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Dramatic effect of PSE clamping on the behaviour of D-glucal under Ferrier I conditions

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Abstract

Clamped by the acid-resistant phenylsulfonylethylidene (PSE) acetal, D-glucal privileged the additive pathway over the Ferrier I rearrangement when confronted with protic nucleophiles.

Keywords: Phenylsulfonylethylidene (PSE) acetals; Glycals; Ferrier I reaction; Glycosylation

Despite the advances of glycochemistry technologies for the synthesis of complex oligosaccharides and the consecutive development of specifically designed chemical tools, a current need remains for original protecting groups in carbohydrate chemistry, and more generally in multistep organic synthesis. Cyclic acetal protecting groups are among the most commonly used groups, for their stability under basic conditions and their standard removability under acid-catalyzed hydrolysis.[1] Phenylsulfonylethylidene (PSE) acetals have recently been introduced as protecting groups with remarkable characteristics.[2] Indeed, those acetals show a strong reluctance to cleavage under standard acidic hydrolysis or alcoholysis conditions ($AcOH–H_2O$, $TFA–H_2O$, BF_3–MeOH); in contrast, they can easily be deprotected under basic ($CsCO_3$–EtOH) or strongly reductive ($LiAlH_4$) conditions.[2] In addition, they display a remarkable stability under oxidative conditions (DDQ)[3] or in the presence of strong Lewis acids.[4]

Considering the stability of the PSE acetal moiety under various acidic conditions, we turned our attention onto one of the most classical carbohydrate transformations: the allylic rearrangement of acylated glycals known as the Ferrier I reaction.[5] This involves the introduction under Lewis acid conditions of a nucleophilic group at the C-1 of a glycal with simultaneous shifting of the double bond between C-2 and C-3. Numerous efforts have been made over decades to avoid or circumvent the Ferrier I reaction in order to selectively favour the regioselective addition process.[6] Modifications of the protecting group array on the glycal substrate might also greatly influence the course of the Ferrier I reaction: because of their sensitiveness to acidic conditions, 4,6-acetal-protected glycals—especially benzylidene—have been scarcely studied,[7] so the influence on the reactivity of glycals of a stable PSE 4,6-*O*-clamping was worth investigating.

PSE D-glucal **2** was prepared in 75% yield from commercially available tri-*O*-acetyl-D-glucal **1** according to the published procedure (Scheme 1).[2b] Three different substrates were synthesized from **2**. Standard O-acylations were performed in excellent yields to produce acetate **3a** and the mixed carbonate **3b**. Applying a routine O-benzylation protocol (NaH, BnBr, DMF, 0 °C) to **2** led to a

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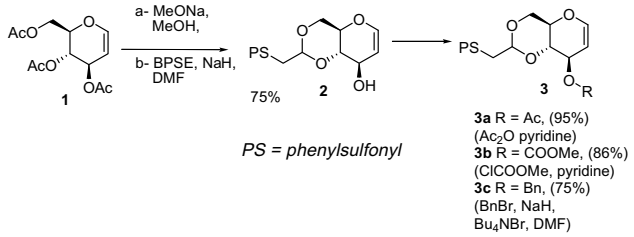


Scheme 1. Preparation of starting material.

mixture of compounds from which the *O*-benzyl ether **3c** could only be obtained in 30% yield.[8] However, carefully controlled alkylation conditions (−78 °C and a slow return to room temperature, 1 equiv Bu_4NBr) allowed an increase of the yield to 75%.

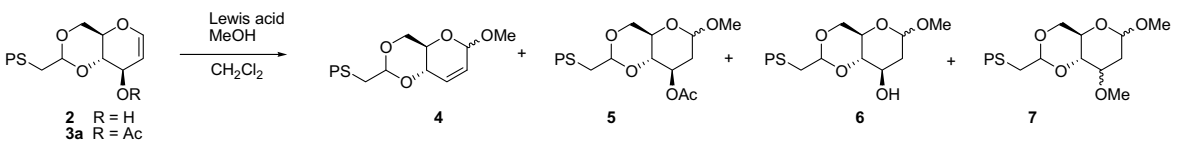
In our first experiments, the acetylated glucal **3a** was chosen as a model (Table 1, entries 1-8) using standard Lewis acid conditions and methanol as the nucleophile (Scheme 2). Unexpected results were obtained: no rearranged compound **4** was detected and a set of three compounds (**5**–**7**) was isolated instead (entry 1).

