Supporting Information for

Stereospecificity in the Au-Catalysed Cyclisation of Allylic Diols. Synthesis of (+)-Isoaltholactone

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(*E*)-Methyl 4-[(4*R*,5*R*)-5-benzoyl-2,2-dimethyl-1,3-dioxolan-4-yl]-2-hydroxybut-3-enoate (12)

Method 1. [used for the chemistry presented in Scheme 3] To an argon-flushed flask containing alkene **10**[1] (875 mg, 3.77 mmol) and alkene **11**[2] (1.31 g, 11.3 mmol) was added a solution of Grubbs II catalyst (320 mg, 0.380 mmol) in degassed dichloromethane (30 mL) and the resulting solution was heated at reflux under argon for 2 h. The reaction mixture was then allowed to cool to RT, concentrated *in vacuo* and purified by column chromatography (petrol/ethyl acetate, 8:1 → 1:1) affording the *title compound* (**12**) as a mixture of diastereoisomers (A & B; *dr* ≈ 1:1) and as a pale yellow oil (870 mg, 72%). See below for data.

Method 2. A solution of Hoveyda–Grubbs II catalyst (10.7 mg, 17.4 μmol) in degassed dichloromethane (1.5 mL) was added *via* cannula to a mixture of alkene **10**[1] (40 mg, 0.172 mmol) and alkene **11**[2] (60 mg, 0.517 mmol) in a vacuum-dried flask. The resulting mixture was stirred at 50 °C for 3.5 h, cooled to RT and then concentrated *in vacuo*. Purification by flash chromatography (petrol/ether, 3:1→2:1) gave the *title compound* (**12**) as a colourless oil (50 mg, 92%) and as a mixture of diastereomers (*dr* ≈ 2:1). R_f 0.20 (petrol/ethyl acetate, 2:1); ν_{max} (thin film)/cm^{-1}

3474br, 1744s, 1697s, 1449w, 1382w, 1217s, 1103m, 1038m, 976m, 934w, 693w; δ_H (400 MHz, $CDCl_3$) 1.49 and 1.70 (2 × 6 H, 2 × s, $(CH_3)_2C$, A & B), 2.57 and 2.64 (2 × 1 H, 2 × br s, OH, A & B) 3.63 and 3.64 (2 × 3 H, 2 × s, OCH_3, A & B), 4.39–4.42 and 4.44–4.47 (2 × 1 H, 2 × m, C*H*OH, A & B), 5.02–5.05 (2 H, m, C*H*CHCOPh, A & B), 5.58–5.61 (2 H, m, C*H*COPh, A & B), 5.63–5.74 (4 H, m, CH=CH, A & B), 7.44–7.48 (4 H, m), 7.55–7.60 (2 H, m) and 7.84–7.86 (4 H, m, Ph, A & B); δ_C (125 MHz, $CDCl_3$) 25.3, 25.4 and 27.1 (2 × CH_3, A & B), 52.8 (CH_3, A & B), 70.0 and 70.1 (CH, A & B), 77.8 (CH, A & B), 80.6 (CH, A & B), 110.7 and 110.8 (C, A & B), 127.5 and 127.7 (CH, A & B), 128.3 (CH, A & B), 128.5 and 128.6 (CH, A & B), 130.9 and 131.0 (CH, A & B), 133.4 (CH, A & B), 136.0 (C, A & B), 172.7 and 172.8 (C, A & B), 194.9 (C, A & B); HRMS (ESI^+) found 343.1148, $C_{17}H_{20}NaO_6$ (MNa^+) requires 343.1152.

(*E*)-Methyl 2-hydroxy-4-{(4*R*,5*S*)-5-[(*S*)-hydroxy(phenyl)methyl]-2,2-dimethyl-1,3-dioxolan-4-yl}but-3-enoate (13)

L-Selectride (2.63 mL, 1.0 M solution in THF, 2.63 mmol) was added dropwise to a solution of ketone **12** (560 mg, 1.75 mmol) in THF (37 ml) at –78 ºC. The resulting solution was stirred at –78 ºC for 30 min and quenched by the addition of sat. aq. NH_4Cl (7.0 mL). Upon warming to RT, the mixture was diluted with water (15 mL) and extracted with ethyl acetate (3 × 25 mL). The combined organic phases were then washed with sat. aq. $NaHCO_3$ (25 mL), dried over $MgSO_4$ and concentrated *in vacuo*. Purification by column chromatography (petrol/ethyl acetate, 2:1→1:1) afforded the *title compound* (**13**) as a colourless oil (388 mg, 69%) and as a mixture of diastereoisomers (A & B, *dr* = 2:1); R_f 0.18 (petrol/ethyl acetate, 2:1); ν_{max} (thin film)/cm^{-1} 3424br, 1742s, 1381w, 1217m, 1055m, 701w; δ_H (400 MHz, $CDCl_3$) 1.31 (3 H, s, CH_3, B), 1.32 (3 H, s, CH_3, A), 1.47 (3 H, s, CH_3, B), 1.49 (3 H, s, CH_3, A), 3.82 (6 H, s, OCH_3, A & B), 4.29–4.42 (2 H, m) and 4.60–4.83 (6 H, m, C*H*C*H*C*H*(OH)Ph and C*H*CO_2Me, A & B), 5.94–6.00 and 6.19–6.30 (2 × 2 H, 2 × m, CH=CH, A & B), 7.28–7.46 (10 H, m, Ph, A & B); δ_C (125 MHz, $CDCl_3$) 25.2 (CH_3, A & B), 27.7 (CH_3, A & B), 53.0 and 53.1 (CH_3, A & B), 70.8 (CH, A), 70.9

(CH, B), 72.2 (CH, A & B), 77.3 (CH, A & B, assigned from HSQC), 80.9 (CH, A & B), 108.9 and 109.0 (C, A & B), 127.0–129.5 (aromatic CH, A & B) including 128.4 and 129.1 (alkenyl CH, A & B, assigned from HSQC), 141.2 (C, A & B), 173.4 (C, B), 173.5 (C, A); HRMS (ESI^+) found 345.1304, $C_{17}H_{22}NaO_6$ (MNa^+) requires 345.1309.

(*E*)-Methyl 3-[(3a*R*,4*S*,6*S*,6a*S*)-2,2-dimethyl-6-phenyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl]acrylate (14), (*E*)-methyl 3-[(3a*R*,4*R*,6*S*,6a*S*)-2,2-dimethyl-6-phenyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl]acrylate (15), and (*Z*)-methyl 3-[(3a*R*,4*S*,6*S*,6a*S*)-2,2-dimethyl-6-phenyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl]acrylate (16)

Dichloromethane (2.0 mL) was added to a foil-covered flask containing activated 4 Å molecular sieves (10 beads), chloro(triphenylphosphine)gold(I) (16.2 mg, 0.0327 mmol) and silver(I) triflate (8.4 mg, 0.0327 mmol) and the mixture was stirred for 2 min at RT. A solution of diol **13** (105 mg, 0.326 mmol, 2:1 mixture of diastereoisomers) in dichloromethane (2.0 mL) was then added and the resulting mixture stirred at RT for 2 h. The crude reaction mixture was then filtered through Celite, concentrated *in vacuo* and purified by column chromatography (petrol/ethyl acetate, 15:1→8:1) to afford the *title compound* (**14**) as a colourless oil (28 mg, 28%). R_f 0.68 (petrol/ether, 2:1); $[\alpha]_D^{23}$ +70 (*c* 0.6, $CHCl_3$); ν_{max} (thin film)/cm^{-1} 2937w, 1726s, 1437w, 1374m, 1271s, 1210s, 1067s, 861m, 701w; δ_H (500 MHz, $CDCl_3$) 1.37 and 1.56 (2 × 3 H, 2 × s, $(CH_3)_2C$), 3.77 (3 H, s, OCH_3), 4.55–4.57 (1 H, m, =CHC*H*(OR)), 4.79 (1 H, dd, *J* 6.0, 4.4, C*H*CH(OR)CH=), 5.00 (1 H, d, *J* 6.0, C*H*CH(OR)Ph), 5.27 (1 H, s, C*H*Ph), 6.23 (1 H, dd, *J* 15.9, 1.6, =C*H*CO_2Me), 7.05 (1 H, dd, *J* 15.9, 5.4, =C*H*CH(OR)), 7.27–7.40 (5 H, m, Ph); δ_C (100 MHz, $CDCl_3$) 25.2 (CH_3), 26.3 (CH_3), 51.6 (CH_3), 80.0 (CH), 82.5 (CH), 84.7 (CH), 87.5 (CH), 113.4 (C), 122.7 (CH), 125.5 (CH), 127.6 (CH), 128.7 (CH), 138.2 (C), 142.0 (CH), 166.4 (C); HRMS (ESI^+) found 327.1206, $C_{17}H_{20}NaO_5$ (MNa^+) requires 327.1203. Also obtained were *stereoisomers* **15** and **16** (58 mg, 59%) as a colourless oil, inseparable, 1:1 ratio. Data for **15** (data from a sample recovered from the isoaltholactone synthesis, see below): R_f 0.75

