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

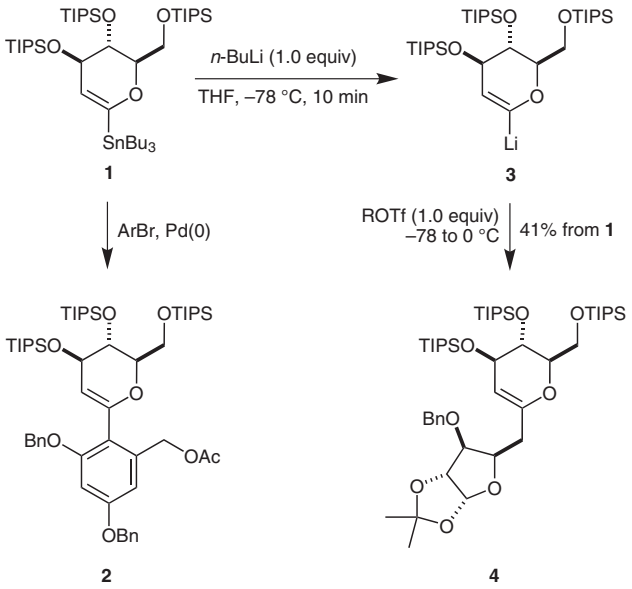
Institute of Process Research and Development, School of Chemistry, Leeds University, Leeds, LS2 9JT, UK
E-mail: p.j.kocienski@leeds.ac.uk

Received 5 May 2008

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.

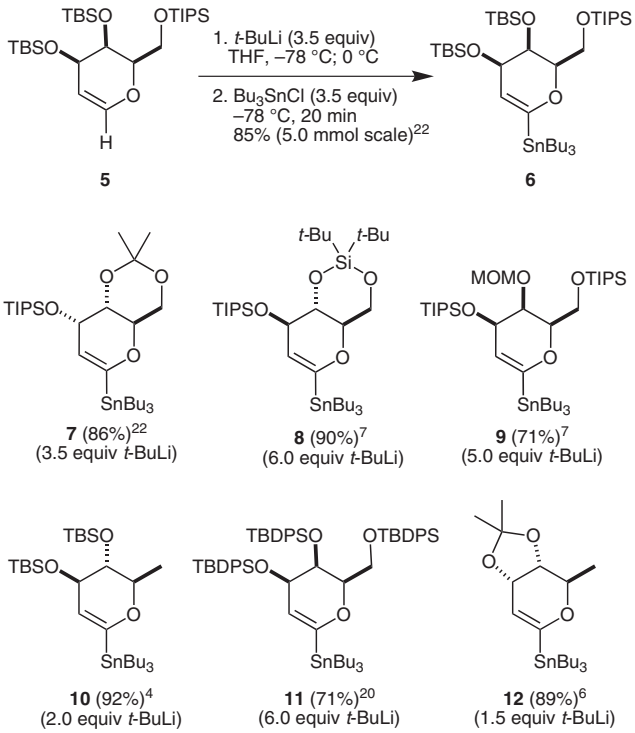
Keywords: lithium, tin, sulfoxides, carbohydrates, glycals

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 glycals[9] (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]



Scheme 1

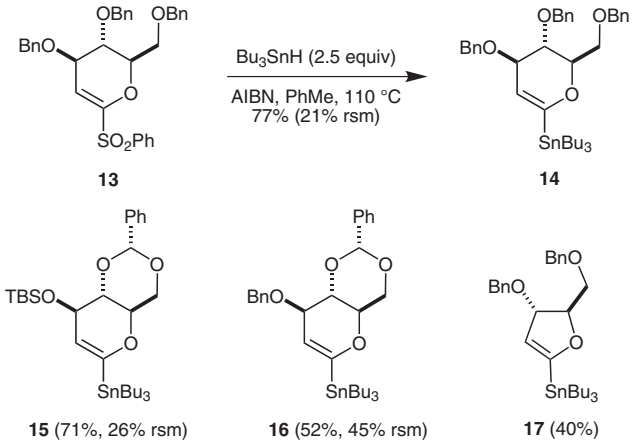
Three general syntheses of 1-tributylstannyl glycals have been reported to date.[17] The first and shortest synthesis entails direct lithiation of a suitably protected glycal with *t*-BuLi in THF at –78 °C followed by quenching with Bu_3SnCl (Scheme 2). The lithiation conditions, first described by Boeckman and Bruza[18] 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 Bu_3SnCl) in order to obtain a yield of 85% of stannane **6** (Scheme 2).[22] The same sequence on 3,4,6- tri-*O*-*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 isopropylidene[6,22] as illustrated by the examples shown in Scheme 2.



Scheme 2

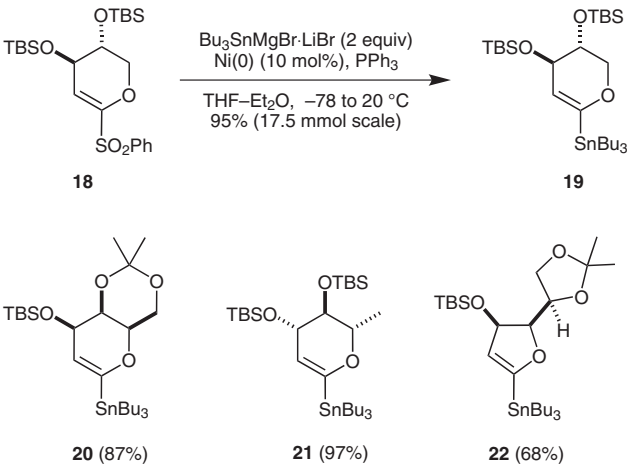
SYNTHESIS 2008, No. 17, pp 2747–2763
Advanced online publication: 13.08.2008
DOI: 10.1055/s-2008-1067226; Art ID: Z10208SS

The second route to 1-tributylstannyl glycals, devised by Beau and co-workers,[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 metallating 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_3SnH (≥2.5 equiv) and even then, it does not go to completion.



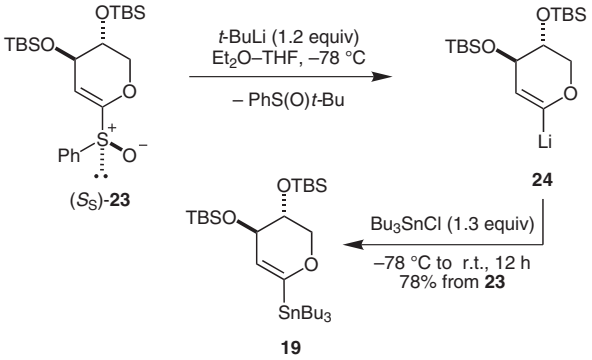
Scheme 3

The 1-phenylsulfonyl glycal substrates at the heart of the Beau protocol are stable, usually crystalline and easy to prepare on large scale and these winning features are preserved in the third route exemplified by the conversion of **18** to **19** (Scheme 4) in which substitution of a phenylsulfonyl group by a tributylstannyl group was accomplished by a Ni(0)-catalysed coupling reaction.[28] The reaction is scalable and efficient, but it requires 2 equivalents of $Bu_3SnMgBr$; hence, there are ≥3 equivalents of tin waste for every equivalent of product formed.[29] The conditions are sufficiently gentle to be applicable to the synthesis of the sensitive dihydrofuran **22**, which is prone to elimination to the corresponding furan.



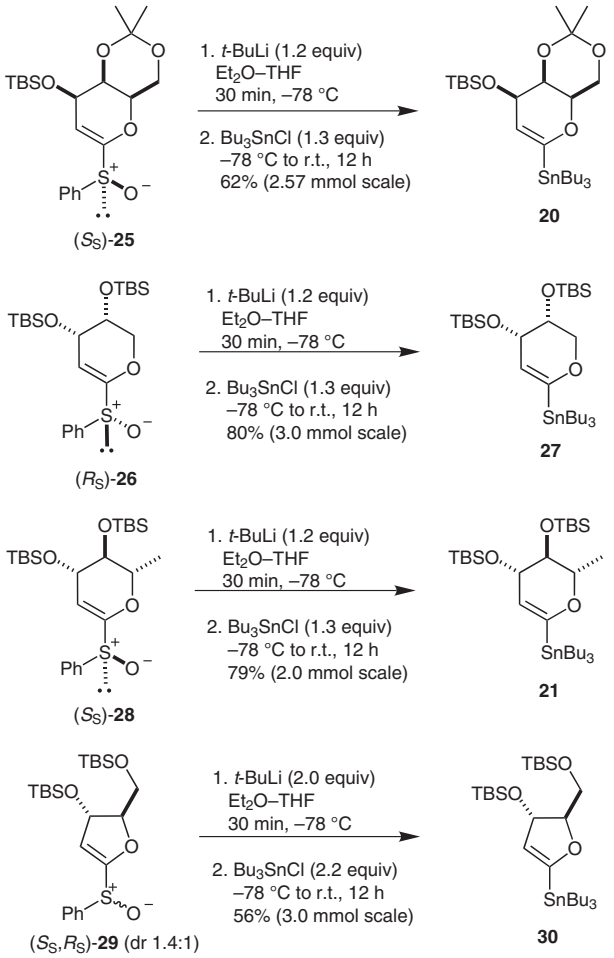
Scheme 4

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).[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,[10] 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_3SnCl (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.

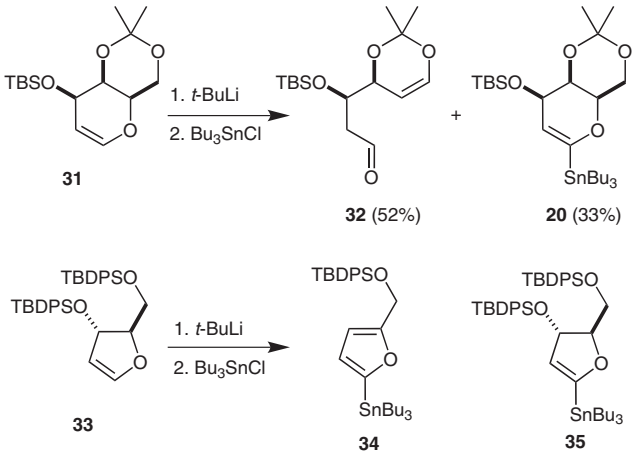


Scheme 5

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[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 coworkers[22] attempted to generate stannane **20** (Scheme 7) by a direct metallation of glycal **31** (*t*-BuLi, Bu_3SnCl), 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[5] resulted in elimination to the furan **34**.[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.

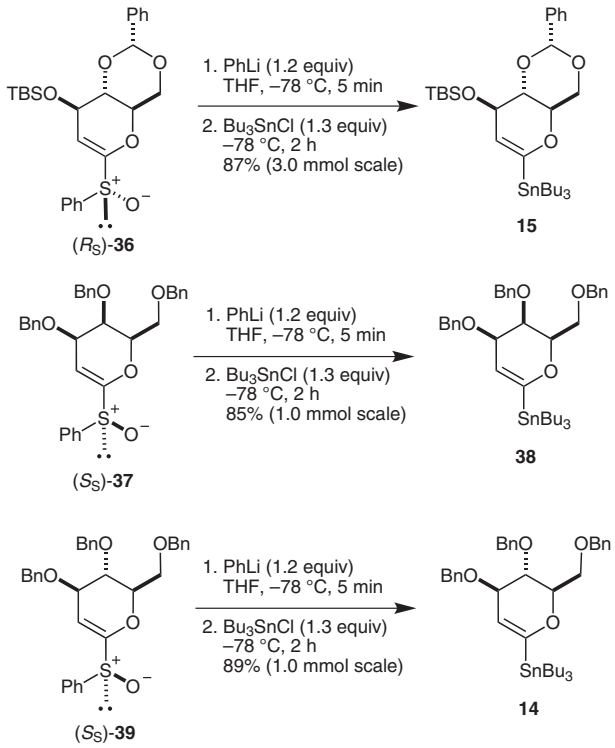


Scheme 6



Scheme 7

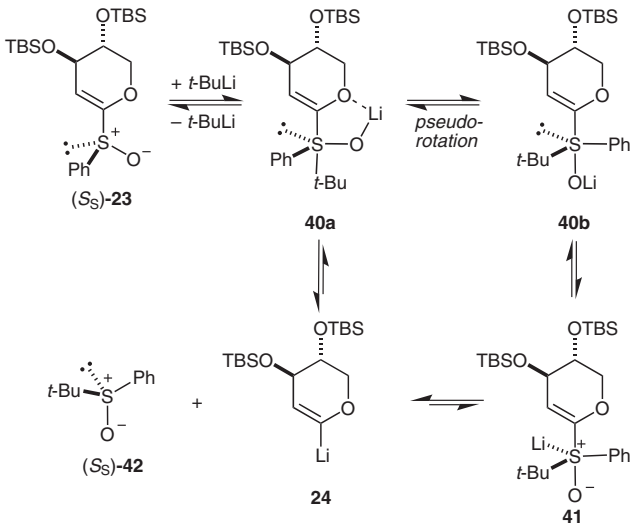
Use of *t*-BuLi to effect sulfoxide–lithium exchange was capricious and messy with substrates bearing benzylidene acetal or benzyl ether protecting groups and we suspected that competing metallation of the benzyl ethers was to blame. However, by using the less basic PhLi in THF instead of *t*-BuLi in Et_2O–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.



Scheme 8

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 (S_S)-**42**.[31] An alternative mechanism based on some deuteration studies by Theobald and Okamura[32] 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 Bu_3SnCl (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-



Scheme 9

spectively. Our method expands the scope of sulfoxide–metal ligand exchange reactions, which have hitherto been used to generate aryllithiums,[33] 1-chloroalkenylmagnesiums,[34] chloroalkyllithiums,[35] chloroalkylmagnesiums,[36] oxiranyllithiums,[37] aziridinyllithiums,[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 calcium hydride; diisopropylethylamine, pyridine and triethylamine from potassium hydroxide. The titre of lithium reagents was determined by the method of Lipton.[39] All reactions were magnetically stirred and were monitored by thin layer chromatography (TLC) using SiO_2 on pre-coated aluminium foil sheets, layer thickness 0.25 mm. Compounds were visualised by UV light (254 and 366 nm) and 20% phosphomolybdic acid in ethanol w/v. Column chromatography was performed on silica gel 60 (35–70 micron). Optical rotations were recorded on an Optical Activity AA-1000 polarimeter (units in 10^{-1} deg·cm^2·g^{-1}). IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer as thin films supported on sodium chloride plates or on a diffuse reflectance sampling cell. Absorptions are reported as values in cm^{-1} followed by the relative intensity: s = strong, m = medium, w = weak. ^{1}H and ^{13}C NMR spectra were recorded on Brüker DPX300 or DRX500 Fourier Transform spectrometers using an internal deuterium lock. The chemical shift in ppm is quoted relative to the residual signals of chloroform (δ_H = 7.26, δ_C = 77.4), methanol (δ_H = 3.34, δ_C = 49.9) or benzene (δ_H = 7.15, δ_C = 128.6) as the internal standard unless otherwise specified. Multiplicities in the ^{1}H NMR spectra are described as: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet, br = broad, and app = apparent. Coupling constants (*J*) are reported in Hz. The numbers of protons attached to carbon in the ^{13}C NMR spectra were revealed by the DEPT spectral editing technique. Signal assignments were based on COSY, HMQC 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 perfluorokerosene or reserpine as a standard. Ion mass/charge (*m*/*z*) ratios are reported as values in atomic mass units followed, in parenthesis, by the peak intensity relative to the base peak (100%). Mass spectra were recorded on samples judged to be ≥95% pure by ^{1}H and ^{13}C NMR spectroscopy unless otherwise stated.

Crystal structure determinations were performed either on a Nonius KappaCCD diffractometer [(*S*$_S$)-**44**, (*R*$_S$)-**36 and** (*S*$_S$)-**28**] (Figures 1, 2, 5, respectively) or a Bruker-Nonius X8 Apex/FR591 rotating anode diffractometer [(*R*$_S$)-**48**, (*R*$_S$)-**55**, (*S*$_S$)-**37** and (*S*$_S$)-**61**] (Figures 3, 4, 7, 6, respectively).[40] In all cases: Mo-Kα radiation and a graphite monochromator were used. *T* = 150(2) K. For all structures, anomalous dispersion effects were sufficient to determine the absolute configuration from the X-ray data since the Flack parameter refined to zero within accepted limits of error. The structures were solved by direct methods and refined by the full matrix least squares method using SHELXS and SHELXL software. 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*$_S$)-**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.

Phenylsufinyl–Lithium Exchange and Stannylation Reactions

1,5-Anhydro-2-deoxy-3,4-bis-*O*-(*tert*-butyldimethylsilyl)-1-*C*-(tributylstannyl)-D-*threo*-pent-1-enitol (19); Typical Procedure 1 (Schemes 5 and 6)

To a solution of the sulfoxide (*S*$_S$)-**23** (4.68 g, 10.0 mmol) in Et_2O (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 Bu_3SnCl (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 $NaHCO_3$ (50 mL).The mixture was extracted with Et_2O (2 × 50 mL) and the combined organic layers were dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by column chromatography (SiO_2, hexanes–Et_2O with 0.5% Et_3N) to give the stannane **19** (4.97 g, 7.83 mmol, 78%) as a colourless oil. The ^{1}H and ^{13}C NMR spectroscopic data were identical to those reported previously.[28]

1,5-Anhydro-2-deoxy-4-*O*-*tert*-butyldimethylsilyl-4,6-*O*-isopropylidene-1-*C*-tributylstannyl-D-*lyxo*-hex-1-enitol (20)

Sulfoxide–lithium exchange of (*S*$_S$)-**25** (1.09 g, 2.6 mmol) with *t*-BuLi (1.74 mL, 1.77 M, 3.1 mmol) in Et_2O (12.9 mL) and THF (0.41 mL, 5.14 mmol) followed by quenching with Bu_3SnCl (1.09 g, 3.34 mmol) according to typical procedure 1 gave the stannane **20** (0.94 g, 1.6 mmol, 62%) as a colourless oil after purification by column chromatography on SiO_2. The ^{1}H and ^{13}C NMR spectroscopic data were identical to those reported previously.[28]

1,5-Anhydro-2-deoxy-3,4-di-*O*-*tert*-butyldimethylsilyl-1-*C*-tributylstannyl-D-*erythro*-pent-1-enitol (27)

Sulfoxide–lithium exchange of (*R*$_S$)-**26** (1.41 g, 3.0 mmol) with *t*-BuLi (2.1 mL, 1.7 M, 3.6 mmol) in Et_2O (15 mL) and THF (0.48 mL, 6.0 mmol) followed by quenching with Bu_3SnCl (1.27 g, 3.9 mmol) according to typical procedure 1 gave the stannane **27** (1.53 g, 2.4 mmol, 80%) as a colourless oil after purification by column chromatography on SiO_2.

