SUPPORTING INFORMATION

Crystallographic Characterisation of Ti(IV) Piperazine Complexes and their exploitation for the Ring Opening Polymerisation of *rac*-Lactide

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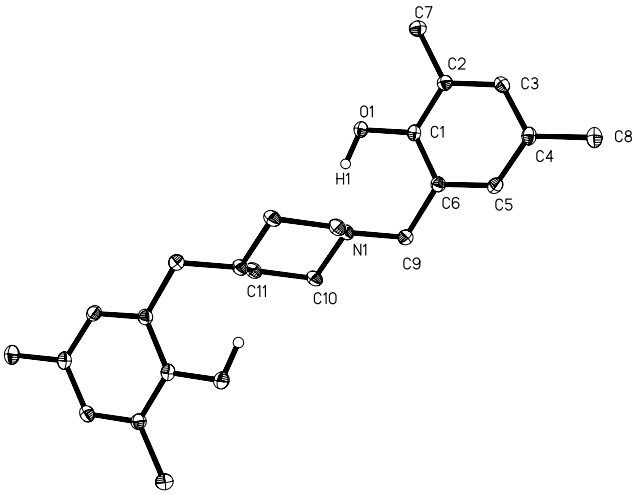
Ligand Characterisation

1H$_2$ (ellipsoids shown at the 30 % probability level) $C_{22}H_{30}N_2O_2$, M = 354.48, 0.30 × 0.30 × 0.30 mm^3, monoclinic, $P2_1/n$, a = 8.4960(3), b = 12.8830(3), c = 8.9960(3) Å, β = 102.393(2)°, V = 961.70(5) Å^3, Z = 2, D_c = 1.224 g/cm^3, F_{000} = 384, MoKα radiation, $2\theta_{max}$ = 55.1°, 17655 reflections collected, 2199 unique (R_{int} = 0.0443). Final *GooF* = 1.040, R_1 = 0.0440, wR_2 = 0.1186, R indices based on 1733 reflections with I >2sigma(I) (refinement on F^2), 124 parameters, 0 restraints.



2H$_2$. Yield = 24 % ^{1}H NMR ($CDCl_3$) δ 1.28 (18H, s, CH_3), 2.24 (6H, s, CH_3), 2.30 – 3.20 (8H, br, CH_2), 3.71 (4H, s, CH_2), 6.84 (2H, d, J = 2.0 Hz, Ar-H), 7.08 (2H, d, J = 2.0 Hz, ArH), 10.67 (2H, br, OH). $^{13}C\{^1H\}$ NMR ($CDCl_3$) 16.1 (CH_3), 31.7 (CH_3), 33.9 (C), 52.5 (CH_2), 61.8 (CH_2), 119.5 (Ar), 123.2 (Ar-H), 124.2 (Ar), 127.1 (Ar-H), 141.6 (Ar), 153.4 (Ar-O). Calc. m/z $[C_{28}H_{42}N_2O_2 + H]^+$ 439.3325. Found 439.3306.

3H$_2$ Yield = 73 %. ^{1}H NMR ($CDCl_3$) 1.28 (18H, s, CH_3), 1.42 (18H, s, CH_3), 2.10 – 3.20 (8H, br, CH_2), 3.72 (4H, s, CH_2), 6.84 (2H, d, J = 2.5 Hz , Ar-H), 7.23 (2H, d, J = 2.5 Hz, Ar-H), 10.68 (2H, br, OH). $^{13}C\{^1H\}$ NMR ($CDCl_3$) 29.7 (CH_3), 31.8 (CH_3), 34.3 (C), 35.0 (C), 52.3 (CH_2), 62.1 (CH_2), 120.4 (Ar), 123.2 (Ar-H), 123.7 (Ar-H), 135.7 (Ar), 140.9 (Ar), 154.2 (Ar-O). Calc. m/z $[C_{22}H_{30}N_2O_2 + H]^+$ 523.4263. Found 523.4366.

4H$_2$ Yield = 56 %. ^{1}H NMR ($CDCl_3$) 1.41 (18H, s, CH_3), 2.25 (6H, s, CH_3), 2.30 – 3.20 (8H, br CH_2), 3.69 (4H, s, CH_2), 6.68 (2H, s, ArH), 7.01 (2H, s, ArH), 10.68 (2H, br, OH). $^{13}C\{^1H\}$ NMR ($CDCl_3$) 20.9 (CH_3), 29.6 (CH_3), 34.7 (C), 52.2 (CH_2), 61.3 (CH_2), 121.0 (Ar), 126.9 (ArH), 127.5 (ArH), 127.1 (Ar), 136.4 (Ar), 154.2 (Ar-O). Calc. *m/z* $[C_{28}H_{42}N_2O_2 + H]^+$ 439.3325. Found 439.3308.

5H$_2$ Yield = 28 %. ^{1}H NMR ($CDCl_3$) 0.62 (6H, t, J = 7.5 Hz, CH_3), 0.64 (6H, t, J = 7.5 Hz, CH_3), 1.24 (12H, s, CH_3), 1.36 (12H, s, CH_3), 1.57 (4H, q, J = 7.5 Hz, CH_2), 1.88 (4H, q, J = 7.5 Hz, CH_2), 2.30 – 3.20 (8H, br, CH_2), 3.67 (4H, s, CH_2), 6.76 (2H, d, J = 2.0 Hz, ArH), 7.08 (2H, d, J = 2.0 Hz, ArH), 10.55 (2H, br, OH). $^{13}C\{^1H\}$ NMR ($CDCl_3$) 9.3 (CH_3), 9.7 (CH_3), 27.7 (CH_2), 28.7 (CH_3), 33.1 (CH_2), 37.3 (C), 38.5 (C), 52.2 (CH_2), 61.2 (CH_2), 120.1 (Ar), 124.3 (ArH), 125.3 (ArH), 133.9 (Ar), 139.0 (Ar), 153.9 (Ar-O). Calc. m/z $[C_{38}H_{63}N_2O_2 + H]^+$ 579.4890. Found 579.4906.

