199. Temporary Protection and Activation in the Regioselective Synthesis of Saccharide Sulfates

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Regioselective sulfation with $Et_3N \cdot SO_3$ of partially protected or unprotected glycosides *via* stannanediyl acetals or stannyl ethers, combined with persistent or temporary protecting groups is described. Stannylation of phenylboronates, followed by sulfation and aqueous workup, is an efficient way for the synthesis of monosulfated monosaccharides. The stannanediyl acetal **2** led in high yields to **3a**, while sulfation of the diol **1** proceeded more slowly and led in lower yield to a mixture **1**/**3a**/**4a**/**5a** (*Scheme 1*). The trehalose disulfate **8a** was obtained in high yields from **7**; reducing the amount of sulfating agent led to a mixture **6**/**8a**/**9a**. Stannylation and sulfation of the galactoside **11** afforded **13a**, while direct sulfation of **11** gave a mixture of the 2- and 3-sulfates **13a**/**14a** besides some disulfate **15a**. Sulfation of the lactose derivative **16** and the stannanediyl acetal **17** gave the 3-sulfate **18a**, with some disulfate **19a** being formed from **16**. The mannopyranoside **21** was selectively sulfated at OH–C(2), leading to **22a**, while the corresponding diol **20** yielded mostly the isomer **23a** and some disulfate **24a**. Sulfation of the stannyl ethers derived from the gluco- and galactopyranosides **25** and **28** and $(Bu_3Sn)_2O$ afforded high yields of the 2,6-disulfate **26a** and the 3,6-disulfate **29a**, respectively. Stannylation of **25** and **28** with Bu_2SnO and sulfation proceeded less satisfactorily. Stannylation of the phenylboronate **32** (Bu_2SnO) and sulfation gave good yields of the 2-sulfate **27a**; stannylation and benzoylation yielded the 2-benzoate **34** (*Scheme 2*). Similarly, the galactose-derived **37** provided high yields of the 3-sulfate **30a** and of the 3-benzoate **39**. Direct sulfation of the phenylboronates **32** and **37** proceeded in lower yields and gave mixtures.

Introduction. – Sulfated saccharides and glycoconjugates occur extensively and are endowed with a number of important biological functions [1–23].

In the preparation of defined carbohydrate sulfates, the sulfate group is, as a rule, introduced near the end of the synthesis to obviate the need of a sulfating agent which introduces the sulfate group in a protected form, such as the phenyl chlorosulfate described by *Penney* and *Perlin* [24]. Consequently, persistent protecting groups such as benzyl ethers have most often used in the synthesis of sulfated oligosaccharides [8] [25–31]. The alcohol is usually treated directly with one of the most common sulfating reagents, complexes of SO_3 and a *Lewis* base such as DMF, pyridine, or a trialkylamine [32], although the $SO_3 \cdot$DMF complex has also been used to form sulfates from nitrite esters [6] [33] or trimethylsilyl ethers [34] of cellulose. The sulfate group has also been introduced by displacing the triflate anion with tetrabutylammonium hydrogensulfate [35][3]). The regioselective sulfation of partially protected glucose [44] or galactose [45] and some disaccharides [46] proceeds similarly to other *O*-acylations. Sulfation at the primary

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[3]) Other reagents include H_2SO_4 in the presence of *N*,*N*′-dicyclohexylcarbodiimide [36–38] or Ac_2O [39], sulfamic acid [40], piperidine-*N*-sulfonic acid [41], chlorosulfonic acid [42] [43], and SO_2Cl_2.

position is preferred, as expected, and goes along with the formation of isomeric monosulfates and higher sulfates. The 4,6-*O*-benzylidene-α-D-glucopyranoside **1** was selectively sulfated at HO–C(2) [47]. An alkyl α-D-glucopyranoside was reported to preferentially form the 2,6-disulfate with the pyridine·SO_3 complex [48][4]).

We became interested in the regioselective activation of carbohydrate OH groups towards sulfating agents *via* dibutylstannanediyl acetals and tributylstannyl ethers, intermediates well known to lead to regioselective *O*-benzylations, *O*-allylations, and *O*-acylations (see [48] [50–52] and ref. cit. therein). It appeared particularly attractive to use this activation in conjunction with temporary protection, such as phenylboronation, as phenylboronates are labile enough to be removed during workup, obviating a separate deprotection step [53]. To the best of our knowledge, this combination of activation and temporary protection is new, while examples of the use of stannanediyl acetals in the regioselective sulfation of partially protected saccharides have recently been reported by *Flitsch et al.* [54].

We report the regioselective sulfation of dibutylstannanediyl acetals prepared from the partially protected glucoside **1**, galactosides **11** and **16**, and mannoside **20**, the use of dibutylstannanediyl acetals and tributylstannyl ethers for the regioselective sulfation of methyl α-D-glucopyranoside (**25**) and methyl β-D-galactopyranoside (**28**), and the results of the combination of the phenylboronate moiety with the butylstannanediyl acetal mediated regioselective sulfation and benzoylation of **25** and **28**.

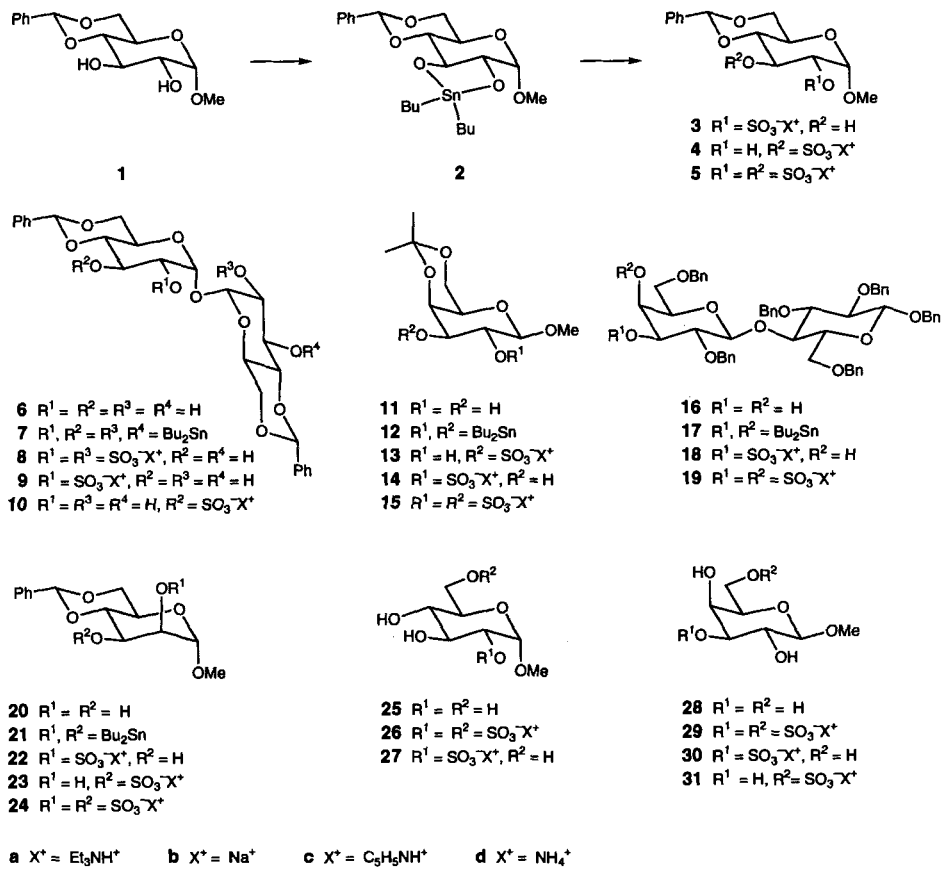
Results and Discussion. – Benzoylation and tosylation of the 2,3-*O*-dibutylstannanediyl acetal **2** [55] [56] of the 4,6-*O*-benzylidene-α-D-glucopyranoside **1** gives good yields of products monofunctionalized at HO–C(2) [57–59]. By analogy, treatment of **2** with 1.1 equiv. of $Et_3N \cdot SO_3$ in DMF yielded 84% of the 2-sulfate **3a**, isolated by flash chromatography on silica gel in the presence of Et_3N [60] (*Scheme 1*). The triethylammonium salt **3a** is easily transformed into the sodium salt **3b** by ion-exchange chromatography. Sulfation of the diol **1** with $Et_3N \cdot SO_3$ in DMF required a longer reaction time, a higher temperature, and the addition of a larger excess of the reagent for completion of the reaction. The reaction gave a 3:1 mixture (68%) of the monosulfates **3a** and **4a**, inseparable by flash chromatography, and the disulfate **5a** (7%) besides recovered **1**. Sulfation of **1** with pyridine·SO_3 [47] [61] or chlorosulfonic acid [62] in pyridine at room temperature gave predominantly the monosulfates **3c**, whereas the disulfate **5c** was obtained in the reaction of **1** with an excess of pyridine·SO_3 at 65° [63].

The bis(dibutylstannanediyl) diacetal **7** derived from 4,6:4′,6′-di-*O*-benzylidene-α,α-trehalose [64] (**6**) was sulfated with 3 equiv. of $Et_3N \cdot SO_3$ in 1,3-dimethylimidazolidin-2-one to give 90% of the crystalline 2,2′-disulfate **8a**. Reaction of **7** with 1.2 equiv. of $Et_3N \cdot SO_3$ in DMF gave recovered **6** (25%), the 2-monosulfate **9a** (50%), and the disulfate **8a** (24%). Direct sulfation of **6** with $C_5H_5N \cdot SO_3$ in pyridine has been reported to lead, after isolation, to the 2-sulfate **9d** and 3-sulfate **10d** in 40 and 8% yield, respectively [65].

The 4,6-*O*-isopropylidene-β-D-galactopyranoside **11** [66] is expected to react at HO–C(3) upon stannylation and sulfation [57] [67]; the 3-sulfate **13a** was indeed ob-

[4]) Azido sulfates were prepared by regioselective ring opening of five-membered cyclic sulfates with lithium azide [49].

Scheme 1



tained in 89% yield as the only product (no **14a** detected). Direct sulfation of **11** with 1.1 equiv. of $Et_3N \cdot SO_3$ gave 51% of a 4:1 mixture of the 3- and 2-sulfates **13a**/**14a** and 10% of the 2,3-disulfate **15a**.

