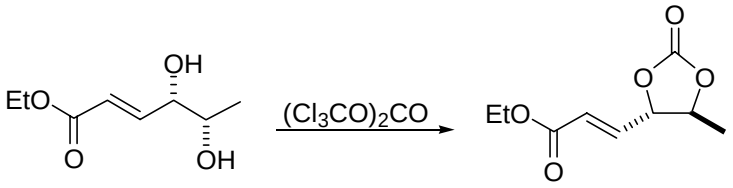
Experimental Section

Materials and Methods. Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on Varian VXR-300 (300 MHz) or Varian VXR-500 (500 MHz) spectrometers. Chemical shifts are reported relative to internal tetramethylsilane (δ 0.00 ppm) or residual solvent signal. Infrared (IR) spectra were obtained on a Prospect MIDAC FT-IR spectrometer. Optical rotations were measured with a Jasco DIP-370 digital polarimeter in the solvent specified. Flash column chromatography was performed on ICN reagent 60 (60-200 mesh) silica gel. Analytical thin-layer chromatography was performed with precoated glass-backed plates (Whatman K6F 60Å, F_{254}) and visualized by quenching of fluorescence and by charring after treatment with *p*-anisaldehyde or potassium permanganate stain. R_f values are obtained by elution in the stated solvent ratios (v/v). Combustion analysis was performed by M-H-W Laboratories, Phoenix, AZ. Ether and THF were distilled from benzophenone and sodium metal. Methylene chloride and triethylamine were distilled from calcium hydride. Unless otherwise noted, solvents were reagent grade and were used without purification. Commercial reagents were used without purification unless otherwise noted.

4a **6**

Ethyl (4*S*, 5*S*)-4,5-dihydroxy-2-hexenoate (6): Into a 250 mL round bottom flask was added 60 mL of *t*-BuOH, 60 mL of water, $K_3Fe(CN)_6$ (49.35 g, 150 mmol), K_2CO_3 (20.70 g, 150 mmol), $MeSO_2NH_2$ (4.75 g, 50 mmol), $(DHQ)_2$-PHAL (390 mg, 0.50 mmol), and OsO_4 (51 mg, 0.20 mmol). The mixture was stirred at room temperature for about 15 minutes and then cooled to 0°C. To this solution was added dienoate **4a** (7.00 g, 50 mmol) and the reaction was stirred vigorously at 0°C overnight. The reaction was quenched with sat. aqueous sodium sulfite (40 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 6.18 g (71 % yield) of **6** 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), 1.24 (d, *J* = 6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.82, 146.90, 122.59, 75.67, 70.23, 60.68, 19.13, 14.21. The enantiomeric excess of compound

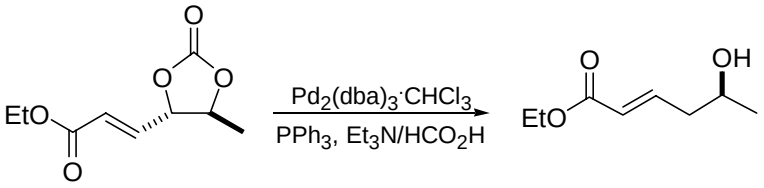
6 was determined by HPLC analysis (Chiralcel OD column), using 8% iPrOH in Hexane at 0.8 mL/min. Retention time (min): *R, R* = 19.3, *S, S* = 24.1.



6 **7**

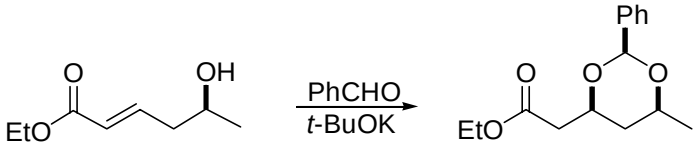
(4*S*, 5*S*)-3-(5-Methyl-2-oxo-[1,3]dioxolan-4-yl)-acrylic acid ethyl ester (7): Into a 250 mL round-bottom flask was placed 9.38 g (31.6 mmol) of triphosgene, 100 mL of dichloromethane, and 10 mL of pyridine. The solution was cooled to 0 °C and 5.50 g (31.6 mmol) of **6** in 40 mL of dichloromethane 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 30 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 **7** as a clear, colorless oil (5.5 g, 87%): $[\alpha]_D$ -21.3° (*c* 2.30, CH_2Cl_2); IR (neat) 2986, 1809, 1722, 1368, 1304, 1271, 1190, 1032 cm^{-1}; ^1H 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. The enantiomeric excess of compound **7** was determined by HPLC

