Supporting Information

Toward Preparative Resolution of Chiral Alcohols by an Organic Chemical Method

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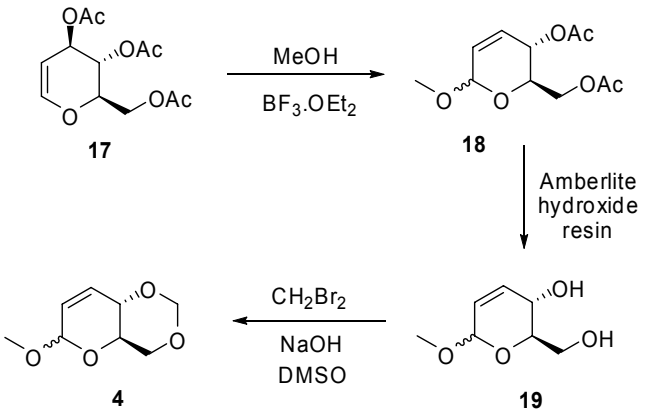
General procedures. Proton nuclear magnetic resonance (^{1}H NMR) and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded with a Varian Mercury 300 Q Spectrometer, Bruker AM-300 Spectrometer and Bruker DRX400 Spectrometer as solutions in deuterated solvents as stated, with chemical shift, measured in parts per million (ppm) relative to the internal reference tetramethylsilane (TMS) (0.00 ppm). Accurate mass measurements were obtained at high resolution with a Bruker BioApex 47 e$^-$ FTMS (4.7 Tesla magnet) fitted with an analytical electrospray source. Flash chromatography was carried out using Merck silica gel 60, 0.063-0.200 mm (70-230 mesh). Analytical gas chromatography (GC) was carried out on a capillary column Model C-002 (column: 0.53 mm x 30 cm, 30QCS/BPX5) and chiral column Model C-024 (column: 0.25 mm x 50 cm, 50 CP2/XE60-SVALSAPEA) using helium as the carrier gas. Temperature programs: (i) 100 °C for 2 mins to 280 °C at 20 °C min^{-1}, 280 °C for 5 mins, or (ii) 150 °C for 10 mins to 280 °C at 2 °C min^{-1}, 280 °C for 15 mins. Chiral alcohols and catalysts were purchased from Sigma-Aldrich at the highest purity available and used as obtained. Solvents were dried and distilled prior to use. 3,4,6-Tri-*O*-acetyl-D-glucal (**17**) was prepared using the procedure of Stick *et al.*[1] Methyl-2,3-dideoxy-4,6-di-*O*-acetyl-α-D-*erythro*-hex-2-enopyranoside (**18**) was prepared by the procedure of

1. R. V. Stick, K. A. Stubbs, D. M. G. Tilbrook, A. G. Watts, *Aust. J. Chem.,* 2002, **55**, 83.

Masson *et al.*[2] and quantitatively *O*-deacetylated to **19** using the method of Pathak.[3] Auxiliary **4** was synthesised by a procedure adapted from Lipták *et al.*[4]



Methyl-2,3-dideoxy-4,6-di-*O*-acetyl-α-D-*erythro*-hex-2-enopyranoside (18). To a solution of 3,4,6-tri-*O*-acetyl-D-glucal (**1**) (10.0 g, 36.73 mmol) and methanol (4.5 mL, 110.2 mmol) in dichloromethane (30 mL) was added boron trifluoride etherate (2.5 mL, 20.11 mmol) dropwise with vigorous stirring at room temperature. The reaction mixture was stirred overnight at room temperature under N_2, after which time the reaction was quenched with $NaHCO_{3\,(aq)}$ (25 mL). The organic layer was then washed with brine, dried with $MgSO_4$, filtered and the solvent removed *in vacuo* to give **18** as a pale orange oil (8.86 g, 99%).

