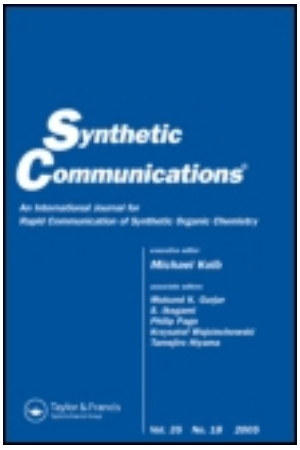

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Introduction of C-Sulfonate Groups into Disaccharide Derivatives

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Published online: 20 Aug 2006.

SYNTHETIC COMMUNICATIONS, 28(13), 2379-2397 (1998)

INTRODUCTION OF *C*-SULFONATE GROUPS INTO DISACCHARIDE DERIVATIVES

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Abstract: To prepare *C*-sulfonate derivatives of disaccharides two different strategies were followed. Thus 6- and 6'-*C*-sulfocellobiosides **4** and **10-12** were prepared starting from a suitably protected cellobioside. The 6'-*C*-sulfoaminocellobioside **18** was prepared by construction of the molecule through a glycosylation reaction. In both cases, the synthetic pathway involves regioselective tosylation, introduction of a sulfur atom by nucleophilic displacement with potassium thioacetate and oxidation with hydrogen peroxide.

Some *C*-sulfosugars have been found in nature. Thus a 6-*C*-sulfoquinovosil diglyceride was isolated from plants and microorganisms[1] and related glycolipids have been also isolated from starfish of the genera *Pseudocentrotus depresus* and *Hemicentrotus pulcherrimus*[2] and of cyanobacteria[3]. The corresponding 2-palmitoyl-3-linolenoyl derivative has recently been synthetised and has shown pharmaceutical anti-HIV-1 activity[4]. The only *C*-sulfoamino monosaccharide isolated from a natural source is a 2-amino-2,6-dideoxyhexose-6-*C*-sulfonic acid that was found in *Haloccocus bacteria* and whose configuration has not been established[5]. Related *C*-sulfoaminohexoses have been identified among the degradation products of glycoproteins[6].

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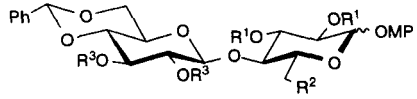
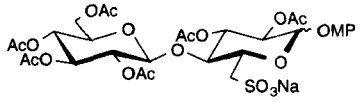
There are some bibliographyc data on the syntehsis of *C*-sulphonate derivatives of monosaccharides, nucleotides and polyols. [7-9] However we have not found data on the preparation of *C*-sulfodisaccharides in spite of the interest of these compounds as building blocks for neo-glycoconjugate syntheses. This fact is probably due to the high number of hydroxyl groups with similar reactivity in the disaccharide molecule.



	R^1	R^2	R^3
1	H	OH	H
2	Ac	OTs	Ac
3	Ac	SAc	Ac



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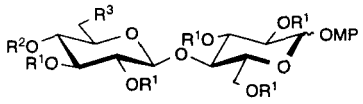
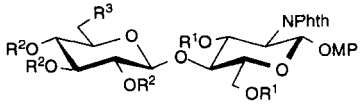


	R^1	R^2	R^3
5	Bn	H	OH
6	Bn	H	OTs
7	Bn	Ac	OTs
8	Bn	H	SAc
9	Bn	Ac	SAc
10	Bn	H	SO_3Na
11	H	H	SO_3Na
12	Ac	Ac	SO_3Na



	R^1	R^2	R^3
13	Bn	Ac	OAc
14	Bn	H	OH
15	Ac	Ac	OAc
16	Bn	Ac	OTs
17	Bn	Ac	SAc
18	Bn	Ac	SO_3Na

At the same time the *p*-methoxyphenyl (MP) group is a useful temporary protecting group for the anomeric position[10] in glycosides and glycoconjugate syntheses. The almost quantitative transformation of *p*-methoxyphenyl glycopyranosides into glycosyl halides and thioglycosides have recently been reported[11].

In this paper we report on the preparation of *C*-sulfo disaccharides with a sulfo group in a primary position. Thus we describe the syntheses of the *p*-

methoxyphenyl *C*-sulfocellobiosides **4**, **10-12** and of the *p*-methoxyphenyl *C*-sulfoaminocellobioside **18**. The starting materials were suitably protected cellobiosides and cellobiosaminides. The sulfo group was introduced by oxidation of the thio group of the corresponding thio-disaccharides, which were obtained from 6(6')-*O*-tosyl esters by nucleophilic displacement of the sulfonyloxy group with potassium thioacetate.

The starting material was the benzylidene derivative **1** as a 1:1 pair of anomers which was obtained by reaction of α-octaacetylcellobiose with *p*-methoxyphenol in the presence of TMSOTf.[12] Regioselective tosylation of **1** with tosyl chloride and pyridine followed by acetylation gave the 6-*O*-tosyl derivatives **2** in 70% yield. Subsequent displacement of the tosyloxy group with potassium thioacetate in butanone gave the thioacetate derivatives **3**. Its reaction with hydrogen peroxide and acetic acid in the presence of sodium acetate[13] produced the oxidation of the thioacetate group into the sulfo group with the simultaneous ring opening of the benzylidene acetal. Subsequent acetylation gave **4** in 43% overall yield from **3**.

The structures of **2-4** were assigned on the basis of analytical, ^{1}H and ^{13}C NMR and MS data. The resonances of H-1β and C-1β[14] appeared at 4.82-4.94 ppm ($J_{1,2}$ ≈7.7 Hz) and ≈ 99.7 ppm respectively in accordance with reported data[13-15] for related cellobiosides. It is worth pointing out that for compounds **3** and **4** the resonances of H-6a, H-6b (3.56-3.03 ppm) and C-6 (30.1 and 50.9 ppm respectively) showed a shielding effect as corresponds to nuclei bonded to thioacetate and sulfo groups respectively.

For the syntheses of the 6'-*C*-sulfocellobiosides a similar sequence was carried out starting from *p*-methoxyphenyl 2,3,6,2',3'-penta-*O*-benzyl-4',6'-*O*-benzylidene-α and β-cellobiosides.[12] Acid treatment of this compound yielded the partially protected cellobioside **5** in 98% yield, which by regioselective tosylation gave **6**. The treatment of **5** with tosyl chloride was tried out at room temperature with different molar ratios and reaction times. The best yield for **6** was obtained after the reaction with 3.5 mol of tosyl chloride for 3.0 hours. Longer reaction times and higher molar ratios of TsCl/**5** produced an increasing formation of the di-*O*-tosyl derivative. The nucleophilic displacement of the tosyloxy group of **6** afforded 6'-*S*-acetyl-2,3,6,2',3'-tetra-*O*-benzyl-6'-thio-α- and β-cellobiosides (**8**)

(70% yield of 1:1 mixture of anomers) which by acetylation originated the 6'-thio derivative **9**. The transformation **6→9** was also accomplished changing the order of reactions, that is, first acetylation to give **7** and then substitution. The *C*-sulfocellobioside **12** was obtained by treatment of **8** with hydrogen peroxide in the presence of sodium acetate to give **10** in 73% yield. Hydrogenolysis in the presence of $Pd(OH)_2$ followed by acetylation gave **12** in 90% yield.

The structures of compounds **5-12** were assigned on the basis of analytical, ^1H and ^{13}C NMR, and MS data. Both ^1H and ^{13}C NMR spectra show the doubling of signals corresponding to ring A[14], confirming the presence of the α and β anomers. In all cases the β-anomer is the major one. The doubling of signal in ring B was practically not observed. For compounds **8**, **9**, **10**, **12** the resonances for H-6'a, H-6'b and C-6' were upfield shifted as described for related compounds. The value of the $^2J_{6a,6b}$ coupling constant for **9**, **10**, **12** is also consistent with a carbon directly joined to a sulfur group.[9]

To construct the *C*-sulfoaminocellobioside **18** we have started from monosaccharide derivatives and used a glycosylation reaction. The *p*-methoxyphenyl 3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside[16] was used as glycosyl acceptor as the phthalimido group usually gives high yields in glycosylation reactions[17] and the benzyl group is the most suitable 3,6-di-*O*-protecting group for 1→4 glycosylations.[18] With the aim of having a high β-stereoselectivity we have chosen as glycosyl donor a thioglycoside with a participating group on C-2.[19] Thus the reaction of the above mentioned glycosyl acceptor and phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside in the presence of *N*-iodosuccinimide[20] gave **13** in 80% yield. The $J_{1',2'}$ value observed for **13** was 7.6 Hz and the chemical shifts for the resonances of H-1' and C-1' were indicative[12,15] of the 100% β-stereoselectivity in the glycosylation reaction. All the analytical and spectroscopic data and experimental) of **13** supported the proposed structure.

