Supporting Information for:

Vinyl Diazophosphonates as Precursors to Quaternary Substituted Indolines and Cyclopentenes

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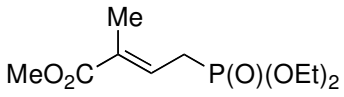
Included are experimental data and preparation information for all new compounds

General Information

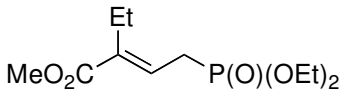
NMR spectra were recorded on either a Varian Inova-500, a Varian Unity-300, a Varian Inova-400 or a Varian VXR-500 spectrometer. Chemical shifts were reported in δ, parts per million (ppm), relative to chloroform (7.25), benzene (7.16), or dichloromethane (5.29) as internal standards. Coupling constants, *J*, were reported in Hertz (Hz) and refer to apparent peak multiplicities and not true coupling constants. Mass spectra were recorded at the Mass Spectrometry Facility at the Department of Chemistry of the University of Utah at Salt Lake City on a Finnigan MAT 95 mass spectrometer. IR spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer. Solvents were purified according to the guidelines in Purification of Common Laboratory Chemicals (Perrin, Armarego, and Perrin: Oxford, 1966). Spectroscopic grade CH_3CN was stored over activated 4Å molecular sieves and used without additional purification. All other reagents were used without purification. Unless otherwise stated, all reactions were run under an atmosphere of dried nitrogen in flame-dried glassware. Concentration refers to removal of solvent under reduced pressure (house vacuum at ca. 20 mmHg).

General procedure for the alkylation of phosphonocrotonate 4. To a solution of phosphonocrotonate **4** (ca. 2.0 mmol) in 10 mL of THF at 0 °C was added LiHMDS (ca. 2.0 mmol) dropwise. After stirring at 0 °C for 0.5 h, the solution was warmed to rt and a solution of alkyl iodide or triflate (ca. 1.0 mmol) in 2 mL of THF was added dropwise. The resulting reaction mixture was stirred for 2 h and the reaction was quenched with sat. NH_4Cl (aq., 10 mL). The organic layer was separated and the aqueous layer was extracted with ethyl acetate (3×10 mL). The organic layers were combined, dried (Na_2SO_4), and concentrated. Flash chromatography provided the corresponding alkylated phosphonates **5-11**.



5

(*E*)-methyl 4-(diethoxyphosphoryl)-2-methylbut-2-enoate (5). Prepared according to the general procedure using phosphonocrotonate **4** (0.472 g, 2.00 mmol), THF (10 mL), LiHMDS (2.0 mL of a 1.0 M solution in THF, 2.0 mmol) and MeI (62.3 μL, 1.00 mmol) in THF (2 mL) to give 0.188 g of **5** (75%) as colorless oil after flash chromatography (1:2 hexanes:ethyl acetate).
5: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.78-6.72 (m, 1H), 4.14 – 4.07 (m, 4H), 3.74 (s, 3H), 2.73 (ddd, *J* = 22.6, 8.3, 0.8 Hz, 2H), 1.90 – 1.87 (m, 3H), 1.38 – 1.25 (m, 6); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.0 (d, *J* = 3.5 Hz), 131.7 (d, *J* = 13.5 Hz), 130.7 (d, *J* = 11.0 Hz), 62.4 (d, *J* = 6.5 Hz), 52.2, 27.8 (d, *J* = 138.2 Hz), 16.7 (d, *J* = 6.0 Hz), 12.8 (d, *J* = 2.6 Hz); IR (neat) 2984, 1716, 1651, 1437, 1252, 1165, 1049, 1024, 965 cm^{-1}; LRMS *m/z* calcd for $C_{10}H_{19}O_5P$ 273.1 (M+Na$^+$), found 273.0



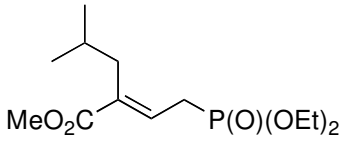
6

(*E*)-methyl 4-(diethoxyphosphoryl)-2-ethylbut-2-enoate (6). Prepared according to the general procedure using phosphonocrotonate **4** (0.472 g, 2.00 mmol), THF (10 mL), LiHMDS (2.0 mL of a 1.0 M solution in THF, 2.0 mmol) and EtI (80.7 μL, 1.00 mmol) in THF (2 mL) to give 0.087 g of **6** (33%) as colorless oil after flash chromatography (1:2 hexanes:ethyl acetate).
6: ^{1}H NMR (300 MHz, $CDCl_3$) δ ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.70 (dt, *J* = 7.6, 7.6 Hz, 1H), 4.16 – 4.05 (m, 4H), 3.73 (s, 3H), 2.73 (dd, *J* = 23.4, 8.2 Hz, 2H), 2.33 (dq, *J* = 7.6, 2.2 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.01 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ δ 167.7, 137.7 (d, *J* = 14.1 Hz), 130.2 (d, *J* = 10.6 Hz), 62.4 (d, *J* = 6.5 Hz), 52.1, 27.5 (d, *J* = 139.5 Hz), 20.4 (d, *J* = 2.0 Hz), 16.7 (d, *J* = 6.1 Hz), 13.7 (d, *J* = 3.5 Hz); IR (neat) 2978, 1714, 1646, 1437, 1392, 1294, 1245, 1192, 1165, 1117, 1094, 1050, 1022, 963 cm^{-1}; LRMS *m/z* calcd for $C_{11}H_{21}O_5P$ 287.1 (M+Na$^+$), found 287.1

7

(*E*)-methyl 2-(2-(diethoxyphosphoryl)ethylidene)pentanoate (7). Prepared according to the general procedure using phosphonocrotonate **4** (0.472 g, 2.00 mmol), THF (10 mL), LiHMDS (2.0 mL of a 1.0 M solution in THF, 2.0 mmol) and PrI (97.5 μL, 1.00 mmol) in THF (2 mL) to give 0.0974 g of **7** (35%) as a colorless oil after flash chromatography (1:2 hexanes:ethyl acetate).

