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Supporting Information

Titanium Complexes with Functional Alkoxido Ligands for Selective Ethylene Dimerization – A High Throughput Experimentation Approach

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SUPPLEMENTARY MATERIAL

Titanium Complexes with Functional Alkoxido Ligands for Selective Ethylene Dimerization. A High Throughput Experimentation Approach

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1. Synthesis and Spectroscopic Data of the Ligand Precursors

3-(Diphenylphosphino)propan-1-ol (19·H).

Triphenylphosphine (40.0 g, 153 mmol, 1.0 equiv.) and lithium (3.17 g,

457 mmol, 3.0 equiv.) were added to a 500 mL round bottom flask. Then THF (200 mL), precooled at -20 °C, was added slowly through a cannula. The mixture turned immediately yellow and became dark red



upon warming to room temperature overnight. The residual lithium was filtered off and the solution was brought to -70 °C before 3-choloropropanol (14.4 g, 153 mmol, 1.0 equiv.) was added dropwise by syringe. The mixture lost its colour upon warming to RT. After 1 h, water (150 mL) was added. The aqueous layer was extracted with THF (3 x 50 mL) and dried over anhydrous MgSO₄. Removal of the volatiles gave a yellowish oil which was purified by vacuum distillation (P = $8 \cdot 10^{-2}$ mbar, *T* = 150 °C) and **19** ·H was obtained as a white solid (23.5 g, 63%). Single crystals were grown from a saturated Et₂O solution. ¹H NMR (300 MHz, CD₂Cl₂): δ (ppm) 1.55 (bs, 1H, OH), 1.71 (m, 2H, H-2), 2.13 (m, 2H, H-1), 3.70 (t, ³*J*_{H3/H2} = 6.4 Hz, 2H, H-3), 7.34 (m, 6H, H-6, H-7), 7.43 (m, 4H, H-5). ¹³C{¹H} NMR (75 MHz, CD₂Cl₂): δ (ppm) 24.2 (d, ¹*J*_{C3/P} = 14.6 Hz, C-3), 28.0 (d, ²*J*_{C2/P} = 16.3 Hz, C-2), 63.5 (d, ³*J*_{C1/P} = 13.0 Hz, C-1), 128.4, 128.5 and 128.6 (C-6 and C-7), 132.7 (d, ²*J*_{C5/P} = 22.4 Hz, C-5), 138.4 (d, ¹*J*_{C4/P} = 16.0 Hz, C-4). ³¹P{¹H} NMR (121 MHz, CD₂Cl₂): δ (ppm) -16.2. Anal. Calcd. for C₁₅H₁₇OP: C, 73.76; H, 7.01. Found: C, 73.76; H, 7.08.



Figure S1. NMR spectra of **19**·H in CD₂Cl₂. Top: ¹H NMR spectrum; middle: ³¹P{¹H} NMR spectrum; bottom: ¹³C{¹H} NMR spectrum.

4-(Diphenylphosphino)butan-1-ol (20·H).

Triphenylphosphine (15.00 g, 57.2 mmol, 1.0 equiv.) and lithium (1.19 g, 171 mmol, 3.0 equiv.) were added under argon to a 250 mL round bottomed flask. Then THF (100 mL), precooled at -20 °C, was added slowly through a cannula. The mixture turned immediately yellow and



became dark red upon warming to room temperature overnight. The residual lithium was filtered off and the solution was placed at -70 °C before 4-cholorobutanol (6.83 g, 62.9 mmol, 1.1 equiv.) was added dropwise by syringe. The mixture lost its colour upon warming to room temperature and was stirred for 1 h at room temperature before addition of water (75 mL). The aqueous layer was extracted with THF (3 x 50 mL), dried over anhydrous MgSO₄. Removal of the volatiles gave a yellowish oil which was purified by vacuum distillation ($P = 8 \cdot 10^{-2}$ mbar, T **20**·H (5.00 g, 34%) was obtained as 155 °C) and a colourless oil. ¹H NMR (300 MHz, CD₂Cl₂): δ (ppm) 1.42 (bs, 1H, OH), 1.54 (m, 2H, H-3), 1.69 (m, 2H, H-2), 2.12 (m, 2H, H-4), 3.62 (t, ${}^{3}J_{H1/H2} = 6.4$ Hz, 2H, H-1), 7.46 (m, 6H, H-7 and H-8), 8.89 (m, 4H, H-6). ¹³C{¹H} NMR (75 MHz, CD₂Cl₂): δ (ppm) 22.7 (d, ³J_{C3/P} = 16.9 Hz, C-3), 20.0 (d, ⁴J_{C2/P} = 11.3 Hz, C-2), 34.5 (d, ${}^{1}J_{C4/P}$ = 12.4 Hz, C-4), 62.6 (C-1), 128.7, 128.8 and 128.9 (C-7 and C-8), 133.0 (d, ${}^{3}J_{C6/P} = 18.4$ Hz, C-6), 139.5 (d, ${}^{3}J_{C5/P} = 13.6$ Hz, C-5). ${}^{31}P{}^{1}H{}$ NMR (121 MHz, CD₂Cl₂): δ (ppm) -16.4. Anal. Calcd. for C₁₆H₁₉OP: C, 74.40; H, 7.41. Found: C, 74.20; H, 7.55.

3-(Methyl(phenyl)phosphino)propan-1-ol (23·H).

Methydiphenylphosphine (10.20 g, 50.9 mmol, 1.0 equiv.) and lithium (1.06 g, 153 mmol, 3.0 equiv.) were added under argon to a 250 mL round bottomed flask. Then THF (80 mL) precooled at -20 °C was added slowly through a cannula. The mixture turned immediately yellow and became dark



red upon warming to room temperature overnight. The residual lithium was filtered off and the solution was placed at -70 °C before 3-choloropropanol (4.82 g, 50.9 mmol, 1.0 equiv.) was added dropwise by syringe. The mixture lost its colour upon warming to room temperature. After 1 h, water (50 mL) was added. The aqueous layer was extracted with THF (3 x 25 mL), dried over anhydrous MgSO₄. Removal of the volatiles gave a yellowish oil which was purified by vacuum distillation ($P = 8 \cdot 10^{-2}$ mbar, T = 150 °C), affording **23** ·H (4.47 g, 48%) as a colourless oil. ¹H NMR (300 MHz, CD₂Cl₂): δ (ppm) 1.34 (d, ²J_{H4/P} = 2.9 Hz, 3H, H-4), 1.53 (bs, 1H, OH), 1.69 (m, 4H, H-2 and H-3), 3.65 (t, ⁴J_{H1/H2} = 6.3 Hz, 2H, H-1), 7.39 (m, 3H, H-7 and H-8), 7.53 (m, 2H, H-6). ¹³C {¹H} NMR (75 MHz, CD₂Cl₂): δ (ppm) 11.7 (d, ¹J_{C4/P} = 13.8 Hz, C-4), 27.1 (d, ²J_{C2/P} = 11.2 Hz, C-2), 29.3 (d, ¹J_{C3/P} = 12.2 Hz, C-3), 63.8 (d, ³J_{C1/P} = 11.8 Hz, C-1), 128.6, 128.7 and 128.8 (C-7 and C-8), 131.7 (d, ²J_{C6/P} = 17.8 Hz, C-6), 132.4 (d, ¹J_{C5/P} = 18.4 Hz, C-5).

³¹P{¹H} NMR (121 MHz, CD₂Cl₂): δ (ppm) -35.4. Anal. Calcd. for C₁₀H₁₅OP: C, 65.92; H, 8.30. Found: C, 65.74; H, 8.35.

3-(Diphenylphosphoryl)propan-1-ol (24·H).

