Stereospecific Deoxygenation of Phosphine Oxides with Retention of Configuration Using Triphenylphosphine as an Oxygen Acceptor

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General methods. All reactions were carried out under a nitrogen atmosphere by using Schlenk techniques. Dry solvents were obtained from Fluka (stored over molecular sieves) or were dried by standard methods prior to use and stored under nitrogen over 4A molecular sieves. Degassed solvents were obtained by the freeze-thaw-freeze circle. Solvents were removed by evaporation on a Buchi rotary evaporator, with vacuum provided by a controlled Teflon-membrane pump. All products were dried at oil-pump vacuum (approximately 0.5 mm Hg or better) for at least one hour before spectroscopic characterization. Thin layer chromatography (TLC) analysis was performed using Merck 60 PF254 (Merck) 0.2 mm plates (glass backed) and were visualized by UV. Flash chromatography was performed using Merck 9385 Kieselgel 60 silica gel.

NMR spectra were obtained on CDCl₃ solution at 25°C using Bruker Avance DPX 400 MHz (400 MHz for ¹H NMR) and Bruker Avance 500 MHz Broadband (500 MHz for ¹H, 125 MHz for ¹³C and 202 MHz for ³¹P) unless stated otherwise. Chemical shifts were reported in δ ppm referenced to the residual solvent peak (δ 7.24 for ¹H and δ 77.0 for ¹³C) and to an external 85% H₃PO₄ standard for ³¹P NMR. IR spectra were recorded using Perkin-Elmer Spectrum One FT-IR with ATR universal sampling accessory as neat solids. Wavelengths were quoted in cm⁻¹. Mass spectra were recorded on Perkin Elmer TurboMass GC-MS (LRMS) and Micromass Q-TOF (HRMS). The parent ion and significant fragments were quoted.

2,2'-Bis(diphenylphosphinyl)-1,1'-binaphthyl (**1c**) and (*R*)-(+)-2,2'-bis(di-*p*-tolyl phosphinyl)-1,1'-binaphthyl (**1d**) were prepared according to the literature method.¹ 1,2-Bis(dipentafluorophenylphosphinyl)ethane (**1g**) was prepared by oxidizing 1,2-bis(dipentafluorophenylphosphino)ethane which is commercially available from Strem Chemical Inc. by the previously reported procedure.² Tris[3,5-bis(trifluoromethyl)phenyl] phosphine oxide (**1h**) was prepared from tris[3,5-bis(trifluoromethyl)phenyl]phosphine using the same method. (*S*)-(-)-(2-Methoxyphenyl)methylphenyl phosphine [(*S*)-PAMP] was purchased from Digital Specialty Chemicals, Inc..

Preparation of phosphine oxides. The preparation of certain BINAP analogue diphosphines has been described elsewhere.¹ Herein we reported a modified procedure which is practical for small scale synthesis. The Ar₂PCl reagents were prepared by treating (Et₂N)PCl₂ with 2 equiv of RMgBr followed by treatment of the resulting (Et₂N)PAr₂ product with HCl.³

Bis[3,5-bis(trifluoromethyl)phenyl]phosphinyl Chloride.

5.0 g (0.010 mol) Bis[3,5-bis(trifluoromethyl)phenyl]-chlorophosphine was dissolved in 25 mL dry benzene under nitrogen atmosphere. Dry oxygen gas was conducted to bubble through the solution for 5 hours. After the bubbling was over benzene was removed under reduced pressure. The crude product (5.08 g) was collected as a white solid of about 98 mol % purity by ³¹P and ¹H NMR spectroscopy and used for next step without purification. ¹H NMR: δ 8.18 (s, 2H), 8.34 (s, 2H), 8.37 (s, 2H). ¹³C NMR: δ 122.3 (q, *J* = 272 Hz, CF₃), 127.6 (d, *J* = 3.25 Hz), 131.1 (d, *J* = 12.6 Hz), 133.2 (dq, *J* = 34.4 Hz, *J* = 14.9 Hz, C-CF₃), 135.0 (d, *J* = 125.6 Hz, C-P), ³¹P NMR: δ 35.56. FT-IR: ν 1360, 1276, 1123, 910, 844, 701, 682 cm⁻¹. LRMS (70eV), 473 [M-Cl].

