

## SUPPORTING INFORMATION

### Group 4 Salalen Complexes and Their Application of the Ring Opening Polymerization of *rac*-Lactide

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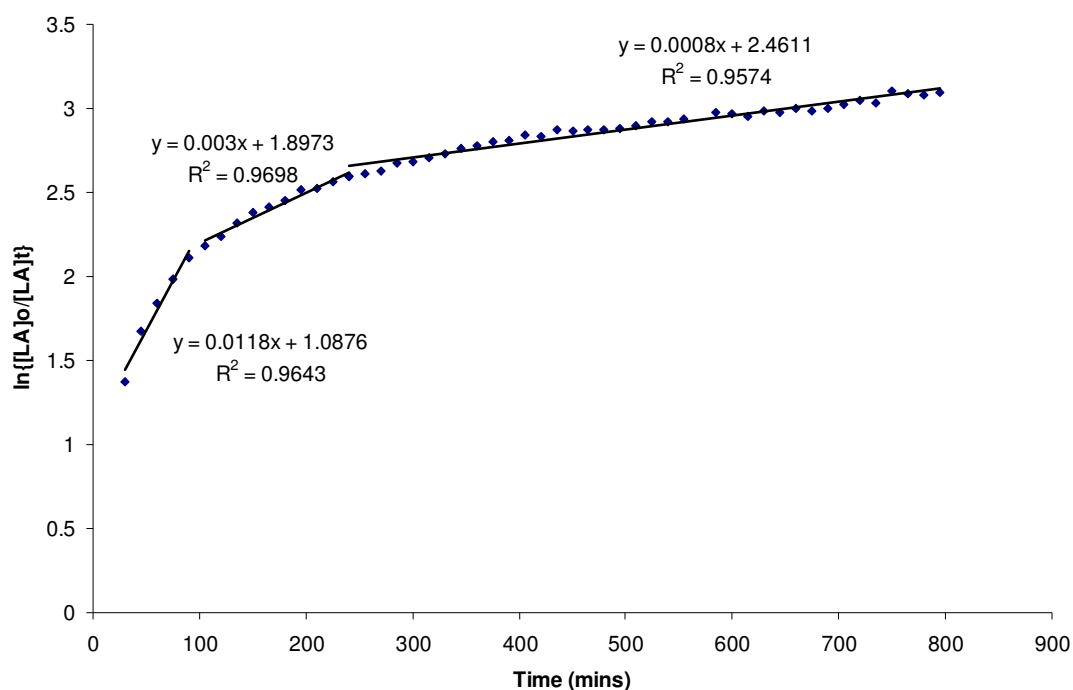
#### Polymerization procedure

For solvent-free polymerizations the monomer: initiator ratio employed was 300:1 at a temperature of 130 °C, in all cases 2 g of *rac*-lactide was used. After the reaction time methanol (20 ml) was added to quench the reaction and the resulting solid was dissolved in dichloromethane. The solvents were removed *in-vacuo* and the resulting solid washed with methanol (3 × 50 ml) to remove any unreacted monomer. For solution polymerizations a monomer:initiator ratio of 100:1 was used. In all cases 0.72 g of lactide and the appropriate amount of initiator were dissolved in toluene (10 ml) these were placed in a pre-heated oil bath and heated for the desired amount of time. The reaction was quenched by the addition of methanol (20 ml). <sup>1</sup>H NMR spectroscopy (CDCl<sub>3</sub>) and GPC (THF) were used to determine tacticity and molecular weights ( $M_n$  and  $M_w$ ) of the polymers produced;  $P_r$  (the probability of heterotactic linkages) were determined by analysis of the methine region of the homonuclear decoupled <sup>1</sup>H NMR spectra. The equations used to calculate  $P_r$  are given by Coates *et al.* In the case where  $P_r \neq 0.5$  the tacticity was also confirmed by <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) spectroscopy by analysis of the methine region. Gel Permeation Chromatography (GPC) analyses were performed on a Polymer Laboratories PL-GPC 50 integrated system using a PLgel 5 µm MIXED-D 300 x 7.5 mm column at 35 °C, THF solvent (flow rate 1.0 ml/min). The polydispersity index (PDI) was determined from  $M_w/M_n$  where  $M_n$  is the number average molecular weight and  $M_w$  the weight average molecular weight. The polymers were referenced to 11 narrow molecular weight polystyrene standards with a range of  $M_w$  615 – 568,000 Da.

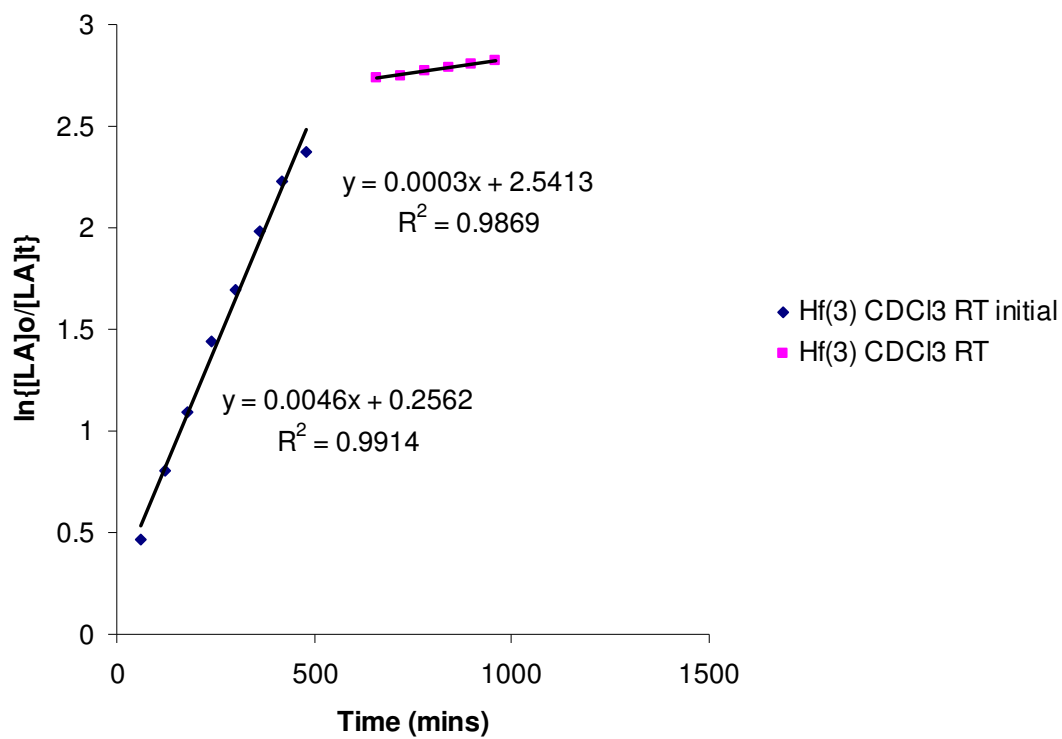
## Kinetic procedure

A 0.6 ml solution of *rac*-lactide in  $d_8$ -toluene was prepared with an initial concentration of  $0.578 \text{ mol dm}^{-3}$  based on 0.05 g of *rac*-lactide with a monomer to initiator ratio of 100:1 using  $\text{Ti}(\mathbf{1}/\mathbf{2})(\text{O}^i\text{Pr})_2$ ,  $\text{Zr}(\mathbf{1}/\mathbf{2})(\text{O}^i\text{Pr})_2$  or  $\text{Hf}(\mathbf{1}/\mathbf{2}/\mathbf{3})(\text{O}^i\text{Pr})_2$  as the initiator. The  $^1\text{H}$  NMR spectra of the sample was obtained at  $80^\circ\text{C}$  over a period of 13 hours at 15 or 30 minute intervals. The relative concentrations of the monomer and polymer were determined from analysis of the  $^1\text{H}$  NMR spectra and a plot of  $\ln\{[\text{LA}]_0/[\text{LA}]_t\}$  vs time was plotted. For the room temperature kinetics the solvent used was  $\text{CDCl}_3$  and the spectra were recorded every hour.

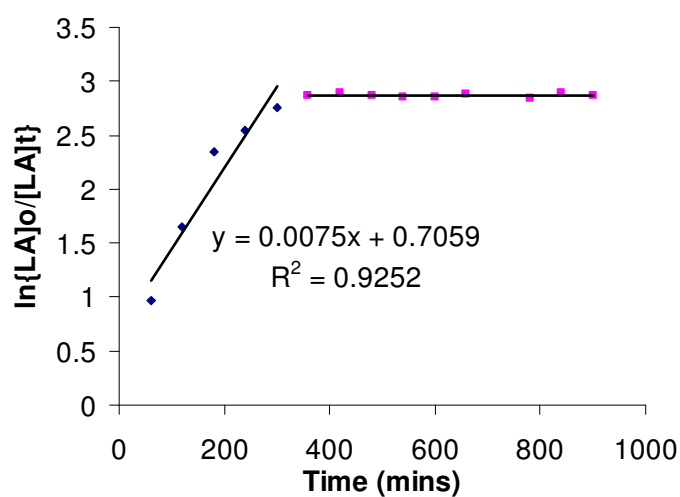
$\text{Hf}(\mathbf{3})(\text{O}^i\text{Pr})_2$  in  $d_8$ -toluene at  $80^\circ\text{C}$  (*rac*-LA) – by the time the sample was shimmed and at temperature 60% conversion was seen.



