A remarkable inversion of structure-activity dependence on imido N-substituents with varying co-ligand topology and the synthesis of a new borate-free zwitterionic polymerisation catalyst

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Supporting information: polymerisation activities and characterising data

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Characterising and room temperature polymerisation data for the catalyst library [Ti(NR){HC(Me$_2$pz)$_3$}Cl$_2$] (1-22)

The library was synthesised using parallel synthesis methodology as reported for the compounds [Ti(NR)(TACN)Cl$_2$] (**V**)[1] and characterised by HRMS or/and ^{1}H NMR spectroscopy in the first instance. Compound **3** has been characterised previously.[2] The compounds showing the most promising polymerisation performance (**6**, **15**, **16**, **20-22**) were fully characterised in the usual way. The poor performance catalyst **9** was also scaled up. The NMR data for samples of the six compounds prepared conventionally were exactly the same as for samples synthesised using parallel synthesis methodology. PE analysis was performed by RAPRA Technology.

Data for [Ti(N^{n}Bu){HC(Me$_2$pz)$_3$}Cl$_2$] (**1**): ^{1}H NMR (CD$_2$Cl$_2$, 300.2 MHz, 298 K): 7.76 (1H, s, HC(Me$_2$pz)$_3$), 6.12 (2H, s, 4-N$_2$C$_3$Me$_2$H *cis* to N$_{imido}$), 5.84 (1H, s, 4-N$_2$C$_3$Me$_2$H *trans* to N$_{imido}$), 3.27 (2H, t, ^{3}J = 7.2 Hz, NCH$_2$CH$_2$), 2.77 (6H, s, N$_2$C$_3$Me$_2$H *cis* to N$_{imido}$), 2.54 (6H, s, N$_2$C$_3$Me$_2$H *cis* to N$_{imido}$), 2.49 (3H, s, N$_2$C$_3$Me$_2$H *trans* to N$_{imido}$), 2.44 (3H, s, N$_2$C$_3$Me$_2$H *trans* to N$_{imido}$), 1.50-1.35 (4H, overlapping signals, NCH$_2$CH$_2$CH$_2$Me), 0.86 (3H, t, ^{3}J = 7.2 Hz, NCH$_2$CH$_2$CH$_2$Me). Productivity = 44 kg(PE).mol^{-1}.h^{-1}.bar^{-1}.

Data for [Ti(NAd){HC(Me$_2$pz)$_3$}Cl$_2$] (**2**): ^{1}H NMR (CD$_2$Cl$_2$, 300.2 MHz, 298 K): 7.75 (1H, s, HC(Me$_2$pz)$_3$), 6.13 (2H, s, 4-N$_2$C$_3$Me$_2$H *cis* to N$_{imido}$), 5.81 (1H, s, 4-N$_2$C$_3$Me$_2$H *trans* to N$_{imido}$), 2.88 (6H, s, N$_2$C$_3$Me$_2$H *cis* to N$_{imido}$), 2.53 (6H, s, N$_2$C$_3$Me$_2$H *cis* to N$_{imido}$), 2.50 (3H, s, N$_2$C$_3$Me$_2$H *trans* to N$_{imido}$), 2.42 (3H, s, N$_2$C$_3$Me$_2$H *trans* to N$_{imido}$), 1.90 (9H, app. s, Adamantyl H), 1.52 (6H, app. s, Adamantyl H). Productivity = 35 kg(PE).mol^{-1}.h^{-1}.bar^{-1}.

Data for [Ti(N^{t}Bu){HC(Me$_2$pz)$_3$}Cl$_2$] (**3**): ^{1}H NMR (CDCl$_3$, 500.0 MHz, 298 K): 7.76 (1H, s, HC(Me$_2$pz)$_3$), 6.08 (2H, s, 4-N$_2$C$_3$Me$_2$H *cis* to N$_{imido}$), 5.76 (1H, s, 4-N$_2$C$_3$Me$_2$H *trans* to N$_{imido}$), 2.87 (6H, s, 3-N$_2$C$_3$Me$_2$H *cis* to N$_{imido}$), 2.58 (3H, s, 3-N$_2$C$_3$Me$_2$H *trans* to N$_{imido}$), 2.52 (6H, s, 5-N$_2$C$_3$Me$_2$H *cis* to N$_{imido}$), 2.38 (3H, s, 5-N$_2$C$_3$Me$_2$H *trans* to N$_{imido}$), 1.20 (9H, s, ^{t}Bu). Productivity = 230

kg(PE).mol^{-1}.h^{-1}.bar^{-1}.

Data for [Ti(NCH$_2$Cy){HC(Me$_2$pz)$_3$}Cl$_2$] (**4**): ^{1}H NMR (CD$_2$Cl$_2$, 300.2 MHz, 298 K): 7.76 (1H, s, HC(Me$_2$pz)$_3$), 6.12 (2H, s, 4-N$_2$C$_3$Me$_2$H *cis* to N$_{imido}$), 5.83 (1H, s, 4-N$_2$C$_3$Me$_2$H *trans* to N$_{imido}$), 3.10 (2H, d, ^{3}J = 6.9 Hz, NCH$_2$), 2.77 (6H, s, N$_2$C$_3$Me$_2$H *cis* to N$_{imido}$), 2.53 (6H, s, N$_2$C$_3$Me$_2$H *cis* to N$_{imido}$), 2.49 (3H, s, N$_2$C$_3$Me$_2$H *trans* to N$_{imido}$), 2.49 (3H, s, N$_2$C$_3$Me$_2$H *trans* to N$_{imido}$), 2.05-1.95 (2H, m, Cy H), 1.76-1.58 (4H, m, Cy H), 1.36-1.04 (3H, m, Cy H), 1.00-0.84 (2H, m, Cy H). Productivity = 13 kg(PE).mol^{-1}.h^{-1}.bar^{-1}.

Data for [Ti(NCH$_2$Ph){HC(Me$_2$pz)$_3$}Cl$_2$] (**5**): ^{1}H NMR (CD$_2$Cl$_2$, 300.2 MHz, 298 K): 7.81 (1H, s, HC(Me$_2$pz)$_3$), 7.43 (2H, m, *o*-Ph), 7.23 (2H, t, ^{3}J = 6.9 Hz, *m*-Ph), 7.14 (1H, m, *p*-Ph), 6.10 (2H, s, 4-N$_2$C$_3$Me$_2$H *cis* to N$_{imido}$), 5.88 (1H, s, 4-N$_2$C$_3$Me$_2$H *trans* to N$_{imido}$), 4.68 (2H, s, NCH$_2$Ph), 2.62 (6H, s, N$_2$C$_3$Me$_2$H *cis* to N$_{imido}$), 2.56 (6H, s, N$_2$C$_3$Me$_2$H *cis* to N$_{imido}$), 2.55 (3H, s, N$_2$C$_3$Me$_2$H *trans* to N$_{imido}$), 2.47 (3H, s, N$_2$C$_3$Me$_2$H *trans* to N$_{imido}$). Productivity = 46 kg(PE).mol^{-1}.h^{-1}.bar^{-1}.

