Transition Metal–Free Stereospecific Access to (E)-(1-fluoro-2-arylvinyl)phosphine Borane Complexes

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1. General information

Commercially available reagents were used without further purification. Anhydrous solvents were purchased from Sigma-Aldrich. Chromatography was carried out using neutral alumina 90 (70-230 mesh); the following solvents were used: DCM = dichloromethane, MeCN = acetonitrile. Melting points (mp) were determined on a Fisher Scientific hot stage melting point apparatus and are uncorrected. $^1$H, $^{11}$B, $^{13}$C, $^{19}$F and $^{31}$P NMR spectra were recorded using a Bruker AC 400 spectrometer operating at 400 MHz ($^1$H), 160 MHz ($^{11}$B), 100 MHz ($^{13}$C), 376 MHz ($^{19}$F), 162 MHz ($^{31}$P), or a Bruker AC 300 spectrometer operating at 300 MHz ($^1$H), 120 MHz ($^{11}$B), 75 MHz ($^{13}$C), 282 MHz ($^{19}$F), 122 MHz ($^{31}$P), respectively. The chemical shifts (δ) were calibrated on residual proton and carbon resonances of CDCl$_3$ ($^1$H, 7.26 ppm and $^{13}$C, 77.2 ppm), on boron resonance of BF$_3$-Et$_2$O ($^{11}$B, 0.0 ppm), on fluorine resonance of CFCl$_3$ ($^{19}$F, 0.0 ppm) and on phosphorus resonance of PPh$_3$ ($^{31}$P, 0.0 ppm). In the $^{13}$C NMR spectra, signals corresponding to CH, CH$_2$, or CH$_3$ groups were assigned from DEPT-135. The multiplicity signals were indicated with the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and b (broad) and the combinations thereof. Proton decoupled $^{13}$C NMR spectra were indicated with the {H} label. IR spectra were recorded on Perkin Elmer Spectrum 100 FT IR spectrometer. High Resolution Mass Spectra (HRMS) were recorded on a JEOL AccuTof 4G spectrometer coupled to a GC HP Agilent 7890 in ElectroSpray Ionisation mode (ESI) or Field Desorption (FD). EPR-ST experiments were carried out using an X-Band spectrometer (MS 400 Magnettech). The ESR spectra simulations were carried out using the WINSIM software. Gem-Bromofluoroalkenes were prepared according to our previous report (X. Lei, G. Dutheuil, X. Pannecoucke, J.-C. Quirion Org. Lett. 2004, 6, 2101).

2. General procedure for the coupling reaction

A. General coupling reaction

\[ \begin{align*}
\text{R}_1^1 & \text{F} \quad \text{Br} \\
\text{1} & \\
\text{R}_2^1 \quad \text{Br} \\
\text{2} & \\
\text{MeCN, rt, 4 h} & \\
\text{Cs}_2\text{CO}_3 & \\
\text{3} & \text{P(R}_2^2\text{)BH}_3 \\
\end{align*} \]

In a dry vial under argon atmosphere was added gem-bromofluoroalkene 1 (1 equiv), phosphine borane 2 (1.1 equiv), and Cs$_2$CO$_3$ (1.2 equiv). The vial was then filled with dry and degassed
MeCN (5 mL/mmol), then was stirred for 4 h at room temperature. The crude was then chromatographed on neutral alumina to afford the pure product 3.

B. One pot coupling/deboration sequence

In a dry vial under argon atmosphere was added gem-bromofluoroalkene 1a (0.20 mmol, 50 mg, 1 equiv), phosphine borane 2a (0.22 mmol, 44 mg, 1.1 equiv), and Cs$_2$CO$_3$ (0.24 mmol, 78 mg, 1.2 equiv). The vial was then filled with dry and degassed MeCN (1 mL, 5 mL/mmol), then was stirred for 12 h at 60 °C. The crude was then chromatographed on silica gel to afford the pure product 3a’ (30 mg, 43%).

3. Optimization of the reaction and control experiments

A. Variation of the phosphine

<table>
<thead>
<tr>
<th>Entry</th>
<th>Y</th>
<th>Yield$^a$</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BH$_3$</td>
<td>21% (3a)</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>O</td>
<td>0%</td>
<td>Products I and II</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>0%</td>
<td>Product I</td>
</tr>
</tbody>
</table>

$^a$ Isolated yields.
B. Optimization of the purification conditions for the phosphine borane

<table>
<thead>
<tr>
<th>Entry</th>
<th>Purification method</th>
<th>Yield(^a)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Filtration(^b)</td>
<td>n.d.</td>
<td>No separation of 3a and HPPH(_2)BH(_3)</td>
</tr>
<tr>
<td>2</td>
<td>Silica gel pad(^b)</td>
<td>n.d.</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>Silica gel column(^b)</td>
<td>25%</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>Dehydrated silica gel column(^b)</td>
<td>14%</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>Basic alumina column(^b)</td>
<td>32%</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>Basic alumina pad(^b)</td>
<td>45%</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>Neutral alumina pad(^b)</td>
<td>49%</td>
<td>Few by-products</td>
</tr>
<tr>
<td>8</td>
<td>Neutral alumina column(^c)</td>
<td>63%</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>Neutral alumina column(^c)</td>
<td>n.d.</td>
<td>Degradation</td>
</tr>
</tbody>
</table>

\(^a\) Isolated yields. \(^b\) With CH\(_2\)Cl\(_2\) stabilized with amylene. \(^c\) With CH\(_2\)Cl\(_2\) stabilized with ethanol. n.d.: not determined.

