Supporting Information

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A Direct Synthesis of Vinylphosphonium Salts from α-Trimethylsilyl Ylides and Non-enolizable Aldehydes

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General:

Reactions were carried out under an Argon atmosphere in oven-dried glassware. All fine chemicals were obtained from Aldrich except tributylphosphane which was obtained from Cytec. THF was distilled from sodium metal with benzophenone indicator. Dichloromethane and ethyl acetate were distilled over calcium hydride. CIMS were run on a Micromass Quattro Ultima spectrometer fitted with a direct injection probe (DIP) with ionization energy set at 70 eV and HRMS (EI) were performed with a Micromass Q-Tof Ultima spectrometer. $^1$H, $^{13}$C and $^{31}$P spectra were recorded on a Bruker 200 or AV 600 spectrometer in CDCl$_3$ with TMS as internal standard, chemical shifts ($d$) are reported in ppm downfield of TMS and coupling constants ($J$) are expressed in Hz. Signal assignments were accomplished via analysis of HMBC, HMQC, COSY, NOSEY experiments where necessary. The ($E$) to ($Z$) ratios are reported from the relative integration of the $^1$H spectra for the olefinic protons and comparison to the $^{31}$P NMR spectra.

Trimethylsilyl-methyl-tributylphosphonium iodide (3):

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\begin{array}{c}
\text{(Bu)}_3\text{P} \\
\text{TMS}
\end{array}
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Into a flame-dried flask, containing a magnetic stirring bar, was weighed (iodomethyl)trimethylsilane (200 µL, 1.346 mmol) under argon and dry THF (2.7 mL) was added to make a 0.5 M solution. The flask was stirred for 15 min. at room temperature whereupon tributylphosphine (353 µL, 1.413 mmol) was added slowly to the reaction flask. The flask was maintained at room temperature for 13 hrs. Solvent was removed under vacuum to yield the title compound, 555 mg, (99%) as a white crystalline solid.

Mp 101–102 °C; H-NMR (600 MHz, CDCl$_3$): d = 0.30 (s, 9H); 0.95 (m, 9H); 1.53 (m, 12H); 1.87 (d, $J_{PH}$=17.0Hz, 2H); 2.36 (m, 6H). $^{13}$C-NMR (150 MHz, CDCl$_3$): d = 1.0; 6.9 (d, $J$=42.3Hz); 13.6; 22.2 (d,
(E)-4-Chlorostyril-2’-tributylphosphonium iodide (Table 1, entry 1):

Into a flame-dried flask, containing a magnetic stirring bar, was weighed trimethylsilyl-methyl-tributylphosphonium salt 3 (200 mg, 0.481 mmol) under argon and dry THF (1 mL) was added to make a 0.5 M solution. The flask was stirred for 15 min. at -78 °C whereupon sBuLi (360µL, 0.505 mmol, 1.4M stock, C₆H₁₂) was added slowly. After 40 mins, a 0.5 M solution (in THF) of 4-chlorobenzaldehyde (71 mg, 0.505 mmol) was added slowly to the reaction flask maintained at -78 °C. The flask was kept at -78 °C for 2 hrs and then slowly warmed to room temperature where it was stirred for a further 2 hr. The resulting mixture was concentrated to remove solvent. Water was added (5 mL) to the residue, and the resulting mixture was extracted with dichloromethane (3 x 15 mL). The combined organic layers were dried over MgSO₄, filtered, and concentrated. Hexane was added (5 mL) to the flask and stirred for 5 mins. The slurry was vacuum filtered and dried to yield the title compound, 211.8 mg, (90%) as yellowish viscous solid.

H-NMR (600 MHz, CDCl₃): d = 0.94 (m, 9H); 1.53 (m, 12H); 2.55 (m, 6H); 7.08 (dd, J_HH=17.2Hz, J_PH=17.2Hz, 1H); 7.34 (d, J_HF=8.3 Hz, 2H); 7.75 (m, 3H). ¹³C-NMR (150 MHz, CDCl₃): d = 13.6; 20.2 (d, J=50.34Hz); 23.7; 23.9 (d, J=18.3Hz); 105.4 (d, J=80.5Hz); 129.3; 130.2; 132.4 (d, 18.1Hz); 137.6; 151.7 (d, J=3.82Hz). ³¹P NMR (80 MHz, CDCl₃): d = 27.9. HRES MS (M)⁺ calcd. for C₁₆H₃₈PSi: 289.2468, found: 289.2480.

