

Supplementary information for:

## Stereospecific debenzylative cycloetherification of carbohydrate-derived allylic alcohols, ethers and esters to form vinyl C-furanosides

Riccardo Cribiù and Ian Cumpstey\*

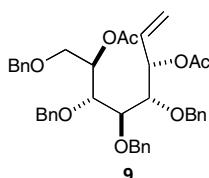
Synthetic procedures and data for acyclic compounds **8**, **9**, **10**, **11**, **17**, **18**, **20**, **21**

General procedure for cyclisation

Data for cyclised compounds **4**, **5**, **12**, **13**, **14**, **15**, **22**, **23**, **24**, **25**

Synthetic procedures and data for peracetylated C-glycosides **26**, **27**, **28**, **29**

Metathesis reaction: synthesis of **30**



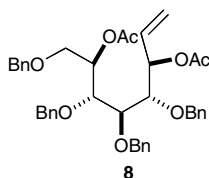
Diol **2** (500 mg, 0.88 mmol), was dissolved in a mixture of pyridine (2 mL) and acetic anhydride (2 mL), and *N,N*-dimethylaminopyridine (53 mg, 0.43 mmol) was added. The reaction mixture was stirred at room temperature for 2 h, after which time TLC (pentane ethyl/acetate, 4:1) showed complete conversion of the starting material ( $R_f$  0.3) into a single product ( $R_f$  0.6). The reaction mixture was cooled to 0 °C and methanol (1.5 mL) was slowly added. The solvent was concentrated under reduced pressure, diluted with ethyl acetate (20 mL) and washed with 0.1 M HCl until acidic pH and with saturated aqueous solution of sodium bicarbonate (25 mL). The organic phase was concentrated under reduced pressure and the residue was purified by flash chromatography (pentane/ethyl acetate, 9:1) to afford **9** (546 mg, 95%).

Colourless oil:  $[\alpha]_D^{25}$   $-1.2$  (*c*, 1 in  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  1.95, 1.98 (6H, 2 x s, 2 x  $\text{CH}_3$ ), 3.65 (1H, dd,  $J_{3,4}$  4.7 Hz,  $J_{2,3}$  6.6 Hz, H-3), 3.73 (1H, dd,  $J_{6,5}$  5.7 Hz,  $J_{6,6'}$  10.8 Hz, H-6), 3.81 (1H, dd,  $J_{1,2}$  3.9 Hz,  $J_{2,3}$  6.6 Hz, H-2), 3.85 (1H, dd,  $J_{6',5}$  3.4 Hz,  $J_{6,6'}$  10.8 Hz, H-6'), 3.88 (1H, at,  $J$  4.8 Hz, H-4), 4.43, 4.50 (2H, ABq,  $J_{\text{AB}}$  12.0 Hz,  $\text{PhCH}_2$ ), 4.54, 4.67 (2H, ABq,  $J_{\text{AB}}$  10.8 Hz,  $\text{PhCH}_2$ ), 4.64-4.69 (4H, m, 2 x  $\text{PhCH}_2$ ), 5.23 (1H, ddd,  $J_{5,6}$  5.7 Hz,  $J_{5,6'}$  3.4 Hz,  $J_{4,5}$  4.8 Hz, H-5), 5.29 (1H, dat,  $J$  1.3 Hz,  $J_{1a,1b}$  10.6 Hz, H-1b), 5.32 (1H, dat,  $J$  1.3 Hz,  $J_{1a,1b'}$  17.4 Hz, H-1b'), 5.38 (1H, dd,  $J_{1,2}$  3.9 Hz,  $J_{1,1a}$  6.9 Hz, H-1), 5.99 (1H, ddd,  $J_{1,1a}$  6.9 Hz,  $J_{1a,1b}$  10.6 Hz,  $J_{1a,1b'}$  17.4 Hz, H-1a), 7.21-7.34 (20H, m, Ar-CH).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  21.1 (2 x q, 2 x  $\text{CH}_3$ ), 68.2 (t, C-

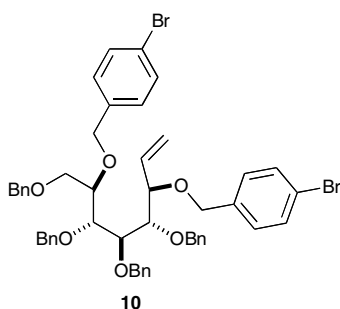
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6), 73.1 (d, C-5), 73.2 (t, PhCH<sub>2</sub>), 74.3 (t, PhCH<sub>2</sub>), 74.4 (t, PhCH<sub>2</sub>) 75.0 (d, C-1), 75.3 (t, PhCH<sub>2</sub>), 78.0 (d, C-4), 78.8 (d, C-3), 80.3 (d, C-2), 119.2 (t, C-1b), 127.5, 127.5, 127.6, 127.6, 127.7, 128.0, 128.1, 128.2, 128.2, 128.2, 128.3, 128.5 (12 x d, Ar-CH), 132.9 (d, C-1a), 137.9, 138.0, 138.1, 138.4 (4 x s, 4 x Ar-C), 169.6, 170.0 (2 x s, 2 x C=O). HRMS (ES<sup>+</sup>) *m/z*: Calcd. for C<sub>44</sub>H<sub>44</sub>O<sub>8</sub>Na (MNa<sup>+</sup>) 675.2928. Found 675.2925.



Following an identical procedure to that described for compound **9**, starting from diol **1** (500 mg, 0.88 mmol), diacetate **8** was obtained (551 mg, 96%). Colourless oil:  $[\alpha]_D^{25} +12.1$  (*c*, 1 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_H$  2.00, 2.01 (6H, 2 x s, 2 x CH<sub>3</sub>), 3.72 (1H, dd, *J*<sub>5,6</sub> 6.3 Hz, *J*<sub>6,6'</sub> 10.9 Hz, H-6), 3.77 (2H, m, H-2, H-3), 3.85 (1H, at, *J* 4.1 Hz, H-4), 3.89 (1H, dd, *J*<sub>5,6'</sub> 3.5 Hz, *J*<sub>6,6'</sub> 10.9 Hz, H-6'), 4.43, 4.49 (2H, ABq, *J*<sub>AB</sub> 11.9 Hz, PhCH<sub>2</sub>), 4.58, 4.66 (2H, ABq, *J*<sub>AB</sub> 11.6 Hz, PhCH<sub>2</sub>), 4.64-4.73 (4H, m, 2 x PhCH<sub>2</sub>), 5.10 (1H, dat, *J* 1.3 Hz, *J*<sub>1a,1b</sub> 10.5 Hz, H-1b), 5.14 (1H, dat, *J* 1.3 Hz, *J*<sub>1a,1b'</sub> 17.5 Hz, H-1b'), 5.23 (1H, ddd, *J*<sub>5,6'</sub> 3.5 Hz, *J*<sub>5,6</sub> 6.3 Hz, *J*<sub>4,5</sub> 4.0 Hz, H-5), 5.40 (1H, dd, *J*<sub>1,2</sub> 4.9 Hz, *J*<sub>1,1a</sub> 6.1 Hz, H-1), 5.65 (1H, ddd, *J*<sub>1,1a</sub> 6.1 Hz, *J*<sub>1a,1b</sub> 10.5 Hz, *J*<sub>1a,1b'</sub> 17.5 Hz, H-1a), 7.22-7.34 (20H, m, Ar-CH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta_C$  21.0, 21.1 (2 x q, 2 x CH<sub>3</sub>), 68.3 (t, C-6), 73.1 (t, PhCH<sub>2</sub>), 73.8 (d, C-5), 74.0 (t, PhCH<sub>2</sub>), 74.4 (d, C-1), 74.9 (t, PhCH<sub>2</sub>), 75.1 (t, PhCH<sub>2</sub>), 78.4 (d, C-4), 78.9 (d, C-2), 80.5 (d, C-3), 117.9 (t, C-1b), 127.6, 127.6, 127.7, 127.9, 128.1, 128.1, 128.2, 128.3 (8 x d, Ar-CH), 133.4 (d, C-1a), 137.9, 137.9, 138.1, 138.2 (4 x s, 4 x Ar-C), 169.9, 170.2 (2 x s, 2 x C=O). HRMS (ES<sup>+</sup>) *m/z*: Calcd. for C<sub>44</sub>H<sub>44</sub>O<sub>8</sub>Na (MNa<sup>+</sup>) 675.2928. Found 675.2949.



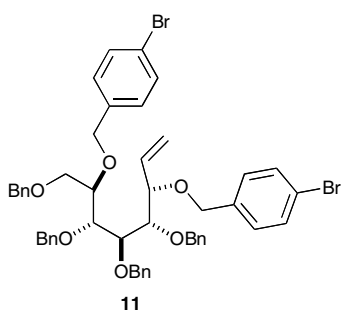
Diol **1** (500 mg, 0.88 mmol) and *para*-bromobenzyl bromide (527 mg, 2.1 mmol) were dissolved in THF (4 mL). The solution was cooled to 0 °C under argon, and sodium hydride (60% in oil,

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100 mg, 2.5 mmol) was then slowly added. The resulting suspension was stirred at room temperature for 5 h, after which time, TLC showed complete conversion of the starting material (pentane/ethyl acetate, 9:1,  $R_f$  0.2) into a single product ( $R_f$  0.8). The reaction mixture was then quenched with methanol (0.5 mL), diluted in ethyl acetate (30 mL) and washed with brine (20 mL). The organic layer was then dried ( $MgSO_4$ ) and evaporated under reduced pressure to give an oily yellowish residue, which was purified by flash chromatography (pentane 100%, then pentane/ethyl acetate, 9:1) to give compound **10** (750 mg, 94%).

