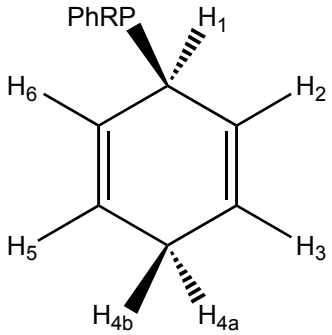
Supplementary Material

*Preparation of (±)-PCy*PhR (where R = Pr^i)*: Ammonia (400 cm^3) was condensed onto PPh_3 (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 cm^3) and dichloromethane (50 cm^3) were added to the residue. The resulting phases were separated and the aqueous phase extracted further with dichloromethane (2 x 25 cm^3). The combined organic extracts were dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. Distillation of the crude oil under reduced pressure gave two fractions: **Fraction I**, (±)-PHPr^{i}Ph (4.97 g, 43%), b.p.65-80 °C, 0.05 mm Hg. ^{1}H NMR ($CDCl_3$): δ 1.10 (dd, 3 H, $^3J_{HH}$ = 6.9 Hz, $^3J_{PH}$ = 15.6 Hz, C*Me*), 1.11 (dd, 3 H, $^3J_{HH}$ = 6.9 Hz, $^3J_{PH}$ = 15.6 Hz, C*Me*), 2.11 (m, 1 H, $^3J_{HH}$ = 6.9 Hz, $^2J_{PH}$ = 6.9 Hz, C*H*Me$_2$), 4.05 (bs, 1 H, P*H*), 7.31–7.68 (m, 5 H, aromatics). ^{31}P{^{1}H} NMR ($CDCl_3$): δ -24.3 (s, 1 P). ^{1}H NMR (C_6D_6): δ 0.96 (dd, 3 H, $^3J_{HH}$ = 6.9 Hz, $^3J_{PH}$ = 15.6 Hz, C*Me*), 0.99 (dd, 3 H, $^3J_{HH}$ = 6.9 Hz, $^3J_{PH}$ = 15.6 Hz, C*Me*), 1.89 (m, 1 H, $^3J_{HH}$ = 6.9 Hz, $^2J_{PH}$ = 6.9 Hz, C*H*Me$_2$), 3.99 (dd, 1 H, $^3J_{HH}$ = 6.9 Hz, $^1J_{PH}$ = 175 Hz, P*H*), 7.07–7.45 (m, 5 H, aromatics). ^{31}P{^{1}H} NMR (C_6D_6): δ -25.2 (s, 1 P). LR-EI MS: *m/z* 152 $(M)^+$, 110 $(M - C_3H_6)^+$, 109 $(M - Pr^i)^+$, 108 $(M - C_3H_8)^+$. **Fraction II**, (±)-PCy*Pr^{i}Ph (9.27 g, 53%), b.p.120-122 °C, 0.05 mm Hg. ^{1}H NMR ($CDCl_3$): δ 0.99 (dd, 6 H, $^3J_{HH}$ = 6.9 Hz, $^3J_{PH}$ = 14.4 Hz, C*Me*), 1.20 (dd, 6 H, $^3J_{HH}$ = 6.9 Hz, $^3J_{PH}$ = 14.4 Hz, C*Me*), 1.87 (m, 1 H, $^3J_{HH}$ = 6.9 Hz, $^2J_{PH}$ = 6.9 Hz, C*H*Me$_2$), 2.39 (m, 2 H, Cy*-*H*$_{4a}$,*H*$_{4b}$), 3.31 (m, 1 H, Cy*-*H*$_1$), 5.58 (m, 1 H, Cy*-*H*$_2$/$_6$), 5.61 (m, 1 H, Cy*-*H*$_2$/$_6$), 5.70 (m, 2 H, Cy*-*H*$_3$, *H*$_5$), 7.26–7.50 (m, 5 H, aromatics). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 8.8 (s, 1 P). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 18.1 (d, 1 C, $^2J_{PC}$ = 18.2 Hz, C*Me*), 18.6 (d, 1 C, $^2J_{PC}$ = 15.4 Hz, C*Me*), 19.9 (d, 1 C, $^2J_{PC}$ = 12.5 Hz, Cy*-*C*$_4$), 24.9 (d, 1 C, $^1J_{PC}$ = 3.5 Hz, *C*HMe$_2$), 34.4 (d, 1 C, $^1J_{PC}$ = 15.5 Hz, Cy*-*C*$_1$), 122.9 (s, 1 C, Cy*-*C*$_3$/*C*$_5$), 123.6 (d, 1 C, $^3J_{PC}$ = 6.8 Hz, Cy*-*C*$_3$/*C*$_5$), 124.4 (d, 1 C, $^2J_{PC}$ = 7.9 Hz, Cy*- *C*$_2$/*C*$_6$), 124.6 (d, 1 C, $^2J_{PC}$ = 10.6 Hz, Cy*- *C*$_2$/*C*$_6$), 126.2 (s, 1 C, aromatic-*C*$_3$/*C*$_5$), 126.3 (s, 1 C, aromatic-*C*$_3$/*C*$_5$), 127.6 (s, 1 C, aromatic-*C*$_4$), 133.3 (s, 1 C, aromatic-*C*$_2$/*C*$_6$), 133.5 (s, 1 C, aromatic-*C*$_2$/*C*$_6$). LR-EI MS: *m/z* 230 $(M)^+$, 201 $(M - Et)^+$, 185 $(M - Et - CH_4)^+$, 152 $(M\text{-}C_6H_6)^+$. HR-EI MS: Found for $(M)^+$ 230.1231 (calc. for $C_{15}H_{19}P$: 230.1224).

