Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Group 4 initiators for the stereoselective ROP of *rac*-β-butyrolactone and its copolymerization with *rac*-lactide

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1.1 Polymerization procedure

For solution polymerizations of *rac*-lactide the monomer:initiator ratio employed was 100:1 at a temperature of 80 °C, in all cases the solvent was toluene and 0.7 g of *rac*-lactide was used. After the reaction time, methanol was added to quench the reaction and any resulting solid dissolved in dichloromethane. The solvents were removed *in-vacuo* and the resulting solid was washed with copious amounts of methanol to remove any unreacted monomer. ^{1}H NMR spectroscopy ($CDCl_3$) 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 ^{1}H NMR spectra.

1.2 Kinetics procedure

A 0.6 ml solution of *rac*-lactide in d_8-toluene was prepared with an initial concentration of 0.578 mol dm^{-3} based on 0.05 g of *rac*-lactide in a monomer to initiator ratio of 100:1 using {Hf(**2**)O^{i}Pr}$_2$, {Hf(**4**)O^{i}Pr}$_2$, {Zr(**2**)O^{i}Pr}$_2$, {Zr(**4**)O^{i}Pr}$_2$, as the initiators. The ^{1}H NMR spectra of the sample was obtained at 80 °C over a period of 13 hours at 15 minute intervals. The relative concentrations of the monomer and polymer were determined from analysis of the ^{1}H NMR spectra and $\ln[A_o]/[A_t]$ *vs* time plotted.

1.3 Butyrolactone Polymerization

General Procedure for BBL polymerization 300:1

BBL (1.0 g, 11.6 mmol) and {Hf(**2**)O^{i}Pr}$_2$ catalyst (30 mg, 38 µmol) were dissolved in toluene (1.0 ml) and heated in a sealed vessel at 80 °C for 24 hours. The reaction was cooled to RT and quenched with MeOH (~1 ml) and CH_2Cl_2 (~5 ml). Solvent was removed and resulting solid dried under vacuum. The solid was dissolved in minimal CH_2Cl_2 and precipitated with MeOH. The precipitate was filtered and dried under vacuum.

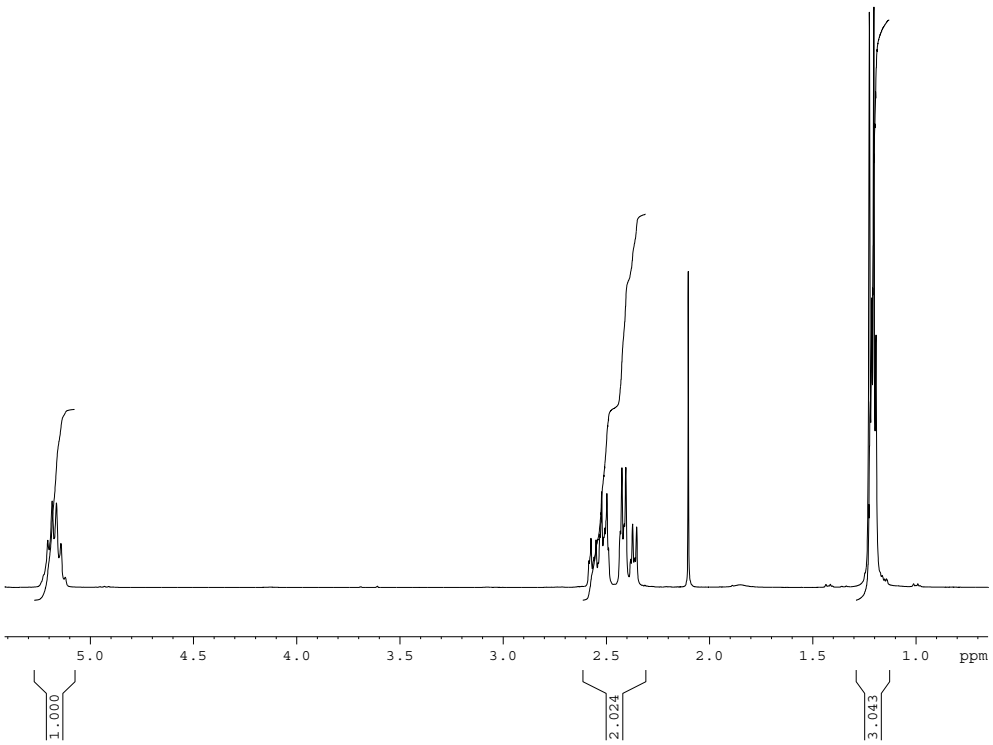


Figure 1: ^{1}H NMR (300MHz, $CDCl_3$) of PHB from {Hf(**2**)O^{i}Pr}$_2$ at 80 °C

General Procedure for copolymerization of BBL:LA 150:150:1

BBL (0.37 g, 4.3 mmol), *rac*-LA (625mg, 4.3mmol) and {Hf(**2**)O^{i}Pr}$_2$ catalyst (22 mg, 28 µmol) were dissolved in toluene (1.0 ml) and heated in a sealed vessel at 80 °C for 24 hours. The reaction was cooled to RT and quenched with MeOH (~1 ml) and CH_2Cl_2 (~5 ml). Solvent was removed and resulting solid dried under vacuum. The solid was dissolved in minimal $CH_2Cl_2$and precipitated with MeOH. The precipitate was filtered and dried under vacuum.

