

SUPPORTING INFORMATION

Supplementary Information:

THP ether 2h: ^1H NMR: δ 1.5-2.0 (m, 11H, 4xCH₂, -CH₃), 3.48-3.52 (m, 1H, -OCH₂-), 3.61-3.62 (m, 1H, -OCH₂), 3.85-3.91 (m, 6H, 3 x -OCH₂-), 4.67 (dd, J = 2.9, 5.8 Hz, 1H, methine). ^{13}C NMR δ 19.26, 19.35, 25.0, 25.39, 30.48, 61.88, 62.01, 66.29, 66.55, 98.54, 98.8. MS m/z (relative intensity) 215 (2) [$\text{M}^+ - 1$], 133 (5) [$\text{M}^+ - 85$], 101 (20) [$\text{M}^+ - 115$], 85 (55) [$\text{M}^+ - 131$]. Analysis Calcd. for C₁₁ H₂₀ O₄: C, 61.08; H, 9.32. Found: C, 61.28; H, 9.23

THP ether 2i: ^1H NMR: δ 0.94 (2 d, J = 6.9 Hz, 6H, 2x-CH₃), 1.54-1.96 (m, 7H, 3x-CH₂, -CHMe₂), 3.49-3.52 (m, 1H, -OCH₂-), 3.75 (s, 3H, -OCH₃), 3.9-3.95 (m, 1H, -OCH₂-), 4.42 (d, J = 4.87 Hz, 1H, -OCH-O-), 4.49 (br s, 1H, -CH-O-), 5.73, 6.34 (2 s, 2H, olefinic). ^{13}C NMR δ 17.34, 19.27, 19.42, 25.47, 30.69, 32.48, 51.7, 62.18, 95.1, 95.42, 126.26, 140.31, 166.99. MS m/z (relative intensity): 243 (2) [$\text{M}^+ + 1$], 141 (10) [$\text{M}^+ - 101$]. Analysis Calcd for C₁₃H₂₂O₄: C, 64.44; H, 9.15. Found: C, 64.51; H, 9.22.

THP ether 2j: ^1H NMR δ 1.45-1.86 (m, 14H, 7 x -CH₂-), 3.47- 4.42 (m, 7H, 3 x -OCH₂-, -CH-O-), 4.85 (t, J = 3.5 Hz, 1H, -O-CH-O-). ^{13}C NMR δ 19.5, 23.1, 25.38, 27.47, 30.5, 31.0, 34.03, 61.0, 62.7, 65.27, 94.43, 100.0, 109.7. MS m/z (relative intensity): 242 (2) [M^+], 157 (100) [$\text{M}^+ - 85$], 101 (30) [$\text{M}^+ - 141$], 85 (95) [$\text{M}^+ - 157$]. Analysis Calcd for C₁₃H₂₂O₄: C, 64.44; H, 9.15. Found: C, 64.56; H, 9.30.

THP ether 2k: ^1H NMR δ 1.5-2.46 (m, 8H, 4x-CH₂-), 2.39-2.70 (m, 2H, epoxy -CH₂-), 2.74-2.82 (m, 1H, epoxy -CH-), 3.49-4.03 (m, 2H, -OCH₂-), 4.43 (t, 1H, J = 3.3 Hz, -OCH-O-), 4.78-4.97 (m, 1H, PhCH-), 7.24-7.42 (m, 5H, aromatic). ^{13}C NMR δ 19.6, 25.39, 30.84, 40.80, 46.83, 49.68, 62.2, 94.7, 95.80, 126.0, -142.89 (6C). MS m/z (relative intensity): 249 (2) [$\text{M}^+ + 1$], 171 (35) [$\text{M}^+ - 77$], 163 (35)

[M⁺-85], 17 (92) [M⁺-101], 101 (100) [M⁺-147]. Analysis Calcd for C₁₅H₂₀O₃: C, 72.55; H, 8.12.

Found: C, 72.62; H, 8.10.

THP ether 2l: ¹H NMR δ 0.88-1.08 (2H, cyclopropyl -CH₂-), 1.4-1.9 (m, 6H, 3 x -CH₂-), 2.08-2.17 (m, 1H, cyclopropyl -CH-), 3.40-4.10 (m, 2H, -OCH₂-), 4.3-4.43 (m, 1H, cyclopropyl PhCH-), 4.46 (t, J = 2.98 Hz, 1H, -O-CH-O-), 5.12 (d, 1H, J = 6 Hz, PhCH-O-), 7.05-7.46 (m, 10H, aromatic). ¹³C NMR δ 11.98, 19.4, 22.2, 30.6, 38.0, 61.95, 79.58, 95.05, 95.80, 123.04-142.78 (12C). MS m/z (relative intensity) 207 (15) [M⁺-101], 191 (30) [M⁺-117], 117 (15) [M⁺-189]. Analysis Calcd for C₂₁H₂₄O₂: C, 81.78; H, 7.84. Found: C, 81.51; H, 7.92.