$[\alpha]_D^{21}$ +128.9 (*c* 1.36, C_6H_6).

IR (film): 2929m, 1597s, 1463s, 1252s cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.78 (1 H, d, *J* = 5.4 Hz, J_{Sn-H} = 26.1 Hz, C2H), 3.94 (1 H, ddd, *J* = 5.4, 3.1, 1.3 Hz, C3H), 3.83 (1 H, ddd, *J* = 10.8, 3.2, 2.8 Hz, C4H), 3.79 (1 H, dd, *J* = 10.8, 8.6 Hz, C5H_AH$_B$), 3.64 (1 H, ddd, *J* = 8.3, 2.8, 1.5 Hz, C5H$_A$$H_B$), 1.61–1.41 (6 H, m, 3 CH_2), 1.31 (6 H, app sextet, *J* = 7.3 Hz, 3 CH_2CH$_3$), 0.95–

0.90 (6 H, m, 3 CH_2Sn), 0.90 [9 H, s, $(CH_3)_3C$], 0.89 [9 H, s, $(CH_3)_3C$], 0.89 (9 H, t, J = 7.7 Hz, 3 CH_3), 0.07 (6 H, s, 2 CH_3Si), 0.07 (3 H, s, CH_3Si), 0.06 (3 H, s, CH_3Si).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.8 (C1), 113.8 (C2H), 69.2 (C4H), 65.5 ($C5H_2$), 65.0 (C3H), 29.5 (J_{Sn-C} = 20.7 Hz, 3 CH_2CH_3,), 27.6 (J_{Sn-C} = 55.7 Hz, 3 $CH_2CH_2CH_3$), 26.35 [$(CH_3)_3C$], 26.33 [$(CH_3)_3C$], 18.6 [2 $C(CH_3)_3$], 14.1 (3 CH_3CH_2), 10.0 (J_{Sn-C} = 345.7, 330.3 Hz, 3 CH_2Sn), –3.7 (CH_3Si), –3.9 (2 CH_3Si), –4.4 (CH_3Si).

HRMS (ES^+): m/z calcd for $C_{29}H_{62}O_3{}^{28}Si_2{}^{120}SnNa$ $(M + Na)^+$: 657.3133; found: 657.3157.

1,5-Anhydro-2,6-dideoxy-3,4-di-*O*-*tert*-butyldimethylsilyl-1-*C*-tributylstannyl-L-*arabino*-hex-1-enitol (21)

Sulfoxide–lithium exchange of (S_S)-**28** (0.97 g, 2.0 mmol) with *t*-BuLi (1.4 mL, 1.7 M, 2.4 mmol) in Et_2O (10 mL) and THF (0.32 mL, 4.0 mmol) followed by quenching with Bu_3SnCl (0.85 g, 2.6 mmol) according to typical procedure 1 gave the stannane **21** (1.02 g, 1.6 mmol, 79%) as a colourless oil after purification by column chromatography on SiO_2. The ^1H and ^{13}C NMR spectroscopic data were identical to those reported previously.[28]

1,4-Anhydro-2-deoxy-3,5-di-*O*-*tert*-butyldimethylsilyl-1-*C*-tributylstannyl-D-*erythro*-pent-1-enitol (30)

Sulfoxide–lithium exchange of (S_S,R_S)-**29** (1.40 g, 3.0 mmol, 1.4:1 mixture of sulfoxide epimers) with *t*-BuLi (3.2 mL, 1.86 M, 6.0 mmol) in Et_2O (15 mL) and THF (0.96 mL, 12.0 mmol) followed by quenching with and Bu_3SnCl (2.15 g, 6.6 mmol) according to typical procedure 1 gave stannane **30** (1.06 g, 1.7 mmol, 56%) as a colourless oil after purification by column chromatography on basic Al_2O_3 deactivated with 5% of H_2O eluting with hexanes–Et_2O containing 0.5% of Et_3N.

$[\alpha]_D{}^{28}$ +83 (c 1.2, C_6H_6).

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

^1H NMR (500 MHz, C_6D_6): δ = 5.36 (1 H, d, J = 2.5 Hz, J_{Sn-H} = 10.1 Hz, C2H), 5.10 (1 H, t, J = 2.5 Hz, C3H), 4.59 (1 H, ddd, J = 7.3, 5.5, 2.6 Hz, C4H), 3.78 (1 H, dd, J = 10.4, 5.5 Hz, $C5H_AH_B$), 3.55 (1 H, dd, J = 10.4, 7.1 Hz, $C5H_AH_B$), 1.72–1.53 (6 H, m, 3 $CH_2CH_2CH_3$), 1.36 (6 H, app sextet, J = 7.3 Hz, 3 CH_2CH_3), 1.08–1.03 (6 H, m, 3 CH_2Sn), 0.99 [9 H, s, $(CH_3)_3C$], 0.96 (9 H, s, $[CH_3)_3C]$, 0.93 (9 H, t, J = 7.3 Hz, 3 CH_3CH_2), 0.17 (3 H, s, CH_3Si), 0.16 (3 H, s, CH_3Si), 0.06 (3 H, s, CH_3Si), 0.05 (3 H, CH_3Si).

^{13}C NMR (75 MHz, C_6D_6): δ = 168.6 (C1), 116.3 (J_{Sn-C} = 55.8 Hz, C2H), 90.8 (C4H), 77.9 (C3H), 64.0 ($C5H_2$), 30.0 (J_{Sn-C} = 21.7 Hz, 3 CH_2CH_3), 28.2 (J_{Sn-C} = 56.7 Hz, 3 CH_2CH_2Sn), 26.73 [$(CH_3)_3C$], 26.71 [$(CH_3)_3C$], 19.2 [$C(CH_3)_3$], 18.9 [$C(CH_3)_3$], 14.5 (3 CH_3CH_2), 10.6 (J_{Sn-C} = 353.6, 338.0 Hz, 3 CH_2Sn), –3.3 (CH_3Si), –3.4 (CH_3Si), –4.6 (CH_3Si), –4.7 (CH_3Si).

HRMS (ES^+): m/z calcd for $C_{29}H_{62}O_3Si_2SnNa$ $(M + Na)^+$: 657.3152; found: 657.3154.

1,5-Anhydro-2-deoxy-3-*O*-*tert*-butyldimethylsilyl-4,6-*O*-[(*R*)-phenylmethylene]-1-*C*-tributylstannyl-D-*arabino*-hex-1-enitol (15); Typical Procedure 2 (Scheme 8)

To a solution of the sulfoxide (R_S)-**36** (1.42 g, 3.0 mmol) in THF (20.0 mL), at –78 °C was added dropwise a solution of PhLi in Bu_2O (2.0 mL, 1.78 M, 3.6 mmol). The reaction mixture was maintained at –78 °C for 5 min and then Bu_3SnCl (1.27 g, 1.1 mL, 3.9 mmol) was added dropwise. After addition was complete, the mixture was stirred at –78 °C for 2 h whereupon the cooling bath was removed and sat. aq NH_4Cl (5 mL) was added. The organic layer was separated and the aqueous layer extracted with Et_2O (3 × 20 mL). The combined organic layers were dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by column chromatography (SiO_2, hexanes–Et_2O) to give diphenyl sulfoxide (0.59 g, 2.92 mmol) as a colourless oil, which solidified on standing, and the stannane **15** (1.66 g, 2.61 mmol, 87%) as a colourless oil. The ^1H and ^{13}C NMR spectroscopic data were identical to those reported previously.[28]

1,5-Anhydro-2-deoxy-3,4,6-*O*-phenylmethyl-1-*C*-tributylstannyl-D-*lyxo*-hex-1-enitol (38)

Stannane **38** (colourless oil) was synthesised in 85% yield on a 1.0 mmol scale according to typical procedure 2.

$[\alpha]_D{}^{23}$ –42 (c 0.914, $CHCl_3$).

IR (film): 2955m, 2924m, 1602m, 1454m, 1094m, 733m, 696m cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.34–7.24 (15 ArH, m), 4.87 (1 H, d, J = 12.0 Hz, CH_AH_BPh), 4.85 (1 H, d, J = 3.0 Hz, J_{Sn-H} = 27.3, 20.5 Hz, C2H), 4.65 (2 H, s, CH_2Ph), 4.63 (1 H, d, J = 12.4 Hz, CH_AH_BPh), 4.52 (1 H, d, J = 12.0 Hz, CH_AH_BPh), 4.44 (1 H, d, J = 12.0 Hz, CH_AH_BPh), 4.17 (1 H, app dt, J = 6.1, 2.7 Hz, C5H), 4.12 (1 H, t, J = 3.6, C3H), 3.95 (1 H, t, J = 3.6 Hz, C4H), 3.78 (1 H, dd, J = 6.4, 10.3 Hz, $C6H_AH_B$), 3.75 (1 H, dd, J = 6.0, 10.0 Hz, $C6H_AH_B$), 1.54–1.48 (6 H, m, 3 $CH_2CH_2CH_3$), 1.30 (6 H, sextet, J = 7.4 Hz, 3 CH_2CH_3), 0.96–0.92 (6 H, m, 3 CH_2Sn), 0.87 (9 H, t, J = 7.3 Hz, 3 CH_3CH_2).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.5 (C1), 139.3 (C_{Ar}), 138.8 (C_{Ar}), 128.7 (3 $C_{Ar}H$), 128.6 (2 $C_{Ar}H$), 128.1 (2 $C_{Ar}H$), 128.0 (2 $C_{Ar}H$), 127.92 ($C_{Ar}H$), 127.87 (2 $C_{Ar}H$), 127.8 (2 $C_{Ar}H$), 127.7 (2 $C_{Ar}H$), 110.7 (C2H), 76.2 (C5H), 73.8 (CH_2), 73.1 (CH_2), 72.5 (C4H), 71.2 (CH_2), 71.1 (C3H), 69.2 ($C6H_2$), 29.3 (J_{Sn-C} = 20.6 Hz, 3 CH_2CH_3), 27.6 (J_{Sn-C} = 56.0 Hz, 3 $CH_2CH_2CH_3$), 14.1 (3 CH_3CH_2), 10.1 (3 CH_2Sn). Signals for 2 carbons in the aromatic region could not be distinguished.

HRMS (ES^+): m/z calcd for $C_{39}H_{55}O_4Sn$ $(M + H)^+$:707.3117; found: 707.3103.

Anal. Calcd for $C_{39}H_{54}O_4Sn$: C, 66.39; H, 7.71. Found: C, 66.6; H, 7.85.

1,5-Anhydro-2-deoxy-3,4,6-*O*-phenylmethyl-1-*C*-tributylstannyl-D-*arabino*-hex-1-enitol (14)

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

$[\alpha]_D{}^{20}$ –10 (c 1.02, $CHCl_3$).

IR (film): 2955s, 2926s, 1454m, 1072s, 1028m, 734s, 696s cm^{-1}.

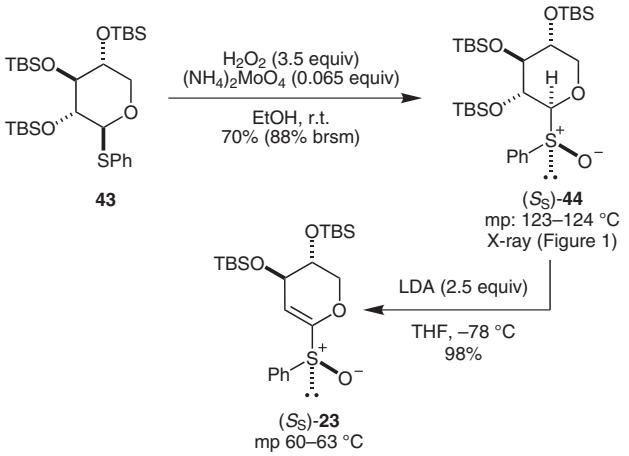
^1H NMR (300 MHz, $CDCl_3$): δ = 7.34–7.27 (15 ArH, m), 4.84 (1 H, d, J = 2.3 Hz, J_{Sn-H} = 28.7, 23.8 Hz, C2H), 4.85 (1 H, d, J = 11.3 Hz, CH_AH_BPh), 4.70 (1 H, d, J = 11.3 Hz, CH_AH_BPh), 4.65 (1 H, d, J = 11.8 Hz, CH_AH_BPh), 4.62 (1 H, d, J = 12.0 Hz, CH_AH_BPh), 4.59 (1 H, d, J = 11.5 Hz, CH_AH_BPh), 4.57 (1 H, d, J = 12.3 Hz, CH_AH_BPh), 4.25–4.22 (1 H, m, C3H), 3.90–3.75 (4 H, m, C4H, C5H, $C6H_2$), 1.58–1.50 (6 H, m, 3 $CH_2CH_2CH_3$), 1.31 (6 H, sextet, J = 7.4 Hz, 3 CH_2CH_3), 0.98–0.93 (6 H, m, 3 CH_2Sn), 0.88 (9 H, t, J = 7.4 Hz, 3 CH_3CH_2).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.3 (C1), 139.1 (C_{Ar}), 139.0 (C_{Ar}), 128.7 (4 $C_{Ar}H$), 128.6 (2 $C_{Ar}H$), 128.3 (2 $C_{Ar}H$), 128.1 (2 $C_{Ar}H$), 128.0 ($C_{Ar}H$), 127.9 ($C_{Ar}H$), 127.8 (2 $C_{Ar}H$), 127.8 ($C_{Ar}H$), 111.3 (C2H), 77.9 (CH), 77.8 (CH), 75.3 (CH), 74.2 (CH_2), 73.8 (CH_2), 70.7 (CH_2), 69.4 ($C6H_2$), 29.3 (J_{Sn-C} = 20.6 Hz, 3 $CH_2CH_2CH_3$), 27.6 (J_{Sn-C} = 44.6 Hz, 3 CH_2CH_3), 14.1 (3 CH_3CH_2), 10.1 (J_{Sn-C} = 84.5 Hz, 3 CH_2Sn). A signal for 1 carbon in the aromatic region could not be distinguished.

HRMS (ES^+): m/z calcd for $C_{39}H_{54}O_4Sn$ $[M^+]$: 729.2936; found: 729.2955.

Anal. Calcd for $C_{39}H_{54}O_4Sn$: C, 66.39; H, 7.71. Found: C, 66.30; H, 7.75.

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



Scheme 10 Synthesis of 1-phenylsulfinyl glycal (S_S)-**23**

1-Deoxy-2,3,4-*tris*-*O*-(*tert*-butyldimethylsilyl)-1-[(S_S)-phenylsulfinyl]-β-D-xylopyranoside (S_S)-44

$(NH_4)_2MoO_4$ (0.25 g, 1.3 mmol, 6.5 mol%) was added to H_2O_2 (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**[21] (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 H_2O (50 mL) was added and the mixture was concentrated in vacuo. The resulting solution was extracted with CH_2Cl_2 (3 × 50 mL). The combined CH_2Cl_2 extracts were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography (SiO_2, hexanes–Et_2O, gradient: 20:1 to 10:1) to give recovered thioether **43** (2.09 g, 3.6 mmol, 18%) and sulfoxide (S_S)-**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).

$[\alpha]_D^{29}$ +32.6 (*c* 1, $CHCl_3$).

IR (diamond compression system): 2953m, 2929m, 2857m, 1256m cm^{-1}.

^1H NMR (500 NMR, $CDCl_3$): 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, C5$H_A$$H_B$), 4.24 (1 H, br s, C1H), 3.86 (1 H, s with fine splitting, C3H), 3.69–3.64 (2 H, m, C4H + C5$H_A$$H_B$), 0.98 [9 H, s, $(CH_3)_3C$], 0.892 [9 H, s, $(CH_3)_3C$], 0.890 [9 H, s, $(CH_3)_3C$], 0.23 (3 H, s, CH_3Si), 0.15 (3 H, s, CH_3Si), 0.14 (3 H, s, CH_3Si), 0.11 (3 H, s, CH_3Si), 0.08 (3 H, s, CH_3Si), 0.07 (3 H, s, CH_3Si).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.2 (C_{Ar}), 131.1 ($C_{Ar}H$), 129.2 (2 $C_{Ar}H$), 124.9 (2 $C_{Ar}H$), 98.1 (C1H), 71.1 (C3H), 69.3 (C4H), 66.7 (C2H), 65.4 (C5H_2), 26.3 [2(*C*H_3)$_3$C], 26.1 [(*C*H_3)$_3$C], 18.6 [*C*(CH$_3$)$_3$], 18.5 [*C*(CH$_3$)$_3$], 18.3 [*C*(CH$_3$)$_3$], –4.15 (CH_3Si), –4.21 (CH_3Si), –4.3 (CH_3Si), –4.38 (CH_3Si), –4.42 (CH_3Si), –4.6 (CH_3Si).