Data for [Ti(NCH(Me)Napthyl){HC(Me$_2$pz)$_3$}Cl$_2$] (**6**): ^{1}H NMR (CD$_2$Cl$_2$, 500.0 MHz, 298 K): 7.97 (1H, d, ^{3}J = 8.0 Hz, Napthyl H3), 7.91 (1H, d, ^{3}J = 7.0 Hz, Napthyl H10), 7.81 (1H, s, HC(Me$_2$pz)$_3$), 7.79 (1H, d, ^{3}J = 8.0 Hz, Napthyl H6), 7.64 (1H, d, ^{3}J = 8.0 Hz, Napthyl H8), 7.39 (1H, ddd, ^{3}J = 8.0 Hz, ^{3}J = 7.0 Hz, ^{4}J = 1.5 Hz, Napthyl H5), 7.34 (1H, ddd, ^{3}J = 8.0 Hz, ^{3}J = 7.0 Hz, ^{4}J = 1.5 Hz, Napthyl H4), 7.31 (1H, dd, ^{3}J = 8.0 Hz, ^{3}J = 7.0 Hz, Napthyl H9), 6.05 (1H, s, 4-N$_2$C$_3$Me$_2$H *cis* to N$_{imido}$), 6.04 (1H, s, 4-N$_2$C$_3$Me$_2$H *cis* to N$_{imido}$), 5.86 (1H, s, 4-N$_2$C$_3$Me$_2$H *trans* to N$_{imido}$), 5.60 (1H, q, ^{3}J = 7.0 Hz, NCH(Me)Ar), 2.54 (6H, s, 5-N$_2$C$_3$Me$_2$H *cis* to N$_{imido}$), 2.53 (3H, s, 3-N$_2$C$_3$Me$_2$H *trans* to N$_{imido}$ or 3-N$_2$C$_3$Me$_2$H *cis* to N$_{imido}$), 2.52 (3H, s, 3-N$_2$C$_3$Me$_2$H *trans* to N$_{imido}$ or 3-N$_2$C$_3$Me$_2$H *cis* to N$_{imido}$), 2.51 (3H, s, 3-N$_2$C$_3$Me$_2$H *cis* to N$_{imido}$), 2.43 (3H, s, 5-N$_2$C$_3$Me$_2$H *trans* to N$_{imido}$), 1.61 (1H, d, ^{3}J = 7.0 Hz, NCH(Me)Ar). ^{13}C-{^{1}H} NMR (CD$_2$Cl$_2$, 125.7 MHz, 298 K): 156.2 (3-N$_2$C$_3$Me$_2$H *cis* to N$_{imido}$), 156.0 (3-N$_2$C$_3$Me$_2$H *cis* to N$_{imido}$), 155.3 (3-N$_2$C$_3$Me$_2$H *trans* to N$_{imido}$), 143.0 (Napthyl C1), 139.8 (5-N$_2$C$_3$Me$_2$H *cis* to N$_{imido}$), 139.7 (5-N$_2$C$_3$Me$_2$H *cis* to N$_{imido}$), 138.2 (5-N$_2$C$_3$Me$_2$H *trans* to N$_{imido}$), 134.0 (Napthyl C7), 130.5 (Napthyl C2), 128.6 (Napthyl C6), 126.6 (Napthyl C8), 125.8 (Napthyl C9), 125.4 (Napthyl C4), 125.2 (Napthyl C5), 124.1 (Napthyl C3), 123.7 (Napthyl C10), 108.8 (4-N$_2$C$_3$Me$_2$H *trans* to N$_{imido}$), 108.4 (4-N$_2$C$_3$Me$_2$H *cis* to N$_{imido}$), 108.4 (4-N$_2$C$_3$Me$_2$H *cis* to N$_{imido}$), 70.9 (CH(Me)Ar), 67.8 (HC(Me$_2$pz)$_3$), 24.5 (CH(Me)Ar), 15.9 (3-N$_2$C$_3$Me$_2$H *cis* to N$_{imido}$), 15.7 (3-N$_2$C$_3$Me$_2$H *cis* to N$_{imido}$), 14.9 (3-N$_2$C$_3$Me$_2$H *trans* to N$_{imido}$), 11.4 (5-N$_2$C$_3$Me$_2$H *cis* to N$_{imido}$), 11.0 (5-N$_2$C$_3$Me$_2$H *trans* to N$_{imido}$). IR (KBr plates, cm^{-1}): 2922 (w, br), 1568 (m), 1462 (s), 1414 (m), 1392 (s), 1384 (s), 1306 (m), 1262 (s), 1198 (w), 1044 (m), 912 (w), 860 (m), 804 (w), 782 (s), 700 (m). Anal. Found (calcd. for C$_{28}$H$_{33}$Cl$_2$N$_7$Ti·0.1C$_{16}$H$_{22}$Cl$_2$N$_6$OTi): C, 56.2 (56.5); H, 5.7 (5.6); N, 16.4 (16.9) %. Productivity = 150 kg(PE).mol^{-1}.h^{-1}.bar^{-1}.

Data for [Ti(N-2-hydroindanyl){HC(Me_2pz)$_3$}Cl_2] (**7**): ^{1}H NMR (CD_2Cl_2, 300.2 MHz, 298 K): 7.78 (1H, s, HC(Me_2pz)$_3$), 7.24 (1H, d, ^{3}J = 7.5 Hz, Aryl H), 7.10-7.02 (2H, overlapping signals, Aryl H), 6.96 (1H, t, ^{3}J = 6.9 Hz, Aryl H), 6.12 (1H, s, 4-$N_2C_3Me_2H$ *cis* to N_{imido}), 5.98 (1H, s, 4-$N_2C_3Me_2H$ *cis* to N_{imido}), 5.86 (1H, s, 4-$N_2C_3Me_2H$ *trans* to N_{imido}), 5.06 (1H, t, ^{3}J = 8.1 Hz, NCH), 2.87-2.80 (2H, overlapping signals, cyclopentane H), 2.64 (3H, s, $N_2C_3Me_2H$), 2.56 (3H, s, $N_2C_3Me_2H$), 2.53 (6H, s, $N_2C_3Me_2H$), 2.45 (3H, s, $N_2C_3Me_2H$), 2.32 (3H, s, $N_2C_3Me_2H$), 2.29-2.09 (2H, overlapping signals, cyclopentane H).

Productivity = 27 kg(PE).mol^{-1}.h^{-1}.bar^{-1}.

Data for [Ti(N-napthyl){HC(Me_2pz)$_3$}Cl_2] (**8**): ^{1}H NMR (CD_2Cl_2, 300.2 MHz, 298 K): 8.93 (1H, m, Aryl H), 7.89 (1H, s, HC(Me_2pz)$_3$), 7.66 (1H, m, Aryl H), 7.40-7.30 (2H, overlapping signals, Aryl H), 7.21 (1H, d, ^{3}J = 8.4 Hz, Aryl H), 7.09 (1H, t, ^{3}J = 7.8 Hz, Aryl H), 6.75 (1H, dd, ^{3}J = 7.2 Hz, ^{4}J = 1.0 Hz, Aryl H), 6.08 (2H, s, 4-$N_2C_3Me_2H$ *cis* to N_{imido}), 5.95 (1H, s, 4-$N_2C_3Me_2H$ *trans* to N_{imido}), 2.65 (3H, s, $N_2C_3Me_2H$ *trans* to N_{imido}), 2.59 (6H, s, $N_2C_3Me_2H$ *cis* to N_{imido}), 2.51 (6H, s, $N_2C_3Me_2H$ *cis* to N_{imido}), 2.48 (3H, s, $N_2C_3Me_2H$ *trans* to N_{imido}). HRMS found (calcd. for $C_{26}H_{29}Cl_2N_7Ti$): *m/z* = 557.1351 (557.1341). Productivity = 9 kg(PE).mol^{-1}.h^{-1}.bar^{-1}.