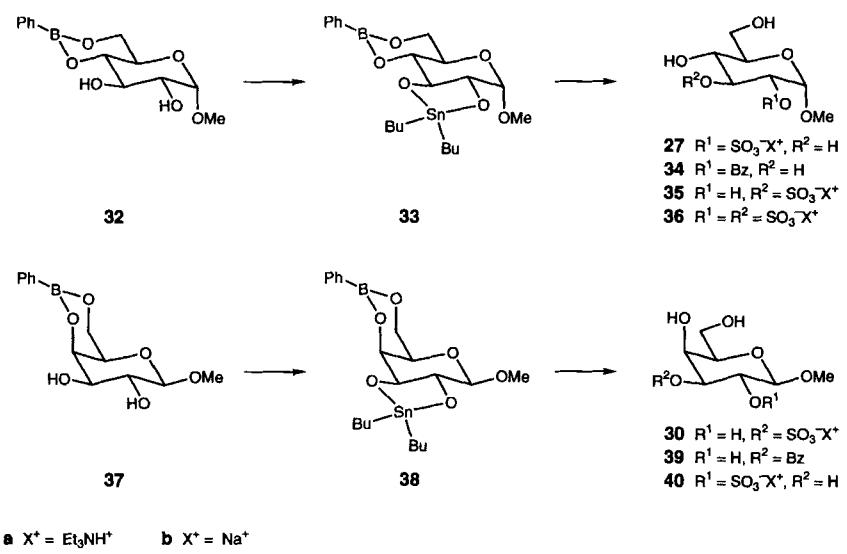
Sulfation of both the lactose derivative **16** [68] and the corresponding stannanediyl acetal **17** gave the 3-sulfate **18a** as the sole monosulfated product in 77 and 83% yield, respectively. Sulfation of **16** occurred more slowly and also gave 11% of the disulfate **19a**. These results are in agreement with the known regioselectivity of 3,4-*O*-(dibutylstannanediyl)galactose derivatives [54] [67] [69–72] and the higher reactivity of HO–C(3) over OH–C(4) in galactose [73] [74].

The stannanediyl acetal **21** [71] [75] of the 4,6-*O*-benzylidene-α-D-mannopyranoside **20** [76] is selectively benzylated at HO–C(3) and benzoylated at HO–C(2) [71] [77]. Similarly, treatment of **21** with $Et_3N \cdot SO_3$ gave predominantly the 2-sulfate **22a** (*ca.* 70%). In agreement with the higher reactivity of the equatorial OH group of **20** upon acylation [78] [79], **20** was sulfated mainly at the equatorial HO–C(3) yielding 55% of **23a**, 15% of **22a**/**23a** 2:1, and 13% of the disulfate **24a** after purification by flash chromatography.

Alcohols were also regioselectively activated towards acylation [80] or alkylation [81–83] *via* their tributylstannyl ethers. Stannylation of the gluco- and the galactopyranoside **25** and **28** with 1.1 equiv. of hexabutyldistannoxane [82] [83] and sulfation of the crude products with 2.5 equiv. of $Et_3N \cdot SO_3$ in DMF yielded 82% of the 2,6-disulfates **26a** and 76% of the 3,6-disulfated **29a**, respectively. Stannylation of **25** or **28** with Bu_2SnO [58] [84] [85], however, followed by sulfation gave only moderate yields of the 2-sulfate **27a**[5]) (38%) and the 3-sulfate **30a** (37%), respectively, besides recovered diol and some 2,6-disulfate **26a** and 3,6-disulfate **29a**. Attempts to force the reaction towards completion, *e.g.* with a larger excess of sulfating agent or using the more reactive $DMF \cdot SO_3$ complex, did not improve the yields. Sulfation of **25** with 4 equiv. of $C_5H_5N \cdot SO_3$ in pyridine, conditions reported to give selectively the 2,6-disulfate of a long-chain α-D-glucoside [87], gave a mixture of three compounds after FC, where the 2,6-disulfate **26a** was present to *ca.* 80% by integration from the ^{1}H-NMR spectrum. The selectivity of sulfation is thus not due to aggregation effects. Sulfation of **28** with H_2SO_4 in the presence of *N,N'*-dicyclohexylcarbodiimide yielded the 6-sulfate **31d** and the 3,6-disulfate **29d** as the main products [88].

The compatibility of phenylboronates [53] with the conditions of stannylation, and subsequent acylation was explored by treating the 4,6-phenylboronates **32** [89] with Bu_2SnO under reflux in toluene with azeotropic removal of H_2O, and subjecting the dried crude material (**33**) to sulfation or benzoylation (*Scheme 2*). High yields of the 2-sulfate **27a** (79%) and of the known 2-benzoate **34** [85] [90] [91] (85%) were obtained after flash chromatography which removed the stannanediyl and boranediyl residues. Similarly, the 4,6-phenylboronate **37** [92] led *via* the stannanediyl acetal **38** to the 3-sulfate **30a** (85%)

Scheme 2



[5]) The brucinium salt of **27** and the barium salt of **36** were obtained by deprotection of **3** [47] and **5** [63], respectively. The ammonium salt of **35** was isolated from the sulfation product of **25** [86].

and the known 3-benzoate **39** [85] [93] (86%). Sulfation of **32** with 1.0 equiv. of $Et_3N \cdot SO_3$ gave the deprotected glucoside **25** (59%), the 2-sulfate **27a** (26%), and the 3-sulfate **35a**[5]) (11%), after medium-pressure chromatography on silica gel. Reaction with 1.5 equiv. of $Et_3N \cdot SO_3$ increased the yield of **27a** to 37%. The 2,3-disulfate **36a**[5]) was obtained in 28% yield besides **25**, while the 3-sulfate **35a** was not observed. Sulfation of **37** with 1.0 equiv. of $Et_3N \cdot SO_3$ gave an inseparable 4:1 mixture of the 3- and 2-sulfates **30a**/**40a** in 34% yield, besides the deprotected galactoside **28**.

The sulfates are characterized as the triethylammonium salts (NMR, see *Exper. Part* and *Tables 1* and *2*) and as the sodium salts (IR spectra, elemental analysis). All sulfates

Table 1. *^{1}H- and ^{13}C-NMR* ($CDCl_3$) *Chemical Shifts* [ppm] *for H–C(2), H–C(3), C(2), and C(3) of the Sulfates Derived from* **1**, **6**, **11**, and **20**, *and for H–C(3), H–C(4), C(3), and C(4) of the Sulfates Derived from* **16**. The shift differences between the sulfates and the corresponding unsulfated compounds [a]) are given in parentheses.

	3a	**4a**	**5a**	**8a**[b])[c])	**9a**[c])
H–C(2)	4.42 (+0.79)	[d])	4.39 (+0.76)	4.02 (+0.59)	4.45, 3.85
H–C(3)	4.13 (+0.19)	4.73 (+0.79)	4.79 (+0.85)	3.80 (+0.04)	4.18, 3.97
C(2)	77.5 (+5.1)		75.5 (+3.1)	78.8 (+5.1)	78.8, 73.7 (+5.3, 0)
C(3)	68.1 (−2.4)		74.9 (+4.5)	70.7 (−0.8)	69.8, 71.8 (−1.7, +0.3)

	13a	**14a**	**15a**	**22a**	**23a**	**24a**[c])
H–C(2)	3.85 (+0.13)	4.42 (+0.80)	4.31 (+0.69)	4.72 (+0.66)	4.64 (+0.56)	5.00 (+0.94)
H–C(3)	4.41 (+0.72)	[d])	4.31 (+0.65)	4.10 (+0.03)	4.64 (+0.57)	4.84 (+0.77)
C(2)	67.1 (−3.0)		67.1 (+3.3)	78.9 (+6.3)	69.0 (−1.6)	76.6 (+6.0)
C(3)	77.5 (+4.9)		67.1 (+3.7)	67.0 (−1.0)	75.7 (+7.7)	73.8 (+5.8)

	18a	**19a**		**18a**	**19a**
H–C(3)	4.33 (+0.83)	4.42 (+0.92)	C(3)	80.7 (+7.3)	78.1 (+4.7)
H–C(4)	4.46 (+0.53)	5.01 (+1.06)	C(4)	66.8 (−1.9)	74.3 (+5.6)

[a]) ^{13}C-NMR Data of **1** and **20** from [97] and of **11** from [98]. [b]) ^{1}H-NMR in (D_6)DMSO. [c]) ^{13}C-NMR in CD_3OD. [d]) Not determined.

Table 2. *^{1}H-* ((D_6)DMSO) *and ^{13}C-NMR* (CD_3OD) *Chemical Shifts* [ppm] *of the Sulfates Derived from* **25** *and* **28**. The shift differences between the sulfates and **25** and **28**[a]), respectively, are given in parentheses.

	26a[b])	**27a**	**36a**	**29a**[c])	**30a**[d])
H–C(1)	4.71 (+0.18)	4.73 (+0.20)	5.06 (+0.53)	4.07 (+0.08)	4.07 (+0.08)
H–C(2)	3.84 (+0.65)	3.81 (+0.62)	3.80 (+0.61)	3.41 (+0.08)	3.33–3.54
H–C(3)	3.44–3.52	3.50 (+0.11)	4.23 (+0.84)	3.95 (+0.67)	3.90–3.95 (+0.65)
H–C(4)	3.20 (+0.01)	3.12 (+0.07)	3.20–3.43	3.85 (+0.21)	3.90–3.95 (+0.29)
H–C(5)	3.44–3.52	3.29 (−0.02)	3.20–3.43	3.58 (+0.30)	3.33–3.54
H–C(6)	4.01 (+0.38)	3.61 (−0.02)	3.47 (−0.20)	3.81 (+0.26)	3.33–3.54
H′–C(6)	3.71 (+0.25)	3.41 (−0.05)	3.20–3.43	3.76 (+0.27)	3.33–3.54
C(1)	99.3 (−0.7)	100.7 (+0.7)	99.3 (−0.7)	105.4 (+0.9)	103.8 (−0.7)
C(2)	78.8 (+6.8)	80.2 (+6.8)	76.1 (+3.9)	70.3 (−1.4)	69.2 (−2.5)
C(3)	72.7 (−1.4)	73.5[e])	80.3 (+6.2)	81.1 (+7.3)	80.7 (+6.9)
C(4)	71.8[e])	74.3[e])	71.6 (+1.0)	68.0 (−1.7)	67.4 (−2.3)
C(5)	71.3[e])	74.6[e])	73.1 (+0.6)	73.6 (−2.4)	75.0 (−1.0)
C(6)	68.1 (+6.5)	64.0 (+2.4)	62.3 (+0.7)	67.1 (+5.1)	61.2 (−0.8)

[a]) ^{13}C-NMR Data of **25** and **28** from [97]. [b]) ^{1}H-NMR of **26b**. [c]) ^{1}H-NMR of **29b**. [d]) ^{13}C-NMR of **30b**. [e]) Assignment may be interchanged.

exhibited strong bands at 1250 cm^{-1} characteristic for S=O stretch and medium-to-strong bands between 820 and 850 cm^{-1} for the C–O–S bend vibration [94] [95] [96]. The number of sulfate groups in the products is easily determined by integration of the MeO and Et_3NH^+ signals in the ^{1}H-NMR spectra.