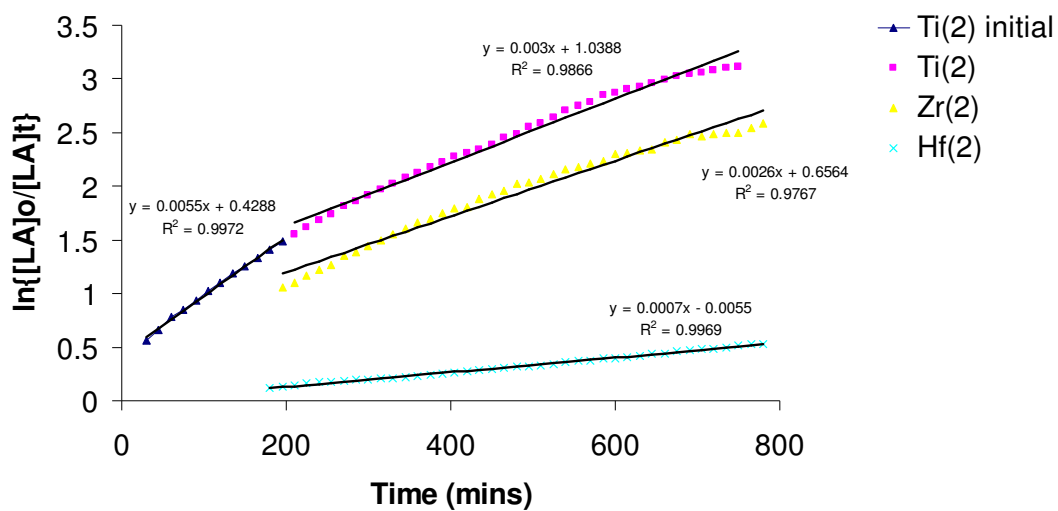
Hf(3)(O<sup>i</sup>Pr)<sub>2</sub> in CDCl<sub>3</sub> at 20 °C (*rac*-LA)



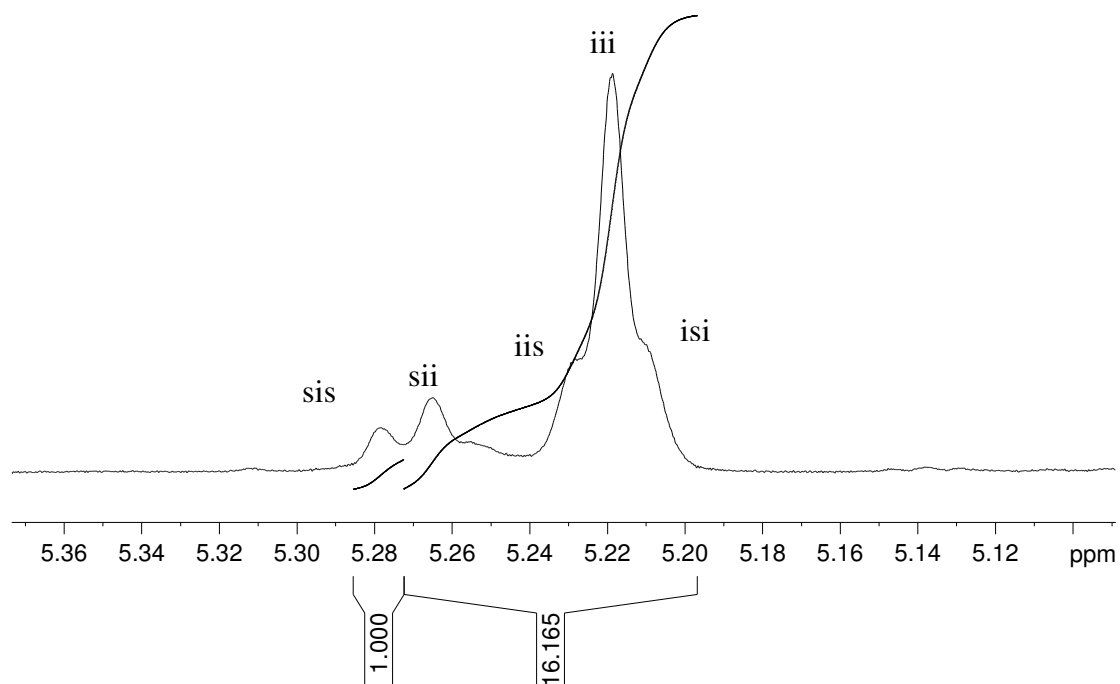
Hf(3)(O<sup>i</sup>Pr)<sub>2</sub> in CDCl<sub>3</sub> at 20 °C (*L*-LA)



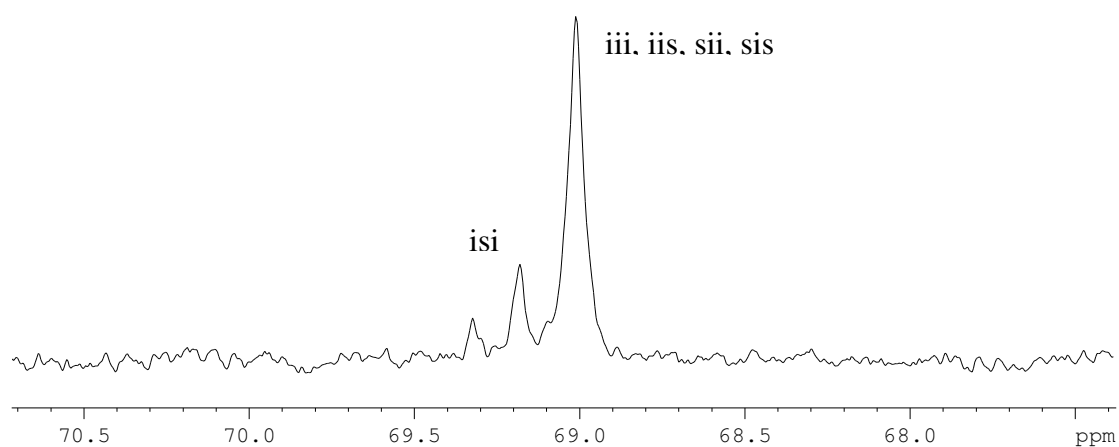
Ti(2)(O<sup>i</sup>Pr)<sub>2</sub>, Zr(2)(O<sup>i</sup>Pr)<sub>2</sub> and Hf(2)(O<sup>i</sup>Pr)<sub>2</sub> in d<sub>8</sub>-toluene at 80 °C (*rac*-LA)



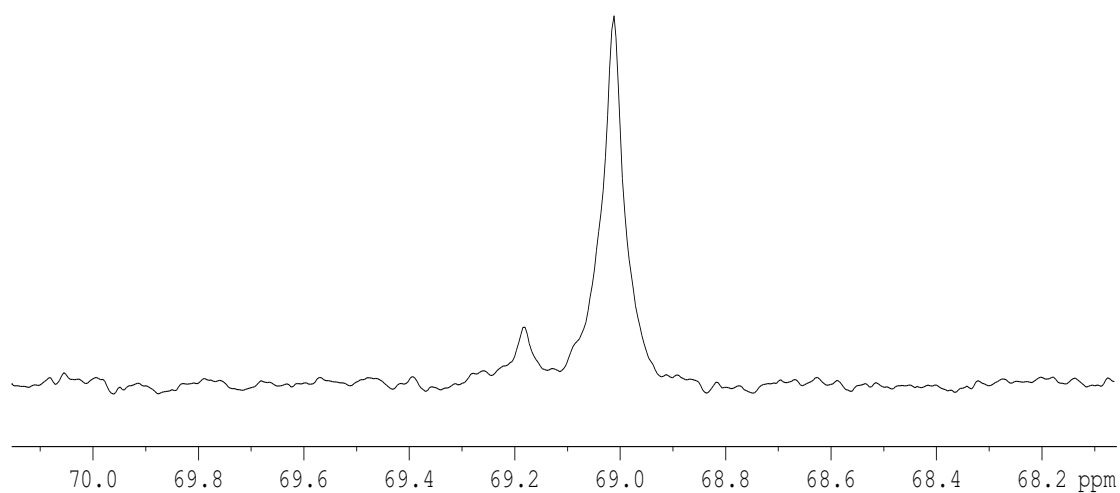
**Selected NMR data for the polymers:**



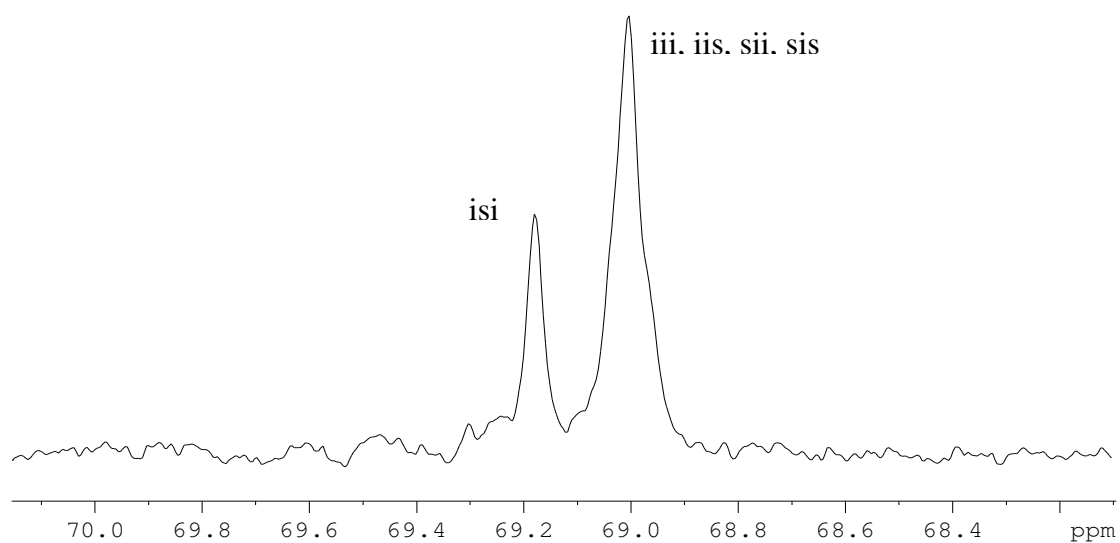
**Fig 1**  $^1\text{H}$  homonuclear decoupled NMR of the methine region of the polymer formed with  $\text{Hf}(\mathbf{1})(\text{O}^i\text{Pr})_2$  using toluene as a solvent for 24 hours at 80 °C.



