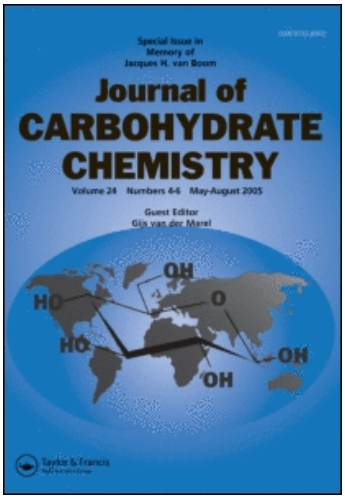


**Journal of Carbohydrate Chemistry**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617200

# Synthesis of 2-(*p*-Trifluoroacetamidophenyl)Ethyl and Methyl Glycosides of *O*-(2-Acetamido-2-Deoxy-α-D-Glucopyranosyl)-(1⟶3)-*O*-α-L-Rhamnopyranosyl-(1⟶3)-*O*-α-L-Rhamnopyranosyl-(2)-α-D-Galactopyranose, Corresponding to the Repeating Unit of the *Shigella Dysenteriae* Type 1 CEll Wall Lipopolysaccharide, and Also of DI- and Trisaccharide Fragments Thereof

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**To cite this Article** Garegg, Per J. and Häullgren, Christer(1992) 'Synthesis of 2-(*p*-Trifluoroacetamidophenyl)Ethyl and Methyl Glycosides of *O*-(2-Acetamido-2-Deoxy-α-D-Glucopyranosyl)-(1⟶3)-*O*-α-L-Rhamnopyranosyl-(1⟶3)-*O*-α-L-Rhamnopyranosyl-(2)-α-D-Galactopyranose, Corresponding to the Repeating Unit of the *Shigella Dysenteriae* Type 1 CEll Wall Lipopolysaccharide, and Also of DI- and Trisaccharide Fragments Thereof', Journal of Carbohydrate Chemistry, 11: 4, 445 — 461
**To link to this Article: DOI:** 10.1080/07328309208017805
**URL:** http://dx.doi.org/10.1080/07328309208017805

J. CARBOHYDRATE CHEMISTRY, 11(4), 445-461 (1992)

# SYNTHESIS OF 2-(*p*-TRIFLUOROACETAMIDOPHENYL)ETHYL AND METHYL GLYCOSIDES OF *O*-(2-ACETAMIDO-2-DEOXY-α-D-GLUCOPYRANOSYL)-(1→3)-*O*-α-L-RHAMNOPYRANOSYL-(1→3)-*O*-α-L-RHAMNOPYRANOSYL-(1→2)-α-D-GALACTOPYRANOSE, CORRESPONDING TO THE REPEATING UNIT OF THE *SHIGELLA DYSENTERIAE* TYPE 1 CELL WALL LIPOPOLYSACCHARIDE, AND ALSO OF DI- AND TRISACCHARIDE FRAGMENTS THEREOF

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*Received September 9, 1991 - Final Form January 29, 1992*



## ABSTRACT

2-(*p*-Trifluoroacetamidophenyl)ethyl and methyl glycosides of a tetrasaccharide repeating unit corresponding to that of the *Shigella dysenteriae* type 1 cell wall lipopolysaccharide, of a rhamnosyl-rhamnosylgalactose trisaccharide, and of a rhamnosylrhamnose and a rhamnosylgalactose disaccharides are described. The main glycosylation method used was activation of thioglycosides with dimethyl(methylthio)-sulfonium triflate (DMTST).

→3)-α-D-Glc*p*NAc-(1→3)-α-L-Rha*p*-(1→3)-α-L-Rha*p*-(1→2)-α-D-Gal*p*-(1-

Figure 1.

## INTRODUCTION

The *Shigella dysenteriae* type 1 O-antigenic cell wall lipopolysaccharide has the repeating unit depicted in Figure 1.[1]

In order to determine the specificity of monoclonal antibodies which recognize this structure, the 2-(*p*-trifluoroacetamidophenyl)ethyl glycoside[2] of the tetrasaccharide unit was synthesized, as earlier reported.[3] Syntheses of the rhamnosylrhamnosylgalactoside, the rhamnosylrhamnoside and the rhamnosylgalactoside, all partial structures, are also described. The corresponding methyl glycosides, destined for inhibition experiments, were also synthesized by parallel routes. The results of the various binding studies will be published elsewhere.



