# Room temperature hydrophosphination using a simple iron salen pre-catalyst

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General considerations
Reagents were purchased from Sigma Aldrich or prepared as stated. CH\textsubscript{3}CN was dried over CaH\textsubscript{2} (reflux), distilled and then degassed using three freeze-pump-thaw cycles. NMR data was collected at 300, 400 or 500 MHz on Bruker instruments in CDCl\textsubscript{3} or CD\textsubscript{3}CN at 293 K and referenced to residual protic solvent. Elemental analyses were carried out by Dr S. Boyer at London Metropolitan University. Mass Spectrometry data was collected by the EPSRC NMSF at the University of Swansea.

4-Methoxystyrene, 4-chlorostyrene, 3-methylstyrene and 4-trifluoromethylstyrene were purchased and purified by trap-to-trap distillation then degassed using three freeze-pump-thaw cycles before transferring to the glove box.

Method of synthesis of styrenes
A benzaldehyde derivative (5 mmol) was added to potassium carbonate (1.1 g, 8 mmol) and methyltriphenylphosphonium bromide (2.1 g, 6 mmol) in anhydrous 1,4-dioxane (5 mL) and heated at reflux for 16 h. The reaction mixture was then cooled, filtered and washed with pentane and then concentrated in vacuo.

Two methods of isolation can be used:
1. The residue was dissolved in hot pentane, cooled to 0 °C, filtered (to remove triphenylphospine oxide: sparingly soluble in cold pentane) and washed with cold pentane. The filtrate was dried (MgSO\textsubscript{4}) and concentrated in vacuo to give the styrene derivative.
2. Isolate via silica gel column chromatography in 40% EtOAc/pentane (ensuring dioxane is removed prior to isolation).

All styrene derivatives were then vacuum distilled (may require gentle heating) and degassed before transferring to the glove box.

Synthesis of 1
A mixture of salicylaldehyde (2.49 g, 18.3 mmol, 3.5 eq) and ethylenediamine (0.31 g, 5.2 mmol, 1 eq) in dry EtOH (40 mL) was heated at reflux for 2 h. The solution was cooled to 0 °C and filtered, and the resultant yellow solid was washed with cold EtOH. The product was then dried in vacuo (1.07 g, 77%). Comparable to the commercially available compound (CAS: 94-93-9).

Synthesis of 2a
Fe(OAc)\textsubscript{2} (109 mg, 0.6 mmol, 1 eq) was weighed into a flask and dissolved in ethanol (5 mL) leaving a brown solution. To this, a solution of N,N’-Bis(salicylidene)ethylenediamine (200 mg, 0.7 mmol, 1.2 eq) in ethanol (10 mL) was added forming a red solution. The mixture was then stirred at 80 °C for 2 h. The flask was allowed to cool to RT before filtering off the solid and washing it with ethanol. The dark red solid was dried under vacuum.

Synthesis of 2b
Manipulations carried out under an inert atmosphere (Ar) with rigorous air sensitive handling. FeCl\textsubscript{2} (142 mg, 1.12 mmol, 1 eq., 99.9% purity) and N,N’-Bis(salicylidene)ethylenediamine (300 mg, 1.12 mmol, 1 eq, dried under vacuum) were combined in an ampule. Freshly dried THF (15 mL) was
cannulated onto the mixture which was then stirred at 80 °C for 2 h before cooling to RT. Using a metal cannula with a glass paper frit, the reaction solution was filtered away from the precipitate leaving a straw yellow solid which was then washed with THF (2 x 5 mL). The solid was then dried under vacuum before storing in a glovebox freezer (-30 °C).

**Method for the conversion of 2b into 2a**

2b (50 mg, 0.155 mmol), stored under an atmosphere of argon, was placed under air, an immediate colour change from yellow to red was observed. The solid was dissolved in MeCN (wet) and filtered using a glass paper cannula to yield 2a as the analytically pure product (18 mg, 18%). Large quantities of black nanoparticulate material were observed to form and are believed to be the major product in the reaction.

**General method for hydrophosphination with 2a**

Carried out under an inert argon atmosphere in an M-Braun glove box.

2a (1.8 mg, 1 mol% Fe-centre) was weighed out into a Schlenk tube. CH$_3$CN (350 µL) was added to this (forming a deep red solution) followed by styrene (1.04 mmol, 1.86 eq) and finally diphenylphosphine (100 µL, 0.57 mmol, 1 eq). After stirring at room temperature for 24 h, the Schlenk tube was placed under vacuum and the excess starting styrene and solvent removed leaving an orange/red oil.

For spectroscopic yields reaction solutions were exposed to air and filtered through a silica gel plug using CH$_2$Cl$_2$. This removed the iron residue leaving a colourless oil. Solvent was removed by blowing nitrogen over the oil before addition of 45 µL 1,2-dichloroethane as an integration standard. CDCl$_3$ was used as the NMR solvent.

Products were then isolated by column chromatography 1 - 5% EtOAc/pentane. The products oxidised slowly over time (this can be observed in some $^{31}$P{^1}H spectra as a peak at ~20 ppm).