C. Reaction with (Z) gem-bromofluoroalkènes

In a dry vial under argon atmosphere was added gem-bromofluoroalkene (Z) 1\(_a\) (1 equiv), phosphine borane 2 (1.1 equiv), and Cs\(_2\)CO\(_3\) (1.2 equiv). The vial was then filled with dry and degassed MeCN (5 mL/mmol), then was stirred for 4 h at room temperature. Degradation of starting material (Z) 1\(_a\) was observed by \(^{19}\)F NMR, probably because of the basic conditions, according to previous report: X. Lei, G. Dutheuil, X. Pannecoucke, J.-C. Quirion Org. Lett. 2004, 6, 2101.
4. Experimental data for compounds 3a-3m

(E)-(1-Fluoro-2-(naphth-2-yl)vinyl)diphenylphosphonio trihydroborate 3a: (E)-2-(2-bromo-2-fluorovinyl)naphthalene (0.2 mmol, 50 mg), diphenylphosphate borane (0.22 mmol, 44 mg), Cs$_2$CO$_3$ (0.24 mmol, 78 mg) in MeCN (1 mL) were reacted according to the general procedure. The crude product was chromatographed on neutral alumina eluting with pure pentane to pentane/DCM 8/2 to afford the desired compound in 63% yield (46 mg) as a colourless solid. mp 173-175 °C. IR: 3058, 2923, 2849, 2392, 2348, 1435, 1054, 910, 821 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.11 (s, 1H), 7.86-7.74 (m, 6H), 7.66-7.40 (m, 10H), 7.04 (dd, $^3$J$_{H-F}$ = 42.7, $^3$J$_{H-P}$ = 8.9 Hz, 1H), 1.7-0.7 (bm, 3H). $^{13}$C NMR ($^1$H) (100 MHz, CDCl$_3$): $\delta$ 153.1 (dd, $^1$J$_{C-F}$ = 295.4, $^1$J$_{C-P}$ = 62.9 Hz, Cq), 133.6 (d, $J$ = 1.7 Hz, Cq), 133.3 (s, Cq), 133.2 (d, $^2$J$_{C-P}$ = 10.0 Hz, 4xCH), 132.0 (d, $^4$J$_{C-P}$ = 2.4 Hz, 2xCH), 130.4 (d, $J$ = 7.7 Hz, CH), 129.3 (dd, $^3$J = 10.9, 2.4 Hz, Cq), 129.1 (d, $^3$J$_{C-P}$ = 10.6 Hz, 4xCH), 128.7 (s, CH), 128.5 (s, CH), 127.8 (s, CH), 127.3 (s, CH), 126.9 (d, $J$ = 7.9 Hz, CH), 126.72 (d, $^1$J$_{C-P}$ = 60.9 Hz, 2xCq), 126.68 (s, CH), 125.3 (d, $^2$J = 26.6 Hz, CH). $^{11}$B NMR (160 MHz, CDCl$_3$): $\delta$ -38.3 (m). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -114.6 (dd, $^3$J$_{F-H}$ = 42.7, $^2$J$_{F-P}$ = 17.5 Hz). $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 21.1 (m). HRMS (ESI-TOF): calcd for C$_{24}$H$_{21}$BFNaP $m/z$ 393.1356 [M+Na]$^+$, found 393.1345.

(E)-(1-Fluoro-2-phenylvinyl)diphenylphosphonio trihydroborate 3b: (E)-2-(2-bromo-2-fluorovinyl)benzene (0.2 mmol, 40 mg), diphenylphosphate borane (0.22 mmol, 44 mg), Cs$_2$CO$_3$ (0.24 mmol, 78 mg) in MeCN (1 mL) were reacted according to the general procedure. The crude product was chromatographed on neutral alumina eluting with pure pentane to pentane/DCM 7/3 to afford the desired compound in 40% yield (25 mg) as a colourless solid.
mp 113-115 °C. IR: 3054, 2387, 1485, 1435, 1052, 875, 829 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ 7.77 (dd, J = 11.1, 7.6 Hz, 4H), 7.68-7.62 (m, 2H), 7.58-7.45 (m, 6H), 7.43- 7.34 (m, 3H), 6.89 (dd, ³J_H-F = 42.7, ³J_H-P = 8.9 Hz, 1H), 1.5-0.7 (bm, 3H). ¹³C NMR {¹H} (75 MHz, CDCl₃): δ 152.9 (d, ¹J_C-P = 10.1 Hz, 4xCH), 131.9 (d, ⁴J_C-P = 2.5 Hz, 2xCH), 131.8 (dd, ³J = 11.4, 1.7 Hz, Cq), 130.1 (d, J = 7.7 Hz, 2xCH), 129.1 (d, J = 2.4 Hz, CH), 129.1 (d, ³J_C-P = 10.6 Hz, 4xCH), 128.9 (s, 2xCH), 126.7 (d, ¹J_C-P = 60.9 Hz, 2xCq), 125.2 (d, ²J = 26.5 Hz, CH). ¹¹B NMR (120 MHz, CDCl₃): δ -38.2 (m). ¹⁹F NMR (282 MHz, CDCl₃): δ -114.7 (dd, ³J_F-H = 42.7, ²J_F-P = 17.8 Hz). ³¹P NMR (122 MHz, CDCl₃): δ 21.1 (m). HRMS (FD-TOF): calcd for C₂₀H₁₆FP m/z 306.0973 [M-BH₃]⁺, found 306.0974.