It can be hypothesized that glycoside **5** is first formed, resulting from an addition process on the enol ether **3a**. The acetyl group is then further methanolyzed to form **6** or C-substituted to afford **7** as mixtures of stereoisomers. The addition process results in a 74% global yield. Replacing $BF_3{\cdot}Et_2O$ by other Lewis acids such as TMSOTf or $Bi(OTf)_3$ only afforded **6** and **7** in improved overall yields. Weaker protic or Lewis acids (entries 4 and 5) proved inefficient in this reaction. In order to limit the side reactions, the amount of acid was reduced to a catalytic level and the nucleophile to a stoichiometric amount; under such conditions the transformations proved far less effective: $BF_3{\cdot}Et_2O$ (entry 6) led to a complex mixture while the other acids (entries 7 and 8) gave a moderate yield of the expected **5**, but still with some nucleophilic substitution. With a view to circumventing the acetate problem (**3a**), the study was pursued starting directly from PSE D-glucal **2**. Applying with a panel of Lewis acids the conditions described above (5 equiv MeOH, 1.1 equiv acid), we observed a high yielding overall transformation of **2** with an 8:1 rough ratio of the addition over the Ferrier rearrangement (entries 9–12). Furthermore, no side formation of **7** was detected. When tested under catalytic conditions with a stoichiometric amount of methanol, the reaction was found still efficient, especially with TMSOTf (entries 13–15).

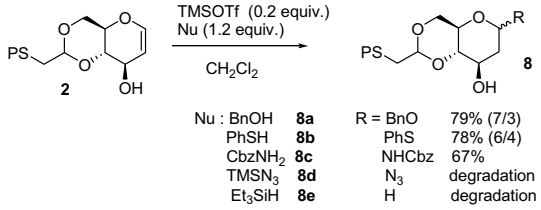
The above preliminary results converged towards the fact that, when placed in Ferrier I conditions, either protected or unprotected PSE D-glucal mainly followed an addition process of the alcohol. Some observations should be emphasized: (a) a stoichiometric amount of Lewis acid increases the reactivity, (b) the catalytic process is effective only with the allyl alcohol **2**, (c) TMSOTf is the most selective reagent for the addition process. On those grounds, we

Table 1
Methanol as a nucleophile

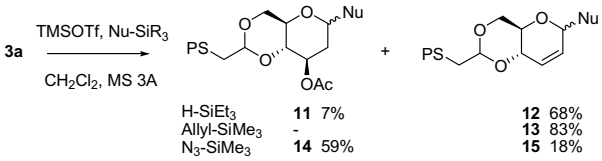
Entry	Glucal	Lewis acid		Methanol	**4**	**5** (α/β)	**6** (α/β)	**7**
1	**3a**	$BF_3{\cdot}Et_2O$	1.1 equiv	5 equiv	—	20%	48% (7/3)	6%
2	**3a**	TMSOTf			—	—	56% (8/2)	21%
3	**3a**	$Bi(OTf)_3$			—	—	77% (8/2)	16%
4	**3a**	CSA			No reaction			
5	**3a**	$ZnCl_2$			No reaction			
6	**3a**	$BF_3{\cdot}Et_2O$	0.2 equiv	1.2 equiv	—	Complex mixture		
7	**3a**	TMSOTf			—	48% (8/2)	—	21%
8	**3a**	$Bi(OTf)_3$			—	45% (8/2)	—	Traces
9	**2**	$BF_3{\cdot}Et_2O$	1.1 equiv	5 equiv	14%		80% (8/2)	—
10	**2**	TMSOTf			Traces	—	88% (8/2)	—
11	**2**	$Bi(OTf)_3$			11%	—	85% (8/2)	—
12	**2**	$InCl_3$			12%	—	75% (8/2)	—
13	**2**	$BF_3{\cdot}Et_2O$	0.2 equiv	1.2 equiv	21%		73% (8/2)	
14	**2**	TMSOTf			Traces		78% (8/2)	
15	**2**	$Bi(OTf)_3$			9%		79% (8/2)	
16	**2**	$InCl_3$			No reaction			



Scheme 2. Attempted Ferrier rearrangement under standard conditions.