Bis[4-(trifluoromethyl)phenyl]phosphinyl Chloride. Yield by NMR: 98% (4.55 g). ^1H NMR: δ 7.68 (d, J = 7.6 Hz, 4H), 7.93 (dd, J = 13.2 Hz, J = 8.0 Hz, 4H). ^{31}P NMR: δ 26.6.

Bis(3,5-dimethylphenyl)phosphinyl Chloride. Yield by NMR: 98% (3.56 g). ^1H NMR: δ 2.38 (s, 12H), 7.22 (s, 2H), 7.48 (s, 2H), 7.51 (s, 2H). ^{13}C NMR: δ 21.2 (s, CH_3), 128.3-138.7. ^{31}P NMR: δ 46.9.

Preparation of 2,2'-Bis{bis[3,5-bis(trifluoromethyl)phenyl]}phosphinyl-1,1'-binaphthyl (1a).

Method a: 0.092 g (3.79 mmol) Magnesium turnings were suspended in 3.0 mL anhydrous, degassed THF under nitrogen atmosphere. A bead of iodine was added to the above mixture and the mixture was stirred at room

temperature until the color of iodine faded. To this was added dropwise a solution of 2,2'-dibromo-1,1'-binaphthyl (0.782 g, 1.90 mmol) in toluene (12 mL) over a period of 2 h at 60 °C. The reaction mixture was further stirred at 75 °C for 2 h and was then cooled down to room temperature. To this was added dropwise a solution of bis[3,5-bis(trifluoromethyl)phenyl]phosphinyl chloride (2.32 g, 4.55 mmol) in THF (5 mL) during 5 min. After the addition was completed, the mixture was further stirred at 60 °C for 3 h and then cooled down to room temperature. To the solution was added 5 mL of 10% aqueous NH_4Cl solution and the mixture was stirred for another 10 min at ambient temperature. The organic layer was separated, washed successively with 10 mL of saturated NaHCO_3 solution and two 10 mL portions of water and then dried over anhydrous MgSO_4 . Solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (diethyl ether/hexane 1:6) to afford 0.455g of the title compound as colourless needle. Yield: 20%. ^1H NMR: δ 6.83 (d, J = 8.8 Hz 2H), 7.09 (dd, J = 7.2 Hz, J = 7.2 Hz, 2H), 7.39 (dd, J = 8.8Hz, J = 12.4 Hz, 2H),

7.47 (dd, $J = 6.8$ Hz, $J = 6.8$ Hz, 2H), 7.82 (m, 4H), 7.93 (m, 8H), 8.21 (d, $J = 11.2$ Hz, 2H). ^{13}C NMR: δ 122.6 (q, $J = 272$ Hz, CF_3), 125.8-141.8. ^{31}P NMR: δ 24.9. FT-IR: ν 1360, 1276, 1181, 1097, 908, 814, 747, 705, 681 cm^{-1} . HRMS (70eV), calcd $[\text{M}+\text{Na}]$ for $\text{C}_{52}\text{H}_{24}\text{O}_2\text{F}_{24}\text{P}_2\text{Na}$: 1221.0766; found: 1221.0873, calcd $[\text{M}+\text{H}]$ for $\text{C}_{52}\text{H}_{25}\text{O}_2\text{F}_{24}\text{P}_2$: 1199.1035; found: 1199.1050

Method b: 0.118 g (4.86 mmol) Magnesium turnings were suspended in 5.0 mL anhydrous, degassed THF under nitrogen atmosphere. A bead of iodine was added to the above mixture and the mixture was stirred at room temperature until the color of iodine faded. To this was added dropwise a solution of 2,2'-dibromo-1,1'-binaphthyl (1.00 g, 2.43 mmol) in toluene (15 mL) over a period of 2 h at 60 °C. The reaction mixture was further stirred at 75 °C for 2 h and was then cooled down to room temperature. To this was added dropwise a solution of bis[3,5-bis(trifluoromethyl)phenyl]bromophosphine (3.13 g, 5.83 mmol) in THF (8 mL) during 30 min. After the addition was completed, the mixture was further stirred at 60 °C for 2 h and then cooled down to room temperature. To the solution was added 5 mL of 10% aqueous NH_4Cl solution and excess H_2O_2 . The mixture was stirred for another 30 min at ambient temperature. Diethyl ether (30 mL) was then added and the organic layer was separated, washed successively with 10 mL of saturated NaHCO_3 solution and two 10 mL portions of water and then dried over anhydrous MgSO_4 . Solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (diethyl ether/hexane 1:6) to afford the phosphine oxide 2.04 g in 70% yield. All the analytical data are identical as method a.