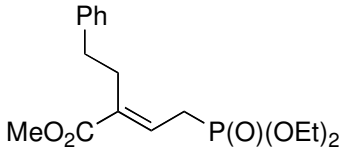
7: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.67 (q, *J* = 7.8 Hz, 1H), 4.11 – 3.98 (m, 4H), 3.67 (s, 3H), 2.67 (dd, *J* = 23.1, 8.1 Hz, 2H), 2.27 – 2.19 (m, 2H), 1.37 (qt, *J* = 7.5, 1.8 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 6H), 0.85 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.8 (d, *J* = 3.0 Hz), 136.2 (d, *J* = 14.0 Hz), 130.7 (d, *J* = 11.0 Hz), 62.4 (d, *J* = 7.0 Hz), 52.0, 28.9 (d, *J* = 2.0 Hz), 27.6 (d, *J* = 138.7 Hz), 22.4 (d, *J* = 3.5 Hz), 16.6 (d, *J* = 6.0 Hz), 14.2; IR (neat) 2961, 1712, 1284, 1251, 1222, 1164, 1018, 957, 853 820 cm^{-1}; LRMS *m/z* calcd for $C_{12}H_{23}O_5P$ 301.1(M+Na$^+$), found 301.1



8

(*E*)-methyl 2-(2-(diethoxyphosphoryl)ethylidene)-4-methylpentanoate (8). Prepared according to the general procedure using phosphonocrotonate **4** (0.472 g, 2.00 mmol), THF (10 mL), LiHMDS (2.0 mL of a 1.0 M solution in THF, 2.0 mmol) and *i*-BuI (0.115 mL, 1.00 mmol) in THF (2 mL) to give 58.3 mg of **8** (20%) as a colorless oil after flash chromatography (1:2 hexanes:ethyl acetate).

8: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.73 (q, *J* = 7.8 Hz, 1H), 4.11 – 3.89 (m, 4H), 3.67 (s, 3H), 2.68 (dd, *J* = 23.1, 8.1 Hz, 2H), 2.16 (dd, *J* = 7.2, 2.1 Hz, 2H), 1.70 (sep, *J* = 6.7 Hz, 1H), 1.25 (t, *J* = 6.9 Hz, 6H), 0.81 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.1, 135.6 (d, *J* = 14.5 Hz), 131.3 (d, *J* = 10.1 Hz), 62.4 (d, *J* = 6.5 Hz), 52.1, 35.7 (d, *J* = 2.0 Hz), 28.4 (d, *J* = 2.6 Hz), 27.9 (d, *J* = 138.8 Hz), 22.6, 16.6 (d, *J* = 6.0 Hz); IR (neat) 2956, 1714, 1289, 1252, 1227, 1163, 1096, 1052, 1021, 961 cm^{-1}; LRMS *m/z* calcd for $C_{13}H_{25}O_5P$ 315.1 (M+Na$^+$), found 315.1

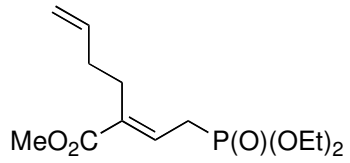


9

(*E*)-methyl 4-(diethoxyphosphoryl)-2-phenethylbut-2-enoate (9). Prepared according to the general procedure using phosphonocrotonate **4** (0.472 g, 2.00 mmol), THF (10 mL), LiHMDS (2.0 mL of a 1.0 M solution in THF, 2.0 mmol) and $PhCH_2CH_2OTf$ (0.300 g, 1.20 mmol) in THF (2 mL) to give 0.191 g of **9** (50%) as a colorless oil after flash chromatography (1:2 hexanes:ethyl acetate).

9: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 2H), 7.19 – 7.16 (m, 3H), 6.76 (q, *J* = 8.1 Hz, 1H), 4.12 – 4.03 (m, 4H), 3.75 (s, 3H), 2.74 – 2.69 (m, 2H), 2.64 – 2.58 (m, 2H), 2.48 (dd, *J* = 23.1, 8.0 Hz, 2H), 1.30 (t, *J* = 7.3 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.6, 141.6, 135.1 (d, *J* = 13.8 Hz), 131.8 (d, *J* = 10.6 Hz), 128.8 (d, *J* = 6.8 Hz), 128.7 (d, *J* = 9.8 Hz), 126.3, 62.4 (d, *J* = 8.3 Hz), 52.1, 35.2 (d, *J* = 3.0 Hz), 29.3 (d, *J* = 2.4 Hz), 27.3 (d, *J* = 138.1 Hz), 16.6 (d, *J* =

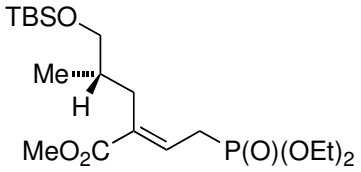
6.1 Hz); IR (neat) 2981, 1712, 1437, 1248, 1195, 1174, 1095, 1019, 958 cm^{-1}; LRMS *m/z* calcd for $C_{17}H_{25}O_5P$ 363.1 ($M+Na^+$), found 363.1.



