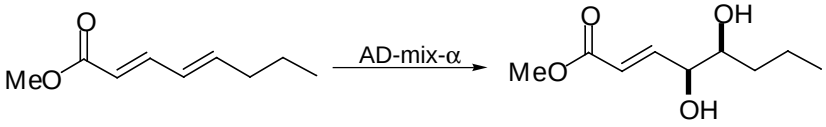
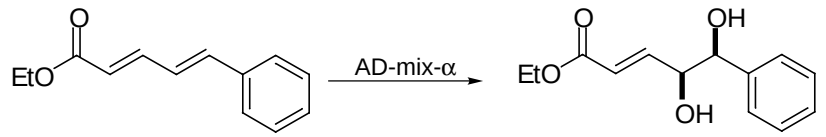
Experimental Procedures



6b **5b**

Representative procedure for preparation of Methyl (4*S*, 5*S*)-4,5-dihydroxy-2-octenoate (5b): Into a 250 mL round bottom flask was added 40 mL of *t*-BuOH, 40 mL of water, $K_3Fe(CN)_6$ (18.75 g, 57 mmol), K_2CO_3 (7.87 g, 57 mmol), $MeSO_2NH_2$ (1.81 g, 19 mmol), $(DHQ)_2$-PHAL (296 mg, 0.38 mmol), and OsO_4 (48 mg, 0.19 mmol). The mixture was stirred at room temperature for about 15 minutes and then cooled to 0°C. To this solution was added dienoate **6b** (3 g, 19 mmol) and the reaction was stirred vigorously at 0°C overnight. The reaction was quenched with sat. aqueous sodium sulfite (30 mL) at room temperature. Ethyl acetate (40 mL) was added to the reaction mixture, and after separation of the layers, the aqueous phase was further extracted with the organic solvent (2 x 30 mL). The combined organic layers were washed with 2N KOH (20 mL) and brine to remove the methanesulfonamide, and dried over anhydrous sodium sulfate. After removal of the solvents in vacuo, flash chromatography on silica gel (7:3 (v/v) hexanes/EtOAc) afforded methyl 4,5-dihydoxy-2-octenoate (**5b**) as a white, waxy solid (2.83 g, 80%): $[\alpha]_D$ -63.9° (*c* 1.07, EtOH); IR (neat) 3424, 2959, 2875, 1717, 1661 1435, 1282, 1173 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 6.95 (dd, *J* = 16.0, 5.0 Hz, 1 H), 6.16 (dd, *J* = 16.5, 2.0 Hz,1 H), 4.14 (ddd, *J* = 10.5, 5, 1.5 Hz, 1 H), 3.76 (s, 1 H), 3.58 (ddd, *J* = 12, 9.5, 4.5 Hz, 1 H), 2.97 (m, 2 H), 1.52 (m, 2 H), 1.40 (m, 2 H), 0.95 (t, *J* = 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 175.96, 147.27, 121.76, 74.04, 73.69, 51.65, 35.06, 18.71, 13.85; HRMS (CI) calcd for $[C_9H_{16}O_4 + NH_4]^+$: 206.1392. Found: 206.1390.



6c **5c**

Ethyl (4*S*, 5*S*)-4,5-dihydroxy-5-phenyl-2-pentenoate (5c): Following the above procedure, the AD of **6c** yielded 1.04 g (79% yield) of **5c** as a clear oil: $[\alpha]_D$ –48.7° (*c* 0.97, EtOH); IR (neat) 3426, 3063, 3031, 2983, 2902, 1955, 1888, 1737, 1651, 1495, 1455, 1368, 1279, 1115 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.36 (m, 5H), 6.75 (dd, *J* = 16, 4.5 Hz, 1 H), 6.10 (dd, *J* = 15.5, 1.5 Hz,1 H), 4.57 (d, *J* = 7 Hz, 1 H), 4.41 (ddd, *J* = 6.5, 4.5, 2 Hz, 1 H), 4.17 (q, *J* = 7 Hz, 2 H), 2.55 (br, 2 H), 1.26 (t, *J* = 7.5 Hz, 3 H); ^{13}C

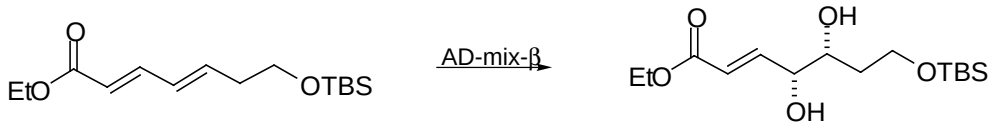
NMR ($CDCl_3$, 125 MHz): δ 166.41, 145.51, 139.65, 128.68, 128.62, 126.68, 122.35, 76.81, 75.32, 60.56, 14.19.

6a **5a**

Ethyl (4*S*, 5*S*)-4,5-dihydroxy-2-hexenoate (5a): Following the above procedure, the AD of 7.0 g of ethyl sorbate (**6a**) yielded 6.182 g (71 % yield) of **5a** as a light yellow oil: $[\alpha]_D$ –52.0° (*c* 1.17, EtOH); IR (neat) 3426, 2978, 1695, 1652, 1464, 1369, 1279, 1179, 1036 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 6.92 (dd, *J* = 16.0, 5.5 Hz, 1 H), 6.14 (dd, *J* = 15.5, 2 Hz, 1 H), 4.20 (q, *J* = 7.5 Hz, 2 H), 4.06 (ddd, *J* = 10.25, 4.5, 1.5 Hz, 1 H), 3.73 (dq, *J* = 10.5, 6.5 Hz, 1 H), 2.89 (br, 1 H), 2.59 (br, 1 H), 1.29 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.82, 146.90, 122.59, 75.67, 70.23, 60.68, 19.13, 14.21.

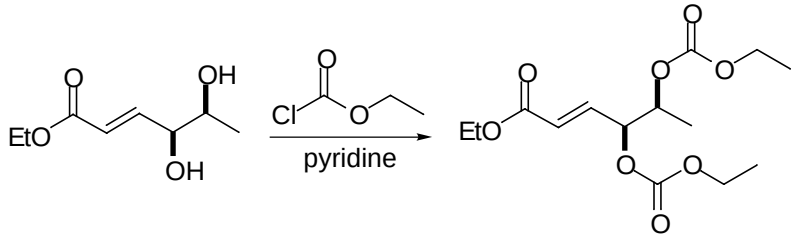
16a **17a**

Ethyl (4*R*, 5*R*)-*6*-(tert-Butyl-dimethyl-siloxy)-4, 5-dihydroxy-2-hexenoate (17a): Following the above procedure, the AD of 6.2 g of **16a** yielded 5.9 g (82 % yield) of **17a** as a clear oil: $[\alpha]_D$ 14.5° (*c* 1.10, EtOH), IR (neat) 3448, 2955, 2932, 2859, 1717, 1659, 1472, 1368, 1259, 1178, 1117 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 6.94 (dd, *J* = 15.6, 4.6 Hz, 1 H), 6.16 (dd, *J* = 15.6, 1.6 Hz, 1 H), 4.34 (m, 1H), 4.20 (q, *J* = 7 Hz, 2 H), 3.77 (m, 2 H), 3.65 (m, 1 H), 2.97 (br, 2 H), 1.29 (t, *J* = 7.2 Hz, 3 H), 0.90 (s, 9 H), 0.08 (s, 6 H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 166.35, 146.55, 122.12, 72.97, 71.71, 64.58, 60.49, 25.80, 18.19, 14.21, -5.52; HRMS (CI) calcd for $[C_{14}H_{28}O_5Si + H]^+$: 305.1784. Found: 305.1795.