6H$_2$ Yield = 51 %. ^{1}H NMR ($CDCl_3$) 1.23 (3H, d, J = 6.5 Hz), 1.28 (9H, s, CH_3), 1.29 (9H, s, CH_3), 1.41 (18H, s, CH_3), 2.10 – 3.20 (7H, br, CH_2/CH), 3.69 (4H, m, CH_2), 6.82, (2H, br Ar-H), 7.21 (1H, d, J = 2.5 Hz, Ar-H), 7.23 (1H, d, J = 2.5 Hz, Ar-H), 10.71 (1H, br, OH), 10.82 (1H, br, OH). $^{13}C\{^1H\}$ NMR ($CDCl_3$) 25.7 (CH_3), 29.7 (CH_3), 31.8 (CH_3), 34.2 (C), 35.0 (C), 52.5 (CH_2),

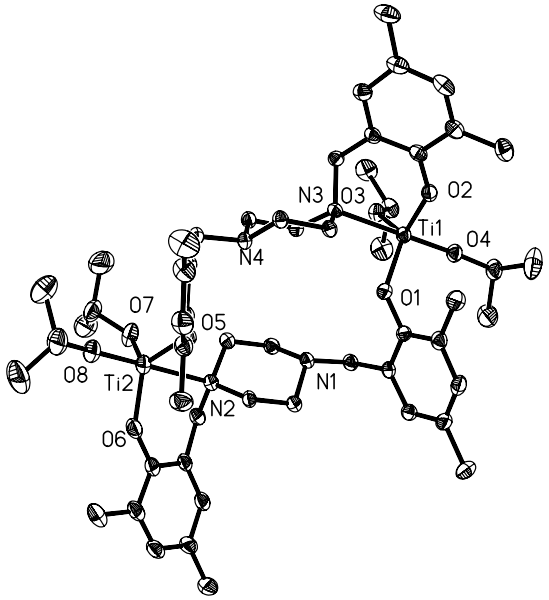
62.1 (CH_2), 120.8 (Ar), 122.9 (Ar-H), 123.0 (Ar-H), 123.5 (Ar-H), 123.6 (Ar-H), 135.6 (Ar), 135.7 (Ar), 140.9 (Ar), 140.9 (Ar), 154.1 (Ar-O). Calc. m/z [$C_{35}H_{56}N_2O_2$ + H]+ 537.4420. Found 537.4413.

7H_2 Yield = 29 %. ^{1}H NMR ($CDCl_3$) 1.21 (3H, d, J = 6.5 Hz, CH_3), 1.42 (18H, s, CH_3), 2.26 (6H, s, CH_3), 2.30 – 3.20 (7H, br, CH_2/CH), 3.30 (1H, br, CH_2), 3.65 (2H, m, CH_2), 4.27 (1H, br, CH_2), 6.68 (1H, s, Ar-H), 6.68 (1H, s, Ar-H), 7.01 (1H, d, J = 2.0 Hz, Ar-H), 7.02 (1H, d, J = 2.0 Hz, Ar-H), 10.67 (2H, br, OH). ^{13}C{^{1}H} NMR ($CDCl_3$) 20.9 (CH_3), 24.1 (CH_3), 29.5 (CH_3), 29.5 (CH_3), 34.6 (C), 34.6 (C), 52.6 (CH_2), 57.4 (CH_2), 61.7 (CH_2), 121.1 (Ar), 126.7 (Ar-H), 127.0 (Ar-H), 127.4 (Ar-H), 127.4 (Ar), 127.5 (Ar-H), 136.4 (Ar), 134.4 (Ar), 154.3 (Ar-O). Calc. *m/z* [$C_{29}H_{44}N_2O_2$ + H]$^+$ 453.3481. Found 453.3462.

8H_2 Yield = 24 %. ^{1}H NMR ($CDCl_3$) 1.28 (18H, s, CH_3), 1.42 (18H, s, CH_3), 1.91 (2H, quintet, J = 6.0 Hz, CH_2), 2.78 (4H, s, CH_2), 2.83 (4H, t, J = 6.0 Hz, CH_2), 3.77 (4H, s, CH_2), 6.84 (2H, d, J = 2.5 Hz, Ar-H), 7.23 (2H, d, J = 2.5 Hz, Ar-H), 10.68 (2H, br, OH). ^{13}C{^{1}H} NMR ($CDCl_3$) 26.9 (CH_2), 29.7 (CH_3), 31.8 (CH_3), 34.2 (C), 35.0 (C), 52.2 (CH_2), 54.6 (CH_2), 62.6 (CH_2), 121.4 (Ar), 123.1 (Ar-H), 123.6 (Ar-H), 135.8 (Ar), 140.7 (Ar), 154.4, (Ar-O). Calc. *m/z* [$C_{35}H_{56}N_2O_2$ + H]$^+$ 537.4420. Found 537.4442.

