General Methods and Materials:

All non-aqueous reactions were run in freshly distilled solvents under an inert Ar atmosphere. Flash chromatography was conducted on silica grade 60, 230-400 mesh (Merck), or on CF-11 fibrous cellulose (Whatman) with the indicated solvent system. Thin layer plates were developed with potassium permanganate or *p*-anisaldehyde. ^{1}H, ^{31}P, and ^{13}C NMR spectra were recorded at 300 MHz in $CDCl_3$ or D_2O, and referenced to either residual $CHCl_3$ (^{1}H NMR, 7.27 ppm; ^{13}C NMR, 77.23 ppm) or residual H_2O (^{1}H NMR, 4.80 ppm). ^{13}C and ^{31}P NMR spectra in D_2O were referenced to external standards of methanol (^{13}C NMR, 50.50 ppm) and phosphoric acid, respectively. 1,2-Propane diol was purchased from Matheson; all other reagents were purchased from Aldrich. All solvents and volatile reagents were distilled prior to use. THF was distilled from Na/benzophenone; CH_2Cl_2 was distilled from CaH_2.

1-(*tert*-Butyldimethylsilyloxy)-propan-2-ol (8). To a solution of 1,2-propane diol **7** (3.00 g, 39.5 mmol, 1 equiv.) in CH_2Cl_2 (100 mL) at room temperature, was added N-ethyldiisopropylamine (7.10 g, 55.2 mmol, 1.4 equiv.) and tertbutyldimethylsilyl chloride (5.90 g, 39.5 mmol, 1 equiv.). The mixture was stirred for 16 h, water was added (50 mL) and the aqueous phase was extracted with ether (3 X 50 mL). The combined organic layers were dried over Mg_2SO_4 and concentrated. Purification by flash chromatography (1:9 (v/v) ethyl acetate in hexanes) gave 7.30 g (97%) of a colorless liquid; ^{1}H NMR (ppm): 0.11 (s, 6H), 0.92 (s, 9H), 1.78 (d, J=6.7 Hz, 3H), 3.52 (dd, J=9.9, 7.8 Hz, 1H), 3.60 (dd, J=9.9, 3.4 Hz, 1H), 3.79-3.84 (m, 1H); ^{13}C NMR (ppm): -5.18, 18.51, 26.10, 61.53, 68.74. IR (thin film) 3410 (br), 2957, 2931, 2859, 1472, 1329, 1097 cm^{-1}.

1-(*tert*-Butyldimethylsilyloxy)-propan-2-one (9). To a solution of **8** (4.00 g, 20.9 mmol, 1 equiv.) in CH_2Cl_2 (210 mL) were added NMO (3.40 g, 29.3 mmol, 1.4 equiv.), finely crushed and activated 4 Å molecular sieves (4.00 g), and TPAP (0.29 g, 0.84 mmol, 0.04 equiv.). The reaction was stirred for 6 h, concentrated, and purified by flash chromatography (1:19 (v/v) ethyl acetate in hexanes) to give 3.60 g (91%) of a colorless oil; ^{1}H NMR (ppm): 0.12 (s, 6H), 0.96 (s, 9H), 2.19 (s. 3H), 4.08 (s, 2H); ^{13}C NMR (ppm): -5.04, 14.75, 24.31, 61.25, 70.12. IR (thin film) 2957, 2931, 2859, 1734, 1355, 1260 cm^{-1}.

Methyl-1-(*tert*-butyldimethylsilyloxy)-2-methyl-4-butenoate (10). To a solution of KH (35% dispersion in mineral oil, 0.240 g, 2.10 mmol, 1.3 equiv.) in THF (13 mL) was added (2,2,2-trifluoroethyl)methoxycarbonylmethyl-phosphonate (0.400 mL. 1.90 mmol, 1.2 equiv.) at 0^{o} over five min. The mixture was then cooled to –78° C before **9** (0.300 g. 1.60 mmol, 1 equiv.) was added over 30 min. The reaction was maintained at –78°for 60 h at which time it was warmed first to –40° C (2 h) and then to room temperature. The mixture was then concentrated and purified by flash chromatography (1:49 (v/v) ethyl acetate in hexanes) to give 0.360 g (93%) of a yellow oil (cis:trans / 7:3); ^{1}H NMR (ppm): 0.08 (s, 6H), 0.90 (s, 9H), 1.98 (s, 3H), 3.68 (s, 3H), 4.80 (s, 2H), 5.69 (dd, J=3.3, 1.6 Hz, 1H); ^{13}C NMR (ppm): -5.24, 18.48, 21.67, 26.07, 51.19, 62.94, 114.63, 161.61, 166.69. IR (thin film) 2957, 2931, 2859, 1719, 1647, 1445, 1252, 1102 cm^{-1}.

