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Regioselective de-*O*-benzylation of phenylsulfonylethylidene (PSE) acetals-containing benzylated monosaccharides using triisobutylaluminum (TIBAL)

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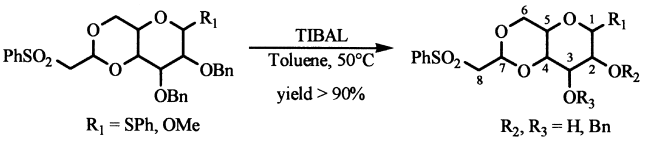
Abstract—A series of benzylated monosaccharidic PSE acetals undergoes regioselective TIBAL-mediated de-*O*-benzylation, to afford monobenzyl ethers, readily available as building blocks for oligosaccharides synthesis.

1. Introduction

A major strategical task in the field of carbohydrate chemistry is the chemical synthesis of selectively protected mono- or oligosaccharides. One of the most classical protecting groups of carbohydrate hydroxyl functions is probably the benzyl ether. It is easily[1] installed, stable to a wide range of reagents and readily removed in the presence of many various functionalities using Lewis/Brönsted acids, dissolving metals or catalytic hydrogenolysis. An attractive access to partially benzylated carbohydrates is provided by selective de-*O*-benzylation of easily available polybenzylated precursors. This has been previously achieved by catalytic hydrogenolysis,[2] controlled acetolysis[3] or by reacting Lewis acids[4] such as $SnCl_4$ and $TiCl_4$ or mixtures[5] like $CrCl_2$/LiI. We recently reported[6] that triisobutylaluminum (TIBAL) led to highly regioselective mono-de-*O*-benzylation of perbenzylated mono- and disaccharide derivatives. We have also discovered[7] that diisobutylaluminum (DIBAL) was a reagent of choice to perform remarkable regioselective mono- and bis-de-*O*-benzylation of either α or β peralkylated (methyl or benzyl ethers) cyclodextrins. As part of our program to evaluate the wider scope and limitations of regioselective de-*O*-benzylation using TIBAL and DIBAL, we have applied this methodology to the recently described[8] phenylsulfonylethylidene (PSE) acetals (Scheme 1) which display various interesting properties as compared to benzylidene acetals.

The scope and regioselectivity of the de-*O*-benzylation reaction were evaluated using a panel of representative monosaccharidic benzylated PSE acetals and the results are compiled in Table 1. The results obtained conform to the mechanism[6] proposed before and give access to selectively modified building blocks suitable for oligosaccharides synthesis.



Scheme 1. TIBAL-promoted regioselective de-*O*-benzylation.

2. Results and discussion

Application of the standard deprotection conditions to methyl 2,3-di-*O*-benzyl-4,6-*O*-(2-phenylsulfonyl)-ethylidene-α-D-glucopyranoside[8] **1** afforded the expected mono-de-*O*-benzylated product **2** in nearly quantitative yield (97%) (entry 1). As in the case[6] of methyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside, we can suggest that two contiguous *cis*-oriented alkoxy groups are necessary for the mono-de-*O*-benzylation reaction. A mono-reduction of the two *cis*-located benzyloxy groups was then observed for methyl 2,3-di-*O*-benzyl-4,6-*O*-(2-phenylsulfonyl)-ethylidene-α-D-mannopyranoside[8] **3**, giving (90% yield) a mixture of monobenzyl ethers **4** and **5** in a 8:1 ratio (entry 2).

According to the known procedure,[8] methyl 2,3-di-*O*-benzyl-4,6-*O*-(2-phenylsulfonyl)-ethylidene-α-D-altropyranoside **6** was then prepared from the related 4,6-diol[9] and the above PSE acetal reacted quickly with TIBAL to afford the monobenzyl ether **7** in almost quantitative yield (97%) (entry 3). However, traces of a side-product resulting

Keywords: monosaccharides; phenylsulfonylethylidene (PSE) acetals; triisobutylaluminum (TIBAL); de-*O*-benzylation; regioselectivity.

