Supporting Information

Simple Unprecedented Conversion of Phosphine Oxides and Sulfides to Phosphine Boranes using Sodium Borohydride

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General Experimental

Melting points were determined on a Reichert Thermovar melting point apparatus and are uncorrected. Elemental analyses were carried out by the Microanalytical Laboratory, University College Dublin. IR spectra were obtained on a Varian 3100 FTIR Excalibur series spectrometer. Routine electrospray mass spectra were obtained on a Micromass Quattro spectrometer. High-resolution mass spectra were run on a Waters Micromass GCT system either in (CI) chemical ionization or (EI) electron ionization mode, also at UCD. The NMR spectra were recorded at 25 °C on Varian VNMRS 300, 400, and 500 MHz spectrometers. $^{13}$C NMR spectra ($^{31}$P decoupled) were recorded on a VNMRS 600 MHz spectrometer. All NMR samples of potentially air-sensitive compounds were made up under nitrogen by syringing a small amount of a solution into an NMR tube contained in a long Schlenk tube that was charged with an atmosphere of nitrogen, and then adding dry CDCl$_3$ to dissolve the compound. The NMR tube was then taken out using tweezers. CDCl$_3$ was purchased from Aldrich, and dried by adding to a Young’s flask containing activated molecular sieves (4 Å) under an atmosphere of nitrogen. It was then stored under nitrogen in the Young’s flask over the molecular sieves.

High-performance liquid chromatography was performed on a Agilent Technologies 1200 series equipped with a 6 column switching device. HPLC grade solvents, purchased from Aldrich and Lennox Supplies Ireland, were used as supplied. All samples were filtered through an Acrodisc CR 13 mm syringe filter with 0.2 µm PTFE prior to injection.

Unless otherwise stated all reactions were carried out under N$_2$ atmosphere in dry glassware using Schlenk-line techniques and all glassware was flame dried prior to use. Air and moisture sensitive liquids and solutions were transferred via syringe. All commercially available solvents were used as supplied unless otherwise stated. All “dry” solvents were dried and distilled by standard procedures or were processed through a Grubbs type still, supplied by Innovative Technology Inc. Pure Solv-400-3-MD solvent purification system. Oxygen free nitrogen was obtained from BOC gases and was used without further drying. Thin layer chromatography (TLC) was performed on Merck pre-coated Kieselgel 60F$_{254}$ aluminium plates with realization by UV irradiation. Flash column chromatography was performed on Merck silica 9385, particle size 0.040-0.063 mm. Magnesium turnings for Grignard reactions were heated to 180 °C for at least 24 hours prior to use. Further activation was achieved by heating and stirring vigorously under vacuum for approximately 10 minutes immediately prior to reaction. 4Å Molecular sieves were kept stored in an oven at 180 °C at all times. Prior to use
sieves were heated to ~300 °C, using a heat gun, for 2 minutes while under vacuum. They were allowed to cool to room temperature and this procedure was then repeated.

Oxalyl chloride, triphenylphosphine oxide, triphenylphosphine sulfide, tributylphosphine oxide, BINAP, Meerwein’s salts, methyl triflate, methyl tosylate, methyl iodide, sulfuryl chloride, methane sulfonyl chloride, thionyl chloride, NaBH₄ and other reagents were purchased from Sigma-Aldrich, Fluka or Merck & Co., Inc. (±)-1,2-ethandiylbis[(o-anisylphenyl)phenylphosphine oxide and (±)-1,2-ethandiylbis[(o-tolylphenyl)phenylphosphine oxide were gifted by Celtic Catalysts Ltd. BINAPO was made from BINAP by oxidation with hydrogen peroxide.²

Enatioenriched methylphenyl-o-tolylphosphine oxide 93% ee (S), o-Anisylmethylphenylphosphine oxide 95% ee (R) were gifted by Celtic Catalysts Ltd. (2-Biphenyl)methylphenylphosphine oxide 81% ee (S), tert-Butylmethylphenylphosphine oxide 46% ee (S); 53% ee (R), methylphenyl(mesityl)phosphine oxide 44% ee (R) were synthesied by asymmetic Appel reaction.²³

A number of the required phosphines, phosphine oxides, and phosphine sulfides were synthesised previously by us as follows.

<table>
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<tr>
<th>Compound</th>
<th>Reference</th>
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<td>Methylphenyl-o-tolylphosphine oxide</td>
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<tr>
<td>o-Anisylmethylphenylphosphine oxide</td>
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<td>Methylphenyl-(2-trifluoromethyl)phenylphosphine oxide</td>
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<td>(2-Biphenyl)methylphenylphosphine oxide</td>
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<td>(4-Fluoro-2-methylphenyl)methylphenylphosphine oxide:</td>
<td>3</td>
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<tr>
<td>(2,4-Dimethylphenyl)methylphenylphosphine oxide</td>
<td>3</td>
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<td>Methylphenyl(2-i-propylphenyl)phosphine oxide:</td>
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<td>(±)-Methyl-(1-naphthyl)phenylphosphine oxide</td>
<td>3</td>
</tr>
</tbody>
</table>
(±)-Cyclohexylmethylphenylphosphine oxide: From Phosphine (2 g, 9.7 mmol), in a yield of (1.8 g, 84%) $^1$H NMR (CDCl$_3$, 300 MHz): $\delta = 7.71$-$7.46$ (m, 5H, Ar) 1.68 (d, $^2J_{PH} = 12.4$ Hz, 3H, PCH$_3$), 1.69-1.16 (m, 11H, c-Hexyl) ppm. $^{31}$P NMR (CDCl$_3$, 300 MHz): $\delta = 40.6$ ppm (Lit.$^4$ -33.1 ppm).

P-phenyldibenzophosphole oxide: From P-phenyl dibenzophosphole$^5$ (2 g, 7.7 mmol), by oxidation with hydrogen peroxide$^2$ gave P-phenyldibenzophosphole oxide (1.82 g, 86%) $^1$H NMR (CDCl$_3$, 300 MHz): $\delta = 7.80$-$7.29$ (m, 13H, Ar) ppm. $^{31}$P NMR (CDCl$_3$, 300 MHz): $\delta = 33.5$ ppm (lit.$^5$ 33.8)

Methylphenyl(mesityl)phosphine oxide$^6$: From methylphenyl (mesityl)phosphine$^7$ (1g, 4.1 mmol) by oxidation with hydrogen peroxide gave methylphenyl(mesityl)phosphine oxide (0.86 g, 81%); $^1$H NMR (CDCl$_3$, 300 MHz): $\delta = 7.64$-$7.46$ (m, 2H, Ar), 7.50-$7.38$ (m, 3H, Ar), 6.90-6.89 (m, 2H, Ar), 2.41 (s, 6H, o-Me), 2.30 (s, 3H, p-Me), 1.21 (d, $^2J_{PH} = 6.0$ Hz, 3H, PCH$_3$); $^{31}$P NMR (CDCl$_3$, 300 MHz): $\delta = 34.6$ ppm.
Synthesis of Required Secondary Phosphine oxides

Exemplar: Synthesis of o-tolylphenylphosphine oxide: A dry 100 mL two-necked round bottom flask fitted with reflux condenser, nitrogen inlet and outlet and septum was charged with magnesium turnings (0.5 g, 18.7 mmol, 1.1 equiv). 2-Bromotoluene (3.0 g, 17 mmol, 1 equiv) was dissolved in THF (10 mL), and approx. 2 mL of this solution was added to the flask via syringe. The mixture was heated to reflux with vigorous stirring until the reaction initiated, at which point the remainder of the solution was added over approximately 30 minutes, also via syringe. After this time the reaction was refluxed for a further 2 hours. The reaction was allowed to cool to room temperature and, it was then transferred through a syringe into a pressure-equalized dropping funnel attached to a flame dried and degassed 100 mL round bottom flask, which had been charged previously with dichlorophenylphosphine (3.0 g, 17 mmol, 1 equiv) and anhydrous THF (10 mL). This solution was cooled to -78 °C using dry ice-acetone mixture and the Grignard solution was added dropwise over 1 hour. The flask was allowed to warm to room temperature and was then stirred for an hour. A 10% aqueous solution of H$_2$SO$_4$ (100 mL) was added dropwise to the reaction mixture at 0 °C and the reaction was allowed stirred for an hour. The solvent was removed in vacuo, and extracted with dichloromethane (3 ×100 mL), which had been stored over anhydrous magnesium sulfate for 30 min under a nitrogen atmosphere. The extracts were filtered through a sintered funnel under nitrogen, the solvent removed in vacuo, phosphine oxide was isolated as colourless oil.

(±)-o-tolylphenylphosphine oxide: (3.35 g, 88 %) $^1$H NMR (CDCl$_3$, 300 MHz): δ = 8.13 (d, $J_{HP} = 483.8$ Hz, 1H), 7.75-7.21 (m, 9H, Ar), 2.35 (s, 3H, ArCH$_3$). $^{13}$C NMR [$^1$H, $^{31}$P] (CDCl$_3$, 151 MHz): δ = 141.4, 132.8, 132.3, 132.2, 131.42, 131.41, 130.8, 129.5, 128.9, 126.0, 20.2. $^{31}$P NMR (CDCl$_3$, 121 MHz): δ =21.6 (lit$^8$ 21.9) ppm. HRMS (Cl) Calc. 216.0704; found: 216.0701. HPLC (CHIRALCEL® IA column, 90:10 Heptane - EtOH, 1 mL/min R$_f$: 18.4 min, 19.9 min.

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(±)-tert-Butyphenylphosphine oxide: From PhPCl₂ (3.0 g, 17 mmol, 1 equiv) and 1BuMgBr (17 mL 1.0 M in THF 1 equiv) by the procedure above gave (±)-tert-Butyphenylphosphine oxide (2.65 g, 85 %) ¹H NMR (CDCl₃, 300 MHz): δ = 7.68-7.38 (m, 5H, Ar), 7.08 (d, JHP = 458.9 Hz, 1H), 1.15(d, JHP= 16.5 Hz, 9H) ¹³C NMR (CDCl₃, 151 MHz): δ = 132.6, 130.9, 128.4, 127.7, 23.7, 23.6. ³¹P NMR (CDCl₃, 121 MHz): δ =47.4 (lit⁸ 47.6) ppm. HRMS (CI) Calc. 182.0861; found: 182.0857. HPLC (CHIRALCEL® IA column, 90:10 Heptane - EtOH, 1 mL/min Ret: 18.4 min, 19.9 min.