Deacylation of **13** with sodium methoxide produced the partially protected cellobioside **14** in high yield. Compound **15**, prepared for spectroscopic characterisation, was obtained by debenzylation and acetylation of **14**.

Regioselective tosylation of **14** in the conditions discussed above for **5**, followed by acetylation gave the 6'-*O*-tosyl ester **16** in 88% yield. The transformation of **16** into the target molecule **18** was accomplished by

nucleophilic displacement of the tosyloxy group with potassium thioacetate and subsequent oxidation with hydrogen peroxide.[13]

The analytical and spectroscopic data of **14-18** were in agreement with proposed structures. Compounds **17** and **18** presented the shielding effects on H-6'a, H-6'b and C-6' and the increase of the $^2J_{6'a,6'b}$ value above described for **8**, **9**, **10** and **12**.

All the measured vecinal coupling constant values for the protons of the sugar rings of **2-18** supported the $^1C_4$ conformation.

EXPERIMENTAL

General. Melting points are uncorrected. Optical rotations were measured at 22±1° for solutions in dichloromethane or chloroform. ^{1}H NMR spectra (300 and 500 MHz) were obtained for solutions in $CDCl_3$ or CD_3OD, *J* values are given in Hz. Assignments were confirmed by decoupling, H-D exchange, and homonuclear 2D COSY correlated experiments. ^{13}C NMR spectra were recorded at 75.4, and 125.7 MHz. Heteronuclear 2D correlated spectra were obtained in order to assist in carbon resonance assignments. EI-Mass spectra (70 eV) were measured with a KRATOS MS-80RFA instrument, with an ionising current or 100 mA, an accelerating voltage of 4 kV, and a resolution of 1000 (10% valley definition). The FABMS spectra were measured with the same instrument. Ions were produced by a beam of xenon atoms (6-7 KeV) using a matrix consisting of glycerol or thioglycerol and NaI as salt, $(CsI)_{37}Cs$ was used as reference. TLC was performed on Silica Gel HF_{254} (Merck), with detection by UV light or charring with H_2SO_4. Silica Gel 60 (Merck, 230 mesh) was used for preparative chromatography.

***p*-Methoxyphenyl 2,3,2',3'-tetra-*O*-acetyl-4',6'-*O*-benzylidene-6-*O*-*p*-toluenesulfonyl-α and β-cellobiosides (2).** To a solution of *p*-methoxyphenyl 4',6'-*O*-benzylidene- α and β-cellobiosides[12] (500 mg, 0.93 mmol) in pyridine (3 mL) at 0°C, *p*-toluenesulfonyl chloride (444 mg, 2.33 mmol) was added. The reaction mixture was kept at r.t. for 2.5 hours. Then acetic anhydride (1.4 mL) was added , and after 15 hours at r.t. the reaction mixture was poured into ice-water to give a white solid which was filtered off and washed sucessively with water and ethanol to give **2** (550 mg, 70%), that recrystallised from ethanol gave

the β-anomer wich had m.p. 216-217°; $[\alpha]_D$ -38° (*c* 1, dichloromethane). ^1H NMR for the β anomer (300 MHz, $CDCl_3$), δ 7.81-7.28 (m, 4H, $C_6H_4CH_3$), 7.45-7.35 (m, 5H, Ph), 6.84-6.73 (m, 4H, C_6H_4OCH3), 5.47 (s, 1H, PhC*H*), 5.19 (t, 2H, $J_{3,4}$=$J_{3',4'}$ 9.5 Hz, H-3, H-3'), 5.01 (dd, 1H, $J_{2,3}$ 9.5 Hz, H-2), 4.99 (dd, 1H, $J_{2',3'}$ 9.5 Hz, H-2'), 4.82 (d, 1H, $J_{1',2'}$ 7.8 Hz, H-1), 4.45 (d, 1H, $J_{1',2'}$ 7.8 Hz, H-1'), 4.40 (dd, 1H, $J_{5,6a}$ 2.0 Hz, $J_{6a,6b}$ 10.8 Hz, H-6a), 4.34 (dd, 1H $J_{5',6'a}$ 4.8 Hz, $J_{6'a,6'b}$ 10.3 Hz, H-6'a), 4.19 (dd, 1H, $J_{5,6b}$ 4.2 Hz, H-6b), 3.78 (t, 1H, $J_{4,5}$ 9.5 Hz, H-4), 3.78 (s, 3H, $C_6H_4OCH_3$), 3.72 (d, 1H, $J_{5',6'a}$ 10.3 Hz, H-6'b), 3.63 (t, 1H, $J_{4',5'}$ 9.5 Hz, H-4'), 3.61 (td, 1H, H-5), 3.36 (td, 1H, H-5'), 2.38 (s, 3H, ArCH_3), 2.08, 2.05, 2.03, 2.02 (4 s, 12H, 4 COCH_3). ^{13}C NMR for the β anomer (75.4 MHz, $CDCl_3$), δ 170.0, 169.4, 169.4, 169.3 (4 $COCH_3$), 155.7 (C-4 of $C_6H_4OCH_3$), 150.6 (C-1 of $C_6H_4OCH_3$), 145.3-114.4 (16C, aromatic), 101.5 (C-1'), 101.0 (Ph*C*H), 99.7 (C-1), 77.8 (C-4'), 75.6, 72.6, 72.4, 72.3 (C-2', C-3', C-3, C-4), 71.1 (C-5), 68.3 (C-6'), 66.7 (C-6), 66.2 (C-5'), 55.5 ($C_6H_4OCH_3$), 21.5 (ArCH_3), 20.8, 20.6, 20.5, 20.5 (4 COCH_3). FABMS: *m/z* 881 [40%, $(M+Na)^+$].

Anal. Calcd. for $C_{41}H_{46}O_{18}S$: C, 57.33; H, 5.40; S, 3.73. Found: C, 57.44; H, 5.47; S, 3.90.

***p*-Methoxyphenyl 2,3,2',3'-tetra-*O*-acetyl-6-*S*-acetyl-4',6'-*O*-benzylidene -6-thio-α and β- cellobiosides (3).** To a solution of **2** (375 mg, 0.44 mmol) in butanone (2 mL) potassium thioacetate (70 mg, 0.61 mmol) was added. The reaction mixture was heated under reflux and Ar atmosphere for 4 hours, then diluted with dichloromethane and filtered. The filtrate was washed with water (2x20 mL), dried ($MgSO_4$) and concentrated to dryness. Column chromatography of the residue on silica gel (toluene) gave **3** (155 mg, 46%) as an amorphous solid; ^1H NMR showed a α/β ratio of 2/5 ; $[\alpha]_D$ -68° (*c* 0.73 dichloromethane), $[\alpha]_{546}$ -82° (*c* 0.73 dichloromethane). ^1H NMR for the β anomer (300 MHz, $CDCl_3$), δ 7.44-7.33 (m, 5H, Ph), 7.00-6.78 (m, 4H, $C_6H_4OCH_3$), 5.49 (s, 1H, PhC*H*), 5.29 (t, 1H, $J_{3',4'}$ 9.1 Hz, H-3'), 5.20 (t, 1H, $J_{3,4}$ 9.5 Hz, H-3), 5.12 (dd, 1H, $J_{2,3}$ 9.5 Hz, H-2), 4.98 (dd, 1H, $J_{2',3'}$ 9.1 Hz, H-2'), 4.70 (d, 1H, $J_{1',2'}$ 7.7 Hz, H-1'), 4.84 (d, 1H $J_{1,2}$ 7.7 Hz, H-1), 4.37 (dd, 1H $J_{5',6'a}$ 4.8 Hz, $J_{6'a,6'b}$ 10.3 Hz, H-6'a), 3.77 (s, 3H, $C_6H_4OCH_3$), 3.73 (m, 1H, H-6'b), 3.70 (t, 1H, $J_{4,5}$ 8.3 Hz, H-4), 3.69 (t, 1H, $J_{4',5'}$ 10.5 Hz, H-4'), 3.61 (m, 1H, H-5), 3.50 (ddd, 1H, $J_{5',6'b}$ 4.8

Hz, $J_{6'a,6'b}$ 10.3 Hz, H-5'), 3.56 (dd, 1H $J_{5,6a}$ 8.1 Hz, $J_{6a,6b}$ 14.0 Hz, H-6a), 3.03 (dd, 1H, $J_{5,6b}$ 8.1 Hz, H-6b), 2.36 (s, 3H, SCOC*H*$_3$), 2.19, 2.06, 2.04, 2.03 (4 s, 12H, 4 COC*H*$_3$). ^{13}C NMR for the β anomer (125.7 MHz, $CDCl_3$), δ 193.8 (S*C*OCH$_3$), 169.9, 169.4, 169.4, 169.3 (4 *C*OCH$_3$), 155.5 (C-4 of *C*$_6$H4OCH$_3$), 150.7 (C-1 of *C*$_6$H$_4$OCH$_3$), 136.4-114.3 (10C aromatic), 101.4 (C-1'), 101.2 (Ph*C*H), 99.8 (C-1), 79.3 (C-4), 77.8 (C-4'), 73.2, 72.8, 72.4, 71.8, 71.4 (C-2', C-3', C-2, C-3, C-5), 68.3 (C-6'), 66.2 (C-5'), 55.5 (C$_6$H$_4$O*C*H$_3$), 30.3 (SCO*C*H$_3$), 30.1 (C-6), 20.9, 20.8, 20.5, 20.4 (4 CO*C*H$_3$). FABMS: *m/z* 785 [100%, $(M+Na)^+$].