(petrol/ethyl acetate, 1:1); $[\alpha]_D^{23}$ +35 (*c* 0.9, CH_2Cl_2); ν_{max} (thin film)/cm^{-1} 2990w, 2950w, 1727s, 1665w, 1374w, 1270m, 1212m, 1081s, 860w, 700w; δ_H (500 MHz, $CDCl_3$) 1.35 and 1.65 (2 × 3 H, 2 × s, $(CH_3)_2C$), 3.78 (3 H, s, OCH_3), 4.54–4.59 (2 H, m, C*H*C*H*CH(OR)Ph), 4.60–4.62 (1 H, m, =CHC*H*(OR)), 4.96 (1 H, d, *J* 4.3, C*H*Ph), 6.24 (1 H, dd, *J* 15.7, 1.7, =C*H*CO_2Me), 7.11 (1 H, dd, *J* 15.7, 4.7, =C*H*CH(OR)), 7.30–7.42 (5 H, m, Ph); δ_C (100 MHz, $CDCl_3$) 25.5 (CH_3), 27.5 (CH_3), 51.7 (CH_3), 82.9 (CH), 84.4 (CH), 85.6 (CH), 86.9 (CH), 115.6 (C), 121.6 (CH), 125.7 (CH), 128.0 (CH), 128.6 (CH), 139.0 (C), 144.2 (CH), 166.5 (C); HRMS (ESI^+) found 327.1197, $C_{17}H_{20}NaO_5$ (MNa^+) requires 327.1203. Characterising ^{1}H NMR data for **16** (not obtained as a pure component): δ_H (500 MHz, $CDCl_3$) 1.35 and 1.56 (2 × 3 H, 2 × s, $(CH_3)_2C$), 3.71 (3 H, s, OCH_3), 5.01 (1 H, d, *J* 6.0, C*H*CH(OR)Ph), 5.05 (1 H, dd, *J* 6.0, 4.0, C*H*CH(OR)CH=), 5.28 (1 H, s, C*H*Ph), 5.42 (1 H, ddd, *J* = 6.5, 4.0, 1.6, =CHC*H*(OR)), 6.01 (1 H, dd, *J* 11.7, 1.6, =C*H*CO_2Me), 6.47 (1 H, dd, *J* 11.7, 6.5, =C*H*CH(OR)), 7.30–7.42 (5 H, m, Ph).

(+)-Isoaltholactone (5)[3]

From 14. To a solution of enoate **14** (26 mg, 0.0856 mmol) in methanol (4.0 mL) was added anhydrous *p*-toluenesulfonic acid (1.6 mg, 8.56 μmol) and the mixture was heated at reflux for 18 h. The mixture was cooled to RT and concentrated *in vacuo* to afford *(*E*)-methyl 3-[(2*S*,3*S*,4*R*,5*S*)-3,4-dihydroxy-5-phenyltetrahydrofuran-2-yl]acrylate* as a colourless oil, used without further purification (23 mg, assumed quant.). R_f 0.29 (ether); $[\alpha]_D^{23}$ +23 (*c* 0.2, $CHCl_3$); ν_{max} (thin film)/cm^{-1} 3440br, 1723s, 1438m, 1262s, 797w, 700w; δ_H (500 MHz, $CDCl_3$) 2.44 and 2.53 (2 × 1 H, 2 × br s, 2 × OH), 3.77 (3 H, s, OCH_3), 4.15–4.20 (1 H, m, C*H*CH(OR)Ph), 4.41 (1 H, app. t, *J* 4.5, C*H*CHCH(OR)Ph), 4.90 (1 H, d, *J* 7.4, C*H*Ph), 4.97 (1 H, app. td, *J* 4.5, 1.7, =CHC*H*(OR)), 6.28 (1 H, dd, *J* 15.8, 1.7, =C*H*CO_2Me), 7.09 (1 H, dd, *J* 15.8, 4.5, =C*H*CH(OR)), 7.30–7.43 (5 H, m, Ph); δ_C (125 MHz, $CDCl_3$) 51.7 (CH_3), 73.2 (CH), 79.3 (CH), 80.0 (CH), 83.3 (CH), 122.8 (CH), 125.6 (CH), 128.0 (CH), 128.6 (CH), 139.8 (C), 143.3 (CH), 166.5 (C); HRMS (ESI^+) found 287.0890, $C_{14}H_{16}NaO_5$ (MNa^+) requires 287.0890. This ester (22.6 mg, 0.0856

mmol) was stirred in a mixture of isopropanol (0.35 mL) and aq. NaOH (2.0 M, 0.175 mL) at RT for 15 min. The reaction mixture was then acidified with hydrochloric acid (1.0 M, 1.0 mL), extracted with ether (3 × 5.0 mL), dried over $MgSO_4$, and concentrated *in vacuo* to afford *(*E*)-3-[(2*S*,3*S*,4*R*,5*S*)-3,4-dihydroxy-5-phenyltetrahydrofuran-2-yl]acrylic acid*, used without further purification (18 mg, 84% from **14**). $[\alpha]_D^{23}$ +17.0 (*c* 0.3, EtOH); ν_{max} (thin film)/cm^{-1} 3418br, 1669s, 1495w, 1267m, 1024m, 700w; δ_H (500 MHz, CD_3OD) 4.08 (1 H, dd, *J* 8.2, 4.2, C*H*CH(OR)Ph), 4.29 (1 H, app. t, *J* 4.2, C*H*CHCH(OR)Ph), 4.85–4.95 (2 H, m, C*H*OC*H*Ph, occluded by the solvated water peak), 6.13 (1 H, d, *J* 15.5, =C*H*CO_2H), 7.09 (1 H, dd, *J* 15.5, 5.4, =C*H*CH(OR)), 7.28–7.45 (5 H, m, Ph); δ_C (125 MHz, CD_3OD) 74.9 (CH), 80.9 (CH), 81.9 (CH), 84.2 (CH), 123.5 (CH), 127.2 (CH), 128.7 (CH), 129.4 (CH), 142.5 (C), 146.5 (CH), 169.7 (C); HRMS (ESI^+) found 273.0734, $C_{13}H_{14}NaO_5$ (MNa^+) requires 273.0733. To a solution of this acid (15 mg, 0.060 mmol) in pyridine (0.24 mL) at 0 °C was added 2,4,6-trichlorobenzoyl chloride (11.3 µl, 0.072 mmol). The solution was warmed to RT and stirred for 18 h. The reaction mixture was then diluted with ether (10 mL), washed sequentially with sat. aq. $NaHCO_3$ (3.0 mL) and sat. aq. $CuSO_4$ (3.0 mL), dried over $MgSO_4$, and concentrated *in vacuo*. Purification by column chromatography (petrol/ethyl acetate, 2:1) afforded the title compound (**5**, 5.5 mg, 40%). See below for data.

From 15/16. To a mixture of enoates **15** and **16** (48 mg, *ca.* 0.079 mmol each of **15** and **16**) in methanol (4.0 mL) was added *p*-toluenesufonic acid (2.0 mg, 0.0116 mmol). The resulting solution was stirred at 50 ºC for 18 h, concentrated *in vacuo* and dissolved in benzene (4.0 mL). The reaction vessel was then sonicated (ultrasonic cleaning bath) for 2 h at RT and then concentrated *in vacuo*. To half of this mixture (the other half being retained for analysis) was added a mixture of 2,2-dimethoxypropane (0.73 mL), acetone (0.22 mL) and methanol (0.05 mL) and the resulting solution was stirred at RT for 10 min. Solid $NaHCO_3$ (50 mg) was added and the mixture then stirred to ensure the pH had reached ≥7.0 (pH paper). The inorganic residues were removed by filtration and rinsed with ethyl acetate (25 mL). The combined

organic portions were washed with water (10 mL), dried over $MgSO_4$ and concentrated *in vacuo*. Purification by column chromatography (petrol/ethyl acetate, 5:1→1:1) afforded recovered acetonide **15** (10 mg, 83% based on **15** originally present) and the title compound (8.0 mg, 87% based on **16** originally present) as a gum. Data for **5**: R_f 0.30 (petrol/ethyl acetate, 1:1); $[\alpha]_D^{20}$ +20 (*c* 0.2, EtOH) [lit.[4,5] values vary: $[\alpha]_D^{21–30}$ +26.1 to + 74.1 (*c* 0.3–0.8, EtOH)]; ν_{max} (thin film)/cm^{-1} 3420br, 1727s, 1391w, 1249m, 1104m, 1040m, 702w; δ_H (500 MHz, $CDCl_3$) 2.66 (1 H, br s, OH), 4.27–4.32 (1 H, m, C*H*OH), 4.79 (1 H, d, 7.6, C*H*Ph), 4.89 (1 H, dd, *J* 5.4, 4.8, =CHC*H*(OR)), 5.08 (1 H, app. t, *J* 5.4, CHOC=O), 6.24 (1 H, d, *J* 10.0, =C*H*CO_2), 6.90 (1 H, dd, *J* 10.0, 4.8, =C*H*CH(OR)), 7.32–7.41 (5 H, m, Ph); δ_C (125 MHz, $CDCl_3$) 67.6 (CH), 78.5 (CH), 78.6 (CH), 83.2 (CH), 123.0 (CH), 125.7 (CH), 128.4 (CH), 128.7 (CH), 138.3 (C), 141.5 (CH), 160.7 (C); HRMS (ESI^+) found 255.0630, $C_{13}H_{12}NaO_4$ (MNa^+) requires 255.0628.

