Supporting Information for:

[3,3]-Rearrangements of Phosphonium Ylides

Marcelle L. Ferguson, Todd D. Senecal, Todd M. Groendyke and Anna K. Mapp

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General. Unless otherwise noted, starting materials were obtained from commercial suppliers and used without further purification. Benzene, acetonitrile, CH₂Cl₂, THF, and toluene were dried by passage through activated alumina columns and degassed by stirring under a dry nitrogen atmosphere.¹ Purification by flash chromatography was carried out with E. Merck Silica Gel 60 (230-400 mesh) according to the procedure of Still, Kahn, and Mitra.² All reactions were performed under a nitrogen atmosphere. ¹H and ¹³C NMR spectra were recorded in CDCl₃ at 400 MHz and 100 MHz, respectively, unless otherwise specified. IR spectra were measured as thin films on NaCl plates. Melting points are uncorrected. Computations were performed with Spartan 4.0³ with the B3LYP/631G* level of theory.

General procedure for the rearrangement: To 25 mL toluene cooled in an ice/H₂O bath was added the allylic alcohol (5 mmol, 1 equiv) and Et₃N (5 mmol, 1 equiv), followed by 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane (5 mmol, 1 equiv). The mixture was allowed to stir with continued cooling until TLC (1:1 hexanes/EtOAc) showed complete consumption of allylic alcohol, typically 25 min. The precipitated Et₃N•HCl was removed by filtration through Celite, and the Celite pad was washed with an additional 25 mL of toluene. To the filtrate was added 5,10,15,20-tetraphenyl-21H,23H-porphine iron (III) chloride (0.05 mmol, 1 mol%) and diazo compound (6 mmol, 1.2 equiv). The reaction mixture was heated to 40 °C for 1 h, then heated at reflux for 12 h. Upon cooling to rt, the reaction mixture was concentrated and subjected to flash chromatography (3:1 → 1:3 hexanes/EtOAc) for isolation of the phosphonate product.

7a

2-(5,5-Dimethyl-2-oxo-2λ5-[1,3,2]dioxaphosphinan-2-yl)-pent-4-enoic acid ethyl ester (7a). Isolated as an oil in 86% yield (1.19 g) from allyl alcohol. ¹H NMR: δ 1.05 (s, 3H), 1.08 (s, 3H), 1.28 (t, *J* = 7.0 Hz, 3H), 2.63-2.82 (m, 2H), 3.14 (ddd, *J* = 4.0, 11.4, 22.3 Hz, 1H), 3.87 (t, *J* = 11.4 Hz, 1H), 4.00 (t, *J* = 11.4 Hz, 1H), 4.15-4.26 (m, 4H), 5.07 (dd, *J* = 1.1, 10.2 Hz, 1H), 5.13 (dd, *J* = 1.5, 16.9 Hz, 1H), 5.72 – 5.82 (m, 1H); ¹³C NMR: δ 14.09, 21.34, 21.50, 30.59 (d, *J* = 4.3 Hz), 32.66 (d, *J* = 6.9 Hz), 44.18 (d, *J* = 128.1 Hz), 61.63, 75.74 (d, *J* = 6.4 Hz), 75.95 (d, *J* = 6.5 Hz), 117.49, 134.10 (d, *J* = 16.4 Hz), 168.04 (d, *J* = 5.1 Hz); IR: 2977, 1735, 1643, 1475, 1280, 1060 cm⁻¹; Anal. calcd for C₁₂H₂₁O₅P: C, 52.17; H, 7.66. Found: C, 52.22; H, 7.87.

2-(5,5-Dimethyl-2-oxo-2λ5-[1,3,2]dioxaphosphinan-2-yl)-hex-4-enoic acid ethyl ester (8a). Isolated as a solid in 79% yield (1.14 g) from 3-buten-2-ol. mp 81-83 °C; ¹H NMR: δ 1.04 (s, 3H), 1.06 (s, 3H), 1.27 (t, *J* = 7.0 Hz, 3H), 1.62 (dd, *J* = 1.1, 6.2 Hz, 3H), 2.54-2.75 (m, 2H), 3.08 (ddd, *J* = 4.0, 11.0, 21.6 Hz, 1H), 3.85 (t, *J* = 12.1 Hz, 1H), 3.98 (t, *J* = 11.9 Hz, 1H), 4.15-4.24 (m, 4H), 5.34- 5.37 (m, 1H), 5.52-5.58 (m, 1H); ¹³C NMR: δ 14.11, 17.77, 21.35, 21.51, 29.62 (d, *J* = 4.3 Hz), 32.64 (d, *J* = 6.7 Hz), 44.80 (d, *J* = 127.3 Hz), 61.50, 75.65 (d, *J* = 6.6 Hz), 75.87 (d, *J* = 6.7 Hz), 126.53 (d, *J* = 16.6 Hz), 128.42, 168.21 (d, *J* = 4.3 Hz); IR: 2968, 1736, 1476, 1280, 1060 cm⁻¹; Anal. calcd for C₁₃H₂₃O₅P: C, 53.79; H, 7.99. Found: C, 53.69; H, 8.31.

2-(5,5-Dimethyl-2-oxo-2λ5-[1,3,2]dioxaphosphinan-2-yl)-hept-4-enoic acid ethyl ester (9a). Isolated as an oil in 84% yield (1.28 g) from 1-penten-3-ol. ¹H NMR: δ 0.93 (t, *J* = 7.5 Hz, 3H), 1.05 (s, 3H), 1.07 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.94-2.01 (m, 2H), 2.58-2.74 (m, 2H), 3.05-3.14 (ddd, *J* = 4.0, 11.4, 22.0 Hz, 1H), 3.86 (t, *J* = 12.1 Hz, 1H), 4.00 (t, *J* = 12.1 Hz, 1H), 4.15-4.26 (m, 4H), 5.30- 5.37 (m, 1H), 5.55-5.60 (m, 1H); ¹³C NMR: δ 13.54, 14.12, 21.34, 21.51, 25.39, 29.60 (d, *J* = 4.4 Hz), 32.64 (d, *J* = 6.3 Hz), 44.86 (d, *J* = 127.2 Hz), 61.50, 75.67 (d, *J* = 6.4 Hz), 75.88 (d, *J* = 6.7 Hz), 124.31 (d, *J* = 16.3 Hz), 135.51, 168.21 (d, *J* = 5.0 Hz); IR: 2965, 1733, 1653, 1474, 1279, 1060 cm⁻¹; HRMS (ESI) calcd for [C₁₄H₂₅O₅P + Na]⁺: 327.1337. Found: 327.1342.

