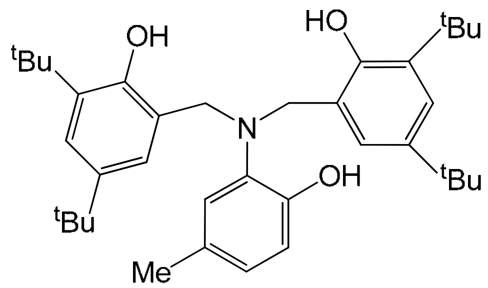
Supporting information:

Novel Ti(IV) and Zr(IV) complexes and their application in the ring opening polymerisation of cyclic esters

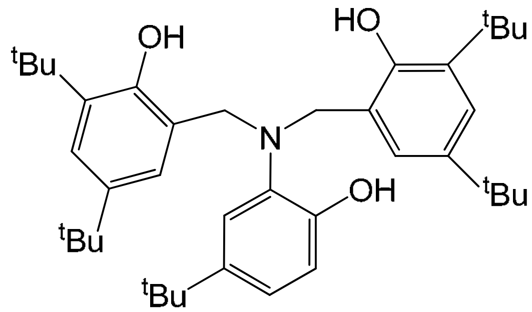
Emma Whitelaw, Matthew D. Jones,* Mary F. Mahon* and Gabriele Kociok-Kohn

1.1 Characterisation of the ligands:

$2H_3$ ^{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. $[C_{37}H_{53}NO_3+Na]^+$ 582.3923, found 582.3913.

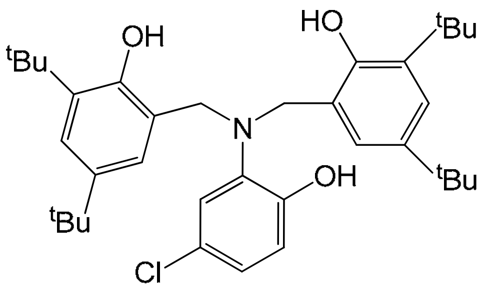


$3H_3$ ^{1}H NMR ($CDCl_3$) 1.28 (9H, s, $C(CH_3)_3$), 1.30 (18H, s, $C(CH_3)_3$), 1.42 (18H, s, $C(CH_3)_3$), 4.19 (4H, s, CH_2), 6.79 (1H, d J = 8.5 Hz, Ar-H), 6.99 (1H, d J = 8.5 Hz, Ar-H), 7.03 (2H, d J = 1.5 Hz, Ar-H), 7.22 (2H, d J = 1.5 Hz, Ar-H), 7.31 (1H, s, Ar-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) 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. $[C_{40}H_{58}NO_3+H]^+$ = 602.4573, found 602.4620



$4H_3$ ^{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)

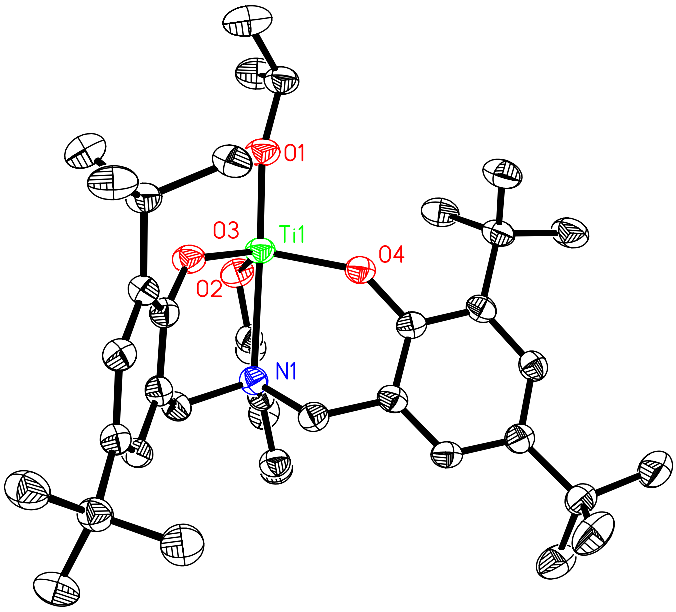
135.6, 136.6, 141.8 (Ar-C), 150.0, 152.0 (Ar-O). m/z calc. $[C_{36}H_{49}NO_3Cl+H]^+$ = 580.3557, found 580.3523



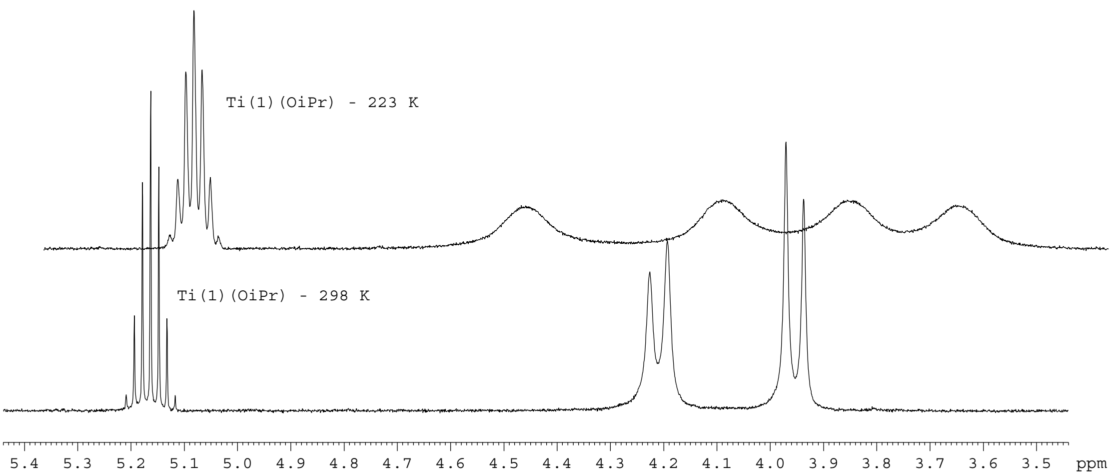
1.2 Characterisation of the Ti(IV) and Zr(IV) complexes.

