Synthesis of a tetrasaccharide repeating unit of $O$-antigenic polysaccharide of *Salmonella enteritidis* by use of unique and odorless dodecyl thioglycosyl donors

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**Supplementary Information**

**General Procedures:** All chemicals were purchased as reagent grade and used without further purification whereas N-iodosuccinimide (NIS) was recrystallized by 1,4-dioxane and diethyl ether (1:1, v/v) before use. Dichloromethane (CH$_2$Cl$_2$) and 1,2-dichloroethane were distilled over calcium hydride (CaH$_2$). Molecular sieves (MS) used for glycosylation were 4Å, which were activated at 200°C under reduced pressure prior to use. Reactions were monitored by thin-layer chromatography (TLC) on a pre-coated plate of silica gel 60F$_{254}$ (layer thickness, 0.25 mm; E. Merck, Germany). Spots were detected under UV (254 nm) and/or by spraying with p-methoxybenzaldehyde–H$_2$SO$_4$–MeOH (1:2:17, v/v/v) and heated for a few minutes. Silica gel 60 with 0.043–0.2 mm (E. Merck, Germany) was used for open column chromatography. Size exclusion column chromatography was performed on Sephadex G-15 (Pharmacia Biotech AB, Uppsala, Sweden) and deionized water as the eluent. $^1$H and $^{13}$C NMR spectra were recorded with a Bruker ASX 300 (300 and 75.1 MHz, respectively) and JEOL ECA 600 (600 and 125 MHz). Chemical shifts (in ppm) were referenced to tetramethylsilane (δ = 0 ppm) in deuterated chloroform (CDCl$_3$). Coupling constant are given in Hertz. $^{13}$C NMR spectra were obtained by using the same NMR spectrometers and were calibrated with CDCl$_3$ (δ = 77.00 ppm). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; brd, broad doublet for $^1$H NMR data. ESI-HR mass spectra were measured on a JEOL JMS-T100LCP and FAB-HR mass was carried out using a JEOL JMS-HX100.
Dodecyl 2,3-O-di-benzoyl-4,6-O-benzylidene-1-thio-α-d-mannopyranoside (4). To a solution of dodecyl 2,3,4,6-tetra-O-acetyl-1-thio-α-d-mannopyranoside 9 (5.0 g, 9.4 mmol) in MeOH (25 mL) was added a 25% solution NaOMe in MeOH (0.5 mL, w/v) at room temperature. After 3 h, the reaction was neutralized with acidic resin and filtered. The filtrate was concentrated to give the deacetylated product. Catalytic amount of camphorsulfonic acid (0.2 g, 0.94 mmol) was added to a solution of the resulting product and benzaldehyde dimethylacetate (2.1 mL, 14.1 mmol) in DMF (20 mL). The solution was stirred for 4 h at 50 ºC under reduced pressure (50 mmHg). The reaction was neutralized with Et3N and then concentrated under reduced pressure. The resulting crude product was purified by column chromatography (toluene–EtOAc, 3:1, v/v) to afford 3.2 g (75%) of dodecyl 4,6-O-benzylidene-1-thio-α-d-mannopyranoside as a colorless oil. The resulting crude benzylidene was dissolved in dry pyridine (20 mL), followed by addition of benzoyl chloride (1.66 mL, 14.2 mmol) and 4-dimethylaminopyridine (0.5 g, 4.1 mmol). After 3 h at 50 ºC, the reaction was poured into crushed ice-water and extracted with CHCl3. The extra was washed successively with 1 M HCl, saturated aqueous (sat. aq.) NaHCO3 and brine, dried with MgSO4, and concentrated. The resulting crude product was purified by column chromatography (hexane–EtOAc, from 20:1 to 10:1, v/v) to afford compound 4 (4.4 g, 71% over three steps) as a colorless oil. 

Dodecyl 2,3-O-di-benzoyl-4-O-benzylidene-1-thio-α-d-mannopyranoside (9). To a solution of benzylidene derivative 4 (3.4 g, 5.1 mmol) and borane dimethylamine complex (1.5 g, 25.5 mmol) in dry CH2Cl2 (20 mL) was dropwise added boron trifluoride diethyl etherate (3.2 mL, 25.5 mmol) at 0 ºC under nitrogen atmosphere. The mixture was stirred at the same temperature for 1 h. The reaction was quenched upon addition slowly into ice-cold sat. aq. NaHCO3. The mixture was diluted with CHCl3. The organic layer was washed successively with 1 M HCl, sat. aq. NaHCO3 and brine, dried with MgSO4, and concentrated. The resulting crude product was purified by column chromatography (hexane–EtOAc, from 10:1 to 7:1, v/v) to afford compound 9 (2.8 g, 82%) as a colorless oil.
