A Synthesis of 1-Lithiated Glycals and 1-Tributylstannyl Glycals from 1-Phenylsulfinyl Glycals via Sulfoxide–Lithium Ligand Exchange

Krzysztof Jarowicki, Colin Kilner, Philip J. Kocienski,* Zofia Komsta, Jacqueline E. Milne, Anna Wojtasiewicz, Victoria Coombs

Institute of Process Research and Development, School of Chemistry, Leeds University, Leeds, LS2 9JT, UK
E-mail: p.j.kocienski@leeds.ac.uk
Received 5 May 2008

SYNTHESIS 2008, No. 17, pp 2747–2763
Advanced online publication: 13.08.2008
DOI: 10.1055/s-2008-1067226; Art ID: Z10208SS
© Georg Thieme Verlag Stuttgart · New York

Abstract: 1-Lithiated glycals generated by reaction of 1-phenylsulfinyl glycals with either t-BuLi or PhLi are transformed to 1-tributylstannyl glycals on reaction with tributyltin chloride.

Keywords: lithium, tin, sulfoxides, carbohydrates, glycals

1-Tributylstannyl glycals (e.g., 1) are versatile reagents for the formation of C–C bonds at C1 of carbohydrates (C-glycosidation).1 For example, they undergo Pd(0)-catalysed Stille cross-coupling reactions with aryl halides (Scheme 1),2–5 alkenyl halides,6 enol triflates,7 acyl halides, and sulfonyl chlorides.8 Equally important, they transmetallate easily with n-BuLi to the corresponding 1-lithiated glycals9 (e.g., 3), which participate in diverse nucleophilic substitutions (e.g., 3 to 4),10,11 nucleophilic additions,12,13 benzannulation reactions,14,15 and 1,2-metallate rearrangements.16

Three general syntheses of 1-tributylstannyl glycals have been reported to date.17 The first and shortest synthesis entails direct lithiation of a suitably protected glycal with t-BuLi in THF at –78 °C followed by quenching with Bu3SnCl (Scheme 2). The lithiation conditions, first described by Boeckman and Bruza18 are harsh,19 and some common protecting groups such as benzyl and tert-butyldimethylsilyl (TBS) ethers may undergo competing lithiation.20,21 However, even when the protected ethers are inert under the reaction conditions, their presence may require 3–6 equivalents of t-BuLi to complete the lithiation, presumably due to complexation effects. For example, C1 lithiation of D-galactal derivative 5 requires 3.5 equivalents of t-BuLi (and a corresponding excess of Bu3SnCl) in order to obtain a yield of 85% of stannane 6 (Scheme 2).22 The same sequence on 3,4,6-tri-tert-butyldimethylsilyl-D-glucal delivers only 12–30% of the stannane.20 Protecting groups that survive the metallation of glycals by t-BuLi are MOM,7,23 TBDPS,7,12,20,22,24 TIPS,7,14,22,25 di-tert-butylsilylene,7,24 TBS (except when it is located at C6),4,22,26 and isopropylidene6,22 as illustrated by the examples shown in Scheme 2.
The second route to 1-tributylstannyl glycals, devised by Beau and co-workers,\textsuperscript{3,27} is longer, but it is compatible with the ubiquitous benzyl ether and benzylidene acetal protecting groups because it avoids the use of harsh metallocating conditions. The key step is a radical substitution on a 1-phenylsulfonyl glycal (e.g., 13) by a tributylstannyl group at elevated temperature (Scheme 3). Unfortunately, the reaction requires an excess of Bu\textsubscript{3}SnH (≥2.5 equiv) and even then, it does not go to completion.

We recently reported a synthesis of D-erythro-sphingosine that featured a 1,2-metallate rearrangement of the 1-lithiated glycal 24 prepared by a novel route (Scheme 5).\textsuperscript{16} A key reaction of the sequence entailed treatment of the stable, storable sulfoxide 23 with t-BuLi at −78 °C whereupon a rapid phenylsulfinyl–lithium exchange occurred to generate the 1-lithiated glycal 24. We reasoned that this reaction, coupled to stannylation with a slight excess of tributyltin chloride,\textsuperscript{30} the cheapest of the tributyltin reagents, would provide a convenient access to 1-tributylstannyl glycals. Thus treatment of 23 with t-BuLi (1.2 equiv) for 30 minutes at −78 °C followed by addition of Bu\textsubscript{3}SnCl (1.3 equiv) and gradual warming to room temperature gave the 1-tributylstannyl glycal 19 in 78% yield on a 10 mmol scale after chromatographic purification.

In order to broaden the scope and generality of the sulfoxide–lithium exchange and stannylation sequence, a further four 1-phenylsulfinyl glycals were prepared using standard methods (see Experimental) and converted to the corresponding 1-tributylstannyl glycals (Scheme 6) in 56–80% yield. A significant improvement arising from these studies over our Ni(0)-catalysed coupling reaction\textsuperscript{28} was the reduction in the number of equivalents of Sn from 4 to 1.3 making the procedure much more atom efficient. Moreover, the speed of the sulfoxide–lithium exchange was sufficient to consume the t-BuLi before it could cause mischief. Thus, the synthesis of stannane 20 (Scheme 6) was accomplished in 62% overall yield from 1-phenylsulfinyl glycal derivative 25 whereas Dötz and co-workers\textsuperscript{22} attempted to generate stannane 20 (Scheme 7) by a direct metallation of glycal 31 (t-BuLi, Bu\textsubscript{3}SnCl), but the yield was low (33%) because of competing elimination to the aldehyde 32 (52%). Similarly, attempts to generate the furanoid stannane 35 by direct metallation of glycal 33 with t-BuLi\textsuperscript{2} resulted in elimination to the furan 34.\textsuperscript{30} By contrast, our method delivered the analogous sensitive stannane 30 from the 1-phenylsulfinyl glycal 29 in 56% yield, although in this case 2 equivalents of t-BuLi were necessary because with 1.2 equivalents of t-BuLi, the stannane 30 was isolated in only 7% yield.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Scheme3}
\caption{Scheme 3}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Scheme4}
\caption{Scheme 4}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Scheme5}
\caption{Scheme 5}
\end{figure}
Use of t-BuLi to effect sulfoxide–lithium exchange was capricious and messy with substrates bearing benzylidene acetal or benzyl ether protecting groups and we suspected that competing metallation of the benzyl ethers was to blame. However, by using the less basic PhLi in THF instead of t-BuLi in Et2O–THF, and shortening the reaction time to just 5 minutes, we were able to generate the stannanes 14, 15, and 38 (Scheme 8) in 85–89% yield cleanly and reproducibly.

A mechanism for the ligand exchange involving sulfoxide (S,S)-23 and t-BuLi is given in Scheme 9. Oxygen-assisted attack of the t-BuLi at sulfur from the back side of the more electronegative glycal ligand forms an unstable trigonal bipyramidal σ-sulfurane 40a, which can fragment with expulsion of the 1-lithio glycal 24 and (SS)-42.31 An alternative mechanism based on some deuteration studies by Theobald and Okamura32 entails pseudorotation of 40a to 40b placing both electronegative groups in their favoured axial positions. Transfer of the lithium from oxygen to the equatorial lone pair juxtaposes the lithium and the glycal ligands in intermediate 41 in preparation for fragmentation to the 1-lithioglycal 24.

In conclusion, the reaction of t-BuLi or PhLi with 1-phenylsulfinyl glycals provides fast tin-free access to 1-lithiated glycals. In contrast to the direct lithiation procedure (see Scheme 2), the sulfoxide–lithium exchange requires only a slight excess of t-BuLi or PhLi and occurs rapidly at low temperature – conditions that are compatible with TBS ethers, benzyl ethers, and benzylidene acetals. The requisite 1-phenylsulfinyl glycals are stable and easily prepared in quantity from commercial carbohydrates in 6–8 steps depending on the protecting group regime required. Finally, the synthesis of 1-tributylstannyl glycals by reaction of 1-lithiated glycals with Bu3SnCl (1.3 equiv Sn) is more atom efficient than the routes based on 1-phenylsulfonyl glycals; that is, the radical substitution route (Scheme 3) and the Ni(0)-catalysed coupling route (Scheme 4) requiring ≥2.5 and 4 equivalents of Sn, re-
spectively. Our method expands the scope of sulfoxide–metal ligand exchange reactions, which have hitherto been used to generate aryllithiums,31 1-chloroalkenylmagnesiums,32 chloroaluminiums,33 chloroalkylmagnesiums,36 oxiranylithiums,37 aziridinylithiums,37 and 1-glycosyllithiums.38

Where appropriate, solvents and reagents were dried by distillation from the usual drying agents prior to use: diethyl ether and tetrahydrofuran from sodium/benzophenone; dichloromethane and toluene from the usual drying agents prior to use: diethyl ether and tetrahydrofuran. The chemical shift in ppm is quoted relative to the residual signals of chloroform (δd = 7.26), methanol (δd = 3.34, δt = 49.9) or benzene (δt = 7.15, δc = 128.6) as the internal standard unless otherwise specified. Multiplicities in the 1H NMR spectra are described as: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, br = broad, and app = apparent. Coupling constants (J) are reported in Hz. The numbers of protons attached to carbon in the 13C NMR spectra were revealed by the DEPT spectral editing technique. Signal assignments were based on COSY, HMOC and HMBC correlations. Mass spectrometry was carried out on a VG autospec mass spectrometer, operating at 70 eV, using electron impact ionisation (EI). Electrospray ionisation (ES) was performed on either a Micromass LCT TOF spectrometer or a Waters-Micromass ZMD spectrometer. High-resolution mass spectrometry (HRMS) was obtained by peak matching using the least squares method using SHELXS and SHELXL software. Crystals were solved by direct methods and refined by the full matrix least squares method using SHELX. Crystallographic data for the structures in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 685328 [(S)-41], 676297 [(S)-36], 676296 [(R)-48], 676300 [(R)-55], 676298 [(S)-28], 676301 [(S)-61], 682926 [(S)-37]. Copies of these data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(1223)336033 or e-mail: deposit@ccdc.cam.ac.uk or via www.ccdc.cam.ac.uk/retrieving.html.