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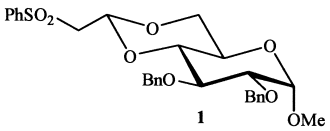
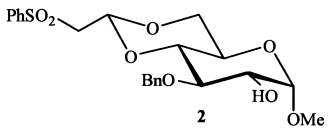
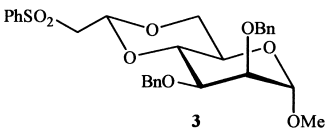
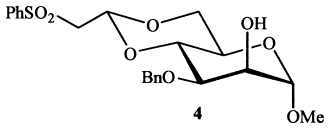
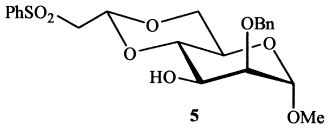
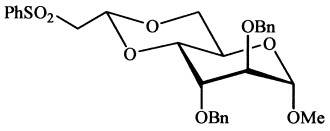
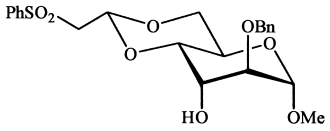
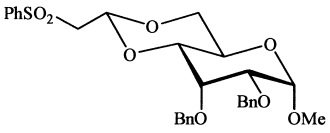
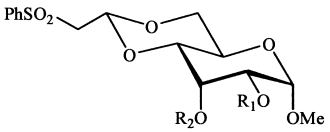
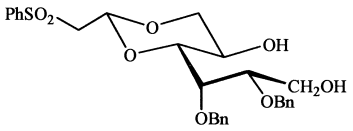
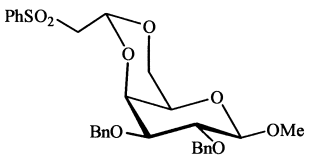
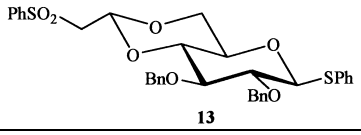
Table 1. Regioselective de-*O*-benzylation using TIBAL in anhydrous toluene at 50°C

Entry	Reactant	Product	Yield	Time
1	 **1**	 **2**	97%	2 h
2	 **3**	 **4**  **5**	90% (8:1), 4:5	2 h
3	 **6**	 **7**	97%[a]	1 h
4	 **8**	 **9** R_1 = H, R_2 = Bn **10** R_1 = Bn, R_2 = H  **11**	99% (1:5:3), 9:10:11	1 h
5	 **12**	Decomposition[b]	None	5 days[c]
6	 **13**	Decomposition[b]	None	5 days[c]

[a] Traces of by-product coming from reduction at the anomeric position were also detected by MS.
[b] No major compound was formed. TLC revealed the formation of many by-products, which were not isolated.
[c] We had to wait 5 days for the complete consumption of starting material.

from reduction at the anomeric position could also be detected by mass spectrometry. Indeed, no de-*O*-benzylation on the 2-position was expected as substituents on the first three positions are all *trans*-oriented. However, mono-de-*O*-benzylation on the 3-position can be accounted for the presence of a *cis*-oriented alkoxy group on either the anomeric position or the 4-position. One can also wonder whether the oxygen atoms on the sulfone may intervene in this reaction. More complex was the case of methyl 2,3-di-*O*-benzyl-4,6-*O*-(2-phenylsulfonyl)-ethylidene-α-D-allo-pyranoside **8**, which reacted also very quickly and efficiently with TIBAL to give a quantitative mixture of compounds **9**, **10** and **11** in a 1:5:3 ratio (entry 4). In this particular case, substituents on the first three positions are now all *cis*-oriented, which can explain why de-*O*-benzylation takes place on both 2- and 3-positions. Moreover, a rather unusual—in such conditions—reduction is observed at the anomeric center to yield the D-allitol derivative **11**.

Entry 5 shows that although located in a *cis* relationship, the benzyloxy group on the 3-position of methyl 2,3-di-*O*-benzyl-4,6-*O*-(2-phenylsulfonyl)-ethylidene-β-D-galacto-pyranoside[8] **12** is not reduced. A similar absence of reactivity has already been observed[6] in the case of methyl 2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranoside. As a result, no major reaction occurs in this case and the starting material is slowly decomposed. A similar slow degradation is observed in the case of phenyl 2,3-di-*O*-benzyl-4,6-*O*-(2-phenylsulfonyl)-ethylidene-1-thio-β-D-glucopyranoside **13**, which contains no *cis*-oriented alkoxy-groups (entry 6).