Dodecyl 2,3-O-di-benzoyl-4-O-benzyl-1-thio-α-D-rhamnopyranoside (10). A solution of compound 9 (1.4 g, 2.1 mmol) in dry pyridine (15 mL) was cooled to 0 º C followed by the addition of tosylchloride (1.6 g, 8.4 mmol) and 4-dimethylaminopyridine (77 mg, 0.63 mmol). The reaction mixture was stirred for overnight under nitrogen atmosphere at 50 º C. The reaction was quenched by addition of ice-water. The mixture was diluted with EtOAc and successively washed with 1 M HCl, sat. aq. NaHCO3 and brine, dried with MgSO4, and concentrated. Co-evaporation with toluene afforded the crude tosylate intermediate as a colorless oil. The crude tosylate was dissolved in DMF (30 mL), followed by addition of sodium borohydride (640 mg, 16.8 mmol) at 70 ºC. The mixture was stirred under nitrogen atmosphere at the same temperature for 3 h. The mixture was diluted with EtOAc and washed with ice-cool 1 M HCl. The organic layer was washed with sat. aq. NaHCO3 and brine, dried with MgSO4, and concentrated. The resulting crude product was purified by column chromatography (hexane–EtOAc, from 10:1 to 7:1, v/v) to afford compound 10 (1.1 g, 81%) as a colorless oil. [α]D26.5 −10.9 (c 1.00, CHCl3); 1H NMR (300 MHz, acetone): δ 8.19-7.14 (m, 15H, CHarom), 5.71 (dd, 1H, J2,3 = 3.3 Hz, H-2), 5.64 (dd, 1H, J3,4 = 9.7 Hz, H-3), 5.65 (dd, 1H, J1,2 = 1.3 Hz, H-1), 4.78 (s, 2H, PHCH2), 4.63 (d, 1H, J = 5.7 Hz, OH), 4.46 (t, 1H, J4,5 = 9.7 Hz, H-4), 4.30-4.18 (m, 1H, H-5), 4.09 (t, 1H, J5,6b = 6.1 Hz, H-6b), 2.89-2.65 (m, 2H, SCHR2), 1.85-1.15 (m, 20H, SCH2(C6H2)10CH3), 0.87 (t, 3H, J = 4.1 Hz, CH2C3); 13C NMR (75 MHz, acetone): δ 165.5, 165.5, 138.7, 133.9, 133.7, 130.2, 130.1, 130.1, 129.8, 129.1, 128.9, 128.5, 128.2, 128.1, 127.9, 82.5, 78.1, 75.0, 73.9, 73.6, 73.4, 72.7, 72.2, 61.3, 32.1, 31.2, 22.8, 13.9; HRMS (FAB) calcd for C39H51O6S [M+H]+: 667.3401, found 667.3401.

Dodecyl 2-O-benzoyl-4-O-benzyl-1-thio-α-D-rhamnopyranoside (11). To a solution of compound 10 (303 mg, 0.47 mmol) in MeOH–CH2Cl2 (10 mL, 1:1, v/v) was added a 25% solution NaOMe in MeOH (0.2 mL, w/v) at room temperature. After 3 h, the reaction was neutralized with acidic resin and filtered. The filtrate was concentrated to give the debenzolated product. The resulting crude mixture was dissolved in dry CH2Cl2 (10 mL),
followed by addition of triethyl orthobenzoate (0.2 mL, 0.9 mmol) and catalytic amount of camphorsulfonic acid (20 mg, 0.05 mmol). After 3 h, the reaction was neutralized with Et₃N and then concentrated under reduced pressure. The crude dodecyl 4-benzyl-2,3-O-(1-ethoxybenzylidene)-1-thio-α-D-rhamnopyranoside was suspended in 80% aqueous acetic acid (10 mL) and the reaction was stirred at 80 ºC for 2 h until the TLC analyses showed complete conversion. The mixture was evaporated to dryness. The residue was dissolved in dry toluene (20 mL) and evaporated again to dryness. This procedure was repeated three times. The resulting crude product was purified by column chromatography (hexane–EtOAc, from 30:1 to 20:1, v/v) to afford compound 11 (212 mg, 79% over three steps) as a colorless oil. 