Data for [Ti(NPh){HC(Me_2pz)$_3$}Cl_2] (**9**): ^{1}H NMR (CD_2Cl_2, 500.0 MHz, 298 K): 7.85 (1H, s, HC(Me_2pz)$_3$), 7.02 (2H, dd, ^{3}J = 8.5 Hz, ^{3}J = 7.5 Hz, *m*-Ph), 6.83 (2H, dd, ^{3}J = 8.5 Hz, ^{4}J = 1.5 Hz, *o*-Ph), 6.74 (1H, tt, ^{3}J = 7.5 Hz, ^{4}J = 1.0 Hz, *p*-Ph), 6.10 (2H, s, 4-$N_2C_3Me_2H$ *cis* to N_{imido}), 5.93 (1H, s, 4-$N_2C_3Me_2H$ *trans* to N_{imido}), 2.59 (9H, overlapping singlets, 5-$N_2C_3Me_2H$ *cis* to N_{imido} and 3-$N_2C_3Me_2H$ *trans* to N_{imido}), 2.55 (6H, s, 3-$N_2C_3Me_2H$ *cis* to N_{imido}), 2.48 (3H, s, 5-$N_2C_3Me_2H$ *trans* to N_{imido}). ^{13}C-{^{1}H} NMR (CD_2Cl_2, 125.7 MHz, 298 K): 159.8 (*i*-Ph), 156.5 (3-$N_2C_3Me_2H$ *cis* to N_{imido}), 155.7 (3-$N_2C_3Me_2H$ *trans* to N_{imido}), 139.8 (5-$N_2C_3Me_2H$ *cis* to N_{imido}), 138.5 (5-$N_2C_3Me_2H$ *trans* to N_{imido}), 128.2 (*m*-Ph), 123.8 (*o*-Ph), 121.5 (*p*-Ph), 108.8 (4-$N_2C_3Me_2H$ *trans* to N_{imido}), 108.5 (4-$N_2C_3Me_2H$ *cis* to N_{imido}), 67.8 (HC(Me_2pz)$_3$), 15.6 (3-$N_2C_3Me_2H$ *cis* to N_{imido}), 14.9 (3-$N_2C_3Me_2H$ *trans* to N_{imido}), 11.3 (5-$N_2C_3Me_2H$ *cis* to N_{imido}), 11.0 (5-$N_2C_3Me_2H$ *trans* to N_{imido}). IR (KBr plates, cm^{-1}): 2916 (w, br), 1568 (m), 1474 (s), 1462 (s), 1412 (m), 1384 (s), 1306 (s), 1264 (s), 1110 (w), 1040 (m), 978 (w), 914 (m), 862 (m), 800 (w), 762 (m), 704 (s), 680 (m), 526 (w). Anal. Found (calcd. for $C_{22}H_{27}Cl_2N_7Ti \cdot 0.5C_6H_6$): C, 54.7 (54.9); H, 5.8 (5.5); N, 17.8 (17.9) %. HRMS found (calcd. for $C_{22}H_{27}Cl_2N_7Ti$): *m/z* = 507.1175 (507.1184). Productivity = 40 kg(PE).mol^{-1}.h^{-1}.bar^{-1}.

Data for [Ti(N-2-C_6H_4Me){HC(Me_2pz)$_3$}Cl_2] (**10**): ^{1}H NMR (CD_2Cl_2, 300.2 MHz, 298 K): 7.85 (1H, s, HC(Me_2pz)$_3$), 6.91 (1H, dd, ^{3}J = 7.2 Hz, ^{4}J = 1.5 Hz, C_6H_4Me), 6.77 (1H, td, ^{3}J = 7.2 Hz, ^{4}J = 1.5 Hz, C_6H_4Me), 6.64-6.54 (2H, overlapping signals, C_6H_4Me), 6.09 (2H, s, 4-$N_2C_3Me_2H$ *cis* to N_{imido}) 5.92 (1H, s, 4-$N_2C_3Me_2H$ *trans* to N_{imido}), 2.60 (3H, s, $N_2C_3Me_2H$ *trans* to N_{imido}), 2.57 (6H, s, $N_2C_3Me_2H$ *cis*

to N_{imido}), 2.55 (6H, s, $N_2C_3\underline{Me}_2H$ *cis* to N_{imido}), 2.49 (3H, s, $N_2C_3\underline{Me}_2H$ *trans* to N_{imido}), 2.46 (3H, s, $C_6H_4\underline{Me}$). HRMS found (calcd. for $C_{23}H_{29}Cl_2N_7Ti$): *m/z* = 521.1363 (521.1341). Productivity = 14 kg(PE).mol^{-1}.h^{-1}.bar^{-1}.

Data for [Ti(N-2-C_6H_4Cl){$HC(Me_2pz)_3$}Cl_2] (**11**): ^{1}H NMR (CD_2Cl_2, 300.2 MHz, 298 K): 7.84 (1H, s, $\underline{H}C(Me_2pz)_3$), 7.36 (1H, m, $C_6\underline{H}_4Cl$), 7.05-6.99 (2H, overlapping signals, $C_6\underline{H}_4Cl$), 6.67 (1H, ddd, ^3J = 7.2 Hz, ^3J = 7.2 Hz, ^4J = 2.0 Hz, $C_6\underline{H}_4Cl$), 6.07 (2H, s, 4-$N_2C_3Me_2\underline{H}$ *cis* to N_{imido}), 5.95 (1H, s, 4-$N_2C_3Me_2\underline{H}$ *trans* to N_{imido}), 2.62 (3H, s, $N_2C_3\underline{Me}_2H$ *trans* to N_{imido}), 2.56 (6H, s, $N_2C_3\underline{Me}_2H$ *cis* to N_{imido}), 2.55 (6H, s, $N_2C_3\underline{Me}_2H$ *cis* to N_{imido}), 2.50 (3H, s, $N_2C_3\underline{Me}_2H$ *trans* to N_{imido}). HRMS found (calcd. for $C_{22}H_{26}Cl_3N_7Ti$): *m/z* = 541.0792 (541.0795). Productivity = 17 kg(PE).mol^{-1}.h^{-1}.bar^{-1}.

Data for [Ti(N-2-C_6H_4Br){$HC(Me_2pz)_3$}Cl_2] (**12**): ^{1}H NMR (CD_2Cl_2, 300.2 MHz, 298 K): 7.84 (1H, s, $\underline{H}C(Me_2pz)_3$), 7.38 (1H, dd, ^3J = 7.5 Hz, ^4J = 1.5 Hz, $C_6\underline{H}_4Br$), 7.20 (1H, dd, ^3J = 7.5 Hz, ^4J = 1.5 Hz, $C_6\underline{H}_4Br$), 7.08 (1H, app. td, ^3J = 7.5 Hz, ^4J = 1.5 Hz, $C_6\underline{H}_4Br$), 6.60 (1H, app. td, ^3J = 7.5 Hz, ^4J = 1.5 Hz, $C_6\underline{H}_4Br$), 6.08 (2H, s, 4-$N_2C_3Me_2\underline{H}$ *cis* to N_{imido}), 5.95 (1H, s, 4-$N_2C_3Me_2\underline{H}$ *trans* to N_{imido}), 2.62 (3H, s, $N_2C_3\underline{Me}_2H$ *trans* to N_{imido}), 2.57 (12H, overlapping singlets, 3-$N_2C_3\underline{Me}_2H$ and 5-$N_2C_3\underline{Me}_2H$ *cis* to N_{imido}), 2.50 (3H, s, $N_2C_3\underline{Me}_2H$ *trans* to N_{imido}). HRMS found (calcd. for $C_{22}H_{26}BrCl_2N_7Ti$): *m/z* = 585.0306 (585.0290). Productivity = 22 kg(PE).mol^{-1}.h^{-1}.bar^{-1}.

Data for [Ti(N-2-C_6H_4Ph){$HC(Me_2pz)_3$}Cl_2] (**13**): ^{1}H NMR (CD_2Cl_2, 300.2 MHz, 298 K): 7.83 (1H, s, $\underline{H}C(Me_2pz)_3$), 7.46-7.40 (3H, overlapping multiplets, Aryl H), 7.06-6.94 (3H, overlapping multiplets, Aryl H), 6.90-6.78 (3H, overlapping multiplets, Aryl H), 5.99 (2H, s, 4-$N_2C_3Me_2\underline{H}$ *cis* to N_{imido}), 5.89 (1H, s, 4-$N_2C_3Me_2\underline{H}$ *trans* to N_{imido}), 2.59 (3H, s, $N_2C_3\underline{Me}_2H$ *trans* to N_{imido}), 2.57 (6H, s, $N_2C_3\underline{Me}_2H$ *cis* to N_{imido}), 2.47 (6H, s, $N_2C_3\underline{Me}_2H$ *cis* to N_{imido}), 2.36 (3H, s, $N_2C_3\underline{Me}_2H$ *trans* to N_{imido}). HRMS found (calcd. for $C_{28}H_{30}ClN_7Ti$ - HCl): *m/z* = 547.1749 (547.1731). Productivity = 18 kg(PE).mol^{-1}.h^{-1}.bar^{-1}.