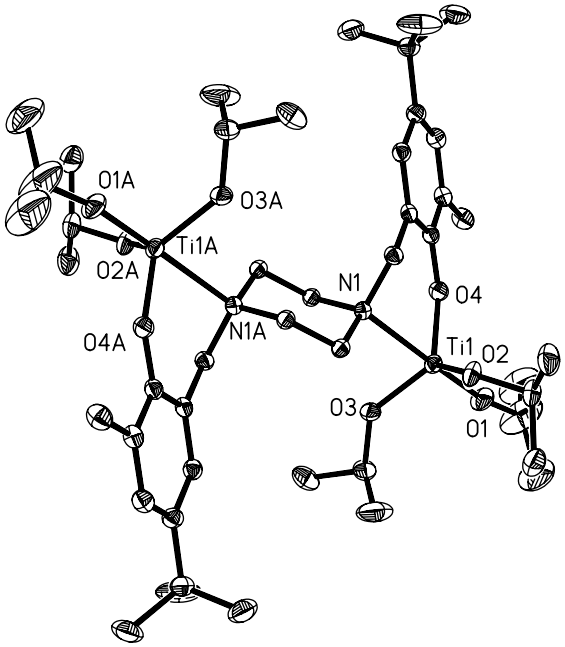
Complex Characterisation

Ti_2(**1**)$_2$(O^iPr)$_4$ All ellipsoids shown at 30% probability level.



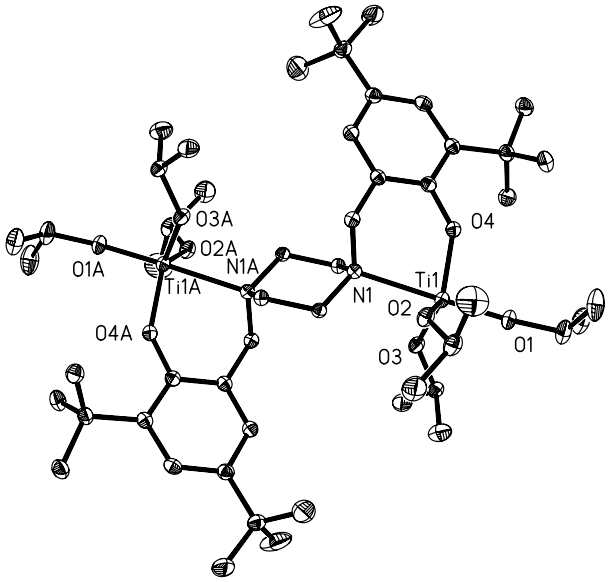
The atoms labelled with the suffix A are related by the -x+1,-y,-z+1 symmetry operation.

Ti_2(**2**)(O^iPr)$_6$ Yield = 41 %. The NMR was a mixture of Ti_2(**2**)(O^iPr)$_6$ and Ti_2(**2**)$_2$(O^iPr)$_4$ and Ti(O^iPr)$_4$ as discussed in the text. The NMRs for the individual components are: Ti_2(**2**)(O^iPr)$_6$ ^{1}H NMR ($CDCl_3$) (233 K) 1.23 (18H, s, CH_3), 1.26 (36H, d, J = 6.0 Hz, CH_3), 2.18 (6H, br, CH_3), 2.30 – 4.00 (8H, br, CH_2), 4.15 (4H, br, CH_2), 4.90 (6H, br, CH), 6.89 (2H, br, Ar-H), 7.10 (2H, br Ar-H), Ti_2(**2**)$_2$(O^iPr)$_4$ ^{1}H NMR ($CDCl_3$) (233 K) 0.85 (3H, d, J = 6.0 Hz, CH_3), 0.87 (3H, d, J = 6.0 Hz, CH_3), 0.97 (3H, d, J = 6.0 Hz, CH_3), δ 1.14 (18H, s, CH_3), 1.10 – 1.50 (15H, br, CH_3), 1.34 (18H, s, CH_3), 2.13 (3H, s CH_3), 2.20 (6H, s, CH_3), 2.26 (3H, s, CH_3), 2.30 – 4.00 (16H, br, CH_2), 4.15 (8H, m, CH_2), 4.90 (4H, br, CH), 6.70 (2H, s, Ar-H), 6.94 (2H, s, Ar-H), 7.05 (2H, s, Ar-H), 7.17 (2H, s, Ar-H). Ti(O^iPr)$_4$ ^{1}H NMR ($CDCl_3$) (233 K) 1.26 (24H, d, J = 6.0 Hz, CH_3), 4.47 (4H, sept, J = 6.0 Hz, CH). ^{13}C{^{1}H} NMR ($CDCl_3$) 17.2 (CH_3), 26.7 (CH_3), 31.8 (C), 43.3 (CH_2), 52.3 (CH_2), 77.8 (CH), 122.3 (Ar), 124.0 (Ar-H), 124.1 (Ar), 127.2 (Ar-H), 140.7 (Ar), 158.3 (Ar-O). Calc.(%) for $C_{46}H_{82}N_2O_8Ti_2$: C 62.30, H 9.32, N 3.16. Found (%); C 61.7, H 9.33, N 3.21.



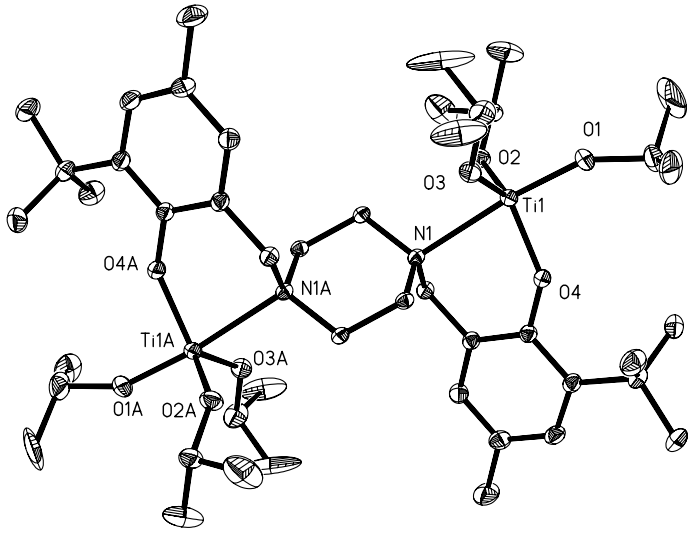
The atoms labelled with the suffix A are related by the -x+1,-y,-z+1 symmetry operation.