(E)-((1-Fluoro-2-(p-tolyl)vinyl)diphenylphosphonio)tri hydroborate 3c: (E)-1-(2-bromo-2-fluorovinyl)-4-methylbenzene (0.20 mmol, 43 mg), diphenylphosphine borane (0.22 mmol, 44 mg), Cs₂CO₃ (0.24 mmol, 78 mg) in MeCN (1 mL) were reacted according to the general procedure. The crude product was chromatographed on neutral alumina eluting with pure pentane to pentane/DCM 8/2 to afford the desired compound in 22% yield (15 mg) as a sticky colourless solid. IR: 2930, 2838, 2388, 1593, 1500, 1291, 1254, 1179, 1107, 1057, 1025, 825, 801 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ 7.74 (dd, J = 11.1, 7.4 Hz, 4H), 7.61-7.33 (m, 8H), 7.18 (d, J = 8.0 Hz, 2H), 6.84 (dd, ³J_H-F = 42.9, ³J_H-P = 8.9 Hz, 1H), 2.36 (s, 3H), 1.4-1.1 (bm, 3H). Selected ¹³C NMR {¹H} (75 MHz, CDCl₃): δ 139.8 (d, J = 2.5 Hz, Cq), 133.2 (d, J = 10.1 Hz, Cq), 133.0 (d, ²J_C-P = 10.0 Hz, 4xCH), 131.7 (d, ⁴J_C-P = 2.5 Hz, 2xCH), 130.0 (d, J = 7.6 Hz, 2xCH), 129.4 (s, 2xCH), 128.9 (d, ³J_C-P = 10.6 Hz, 4xCH), 126.7 (d, ¹J_C-P = 61.0 Hz, 2xCq), 125.1 (d, ²J = 26.7 Hz, CH), 21.5 (s, CH₃). ¹¹B NMR (120 MHz, CDCl₃): δ -37.8 (m). ¹⁹F NMR (282 MHz, CDCl₃): δ -116.1 (dd, ³J_F-H = 43.0, ²J_F-P = 17.5 Hz). ³¹P NMR (122 MHz, CDCl₃): δ 21.1 (m). HRMS (ESI-TOF): calcd for C₂₁H₁₉FP m/z 321.1208 [M-BH₃+H]⁺, found 321.1212.
(E)-((1-Fluoro-2-(o-tolyl)vinyl)diphenylphosphonio)trihydroborate 3d: (E)-1-(2-bromo-2-fluorovinyl)-2-methylbenzene (0.20 mmol, 43 mg), diphenylphosphine borane (0.22 mmol, 44 mg), Cs₂CO₃ (0.24 mmol, 78 mg) in MeCN (1 mL) were reacted according to the general procedure. The crude product was chromatographed on neutral alumina eluting with pure pentane to pentane/DCM 8/2 to afford the desired compound in 84% yield (56 mg) as a sticky colourless solid. IR: 3058, 2924, 2387, 2340, 1482, 1436, 1107, 1053, 830 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ 7.84-7.75 (m, 5H), 7.64-7.56 (m, 2H), 7.55-7.48 (m, 4H), 7.31-7.25 (m, 3H), 7.17 (dd, ³J_H-F = 42.2, ³J_H-P = 9.3 Hz, 1H), 2.41 (s, 3H), 1.6-1.2 (bm, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 160.4 (d, J = 3.1 Hz, Cq), 150.9 (dd, ¹J_C-F = 291.5, ¹J_C-P 64.9 Hz, Cq), 133.0 (d, ²J_C-P = 10.0 Hz, 4xCH), 131.7 (m, 4xCH), 128.9 (d, ³J_C-P = 10.6 Hz, 4xCH), 126.9 (d, ¹J_C-P = 61.2 Hz, 2xCq), 124.8 (d, J = 27.1 Hz, CH), 124.5 (dd, J = 11.8, 1.5 Hz, Cq), 114.2 (s, 2xCH), 55.3 (s, CH₃). ¹¹B NMR (160 MHz, CDCl₃): δ -38.2 (m). ¹⁹F NMR (376 MHz,
CDCl₃): δ -118.9 (dd, 3J_F-H = 43.3, 2J_F-P = 18.8 Hz). ³¹P NMR (162 MHz, CDCl₃): δ 20.4 (m). HRMS (ESI-TOF): calcd for C₂₁H₁₉FOP m/z 337.1158 [M-BH₃+H]⁺, found 337.1161.

(E)-(2-(4-Chlorophenyl)-1-fluorovinyl)diphenylphosphonio)trihydroborate 3f: (E)-1-(2-bromo-2-fluorovinyl)-4-chlorobenzene (0.2 mmol, 47 mg), diphenylphosphine borane (0.22 mmol, 44 mg), Cs₂CO₃ (0.24 mmol, 78 mg) in MeCN (1 mL) were reacted according to the general procedure. The crude product was chromatographed on neutral alumina eluting with pentane/DCM 9/1 to pentane/DCM 8/2 to afford the desired compound in 64% yield (45 mg) as a colourless solid. mp 119-121 °C. IR: 2376, 1492, 1434, 1108, 1091, 1055, 814 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.75 (dd, J = 11.3, 7.5 Hz, 4H), 7.59-7.55 (m, 4H), 7.53-7.45 (m, 4H), 7.35 (d, J = 8.5 Hz, 2H), 6.84 (dd, 3J_H-F = 42.1 Hz, 2J_H-P = 8.8 Hz, 1H), 1.60.9 (bm, 3H). ¹³C NMR {¹H} (100 MHz, CDCl₃): δ 153.6 (dd, 1J_C-F = 296.2, 1J_C-P = 61.8 Hz, Cq), 135.4 (d, J = 3.6 Hz, Cq), 133.1 (d, 2J_C-P = 10.1 Hz, 4xCH), 132.0 (d, 4J_C-P = 2.4 Hz, 2xCH), 131.3 (d, J = 7.9 Hz, 2xCH), 130.2 (dd, 3J = 11.5, 1.5 Hz, Cq), 129.4-128.7 (m, 6xCH), 126.4 (d, 1J_C-P = 61.0 Hz, 2xCq), 123.9 (d, 2J = 26.6 Hz, CH). ¹¹B NMR (160 MHz, CDCl₃): δ -38.3 (m). ¹⁹F NMR (376 MHz, CDCl₃): δ -113.9 (dd, 3J_F-H = 42.1, 2J_F-P = 17.0 Hz). ³¹P NMR (162 MHz, CDCl₃): δ 21.3 (m). HRMS (ESI-TOF): calcd for C₂₀H₁₆³⁵ClF₃P m/z 341.0662 [M-BH₃+H]⁺, found 341.0668.

