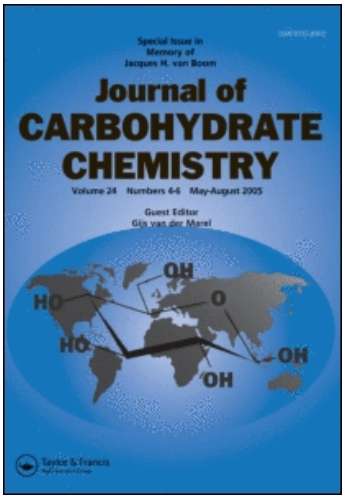

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Synthesis of 2-(*p*-Trifluoroacetamidophenyl)ethyl *O*-β-D-Mannopyranosyl-(2)-*O*-α-D-Mannopyranosyl-(2)-*O*-[α-D-Glucopyranosyl-(1→3)]-*O*-α-D-Mannopyranosyl-(1→2)-*O*-β-D-Manpopyranosyl-(1→3)-2-Acetamido-2-Deoxy-β-D-Gluco-Pyranoside, Corresponding to the Repeating Unit of the *Salmonella Thompson*, Serogroup C_1 O-Antigen Lipopolysaccharide, and of a Pentasaccharide Fragment Thereof

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SYNTHESIS OF 2-(*p*-TRIFLUOROACETAMIDOPHENYL)ETHYL *O*-β-D-MANNOPYRANOSYL-(1→2)-*O*-α-D-MANNOPYRANOSYL-(1→2)-*O*-[α-D-GLUCOPYRANOSYL-(1→3)]-*O*-α-D-MANNOPYRANOSYL-(1→2)-*O*-β-D-MANNOPYRANOSYL-(1→3)-2-ACETAMIDO-2-DEOXY-β-D-GLUCOPYRANOSIDE, CORRESPONDING TO THE REPEATING UNIT OF THE *SALMONELLA THOMPSON*, SEROGROUP C_1 O-ANTIGEN LIPOPOLYSACCHARIDE, AND OF A PENTASACCHARIDE FRAGMENT THEREOF

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ABSTRACT

2-(*p*-Trifluoroacetamidophenyl)ethyl *O*-β-D-mannopyranosyl-(1→2)-*O*-α-D-mannopyranosyl-(1→2)-*O*-[α-D-glucopyranosyl-(1→3)]-*O*-α-D-mannopyranosyl-(1→2)-*O*-β-D-mannopyranosyl-(1→3)-2-acetamido-2-deoxy-β-D-glucopyranoside was synthesized. The main glycosylation method used was activation of thioglycosides with either dimethyl(methylthio)sulfonium triflate (DMTST), *N*-iodosuccinimide (NIS)/silver triflate or iodonium dicollidine perchlorate (IDCP).

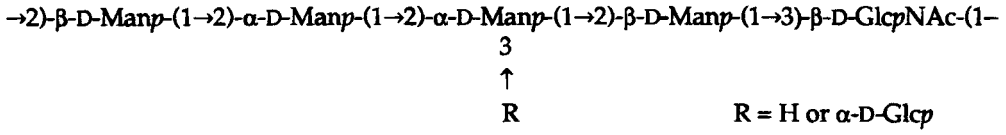


Figure 1.

INTRODUCTION

The structure of the O-antigen lipopolysaccharide of *Salmonella thompson* , serogroup C_1 has the repeating unit depicted in Figure 1.[1]

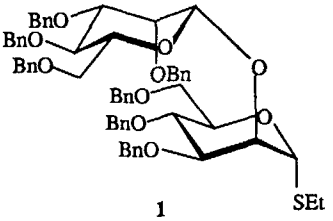
There are two populations of chains, with or without an α-D-glucopyranosyl group 3-linked to the central α-D-mannopyranosyl residue. In order to determine the specificity of monoclonal antibodies which recognize the structure in Figure 1, the 2-(*p*-trifluoroacetamidophenyl)ethyl glycoside[2] of both have been synthesized.

RESULTS AND DISCUSSION

Key intermediates in the synthesis of the title hexasaccharide were the disaccharides **1, 3** and **9**. The 1-thioglycoside disaccharides **1** and **3** were synthesized using totally different strategies, as follows.

The disaccharide **1** was obtained in 77% yield by condensing ethyl 3,4,6-tri-*O*-benzyl-1-thio-α-D-mannopyranoside[3] with 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl bromide[4] using silver silicate[5] as promoter (18% of the corresponding α-isomer was also isolated). Disaccharide **3** was synthesized by a chemoselective condensation of ethyl 2-*O*-benzoyl-4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside[6] **2** ("disarmed acceptor"), with ethyl 2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-glucopyranoside[7] ("armed donor") using IDCP[8] as promoter (59%). (18% of the β-isomer was also formed, but no other disaccharide formed by self-condensation could be detected). It should be noticed that in the preparation of **2** *via* the 2,3-orthoester a 1,2-ethylthio group migration, recently reported by Auzanneau and Bundle,[9] occured if the reaction was performed in acetonitrile yielding **19** (22%).[10] This by-

Scheme 1



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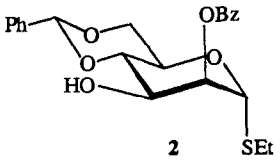

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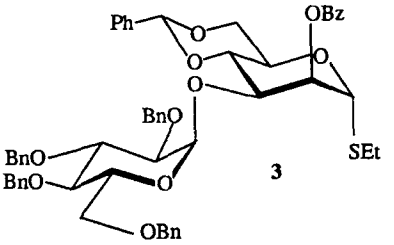

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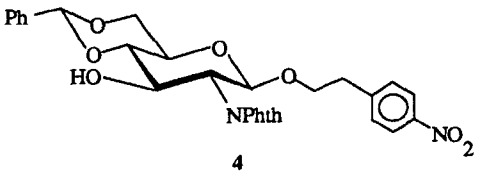

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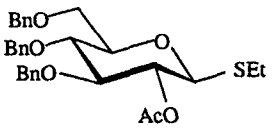

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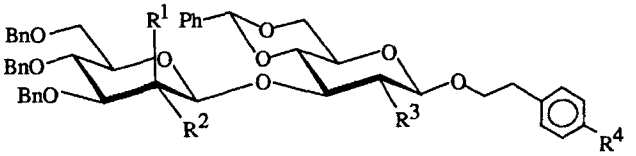


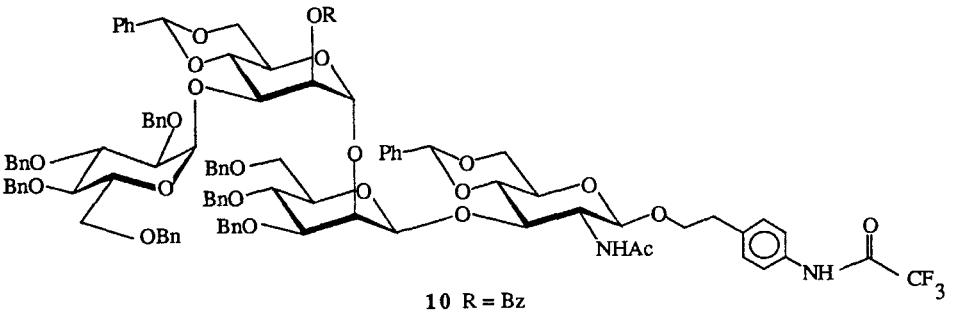
6 R^1 = H, R^2 = OAc, R^3 = NPhth, R^4 = NO_2

