An Enantioselective Synthesis of *N*-Methylfucosamine *via* Tandem C–C/C–O Bond Formation

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Optically pure D-(+)-*N*-methylfucosamine (**8**) has been synthesized from a TBDMS-protected methyl L-serinate benzophenone Schiff base (O'Donnell's Schiff base, **1**) in seven steps in 13% overall yield. Efficient construction of the requisite amino triol acetate **3a** with the proper stereochemical configuration is accomplished in two steps with a chelation-controlled reduction–alkylation reaction using $[Bu_2AlH{\cdot}Al\text{-}iBu_3/E\text{-}LiCH{=}CHCH_3$, followed by oxidation with OsO_4. Conversion of the Schiff base to the *N*-benzhydryl protecting group and methylation (Eschweiler–Clark) is accomplished in one pot with $NaCNBH_3$ in the presence of $H_2C{=}O$. Deprotection and oxidation of the primary alcohol, followed by deacetylation with KCN, provided the desired product **8**.

Amino sugars have attracted much attention as an important class of natural products beginning in the 1950's when 2-deoxy-2-(methylamino)-L-glucosamine was found to be a component of the antibiotic streptomycin.[1] Aminoglycosides are found in glycoproteins and glycolipids,[2] as well as in various antibiotics.[3] 5-Deoxy 5-amino sugars (aza sugars) have been found to be effective glycosidase inhibitors and have been studied intensively.[4] Alkaloids such as castanospermine and swainsonine may be regarded as azasugar analogs. The enediyne class of antibiotics has been of central interest for the past decade,[5] and the aminoglycoside structures (*cf.* Figure 1) of the calicheamicins and the esperamycins have been shown to play a crucial role in the recognition and binding to the DNA substrate.[6] It has also been recently demonstrated that the aminoglycoside moiety participates as an internal base in thiol activation of the neocarzinostatin chromophore.[7]

Unusual sugars have been synthesized *via* transformation of other readily available carbohydrates.[8] Cycloaddition reactions of dienes with carbonyl compounds,[9] or alternatively reactions of enones and alkenes,[10] have provided cyclic intermediates which have been functionalized in a stereoselective manner to yield carbohydrates in an elegant way. Another commonly employed strategy includes elaboration of acyclic allylic alcohol intermediates which are accessible *via* reaction of chiral aldehydes with various nucleophiles such as enolates or organometallic reagents. Despite dependability of this approach, low stereoselectivity has often been a serious shortcoming. One solution to this problem has been the use of double diastereoselection with chiral allylboronates as the nucleophile.[11] Asymmetric epoxidation also provides an access to the starting materials that have been used in the synthesis of carbohydrate derivatives.[12,13] A review of synthetic approaches to carbohydrates starting from acyclic precursors has been recently published.[14]

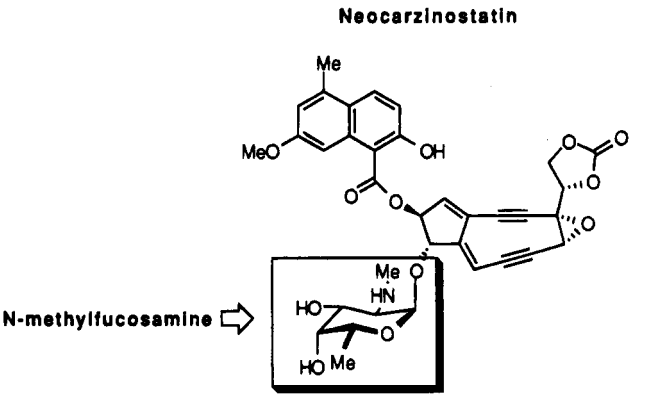

Figure 1

® Abstract published in *Advance ACS Abstracts,* July 15, 1994.

