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## ACS Publications

## Supplementary Material

## THE TOTAL SYNTHESIS OF ALLOSAMIDIN

# Expansions Of The Methodology Of Azaglycosylation Pursuant to the Total Synthesis of 

Allosamidin. A Surprising Enantiotopic Sense for a Lipase Induced De-acetylation

David A. Griffith and Samuel J. Danishefsky ${ }^{* i}$

Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06511.

## Supplementary Material

Experimentals and characterizations which are not part of the pathway leading to allosamidin are provided as Supplementary Material. This includes the procedures for the preparation of compounds ent-8, ent-20, ent-24-ent-27, 41-44, 5058, 64, 66-71, 73-78, and 81-84. (38 Pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.
[1S-(1 $\alpha, 2 \beta, 3 \alpha)]-2-[(B e n z y l o x y) m e t h y l]-4-c y c l o p e n t e n e-1,3-d i o l$ Monocarbamate (ent20).

To a $0{ }^{\circ} \mathrm{C}$ solution of monoacetate ent-19 (4.77 g, 18.2 mmol ) in dichloromethane ( 60 mL ) was added pyridine ( 3.7 mL ) and phenyl chloroformate ( $2.7 \mathrm{~mL}, 22$ mmol ). The mixture was stirred 15 min , then diluted with diethyl ether ( 300 mL ), washed with water $(50 \mathrm{~mL}), 1 \mathrm{M} \mathrm{HCl}(3 \times 50 \mathrm{~mL})$, saturated $\mathrm{NaHCO}_{3}(50 \mathrm{~mL})$, and brine ( 50 mL ), dried $\left(\mathrm{MgSO}_{4}\right)$, and concentrated. The phenyl carbonate thus produced was treated with methanolic ammonia ( 200 mL ) for 4 h , deacetylated with added aq. $\mathrm{K}_{2} \mathrm{CO}_{3}$ ( $4 \mathrm{~g}, 30 \mathrm{mmol}$ ) for an additional 14 h , and quenched with solid $\mathrm{NH}_{4} \mathrm{Cl}(4 \mathrm{~g})$. The mixture was then concentrated to $1 / 3$ volume, diluted with ethyl acetate $(200 \mathrm{~mL})$, filtered through Celite, concentrated, and filtered through a plug of silica ( $33 \rightarrow 50 \%$ ethyl acetate in diethyl ether). The residue was recrystallized to provide the desired carbamate (ent-20; $3.39 \mathrm{~g}, 71 \%$ ) as flaky, colorless crystals: mp $114-114.5^{\circ} \mathrm{C} ;[\alpha]_{\mathrm{D}}-57.7^{\circ}$ (c 1.1, THF); Anal. Calcd for $\mathrm{C}_{14} \mathrm{H}_{17} \mathrm{NO}_{4}: \mathrm{C}, 63.86 ; \mathrm{H}, 6.51 ; \mathrm{N}$, 5.32. Found: C, 63.64; H, 6.23; N, 5.31.
[3aS-(3a $\alpha, 6 \alpha, 6 a \alpha)]-6-[($ Benzyloxy)methyl]-3,3a,6,6a-tetrahydro-2H-cyclopentoxazol-2one (ent-24).

Cyclization of ent-20 ( $518 \mathrm{mg}, 1.97 \mathrm{mmol}$ ), as was described in the synthesis 24, gave the desired oxazolone (ent-24; $1.74 \mathrm{~g}, 63 \%$ ) as an off-white solid (mp 84.5-86 ${ }^{\circ} \mathrm{C}$ ). A portion was recrystallized (diethyl ether/hexanes) to provide colorless
crystals: $\mathrm{mp} 87.5-88^{\circ} \mathrm{C}$; $[\alpha]_{\mathrm{D}}+206^{\circ}$ ( $c 1.0, \mathrm{CHCl}_{3}$ ); Anal. Calcd for $\mathrm{C}_{14} \mathrm{H}_{15} \mathrm{NO}_{3}: \mathrm{C}, 68.56$; H, 6.16; N, 5.71. Found: C, 68.38; H, 6.11; N, 5.99.
[3aS-(3a $\alpha, 6 \alpha, 6 a \alpha)]-6-[(B e n z y l o x y) m e t h y l]-3,6 a-d i h y d r o-N, N$-dimethyl-6H-cyclopent-oxazol-2-amine (ent-25).

Conversion of oxazolone ent-24 ( $310 \mathrm{mg}, 1.26 \mathrm{mmol}$ ) to aminooxazoline ent25 ( $266 \mathrm{mg}, 77 \%$ ) occurred as described in the synthesis of $\mathbf{2 5}$ to provide a yellow oil: $[\alpha]_{D}+209^{\circ}\left(c\right.$ 1.1, $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ ); Anal. Calcd for $\mathrm{C}_{16} \mathrm{H}_{20} \mathrm{~N}_{2} \mathrm{O}_{2}$ : $\mathrm{C}, 70.56 ; \mathrm{H}, 7.40 ; \mathrm{N}, 10.28$. Found: C, 70.84; H, 7.11; N, 10.33.
[1aR-(1a $\alpha, 1 \mathrm{~b} \alpha, \mathbf{4 a \alpha}, 5 \alpha, 5 \mathrm{a} \alpha)]-5-[(B e n z y l o x y) m e t h y l]-N, N$-dimethyl-1a,1b,4a,5a-tetra-hydro-5H-oxireno[4,5]cyclopent[1,2-d]oxazol-3-amine (ent-26) and 6-O-Benzyl-(+)allosamizoline (ent-27).

Oxidation of ent-25 ( $230 \mathrm{mg}, 0.844 \mathrm{mmol}$ ), and subsequent hydrolysis, provided ent-26 ( $79 \mathrm{mg}, 32 \%$ ) and ent-27 ( $118 \mathrm{mg}, 46 \%$ ) as described for 26 and 27. 26: light-yellow syrup: $[\alpha]_{\mathrm{D}}+88.9^{\circ}$ ( c 1.1, $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ ); Anal. Calcd for $\mathrm{C}_{16} \mathrm{H}_{20} \mathrm{~N}_{2} \mathrm{O}_{3}$ : $\mathrm{C}, 66.65$; H, 6.99; N, 9.72. Found: C, 66.43; H, 6.71; N, 9.45. ent-27: A portion of the off-white solid was recrystallized (ethyl acetate/methanol/hexanes) to provide light, colorless crystals: mp 144-145 ${ }^{\circ} \mathrm{C}$; $[\alpha]_{\mathrm{D}}-15.2^{\circ}$ (c 1.2, $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ ); Anal. Calcd for $\mathrm{C}_{16} \mathrm{H}_{22} \mathrm{~N}_{2} \mathrm{O}_{4}$ : C , 62.73; H, 7.24; N, 9.14. Found: C, 62.47; H, 7.39; N, 9.41.

4-O-Acetyl-6-O-benzyl-(+)-allosamizoline (41) and 3,4-Di-O-acetyl-6-O-benzyl-(+)allosamizoline (42).

To a dichloromethane ( 1 mL ) solution of diol ent-27 ( $103 \mathrm{mg}, 0.336 \mathrm{mmol}$ ) was added triethylamine ( $0.94 \mathrm{~mL}, 0.67 \mathrm{mmol}$ ), DMAP ( $2 \mathrm{mg}, 0.02 \mathrm{mmol}$ ), and acetic anhydride ( $35 \mu \mathrm{~L}, 0.37 \mathrm{mmol}$ ). The mixture was stirred 16 h , concentrated, and the residue chromatographed (silica; $1 \% \mathrm{Et}_{3} \mathrm{~N}, 10 \rightarrow 20 \%$ methanol in ethyl acetate) to provide the diacetate ( $42 ; 66.2 \mathrm{mg}, 50 \%$ ) followed by the desired monoacetate ( $41 ; 35.7$ $\mathrm{mg}, 30 \%$ ). 41: colorless oil; $\mathrm{mp} 113-116^{\circ} \mathrm{C} ;[\alpha]_{\mathrm{D}}-21.5^{\circ}\left(c 1.1, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right)$; IR ( KBr ) $v_{\max }$ 3160 (br), 2960, 2910, 2860, 1735, 1650, 1410, 1365, 1240, 1100, $1035 \mathrm{~cm}^{-1}$; 1 H NMR ( 250 $\left.\mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}\right) \delta 7.38-7.23(\mathrm{~m}, 5 \mathrm{H}, \mathrm{ArH}), 6.52(\mathrm{br} \mathrm{s}, 1 \mathrm{H}, \mathrm{OH}), 4.93(\mathrm{dd}, J=7.9,6.6 \mathrm{~Hz}, 1$ $\mathrm{H}, \mathrm{H}-4), 4.82(\mathrm{dd}, J=8.8,5.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1), 4.52\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{Ph}\right), 4.11(\mathrm{dd}, J=8.8,4.3$ $\mathrm{Hz}, 1 \mathrm{H}, \mathrm{H}-2), 3.98(\mathrm{dd}, J=6.4,4.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3), 3.65(\mathrm{dd}, J=9.6,5.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6), 3.55$ (dd, $J=9.6,6.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6), 2.87\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{N}\left(\mathrm{CH}_{3}\right)_{2}\right), 2.42-2.39(\mathrm{~m}, 1 \mathrm{H}, \mathrm{H}-5), 1.96(\mathrm{~s}, 3 \mathrm{H}$, $\left.\mathrm{OCOCH}_{3}\right) ;{ }^{13} \mathrm{C}$ NMR ( $63 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}$ ) $\delta 170.7,162.2,138.7,128.7,128.1,128.0,84.0$, 82.4, 79.1, 74.9, 73.6, 69.2, 50.5, 37.9, 21.1; MS (EI) $m / e$ (rel. intensity) $248\left(\mathrm{M}+\mathrm{H}^{+}, 1\right)$, 288 (18), 167 (15), 113 (30), 112 (100), 91 (14), 72 (9); HRMS (CI) calcd for $\mathrm{C}_{18} \mathrm{H}_{25} \mathrm{~N}_{2} \mathrm{O}_{5}$ $\left(\mathrm{M}+\mathrm{H}^{+}\right) 349.1764$, found 349.1775 .42 : colorless solid; mp $113-116{ }^{\circ} \mathrm{C} ;[\alpha]_{\mathrm{D}}-52.2^{\circ}(\mathrm{c}$ $1.4, \mathrm{CH}_{2} \mathrm{Cl}_{2}$ ); IR (neat) $v_{\max } 2920,2860,1740,1655,1370,1250,1035 \mathrm{~cm}^{-1} ; 1 \mathrm{H}$ NMR ( 250 $\left.\mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}\right) \delta 7.40-7.25(\mathrm{~m}, 5 \mathrm{H}, \mathrm{ArH}), 5.06(\mathrm{t}, J=5.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-4), 5.00(\mathrm{t}, J=3.7 \mathrm{~Hz}$, $1 \mathrm{H}, \mathrm{H}-3), 4.84(\mathrm{dd}, J=8.4,4.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1), 4.52\left(\mathrm{AB}_{\mathrm{q}}, J=11.9 \mathrm{~Hz}, v=5.8 \mathrm{~Hz}, 2 \mathrm{H}\right.$, $\left.\mathrm{OCH}_{2} \mathrm{Ph}\right), 4.24(\mathrm{dd}, J=8.4,3.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-2), 3.60(\mathrm{dd}, J=9.7,3.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6), 3.48(\mathrm{dd}$,
$J=9.7,6.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6), 2.87\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{N}\left(\mathrm{CH}_{3}\right)_{2}\right), 2.55-2.44(\mathrm{~m}, 1 \mathrm{H}, \mathrm{H}-5), 1.98(\mathrm{~s}, 3 \mathrm{H}$, $\left.\mathrm{OCOCH}_{3}\right), 1.95\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCOCH}_{3}\right) ;{ }^{13} \mathrm{C} \mathrm{NMR}\left(63 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}\right) \delta 170.4,170.1,162.3$, $138.7,128.7,128.1,128.0,83.7,83.4,76.8,73.8,73.5,68.0,51.1,37.8,21.1,21.0$; MS (CT) $m / e$ (rel. intensity) $391\left(\mathrm{M}+\mathrm{H}^{+}, 20\right), 331(76), 330(98), 271$ (100), $270(89), 224(21), 224$ (25), 223 (54), $209(27), 208(94), 203(43), 181(48), 167(77), 166(24), 165(95), 164(68), 154$ (25), 113 (64), 112 (42), 91 (83); HRMS ( FAB ) calcd for $\mathrm{C}_{20} \mathrm{H}_{27} \mathrm{~N}_{2} \mathrm{O}_{6}\left(\mathrm{M}+\mathrm{H}^{+}\right)$391.1869, found 391.1869.

## 4-O-Acetyl-6-O-benzyl-3-O-(tert-butyldimethylsilyl)-(+)-allosamizoline (43).

To a $0^{\circ} \mathrm{C}$ DMF solution ( 0.4 mL ) of monoacetate $41(65 \mathrm{mg}, 0.186 \mathrm{mmol})$ was added triethylamine ( $0.13 \mathrm{~mL}, 0.93 \mathrm{mmol}$ ) and tert-butyldimethylsilyl chloride ( 64 $\mathrm{mg}, 0.418 \mathrm{mmol}$ ). The reaction was stirred 1 h , warmed to room temperature for 3 h , and then extracted from 0.5 M aq. $\mathrm{Na}_{2} \mathrm{CO}_{3}(10 \mathrm{~mL})$ with diethyl ether ( $3 \times 8 \mathrm{~mL}$ ). The combined organic layers were dried $\left(\mathrm{MgSO}_{4}\right)$, concentrated, and chromatographed (silica; 2\% $\mathrm{Et}_{3} \mathrm{~N}, 5 \%$ methanol in hexanes) to provide $43(61.4 \mathrm{mg}, 71 \%)$ as a colorless oil: $[\alpha]_{D}-10.6^{\circ}\left(c 1.0, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right)$; $\operatorname{IR}$ (neat) $v_{\max } 2950,2930,2860,1740,1655,1240,1100$ $\mathrm{cm}^{-1}$; ${ }^{1} \mathrm{H}$ NMR $\left(250 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}\right) \delta 7.40-7.25(\mathrm{~m}, 5 \mathrm{H}, \mathrm{ArH}), 4.86(\mathrm{dd}, J=7.8,2.5 \mathrm{~Hz}, 1$ $\mathrm{H}, \mathrm{H}-1), 4.80(\mathrm{t}, \mathrm{J}=5.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-4), 4.51\left(\mathrm{AB}_{\mathrm{q}}, J=11.8 \mathrm{~Hz}, v=15.6 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{Ph}\right)$, $4.19(\mathrm{dd}, J=7.8,2.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-2), 4.01(\mathrm{ddd}, J=3.3,2.2,1.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3), 3.55\left(\mathrm{AB}_{\mathrm{q}}\right.$ of $\mathrm{ABX}, J_{\mathrm{AB}}=9.5 \mathrm{~Hz}, J_{\mathrm{AX}}=8.5 \mathrm{~Hz}, J_{\mathrm{BX}}=6.1 \mathrm{~Hz}, v=11.4 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{H}-6$ and H-6), 2.86 (s, 6 $\left.\mathrm{H}, \mathrm{N}\left(\mathrm{CH}_{3}\right)_{2}\right), 2.53-2.43(\mathrm{~m}, 1 \mathrm{H}, \mathrm{H}-5), 1.94\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCOCH}_{3}\right), 0.87\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{SiC}\left(\mathrm{CH}_{3}\right)_{3}\right)$,
$0.12\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{SiCH}_{3}\right), 0.10\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{SiCH}_{3}\right) ;{ }^{13} \mathrm{C} \mathrm{NMR}\left(63 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}\right) \delta 170.3,162.1$, $139.0,128.8,128.2,128.0,85.6,83.1,80.5,77.3,73.6,69.6,52.0,38.0,26.0,21.2,18.3,-4.6,-$ 4.7; MS (CI) $m / e$ (rel. intensity) 464 (46), $463\left(\mathrm{M}+\mathrm{H}^{+}, 100\right), 405$ (53), 331 (56), 91 (24); HRMS (CI) calcd for $\mathrm{C}_{24} \mathrm{H}_{39} \mathrm{~N}_{2} \mathrm{O}_{5} \mathrm{Si}\left(\mathrm{M}+\mathrm{H}^{+}\right) 463.2628$, found 463.2635 .

## 6-O-Benzyl-3-O-(tert-butyldimethylsilyl)-(+)-allosamizoline (44).

A methanolic solution ( 0.5 mL ) of $43(61.0 \mathrm{mg}, 0.132 \mathrm{mmol})$ was deacetylated for 18 h with $25 \%$ sodium methoxide ( $10 \mu \mathrm{~L}, 0.04 \mathrm{mmol}$ ), and then extracted from saturated aq. $\mathrm{NaHCO}_{3}(10 \mathrm{~mL})$ with diethyl ether $(3 \times 5 \mathrm{~mL})$. The combined extracts were dried $\left(\mathrm{MgSO}_{4}\right)$ and concentrated to provide allosamizoline derivative 44 (55.1 $\mathrm{mg}, 99 \%$ ) as a colorless oil: $[\alpha]_{\mathrm{D}}+22.2^{\circ}\left(c 1.2, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right.$ ); IR (neat) $v_{\max } 3090$ (br), 2930, $2860,1655,1410,1260,1135,1090 \mathrm{~cm}^{-1} ; 1 \mathrm{H}$ NMR $\left(250 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}\right) \delta 7.40-7.25(\mathrm{~m}, 5$ $\mathrm{H}, \mathrm{Ar} H), 4.70(\mathrm{dd}, J=8.1,4.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1), 4.54\left(\mathrm{AB}_{\mathrm{q}}, J=11.8 \mathrm{~Hz}, v=9.5 \mathrm{~Hz}, 2 \mathrm{H}\right.$, $\left.\mathrm{OCH}_{2} \mathrm{Ph}\right), 4.06(\mathrm{dd}, J=8.1,3.5 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-2), 3.89(\mathrm{t}, J=4.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3), 3.70(\mathrm{t}, J=5.8$ $\mathrm{Hz}, 1 \mathrm{H}, \mathrm{H}-4), 3.62\left(\mathrm{AB}_{\mathrm{q}}\right.$ of $\mathrm{A}_{\mathrm{BX}}, J_{\mathrm{AB}}=9.3 \mathrm{~Hz}, J_{\mathrm{AX}}=7.4 \mathrm{~Hz}, J_{\mathrm{BX}}=6.4 \mathrm{~Hz}, v=7.5 \mathrm{~Hz}, 2$ H, H-6 and H-6), 2.87 (s, $\left.6 \mathrm{H}, \mathrm{N}\left(\mathrm{CH}_{3}\right)_{2}\right), 2.31-2.20(\mathrm{~m}, 1 \mathrm{H}, \mathrm{H}-5), 0.90(\mathrm{~s}, 9 \mathrm{H}$, $\left.\mathrm{SiC}\left(\mathrm{CH}_{3}\right)_{3}\right), 0.14\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{SiCH}_{3}\right), 0.12\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{SiCH}_{3}\right) ;{ }^{13} \mathrm{C} \mathrm{NMR}\left(63 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}\right) \delta$ $162.3,139.0,128.8,128.2,128.0,85.4,84.4,78.9,76.1,73.6,70.6,53.2,37.9,26.1,18.4,-4.3$, -4.5 ; MS (CI) $m / e$ (rel. intensity) 422 (66), $421\left(\mathrm{M}+\mathrm{H}^{+}, 100\right), 364(19), 363$ (74), 289 (45), 91 (30); HRMS (CI) calcd for $\mathrm{C}_{22} \mathrm{H}_{36} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{Si}\left(\mathrm{M}+\mathrm{H}^{+}\right) 421.2523$, found 421.2521.