{(4*R*,5*R*)-5-[(*S*,*E*)-4-(*tert*-Butyldimethylsilyloxy)-3-hydroxybut-1-enyl]-2,2-dimethyl-1,3-dioxolan-4-yl]}phenylmethanone (17)

A solution of Hoveyda–Grubbs II catalyst (10.7 mg, 17.4 μmol) in degassed dichloromethane (1.37 mL) was added *via* cannula to a mixture of alkene **10**[1] (40 mg, 0.172 mmol) and alkene **22**[6] (130 mg, 0.345 mmol) in a vacuum-dried flask. The resulting mixture was stirred at 50 °C for 3 h, cooled to RT and then concentrated *in vacuo*. Purification by flash chromatography (toluene/ether, 3:1) gave *alcohol* **17** as a colourless oil (68 mg, 97%). R_f 0.35 (toluene/ether, 3:1); $[\alpha]_D^{25}$ +26.4 (*c* 1.0, $CHCl_3$); ν_{max} (thin film)/cm^{-1} 3502br, 2930s, 2858s, 1696s, 1598w, 1449m, 1381m, 1253s, 1216s, 1163m, 1104br, 936w, 881m, 837s, 777m, 690m; δ_H (500 MHz, $CDCl_3$) 0.00 (6 H, s, $Si(CH_3)_2$), 0.85 (9 H, s, $SiC(CH_3)_3$), 1.48 (3 H, s, CH_3), 1.69 (1 H, br s, OH), 1.71 (3 H, s, CH_3), 3.03 (1 H, dd, *J* 10.0, 8.5) and 3.29 (1 H, dd, *J* 10.0, 4.0, CH_2OSi), 3.88–3.93 (1 H, m, C*H*OH), 4.99–5.02 (1 H, m, =CHC*H*(OR)), 5.50 (1 H, ddd, *J* 15.5, 7.5, 1.0, =C*H*CH(OR)), 5.59–5.65 (2 H, m, CH(OH)C*H*= and C*H*(OR)COPh), 7.46 (2 H, t, *J* 7.5), 7.53–7.59 (1 H, m) and 7.88 (2 H, d, *J* 7.5, Ph); δ_C (125 MHz, $CDCl_3$) –5.6 and –5.4 (2 × CH_3), 18.2 (C), 25.4 (CH_3), 25.8 (3 × CH_3), 27.1 (CH_3), 66.5

(CH_2), 71.5 (CH), 78.4 (CH), 80.5 (CH), 110.7 (C), 126.8 (CH), 128.4 (CH), 128.6 (CH), 133.4 (CH), 133.7 (CH), 136.0 (C), 195.1 (C); HRMS (ESI^+) found 429.2063, $C_{22}H_{34}NaO_5Si$ (MNa^+) requires 429.2068.

{(4*R*,5*R*)-5-[(*R*,*E*)-4-(*tert*-Butyldimethylsilyloxy)-3-hydroxybut-1-enyl]-2,2-dimethyl-1,3-dioxolan-4-yl}phenylmethanone (18)

A solution of Hoveyda–Grubbs II catalyst (27 mg, 44 μmol) in degassed dichloromethane (0.55 mL) was added *via* cannula to a mixture of alkene **10**[1] (100 mg, 0.43 mmol) and alkene **23**[7] (174 mg, 0.86 mmol) in a vacuum–dried flask. The resulting mixture was stirred at 50 °C for 1.5 h then cooled to RT and concentrated *in vacuo*. Purification of the residue by flash chromatography (toluene/ether, 3:1) gave the *title compound* (**18**) as a colourless oil (139 mg, 80%). R_f 0.23 (petrol/ether, 2:1); $[\alpha]_D^{25}$ +18.8 (*c* 1.0, $CHCl_3$); ν_{max} (thin film)/cm^{-1} 3450br, 2931s, 2858s, 1698s, 1598w, 1449m, 1381m, 1254s, 1217s, 1163m, 1105br, 1039m, 838s; δ_H (500 MHz, $CDCl_3$) –0.02 and –0.01 (2 × 3 H, 2 × s, $Si(CH_3)_2$), 0.85 (9 H, s, $SiC(CH_3)_3$), 1.49 and 1.71 (2 × 3 H, 2 × s, $(CH_3)_2C$), 2.30 (1 H, br s, OH), 2.86 (1 H, dd, *J* 10.0, 8.5) and 3.06 (1 H, dd, *J* 10.0, 3.5, CH_2OSi), 3.87–3.91 (1 H, m, C*H*OH), 5.00 (1 H, t, *J* 7.5, =CHC*H*(OR)), 5.46 (1 H, ddd, *J* 15.5, 7.5, 1.0, =C*H*CH(OR)), 5.55 (1 H, dd, *J* 15.5, 6.5, CH(OH)C*H*=), 5.62 (1 H, d, *J* 7.5, C*H*(OR)CO.Ph), 7.46 (2 H, td, *J* 7.5, 1.5), 7.58 (1 H, tt, *J* 7.5, 1.5) and 7.87–7.89 (2 H, m, Ph); δ_C (125 MHz, $CDCl_3$) –5.5 and –5.4 (2 × CH_3), 18.2 (C), 25.3 (CH_3), 25.8 (3 × CH_3), 27.1 (CH_3), 66.4 (CH_2), 71.7 (CH), 78.6 (CH), 80.4 (CH), 110.7 (C), 127.3 (CH), 128.4 (CH), 128.5 (CH), 133.5 (CH), 133.8 (CH), 135.9 (C), 194.8 (C); HRMS (ESI^+) found 429.2069, $C_{22}H_{34}NaO_5Si$ (MNa^+) requires 429.2068. Also isolated was *(6*R*,9*R*,*E*)-2,2,3,3,12,12,13,13-octamethyl-4,11-dioxa-3,12-disilatetradec-7-ene-6,9-diol* (*R*,*R*-**22**) as a white crystalline solid (80 mg, 50%). R_f 0.19 (petrol/ether, 2:1); m.p. 59 °C (lit.[8] m.p. 89–90 °C for (*S*,*S*)-**22**); $[\alpha]_D^{19}$ –2.3 (*c* 5.0, $CHCl_3$) [lit.[8] for (*S*,*S*)-**22** $[\alpha]_D^{20}$ –21 (*c* 0.45, MeOH)]; ν_{max} (KBr disc)/cm^{-1} 3284br, 2928s, 1471m, 1338w, 1256m, 1117s, 1027m, 972w, 939w, 837s, 774s; δ_H (500 MHz, $CDCl_3$) 0.09 (12 H, s, 2 × $Si(CH_3)_2$), 0.91 (18 H, s, 2 × $SiC(CH_3)_3$), 2.56

(2 H, br s, 2 × OH), 3.44 (2 H, dd, *J* 10.0, 8.0) and 3.66 (2 H, dd, *J* 10.0, 3.5, 2 × CH_2OSi), 4.20 (2 H, app. dt, *J* 8.0, 3.5, 2 × C*H*OH), 5.78 (2 H, dd, *J* 3.0, 1.5, CH=CH); δ_C (125 MHz, $CDCl_3$) –5.4 (4 × CH_3), 18.3 (2 × C), 25.8 (6 × CH_3), 67.1 (2 × CH_2), 72.1 (2 × CH), 130.4 (2 × CH); HRMS (ESI^+) found 399.2358, $C_{18}H_{40}NaO_4Si_2$ (MNa^+) requires 399.2357.