(E)-(2-(3-Chlorophenyl)-1-fluorovinyl)diphenylphosphonio)trihydroborate 3g: (E)-1-(2-bromo-2-fluorovinyl)-3-chlorobenzene (0.2 mmol, 47 mg), diphenylphosphine borane (0.22 mmol, 44 mg), Cs₂CO₃ (0.24 mmol, 78 mg) in MeCN (1 mL) were reacted according to the general procedure. The crude product was chromatographed on neutral alumina eluting with pure pentane to pentane/DCM 8/2 to afford the desired compound in 49% yield (34 mg) as a
colourless solid. mp 99-101 °C. IR: 3057, 2924, 2388, 1561, 1472, 1435, 1053, 888, 820 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ 5.75 (dd, J = 11.2, 7.6 Hz, 4H), 7.68 (s, 1H), 7.59-7.54 (m, 2H), 7.53-7.46 (m, 5H), 7.35-7.28 (m, 2H), 6.83 (dd, ³Jₕ,F = 41.7, ³Jₕ,P = 8.7 Hz, 1H), 1.6-0.9 (bm, 3H). ¹³C NMR {¹H} (100 MHz, CDCl₃): δ 154.3 (dd, ¹JC,F = 297.5, ¹JC,P = 61.0 Hz, Cq), 134.8 (s, Cq), 133.3 (dd, ³J = 11.4, 1.3 Hz, Cq), 133.1 (d, ²JC,P = 10.0 Hz, 4xCH), 132.1 (d, ⁴JC,P = 2.5 Hz, 2xCH), 130.1 (s, CH), 129.8 (d, J = 9.1 Hz, CH), 129.6 (d, J = 2.1 Hz, CH), 129.2 (d, ³JC,P = 10.6 Hz, 4xCH), 128.2 (d, J = 6.9 Hz, CH), 126.3 (d, ¹JC,P = 60.9 Hz, 2xCq), 123.7 (d, J = 26.4 Hz, CH). ¹¹B NMR (160 MHz, CDCl₃): δ -38.3 (m). ¹⁹F NMR (376 MHz, CDCl₃): δ -112.3 (dd, ³J,F,H = 41.7, ²J,F,P = 17.2 Hz). ³¹P NMR (162 MHz, CDCl₃): δ 21.6 (m). HRMS (ESI-TOF): calcd for C₂₀H₁₆³⁵ClFP m/z 341.0662 [M-BH₃+H]⁺, found 341.0659.

(E)-(2-(4-(Methoxycarbonyl)phenyl)-1-fluorovinyl)diphenylphosphonio)trihydroborate