To a stirred solution of 3-(diphenylphosphino)propan-1-ol **19**·H (4.40 g, 16.4 mmol, 1.0 equiv.) in acetone (100 mL) was added H₂O₂ (10 mL, 30% in H₂O) dropwise at 0 °C. The mixture was then refluxed (60 °C) for 5 h. CH₂Cl₂ (30 mL) was added and the organic layer was washed with water (3



x 30 mL). Removal of the volatiles gave 24·H (2.60 g, 61%) as a white solid. ¹H NMR (300 MHz, CD₂Cl₂): δ (ppm) 1.84 (m, 2H, H-2), 2.40 (dt, ²*J*_{H3/H3} = 11.3 Hz, ³*J*_{H3/H2} = 7.2 Hz, 2H, H-3), 3.64 (t, ³*J*_{H1/H2} = 5.5 Hz, 2H, H-1), 3.88 (bs, 1H, OH), 7.51 (m, 6H, H-6 and H-7), 7.73 (m, 4H, H-5). ¹³C{¹H} NMR (75 MHz, CD₂Cl₂): δ (ppm) 26.0 (d, ²*J*_{C2/P} = 4.2 Hz, C-2), 27.9 (d, ¹*J*_{C3/P} = 71.1 Hz, C-3), 62.7 (d, ³*J*_{C1/P} = 8.8 Hz, C-1), 129.0 (d, ³*J*_{C6/P} = 11.6 Hz, C-6), 131.1 (d, ²*J*_{C5/P} = 9.4 Hz,C-5), 132.1 (d, ⁴*J*_{C7/P} = 2.8 Hz, C-7), 133.1 (d, ¹*J*_{C4/P} = 98.2 Hz, C-4). ³¹P{¹H} NMR (121 MHz, CD₂Cl₂): δ (ppm) 34.0. Anal. Calcd. for C₁₅H₁₇O₂P: C, 69.22; H, 6.58. Found: C, 68.82; H, 6.77.

3-(Diphenylphosphorothioyl)propan-1-ol (25·H).

To a stirred solution of 3-diphenylphosphinopropan-1-ol $19 \cdot H$ (3.00 g, 12.3 mmol, 1.0 equiv.) in toluene (50 mL) was added S₈ until some yellow solid remains in suspension. The mixture was stirred for 2 days at room temperature. The precipitate formed was dissolved in CH₂Cl₂ and the residual S₈ was filtered off. Removal of the solvent and



recrystallization from CH₂Cl₂/pentane gave **25**·H (2.74 g, 81%) as a white solid. MS (EI⁺): (*m/z*) $[M^+] = 276$. ¹H NMR (300 MHz, CD₂Cl₂): δ (ppm) 1.71 (bs, 1H, OH), 1.82 (m, 2H, H-2), 2.58 (m, 2H, H-3), 3.66 (t, ³*J*_{H1/H2} = 6.0 Hz, 2H, H-1), 7.49 (m, 6H, H-6 and H-7), 7.84 (m, 4H, H-5). ¹³C{¹H} NMR (75 MHz, CD₂Cl₂): δ (ppm) 26.0 (d, ²*J*_{C2/P} = 2.6 Hz, C-2), 29.5 (d, ¹*J*_{C3/P} = 57.8 Hz, C-3), 62.6 (d, ²*J*_{C3/P} = 15.9 Hz, C-1), 129.0 (d, ³*J*_{C6/P} = 11.9 Hz, C-6), 131.4 (d, ²*J*_{C5/P} = 10.0 Hz, C-5), 131.8 (d, ⁴*J*_{C7/P} = 2.9 Hz, C-7), 133.9 (d, ¹*J*_{C4/P} = 79.4 Hz, C-4). ³¹P{¹H} NMR (121 MHz, CD₂Cl₂): δ (ppm) 42.9. Anal. Calcd. for C₁₅H₁₇OSP: C, 65.20; H, 6.20. Found: C, 64.79; H, 6.20.

2. Synthesis and Spectroscopic Data of the Complexes

General procedure.

To a cyclohexane solution of the alcohol $X \cdot H$ (2 equiv.) was added $[Ti(OiPr)_4]$ (or $[Ti(OnBu)_4]$) (1.0 equiv.) at room temperature. The solution was stirred at room temperature overnight. Removal of the volatiles gave the complex $[TiX_2(OiPr \text{ or } OnBu)_2]$ in quantitative yield. This was checked with some complexes but not verified for the whole library. Some residual cyclohexane was often observed at the end of the synthesis. However, complexes were used as obtained without further purification, cyclohexane being the solvent of catalytic tests. These syntheses operated carousel with reaction were in а apparatus 12 parallel tubes (https://www.radleys.com/range/carousel-12-plus-reaction-station/) in line with the HTE approach developed in this work.

[Ti(benzyloxy)₂(O*i*Pr)₂] [Ti(1)₂(O*i*Pr)₂].

The general procedure was applied with $1 \cdot H$ (3.78 g, 35.0 mmol, 2.0 equiv.) and $[Ti(OiPr)_4]$ (5.00 g, 17.5 mmol, 1.0 equiv.), affording $[Ti(1)_2(OiPr)_2]$ (6.66 g, 99%) as a colourless oil. ¹H NMR (300 MHz,



CD₂Cl₂): δ (ppm) 1.17 (d, ${}^{3}J_{H7/H6} = 5.9$ Hz, 12H, H-7), 4.58 (sept., ${}^{3}J_{H6/H7} = 5.9$ Hz, 2H, H-6), 5.42 (s, 4H, H-1), 7.28 (m, 6H, H-3 and H-5), 7.37 (m, 4H, H-4). ${}^{13}C{}^{1}H{}$ NMR (75 MHz, CD₂Cl₂): δ (ppm) 26.5 (C-7), 77.1 (C-1), 78.1 (C-6), 126.8, 127.0, 128.2 (C-3, C-4 and C-5), 143.2 (C-2).



Figure S2. NMR spectra of $[Ti(1)_2(OiPr)_2]$ in CD₂Cl₂. Top: ¹H NMR spectrum; bottom: ¹³C{¹H} NMR spectrum.

[Ti(2-phenylpropan-2-yloxy)₂(OiPr)₂] [Ti(2)₂(OiPr)₂].

The general procedure was applied with **2**·H (4.77 g, 35.0 mmol, 2.0 equiv.) and [Ti(O*i*Pr)₄] (5.00 g, 17.5 mmol, 1.0 equiv.), affording $\begin{pmatrix} 5 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$ [Ti(**2**)₂(O*i*Pr)₂] (7.64 g, 99%) as a yellowish liquid. ¹H NMR (300 MHz, CD₂Cl₂): δ (ppm) 1.28 (broad d, ³*J*_{H8/H7} = 5.9 Hz, 12H, H-8), 1.69 (m, 12H, H-6), 4.59 (m, 2H, H-7), 7.23 (m, 2H, H-5), 7.33 (m, 4H, H-4), 7.59 (m, 4H, H-3). ¹³C{¹H} NMR (75 MHz, CD₂Cl₂): δ (ppm) 26.7 (2s, C-8), 33.6 (2s, C-6), 77.4 (m, C-7), 84.3 (m, C-1), 124.9 (m, C-4), 126.6 (C-5), 128.2 (C-3), 150.4 (m, C-2).



Figure S3. NMR spectra of $[Ti(2)_2(OiPr)_2]$ in CD₂Cl₂. Top: ¹H NMR spectrum; bottom: ¹³C{¹H} NMR spectrum.

[Ti(phenethoxy)₂(O*i*Pr)₂] [Ti(3)₂(O*i*Pr)₂].



Figure S4. NMR spectra of $[Ti(3)_2(OiPr)_2]$ in CD₂Cl₂. Top: ¹H NMR spectrum; bottom: ¹³C{¹H} NMR spectrum.

[Ti(3,3-dyphenylpropoxy)₂(O*i*Pr)₂] [Ti(4)₂(O*i*Pr)₂].