(E)-4-Fluorostyril-2’-tributylphosphonium iodide (Table 1, entry 2):
Into a flame-dried flask, containing a magnetic stirring bar, was weighed trimethylsilyl-methyl-tributylphosphonium salt 3 (200 mg, 0.481 mmol) under argon and dry THF (1 mL) was added to make a 0.5 M solution. The flask was stirred for 15 min. at -78 °C whereupon sBuLi (360µL, 0.505 mmol, 1.4M stock, C₆H₁₂) was added slowly. After 40 mins, a 0.5 M solution (in THF) of 4-fluorobenzaldehyde (53.3µL, 0.505 mmol) was added slowly to the reaction flask maintained at -78 °C. The flask was kept at -78 °C for 2 hrs and then slowly warmed to room temperature where it was stirred for a further 2 hr. The resulting mixture was concentrated to remove solvent. Water was added (5 mL) to the residue, and the resulting mixture was extracted with dichloromethane (3 x 15 mL). The combined organic layers were dried over MgSO₄, filtered, and concentrated. Hexane was added (5 mL) to the flask and stirred for 5 mins. The slurry was vacuum filtered and dried to yield the title compound, 216 mg, (95%) as yellowish viscous solid.

H-NMR (600 MHz, CDCl₃): δ = 0.94 (m, 9H); 1.52 (m, 12H); 2.55 (m, 6H); 7.05 (m, 3H); 7.56 (m, 3H).

¹³C-NMR (150 MHz, CDCl₃): δ = 13.6; 20.2 (d, J=50.3Hz); 23.7; 23.9 (d, J=18.0Hz); 104.3 (d, J=80.3Hz); 116.2; 128.5(18.1 Hz); 131.2; 151.7; 167.2. ³¹P NMR (80 MHz, CDCl₃): δ = 27.8. HRES MS (M) calcd. for C₂₀H₃₃PF: 323.2299, found: 323.2304.

(E)-4-Methylstyryl-2'-tributylphosphonium iodide (Table 1, entry 3):

Into a flame-dried flask, containing a magnetic stirring bar, was weighed trimethylsilyl-methyl-tributylphosphonium salt 3 (200 mg, 0.481 mmol) under argon and dry THF (1 mL) was added to make a 0.5 M solution. The flask was stirred for 15 min. at -78 °C whereupon sBuLi (360µL, 0.505 mmol, 1.4M
stock, C₆H₁₂) was added slowly. After 40 mins, a 0.5 M solution (in THF) of 4-methylbenzaldehyde (60.1µL, 0.505 mmol) was added slowly to the reaction flask maintained at -78 °C. The flask was kept at -78 °C for 2 hrs and then slowly warmed to room temperature where it was stirred for a further 2 hr. The resulting mixture was concentrated to remove solvent. Water was added (5 mL) to the residue, and the resulting mixture was extracted with dichloromethane (3 x 15 mL). The combined organic layers were dried over MgSO₄, filtered, and concentrated. Hexane was added (5 mL) to the flask and stirred for 5 mins. The slurry was vacuum filtered and dried to yield the title compound, 207.3 mg, (92%) as yellowish viscous solid.

H-NMR (600 MHz, CDCl₃): δ 0.95 (m, 9H); 1.52 (m, 12H); 2.35 (s, 3H); 2.55 (m, 6H); 6.86 (dd, J_HH=17.8Hz, J_PH=17.8Hz, 1H); 7.19 (d, J_HH=8.1Hz, 2H); 7.62 (m, 3H). ¹³C-NMR (150 MHz, CDCl₃): δ 13.5; 20.1 (d, J=48.8Hz); 21.5; 23.5; 23.7 (d, J=18.1); 103.0 (d, J=79.1Hz); 128.7; 129.6; 131.2 (16.7Hz); 142.0; 152.8 (2.3Hz). ³¹P NMR (80 MHz, CDCl₃): δ 27.6. HRES MS (M)⁺ calcd. for C₂₁H₃₆P: 319.2570, found: 319.2555.