Phenylsulfanyl–Lithium Exchange and Stannylation Reactions

1.5-Anhydro-deoxy-3,4,6-bis-(O-tert-butyldimethylsilyl)-1-C-(tributylstannyl)-D-threo-pent-1-enitol (19); Typical Procedure

To an optical activity AA-1000 spectrometer using an internal deuterium lock. Optical rotations were recorded on a Perkin Elmer. Spectral editing technique. Signal assignments were based on COSY, HMOC and HMBC correlations. Mass spectrometry was carried out on a VG autospec mass spectrometer, operating at 70 eV, using electron impact ionisation (EI). Electrospray ionisation (ES) was performed on either a Micromass LCT TOF spectrometer or a Waters-Micromass ZMD spectrometer. High-resolution mass spectrometry (HRMS) was obtained by peak matching using the least squares method using SHELXS and SHELXL software. Crystals were solved by direct methods and refined by the full matrix least squares method using SHELX. Crystallographic data for the structures in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 685328 [(S)-41], 676297 [(S)-36], 676296 [(R)-48], 676300 [(R)-55], 676298 [(S)-28], 676301 [(S)-61], 682926 [(S)-37]. Copies of these data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(1223)336033 or e-mail: deposit@ccdc.cam.ac.uk or via www.ccdc.cam.ac.uk/retrieving.html.

Phenylsulfanyl–Lithium Exchange and Stannylation Reactions

1.5-Anhydro-deoxy-3,4,6-bis-(O-tert-butyldimethylsilyl)-1-C-(tributylstannyl)-D-threo-pent-1-enitol (19); Typical Procedure

To a solution of the sulfoxide [(S)-23] (4.68 g, 10.0 mmol) in Et2O (50 mL) and THF (1.60 mL, 20 mmol), at –78 °C, t-BuLi (6.7 mL, 1.8 M, 12 mmol) was added dropwise. The reaction mixture was maintained at –78 °C for 30 min. and then freshly distilled Bu3SnCl (4.24 g, 3.53 mL, 13 mmol) was added dropwise. The mixture was left in the cooling bath and allowed to warm gradually to r.t. over 12 h and then quenched with sat. aq NaHCO3 (50 mL). The mixture was extracted with Et2O (2 × 50 mL) and the combined organic layers were dried (Na2SO4) and concentrated in vacuo. The residue was purified by column chromatography (SiO2, hexanes–Et2O with 0.5% Et3N) to give the stannane [(S)-21] (4.97 g, 7.83 mmol, 78%) as a colourless oil. The 1H and 13C NMR spectroscopic data were identical to those reported previously.28

1.5-Anhydro-deoxy-4-(O-tert-butylidemethylsilyl)-4,6-isopropyliene-1-C-tributylstannyl-D-lyxho-hex-1-enitol (20)

Sulfoxide–lithium exchange of [(S)-25] (1.09 g, 2.6 mmol) with t-BuLi (1.74 mL, 1.77 M, 3.1 mmol) in Et2O (12.9 mL) and THF (0.41 mL, 5.14 mmol) followed by quenching with Bu3SnCl (1.09 g, 3.34 mmol) according to typical procedure 1 gave the stannane [(S)-20] (0.94 g, 1.6 mmol, 62%) as a colourless oil after purification by column chromatography on SiO2. The 1H and 13C NMR spectroscopic data were identical to those reported previously.28

1.5-Anhydro-deoxy-3,4,6-di-O-tert-butyldimethylsilyl-1-C-

tributylstannyl-D-erythro-pent-1-enitol (27)

Sulfoxide–lithium exchange of [(R)-26] (1.41 g, 3.0 mmol) with t-BuLi (2.1 mL, 1.7 M, 3.6 mmol) in Et2O (15 mL) and THF (0.48 mL, 6.0 mmol) followed by quenching with Bu3SnCl (1.27 g, 3.9 mmol) according to typical procedure 1 gave the stannane [(R)-27] (1.53 g, 2.4 mmol, 80%) as a colourless oil after purification by column chromatography on SiO2. The 1H and 13C NMR spectroscopic data were identical to those reported previously.28

0.90 (6 H, m, 3 CH2Sn), 0.90 [9 H, s, (CH3)3C], 0.89 [9 H, s, (CH3)2CH], 0.89 (9 H, t, J = 7.7 Hz, 3 CH3), 0.07 (6 H, s, 2 CH2Si), 0.07 (3 H, s, CHSi), 0.06 (3 H, s, CH3Si).

13C NMR (75 MHz, CDCl3): δ = 65.5 (C3H), 29.5 (J(csp2) = 20.7 Hz, 3 CH2C), 27.6 (J(csp2) = 55.7 Hz, 3 CH2CH2C), 26.35 ([CH3)2C], 26.33 ([CH3)2CH], 18.6 ([2 C(CH3)], 14.1 (3 CH2CH3), 10.0 (J(csp2) = 345.7, 330.3 Hz, 3 CH3Sn), –3.7 (CH3Si), –3.9 (2 CH2Si), –4.4 (CH3Si).

HRMS (ES−): m/z calcd for C29H62O3Sn: 729.2936; found: 729.2955.

IR (film): 2956s, 2929s, 2857s, 1577w, 1463m, 1252s, 1076s, 835s cm−1.


1,5-Anhydro-2-deoxy-3,4-di-O-tetraetylthymidylisilyl-1-C-tributylstannyl-1-arabino-hex-1-enitol (14)

Stannane 14 was synthesised in 89% yield on a 1.0 mmol scale according to typical procedure 2.

1H NMR (500 MHz, CDCl3): δ = 7.34–7.25 (15 ArH, m), 4.87 (1 H, d, J = 12.0 Hz, CH2Ph), 4.85 (1 H, d, J = 3.0 Hz, JABPh = 27.3, 20.5 Hz, CH2), 4.65 (2 H, s, CH2Ph), 4.63 (1 H, d, J = 12.4 Hz, CH2Ph), 4.52 (1 H, d, J = 12.0 Hz, CH2Ph), 4.41 (1 H, d, J = 12.0 Hz, CH2Ph), 4.17 (1 H, app dt, J = 6.1, 2.7 Hz, CH2), 4.12 (1 H, t, J = 3.6, CH3), 3.95 (1 H, t, J = 3.6 Hz, CH2), 3.78 (1 H, dd, J = 6.4, 10.3 Hz, CH2(C6H5)), 3.75 (1 H, dd, J = 6.0, 10.0 Hz, CH2(C6H5)), 1.54–1.48 (6 H, m, 3 CH2CH2CH3), 1.30 (6 H, sextet, J = 7.4 Hz, 3 CH3CH2), 0.96–0.92 (6 H, m, 3 CH3Sn), 0.87 (9 H, t, J = 7.3 Hz, 3 CH3CH2).

13C NMR (75 MHz, CDCl3): δ = 164.5 (C1), 139.3 (C4A), 138.8 (C8A), 128.7 (C3A), 128.6 (2 C6A), 128.1 (2 CH), 128.0 (2 CH), 127.9 (C2A), 127.8 (2 CH), 127.5 (2 CH), 110.7 (C2CH), 76.2 (C3CH), 73.8 (CH2), 73.1 (CH2), 72.5 (C4H), 71.2 (CH1), 71.1 (C3H), 69.2 (C6H2), 29.3 (J(csp2) = 20.6 Hz, 3 CH2CH2), 27.6 (J(csp2) = 56.0 Hz, 3 CH2CH2CH3), 14.1 (3 CH3CH2), 10.1 (3 CH3Sn). Signals for 2 carbons in the aromatic region could not be distinguished.

HRMS (ES−): m/z calcd for C39H55O4Sn (M + H)+: 732.3096; found: 732.3095.


1,5-Anhydro-2-deoxy-3,4,6-O-phenylmethyl-1-C-tributylstannyl-o-dexo-hex-1-enitol (15)

Stannane 15 was synthesised in 89% yield on a 1.0 mmol scale according to typical procedure 2.

1H NMR (500 MHz, CDCl3): δ = 7.34–7.25 (15 ArH, m), 4.87 (1 H, d, J = 12.0 Hz, CH2Ph), 4.85 (1 H, d, J = 3.0 Hz, JABPh = 27.3, 20.5 Hz, CH2), 4.65 (2 H, s, CH2Ph), 4.63 (1 H, d, J = 12.4 Hz, CH2Ph), 4.52 (1 H, d, J = 12.0 Hz, CH2Ph), 4.41 (1 H, d, J = 12.0 Hz, CH2Ph), 4.17 (1 H, app dt, J = 6.1, 2.7 Hz, CH2), 4.12 (1 H, t, J = 3.6, CH3), 3.95 (1 H, t, J = 3.6 Hz, CH2), 3.78 (1 H, dd, J = 6.4, 10.3 Hz, CH2(C6H5)), 3.75 (1 H, dd, J = 6.0, 10.0 Hz, CH2(C6H5)), 1.54–1.48 (6 H, m, 3 CH2CH2CH3), 1.30 (6 H, sextet, J = 7.4 Hz, 3 CH3CH2), 0.96–0.92 (6 H, m, 3 CH3Sn), 0.87 (9 H, t, J = 7.3 Hz, 3 CH3CH2).

13C NMR (75 MHz, CDCl3): δ = 164.5 (C1), 139.3 (C4A), 138.8 (C8A), 128.7 (3 C3A), 128.6 (2 C6A), 128.1 (2 CH), 128.0 (2 CH), 127.9 (C2A), 127.8 (2 CH), 127.5 (2 CH), 110.7 (C2CH), 76.2 (C3CH), 73.8 (CH2), 73.1 (CH2), 72.5 (C4H), 71.2 (CH1), 71.1 (C3H), 69.2 (C6H2), 29.3 (J(csp2) = 20.6 Hz, 3 CH2CH2), 27.6 (J(csp2) = 56.0 Hz, 3 CH2CH2CH3), 14.1 (3 CH3CH2), 10.1 (3 CH3Sn). Signals for 2 carbons in the aromatic region could not be distinguished.

