow solid. This crude product was redissolved in dichloromethane (~5 ml) and subjected to flash chromatography to remove unreacted starting material and triethylamine. Solvent was removed under vacuum and the resulting solid recrystallized in hexane with a small amount of methanol to yield the white solid amine tris(phenolate), H_3**3** (0.98g, 2.20 mmol, 43% yield).

^{1}H NMR ($CDCl_3$) 1.26 (9H, s, ^{t}Bu), 1.36 (9H, s, ^{t}Bu), 3.74 (4H, s, N-CH_2-PH), 3.75 (2H, s, N-CH_2-Ph), 6.80-8.85 (4H, m, Ar-H), 6.93 (1H, d (J = 2.4 Hz), ^{tBu}Ar-H), 7.08-7.16 (4H, m, Ar-H), 7.20 (1H, d (J = 2.4 Hz), ^{tBu}Ar-H).

^{13}C {^{1}H} NMR ($CDCl_3$) 29.9, 31.8 (C(*C*H_3)$_3$), 34.3, 34.9 (*C*(CH_3)$_3$), 56.4, 58.1 (N-*C*H_2-Ph), 116.5, 120.5, 121.6, 122.6, 123.4, 125.4, 129.7, 131.3, 136.2, 141.9 (Ar-*C*), 152.1, 155.3 (Ar-O).

m/z $[C_{29}H_{38}NO_3 + H]^+$ = 448.2852, found 448.2880.

Experimental - Zirconium Complex Synthesis and Characterisation

General Procedure

Amine tris(phenolate) ligands (H_3**X**) could be used crude and charged to a dry Schlenk and placed under an inert atmosphere using standard Schlenk techniques. The ligand was dissolved in dry toluene before adding Zr(O^iPr)(HO^iPr). The reaction was stirred at room temperature for one hour before the solvent was removed under vacuum. Dry hexane was added, giving an orange solution and off white solid. The solid was isolated *via* cannula filtration and dried under vacuum. The crude solid product was dissolved in minimal hot toluene and allowed to recrystallize to yield a white crystalline product.

Zr_2(**1**)$_2$(O^iPr)$_2$

^{1}H NMR ($CDCl_3$) 0.98 (6H, d J = 6.4 Hz, $CH(CH_3)_2$), 1.00 (18H, s, $C(CH_3)_3$), 1.03 (18H, s, $C(CH_3)_3$), 1.18 (18H, s, $C(CH_3)_3$), 1.20 (6H, d J = 6.0 Hz, $CH(CH_3)_2$), 1.28 (18H, s, $C(CH_3)_3$), 2.80 (2H, d J = 12.8 Hz, $PhCH_2N$), 3.21 (2H, d J = 13.2 Hz, $PhCH_2N$), 3.48 (2H, d J = 13.2 Hz, $PhCH_2N$), 3.81 (2H, d J = 12.8 Hz, $PhCH_2N$), 4.51 (2H, sept J = 6.0 Hz, $CH(CH_3)_2$), 5.12 (2H, d J = 13.2 Hz, $PhCH_2N$), 5.40 (2H, d J = 12.8 Hz, $PhCH_2N$), 6.22 (6H, m, Ar-H), 6.52 (2H , m, Ar-H), 6.72 (2H, s, Ar-H), 6.79 (2H, s, Ar-H), 7.02 (2H, s, Ar-H), 7.12 (2H, s, Ar-H).

^{13}C{^{1}H} NMR ($CDCl_3$) 22.7 ($CH(\mathit{C}H_3)_2$), 26.4, 26.6, 29.5, 30.0 ($C(\mathit{C}H_3)_3$), 34.0, 34.3, 34.7, 34.9 ($\mathit{C}(CH_3)_3$), 61.6, 62.3, 64.9 ($Ph\mathit{C}H_2N$), 72.2 ($\mathit{C}H(CH_3)_2$), 120.8, 123.0, 123.6, 123.7, 124.2, 124.5, 125.5, 126.5, 128.3, 130.5 (Ar-*C*H), 134.8, 136.4, 140.2, 140.9 (Ar-C), 154.4, 156.7, 157.4 (Ar-O).

Anal: calc. for $C_{40}H_{57}NO_4Zr$ C, 67.9; H, 8.13; N, 1.98. Found C, 68.6; H, 8.22; N, 1.93.