(E)-4-Methoxystyril-2'-tributylphosphonium iodide (Table 1, entry 4):

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\begin{align*}
&\text{Into a flame-dried flask, containing a magnetic stirring bar, was weighed trimethylsilyl-methyl-tributylphosphonium salt 3 (200 mg, 0.481 mmol) under argon and dry THF (1 mL) was added to make a} \\
&\text{0.5 M solution. The flask was stirred for 15 min. at -78 °C whereupon sBuLi (360µL, 0.505 mmol, 1.4M} \\
&\text{stock, C₆H₁₂) was added slowly. After 40 mins, a 0.5 M solution (in THF) of 4-methoxybenzaldehyde} \\
&\text{(61.5µL, 0.505 mmol) was added slowly to the reaction flask maintained at -78 °C. The flask was kept at -78 °C for 2 hrs and then slowly warmed to room temperature where it was stirred for a further 2 hr. The} \\
&\text{resulting mixture was concentrated to remove solvent. Water was added (5 mL) to the residue, and the} \\
&\text{resulting mixture was extracted with dichloromethane (3 x 15 mL). The combined organic layers were dried} \\
&\text{over MgSO₄, filtered, and concentrated. Hexane was added (5 mL) to the flask and stirred for 5 mins. The}
\end{align*}
\]
slurry was vacuum filtered and dried to yield the title compound, 212.4 mg, (91%) as yellowish viscous solid.

H-NMR (600 MHz, CDCl₃): d = 0.92 (m, 9H); 1.51 (m, 12H); 2.53 (m, 6H); 3.78 (s, 3H); 6.75 (dd, J_HH=17.8Hz, J_PP=17.8Hz, 1H); 6.86 (d, J_HH=7.5Hz, 2H); 7.60 (dd, J_HH=17.8Hz, J_PP=19.3Hz, 1H); 7.72 (d, J_HH=7.5Hz, 2H). ¹³C-NMR (150 MHz, CDCl₃): d = 13.6; 20.3 (d, J=49.7Hz); 23.6; 23.8 (d, J=17.1Hz); 55.1; 100.6 (d, J=83.4Hz); 114.41; 126.7 (d, 18.3Hz); 130.7; 152.4; 162.4. ³¹P NMR (80 MHz, CDCl₃): d = 27.5. HRES MS (M⁺) calcd. for C₂₁H₃₆O₂P: 335.2512, found: 335.2504.

(E)-3,4-Methylenedioxystyryl-2’-tributylphosphonium iodide (Table 1, entry 5):

![Diagram](image)

Into a flame-dried flask, containing a magnetic stirring bar, was weighed trimethylsilyl-methyl-tributylphosphonium salt 3 (200 mg, 0.481 mmol) under argon and dry THF (1 mL) was added to make a 0.5 M solution. The flask was stirred for 15 min. at -78 °C whereupon sBuLi (360 µL, 0.505 mmol, 1.4M stock, C₆H₁₂) was added slowly. After 40 mins, a 0.5 M solution (in THF) of piperonal (75.8 mg, 0.505 mmol) was added slowly to the reaction flask maintained at -78 °C. The flask was kept at -78 °C for 2 hrs and then slowly warmed to room temperature where it was stirred for a further 2 hr. The resulting mixture was concentrated to remove solvent. Water was added (5 mL) to the residue, and the resulting mixture was extracted with dichloromethane (3 x 15 mL). The combined organic layers were dried over MgSO₄, filtered, and concentrated. Hexane was added (5 mL) to the flask and stirred for 5 mins. The slurry was vacuum filtered and dried to yield the title compound, 195 mg, (85%) as yellowish viscous solid.

H-NMR (600 MHz, CDCl₃): d = 0.92 (m, 9H); 1.50 (m, 12H); 2.55 (m, 6H); 5.90 (s, 2H); 6.71 (dd, J_HH=17.5Hz, J_PP=17.5Hz, 1H); 6.84 (d, J_HH=8.5 Hz, 2H); 7.22 (s, 1H); 7.59 (dd, J_HH=17.5, J_PP=20.9Hz, 1H). ¹³C-NMR (150 MHz, CDCl₃): d = 13.6; 20.1 (d, J=47.2Hz); 23.8; 23.9 (d, J=19.3Hz); 101.7 (d, J=64.8Hz); 102.0; 107.0; 108.6; 125.8; 128.6 (d, 18.8Hz); 148.6; 150.8; 152.5 (d, J=3Hz). ³¹P NMR (80 MHz, CDCl₃): d = 27.7. HRES MS (M⁺) calcd. for C₂₁H₃₀O₂P: 349.2282, found: 349.2296.
(E)-4-Cyanostyryl-2’-tributylphosphonium iodide (Table 1, entry 6):

![Chemical Structure](attachment:image.png)