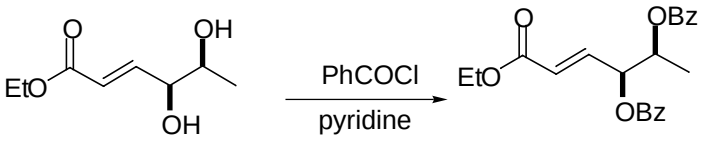
16b **17b**

Ethyl (4*R*, 5*R*)-7-(tert-Butyl-dimethyl-siloxy)-4, 5-dihydroxy-2-heptenoate (17b): Following the above procedure, the AD of 29 g of **16b** yielded 29.5 g (91% yield) of **17b** as a clear oil: $[\alpha]_D$ 37.5° (*c* 1.03, EtOH), IR (neat) 3439, 2931, 2859, 1722, 1660, 1471, 1368, 1257, 1175, 1090 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 6.96 (dd, *J* = 16, 4.5 Hz, 1 H), 6.16 (dd, *J* = 16, 1.5 Hz, 1 H), 4.20 (q, *J* = 7.5 Hz, 2 H), 3.94-3.82 (m, 2H), 3.75 (d, *J* = 3 Hz, 1 H), 3.00 (d, *J* = 5.5 Hz, 1 H), 1.88-1.81 (m, 1 H), 1.78-1.73 (m, 1 H), 1.29 (t, *J* = 7 Hz, 3 H), 0.90 (s, 9 H), 0.10 (s, 6 H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.33, 146.81, 122.27, 81.01, 73.86, 61.88, 60.44, 34.62, 25.82, 20.57, 18.10, 14.22, -5.56; HRMS (FAB) calcd for $[C_{15}H_{30}O_5Si + H]^+$: 318.1863 Found: 305.1795; Anal. Calcd for C, 56.57; H, 9.49. Found: C, 56.66; H, 9.55.



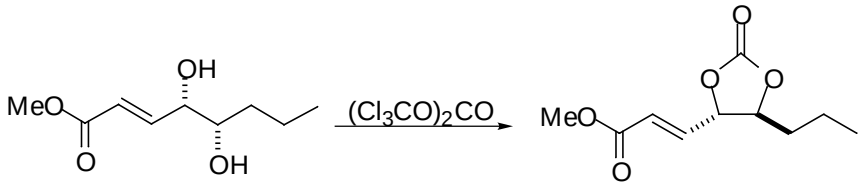
5a **10**

Ethyl (4*S*, 5*S*)-4, 5-bis-ethoxycarbonyloxy-2-hexenoate (10): To a solution of diol **5a** (100 mg, 0.56 mmol) and 0.23 mL of pyridine in 5 mL of CH_2Cl_2 cooled to 0° C was added 0.121 mL of ethyl chloroformate. The reaction was stirred for 2 hours. The reaction was quenched with saturated aqueous ammonium chloride (5 mL). The layers were separated and the aqueous layer was extracted with ether (3 x 10 mL). The organic layers were combined and washed with saturated aqueous sodium bicarbonate (15 mL), brine (15 mL), and then dried over sodium sulfate. Purification on a silica gel column (4:1 hexanes/ethyl acetate) yielded 145 mg (81 % yield) of bis-carbonate **10** as a clear oil: IR (neat) 2985, 1750, 1732, 1666, 1468, 1373, 1245, 1183, 1031 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 6.85 (dd, *J* = 15.5, 5 Hz, 1 H), 6.10 (dd, *J* = 15.5, 1.5 Hz, 1 H), 5.32 (ddd, *J* = 5.5, 5.5, 1.5 Hz, 1 H), 4.94 (dq, *J* = 6.25, 6 Hz, 1 H), 4.19 (m, 6 H), 1.29 (m, 9 H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 165.38, 154.24, 154.08, 140.06, 124.59, 76.54, 64.65, 64.29, 60.77, 15.68, 14.18; HRMS (FAB) calcd for $[C_{14}H_{22}O_8 + H]^+$: 319.1393 Found: 319.1401.



5a **9**

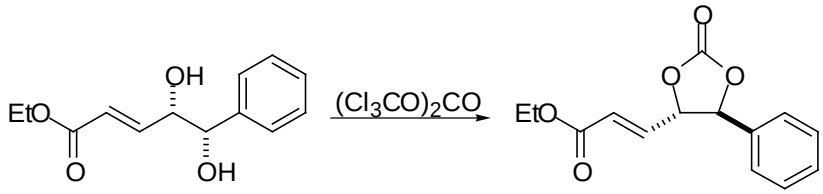
Ethyl (4S, 5S)-4, 5-bis-benzoyloxy-2-hexenoate (9): To a solution of diol **5a** (50 mg, 0.0.29 mmol) and 0.12 mL of pyridine in 3 mL of CH_2Cl_2 cooled to 0° C was added 73 μL of benzoyl chloride. The reaction was stirred for 2 hours. The reaction was quenched with saturated aqueous ammonium chloride (5 mL). The layers were separated and the aqueous layer was extracted with ether (3 x 10 mL). The organic layers were combined and washed with saturated aqueous sodium bicarbonate (15 mL), brine (15 mL), and then dried over sodium sulfate. Purification on a silica gel column (4:1 hexanes/ethyl acetate) yielded 61 mg (56 % yield) of bis-benzoate **9** as a clear oil: IR (neat) 2950, 1771, 1716, 1669, 1651, 1597, 1450, 1311, 1248, 1208, 1172, 1095 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 8.17 (m, 4 H), 7.58-7.40 (m, 6 H), 7.04 (dd, *J* = 15.6, 5.1 Hz, 1 H), 5.90 (ddd, *J* = 5.4, 5.4, 1.5 Hz, 1 H), 5.49 (dq, *J* = 6.6, 6.3 Hz, 1 H), 4.19 (q, *J* = 7.2 Hz, 2 H); 1.45 (d, *J* = 6.6 Hz, 3 H), 1.27 (t, *J* = 7.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 165.62, 165.23, 162.34, 141.09, 133.56, 133.24, 130.59, 129.80, 129.68, 128.91, 128.57, 128.45, 124.20, 73.95, 70.57, 60.80, 16.26, 14.18; HRMS (FAB) calcd for $[C_{22}H_{22}O_6 + H]^+$: 383.1495 Found: 383.1507.



