Supporting Information

“De novo synthesis of 2-substituted *syn* 1,3-diols via an iterative asymmetric hydration strategy”

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General Methods and Materials. ^1H and ^{13}C NMR spectra were recorded on a 600 MHz spectrometer. Chemical shifts are reported relative to internal tetramethylsilane (δ 0.00 ppm) or CDCl_3 (δ 7.26 ppm) for ^1H and CDCl_3 (δ 77.0 ppm) for ^{13}C . Infrared (IR) spectra were obtained on a FT-IR spectrometer. Optical rotations were measured with a digital polarimeter in the solvent specified. Melting points were determined with a standard melting point apparatus and are uncorrected. Flash column chromatography was performed on 60-200 mesh silica gel. Analytical thin-layer chromatography was performed with precoated glass-backed plates and visualized by quenching of fluorescence and by charring after treatment with *p*-anisaldehyde or phosphomolybdic acid or potassium permanganate stain. R_f values are obtained by elution in the stated solvent ratios (v/v). Ether, THF, Methylene chloride and triethylamine were dried by passing through activated alumina column with argon gas pressure. Commercial reagents were used without purification unless otherwise noted. Air and/ or moisture- sensitive reactions were carried out under an atmosphere of argon/nitrogen using oven-dried glassware and standard syringe/septa techniques.

HPLC procedures: HPLC analyses were carried out using a chiral column eluting (flow rate = 1.0 mL/min) with Argon-degassed HPLC grade solvents. Detection was done by UV. Specifically, diol **11b** was analyzed using hexane:EtOH (97:3). Enantiomeric excess of diol **11a** was determined via the HPLC analysis of the resulting homoallylic alcohol **14a** using hexane:EtOH (97:3). Enantiomeric excess of diol **7b** was determined via the HPLC analysis of the resulting homoallylic alcohol **8b** using hexane:EtOH (98:2). Diol **17** was analyzed using hexane:*i*PrOH (97:3). Enantiomeric excess of diol **7a** was

determined via the HPLC analysis of the resulting homoallylic alcohol **8a** using hexane:EtOH (98:2). Enantiomeric excess of diol **11c** was determined via the HPLC analysis of the resulting carbonate **13c** using hexane:*i*PrOH (97:3).

(2E,4E)-Ethyl 7-(*tert*-butyldimethylsilyloxy)-4-methylhepta-2,4-dienoate (6a)

To a flask containing enal (500 mg, 2.19 mmol) in dry CH₂Cl₂ (3.1 mL) was added (carboethoxymethylene)triphenylphosphorane (838 mg, 2.40 mmol) in one portion. The reaction was allowed to stir at RT overnight until determined complete by TLC (UV, anisaldehyde). The solvent was then removed *en vacuo* and the crude mixture was immediately subjected to flash column chromatography (5% EtOAc/Hexanes) to yield 489 mg (75%) of dienoate as a clear oil. Spectral data agreed satisfactorily with literature, see Wang, J.; Hsung, R. P.; Ghosh, S. K. *Org. Lett.* **2004**, 6, 1939-1942.

(2E,4E)-Ethyl 7-(benzyloxy)-4-methylhepta-2,4-dienoate (6b). To a flask containing enal (500 mg, 2.19 mmol) in dry CH₂Cl₂ (3.1 mL) was added (carboethoxymethylene)triphenylphosphorane (838 mg, 2.40 mmol) in one portion. The reaction was allowed to stir at RT overnight until determined complete by TLC (UV, anisaldehyde). The solvent was then removed *en vacuo* and the crude mixture was

immediately subjected to flash column chromatography (5% EtOAc/hexanes) to yield dienoate in 69% as a clear, colorless oil. $R_f = 0.50$ (4:1 hexanes:EtOAc); IR (neat, cm^{-1}) 2934, 1716, 1622, 1463, 1447, 1366, 1267, 1102, 1037, 983; ^1H NMR (CDCl_3 , 600 MHz) δ 7.33 (m, 4H), 7.30 (d, $J = 15.6$ Hz, 1H), 7.28 (m, 1H), 5.93 (t, $J = 7.2$ Hz, 1H), 5.81 (d, $J = 15.6$ Hz, 1H), 4.52 (s, 2H), 4.21 (q, $J = 7.2$ Hz, 2 H), 3.54 (t, $J = 7.2$ Hz, 2H), 2.53 (dt, $J = 7.2, 7.2$ Hz, 2H), 1.79 (s, 3H), 1.30 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 167.4, 149.1, 138.2, 137.7, 134.3, 128.3 (2C), 127.6 (3C), 116.0, 73.0, 69.0, 60.1, 29.5, 14.3, 12.2; HRMS (ESI) calcd for $[\text{C}_{17}\text{H}_{22}\text{O}_3]^+$: 274.1563, Found: 274.1568.

(2E,4E)-Ethyl 4,7-dimethylocta-2,4-dienoate (10a). The corresponding allylic alcohol (858 mg, 6.50 mmol) was placed in a RBF with CH_2Cl_2 (10 mL) followed by addition of 1 equivalent of (carboethoxymethylene)-triphenylphosphorane (2.26 g, 6.50 mmol) in one portion. Next was added 5 mass equivalents of MnO_2 (4.29 g). The reaction was allowed to stir for 3 days at RT. The reaction was then filtered through a plug of celite and the solvent was removed *en vacuo*. The crude mixture was immediately subjected to flash column chromatography on silica gel (10% EtOAc/hexanes) to yield 945 mg (75%) of dienoate as a clear colorless oil. $R_f = 0.60$ (4:1 hexanes:EtOAc); IR (neat, cm^{-1}) 2956, 2870, 1709, 1621, 1465, 1392, 1366, 1301, 1267, 1160, 1095, 1035, 981, 850, 791; ^1H NMR (CDCl_3 , 600 MHz) δ 7.33 (d, $J = 16.2$ Hz, 1H), 5.92 (t, $J = 7.2$ Hz, 1H), 5.78 (d, $J = 16.2$ Hz, 1H), 4.20 (q, $J = 7.2$ Hz, 2H), 2.08 (s, $J = 7.2$ Hz, 2H), 1.76 (s, 3H), 1.71 (septuplet, $J = 6.6$ Hz, 1H), 1.29 (t, $J = 7.2$ Hz, 3H), 0.91 (d, $J = 6.6$ Hz, 6H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 167.6, 149.6, 141.2, 133.3,

115.4, 60.1, 37.8, 28.6, 22.4 (2C), 14.3, 12.2; HRMS (ESI) calcd for $[C_{12}H_{21}O_2]^+$:

197.1536, Found: 197.1541.

(2E,4E)-Ethyl 4,6-dimethylhepta-2,4-dienoate (10b). Allylic alcohol (7.0 g, 61 mmol) was added to a RBF in CH_2Cl_2 (120 mL) followed by addition of 10 mass equivalents of activated MnO_2 (70 g). The reaction was allowed to stir for 24 hours at RT when determined complete by TLC (UV, $KMnO_4$). The reaction mixture was then filtered through celite and concentrated to approximately 100 mL. The reaction mixture was again placed under an inert atmosphere and 10 mol% trifluoroacetic acid (528 μ L, 6.1 mmol) was added via syringe. This isomerization was allowed to take place for 18 hours when determined complete (1H NMR). The TFA in the flask was quenched using sat. aqueous $NaHCO_3$ and the mixture was washed with brine and dried over Na_2SO_4 . The crude mixture was then filtered back into a flask and 1.1 equivalents of (carboethoxymethylene)triphenylphosphorane (22.7 g, 67 mmol) was added to the flask in one portion. The mixture was allowed to stir at RT for 2 days until determined complete by TLC (UV, anisaldehyde stain). The crude mixture was concentrated *en vacuo* and immediately subjected to flash column chromatography on silica gel (10% EtOAc/hexanes) to yield 7.9 g (72%, 3 steps) of dienoate as a clear, colorless oil. R_f = 0.59 (4:1 hexanes:EtOAc); IR (neat, cm^{-1}) 2962, 2870, 1710, 1623, 1465, 1393, 1365, 1305, 1283, 1265, 1249, 1145, 1120, 1096, 1029, 981, 844, 748; 1H NMR ($CDCl_3$, 600 MHz) δ 7.28 (d, J = 15.6 Hz, 1H), 5.77 (d, J = 15.6 Hz, 1H), 5.70 (d, J = 9.0 Hz, 1H), 4.19 (q, J = 7.2 Hz, 2H), 2.66 (m, 1H), 1.77 (d, J = 1.2 Hz, 3H), 1.29 (t, J = 7.2 Hz, 3H),

0.99 (d, $J = 6.6$ Hz, 6H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 167.7, 150.0, 149.3, 130.7, 115.8, 60.2, 28.0, 22.5 (2C), 14.5, 12.2; HRMS (ESI) calcd for $[\text{C}_{11}\text{H}_{19}\text{O}_2]^+$: 183.1379, Found: 183.1385.

(2E,4E)-Ethyl 4-methyl-5-phenylpenta-2,4-dienoate (10c). To a flask containing enal (750 mg, 5.13 mmol) in dry CH_2Cl_2 (5.1 mL) was added (carboethoxymethylene)triphenylphosphorane (1.96 g, 5.65 mmol) in one portion. The reaction was allowed to stir at RT overnight until determined complete by TLC (UV, anisaldehyde). The solvent was then removed *en vacuo* and the crude mixture was immediately subjected to flash column chromatography (10% EtOAc/hexanes) to yield dienoate in 90% as a clear, light yellow oil. Spectral data agreed satisfactorily with literature, see Fleming, I.; Rowley, M. *Tetrahedron* **1986**, 42, 3181-98.