**Method for hydrophosphination with radical trap**

Carried out as in general method for hydrophosphination. The appropriate quantity of Cumene or TEMPO added to the Schlenk tube after loading the pre-catalyst and CH$_3$CN. Monitoring of the rate of reaction of styrene (1.04 mmol) and HPPh$_2$ (0.57 mmol) in the presence of cumene (0.57 mmol) was carried out using the ‘general method for kinetic studies of hydrophosphination’ procedure (below).

**Method for hydrophosphination with 2b**

Carried out as in general method for hydrophosphination. The appropriate quantity of base added to the Schlenk after loading the pre-catalyst and CH$_3$CN. Colour change – yellow to colourless upon addition of NEt$_3$. Addition of diphenylphosphine to NaO’Bu and an orange solution formed which gradually returned to colourless after 30 mins.

**Method for hydrophosphination without catalyst**

Carried out as in general method for hydrophosphination (without catalyst). Addition of diphenylphosphine to NaO’Bu solution an orange solution formed which did not go back to colourless until the solution was opened to air.

**General method for kinetic studies of hydrophosphination.**

2a (1.8 mg, 0.01 eq) was weighed out into a vial. CD$_3$CN (350 µL) was added to this (forming a deep red solution) followed by diphenylphosphine (100 µL, 0.056 mmol). This solution was syringed into a
vial containing an integration standard - 1,3,5-trimethoxybenzene (3.4 mg). This solution was then syringed into a J-Young NMR tube and sealed. Styrene derivative was syringed into a separate J-Young NMR tube and sealed. The two J-Young NMR tubes were then attached to a Schlenk line through vacuum transfer apparatus. The samples were degassed using three freeze-pump-thaw cycles. With the CD$_3$CN containing tube kept frozen, the styrene was allowed to warm to RT and transferred on top of the CD$_3$CN solution. Once all the styrene was transferred, the sample was removed from liquid N$_2$ and placed in acetone/solid CO$_2$ the NMR tube was then refilled with argon and kept frozen. When ready to collect kinetic data the sample was allowed to defrost – the sample was inverted to speed up this process. Once all solid had melted the outside of the tube was wiped down to remove condensation/ ice forming on the outside and placed in the spectrometer.

Table S1: Spectroscopic yields with various solvents using the general conditions for HP with 2a.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Yield (%)</th>
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<tr>
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<tr>
<td>2</td>
<td>THF</td>
<td>84</td>
</tr>
<tr>
<td>3</td>
<td>Toluene</td>
<td>76</td>
</tr>
<tr>
<td>4</td>
<td>CH$_2$Cl$_2$</td>
<td>98</td>
</tr>
<tr>
<td>5</td>
<td>MeCN</td>
<td>89</td>
</tr>
<tr>
<td>6</td>
<td>Methanol</td>
<td>92</td>
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</table>

Products

2a

![Product structure](image)

Dark red solid (143 mg, 72%). IR (solid) ν 3049, 1610, 1597, 851 cm$^{-1}$; m.p. (decomp.) 296 °C.

Crystal structure obtained, with compound data being comparable to other published methods.\textsuperscript{7}
Table S2: Crystal data and structure refinement for 2a.

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<tr>
<td></td>
<td>b = 10.8150(2)Å beta = 85.858 (1)°</td>
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<tr>
<td></td>
<td>c = 13.7380(4)Å gamma = 73.156 (2)°</td>
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<tr>
<td>Volume</td>
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<tr>
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<tr>
<td>Goodness-of-fit on F²</td>
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Final R indices [I>2σ(I)]

\[ R_1 = 0.0404 \quad wR_2 = 0.0837 \]

R indices (all data)

\[ R_1 = 0.0672 \quad wR_2 = 0.0933 \]

Largest diff. peak and hole

-0.319 and 0.365 eÅ\(^{-3}\)

### 2a Elemental analysis:

<table>
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<tr>
<th>Element</th>
<th>Expected (%)</th>
<th>Found (1)</th>
<th>Found (2)</th>
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<tr>
<td>Carbon</td>
<td>59.66</td>
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<td>59.45</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>4.38</td>
<td>4.30</td>
<td>4.26</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>8.70</td>
<td>8.61</td>
<td>8.55</td>
</tr>
</tbody>
</table>

### 2b

Yellow solid (276 mg, 77%). IR (solid) \( \nu \) 2966, 1638, 1606 cm\(^{-1}\); m.p. (decomp.) 174 °C. Compound data is comparable to other published data.\(^8\)

### 2b Elemental Analysis:

<table>
<thead>
<tr>
<th>Element</th>
<th>Expected (%)</th>
<th>Found (1)</th>
<th>Found (2)</th>
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<tbody>
<tr>
<td>Carbon</td>
<td>58.21</td>
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<tr>
<td>Hydrogen</td>
<td>4.27</td>
<td>4.12</td>
<td>4.16</td>
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<tr>
<td>Nitrogen</td>
<td>8.49</td>
<td>8.11</td>
<td>8.17</td>
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</table>