1-(*tert*-butyldimethylsilyloxy)-2-methyl-buten-4-ol (11). To a solution of **10** (0.200 g, 0.780 mmol, 1 equiv.) in CH_2Cl_2 (7 mL)at –40° C was added DIBALH (1.0 M solution in hexanes, 1.70 mL, 1.70 mmol, 2.2 equiv.) and the reaction was stirred for 2 h. Excess DIBALH was quenched by the addition of $NaSO_4$•H_2O / celite (1:1 (w/w)), stirred for 10 h, and filtered. The filtrate was concentrated and purified by flash chromatography (1:8 (v/v) ethyl acetate in hexanes) to give 171 mg (97%) of a colorless liquid; ^{1}H NMR (ppm): 0.09 (s, 6H), 0.92 (s, 9H), 1.78 (s, 3H), 4.15 (d, J=6.7 Hz, 2H), 4.18 (s, 2H), 5.55 (td, J=8.0, 1.0 Hz, 1H); ^{13}C NMR (ppm): -5.16, 19.51, 21.71, 26.09, 58.84, 62.60, 125.92, 139.33. IR (thin film) 3333 (br), 2957, 2931, 2859, 1471, 1253, 1082 cm^{-1}.

Dimethyl 1-(*tert*-butyldimethylsilyloxy)-2-methyl-buten-4-phosphate (12). To a solution of alcohol **11** (80.0 mg, 0.460 mmol, 1 equiv.) in CH_2Cl_2 (6 mL)at 0° C was added dimethylaminopyridine (85.0 mg, 0.690 mmol, 1.5 equiv.), followed by dropwise addition of dimethylchlorophosphate (75.0 μL, 0.690 mmol, 1.5 equiv.). The reaction was stirred for 14 h and concentrated. Flash column chromatography of the residue (1:5 (v/v) ethyl acetate in hexanes) gave 102 mg (85%) of a colorless oil; ^{1}H NMR (ppm): 0.08 (s, 6H), 0.90 (s, 9H), 1.80 (s, 3H), 3.74 (s, 3H), 3.78 (s, 3H), 4.18 (s, 2H), 4.63 (t, J=7.5, 2H), 5.45 (td, J=7.1, 1.2 Hz, 1H); ^{13}C NMR (ppm): -5.19, 18.51, 21.27, 26.06, 54.43, 62.14, 63.72, 120.61, 141.89; ^{31}P NMR (ppm): –0.04. IR (thin film) 2957, 2857, 2370, 1478, 1312, 1056 (br) cm^{-1}.

(2S, 3R)-Dimethyl 1-(*tert*-butyldimethylsilyloxy)-2, 3-dihydroxy-2-methyl-butan-4-phosphate (13). To a stirred solution of water (650 μL) and *tert*-butanol (650 μL), buffered with $NaHCO_3$ (32.0 mg, 0.310 mmol, 3 equiv.) was added AD-mix β (180 mg, 1 equiv.), and $(DHQD)_2PHAL$ (8.0 mg, 0.510 μmol, 0.05 equiv.). The mixture was cooled to 0° C before **12** (32.0 mg, 0.101 mmol, 1 equiv.) and OsO_4 (2.5 % solution in 2-methyl-2-propanol, 8.0 μL, 0.100 μmol, 0.01 equiv.) were added and the resulting mixture was stirred for 24 h, allowed to warm to room temperature, and quenched with Na_2SO_3 (130 mg), after which the aqueous layer was extracted with ethyl acetate (3 X 20 mL), and chloroform (1 X 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated. Flash column chromatography (50-75% (v/v) ethyl acetate/hexanes) gave 20.0 mg (60%) of an opaque yellow oil. ^{1}H NMR (ppm): 0.09 (s, 6H), 0.91 (s, 9H), 1.12 (s, 3H), 3.42 (d, J=10.2 Hz, 1H), 3.72 (d, J=10.2 Hz, 1H), 3.79 (s, 2H), 3.82 (s, 2H), 4.08-4.18 (m, 1H), 4.38 (td, 1H); ^{13}C NMR (ppm): -5.31, 18.41, 19.20, 26.04, 54.39, 67.96, 70.43, 73.12, 74.21; ^{31}P NMR (ppm): –0.04. IR (thin film) 3396 (br), 2957, 2927, 2855, 1460, 1256, 1034 cm^{-1}. $[\alpha]_D^{25}$ = -24.1 °C.

