

SUPPLEMENTARY MATERIAL

Experimental procedures for compounds **6**, **7**, **8** and **10**.

General methods: Organic solutions were dried over MgSO_4 before concentration, which was performed under reduced pressure at <40 °C (bath temperature). NMR spectra were recorded at 25 °C and 300 or 400 MHz (^1H) or 75 or 100 MHz (^{13}C) in CDCl_3 with Me_4Si as the internal standard ($\delta = 0$), unless otherwise stated. TLC was performed on silica gel 60 F₂₅₄ with detection by UV light and charring with 8% sulfuric acid. Silica gel (0.040-0.063 mm) was used for column chromatography.

Methyl (2,3,4-tri-*O*-benzyl- α -L-rhamnopyranosyl)-(1 \rightarrow 4)-(2,3-di-*O*-benzoyl-6-*O*-benzyl- β -D-glucopyranosyl)-(1 \rightarrow 3)-2-*O*-benzyl-4,6-*O*-benzylidene- α -D-glucopyranoside (6). A solution of ethyl 2,3,4-tri-*O*-benzyl-1-thio- α -L-rhamnopyranoside (**1**, 20 mg, 42 μmol) and phenyl 2,3-di-*O*-benzoyl-6-*O*-benzyl-1-thio- β -D-glucopyranoside (**2**, 24 mg, 42 μmol) in dry Et_2O (1 mL) was stirred with powdered molecular sieves (4 \AA) under argon for 30 min. NIS (12.5 mg, 56 μmol) was then added and stirring was continued for a further 30 min, when after addition of a catalytic amount of AgOTf (approx. 1 mg) the colour of the reaction mixture turned deep yellow brown. TLC (toluene/EtOAc 6:1) showed complete conversion into the disaccharide after 45 min. Subsequently methyl 2-*O*-benzyl-4,6-*O*-benzylidene- α -D-glucopyranoside (**3**, 16 mg, 43 μmol) and NIS (12 mg) dissolved in CH_2Cl_2 (3 mL) containing molecular sieves were added. The mixture was stirred for 15 min, when a catalytic amount of AgOTf was added. As soon as the reaction was complete (15 min) the mixture was quenched by addition of Et_3N (50 μl) and stirred for an additional 20 min, whereafter the mixture was diluted, filtered and concentrated. The residue was subjected to silica gel column chromatography (toluene \rightarrow toluene/EtOAc 50:1) to yield **6** (42 mg, 34 μmol , 81 %): $[\alpha]_D +0.5$ (*c* 1.0, CH_2Cl_2); ^{13}C -NMR (CDCl_3): δ 17.7 (Me-Rha), 55.4 (MeO), 62.3, 68.0, 69.0, 69.2, 72.5, 72.6, 73.1, 73.8, 74.1, 74.8, 75.5, 75.6, 79.4, 80.0, 80.2, 80.4 ($\text{C}^{\text{A}2}\text{-C}^{\text{A}6}$, $\text{C}^{\text{B}2}\text{-C}^{\text{B}6}$, $\text{C}^{\text{C}2}\text{-C}^{\text{C}5}$, CH_2Bn), 98.9 ($\text{C}^{\text{A}1}$), 99.4 ($\text{C}^{\text{C}1}$), 100.7 (Bn-acetal), 101.7 ($\text{C}^{\text{B}1}$), 126.2-129.9 (aromatic C), 132.9, 133.0 (aromatic $\text{C}_q\text{-Bz}$), 137.4, 138.1, 138.3, 138.7, 138.9 (aromatic $\text{C}_q\text{-Bn}$), 165.4, 166.0 (PhCO) ppm. $\text{C}_{75}\text{H}_{76}\text{O}_{17}$ (1248.51); MALDI-TOF MS: $m/z = 1271.51$ $[\text{M}+\text{Na}]^+$, $m/z = 1287.49$ $[\text{M}+\text{K}]^+$.