10

(*E*)-methyl 2-(2-(diethoxyphosphoryl)ethylidene)hex-5-enoate (10). Prepared according to the general procedure using phosphonocrotonate **4** (0.472 g, 2.00 mmol), THF (10 mL), LiHMDS (2.0 mL of a 1.0 M solution in THF, 2.0 mmol) and homoallyl triflate (0.124 mg, 0.600 mmol) in THF (2 mL) to give 75.8 mg of **10** (44%) as a colorless oil after flash chromatography (1:2 hexane/ethyl acetate).

10: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.73 (q, *J* = 8.1 Hz, 1H), 5.76 (ddt, *J* = 17.0, 10.3, 6.7 Hz, 1H), 5.03 – 4.88 (m, 2H), 4.15 – 4.00 (m, 4H), 3.70 (s, 3H), 2.70 (dd, *J* = 23.3, 8.2 Hz, 2H), 2.38 (td, *J* = 7.9, 1.6 Hz, 2H), 2.12 (dt, *J* = 7.2, 7.2 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.6, 137.8, 135.5 (d, *J* = 13.6 Hz), 131.3 (d, *J* = 10.6 Hz), 115.4, 62.4 (d, *J* = 7.0 Hz), 52.1, 33.1 (d, *J* = 3.0 Hz), 27.7 (d, *J* = 139.5 Hz), 26.5 (d, *J* = 2.0 Hz), 16.6 (d, *J* = 6.1 Hz); IR (neat) 2981, 1713, 1642, 1249, 1163, 1020, 962 cm^{-1}; LRMS *m/z* calcd for $C_{13}H_{23}O_5P$ 313.1(M+Na$^+$), found 313.1

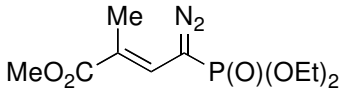


11

(*S,E*)-methyl 5-(tert-butyldimethylsilyloxy)-2-(2-(diethoxyphosphoryl)ethylidene)-4-methylpentanoate (11). Prepared according to the general procedure using phosphonocrotonate **4** (59.3 mg, 2.00 mmol), THF (10 mL), LiHMDS (0.25 mL of a 1.0 M solution in THF, 0.25 mmol) and (R)-3-(tert-butyldimethylsilyloxy)-2-methylpropyl triflate (42.2 mg, 0.125 mmol) in THF (2 mL) to give 27.1 mg of **11** (51%) as a colorless oil after flash chromatography (1:2 hexane/ethyl acetate).

11: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.80 (q, *J* = 8.1 Hz, 1H), 4.14 – 4.03 (m, 4H), 3.71 (s, 3H), 3.40 (d, *J* = 5.4 Hz, 2H), 2.83 (ddd, *J* = 15.1, 15.1, 8.3 Hz, 1 H), 2.71 (ddd, *J* = 15.3m 15.3, 8.1 Hz, 1 H), 2.48 (ddd, *J* = 13.8, 6.4, 2.3 Hz, 1H), 2.14 (ddd, *J* = 13.6, 8.0, 2.0 Hz, 1H), 1.84-1.67 (m, 1H), 1.29 (t, *J* = 7.2 Hz, 6H), 0.875 (s, 9H), 0.83 (d, *J* = 6.9 Hz, 3H), 0.02 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.0, 135.2 (d, *J* = 14.0 Hz), 131.8 (d, *J* = 10.0 Hz), 67.5, 62.4 (d, *J* = 3.0 Hz), 62.3 (d, *J* = 2.6 Hz) , 52.1, 35.9 (d, *J* = 3.0 Hz), 30.1 (d, *J* = 2.6 Hz), 27.7 (d, *J* = 138.6 Hz), 26.1, 18.5, 16.8, 16.6 (d, *J* = 6.5 Hz), -5.2, -5.2; IR (neat) 2954, 2930, 2857, 1717, 1253, 1218, 1165, 1086, 1026, 964 cm^{-1}; LRMS *m/z* calcd for $C_{19}H_{39}O_6PSi$ 445.2 (M+Na$^+$), found 445.1

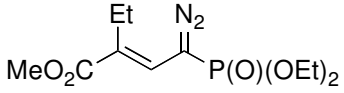
General procedure for diazo formation. To a solution of phosphonate (ca. 0.10 mmol) and ABSA in 5 mL CH_3CN at 0 °C was added DBU dropwise. The resulting reaction mixture was warmed to rt and stirred for 12 h. Following concentration, the resulting residue was taken up in CH_2Cl_2 (9 mL). Concentration and flash chromatography gave diazo substrates **12-19**.



12

(*E*)-methyl 4-diazo-4-(diethoxyphosphoryl)-2-methylbut-2-enoate (12). Prepared according to the general procedure using phosphonate **5** (0.200 g, 0.800 mmol), ABSA (0.211 g, 0. 880 mmol) and DBU (0.143 mL, 0. 960 mmol) to give 0.141 g of **12** (64%) as clear orange oil after flash chromatography (2:1 hexane/ethyl acetate).

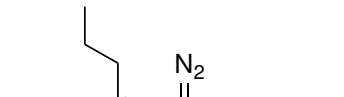
12: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.61 (dq, *J* = 7.9, 1.2 Hz, 1H), 4.25 – 4.06 (m, 4H), 3.73 (s, 3H), 1.96 (d, *J* = 1.1 Hz, 3H), 1.35 (dt, *J* = 7.2, 0.8 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.8, 124.7 (d, *J* = 10.6 Hz), 122.4 (d, *J* = 9.9 Hz), 63.4 (d, *J* = 5.3 Hz), 52.2, 16.3 (d, *J* = 6.9 Hz), 12.5; IR (neat) 2985, 2078, 1705, 1616, 1436, 1259, 1133, 1045, 1015, 973 cm^{-1}; LRMS *m/z* calcd for $C_{10}H_{17}N_2O_5P$ 299.1 (M+Na$^+$), found 299.1.