Anal. Calcd. for $C_{36}H_{42}O_{16}S$: C, 56.68; H, 5.55; S, 4.20. Found: C, 56.81; H, 5.45; S, 4.28.

Sodium *p*-methoxyphenyl 2,3,2',3',4',6'-hexa-*O*-acetyl-6-deoxy-α and β-cellobioside-6-sulfonates (4). To a solution of **3** (510 mg, 0.67 mmol) and sodium acetate (218 mg, 2.68 mmol) in acetic acid (3 mL) aqueous hydrogen peroxide 33% (0.8 mL, 7.8 mmol) was added. The reaction mixture was heated at 60°C for two days, and then evaporated. The residue was disolved in water and extracted with ether (2x20 ml) and the aqueous layer evaporated to dryness. The crude product was conventionally acetylated with pyridine (3 mL) and acetic anhydride (2 mL) for 24 hours at r.t. The solvents were eliminated by coevaporation under reduced pressure with toluene. Column chromatography of the residue on silica gel (toluene-acetone, 1:4) gave **4** (226 mg, 43%) as a syrup; $[\alpha]_D$ -15° (*c* 1, dichloromethane). ^{1}H NMR for the β anomer (500 MHz, $CDCl_3$), δ 7.11-6.78 (m, 4H, C$_6$*H*$_4$OCH$_3$), 5.19 (t, 1H, $J_{3,4}$ 9.0 Hz, H-3), 5.16 (t, 1H, $J_{3',4'}$ 9.4 Hz, H-3'), 5.15 (m, 1H, $J_{2,3}$ 9.6 Hz, H-2), 5.07 (t, 1H, $J_{4',5'}$ 9.5 Hz, H-4'), 4.96 (dd, 1H, $J_{2',3'}$ 9.4 Hz, H-2'), 4.94 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1), 4.65 (d, 1H, $J_{1',2'}$ 8.1 Hz, H-1'), 4.38 (dd, 1H, $J_{5',6'a}$ 4.3 Hz, $J_{6'a,6'b}$ 12.5 Hz, H-6'a), 4.09 (td, 1H, $J_{5,6b}$ 8.5 Hz, H-5), 3.83 (t, 1H, $J_{4,5}$ 9.3 Hz, H-4), 4.04 (dd, 1H, $J_{5',6'b}$ 2.1 Hz, H-6'b), 3.74 (s, 3H, C$_6$H$_4$OC*H*$_3$), 3.70 (m, 1H, H-5'), 3.42 (dd, 1H, $J_{5,6a}$ 2.2 Hz, $J_{6a,6b}$ 14.1 Hz, H-6a), 3.08 (m, 1H, H-6b), 2.17, 2.09, 2.04, 2.02, 2.01, 1.97 (6 s, 18H, 6 COC*H*$_3$). ^{13}C NMR for the β anomer (75.4 MHz, $CDCl_3$), δ 170.5, 170.0, 169.7, 169.6, 169.4, 167.2 (6 *C*OCH$_3$), 155.6 (C-4 of *C*$_6$H$_4$OCH$_3$), 151.3 (C-1 of *C*$_6$H$_4$OCH$_3$), 118.0, 118.0, 114.3, 114.2 (4C, *C*$_6$H$_4$OCH$_3$), 101.1 (C-1'), 99.7 (C-1), 78.3 (C-4), 72.9, 72.5, 72.2, 71.7, 71.3,

71.2 (C-2', C-3', C-5', C-2, C-3, C-5), 67.7 (C-4'), 61.5 (C-6'), 55.5 ($C_6H_4OCH_3$), 50.9 (C-6), 22.5, 20.6, 20.6, 20.4, 20.4, 20.4 (6 $COCH_3$). FABMS: *m/z* 809 [100%, $(M+Na)^+$]. HRFABMS: *m/z* obsd. 809.1549. Calcd. for $C_{31}H_{39}O_{20}SNa$+Na 809.1539.

***p*-Methoxyphenyl 2,3,6,2',3'-penta-*O*-benzyl-α and β-cellobiosides (5).** To a solution of *p*-methoxyphenyl 2,3,6,2',3'-penta-*O*-benzyl-4',6'-*O*-benzylidene-α and β-cellobiosides[12] (4.46 g, 4.53 mmol) in methanol-dioxane (1:1, 40 mL), $TsOH \cdot H_2O$ (86 mg, 0.43 mmol) was added. The reaction mixture was stirred for 1 hour at 60°C and for 45 minutes at 85°C, neutralised with Et_3N and evaporated. Compound **5** (226 mg, 43%) was obtained as a solid that recrystallised from ethanol had m.p 139-141°C; $[\alpha]_D$ +4° (*c* 1, dichloromethane) (3:7 mixture α:β anomers) . ^1H NMR for the *β* anomer (300 MHz, $CDCl_3$), δ 7.40-7.24 (m, 25H, 5Ph), 7.05-6.79 (m, 4H, $C_6H_4OCH_3$), 4.99, 4.93, 4.93, 4.86, 4.84, 4.84, 4.73, 4.68 (8d, 8H, $^2J_{H,H}$ 10.9, 12.6, 11.3, 12.6, 10.9, 11.4, 11.3, 11.4 Hz, 4 CH_2Ph), 4.84 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1), 4.46 (m, 1H, H-1'), 4.43, 4.58 (2d, 2H, $^2J_{H,H}$ 12.0 Hz, CH_2Ph), 3.97 (dd, 1H, $J_{3,4}$ 8.7 Hz, $J_{4,5}$ 9.8 Hz, H-4), 3.83 -3.78 (m, 2H, H-6a, H-6b), 3.44-3.38 (m, 2H, H-6'a, H-6'b), 3.80 (s, 3H, $C_6H_4OCH_3$), 3.72 (m, 1H, H-2), 3.63 (m, 1H, H-3), 3.48 (m, 1H, H-5), 3.32 (m, 3H, H-2', H-3', H-4'), 3.11 (ddd, 1H, H-5'). ^{13}C NMR for the *β* anomer (75.4 MHz, $CDCl_3$), δ 155.2 (C-4 of $C_6H_4OCH_3$), 151.4 (C-1 of $C_6H_4OCH_3$), 138.7-114.4 (m, 34 C aromatic), 102.7 (C-1), 102.5 (C-1'), 84.2 (C-3'), 82.6 (C-3), 82.3 (C-2'), 81.3 (C-2), 76.5 (C-4), 75.4, 75.2, 75.1, 75.0, 74.8 (5C, CH_2Ph), 74.8 (C-5), 73.2 (C-5'), 70.6 (C-4'), 67.9 (C-6), 62.2 (C-6'), 55.5 ($C_6H_4OCH_3$). FABMS: *m/z* 921 [100%, $(M+Na)^+$].

Anal. Calcd. for $C_{54}H_{58}O_{12}$: C, 72.14; H, 6.50 Found: C, 71.83; H, 6.41.