5b **14b**

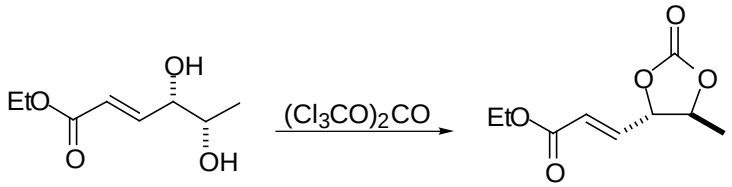
Representative procedure for the preparation of (4*S*, 5*S*)-3-(2-Oxo-5-propyl-[1,3]dioxolan-4-yl)-acrylic acid methyl ester (14b): Into a 250 mL round-bottom flask was placed 2.37 g (8mmol) of triphosgene, 60 mL of dichloromethane, 2 mL of pyridine, and 50 mg of DMAP. The solution was cooled to 0 °C and 1.50 g (8 mmol) of **5b** in 20 mL of dichloromethane was added slowly with an addition funnel. The reaction was stirred for 1.5 h and quenched with saturated aqueous NH_4Cl (40 mL). The layers were separated and the aqueous layer was extracted with ether (3 x 20 mL). The combined organic layers were washed with saturated aqueous sodium bicarbonate (30 mL), brine (25 mL), and dried over anhydrous sodium sulfate. After removal of the solvents in vacuo, flash chromatography on silica gel (7:3 (v/v) hexanes/EtOAc) afforded **14b** as a clear, colorless oil (1.62 g, 95%): $[\alpha]_D$ –59.0° (*c* 1.07, EtOH); IR (neat) 2962, 1809, 1732, 1438, 1279 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 6.83 (dd, *J* = 16, 6 Hz, 1 H), 6.18 (d, *J* = 15.5 Hz, 1H), 4.81 (ddd, *J* = 7.5, 6, 1.5 Hz, 1 H), 4.35 (dt, *J* = 10.5, 7.5 Hz, 1 H), 3.76 (s, 3 H), 1.79 (m, 1 H), 1.71 (m, 1 H), 1.52 (m, 1 H), 1.44 (m, 1 H), 0.97 (td, *J* = 7.5, 1.5 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 165.40, 153.64, 139.65, 124.40, 81.23,

79.85, 52.12, 35.21, 18.04, 13.59; HRMS (CI) calcd for $[C_{10}H_{14}O_5 + NH_4]^+$: 232.1185 Found: 232.1194.



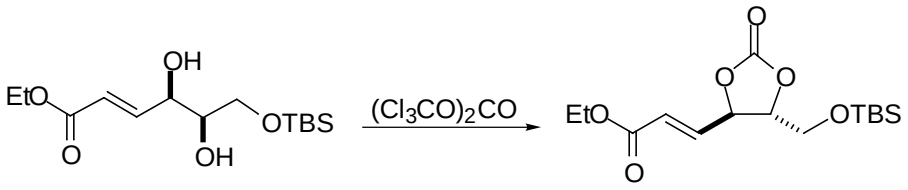
5c **14c**

(4*S*, 5*S*)-3-(2-Oxo-5-phenyl-[1,3]dioxolan-4-yl)-acrylic acid ethyl ester (14c): Following the procedure above, the cyclic carbonate **14c** was produced (605 mg, 2.31 mmol) in 91% yield from diol **5c** as a clear, colorless oil: $[\alpha]_D$ –101.4° (*c* 1.44, EtOH); IR (neat) 3608, 3066, 3037, 2984, 2939, 2906, 1958, 1809, 1717, 1668, 1498, 1456, 1368, 1282, 1165; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.49 (m, 3 H), 7.38 (m, 2 H), 6.95 (dd, *J* = 15.6, 5.4 Hz, 1 H), 6.19 (dd, *J* = 15.9, 1.5 Hz, 1 H), 5.32 (d, *J* = 8.1 Hz, 1 H), 5.07 (ddd, *J* = 7.5, 5.7, 1.5 Hz, 1 H), 4.26 (q, *J* = 7.2 Hz, 2 H), 1.33 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 164.70, 153.22, 138.24, 134.15, 129.98, 129.27, 125.88, 125.46, 82.43, 81.99, 61.09, 14.06 cm^{-1}; HRMS (CI) calcd for $[C_{14}H_{14}O_5 + NH_4]^+$: 280.1185 Found: 280.1164.



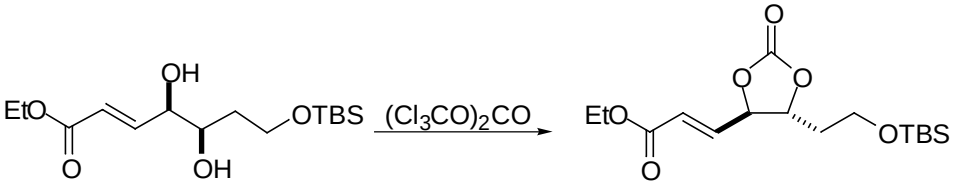
5a **14a**

(4*S*, 5*S*)-3-(5-Methyl-2-oxo-[1,3]dioxolan-4-yl)-acrylic acid ethyl ester (14a): Following the procedure above, the cyclic carbonate **14a** was produced (10.61 g, 53.1 mmol) in 87% yield from diol **5a** as a light yellow oil: $[\alpha]_D$ -21.3° (*c* 2.30, $CHCl_2$); IR (neat) 2986, 1809, 1722, 1368, 1304, 1271, 1190, 1032 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500) δ 6.84 (dd, *J* = 16, 5.5 Hz, 1 H), 6.19 (dd, *J* = 15.5, 1 Hz, 1 H), 4.77 (ddd, *J* = 7, 6, 1 Hz, 1 H), 4.50 (dq, *J* = 6.75, 6.5 Hz, 1 H), 4.24 (q, *J* = 7 Hz, 2 H), 1.54 (d, *J* = 6 Hz, 3H), 1.31 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 164.89, 153.60, 138.78, 125.13, 81.31, 77.93, 61.13, 18.38, 14.12.