HRMS (ES−): m/z calcd for C39H55O4Sn (M + H)+: 732.3096; found: 732.3095.

1-Phenylsulfinyl Glycal (S₆)-23 (Scheme 10)

![Scheme 10 Synthesis of 1-phenylsulfinyl glycal (S₆)-23](image_url)

1-Deoxy-2,3,4-tris-O-(tert-butyldimethylsilyl)-1-[(S₆)-phenylsulfinyl]-β-D-xlyopyranoside (S₄)-44

(NH₄)₂MoO₄ (0.25 g, 1.3 mmol, 6.5 mol%) was added to H₂O₂ (7.2 mL, 30%, 70 mmol, 3.5 equiv) at 0 °C. The resulting yellow solution was then added to a solution of the thioether 43 (11.65 g, 20.0 mmol) in EtOH (160 mL). The reaction was allowed to warm gradually to r.t. over 18 h. A portion of H₂O (50 mL) was added and the mixture was concentrated in vacuo. The resulting solution was extracted with CH₂Cl₂ (3 × 50 mL). The combined CH₂Cl₂ extracts were dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by column chromatography (SiO₂, hexanes–Et₂O, gradient: 20:1 to 10:1) to give recovered thioether 43 (2.09 g, 3.6 mmol, 18%) and sulfoxide (S₆)-44 (8.24 g, 14.0 mmol, 70% or 88% based on recovered starting material) as a colourless crystalline solid; mp 123–124 °C (hexane).

[H₁]ₐ 29 +32.6 (c 1, CHCl₃).

IR (diamond compression system): 2953m, 2928, 2856m, 1648m, 1255m cm⁻¹.

H NMR (500 MHz, CDCl₃): δ = 7.68–7.64 (2 ArH, m), 7.52–7.44 (3 ArH, m), 4.44 (1 H, br d, J = 2.1 Hz, C2H), 4.24 (1 H, dd, J = 12.2, 2.6 Hz, C5H₂), 4.24 (1 H, br s, C1H), 3.86 (1 H, s with fine splitting, C3H), 3.69–3.64 (2 H, m, C4H + C5H₂), 0.98 [9 H, s, (CH₃)₃C], 0.892 [9 H, s, (CH₃)₂C], 0.890 [9 H, s, (CH₃)₃C], 0.23 (3 H, s, CH₃Si), 0.15 (3 H, s, CH₂Si), 0.14 (3 H, s, CH₂Si), 0.11 (3 H, s, CH₃Si), 0.08 (3 H, s, CH₂Si), 0.07 (3 H, s, CH₃Si).

C NMR (75 MHz, CDCl₃): δ = 145.2 (C₆), 131.1 (C₆H), 129.2 (2C₆H), 124.9 (2C₆H), 98.1 (C1H), 71.1 (C3H), 69.3 (C4H), 66.7 (C2H), 65.4 (C5H₂), 26.3 [(CH₃)₂C], 26.1 [(CH₃)₃C], 18.6 [(CH₃)₂C], 18.5 [(CH₃)₂C], 18.3 [(CH₃)₃C], –4.15 (CH₃Si), –4.21 (CH₂Si), –4.3 (CH₂Si), –4.38 (CH₂Si), –4.42 (CH₂Si), –4.6 (CH₃Si).

LRMS (ES⁺): m/z (%) = 623.4 (M + Na)⁺, (100).


The structure and stereochemistry of (S₆)-44 was established by X-ray crystallography (Figure 1).

1,2-Dideoxy-3,4-bis(tert-butyldimethylsilyl)-1-[(S₆)-phenylsulfinyl]-β-D-ribo-hexopyranose ([S₆]-23); Typical Procedure 3

To a solution of i-Pr₂NH (2.91 g, 28.8 mmol, 3.8 equiv) in THF (13 mL) was added n-ButLi (2.36 M in pentane, 8.1 mL, 19.2 mmol, 2.5 equiv) at a rate sufficient to maintain the internal temperature at ~30 °C. After stirring for 15 min, the reaction mixture was cooled to ~78 °C and a solution of sulfoxide (S₆)-44 (4.52 g, 7.52 mmol) in THF (30 mL) was added and the mixture stirred at ~78 °C for 30 min. The cooling bath was removed and a sat. aq NaHCO₃ (5 mL) was added and the mixture allowed to warm to r.t. The product was extracted with Et₂O (3 × 20 mL) and the combined organic extracts were dried over Na₂SO₄, filtered and concentrated in vacuo.

1H NMR spectroscopic analysis of the crude product was 1H NMR (500 MHz, CDCl₃): δ = 7.73–7.70 (2 ArH, m), 7.50–7.43 (3 ArH, m), 5.74 (1 H, dd, J = 5.0, 1.4 Hz, C2H), 4.03 (1 H, dd, J = 11.0, 1.4 Hz, C5H₂), 3.95 (1 H, ddd, J = 5.0, 3.0, 1.4 Hz, C3H), 3.90 (1 H, ddd, J = 11.0, 3.3, 1.4 Hz, C4H₂), 3.66 (1 H, tt, J = 3.1, 1.4 Hz, C4H), 0.90 [9 H, s, (CH₃)₂C], 0.72 [9 H, s, (CH₃)₂C], 0.13 (3 H, s, CH₃Si), 0.11 (3 H, s, CH₂Si), 0.00 (3 H, s, CH₂Si), –0.08 (3 H, s, CH₃Si).

C NMR (75 MHz, CDCl₃): δ = 157.5 (C₁), 142.3 (C₃a), 131.9 (C₆H), 129.4 (2C₆H), 126.4 (2C₆H), 101.3 (C₂H), 69.5 (C4H), 69.0 (C5H₂), 65.5 (C3H), 26.1 [(CH₃)₂C], 25.8 [(CH₃)₃C], 18.3 [(CH₃)₂C], 18.0 [(CH₃)₂C], –4.0 (CH₂Si), –4.4 (CH₂Si), –4.5 (CH₃Si), –4.7 (CH₃Si).

HRMS (ES⁺): m/z calc for C₂₉H₄₀O₅Si₃SNa (M + Na)⁺: 491.2084; found: 491.2103.

1-Phenylsulfinyl Glycal (R₆)-36 (Scheme 11)

4,6-O-Benzylidene-2,3-di-O-tert-butyldimethylsilyl-1-[(R₆)-phenylsulfinyl]-α-D-glucopyranoside ([R₆]-46) and its Epimer (S₆)-46; Typical Procedure 4

To a suspension of the thioether 43 (107.7 g, 18.3 mmol) and NaHCO₃ (18.4 g, 220 mmol) in CH₂Cl₂ (400 mL) at ~78 °C was added dropwise a solution of mCPBA (3.8 g, 70%, 20.1 mmol) in CH₂Cl₂ (100 mL) and the mixture was stirred at ~78 °C for 4 h. The cooling bath was removed and sat. aq solutions of Na₂S₂O₃ (100 mL) and NaHCO₃ (100 mL) were added sequentially in one portion with vigorous stirring. When the mixture reached r.t., the phases were separated and the aqueous phase was extracted with CH₂Cl₂ (3 × 50 mL). The combined organic extracts were dried (Na₂SO₄) and concentrated in vacuo.

1H NMR spectroscopic analysis of the crude product was...
Scheme 11 Synthesis of 1-phenylsulfinyl glycal (R)-36

Product revealed two epimeric sulfoxides (2:1) according to integration of the signals for the benzylidene acetal proton at $\delta = 5.44$ for (R)-46 and $\delta = 5.57$ for (S)-46. The mixture was separated by column chromatography (SiO$_2$, hexanes–Et$_2$O, 20:1, 10:1, 5:1, 2:1) to give (S)-46 (3.86 g, 6.4 mmol, 35%) and (R)-46 (6.43 g, 10.6 mmol, 58%).

(R)-46 (Major Epimer)

White solid; mp 120–121 °C (hexanes); $\left[\alpha\right]_{D}^{20}$ = −117 (c 1.00, CHCl$_3$).

IR (diamond compression system): 2928s, 1582w, 1473s, 1472s, 1256s, 1238s, 1172s, 964s, 760s cm$^{-1}$

HRMS (ES$^+$): m/z calcd for C$_{31}$H$_{49}$O$_6$SSi$_2$: (M + H)$^+$: 605.2788; found: 605.2766.

Anal. Calcd for C$_{31}$H$_{49}$O$_6$SSi$_2$: C, 61.55; H, 8.100. Found: C, 61.80; H, 8.10.

1,5-Anhydro-2-deoxy-4.6-O-[(R)-phenylmethylene]-3-[(R)-3-phenylsulfinyl]-1-arabino-hex-1-enitol ([R]-36) and its Epimer (S)-36

Treatment of sulfoxide (R)-46 (9.85 g, 16.3 mmol) with LDA (2.4 equiv) according to typical procedure 3 gave 1-phenylsulfinyl glycal (R)-36 (6.78 g, 14.3 mmol, 88%) as a white solid; mp 118.5–120.5 °C (hexanes–Et$_2$O).

$\left[\alpha\right]_{D}^{20}$ = −137 (c 1.00, CHCl$_3$).