³h: (E)-methyl 4-(2-bromo-2-fluorovinyl)benzoate (0.2 mmol, 52 mg), diphenylphosphine borane (0.22 mmol, 44 mg), Cs₂CO₃ (0.24 mmol, 78 mg) in MeCN (1 mL) were reacted according to the general procedure. The crude product was chromatographed on neutral alumina eluting with pentane/DCM 9/1 to pentane/DCM 8/2 to afford the desired compound in 85% yield (64 mg) as a colourless solid. mp 147-149 °C. IR: 2924, 2849, 2384, 1717, 1436, 1412, 1280, 1185, 1107, 1053, 894, 828 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 8.04 (d, ³Jₕ,H = 8.4 Hz, 2H), 7.79-7.72 (m, 4H), 7.69 (d, ³Jₕ,H = 8.4 Hz, 2H), 7.59-7.54 (m, 2H), 7.53-7.46 (m, 4H), 6.91 (dd, ³Jₕ,F = 41.9, ³Jₕ,P = 8.7 Hz, 1H), 3.92 (s, 3H), 1.6-0.8 (bm, 3H). ¹³C NMR {¹H} (100 MHz, CDCl₃): δ 166.6 (s, Cq), 155.0 (dd, ¹JC,F = 299.1, ¹JC,P = 60.4 Hz, Cq), 135.9 (d, ³J = 11.2 Hz, Cq), 133.1 (d, ²JC,P = 10.1 Hz, 4xCH), 132.1 (d, ⁴JC,P = 2.5 Hz, 2xCq), 130.6 (d, J = 2.4 Hz, Cq), 130.0 (s, 2xCq), 129.9 (d, J = 7.9 Hz, 2xCq), 129.2 (d, ³JC,P = 10.7 Hz, 4xCH), 126.2 (d, ¹JC,P = 60.8 Hz, 2xCq), 123.9 (d, ²J = 26.2 Hz, CH), 52.4 (s, OCH₃). ¹¹B NMR (160 MHz, CDCl₃): δ -38.5 (m). ¹⁹F NMR (376 MHz, CDCl₃): δ -111.0 (dd, ³J,F,H = 41.9, ²J,F,P = 17.5 Hz). ³¹P NMR (122 MHz, CDCl₃): δ 21.7 (m). HRMS (ESI-TOF): calcd for C₂₂H₁₉FO₂P m/z 365.1107 [M-BH₃+H]⁺, found 365.1106.
(E)-(2-(4-Nitrophenyl)-1-fluorovinyl)diphenylphosphonio)trihydroborate 3i: (E)-1-(2-bromo-2-fluorovinyl)-4-nitrobenzene (0.20 mmol, 49 mg), diphenylphosphine borane (0.22 mmol, 44 mg), Cs$_2$CO$_3$ (0.24 mmol, 78 mg) in MeCN (1 mL) were reacted according to the general procedure. The crude product was chromatographed on neutral alumina eluting with pure pentane to pentane/DCM 1/1 to afford the desired compound in 53% yield (39 mg) as a colourless solid. mp 153-155 °C. IR: 3061, 2418, 1644, 1594, 1511, 1436, 1344, 1289, 1107, 1056, 885, 859, 843, 827 cm$^{-1}$. $^1$H NMR (300 MHz, CDCl$_3$): δ 8.23 (d, $^3$J$_{H,F}$ = 8.8 Hz, 2H), 7.89-7.67 (m, 6H), 7.65-7.38 (m, 6H), 6.94 (dd, $^3$J$_{H,F}$ = 41.0, $^3$J$_{H,P}$ = 8.6 Hz, 1H), 1.4-0.7 (bm, 3H). $^{13}$C NMR ($^1$H) (75 MHz, CDCl$_3$): δ 156.7 (dd, $^1$J$_{C,F}$ = 302.4, $^1$J$_{C,P}$ = 58.1 Hz, Cq), 147.8 (s, Cq), 137.8 (d, $^3$J = 11.3 Hz, Cq), 133.1 (d, $^2$J$_{C,P}$ = 10.1 Hz, 4xCH), 132.3 (s, 2xCH), 130.7 (d, $^1$J = 8.0 Hz, 2xCH), 129.3 (d, $^3$J$_{C,P}$ = 10.7 Hz, 4xCH), 125.8 (d, $^1$J = 60.7 Hz, 2xCq), 124.1 (s, 2xCH), 122.6 (d, $^2$J = 26.1 Hz, CH). $^{11}$B NMR (120 MHz, CDCl$_3$): δ -38.5 (m). $^{19}$F NMR (282 MHz, CDCl$_3$): δ -108.6 (dd, $^3$J$_{F,H}$ = 41.0, $^3$J$_{F,P}$ = 16.5 Hz). $^{31}$P NMR (122 MHz, CDCl$_3$): δ 22.2 (m). HRMS (FD-TOF): calcd for C$_{20}$H$_{15}$FNO$_2$P m/z 351.0824 [M-BH$_3$]$^+$, found 351.0826.

(E)-(2-(4-Cyanophenyl)-1-fluorovinyl)diphenylphosphonio)trihydroborate 3j: (E)-4-(2-bromo-2-fluorovinyl)benzonitrile (0.2 mmol, 45 mg), diphenylphosphine borane (0.22 mmol, 44 mg), Cs$_2$CO$_3$ (0.24 mmol, 78 mg) in MeCN (1 mL) were reacted according to the general procedure. The crude product was chromatographed on neutral alumina eluting with pentane/DCM 8/2 to afford the desired compound in 82% yield (51 mg) as a colourless solid. mp 131-133 °C. IR: 3053, 2401, 2350, 2230, 1435, 1050, 887, 839, 828 cm$^{-1}$. $^1$H NMR (300 MHz, CDCl$_3$): δ 7.98-7.37 (m, 14H), 6.89 (dd, $^3$J$_{H,F}$ = 41.2, $^3$J$_{H,P}$ = 8.2 Hz, 1H), 1.5-0.8 (bm, 3H). $^{13}$C NMR ($^1$H) (75 MHz, CDCl$_3$): δ 156.1 (d, $^1$J$_{C,F}$ = 301.3, $^1$J$_{C,P}$ = 58.6 Hz, Cq), 135.9 (d, $^1$J = 11.3 Hz, Cq), 133.0 (d, $^2$J$_{C,P}$ = 10.1 Hz, 4xCH), 132.5 (s, 2xCH), 132.2 (d, $^4$J$_{C,P}$ = 2.4
Hz, 2xCH), 130.4 (d, J = 8.0 Hz, 2xCH), 129.2 (d, 3J_C-P = 10.7 Hz, 4xCH), 125.8 (d, 1J_C-P = 60.8 Hz, 2xCq), 123.0 (d, J = 26.1 Hz, CH), 118.5 (s, Cq), 112.7 (d, J = 3.0 Hz, Cq). 11B NMR (160 MHz, CDCl3): δ -38.4 (m). 19F NMR (376 MHz, CDCl3): δ -109.7 (dd, 3J_F-H = 41.2, 2J_F-P = 19.2 Hz). 31P NMR (162 MHz, CDCl3): δ -21.9 (m). HRMS (ESI-TOF): calcd for C21H16FNP m/z 332.1004 [M-BH3+H]+, found 332.1002.