The introduction of a sulfate group leads to a downfield ^{1}H-NMR shift of the geminal and vicinal (0.1–0.4 ppm) H-atoms (*ca.* 0.6–0.7 ppm for CH and *ca.* 0.4–0.5 for CH_2) [99–101]. The downfield shift for the vicinal H-atoms depends on the relative orientation of the sulfate group and is strongest for an equatorial H-atom in the neighborhood of an equatorial sulfate group. Similarly, one observes a downfield shift of the C(α)-atoms (*ca.* 6–8 ppm) [25] [99–101]. The C(β)-atoms, however, are shifted upfield (1–2 ppm by an equatorial and 0.5–1 ppm by an axial sulfate group). The position of the sulfate groups is thus revealed by the chemical shift of the geminal H-atoms and of the C(α)-atoms of the sulfated and hydroxylated centers and by signal changes upon D_2O or CD_3OD exchange (see *Exper. Part*). The chemical-shift values for these centers of the partially protected glycosides (^{1}H-NMR in $CDCl_3$) are listed in *Table 1* and the ones for all centers of the sulfates derived from **25** or **28** (^{1}H-NMR in (D_6)DMSO) in *Table 2*. The observed $\Delta\delta$ values agree well with the above mentioned rules. The strong deshielding of the equatorial H vicinal to an equatorial sulfate group (H–C(4) of **18**, H–C(2) of **23**) and the relatively weak deshielding of the C(α)-atoms of the disulfates **5** and **15** due to the opposing α- and β-effects are remarkable. The presence of sulfate groups has no influence upon the conformation of the pyranose ring. The NMR spectra of the trehalose sulfate **8** show only one set of signals, evidencing the presence of a symmetric disulfate, whereas the spectra of **9** exhibit two sets of signals. These were unambiguously assigned by a ^{1}H,^{13}C-HMQC and a TOCSY spectrum and show the presence of a 2-sulfated and an unsulfated glucopyranosyl residue.

We thank *F. Hoffmann-La Roche AG*, Basel, for generous support.

Experimental Part

1. *General Procedure for the Preparation of the Dibutylstannanediyl Derivatives.* An equimolar mixture of the powdered saccharide and Bu_2SnO was refluxed in toluene for 16 h (*Dean-Stark* condenser). Evaporation of the resulting clear soln. (using a water pump equipped with a liq. N_2 trap) gave the crude stannanediyl derivative.

2. *General Procedure for the Sulfation of the Stannanediyl Derivatives.* Under Ar, 0.1M crude stannanediyl derivative in DMF was cooled to 0° and treated dropwise with *ca.* 0.3M $Et_3N \cdot SO_3$ (1.2 equiv.) in DMF within 10 min. Stirring was continued until complete disappearance of the starting material (TLC monitoring; 1–3 h). Evaporation at 30°/0.05 mbar, followed by FC, concentration of the appropriate fractions, membrane filtration, and drying gave the sulfates.

3. *General Procedure for the Conversion of the Triethylammonium Salts to the Sodium Salts.* The triethylammonium salt was dissolved in a minimum volume of MeOH and passed through *Dowex 50 WX8* (strongly acidic ion-exchange resin, Na^+ form, 30 g-equiv.). Elution with MeOH (0.5 ml/min), evaporation, and drying gave the sodium salts. For the preparation of **26b**, **27b**, **29b**, and **30b**, the sodium salt was dissolved in a minimum volume of MeOH and precipitated by the addn. of Et_2O, the mixture centrifuged, the solvent decanted, and the pellet dried to give a white powder. Yields for the conversion to the sodium salts were always greater than 95%.

4. *Sulfation of* **1**. a) The reaction of **1** (1.00 g, 3.53 mmol) with Bu_2SnO (0.88 g, 3.53 mmol) gave crude **2** [55] (1.81 g, 100%; white solid). A part of **2** (400 mg, 0.78 mmol) was treated with $Et_3N \cdot SO_3$ (153 mg, 0.85 mmol) for 1 h. FC (toluene/EtOH/Et_3N 3:1:0.05) gave **1** (14 mg) and **3a** (302 mg, 84%).

b) A soln. of **1** (410 mg, 1.45 mmol) in DMF (10 ml) was treated with $Et_3N \cdot SO_3$ (285 mg, 1.57 mmol) at 25° for 24 h. Additional $Et_3N \cdot SO_3$ (100 mg, 0.55 mmol) was added and the mixture stirred for further 24 h. FC (toluene/EtOH/Et_3N 3:1:0.05) gave **1** (62 mg, 15%), **3a**/**4a** 3:1 (398 mg, 68%), and **5a** (60 mg, 7%). The ratio **3a**/**4a** was determined by integration of the ^{1}H-NMR peaks for PhC*H*, H–C(1), and H–C(3).

*Triethylammonium (Methyl 4,6-*O*-Benzylidene-2-*O*-sulfonato-α-*D*-glucopyranoside)* (= *Methyl 4,6-*O*-Benzylidene-α-*D*-glucopyranoside 2-(Triethylammonium Sulfate)*; **3a**): Amorphous solid. R_f (toluene/EtOH/Et_3N 3:1:0.05) 0.17. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.35 (*t*, *J* = 7.5, 3 Me); 3.13 (*q*, *J* = 7.5, 3 CH_2); 3.41 (*s*, MeO); 3.58 (*t*, *J* ≈ 9.7, H–C(4)); 3.76 (*t*, *J* = 10,1, H_{ax}–C(6)); 3.85 (*dt*, *J* = 4.7, 10.1, H–C(5)); 4.13 (*t*, *J* = 9.3, H–C(3)); 4.27 (*dd*, *J* = 4.7, 10.1, H_{eq}–C(6)); 4.30 (br. *s*, exchange with D_2O, HO–C(3)); 4.42 (*dd*, *J* = 3.8, 9.3, H–C(2)); 4.99 (*d*, *J* = 3.8, H–C(1)); 5.55 (*s*, PhC*H*); 7.31–7.36 (*m*, 3 arom. H); 7.48–7.51 (*m*, 2 arom. H). ^{13}C-NMR (50 MHz, $CDCl_3$): 8.57 (*q*, 3 Me); 46.54 (*t*, 3 CH_2); 55.11 (*q*, MeO); 61.79 (*d*, C(5)); 68.74 (*t*, C(6)); 68.08 (*d*, C(3)); 77.48 (*d*,

C(2)); 81.60 (*d*, C(4)); 98.58 (*d*, C(1)); 101.72 (*d*, PhCH); 126.28 (*d*, 2 arom. C); 127.95 (*d*, 2 arom. C); 128.79 (*d*, 1 arom. C); 137.15 (*s*, 1 arom. C).

Sodium (Methyl 4,6-O-Benzylidene-2-O-sulfonato-α-D-glucopyranoside) (**3b**): $[\alpha]_D^{25} = +4.7$ ($c = 0.315$, MeOH). IR (KBr): 3400*s* (br.), 2965*w*, 2940*w*, 2920*w*, 2865*w*, 1630*m*, 1495*w*, 1460*w*, 1450*m*, 1415*m*, 1385*m*, 1375*m*, 1290*w*, 1250*s*, 1235*s*, 1210*m*, 1190*m*, 1170*w*, 1150*m*, 1130*m*, 1110*m*, 1095*m*, 1080*s*, 1070*s*, 1055*s*, 1040*s*, 1030*s* (sh), 1010*s*, 1000*s*, 975*m*, 935*w*, 890*w*, 830*m*, 815*m* (sh), 750*m*, 695*m*, 675*m*, 660*m*, 650*m*, 615*m*, 605*m*. Anal. calc. for $C_{14}H_{17}NaO_9S$ (384.33): C 43.75, H 4.46, S 8.34; found: C 44.03, H 4.48, S 8.50.

Signals of **4a** *in the* ^{1}*H-NMR of* **3a**/**4a** *76:24*: 3.45 (*s*, MeO); 3.62 (*t*, $J \approx 9.5$, H–C(4)); 4.73 (*t*, $J = 9.3$, H–C(3)); 4.84 (*d*, $J = 3.8$, H–C(1)); 5.23 (br. *s*, exchange with D_2O, OH–C(2)); 5.46 (*s*, PhC*H*).

Bis(triethylammonium) (Methyl 4,6-O-Benzylidene-2,3-di-O-sulfonato-α-D-glucopyranoside) (**5a**): R_f (toluene/EtOH/Et_3N 3:1:0.05) 0.05. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.35 (*t*, $J = 7.5$, 6 Me); 3.13 (*q*, $J = 7.5$, 6 CH_2); 3.39 (*s*, MeO); 3.62 (*t*, $J = 9.6$, H–C(4)); 3.76 (*t*, $J = 10.1$, H_{ax}–C(6)); 3.85 (*m*, H–C(5)); 4.26 (*dd*, $J = 4.0$, 9.5, H_{eq}–C(6)); 4.39 (*dd*, $J = 3.5$, 9.6, H–C(2)); 4.79 (*t*, $J = 9.6$, H–C(3)); 5.30 (*d*, $J = 3.5$, H–C(1)); 5.55 (*s*, PhC*H*); 7.21–7.30 (*m*, 3 arom. H); 7.48–7.51 (*m*, 2 arom. H). ^{13}C-NMR (50 MHz, $CDCl_3$): 8.57 (*q*, 3 Me); 46.21 (*t*, 3 CH_2); 55.38 (*q*, MeO); 62.61 (*d*, C(5)); 68.94 (*t*, C(6)); 74.86 (*d*, C(3)); 75.45 (*d*, C(2)); 80.14 (*d*, C(4)); 99.11 (*d*, C(1)); 101.02 (*d*, PhCH); 126.31 (*d*, 2 arom. C); 127.88 (*d*, 2 arom. C); 128.46 (*d*, 1 arom. C); 137.52 (*s*, 1 arom. C).