(2E,4E)-Ethyl 4-methylhexa-2,4-dienoate (10d). To a flask containing enal (2.00 g, 23.7 mmol) in dry CH_2Cl_2 (23 mL) was added (carboethoxymethylene)triphenylphosphorane (9.94 g, 28.5 mmol) in one portion. The reaction was allowed to stir at RT overnight until determined complete by TLC (UV, anisaldehyde). The solvent was then removed *en vacuo* and the crude mixture was immediately subjected to flash column chromatography (5% EtOAc/hexanes) to yield dienoate in 67% as a clear, colorless oil. Spectral data agreed satisfactorily with literature, see Tholander, J.; Carreira, E. M. *Helv. Chim. Acta* **2001**, 84, 613.

(2E,4Z)-Ethyl 4-methylhexa-2,4-dienoate (16). To a flask containing alcohol (1.00 g, 11.6 mmol) in CH₂Cl₂ (116 mL) was added MnO₂ (10.1 g, 116 mmol) at RT. To the reaction mixture was added (carboethoxymethylene)triphenylphosphorane (7.25 g, 20.9 mmol) in two portions over the course of 24 hours (i.e. 0 h and 24 h). The reaction was then allowed to stir at RT for an additional 24 hours until determined complete by TLC (UV, KMnO₄). The reaction mixture was filtered through a plug of Celite[®] with the aid of CH₂Cl₂ and concentrated en vacuo. The crude mixture was purified using column chromatography (10% EtOAc/Hex) to yield 1.45 g (81%) of (*Z,E*) methyl substituted ethyl sorbate derivative as a fragrant, volatile clear oil. This compound is generally unstable, like the *E,E* isomer, but is stable with respect to olefin isomerization. *R*_f = 0.58 (4:1 hexanes:EtOAc); IR (neat, cm⁻¹) 2980, 2938, 1710, 1635, 1614, 1443, 1368, 1308, 1273, 1177, 1090, 1031, 977, 865, 810, 791, 725; ¹H NMR (CDCl₃, 600 MHz) δ 7.77 (d, *J* = 15.6 Hz, 1H), 5.86 (d, *J* = 15.6 Hz, 1H), 5.80 (q, *J* = 7.2 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 1.84 (d, *J* = 7.2 Hz, 3H), 1.82 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (CDCl₃, 150 MHz) δ 167.8, 140.9, 133.9, 131.7, 118.0, 60.4, 20.1, 14.5, 13.9; HRMS (ESI) calcd for [C₉H₁₄O₂]⁺: 154.0988, Found: 154.0942.

(+)-(E,4S,5S)-Ethyl 7-(tert-butyldimethylsilyloxy)-4,5-dihydroxy-4-methylhept-2-enoate (7a). Into a round bottom flask containing K₃Fe(CN)₆ (1.67 g, 5.1 mmol), K₂CO₃ (703 mg, 5.1 mmol), MeSO₂NH₂ (483 mg, 5.1 mmol) and (DHQ)₂-PHAL

(65 mg, 0.085 mmol) was added 8 mL of *t*-BuOH and 8 mL of water. The mixture was stirred at 0°C for 5 minutes and then to this solution was added OsO₄ (4 mg, 0.017 mmol) immediately followed by addition of dienoate (514 mg, 1.7 mmol). The reaction was stirred vigorously at 0°C for 4 h when determined complete by TLC (UV, PMA stain). Ethyl acetate (15 mL) was added to the reaction mixture followed by quenching with solid sodium sulfite. The layers were separated and the aqueous layer was extracted with EtOAc (2 x 5 mL). The combined organic layers were washed with 10 mL of brine and then dried over Na₂SO₄. After concentration the crude mixture was purified by flash column chromatography (30% EtOAc/hexanes) to yield 380 mg (68%) of diol as a clear, colorless oil. R_f = 0.10 (4:1 hexanes:EtOAc), $[\alpha]_D^{24} +5.2$ (c 0.61, CH₂Cl₂); IR (neat, cm⁻¹) 3459(br), 2932, 2859, 1713, 1658, 1469, 1369, 1257, 1183, 1089, 987, 941, 836, 778, 728; ¹H NMR (CDCl₃, 600 MHz) δ 6.99 (d, J = 15.6 Hz, 1H), 6.11 (d, J = 15.6 Hz, 1H), 4.17 (q, J = 7.2 Hz, 2H), 3.90 (m, 2H), 3.74 (dd, J = 6, 6 Hz, 1H), 1.99 (brs, 2H), 1.71 (m, 2H), 1.27 (t, J = 7.2 Hz, 3H), 1.25 (s, 3H), 0.88 (s, 9H), 0.07 (s, 6H); ¹³C NMR (CDCl₃, 150 MHz) δ 166.6, 152.3, 120.2, 77.2, 74.6, 62.5, 60.3, 32.2, 25.7 (3C), 22.8, 18.0, 14.1, -5.6 (2C); HRMS (ESI) calcd for [C₁₆H₃₂O₅Si + Na]⁺: 355.1911, Found: 355.1909.

(+)-(E,4S,5S)-Ethyl 7-(benzyloxy)-4,5-dihydroxy-4-methylhept-2-enoate (7b).

Into a round bottom flask containing K₃Fe(CN)₆ (1.55 g, 4.71 mmol), K₂CO₃ (650 mg, 4.71 mmol), MeSO₂NH₂ (450 mg, 4.71 mmol) and (DHQ)₂-PHAL (60 mg, 0.0785 mmol) was added 5 mL of *t*-BuOH and 5 mL of water. The mixture was stirred at 0°C for 5

minutes and then to this solution was added OsO₄ (4 mg, 0.0157 mmol) immediately followed by addition of dienoate (430 mg, 1.57 mmol). The reaction was stirred vigorously at 0°C to RT for 8 h when determined complete by TLC (UV, PMA stain). Ethyl acetate (10 mL) was added to the reaction mixture followed by quenching with solid sodium sulfite. The layers were separated and the aqueous layer was extracted with EtOAc (2 x 5 mL). The combined organic layers were washed with 5 mL of brine and then dried over Na₂SO₄. After concentration the crude mixture was purified by flash column chromatography (50% EtOAc/hexanes) with a yield of 71% as a clear, colorless oil. R_f = 0.11 (4:1 hexanes:EtOAc), $[\alpha]_D^{24}$ +5.2 (c 2.0, CH₂Cl₂); IR (neat, cm⁻¹) 3461(br), 2931, 2860, 1715, 1453, 1367, 1282, 1186, 1095, 1031, 987, 698; ¹H NMR (CDCl₃, 600 MHz) δ 7.35 (m, 3H), 7.30 (m, 2H), 6.99 (d, J = 15.6 Hz, 1H), 6.11 (d, J = 15.6 Hz, 1H), 4.52 (s, 2H), 4.18 (q, J = 7.2 Hz, 2H), 3.75 (m, 2H), 3.68 (m, 1H), 3.51 (s, 1H), 2.71 (s, 1H), 1.81 (m, 2H), 1.28 (t, J = 7.2 Hz, 3H), 1.27 (s, 3H); ¹³C NMR (CDCl₃, 150 MHz) δ 166.5, 152.0, 138.1, 128.5 (2C), 127.9, 127.7 (2C), 120.3, 76.7, 74.6, 73.5, 69.2, 60.4, 30.2, 22.8, 14.2; HRMS (ESI) calcd for [C₁₇H₂₄O₅ + Na]⁺: 331.1515, Found: 331.1516.

(-)-(E,4S,5S)-Ethyl 4,5-dihydroxy-4,7-dimethyloct-2-enoate (11a). Into a round bottom flask containing K₃Fe(CN)₆ (251 mg, 0.765 mmol), K₂CO₃ (106 mg, 0.765 mmol), MeSO₂NH₂ (73 mg, 0.765 mmol) and DHQ-4-Me-2-Quinolyl ether (7 mg, 0.0149 mmol) was added 1.3 mL of *t*-BuOH and 1.3 mL of water. The mixture was stirred at 0°C for 5 minutes and then to this solution was added OsO₄ (1 mg, 0.0039 mmol) immediately followed by addition of dienoate (600 mg, 3.06 mmol). The reaction

was stirred vigorously at 0°C to RT for 24 h when determined complete by TLC (UV, PMA stain). Ethyl acetate (5 mL) was added to the reaction mixture followed by quenching with solid sodium sulfite. The layers were separated and the aqueous layer was extracted with EtOAc (2 x 2 mL). The combined organic layers were washed with 3 mL of brine and then dried over Na₂SO₄. After concentration the crude mixture was purified by flash column chromatography (50% EtOAc/hexanes) to yield 44 mg (75%) of diol as a clear oil with no detectable regioisomer. R_f = 0.15 (4:1 hexanes:EtOAc), $[\alpha]_D^{24}$ -21.7 (c 1.0, CH₂Cl₂); IR (neat, cm⁻¹) 3460, 2957, 2870, 1701, 1656, 1466, 1368, 1307, 1282, 1189, 1034, 988, 869, 766, 743, 652; ¹H NMR (CDCl₃, 600 MHz) δ 6.95 (d, J = 15.6 Hz, 1H), 6.10 (d, J = 15.6 Hz, 1H), 4.19 (q, J = 7.2 Hz, 2H), 3.56 (ddd, J = 10.8, 4.2, 2.4 Hz, 1H), 2.53 (brs, 1H), 2.31 (brs, 1H), 1.80 (m, 1H), 1.38 (ddd, J = 13.8, 10.8, 3.6 Hz, 1H), 1.28 (t, J = 7.2 Hz, 3H), 1.26 (s, 3H), 1.20 (ddd, J = 13.8, 10.2, 4.2 Hz, 1H), 0.94 (d, J = 6.6 Hz, 3H), 0.88 (d, J = 6.6 Hz, 3H); ¹³C NMR (CDCl₃, 150 MHz) δ 166.6, 151.9, 120.6, 75.4, 74.7, 60.5, 39.7, 24.6, 23.8, 21.8, 21.2, 14.1; HRMS (ESI) calcd for [C₁₂H₂₂O₄ + Na]⁺: 253.1410, Found: 253.1402.