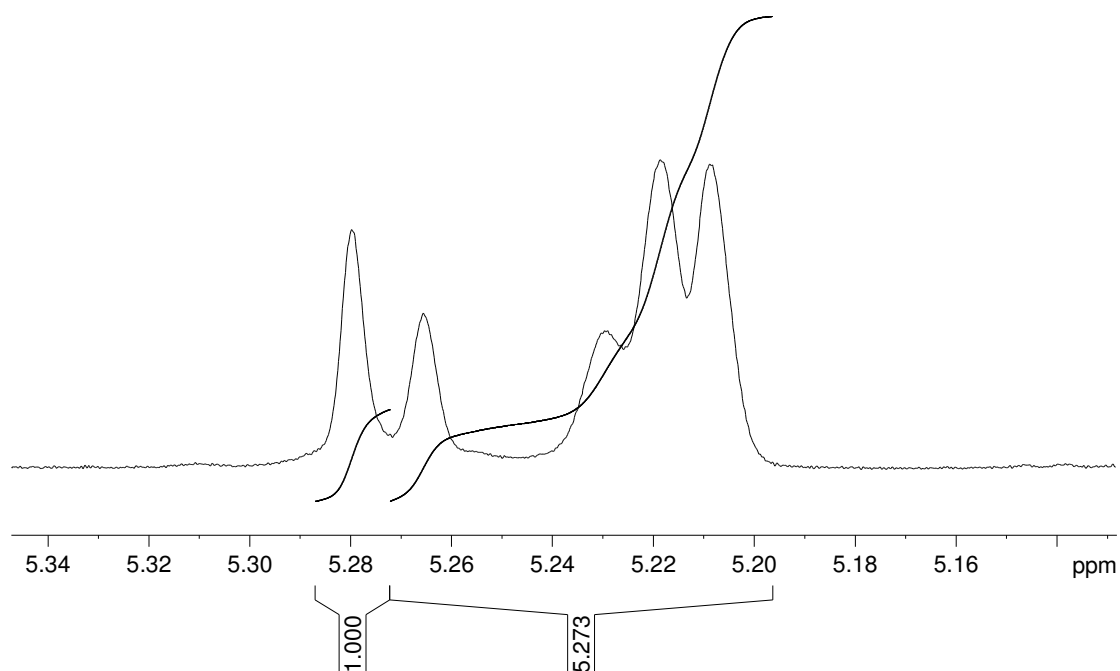
**Fig 2**  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ) of the methine region of the polymer formed with  $\text{Hf}(\mathbf{1})(\text{O}^i\text{Pr})_2$  using toluene as a solvent for 24 hours at 80 °C which favours the formation of isotactic sequences. Further information about the assignment of the tetrads in the  $^{13}\text{C}\{^1\text{H}\}$  NMR can be found in Chisholm et al *Macromolecules*, 1999, **32**, 963 or Thakur et al *Macromolecules*, 1997, **30**, 2422.



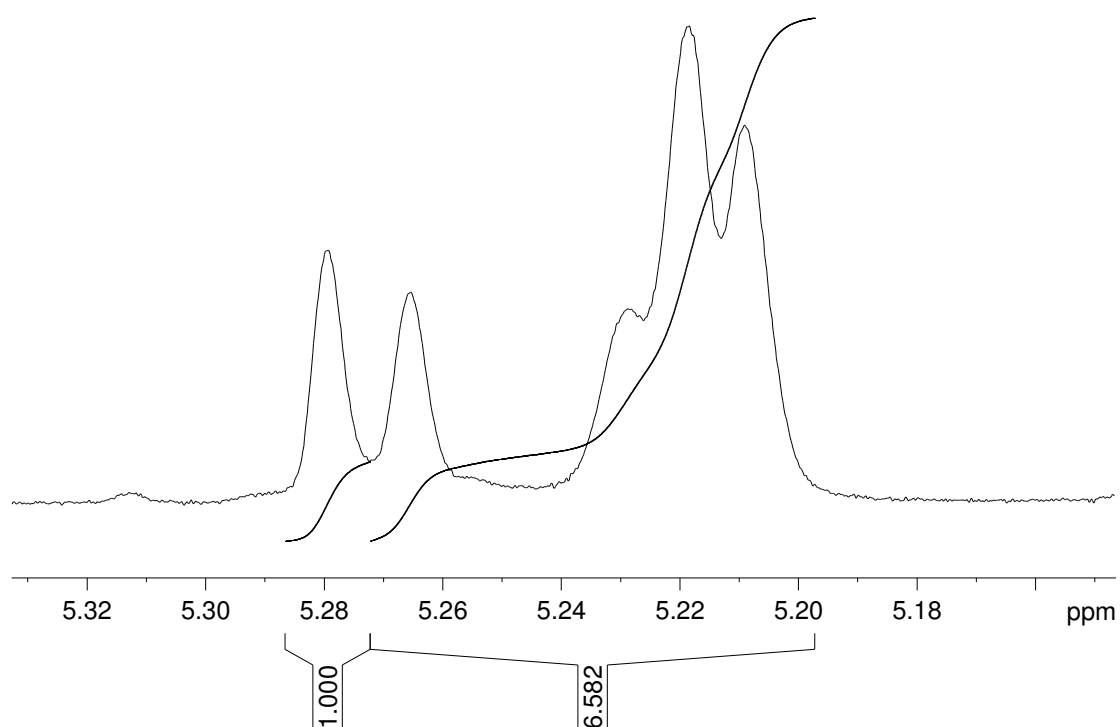
**Fig 3**  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ) of the methine region of the polymer formed with  $\text{Hf}(\mathbf{3})(\text{O}^i\text{Pr})_2$  using  $\text{CH}_2\text{Cl}_2$  as a solvent for 6 hours at room temperature which favours the formation of isotactic sequences.



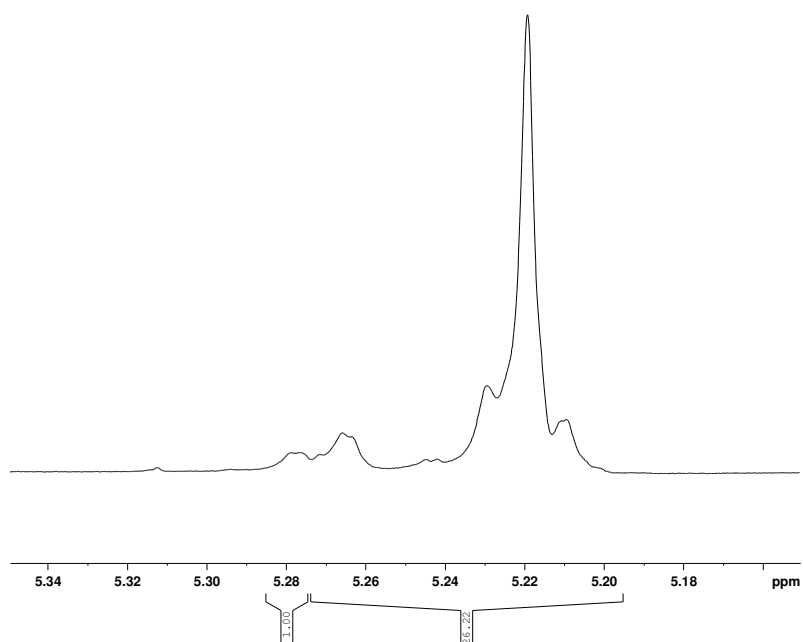
**Fig 4**  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ) of the methine region of the polymer formed with  $\text{Ti}(\mathbf{1})(\text{O}^i\text{Pr})_2$  using toluene as a solvent for 2 hours at  $80\text{ }^\circ\text{C}$  which favours the formation of atactic sequences.



**Fig 5**  $^1\text{H}$  homonuclear decoupled NMR of the methine region of the polymer formed with  $\text{Zr}(\mathbf{1})(\text{O}^i\text{Pr})_2$  polymerization in toluene at 80 °C for 24 hours showing slightly heterotactic bias with  $P_r = 0.56$ .



