D-Allal- and D-Galactal-Derived Vinyl *N*-Mesylaziridines: Regio- and Stereoselectivity in Addition Reactions of O-, C-, N-, and S-Nucleophiles

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Abstract: The regioselectivity and stereoselectivity were examined of the addition reactions of O-, C-, N- and S-nucleophiles to D-allal- and D-galactal-derived *N*-mesylaziridines. The ratio of 1,4-regioselectivity (exclusive *syn*-1,4-addition) to 1,2-regioselectivity (exclusive *anti*-1,2-addition) was strictly and directly dependent on the ability of the nucleophile to coordinate with the nitrogen atom of the aziridine.

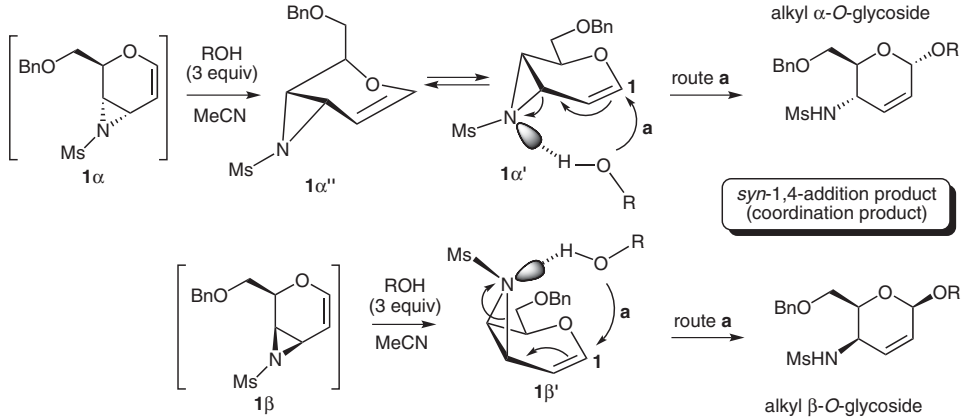
Key words: glycosylations, regioselectivity, stereoselectivity, nucleophilic additions, heterocycles

Glycosides with functionalized amino groups in various positions (amino sugars) form an important category of modified carbohydrate units that are present in several oligosaccharides and glycoconjugates.[1] Amino sugars are also important as essential components of bacterial capsular polysaccharides and as structural elements of aminoglycoside antibiotics that display antiviral and antitumor activities.[2] Because of the biological importance of natural products containing amino sugars,[3] the development of efficient routes for synthesizing these carbohydrates is an attractive goal.

In this context, our interest was directed toward glycal-derived vinyl aziridines as useful tools for the regio- and stereoselective introduction of a nitrogen functionality at the C(4) carbon of glycal systems with simultaneous glycosylation.The addition reactions of alcohols and partially protected monosaccharides (O-nucleophiles) to vinyl D-allal- and D-galactal-derived *N*-mesyl aziridines (**1α** and **1β**, respectively) as new glycosyl donors has been shown to be completely 1,4-regio- and *syn*-stereoselective, with exclusive formation of the corresponding alkyl α-*O*- or β-*O*-glycosides (*syn*-1,4-addition products) with the same configuration as that of the starting aziridines **1α** and **1β**, respectively, in an uncatalyzed, directly substrate-dependent, stereospecific glycosylation process (route a, Scheme 1).[4,5]

During this process, the stereo- and regioselective introduction of an N-substituted amino group at C(4) also occurred (Scheme 1). The *syn*-1,4-addition products have also been termed coordination products, because they are believed to be formed as a result of coordination between the aziridine nitrogen and the O-nucleophile with a subsequent entropically favored attack at C(1) from the same side (Scheme 1).[6] In an unexpected contrast with the results obtained with alcohols, the reactions of aziridines **1α** and **1β** with amines (N-nucleophiles) led exclusively to mixtures of the corresponding *anti*-1,2- and *anti*-1,4-addition products (noncoordination products) (Scheme 2).[7]

These results prompted us to check the corresponding chemical behavior of aziridines **1α** and **1β** with other O-nucleophiles (acetate, methoxide, and hydroxide ions), another N-nucleophile (azide ion), and the previously unexamined C-nucleophiles (organometallic compounds) and S-nucleophiles (thiols). Our aim was to find simple procedures for glycosylating as many nucleophiles as pos-



Scheme 1

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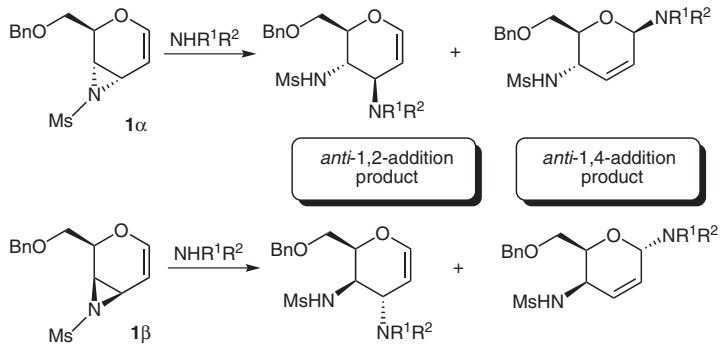


Scheme 2

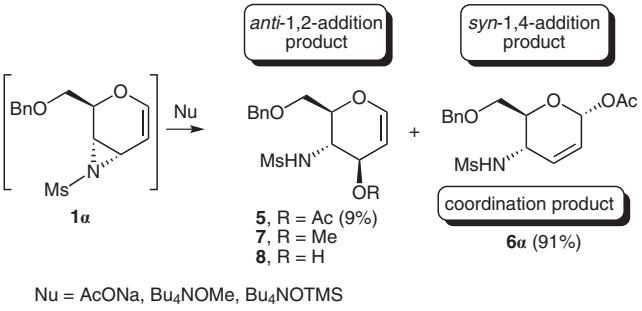
sible with aziridines **1α** and **1β**, preferably with high levels of regio- and stereocontrol.

The aziridines **1α** and **1β** are synthesized from the corresponding epoxides with the opposite configurations (**2β** and **2α**, respectively). Aziridines **1α** and **1β** are unstable and must be prepared in situ by base-catalyzed cyclization of the corresponding stable precursor, the *trans*-*N*,*O*-dimesylates **3** and **4**, respectively, in the presence of potassium *tert*-butoxide or potassium carbonate. The resulting aziridines react immediately with the selected nucleophile (Scheme 3).[4a,4b,8]

A theoretical conformational study carried out on appropriately simplified models has indicated that aziridine **1β** exists only as the corresponding conformer **1β′** with an equatorial side chain,[4b] whereas aziridine **1α** exists as an equilibrium mixture (49:51, calculated in benzene as the solvent) of the corresponding conformers **1α′** and **1α″** (Scheme 1).[7]