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

Anal. Calcd for $C_{29}H_{56}O_5Si_3S$: C, 57.95; H, 9.39. Found: C, 57.75; H, 9.55.

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

1,2-Dideoxy-3,4-bis(*tert*-butyldimethylsilyl)-1-[(S_S)-phenylsulfinyl]-D-*threo*-pent-1-enopyranose [(S_S)-23]; Typical Procedure 3

To a solution of *i*-Pr_2NH (2.91 g, 4.0 mL, 28.8 mmol, 3.8 equiv) in THF (13 mL) was added *n*-BuLi (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 (S_S)-**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 $NaHCO_3$ (5 mL) was added and the mixture allowed to warm to r.t. The product was extracted with Et_2O (3 × 20 mL) and the combined organic extracts were dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography (SiO_2, hexanes–Et_2O, gradient: 20:1 to 2:1, 0.5% Et_3N) to give the 1-phenylsulfinyl glycal (S_S)-**23** (3.47 g, 7.40 mmol, 98%) as a colourless oil which crystallised on standing; mp 60–63 °C.

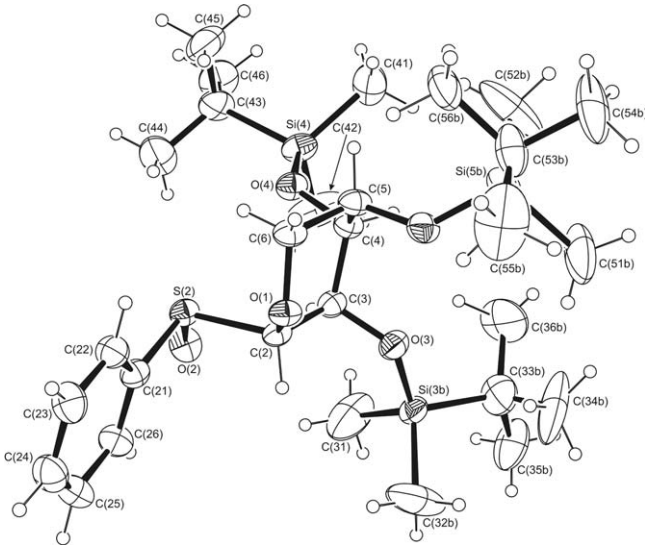


Figure 1 Molecular structure of (S_S)-**44**

$[\alpha]_D^{29}$ –2.5 (c 1.05, $CHCl_3$).

IR (film): 2953m, 2928s, 2856m, 1648m, 1255m cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): 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, C5$H_A$$H_B$), 3.95 (1 H, ddd, *J* = 5.0, 3.0, 1.4 Hz, C3H), 3.90 (1 H, ddd, *J* = 11.0, 3.3, 1.4 Hz, C5$H_A$$H_B$), 3.66 (1 H, tt, *J* = 3.1, 1.4 Hz, C4H), 0.90 [9 H, s, $(CH_3)_3C$], 0.72 [9 H, s, $(CH_3)_3C$], 0.13 (3 H, s, CH_3Si), 0.11 (3 H, s, CH_3Si), 0.00 (3 H, s, CH_3Si), –0.08 (3 H, s, CH_3Si).

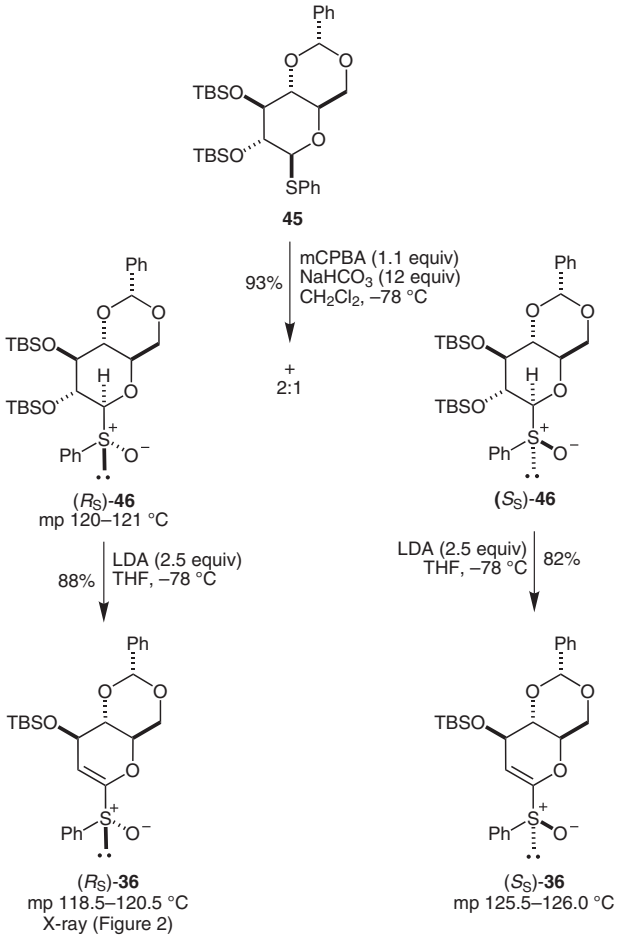
^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.5 (C1), 142.3 (C_{Ar}), 131.9 ($C_{Ar}H$), 129.4 (2 $C_{Ar}H$), 126.4 (2 $C_{Ar}H$), 101.3 (C2H), 69.5 (C4H), 69.0 (C5H_2), 65.5 (C3H), 26.1 [(*C*H_3)$_3$C], 25.8 [(*C*H_3)$_3$C], 18.3 [*C*(CH$_3$)$_3$], 18.0 [*C*(CH$_3$)$_3$], –4.0 (CH_3Si), –4.4 (CH_3Si), –4.5 (CH_3Si), –4.7 (CH_3Si).

HRMS (ES^+): *m*/*z* calcd for $C_{23}H_{40}O_4Si_2SNa$ $(M + Na)^+$: 491.2084; found: 491.2103.

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

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

To a suspension of the thioether **45**[28] (10.7 g, 18.3 mmol) and $NaHCO_3$ (18.4 g, 220 mmol) in CH_2Cl_2 (400 mL) at –78 °C was added dropwise a solution of mCPBA (3.8 g, 70%, 20.1 mmol) in CH_2Cl_2 (100 mL) and the mixture was stirred at –78 °C for 4 h. The cooling bath was removed and sat. aq solutions of $Na_2S_2O_3$ (100 mL) and $NaHCO_3$ (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 CH_2Cl_2 (3 × 50 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated in vacuo. ^1H NMR spectroscopic analysis of the crude



Scheme 11 Synthesis of 1-phenylsulfinyl glycal (R_S)-**36**

product revealed two epimeric sulfoxides (2:1) according to integration of the signals for the benzylidene acetal proton at δ = 5.44 for (R_S)-**46** and δ = 5.57 for (S_S)-**46**. The mixture was separated by column chromatography (SiO_2, hexanes–Et_2O, 20:1, 10:1, 5:1, 2:1) to give (S_S)-**46** (3.86 g, 6.4 mmol, 35%) and (R_S)-**46** (6.43 g, 10.6 mmol, 58%).

(R_S)-46 (Major Epimer)

White solid; mp 120–121 °C (hexanes); $[\alpha]_D^{24}$ –117 (*c* 1.00, $CHCl_3$).

IR (diamond compression system): 2928s, 1582w, 1473s, 1254s, 975s, 933s, 748s, 692s, 564s cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.69–7.68 (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* = 10.7, 5.1 Hz, C6$H_A$$H_B$), 4.07 (1 H, d, *J* = 6.0 Hz, C1H), 3.98 (1 H, t, *J* = 5.1 Hz, C2H), 3.89 (1 H, dd, *J* = 8.1, 5.1 Hz, C3H), 3.79 (1 H, t, *J* = 10.3 Hz, C6$H_A$$H_B$), 3.76 (1 H, dd, *J* = 9.8, 8.1 Hz, C4H), 3.65 (1 H, dt, *J* = 9.8, 5.1 Hz, C5H), 0.90 [9 H, s, $(CH_3)_3C$], 0.85 [9 H, s, $(CH_3)_3C$], 0.10 (3 H, s, CH_3Si), 0.06 (3 H, s, CH_3Si), 0.042 (3 H, s, CH_3Si), 0.037 (3 H, s, CH_3Si).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.5 (C_{Ar}), 137.3 (C_{Ar}), 131.7 ($C_{Ar}H$), 129.5 ($C_{Ar}H$), 129.3 (2 $C_{Ar}H$), 128.5 (2 $C_{Ar}H$), 126.8 (2 $C_{Ar}H$), 125.7 (2 $C_{Ar}H$), 102.5 (CHPh), 97.5 (C1H), 81.8 (C4H), 77.2 (C3H), 72.5 (C2H), 69.1 ($C6H_2$), 68.4 (C5H), 26.6 [(CH_3)$_3$C], 26.3 [(CH_3)$_3$C], 18.8 [$C(CH_3)$], 18.5 [$C(CH_3)$], –2.7 (CH_3Si), –3.1 (CH_3Si), –3.2 (CH_3Si), –4.2 (CH_3Si).

HRMS (ES$^+$): *m*/*z* calcd for $C_{31}H_{49}O_6SSi_2$ (M + H)$^+$: 605.2788.; found: 605.2770.

Anal. Calcd for $C_{31}H_{48}O_6SSi_2$: C, 61.55; S, 5.30; H, 8.00. Found: C, 61.5; H, 8.05.

(S_S)-46 (Minor Epimer)

Colourless oil; $[\alpha]_D^{24}$ +0.2 (*c* 1.00, $CHCl_3$).

IR (film): 3034m, 2927s, 2857s, 1471m, 1375s, 1249m, 1082s, 1039s, 1006s cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.72–7.68 (2 ArH, m), 7.54–7.52 (3 ArH, m), 7.51–7.49 (2 ArH, m), 7.41–7.37 (3 ArH, m), 5.57 (1 H, s, CHPh), 4.54 (1 H, t, *J* = 1.3 Hz, C2H), 4.30 (1 H, dt, *J* = 10.3, 5.1 Hz, C6$H_A$$H_B$), 4.28 (1 H, t, *J* = 1.7 Hz, C1H), 4.12 (1 H, dt, *J* = 10.3, 5.1 Hz, C5H), 3.99 (1 H, dt, *J* = 5.6, 1.3 Hz, C3H), 3.95 (1 H, dd, *J* = 10.3, 5.6 Hz, C4H), 3.58 (1 H, t, *J* = 10.3 Hz, C6$H_A$$H_B$), 1.57 [9 H, s, $(CH_3)_3C$], 0.89 [9 H, s, $(CH_3)_3C$], 0.172 (3 H, s, CH_3Si), 0.170 (3 H, s, CH_3Si), 0.16 (3 H, s, CH_3Si), 0.13 (3 H, s, CH_3Si).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.1 (C_{Ar}), 137.5 (C_{Ar}), 131.7 ($C_{Ar}H$), 129.3 ($C_{Ar}H$), 129.2 (2 $C_{Ar}H$), 128.6 (2 $C_{Ar}H$), 126.3 (2 $C_{Ar}H$), 125.7 (2 $C_{Ar}H$), 101.7 (*C*HPh), 96.7 (C1H), 84.4 (C4H), 75.5 (C3H), 73.3 (C2H), 70.0 ($C6H_2$), 64.0 (C5H), 26.01 [(CH_3)$_3$C], 25.98 [(CH_3)$_3$C], 18.3 [$C(CH_3)$], 18.2 [$C(CH_3)$], –3.9 (CH_3Si), –4.30 (CH_3Si), –4.33 (CH_3Si), –4.8 (CH_3Si).

HRMS (ES$^+$): *m*/*z* calcd for $C_{31}H_{49}O_6SSi_2$ (M + H)$^+$: 605.2706; found: 605.2766.

Anal. Calcd for $C_{31}H_{48}O_6SSi_2$: C, 61.55; H, 8.00. Found: C, 61.80; H, 8.10.

1,5-Anhydro-2-deoxy-4,6-*O*-[(*R*)-phenylmethylene]-3-*O*-*tert*-butyldimethylsilyl-1-[(R_S)-phenylsulfinyl]-D-*arabino*-hex-1-enitol [(R_S)-36] and its Epimer (S_S)-36

Treatment of sulfoxide (R_S)-**46** (9.85 g, 16.3 mmol) with LDA (2.4 equiv) according to typical procedure 3 gave 1-phenylsulfinyl glycal (R_S)-**36** (6.78 g, 14.3 mmol, 88%) as a white solid; mp 118.5–120.5 °C (hexanes–Et_2O).

$[\alpha]_D^{20}$ –137 (*c* 1.00, $CHCl_3$).

IR (diamond compression system): 3061s, 2927s, 2856s, 1632s, 1473s, 1378s, 1170s, 977s, 700s cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.71–7.69 (2 ArH, m), 7.53–7.52 (3 ArH, m), 7.45–7.44 (2 ArH, m) 7.36–7.35 (3 ArH, m), 5.62 (1 H, d, *J* = 2.1 Hz, C2H), 5.51 (1 H, s, CHPh), 4.62 (1 H, dd, *J* = 7.3, 2.1 Hz, C3H), 4.29 (1 H, dd, *J* = 10.3, 5.1 Hz, C6$H_A$$H_B$), 3.99 (1 H, dt, *J* = 10.3, 5.6 Hz, C5H), 3.75 (1 H, dd, *J* = 10.3, 7.7 Hz, C4H), 3.71 (1 H, t, *J* = 10.3 Hz, C6$H_A$$H_B$), 0.89 [9 H, s, $(CH_3)_3C$], 0.11 (3 H, s, CH_3Si), 0.08 (3 H, s, CH_3Si).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.9 (C1), 141.6 (C_{Ar}), 137.2 (C_{Ar}), 132.0 ($C_{Ar}H$), 129.5 (2 $C_{Ar}H$), 129.3 ($C_{Ar}H$), 128.5 (2 $C_{Ar}H$), 126.2 (2 $C_{Ar}H$), 125.7 (2 $C_{Ar}H$), 107.1 (C2H), 101.7 (CHPh), 80.2 (C4H), 71.9 (C5H), 68.0 ($C6H_2$), 67.9 (C3H), 26.0 [(CH_3)$_2$C], 18.5 [$C(CH_3)$], –4.2 (CH_3Si), –4.5 (CH_3Si).

HRMS (ES$^+$): *m*/*z* calcd for $C_{25}H_{33}O_5SSi$ (M + H)$^+$: 473.1818; found: 473.1797.

Anal. Calcd for $C_{25}H_{32}O_5SSi$: C, 63.53; H, 6.82. Found: C, 63.80; H, 7.05.

(S_S)-36

An analogous procedure was used to obtain (S_S)-**36** in 82–84% yield from sulfoxide (S_S)-**46**. (S_S)-**36** was obtained as a white solid; mp 125.5–126.0 °C (hexanes–Et_2O).

$[\alpha]_D^{25}$ +6 (*c* 1.00, $CHCl_3$).

IR (diamond compression system): 3065m, 2926s, 2854s, 1639s, 1376s, 1258s, 1085s, 837s, 746s, 692s cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 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, C2H), 5.54 (1 H, s, CHPh), 4.59 (1 H, dd, *J* = 7.4, 2.3 Hz, C3H), 4.30 (1 H, dd, *J* = 10.5, 5.1 Hz, C6$H_A$$H_B$), 3.86 (1 H, dt, *J* = 10.1, 5.0 Hz, C5H), 3.78 (1 H, dd, *J* = 10.0, 7.3 Hz, C4H), 3.75

(1 H, t, J = 10.3 Hz, C6H$_A$$H_B$), 0.90 [9 H, s, $(CH_3)_3C$], 0.12 (3 H, s, CH_3Si), 0.09 (3 H, s, CH_3Si).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.2 (C1), 141.7 (C_{Ar}), 137.0 (C_{Ar}), 131.7 ($C_{Ar}H$), 129.3 (2 $C_{Ar}H$), 129.2 ($C_{Ar}H$), 128.3 (2 $C_{Ar}H$), 126.1 (2 $C_{Ar}H$), 125.1 (2 $C_{Ar}H$), 107.0 (C2H), 101.6 (*C*HPh), 80.0 (C4H), 71.1 (C5H), 67.9 (C6H_2), 67.9 (C3H), 25.9 [$(CH_3)_2C$], 18.3 [$C(CH_3)$], –4.3 (CH_3Si), –4.7 (CH_3Si).

HRMS (ES$^+$): *m*/*z* calcd for $C_{25}H_{32}O_5SSiNa$ (M + Na)$^+$: 495.1632; found: 495.1636.

Anal. Calcd for $C_{25}H_{32}O_5SSi$: C, 63.53; H, 6.82. Found: C, 63.50; H, 6.85.

The structure and stereochemistry of (R_S)-**36** was established by X-ray crystallography (Figure 2).