*Preparation of (±)-PCy*PhR (where R = Bu^s)*: Ammonia (400 cm^3) was condensed onto PPh_3 (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 cm^3) and dichloromethane (50 cm^3) were added to the residue. The resulting phases were separated and the aqueous phase extracted further with dichloromethane (2 x 25 cm^3). The combined organic extracts were dried ($MgSO_4$),

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*)*-PHBu^{s}Ph (1.30 g, 10%), b.p.89-100 °C, 0.05 mm Hg. ^{1}H NMR ($CDCl_3$): δ 0.99 (t, 3 H, $^3J_{HH}$ = 7.2 Hz, CH_2CMe), 1.09 (dd, 3 H, $^3J_{HH}$ = 7.2 Hz, $^3J_{PH}$ = 13.5 Hz, CHC*Me*), 1.37 (m, 1 H, CH*H*), 1.56 (m, 1 H, C*H*H), 1.91 (m, 1 H, C*H*CMe), 4.05 (bd, 1 H, $^1J_{PH}$ = 203 Hz, PH), 7.32–7.56 (m, 5 H, aromatics). ^{31}P{^{1}H} NMR ($CDCl_3$): δ -32.6 (s, 1 P), -28.5 (s, 1 P). LR-EI MS: *m/z* 166 $(M)^+$, 110 $(M - C_4H_8)^+$. **Fraction II**, (R_P*,R_P*)- & (R_P*,S_P*)-PCy*Bu^{s}Ph (11.98g, 64%), b.p.120-140 °C, 0.05 mm Hg. ^{1}H NMR ($CDCl_3$): δ 0.92 (t, 3 H, $^3J_{HH}$ = 7.5 Hz, CH_2CMe), 0.95 (t, 3 H, $^3J_{HH}$ = 6.9 Hz, CH_2CMe), 1.04 (dd, 3 H, $^3J_{HH}$ = 7.2 Hz, $^3J_{PH}$ = 14.7 Hz, CHC*Me*), 1.19 (dd, 3 H, $^3J_{HH}$ = 6.6 Hz, $^3J_{PH}$ = 14.7 Hz, CHC*Me*), 1.37 (m, 2 H, CH*H*), 1.71 (m, 2 H, C*H*H), 1.94 (m, 2 H, C*H*CMe), 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*-*$H_{2/6}$*), 5.69 (m, 4 H, Cy*-*H_3, H_5*), 7.25–7.51 (m, 10 H, aromatics). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 4.9 (s, 1 P), 5.6 (s, 1 P). LR-EI MS: *m/z* 244 $(M)^+$, 242 $(M - H_2)^+$, 186 $(M\text{-}C_4H_{10})^+$.



Preparation of (±)-1,2-C_6H_8(PPh_2){PPh(3-pentyl)}: The Birch reduced tertiary phosphine (±)-PCy*(3-pentyl)Ph (2.43g, 9.4 mmol) and $PHPh_2$ (1.79g, 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_4Cl (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 (3.75g, 90%). ^{1}H NMR ($CDCl_3$): δ 0.98 (t, 3 H, $^3J_{HH}$ = 7.5 Hz, C*Me*), 1.12 (t, 3 H, $^3J_{HH}$ = 7.5 Hz, C*Me*), 1.51 (m, 4 H, 2 CH_2-Cy), 1.75 (m, 2 H, CH_2Me), 1.85 (m, 2 H, CH_2Me), 2.35 (m, 1 H, C*H*Et_2), 3.76 (m, 4 H, 2 CH_2C=C), 7.28 –7.52 (m, 15 H, aromatics). ^{31}P{^{1}H} NMR ($CDCl_3$): δ -15.6, -8.8 (ABq, 2 P, $^4J_{PP}$ = 216 Hz). LR-EI MS: *m/z* 444 $(M)^+$, 373 $(M - Pe)^+$, 265 $(M - PPePh)^+$. HR-EI MS: Found for $(M)^+$ 444.2130 (calc. for $C_{29}H_{34}P_2$: 444.2136).