[α]D^26.5 +36.2 (c 1.00, CHCl₃); ¹H NMR (300 MHz, acetone): δ 8.19-7.14 (m, 10H, CHarom), 5.40 (dd, 1H, J₂,₃ = 3.4 Hz, H-2), 5.35 (s, 1H, H-1), 5.02 (d, 1H, J = 11.3 Hz, PHCH₂), 4.77 (d, 1H, J = 11.3 Hz, PHCH₂), 4.62 (d, 1H, J = 5.4 Hz, OH), 4.16-4.02 (m, 2H, H-3, 5), 3.65 (t, 1H, J = 5.4 Hz, OH), 3.65 (t, 1H, J = 5.4 Hz, OH), 2.85-2.70 (m, 2H, SC₂H₂), 1.85-1.15 (m, 23H, SCH₂(C₂H₂)₁₀CH₃, H-6), 0.89 (t, 3H, J = 4.1 Hz, CH₂C₃H₃); ¹³C NMR (75 MHz, acetone): δ 166.3, 134.1, 131.2, 130.5, 129.4, 129.0, 128.7, 128.2, 83.4, 82.5, 76.5, 75.4, 71.8, 69.0, 32.6, 32.1, 23.3, 18.4, 14.4; HRMS (FAB) calcd for C₃₂H₄₇O₅S [M+H]+: 543.3139, found 543.3149.

Dodecyl 2-O-benzyloxy-4-O-benzyl-3-O-thiocarbonylimidazole-1-thio-α-D-rhamnopyranoside (12). Compound 11 (323 mg, 0.6 mmol), imidazole (20 mg, 0.3 mmol) and thiocarbonyldiimidazole (214 mg, 1.2 mmol) in 1,2-dichloroethane (10 mL) were stirred at 80 ºC for 18 h until the TLC analyses showed complete conversion. The solvent was removed and the residue purified by column chromatography (hexane–EtOAc, from 10:1 to 3:1, v/v) to afford compound 12 (386 mg, 98%) as a colorless oil. 

[α]D^24.4 +29.8 (c 1.00, CHCl₃); ¹H NMR (300 MHz, acetone): δ 8.24 (t, 1H, J = 0.9 Hz, NCHN), 8.19-7.14 (m, 11H, CHarom, CSNCHCH), 7.02 (dd, 1H, J = 0.9 Hz, J = 1.8 Hz, CSNCHCH), 6.21 (dd, 1H, J₃,₄ = 9.5 Hz, H-3), 5.84 (brd, 1H, H-2), 5.58 (s, 1H, H-1), 4.85 (d, 1H, J = 11.6 Hz, PhCH₂), 4.78 (d, 1H, J = 11.6 Hz, PhCH₂), 4.45-4.29 (m, 1H, H-5), 4.22 (t, 1H, J₄,₅ = 9.4 Hz, H-4), 2.95-2.65 (m, 2H, SCHR₂), 1.85-1.15 (m, 23H, SCHR₂(CH₃)₁₀CH₃, H-6), 0.87 (t, 3H, J = 4.1 Hz, CH₂C₃H₃); ¹³C NMR (75 MHz, acetone): δ 184.0, 165.5, 138.6, 137.0, 134.1, 130.1, 129.9, 129.1, 128.6, 128.0, 128.0, 82.5, 81.6, 79.4, 75.3, 71.8, 69.1, 32.2, 31.5, 30.2, 30.0, 29.9, 29.8, 29.7, 29.7, 29.5, 29.2, 29.0, 28.7, 22.9, 18.0, 14.0; HRMS (FAB) calcd for C₃₆H₄₉N₂O₅S₂ [M+H]+: 653.3077, found 653.3069.

Dodecyl 2-O-benzyloxy-4-O-benzyl-3,6-dideoxy-1-thio-α-D-arabinohexopyranoside (6). Compound 12 (213 mg, 0.33 mmol) and a catalytic amount of AIBN, dissolved in toluene (3 mL), were added dropwise to a refluxing solution of Bu₃SnH (125 μL, 0.4 mmol) in toluene (3
mL). After 30 min the reaction mixture was concentrated and partitioned between MeCN–hexane. The layer were separated and the hexane layer extracted with MeCN twice. The MeCN phase were combined and concentrated. The resulting crude product was purified by column chromatography (hexane–EtOAc, from 50:1 to 40:1, v/v) to afford compound 6 (141 mg, 82%) as a colorless oil. 