2-(5,5-Dimethyl-2-oxo-2λ5-[1,3,2]dioxaphosphinan-2-yl)-4-methyl-pent-4-enoic acid ethyl ester (10a). Isolated as a solid in 71% yield (1.03 g) from 2-propen-2-methyl-1-ol. mp 53-55 °C; ¹H NMR: δ 1.05 (s, 3H), 1.08 (s, 3H), 1.27 (t, *J* = 7.3 Hz, 3H), 1.74 (s, 3H), 2.54-2.61 (m, 1H), 2.75-2.84 (m, 1H), 3.31 (ddd, *J* = 3.3, 12.3, 22.8 Hz, 1H), 3.86 (t, *J* = 11.9 Hz, 1H), 4.00 (t, *J* = 11.9 Hz, 1H), 4.17-4.23 (m, 4H), 4.34 (s, 1H), 4.79 (s, 1H); ¹³C NMR: δ 14.05, 21.35, 21.48, 22.20, 32.67 (d, *J* = 6.5 Hz), 33.96 (d, *J* = 4.1 Hz), 42.97 (d, *J* = 127.85 Hz), 61.58, 75.72 (d, *J* = 6.6 Hz), 75.95 (d, *J* = 6.7 Hz), 111.92, 141.69 (d, *J* = 16.7 Hz), 168.21 (d, *J* = 4.7 Hz); IR: 2973, 1734, 1653, 1473, 1283, 1059 cm⁻¹; Anal. calcd for C₁₃H₂₃O₅P: C, 53.79; H, 7.99. Found: C, 53.98; H, 8.16.

4-Chloro-2-(5,5-dimethyl-2-oxo-2λ5-[1,3,2]dioxaphosphinan-2-yl)-pent-4-enoic acid ethyl ester (11a). Isolated as a solid in 73% yield (1.13 g) from 2-chloro-2-propen-1-ol. mp 43-45 °C; ^1H NMR: δ 1.06 (s, 3H), 1.11 (s, 3H), 1.29 (t, $J = 6.2$ Hz, 3H), 2.84-2.92 (m, 1H), 3.10-3.19 (m, 1H), 3.50 (ddd, $J = 3.7, 11.0, 22.3$ Hz, 1H), 3.93 (t, $J = 11.2$ Hz, 1H), 4.04 (t, $J = 11.7$ Hz, 1H), 4.11-4.28 (m, 4H), 5.25 (s, 1H), 5.30 (s, 1H); ^{13}C NMR: δ 14.03, 21.20, 21.55, 32.62 (d, $J = 6.7$ Hz), 36.06 (d, $J = 3.3$ Hz), 42.09 (d, $J = 126.9$ Hz), 61.91, 76.22 (d, $J = 6.4$ Hz), 76.38 (d, $J = 6.5$ Hz), 115.25, 138.29 (d, $J = 18.6$ Hz), 167.26 (d, $J = 5.2$ Hz); IR: 2976, 1734, 1636, 1473, 1285, 1058 cm^{-1} ; Anal. calcd for $\text{C}_{12}\text{H}_{20}\text{ClO}_5\text{P}$: C, 46.39; H, 6.49. Found: C, 46.35; H, 6.69.

2-(5,5-Dimethyl-2-oxo-2λ5-[1,3,2]dioxaphosphinan-2-yl)-5-phenyl-pent-4-enoic acid ethyl ester (12a). Isolated as a solid in 79% yield (1.39 g) from α -vinyl benzyl alcohol. mp 79-80 °C; ^1H NMR: δ 1.07 (s, 3H), 1.08 (s, 3H), 1.26 (t, $J = 7.1$ Hz, 3H), 2.78-3.00 (m, 2H), 3.21 (ddd, $J = 4.0, 11.0, 22.0$ Hz, 1H), 3.89 (t, $J = 11.9$ Hz, 1H), 4.02 (t, $J = 11.9$ Hz, 1H), 4.17-4.25 (m, 4H), 6.13 (dt, $J = 7.1, 15.8$ Hz, 1H), 6.49 (d, $J = 16.1$ Hz, 1H), 7.18-7.23 (m, 1H), 7.28-7.33 (m, 4H); ^{13}C NMR: δ 14.14, 21.37, 21.54, 30.08 (d, $J = 4.1$ Hz), 32.69 (d, $J = 6.7$ Hz), 44.6 (d, $J = 127.3$ Hz), 61.71, 75.83 (d, $J = 6.5$ Hz), 76.03 (d, $J = 6.7$ Hz), 125.56 (d, $J = 16.2$), 126.16, 127.42, 128.47, 132.82, 136.82, 168.08 (d, $J = 4.6$ Hz); IR: 2975, 1733, 1653, 1473, 1277, 1059 cm^{-1} ; Anal. calcd for $\text{C}_{18}\text{H}_{25}\text{O}_5\text{P}$: C, 61.36; H, 7.15. Found: C, 61.21; H, 7.14.

