Appendix A: Supplementary information

1.0. Synthesis of bis(diphenylphosphino)amine ligands (PNP ligands)

At room temperature, chlorodiphenylphosphine (2.01 mL, 11.2 mmol) was added to a solution containing dichloromethane (50 mL), the corresponding amine (11.2 mmol) and triethylamine (15 mL). The mixture was stirred for 30 minutes after which a second aliquot of chlorodiphenylphosphine (2.01 mL, 11.2 mmol) was added. The reaction mixture was stirred overnight at room temperature. The mixture was filtered to remove the triethylammonium hydrochloride salt formed and the product was isolated as a white solid by removal of the solvent under vacuum.

Bis(diphenylphosphino)methylamine (1):

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.80 (s, 3 H, CH_3), 7.20 – 7.48 (m, 20 H, CH). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 32.5 (t, CH_3), 128.9 (3 CH), 132.4 (t, 2 CH), 138.4 (t, CH). ^{31}P NMR (400 MHz, $CDCl_3$): δ = 73.0 (s). IR (ATR) ν_{max}/cm^{-1}: 3052, 2927, 1585, 1478, 1433, 1277, 858, 741, 694. MS (EI, 70 eV): *m/z* (%) = 400 (13, $[M + H]^+$), 399 (51, $[M]^+$), 384 (15, $[M - CH_3]^+$), 214 (15, $[M - PPh_2]^+$), 185 (6, $[PPh_2]^+$). Anal. Calc. for $C_{25}H_{23}NP_2$: C, 75.18; H, 5.80; N, 3.51; P, 15.51. Found: C, 74.94; H, 5.89; N, 3.31; P, 15.86. Yield: 65 %. Mp: 114 – 116 °C.

Bis(diphenylphosphino)isopropylamine (2):

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.20 (d, 6 H, 2 CH_3), 3.75 (m, 1 H, CH), 7.25 – 7.47 (m, 20 H, CH). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 24.7 (2 CH_3), 51.9 (t, CH), 128.5 (3 CH), 132.8 (t, 2 CH), 139.2 (t, CH). ^{31}P NMR (400 MHz, $CDCl_3$): δ = 48.7 (br s). IR (ATR) ν_{max}/cm^{-1}: 3050, 2965, 1585, 1478, 1431, 1376, 871, 738, 692. MS (EI, 70 eV): *m/z* (%) = 428 (2, $[M + H]^+$), 427 (12, $[M]^+$), 384 (100, $[M - i\text{Pr}]^+$), 242 (10, $[M - PPh_2]^+$), 185 (25, $[PPh_2]^+$). Anal. Calc. for $C_{27}H_{27}NP_2$: C, 75.86; H, 6.37; N, 3.28; P, 14.49. Found: C, 75.67; H, 6.15; N, 3.42; P, 14.76. Yield: 77 %. Mp: 133 – 135 °C.

Bis(diphenylphosphino)pentylamine (3):

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.40 (t, 2 H, CH_2), 0.85 (m, 5 H, CH_2 + CH_3), 1.10 (q, 4 H, 2 CH_2), 3.25 (t, 2H, CH_2), 7.35 – 7.50 (m, 20 H, CH). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 14.3 (CH_3), 22.4 (CH_2), 29.3 (CH_2), 31.3 (CH_2), 53.1 (t, CH_2), 128.5 (3 CH), 132.7 (t, 2 CH), 139.7 (t, CH). ^{31}P NMR (400 MHz, $CDCl_3$): δ = 62.2 (s). IR (ATR) ν_{max}/cm^{-1}: 3051, 2935, 2857, 1584, 1454, 1431, 1280, 878, 740, 693. MS (EI, 70 eV): *m/z* (%) = 456 (2, $[M + H]^+$), 455 (16, $[M]^+$), 384 (32, $[M - C_5H_{11}]^+$), 270 (2, $[M - PPh_2]^+$), 185 (25, $[PPh_2]^+$), 71 (1, $[C_5H_{11}]^+$). Anal. Calc. for $C_{29}H_{31}NP_2$: C, 76.47; H, 6.86; N, 3.07; P, 13.60. Found: C, 76.12; H, 6.93; N, 2.90; P, 14.05. Yield: 83 %. Mp: 78 – 79 °C.