(-)-(E,4S,5S)-Ethyl 4,5-dihydroxy-4,6-dimethylhept-2-enoate (11b). Into a round bottom flask containing K₃Fe(CN)₆ (542 mg, 1.64 mmol), K₂CO₃ (227 mg, 1.64 mmol), MeSO₂NH₂ (157 mg, 1.64 mmol), NaHCO₃ (138 mg, 1.64 mmol) and hydroquinine-4-methyl-2-quinolyl ether (13 mg, 0.0274 mmol) was added 2.7 mL of *t*-BuOH and 2.7 mL of water. The mixture was stirred at 0°C for 5 minutes and then to this solution was added OsO₄ (1.4 mg, 0.00549 mmol) immediately followed by addition of

dienoate (100 mg, 0.549 mmol). The reaction was stirred vigorously at 0°C for 24 hours. Ethyl acetate (5 mL) was added to the reaction mixture followed by quenching with solid sodium sulfite. The layers were separated and the aqueous layer was extracted with EtOAc (2 x 5 mL). The combined organic layers were washed with 10 mL of brine and then dried over NaSO₄. After concentration the crude mixture was purified by silica gel column chromatography (30% EtOAc/hexanes) to yield 72 mg (60%) of diols as a 16:1 mixture of regioisomers. R_f = 0.11 (4:1 hexanes:EtOAc), $[\alpha]_D^{24}$ – 3.0 (c 0.5, CH₂Cl₂); IR (neat, cm⁻¹) 3448, 2962, 2874, 1698, 1655, 1467, 1368, 1303, 1279, 1179, 1096, 1031, 984, 869, 725, 679; ¹H NMR (CDCl₃, 600 MHz) δ 6.89 (d, J = 15.6 Hz, 1H), 5.99 (d, J = 15.6 Hz, 1H), 4.10 (q, J = 7.2 Hz, 2H), 3.27 (dd, J = 4.8, 3.6 Hz, 1H), 2.32 (s, 1H), 1.95 (d, J = 4.8 Hz, 1H), 1.86 (m, 1H), 1.22 (s, 3H), 1.19 (t, J = 7.2 Hz, 3H), 0.90 (d, J = 6.6 Hz, 3H), 0.89 (d, J = 6.6 Hz, 3H); ¹³C NMR (CDCl₃, 150 MHz) δ 166.8, 153.4, 120.2, 80.1, 75.6, 60.7, 29.0, 23.1, 22.0, 16.6, 14.4; HRMS (ESI) calcd for [C₁₁H₂₀O₄ + Na]⁺: 239.1253, Found: 239.1249.

(+)-(S,E)-Ethyl 4-hydroxy-4-((S)-hydroxy(phenyl)methyl)pent-2-enoate (11c).

Into a round bottom flask containing K₃Fe(CN)₆ (3.198 g, 9.72 mmol), K₂CO₃ (1.341 mg, 9.72 mmol), MeSO₂NH₂ (923 mg, 9.72 mmol) and Hydroquinine-4-methyl-2-quinolyl ether (151 mg, 0.324 mmol) was added 8 mL of *t*-BuOH and 8 mL of water. The mixture was stirred at 0°C for 5 minutes and then to this solution was added OsO₄ (16 mg, 0.0648 mmol) immediately followed by addition of dienophile (700 mg, 3.24 mmol). The reaction was stirred vigorously at 0°C for 8 h when determined complete by TLC (UV, PMA

stain). Ethyl acetate (15 mL) was added to the reaction mixture followed by quenching with solid sodium sulfite. The layers were separated and the aqueous layer was extracted with EtOAc (2 x 5 mL). The combined organic layers were washed with 10 mL of brine and then dried over Na₂SO₄. After concentration the crude mixture was purified by flash column chromatography (50% EtOAc/hexanes) to yield 490 mg (60%) of diol as a clear, yellow oil. R_f = 0.10 (4:1 hexanes:EtOAc), $[\alpha]_D^{24}$ +15.7 (c 1.2, CH₂Cl₂); IR (neat, cm⁻¹) 3436, 2981, 1699, 1656, 1453, 1368, 1304, 1278, 1182, 1094, 1026, 985, 910, 868, 721, 700; ¹H NMR (CDCl₃, 600 MHz) δ 7.33 (m, 5H), 7.01 (d, J = 15.6 Hz, 1H), 6.11 (d, J = 15.6 Hz, 1H), 4.60 (d, J = 3.0 Hz, 1H), 4.19 (q, J = 7.2 Hz, 2H), 2.70 (s, 1H), 2.47 (s, 1H), 1.28 (t, J = 7.2 Hz, 3H), 1.17 (s, 3H); ¹³C NMR (CDCl₃, 150 MHz) δ 166.5 151.8, 138.9, 128.2, 128.1 (2C), 127.5 (2C), 120.5, 79.2, 75.5, 60.4, 22.9, 14.1; HRMS (ESI) calcd for [C₁₄H₁₈O₄ + Na]⁺: 273.1097, Found: 273.1091.

(*E*,4*S*,5*S*)-Ethyl 4,5-dihydroxy-4-methylhex-2-enoate (11d). Into a round bottom flask containing K₃Fe(CN)₆ (6.42 g, 19.5 mmol), K₂CO₃ (2.69 g, 19.5 mmol), MeSO₂NH₂ (618 mg, 6.50 mmol) and (DHQ)₂-PHAL (101 mg, 0.13 mmol) was added 15 mL of *t*-BuOH and 15 mL of water. The mixture was stirred at 0°C for 5 minutes and then to this solution was added OsO₄ (16.5 mg, 0.065 mmol) immediately followed by addition of dienolate (1.00 g, 6.50 mmol). The reaction was stirred vigorously at 0°C for 9 h when determined complete by TLC (UV, PMA stain). Ethyl acetate (30 mL) was added to the reaction mixture followed by quenching with solid sodium sulfite. The layers were separated and the aqueous layer was extracted with EtOAc (2 x 10 mL). The

combined organic layers were washed with 15 mL of brine and then dried over Na₂SO₄. After concentration the crude mixture was purified by flash column chromatography (40% EtOAc/hexanes) to yield 65% of diol as a clear, colorless oil. Spectral data agreed satisfactorily with the literature, see Tholander, J.; Carreira, E. M. *Helv. Chim. Acta* **2001**, *84*, 613.

(+)-(E,4R,5S)-Ethyl 4,5-dihydroxy-4-methylhex-2-enoate (17). Into a round bottom flask containing K₃Fe(CN)₆ (1.28 g, 3.89 mmol), K₂CO₃ (537 mg, 3.89 mmol), MeSO₂NH₂ (369 mg, 3.89 mmol), NaHCO₃ (327 mg, 3.89 mmol) and (DHQD)₂-PYR (50 mg, 0.065 mmol) was added 6 mL of *t*-BuOH and 6 mL of water. The mixture was stirred at 0°C for 5 minutes and then to this solution was added OsO₄ (3.2 mg, 0.013 mmol) immediately followed by addition of dienolate (200 mg, 1.29 mmol). The reaction was stirred vigorously at 0°C for 9 h when determined complete by TLC (UV, PMA stain). Ethyl acetate (10 mL) was added to the reaction mixture followed by quenching with solid sodium sulfite. The layers were separated and the aqueous layer was extracted with EtOAc (2 x 5 mL). The combined organic layers were washed with 5 mL of brine and then dried over Na₂SO₄. After concentration the crude mixture was purified by flash column chromatography (30% EtOAc/hexanes) to yield 153 mg (64%) of diol as a clear, colorless oil. R_f = 0.10 (4:1 hexanes:EtOAc), $[\alpha]_D^{24}$ +2.5 (*c* 1.00, CH₂Cl₂); IR (neat, cm⁻¹) 3434(br), 2980, 2936, 1699, 1655, 1449, 1368, 1303, 1276, 1181, 1090, 1033, 985, 920, 887, 729; ¹H NMR (CDCl₃, 600 MHz) δ 6.97 (d, *J* = 15.6 Hz, 1H), 6.11 (d, *J* = 15.6 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 3.71 (q, *J* = 6.6 Hz, 1H), 2.64 (brs, 1H), 2.28 (brs, 1H),

1.31 (s, 3H), 1.28 (t, $J = 7.2$ Hz, 3H), 1.17 (dd, $J = 6.6, 1.2$ Hz, 3H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 166.7, 150.0, 121.2, 75.6, 74.0, 60.7, 24.6, 18.2, 14.4.

(+)-(E)-Ethyl 3-((4S,5S)-5-isobutyl-4-methyl-2-oxo-1,3-dioxolan-4-yl)acrylate (13a). To diol (285 mg, 1.24 mmol) in CH_2Cl_2 (3 mL) in an ice bath was added pyridine (500 μL , 6.20 mmol). Triphosgene (405 mg, 1.37 mmol) in CH_2Cl_2 (3 mL) was added via syringe and the reaction was allowed to stir for 5 min when determined complete by TLC (UV, PMA stain). The reaction was diluted with ether (10 mL) and was placed in a separatory funnel. The crude mixture, including salts, was washed vigorously with a saturated CuSO_4 solution until all salts dissolved. The layers were then separated and the organic layer was washed with brine. After separation the organic layer was dried over Na_2SO_4 and concentrated. The crude mixture was then purified by flash column chromatography (20% EtOAc/hexanes) to yield carbonate in 90% yield as a clear, colorless oil. $R_f = 0.26$ (4:1 hexanes:EtOAc), $[\alpha]_D^{24} +35.6$ (c 1.0, CH_2Cl_2); IR (neat, cm^{-1}) 2961, 1799, 1719, 1663, 1468, 1385, 1367, 1309, 1280, 1232, 1177, 1088, 1063, 1013, 982, 870, 774; ^1H NMR (CDCl_3 , 600 MHz) δ 6.85 (d, $J = 15.6$ Hz, 1H), 6.16 (d, $J = 15.6$ Hz, 1H), 4.41 (dd, $J = 10.8, 2.4$ Hz, 1H), 4.22 (q, $J = 7.2$ Hz, 2H), 1.84 (m, 1H), 1.71 (m, 1H), 1.46 (s, 3H), 1.32 (m, 1H), 1.30 (t, $J = 7.2$ Hz, 3H), 0.99 (d, $J = 6.6$ Hz, 3H), 0.95 (d, $J = 7.2$ Hz, 3H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 165.3, 153.2, 144.0, 122.3, 84.15, 82.0, 61.0, 37.4, 25.1, 23.1, 21.5, 19.2, 14.1; HRMS (ESI) calcd for $[\text{C}_{13}\text{H}_{20}\text{O}_5 + \text{Na}]^+$: 279.1202, Found: 279.1204.