Colourless oil:  $[\alpha]_D^{25}$   $-21.8$  ( $c$ , 1 in  $CHCl_3$ );  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta_H$  3.63-3.69 (2H, m, H-6, H-2), 3.81-3.88 (4H, m, H-1, H-4, H-5, H-6'), 3.96 (1H, dd,  $J$  4.3 Hz,  $J$  5.9 Hz, H-3), 4.17 (1H, d,  $J$  12.0 Hz, ArCH $\underline{H}H'$ ) 4.25 (1H, d,  $J$  12.0 Hz, ArCH $\underline{H}H'$ ), 4.48-4.72 (10H, m, 4 x ArCH $\underline{C}H_2$ , 2 x ArCH $\underline{H}H'$ ) 5.04 (1H, dat,  $J$  1.8 Hz,  $J_{1a,1b}$  17.3 Hz, H-1b), 5.16 (1H, dat,  $J$  1.8 Hz,  $J_{1a,1b'}$  10.5 Hz, H-1b'), 5.67 (1H, ddd,  $J_{1,1a}$  7.7 Hz,  $J_{1a,1b}$  17.3 Hz,  $J_{1a,1b'}$  10.5 Hz, H-1a), 7.06-7.34 (28H, m, Ar-CH).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta_C$  69.5 (t, ArCH $\underline{C}H_2$ ), 69.9 (t, C-6), 71.0 (t, ArCH $\underline{C}H_2$ ), 73.3 (t, ArCH $\underline{C}H_2$ ), 73.6 (t, ArCH $\underline{C}H_2$ ), 74.8 (2 x t, ArCH $\underline{C}H_2$ ), 78.7, 79.3 (2 x d, C-4, C-5), 79.4 (d, C-3), 80.6 (d, C-1), 82.0 (d, C-2), 118.9 (t, C-1b), 121.1, 121.3 (2 x s, 2 x Ar-CBr) 127.3, 127.5, 127.5, 127.6, 127.7, 127.7, 128.0, 128.0, 128.2, 128.2, 128.3, 128.9, 129.7, 131.3, 131.4 (15 x d, Ar-CH), 135.2 (d, C-1a), 137.1, 137.7, 138.2, 138.5, 138.5, 138.8 (6 x s, 6 x Ar-C).  $m/z$  ( $ES^+$ ) Isotope distribution  $MNa^+$ : 933.2 (5), 932.2 (29), 931.2 (66), 930.2 (59), 929.2 (100), 928.2 (30), 927.2 (54).  $C_{50}H_{50}Br_2O_6Na$  requires 933.2 (8), 932.2 (27), 931.2 (59), 930.2 (48), 929.2 (100), 928.2 (24), 927.2 (48%). HRMS ( $ES^+$ )  $m/z$ : Calcd. for  $C_{50}H_{50}Br_2O_6Na$  ( $MNa^+$ ) 927.1866. Found 927.1858.



Following an identical procedure to that described for compound **10**, starting from diol **2** (300 mg, 0.53 mmol), **11** was obtained (455 mg, 94%).

**11** Colourless oil:  $[\alpha]_D^{25}$   $-0.4$  ( $c$ , 1 in  $CHCl_3$ );  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta_H$  3.67 (1H, dd,  $J_{5,6}$  5.2 Hz,  $J_{6,6'}$  10.1, H-6), 3.79-3.86 (5H, m, H-2, H-3, H-4, H-5, H-6'), 3.92 (1H, dd,  $J_{1,2}$  4.6 Hz,  $J_{1,1a}$  7.9 Hz, H-1), 4.03, 4.42 (2H, ABq,  $J_{AB}$  11.9 Hz, ArCH $\underline{C}H_2$ ), 4.26-4.76 (10H, m, 5 x ArCH $\underline{C}H_2$ ), 5.29 (1H, ddd,  $J_{1,1b}$  0.8 Hz,  $J_{1b,1b'}$  1.8 Hz,  $J_{1a,1b}$  17.3, H-1b), 5.35 (1H, ddd,  $J_{1,1b'}$  0.6 Hz,  $J_{1b,1b'}$  1.8 Hz,

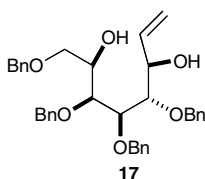
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$J_{1a,1b}$  10.3 Hz, H-1b'), 5.91 (1H, ddd,  $J_{1,1a}$  7.9 Hz,  $J_{1a,1b}$  17.3 Hz,  $J_{1a,1b'}$  10.3 Hz, H-1a), 7.06-7.34 (28H, m, Ar-CH).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  69.1 (t, C-6), 69.9 (t, ArCH<sub>2</sub>), 71.1 (t, ArCH<sub>2</sub>), 73.3 (t, ArCH<sub>2</sub>), 73.9 (t, ArCH<sub>2</sub>), 74.1 (t, ArCH<sub>2</sub>), 75.0 (t, ArCH<sub>2</sub>), 78.9, 79.4, 81.1, 81.5 (4 x d, C-2, C-3, C-4, C-5), 79.5 (d, C-1), 119.7 (t, C-1b), 121.1, 121.1 (2 x s, Ar-CBr), 127.3, 127.4, 127.5, 127.6, 127.6, 127.9, 127.9, 128.0, 128.2, 128.2, 128.2, 128.3, 129.0, 129.1, 131.2, 131.3 (16 x d, Ar-CH), 135.7 (d, C-1a), 137.5, 137.7, 138.2, 138.5, 138.7, 138.8 (6 x s, 6 x Ar-C).  $m/z$  ( $\text{ES}^+$ ) Isotope distribution  $\text{MNa}^+$ : 933.2 (5), 932.2 (23), 931.2 (56), 930.2 (48), 929.2 (100), 928.2 (30), 927.2 (37).  $\text{C}_{50}\text{H}_{50}\text{Br}_2\text{O}_6\text{Na}$  requires 933.2 (8) 932.2 (27), 931.2 (59), 930.2 (48), 929.2 (100), 928.2 (24), 927.2 (48%). HRMS ( $\text{ES}^+$ )  $m/z$ : Calcd. for  $\text{C}_{50}\text{H}_{50}\text{Br}_2\text{O}_6\text{Na}$  ( $\text{MNa}^+$ ) 927.1866. Found 927.1845.

**Synthesis of galactose diols:**

Tetrabenzyl galactose **16** (1.6 g, 2.9 mmol) was dissolved in anhydrous THF (5 mL) and cooled to 0° C under argon. Vinylmagnesium bromide (10.5 mL, 0.7 M in THF, 7.4 mmol) was slowly added to the suspension and the reaction mixture was stirred under argon atmosphere at room temperature. After 12 h, TLC (toluene/ethyl acetate, 8:1) showed starting material ( $R_f$  0.25), and the formation of a minor ( $R_f$  0.25) and a major product ( $R_f$  0.20). Saturated aqueous  $\text{NH}_4\text{Cl}$  (3 mL) was added and the mixture was diluted with ethyl acetate (25 mL) and washed with brine (15 mL). The  $^1\text{H}$  NMR spectrum of the crude material showed a diastomeric ratio of 2:1 of the epimeric diols. Purification by repeated flash chromatography (toluene/ethyl acetate, 10:1) gave minor diastomeric diol **17** (523 mg, 32%), and major diastomeric diol **18** (884 mg, 53%).

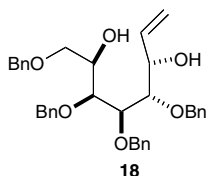


**17** Colourless oil:  $[\alpha]_{\text{D}}^{25}$  -8.9 (c, 1 in  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  2.73 (1H, d,  $J_{1,\text{OH}}$  5.8 Hz, OH-1), 3.35 (1H, d,  $J_{5,\text{OH}}$  4.0 Hz, OH-5), 3.51 (1H, dd,  $J_{5,6}$  6.6 Hz,  $J_{6,6'}$  9.4 Hz, H-6), 3.56 (1H, dd,  $J_{5,6}$  5.5,  $J_{6,6'}$  9.4 Hz, H-6'), 3.64 (1H, dd,  $J_{1,2}$  2.9 Hz,  $J_{2,3}$  6.4 Hz, H-2), 3.88 (1H, dd,  $J_{4,5}$  2.5 Hz,  $J_{3,4}$  3.9 Hz, H-4), 3.99 (1H, dd,  $J_{3,4}$  3.9 Hz,  $J_{2,3}$  6.4 Hz, H-3), 4.06 (1H, m, H-5), 4.29 (1H, m, H-1), 4.40, 4.46 (2H, ABq,  $J_{\text{AB}}$  11.8 Hz,  $\text{PhCH}_2$ ), 4.51, 4.68 (2H, ABq,  $J_{\text{AB}}$  11.5 Hz,  $\text{PhCH}_2$ ), 4.62, 4.74 (4H, m, 2 x  $\text{PhCH}_2$ ), 5.17 (1H, dat,  $J$  1.5 Hz,  $J_{1a,1b}$  10.5 Hz, H-1b), 5.29 (1H, dat,  $J$  1.5 Hz,  $J_{1a,1b'}$  17.2 Hz, H-1b'), 5.91 (1H, ddd,  $J_{1,1a}$  5.9 Hz,  $J_{1a,1b}$  10.5 Hz,  $J_{1a,1b'}$  17.2 Hz, H-1a), 7.23-7.33 (20H,

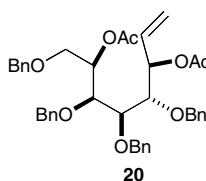
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m, Ar-CH).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  70.1 (d, C-5), 70.8 (t, C-6), 71.8 (d, C-1), 73.3 (t,  $\text{PhCH}_2$ ), 73.3 (t,  $\text{PhCH}_2$ ), 74.6 (t,  $\text{PhCH}_2$ ), 74.7 (t,  $\text{PhCH}_2$ ), 77.5 (d, C-4), 80.7 (d, C-3), 81.5 (d, C-2), 115.9 (t, C-1b), 127.7, 127.7, 127.8, 127.8, 127.9, 128.0, 128.1, 128.3, 128.4, 128.4 (10 x d, Ar-CH), 137.8, 137.9, 137.9, 138.0 (4 x s, 4 x Ar-C), 138.4 (d, C-1a). HRMS ( $\text{ES}^+$ )  $m/z$ : Calcd. for  $\text{C}_{36}\text{H}_{40}\text{O}_6\text{Na}$  ( $\text{MNa}^+$ ) 591.2717. Found 591.2699.