IR (diamond compression system): 3061s, 2927s, 2856s, 1632s, 1473s, 1378s, 1105s, 977s, 700s cm$^{-1}$

1H NMR (500 MHz, CDCl$_3$): $\delta$ = 7.71–7.69 (2 ArH, m), 7.53–7.50 (3 ArH, m), 7.44–7.42 (2 ArH, m), 7.36–7.34 (3 ArH, m), 5.44 (1 H, s, CHPh), 4.18 (1 H, dd, $J$ = 10.1, 5.1 Hz, C$_6$H$_4$H$_2$), 4.07 (1 H, d, $J$ = 6.0 Hz, C$_1$H), 3.98 (1 H, t, $J$ = 5.1 Hz, C$_2$H), 3.89 (1 H, dd, $J$ = 8.1, 5.1 Hz, C$_3$H), 3.79 (1 H, t, $J$ = 10.3 Hz, C$_6$H$_4$H$_2$), 3.76 (1 H, dd, $J$ = 9.8, 8.1 Hz, C$_4$H), 3.63 (1 H, dt, $J$ = 9.8, 5.1 Hz, C$_5$H), 0.90 [9 H, s, (CH$_3$_)$_2$C], 0.85 [9 H, s, (CH$_3$_)$_2$], 0.10 (3 H, s, CH$_3$Si), 0.06 (3 H, s, CH$_3$Si), 0.04 (3 H, s, CH$_3$Si), 0.037 (3 H, s, CH$_3$Si), 0.08 (3 H, s, CH$_3$Si).

13C NMR (75 MHz, CDCl$_3$): $\delta$ = 141.5 (C$_{18}$), 137.3 (C$_{18}$), 131.7 (C$_{18}$), 129.5 (C$_{9}$), 129.3 (2 C$_{5}$H), 128.5 (2 C$_{5}$H), 126.8 (2 C$_{5}$H), 125.7 (2 C$_{5}$H), 102.5 (CHPh), 97.5 (C$_1$H), 81.8 (C$_7$H), 77.2 (C$_2$H), 69.1 (C$_6$H$_4$), 68.4 (C$_6$H), 26.6 [(CH$_3$_)$_2$C], 26.3 [(CH$_3$_)$_2$C], 18.8 [(CH$_3$_)$_2$C], 18.5 [(CH$_3$_)$_2$C], –2.7 (CH$_3$Si), –3.1 (CH$_3$Si), –3.2 (CH$_3$Si), –4.2 (CH$_3$Si).

HRMS (ES$^+$): m/z calcd for C$_1$H$_4$O$_4$SSi$_2$: (M + H)$^+$: 473.1818; found: 473.1797.

Anal. Calcd for C$_1$H$_4$O$_4$SSi$_2$: C, 63.53; H, 6.82. Found: C, 63.80; H, 7.05.

(S)-36

An analogous procedure was used to obtain (S)-36 in 82–84% yield from sulfoxide (S)-46. (S)-36 was obtained as a white solid; mp 125.5–126.0 °C (hexanes–Et$_2$O).

$\left[\alpha\right]_{D}^{20}$ = +46 (c 1.00, CHCl$_3$).

IR (diamond compression system): 3065m, 2926s, 2854s, 1639s, 1376s, 1285s, 857s, 746s, 692s cm$^{-1}$

1H NMR (500 MHz, CDCl$_3$): $\delta$ = 7.73–7.67 (2 ArH, m), 7.54–7.49 (3 ArH, m), 7.46–7.42 (2 ArH, m), 7.37–7.33 (3 ArH, m), 5.63 (1 H, d, $J$ = 2.3 Hz, C$_2$H), 5.54 (1 H, s, CHPh), 4.59 (1 H, dd, $J$ = 7.4, 2.3 Hz, C$_5$H), 3.40 (1 H, dd, $J$ = 10.5, 5.1 Hz, C$_6$H$_4$H$_2$), 3.86 (1 H, dt, $J$ = 10.1, 5.0 Hz, C$_5$H), 3.78 (1 H, dd, $J$ = 10.0, 7.3 Hz, C$_4$H), 3.75

**Figure 2 Molecular structure of (R<sub>6</sub>)-36**

1-Phenylsulfinyl Glycal (S<sub>6</sub>)-25 (Scheme 12)

1-Deoxy-2,3,4,6-di-O-isopropylidene-1-[(S)<sub>6</sub>-phenylsulfinyl]-β-D-galactopyranoside ([S<sub>6</sub>]-48) and its Epimer (R<sub>6</sub>)-48

Oxidation of thioether 47<sup>47</sup> (7.08 g, 20.0 mmol) according to typical procedure 4 gave a mixture of two diastereoisomeric sulfoxides ([S<sub>6</sub>]-48 and (R<sub>6</sub>)-48) in the ratio 4.5:1 according to integration of the <sup>1</sup>H NMR signals for C1H at δ = 4.53 for ([S<sub>6</sub>]-48) and δ = 4.42 for (R<sub>6</sub>)-48. The products were separated by column chromatography (SiO<sub>2</sub>, hexanes–EtOAc with 0.5% of Et<sub>3</sub>N) to give the less polar minor sulf oxide (R<sub>6</sub>)-48 (1.04 g, 2.8 mmol, 14%) followed by a 3.9:1 mixture of ([S<sub>6</sub>]-48 and (R<sub>6</sub>)-48 (1.03 g, 2.8 mmol, 14%), and finally the more polar major sulf oxide ([S<sub>6</sub>]-48 (4.84 g, 13.1 mmol, 66%). The total yield of both epimers was 94%.

([S<sub>6</sub>]-48) (Major Epimer)

White solid; mp 164.5–166.5 °C (hexane–EtOAc).

[α]<sub>D</sub><sup>21</sup> = +5 (c 1.00, CHCl<sub>3</sub>).  

IR (diamond compression system): 3063m, 2989s, 2923s, 1478m, 1382m, 1297m, 1242m, 1224s, 1150s, 972sm−1.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 7.79–7.76 (2 ArH, m), 7.54–7.50 (3 ArH, m), 4.53 (1 H, d, J = 9.6 Hz, C1H), 4.39 (1 H, dd, J = 2.6, 1.5 Hz, C4H), 4.02 (1 H, dd, J = 13.1, 2.2 Hz, C6O1H<sub>2</sub>), 3.95 (1 H, dd, J = 13.1, 1.3 Hz, C6O2H<sub>3</sub>), 3.84 (1 H, t, J = 9.4 Hz, C2H1), 3.59 (1 H, dd, J = 9.2, 2.6 Hz, C3H), 3.52 (1 H, q, J = 7.7 Hz, CSH), 1.46 (3 H, s, CH<sub>3</sub>).  

HRMS (ES<sup>+</sup>): m/z calc'd for C<sub>36</sub>H<sub>42</sub>O<sub>4</sub>Si: 547.2744; found: 547.2745.

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 156.2 (C<sub>1</sub>), 141.7 (C<sub>4</sub>), 137.0 (C<sub>8</sub>), 131.7 (C<sub>1</sub>H), 129.3 (2 C<sub>4</sub>H), 129.2 (C<sub>8</sub>H), 128.3 (2 C<sub>4</sub>H), 126.1 (2 C<sub>4</sub>H), 125.1 (2 C<sub>4</sub>H), 107.0 (C2H<sub>2</sub>), 101.6 (CHPh), 80.0 (C4H), 71.1 (C5H), 67.9 (C6H), 67.9 (C3H), 25.9 [(CH<sub>3</sub>)<sub>2</sub>C], 18.3 [(C3H<sub>3</sub>)<sub>2</sub>], 4.3 (CH<sub>3</sub>Si), 4.7 (CH<sub>3</sub>Si).

**Scheme 12 Synthesis of 1-phenylsulfinyl glycal ([S<sub>6</sub>]-25**

(3 H, s, CH<sub>3</sub>), 1.43 (3 H, s, CH<sub>3</sub>), 1.40 (3 H, s, CH<sub>3</sub>), 1.19 (3 H, s, CH<sub>3</sub>).  

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 139.1 (C<sub>1</sub>), 132.0 (C<sub>4</sub>H), 128.8 (2 C<sub>4</sub>H), 126.7 (2 C<sub>4</sub>H), 112.2 [(CH<sub>3</sub>)<sub>2</sub>C], 98.7 [(CH<sub>3</sub>)<sub>2</sub>C], 92.7 (C1H), 79.7 (C3H), 70.7 (C5H), 69.9 (C4H), 66.4 (C4H), 62.8 (C6H<sub>3</sub>), 28.7 (CH<sub>3</sub>), 26.9 (CH<sub>3</sub>), 26.7 (CH<sub>3</sub>), 18.9 (CH<sub>3</sub>).

IR (diamond compression system): 3063m, 2989s, 2923s, 1478m, 1382m, 1297m, 1242m, 1224s, 1150s, 972sm−1.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 7.74–7.71 (2 ArH, m), 7.50–7.47 (3 ArH, m), 4.42 (1 H, d, J = 9.4 Hz, C1H), 4.38 (1 H, dd, J = 2.8, 1.5 Hz, C4H), 4.01 (1 H, dd, J = 13.1, 2.2 Hz, C6O1H<sub>2</sub>), 3.90 (1 H, dd, J = 13.1, 1.5 Hz, C6O2H<sub>3</sub>), 3.78 (1 H, t, J = 9.4 Hz, C2H<sub>2</sub>), 3.55 (1 H, dd, J = 9.3, 2.7 Hz, C3H), 3.34 (1 H, q, J = 1.7 Hz, C5H<sub>3</sub>), 1.39 (3 H, s, CH<sub>3</sub>), 1.38 (3 H, s, CH<sub>3</sub>), 1.31 (3 H, s, CH<sub>3</sub>), 1.29 (3 H, s, CH<sub>3</sub>).  

HRMS (ES<sup>+</sup>): m/z calc'd for C<sub>36</sub>H<sub>42</sub>O<sub>4</sub>Si: 547.2744; found: 547.2745.

**Scheme 12 Synthesis of 1-phenylsulfinyl glycal ([S<sub>6</sub>]-25**

(3 H, s, CH<sub>3</sub>), 1.45 (3 H, s, CH<sub>3</sub>), 1.40 (3 H, s, CH<sub>3</sub>), 1.19 (3 H, s, CH<sub>3</sub>).  