Methyl-2,3-dideoxy-4,6-*O*-methylene-α-D-*erythro*-hex-2-enopyranoside (4). The method was adapted from the procedure of Lipták *et al.*[4] To a solution of methyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (1.0 g, 6.24 mmol) in DMSO (6 mL) was added NaOH (1.0 g, 24.96 mmol) as a powder. This mixture was stirred at 60 ºC for 30 min under N_2 prior to the addition of CH_2Br_2 (1.14 g, 6.55 mmol). The mixture was stirred for another 1.5 h at 60 ºC then poured into water (20 mL) and extracted with diethyl ether (3 x 20 mL). The organic layer was dried with $MgSO_4$, filtered and the solvent removed *in vacuo* to give a yellow oil. The crude oil was purified by flash chromatography on a short silica column eluting with diethyl ether:pentane (7:2), yielding compound **4** as a colourless crystalline solid (0.46 g, 43%), mp 85.5-85.9 ºC. IR

2. C. Masson, J. Soto, M. Bessodes, *Synlett,* 2000, 1281.
3. V. P. Pathak, *Synth. Commun.,* 1993, **23**, 83.
4. A. Lipták, V. A. Oláh, J. Kerékgyártó, *Synthesis,* 1982, 421.

(Nujol) ν cm^{-1} 2893, 2463, 1737, 1711, 1150, 1107, 1061, 1022, 998, 968, 940, 916, 893, 722, 670. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.07 (m, 1H), 5.71 (ddd, *J* = 2.3, 2.5, 10.3 Hz, 1H), 5.06 (d, *J* = 6.2 Hz, 1H), 4.85 (m, 1H), 4.67 (d, *J* = 6.2 Hz, 1H), 4.18 (m, 1H), 3.86 (m, 1H), 3.73 (m, 1H), 3.54 (t, *J* = 10.3, 1H), 3.44 (s, 3H), ^{13}C NMR ($CDCl_3$, 75 MHz) δ 130.7, 126.9, 96.1, 94.1, 75.3, 69.4, 64.2, 56.1. Mass Spectrum (ESI^+, MeOH) *m/z* calculated for $[C_8H_{12}O_4Na]^+$ 195.0629, found 195.0633.

Transacetalisation of methyl-2,3-dideoxy-4,6-*O*-methylene-α-D-*erythro*-hex-2-enopyranoside (4) with (*S*)-1-phenylethanol (5). Methyl-2,3-dideoxy-4,6-*O*-methylene-α-D-*erythro*-hex-2-enopyranoside (**4**) (0.13 g, 0.73 mmol), (*S*)-1-phenylethanol (**5**) (0.18 mL, 1.45 mmol) and K10 Montmorillonite (0.07 g, 50 wt%) were combined in DCM (1 mL) under nitrogen and stirred at 45 °C. After 50 min, the mixture was filtered through celite and the solvent evaporated. The oily residue was extracted with pentane and partition fluid (methanol:aqueous $NaHCO_3$ in a 1:1 mixture). The pentane layer was separated and the solvent evaporated to give an oil which was then purified by column chromatography with diethyl ether:pentane (1:1) giving a mixture of **5a** and **5b** as a colourless oil (85 mg, 45%). The oil was cooled in a freezer and the surface of the flask scratched, which induced crystallization. Upon warming to room temperature (ca. 23°C) the solid partially melted. Analysis of the purified product by ^{13}C NMR showed the anomeric ratio to be (*S*)-α **5a**:(*S*)-β **5b** = 85:15. Data for (*S*)-α **5a**: ^{13}C NMR ($CDCl_3$, 75 MHz) δ 145.1, 130.5 (overlap), 128.2, 127.1, 125.8, 94.8, 93.6, 77.5, 75.1, 68.6, 63.8, 23.3; Data for (*S*)-β **5b**: ^{13}C NMR ($CDCl_3$, 75 MHz) δ 142.7, 130.5, 128.8, 128.5, 127.8, 126.4, 96.1, 93.9, 75.4, 74.9, 70.6, 68.9, 24.2.