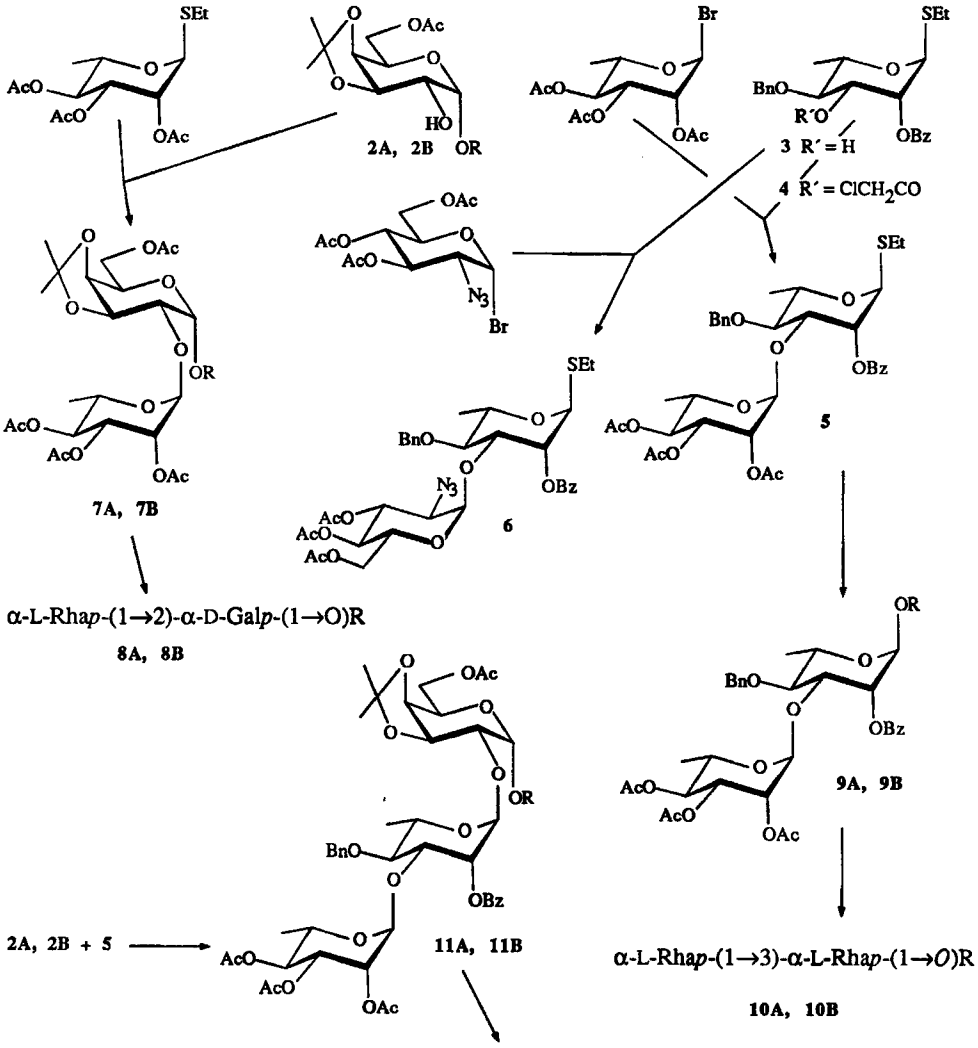
## RESULTS AND DISCUSSION

The various oligosaccharides were made from the readily available glycosyl donors, ethyl 2,3,4-tri-*O*-acetyl-1-thio-α-L-rhamnopyranoside,[4] 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl bromide[5] and 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-D-glucopyranosyl bromide.[6] Monosaccharide glycosyl acceptors were the 6-*O*-acetyl-3,4-*O*-isopropylidene-α-D-galactopyranosides **2A** and **2B**[7] depicted in Scheme 1 and also ethyl 2-*O*-benzoyl-4-*O*-benzyl-1-thio-α-L-rhamnopyranoside **3**. Condensation involving glycosyl bromides were promoted by silver triflate[8] and those involving thioglycosides by dimethyl(methylthio)sulfonium triflate (DMTST).[9]

It should be noticed that in the preparation of **3** *via* the 2,3-orthoester no 1,2-ethylthio group migration, recently reported by Auzanneau and Bundle,[10] could be detected. In our experiment a lower concentration of *p*-toluenesulfonic acid in acetonitrile was used.

Thus, the rhamnosylgalactosides **8A** (90%) and **8B** (96%) were obtained by condensing ethyl 2,3,4-tri-*O*-acetyl-1-thio-α-L-rhamnopyranoside with **2A** or **2B**, giving products **7A** (85%) and **7B** (87%),

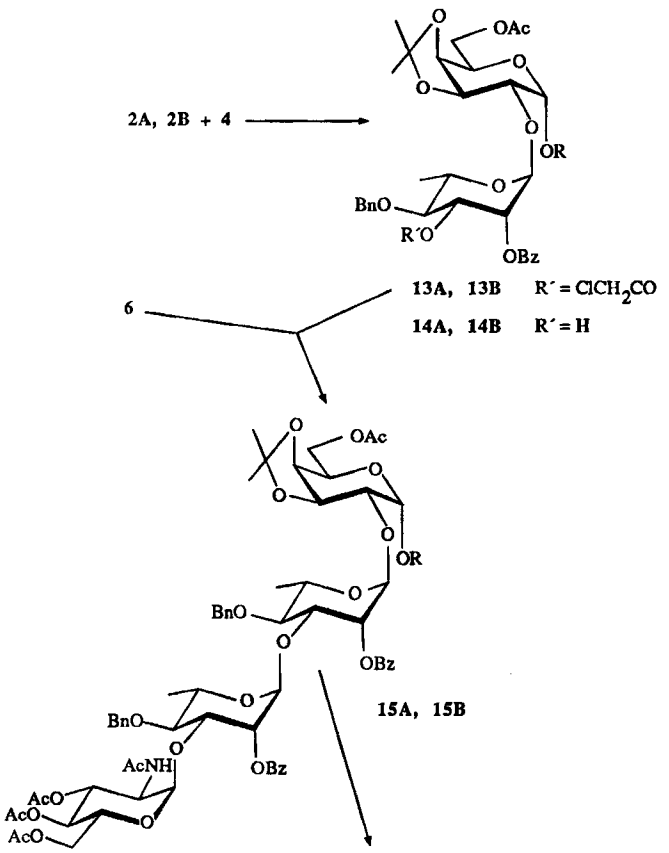
Scheme 1




**A series:** R = $CH_2CH_2$-C$_6$H$_4$-NHCOCF$_3$

**B series:** R = Me

Scheme 2




α-D-Glc*p*NAc-(1→3)-α-L-Rha*p*-(1→3)-α-L-Rha*p*-(1→2)-α-D-Gal*p*-(1→*O*)R

**16A, 16B**

**A series:** R = $CH_2CH_2$-C$_6$H$_4$-NHCOCF$_3$

**B series:** R = Me

followed by standard deprotection. The other two disaccharide glycosides were obtained by first condensing 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl bromide with the thioglycoside **3**, containing a 3-OH group giving **5** (87%). The product **5** was then glycosylated with 2-(*p*-trifluoroacetamidophenyl)-ethanol or with methanol to yield the disaccharide glycosides **9A** (75%)

and **9B** (84%) respectively. Deprotection of these gave the two target compounds **10A** (80%) and **10B** (88%).

Glycosylation of galactosides **2A** and **2B**, both with a 2-OH group, with the thioglycoside **5** afforded the two trisaccharides **11A** (77%) and **11B** (66%), deprotection of which gave the two rhamnosyl-rhamnosyl-galactosides **12A** (82%) and **12B** (85%).

Starting once again from the ethyl 1-thio-rhamnoside **3** with a 3-OH group, and glycosylating this time with 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-D-glucopyranosyl bromide, the disaccharide **6** (59%) was obtained. The other disaccharide building blocks, depicted in Scheme 2 were produced from condensing the galactosides **2A** and **2B** with ethyl 2-*O*-benzoyl-4-*O*-benzyl-3-*O*-chloroacetyl-1-thio-α-L-rhamnopyranoside **4** (79%), obtained by chloroacetylation of **3**. The products **13A** (74%) and **13B** (70%) were dechloroacetylated yielding the corresponding 3′-OH glycosyl acceptors, **14A** (73%) and **14B** (80%). Glycosylation of these with the thioglycoside **6**, then produced the protected tetrasaccharides **15A** (68%) and **15B** (71%), deprotection of which gave the two target tetrasaccharides **16A** (81%) and **16B** (81%). All anomeric configurations are determined either by the homonuclear $^3J_{H,H}$ or the heteronuclear $^1J_{C,H}$ value.



## EXPERIMENTAL

**General methods.** Melting points are corrected. Optical rotations were recorded at room temperature (22-25 °C) using a Perkin-Elmer 241 polarimeter. NMR spectra were recorded at 25 °C for solutions in $CDCl_3$ using a JEOL GSX-270 spectrometer, and chemical shifts are given in ppm downfield from tetramethylsilane, unless otherwise stated. The spectra were invariably in accordance with postulated structures and only selected values are given below. Concentrations were performed at reduced pressure at a bath temperature not exceeding 40 °C. Toluene used for co-evaporation was previously dried over sodium wire. Light petroleum used was the fraction bp 60-71 °C, unless otherwise stated. Column chromatography was performed on silica gel (Matrex Silica Si 60A, 35-70 μ, Amicon). Yields were not subjected to optimization procedures. Elemental analyses were performed by Mikro Kemi AB (Uppsala, Sweden), or Analytische Laboratorien (Engelskirchen, Germany).