5. *Sulfation of* **6**. a) The crude stannanediyl acetal **7** obtained by the reaction of **6** [64] (155 mg, 0.3 mmol) with Bu_2SnO (150 mg, 0.6 mmol) was dissolved in 1,3-dimethylimidazolidin-2-one (3 ml) and treated dropwise (over 10 min) at r.t. with the soln. of $Et_3N \cdot SO_3$ (145 mg, 0.8 mmol) in 2 ml of the same solvent. Stirring for 1 h, evaporation, FC (toluene/EtOH/Et_3N 20:1:0.05→3:2:0.05), and crystallization from CH_2Cl_2/Et_2O gave **8a** (251 mg, 90%).

b) The crude stannanediyl acetal **7** obtained by the reaction of **6** (250 mg, 0.48 mmol) with Bu_2SnO (120 mg, 0.48 mmol) was dissolved in DMF (10 ml) and treated dropwise (over 10 min) at r.t. with 0.3M $Et_3N \cdot SO_3$ (110 mg, 0.61 mmol) in DMF. Stirring for 15 h, evaporation, and FC (toluene/EtOH/Et_3N 3:1:0.05→2:1:0.05) gave **6** (64 mg, 25%), **9a** (173 mg, 50%), and **8a** (105 mg, 24%).

Bis(triethylammonium) (4,6-O-Benzylidene-2-O-sulfonato-α-D-glucopyranosyl 4,6-O-Benzylidene-2-O-sulfonato-α-D-glucopyranoside) (**8a**): Fine needles. M.p. 210°. R_f (AcOEt/MeOH/H_2O/Et_3N 7:2:1:0.05) 0.36. ^{1}H-NMR (400 MHz, (D_6)DMSO): 1.17 (*t*, $J = 7.3$, 6 Me); 2.91 (*q*, $J = 7.3$, 6 CH_2); 3.42 (*t*, $J \approx 9.5$, H–C(4)); 3.57 (*t*, $J = 10.1$, H_{ax}–C(6)); 3.80 (*dt*, $J = 3.6$, 9.3, H–C(3)); 4.02 (*dd*, $J = 3.8$, 9.3, H–C(2)); 4.13 (*dt*, $J = 5.1$, 10.0, H–C(5)); 4.19 (*dd*, $J = 5.1$, 10.0, H_{eq}–C(6)); 5.09 (br. *s*, exchange with D_2O, HO–C(3)); 5.30 (*d*, $J = 3.8$, H–C(1)); 5.57 (*s*, PhC*H*); 7.30–7.33 (*m*, 3 arom. H); 7.51–7.53 (*m*, 2 arom. H). ^{13}C-NMR (50 MHz, CD_3OD): 9.27 (*q*, 3 Me); 47.73 (*t*, 3 CH_2); 64.00 (*d*, C(5)); 69.71 (*t*, C(6)); 70.11 (*d*, C(3)); 78.85 (*d*, C(2)); 82.69 (*d*, C(4)); 95.60 (*d*, C(1)); 102.73 (*d*, PhCH); 127.61 (*d*, 2 arom. C); 128.98 (*d*, 2 arom. C); 129.84 (*d*, 1 arom. C); 139.35 (*s*, 1 arom. C).

Disodium (4,6-O-Benzylidene-2-O-sulfonato-α-D-glucopyranosyl 4,6-O-Benzylidene-2-O-sulfonato-α-D-glucopyranoside) (**8b**): $[\alpha]_D^{25} = +64.4$ ($c = 0.985$, MeOH). IR (KBr): 3430*s* (br.), 3030*w*, 3000*w*, 2940*w*, 2880*w*, 1640*m*, 1460*m*, 1395*m*, 1380*m*, 1260*s* (br.), 1150*s*, 1120*m*, 1100*s*, 1075*s*, 1050*s*, 1010*s* (br.), 930*m*, 880*w*, 820*s*, 815*m*, 790*m*, 760*m*, 705*m*, 680*m*, 660*m*, 640*m*, 610*s*. Anal. calc. for $C_{26}H_{28}Na_2O_{17}S_2$ (722.58): C 43.22, H 3.91, S 8.87; found: C 43.44, H 4.11, S 8.76.

Triethylammonium (4,6-O-Benzylidene-α-D-glucopyranosyl 4,6-O-Benzylidene-2-O-sulfonato-α-D-glucopyranoside) (**9a**): ^{1}H-NMR (400 MHz, $CDCl_3$; assignment based on TOCSY): 1.08 (*t*, $J = 7.3$, 3 Me); 2.81 (*q*, $J = 7.3$, 3 CH_3); 3.44 (*t*, $J = 9.5$, H–C(4′)); 3.54 (*t*, $J = 9.5$, H–C(4)); 3.58 (*t*, $J = 10.1$, H_{ax}–C(6′)); 3.65 (*t*, $J = 10.1$, H_{ax}–C(6)); 3.665 (*dd*, $J \approx 3.5$, 9.5, H–C(2′)); 3.55–3.8 (br. *s*, 2 OH); 3.9–4.1 (br. *s*, OH); 3.97 (*t*, $J = 9.2$, H–C(3′)); 4.06 (*dt*, $J = 5.1$, 9.8, H–C(5)); 4.15 (*dt*, $J = 5.2$, 9.9, H–C(5′)); 4.18 (*t*, $J = 9.5$, H–C(3)); 4.25 (*dd*, $J = 5.0$, 9.8, H_{eq}–C(6)); 4.34 (*dd*, $J = 5.0$, 9.8, H_{eq}–C(6′)); 4.45 (*dd*, $J = 3.8$, 9.5, H–C(2)); 5.10 (*d*, $J = 3.4$, H–C(1′)); 5.41 (*d*, $J = 3.8$, H–C(1)); 5.44 (*s*, PhC*H*); 5.46 (*s*, PhC*H*); 7.26–7.31 (*m*, 6 arom. H); 7.46–7.49 (*m*, 4 arom. H). ^{13}C-NMR (50 MHz, CD_3OD; assignment corroborated by ^{1}H,^{13}C-HMQC): 9.24 (*q*, 3 Me); 47.86 (*t*, 3 CH_2); 63.95 (*d*, C(5)); 64.16 (*d*, C(5′)); 69.78 (*t*, C(6), C(6′)); 69.78 (*d*, C(3)); 71.79 (*d*, C(3′)); 73.72 (*d*, C(2′)); 78.83 (*d*, C(2)); 82.72 (*d*); 82.85 (*d*, C(4), C(4′)); 95.09 (*d*, C(1)); 96.87 (*d*, C(1′)); 102.68 (*d*, PhCH); 102.97 (*d*, PhCH); 127.51 (*d*, 2 arom. C); 127.59 (*d*, 2 arom. C); 128.95 (*d*, 2 arom. C); 129.02 (*d*, 2 arom. C); 129.77 (*d*, 1 arom. C); 129.90 (*d*, 1 arom. C); 139.06 (*s*, 1 arom. C); 139.40 (*s*, 1 arom. C).

6. *Sulfation of* **11**. a) The reaction of **11** [66] (prepared according to [102]; 912 mg, 3.90 mmol) with Bu_2SnO (0.97 g, 3.90 mmol) gave crude **12** (1.81 g, 100%; white solid). A part of **12** (515 mg, 1.11 mmol) was treated with $Et_3N \cdot SO_3$ (220 mg, 1.21 mmol) for 4 h at 0°. FC (toluene/EtOH/Et_3N 3:1:0.05) gave **11** (12 mg, 2%) and **13a** (410 mg, 89%).

b) A soln. of **11** (234 mg, 1.00 mmol) in DMF (10 ml) was treated with $Et_3N \cdot SO_3$ (190 mg, 1.05 mmol) at 25° for 24 h. Evaporation and FC (toluene/EtOH/Et_3N 3:1:0.05) gave **11** (82 mg, 35%), **13a**/**14a** 4:1 (212 mg, 51%; ratio determined by integration of the MeO ^{1}H-NMR signals), and **15a** (64 mg, 10%).

Triethylammonium (Methyl 4,6-O-Isopropylidene-3-O-sulfonato-β-D-galactopyranoside) (**13a**): Amorphous solid. R_f (toluene/EtOH/Et_3N 3:1:0.05) 0.21. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.37 (*t*, *J* = 7.5, 3 Me); 1.41 (*s*, Me); 1.43 (*s*, Me); 3.16 (*q*, *J* = 7.5, 3 CH_2); 3.36 (*q*, *J* ≈ 1.7, H–C(5)); 3.58 (*s*, MeO); 3.85 (*dd*, *J* = 7.7, 9.6, H–C(2)); 3.95 (*dd*, *J* = 1.7, 12.8, H–C(6)); 4.06 (*dd*, *J* = 2.0, 12.8, H–C(6)); 4.10 (br. *s*, exchange with D_2O, HO–C(2)); 4.24 (*d*, *J* = 7.7, H–C(1)); 4.41 (*dd*, *J* = 3.7, 9.6, H–C(3)); 4.43 (*dd*, *J* = 0.9, 3.7, H–C(4)). ^{13}C-NMR (50 MHz, $CDCl_3$): 8.21 (*q*, 3 Me); 18.00 (*q*, Me); 28.71 (*q*, Me); 46.21 (*t*, 3 CH_2); 54.44 (*q*, MeO); 61.94 (*t*, C(6)); 65.41 (*d*, C(5)); 67.05 (*d*, C(4)); 68.44 (*d*, C(2)); 77.54 (*d*, C(3)); 97.87 (*s*, Me_2C); 103.41 (*d*, C(1)).