(±)-tert-Butyphenylphosphine sulfide: From PhPCl₂ (3.0 g, 17 mmol, 1 equiv), 1BuMgBr (17 mL 1.0 M in THF 1 equiv), LiAlH₄ (8.5 mL 2.0 M in THF 1 equiv.) and sulphur (0.65 g, 1.2 equiv, 20.4 mmol) by the procedure above gave (±)-tert-Butyphenylphosphine sulphide as solid (2.64 g, 78 %) ¹H NMR (CDCl₃, 300 MHz): δ = 7.48-7.18 (m, 5H, Ar), 6.83 (d, JHP = 458.9 Hz, 1H), 0.9 (d, JHP= 16.5 Hz, 9H) ³¹P NMR (CDCl₃, 121 MHz): δ =54.0 (lit⁹ 54.0)

Synthesis of methylphenylphosphine oxide⁴

\[
\begin{align*}
\text{PhCl} & \rightarrow \text{PhPO} & \text{MeOH} & \rightarrow \text{MeI} & \rightarrow \text{PhPO} & \rightarrow \text{LiAlH}_4 & \rightarrow \text{PhPH} & \rightarrow \text{O} \\
\end{align*}
\]

Synthesis of dimethylphenylphosphonite: A 500 mL 2 necked round bottom flask equipped with a pressure equalised dropping funnel attached to a Schlenk line was charged with anhydrous pyridine (80 mL, 0.9 mol), dichlorophenylphosphine (84 g, 0.46 mol) and degassed pentane (250 mL). The stirred solution was cooled to 0 °C and anhydrous methanol (38 mL, 0.93 mol) in degassed pentane (25 mL) was added over a period of 2 hours. The pyridine hydrochloride salt was filtered off under N₂ and the filtrate was concentrated under reduced pressure. The crude grainy colourless liquid product was carried onto the next step without further purification. (38 g, 47 %) ³¹P NMR (CDCl₃, 121 MHz): δ =165.09 ppm.
Synthesis of methyl-methylphenylphosphinate: A 3-neck 250 mL round bottom flask was fitted with a thermometer and two condensers, one of which was connected to a pressure equalised dropping funnel which in turn was connected to a Schlenk line via a stop-cock adaptor. The flask was charged with a small amount of dimethylphenylphosphonite (3 mL) and a few drops of methyl iodide. The orange mixture was stirred and warmed carefully under a N\textsubscript{2} atmosphere until a very vigorous exothermic reaction began. The phosphonite (35 g, 0.21 mol) was added at a rate sufficient to keep the temperature at roughly 70 °C. It was necessary to periodically add small amount of methyl iodide to maintain a constant reaction. After complete addition the red mixture was stirred at room temperature overnight. Distillation under reduced pressure (98°C @ 0.4 mm Hg) yielded a colourless oil (27.2 g 78%). \textsuperscript{31}P NMR (CDCl\textsubscript{3}, 121 MHz): \(\delta = 48.7 \text{ ppm}\).

Synthesis of methylphenylphosphine: To a stirred solution of LiAlH\textsubscript{4} (1 M soln. In THF 50 mL, 50 mmol) in dry THF (25 mL) at -78 °C was added a solution of a methylphenylphophinate (5.0 g, 29.4 mmol) in dry THF (75 mL) over 1 hour. After warming to room temperature the solution was then refluxed for 4 hours. After removal of THF under reduced pressure, degassed H\textsubscript{2}O (20 mL) was added very slowly, followed by degassed aqueous NaOH (20% 20 mL) and finally degassed H\textsubscript{2}O (20 mL). The product was extracted into degassed DCM (2 x 100 mL), dried over MgSO\textsubscript{4} and the solvent removed under reduced pressure. \textsuperscript{31}P NMR (CDCl\textsubscript{3}, 121 MHz): \(\delta = -76.4 \text{ ppm}\).

methylphenylphosphine oxide: The phosphine from previous reaction was opened to air and left for 3 days for complete conversion to oxide. (2.9 g 70%) \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 300 MHz): \(\delta = 7.80-7.42 \text{ (m, 5H, Ar), 7.64 (d, } J_{\text{HP}} = 484.4 \text{ Hz, 1H), 1.81 (d, } J_{\text{HP}} = 11 \text{ Hz, 3H) }\textsuperscript{31}P \text{ NMR (CDCl}\textsubscript{3}, 121 MHz): \(\delta = 21.2 \text{ (lit}\textsuperscript{3} \text{ 20.3).} \)
Synthesis of Required Phosphine Sulfides

Exemplar Synthesis of (±)-o-anisylmethylphenylphosphine sulfide: To a stirred solution of phosphine (0.5 g, 2.1 mmol, 1 equiv) in DCM (30 mL, degassed) at 0 °C (ice bath) sulphur (74 mg, 1.2 equiv) was added through powder funnel. After the addition was complete the suspension was stirred for 2 hrs. Excess sulphur was filtered off and the solvent was removed in vacuo to yield light yellow solid. (0.5 g 90%) $^1$H NMR (CDCl$_3$, 300 MHz): δ = 8.20-8.13 (m, 1H, Ar), 7.68-7.63 (m, 2H, Ar), 7.45-7.19 (m, 4H, Ar), 7.07-7.04 (m, 1H, Ar), 6.81-6.78 (m, 1H, Ar), 3.59 (s, 3H, OCH$_3$), 2.29 (d, $^2$J$_{PH}$ = 14.4 Hz, 3H, CH$_3$); $^{31}$P NMR (CDCl$_3$, 121 MHz): δ = 35.2 (lit$^{10}$ 35.9) ppm.

(±)-o-tolylmethylphenylphosphine sulfide: From phosphine$^2$ (2 g, 9.3 mmol), in a yield of (1.9 g, 82%) $^1$H NMR (CDCl$_3$, 300 MHz): δ = 8.48-8.40 (m, 3H, Ar), 8.32-8.24 (m, 4H, Ar), 7.92-7.521 (m, 2H, Ar), 2.75 (s, 3H, ArCH$_3$), 2.32 (d, $^2$J$_{PH}$ = 14.1 Hz, 3H, CH$_3$) ppm. $^{31}$P NMR (CDCl$_3$, 121 MHz): δ = 34.7 (lit$^{11}$ 34.4) ppm.

(±)-(2-Biphenyl)methylphenylphosphine sulfide: From phosphine$^3$ (2 g, 7.2 mmol), in a yield of (1.8 g, 81%) $^1$H NMR (CDCl$_3$, 300 MHz): δ = 8.60-724 (m, 14H, Ar), 2.29 (d, $^2$J$_{PH}$ = 14.1 Hz, 3H, CH$_3$) ppm. $^{31}$P NMR (CDCl$_3$, 121 MHz): δ = 37.2 ppm. $^{13}$C NMR ($^1$H, $^{31}$P) (CDCl$_3$, 151 MHz): δ = 136.5, 132.8, 132.2, 131.5, 130.4, 129.7, 129.3, 128.8, 127.9, 127.7, 127.3, 126.3, 125.3, 121.1, 23.2 ppm. IR: v$^\nu$ =3185, 2468, 1621, 1342, 1292, 585 (P=S) cm$^{-1}$. HRMS (EI): C$_{19}$ H$_{17}$ PS Calculated: 308.0788 Found: 308.0781.
(±)-Methylphenyl(2-trifluoromethylphenyl)phosphine sulfide: From phosphine\(^3\) (1 g, 5.5 mmol), in a yield of (0.55 g, 87%) \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta = 8.01-7.42\) (m, 9H, Ar), 2.4 (d, \(^2\)J\(_{PH}\) = 12.2, Hz, 3H, PCH\(_3\)) ppm. \(^{31}\)P NMR (CDCl\(_3\), 121 MHz): \(\delta = 40.6\) ppm. \(^{13}\)C NMR \(\{^{1}\)H,\(^{31}\)P\} (CDCl\(_3\), 151 MHz): \(\delta = 136.9, 135.4, 133.1, 132.9, 132.7, 131.8, 131.4, 130.0, 129.4, 127.4, 123.5\) (q, \(J = 273.2\) Hz), 17.6 ppm. IR: \(\tilde{\nu} = 3213, 1649, 1521, 1474, 1232, 595\) (P=S) cm\(^{-1}\). HRMS (EI): \(\text{C}_{14}\text{H}_{12}\text{F}_{3}\text{PS}\) Calculated: 300.0349 Found: 300.0342.

(±)-Methylphenyl(2-i-propylphenyl)phosphine sulfide: From phosphine\(^2\) (2 g, 8.2 mmol), in a yield of (1.81 g, 80%) \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta = 7.62-7.12\) (m, 9H, Ar) 3.24 (quintet, \(J = 6.7\) Hz, 1H, CH\(_2\)), 2.21 (d, \(^2\)J\(_{PH}\) = 14.0 Hz, 3H, PCH\(_3\)), 1.34 (d, \(J = 6.8\) Hz 3H, i-Pr-Me), 0.92 \(^{31}\)P NMR (CDCl\(_3\), 121 MHz): \(\delta = 37.3\) ppm. \(^{13}\)C NMR \(\{^{1}\)H,\(^{31}\)P\} (CDCl\(_3\), 151 MHz): \(\delta = 154.3, 136.2, 134.9, 132.9, 131.4, 130.2, 129.2, 128.3, 127.4, 125.5, 32.5, 23.4, 17.6\) ppm. IR: \(\tilde{\nu} = 3385, 2868, 1521, 1592, 1474, 1364, 580\) (P=S) cm\(^{-1}\). HRMS (EI): \(\text{C}_{16}\text{H}_{19}\text{PS}\) Calculated: 274.0945 Found: 274.0939.
General Procedure for Reduction of Achiral Racemic Tertiary and Secondary phosphine oxide and sulfides using oxalyl chloride and sodium borohydride.