3. Conclusion

In summary, the TIBAL-induced regioselective de-*O*-benzylation of benzylated monosaccharidic PSE acetals affords an operationally simple protocol for the regio-selective cleavage of benzyl ethers. Functionalising the free hydroxyl, then selectively removing[8] the PSE protecting group lead to selectively modified monosaccharides which can in turn be protected on the primary position only, to afford useful orthogonally protected building blocks for oligosaccharides synthesis. This process constitutes an elegant alternative to already existing methods requiring regioselective *O*-benzylation[10] or de-*O*-benzylation.[11] Besides, this method may be extended to disaccharides and other polyols. Alternate deprotecting methods and ring-opening abilities of PSE acetals are currently under investigation.

4. Experimental

4.1. General

Optical rotations were measured on a Perkin–Elmer 241 digital polarimeter with a path length of 1 dm. Mass spectra were recorded on a Nermag R10-10 spectrometer, using chemical ionisation with ammonia. Elemental analyses were performed by the Service d'Analyse de l'Université Pierre et Marie Curie, 75252 Paris Cedex 05, France. NMR spectra were recorded on a Bruker AM-400 (400 and 100.6 MHz for ^{1}H and ^{13}C, respectively), using TMS as internal standard. TLC was performed on silica gel 60 F_{254} (Merck) and developed by charring with concentrated H_2SO_4. Flash column chromatography was performed using silica gel 60 (230–400 mesh, Merck).

Recently described PSE acetals **1**, **3**, **12**, **13**, as well as new compounds **6** and **8**, were prepared according to the previously reported[8] procedure.

4.1.1. Methyl 2,3-di-*O*-benzyl-4,6-*O*-(2-phenylsulfonyl)-ethylidene-α-D-altropyranoside (6). An ice-cold THF (19 mL) solution of the 4,6-diol (704 mg, 1.88 mmol) prepared according to Dechaux et al.[9] was treated by NaH (182 mg, 3.8 mmol, 2 equiv., 50% in mineral oil). After 15 min stirring at rt (*E*)-1,2-bis(phenylsulfonyl)-ethylene (580 mg, 1.88 mmol, 1 equiv.) and a few crystals of Bu_4NBr were added. The mixture was stirred 12 h at rt then treated with brine and extracted with EtOAc. After drying over $MgSO_4$, concentration under reduced pressure and silica gel column purification (EtOAc/cyclohexane=1/3), the altroside **6** (732 mg, 72%) was obtained as a colourless foam: $[\alpha]_D^{23}$=+28 (*c* 1.0, $CHCl_3$); MS (CI) *m/z* 563.0 [*M*Na]$^+$, 579.0 [*M*K]$^+$; ^{1}H NMR ($CDCl_3$) δ 7.90–7.86 (m, 2H, *o*-SO_2 H-Ar), 7.62–7.21 (m, 13H, H-Ar), 5.05 (t, 1H, J_{7-8}= 4.8 Hz, H-7), 4.57 (br s, 1H, H-1), 4.50–4.30 (m, 4H, 2×CH_2Ph), 4.07 (m, 2H, H-5+H-6a), 3.74 (dd, 1H, J_{3-4}= 3.0 Hz, J_{4-5}=9.4 Hz, H-4), 3.65 (br t, 1H, J_{2-3}= 2.6 Hz, H-3), 3.58 (br d, 1H, H-2), 3.48 (m 1H, H-6b), 3.47 (d, 2H, J_{7-8}=4.8 Hz, H-8), 3.30 (s, 3H, OMe); ^{13}C NMR ($CDCl_3$) δ 139.9, 138.4, 137.3, (C_{quat}-Ar), 133.7 (*p*-SO_2 CH-Ar), 129.1–127.4 (CH-Ar), 100.0 (C-1), 97.1 (C-7), 77.0 (C-4), 76.1 (C-2), 72.7, 72.5 (CH_2Ph+C-3), 68.9 (C-6), 60.1 (C-8), 57.8 (C-5), 55.5 (OMe); Anal. calcd for $C_{29}H_{32}O_8S$ (540.61): C, 64.43; H, 5.97, found: C, 64.51; H, 6.01%.