O-[2-(Benzenesulfonamido)-3-O-benzyl-4,6-O-benzylidene-2-deoxy-D-allopyranosyl]-$\beta$-(1 $\rightarrow 4$ )-O-[2-(benzenesulfonamido)-6-O-benzyl-2-deoxy-3-O-[[2-(trimethylsilyl)-ethoxy]methyll-D-allopyranosyl]- $\beta$-(1-4)-6-O-benzyl-3-O-(tert-butyldimethylsilyl)-(+)allosamizoline (50), O-[2-(Benzenesulfonamido)-3-O-benzyl-4,6-O-benzylidene-2-deoxy-D-allopyranosyl]- $\beta$-(1 $\rightarrow 4$ )-O-[2-(benzenesulfonamido)-6-O-benzyl-2-deoxy-3-O-[[2-(trimethylsilyl)ethoxy]methyl]-D-allopyranosyl]- $\beta$-( $1 \rightarrow 3$ )-6-O-benzyl-4-O-(tert-butyldimethylsilyl)-(+)-allosamizoline (51), and 6-O-Benzyl-4-O-(tert-butyldi-methylsilyl)-(+)-allosamizoline (52).

To a $-40^{\circ} \mathrm{C}$ solution of trans-bromosulfonamide $49(213 \mathrm{mg}, 0.197 \mathrm{mmol})$ in DMF ( 2 mL ) was added a DMF solution ( 0.5 mL ) of allosamizoline derivative 44 (55 $\mathrm{mg}, 0.131 \mathrm{mmol}$ ), followed by dropwise addition of potassium hexamethyldisilazide ( 0.5 M in toluene, $1.05 \mathrm{~mL}, 0.52 \mathrm{mmol}$ ). The reaction mixture was stirred for 30 min at $-40^{\circ} \mathrm{C}$ and then slowly warmed to room temperature. After 15 h , the reaction was extracted from saturated aq. $\mathrm{NaHCO}_{3}(20 \mathrm{~mL})$ with diethyl ether ( $4 \times 10 \mathrm{~mL}$ ). The combined organic layers were dried $\left(\mathrm{MgSO}_{4}\right)$, concentrated, and the residue chromatographed (silica; $1 \% \mathrm{Et}_{3} \mathrm{~N}, 33 \rightarrow 40 \rightarrow 50 \rightarrow 66 \rightarrow 80 \rightarrow 100 \%$ ethyl acetate in hexanes $\rightarrow 5 \%$ methanol in ethyl acetate) to provide fractions which contained the 4-O-linked pseudotrisaccharide 50, followed by the 3 -O-linked pseudotrisaccharide 51, the 3-O-protected aglycon derivative 44, and finally the 4-O-protected aglycon derivative 52. 50: The residue was rechromatographed (silica, $30 \rightarrow 50 \rightarrow 75 \%$ ethyl acetate in hexanes) to provide material which was extracted from 0.5 M aq. $\mathrm{Na}_{2} \mathrm{CO}_{3}$ ( 5 mL ) with dichloromethane ( $3 \times 2 \mathrm{~mL}$ ). The combined organic layers were dried
$\left(\mathrm{Na}_{2} \mathrm{SO}_{4}\right)$ and concentrated to provide the pseudotrisaccharide ( $50 ; 11.6 \mathrm{mg}, 6.2 \%$ ) as a colorless oil: $[\alpha]_{\mathrm{D}}-54.9^{\circ}$ (c $1.2, \mathrm{CH}_{2} \mathrm{Cl}_{2}$ ); IR (neat) $v_{\max } 3330$ (br), 2920, 2850, 1655, 1335, 1160, 1095, $1050 \mathrm{~cm}^{-1}$; ${ }^{1} \mathrm{H}$ NMR $\left(490 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}\right) \delta 7.86-7.82(\mathrm{~m}, 2 \mathrm{H}$, $\left.\mathrm{SO}_{2} \mathrm{C}(\mathrm{CHCH})_{2} \mathrm{CH}\right), 7.71-7.61\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{SO}_{2} \mathrm{C}(\mathrm{CHCH})_{2} \mathrm{CH}\right), 7.56-7.17(\mathrm{~m}, 26 \mathrm{H}, \mathrm{ArH})$, 5.58-5.51 (br s, $1 \mathrm{H}, \mathrm{NH}$ '), 5.49 ( $\mathrm{s}, 1 \mathrm{H}, \mathrm{O}_{2} \mathrm{CHPh}$ ), $5.15\left(\mathrm{~d}, \mathrm{~J}=8.5 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{NH} H^{\prime \prime}\right), 4.93(\mathrm{~d}$, $J=11.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{OCHHPh}), 4.72(\mathrm{~d}, I=8.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1), 4.65-4.62(\mathrm{~m}, 1 \mathrm{H}, \mathrm{H}-1), 4.64$ $\left(\mathrm{s}, 2 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{OCH}_{2} \mathrm{CH}_{2} \mathrm{Si}\right), 4.61\left(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1^{\prime \prime}\right), 4.46\left(\mathrm{AB}_{\mathrm{q}}, I=12.3 \mathrm{~Hz}, v=7.7\right.$ $\left.\mathrm{Hz}, 2 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{Ph}\right), 4.45(\mathrm{~d}, J=11.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{OCHHPh}), 4.44(\mathrm{~d}, J=11.9 \mathrm{~Hz}, 1 \mathrm{H}$, OCHHPh $), 4.33(\mathrm{~d}, J=11.9 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{OCHHPh}), 4.30\left(\mathrm{dd}, J=10.4,5.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-\mathrm{\sigma}_{\mathrm{e}}{ }^{\prime \prime}\right)$, 3.99-3.94 (m, $3 \mathrm{H}, \mathrm{H}-3^{\prime}, \mathrm{H}-3^{\prime \prime}$, and H-5'), 3.84 (dd, $J=8.5,4.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-2$ ), 3.80 (td, $\mathrm{J}=$ $\left.9.8,7.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{OCHHCH}_{2} \mathrm{Si}\right), 3.77(\mathrm{dd}, J=9.2,6.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-4), 3.68-3.61(\mathrm{~m}, 4 \mathrm{H}$, H-4', H-4", H-6a", and OCHHCH 2 Si ), $3.54(\mathrm{dd}, J=9.6,3.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6), 3.39(\mathrm{dd}, J=$ 9.6, $6.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6$ ), $3.40-3.34$ (br m, $2 \mathrm{H}, \mathrm{H}-3$ and $\mathrm{H}-5$ '), $3.33-3.28$ (m, $3 \mathrm{H}, \mathrm{H}-6$ ', H-6', and H-2'), 3.19-3.14 (br m, $\left.1 \mathrm{H}, \mathrm{H}-2^{\prime}\right), 2.93\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{N}\left(\mathrm{CH}_{3}\right)_{2}\right), 3.12-3.07(\mathrm{~m}, 2 \mathrm{H}$, $\left.\mathrm{OCH}_{2} \mathrm{CH}_{2} \mathrm{Si}\right), 1.74-1.67(\mathrm{~m}, 1 \mathrm{H}, \mathrm{H}-5), 0.94\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{SiC}\left(\mathrm{CH}_{3}\right)_{3}\right), 0.19\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{SiCH}_{3}\right), 0.13$ (s, $\left.3 \mathrm{H}, \mathrm{SiCH}_{3}\right), 0.10\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{3}\right) ;{ }^{13} \mathrm{C}$ NMR $\left(63 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}\right) \delta 161.7,142.3,141.5$, $139.3,138.5,138.5,138.0,133.0,132.6,129.5,129.4,129.2,129.0,128.9,128.8,128.7,128.6$, $128.4,128.3,128.2,127.9,127.5,127.4,126.6,102.6,101.3,97.8,97.1,85.1,82.5,80.4,79.9$, $79.3,76.9,76.8,75.4,75.2,73.9,73.4,72.0,69.5,69.3,68.7,67.0,64.0,57.6,56.8,49.7,38.0$, 26.3, 26.0, 18.6, 18.1, $-1.2,-3.8,-4.4$; MS (FAB) $m / e$ (rel. intensity) $1422\left(\mathrm{M}+\mathrm{H}^{+}, 100\right)$, 535 (11), 449 (9), 283 (8); HRMS (FAB) calcd for $\mathrm{C}_{73} \mathrm{H}_{97} \mathrm{~N}_{4} \mathrm{O}_{17} \mathrm{~S}_{2} \mathrm{Si}_{2}\left(\mathrm{M}+\mathrm{H}^{+}\right)$1421.5830, found 1421.5855. 51: The residue was rechromatographed (silica, $50 \rightarrow 70 \rightarrow 90 \%$
ethyl acetate in hexanes) to provide material which was extracted from 0.5 M aq. $\mathrm{Na}_{2} \mathrm{CO}_{3}(5 \mathrm{~mL})$ with dichloromethane $(3 \times 2 \mathrm{~mL})$. The combined organic layers were dried $\left(\mathrm{Na}_{2} \mathrm{SO}_{4}\right)$ and concentrated to provide the pseudotrisaccharide ( $51 ; 8.7 \mathrm{mg}$, $4.6 \%)$ as a colorless oil: $[\alpha]_{D}-41.4^{\circ}\left(c 0.7, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right)$; IR (neat) $v_{\max } 2920,2850,1655,1340$, $1170,1095 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(490 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}\right) \delta 7.89-7.85\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{SO}_{2} \mathrm{C}(\mathrm{CHCH})_{2} \mathrm{CH}\right)$, 7.70-7.66(m, $\left.\left.2 \mathrm{H}, \mathrm{SO}_{2} \mathrm{C}(\mathrm{CHCH})\right)_{2} \mathrm{CH}\right), 7.57-7.28(\mathrm{~m}, 26 \mathrm{H}, \mathrm{ArH}), 5.85(\mathrm{~d}, J=8.9 \mathrm{~Hz}, 1 \mathrm{H}$, $\left.\mathrm{NH}^{\prime}\right), 5.46\left(\mathrm{~s}, 1 \mathrm{H}, \mathrm{O}_{2} \mathrm{CHPh}\right), 5.04\left(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{NH}{ }^{\prime \prime}\right), 4.91(\mathrm{~d}, J=11.3 \mathrm{~Hz}, 1 \mathrm{H}$, $\mathrm{OCH} H \mathrm{Ph}), 4.81(\mathrm{br} \mathrm{d}, J=7.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1), 4.66\left(\mathrm{~d}, J=6.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{OCHHOCH} 2 \mathrm{CH}_{2} \mathrm{Si}\right)$, $4.56(\mathrm{~d}, J=11.9 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{OCHHPh}), 4.56\left(\mathrm{AB}_{\mathrm{q}}, J=12.2 \mathrm{~Hz}, v=3.8 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{Ph}\right)$, $4.50\left(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1^{\prime \prime}\right), 4.48\left(\mathrm{~d}, J=8.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1^{\prime}\right), 4.43(\mathrm{~d}, J=11.3 \mathrm{~Hz}, 1 \mathrm{H}$, OCHHPh $), 4.43(\mathrm{~d}, J=11.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{OCHHPh}), 4.36(\mathrm{~d}, J=6.6 \mathrm{~Hz}, 1 \mathrm{H}$, $\mathrm{OCHHOCH}_{2} \mathrm{CH}_{2} \mathrm{Si}$ ), 4.26 (br d, $J=7.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-2$ ), 4.10 (dd, $J=10.3,5.2 \mathrm{~Hz}, 1 \mathrm{H}$, H-6e"), 3.92 (br s, $1 \mathrm{H}, \mathrm{H}-3$ or H-4), $3.90-3.88$ (m, $2 \mathrm{H}, \mathrm{H}-3$ or H-4, and H-3'), 3.87 (td, J $\left.=9.9,5.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-5{ }^{\prime}\right), 3.80\left(\mathrm{td}, J=9.3,7.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{OCHHCH}_{2} \mathrm{Si}\right), 3.60(\mathrm{td}, J=9.4,7.8$ $\mathrm{Hz}, 1 \mathrm{H}, \mathrm{OCHHCH} 2 \mathrm{Si}), 3.56\left(\mathrm{dd}, J=9.5,2.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-4{ }^{\prime \prime}\right), 3.53(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{H}-6$ and H-6), $3.52\left(\mathrm{dd}, J=9.5,2.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6^{\prime}\right), 3.49\left(\mathrm{t}, J=10.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6_{\mathrm{a}}{ }^{\prime \prime}\right), 3.43-3.36$ (m, $3 \mathrm{H}, \mathrm{H}-3^{\prime}, \mathrm{H}^{\prime} 5^{\prime}$ and $\mathrm{H}-6$ '), 3.29 (dd, $J=10.6,2.9 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-4$ '), 3.26 (td, $J=8.6,3.1$ $\left.\mathrm{Hz}, 1 \mathrm{H}, \mathrm{H}-2^{\prime \prime}\right), 3.09\left(\mathrm{td}, J=8.5,2.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-2^{\prime}\right), 2.82\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{N}\left(\mathrm{CH}_{3}\right)_{2}\right), 2.41(\mathrm{t}, J=7.5$ $\mathrm{Hz}, 1 \mathrm{H}, \mathrm{H}-5), 2.12-2.06\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{CH}_{2} \mathrm{Si}\right), 0.87\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{SiC}\left(\mathrm{CH}_{3}\right)_{3}\right), 0.09(\mathrm{~s}, 9 \mathrm{H}$, $\left.\mathrm{Si}\left(\mathrm{CH}_{3}\right)_{3}\right), 0.08(\mathrm{~s}, 3 \mathrm{H}, \mathrm{SiCH} 3), 0.08\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{SiCH}_{3}\right) ;{ }^{13} \mathrm{C}$ NMR $\left(63 \mathrm{MHz}^{2}, \mathrm{CD}_{2} \mathrm{Cl}_{2}\right) \delta 161.7$, $142.0,141.6,139.5,138.5,138.4,137.9,133.0,132.9,132.1,129.6,129.4,129.3,129.1,129.0$, $128.8,128.7,128.6,128.4,128.2,127.8,127.7,127.3,126.6,102.6,101.2,99.1,97.7,90.7,86.7$,
$80.7,80.4,77.8,76.7,76.3,76.0,75.4,73.9,73.3,72.2,69.5,69.2,68.9,67.0,63.8,57.5,56.2$, 55.6, $37.8, \quad 25.8, \quad 18.6, \quad 18.1, \quad-1.2, \quad-4.2$, -4.8; HRMS (FAB) calcd for $\mathrm{C}_{73} \mathrm{H}_{97} \mathrm{~N}_{4} \mathrm{O}_{17} \mathrm{~S}_{2} \mathrm{Si}_{2}\left(\mathrm{M}+\mathrm{H}^{+}\right)$1421.5830, found 1421.5829. 44: The residue was rechromatographed (silica, $10 \%$ methanol in ethyl acetate) to provide material which was extracted from 0.5 M aq. $\mathrm{Na}_{2} \mathrm{CO}_{3}$ ( 5 mL ) with dichloromethane $(3 \times 2 \mathrm{~mL})$. The combined organic layers were dried $\left(\mathrm{Na}_{2} \mathrm{SO}_{4}\right)$ and concentrated to provide the aglycon derivative (44; $17.4 \mathrm{mg}, 32 \%$ ) as a colorless oil. 52: The residue was rechromatographed (silica, $20 \rightarrow 30 \%$ methanol in ethyl acetate) to provide material which was extracted from 0.5 M aq. $\mathrm{Na}_{2} \mathrm{CO}_{3}$ ( 5 mL ) with dichloromethane $(3 \times 2 \mathrm{~mL})$. The combined organic layers were dried $\left(\mathrm{Na}_{2} \mathrm{SO}_{4}\right)$ and concentrated to provide the aglycon derivative ( $52 ; 17.3 \mathrm{mg}, 31 \%$ ) as a colorless oil: $[\alpha]_{\mathrm{D}}-7.4^{\circ}\left(c 1.7, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right)$; IR (neat) $v_{\max } 3140(\mathrm{br}), 2920,2850,1645,1405,1140,1090$, $1055 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H}$ NMR $\left(250 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}\right) \delta 7.40-7.24(\mathrm{~m}, 5 \mathrm{H}, \mathrm{ArH}), 4.80(\mathrm{dd}, J=8.8,5.5$ $\mathrm{Hz}, 1 \mathrm{H}, \mathrm{H}-1), 4.53\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{Ph}\right), 4.03-3.96(\mathrm{~m}, 1 \mathrm{H}, \mathrm{H}-2), 3.83-3.74(\mathrm{~m}, 2 \mathrm{H}, \mathrm{H}-3$ and H-4), $3.67(\mathrm{dd}, J=9.5,3.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6), 3.56(\mathrm{dd}, J=9.5,5.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6), 2.85(\mathrm{~s}, 9$ $\left.\left.\mathrm{H}, \mathrm{N}\left(\mathrm{CH}_{3}\right)_{3}\right), 2.23-2.12(\mathrm{~m}, 1 \mathrm{H}, \mathrm{H}-5), 0.86\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{SiC}\left(\mathrm{CH}_{3}\right)_{3}\right), 0.09(\mathrm{~s}, 3 \mathrm{H}, \mathrm{SiCH})_{3}\right), 0.05$ $\left(\mathrm{s}, 3 \mathrm{H}, \mathrm{SiCH}_{3}\right) ;{ }^{13} \mathrm{C}$ NMR $\left(63 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}\right) \delta 162.3,139.0,128.7,128.1,128.0,85.4,83.6$, $77.6,75.5,73.6,68.8,38.0,26.0,18.3,-4.0,-4.8 ; \mathrm{MS}(\mathrm{CI}) m / e$ (rel. intensity) $421\left(\mathrm{M}+\mathrm{H}^{+}\right.$, 51), 363 (20), 91 (100); HRMS (CI) calcd for $\mathrm{C}_{22} \mathrm{H}_{37} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{Si}\left(\mathrm{M}+\mathrm{H}^{+}\right) 421.2523$, found 421.2536.
$O$-[2-(Benzenesulfonamido)-3-O-benzyl-2-deoxy-D-allopyranosyl]- $\beta-(1 \rightarrow 4)-O-[2-$ (benzenesulfonamido)-6-O-benzyl-2-deoxy-3-D-allopyranosyl]- $\beta$-(1-4)-6-O-benzyl-(+)-allosamizoline (53).