2,2'-Bis [bis(4-trifluoromethylphenyl)] phosphinyl -1,1'-binaphthyl (1b). Yield: 25% (0.52 g). ^1H NMR: δ 6.69 (d, $J = 8.5$ Hz 2H), 6.83 (t, $J = 8.2$ Hz, 2H), 7.36–7.44 (m, 4H), 7.51 (d, 6.2 Hz, 8H), 7.59 (dd, $J = 8.2$ Hz, $J = 1.8$ Hz, 4H), 7.84–7.88 (m, 6H), 7.93 (dd, $J = 8.5$ Hz, $J = 2.5$

Hz, 2H). ^{13}C NMR: δ 123.5 (dq, $J = 271$ Hz, $J = 5.5$ Hz), 124.9–142.6. ^{31}P NMR: δ 27.1. FT-IR: ν 1399, 1322, 1121, 1061, 1018, 836, 816, 744, 713, 701 cm^{-1} . HRMS (70eV), calcd $[\text{M}+\text{Na}]$ for $\text{C}_{48}\text{H}_{28}\text{O}_2\text{F}_{12}\text{P}_2\text{Na}$: 949.1265; found: 949.1291. Calcd $[\text{M}+\text{H}]$ for $\text{C}_{48}\text{H}_{29}\text{O}_2\text{F}_{12}\text{P}_2$: 927.1446; found: 927.1526.

2,2'-Bis[bis(3,5-dimethylphenyl)] phosphinyl -1,1'-binaphthyl (1e).

The general procedure was followed by extending the coupling reaction time to 16 h. Yield: 71% (1.24 g). ^1H NMR (CD_2Cl_2): δ 2.13 (s, 12H), 2.23 (s, 12H), 6.85–6.93 (m, 4H), 6.99 (s, 2H), 7.07 (s, 2H), 7.11 (s, 2H), 7.14 (s, 2H), 7.23 (s, 2H), 7.25 (s, 2H), 7.42 (ddd, $J = 8.0$ Hz, $J = 8.0$ Hz and $J = 1.1$ Hz, 2H), 7.56 (dd, $J = 11.6$ Hz, $J = 8.6$ Hz, 2H), 7.84–7.88 (m, 4H). ^{13}C NMR (CD_2Cl_2): δ 20.8 (s, CH_3), 20.9 (s, CH_3), 125.6 – 142.4. ^{31}P NMR (CD_2Cl_2): δ 28.62. FT-IR: ν 2914, 1416, 1198, 1123, 851, 812, 744 cm^{-1} .

2-Bis{bis[3,5-bis(trifluoromethyl)phenyl]}phosphinyl-1,1' - binaphthyl (1f).

Yield: 23% (0.26 g). ^1H NMR: δ 6.90 (d, $J = 8.4$ Hz, 1H), 7.16 (dd, $J = 7.2$ Hz, $J = 7.2$ Hz, 1H), 7.24–7.38 (m, 4H), 7.53–7.67 (m, 6 H), 7.71 (d, $J = 8.2$ Hz, 1H), 7.76 (dd, $J = 7.0$ Hz, $J = 1.1$ Hz, 1H), 7.99–8.03 (m, 2H), 8.09 (dd, $J = 8.6$ Hz, $J = 2.5$ Hz, 1H), 8.23 (s, 1H), 8.25 (s, 1H). ^{13}C NMR: δ 121.22.4 (q, $J = 272$ Hz, CF_3), 122.7 (q, $J = 272$ Hz, CF_3), 124.4–145.8. ^{31}P NMR: δ 22.56 (s). FT-IR: ν 1363, 1279, 1132, 909, 844, 701, 683 cm^{-1} . HRMS (70eV), calcd M for $\text{C}_{36}\text{H}_{19}\text{F}_{12}\text{PO}$: 726.0982; found: 726.0963.