THP ether 2n: ¹H NMR δ 1.48-1.73 (m, 6H, 3 x -CH₂-), 2.06 (s, 3H, -OCOCH₃), 3.25-4.31 (m, 4H, 2 x -OCH₂-), 4.51 (t, J = 4.3 Hz, 1H, -O-CH-O-), 4.95 (dd, J = 4.63, 8.42 Hz, 1H, PhCH-O-), 7.26-7.42 (5H, aromatic). ¹³C NMR δ 18.89, 20.89, 25.35, 30.36, 61.64, 67.68, 95.05, 98.46, 126.7-139.3 (6C), 170.74. MS m/z (relative intensity) 163 (4) [M⁺-101], 120(90) [M⁺-144]. Analysis Calcd for C₁₅H₂₀O₄: C, 68.16; H, 7.63. Found: C, 68.12; H, 7.52

THP ether 2p: ¹H NMR δ 1.51-1.86 (m, 10H, 5 x -CH₂-), 2.20-2.6 (m, 4H, allylic methylenes), 3.51-4.28 (m, 4H, 2 x -OCH₂-), 4.62 (t, J = 3.11 Hz, 1H, -O-CH-O-). ¹³C NMR δ 19.36, 22.18, 24.6, 25.36, 28.9, 30.49, 36.67, 62.1, 70.21, 98.09, 121.56, 133.11. MS m/z (relative intensity) 275(2) [M⁺+1], 195(35) [M⁺-101], 101 (30) [M⁺-174], 85(75)[M⁺-190]. Analysis Calcd for C₁₂H₁₉O₂Br: C, 52.38; H, 6.96. Found: C, 52.40; H, 6.81.

THP ether 2q: ¹H NMR δ 1.5-1.75 (m, 6H, 3 x -CH₂-), 3.49-3.87 (m, 4H, H-6, H-6'), 4.04 (t, J = 10.95 Hz, 1H, -OCH-O-), 4.45-4.96 (m, 11H, 4 x -OCH₂Ph, H-2, H-3, H-4), 4.6 (t, J = 10.95 Hz, 1H, H-5), 5.31 (d, 1H, J = 4.38 Hz, H-1), 7.12-7.35 (m, 20H, aromatic). ¹³C NMR δ 18.25, 25.34, 30.63, 61.87,

68.48, 70.58, 72.53, 73.16, 74.93, 75.5, 77.86, 79.59, 81.74, 93.52, 94.25, 127.44-138.9 (24C). MS m/z (relative intensity) 625(2) [$M^+ + 1$], 523(5) [$M^+ - 101$]. Analysis Calcd for $C_{39}H_{44}O_7$: C, 74.98; H, 7.10. Found: C, 74.92; H, 7.09.

Benzyl 2-deoxy-3,4,6-tri-O-benzyl- α/β -D-galactopyranoside 5d:

1H NMR: δ 2.03-2.06 and 2.21-2.25 (m, 2H, H-2, H-2'), 3.54-3.66 (m, 2H, H-6, H-6'), 3.91-4.01 (m, 3H, H-3, H-4, H-5), 4.41-4.95 (m, 8H, 4 x $PhCH_2$ -), 5.07 (brd, $J = 3.5$ Hz, H-1), 7.24-7.35 (m, 20H, aromatic). ^{13}C NMR: δ 31.10, 68.86, 69.52, 70.02, 70.45, 72.91, 73.44, 74.25, 74.81, 97.06 (C-1), 127.3-138.8 (24 C). Characteristic signals for the β -anomer: 1H NMR: δ 4.53 (brd, $J = 9.5$ Hz, H-1). ^{13}C NMR: δ 93.18 (C-1). MS (FAB) m/z (relative intensity) 524 (20) [M^+], 417 (10) [$M^+ - 107$]. Analysis Calcd. for $C_{34}H_{36}O_5$: C, 77.84, H, 6.92. Found. C, 77.92, H, 6.90.

Cyclohexyl 2-deoxy-3,4,6-tri-O-benzyl- α/β -D-galactopyranoside 5f:

1H NMR: δ 1.2-1.92 (m, 10H, cyclohexyl), 2.0-2.08 and 2.27-2.33 (m, 2H, H-2, H-2'), 3.6-3.7 (m, 3H, H-6, H-6', cyclohexyl methine), 3.98-4.18 (m, 2H, H-3, H-4), 4.08 (t, $J = 6.59$ Hz, 1H, H-5), 4.45-5.03 (m, 6H, 3 x $PhCH_2$ -), 5.2 (brd, $J = 3.3$ Hz, H-1), 7.28-7.39 (m, 15 H, aromatic). ^{13}C NMR: δ 23.95, 24.2, 25.60, 31.51, 31.62, 33.36, 69.39, 69.73, 70.31, 73.1, 73.25, 74.14, 74.33, 74.93, 95.47 (C-1), 127.3-138.88 (18 C). Characteristic signals for the β -anomer: 1H NMR: δ 4.55 (dd, $J = 3.3, 10$ Hz, H-1). ^{13}C NMR: δ 98.08 (C-1). MS (FAB) m/z (relative intensity) 516 (100) [M^+], 417 (10) [$M^+ - 99$]. Analysis Calcd. for $C_{33}H_{40}O_5$: C, 76.71, H, 7.80. Found. C, 76.83, H, 7.92

t-Butyl 2-deoxy-3,4,6-tri-O-benzyl- α/β -D-galactopyranoside 5g:

1H NMR: δ 1.21, (s, 9H, t-Bu-), 2.0-2.25 (m, 2H, H-2, H-2'), 3.50-3.66 (m, 2H, H-6, H-6'), 3.94-4.01 (m, 2H, H-3, H-5), 4.07 (t, $J = 6.52$ Hz, 1H, H-4), 4.39-4.94 (m, 6H, 3 x $PhCH_2$ -), 5.08 (d, 1H, $J = 3$

Hz, H-1), 7.22-7.35 (m, 15H, aromatic). ^{13}C NMR: δ 28.57, 28.62, 28.65, 32.74, 68.87, 69.5, 70.45, 71.0, 71.42, 73.42, 74.21, 75.06, 92.31(C-1), 127.2-128.45 (18 C). Characteristic signals for the β -anomer: ^1H NMR: δ 1.24 (t-Bu), 4.53 (dd, $J = 2.2, 9.03$ Hz, H-1). ^{13}C NMR: δ 94.85(C-1). MS (FAB) m/z (relative intensity) 490 (100) [M^+], 417 (10) [$\text{M}^+ - 73$]. Analysis Calcd. for $\text{C}_{31}\text{H}_{38}\text{O}_5$: C, 75.88, H, 7.81. Found. C, 75.95, H, 7.60

Allyl 2-deoxy-3,4,6-tri-O-benzyl- α/β -D-glucopyranoside 5b:

^1H NMR: δ 1.61-1.76 and 2.28-2.37 (m, 2H, H-2, H-2'), 3.51 (t, $J = 8.8$ Hz, 1H, H-5), 3.59-4.15 (m, 6H, $-\text{OCH}_2\text{CH}=\text{CH}_2$, H-3, H-4, H-6, H-6'), 4.35-4.90 (m, 6H, 3 x PhCH_2 -), 4.5 (d, $J = 2.83$ Hz, H-1), 5.13-5.29 (m, 2H, $-\text{CH}=\text{CH}_2$), 5.83-5.95 (m, 1H, $-\text{CH}=\text{CH}_2$), 7.16-7.35 (m, 15H, aromatic). ^{13}C NMR: δ 35.36, 67.64, 69.29, 71.35, 73.40, 74.9, 77.6, 78.19, 79.38, 96.6 (C-1), 116.99, 127.48-138.65 (18 C), 134.0. Characteristic signals for the β -anomer: ^1H NMR: δ 4.38 (dd, $J = 5.3, 11.9$ Hz, H-1). ^{13}C NMR: δ 98.84 (C-1). MS (FAB) m/z (relative intensity): 475 (30) [$\text{M}^+ + 1$], 474 (100) [M^+], 417 (11) [$\text{M}^+ - 57$]. Analysis Calcd for $\text{C}_{30}\text{H}_{34}\text{O}_5$: C, 75.92; H, 7.22. Found: C, 75.69; H, 7.48.

Cyclohexyl 4,6-di-O-benzyl-2,3-dideoxy- α -D-erythro-hex-2-enopyranoside 7c:

IR(CH_2Cl_2): 1605 cm^{-1} . ^1H NMR: δ 1.14-1.94 (m, 10H, cyclohexyl), 3.62-3.79 (m, 3H, cyclohexyl methine, H-6, H-6'), 4.0-4.04 (m, 1H, H-5), 4.17 (dd, $J = 2.17, 9.52$ Hz, 1H, H-4), 4.48, 4.64 (2q, $J = 12.24$ Hz, 4H, 2 x PhCH_2 -), 5.16 (brd, $J = 2.22$ Hz, 1H, H-1), 5.75, 6.04 (2 brd, $J = 11.1$ Hz, 2H, H-2, H-3), 7.23-7.35 (m, 10H, aromatic). ^{13}C NMR δ 24.41, 25.63, 29.69, 32.12, 33.83, 68.88, 68.99, 70.45, 70.93, 73.29, 76.69, 92.77, 127.3-128.3 (12 C), 130.2, 138.3. MS (FAB) m/z (relative intensity) 427 (15) [$\text{M}^+ + 1$], 426 (55) [M^+], 309 (20) [$\text{M}^+ - 99$]. Analysis Calcd for $\text{C}_{26}\text{H}_{32}\text{O}_4$: C, 76.44; H, 7.89. Found: C, 76.49; H, 7.89.