7 R^1 = H, R^2 = OH, R^3 = NHAc, R^4 = NO_2

8 R^1 = H, R^2 = OH, R^3 = NHAc, R^4 = $NHCOCF_3$

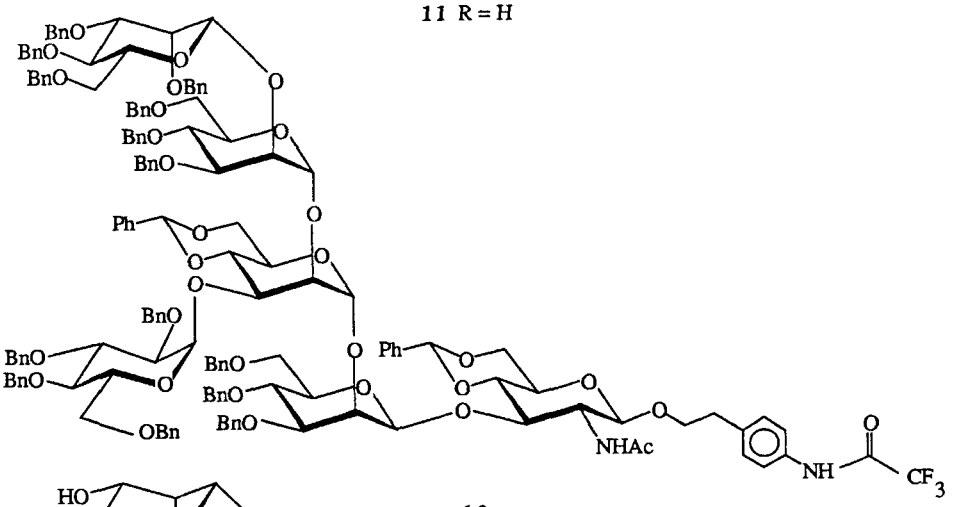
9 R^1 = OH, R^2 = H, R^3 = NHAc, R^4 = $NHCOCF_3$

Scheme 2



10 R = Bz

11 R = H



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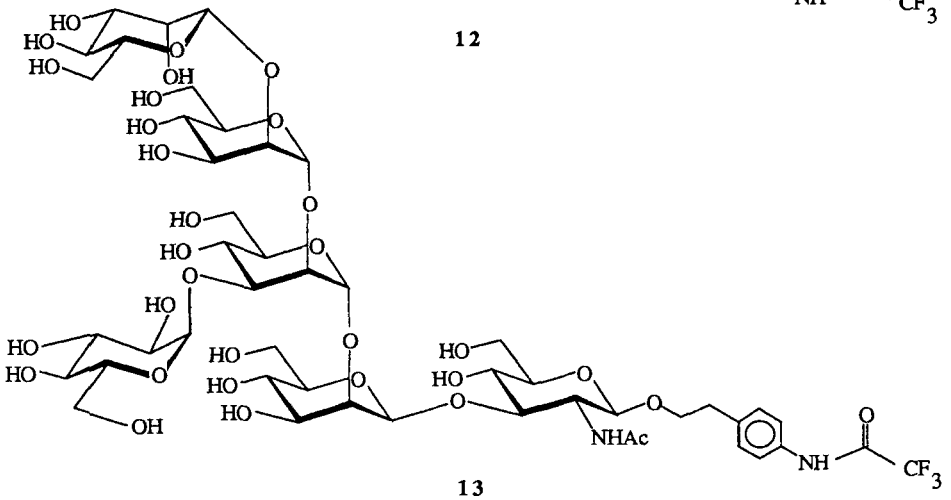

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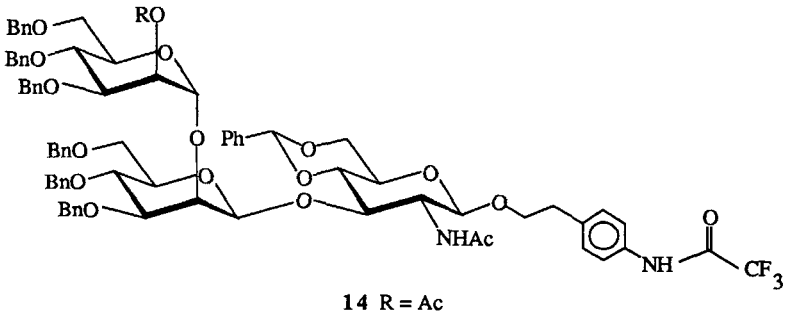
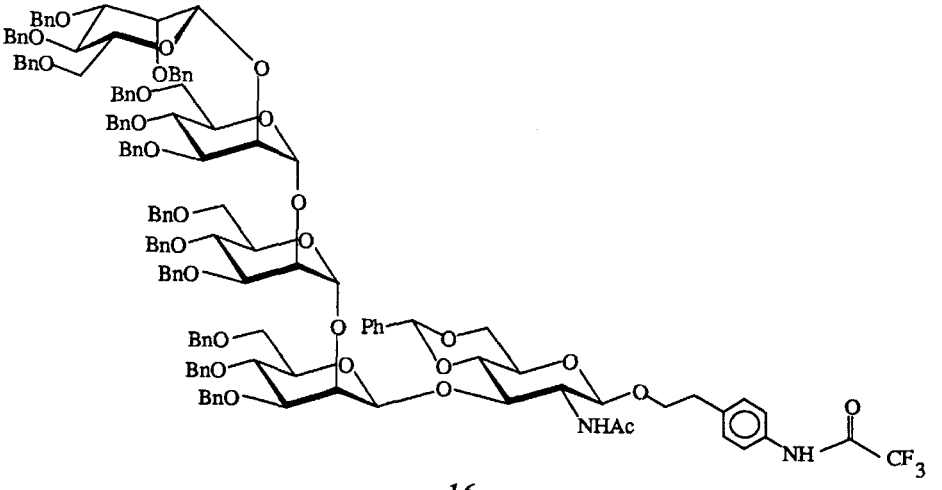
Scheme 3