**18** Colourless oil:  $[\alpha]_{\text{D}}^{25}$   $-17.3$  (c, 1 in  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  2.80 (1H, br s, OH-1), 2.98 (1H, br s, OH-5), 3.51 (1H, dd,  $J_{5,6}$  6.7 Hz,  $J_{6,6'}$  9.5 Hz, H-6), 3.54 (1H, dd,  $J_{5,6'}$  6.0 Hz,  $J_{6,6'}$  9.5 Hz, H-6'), 3.65 (1H, dd,  $J_{1,2}$  4.9 Hz,  $J_{2,3}$  4.3 Hz, H-2), 3.84 (1H, dd,  $J_{4,5}$  1.9 Hz,  $J_{3,4}$  5.8 Hz, H-4), 3.97 (1H, dd,  $J_{3,4}$  5.8 Hz,  $J_{2,3}$  4.3 Hz, H-3), 4.13 (1H, m, H-5), 4.41-4.53 (5H, m, 2 x  $\text{PhCH}_2$ , H-1), 4.60, 4.71 (2H, ABq,  $J_{\text{AB}}$  11.8 Hz,  $\text{PhCH}_2$ ), 4.72, 4.76 (2H, ABq,  $J_{\text{AB}}$  10.9 Hz,  $\text{PhCH}_2$ ), 5.24 (1H, dat,  $J$  1.5 Hz,  $J_{1a,1b}$  10.5 Hz, H-1b), 5.37 (1H, dat,  $J$  1.5 Hz,  $J_{1a,1b'}$  17.2 Hz, H-8'), 5.94 (1H, ddd,  $J_{1,1a}$  5.6 Hz,  $J_{1a,1b}$  10.5 Hz,  $J_{1a,1b'}$  17.2 Hz, H-1a), 7.20-7.33 (20H, m, Ar-CH).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  69.5 (d, C-5), 71.1 (t, C-6), 72.1 (d, C-1), 72.7 (t,  $\text{PhCH}_2$ ), 73.3 (t,  $\text{PhCH}_2$ ), 73.6 (t,  $\text{PhCH}_2$ ), 74.3 (t,  $\text{PhCH}_2$ ), 77.0 (d, C-4), 79.6 (d, C-3), 80.5 (d, C-2), 116.8 (t, C-1b), 127.7, 127.7, 127.8, 127.9, 127.9, 128.1, 128.2, 128.4, 128.4, 128.4, 129.0 (11 x d, Ar-CH), 137.2 (d, C-1a), 137.8, 137.9, 137.9, 138.0 (4 x s, 4 x Ar-C). HRMS ( $\text{ES}^+$ )  $m/z$ : Calcd. for  $\text{C}_{36}\text{H}_{40}\text{O}_6\text{Na}$  ( $\text{MNa}^+$ ) 591.2717. Found 591.2691.



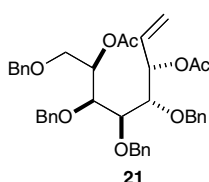
Following an identical procedure to that described for compound **9**, starting from diol **17** (60 mg, 0.11 mmol), diacetate **20** was obtained (66 mg, 92%).

**20** Colourless oil:  $[\alpha]_{\text{D}}^{25}$   $+3.8$  (c, 1 in  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  1.94, 1.98 (6H, 2 x s, 2 x  $\text{CH}_3$ ), 3.61 (1H, dd,  $J_{5,6}$  5.6 Hz,  $J_{6,6'}$  10.1 Hz, H-6) 3.66 (1H, dd,  $J_{5,6'}$  5.7 Hz,  $J_{6,6'}$  10.1 Hz, H-6'), 3.83 (2H, m, H-2, H-3), 3.93 (1H, at,  $J$  4.0 Hz, H-4), 4.45 (2H, s,  $\text{PhCH}_2$ ), 4.53, 4.56 (2H, ABq,  $J_{\text{AB}}$  11.6 Hz,  $\text{PhCH}_2$ ), 4.63, 4.71 (2H, ABq,  $J_{\text{AB}}$  11.5 Hz,  $\text{PhCH}_2$ ), 4.64, 4.66 (2H, m,  $\text{PhCH}_2$ ), 5.18

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(1H, dat,  $J$  1.4 Hz,  $J_{1a,1b}$  10.6 Hz, H-1b), 5.20 (1H, dat,  $J$  1.4 Hz,  $J_{1a,1b'}$  17.2 Hz, H-1b'), 5.40 (1H, dat,  $J$  5.6 Hz,  $J_{4,5}$  3.9 Hz, H-5), 5.55 (1H, dd,  $J_{1,2}$  4.7 Hz,  $J_{1,1a}$  6.1 Hz, H-1), 5.83 (1H, ddd,  $J_{1,1a}$  6.1 Hz,  $J_{1a,1b}$  10.5 Hz,  $J_{1a,1b'}$  17.2, H-1a), 7.23-7.34 (20H, m, Ar-CH).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  21.0, 21.1 (2 x q, 2 x  $\text{CH}_3$ ), 68.7 (t, C-6), 71.7 (d, C-5), 73.1, 73.5 (2 x t,  $\text{PhCH}_2$ ), 74.2 (d, C-1), 74.3 (t,  $\text{PhCH}_2$ ), 77.2 (d, C-4), 79.1, 79.6 (2 x d, C-2, C-3), 118.1 (t, C-1b), 127.5, 127.5, 127.6, 127.7, 127.7, 127.8, 127.9, 128.2, 128.2, 128.3, 128.3 (11 x d, Ar-CH), 133.4 (d, C-1a), 137.7, 138.0, 138.3, 138.4 (4 x s, 4 x Ar-C), 169.8, 170.5 (2 x s, 2 x C=O). HRMS ( $\text{ES}^+$ )  $m/z$ : Calcd. for  $\text{C}_{40}\text{H}_{44}\text{O}_8\text{Na}$  ( $\text{MNa}^+$ ) 675.2928. Found 675.2954.



Following an identical procedure to that described for compound **9**, starting from diol **18** (200 mg, 0.35 mmol), diacetate **21** was obtained (206 mg, 88%).

**21** Colourless oil:  $[\alpha]_{\text{D}}^{25}$   $-10.2$  ( $c$ , 1 in  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  1.96, 1.97 (6H, 2 x s, 2 x  $\text{CH}_3$ ), 3.61 (1H, dd,  $J_{5,6}$  5.9 Hz,  $J_{6,6'}$  10.1 Hz, H-6), 3.65 (1H, dd,  $J_{5,6'}$  6.1 Hz,  $J_{6,6'}$  10.1 Hz, H-6'), 3.73 (1H, at,  $J$  5.6 Hz, H-3), 3.85 (1H, dd,  $J_{1,2}$  3.9 Hz,  $J_{2,3}$  5.7 Hz, H-2), 3.89 (1H, dd,  $J_{4,5}$  3.4 Hz,  $J_{3,4}$  5.6 Hz, H-4), 4.46, 4.56 (4H, 2 x s, 2 x  $\text{PhCH}_2$ ), 4.57-4.68 (4H, m, 2 x  $\text{PhCH}_2$ ), 5.27 (1H, dat,  $J$  1.3 Hz,  $J_{1a,1b}$  10.5 Hz, H-1b), 5.29 (1H, dat,  $J$  1.3 Hz,  $J_{1a,1b'}$  17.2 Hz, H-1b'), 5.42-5.49 (2H, m, H-5, H-1), 5.99 (1H, ddd,  $J_{1,1a}$  6.9 Hz,  $J_{1a,1b}$  10.5 Hz,  $J_{1a,1b'}$  17.2, H-1a), 7.23-7.34 (20H, m, Ar-CH).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  21.1 (2 x q, 2 x  $\text{CH}_3$ ), 68.4 (t, C-6), 71.4 (d, C-5), 72.9, 73.5, 73.8, 74.9 (4 x t, 4 x  $\text{PhCH}_2$ ), 74.7 (d, C-1), 75.0 (d, C-4), 79.2 (d, C-3), 80.1 (d, C-2), 119.4 (t, C-1b), 127.4, 127.5, 127.6, 127.7, 127.8, 127.8, 128.0, 128.2, 128.2, 128.3, 128.3 (11 x d, Ar-CH), 132.8 (d, C-1a), 137.8, 137.9, 138.2, 138.5 (4 x s, 4 x Ar-C), 169.7, 170.5 (2 x s, C=O). HRMS ( $\text{ES}^+$ )  $m/z$ : Calcd. for  $\text{C}_{40}\text{H}_{44}\text{O}_8\text{Na}$  ( $\text{MNa}^+$ ) 675.2928. Found 675.2906.