Cetyl (2,3,4-tri-*O*-benzyl- α -L-rhamnopyranosyl)-(1 \rightarrow 4)-(2,3-di-*O*-benzoyl-6-*O*-benzyl- β -D-glucopyranoside (7). As described above **1** (20 mg, 42 μmol) and **2** (24 mg, 42

μmol) in dry Et_2O (1 mL) were coupled by promotion of NIS (12.5 mg, 56 μmol) together with a catalytic amount of AgOTf (approx. 1 mg). The TLC (toluene/EtOAc 6:1) showed complete conversion into the disaccharide after 45 min. Then cetyl alcohol (**4**, 11 mg, 45 μmol) and NIS (12 mg) dissolved in CH_2Cl_2 (3 mL) and an additional amount of molecular sieves were added, and the mixture was stirred for 15 min, whereafter a catalytic amount of AgOTf was added. As soon as the reaction was complete (15 min) the mixture was quenched by addition of Et_3N (50 μl) and stirred an additional 20 min. The mixture was diluted, filtered and concentrated and the residue subjected to silica gel column chromatography (toluene \rightarrow toluene/EtOAc 50:1) to obtain **7** (36 mg, 32 μmol , 76 %) as an anomeric mixture (9:1 β/α): $[\alpha]_D$ -4.5 (*c* 1.0, CH_2Cl_2); ^{13}C -NMR (CDCl_3): δ 14.3 (*Me*-Cet), 17.6 (*Me*-Rha), 22.8, 26.0, 29.4, 29.5, 29.6, 29.7, 29.8, 32.1 (CH_2 -Cet), 68.6, 69.2, 70.1, 72.5, 72.6, 72.7, 73.8, 73.9, 74.8, 75.5, 75.7, 79.5, 80.5, ($\text{C}^{\text{A}}2\text{-C}^{\text{A}}6$, $\text{C}^{\text{B}}2\text{-C}^{\text{B}}6$, OCH_2 -Cet, CH_2Bn), 99.6 ($\text{C}^{\text{B}}1$), 101.2 ($\text{C}^{\text{A}}1$), 127.5-130.0 (aromatic C), 133.1, 133.3 (aromatic C_q -Bz), 138.2, 138.5, 138.8, 138.9, (aromatic C_q -Bn), 165.4, 166.1 (PhCO) ppm. Anal. Calcd. for $\text{C}_{70}\text{H}_{86}\text{O}_{12}$ (1118.61): C, 75.11; H, 7.74; Found: C, 75.07; H, 7.73); MALDI-TOF MS: *m/z* = 1141.63 [$\text{M}+\text{Na}$] $^+$, *m/z* = 1157.59 [$\text{M}+\text{K}$] $^+$.

Methyl (2,3,4-tri-*O*-benzyl- α -L-rhamnopyranosyl)-(1 \rightarrow 4)-(2,3-di-*O*-benzoyl-6-*O*-benzyl- β -D-glucopyranosyl)-(1 \rightarrow 6)- 2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (8). Analogously to the above described experiment **1** (20 mg, 42 μmol) and **2** (24 mg, 42 μmol) in dry Et_2O (1 mL) were coupled by promotion of NIS (12.5 mg, 56 μmol) and a catalytic amount of AgOTf (approx. 1 mg). The TLC (toluene/EtOAc 6:1) showed complete conversion into the disaccharide after 45 min. Methyl 2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (**5**, 20 mg, 43 μmol) and NIS (12 mg) in CH_2Cl_2 (3 mL) containing molecular sieves were added. The mixture was stirred for 15 min, before a catalytic amount of AgOTf was added. As soon as the reaction was complete (15 min) the mixture was quenched by addition of Et_3N (50 μl) and stirred for a further 20 min. The mixture was diluted, filtered and concentrated and the residue subjected to silica gel column chromatography (toluene \rightarrow toluene/EtOAc 50:1) to give **8** (43 mg, 32 μmol , 76 %): $[\alpha]_D$ +15.2 (*c* 1.0, CH_2Cl_2); ^{13}C -NMR (CDCl_3): δ 17.7 (*Me*-Rha), 55.1 (MeO), 68.3, 68.5, 69.2, 69.7, 72.4, 72.6, 72.8, 73.5, 73.8, 74.8, 75.7, 75.8, 79.4, 79.9, 80.5, 82.0 ($\text{C}^{\text{A}}2\text{-C}^{\text{A}}6$, $\text{C}^{\text{B}}2\text{-C}^{\text{B}}6$, $\text{C}^{\text{C}}2\text{-C}^{\text{C}}5$, CH_2Bn), 98.0 ($\text{C}^{\text{A}}1$), 99.6 ($\text{C}^{\text{C}}1$), 101.3 ($\text{C}^{\text{B}}1$), 127.4-129.9 (aromatic C), 133.0 (aromatic C_q -Bz), 138.1, 138.2, 138.3, 138.6, 138.8 (aromatic C_q -Bn), 165.1, 165.8 (PhCO) ppm. Anal. Calcd. for

