**Supplementary Material**

**Preparation of (±)-PCy*PhR (where R = Pri):** Ammonia (400 cm³) was condensed onto PPh₃ (20.0 g, 0.0763 mol). Sodium foil (3.80 g, 0.169 mol) was added piecewise to the stirred solution. The reaction was allowed to stir in the cold for 0.5 h, 2-bromopropane (18.82 g, 0.153 mol) was added dropwise followed by the further addition of sodium foil (3.90 g, 0.169 mol). The reaction mixture was stirred for a further 2 h. Solid ammonium chloride was added until the colour discharged and the reaction mixture stirred overnight under nitrogen to allow the ammonia to evaporate. Water (150 cm³) and dichloromethane (50 cm³) were added to the residue. The resulting phases were separated and the aqueous phase extracted further with dichloromethane (2 x 25 cm³). The combined organic extracts were dried (MgSO₄), filtered and the solvent removed in vacuo. Distillation of the crude oil under reduced pressure gave two fractions: **Fraction I**, (±)-PHPriPh (4.97 g, 43%), b.p. 65-80 °C, 0.05 mm Hg. 1H NMR (CDCl₃): δ 1.10 (dd, 3 H, 3JHH = 6.9 Hz, 3JPH = 15.6 Hz, CMe), 1.11 (dd, 3 H, 3JHH = 6.9 Hz, 3JPH = 15.6 Hz, CMe), 2.11 (m, 1 H, 3JPH = 6.9 Hz, 2JPH = 6.9 Hz, CMe), 4.05 (bs, 1 H, PH), 7.31–7.68 (m, 5 H, aromatics). 31P{1H} NMR (CDCl₃): δ -24.3 (s, 1 P). LR-EI MS: m/z 152 (M)+, 110 (M – C₃H₆)+, 109 (M – Pr)+, 108 (M – C₃H₈)+.

**Fraction II**, (±)-PCy*PriPh (9.27 g, 53%), b.p. 120-122 °C, 0.05 mm Hg. 1H NMR (CDCl₃): δ 0.99 (dd, 6 H, 3JHH = 6.9 Hz, 3JPH = 14.4 Hz, CMe), 1.20 (dd, 6 H, 3JHH = 6.9 Hz, 3JPH = 14.4 Hz, CMe), 1.87 (m, 1 H, 3JPH = 6.9 Hz, CMe), 1.89 (m, 1 H, 3JHH = 6.9 Hz, 2JPH = 6.9 Hz, CMe), 2.39 (m, 2 H, Cy*-H₄a,H₄b), 3.31 (m, 1 H, Cy*-H₁), 5.58 (m, 1 H, Cy*-H₅/₆), 5.61 (m, 1 H, Cy*-H₅/₆), 5.70 (m, 2 H, Cy*-H₃, H₅), 7.26–7.50 (m, 5 H, aromatics). 31P{1H} NMR (CDCl₃): δ 8.8 (s, 1 P). 13C{1H} NMR (CDCl₃): δ 18.1 (d, 1 C, 2JPC = 18.2 Hz, CMe), 18.6 (d, 1 C, 2JPC = 15.4 Hz, CMe), 19.9 (d, 1 C, 2JPC = 12.5 Hz, Cy*-C₂), 24.9 (d, 1 C, 1JPC = 3.5 Hz, CHMe₂), 34.4 (d, 1 C, 1JPC = 15.5 Hz, Cy*-C₇), 122.9 (s, 1 C, Cy*-C₅/C₃), 123.6 (d, 1 C, 1JPC = 6.8 Hz, Cy*-C₅/C₃), 124.4 (d, 1 C, 2JPC = 7.9 Hz, Cy*-C₅/C₃), 124.6 (d, 1 C, 2JPC = 10.6 Hz, Cy*-C₅/C₃), 126.2 (s, 1 C, aromatic-C₂/C₃), 126.3 (s, 1 C, aromatic-C₂/C₃), 127.6 (s, 1 C, aromatic-C₁), 133.3 (s, 1 C, aromatic-C₅/C₇), 133.5 (s, 1 C, aromatic-C₂/C₆). LR-EI MS: m/z 230 (M)+, 201 (M – Et)+, 185 (M – Et – CH₄)+, 152 (M-C₃H₆)+. HR-EI MS: Found for (M)+ 230.1231 (calc. for C₁₅H₁₉P: 230.1224).