**2-(*p*-Trifluoroacetamidophenyl)ethyl 2,3,4,6-Tetra-*O*-benzyl-α-D-galactopyranoside (1A).** Bromine (110 μL, 2.0 mmol) was added at 0 °C to a solution of ethyl 2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-galactopyranoside[11] (1.20 g, 2.0 mmol) in dichloromethane (2 mL). After 10 min, the solution was concentrated and the residue was co-evaporated with toluene. The residue in dichloromethane (2 mL) was added at room temperature to a solution of 2-(*p*-trifluoroacetamidophenyl)ethanol (0.5 g, 2.2 mmol) and tetraethylammonium bromide (0.44 g, 2.0 mmol) in *N,N*-dimethyl formamide (25 mL) containing molecular sieves (4Å). The mixture was stirred overnight, filtered through a layer of Celite, diluted with toluene, washed with sodium hydrogencarbonate, dried ($MgSO_4$), and concentrated. Column chromatography (chloroform-acetone, 50:1) gave amorphous **1A** (1.1 g, 58 %), $[\alpha]_{578}$ +10° (*c* 0.5, chloroform). $^{13}C$ NMR δ 35.3 ($PhCH_2CH_2$), 68.3-78.7 (ring C, $PhCH_2CH_2$, benzyl), 97.5 (C-1, $^1J_{C,H}$ = 168 Hz), 115.8 ($CF_3C{=}O$, $^1J_{C,F}$ = 289 Hz), 120.7- 138.7 (aromatic C), 154.8 ($CF_3C{=}O$, $^2J_{C,F}$ = 38 Hz).

Anal. Calcd for $C_{44}H_{44}F_3NO_7$: C, 70.0; H, 5.9; N, 1.8. Found: C, 69.7; H, 6.0; N, 1.9.

**2-(*p*-Trifluoroacetamidophenyl)ethyl 6-*O*-Acetyl-3,4-*O*-isopropylidene-α-D-galactopyranoside (2A). 1A** (6.94 g, 9.2 mmol) was hydrogenolyzed in acetic acid (20 mL) over 10% Pd/C at 400 kPa overnight. The product was filtered through Celite and concentrated to give 2-(*p*-trifluoroacetamidophenyl)ethyl α-D-galactopyranoside (3.50 g, 96%), $[\alpha]_{578}$ +81° (*c* 1.0, acetone). $^{13}C$ NMR ($Me_2CO$-$d_6$, 30 °C, $\delta_C$ at 30.3): δ 36.5 ($PhCH_2CH_2$), 63.0-72.2 (ring C, $PhCH_2CH_2$), 100.3 (C-1, $^1J_{C,H}$ = 167 Hz), 117.4 ($CF_3C{=}O$, $^1J_{C,F}$ = 288 Hz), 122.2- 138.4 (aromatic C), 156.1 ($CF_3C{=}O$, $^2J_{C,F}$ = 38 Hz).

Sulfuric acid (200 μL, cat) was added at room temperature to a stirred mixture of 2-(*p*-trifluoroacetamidophenyl)ethyl α-D-galactopyranoside (3.50 g, 8.9 mmol) in acetone (250 mL) containing $CuSO_4$ (~10 g). After 16 h, triethylamine (1 mL) was added and the mixture was filtered through Celite and concentrated. Column chromatography (toluene-ethyl acetate, 1:2) followed by precipitation from dichloromethane, gave 2-(*p*-trifluoroacetamidophenyl)ethyl 3,4-*O*-isopropylidene-α-D-galactopyranoside (2.78 g, 72%), mp 158-163 °C, $[\alpha]_{578}$ +98° (*c* 1.0, acetone). $^{13}C$ NMR ($Me_2CO$-$d_6$, 30 °C, $\delta_C$ at 30.3): δ 26.9, 28.8 (Me isopropylidene), 36.5 ($PhCH_2CH_2$), 62.8-78.0

(ring C, $PhCH_2\underline{C}H_2$), 99.6 (C-1), 109.7 (isopropylidene), 117.4 ($\underline{C}F_3C=O$, $^1J_{C,F}$ = 289 Hz), 122.1- 138.2 (aromatic C), 155.1 ($CF_3\underline{C}=O$, $^2J_{C,F}$ = 38 Hz).

Anal. Calcd for $C_{19}H_{24}F_3NO_7$: C, 52.4; H, 5.6; N, 3.2. Found: C, 52.9; H, 5.6; N, 3.0.

Acetyl chloride (320 μL, 4.5 mmol) was added at 0 °C to a stirred solution of 2-(*p*-trifluoroacetamidophenyl)ethyl 3,4-*O*-isopropylidene-α-D-galactopyranoside (1.8 g, 4.1 mmol) in acetone (100 mL) containing pyridine (1 mL, 12.4 mmol). After 1 h, methanol (10 mL) was added and the solution was stirred for another 5 min and then washed with saturated aqueous sodium hydrogencarbonate, dried ($MgSO_4$), and filtered. Concentration and column chromatography (flash, light petroleum-ethyl acetate, 3:2) gave **2A** (1.41 g, 72%), $[\alpha]_{578}$ +64° (*c* 1.0, chloroform). $^{13}C$ NMR δ 21.0 (Me acetyl), 25.9, 27.6 (Me isopropylidene), 35.7 ($Ph\underline{C}H_2CH_2$), 63.7-75.7 (ring C, $PhCH_2\underline{C}H_2$), 97.0 (C-1), 110.1 (isopropylidene), 115.8 ($\underline{C}F_3C=O$, $^1J_{C,F}$ = 289 Hz), 120.9- 137.1 (aromatic C), 155.1 ($CF_3\underline{C}=O$, $^2J_{C,F}$ = 38 Hz), 171.0 (acetyl C=O).

Anal. Calcd for $C_{21}H_{26}F_3O_8$: C, 52.8; H, 5.5; N, 2.9. Found: C, 52.6; H, 5.5; N, 3.0.