14 R = Ac
15 R = H



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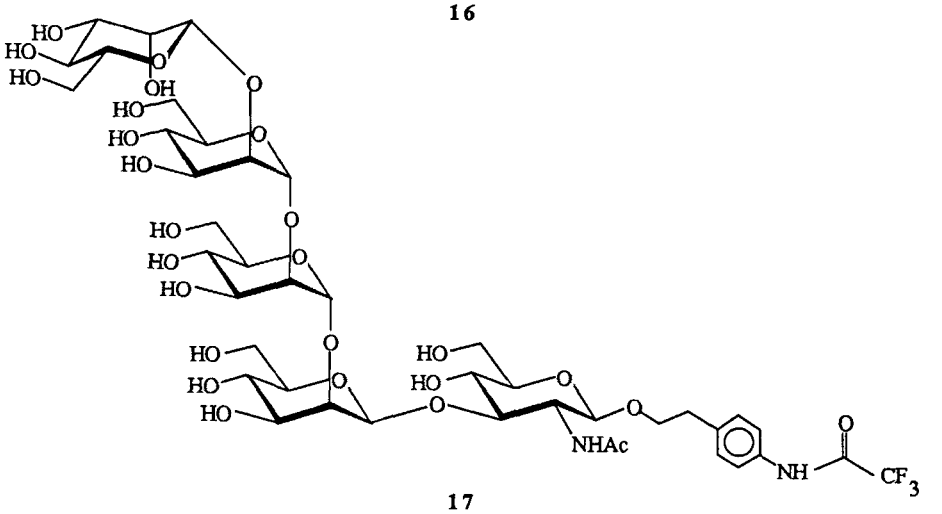

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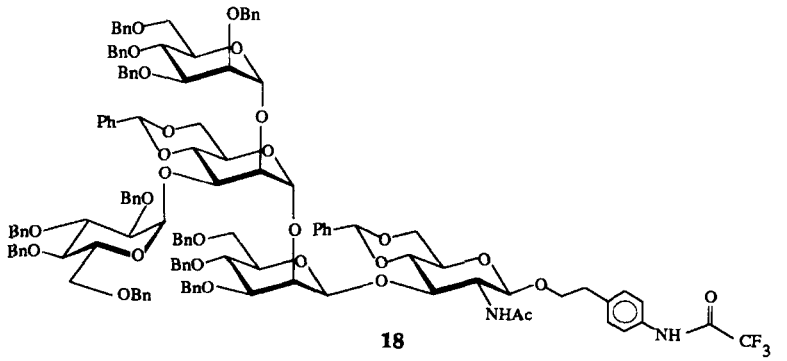
Scheme 4



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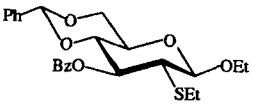

19

product could be avoided if the reaction was performed in *N,N*-dimethylformamide.

In the route to **9**, ethyl 4,6-*O*-benzylidene-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside[11] was condensed with 2-(*p*-nitrophenyl)ethanol, using DMTST[12] as promoter, to give **4** (84%). 1,2-di-*O*-acetyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranose[13] was thioglycosylated[14] to give **5** (84%), which was condensed with **4** using NIS/AgOTf[15] as promoter, and gave **6** (64%). The disaccharide **6** was taken through the following steps: hydrazinolysis, *N*-acetylation, NO_2-reduction, *N*-trifluoroacetylation and gave **8** (61%). The epimerisation of **8** into the desired *manno*-configuration was accomplished by a DMSO/acetic anhydride (Albright-Goldman)[16] oxidation, directly followed by sodium borohydride reduction, giving **9** (80%, *manno:gluco*, 10:1). The β-mannosylglucosamine disaccharide **9** was condensed with **3**, using DMTST as promoter, and gave tetrasaccharide **10** (75%). Debenzoylation followed by DMTST-promoted glycosylation with **1** gave the desired hexasaccharide **12** (24%). Hydrogenolysis of the latter compound gave the title hexasaccharide **13** (43%).

The pentasaccharide **17** was synthesized in a similar way. Starting once again from disaccharide **9**, and glycosylating this time with ethyl 2-*O*-acetyl-

3,4,6-tri-O-benzyl-1-thio-α-D-mannopyranoside,[17] the trisaccharide **14** was obtained (76%). Zemplén deacetylation of **14** gave **15**, which was condensed with **1**, and gave the protected pentasaccharide **16** (56%). Hydrogenolysis of **16** gave the desired pentasaccharide **17** (63%).

Surprisingly, a pentasaccharide **18** was also formed (7 %) in the DMTST-promoted glycosylation of tetrasaccharide **11** with disaccharide **1** (Scheme 1). This "side-reaction" has earlier been encountered at our department, but never reported. Common in all are loss of one glycosyl residue due to cleavage of a glycosidic bond, in the glycosyl donor, under prolonged glycosylating conditions. In this particular case this cleavage gives 2,3,4,6-tetra-O-benzyl-D-mannopyranosylium cation as the glycosylating agent and not the expected 3,4,6-tri-O-benzyl-2-O-(2,3,4,6-tetra-O-benzyl-β-D-mannopyranosyl)-D-mannopyranosylium cation. Both halide- and thioglycoside mediated condensations are prone to this misbehavior.

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. All ^1H assignments are based on 2D experiments and within 0.01 ppm accuracy. For some compounds ^1H shift values and coupling constants (values in parentheses) are given in table form. In these tables the sugar residues are given as α-ManA, α-ManB etc. where A and B designations are arbitrary. The FAB-MS spectra were recorded using a JEOL SX102 instrument. Ions were produced by a beam of xenon atoms (4-6 keV), using a matrix consisting of glycerol, thioglycerol or *m*-nitrobenzyl alcohol. 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 Analytische Laboratorien (Engelskirchen, Germany).

Ethyl 3,4,6-Tri-*O*-benzyl-2-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-mannopyranosyl)-1-thio-α-D-mannopyranoside (1). A mixture of ethyl 3,4,6-tri-*O*-benzyl-1-thio-α-D-mannopyranoside (88 mg, 178 μmol) and silver silicate (355 mg) in dichloromethane (10 mL) containing ground molecular sieves (4Å) was stirred at room temperature for 5 min. 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl bromide[18] (215 mg, 356 μmol) in a minimal amount of dichloromethane was added, and after 16 h the mixture was filtered through Celite and concentrated. Column chromatography (flash, light petroleum-ethyl acetate, 5:1) gave **1** (139 mg, 77%), $[\alpha]_{578}$ -27° (*c* 1.0, chloroform) and the corresponding α-isomer (31 mg, 18%), $[\alpha]_{578}$ +41° (*c* 1.1, chloroform). ^{13}C NMR δ 15.0 ($SCH_2\underline{C}H_3$), 25.6 ($S\underline{C}H_2CH_3$), 68.9-81.4 (ring C, benzyl), 81.7 (C-1, $^1J_{C,H}$ = 163 Hz), 98.6 (C-1', $^1J_{C,H}$ = 154 Hz), 127.2-139.0 (aromatic C); ^1H NMR (400 MHz) data are shown in the following table;

	H-1	H-2	H-3	H-4	H-5	H-6
β-Man	4.63 (NR)	4.06	3.53	3.90	3.48	3.70, 3.75
α-Man	5.45 (1.4)	4.52	3.88	3.95	4.12	3.63, 3.74

Anal. Calcd for $C_{63}H_{68}O_{10}S$: C, 74.4; H, 6.7. Found: C, 74.5; H, 6.7.