Data for [Ti(N-2-$C_6H_4{}^iPr$){$HC(Me_2pz)_3$}Cl_2] (**14**): ^{1}H NMR (CD_2Cl_2, 300.2 MHz, 298 K): 7.86 (1H, s, $\underline{H}C(Me_2pz)_3$), 7.03-7.00 (1H, m, $C_6\underline{H}_4{}^iPr$), 6.72-6.62 (2H, overlapping signals, $C_6\underline{H}_4{}^iPr$), 6.37-6.32 (1H, m, $C_6\underline{H}_4{}^iPr$), 6.10 (2H, s, 4-$N_2C_3Me_2\underline{H}$ *cis* to N_{imido}), 5.92 (1H, s, 4-$N_2C_3Me_2\underline{H}$ *trans* to N_{imido}), 4.22 (1H, septet, ^3J = 6.9 Hz, $C\underline{H}Me_2$), 2.60 (3H, s, $N_2C_3\underline{Me}_2H$ *trans* to N_{imido}), 2.58 (6H, s, $N_2C_3\underline{Me}_2H$ *cis* to N_{imido}), 2.54 (6H, s, $N_2C_3\underline{Me}_2H$ *cis* to N_{imido}), 2.49 (3H, s, $N_2C_3\underline{Me}_2H$ *trans* to N_{imido}), 1.31 (6H, d, ^3J = 6.9 Hz, $CH\underline{Me}_2$). Productivity = 10 kg(PE).mol^{-1}.h^{-1}.bar^{-1}.

Data for [Ti(N-2-$C_6H_4CF_3$){$HC(Me_2pz)_3$}Cl_2] (**15**): ^{1}H NMR (CD_2Cl_2, 500.0 MHz, 298 K): 7.86 (1H, s, $\underline{H}C(Me_2pz)_3$), 7.37 (1H, m, 3-$C_6H_4CF_3$), 7.36-7.25 (2H, overlapping signals, 4-$C_6H_4CF_3$ and 6-$C_6H_4CF_3$), 6.80 (1H, t, ^3J = 7.5 Hz, 5-$C_6H_4CF_3$), 6.10 (2H, s, 4-$N_2C_3Me_2\underline{H}$ *cis* to N_{imido}), 5.93 (1H, s, 4-$N_2C_3Me_2\underline{H}$ *trans* to N_{imido}), 2.60 (3H, s, 3-$N_2C_3\underline{Me}_2H$ *trans* to N_{imido}), 2.56 (6H, s, 5-$N_2C_3\underline{Me}_2H$ *cis* to N_{imido}), 2.50 (6H, s, 3-$N_2C_3\underline{Me}_2H$ *cis* to N_{imido}), 2.47 (3H, s, 5-$N_2C_3\underline{Me}_2H$ *trans* to N_{imido}). ^{13}C-{^{1}H} NMR (CD_2Cl_2, 125.7

MHz, 298 K): 156.7 (3-$N_2\underline{C}_3Me_2H$ *cis* to N_{imido} overlapping with *i*-$C_6H_4CF_3$), 155.7 (3-$N_2\underline{C}_3Me_2H$ *trans* to N_{imido}), 139.6 (5-$N_2\underline{C}_3Me_2H$ *cis* to N_{imido}), 138.5 (5-$N_2\underline{C}_3Me_2H$ *trans* to N_{imido}), 132.0 (4-$C_6H_4CF_3$), 125.1 (q, ^2J = 5.4 Hz, 3-$C_6H_4CF_3$ overlapping with 6-$C_6H_4CF_3$), 120.3 (5-$C_6H_4CF_3$), 108.8 (4-$N_2\underline{C}_3Me_2H$ *trans* to N_{imido}), 108.5 (4-$N_2\underline{C}_3Me_2H$ *cis* to N_{imido}), 67.8 ($H\underline{C}(Me_2pz)_3$), 15.6 (3-$N_2C_3\underline{Me}_2H$ *cis* to N_{imido}), 14.9 (3-$N_2C_3\underline{Me}_2H$ *trans* to N_{imido}), 11.4 (5-$N_2C_3\underline{Me}_2H$ *cis* to N_{imido}), 11.0 (5-$N_2C_3\underline{Me}_2H$ *trans* to N_{imido}). ^{19}F NMR (CD_2Cl_2, 282.4, 298K): -60.4 (CF_3). IR (KBr plates, cm^{-1}): 2918 (w, br), 1590 (w), 1568 (m), 1464 (s,), 1446 (s), 1414 (m), 1394 (m), 1384 (m), 1338 (s), 1308 (s), 1268 (m), 1160 (m), 1126 (m), 1048 (m), 1028 (m), 966 (w), 862 (m), 800 (w), 760 (w), 708 (m), 676 (m). Anal. Found (calcd. for $C_{23}H_{26}Cl_2F_3N_7Ti\cdot0.6C_6H_6$): C, 51.5 (51.3); H, 5.1 (4.8); N, 15.5 (15.7) %. HRMS found (calcd. for $C_{23}H_{26}Cl_2F_3N_7Ti$): *m/z* = 575.1061 (575.1058). Productivity = 1,170 $kg(PE).mol^{-1}.h^{-1}.bar^{-1}$.

Data for [Ti(N-2-$C_6H_4{}^tBu$){$HC(Me_2pz)_3$}Cl_2] (**16**): ^1H NMR (CD_2Cl_2, 500.0 MHz, 298 K): 7.92 (1H, s, $\underline{H}C(Me_2pz)_3$), 7.08 (1H, dd, ^3J = 7.5 Hz, ^5J = 2.0 Hz, 3-$C_6H_4{}^tBu$), 6.59 (1H, td, ^3J = 7.5 Hz, ^5J = 1.5 Hz, 4-$C_6H_4{}^tBu$), 6.55 (1H, td, ^3J = 7.5 Hz, ^5J = 1.5 Hz, 5-$C_6H_4{}^tBu$), 6.09 (2H, s, 4-$N_2C_3Me_2\underline{H}$ *cis* to N_{imido}), 5.94 (1H, dd, ^3J = 7.5 Hz, ^5J = 2.0 Hz, 6-$C_6H_4{}^tBu$), 5.94 (1H, s, 4-$N_2C_3Me_2\underline{H}$ *trans* to N_{imido}), 2.59 (6H, s, 5-$N_2C_3\underline{Me}_2H$ *cis* to N_{imido}), 2.57 (3H, s, 3-$N_2C_3\underline{Me}_2H$ *trans* to N_{imido}), 2.49 (3H, s, 5-$N_2C_3\underline{Me}_2H$ *trans* to N_{imido}), 2.41 (6H, s, 3-$N_2C_3\underline{Me}_2H$ *cis* to N_{imido}), 1.70 (9H, s, ^tBu). ^{13}C-{^1H} NMR (CD_2Cl_2, 125.7 MHz, 298 K): 158.6 (*i*-$C_6H_4{}^tBu$), 156.4 (3-$N_2\underline{C}_3Me_2H$ *cis* to N_{imido}), 155.8 (3-$N_2\underline{C}_3Me_2H$ *trans* to N_{imido}), 140.8 (quartenary, 2-$C_6H_4{}^tBu$), 139.6 (5-$N_2\underline{C}_3Me_2H$ *cis* to N_{imido}), 138.5 (5-$N_2\underline{C}_3Me_2H$ *trans* to N_{imido}), 131.4 (6-$C_6H_4{}^tBu$), 125.3 (3- or 5-$C_6H_4{}^tBu$), 125.2 (3- or 5-$C_6H_4{}^tBu$), 121.1 (4-$C_6H_4{}^tBu$), 108.8 (4-$N_2\underline{C}_3Me_2H$ *trans* to N_{imido} and 4-$N_2\underline{C}_3Me_2H$ *cis* to N_{imido}), 67.8 ($H\underline{C}(Me_2pz)_3$), 35.6 ($\underline{C}Me_3$), 31.0 ($C\underline{Me}_3$), 15.1 (3-$N_2C_3\underline{Me}_2H$ *trans* to N_{imido}), 15.0 (3-$N_2C_3\underline{Me}_2H$ *cis* to N_{imido}), 11.4 (5-$N_2C_3\underline{Me}_2H$ *cis* to N_{imido}), 11.0 (5-$N_2C_3\underline{Me}_2H$ *trans* to N_{imido}). IR (KBr plates, cm^{-1}): 2924 (w, br), 1568 (m), 1466 (s), 1424 (m), 1414 (m), 1392 (m), 1380 (m), 1308 (s), 1270 (s), 1042 (m), 962 (w), 864 (m), 792 (w), 758 (m), 706 (s), 686 (m). Anal. Found (calcd. for $C_{26}H_{35}Cl_2N_7Ti\cdot0.5C_6H_6$): C, 57.3 (57.7); H, 6.3 (6.4), N, 16.0 (16.3) %. HRMS found (calcd. for $C_{26}H_{35}Cl_2N_7Ti$): *m/z* = 563.1798 (563.1810). Productivity = 930 $kg(PE).mol^{-1}.h^{-1}.bar^{-1}$.