### 3a (Table 1, Entry 1)

Colourless oil, 147 mg (88%). \(^1\)H NMR (300 MHz, 298 K, CDCl\(_3\)) \( \delta \) 7.47 – 7.15 (m, 14H), 2.73 - 2.67 (m, 2H), 2.39 - 2.33 (m, 2H); \(^13\)C\(^{1}\)H) NMR (75 MHz, 298 K, CDCl\(_3\)) \( \delta \) 142.7 (d, \( J = 12.7 \) Hz), 138.6 (d, \( J = 19.2 \) Hz), 132.8 (d, \( J = 13.2 \) Hz), 128.9, 128.6 (d, \( J = 6.2 \) Hz), 128.2, 128.0, 126.1, 32.3 (d, \( J = 3.3 \) Hz), 30.2 (d, \( J = 7.7 \) Hz); \(^31\)P\(^{1}\)H) NMR (121.5 MHz, 298 K, CDCl\(_3\)) \( \delta \) -15.0; IR (solid) \( \nu \) 3055, 2936, 1603, 1585, 1481 cm\(^{-1}\); HRMS (EI) 291.1303 (calcd.), 291.1297 (obs.). Unknown impurity present at 20.1 ppm.\(^9\)
3b (Table 1, Entry 2)

Colourless oil, 136 mg (79%). $^1$H NMR (300 MHz, 298 K, CDCl$_3$) δ 7.58 - 7.55 (m, 4H), 7.43 - 7.41 (m, 6H), 7.17 (s, 4H), 2.83 - 2.75 (m, 2H), 2.48 - 2.40 (m, 2H), 2.40 (s, 3H); $^{13}$C{$_1$H} NMR (75 MHz, 298 K, CDCl$_3$) δ 139.6 (d, $J$ = 13.4 Hz), 138.5 (d, $J$ = 12.7 Hz), 135.6, 132.8 (d, $J$ = 18.3 Hz), 129.2, 128.7, 128.6 (d, $J$ = 6.5 Hz), 128.1, 31.8 (d, $J$ = 17.6 Hz), 30.4 (d, $J$ = 12.5 Hz), 21.13; $^{31}$P{$_1$H} NMR (121.5 MHz, 298 K, CDCl$_3$) δ -15.1; IR (solid) ν 3052, 2915, 1590, 1516, 1482, 1437, 801, 862, 738, 693 cm$^{-1}$; HRMS (EI) [M + H]$^+$ 305.1454 (calcd.), 305.1452 (obs.).

3c (Table 1, Entry 3)

Colourless oil, 163 mg (89%). $^1$H NMR (300 MHz, 298 K, CDCl$_3$) δ 7.63 - 7.60 (m, 4H), 7.46 - 7.43 (m, 6H), 7.23 (d, $J$ = 8.7, 2.1 Hz), 6.99 - 6.92 (dd, 2H, $J$ = 8.6, 2.3 Hz), 3.90 (s, 3H), 2.84 - 2.81 (m, 2H), 2.52 - 2.46 (m, 2H); $^{13}$C{$_1$H} NMR (75 MHz, 298 K, CDCl$_3$) δ 158.0, 138.7 (d, $J$ = 13.0 Hz), 134.6 (d, $J$ = 13.3 Hz), 132.8 (d, $J$ = 18.3 Hz), 129.1, 128.6, 128.5 (d, $J$ = 6.5 Hz), 113.9, 55.3, 31.2 (d, $J$ = 17.7 Hz), 30.4 (d, $J$ = 12.7 Hz); $^{31}$P{$_1$H} NMR (121.5 MHz, 298 K, CDCl$_3$) δ -15.3; IR (solid) ν 3053, 2934, 2904, 2833, 1610, 1584, 1510, 1464, 818, 734, 695, 717 cm$^{-1}$; HRMS (EI) [M + H]$^+$ 321.1403 (calcd.), 321.1403 (obs.).

3d (Table 1, Entry 4)

Colourless oil, 136 mg (65%). $^1$H NMR (300 MHz, 298 K, CDCl$_3$) δ 7.54 - 7.33 (m, 12H), 7.09 (d, $J$ = 8.3 Hz), 2.78 - 2.70 (m, 2H), 2.43 - 2.37 (m, 2H); $^{13}$C{$_1$H} NMR (75 MHz, 298 K, CDCl$_3$) δ 141.5 (d, $J$ = 12.7 Hz), 138.3 (d, $J$ = 13.0 Hz), 132.8 (d, $J$ = 18.3 Hz), 131.5, 130.1, 128.8, 128.6 (d, $J$ = 6.5 Hz), 119.9, 31.7 (d, $J$ = 18.0 Hz), 30.1 (d, $J$ = 13Hz); $^{31}$P{$_1$H} NMR (121.5 MHz, 298 K, CDCl$_3$) δ -15.4; IR (solid) ν 3052, 2933, 1487, 1433, 842, 799, 736, 693 cm$^{-1}$; HRMS (EI) [M + H]$^+$ 369.0402 (calcd.), 369.0397 (obs.) Unknown impurity present at 20.1 ppm.