^{13}C NMR (for the α-isomer) δ 15.1 ($SCH_2\underline{C}H_3$), 25.6 ($S\underline{C}H_2CH_3$),69.4-80.5 (ring C, benzyl), 84.0 (C-1, $^1J_{CH}$ 167 Hz), 99.9 (C-1', $^1J_{CH}$ 170 Hz), 127.5-138.7 (aromatic C).

Ethyl 2-*O*-Benzoyl-4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside (2). *p*-Toluenesulphonic acid (5 mg, cat) was added at room temperature to a stirred solution of ethyl 4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside[6] (100 mg, 0.32 mmol) and triethyl orthobenzoate (150 μL, 0.64 mmol) in *N*, *N*-dimethylformamide (1 mL). After 30 min, aqueous trifluoroacetic acid (90%, 50 μL) was added. When TLC (light petroleum-ethyl acetate, 5:2) indicated no further reaction, triethylamine (500 μL) was added and the solution was concentrated. Column chromatography (light petroleum-ethyl acetate, 7:2) gave **2** (111 mg, 83%), mp 59-62 °C (from toluene-light petroleum), $[\alpha]_{578}$ +63° (*c* 0.5, chloroform), lit.[6] $[\alpha]_D$ +49.5°. ^{13}C NMR δ 15.1 ($SCH_2\underline{C}H_3$), 25.9 ($S\underline{C}H_2CH_3$), 64.2-79.8 (ring C), 83.5 (C-1), 102.4 (Ph$\underline{C}$H), 126.4-137.2 (aromatic C), 166.1 (benzoyl C=O).

Ethyl 2-*O*-Benzoyl-4,6-*O*-benzylidene-3-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-1-thio-α-D-mannopyranoside (3). IDCP[20] (126 mg 268 μmol) was added at room temperature to a stirred mixture of ethyl 2,3,4,6-tetra-*O*-

benzyl-1-thio-β-D-glucopyranoside (86 mg, 147 μmol) and **2** (56 mg, 134 μmol) in diethyl ether (10 mL) containing ground molecular sieves (4Å) under nitrogen. When TLC (light petroleum-ethyl acetate, 5:2) indicated no further reaction, the mixture was filtered through Celite. The filtrate was partitioned between dichloromethane and 10% aqueous sodium thiosulfate, the organic layer was dried ($MgSO_4$), filtered, and concentrated. Column chromatography (toluene-ethyl acetate, 40:1) gave **3** (75 mg, 59 %), $[\alpha]_{578}$ +56° (*c* 1.1, chloroform) and the corresponding β-isomer (23 mg, 18 %), $[\alpha]_{578}$ +12° (*c* 1.1, chloroform). ^{13}C NMR δ 15.1 ($SCH_2\underline{C}H_3$), 25.7 ($S\underline{C}H_2CH_3$), 64.4-83.6 (C-1, ring C, benzyl), 97.5 (C-1′), 102.4 (Ph$\underline{C}$H), 126.5-138.9 (aromatic C), 166.1 (benzoyl C=O); ^1H NMR data are shown in the following table;

	H-1	H-2	H-3	H-4	H-5
Man	5.45 (1.1)	5.56	4.46	4.28	ND
Glc	5.43 (3.5)	3.44	3.73	3.54	3.84

Anal. Calcd for $C_{56}H_{58}O_{11}S$: C, 71.6; H, 6.2. Found: C, 71.7; H, 6.3.

^{13}C NMR (for the corresponding β-isomer) δ 15.1 ($SCH_2\underline{C}H_3$), 25.9 ($S\underline{C}H_2CH_3$), 64.9-84.8 (C-1, ring C, benzyl), 101.3, 102.2 (C-1′, Ph$\underline{C}$H), 126.5-138.7 (aromatic C), 165.8 (benzoyl C=O); ^1H-NMR δ 4.62 (d, 1H, $J_{1,2}$ = 7.3 Hz, H-1′), 5.43 (d, 1H. $J_{1,2}$ = 1.5 Hz, H-1).

2-(*p*-Nitrophenyl)ethyl 4,6-*O*-Benzylidene-2-deoxy-2-phthalimido-β-D-glucopyranoside (4). DMTST (4.5 g, 17.4 mmol) was added at room temperature to a stirred mixture of 2-(*p*-nitrophenyl)ethanol (2.90 g, 17.2 mmol) and ethyl 4,6-*O*-benzylidene-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (5.1 g, 11.6 mmol) in dichloromethane (300 mL) containing ground molecular sieves (4Å) under nitrogen. When TLC (light petroleum-ethyl acetate, 5:2) indicated complete reaction, triethylamine (5 mL) was added and the mixture was stirred for another 5 min. 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 (light petroleum-ethyl acetate, 3:2) gave **4** (5.27 g, 84%), mp 109-110 °C (from methanol), $[\alpha]_{578}$ -63° (*c* 0.6, chloroform). ^{13}C NMR δ 35.4 ($Ph\underline{C}H_2CH_2$), 56.4 (C-2), 66.4-82.2 (ring C, $PhCH_2\underline{C}H_2$), 98.8, 102.0 (C-1, Ph$\underline{C}$H), 123.1-146.6 (aromatic C), 167.8, 168.0 (phthalimido C=O).

Anal. Calcd for $C_{29}H_{26}N_2O_9$: C, 63.7; H, 4.8; N, 5.1. Found: C, 63.5; H,4.9; N, 5.0.

Ethyl 2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (5). Boron trifluoride etherate (345 μL, 2.8 mmol) was added at room temperature to a stirred mixture of 1,2-di-*O*-acetyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranose (1.0 g, 1.9 mmol) and ethanethiol (152 μL, 2.0 mmol) in dichloromethane (50 mL) containing ground molecular sieves (4Å). When TLC (toluene-ethyl acetate, 15:1) indicated complete reaction, the mixture was filtered through Celite and 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, 15:1) gave **5** (843 mg, 84%), $[\alpha]_{578}$ +1° (*c* 1.0, chloroform). ^{13}C NMR δ 14.6 ($SCH_2\underline{C}H_3$), 20.3 (Me acetyl), 23.2 ($S\underline{C}H_2CH_3$), 68.4-82.9 (ring C, benzyl), 84.0 (C-1), 127.1-138.2 (aromatic C), 168.9 (acetyl C=O).

Anal. Calcd for $C_{31}H_{36}O_6S$: C, 69.4; H, 6.8. Found: C, 69.1; H, 6.6.