The X-ray structures are shown at the 50 % probability level:

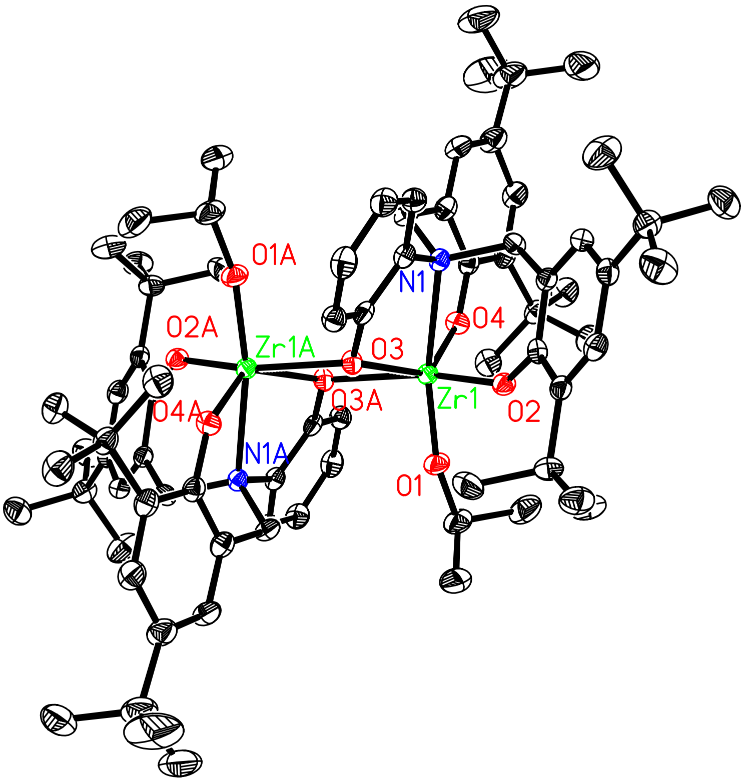
Ti(**1**)(O^{i}Pr) – see main paper for further characterisation data.



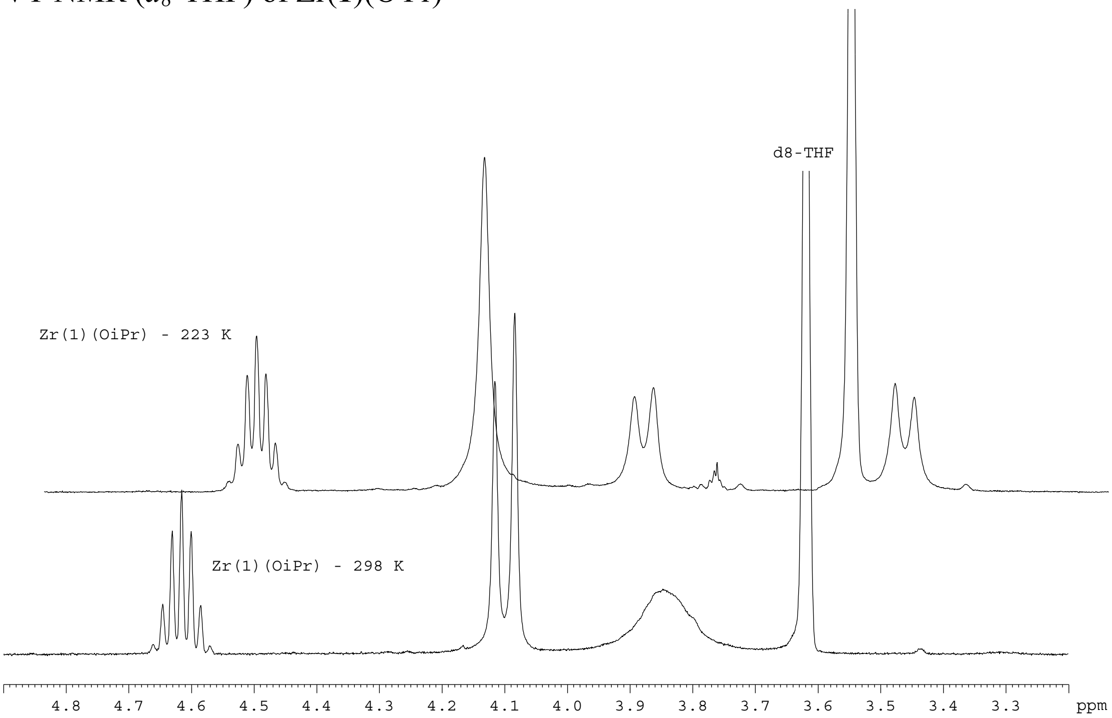
VT NMR ($CDCl_3$) of Ti(**1**)(O^{i}Pr)



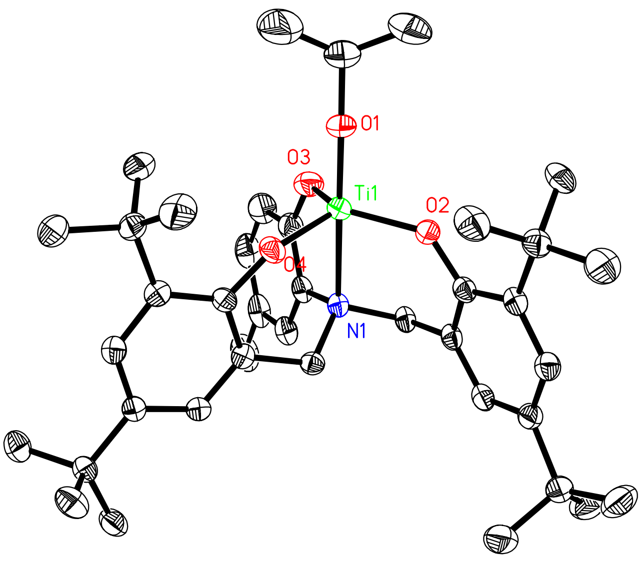
{Zr(**1**)(O^{i}Pr)}$_2$ - see main paper for further characterisation data.