Sodium (Methyl 4,6-O-Isopropylidene-3-O-sulfonato-β-D-galactopyranoside) (**13b**): $[\alpha]_D^{25}$ = +197.5 (*c* = 0.2, MeOH). IR (KBr): 3520*m* (sh), 3485*s* (br.), 3010*w* (sh), 2995*w*, 2990*w*, 2935*w*, 2930*w* (sh), 2895*w*, 1680*w*, 1660*w*, 1630*w*, 1470*m*, 1455*w*, 1420*w*, 1380*m*, 1335*w*, 1310*m*, 1275*s*, 1250*s*, 1235*s* (sh), 1220*s*, 1190*s*, 1180*s* (sh), 1160*m*, 1145*s*, 1125*s*, 1090*s*, 1065*s*, 1010*s*, 990*s*, 960*s*, 930*w*, 880*s*, 845*s*, 820*m*, 795*m*, 780*m*, 710*w*, 640*m*, 620*m*. Anal. calc. for $C_{10}H_{17}NaO_9S$ (336.29): C 35.71, H 55.10, S 9.53; found: C 35.73, H 4.91, S 9.35.

Triethylammonium (Methyl 4,6-O-Isopropylidene-2-O-sulfonato-β-D-galactopyranoside) (**14a**): ^{1}H-NMR (300 MHz, $CDCl_3$; **13a**/**14a** 4:1): signals of **14a**: 3.30 (br. *s*, H–C(5)); 3.53 (*s*, MeO); 4.02 (*dd*, *J* = 1.5, 12.6, H–C(6)); 4.34 (*d*, *J* = 7.6, H–C(1)); 4.42 (*dd*, *J* ≈ 7.6, 9.5, H–C(2)).

Bis(triethylammonium) (Methyl 4,6-O-Isopropylidene-2,3-di-O-sulfonato-β-D-galactopyranoside) (**15a**): R_f (toluene/EtOH/Et_3N 3:1:0.05) 0.05. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.30 (*t*, *J* = 7.5, 6 Me); 1.32 (*s*, Me); 1.41 (*s*, Me); 3.21 (*q*, *J* = 7.5, 6 CH_2); 3.32 (br. *s*, H–C(5)); 3.51 (*s*, MeO); 3.88 (*dd*, *J* = 1.4, 12.6, H–C(6)); 4.00 (*dd*, *J* = 1.7, 12.6, H–C(6)); 4.31 (*d*, *J* = 7.5, H–C(1)); 4.34 (*dd*, *J* = 3.4, 10.0, H–C(3)); 4.51 (*dd*, *J* = 7.6, 10.0, H–C(2)); 4.74 (br. *d*, *J* = 3.3, H–C(4)). ^{13}C-NMR (50 MHz, $CDCl_3$): 8.69 (*q*, 6 Me); 18.62 (*q*, Me); 29.34 (*q*, Me); 46.35 (*t*, 6 CH_2); 56.55 (*q*, MeO); 62.67 (*t*, C(6)); 66.17 (*d*, C(5)); 67.21 (*d*, C(4)); 74.71 (*d*, C(2)); 76.29 (*d*, C(3)); 98.76 (*s*, Me_2C); 102.56 (*d*, C(1)).

7. *Sulfation of* **16**. a) The reaction of **16** [68] (0.5 g, 0.57 mmol) with Bu_2SnO (141 mg, 0.57 mmol) gave crude stannanediyl acetal **17** which was treated with $Et_3N \cdot SO_3$ (120 mg, 0.66 mmol) for 2 h at 25°. FC (toluene/EtOH/Et_3N 4:1:0.05) gave **18a** (453 mg, 83%).

b) A soln. of **16** (312 mg, 0.35 mmol) and $Et_3N \cdot SO_3$ (65 mg, 0.36 mmol) in DMF (10 ml) was stirred at 25° for 24 h, treated with additional $Et_3N \cdot SO_3$ (30 mg, 0.17 mmol), and stirred for a further 16 h. FC (toluene/EtOH/Et_3N 3:1:0.05) gave **18a** (286 mg, 77%) and **19a** (41 mg, 11%).

Triethylammonium [Benzyl 2,3,6-Tri-O-benzyl-4-O-(2,6-di-O-benzyl-3-O-sulfonato-β-D-galactopyranosyl)-β-D-glucopyranoside] (**18a**): Amorphous solid. R_f (toluene/EtOH/Et_3N 3:1:0.05) 0.25. ^{1}H-NMR (400 MHz, $CDCl_3$; assignment corroborated by ^{1}H,^{13}C-HMQC): 1.25 (*t*, *J* = 7.5, 3 Me); 2.99 (*d*, *J* ≈ 6, exchange with D_2O, HO–C(4′)); 3.01 (*q*, *J* = 7.5, 3 CH_2); 3.37 (*ddd*, *J* = 1.8, 4.5, 9.8, H–C(5)); 3.43–3.50 (*m*, H–C(2), H–C(5′)); 3.54 (*dd*, *J* = 5.7, 9.8, H–C(6′)); 3.58 (*t*, *J* ≈ 8.8, H–C(3)); 3.66 (*dd*, *J* = 7.8, 9.5, H–C(2′)); 3.70–3.74 (*m*, H–C(6), H–C(6′)); 3.77 (*dd*, *J* = 4.6, 11.0, H–C(6)); 3.98 (*t*, *J* ≈ 9.3, H–C(4)); 4.32 (*d*, *J* = 11.9, PhC*H*); 4.33 (*dd*, *J* = 3.2, 9.5, H–C(3′)); 4.41 (*d*, *J* = 12.1, PhC*H*); 4.46 (*d*, *J* = 11.9, PhC*H*); 4.47 (*d*, *J* = 7.7, H–C(1)); 4.46–4.50 (*m*, H–C(4′)); 4.51 (*d*, *J* = 11.9, PhC*H*); 4.53 (*d*, *J* = 7.7, H–C(1′)); 4.63 (*d*, *J* = 12.0, PhC*H*); 4.71 (*d*, *J* = 10.9, PhC*H*); 4.72 (*d*, *J* = 11.5, PhC*H*); 4.75 (*d*, *J* = 10.9, PhC*H*); 4.85 (*d*, *J* = 11.5, PhC*H*); 4.89 (*d*, *J* = 10.9, PhC*H*); 4.93 (*d*, *J* = 12.0, PhC*H*); 5.02 (*d*, *J* = 10.9, PhC*H*); 7.17–7.41 (*m*, 30 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$; assignment corroborated by ^{1}H,^{13}C-HMQC): 8.32 (*q*, 3 Me); 46.25 (*t*, 3 CH_2); 66.75 (*d*, C(4′)); 68.03 (*t*, C(6)); 68.67 (*t*, C(6′)); 70.59 (*t*, PhCH_2); 72.75 (*d*, C(5′)); 72.75 (*t*, PhCH_2); 73.04 (*t*, PhCH_2); 74.41 (*t*, PhCH_2); 74.55 (*t*, PhCH_2); 74.67 (*t*, PhCH_2); 74.67 (*d*, C(5)); 76.36 (*d*, C(4)); 77.64 (*d*, C(2′)); 80.71 (*d*, C(3′)); 81.55 (*d*, C(2)); 82.57 (*d*, C(3)); 102.25 (*d*, C(1)); 102.30 (*d*, C(1′)); 126.85–128.70 (several *d*); 137.23 (*s*); 138.06 (*s*); 138.15 (*s*); 138.30 (*s*); 138.66 (*s*); 138.88 (*s*).

Sodium [Benzyl 2,3,6-Tri-O-benzyl-4-O-(2,6-di-O-benzyl-3-O-sulfonato-β-D-galactopyranosyl)-β-D-glucopyranoside] (**18b**): $[\alpha]_D^{25}$ = +6.9 (*c* = 0.475, MeOH). IR (KBr): 3440*s* (br.), 3025*w*, 3015*w*, 2910*w*, 2860*w*, 1630*w* (br.), 1495*w*, 1455*m*, 1365*m*, 1245*s*, 1215*s* (sh), 1130*s*, 1090*s*, 1070*s*, 1050*s*, 1030*s*, 995*s*, 930*w*, 910*w*, 870*w*, 810*w*, 730*s*, 700*s*. Anal. calc. for $C_{54}H_{57}NaO_{14}S$ (384.33): C 65.84, H 5.83, S 3.26; found: C 65.65, H 5.64, S 3.49.

Bis(triethylammonium) [Benzyl 2,3,6-Tri-O-benzyl-4-O-(2,6-di-O-benzyl-3,4-di-O-sulfonato-β-D-galactopyranosyl)-β-D-glucopyranoside] (**19a**): R_f (toluene/EtOH/Et_3N 3:1:0.05) 0.08. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.25 (*t*, *J* = 7.5, 6 Me); 3.10 (*q*, *J* = 7.5, 6 CH_2); 3.34 (*ddd*, *J* = 1.8, 4.6, 9.4, H–C(5)); 3.43 (*dd*, *J* = 7.9, 8.9, H–C(2)); 3.49 (*t*, *J* = 6.0, H–C(5′)); 3.54 (*dd*, *J* = 7.4, 9.9, H–C(2′)); 3.545 (*t*, *J* = 9.8, H–C(3)); 3.57 (*dd*, *J* = 6.0, 10.2, H–C(6′)); 3.67 (*dd*, *J* = 1.3, 11.0, H–C(6)); 3.67 (*dd*, *J* = 4.6, 11.0, H–C(6)); 3.91 (*dd*, *J* = 6.0, 10.2, H–C(6′)); 3.98 (*t*, *J* = 9.3, H–C(4)); 4.31 (*d*, *J* = 11.7, PhC*H*); 4.38 (*d*, *J* ≈ 11.9, 2 PhC*H*); 4.42 (*dd*, *J* = 3.2, 9.7, H–C(3′)); 4.45 (*d*, *J* = 12.1, PhC*H*); 4.46 (*d*, *J* = 7.7, H–C(1)); 4.53 (*d*, *J* = 7.7, H–C(1′)); 4.62 (*d*, *J* = 12.0, PhC*H*); 4.68 (*d*, *J* = 11.5, PhC*H*); 4.68 (*d*, *J* = 10.5, PhC*H*); 4.70 (*d*, *J* = 10.9, PhC*H*); 4.88 (*d*, *J* = 11.2, PhC*H*); 4.91 (*d*, *J* ≈ 11.5, PhC*H*); 4.94 (*d*, *J* = 10.9, PhC*H*); 4.96 (*d*, *J* = 10.2, PhC*H*); 5.01 (*d*, *J* = 3.2, H–C(4′)); 7.17–7.41 (*m*, 30 arom.