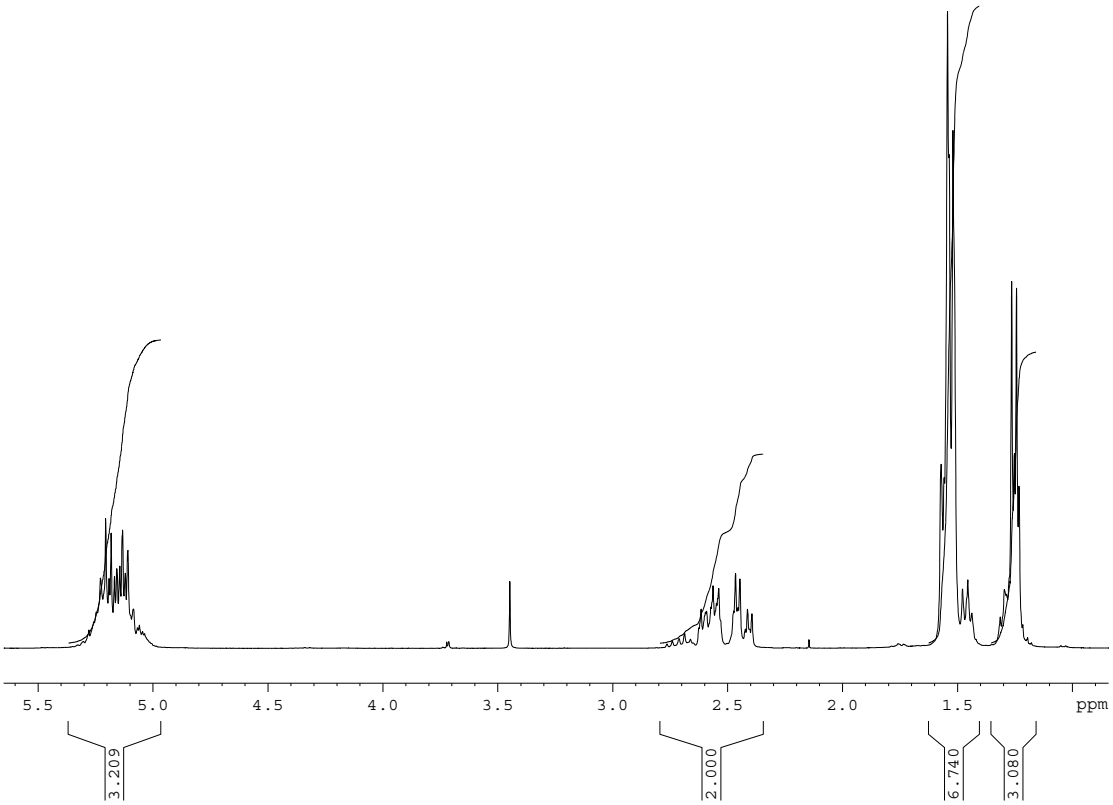


Figure 2 ^{1}H NMR (300MHz, $CDCl_3$) of PHB-*b*-PLA from {Hf(**2**)O^{i}Pr}$_2$ at 80 °C

Determination of Tacticity

The tacticity was determined by deconvolution of carbonyl signal of the $^{13}C\{^{1}H\}$ NMR spectrum (300 MHz in $CDCl_3$).