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These strategies have also been applied to the synthesis of amino sugars.[15] Nitrogen is typically introduced into the molecule during the later stages of the synthetic scheme. Usually, this has been accomplished by a nucleophilic attack with azide N_3^-,[16] NH_3,[17] or Et_2AlNBn_2[18] at an electrophilic position (*cf.* epoxide). Stereoselective amination methods have also been developed using the intramolecular electrophilic addition of carbamoyloxy olefinic systems.[19] Trichloroacetamidate has been applied as an alternative in the intramolecular amination.[20] Nitrogen has been introduced via formation of an imine and subsequent stereoselective reduction of the carbon–nitrogen double bond.[21] Chiral aldol condensation of optically active glycine imines and aldehydes has been the key step in the synthesis of several amino sugars.[22] Nitrone cycloaddition with enol ethers,[23] and the hetero-Diels–Alder reaction of dienes with nitrosyl substrates,[24] have provided effective routes to amino sugars and aminocyclitols. Epoxidation and osmylation have been the most useful methodologies in the elaboration of chiral unsaturated intermediates (*cf. epoxidation of allylic amines*[25] *and osmylation of dihydroisoxazolyl alkenes*[26]).

Amino acids appear to be ideal starting chiral materials for the *de novo* synthesis of amino sugars and related compounds. The introduction of hydroxyl groups with the desired configuration into amino acid-derived substrates may be more efficient than the manipulation of pre-existing hydroxyl-bearing centers in naturally occurring sugars. In addition, the availability of either enantiomer of many amino acids provides access to rare L-sugars. Although L- and D-amino acids have been widely used in synthesis of natural products,[27] they have not yet become common starting materials for the synthesis of amino sugars and related compounds.[28] The more reactive α-amino aldehydes have been used, but there are some problems associated with this approach, since α-amino aldehydes undergo racemization,[29] and *N*-Boc protected amino aldehydes do not give, in many cases, very stereoselective results.[28,30]

Convenient, highly stereoselective reduction–alkylation methods using amino acids as a source of chirality have been developed, and several research groups have now utilized this approach to avoid the isolation of configurationally labile α-amino aldehydes.[31] In our approach, benzophenone imine derivatives of α-amino esters (O'Donnell's Schiff bases)[32] are chilled to −78 °C in CH_2Cl_2, treated with iBu_5Al_2H (1:1 mixture of iBu_3Al and iBu_2AlH), followed by addition of a carbon nucleophile. We have shown that under these conditions, significant reduction of the ester does not occur until after the carbon nucleophile is added, which presumably generates an aluminum "ate" species which is a stronger reducing agent than iBu_2AlH itself. Thus, a one-pot reaction provides access to β-amino alcohols which can be elaborated in a number of different ways to yield a number of nitrogen-containing structures (*i.e.* sphingosines, amino sugars, aza sugars, alkaloids). We have chosen *N*-methyl-2-amino-2,6-dideoxy-D-galactose (*N*-methylfucosamine, Figure 1),the aminoglycoside fragment of the antibiotic neocarzinostatin,[33] as a model system which is also of biological interest.

The synthesis of *N*-methylfucosamine began with the crystalline L-serine Schiff base **1** (Scheme 1). Addition of iBu_5Al_2H to the Schiff base ester, followed by the addition of the alkenyllithium provided the *syn*-amino alcohol **2a** with excellent stereoselectivity (>20:1); the principal byproduct consisting of the over-reduced primary alcohol **2c**. While long-chain *trans*-alkenyllithiums could be easily generated with tBuLi from the corresponding iodides in hexane,[34] the propenyl lithium analog precipitated from hexane when generated from propenylbromide in a similar fashion. The solid *trans*-propenyllithium was isolated and then redissolved in toluene. Chromatographic isolation of pure (*S,S*)-**2a** in 70% yield was facilitated by the equilibrium between the cyclic oxazolidine structure and the more polar hydroxyimine tautomer which is capable of chelation.[35] The undesired *anti*-amino alcohol (*R,S*)-**2b** favors the open chain structure, is much more polar, and is thus retained on SiO_2.

Catalytic osmylation using the Sharpless procedure[36] *in the absence of a chiral auxiliary* gave a mixture of triol diastereomers which was acetylated *in situ* and easily separated by flash chromatography on SiO_2 to provide the protected amino tetrols **3a** and **3b** (70% combined, 6:1 ratio). The yield and stereoselectivity of this reaction did not seem to be affected by changes in concentration or changes in temperature(−20–rt). Osmylation of the corresponding acetate **2d** gave lower selectivity (3:1 ratio). The major diastereomer **3a** has the desired stereochemical configuration. That is, all four contiguous chiral centers were introduced stereoselectively in high yield in two steps.