H). ^{13}C-NMR (50 MHz, $CDCl_3$): 8.44 (*q*, 6 Me); 45.96 (*t*, 6 CH_2); 67.98 (*t*, C(6)); 69.19 (*t*, C(6′)); 70.71 (*t*, Ph*C*H_2); 72.77 (*t*, Ph*C*H_2); 72.98 (*t*, Ph*C*H_2); 73.53 (*d*, C(5′)); 74.32 (*t*, Ph*C*H_2); 74.32 (*d*, C(4′)); 74.80 (*t*, Ph*C*H_2); 75.10 (*d*, C(5)); 75.10 (*t*, Ph*C*H_2); 76.59 (*d*, C(4)); 77.21 (*d*, C(2′)); 78.08 (*d*, C(3′)); 81.58 (*d*, C(2)); 82.71 (*d*, C(3)); 102.31 (*d*, C(1), C(1′)); 126.97–128.70 (several *d*); 137.43 (*s*); 138.26 (*s*); 138.50 (*s*); 138.69 (*s*); 138.88 (*s*); 138.91 (*s*).

8. *Sulfation of* **20**. a) The reaction of **20** [76] (560 mg, 2.0 mmol) with Bu_2SnO (498 mg, 2.0 mmol) gave crude **21** [71] [75] (1.02 g, 100%; white foam). A part (228 mg, 0.44 mmol) was treated with $Et_3N \cdot SO_3$ (88 mg, 0.48 mmol) for 2 h. FC (MeCN/toluene/Et_3N 3:1:0.05) gave **22a** (133 mg, 67%) and **22a**/**23a** 1:4 (35 mg, 17%).

b) At 0°, a soln. of **20** (564 mg, 2.0 mmol) in DMF (15 ml) was treated dropwise with 0.3M $Et_3N \cdot SO_3$ (252 mg, 2.5 mmol) in DMF, allowed to warm to r.t., and stirred for 24 h. Evaporation and FC (toluene/EtOH/Et_3N 3:1:0.05) gave **23a** (505 mg, 55%), **22a**/**23a** 2:1 (136 mg, 15%; ratio determined by integration of the PhC*H* and H–C(1) ^{1}H-NMR signals), and **24a** (170 mg, 13%).

*Triethylammonium (Methyl 4,6-*O*-Benzylidene-2-*O*-sulfonato-α-*D*-mannopyranoside)* (**22a**): ^{1}H-NMR (400 MHz, $CDCl_3$): 1.39 (*t*, *J* = 7.5, 3 Me); 3.13 (*q*, *J* = 7.5, 3 CH_2); 3.40 (*s*, MeO); 3.76–3.83 (*m*, H–C(5), H_{ax}–C(6)); 3.88 (*t*, *J* = 9.8, H–C(4)); 3.95 (br. *s*, exchange with D_2O, HO–C(3)); 4.10 (*dd*, *J* = 3.6, 9.8, H–C(3)); 4.20–4.28 (*m*, H_{eq}–C(6)); 4.72 (*dd*, *J* = 1.7, 3.6, H–C(2)); 4.96 (*d*, *J* = 1.6, H–C(1)); 5.56 (*s*, PhC*H*); 7.31–7.36 (*m*, 3 arom. H); 7.48–7.51 (*m*, 2 arom. H). ^{13}C-NMR (50 MHz, $CDCl_3$): 8.27 (*q*, 3 Me); 46.21 (*t*, 3 CH_2); 54.44 (*q*, MeO); 63.10 (*d*, C(5)); 67.04 (*d*, C(3)); 68.14 (*t*, C(6)); 76.26 (*d*, C(4)); 78.89 (*d*, C(2)); 99.71 (*d*, C(1)); 101.60 (*d*, Ph*C*H); 125.94 (*d*, 2 arom. C); 127.62 (*d*, 2 arom. C); 128.52 (*d*, 1 arom. C); 137.06 (*s*, 1 arom. C).

*Sodium (Methyl 4,6-*O*-Benzylidene-2-*O*-sulfonato-α-*D*-mannopyranoside)* (**22b**): $[\alpha]_D^{25} = -0.5$ (*c* = 2.1, MeOH). IR (KBr): 3420*s* (br.), 2290*w*, 2910*w*, 2880*w*, 1650*w* (br.), 1455*m*, 1445*w* (sh), 1385*m*, 1270*s* (sh), 1250*s*, 1130*s*, 1105*s*, 1075*s*, 1055*s*, 1020*s*, 970*s*, 920*m*, 885*m*, 840*m*, 780*w*, 755*m*, 700*m*, 675*m*, 640*m*. Anal. calc. for $C_{14}H_{17}NaO_9S$ (384.33): C 43.75, H 4.46, S 8.34; found: C 43.50, H 4.52, S 8.15.

*Triethylammonium (Methyl 4,6-*O*-Benzylidene-3-*O*-sulfonato-α-*D*-mannopyranoside)* (**23a**): ^{1}H-NMR (400 MHz, $CDCl_3$): 1.12 (*t*, *J* = 7.5, 3 Me); 3.13 (*q*, *J* = 7.5, 3 CH_2); 3.40 (*s*, MeO); 3.41 (*d*, *J* = 2.5, exchange with D_2O, HO–C(2)); 3.86 (*dd*, *J* = 9.6, 10.2, H_{ax}–C(6)); 3.89 (*dt*, *J* = 4.2, 9.6, H–C(5)); 4.10 (*t*, *J* = 9.4, H–C(4)); 4.24 (*dd*, *J* = 4.2, 10.2, H_{eq}–C(6)); 4.62–4.66 (*m*, addn. of $D_2O \rightarrow$ *dd*, *J* = 1.5, 3.5, H–C(2)); 4.64 (*dd*, *J* = 3.5, 9.4, H–C(3)); 4.79 (*d*, *J* = 1.5, H–C(1)); 5.50 (*s*, PhC*H*); 7.32–7.36 (*m*, 3 arom. H); 7.44–7.48 (*m*, 2 arom. H). ^{13}C-NMR (50 MHz, $CDCl_3$): 8.41 (*q*, 3 Me); 46.35 (*t*, 3 CH_2); 54.96 (*q*, MeO); 63.28 (*d*, C(5)); 68.98 (*t*, C(6)); 69.01 (*d*, C(2)); 75.69 (*d*, C(3)); 76.71 (*d*, C(4)); 101.67 (*d*, C(1)); 102.41 (*d*, Ph*C*H); 126.56 (*d*, 2 arom. C); 128.15 (*d*, 2 arom. C); 129.20 (*d*, 1 arom. C); 137.72 (*s*, 1 arom. C).

*Sodium (Methyl 4,6-*O*-Benzylidene-3-*O*-sulfonato-α-*D*-mannopyranoside)* (**23b**): $[\alpha]_D^{25} = +16.5$ (*c* = 0.5, MeOH). IR (KBr): 3420*s* (br.), 2915*m*, 2905*m* (sh), 2860*w*, 1630*m* (br.), 1455*m*, 1415*w*, 1385*m*, 1250*s* (br.), 1130*s*, 1095*s*, 1060*s* (sh), 1050*s*, 995*s*, 980*s* (sh), 915*m*, 870*m*, 825*s*, 780*m*, 755*m*, 700*m*, 680*m*, 640*m*. Anal. calc. for $C_{14}H_{17}NaO_9S$ (384.33): C 43.75, H 4.46, S 8.34; found: C 44.01, H 4.71, S 8.35.

*Bis(triethylammonium) (Methyl 4,6-*O*-Benzylidene-2,3-di-*O*-sulfonato-α-*D*-mannopyranoside)* (**24a**): ^{1}H-NMR (400 MHz, $CDCl_3$): 1.12 (*t*, *J* = 7.5, 6 Me); 3.13 (*q*, *J* = 7.5, 6 CH_2); 3.35 (*s*, MeO); 3.80–3.87 (*m*, H–C(5), H_{ax}–C(6)); 4.0–4.05 (*m*, H–C(4)); 4.20–4.21 (*m*, H_{eq}–C(6)); 4.84 (*dd*, *J* = 3.4, 10.3, H–C(3)); 5.00 (*dd*, *J* = 1.7, 3.3, H–C(2)); 5.23 (*d*, *J* = 1.7, H–C(1)); 5.50 (*s*, PhC*H*); 7.32–7.36 (*m*, 3 arom. H); 7.44–7.48 (*m*, 2 arom. H). ^{13}C-NMR (50 MHz, CD_3OD): 9.25 (*q*, 6 Me); 47.74 (*t*, 6 CH_2); 55.60 (*q*, MeO); 65.59 (*d*, C(5)); 69.63 (*t*, C(6)); 73.75 (*d*, C(3)); 76.59 (*d*, C(2)); 77.75 (*d*, C(4)); 100.89 (*d*, C(1)); 103.00 (*d*, Ph*C*H); 127.62 (*d*, 2 arom. C); 129.07 (*d*, 2 arom. C); 130.00 (*d*, 1 arom. C); 139.17 (*s*, 1 arom. C).

9. *Sulfation of* **25**. a) A suspension of **25** (500 mg, 2.55 mmol) and $(Bu_3Sn)_2O$ (1.8 g, 3.0 mmol) in toluene (50 ml) was kept under reflux for 16 h (*Dean-Stark* condenser) [82]. Evaporation of the clear soln. gave an oil which was dissolved in DMF, cooled to 0°, and treated dropwise (over 10 min) with 1.0M $Et_3N \cdot SO_3$ (1.0 g, 5.5 mmol) in DMF. Stirring for 16 h at 4°, evaporation, and FC (toluene/EtOH/Et_3N 3:2:0.05) gave **26a** (1.15 g, 82%).

b) According to [58] [84] [85], stannylation of **25** (334 mg, 1.72 mmol) with Bu_2SnO (428 mg, 1.72 mmol) in MeOH (10 ml) gave a residue (732 mg) which was dissolved in DMF and treated with $Et_3N \cdot SO_3$ (371 mg, 2.07 mmol) for 14 h at 5°. FC (toluene/EtOH/Et_3N 3:2:0.05) gave **25** (103 mg, 31%), **27a** (247 mg, 38%), and **26a** (45 mg, 5%).