Ti_2(**3**)(O^iPr)$_6$ Yield = 41 %. ^{1}H NMR ($CDCl_3$) 1.27 (18H, s, CH_3), 1.30 (36H, d, J = 6.0 Hz, CH_3), 1.43 (18H, s, CH_3), 2.10 – 3.80 (8H, br, CH_2), 4.16 (4H, s, CH_2), 4.92 (6H, sept, J = 6.0 Hz, CH), 6.97 (2H, d = 2.3 Hz, Ar-H), 7.20 (2H, d = 2.3 Hz, Ar-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) 27.0 (CH_3), 29.7 (CH_3), 31.9 (CH_3), 34.3 (C), 35.1 (C), 52.2 (CH_2), 77.4 (CH), 123.2 (Ar-H), 123.7 (Ar-H), 124.5 (Ar), 135.5 (Ar), 140.1 (Ar), 154.7 (Ar-O). Calc.(%) for $C_{52}H_{94}N_2O_8Ti_2$: C 64.32, H 9.76, N 2.88. Found (%); C 63.8, H 9.76, N 2.78.



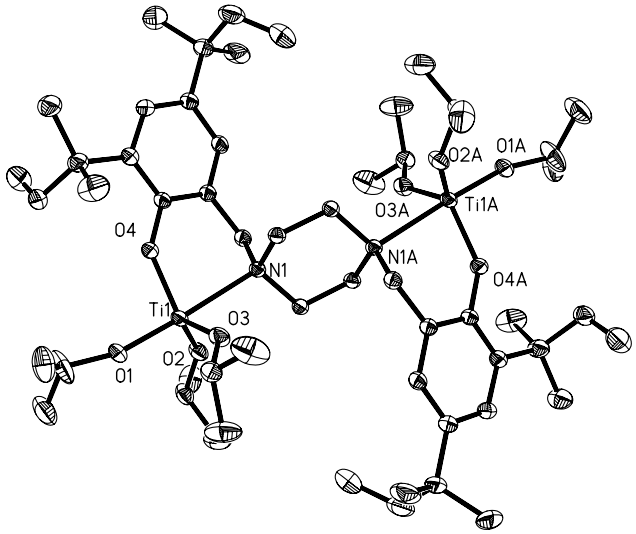
The atoms labelled with the suffix A are related by the 1-x,-y,-z+2 symmetry operation.

Ti_2(**4**)(O^iPr)$_6$ Yield = 52 %. ^{1}H NMR ($CDCl_3$) 1.31 (36H, d, J = 6.0 Hz, CH_3), 1.41 (18H, s, CH_3), 2.21 (6H, s, CH_3), 2.30 – 3.80 (8H, br, CH_2), 4.12 (4H, s, CH_2), 4.93 (6H, sept, J = 6.0 Hz, CH), 6.78 (2H, d, J = 2.0 Hz, Ar-H), 6.97 (2H, d, J = 2.0 Hz, Ar-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) 20.9 (CH_3), 27.0 (CH_3), 29.6 (CH_3), 34.8 (C), 51.9 (CH_2), 77.6 (CH), 124.3 (Ar), 126.7 (Ar), 126.9 (Ar-H), 128.3 (Ar-H), 136.2 (Ar), 158.9 (Ar-O). Calc.(%) for $C_{46}H_{82}N_2O_8Ti_2$: C 62.30, H 9.32, N 3.16. Found (%); C 61.9, H 9.28, N 3.61.



The atoms labelled with the suffix A are related by the -x+1,-y,-z symmetry operation.

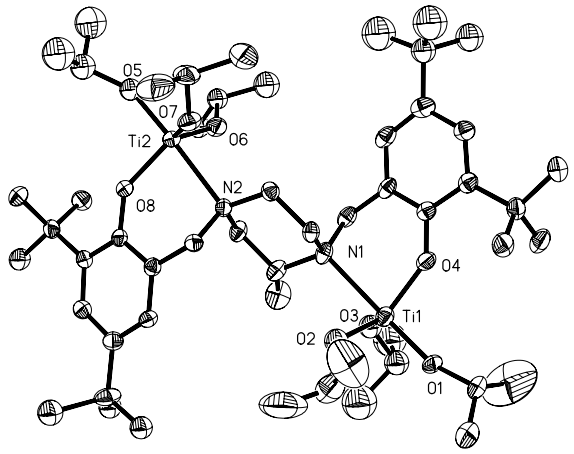
Ti_2(**5**)(O^iPr)$_6$ Yield = 20 %. ^{1}H NMR ($CDCl_3$) 0.61 (12H, m, CH_3), 1.20 – 1.25 (12H, m, CH_3), 1.28 (36H, d, J = 6.0 Hz, CH_3), 1.35 (12H, s, CH_3), 1.54 (4H, m, CH_2), 1.96 (4H, m, CH_2), 2.20 – 2.80 (4H, br, CH_2), 3.30 – 3.80 (4H, br, CH_2), 4.10 (4H, s, CH_2), 4.90 (6H, sept, J = 6.0 Hz, CH), 6.88 (2H, d, J = 2.0 Hz, Ar-H), 7.04 (2H, d, J = 2.0 Hz, Ar-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) 9.28 (CH_3), 9.81 (CH_3), 26.7 (CH_3), 26.8 (CH_3), 27.0 (CH_3), 27.8 (CH_2), 28.8 (CH_3), 32.8 (CH_2), 37.3 (C), 38.6 (C), 43.7 (CH_2), 77.5 (CH), 123.4 (Ar), 125.2 (Ar-H), 125.3 (Ar-H), 133.7 (Ar), 138.1 (Ar), 158.9 (Ar-O). Calc.(%) for $C_{56}H_{102}N_2O_8Ti_2$: (%); C 65.48, H 10.01, N 2.73. Found CHN (%); C 64.2, H 9.98, N 3.02.