Scheme 3.



Scheme 5.

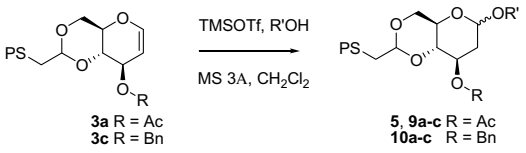
first explored the scope of our reaction, getting simple (O, S, N, H) nucleophiles (Nu) opposed to PSE D-glucal **2** (Scheme 3). With protic reagents, the addition performed well with reasonable to good yields of **8a–c**, whereas non-protic reagents only led to degradations.

We then turned our attention back to protected substrates **3a**, and **3c** reacting with protic nucleophiles; yield optimization was ensured through combining a stoichiometric amount of nucleophile and TMSOTf, associated with 3 Å molecular sieves (Scheme 4).

Under such conditions indeed, an even more efficient addition process was observed. In all cases, side products **6** and **7** were either not detected or only found as traces. Aliphatic alcohols as well as *p*-methoxyphenol gave the desired compounds **5** and **9a–c** in reasonable yields; on the other hand, the O-benzylated substrate **3c** allowed yield improvement for adducts **10b–c** (see Table 2).

The striking efficacy of the above process[9] with protic nucleophiles brought us to reconsider the case of aprotic nucleophiles when confronted with the protected glucal **3a** and preliminary results were found quite contradictory (Scheme 5). Triethylsilane and allyltrimethylsilane unexpectedly underwent the Ferrier rearrangement to afford unsaturated compounds **12** (with a small amount of the adduct **11**) and **13**. In contrast, $TMSN_3$ reacted preferentially in the addition mode, giving a 59% yield of **14** (3:7 α/β mixture) and an 18% yield of the rearranged product **15** (1:1 α/β mixture).[10] It may thus be hypothesized at this stage that the hardness factor of the nucleophilic reagent remains a prominent parameter in the behaviour of PSE glucals under Ferrier I conditions. It is also plausible that a rigidification of the glucal through PSE acetal clamping exerts a dramatic effect on the reaction process; a radiocrystallographic analysis of glucal **2** was performed in order to detect a possible conformational anomaly. However, the X-ray picture obtained (Fig. 1)[11] revealed for **2** a standard half-chair conformation, thus indicating that the PSE-clip should have no distortional impact on the course of the Ferrier I transformation. In other respects, it can also be postulated that the rearrangement process might be hampered by conformational constraints of a 2,3-enopyranoside of type **4**. Therefore diol **16** was reacted with BPSE under standard conditions[2b] to afford the corresponding PSE acetal **17** in 86% yield (Scheme 6).

This is consistent with the results obtained notably with the formation of **12** and **13** (Scheme 5), which indicate that PSE acetal-clamping of a glucal does not create hindrance to the Ferrier I rearrangement. Our attention is rather attracted on the allyloxycarbenium transition state, in which the sulfonyl group is likely to exert a complexation effect on the Lewis acid, thus deviating the reaction towards an additive pathway. Further investigation of the atypical chemical behaviour of PSE-protected glycals is currently under way in our laboratory.



Scheme 4.