Preparation of 1,2-Bis(dipentafluorophenylphosphino)ethane (1g).

To a solution of 0.5 g (0.66 mmol) 1,2-bis(dipentafluorophenylphosphino)ethane in 50 mL of THF was added 3 mL (26.4

mmol) of 30% H₂O₂. The reaction mixture was stirred at room temperature until TLC showed the absence of starting material. Solvent was removed under reduced pressure and the residue was recrystallized from dichloromethane and cyclohexane to afford 0.48 g pure product. Yield: 92%. ¹H NMR: δ 3.04 (s, 4H). ¹³C NMR: δ 25.6 (m, -CH₂-), 106.7, 138.0, 144.0, 147.1. ³¹P NMR: δ 19.16 (s). FT-IR: ν 3198, 1478, 1362, 1279, 1176, 1127, 980, 904, 702, 682 cm⁻¹. HRMS (70eV), calcd [M+Na] for C₂₆H₄O₂F₂₀P₂Na: 812.9259; found: 812.9244.

Tris[3,5-bis(trifluoromethyl)phenyl]phosphine oxide

(1h). The same procedure was followed as **1g**. Yield: 96%

(0.88 g). ¹H NMR: δ 8.14 (s, 3H), 8.16 (s, 3H), 8.21 (s, 3H). ¹³C NMR: δ 122.4 (q, *J* = 272 Hz, CF₃), 127.4 (d, *J* =

3.1 Hz), 131.7 (d, *J* = 10.6 Hz), 132.9 (d, *J* = 105 Hz), 133.4 (dq, *J* = 12.5 Hz, *J* = 34.3 Hz, C-CF₃). ³¹P NMR: δ 22.28. FT-IR: ν 1362, 1278, 1173, 1127, 904, 838, 701, 681 cm⁻¹. HRMS (70eV), calcd [M+Na] for C₂₄H₉OF₁₈PNa: 709.0001; found: 709.0021.

(R)-(+)-(2-Methoxyphenyl)methylphenyl phosphine oxide

[(R)-PAMPO]. The same procedure was followed as **1g**. Yield:

99% (0.36 g), 99.5% e.e.. ¹H NMR: δ 2.05 (d, *J* = 14.1 Hz, 3H), 3.69 (s, 3H), 6.86 (dd, *J* = 8.3 Hz, *J* = 5.6 Hz, 1H), 7.07 (dt, *J* = 7.5

Hz, *J* = 1.6 Hz, 1H), 7.39 (m, 2H), 7.46 (m, 2H), 7.71 (m, 2H), 7.94 (ddd, *J* = 13.3 Hz, *J* = 7.6 Hz, *J* = 1.7 Hz, 1H). ¹³C NMR: δ 16.1 (d, *J* = 74.8 Hz), 55.3, 110.9 (d, *J* = 6.5 Hz), 121.0 (d, *J* = 11 Hz), 121.5 (d, *J* = 99.1 Hz), 128.2 (d, *J* = 12.1 Hz), 130.2 (d, *J* = 10.1 Hz), 131.2 (d, *J* = 2.5 Hz), 133.9 (d, *J* = 2.1 Hz), 135.0 (d, *J* = 103 Hz), 159.9 (d, *J* = 4.1 Hz). ³¹P NMR: δ 28.94. [α]_D²⁵ +25.8 (c 1.0 MeOH). (lit. [α]_D²⁵ +25.9 (c 1.0 MeOH))⁴