(+)-(E)-Ethyl 3-(((4S,5S)-5-isopropyl-4-methyl-2-oxo-1,3-dioxolan-4-yl)acrylate (13b). To diol (1.04 g, 4.81 mmol) in CH_2Cl_2 (14 mL) in an ice bath was added pyridine (1.96 mL, 24.0 mmol). Triphosgene (1.57 g, 5.29 mmol) in CH_2Cl_2 (14 mL) was added via syringe and the reaction was allowed to stir for 5 min when determined complete by TLC (UV, PMA stain). The reaction was diluted with ether (40 mL) and was placed in a separatory funnel. The crude mixture, including salts, was washed vigorously with a saturated CuSO_4 solution until all salts dissolved. The layers were then separated and the organic layer was washed with brine. After separation the organic layer was dried over Na_2SO_4 and concentrated. The crude mixture was then purified by flash column chromatography (20% EtOAc/hexanes) to yield carbonate in 84% yield as a clear, colorless oil. $R_f = 0.22$ (4:1 hexanes:EtOAc), $[\alpha]_D^{24} +18.3$ (c 1.0, CH_2Cl_2); IR (neat, cm^{-1}) 2973, 1801, 1720, 1663, 1472, 1368, 1281, 1245, 1175, 1109, 1062, 1027, 982, 839, 774; ^1H NMR (CDCl_3 , 600 MHz) δ 6.84 (d, $J = 15.6$ Hz, 1H), 6.20 (d, $J = 15.6$ Hz, 1H), 4.23 (q, $J = 7.2$ Hz, 2H), 3.98 (d, $J = 9.6$ Hz, 1H), 2.04 (m, 1H), 1.54 (s, 3H), 1.30 (t, $J = 7.2$ Hz, 3H), 1.11 (d, $J = 6.6$ Hz, 3H), 0.95 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 165.6, 153.1, 144.5, 123.0, 89.1, 84.5, 61.2, 28.2, 19.8, 19.1, 18.7, 14.3; HRMS (ESI) calcd for $[\text{C}_{12}\text{H}_{18}\text{O}_5 + \text{Na}]^+$: 265.1046, Found: 265.1050.

(-)-(E)-Ethyl 3-((4S,5S)-4-methyl-2-oxo-5-phenyl-1,3-dioxolan-4-yl)acrylate

(13c). To diol (400 mg, 1.60 mmol) in CH₂Cl₂ (4 mL) in an ice bath was added pyridine (651 μ L, 8.00 mmol). Triphosgene (523 mg, 1.76 mmol) in CH₂Cl₂ (4 mL) was added via syringe and the reaction was allowed to stir for 5 min when determined complete by TLC (UV, PMA stain). The reaction was diluted with ether (10 mL) and was placed in a separatory funnel. The crude mixture, including salts, was washed vigorously with a saturated CuSO₄ solution until all salts dissolved. The layers were then separated and the organic layer was washed with brine. After separation the organic layer was dried over Na₂SO₄ and concentrated. The crude mixture was then purified by flash column chromatography (20% EtOAc/hexanes) to yield carbonate in 91% yield as a clear, colorless oil. R_f = 0.21 (4:1 hexanes:EtOAc), $[\alpha]_D^{24}$ -24.9 (c 1.3, CH₂Cl₂); IR (neat, cm⁻¹) 2984, 1802, 1718, 1663, 1456, 1367, 1308, 1288, 1245, 1180, 1088, 1069, 1044, 1028, 979, 771, 700; ¹H NMR (CDCl₃, 600 MHz) δ 7.43 (m, 3H), 7.28 (m, 2H), 7.01 (d, J = 15.6 Hz, 1H), 6.20 (d, J = 15.6 Hz, 1H), 5.47 (s, 1H), 4.26 (qd, J = 7.2, 1.2 Hz, 2H), 1.32 (t, J = 7.2 Hz, 3H), 1.12 (s, 3H); ¹³C NMR (CDCl₃, 150 MHz) δ 165.3, 153.0, 144.5, 132.2, 129.5, 128.9 (2C), 125.5 (2C), 122.6, 85.2, 84.4, 61.1, 20.9, 14.1; HRMS (ESI) calcd for [C₁₅H₁₆O₅ + Na]⁺: 299.0889, Found: 299.0897.

(E)-Ethyl 3-((4S,5S)-4,5-dimethyl-2-oxo-1,3-dioxolan-4-yl)acrylate (13d[13e]).

To diol (428 mg, 2.20 mmol) in CH₂Cl₂ (5 mL) in an ice bath was added pyridine (897 μ L, 11.0 mmol). Triphosgene (742 mg, 2.50 mmol) in CH₂Cl₂ (5 mL) was added via syringe and the reaction was allowed to stir for 5 min when determined complete by TLC

(UV, PMA stain). The reaction was diluted with ether (10 mL) and was placed in a separatory funnel. The crude mixture, including salts, was washed vigorously with a saturated CuSO₄ solution until all salts dissolved. The layers were then separated and the organic layer was washed with brine. After separation the organic layer was dried over Na₂SO₄ and concentrated. The crude mixture was then purified by flash column chromatography (20% EtOAc/hexanes) to yield carbonate in 90% yield as a clear, colorless oil. $R_f = 0.25$ (4:1 hexanes:EtOAc), $[\alpha]_D^{24} +12.7$ [-15.1] (c 1.00, CH₂Cl₂); IR (neat, cm⁻¹) 2987, 2941, 2301, 1821, 1726, 1664, 1446, 1390, 1348, 1312, 1235, 1183, 1086, 1034, 868, 774, 630; ¹H NMR (CDCl₃, 600 MHz) δ 6.86 (d, $J = 16.2$ Hz, 1H), 6.15 (d, $J = 16.2$ Hz, 1H), 4.54 (q, $J = 6.6$ Hz, 1H), 4.22 (q, $J = 6.6$ Hz, 2H), 1.48 (s, 3H), 1.41 (d, $J = 6.6$ Hz, 3H), 1.30 (t, $J = 6.6$ Hz, 3H); ¹³C NMR (CDCl₃, 150 MHz) δ 165.3, 153.1, 144.0, 122.3, 84.1, 79.6, 61.0, 19.1, 14.3, 14.1; HRMS (ESI) calcd for [C₁₀H₁₄O₅ + Na]⁺: 237.0733, Found: 237.0726.

(-)-(E)-Ethyl 3-(((4S,5S)-5-(2-(tert-butyldimethylsilyloxy)ethyl)-4-methyl-2-oxo-1,3-dioxolan-4-yl)acrylate (13f). To diol (250 mg, 0.753 mmol) in CH₂Cl₂ (2 mL) in an ice bath was added pyridine (300 μ L, 3.76 mmol). Triphosgene (245 mg, 0.828 mmol) in CH₂Cl₂ (2 mL) was added via syringe and the reaction was allowed to stir for 5 min when determined complete by TLC (UV, PMA stain). The reaction was diluted with ether (6 mL) and was placed in a separatory funnel. The crude mixture, including salts, was washed vigorously with a saturated CuSO₄ solution until all salts dissolved. The layers were then separated and the organic layer was washed with brine. After separation

the organic layer was dried over Na₂SO₄ and concentrated. The crude mixture was then purified by flash column chromatography (20% EtOAc/hexanes) to yield carbonate in 71% yield as a clear, colorless oil. R_f = 0.50 (4:1 hexanes:EtOAc), $[\alpha]_D^{24}$ -52.2 (c 1.00, CH₂Cl₂); IR (neat) 2956, 2858, 1813, 1723, 1665, 1469, 1388, 1309, 1258, 1179, 1088, 1033, 982, 835, 777, 721; ¹H NMR (CDCl₃, 600 MHz) δ 6.89 (d, J = 15.6 Hz, 1H), 6.15 (d, J = 15.6 Hz, 1H), 4.59 (dd, J = 9.6, 3.6 Hz, 1H), 4.22 (q, J = 7.2 Hz, 2H), 3.77 (m, 2H), 1.87 (m, 2H), 1.49 (s, 3H), 1.30 (t, J = 7.2 Hz, 3H), 0.88 (s, 9H), 0.06 (s, 3H), 0.06 (s, 3H); ¹³C NMR (CDCl₃, 150 MHz) δ 165.3, 153.1, 144.1, 122.2, 83.9, 80.3, 61.0, 58.5, 32.1, 25.8 (3C), 19.6, 18.2, 14.1, -5.5 (2C); HRMS (ESI) calcd for [C₁₇H₃₀O₆Si + Na]⁺: 381.1703, Found: 381.1718.