Table 2
Glycosylation reactions on **3a** and **3c** (Scheme 4)

Products	R′	Yield	α/β
5	Methyl	73%	8/2
9a	Heptyl	61%	8/2
9b	Cyclohexyl	55%	9/1
9c	*p*-Methoxyphenyl	64%	>95/5
10a	Methyl	55%	7/3
10b	Heptyl	86%	8/2
10c	Cyclohexyl	96%	8/2

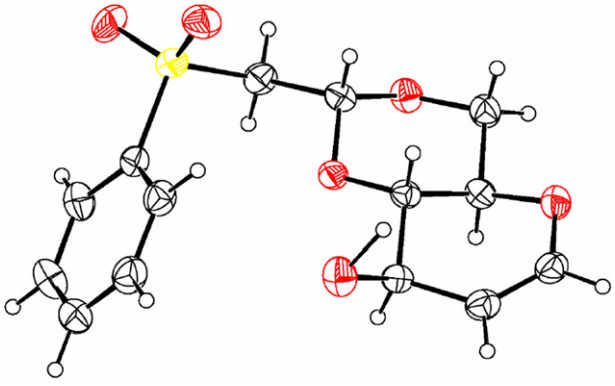
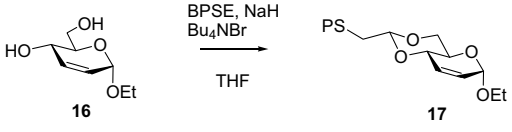


Fig. 1. ORTEP representation of PSE D-glucal **2**.



Scheme 6.