Transacetalisation of methyl-2,3-dideoxy-4,6-*O*-methylene-α-D-*erythro*-hex-2-enopyranoside (4) with (*R*)-3-hydroxytetrahydrofuran (6). Methyl-2,3-dideoxy-4,6-*O*-methylene-α-D-*erythro*-hex-2-enopyranoside (**4**) (0.1 g, 0.58 mmol), (*R*)-3-hydroxytetrahydrofuran (**6**) (0.08 g, 0.87 mmol) and K10 Montmorillonite (0.05 g, 50 wt%) were combined under nitrogen and DCM (1 mL) added. The reaction mixture was heated at 40 °C for 2.5 h. Workup as above afforded an oil which was then passed through a small plug of silica to remove the green colouration. The diethyl ether was evaporated *in vacuo* to give the product **6a** as an oil (77 mg, 58%). Cooling of the viscous oily product **6a** caused it to crystallise and it remained a crystalline solid at room

temperature. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 130.4, 126.8, 94.2, 93.9, 78.0, 75.0, 72.5, 69.2, 67.0, 64.0, 33.9.

Transacetalisation of methyl-2,3-dideoxy-4,6-*O*-methylene-α-D-*erythro*-hex-2-enopyranoside (4) with (*R*)-2-butanol (7). A solution of methyl-2,3-dideoxy-4,6-*O*-methylene-α-D-*erythro*-hex-2-enopyranoside (**4**) (0.20 g, 1.16 mmol) in (*R*)-2-butanol **7** (2.8 mL, 30.19 mmol) together with K10 Montmorillonite (60 mg, 30 wt%) was stirred at 60 °C overnight. Workup as above gave product **7a** as an oil (0.18 g, 72%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.05 (m, 1H), 5.67 (td, *J* = 10.3, 2.4 Hz, 1H), 5.04 (m, 2H), 4.66 (d, *J* = 6.2 Hz, 1H), 4.12 (m, 1H), 3.78 (m, 3H), 3.51 (t, *J* = 9.8 Hz, 1H), 1.52 (m, 2H), 1.04 (d, *J* = 6.2 Hz, 3H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 130.3, 127.6, 94.0, 92.5, 75.2, 74.9, 69.2, 64.1, 30.2, 19.4, 10.2.

Transacetalisation of methyl-2,3-dideoxy-4,6-*O*-methylene-α-D-*erythro*-hex-2-enopyranoside (4) with (*S*)-2-butanol (8). A solution of methyl-2,3-dideoxy-4,6-*O*-methylene-α-D-*erythro*-hex-2-enopyranoside (**4**) (0.10 g, 1.16 mmol) in (*S*)-2-butanol (**8**) (0.6 mL, 6.47 mmol) together with K10 Montmorillonite (30 mg, 30 wt%) was stirred at 60 °C overnight. Workup as above afforded a mixture of products **8a** and **8b** as an oil (0.08 g, 67%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.98 (m, 1H), 5.64 (m, 1H), 4.98 (m, 2H), 4.60 (d, *J* = 6.2 Hz, 1H), 4.14 (m, 1H), 3.64 (m, 3H), 3.45 (t, *J* = 9.5 Hz, 1H), 1.45 (m, 2H), 1.14 (d, *J* = 6.2 Hz, 3H), 0.83 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ ((*S*)-α adduct, **8a**) 130.3, 127.4, 94.8, 94.1, 76.9, 75.4, 69.4, 63.9, 29.5, 21.7, 9.9.