A THF solution ( 0.7 mL ) of pseudotrisaccharide $50(18.2 \mathrm{mg}, 0.0128 \mathrm{mmol})$ was stirred 9 h with tetrabutylammonium fluoride ( 1.0 M in $\mathrm{THF}, 0.1 \mathrm{~mL}, 0.1 \mathrm{mmol}$ ), and then extracted from saturated aq. $\mathrm{NaHCO}_{3}(5 \mathrm{~mL})$ with diethyl ether ( $3 \times 5 \mathrm{~mL}$ ). The combined organic layers were dried $\left(\mathrm{MgSO}_{4}\right)$, concentrated, and the residue treated with $5 \%$ concentrated aq. HCl in methanol ( 1 mL ). The reaction was stirred 6 $h$ and then extracted from $10: 1$ saturated aq. $\mathrm{K}_{2} \mathrm{CO}_{3} /$ water ( 25 mL ) with ethyl acetate $(3 \times 8 \mathrm{~mL})$. The combined organic layers were dried $\left(\mathrm{MgSO}_{4}\right)$, concentrated, and chromatographed (silica; $2 \% \mathrm{Et}_{3} \mathrm{~N}, 10 \rightarrow 20 \%$ methanol in ethyl acetate) to provide 53 ( $10.2 \mathrm{mg}, 73 \%$ ) as a colorless glass: $[\alpha]_{D}-52.8^{\circ}\left(c 0.6, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right)$; IR (neat) $v_{\max } 3310$ (br), 2920, 1645, 1445, 1335, 1160, 1095, $1055 \mathrm{~cm}^{-1}$; ${ }^{1} \mathrm{H}$ NMR ( $490 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}$ ) $\delta 7.88-$ $7.84\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{SO}_{2} \mathrm{C}(\mathrm{CHCH})_{2} \mathrm{CH}\right), 7.81-7.77\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{SO}_{2} \mathrm{C}(\mathrm{CHCH})_{2} \mathrm{CH}\right), 7.58-7.43(\mathrm{~m}, 7$ $\mathrm{H}, \mathrm{ArH}), 7.37-7.20(\mathrm{~m}, 14 \mathrm{H}, \mathrm{ArH}), 4.88-4.83(\mathrm{brm}, 1 \mathrm{H}, \mathrm{H}-1), 4.81(\mathrm{~d}, J=11.1 \mathrm{~Hz}, 1 \mathrm{H}$, OCHHPh $), 4.77\left(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1^{\prime}\right), 4.60\left(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1^{\prime \prime}\right), 4.44\left(\mathrm{AB}_{\mathrm{q}}, J=\right.$ $\left.11.8 \mathrm{~Hz}, v=25.7 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{Ph}\right), 4.43(\mathrm{~d}, J=11.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{OCHHPh}), 4.40(\mathrm{~s}, 2 \mathrm{H}$, $\left.\mathrm{OCH}_{2} \mathrm{Ph}\right), 4.06(\mathrm{t}, J=2.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3$ '), $3.93(\mathrm{dd}, J=8.9,4.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-2), 3.77(\mathrm{dd}, J=$ $8.5,6.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-4), 3.72-3.67$ (m, $4 \mathrm{H}, \mathrm{H}-3^{\prime \prime}, \mathrm{H}-4^{\prime \prime}, \mathrm{H}-6^{\prime \prime}$, and H-6"), 3.66-3.62 (m, 1 H, H-5'), 3.58 (ddd, $\left.J=9.8,4.1,2.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}^{\prime} 5^{\prime}\right), 3.54\left(\mathrm{dd}, J=9.8,2.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-4^{\prime}\right)$, $3.54(\mathrm{dd}, J=9.8,4.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6), 3.52(\mathrm{dd}, J=11.2,2.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6$ '), $3.44(\mathrm{dd}, J=11.2$, $4.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6$ ), 3.43 (dd, $J=9.8,6.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6), 3.42-3.37$ (br m, $1 \mathrm{H}, \mathrm{H}-3$ ), 3.33 (dd,
$\left.J=8.1,2.9 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-2^{\prime \prime}\right), 3.21\left(\mathrm{dd}, J=8.3,3.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-2^{\prime}\right), 3.00\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{N}\left(\mathrm{CH}_{3}\right)_{2}\right)$, $1.84-1.90(\mathrm{~m}, 1 \mathrm{H}, \mathrm{H}-5)$; ${ }^{13} \mathrm{C}$ NMR ( $63 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}$ ) $\delta 163.7,144.3,143.3,140.1,139.9$, $139.7,133.6,133.0,130.3,129.8,129.4,129.3,129.1,128.7,128.6,128.3,127.9,101.5,99.4$, $85.5,83.0,81.4,80.9,78.4,76.7,75.6,74.7,74.0,73.5,73.1,72.3,70.6,69.3,68.9,62.2,58.6$, $58.4,50.0,37.9,30.7,24.8 ; \mathrm{MS}(\mathrm{FAB}) m / e$ (rel. intensity) $1089\left(\mathrm{M}+\mathrm{H}^{+}, 20\right), 307(51), 288$ (28), 243 (19), 242 (100); HRMS (FAB) calcd for $\mathrm{C}_{54} \mathrm{H}_{65} \mathrm{~N}_{4} \mathrm{O}_{16} \mathrm{~S}_{2}\left(\mathrm{M}+\mathrm{H}^{+}\right)$1089.3838, found 1089.3845.
$O$-(2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-D-allopyranosyl)- $\beta$-(1 $\rightarrow 4$ )-O-(2-acetamido-3,6-di-O-acetyl-2-deoxy-D-allopyranosyl)- $\beta$-(1 $\rightarrow 4$ )-3,6-di-O-acetyl-(+)-allosamizoline (54).

To a $-78{ }^{\circ} \mathrm{C}$ solution of 53 ( $17.4 \mathrm{mg}, 0.0 .0160 \mathrm{mmol}$ ) in ammonia ( 3 mL ) were added small pieces of sodium until a deep blue color was maintained for 25 min . The mixture was quenched with solid $\mathrm{NH}_{4} \mathrm{Cl}$, and then concentrated with a stream of nitrogen. The residue was acetylated for 4 days with pyridine ( 4 mL ) and acetic anhydride ( 1.5 mL ), concentrated under reduced pressure, and the residue extracted from 1:1 saturated aq. $\mathrm{K}_{2} \mathrm{CO}_{3}$ /water with ethyl acetate $(3 \times 5 \mathrm{~mL})$. The combined organic layers were dried $\left(\mathrm{MgSO}_{4}\right)$, concentrated, and the residue chromatographed (silica; $10 \rightarrow 20 \rightarrow 35 \%$ methanol in ethyl acetate; then $2 \% \operatorname{Et}_{3} \mathrm{~N}, 10 \%$ methanol in ethyl acetate) to afford $54(2.2 \mathrm{mg}, 15 \%)$ as a glass: $[\alpha] \mathrm{D}-60^{\circ}\left(c 0.2, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right)$; IR (neat) $v_{\max } 3300(\mathrm{br}), 2920,1745,1655,1370,1280,1045 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H} \mathrm{NMR}\left(490 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}\right) \delta$ $6.34\left(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{N} H^{\prime}\right), 6.22\left(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{NH}{ }^{\prime \prime}\right), 5.72(\mathrm{t}, J=2.9 \mathrm{~Hz}, 1 \mathrm{H}$,
$\left.\mathrm{H}-3^{\prime}\right), 5.06(\mathrm{dd}, J=6.0,4.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3), 4.80\left(\mathrm{dd}, J=10.2,2.9 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-4{ }^{\prime \prime}\right), 4.73(\mathrm{dd}, J$ $=8.8,6.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1), 4.59\left(\mathrm{~d}, J=8.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1^{\prime \prime}\right), 4.56\left(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-\mathrm{I}^{\prime}\right), 4.54$ (dd, $J=12.0,3.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6$ ) $, 4.28(\mathrm{dd}, J=11.4,4.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6), 4.26$ (dd, $J=8.8,4.0$ $\mathrm{Hz}, 1 \mathrm{H}, \mathrm{H}-2$ ), 4.17 (dd, $J=11.4,6.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6), 4.12-4.06\left(\mathrm{~m}, 3 \mathrm{H}, \mathrm{H}-2^{\prime \prime}, \mathrm{H}-6^{\prime \prime}\right.$, and H-6"), 4.05-3.99 (m, 2 H, H-6' and H-5'), $3.96(\mathrm{dd}, J=9.2,6.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-4), 3.88-3.84$ ( $\mathrm{m}, 2 \mathrm{H}, \mathrm{H}-2^{\prime}$ and $\mathrm{H}-5^{\prime}$ ), $3.62\left(\mathrm{dd}, J=9.4,3.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-4\right.$ '), $2.86\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{N}\left(\mathrm{CH}_{3}\right)_{2}\right), 2.46-$ $2.39(\mathrm{~m}, 1 \mathrm{H}, \mathrm{H}-5), 2.15\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{COCH}_{3}\right), 2.14\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{COCH}_{3}\right), 2.12\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{COCH}_{3}\right), 2.07$ $\left(\mathrm{s}, 3 \mathrm{H}, \mathrm{COCH}_{3}\right), 2.06\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{COCH}_{3}\right), 2.06\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{COCH}_{3}\right), 1.93\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{COCH}_{3}\right), 1.92(\mathrm{~s}$, $3 \mathrm{H}, \mathrm{COCH}_{3}$ ), $1.91\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{COCH}_{3}\right) ;{ }^{13} \mathrm{C}$ NMR ( $123 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}$ ) $\delta 100.6,98.2,85.6$, $81.6,81.2,74.6,72.7,72.2,70.5,69.9,69.8,67.1,63.1,62.6,62.0,52.4,51.2,50.0,37.8,23.1$, 23.0,21.6, 21.2, 20.9, 20.9, 20.8, 20.7; MS (FAB) $m / e$ (rel. intensity) 919 (15), 918 (44), 917 $\left(\mathrm{M}+\mathrm{H}^{+}, 100\right), 329(10), 307(38), 288(23), 225(14) ; \mathrm{HRMS}(\mathrm{FAB})$ calcd for $\mathrm{C}_{39} \mathrm{H}_{57} \mathrm{~N}_{4} \mathrm{O}_{21}$ $\left(\mathrm{M}+\mathrm{H}^{+}\right) 917.3515$, found 917.3528.

O-(2-Acetamido-2-deoxy-D-allopyranosyl)- $\beta$-(1 $\rightarrow 4$ )-O-(2-acetamido-2-deoxy-D-allo-pyranosyl)- $\beta$-( $1 \rightarrow 4$ )-(+)-allosamizoline (55).

A stream of ammonia was passed over a methanolic solution ( 3 mL ) of heptaacetate 54 ( $1.5 \mathrm{mg}, 0.0016 \mathrm{mmol}$ ) until the solution had returned to room temperature. The reaction was stirred 3 days, concentrated, and chromatographed (Bio-gel P-2; $10 \mathrm{mM} \quad \mathrm{NH}_{4} \mathrm{OAc}-\mathrm{NH}_{3}, \mathrm{pH}$ 9) to provide the deprotected pseudotrisaccharide ( $55 ; 0.9 \mathrm{mg}, 90 \%$ ) as a colorless solid: $[\alpha]_{\mathrm{D}}-15^{\circ}$ (c $0.1,10 \%$ acetic acid in water); ${ }^{1} \mathrm{H}$ NMR ( $\left.490 \mathrm{MHz}, \mathrm{D}_{2} \mathrm{O}+0.5 \% \mathrm{CD}_{3} \mathrm{CO}_{2} \mathrm{D}\right) \delta 5.39$ (dd, $J=8.7,4.5 \mathrm{~Hz}, 1$
$\mathrm{H}, \mathrm{H}-1), 4.86(\mathrm{~d}, J=8.5,1 \mathrm{H}), 4.79(\mathrm{~d}, J=8.7,1 \mathrm{H}), 4.36(\mathrm{dd}, J=8.7,4.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-2), 4.34$ $\left(\mathrm{t}, J=2.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3^{\prime}\right), 4.13(\mathrm{dd}, J=5.5,4.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3), 4.04\left(\mathrm{t}, J=2.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3^{\prime \prime}\right)$, $4.00(\mathrm{t}, J=6.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-4), 3.90-3.69(\mathrm{~m}, 10 \mathrm{H}), 3.68(\mathrm{dd}, J=9.9,2.9 \mathrm{~Hz}, 1 \mathrm{H}), 3.62(\mathrm{dd}, J$ $=12.1,5.9 \mathrm{~Hz}, 1 \mathrm{H}), 3.08\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{NCH}_{3} \mathrm{Me}\right), 3.07\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{NCH}_{3} \mathrm{Me}\right), 2.59-2.65(\mathrm{~m}, 1 \mathrm{H}$, $\mathrm{H}-5), 2.06\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{NHCOCH}_{3}\right), 2.04\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{NHCOCH}_{3}\right) ;{ }^{13} \mathrm{C}$ NMR ( $490 \mathrm{MHz}, \mathrm{D}_{2} \mathrm{O}+$ $\left.0.5 \% \mathrm{CD}_{3} \mathrm{CO}_{2} \mathrm{D}\right) \delta 174.0,173.9,160.7,100.6,99.6,87.6,83.8,81.0,76.6,73.6,72.7,70.1$, $69.0,66.4,64.6,60.9,59.2,52.9,52.7,51.2,37.7,37.4,22.1,22.0 ; \mathrm{MS}$ (FAB) $m / e$ (rel. intensity) $623\left(\mathrm{M}+\mathrm{H}^{+}, 17\right), 299(10), 223(13), 207(100), 205(10)$; HRMS (FAB) calcd for $\mathrm{C}_{25} \mathrm{H}_{43} \mathrm{~N}_{4} \mathrm{O}_{14}\left(\mathrm{M}+\mathrm{H}^{+}\right) 623.2775$, found 623.2780 .
$O$-[2-(Benzenesulfonamido)-3-O-benzyl-2-deoxy-D-allopyranosyl]- $\beta$-(1 $\rightarrow 4$ )-O-[2-(benzenesulfonamido)-6-O-benzyl-2-deoxy-D-allopyranosyl]- $\beta$-(1 $\rightarrow 3$ )-6-O-benzyl-3-(+)-allosamizoline (56).

A THF solution ( 0.7 mL ) of pseudotrisaccharide $51(14.6 \mathrm{mg}, 0.0128 \mathrm{mmol})$ was stirred 22 h with tetrabutylammonium fluoride $(1.0 \mathrm{M}, 0.2 \mathrm{~mL}, 0.2 \mathrm{mmol})$, and then extracted from saturated aq. $\mathrm{NaHCO}_{3}(5 \mathrm{~mL})$ with diethyl ether $(3 \times 5 \mathrm{~mL})$. The combined organic layers were dried $\left(\mathrm{MgSO}_{4}\right)$, concentrated, and the residue treated with $5 \%$ concentrated aq. HCl in methanol $(1 \mathrm{~mL})$. The reaction was stirred 6 h and then extracted from $10: 1$ saturated aq. $\mathrm{K}_{2} \mathrm{CO}_{3} /$ water $(25 \mathrm{~mL})$ with ethyl acetate $(3 \times 8 \mathrm{~mL})$. The combined organic layers were dried $\left(\mathrm{MgSO}_{4}\right)$, concentrated, and chromatographed (silica; 2\% Et3N, $10 \rightarrow 15 \rightarrow 20 \%$ methanol in ethyl acetate) to provide 56 ( $6.5 \mathrm{mg}, 58 \%$ ) as a colorless glass: $[\alpha]_{\mathrm{D}}-47.1^{\circ}\left(c 0.2, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right)$; IR (neat) $v_{\max }$

3300 (br), 2880, 2820, 1640, 1430, 1320, 1150, 1105, 1075, $1040 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H}$ NMR ( 490 MHz , $\left.\mathrm{CD}_{3} \mathrm{COD}\right) \delta 7.86-7.79\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{SO}_{2} \mathrm{C}(\mathrm{CHCH})_{2} \mathrm{CH}\right), 7.60-7.23(\mathrm{~m}, 21 \mathrm{H}, \mathrm{ArH}), 4.85(\mathrm{~d}, J=$ $\left.8.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1^{\prime \prime}\right), 4.81-4.78(\mathrm{~m}, 1 \mathrm{H}, \mathrm{H}-1), 4.79(\mathrm{~d}, J=11.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{OCHHPh}), 4.61(\mathrm{~d}, J$ $\left.=8.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1^{\prime}\right), 4.57\left(\mathrm{AB}_{\mathrm{q}^{\prime}} J=11.7 \mathrm{~Hz}, v=8.6 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{Ph}\right), 4.53\left(\mathrm{AB}_{\mathrm{q}}, J=11.7\right.$ $\left.\mathrm{Hz}, v=18.1 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{Ph}\right), 4.44(\mathrm{~d}, J=11.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{OCHHPh}), 4.07(\mathrm{t}, J=2.8 \mathrm{~Hz}, 1$ $\left.\mathrm{H}, \mathrm{H}-3^{\prime}\right), 3.83(\mathrm{dd}, J=6.4,4.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3), 3.78-3.73(\mathrm{br} \mathrm{m}, 1 \mathrm{H}, \mathrm{H}-2), 3.72-3.61(\mathrm{~m}, 8$ H), $\left.3.57(\mathrm{dd}, J=9.8,6.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6), 3.54-3.45(\mathrm{~m}, 3 \mathrm{H}, \text { includes } \mathrm{H}-4 \text { and } \mathrm{H}-4)^{\prime}\right), 3.33$ (dd, $\left.J=8.0,2.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-2^{\prime \prime}\right), 3.19\left(\mathrm{dd}, J=8.3,3.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-2\right.$ ), $2.81\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{N}\left(\mathrm{CH}_{3}\right)_{2}\right)$, 2.17-2.10 (m, $1 \mathrm{H}, \mathrm{H}-5$ ); ${ }^{13} \mathrm{C}$ NMR (123 MHz, $\mathrm{CD}_{3} \mathrm{COD}$ ) $\delta$ 163.1, 143.7, 143.4, 140.1, $139.8,139.5,133.7,133.3,130.3,130.1,130.0,129.5,129.4,129.3,129.2,129.1,128.8,128.7$, $128.1,127.9,101.3,98.9,90.2,84.9,80.9,78.8,76.7,75.8,75.5,74.9,74.3,72.9,71.5,71.2$, 70.4, 69.2, 68.6, 62.1, 58.4, 58.1, 52.6, 37.9; HRMS (FAB) calcd for $\mathrm{C}_{54} \mathrm{H}_{65} \mathrm{~N}_{4} \mathrm{O}_{16} \mathrm{~S}_{2}(\mathrm{M}+$ $\left.\mathrm{H}^{+}\right)$1089.3838, found 1089.3842 .
$O$-(2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-D-allopyranosyl)- $\beta$-(1 $\rightarrow$ 4)-O-(2-acetamido-3,6-di-O-acetyl-2-deoxy-D-allopyranosyl)- $\beta$-(1 $\rightarrow 3$ )-4,6-di-O-acetyl-(+)-allosamizoline (57).