O-Nucleophiles

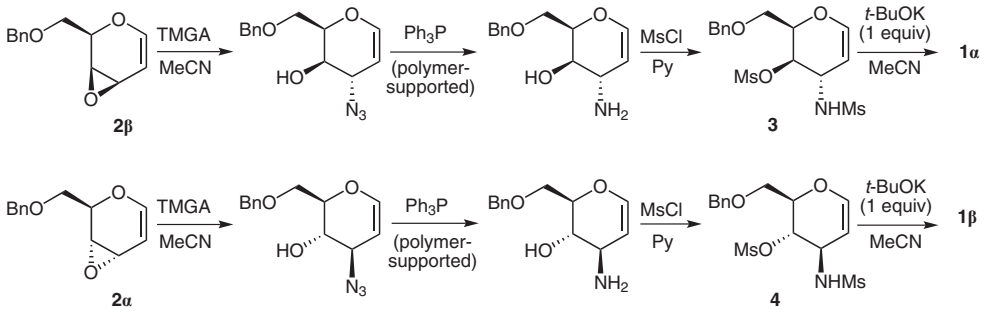
The marked tendency of aziridines **1α** and **1β** to give *syn*-1,4-addition products (coordination products) with O-nucleophiles was further demonstrated by their reactions with sodium acetate in *N*,*N*-dimethylformamide, that is to say, under conditions that should reasonably favor a typical S_N2 process at the allylic C(3) aziridine carbon with the formation of the corresponding *anti*-1,2-addition product (noncoordination product). Actually, in the case of aziridine **1α**, the α-acetyl glycoside **6α** was the main addition product (91%) with only a small amount of the expected *anti*-1,2 addition product, the *trans*-mesylamino acetate **5** (9%, Scheme 4). A selective 1,2-addition process with O-nucleophiles occurred only with reagents such as tetrabutylammonium methoxide or tetrabutylammonium trimethylsilanolate, in which the noncoordinating tetrabutylammonium cation is the counterion of the corresponding O-nucleophile (MeO^- or $TMSO^-$, the synthetic equivalents of OH^-).[9] In this way, the *trans*-methoxy and *trans*-hydroxy mesylamino derivatives **7** and **8**, respectively, were obtained, as the exclusive reaction products in a completely 1,2-regioselective and *anti*-stereoselective fashion (Scheme 4). A corresponding regio- and stereoselective behavior has been previously observed with aziridine **1β** with the same reagents under the same reaction conditions.[4b]



Scheme 4

N-Nucleophiles

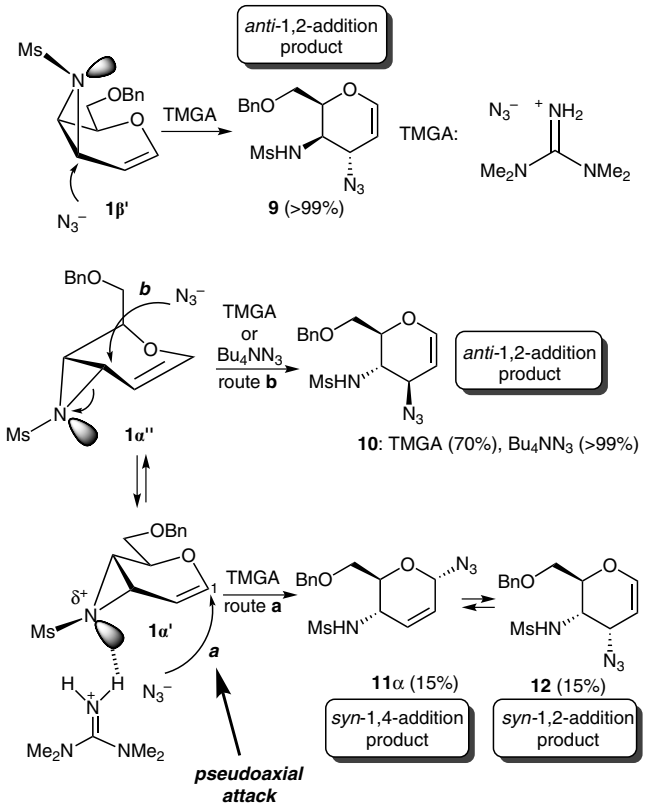
The reaction of aziridines **1α** and **1β** with trimethylsilyl azide, carried out, necessarily, by protocol B,[5] led to complex reaction mixtures. Evidently, the electrophilicity of the reagent is not compatible with the base necessary for



Scheme 3

the formation of the aziridines from their respective precursors.[8]

Before the tetramethylguanidinium ion (TMG^+: $Me_4N_2C{=}NH_2^+$) was identified as being capable of hydrogen bonding,[10] we believed that tetramethylguanidinium azide would serve as an organosoluble noncoordinating source of azide ion and therefore an appropriate reagent for a regioselective, noncoordinated, anti-1,2-addition process. Actually, the reaction of aziridine **1β** with tetramethylguanidinium azide was completely regioselective with exclusive formation of the corresponding noncoordination product, the *trans*-azido mesylamino derivative **9** (*anti*-1,2-addition product), as expected (Scheme 5).[6]



Scheme 5

However, aziridine **1α** showed a decidedly different behavior in the same reaction. In this case, the expected *anti*-1,2-addition product, the *trans*-3-azido-*N*-(mesylamino) derivative **10** (route b, 70%) was not the sole reaction product, but was obtained as a mixture containing a substantial amount (15%) of the corresponding *syn*-1,2-addition product, the *cis*-3-azido-4-*N*-(mesylamino) derivative **12**, and the coordination product (*syn*-1,4-addition product), the α-glycosyl azide **11α** (15%, Scheme 5, route a). On the basis of experimental evidence that clearly indicated that an equilibrium exists between the *syn*-1,2-addition product **12** and the *syn*-1,4-addition product **11α**, together with some previous results,[11] we concluded that *syn*-1,2-addition product **12** is not the primary reaction product, but is the result of an isomerization by suprafacial [3,3]-sigmatropic rearrangement of the corresponding α-glycosyl azide **11α**, which is the actual primary reaction product.

On the basis of these results, we believe that because of the presence of the proton,[10] the TMG ion can coordinate to the aziridine nitrogen of **1α** through a hydrogen bond to give the α-glycosyl azide **11α** by an entropically favored attack on C(1) from the same side (route a). Subsequent azide migration leads to the corresponding *syn*-1,2-addition product, as found experimentally (Scheme 5).[11]

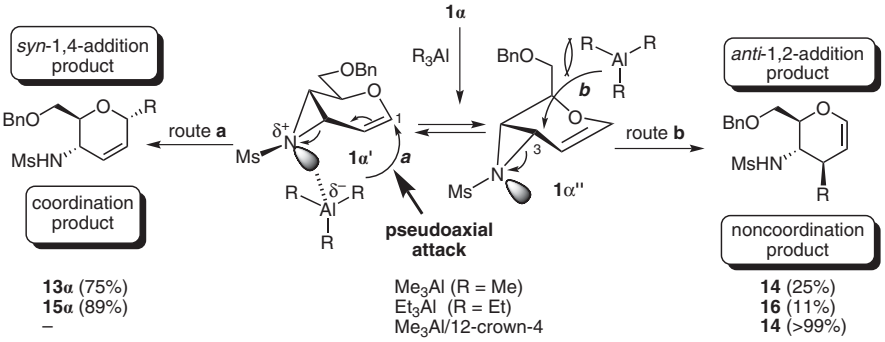
As confirmation of this rationalization, when the azidolysis reaction of **1α** was repeated by using tetrabutylammonium azide, an azide ion species with a noncoordinating and nonprotic counterion (Bu_4N^+), the corresponding noncoordination product, the *trans*-3-azido-4-*N*-(mesylamino) derivative **10** was be the sole reaction product (Scheme 5).

C-Nucleophiles

Alkyl lithium reagents have been shown to react efficiently and stereoselectively with epoxides **2α** and **2β** to give the corresponding *C*-glycosides with the same configuration as that of the starting epoxide (coordination products), in a somewhat rare example of a 1,4-addition of these reagents to a vinyl oxirane system.[9,12,13]

This is not the case with aziridines **1α** and **1β**, where complex reaction mixtures were obtained with both alkyllithium and Grignard reagents. Only trialkylaluminum reagents were effective in transferring a simple alkyl group. In this way, the reaction of **1α** with trimethylaluminum was not regioselective, affording a 75:25 mixture of the *syn*-1,4-α-*C*-glycoside **13α** (the coordination product) and the *anti*-1,2-addition product, the *trans* 3-methyl-4-*N*-mesylamino derivative **14** (the noncoordination product). The ratio of the *syn*-1,4-addition product to the *anti*-1,2-addition product increased to almost 9:1 when triethylaluminum was used, giving the α-*C*-glycoside **15α** and *trans*-3-ethyl-4-*N*-mesylamino derivative **16** as the sole products (Scheme 6).