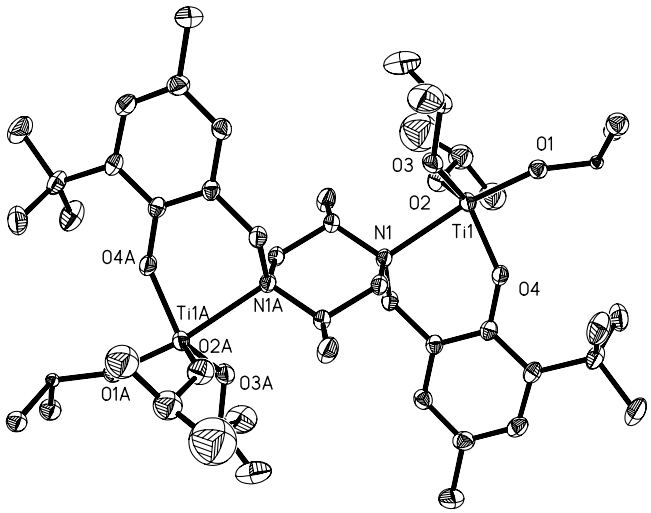
The atoms labelled with the suffix A are related by the -x,-y+1,-z+2 symmetry operation.

Ti_2(**6**)(O^iPr)$_6$ Yield = 65 %. ^{1}H NMR ($CDCl_3$, 233 K) 0.97 (3H, d, J = 6.0 hzCH_3), 1.25 (9H, br, CH_3), 1.28 (36H, d, J = 6.0 Hz, CH_3), 1.31 (9H, br, CH_3), 1.41 (9H, s, CH_3), 1.42 (9H, s, CH_3), 2.40 – 3.70 (7H, br, CH_2), 3.95 (2H, br, CH_2), 4.12 (2H, m, CH_2), 4.80 (3H, sept, J = 6.0 Hz, CH), 4.89 (3H, sept, J = 6.0 Hz, CH), 6.90 (1H, d, J = 2.5 Hz, Ar-H), 7.14 (1H, d, J = 2.5 Hz, Ar-H), 7.18 (2H, br, Ar-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) 26.7 (CH_3), 26.8 (CH_3), 26.8 (CH_3), 26.9 (CH_3), 26.9 (CH_3), 29.7 (C), 29.8 (C), 31.8 (CH_3), 34.3 (C), 34.4 (C), 35.1 (CH_2), 76.5 (CH), 77.4 (CH), 77.8 (CH), 122.0 (Ar-H), 123.1 (Ar-H), 123.6 (Ar-H), 123.9 (Ar), 124.4 (Ar-H), 135.5 (Ar), 135.7 (Ar),

140.0 (Ar), 141.0 (Ar), 158.9 (Ar-O). Calc.(%) for $C_{53}H_{96}N_2O_8Ti_2$; C 64.62, H 9.82, N 2.84. Found (%); C 64.0, H 9.48, N 3.04