(-)-(E)-Ethyl 3-((4S,5S)-5-(2-(benzyloxy)ethyl)-4-methyl-2-oxo-1,3-dioxolan-4-yl)acrylate (13g). To diol (320 mg, 1.04 mmol) in CH₂Cl₂ (4 mL) in an ice bath was added pyridine (424 μ L, 5.20 mmol). Triphosgene (340 mg, 1.14 mmol) in CH₂Cl₂ (4 mL) was added via syringe and the reaction was allowed to stir for 5 min when determined complete by TLC (UV, PMA stain). The reaction was diluted with ether (10 mL) and was placed in a separatory funnel. The crude mixture, including salts, was washed vigorously with a saturated CuSO₄ solution until all salts dissolved. The layers were then separated and the organic layer was washed with brine. After separation the organic layer was dried over Na₂SO₄ and concentrated. The crude mixture was then purified by flash column chromatography (20% EtOAc/hexanes) to yield carbonate in 88% yield as a clear, colorless oil. R_f = 0.23 (4:1 hexanes:EtOAc), $[\alpha]_D^{24}$ -23.8 (c 2.3,

CH₂Cl₂); IR (neat, cm⁻¹) 2985, 2863, 1810, 1720, 1662, 1556, 1495, 1454, 1382, 1188, 1090, 985, 773, 741;; ¹H NMR (CDCl₃, 600 MHz) δ 7.35 (m, 3H), 7.31 (m, 2H), 6.88 (d, *J* = 15.6 Hz, 1H), 6.15 (d, *J* = 15.6 Hz, 1H), 4.62 (t, *J* = 7.2 Hz, 1H), 4.51 (dd, *J* = 27.0, 6.0 Hz, 2H), 4.22 (q, *J* = 7.2 Hz, 2H), 3.63 (m, 2H), 1.95 (dd, *J* = 12.6, 6.0 Hz, 2H), 1.48 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (CDCl₃, 150 MHz) δ 165.3, 153.0, 144.1, 137.5, 128.4 (2C), 127.8, 127.7 (2C), 122.2, 84.0, 80.5, 73.4, 65.4, 61.0, 29.6, 19.5, 14.1; HRMS (ESI) calcd for [C₁₈H₂₂O₆ + Na]⁺: 357.1308, Found: 357.1290.

(+)-(E)-Ethyl 3-((4R,5S)-4,5-dimethyl-2-oxo-1,3-dioxolan-4-yl)acrylate (18).

To diol (170 mg, 0.779 mmol) in CH₂Cl₂ (2 mL) in an ice bath was added pyridine (317 μL, 3.89 mmol). Triphosgene (254 mg, 0.857 mmol) in CH₂Cl₂ (2 mL) was added via syringe and the reaction was allowed to stir for 5 min when determined complete by TLC (UV, PMA stain). The reaction was diluted with ether (6 mL) and was placed in a separatory funnel. The crude mixture, including salts, was washed vigorously with a saturated CuSO₄ solution until all salts dissolved. The layers were then separated and the organic layer was washed with brine. After separation the organic layer was dried over Na₂SO₄ and concentrated. The crude mixture was then purified by flash column chromatography (20% EtOAc/hexanes) to yield carbonate in 89% yield as a clear, colorless oil. *R*_f = 0.20 (4:1 hexanes:EtOAc), [α]_D²⁴ +30.2 (*c* 0.65, CH₂Cl₂); IR (neat, cm⁻¹) 2985, 2940, 1793, 1717, 1662, 1594, 1448, 1387, 1367, 1310, 1287, 1225, 1180, 1097, 1074, 1000, 905, 870, 773, 732, 685; ¹H NMR (CDCl₃, 600 MHz) δ 6.76 (d, *J* = 15.6 Hz, 1H), 6.19 (d, *J* = 15.6 Hz, 1H), 4.55 (dd, *J* = 6.6, 6.6 Hz, 1H), 4.22 (q, *J* = 7.2 Hz, 2H),

1.60 (s, 3H), 1.32 (d, $J = 6.6$ Hz, 3H), 1.30 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 165.4, 153.3, 142.1, 123.2, 84.4, 81.9, 61.2, 24.4, 16.1, 14.3; HRMS (ESI) calcd for $[\text{C}_{10}\text{H}_{14}\text{O}_5 + \text{Na}]^+$: 237.0733, Found: 237.0736.

(-)-(E,4S,5S)-Ethyl 7-(tert-butyldimethylsilyloxy)-5-hydroxy-4-methylhept-2-enoate (8a). To a flask containing carbonate (170 mg, 0.474 mmol) in THF (2.3 mL) was added $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (5.0 mg, 0.00470 mmol), PPh_3 (1.3 mg, 0.00470 mmol), Et_3N (330 μL , 2.37 mmol) and finally formic acid (89 μL , 2.37 mmol). The reaction was then refluxed for 25 min when determined complete by TLC (UV, anisaldehyde). The reaction was then allowed to cool to RT then diluted with ether and filtered through a plug of silica gel to remove $\text{Pd}(0)$ before concentration. The crude mixture was then concentrated and subjected to flash column chromatography (20% EtOAc /hexanes) to yield δ -hydroxy enoate in 95% yield as a clear, colorless oil. $R_f = 0.45$ (4:1 hexanes: EtOAc), $[\alpha]_D^{24} -16.5$ (c 0.63, CH_2Cl_2); IR (neat, cm^{-1}) 3499(br), 2955, 2859, 1720, 1651, 1463, 1368, 1256, 1181, 1144, 1093, 1038, 986, 835, 777, 726; ^1H NMR (CDCl_3 , 600 MHz) δ 6.93 (dd, $J = 16.2, 7.8$ Hz, 1H), 5.84 (dd, $J = 16.2, 1.2$ Hz, 1H), 4.17 (q, $J = 7.2$ Hz, 2H), 3.89 (m, 1H), 3.78 (m, 2H), 2.41 (m, 1H), 1.61 (m, 2H), 1.27 (t, $J = 7.2$ Hz, 3H), 1.10 (d, $J = 7.2$ Hz, 3H), 0.88 (s, 9H), 0.07 (d, $J = 1.2$ Hz, 6H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 166.6, 150.9, 121.4, 75.1, 63.0, 60.2, 42.7, 35.4, 25.8 (3C), 18.0, 14.7, 14.2, -5.6 (2C); HRMS (ESI) calcd for $[\text{C}_{16}\text{H}_{32}\text{O}_4\text{Si} + \text{Na}]^+$: 339.1962, Found: 339.1954.

(-)-(E,4S,5S)-Ethyl 7-(benzyloxy)-5-hydroxy-4-methylhept-2-enoate (8b). To a flask containing carbonate (200 mg, 0.598 mmol) in THF (2.5 mL) was added $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (6.1 mg, 0.00598 mmol), PPh_3 (1.5 mg, 0.00598 mmol), Et_3N (416 μL , 2.99 mmol) and finally formic acid (113 μL , 2.99 mmol). The reaction was then refluxed for 35 min when determined complete by TLC (UV, anisaldehyde). The reaction was then allowed to cool to RT then diluted with ether and filtered through a plug of silica gel to remove $\text{Pd}(0)$ before concentration. The crude mixture was then concentrated and subjected to flash column chromatography (20% EtOAc/hexanes) to yield δ -hydroxy enoate in 96% yield as a clear, colorless oil. $R_f = 0.23$ (4:1 hexanes:EtOAc), $[\alpha]_D^{24} -18.9$ (c 1.20, CH_2Cl_2); IR (neat, cm^{-1}) 3486(br), 2932, 2854, 1725, 1646, 1467, 1273, 1193, 1107, 1090, 741, 705; ^1H NMR (CDCl_3 , 600 MHz) δ 7.31 (m, 5H), 6.95 (dd, $J = 15.6$, 7.8 Hz, 1H), 5.84 (dd, $J = 15.6$, 1.8 Hz, 1H), 4.51 (s, 2H), 4.18 (q, $J = 7.2$ Hz, 2H), 3.74 (m, 2H), 3.64 (ddd, $J = 12.6$, 6.6, 2.4 Hz, 1H), 3.01 (d, $J = 3.0$ Hz, 1H), 2.43 (sextet, $J = 6.6$ Hz, 1H), 1.73 (q, $J = 6.0$ Hz, 2H), 1.29 (t, $J = 7.2$ Hz, 3H), 1.11 (d, $J = 7.2$ Hz, 3H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 166.5, 150.7, 137.7, 128.4 (2C), 127.8, 127.7 (2C), 121.5, 74.4, 73.4, 69.4, 60.2, 42.6, 33.6, 14.6, 14.2; HRMS (ESI) calcd for $[\text{C}_{17}\text{H}_{24}\text{O}_4\text{Si} + \text{Na}]^+$: 315.1566, Found: 315.1568.

(-)-(E,4S,5S)-Ethyl 5-hydroxy-4,7-dimethyloct-2-enoate (14a). To a flask containing carbonate (220 mg, 0.894 mmol) in THF (4.5 mL) was added

$\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (9.2 mg, 0.00894 mmol), PPh_3 (2.3 mg, 0.00894 mmol), Et_3N (622 μL , 4.47 mmol) and finally formic acid (169 μL , 4.47 mmol). The reaction was then refluxed for 40 min when determined complete by TLC (UV, anisaldehyde). The reaction was then allowed to cool to RT then diluted with ether and filtered through a plug of silica gel to remove $\text{Pd}(0)$ before concentration. The crude mixture was then concentrated and subjected to flash column chromatography (20% EtOAc /hexanes) to yield δ -hydroxy enoate in 96% yield as a clear, colorless oil. $R_f = 0.27$ (4:1 hexanes: EtOAc), $[\alpha]_D^{24} -43.7$ (c 1.0, CH_2Cl_2); IR (neat, cm^{-1}) 3436(br), 2957, 2871, 1702, 1651, 1467, 1368, 1272, 1182, 1150, 1095, 1034, 989, 865, 729; ^1H NMR (CDCl_3 , 600 MHz) δ 6.95 (dd, $J = 15.6$, 7.8 Hz, 1H), 5.86 (dd, $J = 15.6$, 1.8 Hz, 1H), 4.21 (q, $J = 7.2$ Hz, 2H), 3.67 (ddd, $J = 9.0$, 8.4, 5.4 Hz, 1H), 2.40 (sextet, $J = 7.2$ Hz, 1H), 1.77 (m, 2H), 1.57 (brs, 1H), 1.35 (m, 1H), 1.29 (t, $J = 7.2$ Hz, 3H), 1.08 (d, $J = 7.2$ Hz, 3H), 0.94 (d, $J = 6.6$ Hz, 3H), 0.90 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 166.5, 150.9, 121.6, 72.4, 60.2, 43.4, 42.8, 24.6, 23.6, 21.6, 14.2, 13.8; HRMS (ESI) calcd for $[\text{C}_{12}\text{H}_{22}\text{O}_3 + \text{Na}]^+$: 237.1461, Found: 237.1460.