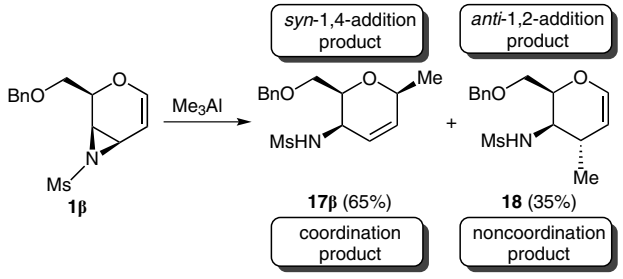
α-*C*-Glycosides **13α** and **15α** are formed as a result of the organometallic nucleophile (which is coordinated to the aziridine nitrogen through the metal) attacking the C(1) carbon from the same side as the coordination, with the aziridine reacting through conformer **1α′**. This attack corresponds to a more favorable pseudoaxial attack (Scheme 6, route a). Even though this process appears to be entropically favored, the presence in the reaction mixture of a proportion of noncoordinated reagent cannot be excluded. The noncoordinated reagent can attack the aziridine at the C(3) allylic carbon in the usual *trans* diaxial fashion, possible with the aziridine reacting through conformer **1α″**, to give the noncoordination products, the *trans*-derivatives **14** (from triethylaluminum) and **16** (from triethyaluminum). In this context, the presence of a certain steric and/or torsional strain between the attacking nucleophile (AlR_3) and the side chain ($-CH_2OBn$, route b) might explain the production of a smaller amount of *anti*-1,2-addition product from triethylaluminum than from trimethylaluminum (Scheme 6).



Scheme 6

We confirmed this rationalization by repeating the reaction of trimethylaluminum with aziridine **1α** in in the presence of 12-crown-4. The presence of the metal-sequestering crown ether prevented coordination of the aziridine nitrogen with the nucleophile and, as a result, the corresponding noncoordination product **14** became the sole reaction product (Scheme 6).

Similar results were obtained in the reaction of the diastereoisomeric aziridine **1β** with trimethylaluminum (*syn*-1,4-addition product **17β**/*anti*-1,2-addition product **18** ratio = 65:35). In this case, the configuration (β) of the starting aziridine and its coordination with the reagent determines the configuration (β) of the only 1,4-addition product that was obtained, the β-*C*-glycoside **17β**, which is the coordination product (Scheme 7).



Scheme 7

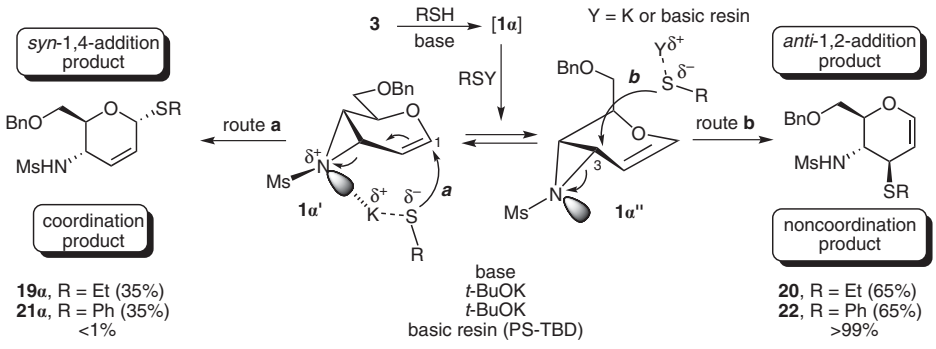
S-Nucleophiles

The reaction of aziridine **1α** with benzenethiol or ethanethiol in the presence of potassium *tert*-butoxide, to effect both the cyclization of the precursor **3** and the deprotonation of the thiol to the corresponding potassium thiolate, gave a 35:65 mixture of the corresponding coordination products, the α-thioglycoside **19α** (R = Et) and **21α** (R = Ph) (Scheme 8, route a; 35%), respectively, and the noncoordination product, the *trans*-4-*N*-(mesylamino)-3-ethylsulfanyl derivative **20** (R = Et) and *trans*-4-*N*-(mesylamino)-3-phenylsulfanyl derivative **22** (R = Ph) (route b, 65%), respectively.

The coordination of the aziridine with the thiolate nucleophile through the metal and attack on the C(1) carbon through conformer **1α′** is responsible, as usual, for the formation of the coordination products.

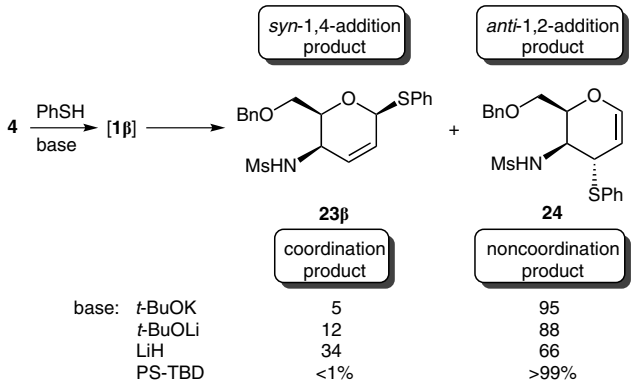
Actually, the noncoordination products **20** (R = Et) and **22** (R = Ph) were the sole products when the reaction was carried out in the presence of a polymer-bound basic catalyst (polystyrene-bound 1,5,7-triazabicyclo[4.4.0]dec-5-ene; TBD resin) to effect both the cyclization of the precursor **3** to aziridine **1α** and the deprotonation of the thiol to give the corresponding thiolate in the absence of any metal counterion.

The same results were also obtained with aziridine **1β** in the reaction with benzenethiol (Scheme 9). In this case, a progressive increase in the yield of the coordination product, the β-phenyl thioglycoside **23β** was observed when base necessary for the formation of the aziridine in situ from *trans N*,*O*-dimesylate **4** was changed from potassi-



Scheme 8

um *tert*-butoxide to lithium *tert*-butoxide and then to lithium hydride, indicating the importance of the metal counterion to the occurrence of a coordination process. The use of the PS-TBD resin simplified the composition of reaction mixture and gave the noncoordination product, the *trans N*-(mesylamino)phenylthio derivative **24**, exclusively (Scheme 9).