Zr_2(**2**)$_2$(O^iPr)$_2$

^{1}H NMR ($CDCl_3$) 0.98 (18H, s, $C(CH_3)_3$), 1.10 (6H, d (J = 6.1 Hz), $CH(CH_3)_2$), 1.15 (6H, d (J = 6.1 Hz), $CH(CH_3)_2$), 1.29 (18H, s, $C(CH_3)_3$), 1.54 (6H, s, Ph-CH_3), 2.06 (6H, s, Ar-CH_3), 2.78 (2H, d (J = 13.0 Hz), Ph-CH_2-N), 3.12 (2H, d (J = 13.0 Hz), Ph-CH_2-N), 3.52 (2H, d (J = 13.7 Hz), Ph-CH_2-N), 3.87 (2H, d (J = 13.0 Hz), Ph-CH_2-N), 4.39 (2H, sept (J = 6.1 Hz), $CH(CH_3)_2$), 5.12 (2H, d (J = 13.7 Hz), Ph-CH_2-N), 5.24 (2H, d (J = 13.0 Hz), Ph-CH_2-N), 6.16-6.25 (6H, m, Ar-H), 6.33 (2H, s, ^{Me}Ar-H), 6.48-6.55 (2H, m, Ar-H), 6.54 (2H, s, ^{Me}Ar-H), 6.69-6.85 (2H, m, Ar-H), 7.02 (2H, d (J = 2.2 Hz), ^{tBu}Ar-H), 7.12 (2H, d (J = 2.2 Hz), ^{tBu}Ar-H).

^{13}C {^{1}H} NMR ($CDCl_3$) 15.1 (Ar-$\mathit{C}H_3$), 19.4 (Ar-$\mathit{C}H_3$), 25.2 ($CH(\mathit{C}H_3)_2$), 25.7 ($CH(\mathit{C}H_3)_2$), 28.4 ($C(\mathit{C}H_3)_3$), 30.8 ($C(\mathit{C}H_3)_3$), 33.3 ($\mathit{C}(CH_3)_3$), 33.7 ($\mathit{C}(CH_3)_3$), 59.8 ($Ph\mathit{C}H_2N$), 60.8 ($Ph\mathit{C}H_2N$), 63.7 ($Ph\mathit{C}H_2N$), 71.4 ($\mathit{C}H(CH_3)_2$), 117.8, 119.7, 119.8, 122.7, 123.0, 123.3, 123.4, 123.5, 125.7, 125.8, 127.3, 128.1, 129.7, 135.5, 139.8 (Ar-H), 154.3, 155.3, 155.9 (Ar-O).

$Zr_2(\mathbf{3})_2(O^iPr)_2$

^{1}H NMR ($CDCl_3$) 1.06 (18H, s, $C(CH_3)_3$), 1.17 (6H, d (J = 6.0 Hz), $CH(CH_3)_2$), 1.28 (6H, d (J = 6.0 Hz), $CH(CH_3)_2$), 1.37 (18H, s, $C(CH_3)_3$), 2.96 (2H, d (J = 13.2 Hz), $PhCH_2N$), 3.24 (2H, d (J = 13.2 Hz), $PhCH_2N$), 3.64 (2H, d (J = 13.7 Hz), $PhNCH_2$), 4.02 (2H, d (J = 13.2 Hz), $PhNCH_2$), 4.45 (2H, sept (J = 6.0 Hz), $CH(CH_3)_2$), 5.22 (2H, d (J = 13.7 Hz), $PhNCH_2$), 5.34 (2H, d (J = 13.2 Hz), $PhNCH_2$), 5.80 (2H, d (J = 7.9 Hz), Ar-H), 6.20-6.29 (4H, m, Ar-H), 6.47-6.56 (2H, m, Ar-H), 6.60-6.72 (4H, m, Ar-H), 6.78-6.93 (4H, m, Ar-H), 7.11 (2H, d (J = 2.2 Hz), ^{tBu}Ar-H), 7.21 (2H, d (J = 2.2 Hz), ^{tBu}Ar-H).

^{13}C {^{1}H} NMR ($CDCl_3$) 25.9 ($CH(\mathit{C}H_3)_2$), 26.6 ($CH(\mathit{C}H_3)_2$), 29.5 ($C(\mathit{C}H_3)_3$), 31.8 ($C(\mathit{C}H_3)_3$), 34.3 ($\mathit{C}(CH_3)_3$), 34.8 ($\mathit{C}(CH_3)_3$), 60.7 ($Ph\mathit{C}H_2N$), 61.9 ($Ph\mathit{C}H_2N$), 64.7 ($Ph\mathit{C}H_2N$), 72.7 ($\mathit{C}H(CH_3)_2$), 116.2, 118.0, 119.3, 121.1 (Ar-H), 123.8, 124.0 (^{tBu}Ar-H), 124.4 (Ar-C), 125.6, 126.5 (Ar-C), 128.3, 128.4, 129.1, 130.2 (Ar-H), 136.6, 141.1 (Ar-C), 155.0, 156.8, 160.2 (Ar-O).

Anal: calc. for $C_{32}H_{41}NO_4Zr$, C, 64.60; H, 6.95; N, 2.35. Found: C, 64.49; H, 7.05; N, 2.26.