4.1.2. Methyl 2,3-di-*O*-benzyl-α-D-allopyranoside (14). A 60% aqueous acetic acid solution (4 mL) of the parent 4,6-*O*-benzylidene acetal (680 mg, 1.47 mmol) prepared according to Collins et al.[12] was stirred at 80°C until complete consumption of the starting material (ca 1 h). Evaporation then co-evaporation with toluene left a residue which was purified by flash chromatography (EtOAc/cyclohexane=1/1) to afford syrupy compound **14** (490 mg, 89%): $[\alpha]_D^{23}$=+81 (*c* 1.0, $CHCl_3$); MS (CI) *m/z* 397.0 [*M*Na]$^+$, 413.0 [*M*K]$^+$; ^{1}H NMR ($CDCl_3$) δ 7.41–7.22 (m, 10H, H-Ar), 5.17 (d, 1H, J_{gem}=11.6 Hz, C*H*HPh); 4.74 (d, 1H, J_{1-2}=3.8 Hz, H-1), 4.65 (s, 2H, CH_2Ph), 4.61 (d, 1H, J_{gem}=11.6 Hz, C*H*HPh); 4.04 (br t, 1H, J_{3-4}= 2.8 Hz, H-3), 3.78 (m, 3H, H-5+2×H-6), 3.57–3.40 (m, 2H, H-2+H-4), 3.42 (s, 3H, OMe), 2.65 (d, 1H, *J*=10.8 Hz, OH-4), 2.34 (br s, 1H, OH-6); ^{13}C NMR ($CDCl_3$) δ 138.7, 137.7 (C_{quat}-Ar), 128.6–127.8 (CH-Ar), 97.9 (C-1), 76.8 (C-2), 75.5 (C-3), 74.3, 71.6 (CH_2Ph), 68.2 (C-5), 66.9 (C-4), 62.3 (C-6), 56.0 (OMe); Anal. calcd for $C_{21}H_{26}O_6$ (374.42): C, 67.36; H, 7.00, found: C, 67.43; H, 7.04%.

4.1.3. Methyl 2,3-di-*O*-benzyl-4,6-*O*-(2-phenylsulfonyl)-ethylidene-α-D-allopyranoside (8). As for the preparation of **6**, an ice-cold THF (13 mL) solution of the above 4,6-diol (491 mg, 1.3 mmol) was reacted with (*E*)-1,2-bis(phenyl-sulfonyl)-ethylene (404 mg, 1.31 mmol, 1 equiv.) to afford after silica gel column purification chromatography (EtOAc/cyclohexane=1/3) the alloside **8** (566 mg, 80%) as a colourless foam: $[\alpha]_D^{23}$=+9 (*c* 1.0, $CHCl_3$); MS (CI) *m/z* 563.0 [*M*Na]$^+$, 579.0 [*M*K]$^+$; ^{1}H NMR ($CDCl_3$) δ 7.89–7.85 (m, 2H, *o*-SO_2 H-Ar), 7.64–7.19 (m, 13H, H-Ar), 4.99 (t, 1H, J_{vic}=4.8 Hz, H-7), 4.62 (d, 1H, J_{1-2}=4.0 Hz, H-1), 4.60–4.43 (m, 4H, CH_2Ph), 4.09 (m, 2H, H-5+H-6a), 3.91 (br t, 1H, J_{2-3}=3.0 Hz, H-3), 3.30–3.50 (m, 4H, H-8+H-2+H-6b), 3.38 (s, 3H, OMe), 3.24 (dd, 1H, J_{3-4}=2.4 Hz, J_{4-5}=9.1 Hz, H-4); ^{13}C NMR ($CDCl_3$) δ 139.9, 139.0, 137.6 (C_{quat}-Ar), 133.8 (*p*-SO_2 CH-Ar), 129.1–127.1 (CH-Ar), 99.9 (C-1), 96.7 (C-7), 79.2 (C-4), 74.8 (C-2), 73.9, 71.1 (CH_2Ph), 73.0 (C-3), 68.9 (C-6), 60.0 (C-8), 57.4 (C-5), 56.2 (OMe); Anal. calcd for $C_{29}H_{32}O_8S$ (540.61): C, 64.43; H, 5.97, found: C, 64.47; H, 6.02%.