**Ethyl 2-*O*-Benzoyl-4-*O*-benzyl-1-thio-α-L-rhamnopyranoside (3).** *p*-Toluenesulfonic acid (10 mg, cat) was added at room temperature to a stirred solution of ethyl 1-thio-α-L-rhamnopyranoside[4] (4.42 g, 21.2 mmol), triethyl orthobenzoate (9.6 mL, 42.4 mmol) in acetonitrile (100 mL). After 20 min, triethylamine (1 mL) was added and the solution was concentrated. Benzyl bromide (3.78 mL, 31.8 mmol) was added to a solution of the residue in *N,N*-dimethylformamide (50 mL). The resulting solution was added at room temperature to sodium hydride (1.85 g, 42.4 mmol) under nitrogen. After 30 min, methanol (10 mL) was added and the reaction mixture was stirred for another 5 min. The reaction mixture was partitioned between toluene and brine. The organic layer was dried ($MgSO_4$), filtered, and concentrated. A solution of the residue in aqueous acetic acid (80 %, 100 mL) was heated at 70 °C for 30 min, cooled and concentrated. Column chromatography (toluene-ethyl acetate, 1:1) gave syrupy **3** (6.09 g, 71%), $[\alpha]_{578}$ -67° (*c* 2.1, chloroform). $^{13}C$ NMR δ 15.1 ($SCH_2\underline{C}H_3$), 18.2 (C-6), 25.7 ($S\underline{C}H_2CH_3$), 68.2-81.9 (ring C, benzyl), 82.3 (C-1), 128.0-138.3 (aromatic C), 166.3 (benzoyl C=O).

**Ethyl 2-*O*-Benzoyl-4-*O*-benzyl-3-*O*-chloroacetyl-1-thio-α-L-rhamnopyranoside (4).** Chloroacetyl chloride (677 μL, 8.5 mmol) was added at 0 °C to a stirred solution of **3** (3.2 g, 7.7 mmol) in dichloromethane (100 mL) and pyridine (1.5 mL). After 5 min, saturated aqueous sodium hydrogencarbonate was added. The organic layer was separated, dried ($MgSO_4$), filtered, and concentrated. Column chromatography (toluene-ethyl acetate, 9:1) gave **4** (3.03 g, 79 %) mp 75-77 °C (from diethyl ether-pentane), $[\alpha]_{578}$ -30° (*c* 1.0, chloroform). $^{13}C$ NMR δ 14.9 ($SCH_2\underline{C}H_3$), 18.0 (C-6), 25.5 ($S\underline{C}H_2CH3$), 40.6 ($Cl\underline{C}H2CO$), 68.4-78.8 (ring C, benzyl), 81.9 (C-1), 127.8-137.9 (aromatic C), 165.6 (chloroacetyl C=O), 166.3 (benzoyl C=O).

Anal. Calcd for $C_{24}H_{27}ClO_6S$: C, 60.1; H, 5.7. Found: C, 59.8; H, 5.7.

**Ethyl 2-*O*-Benzoyl-4-*O*-benzyl-3-*O*-(2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-1-thio-α-L-rhamnopyranoside (5).** Silver triflate (833 mg, 3.2 mmol) was added at -30 °C to a stirred mixture of **3** (543 mg, 1.3 mmol), 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl bromide[12] (916 mg, 2.6 mmol), and 2,6 lutidine (271 μL, 2.3 mmol) in dichloromethane (50 mL) containing ground molecular sieves (4Å) under nitrogen. When TLC (toluene-ethyl acetate, 3:1) indicated complete reaction, 10% aqueous sodium thiosulfate was added. The mixture was allowed to attain room temperature and then filtered through Celite. The organic layer was separated, washed with water, dried ($MgSO_4$), filtered, and concentrated. Column chromatography (toluene-ethyl acetate, 5:1) gave amorphous **5** (761 mg, 87 %), $[\alpha]_{578}$ -61° (*c* 1.0, chloroform). $^{13}C$ NMR δ 15.0 ($SCH_2\underline{C}H_3$), 17.1, 18.0 (C-6, C-6'), 20.7 (Me acetyl), 25.7 ($S\underline{C}H_2CH_3$), 67.3-80.4 (ring C, benzyl), 81.9 (C-1, $^1J_{C,H}$ = 167 Hz), 99.4 (C-1', $^1J_{C,H}$ = 173 Hz), 127.8-137.8 (aromatic C), 166.0 (benzoyl C=O), 169.8 (3 acetyl C=O).

Anal. Calcd for $C_{34}H_{42}O_{12}S$: C, 60.5; H, 6.3. Found: C, 60.4; H, 6.3.

**Ethyl 2-*O*-Benzoyl-4-*O*-benzyl-3-*O*-(3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-D-glucopyranosyl)-1-thio-α-L-rhamnopyranoside (6).** Silver triflate (539 mg, 2.1 mmol) was added at -30 °C to a stirred mixture of 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-D-glucopyranosyl bromide (729 mg, 1.8 mmol), **3** (675 mg, 1.68 mmol), and 2,6 lutidine (175 μL, 1.5 mmol) in dichloromethane (100 mL) containing ground molecular sieves (4Å) under nitrogen. The reaction mixture was processed as described for the preparation of **5**. Column chromatography (toluene-ethyl acetate, 3:1) gave amorphous **6** (708 mg, 59%), $[\alpha]_{578}$ +97° (*c* 0.5, chloroform). $^{13}C$ NMR δ 14.9 ($SCH_2\underline{C}H_3$), 17.9 (C-6), 20.4, 20.5, 20.6 (3 Me acetyl), 25.8 ($S\underline{C}H_2CH_3$), 60.4, 61.5 (C-2', C-6'),

67.4-79.7 (ring C, benzyl), 82.2 (C-1), 92.9 (C-1'), 127.5-137.7 (aromatic C), 165.7 (benzoyl C=O), 169.4, 169.7, 170.4 (3 acetyl C=O).

Anal. Calcd for $C_{34}H_{41}N_3O_{12}S$: C, 57.0; H, 5.8; N, 5.9. Found: C, 57.2; H, 5.8; N, 5.6.

**2-(*p*-Trifluoroacetamidophenyl)ethyl 6-*O*-Acetyl-3,4-*O*-isopropylidene-2-*O*-(2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-α-D-galactopyranoside (7A).** DMTST (300 mg, 1.16 mmol) was added at room temperature to a stirred mixture of **2A** (270 mg, 0.57 mmol) and ethyl 2,3,4-tri-*O*-acetyl-1-thio-α-L-rhamnopyranoside (227 mg, 0.68 mmol) in dichloromethane (50 mL) containing ground molecular sieves (4Å) under nitrogen. When TLC (toluene-ethyl acetate, 3:1) indicated complete reaction, triethylamine (1 mL) was added. The reaction mixture was filtered through Celite, the filtrate was partitioned between dichloromethane and saturated aqueous sodium hydrogencarbonate. The organic layer was dried ($MgSO_4$), filtered, and concentrated. Column chromatography (toluene-ethyl acetate, 3:1) gave syrupy **7A** (360 mg, 85%), $[\alpha]_{578}$ +1° (*c* 1.0, chloroform). $^{13}C$ NMR δ 17.3 (C-6'), 20.6, 20.7, 20.9, 20.9 (4 Me acetyl), 26.4, 28.2 (Me isopropylidene), 35.2 ($PhCH_2CH_2$), 63.5-76.7 (ring C, $PhCH_2CH_2$), 97.7, 98.7 (C-1, C-1', $^1J_{C,H}$ = 170 Hz and 177 Hz, respectively), 109.6 (isopropylidene), 115.9 ($CF_3C=O$, $^1J_{C,F}$ = 290 Hz), 120.7-137.0 (aromatic C), 154.9 ($CF_3C=O$, $^2J_{C,F}$ = 38 Hz), 169.9, 170.0, 170.0, 170.8 (4 acetyl C=O).