3e (Table 1, Entry 5)

Colourless oil, 136 mg (65%). $^1$H NMR (300 MHz, 298 K, CDCl$_3$) δ 7.54 - 7.33 (m, 12H), 7.09 (d, $J$ = 8.3 Hz), 2.78 - 2.70 (m, 2H), 2.43 - 2.37 (m, 2H); $^{13}$C{$_1$H} NMR (75 MHz, 298 K, CDCl$_3$) δ 141.5 (d, $J$ = 12.7 Hz), 138.3 (d, $J$ = 13.0 Hz), 132.8 (d, $J$ = 18.3 Hz), 131.5, 130.1, 128.8, 128.6 (d, $J$ = 6.5 Hz), 119.9, 31.7 (d, $J$ = 18.0 Hz), 30.1 (d, $J$ = 13Hz); $^{31}$P{$_1$H} NMR (121.5 MHz, 298 K, CDCl$_3$) δ -15.4; IR (solid) ν 3052, 2933, 1487, 1433, 842, 799, 736, 693 cm$^{-1}$; HRMS (EI) [M + H]$^+$ 369.0402 (calcd.), 369.0397 (obs.) Unknown impurity present at 20.1 ppm.
Colourless oil, 136 mg (74%, 114 h). $^1$H NMR (300 MHz, 298 K, CDCl$_3$) $\delta$ 7.50 - 7.47 (m, 4H), 7.38 - 7.31 (m, 6H), 7.25 (dd, 2H, $J$ = 8.6, 2.1 Hz), 7.10 (dd, 2H, $J$ = 8.6, 2.1 Hz), 2.76 - 2.68 (m, 2H), 2.39 - 2.34 (m, 2H); $^{13}$C($^1$H) NMR (75 MHz, 298 K, CDCl$_3$) $\delta$ 141.1 (d, $J$ = 13.0 Hz), 138.4 (d, $J$ = 13.0 Hz), 132.9 (d, $J$ = 18.6 Hz), 130.9 (d, $J$ = 9.3 Hz), 129.7, 128.8, 128.7, 128.6 (d, $J$ = 2.8 Hz), 31.7 (d, $J$ = 18.0 Hz), 30.3 (d, $J$ = 13.3 Hz); $^{31}$P($^1$H) NMR (121.5 MHz, 298 K, CDCl$_3$) $\delta$ -15.2; IR (solid) $\nu$ 3064, 2898, 1591, 1492, 1435, 843, 801, 736, 720, 693 cm$^{-1}$; HRMS (EI) [M + H]$^+$ 325.0907 (calcd.), 325.0903 (obs.)

3f (Table 1, Entry 6)

Colourless oil, 77 mg (43%). $^1$H NMR (300 MHz, 298 K, CDCl$_3$) $\delta$ 7.56 (d, 2H, $J$ = 8.4 Hz), 7.49 - 7.43 (m, 4H), 7.38 - 7.35 (m, 6H), 7.28 (d, 2H, $J$ = 8.4 Hz), 2.92 - 2.67 (m, 2H), 2.47 - 2.31 (m, 2H); $^{13}$C($^1$H) NMR (75 MHz, 298 K, CDCl$_3$) $\delta$ 148.1 (d, $J$ = 12.7 Hz), 137.9 (d, $J$ = 12.2 Hz), 132.8 (d, $J$ = 18.6 Hz), 132.4, 130.8 (d, $J$ = 9.3 Hz), 129.1 (d, $J$ = 12.1 Hz), 128.7 (d, $J$ = 6.8 Hz) 119.1, 110.0, 32.5 (d, $J$ = 17.3 Hz), 29.7 (d, $J$ = 13.4 Hz); $^{31}$P($^1$H) NMR (121.5 MHz, 298 K, CDCl$_3$) $\delta$ -15.4; IR (solid) $\nu$ 3060, 2943, 2905, 2227, 1605, 1506, 1480, 1435, 822, 741, 695 cm$^{-1}$; HRMS (EI) [M + H]$^+$ 316.1250 (calcd.), 316.1245 (obs.)

3g (Table 1, Entry 7)

Colourless oil, 170 mg (83%). $^1$H NMR (300 MHz, 298 K, CDCl$_3$) $\delta$ 7.51 - 7.41 (m, 6H), 7.37 - 7.30 (m, 6H), 7.24 (d, 2H, $J$ = 8.1 Hz), 2.80 - 2.72 (m, 2H), 2.38 - 2.33 (m, 2H); $^{13}$C($^1$H) NMR (75 MHz, 298 K, CDCl$_3$) $\delta$ 146.7 (d, $J$ = 12.7 Hz), 138.3 (d, $J$ = 12.7 Hz), 132.8 (d, $J$ = 18.6 Hz), 128.7, 128.5, 128.45, 128.0 (d, $J$ = 10.5 Hz), 126.1, 125.3 (q, $J$ = 3.7 Hz), 32.2 (d, $J$ = 18.3 Hz), 30.0 (d, $J$ = 13.4 Hz); $^{31}$P($^1$H) NMR (121.5 MHz, 298 K, CDCl$_3$) $\delta$ -15.3; IR (solid) $\nu$ 3049, 2922, 1590, 1567, 1480, 1434, 1323, 844, 820, 748, 735, 695 cm$^{-1}$; HRMS (EI) [M + H]$^+$ 359.1171 (calcd.), 359.1166 (obs.) Unknown impurity present at 20.1 ppm.