The general procedure was applied with 4·H (1.00 g, 4.7 mmol, 2.0 equiv.) and $[Ti(OiPr)_4]$ (0.67 g, 2.3 mmol, 1.0 equiv.), leading to $[Ti(4)_2(OiPr)_2]$ as a viscous, beige oil. ¹H NMR (300 MHz,



CD₂Cl₂): δ (ppm) 1.17 (bs, 12H, H-8), 2.33 (bs, 4H, H-2), 3.94 (bs, 2H, H-3), 4.16 (bs, 4H, H-1), 4.52 (m, 2H, H-8), 7.17 (m, 20H, H5, H6 and H7). ¹³C{¹H} NMR (75 MHz, CD₂Cl₂): δ (ppm) 26.6 (C-9), 39.1 (C-2), 48.0 (C-3), 74.1 (bs, C-1), 77.3 (bs, C-8), 126.4 (C-7), 128.1 (C-5), 128.8 (C-6), 145.5 (C-4).



Figure S5. NMR spectra of $[Ti(4)_2(OiPr)_2]$ in CD₂Cl₂. Top: ¹H NMR spectrum; bottom: ¹³C{¹H} NMR spectrum.

[Ti(2-methoxyethoxy)₂(OiPr)₂] [Ti(5)₂(OiPr)₂].

The general procedure was applied with 5·H (2.60 g, 35.0 mmol, $(3 - 2 - 0)_{2^{Ti}} (0 - 4 - 5)_{2^{Ti}} (0 - 4$



Figure S6. NMR spectra of $[Ti(5)_2(OiPr)_2]$ in CD₂Cl₂. Top: ¹H NMR spectrum; middle: blow-up of the 3.8-5.5 ppm region; bottom: ¹³C{¹H} NMR spectrum.

[Ti(3-methoxypropoxy)₂(OiPr)₂] [Ti(6)₂(OiPr)₂].

The general procedure was applied with 6·H (3.15 g, 35.0 mmol, 2.0 equiv.) and [Ti(O*i*Pr)₄] (5.00 g, 17.5 mmol, 1.0 equiv.), affording [Ti(**5**)₂(O*i*Pr)₂] as a colourless liquid. ¹H NMR (300 MHz, CD₂Cl₂): δ (ppm) 1.21 (broad d, ³*J*_{H6/H5} = 6.0 Hz, 12H, H-6), 1.88 (m, 4H, H-2), 3.27 (s, 6H, H-4), 3.47 (t, ³*J*_{H3/H2} = 6.5 Hz, 4H, H-3), 4.28 (bs, 4H, H-1), 4.49 (bs, 2H, H-5). ¹³C{¹H} NMR (75 MHz, CD₂Cl₂): δ (ppm) 26.3 (C-6), 33.6 (C-2), 58.7 (C-4), 71.0 (C-3), 71.6 (bs, C-1), 77.3 (bs, C-5).



Figure S7. NMR spectra of $[Ti(6)_2(OiPr)_2]$ in CD₂Cl₂. Top: ¹H NMR spectrum; bottom: ¹³C{¹H} NMR spectrum.

[Ti(2-furan-2-ylmethoxy)₂(OiPr)₂] [Ti(7)₂(OiPr)₂].

The general procedure was applied with 7·H (3.43 g, 35.0 mmol, 2.0 equiv.) and [Ti(O*i*Pr)₄] (5.00 g, 17.5 mmol, 1.0 equiv.) affording [Ti(7)₂(O*i*Pr)₂] (6.30 g, 99%) as a red oil. ¹H NMR (300 MHz, CD₂Cl₂): δ (ppm) 1.17 (d, ³J_{H7/H6} = 5.7 Hz, 12H, H-7), 4.58 (m, 2H, H-6), 5.26 (s, 4H, H-1), 6.25 and 6.31 (2m, 4H, H-3 and H-4), 7.34 (m, 2H, H-5). ¹³C{¹H} NMR (75 MHz, CD₂Cl₂): δ (ppm) 26.4 (C-7), 69.1 (C-1), 78.0 (bs, C-6), 107.4 (C-3), 110.5 (C-4), 141.6 (C-5), 156.4 (C-2).



Figure S8. NMR spectra of $[Ti(7)_2(OiPr)_2]$ in CD₂Cl₂. Top: ¹H NMR spectrum; bottom: ¹³C{¹H} NMR spectrum.

[Ti(2-tetrahydrofuran-2-ylmethoxy)₂(OiPr)₂] [Ti(8)₂(OiPr)₂].

The general procedure was applied with **8**·H (3.57 g, 35.0 mmol, $\left(\int_{4}^{5} \int_{2}^{1} \int_{2}^$



Figure S9. NMR spectra of $[Ti(8)_2(OiPr)_2]$ in CD₂Cl₂. Top: ¹H NMR spectrum; bottom: ¹³C{¹H} NMR spectrum.

[Ti(2-thiophen-2-ylmethoxy)₂(OiPr)₂] [Ti(9)₂(OiPr)₂].

The general procedure was applied with 9·H (3.99 g, 35.0 mmol, 2.0 equiv.) and [Ti(O*i*Pr)₄] (5.00 g, 17.5 mmol, 1.0 equiv.), $\left(5 + \frac{1}{2} +$

CD₂Cl₂): δ (ppm) 1.20 (d, ${}^{3}J_{H7/H6} = 6.1$ Hz, 12H, H-7), 4.64 (sept, ${}^{3}J_{H6/H7} = 6.1$ Hz, 2H, H-6), 5.52 (s, 4H, H-1), 6.94 (m, 2H, H-4), 6.98 (m, 2H, H-3), 7.22 (m, 2H, H-5). ${}^{13}C{}^{1}H{}$ NMR (75 MHz, CD₂Cl₂): δ (ppm) 26.5 (C-5), 71.8 (C-1), 78.2 (bs, C-6), 124.7 (C-5), 125.2 (C-3), 126.6 (C-4), 146.4 (C-2).



Figure S10. NMR spectra of $[Ti(9)_2(OiPr)_2]$ in CD₂Cl₂. Top: ¹H NMR spectrum; bottom: ¹³C{¹H} NMR spectrum.

[Ti(2-thiophen-2-ylmethoxy)₂(OiPr)₂] [Ti(10)₂(OiPr)₂].

The general procedure was applied with $10 \cdot H$ (4.48 g, 35.0 mmol, 2.0 equiv.) and [Ti(O*i*Pr)₄] (5.00 g, 17.5 mmol, 1.0 equiv.), yielding



[Ti(**10**)₂(O*i*Pr)₂] as an orange viscous oil. ¹H NMR (300 MHz, CD₂Cl₂): δ (ppm) 1.29 (d, ³*J*_{H8/H7} = 6.2 Hz, 12H, H-8), 3.30 (m, 4H, H-2), 4.62 (m, 4H, H-1), 4.82 (bs, 2H, H-7), 6.86 (m, 2H, H-4), 6.95 (dd, ³*J*_{H5/H6} = 5.2 Hz, ³*J*_{H5/H4} = 3.4 Hz 2H, H-5), 7.15 (dd, ³*J*_{H6/H5} = 5.2 Hz, ⁴*J*_{H6/H4} = 1.2 Hz, 2H, H-6). ¹³C{¹H} NMR (75 MHz, CD₂Cl₂): δ (ppm) 28.7 (C-8), 34.0 (C-2), 76.3 (bs, C-1), 78.4 (bs, C-7), 123.5 (C-6), 125.3 (C-4), 127.1 (C-5), 141.8 (C-3).



Figure S11. NMR spectra of $[Ti(10)_2(OiPr)_2]$ in CD₂Cl₂. Top: ¹H NMR spectrum; bottom: ¹³C{¹H} NMR spectrum.

[Ti(2-dimethylaminoethoxy)₂(O*i*Pr)₂] [Ti(11)₂(O*i*Pr)₂].