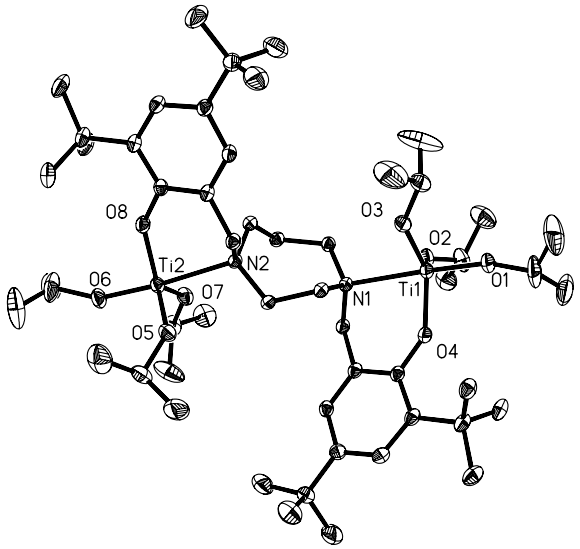


Ti_2(**7**)(O^iPr)$_6$ Yield = 58 %. ^{1}H NMR ($CDCl_3$) 1.07 (3H, d, J = 6.5, CH_3), 1.31 (18H, d, J = 6.0 Hz, CH_3), 1.33 (18H, d, J = 6.0 Hz, CH_3), 1.44 (9H, s, CH_3), 1.45 (9H, s, CH_3), 2.23 (3H, s, CH_3), 2.25 (3H, s, CH_3), 2.48 (1H, br, CH_2), 2.52 (1H, br, CH_2), 2.66, (1H, br, CH_2), 3.04 (1H, m, CH_2), 3.34 (1H, m, CH_2), 3.38 (1H, m, CH_2), 3.55 (1H, br, CH_2) 3.94 (2H, s, CH_2), 4.09 (2H, m, CH_2), 4.83 (3H, sept, J = 6.0 Hz, CH), 4.92 (3H, sept, J = 6.0 Hz, CH), 6.72 (1H, s, Ar-H), 6.95 (1H, s, Ar-H), 6.98 (1H, s, Ar-H), 7.01 (1H, s, Ar-H). ^{13}C{^{1}H} NMR ($CDCl_3$) 17.9 (CH_3), 21.0 (CH_3), 21.1 (CH_3), 26.8 (CH_3), 26.9 (CH_3), 29.7 (C), 30.0 (C), 34.8 (CH_2), 44.9 (CH_2), 49.5 (CH), 50.2 (CH_2), 53.4 (CH_2), 77.5 (CH), 77.9 (CH), 124.4 (Ar), 125.7 (Ar-H), 126.5 (Ar), 126.7 (Ar-H), 127.6 (Ar-H), 127.6 (Ar), 128.2 (Ar-H), 136.2 (Ar), 136.5 (Ar), 159.1 (Ar-O), 159.7 (Ar-O). Calc.(%) for $C_{47}H_{84}N_2O_8Ti_2$; C 62.66, H 9.40, N 3.11. Found (%); C 61.0, H 9.00, N 3.03



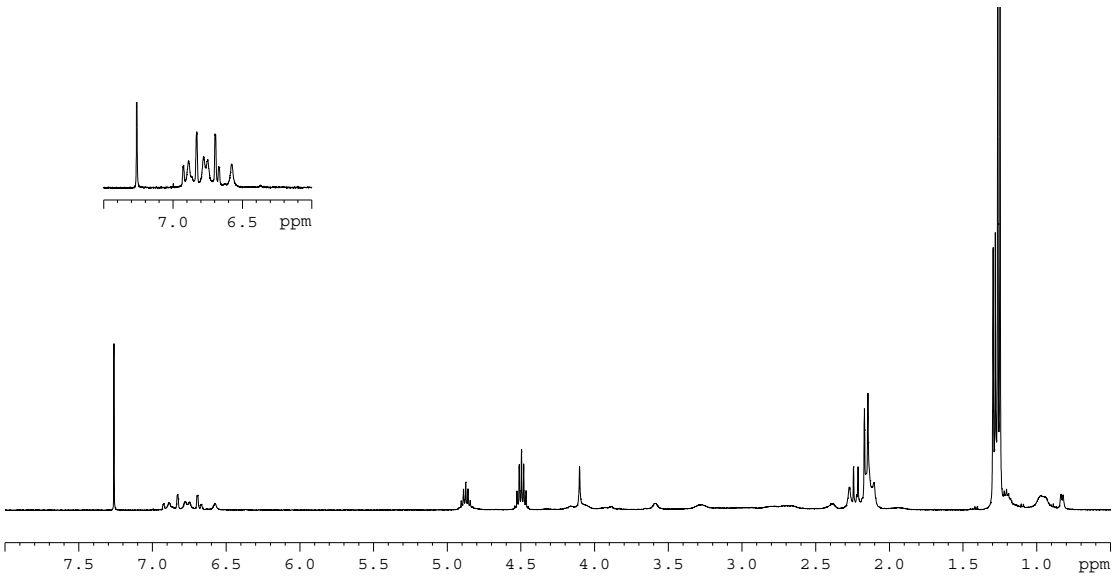
The atoms labelled with the suffix A are related by the -x+1,-y+1,-z+1 symmetry operation.

Ti_2(**8**)(O^iPr)$_6$ Yield = 77 %. ^{1}H NMR ($CDCl_3$) 1.27 (36H, br, CH_3), 1.29 (18H, s, CH_3), 1.45 (18H, s, CH_3), 2.00 (2H, br, CH_2), 2.98 (4H, br, CH_2), 3.14 (4H, br, CH_2), 3.92 (4H, s, CH_2), 4.90 (6H, sept, J = 6.0 Hz, CH), 6.86 (2H, d, J = 2.5 Hz, Ar-H), 7.19 (2H, d, J = 2.5 Hz, Ar-H). ^{13}C{^{1}H} NMR ($CDCl_3$) 26.9 (CH_3), 31.8 (CH_3), 34.3 (C), 35.1 (C), 77.6 (CH), 123.2 (Ar-H), 124.1 (Ar), 124.6 (Ar-H), 135.5 (Ar), 140.0 (Ar), 159.9 (Ar-O). Calc.(%) for $C_{53}H_{96}N_2O_8Ti_2$; C 64.62, H 9.82, N 2.84. Found (%); C 64.4, H 9.61, N 2.95