Transacetalisation of methyl-2,3-dideoxy-4,6-*O*-methylene-α-D-*erythro*-hex-2-enopyranoside (4) with *rac*-2-butanol (9). A solution of methyl-2,3-dideoxy-4,6-*O*-methylene-α-D-*erythro*-hex-2-enopyranoside (**4**) (0.50 g, 2.90 mmol) in dry *rac*-2-butanol (**13**) (7 mL, 75.45 mmol) together with K10 Montmorillonite (0.15 g, 30 wt%) was stirred overnight at 60 °C under nitrogen. Workup as above gave an oil which was then purified by flash chromatography on a silica column eluting with a solvent gradient program involving diethyl ether and hexane. The initial solvent system was 5% diethyl ether for 5 min then increased at the flow rate of 30 mL min^{-1} to 30% diethyl ether for 40 min which eluted the product mixture **9a**, **9b** and **9c** as an oil (0.35 g, 57%). Refer above for characterisation data.

Transacetalisation of methyl-2,3-dideoxy-4,6-*O*-methylene-α-D-*erythro*-hex-2-enopyranoside (4) with *rac*-pantolactone (10). *rac*-Pantolactone (**10**) (450 mg, 3.49 mmol) and methyl-2,3-dideoxy-4,6-*O*-methylene-α-D-*erythro*-hex-2-enopyranoside (**4**) (200 mg, 1.16 mmol) were dissolved in dry toluene (5 mL) followed by the addition of 10M acid-treated K10 Montmorillonite (60 mg, 30% wt) and 4Å molecular sieves. The reaction mixture was heated to 75 ºC. After 20 h the clay was removed by filtration through celite and the solvent evaporated to give a yellow oil. The ratio of (*R*)-α **10a**:(*S*)-α **10b** = 71:29 was assessed by GC (conditions as stated in general data) which showed 93% conversion. The (*R*)-α adduct **10a** precipitated as a colourless solid (126 mg, 41%) by adding methanol. The filtrate was purified by flash chromatography on a silica column eluting with a solvent gradient program involving diethyl ether and hexane. The initial solvent system was 5% diethyl ether for 5 min then increased at the flow rate of 30 mL min^{-1} to 30% diethyl ether for 40 min. This eluted the (*S*)-α adduct **10b** and *rac*-pantolactone (**10**) in the same fraction. Extraction with partition fluid (methanol:aqueous $NaHCO_3$ in the ratio 1:1) gave the (*S*)-α adduct **10b** (12 mg, 4%) as a yellow oil containing trace amounts of *rac*-pantolactone (**10**). Data for (*R*)-α adduct **10a**: mp 192.4-194.6 ºC. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.12 (d, *J* = 10.8 Hz, 1H), 5.85 (m, 1H), 5.44 (bs, 1H), 5.07 (d, *J* = 6.2 Hz, 1H), 4.69 (d, *J* = 6.2 Hz, 1H), 4.16 (s, 1H), 4.12 (dd, *J* = 4.7, 10.3 Hz, 1H), 4.03 (d, *J* = 8.8 Hz, 1H), 3.94 (d, *J* = 8.9 Hz, 1H), 3.89 (bs, 1H), 3.77 (m, 1H), 3.56 (m, 1H), 1.20 (s, 3H), 1.11 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 175.2, 130.9, 126.5, 94.1, 93.9, 78.6, 76.4, 75.1, 69.1, 64.5, 40.1, 22.9, 19.6. Mass Spectrum (ESI^+, MeOH) *m/z* calculated for $[C_{13}H_{18}O_6Na]^+$ 293.1001, found 293.0997. Data for (*S*)-α adduct **10b**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.15 (d, *J* = 10.9 Hz, 1H), 5.77 (td, *J* = 2.5, 10.3 Hz, 1H), 5.06 (bd, 2H), 4.67 (d, *J* = 6.2 Hz, 1H), 4.28 (m, 1H), 4.08-3.88 (m, 5H), 3.48 (m, 1H), 1.20 (s, 3H), 1.11 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 178.5, 132.1, 125.6, 96.3, 94.2, 80.8, 75.9, 75.0, 69.1, 64.5, 40.5, 23.5, 19.5. Mass Spectrum (ESI^+, MeOH) *m/z* calculated $[C_{13}H_{18}O_6Na]^+$ 293.1001, found 293.0990.