Representative ^{1}H NMR Spectra for Zirconium Complexes

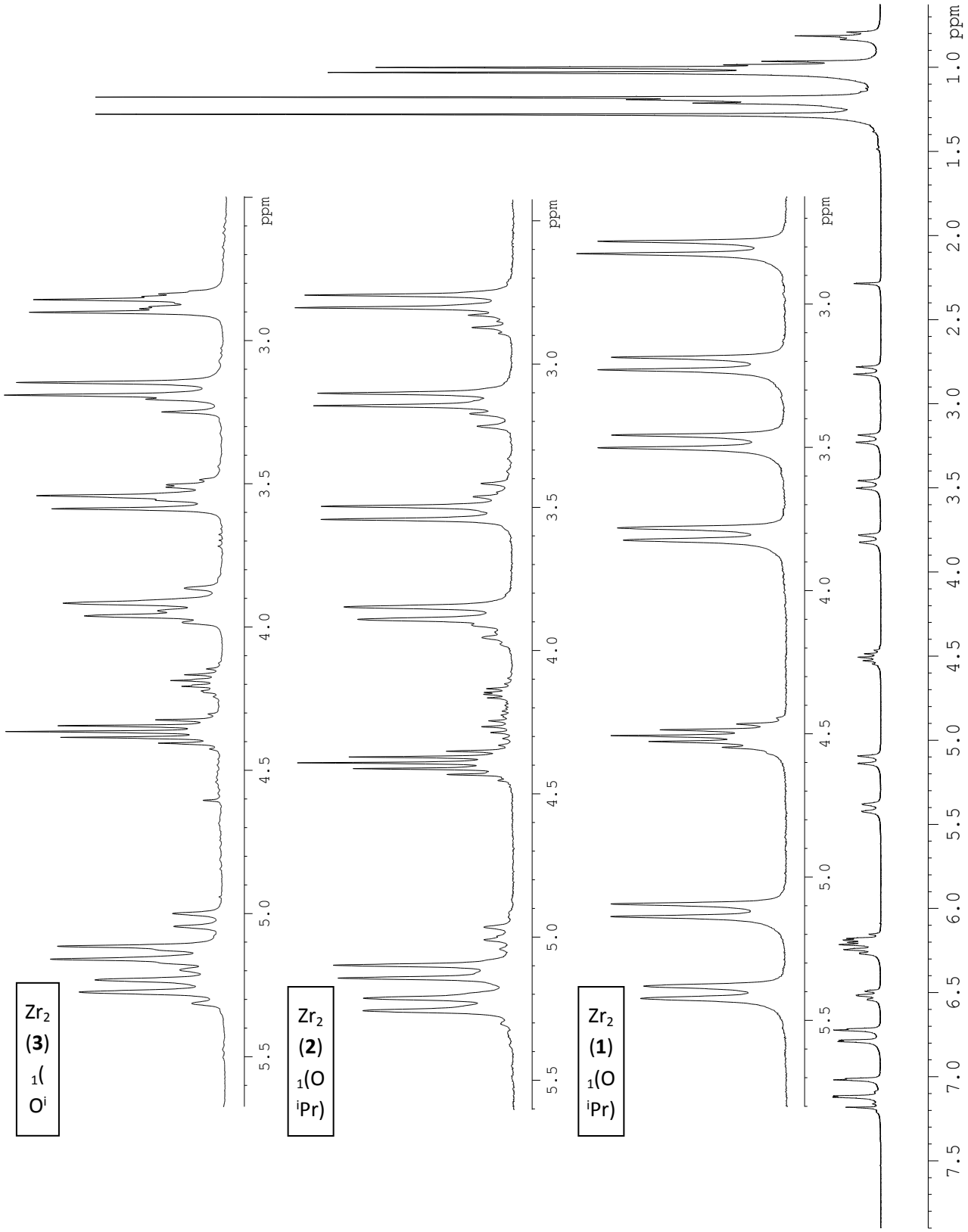


Figure S1. ^{1}H NMR Sepctrum for $Zr_2(\mathbf{1})_2(O^iPr)_2$ in $CDCl_3$. Inserts show AX spin system doublets for methylene bridges of $Zr_2(\mathbf{1\text{-}3})_2(O^iPr)_2$.