4.2. General procedure using TIBAL

TIBAL (1.5 M in toluene, 6 equiv.) was added to a stirred solution of starting material in anhydrous toluene (same

volume as TIBAL) at rt under argon. The reaction mixture was heated at 50°C until TLC (EtOAc/cyclohexane=1/2) indicated no starting material but a major product. The mixture was cooled to 0°C, aqueous 1N HCl was carefully added dropwise, and the mixture was stirred vigorously at rt for 15 min. The mixture was filtered (Celite®) into a separating funnel and washed thoroughly with EtOAc. The organic layer was washed with brine, dried ($MgSO_4$), filtered and the solvent was removed in vacuo. The residue was purified by flash chromatography (EtOAc/cyclohexane=1/1) to afford the de-*O*-benzylated product as a colourless foam.

4.2.1. Methyl 3-*O*-benzyl-4,6-*O*-(2-phenylsulfonyl)-ethylidene-α-D-glucopyranoside (2). Compound **1** (309 mg, 0.57 mmol) was submitted to TIBAL (3.4 mL, 3.4 mmol, 1 M, 6 equiv.) in anhydrous toluene (3.5 mL), to afford, after stirring 2 h at 50°C, the mono-benzyl ether **2** (250 mg, 97%) as a colourless foam: $[\alpha]_D^{23}=+102$ (*c* 1.0, $CHCl_3$); MS (CI) *m/z* 468 $[M\mathrm{NH_4}]^+$; ^{1}H NMR ($CDCl_3$) δ 5.04 (t, 1H, J_{7-8}=4.9 Hz, H-7), 4.86 (d, 1H, J_{gem}=11.6 Hz, C*H*HPh), 4.77 (d, 1H, J_{1-2}=3.0 Hz, H-1), 4.71 (d, 1H, J_{gem}=11.6 Hz, CH*H*Ph), 4.08 (dd, 1H, J_{5-6a}=4.8 Hz, J_{gem}=10.2 Hz, H-6a), 3.68 (m, 2H, H-2+H-4), 3.53 (t, 1H, $J_{5-6b}\sim J_{6a-6b}\sim$10.0 Hz, H-6b), 3.51 (d, 2H, J_{7-8}=4.9 Hz, H-8), 3.43 (m, 1H, H-3), 3.42 (s, 3H, OMe); ^{13}C NMR ($CDCl_3$, TMS) δ 139.7, 138.3 (2×C_{quat}-Ar), 133.9, 129.1, 128.3, 128.1, 127.9, 127.7 (10×CH-Ar), 99.7 (C-1), 96.5 (C-7), 81.6 (C-3), 78.3 (C-4), 74.5 (CH_2Ph), 72.1 (C-2), 68.5 (C-6), 61.9 (C-5), 59.9 (C-8), 55.4 (OMe); Anal. calcd for $C_{22}H_{26}O_8S$ (450.50): C, 58.65; H, 5.82, found: C, 58.51; H, 5.97%.

4.2.2. Methyl 3-*O*-benzyl-4,6-*O*-(2-phenylsulfonyl)-ethylidene-α-D-mannopyranoside (4), methyl 2-*O*-benzyl-4,6-*O*-(2-phenylsulfonyl)-ethylidene-α-D-mannopyranoside (5). The precursor **3** (150 mg, 0.28 mmol) was submitted to TIBAL (1.7 mL, 1.70 mmol, 1 M, 6 equiv.) in anhydrous toluene (1.7 mL), to afford, after stirring 2 h at 50°C, first, side-product **5** (12 mg, 10%), followed by major product **4** (100 mg, 80%) both in the form of colourless foams:

Compound **4**. $[\alpha]_D^{23}=+74$ (*c* 1.0, $CHCl_3$); MS (CI) *m/z* 468 $[M\mathrm{NH_4}]^+$; ^{1}H NMR ($CDCl_3$) δ 7.97–7.38 (m, 10H, 10×CH-Ar), 5.06 (t, 1H, J_{7-8}=4.9 Hz, H-7), 4.78 (d, 1H, J_{gem}=11.9 Hz, C*H*HPh), 4.70 (d, 1H, J_{1-2}=1.3 Hz, H-1), 4.62 (d, 1H, J_{gem}=11.9 Hz, CH*H*Ph), 4.05 (m, 1H, H-6a), 3.98 (dd, 1H, J_{1-2}=1.3 Hz, J_{2-3}=3.4 Hz, H-2), 3.88 (br t, 1H, H-4), 3.74 (dd, 1H, J_{2-3}=3.4 Hz, J_{3-4}=9.5 Hz, H-3), 3.65–3.57 (m, 2H, H-5+H-6b), 3.54 (dd, 1H, J_{gem}=14.5 Hz, J_{7-8a}=4.4 Hz, H-8a), 3.50 (dd, 1H, J_{gem}=14.5 Hz, J_{7-8b}=5.2 Hz, H-8b), 3.34 (s, 3H, OMe); ^{13}C NMR ($CDCl_3$, TMS) δ 139.6, 137.8 (2×C_{quat}-Ar), 133.8, 129.1, 128.4, 128.1, 127.8, 127.7 (10×CH-Ar), 100.9 (C-1), 96.8 (C-7), 78.6 (C-4), 75.1 (C-3), 72.7 (CH_2Ph), 69.5 (C-2), 68.4 (C-6), 62.5 (C-5), 59.9 (C-8), 54.9 (OMe); Anal. calcd for $C_{22}H_{26}O_8S$ (450.50): C, 58.65; H, 5.82, found: C, 58.51; H, 5.87%.

Compound **5**. $[\alpha]_D^{23}=+10$ (*c* 0.5, $CHCl_3$); MS (CI) *m/z* 468 $[M\mathrm{NH_4}]^+$; ^{1}H NMR ($CDCl_3$) δ 7.98–7.30 (m, 10H, 10×CH-Ar), 5.11 (t, 1H, J_{7-8}=4.5 Hz, H-7), 4.74 (d, 1H, J_{gem}=11.7 Hz, C*H*HPh), 4.71 (d, 1H, J_{1-2}=1.3 Hz, H-1), 4.67 (d, 1H, J_{gem}=11.7 Hz, CH*H*Ph), 4.06 (dd, 1H, J_{5-6a}=4.5 Hz, J_{gem}=10.0 Hz, H-6a), 3.85 (dd, 1H, J_{2-3}=3.8 Hz, J_{3-4}=9.8 Hz, H-3), 3.77 (dd, 1H, J_{2-3}=3.8 Hz, J_{1-2}=1.3 Hz, H-2), 3.68 (t, 1H, H-4), 3.62 (t, 1H, H-6b), 3.57 (dd, 1H, J_{gem}=14.7 Hz, J_{7-8a}=4.7 Hz, H-8a), 3.54 (td, 1H, $J_{4-5}\sim J_{5-6b}\sim 2\times J_{5-6a}$, H-5), 3.51 (dd, 1H, J_{gem}=14.7 Hz, J_{7-8b}=5.3 Hz, H-8b), 3.32 (s, 3H, OMe); ^{13}C NMR ($CDCl_3$, TMS) δ 139.8, 137.3 (2×C_{quat}-Ar), 133.8, 129.0, 128.6, 128.4, 128.2, 127.9 (10×CH-Ar), 99.1 (C-1), 97.0 (C-7), 79.4 (C-4), 78.3 (C-2), 73.7 (CH_2Ph), 68.4 (C-6), 68.2 (C-3), 62.6 (C-5), 59.9 (C-8), 55.0 (OMe); Anal. calcd for $C_{22}H_{26}O_8S$ (450.50): C, 58.65; H, 5.82, found: C, 58.86; H, 6.12%.