2-(5,5-Dimethyl-2-oxo-2λ5-[1,3,2]dioxaphosphinan-2-yl)-3-methyl-hex-4-enoic acid ethyl ester (13a). Isolated as a solid in 76% yield (1.16 g) of a 1.3:1 diastereomeric mixture from 3-penten-2-ol. mp 83-85 °C; ^1H NMR: δ 1.01 (s, 2H), 1.02 (s, 3H), 1.08-1.12 (m, 7H), 1.21-1.25 (m, 6H), 1.27 (t, $J = 7.1$ Hz, 2H), 1.60 (dd, $J = 1.4, 6.4$ Hz, 3H), 1.64 (dd, $J = 1.4, 6.4$ Hz, 2H), 2.86-3.01 (m, 3H), 3.82-3.91 (m, 2H), 3.98-4.25 (m, 9H), 5.24-5.30 (m, 1H), 5.39-5.63 (m, 2H); ^{13}C NMR: δ 14.09, 14.13, 17.70, 17.83, 19.09, 19.22, 19.83 (d, $J = 2.5$ Hz), 21.23, 21.27, 21.69, 32.60 (d, $J = 6.8$ Hz), 32.64 (d, $J = 6.9$ Hz), 35.81 (d, $J = 3.9$ Hz), 36.73 (d, $J = 3.4$ Hz), 50.96 (d, $J = 128.4$ Hz), 51.45 (d, $J =$

125.8 Hz), 61.30, 61.42, 75.86 (d, $J = 6.6$ Hz), 75.97 (d, $J = 6.7$ Hz), 75.99 (d, $J = 6.3$ Hz), 76.23 (d, $J = 6.8$ Hz), 126.17, 126.27, 132.53 (d, $J = 6.3$ Hz), 132.89 (d, $J = 17.1$ Hz), 168.25, 168.28; IR: 2968, 2944, 1733, 1475, 1278, 1059 cm^{-1} ; HRMS (ESI) calcd for $[\text{C}_{14}\text{H}_{25}\text{O}_5\text{P} + \text{Na}]^+$: 327.1337. Found: 327.1335.

14a

2-(5,5-Dimethyl-2-oxo-2λ5-[1,3,2]dioxaphosphinan-2-yl)-3-ethyl-pent-4-enoic acid ethyl ester (14a). Isolated as a solid in 68% yield (1.03 g) of a 1:1 diastereomeric mixture from *cis*-2-penten-1-ol. mp 62-64 °C; ^1H NMR: δ 0.87 (t, $J = 7.3$ Hz, 3H), 0.88 (t, $J = 7.3$ Hz, 3H), 1.03 (s, 3H), 1.04 (s, 3H), 1.09 (s, 3H), 1.10 (s, 3H), 1.26 (t, $J = 7.1$ Hz, 3H), 1.30 (t, $J = 7.1$ Hz, 3H), 1.29-1.40 (m, 2H), 1.55-1.63 (m, 1H), 1.89-1.99 (m, 1H), 2.72-2.82 (m, 2H), 3.06 (dd, $J = 10.0, 19.2$ Hz, 1H), 3.10 (dd, $J = 9.5, 20.0$ Hz, 1H), 3.84-3.92 (m, 2H), 4.01-4.26 (m, 10H), 5.08-5.23 (m, 4H), 5.51-5.65 (m, 2H); ^{13}C NMR: δ 11.26, 11.35, 14.06, 21.22, 21.65, 21.69, 25.64 (d, $J = 3.7$ Hz), 25.86 (d, $J = 13.7$ Hz), 32.61 (d, $J = 6.5$ Hz), 32.65 (d, $J = 7.1$ Hz), 44.30 (d, $J = 4.0$ Hz), 44.66 (d, $J = 3.3$ Hz), 48.89 (d, $J = 127.3$ Hz), 50.13 (d, $J = 128.7$ Hz), 61.40, 61.52, 75.91 (d, $J = 6.6$ Hz), 76.02 (d, $J = 6.8$ Hz), 76.09 (d, $J = 7.2$ Hz), 76.25 (d, $J = 6.7$ Hz), 117.70, 117.91, 137.35 (d, $J = 5.1$ Hz), 137.93 (d, $J = 16.3$ Hz), 168.07, 168.11; IR: 2965, 1728, 1642, 1474, 1267, 1058 cm^{-1} ; HRMS (ESI) calcd for $[\text{C}_{14}\text{H}_{25}\text{O}_5\text{P} + \text{Na}]^+$: 327.1337. Found: 327.1333.

15a

Cyclohex-2-enyl-(5,5-dimethyl-2-oxo-2λ5-[1,3,2]dioxaphosphinan-2-yl)-acetic acid ethyl ester (15a). Isolated as a solid in 62% yield (0.97 g) of a 1:1 diastereomeric mixture from 2-cyclohexen-1-ol. mp 88-90 °C; ^1H NMR: δ 1.04 (s, 3H), 1.05 (s, 3H), 1.09 (s, 3H), 1.10 (s, 3H), 1.28 (t, $J = 7.1$ Hz, 3H), 1.29 (t, $J = 7.1$ Hz, 3H), 1.37-1.44 (m, 1H), 1.50-1.64 (m, 3H), 1.67-1.77 (m, 2H), 1.80-1.85 (m, 1H), 1.98 (br s, 4H), 2.04-2.10 (m, 1H), 2.92-3.06 (m, 4H), 3.85-3.92 (m, 2H), 4.02-4.28 (m, 10H), 5.51 (d, $J = 10.3$ Hz, 1H), 5.75-5.81 (m, 2H), 5.90 (dd, $J = 1.9, 10.2$ Hz, 1H); ^{13}C NMR: δ 14.08, 20.60, 20.93, 21.24, 21.28, 21.65, 24.77 (d, $J = 1.3$ Hz), 27.30 (d, $J = 14.0$ Hz), 27.77 (d, $J = 4.4$ Hz), 32.65 (d, $J = 7.1$ Hz), 34.39 (d, $J = 3.8$ Hz), 34.43 (d, $J = 3.2$ Hz), 50.12 (d, $J = 126.1$ Hz), 50.30 (d, $J = 128.5$ Hz), 61.49, 61.52, 75.96 (d, $J = 6.4$ Hz), 76.02 (d, $J = 6.4$ Hz), 76.14 (d, $J = 6.6$ Hz), 76.20 (d, $J = 6.5$ Hz), 127.38 (d, $J = 15.2$ Hz), 127.65 (d, $J = 5.2$ Hz), 129.39, 129.71, 168.30 (d, $J = 4.3$ Hz). IR: 2933, 1732, 1652, 1474, 1274, 1058 cm^{-1} ; HRMS (ESI) calcd for $[\text{C}_{15}\text{H}_{25}\text{O}_5\text{P} + \text{Na}]^+$: 339.1337. Found: 339.1330.