Acknowledgements

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8. Strong bases readily induce ring opening of PSE acetals: Chéry, F.; Tatibouët, A.; De Lucchi, O.; Rollin, P., unpublished results.
9. *Representative procedure*: PSE-glucal **2** or **3a** (0.1 g) was dissolved in DCM (4 mL) under argon. Activated 3 Å molecular sieves (0.2 g) were added, followed by the nucleophile; the resulting slurry was then cooled to 0 °C and stirred for 1 h. TMSOTf (1.2 equiv) was added and the reaction allowed to warm up slowly to room temperature. At the end of the reaction, the solution was quickly filtered over a $MgSO_4$ pad, then diluted with EtOAc (40 mL) and washed with water (3 × 20 mL) then brine (20 mL). The organic solution was dried over $MgSO_4$, evaporated under reduced pressure and purified by silica gel chromatography (petroleum-ether–AcOEt elution).
Selected analytical data for n-heptyl 3-O-benzyl-2-deoxy-4,6-O-(2-phenylsulfonyl)ethylidene-α-D-arabino-hexopyranoside **10b**: Syrup; $[\alpha]_D^{20}$ +54 ($c = 2.1$, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.80$ (3H, m, Me), 1.20 (br s, 8H, heptyl CH_2), 1.45 (m, 2H, heptyl CH_2), 1.62 (ddd, 1H, H-2ax), 2.13 (dd, 2H, $J_{2a-b} = 13.3$ Hz, H-2eq), 3.22 (dt, 1H, $J_{gem} = 9.6$ Hz, $J_{vic} = 4.8$ Hz, H-9b), 3.33–3.56 (m, 6H, H-4, H-5, H-6b, H-8a, H-8b, H-9a), 3.78 (ddd, 1H, $J_{3,4} = 9.1$ Hz, $J_{3,2eq} = 5.0$ Hz, $J_{3,2ax} = 11.1$ Hz, H-3), 3.92 (dd, 1H, $J_{6a,6b} = 10.2$ Hz, $J_{6a,5} = 4.7$ Hz, H-6a), 4.48 and 4.62 (2d, AB system, 2H, $J_{gem} = 11.9$ Hz, $PhCH_2O$), 4.74 (d, 1H, $J_{1,2ax} = 3.2$ Hz, H-1), 4.97 (t, 1H, $J_{7-8} = 5.1$ Hz, H-7), 7.17–7.25 (m, 5H, H–Ph), 7.40–7.42 (m, 2H, *meta*-H–$PhSO_2$), 7.50–7.54 (m, 1H, *para*-H–$PhSO_2$) 7.83–7.86 (d, 2H, *ortho*-H–$PhSO_2$). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.2$ (Me), 22.7, 26.2, 29.1, 29.5, 31.8 (heptyl CH_2), 36.4 (C-2), 61.2 (C-8), 62.4 (C-5), 67.7 (C-9), 68.8 (C-6), 72.5 ($PhCH_2O$), 72.8 (C-3), 83.7 (C-4), 96.9 (C-7), 97.9 (C-1), 127.6–129.2 (CH-Ar), 133.9 (CH-*para*-$PhSO_2$), 138.8 (C_{IV}-Ar), 139.9 (C_{IV}-$PhSO_2$). MS (IS) $m/z = 519.5$ $[M+H]^+$, 542.5 $[M+Na]^+$.
10. *1,5-Anhydro-2,3-dideoxy-4,6-O-(2-phenylsulfonyl)ethylidene-D-erythro-hex-2-enitol* **12**: Syrup; $[\alpha]_D^{20}$ +1 ($c = 0.4$, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 3.25$ (ddd, 1H, $J_{5-6b} = 10.3$ Hz, $J_{5-6a} = 4.8$ Hz, $J_{4-5} = 8.3$ Hz, H-5), 3.48 (d, 2H, $J_{7-8} = 5.0$ Hz, H-8a, H-8b), 3.53 (t, 1H, $J_{5-6b} = J_{6a-6b} = 10.3$ Hz, H-6b), 3.92–3.95 (m, 1H, H-4), 4.06 (dd, 1H, $J_{5-6a} = 4.8$, H-6a), 4.18–4.21 (m, 2H, H-1a, H-1b), 5.11 (t, 1H, $J_{7-8} = 5.0$ Hz, H-7), 5.63 (d, 1H, $J_{2-3} = 10.5$ Hz, H-2), 5.70 (dt, 1H, $J_{3-1} = J_{3-4} = 1.8$ Hz, $J_{3-2} = 10.5$ Hz, H-3), 7.53–7.59 (m, 2H, *meta*-H–$PhSO_2$), 7.64–7.69 (m, 1H, *para*-H–$PhSO_2$), 7.91 (d, 2H, $J = 7.3$, *ortho*-H–$PhSO_2$). ^{13}C NMR (62.5 MHz, $CDCl_3$): $\delta = 60.1$ (C-8), 66.5 (C-1), 69.2 (C-6), 69.7 (C-5), 75.0 (C-4), 97.0 (C-7), 125.3 (C-2), 127.9 (C-3), 128.4 (CH-*ortho*-$PhSO_2$), 129.1 (CH-*meta*-$PhSO_2$), 133.9 (CH-*para*-$PhSO_2$), 139.9 (C_{IV}-$PhSO_2$). MS (IS) $m/z = 314$ $[M+NH_4]^+$, 319 $[M+Na]^+$.