(*S*,*E*)-1-(*tert*-Butyldimethylsilyloxy)-4-{(4*R*,5*S*)-5-[(*S*)-hydroxy(phenyl)methyl]-2,2-dimethyl-1,3-dioxolan-4-yl}but-3-en-2-ol (19) and (*S*,E)-1-(*tert*-butyldimethylsilyloxy)-4-{(4*R*,5*S*)-5-[(*R*)-hydroxy(phenyl)methyl]-2,2-dimethyl-1,3-dioxolan-4-yl}but-3-en-2-ol (21)

L-Selectride (150 μL, 1.0 M in THF, 0.15 mmol) was added to a solution of ketone **17** (40 mg, 0.099 mmol) in THF (2.1 mL) at –78 °C, the mixture stirred for 1 h and then warmed to 0 °C. The reaction was quenched with sat. aq. NH_4Cl (1.5 mL), the aqueous layer was extracted with ethyl acetate (3 × 5.0 mL) and the combined organic phases were washed with sat. aq. $NaHCO_3$ (10 mL), dried ($MgSO_4$) and concentrated *in vacuo*. Purification by flash chromatography (petrol/ether, 1:1) gave *diols* **19** and **21** (40 mg, 99%), an inseparable mixture (*dr* = 7.2:1 by ^1H NMR analysis), as a colourless oil. R_f 0.26 (petrol/ether, 1:1); ν_{max} (thin film)/cm^{-1} 3418br, 2930br, 1462m, 1380s, 1255s, 1217s, 1110br, 1062br, 838s, 779m, 699m; HRMS (ESI^+) found 431.2209, $C_{22}H_{36}NaO_5Si$ (MNa^+) requires 431.2224. NMR data for **19**: δ_H (500 MHz, $CDCl_3$) 0.08 (6 H, s, $Si(CH_3)_2$), 0.91 (9 H, s, $SiC(CH_3)_3$), 1.30 and 1.47 (2 × 3 H, 2 × s, $(CH_3)_2C$), 2.20–2.92 (2 H, br m, 2 × OH), 3.49–3.51 (1 H, m) and 3.70 (1 H, dd, *J* 10.0, 4.0, CH_2OSi), 4.22–4.27 (1 H, m, $SiOCH_2CH(OH)$), 4.28 (1 H, dd, *J* 9.0, 6.5, C*H*(OR)CHPh), 4.62–4.66 (1 H, m, C*H*(OH)Ph), 4.76 (1 H, app. t, *J* 7.0, C*H*(OR)CH=), 5.84 (1 H, dd, *J* 15.5, 6.0, CH(OH)C*H*=), 6.08 (1 H, ddd, *J* 15.5, 7.0, 1.5, =C*H*CH(OR)), 7.24–7.42 (5 H, m, Ph); δ_C (125 MHz, $CDCl_3$) –5.4 and –5.3 (2 × CH_3), 18.3 (C), 25.2 (CH_3), 25.8 (3 × CH_3), 27.8 (CH_3), 66.9 (CH_2), 71.9 (CH), 72.0 (CH), 78.1 (CH), 81.0 (CH), 108.9 (C), 127.0 (CH), 127.8 (CH), 128.2 (CH), 128.4 (CH), 132.1 (CH), 141.6 (C). NMR data for **21**: δ_H (500 MHz, $CDCl_3$) 0.08 (6 H, s, $Si(CH_3)_2$), 0.91 (9 H, s, $SiC(CH_3)_3$), 1.41 and 1.59 (2 × 3 H, 2 × s, $(CH_3)_2C$), 2.20–2.92 (2 H, br m, 2 × OH), 3.38 (1 H, dd, *J* 10.0, 8.0) and 3.61 (1 H, dd, *J*

10.0, 4.0, CH_2OSi), 4.14–4.21 (2 H, m, $SiOCH_2CH(OH)$ and $CH(OR)CHPh$), 4.41 (1 H, app. t, *J* 6.0, $CH(OH)Ph$), 4.56 (1 H, app. t, *J* 7.5, $CH(OR)CH=$), 5.66 (1 H, dd, *J* 15.6, 5.5, $CH(OH)CH=$), 5.89 (1 H, ddd, *J* 15.6, 7.5, 1.5, $=CHCH(OR)$), 7.24–7.42 (5 H, m, Ph); δ_C (125 MHz, $CDCl_3$) –5.4 and –5.3 (2 × CH_3), 18.3 (C), 25.1 (CH_3), 25.9 (3 × CH_3), 27.5 (CH_3), 65.8 (CH_2), 71.9 (CH), 72.3 (CH), 78.0 (CH), 81.5 (CH), 108.9 (C), 127.0 (CH), 127.8 (CH), 128.2 (CH), 128.5 (CH), 133.5 (CH), 140.4 (C).

(*R*,*E*)-1-(*tert*-Butyldimethylsilyloxy)-4-{(4*R*,5*S*)-5-[(*S*)-hydroxy(phenyl)methyl]-2,2-dimethyl-1,3-dioxolan-4-yl}but-3-en-2-ol (20)

L-Selectride (443 μL, 1.0 M in THF, 0.44 mmol) was added to a solution of ketone **18** (120 mg, 0.30 mmol) in THF (6.3 mL) at –78 °C and the mixture stirred for 1 h then warmed to 0 °C and quenched with sat. aq. NH_4Cl (4.5 mL). The aqueous layer was extracted with ethyl acetate (3 × 10 mL) and the combined organic phases were washed successively with sat. aq. $NaHCO_3$ (20 mL) and brine (20 mL), then dried ($MgSO_4$) and concentrated *in vacuo*. Purification by flash chromatography on basic Al_2O_3 (petrol/ether, 1:1) gave *diol* **20** (73 mg, 60%) as a colourless oil. R_f 0.19 (petrol/ether, 1:1); $[\alpha]_D^{25}$ –6.2 (*c* 1.0, $CHCl_3$); ν_{max} (thin film)/cm^{-1} 3418br, 2930br, 2858s, 1724w, 1462m, 1380m, 1257s, 1217m, 1166w, 1108br, 1062br, 838s, 779m, 699m; δ_H (500 MHz, $CDCl_3$) 0.08 (6 H, s, $Si(CH_3)_2$), 0.91 (9 H, s, $SiC(CH_3)_3$), 1.31 and 1.48 (2 × 3 H, 2 × s, $(CH_3)_2C$), 2.41 and 2.57 (2 × 1 H, 2 × br s, 2 × OH), 3.50 (1 H, dd, *J* 10.0, 7.5) and 3.66 (1 H, dd, *J* 10.0, 4.0, CH_2OSi), 4.22–4.27 (1 H, m, $SiOCH_2CH(OH)$), 4.29 (1 H, dd, *J* 8.5, 6.5, $CHCH(OH)Ph$), 4.66 (1 H, d, *J* 8.5, $CH(OH)Ph$), 4.78 (1 H, app. t, *J* 6.5, $CH(OR)CH=$), 5.86 (1 H, ddd, *J* 15.5, 5.5, 1.0, $CH(OH)CH=$), 6.10 (1 H, ddd, *J* 15.5, 6.5, 1.5, $=CHCH(OR)$), 7.27–7.41 (5 H, m, Ph); δ_C (125 MHz, $CDCl_3$) –5.4 (2 × CH_3), 18.3 (C), 25.2 (CH_3), 25.9 (3 × CH_3), 27.8 (CH_3), 66.9 (CH_2), 72.0 (CH), 72.1 (CH), 77.8 (CH), 81.0 (CH), 108.8 (C), 127.0 (CH), 127.8 (CH), 128.2 (2 × CH), 131.9 (CH), 141.3 (C); HRMS (ESI+) found 431.2225, $C_{22}H_{36}NaO_5Si$ (MNa^+) requires 431.2224.

(*R*)-*tert*-Butyldimethyl(oxiran-2-ylmethoxy)silane[9]

(*S*)-Glycidol (300 mg, 4.05 mmol) was added dropwise to a cooled (0 °C) solution of imidazole (441 mg, 6.48 mmol) and *tert*-butyldimethylsilyl chloride (793 mg, 5.26 mmol) in anhydrous DMF (2.40 mL). The mixture was stirred at 0 °C for 0.5 h then warmed to RT and stirred for a further 1.5 h. The reaction was quenched with brine (6.0 mL) and the resulting mixture stirred for 20 min; the layers were separated, the aqueous layer extracted with ether (2 × 15 mL), and the combined organic layers washed with water (10 mL), then dried ($MgSO_4$) and concentrated *in vacuo*. Purification by flash chromatography on neutral Al_2O_3 (petrol/ethyl acetate, 49:1) gave the title silyl ether as a colourless oil (726 mg, 95%). R_f 0.15 (petrol/ethyl acetate, 49:1); $[\alpha]_D^{25}$ –2.1 (*c* 1.0, $CHCl_3$); δ_H (500 MHz, $CDCl_3$) 0.07–0.10 (6 H, s, $Si(CH_3)_2$), 0.91 (9 H, s, $SiC(CH_3)_3$), 2.65 (1 H, dd, *J* 5.0, 2.5) and 2.78 (1 H, dd, *J* 5.0, 4.5, epoxide CH_2), 3.10 (1 H, app. quin, *J* 3.5, CH), 3.67 (1 H, dd, *J* 12.0, 5.0) and 3.86 (1 H, dd, *J* 12.0, 3.0, CH_2OSi); δ_C (125 MHz, $CDCl_3$) –5.4 and –5.3 (2 × CH_3), 18.4 (C), 25.9 (3 × CH_3), 44.5 (CH_2), 52.4 (CH), 63.7 (CH_2).