analysis (Chiralcel OD column), using 8% iPrOH in Hexane at 0.8 mL/min. Retention time (min): *S, S* = 18.1, *R, R* = 20.4.



7 **8**

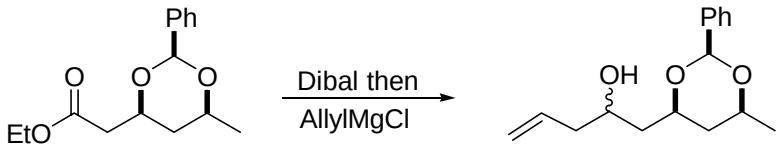
Ethyl (5*S*)-5-hydroxy-2-hexenoate (8): Into a 100 mL, round bottomed flask fitted with a condenser and maintained under nitrogen was placed 1.50 g (7.5 mmol) of **7**, 78 mg (0.075 mmol) of $Pd_2(dba)_3{\cdot}CHCl_3$, 49 mg (0.188 mmol) of PPh_3, and 25 mL of THF. Triethylamine (3.1 mL, 22.5 mmol) and formic acid (0.85 mL, 22.5 mmol) were added and the mixture was allowed to reflux for three hours. The reaction was cooled to room temperature and quenched with saturated aqueous sodium bicarbonate (15 mL). The aqueous layer was extracted with ether (3 x 15 mL). The organic layer was washed with brine (15 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 **8** as a yellow oil (1.08 g, 89 %): IR (neat) 3425, 2976, 2933, 2906, 1721, 1656, 1449, 1370, 1321, 1267, 1217, 1177, 1118, 1043, 983; ^{1}H 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. The enantiomeric excess of compound **8** was determined by conversion of the alcohol to the corresponding Mosher ester and analysis of the ^{19}F NMR.



8 **5a**

(2S, 4S, 6S)-4-(carboethoxymethyl)-2-methyl-6-phenyl-1,3-dioxane (5a): To a solution of alcohol **8** (940 mg, 5.95 mmol) in 60 mL of THF at 0° C was added 0.66 mL (6.5 mmol) of benzaldehyde, followed by 67 mg (0.60 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 30 mL of pH 7 phosphate buffer. The layers were separated, and the aqueous layer was extracted with ether (3 x 30 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, benzylidene protected diol **5a** (1.01 g) in 64 % 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}; ^1H 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.



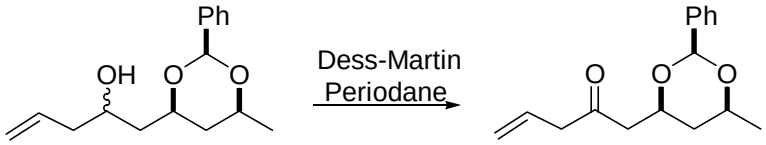
5a **10a + 10b**

(2S, 4S, 6S)-4-(pent-4-en-2-ol)-2-methyl-6-phenyl-1,3-dioxane (10): Into a 5 mL round bottomed flask was added 50 mg of the ester and 1 mL of CH_2Cl_2. This solution was cooled to –78 °C and 0.42 mL (0.42 mmol) of DIBAL (1M solution in hexanes) was added. After 30 minutes, 0.29 mL (0.57 mmol) of allylmagnesium chloride (2M solution in THF) was added. The reaction was allowed to warm to room temperature and stirred for 45 minutes after which 1 mL of a 20% sodium potassium tartrate solution was added. This solution was stirred vigorously until the layers separated rapidly upon cessation of stirring. The aqueous layer was extracted with CH_2Cl_2 (3 x 1 mL). The organic layers were combined and washed with brine and dried over anhydrous sodium sulfate. Removal of the solvents in vacuo followed by passage through a short pad of silica gel yielded the alcohol (45 mg, 91%) as a clear oil and a mixture of diastereomers.