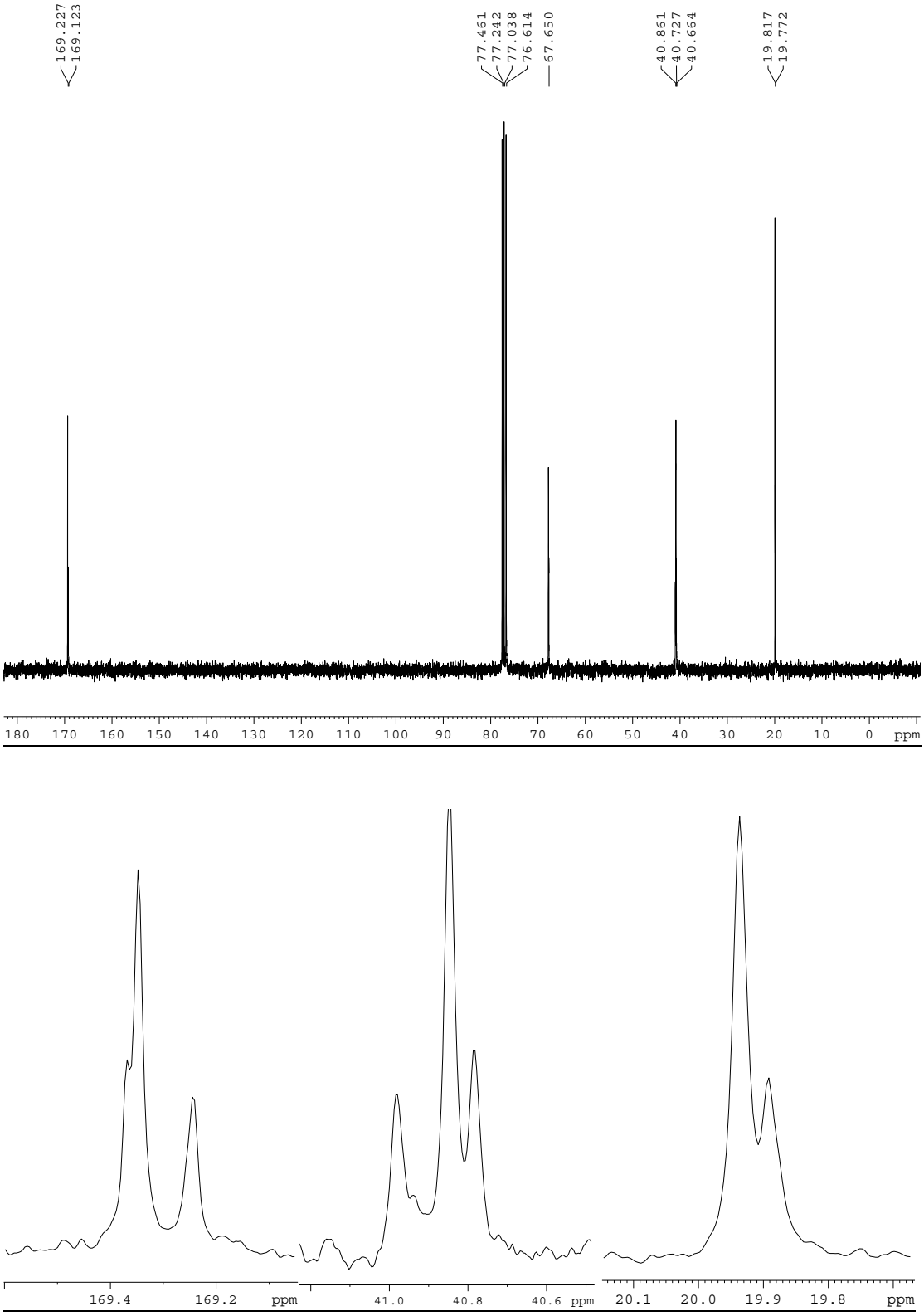


Figure 3 $^{13}C\{^{1}H\}$ NMR (300MHz, $CDCl_3$) of PHB from $\{Hf(\mathbf{2})O^{i}Pr\}_2$ at 40 °C