Orthogonal manipulation of the protecting groups, N-methylation, and oxidation of the primary alcohol

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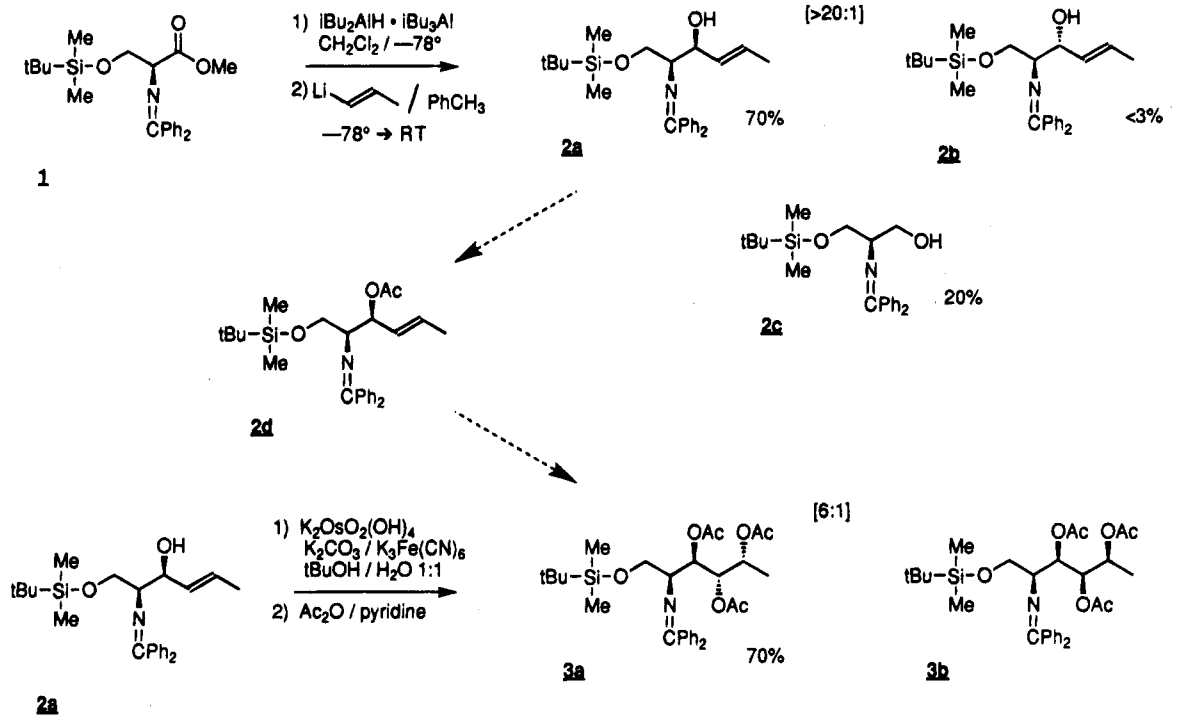
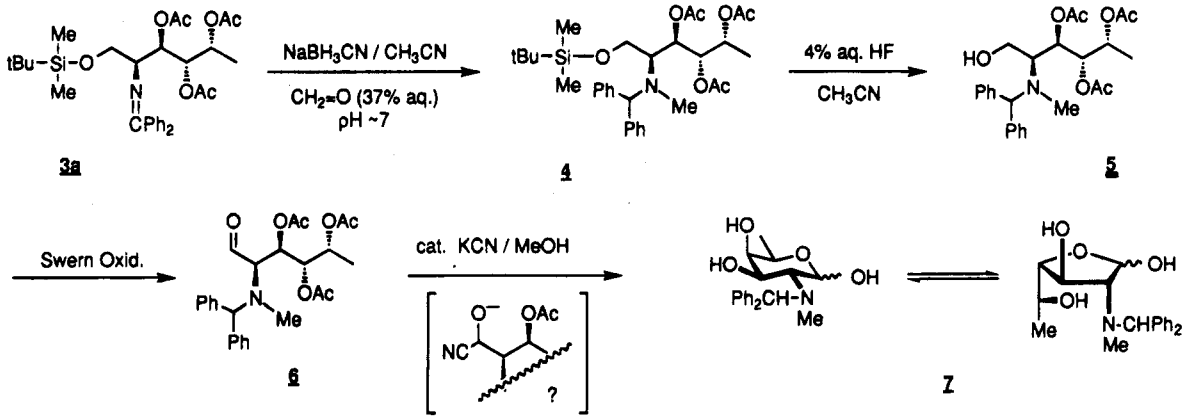
Scheme 1