Data for [Ti(N-3,5-$C_6H_3(CF_3)_2$){$HC(Me_2pz)_3$}Cl_2] (**17**): ^1H NMR (CD_2Cl_2, 300.2 MHz, 298 K): 7.84 (1H, s, $\underline{H}C(Me_2pz)_3$), 7.25 (1H, br. s, $C_6\underline{H}_3(CF_3)_2$), 7.21 (1H, br. s, $C_6\underline{H}_3(CF_3)_2$), 7.06 (1H, br. s, $C_6\underline{H}_3(CF_3)_2$), 6.12 (2H, s, 4-$N_2C_3Me_2\underline{H}$ *cis* to N_{imido}), 5.97 (1H, s, 4-$N_2C_3Me_2\underline{H}$ *trans* to N_{imido}), 2.63 (3H, s, $N_2C_3\underline{Me}_2H$ *trans* to N_{imido}), 2.58 (6H, s, $N_2C_3\underline{Me}_2H$ *cis* to N_{imido}), 2.57 (6H, s, $N_2C_3\underline{Me}_2H$ *cis* to N_{imido}), 2.51 (3H, s, $N_2C_3\underline{Me}_2H$ *trans* to N_{imido}). ^{19}F NMR data (CD_2Cl_2, 282.4 MHz, 298 K): -63.7 (2F, app. s, CF_3), -64.0 (1F, app. s, CF_3). HRMS found (calcd. for $C_{24}H_{25}Cl_2F_6N_7Ti$): *m/z* = 643.0930 (643.0932). Productivity = 20 $kg(PE).mol^{-1}.h^{-1}.bar^{-1}$.

Data for [Ti(NC$_6$F$_5$){HC(Me$_2$pz)$_3$}Cl$_2$] (**18**): ^{1}H NMR (CDCl$_3$, 500.0 MHz, 298 K): 7.85 (1H, s, HC(Me$_2$pz)$_3$), 6.05 (2H, s, 4-N$_2$C$_3$Me$_2$H *cis* to N$_{imido}$), 5.92 (1H, s, 4-N$_2$C$_3$Me$_2$H *trans* to N$_{imido}$), 2.68 (3H, s, 3-N$_2$C$_3$Me$_2$H *trans* to N$_{imido}$), 2.57 (6H, s, 5-N$_2$C$_3$Me$_2$H *cis* to N$_{imido}$), 2.55 (6H, s, 3-N$_2$C$_3$Me$_2$H *cis* to N$_{imido}$), 2.48 (3H, s, 5-N$_2$C$_3$Me$_2$H *trans* to N$_{imido}$). ^{19}F NMR (CDCl$_3$, 500.0 MHz, 298 K): -157.6 (1F, *o*-C$_6$F$_5$), -168.8 (2F, C$_6$F$_5$), -169.7 (2F, C$_6$F$_5$). HRMS found (calcd. for C$_{22}$H$_{22}$Cl$_2$F$_5$N$_7$Ti): *m/z* = 597.0728 (597.0713). Productivity = 40 kg(PE).mol^{-1}.h^{-1}.bar^{-1}.

Data for [Ti(N-2,4,6-C$_6$H$_2$F$_3$){HC(Me$_2$pz)$_3$}Cl$_2$] (**19**): ^{1}H NMR (CD$_2$Cl$_2$, 300.2 MHz, 298 K): 7.84 (1H, s, HC(Me$_2$pz)$_3$), 6.42 (2H, dd, ^{3}J = 8.1Hz, ^{3}J = 9 Hz, *m*-C$_6$H$_2$F$_3$), 6.08 (2H, s, 4-N$_2$C$_3$Me$_2$H *cis* to N$_{imido}$), 5.95 (1H, s, 4-N$_2$C$_3$Me$_2$H *trans* to N$_{imido}$), 2.62 (3H, s, N$_2$C$_3$Me$_2$H *trans* to N$_{imido}$), 2.56 (6H, s, N$_2$C$_3$Me$_2$H *cis* to N$_{imido}$), 2.55 (6H, s, N$_2$C$_3$Me$_2$H *cis* to N$_{imido}$), 2.36 (3H, s, N$_2$C$_3$Me$_2$H *trans* to N$_{imido}$). ^{19}F NMR (CD$_2$Cl$_2$, 282.4 MHz, 298 K): -118.3 (1F, t, ^{4}J = 8.7 Hz, *p*-C$_6$H$_2$F$_3$), -121.0 (2F, d, ^{4}J = 8.7 Hz, *m*-C$_6$H$_2$F$_3$). HRMS found (calcd. for C$_{22}$H$_{24}$Cl$_2$F$_3$N$_7$Ti): *m/z* = 561.0904 (561.0902). Productivity = 36 kg(PE).mol^{-1}.h^{-1}.bar^{-1}.

Data for [Ti(N-2,6-C$_6$H$_3$Me$_2$){HC(Me$_2$pz)$_3$}Cl$_2$] (**20**): ^{1}H NMR (CD$_2$Cl$_2$, 500.0 MHz, 298 K): 7.86 (1H, s, HC(Me$_2$pz)$_3$), 6.81 (1H, d, ^{3}J = 7.4 Hz, *m*-C$_6$H$_3$Me$_2$ dn), 6.60(1H, d, ^{3}J = 7.5 Hz, *m*-C$_6$H$_3$Me$_2$ u), 6.47 (1H, app. t, ^{3}J = 7.5 Hz, *p*-C$_6$H$_3$Me$_2$), 6.11 (2H, s, 4-N$_2$C$_3$Me$_2$H *trans* to Cl), 5.93 (1H, s, 4-N$_2$C$_3$Me$_2$H *trans* to N^{t}Bu), 2.99 (3H, s, C$_6$H$_3$Me$_2$ dn), 2.61 (3H, s, 3-N$_2$C$_3$Me$_2$H *trans* to N^{t}Bu), 2.59 (6H, s, 5-N$_2$C$_3$Me$_2$H *trans* to Cl), 2.58 (6H, s, 3-N$_2$C$_3$Me$_2$H *trans* to Cl), 2.50 (3H, s, 5-N$_2$C$_3$Me$_2$H *trans* to N^{t}Bu), 1.63 (3H, s, C$_6$H$_3$Me$_2$ u). ^{13}C-{^{1}H} NMR (CD$_2$Cl$_2$, 125.7 MHz, 298 K): 158.4 (*i*-C$_6$H$_3$Me$_2$), 156.6 (3-N$_2$C$_3$Me$_2$H *trans* to Cl), 155.6 (3-N$_2$C$_3$Me$_2$H *trans* to N-2,6-C$_6$H$_3$Me$_2$), 139.7 (5-N$_2$C$_3$Me$_2$H *trans* to Cl), 138.3 (5-N$_2$C$_3$Me$_2$H *trans* to N-2,6-C$_6$H$_3$Me$_2$), 137.0 (*o*-C$_6$H$_3$Me$_2$ dn), 131.4 (*o*-C$_6$H$_3$Me$_2$ u), 127.2 (*m*-C$_6$H$_3$Me$_2$ dn), 126.6 (*m*-C$_6$H$_3$Me$_2$ u), 120.6 (*p*-C$_6$H$_3$Me$_2$), 108.8 (4-N$_2$C$_3$Me$_2$H *trans* to N-2,6-C$_6$H$_3$Me$_2$), 108.4 (4-N$_2$C$_3$Me$_2$H *trans* to Cl), 67.8 (HC(Me$_2$pz)$_3$), 20.0 (C$_6$H$_3$Me$_2$ dn), 17.4 (C$_6$H$_3$Me$_2$ u), 15.5 (3-N$_2$C$_3$Me$_2$H *trans* to Cl), 14.9 (3-N$_2$C$_3$Me$_2$H *trans* to N-2,6-C$_6$H$_3$Me$_2$), 11.3 (5-N$_2$C$_3$Me$_2$H *trans* to Cl), 11.0 (5-N$_2$C$_3$Me$_2$H *trans* to N-2,6-C$_6$H$_3$Me$_2$). IR (NaCl plates, Nujol, cm^{-1}): 1567(s), 1512(w), 1415(m), 1392(m), 1308(s), 1272(s), 1159(w), 1095(m), 1040(m), 978(w), 915(m), 866(m), 820(m), 809(m), 752(w), 706(m), 633(w), 583(w), 412(w). Anal. Found (calcd. for C$_{24}$H$_{31}$N$_7$Cl$_2$Ti·0.4CH$_2$Cl$_2$): C, 51.6 (51.4); H, 6.0 (5.6); N, 17.1 (17.2) %. EI-MS *m/z* = 535 (40 %) [M]$^+$, 416 (10 %) [M – N-2,6-C$_6$H$_3$Me$_2$]$^+$. Productivity = 900 kg(PE).mol^{-1}.h^{-1}.bar^{-1}.