To a stirred solution of phosphine oxide/sulfide (1.0 mmol) in toluene (2 mL) was added oxalyl chloride (1.0 mmol) dissolved in toluene (2 mL) dropwise at room temperature under a nitrogen atmosphere. At this point $^{31}$P-NMR of the reaction mixture shows full conversion to chlorophosphosphonium salt (CPS). After 30 min, sodium borohydride (2.1 mmol) dissolved in diglyme (~3 mL) was added dropwise to the reaction mixture. This mixture was stirred for 1 h, where $^{31}$P shows full completion of CPS to phosphine borane. The reaction mixture was washed with deionised water (5 mL) and the isolated organic layer was dried over anhydrous MgSO₄. The drying agent was removed by filtration, and the solvent was removed \textit{in vacuo} to give colourless oil, which was eluted through a silica plug with 50:50 cyclohexane/ethylacetate. Solvent removal \textit{in vacuo} yielded the pure phosphine borane.

Table A. Reduction of achiral and racemic tertiary phosphine oxides and sulfides.

<table>
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<th>Entry</th>
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<td>X= S 35.2</td>
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<td>X= S 40.6</td>
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**Electronic Supplementary Material (ESI) for Chemical Communications**

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[Chemical structures and data]

14  
\[
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O & O \\
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\end{array}
\]

15  
\[
\begin{array}{ccc}
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O & O \\
40.6 & 91.9 & 17.1
\end{array}
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16  
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\]

17  
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\text{n-Bu} & \text{n-Bu} \\
56.2 & 105.1 & 14.1
\end{array}
\]

\[a\]: PX: phosphine oxide or sulfide;  \[b\]: CPS: shift assigned as chlorophosphonium salt;  \[c\]: PB phosphine borane, isolated yield > 85%. No other material was apparent in the \(^{31}\)P NMR of the crude reaction mixture. Unless otherwise noted, these are known compounds - literature references given in ESI;  \[d\]: this work.
Table B. Reduction of racemic secondary phosphine oxides and sulfide.

\[
\begin{align*}
\text{R}^1 & \quad \text{R}^2 & \quad \text{R}^3 & \quad \text{oxalyl chloride} & \quad \text{NaBH}_4 \\
X & \quad \text{Cl} & \quad \text{Cl} & \quad \text{room temp.} & \quad \text{room temp.}
\end{align*}
\]

\[
\begin{align*}
\text{PX}^a & & \text{CPS}^b & & \text{PB}^c \\
21.6 & & 78.4 & & -6.3 \\
21.2 & & 100.9 & & -13.5 \\
\text{X = O 47.4} & & & & \text{X = S 54.0}
\end{align*}
\]

\[\text{PX}: \text{phosphine oxide or sulfide}; \quad \text{CPS}: \text{shift assigned as chlorophosphonium salt}; \quad \text{PB}: \text{phosphine borane, isolated yield > 85%}. \text{No other material was apparent in the }^{31}\text{P nmr of the crude reaction mixture. These are known compounds - literature references given in SI.}\]
**Triphenylphosphine borane**: From triphenylphosphine oxide (0.27 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.) followed by the treatment with NaBH$_4$ in diglyme (3.4 mL, 0.6 M, 2.1 mmol, 2.1 equiv) gave triphenylphosphine borane. (0.24 g, 88%) $^1$H NMR (CDCl$_3$, 300 MHz): $\delta = 7.61–7.40$ (m, 15H, Ph-H), 1.74–0.83 (br, 3H, BH$_3$) ppm. $^{31}$P NMR (CDCl$_3$, 121 MHz): $\delta = 21.5$ (lit.$^{12}$) 20.6 ppm.

**Triphenylphosphine borane**: From triphenylphosphine sulfide (0.29 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.) followed by the treatment with NaBH$_4$ in diglyme (3.4 mL, 0.6 M, 2.1 mmol, 2.1 equiv) gave triphenylphosphine borane. (0.25 g, 92%) $^{31}$P NMR (CDCl$_3$, 121 MHz): $\delta = 21.5$ (lit.$^{12}$ above) 20.6 ppm.

**Methylphenyl(o-tolyl)phosphine borane**: From methylphenyl(o-tolyl)phosphine oxide (0.23 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.) followed by the treatment with NaBH$_4$ in diglyme (3.4 mL, 0.6 M, 2.1 mmol, 2.1 equiv) gave methylphenyl(o-tolyl)phosphine borane (0.20 g, 87%) $^1$H NMR (CDCl$_3$, 300 MHz): $\delta = 7.72–7.14$ (m, 9H, Ar), 2.17 (s, 3H, ArCH$_3$), 1.82 (d, $^2$J$_{PH} = 9.8$ Hz, 3H, CH$_3$) 1.61–0.72 (br, 3H, BH$_3$) ppm ppm. $^{31}$P NMR (CDCl$_3$, 121 MHz): $\delta = 10.2$ (lit.$^{13}$ 10.9) ppm

**Methylphenyl(o-tolyl)phosphine borane**: From methylphenyl(o-tolyl)phosphine sulfide (0.24 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.) followed by the treatment with NaBH$_4$ in diglyme (3.4 mL, 0.6 M, 2.1 mmol, 2.1 equiv) gave methylphenyl(o-tolyl)phosphine borane (0.21 g, 91%) $^{31}$P NMR (CDCl$_3$, 121 MHz): $\delta = 10.5$ (lit.$^{13}$ 10.9) ppm

**Methylphenyl(o-anisyl)phosphine borane**: From methylphenyl(o-anisyl)phosphine oxide (0.24 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.) followed by the treatment with NaBH$_4$ in diglyme (3.4 mL, 0.6 M, 2.1 mmol, 2.1 equiv) gave methylphenyl(o-anisyl)phosphine borane. (0.22 g, 91%) $^1$H NMR
(CDCl₃, 300 MHz): δ = 7.90–6.77 (m, 9 H, Ar), 3.68 (s, 3 H, Ar-OCH₃), 1.94 (d, 2JPH = 10.2 Hz, 3H, CH₃) 1.43–0.50 (br, 3H, BH₃) ppm ³¹P NMR (CDCl₃, 121 MHz): δ = 8.4 (lit. 14 9.2) ppm.

Methylphenyl(o-anisyl)phosphine borane: From methylphenyl(o-anisyl)phosphine sulfide (0.26 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.) followed by the treatment with NaBH₄ in diglyme (3.4 mL, 0.6 M, 2.1 mmol, 2.1 equiv) gave methylphenyl(o-anisyl)phosphine borane. (0.21 g, 87%) ³¹P NMR (CDCl₃, 121 MHz): δ = 8.7 (lit. 14 9.2) ppm.

(±)-1,2-Ethandiylbis[(o-anisylphenyl)phenylphosphine borane: From 1,2-ethandiylbis[(o-anisylphenyl)phenylphosphine oxide (0.49 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.2 mL, 2.0 mmol, 2 equiv.) followed by the treatment with NaBH₄ in diglyme (6.9 mL, 0.6 M, 4.2 mmol, 4.2 equiv) gave 1,2-ethandiylbis[(o-anisylphenyl)phenylphosphine borane (0.42 g, 87%) ¹H NMR (CDCl₃, 300 MHz): δ = 7.90-7.83 (m, 2H, Ar), 7.69-7.64 (m, 4H, Ar), 7.49-7.36 (m, 8H, Ar), 7.05-7.00 (m, 2H, Ar), 6.83-6.80(m, 2H, Ar), 3.62 (s, 6H, OCH₃), 1.87 (m, 4H, P-CH₂), 1.22–0.90 (br, 6H, BH₃) ppm. ³¹P NMR (CDCl₃, 300 MHz): δ = 18.5 ppm (lit. 15 18.8 ppm).

(±)-1,2-Ethandiylbis[(o-tolylphenyl)phenylphosphine borane: From 1,2-ethandiylbis[(o-tolylphenyl)phenylphosphine (0.46 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.2 mL, 2.0 mmol, 2 equiv.) followed by the treatment with NaBH₄ in diglyme (6.9 mL, 0.6 M, 4.2 mmol, 4.2 equiv) gave 1,2-ethandiylbis[(o-tolylphenyl)phenylphosphine borane. (0.43 g, 88%) ¹H NMR (CDCl₃, 300 MHz): δ = 7.66-7.60 (m, 2H, Ar), 7.52-7.37 (m, 8H, Ar), 7.30-7.26 (m, 2H, Ar), 7.20-7.18(m, 6H, Ar), 2.14 (s, 6H, CH₃), 2.48 (m, 4H, P-CH₂), 1.26–0.88 (br, 6H, BH₃) ppm. ³¹P NMR (CDCl₃, 300 MHz): δ = 18.5 ppm (lit. 13 19.1 ppm)
1,1’-Binaphthalene-2,2’-diyl)bis(diphenylphosphineborane): From (1,1’Binaphthalene-2,2’-diyl)bis(diphenylphosphine oxide) (0.33 g, 0.5 mmol, 1 equiv) treated with oxalyl chloride (0.2 mL, 1.0 mmol, 2 equiv.) followed by the treatment with NaBH₄ in diglyme (6.9 mL, 0.6 M, 2.1 mmol, 4.2 equiv) gave 1,1’-Binaphthalene-2,2’-diyl)bis(diphenylphosphine borane) (0.29 g, 87%)

1H NMR (CDCl₃, 300 MHz): δ = 7.94 (d, J = 8.5 Hz, 2H), 7.84 (d, J = 8.2 Hz, 2H), 7.82 (dd, J = 8.5 Hz, J = 2.2Hz, 2H), 7.74-7.52 (m, 20H), 7.41 (m, 2H), 7.39 (m, 2H), 7.36 (d, J = 8.5 Hz, 2H). 1.69–0.72 (br, 6H, BH₃)

31P NMR (CDCl₃, 300 MHz): δ = 23.0 (lit. 16 23.0) ppm.