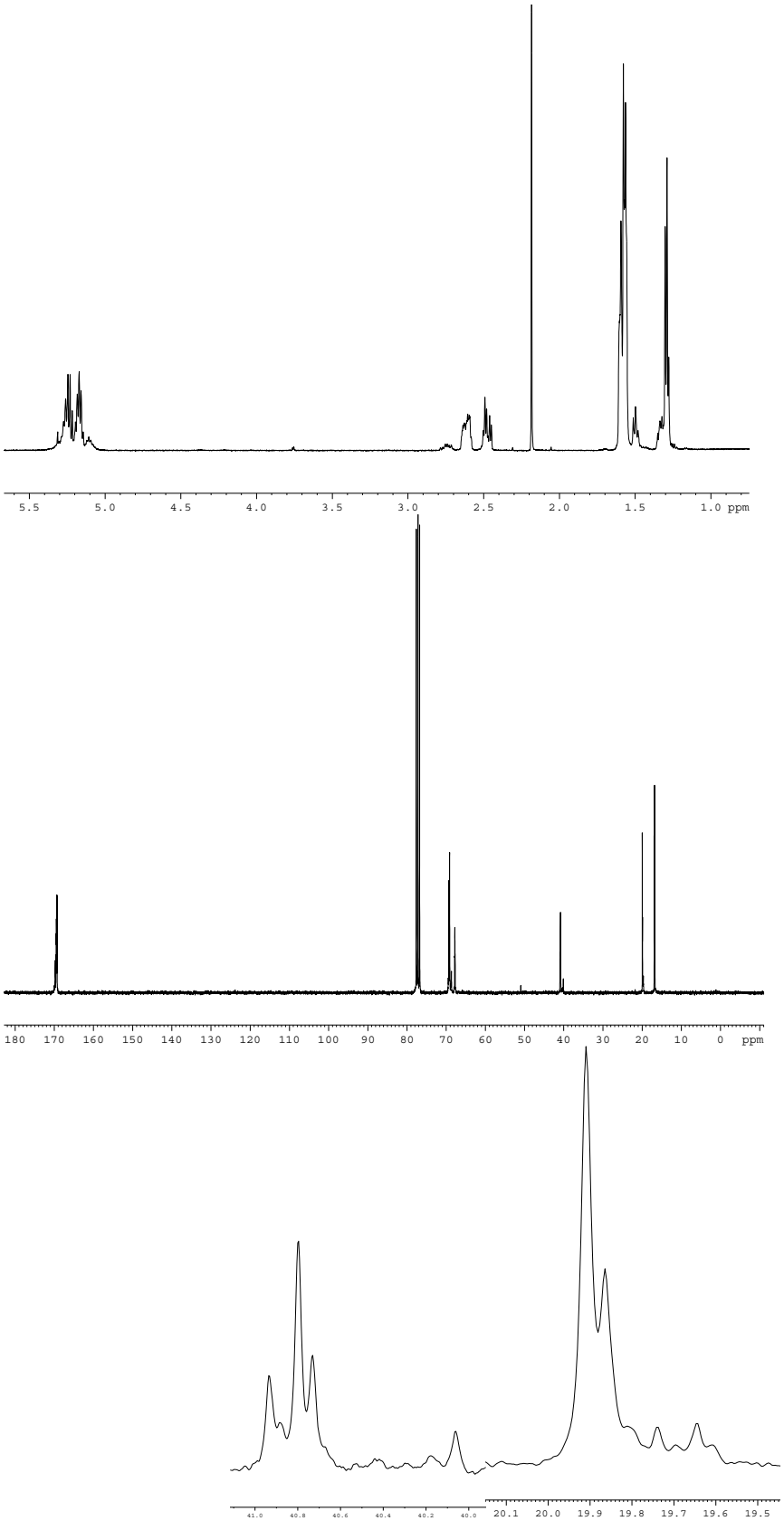


Figure 4 $^{13}C\{^{1}H\}$ and ^{1}H NMR (500MHz, $CDCl_3$) for PLA-*b*-PHB

1.4 GPC

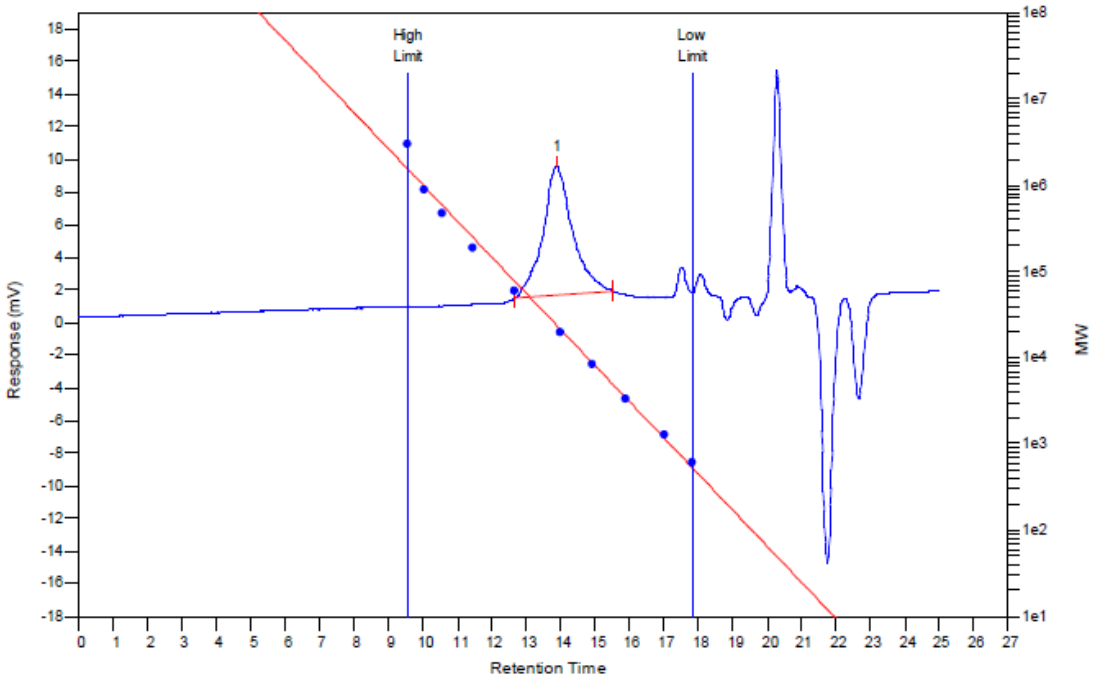
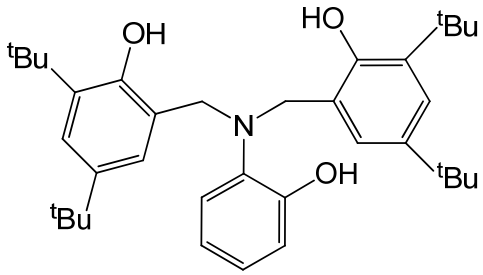


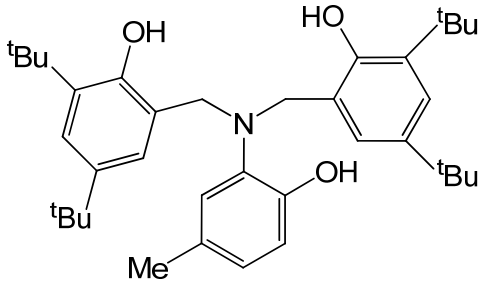
Figure 5 {Hf(**2**)O^{i}Pr}$_2$ solution polymerisation for 24 hours at 80 °C