Transacetalisation of methyl-2,3-dideoxy-4,6-*O*-methylene-α-D-*erythro*-hex-2-enopyranoside (4) with *rac*-α-methylcyclopropanemethanol (11). Methyl-2,3-dideoxy-4,6-*O*-methylene-α-D-*erythro*-hex-2-enopyranoside (**4**) (0.25 g, 1.45 mmol), *rac*-α-methylcyclopropanemethanol (**11**) (0.25 g, 2.90 mmol) and K10 Montmorillonite

(0.13 g, 50 wt%) were combined under nitrogen in DCM (1 mL) and the mixture heated at 40 °C for 2.5 h. Workup as above afforded an oil which was purified by column chromatography (diethyl ether:pentane, 3:1) yielding the bulk transacetalisation adducts **11a-c** as a colourless oil (130 mg, 40%). Cooling of the oil in a freezer overnight did not cause crystallisation and the product remained a liquid. ^{13}C NMR showed an (*R*)-α:(*S*)-α:(*S*)-β adduct ratio of *ca.* 51:41:8 based on relative intensities of signals for the respective anomeric carbons. ^{13}C NMR ($CDCl_3$, 100 MHz) δ ((*R*)-α adduct, **11a**) 130.0, 127.5, 93.9, 92.7 (anomeric-C), 77.6, 75.3, 69.3, 63.7, 21.7, 15.9, 4.1, 0.6; ((*S*)-α adduct, **11b**) 130.2, 127.4, 93.9, 92.2 (anomeric-C), 77.9, 75.3, 69.3, 63.8, 19.4, 17.2, 3.9, 2.7. ((*S*)-β adduct, **11c**) 130.3, 126.9, 94.8 (anomeric-C), 93.9, 78.6, 75.1, 69.2, 63.9, 21.6, 17.9, 4.3, 0.8.

Transacetalisation of methyl-2,3-dideoxy-4,6-*O*-methylene-α-D-*erythro*-hex-2-enopyranoside (4) with *rac*-1-pentyn-3-ol (12). A solution of methyl-2,3-dideoxy-4,6-*O*-methylene-α-D-*erythro*-hex-2-enopyranoside (**4**) (0.15 g, 0.87 mmol), 1-pentyn-3-ol (**12**) (0.22 g, 2.61 mmol) and K10 Montmorillonite (0.08 g, 50 wt%) in dichloromethane (1 mL) was heated at 40 °C for 2 h. Workup as above afforded an oil which was purified by column chromatography (diethyl ether:pentane, 2:1). A mixture containing predominantly (*R*)-α **12a** and trace amounts of (*S*)-β **12c** (78 mg, 40%) eluted first. This oil did not solidify even upon cooling in a freezer for 1 h with scratching. The second fraction contained a mixture of (*R*)-α **12a** and (*S*)-α **12b** (40 mg, 21%) which was highly crystalline at room temperature. Data for (*R*)-α adduct **12a**: ^{13}C NMR ($CDCl_3$, 75 MHz) δ 130.5, 126.9, 93.9, 91.9 (anomeric-C), 82.1, 75.1, 73.9, 69.2, 67.3, 64.3, 28.8, 9.6. Data for (*S*)-α adduct **12b**: ^{13}C NMR ($CDCl_3$, 75 MHz) δ 130.8, 126.6, 94.7 (anomeric-C), 94.0, 83.5, 75.1, 72.9, 69.8, 69.0, 64.1, 29.1, 9.5.