Data for [Ti(N-2,6-C$_6$H$_3$^{i}Pr$_2$){HC(Me$_2$pz)$_3$}Cl$_2$] (**21**): ^{1}H NMR (CD$_2$Cl$_2$, 500.0 MHz, 298 K): 7.89 (1H, s, HC(Me$_2$pz)$_3$), 6.92 (1H, dd, ^{3}J = 7.2 Hz, ^{4}J = 2.0 Hz, *m*-C$_6$H$_3$^{i}Pr$_2$ dn), 6.68 (1H, dd, ^{3}J = 7.9, Hz ^{4}J = 1.9 Hz, *m*-C$_6$H$_3$^{i}Pr$_2$ u), 6.66 (1H, app. t, ^{3}J = 7.4 Hz, *p*-C$_6$H$_3$^{i}Pr$_2$), 6.13 (2H, s, 4-N$_2$C$_3$Me$_2$H *trans* to Cl), 5.89 (1H, s, 4-N$_2$C$_3$Me$_2$H *trans* to N-2,6-C$_6$H$_3$^{i}Pr$_2$), 4.98 (1H, sept., ^{3}J = 6.9 Hz, C$_6$H$_3$(CHMe$_2$)$_2$ dn), 2.85 (1H, sept, ^{3}J = 6.9 Hz, C$_6$H$_3$(CHMe$_2$)$_2$ u), 2.58 (6H, s, 5-N$_2$C$_3$Me$_2$H *trans* to Cl), 2.57 (6H, s, 3-N$_2$C$_3$Me$_2$H *trans* to Cl), 2.56 (3H, s, 3-N$_2$C$_3$Me$_2$H *trans* to N-2,6-C$_6$H$_3$^{i}Pr$_2$), 2.45 (3H, s, 5-N$_2$C$_3$Me$_2$H *trans* to N-2,6-C$_6$H$_3$^{i}Pr$_2$), 1.35 (6H, d,

^{3}J = 6.9 Hz, $C_6H_3(CH\underline{Me}_2)_2$ dn), 0.61 (6H, d, ^{3}J = 6.8 Hz, $C_6H_3(CH\underline{Me}_2)_2$ u). ^{13}C-{^{1}H} NMR (CD_2Cl_2, 125.7 MHz, 298 K): 156.5 (3-$N_2\underline{C}_3Me_2H$ *trans* to Cl), 155.4 (5-$N_2\underline{C}_3Me_2H$ *trans* to N-2,6-$C_6H_3{}^{i}Pr_2$), 147.5 (*o*-$C_6H_3{}^{i}Pr_2$ dn), 143.5 (*o*-$C_6H_3{}^{i}Pr_2$ u), 139.3 (3-$N_2\underline{C}_3Me_2H$ *trans* to Cl), 138.1 (5-$N_2\underline{C}_3Me_2H$ *trans* to N-2,6-$C_6H_3{}^{i}Pr_2$), 122.4 (*m*-$C_6H_3{}^{i}Pr_2$ dn), 121.9 (*m*-$C_6H_3{}^{i}Pr_2$ u), 121.3 (*p*-$C_6H_3{}^{i}Pr_2$), 108.7 (4-$N_2\underline{C}_3Me_2H$ *trans* to Cl), 108.6 (4-$N_2\underline{C}_3Me_2H$ *trans* to N-2,6-$C_6H_3{}^{i}Pr_2$), 67.7 (H$\underline{C}$(Me$_2$pz)$_3$), 27.6 ($C_6H_3(\underline{C}HMe_2)_2$ dn), 26.2 ($C_6H_3(\underline{C}HMe_2)_2$ u), 25.1 ($C_6H_3(CH\underline{Me}_2)_2$ dn), 24.3 ($C_6H_3(CH\underline{Me}_2)_2$ u), 16.4 (3-$N_2C_3\underline{Me}_2H$ *trans* to Cl), 14.8 (3-$N_2C_3\underline{Me}_2H$ *trans* to N-2,6-$C_6H_3{}^{i}Pr_2$), 11.2 (5-$N_2C_3\underline{Me}_2H$ *trans* to Cl), 10.9 (5-$N_2C_3\underline{Me}_2H$ *trans* to N-2,6-$C_6H_3{}^{i}Pr_2$). IR (NaCl plates, Nujol, cm^{-1}): 1567(w), 1414(m), 1330(w), 1306(m), 1262(s), 1094(m), 1038(m), 914(w), 862(m), 800(s), 755(m), 706(w). Anal. Found (calcd. for $C_{28}H_{39}Cl_2N_7Ti{\cdot}1.1CH_2Cl_2$): C, 50.6 (60.0); H, 5.6 (6.1); N, 14.5 (14.3) %. EI-MS *m/z* = 591 (5 %) $[M]^+$. Productivity = 810 kg(PE).mol^{-1}.h^{-1}.bar^{-1}.

Data for [Ti(N-2,6-$C_6H_3Br_2$){HC(Me$_2$pz)$_3$}Cl_2] (**22**): ^{1}H NMR (CD_2Cl_2, 300.0 MHz, 298 K): 7.83 (1H, s, H$\underline{C}$(Me$_2$pz)$_3$), 7.35 (1H, dd, ^{3}J = 7.8 Hz, ^{4}J = 1.2 Hz, *m*-$C_6H_3Br_2$ dn), 7.10 (1H, dd, ^{3}J = 8.1 Hz, ^{4}J = 1.2 Hz, *m*-2,6-$C_6H_3Br_2$ u), 6.36 (1H, app. t, ^{3}J = 7.8 Hz, *p*-2,6-$C_6H_3Br_2$), 6.06 (2H, s, 4-$N_2C_3Me_2\underline{H}$ *cis* to N_{imido}), 5.94 (1H, s, 4-$N_2C_3Me_2\underline{H}$ *trans* to N_{imido}), 2.63 (3H, s, 3-$N_2C_3\underline{Me}_2H$ *trans* to N_{imido}), 2.58 (6H, s, 5-$N_2C_3\underline{Me}_2H$ *cis* to N_{imido}), 2.55 (6H, s, 3-$N_2C_3\underline{Me}_2H$ *cis* to N_{imido}), 2.49 (3H, s, 5-$N_2C_3\underline{Me}_2H$ *trans* to N_{imido}). ^{13}C-{^{1}H} NMR (CD_2Cl_2, 75.5 MHz, 298 K): 157.0 (3-$N_2\underline{C}_3Me_2H$ *cis* to N_{imido}), 155.7 (3-$N_2\underline{C}_3Me_2H$ *trans* to N_{imido}), 139.2 (5-$N_2\underline{C}_3Me_2H$ *cis* to N_{imido}), 138.3 (5-$N_2\underline{C}_3Me_2H$ *trans* to N_{imido}), 132.0 (*m*-$C_6H_3Br_2$ dn), 130.9 (*m*-$C_6H_3Br_2$ u), 121.7 (*p*-$C_6H_3Br_2$), 121.4 (*o*-$C_6H_3Br_2$), 118.9 (*o*-$C_6H_3Br_2$), 108.9 (4-$N_2\underline{C}_3Me_2H$ *trans* to N_{imido}), 108.3 (4-$N_2\underline{C}_3Me_2H$ *cis* to N_{imido}), 67.8 (H$\underline{C}$(Me$_2$pz)$_3$), 15.8 (3-$N_2C_3\underline{Me}_2H$ *cis* to N_{imido}), 15.1 (3-$N_2C_3\underline{Me}_2H$ *trans* to N_{imido}), 11.3 (5-$N_2C_3\underline{Me}_2H$ *cis* to N_{imido}), 11.0 (5-$N_2C_3\underline{Me}_2H$ *trans* to N_{imido}). IR (KBr plates, cm^{-1})**:** 2918 (w, br), 1568 (s), 1462 (s), 1446 (w), 1416 (s), 1382 (m), 1306 (s), 1268 (m), 1040 (m), 964 (m), 916 (w), 862 (m), 808 (w), 720 (m), 706 (m). Anal. Found (calcd. for $C_{22}H_{25}Br_2Cl_2N_7Ti{\cdot}0.25C_6H_6$): C, 41.6 (41.2); H, 4.1 (3.9); N, 14.5 (14.3) %. HRMS found (calcd. for $C_{22}H_{25}Br_2Cl_2N_7Ti$): *m/z* = 662.9443 (662.9395). Productivity = 1,200 kg(PE).mol^{-1}.h^{-1}.bar^{-1}.