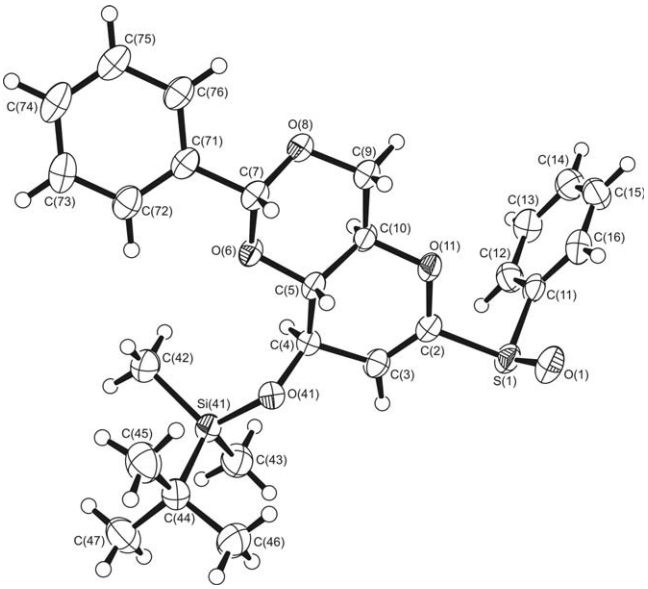


Figure 2 Molecular structure of (R_S)-**36**

1-Phenylsulfinyl Glycal (S_S)-25 (Scheme 12)

1-Deoxy-2,3:4,6-di-*O*-isopropylidene-1-[(S_S)-phenylsulfinyl]-β-D-galactopyranoside [(S_S)-48] and its Epimer (R_S)-48

Oxidation of thioether **47**[41] (7.08 g, 20.0 mmol) according to typical procedure 4 gave a mixture of two diastereoisomeric sulfoxides (S_S)-**48** and (R_S)-**48** in the ratio 4.5:1 according to integration of the ^{1}H NMR signals for C1H at δ = 4.53 for (S_S)-**48** and δ = 4.42 for (R_S)-**48**. The products were separated by column chromatography (SiO_2, hexanes–EtOAc with 0.5% of Et_3N) to give the less polar minor sulfoxide (R_S)-**48** (1.04 g, 2.8 mmol, 14%) followed by a 3.9:1 mixture of (S_S)-**48** and (R_S)-**48** (1.03 g, 2.8 mmol, 14%), and finally the more polar major sulfoxide (S_S)-**48** (4.84 g, 13.1 mmol, 66%). The total yield of both epimers was 94%.

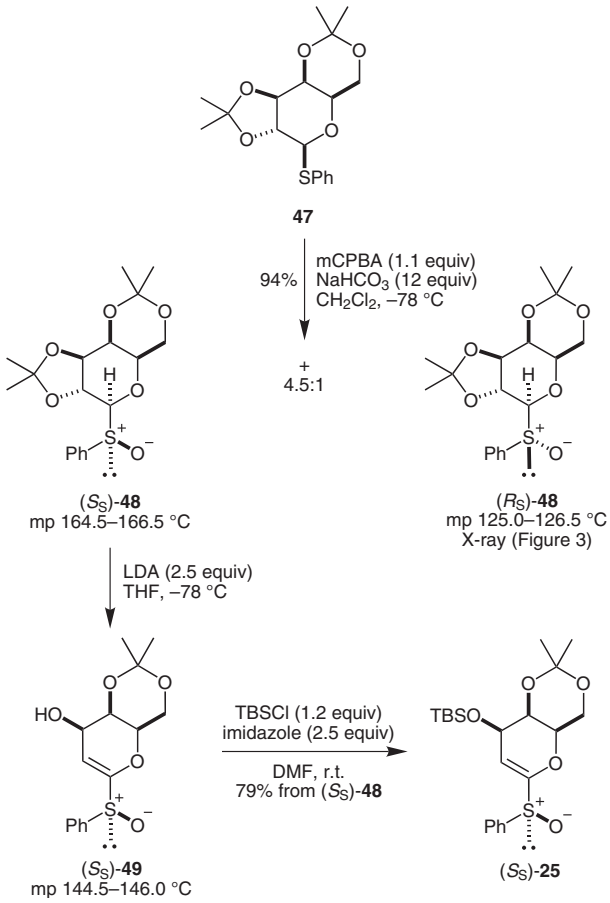
(S_S)-48 (Major Epimer)

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

$[\alpha]_D^{21}$ +5 (*c* 1.00, $CHCl_3$).

IR (diamond compression system): 3063m, 2989s, 2923s, 1478s, 1441s, 1381s, 1322m, 1308m, 1212s cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): 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, C6H_AH$_B$), 3.95 (1 H, dd, J = 13.1, 1.3 Hz, C6H$_A$$H_B$), 3.84 (1 H, t, J = 9.4 Hz, C2H), 3.59 (1 H, dd, J = 9.2, 2.6 Hz, C3H), 3.32 (1 H, q, J = 1.7 Hz, C5H), 1.46 (3 H, s, CH_3), 1.45 (3 H, s, CH_3), 1.40 (3 H, s, CH_3), 1.19 (3 H, s, CH_3).



Scheme 12 Synthesis of 1-phenylsulfinyl glycal (S_S)-**25**

^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.1 (C_{Ar}), 132.0 ($C_{Ar}H$), 128.8 (2 $C_{Ar}H$), 126.7 (2 $C_{Ar}H$), 112.2 [$C(CH_3)_2$], 98.7 [$C(CH_3)_2$], 92.7 (C1H), 79.7 (C3H), 70.7 (C5H), 69.9 (C2H), 66.4 (C4H), 62.8 (C6H_2), 28.7 (*C*H$_3$C), 26.9 (*C*H$_3$C), 26.7 (*C*H$_3$C), 18.9 (*C*H$_3$C).

Anal. Calcd for $C_{18}H_{24}O_6S$: C, 58.68; H, 6.57. Found: C, 58.6; H, 6.75.

(R_S)-48 (Minor Epimer)

White solid; mp 125.0–126.5 °C (hexane–EtOAc).

$[\alpha]_D^{31}$ –92 (*c* 1.36, $CHCl_3$).

IR (diamond compression system): 2990m, 2934m, 1443m, 1382m, 1279m, 1243s, 1224s, 1150s, 1072s cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): 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, C6H_AH$_B$), 3.90 (1 H, dd, J = 13.1, 1.5 Hz, C6H$_A$$H_B$), 3.78 (1 H, t, J = 9.4 Hz, C2H), 3.55 (1 H, dd, J = 9.3, 2.7 Hz, C3H), 3.34 (1 H, q, J = 1.7 Hz, C5H), 1.39 (3 H, s, CH_3), 1.38 (3 H, s, CH_3), 1.31 (3 H, s, CH_3), 1.29 (3 H, s, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.0 (C_{Ar}), 131.8 ($C_{Ar}H$), 128.9 (2 $C_{Ar}H$), 126.2 (2 $C_{Ar}H$), 112.0 [$C(CH_3)_2$], 98.8 [$C(CH_3)_2$], 92.2 (C1H), 79.4 (C3H), 70.7 (C5H), 68.4 (C2H), 66.4 (C4H), 62.8 (C6H_2), 29.0 (*C*H$_3$C), 26.8 (*C*H$_3$C), 26.4 (*C*H$_3$C), 18.8 (*C*H$_3$C).

The structure and stereochemistry of (R_S)-**48** was established by X-ray crystallography (Figure 3).

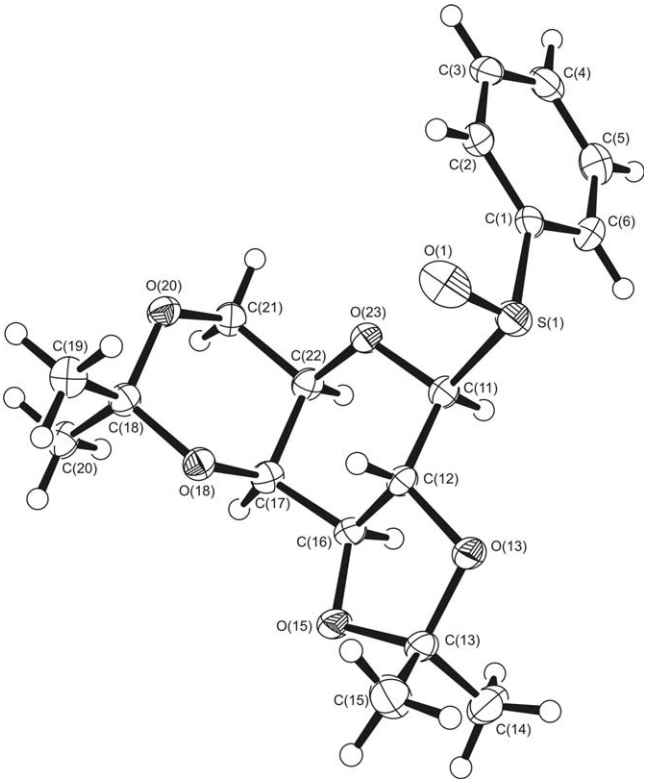


Figure 3 Molecular structure of (R_S)-**48**

1,5-Anhydro-4,6-*O*-isopropylidene-1-[(S_S)-phenylsulfinyl]-D-*lyxo*-hex-1-enitol [(S_S)-49]

Treatment of sulfoxide (S_S)-**48** (1.84 g, 5.0 mmol) with LDA (2.0 equiv) according to typcical procedure 3 gave the 1-phenylsulfinyl glycal (S_S)-**49** (1.22 g) as a pale yellow solid. The crude product was used in the next step without further purification. An analytical sample was obtained by recrystallisation from EtOAc; mp 144.5–146.0 °C.

$[\alpha]_D^{21}$ –23 (*c* 1.00, $CHCl_3$).

IR (diamond compression system): 3500s, 3066m, 2997s, 2938s, 2868m, 1693s, 1478m, 1447m, 1412s, 1381s, 1354m, 1267m, 1236s, 1176s, 1145m, 1112s, 1083s, 1038s, 997m, 959m, 922m, 851m, 813m cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.71–7.67 (2 ArH, m), 7.47–7.43 (3 ArH, m), 5.61 (1 H, t, *J* = 1.7 Hz, C2H), 4.46 (1 H, ddd, *J* = 10.8, 4.7, 1.6 Hz, C3H), 4.14 (1 H, poorly resolved ddd, *J* = 4.9, 1.5, 1.3 Hz, C4H), 3.94 (1 H, dd, *J* = 13.0, 1.6 Hz, C6H_AH$_B$), 3.89 (1 H, dd, *J* = 13.0, 1.9 Hz, C6H$_A$$H_B$), 3.82 (1 H, q, *J* = 1.7 Hz, C5H), 2.74 (1 H, d, *J* = 11.1 Hz, OH), 1.41 (3 H, s, CH_3), 1.19 (3 H, s, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.41 (C1), 141.55 (C_{Ar}), 131.08 (C_{Ar}H), 128.85 (2 C_{Ar}H), 124.89 (2 C_{Ar}H), 104.09 (C2H), 99.16 [$C(CH_3)_2$], 70.60 (C5H), 64.33 (C4H), 63.52 (C3H), 62.09 (C6H), 28.76 (CH_3C), 18.47 (CH_3C).

Anal. Calcd for $C_{15}H_{18}O_5S$: C, 58.05; H, 5.85. Found: C, 57.85; H, 5.95.

1,5-Anhydro-3-*O*-*tert*-butyldimethylsilyl-4,6-*O*-isopropylidene-1-[(S_S)-phenylsulfinyl]-D-*lyxo*-hex-1-enitol [(S_S)-25]

1-Phenylsulfinyl glycal (S_S)-**49** (1.05 g, 3.4 mmol), TBSCl (0.62 g, 4.08 mmol) and imidazole (0.58 g, 8.5 mmol) were dissolved in DMF (23 mL). After stirring at r.t. for 12 h, H_2O (250 mL) was added. The phases were separated and the aqueous layer was extracted with Et_2O (3 × 50 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by column chromatography (SiO_2, hexanes–Et_2O) to give the TBS-protected 1-phenylsulfinyl glycal (S_S)-**25** (1.15 g, 2.7 mmol, 79%) as a colourless, viscous oil.

$[\alpha]_D^{26}$ –10 (*c* 1.00, $CHCl_3$).

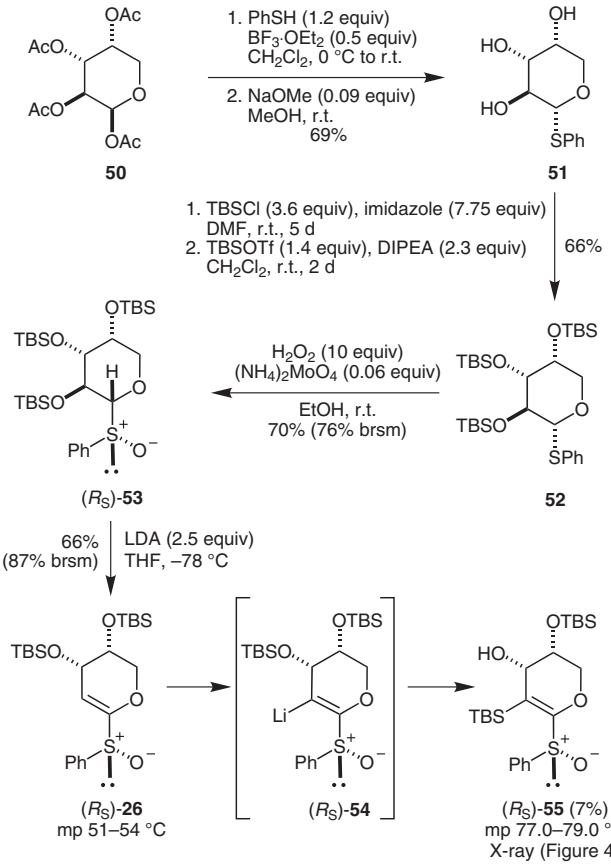
IR (diamond compression system): 3061m, 2992s, 2929s, 2894s, 2857s, 1655s, 1473s, 1463s, 1444s, 1382s, 1361m, 1342m, 1311m, 1261s, 1183s, 1131s, 1090s, 1051s, 1023m, 1006m, 961s, 929s, 881s, 837s, 803s, 778s, 749s, 688s, 666m, 596m, 562m, 538m, 516m, 480m cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): 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 ddd, *J* = 4.5, 1.5, 1.3 Hz, C4H), 3.94 (1 H, dd, *J* = 12.9, 1.7 Hz, C6H_AH$_B$), 3.87 (1 H, dd, *J* = 12.9, 1.9 Hz, C6H$_A$$H_B$), 3.80–3.82 (1 H, m, C5H), 1.40 (3 H, s, CH_3), 1.25 (3 H, s, CH_3), 0.89 [9 H, s, $(CH_3)_3$C], 0.09 (3 H, s, CH_3Si), 0.09 (3 H, s, CH_3Si).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.0 (C1), 142.1 (C_{Ar}), 131.4 (C_{Ar}H), 129.2 (2 C_{Ar}H), 125.5 (2 C_{Ar}H), 105.6 (C2H), 99.3 [$C(CH_3)_2$], 71.4 (C5H), 66.1 (C3H), 65.7 (C4H), 62.8 (C6H), 29.3 (CH_3C), 26.1 [$(CH_3)_3$C]), 18.8 (CH_3C), 18.6 [$(CH_3)_3C$], –4.0 (CH_3Si), –4.1 (CH_3Si).

HRMS (ES$^+$): *m*/*z* calcd for $C_{21}H_{32}O_5SNa$ (M + Na)$^+$: 447.1632; found: 447.1614.

1-Phenylsulfinyl Glycal (R_S)-26 (Scheme 13)



Scheme 13 Synthesis of 1-Phenylsulfinyl Glycal (R_S)-**26**

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

Thiophenol (8.7 mL, 84.3 mmol) and then BF_3·OEt_2 (4.5 mL, 35.1 mmol) were added to a solution of tetra-*O*-acetyl-α-D-arabinopyranose **50**[42] (22.35 g, 70.2 mmol) in CH_2Cl_2 (75 mL) at 0 °C. After 2.5 h at r.t., the reaction mixture was diluted with CH_2Cl_2 (75 mL) and

the mixture washed with sat. aq $NaHCO_3$ (2 × 150 mL), sat. aq. NaOH (2 × 50 mL) and H_2O (2 × 150 mL). The organic layer was dried (Na_2SO_4) 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 (SiO_2, 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. $[\alpha]_D^{21}$ +10.2 (*c* 0.41, $CHCl_3$) {Lit.[43] (for L-enantiomer) $[\alpha]_D^{23}$ –12.6 (*c* 0.4, $CHCl_3$)}. The ^{1}H NMR spectrum of triol **51** recorded at 500 MHz was consistent with the data reported in the literature.[43]

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

Imidazole (10.2 g, 0.155 mol) and TBSCl (10.85 g, 72 mmol) were added to a solution of the triol **51** (4.85 g, 20.0 mmol) in DMF (50 mL) at r.t. After stirring for 5 d, the reaction mixture was poured into H_2O (300 mL) and the aqueous phase extracted with Et_2O (3 × 250 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by column chromatography (SiO_2, petroleum ether–Et_2O, 20:1) to yield a mixture of di- and tri-protected compound (6.06 g). The mixture was dissolved in CH_2Cl_2 (30 mL). DIPEA (8.0 mL, 46.0 mmol) was added, followed by the dropwise addition of TBSOTf (6.4 mL, 28 mmol). After 2 d at r.t., the mixture was washed with aq 5% HCl (2 × 55 mL) and H_2O (2 × 55 mL), and the aqueous layers were combined and extracted with CH_2Cl_2 (3 × 35 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by column chromatography (SiO_2, hexanes–Et_2O) to give the title compound **52** (7.71 g, 13.2 mmol, 66%, 2 steps) as a colourless oil.

$[\alpha]_D^{21}$ +104.0 (*c* 0.54, $CHCl_3$).

IR (film): 2953s, 2930s, 2858s, 1256s cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.46 (2 ArH, d with fine splitting, *J* = 7.0 Hz), 7.26 (2 ArH, t with fine splitting, *J* = 7.5, 2 Hz), 7.19 (1 ArH, tt, *J* = 7.3, 1.2 Hz), 5.12 (1 H, br s, C1H), 4.29 (1 H, t, *J* = 10.7 Hz, C5$H_A$$H_B$), 4.15 (1 H, ddd, *J* = 10.6, 4.5, 2.5 Hz, C4H), 4.04 (1 H, d, *J* = 3.7 Hz, C2H), 3.81 (1 H, t, *J* = 3.0 Hz, C3H), 3.39 (1 H, dd, *J* = 10.4, 4.6 Hz, C5$H_A$$H_B$), 0.99 [9 H, s, $(CH_3)_3C$], 0.91 [9 H, s, $(CH_3)_3C$], 0.89 [9 H, s, $(CH_3)_3C$], 0.15 (3 H, s, CH_3Si), 0.13 (3 H, s, CH_3Si), 0.09 (9 H, s, 3 CH_3Si), 0.07 (3 H, s, CH_3Si).