Spectroscopic data for the ***syn*** diastereomer: $[\alpha]_D$ 24.9° (*c* 1.68, CH_2Cl_2); IR (neat) 3500, 3071, 3035, 2974, 2939, 2912, 2862, 1641, 1497, 1452, 1403, 1376, 1339 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.47 (dd, *J* = 8, 1.5 Hz, 2H), 7.34 (m, 3H), 5.90 (dddd, *J* = 17.5, 10, 7, 7 Hz, 1H), 5.57 (s, 1H), 5.12 (m, 2H), 4.12 (dddd, *J* = 11.5, 9, 3.5, 2.5 Hz, 1H), 3.98 (m, 2H), 3.12 (s, 1H), 2.26 (m, 2H), 1.79 (ddd, *J* = 15, 9.5, 9 Hz, 1H), 1.71 (ddd, *J* = 14, 4, 3 Hz, 1H), 1.64 (ddd, *J* = 13.5, 2.5, 2.5 Hz, 1H), 1.49 (ddd, *J* = 13.5,

11.5, 11 Hz, 1H), 1.32 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 138.26, 134.76, 128.86, 128.33, 126.08, 117.62, 100.84, 76.64, 73.06, 70.39, 41.99, 41.94, 38.73, 21.62; HRMS (CI) calcd for $[C_{16}H_{22}O_3 + H]^+$: 263.1649 Found: 263.1653.

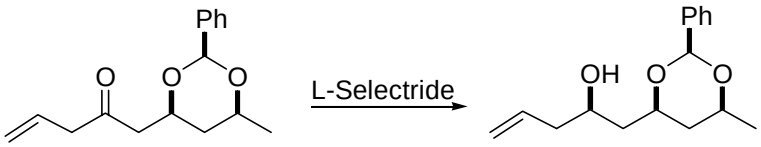
Spectroscopic data for the ***anti*** diastereomer: $[\alpha]_D$ 26.3° (*c* 0.68, CH_2Cl_2); IR (neat) 3460, 2973, 2938, 2911, 2864, 1641, 1452, 1428, 1405, 1373, 1341 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.50 (d, *J* = 8, 2H), 7.35 (m, 3H), 5.84 (dddd, *J* = 17, 10.5, 7, 7 Hz, 1H), 5.55 (s, 1H), 5.14 (m, 2H), 4.17 (dddd, *J* = 11, 8, 3, 3 Hz, 1H), 4.01 (m, 2H), 2.26 (m, 2H), 1.79 (ddd, *J* = 14.5, 8, 2.5 Hz, 1H), 1.69 (ddd, *J* = 14.5, 9, 3 Hz, 1H), 1.58 (m, 2H), 1.52 (ddd, *J* = 13, 10.5, 10.5 Hz, 1H), 1.32 (d, *J* = 6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 138.69, 134.75, 128.71, 128.26, 126.13, 118.01, 100.87, 74.18, 73.09, 67.06, 42.28, 42.08, 38.57, 21.69.



10a + 10b **11**

1-(6-Methyl-2-phenyl-[1,3]dioxan-4-yl)-pent-4-en-2-one (11): Into a 10 mL round bottomed flask was placed 19 mg alcohol in 1 mL of CH_2Cl_2. To this solution was added 37 mg (0.087 mmol) of Dess-Martin periodane. The reaction was stirred for 1.5 hours. Ether was added to the reaction and the solution was filtered through a pad of silica gel to yield 17 mg (90% yield) of ketone as a yellow, low melting solid. $[\alpha]_D$ 17.2° (*c* 0.98, CH_2Cl_2); IR (neat) 2974, 2932, 2911, 2870, 1717, 1637, 1456, 1376, 1343 cm^{-1}; ^{1}H