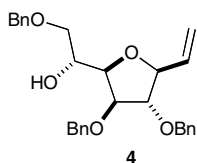
**General procedure for cyclisation:**

Compounds (**1**, **2**, **8**, **9**, **10**, **11**, **17**, **18**, **20**, **21**) (100 mg), were dissolved in acetonitrile (0.6 mL), and toluene (10 eq for compounds **8**, **9**, **10**, **11**, **20**, **21**; 20 eq for compounds **1**, **2**, **17**, **18**), and trifluoroacetic acid (1.4 mL) were added. After complete disappearance of the starting material on TLC (pentane/ethyl acetate, 4:1 for compounds **1**, **2**, **17**, **18**; pentane/ethyl acetate, 9:1 for compounds **8**, **9**, **10**, **11**, **20**, **21**), the solution was diluted with ethyl acetate (10 mL), and washed

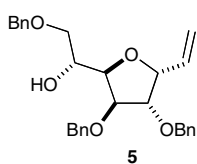
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with saturated aqueous NaHCO<sub>3</sub> until basic pH. The aqueous phase was re-extracted twice with ethyl acetate (5 mL), the organic phases combined and dried (MgSO<sub>4</sub>). Evaporation of the solvent under reduced pressure and purification of the residue by flash chromatography (pentane/ethyl acetate, 4:1 for compounds **4**, **5**, **22**, **23**; pentane/ethyl acetate, 9:1 for compounds **12**, **13**, **14**, **15**, **24**, **25**) gave the C-glycosides (**4**, **5**, **12**, **13**, **14**, **15**, **22**, **23**, **24**, **25**).



**4** Colourless oil:  $[\alpha]_D^{25} -14.1$  (*c*, 1 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_H$  2.74 (1H, br s, OH), 3.62 (1H, dd,  $J_{5,6}$  6.2 Hz,  $J_{6,6'}$  9.8 Hz, H-6), 3.75 (1H, dd,  $J_{5,6'}$  3.2 Hz,  $J_{6,6'}$  9.8 Hz, H-6'), 3.83 (1H, dd,  $J_{2,3}$  1.0 Hz,  $J_{1,2}$  3.2 Hz, H-2), 3.99 (1H, dd,  $J_{3,4}$  3.8 Hz,  $J_{4,5}$  8.1 Hz, H-4), 4.12 (1H, dd,  $J_{2,3}$  1.0 Hz,  $J_{3,4}$  3.8 Hz, H-3), 4.19 (1H, m, H-5), 4.29 (1H, dd,  $J_{1,2}$  3.2 Hz,  $J_{1,1a}$  7.5 Hz, H-1), 4.50 (2H, s, PhCH<sub>2</sub>), 4.50 (1H, d,  $J$  11.7 Hz, PhCHH'), 4.54 (1H, d,  $J$  11.9 Hz, PhCHH'), 4.56-4.60 (2H, m, 2 x PhCHH'), 5.14 (1H, dat,  $J$  1.3 Hz,  $J_{1a,1b}$  10.3 Hz, H-1b), 5.30 (1H, dat,  $J$  1.3 Hz,  $J_{1a,1b'}$  17.3 Hz, H-1b'), 5.93 (1H, ddd,  $J_{1,1a}$  7.5 Hz,  $J_{1a,1b}$  10.3 Hz,  $J_{1a,1b'}$  17.3 Hz, H-1a), 7.19-7.29 (15H, m, Ar-CH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta_C$  68.6 (d, C-5), 71.7 (t, PhCH<sub>2</sub>), 71.8 (t, PhCH<sub>2</sub>), 72.1 (t, C-6), 73.4 (t, PhCH<sub>2</sub>), 80.8 (d, C-4), 83.0 (d, C-3), 85.5 (d, C-1), 87.1 (d, C-2), 116.9 (t, C-1b), 127.6, 127.7, 127.7, 127.8, 127.9, 127.9, 128.4, 128.5 (8 x d, Ar-CH), 137.0 (d, C-1a), 137.5, 137.7, 138.1 (3 x s, 3 x Ar-C). HRMS (ES<sup>+</sup>) *m/z*: Calcd. for C<sub>29</sub>H<sub>32</sub>O<sub>5</sub>Na (MNa<sup>+</sup>) 483.2142. Found 483.2146



**5** Colourless oil:  $[\alpha]_D^{25} -21.5$  (*c*, 1 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_H$  2.33 (1H, br s, OH), 3.60 (1H, dd,  $J_{5,6}$  5.9 Hz,  $J_{6,6'}$  9.7 Hz, H-6), 3.77 (1H, dd,  $J_{5,6'}$  2.6 Hz,  $J_{6,6'}$  9.7 Hz, H-6'), 3.90 (1H, dd,  $J_{1,2}$  3.8 Hz,  $J_{2,3}$  1.2 Hz, H-2), 4.12-4.17 (3H, m, H-3, H-4, H-5), 4.47 (1H, d,  $J$  11.2 Hz, PhCHH'), 4.48-4.58 (6H, m, 2 x PhCH<sub>2</sub>, PhCHH', H-1), 5.25 (1H, ddd,  $J_{1,1b}$  0.9 Hz,  $J_{1b,1b'}$  1.8 Hz,  $J_{1a,1b}$  10.3 Hz, H-1b), 5.34 (1H, ddd,  $J_{1,1b}$  1.1 Hz,  $J_{1b,1b'}$  1.8 Hz,  $J_{1a,1b'}$  17.3 Hz, H-1b'), 6.00 (1H, ddd,  $J_{1,1a}$  7.5 Hz,  $J_{1a,1b}$  10.3 Hz,  $J_{1a,1b'}$  17.3 Hz, H-1a), 7.23-7.37 (15H, m, Ar-CH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta_C$  68.7 (d, C-5), 79.8 (d, C-4), 72.1 (t, PhCH<sub>2</sub>), 72.4 (t, C-6), 72.5 (t, PhCH<sub>2</sub>), 73.4 (t, PhCH<sub>2</sub>), 82.1 (d, C-1), 82.3 (d, C-3), 83.0 (d, C-2), 118.1 (t, C-1b), 127.5, 127.6, 127.8, 127.8,

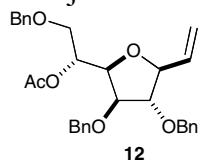
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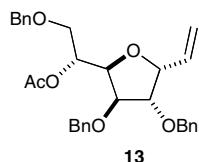
127.8, 127.9, 128.3, 128.4, 128.5 (9 x d, Ar-CH), 133.9 (d, C-1a), 137.6, 137.7, 138.1 (3 x s, 3 x

Ar-C). HRMS (ES<sup>+</sup>) *m/z*: Calcd. for C<sub>29</sub>H<sub>32</sub>O<sub>5</sub>Na (MNa<sup>+</sup>) 483.2142. Found 483.2143.

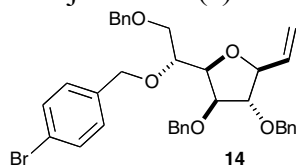




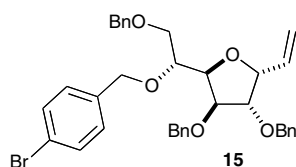
**12** Colourless oil:  $[\alpha]_D^{25} -39.1$  (*c*, 1 in  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  1.97 (3H, s,  $\text{CH}_3$ ), 3.77 (1H, dd,  $J_{5,6}$  5.3 Hz,  $J_{6,6'}$  11.3 Hz, H-6), 3.82 (1H, dd,  $J_{2,3}$  0.9 Hz,  $J_{1,2}$  2.9 Hz, H-2), 3.87 (1H, dd,  $J_{5,6'}$  2.3 Hz,  $J_{6,6'}$  11.3 Hz, H-6'), 3.98 (1H, dd,  $J_{2,3}$  0.9 Hz,  $J_{3,4}$  3.8 Hz, H-3), 4.31 (1H, dd,  $J_{3,4}$  3.8 Hz,  $J_{4,5}$  7.3 Hz, H-4), 4.35 (1H, dd,  $J_{1,2}$  2.9 Hz,  $J_{1,1a}$  7.5 Hz, H-1), 4.39, 4.49 (2H, ABq,  $J_{\text{AB}}$  11.8 Hz,  $\text{PhCH}_2$ ), 4.49, 4.55 (2H, ABq,  $J_{\text{AB}}$  12.1 Hz,  $\text{PhCH}_2$ ), 4.53 (2H, s,  $\text{PhCH}_2$ ), 5.13 (1H, dat,  $J$  1.3 Hz,  $J_{1a',1b}$  10.3 Hz, H-1b), 5.29 (1H, dat,  $J$  1.3 Hz,  $J_{1a,1b'}$  17.4 Hz, H-1b'), 5.38 (1H, ddd,  $J_{5,6}$  5.3 Hz,  $J_{5,6'}$  2.3 Hz,  $J_{4,5}$  7.3 Hz, H-5), 5.89 (1H, ddd,  $J_{1,1a}$  7.5 Hz,  $J_{1a,1b}$  10.3 Hz,  $J_{1a,1b'}$  17.4 Hz, H-1a), 7.22-7.38 (15H, m, Ar-CH).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  21.1 (q,  $\text{CH}_3$ ), 69.3 (t, C-6), 70.4 (d, C-5), 71.6 (t,  $\text{PhCH}_2$ ), 71.7 (t,  $\text{PhCH}_2$ ), 73.1 (t,  $\text{PhCH}_2$ ), 79.1 (d, C-4), 82.1 (d, C-3), 85.6 (d, C-1), 86.4 (d, C-2), 116.7 (t, C-1b), 127.4, 127.5, 127.6, 127.8, 127.9, 128.0, 128.2, 128.4, 128.5 (9 x d, Ar-CH), 136.9 (d, C-1a), 137.4, 137.5, 138.4 (3 x s, 3 x Ar-C), 169.9 (s, C=O). HRMS ( $\text{ES}^+$ )  $m/z$ : Calcd. for  $\text{C}_{31}\text{H}_{34}\text{O}_6\text{Na}$  ( $\text{MNa}^+$ ) 525.2248. Found 525.2229.