3h (Table 1, Entry 8)

Colourless oil, 122 mg (58% at 60°C). $^1$H NMR (300 MHz, 298 K, CDCl$_3$) $\delta$ 7.70 - 7.33 (m, 19H), 2.90 - 2.85 (m, 2H), 2.55 - 2.50 (m, 2H); $^{13}$C($^1$H) NMR (75 MHz, 298 K, CDCl$_3$) $\delta$ 141.7 (d, $J$ = 13.0 Hz), 141.1, 139.0, 138.5 (d, $J$ = 12.4 Hz), 132.7 (d, $J$ = 18.6 Hz), 128.7, 128.62, 128.56, 128.50 (d, $J$ = 6.5 Hz),
127.2, 127.03, 126.98, 31.9 (d, J = 17.7 Hz), 30.2 (d, J = 12.4 Hz); $^{31}$P($^1$H) NMR (121.5 MHz, 298 K, CDCl$_3$) δ -14.9; IR (solid) ν 3050, 2944, 2903, 1586, 1481, 1433, 821, 744, 693 cm$^{-1}$; HRMS (EI) [M + H]$^+$ 367.1610 (calcd.), 367.1606 (obs.).

3i (Table 1, Entry 9)

![Chemical structure of 3i](image)

Colourless oil, 164 mg (95%). $^1$H NMR (300 MHz, 298 K, CDCl$_3$) δ 7.63 - 7.60 (m, 4H), 7.46 - 7.42 (m, 6H), 7.29 (dd, 1H, J = 8.1, 7.2 Hz), 7.13 - 7.09 (m, 3H), 2.88 - 2.80 (m, 2H), 2.53 - 2.42 (m, 2H), 2.44 (s, 3H); $^{13}$C($^1$H) NMR (75 MHz, 298 K, CDCl$_3$) δ 142.6 (d, J = 13.4 Hz), 138.6 (d, J = 13.0 Hz), 138.0, 134.0 (d, J = 16.8 Hz), 132.8 (d, J = 18.6 Hz), 129.0, 128.6 (d, J = 8.1 Hz), 128.4 (d, J = 5.3 Hz), 126.8, 125.2, 32.2, 30.3, 21.5; $^{31}$P($^1$H) NMR (121.5 MHz, 298 K, CDCl$_3$) δ -14.8; IR (solid) ν 3052, 2917, 2856, 1608, 1586, 1480, 1433, 1377, 735, 695 cm$^{-1}$; HRMS (EI) [M + H]$^+$ 305.1454 (calcd.), 305.1454 (obs.).

Unknown impurity present at 20.1 ppm.

3j (Table 1, Entry 10)

![Chemical structure of 3j](image)

Colourless oil, 202 mg (96%). $^1$H NMR (300 MHz, 298 K, CDCl$_3$) δ 7.55 - 7.52 (m, 4H), 7.46 - 7.36 (m, 8H), 7.18 - 7.15 (m, 2H), 2.80 - 2.72 (m, 2H), 2.44 - 2.39 (m, 2H); $^{13}$C($^1$H) NMR (75 MHz, 298 K, CDCl$_3$) δ 144.9 (d, J = 13.4 Hz), 138.1 (d, J = 12.4 Hz), 132.8 (d, J = 18.6 Hz), 131.2, 130.0, 129.2, 128.8, 128.6 (d, J = 6.9 Hz), 126.9, 122.5, 31.9 (d, J = 18.3 Hz), 30.0 (d, J = 12.8 Hz); $^{31}$P($^1$H) NMR (121.5 MHz, 298 K, CDCl$_3$) δ -15.2; IR (solid) ν 3057, 2943, 2923, 2830, 1583, 1567, 1491, 1475, 1464, 1431, 885, 796, 775, 739, 695 cm$^{-1}$; HRMS (EI) 369.0402 (calcd.), 369.0406 (obs.) Unknown impurity present at 20.1 ppm.

3k (Table 1, Entry 11)

![Chemical structure of 3k](image)

Colourless oil, 178 mg (89%). $^1$H NMR (300 MHz, 298 K, CDCl$_3$) δ 7.54 - 7.42 (m, 4H), 7.41 - 7.39 (m, 6H), 6.41 (d, 2H, J = 2.3 Hz), 6.37 (t, 1H, J = 2.3 Hz), 3.81 (s, 6H) 2.78 - 2.70 (m, 2H), 2.47 - 2.41 (m, 2H); $^{13}$C($^1$H) NMR (75 MHz, 298 K, CDCl$_3$) δ 160.9, 145.1 (d, J = 13.4 Hz), 138.5, 133.0 (d, J = 18.6 Hz),...
128.8, 128.6 (d, J = 6.5 Hz), 106.3, 98.0, 55.3, 32.6 (d, J = 12.4 Hz); 31P{1H} NMR (121.5 MHz, 298 K, CDCl₃) δ -14.9; IR (solid) ν 3048, 2920, 2849, 1591, 1567, 1470, 1433, 843, 782 cm⁻¹; HRMS (EI) 351.1508 (calcd.), 351.1505 (obs.)