(*R*)-1-(*tert*-Butyldimethylsilyloxy)but-3-en-2-ol (23)[10]

Butyllithium (3.96 mL, 1.6 M in hexanes, 6.34 mmol) was added to a stirred suspension of trimethylsulfonium iodide (1.34 g, 6.56 mmol) in THF (20 mL) at –10 °C. After 0.5 h (*R*)-*tert*-butyldimethyl(oxiran-2-ylmethoxy)silane[9] (400 mg, 2.13 mmol) was added, the resulting milky suspension warmed to 0 °C over 0.5 h, and then stirring continued at RT for 2 h. The reaction was quenched with water (10 mL), the separated aqueous layer was extracted with ether (3 × 20 mL), and the combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo*. Purification by flash chromatography (petrol/ethyl acetate, 49:1) furnished the title alcohol (**23**) as a colourless oil (310 mg, 72%). R_f 0.09 (petrol/ethyl acetate, 49:1); $[\alpha]_D^{25}$ –3.7 (*c* 1.0, $CHCl_3$) [Lit.[10] $[\alpha]_D^{25}$ 4.6 (no sign given) (*c* 1.0, $CHCl_3$)]; δ_H (500 MHz, $CDCl_3$) 0.09 (6 H, s, $Si(CH_3)_2$), 0.92 (9 H, s, $SiC(CH_3)_3$), 2.57 (1 H, d, *J* 3.5, OH), 3.46 (1 H, dd, *J* 10.0, 8.0) and 3.67 (1 H, dd, *J* 10.0, 4.0, CH_2OSi), 4.15–4.21 (1 H, m, C*H*OH), 5.20 (1 H, d, *J* 10.5) and 5.35 (1 H, d, *J* 17.0, $=CH_2$), 5.82 (1 H, ddd, *J* 17.0,

10.5, 6.0, C*H*=CH_2); δ_C (125 MHz, $CDCl_3$) –5.4 (2 × CH_3), 18.3 (C), 25.9 (3 × CH_3), 66.9 (CH_2), 73.0 (CH), 116.5 (CH_2), 136.6 (CH).

tert-Butyl{(*Z*)-3-[(3a*R*,4*S*,6*S*,6a*S*)-2,2-dimethyl-6-phenyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl]allyloxy}dimethylsilane (24), _tert_-butyl{(*E*)-3-[(3a*R*,4*R*,6*S*,6a*S*)-2,2-dimethyl-6-phenyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl]allyloxy}dimethylsilane (25), and t_ert_-butyl((E)-3-((3a*R*,4*R*,6*R*,6a*S*)-2,2-dimethyl-6-phenyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)allyloxy)dimethylsilane (27)

Dichloromethane (1.0 mL) was added to a foil-covered flask containing chloro(triphenylphosphine)gold(I) (7.9 mg, 16.0 μmol), silver(I) triflate (4.1 mg, 16.0 μmol) and activated 4 Å molecular sieves under argon. The mixture was stirred for 2 min at RT then a solution of diol mixture **19**/**21** (65 mg, *ca.* 0.140 mmol **19** & 0.0194 mmol **21**) in dichloromethane (1.0 mL) was added *via* cannula. The reaction mixture was stirred at RT for 2 h and was then filtered through Celite and concentrated *in vacuo*. Purification by flash chromatography (petrol/ether, 25:1) gave, in order of elution, dioxolanes **25** (12 mg, 22% from **19**), **24** (26 mg, 48% from **19**) and **27** (7.0 mg, 93% from **21**) as colourless oils. Data for **25**: R_f 0.25 (petrol/ether, 25:1); $[\alpha]_D^{25}$ +3.9 (*c* 0.7, $CHCl_3$); ν_{max} (thin film)/cm^{-1} 2931s, 2857s, 1462w, 1373w, 1255m, 1212m, 1080s, 837s, 777m, 699m; δ_H (500 MHz, $CDCl_3$) 0.09 (6 H, s, $Si(CH_3)_2$), 0.93 (9 H, s, $SiC(CH_3)_3$), 1.36 and 1.64 (2 × 3 H, 2 × s, $(CH_3)_2C$), 4.24 (2 H, d, *J* 4.0, CH_2OSi), 4.49 (1 H, app. t, *J* 6.5, =CHC*H*(OR)), 4.53 (1 H, dd, *J* 7.0, 5.0, C*H*CH(OR)CH=), 4.57 (1 H, dd, *J* 7.0, 5.0, C*H*CH(OR)Ph), 4.90 (1 H, d, *J* 5.0, C*H*Ph), 5.89 (1 H, dd, *J* 15.5, 6.5, =C*H*CH(OR)), 6.00 (1 H, dt, *J* 15.5, 4.0, $SiOCH_2CH$=), 7.28–7.42 (5 H, m, Ph); δ_C (125 MHz, $CDCl_3$) –5.3 and –5.3 (2 × CH_3), 18.4 (C), 25.6 (CH_3), 25.9 (3 × CH_3), 27.5 (CH_3), 62.9 (CH_2), 84.4 (CH), 85.2 (CH), 85.3 (CH), 87.1 (CH), 115.3 (C), 125.8 (CH), 126.5 (CH), 127.8 (CH), 128.4 (CH), 132.8 (CH), 139.6 (C); HRMS (ESI^+) found 413.2121, $C_{22}H_{34}NaO_4Si$ (MNa^+) requires 413.2119. Data for **24**: R_f 0.20 (petrol/ether, 25:1); $[\alpha]_D^{25}$ +27.0 (*c* 1.0, $CHCl_3$); ν_{max} (thin film)/cm^{-1} 2931s, 2857s, 1495w, 1463m, 1381m, 1255s, 1210s, 1163m,

1090br, 978m, 838s, 777s, 741m, 701m; δ_H (500 MHz, $CDCl_3$) 0.06 and 0.07 (2 × 3 H, 2 × s, $Si(CH_3)_2$), 0.89 (9 H, s, $SiC(CH_3)_3$), 1.38 and 1.60 (2 × 3 H, 2 × s, $(CH_3)_2C$), 4.28 and 4.34 (2 × 1 H, 2 × ddd, *J* 13.6, 5.5, 1.5, CH_2OSi), 4.63 (1 H, dd, *J* 5.7, 4.0, C*H*CH(OR)CH=), 4.67 (1 H, dd, *J* 7.5, 4.0, =CHC*H*(OR)), 5.00 (1 H, d, *J* 5.7, C*H*CH(OR)Ph), 5.23 (1 H, s, C*H*Ph), 5.79 (1 H, ddt, *J* 11.5, 7.5, 1.5, =C*H*CH(OR)), 5.87 (1 H, dt, *J* 11.5, 5.5, $SiOCH_2CH$=), 7.27–7.39 (5 H, m, Ph); δ_C (125 MHz, $CDCl_3$) –5.3 and –5.2 (2 × CH_3), 18.4 (C), 25.5 (CH_3), 25.9 (3 × CH_3), 26.3 (CH_3), 60.0 (CH_2), 76.4 (CH), 83.0 (CH), 84.5 (CH), 87.6 (CH), 112.8 (C), 124.6 (CH), 125.6 (CH), 127.4 (CH), 128.6 (CH), 134.1 (CH), 138.6 (C); HRMS (ESI^+) found 413.2118, $C_{22}H_{34}NaO_4Si$ (MNa^+) requires 413.2119. Data for **27**: R_f 0.13 (petrol/ether, 25:1); $[\alpha]_D^{25}$ –15.4 (*c* 0.5, $CHCl_3$); ν_{max} (thin film)/cm^{-1} 2934s, 2855m, 1492s, 1218m, 1087s; δ_H (500 MHz, C_6D_6) 0.14 (6 H, s, $Si(CH_3)_2$), 1.07 (9 H, s, $SiC(CH_3)_3$), 1.22 and 1.52 (2 × 3 H, 2 × s, $(CH_3)_2C$), 4.10–4.13 (2 H, m, CH_2OSi), 4.44 (1 H, dd, *J* 5.5, 4.0, C*H*CH(OR)Ph), 4.59 (1 H, d, *J* 5.5, C*H*CH(OR)CH=), 4.93 (1 H, d, *J* 4.0, C*H*Ph), 5.02–5.05 (1 H, m, =CHC*H*(OR)), 5.79 (1 H, dd, *J* 15.6, 4.3, =C*H*CH(OR)), 5.91 (1 H, dt, *J* 15.6, 4.3, $SiOCH_2CH$=), 7.21–7.62 (5 H, m, Ph); δ_C (125 MHz, C_6D_6) –5.1 (2 × CH_3), 18.5 (C), 25.1 (CH_3), 26.1 (3 × CH_3), 26.5 (CH_3), 63.1 (CH_2), 82.5 (CH), 82.9 (CH), 83.7 (CH), 86.1 (CH), 112.4 (C), 126.5 (CH), Ph CHs obscured by solvent, 131.3 (CH), 137.3 (C); HRMS (ESI^+) found 413.2116, $C_{22}H_{34}NaO_4Si$ (MNa^+) requires 413.2119.