$\alpha_D^{21.3} = +59.2$ (c 1.00, CHCl$_3$); $^1$H NMR (300 MHz, acetone): $\delta$ 8.14-7.14 (m, 10H, CHarom), 5.30 (brd, 1H, H -2), 5.24 (s, 1H, H-1), 4.64 (d, 1H, $J = 11.4$ Hz, PhCH$_2$), 4.50 (d, 1H, $J = 11.4$ Hz, PhCH$_2$), 4.22-4.09 (m, 1H, H-5), 3.56-3.45 (m, 1H, H-4), 2.71-2.57 (m, 2H, S$\mathrm{CH}_2$), 2.31-2.35 (m, 1H, H-3), 2.09-1.92 (m, 1H, H-3), 1.42-1.21 (m, 23H, S$\mathrm{CH}_2$($\mathrm{CH}_2$)$_{10}$CH$_3$), 0.87 (t, 3H, $J = 4.1$ Hz, CH$_2$C$_3$); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 167.7, 166.1, 138.6, 133.8, 133.5, 130.6, 130.3, 130.2, 129.0, 128.9, 128.5, 128.4, 83.0, 75.9, 73.3, 71.8, 69.0, 52.7, 32.5, 31.9, 31.1, 30.4, 30.2, 30.1, 29.9, 29.8, 29.4, 23.3, 18.7, 14.7; HRMS (FAB) calcd for C$_{32}$H$_{47}$O$_4$S [M+H]$^+$: 527.3190, found 527.3196.

Dodecyl 2,3,4,6-tetra-O-benzyl-1-thio-β-D-galactopyranoside (7). Dodecyl 2,3,4,6-tetra-O-acetyl-1-thio-β-D-galactopyranoside 17 (0.65 g, 1.19 mmol) in MeOH (10 mL) was added a 25% solution NaOMe in MeOH (30 μL, w/v) at room temperature. After 1 h, the reaction was neutralized with acidic resin and filtered. The filtrate was concentrated to give the deacetylated product. The residue was dissolved in DMF (15 mL) and cooled to 0 ºC. Benzylbromide (1.4 mL, 11.9 mmol) and sodium hydride (60%, in mineral oil, 0.3 g, 7.14 mmol) were added carefully. The solution was allowed to warm to room temperature and stirred overnight. The residue reaction was quenched with MeOH and solvent was evaporated in vacuo. The residue was diluted with EtOAc, and the organic layer was washed with sat. aq. NaHCO$_3$ and brine, dried with MgSO$_4$, and concentrated. The resulting crude product was purified by column chromatography (hexane–EtOAc, 11:1, v/v) to afford compound 7 (0.72 g, 83% over two steps) as a colorless oil. $\alpha_D^{22.1} = +10.5$ (c 1.00, CHCl$_3$); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.40-7.25 (m, 20H, CHarom), 4.88 (d, 1H, $J = 10.1$ Hz, PhCH$_2$), 4.79 (d, 1H, $J = 10.1$ Hz, PhCH$_2$), 4.77 (s, 2H, PhCH$_2$), 4.45 (d, 1H, $J = 10.1$ Hz, PhCH$_2$), 4.40 (d, 1H, $J_{1,2} = 9.6$ Hz, H-1), 4.39 (d, 1H, $J = 11.7$ Hz, PhCH$_2$), 3.95 (d, 1H, $J_{4,5} = 2.7$ Hz, H-4), 3.81 (t, 1H, $J_{2,3} = 9.4$ Hz, H-2), 3.61-3.52 (m, 4H, H-3, 5, 6a, 6b), 2.78-2.61 (m, 2H, S$\mathrm{CH}_2$), 1.64-1.25 (m, 20H, S$\mathrm{CH}_2$(CH$_2$)$_{10}$), 0.88 (t, 3H, $J = 6.5$ Hz, CH$_2$CH$_3$); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 138.9, 138.5, 138.4, 138.0, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.7, 127.6, 127.6, 127.4, 85.6, 84.2.