13

(*E*)-methyl 4-diazo-4-(diethoxyphosphoryl)-2-methylbut-2-enoate (13). Prepared according to the general procedure using phosphonate **6** (0.106 g, 0.401 mmol), ABSA (0.106 g, 0.44 mmol) and DBU (72.2 μL, 0.48 mmol) to give 85 mg of **13** (73%) as clear orange oil after flash chromatography (2:1 hexane/ethyl acetate).

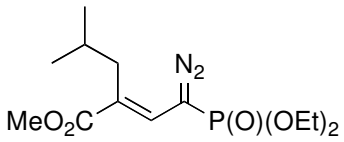
13: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.56 (d, *J* = 8.1 Hz, 1H), 4.25 – 4.06 (m, 4H), 3.73 (s, 3H), 2.37 (q, *J* = 7.6 Hz, 2H), 1.36 (t, *J* = 7.0 Hz, 3H), 1.36 (t, *J* = 7.3 Hz, 3H), 1.04 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.6, 128.5 (d, *J* = 9.9 Hz), 124.1 (d, *J* = 11.4 Hz), 63.5 (d, *J* = 5.3 Hz), 52.1, 20.0, 16.4 (d, *J* = 6.9 Hz), 14.9; IR (neat) 2981, 2078, 1706, 1610, 1436, 1277, 1237, 1134, 1045, 1016, 973 cm^{-1}; LRMS *m/z* calcd for $C_{11}H_{19}N_2O_5P$ 313.1(M+Na$^+$), found 313.0.



14

(*E*)-methyl 4-diazo-4-(diethoxyphosphoryl)-2-methylbut-2-enoate (14). Prepared according to the general procedure using phosphonate **7** (52.7 mg, 0.190 mmol), ABSA (50.0 mg, 0.210 mmol) and DBU (34.0 μL, 0.227 mmol) to give 44.6 mg of **14** (77%) as clear orange oil after flash chromatography (2:1 hexane/ethyl acetate).

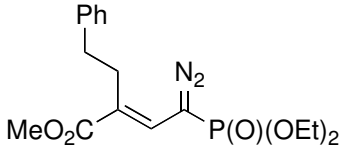
14: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.57 (d, *J* = 8.3 Hz, 1H), 4.25 – 4.06 (m, 4H), 3.72 (s, 3H), 2.34 – 2.29 (m, 2H), 1.49 – 1.35 (partially obscured m, 2H), 1.36 (t, *J* = 7.0 Hz, 3H), 1.36 (t, *J* = 7.1 Hz, 3H), 0.92 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.8, 127.2 (d, *J* = 10.6 Hz), 124.4 (d, *J* = 10.6 Hz), 63.5 (d, *J* = 5.3 Hz), 52.1, 28.5, 23.6, 16.4 (d, *J* = 6.1 Hz), 13.8; IR (neat) 2961, 2074, 1706, 1607, 1436, 1268, 1218, 1190, 1137, 1046, 1017, 973 cm^{-1}; LRMS *m/z* calcd for $C_{12}H_{21}N_2O_5P$ 327.1 (M+Na$^+$), found 327.1.



15

(*E*)-methyl 4-diazo-4-(diethoxyphosphoryl)-2-methylbut-2-enoate (15). Prepared according to the general procedure using phosphonate **8** (29.1 mg, 0.100 mmol), ABSA (26.4 mg, 0.11 mmol) and DBU (18.0 μL, 0.12 mmol) to give 23.6 mg of **15** (74%) as clear orange oil after flash chromatography (2:1 hexane/ethyl acetate).

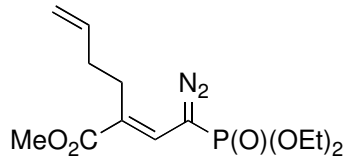
15: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.62 (d, *J* = 8.3 Hz, 1H), 4.25 – 4.06 (m, 4H), 3.73 (s, 3H), 2.24 (d, *J* = 7.4 Hz, 2H), 1.71 (sep, *J* = 6.9 Hz, 1H), 1.36 (t, *J* = 7.2 Hz, 3H), 1.35 (t, *J* = 7.2 Hz, 3H), 0.89 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.1, 126.5 (d, *J* = 10.6 Hz), 124.7 (d, *J* = 11.4 Hz), 63.5 (d, *J* = 5.3 Hz), 52.1, 34.6, 29.1, 22.1, 16.4 (d, *J* = 6.9 Hz); IR (neat) 2958, 2870, 2076, 1707, 1605, 1270, 1221, 1139, 1046, 1017, 973 cm^{-1}; LRMS *m/z* calcd for $C_{13}H_{23}N_2O_5P$ 341.1(M+Na$^+$), found 341.1.



16

(*E*)-methyl 4-diazo-4-(diethoxyphosphoryl)-2-methylbut-2-enoate (16). Prepared according to the general procedure using phosphonate **10** (38.0 mg, 0.112 mmol), ABSA (29.6 mg, 0.120 mmol) and DBU (20.1 μL, 0.135 mmol) to give 35.2 mg of **16** (86%) as clear orange oil after flash chromatography (2:1 hexane/ethyl acetate).