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 139.0 (C<sub>1</sub>), 131.8 (C<sub>4</sub>H), 128.9 (2 C<sub>4</sub>H), 126.2 (2 C<sub>4</sub>H), 112.0 [(CH<sub>3</sub>)<sub>2</sub>C], 98.8 [(CH<sub>3</sub>)<sub>2</sub>C], 92.2 (C1H), 79.4 (C3H), 70.7 (C5H), 68.4 (C4H), 66.4 (C4H), 62.8 (C6H<sub>3</sub>), 29.0 (CH<sub>3</sub>), 26.8 (CH<sub>3</sub>), 26.4 (CH<sub>3</sub>), 18.8 (CH<sub>3</sub>).

The structure and stereochemistry of (R<sub>6</sub>)-48 was established by X-ray crystallography (Figure 3).
(Na₂SO₄) and concentrated in vacuo. The residue was purified by column chromatography (SiO₂, hexanes–Et₂O) to give the TBS-protected 1-phenylsulfinyl glycal (S₅)–25 (1.15 g, 2.7 mmol, 79%) as a colourless, viscous oil.

[a]ᵣ₂⁰ –10 (c 1.00, CHCl₃).

IR (diamond compression system): 3061m, 2929s, 2894s, 2857s, 1655s, 1473s, 1463s, 1444s, 1382s, 1361m, 1342m, 1311m, 1261s, 1183s, 1131s, 1090s, 1051s, 1023m, 1006m, 961s, 929s, 881s, 837s, 803s, 778s, 749s, 688s, 666m, 590m, 562m, 538m, 516m, 480m cm⁻¹.

¹H NMR (500 MHz, CDCl₃): δ = 7.74–7.70 (2 ArH, m), 7.49–7.43 (3 ArH, m), 5.57 (1 H, t, J = 1.7 Hz, C₂H), 4.65 (1 H, dd, J = 4.5, 2.1 Hz, C₃H), 4.05 (1 H, ill-resolved dd, J = 4.5, 1.5, 1.3 Hz, C₄H), 3.94 (1 H, dd, J = 12.9, 1.7 Hz, C₆H₂(H₆)), 3.87 (1 H, dd, J = 12.9, 1.9 Hz, C₆H₂(H₆)), 3.80–3.82 (1 H, m, C₅H), 1.40 (3 H, s, CH₃), 1.25 (3 H, s, CH₂), 0.89 [9 H, s, (CH₃)₂C], 0.09 (3 H, s, CH₃Si), 0.09 (3 H, s, CH₃Si).

¹³C NMR (75 MHz, CDCl₃): δ = 155.0 (C₁), 142.1 (C₁), 131.4 (C₆H), 129.2 (2 C₆H), 125.5 (2 C₆H), 105.6 (C₂H), 99.3 [C(CH₃)₃], 71.4 (C₅H), 66.1 (C₄H), 65.7 (C₃H), 62.8 (C₆H), 29.3 (2C₆H), 26.1 [(CH₃)₂C], 18.8 (CH₃C), 18.6 [(CH₃)₂C], –4.0 (CH₃Si), –4.1 (CH₃Si).

HRMS (ES⁺): m/z calcd for C₂₁H₂₃O₅SNa (M + Na⁺): 447.1632; found: 447.1614.

1-Phenylsulfinyl Glycal (R₅)–26 (Scheme 13)

Scheme 13 Synthesis of 1-Phenylsulfinyl Glycal (R₅)–26

1-Phenylsulfinyl glycal (S₅)–49 (1.05 g, 3.4 mmol) and THF, –78 °C was added. The phases were separated and the aqueous layer was extracted with Et₂O (3 × 50 mL). The combined organic extracts were dried (Na₂SO₄) and concentrated in vacuo. The residue was purified by column chromatography (SiO₂, hexanes–Et₂O) to give the TBS-protected 1-phenylsulfinyl glycal (S₅)–25 (1.15 g, 2.7 mmol, 79%) as a colourless, viscous oil.

[a]ᵣ₂⁰ –10 (c 1.00, CHCl₃).

IR (diamond compression system): 3061m, 2929s, 2894s, 2857s, 1655s, 1473s, 1463s, 1444s, 1382s, 1361m, 1342m, 1311m, 1261s, 1183s, 1131s, 1090s, 1051s, 1023m, 1006m, 961s, 929s, 881s, 837s, 803s, 778s, 749s, 688s, 666m, 590m, 562m, 538m, 516m, 480m cm⁻¹.

¹H NMR (500 MHz, CDCl₃): δ = 7.74–7.70 (2 ArH, m), 7.49–7.43 (3 ArH, m), 5.57 (1 H, t, J = 1.7 Hz, C₂H), 4.65 (1 H, dd, J = 4.5, 2.1 Hz, C₃H), 4.05 (1 H, ill-resolved dd, J = 4.5, 1.5, 1.3 Hz, C₄H), 3.94 (1 H, dd, J = 12.9, 1.7 Hz, C₆H₂(H₆)), 3.87 (1 H, dd, J = 12.9, 1.9 Hz, C₆H₂(H₆)), 3.80–3.82 (1 H, m, C₅H), 1.40 (3 H, s, CH₃), 1.25 (3 H, s, CH₂), 0.89 [9 H, s, (CH₃)₂C], 0.09 (3 H, s, CH₃Si), 0.09 (3 H, s, CH₃Si).

¹³C NMR (75 MHz, CDCl₃): δ = 155.0 (C₁), 142.1 (C₁), 131.4 (C₆H), 129.2 (2 C₆H), 125.5 (2 C₆H), 105.6 (C₂H), 99.3 [C(CH₃)₃], 71.4 (C₅H), 66.1 (C₄H), 65.7 (C₃H), 62.8 (C₆H), 29.3 (2C₆H), 26.1 [(CH₃)₂C], 18.8 (CH₃C), 18.6 [(CH₃)₂C], –4.0 (CH₃Si), –4.1 (CH₃Si).

HRMS (ES⁺): m/z calcd for C₂₁H₂₃O₅SNa (M + Na⁺): 447.1632; found: 447.1614.

1-Phenylsulfinyl Glycal (R₅)–26 (Scheme 13)

Scheme 13 Synthesis of 1-Phenylsulfinyl Glycal (R₅)–26

Phenyl 1-Thio-α-D-arabinopyranoside (51)

Thiophenol (8.7 mL, 84.3 mmol) and then BF₃·OEt₂ (4.5 mL, 35.1 mmol) were added to a solution of tetra-O-acetyl-α-D-arabinopyranose 50(1) (22.35 g, 70.2 mmol) in CH₂Cl₂ (75 mL) at 0 °C. After 2.5 h at r.t., the reaction mixture was diluted with CH₂Cl₂ (75 mL)
the mixture washed with sat. aq NaHCO₃ (2 × 150 mL), sat. aq.
NaOH (2 × 50 mL) and H₂O (2 × 150 mL). The organic layer was
dried (Na₂SO₄) and concentrated in vacuo. The residue was
dissolved in MeOH (60 mL) and a solution of NaOMe in MeOH (0.1 M,
60 mL, 6 mmol) was added. The mixture was stirred for 1 h at
r.t., then neutralised by stirring for 30 min with Amberlite IR-120
(10 g). The suspension was filtered and the filtrate concentrated in
vacuo. The residue was purified by column chromatography (SiO₂,
hexanes–EtOAc gradient, 2:1 to 1:3) to give the title triol 51 (11.8 g,
48.6 mmol, 69%, 2 steps) as a colourless foam: mp 89–92 °C.

**Phenyl 2,3,4-Tri-O-tert-butyldimethylsilyl-1-thio-o-α-arabinopyranoside (52)**

Imidazole (10.2 g, 0.155 mol) and TBSCI (10.85 g, 72 mmol) were
added to a solution of the triol 51 (4.85 g, 20.0 mmol) in DMP
(50 mL) at r.t. After stirring for 5 d, the reaction mixture was
shaken into H₂O (300 mL) and the aqueous phase extracted with Et₂O (3 ×
25 mL). The combined organic extracts were dried (Na₂SO₄) and
concentrated in vacuo. The residue was purified by column chromatography (SiO₂,
petroleum ether–Et₂O, 20:1) to give a mixture of di- and tri-protected compound (6.06 g). The mixture was dissolved
in CH₂Cl₂ (35 mL). The combined organic extracts were
concentrated in vacuo. The residue was purified by column chromatography (SiO₂, hexanes–Et₂O) to give recovered thioether (80 mg,
48.6 mmol, 66% or 87% based on recovered starting material) as a co-
less oil.

IR (film) 2954m, 2930m, 2858m cm⁻¹.

IR (diamond compression system): 3057s, 2929s, 2857s, 1645s,
1628s, 1531s, 1457s, 1308s, 1220s, 1143s, 1076s, 1030s, 958s, 937s.

HRMS (ES +): m/z calcd for C₆H₁₀O₆Si₃Na₂Cl₂ 427.4828; found:
427.4828.

1H NMR (500 MHz, CDCl₃): δ = 7.68–7.64 (2 ArH, m), 7.52–7.46
(3 ArH, m), 4.54 (1 H, d, J = 3.6 Hz, C2H), 4.18 (1 H, ddd, J = 10.6,
4.6, 2.2 Hz, C4H), 4.05 (1 H, t, J = 10.4 Hz, C5H₂), 3.98–3.94 (2 H,
m, C1H and C3H), 3.50 (1 H, ddd, J = 10.0, 4.7, 0.6 Hz, CJH₃,H₄),
1.00 [9 H, s, (CH₃)₃C], 0.91 [9 H, s, (CH₃)₂C], 0.87 [9 H, s,
(CH₃)₃C], 0.23 (3 H, s, CH₃Si), 0.17 (3 H, s, CH₃Si), 0.14 (3 H,
CH₃Si), 0.13 (3 H, s, CH₃Si), 0.10 (3 H, s, CH₃Si), 0.09 (3 H, s,
CH₃Si), 0.08 (3 H, s, CH₃Si).