Anal. Calcd for $C_{33}H_{42}F_3NO_{15}$: C, 52.9; H, 5.6; N, 1.9. Found: C, 53.1; H, 5.7; N, 1.9.

**Methyl 6-*O*-Acetyl-3,4-*O*-isopropylidene-2-*O*-(2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-α-D-galactopyranoside (7B).** DMTST (105 mg, 0.41 mmol) was added at room temperature to a stirred mixture of **2B** (89 mg, 0.32 mmol) and ethyl 2,3,4-tri-*O*-acetyl-1-thio-α-L-rhamnopyranoside (129 mg, 0.39 mmol) in dichloromethane (25 mL) containing ground molecular sieves (4Å) under nitrogen. The reaction mixture was processed as described for the preparation of **7A**. Column chromatography (toluene-ethyl acetate, 1:1) gave syrupy **7B** (152 mg, 87%), $[\alpha]_{578}$ +29° (*c* 0.8, chloroform). $^{13}C$ NMR δ 17.6 (C-6'), 20.8, 21.0, 21.0, 21.1 (4 Me acetyl), 26.5, 28.4 (Me isopropylidene), 55.6 (OMe), 63.8-76.7 (ring C), 98.5, 99.0 (2 C-1), 109.8 (isopropylidene), 170.1, 170.1, 170.2, 170.2 (4 acetyl C=O).

Anal. Calcd for $C_{26}H_{40}O_{14}$: C, 54.2; H, 7.0. Found: C, 54.1; H, 7.1.

**2-(*p*-Trifluoroacetamidophenyl)ethyl 2-*O*-α-L-Rhamnopyranosyl-α-D-galactopyranoside (8A).** Compound **7A** (152 mg, 0.20 mmol) was treated with methanolic sodium methoxide (0.2 M, 10 mL) at room temperature

for 30 min. Dowex 50W-X8 ($H^+$ form) was added and the mixture was stirred for another 5 min. The mixture was filtered and concentrated The residue was treated with aqueous acetic acid (80%, 10 mL) at 60 °C for 1 h, then cooled and concentrated. Column chromatography on Bio-Gel P2 (1% aqueous 1-butanol) gave amorphous **8A** (99 mg, 90%), $[\alpha]_{578}$ +64° (*c* 0.6, water). $^{13}C$ NMR ($D_2O$, 60 °C, $Me_2CO$, $\delta_C$ at 31.07): δ 17.6 (C-6'), 35.5 ($PhCH_2CH_2$), 61.7 (C-6), 69.0-78.0 (ring C, $PhCH_2CH_2$), 98.5, 103.6 (2 C-1), 123.1-138.7 (aromatic C).

**Methyl 2-*O*-α-L-Rhamnopyranosyl-α-D-galactopyranoside (8B).** Compound **7B** (85 mg, 0.16 mmol) was treated with saturated ammoniacal methanol at room temperature for 16 h. Concentration, further deprotection and purification as described for the preparation of **8A**, gave **8B** (51 mg, 96%), $[\alpha]_{578}$ +81° (*c* 2.8, water). $^{13}C$ NMR ($D_2O$, 60 °C, $Me_2CO$ $\delta_C$ at 31.07): δ 17.5 (C-6'), 55.6 (OMe), 61.9 (C-6), 69.2-78.0 (ring C), 99.6, 103.5 (2 C-1, $^1J_{C,H}$ = 171 Hz and 167 Hz, respectively).

**2-(*p*-Trifluoroacetamidophenyl)ethyl 2-*O*-Benzoyl-4-*O*-benzyl-3-*O*-(2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (9A).** DMTST (195 mg, 0.75 mmol) was added at room temperature to a stirred mixture of **5** (255 mg, 0.38 mmol) and 2-(*p*-trifluoroacetamidophenyl)-ethanol (97 mg, 0.42 mmol) in dichloromethane (25 mL) containing ground molecular sieves (4Å) under nitrogen. The reaction mixture was processed as described for the preparation of **7A**. Column chromatography (toluene-ethyl acetate, 7:2) gave syrupy **9A** (240 mg, 75%), $[\alpha]_{578}$ -34° (*c* 1.0, chloroform). $^{13}C$ NMR δ 17.3, 18.2 (C-6, C-6'), 20.8 (3 Me acetyl), 35.5 ($PhCH_2CH_2$), 67.4-80.2 (ring C, benzyl, $PhCH_2CH_2$), 96.8, 99.5 (2 C-1, $^1J_{C,H}$ = 170 Hz and 172 Hz, respectively), 120.8-138.0 (aromatic C), 166.2 (benzoyl C=O), 170.1 (3 acetyl C=O).

Anal. Calcd for $C_{42}H_{46}F_3NO_{14}$: C, 59.6; H, 5.5; N, 1.7. Found: C, 59.6; H, 5.5; N, 1.6.

**Methyl 2-*O*-Benzoyl-4-*O*-benzyl-3-*O*-(2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (9B).** DMTST (60 mg, 0.23 mmol) was added at room temperature to a stirred solution of **5** (72 mg, 0.11 mmol) in dichloromethane (25 mL) containing methanol (22 μL, 0.54 mmol) under nitrogen. The reaction mixture was processed as described for the preparation of **7A**. Column chromatography (toluene-ethyl acetate, 3:1) gave amorphous **9B** (58 mg, 84%), $[\alpha]_{578}$ -14° (*c* 0.9, chloroform). $^{13}C$ NMR δ 17.3, 18.3 (C-6, C-6'), 20.9, 20.9, 21.0 (3 Me acetyl), 55.1 (OMe), 67.4-80.4 (ring

C, benzyl), 98.2, 99.7 (2 C-1), 128.0- 138.0 (aromatic C), 166.2 (benzoyl C=O), 170.0 (3 acetyl C=O).

Anal. Calcd for $C_{33}H_{40}O_{13}$: C, 61.5; H, 6.2. Found: C, 61.8; H, 6.2.

**2-(*p*-Trifluoroacetamidophenyl)ethyl 3-*O*-α-L-Rhamnopyranosyl-α-L-rhamnopyranoside (10A).** Compound **9A** (68 mg, 76 μmol) was deacetylated as described for the preparation of **8A**. The product was hydrogenolyzed in ethyl acetate-ethanol-water (12:3:2, 3 mL) over 10% Pd/C at 400 kPa overnight. The product was filtered through Celite and concentrated. Column chromatography on Bio-Gel P2 (1% aqueous 1-butanol) gave amorphous **10A** (32 mg, 80%), $[\alpha]_{578}$ +91° (*c* 0.4, water). $^{13}C$ NMR ($D_2O$, 60 °C, $Me_2CO$ $\delta_C$ at 31.07): δ 17.3, 17.4 (C-6, C-6'), 35.4 ($PhCH_2CH_2$), 68.8-78.6 (ring C, $PhCH_2CH_2$), 100.2, 102.9 (2 C-1), 117.3-138.9 (aromatic C).