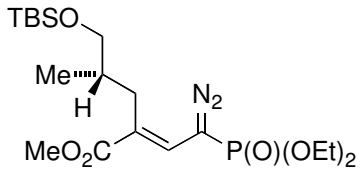
17: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 2H), 7.22 – 7.17 (m, 3H), 6.64 (d, *J* = 8.4 Hz, 1H), 4.22 – 4.02 (m, 4H), 3.76 (s, 3H), 2.76 – 2.60 (m, 4H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.35 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.6, 141.1, 128.7, 128.7, 126.5, 125.9 (d, *J* = 10.0 Hz), 125.2 (d, *J* = 11.0 Hz), 63.5 (d, *J* = 5.5 Hz), 52.2, 36.2, 29.0, 16.4 (d, *J* = 6.5 Hz); IR (neat) 2984, 2951, 2077, 1705, 1609, 1261, 1191, 1165, 1045, 1016, 974 cm^{-1}; LRMS *m/z* calcd for $C_{17}H_{23}N_2O_5P$ 389.1 (M+Na$^+$), found 389.1.



17

(*E*)-methyl 4-diazo-4-(diethoxyphosphoryl)-2-methylbut-2-enoate (17). Prepared according to the general procedure using phosphonate **10** (38.0 mg, 0.120 mmol), ABSA (34.6 mg, 0.144 mmol) and DBU (23.5 μL, 0.160 mmol) to give 31.4 mg of **17** (76%) as clear orange oil after flash chromatography (2:1 hexane/ethyl acetate).

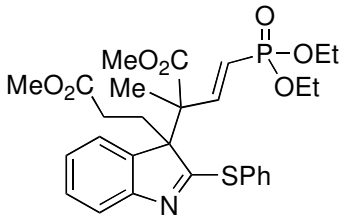
17: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.62 (d, *J* = 8.2 Hz, 1H), 5.78 (ddt, *J* = 16.9, 10.0, 6.7 Hz, 1H), 5.04 (ddt, *J* = 17.0, 1.5, 1.5 Hz, 1H), 4.99 (ddt, *J* = 10.1, 1.8, 1.1 Hz, 1H), 4.26-4.06 (m, 4H), 3.74 (s, 3H), 2.47-2.42 (m, 2H), 2.21 – 2.11 (m, 2H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.36 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.6, 137.1, 126.1 (d, *J* = 10.6 Hz), 124.9 (d, *J* = 11.4 Hz), 115.9, 63.5 (d, *J* = 5.3 Hz), 52.2, 34.1, 26.1, 16.4 (d, *J* = 6.1 Hz); IR (neat) 2982, 2076, 1705, 1608, 1436, 1260, 1198, 1137, 973 cm^{-1}; LRMS *m/z* calcd for $C_{13}H_{21}N_2O_5P$ 339.1 ($M+Na^+$), found 339.1.



18

(*E*)-methyl 4-diazo-4-(diethoxyphosphoryl)-2-methylbut-2-enoate (18). Prepared according to the general procedure using phosphonate **11** (14.5 mg, 0.0343 mmol), ABSA (9.1 mg, 0.0379 mmol) and DBU (6.2 μL, 0.041 mmol) to give 12.8 mg of **18** (83%) as clear orange oil after flash chromatography (2:1 hexane/ethyl acetate).

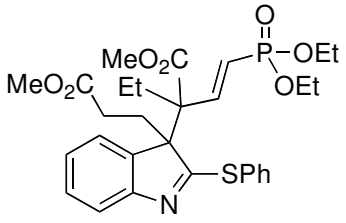
18: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.63 (d, *J* = 8.4 Hz, 1H), 4.26 – 4.06 (m, 4H), 3.73 (s, 3H), 3.45 (d, *J* = 5.9 Hz, 2H), 2.48 (dd, *J* = 14.3, 6.0 Hz, 1H), 2.19 (dd, *J* = 14.2, 9.0 Hz, 1H), 1.87 – 1.70 (m, 1H), 1.37 (t, *J* = 7.2 Hz, 3H), 1.36 (t, *J* = 7.1 Hz, 3H), 0.89 (s, 9H), 0.86 (d, *J* = 6.6 Hz, 3H), 0.03 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.1, 125.8 (d, *J* = 10.5 Hz), 124.9 (d, *J* = 11.0 Hz), 68.2, 63.5 (d, *J* = 5.6 Hz), 52.1, 36.5, 29.7, 26.2, 18.6, 16.4 (d, *J* = 7.0 Hz), 16.1, -5.2, -5.2; IR (neat) 2954, 2930, 2857, 2075, 1708, 1607, 1472, 1435, 1260, 1210, 1090, 1048, 1019, 973 cm^{-1}; LRMS *m/z* calcd for $C_{19}H_{37}N_2O_6PSi$ 471.2 ($M+Na^+$), found 471.1.



20

Quaternary Indoline (20). To a solution of thioindole **19** (0.140 g, 0.450 mmol) and $Rh_2(OAc)_4$ (9.9 mg, 0.022 mmol) at rt was added a solution of diazophosphonate **12** (0.373 g, 1.35 mmol) in CH_2Cl_2 (3.7 mL) over 4 h via syringe pump. After stirring at rt for 24 h, the reaction mixture was concentrated. Flash chromatography (1:2 hexane/ ethyl acetate) gave 89 mg of indoline **20** (86%) as a pale yellow oil.