To a $-78{ }^{\circ} \mathrm{C}$ solution of $56(7.6 \mathrm{mg}, 0.0070 \mathrm{mmol})$ in ammonia ( 3 mL ) were added small pieces of sodium until a deep blue color was maintained for 25 min . The mixture was quenched with solid $\mathrm{NH}_{4} \mathrm{Cl}$, and then concentrated with a stream of nitrogen. The residue was acetylated for 4 days with pyridine ( 4 mL ) and acetic anhydride ( 1.5 mL ), concentrated under reduced pressure, and extracted from 1:1
saturated aq. $\mathrm{K}_{2} \mathrm{CO}_{3} /$ water with ethyl acetate $(3 \times 5 \mathrm{~mL})$. The combined organic layers were dried $\left(\mathrm{MgSO}_{4}\right)$, concentrated, and the residue chromatographed (silica; $10 \rightarrow 20$ $\rightarrow 35 \%$ methanol in ethyl acetate; then $2 \% \operatorname{Et}_{3} \mathrm{~N}, 10 \%$ methanol in ethyl acetate) to afford $57(1.2 \mathrm{mg}, 19 \%)$ as a glass: $[\alpha]_{\mathrm{D}}-53^{\circ}\left(c 0.1, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right)$; IR (neat) $v_{\max } 3270$ (br), $2920,1745,1655,1370,1230,1045 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H}$ NMR $\left(490 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}\right) \delta 6.38-6.30$ (br m, $2 \mathrm{H}, \mathrm{NH} \mathrm{N}^{\prime}$ and $\mathrm{NH}^{\prime \prime}$ ), 5.65 (br s, $1 \mathrm{H}, \mathrm{H}-3^{\prime}$ ), 5.49 (t, $J=2.9 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3^{\prime \prime}$ ), 4.92 (dd, $J=$ $5.0,3.9 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-4), 4.81\left(\mathrm{dd}, J=10.2,2.9 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-4{ }^{\prime \prime}\right), 4.79-4.74$ (br m, $1 \mathrm{H}, \mathrm{H}-1$ ), 4.73 (dd, $\left.J=12.3,3.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6^{\prime}\right), 4.72\left(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1^{\prime}\right), 4.57(\mathrm{~d}, J=8.6 \mathrm{~Hz}, 1 \mathrm{H}$, $\mathrm{H}-1^{\prime \prime}$ ), 4.34 ( $\mathrm{br} \mathrm{d}, J=6.9 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-2$ ), 4.23 (dd, $J=11.4,7.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6$ ), 4.19 (br s, 1 H , H-3), 4.13-3.99(m, 7 H$), 3.93(\mathrm{dt}, J=8.9,2.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-5$ '), $3.65(\mathrm{dd}, J=8.5,3.0 \mathrm{~Hz}, 1 \mathrm{H}$, $\left.\mathrm{H}-4^{\prime}\right), 2.87\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{N}\left(\mathrm{CH}_{3}\right)_{2}\right), 2.61-2.55(\mathrm{~m}, 1 \mathrm{H}, \mathrm{H}-5), 2.20\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{COCH}_{3}\right), 2.15(\mathrm{~s}, 3 \mathrm{H}$, $\left.\mathrm{COCH}_{3}\right), 2.09\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{COCH}_{3}\right), 2.07\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{COCH}_{3}\right), 2.06\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{COCH}_{3}\right), 2.02,(\mathrm{~s}, 3 \mathrm{H}$, $\left.\mathrm{COCH}_{3}\right) 1.93,\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{COCH}_{3}\right) 1.93\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{COCH}_{3}\right), 1.89\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{COCH}_{3}\right) ;{ }^{13} \mathrm{C}$ NMR ( 123 $\left.\mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}\right) \delta 172.1,171.2,170.2,170.1,170.0,169.9,169.7,169.6,161.8,100.6,98.1$, $87.6,83.8,77.7,75.0,74.5,72.5,70.5,70.2,69.6,67.2,63.1,62.7,62.2,51.8,51.3,51.0,37.8$, 23.1, 21.3, 21.3, 21.0, 20.9, 20.8, 20.7; MS (FAB) $m / e$ (rel. intensity) 918 (46), 917 (M + $\left.\mathrm{H}^{+}, 100\right), 307(85), 288(51), 225(24) ;$ HRMS (FAB) calcd for $\mathrm{C}_{39} \mathrm{H}_{57} \mathrm{~N}_{4} \mathrm{O}_{21}\left(\mathrm{M}+\mathrm{H}^{+}\right)$ 917.3515, found 917.3590.

O-(2-Acetamido-2-deoxy-D-allopyranosyl)- $\beta$-(1 $\rightarrow 4$ )-O-(2-acetamido-2-deoxy-D-allo-pyranosyl)- $\beta-(1 \rightarrow 3)-(+)$-allosamizoline (58).

A stream of ammonia was passed over a methanolic solution (3 mL) of heptaacetate 57 ( $1.1 \mathrm{mg}, 0.0012 \mathrm{mmol}$ ) until the solution had returned to room temperature. The reaction was stirred 3 days, concentrated, and chromatographed (Bio-gel P-2; $10 \mathrm{mM} \mathrm{NH}_{4} \mathrm{OAc}_{\mathrm{NH}}^{3}$, pH 9) to provide the deprotected pseudotrisaccharide (58; $0.5 \mathrm{mg}, 71 \%$ ) as a colorless solid: $[\alpha]_{D}-12^{\circ}(c 0.05,10 \%$ acetic acid in water); ${ }^{1} \mathrm{H}$ NMR $\left(490 \mathrm{MHz}, \mathrm{D}_{2} \mathrm{O}+0.5 \% \mathrm{CD}_{3} \mathrm{CO}_{2} \mathrm{D}\right) \delta 5.29(\mathrm{dd}, J=9.4,6.0 \mathrm{~Hz}, 1$ $\mathrm{H}, \mathrm{H}-1), 4.87\left(\mathrm{~d}, J=8.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1^{\prime}\right), 4.77\left(\mathrm{~d}, J=8.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1^{\prime \prime}\right), 4.42(\mathrm{dd}, J=9.4,5.0$ $\mathrm{Hz}, 1 \mathrm{H}, \mathrm{H}-2), 4.38\left(\mathrm{t}, J=2.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3^{\prime}\right), 4.04\left(\mathrm{t}, J=3.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3^{\prime \prime}\right), 4.02(\mathrm{dd}, J=$ $7.8,5.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3), 3.97(\mathrm{td}, \mathrm{J}=9.5,2.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-5$ ), $3.92-3.82(\mathrm{~m}, 6 \mathrm{H}, \mathrm{H}-4, \mathrm{H}-6$, H-2', H-6', H-2', and H-6'), 3.77 (ddd, $\left.J=10.1,4.9,1.9 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-5^{\prime \prime}\right), 3.72$ (dd, $J=12.0$, $\left.4.9 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6^{\prime \prime}\right), 3.69(\mathrm{dd}, J=12.1,7.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6), 3.68$ (dd, $J=9.7,2.6 \mathrm{~Hz}, 1 \mathrm{H}$, $\left.\mathrm{H}-4{ }^{\prime}\right), 3.63\left(\mathrm{dd}, J=11.5,8.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6\right.$ ) , $3.08\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{NCH}_{3} \mathrm{Me}\right), 3.05(\mathrm{~s}, 3 \mathrm{H}$, $\left.\mathrm{NCH}_{3} \mathrm{Me}\right), 3.40-3.34(\mathrm{~m}, 1 \mathrm{H}, \mathrm{H}-5), 2.07\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{COCH}_{3}\right), 2.03\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{COCH}_{3}\right) ;{ }^{13} \mathrm{C}$ NMR ( $\left.123 \mathrm{MHz}, \mathrm{D}_{2} \mathrm{O}+0.5 \% \mathrm{CD}_{3} \mathrm{CO}_{2} \mathrm{D}\right) \delta 174.3,174.2,161.4,100.7,99.7,90.0,85.8,77.7$, $73.6,72.7,72.5,70.1,68.8,66.4,63.4,61.7,60.9,59.2,52.9,52.7,50.4,37.7,22.1$; HRMS (FAB) calcd for $\mathrm{C}_{25} \mathrm{H}_{43} \mathrm{~N}_{4} \mathrm{O}_{14}\left(\mathrm{M}+\mathrm{H}^{+}\right) 623.2775$, found 623.2767 .

## (+)-Allosamizoline (ent-8).

Hydrogenolysis of benzyl ether ent-27 (20.4 mg, 0.0666 mmol ) as was described in the synthesis of 8 provided the acetic acid salt of (-)-allosamizoline (ent-8; 16 mg , $87 \%$ ): colorless glass; $[\alpha]_{\mathrm{D}}+22.2^{\circ}(c 0.7$, water $)$.

## 2,5-Dideoxy-2,5-[(diphenylmethyl)imino]-1,3-O-isopropylidene-D-glucitol (68).

A DMF solution of azasugar $67(452 \mathrm{mg}, 1.37 \mathrm{mmol})$ was treated with 2,2-dimethoxypropane ( $0.50 \mathrm{~mL}, 4.1 \mathrm{mmol}$ ) and $p$-toluenesulfonic acid ( 295 mg , 1.6 $\mathrm{mmol})$. Additional portions of 2,2-dimethoxypropane ( $0.15 \mathrm{~mL}, 1.2 \mathrm{mmol}$ ) were added after 7 h and 19 h . The reaction was stirred for 24 h , then extracted from saturated aq. $\mathrm{NaHCO}_{3}(75 \mathrm{~mL})$ with ethyl acetate $(3 \times 40 \mathrm{~mL})$. The combined organic layers were dried $\left(\mathrm{MgSO}_{4}\right)$, concentrated, and the residue chromatographed (silica; $2 \% \operatorname{Et}_{3} \mathrm{~N}, 33 \rightarrow 50 \rightarrow 66 \rightarrow 75 \%$ ethyl acetate in hexanes) to provide the desired acetonide (68; $392 \mathrm{mg}, 77 \%$ ) as a colorless solid: $\mathrm{mp} 159.5-160.5^{\circ} \mathrm{C}$; $[\alpha]_{\mathrm{D}}-3.1^{\circ}(c 1.0$, $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ ); IR (KBr) $v_{\max } 3450(\mathrm{br}), 3310(\mathrm{v}$ br), 2980, 2930, 2880, 1450, 1375, 1230, 1070 $\mathrm{cm}^{-1}{ }^{1} \mathrm{H}$ NMR $\left(490 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}\right) \delta 7.49-7.45(\mathrm{~m}, 2 \mathrm{H}, \mathrm{ArH}), 7.42-7.48(\mathrm{~m}, 2 \mathrm{H}, \mathrm{ArH})$, 7.44-7.22 (m, 6 H, ArH), $5.13\left(\mathrm{~s}, 1 \mathrm{H}, \mathrm{NCHPh}_{2}\right), 4.15(\mathrm{dt}, J=5.4,1.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3), 4.13$ (dt, $J=3.3,1.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-4), 3.56-3.48(\mathrm{~m}, 2 \mathrm{H}, \mathrm{H}-6$ and $\mathrm{H}-6), 3.46(\mathrm{dd}, J=11.8,6.4 \mathrm{~Hz}, 1$ $\mathrm{H}, \mathrm{H}-1), 3.38$ (dd, $J=11.8,5.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1), 3.25(\mathrm{q}, J=5.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-2), 3.06$ (dddd, $J=$ $6.6,4.8,1.9,1.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-5), 2.48\left(\mathrm{t}, J=5.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{CH}_{2} \mathrm{OH}\right), 2.35(\mathrm{~d}, J=3.4 \mathrm{~Hz}, 1 \mathrm{H}$, $\mathrm{CHOH}), 1.34\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{O}_{2} \mathrm{CH}_{3} \mathrm{Me}\right), 1.31\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{O}_{2} \mathrm{CH}_{3} \mathrm{Me}\right) ;{ }^{13} \mathrm{C}$ NMR ( $63 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}$ ) $\delta$ $143.5,142.7,129.4,129.1,128.9,127.9,127.7,99.1,79.1,78.0,73.3,72.4,63.3,62.6,61.4$, 26.7, 22.1; MS (CI) $m / e$ (rel. intensity) 61 (100), 63 (20), 91 (80), 167 (56), 257 (26), 338 (21), 370 (25); HRMS (CI) calcd for $\mathrm{C}_{22} \mathrm{H}_{28} \mathrm{NO}_{4}\left(\mathrm{M}+\mathrm{H}^{+}\right) 370.2018$, found 370.2034 . Anal. Calcd for $\mathrm{C}_{22} \mathrm{H}_{27} \mathrm{NO}_{4}: \mathrm{C}, 71.52 ; \mathrm{H}, 7.36 ; \mathrm{N}, 3.79$. Found: C, $71.54 ; \mathrm{H}, 7.33 ; \mathrm{N}, 3.74$.

6-O-Benzyl-2,5-dideoxy-2,5-[(diphenylmethyl)imino]-1,3-O-isopropylidene-D-glucitol (69).

A methanolic ( 20 mL ) suspension of diol 68 and dibutyltin oxide ( $354 \mathrm{mg}, 1.42$ mmol) were refluxed until homogeneous ( 1 h ), concentrated under reduced pressure, then concentrated from toluene ( $2 \times 15 \mathrm{~mL}$ ) to remove any methanol still present. The stannylene acetal was rapidly stirred in DMF ( 6 mL ) for 24 h with benzyl bromide ( $0.32 \mathrm{~mL}, 2.7 \mathrm{mmol}$ ) and dry cesium fluoride ( $420 \mathrm{mg}, 2.8 \mathrm{mmol}$ ), and then extracted from $5: 1$ water/saturated aq. $\mathrm{K}_{2} \mathrm{CO}_{3}(150 \mathrm{~mL})$ with ethyl acetate (3 $\times 70 \mathrm{~mL})$. The combined organic layers were dried $\left(\mathrm{MgSO}_{4}\right)$, concentrated, and then concentrated several additional times from toluene ( $10 \times 200 \mathrm{~mL}$ ) to remove benzyl alcohol which was found to co-elute with the product. The residue thus produced was chromatographed (silica; $2 \% \mathrm{Et}_{3} \mathrm{~N}, 33 \rightarrow 50 \rightarrow 70 \rightarrow 100 \%$ ethyl acetate in hexanes) to provide the desired primary benzyl ether ( $69 ; 406 \mathrm{mg}, 65 \%$ ), followed by recovered diol (68; $99 \mathrm{mg}, 20 \%$ ). 69: off-white glass: $[\alpha]_{\mathrm{D}}-55.9^{\circ}$ (c 1.2, $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ ); IR (neat) $v_{\max } 3420,3060,3030,2980,2940,2870,1490,1450,1375,1225,1100,1075 \mathrm{~cm}^{-1} ; 1 \mathrm{H}$ NMR ( $490 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}$ ) $\delta 7.48-7.44(\mathrm{~m}, 2 \mathrm{H}, \mathrm{ArH}), 7.72-7.38(\mathrm{~m}, 2 \mathrm{H}, \mathrm{ArH}), 7.32-7.28$ $(\mathrm{m}, 11 \mathrm{H}, \mathrm{ArH}), 4.32\left(\mathrm{AB}_{\mathrm{q}}, J=12.1, v=13.6 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{Ph}\right), 4.23(\mathrm{dt}, J=3.0,1.5 \mathrm{~Hz}, 1$ $\mathrm{H}, \mathrm{H}-4), 4.16(\mathrm{dt}, J=5.6,1.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3), 3.64(\mathrm{dd}, J=10.3,9.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6), 3.40(\mathrm{dd}, J$ $=9.3,5.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6), 3.38-3.34(\mathrm{~m}, 1 \mathrm{H}, \mathrm{H}-1), 3.29-3.22(\mathrm{~m}, 2 \mathrm{H}, \mathrm{H}-1$ and $\mathrm{H}-2), 3.09$ (dddd, $J=10.2,5.1,1.8,1.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-5), 1.83(\mathrm{~d}, J=3.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{OH}), 1.27(\mathrm{~s}, 6 \mathrm{H}$, $\left.\mathrm{O}_{2} \mathrm{C}\left(\mathrm{CH}_{3}\right)_{2}\right) ;{ }^{13} \mathrm{C} \mathrm{NMR}\left(63 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}\right) \delta 143.9,143.4,139.0,129.0,128.7,127.9,127.8$,
$127.6,127.5,127.2,98.9,78.9,78.2,74.6,73.2,72.5,70.4,63.1,62.1,26.2,22.2 ; \mathrm{MS}(\mathrm{CI}) m / e$ (rel. intensity) $460\left(\mathrm{M}+\mathrm{H}^{+}, 100\right), 338$ (85), 294 (18), 209 (18), 167 (90), 91 (64), 61 (22); HRMS (CI) calcd for $\mathrm{C}_{29} \mathrm{H}_{34} \mathrm{NO}_{4}\left(\mathrm{M}+\mathrm{H}^{+}\right) 460.2488$, found 460.2473. Anal. Calcd for $\mathrm{C}_{29} \mathrm{H}_{33} \mathrm{NO}_{4}: \mathrm{C}, 75.79 ; \mathrm{H}, 7.24 ; \mathrm{N}, 3.05$. Found: C, $75.51 ; \mathrm{H}, 7.47 ; \mathrm{N}, 2.83$.

2-(Trimethylsilyl)ethanesulfonamide (70).