2-C-methyl-erythritol-4-phosphate (4). To a solution of phosphotriester **13** (40.0 mg, 0.110 mmol, 1 equiv.) in CH_2Cl_2 (0.5 mL) at 0° C was added trimethylsilyl bromide (90.0 μL, 0.660 mmol, 6 equiv.). The reaction was allowed to stir for 1 h at 0° C and 2 h at room temperature before it was concentrated. Water (2 mL) was added to the flask and the reaction was stirred for 1 h before the addition of concentrated HCl (150 μL). Stirring was continued for an additional 1 h before solid $NaHCO_3$ was added to pH = 7. The mixture was then frozen and lyophilized to yield a white solid. Cellulose column chromatography (5%-20% (v/v) water/THF) gave 18 mg (79%) of a white solid; ^{1}H NMR (ppm): 1.12 (s, 3H), 3.46 (d, J= 11.7 Hz, 1H), 3.58 (d, J=11.7 Hz, 1H), 3.76-3.90 (m, 2H), 4.05-4.12 (m, 1H); ^{13}C NMR (ppm): 19.8, 67.2, 67.7, 74.9, 75.3; ^{31}P NMR (ppm): 0.28. IR (KBr pellet) 3416 (br), 2974, 2932, 2862, 1692, 1214, 1148, 1112 cm^{-1}. $[\alpha]_D^{25}$ = +6.8 °C (lit[1] = +6.4°C).

Methyl-1-(*tert*-butyldimethylsilyloxy)-4-butynoate (15). To a stirred solution of protected propargyl alcohol **14** (1.00 g, 5.83 mmol, 1 equiv.) in THF (7 mL) at –78° C was added n-butyllithium (2.5 M solution in hexanes, 2.60 mL, 5.83 mmol, 1 equiv.) over 30 min, followed by methyl chloroformate (900 μL, 8.75 mmol, 1.5 equiv) over 10 min. The reaction was allowed to stir at –78° C for 1 h and at room temperature for 2 h. The reaction was quenched with saturated NH_4Cl (10 mL), and flash column chromatography (1:49 (v/v) ethyl acetate: hexanes) gave 0.91 g (72%) of a yellow oil; ^{1}H NMR (ppm): 0.137 (s, 6H), 0.91 (s, 9H), 3.79 (s, 3H), 4.44 (s, 2H); ^{13}C NMR (ppm): -4.61, 18.86, 26.34, 52.01, 53.40, 77.19, 86.81. IR (thin film) 2955, 2931, 2858, 2240, 1721, 1254, 1107 cm^{-1}.

Methyl-1-(*tert*-butyldimethylsilyloxy)-2-methyl-4-butenoate (10). A stirred solution of CuBr-DMS (36.0 mg, 0.210 mmol, 0.8 equiv.) in THF (1 mL) was cooled to –40° C and methyllithium (250 μL, 0.320 mmol, 1.6 equiv.) was added dropwise over 5 min. The mixture was stirred for 20 min, and cooled to -78° C, at which time **15** (50.0 mg, 0.210 mmol, 1 equiv.) was added dropwise

[1] Kuzuyama, T.; Shunji, T.; Watanabe, H; Seto, H. *Tetrahedron Lett.* **1998**, *39*, 4509-4512.

over 10 min. The solution was stirred for 2 h, and warmed to room temperature. Flash column chromatography (1: 49 (v/v) ethyl acetate / hexanes) gave 18 mg (34%) of a yellow oil; ^{1}H NMR (ppm): 0.08 (s, 6H), 0.90 (s, 9H), 1.98 (s, 3H), 3.68 (s, 3H), 4.80 (s, 2H), 5.69 (dd, J=3.3, 1.6 Hz, 1H); ^{13}C NMR (ppm): -5.24, 18.48, 21.67, 26.07, 51.19, 62.94, 114.63, 161.61, 166.69. IR (thin film) 2957, 2931, 2859, 1719, 1647, 1445, 1252, 1102 cm^{-1}.