(-)-(E,4S,5S)-Ethyl 5-hydroxy-4,6-dimethylhept-2-enoate (14b). To a flask containing carbonate (10.0 g, 41.3 mmol) in THF (200 mL) was added $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (420 mg, 0.413 mmol), PPh_3 (110 mg, 0.413 mmol), Et_3N (28.5 mL, 206.50 mmol) and finally formic acid (7.8 mL, 206.50 mmol). The reaction was then refluxed for 35 min when determined complete by TLC (UV, anisaldehyde). The reaction was then allowed to cool to RT then diluted with ether and filtered through a large plug of silica gel to

remove Pd(0) before concentration. The crude mixture was then concentrated and subjected to flash column chromatography (20% EtOAc/hexanes) to yield δ -hydroxy enoate in 98% yield as a clear, yellow oil. Spectral data agreed satisfactorily with the literature, see Schlessinger, R. H.; Iwanowicz, E. J.; Springer, J. P. *J. Org. Chem.* **1986**, *51*, 3070-3

(-)-(S,E)-Ethyl 4-((R)-hydroxy(phenyl)methyl)pent-2-enoate (14c). To a flask containing carbonate (150 mg, 0.543 mmol) in THF (2.7 mL) was added $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (5.5 mg, 0.00543 mmol), PPh_3 (1.4 mg, 0.00543 mmol), Et_3N (377 μL , 2.71 mmol) and finally formic acid (102 μL , 2.71 mmol). The reaction was then refluxed for 10 min when determined complete by TLC (UV, anisaldehyde). The reaction was then allowed to cool to RT then diluted with ether and filtered through a plug of silica gel to remove Pd(0) before concentration. The crude mixture was then concentrated and subjected to flash column chromatography (20% EtOAc/hexanes) to yield δ -hydroxy enoate in 98% yield as a clear, colorless oil.. Spectral data agreed satisfactorily with the literature, see Oshima, M.; Yamazaki, H.; Shimizu, I.; Nisar, M.; Tsuji, J. *J. Am. Chem. Soc.* **1989**, *111*, 6280-7.

(E,4S,5S)-Ethyl 5-hydroxy-4-methylhex-2-enoate (14d[14e]). To a flask containing carbonate (379 mg, 1.70 mmol) in THF (8.0 mL) was added $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (17.6 mg, 0.0170 mmol), PPh_3 (4.4 mg, 0.0170 mmol), Et_3N (1.18 mL, 8.50 mmol) and

finally formic acid (320 μ L, 8.50 mmol). The reaction was then refluxed for 35 min when determined complete by TLC (UV, anisaldehyde). The reaction was then allowed to cool to RT then diluted with ether and filtered through a plug of silica gel to remove Pd(0) before concentration. The crude mixture was then concentrated and subjected to flash column chromatography (20% EtOAc/hexanes) to yield δ -hydroxy enoate in 98% yield as a clear, colorless oil. R_f = 0.40 (4:1 hexanes:EtOAc), $[\alpha]_D^{24}$ -29.8 $[+29.9]$ (c 0.77, CH_2Cl_2); IR (neat, cm^{-1}) 3410(br), 2971, 2850, 1716, 1650, 1273, 1183, 1155, 1093, 1034; ^1H NMR (CDCl_3 , 600 MHz) δ 6.93 (dd, J = 15.6, 7.8 Hz, 1H), 5.86 (dd, J = 15.6, 1.2 Hz, 1H), 4.18 (q, J = 7.2 Hz, 2H), 3.77 (m, 1H), 2.39 (m, 1H), 1.58 (brs, 1H), 1.29 (t, J = 7.2 Hz, 3H), 1.16 (d, J = 6.6 Hz, 3H), 1.08 (d, J = 6.6 Hz, 3H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 166.5, 150.4, 121.8, 70.5, 60.2, 43.7, 20.4, 14.4, 14.2; HRMS (ESI) calcd for $[\text{C}_9\text{H}_{16}\text{O}_3 + \text{Na}]^+$: 195.0991, Found: 195.1000.

(+)-(E,4S,5R)-Ethyl 5-hydroxy-4-methylhex-2-enoate (20). The allylic alcohol from this carbonate was prepared in a similar manner as above with the exception that all reagents were allowed to stir together first for 5 min. Thus, to a flask containing THF (1.0 mL) was added $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (11.2 mg, 0.0108 mmol), PPh_3 (2.8 mg, 0.0108 mmol), Et_3N (301 μ L, 2.16 mmol) and finally formic acid (81 μ L, 2.16 mmol). After 5 minutes carbonate (110 mg, 0.433 mmol) in THF (1.0 ml) was added and the reaction was brought to reflux. The reaction was then refluxed for 5 min when determined complete by TLC (UV, anisaldehyde). The reaction was then allowed to cool to RT then diluted with ether and filtered through a plug of silica gel to remove Pd(0) before

concentration. The crude mixture was then concentrated and subjected to flash column chromatography (30% EtOAc/hexanes) to yield δ -hydroxy enoate in 86% yield as a clear, colorless oil. Spectral data agreed satisfactorily with the literature, see Tholander, J.; Carreira, E. M. *Helv. Chim. Acta* **2001**, *84*, 613.

(-)-Ethyl 2-((2*S*,4*R*,5*R*,6*S*)-6-(2-(*tert*butyldimethylsilyloxy)ethyl)-5-methyl-2-phenyl-1,3-dioxan-4-yl)acetate (9a). Enolate (108 mg, 0.342 mmol) was dissolved in 1.5 mL of THF and cooled to 0 °C. To the reaction was added benzaldehyde (38 μ L, 0.376 mmol) and potassium *tert*-butoxide (6.0 mg, 0.0513 mmol). The addition of base and aldehyde was repeated 3 times at 20 minute intervals. The reaction was allowed to stir at 0 °C, and was quenched after 1 hour by adding 1.0 mL of pH 7 buffered phosphate solution. The layers were separated and the aqueous layer was extracted (3 x 2 mL) with Et₂O. The organic layers were combined and washed with 4 mL of brine, then dried using Na₂SO₄, and the solvent removed under reduced pressure. The product was purified by silica gel chromatography eluting with (5 % EtOAc/hexanes) to yield benzylidene acetal in 58% yield as a clear, colorless oil. R_f = 0.62 (4:1 hexanes:EtOAc), $[\alpha]_D^{24}$ -27.5 (*c* 0.50, CH₂Cl₂); IR (neat, cm⁻¹) 2955, 2930, 2858, 1738, 1461, 1390, 1349, 1314, 1254, 1182, 1098, 1064, 1027, 941, 835, 776, 697; ¹H NMR (CDCl₃, 600 MHz) δ 7.49 (m, 2H), 7.34 (m, 3H), 5.58 (s, 1H), 4.43 (ddd, J = 7.8, 6.0, 2.4 Hz, 1H), 4.16 (dq, J = 7.2, 1.2 Hz, 2H), 4.13 (ddd, J = 8.4, 3.0, 3.0 Hz, 1H), 3.78 (m, 1H), 3.73 (m, 1H), 2.71 (dd, J = 15.6, 8.4 Hz, 1H), 2.48 (dd, J = 15.6, 6.0 Hz, 1H), 1.87 (m, 1H), 1.66 (m, 1H), 1.58 (qdd, J = 7.2, 2.4, 2.4 Hz, 1H), 1.26 (t, J = 7.2 Hz, 3H), 1.01 (d, J = 7.2 Hz, 3H),

0.91 (d, $J = 1.2$ Hz, 9H), 0.06 (d, $J = 6.4$ Hz, 6H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 171.0, 138.6, 128.6, 128.1 (2C), 126.1 (2C), 101.5, 77.3, 77.1, 60.5, 59.2, 38.1, 35.8, 34.6, 25.9 (3C), 18.3, 14.1, 6.2, -5.3(2C); HRMS (ESI) calcd for $[\text{C}_{23}\text{H}_{38}\text{O}_5 + \text{Na}]^+$: 445.2380, Found: 445.2398.