3l (Table 1, Entry 12)

![Chemical structure of 3l](image)

Colourless oil, 113 mg (62%). ¹H NMR (300 MHz, 298 K, CDCl₃) δ 7.64 - 7.59 (m, 2H), 7.47 - 7.42 (m, 6H), 7.32 - 7.23 (m, 2H), 7.01 (app. td, 1H, J = 7.4, 1.0 Hz), 6.93 (d, 1H, J = 8.1 Hz) 3.88 (s, 3H), 2.94 - 2.86 (m, 2H), 2.52 - 2.47 (m, 2H); ¹³C{¹H} NMR (75 MHz, 298 K, CDCl₃) δ 157.3, 138.7 (d, J = 12.7 Hz), 132.8 (d, J = 13.6 Hz), 129.6, 128.4 (d, J = 6.5 Hz), 127.4, 120.4, 110.2, 55.1, 28.4 (d, J = 12.1 Hz), 27.2 (d, J = 18.3 Hz); 31P{¹H} NMR (121.5 MHz, 298 K, CDCl₃) δ -14.5; IR (solid) ν 3059, 2948, 2922, 2902, 2830, 1600, 1583, 1490, 1464, 1432, 856, 742, 696 cm⁻¹; HRMS (EI) [M + H]+ 321.1403 (calcd.), 321.1404 (obs.)

3m (Table 1, Entry 13)

![Chemical structure of 3m](image)

Colourless oil, 125 mg (75%, after 72 h). ¹H NMR (300 MHz, 298 K, CDCl₃) δ 8.46 (dd, 2H, J = 4.3, 1.7 Hz), 7.47 - 7.42 (m, 4H), 7.36 - 7.31 (m, 6H), 7.07 (dd, 2H, J = 4.3, 1.7 Hz), 2.76 - 2.58 (m, 2H), 2.44 - 2.25 (m, 2H); ¹³C{¹H} NMR (75 MHz, 298 K, CDCl₃) δ 151.4 (d, J = 13.0 Hz), 149.9, 138.1 (d, J = 13.0 Hz), 132.8 (d, J = 18.6 Hz), 129.0, 128.7 (d, J = 6.8 Hz), 123.7, 31.6 (d, J = 13.3 Hz); 31P{¹H} NMR (121.5 MHz, 298 K, CDCl₃) δ -15.2; IR (solid) ν 3051, 2928, 1599, 1559, 1480, 1433, 850, 801, 737, 694 cm⁻¹; HRMS (EI) [M + H]+ 292.1250 (calcd.), 292.1246 (obs.) Unknown impurity present at 20.1 ppm.⁹

3n (Table 1, Entry 14)

![Chemical structure of 3n](image)

Colourless oil, 143 mg (86%, after 72 h). ¹H NMR (300 MHz, 298 K, CDCl₃) δ 8.56 (d, 1H, J = 4.1 Hz), 7.62 - 7.43 (m, 5H), 7.43 - 7.29 (m, 6H), 7.20 - 7.03 (m, 2H), 3.05-2.82 (m, 2H), 2.64 - 2.48 (m, 2H); ¹³C{¹H} NMR (75 MHz, 298 K, CDCl₃) δ 161.9 (d, J = 13.3 Hz), 149.5, 138.5 (d, J = 13.0 Hz), 136.4, 132.9 (d, J = 18.6 Hz), 128.7, 128.6 (d, J = 6.8 Hz), 122.8, 121.3, 34.7 (d, J = 17.7 Hz), 28.1 (d, J = 12.4 Hz); 31P{¹H} NMR (121.5 MHz, 298 K, CDCl₃) δ -14.6; IR (solid) ν 3046, 2920, 2949, 1590, 1567, 1470, 1479, 1433, 843, 781, 749, 735, 723, 697, cm⁻¹; HRMS (EI) [M + H]+ 292.1250 (calcd.), 292.1249 (obs.)
3o (Table 1, Entry 15)

![Chemical Structure](image)

Colourless oil, 120 mg (69%). $^1$H NMR (300 MHz, 298 K, CDCl$_3$) δ 7.50 - 7.47 (m, 4H), 7.37 - 7.35 (m, 6H), 3.66 (s, 3H), 2.45 - 2.42 (m, 4H); $^{13}$C($^1$H) NMR (75 MHz, 298 K, CDCl$_3$) δ 173.5 (d, $J = 14.9$ Hz), 137.7 (d, $J = 12.1$ Hz), 132.7 (d, $J = 18.3$ Hz), 128.8, 128.5 (d, $J = 6.5$ Hz), 51.7, 30.5 (d, $J = 19.3$ Hz), 22.9 (d, $J = 11.5$ Hz); $^{31}$P($^1$H) NMR (121.5 MHz, 298 K, CDCl$_3$) δ -14.9; IR (solid) ν 3054, 2950, 1735, 1585, 1481, 1433, 1354, 848, 736, 694 cm$^{-1}$; HRMS (EI) [M + H]$^+$ 273.1039 (calcd.), 273.1040 (obs.)