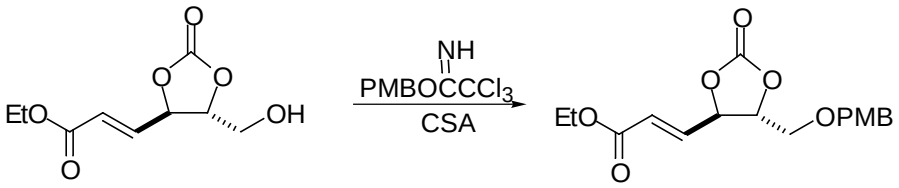
17a **18a**

(4*R*, 5*R*)-3-[5-(tert-Butyl-dimethyl-siloxymethyl)-2-oxo-[1,3]dioxolan-4-yl]-acrylic acid ethyl ester (18a): Following the procedure above, the cyclic carbonate **18a** was produced (2.22 g, 6.72 mmol) in 94% yield from diol **17a** as a light yellow oil: IR (neat) 2932, 2859, 1809, 1732, 1667, 1472, 1368, 1262, 1165, 1038 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300MHz) δ 6.89 (dd, *J* = 15.6, 5.4 Hz, 1 H), 6.20 (dd, *J* = 15.6, 1.5 Hz, 1 H), 5.22 (ddd, *J* = 5.7, 5.4, 1.8 Hz, 1 H), 4.42 (ddd, *J* = 6.0, 3.9, 2.7 Hz, 1 H), 3.95 (dd, *J* = 11.7, 3.9 Hz, 1 H), 3.80 (dd, *J* = 11.7, 2.4 Hz, 1 H), 1.34 (t, *J* = 7.2 Hz, 3 H), 0.92 (s, 9 H), 0.10 (s, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 165.11, 153.80, 140.34, 124.27, 105.00, 80.48, 76.16, 61.78, 61.12, 25.70, 18.18, 14.20, -5.47; HRMS (CI) calcd for $[C_{15}H_{26}O_6Si + NH_4]^+$: 348.1842 Found: 348.1826.



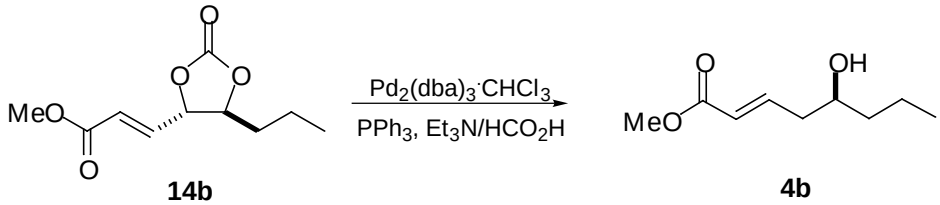
17b **18b**

(4*R*, 5*R*)-3-{5-[2-(tert-Butyl-dimethyl-siloxy)-ethyl]-2-oxo-[1,3]dioxolan-4-yl}-acrylic acid ethyl ester (18b): Following the procedure above, the cyclic carbonate **18b** was produced (26 g, 77.5 mmol) in 95 % yield from diol **17b** as a light yellow oil: $[\alpha]_D$ 34.8° (*c* 1.25, EtOH); IR (neat) 2956, 2932, 2858, 1816, 1726, 1668, 1472, 1390, 1368, 1305, 1261, 1171, 1095, 1043 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.93 (dd, *J* = 15.9, 5.1 Hz, 1 H), 6.25 (dd, *J* = 15.9, 1.5 Hz, 1 H), 5.10 (ddd, *J* = 7.2, 5.1, 1.5 Hz, 1 H), 4.61 (dd, 13.2, 6.6 Hz, 1 H), 4.29 (q, *J* = 7.2 Hz, 2 H), 3.92-3.79 (m, 2 H), 2.13-2.01 (m, 2 H), 1.36 (t, *J* = 6.9 Hz, 3 H), 0.94 (s, 9 H), 0.12 (s, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 164.97, 153.59, 139.49, 124.36, 79.64, 79.23, 60.96, 58.23, 35.82, 25.79, 18.18, 14.10, -5.45; HRMS (CI) calcd for $[C_{16}H_{28}O_6Si + NH_4]^+$: 362.1999 Found: 362.2000; Anal. Calcd for C, 55.79; H, 8.19. Found: C, 55.91; H, 7.96.



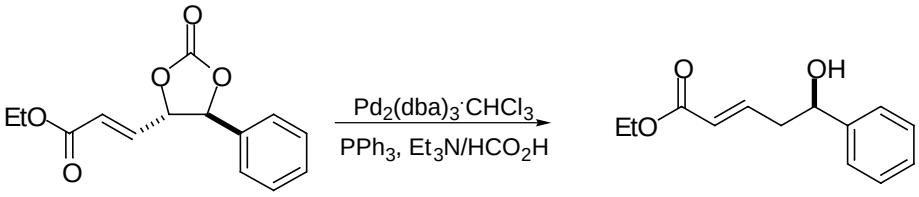
18c

(4R, 5R)-3-[5-(4-Methoxy-benzyloxymethyl)-2-oxo-[1,3]dioxolan-4-yl]-acrylic acid ethyl ester (18c): To a mixture of the alcohol (270 mg, 1.25 mmol) and (S)-(+)-camphorsulfonic acid (29 mg, 0.125 mmol) in methylene chloride (5 mL) was added 4-methoxybenzyl thrichloroacetimidate (425 mg, 1.5 mmol). The mixture was stirred at room temperature for 24 h and concentrated *in vacuo*. Separation on a silica gel column (hexanes: ethylacetate = 4:1) gave 256 mg of the PMB carbonate **18c** (61%): $[\alpha]_D$ 43.8° (*c* 1.70, EtOH); IR (neat) 2937, 2867, 2840, 2053, 1799, 1717, 1668, 1615, 1586, 1516, 1464, 1368; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.24 (d, *J* = 8.5 Hz, 2 H), 6.90 (d, *J* = 8.5 Hz, 2 H), 6.83 (dd, *J* = 16.5, 6 Hz, 1 H), 6.14 (dd, *J* = 15.5, 1.5 Hz, 1 H), 5.14 (ddd, *J* = 6.5, 5.5, 1.5 Hz, 1 H), 4.57 (d, *J* = 11.5 Hz, 1 H), 4.51 (d, *J* = 12 Hz, 1 H), 4.45 (dt, *J* = 6, 4 Hz, 1 H), 4.23 (q, *J* = 7 Hz, 2 H), 3.82 (s, 3 H), 3.71 (dd, *J* = 11.5, 4.5 Hz, 1H), 3.63 (dd, *J* = 11, 3.5 Hz, 1 H), 1.31 (t, 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz), 164.98, 159.63, 153.56, 139.82, 129.55, 128.86, 124.52, 114.03, 79.37, 76.57, 73.48, 67.35, 61.10, 55.31, 14.15; HRMS (FAB) calcd for $[C_{17}H_{20}O_7]^+$: 336.1209 Found: 336.1233.