Scheme 9

The reactions of aziridines **1α** and **1β** with O-nucleophiles (sodium acetate, tetrabutylammonium methoxide, or tetrabutylammonium trimethylsilanolate), C-nucleophiles (trimethylaluminum or triethylaluminum), N-nucleophiles (tetramethylguanidinium azide or tetrabutylammonium azide), or S-nucleophiles (ethanethiol or benzenethiol) confirmed the marked tendency of these activated vinyl aziridines to show a high-to-complete degree of 1,4-regioselectivity in association with complete *syn*-stereoselectivity (coordination products) in nucleophilic addition reactions when the nucleophile can coordinate the aziridine nitrogen through a metal or by means of a hydrogen bond. On the other hand, the use of reaction conditions where no coordinating agent (metal or protic species) is present leads to complete 1,2-regioselectivity and *anti*-stereoselectivity (noncoordination products) in an elegant regioalternating process.[14]

All reactions were performed under a positive pressure of argon in flame-dried, modified, Schlenk (Kjeldahl-shaped) flasks fitted with glass stoppers or rubber septa. Flash column chromatography was performed on 230–400 mesh silica gel (Macherey-Nagel). Analytical TLC was performed on Alugram SIL G/UV$_{254}$ silica gel sheets (Macherey-Nagel) with detection by 0.5% phosphomolybdic acid soln in 95% EtOH. IR spectra were recorded on a Mattson 3000 FTIR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded at 250 and 62.5 MHz, respectively, on a Bruker Avance II 250 spectrometer. Benzene, toluene, Et_2O, and THF were distilled from sodium/benzophenone. *N*-Mesylaziridines **1α** and **1β** were prepared in situ by cyclization under basic conditions (*t*-BuOK) of the corresponding stable precursors, the *trans*-*N*,*O*-dimesylates **3**[4a] and **4**,[4b] respectively, as previously described. Tetramethylguanidinium azide (TMGA),[15] Bu_4NOTMS,[9a] Bu_4NOMe,[9b] and Bu_4NN_3[16] were prepared as previously described. Bu_4NOMe and Bu_4NN_3 are also commercially available (Aldrich). PS-TBD resin was purchased from Aldrich. The structures of the 1,2- and 1,4-addition products were determined by simple examination of their ^{1}H NMR spectra. The configuration of 1,4-addition products was determined by means of appropriate NOE experiments.

1,5-Anhydro-6-*O*-benzyl-2,4-dideoxy-4-(mesylamino)-D-*arabino*-hex-1-enitol (8)

A soln of dimesylate **3** (0.035 g, 0.090 mmol) in anhyd THF (1.0 mL) containing Bu_4NOTMS [4 equiv, prepared from TBAB (0.116 g, 0.36 mmol) and TMSOK (0.046 g, 0.36 mmol)] was treated with *t*-BuOK (0.010 g, 0.090 mmol, 1 equiv), and the mixture was stirred for 30 min at r.t. The mixture was diluted with Et_2O (15 mL), washed with sat. brine (2 × 2 mL), and concentrated to give a crude product [yield: 0.027 g (96%)] that was purified by flash chromatography [hexanes–EtOAc (3:7)] to give a pale yellow liquid; yield: 0.023 g (81%); R_f = 0.26 (hexanes–EtOAc, 3:7).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.22–7.41 (m, 5 H), 6.42 (dd, *J* = 6.1, 1.1 Hz, 1 H), 4.79–4.96 (m, 1 H), 4.84 (dd, *J* = 6.1, 2.9 Hz, 1 H), 4.59 (s, 2 H), 4.52–4.62 (m, 1 H), 4.15–4.26 (m, 1 H), 3.80–3.85 (m, 3 H), 3.55–3.67 (m, 1 H), 3.04 (s, 3 H).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 144.3, 138.0, 128.6, 127.9, 128.1, 102.9, 75.7, 73.7, 69.5, 67.7, 56.2, 41.3.

Anal. Calcd for $C_{14}H_{19}NO_5S$: C, 53.66; H, 6.12; N, 4.47. Found: C, 53.95; H, 5.91; N, 4.18.

3-*O*-Acetyl-1,5-anhydro-6-*O*-benzyl-2,4-dideoxy-4-(mesylamino)-D-*arabino*-hex-1-enitol (5)

A solution of allyl alcohol **8** (0.020 g, 0.064 mmol) in anhydrous pyridine (0.2 mL) was treated at 0 °C with Ac_2O (0.15 mL) and the reaction mixture was stirred at r.t. for 12 h. Dilution with toluene (3 × 10 mL) and co-evaporation of the organic solvent and reagents at reduced pressure (rotating evaporator) afforded a crude pale yellow liquid consisting of acetate **5**, practically pure; yield: 0.019 g (83%); R_f = 0.32 (hexanes–EtOAc, 1:1).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.24–7.37 (m, 5 H), 6.50 (dd, *J* = 6.3, 0.9 Hz, 1 H), 5.14–5.21 (m, 1 H), 4.82 (dd, *J* = 6.3, 3.9 Hz, 1 H), 4.62–4.67 (m, 1 H), 4.58 (s, 2 H), 4.27 (q, *J* = 5.5 Hz, 1 H), 3.85–3.98 (m, 1 H), 3.76–3.80 (m, 2 H), 3.04 (s, 3 H), 2.05 (s, 3 H).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 170.2, 146.5, 137.2, 130.8, 128.6, 128.0, 98.4, 78.2, 73.8, 68.2, 67.8, 51.6, 42.1, 21.2.

Anal. Calcd for $C_{16}H_{21}NO_6S$: C, 54.07; H, 5.96; N, 3.94. Found: C, 54.26; H, 5.74; N, 3.76.

1-*O*-Acetyl-6-*O*-benzyl-2,3,4-trideoxy-4-(mesylamino)-α-D-*erythro*-hex-2-enopyranose (6α)

A soln of dimesylate **3** (0.021 g, 0.050 mmol) in anhyd DMF (0.5 mL) was treated with anhyd NaOAc (0.009 g, 0.10 mmol, 2 equiv), and the mixture was stirred for 16 h at r.t. The resulting mixture was diluted with sat. aq NaCl (2 mL) and extracted with Et_2O (3 × 10 mL). The extracts were concentrated to give a crude product [yield: 0.016 g (89%)] consisting of a 91:9 mixture of α-acetyl glycoside **6α** and the *trans*-acetoxy derivative **5** (^{1}H NMR) that was purified by preparative TLC (hexanes–EtOAc, 4:6). Extraction of the most intense band gave **6α** as a colorless liquid; yield: 0.012 g (67%); R_f = 0.24 (hexanes–EtOAc, 3:7).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.25–7.38 (m, 5 H), 6.30 (unresolved t, *J* = 1,4 Hz, 1 H), 6.12 (d, *J* = 10.0 Hz, 1 H), 5.83 (dt, *J* = 10.0, 2.6 Hz, 1 H), 4.64 (d, *J* = 11.8 Hz, 1 H), 4.55 (d, *J* = 11.8 Hz, 1 H), 4.51–4.69 (m, 1 H), 4.16–4.31 (m, 1 H), 3.71–3.87 (m, 3 H), 2.89 (s, 3 H), 2.08 (s, 3 H).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 170.2, 137.9, 133.4, 128.9, 128.6, 128.5, 126.2, 88.7, 74.6, 71.9, 69.3, 48.8, 41.7, 21.9.

Anal. Calcd for $C_{16}H_{21}NO_6S$: C, 54.07; H, 5.96; N, 3.94. Found: C, 53.88; H, 5.59; N, 3.60.

1,5-Anhydro-6-*O*-benzyl-2,4-dideoxy-3-*O*-methyl-4-(mesylamino)-D-*arabino*-hex-1-enitol (7)

A soln of dimesylate **3** (0.032 g, 0.082 mmol) in anhyd THF (1 mL) containing Bu_4NOMe (0.090 g, 0.33 mmol, 4 equiv) was treated

with *t*-BuOK (0.009 g, 0.083 mmol) and the mixture was stirred for 2 h at r.t. The resulting mixture was diluted with sat. aq NaCl (2 mL) and extracted with Et_2O (3 × 10 mL). The extracts were concentrated to give a crude product [yield: 0.025 g (93%)] that was purified by flash chromatography [hexanes–EtOAc (1:1)] to give a colorless liquid: yield: 0.018 g (67%); R_f = 0.42 (hexanes–EtOAc, 1:1).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.24–7.38 (m, 5 H), 6.44 (d, *J* = 6.2 Hz, 1 H), 4.93 (dd, *J* = 6.2, 3.8 Hz, 1 H), 4.50–4.62 (m, 1 H), 4.57 (s, 2 H), 4.10–4.22 (m, 1 H), 3.71–3.87 (m, 4 H), 3.38 (s, 3 H), 3.06 (s, 3 H).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 145.1, 138.1, 128.6, 128.1, 128.0, 99.2, 75.0, 73.8, 69.0, 55.7, 51.8, 42.0.