General procedure for the reduction of phosphine oxides using triphenylphosphine. In a 20mL pressure tube 0.20 mmol phosphine oxide and 0.80 mmol triphenylphosphine were dissolved in the 6mL mixture of degassed THF and

toluene (1:1) under nitrogen atmosphere. To the solution was added 0.80 mL (8.0 mmol) trichlorosilane at room temperature. The reaction mixture was then stirred at 100 °C. After TLC showed the absence of starting material and the mono-reduced product, the mixture was cooled down to ambient temperature and diluted with diethyl ether or dichloromethane (for 3a, 4a, 5a). To the solution was added 10 g ice and 10 mL 20% NaOH solution. The mixture was transferred to a separating funnel and shaken for 10 min. (For 3a, 4a and 5a the solution was heated to 50 °C to help layers separate.) The organic layer was separated and washed successively with saturated NaHCO₃, brine and water. The solution was then dried over anhydrous Na₂SO₄ and solvent removed under reduced pressure. The residue was purified by flash chromatography on silica gel (diethyl ether/hexane 1:10) to afford the title phosphine.

2,2'-Bis{bis[3,5-bis(trifluoromethyl)phenyl]}phosphino-1,1'-binaphthyl (2a). Reaction time: 96 h. Yield: 90% (0.21 g). ¹H NMR: δ 6.88 (d, *J* = 8.5 Hz, 2H), 7.22 (dd, *J* = 7.4 Hz, *J* = 7.4 Hz, 2H), 7.36 (d, *J* = 8.6 Hz, 2H), 7.49–7.52 (m, 8H), 7.59 (dd, *J* = 7.2 Hz, *J* = 7.2 Hz, 2H), 7.70 (s, 2H), 7.80 (s, 2H), 8.0 (d, *J* = 8.2 Hz, 2H), 8.08 (d, *J* = 8.5 Hz, 2H). ¹³C NMR: δ 122.7 (q, *J* = 272 Hz, CF₃), 122.8 (q, *J* = 272 Hz, CF₃), 122.3–146.4. ³¹P NMR: δ -12.62. FT-IR: ν 1352, 1276, 1174, 1129, 896, 844, 816, 747, 703, 682 cm⁻¹. HRMS (70eV), calcd [M+H] for C₅₂H₂₅F₂₄P₂: 1167.1043; found: 1167.1137.

2-Bis[3,5-bis(trifluoromethyl)phenyl]phosphinyl-2'-bis[3,5-bis(trifluoromethyl)phenyl] phosphino- 1,1'-binaphthyl (3a) was also characterised by spectroscopic measurement. ¹H NMR: δ 6.36 (d, 8.4 Hz, 1H), 6.80 (t, *J* = 7.3 Hz, 1H), 6.87 (d, *J* = 8.6 Hz, 1H), 7.15 (dd, *J* = 7.6 Hz, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 6.8

Hz, 2H), 7.35–7.38 (m, 2H), 7.46–7.49 (m, 2H), 7.56–7.60 (m, 3H), 7.64 (d, $J = 8.2$ Hz, 1H), 7.71 (s, 1H), 7.84 (d, $J = 8.6$ Hz, 1H), 7.90 (s, 1H), 8.08 (m, 3H), 8.14 (dd, $J = 8.6$ Hz, $J = 2.6$ Hz, 1H), 8.37 (d, $J = 11.0$ Hz, 2H). ^{13}C NMR: δ . ^{31}P NMR: δ -11.68 (s), 21.13 (d). FT-IR: ν 2924, 2852, 1736, 1362, 1280, 1185, 1138, 682 cm^{-1} . HRMS (70eV), calcd $[\text{M}+\text{Na}]$ for $\text{C}_{52}\text{H}_{24}\text{OF}_{24}\text{P}_2\text{Na}$: 1205.0811; found 1205.0693.

2,2'-Bis[bis(4-trifluoromethylphenyl)] phosphino-1,1'-binaphthyl (2b).

Reaction time: 18 h. Yield: 88% (0.16 g). ^1H NMR: δ 6.81 (d $J = 8.5$ Hz, 2H), 7.02 – 7.06 (m, 2H), 7.15 – 7.20 (m, 8H), 7.39–7.42 (m, 10H), 7.45–7.48 (m, 2H), 7.91 (d, $J = 8.2$ Hz, 2H), 7.98 (d, $J = 8.5$ Hz, 2H). ^{13}C NMR: δ 123.8 (q, $J = 271$ Hz, CF_3), 124.9–145.7. ^{31}P NMR: δ -14.27(s). FT-IR: ν 1606, 1398, 1322, 1167, 1117, 1060, 1015, 833, 818, 743, 702, 695 cm^{-1} . HRMS (70eV), calcd $[\text{M}+\text{H}]$ for $\text{C}_{48}\text{H}_{25}\text{F}_{12}\text{P}_2$: 895.1547; found 895.1569.