(E)-(1-Fluoro-2-(naphth-2-yl)vinyl)-bis(4-methoxyphenyl)phosphonio)trihydroborate

3k: (E)-2-(2-bromo-2-fluorovinyl)naphthalene (0.20 mmol, 50 mg), bis(4-methoxyphenyl)phosphine borane (0.22 mmol, 57 mg), Cs2CO3 (0.24 mmol, 78 mg) in MeCN (1 mL) were reacted according to the general procedure. The crude product was chromatographed on neutral alumina eluting with pure pentane to pentane/DCM 1/1 to afford the desired compound in 38% yield (30 mg) as a sticky colourless solid. IR: 2923, 2355, 1593, 1569, 1500, 1455, 1300, 1257, 1177, 1108, 1054, 1028, 903, 826 cm⁻¹. 1H NMR (300 MHz, CDCl3): δ 8.08 (s, 1H), 7.84-7.68 (m, 8H), 7.54-7.44 (m, 2H), 7.05-6.83 (m, 5H), 3.85 (s, 6H), 1.4-0.9 (bm, 3H). 13C NMR (1H) (75 MHz, CDCl3): δ 162.6 (d, 4J_C-P = 2.4 Hz, 2xCq), 154.1 (dd, 1J_C-F = 295.0, 1J_C-P = 63.3 Hz, Cq), 134.8 (d, J_C-P = 11.3 Hz, 4xCH), 133.5 (d, J = 1.8 Hz, Cq), 133.3 (s, Cq), 130.2 (d, J = 7.6 Hz, CH), 129.5 (dd, J = 11.2, 1.7 Hz, Cq), 128.6 (s, J = 16.2 Hz, CH), 128.4 (s, CH), 127.7 (s, CH), 127.2 (s, CH), 126.9 (d, J = 7.9 Hz, CH), 126.6 (s, CH), 124.2 (d, 2J = 26.0 Hz, CH), 117.5 (d, 1J_C-P = 66.4 Hz, 2xCq), 114.8 (d, J_C-P = 11.6 Hz, 4xCH), 55.5 (s, 2xOCH3). 11B NMR (120 MHz, CDCl3): δ -38.0 (m). 19F NMR (282 MHz, CDCl3): δ -114.8 (dd, 3J_F-H = 42.8, 2J_F-P = 20.6 Hz). 31P NMR (122 MHz, CDCl3): δ 18.4 (m). HRMS (FD-TOF): calcd for C26H22FO2P m/z 416.1341 [M-BH3]+, found 416.1349.
(E)-[(2-(3-Chlorophenyl)-1-fluorovinyl)-bis(4-methoxyphenyl)phosphonio]trihydroborate 3l: (E)-1-(2-bromo-2-fluorovinyl)-3-chlorobenzene (0.20 mmol, 47 mg), bis(4-methoxyphenyl)phosphine borane (0.22 mmol, 57 mg), Cs₂CO₃ (0.24 mmol, 78 mg) in MeCN (1 mL) were reacted according to the general procedure. The crude product was chromatographed on neutral alumina eluting with pure pentane to pentane/DCM 7/3 to afford the desired compound in 18% yield (12 mg) as a sticky colourless solid. IR: 2924, 2389, 1725, 1436, 1107, 1054, 812 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ 7.66 (m, 5H), 7.44 (m, 1H), 7.30 (m, 2H), 6.98 (m, 4H), 6.72 (dd, 3J_H-F = 41.9, 3J_H-P = 8.5 Hz, 1H), 3.85 (s, 6H), 1.4-0.8 (bm, 3H). Selected ¹³C NMR ¹H (75 MHz, CDCl₃): δ 162.7 (d, 4J_C-P = 2.4 Hz, 2xCq), 134.8 (m, 4xCH+Cq), 133.5 (dd, J = 11.1, 1.3 Hz, Cq), 130.0 (s, CH), 129.8 (d, J = 9.0 Hz, CH), 129.4 (d, J = 2.1 Hz, CH), 128.2 (d, J = 7.0 Hz, CH), 122.6 (d, 2J = 25.9 Hz, CH), 117.1 (d, 1J_C-P = 66.4 Hz, 2xCq), 114.8 (d, 3J_C-P = 11.6 Hz, 4xCH), 55.5 (s, CH₃). ¹¹B NMR (120 MHz, CDCl₃): δ -38.7 (m). ¹⁹F NMR (282 MHz, CDCl₃): δ -112.6 (dd, 3J_F-H = 41.9, 2J_F-P = 20.2 Hz). ³¹P NMR (122 MHz, CDCl₃): δ 18.7 (m). HRMS (ESI-TOF): calcd for C₂₂H₂₀ClFO₂P m/z 401.0873 [M-BH₃+H]+, found 401.0867.