Scheme 2



yielded the desired target structure in 30% overall yield (Scheme 2). Reduction of the Schiff base triacetate **3a** with $NaBH_3CN$ under anhydrous acidic conditions to generate benzhydryl secondary amine[37a] and subsequent reductive methylation[37b] was accomplished in a one-pot reaction sequence to provide compound **4**. Desilylation was accomplished with HF in aqueous acetonitrile[38] and yielded the primary alcohol **5**. Desilylation with basic fluoride ($nBu_4N^+F^-$ or HF·pyridine) was accompanied by migration of the C-3 acetyl group to C-1. The α-amino aldehyde **6** was obtained by standard Swern oxidation of **5**. This key aldehyde intermediate proved to be very labile under basic conditions. The compound decomposed upon attempts at column chromatography, and Zemplèn deacylation (cat. NaOMe/MeOH) led to decomposition of the amino aldehyde. Several attempts to protect the aldehyde as an acetal under acidic conditions also failed. Deacetylation was finally accomplished with KCN in anhydrous MeOH.[39] While the weak Bronsted base CN^- is less likely to attack protons than MeO^- due to simple basicity, it may be that rapid cyanohydrin formation can reduce the acidity of the amino aldehyde **6**, permitting deacetylation without β-elimination of HOAc. In any case, the protected *N*-methyl-*N*-(diphenylmethyl)fucosamine (**7**) was produced in good yield as a mixture of pyranose and furanose anomers.

Conversion of **7** to *N*-methylfucosamine **8** was accomplished by hydrogenolysis of the benzhydryl group (H_2/Pd–C/MeOH). (Scheme 3). Purification of the amino sugar was done on acidic ion–exchange resin,[33a] and the desired product was recovered after lyophilization as the free base. In order to confirm the stereochemical configuration of the product, the compound **7** was also

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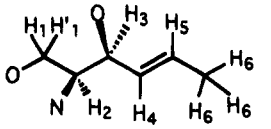
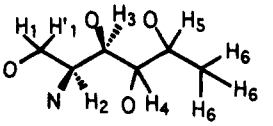
Table 1. ^{1}H NMR Data for Acyclic Compounds (250 MHz, $CDCl_3$)