**Fig. 6:**  $^1\text{H}$  homonuclear decoupled NMR of  $\text{Ti}(\mathbf{1})(\text{O}^i\text{Pr})_2$  polymerization in toluene at 80 °C for 2 hours showing atactic PLA with  $P_r = 0.51$

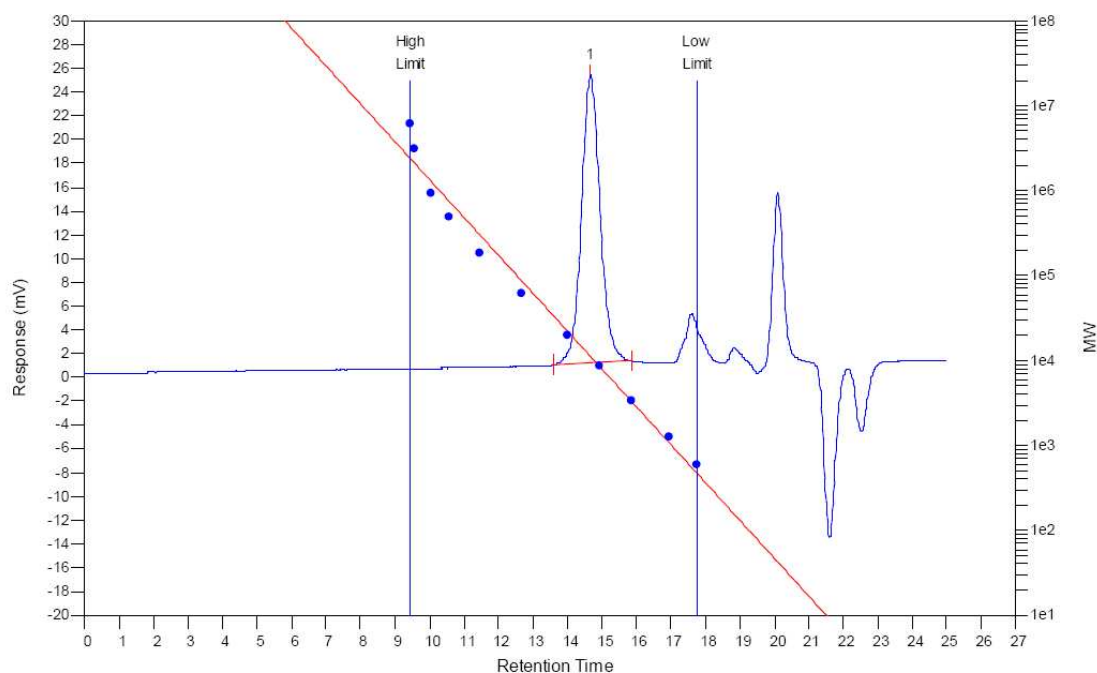


**Fig. 7:**  $^1\text{H}$  homonuclear decoupled NMR of  $\text{Hf}(\mathbf{3})(\text{O}^i\text{Pr})_2$  polymerization in  $\text{CH}_2\text{Cl}_2$  at room temperature for 6 hours showing isotactic PLA with  $P_r = 0.25$

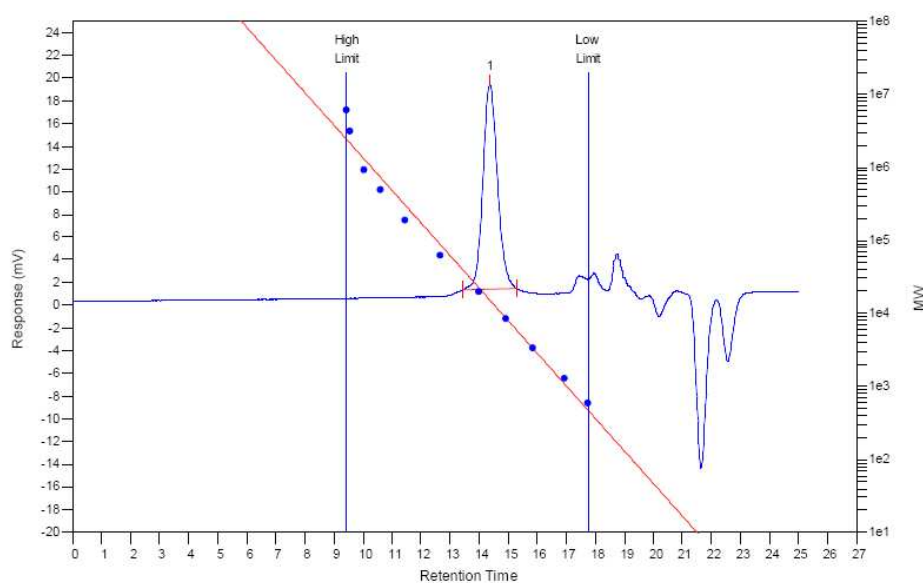


### Selected GPC data:

It is possible to correct the GPC values for PLA by the Mark–Houwink equation [ $M_n(\text{obsd}) = 0.58 \times M_n(\text{GPC})$ ] (I. Barakat, P. Dubois, R. Jerome, P. Teyssie, *J. Polym. Sci. Part A*, 1993, **31**, 505.) However, in these examples the GPC  $M_n$ 's are relative to polystyrene standards.



**Fig 8:**  $\text{Zr}(\text{2})(\text{O}^i\text{Pr})_2$  solution polymerization 24 hours,  $M_n = 10,500$ .



**Fig 9:**  $\text{Hf}(\text{2})(\text{O}^i\text{Pr})_2$  solution polymerization 24 hours,  $M_n = 14,300$ .

## MALDI-TOF MS DATA

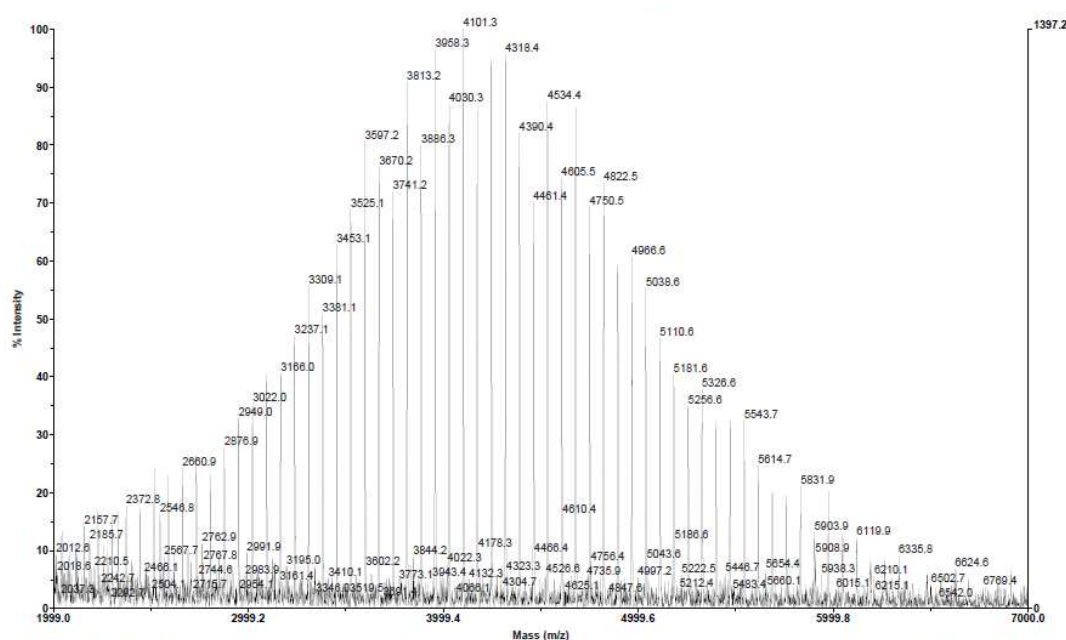


Fig 10: MALDI-TOF MS of PLA formed with  $\text{Zr}(\mathbf{1})(\text{O}^i\text{Pr})_2$  after 2 hrs.

## Full synthetic Procedures and Protocols:

For all crystallographically characterized complexes the ellipsoids are shown at the 50 % probability level and all H-atoms have been removed for clarity.

## Ligands

**1H<sub>2</sub>:** A solution of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (3.23 g, 0.01 mol) and N-methyl-ethylenediamine (1.02 g, 1.2 ml, 0.01 mol) in methanol (20 ml) was prepared. The solution was stirred until a clear solution was observed, and left to stand for 24 hours to yield a yellow oil which was collected and dried (2.68 g, 66 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>) 1.31 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 1.45 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 2.47 (3H, s, CH<sub>3</sub>), 2.92 (2H, t J = 6 Hz, CH<sub>2</sub>), 3.73 (2H, t J = 6 Hz, CH<sub>2</sub>), 7.09 (1H, d J = 2.5 Hz, Ar-H), 7.39 (1H, d J = 2.5 Hz, Ar-H), 8.40 (1H, s, CH). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) 29.8, 31.8 (C(CH<sub>3</sub>)<sub>3</sub>), 34.4, 35.3 (C(CH<sub>3</sub>)<sub>3</sub>), 36.6 (CH<sub>3</sub>), 52.2, 59.8 (CH<sub>2</sub>), 118.1, (Ar-C), 126.3, 127.3 (Ar-CH), 137.0, 140.5 (Ar-C), 158.3 (Ar-O), 167.5 (CH).