tert-Butyl{(*E*)-3-[(3a*R*,4*S*,6*S*,6a*S*)-2,2-dimethyl-6-phenyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl]allyloxy}dimethylsilane (26)

Dichloromethane (0.30 mL) was added to a foil-covered flask containing chloro(triphenylphosphine)gold(I) (2.4 mg, 5.0 μmol), silver(I) triflate (1.3 mg, 5.0 μmol) and activated 4 Å molecular sieves under argon. The mixture was left to stir for 2 min at RT then a solution of diol **20** (20 mg, 0.05 mmol) in dichloromethane (0.30 mL) was added *via* cannula. The reaction mixture was stirred at RT for 1 h and then filtered through Celite and concentrated *in vacuo*. Purification by flash chromatography (petrol/ether, 25:1) gave the *title compound* (**26**) (13

mg, 67%) as a colourless oil. R_f 0.18 (petrol/ether, 25:1); $[\alpha]_D^{25}$ +9.4 (*c* 0.5, $CHCl_3$); ν_{max} (thin film)/cm^{-1} 2930s, 2856s, 1462w, 1381m, 1258m, 1210s, 1096br, 977m, 837s, 778s, 701w; δ_H (500 MHz, $CDCl_3$) 0.09 (6 H, s, $Si(CH_3)_2$), 0.93 (9 H, s, $SiC(CH_3)_3$), 1.37 and 1.59 (2 × 3 H, 2 × s, $(CH_3)_2C$), 4.24–4.26 (2 H, m, CH_2OSi), 4.38 (1 H, dd, *J* 6.0, 4.0, =CHC*H*(OR)), 4.66 (1 H, dd, *J* 6.0, 4.0, C*H*CH(OR)CH=), 4.98 (1 H, dd, *J* 6.0, 1.5, C*H*CH(OR)Ph), 5.21 (1 H, s, C*H*Ph), 5.93 (1 H, dd, *J* 15.5, 4.0, $SiOCH_2CH$=), 5.98 (1 H, ddd, *J* 15.5, 6.0, 1.0, =C*H*CH(OR)), 7.37–7.39 (5 H, m, Ph); δ_C (125 MHz, $CDCl_3$) –5.3 (2 × CH_3), 18.4 (C), 25.2 (CH_3), 25.9 (3 × CH_3), 26.3 (CH_3), 63.2 (CH_2), 81.4 (CH), 83.0 (CH), 84.5 (CH), 87.6 (CH), 112.8 (C), 124.4 (CH), 125.6 (CH), 127.4 (CH), 128.6 (CH), 134.5 (CH), 138.8 (C); HRMS (ESI^+) found 413.2116, $C_{22}H_{34}NaO_4Si$ (MNa^+) requires 413.2119.

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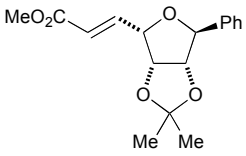
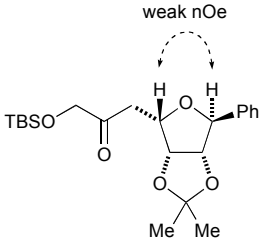
Assignment of stereochemistry for products of Au-catalysed cyclisation of (13) and (19–21)

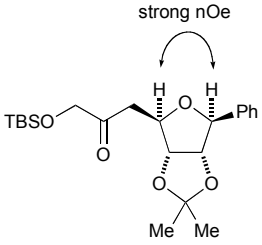
(1) The *endo*- stereochemical assignment in compound **14** was established by comparison with material obtained[11] from ketone **A**, below, whose stereochemistry was confirmed by comparison nOe data with ketone **B**.



14, *endo-E*

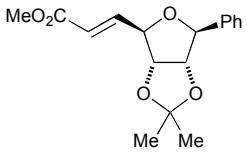


A



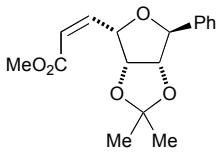
B

(2) Compound **15**, obtained in a pure form by isolation from the reaction to form isoaltholactone was therefore the default structure since it differed from **14**.



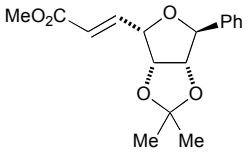
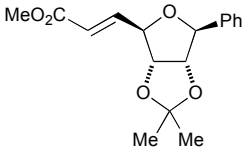
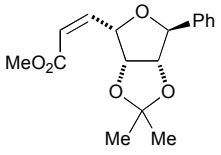
15, *exo-E*

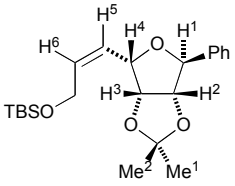
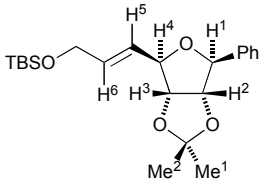
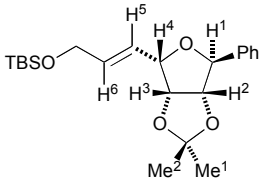
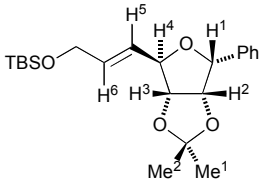
(3) Compound **16** could not be obtained in a pure form but its stereochemistry was inferred on the basis of its conversion into isoaltholactone.



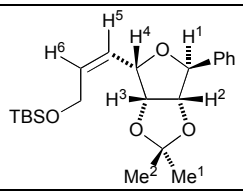
16, *endo-Z*

(4) Furthermore, based on a database of compounds of this sort[11] we find, *inter alia*, that the C*H*Ph resonance in ^{1}H NMR spectra is responsive to the side chain stereochemistry. In the *endo*-configured derivatives, the resonance appears as a broadened singlet at *ca.* 5.2 p.p.m.; the *exo*-configured derivatives display this resonance at *ca.* 4.9 p.p.m. as a distinct doublet, see below. Interestingly, this trend held even in compound **27** (in $CDCl_3$ and C_6D_6). The alkene stereochemistry is clear from the *vicinal* ^{1}H–^{1}H coupling across the C=C. These data are summarised overleaf.

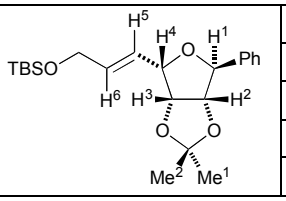
	δ C*H*Ph ^3J for CH=CH
 **14**, *endo-E*	5.27, s 15.9 Hz
 **15**, *exo-E*	4.96, d, *J* 4.3 Hz 15.7 Hz
 **16**, *endo-Z*	5.28, s 11.7 Hz

	δ C*H*Ph ^3J for CH=CH
 **24**, *endo-Z*	5.23, s 11.5 Hz
 **25**, *exo-E*	4.90, d, *J* 5.0 Hz 15.5 Hz
 **26**, *endo-E*	5.21, s 15.5 Hz
 **27**, *exo-E* (*endo*-Ph)	4.93, d, *J* 4.0 Hz 15.6 Hz (data in C_6D_6)

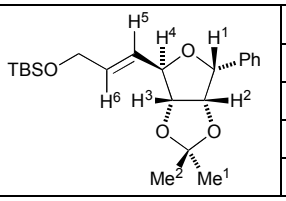
(5) Finally, some substrates were analysed by nOe spectroscopy. In the tables below, rows correspond to the irradiated protons. [Key: ✓ strong, (✓) weak, (×) very weak, × absent]



24	H^1	H^2	H^3	H^4	H^5	H^6	Me^1	Me^2	Ph
H^1	—	✓	×	×	×	×	✓	×	✓
H^2	✓	—	✓	(✓)	×	×	×	✓	✓
$H^{3,4}$	(✓)	✓	—	—	✓	×	×	✓	✓

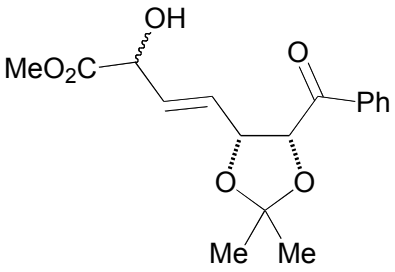


26	H^1	H^2	H^3	H^4	H^5	H^6	Me^1	Me^2	Ph
H^1	—	✓	×	(×)	(×)	(×)	✓	×	✓
H^2	✓	—	✓	(✓)	×	×	×	✓	✓
H^3	(×)	✓	—	✓	(✓)	(✓)	×	✓	(✓)
H^4	(×)	(✓)	✓	—	✓	✓	×	×	✓