**13** Colourless oil:  $[\alpha]_D^{25} -28.2$  (*c*, 1 in  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  1.96 (3H, s,  $\text{CH}_3$ ), 3.76 (1H, dd,  $J_{5,6}$  5.3 Hz,  $J_{6,6'}$  11.3 Hz, H-6), 3.85 (1H, dd,  $J_{5,6'}$  2.3 Hz,  $J_{6,6'}$  11.3 Hz, H-6'), 3.88 (1H, dd,  $J_{2,3}$  1.2 Hz,  $J_{1,2}$  3.7 Hz, H-2), 4.02 (1H, dd,  $J_{2,3}$  1.2 Hz,  $J_{3,4}$  3.9 Hz, H-3), 4.40 (1H, ABq,  $J_{\text{AB}}$  11.8 Hz,  $\text{PhCH}_2$ ), 4.44 (1H, dd,  $J_{3,4}$  3.9 Hz,  $J_{4,5}$  8.2 Hz, H-4), 4.45-4.57 (6H, m, 2 x  $\text{PhCH}_2$ ,  $\text{PhCH}_2$ ), 5.25 (1H, ddd,  $J_{1,1b}$  0.8 Hz,  $J_{1b,1b'}$  1.7 Hz,  $J_{1a,1b}$  10.3 Hz, H-1b), 5.30 (1H, ddd,  $J_{5,6}$  2.3 Hz,  $J_{5,6'}$  5.3 Hz,  $J_{4,5}$  8.2 Hz, H-5), 5.34 (1H, ddd,  $J_{1,1b}$  1.1 Hz,  $J_{1b,1b'}$  1.7 Hz,  $J_{1a,1b'}$  17.4 Hz, H-1b'), 6.00 (1H, ddd,  $J_{1,1a}$  7.5 Hz,  $J_{1a,1b}$  10.3 Hz,  $J_{1a,1b'}$  17.4 Hz, H-1a), 7.23-7.37 (15H, m, Ar-CH).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  21.1 (q,  $\text{CH}_3\text{CO}$ ), 69.5 (t, C-6), 70.6 (d, C-5), 72.2 (t,  $\text{PhCH}_2$ ), 72.4 (t,  $\text{PhCH}_2$ ), 73.0 (t,  $\text{PhCH}_2$ ), 78.2 (d, C-4), 81.6 (d, C-3), 82.3 (d, C-1), 82.6 (d, C-2), 118.1 (t, C-1b), 127.4, 127.5, 127.6, 127.8, 127.9, 128.0, 128.2, 128.4, 128.5 (9 x d, Ar-CH), 133.9 (d, C-1a), 137.3, 137.7, 138.4 (3 x s, 3 x Ar-CH), 169.9 (s, C=O). HRMS ( $\text{ES}^+$ )  $m/z$ : Calcd. for  $\text{C}_{31}\text{H}_{34}\text{O}_6\text{Na}$  ( $\text{MNa}^+$ ) 525.2248. Found 525.2235.



**14** Colourless oil:  $[\alpha]_D^{25} -34.2$  (*c*, 1 in  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  3.69 (1H, dd,  $J_{5,6}$  5.9 Hz,  $J_{6,6'}$  11.6 Hz, H-6), 3.83 (1H, dd,  $J_{2,3}$  0.7 Hz,  $J_{1,2}$  2.7 Hz, H-2), 3.90 (1H, dd,  $J_{5,6'}$  1.8 Hz,  $J_{6,6'}$  11.6 Hz, H-6'), 4.06 (1H, ddd,  $J_{5,6}$  5.9 Hz,  $J_{5,6'}$  1.8 Hz,  $J_{4,5}$  8.9 Hz, H-5), 4.07 (1H, dd,  $J_{2,3}$  0.7 Hz,  $J_{3,4}$  3.3 Hz, H-3), 4.12 (1H, dd,  $J_{3,4}$  3.3 Hz,  $J_{4,5}$  8.9 Hz, H-4), 4.35 (1H, dd,  $J_{1,2}$  2.7 Hz,  $J_{1,1a}$  7.5 Hz, H-1), 4.36, 4.52 (2H, ABq,  $J_{\text{AB}}$  11.6 Hz,  $\text{ArCH}_2$ ), 4.42-4.55 (5H, m, 2 x  $\text{ArCH}_2$ ,  $\text{ArCHH}'$ ), 4.72 (1H, d,  $J$  11.8 Hz,  $\text{ArCHH}'$ ), 5.13 (1H, ddd,  $J_{1,1b}$  1.0 Hz,  $J_{1b,1b'}$  1.6 Hz,  $J_{1a,1b}$  10.3 Hz, H-1b), 5.28 (1H, H, ddd,  $J_{1,1b'}$  1.2 Hz,  $J_{1b,1b'}$  1.6 Hz,  $J_{1a,1b'}$  17.2 Hz, H-1b'), 5.91 (1H, ddd,  $J_{1,1a}$  7.5 Hz,  $J_{1a,1b}$  10.3 Hz,  $J_{1a,1b'}$  17.4 Hz, H-1a), 7.08 (2H, d,  $J$  8.5 Hz, Ar-CH), 7.20-7.34 (15H, m, Ar-CH), 7.37 (2H, d,  $J$  8.5 Hz, Ar-CH).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  71.3, 71.4, 71.6, 71.7, 73, 3 (5 x t, C-6, 4 x  $\text{ArCH}_2$ ), 76.2 (d, C-5), 80.3 (d, C-4), 82.6 (d, C-3), 85.9 (d, C-1), 86.5 (d, C-2), 116.5 (t, C-1b), 121.1 (s, Ar-CBr), 127.4, 127.6, 127.6, 127.7, 127.8, 128.2, 128.3, 128.5, 129.0, 131.2 (10 x d, Ar-CH), 137.1 (C-1a), 137.6, 137.8, 138.1, 138.5 (4 x s, 4 x Ar-C). *m/z* ( $\text{ES}^+$ ) Isotope distribution  $\text{MNa}^+$ : 655.2 (5), 654.2 (38), 653.2 (100), 652.2 (38), 651.2 (96).  $\text{C}_{36}\text{H}_{37}\text{BrO}_5\text{Na}$  requires 655.2 (7), 654.2 (36), 653.2 (100), 652.2 (36), 651.2 (92%). HRMS ( $\text{ES}^+$ ) *m/z*: Calcd. for  $\text{C}_{36}\text{H}_{37}\text{BrO}_5\text{Na}$  ( $\text{MNa}^+$ ) 651.1717. Found 651.1722.

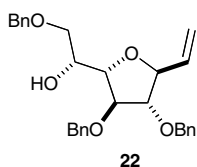


**15** Colourless oil:  $[\alpha]_D^{25} -15.7$  (*c*, 1 in  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  3.70 (1H, dd,  $J_{5,6}$  6.3 Hz,  $J_{6,6'}$  10.6 Hz, H-6), 3.89 (1H, dd,  $J_{2,3}$  1.0 Hz,  $J_{1,2}$  3.7 Hz, H-2), 3.92 (1H, dd,  $J_{5,6'}$  1.9 Hz,  $J_{6,6'}$  10.6 Hz, H-6'), 3.97 (1H, ddd,  $J_{5,6}$  6.3 Hz,  $J_{5,6'}$  1.9 Hz,  $J_{4,5}$  9.2 Hz, H-5), 4.11 (1H, dd,  $J_{2,3}$  1.0 Hz,  $J_{3,4}$  3.6 Hz, H-3), 4.25 (1H, dd,  $J_{3,4}$  3.6 Hz,  $J_{4,5}$  9.2 Hz, H-4), 4.40-4.55 (7H, m, 3 x  $\text{ArCH}_2$ ,  $\text{ArCHH}'$ ), 4.56 (1H, dd,  $J_{1,2}$  3.7 Hz,  $J_{1,1a}$  7.5 Hz, H-1), 4.75 (1H, d,  $J_{\text{AB}}$  11.8 Hz,  $\text{ArCHH}'$ ), 5.25 (1H, ddd,  $J_{1,1b}$  0.8 Hz,  $J_{1b,1b'}$  1.8 Hz,  $J_{1a,1b}$  10.3 Hz, H-1b), 5.33 (1H, ddd,  $J_{1,1b'}$  1.1 Hz,  $J_{1b,1b'}$  1.8 Hz,  $J_{1a,1b'}$  17.3 Hz, H-1b'), 6.01 (1H, ddd,  $J_{1,1a}$  7.5 Hz,  $J_{1a,1b}$  10.3 Hz,  $J_{1a,1b'}$  17.3 Hz, H-1a), 7.09 (2H, d,  $J$  8.5 Hz, Ar-CH), 7.18-7.34 (15H, m, Ar-CH), 7.38 (2H, d,  $J$  8.5 Hz, Ar-CH).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  71.7, 71.9, 72.1, 72.1, 73.4 (5 x t, 4 x  $\text{ArCH}_2$ , C-6), 76.4 (d, C-5), 79.3 (d, C-4), 81.9 (d, C-3), 82.3 (d, C-1), 82.6 (d, C-2), 117.9 (t, C-1b), 121.0 (s, Ar-CBr), 127.4, 127.4, 127.5, 127.6,

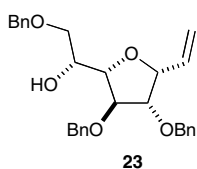
Supplementary Material (ESI) for Chemical Communications

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127.7, 127.8, 127.8, 128.2, 128.4, 128.4, 129.0, 131.2 (12 x d, Ar-CH), 134.1 (C-1a), 137.7, 137.8, 138.1, 138.5 (4 x s, 4 x Ar-C).  $m/z$  ( $ES^+$ ) Isotope distribution  $MNa^+$ : 655.2 (5), 654.2 (30), 653.2 (100), 652.2 (30), 651.2 (93).  $C_{36}H_{37}BrO_5Na$  requires 655.2 (7), 654.2 (36), 653.2 (100), 652.2 (36), 651.2 (92%). HRMS ( $ES^+$ )  $m/z$ : Calcd. for  $C_{36}H_{37}BrO_5Na$  ( $MNa^+$ ) 651.1717. Found 651.1736.