20: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.61 – 7.59 (m, 2H), 7.48 – 7.46 (m, 3H), 7.28 (d, *J* = 4Hz, 2H), 7.15 – 7.03 (m, 3H), 5.86 (dd, *J* = 18, 18 Hz, 1H), 4.05 – 3.98 (m, 4H), 3.74 (s, 3H), 3.52 (s, 3H), 2.95 (ddd, *J* = 14, 12, 5 Hz, 1H), 2.49 (ddd, *J* = 14, 11, 5 Hz, 1H), 1.86 (ddd, *J* = 16, 12, 5 hz, 1H), 1.32 (ddd, *J* = 16, 11, 5 Hz, 1H), 1.31-1.26 (m, 6H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 183.8, 174.9, 157.4, 151.0 (d, *J* = 7 Hz), 140.4, 137.2, 131.8, 131.7, 131.5, 131.2, 130.3, 126.8, 125.2, 123.2 (d, *J* = 184 Hz), 121.5, 70.2, 64.1 (d, *J*= 6Hz), 64.0 (d, *J* = 6 Hz), 55.3, 54.5, 53.6, 30.9, 29.6, 19.2, 18.4 (d, *J* = 2Hz), 18.3 (d, *J* = 2 Hz); IR (neat) 3060, 2985, 2952, 1735, 1515, 1456, 1440, 1251, 1024, 965 cm^{-1}; LRMS *m/z* calcd for $C_{28}H_{35}NO_7PS$ 582.2 ($M+Na^+$), found 582.1



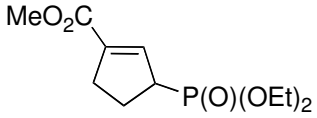
22

(E)-methyl 4-(diethoxyphosphoryl)-2-ethyl-2-(3-(3-methoxy-3-oxopropyl)-2-(phenylthio)-3H-indol-3-yl)but-3-enoate (22).

22: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 – 7.62 (m, 2H), 7.46 – 7.41 (m, 3H), 7.28 (d, *J* = 7.3 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.14 (d, *J* = 7.3 Hz, 1H), 7.07 (dt, *J* = 7.3, 1.0 Hz, 1H), 6.97 (dd, *J* = 23.9, 18.1 Hz, 1H), 5.61 (dd, *J* = 18.3, 18.3 Hz, 1H), 4.02 – 3.88 (m, 4H), 3.75 (s, 3H), 3.54 (s, 3H), 2.74–2.57 (m, 2H), 2.24 – 2.16 (m, 1H), 2.00 – 1.86 (m, 2H), 1.34 – 1.24 (m, 7H), 0.79 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 181.4, 173.3, 171.5, 155.4, 147.2 (d, *J* = 6.9 Hz), 138.3, 134.8, 129.7, 129.6, 129.1, 128.2, 124.5, 123.7, 121.0 (d, *J* = 184.6 Hz), 120.0, 68.7 (d, *J* = 1.5 Hz), 62.1 (d, *J*= 5.3 Hz), 62.0 (d, *J*= 5.3 Hz), 58.5 (d, *J* = 19.9 Hz), 52.2, 51.8, 29.0, 27.4, 24.2, 16.6, 16.5, 9.9 IR (neat) 2981, 1734, 1514, 1456, 1441, 1250, 1213, 1170, 1052, 1023, 965, 849, 748 cm^{-1}; LRMS *m/z* calcd for $C_{28}H_{35}NO_7PS$ 574.2 ($M+H^+$), found 574.2

General procedure for cyclopentene formation. To a solution of vinyl diazophosphonate (ca. 0.10 mmol) in CH_2Cl_2 was added $Rh_2(OAc)_4$ (ca. 0.005 mmol) in one portion. After stirring at rt overnight, the reaction mixture was concentrated. The resulting residue was purified by flash chromatography to give cyclopentenes **23-28**.

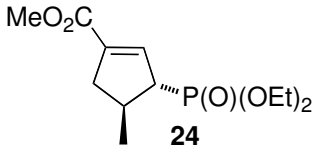
General procedure for equilibration. To a solution of the cyclopentene **24**, **26** and **27** in CH_2Cl_2 was added 0.05 mL of DBU dropwise. The reaction mixture was allowed to stir for 1 h before it was concentrated. Preparative TLC (1:2 hexane/ethyl acetate) gave cyclopentenes **24**, **26** and **27** as single isomers as determined by ^{1}H NMR analysis in 70% ~ 80% yield.



23

Methyl 3-(diethoxyphosphoryl)cyclopent-1-enecarboxylate (23). Prepared according to the general procedure using diazo **13** (147 mg, 0.510 mmol) and $Rh_2(OAc)_4$ (11 mg, 0.025 mmol) to give 91.1 mg of cyclopentene **23** (68%) as a colorless oil after flash chromatography (1:2 to 1:3 hexane/ethyl acetate).

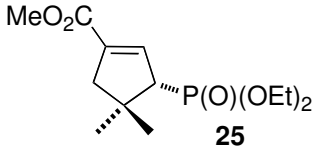
23: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.65 (dddd, *J* = 4.7, 2.2, 2.2, 2.2 Hz, 1H), 4.17 – 4.05 (m, 4H), 3.73 (s, 3H), 3.28-3.13 (m, 1H), 2.80-2.54 (m, 2H), 2.37 – 2.15 (m, 2H), 1.31 (t, *J* = 7.0 Hz, 3H), 1.30 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.2 (d, *J* = 3.0 Hz), 139.5 (d, *J* = 14.0 Hz), 138.4 (d, *J* = 9.0 Hz), 62.5 (d, *J* = 7.0 Hz), 62.3 (d, *J* = 7.1 Hz), 51.9, 44.5 (d, *J* = 143.2 Hz), 31.5 (d, *J* = 3.5 Hz), 24.7 (d, *J* = 3.0 Hz), 16.7 (d, *J* = 5.5 Hz); IR (neat) 2982, 1717, 1438, 1257, 1214, 1163, 1094, 1053, 1023 cm^{-1}; LRMS *m/z* calcd for $C_{11}H_{19}O_5P$ 285.1 (M+Na$^+$), found 285.0



24

Methyl 3-(diethoxyphosphoryl)-4-methylcyclopent-1-enecarboxylate (24). Prepared according to the general procedure using diazo **14** (22.3 mg, 0.0730 mmol) and $Rh_2(OAc)_4$ (1.6 mg, 0.0037 mmol) to give 18.1 mg of cyclopentene **24** (89%) as a colorless oil after flash chromatography (1:2 to 1:3 hexane/ethyl acetate).