**Methyl 3-*O*-α-L-Rhamnopyranosyl-α-L-rhamnopyranoside (10B).** Compound **9B** (33 mg, 51 μmol) was deacetylated as described for the preparation of **8B**. The product was hydrogenolyzed as described for the preparation of **9A**. Column chromatography on Bio-Gel P2 (1% aqueous 1-butanol) gave amorphous **10B** (13 mg, 88%), $[\alpha]_{578}$ +79° (*c* 0.7, water). $^{13}C$ NMR ($D_2O$, 60 °C, $Me_2CO$, $\delta_C$ at 31.07): δ 17.4, 17.4 (C-6, C-6'), 55.5 (OMe), 69.4-78.8 (ring C), 101.6, 102.9 (2 C-1, $^1J_{C,H}$ = 170 Hz and 176 Hz, respectively).

**2-(*p*-Trifluoroacetamidophenyl)ethyl *O*-(2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl)-(1→3)-*O*-(2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranosyl)-(1→2)-6-*O*-acetyl-3,4-*O*-isopropylidene-α-D-galactopyranoside (11A).** DMTST (202 mg, 0.78 mmol) was added at room temperature to a stirred mixture of **2A** (132 mg, 0.28 mmol) and **5** (205 mg, 0.30 mmol) in dichloromethane (25 mL) containing ground molecular sieves (4Å) under nitrogen. The reaction mixture was processed as described for the preparation of **7A**. Column chromatography (light petroleum-ethyl acetate, 3:2) gave syrupy **11A** (223 mg, 77%) $[\alpha]_{578}$ +25° (*c* 1.0, chloroform). $^{13}C$ NMR δ 17.1, 18.1 (C-6', C-6''), 20.7, 20.7, 20.9, 21.0 (4 Me acetyl), 26.4, 28.2 (Me isopropylidene), 35.2 ($PhCH_2CH_2$), 63.6-80.0 (ring C, benzyl, $PhCH_2CH_2$), 97.6, 98.1, 99.1 (3 C-1, $^1J_{C,H}$ = 170 Hz, 177 Hz and 175 Hz, respectively), 109.7 (isopropylidene) 115.9 ($CF_3C=O$, $^1J_{C,F}$ = 289 Hz), 120.9-137.8 (aromatic C), 154.9 ($CF_3C=O$, $^2J_{C,F}$ = 38 Hz), 165.8 (benzoyl C=O), 170.0, 170.0, 170.6, 170.8 (4 acetyl C=O).

Anal. Calcd for $C_{53}H_{62}F_3NO_{20}$: C, 58.4; H, 5.7; N, 1.3. Found: C, 58.3; H, 5.7; N, 1.2.

**Methyl *O*-(2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl)-(1→3)-*O*-(2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranosyl)-(1→2)-6-*O*-acetyl-3,4-*O*-isopropylidene-α-D-galactopyranoside (11B).** DMTST (50 mg, 190 μmol) was added at room temperature to a stirred mixture of **5** (65 mg, 96 μmol) and **2B** (27 mg, 96 μmol) in dichloromethane (50 mL) containing ground molecular sieves (4Å) under nitrogen. The reaction mixture was processed as described for the preparation of **7A**. Column chromatography (toluene-ethyl acetate, 2:1) gave syrupy **11B** (56 mg, 66 %), $[\alpha]_{578}$ +23° (*c* 1.0, chloroform). $^{13}C$ NMR δ 17.3, 18.3 (C-6', C-6''), 20.9, 21.0, 21.0, 21.0 (4 Me acetyl), 26.4, 28.1 (Me isopropylidene), 55.6 (OMe), 63.8-80.3 (ring C, benzyl), 98.0, 99.0, 99.4 (3 C-1, $^1J_{C,H}$ = 172 Hz, 170 Hz and 175 Hz, respectively), 109.8 (isopropylidene), 128,0-137.9 (aromatic C), 165.8 (benzoyl C=O), 170.0, 170.0, 170.1, 170.9 (4 acetyl C=O).

Anal. Calcd for $C_{44}H_{56}O_{19}$: C, 59.4; H, 6.4. Found: C, 58.7; H, 6.3.

**2-(*p*-Trifluoroacetamidophenyl)ethyl *O*-α-L-Rhamnopyranosyl-(1→3)-*O*-α-L-rhamnopyranosyl-(1→2)-α-D-galactopyranoside (12A).** A solution of **11A** (104 mg, 95 μmol) in aqueous acetic acid (80%, 5 mL) was heated at 60 °C for 1 h, then cooled and concentrated. The product was hydrogenolyzed in ethyl acetate-ethanol-water (12:3:2, 3 mL) over 10% Pd/C at 400 kPa overnight. The mixture was filtered through Celite, the filtrate was concentrated and the residue was treated with methanolic sodium methoxide (0.2 M, 10 mL) for 30 min. Dowex 50W-X8 ($H^+$ form) was added and stirring was continued for 5 min. The mixture was filtered and concentrated. Column chromatography on Bio-Gel P2 (1% aqueous 1-butanol) gave amorphous **12A** (54 mg, 82%), $[\alpha]_{578}$ +22° (*c* 1.0, water). $^{13}C$ NMR ($D_2O$, 60 °C, $Me_2CO$, $\delta_C$ at 31.07): δ 17.5, 17.6 (C-6´, C-6´´), 35.5 ($PhCH_2CH_2$), 61.8 (C-6), 69.0-79.2 (ring C, $PhCH_2CH_2$), 98.4, 103.1, 103.4 (3 C-1, $^1J_{C,H}$ = 170 Hz, 170 Hz and 174 Hz respectively), 123.2-138.2 (aromatic C).

**Methyl *O*-α-L-Rhamnopyranosyl-(1→3)-*O*-α-L-rhamnopyranosyl-(1→2)-α-D-galactopyranoside (12B).** Compound **11B** (78 mg, 88 μmol) was deprotected as described above for the preparation of **12A**, except that the order of operations was deacetylation-deisopropylidenation-hydrogenolysis. Column chromatography on Bio-Gel P2 (1% aqueous 1-butanol) gave amorphous **12B** (36 mg, 85%), $[\alpha]_{578}$ +9° (*c* 0.3, water). $^{13}C$

NMR ($D_2O$, 60 °C, $Me_2CO$ $\delta_C$ at 31.07): δ 17.4, 17.7 (C-6', C-6''), 55.7 (OMe), 61.9 (C-6) 69.2-79.1 (ring C), 99.7, 103.2, 103.5 (3 C-1).