The oil (1 g, 3.44 mmol) was dissolved in THF (20 cm<sup>3</sup>), to which a solution of 3,5-di-*tert*-2-hydroxybenzyl bromide (1.03 g, 3.44 mmol) in THF (20 cm<sup>3</sup>) was added. Triethylamine (0.35 g, 0.48 ml, 3.44 mmol) was added and the mixture stirred at 80 °C for three hours. The white precipitate was filtered and the solvent removed under reduced pressure. The product was isolated *via* flash chromatography (CH<sub>2</sub>Cl<sub>2</sub>) to obtain the product (1.33 g, 76 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>) 1.29 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 1.32 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 1.39 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 1.46 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 2.40 (3H, s, CH<sub>3</sub>), 2.85 (2H, t J = 6.5 Hz, CH<sub>2</sub>), 3.76 (2H, s, CH<sub>2</sub>), 3.78 (2H, t J = 6.5 Hz, CH<sub>2</sub>), 6.84 (1H, d J = 2.5 Hz, Ar-H), 7.09 (1H, d J = 2.5 Hz, Ar-H), 7.22 (1H, d J = 2.5 Hz, Ar-H), 7.40 (1H, d J = 2.5 Hz, Ar-H), 8.39 (1H, s, CH). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) 29.4, 29.4, 31.5, 31.7 (C(CH<sub>3</sub>)<sub>3</sub>), 34.1, 35.0 (C(CH<sub>3</sub>)<sub>3</sub>), 41.9 (CH<sub>3</sub>), 57.1, 57.3, 62.2 (CH<sub>2</sub>), 117.8, 120.9, (Ar-C), 122.9, 123.2, 125.9, 127.0 (Ar-CH), 135.6, 136.6, 140.1, 140.4 (Ar-C), 154.3, 158.0 (Ar-O), 167.3 (CH). m/z calc. C<sub>33</sub>H<sub>53</sub>N<sub>2</sub>O<sub>2</sub> = 509.4107, found 509.4145

**2H<sub>2</sub>:** A solution of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (3.23 g, 0.01 mol) and N-phenyl-ethylenediamine (1.91 g, 1.83 ml, 0.01 mol) in methanol (20 ml) was prepared. The solution was stirred until a clear solution was observed, and left to stand for 24 hours to yield a yellow powder which was collected and dried (7.34 g, 91 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>) 1.31 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 1.46 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 3.52 (2H, t J = 6 Hz, CH<sub>2</sub>), 3.81 (2H, t J = 5.5 Hz, CH<sub>2</sub>), 6.66 (2H, d J = 8 Hz, Ar-H), 6.73 (1H, t J = 7.5 Hz, Ar-H), 7.08 (1H, d J = 2.5 Hz, Ar-H), 7.19 (2H, t, J = 8 Hz, Ar-H), 7.40 (1H, d J = 2.5 Hz, Ar-H), 8.35 (1H, s, CH). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) 29.7, 31.8 (C(CH<sub>3</sub>)<sub>3</sub>), 34.4, 35.3 (C(CH<sub>3</sub>)<sub>3</sub>), 44.5, 58.7 (CH<sub>2</sub>), 113.5, 118.0, 126.3, 127.5, 129.6 (Ar-CH), 137.0, 140.5, 147.9 (Ar-C), 158.3 (Ar-O), 168.0 (CH).

The yellow powder (1 g, 2.84 mmol) was dissolved in THF (20 cm<sup>3</sup>), to which a solution of 3,5-di-*tert*-2-hydroxybenzyl bromide (0.85 g, 2.84 mmol) in THF (20 cm<sup>3</sup>) was added. Triethylamine (0.29 g, 0.4 ml, 2.84 mmol) was added and the mixture stirred at 80 °C for three hours. The white precipitate was filtered and the solvent removed under reduced pressure. The product was isolated *via* flash chromatography (CH<sub>2</sub>Cl<sub>2</sub>) to obtain the product (0.958 g, 59 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>) 1.19 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 1.21 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 1.32 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 1.36 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 3.42 (2H, t J = 6.5 Hz, CH<sub>2</sub>), 3.58 (2H, t J = 6.5 Hz, CH<sub>2</sub>), 4.32 (2H, s, CH<sub>2</sub>), 6.87 (1H, d J = 2.5 Hz, Ar-H), 6.90 (1H, d J = 2.5 Hz, Ar-H), 6.93 – 6.99 (1H, m, Ar-H), 7.09 – 7.16 (3H, m, Ar-H), 7.21 – 7.27 (2H, m, Ar-H), 7.29 (1H, d J = 2.5

Hz, Ar-H), 8.07 (1H, s, CH).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ) 29.8, 30.0, 31.8, 32.0 ( $\text{C}(\text{CH}_3)_3$ ), 34.4, 34.5, 35.2, 35.4 ( $\text{C}(\text{CH}_3)_3$ ), 52.8, 56.9, 57.9 ( $\text{CH}_2$ ), 118.1 (Ar-C), 121.0, (Ar-CH), 121.5 (Ar-C), 123.4, 123.7, 124.3, 126.2, 127.4, 129.7 (Ar-CH), 136.2, 137.0, 140.5, 141.7, 149.2 (Ar-C), 154.0, 158.3 (Ar-O), 167.9 (CH).  $m/z$  calc.  $\text{C}_{38}\text{H}_{54}\text{N}_2\text{O}_2 = 571.4264$ , found 571.4270

**3H<sub>2</sub>** A solution of 2-hydroxy-3-methylbenzaldehyde (0.75 g, 0.66 ml, 5.51 mmol) and N-methyl-ethylenediamine (0.41 g, 0.48 ml, 5.51 mol) in methanol (10 ml) was prepared. The solution was stirred until a clear solution was observed, and left to stand for 24 hours to yield a yellow oil which was collected and dried (0.83 g, 78 %).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 2.21 (3H, s,  $\text{CH}_3$ ), 2.39 (3H, s,  $\text{CH}_3$ ), 2.83 (2H, t  $J = 5.5$  Hz,  $\text{CH}_2$ ), 3.64 (2H, t  $J = 5.5$  Hz,  $\text{CH}_2$ ), 6.72 (1H, t  $J = 7.5$  Hz, Ar-H), 7.03 (1H, d  $J = 7.5$  Hz, Ar-H), 7.11 (1H, d  $J = 7.0$  Hz, Ar-H), 8.28 (1H, s, CH).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ) 15.6, 36.4 ( $\text{CH}_3$ ), 51.9, 59.4 ( $\text{CH}_2$ ), 117.9 (Ar-C), 118.2 (Ar-CH), 125.9 (Ar-C), 129.1, 133.3 (Ar-CH), 159.4 (Ar-O), 166.2 (CH).  $m/z$  calc.  $\text{C}_{11}\text{H}_{17}\text{N}_2\text{O} = 193.1341$ , found 193.1352

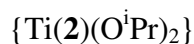
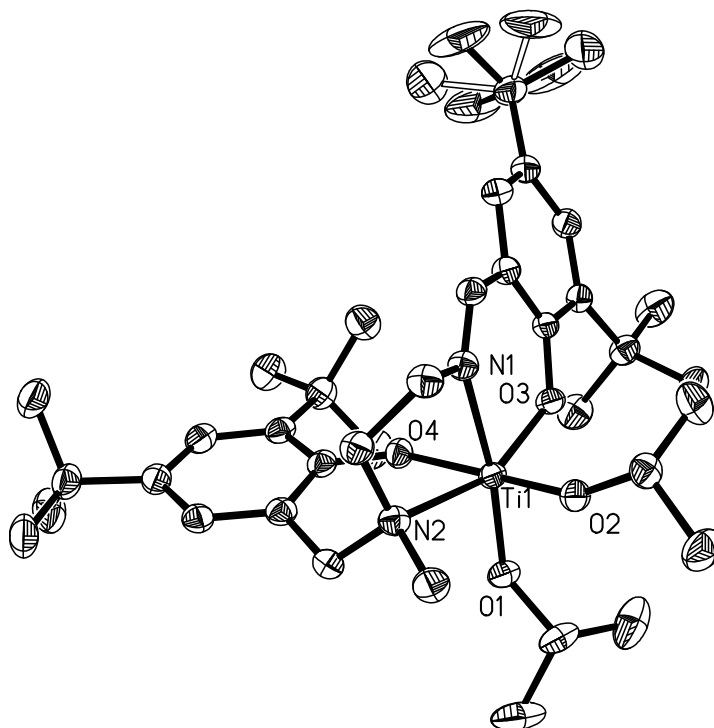
The yellow oil (0.79 g, 4.08 mmol) was dissolved in THF (30  $\text{cm}^3$ ), to which a solution of 3,5-di-*tert*-2-hydroxybenzyl bromide (1.22 g, 4.08 mmol) in THF (30  $\text{cm}^3$ ) was added. Triethylamine (0.41 g, 0.57 ml, 4.08 mmol) was added and the mixture stirred at 80 °C for three hours. The white precipitate was filtered and the solvent removed under reduced pressure. The product was isolated *via* flash chromatography ( $\text{CHCl}_3$ ) to obtain the product (0.21 g, 13 %).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 1.31 (9H, s,  $\text{C}(\text{CH}_3)_3$ ), 1.40 (9H, s,  $\text{C}(\text{CH}_3)_3$ ), 2.30 (3H, s,  $\text{CH}_3$ ), 2.41 (3H, s,  $\text{CH}_3$ ), 2.86 (2H, t  $J = 6.5$  Hz,  $\text{CH}_2$ ), 3.76 (2H, s,  $\text{CH}_2$ ), 3.79 (2H, t  $J = 6.5$  Hz,  $\text{CH}_2$ ), 6.80 (1H, t  $J = 7.5$  Hz, Ar-H), 6.85 (1H, d  $J = 2.5$  Hz, Ar-H), 7.11 (1H, d  $J = 7.5$  Hz, Ar-H), 7.20 (1H, d  $J = 7.5$  Hz, Ar-H), 7.24 (1H, d  $J = 2.5$  Hz, Ar-H), 8.37 (1H, s, CH).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ) 15.8 ( $\text{CH}_3$ ), 29.9, 30.7 ( $\text{C}(\text{CH}_3)_3$ ), 31.9, 32.0 ( $\text{C}(\text{CH}_3)_3$ ), 34.5, 35.2 ( $\text{C}(\text{CH}_3)_3$ ), 42.3 ( $\text{CH}_3$ ), 57.3, 57.8, 62.6 ( $\text{CH}_2$ ), 118.3 (Ar-C), 118.5 (Ar-CH), 121.3 (Ar-C), 123.3, 123.6 (Ar-CH), 126.2 (Ar-C), 129.4, 133.7 (Ar-CH), 136.0, 140.8 (Ar-C), 154.6, 159.6 (Ar-O), 166.8 (CH).  $m/z$  calc.  $\text{C}_{26}\text{H}_{39}\text{N}_2\text{O}_2 = 411.3012$ , found 411.2993