Anal. Calcd for $C_{15}H_{21}NO_5S$: C, 55.03; H, 6.46; N, 4.28. Found: C, 54.71; H, 6.15; N, 4.17.

Reaction of Aziridine 1α with TMGA

A soln of dimesylate **3** (0.051 g, 0.13 mmol) in anhyd benzene (2 mL) was treated with *t*-BuOK (0.015 g, 0.13 mmol, 1 equiv) in the presence of TMGA (0.082 g, 0.52 mmol, 4 equiv), and the mixture was stirred for 4 h at r.t. The resulting mixture was partitioned between Et_2O (15 mL) and brine (3 mL), and the aqueous layer was further extracted with Et_2O (3 × 8 mL). The combined organic extracts were concentrated to give a crude product [yield: 0.042 g (95%)] consisting of a 70:15:15 mixture of *trans*-azido derivative **10**, the *cis*-azido derivative **12**, and the α-glycosyl azide **11α** (^{1}H NMR) that was separated by flash chromatography [CH_2Cl_2–EtOAc (9:1)] to give **10** and **12**.

1,5-Anhydro-3-azido-6-*O*-benzyl-2,3,4-trideoxy-4-(mesylamino)-D-*arabino*-hex-1-enitol (10)

Pale yellow liquid: yield: 0.020 g (45%); R_f = 0.28 (CH_2Cl_2–EtOAc, 9:1).

IR (neat): 2106 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.24–7.41 (m, 5 H), 6.52 (dd, *J* = 6.1, 1.5 Hz, 1 H), 5.10 (d, *J* = 8.6 Hz, 1 H), 4.81 (dd, *J* = 6.1, 2.6 Hz, 1 H), 4.62 (d, *J* = 11.7 Hz, 1 H), 4.55 (d, *J* = 11.7 Hz, 1 H), 3.90–4.12 (m, 2 H), 3.74–3.88 (m, 2 H), 3.65 (q, *J* = 8.8 Hz, 1 H), 3.08 (s, 3 H).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 145.5, 137.8, 128.6, 128.2, 128.1, 97.8, 77.0, 73.9, 69.1, 58.7, 53.3, 42.6.

Anal. Calcd for $C_{14}H_{18}N_4O_4S$: C, 49.69; H, 5.36; N, 16.56. Found: C, 49.50; H, 5.09; N, 16.74.

1,5-Anhydro-3-azido-6-*O*-benzyl-2,3,4-trideoxy-4-(mesylamino)-D-*ribo*-hex-1-enitol (12)

Pale yellow liquid; yield: 0.004 g (9%); R_f = 0.62 (CH_2Cl_2–EtOAc, 9:1).

IR (neat): 2105 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.30–7.38 (m, 5 H), 6.62 (d, *J* = 5.9 Hz, 1 H), 4.96 (t, *J* = 5.9 Hz, 1 H), 4.83 (d, *J* = 8.7 Hz, 1 H), 4.63 (d, *J* = 11.9 Hz, 1 H), 4.56 (d, *J* = 11.9 Hz, 1 H), 4.18–4.25 (m, 1 H), 3.78–3.96 (m, 4 H), 2.94 (s, 3 H).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 147.9, 137.4, 128.7, 128.1, 127.9, 95.7, 74.1, 73.2, 68.7, 55.2, 50.9.

The ^{1}H NMR spectrum of *cis*-azido alcohol **12** showed the presence (10%) of the α-glycosyl azide **11α**. Neither **12** nor **11α** could be obtained in a pure form.

11α: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.05 (dt, *J* = 10.1, 1.2 Hz, 1 H), 5.77 (dt, *J* = 10.1, 2.2 Hz, 1 H), 5.57–5.60 (m, 1 H, H-1).

1,5-Anhydro-3-azido-6-*O*-benzyl-2,3,4-trideoxy-4-(mesylamino)-D-*xylo*-hex-1-enitol (9)

A soln of dimesylate **4** (0.051 g, 0.13 mmol) in anhyd MeCN (1.5 mL) was treated with *t*-BuOK (0.015 g, 0.13 mmol, 1 equiv) in the presence of TMGA (0.082 g, 0.52 mmol, 4 equiv) and the mixture was stirred for 30 min at r.t. The crude reaction product [yield: 0.043 g (98%)] was purified by flash chromatography [hexanes–EtOAc (1:1) to give a pale yellow liquid: yield: 0.034 g (77%); R_f = 0.36 (hexanes–EtOAc, 1:1).

IR (neat): 2106 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.24–7.42 (m, 5 H), 6.67 (d, *J* = 6.0 Hz, 1 H), 4.95 (td, *J* = 6.0, 1.5 Hz, 1 H), 4.75 (d, *J* = 9.3 Hz, 1 H), 4.57 (s, 2 H), 4.07–4.19 (m, 1 H), 3.95 (dd, *J* = 5.3, 2.2 Hz, 1 H), 3.61–3.79 (m, 3 H), 2.90 (s, 3 H).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 148.4, 137.2, 128.8, 128.3, 128.2, 96.0, 74.0, 71.4, 68.2, 55.5, 51.1, 41.4.

Anal. Calcd for $C_{14}H_{18}N_4O_4S$: C, 49.69; H, 5.36; N, 16.56. Found: C, 49.35; H, 5.11; N, 16.29.

Reaction of Aziridine 1α with Tetrabutylammonium Azide

A soln of dimesylate **3** (0.024 g, 0.061 mmol) in anhyd MeCN (1 mL) was treated with *t*-BuOK (0.007 g, 0.061 mmol, 1 equiv) and Bu_4NN_3 (0.052 g, 0.18 mmol, 3 equiv), and the mixture was stirred for 2 h at r.t. The usual workup gave practically pure product **10** (^{1}H NMR); yield: 0.018 g (87%).

Reaction of Aziridine 1α with Me_3Al

A soln of dimesylate **3** (0.056 g, 0.143 mmol) in anhyd toluene (1 mL) was treated with *t*-BuOK (0.016 g, 0.014 mmol, 1 equiv) and a 2.0 M soln of Me_3Al in toluene (0.215 mL, 0.43 mmol, 3 equiv), and the mixture was stirred for 18 h at r.t. The soln was then partitioned between Et_2O (20 mL) and brine (8 mL), and the aqueous layer was extracted with Et_2O (2 × 10 mL). The combined organic extracts were concentrated to give a crude product [yield: 0.042 g (94%)] consisting of a 75:25 mixture of α-*C*-glycoside **13α** and *trans*-methyl derivative **14** (^{1}H NMR). This was separated by preparative TLC [hexanes–EtOAc (6:4)]. Extraction of the two most intense bands gave pure **13α** and **14** (faster band).

(1*R*)-1,5-Anhydro-6-*O*-benzyl-2,3,4-trideoxy-1-methyl-4-(mesylamino)-D-*erythro*-hex-2-enitol (13α)

Colorless liquid: yield: 0.020 g (44%); R_f = 0.23 (hexanes–EtOAc, 1:1).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.24–7.39 (m, 5 H), 5.78–5.82 (m, 2 H), 4.58 (s, 2 H), 4.45–4.60 (m, 1 H), 4.24–4.40 (m, 1 H), 3.77–3.97 (m, 2 H), 3.58–3.74 (m, 2 H), 2.92 (s, 3 H), 1.25 (d, *J* = 6.8 Hz, 3 H).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 137.8, 134.0, 128.6, 128.1, 128.0, 124.7, 73.8, 73.2, 69.1, 67.4, 48.0, 41.9, 19.7.