(E)-[(2-(4-Cyanophenyl)-1-fluorovinyl) bis(4-methoxyphenyl)phosphonio]trihydroborate 3m: (E)-4-(2-bromo-2-fluorovinyl)benzonitrile (0.20 mmol, 45 mg), bis(4-methoxyphenyl)phosphine borane (0.22 mmol, 57 mg), Cs₂CO₃ (0.24 mmol, 78 mg) in MeCN (1 mL) were reacted according to the general procedure. The crude product was chromatographed on neutral alumina eluting with pure pentane to pentane/DCM 1/1 to afford the desired compound in 47% yield (42 mg) as a sticky colourless solid. IR: 2932, 2389, 2228, 1594, 1500, 1292, 1254, 1179, 1107, 826, 800 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ 7.71-...
7.61 (m, 8H), 7.00 (dd, $J = 8.3, 1.7$ Hz, 4H), 6.79 (dd, $^3J_{H-F} = 41.4$, $^3J_{H-P} = 8.3$ Hz, 1H), 3.85 (s, 6H), 1.4-0.9 (bm, 3H). $^{13}$C NMR ($^1$H) (75 MHz, CDCl$_3$): $\delta$ 162.7 (d, $^4J_{C-P} = 2.4$ Hz, 2xCq), 157.1 (dd, $^1J_{C-F} = 301.0$, $^1J_{C-P} = 59.2$ Hz, Cq), 136.1 (d, $J = 11.0$ Hz, Cq), 134.8 (d, $^2J_{C-P} = 11.5$ Hz, 4xCq), 132.5 (s, 2xCq), 130.3 (d, $J = 8.1$ Hz, 2xCq), 121.9 (d, $^2J = 25.5$ Hz, CH), 118.6 (s, Cq), 116.5 (d, $^1J_{C-P} = 66.3$ Hz, 2xCq), 114.9 (d, $^3J_{C-P} = 11.6$ Hz, 4xCq), 112.5 (d, $J = 3.0$ Hz, Cq), 55.5 (s, 2xOCH$_3$). $^{11}$B NMR (120 MHz, CDCl$_3$): $\delta$ -38.1 (m). $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ -109.4 (dd, $^3J_{F-H} = 41.4$, $^2J_{F-P} = 19.8$ Hz). $^{31}$P NMR (122 MHz, CDCl$_3$): $\delta$ 19.1 (m). HRMS (FD-TOF): calcd for C$_{23}$H$_{19}$FNO$_2$P $m/z$ 391.1137 [M-BH$_3$]$^+$, found 391.1148.

$$\text{(E)-(1-Fluoro-2-(naphth-2-yl)vinyl)diphenylphosphine 3a'}: \quad \text{(E)-2-(2-bromo-2-fluorovinyl)naphthalene (0.20 mmol, 50 mg), diphenylphosphine borane (0.22 mmol, 44 mg), Cs$_2$CO$_3$ (0.24 mmol, 78 mg) in MeCN (1 mL) were reacted according to the general procedure, at 60 °C overnight. The crude product was chromatographed on silica gel eluting with pentane/toluene 9/1 to 5/5 to afford the desired compound in 43% yield (31 mg) as a colourless solid. mp 139-141 °C. IR: 3058, 2924, 2852, 1727, 1584, 1479, 1430, 1273, 1042, 906, 828 cm}^{-1}. \  \  \text{1H NMR (300 MHz, CDCl$_3$): $\delta$ 8.04 (s, 1H), 7.9-7.7 (m, 4H), 7.7-7.6 (m, 4H), 7.5-7.3 (m, 8H), 6.51 (dd, $^3J_{H-F} = 41.0$, $^3J_{H-P} = 9.4$ Hz, 1H).} \  \text{13C NMR ($^1$H) (75 MHz, CDCl$_3$): $\delta$ 161.6 (dd, $^1J_{C-F} = 313.6$, $^1J_{C-P} = 28.9$ Hz, Cq), 134.4 (dd, $J = 6.4, 2.8$ Hz, 2xCq), 133.6 (d, $^2J_{C-P} = 19.3$ Hz, 4xCq), 133.4 (s, Cq), 133.1 (d, $J = 1.9$ Hz, Cq), 130.7 (dd, $^3J = 11.9, 2.1$ Hz, Cq), 129.4 (s, 2xCq), 129.0 (d, $J = 8.1$ Hz, CH), 128.8 (d, $^3J_{C-P} = 7.1$ Hz, 4xCq), 128.4 (s, CH), 128.2 (s, CH), 127.7 (s, CH), 126.9 (d, $J = 8.0$ Hz, CH), 126.6 (s, CH), 126.4 (s, CH), 123.8 (dd, $^2J_{C-F} = 39.3$, $^2J_{C-P} = 4.3$ Hz, CH).} \ \text{19F NMR (282 MHz, CDCl$_3$): $\delta$ -104.4 (dd, $^3J_{F-H} = 41.1$, $^2J_{F-P} = 14.5$ Hz).} \ \text{31P NMR (122 MHz, CDCl$_3$): $\delta$ -5.4 (m). HRMS (ESI-TOF): calcd for C$_{24}$H$_{19}$OFP $m/z$ 373.1158 [M(O)+H]$^+$, found 373.1163.}$$
5. NMR spectra for compounds 3a-3m

\((E)-((1\text{-Fluoro-2-(naphth-2-yl)vinyl})\text{diphenylphosphonio})\text{trihydroborate}\) 3a

\(^{1}H\) NMR in CDCl\(_3\)

\(^{19}F\) NMR in CDCl\(_3\)
(E)-((1-Fluoro-2-phenylvinyl)diphenylphosphonio)trihydroborate 3b

\[ \text{chemical structure image} \]

$^1$H NMR in CDCl$_3$

$^{19}$F NMR in CDCl$_3$
$	ext{^31P NMR in CDCl}_3$

$	ext{^11B NMR in CDCl}_3$

$	ext{^13C NMR \{^1H\} in CDCl}_3$
(E)-((1-Fluoro-2-(p-tolyl)vinyl)diphenylphosphonio)trihydroborate 3c