VT NMR (d_8-THF) of Zr(**1**)(O^{i}Pr)



Ti(**2**)(O^{i}Pr)

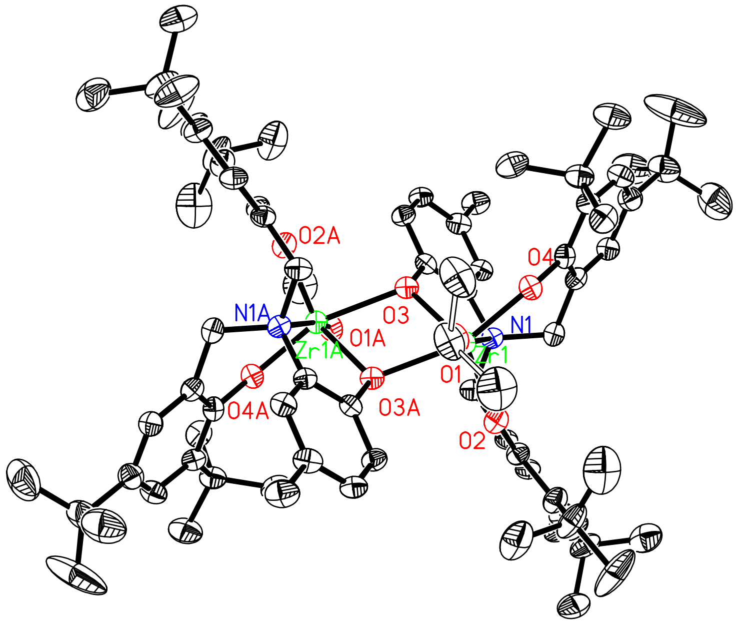


^{1}H ($CDCl_3$) 1.20 (18H, s, C(CH_3)$_3$), 1.42 (18H, s, C(CH_3)$_3$), 1.50 (6H, d J = 6 Hz, CH_3 isopropoxide), 2.21 (3H, s, CH_3), 3.91 (2H, d J = 13.5 Hz, CH_2), 4.15 (2H, d J = 13.5 Hz, CH_2), 5.11 (1H, sept J = 6 Hz, CH isopropoxide), 6.44 (1H, d J = 8.0 Hz, Ar-H), 6.80 (1H, m, Ar-H), 6.99 (3H, dd J = 12.0 Hz, 2.0 Hz Ar-H), 7.17 (2H, d J = 2.5 Hz, Ar-H).

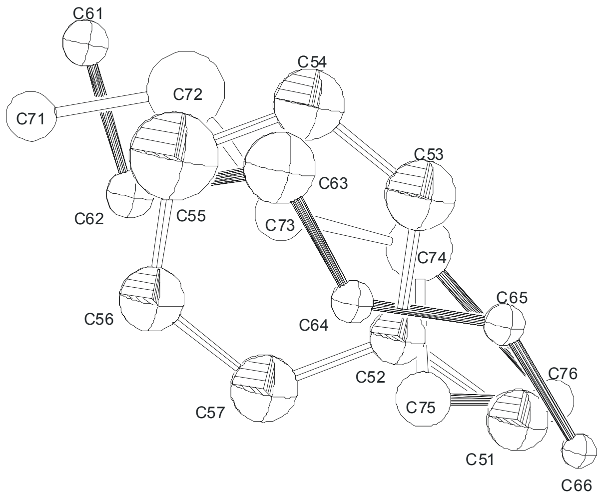
^{13}C{^{1}H} ($CDCl_3$) 20.7 (CH_3) 25.9 (CH_3 isopropoxide), 29.6, 31.6 (C(CH_3)$_3$), 34.3, 34.9 (C(CH_3)$_3$), 59.6 (CH_2), 80.2 (CH isopropoxide), 114.7, 122.3 (Ar-CH), 123.3

(Ar-C), 123.4, 124.7 (Ar-CH), 128.9 (Ar-CH), 129.2, 135.2, 137.5, 142.6 (Ar-C), 158.8, 159.1 (Ar-O). Anal: Calc for $C_{40}H_{57}NO_4Ti$ C, 72.4; H, 8.66; N, 2.11. Found: C, 70.9; H, 8.62; N, 2.26.

$\{Zr(\mathbf{2})(O^iPr)\}_2$



Disordered solvent present:



^1H (d_8-THF) 1.20 (36H, s, C(CH_3)$_3$), 1.37 (12H, d J = 6 Hz, CH_3 isopropoxide), 1.47 (36H, s, C(CH_3)$_3$), 2.21 (6H, s, CH_3), 3.81 (4H, d J = 12.5 Hz, CH_2), 4.04 (4H, d J = 12.5 Hz, CH_2), 4.56 (2H, sept J = 6 Hz, CH isopropoxide), 6.18 (2H, d J = 8.0 Hz, Ar-H), 6.63 (2H, dd J = 8.0 Hz, 2 Hz, Ar-H), 6.86 (4H, m, Ar-H), 7.13 (4H, m, Ar-H), 7.28 (2H, d J = 2H, Ar-H).