2-(*p*-Nitrophenyl)ethyl 3-*O*-(2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-β-D-glucopyranoside (6). NIS (237 mg, 1.0 mmol), immediately followed by a solution of silver triflate (27.1 mg, 0.10 mmol) in toluene (1 mL) were added at room temperature to a stirred mixture of **4** (360 mg, 0.66 mmol) and **5** (530 mg, 0.99 mmol) in dichloromethane (20 mL) containing ground molecular sieves (4Å). When TLC (light petroleum-ethyl acetate, 5:2) indicated complete reaction, the reaction mixture was filtered through Celite. The filtrate was partitioned between dichloromethane and 10% aqueous sodium thiosulfate. The organic layer was dried ($MgSO_4$), filtered and concentrated. Column chromatography (light petroleum-ethyl acetate, 2:1) gave **6** (464 mg, 64%), mp 78-81 °C (from methanol), $[\alpha]_{578}$ -23° (*c* 1.0, chloroform). ^{13}C NMR δ 19.9 (Me acetyl), 35.2 ($PhC\underline{H}_2CH_2$), 55.0 (C-2), 66.5-82.7 (ring C, $PhCH_2\underline{C}H_2$, benzyl), 98.4, 99.9, 101.4 (2 C-1, $Ph\underline{C}H$, $^1J_{C,H}$ = 167 Hz, 161 Hz and 167 Hz, respectively), 122.9-146.5 (aromatic C), 168.6 (acetyl C=O); ^1H NMR (400 MHz) data are shown in the following table;

	H-1	H-2	H-3	H-4	H-5	H-6
GlcN	5.07 (8.5)	4.23	4.57	3.80	3.56	3.77, 4.30
Glc	4.37 (8.0)	4.73	3.34	3.55	2.99	3.37

Anal. Calcd for $C_{58}H_{56}N_2O_{15}$: C, 68.2; H, 5.5; N, 2.7. Found: C, 68.1; H, 5.5; N, 2.7.

2-(*p*-Nitrophenyl)ethyl 2-Acetamido-4,6-*O*-benzylidene-2-deoxy-3-*O*-(3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-β-D-glucopyranoside (7). Hydrazine hydrate (400 mL, 12 mmol) was added to a mixture of **6** (464 mg, 0.45 mmol) in toluene-methanol (1:1, 20 mL). The mixture was refluxed overnight and then concentrated. The residue was partitioned between dichloromethane and water. The organic layer was dried (Na_2SO_4), filtered, and concentrated. The residue was dissolved in dichloromethane-methanol (1:1, 40 mL) and treated with acetic anhydride (3 mL) at room temperature. After 1 h the reaction mixture was concentrated. Column chromatography (chloroform-acetone, 6:1) gave **7** (354 mg, 87%), mp 177-180 °C (from toluene), $[\alpha]_{578}$ -31° (*c* 0.7, chloroform). ^{13}C NMR δ 23.3 (Me *N*-acetyl), 35.9 ($PhCH_2CH_2$), 55.6 (C-2), 66.6-84.0 (ring C, $PhCH_2CH_2$, benzyl), 101.5, 102.0, 102.3 (2 C-1, PhCH), 123.5-147.0 (aromatic C), 171.6 (acetamido C=O).

Anal. Calcd for $C_{50}H_{54}N_2O_{13}$: C, 67.4; H, 6.1; N, 3.1. Found: C, 67.4; H, 6.0; N, 3.1.

2-(*p*-Trifluoroacetamidophenyl)ethyl 2-Acetamido-4,6-*O*-benzylidene-2-deoxy-3-*O*-(3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-β-D-glucopyranoside (8). A solution of **7** (354 mg, 0.40 mmol) in ethyl acetate (50 mL) was hydrogenated over PtO_2 at atmospheric pressure. When TLC (chloroform-acetone, 4:1) indicated complete reaction, the solution was filtered through Celite and concentrated. The residue was dissolved in dichloromethane (25 mL) containing pyridine (0.64 mL). Trifluoroacetic anhydride (234 μL, 1.6 μmol) was added at 0 °C, and after 10 min, methanolic sodium methoxide (1.0 M, 5 mL). When TLC (chloroform-methanol, 5:1) indicated complete reaction, acetic acid (1 mL) was added and the mixture was concentrated. Column chromatography (chloroform-acetone, 5:1) gave **8** (265 mg, 70 %), mp 178-180 °C (from ethyl acetate-isooctane), $[\alpha]_{578}$ -22° (*c* 0.8, chloroform). ^{13}C NMR δ 23.0 (Me *N*-acetyl), 35.2 ($PhCH_2CH_2$), 55.5 (C-2), 66.3-84.2 (ring C, $PhCH_2CH_2$, benzyl), 101.7 (C-1), 101.9 (PhCH), 102.5 (C-1′), 120.8-138.6 (aromatic C), 171.8 (acetamido C=O); ^1H NMR (400 MHz, $CDCl_3$-MeOH-d_4, 9:1, 40 °C) data are shown in the following table;

	H-1	H-2	H-3	H-4	H-5	H-6
GlcN	4.56 (8.4)	3.74	4.08	3.65	3.44	3.77, 4.32
Glc	4.35 (8.1)	3.50	3.475	3.54	3.33	3.54, 3.60

Anal. Calcd for $C_{52}H_{55}F_3N_2O_{12}$: C, 65.3; H, 5.8; N, 2.9. Found: C, 65.2; H, 5.9; N, 2.8.

2-(*p*-Trifluoroacetamidophenyl)ethyl 2-Acetamido-4,6-*O*-benzylidene-2-deoxy-3-*O*-(3,4,6-tri-*O*-benzyl-β-D-mannopyranosyl)-β-D-glucopyranoside (9). A solution of **8** (518 mg, 541 μmol) in DMSO-acetic anhydride (2:1, 50 mL) was stirred for 16 h. The mixture was lyophilized and the crude product [^{13}C NMR δ 22.6 (Me *N*-acetyl), 34.5 ($PhC\underline{H}_2CH_2$), 54.6 (C-2), 65.5-84.8 (ring C, $PhCH_2\underline{C}H_2$, benzyl), 98.5, 100.0, 100.6 (C-1, C-1′, $Ph\underline{C}H$), 120.7-138.0 (aromatic C), 168.9 (acetamido C=O), 197.1 (C-2′)] was dissolved in dichloromethane-ethyl acetate (1:1, 50 mL). Sodium borohydride (50 mg) was added to the stirred solution at 0 °C and after 5 min acetic acid (1 mL). When the evolution of gas ceased, the mixture was concentrated and co-evaporated several times from methanol-acetic acid (10:1). Column chromatography (chloroform-acetone, 4:1) gave **9** (414 mg, 80%), mp >230 °C (from ethyl acetate-isooctane), $[\alpha]_{578}$ -29° (*c* 0.6, chloroform-methanol, 9:1). ^{13}C NMR δ 22.8 (Me *N*-acetyl), 35.3 ($PhC\underline{H}_2CH_2$), 56.5 (C-2), 66.1-81.3 (ring C, $PhCH_2\underline{C}H_2$, benzyl), 99.1 (C-1′), 101.0 (C-1), 101.5 ($Ph\underline{C}H$), 115.9 ($\underline{C}F_3C{=}O$, $^1J_{C,F}$ = 288 Hz) 120.8-138.0 (aromatic C), 155.5 ($CF_3\underline{C}{=}O$, $^2J_{C,F}$ = 38 Hz) 171.7 (acetamido C=O); ^1H NMR (400 MHz, $CDCl_3$-MeOH-d_4, 9:1) data are shown in the following table;

	H-1	H-2	H-3	H-4	H-5	H-6
GlcN	4.71	3.56	4.35	3.69	3.46	3.76, 4.32
Man	4.59	3.97	3.45	3.76	3.25	3.61

Anal. Calcd for $C_{52}H_{55}F_3N_2O_{12}$: C, 65.3; H, 5.8; N, 2.9. Found: C, 65.0; H, 5.9; N, 2.9.