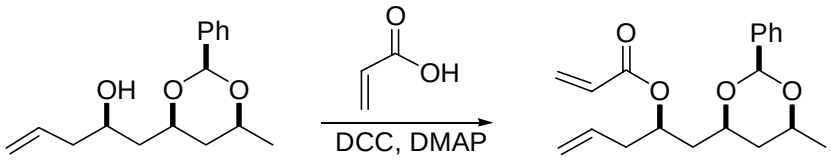
NMR ($CDCl_3$, 500 MHz) δ 7.48 (d, *J* = 7 Hz, 2H), 7.36 (m, 3H), 5.90 (ddt, *J* = 17.5, 11, 7 Hz, 1H), 5.55 (s, 1H), 5.20 (dd, *J* = 10, 1 Hz, 1H), 5.15 (ddd, *J* = 17, 3, 1.5 Hz, 1H), 4.34 (dddd, *J* = 12, 7, 7, 3 Hz, 1H), 4.00 (ddq, *J* = 12.5, 6, 2 Hz, 1H), 3.24 (ddd, *J* = 7, 3, 1.5 Hz, 2H), 2.90 (dd, *J* = 17, 7 Hz, 1H), 2.58 (dd, *J* = 17, 6 Hz, 1H), 1.72 (ddd, *J* = 13, 3, 3 Hz, 1H), 1.41 (ddd, *J* = 13.5, 11.5, 10 Hz, 1H), 1.32 (d, *J* = 7Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 206.47, 138.49, 130.15, 128.70, 128.22, 126.10, 119.16, 100.78, 72.99, 72.86, 48.87, 48.14, 38.41, 21.61; HRMS (CI) calcd for $[C_{16}H_{20}O_3 + H]^+$: 261.1491 Found: 261.1486.



11 **10a**

(2S, 4S, 6S)-4-(pent-4-en-2-ol)-2-methyl-6-phenyl-1,3-dioxane (10a): To a solution of ketone (20 mg, 0.08 mmol) in THF (1 mL) at -90°C was added a 1.0M solution of L-selectride in THF (0.16 mL, 0.16 mmol). After stirring for 3 h a solution of 30% H_2O_2 and 1 M NaOH was added and the reaction was allowed to warm to room temperature and diluted with Et_2O. The organic layer was separated, washed with a saturated solution of sodium thiosulfate, brine, and then dried (Na_2SO_4), filtered, and concentrated. The crude material was purified by flash chromatography (9:1 (v/v) hexanes/EtOAc) to provide 17.5 mg (87%) of a clear oil as a separable mixture (7:1) of diastereomers. $[\alpha]_D$ 24.9° (*c* 1.68, CH_2Cl_2); IR (neat) 3500, 3071, 3035, 2974, 2939, 2912, 2862, 1641, 1497, 1452, 1403, 1376, 1339 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.47 (dd, *J* = 8, 1.5 Hz,

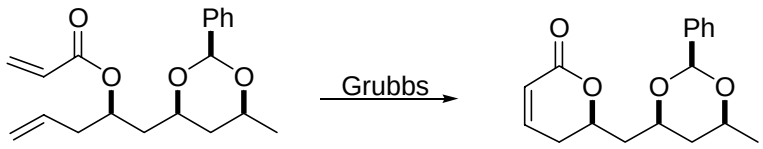
2H), 7.34 (m, 3H), 5.90 (dddd, J = 17.5, 10, 7, 7 Hz, 1H), 5.57 (s, 1H), 5.12 (m, 2H), 4.12 (m, 1H), 3.98 (m, 2H), 3.12 (s, 1H), 2.26 (m, 2H), 1.79 (ddd, J = 15, 9.5, 9 Hz, 1H), 1.71 (ddd, J = 14, 4, 3 Hz, 1H), 1.64 (ddd, J = 13.5, 2.5, 2.5 Hz, 1H), 1.49 (ddd, J = 13.5, 11.5, 11 Hz, 1H), 1.32 (d, J = 6.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 138.26, 134.76, 128.86, 128.33, 126.08, 117.62, 100.84, 76.64, 73.06, 70.39, 41.99, 41.94, 38.73, 21.62; HRMS (CI) calcd for $[C_{16}H_{22}O_3 + H]^+$: 263.1649 Found: 263.1653.