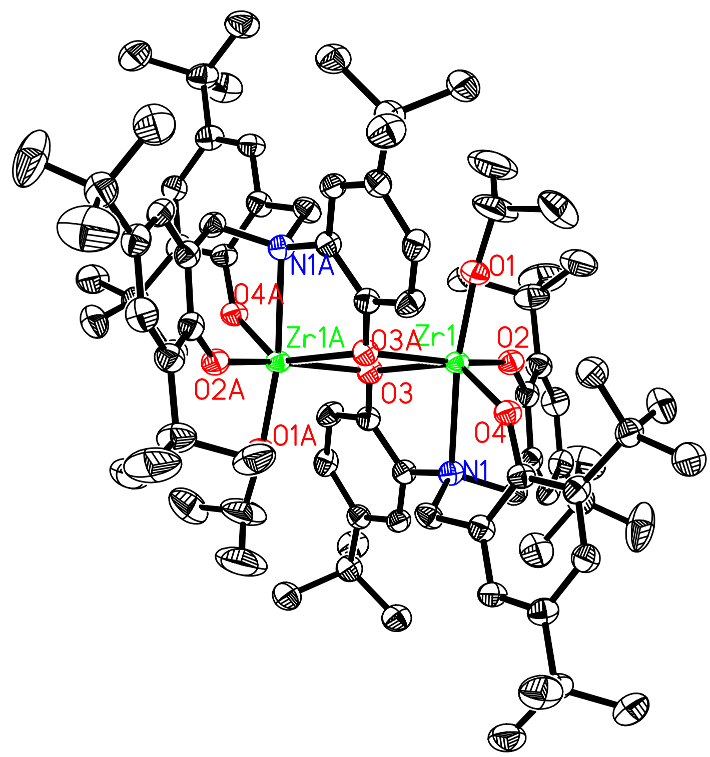
$^{13}C\{^1H\}$ (d_8-THF) 20.9 (CH_3) 28.1 (CH_3 isopropoxide), 30.6, 32.3 (C(CH_3$)_3$), 34.8, 35.9 (C(CH_3)$_3$), 61.9 (CH_2), 72.6 (CH isopropoxide), 117.7, 123.8, 124.4 (Ar-CH), 125.4, 125.9 (Ar-C), 126.6 (Ar-CH), 127.4 (Ar-C), 129.5 (Ar-CH), 136.6, 140.3 (Ar-C), 158.6, 160.4 (Ar-O).

Ti(**3**)(O^{i}Pr)

^{1}H ($CDCl_3$) 1.25 (18H, s, C(CH_3)$_3$), 1.26 (9H, s, C(CH_3)$_3$), 1.43 (18H, s, C(CH_3)$_3$), 1.51 (6H, d J = 6 Hz, CH_3 isopropoxide), 3.91 (2H, d J = 13.5 Hz, CH_2), 4.16 (2H, d J = 13.5 Hz, CH_2), 5.12 (1H, sept J = 6 Hz, CH isopropoxide), 6.46 (1H, d J = 8.5 Hz, Ar-H), 6.98 – 7.03 (3H, m, Ar-H), 7.17 (2H, d J = 2.5 Hz, Ar-H), 7.23 (1H, d J = 2.5Hz, Ar-H),

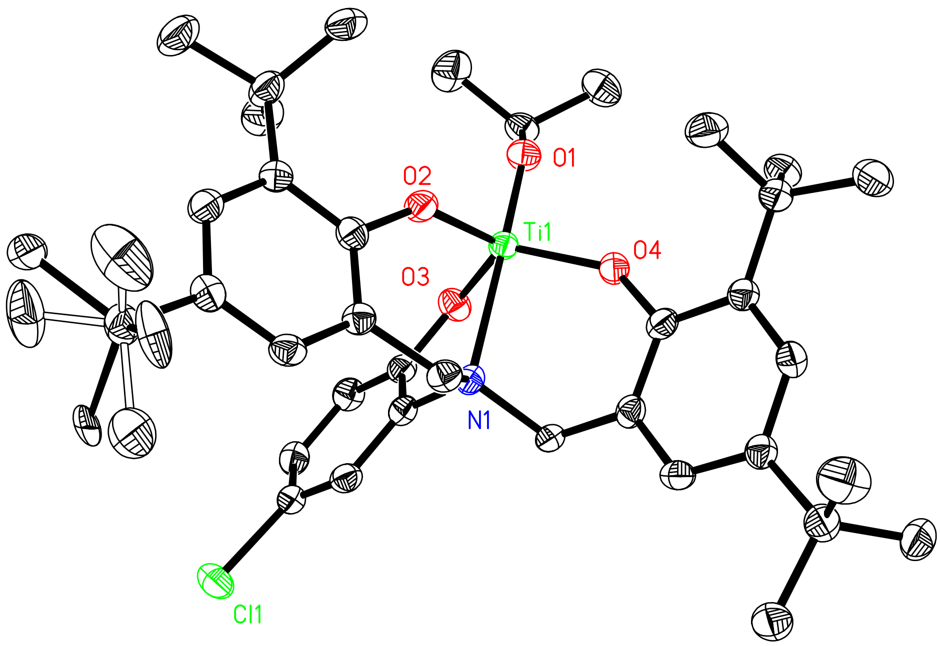
^{13}C{^{1}H} ($CDCl_3$) 25.9 (CH_3 isopropoxide), 29.6, 31.6 (C(CH$_3$)$_3$), 34.3, 34.9 (C(CH$_3$)$_3$), 59.6 (CH_2), 80.2 (CH isopropoxide), 114.2, 118.5 (Ar-CH), 123.3 (Ar-C), 123.5, 124.5, 125.0 (Ar-CH), 135.3, 137.0, 142.5, 142.8 (Ar-C), 158.7, 159.2 (Ar-O). Anal: Calc for $C_{43}H_{63}NO_4Ti$ C, 73.17; H, 9.00; N, 1.98. Found: C, 72.7; H, 8.95; N, 2.16.