4.2.3. Methyl 2-*O*-benzyl-4,6-*O*-(2-phenylsulfonyl)-ethylidene-α-D-altropyranoside (7). Starting material **6** (105 mg, 0.20 mmol) was submitted to TIBAL (1.2 mL, 1.20 mmol, 1 M, 6 equiv.) in anhydrous toluene (1.2 mL), to afford, after stirring 1 h at 50°C, mono-benzyl ether **7** (84 mg, 97%) as a colourless foam: $[\alpha]_D^{23}=+45$ (*c* 1.0, $CHCl_3$); MS (CI) *m/z* 468 $[M\mathrm{NH_4}]^+$; ^{1}H NMR ($CDCl_3$) δ 7.94–7.35 (m, 10H, 10×H-Ar), 5.16 (t, 1H, J_{7-8}=4.9 Hz, H-7), 4.69 (br s, 1H, H-1), 4.63 (br s, 2H, CH_2Ph), 4.11 (dd, 1H, J_{gem}=10.3 Hz, J_{5-6a}=5.1 Hz, H-6a), 3.98 (br s, 1H, H-3), 3.94 (td, 1H, $J_{4-5}\sim J_{5-6b}\sim 2\times J_{5-6a}$, H-5), 3.76 (dd, 1H, J_{3-4}=2.9 Hz, J_{4-5}=9.9 Hz, H-4), 3.67 (br d, 1H, J_{2-3}=3.2 Hz, H-2), 3.63 (t, 1H, $J_{5-6b}=J_{gem}$=10.0 Hz, H-6b), 3.57 (dd, 1H, J_{gem}=14.6 Hz, J_{7-8a}=4.7 Hz, H-8a), 3.53 (dd, 1H, J_{gem}=14.6 Hz, J_{7-8b}=5.1 Hz, H-8b), 3.37 (s, 3H, OMe); ^{13}C NMR ($CDCl_3$, TMS) δ 139.6, 137.0 (2×C_{quat}-Ar), 133.7, 129.1–127.7 (10×CH-Ar), 99.8 (C-1), 97.2 (C-7), 76.4 (C-4), 76.3 (C-2), 72.5 (CH_2Ph), 68.6 (C-6), 66.7 (C-3), 59.9 (C-8), 57.6 (C-5), 55.5 (OMe); Anal. calcd for $C_{22}H_{26}O_8S$ (450.50): C, 58.65; H, 5.82, found: C, 58.65; H, 6.14%.

4.2.4. Methyl 3-*O*-benzyl-4,6-*O*-(2-phenylsulfonyl)-ethylidene-α-D-allopyranoside (9), methyl 2-*O*-benzyl-4,6-*O*-(2-phenylsulfonyl)-ethylidene-α-D-allopyranoside (10) and 2,3-di-*O*-benzyl-4,6-*O*-(2-phenylsulfonyl)-ethylidene-D-allitol (11). The precursor **8** (105 mg, 0.2 mmol) was submitted to TIBAL (1.2 mL, 1.20 mmol, 1 M, 6 equiv.) in anhydrous toluene (1.2 mL), to afford, after stirring 1 h at 50°C, first, a mixture of compounds **9** and **11** (38 mg, 44%, 1:3), followed by **10** (48 mg, 55%), all in the form of colourless foams. NMR data for compounds **9** and **11** were extrapolated from the NMR spectra of a sample of their mixture. As a consequence, neither elemental analysis nor optical rotation are given.

Compound **9**. MS (CI) *m/z* 468 $[M\mathrm{NH_4}]^+$; ^{1}H NMR ($CDCl_3$) δ 7.94–7.30 (m, 10H, 10×H-Ar), 5.08 (t, 1H, J_{7-8}=4.9 Hz, H-7), 4.64 (d, 1H, J_{1-2}=3.7 Hz, H-1), 4.44 (d, 1H, J_{gem}=12.1 Hz, C*H*HPh), 4.26 (d, 1H, J_{gem}=12.1 Hz, CH*H*Ph), 4.16 (m, 1H, H-6a), 4.02 (m, 1H, H-5), 3.86 (br t, 1H, $J_{2-3}\sim J_{3-4}\sim$3.1 Hz, H-3), 3.64 (br m, 1H, H-2), 3.50 (m, 3H, H-8+H-6b), 3.40 (s, 3H, OMe), 3.39 (dd, 1H, J_{4-5}=9.8 Hz, J_{3-4}=3.1 Hz, H-4); ^{13}C NMR ($CDCl_3$, TMS) δ 139.8, 138.6, (2×C_{quat}-Ar), 133.8, 129.0–127.1 (10×CH-Ar), 99.7 (C-1), 96.9 (C-7), 79.1 (C-4), 75.9 (C-3), 74.5 (CH_2Ph), 68.9 (C-6), 67.7 (C-2), 59.9 (C-8), 56.9 (C-5), 56.2 (OMe).