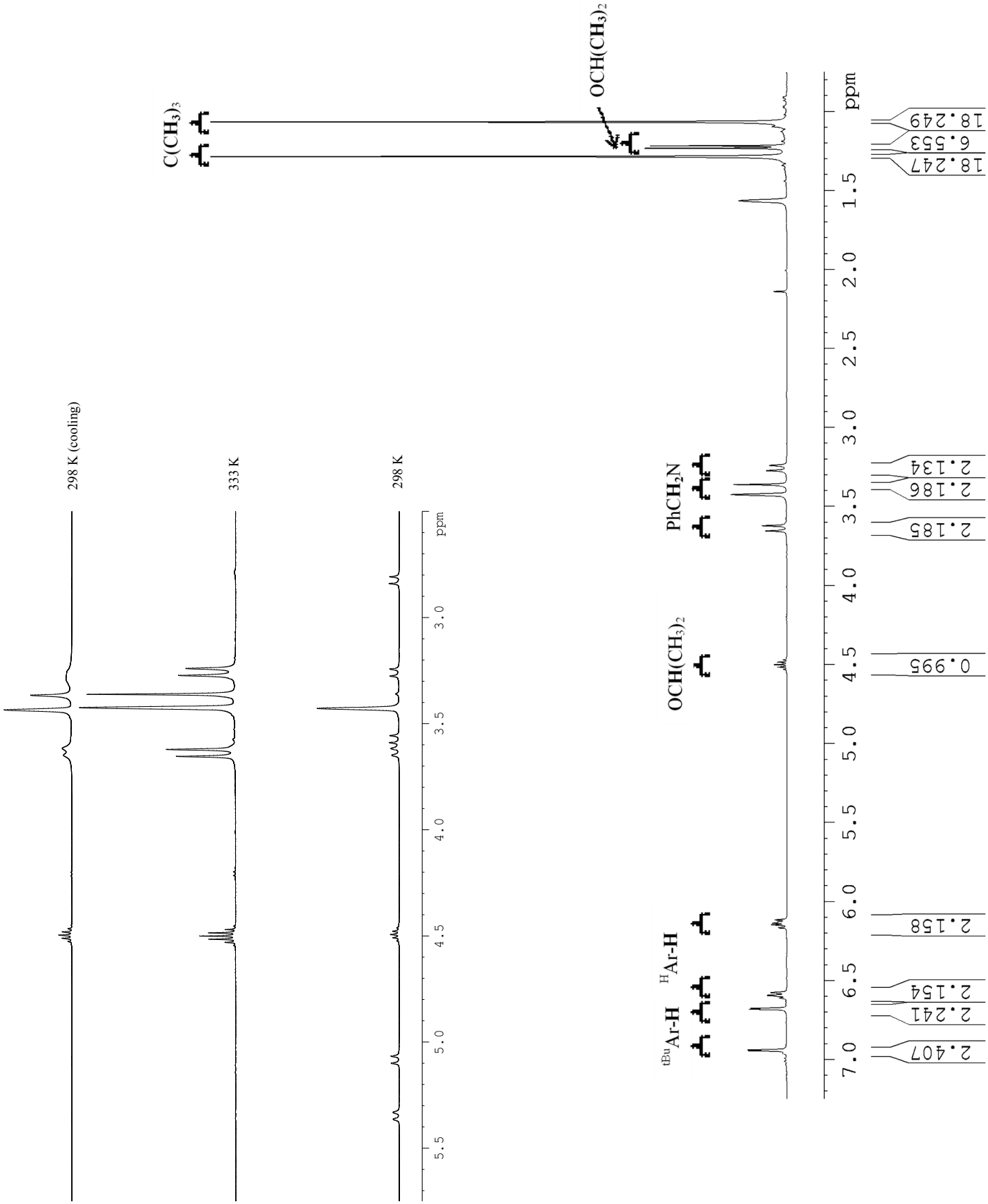


Figure S2. ^{1}H NMR Spectrum for $Zr_2(\mathbf{1})_2(O^iPr)_2$ in THF-d_8 at 333 K. Inset spectra show the persistence of the AX spin system in THF-d_8 until heating to 333 K.

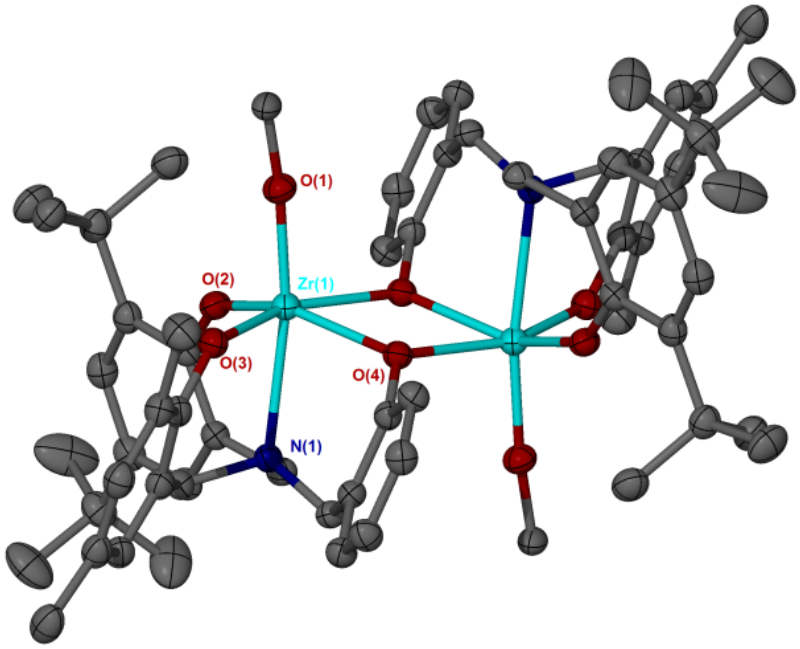
Single Crystal X-ray Crystallography Data