Anal. Calcd for $C_{15}H_{21}NO_4S$: C, 57.86; H, 6.80; N, 4.50. Found: C, 57.55; H, 6.53; N, 4.32.

1,5-Anhydro-6-*O*-benzyl-2,3,4-trideoxy-3-methyl-4-(mesylamino)-D-*arabino*-hex-1-enitol (14)

Colorless liquid: yield: 0.006 g (13%); R_f = 0.38 (hexanes–EtOAc, 1:1).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.24–7.39 (m, 5 H), 6.25 (dd, *J* = 6.1, 2.2 Hz, 1 H), 4.61 (d, *J* = 11.2 Hz, 1 H), 4.52 (d, *J* = 11.2 Hz, 1 H), 4.44–4.53 (m, 2 H), 4.20 (q, *J* = 5.8 Hz, 1 H), 3.61–3.81 (m, 2 H), 3.55 (dd, *J* = 10.0, 6.1 Hz, 1 H), 2.97 (s, 3 H), 2.35–2.54 (m, 1 H), 1.06 (d, *J* = 7.1 Hz, 3 H).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 141.6, 137.7, 128.7, 128.1, 104.3, 75.6, 73.8, 69.2, 51.8, 42.2, 26.9, 16.7.

Anal. Calcd for $C_{15}H_{21}NO_4S$: C, 57.86; H, 6.80; N, 4.50. Found: C, 57.64; H, 6.65; N, 4.26.

Reaction of Aziridine 1α with Et_3Al

By following the typical procedure, a soln of dimesylate **3** (0.062 g, 0.16 mmol) in anhyd toluene (2 mL) was treated with *t*-BuOK (0.018 g, 0.16 mmol, 1 equiv) and a 1.9 M soln of Et_3Al in toluene (0.25 mL, 0.48 mmol, 3 equiv). The crude product [yield: 0.048 g (92%)] consisted of an 89:11 mixture of α-*C*-glycoside **15α** and the *trans*-ethyl derivative **16** (^{1}H NMR), which was subjected to prepar-

ative TLC [hexanes–EtOAc (1:1)]. Extraction of the two most intense bands gave pure **15α** and **16** (faster band).

(1*R*)-1,5-Anhydro-6-*O*-benzyl-2,3,4-trideoxy-1-ethyl-4-(mesylamino)-D-*erythro*-hex-2-enitol (15α)
Colorless liquid; yield: 0.029 g (55%); R_f = 0.30 (hexanes–EtOAc, 1:1).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.27–7.38 (m, 5 H), 5.78–5.89 (m, 2 H), 4.61 (d, *J* = 12.0 Hz, 1 H), 4.55 (d, *J* = 12.0 Hz, 1 H), 4.48 (d, *J* = 9.3 Hz, 1 H, NH), 4.01–4.09 (m, 1 H), 3.88–3.94 (m, 1 H), 3.83 (q, *J* = 5.1 Hz, 1 H), 3.71 (dd, *J* = 10.1, 5.3 Hz, 1 H), 3.63 (dd, *J* = 10.1, 5.1 Hz, 1 H), 2.93 (s, 3 H), 1.58 (q, *J* = 7.4 Hz, 2 H), 0.97 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 138.3, 133.2, 128.8, 128.2, 125.1, 73.9, 73.5, 72.5, 69.4, 48.5, 42.1, 27.1, 10.1.

Anal. Calcd for $C_{16}H_{23}NO_4S$: C, 59.05; H, 7.12; N, 4.30. Found: C, 58.65; H, 6.89; N, 4.11.

1,5-Anhydro-6-*O*-benzyl-2,3,4-trideoxy-3-ethyl-4-(mesylamino)-D-*arabino*-hex-1-enitol (16)
Colorless liquid; yield: 0.003 g (6%); R_f = 0.40 (hexanes–EtOAc, 1:1).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.24–7.38 (m, 5 H), 6.26 (dd, *J* = 6.3, 2.5 Hz, 1 H), 4.62 (d, *J* = 12.0 Hz, 1 H), 4.50 (d, *J* = 12.0 Hz, 1 H), 4.45–4.58 (m, 3 H), 4.23–4.37 (m, 1 H), 3.74–3.89 (m, 1 H), 3.64 (dd, *J* = 10.0, 6.4 Hz, 1 H), 3.48 (dd, *J* = 10.0, 6.1 Hz, 1 H), 2.99 (s, 3 H), 1.30 (q, *J* = 7.4 Hz, 2 H), 0.96 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 141.6, 137.7, 128.7, 128.1, 102.2, 73.8, 68.9, 50.3, 42.5, 33.2, 27.5, 23.9, 11.3.

Anal. Calcd for $C_{16}H_{23}NO_4S$: C, 59.05; H, 7.12; N, 4.30. Found: C, 58.89; H, 6.95; N, 4.15.

Reaction of Aziridine 1β with Me_3Al
By following the typical procedure, a soln of dimesylate **4** (0.031 g, 0.080 mmol) in anhyd toluene (1 mL) was treated with *t*-BuOK (0.009 g, 0.080 mmol, 1 equiv) and a 2.0 M soln of Me_3Al in toluene (0.12 mL, 0.24 mmol, 3 equiv) to give a crude product [yield: 0.024 g (96%)] consisting of a 65:35 mixture of β-*C*-glycoside **17β** and *trans*-methyl derivative **18** (^{1}H NMR), which was subjected to preparative TLC [hexanes–EtOAc, (6:4)]. Extraction of the two most intense bands gave pure **17β** and **18** (faster band).

(1*S*)-1,5-Anhydro-6-*O*-benzyl-2,3,4-trideoxy-1-methyl-4-(mesylamino)-D-*threo*-hex-2-enitol (17β)
Colorless liquid: yield: 0.012 g (48%); R_f = 0.24 (hexanes–EtOAc, 6:4).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.27–7.41 (m, 5 H), 6.02 (ddd, *J* = 10.1, 5.5, 1.9 Hz, 1 H), 5.85 (dd, *J* = 10.1, 2.9 Hz, 1 H), 4.59 (d, *J* = 11.8 Hz, 1 H), 4.53 (d, *J* = 11.8 Hz, 1 H), 4.56 (d, *J* = 10.0 Hz, 1 H, NH), 4.31–4.47 (m, 1 H), 4.04 (td, *J* = 6.1, 2.6 Hz, 1 H), 3.79 (ddd, *J* = 10.0, 5.5, 2.6 Hz, 1 H), 3.69 (dd, *J* = 9.8, 6.5 Hz, 1 H), 3.61 (dd, *J* = 9.8, 6.1 Hz, 1 H), 2.94 (s, 3 H), 1.26 (d, *J* = 6.8 Hz, 3 H).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 137.9, 134.2, 128.6, 128.0, 127.9, 125.1, 73.8, 69.9, 69.8, 68.9, 47.3, 42.0, 18.2.

Anal. Calcd for $C_{15}H_{21}NO_4S$: C, 57.86; H, 6.80; N, 4.50. Found: C, 57.48; H, 6.57; N, 4.32.