2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl (2c).

Reaction time: 3 h. Yield: 95% (0.12 g). ^1H NMR: δ 6.85 (d, $J = 8.4$ Hz, 2H), 6.93 (m, 2H), 7.07–7.25 (m, 20H), 7.37 (m, 2H), 7.47 (dd, $J = 8.5$ Hz, $J = 2.2$ Hz, 2H), 7.85 (d, $J = 8.2$ Hz, 2H), 7.91 (d, $J = 8.5$ Hz, 2H). ^{31}P NMR: δ -14.79.

(R)-(+)-2,2'-Bis(di-*p*-tolylphosphino)-1,1'-binaphthyl (2d).

Reaction time: 2 h. Yield: 92% (0.125 g). $[\alpha]_D^{25} +172.0^\circ$ (c 0.56, benzene) (lit. $[\alpha]_D^{24} +174.0^\circ$ (c 0.886, benzene)). ^1H NMR: δ 2.28 (s, 6H), 2.29 (s, 6H), 6.88 (d, $J = 8.5$ Hz, 2H), 6.95–7.03 (m, 18H), 7.37–7.40 (m, 2H), 7.50 (dd, $J = 8.5$ Hz, $J = 1.9$ Hz, 2H), 7.85 (d, $J = 8.1$ Hz, 2H), 7.89 (d, $J = 8.5$ Hz, 2H). ^{13}C NMR: δ 21.19, 21.25, 125.73–145.32. ^{31}P NMR: δ -16.24.

2,2'-Bis[bis(3,5-dimethylphenyl)]phosphino-1,1'-binaphthyl (2e). Reaction time: 2 h. Yield: 96% (0.135 g). ^1H NMR: δ 2.14 (s, 12H), 2.19 (s, 12H), 6.73-6.77 (m, 4H), 6.82 (s, 2H), 6.89 (s, 2H), 6.93 (d, $J = 8.5$ Hz, 2H), 7.09 (dd, $J = 7.3$ Hz, $J = 7.2$ Hz, 2H), 7.46 (dd, $J = 7.2$ Hz, $J = 7.2$ Hz, 2H), 7.54 (d, $J = 8.5$ Hz, 2H), 7.92-7.95 (m, 4H).

^{13}C NMR: δ 20.89, 20.96, 125.60-145.64. ^{31}P NMR: δ -14.81.

2-Bis[bis[3,5-bis(trifluoromethyl)phenyl]]phosphino-1,1'-binaphthyl (2f). Reaction time: 20 h. Yield: 88% (0.125 g). ^1H NMR: δ 6.93 (d, $J = 8.4$ Hz, 1H), 7.14-7.17 (m, 1H), 7.26-7.46 (m, 5H), 7.50 (d, $J = 6.5$ Hz, 2H), 7.57-7.61 (m, 2H), 7.67 (s, 1H), 7.68 (s, 1H), 7.74 (s, 1H),

7.90-8.02 (m, 5H). ^{13}C NMR: δ 122.8 (q, $J = 273$ Hz, CF_3), 123.0 (q, $J = 273$ Hz, CF_3), 122.85-146.61. ^{31}P NMR: δ -11.06. FT-IR: ν 1351, 1274, 1173, 1118, 1095, 895, 844, 803, 782, 745, 703, 681 cm^{-1} . HRMS (70eV), calcd M for $\text{C}_{36}\text{H}_{19}\text{F}_{12}\text{P}$: 710.1033; found: 710.1001.

1,2-Bis(dipentafluorophenylphosphino) ethane (2g). Reaction time: 4 h. Yield: 90% (0.14 g). ^1H NMR: δ 2.58 (t, $J = 6.95$ Hz, 4H). ^{13}C NMR: δ

20.20, 107.58-148.70. ^{31}P NMR: δ -43.41 (m). FT-IR: ν 1640, 1516, 1466, 1384, 1291, 1086, 970, 840, 744, 684 cm^{-1} .