Bis(diphenylphosphino)cyclohexylamine (4):

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.50 (m, 2 H, CH_2), 1.65 (m, 2 H, CH_2), 1.80 (m, 3 H, CH_2 + CH), 2.80 (q, 4 H, 2 CH_2), 7.25 – 7.40 (m, 20 H, CH). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 25.4 (CH_2), 25.8 (2 CH_2), 37.0 (2 CH_2), 56.0 (t, CH), 128.5 (3 CH), 131.0 (t, 2 CH), 143.2 (t, CH). ^{31}P NMR (400 MHz, $CDCl_3$): δ = 50.8 (br s). IR (ATR) ν_{max}/cm^{-1}: 3052, 2927, 2852, 1584, 1477, 1433, 859, 741, 691. MS (EI, 70 eV): *m/z* (%) = 469 (2.4, $[M + H]^+$), 468 (1.5, $[M]^+$), 385 (0.6, $[M - C_6H_{11}]^+$), 283 (48, $[M - PPh_2]^+$), 185 (13, $[PPh_2]^+$), 83 (2, $[C_6H_{11}]^+$). Anal. Calc. for $C_{30}H_{31}NP_2$: C, 77.07; H, 6.68; N, 3.00; P, 13.25. Found: C, 77.26; H, 6.38; N, 3.27; P, 13.09. Yield: 88 %. Mp: 170 – 171 °C.

Bis(diphenylphosphino)phenylamine (5):

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.70 (d, 2 H, 2 CH), 6.80 (unresolved coupling, CH), 7.00 (m, 2 H, 2 CH), 7.35 – 7.50 (m, 20 H, CH). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 115.9 (CH), 119.4 (CH), 128.0 (CH), 129.1 (CH), 131.2 (t, CH), 139.2 (t, CH), 146.6 (t, CH). ^{31}P NMR (400 MHz, $CDCl_3$): δ = 73.0 (s). IR (ATR) ν_{max}/cm^{-1}: 3055, 1594, 1480, 1432, 871, 738, 690. MS (EI, 70 eV): *m/z* (%) = 462 (0.5, $[M + H]^+$), 461 (1, $[M]^+$), 312 (0.5, $[M - C_6H_5]^+$), 276 (0.5, $[M - PPh_2]^+$), 185 (11, $[PPh_2]^+$), 149 (2, $[C_6H_5]^+$). Anal. Calc. for $C_{30}H_{25}NP_2$: C, 78.08; H, 5.46; N, 3.04; P, 13.42. Found: C, 77.98; H, 5.52; N, 3.14; P, 13.36. Yield: 80 %. Mp: 160 – 163 °C.

2.0. Synthesis of diphenylphosphinoamines

To a stirring ice-cold solution of the corresponding amine (20 mmol) in dichloromethane (50 mL) and triethylamine (2.8 mL, 20 mmol) was added dropwise chlorodiphenylphosphine (3.6 mL, 20 mmol) and the reaction mixture was stirred at room temperature overnight. Amine

hydrochloride was removed by filtration, and the product was isolated as a white solid from the solvent under vacuum.

(Diphenylphosphino)isopropylamine:

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.14 (d, 1 H, CH), 1.80 (s, 1 H, NH), 3.30 (m, 6 H, 2 CH_3), 7.26 – 7.42 (m, 10 H, CH). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 26.2 (2 CH_3), 48.6 (d, CH), 128.2 (3 CH), 132.2 (d, 2 CH), 143.1 (d, CH). ^{31}P NMR (400 MHz, $CDCl_3$): δ = 34.1 (s). IR (ATR) ν_{max}/cm^{-1}: 3058, 2962, 1591, 1471, 1438, 1382, 892, 721, 691. MS (EI, 70 eV): *m/z* (%) = 244 (1, $[M + H]^+$), 243 (1, $[M]^+$), 200 (54, $[M - i\text{Pr}]^+$), 185 (22, $[PPh_2]^+$), 59 (3, $[M - PPh_2]^+$), 44 (79, $[i\text{Pr}]^+$). Anal. Calc. for $C_{15}H_{18}NP$: C, 74.05; H, 7.46; N, 5.76; P, 12.73. Found: C, 74.02; H, 7.42; N, 5.74; P, 12.82. Yield: 85 %. Mp: 98 – 100 °C.