## Complexes

### {Ti(**1**)(O<sup>i</sup>Pr)<sub>2</sub>}

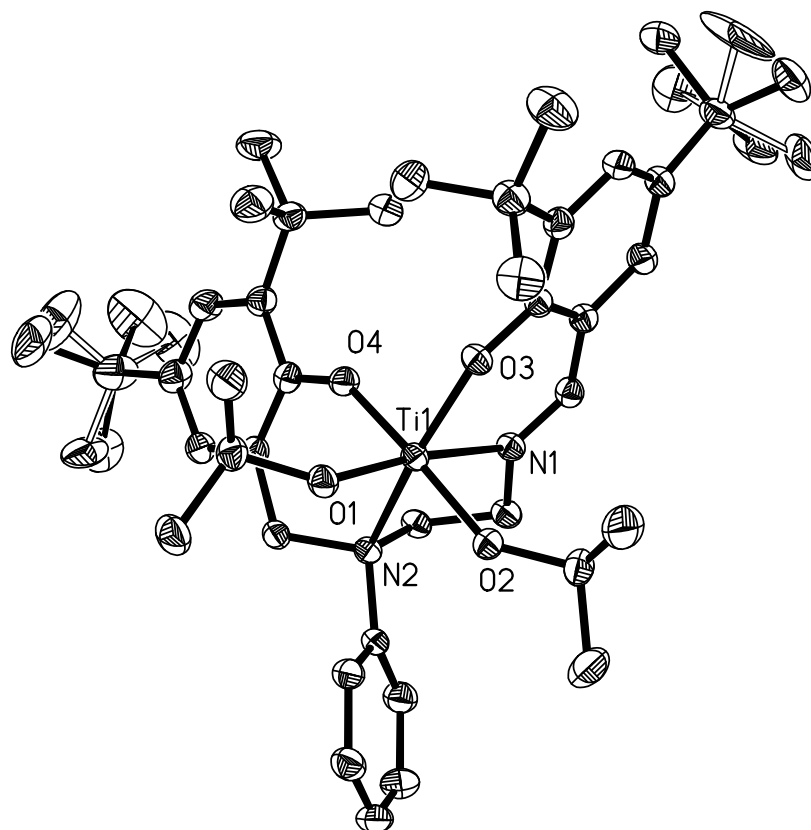
**1**H<sub>2</sub> (0.6513 g, 1.28 mmol) was dissolved in toluene (20 cm<sup>3</sup>) to which Ti(O<sup>i</sup>Pr)<sub>4</sub> (0.4 ml, 1.28 mmol) was added. This was stirred for 2 hours, after which time the solvent was removed in-vacuo and the product was recrystallized in hexane. After 5 days at – 20 °C a crop of crystals were obtained which were filtered and dried.

<sup>1</sup>H (CDCl<sub>3</sub>) 0.91 (3H, d J = 6 Hz, CH<sub>3</sub> isopropoxide), 0.97 (3H, d J = 6 Hz, CH<sub>3</sub> isopropoxide), 1.10 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 1.23 (3H, d J = 6 Hz, CH<sub>3</sub> isopropoxide), 1.27 (18H, s, C(CH<sub>3</sub>)<sub>3</sub>), 1.35 (3H, d J = 6 Hz, CH<sub>3</sub> isopropoxide), 1.52 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 2.08 – 2.87 (2H, m, CH<sub>2</sub>), 3.02 (3H, s, CH<sub>3</sub>), 3.26 – 3.38 (2H, m, CH<sub>2</sub>), 4.38 (1H, sept J = 6 Hz, CH isopropoxide), 4.46 – 4.58 (2H, m, CH<sub>2</sub>), 5.24 (1H, sept J = 6 Hz, CH isopropoxide), 6.88 (1H, d J = 2.5 Hz, Ar-H), 6.94 (1H, d J = 2.5 Hz, Ar-H), 7.14 (1H, d J = 2.5 Hz, Ar-H), 7.44 (1H, d J = 2.5 Hz, Ar-H), 7.92 (1H, s, CH). <sup>13</sup>C{<sup>1</sup>H} (CDCl<sub>3</sub>) 26.3, 26.4, 26.6, 26.9 (CH<sub>3</sub> isopropoxide), 29.9, 30.1, 31.8, 32.2 (C(CH<sub>3</sub>)<sub>3</sub>), 34.4, 35.0, 35.4, 35.7 (C(CH<sub>3</sub>)<sub>3</sub>), 52.3 (CH<sub>3</sub>), 58.6, 58.9, 66.6 (CH<sub>2</sub>), 75.1, 77.1 (CH isopropoxide), 122.3 (Ar-C), 123.5 (Ar-CH), 123.6 (Ar-C), 123.9 (Ar-CH), 127.9, 129.3 (Ar-CH), 136.5, 137.2, 137.9, 139.3 (Ar-C), 161.2, 161.6 (Ar-O), 163.0 (CH). Anal: Calc for C<sub>39</sub>H<sub>64</sub>N<sub>2</sub>O<sub>4</sub>Ti C, 69.62, H 9.59, N 4.16. Found C 68.6, H 9.79, N 4.09.



**2**H<sub>2</sub> (0.2191 g, 0.38 mmol) was dissolved in toluene (10 cm<sup>3</sup>) to which Ti(O<sup>*i*</sup>Pr)<sub>4</sub> (0.1 ml, 1.28 mmol) was added. This was stirred for 2 hours, after which time the solvent was removed in-vacuo and the product was recrystallized in hexane. After 5 days at – 20 °C a crop of crystals were obtained which were filtered and dried.

<sup>1</sup>H (CDCl<sub>3</sub>) 0.30 – 0.71 (6H, br s, CH<sub>3</sub> isopropoxide), 1.20 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 1.26 (6H, s, CH<sub>3</sub> isopropoxide), 1.28 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 1.29 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 1.52 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 3.43 (2H, t J = 5 Hz, CH<sub>2</sub>), 3.66 (2H, br s, CH<sub>2</sub>), 3.88 (1H, sept J = 6 Hz, CH isopropoxide), 4.51 (1H, sept J = 6 Hz, CH isopropoxide), 5.13 (2H, br s, CH<sub>2</sub>), 6.83 (1H, d J = 2.5 Hz, Ar-H), 6.98 (1H, d J = 2.5 Hz, Ar-H), 7.17 – 7.22 (2H, m, Ar-H), 7.40 (2H, t J = 8 Hz, Ar-H), 7.45 (1H, d J = 2.5 Hz, Ar-H), 7.92 (2H, d J = 8 Hz, Ar-H), 7.97 (1H, s, CH). <sup>13</sup>C{<sup>1</sup>H} (CDCl<sub>3</sub>) 26.9 (CH<sub>3</sub> isopropoxide), 30.0, 31.8, 32.2 (C(CH<sub>3</sub>)<sub>3</sub>), 34.4, 35.1, 35.7 (C(CH<sub>3</sub>)<sub>3</sub>), 53.1, 59.2, 69.2 (CH<sub>2</sub>), 76.6 (CH isopropoxide), 122.1 (Ar-C), 123.5, 123.9, 124.3, 125.2, 127.6, 128.8, 129.3 (Ar-CH), 136.6, 137.4, 138.1, 139.5 (Ar-C) 154.4 (C-N), 160.9, 161.8 (Ar-O), 162.8 (CH). Anal: Calc for C<sub>44</sub>H<sub>66</sub>N<sub>2</sub>O<sub>4</sub>Ti C, 71.91, H 9.05, N 3.81. Found C 71.5, H 8.92, N 3.66.