P-Phenyldibenzophosphole borane: From P-phenyldibenzophosphole oxide (0.28 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.) followed by the treatment with NaBH₄ in diglyme (3.4 mL, 0.6 M, 2.1 mmol, 2.1 equiv) gave P-phenyldibenzophosphole borane. (0.25 g, 93%); 1H NMR (CDCl₃, 300 MHz): δ = 7.90-7.29 (m, 13H, Ar), 0.90-1.43 (b, m, 3H, BH₃) ppm. 31P NMR (CDCl₃, 121 MHz): δ = 25.0 ppm. 13C NMR {1H, 31P} (CDCl₃, 151 MHz): δ = 142.3, 132.7, 132.1, 131.0, 130.9, 129.4, 127.9, 127.1, 126.6, 120.3 ppm. 11B NMR (128 MHz, CDCl₃) δ = -39.6 ppm. IR (KBr, cm⁻¹) v: 3053, 2395 (BH₃), 1636, 1593, 1438, 1294, 1164, 1027, 766. HRMS (M –BH₃ + H) + C₁₈H₁₄P Calculated: 261.0833 Found: 261.0828.

(±)-(2-Biphenyl)methylphenylphosphine borane: From (±)-(2-Biphenyl)methylphenylphosphine oxide (0.29 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.) followed by the treatment with NaBH₄ in diglyme (3.4 mL, 0.6 M, 2.1 mmol, 2.1 equiv) gave (2-Biphenyl)methylphenylphosphine borane. (0.26 g, 89%) 1H NMR (CDCl₃, 300 MHz): δ =7.89-7.82 (m, 5H, Ar), 7.70–7.19 (m, 9 H, Ar), 1.41 (d, JₚH = 10.1 Hz, 3 H, CH3), 1.56–0.73 (br, 3H, BH₃) ppm. 31P NMR (CDCl₃, 121 MHz): δ = 13.3 (lit. 17 14.4) ppm.

(±)-(2-Biphenyl)methylphenylphosphine borane: From (±)-(2-Biphenyl)methylphenylphosphine sulfide (0.31 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.)
followed by the treatment with NaBH$_4$ in diglyme (3.4 mL, 0.6 M, 2.1 mmol, 2.1 equiv) gave (2-Biphenyl)methylphenylphosphine borane. (0.24 g, 85%). $^{31}$P NMR (CDCl$_3$, 121 MHz): $\delta = 13.8$ (lit.$^{17}$ 14.4) ppm.

(±)-Methylphenyl(2-iso-propylphenyl)phosphine borane: From methylphenyl -(2-iso-propylphenyl)phosphine oxide (0.26 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.) followed by the treatment with NaBH$_4$ in diglyme (3.4 mL, 0.6 M, 2.1 mmol, 2.1 equiv) gave methylphenyl(2-iso-propylphenyl)phosphine borane. (0.24 g, 92%) $^1$H NMR (CDCl$_3$, 300 MHz): $\delta = 7.67$-$7.26$ (m, 9H, Ar) $3.18$ (quintet, $J = 6.7$ Hz, 1H, CH$_2$), $1.86$ (d, $^2J_{PH} = 10.0$ Hz, 3H, PCH$_3$), $1.08$ (d, $J = 6.8$ Hz 3H, i-Pr-Me), $0.73$ (d, $J = 7.4$ Hz, 3H, i-Pr-Me); $1.62$-$0.51$ (br, m, 3H, BH$_3$) ppm. $^{31}$P NMR (CDCl$_3$, 300 MHz) : $\delta = 9.0$ ppm (lit.$^{13}$ 9.7ppm).

(±)-Methylphenyl(2-iso-propylphenyl)phosphine borane: From methylphenyl -(2-iso-propylphenyl)phosphine sulfide (0.27 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.) followed by the treatment with NaBH$_4$ in diglyme (3.4 mL, 0.6 M, 2.1 mmol, 2.1 equiv) gave methylphenyl(2-iso-propylphenyl)phosphine borane. (0.22 g, 86%) $^{31}$P NMR (CDCl$_3$, 300 MHz) : $\delta = 9.3$ ppm (lit.$^{13}$ 9.7ppm).

(±)-Methylphenyl (2-trifluoromethylphenyl)phosphine borane$^{18}$ : From methylphenyl (2-trifluoromethylphenyl)phosphine oxide (0.28 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.) followed by the treatment with NaBH$_4$ in diglyme (3.4 mL, 0.6 M, 2.1 mmol, 2.1 equiv) gave methylphenyl (2-trifluoromethylphenyl)phosphine borane. (0.26 g, 92%) $^1$H NMR (CDCl$_3$, 300 MHz): $\delta = 7.70$-$7.02$ (m, 9H, Ar), $1.91$ (d, $^2J_{PH} = 9.9$ Hz, 3H, PCH$_3$), $0.65$-$1.53$ (br, m, 3H) ppm. $^{31}$P NMR (CDCl$_3$, 121 MHz): $\delta = 18.3$. (lit.$^{18}$ 18.7)

(±)-Methylphenyl (2-trifluoromethylphenyl)phosphine borane : From methylphenyl (2-trifluoromethylphenyl)phosphine sulfide (0.30 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.) followed by the treatment with NaBH$_4$ in diglyme (3.4 mL, 0.6 M, 2.1
mmol, 2.1 equiv) gave methylphenyl (2-trifluoromethylphenyl)phosphine borane. (0.23 g, 88%) $^{31}$P NMR (CDCl$_3$, 121 MHz): $\delta = 18.5$. (lit$^{18}$ 18.7)

(±)-Methyl(1-naphthyl)phenylphosphine borane: From (±)-methyl(1-naphthyl)phenylphosphine oxide (0.26 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.) followed by the treatment with NaBH$_4$ in diglyme (3.4 mL, 0.6 M, 2.1 mmol, 2.1 equiv) gave methyl(1-naphthyl)phenylphosphine borane. (0.24 g, 91%) $^1$H NMR (CDCl$_3$, 300 MHz): $\delta = 8.22$ (d, $J = 8.4$ Hz, 1H, Ar), 8.00 (d, $J = 8.4$ Hz, 1H, Ar), 7.91-7.37 (m, 10H, Ar), 2.23 (d, $2J_{PH} = 10.2$ Hz, 3H, CH$_3$) 1.53- 0.62 (br, m, 3H) ppm. $^{31}$P NMR (CDCl$_3$, 121 MHz): $\delta = 13.3$ ppm (Lit.$^{17}$ 14.4 ppm).

(±)-(2,4-Dimethylphenyl)methylphenylphosphine borane: From (±)-2,4-dimethylphenyl)methylphenylphosphine oxide (0.26 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.) followed by the treatment with NaBH$_4$ in diglyme (3.4 mL, 0.6 M, 2.1 mmol, 2.1 equiv) gave (±)-2,4-dimethylphenyl)methylphenylphosphine borane. (0.24 g, 92%) $^1$H NMR (CDCl$_3$, 300 MHz): $\delta = 7.64$-7.09 (m, 8H, Ar), 2.55 (s, 3H, ArCH$_3$), 2.33 (s, 3H, ArCH$_3$), 1.99 (d, $2J_{PH} = 9.8$ Hz, 3H, PCH$_3$) 0.62-1.67 (b, m, 3H, BH$_3$) ppm. $^{31}$P NMR (CDCl$_3$, 121 MHz): $\delta = 10.5$ ppm.$^{13}$C NMR {$^1$H, $^{31}$P} (CDCl$_3$, 151 MHz): $\delta = 142.8, 140.6, 138.7, 134.6, 132.6, 133.3, 131.4, 130.7, 128.4, 126.9, 21.3, 21.3, 12.8$ ppm. $^{11}$B NMR (128 MHz, CDCl$_3$) $\delta = -36.5$ ppm) IR (KBr, cm$^{-1}$) v: 3120, 2385 (BH$_3$), 1626, 1583, 1438, 1320, 1236, 1145, 725. HRMS (M–BH$_3$ + H)$^+$ C$_{15}$ H$_{18}$P Calculated: 229.1146 Found: 229.1138; HPLC (CHIRALPAK® ASH column, 98:2 heptane: EtOH, 1 mL/min) $R_t$: 8.0 min, 10.2 min.

(±)-(4-Fluoro-2-methylphenyl)methylphenylphosphine borane: (±)-(4-fluoro-2-methylphenyl)methylphenylphosphine oxide (0.26 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.) followed by the treatment with NaBH$_4$ in diglyme (3.4 mL, 0.6...
M, 2.1 mmol, 2.1 equiv) gave (±)-(4-fluoro-2-methylphenyl)methylphenylphosphine borane. (0.22 g, 84%) \(^{1}\)H NMR (CDCl\(_3\), 300 MHz): \(\delta = 7.74-6.89\) (m, 8H, Ar), 2.18 (s, 3H, ArCH\(_3\)), 1.84 (d, \(^{2}\)J\(_{PH}\) = 9.9 Hz, 3H, CH\(_3\)), 0.90-1.57 (br, m, 3H, BH\(_3\)) ppm. \(^{31}\)P NMR (CDCl\(_3\), 121 MHz): \(\delta = 10.2\) ppm. \(^{13}\)C NMR \{\(^{1}\)H, \(^{31}\)P\} (CDCl\(_3\), 151 MHz): \(\delta = 163.11\) (d, \(^{1}\)J\(_{PF}\) = 249.3 Hz), 145.3, 137.7, 134.8, 131.2, 129.1, 127.9, 125.3, 118.4, 112.9, 21.7, 12.6 ppm. \(^{11}\)B NMR (128 MHz, CDCl\(_3\)) \(\delta = -35.7\) ppm. IR (KBr, cm\(^{-1}\)) \(\nu: 3020, 2345\) (BH\(_3\)), 1650, 1493, 1332, 1294, 1121, 1012, 742. HRMS (M –BH\(_3\) + H)\(^{+}\) C\(_{14}\)H\(_{15}\)PF Calculated: 233.0895 Found: 233.0887 HPLC (CHIRA LPAK\textsuperscript{®} ASH column, 98:2 heptane: EtOH, 1 mL/min) \(R_t\): 9.0 min, 11.0 min.