3-O-Acetyl-1,5-anhydro-2-deoxy-4,6-O-(2-phenylsulfonyl)ethylidene-D-glucitol **11**: Syrup; $[\alpha]_D^{20}$ +3 ($c = 1.0$, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.63$–1.75 (m, 2H, H-2), 2.08–2.17 (m, 4H, H-2, MeCO), 3.21 (dd, 1H, $J_{5-6b} = 9.5$ Hz, $J_{4-5} = 4.8$ Hz, H-5), 3.39–3.57 (m, 3H, H-1ax, H-4, H-6b), 3.47 (d, 2H, $J_{7-8} = 4.8$ Hz, H-8a, H-8b), 3.92 (dd, 1H, $J_{1a-b} = 12.0$ Hz, $J_{1-2} = 4.5$ Hz, H-1eq), 4.04 (dd, 1H, $J_{6a-b} = 10.5$ Hz, $J_{5-6a} = 5.0$ Hz, H-6a), 4.88 (ddd, 1H, $J_{3-4} = 10.8$ Hz, $J_{2ax-3} = 9.5$ Hz, $J_{2eq-3} = 5.4$ Hz, H-3), 5.08 (t, 1H, $J_{7-8} = 4.8$ Hz, H-7), 7.52–7.58 (m, 2H, *meta*-H–$PhSO_2$), 7.63–7.68 (m, 1H, *para*-H–$PhSO_2$) 7.91 (d, 2H, $J = 7.3$ Hz, *ortho*-H–$PhSO_2$). ^{13}C NMR (62.5 MHz, $CDCl_3$): $\delta = 21.3$ (MeCO), 31.5 (C-2), 60.1 (C-8), 66.1 (C-6), 68.5 (C-1), 70.6 (C-3), 71.4 (C-5), 80.4 (C-4), 96.9 (C-7), 128.3 (CH-*ortho*-$PhSO_2$), 129.2 (CH-*meta*-$PhSO_2$), 134.0 (CH-*para*-$PhSO_2$), 140.1 (C_{IV}-$PhSO_2$), 170.5 (CO). MS (IS) $m/z = 357.5$ $[M+H]^+$, 374.5 $[M+NH_4]^+$, 379.5 $[M+Na]^+$.
(1R)-1-C-Allyl-1,5-anhydro-2,3-dideoxy-4,6-O-(2-phenylsulfonyl)-ethylidene-D-erythro-hex-2-enitol **13**: Syrup; $[\alpha]_D^{20}$ +6 (*c* 1.1, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 2.17$–2.45 (m, 2H, allyl CH_2), 3.32 (ddd, 1H, $J_{5-6b} = 10.1$ Hz, $J_{4-5} = 8.3$ Hz, $J_{5-6a} = 4.8$ Hz, H-5), 3.47–3.60 (m, 1H, H-6b), 3.48 (d, 2H, $J_{7-8} = 4.8$ Hz, H-8a, H-8b), 3.85 (dd, 1H, $J_{4-5} = 8.3$ Hz, $J_{1-4} = 2.0$ Hz, H-4), 4.02 (dd, 1H, $J_{6a-b} = 10.3$ Hz, $J_{5-6a} = 4.8$ Hz, H-6a), 4.23 (td, $J_{1\text{-}CH_2} = J_{1\text{-}CH_2} = 6.3$ Hz, $J_{1-4} = 2.5$ Hz, H-1), 5.04–5.11 (m, 3H, H-7, $=CH_2$), 5.63–5.87 (m, 3H, H-2, H-3, =CH), 7.53–7.59 (m, 2H, *meta*-H–$PhSO_2$), 7.63–7.69 (m, 1H, *para*-H–$PhSO_2$), 7.91 (1H, d, $J = 7.3$ Hz, *ortho*-H–$PhSO_2$). ^{13}C NMR (62.5 MHz, $CDCl_3$): $\delta = 38.3$ (allyl CH_2), 60.2 (C-8), 65.0 (C-5), 69.5 (C-6), 73.9 (C-1), 75.0 (C-4), 97.0 (C-7), 117.8 ($=CH_2$), 126.1 (C-2), 128.5 (CH-*ortho*-$PhSO_2$), 129.1 (CH-*meta*-$PhSO_2$), 130.6 (C-3), 133.9 (CH-*para*-$PhSO_2$), 134.2 (=CH), 139.9 (C_{IV}-$PhSO_2$). MS (IS) $m/z = 337.5$ $[M+H]^+$, 354.5 $[M+NH_4]^+$, 359.5 $[M+Na]^+$.
3-O-Acetyl-2-deoxy-4,6-O-(2-phenylsulfonyl)ethylidene-α-D-arabino-hexopyranosyl azide **14α**: Syrup; $[\alpha]_D^{20}$ +24 (*c* 1.0, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.74$ (ddd, 1H, $J_{2ax-2eq} = 13.4$ Hz, $J_{2ax-3} = 11.3$ Hz,$J_{1-2ax} = 4.5$ Hz, H-2ax), 2.10 (s, 3H, MeCO), 2.19 (dd, 1H, $J_{2eq-3} = 5.3$ Hz, $J_{1-2eq} = 1.0$ Hz, H-2eq), 3.43–3.57 (m, 2H, H-4, H-6b), 3.48 (d, 2H, $J_{7-8} = 4.8$ Hz, H-8a, H-8b), 3.78 (dd, 1H, $J_{4-5} = 10.0$ Hz, $J_{5-6} = 5.0$ Hz, H-5), 4.06 (dd, 1H, $J_{6a-b} = 10.3$ Hz, $J_{5-6a} = 4.8$ Hz, H-6a), 5.03–5.15 (m, 2H, H-3, H-7), 5.42 (d, 1H, $J_{1-2ax} = 4.5$ Hz, H-1), 7.52–7.58 (m, 2H, *meta*-H–$PhSO_2$), 7.63–7.69 (m, 1H, *para*-H–$PhSO_2$), 7.91 (d, 1H, $J = 7.0$ Hz, *ortho*-H–$PhSO_2$). ^{13}C (62.5 MHz, $CDCl_3$): $\delta = 21.2$ (MeCO), 34.8 (C-2), 60.0 (C-8), 64.6 (C-5), 66.8 (C-3), 68.3 (C-6), 79.9 (C-4), 87.2 (C-1), 97.0 (C-7), 128.2 (CH-*ortho*-$PhSO_2$), 129.2 (CH-*meta*-$PhSO_2$), 134.0 (CH-*para*-$PhSO_2$), 140.0 (C_{IV}-$PhSO_2$), 170.0 (CO). MS (IS) $m/z = 398.5$ $[M+H]^+$, 415.5 $[M+NH_4]^+$, 420.5 $[M+Na]^+$.
3-O-Acetyl-2-deoxy-4,6-O-(2-phenylsulfonyl)ethylidene-α-D-arabino-hexopyranosyl azide **14β**: Syrup; $[\alpha]_D^{20}$ −25 (*c* 1.1, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.51$–1.65 (m, 1H, H-2ax), 2.09 (s, 3H, MeCO), 2.34 (ddd, 1H, $J_{2ax-2eq} = 13.0$ Hz, $J_{2eq-3} = 5.3$ Hz, $J_{1-2eq} =$