10a **12**

Acrylate ester (12): To the alcohol (20 mg, 0.077 mmol) in anhydrous CH_2Cl_2 (1.5 mL) was added acrylic acid (22 μL, 0.32 mmol) followed by DCC (66mg, 0.32 mmol) and 1 mg of DMAP. The reaction was stirred at room temperature and after 4 h, diluted with ether (1 mL), filtered through a glass wool plug, and washed successively with aq. $NaHSO_4$, saturated aqueous $NaHCO_3$, and brine. The organic layer was dried ($NaSO_4$) and evaporated to yield crude ester. The product was purified with flash chromatography (9:1 (v/v) hexanes/EtOAc) to yield ester **12** as a clear oil (20 mg, 83%). $[\alpha]_D$ 4.6° (*c* 1.25, $CHCl_3$); IR (neat) 3071, 3036, 2974, 2919, 2856, 1722, 1638, 1620, 1453, 1442, 1405 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.49 (dd, J = 8, 2 Hz, 2H), 7.34 (m, 3H), 6.38 (dd, J = 17, 1.5 Hz, 1H), 6.09 (dd, J = 17, 10 Hz, 1H), 5.79 (dd, J = 10.5, 1.5 Hz, 1H), 5.78 (dddd, J = 17, 10, 7, 7 Hz, 1H), 5.49 (s, 1H), 5.22 (dddd, J = 9, 6.5, 6, 4 Hz, 1H),

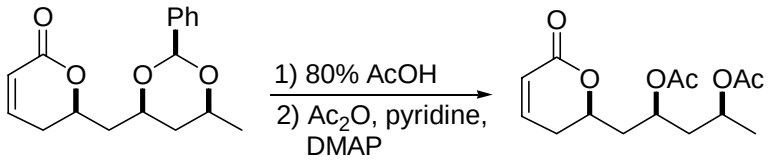
5.10 (m, 2H), 3.93 (m, 2H), 2.42 (m, 2H), 2.08 (ddd, *J* = 14.5, 8.5, 6.5 Hz, 1H), 1.81 (ddd, *J* = 14, 6, 4 Hz, 1H), 1.71 (ddd, *J* = 13, 2.5, 2.5 Hz, 1H), 1.39 (ddd, *J* = 13, 11,11 Hz, 1H), 1.31 (d, *J* = 6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 165.80, 138.63, 133.25, 130.75, 128.65, 128.62, 128.20, 126.22, 118.26, 100.83, 73.98, 72.94, 70.32, 39.77, 39.02, 38.41, 21.70; HRMS (CI) calcd for $[C_{19}H_{24}O_4 + H]^+$: 317.1753 Found: 317.1765.



12 **13**

α, β- Unsaturated Lactone (13): To the acrylate ester (25 mg, 0.085 mmol) in CH_2Cl_2 (5 mL) was added Grubbs' catalyst (1.8 mg, 2.1 μmol). The reaction was allowed to reflux and after five hours the solvent was removed and the crude product was purified with silica gel chromatography (4:1 (v/v) hexanes/EtOAc) to yield lactone **13** as a yellow oil (21 mg, 86%). $[\alpha]_D$ 69.8° (*c* 1.05, $CHCl_3$); IR (neat) 2971, 2924, 2867, 1721, 1496, 1453, 1392, 1380, 1342, 1312, 1247, 1217 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.48 (m, 2H), 7.35 (m, 3H), 6.89 (ddd, *J* = 9.5, 6, 2.5 Hz, 1H), 6.03 (dd, *J* = 9.5, 2 Hz, 1H), 5.54 (s, 1H), 4.68 (dddd, *J* = 12, 6, 6, 4 Hz, 1H), 4.16 (dddd, *J* = 10, 7.5, 5.5, 2.5 Hz, 1H), 3.99 (ddq, *J* = 12, 6, 2 Hz, 1H), 2.51 (dddd, *J* = 18.5, 11.5, 2.5, 2.5 Hz, 1H), 2.41 (ddd, *J* = 18.5, 5.5, 4.5 Hz, 1H), 2.21 (ddd, *J* = 14, 7, 7 Hz, 1H), 1.93 (ddd, *J* = 14, 5.5, 5.5 Hz, 1H), 1.69 (ddd, *J* = 13, 2.5, 2.5 Hz, 1H), 1.49 (ddd, *J* = 13, 11, 11 Hz, 1H), 1.32 (d, *J* = 6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 164.36, 145.36, 138.56, 128.77, 128.27, 126.13,