***p*-Methoxyphenyl 2,3,6,2',3'-penta-*O*-benzyl-6'-*O*-*p*-toluenesulfonyl-a and β-cellobiosides (6).** To a solution of **5** (1.5 g, 1.67 mmol) in pyridine (10 mL) *p*-toluenesulfonyl chloride (1.11 g, 5.86 mmol) was added. The reaction mixture was stirred at r.t. for 3.5 hours, then water (1 mL) was added and stirred for another 10 minutes. The reaction mixture was poured into ice-water and extracted with dichloromethane (3x25 mL). The organic layer was washed with H_2SO_4 2M (2x20 mL), saturated aq $NaHCO_3$ (2x20 mL) and water (3x15 mL),

dried ($MgSO_4$) and concentrated to dryness. The residue was purified by column chromatography on silica gel (toluene) to give **6** (1.19 g, 70%, 3:10 mixture of α:β anomers) as an oil; $[\alpha]_D$ -11° (*c* 1, dichloromethane). ^1H NMR for the β anomer (300 MHz, $CDCl_3$), δ 7.42-7.15 (m, 29H, 5Ph, $C_6H_4CH_3$), 6.92-6.76 (m, 4H, $C_6H_4OCH_3$), 4.98, 4.72 (2d, 2H, $^2J_{H,H}$ 11.0 Hz, CH_2Ph), 4.94, 4.72 (d, 2H, $^2J_{H,H}$ 11.4 Hz, CH_2Ph), 4.87, 4.73 (2d, 2H, $^2J_{H,H}$ 11.7 Hz, CH_2Ph), 4.85 (d, 1H, $J_{1,2}$ 7.3 Hz, H-1), 4.77, 4.70 (2d, 2H, $^2J_{H,H}$ 11.7 Hz, CH_2Ph), 4.63 (d, 1H, $J_{1',2'}$ 7.5 Hz, H-1'), 4.57, 4.38 (2d, 2H, $^2J_{H,H}$ 11.9 Hz, CH_2Ph), 4.21 (dd, 1H, $J_{5',6'a}$ 3.9 Hz, $J_{6'a,6'b}$ 11.1 Hz, H-6'a), 4.11 (dd, 1H, $J_{5',6'b}$ 1.9 Hz, H-6'b), 4.00 (dd, 1H, $J_{4,5}$ 9.5 Hz, H-4), 3.77 (s, 3H, $C_6H_4OCH_3$), 3.80 (dd, 1H $J_{5,6a}$ 3.8 Hz, $J_{6a,6b}$ 11.0 Hz, H-6a), 3.75 (dd, 1H, $J_{5,6b}$ 1.9 Hz, H-6b), 3.66 (m, 1H, H-2), 3.61 (m, 1H, H-3), 3.58 (m, 1H, H-4'), 3.42 (ddd, 1H, H-5), 3.30 (m, 2H, H-2', H-3'), 3.16 (ddd, 1H, $J_{4',5'}$ 9.5 Hz, H-5'), 2.50 (d, 1H, $J_{OH,4'}$ 3.6 Hz, OH), 2.38 (s, 3H, $ArCH_3$). ^{13}C NMR for the β anomer (75.4 MHz, $CDCl_3$), δ 155.1 (C-4 of $C_6H_4OCH_3$), 151.4 (C-1 of $C_6H_4OCH_3$), 138.7-114.4 (40 C aromatic), 102.6 (C-1), 102.2 (C-1'), 83.6 (C-3'), 82.4 (C-3), 81.9 (C-2'), 81.4 (C-2), 76.3 (C-4), 75.1, 74.9, 74.9, 73.1 (4 CH_2Ph), 74.8 (C-5), 73.1 (C-5'), 69.4 (C-4'), 68.1, 67.9 (C-6, C-6'), 55.5 ($C_6H_4OCH_3$), 21.5 ($ArCH_3$). FABMS: *m/z* 1075 [100%, $(M+Na)^+$].

***p*-Methoxyphenyl 4'-*O*-acetyl-2,3,6,2',3'-penta-*O*-benzyl-6'-*O*-*p*-toluenesulfonyl-α and β-cellobiosides (7).** *Procedure a:* To a solution of **5** (517 mg, 0.57 mmol) in pyridine (2 mL), *p*-toluenesulfonyl chloride (384 g, 2.01 mmol) was added. The mixture was stirred at r.t. for 3.5 hours and then acetic anhydride (0.5 mL) was added. The reaction mixture was allowed to stand at r.t. for 15 hours, poured into ice-water and extracted with dichloromethane (3x15 mL). The organic layer was washed with H_2SO_4 2M (2x20 mL), saturated aq $NaHCO_3$ (2x20 mL) and water (3x15 mL), dried ($MgSO_4$) and concentrated to dryness. The residue was purified by column chromatography on silica gel (toluene) to give **7** (315 mg, 50%, 1:4 mixture of α:β anomers) as an oil; $[\alpha]_D$ +30° (*c* 3.4 dichloromethane).

Procedure b: Conventional acetylation of **6** (224 mg, 0.21 mmol) with acetic anhydride (0.5 mL) and pyridine (1 mL) gave **7** (212 mg, 92%). ^1H NMR for the β anomer (500 MHz, $CDCl_3$), δ 7.33-7.02 (m, 29H, 5Ph, $C_6H_4CH_3$), 7.02-6.79

(m, 4H, $C_6H_4OCH_3$), 4.97, 4.78 (2d, 2H, $^2J_{H,H}$ 10.9 Hz, CH_2Ph), 4.85 (d, 1H $J_{1,2}$ 7.6 Hz, H-1), 4.84 (t, 1H, $J_{4',5'}$ 9.5 Hz, H-4'), 4.84, 4.72 (2d, 2H, $^2J_{H,H}$ 10.6 Hz, CH_2Ph), 4.75, 4.67 (2d, 2H, $^2J_{H,H}$ 11.5 Hz, CH_2Ph), 4.73, 4.61 (2d, 2H, $^2J_{H,H}$ 11.4 Hz, CH_2Ph), 4.58, 4.41 (2d, 2H, $^2J_{H,H}$ 12.3 Hz, CH_2Ph), 4.46 (d, 1H, $J_{1',2'}$ 7.8 Hz, H-1'), 3.98 (t, 1H, $J_{4,5}$ 9.5 Hz, H-4), 3.91 (dd, 1H, $J_{5'6'a}$ 4.1 Hz, $J_{6'a,6'b}$ 10.8 Hz, H-6'a), 3.88 (dd, 1H, $J_{5',6'b}$ 5.4 Hz, H-6'b), 3.80 (dd, 1H, $J_{5,6a}$ 4.1 Hz, $J_{6a,6b}$ 10.9 Hz, H-6a), 3.78 (s, 3H, $C_6H_4OCH_3$), 3.72 (dd, 1H, $J_{5,6b}$ 1.8 Hz, H-6b), 2.38 (s, 3H, $ArCH_3$), 3.65 (t, 1H, $J_{2,3}$ 9.3 Hz, H-2), 3.59 (t, 1H, $J_{3,4}$ 8.8 Hz, H-3), 3.43 (t, 1H, $J_{3',4'}$ 9.0 Hz, H-3'), 3.42 (m, 2H, H-5, H-5'), 3.33 (dd, 1H, $J_{2',3'}$ 9.0 Hz, H-2'), 1.94 (s, 3H, $COCH_3$). ^{13}C NMR for the β anomer (75.4 Hz, $CDCl_3$), δ 169.7 ($COCH_3$), 155.0 (C-4 of $C_6H_4OCH_3$), 151.7 (C-1 of $C_6H_4OCH_3$), 144.7-114.4 (40C aromatic), 102.6 (C-1), 101.8 (C-1'), 82.2 (C-3), 82.0 (C-2'), 81.5 (C-2), 81.3 (C-3'), 76.4 (C-4), 75.1, 74.9, 73.2 (5 CH_2Ph), 74.9 (C-5), 71.2 (C-5'), 70.4 (C-4'), 67.8, 67.9 (C-6, C-6'), 55.5 ($C_6H_4OCH_3$), 21.5 ($ArCH_3$), 20.2 ($COCH_3$). FABMS: *m/z* 1117 [100%, $(M+Na)^+$].