2a,2d



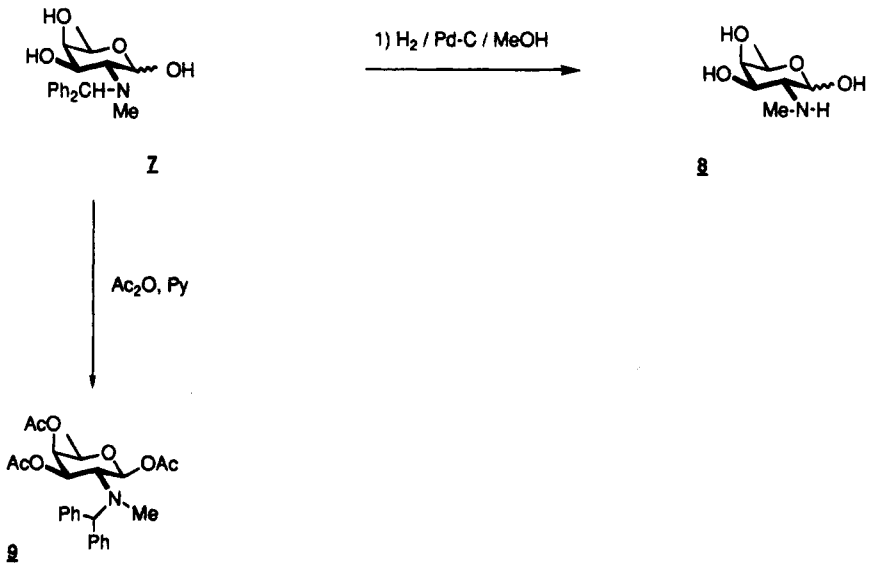
3a - 6

	Chemical Shifts (ppm)								Coupling Constants (ppm)						
number	**2a**	**2d**	**3a**	**3b**	**4**	**5**	**6**	$J_{H,H}$	**2a**	**2d**	**3a**	**3b**	**4**	**5**	**6**
H_1	3.62	3.78	3.79	3.75	3.69	3.59	9.46	1,1'	10.6	-	-	-	-	-	
H'_1	3.84	3.78	3.79	3.75	3.69	3.59		1',2	3.5	-	-	-	-	-	
H_2	2.92	3.70	3.67	3.66	3.05	3.09	3.45	1,2	2.2	-	-	-	-	-	0.0
H_3	4.29	5.38	5.39	5.50	5.32	5.31	5.65	2,3	8.3	-	3.3	3.6	4.7	5.8	5.5
H_4	5.27	5.38	5.20	5.20	5.38	5.48	5.45	3,4	6.7	-	7.0	7.0	7.4	7.3	8.5
H_5	5.69	5.73	5.13	4.89	5.15	5.17	5.07	4,5	15.2	15.2	3.7	3.6	4.5	3.1	2.7
H_6	1.67	1.66	1.09	1.23	1.07	1.14	1.12	5,6	6.5	6.6	6.4	6.4	6.5	6.5	6.6
NMe					2.24	2.27	2.44								
Ph_2CH					4.83	4.79	5.10								

Table 2. ^{13}C NMR Shifts for Acyclic Compounds ($CDCl_3$)

	2a	**2d**	**3a**	**3b**	**4**	**5**	**6**
C-1	59.5	64.1	63.4	63.4	59.8	56.7	200.7
C-2	65.1	66.8	63.6	63.7	59.4	58.5	58.9
C-3	80.8	75.0	72.9	73.2	73.6	73.1	72.0
C-4	-	-	70.5	70.8	71.6	71.3	68.3
C-5	-	-	68.2	69.2	68.6	68.4	68.0
C-6	17.8	17.8	16.6	16.4	16.9	16.8	16.7
N-Me					34.9	35.2	36.8
Ph_2C					74.3	74.2	73.6

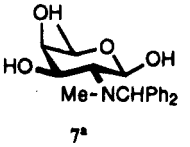
Scheme 3



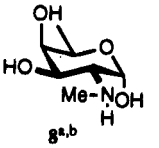
acetylated (pyridine, Ac_2O) to give the protected pyranose structure **9**. Vicinal coupling constants observed in 250 MHz ^{1}H-NMR spectra of **9** in $CDCl_3$ clearly indicate that the product has the desired galacto configuration. Similar coupling constants are observed with *N*-methylfucosamine (**8**) itself in D_2O, although the presence of anomeric species complicates the analysis of this sugar in solution.

Ido, *et al.* have previously reported the deoxygenation and methylation of galactosamine, to provide *N*-methylfucosamine in seven steps in low yield.[33a] The present *de novo* synthesis of **8** in 13% overall yield in seven steps is not only much more efficient than the previous one, but begins with readily-available starting materials, and has the potential for modification to produce a number of fucosamine analogs in *either enantiomeric series*. Now that the efficiency and stereochemical outcome of this tandem C—C/C—O bond formation has been established, this appraoch can be used for more elaborate syntheses, and for quite sensitive functionality.

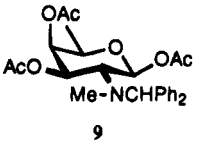
Table 3. ^{1}H NMR and ^{13}C NMR Data for Cyclic Compounds 6–8



7[a]



8[a,b]



9

	^{1}NMR ($CDCl_3$) δ (J,Hz)	^{13}C NMR ($CDCl_3$) δ	^{1}H NMR (D2O) δ (J,Hz)	^{13}C NMR (D_2O) δ	^{1}HNMR ($CDCl_3$) δ (J,Hz)
1	4.83 (8.2)	92.9	5.50 (3.5)	87.8	5.79 (8.8)
2	2.91 (8.3,9.9)	59.6	3.21 (3.2, 11.2)	60.4	3.30 (8.8,11.2)
3	3.82 (undet.)	70.7	4.03 (11.2, 3.2)	67.4	5.16 (11.2, 3.1)
4	3.76 (undet.)	72.9	3.80 (undet.)	72.9	5.08 (3.0)
5	3.60 (6.5)	72.7	4.22 (6.3)	69.2	3.75 (6.5)
6	1.28 (6.5)	16.4	1.20 (6.7)c	16.7	1.06 (6.5)
NMe	2.26	34.0	2.73c	33.9	2.23
Ph_2CH	4.83	74.4			4.75