^{13}C NMR (75MHz, $CDCl_3$): δ = 138.8 (C_{Ar}), 130.6 (2 C_{Ar}H), 129.1 (2 C_{Ar}H), 126.7 (C_{Ar}H), 88.3 (C1H), 75.5 (C2H), 73.3 (C3H), 66.9 (C4H), 59.9 (C5H_2), 26.5 [$(CH_3)_3C$], 26.4 [$(CH_3)_3C$], 26.1 [$(CH_3)_3C$], 18.8 [2 × $C(CH_3)_3$], 18.3 [$C(CH_3)_3$], –4.0 (CH_3Si), –4.1 (CH_3Si), –4.2 (CH_3Si), –4.4 (2 CH_3Si), –4.6 (CH_3Si).

HRMS (ES$^+$): *m*/*z* calcd for $C_{29}H_{56}O_4Si_3SNa$ (M + Na)$^+$: 607.3099; found: 607.3079.

1-Deoxy-2,3,4-tri-*O*-*tert*-butyldimethylsilyl-1-[(R_S)-phenylsulfinyl]-α-D-arabinopyranoside [(R_S)-53]

Ammonium molybdate (26 mg, 0.132 mmol) was added to 30% H_2O_2 (0.80 g, 22 mmol) at 0 °C. The resulting yellow solution was then added to a solution of the thioether **52** (1.29 g, 2.20 mmol) in EtOH (20 mL). The reaction was stirred at r.t. for 20 h. H_2O (25 mL) was added and the resulting solution extracted with CH_2Cl_2 (3 × 25 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by column chromatography (SiO_2, hexanes–Et_2O) to give recovered thioether (80 mg, 0.13 mmol, 6%) and the title sulfoxide (R_S)-**53** (0.94 g, 1.56 mmol, 70% or 76% based on recovered thioether **52**) as a colourless oil.

$[\alpha]_D^{24}$ –12.1 (*c* 0.70, $CHCl_3$).

IR (film): 2954m, 2930m, 2858m cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): 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, C5$H_A$$H_B$), 3.98–3.94 (2 H, m, C1H and C3H), 3.50 (1 H, ddd, *J* = 10.0, 4.7, 0.6 Hz, C5$H_A$$H_B$), 1.00 [9 H, s, $(CH_3)_3C$], 0.91 [9 H, s, $(CH_3)_3C$], 0.87 [9 H, s, $(CH_3)_3C$], 0.23 (3 H, s, CH_3Si), 0.17 (3 H, s, CH_3Si), 0.14 (3 H, s, CH_3Si), 0.10 (3 H, s, CH_3Si), 0.09 (3 H, s, CH_3Si), 0.08 (3 H, s, CH_3Si).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.2 (C_{Ar}), 131.2 (C_{Ar}H), 129.2 (2 C_{Ar}H), 124.9 (2 C_{Ar}H), 97.1 (C1H), 73.0 (C3H), 69.1 (C4H), 65.6 (C2H), 63.7 (C5H_2), 26.4 [$(CH_3)_3C$], 26.2 [$(CH_3)_3C$], 26.0 [$(CH_3)_3C$], 18.7 [$C(CH_3)_3$], 18.7 [$C(CH_3)_3$], 18.2 [$C(CH_3)_3$], –4.2 (2 CH_3Si), –4.3 (CH_3Si), –4.6 (2 CH_3Si), –4.7 (CH_3Si).

HRMS (ES$^+$): *m*/*z* calcd for $C_{29}H_{57}O_5Si_3S$ (M + H)$^+$: 601.3239; found: 601.3235.

1,5-Anhydro-2-deoxy-3,4-di-*O*-*tert*-butyldimethylsilyl-1-[(R_S)-phenylsulfinyl]-D-*erythro*-pent-1-enitol [(R_S)-26]

Reaction of sulfoxide (R_S)-**53** (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 (SiO_2, hexanes–Et_2O) to give the recovered starting material (R_S)-**53** (1.10 g, 1.83 mmol, 21%) followed by the 1-phenylsulfinyl glycal (R_S)-**26** (2.745 g, 5.8 mmol, 66% or 87% based on recovered starting material) as a colourless oil which solidified on standing; mp 51–54 °C.

$[\alpha]_D^{21}$ +110 (*c* 1.1, $CHCl_3$).

IR (diamond compression system): 3057s, 2929s, 2857s, 1645s, 1471s, 1253s cm^{-1}.

^{1}H NMR (500 MHz, $CHCl_3$): 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 with fine splitting, *J* = 9.8 Hz, C5$H_A$$H_B$), 3.87–3.80 (2 H, m, C4H and C5$H_A$$H_B$), 0.89 [9 H, s, $(CH_3)_3C$], 0.82 [9 H, s, $(CH_3)_3C$], 0.11 (3 H, s, CH_3Si), 0.09 (3 H, s, CH_3Si), 0.04 (3 H, s, CH_3Si), 0.00 (3 H, s, CH_3Si).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.8 (C1), 141.7 (C_{Ar}), 131.5 (C_{Ar}H), 129.3 (2 C_{Ar}H), 125.3 (2 C_{Ar}H), 105.9 (C2H), 68.4 (C5H_2), 67.7 (C4H), 64.6 (C3H), 26.1 [$(CH_3)_3C$], 26.1 [$(CH_3)_3C$], 18.5 [$C(CH_3)_3$], 18.4 [$C(CH_3)_3$], –4.0 (CH_3Si), –4.1 (CH_3Si), –4.2 (CH_3Si), –4.6 (CH_3Si).

HRMS (ES$^+$): *m*/*z* calcd for $C_{23}H_{40}O_4{}^{28}Si_2{}^{32}SNa$ (M + Na)$^+$: 491.2078; found: 491.2084.

(R_S)-55

The last component to elute was 1,5-anhydro-2-deoxy-3-*tert*-butyldimethylsilyl-4-*O*-*tert*-butyldimethylsilyl-1-[(R_S)-phenylsulfinyl]-D-*erythro*-pent-1-enitol [(R_S)-**55**] (0.27 g, 0.58 mmol, 7%); colourless solid; mp 77–79 °C (hexane).

$[\alpha]_D^{25}$ +158 (*c* 1.52, $CHCl_3$).

IR (diamond compression system): 3306brm, 2927m, 2159s, 2027s, 1972s, 1586m, 1471m cm^{-1}.

^{1}H NMR (500 MHz, $CHCl_3$): 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, C5$H_A$$H_B$), 3.76 (1 H, t, *J* = 10.0 Hz, C5$H_A$$H_B$), 2.54 (1 H, br s, OH), 1.03 [9 H, s, $(CH_3)_3C$], 0.86 [9 H, s, $(CH_3)_3C$], 0.39 (3 H, s, CH_3Si), 0.38 (3 H, s, CH_3Si), 0.08 (3 H, s, CH_3Si), 0.03 (3 H, s, CH_3Si).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.5 (C1), 141.3 (C_{Ar}), 130.8 (C_{Ar}H), 129.2 (2 C_{Ar}H), 125.3 (2 C_{Ar}H), 115.2 (C2), 66.6 (CH), 66.4 (CH), 66.1 (C5H_2), 27.4 [$(CH_3)_3C$], 25.9 [$(CH_3)_3C$], 18.6 [$(CCH_3)_3$], 18.2 [$CCH_3)_3$], –1.0 (CH_3Si), –4.0 (CH_3Si), –4.5 (CH_3Si), –4.7 (CH_3Si).

HRMS (ES$^+$): *m*/*z* calcd for $C_{23}H_{40}O_4{}^{28}Si_2{}^{32}SNa$ (M + Na)$^+$: 491.2078; found: 491.2078.

The structure and stereochemistry of (R_S)-**55** was established by X-ray crystallography (Figure 4).

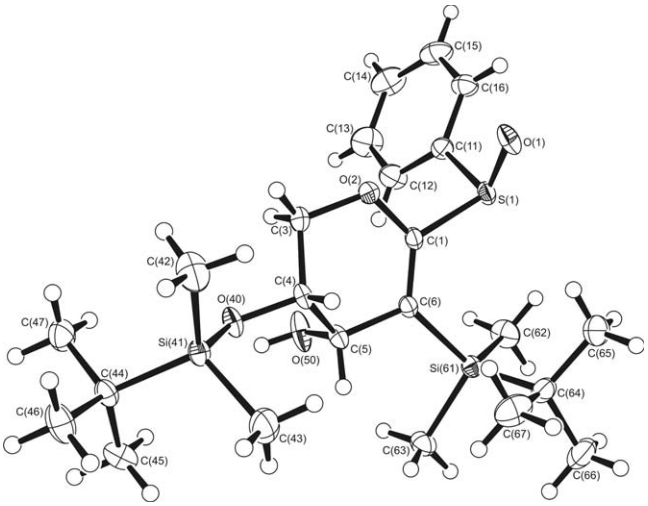
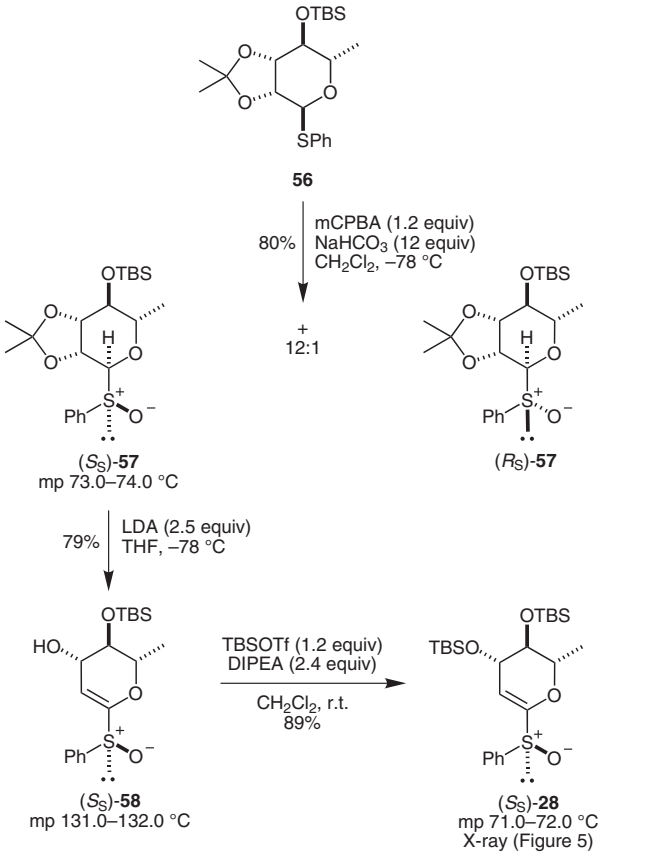


Figure 4 Molecular structure of (R_S)-**55**

When the elimination reaction was carried out according to typical procedure 3 starting from the sulfoxide (R_S)-**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_S)-**26** (0.30 g, 0.64 mmol) was obtained in 40% yield along with sulfoxide (R_S)-**55** (0.29 g, 0.61 mmol) in 38% yield.

1-Phenylsulfinyl Glycal (S_S)-28 (Scheme 14)



Scheme 14 Synthesis of 1-phenylsulfinyl glycal (S_S)-**28**

1,6-Dideoxy-2,3-*O*-isopropylidene-4-*O*-*tert*-butyldimethylsilyl-1-[(S_S)-phenylsulfinyl]-α-L-mannopyranose [(S_S)-57] and its Epimer (R_S)-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_2Cl_2 (70 mL) at –78 °C for 2 h according to typical procedure 4 gave a mixture of two diastereoisomeric sulfoxides (S_S)-**57** (less polar, major) and (R_S)-**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 (S_S)-**57** and 4.23 ppm for (R_S)-**57**. The crude mixture was separated by column chromatography (SiO_2, hexanes–Et_2O) to give first the less polar major sulfoxide (S_S)-**57** (1.20 g, 2.8 mmol, 70%), then a mixture of (S_S)-**57** and (R_S)-**57** (1:1.3, 0.159 g, 0.37 mmol, 9%) and finally the pure minor sulfoxide (R_S)-**57** (0.023 g, 0.053 mmol, 1%).

(S_S)-57 (Major Epimer)

Mp 73–74 °C (MeOH–H_2O); $[\alpha]_D^{21}$ +55 (*c* 1.00, $CHCl_3$).

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

^{1}H NMR (500 MHz, $CHCl_3$): δ = 7.68–7.63 (2 ArH, m), 7.58–7.51 (3 ArH, m), 4.75 (1 H, s, C1H), 4.74 (1 H, d, *J* = 5.8 Hz, C2H), 4.19 (1 H, dd, *J* = 7.2, 6.1 Hz, C3H), 3.84 (1 H, dq, *J* = 9.6, 6.2 Hz, C5H), 3.38 (1 H, dd, *J* = 9.4, 7.3 Hz, C4H), 1.49 (3 H, s, CH_3C), 1.34 (3 H, s, CH_3C), 1.25 (3 H, d, *J* = 6.2 Hz, CH_3CH), 0.91 [9 H, s, $(CH_3)_3$C], 0.17 (3 H, s, CH_3Si), 0.10 (3 H, s, CH_3Si).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.1 (C_{Ar}), 131.9 (C_{Ar}H), 129.6 (2 C_{Ar}H), 124.9 (2 C_{Ar}H), 109.2 [*C*$(CH_3)_2$], 96.5 (C1H), 79.0 (C3H), 75.4 (C4H), 73.4 (C5H), 71.4 (C2H), 28.4 (*C*H_3C), 26.6 (*C*H_3C), 26.2 [(*C*$H_3)_3$C], 18.5 [*C*$(CH_3)_3$], 18.2 (CH_3CH), –3.6 (CH_3Si), –4.6 (CH_3Si).

HRMS (ES$^+$): *m*/*z* calcd for $C_{21}H_{34}O_5NaSSi$ (M + Na)$^+$: 449.1794; found: 449.1794.

Anal. Calcd for $C_{21}H_{34}O_5SSi$: C, 59.12; H, 8.03. Found: C, 59.0; H, 8.05.

(R_S)-57 (Minor Epimer)

Colourless oil; $[\alpha]_D^{26}$ –273 (*c* 0.88, $CHCl_3$).

IR (film): 3060s, 2932s, 2857s, 1472s, 1381s, 1247s, 1219s, 837s, 778s cm^{-1}.

^{1}H NMR (500 MHz, $CHCl_3$): δ = 7.67 (2 ArH, dd, *J* = 7.9, 1.5 Hz), 7.60–7.51 (3 ArH, m), 4.71 (1 H, d, *J* = 1.7 Hz, C1H), 4.69 (1 H, dd, *J* = 6.0, 1.7 Hz, C2H), 4.23 (1 H, dd, *J* = 6.8, 6.4 Hz, C3H), 4.09 (1 H, qd, *J* = 9.4, 6.3 Hz, C5H), 3.34 (1 H, dd, *J* = 9.4, 7.3 Hz, C4H), 1.50 (3 H, s, CH_3C), 1.35 (3 H, s, CH_3C), 1.06 (3 H, d, *J* = 6.0 Hz, CH_3CH), 0.88 [9 H, s, $(CH_3)_3$C], 0.13 (3 H, s, CH_3Si), 0.06 (3 H, s, CH_3Si).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.4 (C_{Ar}), 131.8 (C_{Ar}H), 129.6 (2 C_{Ar}H), 125.5 (2 C_{Ar}H), 109.5 [*C*$(CH_3)_2$], 93.3 (C1H), 79.6 (C3H), 75.4 (C4H), 73.7 (C5H), 73.3 (C2H), 28.3 (*C*H_3C), 26.6 (*C*H_3C), 26.2 [(*C*$H_3)_3$C], 18.5 [*C*$(CH_3)_3$], 18.1 (*C*H_3C5H), –3.6 (CH_3Si), –4.6 (CH_3Si).

HRMS (ES$^+$): *m*/*z* calcd for $C_{21}H_{35}O_5SSi$ (M + H)$^+$: 427.1969; found: 427.1968.

1,5-Anhydro-2,6-dideoxy-4-*O*-*tert*-butyldimethylsilyl-1-[(S_S)-phenylsulfinyl]-l-*arabino*-hex-1-enitol [(S_S)-58]

Reaction of sulfoxide (S_S)-**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_2O gave the 1-phenylsulfinyl glycal (S_S)-**58** (1.17 g, 3.2 mmol, 79%) as a colourless solid; mp 131–132 °C.

$[\alpha]_D^{28}$ +91 (*c* 1.00, $CHCl_3$).

IR (film): 3429brs, 3059m, 2935s, 2855s, 1639s, 1444s, 1252s, 1111s, 844s cm^{-1}.

^1H NMR (500 MHz, $CHCl_3$): 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, C3H), 3.96 (1 H, qd, *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_3CH), 0.87 [9 H, s, $(CH_3)_3C$], 0.12 (3 H, s, CH_3Si), 0.06 (3 H, s, CH_3Si).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.3 (C1), 141.6 (C_{Ar}), 131.8 ($C_{Ar}H$), 129.4 (2 $C_{Ar}H$), 125.8 (2 $C_{Ar}H$), 105.6 (C2H), 79.5 (C5H), 75.7 (C4H), 70.5 (C3H), 26.2 [$(CH_3)_3C$], 18.4 [$C(CH_3)_3$], 17.5 (CH_3CH), –3.6 (CH_3Si), –4.5 (CH_3Si).