***p*-Methoxyphenyl 6'-*S*-acetyl-2,3,6,2',3'-penta-*O*-benzyl-6'-thio-α and β-cellobiosides (8).** To a solution of **6** (995 mg, 0.90 mmol) in butanone (4 mL), potassium thioacetate (140 mg, 1.23 mmol) was added. The reaction mixture was heated under reflux in Ar atmosphere for 5 hours, then diluted with dichloromethane and filtered. The filtrate was washed with water (2x15 mL), dried ($MgSO_4$) and concentrated to dryness. Column chromatography of the residue on silica gel (toluene) gave **8** (601 mg, 70%, 1:3 mixture of α:β anomers) as an amorphous solid; $[\alpha]_D$ +16° (*c* 2.5, dichloromethane). ^1H NMR for the β anomer (500 MHz, $CDCl_3$), δ 7.42-7.21 (m, 25H, 5Ph), 7.02-6.77 (m, 4H, $C_6H_4OCH_3$), 5.06, 5.01, 4.96, 4.63 (4d, 2H, CH_2Ph), 4.84 (d, 1H, $J_{1,2}$ 7.7 Hz, H-1), 4.85-4.75 (m, 6H, 3 CH_2Ph), 4.83, 4.81, 4.72 (3s, 6H, 3 CH_2Ph), 4.56, 4.30 (d, 2H, $^2J_{H,H}$ 12.0 Hz,CH_2Ph), 4.55, 4.41 (2d, 2H, $^2J_{H,H}$ 12.0 Hz, CH_2Ph), 4.47 (d, 1H, $J_{1',2'}$ 7.7 Hz, H-1'), 4.02 (m, 1H, H-4), 3.81 (m, 1H, H-6a), 3.77 (s, 3H, $C_6H_4OCH_3$), 3.74 (m, 1H, H-6b), 3.68 (dd, 1H, $J_{2,3}$ 9.0 Hz, H-2), 3.61 (t, 1H, $J_{3,4}$ 9.0 Hz, H-3), 3.42 (m, 1H, H-5), 3.36 (m, 1H, H-3'), 3.32 (m, 1H, H-4'), 3.27 (m, 1H, H-2'), 3.20-3.14 (m, 2H, H-5', H-6'a), 3.14 (bs, 1H, O*H*), 3.06 (m, 1H, H-6'b), 2.30 (s, 3H, $SCOCH_3$). ^{13}C NMR for the β anomer (125.7 MHz, $CDCl_3$), δ 198.7 (SCOCH3), 155.1 (C-4 of $C_6H_4OCH_3$), 151.4 (C-1 of

$C_6H_4OCH_3$), 139.4-114.3 (34C aromatic), 102.6 (C-1), 102.0 (C-1'), 83.4 (C-3'), 82.4 (C-3), 81.9 (C-2'), 81.3 (C-2), 79.9-70.4 (5CH_2Ph), 76.4 (C-4), 74.7 (C-5), 73.5 (C-5'), 71.8 (C-4'), 67.9 (C-6), 55.5 ($C_6H_4OCH_3$), 30.4 (C-6'), 30.2 (SCOCH_3). FABMS: *m/z* 980 [100%, $(M+Na)^+$].

Anal.: Calcd. for $C_{56}H_{60}O_{12}S$: C, 70.27; H, 6.32; S, 3.35. Found: C, 70.48, H, 6.30; S, 3.63.

p-Methoxyphenyl 4'-*O*-acetyl-6'-*S*-acetyl-2,3,6,2',3'-penta-*O*-benzyl-6'-thio-α and β-cellobiosides (9). *Procedure a:* To a solution of **7** (212 mg, 0.19 mmol) in butanone (3 mL), potassium thioacetate (30 mg, 0.26 mmol) was added. The reaction mixture was heated under reflux for 6 hours, diluted with dichloromethane and filtered. The filtrate was washed with water (2x15 mL), dried ($MgSO_4$) and concentrated to dryness. Column chromatography of the residue on silica gel (toluene) gave **9** (141 mg, 72% of pure β anomer) as an amorphous solid. $[\alpha]_D$ -8° (*c* 1, dichloromethane).

Procedure β: Conventional acetylation of **8** (23 mg, 0.02 mmol) with acetic anhydride (0.5 mL) and pyridine (1 mL) gave **9** (22 mg, 92%). ^{1}H NMR for the β anomer (300 MHz, $CDCl_3$), δ 7.32-7.23 (m, 25H, 5Ph), 7.03-6.79 (m, 4H, $C_6H_4OCH_3$), 4.98, 4.77 (2d, 2H, $^2J_{H,H}$ 12.0 Hz, CH_2Ph), 4.97, 4.48 (2d, 2H, $^2J_{H,H}$ 11.3 Hz, CH_2Ph), 4.86 (t, 1H, $J_{3',4'}$ 9.4 Hz, H-4'), 4.86 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1), 4.81, 4.69 (2d, 2H, $^2J_{H,H}$ 11.4 Hz, CH_2Ph), 4.75 (s, 2H, CH_2Ph), 4.61, 4.42 (2d, 2H, $^2J_{H,H}$ 11.5 Hz, CH_2Ph), 4.42 (d, 1H, $J_{1',2'}$ 7.4 Hz, H-1'), 4.05 (t, 1H, $J_{4,5}$ 9.4 Hz, H-4), 3.82 (dd, 1H, $J_{5,6a}$ 4.1 Hz, $J_{6a,6b}$ 11.0 Hz, H-6a), 3.78 (s, 3H, $C_6H_4OCH_3$), 3.73 (dd, 1H, $J_{5,6b}$ 2.2 Hz, $J_{5,6b}$ 2.2 Hz, H-6b), 3.71 (dd, 1H, $J_{2,3}$ 9.1 Hz, H-2), 3.61 (t, 1H, $J_{3,4}$ 8.8 Hz, H-3), 3.42 (m, 1H, H-5), 3.41 (t, 1H, H-3'), 3.37 (t, 1H, $J_{2',3'}$ 9.1 Hz, H-2'), 3.22 (m, 1H, H-5'), 3.10 (dd, 1H, $J_{5',6'a}$ 2.7 Hz, $J_{6'a,6'b}$ 14.2 Hz, H-6'a), 2.69 (dd, 1H $J_{5',6'b}$ 7.4 Hz, H-6'b), 2.27 (s, 3H, SCOCH_3), 1.99 (s, 3H, COCH_3). ^{13}C NMR for the β anomer (75.4 MHz, $CDCl_3$), δ 193.4 (S*C*OCH_3), 169.5 (*C*OCH_3), 155.4 (C-4 of $C_6H_4OCH_3$), 151.5 (C-1 of $C_6H_4OCH_3$), 139.8-112.7 (34C aromatic), 101.8 (C-1'), 102.7 (C-1), 82.3, 82.2, 81.3, 80.8 (C-2', C-3', C-2, C-3), 76.2 (C-4), 75.0 (C-5') 75.1-74.6 (5 CH_2Ph), 73.2 (C-4'), 70.4 (C-5), 67.6 (C-6), 55.5 ($C_6H_4OCH_3$), 30.3 (S*C*OCH_3), 30.0 (C-6'), 20.8 (CO*C*H_3). FABMS: *m/z* 1021 [100%, $(M+Na)^+$].

Anal. Calcd. for $C_{58}H_{62}O_{13}S$: C, 69.72; H, 6.25; S, 3.21. Found: C, 69.72; H, 6.25; S, 3.31.

Sodium *p*-methoxyphenyl 2,3,6,2',3'-penta-*O*-benzyl-6'-deoxy-α and β-cellobioside-6'-sulfonates (10). To a mixture of **8** (345 mg, 0.36 mmol) and sodium acetate (44.4 mg, 0.54 mmol) in acetic acid (4 mL), aqueous hydrogen peroxide 33% (0.43 mL, 4.2 mmol) was added. The reaction mixture was heated at 60°C for 4 hours and then concentrated to dryness. The crude product was purified by column chromatography on silica gel (dichloromethane-methanol, 10:1) to give **10** (259 mg, 73%) as a white solid that recrystallised from dichloromethane-methanol (1:2 mixture of anomers) had m.p. 92-93°; $[\alpha]_D$ +7° (*c* 1, dichloromethane). ^{1}H NMR for the *β* anomer (500 MHz, CD_3OD), δ 7.46-7.13 (m, 25H, 5Ph), 7.05-6.75 (m, 4H, $C_6H_4OCH_3$), 5.01 (d, 1H, $J_{1,2}$ 7.7 Hz, H-1), 4.97, 4.94, 4.89, 4.81, 4.78, 4.78, 4.74, 4.63 (8d, 8H, $^2J_{H,H}$ 11.2, 11.1, 11.2, 11.2, 11.7, 11.7, 11.5, 12.1 Hz, 4 CH_2Ph), 4.55 (d, 1H, $J_{1',2'}$ 7.6 Hz, H-1'), 4.04 (t, 1H, $J_{3,4}$ 9.0 Hz, H-4), 3.80 (t, 1H, H-3), 3.83-3.74 (m, 3H, H-5, H-6a, H-6b), 3.72 (m, 1H, H-5'), 3.71 (s, 3 H, $C_6H_4OCH_3$), 3.63 (dd, 1H, $J_{2,3}$ 9.0 Hz, H-2), 3.40 (t, 1H, $J_{3',4'}$ 8.9 Hz, H-3'), 3.33 (t, 1H, $J_{4',5'}$ 9.4 Hz, H-4'), 3.27 (m, 1H, H-2'), 3.25 (m, 1H, H-6'a), 3.01 (dd, 1H, $J_{5'6'b}$ 6.3 Hz, H-6'b). ^{13}C NMR for the *β* anomer (75.4 MHz, $CDCl_3$), δ 155.0 (C-4 of $C_6H_4OCH_3$), 151.4 (C-1 of $C_6H_4OCH_3$), 138.7-114.3 (34 C aromatic), 102.7 (C-1), 102.2 (C-1'), 83.8 (C-3'), 81.9, 81.7 (C-2', C-3), 81.2 (C-2), 76.4 (C-4), 74.2 (C-5), 72.9 (C-5'), 71.8 (C-4'), 75.1, 74.8, 74.2, 72.9, 71.8 (5C, CH_2Ph), 67.9 (C-6), 55.4 ($C_6H_4OCH_3$), 54.0 (C-6').