[a] A mixture of pyranose and furanose anomers is observed in D_2O solution; resonances of major anomers are listed in the table. [b] NMR data is in a good agreement with published data.[33a,b] [c] These resonances differ from published data by Edo *et al.* (1.65, 3.23 ppm).[33a]

Experimental Section

General Methods. All air- and moisture-sensitive reactions were performed under an argon atmosphere in flame-dried reaction flasks using standard Schlenk methods. All solvents were dried over the standard drying agents and freshly distilled prior to use. For flash chromatography, 400–230 mesh silica gel 60 (E. Merck No. 9385) was employed. All compounds described were characterized by IR as well as ^{1}H- and ^{13}C-NMR. The ^{1}H- and ^{13}C-NMR spectra were obtained on at 250 and 62.9 MHz. Chemical shifts are reported in δ *vs* Me_4Si in ^{1}H spectra and *vs* $CDCl_3$ in ^{13}C spectra.

Methyl *O*-(*tert*-Butyldimethylsilyl)-*N*-(Diphenylmethylene)-L-serinate (1). Compound **1** was prepared following the published procedure.[31]

(*E*)-1-Lithio-1-propene. Distilled (*E*)-1-bromopropene[40] (4.0 mmol, 484 mg) and 8 mL of hexane was cooled to 0 °C and tBuLi (4.8 mL, 8.8 mmol) was added dropwise with vigorous stirring.[34] The mixture was stirred for 30 min at 0 °C and then warmed to rt and stirred for another 1 h to form a white precipitate (LiBr and propenyllithium). The mixture was allowed to stand at rt for 30 min and the upper hexane layer removed, and 12 mL of $PhCH_3$ was added to the precipitate. The mixture was stirred vigorously for 15 min before use. Gilman titration[41] showed that the solubility of propenyllithium is at least four times greater in toluene than in hexane.

(2*S*,3*S*,4*E*)-2-[*N*-(Diphenylmethylene)amino]-1-*O*-(*tert*-butyldimethylsilyl)-4-hexene-1,3-diol (2a). Schiff base ester **1** (1.0 mmol, 398 mg) and 10 mL of CH_2Cl_2 were cooled to −78 °C and Dibal–Tribal[31a] (1.1 mmol, 2.2 mL of 0.5 M solution in hexane) was added *via* syringe pump over 15–20 min. After addition was complete, (*E*)-1-lithio-1-propene (4.0 mmol, 12 mL of 1.6 M solution in $PhCH_3$[26]) was slowly cannulated into the reaction flask, stirred for 1 h at −78 °C, and then warmed to rt. After stiring for 1 h at rt, the reaction mixture was quenched by pouring into 1% $NaHCO_3$. The reaction mixture was extracted with Et_2O, dried over K_2CO_3, and filtered through Celite and the solvent was removed *in vacuo*. The crude product was purified *via* flash chomatography (5% EtOAc/C_6H_{14}) to provide pure **2a** (570 mg, 70%). **2a:** IR (neat) 3310, 3059, 2928, 1664, 1598, 1450 cm^{-1}; MS (CI) *m/z* 411(MH^+, bp), 410, 394, 392, 368, 352, 339, 338.

(2*S*,3*S*,4*E*)-3-Acetoxy-2-[*N*-(Diphenylmethylene)amino]-1-*O*-(*tert*-butyldimethylsilyl)-4-hexen-1-ol (2d). Compound **2a** (0.49 mmol, 200 mg) was dissolved in pyridine (1 mL), a catalytic amount of DMAP was added, and the mixture was cooled to 0 °C. Acetic anhydride (1 mL) was added dropwise and the reaction mixture was stirred for 24 h at rt. Toluene was added and the solvent was removed *in vacuo*. The crude product was purified by flash chromatography (5% EtOAc/C_6H_{14}) to yield 220 mg (95%) of pure **2d**: colorless oil; IR (neat) 3060, 2929, 1740, 1662, 1595, 1371, 1221 cm^{-1}; $[\alpha]_D$ +2.7 (*c* = 1.1, $CHCl_3$).