{Zr(**3**)(O^{i}Pr)}$_2$



^{1}H (d_8-THF) 1.96 (36H, s, C(CH_3)$_3$), 1.29 (9H, s, C(CH_3)$_3$), 1.37 (12H, d J = 6 Hz, CH_3 isopropoxide), 1.47 (36H, s, C(CH_3)$_3$), 3.83 (4H, d J = 12.5 Hz, CH_2), 4.05 (4H, d J = 12.5 Hz, CH_2), 4.57 (2H, sept J = 6 Hz, CH isopropoxide), 6.24 (2H, d J = 8.5 Hz, Ar-H), 6.86 – 6.96 (6H, m, Ar-H), 7.14 (4H, m, Ar-H), 7.47 (2H, d J = 2H, Ar-H). ^{13}C{^{1}H} (d_8-THF) 20.9 (CH_3) 28.1 (CH_3 isopropoxide), 30.6, 32.3 (C(CH$_3$)$_3$), 34.8, 35.9 (C(CH$_3$)$_3$), 61.9 (CH_2), 72.6 (CH isopropoxide), 117.7, 123.8, 124.4 (Ar-CH), 125.4, 125.9 (Ar-C), 126.6 (Ar-CH), 127.4 (Ar-C), 129.5 (Ar-CH), 136.6, 140.3 (Ar-C), 158.6, 160.4 (Ar-O). Calc for $C_{43}H_{63}NO_4Zr$ C, 68.94; H, 8.48; N, 1.87. Found: C, 68.7; H, 9.04; N, 1.67.

Ti(**4**)(O^{i}Pr)



^{1}H ($CDCl_3$) 1.28 (18H, s, C(CH_3)$_3$), 1.44 (18H, s, C(CH_3)$_3$), 1.52 (6H, d J = 6 Hz, CH_3 isopropoxide), 2.21 (3H, s, CH_3), 3.94 (2H, d J = 13.5 Hz, CH_2), 4.14 (2H, d J = 13.5 Hz, CH_2), 5.13 (1H, sept J = 6 Hz, CH isopropoxide), 6.50 (1H, d J = 8.5 Hz, Ar-H), 6.96 – 7.01 (3H, m, Ar-H), 7.21 (3H, m, Ar-H).

^{13}C{^{1}H} ($CDCl_3$) 25.8 (CH_3 isopropoxide), 29.6, 31.6 (C(CH$_3$)$_3$), 34.3, 34.9 (C(CH$_3$)$_3$), 59.5 (CH_2), 80.7 (CH isopropoxide), 116.3, 122.4 (Ar-CH), 122.8 (Ar-C), 123.6, (Ar-CH), 124.2 (Ar-C), 124.7, 128.6 (Ar-CH) 135.2, 138.6, 143.0 (Ar-C), 159.1, 159.8 (Ar-O)

Zr(**4**)(O^{i}Pr)

^{1}H (d_8-THF) 1.21 (36H, s, C(CH_3)$_3$), 1.30 (12H, s, CH_3 isopropoxide), 1.37 (12 H, d J = 6 Hz, CH_3 isopropoxide) 1.47 (36H, s, C(CH_3)$_3$), 3.82 (4H, s, CH_2), 4.07 (4H, d J = 12.5 Hz, CH_2), 4.57 (2H, sept J = 6 Hz, CH isopropoxide), 6.26 (2H, d J = 8.5 Hz, Ar-H), 6.78 – 6.82 (2H, dd J = 8.5 Hz, 2.5 Hz, Ar-H), 6.89 – 7.00 (4H, m, Ar-H), 7.06 – 7.21 (6H, m, Ar-H), 7.54 (2H, d J = 2.5 Hz, Ar-H).

^{13}C{^{1}H} (d_8-THF) 28.0 (CH_3 isopropoxide), 30.5, 32.2 (C(CH$_3$)$_3$), 34.8, 35.8 (C(CH$_3$)$_3$), 61.9 (CH_2), 72.8 (CH isopropoxide), 119.0 (Ar-CH), 122.6 (Ar-C), 124.0, 124.8 (Ar-CH), 125.1 (Ar-C), 126.6, 129.0 (Ar-CH), 136.7, 140.6, 141.7 (Ar-C), 158.4, 161.7 (Ar-O). Calc for $C_{39}H_{54}NO_4ClZr$ C, 64.38; H, 7.48; N, 1.92. Found: C, 62.4; H, 7.44; N, 1.77.

1.3 Polymerisation procedures:

For the polymerisation of *rac*-lactide see the main paper. The table is a comparison of molecular weights from GPC and NMR.

	Mn GPC	Mn NMR
Ti(1)O^{i}Pr	12100	4860
Ti(2)O^{i}Pr	11300	7,000
Ti(3)O^{i}Pr	-	-
Ti(4)O^{i}Pr	23100	10,000
{Zr(1)(O^{i}Pr)}$_2$	26300	9000
{Zr(2)(O^{i}Pr)}$_2$	28700	9060
{Zr(3)(O^{i}Pr)}$_2$	21300	7400
{Zr(4)(O^{i}Pr)}$_2$	13100	8900

Copolymerisation of isosorbide and *rac*-lactide

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 were used. The amount of isosorbide was varied to give a 300:1:10, 300:1:20 and 300:1:30 ratio of *rac*-lactide:initiator:isosorbide. After the reaction time (120 minutes) 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 was washed with copious amounts of methanol to remove any unreacted lactide monomer and copious amounts of water to remove any unreacted isosorbide. ^{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.