An unassigned peak is present at 3.59 ppm (0.3H). ${}^{13}C{}^{1}H$ NMR (75 MHz, CD₂Cl₂): δ (ppm) 26.6 (C-5), 46.5 (C-3), 62.8 (C-2), 70.9 (bs, C-1), 76.4 (C-4).



Figure S12. NMR spectra of $[Ti(11)_2(OiPr)_2]$ in CD₂Cl₂. Top: ¹H NMR spectrum; bottom: ¹³C{¹H} NMR spectrum.

[Ti(2-dimethylaminopropoxy)2(OiPr)2] [Ti(12)2(OiPr)2].

The general procedure was applied with $12 \cdot H$ (3.61 g, 35.0 mmol, 2.0 equiv.) and $[Ti(OiPr)_4]$ (5.00 g, 17.5mmol, 1.0 equiv.), yielding



[Ti(12)₂(O*i*Pr)₂] as an orange liquid. ¹H NMR (300 MHz, CD₂Cl₂): δ (ppm) 1.21 (d, ³*J*_{H6/H5} = 6.0 Hz, 12H, H-6), 1.75 (p, ³*J*_{H2/H1} = ³*J*_{H2/H3} = 6.7 Hz, 4H, H-2), 2.22 (s, 12H, H-4); 2.40 (t, ³*J*_{H3/H2} = 6.7 Hz, 4H, H-3), 4.32 (t, ³*J*_{H1/H2} = 6.7 Hz, 4H, H-1), 4.68 (m, 2H, H-5). An unassigned peak is present at 3.52 ppm (0.6H). ¹³C{¹H} NMR (75 MHz, CD₂Cl₂): δ (ppm) 26.7 (C-6), 31.0 (C-2), 46.5 (C-4), 58.4 (C-3), 72.8 (C-1), 76.7 (bs, C-5).



Figure S13. NMR spectra of $[Ti(12)_2(OiPr)_2]$ in CD₂Cl₂. Top: ¹H NMR spectrum; bottom: ¹³C{¹H} NMR spectrum.

[Ti(pyridine-2-ylmethoxy)₂(OiPr)₂] [Ti(13)₂(OiPr)₂].

The general procedure was applied with $13 \cdot H$ (3.80 g, 35.0 mmol, 2.0 equiv.) and $[Ti(OiPr)_4]$ (5.00 g, 17.5 mmol, 1.0 equiv.), affording



[Ti(**13**)₂(O*i*Pr)₂] as a white solid. Single crystals were obtained from a cold saturated pentane solution. ¹H NMR (300 MHz, CD₂Cl₂): δ (ppm) 0.96 (d, ³*J*_{H8/H7} = 6.4 Hz,12H H-8), 4.57 (sept., ³*J*_{H7/H8} = 6.4 Hz, 2H, H-7), 5.53 (s, 4H, H-1), 7.16 (m, 4H, H-5, H-3), 7.64 (m, 2H, H-4), 8.54 (m, 2H, H-6). ¹³C{¹H} NMR (75 MHz, CD₂Cl₂): δ (ppm) 25.8 (C-8), 74.4 (C-1), 75.3 (C-7), 119.5 (C-5), 122.3 (C-3), 138.0 (C-4), 147.6 (C-6), 166.8 (C-2).



Figure S14. NMR spectra of $[Ti(13)_2(OiPr)_2]$ in CD₂Cl₂. Top: ¹H NMR spectrum; middle: blow-up of the 4.3-6 ppm region; bottom: ¹³C{H} NMR spectrum.

[Ti(pyridine-2-ylmethoxy)₂(OnBu)₂] [Ti(13)₂(OnBu)₂].

The general procedure was applied with $13 \cdot H$ (1.92 g, 17.6 mmol, 2.0 equiv.) and $[Ti(OnBu)_4]$ (3.00 g, 8.80 mmol, 1.0 equiv.), yielding $[Ti(13)_2(OnBu)_2]$ as a white solid. Single



crystals were obtained from a cold saturated pentane solution. ¹H NMR (300 MHz, CD₂Cl₂): δ (ppm) 0.77 (t, ³*J*_{H10/H9} = 7.2 Hz, 6H, H-10), 1.15 (m, 4H, H-9), 1.28 (m, 4H, H-8), 4.12 (t, ³*J*_{H7/H8} = 6.6 Hz, H-7), 5.53 (s, 4H, H-1), 7.18 (m, 4H, H-3, H-5), 7.67 (m, 2H, H-4), 8.54 (m, 2H, H-6). ¹³C{¹H} NMR (75 MHz, CD₂Cl₂): δ (ppm) 14.2 (C-10), 19.4 (C-9), 36.1 (C-8), 74.3 (C-7), 74.8 (C-1), 119.5 (C-3), 122.4 (C-5), 138.2 (C-4), 147.5 (C-6), 166.8 (C-1).



Figure S15. NMR spectra of $[Ti(13)_2(OnBu)_2]$ in CD₂Cl₂. Top: ¹H NMR spectrum; middle: blow-up of the 4.3-6 ppm region; bottom: ¹³C{H} NMR spectrum.

[Ti(pyridine-3-ylmethoxy)₂(OiPr)₂] [Ti(14)₂(OiPr)₂].

The general procedure was applied with 14·H (3.80 g, 35.0 mmol, 2.0 equiv.) and $[Ti(OiPr)_4]$ (5.00 g, 17.5 mmol, 1.0 equiv.), affording



[Ti(14)₂(O*i*Pr)₂] as a viscous yellow oil. ¹H NMR (300 MHz, CD₂Cl₂): δ (ppm) 1.15 (bs, 12H, H-8), 4.52 (bs, 2H, H-7), 5.35 (bs, 4H, H-1), 7.14 (m, 2H, H-4), 7.65 (bs, 2H, H-3), 8.45 (m, 2H, H-6), 8.57 (bs, 2H, H-5). ¹³C{¹H} NMR (75 MHz, CD₂Cl₂): δ (ppm) 26.4 (C-8), 73.9 (bs, C-7), 77.4 (bs, C-1), 123.3 (C-4), 135.2 (C-3), 138.8 (C-2), 148.3 (C-6), 149.0 (C-5).



Figure S16. NMR spectra of $[Ti(14)_2(OiPr)_2]$ in CD₂Cl₂. Top: ¹H NMR spectrum; bottom: ¹³C{¹H} NMR spectrum.

[Ti(pyridine-4-ylmethoxy)₂(OiPr)₂] [Ti(15)₂(OiPr)₂].

The general procedure was applied with **15**·H (2.30 g, 21.1 mmol, 2.0 $\left(\begin{array}{c} \sum_{4=3}^{N} \sum_{2=1}^{N} \sum_{2=1}^{N$



Figure S17. NMR spectra of $[Ti(15)_2(OiPr)_2]$ in CD₂Cl₂. Top: ¹H NMR spectrum; bottom: ¹³C{¹H} NMR spectrum.

[Ti(2-(pyridine-2-yl)ethoxy)₂(OiPr)₂] [Ti(16)₂(OiPr)₂].

The general procedure was applied with $16 \cdot H$ (4.31 g, 35.0 mmol, 2.0 equiv.) and $[Ti(OiPr)_4]$ (5.00 g, 17.5 mmol, 1.0 equiv.), affording



[Ti(**16**)₂(O*i*Pr)₂] as a viscous brown oil. ¹H NMR (300 MHz, CD₂Cl₂): δ (ppm) 1.10 (bs, 12H, H-9), 2.90 (bs, 4H, H-1), 4.39 (bs, 4H, H-2), 4.66 (bs, 2H, H-8), 7.09 (bs, 4H, H-6 and H-4), 7.61 (bs, 2H, H-5), 8.82 (bs, 2H, H-7). ¹³C{¹H} NMR (75 MHz, CD₂Cl₂): δ (ppm) 26.4 (C-9), 41.1 (C-2), 69.9 (bs, C-1), 76.2 (bs, C-8), 121.3 (C-6), 124.3 (C-4), 137.4 (C-5), 150.4 (C-7), 161.0 (C-3).