Phosphorous pentachloride ( $77 \mathrm{~g}, 0.37 \mathrm{~mol}$ ) was added in portions over 10 minutes to a suspension of sodium 2-(trimethylsilyl)ethanesulfonate ( $22.8 \mathrm{~g}, 0.112$ mol) in carbon tetrachloride ( 80 mL ). The reaction was stirred for 4 h , poured into ice water ( 100 mL ) and extracted with dichloromethane $(2 \times 150 \mathrm{~mL})$. The combined organic layers were washed with saturated aq. $\mathrm{NaHCO}_{3}(150 \mathrm{~mL})$, dried $\left(\mathrm{Na}_{2} \mathrm{SO}_{4}\right)$, and filtered. Ammonia was bubbled through the solution for 10 minutes at $0^{\circ} \mathrm{C}$. The reaction was stirred 1 h , concentrated, and the residue extracted from water (200 $\mathrm{mL})$ with diethyl ether $(3 \times 200 \mathrm{~mL})$. The combined organic layers were dried $\left(\mathrm{MgSO}_{4}\right)$ and concentrated to afford 2-(trimethylsilyl)ethanesulfonamide (70; 12.6 g , $62 \%$ ) as an off-white solid: $\operatorname{mp} 86-89^{\circ} \mathrm{C}$; IR (KBr) $v_{\max } 3310,3220,2950,1335,1315$, $1225,1200,1185,1150,1135 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H}$ NMR $\left(250 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 5.02(\mathrm{~s}, 2 \mathrm{H}, \mathrm{NH}), 3.09-$ $2.99\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{SO}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{Si}\right), 0.11-0.01\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{SO}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{Si}\right), 0.06\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{3}\right)$; ${ }^{13} \mathrm{C} \mathrm{NMR}\left(63 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 51.4,10.8,-2.0 ; \mathrm{MS}(\mathrm{CI}) m / e$ (rel. intensity) $182\left(\mathrm{M}+\mathrm{H}^{+}\right.$, 5), 166 (100), 138 (35), 101 (23), 74 (24), 73 (24); Anal. Calcd for $\mathrm{C}_{5} \mathrm{H}_{15} \mathrm{NSO}_{2} \mathrm{Si}: \mathrm{C}, 33.12$; H, 8.34; N, 7.72; S, 17.68. Found: C, 33.35; H, 8.60; N, 7.97; S, 17.42 .
$N_{r} N$-Dibromo-2-(trimethylsilyl)ethanesulfonamide (71).

Bromine ( $7.5 \mathrm{~mL}, 0.15 \mathrm{~mol}$ ) was added to a solution of 2(trimethylsilyl)ethanesulfonamide ( $70 ; 12.7 \mathrm{~g}, 70.0 \mathrm{mmol}$ ) in $4 \%$ aqueous sodium hydroxide $(220 \mathrm{~mL})$. The precipitate that formed was dissolved in chloroform (100 mL ), the organic layer was separated, dried $\left(\mathrm{MgSO}_{4}\right)$, and concentrated to 25 mL . Hexanes was added until the product began to crystallize, at which time the suspension was placed in a freezer. The crystals were collected by filtration and dried overnight under high vacuum over $\mathrm{P}_{2} \mathrm{O}_{5}$ to give dibromosulfonamide 71 as orange needles ( $8.31 \mathrm{~g}, 35 \%$ ): mp $90-92{ }^{\circ} \mathrm{C}$; IR (KBr) $v_{\max } 2930,2870,1400,1325,1240,1165$, $1130 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H}$ NMR ( $250 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 3.60-3.52\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{SO}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{Si}\right), 1.24-1.14$ $\left(\mathrm{m}, 2 \mathrm{H}, \mathrm{SO}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{Si}\right), 0.12\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{3}\right) ;{ }^{13} \mathrm{C}$ NMR $\left(63 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 43.3,10.6$, -2.1; MS (EI) $m / e$ (rel. intensity) 343 (0.7), 341 (1.0), $339\left(0.6, \mathrm{M}+\mathrm{H}^{+}\right.$), 257 (22), 166 (22), 91 (100), 69 (32), 67 (19), 63 (18), 61 (50); Anal. Calcd for $\mathrm{C}_{5} \mathrm{H}_{13} \mathrm{Br}_{2} \mathrm{NO}_{2} \mathrm{SSi}$ C, 17.71; H, 3.86; N, 4.13; S, 9.45. Found: C, 17.95; H, 3.97; N, 4.14; S, 9.45.

## 3-O-Benzyl-4,6-O-benzylidene-2-bromo-2-deoxy- $\alpha$-D-altropyranosyl 2-(Trimethylsilyl)ethanesulfonamide (67) and 3-O-Benzyl-4,6-O-benzylidene-2-bromo-2-deoxy- $\beta$ -D-altropyranosyl 2-(Trimethylsilyl)ethanesulfonamide.

A solution of 3-O-benzyl-4,6-O-benzylidene-D-allal (32; $248 \mathrm{mg}, 0.764 \mathrm{mmol}$ ) in dichloromethane ( 2 mL ) was added dropwise to a stirred suspension of $N, N-$ dibromo-2-(trimethylsilyl)ethanesulfonamide (71; $293 \mathrm{mg}, 0.864 \mathrm{mmol}$ ) in
dichloromethane ( 0.5 mL ) at $0^{\circ} \mathrm{C}$. After 1 h , ethanol ( 6 mL ) and $\mathrm{NH}_{4} \mathrm{I}(120 \mathrm{mg}, 1.04$ mmol ) were added to the reaction, the resultant mixture was stirred an additional 1 $h$ at room temperature, diluted with diethyl ether ( 80 mL ), reduced with saturated aq. $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}(20 \mathrm{~mL})$, and washed with brine ( 20 mL ). The organic layer was dried $\left(\mathrm{MgSO}_{4}\right)$, concentrated, and the residue chromatographed (silica, 20\% ethyl acetate in hexanes) to provide trans-sulfonamide 72 ( $205 \mathrm{mg}, 46 \%$ ) followed by a $1: 1.8$ mixture of trans-sulfonamide:cis-sulfonamide ( $72: \beta$-anomer $118 \mathrm{mg}, 26 \%$ ) as colorless foams. 72: $[\alpha]_{\mathrm{D}}+25.7^{\circ}\left(c 1.2, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right)$; IR (neat) $v_{\max } 3340,3050,3020,2950,1415,1335,1125$, $1035 \mathrm{~cm}^{-1}$; ${ }^{1} \mathrm{H}$ NMR ( $250 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.56-7.34(\mathrm{~m}, 10 \mathrm{H}, \mathrm{ArH}), 6.65(\mathrm{~d}, J=10.0 \mathrm{~Hz}$, $1 \mathrm{H}, \mathrm{NH}), 5.66\left(\mathrm{~s}, 1 \mathrm{H}, \mathrm{O}_{2} \mathrm{CHPh}\right), 5.40(\mathrm{~d}, J=10.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1), 4.84\left(\mathrm{AB}_{\mathrm{q}}, J=11.8 \mathrm{~Hz}, v\right.$ $\left.=38.2 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{Ph}\right), 4.47(\mathrm{dd}, \mathrm{J}=9.6,2.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-4), 4.37-4.17(\mathrm{~m}, 4 \mathrm{H}, \mathrm{H}-2, \mathrm{H}-3$, $\mathrm{H}-5$, and $\left.\mathrm{H}-\mathrm{\sigma}_{\mathrm{e}}\right), 3.91(\mathrm{t}, \mathrm{J}=9.9 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6 \mathrm{a}), 3.13-2.90\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{SO}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{Si}\right), 1.18-$ $0.91\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{SO}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{Si}\right), 0.07\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{3}\right) ;{ }^{13} \mathrm{C} \mathrm{NMR}\left(63 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 137.1$, $136.6,129.2,128.7,128.4,128.3,128.0,126.1,102.4,82.3,76.2,75.2,74.4,69.0,60.5,51.4$, 45.7, 10.2, -2.0 ; MS (FAB) $m / e$ (rel. intensity) $587(28), 586(83), 585(35), 584\left(\mathrm{M}+\mathrm{H}^{+}\right.$, 100), 406 (19), 405 (83), 404 (19), 403 (82), 307 (58), 289 (42), 270 (20), 226 (64), 219 (22); HRMS (FAB) calcd for $\mathrm{C}_{25} \mathrm{H}_{35} \mathrm{BrNO}_{6} \mathrm{SSi}\left(\mathrm{M}+\mathrm{H}^{+}\right)$584.1138, found 584.1155. Anal. Calcd for $\mathrm{C}_{25} \mathrm{H}_{34} \mathrm{BrNO}_{6} \mathrm{SSi}: \mathrm{C}, 51.36 ; \mathrm{H}, 5.86 ; \mathrm{N}, 2.40 ; \mathrm{S}, 5.48$. Found: C, $51.60 ; \mathrm{H}, 5.68$; $\mathrm{N}, 2.25 ; \mathrm{S}, 5.44 . \beta$-anomer: ${ }^{1} \mathrm{H}$ NMR ( $250 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.55-7.30(\mathrm{~m}, 10 \mathrm{H}, \mathrm{ArH}), 5.57$ $\left(\mathrm{s}, \mathrm{O}_{2} \mathrm{CHPh}\right), 5.35(\mathrm{~d}, J=10.9 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{NH}), 5.22(\mathrm{dd}, J=10.9,1.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1), 4.79$ $\left(\mathrm{AB}_{\mathrm{q}}, J=12.0 \mathrm{~Hz}, v=34.6 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{Ph}\right), 4.34-4.17(\mathrm{~m}, 5 \mathrm{H}), 3.77(\mathrm{t}, J=9.3 \mathrm{~Hz}, 1 \mathrm{H}$, $\mathrm{H}-6 \mathrm{a}$ ), 3.12-2.95 (m, $\left.2 \mathrm{H}, \mathrm{SO}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{Si}\right), 1.18-0.90\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{SO}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{Si}\right), 0.07$ (s, 9
$\left.\mathrm{H}, \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{3}\right) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(63 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 137.3,137.2,128.7,128.4,128.2,128.0,127.8$, 126.1, 102.3, 78.2, 76.6, 75.2, 73.8, 68.6, 65.8, 53.0, 51.8, 10.4, -2.1; Anal. Calcd for $\mathrm{C}_{25} \mathrm{H}_{34} \mathrm{BrNO}_{6} \mathrm{SSi}: \mathrm{C}, 51.36 ; \mathrm{H}, 5.86 ; \mathrm{N}, 2.40 ; \mathrm{S}, 5.48$. Found: C, $51.60 ; \mathrm{H}, 5.68 ; \mathrm{N}, 2.25 ; \mathrm{S}$, 5.44.

O-[3-O-Benzyl-4,6-O-benzylidene-2-deoxy-2-[2-(trimethylsilyl)ethanesulfonamido]- $\alpha$ -D-allopyranosyl]- $\beta$-(1 $\rightarrow 4$ )-6-O-benzyl-2,5-dideoxy-2,5-[(diphenylmethyl)imino]-1,3-O-isopropylidene-D-glucitol (73).

Potassium hexamethyldisilazide ( 0.5 M in toluene, 0.225 mmol ) was added dropwise to $\mathrm{a}-40^{\circ} \mathrm{C}$ stirred solution of trans-bromosulfonamide $72(61.0 \mathrm{mg}, 0.104$ $\mathrm{mmol})$ and azasugar $69(55.7 \mathrm{mg}, 0.121 \mathrm{mmol})$ in $\mathrm{DMF}(1 \mathrm{~mL})$. The reaction mixture was stirred for 30 min at $-40^{\circ} \mathrm{C}$, slowly warmed to room temperature, stirred an additional 15 h , and extracted from brine ( 10 mL ) with diethyl ether ( $3 \times 6 \mathrm{~mL}$ ). The combined organic layers were dried $\left(\mathrm{MgSO}_{4}\right)$, concentrated, and the residue chromatographed (silica; $2 \% \mathrm{Et}_{3} \mathrm{~N}, 20 \rightarrow 40 \rightarrow 50 \%$ ethyl acetate in hexanes) to provide disaccharide 73 ( $80.3 \mathrm{mg}, 80 \%$ ), followed by recovered alcohol 69 ( 14 mg , $25 \%$ 73: colorless foam; $[\alpha]_{D}$ $-64.9^{\circ}\left(c 1.1, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right)$; IR (neat) $v_{\max } 3350,3060,3030,2980,2940,2870,1455,1380,1335$, $1255,1225,1170,1145,1090,1030 \mathrm{~cm}^{-1} ; 1 \mathrm{H} \mathrm{NMR}\left(490 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}\right) \delta 7.56-7.19(\mathrm{~m}, 25$ $\mathrm{H}, \mathrm{ArH}), 5.54\left(\mathrm{~s}, 1 \mathrm{H}, \mathrm{O}_{2} \mathrm{CHPh}\right), 5.15(\mathrm{~s}, 1 \mathrm{H}, \mathrm{NCHPh} 2), 5.07(\mathrm{~d}, J=11.4 \mathrm{~Hz}, 1 \mathrm{H}$, OCHHPh $\left.), 4.77(\mathrm{~d}, J=9.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{NH}), 4.66(\mathrm{~d}, J=7.9 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1)^{\prime}\right), 4.66(\mathrm{~d}, J=11.4$ $\mathrm{Hz}, 1 \mathrm{H}, \mathrm{OCHHPh}), 4.36(\mathrm{~d}, J=5.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3), 4.34-4.32\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{Ph}\right), 4.30(\mathrm{~s}, 1$
$\mathrm{H}, \mathrm{H}-4), 4.27-4.20\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{H}-3^{\prime}\right.$ and $\left.\mathrm{H}-\mathrm{6}_{\mathrm{e}}{ }^{\prime}\right), 3.95(\mathrm{td}, \mathrm{J}=9.9,5.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-5$ ), 3.77 (dd, $\left.J=9.5,2.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-4^{\prime}\right), 3.73\left(\mathrm{t}, J=10.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-\mathrm{G}_{\mathrm{a}}{ }^{\prime}\right), 3.63(\mathrm{t}, J=9.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6)$, 3.48 (dd, $J=9.2,5.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6), 3.47$ (td, $J=8.8,3.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-2$ ), 3.39 (dd, $J=11.8$, $6.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1), 3.33(\mathrm{dd}, \mathrm{J}=11.8,5.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1), 3.26(\mathrm{dd}, J=10.3,5.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-5)$, $3.18(\mathrm{q}, J=5.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-2), 2.90-2.84\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{SO}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{Si}\right), 1.31(\mathrm{~s}, 3 \mathrm{H}$, $\left.\mathrm{O}_{2} \mathrm{CCH}_{3} \mathrm{Me}\right), 1.29\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{O}_{2} \mathrm{CCH}_{3} \mathrm{Me}\right), 1.09-1.02\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{SO}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{Si}\right), 0.04(\mathrm{~s}, 9 \mathrm{H}$, $\left.\mathrm{Si}\left(\mathrm{CH}_{3}\right)_{3}\right) ;{ }^{13} \mathrm{C}$ NMR $\left(63 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}\right) \delta 143.8,143.1,138.9,138.3,137.9,129.2,128.9$, $128.8,128.7,128.5,128.2,127.5,127.4,127.3,126.4,102.3,98.6,98.2,84.5,80.5,77.2,76.9$, $75.1,73.5,72.8,71.5,69.2,67.4,63.9,62.7,61.8,56.9,50.5,26.2,21.6,10.4,-2.0 ;$ MS (FAB) $m / e$ (rel. intensity) $965(29), 964(43), 963\left(\mathrm{M}+\mathrm{H}^{+}, 66\right), 843(29), 842$ (63), 841 (100); HRMS (FAB) calcd for $\mathrm{C}_{54} \mathrm{H}_{67} \mathrm{~N}_{2} \mathrm{O}_{10} \mathrm{SSi}\left(\mathrm{M}+\mathrm{H}^{+}\right) 963.4286$, found 963.4293. Anal. Calcd for $\mathrm{C}_{54} \mathrm{H}_{66} \mathrm{~N}_{2} \mathrm{O}_{10}$ SSi: C, 67.33; H, 6.90; N, 2.91; S, 3.33. Found: C, 67.16; H, 7.01; N, 2.63; S, 3.33.
$O$-[2-Acetamido-3-O-benzyl-4,6-O-benzylidene-2-deoxy- $\alpha$-D-allopyranosyl]- $\beta$-(1 $\rightarrow 4$ )-6-$O$-benzyl-2,5-dideoxy-2,5-[(diphenylmethyl)imino]-1,3-O-isopropylidene-D-glucitol (74).

A suspension of sulfonamide $73(233 \mathrm{mg}, 0.242 \mathrm{mmol})$ and cesium fluoride ( $200 \mathrm{mg}, 1.3 \mathrm{mmol}$ ) in DMF ( 1 mL ) was rapidly stirred for 19 h at $95^{\circ} \mathrm{C}$, cooled, acetylated for 4 h with pyridine $(1.0 \mathrm{~mL})$ and acetic anhydride $(0.5 \mathrm{~mL})$, concentrated under reduced pressure, and extracted from saturated aq. $\mathrm{Na}_{2} \mathrm{CO}_{3}(50 \mathrm{~mL})$ with ethyl acetate $(3 \times 30 \mathrm{~mL})$. The combined organic layers were dried $\left(\mathrm{MgSO}_{4}\right)$, concentrated,
and the residue chromatographed (silica; $E t_{3} \mathrm{~N}, 40 \rightarrow 50 \%$ ethyl acetate in hexanes) to afford the desired N -acetylated disaccharide ( $74 ; 161 \mathrm{mg}, 79 \%$ ) as a colorless foam: $[\alpha]_{\mathrm{D}}-89.8^{\circ}\left(c 1.1, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right) ; \mathrm{IR}$ (neat) $v_{\max } 3410,3050,3020,2980,2920,2860,1685,1495$, $1455,1375,1225,1170,1095 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H}$ NMR $\left(490 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}\right) \delta 7.56-7.19(\mathrm{~m}, 25 \mathrm{H}$, $\operatorname{ArH}), 5.72(\mathrm{~d}, J=9.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{NH}), 5.57\left(\mathrm{~s}, 1 \mathrm{H}, \mathrm{O}_{2} \mathrm{CHPh}\right), 5.04(\mathrm{~d}, J=11.6 \mathrm{~Hz}, 1 \mathrm{H}$, OCHHPh $), 4.98\left(\mathrm{~s}, 1 \mathrm{H}, \mathrm{NCHPh}_{2}\right), 4.72(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1), 4.58(\mathrm{~d}, J=11.6 \mathrm{~Hz}, 1 \mathrm{H}$, OCHHPh $), 4.45(\mathrm{dt}, J=5.5,1.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3), 4.36(\mathrm{~d}, J=12.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{OCH} H \mathrm{Ph}), 4.34$ (dd, $\left.J=10.4,5.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-\mathrm{G}_{\mathrm{e}}{ }^{\prime}\right), 4.27(\mathrm{~d}, J=12.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{OCHHPh}), 4.18$ (ddd, $J=9.4$, $8.6,3.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-2$ '), $4.15(\mathrm{~s}, 1 \mathrm{H}, \mathrm{H}-4), 4.13(\mathrm{t}, J=2.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3$ '), $4.08(\mathrm{td}, I=9.9,5.2$ $\left.\mathrm{Hz}, 1 \mathrm{H}, \mathrm{H}-5^{\prime}\right), 3.80\left(\mathrm{dd}, J=9.8,2.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-4^{\prime}\right), 3.79\left(\mathrm{t}, J=10.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6_{\mathrm{a}}{ }^{\prime}\right), 3.68$ $(\mathrm{d}, J=10.7,9.5 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6), 3.44(\mathrm{dd}, J=9.5,5.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6), 3.33(\mathrm{~d}, J=6.5 \mathrm{~Hz}, 2 \mathrm{H}$, $\mathrm{H}-1), 3.18(\mathrm{q}, J=6.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-2), 3.14(\mathrm{ddt}, J=10.7,5.2,1.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-5), 1.84(\mathrm{~s}, 3 \mathrm{H}$, $\mathrm{COCH}_{3}$ ), $1.29\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{O}_{2} \mathrm{CCH}_{3} \mathrm{Me}\right), 1.28\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{O}_{2} \mathrm{CCH}_{3} \mathrm{Me}\right)$; ${ }^{13} \mathrm{C} \mathrm{NMR}(63 \mathrm{MHz}$, $\left.\mathrm{CD}_{2} \mathrm{Cl}_{2}\right) \delta 169.2,144.6,143.7,139.3,138.9,138.2,129.4,129.1,129.0,128.8,128.7,128.6$, $128.4,127.8,127.6,127.4,126.6,102.5,101.4,98.9,86.6,80.7,77.5,76.6,75.1,74.8,73.1$, $72.0,69.6,69.4,64.2,63.3,62.3,52.6,26.2,23.7,22.0 ; \mathrm{MS}$ (FAB) $m / e$ (rel. intensity) 842 (20), $841\left(\mathrm{M}+\mathrm{H}^{+}, 34\right), 783(16), 720(19), 719(39), 168(63), 167(100), 166(25), 165(41) ;$ HRMS (FAB) calcd for $\mathrm{C}_{51} \mathrm{H}_{57} \mathrm{~N}_{2} \mathrm{O}_{9}\left(\mathrm{M}+\mathrm{H}^{+}\right)$841.4064, found 841.4079. Anal. Calcd for $\mathrm{C}_{51} \mathrm{H}_{56} \mathrm{~N}_{2} \mathrm{O}_{9}: \mathrm{C}, 72.84 ; \mathrm{H}, 6.71 ; \mathrm{N}, 3.33$. Found: C, $73.08 ; \mathrm{H}, 6.96 ; \mathrm{N}, 3.09$. dideoxy-2,5-[(diphenylmethyl)imino]-D-glucitol (75).