Into a flame-dried flask, containing a magnetic stirring bar, was weighed trimethylsilyl-methyl-tributylphosphonium salt 3 (200 mg, 0.481 mmol) under argon and dry THF (1 mL) was added to make a 0.5 M solution. The flask was stirred for 15 min. at -78 °C whereupon sBuLi (360µL, 0.505 mmol, 1.4M stock, C₆H₁₂) was added slowly. After 40 mins, a 0.5 M solution (in THF) of 4-cyanobenzaldehyde (66.2 mg, 0.505 mmol) was added slowly to the reaction flask maintained at -78 °C. The flask was kept at -78 °C for 2 hrs and then slowly warmed to room temperature where it was stirred for a further 2 hr. The resulting mixture was concentrated to remove solvent. Water was added (5 mL) to the residue, and the resulting mixture was extracted with dichloromethane (3 x 15 mL). The combined organic layers were dried over MgSO₄, filtered, and concentrated. Hexane was added (5 mL) to the flask and stirred for 5 mins. The slurry was vacuum filtered and dried to yield the title compound, 208 mg, (90%) as yellowish viscous solid.

H-NMR (600 MHz, CDCl₃): d = 0.94 (m, 9H); 1.54 (m, 12H); 2.60 (m, 6H); 7.50 (dd, J_HH=17.4Hz, J_PH=17.4Hz, 1H); 7.65 (d, J_HH=8.4 Hz, 2H); 8.0 (m, 3H). ¹³C-NMR (150 MHz, CDCl₃): d = 13.6; 20.5 (d, J=49.3Hz); 23.8; 23.9 (d, J=18.1Hz); 29.0 (m, 110; d, J=81.1Hz); 114.1; 118.3; 132.6; 135.6; 138.0 (d, 19.7Hz); 150.8. ³¹P NMR (80 MHz, CDCl₃): d = 28.4. HRES MS (M)⁺ calcd. for C₂₁H₃₁NP: 330.2344, found: 330.2351.

(E)-2,3-Dimethoxystyryl-2’-tributylphosphonium iodide (Table 1, entry 7):

![Chemical Structure](attachment:image.png)
Into a flame-dried flask, containing a magnetic stirring bar, was weighed trimethylsilyl-methyl-tributylphosphonium salt 3 (200 mg, 0.481 mmol) under argon and dry THF (1 mL) was added to make a 0.5 M solution. The flask was stirred for 15 min. at -78 °C whereupon sBuLi (360 µL, 0.505 mmol, 1.4M stock, C₆H₁₂) was added slowly. After 40 mins, a 0.5 M solution (in THF) of 2,3-dimethoxybenzaldehyde (83.9 mg, 0.505 mmol) was added slowly to the reaction flask maintained at -78 °C. The flask was kept at -78 °C for 2 hrs and then slowly warmed to room temperature where it was stirred for a further 2 hr. The resulting mixture was concentrated to remove solvent. Water was added (5 mL) to the residue, and the resulting mixture was extracted with dichloromethane (3 x 15 mL). The combined organic layers were dried over MgSO₄, filtered, and concentrated. Hexane was added (5 mL) to the flask and stirred for 5 mins. The slurry was vacuum filtered and dried to yield the title compound, 223.7 mg, (90%) as brownish viscous solid. H-NMR (600 MHz, CDCl₃): δ = 0.93 (m, 9H); 1.52 (m, 12H); 2.55 (m, 6H); 3.91 (s, 6H); 7.10 (m, 3H); 7.51 (d, 7.8Hz, 2H); 7.74 (dd, J_HH=17.9, J_PH=19.4Hz, 1H). ¹³C-NMR (150 MHz, CDCl₃): δ = 13.7; 20.0 (d, J=50.6Hz); 23.6; 23.7 (d, J=15.2Hz); 56.2; 61.7; 106.3 (d, J=79.8Hz); 115.1; 119.7; 124.8; 127.5 (d, J=18.4Hz); 146.4; 148.0; 152.8. ³¹P NMR (80 MHz, CDCl₃): δ = 27.8. HRES MS (M⁺) calcd. for C₂₂H₃₈O₃P: 365.2599, found: 365.2609.