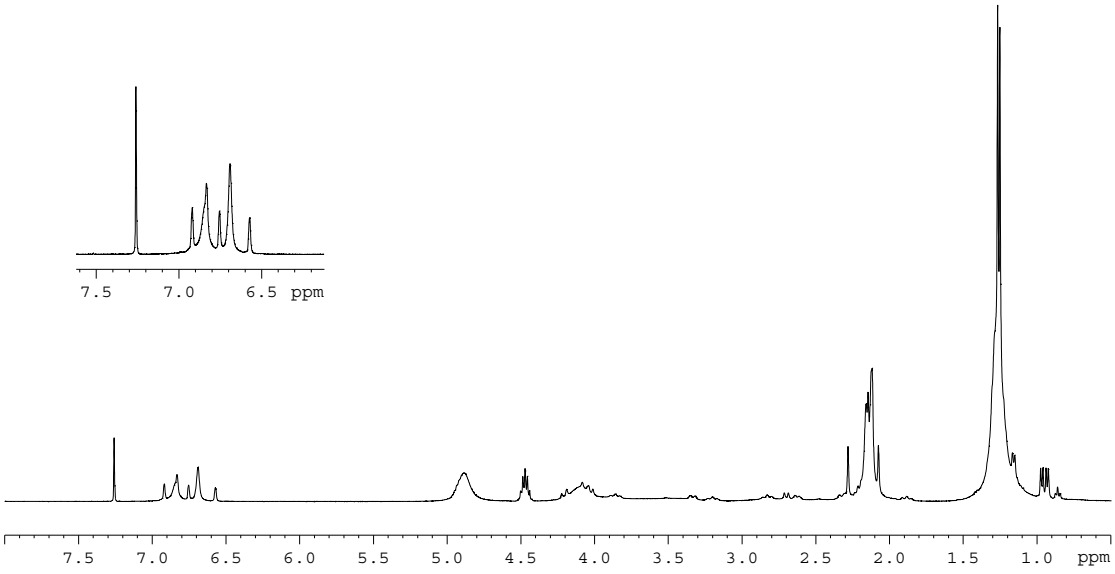


The atoms labelled with the suffix A are related by the -x+1,-y+1,-z+1 symmetry operation.