**2-(*p*-Trifluoroacetamidophenyl)ethyl 6-*O*-Acetyl-3,4-*O*-isopropylidene-2-*O*-(2-*O*-benzoyl-4-*O*-benzyl-3-*O*-chloroacetyl-α-L-rhamnopyranosyl)-α-D-galactopyranoside (13A).** DMTST (466 mg, 1.8 mmol) was added at room temperature to a stirred mixture of **4** (433 mg, 0.90 mmol) and **2A** (431 mg, 0.90 mmol) in dichloromethane (50 mL) containing ground molecular sieves (4Å) under nitrogen. The reaction mixture was processed as described for the preparation of **7A**. Column chromatography (toluene-ethyl acetate, 4:1) gave syrupy **13A** (596 mg, 74%), $[\alpha]_{578}$ +46° (*c* 1.0, chloroform). $^{13}C$ NMR δ 18.1 (C-6'), 21.0 (Me acetyl), 26.5, 28.3 (Me isopropylidene), 35.4 ($PhCH_2CH_2$), 40.8 ($ClCH_2CO$), 63.7- 78.6 (ring C, $PhCH_2CH_2$), 97.8, 98.2, (2 C-1, $^1J_{C,H}$ = 170 Hz and 176 Hz, respectively), 109.7 (isopropylidene), 121.3- 137.6 (aromatic C), 165.7, 166.9 (benzoyl and chloroacetyl C=O), 170.9 (acetyl C=O).

Anal. Calcd for $C_{43}H_{47}ClF_3NO_{14}$: C, 57.7; H, 5.3; N, 1.6. Found: C, 57.6; H, 5.2; N, 1.6.

**Methyl 6-*O*-Acetyl-3,4-*O*-isopropylidene-2-*O*-(2-*O*-benzoyl-4-*O*-benzyl-3-*O*-chloroacetyl-α-L-rhamnopyranosyl)-α-D-galactopyranoside (13B).** DMTST (600 mg, 2.32 mmol) was added at room temperature to a stirred mixture of **4** (764 mg, 1.59 mmol) and **2B** (440 mg, 1.59 mmol) in dichloromethane (50 mL) containing ground molecular sieves (4Å) under nitrogen. The reaction mixture was processed as described for the preparation of **7A**. Column chromatography (toluene-ethyl acetate, 3:1) gave syrupy **13B** (500 mg, 70%), $[\alpha]_{578}$ +70° (*c* 0.7, chloroform). $^{13}C$ NMR δ 18.2 (C-6'), 20.9 (Me acetyl), 26.4, 28.3 (Me isopropylidene), 40.7 ($ClCH_2CO$), 55.5 (OMe), 63.7-78.7 (ring C, benzyl), 98.3, 98.9 (2 C-1, $^1J_{C,H}$ = 173 Hz and 170 Hz, respectively), 109.6 (isopropylidene), 128.1-137.8 (aromatic C), 165.5, 166.2 (benzoyl and chloroacetyl C=O), 170.8 (acetyl C=O).

Anal. Calcd for $C_{34}H_{41}ClO_{13}$: C, 58.8; H, 6.0. Found: C, 59.0; H, 6.0.

**2-(*p*-Trifluoroacetamidophenyl)ethyl *O*-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranosyl)-(1→3)-*O*-(2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-*O*-(2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranosyl)-(1→2)-6-*O*-acetyl-3,4-*O*-isopropylidene-α-D-galactopyranoside (15A).** Hydrazine acetate (58 mg, 630 μmol) was added at room temperature to a stirred solution of **13A** (56 mg, 63 μmol) in ethyl acetate-methanol (1:1, 5 mL). After 16 h the solution was concentrated. Column chromatography

(toluene-ethyl acetate, 2:1) gave 2-(*p*-trifluoroacetamidophenyl)ethyl 6-*O*-acetyl-2-*O*-(2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranosyl)-3,4-*O*-isopropylidene-α-D-galactopyranoside (**14A**) (38 mg, 73%), $[\alpha]_{578}$ +23° (*c* 1.1, chloroform). $^{13}C$ NMR δ 18.3 (C-6′), 21.0 (Me acetyl), 26.5, 28.3 (Me isopropylidene), 35.5 ($Ph\underline{C}H_2CH_2$), 63.7-81.5 (ring C, $PhCH_2\underline{C}H_2$), 97.2, 98.3 (2 C-1), 109.7 (isopropylidene), 115.9 ($\underline{C}F_3C{=}O$, $^1J_{C,F}$ = 289 Hz), 121.4-138.1 (aromatic C), 155.2 ($CF_3\underline{C}{=}O$, $^2J_{C,F}$ = 38 Hz), 166.4 (benzoyl C=O), 170.9 (acetyl C=O).

DMTST (23 mg, 88 μmol) was added at room temperature to a stirred mixture of the latter compound (23 mg, 88 μmol) and **6** (31 mg, 44 μmol) in dichloromethane (10 mL) containing ground molecular sieves (4Å) under nitrogen. The reaction mixture was processed as described for the preparation of **7A**. Column chromatography (toluene-ethyl acetate, 5:2) gave syrupy 2-(*p*-trifluoroacetamidophenyl)ethyl *O*-(3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-D-glucopyranosyl)-(1→3)-*O*-(2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-*O*-(2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranosyl)-(1→2)-6-*O*-acetyl-3,4-*O*-isopropylidene-α-D-galactopyranoside (44 mg, 68%), $[\alpha]_{578}$ +108° (*c* 1.0, chloroform). $^{13}C$ NMR δ 17.9, 18.2 (C-6′, C-6″), 20.6, 20.8, 21.0, 21.6 (4 Me acetyl), 26.5, 28.3 (Me isopropylidene), 35.4 ($Ph\underline{C}H_2CH_2$), 60.7-80.3 (ring C, benzyl, $PhCH_2\underline{C}H_2$), 93.3, 97.8, 98.3, 99.2 (4 C-1, $^1J_{C,H}$ = 174 Hz, 170 Hz, 175 Hz and 171 Hz, respectively), 109.8 (isopropylidene), 120.9-138.0 (aromatic C), 165.6, 166.3 (2 benzoyl C=O), 169.6, 170.0, 170.6, 170.9 (4 acetyl C=O).

A slow stream of hydrogen sulfide was at room temperature passed through a solution of the latter compound (32 mg, 22 μmol) in pyridine-triethylamine (2:1, 5 mL). After 6 h acetic anhydride (100 μL) was added slowly and the solution was concentrated several times from water. Column chromatography (toluene-ethyl acetate, 1:2) gave syrupy **15A** (22 mg, 67%), $[\alpha]_{578}$ +93° (*c* 0.8, chloroform). $^{13}C$ NMR δ 18.0, 18.2 (C-6′, C-6″), 20.5, 20.7, 20.7, 20.9 (4 Me acetyl), 22.4 (Me *N*-acetyl), 26.4, 28.3 (Me isopropylidene), 35.4 ($Ph\underline{C}H_2CH_2$), 51.1 (C-2‴), 61.1-80.4 (ring C, benzyl, $PhCH_2\underline{C}H_2$), 93.6, 97.7, 98.2, 99.0 (4 C-1, $^1J_{C,H}$ = 173 Hz, 170 Hz, 173 Hz and 171 Hz, respectively), 109.7 (isopropylidene), 115.8 ($\underline{C}F_3C{=}O$, $^1J_{C,F}$ = 289 Hz), 121.0-137.7 (aromatic C), 154.9 ($CF_3\underline{C}{=}O$, $^2J_{C,F}$ = 37 Hz), 165.6 (2 benzoyl C=O), 169.1, 169.9, 170.6, 170.8, 171.3 (4 acetyl C=O, acetamido C=O).