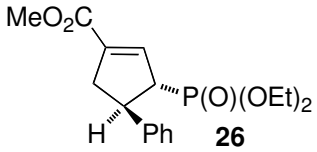
24 (after equilibration using DBU): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.60 (dddd, *J* = 4.6, 2.2, 2.2, 2.2 Hz, 1H), 4.18 – 4.05 (m, 4H), 3.74 (s, 3H), 2.99 – 2.86 (m, 1H), 2.84 – 2.65 (m, 2H), 2.32 – 2.18 (m, 1H), 1.31 (dt, *J* = 7.2, 0.3 Hz 3 H), 1.30 (dt, *J* = 7.4, 0.3 Hz, 3H), 1.14 (dd, *J* = 6.8, 0.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.3, 138.1 (d, *J* = 13.5 Hz), 137.5 (d, *J* = 9.0 Hz), 62.4 (d, *J* = 7.1 Hz), 62.3 (d, *J* = 6.9 Hz), 52.5 (d, *J* = 141.6 Hz), 51.9, 39.9 (d, *J* = 4.0 Hz), 33.8 (d, *J* = 2.0 Hz), 22.2 (d, *J* = 9.5 Hz), 16.7 (d, *J* = 5.6 Hz); IR (neat) 2959, 1718, 1635, 1438, 1249, 1092, 1052, 1024, 959 cm^{-1}; LRMS *m/z* calcd for $C_{12}H_{21}O_5P$ 299.1 (M+Na$^+$), found 299.0



25

Methyl 3-(diethoxyphosphoryl)-4,4-dimethylcyclopent-1-enecarboxylate (25). Prepared according to the general procedure using diazo **15** (11.8 mg, 0.037 mmol) and $Rh_2(OAc)_4$ (0.8 mg, 0.0018 mmol) to give 9.3 mg of cyclopentene **25** (86%) as a colorless oil after flash chromatography (1:2 to 1:3 hexane/ethyl acetate).

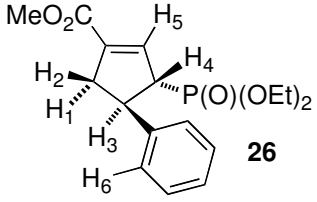
25: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.64 – 6.59 (m, 1H), 4.18 – 4.02 (m, 4H), 3.73 (s, 3H), 2.82 (dddd, *J* = 25.8, 2.6, 2.6, 1.6 Hz, 1H), 2.58 (dddd, *J* = 16.1, 6.9, 2.3, 2.3 Hz, 1H), 2.37 (dddd, *J* = 16.2, 7.4, 1.6, 1.6 Hz, 1H), 1.34 – 1.27 (m, 9H), 1.18 (d, *J* = 1.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.4 (d, *J* = 3.0 Hz), 138.7 (d, *J* = 9.5 Hz), 137.9 (d, *J* = 13.1 Hz), 62.1 (d, *J* = 7.0 Hz), 62.0 (d, *J* = 7.5 Hz), 55.1 (d, *J* = 138.7 Hz), 51.8, 46.7 (d, *J* = 2.6 Hz), 42.3, 31.3 (d, *J* = 10.5 Hz), 25.6 (d, *J* = 5.5 Hz), 16.7 (d, *J* = 6.0 Hz); IR (neat) 2980, 1718, 1437, 1247, 1164, 1053, 1025 cm^{-1}; LRMS *m/z* calcd for $C_{13}H_{23}O_5P$ 313.1 ($M+Na^+$), found 313.0.



26

Methyl 3-(diethoxyphosphoryl)-4-phenylcyclopent-1-enecarboxylate (26). Prepared according to the general procedure using diazo **16** (17.6 mg, 0.0480 mmol) and $Rh_2(OAc)_4$ (1.1 mg, 0.0024 mmol) to give 11.9 mg of cyclopentene **26** (78%) as colorless oil after flash chromatography (1:2 to 1:3 hexane/ethyl acetate).

26 (after DBU equilibration): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 – 7.16 (m, 5H), 6.72 (dddd, *J* = 6.2, 2.3, 2.3, 2.3 Hz, 1H), 4.13 – 3.98 (m, 4H), 3.90 – 3.77 (m, 1H), 3.77 (s, 3H), 3.35 – 3.16 (m, 2H), 2.86 – 2.72 (m, 1H), 1.25 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.9 (d, *J* = 3.0 Hz), 145.5 (d, *J* = 8.4 Hz), 138.2 (d, *J* = 13.7 Hz), 137.4 (d, *J* = 8.4 Hz), 129.0, 127.1, 126.9, 62.6 (d, *J* = 6.9 Hz), 62.4 (d, *J* = 6.9 Hz), 53.6 (d, *J* = 141.9 Hz), 51.9, 44.1 (d, *J* = 1.5 Hz), 40.8 (d, *J* = 4.6 Hz), 16.7 (d, *J* = 6.1 Hz), 16.6 (d, *J* = 6.1 Hz); IR (neat) 2983, 2951, 1718, 1634, 1495, 1438, 1391, 1349, 1250, 1195, 1162, 1097, 1023 cm^{-1}; LRMS *m/z* calcd for $C_{17}H_{23}O_5P$ 361.1 ($M+Na^+$), found 361.0.