(2*S*,3*S*,4*S*,5*R*)-3,4,5-Triacetoxy-2-[*N*-(Diphenylmethylene)amino]-1-*O*-(*tert*-butyldimethylsilyl)hexan-1-ol (3a). $K_3Fe(CN)_6$ (0.49 g,1.5 mmol), K_2CO_3 (0.21 g, 1.5 mmol), and $K_2OsO_2(OH)_4$ (5.6 mg, 3 mol %) were dissolved in 6.7 mL of H_2O. Compound **2a** was dissolved in 6.7 mL of tBuOH and added to the aqueous solution. The mixture was stirred vigorously at rt for 24 h. Solid Na_2SO_3 (0.375 g) was added and the mixture was stirred for 20 min. The aqueous layer was extracted with three portions of $CHCl_3$ and the combined organic phase was dried over $MgSO_4$, filtered through Celite, and dried *in vacuo*. The mixture was dissolved in 1 mL of pyridine, a crystal of DMAP was added, and the mixture was cooled to 0 °C. A volume of 1 mL of Ac_2O was added dropwise. Solvent was removed and **3a** and **3b** were separated by gradient flash chromatography (5% → 25% EtOAc/C_6H_{14}) to yield pure **3a** (170 mg, 60%) and pure **3b** (28 mg, 10%). **3a**: colorless oil; IR (neat) 2928, 2857, 1742, 1370, 1221 cm^{-1}; MS (CI) *m/z* 570 (MH^+), 512, 424, 364, 338, 280; $[\alpha]^{25}_D$ +5.4 (*c* = 0.4, $CHCl_3$).

(2*S*,3*S*,4*S*,5*R*)-3,4,5-Triacetoxy-2-[*N*-Methyl-*N*-(diphenylmethyl)amino]-1-*O*-(*tert*-butyldimethylsilyl)hexan-1-ol (4). Compound **3a** (150 mg, 0.26 mmol) in 1.2 mL of anhydrous CH_3CN was added to solid $NaBH_3CN$ (26.4 mg, 0.42 mmol) *via* syringe, and glacial HOAc was added dropwise to keep the pH near neutrality. After the reduction was complete (~10 min by TLC), 37% aqueous CH_2=O (420 μL, 5.2 mmol) and additional $NaBH_3CN$ (102 mg, 1.6 mmol) were added. The resulting exothermic reaction was allowed to cool to rt while stirring, and glacial HOAc was added until the solution was neutral to wet pH paper. After 2 h the reaction mixture was diluted with Et_2O and washed with concd $NaHCO_3$ and then H_2O. The organic phase was dried over K_2CO_3, filtered through Celite, and dried *in vacuo*. The crude product was purified by flash chromatography (5% EtOAc/C_6H_{14}) to yield pure **4** (140 mg, 89%). **4**: colorless oil; IR (neat) 2929, 1742, 1370, 1251, 1221 cm^{-1}; MS (CI) *m/z* 586 (MH^+, bp), 508, 354, 167; $[\alpha]^{25}_D$ +5.4 (*c* = 0.7, $CHCl_3$).

(2*S*,3*S*,4*S*,5*R*)-3,4,5-Triacetoxy-2-[*N*-Methyl-*N*-(diphenylmethyl)amino]hexan-1-ol (5). Compound **4** (140 mg, 0.24 mmol) was added to 2.8 mL of 4% HF/CH_3CN (0.4 mL of 49% aqueous HF + 9.6 mL of CH_3CN) and stirred at rt for 2 h. The reaction mixture was quenched with concd $NaHCO_3$ solution. The mixture was extracted 3× with $CHCl_3$, dried over K_2CO_3, filtered through Celite, and concentrated *in vacuo*. The pure alcohol **5** (100 mg, 92%) was obtained by flash chromatography (35% EtOAc/C_6H_{14}). **5**: colorless oil; IR (neat) 3519, 2969, 1740, 1371, 1227, 1029; MS (CI) *m/z* 472 (MH^+), 412, 394, 334, 282, 240, 167; $[\alpha]^{25}_D$ +4.4 (*c* = 0.5, $CHCl_3$).