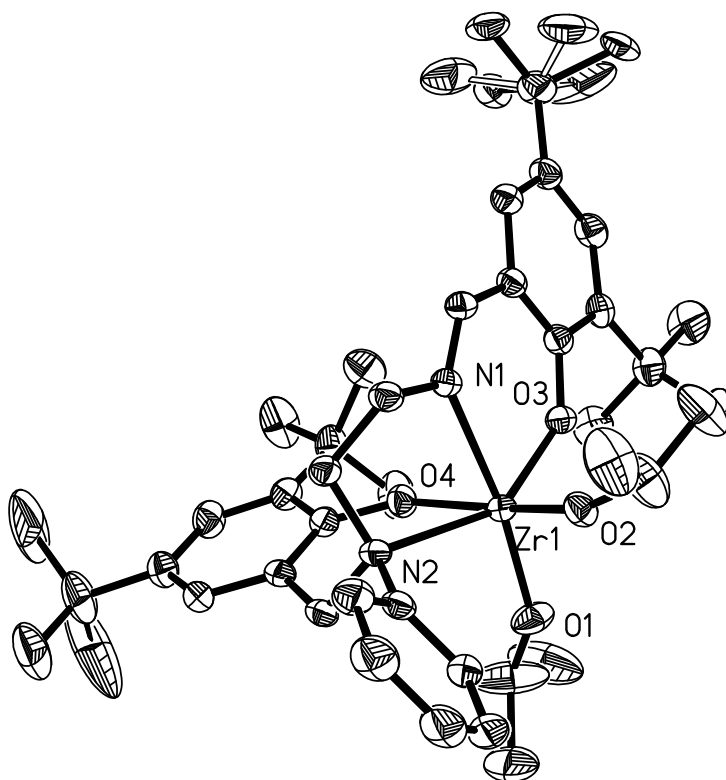


$\text{Zr}(\text{O}^i\text{Pr})_2^i\text{PrOH}$  (0.5 g, 1.28 mmol) was dissolved in toluene (20 cm<sup>3</sup>) to which  $\mathbf{1H}_2$  (0.6513 g, 1.28 mmol) was added. This was stirred for 2 hours, after which time the solvent was removed *in-vacuo* and the product was recrystallized in hexane. After 4 days at – 20 °C a crop of crystals were obtained which were filtered and dried.

$^1\text{H}$  ( $\text{CDCl}_3$ ) 0.87 (3H, d  $J$  = 6.0 Hz,  $\text{CH}_3$  isopropoxide), 1.04 (3H, d  $J$  = 6.0 Hz,  $\text{CH}_3$  isopropoxide), 1.11 (9H, s,  $\text{C}(\text{CH}_3)_3$ ), 1.22 – 1.23 (6H, m,  $\text{CH}_3$  isopropoxide), 1.26 (18H, d  $J$  = 2.5 Hz,  $\text{C}(\text{CH}_3)_3$ ), 1.51 (9H, s,  $\text{C}(\text{CH}_3)_3$ ), 2.65 – 2.74 (1H, m,  $\text{CH}_2$ ), 2.92 (3H, s,  $\text{CH}_3$ ), 3.31 (2H, d  $J$  = 13.0 Hz,  $\text{CH}_2$ ), 3.30 – 3.38 (1H, m,  $\text{CH}_2$ ), 3.56 – 3.65 (1H, m,  $\text{CH}_2$ ), 4.14 (1H, sept  $J$  = 6.0 Hz, CH isopropoxide), 4.41 (1H, sept  $J$  = 6.0 Hz, CH isopropoxide), 4.47 (1H, d  $J$  = 12.5 Hz,  $\text{CH}_2$ ), 6.85 (1H, d  $J$  = 2.5 Hz, Ar-H), 6.92 (1H, d  $J$  = 2.5 Hz, Ar-H), 7.15 (1H, d  $J$  = 2.5 Hz, Ar-H), 7.44 (1H, d  $J$  = 2.5 Hz, Ar-H), 7.92 (1H, s, CH).  $^{13}\text{C}\{^1\text{H}\}$  ( $\text{CDCl}_3$ ) 27.4, 27.7 ( $\text{CH}_3$  isopropoxide), 29.7, 30.0, 31.8, 32.2 ( $\text{C}(\text{CH}_3)_3$ ), 34.3, 35.1 ( $\text{C}(\text{CH}_3)_3$ ), 49.8 ( $\text{CH}_3$ ), 57.7, 58.2, 66.0 ( $\text{CH}_2$ ), 70.2, 70.9 (CH isopropoxide), 122.2, 123.1 (Ar-C), 124.1, 124.2, 128.4, 129.5 (Ar-CH), 136.9, 137.6, 138.6, 138.9 (Ar-C), 159.9, 160.0 (Ar-O), 165.7 (CH). Anal: Calc for  $\text{C}_{39}\text{H}_{64}\text{N}_2\text{O}_4\text{Zr}$  C, 64.41, H 9.01, N 3.91. Found C 63.4, H 8.73, N 3.76.

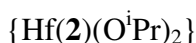
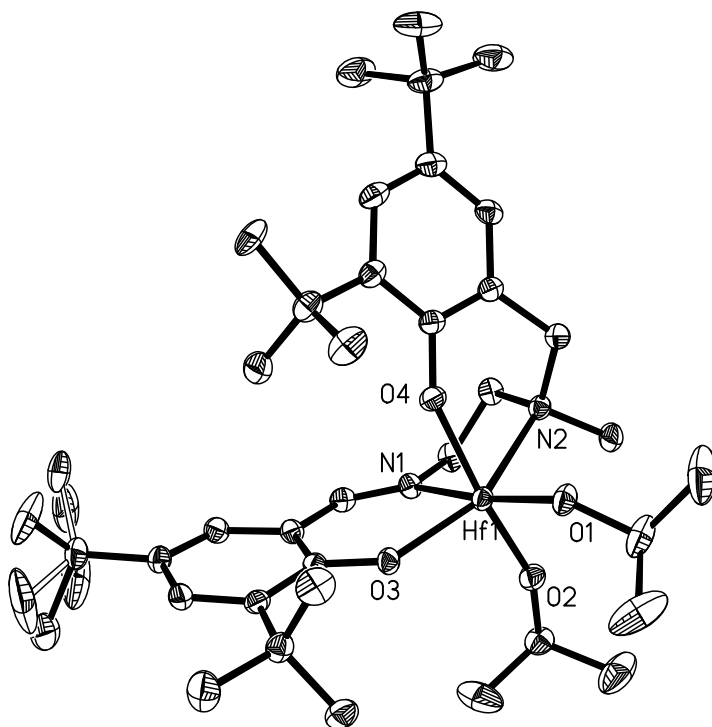






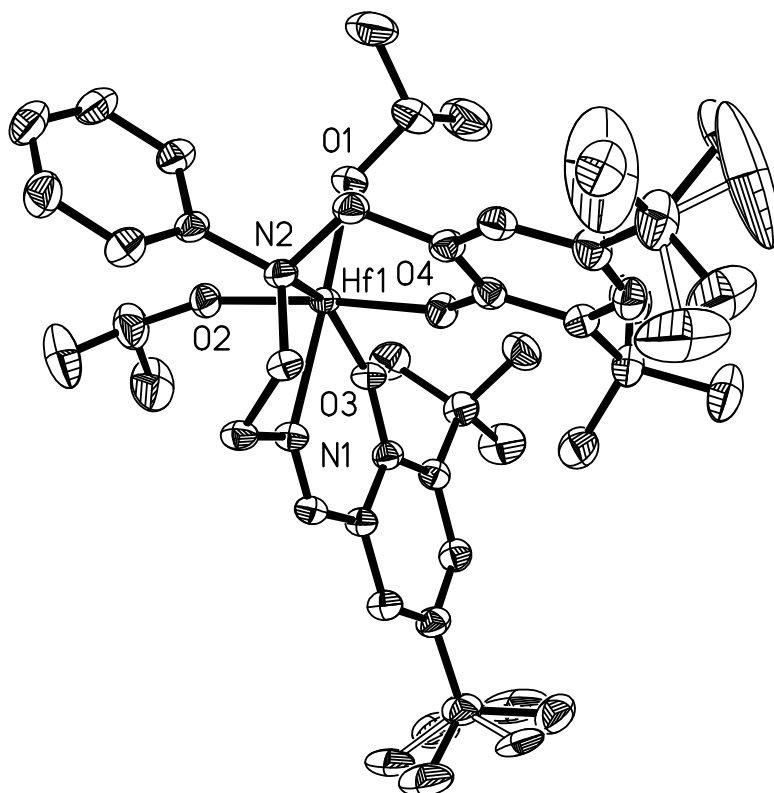
$\text{Hf}(\text{O}^i\text{Pr})_4(\text{OH}^i\text{Pr})$  (0.608 g, 1.28 mmol) was dissolved in toluene (20 cm<sup>3</sup>) to which  $\mathbf{1H}_2$  (0.5 g, 1.28 mmol) was added. This was stirred for 2 hours, after which time the solvent was removed *in-vacuo* and the product was recrystallized in hexane. After 4 days at  $-20\text{ }^\circ\text{C}$  a crop of crystals were obtained which were filtered and dried.