HRMS (ES$^+$): *m*/*z* calcd for $C_{18}H_{29}O_4SSi$ (M + H)$^+$: 369.1556; found: 369.1573

Anal. Calcd for $C_{18}H_{28}O_4SSi$: C, 58.66; H, 7.66. Found: C, 58.45; H, 7.80.

1,5-Anhydro-2,6-dideoxy-3,4-di-*O*-*tert*-butyldimethylsilyl-1-[(S_S)-phenylsulfinyl]-L-*arabino*-hex-1-enitol [(S_S)-28]

To a solution of alcohol (S_S)-**58** (0.94 g, 2.5 mmol) in CH_2Cl_2 (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 12 h at r.t., the reaction mixture was washed with H_2O (100 mL) and the aqueous layer extracted with CH_2Cl_2 (2 × 50 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by column chromatography (SiO_2, hexanes–Et_2O) to give the 1-phenylsulfinyl glycal (S_S)-**28** (1.07 g, 2.2 mmol, 89%) as a white solid; mp 71–72 °C (MeOH–H_2O).

$[\alpha]_D^{28}$ +136 (*c* 1.00, $CHCl_3$).

IR (film): 3057s, 2951s, 2928s, 2887s, 1641s, 1464s, 1246s, 1078s, 895s, 834s, 770s cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.70–7.65 (2 ArH, m), 7.47–7.42 (3 ArH, m), 5.66 (1 H, dd, *J* = 4.5, 1.3 Hz, C2H), 4.18 (1 H, ddq, *J* = 6.9, 3.1, 1.5 Hz, C5H), 4.01 (1 H, ddd, *J* = 4.4, 2.8, 1.5 Hz, C3H), 3.60 (1 H, dt, *J* = 3.0, 1.3 Hz, C4H), 1.04 (3 H, d, *J* = 7.0 Hz, CH_3CH), 0.86 [9 H, s, $(CH_3)_3C$], 0.80 [9 H, s, $(CH_3)_3C$], 0.11 (3 H, s, CH_3Si), 0.08 (3 H, s, CH_3Si), 0.04 (3 H, s, CH_3Si), –0.01 (3 H, s, CH_3Si).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.5 (C1), 142.5 (C_{Ar}), 131.4 ($C_{Ar}H$), 129.2 (2 $C_{Ar}H$), 125.4 (2 $C_{Ar}H$), 102.2 (C2H), 78.5 (C5H), 73.7 (C4H), 67.4 (C3H), 26.0 [$(CH_3)_3C$], 26.0 [$(CH_3)_3C$], 18.2 [2 $C(CH_3)_3$], 15.4 (CH_3CH), –4.0 (CH_3Si), –4.2 (CH_3Si), –4.3 (CH_3Si), –4.4 (CH_3Si).

HRMS (ES$^+$): *m*/*z* calcd for $C_{24}H_{43}O_4SSi_2$ (M + H)$^+$: 483.2421; found: 483.2425.

Anal. Calcd for $C_{24}H_{42}O_4SSi_2$: C, 59.70; H, 8.77. Found: C, 59.65; H, 8.95.

The structure and stereochemistry of (S_S)-**28** were established by X-ray crystallography (Figure 5).

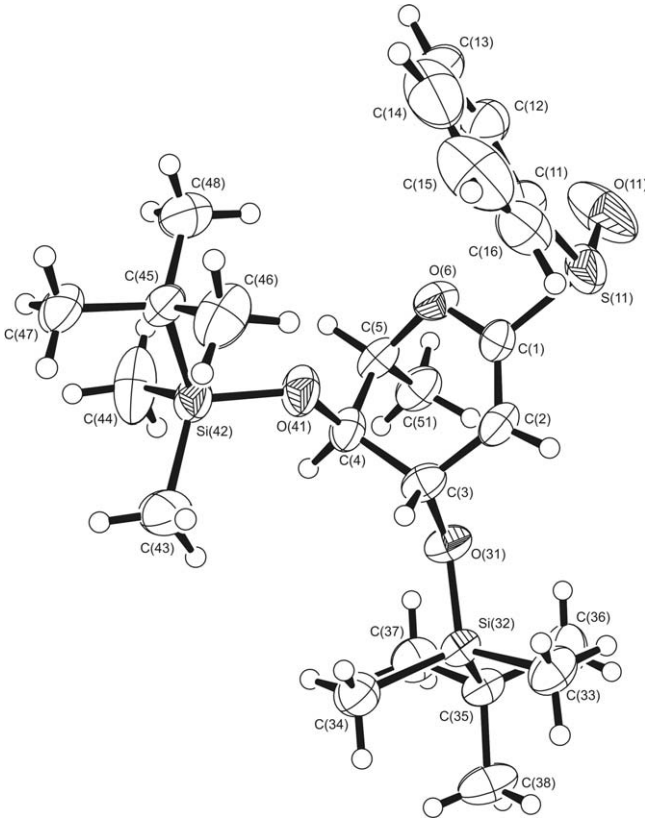


Figure 5 Molecular structure of (S_S)-**28**

1,5-Anhydro-2,6-dideoxy-3,4-di-*O*-*tert*-butyldimethylsilyl-1-[(S_S)-phenylsulfinyl]-L-*arabino*-hex-1-enitol [(S_S)-28]

To a solution of alcohol (S_S)-**58** (0.94 g, 2.5 mmol) in CH_2Cl_2 (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 12 h at r.t., the reaction mixture was washed with H_2O (100 mL) and the aqueous layer extracted with CH_2Cl_2 (2 × 50 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by column chromatography (SiO_2, hexanes–Et_2O) to give the 1-phenylsulfinyl glycal (S_S)-**28** (1.07 g, 2.2 mmol, 89%) as a white solid; mp 71–72 °C (MeOH–H_2O).

$[\alpha]_D^{28}$ +136 (*c* 1.00, $CHCl_3$).

IR (film): 3057s, 2951s, 2928s, 2887s, 1641s, 1464s, 1246s, 1078s, 895s, 834s, 770s cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.70–7.65 (2 ArH, m), 7.47–7.42 (3 ArH, m), 5.66 (1 H, dd, *J* = 4.5, 1.3 Hz, C2H), 4.18 (1 H, ddq, *J* = 6.9, 3.1, 1.5 Hz, C5H), 4.01 (1 H, ddd, *J* = 4.4, 2.8, 1.5 Hz, C3H), 3.60 (1 H, dt, *J* = 3.0, 1.3 Hz, C4H), 1.04 (3 H, d, *J* = 7.0 Hz, CH_3CH), 0.86 [9 H, s, $(CH_3)_3C$], 0.80 [9 H, s, $(CH_3)_3C$], 0.11 (3 H, s, CH_3Si), 0.08 (3 H, s, CH_3Si), 0.04 (3 H, s, CH_3Si), –0.01 (3 H, s, CH_3Si).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.5 (C1), 142.5 (C_{Ar}), 131.4 ($C_{Ar}H$), 129.2 (2 $C_{Ar}H$), 125.4 (2 $C_{Ar}H$), 102.2 (C2H), 78.5 (C5H), 73.7 (C4H), 67.4 (C3H), 26.0 [$(CH_3)_3C$], 26.0 [$(CH_3)_3C$], 18.2 [2 $C(CH_3)_3$], 15.4 (CH_3CH), –4.0 (CH_3Si), –4.2 (CH_3Si), –4.3 (CH_3Si), –4.4 (CH_3Si).

HRMS (ES$^+$): *m*/*z* calcd for $C_{24}H_{43}O_4SSi_2$ (M + H)$^+$: 483.2421; found: 483.2425.

Anal. Calcd for $C_{24}H_{42}O_4SSi_2$: C, 59.70; H, 8.77. Found: C, 59.65; H, 8.95.

The structure and stereochemistry of (S_S)-**28** were established by X-ray crystallography (Figure 5).

1-Phenylsulfinyl Glycals (S_S)- and (R_S)-29 (Scheme 15)

Phenyl 5-*O*-*tert*-Butyldimethylsilyl-2,3-*O*-isopropylidene-1-thio-α-D-ribofuranoside (61)

The reaction of 5-*O*-(*tert*-butyldimethylsilyl)-2,3-*O*-isopropylidene-D-ribofuranose (**59**)[45] (12.9 g, 42.0 mmol) with PhSSPh (10.0 g, 46.0 mmol) and Bu_3P (17.0 g, 21.0 mL, 84.0 mmol) in CH_2Cl_2 (70 mL) according to the procedure of Fürstner[46] gave, after column chromatography (SiO_2, hexanes–Et_2O), 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]

5-*O*-*tert*-Butyldimethylsilyl-1-deoxy-2,3-*O*-isopropylidene-1-[(R_S)-phenylsulfinyl-α-D-ribofuranose [(R_S)-61] and its Epimer (S_S)-61

Oxidation of the thioether **60** (6.55 g, 16.5 mmol) with mCPBA (4.08 g, 77%, 18.1 mmol) and $NaHCO_3$ (16.5 g, 196 mmol) in CH_2Cl_2 (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 (SiO_2, hexanes–Et_2O). The ratio was determined by integration of the ^1H NMR signals for C4H at 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 (R_S)-**61** and (S_S)-**61**.

(R_S)-61 (Major Epimer)

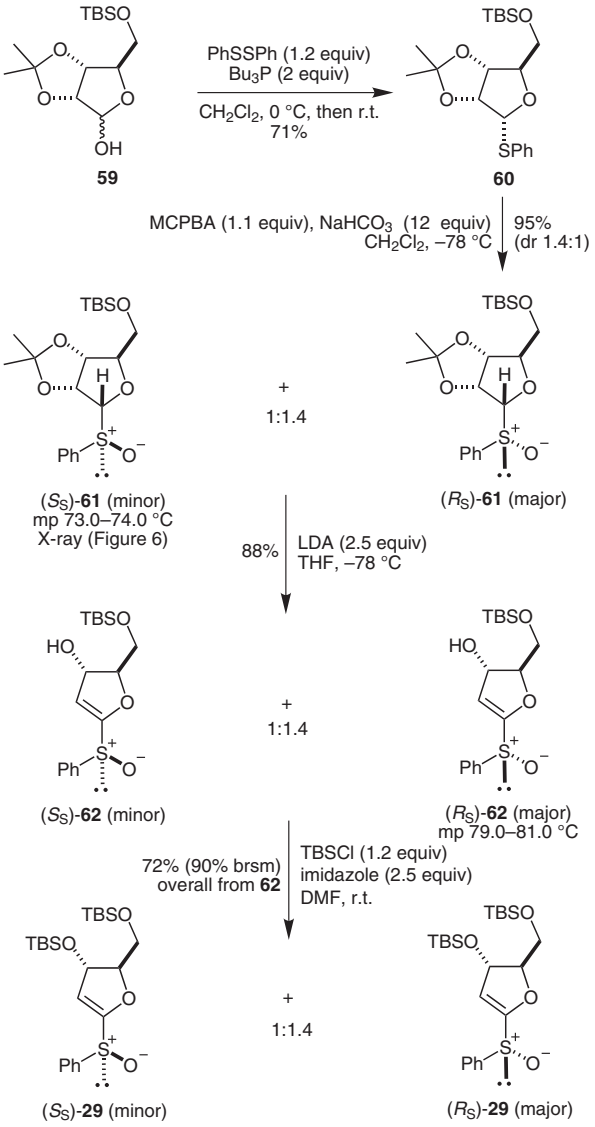
Colourless oil; $[\alpha]_D^{23}$ –80 (*c* 0.4, $CHCl_3$).

IR (film): 2953s, 2931s, 2857s, 1471m, 1382m, 1255s, 1212s, 1083s 1043s, 836s cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): 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_AH_B), 3.57 (1 H, dd, *J* = 11.1, 2.6 Hz, C5H_AH_B), 1.69 (3 H, s, CH_3C), 1.44 (3 H, s, CH_3C), 0.80 [9 H, s, $(CH_3)_3C$], –0.09 (3 H, s, CH_3Si), –0.12 (3 H, s, CH_3Si).

^{13}C (75 MHz, $CDCl_3$): δ = 143.0 (C_{Ar}), 131.6 ($C_{Ar}H$), 129.1 (2 $C_{Ar}H$), 126.2 (2 $C_{Ar}H$), 114.6 [$C(CH_3)_2$], 101.0 (C1H), 86.9 (C4H), 83.2 (C3H), 81.9 (C2H), 65.3 (C5H_2), 26.4 (CH_3C), 26.2 [$(CH_3)_3C$], 25.1 (CH_3C), 18.5 [$C(CH_3)_3$], –5.3 (CH_3Si), –5.4 (CH_3Si).

HRMS (ES$^+$): *m*/*z* calcd for $C_{20}H_{32}O_5SSiNa$ (M + Na)$^+$: 435.1632; found: 435.1639.



Scheme 15 Synthesis of 1-phenylsulfinyl glycal (S_S,R_S)-**29**

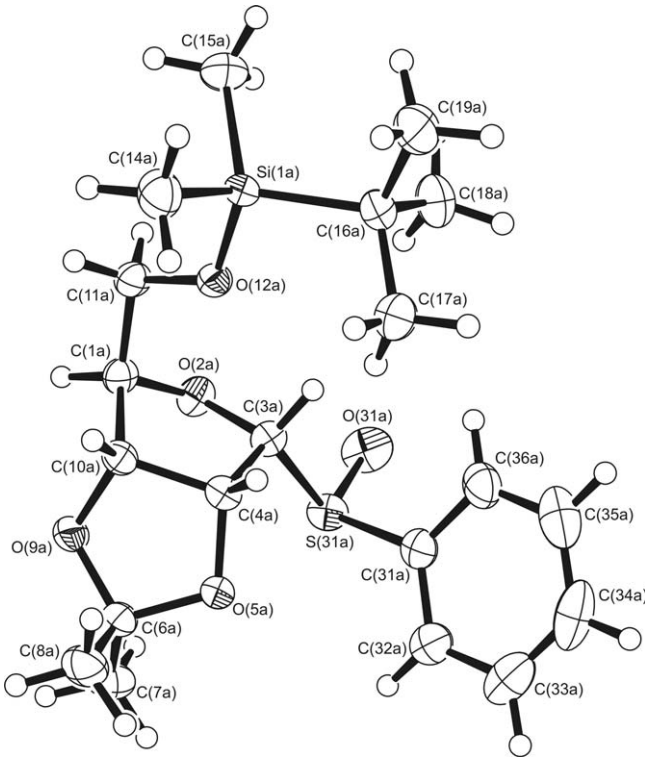


Figure 6 Molecular structure of (S_S)-**61**

(S_S)-61 (Minor Epimer)

White crystalline solid; mp 73–74 °C (hexane); $[\alpha]_D^{23}$ +19 (*c* 0.78, $CHCl_3$).

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

^1H NMR (500 MHz, $CDCl_3$): δ = 7.84–7.81 (2 ArH, m), 7.51–7.47 (3 ArH, m), 4.81 (1 H, d, *J* = 4.7 Hz, C1H), 4.80 (1 H, dd, *J* = 6.2, 1.5 Hz, C3H), 4.60 (1 H, dd, *J* = 6.2, 4.7 Hz, C2H), 4.48 (1 H, app dt, *J* = 2.2, 1.7 Hz, C4H), 3.83 (1 H, dd, *J* = 11.1, 2.7 Hz, C5H_AH_B), 3.69 (1 H, dd, *J* = 11.1, 2.1 Hz, C5H_AH_B), 1.65 (3 H, s, CH_3C), 1.32 (3 H, s, CH_3C), 0.78 [9 H, s, $(CH_3)_3C$], 0.00 (3 H, s, CH_3Si), –0.01 (3 H, s, CH_3Si).

^3C NMR (75 MHz, $CDCl_3$): δ = 142.2 (C_{Ar}), 131.7 ($C_{Ar}H$), 129.2 (2 $C_{Ar}H$), 126.2 (2 $C_{Ar}H$), 114.5 [$C(CH_3)_2$], 102.9 (C1H), 86.5 (C4H), 83.2 (C3H), 81.5 (C2H), 65.1 ($C5H_2$), 26.4 (CH_3C), 26.1 [$(CH_3)_3C$], 25.3 (CH_3C), 18.3 [$C(CH_3)_3$], –5.2 (CH_3Si), –5.4 (CH_3Si).

HRMS (ES^+): *m*/*z* calcd for $C_{20}H_{32}O_5SSiNa$ $(M + Na)^+$: 435.1632; found: 435.1639.

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

1,4-Anhydro-2-deoxy-5-*O*-*tert*-butyldimethylsilyl-1-[(R_S)-phenylsulfinyl]-D-*erythro*-pent-1-enitol [(R_S)-62] and its Epimer (S_S)-62

Reaction of sulfoxide **61** (6.2 g, 15.0 mmol, 1.4:1 mixture of diastereoisomers) with LDA (2.5 equiv) in THF (114 mL) according to typical procedure 3 gave alcohol **62** (4.66 g, 13.0 mmol, 88%) as a colourless oil after column chromatography (SiO_2, hexanes–Et_2O). Integration of the ^1H NMR signals (C_6D_6) for C4H at δ = 4.59 and δ = 4.44 indicated that the product was a 1.4:1 mixture of two epimers (R_S)-**62** and (S_S)-**62** respectively. A second column chromatography achieved partial separation of the epimers and gave analytic samples of pure (R_S)-**62** and (S_S)-**62**.

(R_S)-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_2O–hexane). This isomer decomposed over 24 h at r.t. in $CDCl_3$ that had been stored over K_2CO_3; therefore, spectroscopic data was best acquired in C_6D_6.

$[\alpha]_D^{28}$ +14 (*c* 0.84, C_6H_6).