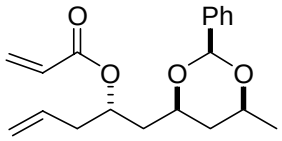
121.27, 100.78. 74.61, 72.99, 72.56, 40.31, 38.18, 29.31, 21.68; HRMS (CI) calcd for $[C_{17}H_{20}O_4 + H]^+$: 289.1440 Found: 289.1445.



13 **1**

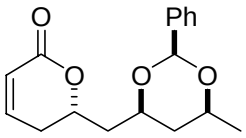
Cryptocarya Diacetate (1): The α, β-unsaturated lactone (20 mg, 0.069 mmol) was added to 3 mL of an 80% solution of AcOH. The reaction was heated to 60°C. After three hours, the solvent was evaporated and the resulting diol was added to CH_2Cl_2 (1 mL), Ac_2O (0.1 mL, 1.1 mmol), pyridine (0.2 mL), and a catalytic amount of DMAP. The reaction was stirred for an hour, after which 1 mL of a saturated solution of sodium bicarbonate was added. The layers were separated and the aqueous layer was extracted with ether (3 x 1 mL). The organic layers were combined and dried over anhydrous $NaSO_4$. The solvent was removed and the crude product was purified by silica gel chromatography (4:1 (v/v) hexanes/EtOAc) to yield cryptocarya diacetate as a clear oil (15 mg, 77%). $[\alpha]_D$ 47.5° (*c* 0.6, $CHCl_3$); lit[2] $[\alpha]_D$ 55.8° (*c* 1.06, $CHCl_3$); IR (neat) 2979, 1731, 1434, 1372, 1238, 1037 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.91 (ddd, *J* = 9.5, 6, 2.5 Hz, 1H), 6.06 (ddd, *J* = 9.5, 2.5, 1 Hz, 1H), 5.14 (dddd, *J* = 8.5, 7, 6, 4 Hz, 1H), 5.03 (ddq, *J* = 7, 6.5, 6.5 Hz, 1H), 4.54 (ddd, *J* = 11.5, 6.5, 6.5, 4 Hz, 1H), 2.50 (ddd, *J* = 18, 6, 5, 1 Hz, 1H), 2.35 (dddd, *J* = 18, 11.5, 2.5, 2.5 Hz, 1H), 2.21 (ddd, *J* = 14.5, 8.5, 6.5 Hz, 1H), 2.13 (s, 3H), 2.08 (s, 3H), 2.05 (ddd, *J* = 14.5, 7, 7 Hz, 1H), 1.99 (ddd, *J* = 14.5, 6.5, 4 Hz, 1H), 1.83 (ddd, *J* = 14.5, 6, 6 Hz, 1H), 1.30 (d, *J* = 6.5 Hz, 3H);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.53, 170.40, 163.62, 144.53, 121.38, 74.85, 67.75, 67.68, 40.46, 39.18, 29.19, 21.24, 21.10, 20.13.