All data were collected on a Nonius kappa CCD diffractometer with MoKα radiation (λ = 0.71073 Å) see Table. T = 150(2) K throughout and all structures were solved by direct methods and refined on F^2 data using the SHELXL-97 suite of programs. Hydrogen atoms, were included in idealised positions and refined using the riding model. All solutions were relatively straightforward expect the following: Zr_2(**1**)$(O^iPr)_2$ The asymmetric unit was also seen to contain some extensively disordered solvent, which was treated using the Platon SQUEEZE algorithm. Based on the results from same and the pre-SQUEEZE difference electron-density map 1.2 molecules of $CDCl_3$ are present. The carbon and hydrogen atoms of the isopropoxide are disordered over two sites in a 60:40 ratio, one tBu moiety is disordered over two sites in a 60:40 ratio. Zr_2(**2**)$(O^iPr)_2$ the data was truncated to a 2θ value of 50.0º due to their small size. The carbon and hydrogen atoms of the isopropoxide are disordered over two sites in a 50:50 ratio, a molecule of toluene is also present in the asymmetric unit.

X-ray Parameters

Compound reference	Zr_2(**1**)$_2(O^iPr)_2$	Zr_2(**2**)$(O^iPr)_2$
Chemical formula	$C_{80}H_{114}N_2O_8Zr_2$	$C_{82}H_{106}N_2O_8Zr_2$
Formula Mass	1414.17	1430.13
Crystal system	Triclinic	Trigonal
a/Å	10.2690(2)	29.3650(6)
b/Å	13.0450(3)	29.3650(6)
c/Å	18.1870(4)	23.3020(6)
α/°	83.0580(10)	90.00
β/°	85.0540(10)	90.00
γ/°	69.3200(10)	120.00
Unit cell volume/Å^3	2260.14(8)	17401.4(7)
Temperature/K	150(2)	150(2)
Space group	*P*Error!	*R*Error!
No. of formula units per unit cell, *Z*	1	9
No. of reflections measured	10318	59569
No. of independent reflections	10318	6767
R_{int}	0.0000***	0.1093
Final R_1 values ($I > 2\sigma(I)$)	0.0501	0.0572
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1384	0.1503
Final R_1 values (all data)	0.0666	0.0938
Final $wR(F^2)$ values (all data)	0.1460	0.1859
Goodness of fit on F^2	1.093	1.124

*** pre squeezed 0.0529



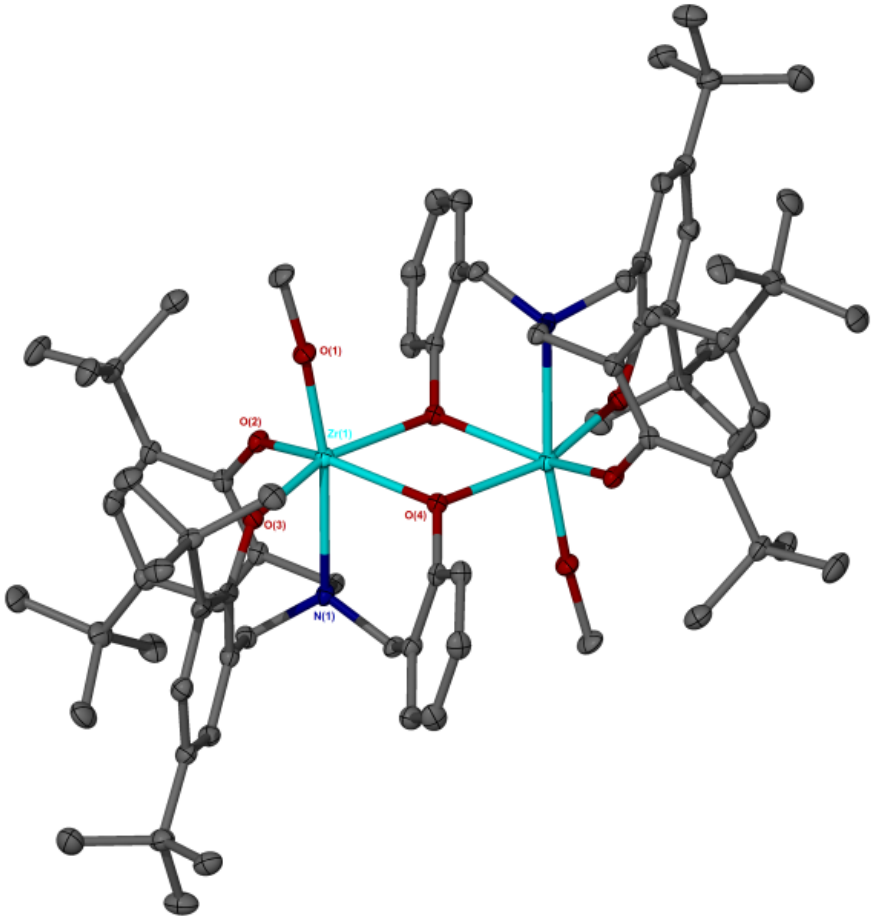


Figure S3. $Zr_2(\mathbf{1/2})_2(O^iPr)_2$ ellipsoids are shown at the 30% probability level. All disorder, hydrogen atoms and methyl groups of the isopropoxide moiety have been removed for clarity.