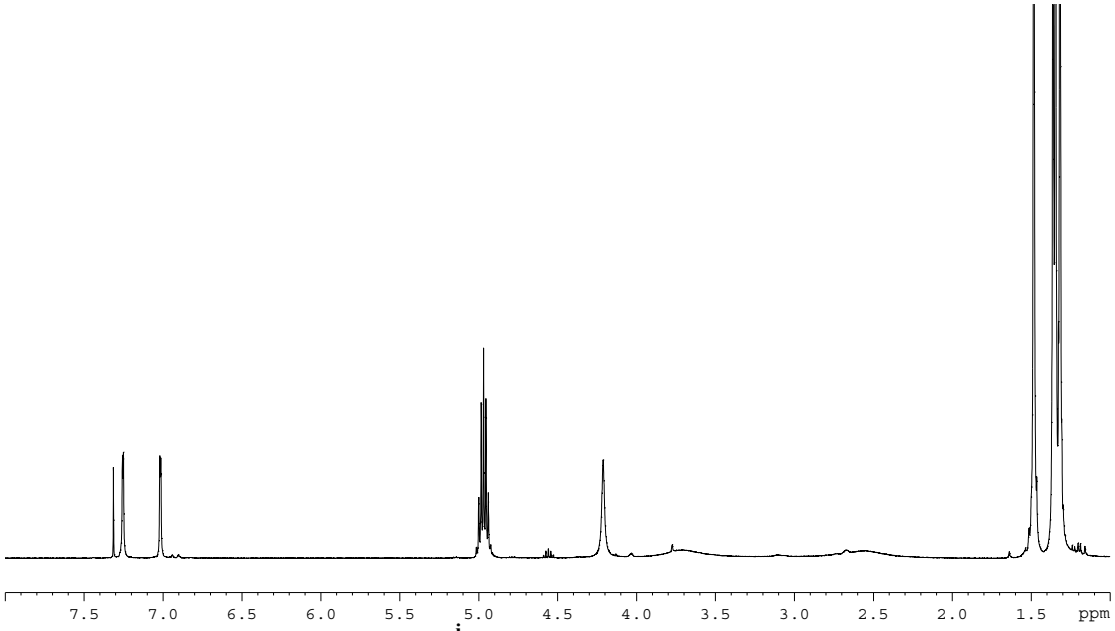
Selected NMR data



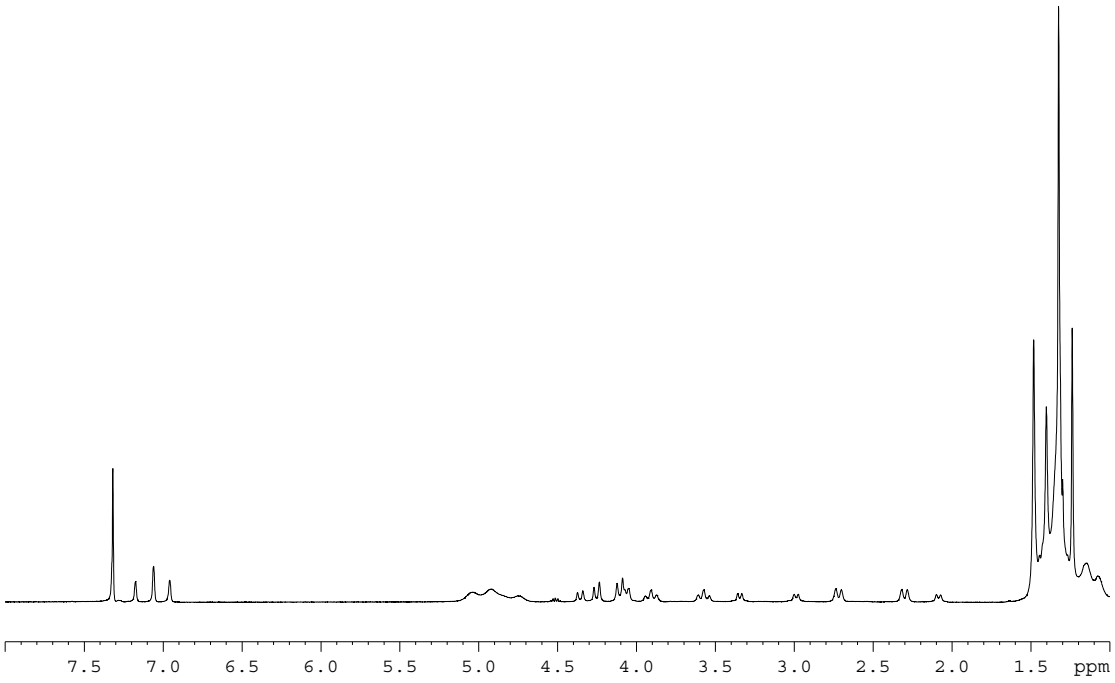
$Ti(O^iPr)_4 + 1H_2$ at 298 K



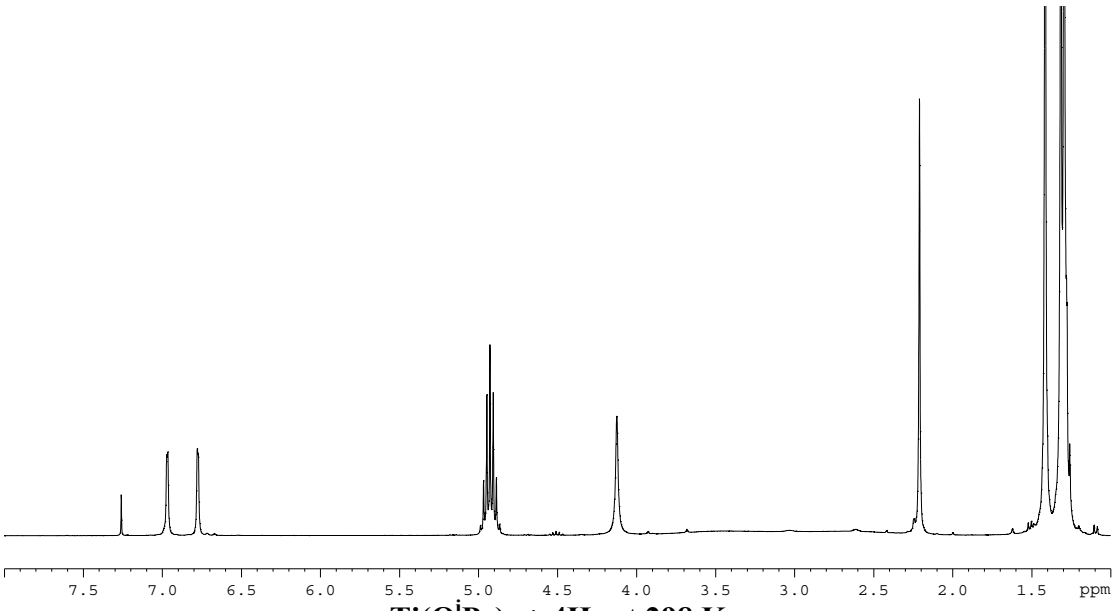
$Ti(O^iPr)_4 + 1H_2$ at 233 K



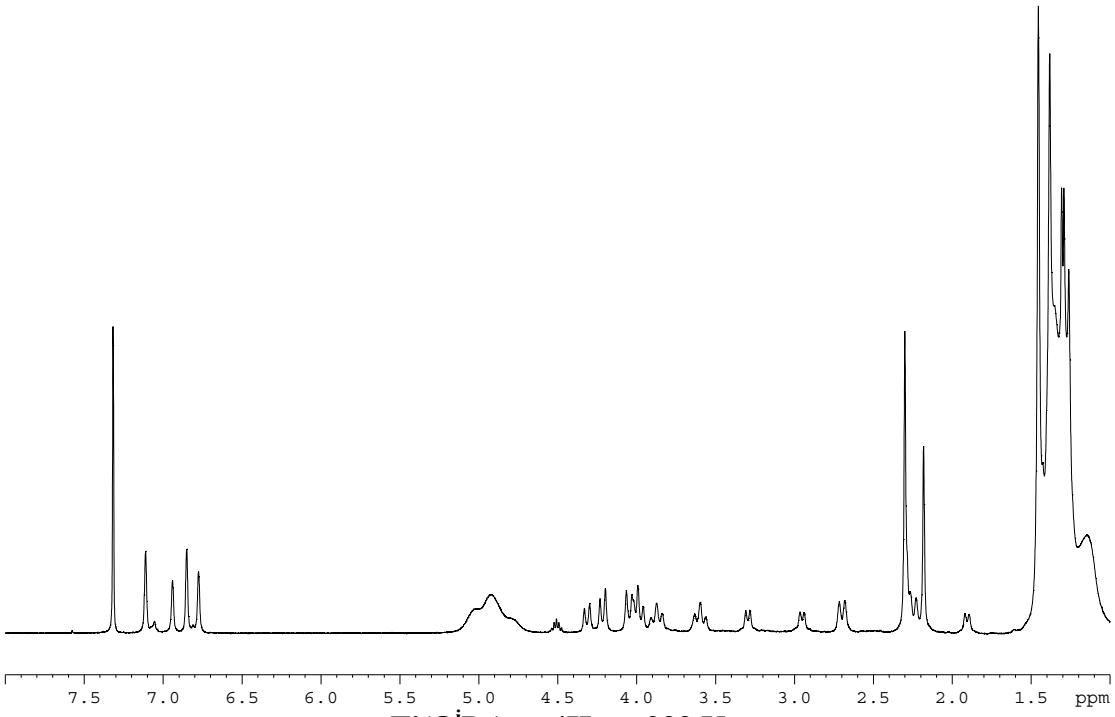
$Ti(O^iPr)_4 + 3H_2$ at 298 K



$Ti(O^iPr)_4 + 3H_2$ at 233 K



$Ti(O^iPr)_4 + 4H_2$ at 298 K



$Ti(O^iPr)_4 + 4H_2$ at 233 K