Figure S18. NMR spectra of $[Ti(16)_2(OiPr)_2]$ in CD₂Cl₂. Top: ¹H NMR spectrum; bottom: ¹³C{¹H} NMR spectrum.

[Ti(2-diphenylphosphinoethoxy)₂(OiPr)₂] [Ti(17)₂(OiPr)₂].

The general procedure was applied with $17 \cdot H$ (3.24 g, 14.1 mmol, 2.0 equiv.) and [Ti(O*i*Pr)₄] (2.00 g, 7.05 mmol, 1.0 equiv.), leading to [Ti(17)₂(O*i*Pr)₂] as a yellowish viscous oil. ¹H NMR (300 MHz,



CD₂Cl₂): δ (ppm) 1.14 (m, 12H, H-8), 2.47 (bs, 4H, H-2), 4.34 (bs, 4H, H-1), 4.42 (m, 2H, H-7), 7.30 (m, 12H, H-6 and H-5), 7.37 (m, 8H, H-4). ¹³C{¹H} NMR (75 MHz, CD₂Cl₂): δ (ppm) 26.6 (C-8), 32.4 (d, ¹*J*_{C2/P} = 12.7 Hz, C-2), 72.5 (bs, C-1), 77.6 (bs, C-7), 128.7, 128.8 (C-5 and C-6), 133.0 (d, ²*J*_{C4/P} = 18.7 Hz, C-4), 139.2 (d, ¹*J*_{C3/P} = 13.3 Hz, C-3). ³¹P{¹H} NMR (121 MHz, CD₂Cl₂): δ (ppm) -23.1 (bs).



Figure S19. NMR spectra of $[Ti(17)_2(OiPr)_2]$ in CD₂Cl₂. Top: ¹H NMR spectrum; middle: ¹³C{¹H} NMR spectrum; bottom: ³¹P{¹H} NMR spectrum.

[Ti(2-diphenylphosphinoethoxy)₂(OnBu)₂] [Ti(17)₂(OnBu)₂].

The general procedure was applied with $17 \cdot H$ (2.70 g, 11.7 mmol, 2.0 equiv.) and $[Ti(OnBu)_4]$ (2.00 g, 5.80 mmol, 1.0 equiv.), leading to $[Ti(17)_2(OnBu)_2]$ as a yellowish viscous



oil. ¹H NMR (300 MHz, CD₂Cl₂): δ (ppm) 0.86 (bs, 6H, H-10), 1.27 (bs, 4H, H-9), 1.50 (bs, 4H, H-8), 2.46 (bs, 4H, H-2), 4.15 (bs, 4H, H-7), 4.32 (bs, 4H, H-1), 7.26 (m, 10H, H-5 and H-6), 7.40 (m, 8H, H-4). ¹³C{¹H} NMR (75 MHz, CD₂Cl₂): δ (ppm) 14.3 (C-10), 19.5 (C-9), 32.4 (d, ¹*J*_{C2/P} = 13.5 Hz, C-2), 36.1 (C-8), 72.7 (bs, C-1), 75.6 (bs, C-7), 128.7, 128.8 (C-5 and C-6), 133.0 (d, ¹*J*_{C2/P} = 18.7 Hz, C-4), (d, ¹*J*_{C3/P} = 15.1 Hz, C-3). ³¹P{¹H} NMR (121 MHz, CD₂Cl₂): δ (ppm) -23.7 (bs).



Figure S20. NMR spectra of $[Ti(17)_2(OnBu)_2]$ in CD₂Cl₂. Top: ¹H NMR spectrum; middle: ¹³C{¹H} NMR spectrum; bottom: ³¹P{¹H} NMR spectrum.

[Ti(1-(diphenylphosphino)-2-methylpropan-2-yloxy)₂(OiPr)₂] [Ti(18)₂(OiPr)₂].

The general procedure was applied with $18 \cdot H$ (1.80 g, 7.00 mmol, 2.0 equiv.) and $[Ti(OiPr)_4]$ (1.00 g, 3.50 mmol, 1.0 equiv.), yielding $[Ti(18)_2(OiPr)_2]$ as a yellowish viscous oil. ¹H NMR (300 MHz, CD₂Cl₂): δ (ppm) 1.22 (m, 12H, H-9), 1.34 (m,

$$\left(\begin{array}{c} 7 & 6 & 5 \\ 4 & p & 1 \\ 4 & p & 1 \\ 1 & 3 & 3 \\ \end{array}\right) Ti \left(\begin{array}{c} 0 & 8 & 9 \\ 9 & 9 \\ 9 & 2 \\ \end{array}\right)_2$$

12H, H-3), 2.50 (m, 4H, H-2), 4.50 (m, 2H, H-8), 7.29 (m, 12H, H-6 and H-7), 7.46 (m, 8H, H-7). ¹³C{¹H} NMR (75 MHz, CD₂Cl₂): δ (ppm) 26.8 (C-9), 32.0 (d, ³*J*_{C3/P} = 8.2 Hz, C-3), 45.5 (d, ¹*J*_{C1/P} = 16.1 Hz, C-2), 76.9 (m, C-8), 83.0 (m, C-1), 128.6, 128.7 (C-6 and C-7), 133.3 (d, ²*J*_{C5/P} = 16.1 Hz, C-5), 140.8 (d, ¹*J*_{C4/P} = 14.4 Hz, C-4). ³¹P{¹H} NMR (121 MHz, CD₂Cl₂): δ (ppm) –21.9 (m).



Figure S21. NMR spectra of $[Ti(18)_2(OiPr)_2]$ in CD₂Cl₂. Top: ¹H NMR spectrum; middle: ¹³C{¹H} NMR spectrum; bottom: ³¹P{¹H} NMR spectrum.

[Ti(3-diphenylphosphinopropoxy)₂(OiPr)₂] [Ti(19)₂(OiPr)₂].

The general procedure was applied with **19**·H (3.44 g, 14.1 mmol, 2.0 equiv.) and $[Ti(OiPr)_4]$ (2.00 g, 7.00 mmol, 1.0 equiv.), affording $[Ti(19)_2(OiPr)_2]$ as a yellowish viscous oil. ¹H NMR (300 MHz, CD₂Cl₂): δ (ppm) 1.14 (bs, 12H, H-9), 1.68 (bs, 4H, H-2),



1.98 (bs, 4H, H-3), 4.22 (bs, 4H, H-1), 4.50 (sept, ${}^{3}J_{H8/H9} = 6.0$ Hz, 2H, H-8), 7.27 (m, 12H, H-6 and H-7), 7.40 (m, 8H, H-5). ${}^{13}C\{{}^{1}H\}$ NMR (75 MHz, CD₂Cl₂): δ (ppm) 24.3 (d, ${}^{1}J_{C3/P} = 11.7$ Hz, C-3), 36.6 (C-5), 30.1 (d, ${}^{2}J_{C2/P} = 15.8$ Hz, C-2), 76.0 (bs, C-1), 77.3 (bs, C-8), 128.7, 128.8 (C-6 and C-7), 133.0 (d, ${}^{2}J_{C5/P} = 18.4$ Hz, C-5), 13.7 (d, ${}^{1}J_{C4/P} = 14.1$ Hz, C-4). ${}^{31}P\{{}^{1}H\}$ NMR (121 MHz, CD₂Cl₂): δ (ppm) -16.0. Anal. Calcd. for C₃₆H₄₆O₄P₂Ti: C, 66.26; H, 7.11; P, 9.49. Found: C, 65.24; H, 6.99; P, 9.42.