(E)-3-Furanylvinyl-2’-tributylphosphonium iodide (Table 1, entry 8):

![Structure of (E)-3-Furanylvinyl-2’-tributylphosphonium iodide](image)

Into a flame-dried flask, containing a magnetic stirring bar, was weighed trimethylsilyl-methyl-tributylphosphonium salt 3 (200 mg, 0.481 mmol) under argon and dry THF (1 mL) was added to make a 0.5 M solution. The flask was stirred for 15 min. at -78 °C whereupon sBuLi (360 µL, 0.505 mmol, 1.4M stock, C₆H₁₂) was added slowly. After 40 mins, a 0.5 M solution (in THF) of 3-furaldehyde (43.7 µL, 0.505 mmol) was added slowly to the reaction flask maintained at -78 °C. The flask was kept at -78 °C for 2 hrs and then slowly warmed to room temperature where it was stirred for a further 2 hr. The resulting mixture
was concentrated to remove solvent. Water was added (5 mL) to the residue, and the resulting mixture was
extracted with dichloromethane (3 x 15 mL). The combined organic layers were dried over MgSO₄, filtered,
and concentrated. Hexane was added (5 mL) to the flask and stirred for 5 mins. The slurry was vacuum
filtered and dried to yield the title compound, 181.2 mg, (85%) as brownish viscous solid.

H-NMR (600 MHz, CDCl₃): δ = 0.92 (m, 9H); 1.52 (m, 12H); 2.55 (m, 6H); 6.20 (dd, J_HH=17.9Hz, J_PH=17.9Hz, 1H); 6.46 (s, 1H); 6.99 (s, 1H); 7.50 (s, 1H); 7.76 (dd, J_HH=17.9, J_PH=17.9Hz, 1H). ¹³C-NMR
(150 MHz, CDCl₃): δ = 13.5; 20.3 (d, J=47.5Hz); 23.6; 23.8 (d, J=18.2Hz); 99.2 (d, J=79.2Hz); 112.8;
118.0; 139.8; 146.0; 150.1 (d, J=7.1Hz). ³¹P NMR (80 MHz, CDCl₃): δ = 27.7. HRES MS (M⁺) calcd. for

(E) and (Z)-N(Boc)-3-vinylindolyl-2'-tributylphosphonium iodide (Table 1, entry 9):

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\text{\includegraphics[width=0.2\textwidth]{image}}
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Into a flame-dried flask, containing a magnetic stirring bar, was weighed trimethylsilyl-methyl-
tributylphosphonium salt 3 (200 mg, 0.481 mmol) under argon and dry THF (1 mL) was added to make a
0.5 M solution. The flask was stirred for 15 min. at -78 °C whereupon sBuLi (360µL, 0.505 mmol, 1.4M
stock, C₆H₁₂) was added slowly. After 40 mins, a 0.5 M solution (in THF) of N-(t-butoxycarbonyl)indole-3-
carboxaldehyde (123.8mg, 0.505 mmol) was added slowly to the reaction flask maintained at -78 °C. The
flask was kept at -78 °C for 2 hrs and then slowly warmed to room temperature where it was stirred for a
further 2 hr. The resulting mixture was concentrated to remove solvent. Water was added (5 mL) to the
residue, and the resulting mixture was extracted with dichloromethane (3 x 15 mL). The combined organic
layers were dried over MgSO₄, filtered, and concentrated. Hexane was added (5 mL) to the flask and stirred
for 5 mins. The slurry was vacuum filtered and dried to yield the title compound, 285.6 mg, (99%) as
brownish viscous solid. (E)-isomer: H-NMR (600 MHz, CDCl₃): δ = 0.91 (m, 9H); 1.52 (m, 12H); 1.63 (s,
9H); 2.58 (m, 6H); 6.71 (dd, J_HH=18.1, J_PH=18.1Hz, 1H); 7.33 (m, 2H); 7.9 (dd, J_HH=18.1, J_PH=20.6Hz, 1H); 8.10 (m, 1H); 8.15 (m, 1H); 8.24 (s, 1H). \(^{13}\)C-NMR (150 MHz, CDCl\(_3\)): d = 13.6; 20.4 (d, =50.2Hz); 23.8; 23.9 (d, J=15.0Hz); 28.2; 82.3; 101.5 (d, J=83.4Hz); 115.6; 117.0 (d, J=20.5Hz); 120.8; 124.2; 125.6; 127.0; 131.5, 136.2, 145.5; 148.9. \(^{31}\)P NMR (80 MHz, CDCl\(_3\)): d = 27.9. HRES MS (M\(^{+}\)) calcd. for C\(_{27}\)H\(_{43}\)NO\(_2\)P: 444.3015, found: 444.3031. (Z)-isomer: H-NMR (600 MHz, CDCl\(_3\)): d = 0.91 (m, 9H); 1.52 (m, 12H); 1.63 (s, 9H); 2.42 (m, 6H); 5.99 (dd, J_HH=17.6, J_PH=19.5Hz, 1H); 7.14 (m, 2H); 7.64 (m, 1H); 7.75 (dd, J_HH=17.6, J_PH=20.6Hz, 1H); 7.84 (m, 2H). \(^{13}\)C-NMR (150 MHz, CDCl\(_3\)): d = 13.6; 20.8 (d, =51.4Hz); 23.8; 23.9 (d, J=15.0Hz); 28.2; 82.3; 92.2 (d, J=88.0Hz); 112.94 (d, J=19.9Hz); 113.3; 119.6; 121.8; 123.2; 124.8; 132.8; 137.5; 147.5; 148.9. \(^{31}\)P NMR (80 MHz, CDCl\(_3\)): d = 26.6. HRES MS (M\(^{+}\)) calcd. for C\(_{27}\)H\(_{43}\)NO\(_2\)P: 444.3015, found: 444.3031.