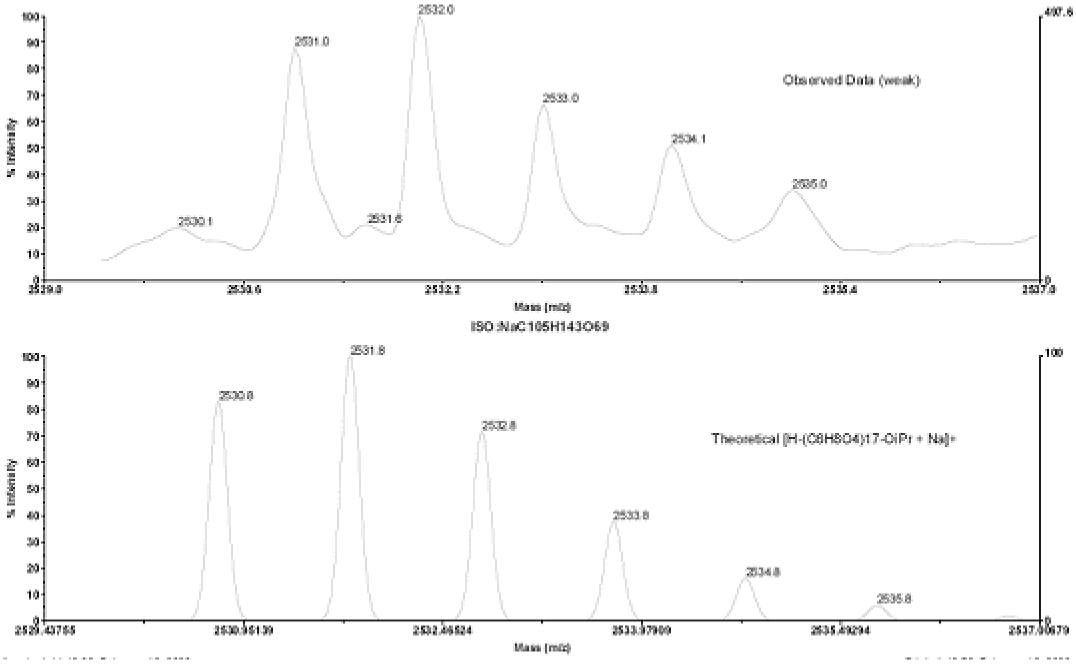
Polymerisation of 1,3-dioxan-2-one

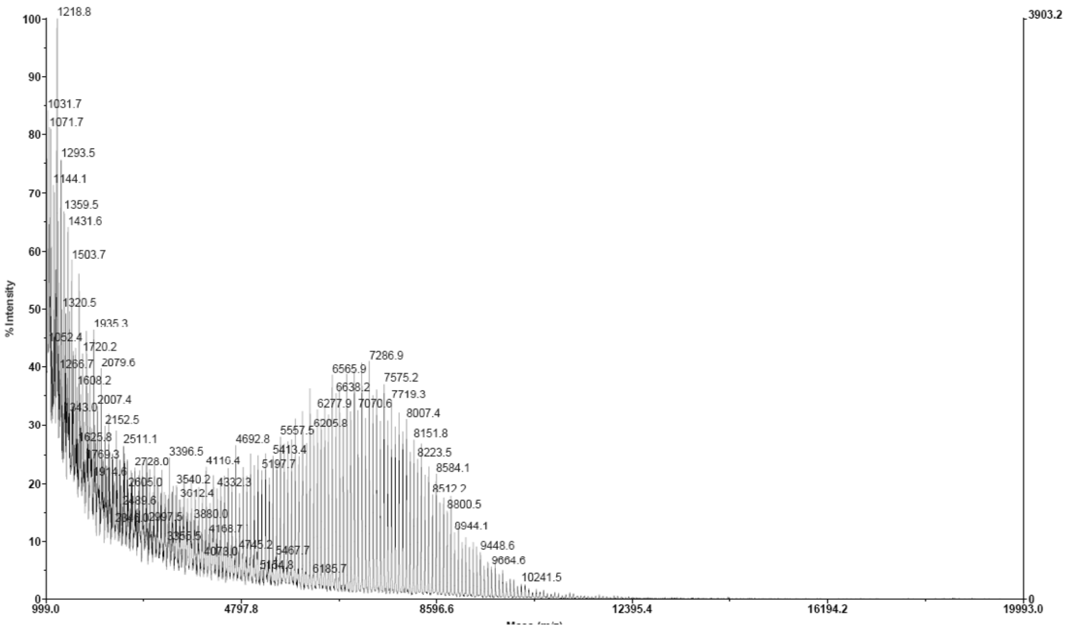
For solution polymerizations the monomer:initiator ratio employed was 100:1 at a temperature of 80 °C, in all cases 0.493 g of 1,3-dioxan-2-one were used and toluene as the solvent. After the reaction time (24 hours) the solvents were removed in vacuo and the resulting solid was washed with copious amounts of methanol to remove any unreacted monomer. GPC (THF) was used to determine molecular weights (*Mn* and *Mw*) of the polymers produced.

1.4 Selected NMR spectra and MALDI-TOF spectra of the polymers:

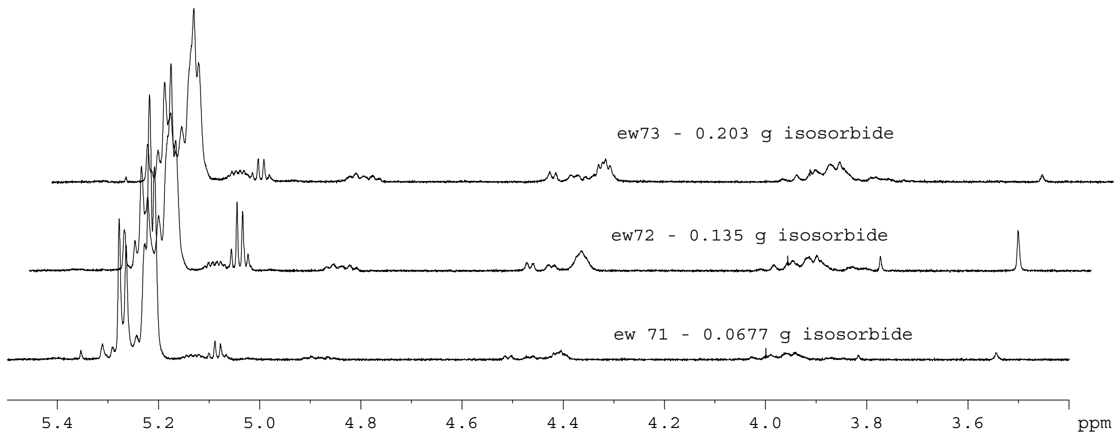
Melt polymerisation of *rac*-lactide initiated with Ti(1)(O^{i}Pr)