Anal. Calcd. for $C_{54}H_{57}O_{14}SNa$: C, 65.84; H, 5.83; S, 3.25. Found: C, 65.96; H, 5.66; S, 3.16.

Sodium *p*-methoxyphenyl 2,3,6,2',3',4'-hexa-*O*-acetyl-6'-deoxy-α and β-cellobioside-6'-sulfonates (12). To a solution of **10** (58 mg, 0,06 mmol) in methanol (2 mL), $Pd(OH)_2$-C, 20% (41 mg) was added. After 36 hours under H_2 (1 atm) at r.t. and 1 atm the reaction mixture was filtered through Celite and the solution concentrated to dryness to give a residue {**11**, 29 mg, [FABMS: *m/z* 557, 35% $(M+Na)^+$]}, that was conventionally acetylated with 1:1 pyridine-acetic anhydride (2 mL) for 24 hours. The residue was crystallised from

dichloromethane-ethyl ether to give **12** (41 mg, 90%, 1:3 mixture of α:β anomers) as a solid had m.p. 185-186°; $[\alpha]_D$ +7° (*c* 1, dichloromethane). ^{1}H NMR for the β anomer (300 MHz, CD_3OD), δ 6.94-6.79 (m, 4H, $C_6H_4OCH_3$), 5.37 (m, 1H, H-3), 5.19 (t, 1H, $J_{2',3'}$=$J_{3',4'}$ 9.0 Hz, H-3'), 5.07 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 5.05 (t, 1H, H-4'), 4.88-4.76 (m, 2H, H-2', H-2), 4.68 (d, 1H, $J_{1',2'}$ 8.0 Hz, H-1'), 4.50 (t, 1H, $J_{3,4}$ 10.8 Hz, H-4), 4.25 (m, 1H, H-6a), 4.10-4.01 (m, 3H, H-5', H-5, H-6b), 3.73 (s, 3H, $C_6H_4OCH_3$), 3.02 (dd, 1H, $J_{5',6'a}$ 2.8 Hz, $J_{6'a,6'b}$ 14.7 Hz, H-6'a), 2.98 (dd, 1H, $J_{5',6'b}$ 5.8 Hz, H-6'b), 2.11, 2.10, 2.03, 2.02, 2.01, 1.94 (6s, 18 H, 6 $COCH_3$). ^{13}C NMR for the β anomer (75.4 MHz, CD_3OD), δ 172.5, 172.2, 171.8, 171.5, 171.2, 171.0 (6 $COCH_3$), 156.9 (C-4 of $C_6H_4OCH_3$), 152.4 (C-1 of $C_6H_4OCH_3$), 119.1, 119.1, 115.5, 115.5 (4C, $C_6H_4OCH_3$), 101.3 (C-1), 100.9 (C-1'), 77.0 (C-4), 74.5 (C-5'), 73.9 (C-5), 73.2, 73.2, 72.3, 71.8 (C-2', C-3', C-2, C-3), 70.5 (C-4'), 63.6 (C-6), 56.0 ($C_6H_4OCH_3$), 54.1 (C-6'), 21.5, 21.3, 20.8, 20.7, 20.6, 20.5 (6 $COCH_3$). FABMS: *m/z* 809 [100%, $(M+Na)^+$]. HRFABMS: *m/z* obsd. 919.0716. Calcd. for $C_{31}H_{39}O_{20}SNa$ + Cs 919.0691.

***p*-Methoxyphenyl 3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-β-D-glucopyranoside (13).** To a solution of phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside[21] (1.24 g, 2.82 mmol) and *p*-methoxyphenyl 3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside[24] (840 mg, 1.42 mmol) in dry dichloromethane (5 mL), containing 4Å molecular sieves, *N*-iodosuccinimide (1.3 g, 5.68 mmol) under Ar and in the dark was added. The reaction mixture was stirred at r.t. for 30 minutes and then cooled to 0°C. A solution of TfOH (25 mL, 0.31 mmol) in dichloromethane (0.3 mL) was added. The reaction mixture was stirred at 0°C for 3.5 hours, diluted with dichloromethane (15 mL) and then filtered trough Celite. The solution was washed sucessively with water, saturated aq $NaHCO_3$, aq $Na_2S_2O_3$ (10%) and water, dried (Na_2SO_4) and concentrated to dryness. Column chromatograpy of the residue on silica gel (ethyl ether-petroleum ether, 3:1) gave **13** (927 mg, 80%) as a white solid that recrystallised from ethyl ether had m.p. 78-80°; $[\alpha]_D$ +20° (*c* 1, dichloromethane). ^{1}H NMR (300 MHz, $CDCl_3$), δ 7.67 (m, 4H, NPhth), 7.43-6.80 (m, 10H, 2Ph), 6.80-6.66 (m, 4H, $C_6H_4OCH_3$), 4.79, 4.51 (d, 2H, $^2J_{H,H}$ 12.0 Hz, CH_2Ph), 5.08 (t, 1H, $J_{3',4'}$ 8.9 Hz, H-3'), 5.03 (m, 1H, H-4'), 5.00 (dd, 1H, $J_{2',3'}$ 9.8 Hz, H-2'), 4.79, 4.42 (d, 2H, $^2J_{H,H}$ 12.5 Hz, CH_2Ph), 4.66 (d, 1H,

$J_{1'2'}$ 7.6 Hz, H-1'), 4.37 (dd, 1H, $J_{2,3}$ 10.5 Hz, H-2), 4.27 (dd, 1H, $J_{3,4}$ 8.3 Hz, H-3), 4.25 (dd, 1H, $J_{5',6'a}$ 4.6 Hz, $J_{6'a,6'b}$ 12.2 Hz, H-6'a), 4.13 (t, 1H, $J_{4,5}$ 9.8 Hz, H-4), 3.99 (dd, 1H, $J_{5'6'b}$ 2.2 Hz, H-6'b), 3.80 (m, 2H, H-6a, H-6b), 3.70 (s, 3H, $C_6H_4OCH_3$), 3.61 (m, 1H, H-5), 3.46 (ddd, 1H, $J_{4',5'}$ 9.5 Hz, H-5'), 2.02, 2.02, 2.00, 1.97 (s, 3 $COCH_3$). ^{13}C NMR (75.4 MHz, $CDCl_3$), δ 170.5, 170.1, 169.3, 169.0 (4C, $COCH3$), 167.9, 167.6 (CO, NPhth), 155.2 (C-4 of $C_6H_4OCH_3$), 150.7 (C-1 of $C_6H_4OCH_3$), 138.3-114.2 (22C aromatic), 99.9 (C-1'), 78.2 (C-4), 76.5 (C-3), 74.5 (C-5), 72.9 (C-3'), 73.5, 74.8 (2C, CH_2Ph), 71.7 (C-2'), 71.4 (C-5'), 68.2 (C-4'), 67.3 (C-6), 61.5 (C-6'), 55.4 (C-2), 55.4 ($C_6H_4OCH_3$), 20.5, 20.4 (2 $COCH_3$). FABMS: *m/z* 948 [100%, $(M+Na)^+$].

Anal. Calcd. for $C_{49}H_{51}NO_{17}$: C, 63.50; H, 5.55; N, 1.51. Found: C, 62.86; H, 5.86; N, 1.22.