**22** Colourless oil:  $[\alpha]_D^{25} -22.3$  (*c*, 1 in  $CHCl_3$ );  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta_H$  2.63 (1H, br s, OH), 3.54 (1H, dd,  $J_{5,6}$  5.5 Hz,  $J_{6,6'}$  9.8 Hz, H-6) 3.57 (1H, dd,  $J_{5,6'}$  6.3 Hz,  $J_{6,6'}$  9.8 Hz, H-6'), 3.90 (1H, m, H-5), 3.95 (1H, dd,  $J_{2,3}$  3.1 Hz,  $J_{1,2}$  4.0 Hz, H-2), 4.11 (1H, at,  $J$  4.5 Hz, H-4), 4.19 (1H, dd,  $J_{2,3}$  3.1 Hz,  $J_{3,4}$  4.6 Hz, H-3), 4.50 (1H, m, H-1), 4.51-4.58 (6H, m, 3 x  $Ph\text{CH}_2$ ), 5.20 (1H, dat,  $J$  1.2 Hz,  $J_{1a,1b}$  10.3 Hz, H-1b), 5.32 (1H, dat,  $J$  1.2 Hz,  $J_{1a,1b'}$  17.2 Hz, H-1b'), 5.94 (1H, ddd,  $J_{1,1a}$  6.9 Hz,  $J_{1a,1b}$  10.3 Hz,  $J_{1a,1b'}$  17.2 Hz, H-1a), 7.24-7.36 (15H, m, Ar-CH).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta_C$  70.4 (d, C-5), 71.5 (t, C-6), 71.9, 72.0, 73.4 (3 x t, 3 x  $Ph\text{CH}_2$ ), 82.7 (d, C-4), 84.2, 84.3 (2 x d, C-1, C-3), 87.4 (d, C-2), 117.1 (t, C-1b), 127.6, 127.7, 127.7, 127.8, 127.8, 127.9, 128.4, 128.4, 128.5 (9 x d, Ar-CH), 136.3 (d, C-1a), 137.4, 137.7, 138.0 (3 x s, 3 x Ar-C). HRMS ( $ES^+$ )  $m/z$ : Calcd. for  $C_{29}H_{32}O_5Na$  ( $MNa^+$ ) 483.2142. Found 483.2147

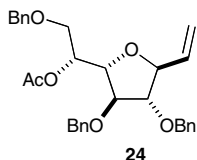


**23** Colourless oil:  $[\alpha]_D^{25} -30.7$  (*c*, 1 in  $CHCl_3$ );  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta_H$  2.87 (1H, br s, OH-5), 3.54 (1H, dd,  $J_{5,6}$  5.8 Hz,  $J_{6,6'}$  9.8 Hz, H-6), 3.57 (1H, dd,  $J_{5,6'}$  6.5 Hz,  $J_{6,6'}$  9.8 Hz, H-6'), 3.87 (1H, dd,  $J_{2,3}$  0.9 Hz,  $J_{1,2}$  3.5 Hz, H-2), 3.90 (1H, m, H-5), 4.08 (1H, at,  $J$  3.3 Hz, H-4), 4.12 (1H, dd,  $J_{2,3}$  0.9 Hz,  $J_{3,4}$  3.1 Hz, H-3), 4.45 (1H, dd,  $J_{1,2}$  3.5 Hz,  $J_{1,1a}$  7.4 Hz, H-1), 4.46-4.54 (6H, m, 3 x  $Ph\text{CH}_2$ ), 5.30 (1H, ddd,  $J_{1,1b}$  0.7 Hz,  $J_{1b,1b'}$  1.7 Hz,  $J_{1a,1b}$  10.4 Hz, H-1b), 5.39 (1H, ddd,  $J_{1,1b'}$  1.1 Hz,  $J_{1b,1b'}$  1.7 Hz,  $J_{1a,1b'}$  17.3 Hz, H-1b'), 6.05 (1H, ddd,  $J_{1,1a}$  7.4 Hz,  $J_{1a,1b}$  10.4 Hz,  $J_{1a,1b'}$  17.3 Hz, H-1a), 7.24-7.36 (15H, m, Ar-CH).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta_C$  70.6 (d, C-5), 71.6, 71.6, 71.8, 73.4 (4 x t, 3 x  $Ph\text{CH}_2$ , C-6), 82.6 (d, C-1), 83.5 (d, C-2), 83.8, 83.9 (2 x d, C-3, C-4), 119.0 (t, C-1b), 127.5, 127.6, 127.6, 127.7, 127.9, 127.9, 128.3, 128.4, 128.5 (9 x d, 15 x Ar-CH), 133.0 (d, C-

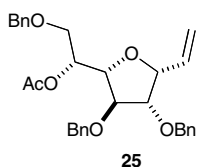
## Supplementary Material (ESI) for Chemical Communications

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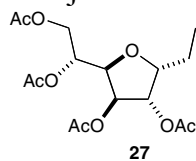
1a), 137.3, 137.5, 138.2 (3 x s, 3 x Ar-C). HRMS (ES<sup>+</sup>) *m/z*: Calcd. for C<sub>29</sub>H<sub>32</sub>O<sub>5</sub>Na (MNa<sup>+</sup>) 483.2142. Found 483.2118.



**24** Colourless oil:  $[\alpha]_D^{25} -7.8$  (*c*, 1 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_H$  2.04 (3H, s, CH<sub>3</sub>), 3.63 (2H, d, *J* 5.7 Hz, H-6, H-6'), 3.92 (1H, dd, *J*<sub>2,3</sub> 3.6 Hz, *J*<sub>1,2</sub> 5.2 Hz, H-2), 4.03 (1H, dd, *J*<sub>2,3</sub> 3.6 Hz, *J*<sub>3,4</sub> 4.8 Hz, H-3), 4.22 (1H, at, *J* 4.6 Hz, H-4), 4.44-4.57 (7H, m, 3 x PhCH<sub>2</sub>, H-1), 5.20 (1H, dat, *J* 1.3 Hz, *J*<sub>1a,1b</sub> 10.3 Hz, H-1b), 5.31 (1H, m, H-5), 5.34 (1H, dat, *J* 1.3 Hz, *J*<sub>1a,1b'</sub> 17.2 Hz, H-1b'), 5.91 (1H, ddd, *J*<sub>1,1a</sub> 6.9 Hz, *J*<sub>1a,1b</sub> 10.3 Hz, *J*<sub>1a,1b'</sub> 17.2 Hz, H-1a), 7.24-7.36 (15H, m, Ar-CH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta_C$  21.1 (q, CH<sub>3</sub>), 68.9 (t, C-6), 71.6 (d, C-5), 72.1, 72.1, 73.1 (3 x t, 3 x PhCH<sub>2</sub>), 80.8 (d, C-4), 83.8 (d, C-1), 84.5 (d, C-3), 87.9 (d, C-2), 117.4 (t, C-1b), 127.5, 127.6, 127.7, 127.8, 127.8, 128.3, 128.4, 128.4 (8 x d, Ar-CH), 136.5 (d, C-1a), 137.5, 137.6, 137.9 (3 x s, 3 x Ar-C), 170.6 (s, C=O). HRMS (ES<sup>+</sup>) *m/z*: Calcd. for C<sub>31</sub>H<sub>34</sub>O<sub>6</sub>Na (MNa<sup>+</sup>) 525.2248. Found 525.2249