Methyl 2,3-O-di-benzoyl-4,6-O-benzylidene-α-D-mannopyranosyl-(1→4)-2,3-O-isopropylidene-α-L-rhamnopyranoside (13). A solution of the glycosyl donor 4 (234 mg, 0.36 mmol), glycosyl acceptor 3 (65 mg, 0.30 mmol) and freshly recrystallized NIS (97.2 mg, 0.43 mmol) in dry CH₂Cl₂ was stirred, for 30 min over activated MS4 Å under nitrogen atmosphere. TfOH (10 μL) was added at –20 ºC with micro syringe. The reaction mixture was stirred and the temperature was warmed slowly to 0 ºC over 30 min. After TLC analyses (toluene–EtOAc, 5:1, v/v) to check the glycosyl donor was consumed, the reaction was quenched with Et₃N (about 2 mL) and the diluted with CHCl₃. The mixture was filtered through a Celite pad, and the filtrate was washed successively with sat. aq. Na₂S₂O₃, sat. aq. NaHCO₃, and brine, dried (MgSO₄), and concentrated. The resulting crude product was purified by column chromatography (toluene–EtOAc, from 15:1 to 9:1, v/v) to afford compound 13 (183 mg, 90%) as a colorless oil. [α]₀D 20.0 –94.3 (c 1.00, CHCl₃); ¹H NMR (300 MHz, CDCl₃): δ 8.12-7.21 (m, 15H, CHarom), 5.81 (dd, 1H, J₃′, 4′ = 3.4 Hz, H-3′), 5.69 (s, 1H, PhCH), 5.65 (dd, 1H, J₂, 3 = 3.5 Hz, H-2′), 5.12 (s, 1H, H-1′), 4.88 (s, 1H, H-1), 4.61-4.31 (m, 3H, H-4′, 6′a, 6′b), 4.23 (t, 1H, J₃, 4 = 7.2 Hz, H-3), 4.15 (d, 1H, J₂, ₃ = 5.5 Hz, H-2), 3.99-3.91 (m, 1H, H-5′), 3.82-3.72 (m, 1H, H₅), 3.42 (dd, 1H, J₄, ₅ = 7.5 Hz, H-4), 3.39 (s, 3H, OMe), 1.53 (s, 3H, CH₃), 1.37 (d, 3H, J = 6.1 Hz, H-6), 1.36 (s, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃): δ 171.1, 137.1, 136.7, 133.6, 133.1, 129.8, 129.7, 129.6, 129.4, 129.0, 128.6, 128.2, 128.2, 109.2, 101.8, 99.0, 97.8, 81.5, 76.0, 71.0, 68.9, 64.6, 63.9, 60.4, 54.9, 28.2, 26.4, 17.4; HRMS (FAB) calcd for C₃₇H₄₁O₁₂ [M+H]⁺: 677.2593, found 677.2592.

Methyl 4,6-O-benzylidene-α-D-mannopyranosyl-(1→4)-2,3-O-isopropylidene-α-L-rhamnopyranoside (5). To a solution of compound 13 (183 mg, 0.27 mmol) in MeOH–CH₂Cl₂ (10 mL, 1:1, v/v) was added a 25% solution NaOMe in MeOH (100 μL, w/v) at room temperature. After 3 h, the reaction was neutralized with acidic resin and filtered. The filtrate was concentrated and purified by column chromatography (toluene–EtOAc, from 5:1 to 1:1, v/v) to afford compound 5 (120 mg, 96%) as a colorless oil. [α]₀D 20.0 –43.9 (c 1.00, CHCl₃); ¹H NMR (300 MHz, CDCl₃): δ 7.65-7.31 (m, 5H, CHarom), 5.54 (s, 1H, PhCH), 4.90 (s, 1H, H-1′), 4.85 (s, 1H, H-1), 4.26 (dd, 1H, J₅, ₆a = 4.9 Hz, J₆b, ₆b = 9.9 Hz, H-6′a), 4.13-3.95 (m, 5H, H-2, 3, 2′, 3′, 5′), 3.90 (t, 1H, J₄, ₅ = 3.4 Hz, H-4′), 3.78 (t, 1H, J₅, ₆b = 10.0 Hz, H-6′b), 3.72-3.59 (m, 1H, H-5), 3.43-3.32 (m, 1H, H-4), 3.36 (s, 3H, OMe), 3.12 (d, 3H, J = 2.8 Hz, OH), 3.03 (d, 1H, J = 2.0 Hz, OH),
1.52 (s, 3H, CH₃), 1.34 (s, 3H, CH₃), 1.27 (d, 1H, J = 6.3 Hz, H-6); ¹³C NMR (75 MHz, CDCl₃): δ 137.8, 129.8, 128.6, 127.2, 109.8, 102.8, 101.4, 98.5, 81.2, 79.4, 76.5, 71.4, 69.4, 69.1, 65.2, 63.6, 55.5, 28.7, 27.0, 18.0; HRMS (FAB) calcd for C₂₃H₃₃O₁₀ [M+H]+: 469.2068, found 469.2075.