Transacetalisation of methyl-2,3-dideoxy-4,6-*O*-methylene-α-D-*erythro*-hex-2-enopyranoside (4) with *rac*-1-octyn-3-ol (13). A mixture of methyl-2,3-dideoxy-4,6-*O*-methylene-α-D-*erythro*-hex-2-enopyranoside (**4**) (200 mg, 1.16 mmol), 1-octyn-3-ol (**13**) (0.51 mL, 3.48 mmol) and 10M acid-treated K10 Montmorillonite (60 mg, 30% wt) in dry toluene (5 mL) was heated to 50 ºC. After 2.5 h, the reaction was worked up as above and the solvent evaporated to give a yellow oil. At 100% conversion, the ratio of (*R*)-α **13a**:(*S*)-α **13b:** by-product as assessed by GC (conditions as stated in general data)

was 70:20:10 respectively. The crude oil was purified by flash chromatography on a silica column eluting with solvent gradient program involving diethyl ether and hexane: the initial solvent system was 5% diethyl ether for 5 min then increased at the flow rate of 30 mL min^{-1} to 30% diethyl ether for 40 min which subsequently eluted the (*R*)-α adduct **13a** (18 mg, 9%) and a mixture of (*R*)-α adduct **13a** and (*S*)-α adduct **13b** in one fraction. The mixture was purified again by flash chromatography on a silica column with solvent gradient program as stated above to give pure (*R*)-α adduct **13a** as an oil (101 mg, 30%) and the (*S*)-α adduct **13b** which contained a trace amount of unidentified impurities (38 mg, 12%). The (*S*)-α adduct **13b** slowly crystallized as needles. Data for (*R*)-α adduct **13a**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.07 (m, 1H), 5.70 (m, 1H), 5.32 (m, 1H), 5.05 (d, *J* = 6.1 Hz, 1H), 4.67 (d, *J* = 6.2 Hz, 1H), 4.42 (m, 1H), 4.12 (m, 1H), 3.87 (m, 1H), 3.71 (m, 1H), 3.53 (t, *J* = 10.3 Hz, 1H), 2.42 (d, *J* = 2.1 Hz, 1H), 1.80-1.60 (m, 2H), 1.50-1.37 (m, 2H), 1.37-1.26 (m, 4H), 0.90 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 130.6, 127.0, 94.1, 92.0 (anomeric-C), 75.3, 73.9, 69.3, 65.9, 64.4, 35.6, 31.4, 24.9, 22.6, 14.1. Mass Spectrum (ESI^+, MeOH) *m/z* calculated for $[C_{15}H_{22}O_4Na]^+$ 289.1416, found 289.1417. Data for (*S*)-α adduct **13b**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.07 (m, 1H), 5.69 (m, 1H), 5.13 (m, 1H), 5.04 (m, 1H), 4.66 (d, *J* = 6.2 Hz, 1H), 4.19-4.08 (m, 2H), 3.91 (m, 2H), 3.42 (m, 1H), 2.43 (d, *J* = 2.2 Hz, 1H), 1.82-1.61 (m, 2H), 1.57-1.42 (m, 2H), 1.40-1.26 (m, 4H), 0.90 (m, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 130.9, 126.8, 94.9 (anomeric-C), 94.2, 75.3, 72.9, 69.2, 64.3, 36.1, 31.6, 22.7, 15.0, 14.1. Mass Spectrum (ESI^+, MeOH): *m/z* calculated for $[C_{15}H_{22}O_4Na]^+$ 289.1416, found 289.1408

Transacetalisation of methyl-2,3-dideoxy-4,6-*O*-methylene-α-D-*erythro*-hex-2-enopyranoside (4) with *rac*-3-methyl-1-pentyn-3-ol (14). A mixture of methyl-2,3-dideoxy-4,6-*O*-methylene-α-D-*erythro*-hex-2-enopyranoside (**4**) (200 mg, 1.16 mmol), *rac*-3-methyl-1-pentyn-3-ol (**14**) (0.40 mL, 3.48 mmol) and 10M acid-treated K10 Montmorillonite (200 mg, 100% wt) in dry toluene (12 mL) was heated at 60 ºC overnight. The reaction was worked up as above and the solvent evaporated to give a yellow oil which was purified by flash chromatography (diethyl ether:hexane, 5:95). Partial separation of the major anomer of **14a** was achieved and a pure adduct isolated as an oil (40 mg, 15%). The remainder of the material, major and minor anomers**,** eluted as a mixture (141 mg, 51%). Data for major anomer: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.06-6.01 (m, 1H), 5.66 (dt, *J* = 10.2, 2.5 Hz, 1H), 5.59 (m, 1H), 5.04 (d, *J* = 6.2 Hz, 1H), 4.66 (d, *J* = 6.2 Hz, 1H), 4.13-4.09 (dd, *J* = 10.3, 4.2 Hz, 2H), 3.86-3.73 (m, 1H), 3.55-3.49 (m,