7b

5,5-Dimethyl-2-(1-trimethylsilanyl-but-3-enyl)-[1,3,2]dioxaphosphinane 2-oxide (7b). Isolated as a solid in 90% yield (1.24 g) from allyl alcohol. mp 91-92 °C; ^1H NMR: δ 0.19 (s, 9H), 0.91 (s, 3H), 1.17 (s, 3H), 1.30 (ddd, $J = 4.8, 7.7, 23.8$ Hz, 1H), 2.30-2.43 (m, 1H), 2.52-2.63 (m, 1H), 3.69 (dd, $J = 11.0, 17.2$ Hz, 2H), 4.23-4.29 (m, 2H), 4.98 (d, $J = 11.0$ Hz, 1H), 5.06 (d, $J = 16.8$ Hz, 1H), 5.88-5.99 (m, 1H); ^{13}C NMR: δ -1.18 (d, $J = 2.9$ Hz), 21.38, 22.10, 24.51 (d, $J = 121.2$ Hz), 29.16 (d, $J = 5.9$ Hz), 32.47 (d, $J = 5.2$ Hz), 73.81 (d, $J = 6.0$ Hz), 74.01 (d, $J = 6.3$ Hz), 115.37, 138.16 (d, $J = 6.9$ Hz); IR: 2960, 1653, 1474, 1251, 1059, 839 cm^{-1} ; Anal. calcd for $\text{C}_{12}\text{H}_{25}\text{O}_3\text{PSi}$: C, 52.15; H, 9.12. Found: C, 52.11; H, 9.14.

8b

5,5-Dimethyl-2-(1-trimethylsilanyl-pent-3-enyl)-[1,3,2]dioxaphosphinane 2-oxide (8b). Isolated as a solid in 88% yield (1.28 g) from 3-buten-2-ol. mp 66-68 °C; ^1H NMR: δ 0.18 (s, 9H), 0.91 (s, 3H), 1.16 (s, 3H), 1.22-1.29 (m, 1H), 1.64 (d, $J = 5.9$ Hz, 3H), 2.24-2.36 (m, 1H), 2.45-2.58 (m, 1H), 3.66 (dd, $J = 11.4, 16.8$ Hz, 2H), 4.21-4.28 (m, 2H), 5.41-5.57 (m, 2H); ^{13}C NMR: δ -1.15 (d, $J = 2.9$ Hz), 17.68, 21.39, 22.05, 24.81 (d, $J = 119.9$ Hz), 27.95 (d, $J = 6.0$ Hz), 32.45 (d, $J = 5.3$ Hz), 73.76 (d, $J = 6.0$ Hz), 74.00 (d, $J = 6.3$ Hz), 125.93, 130.65 (d, $J = 7.2$ Hz); IR: 2959, 1653, 1476, 1250, 1060, 844 cm^{-1} ; Anal. calcd for $\text{C}_{13}\text{H}_{27}\text{O}_3\text{PSi}$: C, 53.76; H, 9.37. Found: C, 53.99; H, 9.57.

9b

5,5-Dimethyl-2-(1-trimethylsilanyl-hex-3-enyl)-[1,3,2]dioxaphosphinane 2-oxide (9a). Isolated as a solid in 83% yield (1.26 g) from 1-penten-3-ol. mp 60-61 °C; ^1H NMR: δ 0.18 (s, 9H), 0.91 (s, 3H), 0.96 (t, $J = 7.5$ Hz, 3H), 1.16 (s, 3H), 1.22-1.31 (m, 1H), 1.96-2.02 (m, 2H), 2.25-2.38 (m, 1H), 2.46-2.58 (m, 1H), 3.65-3.72 (m, 2H), 4.21-4.28 (m, 2H), 5.48-5.51 (m, 2H); ^{13}C NMR: δ -1.07 (d, $J = 2.9$ Hz), 13.56, 21.39, 22.07, 24.89 (d, $J = 119.8$ Hz), 25.31, 27.94 (d, $J = 5.9$ Hz), 32.44 (d, $J = 5.2$ Hz), 73.77 (d, $J = 6.1$ Hz), 74.00 (d, $J = 6.3$ Hz), 128.45 (d, $J = 7.2$ Hz), 133.04; IR: 2962, 1653, 1474, 1248, 1063, 844 cm^{-1} ; Anal. calcd for $\text{C}_{14}\text{H}_{29}\text{O}_3\text{PSi}$: C, 55.23; H, 9.60. Found: C, 55.35; H, 9.94.

5,5-Dimethyl-2-(3-methyl-1-trimethylsilylbut-3-enyl)-[1,3,2]dioxaphosphinane 2-oxide (10b). Isolated as a solid in 82% yield (1.19 g) from 2-methyl-2-propen-1-ol. mp 106-108 °C; ^1H NMR: δ 0.19 (s, 9H), 0.90 (s, 3H), 1.17 (s, 3H), 1.51 (dt, $J = 6.4$, 24.2 Hz, 1H), 1.74 (s, 3H), 2.22-2.34 (m, 1H), 2.52-2.63 (m, 1H), 3.63-3.72 (m, 2H), 4.21-4.28 (m, 2H), 4.80 (s, 2H); ^{13}C NMR: δ -1.25 (d, $J = 2.8$ Hz), 21.96, 21.97 (d, $J = 121.0$ Hz), 22.14, 32.44 (d, $J = 5.8$ Hz), 32.45 (d, $J = 4.8$ Hz), 73.82 (d, $J = 6.1$ Hz), 74.00 (d, $J = 6.2$ Hz), 111.51, 143.95 (d, $J = 7.8$ Hz); IR: 2965, 1653, 1473, 1254, 1059, 849 cm^{-1} ; Anal. calcd for $\text{C}_{13}\text{H}_{27}\text{O}_3\text{PSi}$: C, 53.76; H, 9.37. Found: C, 53.91; H, 9.37.