Methyl 2-O-benzoyl-4-O-benzyl-3,6-dideoxy-α-D-arabino-hexopyranosyl-(1→3)-4,6-O-benzylidene-α-D-mannopyranosyl-(1→4)-2,3-O-isopropylidene-α-L-rhamnopyranoside (14). A solution of the glycosyl donor 6 (69 mg, 0.13 mmol), glycosyl acceptor 5 (117 mg, 0.25 mmol) and freshly recrystallized NIS (36 mg, 0.16 mmol) in dry CH₂Cl₂ was stirred for 30 min over activated MS4 Å under nitrogen atmosphere. TfOH (10 μL) was added at –40 ºC with micro syringe. The reaction mixture was stirred at the same temperature for 30 min. After TLC analyses (hexane–EtOAc, 2:1, v/v) to check the glycosyl donor was consumed, the reaction was quenched with Et₃N (about 2 mL) and the diluted with CHCl₃. The mixture was filtered through a Celite pad, and the filtrate was washed successively with sat. aq. Na₂S₂O₃, sat. aq. NaHCO₃, and brine, dried (MgSO₄), and concentrated. The resulting crude product was purified by column chromatography (hexane–EtOAc, from 10:1 to 2:1, v/v) to afford compound 14 (94 mg, 92%) as a colorless oil. [α]D²¹.₈ +38.6 (c 1.00, CHCl₃); ¹H NMR (600 MHz, CDCl₃): δ 8.01–7.18 (m, 15H, CHarom), 5.59 (s, 1H, PhCH), 5.31 (s, 1H, H-2″), 4.95 (s, 1H, H-1″), 4.62 (d, 1H, J = 11.0 Hz, PhCH₂), 4.47 (d, 1H, J = 11.6 Hz, PhCH₂), 4.31–4.28 (m, 1H, H-6′a), 4.25–4.18 (m, 1H, H-6′b), 4.16–4.02 (m, 5H, H-2, 3, 2′, 3′, 4′), 3.89–3.85 (m, 1H, H-5″), 3.84–3.78 (m, 1H, H-5′), 3.69–3.62 (m, 1H, H-5), 3.49–3.44 (m, 1H, H-4″), 3.58–3.42 (m, 1H, H-4), 3.36 (s, 3H, OMe), 2.53 (s, 1H, OH), 2.40–2.34 (m, 1H, H-3″), 2.04–1.96 (m, 1H, H-3″), 1.52 (s, 3H, CH₃), 1.35 (d, 3H, J = 6.6 Hz, H-6″), 1.33 (s, 3H, CH₃), 1.27 (d, 3H, J = 6.6 Hz, H-6); ¹³C NMR (75 MHz, CDCl₃): δ 165.9, 138.4, 137.9, 133.7, 130.4, 130.3, 129.1, 129.0, 128.9, 128.6, 128.4, 125.3, 109.7, 101.7, 101.2, 98.5, 97.6, 81.3, 79.2, 77.2, 76.5, 75.4, 73.4, 71.8, 71.7, 71.0, 69.2, 65.1, 63.9, 55.4, 29.8, 28.7, 27.0, 18.8, 18.0; HRMS (FAB) calcd for C₄₃H₅₃O₁₄ [M+H]+: 793.3430, found 793.3437.