**Preparation of (±)-PCy*PhR (where R = Bu):** Ammonia (400 cm³) was condensed onto PPh₃ (20.0 g, 0.0763 mol). Sodium foil (3.96 g, 0.172 mol) was added piecewise to the stirred solution. The reaction was allowed to stir in the cold for 0.5 h, 2-bromobutane (20.90 g, 0.153 mol) was added dropwise followed by the further addition of sodium foil (3.94 g, 0.171 mol). The reaction mixture was stirred for a further 2 h. Solid ammonium chloride was added until the colour discharged and the reaction mixture stirred overnight under nitrogen to allow the ammonia to evaporate. Water (150 cm³) and dichloromethane (50 cm³) were added to the residue. The resulting phases were separated and the aqueous phase extracted further with dichloromethane (2 x 25 cm³). The combined organic extracts were dried (MgSO₄),
filtered and the solvent removed in vacuo. Distillation of the crude oil under reduced pressure gave two fractions: **Fraction I**, (\(R_p^*,R_p^*\)- & \(R_p^*,S_p^*\)-PHBuPh (1.30 g, 10%), b.p.89-100 °C, 0.05 mm Hg. \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 0.99 (t, 3 H, \(3J_{HH} = 7.2\) Hz, CH\(_2\)CMe), 1.09 (dd, 3 H, \(3J_{HH} = 7.2\) Hz, \(3J_{PH} = 13.5\) Hz, CHCMe), 1.37 (m, 1 H, CHH), 1.56 (m, 1 H, CHH), 1.91 (m, 1 H, CHCMe), 4.05 (bd, 1 H, \(1J_{PH} = 203\) Hz, PH), 7.32–7.56 (m, 5 H, aromatics). \(^{31}\)P{\(^1\)H} NMR (CDCl\(_3\)): \(\delta\) -32.6 (s, 1 P), -28.5 (s, 1 P). LR-EI MS: \(m/z\) 166 (M\(^+\)), 110 (M – C\(_4\)H\(_8\))^\textsuperscript{+}.

**Fraction II**, (\(R_p^*,R_p^*\)- & (\(R_p^*,S_p^*\)-PCy*BuPh (11.98 g, 64%), b.p.120-140 °C, 0.05 mm Hg. \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 0.92 (t, 3 H, \(3J_{HH} = 7.5\) Hz, CH\(_2\)CMe), 0.95 (t, 3 H, \(3J_{HH} = 6.9\) Hz, CH\(_2\)CMe), 1.04 (dd, 3 H, \(3J_{HH} = 7.2\) Hz, \(3J_{PH} = 14.7\) Hz, CHCMe), 1.19 (dd, 3 H, \(3J_{HH} = 6.6\) Hz, \(3J_{PH} = 14.7\) Hz, CHCMe), 1.37 (m, 2 H, CHH), 1.71 (m, 2 H, CHH), 1.94 (m, 2 H, CHCMe), 2.21 (m, 2 H, Cy*-H\(_{4b}\)), 2.39 (m, 2 H, Cy*-H\(_{4a}\)), 3.31 (m, 1 H, Cy*-H\(_1\)), 3.38 (m, 1 H, Cy*-H\(_1\)), 5.60 (m, 4 H, Cy*-H\(_{3,5}\)), 5.69 (m, 4 H, Cy*-H\(_{3,5}\)), 7.25–7.51 (m, 10 H, aromatics). \(^{31}\)P{\(^1\)H} NMR (CDCl\(_3\)): \(\delta\) 4.9 (s, 1 P), 5.6 (s, 1 P). LR-EI MS: \(m/z\) 244 (M\(^+\)), 242 (M – H\(_2\))^\textsuperscript{+}, 186 (M-C\(_4\)H\(_{10}\))^\textsuperscript{+}.

**Preparation of (\(\pm\)-1,2-C\(_6\)H\(_8\)(PPh\(_2\)){PPh(3-pentyl)}**: The Birch reduced tertiary phosphine (\(\pm\)-PCy*(3-pentyl)Ph (2.43 g, 9.4 mmol) and PHPh\(_2\) (1.79 g, 9.6 mmol) were stirred in thf (50 cm\(^3\)). KOBu\(_t\) was added and the resulting yellow solution heated under reflux. More KOBu\(_t\) was added after 72 h and the solution heated under reflux for a further 4 days. Saturated aqueous NH\(_4\)Cl (3 drops) was added and the solvent was removed. Dichloromethane (50 cm\(^3\)) and water (20 cm\(^3\)) were added to the residue. The resulting phases were separated and the aqueous phase extracted further with dichloromethane (2 x 10 cm\(^3\)). The combined organic extracts were dried (MgSO\(_4\)), filtered and the solvent removed in vacuo. Vacuum distillation was employed to remove unreacted PHPh\(_2\) and leave the product as a viscous yellow oil (3.75 g, 90%). \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 0.98 (t, 3 H, \(3J_{HH} = 7.5\) Hz, CH\(_2\)CMe), 1.12 (t, 3 H, \(3J_{HH} = 7.5\) Hz, CMe), 1.51 (m, 4 H, 2 CH\(_2\)-Cy), 1.75 (m, 2 H, CH\(_2\)-CMe), 1.85 (m, 2 H, CH\(_2\)-CMe), 2.35 (m, 1 H, CyEt\(_2\)), 3.76 (m, 4 H, 2 CH\(_2\)=C), 7.28–7.52 (m, 15 H, aromatics). \(^{31}\)P{\(^1\)H} NMR (CDCl\(_3\)): \(\delta\) -15.6, -8.8 (ABq, 2 P, \(4J_{PP} = 216\) Hz). LR-EI MS: \(m/z\) 444 (M\(^+\)), 373 (M – Pe)^\textsuperscript{+}, 265 (M – PPePh)^\textsuperscript{+}. HR-EI MS: Found for (M\(^+\)) 444.2130 (calc. for C\(_{29}\)H\(_{34}\)P\(_2\): 444.2136).