2-(*p*-Trifluoroacetamidophenyl)ethyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→3)-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-benzyl-β-D-mannopyranosyl)-(1→3)-2-acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (10). DMTST (18 mg, 68 μmol) was added at room temperature to a stirred mixture of **9** (65 mg, 68 μmol) and **3** (64 mg, 68 μmol) in dichloromethane (5 mL) containing ground molecular sieves (4Å) under nitrogen. After 6 h, DMTST (18 mg, 68 μmol) and **3** (64 mg, 68 μmol) were added and the mixture was stirred overnight. The reaction mixture was processed as described for the preparation of **4**. Column chromatography (toluene-ethyl acetate, 3:2) gave

10 (94 mg, 75%), $[\alpha]_{578}$ -6° (*c* 1.1, chloroform). ^{13}C NMR δ 23.4 (Me *N*-acetyl), 35.6 ($PhCH_2CH_2$), 59.3 (C-2), 62.8-83.1 (ring C, $PhCH_2CH_2$, benzyl), 97.1 (C-1 α-Glc, $^1J_{C,H}$ = 171 Hz), 98.2 (C-1 α-Man, $^1J_{C,H}$ = 178 Hz), 99.1 (C-1 β-Man, $^1J_{C,H}$ = 156 Hz), 99.4 (C-1 β-GlcN, $^1J_{C,H}$ = 165 Hz), 101.2 (PhCH, $^1J_{C,H}$ = 164 Hz), 102.7 (PhCH, $^1J_{C,H}$ = 164 Hz) 115.9 (CF_3C=O, $^1J_{C,F}$ = 289 Hz), 120.5-139.0 (aromatic C), 154.8 (CF_3C=O, $^2J_{C,F}$ = 38 Hz), 165.9 (benzoyl C=O), 171.3 (acetamido C=O); ^1H NMR data are shown in the following table;

	H-1	H-2	H-3	H-4
α-Glc	5.46 (3.7)	3.38	3.68	3.60
β-GlcN	5.11 (8.1)	3.15	4.74	3.87
α-Man	5.55 (NR)	5.73	4.66	4.24
β-Man	4.59 (NR)	4.18	3.48	ND

2-(*p*-Trifluoroacetamidophenyl)ethyl *O*-(2,3,4,6-Tetra-*O*-benzyl-β-D-mannopyranosyl)(1→2)-*O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-*O*-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→3)]-*O*-(4,6-*O*-benzylidene-*O*-α-D-mannopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-benzyl-β-D-mannopyranosyl)-(1→3)-2-acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (12). Methanolic sodium methoxide (1.0 M, 4 mL) was added at room temperature to a solution of **10** (63 mg, 34 μmol) in dichloromethane (4 mL). After 1.5 h, Dowex 50W-X8 (H^+ form) was added and the mixture was stirred for another 5 min. The reaction mixture was filtered, concentrated and gave crude 2-(*p*-trifluoroacetamidophenyl)ethyl *O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→3)-*O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-benzyl-β-D-mannopyranosyl)-(1→3)-2-acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside **11** which was used without any further purification. An analytical sample was obtained after column chromatography (toluene-ethyl acetate, 1:1), $[\alpha]_{578}$ +11° (*c* 0.6, chloroform). ^{13}C NMR δ 23.5 (Me *N*-acetyl), 35.6 ($PhCH_2CH_2$), 59.3 (C-2), 63.0-83.2 (ring C, $PhCH_2CH_2$, benzyl), 97.1, 99.4, 99.4, 100.0, 101.2, 102.7 (4 C-1, 2 PhCH), 115.9 (CF_3C=O, $^1J_{C,F}$ = 289 Hz), 120.5-138.9 (aromatic C), 154.8 (CF_3C=O, $^2J_{CF}$ = 37 Hz), 171.2 (acetamido C=O).

DMTST (19 mg, 76 μmol) was added at room temperature to a stirred mixture of **11** (65 mg, 38 μmol) and **1** (76 mg, 76 μmol) in dichloromethane (5 mL) containing ground molecular sieves (4Å) under nitrogen. After 6 h, DMTST (19 mg, 76 μmol) and **1** (76 mg, 76 μmol) were added and the

mixture was stirred overnight. The reaction mixture was processed as described for the preparation of **4**. Column chromatography (toluene-ethyl acetate, 5:2) gave **12** (24 mg, 24%), $[\alpha]_{578}$ -13° (*c* 0.6, chloroform); 11 mg **11** (17%) was recovered. ^{13}C NMR δ 23.5 (Me *N*-acetyl), 35.6 ($PhCH_2CH_2$), 59.6 (C-2), 63.7-83.3 (ring C, $PhCH_2CH_2$, benzyl), 97.2 (C-1 α-Glc, $^1J_{C,H}$ = 172 Hz), 98.8 (C-1 β-ManB, $^1J_{C,H}$ = 158 Hz), 99.3† (C-1 α-ManB, $^1J_{C,H}$ = 167 Hz), 99.9 (C-1 β-ManA, $^1J_{C,H}$ = 152 Hz), 100.0 (C-1 α-ManA, $^1J_{C,H}$ = 176 Hz), 100.1† (PhCH, $^1J_{C,H}$ = 168 Hz), 101.3 (C-1 β-GlcN, $^1J_{C,H}$ = 163 Hz),102.9 (PhCH, $^1J_{C,H}$ = 163 Hz), 120.6-139.2 (aromatic C), 171.4 (acetamido C=O); ^1H NMR (270 MHz) data are shown in the following table;

	H-1	H-2	H-3	H-4	H-5
α-Glc	5.44 (4.0)	3.46	3.81	3.63	ND
β-GlcN	5.27 (8.8)	3.07	4.69	3.82	3.52
α-ManA	5.40 (NR)	4.21	4.50	4.22	ND
α-ManB	5.25 (NR)	4.66	4.03	3.90	ND
β-ManA	4.72 (NR)	3.98	3.39	3.82	ND
β-ManB	4.42 (NR)	4.00	3.33	3.73	ND

† could be interchanged.

No destructive elemental analysis was performed on this precious compound.