2.3 Hz, H-2eq), 3.34 (dd, 1H, $J_{5-6b} = 9.8$ Hz, $J_{5-6a} = 4.8$ Hz, H-5), 3.47 (d, 2H, $J_{7-8} = 4.8$ Hz, H-8a, H-8b), 3.43–3.50 (m, 1H, H-4), 3.58 (t, 1H, $J_{6a-6b} = J_{5-6b} = 10.0$ Hz, H-6b), 4.07 (dd, 1H, $J_{6a-6b} = 10.5$ Hz, $J_{5-6a} = 4.8$ Hz, H-6a), 4.78 (dd, 1H, $J_{1-2} = 10.8$ Hz, $J_{1-2} = 2.3$ Hz, H-1), 4.90 (ddd, 1H, $J_{3-4} = 11.3$ Hz, $J_{2-3} = 9.5$ Hz, $J_{2-3} = 5.3$ Hz, H-3) 5.09 (t, 1H, $J_{7-8} = 4.8$ Hz, H-7), 7.52–7.58 (m, 2H, *meta*-H–$PhSO_2$) 7.63–7.69 (m, 1H, *para*-H–$PhSO_2$) 7.91 (d, 2H, $J = 7.3$, *ortho*-H–$PhSO_2$). ^{13}C (62.5 MHz, $CDCl_3$): $\delta = 21.2$ (MeCO), 36.1 (C-2), 60.0 (C-8), 68.1 (C-6), 68.4 (C-5), 68.9(C-3), 79.2 (C-4), 86.5 (C-1), 97.1 (C-7), 128.2 (CH-*ortho*-$PhSO_2$), 129.2 (CH-*meta*-$PhSO_2$), 134.0 (CH-*para*-$PhSO_2$), 140.0 (C_{IV}-$PhSO_2$), 170.2 (CO). MS (IS) $m/z = 398.5$ $[M+H]^+$, 415.5 $[M+NH_4]^+$, 420.5 $[M+Na]^+$.

11. CCDC 656182 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.