Data for [Ti(N^{t}Bu){HC(Bupz)$_3$}Cl_2] (**23**): ^{1}H NMR (CD_2Cl_2, 299.9 MHz, 298 K): 10.14 (1H, s, H$\underline{C}$(4-^{n}Bupz)$_3$), 8.71 (2H, s, 5-$N_2C_3{}^{n}Bu\underline{H}_2$ *cis* to N_{imido}), 8.45 (1H, s, 5-$N_2C_3{}^{n}Bu\underline{H}_2$ *trans* to N_{imido}), 8.25 (2H, s, 3-$N_2C_3{}^{n}Bu\underline{H}_2$ *cis* to N_{imido}), 7.52 (1H, s, 3-$N_2C_3{}^{n}Bu\underline{H}_2$ *trans* to N_{imido}), 2.58 (4H, t, ^{3}J = 7.6 Hz, $C\underline{H}_2CH_2CH_2CH_3$ *cis* to N_{imido}), 2.38 (2H, t, ^{3}J = 7.7 Hz, $C\underline{H}_2CH_2CH_2CH_3$ *trans* to N_{imido}), 1.66-1.29, (12H, m, overlapping signals, $CH_2C\underline{H}_2C\underline{H}_2CH_3$ *cis* and *trans* to N_{imido}), 1.08 (9H, s, ^{t}Bu), 0.93 (6H, t, ^{3}J = 7.2 Hz, $CH_2CH_2CH_2C\underline{H}_3$ *cis* to N_{imido}), 0.84 (3H, t, ^{3}J = 7.3 Hz, $CH_2CH_2CH_2C\underline{H}_3$ *trans* to N_{imido}). ^{13}C-{^{1}H} NMR (CD_2Cl_2, 75.4 MHz, 298 K): 145.8 (3-$N_2\underline{C}_3{}^{n}BuH_2$ *cis* to N_{imido}), 143.2 (3-$N_2\underline{C}_3{}^{n}BuH_2$ *trans* to N_{imido}), 130.6 (5-$N_2\underline{C}_3{}^{n}BuH_2$ *cis* to N_{imido}), 129.6 (5-$N_2\underline{C}_3{}^{n}BuH_2$ *trans* to N_{imido}), 123.2 (4-$N_2\underline{C}_3{}^{n}BuH_2$), 72.9 (H$\underline{C}$(4-^{n}Bupz)$_3$), 69.6 ($\underline{C}Me_3$), 32.9 ($CH_2\underline{C}H_2CH_2CH_3$), 31.0 ($C\underline{Me}_3$), 23.9 ($\underline{C}H_2CH_2CH_2CH_3$), 22.7 ($CH_2CH_2\underline{C}H_2CH_3$), 13.91 ($CH_2CH_2CH_2\underline{C}H_3$). IR (NaCl plates, Nujol, cm^{-1}): 3094 (s), 2920 (s, br), 2854

(w), 1570 (w), 1457 (s), 1402 (s), 1378 (s), 1351 (s), 1248 (m), 1209 (s), 1172 (w), 1097 (s), 1019 (s), 913 (w), 872 (w), 807 (s), 723 (s), 679 (w), 663 (w), 621 (m), 538 (s). Anal. Found (calcd. for $C_{26}H_{43}Cl_2N_7Ti$): C, 54.6 (54.6); H, 7.5 (7.6); N, 17.0 (17.1) %.

Data for [Ti(N-2,6-$C_6H_3{}^iPr_2$){HC(Bupz)$_3$}Cl_2] (**24**): ^{1}H NMR (CD_2Cl_2, 299.9 MHz, 298 K): 9.92 (1 H, s, HC(4-^{n}Bupz)$_3$), 8.57 (2 H, s, 5-$N_2C_3{}^nBuH_2$ *cis* to N_{imido}), 8.20 (1 H, s, 5-$N_2C_3{}^nBuH_2$ *trans* to N_{imido}), 8.17 (2 H, s, 3-$N_2C_3{}^nBuH_2$ *cis* to N_{imido}), 7.69 (1 H, s, 3-$N_2C_3{}^nBuH_2$ *trans* to N_{imido}), 6.83 (2 H, d, ^{3}J = 7.6 Hz, *m*-$C_6H_3{}^iPr_2$), 6.70 (1 H, t, ^{3}J = 7.5 Hz, *p*-$C_6H_3{}^iPr_2$), 4.15 (2 H, sept., CHMe$_2$), 2.41 (4 H, m, $CH_2CH_2CH_2CH_3$ *cis* to N_{imido}), 2.38 (2 H, m, $CH_2CH_2CH_2CH_3$ *trans* to N_{imido}), 1.54-1.22 (12 H, m, overlapping signals, $CH_2CH_2CH_2CH_3$ *cis* and *trans* to N_{imido}), 0.96 (12 H, d, ^{3}J = 6.8 Hz, CHMe$_2$), 0.88 - 0.78 (9 H, m, overlapping peaks, $CH_2CH_2CH_2CH_3$ *cis* and *trans* to N_{imido}). ^{13}C-{^{1}H} NMR (CD_2Cl_2, 75.4 MHz, 298 K): 155.6 (*i*-$C_6H_3{}^iPr_2$), 145.9 (3-$N_2C_3{}^nBuH_2$ *cis* to N_{imido}), 145.6 (*o*-$C_6H_3{}^iPr_2$), 143.9 (3-$N_2C_3{}^nBuH_2$ *trans* to N_{imido}), 130.3 (5-$N_2C_3{}^nBuH_2$ *cis* to N_{imido}), 129.2 (5-$N_2C_3{}^nBuH_2$ *trans* to N_{imido}), 123.8 (4-$N_2C_3{}^nBuH_2$ *cis* to N_{imido}), 123.4 (4-$N_2C_3{}^nBuH_2$ *trans* to N_{imido}), 122.5 (*m*-$C_6H_3{}^iPr_2$), 122.3 (*p*-$C_6H_3{}^iPr_2$), 75.8 (HC(4-^{n}Bupz)$_3$), 32.7 ($CH_2CH_2CH_2CH_3$), 27.4 (CHMe$_2$), 24.8 (CHMe$_2$), 23.7 ($CH_2CH_2CH_2CH_3$), 22.7 ($CH_2CH_2CH_2CH_3$), 13.8 ($CH_2CH_2CH_2CH_3$). IR (NaCl plates, Nujol, cm^{-1}): 3076 (w), 2958 (s, br), 2855 (s), 1458 (s), 1403 (m), 1378 (m), 1353 (w), 1319 (w), 1261 (s), 1175 (m), 1097 (m), 1020 (s), 963 (w), 933 (w), 873 (m), 805 (s), 755 (w), 663 (w). Anal. Found (calcd. for $C_{34}H_{51}Cl_2N_7Ti$): C, 60.2 (60.4); H, 7.6 (7.6); N, 14.4 (14.5) %.