2-(*p*-Trifluoroacetamidophenyl)ethyl *O*-β-D-Mannopyranosyl-(1→2)-*O*-α-D-mannopyranosyl-(1→2)-*O*-[α-D-glucopyranosyl-(1→3)]-*O*-α-D-mannopyranosyl-(1→2)-*O*-β-D-mannopyranosyl-(1→3)-2-acetamido-2-deoxy-β-D-glucopyranoside (13). **12** (16 mg, 6.0 μmol) was hydrogenolyzed in acetic acid (1 mL) over 10% Pd/C at 400 kPa overnight. The mixture was filtered through Celite and concentrated. Column chromatography on Bio-Gel P2 (1% aqueous 1-butanol) gave amorphous **13** (3.2 mg, 43%), $[\alpha]_{578}$ +34° (*c* 0.25, water); Negative ion FAB-MS showed an M-H ion at m/z 1246. ^{13}C NMR (D_2O, 30 °C, Me_2CO, δ_C at 31.07): δ 22.8 (Me *N*-acetyl), 35.2 ($PhCH_2CH_2$), 55.9 (C-2), 61.9-82.0 (ring C, $PhCH_2CH_2$), 99.8 (C-1 β-ManA, $^1J_{C,H}$ = 158 Hz), 100.2 (C-1 α-ManB, $^1J_{C,H}$ = 172 Hz), 100.5 (C-1 α-ManA, $^1J_{C,H}$ = 172 Hz), 100.7 (C-1 β-ManB, $^1J_{C,H}$ = 162 Hz), 101.3† (C-1 α-Glc $^1J_{C,H}$ = 172 Hz), 101.4† (C-1 β-GlcN, $^1J_{C,H}$ = 159 Hz), 123.1-138.8 (aromatic C), 174.6 (acetamido C=O); ^1H NMR (270 MHz, D_2O, 25 °C, Me_2CO, δ_H at 2.2307) data are shown in the following table;

	H-1	H-2	H-3	H-4
α-Glc	5.27 (3.5)	3.58	3.65	3.41
β-GlcN	4.51 (8.2)	3.67	ND	ND
α-ManA	5.31 (1.6)	4.28	4.18	3.98
α-ManB	5.26 (1.8)	4.24	3.90	3.75
β-ManA	4.76 (NR)	4.05	3.68	3.59
β-ManB	4.69 (NR)	3.93	3.70	3.58

† could be interchanged.

2-(*p*-Trifluoroacetamidophenyl)ethyl *O*-(2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-benzyl-β-D-mannopyranosyl)-(1→3)-2-acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (14). DMTST (48 mg, 180 μmol) was added at room temperature to a stirred mixture of **9** (88 mg, 92 μmol) and ethyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-1-thio-α-D-mannopyranoside (74 mg, 138 μmol) in dichloromethane (5 mL) containing ground molecular sieves (4Å) under nitrogen. The reaction mixture was processed as described for the preparation of **4**. Column chromatography (toluene–ethyl acetate, 3:2) followed by precipitation from dichloromethane–isooctane gave **14** (106 mg, 76%), $[\alpha]_{578}$ -7° (*c* 0.5, chloroform). ^{13}C NMR δ 21.2 (Me acetyl), 23.3 (Me *N*-acetyl), 35.4 ($PhCH_2CH_2$), 58.7 (C-2), 66.2-82.8 (ring C, $PhCH_2CH_2$, benzyl), 98.9 (C-1′′), 99.6 (C-1), 101.1 (PhCH), 101.5 (C-1′), 116.0 ($CF_3C=O$, $^1J_{C,F}$ = 289 Hz), 120.6-138.5 (aromatic C), 154.8 ($CF_3C=O$, $^2J_{C,F}$ = 37 Hz), 169.9 (acetyl C=O), 171.2 (acetamido C=O); ^1H NMR (400 MHz) data are shown in the following table;

	H-1	H-2	H-3	H-4	H-5	H-6
β-GlcN	5.34 (7.1)	3.00	4.62	3.68	3.51	3.71, 4.26
β-Man	4.45 (NR)	3.91	3.45	3.83	3.20	3.47, 3.59
α-Man	5.10 (1.1)	5.61	4.05	3.35	4.28	3.42, 3.64

Anal. Calcd for $C_{81}H_{85}F_3N_2O_{18}$: C, 68.0; H, 6.0; N, 2.0. Found: C, 67.9; H, 6.1; N, 1.9.

2-(*p*-Trifluoroacetamidophenyl)ethyl *O*-(2,3,4,6-tetra-*O*-benzyl-β-D-mannopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-benzyl-β-D-mannopyranosyl)-(1→3)-2-acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (16). Methanolic sodium methoxide (5 mL, 0.2 M) was added at room temperature to a stirred solution of **14** (79 mg, 55 μmol) in

dichloromethane (5 mL). After 1 h, Dowex 50W-X8 (H^+ form) was added and the mixture was stirred for another 5 min. The reaction mixture was filtered, concentrated and gave crude 2-(*p*-trifluoroacetamidophenyl)ethyl *O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-benzyl-β-D-mannopyranosyl)-(1→3)-2-acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside **15** which was used without any further purification. An analytical sample was obtained after column chromatography (chloroform-acetone, 6:1), $[\alpha]_{578}$ +6° (*c* 1.9, chloroform). ^{13}C NMR δ 23.4 (Me *N*-acetyl), 35.4 ($PhCH_2CH_2$), 58.7 (C-2), 66.1-82.8 (ring C, $PhCH_2CH_2$, benzyl), 99.6, 100.5, 101.1, 102.0 (3 C-1, PhCH), 116.0 ($CF_3C{=}O$, $^1J_{C,F}$ = 289 Hz), 120.6-138.5 (aromatic C), 154.7 ($CF_3C{=}O$, $^2J_{C,F}$ = 38 Hz), 171.4 (acetamido C=O).

DMTST (56 mg, 220 μmol) was added at room temperature to a stirred mixture of **15** (76 mg, 55 μmol) and **1** (111 mg, 110 μmol) in dichloromethane (3 mL) containing ground molecular sieves (4Å) under nitrogen. The reaction mixture was processed as described for the preparation of **4**. Column chromatography (toluene-ethyl acetate, 2:1) gave **16** (72 mg, 56%), $[\alpha]_{578}$ -17° (*c* 1.0, chloroform). ^{13}C NMR δ 23.5 (Me *N*-acetyl), 35.4 ($PhCH_2CH_2$), 59.0 (C-2), 66.3-82.4 (ring C, $PhCH_2CH_2$, benzyl), 99.0 (C-1 α-ManB, $^1J_{C,H}$ = 170 Hz), 99.5 (C-1 β-GlcN, $^1J_{C,H}$ = 165 Hz), 99.5 (C-1 β-ManB, $^1J_{C,H}$ = 153 Hz), 99.9 (C-1 α-ManA, $^1J_{C,H}$ = 172 Hz), 101.2 (PhCH, $^1J_{C,H}$ = 162 Hz), 101.4 (C-1 β-ManA, $^1J_{C,H}$ = 156 Hz), 115.9 ($CF_3C{=}O$, $^1J_{C,F}$ = 289 Hz), 120.7-139.1 (aromatic C), 154.7 ($CF_3C{=}O$, $^2J_{C,F}$ = 38 Hz), 171.2 (acetamido C=O); ^1H NMR (400 MHz) data are shown in the following table;

	H-1	H-2	H-3	H-4	H-5
β-GlcN	5.32 (8.2)	2.89	4.54	3.60	3.43
α-ManA	5.10 (NR)	4.16	3.93	3.23	ND
α-ManB	4.93 (1.1)	4.25	3.84	ND	ND
β-ManA	4.26 (NR)	3.73	3.22	3.92	ND
β-ManB	4.07 (NR)	3.77	3.13	3.71	ND

No destructive elemental analysis was performed on this precious compound.