3p (Table 1, Entry 16)

![Chemical Structure](image)

Colourless oil, 142 mg (76%). $^1$H NMR (300 MHz, 298 K, CDCl$_3$) δ 7.49 - 7.46 (m, 4H), 7.37 - 7.35 (m, 6H), 4.08 (t, 2H, $J = 6.7$ Hz), 2.44 - 2.39 (m, 4H), 1.61 (app. tt, 2H, $J = 15.5, 6.7$ Hz), 1.37 (app. tq, 2H, $J = 15.5, 7.4$ Hz), 0.95 (t, 3H, $J = 7.4$ Hz); $^{13}$C($^1$H) NMR (75 MHz, 298 K, CDCl$_3$) δ 173.3 (d, $J = 15.2$ Hz), 137.8 (d, $J = 18.6$ Hz), 132.8 (d, $J = 18.6$ Hz), 128.9, 128.6 (d, $J = 6.8$ Hz), 64.6, 30.9, 30.7, 23.0 (d, $J = 11.5$ Hz), 19.2, 13.8; $^{31}$P($^1$H) NMR (121.5 MHz, 298 K, CDCl$_3$) δ -14.9; IR (solid) ν 3054, 2958, 2872, 1731, 1586, 1481, 1465, 1433, 1348, 737, 696 cm$^{-1}$; HRMS (EI) 315.1508 (calcd.), 315.1509 (obs.)
$^1$H NMR, 3a (Table 1, Entry 1)
\(^{13}\text{C}^1\text{H}\) NMR, 3a (Table 1, Entry 1)
$^{31}\text{P}$\textsuperscript{[1]H} NMR, 3a (Table 1, Entry 1)

![NMR Spectrum]

- 3a-oxide
- Unknown
$^1$H NMR, 3b (Table 1, Entry 2)
$^{13}$C[$^1$H] NMR, 3b (Table 1, Entry 2)
$^{31}\text{P}[^1\text{H}] \text{NMR, 3b (Table 1, Entry 2)}$
$^1$H NMR, 3c (Table 1, Entry 3)
$^{13}$C$^{[1]}$H NMR, 3c (Table 1, Entry 3)
$^{31}\text{P}^{[1\text{H}]}$ NMR, 3c (Table 1, Entry 3)
$^1$H NMR, 3d (Table 1, Entry 4)
$^{13}$C($^3$H) NMR, 3d (Table 1, Entry 4)
$^{31}$P$[\text{H}]$ NMR, 3d (Table 1, Entry 4)
$^1$H NMR, **3e** (Table 1, Entry 5)

![Chemical structure](image)

**Normalized intensity**

<table>
<thead>
<tr>
<th>Chemical Shift (ppm)</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.47</td>
<td>1.0</td>
</tr>
<tr>
<td>7.48</td>
<td>0.9</td>
</tr>
<tr>
<td>7.12</td>
<td>0.8</td>
</tr>
<tr>
<td>7.09</td>
<td>0.7</td>
</tr>
<tr>
<td>2.76</td>
<td>2.73</td>
</tr>
<tr>
<td>2.38</td>
<td>2.35</td>
</tr>
<tr>
<td>1.95</td>
<td>2.00</td>
</tr>
</tbody>
</table>

**Chemical shift values:**
- $^1$H NMR (Table 1, Entry 5)
$^{13}$C\textsuperscript{1}H NMR, 3e (Table 1, Entry 5)
$^{31}$P$^{[1]}$H NMR, 3e (Table 1, Entry 5)
$^1$H NMR, 3f (Table 1, Entry 6)
$^{13}$C(H) NMR, 3f (Table 1, Entry 6)
$^{31}$P$^{[1]}$H NMR, 3f (Table 1, Entry 6)
$^1$H NMR, 3g (Table 1, Entry 7)
$^{13}$C$^{[1]}$H NMR, 3g (Table 1, Entry 7)
$^{31}\text{P}[^1\text{H}]$ NMR, 3g (Table 1, Entry 7)

![Chemical structure and NMR spectrum](image)
$^1$H NMR, 3h (Table 1, Entry 8)

![NMR Spectrogram]
$^{13}\text{C}^{[1}\text{H}] \text{ NMR, 3h (Table 1, Entry 8)}$

![Chemical Structure: \text{PPh}_2](image)
$^{31}\text{P}^{[1]}\text{H} \text{NMR, 3h (Table 1, Entry 8)}$

![Diagram of phosphorus compound with chemical shifts]
$^1$H NMR, 3i (Table 1, Entry 9)
$^{13}$C[{}^1H] NMR, 3i (Table 1, Entry 9)

\[
\text{Me}
\]

\[
P\text{Ph}_2
\]
$^{31}$P($^1$H) NMR, 3i (Table 1, Entry 9)
$^1$H NMR, 3j (Table 1, Entry 10)
$^{13}$C[1H] NMR, 3j (Table 1, Entry 10)
$^{31}$P$^{[1]H}$ NMR, 3j (Table 1, Entry 10)
$^1$H NMR, 3k (Table 1, Entry 11)

\[
\text{MeO-PPh}_2
\]

\[
\text{OMe}
\]
$^{13}$C\((^{1}H)\) NMR, 3k (Table 1, Entry 11)
$^{13}$C($^1$H) NMR, 3k (Table 1, Entry 11)
$^1$H NMR, 3I (Table 1, Entry 12)
$^{13}$C($^1$H) NMR, 3I (Table 1, Entry 12)
$^{31}$P[¹H] NMR, 3I (Table 1, Entry 12)
$^1$H NMR, 3m (Table 1, Entry 13)
\( ^{13}\text{C}[^{1}\text{H}] \text{NMR, 3m (Table 1, Entry 13)} \)
$^{31}$P$^{[1]H}$ NMR, 3m (Table 1, Entry 13)