27	H^1	H^2	H^3	H^4	H^5	H^6	Me^1	Me^2	Ph
H^1	—	✓	(✓)	×	✓	✓	×	×	✓
H^2	✓	—	✓	×	×	×	×	✓	(✓)
H^3	(✓)	✓	—	(✓)	✓	(✓)	×	✓	×
H^4	×	×	(✓)	—	✓	✓	(✓)	×	(×)

11. W. P. Unsworth, *D.Phil. Thesis*, University of Oxford, 2009.



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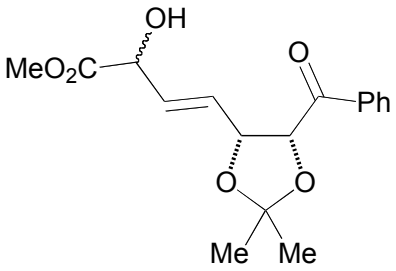

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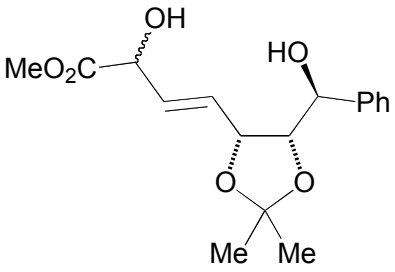

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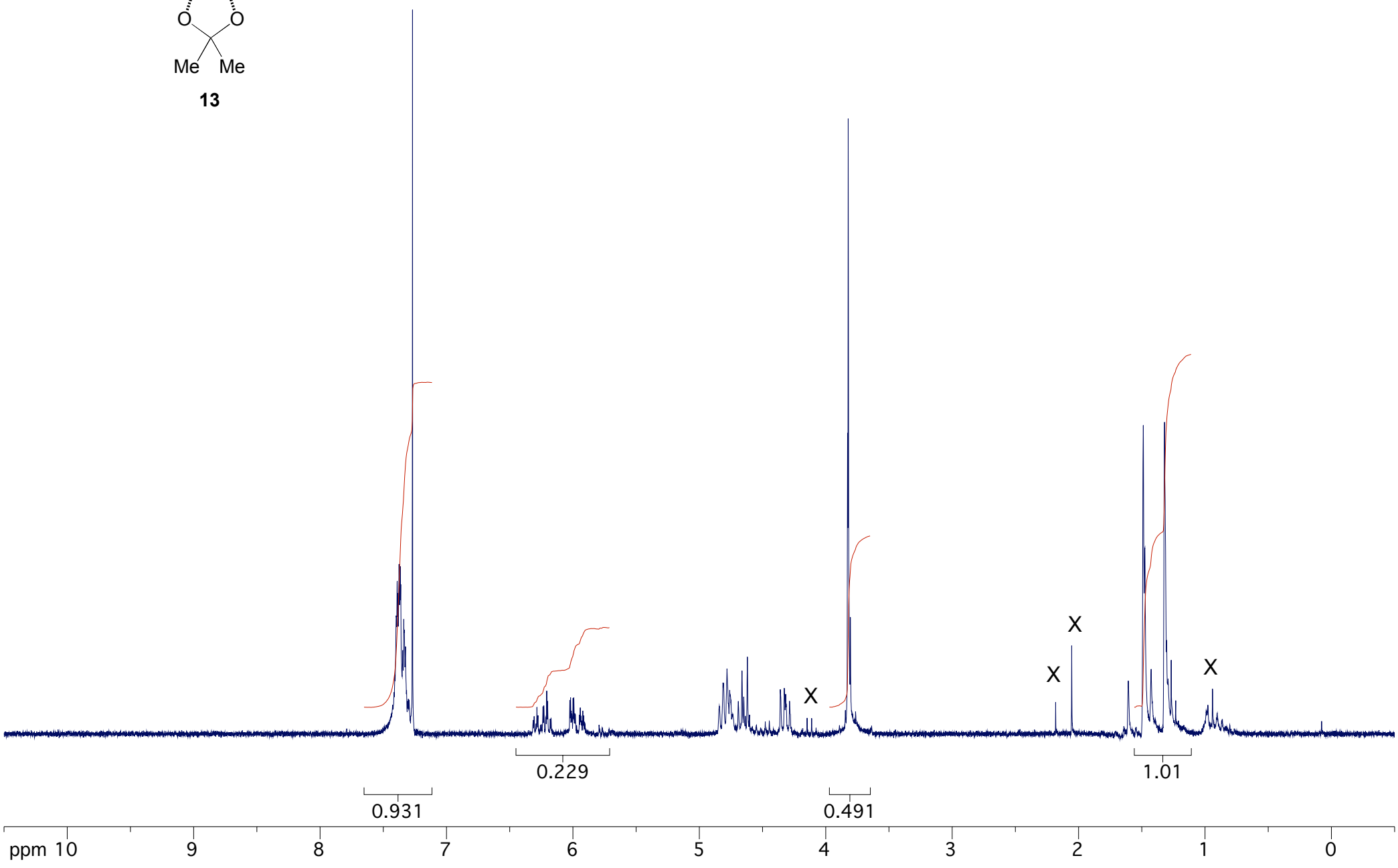
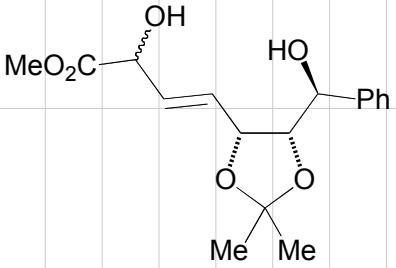
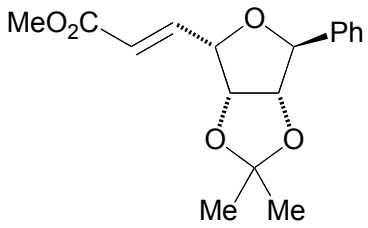




13

HSQC spectrum



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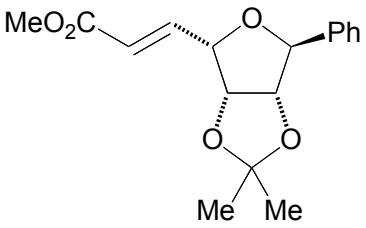

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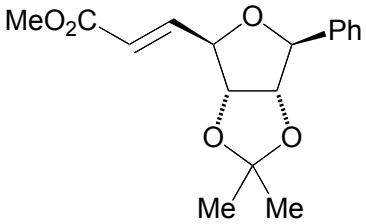
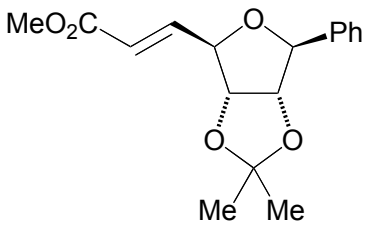


15

(recovered from isoaltholactone prep.; contains a little **16**)



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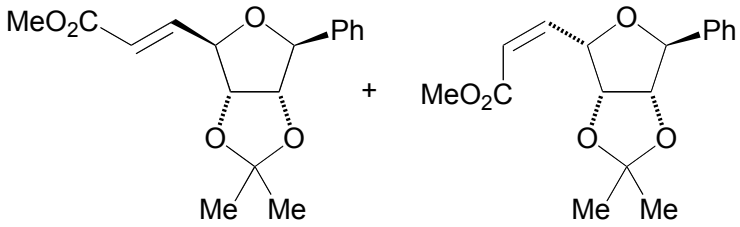
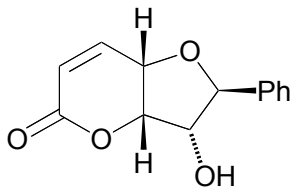
(recovered from isoaltholactone prep.; contains a little **16**)