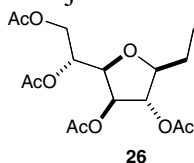


**25** Colourless oil:  $[\alpha]_D^{25} -16.5$  (*c*, 1 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_H$  2.01 (3H, s, CH<sub>3</sub>), 3.59 (1H, dd, *J*<sub>5,6</sub> 6.4 Hz, *J*<sub>6,6'</sub> 10.7 Hz, H-6), 3.65 (1H, dd, *J*<sub>5,6'</sub> 4.7 Hz, *J*<sub>6,6'</sub> 10.7 Hz, H-6'), 3.91 (1H, dd, *J*<sub>2,3</sub> 1.7 Hz, *J*<sub>1,2</sub> 4.3 Hz, H-2), 3.99 (1H, dd, *J*<sub>2,3</sub> 1.7 Hz, *J*<sub>3,4</sub> 4.0 Hz, H-3), 4.07 (1H, dd, *J*<sub>4,5</sub> 4.9 Hz, *J*<sub>3,4</sub> 4.0 Hz, H-4), 4.42 (1H, dd, *J*<sub>1,2</sub> 4.3 Hz, *J*<sub>1,1a</sub> 7.5 Hz, H-1), 4.45-4.52 (6H, m, 3 x PhCH<sub>2</sub>), 5.29 (1H, ddd, *J*<sub>1,1b</sub> 0.8 Hz, *J*<sub>1b,1b'</sub> 1.7 Hz, *J*<sub>1a,1b</sub> 10.3 Hz, H-1b), 5.33 (1H, m, H-5), 5.38 (1H, ddd, *J*<sub>1,1b</sub> 1.0 Hz, *J*<sub>1b,1b'</sub> 1.7 Hz, *J*<sub>1a,1b'</sub> 17.3 Hz, H-1b'), 6.05 (1H, ddd, *J*<sub>1,1a</sub> 7.5 Hz, *J*<sub>1a,1b</sub> 10.3 Hz, *J*<sub>1a,1b'</sub> 17.3 Hz, H-1a), 7.24-7.35 (15H, m, Ar-CH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta_C$  21.0 (q, CH<sub>3</sub>), 69.0 (t, C-6), 71.6 (t, PhCH<sub>2</sub>), 71.8 (d, C-5), 71.9, 73.0 (2 x t, 2 x PhCH<sub>2</sub>), 82.0 (d, C-4), 82.4 (d, C-1), 83.5 (d, C-3), 84.0 (d, C-2), 118.8 (t, C-1b), 127.5, 127.7, 127.7, 127.8, 128.3, 128.3, 128.4 (7 x d, Ar-CH), 133.4 (d, C-1a), 137.5, 137.7, 137.9 (3 x s, 3 x Ar-C), 170.6 (s, CH<sub>3</sub>CO). HRMS (ES<sup>+</sup>) *m/z*: Calcd. for C<sub>31</sub>H<sub>34</sub>O<sub>6</sub>Na (MNa<sup>+</sup>) 525.2248. Found 525.2230.



Compound **5** (55 mg, 0.119 mmol) was dissolved in a mixture of ethyl acetate/methanol/water 2:4:1 and Pd/C catalyst (10%, 12 mg) was added. The mixture was stirred at RT under hydrogen. After 12 h, TLC showed complete conversion of the starting material and of the intermediate products into a single product ( $R_f$  0.2, ethyl acetate/methanol, 10:1). The mixture was filtered through Celite and the solvent evaporated under reduced pressure to give the deprotected C-glycoside as a colourless oil (22 mg, 99%).  $[\alpha]_D^{25}$   $-18.4$  ( $c$ , 1 in  $\text{CH}_3\text{OH}$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ )  $\delta_{\text{H}}$  0.95 (3H, t,  $J$  7.4 Hz,  $\text{CH}_3$ -1b), 1.61 (2H, m,  $\text{CH}_2$ -1a), 3.59 (1H, dd,  $J_{5,6}$  6.3 Hz,  $J_{6,6'}$  11.4 Hz, H-6), 3.77 (1H, dd,  $J_{5,6'}$  3.4 Hz,  $J_{6,6'}$  11.4 Hz, H-6'), 3.86 (1H, ddd,  $J_{5,6'}$  3.4 Hz,  $J_{5,6}$  6.3 Hz,  $J_{4,5}$  8.2 Hz, H-5), 3.94 (1H, dd,  $J_{3,4}$  3.4 Hz,  $J_{4,5}$  8.2 Hz, H-4), 3.95 (1H, dd,  $J_{1,2}$  3.0 Hz,  $J_{2,3}$  1.1 Hz, H-2), 3.98 (1H, dd,  $J_{1,2}$  3.0 Hz,  $J_{1,1a}$  7.1 Hz, H-1), 4.20 (1H, dd,  $J_{3,4}$  3.4 Hz,  $J_{2,3}$  1.1 Hz, H-3).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{OD}$ )  $\delta_{\text{C}}$  10.9 (q, C-1b), 22.9 (t, C-1a), 65.7 (t, C-6), 71.6 (d, C-5), 78.1 (d, C-2), 78.6 (d, C-3), 80.9 (d, C-4), 83.9 (d, C-1), HRMS ( $\text{ES}^+$ )  $m/z$ : Calcd. for  $\text{C}_8\text{H}_{16}\text{O}_5\text{Na}$  ( $\text{MNa}^+$ ) 215.0890. Found 215.0881.

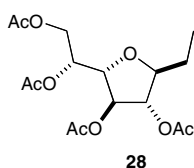
Deprotected THF (22 mg) was dissolved in acetic anhydride (0.3 mL) and pyridine (0.3 mL), and DMAP (2 mg) was added. After 3h, TLC showed complete conversion of the starting material into a single product. The reaction mixture was cooled to 0 °C and methanol (0.2 mL) was slowly added. The solvent was concentrated under reduced pressure, diluted with ethyl acetate (3 mL) and washed with 0.1 M HCl until acidic pH and with saturated aqueous solution of sodium bicarbonate (1.5 mL). The organic layer was concentrated under reduced pressure and the residue was purified by flash chromatography (pentane/ethyl acetate, 90:10) to give **27** (39 mg, 95%). Colourless oil:  $[\alpha]_D^{25}$   $+37.4$  ( $c$ , 1 in  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  0.93 (3H, t,  $J$  7.4 Hz,  $\text{CH}_3$ -1b), 1.54 (2H, m,  $\text{CH}_2$ -1a), 1.98, 2.06, 2.07, 2.12 (12H, 4 x s, 4 x  $\text{CH}_3\text{CO}$ ), 4.10 (1H, m, H-1) 4.13 (1H, dd,  $J_{5,6}$  5.5 Hz,  $J_{6,6'}$  12.1 Hz, H-6), 4.30 (1H, dd,  $J_{3,4}$  3.9 Hz,  $J_{4,5}$  9.6 Hz, H-4), 4.59 (1H, dd,  $J_{5,6'}$  2.5 Hz,  $J_{6,6'}$  12.1 Hz, H-6'), 5.16-5.17 (2H, m, H-2, H-5), 5.40 (1H, dd,  $J_{3,4}$  3.9 Hz,  $J_{2,3}$  1.2 Hz, H-3).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  10.3 (q, C-1b), 20.6, 20.7, 20.8, 21.8 (4 x q,  $\text{CH}_3\text{CO}$ , 1 x t, C-1a), 63.6 (t, C-6), 68.1 (d, C-5), 75.1 (d, C-3), 76.4 (d, C-4), 76.5 (d, C-2), 82.1 (d, C-1) 169.4, 169.5, 169.6, 169.7 (4 x s, 4 x C=O). HRMS ( $\text{ES}^+$ )  $m/z$ : Calcd. for  $\text{C}_{16}\text{H}_{24}\text{O}_9\text{Na}$  ( $\text{MNa}^+$ ) 383.1313. Found 383.1327.



Following the same procedure as for compound **27**, starting from compound **4** (100 mg, 0.22 mmol), the deprotected THF (42 mg, quant.) was obtained:

Colourless oil:  $[\alpha]_D^{25} -9.2$  (*c*, 1 in CH<sub>3</sub>OH); <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD)  $\delta_H$  0.97 (3H, t, *J* 7.4 Hz, CH<sub>3</sub>-1b), 1.65 (2H, m, CH<sub>2</sub>-1a), 3.51 (1H, m, H-1), 3.61 (1H, dd, *J*<sub>5,6</sub> 6.1 Hz, *J*<sub>6,6'</sub> 11.3 Hz, H-6), 3.76-3.82 (3H, m, H-2, H-4, H-6'), 3.90 (1H, ddd, *J* 3.3 Hz, *J*<sub>5,6'</sub> 6.1 Hz, *J* 7.9 Hz, H-5), 4.09 (1H, dd, *J* 1.3 Hz, *J* 3.7 Hz, H-3). <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>OD)  $\delta_C$  10.8 (q, C-1b), 27.8 (t, C-1a), 65.3 (t, C-6), 71.4 (d, C-5), 79.5 (d, C-3), 81.6 (d, C-2), 83.0 (d, C-4), 88.5 (d, C-1). HRMS (ES<sup>+</sup>) *m/z*: Calcd. for C<sub>8</sub>H<sub>16</sub>O<sub>5</sub>Na (MNa<sup>+</sup>) 215.0890. Found 215.0891.

Acetylation of the deprotected THF (20 mg), following an identical procedure to that described for compound **27**, gave peracetylated THF **26** (25 mg, 66%). Colourless oil:  $[\alpha]_D^{25} +10.7$  (*c*, 1 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_H$  0.97 (3H, t, *J* 7.4 Hz, CH<sub>3</sub>-1b), 1.69 (2H, m, CH<sub>2</sub>-1a), 2.00, 2.06, 2.07, 2.09 (12H, 4 x s, 4 x CH<sub>3</sub>CO), 3.77 (1H, m, H-1), 4.13 (1H, dd, *J*<sub>5,6</sub> 5.4 Hz, *J*<sub>6,6'</sub> 12.2 Hz, H-6), 4.17 (1H, dd, *J*<sub>3,4</sub> 3.6 Hz, *J*<sub>4,5</sub> 9.2 Hz, H-4), 4.58 (1H, dd, *J*<sub>5,6'</sub> 2.4 Hz, *J*<sub>6,6'</sub> 12.1 Hz, H-6'), 4.80 (1H, dd, *J*<sub>1,2</sub> 3.0 Hz, *J*<sub>2,3</sub> 0.8 Hz, H-2), 5.23 (1H, ddd, *J*<sub>5,6</sub> 5.3 Hz, *J*<sub>5,6'</sub> 2.4 Hz, *J*<sub>4,5</sub> 9.2 Hz, H-5), 5.33 (1H, dd, *J*<sub>3,4</sub> 3.6 Hz, *J*<sub>2,3</sub> 0.8 Hz, H-3). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta_C$  9.9 (q, C-1b), 20.7, 20.8, 20.8, 20.9 (4 x q, 4 x CH<sub>3</sub>CO), 26.3 (t, C-1a), 63.3 (t, C-6), 68.0 (d, C-5), 75.7 (d, C-3), 77.6 (d, C-4), 80.9 (d, C-2), 85.9 (d, C-1), 169.4, 169.5, 169.6, 169.7 (4 x s, 4 x C=O). HRMS (ES<sup>+</sup>) *m/z*: Calcd. for C<sub>16</sub>H<sub>24</sub>O<sub>9</sub>Na (MNa<sup>+</sup>) 383.1313. Found 383.1311.