Compound 15: ¹H NMR (300 MHz, CDCl₃): δ 7.97–7.22 (m, 15H, CHarom), 5.63 (s, 1H, PhCH), 5.26 (brd, 1H, H-2″), 5.21 (dd, 1H, J₂,₃ = 3.5 Hz, H-2′), 5.16 (s, 1H, H-1″), 4.91 (d, 1H, J₁,₂ = 1.2 Hz, H-1′), 4.85 (s, 1H, H-1), 4.62 (d, 1H, J = 11.6 Hz, PhCH₂), 4.47 (d, 1H, J = 11.6 Hz, PhCH₂), 4.34 (dd, 1H, J₂,₃ = 9.5 Hz, H-3′), 4.27 (dd, 1H, J₅,₆b = 4.2 Hz, H-6″), 4.18–4.06 (m, 4H, H-2, 3, 4′, 6″), 3.87–3.76 (m, 2H, H-5′, 5″), 3.70–3.61 (m, 1H, H-5), 3.55–3.33 (m, 2H, H-4, 4″), 3.35 (s, 3H, OMe), 2.33–2.26 (m, 1H, H-3″), 2.18 (s, 3H, acetyl), 2.08–1.92 (m, 1H, H-3″), 1.51 (s, 3H, CH₃), 1.33 (s, 3H, CH₃), 1.32 (d, 3H, J = 6.3 Hz, H-6″), 1.31 (d, 3H, J = 6.3 Hz, H-6); ¹³C NMR (150.9 MHz, CDCl₃): δ 170.3, 165.4, 138.2, 137.3, 133.2, 130.1, 129.8,
128.7, 128.4, 128.4, 127.9, 127.7, 126.0, 109.2, 101.3, 99.0 (JC1, H1 = 175.9 Hz, C-1'),
97.8 (JC1, H1 = 170.0 Hz, C-1), 97.7 (JC1', H1' = 172.9 Hz, C-1'), 81.2, 78.7, 76.7, 76.0, 74.9, 72.1,
71.4, 71.0, 70.8, 68.8, 68.7, 64.6, 63.8, 54.9, 29.3, 28.1, 26.4, 21.0, 18.2, 17.4.

Methyl 2-O-benzoyl-4-O-benzyl-3,6-dideoxy-α-D-arabino-hexopyranosyl-(1→3)-[2,3,4,6-tetra-O-be
nzyl-α-D-galactopyranosyl-(1→2)]-4,6-benzylidene-α-D-mannopyranosyl-(1→4)-2,3-O-is
opropylidene-α-L-rhamnopyranoside (16).  A solution of the glycosyl donor 7 (78.3 mg, 0.11 mmol),
BSP (25 mg, 0.12 mmol), DTBM (49 mg, 0.24 mmol) and MS4Å (500 mg) was
stirred in dry CH2Cl2 (3 mL) at room temperature for 30 min under nitrogen atmosphere.  The
reaction mixture was cooled to –78 ºC, followed by addition of Tf2O (24 μL, 0.14 mmol) and
stirred at this temperature for 15 min.  Then a solution of glycosyl acceptor 14 (43 mg, 0.054
mmol) in dry CH2Cl2 (2 mL) was added and the reaction mixture was stirred at the same
temperature for 30 min.  After TLC analyses (hexane–EtOAc, 3:1, v/v) to check the glycosyl
acceptor was consumed, the reaction was quenched with Et3N (about 2 mL) and the diluted with
CHCl3.  The mixture was filtered thought a Celite pad, and the filtrate was washed
successively with sat. aq. NaHCO3, and brine, dried (MgSO4), and concentrated.  The resulting
 crude product was purified by column chromatography (hexane/EtOAc, from 10:1 to 3:1, v/v) to
afford compound 16 (52.4 mg, 72%) as a colorless oil.  [α]D21.0 +34.1 (c 1.00, CHCl3); 1H
NMR (600 MHz, CDCl3): δ 7.99–7.12 (m, 35H, CH arom), 5.62 (d, 1H, J1′′′, 2′′′ = 3.8 Hz, H -1′′′),
5.37 (s, 1H, PhCHH), 5.29 (s, 1H, H-1′′), 5.28 (s, 1H, H-2′′), 4.95 (d, 1H, J = 11.5 Hz, PhCH2),
4.93 (s, 1H, H-1'), 4.91 (d, 1H, J = 12.1 Hz, PhCH2), 4.89 (d, 1H, J = 11.5 Hz, PhCH2), 4.83 (s,
1H, H-1), 4.76 (d, 1H, J = 11.0 Hz, PhCH2), 4.71 (d, 1H, J = 11.0 Hz, PhCH2), 4.59 (d, 1H, J =
11.5 Hz, PhCH2), 4.58 (d, 1H, J = 11.5 Hz, PhCH2), 4.45 (d, 1H, J = 11.5 Hz, PhCH2), 4.42 (d,
1H, J = 11.5 Hz, PhCH2), 4.39 (dd, 1H, J1= 10.4 Hz, H-3'), 4.37 (d, 1H, J = 12.1 Hz, PhCH2),
4.28 (t, 1H, J3′, 4′ = 9.9 Hz, H-4'), 4.17 (dd, 1H, J2′, 3′ = 5.0 Hz, H-2'), 4.13 (dd, 1H, J2′′, 3′′ = 10.4