Indicates the presence of the isopropoxide end group

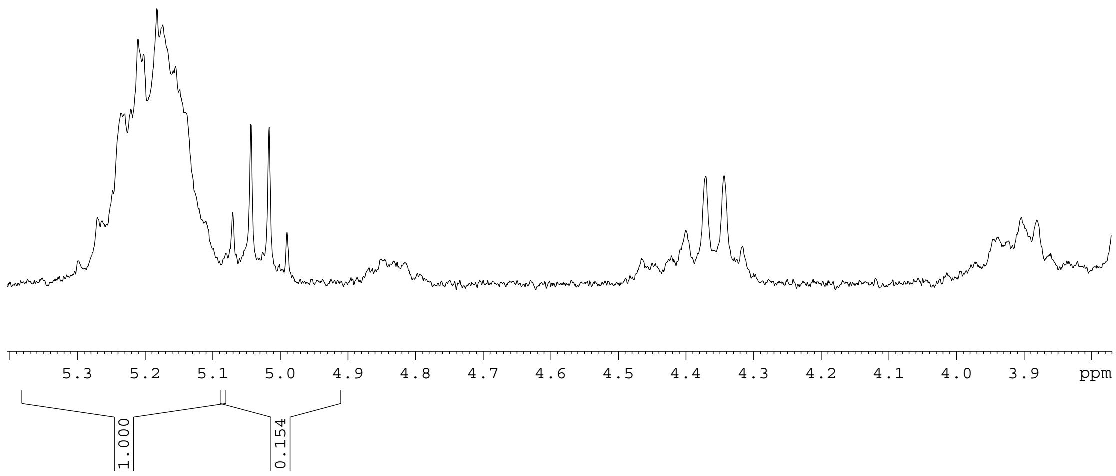




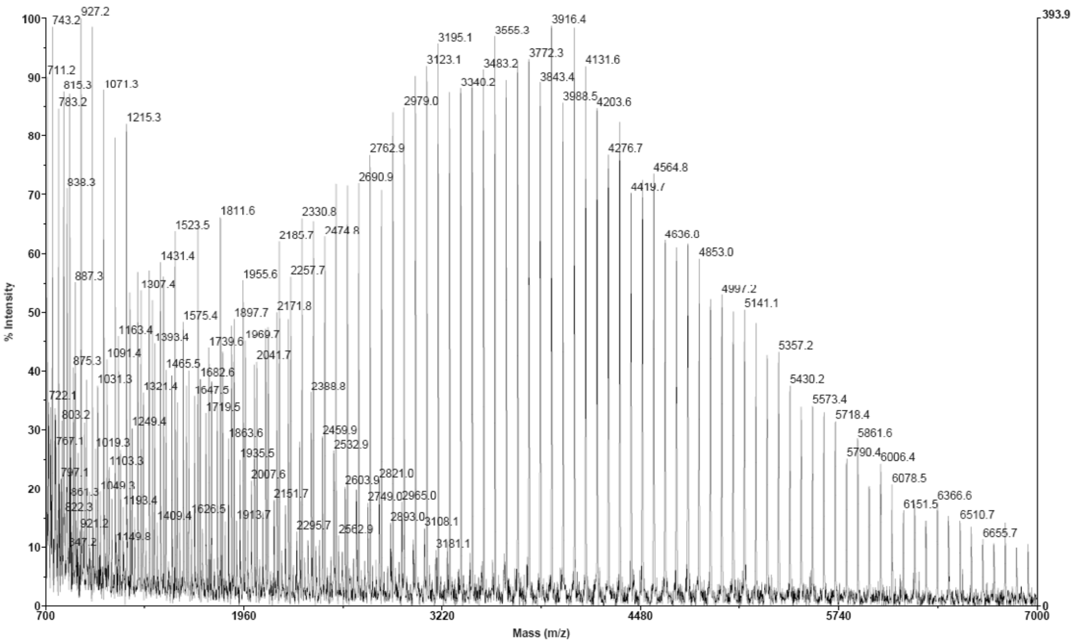
Melt polymerisation of *rac*-lactide and isosorbide initiated with Ti(**1**)O^{i}Pr, ^{1}H homonuclear decoupled NMR, with increasing amounts of isosorbide.