***p*-Methoxyphenyl 3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-4-*O*-(β-D-glucopyranosyl)-β-D-glucopyranoside (14).** To a solution of **13** (452 mg, 0.49 mmol) in methanol-toluene (1:1, 2 mL), NaOMe in MeOH (1M) was added until basic pH. The reaction mixture was stirred at r.t. for 90 minutes, made neutral with Amberlyst IR-120 (H^+) filtered and concentrated to dryness. Column chromatography of the residue on silica gel (dichloromethane-acetone, 1:1) gave **13** (311mg, 84%) as a white solid that recrystallised from dichloromethane-acetone had m.p. 89-91°; $[\alpha]_D$ +51° (*c* 1, dichloromethane). ^1H NMR (300 MHz, CD_3OD), δ 7.78 (m, 4H, NPhth), 7.39-6.80 (m, 10H, 2Ph), 6.80-6.65 (m, 4H, $C_6H_4OCH_3$), 4.84, 4.58 (d, 2H, $^2J_{H,H}$ 12.0 Hz, CH_2Ph), 4.66, 4.58 (d, 1H, $^2J_{H,H}$ 11.8 Hz, CH_2Ph), 4.51 (d, 1H, $J_{1'2'}$ 7.4 Hz, H-61'), 4.35 (dd, 1H, $J_{3,4}$ 8.6 Hz, H-3), 4.23 (dd, 1H, $J_{2,3}$ 10.7 Hz, H-2), 4.16 (t, 1H, $J_{4,5}$ 9.9 Hz, H-4), 3.79 (ddd, 1H, H-5), 4.03 (dd, 1H, $J_{5,6a}$ 4.0 Hz, $J_{6a,6b}$ 11.2 Hz, H-6a), 3.91 (dd, 1H, $J_{5,6b}$ 1.5 Hz, H-6b), 3.85 (dd, 1H, $J_{5',6'a}$ 1.6 Hz, $J_{6'a,6'b}$ 12.3 Hz, H-6'a), 3.65 (s, 3H, $C_6H_4OCH_3$), 3.60 (dd, 1H, $J_{5',6'b}$ 6.1 Hz, H-6'a), 3.34 (t, 1H, $J_{3',4'}$ 8.9 Hz, H-3'), 3.27 (dd, 1H, $J_{2',3'}$ 8.9 Hz, H-2'), 3.24-3.20 (m, 2H, H-4', H-5'). ^{13}C NMR (75.4 MHz en CD_3OD), δ 169.2, 169.2 (CO, NPhth), 158.7 (C-4, $C_6H_4OCH_3$), 152.2 (C-1, $C_6H_4OCH_3$), 139.6-114.4 (m, 16H, 2 Ph, NPhth, $C_6H_4OCH_3$), 103.8 (C-1'), 78.8, 78.4, 78.4, 77.9 (C-3', C-5', C-3, C-4), 76.6, 75.7 (2 CH_2Ph), 76.5 (C-5), 74.3 (C-2'), 71.9 (C-4'), 57.0 (C-2), 69.1 (C-6), 63.2 (C-6'), 56.0 ($C_6H_4OCH_3$). FABMS: *m/z* 780 [100%, $(M+Na)^+$].

Anal. Calcd. for $C_{41}H_{43}NO_{13}$: C, 64.98; H, 5.72; N, 1.85. Found: C, 64.69; H, 5.43; N, 1.73.

p-Methoxyphenyl 3,6-di-*O*-acetyl-2-deoxy-2-phthalimido-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-β-D-glucopyranoside (15). To a solution of **14** (44 mg, 0.06 mmol) was dissolved in methanol (3 mL) and $Pd(OH)_2$-C, 20% (40 mg) was added. After 3 hours under H_2 (1 atm) at r.t., the reaction mixture was filtered through Celite and the solution concentrated to dryness to give a residue {31 mg, [FABMS: *m/z* 600, 100% $(M+Na)^+$]}, that was conventionally acetylated with 1:1 pyridine-acetic anhydride (2 mL) for 24 hours. The residue was crystallised from dichloromethane-ethyl ether to give **15** (37 mg, 85%) as a white solid, wich crystallysed from dihcloromethane-ethyl ether had m.p. 88-90°; $[\alpha]_D$ +10° (*c* 1, dichloromethane). ^1H NMR (300 MHz, $CDCl_3$), δ 7.88-7.33 (m, 4H, NPhth), 6.86-6.70 (m, 4H, $C_6H_4OCH_3$), 5.16 (t, 2H, $J_{3,4}$=$J_{3',4'}$ 9.4 Hz, H-3', H-3), 5.07 (t, 1H, $J_{4',5'}$ 9.4 Hz, H-4'), 4.94 (dd, 1H, $J_{2',3'}$ 9.4 Hz, H-2'), 4.53 (m, 1H, H-4), 4.57 (d, 1H, $J_{1'2'}$ 7.9 Hz, H-1'), 4.46 (dd, 1H, $J_{2,3}$ 9.4 Hz, H-2), 4.35 (dd, 1H, $J_{5'6'a}$ 4.2 Hz, $J_{6',6'b}$ 12.4 Hz, H-6'a), 4.20 (dd, 1H, $J_{5,6a}$ 4.7 Hz, $J_{6a,6b}$ 11.8 Hz, H-6a), 4.03 (dd, 1H, $J_{5',6'b}$ 2.2 Hz, H-6'b), 3.90 (m, 2H, H-5, H-6b), 3.72 (s, 3H, $C_6H_4OCH_3$), 3.67 (ddd, 1H, H-5'), 2.14, 2.07, 2.06, 2.01, 1.99, 1.90 (s, 18H, 6 $COCH_3$). ^{13}C NMR (75.4 MHz, $CDCl_3$), δ 170.4, 170.2, 170.1, 169.7, 169.2, 168.9 (6 $COCH_3$), 167.6 (2 CO of NPhth), 155.6 (C-4 of$C_6H_4OCH_3$), 150.4 (C-1 of $C_6H_4OCH_3$), 134.2-114.3 (10C, NPhth, $C_6H_4OCH_3$), 100.5 (C-1'), 77.1 (C-4), 72.8 (C-3'), 72.6 (C-3), 71.8 (C-2'), 71.5 (C-5'), 70.5 (C-5), 67.7 (C-4'), 61.9, 61.4 (C-6, C-6'), 55.5 ($C_6H_4OCH_3$), 54.7 (C-2), 20.7, 20.5, 20.4, 20.4, 20.4, 20.2 (6 $COCH_3$). FABMS: *m/z* 852 100%, $(M+Na)^+$]

p-Methoxyphenyl 3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-4-*O*-(2,3,4-tri-*O*-acetyl-6-*O*-*p*-toluenesulfonyl-β-D-glucopyranosyl)-β-D-glucopyranoside (16).

To a solution of **14** (50 mg, 0.07 mmol) in pyridine (2 mL) *p*-toluenesulfonyl chloride (44 mg, 0.23 mmol) was added at 0°C. The reaction mixture was stirred at r.t. for 3.5 hours, then acetic anhydride (1 mL) was added and stirred for another 16 hours at r.t. The reaction mixture was poured into ice-water and extracted with dichloromethane (3x10 mL). The organic layer was washed with

H_2SO_4 1N (15 mL), saturated aq $NaHCO_3$ (15 mL) and water (2x15 mL), dried ($MgSO_4$) and concentrated to dryness. Column chromatography of the residue on silica gel (dichloromethane-acetone, 80:1) gave **16** (60 mg, 88%) as a white solid that crystallised from dichloromethane-acetone had m.p. 85-87°; $[\alpha]_D$ +37° (*c* 0.75, dichloromethane). ^1H NMR (300 MHz, $CDCl_3$), δ 7.73-7.28 (m, 4H, $C_6H_4CH_3$), 7.67 (m, 4H, NPhth), 7.40-6.76 (m, 10H, 2Ph), 6.80-6.66 (m, 4H, $C_6H_4OCH_3$), 5.05 (t, 1H, $J_{3',4'}$ 9.3 Hz, H-3'), 4.99 (t, 1H, $J_{4',5'}$ 9.3 Hz, H-4'), 4.94 (dd, 1H, $J_{2',3'}$ 9.3 Hz, H-2'), 4.78, 4.48 (d, 2H, $^2J_{H,H}$ 11.9 Hz, CH_2Ph), 4.63, 4.36 (d, 2H, $^2J_{H,H}$ 11.7 Hz, CH_2Ph), 4.59 (d, 1H, $J_{1'2'}$ 7.9 Hz, H-1'), 4.33 (dd, 1H, $J_{2,3}$ 10.6 Hz, H-2), 4.22 (dd, 1H, $J_{3,4}$ 8.3 Hz, H-3), 4.05 (m, 3H, H-4, H-6'a, H-6'b), 3.77 (m, 2H, H-6a, H-6b), 3.69 (s, 3H, $C_6H_4OCH_3$), 3.57 (m, 1H, H-5), 3.52 (m, 1H, H-5'), 2.41 (s, 3H, $ArCH_3$), 2.03, 2.00, 1.99 (s, 9H, 3 $COCH_3$). ^{13}C NMR (75.4 MHz, $CDCl_3$), δ 170.0, 169.3, 168.8 (3C, *C*OCH3), 167.7, 167.5 (CO, NPhth), 155.2 (C-4 de $C_6H_4OCH_3$), 150.6 (C-1 de $C_6H_4OCH_3$), 144.9-114.2 (28 C aromatic), 99.7 (C-1'), 78.0 (C-4), 76.3 (C-3), 74.6, 74.5 (2 CH_2Ph), 74.6 (C-5), 72.6 (C-3'), 71.5 (C-2'), 71.0 (C-5'), 68.4 (C-4'), 67.2 (C-6), 66.6 (C-6'), 55.4 (C-2), 55.4 ($C_6H_4OCH_3$), 21.5 ($ArCH_3$), 20.5 ($COCH_3$), 20.4 (2 $COCH_3$). FABMS: *m/z* 1070 [100%, $(M+Na)^+$].