2-(3-Chloro-1-trimethylsilylbut-3-enyl)-5,5-dimethyl-[1,3,2]dioxaphosphinane 2-oxide (11b). Isolated as a solid in 77% yield (1.19 g) from 2-chloro-2-propen-1-ol. mp 92-94 °C; ^1H NMR: δ 0.22 (s, 9H), 1.00 (s, 3H), 1.10 (s, 3H), 1.81 (ddd, $J = 5.1$, 7.7, 22.3 Hz, 1H), 2.57 (ddd, $J = 4.4$, 15.0, 25.3 Hz, 1H), 2.86-2.95 (m, 1H), 3.76 (dd, $J = 13.7$, 11.0 Hz, 2H), 4.12-4.21 (m, 2H), 5.22 (d, $J = 1.5$ Hz, 1H), 5.31 (d, $J = 1.1$ Hz, 1H); ^{13}C NMR: δ -1.36 (d, $J = 2.2$ Hz), 21.45 (d, $J = 120.8$ Hz), 21.50, 21.81, 32.40 (d, $J = 5.6$ Hz), 32.38 (d, $J = 5.2$ Hz), 74.51 (d, $J = 6.1$ Hz), 74.78 (d, $J = 6.4$ Hz), 113.90, 141.41 (d, $J = 8.4$ Hz); IR: 2971, 1636, 1487, 1252, 1058, 847 cm^{-1} ; Anal. calcd for $\text{C}_{12}\text{H}_{24}\text{ClO}_3\text{PSi}$: C, 46.37; H, 7.78. Found: C, 46.14; H, 8.05.

5,5-Dimethyl-2-(4-phenyl-1-trimethylsilylbut-3-enyl)-[1,3,2]dioxaphosphinane 2-oxide (12b). Isolated as a solid in 78% yield (1.38 g) from α -vinyl benzyl alcohol. mp 80-82 °C; ^1H NMR: δ 0.22 (s, 9H), 0.92 (s, 3H), 1.17 (s, 3H), 1.39 (ddd, $J = 4.8$, 7.7, 23.8 Hz, 1H), 2.48-2.51 (m, 1H), 2.68-2.81 (m, 1H), 3.71 (dd, $J = 11.0$, 16.8 Hz, 2H), 4.24-4.31 (m, 2H), 6.32 (dt, $J = 6.8$, 16.1 Hz, 1H), 6.41 (d, $J = 16.1$ Hz, 1H), 7.19-7.22 (m, 1H), 7.28-7.35 (m, 4H); ^{13}C NMR: δ -1.10 (d, $J = 2.7$ Hz), 21.40, 22.11, 24.90 ($J = 120.5$ Hz), 28.53 (d, $J = 5.9$ Hz), 32.51 (d, $J = 5.3$ Hz), 73.88 (d, $J = 6.0$ Hz), 74.12 (d, $J = 6.2$ Hz), 126.02, 127.08, 128.47, 129.91 (d, $J = 6.8$ Hz), 130.63, 137.30; IR: 2962, 1473, 1249, 1062, 847 cm^{-1} ; Anal. calcd for $\text{C}_{18}\text{H}_{29}\text{O}_3\text{PSi}$: C, 61.33; H, 8.29. Found: C, 61.30; H, 8.54.

13b

5,5-Dimethyl-2-(2-methyl-1-trimethylsilanyl-pent-3-enyl)-[1,3,2]dioxaphosphinane 2-oxide (13b). Isolated as a solid in 72% yield (1.09 g) of a 2:1 diastereomeric mixture from 3-penten-2-ol. mp 90-92 °C; ^1H NMR: δ 0.16 (s, 6H), 0.17 (s, 3H), 0.86 (s, 2H), 0.90 (s, 1H), 1.10 (s, 1H), 1.14 (s, 2H), 1.23-1.27 (m, 3H), 1.35-1.47 (m, 1H), 1.61 (d, J = 6.4 Hz, 3H), 2.65-2.84 (m, 1H), 3.59-3.71 (m, 2H), 4.15-4.26 (m, 2H), 5.33-5.41 (m, 1H), 5.64-5.72 (m, 1H); ^{13}C NMR: δ 0.04 (d, J = 2.7 Hz), 0.05 (d, J = 2.6 Hz), 17.67, 17.71, 20.07 (d, J = 8.4 Hz), 21.38, 21.51, 21.71 (d, J = 1.7 Hz), 22.18, 22.26, 31.28, 31.30, 32.42, 32.43, 34.22 (d, J = 5.2 Hz), 34.89 (d, J = 5.1 Hz), 73.71 (d, J = 6.3 Hz), 73.85 (d, J = 6.0 Hz), 73.91 (d, J = 6.0 Hz), 74.12 (d, J = 6.1 Hz), 123.08, 124.22, 135.85 (d, J = 10.6 Hz), 136.89; IR: 2961, 2882, 1482, 1250, 1059, 841 cm^{-1} ; HRMS (ESI) calcd for $[\text{C}_{14}\text{H}_{29}\text{O}_3\text{PSi} + \text{Na}]^+$: 327.1521. Found 327.1514.