1,5-Anhydro-6-*O*-benzyl-2,3,4-trideoxy-3-methyl-4-(mesylamino)-D-*xylo*-hex-1-enitol (18)
Pale yellow liquid: yield: 0.005 g (20%); R_f = 0.30 (hexanes–EtOAc, 1:1).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.28–7.40 (m, 5 H), 6.37 (t, *J* = 2.5 Hz, 1 H), 4.81 (t, *J* = 2.5 Hz, 1 H), 4.59 (d, *J* = 12.0 Hz, 1 H), 4.53 (d, *J* = 12.0 Hz, 1 H), 4.38 (d, *J* = 10.7 Hz, 1 H, NH), 4.20–4.30 (m, 1 H), 3.77–3.90 (m, 1 H), 3.56–3.70 (m, 2 H), 3.34–3.46 (m, 1 H), 2.92 (s, 3 H), 1.24 (d, *J* = 6.7 Hz, 3 H).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 143.0, 135.0, 128.7, 128.1, 128.0, 99.7, 79.4, 75.4, 72.2, 52.4, 42.1, 29.9, 21.1.

Anal. Calcd for $C_{15}H_{21}NO_4S$: C, 57.86; H, 6.80; N, 4.50. Found: C, 57.55; H, 6.51; N, 4.25.

Reaction of Aziridine 1α with Trimethylaluminum in the Presence of 12-Crown-4
A 2.0 M soln of Me_3Al in toluene (0.12 mL, 0.24 mmol, 3 equiv) was treated with 12-crown-4 (0.044 g, 0.040 mL, 0.25 mmol) in anhyd toluene (1 mL), and the mixture was stirred for 18 h at r.t. Dimesylate **3** (0.031 g, 0.080 mmol) and *t*-BuOK (0.009 g, 0.080 mmol, 1 equiv) were added and the mixture was stirred for a further 18 h at r.t. The mixture was then diluted with Et_2O and the organic phase was washed with sat. brine, and concentrated to give a mixture of the *trans*-methyl derivative **14** and excess crown ether (^{1}H NMR).

Reaction of Aziridine 1α with EtSH
By following the typical procedure; a soln of dimesylate **3** (0.031 g, 0.080 mmol) in anhyd benzene (2.2 mL) was treated with *t*-BuOK (0.009 g, 0.080 mmol) and EtSH (0.015 g, 0.018 mL, 0.24 mmol, 3 equiv) to give a crude product [yield: 0.027 g (94%)] consisting of a 35:65 mixture of thioglycoside **19α** and *trans*-ethysulfanyl derivative **20** (^{1}H NMR), which was subjected to preparative TLC [hexanes–CH_2Cl_2–*i*-Pr_2O (3:5:2)]. Extraction of the two most intense bands gave pure **19α** and **20** (faster band).

Ethyl 6-*O*-Benzyl-2,3,4-trideoxy-4-(mesylamino)-1-thio-α-D-*erythro*-hex-2-enopyranoside (19α)
Pale yellow liquid; yield: 0.006 g (21%); R_f = 0.25 (hexanes–EtOAc, 1:1).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.22–7.41 (m, 5 H), 5.94 (dd, *J* = 10.7, 2.3 Hz, 1 H), 5.85 (d, *J* = 10.7 Hz, 1 H), 5.58 (br s, 1 H), 4.67 (d, *J* = 11.8 Hz, 1 H), 4.56 (d, *J* = 11.8 Hz, 1 H), 4.24–4.31 (m, 2 H), 3.94–4.05 (m, 1 H), 3.83 (dd, *J* = 10.8, 3.5 Hz, 1 H), 3.71 (dd, *J* = 10.8, 2.7 Hz, 1 H), 2.88 (s, 3 H), 2.55–2.81 (m, 2 H), 1.29 (t, *J* = 7.5 Hz, 3 H).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 137.9, 129.3, 129.2, 128.7, 128.2, 128.1, 80.0, 74.0, 69.5, 69.3, 48.6, 41.7, 26.3, 15.5.

Anal. Calcd for $C_{16}H_{23}NO_4S_2$: C, 53.76; H, 6.49; N, 3.92. Found: C, 53.39; H, 6.24; N, 3.77.

1,5-Anhydro-6-*O*-benzyl-2,3,4-trideoxy-3-(ethylsulfanyl)-4-(mesylamino)-*arabino*-hex-1-enitol (20)
Pale yellow liquid; yield: 0.015 g (52%); R_f = 0.38 (hexanes–EtOAc, 1:1).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.24–7.40 (m, 5 H), 6.44 (dd, *J* = 6.0, 1.9 Hz, 1 H), 4.80 (dd, *J* = 6.0, 3.2 Hz, 1 H), 4.49–4.61 (m, 1 H), 4.62 (d, *J* = 11.7 Hz, 1 H), 4.55 (d, *J* = 11.7 Hz, 1 H), 3.70–4.10 (m, 4 H), 3.29–3.37 (m, 1 H), 3.13 (s, 3 H), 2.61 (q, *J* = 7.4 Hz, 2 H), 1.26 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 144.4, 137.9, 128.6, 128.2, 128.0, 101.9, 78.0, 73.7, 69.6, 53.5, 43.5, 43.0, 23.8, 14.8.

Anal. Calcd for $C_{16}H_{23}NO_4S_2$: C, 53.76; H, 6.49; N, 3.92. Found: C, 53.41; H, 6.18; N, 3.71.

Reaction of Aziridine 1α with PhSH
By following the typical procedure, a soln of dimesylate **3** (0.040 g, 0.10 mmol) in anhyd benzene (3 mL) was treated with *t*-BuOK (0.011 g, 0.10 mmol) and PhSH (0.033 g, 0.030 mL, 0.30 mmol, 3 equiv) to give, after 48 h stirring at r.t., a crude product [yield: 0.038 g (94%)] consisting of a 35:65 mixture of thioglycoside **21α** and *trans*-phenylsulfanyl derivative **22** (^{1}H NMR), which was subjected to preparative TLC [hexanes–CH_2Cl_2–*i*-Pr_2O (4:3:3)]. Extraction of the two most intense bands gave pure **21α** (faster band) and **22**.

Phenyl 6-*O*-Benzyl-2,3,4-trideoxy-4-(mesylamino)-1-thio-α-D-*erythro*-hex-2-enopyranoside (21α)
Pale yellow liquid; yield: 0.010 g (24%); R_f = 0.28 (hexanes–CH_2Cl_2–*i*-Pr_2O, 4:3:3).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.47–7.58 (m, 2 H), 7.21–7.40 (m, 8 H), 6.06 (ddd, *J* = 10.0, 2.9, 1.8 Hz, 1 H), 5.93 (dt, *J* = 10.0, 1.4 Hz, 1 H), 5.73–5.80 (m, 1 H), 4.66 (d, *J* = 11.8 Hz, 1 H), 4.56 (d, *J* = 11.8 Hz, 1 H), 4.08–4.45 (m, 3 H), 3.86 (dd, *J* = 10.8, 3.8 Hz, 1 H), 3.78 (dd, *J* = 10.8, 2.6 Hz, 1 H), 2.91 (s, 3 H).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 137.9, 134.9, 132.0, 129.2, 128.7, 128.6, 128.2, 128.1, 127.8, 83.7, 73.9, 70.1, 69.3, 48.6, 41.8.

Anal. Calcd for $C_{20}H_{23}NO_4S_2$: C, 59.24; H, 5.72; N, 3.45. Found: C, 59.05; H, 5.41; N, 3.12.

1,5-Anhydro-6-*O*-benzyl-2,3,4-trideoxy-3-(phenylsulfanyl)-4-(mesylamino)-D-*arabino*-hex-1-enitol (22)
Pale yellow liquid: yield: 0.021 g (51%); R_f = 0.24 (hexanes–CH_2Cl_2–*i*-Pr_2O, 4:3:3).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.41–7.53 (m, 2 H), 7.23–7.40 (m, 8 H), 6.42 (dd, *J* = 6.0, 1.4 Hz, 1 H), 4.81–4.94 (m, 2 H), 4.64 (d, *J* = 11.8 Hz, 1 H), 4.57 (d, *J* = 11.8 Hz, 1 H), 4.06–4.24 (m, 2 H), 3.71–3.98 (m, 3 H), 2.93 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 144.5, 137.9, 133.2, 133.1, 129.5, 128.6, 128.2, 128.0, 100.7, 77.8, 73.7, 69.4, 52.8, 46.4, 42.6.