Anal. Calcd. for $C_{54}H_{55}NO_{18}S$: C, 62.49; H, 5.34; N, 1.35; S, 3.09. Found: C, 62.58; H, 5.29; N, 1.47; S, 3.31.

***p*-Methoxyphenyl 3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-4-*O*-(2,3,4-tri-*O*-acetyl-6-*S*-acetyl-6-thio-β-D-glucopyranosyl)-β-D-glucopyranoside (17).**

A mixture of **16** (190 mg, 0.18 mmol) and potassium thioacetate (42 mg, 0.36 mmol) in DMF (3 mL) was heated at 80°C for 5 hours and then diluted with dichloromethane (50 mL). The organic layer was washed with water (3x25 mL), dried (Na_2SO_4) and evaporated. Column chromatography on silica gel of the residue (ethyl ether-petroleum ether, 4:1) gave **17** (116 mg, 70%) as a white solid that crystallised from ethyl ether and petroleum ether had m.p. 74-76°; $[\alpha]_D$ 19° (*c* 1, dichloromethane). ^1H NMR (300 MHz, $CDCl_3$), δ 7.66 (m, 4H, NPhth), 7.43-6.81 (m, 10H, 2Ph), 6.81-6.58 (m, 4H, $C_6H_4OCH_3$), 5.03 (dd, 1H, $J_{3',4'}$ 8.8 Hz, H-3'), 4.96 (dd, 1H, $J_{4',5'}$ 9.3 Hz, H-4'), 4.94 (dd, 1H, $J_{2',3'}$ 9.3 Hz, H-2'), 4.80, 4.50 (d, 2H, $^2J_{H,H}$ 12.0 Hz, CH_2Ph), 4.78, 4.44 (d, 2H, $^2J_{H,H}$ 12.7 Hz, CH_2Ph), 4.59 (d, 1H, $J_{1'2'}$ 7.8 Hz, H-1'), 4.37 (dd, 1H, $J_{2,3}$ 10.5 Hz, H-2), 4.24

(dd, 1H, $J_{3,4}$ 8.4 Hz, H-3), 4.13 (dd, 1H, $J_{4,5}$ 9.8 Hz, H-4), 3.79 (m, 2H, H-6a, H-6b), 3.70 (s, 3H, $C_6H_4OCH_3$), 3.59 (m, 1H, H-5), 3.43 (m, 1H, H-5'), 3.12 (m, 1H, $J_{5',6'a}$ 3.0 Hz†, $J_{6'a,6'b}$ 14.4 Hz†, H-6'a), 3.08 (m, 1H, $J_{5',6'b}$ 6.1 Hz†, H-6'b), 2.30 (s, 3H, $SCOCH_3$), 2.07, 2.01, 1.98 (s, 3 $COCH_3$). ^{13}C NMR (75.4 MHz, $CDCl_3$), δ 194.8 ($SCOCH_3$) 169.6, 168.9, 167.5 (3C, $COCH_3$), 167.5, 167.4 (CO, NPhth), 155.2 (C-4 of $C_6H_4OCH_3$), 150.7 (C-1 of $C_6H_4OCH_3$), 138.9-114.2 (22 C aromatic), 99.6 (C-1'), 77.8 (C-4), 76.0 (C-3), 74.7, 74.1 (2 CH_2Ph), 74.4 (C-5), 72.9 (C-3'), 72.4 (C-2'), 71.7 (C-5'), 69.9 (C-4'), 67.2 (C-6), 55.4 (C-2), 55.4 ($C_6H_4OCH_3$), 30.3 ($SCOCH_3$), 29.5 (C-6'), 22.5 ($COCH_3$), 20.5 (2 $COCH_3$). FABMS: *m/z* 964 [100%, $(M+Na)^+$].

Anal. Calcd. for $C_{49}H_{51}NO_{16}S$: C, 62.48; H, 5.46; N, 1.49; S, 3.40. Found: C, 62.58; H, 5.71; N, 1.45; S, 3.27.

† *Calculated by resolution of the AB part in a ABX system.*

Sodium *p*-methoxyphenyl 3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-4-*O*-(2,3,4-tri-*O*-acetyl-6-deoxy-6-sulfonato-β-D-glucopyranosyl)-β-D-glucopyranoside (18). To a mixture of **17** (68 mg, 0.07 mmol) and sodium acetate (18 mg, 0.2 mmol) in acetic acid (1 mL), aqueous hydrogen peroxide 33% (86 mL, 0.83 mmol) was added. The reaction mixture was heated at 60°C for 8 hours and evaporated to dryness. Column chromatography of the residue on silica gel (dichloromethane-methanol, 20:1) gave **18** (44 mg, 65%) as an oil; $[\alpha]_D$ +12° (*c* 1, dichloromethane). ^1H NMR (300 MHz, $CDCl_3$), δ 7.83-6.57 (m, 14H, NPhth, 2Ph), 6.70-6.49 (m, 4H, $C_6H_4OCH_3$), 5.11 (t, 1H, $J_{3',4'}$ 9.4 Hz, H-3'), 4.99 (t, 1H, $J_{2',3'}$ 9.4 Hz, H-2'), 4.94, 4.61 (d, 2H, $^2J_{H,H}$ 12.6 Hz, CH_2Ph), 4.89 (t, 1H, $J_{4',5'}$ 9.4 Hz, H-4'), 4.73 (d, 1H, $J_{1'2'}$ 8.0 Hz, H-1'), 4.69, 4.46 (d, 2H, $^2J_{H,H}$ 12.2 Hz, CH_2Ph), 4.51 (dd, 1H, $J_{2,3}$ 10.6 Hz, H-2), 4.45 (m, 1H, H-4), 4.26 (m, 1H, H-5'), 4.03 (dd, 1H, $J_{3,4}$ 8.5 Hz, H-3), 3.79 (m, 2H, H-6a, H-6b), 3.63 (s, 3H, $C_6H_4OCH_3$), 3.60 (m, 1H, H-5), 3.29 (dd, 1H, $J_{5'6'a}$ 9.4 Hz, $J_{6'a6'b}$ 14.9 Hz, H-6'a), 3.22 (dd, 1H, $J_{5'6'b}$ 2.0 Hz, H-6'b), 1.96, 1.95, 1.88 (s, 9H 3 $COCH_3$). ^{13}C NMR (75.4 MHz, $CDCl_3$), δ 170.0, 169.7, 169.1 (3 $COCH_3$), 167.1 (2 CO, NPhth), 155.1 (C-4 of $C_6H_4OCH_3$), 150.0 (C-1 of $C_6H_4OCH_3$), 137.6-114.5 (22 C aromatic), 100.2 (C-1'), 78.3 (C-4), 75.8 (C-5), 75.2 (C-3), 74.7, 73.4 (2 CH_2Ph), 73.0 (C-3'), 71.9 (C-2'), 71.2 (C-5'), 70.9 (C-4'), 67.6 (C-6), 55.4 ($C_6H_4OCH_3$), 55.2 (C-2), 52.0 (C-6'), 20.5, 20.4, 20.4 (3 $COCH_3$). FABMS: *m/z*

992 [100%, $(M+Na)^+$]. HRFABMS: *m/z* obsd. 1102.1599. Calcd. for $C_{47}H_{48}O_{18}SNa + Cs$ 1102.1526.

ACKNOWLEDGEMENTS

We thank the Dirección General de Investigación Científica y Técnica for financial support (grant number PB94/1440-C02-01).

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(Received in the UK 10 November 1997)