$C_{82}H_{84}O_{17}$ (1340.57): C, 73.41; H, 6.31; Found: C, 73.25; H, 6.44; MALDI-TOF MS: m/z = 1363.65 [M+Na]⁺, m/z = 1379.62 [M+K]⁺.

Methyl (2,3,4-tri-*O*-benzyl- α -L-rhamnopyranosyl)-(1 \rightarrow 6)-(2,3,4-tri-*O*-benzyl- α -D-mannopyranosyl)-(1 \rightarrow 3)-2-*O*-benzyl-4,6-*O*-benzylidene- α -D-glucopyranoside (10). A solution of **1** (80 mg, 167 μ mol) and phenyl 2,3,4-tri-*O*-benzyl-1-thio- α -D-mannopyranoside (**9**, 90 mg, 165 μ mol) in dry Et₂O (1 mL) was stirred with powdered molecular sieves (4 \AA) under argon for 30 min. NIS (50 mg, 222 μ mol) was then added and stirring continued for another 30 min. After addition of a catalytic amount of AgOTf (approx. 5 mg), the mixture was stirred until all acceptor was consumed (toluene/EtOAc 6:1, approx 60 min). Then **3** (65 mg, 173 μ mol) dissolved in dry CH₂Cl₂ (15 mL) together with NIS (12 mg) and an additional amount of molecular sieves was added. The mixture was stirred for 30 min, whereafter a catalytic amount of AgOTf (5 mg) was added. As soon as the reaction was complete (30 min) the mixture was quenched by addition of Et₃N (100 μ L) and stirred for a further 20 min. The mixture was diluted, filtered and concentrated. The residue was subjected to silica gel column chromatography (toluene \rightarrow toluene/EtOAc 50:1, toluene containing 0.5 % vol Et₃N) to give **10** (169 mg, 138 μ mol, 84 %): $[\alpha]_D$ +15 (*c* 1.0, CH₂Cl₂); ¹³C-NMR (CDCl₃): δ 18.2 (Me-Rha), 55.5 (MeO), 61.9, 66.7, 68.1, 69.3, 71.6, 71.7, 72.6, 72.8, 73.6, 74.2, 74.4, 74.7, 75.1, 75.5, 75.6, 78.0, 79.6, 80.4, 80.9, 82.8 (C^A2-C^A6, C^B2-C^B6, C^C2-C^C5, CH₂Bn), 97.8, 98.5, 98.9, 102.0 (C^A1, C^B1, C^C1, O₂Ph), 126.3-129.5 (aromatic C), 137.3, 137.8, 138.4, 138.6, 138.8, 138.9, 139.1 (aromatic C_q-Bn) ppm. C₇₅H₈₀O₁₅ (1220.55); MALDI-TOF MS: m/z = 1243.41 [M+Na]⁺, m/z = 1259.36 [M+K]⁺.