Polymerisation Experimental Procedures

Solvent-free polymerisations of *rac*-lactide initiated by group IV amine tris(phenolate) complexes

For solvent-free polymerisation of *rac*-lactide the monomer/ initiator ratio was 300:1. 0.50 g of monomer was used (recrystallised and doubly sublimed). Reactions were prepared air-sensitively and sealed before being carried out at 130 °C. After the reaction time, methanol (1 ml) was added to quench the reaction and the resulting solid dissolved in dichloromethane (~20 ml). The solvents were removed under reduced pressure and the resulting solid was analysed by ^{1}H NMR ($CDCl_3$) to determine conversion. Quantification was achieved through the integration of the monomer methine quartet (4.9 ppm) and the polymer methine multiplet (5.1 ppm) with conversion calculated using the following equation: $conv. = \frac{[PLA]}{[LA] + [PLA]} \times 100$. The solid was washed with methanol to remove all unreacted monomer. Homonuclear decoupled ^{1}H NMR spectroscopy ($CDCl_3$) was used to determine the polymer tacticity, with quantification as a P_r value (probability of racemic enchainment). GPC (THF, referenced to polystyrene standards) provided relative molecular weights (M_n) and polydispersity index (PDI) of the polymers produced.

Solvent-based polymerisations of *rac*-lactide initiated by group IV amine tris(phenolate) complexes

Solvent-based polymerisations were carried out in toluene at a lactide concentration of 0.5 M. The monomer/initator ratio used was 100:1 with monomer (1.0 g) purified through recrystallisation and double sublimation. Reactions were prepared air-sensitively and sealed before being carried out at 80 °C. After the desired reaction time, the reaction was quenched with methanol (1 ml). Solvents were then removed under reduced pressure and the resulting solid analysed by ^{1}H NMR to determine conversion. Quantification was achieved through the integration of the monomer methine quartet (4.9 ppm) and the polymer methine multiplet (5.1 ppm) with conversion calculated using the following equation: $conv. = \frac{[PLA]}{[LA] + [PLA]} \times 100$. The solid was washed with methanol to remove all unreacted monomer. Homonuclear decoupled ^{1}H NMR spectroscopy ($CDCl_3$) was used to determine the polymer tacticity, with quantification as a P_r value (probability of racemic enchainment). GPC (THF, referenced to polystyrene standards) provided relative molecular weights (M_n) and polydispersity index (PDI) of the polymers produced.

Kinetics-scale solvent-based polymerisations of *rac*-lactide

Polymerisations were carried out in a Young's NMR tube, prepared under an inert atmosphere using standard glove-box techniques. Monomer/initiator ratio was 100:1 with a monomer concentration of 0.5 M. 0.5ml of solvent (toluene-d_8) was added to the monomer in the Young's NMR tube. A solution of initiator was prepared containing five times the amount required in 0.50 ml of toluene-d_8. 0.10 ml

of this solution was then transferred to the NMR tube. Kinetic experiments were carried out at 80 °C in the NMR spectrometer. To aid accuracy, the instrument was pre-heated and shimmed to a sample of 0.5 M lactide in toluene-d_8. ^{1}H NMR spectra were obtained at regular intervals and the conversion calculated based on relative integrals of monomeric and polymeric signals for the lactide methine. $[M]_t = [M]_0 \times conv.$ The pseudo first-order rate constant (k_{app}) was calculated from the gradient of $\ln\left(\frac{[M]_0}{[M]_t}\right) vs.\ t$.

Polymerisations to investigate reaction order

Polymerisations were carried out in a Young's NMR tube, prepared under an inert atmosphere using standard glove-box techniques. For all experiments the lactide concentration ($[LA]_0$) was 0.5 M and the monomer/initiator ratio was varied between 400:1 and 50:1. To achieve this and minimise the experimental error incurred at such a small reaction scale, the amount of initiator was calculated for a [LA]:[I] of 100:1 and six times the amount was added to a 1.2 ml of toluene-d_8. The following dilutions were used to achieve each initiator loading:

[M]:[I]	lactide	toluene-d_8	Initiator stock solution
50:1	43 mg	0.2 ml	0.4 ml
100:1	43 mg	0.4 ml	0.2 ml
200:1	43 mg	0.5 ml	0.1 ml
400:1	43 mg	0.55 ml	0.05 ml

Experiments were carried out at 80 °C in the NMR instrument. To aid accuracy, the instrument was pre-heated and shimmed to a sample of 0.5 M lactide in toluene-d_8. ^{1}H NMR spectra were obtained at regular intervals and the conversion calculated based on relative integrals of monomeric and polymeric signals for the lactide methine (4.21 ppm → 5.15 ppm). $[LA]_t = [LA]_0 \times conv.$ The pseudo first-order rate constant (k_{app}) was calculated from the gradient of $\ln\left(\frac{[LA]_0}{[LA]_t}\right) vs.\ t$. Order with respect to [I] was found through the plot of $\ln(k_{app})\ vs.\ \ln([I])$ where the gradient of the plot is equal to the order with respect to [I].