14b

2-(2-Ethyl-1-trimethylsilanyl-but-3-enyl)-5,5-dimethyl-[1,3,2]dioxaphosphinane 2-oxide (14b). Isolated as a solid in 83% yield (1.26 g) of a 1:1 diastereomeric mixture from *cis*-2-penten-1-ol. mp 98-100 °C; ^1H NMR: δ 0.20 (s, 9H), 0.23 (s, 9H), 0.83-0.88 (m, 6H), 0.89 (s, 3H), 0.94 (s, 3H), 1.14 (s, 3H), 1.19 (s, 3H), 1.44-1.56 (m, 2H), 1.59-1.75 (m, 4H), 2.29-2.46 (m, 2H), 3.63-3.75 (m, 4H), 4.20-4.25 (m, 2H), 4.27-4.31 (m, 2H), 4.96-5.07 (m, 4H), 5.92-6.01 (m, 1H), 6.07-6.16 (m, 1H); ^{13}C NMR: δ -0.05 (d, J = 2.4 Hz), 0.11 (d, J = 2.4 Hz), 12.52, 12.82, 21.35, 21.48, 22.20, 22.33, 25.85, 25.93, 28.69 (d, J = 2.0 Hz), 30.71 (d, J = 116.3 Hz), 32.51 (d, J = 5.1 Hz), 32.53 (d, J = 5.2 Hz), 43.82 (d, J = 5.0 Hz), 44.53 (d, J = 4.8 Hz), 73.71 (d, J = 6.3 Hz), 73.83 (d, J = 6.0 Hz), 73.99 (d, J = 6.2 Hz), 74.13 (d, J = 6.2 Hz), 114.59, 115.89, 140.75 (d, J = 7.0 Hz), 142.45 (d, J = 1.8 Hz); IR: 2963, 2883, 1636, 1477, 1250, 1060, 840 cm^{-1} ; HRMS (ESI) calcd for $[\text{C}_{14}\text{H}_{29}\text{O}_3\text{PSi} + \text{Na}]^+$: 327.1521. Found 327.1513.

15b

2-(Cyclohex-2-enyl-trimethylsilanyl-methyl)-5,5-dimethyl-[1,3,2]dioxaphosphinane 2-oxide (15b). Isolated as a solid in 73% yield (1.16 g) of a 2:1 diastereomeric mixture from 2-cyclohexen-1-ol. mp 136-138 °C; ^1H NMR (major diastereomer): δ 0.23 (s, 9H), 0.90 (s, 3H), 1.17 (s, 3H), 1.42 (dd, J = 1.9, 26.7 Hz, 1H), 1.51-1.58 (m, 1H), 1.61-1.68

(m, 1H), 1.80-1.84 (m, 1H), 1.96- 2.03 (m, 3H), 2.77- 2.88 (m, 1H), 3.63-3.73 (m, 2H), 4.25-4.30 (m, 2H), 5.57 (d, $J = 10.2$ Hz, 1H), 5.65-5.70 (m, 1H); ^{13}C NMR (major diastereomer): δ 0.39 (d, $J = 2.9$ Hz), 21.38, 22.22, 22.97, 24.70, 29.81, 31.17 (d, $J = 115.7$ Hz), 32.53 (d, $J = 5.2$ Hz), 34.30 (d, $J = 4.9$ Hz), 73.81 (d, $J = 5.8$ Hz), 73.86 (d, $J = 6.0$ Hz), 127.44, 131.74 (d, $J = 14.4$ Hz); IR: 2931, 1683, 1473, 1251, 1057, 847 cm^{-1} ; HRMS (ESI) calcd for $[\text{C}_{15}\text{H}_{29}\text{O}_3\text{PSi} + \text{Na}]^+$: 339.1521. Found: 339.1514.

Table S1. Horner-Wadsworth-Emmons Olefinations

Entry	Substrate	Product	Yield	E:Z
1	 7a	 S1	89%	98:2
2	 8a	 S2	92%	98:2
3	 9a	 16	92%	98:2
4	 10a	 S3	87%	94:6
5	 11a	 S4	80%	93:7

General procedure for Horner-Wadsworth-Emmons olefinations: To 7 mL THF was added the phosphonate (0.5 mmol, 1 equiv), and 18-crown-6 (661 mg, 2.5 mmol, 5 equiv). The reaction was cooled in dry ice/acetone bath, after which a 0.5 M solution of $\text{KN}(\text{TMS})_2$ in toluene (1 mL, 0.5 mmol, 1 equiv) was added dropwise. The mixture was allowed to stir for 1 h at -78°C after which a solution of benzaldehyde (56 μL , 0.55 mmol, 1.1 equiv) in 3 mL THF was added dropwise. The reaction mixture was warmed to 0°C over 3 h until TLC (19:1 hexanes:EtOAc) indicated consumption of the phosphonate. The reaction mixture was poured onto 50 mL of sat. NH_4Cl . The resulting mixture was extracted with Et_2O (2 x 25 mL). The combined organic layers were dried over MgSO_4 , filtered, and concentrated. The resulting oil was subjected to flash chromatography (19:1 hexanes/EtOAc) for isolation of the olefin product.

2-Benzylidene-pent-4-enoic acid ethyl ester (S1). Isolated as an oil in 89% yield (0.096 g) from **7a** as a 98:2 mixture of E/Z isomers. Spectral data for **S1** were consistent with the literature reported values.⁴

2-Benzylidene-hex-4-enoic acid ethyl ester (S2). Isolated as an oil in 92% yield (0.106 g) from **8a** as a 98:2 mixture of E/Z isomers. ^1H NMR: δ 1.32 (t, $J = 7.1$ Hz, 3 H), 1.67 (dd, $J = 1.1, 5.9$ Hz, 3 H), 3.19 (d, $J = 5.13$ Hz, 2H), 4.24 (q, $J = 7.1$ Hz, 2 H), 5.40-5.61 (m, 2 H), 7.25-7.21 (m, 5H), 7.91 (s, 1H); ^{13}C NMR: δ 14.2, 17.9, 30.4, 61.0, 126.2, 128.0, 128.3, 128.4, 129.2, 131.4, 135.6, 139.3, 168.1; IR (film): 3023, 2978, 2934, 2916, 2854, 1709, 1631, 1257, 1218, 1196 cm^{-1} ; Anal. calcd for $\text{C}_{15}\text{H}_{18}\text{O}_2$: C, 78.23; H, 7.88. Found: C, 78.09; H, 7.81.