Disaccharide 74 ( $136 \mathrm{mg}, 0.162 \mathrm{mmol}$ ) was stirred 15 h with $5 \%$ concentrated aq. HCl in methanol, poured into concentrated aq. $\mathrm{NaHCO}_{3}(10 \mathrm{~mL})$, and extracted with 1:2 isopropanol/dichloromethane $(3 \times 4 \mathrm{~mL})$. The combined organic layers were dried $\left(\mathrm{Na}_{2} \mathrm{SO}_{4}\right)$, concentrated, and the residue chromatographed ( $2 \% \mathrm{Et}_{3} \mathrm{~N}$, 10 $\rightarrow 15 \%$ methanol in ethyl acetate) to provide the tetraol ( $75 ; 106 \mathrm{mg}, 92 \%$ ) as a colorless solid: $\mathrm{mp} 156-159^{\circ} \mathrm{C}(\mathrm{dec})$; $[\alpha]_{\mathrm{D}}-18.8^{\circ}\left(c 1.1, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right)$; $\mathrm{IR}(\mathrm{KBr}) v_{\max } 3490$ (br), 3050, 3020, 2910, 2860, 1660, 1520, 1490, 1450, 1365, 1160, 1090, $1055 \mathrm{~cm}^{-1}{ }^{1}{ }^{1} \mathrm{H}$ NMR (490 MHz, $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ ) $\delta 7.41-7.19(\mathrm{~m}, 20 \mathrm{H}, \mathrm{ArH}), 5.38(\mathrm{~d}, \mathrm{~J}=8.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{NH}), 5.01(\mathrm{~s}, 1 \mathrm{H}$, $\mathrm{NCHPh} 2), 4.91(\mathrm{~d}, J=11.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{OCHHPh}), 4.61(\mathrm{~d}, J=11.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{OCHHPh}), 4.59$ $(\mathrm{d}, J=8.5 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1$ ') $4.59(\mathrm{~d}, J=12.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{OCHHPh}), 4.44(\mathrm{~d}, J=3.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{C}-3$ $\mathrm{OH}), 4.28(\mathrm{~d}, \mathrm{~J}=12.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{OCHHPh}), 4.26(\mathrm{td}, J=8.1,3.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3), 4.20(\mathrm{t}, \mathrm{J}=7.5$ $\mathrm{Hz}, 1 \mathrm{H}, \mathrm{H}-4), 3.95\left(\mathrm{t}, \mathrm{J}=3.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3^{\prime}\right), 3.94-3.89(\mathrm{~m}, 2 \mathrm{H}, \mathrm{H}-5$ and $\mathrm{H}-6$ '), $3.88(\mathrm{td}, J$ $=8.7,3.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-2$ ) , $3.82(\mathrm{~d}, J=9.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{C}-1 \mathrm{OH}), 3.73$ (ddd, $J=10.2,7.9,2.8 \mathrm{~Hz}$, $\left.\left.1 \mathrm{H}, \mathrm{H}-4)^{\prime}\right), 3.71-3.68(\mathrm{~m}, 1 \mathrm{H}, \mathrm{H}-6)^{\prime}\right), 3.47(\mathrm{t}, J=9.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1), 3.32(\mathrm{~d}, J=7.9 \mathrm{~Hz}, 1 \mathrm{H}$, C-4' OH ), $3.31-3.24(\mathrm{~m}, 2 \mathrm{H}, \mathrm{H}-2$ and C-6' OH ), $3.15(\mathrm{dd}, J=11.0,4.9 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1), 3.12$ (dd, $J=9.7,2.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6), 3.06(\mathrm{dd}, J=9.7,4.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6$ ), 2.95-2.91 (m, $1 \mathrm{H}, \mathrm{H}-5$ ), 1.42 ( $\mathrm{s}, 3 \mathrm{H}, \mathrm{COCH}_{3}$ ); ${ }^{13} \mathrm{C}$ NMR ( $123 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}$ ) $\delta 170.2,142.7,142.5,138.8,138.6$, $129.2,129.1,128.9,128.7,128.6,128.5,128.2,128.1,127.7,127.7,101.0,88.5,79.4,76.3,74.9$, $74.8,73.3,73.1,69.6,69.2,65.0,62.8,62.7,61.8,52.6,23.0$; MS (FAB) $m / e$ (rel. intensity) 714 (20), $713\left(\mathrm{M}+\mathrm{H}^{+}, 43\right), 591(10), 307(27), 289(15), 176$ (19), 168 (47), 167 (100), 166 (18), 165 (27); HRMS (FAB) calcd for $\mathrm{C}_{41} \mathrm{H}_{49} \mathrm{~N}_{2} \mathrm{O}_{9}\left(\mathrm{M}+\mathrm{H}^{+}\right) 713.3438$, found 713.3455. Anal. Calcd for $\mathrm{C}_{41} \mathrm{H}_{48} \mathrm{~N}_{2} \mathrm{O}_{9}$ : C, 69.05; H, $6.72 ; \mathrm{N}, 3.86$. Found: C, 69.08; H, 6.79; N, 3.93.

O-[2-Acetamido-2-deoxy- $\alpha$-D-allopyranosyl]- $\beta$-(1 $\rightarrow 4$ )-2,5-dideoxy-2,5-imino-D-glucitol (64).

A mixture of disaccharide $75(90.2 \mathrm{mg}, 0.126 \mathrm{mmol})$ and $10 \% \mathrm{Pd}-\mathrm{C}$ catalyst ( 67 mg ) in $1: 9$ acetic acid/methanol ( 1.5 mL ) was shaken 1 day under hydrogen ( 50 psi ), a second portion of catalyst ( 52 mg ) was added, the hydrogenolysis was continued an additional day, then filtered through Celite, concentrated, and the residue chromatographed (Bio-gel P-2; $10 \mathrm{mM} \mathrm{NH}_{4} \mathrm{OAc}_{\mathrm{OA}}^{\mathrm{NH}} 3$, pH 9). Treatment of an aqueous solution of the salt thus produced with Amberlite IRA-400(OH) afforded the free base of azasugar 64 (amorphous solid; $39.3 \mathrm{mg}, 85 \%$ ) after lyophilization: $[\alpha]_{\mathrm{D}}$ $-19.1^{\circ}$ (c 1.2, water); IR (KBr) $v_{\max } 3350(\mathrm{v} \mathrm{br}), 2920,2880,1650,1555,1405,1380,1065$ $\mathrm{cm}^{-1} ;{ }^{1} \mathrm{H}$ NMR $\left(490 \mathrm{MHz}, \mathrm{D}_{2} \mathrm{O}+0.5 \% \mathrm{CD}_{3} \mathrm{CO}_{2} \mathrm{D}\right) \delta 4.83(\mathrm{~d}, J=8.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1$ '), 4.55 $(\mathrm{dd}, J=3.6,1.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3), 4.14(\mathrm{dd}, J=3.3,1.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-4), 4.08(\mathrm{t}, J=3.0 \mathrm{~Hz}, 1 \mathrm{H}$, H-3'), 4.02 (dd, $\left.J=12.2,4.9 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6^{\prime}\right), 3.94(\mathrm{dd}, J=11.9,5.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6$ ), 3.93 (dd, $J$ $=12.2,8.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6$ ), $3.92(\mathrm{dd}, J=12.2,2.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1), 3.88(\mathrm{dd}, J=11.9,8.1 \mathrm{~Hz}, 1$ H, H-6), 3.87 (dd, $J=8.7,3.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-2$ '), $3.85-3.81(\mathrm{~m}, 2 \mathrm{H}, \mathrm{H}-2$ and $\mathrm{H}-5$ '), 3.73 (dd, $J$ $\left.=12.2,5.9 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1), 3.67(\mathrm{dd}, J=10.0,3.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-4)^{\prime}\right), 3.64(\mathrm{ddd}, J=8.1,5.6,3.3$ $\mathrm{Hz}, 1 \mathrm{H}, \mathrm{H}-5), 2.06\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{COCH}_{3}\right) ;{ }^{13} \mathrm{C}$ NMR ( $123 \mathrm{MHz}, \mathrm{D}_{2} \mathrm{O}+0.5 \% \mathrm{CD}_{3} \mathrm{CO}_{2} \mathrm{D}$ ) $\delta$ $174.1,99.6,84.5,73.9,73.3,69.8,66.6,65.9,63.8,61.0,59.4,56.8,52.8,22.0$; MS (FAB) $m / e$ (rel. intensity) $367\left(\mathrm{M}+\mathrm{H}^{+}, 9\right), 329(63), 308(24), 307(100), 290(15), 289$ (54); HRMS ( FAB ) calcd for $\mathrm{C}_{14} \mathrm{H}_{27} \mathrm{~N}_{2} \mathrm{O}_{9}\left(\mathrm{M}+\mathrm{H}^{+}\right)$367.1717, found 367.1727.

O-[3-O-Benzyl-4,6-O-benzylidene-2-deoxy-2-[2-(trimethylsilyl)ethanesulfonamido]-D-allopyranosyl]- $\beta-(1 \rightarrow 4)$-6-O-benzyl-3-O-[[2-(trimethylsilyl)ethoxy]methyl]-D-ribo-hex-1-enopyranose (76).

Potassium hexamethyldisilazide ( 0.5 M in toluene, 2.98 mmol ) was added dropwise to a $-40^{\circ} \mathrm{C}$ stirred solution of trans-bromosulfonamide 72 ( $833 \mathrm{mg}, 1.42$ mmol ) and allal derivative $47(578 \mathrm{mg}, 1.58 \mathrm{mmol})$ in DMF ( 12 mL ). The reaction mixture was stirred for 30 min at $-40^{\circ} \mathrm{C}$ and then allowed to slowly warm to room temperature. After 15 h , the reaction was poured into $4: 1$ saturated aq. $\mathrm{NH}_{4} \mathrm{Cl} /$ water $(250 \mathrm{~mL})$ and extracted with diethyl ether $(2 \times 200 \mathrm{~mL})$. The combined organic layers were dried $\left(\mathrm{Na}_{2} \mathrm{SO}_{4}\right)$, concentrated, and the residue chromatographed (silica, $15 \rightarrow$ $20 \%$ ethyl acetate in hexanes) to provide disaccharide 76 (foam; $780 \mathrm{mg}, 63 \%$ ), followed by impure recovered alcohol 47 (215 mg). The alcohol was rechromatographed (silica, $35 \rightarrow 50 \%$ diethyl ether in hexanes) to provide pure material (147 mg, 25\%). 76: $[\alpha]_{\mathrm{D}}+34.5^{\circ}\left(c 1.6, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right.$ ); IR (neat) $v_{\max } 3420,3060,3030$, $2950,2890,1640,1330,1250,1170,1145,1090,1030 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H} \mathrm{NMR}\left(490 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ $7.51-7.20(\mathrm{~m}, 15 \mathrm{H}, \mathrm{ArH}), 6.43(\mathrm{~d}, J=5.9 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1), 5.53\left(\mathrm{~s}, 1 \mathrm{H}, \mathrm{O}_{2} \mathrm{CHPh}\right), 5.07(\mathrm{~d}, J$ $=11.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{OCHHPh}), 4.90(\mathrm{t}, J=5.9 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-2), 4.89(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 1 \mathrm{H}$, $\left.\mathrm{OCHHOCH}_{2} \mathrm{CH}_{2} \mathrm{Si}\right), 4.78(\mathrm{~d}, \mathrm{~J}=8.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1), 4.74(\mathrm{~d}, \mathrm{~J}=6.8 \mathrm{~Hz}, 1 \mathrm{H}$, $\left.\mathrm{OCHHOCH}_{2} \mathrm{CH}_{2} \mathrm{Si}\right), 4.70(\mathrm{~d}, J=9.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{NH}), 4.66(\mathrm{~d}, J=11.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{OCHHPh})$, $4.60(\mathrm{~d}, J=12.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{OCHHPh}), 4.50(\mathrm{~d}, J=12.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{OCHHPh}), 4.37(\mathrm{dd}, J=$ $\left.10.4,2.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6_{\mathrm{e}}{ }^{\prime}\right), 4.27\left(\mathrm{t}, J=2.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3^{\prime}\right), 4.18(\mathrm{dd}, J=5.9,3.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3)$,
$4.11(\mathrm{dt}, J=10.7,2.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-5), 4.06(\mathrm{dd}, J=10.7,3.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-4), 4.04(\mathrm{td}, J=10.0$, $5.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-5$ '), $3.82(\mathrm{dd}, J=10.8,3.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6), 3.77(\mathrm{td}, J=9.9,6.5 \mathrm{~Hz}, 1 \mathrm{H}$, $\left.\mathrm{OCHHCH}_{2} \mathrm{Si}\right), 3.75\left(\mathrm{t}, \mathrm{J}=10.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6_{\mathrm{a}}{ }^{\prime}\right), 3.74-3.71(\mathrm{~m}, 2 \mathrm{H}, \mathrm{H}-4$ and H-6), 3.56 $(\mathrm{td}, J=9.9,6.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{OCHHCH} 2 \mathrm{Si}), 3.41(\mathrm{td}, J=8.9,3.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-2$ ), $2.93(\mathrm{td}, J=$ $\left.13.8,4.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{SO}_{2} \mathrm{CHHCH}_{2} \mathrm{Si}\right), 2.79\left(\mathrm{td}, J=13.8,4.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{SO}_{2} \mathrm{CHHCH}_{2} \mathrm{Si}\right), 1.07$ $\left(\mathrm{td}, J=13.8,4.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{SO}_{2} \mathrm{CH}_{2} \mathrm{CHHSi}\right), 1.11-0.92\left(\mathrm{~m}, 3 \mathrm{H}, \mathrm{CH}_{2} \mathrm{CHHSi}\right), 0.07(\mathrm{~s}, 9 \mathrm{H}$, $\left.\mathrm{Si}\left(\mathrm{CH}_{3}\right)_{3}\right), 0.04\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{3}\right) ;{ }^{13} \mathrm{C}$ NMR $\left(123 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 145.6,137.6,137.2$, $137.0,128.8,128.2,128.1,127.9,127.6,125.8,101.7,100.2,99.7,94.1,79.8,77.0,74.8,74.4$, $73.3,72.4,68.7,68.0,67.6,64.5,63.3,56.9,50.3,17.8,9.7,-1.6,-2.3$; MS (FAB) $m / e$ (rel. intensity) $892\left(\mathrm{M}+\mathrm{Na}^{+}, 5\right), 722(23), 412(25), 396(36), 304(22), 278(100), 227(10), 226$ (76), 210 (32), 201 (31); HRMS (FAB) calcd for $\mathrm{C}_{44} \mathrm{H}_{63} \mathrm{NNaO}_{11} \mathrm{SSi}_{2}\left(\mathrm{M}+\mathrm{Na}^{+}\right) 892.3560$, found 892.3624. Anal. Calcd for $\mathrm{C}_{44} \mathrm{H}_{63} \mathrm{NO}_{11} \mathrm{SSi}_{2}: \mathrm{C}, 60.73 ; \mathrm{H}, 7.30 ; \mathrm{N}, 1.61 ; \mathrm{S}, 3.68$. Found: C, 60.58; H, 7.36; N, 1.41; S, 3.70.
$O$-[3-O-Benzyl-4,6-O-benzylidene-2-deoxy-2-[2-(trimethylsilyl)ethanesulfonamido]-D-allopyranosyl]- $\beta-(1 \rightarrow 4)$-6-O-benzyl-2-bromo-2-deoxy-3-O-[[2-(trimethylsilyl)-ethoxylmethyll-D-altropyranosyl 2-(Trimethylsilyl)ethanesulfonamide (77).