(Diphenylphosphino)cyclohexylamine:

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.17 (m, 2 H, CH_2), 1.57 (m, 2 H, CH_2), 1.90 (m, 3 H, CH_2 + CH), 2.92 (q, 4 H, 2 CH_2), 7.30 – 7.49 (m, 10 H, CH). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 24.9 (CH_2), 25.4 (2 CH_2), 36.8 (2 CH_2), 56.1 (d, CH), 128.5 (3 CH), 130.8 (d, 2 CH), 143.2 (d, CH). ^{31}P NMR (400 MHz, $CDCl_3$): δ = 34.4 (s). IR (ATR) ν_{max}/cm^{-1}: 3059, 2926, 2851, 1548, 1435, 887, 740, 693. MS (EI, 70 eV): *m/z* (%) = 284 (10, $[M + H]^+$), 283 (24, $[M]^+$), 200 (26, $[M - C_6H_{11}]^+$), 185 (10, $[PPh_2]^+$), 98 (17, $[M - PPh_2]^+$), 83 (4, $[C_6H_{11}]^+$). Anal. Calc. for $C_{18}H_{22}NP$: C, 76.30; H, 7.83; N, 4.94; P, 10.93. Found: C, 76.35; H, 7.79; N, 4.97; P, 10.89. Yield: 94 %. Mp: 48 – 50 °C.

(Diphenylphosphino)phenylamine:

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.63 (s, 1 H, NH), 6.68 (d, 2 H, 2 CH), 6.90 (d, 1 H, CH), 7.02 (m, 2 H, 2 CH), 7.28 – 7.33 (m, 10 H, CH). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 115.9 (CH), 119.4 (CH), 128.5 (CH), 129.3 (CH), 131.2 (d, CH), 139.3 (d, CH), 147.5 (d, CH). ^{31}P NMR (400 MHz, $CDCl_3$): δ = 28.0 (s). IR (ATR) ν_{max}/cm^{-1}: 3055, 1598, 1480, 1433, 871, 738, 689. MS (EI, 70 eV): *m/z* (%) = 278 (12, $[M + H]^+$), 277 (39, $[M]^+$), 200 (5, $[M - C_6H_5]^+$), 185 (22, $[PPh_2]^+$), 149 (62, $[C_6H_5]^+$), 92 (99, $[M - PPh_2]^+$). Anal. Calc. for $C_{18}H_{16}NP$: C, 77.96; H, 5.82; N, 5.05; P, 11.17. Found: C, 77.93; H, 5.86; N, 5.08; P, 11.13. Yield: 72 %. Mp: 68 – 70 °C.

3.0. Functionalising of Merrifield's resin

A solution of tert-butylamine (21 mmol) and potassium iodide (0.3 mmol) in 50 mL of tetrahydrofuran was treated with Merrified resin (2.5 mmol/g, 1 mmol) while stirring at room temperature for 30 minutes. The suspension was then heated under reflux for 48 hours before the resin was filtered off. The resulting resin was washed with water (3 x 15 mL), tetrahydrofuran (3 x 10 mL) and hexane (3 x 12 mL). The resin was then dried overnight under vacuum.

^{13}C MAS SS-NMR (600 MHz): δ = 28.2, 41.0, 46.7, 128.6, 145.8. IR (ATR) ν_{max}/cm^{-1}: 3025, 2923, 1602, 1493, 1452, 1360, 868, 757, 697.

4.0. Heterogeneous catalytic testing

These were done using supported ligands **9 – 11**. The loading of the ligand on the polymer was determined by ICP-OES and reported as mmol P/gram of supported ligand (Table 1). From this information, the appropriate amount of supported ligand could be weighed out using the same mole quantities as those of the homogeneous runs.

Table 1. Loadings of the supported ligands as determined by ICP-OES.

Ligand	Loading / mmol P per gram
9	**0.77**
10	**2.74**
11	**0.30**

A solution of supported ligand (0.005 mmol) in methylcyclohexane (2 mL) was added to a solution of Cr(acac)$_3$ (0.005 mmol) in methylcyclohexane (2 mL). The mixture was stirred for 5 minutes at room temperature after which MMAO (9.6 mmol, 2.50 mL) was added. The mixture was then transferred to a pressure reactor containing methylcyclohexane (93.5 mL) at the

required temperature. The pressure reactor was charged with ethylene at 45 bar and the temperature was controlled. The reaction was terminated after 30 minutes by discontinuing the ethylene feed and quenching with ethanol (10 mL). The liquid phase was analysed by GC-FID using nonane as the internal standard.