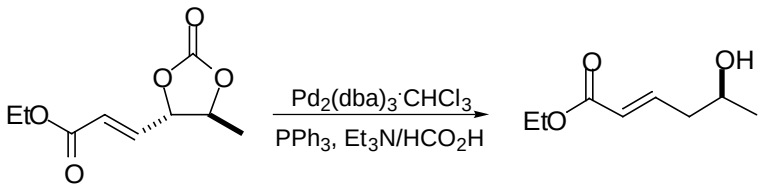
14b **4b**

Representative procedure for the preparation of Methyl (5*S*)-5-Hydroxy-2-octenoate (4b): Into a two-necked, 50 mL, round bottomed flask fitted with a condenser and maintained under nitrogen was placed 480 mg (2.24 mmol) of **14b**, 60 mg of $Pd_2(dba)_3{\cdot}CHCl_3$, 38 mg of PPh_3, and 15 mL of THF. Triethylamine (1 mL, 7.02 mmol) and formic acid (0.26 mL, 7.02 mmol) were added and the mixture was allowed to reflux for 2 hours. The reaction was cooled to room temperature and quenched with saturated aqueous sodium bicarbonate (10 mL). The aqueous layer was extracted with ether (3 x 10 mL). The organic layer was washed with brine (10 mL) and dried with anhydrous sodium sulfate. After removal of the solvents *in vacuo*, flash chromatography on silica gel (7:3 (v/v) hexanes/EtOAc) afforded **4b** as a yellow oil (285 mg, 74 %): $[\alpha]_D$ 2.8° (*c* 0.93, EtOH); IR (neat) 3450, 2958, 2933, 2874, 1725, 1658, 1436, 1325, 1275, 1209, 1169 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500) δ 7.00 (dt, *J* = 15.5, 7.5 Hz, 1 H), 5.92 (dt, *J* = 15.5, 1.5 Hz, 1 H), 3.78 (m, 1 H), 3.74 (s, 3 H), 2.41 (m, 1 H), 2.33 (m, 1 H), 1.48 (m, 3 H), 1.36 (m, 1 H), 0.94 (t, *J* = 6.5 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.62, 145.41, 123.31, 70.19, 51.36, 40.10, 39.19, 18.68, 13.86; HRMS (CI) calcd for $[C_{17}H_{20}O_7 + H]^+$: 173.1178 Found: 173.1177.



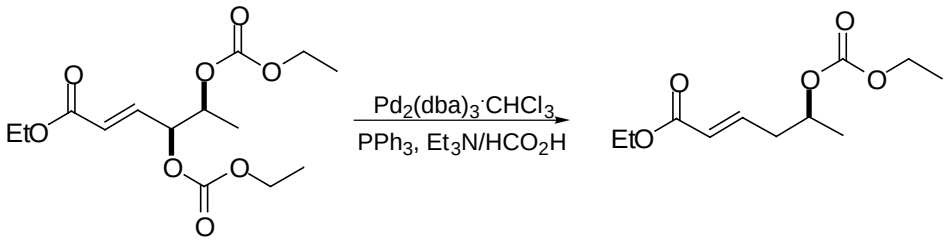
14c **4c**

Ethyl (5*R*)-5-Hydroxy-5-phenyl-2-pentenoate (4c): Following the procedure above, alcohol **14c** was produced (198 mg, 0.9 mmol) in 72% yield as a light yellow oil: $[\alpha]_D$ 10.4° (*c* 1.13, EtOH); IR (neat) 3250, 2981, 1706, 1700, 1603, 1494, 1198 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.34 (m, 5 H), 6.99 (dt, *J* = 15.6, 7.5 Hz, 1 H), 5.92 (dt, *J* = 15.9, 1.5, Hz, 1 H), 4.85 (ddd, *J* = 8.4, 5.1, 3.3 Hz, 1 H), 4.19 (q, *J* = 7.2 Hz, 2 H), 2.66 (m, 2 H), 2.02 (m, 1 H), 1.29 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 166.20, 144.56, 143.41, 128.49, 127.77, 125.62, 123.90, 72.98, 60.20, 41.77, 14.15; HRMS (CI) calcd for $[C_{13}H_{16}O_3 + H]^+$: 238.1443 Found: 238.1431.



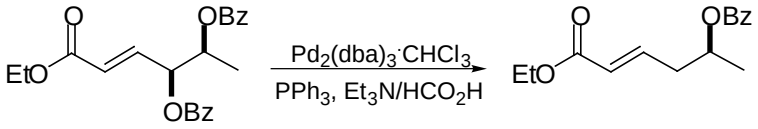
14a **4a**

Ethyl (5*S*)-5-hydroxy-2-hexenoate (4a): The procedure above was followed except that 0.75% $Pd_2(dba)_3{\cdot}CHCl_3$ was used. Alcohol **4a** was produced (4.32 g, 27.3 mmol) in 68% yield as a light yellow oil: IR (neat) 3425, 2976, 2933, 2906, 1721, 1656, 1449, 1370, 1321, 1267, 1217, 1177, 1118, 1043, 983; ^1H NMR ($CDCl_3$, 500 MHz) δ 6.96 (dt, *J* = 15.5, 7 Hz, 1 H), 5.90 (dd, *J* = 15.5, 1.5 Hz, 1 H), 4.18 (q, *J* = 7 Hz, 2 H), 3.96 (dq, *J* = 12, 6 Hz, 1 H), 2.36 (ddd, *J* = 7, 7, 1 Hz, 2 H), 1.77 (s, 1 H), 1.28 (t, *J* = 7 Hz, 3 H), 1.24 (d, *J* = 5.5 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.37, 144.98, 123.95, 66.74, 60.34, 41.85, 23.23, 14.26.



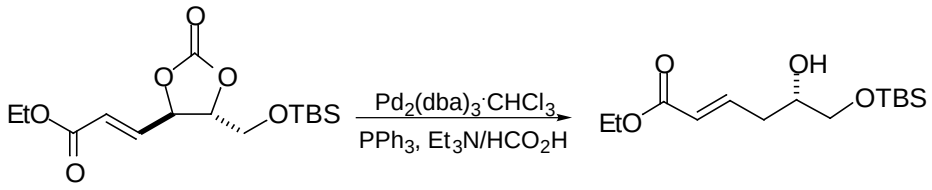
8 **10**

Ethyl (5*S*)-5-Ethoxycarbonyloxy-2-hexenoate (10): Following the procedure above(using 2.5% $Pd_2(dba)_3{\cdot}CHCl_3$), mono carobonate **10** was produced (24 mg, 0.10 mmol) in 43 % yield as a light yellow oil: $[\alpha]_D$ –13.6° (*c* 0.80, EtOH); IR (neat) 2983, 2938, 1742, 1722, 1658, 1623, 1466, 1448, 1373, 1320, 1260, 1181, 1136, 1097, 1048, 1008, 988 cm^{-1}, ^1H NMR ($CDCl_3$, 500 MHz) δ 6.89 (dt, *J* = 15.5, 7.5 Hz, 1 H), 5.89 (ddd, *J* = 15.5, 1.5, 1.5 Hz, 1 H), 4.87 (dq, *J* = 12, 6 Hz, 1 H), 4.18 (q, *J* = 7 Hz, 2 H), 4.18 (q, *J* = 6.5 Hz, 2 H), 2.54 (m, 1 H), 2.46 (m, 1 H), 1.30 (t, *J* = 6.5 Hz, 3 H), 1.28 (t, *J* = 6.5 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.09, 154.51, 143.00, 124.47. 73.06, 63.91, 60.34, 38.38, 19.65, 14.24, 14.23; HRMS (CI) calcd for $[C_{11}H_{18}O_5 + NH_4]^+$: 248.1498 Found: 248.1500.