Figure S22. NMR spectra of $[Ti(19)_2(OiPr)_2]$ in CD₂Cl₂. Top: ¹H NMR spectrum; middle: ¹³C{¹H} NMR spectrum; bottom: ³¹P{¹H} NMR spectrum.

[Ti(3-diphenylphosphinopropoxy)₂(OnBu)₂] [Ti(19)₂(OnBu)₂].

The general procedure was applied with **19**·H (2.87 g, 11.7 mmol, 2.0 equiv.) and $[Ti(OnBu)_4]$ (2.00 g, 5.85 mmol, 1.0 equiv.), yielding $[Ti(19)_2(OnBu)_2]$ (3.96 g, 99%) as a yellowish oil. ¹H NMR (300 MHz, CD₂Cl₂): δ (ppm) 0.90 (m,



6H, H-11), 1.29 (bs, 4H, H-10), 1.51 (bs, 4H, H-9), 1.97 (bs, 4H, H-2), 2.01 (bs, 4H, H-3), 4.19 (bs, 8H, H-1 and H-8), 7.29 (m, 12H, H-6 and H-7), 7.41 (m, 8H, H-5). ${}^{13}C{}^{1H}$ NMR (75 MHz, CD₂Cl₂): δ (ppm) 14.3 (C-11), 19.5 (C-10), 24.4 (d, ${}^{1}J_{C3/P} = 11.6$ Hz, C-3), 30.1 (d, ${}^{2}J_{C2/P} = 15.7$ Hz, C-2), 36.0 (C-9), 72.3 (bs, C-8), 75.9 (bs, C-1), 128.7, 128.8 (C-6 and C-7), 133.0 (d, ${}^{2}J_{C5/P} = 18.4$ Hz, C-5), 139.7 (d, ${}^{1}J_{C4/P} = 14.1$ Hz, C-4). ${}^{31}P{}^{1}H{}$ NMR (121 MHz, CD₂Cl₂): δ (ppm) -16.0. IR: v(cm⁻¹) 3073(w), 2927(w), 2858(w), 1585(w), 1482(w), 1435(m), 1123(m), 906(w), 740(s), 697(s), 600(s), 497(s). Anal. Calcd. for C₃₈H₅₀O₄P₂Ti: C, 67.06; H, 7.40. Found: C, 67.01; H, 7.18.



Figure S23. NMR spectra of complex $[Ti(19)_2(OnBu)_2]$. Top ¹H NMR spectra in toluene-d₈ at 40 °C (a) and 60 °C (b); middle: ¹³C{¹H} NMR spectrum; bottom: ³¹P{¹H} NMR spectrum.

[Ti(4-diphenylphosphinobutoxy)₂(OiPr)₂] [Ti(20)₂(OiPr)₂].

The general procedure was applied with **20**·H (1.00 g, 3.90 mmol, 2.0 equiv.) and [Ti(O*i*Pr)₄] (0.500 g, 1.95 mmol, 1.0 equiv.), yielding [Ti(**20**)₂(O*i*Pr)₂] as a yellow sticky oil. ¹H NMR (300 MHz, CD₂Cl₂): δ (ppm) 1.20 (d, ³*J*_{H10/H9} = 6.2 Hz, 12H, H-10), 1.46 (m, 4H, H-3), 1.73 (m, 4H, H-2), 2.06 (m, 4H,



H-4), 4.20 (t, ${}^{3}J_{\text{H1/H2}} = 6.8$ Hz, 4H, H-1), 4.52 (sept, ${}^{3}J_{\text{H9/H10}} = 6.2$ Hz, 2H, H-9), 7.28 (m, 12H, H-7 and H-8), 7.39 (m, 8H, H-6). ${}^{13}C{}^{1}H$ NMR (75 MHz, CD₂Cl₂): δ (ppm) 22.9 (d, ${}^{2}J_{C3/P} = 14.9$ Hz, C-3), 26.7 (C-10), 28.2 (d, ${}^{1}J_{C4/P} = 14.9$ Hz, C-4), 35.6 (bs, C-2), 75.1 (bs, C-9), 77.0 (bs, C-1), 128.7 and 128.8 (C-7 and C-8), 133.0 (d, ${}^{2}J_{C6/P} = 18.4$ Hz, C-6), 139.7 (d, ${}^{1}J_{C5/P} = 14.2$ Hz, C-5). ${}^{31}P{}^{1}H$ NMR (121 MHz, CD₂Cl₂): δ (ppm) -16.5. Anal. Calcd. for C₃₈H₅₀O₄P₂Ti: C, 67.06; H, 7.40; P, 9.10. Found: C, 64.63; H, 6.99; P, 9.66. Despite many attempts, no better elemental analyses could be obtained.



Figure S24. NMR spectra of $[Ti(20)_2(OiPr)_2]$ in CD₂Cl₂. Top: ¹H NMR spectrum; middle: ³¹P{¹H} NMR spectrum; bottom ¹³C{¹H} NMR spectrum.

[Ti(4-diphenylphosphinobutoxy)₂(OnBu)₂] [Ti(20)₂(OnBu)₂].

The general procedure was applied with **20**·H (1.00 g, 3.90 mmol, 2.0 equiv.) and [Ti(O*n*Bu)₄] (0.66 g, 1.95 mmol, 1.0 equiv.), affording [Ti(**20**)₂(O*n*Bu)₂] as a yellow oil. ¹H NMR (300 MHz, CD₂Cl₂): δ (ppm) 0.89 (t, ³*J*_{H12/H11} = 7.6 Hz, 6H, H-12), 1.33 (m, 4H, H-11), 1.45 (m, 4H, H-3), 1.56



(m, 4H, H-10), 1.71 (m, 4H, H-2), 2.05 (t, ${}^{3}J_{H4/H3} = 6.5$ Hz, 4H, H-4), 4.24 (m, 8H, H-1 and H-9), 7.28 (m, 12H, H-7 and H-8), 7.39 (m, 8H, H-6). ${}^{13}C{}^{1}H$ NMR (75 MHz, CD₂Cl₂): δ (ppm) 14.3 (C-12), 19.5 (C-11), 22.9 (d, ${}^{2}J_{C3/P} = 16.8$ Hz, C-3), 28.3 (d, ${}^{1}J_{C4/P} = 11.6$ Hz, C-4), 35.4 (d, ${}^{3}J_{C2/P} = 12.0$ Hz, C-2), 36.2 (C-10), 75.1 and 75.5 (C-1 and C-9), 128.7 and 128.8 (C-7 and C-8), 133.0 (d, ${}^{2}J_{C6/P} = 18.4$ Hz, C-6), 139.7 (d, ${}^{1}J_{C5/P} = 14.1$ Hz, C-5). ${}^{31}P{}^{1}H{}$ NMR (121 MHz, CD₂Cl₂): δ (ppm) -16.4. Anal. Calcd. for C₄₀H₅₄O₄P₂Ti: C, 67.79; H, 7.68; P, 8.74. Found: C, 65.43; H, 7.45; P, 8.94. Despite many attempts, no better elemental analyses could be obtained.



Figure S25. NMR spectra of $[Ti(20)_2(OnBu)_2]$ in CD₂Cl₂. Top: ¹H NMR spectrum; middle: ³¹P{¹H} NMR spectrum; bottom ¹³C{¹H} NMR spectrum.

[Ti(*trans*-2-(diphenylphosphino)cyclohexyloxy)₂(O*i*Pr)₂] [Ti(21)₂(O*i*Pr)₂].