IR (diamond compression system): 3374m, 2951m, 2930m, 2856m, 1600m, 1445m, 1387m, 1251m, 1108s, 1080s, 1014s, 839m cm^{-1}.

^1H NMR (500 MHz, C_6D_6): δ = 7.66 (2 ArH, d with fine splitting, *J* = 7.1 Hz), 7.03 (2 ArH, t with extra splitting, *J* = 7.4 Hz), 6.97 (1 ArH, t with fine splitting, *J* = 7.3 Hz), 5.92 (1 H, d, *J* = 2.7 Hz, C2H), 4.81–4.76 (1 H, m, C3H), 4.59 (1 H, ddd, *J* = 5.3, 5.1, 3.6 Hz, C4H), 3.43 (1 H, d, *J* = 7.5 Hz, OH), 3.30 (1 H, dd, *J* = 11.2, 5.6 Hz, C5H_AH_B), 3.27 (1 H, dd, *J* = 11.2, 4.9 Hz, C5H_AH_B), 0.82 [9 H, s, $(CH_3)_3C$)], –0.15 (3 H, s, CH_3Si), –0.18 (3 H, s, CH_3Si).

^{13}C NMR (75 MHz, C_6D_6): δ = 163.6 (C1), 142.7 (C_{Ar}), 132.0 ($C_{Ar}H$), 129.9 (2 $C_{Ar}H$), 125.9 (2 $C_{Ar}H$), 107.2 (C2H), 94.5 (C4H), 75.2 (C3H), 63.5 ($C5H_2$), 26.5 [$(CH_3)_3C$], 18.9 [$C(CH_3)_3$], –4.92 (CH_3Si), –4.95 (CH_3Si).

HRMS (ES^+): *m*/*z* calcd for $C_{17}H_{27}O_4SSi$ $(M + H)^+$: 355.1394; found: 355.1396.

Anal. Calcd for $C_{17}H_{26}O_4SSi$: C, 57.63; H, 7.34. Found: C, 57.65; H, 7.45.

(S_S)-62 (Minor Epimer)
Less polar; colourless oil; $[\alpha]_D^{28}$ +160 (*c* 1.28, C_6H_6).

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

^1H NMR (500 MHz, $CDCl_3$): δ = 7.75–7.69 (2 ArH, m), 7.54–7.49 (3 ArH, m), 5.81 (1 H, d, *J* = 2.8 Hz, C2H), 4.95–4.90 (1 H, m, C3H), 4.46 (1 H, dt, *J* = 5.0, 3.5 Hz, C4H), 3.68 (1 H, dd, *J* = 11.1, 4.9 Hz, C5H_AH_B), 3.58 (1 H, dd, *J* = 11.1, 5.1 Hz, C5H_AH_B), 2.45 (1 H, br s, OH), 0.84 [9 H, s, $(CH_3)_3C$)], 0.00 (3 H, s, CH_3Si), –0.02 (3 H, s, CH_3Si).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.7 (C1), 141.0 (C_{Ar}), 132.2 ($C_{Ar}H$), 129.7 (2 $C_{Ar}H$), 125.7 (2 $C_{Ar}H$), 106.9 (C2H), 93.0 (C4H), 75.0 (C3H), 62.8 (C5H_2), 26.1 [($CH_3)_3C$], 18.6 [$C(CH_3)_3$], –5.1 (2 CH_3Si).

HRMS (ES^+): *m*/*z* calcd for $C_{17}H_{27}O_4SSi$ (M + H)$^+$: 355.1394; found: 355.1406.

1,4-Anhydro-2-deoxy-3,5-di-*O*-*tert*-butyldimethylsilyl-1-[(R_S)-phenylsulfinyl]-D-*erythro*-pent-1-enitol [(R_S)-29] and its Epimer (S_S)-29
Following typical procedure 3 described above, addition of the sulfoxide **61** (2.06 g, 5.0 mmol, 1.4:1 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 DMF (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 r.t. for 12 h, then poured into H_2O (350 mL) and extracted with Et_2O (2 × 100 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by column chromatography (SiO_2, hexanes–Et_2O) to give the title 1-phenylsulfinyl 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 ^1H NMR signals (doublets) for C2H at δ = 5.82 ppm for (R_S)-**29** (major) and δ = 5.87 ppm for (S_S)-**29** (minor). The spectroscopic data were recorded on the mixture of epimers.

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

HRMS (ES^+): *m*/*z* calcd for $C_{23}H_{41}O_4SSi_2$ (M + H)$^+$: 469.2259; found: 469.2253.

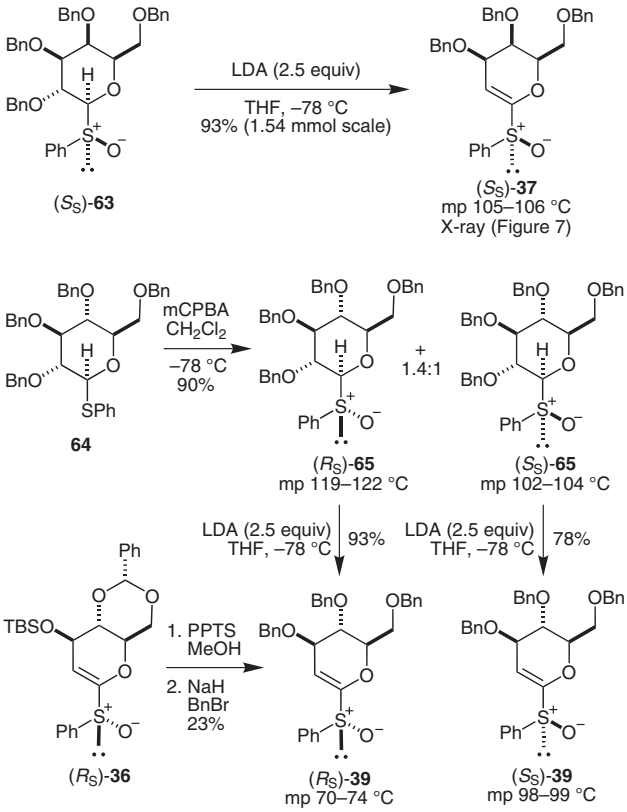
(R_S)-29 (Major Epimer)
^1H NMR (500 MHz, C_6D_6): δ = 7.69 (2 ArH, d with extra splitting, *J* = 7.1 Hz), 7.03–6.91 (3 ArH, m), 5.82 (1 H, d, *J* = 2.6 Hz, C2H), 4.94 (1 H, dd, *J* = 3.0, 2.8 Hz, C3H), 4.49 (1 H, ddd, *J* = 6.1, 5.2, 3.3 Hz, C4H), 3.37 (1 H, dd, *J* = 11.1, 5.1 Hz, C5H_AH_B), 3.22 (1 H, dd, *J* = 11.0, 6.2 Hz, C5H_AH_B), 0.90 [9 H, s, $(CH_3)_3C$], 0.83 [9 H, s, $(CH_3)_3C$], 0.009 (3 H, s, CH_3Si), 0.012 (3 H, s, CH_3Si), –0.11 (3 H, s, CH_3Si), –0.13 (3 H, s, CH_3Si).

^{13}C NMR (75 MHz, C_6D_6): δ = 164.5 (C1), 143.5 (C_{Ar}), 131.6 ($C_{Ar}H$), 129.7 (2 $C_{Ar}H$), 125.7 (2 $C_{Ar}H$), 106.7 (C2H), 93.5 (C4H), 76.2 (C3H), 62.7 (C5H_2), 26.6 [($CH_3)_3C$], 26.5 [($CH_3)_3C$], 19.0 [$C(CH_3)_3$], 18.7 [$C(CH_3)_3$], –3.7 (CH_3Si), –3.9 (CH_3Si), –4.9 (2 CH_3Si).

(S_S)-29 (Minor Epimer)
^1H NMR (500 MHz, C_6D_6): δ = 7.74 (2 ArH, d with extra splitting, *J* = 7.1 Hz), 7.03–6.91 (3 ArH, m), 5.87 (1 H, d, *J* = 2.7 Hz, C2H), 4.99 (1 H, t, *J* = 3.0 Hz, C3H), 4.40 (1 H, ddd, *J* = 5.3, 5.1, 3.3 Hz, C4H), 3.48 (1 H, dd, *J* = 11.1, 4.9 Hz, C5H_AH_B), 3.40 (1 H, dd, *J* = 11.4, 5.8 Hz, C5H_AH_B), 0.90 [9 H, s, $(CH_3)_3C$], 0.86 [9 H, s, $(CH_3)_3C$], –0.020 (3 H, s, CH_3Si), –0.024 (3 H, s, CH_3Si), –0.03 (3 H, s, CH_3Si), –0.05 (3 H, s, CH_3Si).

^{13}C NMR (75 MHz, C_6D_6): δ = 164.8 (C1), 143.2 (C_{Ar}), 132.0 ($C_{Ar}H$), 129.8 (2 $C_{Ar}H$), 126.1 (2 $C_{Ar}H$), 106.2 (C2H), 93.7 (C4H), 76.1 (C3H), 63.2 (C5H_2), 26.6 [($CH_3)_3C$], 26.5 [($CH_3)_3C$], 19.0 [$C(CH_3)_3$], 18.7 [$C(CH_3)_3$], –3.7 (CH_3Si), –3.8 (CH_3Si), –4.72 (CH_3Si), –4.74 (CH_3Si).

1-Phenylsulfinyl Glycals (S_S)-37, (S_S)-39, and (R_S)-39 (Scheme 16)



Scheme 16 Synthesis of 1-phenylsulfinyl glycals (S_S)-**37**, (S_S)-**39** and (R_S)-**39**

1,5-Anhydro-2-deoxy-3,4,6-*O*-phenylmethyl-1-[(S_S)-phenylsulfinyl]-D-*lyxo*-hex-1-enitol (S_S)-37
Reaction of sulfoxide (S_S)-**63**[47] (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 (SiO_2, hexanes–Et_2O) to give the 1-phenylsulfinyl galactal (S_S)-**37** (0.77 g, 1.43 mmol, 93%) as a white solid; mp 105–106 °C (Et_2O).

$[\alpha]_D^{23}$ –66 (*c* 0.924, $CHCl_3$).

IR (film): 1454m, 1353m, 1052s, 733s, 695s cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.59–7.55 (2 ArH, m), 7.37–7.12 (18 ArH, m), 5.76 (1 H, dd, *J* = 2.6, 1.3 Hz, C2H), 4.81 (1 H, d, *J* = 11.6 Hz, CH_AH_BPh), 4.65 (1 H, d, *J* = 12.0 Hz, CH_AH_BPh), 4.55 (1 H, d, *J* = 12.3 Hz, CH_AH_BPh), 4.46 (1 H, d, *J* = 12.3 Hz, CH_AH_BPh), 4.29 (1 H, d, *J* = 11.7 Hz, CH_AH_BPh), 4.23 (1 H d, *J* = 12.5 Hz, CH_AH_BPh), 4.21 (1 H, ddd, *J* = 4.9, 2.8, 1.1 Hz, C3H), 4.12 (1 H, tdd, *J* = 6.4, 2.0, 1.0 Hz, C5H), 3.87 (1 H, app quintet, *J* = 2.0 Hz, C4H), 3.55 (2 H, d, *J* = 6.4 Hz, C6H_2).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.2 (C1), 141.9 (C_{Ar}), 138.5 (C_{Ar}), 138.1 (C_{Ar}), 131.3 ($C_{Ar}H$), 129.2 (2 $C_{Ar}H$), 128.8 (2 $C_{Ar}H$), 128.7 (2 $C_{Ar}H$), 128.6 (2 $C_{Ar}H$), 128.2 ($C_{Ar}H$), 128.1 (4 $C_{Ar}H$),

128.04 (2 $C_{Ar}H$), 127.95 ($C_{Ar}H$), 127.9 (2 $C_{Ar}H$), 125.4 (2 $C_{Ar}H$), 103.2 (C2H), 78.9 (C5H), 74.0 (CH_2Ph), 73.7 (CH_2Ph), 72.1 (C3H), 71.5 (CH_2Ph), 71.0 (C4H), 67.7 ($C6H_2$).

HRMS (ES^+): *m/z* calcd for $C_{33}H_{32}O_5SNa$ $(M + Na)^+$: 563.1863; found: 563.1858.

Anal. Calcd for $C_{33}H_{32}O_5S$: C, 73.31; H, 5.97; S, 5.93. Found: C, 73.05; H, 5.95; S, 5.80.

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

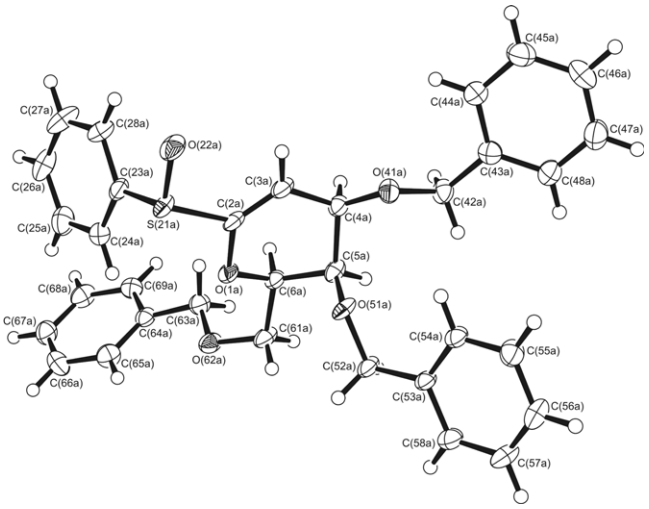


Figure 7 Molecular structure of (S_S)-**37**

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

Oxidation of phenyl 2,3,4,6-tetra-*O*-benzyl-1-thio-β-glucopyranoside[48] (**64**) (7.2 g, 11.4 mmol) with mCPBA according to typical procedure 4 gave a mixture of diastereoisomeric sulfoxides (R_S)-**65** and (S_S)-**65** in the ratio 1.4:1 according to integration of the ^{1}H NMR signal at δ = 4.32 for (R_S)-**65** and 4.53 for (S_S)-**65**. The mixture was separated by column chromatography (SiO_2, hexanes–EtOAc) to give first the major diastereoisomer (R_S)-**65** (1.97 g, 3.04 mmol, 27%), then a mixture of the diastereoisomers (2.15 g, 3.31 mmol, 29%), and finally the minor diastereoisomer (S_S)-**65** (2.51 g, 3.87 mmol, 34%).

(R_S)-65

Mp 119–122 °C (MeOH) (Lit.[47] mp 116–117 °C); $[\alpha]_D^{20}$ –48 (*c* 1.1, $CHCl_3$) {Lit.[47] $[\alpha]_{Hg}^{23}$ –94.0 (*c* $CHCl_3$)}.

IR (film): 3031m, 2871m, 1452s, 1361s, 1154s, 1037s, 732s, 696s cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.67–7.63 (2 ArH, m), 7.47–7.24 (19 ArH), 7.19–7.17 (4 ArH, m), 5.03 (1 H, d, *J* = 10.2 Hz, CH_AH_BPh), 4.97 (1 H, d, *J* = 11.0 Hz, CH_AH_BPh), 4.97 (1 H, d, *J* = 11.0 Hz, CH_AH_BPh), 4.91 (1 H, d, *J* = 11.0 Hz, CH_AH_BPh), 4.80 (1 H, d, *J* = 11.0 Hz, CH_AH_BPh), 4.58 (1 H, d, *J* = 10.7 Hz, CH_AH_BPh), 4.32 (1 H, d, *J* = 12.0 Hz, CH_AH_BPh), 4.21 (1 H, d, *J* = 12.0 Hz, CH_AH_BPh), 4.11 (1 H, t, *J* = 9.3 Hz, C2H), 3.98 (1 H, d, *J* = 9.7 Hz, C1H), 3.80 (1 H, t, *J* = 9.0 Hz, C3H), 3.57 (1 H, t, *J* = 9.5 Hz, C4H), 3.53–3.48 (2 H, m, $C6H_2$), 3.35–3.29 (1 H, m, C5H).

^{3}C NMR (75 MHz, $CDCl_3$): δ = 139.9 (C_{Ar}), 138.6 (C_{Ar}), 138.1 (C_{Ar}), 137.9(C_{Ar}), 131.3 ($C_{Ar}H$), 129.2 (2 $C_{Ar}H$), 128.91(2 $C_{Ar}H$), 128.87 (2 $C_{Ar}H$), 128.8 (2 $C_{Ar}H$), 128.6 (2 $C_{Ar}H$), 128.5 ($C_{Ar}H$), 128.4 (2 $C_{Ar}H$), 128.3 ($C_{Ar}H$), 128.13 ($C_{Ar}H$), 128.0 (2 $C_{Ar}H$), 127.9 (2 $C_{Ar}H$), 125.6 (2 $C_{Ar}H$), 93.8 (C1H), 86.9 (C3H), 81.1 (C5H), 77.9 (C4H), 77.2 (C2H), 76.2 (CH_2), 76.0 (CH_2), 75.5 (CH_2), 73.8 (CH_2), 69.2 ($C6H_2$). Signals for 4 carbons in the aromatic region could not be distinguished.

HRMS (ES^+): *m/z* calcd for $C_{40}H_{40}O_6SNa$ $(M + Na)^+$: 671.2438; found: 671.2451.

Sulfoxide (R_S)-**65** failed to give a satisfactory microanalysis.

(S_S)-65

Mp 102–104 °C (MeOH) (Lit.[47] mp 101–102 °C); $[\alpha]_D^{20}$ +18 (*c* 0.612, $CHCl_3$) {Lit.[47] $[\alpha]_{Hg}^{23}$ +39.0 (*c* $CHCl_3$)}.