(±)-Methylphenyl(mesityl)phosphine borane: From (±)-methylphenyl(mesityl)phosphine oxide (0.26 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.) followed by the treatment with NaBH\(_4\) in diglyme (3.4 mL, 0.6 M, 2.1 mmol, 2.1 equiv) gave (±)-methylphenyl(mesityl)phosphine borane. (0.21 g, 84%) \(^{1}\)H NMR (CDCl\(_3\), 300 MHz): \(\delta = 7.49-7.42\) (m, 2H, Ar), 7.36-7.08 (m, 3H, Ar), 6.84-6.78 (m, 2H, Ar), 2.23 (s, 6H, o-Me), 2.20 (s, 3H, p-Me), 1.86 (d, \(^{2}\)J\(_{PH}\) = 9.6 Hz, 3H, PCH\(_3\)); 1.38-0.82 (b, m, 3H, BH\(_3\)) ppm. \(^{31}\)P NMR (CDCl\(_3\), 121 MHz): \(\delta = 11.6\) ppm. \(^{13}\)C NMR \{\(^{1}\)H, \(^{31}\)P\} (CDCl\(_3\), 151 MHz): \(\delta = 142.5, 140.0, 134.4, 133.6, 129.9, 129.4, 129.1, 127.7, 127.1, 124.2, 22.9, 19.8, 16.0 ppm. \(^{11}\)B NMR (128 MHz, CDCl\(_3\)) \(\delta = -32.5\) ppm); IR (KBr, cm\(^{-1}\)) \(\nu: 3010, 2356\) (BH\(_3\)), 1746, 1623, 1336, 1320, 1136, 765.

(±)-Cyclohexylmethylphenylphosphine borane: From (±)-(2-Cyclohexylmethylphenylphosphine oxide (0.23 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.) followed by the treatment with NaBH\(_4\) in diglyme (3.4 mL, 0.6 M, 2.1 mmol, 2.1 equiv) gave (±)-cyclohexylmethylphenylphosphine borane. (0.20 g, 90%) \(^{1}\)H NMR (CDCl\(_3\), 300 MHz): \(\delta = 7.73-7.46\) (m, 4H, Ar) 1.68 (d, \(^{2}\)J\(_{PH}\) = 10.4 Hz, 3H, PCH\(_3\)), 1.69-1.16 (m, 11H, c-Hexyl); 1.46-0.38 (br, m, 3H) ppm \(^{31}\)P NMR (CDCl\(_3\), 300 MHz): \(\delta = 17.1\) ppm (Lit.\(^{17}\) 16.2 ppm).
**(+)-tert-Butylmethylphenylphosphine borane:** From (+)-tert-Butylmethylphenylphosphine oxide (0.20 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.) followed by the treatment with NaBH₄ in diglyme (3.4 mL, 0.6 M, 2.1 mmol, 2.1 equiv) gave (+)-tert-Butylmethylphenylphosphine borane. (0.17 g, 89%)

**¹H NMR (CDCl₃, 300 MHz):** δ = 7.68-7.38 (m, 5H, Ar), 1.45 (d, JₚH = 10.2 Hz, 3H), 1.09(d, JₚH = 16.5 Hz, 9H), 1.12-0.88 (br, m, 3H) ppm. **³¹P NMR (CDCl₃, 121 MHz):** δ = 25.8 (lit.²⁹ 25.3) ppm.

**Tri-n-butylphosphine borane:** From tri-n-butylphosphine oxide (0.21 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.) followed by the treatment with NaBH₄ in diglyme (3.4 mL, 0.6 M, 2.1 mmol, 2.1 equiv) gave tri-n-butylphosphine borane. (0.19 g, 86%)

**¹H NMR (CDCl₃, 300 MHz):** δ = 1.55-1.47 (m, 6H), 1.45-1.32 (m, 12H), 0.85 (t, JₚH = 7.5 Hz, 9H), 0.55-0.15(br, m, 3H) ppm. **³¹P NMR (CDCl₃, 121 MHz):** δ = 14.1 (lit.²⁰ 14.7) ppm.

**Phenyl(o-tolyl)phosphine borane:** From methylphenyl(o-tolyl)phosphine oxide (0.15 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.) followed by the treatment with NaBH₄ in diglyme (3.4 mL, 0.6 M, 2.1 mmol, 2.1 equiv) gave phenyl(o-tolyl)phosphine borane. (0.13 g, 87%)

**¹H NMR (CDCl₃, 300 MHz):** δ = 7.82-7.30 (m, 9H, Ar), 6.58 (d, JₚH = 385 Hz, 1H), 2.46(s, 3H), 1.65-0.45 (br, m, 3H) ppm. **³¹P NMR (CDCl₃, 121 MHz):** δ = -6.3 (lit.²¹ -3.8) ppm.

**Methylphenylphosphine borane:** From Methylphenylphosphine oxide (0.14 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.) followed by the treatment with NaBH₄ in diglyme (3.4 mL, 0.6 M, 2.1 mmol, 2.1 equiv) gave methylphenylphosphine borane. (0.12 g, 86%)

**¹H NMR (CDCl₃, 300 MHz):** δ = 7.75-7.44 (m, 9H, Ar), 5.35 (d, JₚH = 375 Hz, 1H), 1.67 (d, JₚH = 12.1 Hz, 3H), 0.68-0.45 (br, m, 3H) ppm. **³¹P NMR (CDCl₃, 121 MHz):** δ = -13.5 (lit.²² -14.6).
(±)-tert-Butylphenylphosphine borane: From tert-butylphenylphosphine oxide (0.18 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.) followed by the treatment with NaBH₄ in diglyme (3.4 mL, 0.6 M, 2.1 mmol, 2.1 equiv) gave tert-butylphenylphosphine borane. (0.16 g, 88%) ¹H NMR (CDCl₃, 300 MHz): δ 7.80-7.45 (m, 5H, Ph), 5.25 (q, J₉P = 375 Hz, 1H), 1.21 (d, J₉P = 15.2 Hz, t-Bu, 9H) 1.58-0.32 (m, 3H, BH₃). ³¹P NMR (CDCl₃, 121 MHz): δ = 31.0 (lit 32.0) ppm.

(±)-tert-Butylphenylphosphine borane: From tert-butylphenylphosphine sulfide (0.20 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.) followed by the treatment with NaBH₄ in diglyme (3.4 mL, 0.6 M, 2.1 mmol, 2.1 equiv) gave tert-butylphenylphosphine borane. (0.15 g, 86%) ³¹P NMR (CDCl₃, 121 MHz): δ = 31.4 (lit 31.9) ppm.
Reduction of Enantioenriched phosphine oxide

Using electrophilic chlorides (S)-methylphenyl-o-tolylphosphine oxide of 93% ee was subject to the general procedure for reduction with oxalyl chloride and sodium borohydride described above. The results are shown in Table 1.

**Table C** Reduction of enantiomerically enriched phosphine oxide with electrophilic chlorides under various conditions.

![Chemical structure diagram showing reduction process]

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<sup>a</sup> = Both steps in the reaction were done at -78 °C for entries 2-10, r.t. for entry 1.; CPS (by <sup>31</sup>P NMR) was same for entries 1-9; for entry 10 CPS was observed at -31 and 71 ppm which found to be covalent and ionic form respectively.<sup>23</sup> <sup>b</sup> = (PB) phosphine borane; % ee was determined by CSP HPLC; yield > 95% except for entry 8 which was 65% (by <sup>31</sup>P NMR). <sup>c</sup> = Very slow addition addition of both oxalyl chloride and NaBH<sub>4</sub>; <sup>d</sup> = DME: dimethoxy ethane <sup>e</sup> = (IL) Ionic liquid (1-methyl-3-octylimidazolium tetrafluoroborate;
General Procedure for the Stereospecific Conversion of Enantioenriched Phosphine oxide to phosphine borane

To a stirred solution of alkylation agent (1.2 mmol) in DCM or DME (2 mL) phosphine oxide (1.0 mmol) dissolved in DCM or DME (2 mL) was added dropwise at room temperature under a nitrogen atmosphere. The reaction mixture was refluxed gently for 2 hrs at which point $^{31}$P NMR showed the complete conversion of phosphine oxide to the alkoxyphosphonium salt. After cooling to room temperature, sodium borohydride (3 mmol) dissolved in diglyme (5 mL) was added dropwise to the reaction mixture. This mixture was refluxed gently for 2 h. Once the $^{31}$P NMR showed the full conversion of salt to phosphine borane the reaction mixture was washed with deionised water (5 mL), and the isolated organic layer was dried over anhydrous MgSO$_4$. The drying agent was removed by filtration, and the solvent was removed in vacuo to give colourless oil, which was eluted through a silica plug using 50:50 cyclohexane/ethylacetate as eluting solvent. Solvent removal in vacuo yielded the pure phosphine borane.

Table D. Stereospecific reduction/boronation$^a$ of enantioenriched phosphine oxide.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Phosphine oxide</th>
<th>Alkyl. agent</th>
<th>Yield (%)$^b$</th>
<th>% ee$^c$ (config)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1$^{d,e}$</td>
<td>Ph</td>
<td>MeOTf</td>
<td>62</td>
<td>93 (S)</td>
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<tr>
<td>2$^e$</td>
<td>Ph</td>
<td>MeOTf</td>
<td>73</td>
<td>93 (S)</td>
</tr>
<tr>
<td>3$^f$</td>
<td>[Et$_3$O]BF$_4$</td>
<td>76</td>
<td>93 (S)</td>
<td></td>
</tr>
</tbody>
</table>
Unless otherwise specified the addition of alkylating agent (in DCM) and NaBH$_4$ (in diglyme) was carried at room temperature followed by refluxing; b isolated yield; c by CSP HPLC, configuration determined as described below; d NaBH$_4$ was added at -78 °C; e in DME solvent, methoxyphosphonium salt was observed at δ 75.9 ppm in $^{31}$P NMR; f ethoxyphosphonium salt was observed at δ 70.3 ppm in $^{31}$P NMR; g ethoxyphosphonium salt was observed at δ 78.3 ppm in $^{31}$P NMR; h methoxyphosphonium salt was observed at δ 71.9 ppm in $^{31}$P NMR; i ethoxyphosphonium salt was observed at δ 73.8 ppm in $^{31}$P NMR; j ethoxyphosphonium salt was observed at δ 67.8 ppm in $^{31}$P NMR; k % ee of phosphine oxide obtained by converting scalemic phosphine borane to scalemic phosphine oxide using DABCO and H$_2$O$_2$; config remains to be assigned; l ethoxyphosphonium salt was observed at δ 89.8 ppm in $^{31}$P NMR.
Table D