The general procedure was applied with **21**·H (0.50 g, 1.76 mmol, 2.0 equiv.) and $[Ti(OiPr)_4]$ (0.25 g, 0.88 mmol, 1.0 equiv.) leading to $[Ti(21)_2(OiPr)_2]$ as a white powder. ¹H NMR (300 MHz, CD₂Cl₂): δ (ppm) 0.95 (m, 2H, H-3a), 1.20 (m, 18H, H-4, H-6a and H-12), 1.70 (m, 6H, H-3b and H-5), 2.12 (m, 2H,



H-6b), 2.48 (m, 2H, H-2), 4.10 (m, 2H, H-1), 4.8 (sept, ${}^{3}J_{H11/H12} = 6.1$ Hz, 2H, H-11), 7.29 (m, 12H, H-9 and H-10), 7.47 (m, 8H, H-8). ${}^{13}C{}^{1}H$ NMR (75 MHz, CD₂Cl₂): δ (ppm) 23.5 (bs, C-5), 24.9 (bs, C-4), 25.7 (bs, C-3), 26.7 (C-12), 35.8 (bs, C-6), 43.2 (C-2), 76.9 (d, ${}^{2}J_{C1/P} = 19.6$ Hz, C-1), 83.4 (bs, C-11), 128.4 (2d, ${}^{3}J_{C9/P} = 8.2$ and 9.7 Hz, C-9), 128.5 (d, ${}^{3}J_{C2/P} = 67.2$ Hz, C-10), 135.0 and 133.0 (2d, ${}^{2}J_{C8/P} = 20.5$ and 17.7 Hz, C-8), 138.8 (C-7). ${}^{31}P{}^{1}H$ NMR (121 MHz, CD₂Cl₂): δ (ppm) -9.9 (m, see text).



Figure S26. NMR spectra of complex $[Ti(21)_2(OiPr)_2]$ in CD₂Cl₂. Top: ¹H NMR spectrum; middle: ¹³C{¹H} NMR spectrum; bottom: ³¹P{¹H} NMR spectrum (see text).

[Ti(2-(diphenylphosphino)benzyloxy)₂(OiPr)₂] [Ti(22)₂(OiPr)₂].

The general procedure was applied in dichloromethane with **22**·H (0.58 g, 1.76 mmol, 2.0 equiv.) and $[Ti(OiPr)_4]$ (0.28 g, 0.88 mmol, 1.0 equiv.), yielding $[Ti(22)_2(OiPr)_2]$ as an orange foam. The NMR analysis displayed complex, broad signals. ¹H NMR (300 MHz, CD₂Cl₂): δ (ppm) 1.09 (bs, 12H, H-12), 4.40



and 5.58 (2bs, 2H+2H, H-1); 5.47 (bs, 2H, H-11), 7.25 (m, 28H, H_{arom}). ¹³C{¹H} NMR (75 MHz, CD₂Cl₂): the broad peaks were not be assigned precisely, except the peak at 26.2 ppm (bs, C-12). δ (ppm) 74.6 (bs), 77.0 (bs), 126.9 (bs), 128.8 (m), 132.8 (bs), 134.3 (d, *J*_{C/P} = 21.2 Hz), 136.8 (d, *J*_{C/P} = 9.9 Hz). ³¹P{¹H} NMR (121 MHz, CD₂Cl₂): δ (ppm) -16.9 (bs), -18.0 (m) (the smaller signal was not unambiguously assigned).



Figure S27. NMR spectra of complex $[Ti(22)_2(OiPr)_2]$ in CD₂Cl₂. Top: ¹H NMR spectrum; middle: ¹³C{¹H} NMR spectrum; bottom: ³¹P{¹H} NMR spectrum (the smaller signal was not unambiguously assigned).

[Ti(3-methyl(phenyl)phosphinopropoxy)₂(OiPr)₂] [Ti(23)₂(OiPr)₂].

The general procedure was applied with **23**·H (0.73 g, 4.0 mmol, 2.0 equiv.) and $[Ti(OiPr)_4]$ (0.57 g, 7.00 mmol, 1.0 equiv.), leading to $[Ti(23)_2(OiPr)_2]$ as a colourless oil. ¹H NMR (300 MHz, CD₂Cl₂): δ (ppm) 1.20 (d, ³J_{H10/H9} = 6.1 Hz, 12H, H-10),



1.32 (d, ${}^{2}J_{H8/P} = 3.1$ Hz, 6H, H-8), 1.64 (m, 8H, H-2 and H-3), 4.25 and 4.15 (2bs, 3H+1H, H-1), 4.60 (bs, 2H, H-9), 7.33 (m, 6H, H-6 and H-7), 7.51 (m, 4H, H-5). ${}^{13}C\{{}^{1}H\}$ NMR (75 MHz, CD₂Cl₂): δ (ppm) 11.8 (d, ${}^{1}J_{C8/P} = 14.5$ Hz, C-8), 26.7 (C-10), 27.1 (d, ${}^{1}J_{C3/P} = 11.4$ Hz, C-3), 29.8 (d, ${}^{2}J_{C2/P} = 12.4$ Hz, C-2), 76.2 (d, ${}^{3}J_{C1/P} = 10.0$ Hz, C-1), 77.3 (C-9), 128.5 (C-7), 128.6 (d, ${}^{3}J_{C6/P} = 6.4$ Hz, C-6), 131.7 (d, ${}^{2}J_{C5/P} = 17.8$ Hz, C-5), 141.4 (d, ${}^{1}J_{C4/P} = 14.9$ Hz, C-4). ${}^{31}P\{{}^{1}H\}$ NMR (121 MHz, CD₂Cl₂): δ (ppm) -35.2 (bs).



Figure S28. NMR spectra of complex $[Ti(23)_2(OiPr)_2]$ in CD₂Cl₂. Top: ¹H NMR spectrum; middle: ¹³C{¹H} NMR spectrum; bottom: ³¹P{¹H} NMR spectrum (the smaller signals were not unambiguously assigned).

[Ti(3-diphenylphosphorylpropoxy)₂(OiPr)₂] [Ti(24)₂(OiPr)₂].

The general procedure was applied in dichloromethane with **24**·H (0.50 g, 1.9 mmol, 2.0 equiv.) and $[Ti(OiPr)_4]$ (0.27 g, 0.96 mmol, 1.0 equiv.), leading to $[Ti(24)_2(OiPr)_2]$ as a white foam. ¹H NMR (300 MHz, CD₂Cl₂): δ (ppm) 1.15 (m, 12H, H-



9), 1.74 (bs, 4H, H-2), 2.29 (bs, 4H, H-3), 3.65 and 4.53 (2bs, 1.5H+0.5H, H-8), 3.98 and 4.20 (2bs, 3H+1H, H-1), 7.42 (m, 12H, H-6 and H-7), 7.72 (m, 8H, H-5). ${}^{13}C{}^{1}H{}$ NMR (75 MHz, CD₂Cl₂): δ (ppm) 26.1, 26.4, 26.6 and 27.4 (4m, C-2, C-3 and C-9), 74.1 (bs, C-8), 76.7 (bs, C-1), 128.9 (d, ${}^{3}J_{C6/P} = 11.4$ Hz, C-6), 131.2 (d, ${}^{2}J_{C5/P} = 9.2$ Hz, C-5), 131.8 (C-7), 133.8 (d, ${}^{1}J_{C4/P} = 97.1$ Hz). ${}^{31}P{}^{1}H{}$ NMR (121 MHz, CD₂Cl₂): δ (ppm) 33.7 (bs), 27.3 (bs) (see text).



Figure S29. NMR spectra of complex $[Ti(24)_2(OiPr)_2]$ in CD₂Cl₂. Top: ¹H NMR spectrum; bottom: ¹³C{¹H} NMR spectrum.

[Ti(3-diphenylphosphorothioylpropoxy)2(OiPr)2] [Ti(25)2(OiPr)2].