2-(*p*-Trifluoroacetamidophenyl)ethyl *O*-(β-D-Mannopyranosyl)-(1→2)-*O*-(α-D-mannopyranosyl)-(1→2)-*O*-(α-D-mannopyranosyl)-(1→2)-*O*-(β-D-mannopyranosyl)-(1→3)-2-acetamido-2-deoxy-β-D-glucopyranoside (17). 16 (27 mg, 12 μmol) was hydrogenolyzed in acetic acid (1 mL) over 10% Pd/C at 400 kPa overnight. The mixture was filtered through Celite and

concentrated. Column chromatography on Bio-Gel P2 (1% aqueous 1-butanol) gave amorphous **17** (8.0 mg, 63%), $[\alpha]_{578}$ +6° (*c* 0.5, water); Negative ion FAB-MS showed an M-H ion at m/z 1084. ^{13}C NMR (D_2O, 25°C, Me_2CO, δ_C at 31.07): δ 22.8 (Me *N*-acetyl), 35.3 ($PhCH_2CH_2$), 55.9 (C-2), 61.3-82.7 (ring C, $PhCH_2CH_2$), 99.4 (C-1 β-ManA, $^1J_{C,H}$ = 160 Hz), 100.4 (C-1 α-ManA, $^1J_{C,H}$ = 176 Hz), 100.7 (C-1 β-ManB, $^1J_{C,H}$ = 160 Hz), 100.8 (C-1 α-ManB, $^1J_{C,H}$ = 172 Hz), 101.4 (C-1 β-GlcN $^1J_{C,H}$ = 155 Hz), 123.1-138.8 (aromatic C), 174.6 (acetamido C=O); ^1H NMR (400 MHz, D_2O, 30 °C, Me_2CO, δ_H at 2.228) data are shown in the following table;

	H-1	H-2	H-3	H-4
β-GlcN	4.50 (8.0)	3.68	ND	ND
α-ManA	5.34 (1.4)	4.11	4.01	3.75
α-ManB	5.15 (1.2)	4.28	3.88	3.74
β-ManA	4.79 (NR)	4.04	3.66	3.58
β-ManB	4.68 (NR)	3.94	3.69	3.60

2-(*p*-Trifluoroacetamidophenyl)ethyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-*O*-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→3)]-*O*-(4,6-*O*-benzylidene-α-D-mannopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-benzyl-β-D-mannopyranosyl)-(1→3)-2-acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (18). This compound was isolated as a by-product (7%) in the preparation of **12**. Physical data: $[\alpha]_{578}$ +2° (*c* 0.5, chloroform); Positive ion FAB-MS showed an M+H ion at m/z 2252. ^{13}C NMR δ 23.6 (Me *N*-acetyl), 35.6 ($PhCH_2CH_2$), 59.6 (C-2), 63.5-83.2 (ring C, $PhCH_2CH_2$, benzyl), 97.3 (C-1 α-Glc, $^1J_{C,H}$ = 174 Hz), 98.8 (C-1 β-Man, $^1J_{C,H}$ = 158 Hz), 99.3 (C-1 β-GlcN, $^1J_{C,H}$ = 167 Hz), 100.3 (C-1 α-ManA, $^1J_{C,H}$ = 174 Hz), 100.4 (C-1 α-ManA, $^1J_{C,H}$ = 168 Hz), 101.2 (PhCH, $^1J_{C,H}$ = 163 Hz), 102.7 (PhCH, $^1J_{C,H}$ = 163 Hz), 120.6-138.9 (aromatic C), 171.4 (acetamido C=O); ^1H NMR (270 MHz) data are shown in the following table;

	H-1	H-2	H-3	H-4	H-5
α-Glc	5.45 (3.7)	3.47	3.85	3.61	ND
β-GlcN	5.26 (8.2)	3.06	4.67	3.82	3.51
α-ManA	5.40 (NR)	4.21	4.50	4.22	ND
α-ManB	5.25 (NR)	4.66	4.03	3.90	ND
β-Man	4.42 (NR)	3.96	3.31	3.72	2.98

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10. Ethyl 3-*O*-Benzoyl-4,6-*O*-benzylidene-2-deoxy-2-*S*-ethyl-2-thio-β-D-glucopyranoside (**19**, Scheme 4); $[\alpha]_{578}$ -41° (*c* 1.0, chloroform), Positive ion FAB-MS showed an M+H ion at m/z 445. ^{13}C NMR δ 15.1 ($SCH_2\underline{C}H_3$), 15.3 ($OCH_2\underline{C}H_3$), 26.8 ($S\underline{C}H_2CH_3$), 51.3 (C-2), 66.3 (C-5), 66.5 ($O\underline{C}H_2CH_3$), 68.9 (C-6), 71.5 (C-3), 80.2 (C-4), 101.6 (Ph$\underline{C}$H, $^1J_{C,H}$ = 165 Hz), 105.4 (C-1, $^1J_{C,H}$ = 163 Hz), 126.3-137.1 (aromatic C), 165.8 (benzoyl C=O); ^1H NMR δ 1.18 (t, 3H, $SCH_2\underline{CH_3}$), 1.29 (t, 3H, $OCH_2\underline{CH_3}$), 2.70 (m, 2H, $SC\underline{H_2}CH_3$), 2.88 (dd, 1H, $J_{1,2}$ = 8.7 Hz, $J_{2,3}$ = 11.1 Hz, H-2), 3.56 (ddd, 1H, $J_{4,5}$ = 9.2 Hz, $J_{5,6a}$ = 9.5 Hz, $J_{5,6b}$ = 5.0 Hz, H-5), 3.71 (m, 1H, $OC\underline{H_2}CH_3$), 3.79 (t, 1H, $J_{3,4}$ = 9.2 Hz, H-4), 3.83 (dd, 1H, $J_{6a,6b}$ = 10.4 Hz,

H-6a), 4.01 (m, 1H, OCH_2CH_3), 4.37 (dd, 1H, H-6b), 4.61 (d, 1H, H-1), 5.37 (dd, 1H, H-3), 5.51 (s, 1H, PhCH).

Anal. Calcd for $C_{24}H_{28}O_6S$: C, 64.8; H, 6.4; S, 7.2. Found: C, 64.7; H, 6.3; S, 7.3.

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