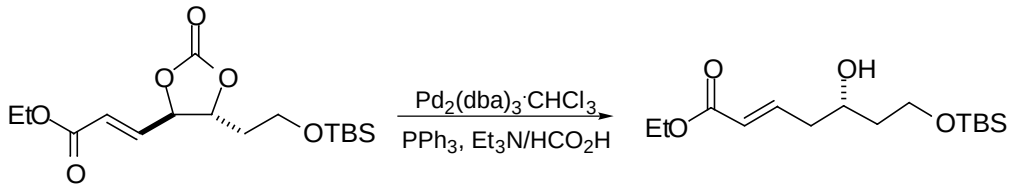
7 **6a**

(1*S*)-Benzoic acid 4-ethoxycarbonyl-1-methyl-but-3-enyl ester (6a): Following the procedure above(using 2.5% $Pd_2(dba)_3{\cdot}CHCl_3$), mono benzoate **6a** was produced (32 mg, 0.12 mmol) in 47 % yield as a light yellow oil: $[\alpha]_D$ 25.3° (*c* 0.80, EtOH); IR (neat) 3063, 2982, 2935, 1717, 1657, 1623, 1603, 1451, 1368, 1315, 1275, 1231, 1180, 1110, 1070 cm^{-1}, ^1H NMR ($CDCl_3$, 500 MHz) δ 8.03 (dd, *J* = 8.5, 1.5 Hz, 2 H), 7.43 (m, 3 H), 6.97 (dt, *J* = 15.5, 7.5 Hz, 1 H), 5.93 (ddd, *J* = 15.5, 1.5, 1.5 Hz, 1 H), 5.28 (dq, *J* = 12.5, 6 Hz, 1 H), 4.18 (q, *J* = 7 Hz, 2 H), 2.67-2.55 (m, 2 H), 1.39 (d, *J* = 6.5 Hz, 3 H), 1.28 (t, *J* = 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.16, 165.92, 143.41, 132.96, 130.52, 129.57, 128.41, 124.36, 69.81, 60.35, 38.52, 19.73, 14.24, 7.38; HRMS (CI) calcd for $[C_{15}H_{18}O_4 + NH_4]^+$: 280.1549 Found: 280.1553.



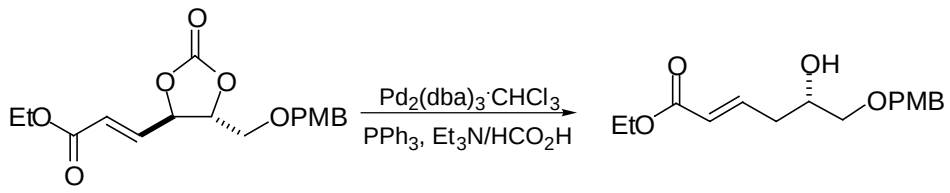
18a **19a**

Ethyl (5*S*)-6-(tert-Butyl-dimethyl-siloxy)-5-hydroxy-2-hexenoate (19a): Following the procedure above, alcohol **19a** was produced (779 mg, 2.7 mmol) in 88 % yield as a light yellow oil: $[\alpha]_D$ –12.8° (*c* 1.22, EtOH); IR (neat) 3464, 2955, 2930, 2858, 1722, 1656, 1472, 1463, 1368, 1320, 1258, 1206, 1165, 1122, 1045 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.02 (dt, *J* = 15.6, 7.2 Hz, 1 H), 5.94 (dt, *J* = 15.6, 1.2 Hz, 1 H), 4.22 (q, *J* = 7.2 Hz, 2 H), 3.87-3.78 (m, 1 H), 3.66 (dd, *J* = 9.9, 3.9 Hz, 1 H), 3.50 (dd, *J* = 9.9, 6.6 Hz, 1 H), 2.54 (dd, *J* = 4.5, 1.2 Hz, 1 H), 2.41 (ddd, *J* = 7.8, 6, 1.5 Hz, 1 H), 1.32 (t, *J* = 7.2 Hz, 3 H), 0.94 (s, 9 H), 0.11 (s, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.40, 144.63, 123.58, 70.47, 66.44, 60.16, 35.96, 25.79, 18.10, 14.20, -5.56; HRMS (CI) calcd for $[C_{14}H_{28}O_4Si + NH_4]^+$: 306.2101 Found: 306.2106.



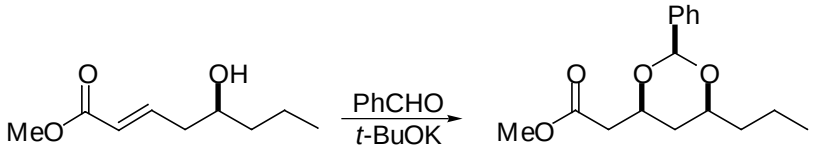
18b **19b**

Ethyl (5*S*)-7-(tert-Butyl-dimethyl-siloxy)-5-hydroxy-2-heptenoate (19b): The procedure above was followed except that 0.5 % of $Pd_2(dba)_3{\cdot}CHCl_3$ was used. Alcohol **19b** was produced (761 mg, 2.9 mmol) in 87% yield as a light yellow oil: $[\alpha]_D$ 2.6° (*c* 1.22, EtOH); IR (neat) 3499, 2929, 2858, 1722, 1654, 1472, 1464, 1368, 1319, 1258, 1164, 1090, 1045; ^1H NMR ($CDCl_3$, 500 MHz) δ 6.98 (dt, *J* = 15.5, 7.5 Hz, 1 H), 5.89 (dt, *J* = 15.5, 1.5, 1 H), 4.17 (q, *J* = 7.5 Hz, 2 H), 3.99 (m, 1 H), 3.90 (ddd, *J* = 10.5, 10, 5 Hz, 1 H), 3.81 (ddd, *J* = 10.5, 8, 4.5 Hz, 1 H), 2.38 (m, 2 H), 1.67 (m, 2 H), 1.28 (t, *J* = 7.5 Hz, 3 H), 0.87 (s, 9 H), 0.07 (s, 6 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.37, 145.26, 123.56, 71.00, 62.65, 60.22, 40.21, 37.73, 25.83, 18.10, 14.26, -5.56; HRMS (FAB) calcd for $[C_{15}H_{30}O_4Si + H]^+$: 303.1913 Found: 303.2015; Anal. Calcd for C, 59.56; H, 10.00; Found: C, 59.71; H, 9.95.