Polymerisation Ki

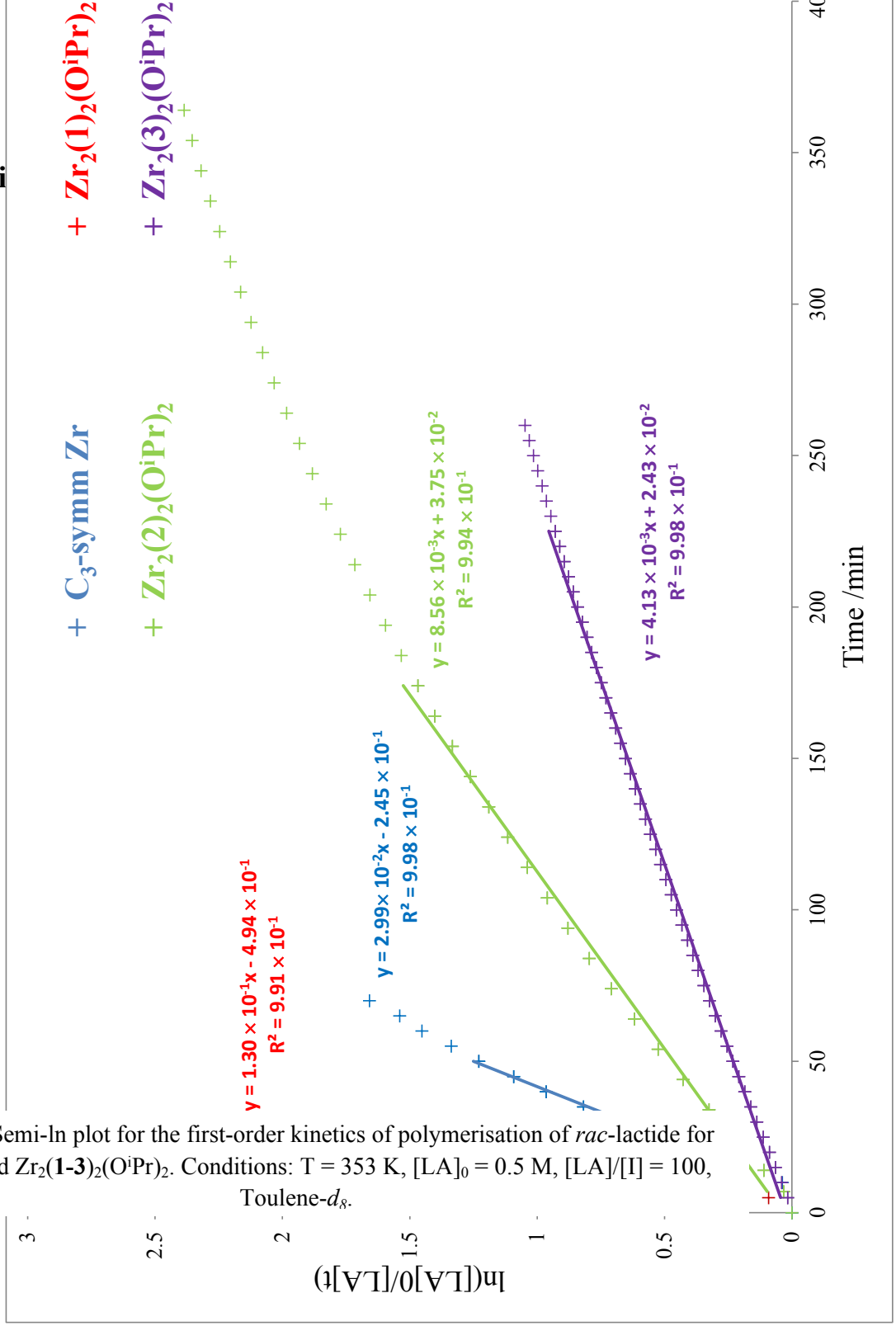


Figure S4. Semi-ln plot for the first-order kinetics of polymerisation of *rac*-lactide for Zr-$C_3{}^t$Bu and Zr_2(**1-3**)$_2$(O^iPr)$_2$. Conditions: T = 353 K, $[LA]_0$ = 0.5 M, [LA]/[I] = 100, Toulene-d_8.