(-)-Ethyl 2-((2*S*,4*R*,5*R*,6*S*)-6-(2-(benzyloxy)ethyl)-5-methyl-2-phenyl-1,3-dioxan-4-yl)acetate (9b). Enolate (150 mg, 0.514 mmol) was dissolved in 2.0 mL of THF and cooled to 0 °C. To the reaction was added benzaldehyde (57 μL , 0.565 mmol) and potassium *tert*-butoxide (8.6 mg, 0.0771 mmol). The addition of base and aldehyde was repeated 3 times at 20 minute intervals. The reaction was allowed to stir at 0 °C, and was quenched after 2 hours by adding 1.5 mL of pH 7 buffered phosphate solution. The layers were separated and the aqueous layer was extracted (3 x 3 mL) with Et_2O . The organic layers were combined and washed with 5 mL of brine, then dried using Na_2SO_4 , and the solvent removed under reduced pressure. The product was purified by silica gel chromatography eluting with (5 % EtOAc /hexanes) to yield benzylidene acetal in 69% yield as a clear, colorless oil. $R_f = 0.39$ (4:1 hexanes: EtOAc), $[\alpha]_{\text{D}}^{24} -20.5$ (c 1.0, CH_2Cl_2); IR (neat, cm^{-1}) 2978, 2869, 1735, 1496, 1454, 1369, 1350, 1264, 1182, 1151, 1100, 1066, 1027, 754, 697; ^1H NMR (CDCl_3 , 600 MHz) δ 7.33 (m, 10H), 5.5 (s, 1H), 4.54 (d, $J = 12.0$ Hz, 1H), 4.50 (d, $J = 12.0$, Hz, 1H), 4.42 (ddd, $J = 8.4, 5.4, 2.4$ Hz, 1H), 4.18 (qd, $J = 7.2, 1.8$ Hz, 1H), 4.17 (ddd, $J = 8.4, 3.6, 2.4$ Hz, 1H), 4.15 (qd, $J = 7.2, 1.8$ Hz, 1H), 3.65 (ddd, $J = 13.2, 9.0, 4.8$ Hz, 1H), 3.59 (ddd, $J = 12.0, 9.0, 6.0$ Hz, 1H), 2.71 (dd, $J = 15.6, 7.8$ Hz, 1H), 2.47 (dd, $J = 15.6, 5.4$ Hz, 1H), 1.97 (m, 1H), 1.76

(m, 1H), 1.58 (qdd, $J = 6.6, 2.4, 2.4$ Hz, 1H), 1.27 (t, $J = 7.2$ Hz, 3H), 1.01 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 170.9, 138.6, 138.4, 128.6, 128.3 (2C), 128.1 (2C), 127.6 (2C), 127.5, 126.1 (2C), 101.4, 77.5, 77.2, 73.0, 66.4, 60.5, 38.1, 34.5, 33.1, 14.1, 6.1; HRMS (ESI) calcd for $[\text{C}_{24}\text{H}_{30}\text{O}_5 + \text{Na}]^+$: 421.1985, Found: 421.2014.

(–)-Ethyl 2-((2*S*,4*R*,5*R*,6*S*)-6-isobutyl-5-methyl-2-phenyl-1,3-dioxan-4-yl)acetate (15a). Enolate (90 mg, 0.42 mmol) was dissolved in 1.7 mL of THF and cooled to 0 °C. To the reaction was added benzaldehyde (47 μL , 0.46 mmol) and potassium *tert*-butoxide (7 mg, 0.063 mmol). The addition of base and aldehyde was repeated 3 times at 20 minute intervals. The reaction was allowed to stir at 0 °C, and was quenched after 1.5 hours by adding 1 mL of pH 7 buffered phosphate solution. The layers were separated and the aqueous layer was extracted (3 x 3 mL) with Et_2O . The organic layers were combined and washed with 5 mL of brine, then dried using Na_2SO_4 , and the solvent removed under reduced pressure. The product was purified by silica gel chromatography eluting with (5-10 % EtOAc /hexanes) to yield benzylidene acetal in 75% yield as a clear, colorless oil. $R_f = 0.39$ (4:1 hexanes: EtOAc), $[\alpha]_D^{24} -7.3$ (c 0.50, CH_2Cl_2); IR (neat, cm^{-1}) 2955, 2870, 1734, 1456, 1391, 1368, 1349, 1259, 1180, 1102, 1056, 1021, 993, 922, 853, 755, 696; ^1H NMR (CDCl_3 , 600 MHz) δ 7.48 (m, 2H), 7.33 (m, 3H), 5.58 (s, 1H), 4.42 (ddd, $J = 7.8, 5.4, 2.4$ Hz, 1H), 4.16 (q, $J = 7.2$ Hz, 2H), 3.99 (ddd, $J = 8.4, 4.8, 2.4$ Hz, 1H), 2.71 (dd, $J = 15.6, 7.8$ Hz, 1H), 2.48 (dd, $J = 15.6, 6.0$ Hz, 1H), 1.78 (m, 1H), 1.64 (m, 1H), 1.54 (qdd, $J = 7.2, 2.4, 2.4$ Hz, 1H), 1.27 (t, $J = 7.2$ Hz, 3H), 1.26 (m, 1H), 0.99 (d, $J = 7.2$ Hz, 3H), 0.95 (d, $J = 6.6$ Hz, 6H); ^{13}C NMR (CDCl_3 ,

150 MHz) δ 171.1, 138.7, 128.5, 128.1 (2C), 126.0 (2C), 101.4, 79.0, 77.4, 60.5, 41.5, 38.1, 34.6, 24.3, 23.0, 22.6, 14.2, 6.0; HRMS (ESI) calcd for $[C_{19}H_{28}O_4 + Na]^+$: 343.1879, Found: 343.1880.

Ethyl 2-((2R,4R,5S,6S)-6-isopropyl-5-methyl-2-phenyl-1,3-dioxan-4-yl)acetate (15b). Enolate (98 mg, 0.490 mmol) was dissolved in 2.0 mL of THF and cooled to 0 °C. To the reaction was added benzaldehyde (55 μ L, 0.539 mmol) and potassium *tert*-butoxide (8.2 mg, 0.0735 mmol). The addition of base and aldehyde was repeated 3 times at 20 minute intervals. The reaction was allowed to stir at 0 °C, and was quenched after 2 hours by adding 1.5 mL of pH 7 buffered phosphate solution. The layers were separated and the aqueous layer was extracted (3 x 3 mL) with Et₂O. The organic layers were combined and washed with 5 mL of brine, then dried using Na₂SO₄, and the solvent removed under reduced pressure. The product was purified by silica gel chromatography eluting with (5 % EtOAc/hexanes) to yield benzyldiene acetal in 57% yield as a clear, colorless oil. Spectral data agreed satisfactorily with the literature, see Evans, D. A.; Gauchet-Prunet, J. A. *J. Org. Chem.* **1993**, 58, 2446-2453.

(+)-Ethyl 2-((2R,4R,5S,6R)-5-methyl-2,6-diphenyl-1,3-dioxan-4-yl)acetate (15c). Enolate (36 mg, 0.153 mmol) was dissolved in 0.75 mL of THF and cooled to 0 °C. To the reaction was added benzaldehyde (17 μ L, 0.169 mmol) and potassium *tert*-

butoxide (2.6 mg, 0.0229 mmol). The addition of base and aldehyde was repeated 3 times at 20 minute intervals. The reaction was allowed to stir at 0 °C, and was quenched after 1.5 hours by adding 1 mL of pH 7 buffered phosphate solution. The layers were separated and the aqueous layer was extracted (3 x 2 mL) with Et₂O. The organic layers were combined and washed with 3 mL of brine, then dried using Na₂SO₄, and the solvent removed under reduced pressure. The product was purified by silica gel chromatography eluting with (10 % EtOAc/hexanes) to yield benzylidene acetal in 33% yield as a clear, colorless oil. R_f = 0.26 (4:1 hexanes:EtOAc), $[\alpha]_D^{24}$ +11.1 (c 1.0, CH₂Cl₂); IR (neat, cm⁻¹) 2982, 2165, 1734, 1497, 1452, 1348, 1260, 1183, 1135, 1100, 1052, 1027, 993, 755, 698; ¹H NMR (CDCl₃, 600 MHz) δ 7.59 (d, J = 7.2 Hz, 1H), 7.37 (m, 9H), 5.79 (s, 1H), 5.15 (d, J = 2.4 Hz, 1H), 4.65 (ddd, J = 7.8, 6.0, 2.4 Hz, 1H), 4.19 (q, J = 7.2 Hz, 2H), 2.76 (dd, J = 15.6, 8.4 Hz, 1H), 2.53 (dd, J = 15.6, 6.0 Hz, 1H), 1.97 (qdd, J = 6.6, 2.4, 2.4 Hz, 1H), 1.28 (t, J = 7.2 Hz, 3H), 0.79 (d, J = 6.6 Hz, 3H); ¹³C NMR (CDCl₃, 150 MHz) δ 170.9, 140.1, 138.5, 128.8, 128.1 (2C), 128.1 (2C), 127.0, 126.2 (2C), 125.3 (2C), 101.5, 81.7, 77.1, 60.6, 38.2, 36.6, 14.2, 6.1; HRMS (ESI) calcd for [C₂₁H₂₄O₄ + Na]⁺: 363.1566, Found: 363.1562.

(+)-Ethyl 2-((2*S*,4*R*,5*R*,6*S*)-5,6-dimethyl-2-phenyl-1,3-dioxan-4-yl)acetate

(15d). Enoate (100 mg, 0.58 mmol) was dissolved in 2 mL of THF and cooled to 0 °C. To the reaction was added benzaldehyde (65 μ L, 0.63 mmol) and potassium *tert*-butoxide (9.7 mg, 87 μ mol). The addition of base and aldehyde was repeated 3 times at 20 minute intervals. The reaction was allowed to stir at 0 °C, and was quenched after 2 hours by

adding 5 mL of pH 7 buffered phosphate solution. The layers were separated and the aqueous layer was extracted (3 x 5 mL) with Et₂O. The organic layers were combined and washed with 8 mL of brine, then dried using Na₂SO₄, and the solvent removed under reduced pressure. The product was purified by silica gel chromatography eluting with (10 % EtOAc/hexanes) to yield benzylidene acetal in 63% yield as a clear, colorless oil. $R_f = 0.42$ (9:1 hexanes:EtOAc), $[\alpha]_D^{24} +21.6$ (c 1.00, CH₂Cl₂); IR (neat, cm⁻¹) 3453, 3066, 3037, 2980, 2935, 2890, 2360, 1958, 1882, 1732, 1496, 1375, 1263, 1183, 1062, 918, 851, 757, 699, 650, 584; ¹H NMR (CDCl₃, 600 MHz) δ 7.49 (m, 2H), 7.33 (m, 3H), 5.58 (s, 1H), 4.40 (ddd, $J = 7.8, 6.0, 2.4$ Hz, 1H), 4.14 (dq, $J = 7.2, 2.4$ Hz, 2H), 4.10 (dq, $J = 6.6, 2.4$ Hz, 1H), 2.69 (dd, $J = 15.6, 7.8$ Hz, 1H), 2.48 (dd, $J = 15.6, 6.0$ Hz, 1H), 1.54 (qdd, $J = 7.2, 2.4, 2.4$ Hz, 1H), 1.27 (d, $J = 6.6$ Hz, 3H), 1.26 (t, $J = 7.2$ Hz, 3H), 1.01 (d, $J = 7.2$ Hz, 3H); ¹³C NMR (CDCl₃, 150 MHz) δ 170.9, 138.5, 128.6, 128.1 (2C), 126.1 (2C), 101.6, 77.2, 76.4, 60.4, 37.9, 35.4, 18.5, 14.1, 5.5; HRMS (ESI) calcd for [C₁₆H₂₂O₄ + Na]⁺: 301.1410, Found: 301.1422.