13C NMR (75 MHz, CDCl₃): δ = 145.2 (C₆H), 131.2 (C₆H), 129.2
(2 C₆H), 124.9 (2 C₆H), 97.1 (C3H), 73.0 (C4H), 69.1 (C4H),
65.6 (C2H), 63.7 (C5H), 62.4 [(CH₃)₃C], 62.6 [(CH₃)₂C], 62.6
[(CH₃)₃C], 18.7 [(CH₃)₃C], 18.7 [(CH₃)₃C], 18.2 [(CH₃)₃C], –4.2 (2
CH₃Si), –4.3 (CH₃Si), –4.6 (2 CH₃Si), –4.7 (CH₃Si).

HRMS (ES +): m/z calcd for C₂₃H₇₀O₇Si₄Na₂ 741.4774; found:
741.4776.

1.5-Anhydro-2-deoxy-3,4-di-O-tert-butyldimethylsilyl-1-[(R)-
phensulfinyl]-o-erythro-pent-1-enitol ([R]-55)

Reaction of sulfoxide (R₅) (5.17 g, 8.9 mmol) with LDA (2.5 equiv)
according to typical procedure 3 gave a crude product that was
purified by column chromatography (SiO₂, hexanes–Et₂O) to
give the recovered starting material (R₅) (5.17 g, 1.83 mmol,
66%) or 87% based on recovered starting material) as a co-
less oil which solidified on standing; mp 51–54 °C.

IR (diamond compression system) 3057s, 2929s, 2857s, 1471s,
1253s cm⁻¹.

1H NMR (500 MHz, CDCl₃): δ = 7.68–7.63 (2 ArH, m), 7.50–7.46
(3 ArH, m), 7.26 (1 H, s), 5.65 (1 H, d, J = 4.9 Hz, C₂H), 4.26–4.22
(1 H, m, C3H), 3.94 (1 H, t, J = 9.8 Hz, C5H₃,H₄), 3.87–3.80 (2 H,
m, C4H and C5H₂), 0.89 [9 H, s, (CH₃)₃C], 0.82 [9 H, s,
(CH₃)₂C], 0.11 (3 H, s, CH₃Si), 0.09 (3 H, s, CH₃Si), 0.04 (3
H, s, CH₃Si), 0.00 (3 H, s, CH₃Si).

13C NMR (75 MHz, CDCl₃): δ = 156.8 (C₁), 141.7 (C₁₅), 131.5
(C₂₃H₉O₇Si₄Na₂) 129.3 (2 C₆H), 125.3 (2 C₆H), 105.9 (C₂H), 68.4 (C₅H),
67.7 (C₄H), 64.6 (C₅H), 26.1 [(CH₃)₃C], 26.1 [(CH₃)₂C], 18.5
[(CH₃)₃C], 18.4 [(CH₃)₃C], –4.0 (CH₃Si), –4.1 (CH₃Si),
–4.2 (CH₃Si), –4.6 (CH₃Si).

HRMS (ES +): m/z calcd for C₂₃H₇₀O₇Si₄Na₂ 741.4774; found:
741.4776.

I R (diamond compression system): 3057s, 2929s, 2857s, 1471s,
1253s cm⁻¹.

1H NMR (500 MHz, CDCl₃): δ = 7.52–7.43 (2 ArH, m), 7.68–7.63
(3 ArH, m), 4.13 (1 H, dd, J = 3.5, 1.2 Hz, C₃H), 3.98 (1 H, td, J =
9.8, 3.9 Hz, C₄H), 3.94 (1 H, ddd, J = 10.1, 4.2, 1.2 Hz, C₅H₃,H₄),
3.76 (1 H, t, J = 10.0 Hz, C₅H₃,H₄), 2.54 (1 H, br s, OH), 1.03 [9
H, s, (CH₃)₂C], 0.86 [9 H, s, (CH₃)₃C], 0.39 (3 H, s, CH₃Si), 0.38 (3
H, s, CH₃Si), 0.08 (3 H, s, CH₃Si), 0.03 (3 H, s, CH₃Si).

13C NMR (75 MHz, CDCl₃): δ = 161.5 (C₁), 141.3 (C₁₅), 130.8
(C₂₃H₉O₇Si₄Na₂) 129.2 (2 C₆H), 125.3 (2 C₆H), 115.2 (C₂H), 66.6 (C₄H),
66.4 (C₅H), 27.4 [(CH₃)₃C], 25.9 [(CH₃)₃C], 18.6 [(CH₃)₃C],
18.2 [(CH₃)₃C], –1.0 (CH₃Si), –4.0 (CH₃Si), –4.5 (CH₃Si),
–4.7 (CH₃Si).

HRMS (ES +): m/z calcd for C₂₃H₇₀O₇Si₄Na₂ 741.4774; found:
741.4776.

PAPER

The structure and stereochemistry of \((R)_5\)-55 was established by X-ray crystallography (Figure 4).

![Figure 4 Molecular structure of \((R)_5\)-55](image)

When the elimination reaction was carried out according to typical procedure 3 starting from the sulfoxide \((R)_5\)-53 (0.97 g, 1.6 mmol) and LDA (2.5 equiv), but for 4 h at –78 °C instead of 1 h, the 1-phenylsulfinyl glycal \((R)_5\)-26 (0.30 g, 0.64 mmol) was obtained in 40% yield along with sulfoxide \((R)_5\)-55 (0.29 g, 0.61 mmol) in 38% yield.

1-Phenylsulfinyl Glycal \((S)_5\)-28 (Scheme 14)

![Scheme 14 Synthesis of 1-phenylsulfinyl glycal \((S)_5\)-28](image)

1,6-Dideoxy-2,3-O-isopropylidene-4-O-tert-butyldimethylsilyl-1-[(\(S)_5\)-phenylsulfinyl]-\(\alpha\)-l-mannopyranose \([(\(S)_5\)-57] and its Epimer \((R)_5\)-57

Oxidation of the thioether 56\(^{28}\) (1.64 g, 4.0 mmol) with mCPBA (1.08 g, 77%, 4.8 mmol) and NaHCO\(_3\) (4.0 g, 48 mmol) in CH\(_2\)Cl\(_2\) (70 mL) at –78 °C for 2 h according to typical procedure 4 gave a mixture of two diastereoisomeric sulfoxides \((S)_5\)-57 (less polar, major) and \((R)_5\)-57 (more polar, minor) in a ratio of 12:1 as determined by integration of the \(^1\)H NMR signal for C3H at 4.19 ppm for \((R)_5\)-57 and 4.23 ppm for \((S)_5\)-57. The crude mixture was separated by column chromatography (SiO\(_2\), hexanes-Et\(_2\)O) to give first the less polar major sulfoxide \((S)_5\)-57 (1.20 g, 2.8 mmol, 70%), then a mixture of \((S)_5\)-57 and \((R)_5\)-57 (1:1.3, 0.159 g, 0.37 mmol, 9%) and finally the pure minor sulfoxide \((R)_5\)-57 (0.023 g, 0.053 mmol, 1%).

\((S)_5\)-57 (Major Epimer)

Mp 73–74 °C (MeOH-H\(_2\)O); \([\alpha]_D^{21}\) +55 (c 1.00, CHCl\(_3\)).

IR (film): 3055s, 2931s, 2857s, 1473s, 1380s, 1250s, 1216s, 836s, 776s cm\(^{-1}\).

HRMS (ES\(^{\ast}\)): \(m/z\) calc for C\(_{23}\)H\(_{36}\)O\(_5\)SSi: 449.1794; found: 449.1794.

Anal. Calcd for C\(_{23}\)H\(_{36}\)O\(_5\)SSi: C, 59.12; H, 8.03. Found: C, 59.0; H, 8.05.

\((R)_5\)-57 (Minor Epimer)

Colourless oil; \([\alpha]_D^{26}\) –273 (c 0.88, CHCl\(_3\)).

IR (film): 3060s, 2925s, 2857s, 1472s, 1427s, 1381s, 1247s, 1219s, 837s, 778s cm\(^{-1}\).

HRMS (ES\(^{\ast}\)): \(m/z\) calc for C\(_{23}\)H\(_{36}\)O\(_5\)SSi: C, 59.12; H, 8.03. Found: C, 59.0; H, 8.05.

1,5-Anhydro-2,6-dideoxy-4-O-tert-butyldimethylsilyl-1-[(\(S)_5\)-phenylsulfinyl]-\(\alpha\)-l-arabinopyranose \([(\(S)_5\)-58] and its Epimer \([(R)_5\)-58]

Reaction of sulfoxide \((S)_5\)-57 (1.71 g, 4.0 mmol) in THF (45 mL) with LDA (2.5 equiv) in THF (14 mL) at –78 °C according to typical procedure 3 gave a solid residue. Recrystallisation from hexanes–Et\(_2\)O gave the 1-phenylsulfinyl glycal \((S)_5\)-58 (1.17 g, 3.2 mmol, 79%) as a colourless solid; mp 131–132 °C.

\([\alpha]_D^{24}\) +41 (c 1.00, CHCl\(_3\)).
IR (film): 2953s, 2978s, 2931s, 2870s, 1471m, 1382m, 1255s, 1212s, 1047s, 834s cm⁻¹.

1H NMR (500 MHz, CDCl₃): δ = 7.72–7.68 (2 ArH, m), 7.53–7.46 (3 ArH, m), 5.66 (1 H, d, J = 2.9 Hz, C2H), 4.25 (1 H, dt, J = 6.3, 2.9 Hz, CH3), 3.96 (1 H, qu, J = 8.6, 6.4 Hz, C5H), 3.41 (1 H, dd, J = 8.7, 6.3 Hz, C4H), 1.86 (1 H, d, J = 6.3 Hz, OH), 1.22 (1 H, d, J = 6.5 Hz, CH(CH3)), 0.87 [9 H, s, (CH3)3C], 0.12 (3 H, s, CH3Si), 0.06 (3 H, s, CH3Si).

13C NMR (75 MHz, CDCl₃): δ = 156.3 (C1), 141.6 (CAr), 131.8 (C1H), 129.4 (2 C1H), 125.8 (2 C2H), 105.6 (C5H), 79.5 (C3H), 75.7 (C4H), 70.5 (C2H), 26.2 [(CH3)3C], 18.4 [(CH3)2C], 17.5 (CH3CH2), –3.6 (CH3Si), –4.5 (CH3Si).