*Bis(triethylammonium) (Methyl 2,6-Di-*O*-sulfonato-α-*D*-glucopyranoside)* (**26a**): R_f (toluene/EtOH 3:2) 0.05. ^{13}C-NMR (50 MHz, CD_3OD): 9.53 (*q*, 3 Me); 47.84 (*t*, 3 CH_3); 57.71 (*q*, MeO); 68.09 (*t*, C(6)); 71.29 (*d*); 71.84 (*d*); 72.71 (*d*, C(3)); 78.78 (*d*, C(2)); 99.30 (*d*, C(1)).

*Disodium (Methyl 2,6-Di-*O*-sulfonato-α-*D*-glucopyranoside)* (**26b**): $[\alpha]_D^{25} = +69.2$ (*c* = 0.49, MeOH). IR (KBr): 3430*s* (br.), 2980*w*, 2950*w*, 2910*w*, 1640*m*, 1560*w*, 1540*w*, 1460*w*, 1390*w*, 1250*s* (br.), 1150*w*, 1135*w*, 1115*w*, 1075*s*, 1065*s*, 1015*s*, 1000*s*, 950*w*, 910*w*, 840*m*, 815*m*, 770*m*, 695*m*, 640*m*. ^{1}H-NMR (400 MHz, (D_6)DMSO): 3.06 (*ddd*, *J* = 5.9, 8.7, 10.0, addn. of $CD_3OD \rightarrow$ *dd*, *J* = 8.8, 9.9, H–C(4)); 3.31 (*s*, MeO); 3.44–3.52 (*m*, addn. of

CD_3OD→change, H–C(3), H–C(5)); 3.71 (*dd*, J = 6.7, 10.9, H–C(6)); 3.84 (*dd*, J = 3.7, 9.9, H–C(2)); 4.01 (*dd*, J = 1.9, 10.8, H–C(6)); 4.71 (*d*, J = 3.6, H–C(1)); 4.91 (*d*, J = 3.0, exchange with CD_3OD, HO–C(3)); 5.06 (*d*, J = 5.9, exchange with CD_3OD, OH–C(4)). Anal. calc. for $C_7H_{12}Na_2O_{12}S_2$ (384.33): C 21.11, H 3.04, S 16.10; found: C 20.85, H 3.29, S 16.30.

*Triethylammonium (Methyl 2-*O*-Sulfonato-α-*D*-glucopyranoside)* (**27a**): Amorphous solid. R_f (toluene/EtOH/Et_3N 3:2:0.05) 0.11. ^{1}H-NMR (400 MHz, (D_6)DMSO): 1.16 (*t*, J = 7.5, 3 Me); 3.07 (*q*, J = 7.5, 3 CH_2); 3.12 (*dt*, $J \approx$ 5.8, 8.9, addn. of CD_3OD→*t*, $J \approx$ 8.9, H–C(4)); 3.24 (*s*, MeO); 3.29 (hidden by HDO, addn. of CD_3OD→*ddd*, J = 1.8, 5.7, 9.9, H–C(5)); 3.41 (*td*, $J \approx$ 5.8, 11.6, addn. of CD_3OD→*dd*, J = 5.8, 11.8, H–C(6)); 3.50 (*dt*, $J \approx$ 2.6, 9.2, addn. of CD_3OD→*t*, $J \approx$ 9.4, H–C(3)); 3.61 (br. *ddd*, $J \approx$ 1.8, 5.7, 11.6, addn. of CD_3OD→*dd*, J = 1.9, 11.9, H–C(6)); 3.81 (*dd*, J = 3.6, 9.9, H–C(2)); 4.47 (*t*, $J \approx$ 5.8, exchange with CD_3OD, HO–C(6)); 4.73 (*d*, J = 3.6, H–C(1)); 4.84 (*d*, J = 2.6, exchange with CD_3OD, HO–C(3)); 4.96 (*d*, J = 5.7, exchange with CD_3OD, HO–C(4)). ^{13}C-NMR (50 MHz, CD_3OD): 10.89 (*q*, 3 Me); 49.48 (*t*, 3 CH_2); 57.17 (*q*, MeO); 63.97 (*t*, C(6)); 73.47 (*d*); 74.35 (*d*); 74.62 (*d*); 80.27 (*d*, C(2)); 100.71 (*d*, C(1)).

*Sodium (Methyl 2-*O*-Sulfonato-α-*D*-glucoypranoside)* (**27b**): $[\alpha]_D^{25}$ = +87.0 (c = 0.5, MeOH). IR (KBr): 3600–3100*s*, 2945*w*, 2850*w*, 1455*w*, 1350*w*, 1260*s* (br.), 1200*m* (sh), 1155*m*, 1105*m*, 1080*s*, 1040*s*, 995*m*, 910*w*, 825*m*, 715*w*, 710*w*. Anal. calc. for $C_7H_{13}NaO_9S$ (296.22): C 28.38, H 4.42, S 10.82; found: C 28.25, H 4.35, S 10.70.

10. *Sulfation of* **28**. a) As described for **26a**, the reaction of **28** (0.35 g, 1.88 mmol) and $(Bu_3Sn)_2O$ (1.15 g, 1.9 mmol) [83] gave a yellow residue which was treated with $Et_3N \cdot SO_3$ (720 mg, 4.0 mmol) for 2.5 h at 25°. Evaporation and FC (toluene/EtOH/Et_3N 3:2:0.05) gave **29a** (720 mg, 76%).

b) According to [58] [84] [85], stannylation of **28** (388 mg, 2.0 mmol) with Bu_2SnO (500 mg, 2.08 mmol) in MeOH (10 ml) gave a yellow residue which was dissolved in DMF (10 ml) and treated with $Et_3N \cdot SO_3$ (450 mg, 2.5 mmol) for 5 h at r.t. FC (toluene/EtOH/Et_3N 3:2:0.05) gave **28** (176 mg, 45%), **30a** (277 mg, 37%), and **29a** (75 mg, 7%).

*Bis(trietylammonium) (Methyl 3,6-Di-*O*-sulfonato-β-*D*-galactopyranoside)* (**29a**): R_f (toluene/EtOH 3:2) 0.05. ^{13}C-NMR (50 MHz, CD_3OD): 9.24 (*q*, 3 Me); 47.78 (*t*, 3 CH_2); 57.18 (*q*, MeO); 67.04 (*t*, C(6)); 68.00 (*d*, C(4)); 70.31 (*d*, C(2)); 73.55 (*d*, C(5)); 81.27 (*d*, C(3)); 105.43 (*d*, C(1)).

*Disodium (Methyl 3,6-Di-*O*-sulfonato-β-*D*-galactopyranoside)* (**29b**): $[\alpha]_D^{25}$ = +5.1 (c = 0.77, MeOH). IR (KBr): 3430*s* (br.), 2980*w*, 2950*w*, 2910*w*, 1640*m*, 1560*w*, 1540*w*, 1460*w*, 1390*w*, 1250*s* (br.), 1150*w*, 1135*w*, 1115*w*, 1075*s*, 1065*s*, 1015*s*, 1000*s*, 950*w*, 910*w*, 840*m*, 815*m*, 770*m*, 695*m*, 640*m*. ^{1}H-NMR (400 MHz, (D_6)DMSO): 3.35 (*s*, MeO); 3.41 (*ddd*, J = 2.8, 7.5, 10.0, addn. of CD_3Od→*dd*, J = 7.8, 9.8, H–C(2)); 3.58 (br. *t*, J = 6.1, H–C(5)); 3.76 (*dd*, J = 6.2, 10.6, H–C(6)); 3.81 (*dd*, J = 5.9, 10.6, H–C(6)); 3.85 (br. *t*, $J \approx$ 4.4, addn. of CD_3OD→br. *d*, J = 3.3, H–C(4)); 3.95 (*dd*, J = 3.3, 9.9, H–C(3)); 4.07 (*d*, J = 7.6, H–C(1)); 4.60 (*d*, J = 5.2, exchange with CD_3OD, HO–C(4)); 4.97 (*d*, J = 2.8, exchange with CD_3OD, HO–C(2)). Anal. calc. for $C_7H_{12}Na_2O_{12}S_2$ (384.33): C 21.11, H 3.04, S 16.10; found: C 21.39, H 3.25, S 16.24.

*Triethylammonium (Methyl 3-*O*-Sulfonato-β-*D*-galactopyranoside)* (**30a**): Amorphous solid. R_f 0.10. ^{1}H-NMR (400 MHz, (D_6)DMSO): 1.15 (*t*, J = 7.3, 3 Me); 3.13 (*q*, J = 7.3, 3 CH_2); 3.33–3.54 (*m*, H–C(2), H–C(5), 2 H–C(6)); 3.36 (*s*, MeO); 3.90–3.95 (*m*, addn. of CD_3OD→change, H–C(3), H–C(4)); 4.07 (*d*, J = 7.7, H–C(1)); 4.46 (*d*, J = 4.8, exchange with CD_3OD, OH); 4.58 (*t*, J = 5.7, exchange with CD_3OD, HO–C(6)); 4.96 (*d*, J = 2.6, exchange with CD_3OD, OH). ^{1}H-NMR (400 MHz, D_2O): 1.32 (*t*, J = 7.3, 3 Me); 3.24 (*q*, J = 7.3, 3 CH_2); 3.63 (*s*, MeO); 3.69 (*dd*, J = 7.8, 9.5, H–C(2)); 3.785 (br. *dd*, J = 4.0, 9.0, H–C(5)); 3.81 (*dd*, J = 4.0, 12.0, H–C(6)); 3.95 (*dd*, J = 9.0, 12.0, H–C(6)); 4.33 (br. *d*, J = 3.8, H–C(4)); 4.37 (*dd*, J = 3.8, 7.8, H–C(3)); 4.45 (*d*, J = 7.8, H–C(1)).

*Sodium (Methyl 3-*O*-Sulfonato-β-*D*-galactopyranoside)* (**30b**): $[\alpha]_D^{25}$ = +8.5 (c = 1.23, MeOH). ^{13}C-NMR (50 MHz, D_2O): 57.61 (*q*, MeO); 61.24 (*t*, C(6)); 67.34 (*d*, C(4)); 69.20 (*d*, C(2));75.04 (*d*, C(5)); 80.65 (*d*, C(3)); 103.81 (*d*, C(1)). Anal. calc. for $C_7H_{13}NaO_9S$ (296.22): C 28.38, H 4.42, S 10.82; found: C 28.45, H 4.67, S 10.61.