15

+

16



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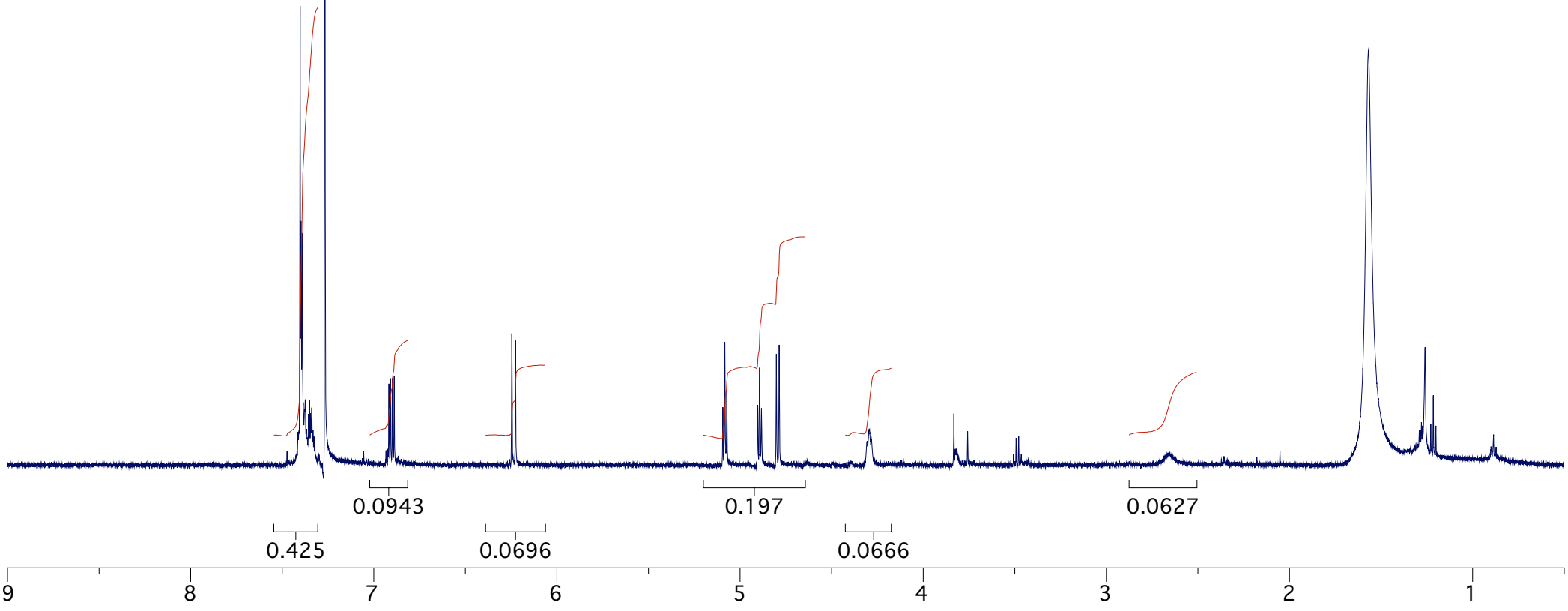

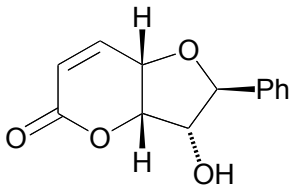

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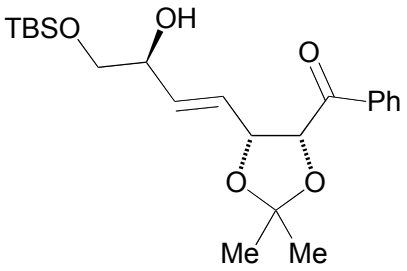

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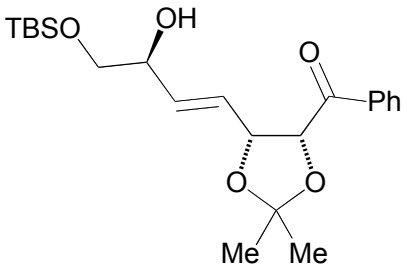

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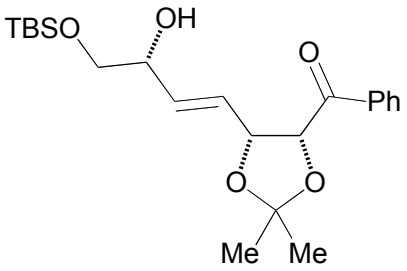

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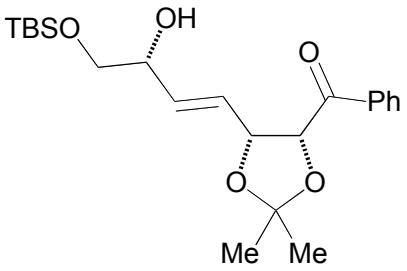

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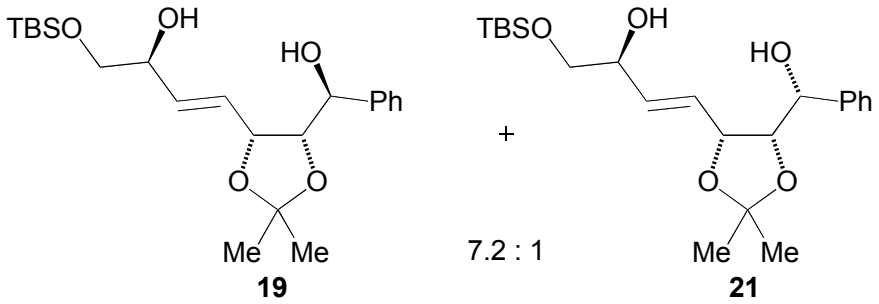

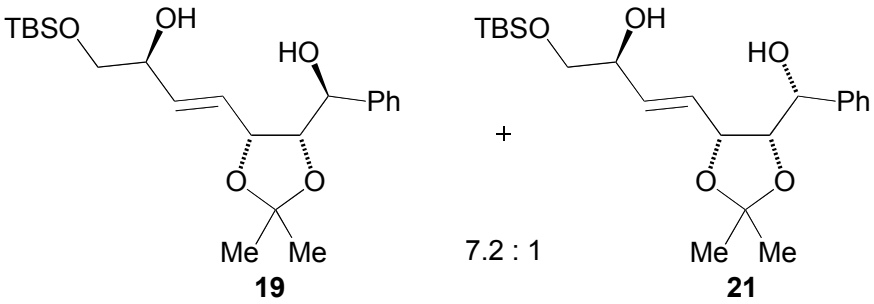

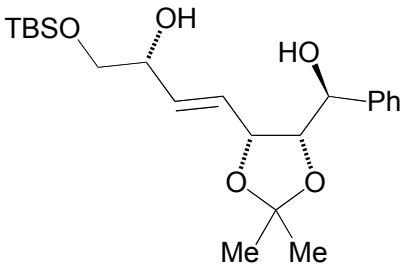

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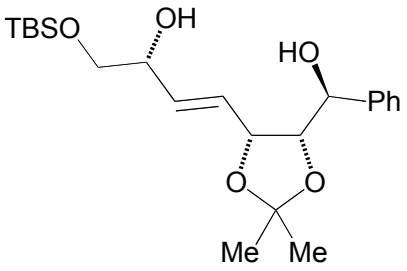

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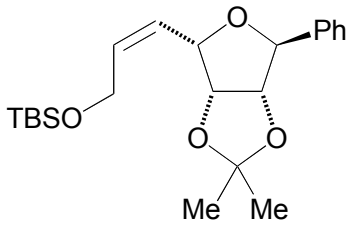

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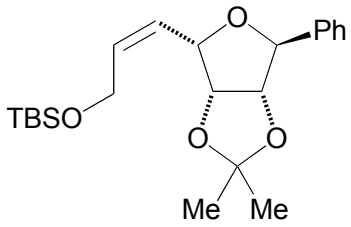

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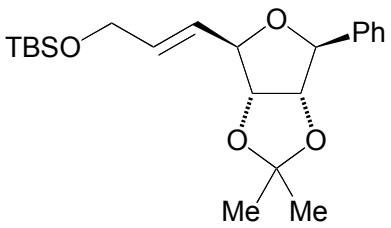

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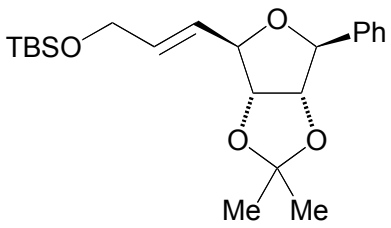

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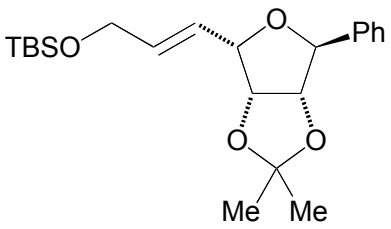

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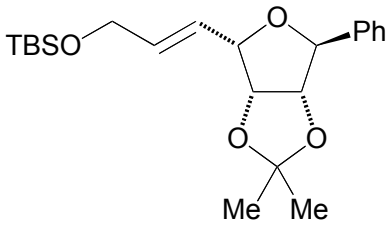

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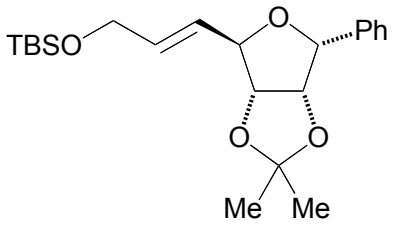
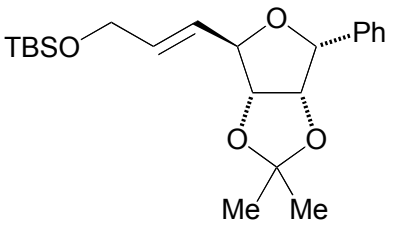


27

(in C_6D_6, + a little **26**)



27

(in C_6D_6, + a little **26**)