Hz, H-2''), 4.18–4.13 (m, 1H, H-6'a), 4.09-4.02 (m, 3H, H-2, 3, 5), 4.00-3.97 (m, 2H, H-3'',
4''), 3.94 (t, 1H, J5′, 6′b = 6.0 Hz, H-6''b), 3.89-3.83 (m, 1H, H-5''), 3.75 (t, 1H, J3′, 6b = 10.4 Hz,
H-6'b), 3.59-3.41 (m, 4H, H-5, 4', 5'', 6''a), 3.37-3.29 (m, 1H, H-4), 3.34 (s, 3H, OMe),
2.29-2.23 (m, 1H, H-3''), 1.90-1.84 (m, 1H, H-3''), 1.48 (s, 3H, CH3), 1.32 (d, 3H, J = 6.1 Hz,
H-6''), 1.30 (s, 3H, CH3), 1.18 (d, 3H, J = 6.1 Hz, H-6); 13C NMR (75 MHz, CDCl3): δ 165.6, 139.5,
139.2, 139.1, 138.6, 138.4, 138.1, 133.6, 130.6, 130.3, 129.0, 128.9, 128.8, 128.4, 128.3,
128.2, 128.0, 126.5, 109.7, 101.4, 101.2, 98.5, 98.3, 98.0, 80.9, 79.5, 79.0, 77.8, 76.8, 76.5, 75.4,
74.1, 73.7, 73.4, 72.4, 71.5, 71.1, 70.6, 70.0, 69.3, 69.1, 29.8, 28.8, 26.9, 18.8, 17.8; HRMS
(FAB) calcd for C77H87O19 [M+H]': 1315.5836, found 1315.5829.
Methyl 3,6-dideoxy-α-D-arabino-hexopyranosyl-(1→3)-[α-D-galactopyranosyl-(1→2)]-α-D-manno pyranosyl-(1→4)-α-L-rhamnopyranoside (2). To a solution of compound 16 (30 mg, 23 μmol) in AcOH (3 mL) was added few drops water at 50 ºC. The reaction mixture was stirred at the same temperature for 24 h, after which TLC analyses (CHCl3–MeOH, 10:1) indicated the presence of a single product. The reaction mixture was partitioned between CH2Cl2–water (40 mL, 1:1, v/v). The water layer was washed with CH2Cl2 (10 mL) five times. The organic phase were combined and concentration. The crude product was dissolved in dry MeOH (3 mL) and treated with NaOH (pH value adjusted to 12.0). The reaction was stirred for 6 h at room temperature, after which it was neutralized with weakly acidic resin (Dowex-H⁺). After filtration and concentration in vacuo, the residue was purified by silica gel column chromatography (CH2Cl2–MeOH, from 50:1 to 30:1, v/v). The containing fractions were combined and concentrated affording 20 mg (80%) of a colorless film. 5% Pd/C (8 mg) was added to a solution of the above obtained intermediate in a MeOH, water and AcOH (2 mL, 1:1:0.1, v/v/v) under an atmosphere of H2. The mixture was stirred for 24 h, after which TLC analyses (t-BuOH–EtOH–H2O, 5:3:2, v/v/v) indicated the presence of a single product. The reaction mixture was filtered through Celite pad and the residue was purified by column chromatography on Sephadex G-15 (water elution) to afford compound 2 (11 mg, 76% over three steps). 1H NMR (300 MHz, D2O, 333 K): (selected data) δ 5.25 (d, 1H, J1′, 2′ = 1.5 Hz, H-1′), 5.21 (d, 1H, J1″′, 2″′ = 3.7 Hz, H-1″′), 4.90 (brd, 1H, H -1), 4.70 (d, 1H, J1′′, 2′′ = 1.4 Hz, H-1′′), 4.18-3.52 (m, 29H), 3.40 (s, 3H, OMe), 2.08 -2.01 (m, 1H, H -3′′), 1.90- 1.78 (m, 1H, H-3″), 1.34 (d, 3H, J5, 6 = 6.4 Hz, H-6), 1.28 (d, 3H, J5, 6′ = 6.2 Hz, H-6′) ; 13C NMR (75 MHz, D2O): δ 104.1, 104.0, 103.5, 102.5, 84.4, 81.8, 80.1, 76.3, 74.3, 73.2, 73.1, 72.1, 72.1, 71.5, 70.2, 70.2, 70.0, 69.1, 64.0, 63.3, 57.6, 19.9, 19.6; HRMS (ESI) calcd for C25H44O18 [M–H+]': 631.2455, found 631.2452.