**Entry 1:** (S)-Methylphenyl(o-tolyl)phosphine oxide (0.23 g, 1.0 mmol, 1 equiv) was treated with methyl triflate (0.13 mL, 1.2 mmol, 1.2 equiv.) in DME solvent followed by the treatment with NaBH₄ in diglyme (6 mL, 0.5 M, 3.0 mmol, 3.0 equiv) gave methylphenyl(o-tolyl)phosphine borane (0.14 g, 62%, 93 % ee (S))

**Entry 2:** (S)-Methylphenyl(o-tolyl)phosphine oxide (0.23 g, 1.0 mmol, 1 equiv) was treated with methyl triflate (0.13 mL, 1.2 mmol, 1.2 equiv.) in DME solvent followed by the treatment with NaBH₄ in diglyme (6 mL, 0.5 M, 3.0 mmol, 3.0 equiv) gave (S)-methylphenyl(o-tolyl)phosphine borane (0.16 g, 73%, 93 % ee (S))

**Entry 3:** (S)-Methylphenyl(o-tolyl)phosphine oxide (0.23 g, 1.0 mmol, 1 equiv) was treated with (triethyloxonium tetrafluoroborate) [Et₃O]BF₄ (0.22 g, 1.2 mmol, 1.2 equiv.) in DCM solvent followed by the treatment with NaBH₄ in diglyme (6 mL, 0.5 M, 3.0 mmol, 3.0 equiv) gave methylphenyl(o-tolyl)phosphine borane (0.17 g, 76%; 93 % ee (S))

**Entry 4:** (S)-Methylphenyl(o-tolyl)phosphine oxide (0.23 g, 1.0 mmol, 1 equiv) was treated with (trimethyloxonium tetrafluoroborate) [Me₃O]BF₄ (0.17 g, 1.2 mmol, 1.2 equiv.) in DCM solvent followed by the treatment with NaBH₄ in diglyme (6 mL, 0.5 M, 3.0 mmol, 3.0 equiv) gave methylphenyl(o-tolyl)phosphine borane (0.16 g, 71%; 93 % ee (S))

**Entry 5:** (R)-Methylphenyl(anisyl)phosphine oxide (0.25 g, 1.0 mmol, 1 equiv) was treated with (triethyloxonium tetrafluoroborate) [Et₃O]BF₄ (0.22 g, 1.2 mmol, 1.2 equiv.) in DCM solvent followed by the treatment with NaBH₄ in diglyme (6 mL, 0.5 M, 3.0 mmol, 3.0 equiv) gave methylphenyl(anisyl)phosphine borane (0.16 g, 67%; 95 % ee (R))

**Entry 6:** (R)-Methylphenyl(anisyl)phosphine oxide (0.25 g, 1.0 mmol, 1 equiv) was treated with (trimethyloxonium tetrafluoroborate) [Me₃O]BF₄ (0.17 g, 1.2 mmol, 1.2 equiv.) in DCM solvent followed by the treatment with NaBH₄ in diglyme (6 mL, 0.5 M, 3.0 mmol, 3.0 equiv) gave methylphenyl(anisyl)phosphine borane (0.17 g, 71%; 95 % ee (R))

**Entry 7:** (S)-Methylphenyl(biphenyl)phosphine oxide (0.14 g, 0.5 mmol, 1 equiv) was treated with (triethyloxonium tetrafluoroborate) [Et₃O]BF₄ (0.11 g, 0.6 mmol, 1.2 equiv.) in DCM solvent followed by the treatment with NaBH₄ in diglyme (3 mL, 0.5 M, 1.5 mmol, 3.0 equiv) gave methylphenyl(biphenyl)phosphine borane (95 mg, 68%; 81 % ee (S))
**Entry 8**: (R)-Methylphenyl(mesityl)phosphine oxide (85 mg, 0.3 mmol, 1 equiv) was treated with (triethylloxonium tetrafluoroborate) [Et$_3$O]BF$_4$ (73 mg, 0.4 mmol, 1.2 equiv.) in DCM solvent followed by the treatment with NaBH$_4$ in diglyme (2 mL, 0.5 M, 1.0 mmol, 3.0 equiv) gave methylphenyl(mesityl)phosphine borane (52 mg, 67%). For HPLC analysis methylphenyl(mesityl)phosphine borane was treated with DABCO (1.2 equiv) followed by hydrogen peroxide (1.2 equiv) to give (S)-Methylphenyl(mesityl)phosphine oxide 44 % ee.

**Entry 9**: (R)-tert-Butylmethylphenylphosphine oxide (0.19 g, 1.0 mmol, 1 equiv) was treated with (triethylloxonium tetrafluoroborate) [Et$_3$O]BF$_4$ (0.22 g, 1.2 mmol, 1.2 equiv.) in DCM solvent followed by the treatment with NaBH$_4$ in diglyme (6 mL, 0.5 M, 3.0 mmol, 3.0 equiv) gave tert-Butylmethylphenylphosphine borane (0.12 g, 63%; 53 % ee (R).

**Entry 10**: (S)-tert-Butylmethylphenylphosphine oxide (0.19 g, 1.0 mmol, 1 equiv) was treated with (triethylloxonium tetrafluoroborate) [Et$_3$O]BF$_4$ (0.22 g, 1.2 mmol, 1.2 equiv.) in DCM solvent followed by the treatment with NaBH$_4$ in diglyme (6 mL, 0.5 M, 3.0 mmol, 3.0 equiv) gave tert-Butylmethylphenylphosphine borane (0.13 g, 68%; 46 % ee (S).
Determination of absolute configurations of phosphine oxide and borane

These were assigned according to the literature reported data. Thus 93% (S)-methylphenylo-tolyl phosphine oxide and 95 % (R)-methylphenylanisylphosphine oxide obtained from Celtic Catalysts Ltd. was confirmed as the (S) and (R) enantiomer respectively by HPLC comparison with the phosphine oxide obtained from an asymmetric Appel reaction on racemic methylphenylo-tolylphosphine with (+)-menthol and HCA, which gave (S)-enantiomer of phosphine oxide, reaction on racemic methylphenylanisylphosphine with (-)-menthol and HCA, which gave (R)-enantiomer of phosphine oxide.

The Absolute configuration of phosphine oxide and phosphine borane were assigned by comparison with the literature reported (cited near the entry no. ) HPLC data.

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<th>Entry</th>
<th>Phosphine oxide and Phosphine borane</th>
<th>Column</th>
<th>Condition</th>
<th>t1 (min)</th>
<th>t2 (min)</th>
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<td>Chiralpak IA</td>
<td>Heptane/Et-OH = 80/20 1 mL/min</td>
<td>7.4 (S)</td>
<td>8.4 (R)</td>
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<td>2.13</td>
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<td>Chiralpak AS-H</td>
<td>Heptane/Et-OH = 98/02 1 mL/min</td>
<td>10.1 (R)</td>
<td>12.5 (S)</td>
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<td><img src="image3" alt="Phosphine oxide" /></td>
<td>Chiralpak IA</td>
<td>Heptane/Et-OH = 90/10 1 mL/min</td>
<td>14.6(R)</td>
<td>15.9(S)</td>
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<td>Heptane/Et-OH = 70/30 1 mL/min</td>
<td>9.0(S) 10.2(R)</td>
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NMR spectra and HPLC traces of phosphine boranes.
Electronic Supplementary Material (ESI) for Chemical Communications
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PROTON_001

MeO

BH₃ BH₃
Ph-P Ph

OMe

O-anisyl-dipamp-BH₃

0.90 0.93 0.95 1.15 1.17 1.22 1.87 3.62 6.80 6.83 7.00 7.03 7.05 7.26 7.26 7.36 7.38 7.40 7.42 7.44 7.46 7.49 7.64 7.66 7.67 7.67 7.69 7.83 7.86 7.88 7.90

PHOSPHORUS_001

MeO

BH₃ BH₃
Ph-P Ph

OMe

A (ppm) 18.52
Supporting HPLC Traces

Entry 2 in Table A

Racemic methylphenyl-o-tolylphosphine oxide

Acq. Operator : General sequence  Seq. Line :  4
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Injection Volume : 5 ul
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(modified after loading)
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Last changed : 7/9/2009 9:49:45 AM by General sequence
Method Info : Isocratic at 80/20 heptane/eton 30min at 1ml/min

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 D. Smp=230.8 Ref=360.100
Entry 1-4 in Table D

Scalemic methylphenyl-o-tolylphosphine oxide used as starting material

---

Acq. Operator : General sequence
Acq. Instrument : Kev HPLC 1
Injection Date : 3/13/2010 7:04:04 PM
Inj Vol : 5 µl
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Last changed : 3/13/2010 7:03:52 PM by General sequence
(modified after loading)
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Last changed : 3/15/2010 10:58:35 AM by General sequence
Method Info : Isocratic at 80/20 heptane/EtOH for 30min at 1ml/min

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Area Percent Report

Sorted By : Signal
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Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DADl D, Sig=230,8 Ref=360,100

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93% ee (S)
Entry 2 in Table A

Racemic methylphenyl-o-tolylphosphine phosphine borane

Instrument Conditions : At Start At Stop
Column Temp. (left) : 24.9 24.9 °C
Column Temp. (right) : 26.0 26.0 °C
Pressure : 54.1 54.5 bar
Flow : 1.000 1.000 ml/min
Valve 1 Position : 4 4

Detector Lamp Burn Times: Current On-Time Accumulated On-Time
DAD 1, UV Lamp : 1.75 1193.6 h
DAD 1, Visible Lamp : OFF 11.2 h

Solvent Description :
PMP1, Solvent A : Heptane
PMP1, Solvent B : EtOH

---

![Graph](image-url)

---

Electronic Supplementary Material (ESI) for Chemical Communications
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Entry 1 and 2 in Table D

Scalemic methylphenylortho-tolylphosphine borane obtained by using MeOTF as alkylating agent and NaBH₄ as reductant