1.5 Ligand and Complex Synthesis:



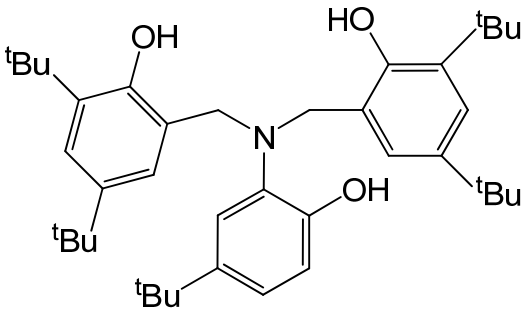
2H_3

2-hydroxyaniline (1 g, 9.16 mmol) was dissolved in THF (20 cm^3), to which a solution of 3,5-di-tert-2-hydroxybenzyl bromide (5.49 g, 18.35 mmol) in THF (20 cm^3) was added. Triethylamine (1.86 g, 3 ml, 18.35 mmol) was added and the mixture stirred at 80 °C for three hours. The precipitate was filtered and the solvent removed under reduced pressure. The product was isolated *via* flash chromatography (CH_2Cl_2) to obtain the product (3.82 g, 76 %). ^{1}H NMR ($CDCl_3$) 1.28 (18H, s, $C(CH_3)_3$), 1.40 (18H, s, $C(CH_3)_3$), 4.14 (4H, s, CH_2), 6.82 – 6.87 (2H, m, Ar-H), 6.97 (3H, d J = 2.5 Hz, Ar-H), 7.20 (2H, d J = 2.5 Hz, Ar-H) and 7.24 (1H, d J = 1.5 Hz, Ar-H) $^{13}C\{^1H\}$ NMR ($CDCl_3$) 29.8, 31.6 ($C(CH_3)_3$), 34.1, 34.6 ($C(CH_3)_3$), 56.4 (CH_2), 114.7, 116.1, 120.6 (Ar-CH), 121.8 (Ar-C), 122.1, 123.5, 125.8 (Ar-CH), 135.5, 135.6, 141.7 (Ar-C), 151.3, 152.1 (Ar-O). m/z calc. $C_{36}H_{51}NO_3^+$ 546.3947, found 546.3985



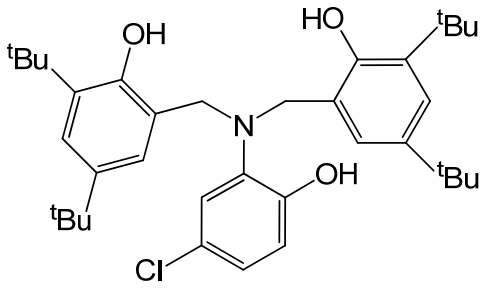
3H_3

2-amino-*p*-cresol (1 g, 8.12 mmol) was dissolved in THF (20 cm^3), to which a solution of 3,5-di-tert-2-hydroxybenzyl bromide (4.84 g, 16.17 mmol) in THF (20 cm^3) was added. Triethylamine (1.64 g, 2.5 ml, 16.17 mmol) was added and the mixture stirred at 80 °C for three hours. The precipitate was filtered and the solvent removed under reduced pressure. The product was isolated *via* flash chromatography (CH_2Cl_2) to obtain the product (3.46 g, 76 %). ^{1}H NMR ($CDCl_3$) 1.29 (18H, s, $C(CH_3)_3$), 1.40 (18H, s, $C(CH_3)_3$), 2.23 (3H, s, CH_3), 4.13 (4H, s, CH_2), 6.74 (2H, dd J = 4.5 Hz, 1.5 Hz, Ar-H), 7.00 (2H, d J = 2.5 Hz, Ar-H), 7.04 (1H, d J = 1.5 Hz, Ar-H) and 7.20 (2H, d J = 2.5 Hz, Ar-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) 20.7 (CH_3), 29.7, 31.6 ($C(CH_3)_3$), 34.1, 34.6 ($C(CH_3)_3$), 56.3 (CH_2), 114.6, 115.7, 120.7 (Ar-CH), 121.7 (Ar-C), 123.4, 125.8 (Ar-CH), 129.8, 135.2, 135.6, 141.5 (Ar-C), 148.6, 152.2 (Ar-O). m/z calc. $C_{37}H_{53}NO_3Na$ 582.3923, found 582.3913.



4H_3

2-amino-4-*tert*-butylphenol (1 g, 8.12 mmol) was dissolved in THF (20 cm^3), to which a solution of 3,5-di-tert-2-hydroxybenzyl bromide (3.62 g, 12.10 mmol) in THF (20 cm^3) was added. Triethylamine (1.23 g, 2.0 ml, 12.10 mmol) was added and the mixture stirred at 80 °C for three hours. The precipitate was filtered and the solvent removed under reduced pressure. The product was isolated *via* flash chromatography (CH_2Cl_2) to obtain the product (2.12 g, 58 %). ^{1}H NMR ($CDCl_3$) 1.28 (9H, s, $C(CH_3)_3$), 1.30 (18H, s, $C(CH_3)_3$), 1.42 (18H, s, $C(CH_3)_3$), 4.19 (4H, s, CH_2), 6.79 (1H, d J = 8.5 Hz, Ar-H), 6.99 (1H, d J = 8.5 Hz, Ar-H), 7.03 (2H, d J = 1.5 Hz, Ar-H), 7.22 (2H, d J = 1.5 Hz, Ar-H), 7.31 (1H, s, Ar-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) 29.8, 31.5, 31.6 ($C(CH_3)_3$), 34.1, 34.3, 34.6 ($C(CH_3)_3$), 56.4 (CH_2), 115.3, 119.2, (Ar-CH), 121.8 (Ar-C), 122.2, 123.5, 125.6 (Ar-CH), 134.7, 135.6, 141.5, 143.3 (Ar-C), 148.5, 152.2 (Ar-O). m/z calc. $C_{40}H_{59}NO_3^+$ = 602.4573, found 602.4620