![Chemical structure of compound 3m with phosphine oxide and vinyl group]
$^1$H NMR, 3n (Table 1, Entry 14)
$^{13}$C($^1$H) NMR, 3n (Table 1, Entry 14)
$^{31}\text{P}[\text{H}]$ NMR, 3n (Table 1, Entry 14)
$^1$H NMR, 3o (Table 1, Entry 15)
$^{13}$C[1H] NMR, 3o (Table 1, Entry 15)
$^{31}$P$^1$H NMR, 3o (Table 1, Entry 15)
\(^1\text{H NMR, 3p (Table 1, Entry 16)}\)

\[
\text{\begin{tabular}{c}
\text{O} \\
\text{O} \\
\text{PPh}_2 \\
\end{tabular}}
\]

![NMR spectrum](image)

Chemical Shift (ppm): 3.90, 5.70, 1.96, 5.97, 2.00, 2.03, 2.96
$^{13}$C[$^1$H] NMR, 3p (Table 1, Entry 16)
$^{31}\text{P} [^1\text{H}]$ NMR, 3p (Table 1, Entry 16)
Mechanistic studies

1. **Reaction monitoring:** comparison of standard reaction vs. radical trap experiment (standard reaction + 0.57 mmol cumene)

   - **Standard reaction:**
     
     ![Standard reaction](image)

     - HPPh₂ (0.5 mol%)
     - 1,3,5-TMB (standard)
     - CD₃CN
     - RT, time
     - Reaction monitored

   - **Radical trap experiment:**
     
     ![Radical trap experiment](image)

     - HPPh₂ (0.5 mol%)
     - 1,3,5-TMB (standard)
     - CD₃CN
     - RT, time
     - Reaction monitored

   where TMB = trimethoxybenzene

---

**Graphical Representation:**

- Linear regression for standard reaction and radical trap experiment:
  
  - Standard reaction:
    
    \[ y = 6.26E-05x + 4.14E-04 \]
    
    \[ R^2 = 9.90E-01 \]

  - Radical trap experiment:
    
    \[ y = 6.16E-05x - 2.70E-02 \]
    
    \[ R^2 = 9.90E-01 \]
2. Reaction progress at different pre-catalyst loadings:

\[
\begin{align*}
\text{1,3,5-TMB (standard)} & \quad 2a \text{ (mol\%)} \\
\text{PPh}_2 & \quad \text{CD}_3\text{CN} \\
\text{RT, time} & \quad \text{TMB = trimethoxybenzene}
\end{align*}
\]
3. Initial rates at various pre-catalyst loadings:

\[
\begin{align*}
\text{HPPh}_2 & \quad \text{1,3,5-TMB (standard)} \\
1.04 \text{ mmol} & \quad 0.57 \text{ mmol} \\
\text{CD}_2\text{CN} & \quad \text{RT, time} \\
\end{align*}
\]

where TMB = trimethoxybenzene

\[
\begin{align*}
\text{1 mol\% 2a} & \quad y = 5.90E-04x - 2.56E-02 \\
R^2 &= 9.92E-01 \\
\text{0.5 mol\% 2a} & \quad y = 1.70E-04x + 1.12E-03 \\
R^2 &= 9.90E-01 \\
\text{0.25 mol\% 2a} & \quad y = 5.44E-05x + 4.99E-02 \\
R^2 &= 9.90E-01 \\
\text{0.125 mol\% 2a} & \quad y = 2.00E-05x - 6.64E-03 \\
R^2 &= 1.00E+00
\end{align*}
\]
4. **Log-log plot to determine order in 2a** (using initial rates from page 45)

Order in 2a = 1.6

\[ \ln([2a]) \]

\[ \ln(\text{initial rate}) \]

\[ y = 1.6316x - 0.7433 \]

\[ R^2 = 0.997 \]

- 0.125 mol%
- 0.25 mol%
- 0.5 mol%
- 1 mol%
5. Initial rates (styrenes)

\[ \text{R} \rightarrow \text{R} \]

\[ \begin{align*}
\text{HPPh}_2 & \quad \text{1,3,5-TMB (standard)} \\
0.5 \text{ mol%} & \quad \text{CD}_3 \text{CN} \\
\text{RT, time} & \quad \text{PPh}_2 \\
\end{align*} \]

\[ \text{TMB} = \text{trimethoxybenzene} \]

N.B. Reaction monitoring carried \textit{in situ} by $^1$H NMR, earliest data point collected is dependent on the time taken for the instrument to lock and shim.
6. Hammett plot

\[ y = 7.49x \]
\[ y = -0.9181x \]

Notes and references

1) In the case of 4-phenyl-styrene, 750 µL CH\(_3\)CN were used to wash the insoluble styrene into an ampule which was then heated at 60 °C for 24 h.

2) Upon addition of diphenylphosphine to 2-vinylpyridine reaction, solution turned aubergine purple.
   In the case of 2-vinylstyrene a lavender-coloured oil remained.

3) 4-vinylstyrene and 2-vinylstyrene reacted for 72 h; 4-chlorostyrene reacted for 114 h.

4) In the case of 4-vinylstyrene a yellow oil remained.

5) In the case of 3-methylstyrene, 4-vinylstyrene and 2-vinylstyrene no additional purification was necessary.

6) Non deutero THF (4.1 mg) was used for an integration standard in the case of 4-MeO-, 4-Me- and 3-methylstyrene.