2-Benzylidene-hept-4-enoic acid ethyl ester (16). Isolated as an oil in 92% yield (0.112 g) from **9a** as a 98:2 mixture of E/Z isomers. ^1H NMR: δ 0.96 (t, $J = 7.5$ Hz, 3H), 1.32 (t, $J = 7.1$ Hz, 3H), 2.00-2.05 (m, 2H), 3.20 (s, 2H), 4.25 (q, $J = 7.1$ Hz, 2H), 5.52-5.54 (m, 2H), 7.28-7.41 (m, 5H), 7.71 (s, 1H); ^{13}C NMR: δ 13.9, 14.5, 25.8, 30.7, 60.9, 126.0, 128.5, 128.6, 129.5, 131.7, 133.6, 135.8, 139.6, 168.4; IR (film): 3058, 3025, 2962, 2931, 2872, 2849, 1708, 1631, 1260, 1217, 1195 cm^{-1} ; Anal. calcd for $\text{C}_{16}\text{H}_{20}\text{O}_2$: C, 78.65; H, 8.25. Found: C, 78.92; H, 8.30.

2-Benzylidene-4-methyl-pent-4-enoic acid ethyl ester (S3). Isolated as an oil in 87% yield (0.100 g) from **10a** as a 94:6 mixture of E/Z isomers. ^1H NMR: δ 1.31 (t, $J = 7.1$ Hz, 3 H), 1.82 (d, $J = 0.6$ Hz, 3H), 3.17 (s, 2H), 4.24 (q, $J = 7.1$ Hz, 2H), 4.67 (dd, $J = 0.8, 1.6$ Hz, 1H), 4.82 (td, $J = 1.5, 2.9$ Hz, 1H), 7.25-7.39 (m, 5H), 7.80 (s, 1H); ^{13}C NMR: δ 14.4, 23.7, 35.5, 61.0, 110.4, 128.6, 128.7, 129.3, 130.9, 135.7, 140.4, 143.7, 168.4; IR (film): 3077, 3024, 2974, 2915, 2848, 1706, 1652, 1634, 1217, 1197, 1091 cm^{-1} ; Anal. calcd for $\text{C}_{15}\text{H}_{18}\text{O}_2$: C, 78.23; H, 7.88. Found: C, 78.07; H, 7.88.

2-Benzylidene-4-chloro-pent-4-enoic acid ethyl ester (S4). Isolated as an oil in 80% yield (0.100 g) from **11a** as a 93:7 mixture of E/Z isomers. ^1H NMR: δ 1.33 (t, J = 7.1 Hz, 3H), 3.53 (s, 2H), 4.27 (q, J = 7.1 Hz, 2H), 5.16 (q, J = 1.7 Hz, 1H), 5.27 (q, J = 1.4 Hz, 1H), 7.34-7.39 (m, 5H), 7.87 (s, 1H); ^{13}C NMR: δ 14.4, 37.6, 61.3, 112.6, 128.3, 128.8, 129.3, 129.4, 135.0, 140.1, 142.3, 167.6; IR (film): 2979, 2916, 2848, 1708, 1633, 1265, 1219, 1199, 1090 cm^{-1} , Anal. calcd for $\text{C}_{14}\text{H}_{15}\text{ClO}_2$: C, 67.07; H, 6.03. Found: C, 67.29; H, 5.90.

Procedure for amination of phosphonate **8a:** In a glove box, to 6 mL CH_2Cl_2 was added (*R*)-(+)-2,2'-isopropylidene-bis(4-phenyl-2-oxazoline) (0.084 mmol, 28.1 mg, 0.2 equiv) and zinc triflate (0.084 mmol, 30.6 mg, 0.2 equiv). The reaction mixture was stirred at rt for 1 h after which phosphonate **8a** (0.42 mmol, 121.7 mg, 1 equiv) and diisopropyl azodicarboxylate (0.63 mmol, 1.5 equiv) were added. The reaction mixture was heated at reflux for 4 d. The reaction mixture was concentrated and the residue was subjected to flash chromatography (1:2 $\rightarrow$ 1:4 hexanes/ Et_2O) to afford 125 mg α -aminophosphonic ester **17** (52% yield) contaminated with bisoxazoline ligand as a clear viscous oil. A second chromatographic purification could be used to isolate analytically pure product. ^1H NMR: δ 0.86 (s, 3H), 1.17-1.31 (m, 18H), 1.60 (d, J = 6.0 Hz, 3H), 2.60-3.00 (m, 2H), 3.71-3.91 (m, 2H), 4.10-4.25 (m, 2H), 4.52-4.61 (m, 1H), 4.70-5.01 (m, 3H), 5.34-5.57 (m, 2H), 6.67 (s, N-H), 6.90 (s, N-H); ^{13}C NMR: δ 14.2, 18.1, 21.7, 21.9 (d, J = 5.9 Hz), 22.0 (d, J = 9.7 Hz), 22.2 (d, J = 6.3 Hz), 23.0 (d, J = 10.3 Hz), 32.6 (d, J = 9.5 Hz), 37.1, 61.6 (d, J = 19.2 Hz), 69.4 (d, J = 8.6 Hz), 71.0 (d, J = 3.9 Hz), 78.1 (d, J = 17.4 Hz), 78.2 (d, J = 17.1 Hz), 123.1, 130.5, 155.4, 155.5, 168.8; IR (film): 3360, 2980, 2938, 1732, 1180, 1145, 1109, 1069 cm^{-1} ; HRMS (ESI) calcd for $[\text{C}_{21}\text{H}_{37}\text{N}_2\text{O}_9\text{P} + \text{Na}]^+$: 515.2134. Found: 515.2131.