5H_3

2-amino-4-chlorophenol (1 g, 6.97 mmol) was dissolved in THF (20 cm^3), to which a solution of 3,5-di-tert-2-hydroxybenzyl bromide (4.17 g, 13.94 mmol) in THF (20 cm^3) was added. Triethylamine (1.41 g, 2.0 ml, 13.94 mmol) was added and the mixture stirred at 80 °C for three hours. The precipitate was filtered and the solvent removed under reduced pressure. The product was isolated *via* flash chromatography (CH_2Cl_2) to obtain the product (2.30 g, 57 %).^{1}H NMR ($CDCl_3$) 1.30 (18H, s, $C(CH_3)_3$), 1.41 (18H, s, $C(CH_3)_3$), 4.12 (4H, s, CH_2), 6.76 (1H, d J = 8.5 Hz, Ar-H), 6.91 (1H, dd J = 8.5 Hz, 2.5 Hz, Ar-H), 7.01 (2H, d J = 2.5 Hz, Ar-H), 7.20 (1H, d J=2.5 Hz, Ar-H), 7.22 (2H, d J = 2.5 Hz, Ar-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) 29.7, 31.6 ($C(CH_3)_3$), 34.1, 34.6 ($C(CH_3)_3$), 56.1 (CH_2), 116.8, (Ar-CH), 121.4 (Ar-C), 122.7, 123.6 (Ar-CH), 124.9 (Ar-C), 125.3, 126.0 (Ar-CH) 135.6, 136.6, 141.8 (Ar-C), 150.0, 152.0 (Ar-O). m/z calc. $C_{36}H_{50}NO_3Cl^+$ = 580.3557, found 580.3523.

{Hf(**2**)(O^iPr)$_2$}$_2$ Hf(O^iPr)$_4$.^{i}PrOH (0.5 g, 1.05 mmol) was dissolved in toluene (20 cm^3) to which **2**H_3 (0.57 g, 1.05 mmol) was added. The solution was stirred for 2 hours, after which time the solvent was removed *in-vacuo* and the product was recrystallised in hexane. After 4 days at -20 °C a crop of crystals were obtained which were filtered and dried. ^{1}H (d_8-THF) 1.20 (36H, s, $C(CH_3)_3$), 1.38 (12H, d J = 6 Hz, CH_3 isopropoxide), 1.48 (36H, s, $C(CH_3)_3$), 3.82 (4H, br s, CH_2), 4.12 (4H, d J = 12.5 Hz, CH_2), 4.67 (2H, sept J = 6 Hz, CH isopropoxide), 6.33 (2H, dd J = 1.5 Hz, 8.0 Hz, Ar-H), 6.62 (2H, td J = 1.5 Hz, 8.0 Hz, Ar-H), 6.84 (4H, td J = 1.5 Hz, 8.0 Hz, Ar-H), 7.13 – 7.19 (6H, m, Ar-H), 7.47 (2H, dd J = 1.5 Hz, 8.0 Hz, Ar-H). $^{13}C\{^1H\}$ (d_8-THF) 28.3 (CH_3 isopropoxide), 32.2 ($C(CH_3)_3$), 34.7, 35.7 ($C(CH_3)_3$), 60.0 (CH_2), 72.4 (CH isopropoxide), 118.2, 119.0, 123.9 (Ar-CH), 125.1 (Ar-C), 126.3,

129.1, 129.7 (Ar-CH), 137.1, 140.2, 140.4 (Ar-C), 132.8, 163.0 (Ar-O). Anal: Calc for $C_{39}H_{55}NO_4Hf$ C, 60.03; H, 7.10; N, 1.79. Found: C, 60.7; H, 7.41; N, 1.69.

{Hf(**3**)O^{i}Pr}$_2$ Hf(O^{i}Pr)$_4$.^{i}PrOH (0.5 g, 1.05 mmol) was dissolved in toluene (20 cm^3) to which **3**H$_3$ (0.59 g, 1.05 mmol) was added. The solution was stirred for 2 hours, after which time the solvent was removed *in-vacuo* and the product was recrystallised in hexane. After 7 days at -20 °C a crop of crystals were obtained which were filtered and dried. ^{1}H (d$_8$-THF) 1.20 (36H, s, C(*CH$_3$*)$_3$), 1.37 (12H, d J = 6 Hz, CH$_3$ isopropoxide), 1.48 (36H, s, C(*CH$_3$*)$_3$), 2.23 (3H, s, CH$_3$), 3.84 (4H, br s, CH$_2$), 4.10 (4H, d J = 12.5 Hz, CH$_2$), 4.66 (2H, sept J = 6.0 Hz, CH isopropoxide), 6.21 (2H, d J = 8.0 Hz, Ar-H), 6.62 (2H, dd J = 2.0 Hz, 8.5 Hz, Ar-H), 6.77 – 6.95 (4H, m, Ar-H), 7.14 – 7.23 (4H, m, Ar-H), 7.28 (2H, d J = 2.0 Hz, Ar-H). ^{13}C{^{1}H} (d$_8$-THF) 20.9 (CH$_3$), 29.4 (CH$_3$ isopropoxide), 32.3 (C(*C*H$_3$)$_3$), 34.8, 35.8 (*C*(CH$_3$)$_3$), 63.8 (CH$_2$), 72.4 (CH isopropoxide), 118.6, 123.9, 124.2 (Ar-CH), 125.3 (Ar-C), 126.4, 129.7 (Ar-CH), 137.2, 139.9, 140.2 (Ar-C), 158.6, 160.7 (Ar-O). Anal: Calc for $C_{40}H_{57}NO_4Hf$ C, 60.48; H, 7.23; N, 1.76. Found: C, 59.4; H, 7.17; N, 1.74.