HRMS (ES⁺): m/z calc’d for C₈H₁₃O₃SSi (M + H)⁺: 369.1556; found: 369.1573.


1-Phenylsulfinyl Glycals (S₅)-28

To a solution of alcohol (S₅)-28 (0.94 g, 2.5 mmol) in CH2Cl2 (66 mL) at 0 °C was added DIPEA (0.74 g, 1.0 mL, 5.8 mmol) followed by the dropwise addition of TBSOTf (0.79 g, 0.68 mL, 3.0 mmol). After 1 h at r.t., the reaction mixture was washed with H2O (100 mL) and the aqueous layer extracted with CH2Cl2 (2 × 50 mL). The combined organic extracts were dried (Na2SO4) and concentrated in vacuo. The residue was purified by column chromatography (SiO2, hexanes–Et2O) to give the 1-phenylsulfinyl glycal (S₅)-28 (1.07 g, 2.2 mmol, 89%) as a white solid; mp 71–72 °C (MeOH–H2O).

1-Phenylsulfinyl Glycals (S₅)-61 and its Epimer (S₅)-61

Oxidation of the thioether 60 (6.55 g, 16.5 mmol) with mCPBA (4.08 g, 77%, 18.1 mmol) and NaHCO₃ (16.5 g, 196 mmol) in CH2Cl2 (70 mL) at –78 °C for 2 h according to typical procedure 4 gave sulfoxide 61 (7.0 g, 15.7 mmol, 95%) as a 1.4:1 mixture of two epimers after column chromatography (SiO2, hexanes–Et2O). The ratio was determined by integration of the 1H NMR signals for C4H (δ = 4.25 (major, more polar) and δ = 4.48 (minor, less polar). A second column chromatography achieved partial separation of the epimers and gave analytical samples of pure of (R₅)-61 and (S₅)-61.

(15) 5-O-tet-Butyldimethylsilyl-1-deoxy-2,3-O-isopropylidene-1-thio-D-ribofuranose (61)

The reaction of 5-O-(tet-butyldimethylsilyl)-2,3-O-isopropylidene-1-thio-D-ribofuranose (59) (12.9 g, 42.0 mmol) with PhSSPh (10.0 g, 46.0 mmol) and Bu₂P (17.0 g, 21.0 mL, 84.0 mmol) in CH2Cl2 (70 mL) according to the procedure of Fürstner46 gave, after column chromatography (SiO2, hexanes–Et2O), the thioether 60 (11.8 g, 30.0 mmol, 71%) as a single diastereoisomer (colourless oil). The spectroscopic data were consistent with those reported.46

Figure 5 Molecular structure of (S₅)-28

5-O-tet-Butyldimethylsilyl-1-deoxy-2,3-O-isopropylidene-1-[(R₅)-phenylsulfinyl]-alpha-D-ribofuranose [(R₅)-61] and its Epimer (S₅)-61

Colourless oil: [α]D²⁵ +136 (c 1.00, CHCl₃).

IR (film): 2953s, 2978s, 2931s, 2870s, 1471m, 1382m, 1255s, 1212s, 1047s, 834s cm⁻¹.

1H NMR (500 MHz, CDCl₃): δ = 7.77–7.73 (2 ArH, m), 7.51–7.47 (3 ArH, m), 5.18 (1 H, dd, J = 6.0, 4.6 Hz, C2H), 4.86 (1 H, dd, J = 6.1, 1.3 Hz, C3H), 4.64 (1 H, d, J = 4.6 Hz, C1H), 4.25 (1 H, dt, J = 2.6, 1.2 Hz, C4H), 3.59 (1 H, dd, J = 11.1, 2.6 Hz, C5H[H₃]), 3.57 (1 H, dd, J = 11.1, 2.6 Hz, C5H[H₅]), 1.69 (3 H, s, CH3C), 1.44 (3 H, s, CH₂C), 0.80 [9 H, s, (CH₃)₃C], –0.09 (3 H, s, CH₃Si), –0.12 (3 H, s, CH₃Si).

13C NMR (75 MHz, CDCl₃): δ = 143.0 (C₆H), 131.6 (C₅H), 129.1 (2 C₄H), 126.2 (2 C₃H), 114.6 [(CH₃)₃C], 101.0 (CH1), 86.9 (C4H), 83.2 (C3H), 81.9 (C2H), 65.3 (C5H), 26.4 [(CH₃)₂C], 25.1 (CH3C), 18.5 [(CH₃)₃C], –5.3 (CH3Si), –5.4 (CH3Si).

HRMS (ES⁺): m/z calc’d for C₉H₁₅O₃SSiNa (M + Na)⁺: 435.1632; found: 435.1639.
\( (S_6)-61 \) (Minor Epimer)

White crystalline solid; mp 73–74 °C (hexane); \([\alpha]_D^{23} +19\ (c\ 0.78,\ \text{CHCl}_3)\).

IR (diamond compression system): 2928s, 2856s, 1471s, 1213s, 1163m, 1056s, 1014s, 839m cm\(^{-1}\).

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 7.84–7.81\ (2 \text{ ArH, m}), 7.51–7.47\ (3 \text{ ArH, m}), 4.81\ (1 \text{ H, d, } J = 4.7\ \text{ Hz, C1H}), 4.80\ (1 \text{ H, dd, } J = 6.2, 1.5\ \text{ Hz, C3H}), 4.60\ (1 \text{ H, dd, } J = 6.2, 4.7\ \text{ Hz, C2H}), 4.48\ (1 \text{ H, app dt}, J = 2.2, 1.7\ \text{ Hz, C4H}), 3.83\ (1 \text{ H, dd, } J = 11.1, 2.7\ \text{ Hz, CSH}_2\text{H}_2\text{O}), 3.69\ (1 \text{ H, dd, } J = 11.1, 2.1\ \text{ Hz, CSH}_2\text{H}_2\text{O}), 1.65\ (3 \text{ H, s, CH}_3\text{C}), 1.32\ (3 \text{ H, s, CH}_3\text{C}), 0.78\ [9\ \text{ H, s, (CH}_3\text{C)}\text{Cl}], 0.00\ (3\ \text{ H, s, CH}_3\text{Si}), –0.01\ (3\ \text{ H, s, CH}_3\text{Si}).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \( \delta = 142.2\ (C_\text{Ar}), 131.7\ (C_\text{Ar}), 129.2\ (2\ C_\text{Ar}), 126.2\ (2\ C_\text{Ar}), 114.5\ (C(CH}_3\text{C})\text{], 102.9\ (C(CH}_3\text{C})\text{], 86.5\ (C4H), 83.2\ (C3H), 81.5\ (C2H), 65.1\ (C1H, C26), 26.4\ (CH}_3\text{C}), 26.1\ [(CH}_3\text{C)], 25.3\ (CH}_3\text{C}), 18.3\ [C(CH}_3\text{C})\text{], –5.2\ (CH}_3\text{Si}), –5.4\ (CH}_3\text{Si}).

HRMS (ES\(^+\)): \( m/z \) calcd for \( (\text{C}_3\text{H}_2\text{O}_3\text{SSi})\text{Na (M + Na)}^+ \): 435.1632; found: 435.1639.

The structure and stereochemistry of the minor sulfoxide \( (S_6)-61 \) was established by X-ray crystallography (Figure 6).

**Figure 6** Molecular structure of \( (S_6)-61 \)

---

\( (R_6)-62 \) (Major Epimer)

This product was the more polar of the two and was obtained as a white solid, with mp 79–81 °C (Et\(_2\)O–hexane). This isomer decomposed over 24 h at r.t. in CDCl\(_3\) that had been stored over K\(_2\)CO\(_3\); therefore, spectroscopic data was best acquired in C\(_6\)D\(_6\).

\([\alpha]_D^{23} +14\ (c\ 0.84,\ \text{C}_6\text{H}_6)\).

IR (diamond compression system): 3374m, 2951m, 2930m, 2856m, 1600m, 1445m, 1387m, 1251m, 1080s, 1014s, 839m cm\(^{-1}\).

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 7.76\ (2\ \text{ ArH, m}), 7.03\ (2\ \text{ ArH, t with extra splitting, } J = 7.4\ \text{ Hz}), 6.97\ (1\ \text{ ArH, t with fine splitting, } J = 7.3\ \text{ Hz}), 5.92\ (1\ \text{ H, d, } J = 2.7\ \text{ Hz, C2H}), 4.81–4.76\ (1\ \text{ H, m, C3H}), 4.59\ (1\ \text{ H, ddd, } J = 5.3, 5.1, 3.6\ \text{ Hz, C4H}), 3.43\ (1\ \text{ H, d, } J = 7.5\ \text{ Hz, OH}), 3.30\ (1\ \text{ H, dd, } J = 11.2, 5.6\ \text{ Hz, CSH}_2\text{H}_2\text{O}), 2.71\ (1\ \text{ H, dd, } J = 11.2, 4.9\ \text{ Hz, CSH}_2\text{H}_2\text{O}), 0.82\ [9\ \text{ H, s, (CH}_3\text{C)}\text{Cl}], –0.15\ (3\ \text{ H, s, CH}_3\text{Si}), –0.18\ (3\ \text{ H, s, CH}_3\text{Si}).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \( \delta = 142.9\ (C_\text{Ar}), 132.0\ (2\ C_\text{Ar}), 129.9\ (2\ C_\text{Ar}), 125.9\ (2\ C_\text{Ar}), 107.2\ (C2H), 94.5\ (C4H), 75.2\ (C3H), 63.5\ (C1H, C26), 26.5\ [(CH}_3\text{C)], 18.9\ [C(CH}_3\text{C})\text{], –4.92\ (CH}_3\text{Si), –4.95\ (CH}_3\text{Si}).