1H), 2.53 (s, 1H), 1.82-1.52 (m, 2H), 1.51 (s, 3H), 0.98-1.03 (t, J = 7.4 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 129.9, 127.9, 93.9 (overlap), 91.6, 75.0, 74.7, 69.3, 64.1, 35.9, 28.3, 8.6. Mass Spectrum (ESI^+, MeOH): *m/z* calculated for $[C_{13}H_{18}O_4Na]^+$ 261.1103, found 261.1100. Data for the minor anomer: ^{13}C NMR ($CDCl_3$, 75 MHz) δ 130.0, 128.0, 93.9 (overlap), 91.2 (anomeric-C), 75.0, 73.9, 69.2, 64.4, 34.9, 26.7, 8.4.

Release of (*R*)-pantolactone (10c). (*R***)-α-Adduct 10a** (160 mg, 0.59 mmol) was dissolved in dry methanol (20 mL) followed by the addition of 10M acid-treated K10 Montmorillonite (1.28 g, 800% wt). The reaction mixture was heated to 40 ºC. After 8 hours the clay was removed by filtration through celite and the solvent was evaporated to give a yellow oil. The reaction had gone to 100% conversion. The ratio of auxiliary:acetal (ring-opened by-product) was 60:40 respectively according to GC analysis (conditions as stated in general data). The crude oil was purified by column chromatography on a silica column eluting with ethyl acetate:hexane in a ratio of 1:2. Methyl-2,3-dideoxy-4,6-*O*-methylene-α-D-*erythro*-hex-2-enopyranoside (**4**) (31 mg, 18%) eluted first, followed by (*R*)-pantolactone (**10c**) (45 mg, 35%) and lastly the acetal by-product **16** (26 mg, 13%). The enantiomeric excess was assessed by chiral GC (temperature program: initial column temperature was 110 °C for 10 min, then heated to 200 °C at 20 °C min^{-1} and maintained at 200 ºC for 5 min) which gave > 99% *ee*.

Release of (*R*)-1-octyn-3-ol (13c). (*R*)-α-Adduct **13a** (60 mg, 0.23 mmol) was dissolved in dry methanol (10 mL) and 10M acid-treated K10 Montmorillonite (480 mg, 800 wt%) added. The reaction mixture was heated to 40 ºC. After 20 h the clay was filtered off through a pad of celite and the solvent evaporated to give a yellow oil. At 100% conversion, the ratio of auxiliary **4** and acetal (ring-opened by-product) **16**, as assessed by GC (conditions as stated in general data) was 60:40, respectively. The crude oil was purified by column chromatography (ethyl acetate:hexane, 1:2). Methyl-2,3,-dideoxy-4,6-*O*-methylene-α-D-*erythro*-hex-2-enopyranoside (**4**) and (*R*)-1-octyn-3-ol (**13c**) co-eluted, followed by the acetal by-product **16** (10 mg, 22%). The mixture of auxiliary and alcohol was redissolved in methanol (10 mL) and extracted with hexane (2 x 5 mL) to give auxiliary **4** (9 mg, 23%) and (*R*)-1-octyn-3-ol (**13c**) (11 mg, 38%) which was isolated from the methanol layer. The enantiomeric excess was assessed by chiral GC (temperature program: the initial column temperature was 75 °C for 20 min, then

heated to 200 °C at 20 °C min^{-1} and maintained at 200 ºC for 5 min) which gave > 99% *ee*.