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(2*S*,3*S*,4*S*,5*R*)-3,4,5-Triacetoxy-2-[*N*-Methyl-*N*-(diphenylmethyl)amino]hexan-1-al (6). The mixture of 22 μL of ClCOCOCl and 0.55 mL of CH_2Cl_2 was cooled to −65 °C ($CHCl_3$/solid CO_2) and 37 μL of DMSO in 110 μL of CH_2Cl_2 was added. The reagent was stirred for 2 min and alcohol **5** (100 mg, 0.212 mmol) in 0.22 mL of CH_2Cl_2 was added. Stirring was continued for 15 min, and 154 μL of Et_3N was added. After stirring for an additional 10 min at −65 °C, and the mixture was allowed to warm to rt and quenched with 6 mL of H_2O. The mixture was extracted twice with $CHCl_3$ and washed with 1% HCl, H_2O, and then 3% $NaHCO_3$ and H_2O. Crude aldehyde **6** (70 mg, 70%) was obtained by drying over $MgSO_4$ and solvent removal. Aldehyde **6** decomposed on SiO_2, precluding further purification. Aldehyde **6** was used for the subsequent step without storage for longer than 12 h. **6**: colorless oil; IR (neat) 2931, 2731, 1747, 1371, 1215, 1024 cm^{-1}.

2-[*N*-Methyl-*N*-(diphenylmethyl)amino]-2,6-dideoxy-D-galactopyranose (*N*-Benzhydryl-*N*-methylfucosamine (7)). Aldehyde **6** (70 mg, 0.15 mmol) was dissolved in freshly distilled MeOH, and KCN (75 μmol, 5 mg, dried *in vacuo* over P_2O_5) was added. After 12 h the reaction mixture was diluted with MeOH, filtered through a pad of SiO_2, and dried *in vacuo*. Flash chromatography of the crude material (2.5% MeOH/$CHCl_3$) yielded **7** (40 mg, 78%) as a mixture of pyranose and furanose anomers. **7**: colorless oil; IR (neat) 3565, 2974, 1598, 1033; MS (EI) *m/z* 343 (M^+), 314, 252, 239, 210, 167, 42.

2-*N*-Methyl-D-(+)-2,6-dideoxygalactose (*N*-Methylfucosamine (8)). Amino sugar **7** (20 mg, 0.050 mmol) was dissolved in 15 mL of MeOH and the solution added to 5% Pd/C (5 mg) under argon. The mixture was vigorously stirred under H_2 (1 atm) for 5 h. The flask was then flushed with argon several times, the Pd catalyst was filtered off, and the solvent was removed. The crude product was dissolved in H_2O, acidified to pH = 2 with 2 M HCl, and extracted with $PhCH_3$. Lyophilization of the aqueous phase provided crude material which was dissolved in 1 M NaOH and purified on Dowex 50 (H^+ form). Elution with MeOH/3 M NH_4OH/H_2O (2:5:3)[33a] yielded crystalline product **8** (6 mg, 68%). **8**: colorless crystals, mp 158.5–162 °C (lit.[33a] 158–161 °C); MS (FAB)[42] *m/z* 178 (MH^+), 176, 160, 132, 130, 103.

1,3,4-Tri-*O*-acetyl-2-[*N*-Methyl-*N*-(Diphenylmethyl)amino]-2,6-dideoxy-β-D-(+)-galactopyranose (9). Amino sugar **7** (5 mg, 14.6 μmol) was dissolved in 0.5 mL of dry pyridine and cooled to 0 °C, and 0.5 mL of Ac_2O was added. The reaction mixture was stirred at 0 °C for 3 h, and the solvent was removed *in vacuo*. The crude material was purified by preparative TLC (Kieselgel 60, F_{254}, 1 mm; $CHCl_3$, developed twice) to yield pure **9** (4 mg, 58%). **9**: colorless oil; R_f 0.11 ($CHCl_3$); MS (EI) *m/z* 469 (M^+), 409, 392, 349, 322, 281, 237, 222, 167; IR (neat) 2934, 1748, 1372, 1224.9, 1046 cm^{-1}.

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Supplementary Material Available: The ^{1}H-NMR and ^{13}C-NMR spectra are available for compounds **2a**–**9**, and the FAB-MS fragmentation scheme for *N*-methylfucosamine (**8**) (20 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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