Compound **11**. MS (CI) *m/z* 546 $[M\mathrm{NH_4}]^+$; ^{1}H NMR ($CDCl_3$) δ 7.94–7.30 (m, 15H, 15×H-Ar), 4.97 (t, 1H, J_{7-8}=4.9 Hz, H-7), 4.68 (d, 1H, J_{gem}=11.5 Hz, C*H*HPh), 4.62 (d, 2H, 2×CH*H*Ph), 4.57 (d, 1H, J_{gem}=11.3 Hz, C*H*HPh), 4.10 (dd, 1H, J_{5-6a}=5.4 Hz, J_{gem}=11.0 Hz, H-6a), 3.78 (m, 5H, 2×H-1+H-2+H-3+H-5), 3.66 (dd, 1H, J_{3-4}=3.6 Hz, J_{4-5}=9.2 Hz, H-4), 3.50 (m, 2H, H-8), 3.36 (t, 1H, $J_{5-6b}\sim J_{gem}$, H-6b); ^{13}C NMR ($CDCl_3$, TMS) δ 139.6, 137.6, 137.3 (3×C_{quat}-Ar), 133.8, 129.1–128.1 (15×CH-Ar), 96.0 (C-7), 80.6, 78.8 (C-2+C-3), 79.9 (C-4), 73.8, 73.0 (2×CH_2Ph), 70.2 (C-6), 62.3 (C-5), 61.0 (C-1), 59.9 (C-8).

Compound **10**. $[\alpha]_D^{23}$=+24 (*c* 1.0, $CHCl_3$); MS (CI) *m/z* 468 $[M\mathrm{NH_4}]^+$; ^{1}H NMR ($CDCl_3$) δ 7.93–7.37 (m, 10H, 10×H-Ar), 5.10 (t, 1H, $J_{7-8}\sim$4.8 Hz, H-7), 4.77 (d, 1H, J_{gem}=12.3 Hz, C*H*HPh), 4.71 (d, 1H, J_{1-2}=3.5 Hz, H-1), 4.61 (d, 1H, J_{gem}=12.3 Hz, CH*H*Ph), 4.24 (br s, 1H, H-3), 4.12 (dd, 1H, J_{gem}=10.1 Hz, J_{5-6a}=4.9 Hz, H-6a), 3.93 (dt, 1H, $J_{4-5}\sim J_{56b}\sim 2\times J_{5-6a}$=10.0 Hz, H-5), 3.58 (dd, 1H, J_{gem}= 14.7 Hz, H-8a), 3.54 (dd, 1H, J_{gem}=14.7 Hz, H-8b), 3.50 (t, 1H, $J_{5-6b}\sim J_{gem}$=10.0 Hz, H-6b), 3.45 (t, 1H, H-2), 3.40 (s, 3H, OMe), 3.22 (dd, 1H, J_{3-4}=2.5 Hz, J_{4-5}=9.7 Hz, H-4), 3.16 (br s, 1H, OH); ^{13}C NMR ($CDCl_3$, TMS) δ 139.6, 137.0 (2×C_{quat}-Ar), 137.0, 133.8, 128.9, 128.6, 128.2, 128.1, 127.9 (10×CH-Ar), 99.3 (C-1), 97.0 (C-7), 78.5 (C-4), 73.5 (C-2), 70.5 (CH_2Ph), 68.6 (C-6), 66.7 (C-3), 59.8 (C-8), 57.1 (C-5), 55.8 (OMe); Anal. calcd for $C_{22}H_{26}O_8S$ (450.50): C, 58.65; H, 5.82, found: C, 58.38; H, 6.30%.

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