$\text{Me}$

$\text{F}$

$\text{P}^+$

$\text{BH}_3$

$\text{H NMR in } \text{CDCl}_3$

$\text{F NMR in } \text{CDCl}_3$
(E)-((1-Fluoro-2-((o-tolyl)vinyl)diphenylphosphonio)trihydroborate 3d

\[
\text{Me} \quad \begin{array}{c}
\text{Ph} \\
\text{Ph} \\
\text{F} \\
\text{H} \quad \text{P} \quad \text{BH}_3
\end{array}
\]

\[\text{^1H NMR in CDCl}_3\]

\[\text{^19F NMR in CDCl}_3\]
(E)-((2-[(4-Methoxyphenyl)-1-fluorovinyl]diphenylphosphonio)trihydroborate 3e

$^{1}H$ NMR in CDCl$_3$

$^{19}F$ NMR in CDCl$_3$
$^{31}$P NMR in CDCl$_3$

$^{11}$B NMR in CDCl$_3$

$^{13}$C NMR ($^1$H) in CDCl$_3$
(E)-((2-(4-Chlorophenyl)-1-fluorovinyl)diphenylphosphonio)trihydroborate 3f
$^{31}$P NMR in CDCl$_3$

$^{11}$B NMR in CDCl$_3$

$^{13}$C NMR [$^1$H] in CDCl$_3$
(E)-(2-(3-Chlorophenyl)-1-fluorovinyl)diphenylphosphonio)trihydroborate 3g
$^{31}$P NMR in CDCl$_3$

$^{11}$B NMR in CDCl$_3$

$^{13}$C NMR {$^1$H} in CDCl$_3$
(E)-(2-(4-(Methoxycarbonyl)phenyl)-1-fluorovinyl)diphenylphosphonio)trihydroborate 3h
$^{31}$P NMR in CDCl$_3$

$^{11}$B NMR in CDCl$_3$

$^{13}$C NMR (H) in CDCl$_3$
(E)-(2-(4-Nitrophenyl)-1-fluorovinyl)diphenylphosphonio)trihydroborate 3i

$\text{^1H NMR in CDCl}_3$

$\text{^{19}F NMR in CDCl}_3$
$^{31}$P NMR in CDCl$_3$

$^{11}$B NMR in CDCl$_3$

$^{13}$C NMR {$^1$H} in CDCl$_3$
(E)-((2-(4-Cyanophenyl)-1-fluorovinyl)diphenylphosphonio)trihydroborate 3j

$^1$H NMR in CDCl$_3$

$^{19}$F NMR in CDCl$_3$
$^{31}\text{P NMR in CDCl}_3$

$^{11}\text{B NMR in CDCl}_3$

$^{13}\text{C NMR \{^{1}\text{H}\} in CDCl}_3$
(E)-((1-Fluoro-2-(naphth-2-yl)vinyl)-bis(4-methoxyphenyl)phosphonio)trihydroborate 3k
\((E)-(2-(3\text{-Chlorophenyl})-1\text{-fluorovinyl})\text{-bis(4\text{-methoxyphenyl})phosphonio} \text{trihydroborate 3l}\)

\begin{center}
\includegraphics[width=0.8\textwidth]{nmr_spectra}
\end{center}

\textbf{\(^1H NMR in CDCl\textsubscript{3}\)}

\textbf{\(^{19}F NMR in CDCl\textsubscript{3}\)}
$^31$P NMR in CDCl$_3$

$^{11}$B NMR in CDCl$_3$

$^{13}$C NMR {$^1$H} in CDCl$_3$
(E)-((2-(4-Cyanophenyl)-1-fluorovinyl) bis(4-methoxyphenyl)phosphonio)trihydroborate

3m

$^1$H NMR in CDCl$_3$

$^{19}$F NMR in CDCl$_3$
(E)-(1-Fluoro-2-(naphth-2-yl)vinyl)diphenylphosphine 3a'

\[
\begin{align*}
\text{H NMR in CDCl}_3 \\
\text{F NMR in CDCl}_3
\end{align*}
\]
$^{31}$P NMR in CDCl$_3$

$^{12}$C NMR ($^1$H) in CDCl$_3$
6. Electron paramagnetic resonance (EPR) experiment

\[
\begin{align*}
1a & \quad 1 \text{ equiv} \\
2a & \quad 1 \text{ equiv}
\end{align*}
\]

\[
\begin{align*}
1 \text{ equiv} & \quad \text{Cs}_2\text{CO}_3 \\
1 \text{ equiv} & \quad \text{tert-butylbenzene}
\end{align*}
\]

\[
\begin{align*}
1 \text{ equiv} & \quad \text{HPPh}_2\text{BH}_3 \\
1 \text{ equiv} & \quad \text{4}
\end{align*}
\]

\[
\begin{align*}
\text{Br} & \quad \text{F} \\
\text{Ph} & \quad \text{N}^+ \text{t-Bu} \quad \text{t-Bu}
\end{align*}
\]

\[a_N = 14.5; \ a_H = 2.3 \ G\]
7. X-Ray structures

\((E)\)-((1-Fluoro-2-(naphth-2-yl)vinyl)diphenylphosphonio)trihydroborate 3a

Hydrogen atoms are omitted for clarity.

\[\text{CCDC: 1496850}\]

Figure 1: X-Ray Structure of 3a

\((E)\)-((2-(4-Chlorophenyl)-1-fluorovinyl)diphenylphosphonio)trihydroborate 3f

Hydrogen atoms are omitted for clarity.

\[\text{CCDC: 1496851}\]

Figure 2: X-Ray Structure of 3f

\((E)\)-((2-(3-Chlorophenyl)-1-fluorovinyl)diphenylphosphonio)trihydroborate 3g

Hydrogen atoms are omitted for clarity.

\[\text{CCDC: 1496852}\]

Figure 3: X-Ray Structure of 3g