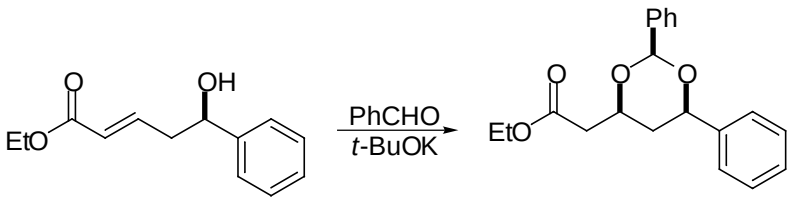
18c **19c**

Ethyl (5*S*)-5-Hydroxy-6-(4-methoxy-benzyloxy)-2-hexenoate (19c): Following the procedure above using 2.5 % $Pd_2(dba)_3 \cdot CHCl_3$, alcohol **19c** was produced (87 mg, 0.30 mmol) in 66 % yield as a light yellow oil: $[\alpha]_D$ –5.8° (*c* 1.50, EtOH); IR (neat) 3469, 2960, 2926, 2854, 1716, 1653, 1616, 1586, 1516, 1464, 1457, 1302, 1172, 1034 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.26 (d, *J* = 8 Hz, 2 H), 6.96 (dt, *J* = 16, 7 Hz, 1 H), 6.89 (d, *J* = 8.5 Hz, 2 H), 5.89 (dt, *J* = 15.5, 1.5 Hz, 1 H), 4.51 (s, 2 H), 4.19 (q, *J* = 7 Hz, 2 H), 3.94 (m, 1 H), 3.49 (dd, *J* = 9.5, 3.5 Hz, 1 H), 3.35 (dd, *J* = 9, 7 Hz, 1 H), 2.39 (m, 2 H), 1.29 (t, J = 7.5 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.28, 159.39, 144.47, 129.45, 123.81, 113.90, 73.38, 73.12, 69.20, 60.29, 55.28, 36.21, 29.72, 14.27; HRMS (CI) calcd for $[C_{16}H_{22}O_5 + NH_4]^+$: 312.1811 Found: 312.1822.



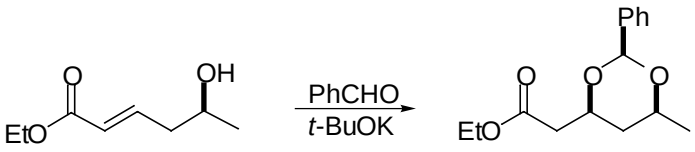
5b **3b**

(2*S*, 4*S*, 6*S*)-4-(carbomethoxymethyl)-2-phenyl-6-propyl-1,3-dioxane (3b): To a solution of alcohol **5b** (113 mg, 0.66 mmol) in 6 mL of THF at 0° C was added 73 μL (0.72 mmol) of benzaldehyde, followed by 8 mg (0.072 mmol) of *t*-BuOK. The solution was stirred for 15 min. The addition of benzaldehyde/*t*-BuOK was repeated 3 more times and the reaction was quenched with 5 mL of pH 7 phosphate buffer. The layers were separated, and the aqueous layer was extracted with ether (3 x 10 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by silica gel chromatography in 9:1 hexanes/ethyl acetate to produce 110 mg (0.40 mmol) of benzylidene protected diol **3b** in 60 % yield as a yellow oil: $[\alpha]_D$ 2.6° (*c* 1.25, EtOH); IR (neat) 3035, 2956, 2872, 1738, 1452, 1436, 1404, 1346, 1312, 1281, 1214, 1169, 1104, 1027 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.49 (m, 2 H), 7.33 (m, 3 H), 5.56 (s, 1 H), 4.31 (m, 1 H), 3.85 (m, 1 H), 3.71 (s, 3 H), 2.75 (dd, *J* = 15.6, 6.9 Hz, 1 H), 2.52 (dd, *J* = 15.6, 6.3 Hz, 1 H), 1.75-1.61 (m, 2 H), 1.54-1.41 (m, 4 H), 0.94 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.10, 138.54, 128.46, 128.02, 125.97, 100.48, 76.32, 73.13, 51.61, 40.74, 37.90, 36.52, 18.19, 13.96; HRMS (CI) calcd for $[C_{16}H_{22}O_4 + NH_4]^+$: 296.1862 Found: 296.1848.



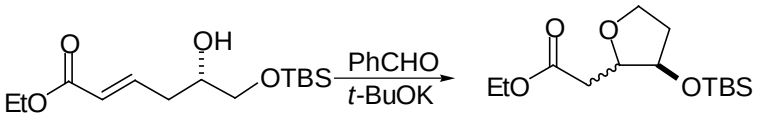
5c **3c**

(2*R*, 4*S*, 6*R*)-4-(carboethoxymethyl)-2,6-diphenyl-1,3-dioxane (3c): Following the procedure above, benzylidene protected diol **3c** was produced (55 mg, 0.17 mmol) in 50 % yield as a clear oil: $[\alpha]_D$ 41.4° (*c* 1.23, EtOH); IR (neat) 3064, 3034, 2983, 2915, 1956, 1883, 1733, 1496, 1456; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.56 (d, *J* = 8 Hz, 2 H), 7.43 (d, *J* = 7.5 Hz, 2 H), 7.39-7.30 (m, 6 H), 5.78 (s, 1 H), 4.95 (dd, *J* = 11, 2 Hz, 1 H), 4.50 (dddd, J = 11.5, 7, 6.5, 2.5 Hz, 1 H), 4.18 (q, J = 7 Hz, 2 H), 2.78 (dd, J = 16, 7 Hz, 1 H), 2.55 (dd, J = 15.5, 6.5 Hz), 2.01 (ddd, J = 13, 2.5, 2.5 Hz, 1 H), 1.27 (t, J = 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.56, 141.32, 138.36, 128.71, 128.40, 128.12, 127.74, 126.21, 125.82, 100.97, 78.48, 73.48, 60.62, 40.92, 38.68, 14.22; HRMS (CI) calcd for $[C_{20}H_{22}O_4 + NH_4]^+$: 344.1862 Found: 344.1856.



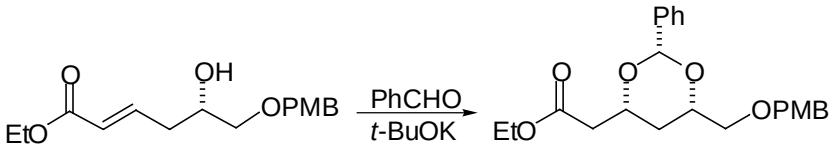
5a **3a**

(2S, 4S, 6S)-4-(carboethoxymethyl)-2-methyl-6-phenyl-1,3-dioxane (3a): Following the procedure above, benzylidene protected diol **3a** was produced (245 mg, 0.93 mmol) in 60 % yield as a clear oil: : IR (neat) 2978, 2873, 1733, 1639, 1602, 1452, 1376, 1344, 1323, 1256, 1227, 1180, 1152, 1102, 1054, 1027 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.49 (dd, *J* = 8, 2 Hz, 2 H), 7.37-7.30 (m, 3 H), 5.60 (s, 1 H), 4.31 (dddd, *J* = 11, 7, 6, 2.5 Hz, 1 H), 4.16 (q, *J* = 7.5 Hz, 2 H), 4.01 (ddq, *J* = 12, 6, 2 Hz, 1 H), 2.73 (dd, *J* = 16, 7 Hz, 1 H), 2.50 (dd, *J* = 15.5, 6.5 Hz, 1 H), 1.74 (ddd, *J* = 13, 2.5, 2.5 Hz, 1 H), 1.44 (ddd, *J* = 13.5, 11.5, 10.5 Hz, 1 H), 1.32 (d, *J* = 6 Hz, 3 H), 1.27 (t, *J* = 6.5 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 192.40, 170.80, 138.53, 129.76, 129.02, 126.17, 100.78, 73.24, 60.61, 41.00, 38.19, 21.64, 14.24; HRMS (CI) calcd for $[C_{15}H_{20}O_4 + NH_4]^+$: 282.1705 Found: 282.1701.