\((E)\) and \((Z)\)-2-Vinylpyridyl-2'-tributylphosphonium iodide (Table 1, entry 10):

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Into a flame-dried flask, containing a magnetic stirring bar, was weighed trimethylsilyl-methyl-tributylphosphonium salt 3 (200 mg, 0.481 mmol) under argon and dry THF (1 mL) was added to make a 0.5 M solution. The flask was stirred for 15 min. at -78 °C whereupon sBuLi (360µL, 0.505 mmol, 1.4M stock, C\(_6\)H\(_{12}\)) was added slowly. After 40 mins, a 0.5 M solution (in THF) of 2-pyridinecarboxaldehyde (48.1µL, 0.505 mmol) was added slowly to the reaction flask maintained at -78 °C. The flask was kept at -78 °C for 2 hrs and then slowly warmed to room temperature where it was stirred for a further 2 hr. The resulting mixture was concentrated to remove solvent. Water was added (5 mL) to the residue, and the resulting mixture was extracted with dichloromethane (3 x 15 mL). The combined organic layers were dried over MgSO\(_4\), filtered, and concentrated. Hexane was added (5 mL) to the flask and stirred for 5 mins. The slurry was vacuum filtered and dried to yield the title compound, 197 mg, (90%) as yellowish viscous solid.
(E)-isomer: H-NMR (600 MHz, CDCl₃): δ = 0.92 (m, 9H); 1.53 (m, 12H); 2.60 (m, 6H); 7.19 (dd, J₉₁₇.₄, J₉₁₉.₇Hz, 1H); 7.30 (dd, J₉₁₇.₅Hz, J₉₁₄.₉Hz, 1H); 7.74 (dt, J₉₁₇.₇Hz, J₉₁₁.₇Hz, 1H); 8.0 (d, J₉₁₇.₇Hz, 1H); 8.13 (dd, J₉₁₇.₄, J₉₁₉.₃Hz, 1H); 8.57 (d, J₉₁₄.₈Hz, 1H). ¹³C-NMR (150 MHz, CDCl₃): δ = 13.6; 20.4 (d, J₉₁₅₀.₃Hz); 23.8; 23.9 (d, J₉₁₂₀.₀Hz); 108.3 (d, J₉₁₇₉.₈Hz); 125.6; 126.4; 137.0; 149.9; 151.2 (d, J₉₁₇₀.₀Hz); 153.1. ³¹P NMR (80 MHz, CDCl₃): δ = 27.9. HRES MS (M⁺) calcd. for C₁₉H₃₃NP: 306.2340, found: 306.2351. (Z)-isomer: H-NMR (600 MHz, CDCl₃): δ = 0.81 (m, 9H); 1.37 (m, 12H); 2.53 (m, 6H); 6.20 (dd, J₉₁₁₂.₆, J₉₁₉.₁Hz, 1H); 7.43 (dd, J₉₁₇.₅Hz, J₉₁₄.₉Hz, 1H); 7.62 (d, J₉₁₇.₇Hz, 1H); 7.86 (m, 2H); 8.67 (d, J₉₁₄.₉Hz, 1H). ¹³C-NMR (150 MHz, CDCl₃): δ = 13.5; 22.8 (d, J₉₁₄₉.₈Hz); 23.7; 23.9 (d, J₉₁₂₀.₁Hz); 112.2 (d, J₉₁₇₇.₅Hz); 125.9; 127.6; 138.5; 148.8; 150.8; 152.2. ³¹P NMR (80 MHz, CDCl₃): δ = 25.1. HRES MS (M⁺) calcd. for C₁₉H₃₃NP: 306.2340, found: 306.2351.