$^1\text{H}$  ( $\text{CDCl}_3$ ) 0.89 (3H, d  $J = 6\text{ Hz}$ ,  $\text{CH}_3$  isopropoxide), 1.04 (3H, d  $J = 6\text{ Hz}$ ,  $\text{CH}_3$  isopropoxide), 1.11 (9H, s,  $\text{C}(\text{CH}_3)_3$ ), 1.21 – 1.25 (6H, m,  $\text{CH}_3$  isopropoxide), 1.26 – 1.29 (18H, m,  $\text{C}(\text{CH}_3)_3$ ), 1.52 (9H, s,  $\text{C}(\text{CH}_3)_3$ ), 2.74 – 2.82 (1H, m,  $\text{CH}_2$ ), 2.88 – 2.94 (1H, m,  $\text{CH}_2$ ), 3.36 (2H, d  $J = 13.0\text{ Hz}$ ,  $\text{CH}_2$ ), 3.64 (1H, sept  $J = 6.0\text{ Hz}$ , CH isopropoxide), 4.20 (1H, sept  $J = 6.0\text{ Hz}$ , CH isopropoxide), 4.48 – 4.58 (2H, m,  $\text{CH}_2$ ), 6.88 (1H, d  $J = 2.5\text{ Hz}$ , Ar-H), 6.94 (1H, d  $J = 2.5\text{ Hz}$ , Ar-H), 7.20 (1H, d  $J = 2.5\text{ Hz}$ , Ar-H), 7.50 (1H, d  $J = 2.5\text{ Hz}$ , Ar-H), 7.93 (1H, s, CH).  $^{13}\text{C}\{^1\text{H}\}$  ( $\text{CDCl}_3$ ) 27.6, 27.7, 27.9, 28.0 ( $\text{CH}_3$  isopropoxide), 29.7, 30.0, 31.8, 32.2 ( $\text{C}(\text{CH}_3)_3$ ), 34.2, 34.3, 35.0, 35.6 ( $\text{C}(\text{CH}_3)_3$ ), 50.1 ( $\text{CH}_3$ ), 57.9, 58.2, 66.0 ( $\text{CH}_2$ ), 69.9, 70.6 (CH isopropoxide), 122.4, 123.0 (Ar-C), 124.0, 124.3, 128.4, 129.8 (Ar-CH), 137.4, 137.6, 139.0, 139.2 (Ar-C), 160.2, 160.4 (Ar-O), 166.1 (CH). Anal: Calc for  $\text{C}_{39}\text{H}_{64}\text{N}_2\text{O}_4\text{Hf}$  C, 58.30, H 8.03, N 3.49. Found C 57.9, H 8.03, N 3.41.



$\text{Hf}(\text{O}^i\text{Pr})_4(\text{OH}^i\text{Pr})$  (0.233 g, 0.491 mmol) was dissolved in toluene (10 cm<sup>3</sup>) to which  $2\text{H}_2$  (0.28 g, 0.491 mmol) was added. This was stirred for 2 hours, after which time the solvent was removed *in-vacuo* and the product was recrystallized in hexane. After 7 days at -20 °C, a crop of crystals were obtained which were filtered and dried.

<sup>1</sup>H (CDCl<sub>3</sub>) 0.40 (3H, d J = 6 Hz, CH<sub>3</sub> isopropoxide), 0.51 (3H, d J = 6 Hz, CH<sub>3</sub> isopropoxide), 1.17 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 1.27 (18H, d J = 5.5 Hz, C(CH<sub>3</sub>)<sub>3</sub>), 1.32 (6H, dd J = 5.5 Hz, 2.5 Hz, CH<sub>3</sub> isopropoxide), 1.52 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 3.33 (1H, sept J = 6.0 Hz, CH isopropoxide), 3.38 – 3.46 (1H, m, CH<sub>2</sub>), 3.48 – 3.60 (2H, m, CH<sub>2</sub>), 3.64 (1H, d J = 13 Hz, CH<sub>2</sub>), 3.78 – 3.88 (1H, m, CH<sub>2</sub>), 4.68 (1H, sept J = 6.0 Hz, CH isopropoxide), 5.13 (1H, d J = 12.5 Hz, CH<sub>2</sub>), 6.82 (1H, d J = 2.5 Hz, Ar-H), 6.94 (1H, d J = 2.5 Hz, Ar-H), 7.23 (2H, t J = 8.0 Hz, Ar-H), 7.44 (2H, t J = 8.0 Hz, Ar-H), 7.49 (1H, d J = 2.5 Hz, Ar-H), 7.76 (2H, d J = 8 Hz, Ar-H), 7.95 (1H, s, CH). <sup>13</sup>C{<sup>1</sup>H} (CDCl<sub>3</sub>) 26.9, 27.8 (CH<sub>3</sub> isopropoxide), 29.7, 30.0, 31.8, 32.2 (C(CH<sub>3</sub>)<sub>3</sub>), 34.3, 34.4, 35.1, 35.6 (C(CH<sub>3</sub>)<sub>3</sub>), 49.9, 58.4, 69.2 (CH<sub>2</sub>), 69.7, 70.9 (CH isopropoxide), 122.1 (Ar-C), 122.4 (Ar-CH), 123.3 (Ar-C), 124.1, 124.4, 125.7, 128.2, 129.2, 129.8 (Ar-CH), 137.5, 137.9, 139.0, 139.3, 152.6 (Ar-C), 159.9, 160.5 (Ar-O), 166.0 (CH). Anal: Calc for C<sub>44</sub>H<sub>66</sub>N<sub>2</sub>O<sub>4</sub>Hf, C 61.06, H 7.69, N 3.24. Found C 60.9, H 7.67, N 3.15.



$\{\text{Hf}(\mathbf{3})(\text{O}^i\text{Pr})_2\}$

$\text{Hf}(\text{O}^i\text{Pr})_2$  (0.61 g, 1.28 mmol) was dissolved in toluene (20 cm<sup>3</sup>) to which  $\mathbf{3H}_2$  (0.519 g, 1.28 mmol) was added. This was stirred for 2 hours, after which time the solvent was removed *in-vacuo* and the product was recrystallized in hexane. After 4 days at  $-20\text{ }^\circ\text{C}$  a crop of crystals were obtained which were filtered and dried.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 0.91 (3H, d  $J = 6\text{ Hz}$ ,  $\text{CH}_3$  isopropoxide), 0.97 (9H, s,  $\text{CH}_3$  isopropoxide), 1.04 (3H, d  $J = 6\text{ Hz}$ ,  $\text{CH}_3$  isopropoxide), 1.10 (9H, s,  $\text{CH}_3$  isopropoxide), 1.24 (18H, s,  $\text{C}(\text{CH}_3)_3$ ), 1.27 (18H, s,  $\text{C}(\text{CH}_3)_3$ ), 2.19 (3H, s,  $\text{CH}_3$ ), 2.29 (3H, s,  $\text{CH}_3$ ), 2.76 (2H, sept  $J = 4.5\text{ Hz}$ , CH isopropoxide), 2.89 – 2.94 (1H, m,  $\text{CH}_2$ ), 2.96 (3H, s,  $\text{CH}_3$ ), 3.00 – 3.14 (1H, m,  $\text{CH}_2$ ), 3.23 (1H, sept  $J = 4.5\text{ Hz}$ , CH isopropoxide), 3.29 (1H, s,  $\text{CH}_2$ ), 3.34 (3H, s,  $\text{CH}_3$ ), 3.35 (2H, s,  $\text{CH}_2$ ), 3.36 – 3.41 (2H, m,  $\text{CH}_2$ ), 3.65 – 3.73 (1H, m,  $\text{CH}_2$ ), 4.20 (1H, sept  $J = 6.0\text{ Hz}$ , CH isopropoxide), 4.42 – 4.57 (4H, m,  $\text{CH}_2$ ), 6.38 – 6.47 (2H, m, Ar-H), 6.64 (1H, t  $J = 7.5\text{ Hz}$ , Ar-H), 6.85 (2H, dd  $J = 8.0, 2.5\text{ Hz}$ , Ar-H), 6.87 (1H, s, CH), 6.99 (1H, dd  $J = 7.5, 1.5\text{ Hz}$ , Ar-H), 7.09 (1H, d  $J = 2.5\text{ Hz}$ , Ar-H), 7.13 – 7.16 (1H, m, Ar-H), 7.18 (1H, d  $J = 2.5\text{ Hz}$ , Ar-H), 7.30 – 7.34 (1H, m, Ar-H), 7.92 (1H, s, CH).

$^{13}\text{C}\{^1\text{H}\}$  ( $\text{CDCl}_3$ ) 16.6, 16.7 ( $\text{CH}_3$ ), 27.4, 27.5, 27.7, 27.9 ( $\text{CH}_3$  isopropoxide), 29.5, 29.6, 32.2 ( $\text{C}(\text{CH}_3)_3$ ), 34.2, 34.3, 34.7, 34.8 ( $\text{C}(\text{CH}_3)_3$ ), 49.9, 50.6 ( $\text{CH}_3$ ), 57.6, 57.8, 58.0, 58.1, 66.0, 66.1 ( $\text{CH}_2$ ), 69.9, 70.1, 70.4, 70.6 ( $\text{CH}$  isopropoxide), 116.5, 117.0 ( $\text{Ar-CH}$ ), 122.0, 122.2, 122.8, 123.5 ( $\text{Ar-C}$ ), 123.8, 124.0, 124.3 ( $\text{Ar-CH}$ ), 128.1, 129.6 ( $\text{Ar-C}$ ), 131.7, 132.2, 132.3, 134.6, 135.5 ( $\text{Ar-CH}$ ), 136.9, 137.1, 137.3, 137.7 ( $\text{Ar-C}$ ), 159.9, 160.3, 160.9, 161.9 ( $\text{Ar-O}$ ), 164.8, 165.1 ( $\text{CH}$ ). Anal: Calc for  $\text{C}_{32}\text{H}_{50}\text{N}_2\text{O}_4\text{Hf}$  C, 54.50, H 7.15, N 3.97. Found C 54.0, H 7.01, N 3.81