**Acq. Operator**: General sequence  
**Seq. Line**: 5  
**Acq. Instrument**: Key HPLC 1  
**Location**: Vial 11  
**Injection Date**: 1/27/2010 5:27:07 PM  
**Inj**: 1  
**Inj Volume**: 5 µl  
**Acq. Method**: C:\Chem32\DATA\RUN QUEUE 2010-01-27 16-52-30\ISO_98_02_60MIN_1MLMIN.M  
**Last changed**: 1/27/2010 5:26:56 PM by General sequence  
(modified after loading)  
**Analysis Method**: C:\CHEM32\METHODS\03 QUICKSTART 1 MLMIN METHODS\ISO_98_02_30MIN_1MLMIN.M  
**Last changed**: 6/28/2010 8:54:49 AM by General sequence  
**Method Info**: Isocratic at 98/02 heptane/EtOH for 30min at 1ml/min

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**Area Percent Report**

**Sorted By**: Signal  
**Multiplier**: 1.0000  
**Dilution**: 1.0000  
Use Multiplier & Dilution Factor with ISTDs

**Signal 1: DAD1 D, Sig=230,8 Ref=360,100**

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Entry 3 in Table D

Scalemic methylphenyl-o-tolylphosphine borane obtained by using [Et₂O]⁻BF₄⁺ as alkylating agent and NaBH₄ as reductant

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<td>Inj Volume</td>
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**Signal 1:** DAD1 D, Sig=230.8 Ref=360,100 (C:\CHEM32\DATA\RUN QUEUE 2010-01-30 13-49-46\1101.D)

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Entry 4 in Table D

Sclaremic methylphenyl-o-tolylphosphine borane obtained by using Me₃O⁺BF₄⁻ as alkylating agent and NaBH₄ as reductant

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Area Percent Report

Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000

Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 D, Sig=230,8 Ref=360,100

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Entry 3 in Table A

Racemic (±)anisylmethylphenylphosphine oxide
Entry 5-6 in Table D

Scalemic anisylmethylphenylphosphine oxide 95.7 % ee (R)
Entry 3 in Table A

Racemic (±)anisylmethylphenylphosphine borane

Acq. Operator : General sequence
Seq. Line : 3
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Injection Date : 6/29/2010 10:17:16 PM
Inj : 1
Inj Volume : 5 µl
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Last changed : 6/29/2010 10:17:05 PM by General sequence
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Method Info : Stabilise column at 99/1 heptane/EtOH for 10 min at 1ml/min

Signal 1: DAD1 D, Slg=230.8 Ref=360.100 (C:\CHEM32\DATA\RUN QUEUE 2010-06-29 21-42-34\011-3961.D)
Entry 5 and 6 in Table D

Scalemic anisylmethylphenylphosphine borane 95.6 % ee

---

Acq. Operator : DGG  
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Acq. Instrument : HPLC1  
Location : Vial 22  
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Inj Vol : 5.000 µl  
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(modified after loading)  
Method Info : Isocratic at 99/01 heptane/EtOH for 15min at 0.5ml/min  
Additional Info : Peak(s) manually integrated

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Area Percent Report

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Sorted By : Signal  
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Dilution : 1.0000  
Use Multiplier & dilution factor with ratios

Signal 1: DAD 4, Sig=230.8 Ref=360.100

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<thead>
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<th>Peak RetTime</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 15.755 min</td>
<td>0.321</td>
<td>6156.71533</td>
<td>428.82746</td>
<td>97.7988</td>
</tr>
<tr>
<td>2 16.720 min</td>
<td>0.449</td>
<td>184.48784</td>
<td>6.84908</td>
<td>1.2112</td>
</tr>
</tbody>
</table>

Totals : 8343.20317 435.67657

---

*** End of Report ***
Entry 7 in Table D

Scalemic (2-Biphenyl)methylphenylphosphine oxide 81 % ee (S)

---

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Entry 8 in Table A

Racemic (±)-(2-Biphenyl)methylphenylphosphine borane

Acq. Operator : General sequence  Seq. Line : 6
Acq. Instrument : Kev HPLC 1  Location : Vial 2
Injection Date : 6/2/2010 10:34:56 PM  Inj : 1
  Inj Volume : 5 μl
Acq. Method : C:\Chem32\DATA\RUN QUEUE 2010-04-21 18-10-30\RUN QUEUE 2010-06-02 20-48-45\ISO_98_02_30MIN_1MLMIN.M
Last changed : 6/2/2010 10:34:46 PM by General sequence
  (modified after loading)
Analysis Method : C:\CHEM32\DATA\METHODS\03 QUICKSTART 1 1MLMIN METHODS\ISO_98_02_30MIN_1MLMIN.M
Last changed : 5/20/2010 11:50:38 AM by General sequence
Method Info : Isocratic at 98/02 heptane/EtOH for 30min at 1ml/min

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 D, Sig=230.8 Ref=360.100

<table>
<thead>
<tr>
<th>#</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.746</td>
<td>VB</td>
<td>3.006</td>
<td>2148</td>
<td>0.2174</td>
<td>49.6276</td>
</tr>
<tr>
<td>2</td>
<td>10.063</td>
<td>BB</td>
<td>3.053</td>
<td>1767</td>
<td>0.2695</td>
<td>50.3724</td>
</tr>
</tbody>
</table>
Entry 7 in Table D

Scalemic (2-Biphenyl)methylphenylphosphine borane 81 % ee($S$)

---

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---
Entry 14 in Table A

Racemic methylphenyl(mesityl)phosphine oxide

---

Instrument Conditions
- At Start: 14.0
- At Stop: 23.9 °C

Column resp. (left): 12.0 m
- pressure: 10.9 Bar
- flow: 1.000 mL/min

Valve 1 Position: 1

Detector Lamp Burn Times: Current On-Time Accumulated On-Time
- DAD 1, UV lamp: 9.01 h 3128.3 h
- DAD 1, Visible lamp: OFF 87.5 h

Solvant Description:
- PXPI, Solvent A: Heptane
- PXPI, Solvent B: EtOH

---

Peak RetTime Type Width Area Height Area [%]
--- --- --- --- --- --- --- --- --- ---
1 15.561 min 0.3886 1.1232% 653.3940 54.2340
2 17.194 min 0.4407 1.2814% 486.1792 45.7660

Totals: 2.8297% 1129.5725
Entry 8 in Table D

Scalemic methylphenyl(mesityl)phosphine oxide 44 % ee (R)
Entry 8 in Table D

Scalemic methylphenyl(mesityl)phosphine oxide 44 % ee (S)
Entry 16 in Table A

Racemic *-tert*-Butylmethylphenylphosphine oxide

<table>
<thead>
<tr>
<th>Instrument Conditions</th>
<th>At Start</th>
<th>At Stop</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column Temp. (left)</td>
<td>28.3</td>
<td>28.4 °C</td>
</tr>
<tr>
<td>Column Temp. (right)</td>
<td>28.3</td>
<td>28.4 °C</td>
</tr>
<tr>
<td>Pressure</td>
<td>70.1</td>
<td>71.1 bar</td>
</tr>
<tr>
<td>Flow</td>
<td>1.000</td>
<td>1.000 ml/min</td>
</tr>
<tr>
<td>Valve 1 Position</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

Detector Lamp Burn Times: Current On-Time Accumulated On-Time
DAD 1, UV Lamp: 4.88 1156.3 h
DAD 1, Visible Lamp: OFF 11.2 h

Solvent Description:
PMP1, Solvent A: Heptane
PMP1, Solvent B: EtOH

---

Peak RetTime Width Area Height Area
# [min] [min] [mAU*s] [mAU] %
---|---|---|---|---|
1 8.017 VB 0.1821 1.09237e4 923.13629 48.4947
2 10.219 BB 0.2665 1.16018e4 661.75677 51.5053
Totals: 2.25255e4 1584.89307

---
Entry 9 in Table D

Scalemic (R)-\textit{tert}-Butylmethylphenylphosphine oxide 53 % ee

Detector Lamp Burn Times: Current On-Time Accumulated On-Time
DAD 1, UV Lamp : 3.66 1155.1 h
DAD 1, Visible Lamp : OFF 11.2 h

Solvent Description :
PME, Solvent A : Heptane
PME, Solvent B : EOH

Signal 1: DAD D, Sig=230,8 Ref=360,100

Peak RetTime Type Width Area Height Area %
--- --- ------ ------ ------- ------- ------
1 12.379 EV 0.4211 5409.17627 188.34339 23.2056
2 14.111 VB 0.6644 1.79007e4 398.26746 76.7944

Totals : 2.33098e4 596.61081

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Entry 10 in Table D

**Scalemic (S)-**<sup>**tert**</sup>-Butylmethylphenylphosphine oxide 46 % ee
## Entry 16 in Table A

### Racemic -tert-Butylmethylphenylphosphine borane

<table>
<thead>
<tr>
<th>Instrument Conditions</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>At Start</td>
<td>At Stop</td>
<td></td>
</tr>
<tr>
<td>Column Temp. (left)</td>
<td>18.3</td>
<td>28.4</td>
</tr>
<tr>
<td>Column Temp. (right)</td>
<td>19.3</td>
<td>29.4</td>
</tr>
<tr>
<td>Pressure</td>
<td>70.1</td>
<td>71.1</td>
</tr>
<tr>
<td>Flow</td>
<td>1.000</td>
<td>1.000 ml/min</td>
</tr>
<tr>
<td>Valve 1 Position</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Detector Lamp Burn Times</th>
<th>Current On-Time</th>
<th>Accumulated On-Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>TAC 1, UV Lamp</td>
<td>4.00</td>
<td>1584.3 h</td>
</tr>
<tr>
<td>TAC 1, Visible Lamp</td>
<td>OFF</td>
<td>11.2 h</td>
</tr>
</tbody>
</table>

### Solvent Description

- MTBE, Solvent A: Hexane
- MTBE, Solvent B: EGC

![Graph](attachment:image.png)

**Signal 1:** DAD1 D, Sig=230,8 Ref=360,100

<table>
<thead>
<tr>
<th>Peak RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.017 VB</td>
<td></td>
<td>0.1821</td>
<td>1.0937e4</td>
<td>923.13629</td>
<td>48.4947</td>
</tr>
<tr>
<td>10.219 BB</td>
<td></td>
<td>0.2665</td>
<td>1.16018e4</td>
<td>661.75677</td>
<td>51.5053</td>
</tr>
</tbody>
</table>