26

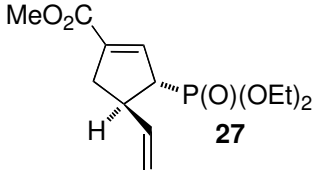
Summary of 1D nOe data for the single isomer of compound **26** after equilibration (500 Hz, C_6D_6):

Irradiation at 2.80 ppm (H-1) resulted in enhancement at 3.30 ppm (H-3) and 7.05 ppm (H-5);

Irradiation at 3.30 ppm (H-3) resulted in enhancement at 2.80 ppm (H-1);

Irradiation at 3.20 ppm (H-2) resulted in enhancement at 7.05 ppm (H-5), 6.85 ppm (H-6), 3.80 ppm (H-4) and 2.80 ppm (H-1);

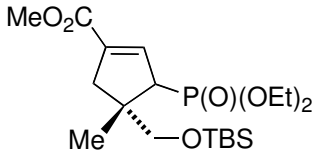
Irradiation at 3.90 ppm (H-4) resulted in enhancement at 7.05 ppm (H-5) and 3.20 ppm (H-2).



27

Methyl 3-(diethoxyphosphoryl)-4-vinylcyclopent-1-enecarboxylate (27). Prepared according to the general procedure using diazo **17** (15.7 mg, 0.0496 mmol) and $Rh_2(OAc)_4$ (1.1 mg, 0.0025 mmol) to give 11.9 mg of cyclopentene **27** (83%) as colorless oil after flash chromatography (1:2 to 1:3 hexane/ethyl acetate).

27 (after DBU equilibration): ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.62 – 6.60 (m, 1H), 5.85 (ddd, *J* = 17.6, 10.3, 7.8 Hz, 1H), 5.12-5.08 (m, 1H), 5.01 (d, *J* = 10.3 Hz, 1H), 4.15 – 4.07 (m, 4H), 3.74 (s, 3H), 3.35 – 3.25 (m, 1H), 3.04 (ddd, *J* = 7.9, 5.4, 3.2 Hz, 1H), 3.00-2.93 (m, 1 H), 2.55 – 2.48 (m, 1H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.0 (d, *J* = 3.1 Hz), 140.5 (d, *J* = 8.4 Hz), 138.0 (d, *J* = 13.7 Hz), 137.4 (d, *J* = 9.2 Hz), 114.7 (d, *J* = 2.3 Hz), 62.6 (d, *J* = 7.0 Hz), 62.4 (d, *J* = 6.9 Hz), 51.9, 50.7 (d, *J* = 142.7 Hz), 42.7 (d, *J* = 2.3 Hz), 37.9 (d, *J* = 3.8 Hz), 16.7 (d, *J* = 1.5 Hz), 16.7 (d, *J* = 2.3 Hz); IR (neat) 2982, 1719, 1635, 1438, 1249, 1096, 1053, 1024, 962 cm^{-1}; LRMS *m/z* calcd for $C_{13}H_{21}N_2O_5P$ 311.1 ($M+Na^+$), found 311.1.



28

(4S)-methyl 4-((tert-butyldimethylsilyloxy)methyl)-3-(diethoxyphosphoryl)-4-methylcyclopent-1-enecarboxylate (28). Prepared according to the general procedure using diazo **18** (93.1 mg, 0.21 mmol) and $Rh_2(OAc)_4$ (4.6 mg, 0.010 mmol) to give 79.0 mg of cyclopentene **28** (91%, 3:2 mixture of isomers) as a colorless oil after flash chromatography (1:2 to 1:3 hexanes/ethyl acetate). Analytically pure **28** (major isomer) was obtained following preparatory TLC (1:2 hexanes/ethyl acetate). The minor isomer could not be separated from the major isomer.

28 (major isomer): $[\alpha]_D^{25}$ =- 48.0 (c = 0.125, $CHCl_3$) ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.63 – 6.60 (m, 1H), 4.15 – 4.04 (m, 4H), 3.82 (d, *J* = 9.8 Hz, 1H), 3.74 (s, 3H), 3.70 (d, *J* = 8.8 Hz, 1H), 2.89 – 2.78 (m, 2H), 2.32 (dddd, *J* = 17.1, 7.8, 2.0, 2.0 Hz,1H), 1.31 (t, *J* = 7.1 Hz, 6H), 1.21 (broad s, 3H), 0.90 (s, 9H), 0.04 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.5, 138.0 (d, *J* = 9.1 Hz), 137.9, 67.8 (d, *J* = 6.0 Hz), 62.3 (d, *J* = 7.1 Hz), 62.0 (d, *J* = 7.6 Hz), 53.6 (d, *J* = 137.6 Hz), 51.8, 47.8, 42.2 (d, *J* = 3.0 Hz), 26.1, 25.8 (d, *J* = 9.6 Hz), 18.5, 16.7 (d, *J* = 6.0 Hz), -5.2 (d, *J* =

1.5 Hz); IR (neat) 2954, 2929, 2856, 1721, 1472, 1438, 1249, 1198, 1086, 1053, 1027 cm^{-1}; LRMS *m/z* calcd for $C_{19}H_{37}O_6PSi$ 443.2 ($M+Na^+$), found 443.1.
Complete chirality retention in C-H insertion reactions is identified by HPLC separation of compound **28** (chiral OD-H column, 0.5 ml/min, 98:2 hexane/isopropanol)

28 from racemic diazo **18**: t_R = 7.92 min (50%), 24.68 (50%)

28 from chiral diazo **18**: t_R = 7.80 min