11. *Sulfation of* **32**. a) The reaction of **32** (280 mg, 1.0 mmol) with Bu_2SnO (250 mg, 1.0 mmol) for 6 h gave crude **33** (white solid) which was dissolved in 1,3-dimethylimidazolidin-2-one (10 ml), treated dropwise (over 10 min) with a soln. of $Et_3N \cdot SO_3$ (240 mg, 1.3 mmol) in 2 ml of the same solvent, and stirred for 2 h at 25°. FC (toluene/EtOH/Et_3N 20:1:0.05→3:2:0.05) gave **27a** (295 mg, 79%).

b) A soln. of **32** (500 mg, 1.78 mmol) and $Et_3N \cdot SO_3$ (325 mg, 1.80 mmol) in DMF (10 ml) was stirred at 25° for 16 h. Evaporation and FC (toluene/EtOH/Et_3N 3:2:0.05) gave **25** (205 mg, 59%), **35a** (73 mg, 11%), and **27a** (173 mg, 26%).

c) A soln. of **32** (500 mg, 1.78 mmol) and $Et_3N \cdot SO_3$ (489 mg, 2.70 mmol) in DMF (10 ml) was stirred at 25° for 18 h. Evaporation and FC (toluene/EtOH/Et_3N 3:2:0.05) gave **25** (74 mg, 21%), **27a** (246 mg, 37%), a mixture of unknown compounds (126 mg), and **36a** (278 mg, 28%).

Triethylammonium (Methyl 3-O-Sulfonato-α-D-glucopyranoside) (**35a**): ^{1}H-NMR (400 MHz, D_2O): 1.25 (*t*, *J* = 7.3, 3 Me); 3.17 (*q*, *J* = 7.3, 3 CH_2); 3.40 (*s*, MeO); 3.58 (*dd*, *J* = 8.5, 9.6, H–C(4)); 3.67 (*ddd*, *J* = 2.0, 4.0, 9.6, H–C(5)); 3.71 (*dd*, *J* = 4.0, 10.8, H–C(6)); 3.74 (*dd*, *J* = 3.5, 10.0, H–C(2)); 3.84 (*dd*, *J* = 2.0, 10.8, H–C(6)); 4.41 (*dd*, *J* = 8.5, 10.0, H–C(3)); 4.82 (*d*, *J* = 3.6, H–C(1)).

Bis(triethylammonium) (Methyl 2,3-Di-O-sulfonato-α-D-glucopyranoside) (**36a**): ^{1}H-NMR (400 MHz, (D_6)DMSO): 1.16 (*t*, *J* = 7.2, 6 Me); 3.07 (*q*, *J* = 7.2, 6 CH_2); 3.20–3.43 (*m*, partially hidden by HDO signal, H–C(4), H–C(5), H–C(6), MeO); 3.47 (*td*, *J* ≈ 5.3, 11.0, H–C(6)); 3.80 (*dd*, *J* = 3.3, 10.0, H–C(2)); 4.23 (*dd*, *J* = 8.3, 10.1, H–C(3)); 4.47–4.55 (*m*, exchange with D_2O, 2 OH); 5.06 (*d*, *J* = 3.2, H–C(1)). ^{1}H-NMR (200 MHz, D_2O): 1.17 (*t*, *J* = 7.3, 6 Me); 3.09 (*q*, *J* = 7.3, 6 CH_2); 3.27 (*s*, MeO); 3.44 (*ddd*, *J* = 1.8, 4.0, 9.5, H–C(5)); 3.49 (*dd*, *J* = 7.8, 9.6, H–C(4)); 3.54 (*dd*, *J* = 4.0, 10.8, H–C(6)); 3.66 (*dd*, *J* = 2.0, 10.7, H–C(6)); 4.03 (*dd*, *J* = 3.6, 10.0, H–C(2)); 4.42 (*dd*, *J* = 7.8, 10.0, H–C(3)); 5.05 (*d*, *J* = 3.6, H–C(1)). ^{13}C-NMR (50 MHz, CD_3OD): 9.27 (*q*, 6 Me); 49.00 (*t*, 6 CH_2); 55.67 (*q*, MeO); 62.32 (*t*, C(6)); 71.59 (*d*, C(4)); 73.09 (*d*, C(5)); 76.08 (*d*, C(2)); 80.26 (*d*, C(3)); 99.29 (*d*, C(1)).

Methyl 2-O-Benzoyl-α-D-glucopyranoside [85] [90] [91] (**34**). Reaction of **32** (238 mg, 0.85 mmol) with Bu_2SnO (212 mg, 0.85 mmol) for 6 h gave crude **33** (white solid) which was dissolved in toluene (15 ml), cooled to 0°, and treated dropwise (over 10 min) with 0.4M benzoyl chloride (132 mg, 0.95 mmol) in toluene. The soln. was allowed to warm to r.t. and stirred for 2 h. Evaporation and FC (toluene/EtOH 20:3) gave a colorless amorphous residue which was crystallized from MeOH/Et_2O: **34** (218 mg, 85%). Fine needles, R_f (toluene/EtOH 15:3) 0.20. M.p. 175° ([90]: 174–175°; [91]: 181–182°; [85]: 177–179°). $[\alpha]_D^{25}$ = +147.0 (*c* = 0.50, EtOH; [91]: +152.3). ^{1}H-NMR (400 MHz, (D_6)DMSO): 3.25 (*dt*, *J* ≈ 6.0, 9.3, after addn. of CD_3OD→*t*, *J* ≈ 9.3, H–C(4)); 3.26 (*s*, MeO); 3.41 (*ddd*, *J* = 2.0, 5.6, 9.9, H–C(5)); 3.51 (*td*, *J* = 5.8, 11.8, addn. of CD_3OD→*dd*, *J* = 5.6, 11.8, H–C(6)); 3.68 (*ddd*, *J* = 2.0, 5.9, 11.8, addn. of CD_3OD→*dd*, *J* = 2.0, 11.8, H–C(6)); 3.76 (*ddd*, *J* = 5.5, 8.8, 9.8, addn. of CD_3OD→*dd*, *J* = 8.8, 9.8, H–C(3)); 4.59 (*t*, *J* = 5.9, exchange with CD_3OD, HO–C(6)); 4.67 (*dd*, *J* = 3.7, 10.1, H–C(2)); 4.85 (*d*, *J* = 3.7, H–C(1)); 5.17 (*d*, *J* = 5.8, exchange with CD_3OD, HO–C(4)); 5.27 (*d*, *J* = 5.5 exchange with CD_3OD, HO–C(3)); 7.51 (*t*, *J* ≈ 7.7, 2 arom. H); 7.64 (*tt*, *J* = 1.0, 7.5, 1 arom. H); 7.99 (*dd*, *J* = 1.0, 8.0, 2 arom. H). ^{13}C-NMR (50 MHz, CD_3OD): similar to the published one in C_5D_5N [86]: $\Delta\delta$ values < 0.7 ppm.

12. *Sulfation of* **37**. a) Reaction of **37** (115 mg, 0.41 mmol) with Bu_2SnO (105 mg, 0.41 mmol) for 6 h gave crude **38** (white solid) which was dissolved in 1,3-dimethylimidazolidin-2-one (5 ml), treated dropwise (over 10 min) with a soln. of $Et_3N \cdot SO_3$ (90 mg, 0.5 mmol) in 2 ml of the same solvent, and stirred for 3 h at 25°. FC (toluene/EtOH/Et_3N 20:1:0.05→3:2:0.05) gave **30a** (132 mg, 85%).

b) A soln. of **37** (500 mg, 1.78 mmol) and $Et_3N \cdot SO_3$ (325 mg, 1.80 mmol) in DMF (10 ml) was stirred at 25° for 16 h. Evaporation and FC (toluene/EtOH/Et_3N 3:2:0.05) gave **28** (173 mg, 50%) and **30a**/**40a** 4:1 (227 mg, 34%).

Triethylammonium (Methyl 2-O-Sulfonato-β-D-galactopyranoside) (**40a**): ^{1}H-NMR (300 MHz, D_2O; **30a**/**40a** 4:1): signals of **40a**: 3.60 (*s*, MeO); 4.03 (*dd*, *J* = 1.0, 3.4, H–C(4)); 4.29 (*dd*, *J* = 7.8, 10.0, H–C(2)); 4.50 (*d*, *J* = 7.7, H–C(1)).

Methyl 3-O-Benzoyl-β-D-galactopyranoside [85] [93] (**39**). As described for **34**, reaction of **37** (137 mg, 0.49 mmol) with Bu_2SnO (122 mg, 0.49 mmol) gave **38**, which was treated with benzoyl chloride (80 mg, 0.6 mmol) to yield crude **39**. FC (toluene/EtOH 20:3) gave a solid which was dissolved in H_2O (5 ml), treated with active charcoal (20 mg) for 2 min, and filtered. Concentration of the filtrate gave small crystals of **39** (126 mg, 86%). R_f (toluene/EtOH 15:3) 0.18. M.p. 60–100° ([93]: 106–109°; [85]: 127–128°). $[\alpha]_D^{25}$ = +53.5 (*c* = 0.72, EtOH; [93]: +56.7). ^{1}H-NMR (400 MHz, (D_6)DMSO): 3.41 (*s*, MeO); 3.48–3.56 (*m*, H–C(5), 2 H–C(6)); 3.69 (*ddd*, *J* = 5.5, 7.7, 10.0, addn. of CD_3OD→*dd*, *J* = 7.9, 9.8, H–C(2)); 3.96 (*dd*, *J* = 3.3, 6.0, addn. of CD_3OD→*d*, *J* = 3.2, H–C(4)); 4.20 (*d*, *J* = 7.7, H–C(1)); 4.63 (*t*, *J* ≈ 4.7, exchange with CD_3OD, HO–C(6)); 4.78 (*dd*, *J* = 3.3, 10.1, H–C(3)); 4.94 (*d*, *J* = 6.0, exchange with CD_3OD, OH–C(4)); 5.27 (*d*, *J* = 5.5, exchange with CD_3OD, HO–C(2)); 7.51 (*t*, *J* ≈ 7.7, 2 arom. H); 7.64 (*tt*, *J* = 1.0, 7.5, 1 arom. H); 7.99 (*dd*, *J* = 1.0, 7.5, 2 arom. H). ^{13}C-NMR (50 MHz, CD_3OD): similar to the spectrum in C_5D_5N [86]; $\Delta\delta$ values < 0.7 ppm.

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