To a solution of glycal $76(749 \mathrm{mg}, 0.861 \mathrm{mmol})$ in dichloromethane ( 2 mL ) was added solid $\mathrm{N}, \mathrm{N}$-dibromo-2-(trimethylsilyl)ethanesulfonamide (71; 315 mg , $0.929 \mathrm{mmol})$ at $0^{\circ} \mathrm{C}$. After 1 h , ethanol ( 10 mL ) and $\mathrm{NH}_{4} \mathrm{I}(120 \mathrm{mg}, 1.04 \mathrm{mmol})$ were added to the reaction, the mixture was stirred an additional 1 h at room temperature, then diluted with diethyl ether ( 100 mL ), reduced with saturated aq.
$\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}(30 \mathrm{~mL})$, dried $\left(\mathrm{Na}_{2} \mathrm{SO}_{4}\right)$, concentrated, and the residue chromatographed (silica, 20\% ethyl acetate in hexanes) to provide a 6.5:1 $\alpha: \beta$ anomeric mixture of sulfonamides (colorless foam; $205 \mathrm{mg}, 46 \%$ ). 76: IR (neat) $v_{\max } 3360,3060,3030,2950$, $2900,1420,1335,1250,1145,1110,1090 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H}$ NMR ( $490 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.50-7.19$ $(\mathrm{m}, 15 \mathrm{H}, \operatorname{ArH}), 6.49(\mathrm{~d}, J=10.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{NH}), 5.51\left(\mathrm{~s}, 1 \mathrm{H}, \mathrm{O}_{2} \mathrm{CHPh}\right), 5.39(\mathrm{~d}, J=10.1$ $\mathrm{Hz}, 1 \mathrm{H}, \mathrm{H}-1), 5.05(\mathrm{~d}, \mathrm{~J}=11.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{OCHHPh}), 4.80\left(\mathrm{AB}_{\mathrm{q}}, J=6.8 \mathrm{~Hz}, \mathrm{v}=20.2 \mathrm{~Hz}, 2 \mathrm{H}\right.$, $\left.\mathrm{OCH}_{2} \mathrm{OCH}_{2} \mathrm{CH}_{2} \mathrm{Si}\right), 4.68(\mathrm{~d}, J=12.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{OCHHPh}), 4.66(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1)$, $4.62(\mathrm{~d}, J=11.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{OCHHPh}), 4.53(\mathrm{~d}, J=9.5 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{NH}), 4.50(\mathrm{~d}, J=12.1 \mathrm{~Hz}, 1$ $\mathrm{H}, \mathrm{OCH} H \mathrm{Ph}), 4.42(\mathrm{dd}, J=10.0,3.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-4), 4.36\left(\mathrm{dd}, J=10.4,5.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-\mathrm{be}^{\prime}\right)$, $4.33(\mathrm{t}, J=3.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3), 4.23(\mathrm{dd}, J=3.6,1.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-2), 4.18(\mathrm{t}, J=2.6 \mathrm{~Hz}, 1 \mathrm{H}$, H-3'), 4.06 (td, J = 9.7, $5.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-5 '), 4.03$ (ddd, $J=10.0,4.1,1.9 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-5$ ), 3.81 $(\mathrm{td}, J=9.9,7.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{OCHHCH} 2 \mathrm{Si}), 3.77(\mathrm{dd}, J=10.6,4.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6), 3.72(\mathrm{t}, J=10.4$ $\left.\mathrm{Hz}, 1 \mathrm{H}, \mathrm{H}-6 \mathrm{a}^{\prime}\right), 3.69$ (dd, $J=9.7,2.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-4$ ), 3.59 ( $\mathrm{td}, J=9.5,7.2 \mathrm{~Hz}, 1 \mathrm{H}$, $\left.\mathrm{OCHHCH}_{2} \mathrm{Si}\right), 3.54(\mathrm{dd}, J=10.7,1.9 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6), 3.35(\mathrm{ddd}, J=9.4,8.5,3.2 \mathrm{~Hz}, 1 \mathrm{H}$, $\mathrm{H}^{2}$ '), 3.07 (td, $J=13.8,4.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{SO}_{2} \mathrm{CHHCH}_{2} \mathrm{Si}$ ), 2.93 (td, $J=13.8,4.4 \mathrm{~Hz}, 1 \mathrm{H}$, $\left.\mathrm{SO}_{2} \mathrm{CHHCH}_{2} \mathrm{Si}\right), 2.80\left(\mathrm{td}, J=13.5,4.9 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{SO}_{2} \mathrm{CHHCH}_{2} \mathrm{Si}\right), 2.69(\mathrm{td}, J=13.5,4.7 \mathrm{~Hz}$, $1 \mathrm{H}, \mathrm{SO}_{2} \mathrm{CHHCH}_{2} \mathrm{Si}$ ), 1.11 ( $\mathrm{td}, J=13.8,4.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{SO}_{2} \mathrm{CH}_{2} \mathrm{CHHSi}$ ), $1.07-0.90(\mathrm{~m}, 5 \mathrm{H}$, $\left.\mathrm{CH}_{2} \mathrm{CHHSi}\right), 0.07\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{3}\right), 0.05\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{3}\right), 0.04\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{3}\right) ;{ }^{13} \mathrm{C}$ NMR ( $63 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 137.5,137.2,136.9,128.9,128.3,128.2,128.0,127.8,127.8,125.9$, $101.9,100.7,96.0,81.4,79.8,77.4,76.7,74.8,73.4,70.8,68.6,68.3,67.8,66.3,63.4,56.6,51.0$, 50.4, 46.6, 17.9, 9.8, -1.6, -2.1, -2.2; Anal. Calcd for $\mathrm{C}_{49} \mathrm{H}_{77} \mathrm{BrN}_{2} \mathrm{O}_{13} \mathrm{~S}_{2} \mathrm{Si}_{3}$ : $\mathrm{C}, 52.06 ; \mathrm{H}$, 6.86; N, 2.48; S, 5.67. Found: C, $52.40 ; H, 7.04 ; \mathrm{N}, 2.31 ; \mathrm{S}, 5.67$.

O-[3-O-Benzyl-4,6-O-benzylidene-2-deoxy-2-[2-(trimethylsilyl)ethanesulfonamido]-D-allopyranosyl]- $\beta-(1 \rightarrow 4)-O-[6-O-b e n z y l-2-d e o x y-2-[2-(t r i m e t h y l s i l y l) e t h a n e s u l f o n-~$ amido]-3-O-[[2-(trimethylsilyl)ethoxy]methyl]-D-allopyranosyl]- $\beta$-(1 $\rightarrow 4$ )-6-O-benzyl-2,5-dideoxy-2,5-[(diphenylmethyl)imino]-1,3-O-isopropylidene-D-glucitol (78).

Potassium hexamethyldisilazide ( 0.5 M in toluene, 0.322 mmol ) was added dropwise to $\mathrm{a}-40^{\circ} \mathrm{C}$ stirred solution of bromosulfonamide $77(120 \mathrm{mg}, 0.106 \mathrm{mmol})$ and azasugar $69(50.7 \mathrm{mg}, 0.110 \mathrm{mmol})$ in DMF ( 1 mL ). The reaction mixture was stirred for 30 min at $-40^{\circ} \mathrm{C}$ and then allowed to slowly warm to room temperature. After 18 h , the reaction was poured into brine $(15 \mathrm{~mL})$ and was extracted with diethyl ether ( $3 \times 8 \mathrm{~mL}$ ). The combined organic layers were dried $\left(\mathrm{MgSO}_{4}\right)$, concentrated, and the residue chromatographed (silica; $2 \% \mathrm{Et}_{3} \mathrm{~N}, 10 \rightarrow 15 \rightarrow 20 \%$ ethyl acetate in toluene) to provide trisaccharide 78 ( $69 \mathrm{mg}, 43 \%$ ), followed by recovered alcohol 69 (27 mg, 54\%). 78: colorless foam; [ $\alpha]_{\mathrm{D}}-63.7^{\circ}\left(c 0.8, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right.$ ); IR (neat) $v_{\max } 2830,3060$, $3030,2950,1455,1330,1255,1170,1145,1030,1045 \mathrm{~cm}^{-1} ; 1 \mathrm{H} \mathrm{NMR}\left(490 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}\right) \delta$ 7.58-7.15 (m, $30 \mathrm{H}, \mathrm{ArH}), 5.53\left(\mathrm{~s}, 1 \mathrm{H}, \mathrm{O}_{2} \mathrm{CHPh}\right), 5.48(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{NH}$ ) , $5.17(\mathrm{~s}, 1$ $\mathrm{H}, \mathrm{NCHPh} 2), 5.04(\mathrm{~d}, J=11.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{OCHHPh}), 4.83\left(\mathrm{AB}_{\mathrm{q}^{\prime}} J=6.4 \mathrm{~Hz}, \mathrm{v}=19.2 \mathrm{~Hz}, 2 \mathrm{H}\right.$, $\left.\mathrm{OCH}_{2} \mathrm{OCH}_{2} \mathrm{CH}_{2} \mathrm{Si}\right), 4.72\left(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1^{\prime}\right), 4.71\left(\mathrm{~d}, J=9.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1{ }^{\prime \prime}\right), 4.64(\mathrm{~d}$, $J=11.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{OCH} H \mathrm{Ph}), 4.55\left(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{NH} H^{\prime \prime}\right), 4.53(\mathrm{~d}, J=11.8 \mathrm{~Hz}, 1 \mathrm{H}$, OCHHPh $), 4.45(\mathrm{~d}, J=5.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3), 4.42(\mathrm{~d}, J=11.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{OCHHPh}), 4.37(\mathrm{dd}, J=$ $\left.10.3,5.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6 \mathrm{e}^{\prime \prime}\right), 4.30\left(\mathrm{AB}_{\mathrm{q}}, J=12.4 \mathrm{~Hz}, v=24.2 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{OCH} 2 \mathrm{Ph}\right), 4.30(2,1 \mathrm{H}$, $\mathrm{H}-4), 4.19\left(\mathrm{t}, \mathrm{J}=2.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3^{\prime \prime}\right), 4.16\left(\mathrm{t}, J=2.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3^{\prime}\right), 4.03(\mathrm{td}, J=9.8,5.1 \mathrm{~Hz}$, $\left.1 \mathrm{H}, \mathrm{H}-5^{\prime}\right), 3.90\left(\mathrm{dd}, J=9.8,2.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-4^{\prime}\right), 3.82(\mathrm{td}, J=9.9,6.8 \mathrm{~Hz}, 1 \mathrm{H}$,
$\left.\mathrm{OCHHCH}_{2} \mathrm{Si}\right), 3.75\left(\mathrm{br} \mathrm{d}, J=9.9 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-5{ }^{\prime}\right), 3.75\left(\mathrm{dd}, J=9.5,2.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-4{ }^{\prime \prime}\right), 3.73$ $\left(\mathrm{t}, J=10.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-\mathrm{Ga}^{\prime \prime}\right), 3.68\left(\mathrm{dd}, J=10.6,3.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6^{\prime}\right), 3.65(\mathrm{td}, J=10.2,6.8 \mathrm{~Hz}$, $1 \mathrm{H}, \mathrm{OCHHCH} 2 \mathrm{Si}), 3.63(\mathrm{dd}, J=10.4,9.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6), 3.59(\mathrm{dd}, J=10.6,2.2 \mathrm{~Hz}, 1 \mathrm{H}$, $\mathrm{H}^{\prime}$ '), $3.44(\mathrm{dd}, J=9.1,5.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6), 3.42-3.36\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{H}-2^{\prime}\right.$ and $\left.\mathrm{H}-2^{\prime \prime}\right), 3.31\left(\mathrm{AB}_{\mathrm{q}}\right.$ of $\mathrm{ABX}, J_{\mathrm{AB}}=11.8 \mathrm{~Hz}, J_{\mathrm{AX}}=7.0 \mathrm{~Hz}, J_{\mathrm{BX}}=5.8 \mathrm{~Hz}, v=9.2 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{H}-1$ and $\left.\mathrm{H}-1\right), 3.30-3.26$ (m, $1 \mathrm{H}, \mathrm{H}-5), 3.19(\mathrm{q}, \mathrm{J}=5.9 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-2), 3.04-2.73(\mathrm{~m}, 4 \mathrm{H}), \mathrm{SO}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{Si}, 1.24(\mathrm{~s}, 3$ $\left.\mathrm{H}, \mathrm{O}_{2} \mathrm{CCH}_{3} \mathrm{Me}\right), 1.22\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{O}_{2} \mathrm{CCH}_{3} \mathrm{Me}\right), 1.10-0.85\left(\mathrm{~m}, 6 \mathrm{H}, \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{Si}\right), 0.05(\mathrm{~s}, 9 \mathrm{H}$, $\left.\mathrm{Si}\left(\mathrm{CH}_{3}\right)_{3}\right),-0.01\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{3}\right),-0.02\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{3}\right) ;{ }^{13} \mathrm{C} \mathrm{NMR}\left(63 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}\right)$ $\delta 144.8,143.8,139.3,138.5,138.4,138.0,129.5,129.2,129.0,128.8,128.7,128.6,128.5,128.3$, $128.2,127.8,127.7,127.6,127.4,126.6,102.6,101.3,98.9,98.8,97.6,84.8,80.7,77.6,77.2$, $75.5,74.4,74.0,73.1,72.8,71.9,69.6,69.3,68.2,67.0,64.3,63.4,62.3,57.5,56.4,51.1,50.8$, $26.2,22.1,18.7,10.6,10.5,-1.2,-1.8$; HRMS (FAB) calcd for $\mathrm{C}_{78} \mathrm{H}_{110} \mathrm{~N}_{3} \mathrm{O}_{17} \mathrm{~S}_{2} \mathrm{Si}_{3}(\mathrm{M}+$ $\left.\mathrm{H}^{+}\right) 1508.6585$, found 1508.6572. Anal. Calcd for $\mathrm{C}_{78} \mathrm{H}_{109} \mathrm{~N}_{3} \mathrm{O}_{17} \mathrm{~S}_{2} \mathrm{Si}_{3}: \mathrm{C}, 62.08 ; \mathrm{H}, 7.28$; N, 2.78; S, 4.25. Found: C, 61.85; H, 7.29; N, 2.55; S, 4.20.

## 3,4,6-Tri-O-benzyl-2-deoxy-2-iodo- $\alpha$-D-mannopyranosyl 2-(Trimethylsilyl)ethanesul-

 fonamide (81).To a $0^{\circ} \mathrm{C}$ suspension of $3,4,6$-tri-O-benzyl-D-glucal ( $80 ; 1.01 \mathrm{~g}, 2.42 \mathrm{mmol}$ ), 2-(trimethylsilyl)ethanesulfonamide ( $70 ; 538 \mathrm{mg}, 2.97 \mathrm{mmol}$ ), and powdered $4-\AA$ molecular sieves ( 1.1 g ) in dichloromethane ( 20 mL ) was added solid I(sym-collidine $)_{2} \mathrm{ClO}_{4}(1.79 \mathrm{~g}, 3.82 \mathrm{mmol})$. The mixture was stirred for 30 min , diluted with diethyl ether ( 20 mL ), filtered through Celite, diluted with additional diethyl ether
$(120 \mathrm{~mL})$, washed with saturated aq. $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}(2 \times 20 \mathrm{~mL})$, saturated aq. $\mathrm{CuSO}_{4}(3 \times 20$ mL ), and brine ( 20 mL ), dried $\left(\mathrm{MgSO}_{4}\right)$, concentrated, and chromatographed (silica, $20 \%$ ethyl acetate in hexanes) to provide iodosulfonamide 81 ( $858 \mathrm{mg}, 78 \%$ ) as a pink gum: $[\alpha]_{D}$
$-14.5^{\circ}\left(c 1.9, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right)$; IR (neat) $v_{\max } 3250,3060,3030,2950,2890,2760,1455,1330,1255$, $1115 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H}$ NMR $\left(250 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.41-7.28(\mathrm{~m}, 13 \mathrm{H}, \mathrm{ArH}), 7.24-7.17(\mathrm{~m}, 2 \mathrm{H}$, $\operatorname{Ar} H), 5.99(\mathrm{~d}, J=8.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{NH}), 5.50(\mathrm{dd}, J=8.6,5.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1), 4.68(\mathrm{~d}, J=11.4$ $\mathrm{Hz}, 2 \mathrm{H}, \mathrm{OCHHPh}), 4.60(\mathrm{dd}, J=5.1,3.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-2), 4.54\left(\mathrm{AB}_{\mathrm{q}}, J=12.1 \mathrm{~Hz}, v=9.0 \mathrm{~Hz}\right.$, $\left.2 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{Ph}\right), 4.50(\mathrm{~d}, J=11.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{OCHHPh}), 4.48(\mathrm{~d}, I=11.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{OCHHPh})$, $4.03(\mathrm{td}, J=6.3,3.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-5), 3.80(\mathrm{dd}, J=10.4,6.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6), 3.70(\mathrm{t}, J=6.4 \mathrm{~Hz}, 1$ $\mathrm{H}, \mathrm{H}-4), 3.63(\mathrm{dd}, J=10.4,3.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6), 3.41(\mathrm{dd}, J=6.4,3.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3), 3.11-3.02$ $\left(\mathrm{m}, 2 \mathrm{H}, \mathrm{SO}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{Si}\right), 1.07-0.98\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{SO}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{Si}\right), 0.01\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{3}\right) ;{ }^{13} \mathrm{C}$ NMR ( $63 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 138.0,137.6,137.2,128.4,128.2,128.0,127.9,127.8,127.6,81.6$, $77.9,74.4,73.8,73.5,72.2,68.3,51.2,30.9,10.1,-2.0 ; \mathrm{MS}$ (FAB) $m / e$ (rel. intensity) 746 (M + Na+ 15), 326 (9), 271 (11), 262 (8), 239 (11), 234 (14), 226 (15), 181 (100); HRMS (FAB) calcd for $\mathrm{C}_{32} \mathrm{H}_{42} \mathrm{INNaO}_{6} \mathrm{SSi}\left(\mathrm{M}+\mathrm{Na}^{+}\right)$746.1447, found 746.1489. Anal. Calcd for $\mathrm{C}_{32} \mathrm{H}_{42} \mathrm{INO}_{6} \mathrm{SSi}: \mathrm{C}, 53.11 ; \mathrm{H}, 5.85 ; \mathrm{N}, 1.94 ; \mathrm{S}, 4.43$. Found: $\mathrm{C}, 53.22 ; \mathrm{H}, 5.60 ; \mathrm{N}, 1.89$; S, 4.50.
$O$-[3,4,6-Tri-O-benzyl-2-deoxy-2-[2-(trimethylsilyl)ethanesulfonamido]-D-allopyran-osyll- $\beta$-(1 $\rightarrow 4$ )-6-O-benzyl-2,5-dideoxy-2,5-[(diphenylmethyl)imino]-1,3-O-isopropyl-idene-D-glucitol (82).