Tris[3,5-bis(trifluoromethyl)phenyl]phosphine (2h).

Reaction time: 15 h. Yield: 93% (0.13 g). ^1H NMR: δ 7.73 (s, 3H), 7.74 (s, 3H), 7.98 (s, 3H). ^{31}P NMR: δ -2.89. FT-IR: ν 1355, 1277, 1172, 1122, 900, 840, 701, 681 cm^{-1} .

(S)-(-)-(2-Methoxyphenyl)ethylphenylphosphine [(S)-PAMP].

This reaction was conducted at the temperature of 80°C using 0.80 mmol (S)-PAMPO. Reaction time: 3h. Yield: 95% (0.175 g).

^1H NMR: δ 1.62 (d, J = 4.1 Hz, 3H), 3.81 (s, 3H), 6.88 (dd, J = 8.2 Hz, J = 4.1 Hz, 1H), 6.94 (t, J = 7.4 Hz, 1H), 7.07 (m, H), 7.31-7.39 (m, 4H), 7.49 (m, 2H). ^{13}C NMR: δ 11.1 (d, J = 13.2 Hz), 55.5, 110.1 (d, J = 33.6 Hz), 120.9, 128.2 (d, J = 6.8 Hz), 128.4, 129.8, 131.5 (d, J = 3.4 Hz), 132.6 (d, J = 19.4 Hz), 161.0 (d, J = 13.3 Hz). ^{31}P NMR: δ -36.04. $[\alpha]^{25}_{\text{D}}$ -42.7 (*c* 1.3 MeOH), e.e. 99% compared with literature ($[\alpha]^{25}_{\text{D}}$ -38.3 (*c* 1.7 MeOH), 89% e.e.).⁵

General procedure for the reduction of phosphine oxides using triethylphosphite.

In a 20mL pressure tube 0.24 g (0.20 mmol) phosphine oxide **1a** and 0.33 g (2.00 mmol) triethylphosphite were dissolved in the 6mL mixture of degassed THF and Toluene (1:1) under nitrogen atmosphere. To the solution was added 0.80 mL (8.0 mmol) trichlorosilane at room temperature. The reaction mixture was then stirred at 100 °C. After TLC showed the absence of starting material and the mono-reduced product (88 hours), the mixture was cooled down to ambient temperature and diluted with diethyl ether. To the solution was added 10 g ice and 10 mL 20% NaOH solution. The mixture was transferred to a separating funnel and shaken for 10 min. The organic layer was separated and washed successively with saturated NaHCO_3 , brine and water. The solution was then dried over anhydrous Na_2SO_4 and solvent removed under reduced pressure. The residue was purified by a short pad of silica gel (diethyl ether/hexane 1:10) to afford the phosphine **1b** (0.21 g). Yield: 90%.

All the analytical data of the phosphines were identical as outlined above.

^{18}O -labelling experiments. ^{18}O -**1a** was prepared according to **method a** (vide supra) and reduced with the general procedure. HRMS (70eV), calcd $[\text{M}+\text{H}]$ for $\text{C}_{52}\text{H}_{25}^{18}\text{O}_2\text{F}_{24}\text{P}_2$: 1203.1026; found: 1203.1054.

$^{18}\text{OPPh}_3$ HRMS (70eV) calcd $[\text{M}+\text{H}]$ for $\text{C}_{18}\text{H}_{15}^{18}\text{OP}$: 281.0983; found: 281.1013.

From the mass spectrum it clearly shows the ^{18}O transferred from the ^{18}O -labeled substrate to triphenylphosphine. The presence of ^{16}O triphenylphosphine oxide was due to the aerobic workup conditions.

X-ray crystal structures of phosphine oxides **1a**, **1b** and phosphines **2a**, **2b** (requisite CIF files have been submitted to the journal).

X-ray structure of **1a**

X-ray structure of **2a**

X-ray structure of **1b**

X-ray structure of **2b**

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