14

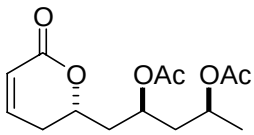
Acrylate Ester (14): $[\alpha]_D$ 47.3° (*c* 1.0, $CHCl_3$); IR (neat) 3078, 3038, 2974, 2977, 2934, 2860, 1729, 1640, 1622, 1456, 1407 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.50 (m, 2H), 7.34 (m, 3H), 6.41 (dd, *J* = 17, 1.5 Hz, 1H), 6.12 (dd, *J* = 17, 10.5 Hz, 1H), 5.83 (dd, *J* = 10.5, 1.5 Hz, 1H), 5.77 (m, 1H), 5.48 (s, 1H), 5.36 (dddd, *J* = 9, 6, 6, 3 Hz, 1H), 5.08 (m, 2H), 4.00-3.82 (m, 2H), 2.41 (m, 2H), 1.94-1.73 (m, 2H), 1.57 (ddd, *J* = 13, 3, 3 Hz, 1H), 1.42 (ddd, *J* = 13, 11,11 Hz, 1H), 1.31 (d, *J* = 6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 165.56, 138.64, 133.26, 130.41, 128.72, 128.39, 128.05, 125.99, 117.93, 100.37, 73.35, 72.78, 70.19, 40.15, 39.21, 38.90, 21.61; HRMS (CI) calcd for $[C_{19}H_{24}O_4 + H]^+$: 317.1753 Found: 317.1738.



15

α, β- Unsaturated Lactone (15): $[\alpha]_D$ 20.1° (*c* 0.9, $CHCl_3$); IR (thin film) 2971, 2919, 2854, 1722, 1454, 1393, 1378, 1342, 1312, 1251, 1216 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.49 (m, 2H), 7.35 (m, 3H), 6.88 (ddd, *J* = 9, 6, 2 Hz, 1H), 6.04 (ddd, *J* = 10, 2.5, 1.5 Hz, 1H), 5.58 (s, 1H), 4.79 (dddd, *J* = 10, 10, 5, 2.5 Hz, 1H), 4.25 (dddd, *J* =

10.5, 10.5, 2.5, 2.5 Hz, 1H), 4.00 (ddq, *J* = 12, 5.5, 1.5 Hz, 1H), 2.41-2.30 (m, 2H), 1.95 (ddd, *J* = 14.5, 10, 2.5 Hz, 1H), 1.87 (ddd, *J* = 14.5, 10, 2.5 Hz, 1H), 1.63 (ddd, *J* = 13.5, 2.5, 2.5 Hz, 1H), 1.43 (ddd, *J* = 13, 11, 11 Hz, 1H), 1.33 (d, *J* = 6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 164.42, 145.21, 138.64, 128.75, 128.26, 126.17, 121.42, 100.69. 74.04, 72.91, 72.00, 41.56, 38.89, 29.92, 21.68; HRMS (CI) calcd for $[C_{17}H_{20}O_4 + H]^+$: 289.1440 Found: 289.1461.



16

5-*epi*-Cryptocarya Diacetate (16): $[\alpha]_D$ –35.6° (*c* 0.75, $CHCl_3$); IR (neat) 2978, 2927, 1731, 1434, 1384, 1229, 1019 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.91 (ddd, *J* = 10, 4.5, 3.5 Hz, 1H), 6.06 (ddd, *J* = 10, 2, 2 Hz, 1H), 5.23 (dddd, *J* = 9, 7, 5.5, 3.5 Hz, 1H), 5.03 (ddq, *J* = 6, 6, 6 Hz, 1H), 4.53 (ddd, *J* = 9, 9, 6, 3.5 Hz, 1H), 2.39 (m, 2H), 2.15-2.02 (m, 2H), 2.09 (s, 3H), 2.08 (s, 3H), 1.92 (ddd, *J* = 14.5, 9, 3 Hz, 1H), 1.81 (ddd, *J* = 14, 6, 6 Hz, 1H), 1.30 (d, *J* = 6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.38, 170.21, 163.44, 144.34, 121.52, 74.46, 67.89, 67.61, 40.47, 39.62, 29.57, 21.26, 21.09, 20.07; HRMS (CI) calcd for $[C_{14}H_{20}O_6 + H]^+$: 285.1338 Found: 285.1334.