{Hf(**4**)O^{i}Pr}$_2$ Hf(O^{i}Pr)$_4$.^{i}PrOH (0.5 g, 1.05 mmol) was dissolved in toluene (20 cm^3) to which **4**H$_3$ (0.63 g, 1.05 mmol) was added. The solution was stirred for 2 hours, after which time the solvent was removed *in-vacuo* and the product was recrystallised in hexane. After 2 days at -20 °C a crop of crystals were obtained which were filtered and dried. ^{1}H (d$_8$-THF) 1.20 (18H, s, C(*CH$_3$*)$_3$), 1.30 (36H, s, C(*CH$_3$*)$_3$), 1.37 (12H, d J = 6 Hz, CH$_3$ isopropoxide), 1.47 (36H, s, C(*CH$_3$*)$_3$), 3.90 (4H, br s, CH$_2$), 4.11 (4H, d J = 12.5 Hz, CH$_2$), 4.66 (2H, sept J = 6 Hz, CH isopropoxide), 6.26 (2H, d J = 8.5 Hz, Ar-H), 6.90 (4H, dd J = 2.0 Hz, 8.5 Hz, Ar-H), 7.04 – 7.29 (6H, m, Ar-H), 7.46 (2H, d J = 2.0 Hz, Ar-H). ^{13}C{^{1}H} (d$_8$-THF) 26.1 (CH$_3$ isopropoxide), 32.3, 32.4 (C(*C*H$_3$)$_3$), 34.8, 35.0, 35.8 (*C*(CH$_3$)$_3$), 64.6 (CH$_2$), 72.4 (CH isopropoxide), 118.2, 120.5, 124.0 (Ar-CH), 125.3 (Ar-C), 125.9, 126.3 (Ar-CH), 135.0, 137.2, 139.5, 141.1 (Ar-C), 158.7, 160.6 (Ar-O). Anal: Calc for $C_{43}H_{63}NO_4Hf$ C, 61.74; H, 7.59; N, 1.67. Found: C, 60.3; H, 7.83; N, 1.52.

{Hf(**5**)O^{i}Pr}$_2$ Hf(O^{i}Pr)$_4$.^{i}PrOH (0.5 g, 1.05 mmol) was dissolved in toluene (20 cm^3) to which **5**H$_3$ (0.61 g, 1.05 mmol) was added. The solution was stirred for 2 hours, after which time the solvent was removed *in-vacuo* and the product was recrystallised in hexane. After 20 days at -20 °C a crop of crystals were obtained which were filtered and dried. ^{1}H (d$_8$-THF) 1.08 (12H, d J = 6 Hz, CH$_3$ isopropoxide), 1.21 (36H, s, C(*CH$_3$*)$_3$), 1.37 (12H, d J = 6 Hz, CH$_3$ isopropoxide), 1.47 (36H, s, C(*CH$_3$*)$_3$), 3.84 (4H, br s, CH$_2$), 4.11 (4H, dd J = 6.5 Hz, 12.5 Hz, CH$_2$), 4.65 (2H, sept J = 6 Hz, CH isopropoxide), 6.28 (2H, dd J = 2.5 Hz, 8.5 Hz, Ar-H), 6.84 (4H, td J = 2.5 Hz, 8.5 Hz, Ar-H), 7.15 – 7.23 (4H, m, Ar-H), 7.53 (2H, d J = 2.5 Hz, Ar-H), 7.59 (2H, d J = 2.5 Hz, Ar-H). ^{13}C{^{1}H} (d$_8$-THF) 26.1 (CH$_3$ isopropoxide), 28.2, 30.8 (*C*(CH$_3$)$_3$), 32.2, 32.3 (C(*C*H$_3$)$_3$), 34.8, 35.8 (*C*(CH$_3$)$_3$), 61.9 (CH$_2$), 72.6 (CH isopropoxide), 119.9 (Ar-CH), 122.5, 123.0 (Ar-C), 124.1, 124.9 (Ar-CH), 125.0 (Ar-C), 126.5, 129.1 (Ar-CH), 137.4, 140.5 (Ar-C), 162.1, 162.3 (Ar-O). Anal: Calc for $C_{39}H_{54}NO_4Cl_1Hf$ C, 57.49; H, 6.67; N, 1.72. Found: C, 57.6; H, 6.77; N, 1.70.