HRMS (ES\(^+\)): \( m/z \) calcd for \( (\text{C}_7\text{H}_2\text{O}_3\text{SSi})\text{Na (M + Na)}^+ \): 355.1396; found: 355.1396.
1,4-Anhydro-2-deoxy-3,5-di-\textit{O}-\textit{t}ert-butyldimethylsilyl-1-\{[(R)_-\textit{S}] or \textit{S}]-phenylsulfanyl\}-\textit{L}-erythro-\textit{pent}-1-enitol ([\(R\)-\(S\)]-29) and Its Epimer ([\(S\)-\(R\)]-29)

Following typical procedure 3 described above, addition of the sulfoxide 61 (2.06 g, 5.0 mmol, 1:1 mixture of epimers) to LDA (2.5 equiv) gave crude alcohol 62 (1.85 g, 5.0 mmol, 100%) as a colourless oil. Without purification, crude 62 was dissolved in DMP (35 mL) and treated with imidazole (0.85 g, 12.5 mmol) and TBSCl (0.91 g, 6.0 mmol). The solution was stirred at rt. for 12 h, then poured into \(\text{H}_2\text{O}\) (350 mL) and extracted with \(\text{Et}_2\text{O}\) (2 x 100 mL). The combined organic extracts were dried (\(\text{Na}_2\text{SO}_4\)) and concentrated in vacuo. The residue was purified by column chromatography (\(\text{SiO}_2\), hexanes–Et\(\text{O}\)) to give the title 1-phenylsulfanyl glycal 29 (1.69 g, 3.6 mmol, 72%) as an inseparable mixture of epimers and recovered starting material 62 (0.31 g, 0.9 mmol, 18%). The ratio of epimers was determined by integration of the \(^1\text{H}\) NMR signals (doubles for \(\text{C}_2\text{H}_6\) at \(\delta = 5.82\) ppm for ([\(R\)-\(S\)]-29) major) and \(\delta = 5.87\) ppm for ([\(S\)-\(R\)]-29) minor). The spectroscopic data were recorded on the mixture of epimers.

IR (film): \(\text{3387m, 2955s, 2928s, 2856s, 1618w, 1472m, 1444m, 1253s, 1087s, 932m, 733s, 695s cm}^{-1}\).

HRMS (ES\(^+\)): \(m/z\) calc'd for \(\text{C}_1\text{H}_2\text{O}_5\text{SSi} (\text{M} + \text{H})^+\): 355.1394; found: 355.1406.

\section*{1-Phenylsulfanyl Glycal (S)-37, (S)-39, and (R)-39 (Scheme 16)}

The reaction of sulfoxide 33\(^6\) (1.00 g, 1.54 mmol) with LDA (2.5 equiv) according to typical procedure 3 gave a crude product that was purified by column chromatography (\(\text{SiO}_2\), hexanes–Et\(\text{O}\)) to give the 1-phenylsulfanyl galactal 37 (0.77 g, 1.43 mmol, 93%) as a white solid: mp 105–106 °C (Et\(\text{O}\)).

IR (film): 1545m, 1353m, 1052s, 733s, 695s cm\(^{-1}\).

HRMS (ES\(^+\)): \(m/z\) calc'd for \(\text{C}_1\text{H}_2\text{O}_4\text{SSi} (\text{M} + \text{H})^+\): 469.2259; found: 469.2253.

\section*{(R)-39 (Major Epimer)}

\section*{(S)-39 (Minor Epimer)}

IR (film): 2954s, 2929s, 2886s, 2857s, 1618m, 1472s, 1253s, 1087s, 1054s, 836s, 778s cm\(^{-1}\).

HRMS (ES\(^+\)): \(m/z\) calc'd for \(\text{C}_1\text{H}_2\text{O}_5\text{SSi} (\text{M} + \text{H})^+\): 469.2259; found: 469.2253.

IR (film): 3387m, 2955s, 2928s, 2856s, 1618m, 1472m, 1444m, 1254s, 1084s, 837s cm\(^{-1}\).

\section*{(S)-62 (Minor Epimer)}

Less polar; colourless oil; \(\delta = 7.75–7.69 (2 \text{ ArH, m}), 7.54–7.49 (3 \text{ ArH, m}), 5.81 (1 \text{ H, d, } J = 2.8 \text{ Hz, CH}_2), 4.95–4.90 (1 \text{ H, m, C}_3\text{H}), 4.46 (1 \text{ H, dt, } J = 5.0, 3.5 \text{ Hz, C}_4\text{H}), 3.68 (1 \text{ H, dd, } J = 11.1, 4.9 \text{ Hz, C}_6\text{H}_2\text{Si}), 3.58 (1 \text{ H, dd, } J = 11.1, 5.1 \text{ Hz, C}_5\text{H}_2\text{Si}), 2.45 (1 \text{ H, br s, OH}), 0.84 [9 \text{ H, s, (CH}_3)_3\text{C}], 0.00 (3 \text{ H, s, CH}_3\text{Si}), –0.02 (3 \text{ H, s, CH}_3\text{Si}).

IR (film): \(\text{3387m, 2954s, 2929s, 2886s, 2857s, 1618m, 1472m, 1253s, 1087s, 1054s, 836s, 778s cm}^{-1}\).

HRMS (ES\(^+\)): \(m/z\) calc'd for \(\text{C}_1\text{H}_2\text{O}_5\text{SSi} (\text{M} + \text{H})^+\): 355.1394; found: 355.1406.
128.04 (2 C ArH), 127.95 (C Ar), 127.9 (2 C ArH), 125.4 (2 C ArH),
103.2 (C2H), 78.9 (C5H), 74.0 (CHPh), 73.7 (ArH), 72.1 (C3H),
71.5 (CHPh), 71.0 (C4H), 67.7 (C6H).

HRMS (ES+): m/z calculated for C13;H20;O2;SNa (M + Na+): 563.1863; found: 563.1858.

Anal. Calculated for C13;H20;O2;S: C, 73.11; H, 5.97; S, 5.93. Found: C,
73.05; H, 5.95; S, 5.80.

The structure and stereochemistry of (S)–37 was established by X-
ray crystallography (Figure 7).

1-Deoxy-2,3:4,6-tetra-O-phenylmethyl-1-[(R*)-phenylsulfinyl]-
β-D-glucopyranoside ([R*]–65) and its Epimer (S*)–65

Oxidation of phenyl 2,3,4,6-tetra-
[500 MHz, CDCl3]) {Lit.47 [C13H20;O2;SNa (M + Na+)]: 671.2438;}
found: 671.2451.

Sulfoxide (R*)–65 failed to give a satisfactory microanalysis.

HRMS (ES+): m/z calculated for C13;H20;O2;SNa (M + Na+): 671.2438; found: 671.2451.

Sulfoxide (S*)–65

Mp 102–104 °C (MeOH) (Lit.47 mp 101–102 °C); [α]D20 +18 (c 0.612, CHCl3) [Lit.47 [α]D20 –16 9 (c 1.0 CHCl3)].

IR (film): 1637m, 1452m, 1300m, 1097s, 1048s, 845m, 741s, 694s cm–1.

HRMS (ES+): m/z calculated for C13;H20;O2;SNa (M + Na+): 671.2438; found: 671.2443.

Anal. Calculated for C13;H20;O2;S: C, 74.05; H, 6.21; S, 4.94. Found: C,
73.80; H, 6.20; S, 4.75.
gave ($S_\text{S}$)-39 (1.63 g, 3.0 mmol, 78%) as a white solid after purification by column chromatography (SiO$_2$, hexanes–EtOAc). A sample recrystallised from EtOAc–hexanes gave white needles: mp 98–99 °C.

IR (film): 3027m, 2900m, 2858m, 1655m, 1453m, 1273m, 1122s, 1090s, 868m, 731s, 694s, 612m cm$^{-1}$.

Sulfoxide (39): 541.2052.

HRMS (ES+): [M + H]$^+$ calculated for C$_{14}$H$_{13}$O$_2$S: 276.0134; found: 276.0125.

1$^3$C NMR (75 MHz, CDCl$_3$): $\delta$ = 77.1–77.7 (2 CH$_2$), 68.0 (C$_6$H$_2$). Signals for 2 carbons could not be distinguished.

Conversion of ($R_\text{S}$)-36 into ($R_\text{S}$)-39

A solution of the sulfoxide ($R_\text{S}$)-36 (100 mg, 0.21 mmol) and PPTS (53 mg, 0.21 mmol) in MeOH (6 mL) and THF (1 mL) was refluxed for 2 d. The solution was redissolved in anhyd DMF (0.4 mL) and added dropwise via syringe to a stirred suspension of NaH (55% in mineral oil; 46 mg, ca. 1.05 mmol) in DMF (0.6 mL) at 0 °C. Then a solution of benzylic bromide (144 mg, 0.1 mL, 0.84 mmol) in DMF (0.4 mL) was added dropwise at 0 °C. The cooling bath was removed and the mixture was allowed to stir at r.t. for 4 h. The reaction was quenched with H$_2$O (5 mL) and extracted with EtO (3 × 10 mL). The combined organic layers were dried over Na$_2$SO$_4$ and the solvent removed in vacuo. The residue was purified by column chromatography (SiO$_2$, hexanes–Et$_2$O) to give the 1-phenylsulfinyl glycal ($R_\text{S}$)-39 (26 mg, 0.0481 mmol, 23% over two steps) as a white solid. The $^1$H and $^{13}$C NMR spectroscopic data were identical to those recorded for sulfoxide ($R_\text{S}$)-39 prepared from ($R_\text{S}$)-65 as shown in Scheme 16.

Acknowledgment

We thank the Carnegie Trust for a studentship (J.E.M.) and the Wellcome Trust for a studentship (V.C.).

References


(40) Crystallographic data for the structures in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 685328 [(S,S)-44], 676297 [(R,S)-36], 676296 [(R,S)-48], 676300 [(R,S)-55], 676298 [(S,S)-28], 676301 [(S,S)-61], 682926 [(S)-37]. Copies of these data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(1223)336033 or e-mail: deposit@ccdc.cam.ac.uk or via www.ccdc.cam.ac.uk/conts/retrieving.html.