(E) and (Z)-6,6-Dimethyl-2-vinyl-bicyclo[3.1.1]hept-2-ene-2’-tributylphosphonium iodide (Table 1, entry 11):

Into a flame-dried flask, containing a magnetic stirring bar, was weighed trimethylsilyl-methyl-tributylphosphonium salt 3 (200 mg, 0.481 mmol) under argon and dry THF (1 mL) was added to make a 0.5 M solution. The flask was stirred for 15 min. at -78 °C whereupon sBuLi (360µL, 0.505 mmol, 1.4M stock, C₆H₁₂) was added slowly. After 40 mins, a 0.5 M solution (in THF) of (1R)-(−)-Myrtenal (78.6µL, 0.505 mmol) was added slowly to the reaction flask maintained at -78 °C. The flask was kept at -78 °C for 2 hrs and then slowly warmed to room temperature where it was stirred for a further 2 hr. The resulting mixture was concentrated to remove solvent. Water was added (5 mL) to the residue, and the resulting mixture was extracted with dichloromethane (3 x 15 mL). The combined organic layers were dried over MgSO₄, filtered, and concentrated. Hexane was added (5 mL) to the flask and stirred for 5 mins. The slurry was vacuum filtered and dried to yield the title compound, 187.6 mg, (78%) as a yellow solid film.
(E)-isomer: H-NMR (600 MHz, CDCl₃): d = 0.62 (s, 3H); 0.84 (m, 9H); 1.05 (m, 1H); 1.25 (s, 3H); 1.43 (m, 12H); 2.03 (m, 1H); 2.39 (m, 10H); 5.61 (m, 1H); 6.30 (s, 1H); 7.24 (dd, J_HH=19.5, J_PH=19.5 Hz, 1H). ^{13}C-NMR (150 MHz, CDCl₃): d = 13.2; 20.2 (d, J=50.2 Hz); 20.5; 23.6 (d, J=16.3 Hz); 24.0; 25.6; 30.9; 32.5; 37.7; 40.4; 44.5; 98.7 (d, J=82.3 Hz); 138.4, 145.8 (d, J=7.0 Hz); 153.1. ^{31}P NMR (80 MHz, CDCl₃): d = 26.7. (Z)-isomer: H-NMR (600 MHz, CDCl₃): d = 0.71 (s, 3H); 0.84 (m, 9H); 1.07 (m, 1H); 1.23 (s, 3H); 1.43 (m, 12H); 2.06 (m, 1H); 2.39 (m, 10H); 5.67 (m, 1H); 5.88 (s, 1H); 7.05 (dd, J_HH=13.6 Hz, J_PH=42.7 Hz, 1H). ^{13}C-NMR (150 MHz, CDCl₃): d = 13.2; 22.3 (d, J=49.6 Hz); 20.5; 23.6 (d, J=16.3 Hz); 24.0; 25.8; 30.5; 32.3; 37.8; 39.6; 44.5; 102.4 (d, J=74.8 Hz); 131.9, 144.6; 155.8. ^{31}P NMR (80 MHz, CDCl₃): d = 22.0.

HRES MS (M) calcd. for C₂₃H₄₂P: 349.3013, found: 349.3024.

(E) and (Z)-(4S)-4-(prop-1-en-2-yl)-cyclohex-1-en-1-vinyl-2'-tributylphosphonium iodide (Table 1, entry 12):