References

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Theoretical computations

Theoretical computations (B3LYP/631G*) were carried out on the following reaction:

Starting material

Energy: -1038.1252320

P	-0.0072398	0.0097015	-0.0185082
C	0.0585566	0.0998474	0.0613203
O	-0.0027750	0.0937386	-0.1600278
O	-0.0020142	-0.1469196	-0.1103370
O	-0.0018465	0.0897825	0.1678446
C	-0.0300380	-0.0456487	-0.0117352
H	0.0097016	0.1128493	0.1368145
C	-0.1530114	-0.0979423	-0.0313253
H	0.0058732	-0.1027002	-0.1485489
C	0.1739527	0.1040308	0.0249950
H	-0.0106966	0.1044045	0.1476738
C	-0.0031780	0.0009573	0.0059807
H	0.0322933	0.1645799	-0.0523562
H	0.1358115	-0.0486680	0.0986075
H	-0.0048916	-0.1043944	-0.1436958
C	0.0066022	0.0236189	-0.0020884
H	-0.1492731	-0.0035389	0.0943973
H	-0.0147895	-0.1149729	-0.1344841
H	0.1321782	-0.0528331	0.1038966
C	-0.0342574	0.0091421	0.0344898
H	-0.0917553	0.0190847	-0.1559934
H	0.0781135	-0.1564915	-0.0039551
C	-0.0327874	0.0077781	-0.0415152
H	0.0696390	-0.1570539	0.0182665
H	-0.0982456	0.0331243	0.1502073
C	-0.0100294	-0.0069354	0.0002793
H	0.1625370	-0.0085973	-0.0886072
C	0.0079611	-0.0038503	-0.0141245
H	-0.1502913	-0.0130577	0.0880963
H	0.1158438	0.0630161	0.1102606
H	-0.0232251	0.1152103	-0.1222608
C	0.0359058	0.0355244	-0.0003696
H	-0.1041529	-0.0011289	-0.1424298
H	0.0831326	-0.1532976	0.0043793
H	-0.1049276	0.0068559	0.1409463
C	0.0195517	-0.0441232	0.0028043

H	-0.1003021	0.0082491	-0.1436253
H	-0.1055295	0.0175988	0.1379595
H	0.1076035	0.1430591	-0.0032316

Transition state with equatorial ylide substituent

Energy: -1038.1107450

P	0.0214026	0.0521115	0.0083777
C	-0.0717889	0.0649721	-0.0687396
O	0.0226210	0.1062183	0.1536928
O	-0.0815237	-0.2654957	0.0655825
O	-0.0737493	0.0924948	-0.1444703
C	0.0789059	-0.0406655	0.0721165
H	0.1128759	0.0167364	-0.1413435
C	-0.0727746	-0.0932301	0.0109667
H	-0.1336592	-0.0341087	0.1157010
C	-0.0091250	0.1451909	-0.0187100
H	0.1323297	0.0321804	-0.1223317
C	0.0004286	-0.0011403	-0.0057164
H	0.0591443	0.1656326	0.0068571
H	-0.0925205	-0.0133831	-0.1448123
H	-0.1093855	-0.0275627	0.1379827
C	0.0013205	-0.0044079	-0.0103908
H	0.1634333	-0.0702983	0.0327191
H	-0.0940074	0.0015702	0.1546046
H	-0.0819309	-0.1028330	-0.1127123
C	0.0166605	0.0145344	-0.0432883
H	0.1265613	0.0540523	0.1188347
H	-0.0274768	-0.1711089	0.0267341
C	0.0400276	0.0179036	0.0257319
H	-0.0300188	-0.1702778	0.0064637
H	0.0359756	0.0416077	-0.1730048
C	0.0125862	-0.0040671	-0.0043308

H	-0.1292588	-0.0370964	0.1305362
C	-0.0029205	-0.0090949	0.0172208
H	0.1178728	0.0184253	-0.1268280
H	-0.1402885	0.0772472	-0.0526801
H	0.0562315	0.0875953	0.1347220
C	-0.0428695	0.0250290	0.0122139
H	0.1379700	0.0342259	0.1040858
H	-0.0368286	-0.1697723	0.0170045
H	0.0525637	0.0260317	-0.1654897
C	-0.0065622	-0.0466811	0.0028146
H	0.1350301	0.0427213	0.1025847
H	0.0467758	0.0351979	-0.1644972
H	-0.1340283	0.1095448	0.0417982

Transition state with axial ylide substituent

Energy: -1038.1087488

P	0.0221158	-0.0581166	-0.0068184
C	-0.1151784	-0.0115157	0.0419899
O	0.0143905	-0.1196766	-0.1460468
O	-0.0755889	0.2602666	-0.0804022
O	-0.0636536	-0.0852118	0.1563986
C	0.0723596	0.0292099	-0.0829659
H	0.1229665	-0.0001848	0.1332822
C	-0.0730305	0.0914902	-0.0121253
H	-0.1445103	0.0235127	-0.1050495
C	-0.0071897	-0.1421642	0.0340031
H	0.1436674	-0.0205768	0.1095260
C	0.0010508	0.0031559	0.0055079
H	0.0614196	-0.1680425	0.0130087
H	-0.0815042	0.0355956	0.1473797
H	-0.1203820	0.0072836	-0.1306062

C	0.0011602	0.0055868	0.0097799
H	0.1610239	0.0675436	-0.0468479
H	-0.0996642	-0.0194203	-0.1495949
H	-0.0787818	0.1140058	0.1036827
C	0.0202678	-0.0120343	0.0427451
H	0.1204642	-0.0611097	-0.1220455
H	-0.0304144	0.1691063	-0.0358667
C	0.0395151	-0.0203122	-0.0267984
H	-0.0302491	0.1696704	-0.0159755
H	0.0457402	-0.0305334	0.1735366
C	0.0116507	0.0045534	0.0026608
H	0.0487687	-0.1581129	0.0781823
C	0.0123869	-0.0134501	0.0011306
H	0.0535610	-0.0867011	-0.1366729
H	-0.1398356	-0.0782223	0.0564105
H	-0.0464945	0.1576090	-0.0561394
C	-0.0066085	0.0463942	-0.0052640
H	0.1290156	-0.0500195	-0.1072728
H	0.0561016	-0.0242865	0.1633757
H	-0.1369503	-0.1121046	-0.0263703
C	-0.0434447	-0.0258917	-0.0077959
H	0.1324438	-0.0415888	-0.1086448
H	-0.0381460	0.1681045	-0.0270626
H	0.0615569	-0.0138119	0.1637656

13b

14b

15b

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