1.6 NMR of complexes

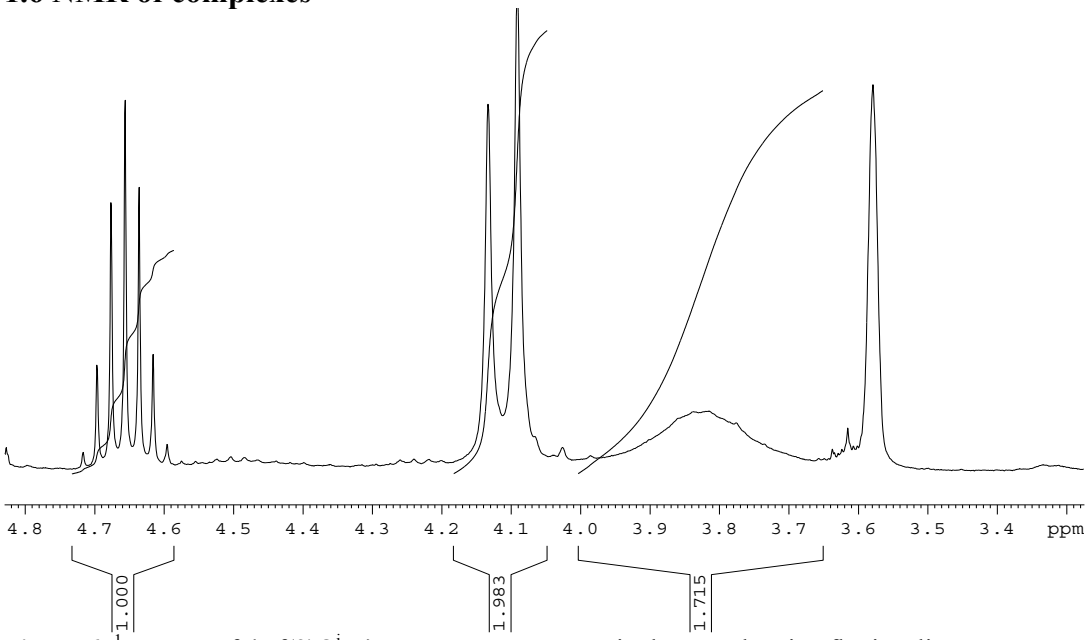


Figure 6: ^{1}H NMR of {Hf(**2**)O^{i}Pr}$_2$ at room temperature in d_8-THF showing fluxionality

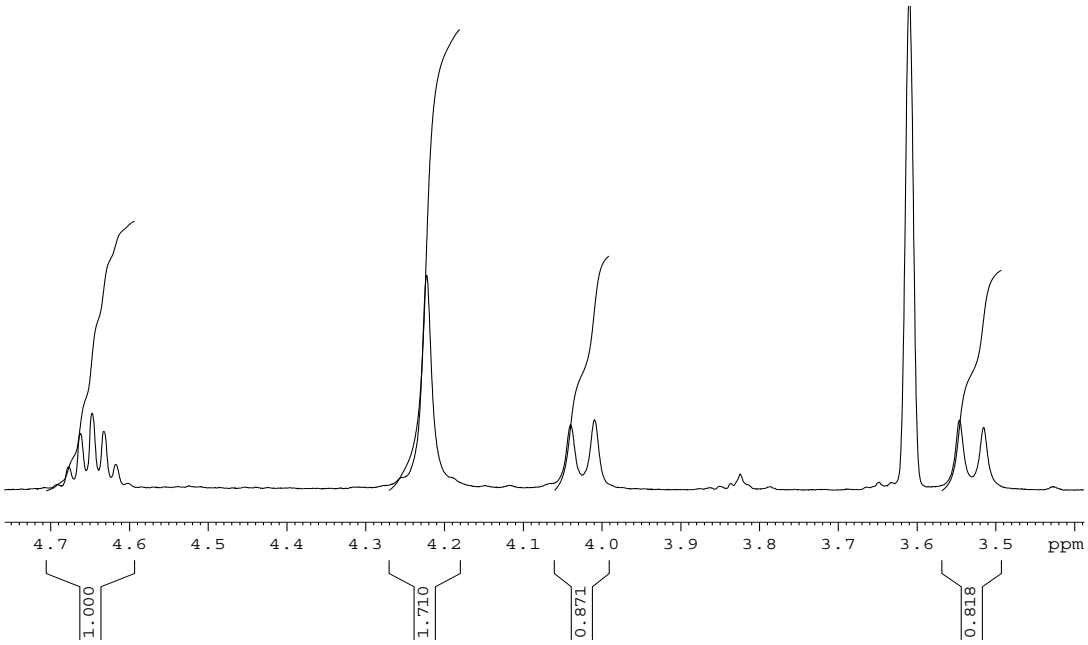


Figure 7: ^{1}H NMR of {Hf(**2**)O^{i}Pr}$_2$ at 230 K in d_8-THF showing that the complex has been isolated in its monomeric form at low temperature with the possibility of a THF molecule coordinated to the metal centre differentiating all protons of the CH_2 groups to be in equivalent.

The investigation of variable temperature shows that with the bulkier ligand with a ^{t}Bu at the para position to the oxygen on the amine phenyl ring differentiates all protons into 4 doublets at 233 K indicating the all the protons are in different environments. However, with the less steric bulky ligand with a H at the para position to the oxygen on the amine phenyl ring, at low temperature, two protons are still seen as equivalent, and the other two are inequivalent shown by a singlet and two doublets.