To a $-78{ }^{\circ} \mathrm{C}$ solution of tetramethylpiperidine ( $99 \mu \mathrm{~L}, 0.62 \mathrm{mmol}$ ) in THF ( 0.5 mL ) was added a 1.3 M hexanes solution of butyllithium ( $475 \mu \mathrm{~L}, 0.62 \mathrm{mmol}$ ). The mixture was warmed to $0^{\circ} \mathrm{C}$ and added dropwise to a $-78^{\circ} \mathrm{C}$ solution of iodosulfonamide 81 ( $212 \mathrm{mg}, 0.293 \mathrm{mmol}$ ) and azasugar $69(149 \mathrm{mg}, 0.324 \mathrm{mmol})$ in THF ( 1 mL ), followed after 15 min by dropwise addition of silver trifluoromethanesulfonate (181 $\mathrm{mg}, 0.70 \mathrm{mmol})$ in THF ( 0.7 mL ). The reaction was covered with foil and allowed to slowly warm to room temperature. After 8 h , the reaction was poured into brine ( 15 mL ) and extracted with diethyl ether ( $3 \times 10 \mathrm{~mL}$ ). The combined organic layers were dried $\left(\mathrm{Na}_{2} \mathrm{SO}_{4}\right)$, concentrated, and the residue chromatographed (silica; $2 \% \mathrm{Et}_{3} \mathrm{~N}, 25$ $\rightarrow 30 \rightarrow 40 \%$ ethyl acetate in hexanes) to provide disaccharide 82 ( $152 \mathrm{mg}, 49 \%$ ), followed by recovered alcohol $69(69 \mathrm{mg}, 46 \%) .82$ : colorless foam; $[\alpha]_{\mathrm{D}}-36.8^{\circ}$ (c 1.2, $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ ); IR (neat) $v_{\max } 3260,3060,3030,2940,2870,1495,1455,1330,1250,1220,1145$, $1095,1070 \mathrm{~cm}^{-1} ; 1 \mathrm{H}$ NMR ( $490 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}$ ) $\delta 7.60-7.56(\mathrm{~m}, 2 \mathrm{H}, \mathrm{ArH}), 7.44-7.13(\mathrm{~m}$, $28 \mathrm{H}, \mathrm{ArH}), 5.18\left(\mathrm{~s}, 1 \mathrm{H}, \mathrm{NCHPh}_{2}\right), 4.87\left(\mathrm{AB}_{\mathrm{q}}, J=11.4, \mathrm{v}=35.7 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{Ph}\right), 4.73$ $(\mathrm{d}, J=10.9 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{OCH} H \mathrm{Ph}), 4.58(\mathrm{~d}, J=10.9 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{OCHHPh}), 4.52\left(\mathrm{AB}_{\mathrm{q}}, J=12.0\right.$ $\left.\mathrm{Hz}, v=35.2 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{Ph}\right), 4.44(\mathrm{~d}, J=5.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3), 4.29\left(\mathrm{AB}_{\mathrm{q}}, J=12.0 \mathrm{~Hz}, v=\right.$ $\left.21.0 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{Ph}\right), 4.27(\mathrm{~s}, 1 \mathrm{H}, \mathrm{H}-4), 4.25(\mathrm{~d}, J=7.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1), 4.07(\mathrm{~d}, J=7.8$ $\mathrm{Hz}, 1 \mathrm{H}, \mathrm{NH}), 3.74\left(\mathrm{dd}, J=9.2,8.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-4^{\prime}\right), 3.69\left(\mathrm{dd}, J=10.8,3.9 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6^{\prime}\right)$, 3.65 (dd, $\left.J=10.8,2.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6^{\prime}\right), 3.64(\mathrm{dd}, J=10.7,9.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6), 3.48(\mathrm{dd}, J=9.2$, $5.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6), 3.45-3.36\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{H}-2^{\prime}\right.$ and $\mathrm{H}-3$ '), $3.34(\mathrm{ddd}, J=9.1,3.9,2.4 \mathrm{~Hz}, 1 \mathrm{H}$, $\left.\mathrm{H}^{\prime} 5^{\prime}\right), 3.30\left(\mathrm{AB}_{\mathrm{q}}\right.$ of $\mathrm{ABX}, J_{\mathrm{AB}}=11.9 \mathrm{~Hz}, J_{\mathrm{AX}}=6.4 \mathrm{~Hz}, J_{\mathrm{BX}}=5.3 \mathrm{~Hz}, v=8.6 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{H}-1$ and H-1), $3.23(\mathrm{dd}, J=10.6,5.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-5), 3.19(\mathrm{q}, J=5.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-2), 2.99-2.83(\mathrm{~m}$, $\left.2 \mathrm{H}, \mathrm{SO}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{Si}\right), 1.27\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{O}_{2} \mathrm{CCH}_{3} \mathrm{Me}\right), 1.24\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{O}_{2} \mathrm{CCH}_{3} \mathrm{Me}\right), 1.10-0.98(\mathrm{~m}, 2$
$-0.12\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{3}\right) ;{ }^{13} \mathrm{C}$ NMR ( $63 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}$ ) $\delta 144.6,143.6,139.4,138.8,138.7$, $129.4,129.0,128.8,128.3,128.2,128.1,128.0,127.8,127.7,127.5,101.1,98.9,85.5,82.8,78.8$, $77.2,75.6,75.0,74.1,74.0,73.4,72.4,69.4,68.9,63.2,62.0,58.9,51.3,26.7,21.9,10.7,-1.8 ;$ MS (FAB) $m / e$ (rel. intensity) 1056 (66), 1055 ( $\mathrm{M}+\mathrm{H}^{+}, 72$ ), 935 (12), 934 (74), 933 (100); HRMS (FAB) calcd for $\mathrm{C}_{61} \mathrm{H}_{75} \mathrm{~N}_{2} \mathrm{O}_{10} \mathrm{SSi}\left(\mathrm{M}+\mathrm{H}^{+}\right)$1055.4912, found 1055.4981. Anal. Calcd for $\mathrm{C}_{61} \mathrm{H}_{74} \mathrm{~N}_{2} \mathrm{O}_{10}$ SSi: C, 69.42; H, 7.07; N, 2.65; S, 3.04. Found: C, 69.06; H, 7.19; N, 2.43; S, 3.42.

## O-(2-Acetamido-3,4,6-tri-O-benzyl-2-deoxy-D-allopyranosyl)- $\beta$-(1 $\rightarrow 4$ )-6-O-benzyl-2,5-dideoxy-2,5-[(diphenylmethyl)imino]-1,3-O-isopropylidene-D-glucitol (83).

A suspension of sulfonamide $82(120 \mathrm{mg}, 0.114 \mathrm{mmol})$ and cesium fluoride ( $220 \mathrm{mg}, 1.4 \mathrm{mmol}$ ) in DMF ( 1 mL ) was rapidly stirred at $95^{\circ} \mathrm{C}$, acetic anhydride ( 11 $\mu \mathrm{L}, 0.15 \mathrm{mmol}$ ) was added to the mixture after 12 h , the mixture was stirred an additional 12 h , cooled, acetylated for 4 h with pyridine ( 1 mL ) and acetic anhydride $(0.3 \mathrm{~mL})$, concentrated under reduced pressure, and extracted from saturated aq. $\mathrm{Na}_{2} \mathrm{CO}_{3}(8 \mathrm{~mL})$ with ethyl acetate $(3 \times 4 \mathrm{~mL})$. The combined organic layers were dried ( $\mathrm{MgSO}_{4}$ ), concentrated, and the residue chromatographed (silica; 2\% Et3 $\mathrm{N}, 30 \rightarrow 40 \%$ ethyl acetate in hexanes) to afford the desired $N$-acetylated disaccharide ( $83 ; 81 \mathrm{mg}$, $76 \%$ ) as a colorless foam: $[\alpha]_{\mathrm{D}}-40.3^{\circ}\left(c 1.2, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right.$ ); IR (neat) $v_{\max } 3280,3060,3030$, $2980,2930,2860,1655,1455,1375,1220,1095,1075 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H}$ NMR ( $490 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}$ ) $\delta$ 7.54-7.50 (m, $2 \mathrm{H}, \mathrm{ArH}$ ), 7.46-7.17 (m, $28 \mathrm{H}, \mathrm{ArH}$ ), $5.23(\mathrm{~d}, \mathrm{~J}=9.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{NH}), 5.02(\mathrm{~s}$,
$1 \mathrm{H}, \mathrm{NCHPh} 2), 4.84(\mathrm{~d}, J=11.2 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{OCHHPh}), 4.68(\mathrm{~d}, J=11.5 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{OCHHPh})$, $4.65(\mathrm{~d}, J=11.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{OCHHPh}), 4.57\left(\mathrm{AB}_{\mathrm{q}}, J=12.0 \mathrm{~Hz}, v=22.8 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{Ph}\right)$, $\left.4.52(\mathrm{~d}, J=5.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3), 4.51(\mathrm{~d}, 8.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1)^{\prime}\right), 4.32\left(\mathrm{AB}_{\mathrm{q}}, J=12.1 \mathrm{~Hz}, \mathrm{v}=28.3\right.$ $\left.\mathrm{Hz}, 2 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{Ph}\right), 4.16(\mathrm{~s}, 1 \mathrm{H}, \mathrm{H}-4), 3.86\left(\mathrm{q}, J=9.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-2^{\prime}\right), 3.77(\mathrm{dd}, J=10.8,4.2$ $\left.\mathrm{Hz}, 1 \mathrm{H}, \mathrm{H}-6^{\prime}\right), 3.74-3.63$ ( $\mathrm{m}, 4 \mathrm{H}, \mathrm{H}-6, \mathrm{H}-3^{\prime}, \mathrm{H}-4^{\prime}$, and H-6'), 3.49 (ddd, $J=9.3,4.2,2.4$ $\left.\mathrm{Hz}, 1 \mathrm{H}, \mathrm{H}-5^{\prime}\right), 3.46(\mathrm{dd}, \mathrm{J}=9.4,5.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6), 3.34(\mathrm{~d}, \mathrm{~J}=6.4 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{H}-1$ and $\mathrm{H}-1)$, $3.22(\mathrm{q}, J=5.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-2), 3.18(\mathrm{dd}, J=10.6,5.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-5), 1.84\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{COCH}_{3}\right)$, $1.27\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{O}_{2} \mathrm{CCH}_{3} \mathrm{Me}\right), 1.25\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{O}_{2} \mathrm{CCH}_{3} \mathrm{Me}\right) ;{ }^{13} \mathrm{C} \mathrm{NMR}\left(63 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}\right) \delta 169.9$, $144.5,143.7,139.6,139.1,138.8,129.2,128.8,128.7,128.5,128.3,128.2,128.0,127.8,127.6$, $127.4,101.9,98.8,86.7,82.0,78.8,77.4,75.4,75.0,74.7,74.0,73.2,72.3,69.6,69.4,63.2,62.1$, $55.8,26.4,23.9,21.9$; MS (FAB) $m / e$ (rel. intensity) 935 (22), $934(58), 933\left(\mathrm{M}+\mathrm{H}^{+}, 89\right)$, $876(24), 875(39), 812(56), 811$ (100), 307 (33), 288 (20), 220 (39), 205 (29); HRMS (FAB) calcd for $\mathrm{C}_{58} \mathrm{H}_{65} \mathrm{~N}_{2} \mathrm{O}_{9}\left(\mathrm{M}+\mathrm{H}^{+}\right)$933.4690, found 933.4708. Anal. Calcd for $\mathrm{C}_{58} \mathrm{H}_{64} \mathrm{~N}_{2} \mathrm{O}_{9}: \mathrm{C}, 74.65 ; \mathrm{H}, 6.91 ; \mathrm{N}, 3.00$. Found: C, $74.46 ; \mathrm{H}, 7.00 ; \mathrm{N}, 2.79$.

O-(2-Acetamido-3,4,6-tri-O-benzyl-2-deoxy-D-allopyranosyl)- $\beta$-(1 $\rightarrow 4$ )-6-O-benzyl-2,5-dideoxy-2,5-[(diphenylmethyl)imino]-D-glucitol (84).

Disaccharide $83(80.8 \mathrm{mg}, 0.0866 \mathrm{mmol})$ was stirred 15 h with $5 \%$ concentrated aq. HCl in methanol, poured into concentrated aq. $\mathrm{NaHCO}_{3}(10 \mathrm{~mL})$, and extracted with 1:2 isopropanol/dichloromethane ( $3 \times 4 \mathrm{~mL}$ ). The combined organic layers were dried $\left(\mathrm{Na}_{2} \mathrm{SO}_{4}\right)$, concentrated, and the residue chromatographed ( $2 \% \mathrm{Et}_{3} \mathrm{~N}, 50$ $\rightarrow 60 \rightarrow 80 \%$ ethyl acetate in hexanes) to provide the diol ( $84 ; 63.5 \mathrm{mg}, 82 \%$ ) as a
colorless solid: $[\alpha]_{D}+17.8^{\circ}\left(c 1.0, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right)$; $\mathrm{IR}(\mathrm{KBr}) v_{\max } 3460,3280,3060,3030,2870$, $1655,1450,1365,1120,1070 \mathrm{~cm}^{-1}$; ${ }^{1} \mathrm{H}$ NMR $\left(490 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}\right) \delta 7.42-7.28(\mathrm{~m}, 30 \mathrm{H}$, $\mathrm{ArH}), 5.05(\mathrm{~s}, 1 \mathrm{H}, \mathrm{NCHPh} 2), 4.78(\mathrm{~d}, J=11.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{OCHHPh}), 4.77(\mathrm{~d}, J=11.4 \mathrm{~Hz}, 1$ $\mathrm{H}, \mathrm{OCHHPh}), 4.63(\mathrm{~d}, J=9.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{NH}), 4.58(\mathrm{~d}, J=11.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{OCHHPh}), 4.56(\mathrm{~d}, J$ $=12.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{OCH} H \mathrm{Ph}), 4.51(\mathrm{~d}, J=11.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{OCHHPh}), 4.50\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{Ph}\right)$, $4.27(\mathrm{~d}, J=12.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{OCHHPh}), 4.26(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1), 4.29-4.18(\mathrm{~m}, 2 \mathrm{H}, \mathrm{H}-3$ and C-2 OH), $\left.4.10(\mathrm{t}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-4), 3.69(\mathrm{dd}, J=10.0,2.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6)^{\prime}\right), 3.64(\mathrm{dt}, J$ $\left.=10.2,8.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-2 '), 3.61\left(\mathrm{ddd}^{\prime}, J=9.6,8.0,2.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-5\right)^{\prime}\right), 3.48(\mathrm{dd}, J=4.48,10.2$, $\left.8.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3^{\prime}\right), 3.47\left(\mathrm{dd}, J=10.0,8.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6^{\prime}\right), 3.45(\mathrm{dd}, J=10.9,1.2 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{C}-1$ $\left.\mathrm{OH}), 3.38(\mathrm{td}, J=10.6,2.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1), 3.37(\mathrm{dd}, J=9.7,8.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-4)^{\prime}\right), 3.26(\mathrm{ddd}, J=$ $8.2,5.8,2.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-2), 3.15(\mathrm{ddd}, J=10.6,5.7,1.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1), 3.13(\mathrm{dd}, J=9.7,3.9$ $\mathrm{Hz}, 1 \mathrm{H}, \mathrm{H}-6), 3.10$ (dd, $J=9.7,2.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6$ ), 2.94 (ddd, $J=7.6,3.9,2.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-5$ ), $1.54\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{COCH}_{3}\right) ;{ }^{13} \mathrm{C}$ NMR ( $63 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}$ ) $\delta 169.9,142.8,142.6,139.1,138.8$, $138.3,138.0,129.4,128.9,128.8,128.6,128.5,128.3,128.2,127.7,102.2,89.1,82.4,79.5,75.3$, $75.2,75.0,74.6,73.9,73.4,72.9,69.9,69.6,65.0,62.8,62.0,55.7,23.4 ; \mathrm{MS}$ (FAB) $m / e$ (rel. intensity) $895(21), 894(61), 893\left(\mathrm{M}+\mathrm{H}^{+}, 100\right), 771(27), 307(22), 220(29), 205(27)$; HRMS (FAB) calcd for $\mathrm{C}_{55} \mathrm{H}_{60} \mathrm{~N}_{2} \mathrm{O}_{9}\left(\mathrm{M}+\mathrm{H}^{+}\right)$893.4377, found 893.4409.
$O$-(2-Acetamido-D-allopyranosyl)- $\beta$-( $1 \rightarrow 4$ )-2,5-dideoxy-2,5-imino-D-glucitol (66).
A mixture of disaccharide $84(63.5 \mathrm{mg}, 0.0709 \mathrm{mmol})$ and $10 \% \mathrm{Pd}-\mathrm{C}$ catalyst ( 43 mg ) in $1: 9$ acetic acid/methanol ( 1.5 mL ) was shaken 1 day under hydrogen ( 50 psi ), a second portion of catalyst ( 35 mg ) was added, the hydrogenolysis was continued an additional day, then filtered
through Celite, concentrated, and the residue chromatographed (Bio-gel P-2; $10 \mathrm{mM} \mathrm{NH} 44 \mathrm{OAc}-$ $\mathrm{NH}_{3}, \mathrm{pH} 9$ ). Treatment of an aqueous solution of the salt thus produced with Amberlite IRA-400 $(\mathrm{OH})$ afforded the free base of azasugar 66 (amorphous solid; $21.0 \mathrm{mg}, 81 \%$ ) after lyophilization: $[\alpha]_{\mathrm{D}}+9.0^{\circ}(c 0.3$, water $) ;$ IR (KBr) $v_{\max } 3370\left(\mathrm{v}\right.$ br), 2910, 2870, 1645, 1555, 1405, $1070 \mathrm{~cm}^{-1}$; ${ }^{1} \mathrm{H}$ NMR ( $490 \mathrm{MHz}, \mathrm{D}_{2} \mathrm{O}+0.5 \% \mathrm{CD}_{3} \mathrm{CO}_{2} \mathrm{D}$ ) $\delta 4.57(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1$ ) $) 4.34(\mathrm{dd}, J=$ $4.4,2.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3), 3.92(\mathrm{dd}, J=4.2,2.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-4), 3.86(\mathrm{dd}, J=12.3,2.1 \mathrm{~Hz}, 1 \mathrm{H}$, H-6'), 3.81 (dd, $J=11.8,5.5 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1$ ), $3.73-3.64$ ( $\mathrm{m}, 4 \mathrm{H}, \mathrm{H}-1, \mathrm{H}-6, \mathrm{H}-6$, and H-6'), 3.62 (dd, $\left.J=10.4,8.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-2^{\prime}\right), 3.49\left(\mathrm{dd}, J=10.4,8.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3^{\prime}\right), 3.46-3.22(\mathrm{~m}, 2 \mathrm{H}, \mathrm{H}-2$ and H-5'), 3.36 (dd, $J=9.8,8.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-4$ '), 3.21 (q, $J=5.5 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-5$ ), 1.98 (s, 3 H , $\mathrm{COCH}_{3}$ ) ${ }^{13} \mathrm{C}$ NMR ( $63 \mathrm{MHz}, \mathrm{D}_{2} \mathrm{O}+0.5 \% \mathrm{CD}_{3} \mathrm{CO}_{2} \mathrm{D}$ ) $\delta 174.7,101.4,86.4,76.0,74.6,73.5$, 69.9, 64.7, 62.3, 60.7, 58.4, 55.6, 22.0; MS (FAB) m/e (rel. intensity) $367\left(\mathrm{M}+\mathrm{H}^{+}, 10\right), 308$ (32), 307 (100), 290 (15), 289 (57); HRMS (FAB) calcd for $\mathrm{C}_{14} \mathrm{H}_{27} \mathrm{~N}_{2} \mathrm{O}_{9}\left(\mathrm{M}+\mathrm{H}^{+}\right.$) 367.1717, found 367.1732.
i Current address: Laboratory for Bioorganic Chemistry, Sloan-Kettering Institute for Cancer Research, Memorial Sloan-Kettering Cancer Center, New York, New York 10021 and the Department of Chemistry, Columbia University, New York, New York 10027.