IR (film): 1452m, 1093s, 1036s, 744s, 698s cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.60–7.59 (2 ArH, m), 7.39–7.24 (19 ArH, m), 7.19–7.16 (4 ArH, m), 4.83 (2 H, s, CH_2Ph), 4.82 (1 H, d, *J* = 10.9 Hz, CH_AH_BPh), 4.78 (1 H, d, *J* = 10.9 Hz, CH_AH_BPh), 4.74 (1 H, d, *J* = 10.9 Hz, CH_AH_BPh), 4.52 (1 H, d, *J* = 10.9 Hz, CH_AH_BPh), 4.49 (1 H, d, *J* = 8.8 Hz, C1H), 4.45 (2 H, s, CH_2Ph), 3.80 (2 H, m, C2H + C3H or C4H), 3.73 (2 H, d, *J* = 2.6 Hz, $C6H_2$), 3.63–3.56 (2 H, m, C5H + C3H or C4H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.4 (C_{Ar}), 138.5 (C_{Ar}), 138.3 (C_{Ar}), 138.2 (C_{Ar}), 138.0 (C_{Ar}), 131.4 ($C_{Ar}H$), 129.1 (2 $C_{Ar}H$), 128.83 (2 $C_{Ar}H$), 128.80 (2 $C_{Ar}H$), 128.7 (2 $C_{Ar}H$), 128.6 (2 $C_{Ar}H$), 128.3 (2 $C_{Ar}H$), 128.21 ($C_{Ar}H$), 128.16 ($C_{Ar}H$), 128.1 (2 $C_{Ar}H$), 128.0 ($C_{Ar}H$), 128.00 (2 $C_{Ar}H$), 127.96 (2 $C_{Ar}H$), 126.0 (2 $C_{Ar}H$), 95.8 (C1), 86.6 (CH), 79.6 (CH), 77.6 (CH), 76.6 (CH), 75.7 (CH_2), 75.2 (CH_2), 74.2 (CH_2), 73.9 (CH_2), 68.9 ($C6H_2$). A signal for 1 carbon could not be distinguished.

HRMS (ES^+): *m/z* calcd for $C_{40}H_{40}O_6SNa$ $(M + Na)^+$: 671.2438; found: 671.2443.

Anal. Calcd for $C_{40}H_{40}O_6S$: C, 74.05; H, 6.21; S, 4.94. Found: C, 73.80; H, 6.20; S, 4.75.

1,5-Anhydro-3,4,6-tri-*O*-phenylmethyl-1,2-dideoxy-1-[(R_S)-phenylsulfinyl]-D-*arabino*-hex-1-enitol [(R_S)-39] and its Epimer (S_S)-39

Treatment of sulfoxide (R_S)-**65** (2.0 g, 3.0 mmol) with LDA (2.6 equiv) in THF at –78 °C according to typical procedure 3 outlined above gave (R_S)-**39** (1.55 g, 2.9 mmol, 93%) as a white solid after purification by column chromatography (SiO_2, hexanes–EtOAc). A sample recrystallised from EtOAc–hexanes gave mp 70–74 °C.

$[\alpha]_D^{23}$ –150 (*c* 0.6 $CHCl_3$) {Lit.[47] $[\alpha]_{Hg}^{22}$ –116.9 (*c* 1.0 $CHCl_3$)}.

IR (film): 1637m, 1452m, 1300m, 1097s, 1048s, 845m, 741s, 694s, 530m cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.74–7.73 (2 ArH, m), 7.46–7.41 (3 ArH, m), 7.34–7.22 (13 ArH, m), 7.12–7.10 (2 ArH, m), 5.92 (1 H, d, *J* = 3.0 Hz, C2H), 4.73 (1 H, d, *J* = 11.5 Hz, CH_AH_BPh), 4.68 (1 H, d, *J* = 11.5 Hz, CH_AH_BPh), 4.60 (1 H, d, *J* = 11.5 Hz, CH_AH_BPh), 4.55 (1 H, d, *J* = 11.5 Hz, CH_AH_BPh) 4.30–4.27 (2 H, m, C3H and C5), 4.22 (1 H, d, *J* = 12.0 Hz, CH_AH_BPh), 4.17 (1 H, d, *J* = 12.0 Hz, CH_AH_BPh), 4.81 (1 H, app t, *J* = 6.0 Hz, C4H), 3.58–3.52 (2 H, m, $C6H_2$).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.8 (C1), 142.4 (C_{Ar}), 138.3 (C_{Ar}), 138.1 (C_{Ar}), 138.0 (C_{Ar}), 131.9 ($C_{Ar}H$), 129.4 (2 $C_{Ar}H$), 128.9 (2 $C_{Ar}H$), 128.8 (2 $C_{Ar}H$), 128.6 (2 $C_{Ar}H$), 128.2 (4 $C_{Ar}H$), 127.9 ($C_{Ar}H$), 127.7 (2 $C_{Ar}H$), 125.9 (2 $C_{Ar}H$), 99.3 (C2H), 80.2 (C5H), 74.3 (C3H and C4H), 73.8 (CH_2), 73.5 (CH_2), 71.2 (CH_2), 68.0 ($C6H_2$).

HRMS (ES^+): *m/z* calcd for $C_{33}H_{32}NaO_5S$ $(M + Na)^+$: 563.1863; found: 563.1870.

Anal. Calcd for $C_{33}H_{32}O_5S$: C, 73.31; H, 5.97; S, 5.93. Found: C, 73.30; H, 6.10; S, 5.70.

(S_S)-39

Similarly, treatment of sulfoxide (S_S)-**65** (2.5 g, 3.85 mmol) with LDA (2.5 equiv) in THF at –78 °C according to typical procedure 4

gave (S_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.

$[\alpha]_D^{20}$ +21 (*c* 1.30, $CHCl_3$) {Lit.[47] $[\alpha]_{Hg}^{22}$ +16.3 (*c* 1.0 $CHCl_3$)}.

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

^1H NMR (500 MHz, $CDCl_3$): δ = 7.71–7.70 (2 ArH, m), 7.45–7.39 (3 ArH, m), 7.33–7.25 (11 ArH, m), 7.21–7.16 (4 ArH, m), 5.91 (1 H, d, *J* = 3.0 Hz, C2H), 4.75 (1 H, d, *J* = 11.1 Hz, CH_AH$_B$Ph), 4.71 (1 H, d, *J* = 11.5 Hz, CH$_A$$H_B$Ph), 4.60 (1 H, d, *J* = 11.5 Hz, CH_AH$_B$Ph), 4.56 (1 H, d, *J* = 11.6 Hz, CH$_A$$H_B$Ph), 4.38 (2 H, s, CH_2Ph), 4.28 (1 H, dd, *J* = 6.4, 3.0 Hz, C3H), 4.04–4.01 (1 H, m, C5H), 3.91 (1 H, dd, *J* = 8.6, 6.5 Hz, C4H), 3.78 (1 H, dd, *J* = 11.6, 4.7 Hz, C6H_AH$_B$), 3.67 (1 H, dd, *J* = 11.6, 2.6 Hz, C6H$_A$$H_B$).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.7 (C1), 142.1(C_{Ar}), 138.23 (C_{Ar}), 138.20 (C_{Ar}), 138.0 (C_{Ar}), 131.7 (C_{Ar}H), 129.4 (2 C_{Ar}H), 128.8 (2 C_{Ar}H), 128.6 (4 C_{Ar}H), 128.2 (2 C_{Ar}H), 128.0 (2 C_{Ar}H), 127.9 (C_{Ar}H), 127.8 (2 C_{Ar}H), 125.4 (2 C_{Ar}H), 101.1 (C2H), 80.0 (C5H), 75.7 (C3H), 74.4 (C4H), 74.0 (CH_2), 73.6 (CH_2), 71.2 (CH_2), 68.0 (C6H_2). Signals for 2 carbons could not be distinguished.

HRMS (ES^+): *m*/*z* calcd for $C_{33}H_{33}O_5S$ $(M + H)^+$: 541.2043; found: 541.2052.

Sulfoxide (S_S)-**39** failed to give a satisfactory microanalysis. Neither (R_S)-**39** nor (S_S)-**39** gave crystals suitable for X-ray diffraction. Therefore the stereochemistry of the 1-phenylsulfinyl glycal (R_S)-**39** was established by a chemical correlation with (R_S)-**36** whose stereochemistry had been established (see Scheme 11 above).

Conversion of (R_S)-36 into (R_S)-39

A solution of the sulfoxide (R_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 solvent was removed in vacuo and the residue was dissolved 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 benzyl 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_2O (5 mL) and extracted with Et_2O (3 × 10 mL). The combined organic layers were dried over Na_2SO_4 and the solvent removed in vacuo. The residue was purified by column chromatography (SiO_2, hexanes–Et_2O) to give the 1-phenylsulfinyl glycal (R_S)-**39** (26 mg, 0.0481 mmol, 23% over two steps) as a white solid. The ^1H and ^{13}C NMR spectroscopic data were identical to those recorded for sulfoxide (R_S)-**39** prepared from (R_S)-**65** as shown in Scheme 16.

Primary Data for this article are available online at http://www.thieme-connect.com/ejournals/toc/synthesis (added August 26th, 2009) and can be cited using the following DOI: 10.4125/pd0001th.

FIDs and associated files for the ^1H, ^{13}C and DEPT NMR spectra for compounds **14**, (S_S)-**23**, (S_S)-**25**, (R_S)-**26**, **27**, (S_S)-**28**, (R_S,S_S)-**29**, **30**, (R_S)-**36**, (S_S)-**36**, (S_S)-**37**, **38**, (R_S)-**39**, (S_S)-**39**, (S_S)-**44**, (R_S)-**46**, (S_S)-**46**, (R_S)-**48**, (S_S)-**48**, (S_S)-**49**, **52**, (R_S)-**53**, (R_S)-**55**, (R_S)-**57**, (S_S)-**57**, (S_S)-**58**, (R_S)-**61**, (S_S)-**61**, (R_S)-**62**, (S_S)-**62**, (R_S)-**65** and (S_S)-**65** are summarized.

Acknowledgment

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

References

(1) (a) Jarosz, S.; Zamojski, A. *Curr. Org. Chem.* **2003**, *7*, 13. (b) Somsák, L. *Chem. Rev.* **2001**, *101*, 81.
(2) (a) Friesen, R. W.; Loo, R. W. *J. Org. Chem.* **1991**, *56*, 4821. (b) Dubois, E.; Beau, J.-M. *Carbohydr. Res.* **1992**, *223*, 157.
(3) Dubois, E.; Beau, J.-M. *Carbohydr. Res.* **1992**, *228*, 103.
(4) Tius, M. A.; Gomez-Galeno, J.; Gu, X.-q. Z.; Javid, H. *J. Am. Chem. Soc.* **1991**, *113*, 5775.
(5) Zhang, H.-C.; Brakta, M.; Doyle Daves, G. *Tetrahedron Lett.* **1993**, *34*, 1571.
(6) Koo, B.; McDonald, F. E. *Org. Lett.* **2005**, *7*, 3621.
(7) Steunenberg, P.; Jeanneret, V.; Zhu, Y.-H.; Vogel, P. *Tetrahedron Asymmetry* **2005**, *16*, 337.
(8) Dubbaka, S. R.; Steunenberg, P.; Vogel, P. *Synlett* **2004**, 1235.
(9) Lesimple, P.; Beau, J.-M.; Sinaÿ, P. *J. Chem. Soc., Chem. Commun.* **1985**, 894.
(10) Hanessian, S.; Martin, M.; Desai, R. C. *J. Chem. Soc., Chem. Commun.* **1986**, 926.
(11) Bearder, J. R.; Dewis, M. L.; Whiting, D. A. *J. Chem. Soc., Perkin Trans.1* **1995**, 227.
(12) Parker, K. A.; Su, D.-S. *J. Carbohydr. Chem.* **2005**, *24*, 187.
(13) (a) Parker, K. A.; Coburn, C. A.; Koh, Y. *J. Org. Chem.* **1995**, *60*, 2938. (b) Koyama, Y.; Yamaguchi, R.; Suzuki, K. *Angew. Chem. Int. Ed.* **2008**, *47*, 1084.
(14) Dötz, K. H.; Otto, F.; Nieger, M. *J. Organomet. Chem.* **2001**, *621*, 77.
(15) Hallett, M. R.; Painter, J. E.; Quayle, P.; Ricketts, D. *Tetrahedron Lett.* **1998**, *39*, 2851.
(16) Milne, J. E.; Jarowicki, K.; Kocienski, P. J.; Alonso, J. *Chem. Commun.* **2002**, 426.
(17) Review: Friesen, R. W. *J. Chem. Soc., Perkin Trans. 1* **2001**, 1969.
(18) Boeckman, R. K.; Bruza, K. J. *Tetrahedron* **1981**, *37*, 3997.
(19) Glycals with heteroatom substituents (Cl, OR, SR) at C2 rapidly metallate with *n*-BuLi, conditions that are compatible with benzyl ether protecting groups: Boyd, E.; Hallet, M. R.; Jones, R. V. H.; Painter, J. E.; Patel, P.; Quayle, P.; Waring, A. J. *Tetrahedron Lett.* **2006**, *47*, 8337; and references cited therein.
(20) Friesen, R. W.; Sturino, C. F.; Daljeet, A. K.; Kolaczewska, A. *J. Org. Chem.* **1991**, *56*, 1944.
(21) (a) Friesen, R. W.; Trimble, L. A. *J. Org. Chem.* **1996**, *61*, 1165. (b) Imanieh, H.; Quayle, P.; Voaden, M.; Street, S. D. A. *Tetrahedron Lett.* **1992**, *33*, 543. (c) Crich, D.; Ritchie, T. J. *Tetrahedron* **1988**, *44*, 2319.
(22) Jäkel, C.; Dötz, K. H. *J. Organomet. Chem.* **2001**, *624*, 172.
(23) Paquette, L. A.; Oplinger, J. A. *Tetrahedron* **1989**, *45*, 107.
(24) Majumder, U.; Cox, J. M.; Johnson, H. W. B.; Rainier, J. D. *Eur. J. Org. Chem.* **2006**, *12*, 1736.
(25) (a) Friesen, R. W.; Loo, R. W.; Sturino, C. F. *Can. J. Chem.* **1994**, *72*, 1262. (b) Jäkel, C.; Dötz, K. H. *Tetrahedron* **2000**, *56*, 2167.
(26) Parker, K. A.; Su, D.-S. *J. Org. Chem.* **1996**, *61*, 2191.
(27) Lesimple, P.; Beau, J.-M.; Jaurand, G.; Sinaÿ, P. *Tetrahedron Lett.* **1986**, *27*, 6201.
(28) Gunn, A.; Jarowicki, K.; Kocienski, P.; Lockhart, S. *Synthesis* **2001**, 331.
(29) The $Bu_3SnMgBr$ was prepared by transmetallation of Bu_3SnLi with $MgBr_2$. The Bu_3SnLi was prepared, in turn, by the reaction of BuLi with $Bu_3SnSnBu_3$ thereby generating 1 equiv of Bu_4Sn waste for each equiv of Bu_3SnLi.
(30) Parker and Su (reference 26) reported a successful metallation of the bis-TBS-protected analogue of **35** using 3 equiv of *t*-BuLi in THF at –78 °C.

(31) Furukawa, N.; Sato, S. In *Topics in Current Chemistry*, Vol. 205; Page, P. C. B., Ed.; Springer: Berlin, **1999**, 89–129.
(32) Theobald, P.; Okamura, W. H. *J. Org. Chem.* **1990**, *55*, 741.
(33) (a) Lockard, J. P.; Schroeck, C. W.; Johnson, C. R. *Synthesis* **1973**, 485. (b) Durst, T.; LeBelle, M. J.; Elzen, R. v. d.; Tin, K. C. *Can. J. Chem.* **1974**, *52*, 761. (c) Clayden, J.; Mitjans, D.; Youssef, L. H. *J. Am. Chem. Soc.* **2002**, *124*, 5266.
(34) Sakurada, J.; Satoh, T. *Tetrahedron* **2007**, *63*, 3806.
(35) Blakemore, P. R.; Burge, M. S. *J. Am. Chem. Soc.* **2007**, *129*, 3068.
(36) Hoffmann, R. W. *Chem. Soc. Rev.* **2003**, *32*, 225.
(37) Satoh, T. *Chem. Rev.* **1996**, *96*, 3303.
(38) Carpintero, M.; Nieto, I.; Fernández-Mayoralas, A. *J. Org. Chem.* **2001**, *66*, 1768.
(39) Lipton, M. F.; Sorenson, C. M.; Sadler, A. C.; Shapiro, R. H. *J. Organomet. Chem.* **1980**, *186*, 155.
(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_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.
(41) Fernández-Mayoralas, A.; Marra, A.; Trumtel, M.; Veyrieres, A.; Sinaÿ, P. *Carbohydr. Res.* **1989**, *188*, 81.
(42) Chen, X.-T.; Bhattacharya, S. K.; Zhou, B.; Gutteridge, C. E.; Pettus, T. R. R.; Danishefsky, S. J. *J. Am. Chem. Soc.* **1999**, *121*, 6563.
(43) Yu, W.; Jin, Z. *J. Am. Chem. Soc.* **2002**, *124*, 6576.
(44) Nicolaou, K. C.; Trujillo, J. I.; Chibale, K. *Tetrahedron* **1997**, *53*, 8751.
(45) Jin, Y. H.; Liu, P.; Wang, J.; Baker, R.; Huggins, J.; Chu, C. K. *J. Org. Chem.* **2003**, *68*, 9012.
(46) Fürstner, A. *Liebigs Ann. Chem.* **1993**, 1211.
(47) Kast, J.; Hoch, M.; Schmidt, R. R. *Liebigs Ann. Chem.* **1991**, 481.
(48) Damager, I.; Olsen, C. E.; Moller, B. L.; Motawia, M. S. *Carbohyr. Res.* **1999**, *320*, 19.