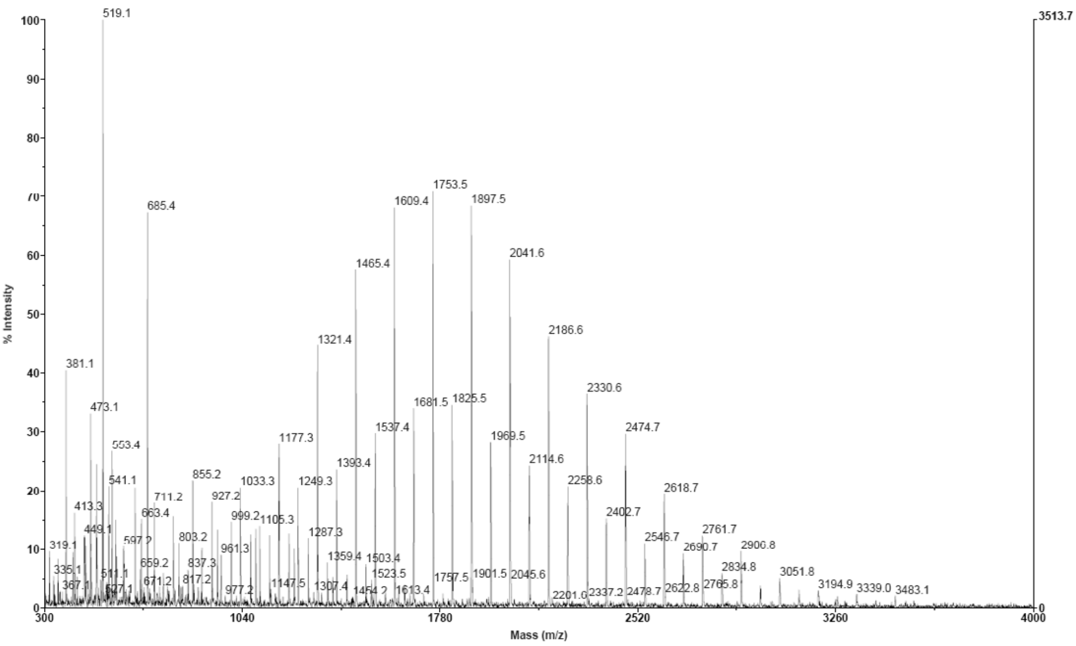
^{1}H NMR of the **MeOH soluble component** with Ti(**1**)(O^{i}Pr) 0.203 g of isosorbide (EW 73). The GPC data Mn = 1800 and PDI = 1.13. Since little unreacted lactide is observed in the washings it is unlikely that the isosorbide is coordinating to the metal centre hindering reactivity.



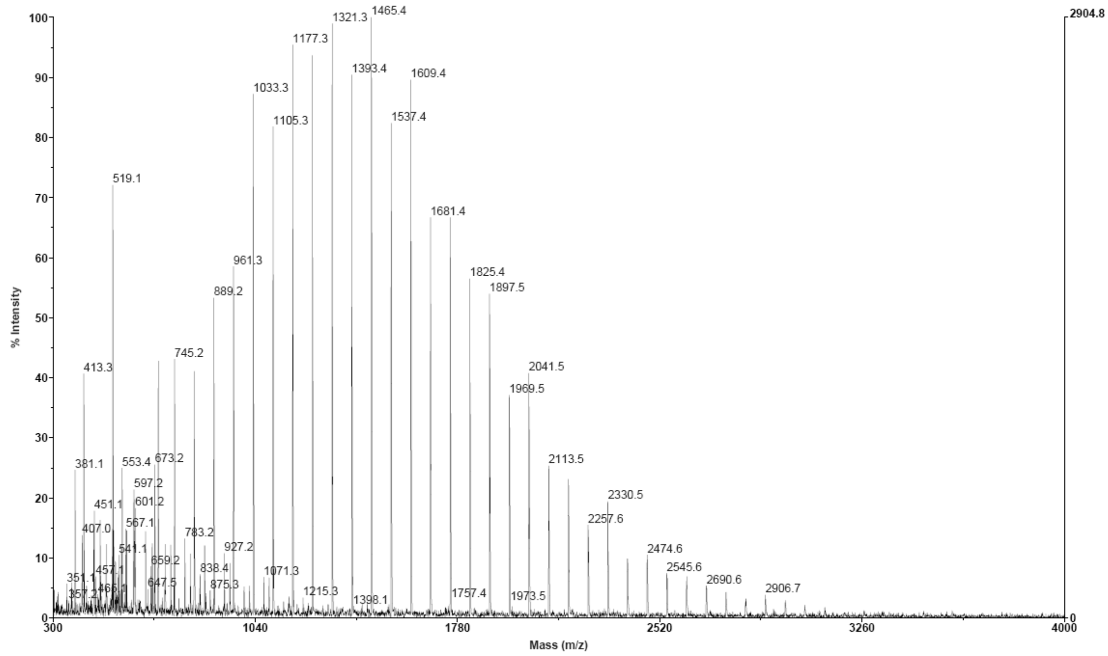
EW71


% Intensity
Mass (m/z)
700
1960
3220
4480
5740
7000
393.9

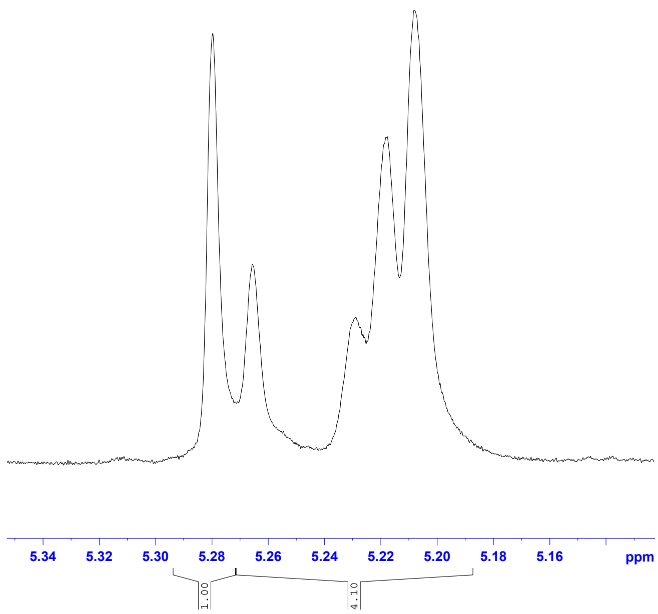
EW72


% Intensity
Mass (m/z)
300
1040
1780
2520
3260
4000
3513.7

EW73



Methine region of the [1]H homonuclear decoupled NMR of the polymer from the polymerisation of *rac*-lactide in solution for 24 hours at 80 °C using Zr-^{t}Bu catalyst



[1]H NMR analysis of the polymerisation of 1,3-dioxan-2-one