The general procedure was applied in dichloromethane with **25**·H (1.00 g, 3.60 mmol, 2.0 equiv.) and $[Ti(OiPr)_4]$ (0.51 g, 1.8 mmol, 1.0 equiv.), yielding $[Ti(25)_2(OiPr)_2]$ as a white powder. ¹H NMR (300 MHz, CD₂Cl₂): δ (ppm) 1.13 (bs, 12H, H-10), 1.80 (bs, 4H, H-2), 2.46 (bs, 4H, H-3), 4.06 and 4.44 (2bs,



2H+2H, H-1), 4.19 (bs, 2H, H-9), 7.44 (m, 12H, H-7 and H-8), 7.81 (m, 8H, H-6). ¹³C{¹H} NMR (75 MHz, CD₂Cl₂): δ (ppm) 26.4 (d, ²*J*_{C2/P} = 43.7 Hz, C-2), 26.7 (C-9), 29.5 (d, ¹*J*_{C3/P} = 57.3 Hz, C-3), 75.1 (bs, C-8), 77.5 (bs, C-1), 131.4 (d, ³*J*_{C6/P} = 11.7 Hz, C-6), 131.4 (d, ²*J*_{C5/P} = 10.0 Hz, C-5), 131.7 (d, ⁴*J*_{C7/P} = 2.8 Hz, C-7), 133.6 (d, ³*J*_{C4/P} = 78.9 Hz). ³¹P{¹H} NMR (121 MHz, CD₂Cl₂): δ (ppm) 43.0. Anal. Calcd. for C₃₆H₄₆O₄P₂S₂Ti: C, 60.33; H, 6.47. Found: C, 58.47; H, 5.98. Despite many attempts, no better elemental analyses could be obtained.



Figure S30. NMR spectra of complex $[Ti(25)_2(OiPr)_2]$ in CD₂Cl₂. Top: ¹H NMR spectrum; middle: ¹³C{¹H} NMR spectrum; bottom: ³¹P{¹H} NMR spectrum.

3. Catalytic Set-Up



Figure S31. Equipment used for catalyst screening consisting of 6 parallelized 35 mL reactors (<u>www.top-industrie.com</u>)



Figure S32. Monitoring of a reference test with [Ti(O*i*Pr)₄]

4. Optimization of the Operating Conditions by Design of Experiments (DoE)

Entries **1-8** and **10-15** in Table 6 were used to build an order 2 model for the activity thanks to a multilinear regression.

$$y = a_0 + a_1x_1 + a_2x_2 + a_3x_3 + a_{11}x_1^2 + a_{22}x_2^2 + a_{33}x_3^2 + a_{12}x_1x_2 + a_{13}x_1x_3 + a_{23}x_2x_3$$

Despite various attempts, entry **9** generated an unsure response and was not used. The model generated led to a good R² value of 0.99 and was globally validated since m_0 - $\sigma_0 < a_0 < m_0 + \sigma_0$, where m_0 is the mean value of the activity at the centre and σ_0 is the standard deviation at the centre. Coefficients of the model are reported below as well as 3D-representations of the experimental domain (Figure S33).

<i>a</i> ₀	a 1	<i>a</i> ₂	<i>a</i> ₃	a 11	a 22	a 33	a ₁₂	a 13	a 23
11129	2414	912	3866	1082	-3481	-5401	2	1370	-2440



Figure S33. Example of surface response representation

5. Crystal Structures

The complex $[Ti(\mu-OPh)(OPh)_2(OiPr)(OHiPr)]_2$ was obtained following the general procedure described in Eq. 1 starting from $[Ti(OiPr)_4]$ and 2 equiv. of phenol in cyclohexane at 90 °C for 0.5 h. Removal of the solvent under vacuum gave a very viscous yellow to orange oil (1.00 g, 99.9%) which crystallized partially. Single crystals of $[Ti(\mu-OPh)(OPh)_2(OiPr)(OHiPr)]_2$ suitable for X-ray diffraction were manually extracted from this mixture.

Crystallographic details are provided in Table S1 and an ORTEP view in shown below in Figure S34.

In the centrosymmetric complex $[Ti(\mu-OPh)(OPh)_2(OiPr)(OHiPr)]_2$, each Ti centre is octahedrally coordinated by two bridging phenoxy ligands, one terminal phenoxy ligand trans to a μ -OPh and another cis to it, a OiPr ligand and a *i*PrOH molecule trans to the terminal OPh ligand. Intramolecular H-bonding interactions occur between the OH proton of the *i*PrOH molecule and the oxygen atom of the *syn* phenoxy ligand on the adjacent Ti centre. Owing to the presence of an inversion centre in the unit cell, another dinuclear complex is present, as shown in Figure S34. Table S1. Crystal data, data collection and structure refinement details for

 $[Ti(\mu-OPh)(OPh)_2(OiPr)(OHiPr)]_2.$

Compound code	pbpb100204_01_Ti
Chemical formula	$C_{48}H_{60}O_{10}Ti_2$
CCDC	2044622
$M_{ m r}$	892.76
Crystal system, space group	Triclinic, <i>P</i> ⁻¹
Temperature (K)	173
<i>a</i> , <i>b</i> , <i>c</i> (Å)	12.0624(6), 13.7104(6), 16.1106(8)
α, β, γ (°)	89.233(1), 68.582(1), 74.202(1)
$V(Å^3)$	2375.7 (2)
Ζ	2
Radiation type	Μο Κα
$\mu \text{ (mm}^{-1}\text{)}$	0.39
Crystal size (mm)	$0.26\times0.14\times0.12$
Data collection	
Diffractometer	Bruker APEX-II CCD
Absorption correction	Multi-scan SADABS
T_{\min}, T_{\max}	0.619, 0.746
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	28057, 10299, 6395
R _{int}	0.051
$(\sin \theta / \lambda)_{max} (\text{\AA}^{-1})$	0.639
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.052, 0.131, 1.02
No. of reflections	10299
No. of parameters	549
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta \rho_{max}, \Delta \rho_{min} (e \text{ Å}^{-3})$	0.77, -0.56

Computer programs: Bruker *APEX2*, Bruker *SAINT*, *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 1997), Bruker *SHELXTL*.



Figure S34. ORTEP views of both asymmetric units with partial labelling scheme of $[Ti(\mu - OPh)(OPh)_2(OiPr)(OHiPr)]_2$. Thermal ellipsoids include 50% of the electron density. Symmetry code for equivalent positions ('): -x, -y, -z or $\frac{1}{2}$ -x, -y, $\frac{1}{2}$ -z (symmetry centers of the space group *P*-1). Selected bond distances and angles: Ti₁-O₁ 2.0777(18), Ti₁'-O₁ 2.0387(17), Ti₁-O₂ 1.8203(19), Ti₁-O₃ 1.9189(17), Ti₁-O₄ 1.7592(19), Ti₁-O₅ 2.1583(19), Ti₂'-O₆ 2.0569(17), Ti₂-O₆ 2.0764(18), Ti₂-O₇ 1.8309(18), Ti₂-O₈ 1.9158(17), Ti₂-O₉ 1.7530(18), Ti₂-O₁₀ 2.1670(19), Ti₁···Ti₁' 3.3454(9), Ti₂···Ti₂' 3.3472(9) Å, Ti₁-O₁-Ti₁' 108.72(8), Ti₂-O₆-Ti₂' 108.16(8)° (for additional distances and angles, see the corresponding CIF file). Hydrogen bonds (dashed red lines): O₅'-H₅···O₃: 2.791(9) / 159.1(5)°, O₁₀'-H₁₀···O₈: 2.801(9) / 156.2(5)°.

Figure S35. ORTEP view with full labelling scheme of $[Ti(13)_2(OiPr)_2 \cdot 1/2(C_5H_{12})]$. Thermal ellipsoids include 50% of the electron density.

Figure S36. ORTEP view with full labelling scheme of $[Ti(13)_2(OnBu)_2]$. Thermal ellipsoids include 50% of the electron density. Symmetry code for equivalent positions ('): 1-x, y, $\frac{1}{2}$ -z. (*C*2 axis passing through the Ti atom).