**Totals:** 2.25285e4 1584.89307
Entry 9 in Table D

Scalemic (R)-tert-Butylmethylphenylphosphine borane 53 % ee

<table>
<thead>
<tr>
<th>Instrument Conditions</th>
<th>At Start</th>
<th>At Stop</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column Temp. (left)</td>
<td>29.2</td>
<td>29.2</td>
</tr>
<tr>
<td>Column Temp. (right)</td>
<td>30.6</td>
<td>30.7</td>
</tr>
<tr>
<td>Pressure</td>
<td>71.5</td>
<td>76.8</td>
</tr>
<tr>
<td>Flow</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>Valve 1 Position</td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>

Detector Lamp Burn Times: Current On-Time Accumulated On-Time

| SAD 1, UV lamp | 1.41 | 1101.6 h |
| SAD 1, Visible lamp | OFF | 11.2 h   |

Solvent Description:
- ROPI, Solvent A: Heptane
- ROPI, Solvent B: ECN

Signal 1: DAD1 A, Siz=254.9 Ref=360.100

Peak RetTime Type Width Area Height Area %

<table>
<thead>
<tr>
<th></th>
<th>[min]</th>
<th>[min]</th>
<th>[nAU's]</th>
<th>[nAU]</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>9.164</td>
<td>0.2163</td>
<td>5851.10459</td>
<td>495.31163</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>10.857</td>
<td>0.2993</td>
<td>1.8474964</td>
<td>109.89684</td>
</tr>
</tbody>
</table>

Totals: 2.4126164 1464.46817
Entry 10 in Table D

Scalemic (S)-tert-Butylmethylphenylphosphine borane 46 % ee

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Entry 9 in Table A

Racemic (±)-methylphenyl(2-i-propylphenyl)phosphine borane

---

Acq. Operator : General sequence  
Seq. Line : 3  
Acq. Instrument : Hewlett Packard 1100  
Location : Vial 16  
Injection Date : 12/9/2010 10:41:45 AM  
Inj : 1  
Inj Volume : 5 μl  
Acq. Method : C:\Chem32\DATA\RUN QUEUE 2010-12-09 10-08-43\ISO_59_01_30MIN_1MLMIN.M  
Last changed : 12/9/2010 10:41:34 AM by General sequence  
(modified after loading)  
Analysis Method : C:\Chem32\METROLOGY\01_COLUMN METHODS\SELECT IA COLUMN.M  
Last changed : 11/30/2010 9:11:53 AM by General sequence  
(modified after loading)  
Method Info : Select IA column

---

Area Percent Report

---

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Use Multiplier & Dilution Factor with ISTDs

---

Signal 1: DAD1 D, Sig=230, # Ref=360, 100

---

Peak RetTime Type Width Area Height Area
--- | --- | --- | --- | --- |
1 | 7.995 | BB | 0.3106 1309.54749 | 60.43586 | 49.93624 |
2 | 11.376 | BV | 0.4867 1403.12354 | 44.63798 | 50.06386

---
Entry 1 in Table B

Racemic (±)methyl(α-tolyl)phosphine borane

---

Acq. Operator : General sequence
Acq. Instrument : Kev HPLC 1
Inj. : 1
Injection Date : 4/3/2010 8:07:36 PM
Inj Volume : 5 μl
Acq. Method : C:\\Chem32\\DATA\RUN QUEUE 2010-04-03 14-55-48\\ISO_97_03_30MIN_1MLMIN.M
Analysis Method : C:\\CHEM32\\DATA\RUN QUEUE 2010-04-03 14-55-48\005-1101.D\DA.M (ISO_97_03_30MIN_1MLMIN.M)
Last changed : 3/22/2010 9:23:07 AM by General sequence
Method Info : Isocratic at 97/3 heptane/EtOH for 30min at 1ml/min

---

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 D, Sig=230, & Ref=360,100

<table>
<thead>
<tr>
<th>Peak RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
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</thead>
<tbody>
<tr>
<td># [min]</td>
<td>[min]</td>
<td>[mAU*]</td>
<td>[mAU]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>---------------</td>
<td>-------</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
</tr>
<tr>
<td>1 11.231</td>
<td>BB</td>
<td>0.2433</td>
<td>8590.73535</td>
<td>50.99377</td>
<td>50.5975</td>
</tr>
<tr>
<td>2 12.857</td>
<td>VB</td>
<td>0.2840</td>
<td>8387.83105</td>
<td>457.26364</td>
<td>49.4025</td>
</tr>
</tbody>
</table>
Entry 15 in Table A

Racemic(±)-Cyclohexymethylphenylphosphine borane

Acq. Operator: General sequence  Seq. Line: 3
Acq. Instrument: Kev APLC 1  Location: Vial 11
Injection Date: 12/19/2009 12:54:02 PM  Inj: 1
                Inj Volumes: 5 μl
Acq. Method: C:\Chem32\DATA\RUN QUEUE 2009-12-19 12-39-51\ISO_96_04_15MIN_1MLMIN.M
Last changed: 12/19/2009 12:53:52 PM by General sequence
             (modified after loading)
Analysis Method: C:\\CHEM32\DATA\RUN QUEUE 2009-12-19 12-39-51\011-0301.D\DA.M (ISO_96_04_15MIN_1MLMIN.M)
Last changed: 12/19/2009 3:45:55 PM by General sequence
Method Info: Isocratic at 95/04 heptane/EtOH for 15min at 1ml/min
Sample Info: ASH 96 4 pen ethan

---

Area Percent Report
---
Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 D, Sig=230,8 Ref=360,100

| Peak RetTime Type Width Area Height Area % |
|------|------|------|-------|
| 1    | 6.966 BV 0.1260 1.20409e4 1451.20239 49.6250 |
| 2    | 7.851 VV 0.1619 1.22229e4 1049.30774 50.3750 |
Entry 13 in Table A

Racemic(±)-(4-Fluoro-2-methylphenyl)methylphenylphosphine borane

Acq. Operator : General sequence
Acq. Instrument : Kev HPLC 1
Injection Date : 6/27/2010 7:23:21 PM
Inj Volume : 5 µl
Analysis Method : C:\Chem32\1\DATA\RUN QUEUE 2010-06-27 18-09-05\ISO_98_02_30MIN_1MLMIN.M
Method Info : Isocratic at 98/02 heptane/EtOH for 30min at 1ml/min

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 D, S1g=230,8 Ref=360,100

<table>
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<tr>
<th>#</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.057</td>
<td>VB</td>
<td>2.5519</td>
<td>1933.06</td>
<td>49.0175</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>11.005</td>
<td>VBA</td>
<td>2.6542</td>
<td>1545.97</td>
<td>50.9825</td>
<td></td>
</tr>
</tbody>
</table>
Entry 12 in Table A

Racemic(±)-(4-methyl-2-methylphenyl)methylphenylphosphine borane

<table>
<thead>
<tr>
<th>Entry</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>Racemic(±)-(4-methyl-2-methylphenyl)methylphenylphosphine borane</td>
</tr>
</tbody>
</table>

**Acq. Operator**: General sequence  
**Seq. Line**: 12  
**Acq. Instrument**: Kev HPLC  
**Location**: Vial 13  
**Injection Date**: 7/21/2010 4:03:40 PM  
**Inj Vol**: 1 μl  
**Acq. Method**: C:\Chem32\DATA\RUN QUEUE 2010-07-21 11-21-13\ISO_70_30_30MIN_1MLMIN.M  
**Last changed**: 7/21/2010 4:03:30 PM by General sequence  
**Analysis Method**: C:\CHEM32\METHODS\01_COLUMN METHODS\STABILISE_98_02_10MIN_1MLMIN.M  
**Last changed**: 7/5/2010 9:52:01 AM by General sequence  
**Method Info**: Stabilise column at 99/1 heptane/EtOH for 10min at 1ml/min

**Instrument Conditions**:  
- **At Start**  
  - Column Temp. (left): 28.3 °C  
  - Column Temp. (right): 29.3 °C  
  - Pressure: 70.1 bar  
  - Flow: 1.000 ml/min  
  - Valve 1 Position: 5  
- **At Stop**  
  - Column Temp. (left): 28.4 °C  
  - Column Temp. (right): 29.4 °C  
  - Pressure: 71.1 bar  
  - Flow: 1.000 ml/min  
  - Valve 1 Position: 5

**Detector Lamp Burn Times**:  
- **Current On-Time**  
  - DAD 1, UV Lamp: 4.88 h  
  - DAD 1, Visible Lamp: OFF  
- **Accumulated On-Time**  
  - DAD 1, UV Lamp: 1156.3 h  
  - DAD 1, Visible Lamp: 11.2 h

**Solvent Description**:  
- PMF1, Solvent A: Heptane  
- PMF1, Solvent B: EtOH

---

**Graph**

---

**Graph**

---

**Graph**

---

89
Entry 11 in Table A

Racemic(±)-(±)-methyl-(1-naphthyl)phenylphosphine borane

Acq. Operator : General sequence  
Seq. Line : 4
Acq. Instrument : Kev HPLC I  
Location : Vial 11
Injection Date : 2/15/2010 10:40:38 PM
Inj : 1
Inj Volume : 5 µl
Acq. Method : C:\Chem32\1\DATA\RUN QUEUE 2010-02-15 21-45\18\ISO_98_02_45MIN_1MLMIN.M
Last changed : 2/15/2010 10:42:28 PM by General sequence
(modified after loading)
Analysis Method : C:\CHEM32\1\DATA\RUN QUEUE 2010-02-15 21-45\18\011-0401.D\A.M (ISO_98_02_45MIN_1MLMIN.M)
Last changed : 2/16/2010 10:09:50 AM by General sequence
Method Info : Isocratic at 98/02 heptane/EtOH for 45min at 1ml/min

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 D, Sig=230.8 Ref=360.100 (RUN QUEUE 2010-02-15 21-45-16/011-0401.D)

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<th>RetTime [min]</th>
<th>Width [min]</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area %</th>
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<td>49.8742</td>
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<tr>
<td>2</td>
<td>11.251</td>
<td>0.2462</td>
<td>2.1553e4</td>
<td>1365.22644</td>
<td>50.1258</td>
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</tbody>
</table>
References


26. Configuration remains to be assigned.