19a **20**

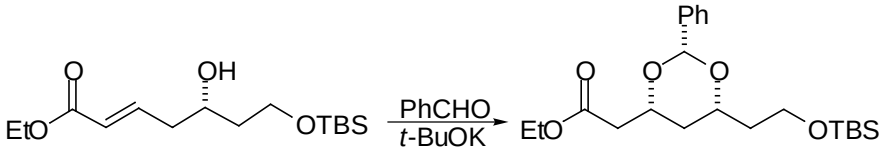
[3-(tert-Butyl-dimethyl-siloxy)-tetrahydro-furan-2-yl]-acetic acid ethyl ester (20): To a solution of alcohol **19a** (250 mg, 0.87 mmol) in 8 mL of THF at 0° C was added 97 μL (0.96 mmol) of benzaldehyde, followed by 10 mg (0.087 mmol) of *t*-BuOK. The solution was stirred for 15 min. The addition of benzaldehyde/*t*-BuOK was repeated once more until TLC showed no starting material left. The reaction was quenched with 10 mL of pH 7 phosphate buffer. The layers were separated, and the aqueous layer was extracted with ether (3 x 10 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by silica gel chromatography in 9:1 hexanes/ethyl acetate to produce 220 mg (0.76 mmol) of **20** in 88 % yield as a mixture of diastereomers. Less polar diastereomer: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.49-4.42 (m, 2 H), 4.15 (q, *J* = 7.5 Hz, 2 H), 3.99 (dd, *J* = 9.5, 5 Hz, 1 H), 3.61 (dd, *J* = 9, 2.5 Hz, 1 H), 2.58 (dd, *J* = 15, 7 Hz, 1 H), 2.48 (dd, *J* = 15.5, 6 Hz, 1 H), 2.00 (ddd, *J* = 12.5, 5.5, 1.5 Hz, 1 H), 1.66 (m, 1 H), 1.26 (t, *J* = 7.5 Hz, 3 H), 0.87 (s, 9 H), 0.46 (s, 6 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 171.12, 76.07, 74.43, 72.58, 60.50, 41.80, 40.39, 25.78, 18.04, 14.20, -4.76; More polar diastereomer: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.33 (m, 1 H), 4.36 (m, 1 H), 4.15 (q, *J* = 7 Hz, 2 H), 3.78 (m, 1 H), 3.75 (m,1 H), 2.77 (dd, *J* = 15.5, 7.5 Hz, 1 H), 2.59 (dd, *J* = 15.5, 7 Hz, 1 H), 2.27 (m, 1 H), 1.65 (m, 1 H), 1.26 (t, *J* = 7.5 Hz, 3 H), 0.86 (s, 9 H), 0.05 (s, 6 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 171.45, 75.58, 75.01, 72.59, 60.39, 41.11, 40.95, 25.78, 17.99, 14.21, -4.86.



19c **21**

(2*S*, 4*R*, 6*S*)-4-(carboethoxymethyl)-6-(methoxy-benzyloxymethyl)-2-phenyl-1,3-dioxane (21): Following the procedure above, benzylidene protected diol **21** was produced (41 mg, 0.10 mmol) in 51 % yield as a clear oil: $[\alpha]_D$ –6.3° (*c* 1.50, EtOH); IR (neat) 2912, 2858, 2056, 1956, 1881, 1732, 1613, 1586, 1514, 1455, 1344, 1302, 1248 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.49 (dd, *J* = 8, 2 Hz, 2 H), 7.38-7.32 (m, 3 H), 7.28 (d, *J* = 8 Hz, 2 H), 6.88 (d, *J* = 9 Hz, 2 H), 5.83 (s, 1 H), 4.55 (d, *J* = 18 Hz, 1 H), 4.52 (d, J = 18 Hz, 1 H), 4.34 (ddd, *J* = 11, 6.5, 2 Hz, 1 H), 4.16 (q, *J* = 7.5 Hz, 2 H), 4.12 (m, 1 H), 3.81 (s, 3 H), 3.64 (dd, *J* = 10, 5.5 Hz, 1 H), 3.51 (dd, *J* = 10.5, 4.5 Hz, 1 H), 2.73 (dd, *J* = 16, 7.5 Hz, 1 H), 2.52 (dd, *J* = 16, 6.5 Hz, 1 H), 1.78 (ddd, J = 13.5, 2.5, 2.5 Hz, 1 H), 1.52 (ddd, *J* = 12.5, 11.5, 11.5 Hz, 1 H), 1.27 (t, *J* = 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.65, 159.26, 138.26,130.21, 129.42, 128.73, 128.14, 126.19, 113.82,

100.73, 75.90, 73.20, 73.14, 72.46, 60.63, 55.29, 41.07, 33.31, 14.23; HRMS (FAB) calcd for $[C_{23}H_{28}O_6 + Na]^+$: 423.1784 Found: 423.1775.



19b **2**

(2*R*, 4*R*, 6*S*)-4-(carboethoxymethyl)-2-phenyl-6-[(tert-Butyl-dimethyl-siloxy)-ethyl]-1,3-dioxane (2): Following the procedure above, benzylidene protected diol **2** was produced (696 mg, 1.71 mmol) in 68 % yield as a clear oil: $[\alpha]_D$ 19.2° (*c* 1.46, EtOH); IR (neat) 3036, 2954, 2929, 2857, 1738, 1472, 1463, 1389, 1373, 1310, 1256, 1211, 1161, 1098, 1028 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.48 (dd, *J* = 8.5, 2 Hz, 2 H), 7.34 (m, 3 H), 5.56 (s, 1 H), 4.33 (dddd, *J* = 11.5, 7.5, 6.5, 2.5 Hz, 1 H), 4.17 (q, *J* = 7 Hz, 2 H), 4.06 (dddd, *J* = 10.5, 8, 4.5, 2.5 Hz, 1 H), 3.83 (ddd, *J* = 10, 9, 5 Hz, 1H), 3.73 (dt, *J* = 10, 5.5 Hz, 1 H), 2.73 (dd, *J* = 15.5, 7.5 Hz, 1 H), 2.51 (dd, 15, 6 Hz, 1 H), 1.84 (m, 1 H), 1.76-1.72 (m, 2 H), 1.48 (ddd, *J* = 12.5, 11.5, 10.5 Hz, 1 H), 1.27 (t, *J* = 7 Hz, 3 H), 0.90 (s, 9 H), 0.05 (s, 6 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.68, 138.55, 128.50, 128.04, 125.99, 100.49, 73.27, 60.53, 58.76, 41.05, 38.87, 36.68, 25.93, 18.31, 14.20, -5.56; HRMS (FAB) calcd for $[C_{22}H_{36}O_5 + H]^+$: 409.2410 Found: 409.2394.