Into a flame-dried flask, containing a magnetic stirring bar, was weighed trimethylsilyl-methyl-tributylphosphonium salt 3 (200 mg, 0.481 mmol) under argon and dry THF (1 mL) was added to make a 0.5 M solution. The flask was stirred for 15 min. at -78 °C whereupon sBuLi (360µL, 0.505 mmol, 1.4M stock, C₆H₁₂) was added slowly. After 40 mins, a 0.5 M solution (in THF) of (1S)-(−)-Perilaldehyde (78.6µL, 0.505 mmol) was added slowly to the reaction flask maintained at -78 °C. The flask was kept at -78 °C for 2 hrs and then slowly warmed to room temperature where it was stirred for a further 2 hr. The resulting mixture was concentrated to remove solvent. Water was added (5 mL) to the residue, and the resulting mixture was extracted with dichloromethane (3 x 15 mL). The combined organic layers were dried over MgSO₄, filtered, and concentrated. Hexane was added (5 mL) to the flask and stirred for 5 mins. The slurry was vacuum filtered and dried to yield the title compound, 180.4 mg, (75%) as yellow solid film. (E)-
isomer: H-NMR (600 MHz, CDCl₃): d = 0.93 (m, 9H); 1.52 (m, 12H); 1.71 (s, 3H), 1.92 (m, 1H); 2.12 (m, 4H); 2.37 (m, 1H); 2.52 (m, 6H); 4.69 (s, 1H); 4.74 (s, 1H); 5.92 (m, 1H); 6.47 (m, 1H); 7.24 (m, 1H). ¹³C-NMR (150 MHz, CDCl₃): d = 13.7; 20.4 (d, J=50.2Hz); 23.8; 23.9 (d, J=19.0Hz); 26.8; 29.8; 32.0; 40.5; 100.2 (d, J=82.8Hz); 109.5; 135.6; 142.5; 148.6; 155.8. ³¹P NMR (80 MHz, CDCl₃): d = 26.1. (Z)-isomer: H-NMR (600 MHz, CDCl₃): d = 0.93 (m, 9H); 1.52 (m, 12H); 1.73 (s, 3H), 1.92 (m, 1H); 2.12 (m, 4H); 2.37 (m, 1H); 2.52 (m, 6H); 4.70 (s, 1H); 4.77 (s, 1H); 5.79 (m, 1H); 5.92 (m, 1H); 7.24 (m, 1H). ¹³C-NMR (150 MHz, CDCl₃): d = 13.7; 22.3 (d, J=49.7Hz); 24.0; 24.1 (d, J=19.0Hz); 26.9; 28.2; 30.9; 40.1; 106.6 (d, J=74.6Hz); 109.9; 130.6; 135.6; 148.1; 158.2. ³¹P NMR (80 MHz, CDCl₃): d = 23.7. HRES MS (M) calcd. for C₂₃H₄₂P: 349.3013, found: 349.3024.

(1E) and (1Z)-(3E)-Hexa-1,3-dienyl-1-tributylphosphonium iodide (Table 1, entry 13):

Into a flame-dried flask, containing a magnetic stirring bar, was weighed trimethylsilyl-methyl-tributylphosphonium salt 3 (200 mg, 0.481 mmol) under argon and dry THF (1 mL) was added to make a 0.5 M solution. The flask was stirred for 15 min. at -78 °C whereupon sBuLi (360µL, 0.505 mmol, 1.4M stock, C₆H₁₂) was added slowly. After 40 mins, a 0.5 M solution (in THF) of 2-hexeneal (58.6µL, 0.505 mmol) was added slowly to the reaction flask maintained at -78 °C. The flask was kept at -78 °C for 2 hrs and then slowly warmed to room temperature where it was stirred for a further 2 hr. The resulting mixture was concentrated to remove solvent. Water was added (5 mL) to the residue, and the resulting mixture was extracted with dichloromethane (3 x 15 mL). The combined organic layers were dried over MgSO₄, filtered, and concentrated. Hexane was added (5 mL) to the flask and stirred for 5 mins. The slurry was vacuum filtered and dried to yield the title compound, 166.1 mg, (77%) as yellow solid film. (1E)-isomer: H-NMR (600 MHz, CDCl₃): d = 0.91 (m, 12H); 1.50 (m, 14H); 2.25 (m, 2H); 2.56 (m, 6H); 6.02 (dd, J_HH=17.5, J_PH=17.5Hz, 1H); 6.35 (m, 2H); 7.28 (m, 1H). ¹³C-NMR (150 MHz, CDCl₃): d = 13.5; 20.3 (d, J=50.3Hz); 23.7; 23.9 (d, J=20.2Hz); 35.0; 104.4; (d, J=82.01Hz); 129.3 (d, J=21.0Hz); 148.3; 153.6. ³¹P NMR (80
MHz, CDCl$_3$): $d = 26.4$. (1Z)-isomer: H-NMR (600 MHz, CDCl$_3$): $d = 0.90$ (m, 12H); 1.50 (m, 14H); 2.14 (m, 2H); 2.47 (m, 6H); 5.61 (dd, $J_{HH} = 14.2$, $J_{PH} = 19.1$Hz, 1H); 6.30 (m, 2H); 7.21 (m, 1H). $^{13}$C-NMR (150 MHz, CDCl$_3$): $d = 13.6$; 21.9 (d, $J = 49.4$Hz); 23.7; 23.9 (d, $J = 20.2$Hz); 35.1; 102.1; (d, $J = 74.6$Hz); 125.2 (d, $J = 9.1$Hz); 151.6; 154.2. $^{31}$P NMR (80 MHz, CDCl$_3$): $d = 23.2$. HRES MS (M) calcd. for C$_{19}$H$_{38}$P: 297.2707, found: 297.2711.