Anal. Calcd for $C_{20}H_{23}NO_4S_2$: C, 59.24; H, 5.72; N, 3.45. Found: C, 59.19; H, 5.54; N, 3.39.

Reaction of Aziridine 1β with PhSH
By following the typical procedure, a soln of dimesylate **4** (0.050 g, 0.13 mmol) in anhyd benzene (3.0 mL) was treated with *t*-BuOK (0.015 g, 0.13 mmol) and PhSH (0.014 g, 0.013 mL, 0.39 mmol, 3 equiv) to give a crude product [yield: 0.051 g (97%)] consisting of a 5:95 mixture of thioglycoside **23β** and *trans*-phenylsulfanyl derivative **24** (^{1}H NMR), which was subjected to preparative TLC [hexanes–CH_2Cl_2–*i*-Pr_2O (4:3:3)]. Extraction of the two most intense bands (the faster band contained **23β**) gave pure **24**.

1,5-Anhydro-6-*O*-benzyl-2,3,4-trideoxy-3-(phenylsulfanyl)-4-(mesylamino)-D-*xylo*-hex-1-enitol (24)
Pale yellow liquid; yield: 0.035 g (66%)]; R_f = 0.26 (hexanes–CH_2Cl_2–*i*-Pr_2O, 4:3:3).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.45–7.57 (m, 2 H), 7.23–7.42 (m, 8 H), 6.55 (d, *J* = 6.1 Hz, 1 H), 4.94 (t, *J* = 6.1 Hz, 1 H), 4.71 (d, *J* = 9.3 Hz, 1 H, NH), 4.54–4.65 (m, 1 H), 4.57 (s, 2 H), 3.61–3.83 (m, 4 H), 2.64 (s, 3 H).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 146.6, 137.6, 133.6, 132.2, 129.5, 128.7, 128.2, 128.0, 98.5, 73.8, 70.9, 68.8, 51.2, 45.7, 41.1.

Anal. Calcd for $C_{20}H_{23}NO_4S_2$: C, 59.24; H, 5.72; N, 3.45. Found: C, 59.11; H, 5.35; N, 3.22.

Reaction of Aziridine 1α with Benzenethiol in the Presence of a Polymer-Bound Basic Catalyst (PS-TBD); Typical Procedure
A soln of dimesylate **3** (0.016 g, 0.040 mmol) in anhyd THF (1 mL) was treated with PS-TBD resin (0.080 g) and PhSH (0.018 g, 0.016 mL, 0.16 mmol, 4 equiv), and the mixture was stirred for 18 h at r.t. The mixture was then diluted with Et_2O (15 mL) and the organic phase was filtered, washed with sat. brine (2 × 2 mL), and concentrated to give crude product consisting of practically pure *trans*-phenylsulfanyl derivative **22** (^{1}H NMR); yield: 0.015 g (92%).

Reaction of Aziridine 1α with Ethanethiol in the Presence of PS-TBD
By following the typical procedure, a soln of dimesylate **3** (0.036 g, 0.092 mmol) in anhyd THF (1.4 mL) was treated with PS-TBD resin (0.19 g) and EtSH (0.017 g, 0.020 mL, 0.27 mmol, 3 equiv) to give a crude product consisting of practically pure *trans*-ethylsulfanyl derivative **20** (^{1}H NMR); yield: 0.028 g (85%).

Reaction of Aziridine 1β with Benzenethiol in the Presence of PS-TBD
By following the typical procedure, a soln of dimesylate **4** (0.014 g, 0.035 mmol) in anhyd THF (0.5 mL) was treated with PS-TBD resin (0.076 g) and PhSH (0.016 g, 0.014 mL, 0.14 mmol, 4 equiv) to give a crude product consisting of practically pure *trans*-phenylsulfanyl derivative **24** (^{1}H NMR); yield: 0.030 g (91%).

Reaction of Aziridine 1β with Benzenethiol in the Presence of Lithium *tert*-Butoxide
A soln of dimesylate **4** (0.017 g, 0.043 mmol) in anhyd benzene (1.2 mL) was treated with *t*-BuOLi (0.0034 g, 0.042 mmol, 1 equiv) and PhSH (0.014 g, 0.013 mL, 0.13 mmol, 3 equiv), and the mixture was stirred for 2 h at r.t. The resulting mixture was diluted with sat. aq NaCl (2 mL) and extracted with Et_2O (2 × 10 mL). The extracts were concentrated to give a crude product [yield: 0.014 g (80%)] consisting of a 12:88 mixture of thioglycoside **23β** and *trans*-phenylsulfanyl derivative **24** (^{1}H NMR).

Reaction of Aziridine 1β with Benzenethiol in the Presence of Lithium Hydride
A soln of dimesylate **4** (0.052 g, 0.132 mmol) in anhyd toluene (4 mL) was treated with LiH (0.004 g, 0.53 mmol, 4 equiv) and PhSH (0.044 g, 0.040 mL, 0.40 mmol, 3 equiv), and the mixture was stirred for 48 h at r.t. The resulting mixture was diluted with sat. aq NaCl (2 mL) and extracted with Et_2O (2 × 10 mL). The extracts were concentrated to give a crude product [yield: 0.047 g (88%)] consisting of a 66:34 mixture of *trans*-phenylsulfanyl derivative **24** and thioglycoside **23β** (^{1}H NMR), which was subjected to preparative TLC [hexanes–CH_2Cl_2–*i*-Pr_2O (4:3:3)]. Extraction of the two most intense bands gave **24** [yield: 0.021 g (39%)] and **23β**.

Phenyl 6-*O*-Benzyl-2,3,4-trideoxy-4-(mesylamino)-1-thio-β-D-*threo*-hex-2-enopyranoside (23β)
Pale yellow liquid: yield: 0.009 g (16%); R_f = 0.34 (hexanes–CH_2Cl_2–*i*-Pr_2O, 4:3:3).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.48–7.60 (m, 2 H), 7.22–7.45 (m, 8 H), 5.88–6.07 (m, 2 H), 5.51 (s, 1 H, H-1), 4.55 (s, 2 H), 3.87–3.98 (m, 1 H), 3.59–3.78 (m, 3 H), 3.43 (d, *J* = 10.6 Hz, 1 H, NH), 2.75 (s, 3 H).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 137.9, 135.5, 131.2, 130.7, 129.4, 129.1, 128.7, 128.4, 128.0, 81.4, 75.9, 73.9, 69.6, 46.7, 42.0.

Anal. Calcd for $C_{20}H_{23}NO_4S_2$: C, 59.24; H, 5.72; N, 3.45. Found: C, 58.91; H, 5.49; N, 3.17.

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(5) *Reaction conditions*: Protocol A: the nucleophile is also the solvent for the reaction. Protocol B: only 3–4 equiv of the nucleophile are present in MeCN or benzene as the solvent. The complete 1,4-regioselectivity and directly substrate-dependent; stereoselectivity found in the glycosylation of alcohols by aziridines **1α** and **1β** was always observed under Protocol B conditions and, in the case of *t*-BuOH, also under Protocol A conditions; see also ref. 4.
(6) In this framework, *anti*-1,2- and *anti*-1,4-addition products, which are assumed to derive from attack of a free noncoordinated nucleophile, are simply named noncoordination products. The coordination and noncoordination product nomenclature is used throughout the text for appropriate modes of formation.
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