Data for [Ti(N-2-$C_6H_4CF_3$){HC(Bupz)$_3$}Cl_2] (**25**): ^{1}H NMR (CD_2Cl_2, 299.9 MHz, 298 K): 10.07 (1 H, s, HC(4-^{n}Bupz)$_3$), 8.52 (2 H, s, 5-$N_2C_3{}^nBuH_2$ *cis* to N_{imido}), 8.34 (1 H, s, 5-$N_2C_3{}^nBuH_2$ *trans* to N_{imido}), 8.15 (2 H, s, 3-$N_2C_3{}^nBuH_2$ *cis* to N_{imido}), 7.76 (1 H, s, 3-$N_2C_3{}^nBuH_2$ *trans* to N_{imido}), 7.65 (1 H, d, ^{3}J = 7.9 Hz, 3-$C_6H_4CF_3$), 7.30-7.35 (2 H, m, overlapping signals, 4- and 6-$C_6H_4CF_3$), 6.80 (1 H, app. t, ^{3}J = 7.6 Hz, 5-$C_6H_4CF_3$), 2.46-2.36 (6 H, m, overlapping signals, $CH_2CH_2CH_2CH_3$ *cis* and *trans* to N_{imido}), 1.57 - 1.24 (12 H, m, overlapping signals, $CH_2CH_2CH_2CH_3$ *cis* and *trans* to N_{imido}), 0.87 - 0.84 (9 H, m, overlapping signals, $CH_2CH_2CH_2CH_3$ *cis* and *trans* to N_{imido}). ^{13}C-{^{1}H} NMR (CD_2Cl_2, 75.4 MHz, 298 K): 155.5 (*i*-$C_6H_4CF_3$), 145.1 (3-$N_2C_3{}^nBuH_2$ *cis* to N_{imido}), 143.8 (3-$N_2C_3{}^nBuH_2$ *trans* to N_{imido}), 132.3 (4-$C_6H_4CF_3$), 130.9 (5-$N_2C_3{}^nBuH_2$ *cis* to N_{imido}), 129.9 (5-$N_2C_3{}^nBuH_2$ *trans* to N_{imido}), 126.2 (3-$C_6H_4CF_3$), 125.4 (2- or 6-$C_6H_4CF_3$), 125.2 (2- or 6-$C_6H_4CF_3$), 123.8 (4-$N_2C_3{}^nBuH_2$ *cis* to N_{imido}), 123.3 (4-$N_2C_3{}^nBuH_2$ *trans* to N_{imido}), 120.9 (5-$C_6H_4CF_3$), 75.6 (HC(4-^{n}Bupz)$_3$), 32.8 ($CH_2CH_2CH_2CH_3$), 23.6 ($CH_2CH_2CH_2CH_3$), 22.7 ($CH_2CH_2CH_2CH_3$), 13.8 ($CH_2CH_2CH_2CH_3$). ^{19}F NMR (CD_2Cl_2, 141.2 MHz, 298 K): -60.4 (CF_3). IR (NaCl plates, Nujol, cm^{-1}): 2923 (s), 2853 (s, br), 1591 (w), 1557 (w), 1459 (s), 1446 (m), 1403 (s), 1377 (s), 1336 (s), 1312 (s), 1260 (s), 1163 (s), 1123 (s), 1104 (s), 1054 (s), 1021 (s), 969 (w), 896 (m), 871 (s), 804 (s),

759 (m), 723 (w), 663 (w). Anal. Found (calcd. for $C_{29}H_{38}Cl_2F_3N_7Ti$): C, 52.7 (52.5); H, 5.9 (5.8); N, 14.8 (14.9) %.

Data for [Ti(N-2-$C_6H_4{}^tBu$){$C(Me_2pz)_3$}Cl(THF)] (**16-zwitt**): ^{1}H NMR (C_7D_8, 499.9 MHz, 298 K): 7.16 (1H, d, ^3J = 7.3 Hz, 3-$C_6H_4{}^tBu$), 6.60 (2H, overlapping multiplets, 4-$C_6H_4{}^tBu$ and 5-$C_6H_4{}^tBu$), 6.29 (1H, d, ^3J = 6.8 Hz, 6-$C_6H_4{}^tBu$), 5.71 (1H, s, 4-$N_2C_3Me_2\underline{H}$ *trans* to Cl), 5.45 (1H, s, 4-$N_2C_3Me_2\underline{H}$ *trans* to THF), 5.44 (1H, s, 4-$N_2C_3Me_2\underline{H}$ *trans* to N-2-$C_6H_4{}^tBu$), 4.00 (4H, br. m, O-$C\underline{H}_2CH_2$), 2.49 (3H, s, 5-$N_2C_3\underline{Me}_2H$ *trans* to Cl), 2.42 (6H, overlapping singlets, 5-$N_2C_3\underline{Me}_2H$ *trans* to N-2-$C_6H_4{}^tBu$ and 3-$N_2C_3\underline{Me}_2H$ *trans* to THF), 2.40 (3H, s, 5-$N_2C_3\underline{Me}_2H$ *trans* to THF), 2.37 (3H, s, 3-$N_2C_3\underline{Me}_2H$ *trans* to N-2-$C_6H_4{}^tBu$), 2.16 (3H, s, 3-$N_2C_3\underline{Me}_2H$ *trans* to Cl), 1.86 (9H, s, $^t\underline{Bu}$), 1.35 (4H, br. m, O-$CH_2C\underline{H}_2$). ^{13}C-{^{1}H} NMR (C_7D_8, 499.9 MHz, 298 K): 158.3 (*i*-$C_6H_4{}^tBu$), 151.2 (3-$N_2\underline{C}_3Me_2H$ *trans* to THF), 149.6 (3-$N_2\underline{C}_3Me_2H$ *trans* to Cl), 149.1 (3-$N_2\underline{C}_3Me_2H$ *trans* to N-2-$C_6H_4{}^tBu$), 145.7 (5-$N_2\underline{C}_3Me_2H$ *trans* to Cl), 144.6 (5-$N_2\underline{C}_3Me_2H$ *trans* to THF), 144.2 (5-$N_2\underline{C}_3Me_2H$ *trans* to N-2-$C_6H_4{}^tBu$), 138.3 (2-$C_6H_4{}^tBu$), 134.3 (6-$C_6H_4{}^tBu$), 125.4 (3-$C_6H_4{}^tBu$), 121.4 (4- or 5-$C_6H_4{}^tBu$), 104.6 (overlapping 4-$N_2\underline{C}_3Me_2H$ *trans* to THF and 4-$N_2\underline{C}_3Me_2H$ *trans* to N-2-$C_6H_4{}^tBu$), 104.5 (4-$N_2\underline{C}_3Me_2H$ *trans* to Cl), 73.9 (O-$\underline{C}H_2CH_2$), 72.2 ($\underline{C}(Me_2pz)_3$), 35.6 ($\underline{C}Me_3$), 31.5 ($C\underline{Me}_3$), 25.4 (O-$CH_2\underline{C}H_2$), 15.3 (3-$N_2C_3\underline{Me}_2H$ *trans* to N-2-$C_6H_4{}^tBu$), 14.4 (3-$N_2C_3\underline{Me}_2H$ *trans* to Cl), 12.6 (overlapping 5-$N_2C_3\underline{Me}_2H$ *trans* to Cl, 5-$N_2C_3\underline{Me}_2H$ *trans* to N-2-$C_6H_4{}^tBu$ and 3-$N_2C_3\underline{Me}_2H$ *trans* to THF), 12.2 (5-$N_2C_3\underline{Me}_2H$ *trans* to THF). IR (NaCl plates, Nujol, cm^{-1}): 1551(m), 1424(s), 1392(s), 1293(m), 1271(s), 1103(m), 1049(s), 1039(s), 1016(s), 954(m), 871(m), 800(m), 778(m), 758(m), 748(m), 677(m), 656(w). Anal. Found (calcd. for $C_{30}H_{42}ClN_7OTi$): C, 59.9 (60.0); N, 16.2 (16.3); H, 7.0 (7.1) %. EI-HRMS found (calcd. for $C_{30}H_{42}ClN_7OTi$): 599.2608 (599.2619).

Summary of polymerisation conditions

(a) Room temperature screening: 20 - 2.5 μmol precatalyst; 250 mL toluene; 5 bar C_2H_4; 60 mins; MAO (Al/Ti = 1500).

(b) Higher temperature screening: 1 - 0.05 μmol precatalyst; 750 mL PMH; 7 bar C_2H_4; 10 mins; MAO (Al/Ti = 1600 or 3200).

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