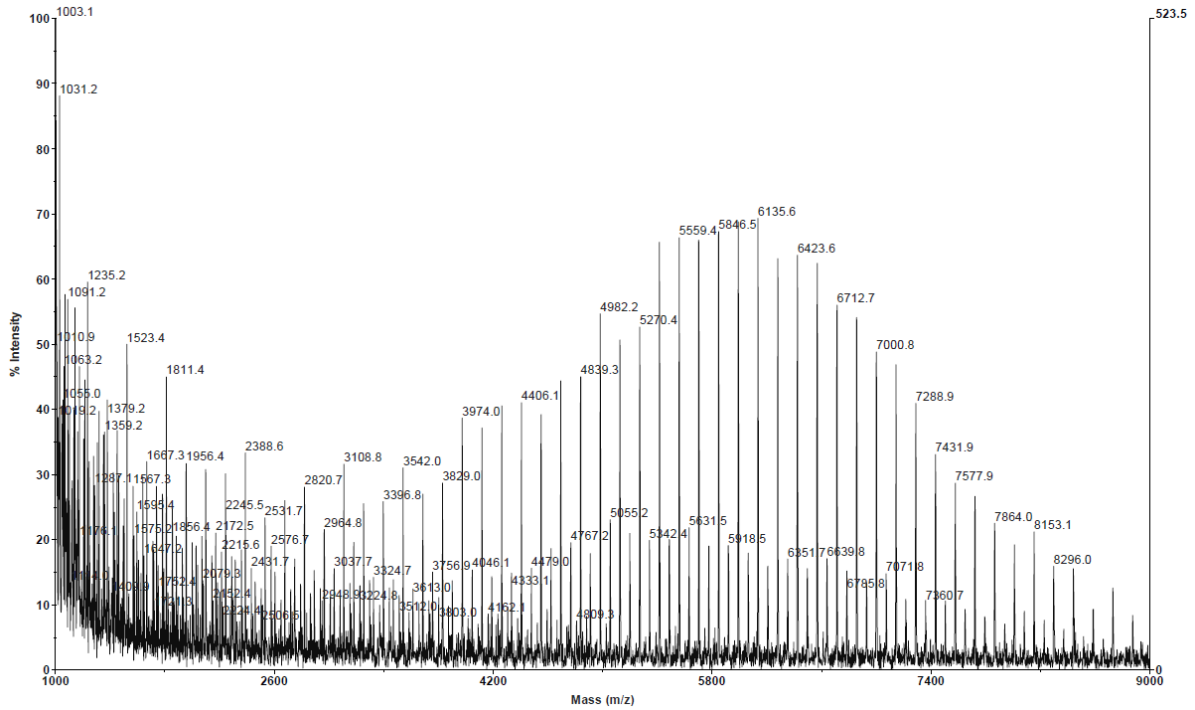


Figure S5. MALDI-TOF MS for Zr_2**3**$(O^iPr)_2$. The peak at 6135.6 m/z corresponds to $H(C_6H_8O_4)nOC_3H_7$-Na where n is 42, evidence for the coordination insertion mechanism

DOSY NMR Analysis:

Pulsed gradient spin echo (PGSE)[1] experiments allow for the determination of the self-diffusion coefficient D_t. It is intuitive that D_t is related to the size of the diffusing species, and provided that the size of the molecules under consideration is substantially greater than the size of the solvent molecules then the Stokes-Einstein equation may be reasonably be applied to gain information on the hydrodynamic radius (r_H).

$$Dt = \frac{kT}{6\pi\eta r_H}$$

where k is the Boltzmann constant, T is the temperature, and η is the solution viscosity.[2] However when the molecules of interest are considerably closer in size to the solvent molecules then a modified form of the Stokes-Einstein equation must be used:

$$Dt = \frac{kT}{c\pi\eta r_H}$$

In this case c is a numerical factor that can be expressed as a function of r_H and the van der Waals radius of the solvent.[3]

$$c = \frac{6}{[1 + 0.695(\frac{r_{solv}}{r_H})^{2.234}}$$

It can also be shown that

$$\frac{D_t^{sa}}{D_t^{so}} = \frac{c^{so} r_H^{so}}{c^{sa} r_H^{sa}}$$

where sa denotes sample and so solvent.[4] As D_t^{sa} and D_t^{so} can be experimentally determined and $c^{so} r_H^{so}$ can be calculated from known values, an estimate of $c^{sa} r_H^{sa}$ can be achieved; using a plot of $c^{sa} r_H^{sa}$ versus r_H^{sa}, r_H^{sa} may be found and thus V_H. The advantage of this method is that data can be obtained without the need for viscosity measurements using the solvent as an internal standard, combined with the known hydrodynamic radii of the solvents.

Experimental details

Data were acquired using a Bruker Avance III NMR spectrometer operating at 500.13 MHz (^{1}H) at 22 ºC with a BBFO+ probe. The standard Bruker pulse sequence ledgp2s[5] 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.[6]

Diffusion coefficients D_t (10^{-10} m^2 s^{-1}), hydrodynamic radii r_H (Å), hydrodynamic volume V_H (Å^3) and *c* factors for solutions in toluene-d_8 or thf-d_8.

Sample	**Solvent**	D_t^{so}/D_t^{sa}	r_H	c	V_H
Zr(C_3-trisPhenolate)(O^{i}Pr)	toluene-d_8	2.59	4.94	5.09	505
Zr$_2$(**1**)$_2$(O^{i}Pr)$_2$	toluene-d_8	2.85	5.33	5.19	635
Zr$_2$(**1**)$_2$(OiPr)$_2$	tetrahydrofuran-d_8	2.64	4.87	5.10	487
Zr$_2$(**3**)$_2$(OiPr)$_2$	toluene-d_8	2.81	5.25	5.19	606

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