Ethyl 2-((2S,4R,5S,6S)-5,6-dimethyl-2-phenyl-1,3-dioxan-4-yl)acetate (21).

Enoate (100 mg, 0.58 mmol) was dissolved in 2 mL of THF and cooled to 0 °C. To the reaction was added benzaldehyde (65 μ L, 0.63 mmol) and potassium *tert*-butoxide (9.7 mg, 87 μ mol). The addition of base and aldehyde was repeated 3 times at 20 minute intervals. The reaction was allowed to stir at 0 °C, and was quenched after 2.5 hours by adding 5 mL of pH 7 buffered phosphate solution. The layers were separated and the aqueous layer was extracted (3 x 4 mL) with Et₂O. The organic layers were combined

and washed with 6 mL of brine, then dried using Na₂SO₄, and the solvent removed under reduced pressure. The product was purified by silica gel chromatography eluting with (10 % EtOAc/hexanes) to yield benzylidene acetal in 80% yield as a clear, colorless oil. Spectral data agreed satisfactorily with the literature, see Tholander, J.; Carreira, E. M. *Helv. Chim. Acta* **2001**, 84, 613.

(+)-(E)-Ethyl 3-((2S,3R)-2,3-dimethyloxiran-2-yl)acrylate (19). To a solution of *Z,E*-dienoate (**16**) (100 mg, 0.649 mmol) and D-Epoxone (100 mg, 0.389 mmol) in CH₃CN/EtOH/CH₂Cl₂ (1:1:2) (1.0 mL) at 0°C was added 0.5 mL of a 2 M solution of K₂CO₃ in 4 x 10⁻⁴ M EDTA. Then a 30% H₂O₂ solution (0.260 mL, 2.59 mmol) was added. The reaction was allowed to stir at 0°C for 23 h when determined complete by TLC (UV, anisaldehyde stain). The reaction mixture was then extracted with ether (3 x 2 mL) and washed with 1 M aqueous Na₂S₂O₃ (2 mL) and brine (2 mL). The organic layers were then dried using Na₂SO₄, and the solvent removed under reduced pressure. The product was purified by silica gel chromatography eluting with (5 % EtOAc/hexanes) to give 70 mg (64 %) of epoxide as a clear, colorless oil. Spectral data agreed satisfactorily with literature, see Tholander, J.; Carreira, E. M. *Helv. Chim. Acta* **2001**, 84, 613.

***Study of the stereospecificity of the Pd(0)/HCOOH reduction reaction:**

(-)-(R,E)-Ethyl 6-(benzyloxy)-4-deutero-5-hydroxyhex-2-enoate: Into a 25 mL, round bottomed flask fitted with a condenser and maintained under nitrogen was placed 300 mg (0.98 mmol) of (*E*)-ethyl 3-((4*S*,5*S*)-5-ethyl-2-oxo-1,3-dioxolan-4-yl)acrylate, 5.1 mg (0.005 mmol, 0.5 mol%) of Pd₂(DBA)₃·CHCl₃, 2.6 mg (0.01 mmol, 1 mol%) of PPh₃, and 5 mL of THF. Triethylamine 0.4 mL, (2.9 mmol) and DCO₂H 138 mg (2.9 mmol) were added and the mixture was allowed to reflux for 30 minutes. The reaction was cooled to room temperature and quenched with saturated aqueous sodium bicarbonate (5 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 (*R,E*)-ethyl 6-(benzyloxy)-4-deutero-5-hydroxyhex-2-enoate as a viscous oil (194 mg, 75 %): *R_f* (30% EtOAc/hexanes) = 0.2; [α]_D²⁵ -2.1 (*c* 1.2, CH₂Cl₂); IR (thin film, cm⁻¹) 3428, 2982, 2902, 1715, 1654, 1454, 1392, 1368, 1313, 1269, 1177, 1095, 1041, 985; ¹H NMR (CDCl₃, 600 MHz) δ 7.34 (m, 5H), 6.96 (dd, *J* = 15.6, 7.2 Hz, 1H), 5.89 (dd, *J* = 15.6, 1.8 Hz, 1H), 4.56 (d, *J* = 12 Hz, 1 H), 4.54 (d, *J* = 12 Hz, 1 H), 4.18 (q, *J* = 7.2 Hz, 2 H), 3.95 (m, 1H), 3.51 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.38 (dd, *J* = 9.6, 7.2 Hz, 1H), 2.46 (brs, 1H), 2.38 (ddd, *J* = 7.8, 7.2, 1.8 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (CDCl₃, 150 MHz) δ 166.2, 144.3, 137.6, 128.4 (2C), 127.8, 127.7 (2C), 123.8, 73.6, 73.4, 69.1, 60.2, 35.8 (t, *J* = 19.1), 14.2; CIHRMS: Calculated for [C₁₅H₁₉DO₄+Na]⁺: 288.1316, Found: 288.1322.

(+)-Ethyl 2-((2S,4R,5R,6R)-6-((benzyloxy)methyl)-5-deutero-2-phenyl-1,3-dioxan-4-yl)acetate: Following general procedure for the Evans' hemiacetal addition, the Ethyl 2-((2S,4R,5R,6R)-6-((benzyloxy)methyl)-5-deutero-2-phenyl-1,3-dioxan-4-yl)acetate was produced (93 mg, >95:5 dr) in 66% yield from (100 mg, 0.38 mmol) (*R,E*)-ethyl 6-(benzyloxy)-4-deutero-5-hydroxyhex-2-enoate as a viscous oil. R_f (30% EtOAc/hexanes) = 0.42; $[\alpha]_D^{25} +6.6$ (c 2.0, CH₂Cl₂); IR (thin film, cm⁻¹) 2864, 1733, 1455, 1396, 1309, 1142, 1115, 1026, 751; ¹H NMR (CDCl₃, 600 MHz) δ 7.48 (m, 2H), 7.33 (m, 8H), 5.59 (s, 1H), 4.62 (d, J = 12.0 Hz, 1 H), 4.58 (d, J = 12.0 Hz, 1 H), 4.33 (ddd, J = 11.4, 6.6, 6.6 Hz, 1 H), 4.16 (q, J = 7.2 Hz, 2 H), 4.13 (ddd, J = 11.4, 6.0, 4.8 Hz, 1 H), 3.66 (dd, J = 10.2, 6.0 Hz, 1H), 3.54 (dd, J = 10.2, 4.8 Hz, 1H), 2.73 (dd, J = 15.6, 7.2 Hz, 1H), 2.52 (dd, J = 15.6, 6.6 Hz, 1H), 1.51 (dd, J = 11.4, 11.4 Hz, 1H), 1.26 (t, J = 7.2 Hz, 3H); ¹³C NMR (CDCl₃, 150 MHz) δ 170.6, 138.2, 138.1, 128.7, 128.4 (2C), 128.1 (2C), 127.7 (2C), 127.6, 126.1 (2C), 100.7, 75.8, 73.5, 73.0, 72.7, 60.6, 41.0, 32.9 (t, J = 19.1), 14.2; CIHRMS: Calculated for [C₂₂H₂₅DO₅+Na]⁺: 394.4348, Found: 394.4352.

Stereochemistry was confirmed by coupling constants between H₂-H₃, H₃-H₄ and nOe experiment:

In the NOESY spectrum, the H-1 at 5.59 ppm shows strong nOe to H-2 and H-4 and no nOes to H-3. Therefore H-1 proton is *cis* to H-2 and H-4. In addition, H-3 shows strong nOes to H-5 and H-6. Finally we can conclude the H-3 is *trans* to H-2 and H-4.

^1H NMR (600 MHz, CDCl_3)

^{13}C NMR (150 MHz, CDCl_3)

^1H NMR (600 MHz, CDCl_3)

^1H NMR (600 MHz, CDCl_3)

^{13}C NMR (150 MHz, CDCl_3)

^{13}C NMR (150 MHz, CDCl_3)

^{13}C NMR (150 MHz, CDCl_3)

^1H NMR (600 MHz, CDCl_3)

^1H NMR (600 MHz, CDCl_3)

^1H NMR (600 MHz, CDCl_3)

^{13}C NMR (150 MHz, CDCl_3)

^1H NMR (600 MHz, CDCl_3)

^1H NMR (600 MHz, CDCl_3)

^1H NMR (600 MHz, CDCl_3)

^{13}C NMR (150 MHz, CDCl_3)

^1H NMR (600 MHz, CDCl_3)

^{13}C NMR (150 MHz, CDCl_3)

^{13}C NMR (150 MHz, CDCl_3)

^1H NMR (600 MHz, CDCl_3)

^{13}C NMR (150 MHz, CDCl_3)

^1H NMR (600 MHz, CDCl_3)

¹³C NMR (150 MHz, CDCl₃)

^1H NMR (600 MHz, CDCl_3)