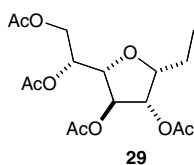


Compound **22** (55 mg, 0.119 mmol) was dissolved in a mixture of ethyl acetate/methanol/water 2:4:1 and Pd/C (10%, 10 mg) was added. The mixture was stirred at RT under hydrogen. After 12 h, TLC showed complete conversion of the starting material and of the intermediate products into a single product. The mixture was filtered through Celite and the solvent evaporated under reduced pressure to give the deprotected C-glycoside, which was directly dissolved in a mixture of acetic anhydride (0.5 mL) and pyridine (0.5 mL) in the presence of DMAP (2 mg). After 3h, TLC showed complete conversion of the starting material into a single product. The reaction mixture was cooled

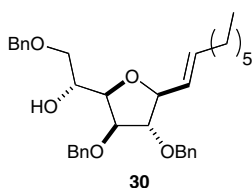
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to 0 °C and methanol (0.2 mL) was slowly added. The solvent was concentrated under reduced pressure, diluted with ethyl acetate (3 mL) and washed with 0.1 M HCl until acidic pH and with saturated aqueous solution of sodium bicarbonate (1.5 mL). The organic layer was concentrated under reduced pressure and the residue was purified by flash chromatography (pentane/ethyl acetate, 9:1) to give compound **28** (39 mg, 95%). Colourless oil:  $[\alpha]_D^{25} -9.6$  (*c*, 0.5 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_H$  0.96 (3H, t, *J* 7.4 Hz, CH<sub>3</sub>-1b), 1.69 (2H, m, CH<sub>2</sub>-1a), 2.05, 2.08, 2.09, 2.14 (12H, 4 x s, 4 x CH<sub>3</sub>CO), 3.96 (1H, m, H-1), 4.08 (1H, dd, *J*<sub>3,4</sub> 4.1 Hz, *J*<sub>4,5</sub> 5.2 Hz, H-4), 4.19 (1H, dd, *J*<sub>5,6</sub> 6.9 Hz, *J*<sub>6,6'</sub> 11.9 Hz, H-6), 4.36 (1H, dd, *J*<sub>5,6'</sub> 4.1 Hz, *J*<sub>6,6'</sub> 11.9 Hz, H-6'), 5.02 (1H, dd, *J*<sub>1,2</sub> 4.5 Hz, *J*<sub>2,3</sub> 2.7 Hz, H-2), 5.12 (1H, dd, *J*<sub>3,4</sub> 4.1 Hz, *J*<sub>2,3</sub> 2.7 Hz, H-3), 5.35 (1H, ddd, *J*<sub>5,6</sub> 6.9 Hz, *J*<sub>5,6'</sub> 4.1 Hz, *J*<sub>4,5</sub> 5.2 Hz, H-5). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta_C$  9.6 (q, C-1b), 20.7, 20.7, 20.8, 20.9 (4 x q, 4 x CH<sub>3</sub>CO), 25.5 (t, C-1a), 62.7 (t, C-6), 69.9 (d, C-5), 78.6 (d, C-3), 80.5 (d, C-4), 80.6 (d, C-2), 84.1 (d, C-1), 169.9, 170.0, 170.1, 170.5 (4 x s, 4 x C=O). HRMS (ES<sup>+</sup>) *m/z*: Calcd. for C<sub>16</sub>H<sub>24</sub>O<sub>9</sub>Na (MNa<sup>+</sup>) 383.1313. Found 383.1309.



Following the same procedure as for compound **28**, starting from compound **25** (49 mg), peracetylated THF **29** (29 mg, 88%) was obtained. Colourless oil:  $[\alpha]_D^{25} +8.6$  (*c*, 0.5 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_H$  0.95 (3H, t, *J* 7.4 Hz, CH<sub>3</sub>-1b), 1.59 (2H, m, CH<sub>2</sub>-1a), 2.06, 2.09, 2.13, 2.14 (12H, 4 x s, 4 x CH<sub>3</sub>CO), 3.91 (1H, m, H-1), 3.93 (1H, dd, *J*<sub>3,4</sub> 4.0 Hz, *J*<sub>4,5</sub> 5.2 Hz, H-4), 4.17 (1H, dd, *J*<sub>5,6</sub> 7.3 Hz, *J*<sub>6,6'</sub> 11.9 Hz, H-6), 4.40 (1H, dd, *J*<sub>5,6'</sub> 3.8 Hz, *J*<sub>6,6'</sub> 11.9 Hz, H-6'), 5.03 (1H, dd, *J*<sub>2,3</sub> 1.2 Hz, *J*<sub>3,4</sub> 4.0 Hz, H-3), 5.22 (1H, dd, *J*<sub>1,2</sub> 3.8 Hz, *J*<sub>2,3</sub> 1.2 Hz, H-2), 5.35 (1H, ddd, *J*<sub>5,6</sub> 7.3 Hz, *J*<sub>5,6'</sub> 3.8 Hz, *J*<sub>4,5</sub> 5.2 Hz, H-5). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta_C$  10.3 (q, C-1b), 20.7, 20.7, 20.7, 20.8 (4 x q, CH<sub>3</sub>CO), 21.5 (t, C-1a), 62.8 (t, C-6), 69.9 (d, C-5), 76.9 (d, C-2), 78.3 (d, C-3), 81.2 (d, C-4), 82.1 (d, C-1), 169.5, 169.7, 170.1, 170.6 (4 x s, 4 x C=O). HRMS (ES<sup>+</sup>) *m/z*: Calcd. for C<sub>16</sub>H<sub>24</sub>O<sub>9</sub>Na (MNa<sup>+</sup>) 383.1313. Found 383.1303.



Supplementary Material (ESI) for Chemical Communications

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Tetrahydrofuran **4** (100 mg, 0.21 mmol) was dissolved in dichloromethane (3 mL), and Grubbs II generation catalyst (5 mg, 0.006 mmol) and then 1-Octene (200  $\mu$ L, 1.27 mmol) were added. The mixture was stirred under reflux for 8 h, after which time TLC (pentane/ethyl acetate 4:1) showed complete conversion of the starting material ( $R_f$  0.2) into a single product ( $R_f$  0.3). Evaporation of the solvent and purification of the residue by flash column chromatography (pentane/ethyl acetate 80:20) gave compound **30** (102 mg, 89%). Colourless oil:  $[\alpha]_D^{25}$   $-12.4$  ( $c$ , 2 in  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  0.88 (3H, t,  $J$  6.6 Hz,  $\text{CH}_3$ -1h), 1.26, 1.36 (8H, m,  $\text{CH}_2$ -1d-g), 2.02 (2H, m,  $\text{CH}_2$ -1c), 2.65 (1H, br s, OH-5), 3.61 (1H, dd,  $J_{5,6}$  6.1 Hz,  $J_{6,6'}$  9.8 Hz, H-6), 3.75 (1H, dd,  $J_{5,6'}$  3.2 Hz,  $J_{6,6'}$  9.8 Hz, H-6'), 3.79 (1H, dd,  $J_{2,3}$  1.2 Hz,  $J_{1,2}$  3.5 Hz, H-2), 3.95 (1H, dd,  $J_{3,4}$  3.9 Hz,  $J_{4,5}$  8.0 Hz, H-4), 4.12 (1H, dd,  $J_{2,3}$  1.2 Hz,  $J_{3,4}$  3.9 Hz, H-3), 4.19 (1H, ddd,  $J_{5,6'}$  3.2 Hz,  $J_{5,6}$  6.1 Hz,  $J_{4,5}$  8.0 Hz, H-5), 4.23 (1H, dd,  $J_{1,2}$  3.5 Hz,  $J_{1,1a}$  8.2 Hz, H-1), 4.47-4.60 (6H, m, 3 x  $\text{PhCH}_2$ ), 5.54 (1H, ddt,  $J_{1a,1c}$  1.3 Hz,  $J_{1a,1b}$  15.3 Hz,  $J_{1a,1b}$  8.2 Hz, H-1a), 5.75 (1H, dt,  $J_{1b,1c}$  6.5 Hz,  $J_{1a,1b}$  15.3 Hz, H-1b), 7.24-7.37 (15H, m, Ar-CH).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  14.1 (q, C-1h), 22.6, 28.9, 28.9, 31.6 (4 x d, C-1d, C-1e, C-1f, C-1g), 32.2 (C-1c), 68.7 (d, C-5), 71.7, 71.7, 72.1, 73.4 (4 x t,  $\text{PhCH}_2$ , C-6), 80.4 (d, C-4), 83.3 (d, C-3), 85.4 (d, C-1), 87.4 (d, C-2), 127.6, 127.6, 127.8, 127.8, 127.8, 128.3, 128.4, 128.4, 128.6 (9 x d, Ar-CH, C-1a), 134.6 (d, C-1b), 137.6, 137.7, 138.1 (3 x s, 3 x Ar-C). HRMS ( $\text{ES}^+$ )  $m/z$ : Calcd. for  $\text{C}_{35}\text{H}_{44}\text{O}_5\text{Na}$  ( $\text{MNa}^+$ ) 567.3081. Found 567.3084.