Anal. Calcd for $C_{75}H_{85}F_3N_2O_{26}$: C, 60.6; H, 5.8; N, 1.9. Found: C, 60.8; H, 5.7; N, 1.8.

**Methyl *O*-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranosyl)-(1→3)-*O*-(2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-*O*-(2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranosyl)-(1→2)-6-*O*-acetyl-3,4-*O*-isopropylidene-α-D-galactopyranoside (15B).** Compound **13B** was taken through the same steps, *i.e.*; dechloroacetylation to give (**14B**), glycosylation with glycosyl donor **6**, and conversion of the 2-azido-2-deoxy to a 2-acetamido-2-deoxy group. The same relative molar proportional and procedures as those described for the preparation of **15A** were used. The following compounds and yields were obtained:

Methyl 6-*O*-acetyl-2-*O*-(2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranosyl)-3,4-*O*-isopropylidene-α-D-galactopyranoside (**14B**) (80%), $[\alpha]_{578}$ +55° (*c* 1.0, chloroform). $^{13}C$ NMR δ 18.4 (C-6'), 21.0 (Me acetyl), 26.5, 28.4 (Me isopropylidene), 55.6 (OMe), 63.8-81.6 (ring C, benzyl), 98.4, 99.0 (2 C-1), 110.1 (isopropylidene), 128.1-138.2 (aromatic C), 166.4 (benzoyl C=O), 171.0 (acetyl C=O).

Methyl *O*-(3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-D-glucopyranosyl)-(1→3)-*O*-(2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-*O*-(2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranosyl)-(1→2)-6-*O*-acetyl-3,4-*O*-isopropylidene-α-D-galactopyranoside (71%), $[\alpha]_{578}$ +120° (*c* 1.1, chloroform). $^{13}C$ NMR δ 18.0, 18.2 (C-6´, C-6´´), 20.5, 20.7, 20.7, 20.9 (4 Me acetyl), 26.5, 28.3 (Me isopropylidene), 55.5 (OMe), 60.3-80.6 (ring C, benzyl), 93.2, 98.1, 99.0, 99.3 (4 C-1, $^1J_{C,H}$ = 174 Hz, 173 Hz, 170 Hz and 171 Hz, respectively), 109.7 (isopropylidene), 127.3-138.0 (aromatic C), 165.6, 165.7 (2 benzoyl C=O), 169.6, 179.9, 170.5, 170.9 (4 acetyl C=O).

Anal. Calcd for $C_{64}H_{75}N_3O_{24}$: C, 60.5; H, 6.0; N, 3.3. Found: C, 60.4; H, 5.9; N, 3.2.

Methyl *O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranosyl)-(1→3)-*O*-(2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-*O*-(2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranosyl)-(1→2)-6-*O*-acetyl-3,4-*O*-isopropylidene-α-D-galactopyranoside (72%), $[\alpha]_{578}$ +96° (*c* 1.0, chloroform). $^{13}C$ NMR δ 17.9, 18.3 (C-6´, C-6´´), 20.6, 20.7, 20.7, 21.0 (4 Me acetyl), 22.4 (Me *N*-acetyl), 26.5, 28.3 (Me isopropylidene), 51.1 (C-2´´´) 55.5 (OMe), 61.1-80.5 (ring C, benzyl), 93.7, 98.1, 99.0, 99.1 (4 C-1, $^1J_{C,H}$ = 172 Hz, 173 Hz, 171 Hz and 171 Hz, respectively), 109.7 (isopropylidene), 127.0-137.7 (aromatic C), 165.3, 165.6 (2 benzoyl C=O), 169.1, 169.9, 170.6, 171.3 (4 acetyl C=O).

Anal. Calcd for $C_{66}H_{79}NO_{25}$: C, 61.6; H, 6.2; N, 1.1. Found: C, 62.3; H, 6.5; N, 1.1.

**2-(*p*-Trifluoroacetamidophenyl)ethyl *O*-(2-Acetamido-2-deoxy-α-D-glucopyranosyl)-(1→3)-*O*-α-L-rhamnopyranosyl-(1→3)-*O*-α-L-rhamnopyranosyl-(1→2)-α-D-galactopyranoside (16A).** Compound **15A** (15 mg, 10 μmol) was deprotected as described for the preparation of **12A**. Chromatography on Bio-Gel P2 (1% aqueous 1-butanol) gave **16A** (7.3 mg, 81%), $[\alpha]_{578}$ +74° (*c* 1.0, water). $^{13}C$ NMR ($D_2O$, 60 °C, $Me_2CO$, $\delta_C$ at 31.07): δ 17.6 (C-6′, C-6′′), 22.8 (Me *N*-acetyl), 35.5 ($PhCH_2CH_2$), 54.5 (C-2′′′), 61.4, 61.8 (C-6, C-6′′′), 67.9-79.2 (ring C, $PhCH_2CH_2$), 95.3, 98.4, 102.8, 103.4 (4 C-1, $^1J_{C,H}$ = 170 Hz, 170 Hz, 172 Hz and 169 Hz, respectively), 123.2-138.8 (aromatic C), 175.2 (acetamido C=O).

**Methyl *O*-(2-Acetamido-2-deoxy-α-D-glucopyranosyl)-(1→3)-*O*-α-L-rhamnopyranosyl-(1→3)-*O*-α-L-rhamnopyranosyl-(1→2)-α-D-galactopyranoside (16B).** Compound **15B** (22 mg, 17 μmol) was deprotected as described for the preparation of **12B**. Chromatography on Bio-Gel P2 (1% aqueous *n*-butanol) gave **16B** (9.6 mg, 81%), $[\alpha]_{578}$ +81° (*c* 1.0, water). $^{13}C$ NMR ($D_2O$, 60 °C, $Me_2CO$, $\delta_C$ 31.07): δ 17.6 (C-6', C-6"), 22.8 (Me *N*-acetyl, 54.4 (OMe), 55,7 (C-2'"), 61.5 (C-6'") 61.9 (C-6), 67.9-72.8 (ring C), 76.6 (C-3"), 78.0 (C-2), 78.7 (C-3'), 95.3 (C-1'"), 99.7 (C-1), 102.7 (C-1"), 103.3 (C-1'), 175.1 (acetamido C=O).



## ACKNOWLEDGEMENT

We thank the Swedish National Board for Technical Development and the Swedish Natural Science Research Council for financial support.

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